0.12 g (0.3 mmol) of I was added. Dry HCl gas was then bubbled. Bubbling for 15 min. of the solution resulted in brown. GC analysis showed the formation of V.

Preparation of 2,3,7,7-tetramethyl-5-(phenylmethylchlorosilyl)-1-octene, VI. 5. An one-necked 10 mL flask was charged with 0.14 g (0.5 mmol) of a mixture of II diluted in 2 mL of hexane and then few drops of c.-HCl. After vigorous stirring for 12 hours the ring cleavage product, VI, was obtained in quantitatative yield. MS (EI, 70 eV) m/z (relative intensity) 322 (M^+, 1), 157 (35), 155 ([PhMeSiCl]$^+$, 100), 57 (33).

6. In the same conditions as experiment 5, dry HCl gas instead of c.-HCl was bubbled until pH paper showed the solution to be acidic. After bubbling of HCl gas for 15 min. the product, VI was obtained in quantitatitative yield.

Preparation of 2,3,7,7-tetramethyl-5-(phenylmethylmethoxysilyl)-1-octene, VII. 7. In a dry 10 mL one-necked flask was placed 0.14 g (0.5 mmol) of a mixture of 20% *Z*-II and 80% of *E*-II and 2 mL of absolute methanol and then few drops of c.-HCl. The mixture was vigorously stirred for 10 hours. A GC/MS analysis of reaction mixture showed a quantitative yields of the two diastereomeric ring opened products, VII in 50 to 50 ratio. MS (EI, 70 eV) m/z (relative intensity) 318 (M^+, 1), 261 (3), 151 ([PhMeSiOMe]$^+$, 100), 121 (19), 57 (9).

8. In a dry 25 mL three-necked flask equipped with a reflux condensor/gas inlet and septum was placed 0.14 g (0.5 mmol) of a mixture of 20% *Z*-II and 80% of *E*-II and 3 mL of absolute methanol. After bubbling of dry HCl gas for 15 min. the diastereomeric mixture of VII in 50 to 50 ratio was also obtained in experiments, 5, 6 by quenching with 2 mL of absolute methanol.

Preparation of 2,3,7,7-tetramethyl-5-(phenylmethylhydroxysilyl)-1-octene, VIII. 9. The diastereomeric mixture of VIII was prepared in experiments, 7, 8 by quenching with 1-2 mL of distilled water. After stirring vigorously for 2 hours, the reaction went to completion giving the diastereomeric mixture of VIII in 50 to 50 ratio. MS (EI, 70 eV) m/z (relative intensity) 304 (parent, 1), 247 (4), 137 ([PhMeSiOH]$^+$, 100), 57 (22).

Acknowledgement. This work was supported by the grant provided from the Korea Science and Engineering Foundaton.

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Asymmetric [2,3]-Witting Rearrangements in the Presence of Sparteine Derivatives

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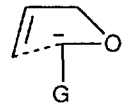
Asymmetric [2,3]-Wittig rearrangements of allyl propargyl ethers in hexane were performed in the presence of *s*-butyllithium and (−)-α-isosparteine which is a C_2-symmetric chiral ligand for the alkyllithium reagent. The reactions of (*Z*)-or (*E*)-allyl 3-trimethylsilylpropargyl ethers at −78℃ showed good diastereoselectivities (74-100%) and moderate enantioselectivities (29-71%). The absolute configurations of the rearrangement products were determined by the corresponding Mosher's esters. It was found that (−)-α-isosparteine induced (*R*) configuration at the hydroxy carbon and *syn* stereochemistry more favorably. The possible transition state is discussed.

Introduction

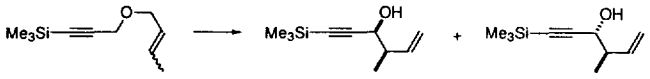
Considerable efforts have been directed toward the development of the stereoselective [2,3]-Wittig sigmatropic rearrangement of allyl ethers as a basic strategy for acyclic stereocontrol.[1] This [2,3]-Wittig rearrangement possesses several valuable features[2]: the regiospecific carbon-carbon bond formation with the allylic transposition of oxygen function, the

generation of specific olefin geometries, and the stereoselective creation of vicinal chiral centers. This reaction usually proceeds through a highly ordered cyclic folded-envelope type transition state like following figure (**1**), to accommodate the stereochemical outcomes.[3]



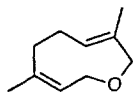
1

As a general rule, *E*-substrates exhibit *anti* selection, whereas *Z*-substrates show *syn* selection. The degree of conversion of *Z* isomers with *syn* selection is greater than that of *E* with *anti* selection. The general selection rule is rationalized by the *pseudo*-1,3-diaxial interaction. In case of G $=C\equiv C\text{-}SiMe_3$, the *Z* substrate exhibits high *syn* selectivity (98%), and the *E* counterpart also shows *syn* selection, which is opposite to the general selection rule, though the degree is moderate (75%).[4]



(*E*)- or (*Z*)-**2** *syn*-**3** (major) *anti*-**3**

Recently, Marshall showed that the asymmetric [2,3]-Wittig ring contraction of fairly rigid cyclic diallylic and allylic propargylic ethers **4** and **5** in the presence of an optically active alkylamide base provided optically active rearranged alcohols of 30-80% *ee*.[5] However, the method could not be extended to flexible and non-activated acyclic systems, which resulted only in racemic products.



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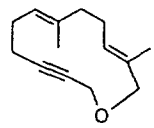
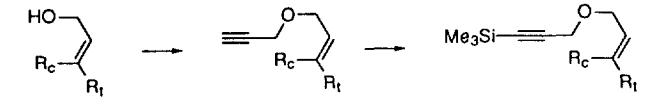


5

Asymmetric [2,3]-Wittig rearrangements of (*E*)- or (*Z*)-allylic 3-trimethylsilylpropargylic ethers were attempted in the presence of the readily available (−)-α-isosparteine as a chiral ligand for alkyllithium in order to develop the reaction on acyclic and non-activated prochiral substrates and to study factors associated with chiral ligands for alkyllithiums. The underlying assumption was that an alkyllithium would form a tetrahedral complex with isosparteine and allyl ether molecules.

Results and Discussion

(*Z*)- or (*E*)-allylic 3-trimethylsilylpropargyl ethers (**6a-d**) were prepared from the corresponding allylic alcohols as shown below.



R_t = Me R_c = H **6a**
R_t = H R_c = Me **6b**
R_t = Me R_c = Me **6c**
R_t = H R_c = Ph **6d**

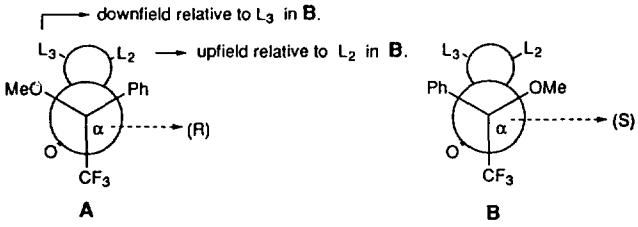
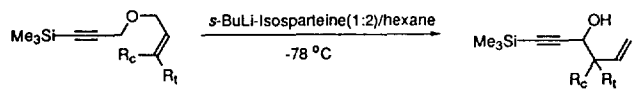


Figure 1. Relative chemical shifts of esters of an enantiopure alcohol with (*R*)- and (*S*)-MTPA.

These substrates were subjected to reaction with *s*-BuLi at −78℃ in an inert solvent to produce the corresponding secondary alcohols. Both ^1H NMR spectra and GC data were used to determine the diastereoselectivity. In our cases, the observed coupling constants were 4.9-6.2 Hz for the *syn* and 6.4-8.6 Hz for the *anti* forms of **6a-d**, which was in accordance with reported cases, 3.0-6.5 Hz for *syn* form and 7.0-9.0 Hz for *anti* forms.[6,7] The diastereoselectivity for the *cis*-crotyl derivative **6b** was better than that of the corresponding *trans*-crotyl analog **6a**. The *cis*-cinnamyl derivative **6d** gave the best diastereoselectivity as expected by the reported results.[4]

A number of experiments with **6a** as a model substrate in the presence of (−)-α-isosparteine were carried out to find out the optimum condition. The main difficulty in the reaction was that since isosparteine contains one molecule of hydrated water and free isosparteine was very hydroscopic, it was difficult to remove water molecule from the isosparteine ligand before the reaction. It was found that, among the various drying methods examined, drying the solution of isosparteine by stirring with CaH_2 for a few hours followed by transfer of the solution to reaction flask was the best. For reaction solvent, nonpolar solvent like hexane was better than ethereal solvents like ether and THF, which might affect the reaction by coordination to the metal. Also, it was found that the optimum ratio of substrate: (−)-α-isosparteine: *s*-BuLi was 1 : 3 : 2. Thus, *s*-BuLi was added to isosparteine in hexane at −78℃, and the mixture was warmed up to *ca.* −30℃ to ensure a good complexation. After stirring for *ca.* 1h at the temperature, the muddy color of the solution changed to clear yellow. The substrate was added after this solution was cooled down −78℃ again. The [2,3]-Wittig rearrangement was carried out with 4 substrates (**6a-d**) under this standard condition and a moderate enantioselectivity was obtained as described in experimental section. Therein are also listed the structures of products modified for GC analysis and detailed GC conditions.



R_t = Me R_c = H **6a** **7a**
R_t = H R_c = Me **6b** **7b**
R_t = Me R_c = Me **6c** **7c**
R_t = H R_c = Ph **6d** **7d**

After determining suitable conditions for analysis of expected products, the absolute configurations of the product alcohols **7** were determined by extended Mosher's method with α-methoxy-α-trifluoromethylphenylacetic acid (MTPA) esters, the assumption of which is that the carbinyl proton and ester

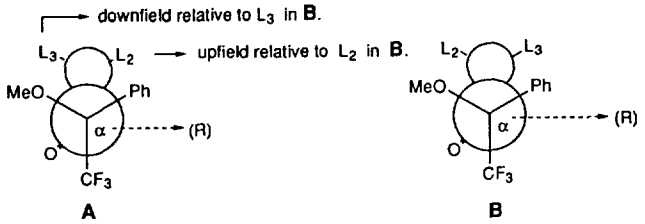
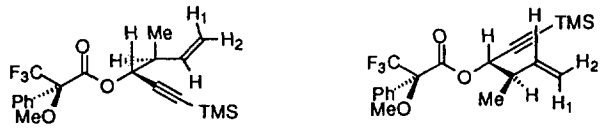


Figure 2. Relative chemical shifts of esters of a racemic alcohol with (*R*)-MTPA.

Table 1. ^{1}H NMR Chemical Shift Differences for (*R*)-MTPA Ester of Alcohol **7b**



Group	**B** (3*S*, 4*R*)	**A** (3*R*, 4*S*)	$\Delta\delta=\delta_B-\delta_A$
-OCH_3	3.540	3.587	−0.047
-$Si(CH_3)_3$	0.155	0.178	−0.023
-CH_3	1.145	1.083	0.062
-C=C-CH	2.645	2.583	0.062
-C≡C-CH	5.450	5.479	−0.029
-CH=C	5.834	5.740	0.094
-C=CH_1	5.123	5.038	0.085
-C=CH_2	5.118	5.054	0.064

carbonyl and trifluoromethyl groups of MTPA moiety all lie in the same plane.[8] Therefore, ^{1}H NMR signal of L_2 of the (*R*)-MTPA ester will appear upfield relative to that of the (*S*)-MTPA ester due to the diamagnetic effect of the benzene ring (Figure 1).[8] When $\Delta\delta=\delta_S-\delta_R$ (ppm) is calculated, the protons on the right side of the plane must have positive value ($\Delta\delta>0$) and protons on the left side of the plane negative value ($\Delta\delta<0$). After the position of each group was settled, absolute configuration was predicted according to the priority.

Conversely, the same reasoning could be true with a diastereomeric ester pair of a pure racemic alcohol with a specific MTPA, either (*R*) or (*S*). As described in Figure 2, when pure (*R*)-MTPA was used, two isomers A and B would be produced, and the chemical shift of L_2 and L_3 would show up differently. When each group was fixed as A and B according to the relative chemical shift by Mosher's assumption, the priority led to their absolute configuration such as A to (*R*) and B to (*S*) or *vice versa*.

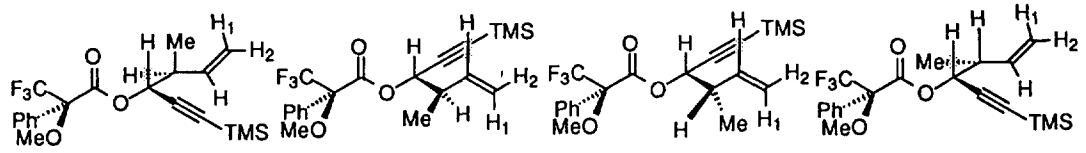
Consequently, the rearranged alcohol products were individually converted to the corresponding diastereomeric mixtures of (*R*)-MTPA esters, which were separated by preparative TLC (several elutions). Gratifyingly, no irregularity was observed in $\Delta\delta$ values of all the cases, which eliminated ambiguity.[8] Thus, ^{1}H NMR signal of L_2 of the (*R*)-MTPA ester appeared upfield relative to that of the (*S*)-MTPA ester (Figure 2).[8] The assignments of ^{1}H NMR spectra of MTPA esters and $\Delta\delta$ values were described in Table 1-4.

Thus, it was possible to assign the absolute configurations of all the products. All the major enantiomers had (*R*) configuration at the carbinyl carbon. Also, the chemical shift change of the proton attached to the hydroxy carbon provided valuable information about the ratio of *syn* : *anti* isomers.

Finally, the same experiments were carried out with sparteine to compare the degree of asymmetric induction and aspect of stereoselectivity of the reactions with those of isosparteine. The results and comparison with isosparteine reactions are summarized in Table 5. The most interesting point was that when the *cis*-cinnamyl derivative **6d** was used as the substrate, *anti* form was a major product in sparteine reaction, which was opposite to the results with isosparteine.

Based on the above experimental results, it was proved

Table 2. ^{1}H NMR Chemical Shift Differences for (*R*)-MTPA Ester of Alcohol **7a**

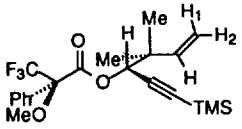


syn isomers *anti* isomers

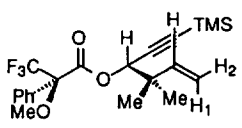
Group	**B** (3*S*, 4*R*)	**A** (3*R*, 4*S*)	$\Delta\delta_{B-A}$ (ppm)	**C** (3*S*, 4*S*)	**D** (3*R*, 4*R*)	$\Delta\delta_{C-D}$ (ppm)
-OCH_3	3.545	3.590	−0.045	[a]	[a]	
-$SiMe_3$	0.159	0.181	−0.022	[a]	0.095	
-CH_3	1.150	1.085	0.065	1.169	1.089	0.080
-C=C-CH	2.646	2.584	0.062	[a]	[a]	
-C≡C-CH	5.461	5.487	−0.026	5.412	5.466	−0.054
-CH=C	5.836	5.742	0.094	5.743	5.682	0.061
-CH=CH_1	5.127	5.029	0.098	[a]	[a]	
-C=CH_2	5.116	5.050	0.066	[a]	[a]	
-C_6H_5	7.536	7.575	−0.034	[a]	[a]	

[a] The peak was obscured by other multiplets.

Table 3. ^{1}H NMR Chemical Shift Differences for (*R*)-MTPA Ester of Alcohol **7c**



A (3*R*)



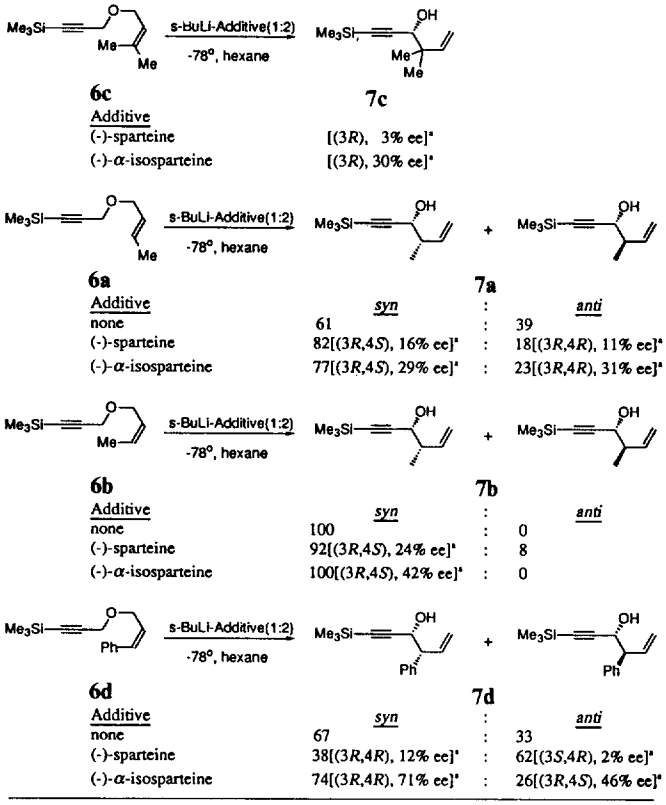
B (3*S*) **8c**

Group	B (3*S*)	A (3*R*)	$\Delta\delta=\delta_B-\delta_A$
-OMe	3.529	3.581	−0.052
-$SiMe_3$	0.156	0.182	−0.026
-Me	1.131	1.089	0.044
-C≡C-CH	5.273	5.317	−0.044
-CH=C	5.859	5.806	0.053
-C=CH_1	5.079	5.019	0.060
-C=CH_2	5.081	5.032	0.049
-C_6H_5	7.455	7.489	−0.034

that the isosparteine played an important role in the reaction. A similar transition state can be proposed for the present chiral ligand system as Marshall's transition states in the [2,3]-Wittig reaction,[9] which are shown in Figure 3. The oxygen in the substrate is coordinated to the lithium in isosparteine-*s*-BuLi complex. Then the coordinating *s*-BuLi faces one of the enantiotopic hydrogens (H_S and H_R). The abstraction of either hydrogens will determine the absolute configuration of the hydroxy carbon. Because the anion is to be created to the opposite direction of the hydrogen abstraction, the allylic group should be arranged at this opposite side to form a five membered cyclic transition state. Consequently, the relative stereochemistry will be dependent on the conformation of the ether moiety, *i.e.* which side of the allylic plane would be attacked by the incipient carbanion.

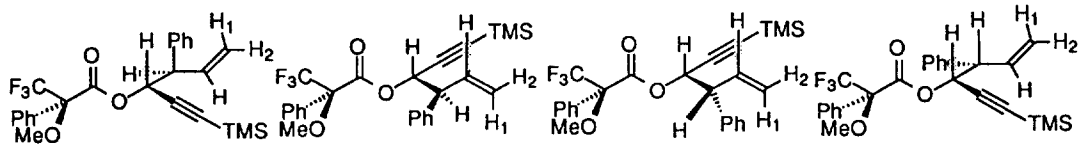
Thus, the transition state accomodates the facts, the *syn*-directing transition state previously reported[4] and that the pro-R hydrogen was preferentially abstracted in the present reaction. Thus, the *a priori* conjecture about the importance of interaction of the methylene groups of substrates with the C_2-symmetric wings of isosparteine to determine the enantioselectivity was realized although the pocket depth of the bidentate ligand was not sufficiently big.

Table 5. Diastereo- and Enantioselectivity of 2,3-Wittig Reactions



[a] Major enantiomer formed in the reaction. [b] Not determined.

Table 4. ^{1}H NMR Chemical Shift Differences for (*R*)-MTPA Ester of Alcohol **7d**



A (3*R*,4*R*) B (3*S*,4*S*) C (3*S*,4*R*) D (3*R*,4*S*)

syn isomer *anti* isomer

Group	B (3*S*, 4*S*))	A (3*R*, 4*R*)	$\Delta\delta_{B-A}$ (ppm)	C (3*S*, 4*R*)	D (3*R*, 4*S*)	$\Delta\delta_{C-D}$ (ppm)
-OMe	3.447	3.543	−0.097	3.161	3.449	−0.288
-$SiMe_3$	0.066	0.070	−0.004	0.153	0.156	−0.003
-C≡C-CH	5.741	5.767	−0.026	5.784	5.844	−0.060
-C=C-CH	3.771	3.702	0.069	3.733	3.711	0.062
-CH=C	6.096	6.012	0.084	6.123	6.075	0.048
-C=CH_1	5.189	5.109	0.080	5.111	5.049	0.062
-C=CH_2	5.226	5.147	0.079	5.226	5.171	0.055
-Ph_1	7.117	7.124		7.117	7.124	
-Ph_2	7.423	7.386		7.423	7.386	

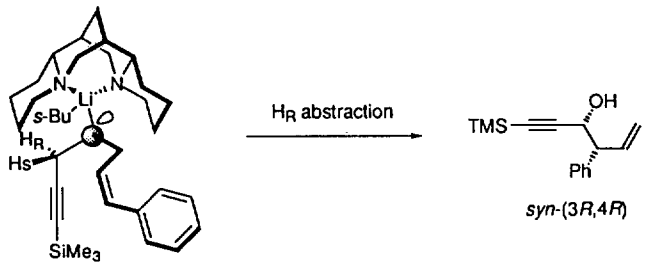


Figure 3. Assumed transition states of isosparteine-**6d** complex.

Experimental Section

General

All reactions involving organometallic reagents were carried out under an inert atmosphere of Nitrogen. Tetrahydrofuran and diethyl ether were freshly distilled from sodium benzophenone ketyl, and methylene chloride and hexane from calcium hydride prior to use. Liquid reagents were transferred using hypodermic syringes. Alkyllithium solutions (Aldrich) were assayed for active alkyl by titration with 2-butanol in tetrahydrofuran using 1,10-phenanthroline as an indicator. All allyl 3-trimethylsilylpropargyl ethers were purified by flash column chromatography and dried over molecular sieves (Linde 4 A, 600 mesh) before use. The term "usual workup" refers to the following product isolation procedure: dilution and successive extraction with ether and brine; treatment of the organic extracts with anhydrous magnesium sulfate ($MgSO_4$); and the solvent removal under reduced pressure. Flash chromatography was performed on a Tokyo Rikakikai EF-10 with Merck 230-400 mesh silica gel.

^{1}H NMR spectra were obtained on a Varian EM-360A (60 MHz), Varian Gemini 300 (300 MHz) or 200 (200 MHz) instruments, recorded in ppm (δ) relative to tetramethylsilane (δ 0.00) as an internal as follows: chemical shift, multiplicity (br=broad, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet), coupling constant and integration. Mass spectra were taken on a VG Trio 2000 (low resolution) spectrometer with an electron beam energy of 70 eV (EI). Diastereomeric excess and enantiomeric excess (%) were taken on Hewlett Packard 5890 Series II Gas chromatograph, equipped with chiral GC columns; Chiraldex B-TA (30 m×0.25 mm), G-TA (30 m×0.25 mm) or HP-1 (25 m×0.32 mm), Nonpolar column was also used to measure the completion of reaction. The ligand, (−)-α-isosparteine monohydrate was prepared in overall 50% yield by formic acid reduction[10] of (−)-α-$\Delta^{5,11}$-didehydrosparteine.[10,11] GC (HP-1) 250℃ (5 min)/10℃ /min/280℃ (30 min) t=2.69 min [*cf.* (−)-sparteine: t=3.23 min]. MS m/e 234 (M^+), 137, 98.

Preparation of (*E*)-Crotyl Propargyl Ether.[4]

Into a 20% aqueous sodium hydroxide solution (50.0 g in 150 m*l* water) was added catalytic amount of tetrabutylammonium hydrogen sulfate (5.5 g, 0.02 mol) and (*E*)-crotyl alcohol (21.0 g, 0.29 mol). After vigorous stirring of the mixture for 1h was added propargyl bromide (45.0 g, 0.38 mol) dropwise over 0.5h and the resulting mixture was stirred overnight at rt. Then usual workup was carried out. Distillation under a low pressure (120℃ /60-70 mmHg) gave the product (20.1 g, 63.1%). TLC (10% ethyl acetate/hexane) R_f, 0.70. GC (HP-1) 80℃ (5 min)/10℃ /min/200℃ (5 min)/10℃ /min/280℃ (10 min) t=3.25 min. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.728 (dd, J=6.4 Hz, 1.44 Hz, 3H), 2.431 (t, J=2.4 Hz, 1H), 3.998 (dd, J=6.4 Hz, 1.10 Hz, 2H), 4.122 (d, J=2.4 Hz, 2H), 5.568 (dt, J=15.3 Hz, 6.4 Hz, 1H), 5.757 (dq, J=15.3 Hz, 6.5 Hz, 1H). Likewise, following products were prepared.

(*Z*)-Crotyl Propargyl Ether

Yield=54% (rt, 24h). bp. 45-48℃ /20 mmHg. TLC (5% ether/hexane) R_f 0.60. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.695 (dd, J=6.5 Hz, 1.6 Hz, 3H), 2.439 (d, J=2.4 Hz, 1H), 4.146 (d, J=6.6 Hz, 2H), 4.321 (d, J=2.5 Hz, 2H), 5.506-5.593 (m, 1H), 5.670-5.757 (m, 1H).

Prenyl Propargyl Ether

Yield=68% (rt, 18h), bp=120-121℃. TLC (30% ethyl acetate/hexane) R_f 0.80. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.620 (s, 3H), 1.700 (s, 3H), 1.700 (s, 3H), 2.300 (t, J=2.5 Hz, 1H), 3.900 (d, 2H), 4.200 (d, J=2.4 Hz, 2H), 5.100 (m, 1H).

(*Z*)-Cinnamyl Propargyl Ether. Yield=89.2% (30℃, 12 h). bp=96-98℃ /10 mmHg. TLC (30% ethyl acetate/hexane) R_f 0.80. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 2.430 (t, J=2.2 Hz, 1H), 4.196 (d, J=2.4 Hz, 2.0H), 5.866 (dd, J=6.5 Hz, 11.8 Hz, 1H), 6.661 (d, J=11.9 Hz, 1H), 7.232-7.417 (m, 5H).

Preparation of (*E*)-Crotyl 3-Trimethylsilylpropargyl Ether 6a

To a solution of ethylmagnesium bromide (0.19 mol) in tetrahydrofuran (150 m*l*) was added a solution of (*E*)-crotyl propargyl ether (11.0 g, 0.10 mol) at 0℃ and the mixture was stirred for 1.5 h at 15-18℃. Chlorotrimethylsilane (19 m*l*, 0.15 mol) was added dropwise to the resulting mixture at 0℃ over 20 min and the mixture was stirred at 20℃ for 11h. Usual workup gave the product (13.0 g) in 68% yield. bp 60℃ /3 mmHg. TLC (5% ethyl acetate/hexane) R_f 0.53. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.166 (s, 9H), 1.710 (dd, J=1.4 Hz, 6.4 Hz, 3H), 3.974 (dd, J=6.4 Hz, 1.1 Hz, 2H), 4.108 (s, 2H), 5.517-5.615 (dqt, J=16.0 Hz, 7.9 Hz, 1.5 Hz, 1H), 5.692-5.789 (dqt, J=16.0 Hz, 6.4 Hz, 1.1 Hz, 1H) [lit.[4] (CCl_4), δ 0.07 (s, 9H), 1.63 (d, J=5.4 Hz, 3H), 3.90 (d, J=5.7 Hz, 2H), 4.03 (s, 2H), 5.23-5.82 (m, 2H)]. Likewise, the following products were prepared.

(*Z*)-Crotyl 3-Trimethylsilylpropargyl Ether 6b

Yield=50.3% (0℃, 30 min). TLC (2% ether/hexane) R_f 0.30. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.168 (s, 9H), 1.681 (d, J=5.9 Hz, 3H), 4.104 (s, 2H), 4.127 (s, 2H), 5.504-5.751 (m, 2H). [lit.[4] (CCl_4), δ 0.18 (s, 9H), 1.66 (d, J=5.4 Hz, 3H), 4.00 (s, 2H), 4.03 (d, J=4.8 Hz, 2H), 5.23-5.82 (m, 2H)].

(*Z*)-Cinnamyl 3-Trimethylsilylpropargyl Ether 6d

Yield=79% (0℃, 1h, rt, 12h). TLC (5% ethyl acetate/hexane) R_f 0.35. ^{1}H NMR (Acetone-d_6, 300 MHz): δ 0.125 (s, 9H), 4.195 (s, 2H), 4.347 (dd, J=6.4 Hz, 1.8 Hz, 2H), 5.830 (dt, J=11.9 Hz, 6.2 Hz, 1H), 6.632 (d, J=11.8 Hz, 1H), 7.269-7.382 (m, 5H). GC (HP-1) 200℃ (5 min)/10℃ /min/280℃ (20 min) split 80 : 1 R_t=5.02 min. MS m/e 244 (M^+), 229, 105, 154, 73.

Prenyl 3-Trimethylsilylpropargyl Ether 6c

Yield=81.9% (0℃, 30 min). TLC (5% ethyl acetate/hexane) R_f 0.40. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.171 (s, 9H), 1.697 (s, 3H), 1.750 (s, 3H), 4.048 (d, J=7.1 Hz, 2H), 4.117 (s, 2H), 5.340 (m, 1H). GC (HP-1) 180℃ (5 min)/10℃ /min/280℃ (20 min) split 80 : 1 R_t=2.38 min. MS m/e 196 (M^-), 181, 151, 103, 83, 73.

Rearrangement of (*E*)-Crotyl 3-Trimethylsilylpropargyl Ether: *syn*- and *anti*-4-Methyl-1-trimethylsilyl-5-

hexen-1-yn-3-ol

To a cold (−75∼−78℃) solution of (*E*)-crotyl 3-trimethylsilylpropargyl ether (40.5 mg, 220 mmol) in dry ether (3 m*l*) was added a solution of *sec*-butyllithium (330 mmol) dropwise. This resulting mixture was stirred at −78℃ for 1h and quenched at the temperature with saturated sodium bicarbonate solution. Usual workup followed by flash column chromatography afforded a diastereomeric mixture of the rearranged alcohols (30.0 mg, 74%). TLC (5% ethyl acetate/hexane) R_f 0.30. ^{1}H NMR ($CDCl_3$, 300 MHz): *syn*: δ 0.166 (s, 9H), 1.108 (d, J=6.8 Hz, 3H), 1.932 (br s, 1H), 2.413-2.479 (m, 1H), 4.255 (d, J=4.91H), 5.132-5.185 (m, 2H), 5.790-5.909 (m, 1H); *anti*: δ 0.177 (s, 9H), 1.124 (d, J=6.8 Hz, 3H), 1.932 (br s, 1H), 2.413-2.479 (m, 1H), 4.188 (d, J=6.4 Hz, 1H), 5.132-5.182 (m, 2H), 5.132-5.840 (m, 1H). Similar reactions for other substrates afforded the following rearranged products, respectively.

Rearrangement Product from (*Z*)-Crotyl 3-Trimethylsilylpropargyl Ether: *syn*-4-Methyl-1-trimethylsilyl-5-hexen-1-yn-3-ol

TLC (5% ethyl acetate/hexane) R_f 0.30. ^{1}H NMR ($CDCl_3$, 300 MHz): *only syn*: δ 0.171 (s, 9H), 1.114 (d, J=6.9 Hz, 3H), 1.256 (br s, 1H), 2.418-2.484 (m, 1H), 4.261 (d, J=4.9 Hz, 1H), 5.144 (dd, J=3.2 Hz, 4.2 Hz, 1H), 5.193 (s, 1H), 5.794-5.913 (m, 1H). GC (HP-1) 160℃ (5 min)/10℃/min/280℃ (20 min) R_t=2.29 min. MS m/e 182 (M^+), 167, 127, 99, 73.

Rearrangement Product from (*Z*)-Cinnamyl 3-Trimethylsilylpropargyl Ether: *syn*- and *anti*-4-Phenyl-1-trimethylsilyl-5-hexen-1-yn-3-ol

TLC (10% ethyl acetate/hexane) R_f 0.40. ^{1}H NMR ($CDCl_3$, 300 MHz): *syn*: δ 0.165 (s, 9H), 1.914 (s, 1H), 3.562-3.619 (m, 1H), 4.538-4.593 (m, 1H), 5.292 (d, J=11.1 Hz, 1H), 5.287 (d, J=15.4 Hz, 1H), 6.265 (ddd, J=17.1 Hz, 10.3 Hz, 8.4 Hz, 1H), 7.245-7.381 (m, 5H); *anti*: δ 0.166 (s, 9H), 1.938 (s, 1H), 5.292 (d, J=11.1 Hz, 1H), 5.287 (d, J=15.4 Hz, 1H), 6.198 (ddd, J=17.0 Hz, 10.5 Hz, 8.3 Hz, 1H), 7.245-7.381 (m, 5H). GC (HP-1) 160℃ (5 min)/10℃/min/280℃ (30 min) R_t=8.59 min (*syn*), 8.72 min (*anti*). MS m/e 244 (M^+), 154, 118, 115, 99.

Rearrangement Product from Prenyl 3-Trimethylsilylporpargyl Ether: 4,4-Dimethyl-1-trimethylsilyl-5-hexen-1-yn-3-ol

TLC (5% ethyl acetate/hexane) R_f 0.30. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.174 (s, 9H), 1.103 (s, 3H), 1.120 (s, 3H), 1.713 (br s, 1H), 4.045 (s, 1H), 5.122 (dd, J=17.5 Hz, 1.6 Hz, 1H), 5.157 (dd, J=10.9 Hz, 1.3 Hz, 1H), 5.930 (dd, J=17.5 Hz, 10.9 Hz, 1H).

Asymmetric Rearrangement of (*E*)-Crotyl 3-Trimethylsilylpropargyl Ether

Sublimed (−)-α-isosparteine (0.75 g, 3.20 mmol) was mixed with calcium hydride (2.00 g) in a 25 m*l* flask which was dried *in vacuo* for 10 min. To that mixture was poured dried hexane (10 m*l*) and the mixture was stirred for 3-4h. The stirring was stopped to settle calcium hydride down to make the solution clear. To a vacuum dried flask was transferred 5 m*l* of that clear isosparteine solution. The solution was cooled down to −78℃ and *sec*-butyllithium (1.07 mmol) was added at the temperature. The mixture was warmed up to −30℃ and stirred for 20-30 min at that temperature. After cooling down to −78℃ again, (*E*)-Crotyl 3-trimethylsilylpropargyl ether (0.09 g, 0.47 mmol) was added dropwise to that solution and the mixture was stirred for 15 min at that temperature. 4N HCl solution was added to the reaction mixture at −78℃, and was warmed up to rt slowly. Isosparteine was recovered as a HCl salt dissolved in acidic aqueous solution, and the residue was followed by a usual workup which gave the product (0.02 g) in 23% yield.

Likewise, this procedure was applied with (−)-sparteine as well as (−)-α-isosparteine to other substrates. The ^{1}H NMR data were the same as those of previously presented products from the reaction without any chiral ligands.

Desilylation of 4-Hydroxy-3-phenyl-6-trimethylsilyl-1-hexen-5-yne[4]

To a solution of 4-hydroxy-3-phenyl-6-trimethylsilyl-1-hexen-5-yne (0.020 g, 0.11 mmol) in water (0.5 m*l*) and methanol (2.0 m*l*) was added cesium fluoride (0.010 g) and the mixture was stirred overnight at 25-30℃. Usual workup followed by flash column chromatography (10% ether/hexene) gave the product. TLC (30% ethyl acetate/hexane) R_f 0.5. ^{1}H NMR ($CDCl_3$, 300 MHz): *syn*: δ 1.986 (d, J=7.2 Hz, 1H), 2.509 (d, J=2.1 Hz, 1H), 3.600 (d, J=6.2 Hz, 1H), 4.612 (dd, J=4.5 Hz, 6.5 Hz, 1H), 5.248 (dd, J=8.6 Hz, 0.9 Hz, 1H), 6.255 (ddd, J=17.1 Hz, 10.5 Hz, 8.5 Hz, 1H), 7.249-7.388 (m, 5H): *anti*: δ 1.971 (d, J=6.5 Hz, 1H), 2.451 (d, J=2.2 Hz, 1H), 3.634 (d, J=8.4 Hz, 1H), 4.612 (dd, J=6.6 Hz, 8.6 Hz, 1H), 5.248 (dd, J=17.1 Hz, 1.2 Hz, 1H), 5.310 (dd, J=8.6 Hz, 0.9 Hz, 1H), 6.192 (ddd, J=17.2 Hz, 10.8 Hz, 1H), 7.249-7.388 (m, 5H).

Preparation of Mosher's ester

Method A.[12] To a solution of (+)- or (−)-α-Methoxy-α-trifluoromethylphenylacetic acid (MTPA) (70 mg, 0.30 mmol) and 4-dimethylaminopyridine (DMAP) (33.0 mg, 0.28 mmol) in methylene chloride (0.3 m*l*) was added a solution of an alcohol of interest (0.05 g) in CH_2Cl_2 (0.3 m*l*), which was followed by slow addition of a solution of dicyclohexylcarbodiimide (DCC) (68.1 mg, 0.33 mmol) in CH_2Cl_2 (0.1 m*l*) at 0℃. The mixture was warmed up to room temperature and then stirred for 2-24h. The resulting white solid was filtered off and the solution was evaporated. The residue was subjected to preparative TLC (Merck, Kieselgel 60, F_{254}, 2% ether in hexane, 4 elutions), affording the diastereomeric esters.

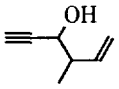
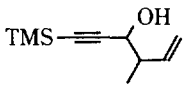
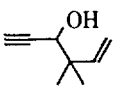
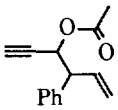
Method B.[13] (+)- or (−)-MTPA (320 g, 1.34 mmol) and thionyl chloride (5 m*l*) were refluxed together for 12h. After excess thionyl chloride was removed by vacuum evaporation and addition of pyridine (1.73 m*l*) at 0℃. A solution of an alcohol of interest (0.05 g) in CH_2Cl_2 (1 m*l*) was added to the (+)- or (−)-MTPA chloride and this mixture was stirred at rt for 3h. After usual workup, the crude product was subjected to preparative TLC (Merck, Kieselgel 60, F_{254}, 2% ether in hexane, 4 elutions), affording the diastereomeric esters.

The MTPA esters of **7b** was prepared by Method B and those of **7a**, **7c** and **7d** were obtained by Method A. The NMR data are listed below.

(*R*)-MTPA Ester of (3*R*, 4*S*)-4-Methyl-1-trimethylsilyl-5-hexen-1-yn-3-ol

^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.178 (s, 9H), 1.083 (d, J=6.9 Hz, 3H), 2.548-2.613 (m, 1H), 3.587 (d, J=1.1 Hz, 3H), 5.038 (dd, J=17.5 Hz, 1.2 Hz, 1H), 5.054 (dd, J=10.2 Hz, 1.2 Hz, 1H), 5.479 (d, J=5.1 Hz, 1H), 5.740 (ddd, J=17.5 Hz, 10.2

Table 6. Determination of Diastereoselectivity and Enantioselectivity

Substrate	**6b**	**6a**	**6c**	**6d**
Product	**7b**	**7a**	**7c**	**7d**
Molecules Actually Analyzed				
Chiral column	B-TA	B-TA	G-TA	G-TA
GC condition	0.986 ml/min	1.35 ml/min	0.798 ml/min	1.0 ml/min
	122 : 1 split	89 : 1 split	100 : 1 split	120 : 1 split
	70℃ isothermal	80℃ isothermal	80℃ isothermal	100℃ isothermal
t_R (min)	18.015	28.688	23.424	94.980
	18.583	29.093	23.984	96.887
		32.830		103.336
		33.328		104.763
Racemic Rxn	50.0[a]	28.5[a]	49.9[a]	33.2[a]
Area ratio	50.0[a]	32.4[a]	50.1[a]	33.3[a]
(normalized)		18.8[a]		11.5[a]
		20.3[a]		22.0[a]
Chiral Rxn	28.8[a,b] (*syn*-3*R*, 4*S*)[c]	46.9[a] (*syn*-3*R*, 4*S*)[c]	34.8[a] (3*S*)[c]	63.4[a] (*syn*-3*R*, 4*R*)[c]
with isosparteine	71.2[a,b] (*syn*-3*S*, 4*R*)[c]	29.6[a](*syn*-3*S*, 4*R*)[c]	65.2[a] (3*R*)[c]	10.7[a] (*syn*-3*S*, 4*S*)[c]
Area ratio		15.0[a] (*anti*-3*R*, 4*R*)[c]		13.6[a] (*anti*-3*R*, 4*S*)[c]
(normalized)		8.5[a] (*anti*-3*S*, 4*S*)[c]		12.3[a] (*anti*-3*S*, 4*R*)[c]
syn/*anti*	100 : 0	77 : 23		74 : 26
ee% (*syn*)	42 (3*R*, 4*S*)[d]	29 (3*R*, 4*S*)	30(*R*)[d]	71 (3*R*, 4*R*)
ee% (*anti*)		31 (3*R*, 4*R*)		46 (3*R*, 4*S*)

[a] In order of elution. [b] The order of elution of *syn* and *anti* isomers changed after desilylation. [c] Assignment of absolute configuration. (*vide infra*). [d] Chiroptical properties: (3*R*, 4*S*)-*syn*-4-Methyl-1-trimethylsilyl-5-hexen-1-yn-3-ol, $[\alpha]_D^{23}=6.0$ (*c* 0.4, CH_2Cl_2) as 42.3% *ee*; (3*R*, 4*S*)-*syn*-4-Methyl-5-hexen-1-yn-3-ol, $[\alpha]_D^{23}=2.5$ (*c* 0.2, CH_2Cl_2) as 42.3% *ee*; (3*R*)-4,4-Dimethyl-1-trimethylsilyl-5-hexen-1-yn-3-ol, $[\alpha]_D^{23}=5.0$ (*c* 0.2, CH_2Cl_2) as 30.0% *ee*; (3*R*)-4,4-Dimethyl-5-hexen-1-yn-3-ol, $[\alpha]_D^{23}=2.3$ (*c* 0.3, CH_2Cl_2) as 30.0% *ee*.

Hz, 7.1 Hz, 1H), 7.389-7.550 (m, 5H).

(*R*)-MTPA Ester of (3*S*, 4*R*)-4-Methyl-1-trimethylsilyl-5-hexen-1-yn-3-ol

^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.155 (s, 9H), 1.145 (d, *J*=6.9 Hz, 3H), 2.613-2.676 (m, 1H), 3.540 (d, *J*=1.1 Hz, 3H), 5.118 (dd, *J*=10.5 Hz, 1.4 Hz, 1H), 5.123 (dd, *J*=16.2 Hz, 1.4 Hz, 1H), 5.450 (d, *J*=5.1 Hz, 1H), 5.834 (ddd, *J*=16.2 Hz, 11.5 Hz, 7.3 Hz, 1H), 7.384-7.559 (m, 5H).

(*R*)-MTPA Ester of (3*R*)-4,4-Dimethyl-1-trimethylsilyl-5-hexen-1-yn-3-ol

^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.182 (s, 9H), 1.089 (s, 6H), 3.581 (d, *J*=1.1 Hz, 3H), 5.019 (dd, *J*=16.0 Hz, 1.1 Hz, 1H), 5.032 (dd, *J*=10.4 Hz, 1.1 Hz, 1H), 5.317 (s, 1H), 5.906 (dd, *J*=16.0 Hz, 10.4 Hz, 1H), 7.348-7.570 (m, 5H).

(*R*)-MTPA Ester of (3*S*)-4,4-Dimethyl-1-trimethylsilyl-5-hexen-1-yn-3-ol

^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.156 (s, 9H), 1.133 (s, 6H), 3.529 (d, *J*=1.1 Hz, 3H), 5.079 (dd, *J*=16.8 Hz, 1.1 Hz, 1H), 5.081 (dd, *J*=10.9 Hz, 1.1 Hz, 1H), 5.273 (s, 1H), 5.273 (s, 1H), 5.859 (dd, *J*=16.8 Hz, 10.9 Hz, 1H), 7.357-7.555 (m, 5H).

(*R*)-MTPA Ester of (3*R*, 4*R*)-4-Phenyl-1-trimethylsilyl-5-hexen-1-yn-3-ol

^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.070 (s, 9H), 3.543 (d, *J*=1.2 Hz, 3H), 3.702 (m, 1H), 5.109 (dd, *J*=17.0 Hz, 1.3 Hz, 1H), 5.147 (dd, *J*=10.4 Hz, 1.3 Hz, 1H), 5.767 (d, *J*=6.9 Hz, 1H), 6.012 (ddd, *J*=17.0 Hz, 10.4 Hz, 6.9 Hz, 1H), 7.124-7.386 (m, 10H).

(*R*)-MTPA Ester of (3*S*, 4*S*)-4-Phenyl-1-trimethylsilyl-5-hexen-1-yn-3-ol

^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.066 (s, 9H), 3.447 (d, *J*=1.3 Hz, 3H), 3.771 (m, 1H), 5.189 (dd, *J*=10.4 Hz, 1.3 Hz, 1H), 5.226 (dd, *J*=10.4 Hz, 1.3 Hz, 1H), 5.741 (d, *J*=7.1 Hz, 1H), 6.096 (ddd, *J*=18.2 Hz, 10.4 Hz, 7.1 Hz, 1H), 7.117-7.423 (m, 10H).

(*R*)-MTPA Ester of (3*R*, 4*S*)-4-Phenyl-1-trimethylsilyl-5-hexen-1-yn-3-ol

^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.156 (s, 9H), 3.449 (d, *J*=1.2 Hz, 3H), 3.711 (m, 1H), 5.049 (dd, *J*=17.1 Hz, 1.3 Hz, 1H), 5.171 (dd, *J*=10.3 Hz, 1.3 Hz, 1H), 5.844 (d, *J*=7.6 Hz, 1H), 6.075 (ddd, *J*=17.1 Hz, 10.3 Hz, 7.4 Hz, 1H), 7.124-7.386 (m, 10H).

(*R*)-MTPA Ester of (3*S*, 4*R*)-4-Phenyl-1-trimethylsilyl-5-hexen-1-yn-3-ol

^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.153 (s, 9H), 3.161 (d, *J*=1.2 Hz, 3H), 3.773 (m, 1H), 5.111 (dd, *J*=17.1 Hz, 1.3 Hz, 1H), 5.226 (dd, *J*=10.3 Hz, 1.3 Hz, 1H), 5.784 (d, *J*=9.0 Hz, 1H), 6.123 (ddd, *J*=17.1 Hz, 10.3 Hz, 7.6 Hz, 1H), 7.117-7.423 (m, 10H).

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Real Time Spectroelectrochemical Experiments with a Multichannel Detector

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A spectroelectrochemical system assembled with a white light source, bifurcated optical fiber, Oriel Multispec® spectrograph, and a charge-coupled device (CCD) detector is described. The system is shown to be capable of acquiring a whole spectrum in the spectral range of 290-800 nm in 25 ms or a longer period during electrochemical experiments at reflective working electrodes such as platinum or mercury. The utility of the system in studying electrochemical reactions during the potential scan, galvanostatic electrolysis, or after the potential step is demonstrated.

Introduction

The *in-situ* spectroelectrochemical technique has been used extensively to probe intermediate species during electrochemical studies of electron transfer reactions since its inception by Kuwana *et al.*[1-6] Although the technique has been developed for a variety of electrochemical cells, the most widely used mode of operation is the transmittance measurement at optically transparent electrodes made of conductive metal oxides such as indium-tin oxide (ITO) glass or metal minigrids inside a spectrophotometric cell cuvette. In many of these experiments, the electrochemistry itself presents a limit for fast spectroelectrochemical measurements primarily due to the distorted current path resulting from unfavorable cell geometry among many other parameters. Efforts have been made to improve electrochemical response times by using reflective platinum disk working electrodes and the reflected light beam is measured at glancing angles.[7] Absorbance signals have been measured by this method in microsecond time domains[8]; however, the measurements were made at a single wavelength, which lacks the spectroscopic information. Modification of this method led to a cell, in which a bifurcated optical fiber is located above the reflective working electrode such that the probing and reflected beams would be nearly normal to the working electrode.[9-11] While this geometry allows a spectrum to be measured in a shorter time period, the mechanically driven monochromator now presents a limit to how fast a spectroscopic measurement can be made.

Semiconductor array detectors have been used for spectroscopic measurements for the last decade or so by recording spectrally dispersed light from monochromators.[12] Compared to traditional detectors such as photomultiplier tubes (PMTs), photodiode arrays can acquire data in a multiplexed mode. Of two types of array detectors, *i.e.*, photodiode and charge-coupled device (CCD), the latter has a number of superior features to the former as well as other photon detectors.[13,14] The CCD detectors have a simple dynamic range approaching 1×10^6, spectral response range of about 200-1000 nm, and quantum efficiency of 35-90%. Also, spectral measurements can be made in a microsecond or slower time domain for the whole spectral range by operating in the spectral framing mode. Because of the wide dynamic range of its

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