# Carbonylative [5 + 1] Cycloaddition of Cyclopropyl Imines Catalyzed by Ruthenium Carbonyl Complex

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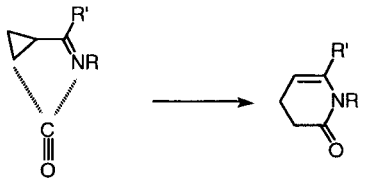
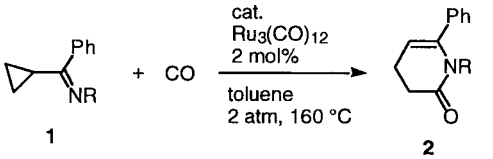
Transition-metal-catalyzed cycloaddition reactions which use carbon monoxide as a one-carbon unit represent one of the attractive methods for the preparation of cyclic carbonyl compounds.[1−4] Of the carbonylative cycloaddition reactions, a [2 + 2 + 1] cycloaddition reaction, which leads to the construction of five-membered carbonyl compounds, is the most popular. We recently reported the first use of a ruthenium complex[4] in the catalytic Pauson−Khand-type reaction,[3] which can be used for the [2 + 2 + 1] cycloaddition of alkynes, alkenes, and carbon monoxide leading to the formation of α,β-unsaturated cyclopentenones. A [2 + 2 + 1] cycloaddition of alkynes (or alkenes), aldehydes (or ketones), and carbon monoxide leading to γ-butyrolactone derivatives was achieved by the use of a ruthenium complex[5−8] or titanium complex.[9] We also reported the Ru-catalyzed [4 + 1] cycloaddition of α,β-unsaturated imines with carbon monoxide, which gives γ-butyrolactams.[10] It is also noteworthy that there

**Scheme 1**




are rare examples of catalytic carbonylative cycloadditions to give six-membered carbonyl compounds.[11] A [5 + 1] mode, which involves the ring-opening of cyclopropane, would be of great potential for the construction of six-membered carbonyl compounds. Wender extensively studied catalytic cycloaddition reactions which involve the opening of a cyclopropane ring.[12] We expected that cyclopropyl imines might function as a five-assembling unit on their ring-opening. We report herein the $Ru_3(CO)_{12}$-catalyzed carbonylative [5 + 1] mode of cycloaddition of cyclopropyl imines leading to six-membered unsaturated lactams (Scheme 1).

The reaction of the cyclopropyl imine **1a** (anti/syn = 3.3/1, 1 mmol), which was derived from cyclopropyl phenyl ketone and *tert*-butylamine, with CO (initial pressure 2 atm at 25 °C) in toluene (3 mL) in the presence of a catalytic amount of $Ru_3(CO)_{12}$ (0.02 mmol) at 160 °C for 20 h gave 3,4-dihydro-1-(1,1-dimethylethyl)-6-phenyl-2(1*H*)-pyridinone (**2a**)[13] in 57% isolated yield after silica gel column chromatography (eq 1). No other carbonylation products could be detected. Prolongation of the reaction time (60 h) resulted in complete consumption of **1a**, and the yield increased to 76%. When the reaction was carried out at 140 or 180 °C, only traces of **2a** were formed in both cases. A higher pressure (10 atm) at 160 °C also gave only trace amounts of **2a**. Of the solvents examined (dioxane 26% yield, $CH_3CN$ 0%, cyclohexane 30%), toluene (57%) was the solvent of choice when the reaction was run at 160 °C under 2 atm of CO for 20 h. Changing the substituent on the imine nitrogen to $PhCH_2$, *p*-$MeOC_6H_4$, or OMe resulted in no detectable corresponding product formation. However, the use of a cyclohexyl group as the N-substituent, such as in **1b**, gave a comparable yield (61%) of the corresponding γ-lactam **2b**. The N-substituent of choice is dependent on the structure of substrates used (vide infra).




(1)

| | | | |
|---|---|---|---|
| **a**: R = $Bu^t$ | 20 h | 57% |
| | 60 h | 76% |
| **b**: R = Cy | 20 h | 61% |
| | 60 h | 65% |
| **c**: R = Bu | 20 h | 10% |
| **d**: R = $PhCH_2$ | 20 h | trace |
| **e**: R = *p*-$MeOC_6H_4$ | 20 h | trace |
| **f**: R = OMe | 20 h | no reaction |

No reaction was observed when other transition metal complexes, such as Cp*RuCl(cod), $Ru(CO)_2(PPh_3)_3$, $RuH_2$-

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(2) For recent papers on carbonylative cycloaddition reactions see the following. [2 + 2 + 1]: Suzuki, N.; Kondo, T.; Mitsudo, T. *Organometallics* **1998**, *17*, 766. [4 + 1]: Murakami, M.; Itami, K.; Ito, Y. *J. Am. Chem. Soc.* **1999**, *121*, 4130. [4 + 4 + 1]: Murakami, M.; Itami, K.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3418.

(3) For a recent review on the Pauson−Khand type reaction, see: Chung, Y. K. *Coord. Chem. Rev.* **1999**, *188*, 297. For recent papers on the catalytic Pauson−Khand type reaction, see: Koga, Y.; Kobayashi, T.; Narasaka, K. *Chem. Lett.* **1998**, 249. Jeong, N.; Lee, S.; Sung, B. K. *Organometallics* **1998**, *17*, 3642. Belanger, D. B.; Livinghouse, T. *Tetrahedron Lett.* **1998**, *39*, 7641. Sugihara, T.; Yamaguchi, M. *J. Am. Chem. Soc.* **1998**, *120*, 10782. Kraft, M. E.; Hirosawa, C.; Bonaga, L. V. R. *Tetrahedron Lett.* **1999**, *40*, 9177. Hicks, F. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 7026. Hiroi, K.; Watanabe, T.; Kawagishi, R.; Abe, I. *Tetrahedron Lett.* **2000**, *41*, 891. Kim, S.-W.; Son, S. U.; Lee, S. I.; Hyeon, T.; Chung, Y. K. *J. Am. Chem. Soc.* **2000**, *122*, 1550.

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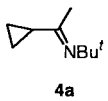
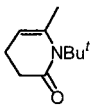
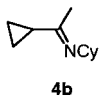
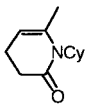
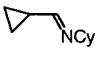
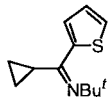
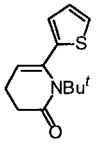
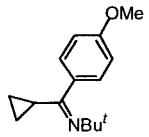
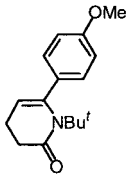
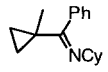
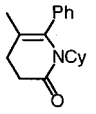
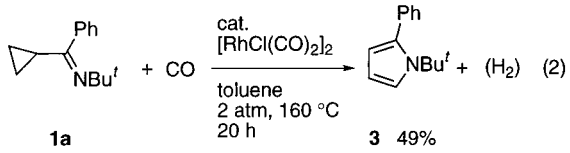
**Table 1. $Ru_3(CO)_{12}$-Catalyzed Reaction of Cyclopropyl Imines with CO[a]**

| entry | cyclopropyl imine | time/h | product |
|---|---|---|---|
| 1 |  **4a** | 40 |  **5a** 34% |
| 2 |  **4b** | 20 |  **5b** 71% |
| 3 |  **6** | 40 |  **7** 64% |
| 4[b] |  **8** | 20 |  **9** 27% |
| 5 |  **10** | 40 |  **11** 64% |
| 6 |  **12** | 40 |  **13** 56% |

[a] Reaction conditions: imine (1 mmol), CO (2 atm at 25 °C), $Ru_3(CO)_{12}$ (0.05 mmol) in toluene (3 mL) at 160 °C. [b] $Ru_3(CO)_{12}$ (0.02 mmol).

$(CO)(PPh_3)_3$, $Ru(acac)_3$, $[RuCl_2(CO)_3]_2$, $Co_2(CO)_8$, $IrCl(CO)(PPh_3)_2$, and $[IrCl(CO)_3]_n$, were used as catalysts. When the reaction was run in the presence of $[RhCl(CO)_2]_2$ as the catalyst, no carbonylation products were obtained, but instead, the pyrrole derivative **3** was formed in 49% yield (eq 2). Product **3** was formed by the dehydrogenation of dihydropyrrole, which would be formed by an aza-version of the vinylcyclopropane rearrangement.

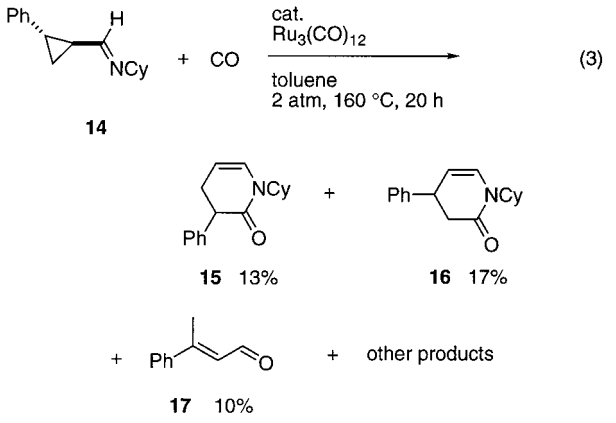
The results of the reaction of some cyclopropyl imines[15] with CO are shown in Table 1. The reaction of imine **4a**,




**1a** **3** 49% (2)

derived from cyclopropyl methyl ketone and *tert*-butylamine, under the same reaction conditions as in eq 1 for 20 h gave the corresponding lactam **5a** in 25% yield. The use of additional catalyst (0.05 mmol) and a longer reaction time (40 h) led to a slight increase in the yield of **5a** to a 34% yield (entry 1). The replacement of the *tert*-butyl group in **4a** with a cyclohexyl group as the N-protecting group, as in **4b**, gave **5b** in 71% yield (entry 2). Cyclopropyl aldimine **6** was also used in this present cyclocarbonylation reaction (entry 3). The reaction of **8** gave **9** in 27% yield, along with 61% of the starting **8** which was recovered as the corresponding ketone after column chromatography on silica gel (entry 4). Use of additional catalyst (0.05 mmol) and a prolonged reaction time (40 h) did not result in an increased yield of **9**, although **8** was completely consumed. In the case of substrates **8** and **10** (entries 4 and 5), the replacement of the *tert*-butyl group by a cyclohexyl group had no effect on the product yields (not shown). The introduction of a methyl group at the 1-position (α to the imine carbonyl carbon) of the cyclopropane ring, as in **12**, resulted in the formation of the corresponding lactam **13** in good yield (entry 6).

In contrast to **12**, cyclopropyl phenyl ketimines which contain a methyl or phenyl group at the 2-position on the cyclopropane ring could not be used in the present reaction. In these cases, complex mixtures were obtained and it was not possible to isolate the corresponding lactams in a pure form. In the case of the reaction of aldimine **14**, a mixture of the expected lactams **15** and **16** was obtained in a total yield of 30% and the aldehyde **17** in 10%, along with 23% of the imine being recovered as *trans*-2-phenylcyclopropancarboxaldehyde (eq 3). We propose that aldehyde **17** is formed from the same key intermediate, leading to **16**. The course of the reaction in which aldehyde **17** is formed will be discussed below.




**14** (3)

**15** 13% **16** 17%

**17** 10%

A proposed mechanism for the reaction is shown in Scheme 2. The coordination of a nitrogen to ruthenium facilitates the conversion to metallacycle **A** via an oxidative cyclization of the cyclopropyl imine.[16] The insertion

(11) [5 + 1]: Murakami, M.; Itami, K.; Ubukata, M.; Tsuji, I.; Ito, Y. *J. Org. Chem.* **1998**, *63*, 4. For a paper on $Fe(CO)_5$-mediated [5 + 1] cycloaddition of vinylcyclopropane and CO, see: Sarel, S.; Felzenstein, A.; Victor, R.; Yovell, J. *J. Chem. Soc., Chem. Commun.* **1974**, 1025.

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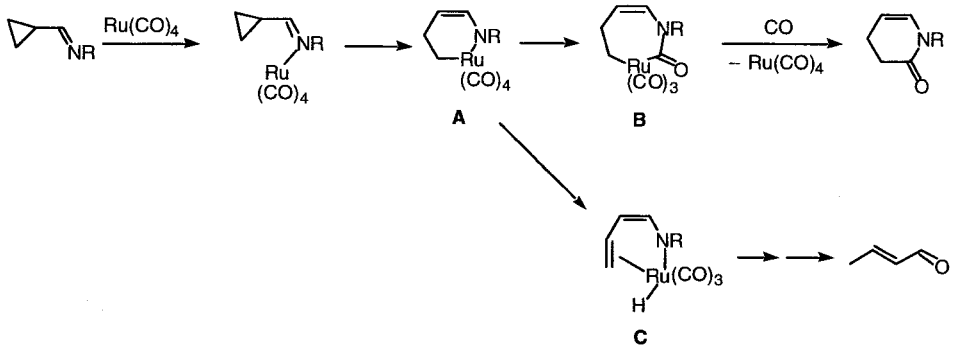
(13) All new compounds were characterized by NMR, IR, mass spectral data and by elemental analyses or high-resolution mass spectra. See Supporting Information.

(14) Ben-Shoshan, R.; Sarel, S. *Chem. Commun.* **1996**, 883.

(15) Ketimines were used as a syn and anti mixture.

**Scheme 2**




of CO in **A** gives the acyl complex **B**,[17] which undergoes a reductive elimination to give the lactam. Compared with the carbonylative [4 + 1] cycloaddition of α,β-unsaturated imines which leads to the formation of unsaturated γ-butyrolactams reported previously,[10] the efficiency of the present reaction is relatively low. The reason for this may be the formation of aldehydes as byproducts. The latter are probably formed via a β-hydride elimination from **A**. The presence of a substituent at the 2-position on the cyclopropane ring facilitates the β-hydride elimination from **A** because the resulting alkene complex **C** is more stable than that derived from the nonsubstituted substrate. In contrast, there is no β-hydrogen available for elimination in a similar metallacycle complex derived from α,β-unsaturated imines. When a rhodium complex is used as the catalyst, the pyrrole **3** is formed (eq 2) by reductive elimination from the Rh complex corresponding to **A**, followed by dehydrogenation and subsequent aromatization.

In summary, we have demonstrated a new Ru-catalyzed [5 + 1] cycloaddition of cyclopropyl imines with carbon monoxide leading to γ,δ-unsaturated six-membered lactam derivatives. Catalytic carbonylative cyclocoupling holds considerable promise for the preparation of cyclic carbonyl compounds.

## Experimental Section

**Materials.** Toluene, dioxane, $CH_3CN$, and cyclohexane were distilled from $CaH_2$. $Ru_3(CO)_{12}$ and $[RhCl(CO)_2]_2$ were purchased from Aldrich Chemical Co. and used after recrystallization from hexane. Ketimines **1**, **4**, **8**, **10**, and **12** were prepared by the treatment of the corresponding ketones with amines in the presence of $TiCl_4$.[18] Aldimines **6** and **13** were prepared by the treatment of the corresponding aldehydes with amines in the presence of $MgSO_4$.[19]

**Typical Procedure.** A 50-mL stainless autoclave was charged with cyclopropyl phenyl *N*-(1,1-dimethylethyl) ketimine (**1a**) (1 mmol, 201 mg), toluene (3 mL), and $Ru_3(CO)_{12}$ (0.02 mmol, 13 mg). The system was flushed with 10 atm of CO three times, after which it was pressurized to 2 atm and immersed in an oil bath at 160 °C. After 60 h had elapsed, the autoclave was removed from the oil bath and cooled for 1 h, followed by release of the CO. The contents were transferred to a round-bottomed flask with ether and the volatiles removed in vacuo. The residue was subjected to column chromatography on silica gel (eluent, hexane/$Et_2O$ = 3/1) to give 3,4-dihydro-1-(1,1-dimethylethyl)-6-phenyl-2(1*H*)-pyridinone (**2a**) (175 mg, 76% yield) as a white solid.

**3,4-Dihydro-1-(1,1-dimethylethyl)-6-phenyl-2(1*H*)-pyridinone (2a).** White solid; mp 78−80 °C (hexane); $R_f$ 0.14 (hexane/ether = 3/1); $^1$H NMR ($CDCl_3$) δ 1.35 (s, 9H), 2.17−2.24 (m, 2H), 2.44−2.49 (m, 2H), 5.69 (t, $J$ = 5.7 Hz, 1H), 7.25−7.35 (m, 5H); $^{13}$C NMR ($CDCl_3$) δ 19.8, 30.3, 37.3, 59.9, 119.1, 125.6, 127.2, 128.2, 141.3, 145.3, 176.2; IR (KBr) 1688 s, 1598 m; MS *m*/*z* (relative intensity, %) 229 ($M^+$, 7), 173 (100); exact mass calcd for $C_{15}H_{19}NO$ 229.1467, found 229.1473.

**1-Cyclohexyl-3,4-dihydro-6-phenyl-2(1*H*)-pyridinone (2b).** White solid; mp 106−108 °C (hexane); $R_f$ 0.16 (hexane/ether = 3/1); $^1$H NMR ($CDCl_3$) δ 0.84−1.67 (m, 8H), 2.23−2.38 (m, 4H), 2.47−2.53 (m, 2H), 3.09 (tt, $J$ = 3.2 Hz, $J$ = 12.2 Hz, 1H), 5.34 (t, $J$ = 4.9 Hz, 1H), 7.27−7.37 (m, 5H); $^{13}$C NMR ($CDCl_3$) δ 19.9, 25.2, 26.5, 29.9, 34.2, 59.7, 111.5, 127.1, 127.9, 128.2, 137.5, 144.4, 172.3; IR (KBr) 1674 s; MS *m*/*z* (relative intensity, %) 255 ($M^+$, 20), 173 (100); exact mass calcd for $C_{17}H_{21}NO$ 255.1623, found 255.1625.

**1-Butyl-3,4-Dihydro-6-phenyl-2(1*H*)-pyridinone (2c).** White solid; mp 64−65 °C (hexane); $R_f$ 0.09 (hexane/ether = 3/1); $^1$H NMR ($CDCl_3$) δ 0.74 (t, $J$ = 7.3 Hz, 3H), 1.04−1.18 (m, 2H), 1.26−1.36 (m, 2H), 2.30−2.37 (m, 2H), 2.54−2.59 (m, 2H), 3.54 (t, $J$ = 7.3 Hz, 2H), 5.36 (t, $J$ = 4.9 Hz, 1H), 7.24−7.38 (m, 5H); $^{13}$C NMR ($CDCl_3$) δ 13.7, 19.7, 19.9, 30.7, 32.3, 42.3, 110.4, 127.6, 128.0, 128.1, 136.1, 142.8, 171.4; IR (KBr) 1662 s; MS *m*/*z* (relative intensity, %) 229 ($M^+$, 47), 158 (100); exact mass calcd for $C_{15}H_{19}NO$ 229.1467, found 229.1463.

**1-(1,1-Dimethylethyl)-2-phenyl-(1*H*)-pyrrole (3).** White solid; mp 57−59 °C (hexane); $R_f$ 0.67 (hexane/ether = 3/1); $^1$H NMR ($CDCl_3$) δ 1.43 (s, 9H), 6.01 (dd, $J$ = 3.2 Hz, $J$ = 1.9 Hz, 1H), 6.14 (dd, $J$ = 3.2 Hz, $J$ = 3.0 Hz, 1H), 6.91 (dd, $J$ = 3.0 Hz, $J$ = 1.9 Hz, 1H), 7.31−7.41 (m, 5H); $^{13}$C NMR ($CDCl_3$) δ 31.9, 57.1, 105.6, 111.7, 118.7, 127.2, 127.4, 131.7, 133.9, 137.2; IR (KBr) 1693 w, 1628 w; MS *m*/*z* (relative intensity, %) 199 ($M^+$, 11), 143 (100); exact mass calcd for $C_{14}H_{17}N$ 199.1361, found 199.1365.

**3,4-Dihydro-1-(1,1-dimethylethyl)-6-methyl-2(1*H*)-pyridinone (5a).** Colorless oil; $R_f$ 0.14 (hexane/ether = 3/1); $^1$H NMR ($CDCl_3$) δ 1.50 (s, 9H), 1.92−1.99 (m, 2H), 2.00 (d, $J$ = 1.4 Hz, 3H), 2.31 (t, $J$ = 6.8 Hz, 2H), 5.40 (dt, $J$ = 1.4 Hz, $J$ = 4.9 Hz, 1H); $^{13}$C NMR ($CDCl_3$) δ 19.4, 23.0, 30.3, 37.6, 57.4, 115.4, 139.1, 175.5; IR (neat) 1672 s; MS *m*/*z* (relative intensity, %) 167 ($M^+$, 10), 83 (100); exact mass calcd for $C_{10}H_{17}NO$ 167.1310, found 167.1311.

**1-Cyclohexyl-3,4-dihydro-6-methyl-2(1*H*)-pyridinone (5b).** Colorless oil; $R_f$ 0.06 (hexane/ether = 3/1); $^1$H NMR ($CDCl_3$) δ 1.18−1.77 (m, 8H), 1.93 (d, $J$ = 1.4 Hz, 3H), 2.04−2.07 (m, 2H), 2.27−2.44 (m, 4H), 3.56 (tt, $J$ = 3.2 Hz, $J$ = 11.9 Hz, 1H), 5.01 (dt, $J$ = 1.4 Hz, $J$ = 4.3 Hz, 1H); $^{13}$C NMR ($CDCl_3$) δ 19.3, 19.9, 25.3, 26.5, 32.3, 33.7, 56.3, 106.8, 137.1, 171.5; IR (neat) 1675 s, 1626 m; MS *m*/*z* (relative intensity, %) 193 ($M^+$, 16), 111 (100); exact mass calcd for $C_{12}H_{19}NO$ 193.1466, found 193.1470.

(16) We have developed the ruthenium carbonyl-catalyzed carbonylation reactions in which the coordination of an $sp^2$-nitrogen atom to a ruthenium is proposed to be a key step. Ie, Y.; Chatani, N.; Ogo, T.; Marshall, D. R.; Fukuyama, T.; Kakiuchi, F.; Murai, S. *J. Org. Chem*. **2000**, *65*, 1475 and references therein.

(17) We do not know whether CO insertion takes place into a Ru−C bond or Ru−N bond in complex **A**. A stoichiometric reaction of related complexes involved CO insertion into an Fe−N bond has been reported. Freiken, N.; Schreuder, P.; Siebenlist, R.; Frühauf, H.-W.; Vrieze, K.; Kooijman, H.; Veldman, N.; Spek, A. L.; Fraanje, J.; Goubitz, K. *Organometallics* **1996**, *15*, 2148.

(18) Kimpe, N. D.; Smaele, D. D.; Hofkens, A.; Dejaegher, Y.; Kesteleyn, B. *Tetrahedron* **1997**, *53*, 10803.

(19) Sulmon, P.; Kimpe, N. D.; Verhe, R.; Buyck, L. D.; Schamp, N. *Synthesis* **1986**, 192.

**1-Cyclohexyl-3,4-dihydro-2(1*H*)-pyridinone (7).** White solid; mp 46−47 °C (hexane); $R_f$ 0.11 (hexane/ether = 3/1); $^1$H NMR ($CDCl_3$) $\delta$ 0.95−1.77 (m, 10H), 2.17−2.24 (m, 2H), 2.45 (t, $J$ = 8.1 Hz, 2H), 4.36−4.46 (m, 1H), 5.10 (dt, $J$ = 4.1 Hz, $J$ = 8.1 Hz, 1H), 6.08 (dt, $J$ = 1.4 Hz, $J$ = 8.1 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ 19.8, 25.4, 25.7, 30.9, 31.8, 51.0, 105.9, 125.2, 168.5; IR (KBr) 1659 s; MS *m*/*z* (relative intensity, %) 179 ($M^+$, 23), 97 (100). Anal. Calcd for $C_{11}H_{17}NO$: C, 73.69; H, 9.56; N, 7.82. Found: C, 73.53; H, 9.54; N, 7.79.

**3,4-Dihydro-1-(1,1-dimethylethyl)-6-(2-thienyl)-2(1*H*)-pyridinone (9).** White solid; mp 91−93 °C (hexane); $R_f$ 0.19 (hexane/ether = 3/1); $^1$H NMR ($CDCl_3$) $\delta$ 1.42 (s, 9H), 2.12−2.23 (m, 2H), 2.44−2.49 (m, 2H), 5.84 (t, $J$ = 3.2 Hz, 1H), 6.92−6.99 (m, 2H), 7.16 (dd, $J$ = 4.9 Hz, $J$ = 1.4 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ 19.9, 30.2, 37.4, 60.3, 119.4, 123.5, 123.6, 126.8, 138.7, 144.1, 176.0; IR (KBr) 1672 s, 1626 s; MS *m*/*z* (relative intensity, %) 235 ($M^+$, 8), 179 (100); exact mass calcd for $C_{13}H_{17}NOS$ 235.1029, found 235.1030.

**3,4-Dihydro-1-(1,1-dimethylethyl)-6-(4-methoxyphenyl)-2(1*H*)-pyridinone (11).** White solid; mp 124−125 °C (hexane); $R_f$ 0.14 (hexane/ether = 3/1); $^1$H NMR ($CDCl_3$) $\delta$ 1.34 (s, 9H), 2.14−2.21 (m, 2H), 2.42−2.47 (m, 2H), 3.81 (s, 3H), 5.61 (t, $J$ = 5.7 Hz, 3H), 6.85 (d, $J$ = 8.6 Hz, 2H), 7.22 (d, $J$ = 8.6 Hz, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$ 19.8, 30.4, 37.5, 55.3, 59.8, 113.6, 117.7, 126.9, 133.9, 144.9, 158.8, 176.3; IR (KBr) 1673 s, 1636 m; MS *m*/*z* (relative intensity, %) 259 ($M^+$, 5), 203 (100). Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 74.08; H, 8.19; N, 5.31.

**1-Cyclohexyl-3,4-dihydro-5-methyl-6-phenyl-2(1*H*)-pyridinone (13).** White solid; mp 79−81 °C (hexane); $R_f$ 0.10 (hexane/ether = 3/1); $^1$H NMR ($CDCl_3$) $\delta$ 0.73−1.58 (m, 8H), 1.61 (s, 3H), 2.13−2.27 (m, 4H), 2.46−2.51 (m, 2H), 2.96 (tt, $J$ = 3.5 Hz, $J$ = 11.9 Hz, 1H), 7.18 (dd, $J$ = 1.9 Hz, $J$ = 7.8 Hz, 2H), 7.28−7.40 (m, 3H); $^{13}$C NMR ($CDCl_3$) $\delta$ 19.4, 25.2, 26.4, 27.0, 29.6, 33.5, 59.0, 117.1, 127.5, 128.0, 129.5, 135.9, 136.6, 171.2; IR (KBr) 1602 m; MS *m*/*z* (relative intensity, %) 269 ($M^+$, 24), 172 (100). Anal. Calcd for $C_{18}H_{23}NO$: C, 80.26; H, 8.60; N, 5.20. Found: C, 80.11; H, 8.61; N, 5.19.

**1-Cyclohexyl-3,4-dihydro-3-phenyl-2(1*H*)-pyridinone (15) and 1-Cyclohexyl-3,4-dihydro-4-phenyl-2(1*H*)-pyridinone (16).** The $^1$H and $^{13}$C NMR spectra and IR data were obtained as a 1.3:1 mixture of **15** and **16**: yellow solid; mp 75−77 °C (hexane); $R_f$ 0.19−0.23 (hexane/ether = 3/1); $^1$H NMR ($CDCl_3$) $\delta$ 1.12−1.58 (m, 10H), 2.55−2.89 (m, 2H), 3.69−3.75 (m, 1H), 4.48−4.50 (m, 1H), [5.20 (dt, $J$ = 4.3 Hz, $J$ = 7.8 Hz, **15**), 5.27 (dt, $J$ = 1.4 Hz, $J$ = 7.8 Hz, **16**), 1H], [6.20 (dt, $J$ = 1.6 Hz, $J$ = 7.8 Hz, **15**), 6.29 (dt, $J$ = 1.9 Hz, $J$ = 7.8 Hz, **16**), 1H], 7.12−7.34 (m, 5H); $^{13}$C NMR ($CDCl_3$) $\delta$ 25.5, 25.8, 28.0, 31.0, 31.1, 40.3, 47.2, 51.2, 51.8, [105.2 (**15**), 109.0 (**16**)], 125.4, 126.7, 126.9, 127.7, 128.3, 128.6, 139.7, 142.8, 167.5, 169.1; IR (KBr) 1670 s; MS *m*/*z* (relative intensity, %) [255 ($M^+$, 12), 118 (100), **15**], [255 ($M^+$, 42), 55 (100), **16**]. Anal. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 79.70; H, 8.40; N, 5.26.

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**Supporting Information Available:** Full characterization of all the new compounds obtained including $^1$H NMR spectra for all previously unknown starting materials and cycloaddition products **2**, **3**, **5**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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