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Enantiospecific synthesis of 1,3-disubstituted allenes by palladium-catalyzed coupling of propargylic compounds with arylboronic acids

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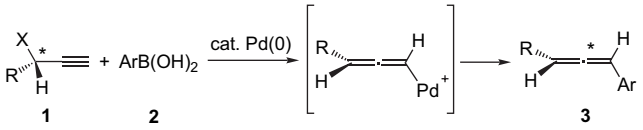
Abstract—An enantiospecific coupling of propargylic esters and carbonates with arylboronic acids has been developed using a palladium catalyst. Optically active 1,3-disubstituted allenes were synthesized with high enantiomeric excesses by carrying out the reactions under basic aqueous conditions.

1. Introduction

Functionalized allenes are versatile building blocks for organic synthesis because of the inherent reactivity of their axially chiral backbones.[1] Most of the natural products containing an allene moiety that have been isolated have axial chirality.[2] Consequently, much attention and extensive study have been focused on the synthesis of optically active allenes,[1] with palladium-catalyzed couplings of propargylic substrates being one of the most useful and efficient methodologies. In these couplings, substituted allenes having an overall *anti*-substitution are normally produced via an *anti*-S_N2' attack of palladium on the propargylic substrates. It has been reported that palladium complexes catalyze the coupling of propargylic substrates with organozinc reagents[3] yielding the substituted optically active allenes with high enantiospecificities. However, these reactions usually have to be conducted under anhydrous conditions.

Organoboron compounds are popular reagents in organic synthesis owing to their stability, commercial availability, and nontoxicity,[4] and some propargylic couplings using organoboron compounds have been reported.[5] We reported a coupling reaction of propargylic oxiranes with arylboronic acids by palladium catalyst. The reactions can be carried out in aqueous media to produce the aryl-substituted 2,3-allenols with high *anti*-diastereoselectivity.[5a] Molander developed a palladium-catalyzed synthesis of chiral ene-allenes employing optically active propargylic substrates with alkenyl trifluoroborates.[5b] Following his method, various substituted allenes were synthesized, but in most cases the enantiomeric excesses turned out to be modest. We reported a direct coupling of propargylic alcohols with arylboronic acids using a palladium catalyst, in which a practical and efficient synthesis of various substituted allenes has been achieved.[5c] However, when an optically active propargylic alcohol was used, the corresponding product was nearly racemic. During the course of our studies on the enantiospecific coupling with organoboron compounds, it became clear that, when the propargylic carbonate was employed, the chirality was successfully transferred to the allenic axial chirality.[5c] Since we anticipated that the enantiospecificity in this type of coupling would be influenced by the propargylic leaving group, we set about examining various ways to improve the reaction. Herein, we describe a methodology for the enantiospecific synthesis of 1,3-disubstituted allenes **3** by palladium-catalyzed coupling of propargylic esters **1** with arylboronic acids **2** (Scheme 1), in which various aryl-substituted allenes were synthesized in high enantiomeric excess under basic aqueous conditions.



Scheme 1.

2. Results and discussion

The propargylic substrates **1a**–**g** for the coupling reaction were synthesized as follows (Scheme 2). (*R*)-1-Phenyl-2-

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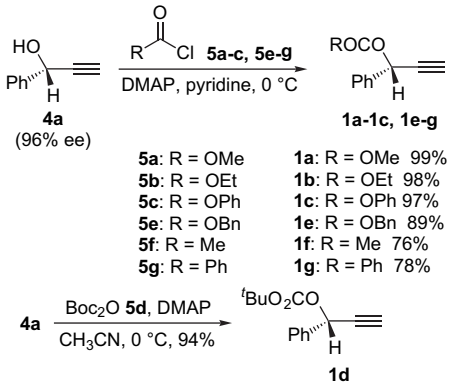
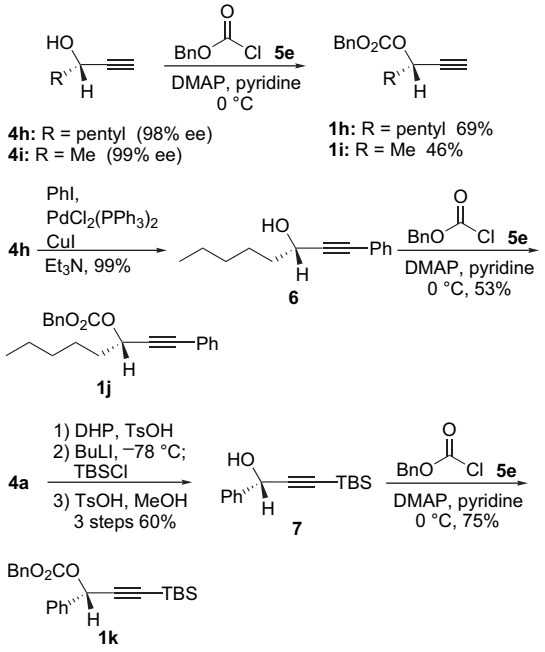
propyn-1-ol (**4a**) was subjected to esterification with the chlorocarbonates **5a–c** and **5e** and the acid chlorides **5f** and **5g** leading to the corresponding propargylic carbonates **1a–c** and **1e** and the esters **1f** and **1g** in high yields. Additionally, the *tert*-butyl carbonate **1d** was prepared from the reaction of **4a** with di-*tert*-butyl dicarbonate (**5d**) in 94% yield.



Scheme 2.

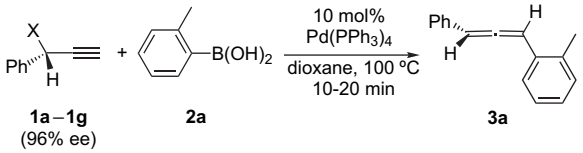
We also prepared various substituted propargylic carbonates **1h–k** (Scheme 3). Pentyl- and methyl-substituted substrates **1h** and **1i** were synthesized from the reactions of (*S*)-1-octyn-3-ol (**4h**) and (*S*)-3-butyn-1-ol (**4i**) with benzyl chlorocarbonate (**5e**). Propargylic alcohol **4h** was subjected to the Sonogashira coupling with iodobenzene to afford the coupled product **6**, which was transformed to the phenyl-substituted substrate **1j**. The TBS-substituted propargylic alcohol **7**, after being synthesized in three steps from **4a** by the selective introduction of the TBS group, was further transformed to the corresponding benzyl carbonate **1k** by reaction with **5e**.



Scheme 3.

The couplings of the optically active propargylic substrates **1a–g** with 2-methylphenylboronic acid (**2a**) were initially examined (Table 1). When methyl carbonate **1a** (96% ee) and **2a** were subjected to the reaction with 10 mol % of $Pd(PPh_3)_4$ in dioxane at 100 °C for 10 min, the optically active aryl-substituted allene **3a** was produced in 76% yield with 92% ee (entry 1).[6] However, the enantiomeric excesses decreased when ethyl, phenyl, *tert*-butyl and benzyl carbonates **1b–e** were employed (entries 2–5). Furthermore, the nearly racemic **3a** was obtained in low yields in the case of the propargylic acetate **1f** and the benzoate **1g** (entries 6 and 7). These results suggested that improvement of the reaction conditions would be essential to increase the enantiomeric excesses of the coupling reactions.

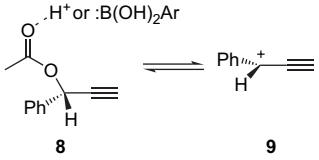
Table 1. Initial attempts to synthesize the optically active allene **3a**



Entry	X	Yield (%)	ee[a] (%)
1	OCO_2Me (**1a**)	76	92
2	OCO_2Et (**1b**)	81	28
3	OCO_2Ph (**1c**)	61	39
4	$OCO_2{}^tBu$ (**1d**)	87	12
5	OCO_2Bn (**1e**)	81	8
6	OAc (**1f**)	27	3
7	OBz (**1g**)	12	0

[a] Enantiomeric excess was determined by HPLC using a chiral column.

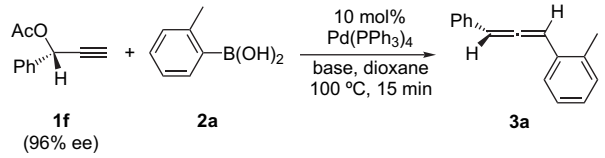
One possible explanation for the racemization of the resulting allenes derived from propargylic esters **1f** and **1g** might be that the attack of palladium proceeded in a stepwise fashion via the achiral propargylic cation intermediate **9** (Scheme 4). Thus, these reactions produce the corresponding carboxylic acids as co-products, which could promote an S_N1' attack of palladium (**8** to **9**) to afford the racemic allenylpalladium. To overcome this problem, we examined the reactions in the presence of base (Table 2). Although KOH or Na_2CO_3 were ineffective (entries 2 and 3), the enantiomeric excesses of the resulting allene **3a** were dramatically increased when Cs_2CO_3 or K_3PO_4 was used (entries 4 and 5).[7]



Scheme 4.

It is known that Suzuki–Miyaura reactions often proceed rapidly and efficiently in aqueous solvent.[8,5a] To examine the effect of water on our coupling process, we next investigated the reactions in aqueous solvent (Table 3). When propargylic carbonate **1b** was reacted with **2a** in dioxane/H_2O mixed solvent, the enantiomeric excesses of the resulting allene **3a** were improved (entries 2–4). The best results were obtained by carrying out the reaction in a 2:1 ratio of dioxane/H_2O (89% ee in entry 3).

Table 2. Effects of base on the coupling of propargylic ester **1f** with **2a**

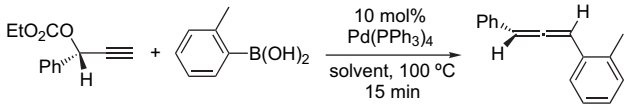


1f (96% ee) **2a** **3a**

Entry	Base[a]	Yield (%)	ee[b] (%)
1	None	27	3
2	KOH	60	2
3	Na_2CO_3	60	5
4	Cs_2CO_3	75	62
5	K_3PO_4	87	74

[a] 5 equiv of base was used.
[b] Enantiomeric excess was determined by HPLC using a chiral column.

Table 3. Effects of water on the coupling of **1b** with **2a**



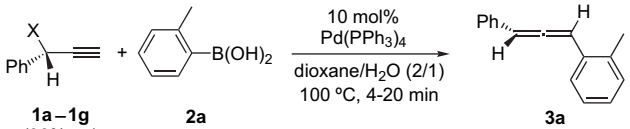
1b (96% ee) **2a** **3a**

Entry	Solvent	Yield (%)	ee[a] (%)
1	Dioxane	81	28
2	Dioxane/H_2O (3:1)	71	51
3	Dioxane/H_2O (2/1)	71	89
4	Dioxane/H_2O (1:1)	36	68

[a] Enantiomeric excess was determined by HPLC using a chiral column.

Table 4 shows the results of the reactions of the propargylic substrates **1a–g** with **2a** under optimized conditions. Under aqueous conditions (dioxane/H_2O=2:1), the reactions of the propargylic carbonates **1a–e** successfully proceeded to give the optically active **3a** in good enantiomeric excesses (entries 1–5). The propargylic esters **1f** and **1g** were also successfully transformed to the optically active **3a** in the presence of K_3PO_4 under aqueous conditions (entries 6 and 7). After several attempts, when the propargylic benzoate **1e** was subjected to the reaction with K_3PO_4 in dioxane/H_2O, **3a** was produced in 93% yield with 94% ee (entry 8). The reaction can be performed in the presence of 2 mol % palladium catalyst without loss of reactivity (83% yield with 94% ee, entry 10), and **3a** is efficiently obtained even when the catalyst loading is decreased to 1 mol % (69% yield with 81% ee, entry 11).

Table 4. Synthesis of chiral allene **3a** under optimized conditions



1a–1g (96% ee) **2a** **3a**

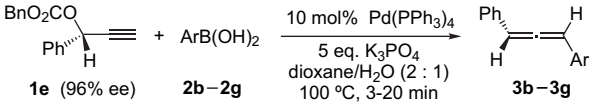
Entry	X	K_3PO_4[a]	Yield (%)	ee[b] (%)
1	OCO_2Me (**1a**)	–	69	93
2	OCO_2Et (**1b**)	–	71	89
3	OCO_2Ph (**1c**)	–	61	91
4	$OCO_2{}^tBu$ (**1d**)	–	73	93
5	OCO_2Bn (**1e**)	–	64	87
6	OAc (**1f**)	+	73	86
7	OBz (**1g**)	+	82	88
8	OCO_2Bn (**1e**)	+	93	94
9[c]	OCO_2Bn (**1e**)	+	85	94
10[d]	OCO_2Bn (**1e**)	+	83	94
11[e]	OCO_2Bn (**1e**)	+	69	81

[a] 5 equiv of K_3PO_4 was used.
[b] Enantiomeric excess was determined by HPLC using a chiral column.
[c] 5 mol % of $Pd(PPh_3)_4$ was used.
[d] 2 mol % of $Pd(PPh_3)_4$ was used.
[e] 1 mol % of $Pd(PPh_3)_4$ was used.

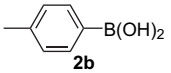
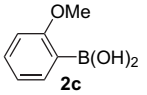
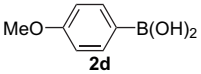
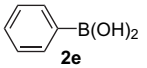
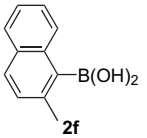
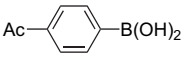
The reactions of the propargylic benzyl carbonate **1e** with the arylboronic acids **2b–g** under optimized conditions are summarized in Table 5. The corresponding substituted allenes **3b–g** were obtained in good yields with high optical purities from reactions with the various methyl- and methoxy-substituted phenylboronic acids **2b–d** (entries 1–3). Phenyl- and 2-methylnaphthaleneboronic acids (**2e** and **2f**) also afforded **3e** and **3f** with high enantiomeric excesses (entries 4 and 5). In contrast, the optical purity was lowered when 4-acetylphenylboronic acid (**2g**) was employed (entry 6).

Table 6 shows our attempts at using the propargylic carbonates **1h–k** having various substituents at the propargylic position and alkyne terminus. When the pentyl- and methyl-substituted substrates **1h** and **1i** were reacted with 2-methylphenylboronic acid (**2a**) and 1-naphthaleneboronic acid (**2h**), the coupled allenes **3h** and **3i** were produced in 83% ee and 74% ee, respectively (entries 1 and 2). On the other hand, the enantiomeric excesses of the corresponding allenes **3j** and **3k** were lower in the reaction of **2a** with **1j** and **1k**, which have a substituent at the alkyne terminus (entries 3 and 4). In the reaction of **1k**, the propargylic arene

Table 5. Reactions using various arylboronic acids **2b–g**

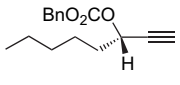
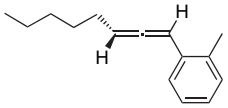
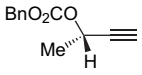
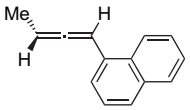
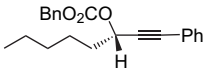
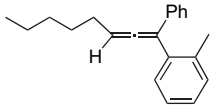
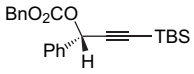
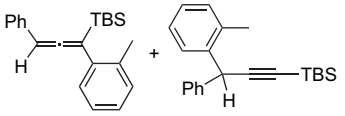


1e (96% ee) **2b–2g** **3b–3g**

Entry	$ArB(OH)_2$	Product	Yield (%)	ee[a] (%)
1	 **2b**	**3b**	61	92
2	 **2c**	**3c**	85	75
3	 **2d**	**3d**	71	90
4	 **2e**	**3e**	64	94
5	 **2f**	**3f**	99	86
6	 **2g**	**3g**	50	66

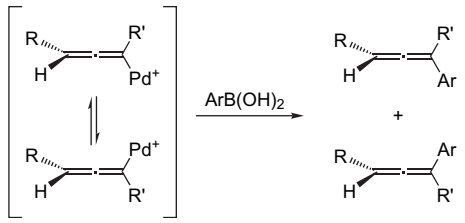
[a] Enantiomeric excess was determined by HPLC chiral column.

Table 6. Reactions using various substituted propargylic carbonates **1h–k**[a]

Entry	Substrate	Product[b]
1[c]	 **1h** (98% ee)	 **3h** 79%, 83% ee
2[d]	 **1i** (99% ee)	 **3i** 75%, 74% ee
3[c,e]	 **1j** (98% ee)	 **3j** 92%, 6% ee
4[c,e]	 **1k** (96% ee)	 **3k** 60%, 38% ee **10** 34%, 20% ee

[a] The reactions were carried out using 10 mol % of $Pd(PPh_3)_4$ and 5 equiv of K_3PO_4 in dioxane/H_2O (2:1) at 100 °C for 5–10 min.
[b] Enantiomeric excess was determined by HPLC chiral column.
[c] 2-Methylphenylboronic acid (**2a**) was used.
[d] 1-Naphthaleneboronic acid (**2h**) was used.
[e] Absolute configurations of **3j**, **3k**, and **10** are not determined.

10 was obtained in 34% yield with 20% ee as a by-product (entry 4).[5c] The reason for the observed low enantiomeric excesses is unclear, but it could be speculated that isomerization of the allenylpalladium occurred. It has been reported that optically active allenylpalladium is rapidly racemized.[9] We anticipated that the transmetallation of the allenylpalladium with the arylboronic acids could be retarded by alkynyl substitution, which promotes the racemization of the allenylpalladium in the coupling process (Scheme 5).



Scheme 5.

3. Conclusion

In conclusion, the studies described above have resulted in the synthesis of optically active 1,3-disubstituted allenes using palladium-catalyzed coupling of propargylic carbonates and esters with arylboronic acids. High enantiospecificity was achieved by conducting the reactions under optimized basic aqueous conditions. The reaction can be carried out under simple and mild reaction conditions to afford various coupled optically active allenes conveniently.

4. Experimental section

4.1. General

All nonaqueous reactions were carried out under a positive atmosphere of argon or nitrogen in dried glassware unless otherwise indicated. Materials were obtained from commercial suppliers and used without further purification except when otherwise noted. Solvents were dried and distilled according to standard protocols. The phrase 'residue upon workup' refers to the residue obtained when the organic layer was separated and dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure.

4.2. General procedure for the preparation of propargylic compounds: synthesis of propargylic carbonate 1e

To a stirred solution of (*R*)-1-phenyl-2-propyn-1-ol (**4a**) (313 mg, 2.37 mmol, 96% ee) and pyridine (1.5 mL, 19.0 mmol) in CH_2Cl_2 (30 mL) was added dropwise benzyl chloroformate (**5e**) (1.21 g, 7.11 mmol) at 0 °C, and stirring was continued for 2.5 h at the same temperature. The reaction mixture was diluted with saturated aq NH_4Cl and extracted with AcOEt. The combined extracts were washed with brine, and the residue upon workup was chromatographed on silica gel with hexane/AcOEt (95:5 v/v) as eluent to give propargylic carbonate **1e** (562 mg, 89%) as a colorless oil.

4.2.1. (*R*)-*O*-Methoxycarbonyl-1-phenyl-2-propyn-1-ol (1a). Yield 99%; 96% ee; $[\alpha]_D^{29}$ −6.2 (*c* 14.4, $CHCl_3$); IR (neat) 3290, 2958, 1752, 1495, 789, 766 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56–7.25 (5H, m), 6.29 (1H, d, *J*=2.4 Hz), 3.81 (3H, s), 2.72 (1H, d, *J*=2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 136.0, 129.4, 128.8, 128.8, 127.8, 127.8, 79.7, 76.7, 69.3, 55.1; MS *m*/*z* 190 (M^+); HRMS *m*/*z* calcd for $C_{11}H_{10}O_3$ 190.0630 (M^+), found 190.0638.

4.2.2. (*R*)-*O*-Ethoxycarbonyl-1-phenyl-2-propyn-1-ol (1b). Yield 98%; 96% ee; colorless oil; $[\alpha]_D^{28}$ −5.78 (*c* 8.88, $CHCl_3$); IR (neat) 3290, 1748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57–7.38 (5H, m), 6.28 (1H, d, *J*=2.0 Hz), 4.24 (2H, q, *J*=7.2 Hz), 2.71 (1H, d, *J*=2.0 Hz), 1.31 (3H, t, *J*=7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 135.8, 129.2, 128.6, 128.6, 127.6, 127.6, 79.6, 76.3, 68.9, 64.4, 14.1; MS *m*/*z* 204 (M^+); HRMS *m*/*z* calcd for $C_{12}H_{12}O_3$ 204.0786 (M^+), found 204.0771.

4.2.3. (*R*)-*O*-Phenyloxycarbonyl-1-phenyl-2-propyn-1-ol (1c). Yield 97%; 96% ee; colorless oil; $[\alpha]_D^{27}$ +13.5 (*c* 9.56, $CHCl_3$); IR (neat) 3306, 1758, 1594, 1494 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62–7.18 (10H, m), 6.38 (1H, d, *J*=2.0 Hz), 2.78 (1H, d, *J*=2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 151.0, 135.4, 129.5, 129.4, 129.4, 128.7, 128.7, 127.8, 127.8, 126.1, 120.8, 120.8, 79.2, 76.9, 70.0; MS *m*/*z* 252 (M^+); HRMS *m*/*z* calcd for $C_{16}H_{12}O_3$ 252.0786 (M^+), found 262.0802.

4.2.4. (*R*)-*O*-*tert*-Butylcarbonyl-1-phenyl-2-propyn-1-ol (1d). Yield 94%; 96% ee; $[\alpha]_D^{27}$ −3.08 (*c* 2.0, $CHCl_3$); IR (neat) 3290, 1743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56–7.26 (5H, m), 6.24 (1H, d, *J*=2.4 Hz), 2.69 (1H, d,

J=2.4 Hz), 1.49 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 136.1, 129.0, 128.6, 128.6, 127.6, 127.6, 83.0, 79.9, 75.9, 68.1, 27.6, 27.6, 27.6; HRMS (ESI) m/z calcd for $C_{14}H_{17}O_3$ 233.1178 (M^++H), found 233.1184.

4.2.5. (*R*)-*O*-Benzyloxycarbonyl-1-phenyl-2-propyn-1-ol (1e). Yield 89%; 96% ee; colorless oil; $[\alpha]_D^{28}$ −10.7 (c 2.64, $CHCl_3$); IR (neat) 3290, 1750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.33 (10H, m), 6.29 (1H, d, J=2.0 Hz), 5.21 (1H, d, J=12.0 Hz), 5.17 (1H, d, J=12.0 Hz), 2.71 (1H, d, J=2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 135.8, 134.9, 129.3, 128.7, 128.7, 128.6, 128.6, 128.6, 128.3, 128.3, 127.7, 127.7, 79.6, 76.5, 70.1, 69.4; HRMS (ESI) m/z calcd for $C_{17}H_{15}O_3$ 267.1022 (M^++H), found 267.1021.

4.2.6. (*R*)-1-Acetoxy-1-phenyl-2-propyne (1f). Yield 76%; 96% ee; $[\alpha]_D^{27}$ +4.3 (c 15.0, $CHCl_3$); IR (neat) 3289, 1742, 1495 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.26 (5H, m), 6.45 (1H, d, J=2.4 Hz), 2.65 (1H, d), 2.11 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 136.4, 129.1, 128.7, 128.7, 127.7, 127.7, 80.2, 75.3, 65.3, 21.0; HRMS (ESI) m/z calcd for $C_{11}H_{11}O_2$ 175.0759 (M^++H), found 175.0759.

4.2.7. (*R*)-1-Benzoxy-1-phenyl-2-propyne (1g). Yield 78%; 96% ee; $[\alpha]_D^{27}$ −21.4 (c 3.74, $CHCl_3$); IR (neat) 3292, 1722, 1601, 1494 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (2H, d, J=8.0 Hz), 7.64–7.26 (8H, m), 6.70 (1H, d, J=2.0 Hz), 2.69 (1H, d, J=2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 136.5, 133.3, 129.9, 129.9, 129.5, 129.0, 128.7, 128.7, 128.4, 128.4, 127.6, 127.6, 80.2, 75.6, 65.8; MS m/z 236 (M^+); HRMS m/z calcd for $C_{16}H_{12}O_2$ 236.0837 (M^+), found 236.0840.

4.2.8. (*S*)-*O*-Benzyloxycarbonyl-1-octyn-3-ol (1h). Yield 69%; 98% ee; colorless oil; $[\alpha]_D^{27}$ −51.2 (c 2.28, $CHCl_3$); IR (neat) 3293, 2956, 1749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.33 (5H, m), 5.21 (1H, td, J=6.8 and 2.0 Hz), 5.19 (2H, s), 2.51 (1H, d, J=2.0 Hz), 1.85–1.78 (2H, m), 1.46 (2H, quint, J=7.2 Hz), 1.33–1.28 (4H, m), 0.89 (3H, t, J=7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 134.9, 128.4, 128.4, 128.3, 128.1, 128.1, 80.4, 74.4, 69.6, 67.7, 34.4, 31.0, 24.2, 22.2, 13.7; HRMS (ESI) m/z calcd for $C_{16}H_{20}O_3Na$ 283.1310 (M^++Na), found 283.1310.

4.2.9. (*S*)-*O*-Benzyloxycarbonyl-3-butyn-1-ol (1i). Yield 46%; 99% ee; colorless oil; $[\alpha]_D^{28}$ −63.2 (c 11.8, $CHCl_3$); IR (neat) 3293, 1749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.26 (5H, m), 5.32 (1H, qd, J=6.8 and 2.0 Hz), 5.21 (1H, d, J=12.4 Hz), 5.17 (1H, d, J=12.4 Hz), 2.52 (1H, d, J=2.0 Hz), 1.56 (3H, d, J=6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 134.9, 128.5, 128.5, 128.5, 128.3, 128.3, 81.3, 73.8, 69.8, 64.0, 21.1; HRMS (ESI) m/z calcd for $C_{12}H_{13}O_3$ 205.0865 (M^++H), found 205.0865.

4.2.10. (*S*)-1-Phenyl-1-octyn-3-ol (6). To a stirred solution of (*S*)-1-octyn-3-ol (**4h**) (133 mg, 1.05 mmol, 98% ee) in Et_3N (15 mL) were added iodobenzene (701 mg, 3.44 mmol), CuI (26.0 mg, 0.137 mmol), and $PdCl_2(PPh_3)_2$ (48.2 mg, 0.0687 mmol) at rt, and stirring was continued for 3 h at the same temperature. The reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with brine, and the residue upon workup was chromatographed on silica gel with hexane/AcOEt (90:10 v/v) as eluent to give propargylic alcohol **6** (211 mg, 99%) as a colorless oil; $[\alpha]_D^{28}$ +3.91 (c 4.07, $CHCl_3$); IR (neat) 3337, 2930, 1599, 1490 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.29 (5H, m), 4.60 (1H, q, J=6.0 Hz), 1.85–1.33 (9H, m), 0.91 (3H, t, J=6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.6, 131.6, 128.3, 128.3, 128.2, 122.7, 90.3, 84.8, 63.0, 37.9, 31.4, 24.9, 22.5, 14.0; HRMS (ESI) m/z calcd for $C_{14}H_{18}O$ 203.1436 (M^++H), found 203.1434.

4.2.11. (*S*)-*O*-Benzyloxycarbonyl-1-phenyl-1-octyn-3-ol (1j). Yield 53%; 98% ee; colorless oil; $[\alpha]_D^{29}$ −56.6 (c 1.95, $CHCl_3$); IR (neat) 2955, 1748, 1599, 1491 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.25 (10H, m), 5.46 (1H, t, J=6.4 Hz), 5.20 (2H, s), 1.93–1.31 (8H, m), 0.90 (3H, t, J=7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 135.2, 131.9, 131.9, 128.6, 128.6, 128.6, 128.5, 128.5, 128.3, 128.2, 128.2, 122.2, 86.2, 85.9, 69.8, 68.9, 34.9, 31.3, 24.6, 22.5, 13.9; HRMS (ESI) m/z calcd for $C_{22}H_{25}O_3$ 337.1804 (M^++H), found 337.1805.

4.2.12. (*S*)-3-*tert*-Butyldimethylsilyl-1-phenyl-2-propyn-1-ol (7). To a stirred solution of (*R*)-1-phenyl-2-propyn-1-ol (1.07 g, 8.10 mmol, 96% ee) and 3,4-dihydro-2*H*-pyran (2.5 mL, 27 mmol) in CH_2Cl_2 (100 mL) was added *p*-toluenesulfonic acid (200 mg, 1.05 mmol) at rt, and stirring was continued for 1 h at the same temperature. The reaction mixture was quenched with saturated aq $NaHCO_3$ and extracted with AcOEt. The combined extracts were washed with brine. The residue upon workup was chromatographed on silica gel with hexane/AcOEt (95:5 v/v) as eluent to give THP ether as a colorless oil. To a stirred solution of the resulting THP ether in THF (60 mL) was added dropwise *n*-BuLi (2.18 M) (5.0 mL, 10.9 mmol) at −78 °C, and stirring was continued for 1 h at the same temperature. To the stirred solution was added dropwise *tert*-butyldimethylsilyl chloride (1.38 g, 9.15 mmol) in THF (15 mL); stirring was continued for 1 h at the same temperature and for 1 h at rt. The reaction mixture was quenched with saturated aq NH_4Cl and extracted with hexane. The combined extracts were washed with brine. To a stirred solution of the residue upon workup in MeOH (200 mL) was added *p*-toluenesulfonic acid (77.0 mg, 0.405 mmol) at rt, and stirring was continued for 10 h at the same temperature. The reaction mixture was quenched with saturated aq $NaHCO_3$ and extracted with AcOEt. The combined extracts were washed with brine, and the residue upon workup was chromatographed on silica gel with hexane/AcOEt (97:3 v/v) as eluent to give propargylic alcohol **7** (1.20 g, three steps 60%) as a colorless oil; $[\alpha]_D^{26}$ −16.6 (c 10.7, $CHCl_3$); IR (neat) 3367, 2954, 2929, 1603, 1494 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (2H, d, J=7.6 Hz), 7.55–7.33 (3H, m), 5.47 (1H, d, J=6.4 Hz), 2.13 (1H, d, J=6.4 Hz), 0.95 (9H, s), 0.15 (3H, s), 0.13 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 128.5, 128.5, 128.3, 126.7, 126.7, 105.7, 89.9, 65.0, 26.0, 26.0, 26.0, 16.5, −4.7, −4.7; HRMS (ESI) m/z calcd for $C_{15}H_{23}OSi$ 247.1518 (M^++H), found 247.1518.

4.2.13. (*S*)-*O*-Benzyloxycarbonyl-3-*tert*-butyldimethylsilyl-1-phenyl-2-propyn-3-ol (1k). Yield 75%; 96% ee; colorless oil; $[\alpha]_D^{30}$ −19.8 (c 5.0, $CHCl_3$); IR (neat) 2953, 2929, 1748 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.33 (10H, m), 6.31 (1H, s), 5.21 (1H, d, J=12.0 Hz), 5.14 (1H, d,

J=12.0 Hz), 0.92 (9H, s), 0.14 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 136.3, 135.0, 129.1, 128.6, 128.6, 128.5, 128.5, 128.5, 128.3, 128.3, 127.9, 127.9, 101.2, 92.1, 70.1, 69.9, 26.0, 26.0, 26.0, 16.5, −4.9, −4.9; HRMS (ESI) m/z calcd for $C_{23}H_{29}O_3Si$ 381.1886 (M^++H), found 381.1879.

4.3. General procedure for the palladium-catalyzed reaction of propargylic compounds with arylboronic acids: reaction of 1e with 2a

To a stirred solution of propargylic carbonate **1e** (32.0 mg, 0.120 mmol) in 1,4-dioxane (0.8 mL) and H_2O (0.4 mL) were added 2-methylphenylboronic acid (**2a**) (32.6 mg, 0.240 mmol), K_3PO_4 (127 mg, 0.60 mmol), and $Pd(PPh_3)_4$ (13.9 mg, 0.012 mmol) at rt, and stirring was continued for 4 min at 100 °C. The reaction mixture was filtered through a small amount of silica gel and concentrated. The residue was chromatographed on silica gel with hexane as eluent to give allene **3a** (23.0 mg, 93%, 94% ee) as a colorless oil.

4.3.1. (*R*)-1-(2-Methylphenyl)-3-phenylpropadiene (3a). Yield 93%; 94% ee; colorless oil; $[\alpha]_D^{26}$ −660.3 (c 2.1, $CHCl_3$); enantiomeric excess was determined by HPLC analysis [CHIRALCEL OJ-H column, 100% hexane, 0.5 mL/min, λ=254 nm, retention times 16.8 min (*R*) and 20.0 min (*S*)]; IR (neat) 3026, 1935, 1598, 1492, 1455 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.12 (9H, m), 6.78 (1H, d, J=6.8 Hz), 6.56 (1H, d, J=6.8 Hz), 2.42 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 135.3, 133.9, 131.9, 130.6, 128.7, 128.7, 127.6, 127.2, 127.2, 126.9, 126.9, 126.2, 97.6, 95.9, 20.0; MS m/z 206 (M^+); HRMS m/z calcd for $C_{16}H_{14}$ 206.1096 (M^+), found 206.1077.

4.3.2. (*R*)-1-(4-Methylphenyl)-3-phenylpropadiene (3b). Yield 61%; 92% ee; colorless oil; $[\alpha]_D^{29}$ −475.8 (c 1.2, $CHCl_3$); enantiomeric excess was determined by HPLC analysis [CHIRALCEL OD-H column, 1% ^{i}PrOH/hexane, 0.5 mL/min, λ=254 nm, retention times 9.74 min (*R*) and 14.8 min (*S*)]; IR (neat) 3023, 1935, 1598, 1492 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.11 (9H, m), 6.57 (2H, s), 2.33 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 137.2, 133.8, 130.6, 129.5, 129.5, 128.7, 128.7, 127.2, 127.2, 127.0, 126.9, 126.9, 98.3, 98.2, 21.2; MS m/z 206 (M^+); HRMS m/z calcd for $C_{16}H_{14}$ 206.1096 (M^+), found 206.1085.

4.3.3. (*R*)-1-(2-Methoxyphenyl)-3-phenylpropadiene (3c). Yield 85%; 75% ee; colorless oil; $[\alpha]_D^{28}$ −346.8 (c 1.9, $CHCl_3$); enantiomeric excess was determined by HPLC analysis [CHIRALCEL OD-H column, 5% ^{i}PrOH/hexane, 0.5 mL/min, λ=254 nm, retention times 9.2 min (*R*) and 12.4 min (*S*)]; IR (neat) 1935, 1596, 1493 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.18 (7H, m), 6.99 (1H, d, J=6.8 Hz), 6.91–6.88 (2H, m), 6.56 (1H, d, J=6.8 Hz), 3.87 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 156.2, 134.0, 128.7, 128.7, 128.4, 128.0, 127.0, 126.9, 126.9, 122.0, 120.8, 111.1, 97.7, 92.4, 55.6; MS m/z 222 (M^+); HRMS m/z calcd for $C_{16}H_{14}O$ 222.1045 (M^+), found 222.1036.

4.3.4. (*R*)-1-(4-Methoxyphenyl)-3-phenylpropadiene (3d). Yield 71%; 90% ee; colorless oil; $[\alpha]_D^{29}$ −494.0 (c 1.2, $CHCl_3$); enantiomeric excess was determined by HPLC analysis [CHIRALCEL OD-H column, 5% ^{i}PrOH/hexane, 0.5 mL/min, λ=254 nm, retention times 10.4 min (*R*) and 12.4 min (*S*)]; IR (neat) 2957, 1934, 1606, 1509, 1494, 1459 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.21 (7H, m), 6.86 (2H, dt, J=8.8 and 2.5 Hz), 6.56 (2H, s), 3.80 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.2, 159.1, 133.9, 128.7, 128.7, 128.1, 128.1, 127.2, 126.9, 126.9, 125.8, 114.2, 114.3, 98.3, 97.8, 55.3; HRMS (ESI) m/z calcd for $C_{16}H_{15}O$ 223.1123 (M^++H), found 223.1114.

4.3.5. (*R*)-1,3-Diphenylpropadiene (3e). Yield 64%, 94% ee; colorless crystals; mp 48–50 °C; $[\alpha]_D^{29}$ −866.9 (c 0.59, $CHCl_3$); enantiomeric excess was determined by HPLC analysis [CHIRALCEL OD-H column, 1% ^{i}PrOH/hexane, 0.5 mL/min, λ=254 nm, retention times 10.2 min (*R*) and 13.6 min (*S*)]; IR (abs KBr) 3013, 1937, 1597, 1493 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.21 (10H, m), 6.60 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 133.6, 133.6, 128.7, 128.7, 128.7, 128.7, 127.3, 127.3, 127.0, 127.0, 127.0, 127.0, 98.4, 98.4; MS m/z 192 (M^+); HRMS m/z calcd for $C_{15}H_{12}$ 192.0939 (M^+), found 192.0943.

4.3.6. (*R*)-1-(2-Methylnaphthyl)-3-phenylpropadiene (3f). Yield 99%; 86% ee; colorless oil; $[\alpha]_D^{27}$ −538.4 (c 1.3, $CHCl_3$); enantiomeric excess was determined by HPLC analysis [CHIRALCEL OD-H column, 100% hexane, 1.2 mL/min, λ=254 nm, retention times 44.5 min (*S*) and 49.5 min (*R*)]; IR (neat) 3051, 1940, 1597, 1495 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (1H, d, J=8.0 Hz), 7.80 (1H, d, J=8.0 Hz), 8.30 (1H, d, J=8.0 Hz), 7.69 (1H, d, J=8.0 Hz), 7.48–7.22 (7H, m), 7.10 (1H, d, J=6.8 Hz), 6.47 (1H, d, J=6.8 Hz), 2.58 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 134.2, 134.0, 132.4, 131.8, 129.3, 128.7, 128.7, 128.3, 127.6, 127.4, 127.1, 127.1, 127.1, 126.2, 124.9, 124.5, 95.4, 92.9, 21.5; MS m/z 256 (M^+); HRMS m/z calcd for $C_{20}H_{16}$ 256.1252 (M^+), found 256.1255.

4.3.7. (*R*)-1-(4-Acetylphenyl)-3-phenylpropadiene (3g). Yield 50%; 66% ee; colorless oil; $[\alpha]_D^{30}$ −359.7 (c 0.72, $CHCl_3$); enantiomeric excess was determined by HPLC analysis [CHIRALCEL OD-H column, 1% ^{i}PrOH/hexane, 0.5 mL/min, λ=254 nm, retention times 15.3 min (*R*) and 17.1 min (*S*)]; IR (neat) 3019, 1935, 1679, 1602 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (2H, d, J=8.4 Hz), 7.43 (2H, d, J=8.4 Hz), 7.35–7.33 (5H, m), 6.66 (1H, d, J= 2.4 Hz), 6.63 (1H, d, J=2.4 Hz), 2.59 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.1, 197.4, 138.8, 135.9, 132.8, 128.9, 128.9, 128.8, 128.8, 127.6, 127.1, 127.1, 127.0, 127.0, 98.4, 97.9, 26.5; MS m/z 234 (M^+); HRMS m/z calcd for $C_{17}H_{14}O$ 234.1045 (M^+), found 234.1034.

4.3.8. (*R*)-1-(2-Methylphenyl)-1,2-octadiene (3h). Yield 79%; 83% ee; colorless oil; $[\alpha]_D^{22}$ −190.0 (c 0.49, $CHCl_3$); enantiomeric excess was determined by HPLC analysis [CHIRALCEL OD-H column, 100% hexane, 0.5 mL/min, λ=254 nm, retention times 12.3 min (*R*) and 14.2 min (*S*)]; IR (neat) 2926, 1947 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (1H, d, J=7.6 Hz), 7.16–7.07 (3H, m), 6.23 (1H, dt, J=6.8 and 9.2 Hz), 5.52 (1H, q, J=6.8 Hz), 2.36 (3H, s), 2.12 (2H, m), 1.49 (2H, quint, J=7.2 Hz), 1.36–1.32 (4H, m), 0.89 (3H, t, J=7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.8, 134.8, 133.3, 130.4, 127.0, 126.5, 126.0, 94.2, 91.7, 31.4, 28.9, 28.8, 22.5, 19.8, 14.1; MS m/z 200 (M^+); HRMS m/z calcd for $C_{15}H_{20}$ 200.1565 (M^+), found 200.1572.

4.3.9. (*R*)-1-Naphthyl-1,2-propadiene (3i). Yield 75%; 74% ee; colorless oil; $[\alpha]_D^{22}$ −53.4 (*c* 0.16, $CHCl_3$); enantiomeric excess was determined by HPLC analysis [CHIRALCEL OB-H column, 100% hexane, 0.3 mL/min, λ=254 nm, retention times 24.2 min (*S*) and 25.4 min (*R*)]; IR (neat) 1947, 1591, 1509 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (1H, d, *J*=8.0 Hz), 7.85 (1H, d, *J*=7.2 Hz), 7.73 (1H, d, *J*=8.0 Hz), 7.72–7.4 (4H, m), 6.81 (1H, dq, *J*=3.2 and 7.2 Hz), 5.58 (1H, quint, *J*=7.2 Hz), 1.85 (3H, dd, *J*=3.2 and 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.5, 133.9, 131.2, 130.8, 128.6, 127.2, 125.9, 125.6, 125.6, 125.2, 123.6, 90.6, 88.5, 14.2; MS *m*/*z* 180 (M^+); HRMS *m*/*z* calcd for $C_{14}H_{12}$ 180.0939 (M^+), found 180.0941.

4.3.10. 1-(2-Methylphenyl)-1-phenyl-1,2-octadiene (3j). Yield 92%; 6% ee; colorless oil; $[\alpha]_D^{25}$ +7.48 (*c* 1.64, $CHCl_3$); enantiomeric excess was determined by HPLC analysis [CHIRALCEL OF column, 100% hexane, 0.2 mL/min, λ=254 nm, retention times 26.4 min (*R*) and 28.4 min (*S*)]; IR (neat) 2955, 2926, 1945, 1491 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29–7.16 (9H, m), 5.60 (1H, t, *J*=6.6 Hz), 2.20 (3H, s), 2.16 (2H, td, *J*=8.0 and 6.6 Hz), 1.54–1.26 (6H, m), 0.86 (3H, t, *J*=6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.9, 137.4, 136.8, 136.5, 130.3, 130.2, 128.3, 128.3, 127.4, 126.5, 126.5, 126.4, 125.9, 125.5, 107.7, 94.0, 31.4, 28.9, 28.8, 22.5, 20.1, 14.0; HRMS (ESI) *m*/*z* calcd for $C_{21}H_{24}$ 277.1956 (M^++H), found 277.1954.

4.3.11. 1-(2-Methylphenyl)-1-*tert*-butyldimethylsilyl-3-phenylpropadiene (3k). Yield 60%; 38% ee; colorless oil; $[\alpha]_D^{27}$ −13.9 (*c* 0.7, $CHCl_3$); enantiomeric excess was determined by HPLC analysis [CHIRALCEL OD-H column, 100% hexane, 0.3 mL/min, λ=254 nm, retention times 18.1 min (*R*) and 19.0 min (*S*)]; IR (neat) 2955, 2927, 1920 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.28–7.11 (9H, m), 5.96 (1H, s), 2.35 (3H, s), 0.94 (9H, s), 0.17 (3H, s), 0.13 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.7, 137.1, 135.1, 134.8, 130.4, 128.5, 128.5, 128.5, 126.4, 126.4, 126.1, 126.1, 125.5, 101.4, 88.9, 26.9, 26.9, 21.0, 21.0, 18.4, −4.5, −4.9; HRMS (ESI) *m*/*z* calcd for $C_{22}H_{28}NaSi$ 343.1858 (M^++Na), found 343.1858.

4.3.12. 3-*tert*-Butyldimethylsilyl-1-(2-methylphenyl)-1-phenyl-2-propyne (10). Yield 34%; 20% ee; colorless oil; $[\alpha]_D^{28}$ −7.3 (*c* 0.7, $CHCl_3$); enantiomeric excess was determined by HPLC analysis [CHIRALPAC IA column, 100% hexane, 0.2 mL/min, λ=254 nm, retention times 22.1 min (*minor*) and 23.2 min (*major*)]; IR (neat) 2952, 2928, 2170, 1601, 1493 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (1H, d, *J*=8.0 Hz), 7.42–7.12 (8H, m), 5.19 (1H, s), 2.28 (3H, s), 0.93 (9H, s), 0.11 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 139.3, 135.9, 130.6, 128.8, 128.4, 128.4, 127.9, 127.9, 127.0, 126.6, 126.2, 107.2, 87.0, 41.3, 26.1, 26.1, 26.1, 19.6, 16.7, −4.5, −4.5; HRMS (ESI) *m*/*z* calcd for $C_{22}H_{29}Si$ 321.2042 (M^++H), found 321.2041.

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