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# Stereoselective reductive radical cyclization of ketonitriles catalyzed by $Cp_2TiCl_2$ in the presence of chlorosilane and zinc

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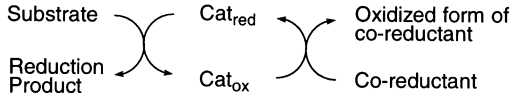
**Abstract**—Reductive radical cyclization of ketonitriles was catalyzed by $Cp_2TiCl_2$ in the presence of $Me_3SiCl$, zinc powder and imidazole, giving the 2-amino-3-cyano-2-cyclopenten-1-ols in moderate to good yields with high *trans* selectivity (up to 94% *trans*). The influence of the catalyst, chlorosilane, co-reductant, solvent, and temperature on both the yield and diastereoselectivity of the cyclized products was investigated in detail. © 2001 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

During the last two decades much attention has been focused on the development of efficient methods for the carbon–carbon bond formation, especially for the construction of carbocyclic skeletons, by using radical reactions.[1] One-electron reduction or oxidation of organic compounds provides a useful route to generate anion radicals or cation radicals, respectively. These routes afford a key process used in radical reactions. A redox of transition metals can be employed for the efficient one-electron reduction or oxidation. In particular, the redox of early transition metals including titanium and vanadium is of synthetic potential.[2,3] For example, titanocene chloride dimers, which is generated from titanocene dichloride, has been used as a useful one-electron transfer reductant.[4] More than stoichiometric amounts of the reductant are usually required to accomplish these reactions, which is clearly disadvantageous from the synthetic viewpoints.[5] Construction of a catalytic system is of great importance (Scheme 1). This concept has been demonstrated in the pinacol coupling reaction catalyzed by cat. $Cp_2TiCl_2$/RMgBr[6] and electrochemical coupling using cat. $SmCl_3$.[7] It has recently been reported that the use of a chlorosilane in combination with a catalytic amount of transition metal salt such as titanium and vanadium, and a stoichiometric co-reductant successfully effects the catalytic pinacol coupling reactions.[8,9] Among these catalytic reactions, our system has been revealed to work in the diastereoselective pinacol coupling reactions of aldehydes and aldimines, giving vicinal diols and diamines with excellent dl- and *meso*-selectivity, respectively. Very recently, a catalytic stereoselective cyclodimerization of arylidene malononitriles has been accomplished by using this catalytic system.[10]

Although several intramolecular radical cyclization reactions of ketonitriles have been reported by using one-electron transfer reagents such as samarium(II) diiodide and low-valent titanium or by using electroreductive method,[11] to our knowledge, there are no examples for catalytic carbon–carbon bond formation by attack of radical species onto carbon–nitrogen triple bond. A diastereoselective catalytic reductive cyclization of γ-ketonitriles promoted by cat. $Cp_2TiCl_2/Me_3SiCl/Zn$ is herein described.




**Scheme 1.**

## 2. Results and discussion

At first, the intramolecular reductive cyclization of γ-ketonitrile **1a** was examined with $Cp_2TiCl_2$ in the presence or absence of additives such as $Me_3SiCl$ and imidazole (Eq. (1), Table 1). When the reaction of **1a** with a stoichiometric amount of $Cp_2TiCl_2$ and 4 molar equiv. of zinc powder in THF was conducted at room temperature for 3 h, the desired 2-amino-3-cyano-2-cyclopenten-1-ol **2a** was stereoselectively obtained in 85% yield (entry 1). Although Zn/$Me_3SiCl$ has been reported to promote intramolecular

*Keywords*: titanium catalyst; one-electron reduction; diastereoselective cyclization; silylating reagent; co-reductant.

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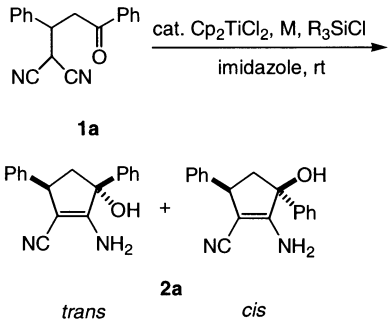
**Table 1.** The $Cp_2TiCl_2$-catalyzed coupling of **1a**

| Entry | Catalyst | Metal | Imidazole | Reaction time (h) | Isolated yield of **2a** (%) | *trans*/*cis* |
|---|---|---|---|---|---|---|
| 1[a] | + | Zn | − | 3 | 85 | 75:25 |
| 2 | − | Zn | − | 24 | 0 | – |
| 3[b] | − | Zn | − | 24 | 0 | – |
| 4[c] | + | Zn | + | 24 | 0 | – |
| 5 | + | Zn | − | 48 | 59 | 75:25 |
| 6 | + | Zn | + | 24 | 65 | 85:15 |
| 7 | + | Al | + | 24 | 76 | 62:38 |
| 8 | + | Mn | + | 24 | 35 | 50:50 |
| 9 | + | Mg | + | 24 | 35 | 64:36 |
| 10[d] | + | Zn | − | 24 | 0 | – |

Reaction conditions: **1a** (1.0 mmol), $Cp_2TiCl_2$ (0.05 mmol), metal (4.0 mmol), $Me_3SiCl$ (2.0 mmol), imidazole (1.0 mmol), THF (5 mL), rt, argon.
[a] A stoichiometric amount of $Cp_2TiCl_2$ was used in the absence of $Me_3SiCl$.
[b] 55°C. Olefin **3** was obtained in 19% yield.
[c] In the absence of $Me_3SiCl$.
[d] DMF was employed as a solvent.

reductive radical cyclization and pinacol coupling of aldehydes and ketones,[11a,12] no desired product was detected by using Zn/$Me_3SiCl$ in the absence of $Cp_2TiCl_2$ at room temperature or even at 55°C (entries 2 and 3). The coupling reaction did not proceed with cat. $Cp_2TiCl_2$/Zn/imidazole in the absence of $Me_3SiCl$ (entry 4). The addition of $Me_3SiCl$ to cat. $Cp_2TiCl_2$/Zn system successfully promoted the reductive coupling of **1a** to **2a** with a moderate yield and good stereoselectivity (entry 5), indicating that the coupling reaction requires a combination of cat. $Cp_2TiCl_2$, $Me_3SiCl$, and Zn. The presence of imidazole could improve the reaction yield.[9i] Although the reason has not been clarified yet, it might be related to the reported suppression of the zinc chloride-catalyzed elimination of a tertiary titanoxy group (entry 6).[11a] The use of aluminum powder as a co-reductant gave a good yield of product **2a**, but the diastereoselectivity decreased considerably (entry 7). A combination with Mn or Mg only resulted in a low yield and poor stereoselectivity (entries 8 and 9). The capability of other catalysts on this reductive cyclization was studied. $Cp_2VCl_2$, which is an effective catalyst for the cyclodimerization of arylidene malononitriles in DMF,[10] did not promote the reductive cyclization of **1a** in DMF in the presence of zinc powder and $Me_3SiCl$ (entry 10). Two cyano groups are required for catalytic reductive cyclization. When one cyano group of **1a** is replaced with the methoxycarbonyl group, the catalytic cyclization was not observed using cat. $Cp_2TiCl_2$/$Me_3SiCl$/Zn system. Futhermore, the attempted reaction of acetophenone or cyclopentanone with a slightly excess of benzyl cyanide did not give the cross-coupling product under the similar reaction conditions.




(1)

Since cat. $Cp_2TiCl_2$/$Me_3SiCl$/Zn/imidazole system in THF was revealed to be a good combination for the keto–nitrile reductive coupling of **1a**, the influence of silyl compounds and solvent was also examined (Table 2). Use of $Et_3SiCl$ as a silylating reagent lowered the yield despite the good stereoselectivity (entry 1). Only moderate stereoselectivity and yield were observed with $PhMe_2SiCl$ (entry 2). Use of the more sterically bulky $Ph_2MeSiCl$ in place of $PhMe_2SiCl$ resulted in a lower yield (entry 3). The reductive coupling proceeded very slowly with a moderate yield by switching a solvent from THF to DME (entry 5). Only a trace of the desired product **2a** was obtained in $Et_2O$ (entry 6). When the reaction was conducted in DMF, **2a** was not detected with 7% yield of olefin **3** and 56% recovery of the starting

**Table 2.** The influence of silyl compounds and solvent on the $Cp_2TiCl_2$-catalyzed coupling of **1a**

| Entry | Silyl compound | Solvent | Reaction time (h) | Isolated yield of **2a** (%) | *trans*/*cis*[a] |
|---|---|---|---|---|---|
| 1 | $Et_3SiCl$ | THF | 24 | 46 | 86:14 |
| 2 | $PhMe_2SiCl$ | THF | 24 | 58 | 71:29 |
| 3 | $Ph_2MeSiCl$ | THF | 24 | 29 | 72:28 |
| 4 | $Me_3SiCl$ | THF | 24 | 65 | 85:15 |
| 5 | $Me_3SiCl$ | DME | 60 | 49 | 85:15 |
| 6 | $Me_3SiCl$ | $Et_2O$ | 48 | Trace | – |
| 7 | $Me_3SiCl$ | DMF | 36 | – | – |
| 8 | $Me_3SiCl$ | $CH_2Cl_2$ | 48 | – | – |

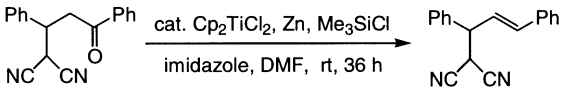
Reaction conditions: **1a** (1.0 mmol), $Cp_2TiCl_2$ (0.05 mmol), Zn (4.0 mmol), $R_3SiCl$ (2.0 mmol), imidazole (1.0 mmol), solvent (5 mL), rt, argon.
[a] Determined by $^1H$ NMR.

**Table 3.** The cat. $Cp_2TiCl_2/Me_3SiCl/Zn$/imidazole induced coupling of **1**

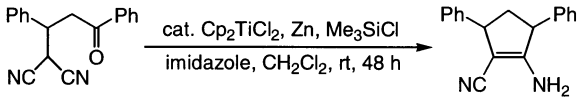
| Entry | 1 | R | Ar | Reaction time (h) | 2 | Isolated yield (%) | *trans*/*cis*[a] |
|---|---|---|---|---|---|---|---|
| 1 | **1a** | $C_6H_5$ | $C_6H_5$ | 24 | **2a** | 65 | 85:15 |
| 2 | **1b** | 3,4-$OCH_2OC_6H_3$ | $C_6H_5$ | 36 | **2b** | 66 | 75:25 |
| 3 | **1c** | *p*-$BrC_6H_4$ | $C_6H_5$ | 24 | **2c** | 56 | 84:16 |
| 4 | **1d** | *p*-$ClC_6H_4$ | $C_6H_5$ | 24 | **2d** | 67 | 83:17 |
| 5 | **1e** | $C_6H_5$ | *p*-$CH_3OC_6H_4$ | 24 | **2e** | 45 | 83:17 |
| 6 | **1f** | *p*-$CH_3C_6H_4$ | *p*-$ClC_6H_4$ | 48 | **2f** | 51 | 94:6 |
| 7 | **1g** | $C_6H_5$ | *p*-$ClC_6H_4$ | 36 | **2g** | 52 | 88:12 |
| 8 | **1h** | α-Naphthyl | $C_6H_5$ | 45 | **2h** | 42 | 84:16 |
| 9 | **1i** | β-Naphthyl | $C_6H_5$ | 45 | **2i** | 40 | 79:21 |
| 10 | **1j** | *o*-$ClC_6H_4$ | $C_6H_5$ | 48 | **2j** | 50 | 58:42 |
| 11 | **1k** | $CH_3$ | $C_6H_5$ | 72 | **2k** | 46 | 67:33 |
| 12 | **1l** | *p*-$BrC_6H_4$ | β-Naphthyl | 24 | **2l** | 40 | 67:33 |

Reaction conditions: **1a** (1.0 mmol), $Cp_2TiCl_2$ (0.05 mmol), Zn (4.0 mmol), $Me_3SiCl$ (2.0 mmol), imidazole (1 mmol), THF (5 mL), rt, argon.
[a] Determined by $^1H$ NMR.

substrate **1a** (entry 7, Eq. (2)). The cyclized cyclopentene **4** was only formed using $CH_2Cl_2$ as a solvent at room temperature (entry 8, Eq. (3)).

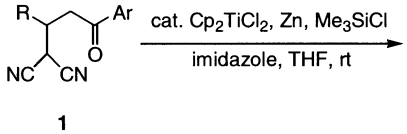



**1a** **3** 7 % (2)

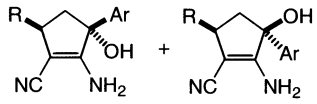



**1a** **4** 28% (3)

Using optimized reaction conditions, reductive coupling of γ-ketonitriles **1** induced by the cat. $Cp_2TiCl_2/Me_3SiCl/Zn$/imidazole system in THF afforded the desired product **2** successfully (Eq. (4), Table 3). The cyclization product **2b** was obtained in a good yield with diastereoselectivity (entry 2). In particular, good *trans* selectivity was observed with **1c** to **1g** bearing a *p*-substituted group on the benzene ring (entries 3–7), although good stereoselectivity is generally less accessible in radical reactions. In the case of **1j** bearing an *o*-substituent, the diastereoselectivity considerably decreased (entry 10).[10,13,14] Similar lower stereoselectivity was observed with the substrates **1k** and **1l** (entries 11 and 12). These findings suggest that the diastereoselectivity also strongly depends on the electronic and steric effects of the substituent on the benzene ring at one-electron reduction or coupling step. The structure and relative configuration of **2** were readily confirmed by the spectral data. Furthermore, the X-ray diffraction study on a single crystal of the major isomer of **2d** supported the formation the *trans*-isomer (Fig. 1).




**1**




**2** (4)

*trans* *cis*

The observed stereochemistry of the products might be related to conformational effect on the intermediates.[15,16] 4-Cyanobutyl radical, which is known to comprise a structure somewhat similar in dimensions to hex-5-enyl radical,[4e] exists preferentially in a chair-like conformation. Consequently, four 'chair-like' intermediates, **A** and **C** where the Ar group lies down and **B** and **D** where the Ar group

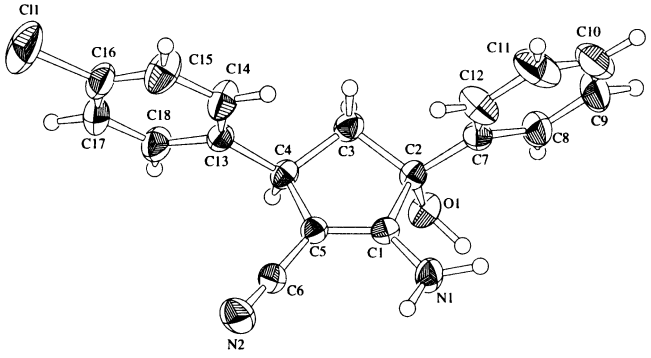



**Figure 1.** ORTEP diagram of the major isomer of **2d**.

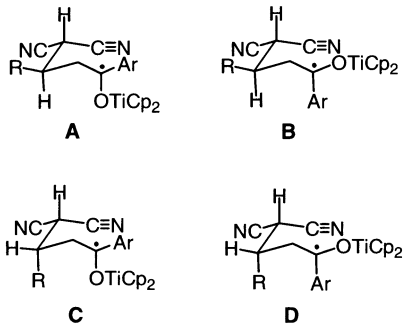



**Figure 2.** The plausible intermediates in the reductive cyclization of **1**.

lies up, are possible (Fig. 2). **A** and **B**, in which R is equatorially substituted β to the radical, should be more stable than the axially substituted intermediates **C** and **D**. When R is the methyl group instead of the phenyl group, the stereoselectivity of the reaction decreased (entries 1 and 11). From the results shown in Table 3, **A** with the Ar group in an equatorial position appears to be a proper intermediate to explain the stereochemistry.

In conclusion, the intramolecular keto–nitrile reductive coupling reaction was demonstrated to be catalyzed efficiently by $Cp_2TiCl_2$ in the presence of $Me_3SiCl$, zinc metal, and imidazole to give the 2-amino-3-cyano-2-cyclopenten-1-ol via stereoselective cyclization.

## 3. Experimental

### 3.1. General

Melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin–Elmer 1600. $^1H$ or $^{13}C$ NMR spectra were recorded on a Varian MERCURY300 spectrometer in chloroform-*d* with tetramethylsilane or residual chloroform as an internal standard. Mass spectra were recorded on a Varian Saturn 3 or JEOL JMS-DX-303. Elemental analyses were performed on a CHN-Corder MT-5 instrument. X-ray analysis of **2d** was performed on a Rigaku RAXIS-RAPID Imaging Plate diffractometer. TLC was carried out on aluminum sheets precoated with silica gel $60F_{254}$ (E. Merck). Column chromatography was performed on silica gel 60 (E. Merck). $Me_3SiCl$ was distilled under argon over calcium hydride. All reagents are of commercial quality and used without purification. All dry solvents were freshly distilled under argon over an appropriate drying agent before use. The reactions were carried out under argon, using syringes and Schlenk-type techniques.

### 3.2. Preparation of γ-ketonitrile 1

The γ-ketonitrile **1** was prepared according to the literature procedure and references cited therein.[17] To a mixture of α,β-unsaturated ketone (10 mmol) and malononitrile (660 mg, 10 mmol) in DMF (10 mL) was added a catalytic amount of piperidine (50 mg, 0.6 mmol). Then, the mixture was stirred at room temperature for 24 h. After the reaction was completed, the mixture was poured into 100 mL of water. The collected crude γ-ketonitrile **1** was purified by recrystallization from ethanol or column chromatography on silica gel (eluent, hexane/ethyl acetate=4:1).

### 3.3. Representative procedure for the intramolecular reductive cyclization of γ-ketonitrile 1

To a mixture of $Cp_2TiCl_2$ (12.5 mg, 0.050 mmol) and zinc powder (131 mg, 2.0 mmol) in THF (5 mL) was added $Me_3SiCl$ (0.27 mL, 2.0 mmol) at room temperature under argon. After stirring for 30 min, a solution of **1** in THF (3 mL) was added to the mixture. The mixture was kept at room temperature with magnetic stirring for the time indicated in the table. Then, the reaction mixture was treated with tetrabutylammonium fluoride (3.0 mL of a 1.0 M solution in THF) for 4 h at room temperature and then subjected to workup with 1 M HCl (3 mL) and ether (50 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ (10 mL), water (10 mL), and brine (10 mL), dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography on silica gel (20 g; eluent, hexane/ethyl acetate=50:0, 48:2, 46:4, 44:6, 42:8, 40:10, 38:12, 35:15, 32:18, 28:22, 25:25, 50 mL× each), giving **2**.

**3.3.1. *trans*-2-Amino-3-cyano-1,4-diphenyl-2-cyclopenten-1-ol (*trans*-2a).** Mp 167–169°C (lit.[11j] 164–165°C), IR (neat) 3462, 3366, 2194, 1639, 1595 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 2.11 (dd, *J*=14.1, 7.2 Hz, 1H), 2.54 (br s, 1H), 2.71 (dd, *J*=14.1, 6.9 Hz, 1H), 4.31 (t, *J*=7.5, 7.2 Hz, 1H), 4.40 (br s, 2H), 7.25–7.51 (m, 10H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 46.4, 52.2, 82.7, 84.9, 117.5, 125.5, 127.0, 127.1, 128.0, 128.6, 128.7, 141.4, 142.1, 163.1; *m/z* 276 ($M^+$, 100), 275 (35), 258 (58), 257 (60), 105 (46), 77 (20); HRMS (EI) 270.1262 (Calcd for $C_{18}H_{16}N_2O$ 270.1263).

**3.3.2. *cis*-2-Amino-3-cyano-1,4-diphenyl-2-cyclopenten-1-ol (*cis*-2a).** Mp 168–170°C (lit.[11j] 168–170°C), IR (neat) 3409, 3340, 2173, 1662, 1599 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 2.11 (dd, *J*=13.2, 7.5 Hz, 1H), 2.45 (br s, 1H), 2.80 (dd, *J*=13.2, 7.2 Hz, 1H), 3.92 (t, *J*=7.5, 6.9 Hz, 1H), 4.66 (br s, 2H), 7.24–7.49 (m, 10H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 45.6, 52.6, 80.7, 84.2, 117.4, 124.8, 127.2, 128.1, 128.7, 128.8, 141.8, 142.2, 163.5; *m/z* 276 ($M^+$, 100), 275 (40), 258 (85), 257 (65), 105 (39), 77 (22); HRMS (EI) 270.1270 (Calcd for $C_{18}H_{16}N_2O$ 270.1263); Anal. Calcd for $C_{18}H_{16}N_2O$: C, 78.24; H, 5.84; N, 10.14. Found: C, 77.99; H, 5.72; N, 9.96.

**3.3.3. *trans*-2-Amino-3-cyano-4-(3′,4′-methylenedioxyphenyl)-1-phenyl-2-cyclopenten-1-ol (*trans*-2b).** Mp 166–167°C (lit.[11j] 162–164°C), IR (neat) 3479, 3376, 2191, 1640, 1485 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 2.13 (dd, *J*=14.1, 7.5 Hz, 1H), 2.66 (dd, *J*=14.4, 7.5 Hz, 2H), 4.22 (t, *J*=7.5 Hz, 1H), 4.43 (br s, 2H), 5.94 (s, 2H), 6.76 (m, 3H), 7.32–7.50 (m, 5H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 46.3, 52.3, 82.7, 84.9, 100.9, 107.2, 108.3, 117.5, 120.3, 125.5, 128.0, 128.6, 136.1, 141.4, 146.5, 147.9, 163.1; MS (EI) *m/z* 320 ($M^+$, 100), 302 (31), 105 (28), 77 (11). Anal. Calcd for $C_{19}H_{16}N_2O_3$: C, 71.24; H, 5.03; N, 8.74. Found: C, 70.97; H, 5.05; N, 8.72.

**3.3.4. *cis*-2-Amino-3-cyano-4-(3′,4′-methylenedioxyphenyl)-1-phenyl-2-cyclopenten-1-ol (*cis*-2b).** Mp 170–172°C (lit.[11j] 164–166°C), IR (neat) 3404, 3344, 2172, 1664, 1600 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 2.07 (dd, $J$= 13.2, 7.5 Hz, 1H), 2.49 (br s, 1H), 2.77 (dd, $J$=13.2, 7.2 Hz, 1H), 3.84 (t, $J$=7.2, 6.9 Hz, 1H), 4.67 (br s, 2H), 5.94 (s, 2H), 6.71–6.79 (m, 3H), 7.33–7.44 (m, 5H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 45.5, 52.6, 80.9, 84.1, 100.9, 107.5, 108.3, 117.4, 120.4, 124.8, 128.1, 128.7, 136.2, 141.9, 146.6, 147.9, 163.4; MS (EI) $m/z$ 320 ($M^+$, 100), 302 (37), 105 (28), 77 (11). Anal. Calcd for $C_{19}H_{16}N_2O_3$: C, 71.24; H, 5.03; N, 8.74. Found: C, 71.13; H, 5.05; N, 8.77.

**3.3.5. *trans*-2-Amino-4-(4′-bromophenyl)-3-cyano-1-phenyl-2-cyclopenten-1-ol (*trans*-2c).** Mp 141–143°C, IR (neat) 3408, 3343, 2189, 1661, 1608 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 2.12 (dd, $J$=14.1, 7.2 Hz, 1H), 2.68 (dd, $J$=14.1, 7.5 Hz, 1H), 2.88 (br s, 1H), 4.25 (t, $J$=7.2 Hz, 1H), 4.51 (br s, 2H), 7.13–7.47 (m, 9H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 45.9, 51.9, 81.5, 84.8, 117.5, 120.8, 125.5, 128.1, 128.6, 128.7, 131.8, 141.2, 141.3, 163.5; MS (EI) $m/z$ 356 (M+2, 81), 355 (32), 354 ($M^+$, 82), 338 (68), 337 (59), 336 (75), 335 (47), 275 (100), 257 (72), 230 (23), 181 (23), 128 (28), 105 (79), 77 (38). Anal. Calcd for $C_{18}H_{15}BrN_2O$: C, 60.86; H, 4.26; N, 7.89. Found: C, 60.78; H, 4.27; N, 7.74.

**3.3.6. *cis*-2-Amino-4-(4′-bromophenyl)-3-cyano-1-phenyl-2-cyclopenten-1-ol (*cis*-2c).** Mp 170–172°C, IR (neat) 3461, 3389, 3230, 2173, 1663, 1602 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 2.06 (dd, $J$=13.2, 7.5 Hz, 1H), 2.40 (br s, 1H), 2.79 (dd, $J$=13.2, 7.2 Hz, 1H), 3.87 (t, $J$=7.2 Hz, 1H), 4.69 (br s, 2H), 7.16–7.48 (m, 9H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 40.7, 47.9, 79.7, 104.7, 112.7, 116.6, 120.3, 123.8, 124.4, 124.5, 127.4, 136.8, 137.3, 159.2; MS (EI) $m/z$ 356 (M+2, 80), 355 (35), 354 ($M^+$, 79), 338 (93), 337 (63), 336 (100), 275 (74), 257 (61), 230 (21), 181 (21), 128 (25), 105 (92), 77 (43); HRMS (EI) 354.0370 (Calcd for $C_{18}H_{15}BrN_2O$ 354.0367).

**3.3.7. 2-Amino-4-(4′-chlorophenyl)-3-cyano-1-phenyl-2-cyclopenten-1-ol (2d).** Mp 133–135°C, IR (neat) 3461, 3360, 2192, 1648, 1595, 1490 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) (*trans*) $\delta$ 2.14 (dd, $J$=14.1, 7.2 Hz, 1H), 2.61 (br s, 1H), 2.69 (dd, $J$=14.1, 7.5 Hz, 1H), 4.28 (t, $J$=7.5, 7.2 Hz, 1H), 4.46 (br s, 2H), 7.20–7.48 (m, 9H); (*cis*) $\delta$ 2.06 (dd, $J$=13.8, 7.8 Hz, 1H), 2.78 (dd, $J$=13.8, 7.5 Hz, 2H), 3.88 (t, $J$=7.8, 7.5 Hz, 1H), 4.74 (br s, 2H), 7.20–7.48 (m, 9H); $^{13}C$ NMR (75 MHz, $CDCl_3$) (*trans*) $\delta$ 45.9, 52.0, 82.0, 84.9, 117.3, 125.4, 128.1, 128.4, 128.7, 128.9, 132.8, 140.6, 141.2, 163.4; MS (EI) $m/z$ 312 (M+2, 35), 311 (27), 310 ($M^+$, 100), 292 (62), 291 (54), 275 (89), 257 (44), 105 (50), 77 (23). Anal. Calcd for $C_{18}H_{15}ClN_2O$: C, 69.57; H, 4.86; N, 9.01. Found: C, 69.12; H, 4.91; N, 8.86.

**3.3.8. *trans*-2-Amino-3-cyano-1-(4′-methoxyphenyl)-4-phenyl-2-cyclopenten-1-ol (*trans*-2e).** Mp 152–154°C, IR (neat) 3434, 3347, 2188, 1661, 1606 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 2.18 (dd, $J$=14.4, 7.5 Hz, 1H), 2.51 (br s, 1H), 2.68 (dd, $J$=14.4, 7.5 Hz, 1H), 3.81 (s, 3H), 4.28 (t, $J$=7.5 Hz, 1H), 4.41 (br s, 2H), 6.90–6.94 (m, 2H), 7.21–7.42 (m, 7H); MS (EI) $m/z$ 306 ($M^+$, 21), 289 (28), 288 (100), 271 (44), 135 (13); HRMS (EI) 306.1369 (Calcd for $C_{19}H_{18}N_2O_2$ 306.1368).

**3.3.9. *cis*-2-Amino-3-cyano-1-(4′-methoxyphenyl)-4-phenyl-2-cyclopenten-1-ol (*cis*-2e).** Mp 151–153°C, IR (neat) 3432, 3346, 2188, 1661, 1606 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 2.09 (dd, $J$=12.9, 7.5 Hz, 1H), 2.32 (br s, 1H), 2.78 (dd, $J$=12.9, 7.2 Hz, 1H), 3.83 (s, 3H), 3.88 (t, $J$= 7.2 Hz, 1H), 4.68 (br s, 2H), 6.92–6.94 (m, 2H), 7.27–7.41 (m, 7H); MS (EI) $m/z$ 306 ($M^+$, 45), 289 (31), 288 (100), 287 (41), 273 (27), 198 (39), 135 (33); HRMS (EI) 306.1363 (Calcd for $C_{19}H_{18}N_2O_2$ 306.1368).

**3.3.10. 2-Amino-1-(4′-chlorophenyl)-3-cyano-4-(4′-methylphenyl)-2-cyclopenten-1-ol (2f).** Mp 160°C (decomp.), IR (neat) 3449, 3362, 3220, 2193, 1644, 1599 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 2.08 (dd, $J$=14.4, 7.5 Hz, 1H), 2.33 (s, 3H), 2.64 (dd, $J$=14.4, 7.5 Hz, 1H), 3.49 (br s, 1H), 4.23 (t, $J$=7.2 Hz, 1H), 4.51 (br s, 2H), 7.14–7.41 (m, 8H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 21.1, 45.9, 52.1, 81.7, 84.5, 117.9, 126.8, 127.1, 128.6, 129.4, 133.7, 136.6, 139.0, 140.3, 163.2; MS (EI) $m/z$ 326 (M+2, 38), 325 (33), 324 ($M^+$, 100), 306 (54), 271 (39), 270 (26), 269 (26), 256 (26), 139 (43); HRMS (EI) 324.1025 (Calcd for $C_{19}H_{17}ClN_2O$ 324.1029).

**3.3.11. 2-Amino-1-(4′-chlorophenyl)-3-cyano-4-phenyl-2-cyclopenten-1-ol (2g).** Mp 144–146°C, IR (neat) 3460, 3366, 2194, 2165, 1643, 1600, 1490 $cm^{-1}$; $^1H$ NMR (300 MHz, $CD_3CN$) (*trans*) $\delta$ 2.11–2.18 (m, 1H), 2.67–2.74 (m, 1H), 3.27 (br s, 1H), 4.30 (t, $J$=7.5, 6.9 Hz, 1H), 4.51 (br s, 2H), 7.23–7.45 (m, 9H); (*cis*) $\delta$ 2.11–2.18 (m, 1H), 2.67–2.74 (m, 1H), 3.27 (br s, 1H), 3.89 (t, $J$=7.5, 7.2 Hz, 1H), 4.81 (br s, 2H), 7.23–7.45 (m, 9H); $^{13}C$ NMR (75 MHz, $CD_3CN$) (*trans*) $\delta$ 46.3, 52.1, 81.9, 84.5, 117.7, 126.9, 127.1, 127.2, 128.6, 128.7, 133.8, 140.2, 142.0, 163.1; MS (EI) $m/z$ 312 (M+2, 38), 311 (35), 310 ($M^+$, 100), 292 (57), 257 (65), 171 (12), 155 (14), 139 (42), 77 (10); HRMS (EI) 310.0869 (Calcd for $C_{18}H_{15}ClN_2O$ 310.0873).

**3.3.12. 2-Amino-3-cyano-4-(1′-naphthyl)-1-phenyl-2-cyclopenten-1-ol (2h).** Mp 173–175°C, IR (neat) 3412, 3337, 3216, 2179, 1653, 1598 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) (*trans*) $\delta$ 2.21 (dd, $J$=14.4, 6.3 Hz, 1H), 3.00 (dd, $J$=14.4, 6.6 Hz, 1H), 3.17 (br s, 1H), 4.61 (br s, 2H), 5.12 (dd, $J$=6.9, 6.6 Hz, 1H), 7.21–8.05 (m, 12H); (*cis*) $\delta$ 2.17 (dd, $J$=13.8, 5.4 Hz, 1H), 2.69 (br s, 1H), 3.00 (dd, $J$=13.8, 8.1 Hz, 1H), 4.71 (br s, 2H), 4.81 (dd, $J$=7.5, 5.4 Hz, 1H), 7.21–8.05 (m, 12H); $^{13}C$ NMR (75 MHz, $CDCl_3$) (mixture) $\delta$ 42.2, 51.2, 80.2, 84.9, 118.1, 122.9, 125.4, 125.5, 125.6, 125.9, 127.4, 127.8, 128.4, 128.8, 131.3, 133.8, 138.4, 141.7, 164.0; MS (EI) $m/z$ 327 (M+1, 28), 326 ($M^+$, 100), 308 (98), 307 (62), 153 (18), 105 (22), 77 (8); HRMS (EI) 326.1425 (Calcd for $C_{22}H_{18}N_2O$ 326.1419).

**3.3.13. 2-Amino-3-cyano-4-(2′-naphthyl)-1-phenyl-2-cyclopenten-1-ol (2i).** Mp 163–166°C, IR (neat) 3450, 3381, 3337, 3225, 2195, 2174, 1654, 1601 $cm^{-1}$; $^1H$ NMR (300 MHz, $CD_3CN$) (*trans*) $\delta$ 2.27 (dd, $J$=14.1, 7.2 Hz, 1H), 2.79 (dd, $J$=14.1, 7.5 Hz, 1H), 4.15 (s, 1H), 4.53 (t, $J$=7.2 Hz, 1H), 5.12 (br s, 2H), 7.39–7.66 (m, 8H), 7.91–8.03 (m, 4H); (*cis*) $\delta$ 2.30 (dd, $J$=13.2, 6.6 Hz, 1H), 2.78

(dd, $J$=13.2, 7.2 Hz, 1H), 4.17 (m, 2H), 4.12 (br s, 2H), 7.39–7.66 (m, 8H), 7.91–8.03 (m, 4H); $^{13}$C NMR (75 MHz, $CD_3CN$) $\delta$ 47.5, 53.0, 80.6, 85.3, 126.4, 126.5, 126.6, 126.7, 126.9, 128.3, 129.0, 129.2, 133.3, 134.2, 141.9, 143.8, 165.4; MS (EI) *m/z* 327 (M+1, 33), 326 ($M^+$, 100), 308 (49), 280 (10), 154 (10), 105 (31), 77 (12); HRMS (EI) 326.1418 (Calcd for $C_{22}H_{18}N_2O$ 326.1419).

**3.3.14. *trans*-2-Amino-4-(2′-chlorophenyl)-3-cyano-1-phenyl-2-cyclopenten-1-ol (*trans*-2j).** Mp 184–185°C, IR (neat) 3407, 3330, 2171, 1661, 1597 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 2.07 (dd, $J$=14.4, 6.9 Hz, 1H), 2.87 (dd, $J$=14.4, 7.8 Hz, 1H), 3.05 (br s, 1H), 4.60 (br s, 2H), 4.47 (t, $J$=7.5, 6.9 Hz, 1H), 7.15–7.43 (m, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 43.2, 50.1, 79.7, 84.7, 117.7, 125.4, 127.2, 127.3, 127.9, 128.1, 128.5, 129.6, 133.6, 139.7, 141.5, 164.3; MS (EI) *m/z* 312 (M+2, 37), 311 (25), 310 ($M^+$, 100), 293 (35), 292 (66), 291 (53), 258 (20), 257 (54), 230 (15), 181 (18), 130 (23), 105 (56), 77 (24). Anal. Calcd for $C_{18}H_{15}ClN_2O$: C, 69.57; H, 4.86; N, 9.01. Found: C, 69.54; H, 4.87; N, 8.94.

**3.3.15. *cis*-2-Amino-4-(2′-chlorophenyl)-3-cyano-1-phenyl-2-cyclopenten-1-ol (*cis*-2j).** Mp 171–173°C, IR (neat) 3450, 3340, 2185, 1648 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 2.02 (dd, $J$=13.5, 6.3 Hz, 1H), 2.35 (br s, 1H), 2.97 (dd, $J$=13.5, 7.5 Hz, 1H), 4.49 (t, $J$=7.5, 6.3 Hz, 1H), 4.68 (br s, 2H), 7.20–7.49 (m, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 42.5, 50.4, 78.9, 84.2, 117.3, 124.8, 127.4, 127.6, 128.1, 128.2, 128.7, 129.7, 133.5, 139.9, 141.8, 164.2; MS (EI) *m/z* 312 (M+2, 36), 311 (25), 310 ($M^+$, 100), 293 (28), 292 (54), 291 (45), 257 (41), 181 (12), 130 (20), 105 (45), 77 (19). Anal. Calcd for $C_{18}H_{15}ClN_2O$: C, 69.57; H, 4.86; N, 9.01. Found: C, 69.37; H, 4.74; N, 8.85.

**3.3.16. 2-Amino-3-cyano-4-methyl-1-phenyl-2-cyclopenten-1-ol (2k).** Mp 60–63°C, IR (neat) 3417, 3336, 3235, 2176, 1658, 1609, 1448 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) (*trans*) $\delta$ 1.18 (d, $J$=6.9 Hz, 3H), 1.85 (dd, $J$=14.1, 6.6 Hz, 1H), 2.44 (dd, $J$=14.1, 7.2 Hz, 1H), 2.80 (br s, 1H), 3.10 (m, 1H), 4.32 (br s, 2H), 7.27–7.45 (m, 5H); (*cis*) $\delta$ 1.22 (d, $J$=6.9 Hz, 3H), 1.76 (dd, $J$=12.9, 7.5 Hz, 1H), 2.53 (dd, $J$=12.9, 6.3 Hz, 1H), 2.78 (m, 2H), 4.59 (br s, 2H), 7.27–7.45 (m, 5H); $^{13}$C NMR (75 MHz, $CDCl_3$) (*trans*) $\delta$ 20.3, 35.1, 50.5, 84.4, 85.2, 117.8, 125.4, 127.8, 128.4, 142.3, 161.8; (*cis*) $\delta$ 20.5, 34.2, 50.8, 84.4, 85.2, 117.8, 124.7, 127.7, 128.5, 142.3, 161.8; MS (EI) *m/z* 214 ($M^+$, 76), 199 (57), 196 (33), 195 (29), 182 (50), 181 (100), 154 (41), 130 (10), 105 (24), 77 (24); HRMS (EI) 214.1109 (Calcd for $C_{13}H_{14}N_2O$ 214.1106).

**3.3.17. *trans*-2-Amino-4-(4′-bromophenyl)-3-cyano-1-(2′-naphthyl)-2-cyclopenten-1-ol (*trans*-2l).** Mp 128–130°C, IR (neat) 3450, 3374, 2195, 1643, 1599 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 2.26 (dd, $J$=14.4, 7.5 Hz, 1H), 2.64 (br s, 1H), 2.75 (dd, $J$=14.4, 7.5 Hz, 1H), 4.32 (t, $J$=7.5 Hz, 1H), 4.47 (br s, 2H), 7.18–8.04 (m, 11H); MS (EI) *m/z* 406 (M+2, 98), 405 (35), 404 ($M^+$, 98), 389 (33), 388 (95), 387 (74), 386 (100), 385 (49), 325 (57), 307 (55), 231 (21), 163 (23), 155 (63), 127 (42); HRMS (EI) 404.0522 (Calcd for $C_{22}H_{17}BrN_2O$ 404.0524).

**3.3.18. *cis*-2-Amino-4-(4′-bromophenyl)-3-cyano-1-(2′-naphthyl)-2-cyclopenten-1-ol (*cis*-2l).** Mp 153–156°C, IR (neat) 3459, 3347, 3220, 2190, 1647, 1598 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 2.12 (dd, $J$=13.5, 7.5 Hz, 1H), 2.60 (br s, 1H), 2.87 (dd, $J$=13.5, 7.2 Hz, 1H), 3.92 (t, $J$= 7.5, 7.2 Hz, 1H), 4.75 (br s, 2H), 7.16–7.91 (m, 11H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 45.2, 52.2, 80.4, 84.4, 109.2, 117.3, 121.0, 122.7, 123.7, 126.5, 126.6, 127.5, 128.1, 128.9, 129.0, 131.9, 132.9, 138.8, 141.3, 163.6; MS (EI) *m/z* 406 (M+2, 34), 405 (13), 404 ($M^+$, 34), 389 (37), 388 (99), 387 (51), 386 (100), 307 (17), 278 (17), 155 (38), 127 (29); HRMS (EI) 404.0524 (Calcd for $C_{22}H_{17}BrN_2O$ 404.0524).

**3.3.19. 4,4-Dicyano-1,3-diphenyl-1-butene (3).** Colorless oil, IR (neat) 3030, 2901, 2254, 1496, 1454 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.06–4.12 (m, 2H), 6.48 (dd, $J$=15.9, 7.8 Hz, 1H), 6.72 (d, $J$=15.6 Hz, 1H), 6.27–7.45 (m, 10H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 30.3, 49.9, 111.5, 111.6, 123.7, 126.7, 127.6, 128.5, 128.6, 128.9, 129.3, 135.3, 135.7, 136.4; MS (EI) *m/z* 258 ($M^+$, 6), 193 (100), 178 (16), 115 (55), 91 (13); HRMS (EI) 258.1162 (Calcd for $C_{18}H_{14}N_2$ 258.1157).

**3.3.20. 1-Amino-2-cyano-3,5-diphenylcyclopentene (4).** Mp 183–184°C (lit.[17] 185–186°C), IR (neat) 3457, 3334, 3254, 3215, 2193, 1648, 1600 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.78–2.87 (dd, $J$=13.5, 7.5 Hz, 1H), 2.60 (br s, 1H), 2.87 (dd, $J$=13.5, 7.2 Hz, 1H), 3.92 (t, $J$=7.5, 7.2 Hz, 1H), 4.75 (br s, 2H), 7.16–7.91 (m, 10H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 44.2, 48.2, 52.1, 80.6, 109.1, 118.1, 126.7, 126.9, 127.1, 127.6, 127.7, 127.8, 128.2, 128.6, 129.0, 139.5, 143.0, 163.7; MS (EI) *m/z* 261 (M+1, 18), 260 ($M^+$, 86), 259 (100), 183 (27), 91 (5), 77 (3); MS (EI) *m/z* 260 ($M^+$, 86), 259 (100), 183 (27); HRMS (EI) 260.1313 (Calcd for $C_{18}H_{16}N_2$ 260.1314). Anal. Calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.19; N, 10.76. Found: C, 82.89; H, 6.11; N, 10.79.

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## References

1. (a) Giese, B. *Radical in Organic Synthesis: Formation of C–C Bonds*; Pergamon: Oxford, 1986 23. (b) Curran, D. P. *Synthesis* **1988**, 417 and 489. (c) Curran, D. P. *Comprehensive Organic Synthesis*; Trost, B. M., Flamin, I., Semmelhack, M. F., Eds.; Pergamon: Oxford, 1991; Vol. 4, p. 715 and 779. (d) Motherwell, W. B.; Crich, D. *Free Radical Chain Reactions in Organic Synthesis*; Academic: London, 1992. (e) Fossey, J.; Lefort, D.; Sorba, J. *Free Radical in Organic Chemistry*; Wiley: New York, 1995.

2. (a) Ho, T.-L. *Synthesis* **1979**, 1. (b) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic: New York, 1981. (c) Freeman, F. In *Organic Syntheses by Oxidation with Metal Compounds*; Mijs, W. J., de Jonge, C. R. H. I., Eds.; Plenum: New York, 1986; Chapter 1. (d) Pons, J.-M.; Santelli, M. *Tetrahedron* **1988**, *44*, 4295. (e) Rehder, D.; Gailus, H. *Trends Organomet. Chem.* **1994**, *1*, 397. (f) Iqbal, J.; Bhatia, B.; Nayyar, N. K. *Chem. Rev.* **1994**, *94*, 519. (g) Dalko, P. I. *Tetrahedron* **1995**, *51*, 7579.
3. (a) Hirao, T. *Chem. Rev.* **1997**, *97*, 2707. (b) Hirao, T. *Synlett* **1999**, 175.
4. (a) Nugent, W. A.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1988**, *110*, 8561. (b) RajanBabu, T. V.; Nugent, W. A. *J. Am. Chem. Soc.* **1989**, *111*, 4525. (c) RajanBabu, T. V.; Nugent, W. A. *J. Am. Chem. Soc.* **1990**, *112*, 6408. (d) RajanBabu, T. V.; Nugent, W. A. *J. Am. Chem. Soc.* **1994**, *116*, 986. (e) Mandal, P. K.; Maiti, G.; Roy, S. C. *J. Org. Chem.* **1998**, *63*, 2829. (f) Gansäuer, A.; Pierobon, M.; Bluhm, H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 101.
5. Halterman, R. L. *Chem. Rev.* **1992**, *92*, 965.
6. Zhang, Y.; Liu, T. *Synth. Commun.* **1988**, *18*, 2173.
7. Léonard, E.; Duñach, E.; Périchon, J. *J. Chem. Soc., Chem. Commun.* **1989**, 276.
8. Fürstner, A.; Hupperts, A. *J. Am. Chem. Soc.* **1995**, *117*, 4468.
9. (a) Hirao, T.; Hasegawa, T.; Muguruma, Y.; Ikeda, I. *Abstr. 6th Int. Conf. New Aspects Org. Chem.* **1994**, 175 and *J. Org. Chem.* **1996**, *61*, 366. (b) Lipski, T. A.; Hilfiker, M. A.; Nelson, S. G. *J. Org. Chem.* **1997**, *62*, 4566. (c) Gansäuer, G. *J. Chem. Soc., Chem. Commun.* **1997**, 457. (d) Gansäuer, A. *Synlett* **1997**, 363. (e) Liao, P.; Huang, Y.; Zhang, Y. *Synth. Commun.* **1997**, *27*, 1483. (f) Hirao, T.; Asahara, M.; Muguruma, Y.; Ogawa, A. *J. Org. Chem.* **1998**, *63*, 2812. (g) Hatano, B.; Ogawa, A.; Hirao, T. *J. Org. Chem.* **1998**, *63*, 9421. (h) Gansäuer, A.; Bauer, D. *J. Org. Chem.* **1998**, *63*, 2070. (i) Hirao, T.; Hatano, B.; Imamoto, Y.; Ogawa, A. *J. Org. Chem.* **1999**, *64*, 7665.
10. Zhou, L.; Hirao, T. *Tetrahedron Lett.* **2000**, *41*, 8517.
11. (a) Corey, E. J.; Pyne, S. G. *Tetrahedron Lett.* **1983**, *24*, 2821. (b) Clive, D. L. J.; Beaulieu, P. L. *J. Org. Chem.* **1984**, *49*, 1313. (c) Molander, G. A.; Kenny, C. *J. Am. Chem. Soc.* **1989**, *111*, 8236. (d) Shono, T.; Kise, N.; Fujimoto, T.; Tominaga, N.; Morita, H. *J. Org. Chem.* **1992**, *57*, 7175. (e) Chen, J.; Chen, W.; Zhang, J.; Kao, T. *Youji Huaxue* **1992**, *12*, 26. (f) Yamamoto, Y.; Matsumi, D.; Ito, K. *J. Chem. Soc., Chem. Commun.* **1998**, 875. (g) Molander, G. A.; Wolfe, C. N. *J. Org. Chem.* **1998**, *63*, 9031. (h) Zhou, L.; Zhang, Y.; Shi, D. *Tetrahedron Lett.* **1998**, *39*, 8491. (i) Yamamoto, Y.; Matsumi, D.; Hattori, R.; Ito, K. *J. Org. Chem.* **1999**, *64*, 3224. (j) Zhou, L.; Zhang, Y.; Shi, D. *Synthesis* **2000**, 91. (k) Jiang, X.; Wang, C.; Hu, Y.; Hu, H. *J. Org. Chem.* **2000**, *65*, 3555.
12. So, J. H.; Park, M. K.; Boudjouk, P. *J. Org. Chem.* **1988**, *53*, 587.
13. Matsubara, S.; Hashimoto, Y.; Okano, T.; Utimoto, K. *Synlett* **1999**, 1411.
14. Tsuritani, T.; Ito, S.; Shinokubo, H.; Oshima, K. *J. Org. Chem.* **2000**, *65*, 5066.
15. Beckwith, A. L. J.; Easton, C. J.; Lawrence, T.; Serelis, A. K. *Aust. J. Chem.* **1983**, *36*, 545.
16. RajanBabu, T. V. *Acc. Chem. Res.* **1991**, *24*, 139.
17. Zhou, L.; Zhang, Y. *Tetrahedron* **2000**, *56*, 2953.
18. Crystallographic data (including structure factors) for the structure of **2d** have been deposited as supplementary publication no. CCDC-164919 with the Cambridge Crystallographic Data Centre. Copies of the Data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).