Highly Regio- and Stereoselective Palladium(0)-Catalyzed Addition of Organoboronic Acids with 1,2-Allenic Sulfones, Sulfoxides, or Alkyl- or Aryl-Substituted Allenes in the Presence of Acetic Acid: An Efficient Synthesis of *E*-Alkenes

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Abstract: Two sets of reaction conditions were established to enable the palladium(0)-catalyzed addition of organoboronic acids with 1,2-allenic sulfones, sulfoxides, or alkyl- or aryl-substituted allenes in the presence of acetic acid. This reaction provides a new way for the stereoselective synthesis of tri- or tetrasubstituted *E*-alkenes. With arylboronic acids, the reactions of 1,2-allenic sulfones, sulfoxides, and alkyl-substituted allenes gave only 1-12% of specific regioisomers; the reactions of aryl-substituted allenes afforded only *E*-alkenes in very high regioselectivity.

Key words: allenes, sulfones, sulfoxides, palladium, addition reactions, boron

Introduction

The highly stereoselective synthesis of multisubstituted alkenes is one of the most important topics in organic chemistry, since many issues need be considered. Recently, transition-metal-catalyzed addition of organic boronic reagents with allenes has caught the attention of synthetic organic chemists. We¹ and Oh et al.² have reported the palladium-catalyzed reaction of functionalized allenes with organoboronic acids in the presence of acetic acid. It provides a new synthetic method for the formation of trior tetrasubstituted E-alkenes. However, the regio- and stereoselectivities have not been satisfactory. Yoshida and Ihara et al.³ reported the palladium-catalyzed coupling reaction of allenic alcohols with organoboronic acids, in which the hydroxy group was used as a leaving group, and which yielded substituted dienes and trienes. Oh et al.⁴ also reported the palladium-catalyzed reaction of 1,6-allenynes with organoboronic acids in the presence of acetic acid, which afforded six-membered-ring products. In the meantime, some palladium-catalyzed three-component coupling reactions involving boronic reagents and allenes have also been reported.⁵ Very recently, Hayashi et al.⁶ reported the rhodium-catalyzed asymmetric addition of allenes with arylboronic acids affording (S)-2-aryl-3-(diphenylphosphinyl)alkenes in high yields and enantioselectivity. We wish to report here, as part of our research program on the chemistry of allenes,⁷ the palladium-catalyzed addition of 1,2-allenic sulfones, sulfoxides, or alkyl- or aryl-substituted allenes with organoboronic acids in the presence of acetic acid.

Results and Discussion

Reactions of 1,2-Allenic Sulfones or Sulfoxides

Multisubstituted alk-1-envl sulfoxides or sulfones are very important in organic synthesis,⁸ and therefore highly stereoselective methods for their preparation are highly desirable. On the other hand, 1,2-allenic sulfones or sulfoxides show good reactivities.^{9–11} For example, we have reported the hydrohalogenation of 1,2-allenic sulfones^{9a} and sulfoxides^{9b} and the *E*-halohydroxylation reaction of 1,2-allenic sulfoxides.^{9c} We have also recently reported the first Heck-type cross-coupling reaction of 1,2-allenic sulfones with aryl halides.¹⁰ Mukai et al. have reported the intramolecular nucleophilic addition of 1,2-allenic sulfones.¹¹ Considering their useful reactivities, we were interested to see whether we could control the regio- and stereoselectivities in the addition of 1,2-allenic sulfones or sulfoxides with organoboronic acids in the presence of acetic acid.

1,2-Allenic sulfones **2** are readily available by oxidation of the corresponding sulfoxides **1**, which are easily prepared by the reaction of the corresponding propargylic alcohols with benzenesulfenyl chloride (PhSCl) (Scheme 1).¹² Six compounds have been synthesized by this literature procedure.¹²

Under the catalysis of 10 mol% of tetrakis(triphenylphosphine)palladium, the reaction of phenyl propa-1,2-dienyl sulfone (**2a**) with phenylboronic acid (**3a**) in the presence of 100 mol% acetic acid failed to afford the addition products in dimethyl sulfoxide, dioxane, *N*,*N*-dimethylformamide, dimethylacetamide (DMA), or ethanol (Table 1, entries 1–5). Fortunately, the same reaction afforded the hydroarylation product in solvents such as, acetone, acetonitrile, diethyl ether, toluene, dichloromethane, and tetrahydrofuran (Table 1, entries 6–11). The best result was obtained in tetrahydrofuran, with product (*E*)-**4aa** form-

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Scheme 1 Preparation of 1,2-allenic sulfones and sulfoxides

ing in a regioselectivity of 91:9 (4aa/5aa) and a stereoselectivity of >99:1 [(E)-4aa/(Z)-4aa] (Table 1, entry 11).

With tetrahydrofuran as the solvent, the same reaction with other catalysts was also studied. Unfortunately, no better results were observed (Table 2).

We next studied the effect of the amount of acetic acid on this reaction (Table 3, entries 1–4), and found that 100 mol% acetic acid was necessary (Table 3, entry 3). The reaction under reflux afforded the product in lower yield (Table 3, entry 5).

The results obtained thus far were combined into conditions A [Pd(PPh₃)₄ (10 mol%), AcOH (100 mol%), THF, r.t.] and applied in the regio- and stereoselective formation of *E*-alkenyl sulfones (*E*)-4; some of the typical results are summarized in Table 4. The configurations of the C=C bonds in 4 were determined by an X-ray diffraction study of (*E*)-4ca¹³ (Figure 1).

Considering that the reactivities of 1,2-allenic sulfoxides are nearly always the same as those of 1,2-allenic sulfones, we tried the addition of phenyl propa-1,2-dienyl

sulfoxide (1a) with phenylboronic acid (3a) under conditions A (Table 5, entry 1). This showed that, fortunately, the reaction can be extended to 1,2-allenic sulfoxides. The reaction of phenyl propa-1,2-dienyl sulfoxide (1a) with different organoboronic acids 3 under conditions A afforded products 6 in slightly lower yields than those of products 4 from 2a (Table 5, cf. Table 4). However, when we tried the reaction of 1,2-allenic sulfoxides 5b and 5c with phenylboronic acid (3a), none of the expected products formed (Scheme 2). Sulfoxide (*E*)-6ab can be converted into sulfone (*E*)-4ab in 52% yield by treatment with hydrogen peroxide in acetic acid (Scheme 3).



Scheme 2 Reactions of 1,2-allenic sulfoxides 1b and 1c with phenylboronic acid (3a) under conditions A

Biographical Sketches



Hao Guo was born in Tianjin, China in 1980. After graduation from Nankai University with a bachelor's degree in 2003, he joined the graduate school of the Shanghai Institute of Organic Chemistry. He is currently a Ph.D. student in Professor Shengming Ma's research group.



Shengming Ma is originally from Zhejiang Province, China. He received a B.S. degree in Chemistry from Hangzhou University (1986), and an M.S. (1988) and a Ph.D. degree (1990) from the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. After postdoctoral research at the ETH in Switzerland and the Purdue University in the USA, he joined the faculty of the Shanghai Institute of Organic Chemistry (1997), where he is now the director of the State Key Laboratory of Organometallic Chemistry. Since February 2003 he has been jointly appointed by the SIOC and Zhejiang University, as Research Professor of Chemistry at SIOC and Cheung Kong Scholars Program Professor at Zhejiang University.

Table 1 Tetrakis(triphenylphosphine)palladium-Catalyzed Addition of Phenyl Propa-1,2-dienyl Sulfone (2a) with Phenylboronic Acid (3a)in Different Solvents^a



^a Reagents and conditions: **2a** (0.25 mmol), **3a** (2.0 equiv), Pd(PPh₃)₄ (10 mol%), AcOH (100 mol%), solvent (3 mL), r.t., under N₂.

^b Determined by ¹H NMR (300 MHz) analysis of the crude reaction mixture obtained after filtration and evaporation.

^c Isolated yield.

^d Allene 2a (32%) was recovered.

^e Allene 2a (56%) was recovered.



Figure 1 ORTEP representation of (E)-4ca



Scheme 3 The formation of sulfone (*E*)-4ab from sulfoxide (*E*)-6ab

Reactions of Alkyl- or Aryl-Substituted Allenes

Non-functionalized allenes are also readily available, but the reaction of deca-1,2-diene with (4-methoxyphenyl)boronic acid afforded the addition products in low selectivities.^{1a} To further improve the selectivity, we studied the addition of alkyl-substituted allene **8a** with phenylboronic acid (**3a**) under conditions A (Table 6, entry 1). However, this reaction afforded a mixture of regioisomeric products **9aa** and **10aa** in low yield (Table 6, entry 1). After some screening (Table 6, entries 2–8), conditions B [Pd(PPh₃)₄ (10 mol%), AcOH (100 mol%), dioxane, reflux] (Table 6, entry 4) were established for the highly stereoselective addition of organoboronic acids with alkyl-

 Table 2
 Addition of Phenyl Propa-1,2-dienyl Sulfone (2a) with Phenylboronic Acid (3a) Catalyzed by Different Palladium Complexes^a



^a Reagents and conditions: 2a (0.25 mmol), 3a (2.0 equiv), Pd catalyst (10 mol%), AcOH (100 mol%), THF (3 mL), r.t., under N₂.
 ^b Determined by ¹H NMR (300 MHz) analysis of the crude reaction mixture obtained after filtration and evaporation.

^c Isolated yield.

^d Allene 2a (57%) was recovered.

^e Allene **2a** (67%) was recovered.

^f Allene 2a (79%) was recovered.

^g PPh₃ (20 mol%) was also used.

^h Allene **2a** (44%) was recovered.

ⁱ Allene **2a** (84%) was recovered.

^j Complex mixture.

PhO ₂ S				
2a + B(OH) ₂	Pd(PPh ₃) ₄ (10 mol%) AcOH THF, r.t.	+ SO ₂ Ph	SO ₂ Ph	+ SOaPh
\/ 3a		(<i>E</i>)-4aa	(<i>Z</i>)-4aa	5aa

Table 3	Palladium(0)-Catalyzed Addition of Phenyl Propa-1,2-dienyl Sulfone (2a) with Phenylboronic Acid (3a) in the Presence of Differen
Amounts	of Acetic Acid ^a

Entry	Amount of AcOH (mol%)	Time (h)	Ratio ^b 4aa/5aa	Yield ^c (%) of (<i>E</i>)- 4aa	Ratio ^b (E)-4aa/(Z)-4aa
1	20	24	86:14	65	>99:1
2	50	24	87:13	68	>99:1
3	100	22	91:9	68	>99:1
4	200	24	90:10	57	>99:1
5 ^d	100	7	90:10	54	>99:1

^a Reagents and conditions: **2a** (0.25 mmol), **3a** (2.0 equiv), Pd(PPh₃)₄ (10 mol%), AcOH, THF (3 mL), r.t., 24 h, under N₂. ^b Determined by ¹H NMR (300 MHz) analysis of the crude reaction mixture obtained after filtration and evaporation.

^c Isolated yield.

^d The reaction was carried out under reflux.

 Table 4
 Palladium(0)-Catalyzed Addition Reactions of 1,2-Allenic Sulfones 2 with Organoboronic Acids 3 under Conditions A^a

PhO ₂ S			R ²	R	2				
R ¹	2 +	Pd(PPh ₃)/ AcOH (1	$\begin{array}{c} (10 \text{ mol}\%) \\ \hline 00 \text{ mol}\%) \\ \hline SO_2 Ph \\ \hline \end{array}$	+	R^1 SO ₂ Ph				
R ² -E	3(OH) ₂		(<i>E</i>)- 4		5				
Entry	R ¹	2	R ²	3	Time (h)	Product 4	Ratio ^b 4/5	Yield ^c (%) of (<i>E</i>)- 4	Ratio ^b (<i>E</i>)-4/(<i>Z</i>)-4
1	Н	2a	Ph	3 a	22	4aa	91:9	68	>99:1
2	Н	2a	4-Tol	3b	22	4ab	>99:1	62	>99:1
3	Н	2a	3-MeOC ₆ H ₄	3c	59	4ac	>97:3	35	>99:1
4	Н	2a	$4-MeOC_6H_4$	3d	17.5	4ad	93:7	78	>99:1
5	Н	2a	$3-O_2NC_6H_4$	3e	19	4ae	94:6	66	>99:1
6	Н	2a	$3-AcC_6H_4$	3f	22	4af	>99:1	80	>99:1
7	Н	2a	$4-AcC_6H_4$	3g	22	4ag	94:6	80	>99:1
8	Н	2a	1-Naph	3h	21.5	4ah	91:9	73	>99:1
9	Н	2a	(E)-CH=CH(CH ₂) ₄ Me	3i	25	4ai	90:10	72	>99:1
10	Н	2a	(E)-CH=CHPh	3j	11	4aj	94:6	52	>99:1
11	Me	2b	Ph	3 a	72	4ba	>99:1	50	>99:1
12	<i>n</i> -Bu	2c	Ph	3 a	96	4ca	>99:1	55	>99:1

^a Reagents and conditions (conditions A): **2** (0.25 mmol), **3** (2.0 equiv), Pd(PPh₃)₄ (10 mol%), AcOH (100 mol%), THF, r.t., under N₂. ^b Determined by ¹H NMR (300 MHz) analysis of the crude reaction mixture obtained after filtration and evaporation.

^c Isolated yield.

substituted allenes. The configurations of the C=C bonds in **9** were determined by the ${}^{1}H{-}^{1}H$ NOESY spectra of (*E*)-**9aa** (Figure 2). The highest regioselectivity observed was 92:8 (Table 6, entry 4).

Some typical results of the reactions between alkyl-substituted allenes **8** and organoboronic acids **3** under conditions B are shown in Table 7. We then tried to extend conditions B to aryl-substituted allenes; typical results are shown in Table 8. It should be noted that both the regioand stereoselectivities are excellent. Both electron-donating and electron-withdrawing groups can be attached to the aryl group (Table 8, entries 6–8).



Figure 2 ${}^{1}\text{H}{-}^{1}\text{H}$ NOESY interaction of (*E*)-9aa

Conclusion

We have succeeded in establishing two sets of reaction conditions for the addition reaction of allenes with organoboronic acids: conditions A for the addition of organoboronic acids with 1,2-allenic sulfones or sulfoxides affording *E*-alkenyl sulfones or sulfoxides; conditions B for the addition of organoboronic acids with alkyl- or arylsubstituted allenes affording *E*-alkenes. The generality of this reaction was studied, with some typical results reported. Further studies in this area and the synthetic applications of this reaction are being carried out in our laboratory.

Melting points were determined on a SGW X-4 apparatus. IR spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer. ¹H (300 MHz) and ¹³C (75.4 MHz) NMR spectra of samples in CDCl₃ (unless stated otherwise) were recorded on a Varian Mercury VX300 spectrometer. MS (EI, 70 eV) determinations were carried out on a HP 5973 spectrometer. HRMS (MALDI) determinations were carried out on a Ionspec MALDI-FTMS spectrometer. HRMS (EI) determinations were carried out on a Water GCT CA176 spectrometer. Elemental analyses were carried out on a Elementar Vario EL instrument. Column chromatography was performed on silica gel (10–40 u). The starting materials **1a**,¹² **1b**,¹² **1c**,¹² **2a**,¹² **2b**,¹² **8a**,¹⁴ **8b**,¹⁴ **8c**,¹⁴ **8e**,¹⁴ **11a**,¹⁵ **11b**,¹⁵**11c**,¹⁵ and **11d**¹⁵ were prepared according to literature procedures.

Table 5 Palladium(0)-Catalyzed Addition Reaction of Phenyl Propa-1,2-dienyl Sulfoxide (1a) with Different Organoboronic Acids 3 underConditions A^a

PhOS



Entry	R	3	Time (h)	Product 6	Ratio ^b 6/7	Yield ^c (%) of (<i>E</i>)- 6	Ratio ^b (<i>E</i>)- $6/(Z)-6^{b}$
1	Ph	3a	72	6aa	94:6	50	>99:1
2	4-Tol	3b	36	6ab	>97:3	58	>99:1
3	3-MeOC ₆ H ₄	3c	12	6ac	99:1	59	>99:1
4	4-MeOC ₆ H ₄	3d	24.5	6ad	95:5	52	>99:1
5	$3-O_2NC_6H_4$	3e	48	6ae	>96:4	49	>99:1
6	$4-AcC_6H_4$	3g	48	6ag	>99:1	48	>99:1
7	1-Naph	3h	24	6ah	>94:6	41	>99:1
8	(E) -CH=CH $(CH_2)_3$ Me	3k	72	6ak	>92:8	53	>99:1
9	(E)-CH=CHPh	3j	50	6aj	>94:6	46	>99:1

^a Reagents and conditions (conditions A): 1a (0.25 mmol), 3 (2.0 equiv), Pd(PPh₃)₄ (10 mol%), AcOH (100 mol%), THF, r.t., under N₂.

^b Determined by ¹H NMR (300 MHz) analysis of the crude reaction mixture obtained after filtration and evaporation.

^c Isolated yield.

 Table 6
 Palladium(0)-Catalyzed Addition of Alkyl-Substituted Allene 8a with Phenylboronic Acid (3a) in the Presence of Acetic Acid^a



Entry	Amount of AcOH (mol%)	Temperature	Time (h)	$Yield^b(\%) \text{ of } \textbf{9aa} + \textbf{10aa}$	Ratio ^c 9aa/10aa	Ratio ^c (<i>E</i>)-9aa/(<i>Z</i>)-9aa
1 ^d	100	r.t.	60	38	91:9	>99:1
2^d	100	reflux	8	75	90:10	>99:1
3	100	50 °C	18	64	90:10	>99:1
4	100	reflux	9	75	92:8	>99:1
5	100	130 °Ce	5	68	90:10	>99:1
6	20	reflux	9	42	90:10	>99:1
7	50	reflux	9	45	92:8	>99:1
8	200	reflux	9	44	91:9	>99:1

^a Reagents and conditions: 8a (0.25 mmol), 3a (2.0 equiv), Pd(PPh₃)₄ (10 mol%), dioxane (3 mL), under N₂.

^b Isolated yield; the isomers could not be separated by flash chromatography (silica gel).

^c Determined by ¹H NMR (300 MHz) analysis of the crude reaction mixture obtained after evaporation.

^d THF was used as solvent.

^e The reaction was conducted in a Schlenk tube with a screw cap.

Table 7Palladium(0)-Catalyzed Addition of Alkyl-Substituted Allenes 8 with Organoboronic Acids 3 under Conditions Ba

R ¹ 8 + R ² -B(O 3	Pd(PPh ₃ AcOH (dioxane, H) ₂	3)₄ (10 mol (100 mol% , reflux, 9 ł	$\stackrel{(E)-S}{}$	+ 1	R ² F (<i>Z</i>)-9 1	n ² R ¹ 0		
Entry	\mathbf{R}^1	8	R ²	3	Products 9 and 10	Yield ^b (%) of $9 + 10$	Ratio ^c 9/10	Ratio ^c (<i>E</i>)- 9 /(<i>Z</i>)- 9
1	(CH ₂) ₇ Me	8a	Ph	3a	9aa, 10aa	75	92:8	>99:1
2	(CH ₂) ₇ Me	8a	4-Tol	3b	9ab, 10ab	75	91:9	>99:1
3	(CH ₂) ₇ Me	8a	2-MeOC ₆ H ₄	31	9al, 10al	66	91:9	>99:1
4	(CH ₂) ₇ Me	8a	$4-MeOC_6H_4$	3d	9ad, 10ad	77	91:9	>99:1
5	(CH ₂) ₇ Me	8a	$3-O_2NC_6H_4$	3e	9ae, 10ae	67	89:11	>99:1
6	(CH ₂) ₇ Me	8a	$4-AcC_6H_4$	3g	9ag, 10ag	62	93:7	>99:1
7	(CH ₂) ₇ Me	8a	1-Naph	3h	9ah, 10ah	74	90:10	>99:1
8	(CH ₂) ₁₁ Me	8b	Ph	3a	9ba, 10ba	50	92:8	>99:1
9	(CH ₂) ₁₅ Me	8c	4-MeOC ₆ H ₄	3d	9cd, 10cd	34	93:7	>99:1
10	Су	8d	4-MeOC ₆ H ₄	3d	9dd, 10dd	44	88:12	>99:1
11 ^d	Bn	8e	4-MeOC ₆ H ₄	3d	9ed, 10ed	76	>93:7	95:5

^a Reagents and conditions (conditions B): 8 (0.25 mmol), 3 (2.0 equiv), Pd(PPh₃)₄ (10 mol%), AcOH (100 mol%), dioxane, reflux, 9 h.

^b Isolated yield; the isomers could not be separated by flash chromatography (silica gel).

^c Determined by ¹H NMR (300 MHz) analysis of the crude reaction mixture obtained after evaporation.

^d Reaction time: 6 h.

Hepta-1,2-dien-3-yl Phenyl Sulfone (2c)

A soln of **1c** (441 mg, 2 mmol) and 30% H_2O_2 (0.6 mL) in AcOH (5 mL) was stirred at 100 °C for 0.5 h. After complete conversion of the starting material as monitored by TLC, the mixture was quenched with ice-water (15 mL) and extracted with CHCl₃ (4 × 15 mL). The organic layer was then neutralized by washing with sat. aq NaHCO₃ (4 × 15 mL). The combined organic layer was dried (MgSO₄). Evaporation of the solvent and flash chromatography (silica gel, PE–Et₂O, 2:1) afforded **2c**. Yield: 251 mg (53%); solid; mp 41–42 °C (Et₂O).

IR (neat): 1968, 1943, 1584, 1466, 1447, 1421, 1152 cm⁻¹.

¹H NMR (300 MHz, $CDCl_3$): $\delta = 7.88-7.80$ (m, 2 H), 7.59–7.44 (m, 3 H), 5.31 (t, J = 3.6 Hz, 2 H), 2.21–2.11 (m, 2 H), 1.34–1.28 (m, 2 H), 1.27–1.17 (m, 2 H), 0.77 (t, J = 7.2 Hz, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 207.5, 139.9, 133.3, 128.9, 127.8, 113.1, 84.2, 29.2, 26.1, 21.7, 13.5.

MS (EI, 70 eV): m/z (%) = 236 [M⁺] (8.26), 67 (100).

Anal. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82. Found: C, 66.06; H, 6.74.

Phenyl (E)-2-Phenylprop-1-en-1-yl Sulfone [(E)-4aa] under Conditions A; Typical Procedure

Compound **3a** (62 mg, 0.51 mmol), **2a** (45 mg, 0.25 mmol), Pd(PPh₃)₄ (30 mg, 0.026 mmol), AcOH (14 μ L, 0.24 mmol), and THF (3 mL) were added into a dried reaction tube under a N₂ atmosphere. The resulting mixture was stirred at r.t. and monitored by TLC (PE–Et₂O, 1:1). After evaporation of the solvent, filtration

though a pad of silica gel, and evaporation to dryness, the resulting mixture was analyzed by ¹H NMR spectroscopy, from which the **4aa/5aa** ratio of 91:9 and (*E*)-**4aa**/(*Z*)-**4aa** ratio of >99:1 were obtained (see Table 4). Purification of the residue by flash chromatography (silica gel, PE–Et₂O, 20:1) gave (*E*)-**4aa**. Yield: 44 mg (68%); solid; mp 71–73 °C (Et₂O).

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IR (neat): 1601, 1571, 1445, 1303, 1145 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 8.01–7.94 (m, 2 H), 7.65–7.51 (m, 3 H), 7.45–7.30 (m, 5 H), 6.61 (q, *J* = 1.2 Hz, 1 H), 2.53 (d, *J* = 1.2 Hz, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 153.5, 142.1, 140.0, 133.2, 129.9, 129.2, 128.7, 127.4, 127.2, 126.3, 17.2.

MS (EI, 70 eV): m/z (%) = 258 [M⁺] (5.96), 115 (100).

Anal. Calcd for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46. Found: C, 69.72; H, 5.40.

Phenyl (E)-2-(4-Tolyl)prop-1-en-1-yl Sulfone [(E)-4ab]

Compound (*E*)-**4ab** was prepared similarly to compound (*E*)-**4aa** by conditions A. The reaction of **2a** (45 mg, 0.25 mmol), **3b** (69 mg, 0.51 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in THF (3 mL) afforded crude **4ab** after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness [**4ab/5ab** > 99:1, (*E*)-**4ab**/(*Z*)-**4ab** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**4ab** was isolated by flash chromatography (silica gel). Yield: 42 mg (62%); solid; mp 70–72 °C (Et₂O–PE).

IR (neat): 1601, 1562, 1510, 1446, 1314, 1289, 1143 cm⁻¹.

 Table 8
 Palladium(0)-Catalyzed Addition of Aryl-Substituted Allenes 11 with Organoboronic Acids 3 under Conditions B^a

Ar 11 + R—B(O 3	Pd(PPh ₃) ₄ (1 AcOH (100 dioxane, re	0 mol%) mol%) flux, 5 h	R Ar (E)-12 (Z)	Ar -12	Ar 13			
Entry	Ar	11	R	3	Product 12	Yield ^b (%) of (<i>E</i>)-12	Ratio ^c 12/13	Ratio ^c (<i>E</i>)- 12 /(<i>Z</i>)- 12
1	Ph	11a	Ph	3a	12aa	41	>99:1	>99:1
2	Ph	11a	4-Tol	3b	12ab	73	>99:1	>99:1
3	Ph	11a	4-MeOC ₆ H ₄	3d	12ad	79	>99:1	>99:1
4	Ph	11a	$4-AcC_6H_4$	3g	12ag	44	>99:1	>99:1
5	Ph	11a	1-Naph	3h	12ah	87	>99:1	>99:1
6	4-MeOC ₆ H ₄	11b	4-MeOC ₆ H ₄	3d	12bd	60	>99:1	>99:1
7 ^d	4-t-BuC ₆ H ₄	11c	4-MeOC ₆ H ₄	3d	12cd	66	>99:1	>99:1
8 ^d	$4-AcC_6H_4$	11d	4-MeOC ₆ H ₄	3d	12dd	62	>99:1	>99:1

^a Reagents and conditions (conditions B): 11 (0.25 mmol), 3 (2.0 equiv), Pd(PPh₃)₄ (10 mol%), AcOH (100 mol%), dioxane, reflux, 5 h, under N₂. ^b Isolated yield.

^c Determined by ¹H NMR (300 MHz) analysis of the crude reaction mixture obtained after evaporation.

^d Reaction time: 2 h.

¹H NMR (300 MHz, $CDCl_3$): $\delta = 8.01-7.94$ (m, 2 H), 7.67–7.50 (m, 3 H), 7.30 (d, J = 8.0 Hz, 2 H), 7.16 (d, J = 8.0 Hz, 2 H), 6.60 (q, J = 1.2 Hz, 1 H), 2.51 (d, J = 1.2 Hz, 3 H), 2.35 (s, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 153.4, 142.3, 140.3, 137.0, 133.1, 129.4, 129.2, 127.2, 126.4, 126.2, 21.2, 17.1.

MS (EI, 70 eV): m/z (%) = 272 [M⁺] (92.36), 115 (100).

Anal. Calcd for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92. Found: C, 70.16; H, 5.90.

(*E*)-2-(3-Methoxyphenyl)prop-1-en-1-yl Phenyl Sulfone [(*E*)-4ac]

Compound (*E*)-**4ac** was prepared similarly to compound (*E*)-**4aa** by conditions A. The reaction of **2a** (45 mg, 0.25 mmol), **3c** (76 mg, 0.50 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in THF (3 mL) afforded crude **4ac** after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness [**4ac/5ac** > 97:3, (*E*)-**4ac**/(*Z*)-**4ac** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**4ac** was isolated by flash chromatography (silica gel). Yield: 25 mg (35%); liquid.

IR (neat): 1602, 1576, 1483, 1446, 1430, 1303, 1145 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.99–7.92 (m, 2 H), 7.64–7.50 (m, 3 H), 7.29–7.21 (m, 1 H), 6.98–6.85 (m, 3 H), 6.59 (q, *J* = 1.5 Hz, 1 H), 3.79 (s, 3 H), 2.49 (d, *J* = 1.5 Hz, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 159.6, 153.4, 142.0, 141.5, 133.2, 129.7, 129.2, 127.5, 127.2, 118.7, 115.1, 112.1, 55.3, 17.3.

MS (EI, 70 eV): m/z (%) = 288 [M⁺] (100).

HRMS (MALDI): m/z calcd for $C_{16}H_{16}O_3SNa^+$ [M⁺ + Na]: 311.0712; found: 311.0712.

(*E*)-2-(4-Methoxyphenyl)prop-1-en-1-yl Phenyl Sulfone [(*E*)-4ad]

Compound (*E*)-**4ad** was prepared similarly to compound (*E*)-**4aa** by conditions A. The reaction of **2a** (45 mg, 0.25 mmol), **3d** (77 mg, 0.51 mmol), Pd(PPh₃)₄ (30 mg, 0.026 mmol), and AcOH (14 μ L, 0.24 mmol) in THF (3 mL) afforded a crude mixture of **4ad** and **5ad** after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness [**4ad/5ad** = 93:7, (*E*)-**4ad**/(*Z*)-**4ad** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**4ad** was isolated by flash chromatography (silica gel). Yield: 56 mg (78%); liquid.

IR (neat): 1599, 1568, 1511, 1445, 1297, 1258, 1143 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 8.01–7.93 (m, 2 H), 7.65–7.49 (m, 3 H), 7.37 (d, *J* = 9.0 Hz, 2 H), 6.87 (d, *J* = 9.0 Hz, 2 H), 6.58 (q, *J* = 1.2 Hz, 1 H), 3.81 (s, 3 H), 2.49 (d, *J* = 1.2 Hz, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 161.1, 152.9, 142.4, 133.0, 131.9, 129.1, 127.8, 127.1, 125.3, 114.0, 55.4, 16.9.

MS (EI, 70 eV): m/z (%) = 288 [M⁺] (100).

HRMS (EI): m/z calcd for $C_{16}H_{16}O_3S^+$ [M⁺]: 288.0815; found: 288.0828.

(*E*)-2-(3-Nitrophenyl)prop-1-en-1-yl Phenyl Sulfone [(*E*)-4ae]

Compound (*E*)-**4ae** was prepared similarly to compound (*E*)-**4ae** by conditions A. The reaction of **2a** (45 mg, 0.25 mmol), **3e** (84 mg, 0.50 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in THF (3 mL) afforded a crude mixture of **4ae** and **5ae** after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness [**4ae/5ae** = 94:6, (*E*)-**4ae**/(*Z*)-**4ae** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**4ae** was isolated by flash chromatography (silica gel). Yield: 50 mg (66%); liquid.

IR (neat): 1611, 1530, 1479, 1446, 1352, 1306, 1148, 1085 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): $\delta = 8.27-8.20$ (m, 2 H), 8.03–7.96 (m, 2 H), 7.77–7.53 (m, 5 H), 6.67 (q, J = 1.5 Hz, 1 H), 2.60 (d, J = 1.5 Hz, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 150.4, 148.4, 141.8, 141.4, 133.7, 132.2, 129.9, 129.8, 129.4, 127.4, 124.4, 121.3, 17.2.

MS (EI, 70 eV): m/z (%) = 303 [M⁺] (29.41), 115 (100).

HRMS (MALDI): m/z calcd for $C_{15}H_{13}NO_4SNa^+$ [M⁺ + Na]: 326.0458; found: 326.0477.

(*E*)-2-(3-Acetylphenyl)prop-1-en-1-yl Phenyl Sulfone [(*E*)-4af] Compound (*E*)-4af was prepared similarly to compound (*E*)-4aa by conditions A. The reaction of 2a (45 mg, 0.25 mmol), 3f (82 mg, 0.50 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in THF (3 mL) afforded crude 4af after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness [4af/5af > 99:1, (*E*)-4af/(*Z*)-4af > 99:1; by ¹H NMR analysis]. Pure (*E*)-4af was isolated by flash chromatography (silica gel). Yield: 60 mg (80%); liquid.

IR (neat): 1686, 1608, 1479, 1446, 1424, 1305, 1147 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 8.02–7.91 (m, 4 H), 7.69–7.47 (m, 4 H), 7.48 (t, *J* = 8.1 Hz, 1 H), 6.64 (q, *J* = 1.1 Hz, 1 H), 2.61 (s, 3 H), 2.57 (d, *J* = 1.1 Hz, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 197.4, 152.3, 141.8, 140.8, 137.5, 133.4, 130.7, 129.6, 129.3, 129.1, 128.6, 127.3, 125.9, 26.7, 17.3.

MS (EI, 70 eV): m/z (%) = 300 [M⁺] (66.66), 285 (100).

HRMS (MALDI): m/z calcd for $C_{17}H_{17}O_3S^+$ [M⁺ + H]: 301.0893; found: 301.0880.

(*E*)-2-(4-Acetylphenyl)prop-1-en-1-yl Phenyl Sulfone [(*E*)-4ag] Compound (*E*)-4ag was prepared similarly to compound (*E*)-4aa by conditions A. The reaction of 2a (45 mg, 0.25 mmol), 3g (82 mg, 0.50 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in THF (3 mL) afforded a crude mixture of 4ag and 5ag after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness [4ag/5ag = 94:6, (*E*)-4ag/(*Z*)-4ag > 99:1; by ¹H NMR analysis]. Pure (*E*)-4ag was isolated by flash chromatography (silica gel). Yield: 60 mg (80%); solid; mp 124– 126 °C (CH₂Cl₂–pentane).

IR (neat): 1685, 1604, 1559, 1446, 1405, 1304, 1146 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): $\delta = 8.01-7.96$ (m, 2 H), 7.94 (d, J = 8.6 Hz, 2 H), 7.72–7.53 (m, 3 H), 7.47 (d, J = 8.6 Hz, 2 H), 6.64 (q, J = 1.2 Hz, 1 H), 2.60 (s, 3 H), 2.56 (d, J = 1.2 Hz, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 197.3, 152.1, 144.5, 141.7, 137.8, 133.5, 129.3, 129.1, 128.7, 127.3, 126.6, 26.7, 17.2.

MS (EI, 70 eV): m/z (%) = 300 [M⁺] (58.00), 285 (100).

Anal. Calcd for $C_{17}H_{16}O_3S$: C, 67.98; H, 5.37. Found: C, 67.74; H, 5.42.

(E)-2-(1-Naphthyl)prop-1-en-1-yl Phenyl Sulfone [(E)-4ah]

Compound (*E*)-**4ah** was prepared similarly to compound (*E*)-**4aa** by conditions A. The reaction of **2a** (45 mg, 0.25 mmol), **3h** (87 mg, 0.51 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in THF (3 mL) afforded a crude mixture of **4ah** and **5ah** after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness [**4ah/5ah** = 91:9, (*E*)-**4ah**/(*Z*)-**4ah** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**4ah** was isolated by flash chromatography (silica gel). Yield: 56 mg (73%); liquid.

IR (neat): 1614, 1508, 1442, 1308, 1148 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 8.07–8.01 (m, 2 H), 7.88–7.78 (m, 2 H), 7.72–7.56 (m, 4 H), 7.53–7.37 (m, 3 H), 7.27–7.20 (m, 1 H), 6.49 (q, *J* = 1.5 Hz, 1 H), 2.62 (d, *J* = 1.5 Hz, 3 H).

 13 C NMR (75.4 MHz, CDCl₃): δ = 154.6, 141.9, 139.6, 133.6, 133.4, 130.4, 129.6, 129.3, 128.9, 128.5, 127.2, 126.7, 126.2, 125.1, 124.5, 124.2, 20.6.

MS (EI, 70 eV): m/z (%) = 308 [M⁺] (6.57), 167 (100).

HRMS (MALDI): m/z calcd for $C_{19}H_{16}O_2SNa^+$ [M⁺ + Na]: 331.0763; found: 331.0783.

(1E,3E)-2-Methylnona-1,3-dien-1-yl Phenyl Sulfone [(E)-4ai]

Compound (*E*)-**4ai** was prepared similarly to compound (*E*)-**4aa** by conditions A. The reaction of **2a** (45 mg, 0.25 mmol), **3i** (72 mg, 0.51 mmol), Pd(PPh₃)₄ (30 mg, 0.026 mmol), and AcOH (14 μ L, 0.24 mmol) in THF (3 mL) afforded a crude mixture of **4ai** and **5ai** after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness [**4ai/5ai** = 90:10, (*E*)-**4ai**/(*Z*)-**4ai** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**4ai** was isolated by flash chromatography (silica gel). Yield: 50 mg (72%); liquid.

IR (neat): 1637, 1587, 1461, 1446, 1305, 1145, 1085 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.95–7.88 (m, 2 H), 7.63–7.48 (m, 3 H), 6.20 (s, 1 H), 6.17 (dt, *J* = 6.6, 15.0 Hz, 1 H), 5.98 (d, *J* = 15.0 Hz, 1 H), 2.21 (d, *J* = 0.9 Hz, 3 H), 2.19–2.08 (m, 2 H), 1.46–1.18 (m, 6 H), 0.87 (t, *J* = 6.6 Hz, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 150.4, 142.5, 139.8, 133.0, 131.3, 129.1, 127.2, 127.1, 33.0, 31.3, 28.4, 22.4, 14.0, 13.2.

MS (EI, 70 eV): m/z (%) = 278 [M⁺] (14.12), 77 (100).

HRMS (MALDI): m/z calcd for $C_{16}H_{22}O_2SNa^+$ [M⁺ + Na]: 301.1233; found: 301.1257.

(1E,3E)-2-Methyl-4-phenylbuta-1,3-dien-1-yl Phenyl Sulfone[(E)-4aj]^{8b}

Compound (*E*)-**4aj** was prepared similarly to compound (*E*)-**4aa** by conditions A. The reaction of **2a** (45 mg, 0.25 mmol), **3j** (77 mg, 0.49 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in THF (3 mL) afforded a crude mixture of **4aj** and **5aj** after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness [**4aj/5aj** = 94:6, (*E*)-**4aj**/(*Z*)-**4aj** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**4aj** was isolated by flash chromatography (silica gel). Yield: 37 mg (52%); solid; mp 123–124 °C (Et₂O) (Lit.^{8b} 128–130 °C).

IR (neat): 1623, 1579, 1494, 1447, 1303, 1144 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): $\delta = 8.00-7.92$ (m, 2 H), 7.66–7.49 (m, 3 H), 7.46–7.39 (m, 2 H), 7.38–7.28 (m, 3 H), 6.96 (d, J = 16.1 Hz, 1 H), 6.68 (d, J = 16.1 Hz, 1 H), 6.42 (s, 1 H), 2.36 (s, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 149.7, 142.4, 135.8, 135.53, 135.51, 133.1, 129.4, 129.2, 129.1, 128.8, 127.2, 127.1, 13.2.

MS (EI, 70 eV): m/z (%) = 284 [M⁺] (11.16), 55 (100).

Phenyl (E)-3-Phenylbut-2-en-2-yl Sulfone [(E)-4ba]

Compound (*E*)-**4ba** was prepared similarly to compound (*E*)-**4aa** by conditions A. The reaction of **2b** (49 mg, 0.25 mmol), **3a** (61 mg, 0.50 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in THF (3 mL) afforded crude **4ba** after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness [**4ba/5ba** > 99:1, (*E*)-**4ba**/(*Z*)-**4ba** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**4ba** was isolated by flash chromatography (silica gel). Yield: 34 mg (50%); liquid.

IR (neat): 1620, 1598, 1490, 1445, 1303, 1159, 1127, 1080 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.99–7.92 (m, 2 H), 7.67–7.52 (m, 3 H), 7.40–7.24 (m, 3 H), 7.10–7.03 (m, 2 H), 2.47 (q, *J* = 1.5 Hz, 3 H), 1.86 (q, *J* = 1.5 Hz, 3 H).

 ^{13}C NMR (75.4 MHz, CDCl₃): δ = 149.8, 142.8, 141.4, 133.7, 133.1, 129.1, 128.5, 127.7, 127.1, 126.5, 22.6, 17.7.

MS (EI, 70 eV): m/z (%) = 272 [M⁺] (27.39), 91 (100).

HRMS (MALDI): m/z calcd for $C_{16}H_{17}O_2S^+$ [M⁺ + H]: 273.0944; found: 273.0945.

Phenyl (E)-2-Phenylhept-2-en-3-yl Sulfone [(E)-4ca]

Compound (*E*)-**4ca** was prepared similarly to compound (*E*)-**4aa** by conditions A. The reaction of **2c** (59 mg, 0.25 mmol), **3a** (61 mg, 0.50 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in THF (3 mL) afforded crude **4ca** after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness [**4ca/5ca** > 99:1, (*E*)-**4ca**/(*Z*)-**4ca** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**4ca** was isolated by flash chromatography (silica gel). Yield: 43 mg (55%); solid; mp 83–85 °C (Et₂O).

IR (neat): 1612, 1598, 1490, 1445, 1301, 1154, 1132, 1083 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): $\delta = 8.00-7.92$ (m, 2 H), 7.66–7.51 (m, 3 H), 7.39–7.24 (m, 3 H), 7.09–7.02 (m, 2 H), 2.32–2.21 (m, 5 H), 1.49–1.36 (m, 2 H), 1.13–0.99 (m, 2 H), 0.66 (t, J = 7.2 Hz, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 150.5, 142.7, 142.6, 139.7, 132.9, 129.0, 128.5, 127.6, 127.0, 126.1, 32.2, 30.7, 23.4, 22.5, 13.4.

MS (EI, 70 eV): m/z (%) = 314 [M⁺] (30.10), 91 (100).

Anal. Calcd for $C_{19}H_{22}O_2S$: C, 72.57; H, 7.05. Found: C, 72.38; H, 7.07.

Phenyl (E)-2-Phenylprop-1-en-1-yl Sulfoxide [(E)-6aa]¹⁶

Compound (*E*)-**6aa** was prepared similarly to compound (*E*)-**4aa** by conditions A. The reaction of **1a** (41 mg, 0.25 mmol), **3a** (61 mg, 0.50 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in THF (3 mL) afforded a crude mixture of **6aa** and **7aa** after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness [**6aa/7aa** = 94:6, (*E*)-**6aa**/(*Z*)-**6aa** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**6aa** was isolated by flash chromatography (silica gel). Yield: 30 mg (50%); liquid.

IR (neat): 1597, 1571, 1475, 1442, 1083, 1038 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.70–7.63 (m, 2 H), 7.57–7.41 (m, 5 H), 7.40–7.31 (m, 3 H), 6.54 (q, *J* = 1.2 Hz, 1 H), 2.58 (d, *J* = 1.2 Hz, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 148.0, 144.6, 139.3, 133.2, 130.6, 129.5, 129.3, 128.6, 126.2, 124.1, 18.1.

MS (EI, 70 eV): m/z (%) = 242 [M⁺] (2.27), 194 (100).

Phenyl (E)-2-(4-Tolyl)prop-1-en-1-yl Sulfoxide [(E)-6ab]

Compound (*E*)-**6ab** was prepared similarly to compound (*E*)-**4aa** by conditions A. The reaction of **1a** (41 mg, 0.25 mmol), **3b** (69 mg, 0.51 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in THF (3 mL) afforded a crude mixture of **6ab** and **7ab** after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness [**6ab/7ab** > 97:3, (*E*)-**6ab**/(*Z*)-**6ab** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**6ab** was isolated by flash chromatography (silica gel). Yield: 37 mg (58%); liquid.

IR (neat): 1608, 1582, 1563, 1514, 1475, 1442, 1083, 1039 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.69–7.62 (m, 2 H), 7.55–7.41 (m, 3 H), 7.35 (d, *J* = 8.1 Hz, 2 H), 7.16 (d, *J* = 8.1 Hz, 2 H), 6.52 (q, *J* = 0.9 Hz, 1 H), 2.56 (d, *J* = 0.9 Hz, 3 H), 2.35 (s, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 148.0, 144.7, 139.7, 136.3, 132.2, 130.6, 129.8, 129.3, 126.1, 124.1, 21.2, 18.0.

MS (EI, 70 eV): m/z (%) = 256 [M⁺] (2.95), 208 (100).

HRMS (MALDI): m/z calcd for $C_{16}H_{17}OS^+$ [M⁺ + H]: 257.0995; found: 257.0985.

(*E*)-2-(3-Methoxyphenyl)prop-1-en-1-yl Phenyl Sulfoxide [(*E*)-6ac]

Compound (*E*)-**6ac** was prepared similarly to compound (*E*)-**4aa** by conditions A. The reaction of **1a** (41 mg, 0.25 mmol), **3c** (76 mg, 0.50 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in THF (3 mL) afforded crude **6ac** after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness [**6ac**/**7ac** = 99:1, (*E*)-**6ac**/(*Z*)-**6ac** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**6ac** was isolated by flash chromatography (silica gel). Yield: 41 mg (59%); liquid.

IR (neat): 1601, 1574, 1485, 1475, 1443, 1428, 1039 cm⁻¹.

¹H NMR (300 MHz, $CDCl_3$): $\delta = 7.67-7.61$ (m, 2 H), 7.55-7.41 (m, 3 H), 7.26 (t, J = 7.8 Hz, 1 H), 7.04–6.99 (m, 1 H), 6.96–6.93 (m, 1 H), 6.91–6.85 (m, 1H), 6.53 (q, J = 1.5 Hz, 1 H), 3.78 (s, 3 H), 2.55 (d, J = 1.5 Hz, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 159.6, 147.9, 144.4, 140.7, 133.2, 130.6, 129.6, 129.3, 124.0, 118.6, 114.7, 111.9, 55.3, 18.1.

MS (EI, 70 eV): m/z (%) = 272 [M⁺] (1.91), 224 (100).

HRMS (MALDI): m/z calcd for $C_{16}H_{16}O_2SNa^+$ [M⁺ + Na]: 295.0763; found: 295.0759.

(*E*)-2-(4-Methoxyphenyl)prop-1-en-1-yl Phenyl Sulfoxide [(*E*)-6ad]

Compound (*E*)-**6ad** was prepared similarly to compound (*E*)-**4aa** by conditions A. The reaction of **1a** (41 mg, 0.25 mmol), **3d** (76 mg, 0.50 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in THF (3 mL) afforded a crude mixture of **6ad** and **7ad** after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness [**6ad/7ad** = 95:5, (*E*)-**6ad**/(*Z*)-**6ad** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**6ad** was isolated by flash chromatography (silica gel). Yield: 35 mg (52%); liquid.

IR (neat): 1604, 1567, 1513, 1463, 1442, 1255, 1183, 1034 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.69–7.61 (m, 2 H), 7.56–7.44 (m, 3 H), 7.42 (d, *J* = 9.0 Hz, 2 H), 6.87 (d, *J* = 9.0 Hz, 2 H), 6.49 (q, *J* = 0.9 Hz, 1 H), 3.81 (s, 3 H), 2.56 (d, *J* = 0.9 Hz, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 160.6, 147.5, 144.9, 131.3, 131.1, 130.5, 129.2, 127.6, 124.0, 113.9, 55.3, 17.8.

MS (EI, 70 eV): m/z (%) = 273 (3.15), 272 [M⁺] (1.82), 224 (100).

HRMS (MALDI): m/z calcd for $C_{16}H_{17}O_2S^+$ [M⁺ + H]: 273.0944; found: 273.0961.

(*E*)-2-(3-Nitrophenyl)prop-1-en-1-yl Phenyl Sulfoxide [(*E*)-6ae] Compound (*E*)-6ae was prepared similarly to compound (*E*)-4aa by conditions A. The reaction of 1a (41 mg, 0.25 mmol), 3e (85 mg, 0.51 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in THF (3 mL) afforded a crude mixture of 6ae and 7ae after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness [6ae/7ae > 96:4, (*E*)-6ae/(*Z*)-6ae > 99:1; by ¹H NMR analysis]. Pure (*E*)-6ae was isolated by flash chromatography (silica gel). Yield: 35 mg (49%); liquid.

IR (neat): 1615, 1530, 1476, 1443, 1351, 1083, 1038 cm⁻¹.

¹H NMR (300 MHz, $CDCl_3$): $\delta = 8.27-8.24$ (m, 1 H), 8.20–8.15 (m, 1 H), 7.79–7.72 (m, 1 H), 7.69–7.62 (m, 2 H), 7.57–7.43 (m, 4 H), 6.61 (q, J = 1.5 Hz, 1 H), 2.60 (d, J = 1.5 Hz, 3 H).

 ^{13}C NMR (75.4 MHz, CDCl₃): δ = 144.8, 144.0, 142.2, 140.8, 135.9, 131.9, 131.0, 129.7, 129.5, 123.94, 123.90, 121.1, 18.0.

MS (EI, 70 eV): m/z (%) = 288 (5.97), 287 [M⁺] (2.64), 239 (100).

HRMS (MALDI): m/z calcd for C₁₅H₁₄O₃SN⁺ [M⁺ + H]: 288.0689; found: 288.0672.

(*E*)-2-(4-Acetylphenyl)prop-1-en-1-yl Phenyl Sulfoxide [(*E*)-6ag]

Compound (*E*)-**6ag** was prepared similarly to compound (*E*)-**4aa** by conditions A. The reaction of **1a** (41 mg, 0.25 mmol), **3g** (83 mg, 0.51 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in THF (3 mL) afforded crude **6ag** after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness [**6ag/7ag** > 99:1, (*E*)-**6ag**/(*Z*)-**6ag** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**6ag** was isolated by flash chromatography (silica gel). Yield: 34 mg (48%); liquid.

IR (neat): 1683, 1604, 1557, 1475, 1443, 1405, 1358, 1268, 1039 $\rm cm^{-1}.$

¹H NMR (300 MHz, CDCl₃): δ = 7.93 (d, *J* = 8.4 Hz, 2 H), 7.70– 7.63 (m, 2 H), 7.57–7.46 (m, 5 H), 6.60 (q, *J* = 1.2 Hz, 1 H), 2.59 (d, *J* = 1.2 Hz, 3 H), 2.59 (s, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 197.3, 146.6, 144.2, 143.7, 137.4, 135.1, 130.9, 129.4, 128.6, 126.4, 124.1, 26.7, 18.1.

MS (EI, 70 eV): m/z (%) = 285 (3.31), 284 [M⁺] (1.43), 236 (100).

HRMS (MALDI): m/z calcd for $C_{17}H_{17}O_2S^+$ [M⁺ + H]: 285.0944; found: 285.0928.

(E)-2-(1-Naphthyl)prop-1-en-1-yl Phenyl Sulfoxide [(E)-6ah]

Compound (*E*)-**6ah** was prepared similarly to compound (*E*)-**4aa** by conditions A. The reaction of **1a** (41 mg, 0.25 mmol), **3h** (86 mg, 0.50 mmol; should be recrystallized from H₂O immediately before use), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in THF (3 mL) afforded a crude mixture of **6ah** and **7ah** after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness [**6ah/7ah** > 94:6, (*E*)-**6ah**/(*Z*)-**6ah** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**6ah** was isolated by flash chromatography (silica gel). Yield: 30 mg (41%); liquid.

IR (neat): 1613, 1590, 1507, 1475, 1442, 1083, 1040 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.91–7.72 (m, 5 H), 7.62–7.40 (m, 6 H), 7.30–7.26 (m, 1 H), 6.41 (q, *J* = 1.2 Hz, 1 H), 2.67 (d, *J* = 1.2 Hz, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 149.4, 144.6, 139.0, 136.6, 133.6, 130.7, 129.8, 129.4, 128.6, 128.5, 126.5, 126.1, 125.1, 124.7, 124.4, 124.0, 21.4.

MS (EI, 70 eV): m/z (%) = 293 (3.07), 292 [M⁺] (6.94), 165 (100).

HRMS (MALDI): m/z calcd for $C_{19}H_{17}OS^+$ [M⁺ + H]: 293.0995; found: 293.0981.

(1*E*,3*E*)-2-Methylocta-1,3-dien-1-yl Phenyl Sulfoxide [(*E*)-6ak] Compound (*E*)-6ak was prepared similarly to compound (*E*)-4aa by conditions A. The reaction of 1a (41 mg, 0.25 mmol), 3k (64 mg, 0.50 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in THF (3 mL) afforded a crude mixture of 6ak and 7ak after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness [6ak/7ak > 92:8, (*E*)-6ak/(*Z*)-6ak > 99:1; by ¹H NMR analysis]. Pure (*E*)-6al was isolated by flash chromatography (silica gel). Yield: 33 mg (53%); liquid.

IR (neat): 1638, 1581, 1475, 1466, 1443, 1379, 1183, 1039 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.63–7.55 (m, 2 H), 7.54–7.39 (m, 3 H), 6.13–6.03 (m, 3 H), 2.25 (d, *J* = 0.6 Hz, 3 H), 2.19–2.08 (m, 2 H), 1.45–1.19 (m, 4 H), 0.88 (t, *J* = 7.2 Hz, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 146.1, 144.8, 138.1, 133.5, 131.1, 130.5, 129.2, 124.1, 32.6, 31.0, 22.2, 14.7, 13.8.

MS (EI, 70 eV): m/z (%) = 249 (3.30), 248 [M⁺] (1.39), 143 (100).

HRMS (MALDI): m/z calcd for $C_{15}H_{21}OS^+$ [M⁺ + H]: 249.1308; found: 249.1299.

(1*E*,3*E*)-2-Methyl-4-phenylbuta-1,3-dien-1-yl Phenyl Sulfoxide [(*E*)-6aj]

Compound (*E*)-**6aj** was prepared similarly to compound (*E*)-**4aa** by conditions A. The reaction of **1a** (40 mg, 0.24 mmol), **3j** (78 mg, 0.50 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in THF (3 mL) afforded a crude mixture of **6aj** and **7aj** after evaporation of the solvent, filtration though a pad of silica gel, and evaporation to dryness **[6aj/7aj** > 94:6, (*E*)-**6aj**/(*Z*)-**6aj** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**6aj** was isolated by flash chromatography (silica gel). Yield: 31 mg (46%); liquid.

IR (neat): 1623, 1599, 1579, 1494, 1474, 1443, 1082, 1036 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.67–7.60 (m, 2 H), 7.55–7.37 (m, 5 H), 7.38–7.24 (m, 3 H), 6.87 (d, *J* = 16.2 Hz, 1 H), 6.73 (d, *J* = 16.2 Hz, 1 H), 6.32 (s, 1 H), 2.39 (s, 3 H).

 ^{13}C NMR (75.4 MHz, CDCl₃): δ = 145.3, 144.6, 135.9, 135.8, 134.4, 130.6, 129.24, 129.16, 128.75, 128.72, 126.9, 124.0, 14.7.

MS (EI, 70 eV): m/z (%) = 268 [M⁺] (1.03), 91 (100).

HRMS (EI): m/z calcd for $C_{17}H_{16}OS^+$ [M⁺]: 268.0922; found: 268.0923.

(*E*)-2-Phenylundec-2-ene [(*E*)-9aa] under Conditions B; Typical Procedure¹⁷

Compound **3a** (61 mg, 0.50 mmol), **8a** (38 mg, 0.25 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), AcOH (14 μ L, 0.24 mmol), and dioxane (3 mL) were added into a dried reaction tube under a N₂ atmosphere. The resulting mixture was stirred under reflux and monitored by TLC (PE). After evaporation to dryness, the crude mixture was analyzed by ¹H NMR spectroscopy, from which the **9aa/10aa** ratio of 92:8 and (*E*)-**9aa**/(*Z*)-**9aa** ratio of >99:1 was obtained (see Table 7). Purification of the residue by flash chromatography (silica gel, PE) gave a mixture of (*E*)-**9aa** and **10aa**. Yield: 43 mg (75%); (*E*)-**9aa/10aa** = 96:4; liquid.

IR (neat): 1597, 1494, 1465, 1445, 1378 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ [(*E*)-**9aa**] = 7.43–7.36 (m, 2 H), 7.35–7.25 (m, 2 H), 7.25–7.17 (m, 1 H), 5.80 (qt, *J* = 1.1, 6.6 Hz, 1 H), 2.26–2.15 (m, 2 H), 2.04 (d, *J* = 1.1 Hz, 3 H), 1.51–1.20 (m, 12 H), 0.90 (t, *J* = 6.6 Hz, 3 H); δ (**10aa**) = 5.27 (s, 1 H), 5.07 (s, 1 H), 2.51 (t, *J* = 7.5 Hz, 2 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 144.0, 134.4, 128.8, 128.1, 126.4, 125.5, 31.9, 29.62, 29.56, 29.4, 29.3, 28.8, 22.7, 15.7, 14.1. MS (EI, 70 eV): m/z (%) = 230 [M⁺] (35.01), 118 (100).

(*E*)-2-(4-Tolyl)undec-2-ene [(*E*)-9ab]

Compound (*E*)-**9ab** was prepared similarly to compound (*E*)-**9aa** by conditions B. The reaction of **3b** (68 mg, 0.50 mmol), **8a** (38 mg, 0.25 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in dioxane (3 mL) afforded a crude mixture of **9ab** and **10ab** after evaporation [**9ab/10ab** = 91:9, (*E*)-**9ab/**(*Z*)-**9ab** > 99:1; by ¹H NMR analysis]. A mixture of (*E*)-**9ab** and **10ab** was isolated by flash chromatography (silica gel). Yield: 46 mg (75%); (*E*)-**9ab/10ab** = 93:7; liquid.

IR (neat): 1512, 1465, 1377 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ [(*E*)-**9ab**] = 7.29 (d, *J* = 8.4 Hz, 2 H), 7.13 (d, *J* = 8.4 Hz, 2 H), 5.77 (qt, *J* = 1.2, 7.2 Hz, 1 H), 2.35 (s, 3 H), 2.25–2.14 (m, 2 H), 2.02 (d, *J* = 1.2 Hz, 3 H), 1.54–1.17 (m, 12 H), 0.90 (t, *J* = 6.9 Hz, 3 H); δ (**10ab**) = 5.25 (s, 1 H), 5.02 (s, 1 H), 2.49 (t, *J* = 7.5 Hz, 2 H).

 ^{13}C NMR (75.4 MHz, CDCl₃): δ = 141.2, 136.0, 134.2, 128.8, 128.0, 125.4, 31.9, 29.7, 29.6, 29.4, 29.3, 28.8, 22.7, 21.0, 15.7, 14.1.

MS (EI, 70 eV): m/z (%) = 244 [M⁺] (24.78), 145 (100).

HRMS (EI): *m/z* calcd for C₁₈H₂₈ [M⁺]: 244.2191; found: 244.2184.

(E)-2-(2-Methoxyphenyl)undec-2-ene [(E)-9al]

Compound (*E*)-**9al** was prepared similarly to compound (*E*)-**9aa** by conditions B. The reaction of **3l** (76 mg, 0.50 mmol), **8a** (38 mg, 0.25 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in dioxane (3 mL) afforded a crude mixture of **9al** and **10al** after evaporation [**9al**/**10al** = 91:9, (*E*)-**9al**/(*Z*)-**9al** > 99:1; by ¹H NMR analysis]. A mixture of (*E*)-**9al** and **10al** was isolated by flash chromatography (silica gel). Yield: 43 mg (66%); (*E*)-**9al**/**10al** = 91:9; liquid.

IR (neat): 1597, 1578, 1489, 1464, 1434, 1031 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ [(*E*)-**9al**] = 7.20–7.12 (m, 1 H), 7.10–7.03 (m, 1 H), 6.90–6.77 (m, 2 H), 5.41 (qt, *J* = 1.5, 7.2 Hz, 1 H), 3.76 (s, 3 H), 2.17–2.06 (m, 2 H), 1.92 (d, *J* = 1.5 Hz, 3 H), 1.45–1.08 (m, 12 H), 0.84 (t, *J* = 7.2 Hz, 3 H); δ (**10a**) = 5.08 (s, 1 H), 4.95 (s, 1 H), 2.42 (t, *J* = 6.9 Hz, 2 H).

 ^{13}C NMR (75.4 MHz, CDCl₃): δ = 156.6, 135.1, 134.6, 130.3, 129.7, 127.7, 120.5, 110.6, 55.4, 31.9, 29.6, 29.5, 29.40, 29.36, 28.3, 22.7, 17.0, 14.1.

MS (EI, 70 eV): m/z (%) = 260 [M⁺] (51.17), 161 (100).

HRMS (EI): m/z calcd for $C_{18}H_{28}O^{+1}$ [M⁺]: 260.2140; found: 260.2162.

(*E*)-2-(4-Methoxyphenyl)undec-2-ene [(*E*)-9ad]

Compound (*E*)-**9ad** was prepared similarly to compound (*E*)-**9aa** by conditions B. The reaction of **3d** (76 mg, 0.50 mmol), **8a** (38 mg, 0.25 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in dioxane (3 mL) afforded a crude mixture of **9ad** and **10ad** after evaporation [**9ad/10ad** = 91:9, (*E*)-**9ad**/(*Z*)-**9ad** > 99:1; by ¹H NMR analysis]. A mixture of (*E*)-**9ad** and **10ad** was isolated by flash chromatography (silica gel). Yield: 50 mg (77%); (*E*)-**9ad**/**10ad** = 97:3; liquid.

IR (neat): 1608, 1512, 1464, 1441, 1246 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ [(*E*)-**9ad**] = 7.32 (d, *J* = 9.0 Hz, 2 H), 6.85 (d, *J* = 9.0 Hz, 2 H), 5.71 (qt, *J* = 1.2, 6.9 Hz, 1 H), 3.81 (s, 3 H), 2.23–2.11 (m, 2 H), 2.00 (d, *J* = 1.2 Hz, 3 H), 1.50–1.20 (m, 12 H), 0.89 (t, *J* = 6.6 Hz, 3 H); δ (**10ad**) = 5.19 (s, 1 H), 4.96 (s, 1 H), 2.46 (t, *J* = 7.5 Hz, 2 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 158.3, 136.6, 133.7, 127.2, 126.5, 113.4, 55.2, 31.9, 29.7, 29.6, 29.4, 29.3, 28.8, 22.7, 15.8, 14.1.

MS (EI, 70 eV): m/z (%) = 260 [M⁺] (48.79), 161 (100).

HRMS (EI): m/z calcd for $C_{18}H_{28}O^+$ [M⁺]: 260.2140; found: 260.2128.

(E)-2-(3-Nitrophenyl)undec-2-ene [(E)-9ae]

Compound (*E*)-**9ae** was prepared similarly to compound (*E*)-**9aa** by conditions B. The reaction of **3e** (84 mg, 0.50 mmol), **8a** (38 mg, 0.25 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in dioxane (3 mL) afforded a crude mixture of **9ae** and **10ae** after evaporation [**9ae/10ae** = 89:11, (*E*)-**9ae/**(*Z*)-**9ae** > 99:1; by ¹H NMR analysis]. A mixture of (*E*)-**9ae** and **10ae** was isolated by flash chromatography (silica gel). Yield: 46 mg (67%); (*E*)-**9ae/10ae** = 93:7; liquid.

IR (neat): 1530, 1465, 1349 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ [(*E*)-**9ae**] = 8.24–8.20 (m, 1 H), 8.09–8.03 (m, 1 H), 7.72–7.66 (m, 1 H), 7.45 (t, *J* = 8.1 Hz, 1 H), 5.92 (qt, *J* = 1.2, 7.5 Hz, 1 H), 2.28–2.17 (m, 2 H), 2.07 (d, *J* = 1.2 Hz, 3 H), 1.51–1.22 (m, 12 H), 0.89 (t, *J* = 6.9 Hz, 3 H); δ (**10ae**) = 5.38 (s, 1 H), 5.20 (s, 1 H), 2.52 (t, *J* = 7.2 Hz, 2 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 145.5, 132.6, 131.57, 131.48, 128.9, 121.1, 120.4, 31.9, 29.5, 29.41, 29.37, 29.28, 28.9, 22.7, 15.6, 14.1.

MS (EI, 70 eV): m/z (%) = 275 [M⁺] (4.11), 163 (100).

HRMS (EI): m/z calcd for $C_{17}H_{25}NO_2^+$ [M⁺]: 275.1885; found: 275.1888.

(E)-2-(4-Acetylphenyl)undec-2-ene [(E)-9ag]

Compound (*E*)-**9ag** was prepared similarly to compound (*E*)-**9aa** by conditions B. The reaction of **3g** (82 mg, 0.50 mmol), **8a** (38 mg, 0.25 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in dioxane (3 mL) afforded a crude mixture of **9ag** and **10ag** after evaporation [**9ag/10ag** = 93:7, (*E*)-**9ag**/(*Z*)-**9ag** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**9ag** was isolated by flash chromatography (silica gel). Yield: 42 mg (62%); liquid.

IR (neat): 1684, 1602, 1466, 1408, 1267 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.90 (d, *J* = 8.7 Hz, 2 H), 7.46 (d, *J* = 8.7 Hz, 2 H), 5.92 (qt, *J* = 1.2, 7.2 Hz, 1 H), 2.59 (s, 3 H), 2.27–2.16 (m, 2 H), 2.05 (d, *J* = 1.2 Hz, 3 H), 1.54–1.22 (m, 12 H), 0.89 (t, *J* = 6.6 Hz, 3 H).

 ^{13}C NMR (75.4 MHz, CDCl₃): δ = 197.8, 148.7, 135.1, 133.7, 131.4, 128.4, 125.5, 31.9, 29.5, 29.4, 29.3, 28.9, 26.6, 22.7, 15.5, 14.1.

MS (EI, 70 eV): m/z (%) = 272 [M⁺] (3.45), 181 (100).

HRMS (MALDI): m/z calcd for $C_{19}H_{29}O^+$ [M⁺ + H]: 273.2213; found: 273.2222.

(E)-2-(1-Naphthyl)undec-2-ene [(E)-9ah]

Compound (*E*)-**9ah** was prepared similarly to compound (*E*)-**9aa** by conditions B. The reaction of **3h** (86 mg, 0.50 mmol), **8a** (38 mg, 0.25 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in dioxane (3 mL) afforded a crude mixture of **9ah** and **10ah** after evaporation [**9ah/10ah** = 90:10, (*E*)-**9ah**/(*Z*)-**9ah** > 99:1; by ¹H NMR analysis]. A mixture of (*E*)-**9ah** and **10ah** was isolated by flash chromatography (silica gel). Yield: 52 mg (74%), (*E*)-**9ah**/**10ah** = 92:8; liquid.

IR (neat): 1591, 1578, 1506, 1465, 1394, 1376 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ [(*E*)-**9ah**] = 8.07–7.97 (m, 1 H), 7.92–7.83 (m, 1 H), 7.77 (d, *J* = 7.8 Hz, 1 H), 7.59–7.38 (m, 3 H), 7.30 (d, *J* = 6.9 Hz, 1 H), 5.56 (t, *J* = 6.9 Hz, 1 H), 2.38–2.27 (m, 2 H), 2.13 (s, 3 H), 1.64–1.24 (m, 12 H), 0.95 (t, *J* = 6.6 Hz, 3 H); δ (**10ah**) = 5.43 (s, 1 H), 5.11 (s, 1 H), 2.55 (t, *J* = 7.5 Hz, 2 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 144.3, 134.6, 133.7, 131.3, 128.3, 127.8, 126.6, 125.9, 125.8, 125.5, 125.4, 124.9, 31.9, 29.61, 29.57, 29.45, 29.39, 28.5, 22.7, 18.9, 14.2.

MS (EI, 70 eV): m/z (%) = 280 [M⁺] (51.05), 181 (100).

HRMS (MALDI): m/z calcd for $C_{21}H_{29}^+$ [M⁺ + H]: 281.2264; found: 281.2256.

(E)-2-Phenylpentadec-2-ene [(E)-9ba]

Compound (*E*)-**9ba** was prepared similarly to compound (*E*)-**9aa** by conditions B. The reaction of **3a** (61 mg, 0.50 mmol), **8b** (52 mg, 0.25 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in dioxane (3 mL) afforded a crude mixture of **9ba** and **10ba** after evaporation [**9ba/10ba** = 92:8, (*E*)-**9ba/**(*Z*)-**9ba** > 99:1; by ¹H NMR analysis]. A mixture of (*E*)-**9ba** and **10ba** was isolated by flash chromatography (silica gel). Yield: 36 mg (50%); (*E*)-**9ba/10ba** = 93:7; liquid.

IR (neat): 1597, 1493, 1465, 1442 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ [(*E*)-**9ba**] = 7.43–7.35 (m, 2 H), 7.36–7.27 (m, 2 H), 7.26–7.17 (m, 1 H), 5.80 (t, *J* = 7.2 Hz, 1 H), 2.26–2.14 (m, 2 H), 2.04 (s, 3 H), 1.60–1.18 (m, 20 H), 0.89 (t, *J* = 6.6 Hz, 3 H); δ (**10ba**) = 5.27 (s, 1 H), 5.06 (s, 1 H), 2.50 (t, *J* = 7.5 Hz, 2 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 144.0, 134.4, 128.8, 128.1, 126.4, 125.6, 31.9, 29.69, 29.66, 29.63, 29.60, 29.43, 29.37, 28.8, 22.7, 15.7, 14.1.

MS (EI, 70 eV): m/z (%) = 286 [M⁺] (37.23), 118 (100).

HRMS (EI): m/z calcd for $C_{21}H_{34}^+$ [M⁺]: 286.2661; found: 286.2651.

(E)-2-(4-Methoxyphenyl)nonadec-2-ene [(E)-9cd]

Compound (*E*)-**9cd** was prepared similarly to compound (*E*)-**9ca** by conditions B. The reaction of **3d** (76 mg, 0.50 mmol), **8c** (66 mg, 0.25 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in dioxane (3 mL) afforded a crude mixture of **9cd** and **10cd** after evaporation [**9cd/10cd** = 93:7, (*E*)-**9cd**/(*Z*)-**9cd** > 99:1; by ¹H NMR analysis]. A mixture of (*E*)-**9cd** and **10cd** was isolated by flash chromatography (silica gel); yield: 32 mg (34%); (*E*)-**9cd**/**10cd** = 95:5. Pure (*E*)-**9cd** was obtained by recrystallization (Et₂O); solid; mp 45–47 °C (Et₂O).

IR (neat): 1609, 1516, 1471, 1464 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.33 (d, *J* = 9.2 Hz, 2 H), 6.86 (d, *J* = 9.2 Hz, 2 H), 5.70 (t, *J* = 6.9 Hz, 1 H), 3.80 (s, 3 H), 2.24–2.12 (m, 2 H), 2.00 (s, 3 H), 1.51–1.18 (m, 28 H), 0.88 (t, *J* = 6.9 Hz, 3 H).

 ^{13}C NMR (75.4 MHz, CDCl₃): δ = 158.3, 136.6, 133.7, 127.3, 126.5, 113.4, 55.2, 31.9, 29.70, 29.66, 29.60, 29.43, 29.37, 28.8, 22.7, 15.8, 14.1.

MS (EI, 70 eV): m/z (%) = 372 [M⁺] (36.55), 161 (100).

Anal. Calcd for $C_{26}H_{44}O$: C, 83.80; H, 11.90. Found: C, 83.52; H, 11.82

(E)-1-Cyclohexyl-2-(4-methoxyphenyl)prop-1-ene [(E)-9dd]

Compound (*E*)-9dd was prepared similarly to compound (*E*)-9aa by conditions B. The reaction of 3d (76 mg, 0.50 mmol), 8d (31 mg, 0.25 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in dioxane (3 mL) afforded a crude mixture of 9dd and 10dd after evaporation [9dd/10dd = 88:12, (*E*)-9dd/(*Z*)-9dd > 99:1; by ¹H NMR analysis]. A mixture of (*E*)-9dd and 10dd was isolated by flash chromatography (silica gel). Yield: 25 mg (44%); (*E*)-9dd/10dd = 92:8; liquid.

IR (neat): 1607, 1511, 1463, 1447, 1246 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ [(*E*)-**9dd**] = 7.33 (d, J = 8.4 Hz, 2 H), 6.85 (d, J = 8.4 Hz, 2 H), 5.56 (d, J = 9.0 Hz, 1 H), 3.81 (s, 3 H), 2.40–2.26 (m, 1 H), 2.02 (s, 3 H), 1.81–1.50 (m, 4 H), 1.42–1.04 (m, 6 H); δ (**10dd**) = 5.20 (s, 1 H), 4.93 (s, 1 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 158.3, 136.6, 133.1, 132.0, 126.5, 113.4, 55.3, 37.7, 33.2, 26.1, 26.0, 15.8.

MS (EI, 70 eV): m/z (%) = 230 [M⁺] (100).

HRMS (EI): m/z calcd for $C_{16}H_{22}O^+$ [M⁺]: 230.1671; found: 230.1683.

(E)-3-(4-Methoxyphenyl)-1-phenylbut-2-ene [(E)-9ed]

Compound (*E*)-**9ed** was prepared similarly to compound (*E*)-**9aa** by conditions B. The reaction of **3d** (76 mg, 0.50 mmol), **8e** (33 mg, 0.25 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in dioxane (3 mL) afforded a crude mixture of **9ed** and **10ed** after evaporation [**9ed/10ed** > 93:7, (*E*)-**9ed**/(*Z*)-**9ed** 95:5; by ¹H NMR analysis]. Pure (*E*)-**9ed** was isolated by flash chromatography (silica gel). Yield: 45 mg (76%); liquid.

IR (neat): 1607, 1574, 1511, 1494, 1453, 1441, 1245 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.41–7.17 (m, 7 H), 6.84 (d, J = 8.7 Hz, 2 H), 5.92 (t, J = 7.5 Hz, 1 H), 3.81 (s, 3 H), 3.56 (d, J = 7.5 Hz, 2 H), 2.13 (s, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 158.5, 141.2, 136.1, 134.9, 128.42, 128.40, 126.7, 125.9, 125.1, 113.5, 55.3, 34.9, 16.0.

MS (EI, 70 eV): m/z (%) = 238 [M⁺] (94.32), 223 (100).

HRMS (EI): m/z calcd for $C_{17}H_{18}O^+$ [M⁺]: 238.1358; found: 238.1378.

(E)-1,2-Diphenylprop-1-ene [(E)-12aa]¹⁸

Compound (*E*)-**12aa** was prepared similarly to compound (*E*)-**9aa** by conditions B. The reaction of **3a** (61 mg, 0.50 mmol), **11a** (29 mg, 0.25 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in dioxane (3 mL) afforded crude **12aa** after evaporation [**12aa/13aa** > 99:1, (*E*)-**12aa/**(*Z*)-**12aa** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**12aa** was isolated by flash chromatography (silica gel). Yield: 20 mg (41%); solid; mp 84–86 °C (Et₂O) (Lit.^{18a} 83.5–84 °C).

IR (neat): 1598, 1566, 1494, 1483, 1444 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.57–7.51 (m, 2 H), 7.43–7.35 (m, 6 H), 7.34–7.25 (m, 2 H), 6.85 (q, *J* = 0.9 Hz, 1 H), 2.30 (d, *J* = 0.9 Hz, 3 H).

 ^{13}C NMR (75.4 MHz, CDCl₃): δ = 143.9, 138.3, 137.4, 129.1, 128.3, 128.2, 127.7, 127.2, 126.5, 126.0, 17.5.

MS (EI, 70 eV): m/z (%) = 194 [M⁺] (100).

(E)-1-Phenyl-2-(4-tolyl)prop-1-ene [(E)-12ab]¹⁹

Compound (*E*)-**12ab** was prepared similarly to compound (*E*)-**9aa** by conditions B. The reaction of **3b** (67 mg, 0.49 mmol), **11a** (29 mg, 0.25 mmol), Pd(PPh₃)₄ (30 mg, 0.026 mmol), and AcOH (14 μ L, 0.24 mmol) in dioxane (3 mL) afforded crude **12ab** after evaporation [**12ab/13ab** > 99:1, (*E*)-**12ab**/(*Z*)-**12ab** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**12ab** was isolated by flash chromatography (silica gel). Yield: 38 mg (73%); solid; mp 67–69 °C (Et₂O), (Lit.¹⁹ 66–66.5 °C).

IR (neat): 1510, 1486, 1444 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.43 (d, *J* = 8.1 Hz, 2 H), 7.40– 7.33 (m, 4 H), 7.29–7.20 (m, 1 H), 7.19 (d, *J* = 8.1 Hz, 2 H), 6.83 (q, *J* = 1.2 Hz, 1 H), 2.38 (s, 3 H), 2.28 (d, *J* = 1.2 Hz, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 141.0, 138.4, 137.2, 136.9, 129.1, 129.0, 128.1, 126.9, 126.3, 125.8, 21.1, 17.4.

MS (EI, 70 eV): m/z (%) = 208 [M⁺] (100).

(E)-2-(4-Methoxyphenyl)-1-phenylprop-1-ene [(E)-12ad]²⁰

Compound (*E*)-**12ad** was prepared similarly to compound (*E*)-**9aa** by conditions B. The reaction of **3d** (76 mg, 0.50 mmol), **11a** (29 mg, 0.25 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in dioxane (3 mL) afforded crude **12ad** after evaporation [**12ad/13ad** > 99:1, (*E*)-**12ad**/(*Z*)-**12ad** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**12ad** was isolated by flash chromatography (silica gel). Yield: 44 mg (79%); solid; mp 93–94 °C (Et₂O) (Lit.²⁰ 95–98 °C).

IR (neat): 1619, 1605, 1514, 1446, 1414, 1261, 1181, 1028 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.49 (d, *J* = 9.0 Hz, 2 H), 7.43– 7.34 (m, 4 H), 7.30–7.20 (m, 1 H), 6.93 (d, *J* = 9.0 Hz, 2 H), 6.81 (q, *J* = 1.2 Hz, 1 H), 3.85 (s, 3 H), 2.28 (d, *J* = 1.2 Hz, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 158.9, 138.5, 136.7, 136.3, 129.1, 128.1, 127.0, 126.22, 126.18, 113.6, 55.3, 17.4.

MS (EI, 70 eV): m/z (%) = 224 [M⁺] (100).

Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.38; H, 7.21.

(E)-2-(4-Acetylphenyl)-1-phenylprop-1-ene [(E)-12ag]

Compound (*E*)-12ag was prepared similarly to compound (*E*)-9aa by conditions B. The reaction of 3g (82 mg, 0.50 mmol), 11a (29

mg, 0.25 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in dioxane (3 mL) afforded crude **12ag** after evaporation [**12ag/13ag** > 99:1, (*E*)-**12ag**/(*Z*)-**12ag** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**12ag** was isolated by flash chromatography (silica gel). Yield: 26 mg (44%); solid; mp 104–106 °C (Et₂O).

IR (neat): 1677, 1599, 1450, 1410, 1357, 1272 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.96 (d, *J* = 8.4 Hz, 2 H), 7.61 (d, *J* = 8.4 Hz, 2 H), 7.45–7.35 (m, 4 H), 7.32–7.25 (m, 1 H), 6.95 (q, *J* = 1.5 Hz, 1 H), 2.63 (s, 3 H), 2.31 (d, *J* = 1.5 Hz, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 197.7, 148.5, 137.7, 136.3, 135.7, 129.6, 129.1, 128.5, 128.2, 126.9, 126.0, 26.6, 17.3.

MS (EI, 70 eV): m/z (%) = 236 [M⁺] (93.22), 43 (100).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.47; H, 6.96.

(E)-2-(1-Naphthyl)-1-phenylprop-1-ene [(E)-12ah]

Compound (*E*)-**12ah** was prepared similarly to compound (*E*)-**9aa** by conditions B. The reaction of **3h** (85 mg, 0.49 mmol), **11a** (29 mg, 0.25 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in dioxane (3 mL) afforded crude **12ah** after evaporation [**12ah/13ah** > 99:1, (*E*)-**12ah**/(*Z*)-**12ah** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**12ah** was isolated by flash chromatography (silica gel). Yield: 53 mg (87%); liquid.

IR (neat): 1598, 1506, 1491, 1443 cm⁻¹.

¹H NMR (300 MHz, $CDCl_3$): $\delta = 8.21-8.13$ (m, 1 H), 8.00–7.87 (m, 1 H), 7.88 (d, J = 8.1 Hz, 1 H), 7.62–7.46 (m, 8 H), 7.41–7.34 (m, 1 H), 6.70 (q, J = 1.2 Hz, 1 H), 2.48 (d, J = 1.2 Hz, 3 H).

 ^{13}C NMR (75.4 MHz, CDCl₃): δ = 144.1, 137.9, 137.8, 133.8, 131.0, 130.4, 129.0, 128.4, 128.3, 127.2, 126.6, 125.82, 125.75, 125.7, 125.4, 124.8, 20.9.

MS (EI, 70 eV): m/z (%) = 244 [M⁺] (94.43), 229 (100).

HRMS (EI): m/z calcd for $C_{19}H_{16}^+$ [M⁺]: 224.1252; found: 244.1255.

(E)-1,2-Bis(4-methoxyphenyl)prop-1-ene [(E)-12bd]²¹

Compound (*E*)-**12bd** was prepared similarly to compound (*E*)-**9aa** by conditions B. The reaction of **3d** (75 mg, 0.49 mmol), **11b** (37 mg, 0.25 mmol), Pd(PPh₃)₄ (30 mg, 0.026 mmol), and AcOH (14 μ L, 0.24 mmol) in dioxane (3 mL) afforded crude **12bd** after evaporation [**12bd/13bd** > 99:1, (*E*)-**12bd**/(*Z*)-**12bd** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**12bd** was isolated by flash chromatography (silica gel). Yield: 38 mg (60%); solid; mp 121–122 °C (Et₂O) (Lit.^{21a} 122–123 °C).

IR (neat): 1608, 1511, 1452, 1252 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.47 (d, *J* = 8.7 Hz, 2 H), 7.31 (d, *J* = 8.7 Hz, 2 H), 6.96–6.87 (m, 4 H), 6.74 (s, 1 H), 3.84 (s, 6 H), 2.26 (s, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 158.7, 158.0, 136.6, 135.3, 131.1, 130.3, 126.9, 125.8, 113.6, 113.5, 55.3, 55.2, 17.4.

MS (EI, 70 eV): m/z (%) = 254 [M⁺] (100).

(*E*)-1-(4-*tert*-Butylphenyl)-2-(4-methoxyphenyl)prop-1-ene [(*E*)-12cd]

Compound (*E*)-**12cd** was prepared similarly to compound (*E*)-**9aa** by conditions B. The reaction of **3d** (77 mg, 0.51 mmol), **11c** (43 mg, 0.25 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), and AcOH (14 μ L, 0.24 mmol) in dioxane (3 mL) afforded crude **12cd** after evaporation [**12cd/13cd** > 99:1, (*E*)-**12cd**/(*Z*)-**12cd** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**12cd** was isolated by flash chromatography (silica gel). Yield: 46 mg (66%); solid; mp 100–101 °C (Et₂O).

IR (neat): 1605, 1513, 1463, 1247 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.49 (d, *J* = 8.6 Hz, 2 H), 7.42 (d, *J* = 8.3 Hz, 2 H), 7.32 (d, *J* = 8.3 Hz, 2 H), 6.93 (d, *J* = 8.6 Hz, 2 H), 6.78 (s, 1 H), 3.85 (s, 3 H), 2.30 (s, 3 H), 1.37 (s, 9 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 158.8, 149.1, 136.6, 136.1, 135.6, 128.8, 127.0, 126.0, 125.0, 113.6, 55.3, 34.5, 31.3, 17.5.

MS (EI, 70 eV): m/z (%) = 280 [M⁺] (80.12), 265 (100).

Anal. Calcd for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.95; H, 8.66.

(*E*)-1-(4-Acetylphenyl)-2-(4-methoxyphenyl)prop-1-ene [(*E*)-12dd]

Compound (*E*)-**12dd** was prepared similarly to compound (*E*)-**9aa** by conditions B. The reaction of **3d** (75 mg, 0.49 mmol), **11d** (40 mg, 0.25 mmol), Pd(PPh₃)₄ (30 mg, 0.026 mmol), and AcOH (14 μ L, 0.24 mmol) in dioxane (3 mL) afforded crude **12dd** after evaporation [**12dd/13dd** > 99:1, (*E*)-**12dd**/(*Z*)-**12dd** > 99:1; by ¹H NMR analysis]. Pure (*E*)-**12dd** was isolated by flash chromatography (silica gel). Yield: 41 mg (62%); solid; mp 110–113 °C (Et₂O).

IR (neat): 1678, 1597, 1514, 1406, 1262 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.96 (d, *J* = 8.7 Hz, 2 H), 7.48 (d, *J* = 8.6 Hz, 2 H), 7.43 (d, *J* = 8.6 Hz, 2 H), 6.92 (d, *J* = 8.7 Hz, 2 H), 6.79 (s, 1 H), 3.84 (s, 3 H), 2.62 (s, 3 H), 2.29 (s, 3 H).

¹³C NMR (75.4 MHz, CDCl₃): δ = 197.7, 159.2, 143.5, 139.2, 135.8, 134.8, 129.2, 128.3, 127.1, 125.2, 113.7, 55.3, 26.6, 17.7.

MS (EI, 70 eV): m/z (%) = 266 [M⁺] (100).

Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.15; H, 6.83.

Synthesis of Sulfone (E)-4ab from Sulfoxide (E)-6ab

A soln of (*E*)-**6ab** (101 mg, 0.4 mmol) and 30% H_2O_2 (5 mL) in AcOH (5 mL) was stirred at 40 °C for 24 h. After complete conversion of the starting material as monitored by TLC (PE–Et₂O, 1:1), the mixture was quenched with H_2O (15 mL), and extracted with CHCl₃ (6 × 25 mL). The organic layer was then neutralized by washing with sat. aq NaHCO₃. The combined organic layer was dried (MgSO₄). Evaporation of the solvent and flash chromatography (silica gel, PE–Et₂O, 3:1) afforded of (*E*)-**4ab**; yield: 57 mg (52%).

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- (13) Crystal structure data for (*E*)-4ca: $C_{19}H_{22}O_2S$, MW = 314.43, triclinic, space group *P*-1, Mo Ka, final *R* indices [*I* > 2 σ (*I*)], *R*1 = 0.0464, *wR*2 = 0.1016, *a* = 9.56611 (11) Å, *b* = 9.9879 (11) Å, *c* = 10.6025 (12) Å, *a* = 102.675 (2)°, β = 101.020 (2)°, γ = 116.035 (2)°, *V* = 838.98 (16) Å³, *T* = 293 (2) K, *Z* = 2, reflections collected/unique: 5004/ 3565 (*R*_{int} = 0.0485), no observation [*I* > 2 σ (*I*)] 3565, parameters 234. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Centre under CCDC 613372.
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