Supporting Information

Reactivity of a NHC-Stabilized Silylene towards Ketones. Formation of Silicon Bis-enolates vs. Bis-silylation of C=O Bond

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$^1$H NMR and $^{13}$C NMR Spectra of Products 2a-o and 3

Figure 1. $^1$H NMR spectra of 2a.

Figure 2. $^{13}$C NMR spectra of 2a.
Figure 3. $^1$H NMR spectra of 2b.

Figure 4. $^{13}$C NMR spectra of 2b.
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Figure 6. $^{13}$C NMR spectra of 2c.
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Figure 12. $^{13}$C NMR spectra of 2f.
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Figure 14. $^{13}$C NMR spectra of 2g.
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Figure 16. $^{13}$C NMR spectra of 2h.
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Figure 20. $^{13}$C NMR spectra of 2j.
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Figure 30. $^{13}$C NMR spectra of 2o.
Figure 31. $^1$H NMR spectra of 3.

Figure 32. $^{13}$C NMR spectra of 3.
NOESY Spectra of Selected Products 2h-n (Ar = 2,6-iPr$_2$C$_6$H$_3$):

Figure 33. NOESY spectrum of compound 2h. The hydrogen atom of the tertiary butyl ($\delta = 1.08$ ppm) couple strongly only with the hydrogen atom of CH= ($\delta = 5.64$ ppm) and do not couple with the hydrogen atom of phenyl, indicating that the tertiary butyl and the hydrogen atom of CH= on the same side of the C=C double bond. The configuration of product 2h is cis isomer.
Figure 34. NOESY spectrum of compound 2i. The hydrogen atom of the ethyl ($\delta = 0.87, 2.09$ ppm) couple strongly only with the hydrogen atom of $CH= (\delta = 5.40$ ppm) and do not couple with the hydrogen atom of phenyl, indicating that the ethyl and the hydrogen atom of $CH=$ on the same side of the $C=C$ double bond. The configuration of product 2i is cis isomer.
Figure 35. NOESY spectrum of compound 2j. The hydrogen atom of the phenyl (δ = 7.63 ppm, PhOC=) couple strongly with the hydrogen atom of CH= (δ = 5.79 ppm), indicating that the phenyl (PhOC=) and the hydrogen atom of CH= on the same side of the C=C double bond. The configuration of product 2j is cis isomer.
Figure 36. NOESY spectrum of compound 2k. The hydrogen atom of the benzyl ($\delta = 3.36$ ppm, PhCH$_2$) couple strongly with the hydrogen atom of CH= ($\delta = 5.36$ ppm), indicating that the benzyl(PhCH$_2$) and the hydrogen atom of CH= on the same side of the C=C double bond. The configuration of product 2k is cis isomer.
Figure 37. NOESY spectrum of compound 2l. The hydrogen atom of the phenyl ($\delta = 7.25$ ppm) couple strongly only with the hydrogen atom of $=CH$ ($\delta = 4.97$ ppm) and do not couple with the hydrogen atom of $=CCH_3$ ($\delta = 1.53$ ppm), indicating that the hydrogen atom of $=CH$ and the phenyl group on the same side of the C=C double bond. The configuration of product 2l is cis isomer.
Figure 38. NOESY spectrum of compound 2m. The hydrogen atom of the phenyl ($\delta = 7.31$ ppm) couple strongly only with the hydrogen atom of $\equiv CH$ ($\delta = 5.01$ ppm) and do not couple with the hydrogen atom of the propyl, indicating that the hydrogen atom of $\equiv CH$ and the phenyl group on the same side of the C=C double bond. The configuration of product 2m is cis isomer.
Figure 39. NOESY spectrum of compound 2n. The hydrogen atom of the phenyl ($\delta = 7.01$ ppm) couple strongly only with the hydrogen atom of $CH= (\delta = 5.15$ ppm) and do not couple with the hydrogen atom of $CH_2CO_2CH_3 (\delta = 3.12, 3.32$ ppm), indicating that the hydrogen atom of $CH= (\delta = 5.15$ ppm) and the phenyl group on the same side of the C=C double bond. The configuration of product 2n is cis isomer.