Nickel(0)-catalyzed asymmetric cross-coupling reactions of allylic compounds with arylboronic acids

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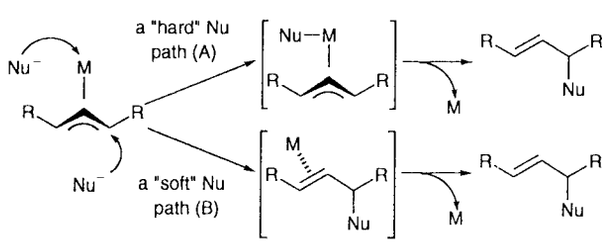
Optically active oxazolinylferrocenylphosphines have been found to work quite effectively as chiral ligands in nickel(0)-catalyzed cross-coupling reactions of allylic compounds with arylboronic acids, which are known to behave as "hard" nucleophiles. The expected coupling products have been obtained in good yields with moderate enantioselectivities (up to 53% ee). This is the first example of asymmetric allylic substitution using organoboron compounds.

Introduction

Organoboron compounds are well-known as versatile reagents in organic synthesis. A number of studies on transition-metal catalyzed carbon–carbon bond forming reactions using these compounds have recently appeared such as the Suzuki-coupling reaction,[1] conjugate addition to enones,[2] addition to aldehydes,[3] allylic substitution,[4] carbonylation[5] and cross-coupling reaction with alkenes or acid chlorides.[6] Each reaction proceeds *via* either transmetallation between a boron atom and a transition metal or oxidative addition of a carbon–boron bond to a lower valence transition metal. Quite recently, asymmetric versions of these reactions have appeared,[2d,2e,3,7] but to the best of our knowledge there are no reports until now on the catalytic asymmetric allylic substitution using such compounds.

The allylic substitution reaction is a powerful method used to construct a new carbon–carbon bond and, so far, excellent selectivities have been attained using palladium catalysts with various chiral ligands in the allylation with "soft" nucleophiles.[8] However, examples of the reaction with corresponding "hard" nucleophiles are quite limited, most of which are nickel-catalyzed allylic substitutions with Grignard reagents in the presence of chiral P–P ligands.[9] Mechanistically speaking, the allylic substitution reaction with a "hard" nucleophile is considered to proceed differently from that with a "soft" nucleophile; a hard nucleophile attacks a transition metal first (Scheme 1, path (A)), while a "soft" one attacks an allylic carbon directly (Scheme 1, path (B)).[10] In this paper, we disclose



Scheme 1

that optically active alkenes having an aryl group at the allylic position can be obtained stereoselectively in nickel(0)-catalyzed asymmetric cross-coupling reactions of allylic compounds with "hard" nucleophiles, arylboronic acids, in the presence of a chiral oxazolinylferrocenylphosphine (Chart 1).[11] These ligands have been found to work quite effectively in rhodium(I)-, iridium(I)- or ruthenium(II)-catalyzed hydrosilylation of ketones or imines[12] and ruthenium(II)-catalyzed transfer hydrogenation of ketones.[13]

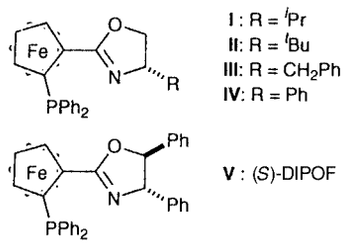
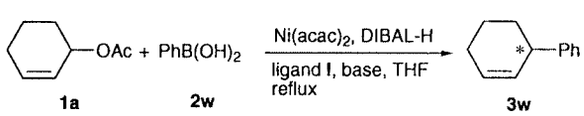


Chart 1

Results and discussion

3-Acetoxycyclohexene (**1a**) and sodium tetraphenylborate ($NaBPh_4$) were chosen first as substrates according to the report by Legros and Fiaud.[4a] The cross-coupling reaction was attempted in tetrahydrofuran (THF) at reflux with **1a** (1 equiv.) and $NaBPh_4$ (1.5 equiv.) in the presence of nickel(II) acetylacetonate [$Ni(acac)_2$] (5 mol%), diisobutylaluminium hydride (DIBAL-H) (16 mol%), and a chiral oxazolinylferrocenylphosphine (**I**, 5 mol%) as a ligand. 3-Phenylcyclohexene (**3w**) was obtained in 28% yield and 1% ee after 42 h, no improvement being shown even by the addition of a base which is indispensable in many cases of Suzuki coupling reactions.[1] Then, hoping to obtain higher chemical yields, we switched from $NaBPh_4$ to phenylboronic acid (**2w**) (Scheme 2), which is



Scheme 2

usually employed in Suzuki coupling reactions. In the presence of base, the nucleophilicity of an organic group on the boron atom is considered to be enhanced by forming "ate" complexes. As summarized in Table 1, the yield of **3w** was greatly increased. In each case a very small amount of the by-product, biphenyl, was detected on GLC analysis (below 3%). Many inorganic bases such as $K_3PO_4 \cdot nH_2O$ and KOH significantly enhanced the chemical yields of **3w**, with **3w** scarcely being obtained in the absence of base as expected (entry 1). In order to obtain a higher stereoselectivity it was necessary to use KOH and further investigation showed that the optical yield was dependent on the concentration of the substrate as well as the nickel : ligand ratio. Thus, the desired product was obtained more stereoselectively (50% ee, entry 9) by using a chiral ligand and nickel in a ratio of 2 : 1 with a higher concentration of **1a**

Table 1 Effect of base on nickel-catalyzed asymmetric allylic substitution[a]

Entry	Base	Time/h	Yield (%)[b]	Ee (%)[c]
1	None	17	3	—[d]
2	Et_3N	65	Trace	—[d]
3	$K_3PO_4 \cdot nH_2O$	17	87	4
4	KO^{t}Bu	17	32	4
5	$Ca(OH)_2$	118	22	1
6	NaOH	17	57	8
7	KOH	17	65	21
8[e]	KOH	17	46	28
9[e,f]	KOH	17	81	50

[a] Reaction conditions; **1a** (0.50 mmol), **2w** (1.5 mmol), $Ni(acac)_2$ (0.025 mmol), DIBAL-H (0.080 mmol), ligand **I** (0.026 mmol, Ni : ligand = 1 : 1), base (1.5 mmol), THF (2.5 mL, 0.20 M of **1a**), at reflux. [b] Determined by GLC. [c] Determined by optical rotation; (*S*)-configuration predominated in either case. [d] Not determined. [e] THF (1.5 mL, 0.33 M of **1a**). [f] Ligand **I** (0.050 mmol, Ni : ligand = 1 : 2).

Table 2 Effect of chiral ligand on nickel-catalyzed asymmetric allylic substitution[a]

Entry	Ligand	Yield (%)[b]	Ee (%)[c]
1	None	2	—[d]
2	**I**	81	50
3	**II**	55	9
4	**III**	56	53
5	**IV**	20	48
6	**V**	41	48

[a] Reaction conditions; **1a** (0.50 mmol), **2w** (1.5 mmol), $Ni(acac)_2$ (0.025 mmol), DIBAL-H (0.080 mmol), ligand (0.050 mmol), KOH (1.5 mmol), THF (1.5 mL, 0.33 M of **1a**), reflux for 17 h. [b] Determined by GLC. [c] Determined by optical rotation; (*S*)-configuration predominated in either case. [d] Not determined.

(0.33 M instead of 0.20 M). In this reaction system, heating to reflux temperature was essential, otherwise **3w** could not be detected at all in GLC analysis (at rt or even at 50 °C). In addition, **3w** was scarcely obtained either by the use of $Pd(dba)_2$ or $Pt(dba)_2$ in place of $Ni(acac)_2$ and DIBAL-H,[14] or by the use of some other organoboron and organoheteroatom compounds such as Ph_3B–KOH, phenylboronic acid ethylene glycol ester [$PhB(OCH_2CH_2O)$]–KOH or MeLi, Ph_3Sb–KOH, Ph_3Bi–KOH and $PhSnBu^n_3$.[15,16]

Next, various other chiral oxazolinylferrocenylphosphines (Chart 1) were used for this reaction (Table 2). Similar enantioselectivities were observed with most ligands including **V** (*S*,*S*,*S*)-[2-(4,5-diphenyl-4,5-dihydro-1,3-oxazol-2-yl)ferrocenyl]-diphenylphosphine (abbreviated as **(*S*)-DIPOF**), which is the best ligand in rhodium(I)- and iridium(I)-catalyzed hydrosilylation of ketones,[12a,b] although the use of **II** resulted in lower enantioselectivity (entry 3). As to the effect of the nature of the leaving group of cyclohexenyl compounds (Chart 2), the acetoxy group gave the best result both in chemical and optical yields (Table 3, entry 1), followed by the hydroxy group (entry

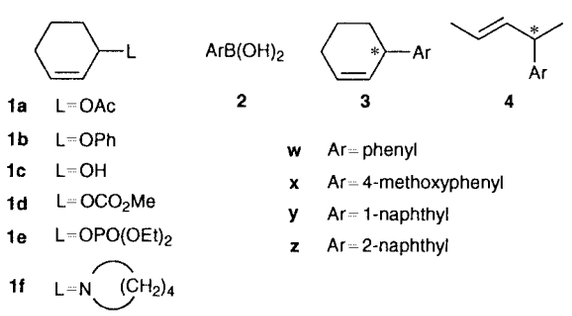


Chart 2

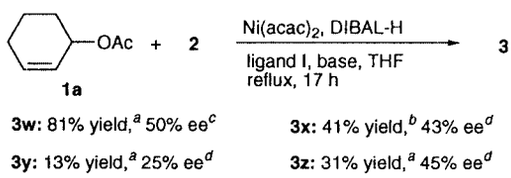
Table 3 Effect of leaving group on nickel-catalyzed asymmetric allylic substitution[a]

Entry	Y	Yield (%)[b]	Ee (%)[c]
1	**1a**	81	50
2	**1b**	8	—[d]
3	**1c**	50	32
4	**1d**	7	—[d]
5	**1e**	6	—[d]
6	**1f**	34	37

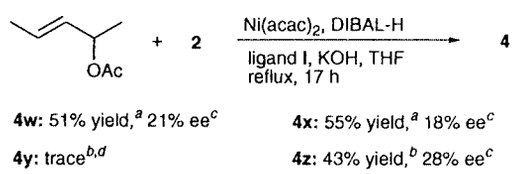
[a] Reaction conditions; **1** (0.50 mmol), **2w** (1.5 mmol), $Ni(acac)_2$ (0.025 mmol), DIBAL-H (0.080 mmol), ligand **I** (0.050 mmol), KOH (1.5 mmol), THF (solvent, 0.33 M of an allylic substrate), at reflux for 17 h. [b] Determined by GLC. [c] Determined by optical rotation; (*S*)-configuration predominated in either case. [d] Not determined.

3) and pyrrolidinyl group employed by Trost and Spagnol[4b] (entry 6). In the absence of KOH, compound **1f** hardly reacted with **2w**, although this type of amine is known to work as a base as well.[4b]

Using the conditions described above, the reactions of other arylboronic acids (Chart 2) with **1a** (Scheme 3) and an acyclic substrate, 4-acetoxypent-2-ene (Scheme 4) were carried out. In

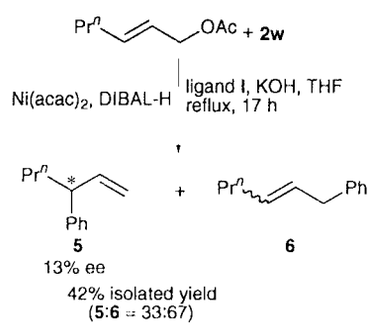


Scheme 3 [a] GLC yield. [b] Isolated yield. [c] Determined by optical rotation. [d] Determined by HPLC using a suitable chiral column.



Scheme 4 [a] Isolated yield. [b] GLC yield. [c] Determined by HPLC using a suitable chiral column. [d] The ee value was not determined.

all cases the expected coupling products were obtained, but both the chemical yield and enantioselectivity were lower, unfortunately. An unsymmetrical substrate, 1-acetoxyhex-2-ene, reacted with **2w** to afford the coupling products **5** and **6** (Scheme 5), albeit the selectivity for **5** as well as its enantioselectivity was not high (**5** : **6** = 33 : 67, 13% ee).[17,18]



Scheme 5

In conclusion, we have found that optically active oxazolinylferrocenylphosphines work as chiral ligands in nickel(0)-catalyzed cross-coupling reactions of allylic compounds with arylboronic acids to afford the desired arylated products with moderate enantioselectivities (up to 53% ee).

Experimental

General

^{1}H- and ^{13}C-NMR spectra were measured on JEOL EX-400, JEOL JNM-AL300 and JEOL JNM-GSX270 spectrometers for solutions in $CDCl_3$ with Me_4Si as an internal standard. GLC analyses were carried out with a Shimadzu GC-14A instrument equipped with a CPB 10-S25-050 column (Shimadzu, fused silica capillary column, 0.33 mm × 25 m, 5.0 mm film thickness) using helium as carrier gas. GLC yields were determined using bibenzyl as an internal standard. Optical rotations were measured on a JASCO DIP-1000 instrument. HPLC analyses were carried out on an HLC-803A instrument (Tosoh) with a UV-8011 detector using a Daicel Chiralcel OB, OD or OJ column. $[\alpha]_D$ values are measured in 10^{-1} deg cm^2 g^{-1}. Analytical thin layer chromatography (TLC) was performed with silica gel 60 Merck F-254 plates. Column chromatography was performed with Merck silica gel 60.

Materials

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon. Triethylamine was distilled from calcium hydride. Other commercially available organic and inorganic compounds including $Ni(acac)_2$ and DIBAL-H (diisobutylaluminium hydride) were used without further purification. Chiral oxazolinylferrocenylphosphines (**I**–**V**) were prepared by reported methods.[11] Cyclohex-2-enol (**1c**) was prepared by the reduction of cyclohex-2-en-1-one with $NaBH_4$ and $CeCl_3 \cdot 7H_2O$ in methanol.[19] 3-Acetoxycyclohexene (**1a**) and 1-acetoxyhex-2-ene were prepared from the corresponding alcohol and acetic anhydride. Cyclohex-2-enyl carbonate (**1d**) was prepared from **1c** and methyl chlorocarbonate. Cyclohex-2-enyl diethyl phosphate (**1e**) was prepared from **1c** and chlorophosphoric acid diethyl ester. 3-Phenoxycyclohexene (**1b**),[20] 3-pyrrolidin-1-ylcyclohexene (**1f**),[4b] 4-acetoxypent-2-ene[21] and arylboronic acids (**3x**, **3y**, **3z**)[22] as well as $Pd(dba)_2$[23] and $Pt(dba)_2$[24] were prepared according to literature procedures.

General procedure for Ni(0)-catalyzed cross-coupling reaction of 3-acetoxycyclohexene (1a) with phenylboronic acid (2w) (Table 1, entry 9)

A mixture of $Ni(acac)_2$ (6.5 mg, 0.025 mmol), (*S*,*S*)-[2-(4-isopropyl-4,5-dihydro-1,3-oxazol-2-yl)ferrocenyl]diphenylphosphine (**I**, 24.2 mg, 0.050 mmol) and bibenzyl (as an internal standard; 19.9 mg) was stirred for 1 h in THF (0.5 mL) at room temperature under nitrogen. After cooling to 0 °C, DIBAL-H (1.0 M solution in hexane; 0.08 mL, 0.08 mmol) was added to the mixture which was stirred for another 30 min. A solution of 3-acetoxycyclohexene (**1a**, 70.0 mg, 0.50 mmol) in THF (0.5 mL), phenylboronic acid (**2w**, 183 mg, 1.5 mmol), potassium hydroxide (85.5 mg, 1.5 mmol) and THF (0.5 mL) were added successively to the mixture and the resulting mixture was heated under reflux for 17 h. The resulting mixture was diluted with hexane and filtered through Florisil. The amount of product **3w** was determined by GLC analysis. For isolation of **3w** the solvent was evaporated and the residue was purified by column chromatography using hexane as an eluent. Typical spectroscopic data of the obtained coupling products are as follows.

3-Phenylcyclohexene (3w). A colorless liquid; ^{1}H-NMR δ = 1.49–2.11 (6H, m), 3.42 (1H, m), 5.71 (1H, m), 5.89 (1H, m), 7.16–7.33 (5H, m); ^{13}C-NMR δ = 21.19, 25.01, 32.60, 41.85, 125.94, 127.71, 128.24, 128.33, 130.18, 146.64. The ee value and the configuration of the product were determined by a polarimeter based on the reported rotation of an optically pure (*R*)-**3w**, $[\alpha]_D^{29}$ = +159.6 (*c* 0.53, benzene).[25]

3-(4-Methoxyphenyl)cyclohexene (3x). A colorless liquid; ^{1}H-NMR δ = 1.48–1.67 (3H, m), 1.69–1.77 (1H, m), 1.95–2.01 (1H, m), 2.06–2.10 (2H, m), 3.32–3.38 (1H, m), 3.79 (3H, s), 5.69 (1H, dd, *J* = 10.0, 2.2 Hz), 5.83–5.89 (1H, m), 6.84 (2H, d, *J* = 8.5 Hz), 7.13 (2H, d, *J* = 8.5 Hz); ^{13}C-NMR δ = 21.13, 25.03, 32.73, 40.97, 55.27, 113.69, 128.13, 128.61, 130.53, 138.81, 157.89. The ee value was determined by HPLC analysis with a Daicel Chiralcel OB column using hexane as an eluent.

3-(1-Naphthyl)cyclohexene (3y). A colorless liquid; ^{1}H-NMR δ = 1.64–1.78 (3H, m), 2.15–2.21 (3H, m), 4.19–4.26 (1H, m), 5.83 (1H, dd, *J* = 10.0, 2.6 Hz), 5.98–6.05 (1H, m), 7.37–7.54 (4H, m), 7.72 (1H, dd, *J* = 7.4, 2.1 Hz), 7.87 (1H, dd, *J* = 7.4, 2.2 Hz), 8.13 (1H, d, *J* = 7.7 Hz); ^{13}C-NMR δ = 20.86, 25.25, 30.91, 37.00, 123.41, 125.06, 125.27, 125.42, 125.71, 126.60, 126.77, 128.92, 130.22, 131.40, 134.10, 141.92; IR (neat) 724, 761, 778, 796, 2834, 2858, 2930, 3018, 3045, 3059 cm^{-1} (Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.50; H, 7.83%). The ee value was determined by HPLC analysis with a Daicel Chiralcel OB column using hexane as an eluent.

3-(2-Naphthyl)cyclohexene (3z). A colorless liquid; ^{1}H-NMR δ = 1.62–2.23 (6H, m), 3.56–3.60 (1H, m), 5.81 (1H, dd, *J* = 10.0, 2.1 Hz), 5.92–6.00 (1H, m), 7.35–7.61 (3H, m), 7.64 (1H, s), 7.76–7.88 (3H, m); ^{13}C-NMR δ = 21.12, 25.09, 32.41, 41.91, 125.14, 125.79, 125.81, 126.71, 127.55, 127.58, 127.84, 128.64, 130.06, 132.16, 133.55, 144.06; IR (neat) 723, 744, 757, 815, 853, 2835, 2856, 2927, 3018, 3052 cm^{-1} (Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.45; H, 7.70%). The ee value was determined by HPLC analysis with a Daicel Chiralcel OJ column using hexane as an eluent.

4-Phenylpent-2-ene (4w). A colorless liquid; ^{1}H-NMR δ = 1.33 (3H, d, *J* = 7.3 Hz), 1.67 (3H, d, *J* = 7.3 Hz), 3.41 (1H, m, *trans* isomer), 3.79 (1H, m, *cis* isomer), 5.42–5.65 (2H, m), 7.16–7.31 (5H, m); ^{13}C-NMR δ = 17.88, 21.46, 42.33, 123.63, 125.90, 127.13, 128.32, 136.24, 146.48. The diastereomeric ratio of **4w** (*trans*:*cis* = 92:8) was determined by ^{1}H-NMR analysis and the ee value was determined by HPLC analysis with a Daicel Chiralcel OJ column using hexane as an eluent.

4-(4-Methoxyphenyl)pent-2-ene (4x). A colorless liquid; ^{1}H-NMR δ = 1.30 (3H, d, *J* = 7.0 Hz), 1.66 (3H, d, *J* = 6.1 Hz), 3.36 (1H, m, *trans* isomer), 3.76 (1H, m, *cis* isomer), 3.78 (3H, s), 5.39–5.49 (1H, m), 5.55–5.62 (1H, m), 6.84 (2H, d, *J* = 8.7 Hz), 7.12 (2H, d, *J* = 8.7 Hz); ^{13}C-NMR δ = 17.88, 21.57, 41.45, 55.25, 113.73, 123.33, 128.00, 136.58, 138.62, 157.79. The diastereomeric ratio was not determined because the peak of the allylic proton of the *cis* isomer overlaps with that of the methyl protons of the methoxy group in the ^{1}H-NMR spectrum. The ee value was determined by HPLC analysis with a Daicel Chiralcel OJ column using hexane as an eluent.

4-(1-Naphthyl)pent-2-ene (4y). A colorless liquid; ^{1}H-NMR δ = 1.47 (3H, d, *J* = 6.8 Hz, *trans* isomer), 1.48 (3H, d, *J* = 7.0 Hz, *cis* isomer), 1.69 (3H, dt, *J* = 6.4, 1.4 Hz, *trans* isomer), 1.74 (3H, dd, *J* = 6.6 Hz, *cis* isomer), 4.24 (1H, m, *trans* isomer), 4.53 (1H, m, *cis* isomer), 5.46–5.80 (2H, m), 7.36–7.53 (4H, m), 7.70 (1H, d, *J* = 7.7 Hz), 7.84 (1H, m), 8.13 (1H, d, *J* = 7.7 Hz); ^{13}C-NMR δ = 17.98, 21.06, 37.02, 123.43, 123.61, 124.13, 125.25, 125.58, 125.63, 126.56, 128.84, 131.44, 133.96, 135.82, 142.34.

4-(2-Naphthyl)pent-2-ene (4z). A colorless liquid; ^{1}H-NMR δ = 1.42 (3H, d, *J* = 6.9 Hz), 1.69 (3H, dt, *J* = 6.0, 1.2 Hz, *trans* isomer), 1.73 (3H, d, *J* = 1.4 Hz, *cis* isomer), 3.53–3.63 (1H, m, *trans* isomer), 3.89–4.01 (1H, m, *cis* isomer), 5.44–5.57 (1H, m), 5.65–5.74 (1H, ddq, *J* = 15.3, 6.6, 1.4 Hz), 7.36 (1H, dd, *J* = 8.5, 1.9 Hz), 7.40–7.47 (2H, m), 7.62 (1H, s), 7.75–7.81 (3H, m); ^{13}C-NMR δ = 17.94, 21.37, 42.41, 124.01, 124.93, 125.15, 125.81, 126.31, 127.55, 127.60, 127.84, 132.14, 133.64, 136.10, 143.91. The diastereomeric ratio of **4z** (*trans*:*cis* = 92:8) was

determined by ^{1}H-NMR analysis and the ee value was determined by HPLC analysis with a Daicel Chiralcel OD column using hexane as an eluent.

3-Phenylhex-1-ene (5). A colorless liquid; ^{1}H-NMR δ = 0.89 (3H, t, J = 7.8 Hz), 1.16–1.42 (2H, m), 1.65–1.71 (2H, m), 3.25 (1H, dt, J = 7.6, 7.6 Hz), 5.01 (1H, d, J = 13.9 Hz), 5.03 (1H, d, J = 8.9 Hz), 5.95 (1H, ddd, J = 13.9, 8.9, 7.6 Hz), 7.17–7.19 (3H, m), 7.26–7.31 (2H, m); ^{13}C-NMR δ = 13.98, 20.62, 37.63, 49.62, 113.80, 126.05, 127.60, 128.39, 142.53, 144.67. The ee value was determined by HPLC analysis with a Daicel Chiralcel OJ column using hexane as an eluent.

1-Phenylhex-2-ene (6). A colorless liquid; ^{1}H-NMR δ = 0.90 (3H, t, J = 7.3 Hz), 1.35–1.44 (2H, m), 2.00 (2H, dt, J = 6.8, 7.3 Hz, *trans* isomer), 2.14 (2H, dt, J = 7.1, 7.3 Hz, *cis* isomer), 3.33 (2H, d, J = 6.3 Hz, *trans* isomer), 3.40 (2H, d, J = 6.4 Hz, *cis* isomer), 5.47–5.61 (2H, m), 7.17–7.19 (3H, m), 7.25–7.30 (2H, m); ^{13}C-NMR δ = 13.67, 22.59, 34.59, 39.05, 125.83, 128.30, 128.46, 128.88, 131.88, 141.14. The diastereomeric ratio of **6** (*trans*:*cis* = 90:10) was determined by ^{1}H-NMR analysis.

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