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$Ru_3(CO)_{12}$-catalyzed reaction of yne–imines with carbon monoxide leading to bicyclic α,β-unsaturated lactams

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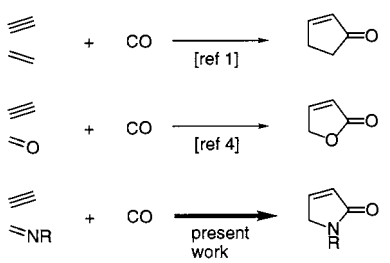
Abstract

The cyclocarbonylation of 1,6- and 1,7-yne–imines leading to bicyclic α,β-unsaturated lactams can be achieved in the presence of a catalytic amount of $Ru_3(CO)_{12}$. The reaction, a [2 + 2 + 1] cycloaddition, incorporates the acetylene π-bond, the imine π-bond, and the carbon atom of CO. The presence of substituents, such as alkyl, aryl, and silyl on the acetylenic terminal carbon is essential for yne–imines to undergo cyclocarbonylation to give bicyclic α,β-unsaturated lactams. An yne–imine having no substituents on the acetylenic terminal carbon does not give the corresponding lactam, but rather a dihydropyridine derivative without incorporating CO.

Keywords: Ruthenium carbonyl; Cyclocarbonylation; Yne–imine; Carbon monoxide; Lactam

1. Introduction

In the course of our studies on transition metal-catalyzed carbonylative cycloaddition reactions, we discovered that $Ru_3(CO)_{12}$ catalyzes the reaction of enynes with CO to give bicyclic α,β-unsaturated ketones [1]. This reaction, the so-called Pauson–Khand reaction, is a three component [2 + 2 + 1] cycloaddition reaction, which incorporates the acetylene π-bond, the olefin π-bond, and the carbon atom of CO into the five-membered ring. Although it is known that a variety of transition metal complexes are capable of catalyzing this transformation [2], our reaction [1] represents the first use of a ruthenium complex for the reaction [3]. If one of the olefinic carbons is replaced with an oxygen atom, the production of α,β-unsaturated lactones would be expected to take place (Scheme 1), and we find this to be true. We have reported that the reaction of yne–aldehydes with CO in the presence of $Ru_3(CO)_{12}$ results in an analogous cyclocarbonylation to give bicyclic α,β-unsaturated lactones [4]. The reaction is synthetically useful because a variety of yne–aldehydes can be used for the cycloaddition reaction leading to bicyclic α,β-unsaturated lactones having various ring systems as well as various substituents. We next examined the possibility of extending this reaction to the synthesis of α,β-unsaturated lactams via the replacement of oxygen with nitrogen, since the lactam skeleton is one of the most important nitrogen heterocycles in pharmaceutical agents [5]. We now wish to report the cyclocarbonylation of yne–imines in the presence of $Ru_3(CO)_{12}$ to give bicyclic α,β-unsaturated lactams.



Scheme 1.

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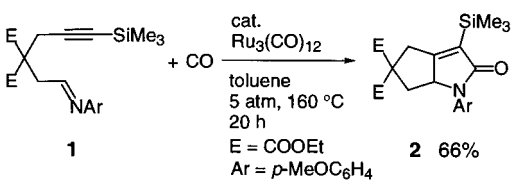
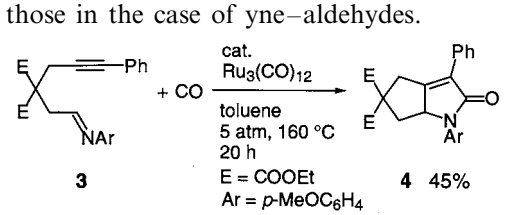
2. Results and discussion

The catalytic reaction proceeded smoothly and efficiently. Again $Ru_3(CO)_{12}$ exhibits catalytic activity for the desired carbonylation. The reaction of the yne–imine **1** (1 mmol), which was obtained by the condensation of the 5-hexynal derivative with *p*-anisidine in the presence of $MgSO_4$, and CO (5 atm) in the presence of $Ru_3(CO)_{12}$ (0.05 mmol) in toluene (5 ml) at 160°C for 20 h, gave a bicyclic α,β-unsaturated lactam **2** in 66% isolated yield (Eq. (1)). A higher CO pressure (10 atm) decreased the yield to 43%. A comparable yield (64%) was obtained when cyclohexane replaced toluene as the solvent. The use of dioxane (51%) and CH_3CN (24%) as the solvents resulted in a decreased yield of **2**. When the reaction was carried out at 140°C, the yield of **2** was decreased to 37% yield. The reaction at 180°C gave a complex mixture. It was found that a *p*-$CH_3OC_6H_4$ group is the *N*-protecting group of choice. Replacement of the *p*-$CH_3OC_6H_4$ group with other *N*-protecting groups such as *n*-Bu (39%), *iso*-Pr (35%), Ph (28%), and *p*-$Me_2NC_6H_4$ (45%) gave decreased yields. The use of a *tert*-Bu group resulted in no product.

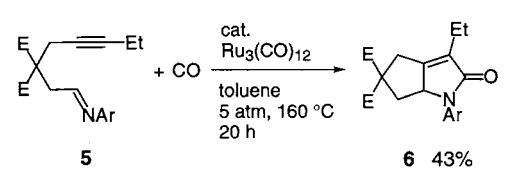


1 2 66% (1)

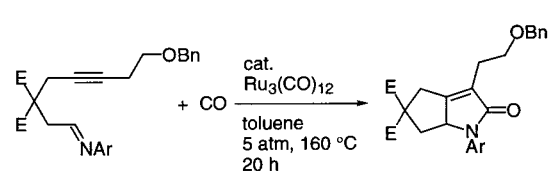
The reaction of phenyl-substituted yne–imine **3** gave the corresponding lactam **4** in 45% yield (Eq. (2)). Alkyl-substituted yne–imines **5** and **7** also underwent cyclocarbonylation to give lactams **6** and **8** in good yields (Eqs. (3) and (4)). The reaction can also be applied to the formation of a cyclohexane-fused γ-lactam (Eq. (5)). In all cases, yields were somewhat lower than those in the case of yne–aldehydes.



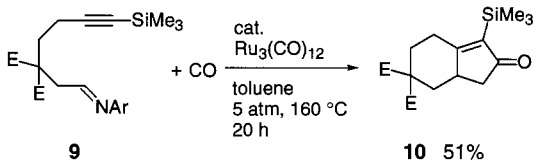
3 4 45% (2)



5 6 43% (3)

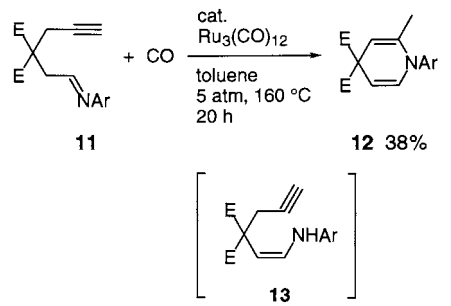


7 8 43% (4)



9 10 51% (5)

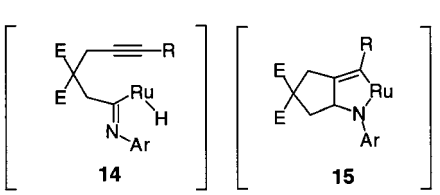
The reaction of an yne–imine having a terminal acetylenic moiety gave the dihydropyridine derivative **12** (Eq. (6)), rather than the expected lactam. Although the mechanism is presently not clear, **12** would have been formed via an intramolecular hydroamination [6] of **13**, which is the enamine-form of **11**, followed by the isomerization of the *exo* olefinic bond to an *endo* isomer. When a substituent is present on the terminal acetylenic carbon, cyclocarbonylation takes place because the addition of N–H bond to an acetylene is retarded by steric hindrance.



11 12 38%

13 (6)

The mechanism of the cyclocarbonylation reactions examined herein should be similar to that which operates in the reaction of yne–aldehydes [4]. Thus, the key step in the present reaction is the oxidative addition of an imine C–H bond to ruthenium, to give **14**. In contrast to aldehyde C–H bonds [7] however, no example of the oxidative addition of imine C–H bonds to a transition metal complex has been reported, except for limited cases [8,9]. Suggs reported the chelation assisted oxidative addition of imine C–H bonds in 2-aminopyridyl aldimines to $Rh(PPh_3)_3Cl$ [8]. Jun developed some Rh-catalyzed reactions which involve the oxidative addition of imine C–H bonds in 2-aminopyridyl aldimines to a rhodium complex as the key step [9]. To our knowledge, no report of the oxidative addition of a simple imine C–H bond to a transition metal complex exists. On the other hand, an alternative mechanism for the present catalytic reaction involves the oxidative cyclization of an yne–imine to a ruthenium leading to metallacycle **15**. This also has no precedent, to our knowledge. A mechanistic study of this reaction is now underway.



14 15

In summary, we have demonstrated a new $Ru_3(CO)_{12}$-catalyzed cyclocarbonylation of yne–imines leading to α,β-unsaturated lactams. This is the first example of the catalytic cyclocoupling of acetylenes, imines, and CO [10].

3. Experimental

3.1. General

^{1}H- and ^{13}C-NMR spectra were recorded on a Jeol JMN-270 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (Hz), integration, and interpretation. IR spectra were obtained on a Hitachi 270-50 spectrometer; absorptions are reported in cm^{-1} with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained on a Shimadzu GCMS-QP 5000 instrument with ionization voltages of 70 eV. Elemental analyses were performed by the Elemental Analysis Section of Osaka University. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-DX303. Analytical GC was carried out on a Shimadzu GC-14B gas chromatography, equipped with a flame ionization detector. Column chromatography was performed with SiO_2 (Merck).

3.2. Materials

Toluene, dioxane, and CH_3CN were distilled from CaH_2. $Ru_3(CO)_{12}$ was purchased from Aldrich and used after recrystallization from hexane. All yne–imines were prepared by the reaction of the corresponding yne–aldehydes [4] with *p*-anisidine in the presence of $MgSO_4$ [11].

3.3. Typical procedure

A 50 ml stainless autoclave was charged with yne–imine **1** (1 mmol, 417 mg), toluene (5 ml), and $Ru_3(CO)_{12}$ (0.05 mmol, 32 mg). The system was flushed three times with 5 atm of CO and was then pressurized to 5 atm and immersed in an oil bath at 160°C. After 20 h had elapsed, the autoclave was removed from the oil bath and allowed to cool for 1 h. The CO was then released. 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/ether = 3/1) to give 4,5,6,6a-tetrahydro-1-(4-methoxyphenyl)-3-(trimethylsilyl)-2*H*-cyclopenta[b]pyrrol-2-one-5,5-dicarboxylic acid diethyl ester (**2**) (294 mg, 66% yield) as a white solid.

3.4. 4,5,6,6a-Tetrahydro-1-(4-methoxyphenyl)-3-(trimethylsilyl)-2H-cyclopenta[b]pyrrol-2-one-5,5-dicarboxylic acid diethyl ester (2)

White solid; m.p. 86–87°C (hexane); R_f 0.16 (hexane/ether = 3/1); ^{1}H-NMR ($CDCl_3$): δ 0.29 (s, 9H, $SiMe_3$), 1.24 (t, $J = 7.3$ Hz, 3H, CH_3), 1.31 (t, $J = 7.3$ Hz, 3H, CH_3), 1.67 (t, $J = 12$ Hz, 1H, 6-H), 3.03 (dd, $J = 7.3$ Hz, $J = 12$ Hz, 1H, 6-H), 3.19 (d, $J = 18$ Hz, 1H, 4-H), 3.39 (d, $J = 18$ Hz, 1H, 4-H), 3.79 (s, 3H, OCH_3) 4.20 (dq, $J = 2.7$ Hz, $J = 7.3$ Hz, 2H, CH_2), 4.28 (dq, $J = 2.7$ Hz, $J = 7.3$ Hz, 2H, CH_2), 4.76 (dd, $J = 7.3$ Hz, $J = 12$ Hz, 1H, 6a-H), 6.88 (d, $J = 8.4$ Hz, 2H, Ar), 7.31 (d, $J = 8.4$ Hz, 2H, Ar); ^{13}C-NMR ($CDCl_3$): δ −1.3 ($SiMe_3$), 13.9 (CH_3), 14.0 (CH_3), 32.7 (4-C), 37.2 (6-C), 55.5 (OCH_3), 60.8 (5-C), 62.1 (CH_2), 62.3 (CH_2), 66.7 (6a-C), 114.2 (Ar), 121.3 (Ar), 131.3 (Ar), 132.2 (3-C), 156.1 (Ar), 170.2 ($COCH_2CH_3$), 171.0 (3a-C), 171.4 ($COCH_2CH_3$), 174.7 (2-C); IR (KBr): 2964 m, 2906 m, 2844 w, 1742 s, 1674 s, 1639 m, 1515 s, 1461 m, 1449 m, 1427 m, 1373 m, 1320 m, 1300 s, 1274 s, 1249 s, 1180 s, 1159 s, 1133 m, 1114 m, 1089 m, 1080 m, 1055 m, 1036 m, 1024 m, 1009 m, 911 w, 842 s, 829 s, 780 m, 767 m, 743 w, 687 w, 669 w, 630 w, 618 w; MS, *m*/*z* (relative intensity, %): 445 (M^+, 36), 372 (12), 134 (11), 77 (18), 75 (34), 73 (100), 59 (10). Anal. Calc. for $C_{23}H_{31}NO_6Si$: C, 62.00; H, 7.02; N, 3.15. Found: C, 61.87; H, 7.02; N, 3.09.

3.5. 4,5,6,6a-Tetrahydro-1-(4-methoxyphenyl)-3-phenyl-2H-cyclopenta[b]pyrrol-2-one-5,5-dicarboxylic acid diethyl ester (4)

White solid; m.p. 97–98°C (hexane); R_f 0.20 (hexane/ether = 3/1); ^{1}H-NMR ($CDCl_3$): δ 1.21 (t, $J = 7.0$ Hz, 3H, CH_3), 1.33 (t, $J = 7.0$ Hz, 3H, CH_3), 1.76 (t, $J = 12$ Hz, 1H, 6-H), 3.05 (dd, $J = 6.8$ Hz, $J = 12$ Hz, 1H, 6-H), 3.48 (d, $J = 18$ Hz, 1H, 4-H), 3.53 (d, $J = 18$ Hz, 1H, 4-H), 3.82 (s, 3H, OCH_3) 4.16 (q, $J = 7.0$ Hz, 2H, CH_2), 4.31 (q, $J = 7.0$ Hz, 2H, CH_2), 4.86 (dd, $J = 7.0$ Hz, $J = 12$ Hz, 1H, 6a-H), 6.94 (d, $J = 8.9$ Hz, 2H, Ar), 7.36–7.47 (m, 3H, Ar), 7.76 (d, $J = 8.9$ Hz, 2H, Ar), 7.78 (d, $J = 7.8$ Hz, 2H, Ar); ^{13}C-NMR ($CDCl_3$): δ 13.4 (CH_3), 13.5 (CH_3), 32.2 (4-C), 36.9 (6-C), 55.0 (OCH_3), 60.9 (5-C), 61.7 (CH_2), 61.9 (CH_2), 63.6 (6a-C), 113.9 (Ar), 121.7 (Ar), 127.9 (Ar), 128.0 (Ar),129.3 (3-C), 130.5 (Ar), 131.5 (Ar), 155.5 (3a-C), 156.2 (Ar), 169.4 ($COCH_2CH_3$), 169.7 (2-C), 170.9 ($COCH_2CH_3$); IR (KBr): 2982 m, 2840 w, 2220 w, 1735 s, 1693 s, 1583 w, 1515 s, 1470 m, 1447 m, 1371 m, 1296 m, 1266 m, 1243 s, 1182 m, 1147 m, 1136 m, 1092 m, 1056 m, 1022 m, 959 w, 858 w, 829 w, 788 m, 757 w, 701 w, 669 m, 654 m, 610 w; MS, *m*/*z* (relative intensity, %): 449 (M^+, 71), 421 (26), 420 (76), 346 (28), 303 (21), 302 (100), 274 (14), 153 (15), 152 (14), 141 (15), 134 (36), 122 (11), 115 (36), 108 (25), 107 (20), 92 (19), 77 (48), 64 (16). Anal.

Calc. for $C_{26}H_{27}NO_6$: C, 69.46; H, 6.06; N, 3.12. Found: C, 69.31; H, 6.06; N, 3.16.

3.6. 4,5,6,6a-Tetrahydro-3-ethyl-1-(4-methoxyphenyl)-2H-cyclopenta[b]pyrrol-2-one-5,5-dicarboxylic acid diethyl ester (**6**)

White solid; m.p. 87–88°C (hexane); R_f 0.07 (hexane/ether = 2/1); ^{1}H-NMR ($CDCl_3$): δ 1.16 (t, $J = 7.8$ Hz, 3H, CH_3), 1.22 (t, $J = 7.3$ Hz, 3H, CH_3), 1.29 (t, $J = 7.3$ Hz, 3H, CH_3), 1.62 (t, $J = 12$ Hz, 1H, 6-H), 2.22–2.46 (m, 2H, CH_2), 3.00 (dd, $J = 6.8$ Hz, $J = 12$ Hz, 1H, 6-H), 3.10 (d, $J = 18$ Hz, 1H, 4-H), 3.36 (d, $J = 18$ Hz, 1H, 4-H), 3.78 (s, 3H, OCH_3) 4.18 (dq, $J = 2.2$ Hz, $J = 7.3$ Hz, 2H, CH_2), 4.26 (dq, $J = 2.7$ Hz, $J = 7.3$ Hz, 2H, CH_2), 4.67 (dd, $J = 6.8$ Hz, $J = 12$ Hz, 1H, 6a-H), 6.88 (d, $J = 8.9$ Hz, 2H, Ar), 7.51 (d, $J = 8.9$ Hz, 2H, Ar); ^{13}C-NMR ($CDCl_3$): δ 12.5 (CH_3), 13.8 (CH_3), 13.9 (CH_3), 18.0 (CH_2), 30.6 (4-C), 37.5 (6-C), 55.4 (OCH_3), 61.2 (5-C), 62.0 (CH_2), 62.2 (CH_2), 63.9 (6a-C), 114.2 (Ar), 121.1 (Ar), 132.3 (3-C), 132.6 (Ar), 153.8 (3a-C), 156.2 (Ar), 170.2 (COCH$_2$CH$_3$), 171.4 (COCH$_2$CH$_3$), 171.8 (2-C); IR (KBr): 2972 w, 2840 w, 1732 s, 1689 s, 1582 w, 1512 s, 1470 w, 1448 w, 1434 w, 1383 m, 1296 m, 1242 s, 1190 m, 1144 m, 1115 w, 1092 m, 1062 m, 1029 m, 960 w, 859 w, 835 m, 792 w, 762 w, 725 w, 669 w, 624 w; MS, m/z (relative intensity, %): 401 (M^+, 100), 373 (24), 372 (14), 356 (17), 328 (14), 300 (11), 299 (19), 298 (76), 282 (12), 255 (17), 254 (89), 226 (17), 214 (24), 200 (12), 134 (26), 122 (11), 108 (18), 107 (14), 105 (14), 92 (17), 91 (18), 79 (15), 78 (11), 77 (48), 65 (12). Anal. Calc. for $C_{22}H_{27}NO_6$: C, 65.82; H, 6.78; N, 3.49. Found: C, 65.79; H, 6.82; N, 3.56.

3.7. 4,5,6,6a-Tetrahydro-3-(2-benzyloxyethyl)-1-(4-methoxyphenyl)-2H-cyclopenta[b]pyrrol-2-one-5,5-dicarboxylic acid diethyl ester (**8**)

Yellow oil; R_f 0.10 (hexane/ether = 1/1); ^{1}H-NMR ($CDCl_3$): δ 1.22 (t, $J = 7.0$ Hz, 3H, CH_3), 1.29 (t, $J = 7.0$ Hz, 3H, CH_3), 1.65 (t, $J = 12$ Hz, 1H, 6-H), 2.53–2.77 (m, 2H, CH_2CH$_2$OBn), 3.00 (dd, $J = 7.0$ Hz, $J = 12$ Hz, 1H, 6-H), 3.11 (d, $J = 18$ Hz, 1H, 4-H), 3.36 (d, $J = 18$ Hz, 1H, 4-H), 3.60–3.77 (m, 2H, CH$_2$CH_2OBn), 3.80 (s, 3H, OCH_3) 4.16 (q, $J = 7.0$ Hz, 2H, CH_2), 4.26 (dq, $J = 1.4$ Hz, $J = 7.0$ Hz, 2H, CH_2), 4.53 (s, 2H, OCH_2Ph), 4.71 (dd, $J = 7.0$ Hz, $J = 12$ Hz, 1H, 6a-H), 6.90 (d, $J = 8.9$ Hz, 2H, Ar), 7.22–7.37 (m, 5H, Ph), 7.51 (d, $J = 8.9$ Hz, 2H, Ar); ^{13}C-NMR ($CDCl_3$): δ 13.8 (CH_3), 13.9 (CH_3), 25.3 (CH$_2$CH$_2$OBn), 30.9 (4-C), 37.5 (6-C), 55.4 (OCH_3), 61.0 (5-C), 62.0 (CH_2), 62.2 (CH_2), 64.1 (6a-C), 67.9 (CH$_2$$CH_2$OBn), 72.8 (O$CH_2$Ph), 114.2 (Ar), 121.2 (Ar), 127.4 (Ph), 127.8 (Ph), 128.0 (Ar), 128.1 (Ph), 132.2 (3-C), 138.3 (Ph), 156.2 (Ar), 156.6 (3a-C), 170.0 (COCH$_2$CH$_3$), 171.4 (COCH$_2$CH$_3$), 171.7 (2-C); IR (neat): 2982 m, 2936 m, 2866 m, 1730 s, 1686 s, 1612 s, 1585 m, 1513 s, 1457 s, 1376 s, 1248 s, 1184 s, 1140 s, 1103 s, 1035 s, 910 w, 860 m, 830 m, 778 m, 737 m, 698 m; MS, m/z (relative intensity, %): 507 (M^+, 8), 416 (18), 410 (11), 342 (11), 92 (11), 91 (100), 77 (13), 65 (12). Anal. Calc. for $C_{29}H_{33}O_7N$: C, 68.62; H, 6.55; N, 2.76. Found: C, 68.34; H, 6.38; N, 2.81.

3.8. 5,6,7,7a-Tetrahydro-1-(4-methoxyphenyl)-3-(trimethylsilyl)-3H-indol-2-one-6,6-dicarboxylic acid diethyl ester (**10**)

White solid; m.p. 106–108°C (hexane); R_f 0.10 (hexane/ether = 4/1); ^{1}H-NMR ($CDCl_3$): δ 0.30 (s, 9H, $SiMe_3$), 1.21 (t, $J = 7.0$ Hz, 3H, CH_3), 1.35 (t, $J = 7.0$ Hz, 3H, CH_3), 1.40 (t, $J = 12$ Hz, 1H, 7-H), 1.92 (dt, $J = 4.9$ Hz, $J = 14$ Hz, 1H, 5-H), 2.38 (dt, $J = 4.9$ Hz, $J = 14$ Hz, 1H, 4-H), 2.60–2.71 (m, 1H, 5-H), 2.93–3.05 (m, 2H, 4-H, 7-H), 3.80 (s, 3H, OCH_3), 4.04–4.22 (m, 2H, CH_2), 4.23–4.42 (m, 2H, CH_2), 4.57 (dd, $J = 5.1$ Hz, $J = 12$ Hz, 1H, 7a-H), 6.91 (d, $J = 9.2$ Hz, 2H, Ar), 7.47 (d, $J = 9.2$ Hz, 2H, Ar); ^{13}C-NMR ($CDCl_3$): δ −0.48 ($SiMe_3$), 13.9 (CH_3), 14.1 (CH_3), 25.2 (4-C), 33.0 (5-C), 37.7 (7-C), 54.3 (6-C), 55.5 (OCH_3), 60.3 (7a-C), 61.9 (CH_2), 62.0 (CH_2), 114.2 (Ar), 122.4 (Ar), 130.4 (3-C), 130.5 (Ar), 156.3 (Ar), 167.1 (3a-C), 170.2 (COCH$_2$CH$_3$), 170.4 (COCH$_2$CH$_3$), 172.7 (2-C); IR (KBr): 2980 m, 2836 w, 1747 s, 1673 s, 1627 w, 1516 s, 1455 w, 1384 m, 1336 m, 1297 m, 1241 s, 1189 m, 1161 w, 1092 w, 1043 w, 1018 w, 841 m, 813 m, 781 w, 693 w, 629 w; MS, m/z (relative intensity, %): 459 (M^+, 46), 288 (20), 287 (100), 77 (13), 75 (21), 73 (67). Anal. Calc. for $C_{24}H_{33}NO_6Si$: C, 62.72; H, 7.24; N, 3.05. Found: C, 62.57; H, 7.18; N, 3.10.

3.9. 1,4-Dihydro-1-(4-methoxyphenyl)-2-methyl-pyridine-4,4-dicarboxylic acid diethyl ester (**12**)

Yellow oil; R_f 0.11 (hexane/ether = 3/1); ^{1}H-NMR ($CDCl_3$): δ 1.26 (t, $J = 7.0$ Hz, 6H, CH_3), 1.64 (d, $J = 1.1$ Hz, 3H, CH_3), 4.20 (q, $J = 7.0$ Hz, 4H, CH_2), 4.69 (dd, $J = 1.1$ Hz, $J = 2.7$ Hz, 1H, 3-H), 4.80 (dd, $J = 2.7$ Hz, $J = 7.8$ Hz, 1H, 5-H), 6.23 (d, $J = 7.8$ Hz, 1H, 6-H), 6.84 (d, $J = 8.9$ Hz, 2H, Ar), 7.05 (d, $J = 8.9$ Hz, 2H, Ar); ^{13}C-NMR ($CDCl_3$): δ 14.0 (CH_3), 20.4 (CH_3), 55.1 (4-C), 55.4 (OCH_3), 61.4 (CH_2), 94.0 (3-C), 94.8 (5-C), 114.1 (Ar), 128.9 (Ar), 133.0 (6-C), 136.3 (Ar), 136.9 (2-C), 158.3 (Ar), 171.5 (COCH$_2$CH$_3$); IR (neat): 2986 m, 2938 m, 2842 w, 2056 w, 1981 w, 1733 s, 1684 s, 1622 m, 1583 w, 1515 s, 1468 m, 1448 m, 1408 m, 1388 m, 1363 m, 1273 s, 1248 s, 1194 s, 1175 s, 1107 s, 1063 m, 1032 s, 879 m, 840 m, 802 m, 772 m, 721 m, 664 w, 638 w, 607 w; MS, m/z (relative intensity, %): 345 (M^+, 1), 273 (12), 272 (100), 245 (10), 244 (62), 200 (10), 92 (12), 77 (17).

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