

# The Transition Metal-Catalyzed Addition of C-H Bonds in Aromatic Hydrazones to Olefins

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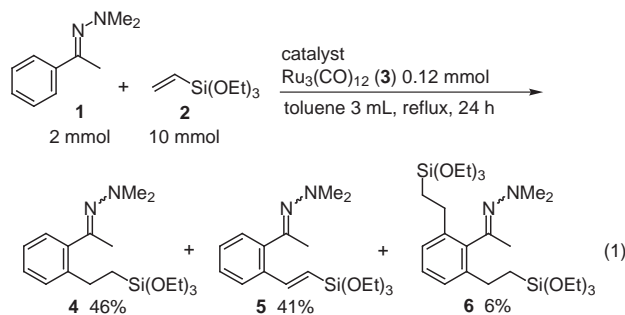
**Abstract:** Catalytic additions of C-H bonds in aromatic hydrazones to olefins proceeded with the aid of ruthenium or rhodium complexes. Several hydrazones can be used in the chelation-assisted C-H/olefin coupling described herein. When a  $\text{Ru}_3(\text{CO})_{12}$  complex was used as the catalyst, a mixture of the 1:1 addition product, along with the corresponding dehydrogenated coupling products was obtained. In the case of the reaction using  $\text{RhCl}(\text{PPh}_3)_3$ -catalyst, no dehydrogenated coupling product was obtained and the 1:2 addition product was produced as the major product.

**Key words:** ruthenium catalysts, rhodium catalysts, C-H bond cleavage, aromatic hydrazones, C-H/olefin coupling

As the result of recent progress in the area, catalytic reactions involving C-H bond cleavage has been found to be one of the most useful protocols for the C-C bond formation.<sup>1</sup> We have been investigating the transition metal-catalyzed addition of C-H bonds to C-C multiple bonds in which chelation-assistance by directing groups is believed to play a major role in the catalytic cycle, especially in the C-H bond cleavage step.<sup>1-12</sup> To date, we have demonstrated that various types of aromatic and olefinic compounds having ketone,<sup>2</sup> ester,<sup>4</sup> imine,<sup>6</sup> imidate,<sup>7</sup> nitrile,<sup>8</sup> aldehyde,<sup>9</sup> and pyridyl moieties<sup>10</sup> can be applied to chelation-assisted C-H/olefin coupling. In this communication, we wish to report that an  $sp^2$  nitrogen in hydrazones, which are often used in organic synthesis for the preparation of nitriles<sup>13</sup> and chiral amines,<sup>14</sup> can also be used as a directing group for C-H/olefin coupling, giving the corresponding *ortho* alkylated products.

The reaction of hydrazone **1**, derived from acetophenone, with triethoxyvinylsilane (**2**) was carried out using  $\text{Ru}_3(\text{CO})_{12}$  (**3**) as a catalyst (eq 1).<sup>15</sup> The 1:1 addition product **4** and the corresponding dehydrogenative coupling products **5** were obtained in 46% and 41% yields, respectively.<sup>16,17</sup>

The catalytic activities of the  $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$  and  $\text{RhCl}(\text{PPh}_3)_3$  complexes were also examined, and the results are shown in Table 1. When the ruthenium-phosphine complex,  $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ , was used instead of complex **3**, **1** was completely consumed and **4** and **5** were obtained in 89% and 11% yields, respectively, with no 1:2 addition product (run 2). In contrast to the case of the reaction of aromatic ketimine **8** with **2** which gave no dehydrogenated products,<sup>6a</sup> the reaction of the ketone hydrazone **1** afforded a considerable amount of dehydrogenated product **5** (runs 1 and 2). When Wilkinson's cat-



**Scheme 1**

alyst (**7**) was used, the 1:2 addition product **6** was obtained as a major product, after prolonged reaction period (48 h) (run 3). Although the  $\text{Ru}_3(\text{CO})_{12}$ -catalyzed reaction of the aromatic ketimine **8** with **2** gave only the corresponding 1:1 addition product,<sup>6a</sup> the use of catalyst **7** for the reaction of **1** with **2** resulted in the 1:2 addition product **6** as a major product (runs 3-5). Under forcing reaction conditions, i.e., using refluxing mesitylene as the solvent, a high total yield of coupling products **4** and **6** (98% combined yield) was achieved. Even when a smaller amount of the olefin **2** was used (run 5), the 1:2 coupling product was obtained as a major product (**4**, 34% yield and **6**, 55% yield). The predominant formation of the 1:2 addition product **6** can be attributed to the binding affinity of the nitrogen atom for the rhodium center, in which the second C-H bond cleavage leading to the formation of 1:2 addition product took place without the dissociation of the 1:1 product from the rhodium center.<sup>18</sup>

**Table 1** The Reaction of Ketone Hydrazone **1** with Triethoxyvinylsilane (**2**) Using a Ruthenium or Rhodium Catalyst<sup>a</sup>

run	catalyst	solvent	time	yields, %		
				<b>4</b>	<b>5</b>	<b>6</b>
1	$\text{Ru}_3(\text{CO})_{12}$ ( <b>3</b> )	toluene	24 h	46	41	6
2	$\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$	toluene	48 h	89	11	0
3	$\text{RhCl}(\text{PPh}_3)_3$ ( <b>7</b> )	toluene	48 h	16	0	75
4	$\text{RhCl}(\text{PPh}_3)_3$	mesitylene	6 h	27	0	71
5 <sup>b</sup>	$\text{RhCl}(\text{PPh}_3)_3$	mesitylene	24 h	34	0	55

<sup>a</sup>Reaction conditions: hydrazone **1** (2 mmol), vinylsilane **2** (10 mmol), catalyst (0.12 mmol), solvent 3 mL, reflux.

<sup>b</sup>Two equivalents of **2** was used.

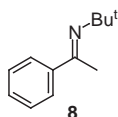


Figure 1

The reaction of several hydrazones with olefins was examined, and some selected results are listed in Table 2. The ketone hydrazone **9** gave the 1:1 (**10**) and 1:2 addition products (**11**) in 27% and 73% yields, respectively (Table 2, run 1). In this case, the reactivity of the hydrazone was very similar to the *N,N*-dimethylamino derivative **1**. The reaction of hydrazone **1** with ethylene gave the *ortho* ethylated products **12** and **13** in 5% and 88% yields, respectively (Table 2, run 2). The reaction with *o*-methylstyrene proceeded smoothly to give only the 1:1 addition product **14** (Table 2, run 3). In the course of our studies of C-H/olefin coupling, the use of aromatic olefins such as styrenes usually resulted in the exclusive formation of the corresponding 1:1 addition product. The reaction of hydrazone **15**, derived from *o*-methylbenzaldehyde, with vinylsilane **2** was carried using the Ru<sub>3</sub>(CO)<sub>12</sub>-catalyst. The 1:1 addition product **16** and the dehydrogenated product **17** were obtained in 30% and 8% yields, respectively (Table 2, run 4). The catalytic activities of several other ruthenium complexes were also examined. Of the catalysts screened, RuH<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>3</sub> (**16**, 13%; **17**, 15%; 48 h) and Ru(cod)(cot) (cod = 1,5-cyclooctadiene; cot = 1,3,5-cyclooctatriene) (**16**, 16%; **17**, 1%; 24 h) were found to be active catalysts, but their activities were low compared with **3**. In the case of the reaction of **15** with **2**, RhCl(PPh<sub>3</sub>)<sub>3</sub> (**7**), which was the active catalyst for the reaction of the ketone hydrazone **1** with olefins, did not serve as a catalyst. To find a more reactive hydrazone derivative, we further examined the present coupling reaction using several additional hydrazones. In the case of the reaction of a hydrazone having an *N*-piperidyl group on the *sp*<sup>2</sup> nitrogen atom, the reactivity of the hydrazone was slightly increased (Table 2, run 5). However, when a sterically hindered piperidyl group, i.e., 2,6-dimethylpiperidyl group, was introduced on the *sp*<sup>2</sup> nitrogen, the yield was decreased considerably to 15% (Table 2, run 6).

In summary, we report on a new procedure for chelation-assisted C-H/olefin coupling using transition metal-catalysts, which enables the site-selective alkylation of an aromatic hydrazone with olefins. Further studies to address the scope of this type of coupling reaction are now in progress.

### Acknowledgement

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**Table 2** The Transition Metal-catalyzed Reaction of Hydrazones with Olefins<sup>a</sup>

run	hydrazone	olefin	cat.	time	yields <sup>b</sup>	
	R <sup>1</sup> R <sup>2</sup> NR <sup>3</sup> <sub>2</sub>	Y				
1	<b>9</b> : H Me N(CH <sub>2</sub> ) <sub>5</sub>	Si(OEt) <sub>3</sub>	<b>7</b>	8 h	<b>10</b> 27%	<b>11</b> 73%
2 <sup>c</sup>	<b>1</b> : H Me NMe <sub>2</sub>	H	<b>7</b>	24 h	<b>12</b> 5%	<b>13</b> 88%
3	<b>1</b> : H Me NMe <sub>2</sub>	<i>o</i> -tolyl	<b>7</b>	24 h	<b>14</b> 77%	0%
4 <sup>d,e</sup>	<b>15</b> : Me H NMe <sub>2</sub>	Si(OEt) <sub>3</sub>	<b>3</b>	48 h	<b>16</b> 30%	—
5 <sup>d,f</sup>	<b>18</b> : Me H N(CH <sub>2</sub> ) <sub>5</sub>	Si(OEt) <sub>3</sub>	<b>3</b>	48 h	<b>19</b> 51%	—
6 <sup>d</sup>	<b>21</b> : Me H	Si(OEt) <sub>3</sub>	<b>3</b>	48 h	<b>22</b> 15%	—

<sup>a</sup>Reaction conditions: hydrazone (2 mmol), olefin (10 mmol), catalyst (0.12 mmol), mesitylene 3 mL, reflux.

<sup>b</sup>GC yield.

<sup>c</sup>The reaction with ethylene (7 atm, 14 mmol) was carried out in autoclave at 150 °C (oil bath temperature).

<sup>d</sup>The reaction was carried out in toluene.

<sup>e</sup>The corresponding dehydrogenated product **17** was also obtained in 8% yield. <sup>f</sup>The corresponding dehydrogenated product **20** was also obtained in 7% yield.

### References and Notes

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- (15) **General procedure for the reaction of aromatic hydrazones with olefins.** An apparatus consisting of a 10 mL two-necked flask, a reflux condenser connected to a nitrogen line, a magnetic stirring bar, and an inlet-tube sealed with a rubber septum was flame-dried under a flow of nitrogen. After cooling to room temperature, the following reagents were placed in the flask: catalyst (0.12 mmol), 3 mL of toluene, hydrazone (2 mmol), olefin (10 mmol), and hexadecane (an internal standard for GC analysis). The resulting solution was then refluxed with stirring. The reaction was monitored by GC analysis. After heating for the appropriate reaction period, the solution was then concentrated in vacuo, and the residue purified by bulb-to-bulb distillation and/or silica gel column chromatography.
- (16) **4** (*anti* isomer):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  0.92-1.00 (c, 2 H,  $\text{SiCH}_2$ ), 1.22 (t,  $J = 7.02$  Hz, 9 H,  $\text{CH}_2\text{CH}_3$ ), 2.30 (s, 3 H,  $\text{CH}_3$ ), 2.61 (s, 6 H,  $\text{NCH}_3$ ), 2.74-2.80 (c, 2 H,  $\text{CH}_2$ ), 3.82 (q,  $J = 7.02$  Hz, 6 H,  $\text{OCH}_2$ ), 7.0-7.3 (m, 4 H, ArH);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 67.5 MHz)  $\delta$  12.85, 18.26, 19.48, 26.22, 46.96, 58.33, 125.71, 127.51, 128.27, 128.95, 139.59, 141.76, 166.00; MS (% relative intensity) 352 ( $\text{M}^+$ , 13), 163 ( $[\text{Si}(\text{OEt})_3]^+$ , 100). HRMS: Calcd for  $\text{C}_{18}\text{H}_{32}\text{N}_2\text{O}_3\text{Si}$ : 352.2182. Found: 352.2198. **4** (*syn* isomer):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  0.92-0.99 (c, 2 H,  $\text{SiCH}_2$ ), 1.23 (t,  $J = 7.02$  Hz, 9 H,  $\text{CH}_2\text{CH}_3$ ), 2.20 (s, 3 H,  $\text{CH}_3$ ), 2.35 (s, 6 H,  $\text{NCH}_3$ ), 2.74-2.80 (c, 2 H,  $\text{CH}_2$ ), 3.84 (q,  $J = 7.02$  Hz, 6 H,  $\text{OCH}_2$ ), 7.0-7.3 (m, 4 H, ArH);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 67.5 MHz)  $\delta$  11.45, 18.26, 26.02, 26.22, 46.96, 58.37, 125.50, 126.09, 127.94, 128.14, 138.74, 140.07, 163.09. **5**:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  1.22 (t,  $J = 7.02$  Hz, 9 H,  $\text{CH}_2\text{CH}_3$ ), 2.19 (s, 3 H,  $\text{CH}_3$ ), 2.35 (s, 6 H,  $\text{NCH}_3$ ), 3.84 (q,  $J = 7.02$  Hz,  $\text{OCH}_2$ ), 6.10 (d,  $J = 17.8$  Hz, 1 H,  $\text{SiCH} =$ ), 7.0-7.4 (m, 4 H, ArH), 7.40 (d,  $J = 1$  H,  $\text{CH} =$ ). **6** (*anti* isomer):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  0.84-1.08 (c, 4 H,  $\text{SiCH}_2$ ), 1.22 (t,  $J = 7.02$  Hz, 18 H,  $\text{CH}_2\text{CH}_3$ ), 2.26 (s, 3 H,  $\text{CH}_3$ ), 2.60 (s, 6 H,  $\text{NCH}_3$ ), 2.57-2.63 (c, 4 H,  $\text{CH}_2$ ), 3.81 (q,  $J = 7.02$  Hz, 12 H,  $\text{OCH}_2$ ), 7.0-7.3 (m, 3 H, ArH);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 67.5 MHz)  $\delta$  12.67, 18.28, 19.97, 25.99, 46.90, 58.33, 125.32, 125.82, 139.48, 141.29, 166.65; MS (% relative intensity) 542 ( $\text{M}^+$ , 20), 163 ( $[\text{Si}(\text{OEt})_3]^+$ , 100). Anal Calcd for  $\text{C}_{26}\text{H}_{50}\text{N}_2\text{O}_6\text{Si}_2$ : C, 57.53; H, 9.28; N, 5.16. Found: C, 57.48; H, 9.07; N, 5.25. **6** (*syn* isomer):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  0.84-1.08 (c, 4 H,  $\text{SiCH}_2$ ), 1.24 (t,  $J = 7.02$  Hz, 18 H,  $\text{CH}_2\text{CH}_3$ ), 2.17 (s, 3 H,  $\text{CH}_3$ ), 2.35 (s, 6 H,  $\text{NCH}_3$ ), 2.57-2.63 (c, 4 H,  $\text{CH}_2$ ), 3.84 (q,  $J = 7.02$  Hz, 12 H,  $\text{OCH}_2$ ), 7.0-7.3 (m, 3 H, ArH);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 67.5 MHz)  $\delta$  11.70, 18.28, 25.86, 26.04, 46.60, 58.40, 128.00, 128.10, 137.65, 138.19, 161.81. **10** (*anti* isomer):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  0.88-1.04 (c, 2 H,  $\text{SiCH}_2$ ), 1.23 (t,  $J = 7.02$  Hz, 9 H,  $\text{CH}_2\text{CH}_3$ ), 1.35 (quintet,  $J = 5.67$  Hz, 2 H,  $\text{CH}_2$ ), 1.73 (quintet,  $J = 5.67$  Hz, 4 H,  $\text{NCH}_2\text{CH}_2$ ), 2.30 (s, 3 H,  $\text{CH}_3$ ), 2.64-2.80 (c, 2 H,  $\text{ArCH}_2$ ), 2.80 (t,  $J = 5.67$  Hz, 4 H,  $\text{NCH}_2$ ), 3.82 (q,  $J = 7.02$  Hz, 6 H,  $\text{OCH}_2$ ), 7.0-7.3 (m, 4 H, ArH);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 67.5 MHz)  $\delta$  12.89, 18.26, 19.61, 25.25, 25.39, 26.06, 55.90, 58.31, 125.68, 127.55, 128.16, 128.93, 139.69, 141.80, 165.97; MS (% relative intensity) 392 ( $\text{M}^+$ , 49), 163 ( $[\text{Si}(\text{OEt})_3]^+$ , 100). Anal Calcd for  $\text{C}_{21}\text{H}_{36}\text{N}_2\text{O}_3\text{Si}$ : C, 64.24; H, 9.24; N, 7.13. Found: C, 64.26; H, 9.46; N, 6.83. **10** (*syn* isomer):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  0.88-1.04 (c, 2 H,  $\text{SiCH}_2$ ), 1.23 (t,  $J = 7.02$  Hz, 9 H,  $\text{CH}_2\text{CH}_3$ ), 1.29 (quintet,  $J = 5.67$  Hz, 2 H,  $\text{CH}_2$ ), 1.48 (quintet,  $J = 5.67$  Hz, 4 H,  $\text{NCH}_2\text{CH}_2$ ), 2.21 (s, 3 H,  $\text{CH}_3$ ), 2.59 (t,  $J = 5.67$  Hz, 4 H,  $\text{NCH}_2$ ), 2.64-2.80 (c, 2 H,  $\text{ArCH}_2$ ), 3.83 (q,  $J = 7.02$  Hz, 6 H,  $\text{OCH}_2$ ), 7.0-7.3 (m, 4 H, ArH);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 67.5 MHz)  $\delta$  12.89, 18.26, 23.78, 23.90, 26.06, 26.17, 55.71, 58.31, 125.21, 126.13, 127.64, 127.91, 138.72, 140.36, 163.68. **11** (*anti* isomer):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  0.80-1.11 (c, 4 H,  $\text{SiCH}_2$ ), 1.22 (t,  $J = 7.02$  Hz, 18 H,  $\text{CH}_3$ ), 1.48 (quint,  $J = 5.67$  Hz, 2 H,  $\text{CH}_2$ ), 1.72 (quint,  $J = 5.67$  Hz, 4 H,  $\text{NCH}_2\text{CH}_2$ ), 2.27 (s, 3 H,  $\text{CH}_3$ ), 2.57-2.63 (c, 4 H,  $\text{ArCH}_2$ ), 2.80 (t,  $J = 5.67$  Hz, 4 H,  $\text{NCH}_2$ ), 3.82 (q,  $J = 7.02$  Hz, 12 H,  $\text{OCH}_2$ ), 7.0-7.3 (m, 3 H, ArH);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 67.5 MHz)  $\delta$  13.19, 18.74, 20.52, 24.40, 25.88, 26.42, 56.28, 58.78, 126.27, 128.50, 138.74, 141.82, 167.12; MS (% relative intensity) 582 ( $\text{M}^+$ , 100), 163 ( $[\text{Si}(\text{OEt})_3]^+$ , 41). Anal Calcd for  $\text{C}_{29}\text{H}_{54}\text{N}_2\text{O}_6\text{Si}_2$ : C, 59.75; H, 9.34; N, 4.81. Found: C, 59.92; H, 9.42; N, 4.90. **11** (*syn* isomer):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  0.80-1.11 (c, 4 H,  $\text{SiCH}_2$ ), 1.23 (quintet,  $J = 5.67$  Hz, 2 H,  $\text{CH}_2$ ), 1.24 (t,  $J = 7.02$  Hz, 18 H,  $\text{CH}_3$ ), 1.35 (quintet,  $J = 5.67$  Hz, 4 H,  $\text{NCH}_2\text{CH}_2$ ), 2.17 (s, 3 H,  $\text{CH}_3$ ), 2.57-2.63 (c, 4 H,  $\text{ArCH}_2$ ), 2.66 (t,  $J = 5.67$  Hz, 4 H,  $\text{NCH}_2$ ), 3.84 (q,  $J = 7.02$  Hz, 12 H,  $\text{OCH}_2$ ), 7.0-7.3 (m, 3 H, ArH);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 67.5 MHz)  $\delta$  13.19, 18.74, 24.28, 25.77, 26.42, 55.76, 58.85, 125.61, 128.12, 138.20, 140.00, 167.12. **12**:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  1.25 (t,  $J = 7.56$  Hz, 6 H,  $\text{CH}_2\text{CH}_3$ ), 2.15 (s, 3 H,  $\text{CH}_3$ ), 2.60 (s, 6 H,  $\text{NCH}_3$ ), 2.69 (q,  $J = 7.56$  Hz, 4 H,  $\text{CH}_2$ ), 7.0-7.3 (m, 3 H, ArH); MS (% relative intensity) 190 ( $\text{M}^+$ , 14), 148 ( $(\text{M}-\text{NMe}_2)^+$ , 48). **13** (*anti* isomer):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  1.25 (t,  $J = 7.56$  Hz, 6 H,  $\text{CH}_2\text{CH}_3$ ), 2.25 (s, 3 H,  $\text{CH}_3$ ), 2.52 (q,  $J = 7.56$  Hz, 4 H,  $\text{CH}_2$ ), 2.60 (s, 6 H,  $\text{NCH}_3$ ), 7.0-7.3 (m, 3 H, ArH). **13** (*syn* isomer):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  1.22 (t,  $J = 7.56$  Hz, 6 H,  $\text{CH}_2\text{CH}_3$ ), 2.15 (s, 3 H,  $\text{CH}_3$ ), 2.35 (s, 6 H,  $\text{NCH}_3$ ), 2.55 (q,  $J = 7.56$  Hz, 4 H,  $\text{CH}_2$ ), 7.0-7.3 (m, 3 H, ArH). MS (% relative intensity) 218 ( $\text{M}^+$ , 26), 174 ( $[\text{M}-\text{NMe}_2]^+$ , 15). **14** (*anti* isomer):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  2.23 (s, 3 H,  $\text{CH}_3$ ), 2.30 (s, 3 H,  $\text{ArCH}_3$ ), 2.59 (s, 6 H,  $\text{NCH}_3$ ), 2.88-2.96 (c, 4 H,  $\text{CH}_2$ ), 7.0-7.3 (m, 8 H, ArH).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 67.5 MHz) (*anti* and *syn* isomers):  $\delta$  19.14, 19.23, 19.43, 26.31, 33.55, 33.98, 34.34, 35.31, 46.97, 125.80, 125.89, 125.97, 126.02, 126.33, 127.64, 127.85, 128.16, 128.55, 128.79, 129.00, 129.83, 130.06, 130.12, 135.78, 137.54, 138.89, 139.16, 139.93, 139.98, 162.26, 165.62; MS (% relative intensity) 280 ( $\text{M}^+$ , 2), 221 ( $[\text{M}-\text{NMe}_2]^+$ , 11). Anal Calcd for  $\text{C}_{19}\text{H}_{24}\text{N}_2$ : C, 81.38; H, 8.63; N, 9.99. Found: C, 81.29; H, 8.59; N, 9.94. **14** (*syn* isomer):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  2.14 (s, 3 H,  $\text{CH}_3$ ), 2.32 (s, 3 H,  $\text{ArCH}_3$ ), 2.35 (s, 6 H,  $\text{NCH}_3$ ), 2.88-2.96 (c, 4 H,  $\text{CH}_2$ ), 7.0-7.3 (m, 8 H, ArH). **16**:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  0.94-1.00 (c, 2 H,  $\text{SiCH}_2$ ), 1.23 (t,  $J = 7.02$  Hz, 9 H,  $\text{CH}_3$ ), 2.39 (s, 3 H,  $\text{ArCH}_3$ ), 2.81-2.88 (c, 2 H,  $\text{CH}_2$ ), 2.95 (s, 6 H,  $\text{NCH}_3$ ), 3.83 (q,  $J = 7.02$  Hz, 6 H,  $\text{OCH}_2$ ), 7.06 (m, 3 H, ArH), 7.46 (s, 1 H,  $\text{CH} = \text{N}$ );  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 67.5 MHz)  $\delta$  12.65, 18.31, 21.19, 26.99, 42.88, 58.33, 126.79, 127.21, 128.36, 132.88, 133.05, 136.62, 143.29; MS (% relative intensity) 352 ( $\text{M}^+$ , 9), 163 ( $[\text{Si}(\text{OEt})_3]^+$ , 100). Anal Calcd for  $\text{C}_{18}\text{H}_{32}\text{N}_2\text{O}_3\text{Si}$ : C, 61.32; H, 9.15; N, 7.94. Found: C, 61.43; H, 9.15; N, 7.72. **17**:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  1.10 (t,  $J = 7.02$  Hz, 9 H,  $\text{CH}_3$ ), 2.38 (s, 3 H,  $\text{ArCH}_3$ ), 2.97 (s, 6 H,  $\text{NCH}_3$ ), 3.88 (q,  $J = 7.02$  Hz, 6 H,  $\text{CH}_2$ ), 6.03 (d,  $J = 18.9$  Hz,  $\text{SiCH} =$ ), 7.0-7.3 (m, 3 H, ArH), 7.43 (s, 1 H,  $\text{CH} = \text{N}$ ), 7.66 (d,  $J = 18.9$  Hz,  $\text{CH} =$ ). HRMS Calcd for  $\text{C}_{18}\text{H}_{30}\text{N}_2\text{O}_3\text{Si}$ : 350.2026. Found: 350.2030.

**19:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  0.93-1.00 (c, 2 H,  $\text{SiCH}_2$ ), 1.23 (t,  $J = 7.02$  Hz, 9 H,  $\text{CH}_3$ ), 1.55 (quintet,  $J = 5.67$  Hz, 2 H,  $\text{CH}_2$ ), 1.76 (quintet,  $J = 5.67$  Hz, 4 H,  $\text{NCH}_2\text{CH}_2$ ), 2.39 (s, 3 H,  $\text{ArCH}_3$ ), 2.80-2.87 (c, 2 H,  $\text{ArCH}_2$ ), 3.15 (t,  $J = 5.67$  Hz, 4 H,  $\text{NCH}_2$ ), 3.82 (q,  $J = 7.02$  Hz, 6 H,  $\text{OCH}_2$ ), 7.0-7.3 (m, 3 H,  $\text{ArH}$ ), 7.78 (s, 1 H,  $\text{CH} = \text{N}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz)  $\delta$  12.71, 18.28, 21.13, 24.23, 25.09, 26.92, 52.24, 58.29, 126.76, 127.40, 128.32, 133.05, 134.90, 136.71, 143.41; MS (% relative intensity) 392 ( $\text{M}^+$ , 9), 163 ( $[\text{Si}(\text{OEt})_3]^+$ , 100). HRMS Calcd for  $\text{C}_{21}\text{H}_{36}\text{N}_2\text{O}_3\text{Si}$ : 392.2495. Found: 392.2483.

**22:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  0.95-1.02 (c, 2 H,  $\text{SiCH}_2$ ), 1.06 (d,  $J = 6.48$  Hz, 6 H,  $\text{CHCH}_3$ ), 1.23 (t,  $J = 7.02$  Hz, 9 H,  $\text{CH}_3$ ), 1.5-1.6 (m, 3 H,  $\text{CH}_2$ ), 1.7-1.8 (m, 3 H,  $\text{CH}_2$ ), 2.47 (s, 3 H,  $\text{ArCH}_3$ ), 2.89-2.96 (c, 2 H,  $\text{ArCH}_2$ ), 3.0-3.1 (m, 2 H,  $\text{CH}$ ),

3.87 (q,  $J = 7.02$  Hz, 6 H,  $\text{OCH}_2$ ), 7.0-7.3 (m, 3 H,  $\text{ArH}$ ), 8.43 (s, 1 H,  $\text{CH} = \text{N}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz)  $\delta$  12.72, 18.31, 20.88, 21.57, 21.76, 27.05, 32.83, 57.14, 58.33, 126.92, 128.55, 128.61, 131.52, 137.68, 144.38, 153.57; MS (% relative intensity) 420 ( $\text{M}^+$ , 8), 163 ( $[\text{Si}(\text{OEt})_3]^+$ , 100). HRMS Calcd for  $\text{C}_{23}\text{H}_{40}\text{N}_2\text{O}_3\text{Si}$ : 420.2808. Found: 420.2807.

- (17) Thermal *syn-anti* isomerization in the hydrazone appeared to occur during the reaction.
- (18) We previously mentioned the possibility of cleavage of the second C-H bond without dissociation of the 1:1 addition product from the metal center. See, ref. 2a.

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