

HETEROCYCLES, Vol. 84, No. 1, 2012, pp. 339 - 347. © 2012 The Japan Institute of Heterocyclic Chemistry  
Received, 23rd June, 2011, Accepted, 1st August, 2011, Published online, 8th August, 2011  
DOI: 10.3987/COM-11-S(P)49

## NI-CATALYZED MULTI-COMPONENT COUPLING REACTION OF NORBORNENE, DIMETHYLZINC, BUTADIENE, AND ALDIMINE

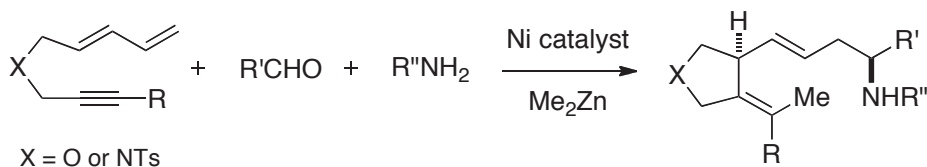
Toshiyuki Nakamura, Takamichi Mori, Mariko Togawa, and Masanari Kimura\*

Graduate School of Engineering, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki, 852-8521, Japan. E-mail; masanari@nagasaki-u.ac.jp

Dedicated to Prof. Dr. Albert Padwa on the occasion of his 75<sup>th</sup> birthday.

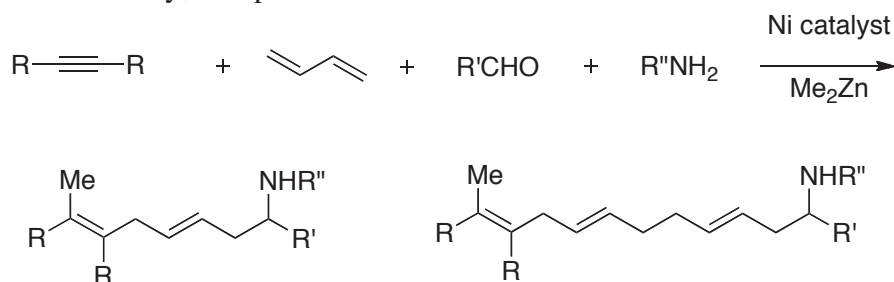
**Abstract** – In the presence of a Ni catalyst and dimethylzinc, aldimines, which are prepared from aldehydes and primary amines, undergo a multi-component coupling reaction with 1,3-butadiene and norbornene to provide homoallylamines in good to excellent yields. Under similar conditions, the reaction can be successfully extended to the *N,O*-acetals prepared from lactols and amines, giving rise to  $\omega$ -hydroxyhomoallylamines.

Sequential transition metal-catalyzed coupling reactions of C-C  $\pi$ -components with carbonyl electrophiles are a versatile strategy for the C-C bond transformation.<sup>1</sup> Particularly, Ni-catalyzed C-C bond formations involving alkynes, alkenes, and dienes as carbon nucleophiles have been well utilized for the synthesis of both complicated and physiologically active molecules.<sup>2</sup> Although aldimines are among the most important carbonyl electrophiles involved in the vital skeleton elongations of the carbon chains of nitrogen containing compounds, it is problematic that they tend to be less reactive than aldehydes.<sup>3</sup> As an effective solution for these problems we have developed Ni-catalyzed five-component connection reactions of dimethylzinc, alkynes, conjugated diene moieties of 1,3-dien-8-yne, aldehydes, and primary amines to furnish heterocyclic compounds bearing dienylyhomoallylamines in good to excellent yields (Scheme 1).<sup>4</sup> Interestingly, these coupling reactions proceed smoothly at room temperature to provide homoallylamine framework with excellent 1,5-*anti* stereoselectivity.



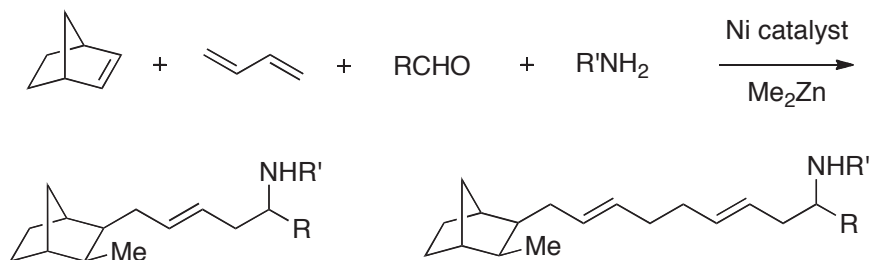
**Scheme 1.** Ni-Catalyzed Multi-component Coupling Reactions with Dienyne, Dimethylzinc, and Aldimine

Furthermore, we have developed the Ni-catalyzed intermolecular five-component connection reaction of dimethylzinc, alkyne, butadiene, aldehydes, and primary amines, furnishing octadienylamines and dodecatrienylamines (Scheme 2).<sup>5</sup> In this case, the reaction outcome was strictly subject to the influence of the amines. Aromatic amines led to octadienylamines, whereas aliphatic amines provided dodecatrienylamines *via* dimerization of butadiene through the bis-butadiene nickel activated species. We have also developed a Ni/phosphine ligand system that can readily promote the dimerization of butadiene to generate  $\eta^1, \eta^3$ -allylnickel species predominantly. Formation of these species then allowed a multi-component coupling reaction involving an alkyne, an aldimine, and dimethylzinc to furnish dodecatrienylamines selectively, irrespective of the kind of amines.<sup>6</sup>



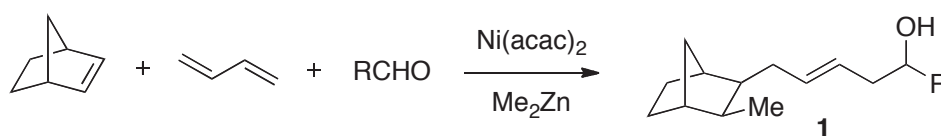
**Scheme 2.** Ni-Catalyzed Multi-Component Coupling Reaction of Alkyne, Dimethylzinc, Butadiene, and Aldimine

Herein, we report that a similar Ni-catalyzed reaction system has been successfully extended to multi-component coupling reactions involving norbornene to provide homoallylamines by means of coupling with aldimines as carbonyl electrophiles (Scheme 3). The reactivity and selectivity associated with the similar reaction of *N,O*-acetals prepared from lactols and primary amines are also reported.



**Scheme 3.** Ni-Catalyzed Multi-Component Coupling Reaction of Norbornene, Dimethylzinc, Butadiene, and Aldimine

We examined the Ni-catalyzed coupling reaction of norbornene with aldehydes prior to investigation of the coupling reaction with aldimines. The reaction was undertaken with great ease simply by exposing dimethylzinc to a mixture of Ni(acac)<sub>2</sub> catalyst, aldehyde, butadiene, and norbornene in THF under a nitrogen atmosphere. Among these investigations with 4 equivalents of butadiene and norbornene, the reaction required 2.4 equivalents of dimethylzinc to consume the aldehyde completely at room temperature. Table 1 summarizes the results obtained from using a wide variety of structurally diverse aldehydes, including electron-donating and electron-withdrawing group substituted aromatic aldehydes and aliphatic aldehydes. All of these reactions were conducted to provide the coupling product **1** as a mixture of diastereomeric isomers in 1:1 to 2:1 ratios with respect to configuration of the hydroxy group. In the presence of dppf ligand, an intractable mixture was formed, and the desired product **1** was not obtained at all (run 2, Table 1).



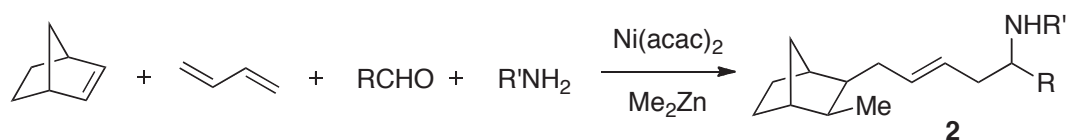
**Table 1.** Ni-Catalyzed Coupling Reaction of Norbornene, Me<sub>2</sub>Zn, Butadiene, and Aldehyde<sup>a</sup>

run	RCHO	yield (%) [ratio]
1	PhCHO	<b>1a</b> : 94 [2:1]
2 <sup>b</sup>	PhCHO	intractable mixture
3	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> CHO	<b>1b</b> : 87 [2:1]
4	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CHO	<b>1c</b> : 92 [2:1]
5	<i>i</i> -PrCHO	<b>1d</b> : 81 [1:1]
6	<i>c</i> -HexCHO	<b>1e</b> : 78 [1:1]

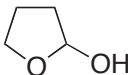
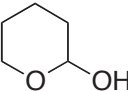
<sup>a</sup> The reaction was undertaken in the presence of Ni(acac)<sub>2</sub> (0.1 mmol), norbornene (4 mmol), butadiene (4 mmol), RCHO (1 mmol), and Me<sub>2</sub>Zn (2.4 mmol) in dry THF (5 mL) at room temperature for 24 h under nitrogen atmosphere. <sup>b</sup> Bidentate ligand, dppf (0.1 mmol) was added.

Next, the similar coupling reaction with norbornene, butadiene, and dimethylzinc was applied to C-C bond formation using aldimines. The reaction was undertaken in one flask as described. A mixture of aldehyde and primary amine in dry THF was stirred at room temperature for 10 hours under a nitrogen atmosphere. Into this mixture, Ni(acac)<sub>2</sub> catalyst, butadiene, norbornene, and dimethylzinc dissolved in THF were added without removal of the water produced. The reaction was complete after 24 hours and

provided the five-component coupling homoallylamines **2** in good to reasonable yields after the usual workup and purification by column chromatography over silica gel (Table 2).<sup>7</sup> Irrespective of the kind of aldehydes employed, the reaction proceeds smoothly at room temperature providing the desired homoallylamines **2a-g** as a mixture of diastereomers in 1:1 to 2:1 ratios. These reactions of aldimines prepared from aromatic and aliphatic aldehydes encouraged us to investigate the coupling reaction using *N,O*-acetals.<sup>8</sup> The five-component coupling reaction of *N,O*-acetals prepared from 2-hydroxytetrahydrofuran and 2-hydroxytetrahydropyran with *p*-anisidine provided the desired products **2f** and **2g** in moderate yields (runs 6 and 7, Table 2).



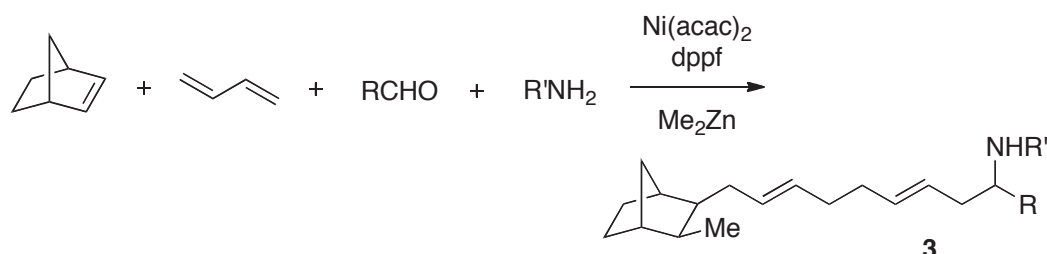
**Table 2.** Ni-Catalyzed Coupling Reaction of Norbornene,  $\text{Me}_2\text{Zn}$ , Butadiene, and Aldimine<sup>a</sup>

run	RCHO	R'NH <sub>2</sub>	yield (%) [ratio]
1	PhCHO	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>2a</b> : 50 [2:1]
2	PhCHO	PhNH <sub>2</sub>	<b>2b</b> : 74 [1:1]
3	PhCHO	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>2c</b> : 71 [1:1]
4	<i>i</i> -PrCHO	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>2d</b> : 58 [1:1]
5	<i>c</i> -HexCHO	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>2e</b> : 50 [2:1]
6		<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>2f</b> : 40 [1:1]
7		<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>2g</b> : 45 [1:1]

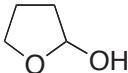
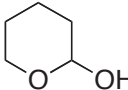
<sup>a</sup> Reaction conditions: RCHO (1 mmol), primary amine (2 mmol) in THF (2 ml) at room temperature for 10 h, and then Ni(acac)<sub>2</sub> (0.1 mmol), norbornene (4 mmol), butadiene (4 mmol), and Me<sub>2</sub>Zn (2.4 mmol) in dry THF (3 mL) at room temperature for 24 h under nitrogen atmosphere.

In the presence of a bidentate phosphine ligand, such as dppf, the dimerization of butadiene was predominant. This was followed by the multi-component coupling reaction with norbornene, aldimine, and dimethylzinc to provide the dienylylhomoallylamines **3a-h**, irrespective of the kinds of aldehydes and amines (Table 3). All of these reactions with various aldimines prepared from aromatic and aliphatic

aldehydes and lactols provided the desired dienylylhomoallylamines **3a-h** in good to excellent yields with a mixture of diastereoisomers in a 1:1 ratio.



**Table 3.** Ni-Catalyzed Coupling Reaction of Norbornene, Me<sub>2</sub>Zn, Butadiene, and Aldimine<sup>a</sup>

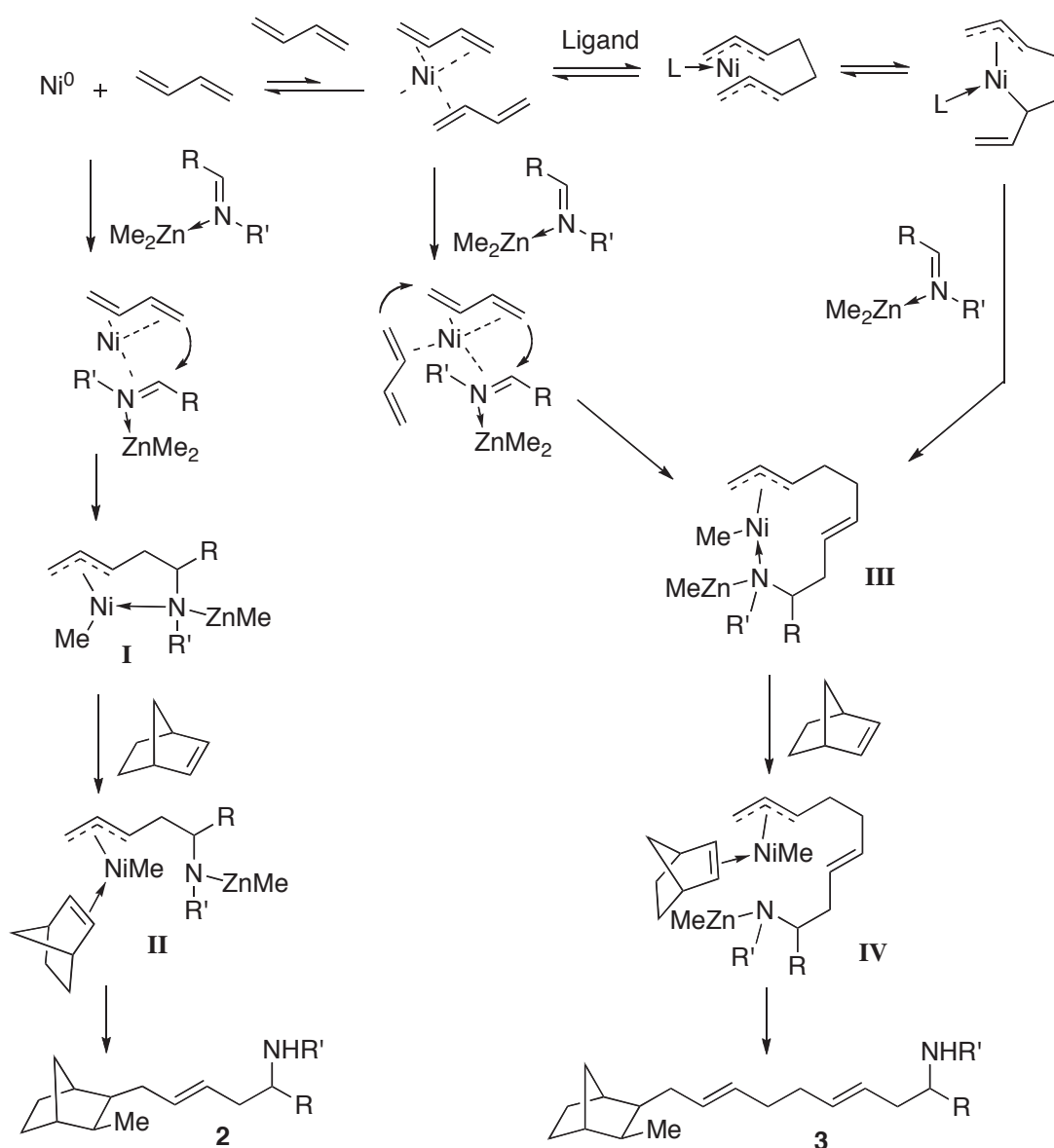
run	RCHO	R'NH <sub>2</sub>	yield (%) [ratio]
1	PhCHO	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3a</b> : 96 [1:1]
2	PhCHO	PhNH <sub>2</sub>	<b>3b</b> : 93 [1:1]
3	PhCHO	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3c</b> : 85 [1:1]
4	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CHO	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3d</b> : 85 [1:1]
5	<i>i</i> -PrCHO	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3e</b> : 76 [1:1]
6	<i>c</i> -HexCHO	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3f</b> : 89 [1:1]
7		<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3g</b> : 79 [1:1]
8		<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	<b>3h</b> : 90 [1:1]

<sup>a</sup> Reaction conditions: RCHO (1 mmol), primary amine (2 mmol) in THF (2 mL) at room temperature for 10 h, and then Ni(acac)<sub>2</sub> (0.1 mmol), dppf (0.1 mmol), norbornene (4 mmol), butadiene (4 mmol), and Me<sub>2</sub>Zn (2.4 mmol) in dry THF (3 mL) at room temperature for 24 h under nitrogen atmosphere.

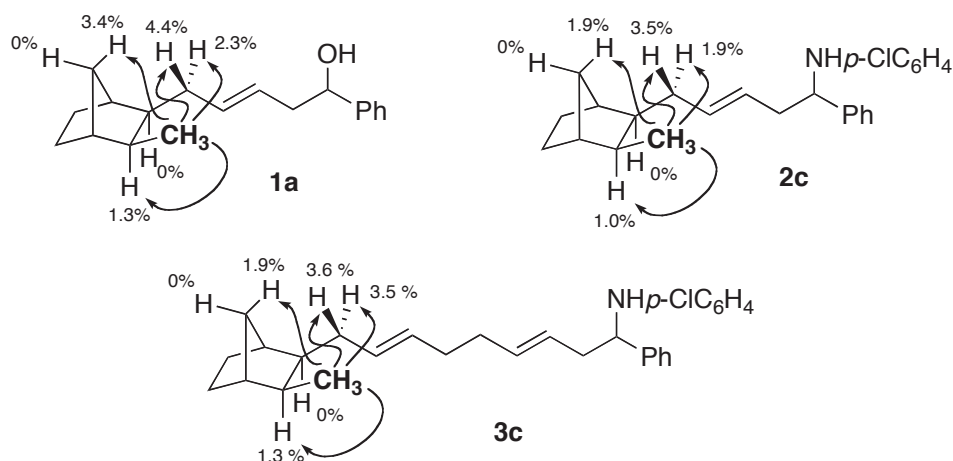
The structure and relative stereochemistry of the products were determined on the basis of spectral data. It was apparent that the olefin geometry is *E*-form by coupling constants in <sup>1</sup>H NMR spectra.<sup>7</sup> In Figure 1 are listed the selected data of NOE obtained by irradiation at methyl protons. Judging from these results, the configuration of the side chains of norbornane skeleton was determined to be *cis-exo* form (Figure 1).

The proposed reaction mechanism for the multi-component coupling reaction utilizing the Ni catalytic system is shown in Scheme 4. In the absence of phosphine ligand, aldimines would react with the mono

butadiene-Ni(0) species to form azanickelacyclo intermediate **I**, providing homoallylamine **2** by virtue of the insertion of norbornene as an allylnickel species **II**. On the other hand, in the presence of ligand, the butadiene tends to readily dimerize to give the more nucleophilic bis- $\pi$ -allylnickel species,<sup>6</sup> which would readily participate in the coupling reaction with aldimines to give rise to the dienylamine **3** through the allylnickel key intermediate **IV** *via* insertion of norbornene as an electron-donating ligand into the allylnickel intermediate **III**, irrespective of the nature of the amines that were employed.



**Scheme 4.** A Plausible Reaction Mechanism for Ni-Catalyzed Coupling of Norbornene, Butadiene, Aldehyde, Amine, and  $\text{Me}_2\text{Zn}$



**Figure 1.** Percent Increment in NOE Observed by Irradiation at Boldface Protons

In summary, we have shown that a combination of a Ni-catalyst and dimethylzinc effectively activates aldimines that are prepared from aldehydes and primary amines to undergo the multi-component coupling reaction of norbornene, butadiene, and a methyl group to form homoallylamines in excellent yields. Under similar conditions, a bidentate phosphine ligand, such as dppf, promotes the dimerization of butadiene to provide predominantly dienylnhomoallylamines. The present methodology could be utilized for the convenient and stereodefined construction of physiologically active molecules involving carbohydrates and amino sugars with great operational ease.

## ACKNOWLEDGEMENTS

Financial support from the Ministry of Education, Culture, Sports, Science, and Technology, Japanese Government (Grant-in-Aid for Scientific Research (B) 21350055 and Scientific Research on Innovative Areas, “Molecular Activation Directed toward Straightforward Synthesis”), is gratefully acknowledged.

## REFERENCES AND NOTES

1. H. Kurosawa and A. Yamamoto, *Fundamentals of Molecular Catalysis*, Elsevier: Amsterdam, 2003; J. Zhu and H. Bienaymé, *Multicomponent Reactions*, Wiley-VCH: Weinheim, 2005; M. J. Krische, *Topics in Current Chemistry*, Springer-Verlag: Berlin, Heidelberg, 2007; M. Kimura and Y. Tamaru, *Mini-Rev. Org. Chem.*, 2009, **6**, 392.
2. P. W. Jolly and G. Wilke, *The Organic Chemistry of Nickel*, Academic: New York, 1975; Y. Tamaru, *Modern Organonickel Chemistry*, Wiley-VCH: Weinheim, 2005; M. Catellani, E. Motti, and N. D. Ca, *Acc. Chem. Res.*, 2008, **41**, 1512.
3. S. Kobayashi, T. Wakatsuki, and H. Oyamada, *Chem. Lett.*, 1997, 831; H. Nakamura, M. Bao, and Y. Yamamoto, *Angew. Chem. Int. Ed.*, 2001, **40**, 3208; C. Wei, Z. Li, and C.-J. Li, *Synlett*, 2004,

- 1472; M. Shimizu, M. Kimura, T. Watanabe, and Y. Tamaru, *Org. Lett.*, 2005, **7**, 637; M. Kimura, T. Tamaki, M. Nakata, K. Tohyama, and Y. Tamaru, *Angew. Chem. Int. Ed.*, 2008, **47**, 5803.
4. M. Kimura, A. Ezoe, M. Mori, and Y. Tamaru, *J. Am. Chem. Soc.*, 2005, **127**, 201.
  5. M. Kimura, K. Kojima, Y. Tatsuyama, and Y. Tamaru, *J. Am. Chem. Soc.*, 2006, **128**, 6332.
  6. M. Kimura, M. Togawa, Y. Tatsuyama, and K. Matsufuji, *Tetrahedron Lett.*, 2009, **50**, 3982.
  7. General procedure for the Ni-catalyzed multi-component coupling reaction (run 3, Table 2): A solution of benzaldehyde (106 mg, 1 mmol) and *p*-chloroaniline (255 mg, 2 mmol) in dry THF (2 mL) was stirred for 10 h under nitrogen. A mixture of Ni(acac)<sub>2</sub> (26 mg, 0.1 mmol), norbornene (377 mg, 4 mmol), butadiene (350  $\mu$ L, 4 mmol) dissolved in dry THF (3 mL) *via* cannula, and dimethylzinc (2.4 mmol, 1.0 M hexane solution) *via* a syringe were successively added to the aldimine residue. The mixture was stirred at room temperature for 24 h. The reaction mixture was diluted with 30 mL of EtOAc and washed with sat. aq. NaHCO<sub>3</sub> and brine. The organic phase was dried (MgSO<sub>4</sub>) and concentrated in vacuo to give a brown oil, which was subjected to column chromatography over silica gel (hexane/EtOAc = 64/1 v/v) to give **2c** (270 mg, 71%, *R<sub>f</sub>* = 0.83; hexane/EtOAc = 4/1 v/v).

**4-Chloro-*N*-[(*E*)-5-(3-methylbicyclo[2.2.1]heptan-2-yl)-1-phenylpent-3-enyl]benzenamine (2c):** a mixture of diastereomers in a ratio of 1:1; IR (neat) 3416 (m), 2870 (s), 2845 (m), 1601 (m), 1260 (w), 972 (m), 814 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, a mixture of isomers in a 1:1 ratio)  $\delta$  0.83 (d, *J* = 7.6 Hz, 3 H), 0.92 (dm, *J* = 4.4 Hz, 1 H), 1.13 - 1.20 (m, 2 H), 1.42 (dm, *J* = 7.6 Hz, 1 H), 1.50 (dm, *J* = 4.4 Hz, 3 H), 1.67 - 1.72 (m, 2 H), 1.94 - 2.00 (m, 1 H), 1.94 - 2.12 (m, 2 H), 2.40 (dm, *J* = 7.8 Hz, 1 H), 2.55 (dm, *J* = 6.6 Hz, 1 H), 4.18 (br s, 1 H), 4.27 (dm, *J* = 7.8 Hz, 1 H), 5.31 (dd, *J* = 6.6, 15.0 Hz, 1 H), 5.54 (dm, *J* = 15.0 Hz, 1 H), 6.37 (d, *J* = 8.8 Hz, 2 H), 6.99 (d, *J* = 8.8 Hz, 2 H), 7.22 - 7.31 (m, 5 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, one isomer)  $\delta$  15.7, 29.6, 29.9, 33.2, 40.1, 40.8, 42.1, 44.6, 45.7, 45.9, 57.5, 114.4, 121.8, 125.6, 125.8, 126.1, 126.9, 128.4, 135.5, 135.6, 145.8; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, the other isomer)  $\delta$  15.7, 29.6, 29.9, 32.2, 40.7, 40.8, 42.3, 44.6, 45.7, 45.9, 57.5, 114.4, 121.8, 125.6, 125.8, 126.1, 126.9, 128.7, 135.5, 135.6, 145.8; HRMS, calcd for C<sub>25</sub>H<sub>30</sub>NCl: 379.2067. Found *m/z* (relative intensity): 380 (M<sup>+</sup>+1, 28), 379.2075 (M<sup>+</sup>, 100).

**(*E*)-5-(3-Methylbicyclo[2.2.1]heptan-2-yl)-1-phenylpent-3-en-1-ol (1a):** a mixture of diastereomers in a ratio of 2:1; IR (neat) 3344 (br s), 2949 (m), 2870 (m), 1456 (w), 1028 (m), 970 (m), 698 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, major isomer)  $\delta$  0.82 (d, *J* = 7.3 Hz, 3 H), 0.94 (m, 1 H), 1.10 - 1.21 (m, 2 H), 1.38 - 1.51 (m, 5 H), 1.68 (dt, *J* = 14.1, 7.3 Hz, 1 H), 1.77 (m, 1 H), 2.02 - 2.12 (m, 2 H), 2.04 (br dt, *J* = 14.1, 7.3 Hz, 1 H), 2.42 (dt, *J* = 14.0, 6.7 Hz, 2 H), 4.68 (dd, *J* = 14.0, 8.3 Hz, 1 H), 5.36 (dt, *J* = 13.8, 7.3 Hz, 1 H), 5.51 (dt, *J* = 13.8, 7.3 Hz, 1 H), 7.23 - 7.38 (m, 5 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz major isomer)  $\delta$  15.7, 29.6, 29.8, 33.2, 40.0, 40.8, 42.8, 44.5, 45.6,

73.3, 125.3, 125.5, 127.0, 127.1, 128.0, 135.5, 143.7;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, minor isomer)  $\delta$  0.82 (d,  $J = 7.3$  Hz, 3 H), 0.94 (m, 1 H), 1.10 - 1.21 (m, 2 H), 1.38 - 1.51 (m, 5 H), 1.74 (dt,  $J = 14.1$ , 6.5 Hz, 1 H), 1.77 (m, 1 H), 2.02 - 2.12 (m, 2 H), 2.06 (br dt,  $J = 14.1$ , 6.5 Hz, 1 H), 2.50 (dt,  $J = 12.1$ , 6.1 Hz, 2 H), 4.67 (dd,  $J = 12.1$ , 5.2 Hz, 1 H) 5.36 (dt,  $J = 12.9$ , 6.5 Hz, 1 H), 5.53 (dt,  $J = 12.9$ , 6.1 Hz, 1 H), 7.23 - 7.38 (m, 5 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz minor isomer)  $\delta$  15.7, 29.6, 29.8, 32.1, 40.0, 40.7, 42.8, 44.5, 45.6, 73.4, 125.3, 125.6, 127.0, 127.1, 128.0, 135.4, 143.7; HRMS, calcd for  $\text{C}_{19}\text{H}_{26}\text{O}$ : 270.1984, Found  $m/z$  (relative intensity): 271 ( $\text{M}^+ + 1$ , 14), 270.1974 ( $\text{M}^+$ , 43), 252 (100), 216 (90).

**4-Chloro-*N*-[(3*E*,7*E*)-9-(3-methylbicyclo[2.2.1]heptan-2-yl)-1-phenylnona-3,7-dienyl]benzamine (3c)**: a mixture of diastereomers in a ratio of 1:1; IR (neat) 3414 (w), 2951 (s), 2870 (s), 1601 (s), 1497 (s), 968 (s), 814 (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400MHz, a mixture of isomers in a 1:1 ratio)  $\delta$  0.83 (d,  $J = 6.8$  Hz, 3 H), 0.91 (m, 1 H), 1.15 (dm,  $J = 2.3$  Hz, 2 H), 1.39 - 1.45 (m, 3 H), 1.48 (dm,  $J = 2.3$  Hz, 2 H), 1.68 (dm,  $J = 6.5$  Hz, 1 H), 1.70 (dm,  $J = 5.0$  Hz, 1 H), 1.79 (br s, 1 H), 1.97 - 2.09 (m, 5 H), 2.01 (br s, 1 H), 2.41 (ddm,  $J = 5.4$ , 14.3 Hz, 1 H), 2.53 (ddm,  $J = 5.4$ , 14.3 Hz, 1 H), 4.17 (br s, 1 H), 4.26 (br t,  $J = 5.4$  Hz, 1 H), 5.34 (dm,  $J = 15.0$  Hz, 1 H), 5.36 (dm,  $J = 15.3$  Hz, 1 H), 5.41 (dm,  $J = 15.0$  Hz, 1 H), 5.56 (ddd,  $J = 5.0$ , 6.5, 15.3 Hz, 1 H), 6.34 (d,  $J = 8.9$  Hz, 2 H), 6.99 (d,  $J = 8.9$  Hz, 2 H), 7.20 - 7.31 (m, 5 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, one isomer)  $\delta$  15.7, 29.7, 29.9, 32.2, 32.5, 32.7, 33.2, 40.1, 40.8, 42.0, 44.6, 45.9, 57.5, 114.5, 121.8, 125.7, 126.1, 126.9, 128.4, 128.7, 129.4, 131.5, 134.2, 143.1, 145.8;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, the other isomer)  $\delta$  15.7, 29.7, 29.9, 32.2, 32.5, 32.7, 33.2, 40.1, 40.7, 42.1, 44.6, 45.9, 57.5, 114.5, 121.8, 125.8, 126.1, 126.9, 128.4, 128.7, 129.4, 131.5, 134.2, 143.1, 145.8; HRMS, calcd for  $\text{C}_{29}\text{H}_{36}\text{NCl}$ : 433.2536. Found  $m/z$  (relative intensity): 433.2537 ( $\text{M}^+$ , 100), 356 (11).

8. Y. Yamaguchi, M. Hashimoto, K. Toyama, and M. Kimura, *Tetrahedron Lett.*, 2011, **52**, 913.