Catalytic and thermal hydrocarbonation of methyleneaziridines

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Dedicated to Professor Keiichiro Fukumoto on the occasion of his 70th birthday
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Abstract
Reaction of the methyleneaziridine 1 with carbon pronucleophiles (2, H-CR3) proceeds smoothly in the presence of a palladium catalyst affording the corresponding hydrocarbonation products 5 in good to high yields. In the absence of palladium catalysts, the reaction of 1a with 2a at 120 °C afforded the ring opened product 9 in good yield.

Keywords: Methyleneaziridine, pronucleophile, palladium, hydrocarbonation

Introduction
2-Methyleneaziridines are small-ring compounds containing a nitrogen atom, which have high ring strain. It is known that the ring opening of methyleneaziridines with Grignard reagents (or organolithium compounds),[1a-d] acid chlorides,[1e-f] and HCl[1g] occurs through N-C3 bond cleavage (eq 1), while ring opening with HOPh proceeds through N-C2 bond cleavage[1h] (eq 2). Accordingly, the normal reaction of 2-methyleneaziridines with nucleophiles produces ring-opened derivatives. Recently we reported that the reaction of the methyleneaziridines 1 with carbon pronucleophiles 2 proceeds smoothly in the presence of a palladium catalyst to give, in good- to high yields, the ring products 5 (eq 3).[2] Formally, this is a hydrocarbonation reaction of the double bond of 1 with carbon pronucleophiles. In this paper, we report the detailed study of the palladium-catalyzed hydrocarbonation of methyleneaziridines together with an attempt at asymmetric hydrocarbonation using chiral phosphine ligands.
Results and Discussion

The results are summarized in Table 1. In the presence of catalytic amounts of Pd(PPh₃)₄ (5 mol %) and triphenylphosphine oxide (10 mol %), the reaction of 1-benzyl-2-methyleneaziridine 1a (0.75 mmol) with methylmalononitrile 2a (0.5 mmol) in THF at 120 °C for 4 h gave 5a in 87% yield (entry 1). The catalytic system Pd(dba)₂/PPh₃ was less effective, and Pd₂(dba)₃.CHCl₃ or Pd(PPh₃)₂Cl₂ did not promote the reaction. The reaction using Pd(OAc)₂/PPh₃ as a catalyst gave 5a in a moderate yield. The combination of Pd(PPh₃)₄ and monodentate phosphine ligands such as PPh₃, P(O)Bu₃, and P(o-tolyl)₃, gave 5a in moderate to good yields. In the presence of only Pd(PPh₃)₄, without additional phosphine ligands, 5a was obtained in good yield (80%). However, even in the presence of Pd(PPh₃)₄, if bidentate ligands such as bis-(diphenylphosphino)methane (dppm), 1,2-bis-(diphenylphosphino)ethane (dppe), 1,3-bis-(diphenylphosphino)propane (dppp) were used as a ligand, only small amounts of 5a were obtained. The best results were obtained with the catalytic system, Pd(PPh₃)₄ and P(O)Ph₃. The reactions of 1-hexyl-2-methyleneaziridine 1b with 2a, and 1-butyl-2-methyleneaziridine 1c with 2a afforded 5b and 5c in yields of 71 and
63%, respectively (entries 2, 3). The reactions of 1d with 2a, and 1e with 2a proceeded smoothly and the corresponding hydrocarbonation products 5d and 5e were produced in 65 and 79% yield, respectively (entries 4, 5). The reaction of 1-p-chlorobenzyl-2-methyleneaziridine, 1f, which has an electron withdrawing group on the nitrogen atom, with 2a required longer reaction times and gave 5f in a lower yield (entry 6). The reaction of 1a with 2-cyanopropionate 2b afforded 5g in 63% yield (entry 7). Other activated methines such as i-propylmalononitrile 2c and benzylmalononitrile 2d, upon treatment with 1a, gave products 5h and 5i in 71 and 61% yield, respectively (entries 8, 9).

**Table 1.** Palladium catalyzed hydrocarbonation of 1 with 2

<table>
<thead>
<tr>
<th>Entry</th>
<th>1</th>
<th>2</th>
<th>Time(h)</th>
<th>3</th>
<th>Yield(%)b</th>
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<tr>
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<td>1a</td>
<td>2a</td>
<td>4</td>
<td>5a</td>
<td>87</td>
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<td>5b</td>
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<tr>
<td>3</td>
<td>1c</td>
<td>2a</td>
<td>5</td>
<td>5c</td>
<td>63</td>
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<tr>
<td>4</td>
<td>1d</td>
<td>2a</td>
<td>4</td>
<td>5d</td>
<td>65</td>
</tr>
<tr>
<td>5</td>
<td>1e</td>
<td>2a</td>
<td>4</td>
<td>5e</td>
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<tr>
<td>6</td>
<td>1f</td>
<td>2a</td>
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</tr>
<tr>
<td>7</td>
<td>1a</td>
<td>2b</td>
<td>15</td>
<td>5g</td>
<td>63(1:1)c</td>
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<tr>
<td>8</td>
<td>1a</td>
<td>2c</td>
<td>5</td>
<td>5h</td>
<td>71</td>
</tr>
<tr>
<td>9</td>
<td>1a</td>
<td>2d</td>
<td>5</td>
<td>5i</td>
<td>61</td>
</tr>
</tbody>
</table>

aThe reaction of 1 (0.75 mmol) with 2 (0.5 mmol) was carried out in the presence of 5 mol% of Pd(PPh₃) and 10 mol% of triphenyl phosphine oxide in THF at 120°C. bisolated yield based on 2. 

cthe diastereomeric ratio of 5g.

Significantly high de’s (82%) were obtained in the reaction of (S)-N-(1-naphthylethyl)-2-methylene-aziridine 1h with 2a, although (S)-N-(1-phenylethyl)-2-methyleneaziridine 1g produced only a moderate de (54%) (eq 4). The absolute stereochemistry of 5k was determined unambiguously by X-ray analysis and NOE experiments.

![Reaction Diagram](image)

Next, we examined the asymmetric hydrocarbonation of methyleneaziridine 1a with 2a using several chiral phosphine ligands (eq 5). The results are summarized in Table 2. In the presence of
5 mol.% of Pd(OAc)$_2$ and 5 mol.% of 1-[1-(acetyloxy)ethyl]-1',2-bis(diphenylphosphino)ferrocene (BPPFOAc), the reaction of 1a with 2a afforded the hydrocarbonation product 5a in 56% yield with the enantiomeric excess of 22% (entry 1). The reaction of 1a with 2a using 1-[1-(dimethylamino)ethyl]-2-(diphenylphosphino)ferrocene (BPPFA) instead of BPPFOAc gave 5a with the same level of ee. The reaction of 1a with 2a using other ligands, such as 1,1'-bis(diphenylphosphino)-2-(1-hydroxyethyl)ferrocene (BPPFOH) and [5-methyl-2-(1-methylethyl)cyclohexyl]diphenylphosphine (NMDPP), gave the product 5a in ~0% ee (entries 3 and 4).

A plausible mechanism for the hydrocarbonation is illustrated in Scheme 1. The oxidative addition of palladium(0) into a C-H bond of the pronucleophile 2a would give the hydridopalladium complex 6. The hydropalladation of the methyleneaziridines 1 with 6 would be facilitated by a chelation effect of the nitrogen atom 7, giving the H-Pd addition product 8. Reductive elimination of palladium(0) could then give the hydrocarbonation products 5.

**Table 2. Asymmetric hydrocarbonation of 1a with 2a**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Yield/ %$^b$</th>
<th>ee/ %$^c$</th>
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<tbody>
<tr>
<td>1</td>
<td>BPPFOH</td>
<td>56</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>BPPFA</td>
<td>55</td>
<td>23</td>
</tr>
<tr>
<td>3</td>
<td>BPPFOH</td>
<td>66</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>NMDPP$^d$</td>
<td>64</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$The reaction of 1a (0.75 mmol) with 2a (0.5 mmol) was carried out in the presence of 5 mol% of Pd(OAc)$_2$ and 10 mol% of chiral phosphine in THF at 100°C. $^b$NMR yield based on 2 using p-xylene as an internal standard. $^c$Determined by a chiral HPLC analysis (column: Daicel, chiralcel OD-R). $^d$Ten mol% of NMDPP was used.
Scheme 1

The reaction with deuterated methylmalononitrile (2a-d, 90% D) substantiated the proposed mechanism. The reaction of 1a with 2a-d under the same reaction conditions as above gave 5a-d in 82% yield, in which the deuterium content was 76% (eq 6).

Interestingly, the thermal reaction of 1a with 2a without any palladium catalyst in THF at 120 °C for 4 days gave the vinylic amine 9 in 73% yield (eq 7). These ring opening reactions of the methyleneaziridine most probably occurred by the nucleophilic addition of the carbanion derived from 2a to the C-3 position of the protonated methyleneaziridine, 10.1 It is now clear that
the palladium catalyzed and thermal reactions of 2a with 1a take totally different reaction courses; the Lewis acidic Pd(II)-nitrogen interaction (7) leads to 5a while the Brønsted acid H⁺-nitrogen interaction (10) gives 9. The addition of carbon pronucleophiles to activated alkenes catalyzed by transition metals, that is the Michael addition, is known. Recently, we and other groups reported the palladium catalyzed addition of carbon pronucleophiles 2 to unactivated olefins such as allenes, enynes, methylenecyclopropanes, and 1,3-dienes. The driving force for these reactions originates in the formation of stable π-allylpalladium complexes. The present hydrocarbonation reaction does not proceed through the formation of a π-allylpalladium intermediate, but most probably proceeds via a chelation effect of the nitrogen atom of the aziridine moiety.

![Chemical structure](image)

**Conclusions**

We have developed the direct hydrocarbonation of methyleneaziridines using carbon pronucleophiles in the presence of a palladium catalyst. The palladium-catalyzed reaction provides geminally disubstituted functionalized aziridines, while traditional reactions give ring-opening products upon treatment with nucleophiles.

**Experimental Section**

**General Procedures.** Spectroscopic measurements were carried out with the following instruments: JEOL JNM LA-300 and JEOL α-500 (¹H- and ¹³C NMR), SHIMADZU FTIR-8200A (FT-IR), HITACHI M-2500s (HRMS). All methyleneaziridines were prepared following the reported procedure. Daicel Chiralcel OD-R was used to analyze the enantiomeric excess of 5a.
General procedure for the addition of the active methyne 1 to methyleneaziridines 4

To a solution of Pd(PPh₃)₄ (28.9 mg, 0.025 mmol), triphenylphosphine oxide (13.9 mg, 0.05 mmol) and active methyne 1 (0.5 mmol) in THF (1 mL) was added methyleneaziridine 4 (0.75 mmol) under Ar atmosphere in pressure vial. After heating at 120 °C for 4-15 hours, the reaction mixture was filtered through a short Florisil column using ethyl acetate as an eluent. Separation by passing through a Florisil column using n-hexane-ethyl acetate as eluent.

2-(1-Benzyl-2-methylaziridin-2-yl)-2-methylmalononitrile (5a). Pale yellow oil: IR (neat) 3062, 3031, 2997, 2935, 2858, 2250, 1496, 1454, 1392, 1342, 1245, 1182, 1159, 1126, 1076, 1028, 736, 698 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.48 (s, 1H), 1.53 (s, 3H), 1.64 (s, 3H), 2.31 (s, 1H), 3.70 (d, J = 2.5 Hz, 2H), 7.25-7.39 (m, 5H); ¹³C NMR (125 MHz, CDCl₃) δ 11.64, 20.79, 37.14, 39.69, 41.87, 56.49, 115.03, 115.22, 127.34, 127.91, 128.44, 138.50. HRMS (EI) Calcd for C₁₄H₁₅N₃; m/z 225.1266: found, 225.1271.

2-(1-Hexyl-2-methylaziridin-2-yl)-2-methylmalononitrile (5b). Pale yellow oil: IR (neat) 2931, 2858, 2250, 1456, 1392, 1377, 1342, 1182, 1164, 1126 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.89 (t, J = 6.9 Hz, 3H), 1.29-1.57 (m, 12H), 1.72 (s, 3H), 2.19 (s, 1H), 2.47 (td, J = 6.6 and 2.0 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 11.22, 13.98, 20.64, 22.54, 26.83, 30.25, 31.61, 36.97, 39.68, 41.37, 52.91, 115.30, 115.34. HRMS (EI) Calcd for C₁₃H₂₁N₃; m/z 219.1735: found, 219.1727.

2-(1-Butyl-2-methylaziridin-2-yl)-2-methylmalononitrile (5c). Pale yellow oil: IR (neat) 2958, 2935, 2864, 2252, 1456, 1392, 1377, 1340, 1244, 1184, 1168, 1145, 1126, 1070, 1045 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.93 (t, J = 6.9 Hz, 3H), 1.29 (s, 1H), 1.32-1.62 (m, 7H), 1.72 (s, 3H), 2.19 (s, 1H), 2.48 (t, J = 6.6 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 11.13, 13.86, 20.27, 20.60, 32.33, 36.92, 39.68, 41.31, 52.52, 115.26, 115.30. HRMS (EI) Calcd for C₁₁H₁₇N₃; m/z 191.1422: found, 191.1422.

2-[1-(3-Methoxypropyl)-2-methylaziridin-2-yl]-2-methylmalononitrile (5d). Pale yellow oil: IR (neat) 2931, 2873, 2831, 2250, 1456, 1392, 1342, 1245, 1182, 1164, 1126 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.33 (s, 1H), 1.50 (s, 3H), 1.73 (s, 3H), 1.78-1.89 (m, 2H), 2.22 (s, 1H), 2.47-2.66 (m, 2H), 3.34 (s, 3H), 3.51 (t, J = 2.4 Hz, 6H), 4.54 (t, J = 5.4 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 11.23, 20.68, 30.34, 37.13, 39.74, 41.41, 49.55, 58.59, 70.11, 115.27, 115.29. HRMS (EI) Calcd for C₁₁H₁₇N₃O₄; m/z 207.1372: found, 207.1376.

2-[1-(2,2-Dimethoxyethyl)-2-methylaziridin-2-yl]-2-methylmalononitrile (5e). Pale yellow oil: IR (neat) 2993, 2945, 2912, 2835, 1454, 1888, 1346, 1313, 1247, 1188, 1166, 1134, 1076, 968, 854 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.41 (s, 1H), 1.48 (s, 3H), 1.74 (s, 3H), 2.25 (s, 1H), 2.57-2.72 (m, 2H), 3.43 (d, J = 2.4 Hz, 6H), 4.54 (t, J = 5.4 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 11.86, 20.64, 36.81, 39.59, 41.21, 54.14, 54.54, 54.73, 104.44, 115.06, 115.16. HRMS (EI) Calcd for C₁₁H₁₇N₃O₂; m/z 223.1321: found, 223.1327.

2-[1-(4-Chloro-benzyl)-2-methylaziridin-2-yl]-2-methylmalononitrile (5f). Pale yellow oil: IR (neat) 2977, 2937, 2860, 2250, 1596, 1492, 1454, 1409, 1340, 1245, 1182, 1161, 1087, 1014,
842, 806, 773 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.48 (s, 1H), 1.54 (s, 3H), 1.67 (s, 3H), 2.32 (s, 1H), 3.67 (q, J = 13.7 Hz, 2H), 7.32 (s, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 11.60, 20.83, 37.12, 39.65, 41.92, 55.75, 114.93, 115.08, 128.58, 129.17, 133.04, 136.98. HRMS (EI) Calcd for C₁₄H₁₄N₃Cl, m/z 259.0876; found, 259.0873.

(1-Benzyl-2-methylaziridin-2-yl)-cyanomethylacetic acid ethyl ester (5g). Diastereoisomer A. Pale yellow oil: IR (neat) 2985, 2240, 1741, 1452, 1257, 1174, 1153, 1114, 1064, 1016, 736, 698 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.48 (s, 1H), 1.54 (s, 3H), 1.67 (s, 3H), 2.32 (s, 1H), 3.67 (q, J = 13.7 Hz, 2H), 7.32 (s, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 11.60, 20.83, 37.12, 39.65, 41.92, 55.75, 114.93, 115.08, 128.58, 129.17, 133.04, 136.98. HRMS (EI) Calcd for C₁₄H₁₄N₃Cl, m/z 259.0876; found, 259.0873.

Diastereoisomer B. Pale yellow oil: IR (neat) 2932, 2241, 1741, 1452, 1259, 1174, 1153, 1114, 1066, 1018, 734, 698 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.48 (s, 1H), 1.54 (s, 3H), 2.32 (s, 1H), 3.67 (q, J = 13.7 Hz, 2H), 7.32 (s, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 11.60, 20.83, 37.12, 39.65, 41.92, 55.75, 114.93, 115.08, 128.58, 129.17, 133.04, 136.98. HRMS (EI) Calcd for C₁₄H₁₄N₃Cl, m/z 259.0876; found, 259.0873.

2-(1-Benzyl-2-methylaziridin-2-yl)-2-isopropyl-malononitrile (5h). Pale yellow oil: IR (neat) 3087-2858, 2240, 1741, 1452, 1257, 1174, 1153, 1114, 1064, 734, 698 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.48 (s, 1H), 1.54 (s, 3H), 2.32 (s, 1H), 3.67 (q, J = 13.7 Hz, 2H), 7.32 (s, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 11.60, 20.83, 37.12, 39.65, 41.92, 55.75, 114.93, 115.08, 128.58, 129.17, 133.04, 136.98. HRMS (EI) Calcd for C₁₄H₁₄N₃Cl, m/z 259.0876; found, 259.0873.

2-Benzyl-2-(1-benzyl-2-methyl-aziridin-2-yl)-malononitrile (5i). White solid: IR (KBr) 3085-2889, 2253, 1604, 1496, 1455, 1398, 1336, 1249, 1228, 1151, 1028, 740, 704 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.50 (s, 1H), 1.62 (s, 3H), 2.26 (s, 1H), 2.92 (d, J = 13.5 Hz, 1H), 3.12 (d, J = 13.5 Hz, 1H), 3.73 (s, 2H), 7.23-7.43 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 12.20, 37.73, 39.36, 41.94, 48.11, 56.45, 113.45, 113.99, 127.17, 127.85, 128.31, 138.30. HRMS (EI) Calcd for C₂₀H₁₉N₃, m/z 253.1579; found, 253.1581.

2-Methyl-2-[2-methyl-1-(1-Phenyl-ethyl)-aziridine-2-yl]-malononitrile(5j). Major diastereoisomer. Pale yellow oil: IR (neat) 2974, 2250, 1492, 1450, 1394, 1373, 1340, 1168, 1128, 1110, 1089, 1028, 1158, 702; ¹H NMR (300 MHz, CDCl₃) δ 1.28 (s, 1H), 1.41 (d, J = 6.6 Hz, 3H), 1.63 (s, 3H), 1.79(s, 3H), 2.10 (s, 1H), 3.19 (q, J = 6.5 Hz, 1H), 7.24-7.41 (m, 5H); ¹³C NMR (125 MHz, CDCl₃) δ 11.38, 20.74, 25.13, 35.80, 39.96, 42.95, 61.42, 115.30, 115.31, 126.75, 127.28, 128.43, 144.04; HRMS (EI) Calcd for C₁₅H₁₇N₃: m/z 239.1422; found 239.1420.

Minor diastereoisomer. Pale yellow oil: IR (neat) 2974, 2250, 1492, 1452, 1392, 1377, 1340, 1163, 1128, 1099, 1068, 1028, 758, 702; ¹H NMR (300 MHz, CDCl₃) δ 1.48 (s, 1H), 1.48 (s, 3H), 2.29 (s, 1H), 3.18 (q, J = 6.4 Hz, 1H), 7.21-7.38 (m, 5H);
$^{13}$C NMR (125 MHz, CDCl$_3$) δ 11.67, 21.09, 24.07, 35.89, 39.91, 42.40, 62.30, 114.89, 115.30, 126.80, 127.54, 128.57, 144.47; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{17}\text{N}_3$: $m/z$ 239.1422; found 239.1419.

The stereochemistry of $5j$ was determined by NOE experiment as shown in Figure 1.

![Figure 1. NOE experiment of 5j.](image)

2-Methyl-2-[2-methyl-1-(1-naphthalen-1-yl-ethyl)-aziridine-2-yl]-malononitrile ($5k$)

**Major diastereoisomer.** White solid: IR (KBr) 2977, 2931, 2247, 1596, 1473, 1452, 1340, 1230, 118, 1110, 779; $^1$H NMR (300 MHz, CDCl$_3$) δ 1.29 (s, 1H), 1.59 (d, $J$ = 6.4 Hz, 3H), 1.75 (s, 3H), 1.87 (s, 3H), 2.22 (s, 1H), 3.97 (s, 1H), 7.46-7.54 (m, 4H), 7.78 (d, $J$ = 8.2 Hz, 1H), 7.87-8.08 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) 11.37, 20.97, 24.47, 36.16, 40.29, 43.59, 57.54, 115.37, 115.38, 122.82, 124.32, 125.40, 125.89, 125.93, 127.69, 129.12, 130.58, 133.87, 139.66; HRMS (EI) Calcd for $\text{C}_{19}\text{H}_{19}\text{N}_3$: $m/z$ 289.1579; found 289.1580.

**Minor diastereoisomer.** Pale yellow oil: IR (neat) 2972, 2952, 2247, 1596, 1450, 1394, 1340, 1247, 1178, 1155, 802, 779; $^1$H NMR (300 MHz, CDCl$_3$) δ 1.26 (s, 3H), 1.56-1.60 (m, 7H), 2.43 (s, 1H), 3.92 (s, 1H), 7.46-7.54 (m, 4H), 7.77-7.90 (m, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) 11.71, 21.34, 23.43, 36.35, 40.17, 42.80, 57.69, 115.22, 115.30, 122.91, 124.86, 125.42, 125.57, 125.92, 127.84, 129.07, 129.97, 133.92, 140.08; HRMS (EI) Calcd for $\text{C}_{19}\text{H}_{19}\text{N}_3$: $m/z$ 289.1579; found 289.1582.

The stereochemistry of $5k$ was determined by NOE experiment as shown in Figure 2.

![Figure 2. NOE experiment of 5k.](image)
We could not measure an NOE experiment for the minor diastereoisomer of 5k because of overlap of the peaks. The ORTEP drawing of the major diastereomer of 5k is shown in Figure 3.

![ORTEP drawing of the major isomer of 5k.](image)

**Figure 3.** ORTEP drawing of the major isomer of 5k.

2-[1-(Benzylamino-methyl)-vinyl]-2-methyl-malononitrile (9). Pale yellow oil: IR (neat) 3307, 2931, 2247, 1651, 1496, 1454, 1404, 1344, 1201, 1114, 981, 808, 727, 696; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.67 (s, 1H), 2.71 (td, J = 1.5 and 15.5 Hz, 1H), 3.21 (td, J = 1.5 and 15.5 Hz, 1H), 4.14 (ddd, J = 2.0, 3.5 and 39.0 Hz, 2H), 4.76 (d, J = 4.2 Hz, 2H), 7.21-7.33 (m, 5H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$24.64, 39.16, 39.46, 44.89, 84.59, 120.57, 126.16, 126.75, 127.42, 128.75, 128.82, 142.64; HRMS (EI) Calcd for C$_{14}$H$_{15}$N$_3$: m/z 225.1266. found: 225.1261.

**References and Notes**


3. The anionic structure, H-Pd\(^{+}\)CR\(_3\), is also conceivable.


