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Cationic Rhodium(I)/Modified-BINAP Catalyzed [2+2+2] Cycloaddition of Alkynes with Nitriles

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Cationic rhodium(I)/modified-BINAP complexes catalyze a chemo- and regioselective [2+2+2] cycloaddition of a wide variety of alkynes and nitriles leading to highly functionalized pyridines under mild reaction conditions. The asymmetric variant of this reaction, enantioselective desymmetrization of substituted malononitriles, also proceeded to give enantio-enriched bicyclic pyridines which possess a tertiary or quaternary stereocenter.

Introduction

Transition-metal-catalyzed or -mediated [2+2+2] cycloadditions of alkynes with nitriles leading to substituted pyridines have been developed using a number of transition-metal complexes.[1] Since the pioneering works by Yamazaki and Wakatsuki,[2] Vollhardt,[3] and Bönnemann,[4] cobalt catalysts have been most widely used for this transformation, and numerous examples, including the synthesis of natural products[5] and oligopyridines,[6] have been reported.[7]

Ruthenium catalysts are highly efficient for activated nitriles (e.g., electron-deficient nitriles, dicyanides, and α-halo nitriles) and tethered 1,6-diynes under mild reaction conditions.[8] Nickel,[9] titanium,[10] and tantalum[11] complexes are also effective for this transformation, although stoichiometric amounts of metals are required. Recently, (N-heterocyclic carbene)nickel complexes have been found to catalyze the [2+2+2] cycloaddition of internal alkynes with inactivated nitriles at room temperature.[12] Although rhodium catalysts can catalyze pyridine annulation at elevated temperature, the efficiency is low due to the formation of a large amount of arene by-products other than the desired pyridines.[13] Recently, the novel enantioselective [2+2+2] cycloaddition of alkynes with nitriles leading to axially chiral pyridines was reported by using chiral (cyclopentadienyl)cobalt complexes.[14] In view of the application to such enantioselective [2+2+2] cycloaddition, the development of Rh-based catalysts is an attractive target.

We recently reported the cationic rhodium(I)/H_8-BINAP [2,2′-bis(diphenylphosphanyl)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl] catalyzed chemo-, regio-, and enantioselective cross cyclotrimerization of two different alkynes.[15] This catalyst was successfully applied to the [2+2+2] cycloaddition of alkynes with isocyanates, isothiocyanates, and carbon disulfide leading to substituted heterocycles.[16] In this paper, we describe a cationic rhodium(I)/modified-BINAP catalyzed [2+2+2] cycloaddition of a wide variety of alkynes and nitriles under mild reaction conditions.

Results and Discussion

We first examined various rhodium catalysts to promote [2+2+2] cycloaddition of the malonate-derived internal 1,6-diyne **1a** with the nitrile **2a**, activated by the electron-deficient ethoxycarbonyl group. Among the rhodium catalysts examined, $[Rh(cod)_2]BF_4$/BINAP showed the highest catalytic activity. The use of neutral Rh^I complexes or conventional phosphane ligands (e.g., dppe, dppb, dppf, Ph_3P) showed no catalytic activity.

Thus, we explored the scope of this process with respect to 1,6-diynes using 3% $[Rh(cod)_2]BF_4$/BINAP as catalyst (Table 1). The reaction of the malonate-derived 1,6-diyne **1a**, dimethoxypropane-derived 1,6-diyne **1b**, and tosylamide-derived 1,6-diyne **1c** with **2a** afforded the corresponding pyridines in excellent yield (Entries 1–3). The dipropargyl ether derivative **1d**, which has no tertiary center on the tether chain, also reacted with **2a** to afford the expected pyridine in excellent yield (Entry 4). The use of terminal 1,6-diyne **1e** lowered the yield of the desired pyridine due to the competitive diyne cyclotrimerization (Entry 5).

Next, the scope of nitriles was investigated by using 3% $[Rh(cod)_2]BF_4$/BINAP as catalyst. The reactions of the electron-deficient nitriles **2a**–**c** with **1a** afforded the corresponding pyridines in almost quantitative yield (Entries 1,

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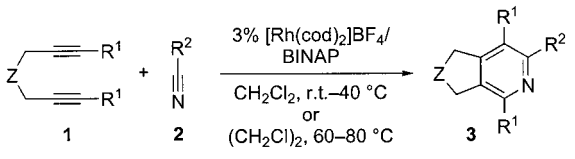
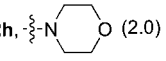
Table 1. Rhodium-catalyzed [2+2+2] cycloaddition of 1,6-diynes with nitriles.



1 2 3

1a R^1 = Me, Z = $C(CO_2Me)_2$ **1d** R^1 = Et, Z = O
1b R^1 = Me, Z = $C(CH_2OMe)_2$ **1e** R^1 = H, Z = $C(CO_2Me)_2$
1c R^1 = Me, Z = NTs

Entry	1	2, R^2 (equiv.)	Conditions	3	Yield [%][a]
1	**1a**	**2a**, CO_2Et (1.1)	r.t./3 h	**3aa**	>99
2	**1b**	**2a**, CO_2Et (1.1)	r.t./5 h	**3ba**	91
3	**1c**	**2a**, CO_2Et (1.1)	r.t./1 h	**3ca**	>99
4	**1d**	**2a**, CO_2Et (1.1)	r.t./1 h	**3da**	>99
5	**1e**	**2a**, CO_2Et (2.0)	60 °C/6 h	**3ea**	69
6	**1a**	**2b**, COPh (1.1)	60 °C/16 h	**3ab**	>99
7	**1a**	**2c**, Ac (1.1)	80 °C/40 h	**3ac**	98
8[b]	**1e**	**2d**, Ph (5.0)	60 °C/1 h	**3ed**	87
9	**1e**	**2e**, CH_3 (solvent)	80 °C/1 h	**3ee**	63
10[b,c]	**1e**	**2f**, Ts (1.1)	80 °C/16 h	**3ef**	60
11[d]	**1e**	**2g**, SMe (2.0)	80 °C/36 h	**3eg**	35
12[e]	**1e**	**2h**,  (2.0)	40 °C/5 h	**3eh**	47

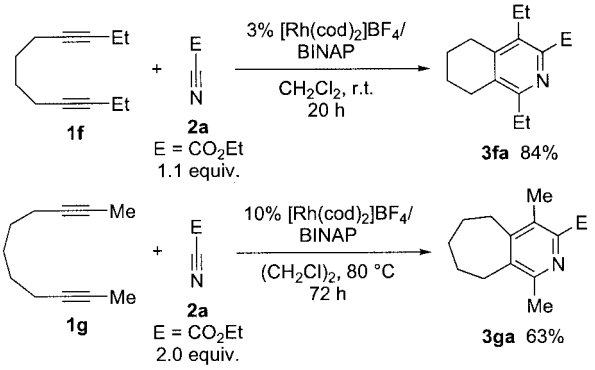
[a] Yield of isolated products. [b] Ligand: Segphos [(4,4′-bi-1,3-benzodioxiol)-5,5′-diylbis(diphenylphosphane)]. [c] Catalyst: 10%. [d] Catalyst: 20%. [e] Ligand: H_8-BINAP.

6, and 7). In the cases of inactivated nitriles **2d** and **2e**, the reactions proceeded in good yield using terminal diyne **1e** and excess nitriles (**2d**: 5.0 equiv., Entry 8; **2e**: solvent, Entry 9). The reactions of heteroatom-substituted nitriles **2f**–**h** were also investigated. Although high catalyst loading (10–20%) and elevated temperature (80 °C) were required, the sulfur-containing nitriles **2f** and **2g** could participate in this cycloaddition to give the corresponding pyridines (Entries 10 and 11).[17] Cyanamide **2h** was a reactive substrate to give the corresponding aminopyridine at 40 °C (Entry 12).[18]

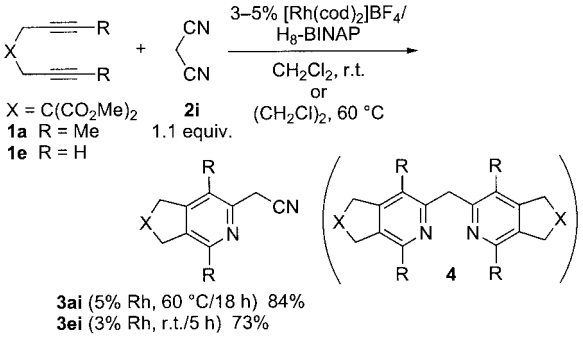
The formation of not only a five-membered ring but also six- and seven-membered rings was possible using the 1,7-diyne **1f** and 1,8-diyne **1g**, respectively (Scheme 1).

The present Rh^I-catalyzed reaction exhibited an interesting chemoselectivity. The reaction of the 1,6-diynes **1a** and **1e** with malononitrile (**2i**) in the presence of 3–5% [Rh(cod)$_2$]BF_4/H_8-BINAP selectively afforded the corresponding monopyridines **3ai** and **3ei**, respectively, without the formation of bipyridines **4** (Scheme 2).[19]

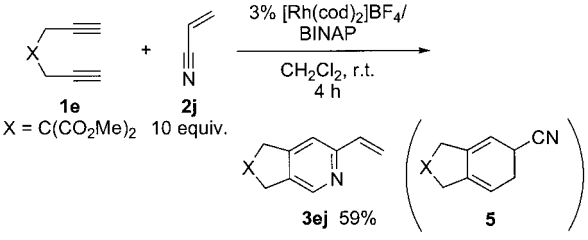
Another interesting chemoselectivity is shown in Scheme 3. Grigg et al. reported that a 1,6-diyne selectively reacted with the double bond of acrylonitrile (**2j**) in the presence of 2% $RhCl(PPh_3)_3$ at 82 °C for 6 h which afforded a nitrile in 59% yield.[20] On the other hand, the 1,6-diyne **1e** selectively reacted with the cyano group of **2j** in the presence of 3% [Rh(cod)$_2$]BF_4/BINAP at room temperature which afforded the vinylpyridine **3ej** in good yield without the formation of nitrile **5**.[21]



Scheme 1. Rhodium-catalyzed [2+2+2] cycloaddition of 1,7- and 1,8-diynes with ethyl cyanoformate.



Scheme 2. Rhodium-catalyzed chemoselective [2+2+2] cycloaddition of 1,6-diynes with malononitrile.

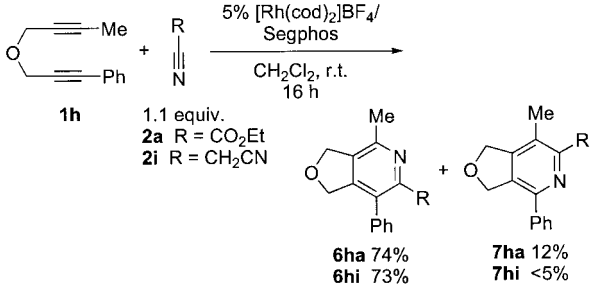


Scheme 3. Rhodium-catalyzed chemoselective [2+2+2] cycloaddition of a 1,6-diyne with acrylonitrile.

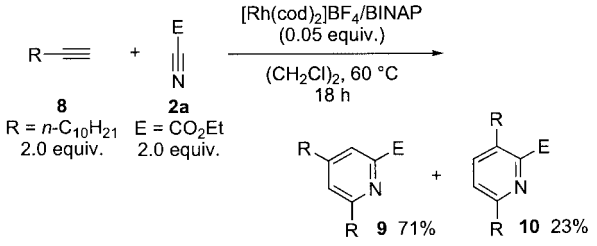
The regioselectivity of the present pyridine synthesis was then investigated using the unsymmetrical 1,6-diyne **1h** which has a methyl and a phenyl group at each terminal position. The reaction of **1h** with ethyl cyanoformate (**2a**) in the presence of 5% [Rh(cod)$_2$]BF_4/Segphos at room temperature afforded the corresponding pyridines **6ha** and **7ha** in good yield, preferably **6ha** over **7ha**. Similarly, the reaction of **1h** with malononitrile (**2i**) afforded **6hi** as the predominant isomer (Scheme 4).

We also investigated the pyridine synthesis by cycloaddition of an untethered monoalkyne with **2a**. The reaction of 1-dodecyne (**8**, 2.0 equiv.) with **2a** (2.0 equiv.) in the presence of [Rh(cod)$_2$]BF_4/BINAP (0.05 equiv.) at 60 °C afforded the corresponding pyridines **9** and **10** in high yields; **9** was obtained as the major isomer (Scheme 5).

Finally, the asymmetric variant of this reaction, the enantioselective desymmetrization of substituted malononi-

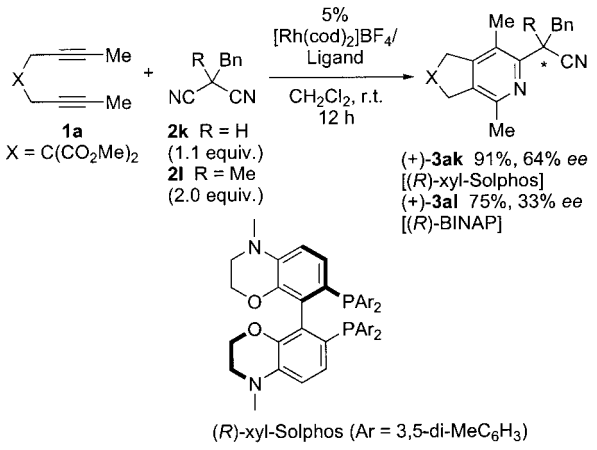


Scheme 4. Rhodium-catalyzed regioselective [2+2+2] cycloaddition of an unsymmetrical 1,6-diyne with nitriles.



Scheme 5. Rhodium-catalyzed regioselective [2+2+2] cycloaddition of 1-dodecyne with ethyl cyanformate.

triles, is shown in Scheme 6.[22] The 1,6-diyne **1a** smoothly reacted with monosubstituted malononitrile (**2k**, 1.1 equiv.) in the presence of 5% $[Rh(cod)_2]BF_4$/(*R*)-xyl-Solphos[23] at room temperature to give the enantio-enriched bicyclic pyridine (+)-**3ak**, which has a tertiary stereocenter, in 91% yield with 64% *ee*. Furthermore, the reaction of **1a** with sterically demanding disubstituted malononitrile (**2l**, 2.0 equiv.) proceeded in the presence of 5% $[Rh(cod)_2]BF_4$/(*R*)-BINAP at room temperature to give the enantio-enriched bicyclic pyridine (+)-**3al**, which possesses a quaternary stereocenter, in 75% yield with 33% *ee*.



Scheme 6. Rhodium-catalyzed enantioselective [2+2+2] cycloaddition of a 1,6-diyne with substituted malononitriles.

Conclusions

In conclusion, we have determined that cationic rhodium(I)/modified-BINAP complexes are versatile new catalysts for chemo- and regioselective [2+2+2] cycloaddition of a wide variety of alkynes and nitriles leading to highly functionalized pyridines under mild reaction conditions. The asymmetric variant of this reaction, enantioselective desymmetrization of substituted malononitriles, was also demonstrated to give enantio-enriched bicyclic pyridines which possess a tertiary or quaternary stereocenter.

Experimental Section

General Methods: ^1H NMR spectra were recorded with a JEOL AL 300 (300 MHz) spectrometr. ^{13}C NMR spectra were obtained with complete proton decoupling with a JEOL AL 300 (75 MHz) spectrometer. HRMS data were obtained with a JEOL JMS-700 spectrometer. Infrared spectra were obtained with a JASCO A-302 spectrometer. (*R*)-Xyl-Solphos was obtained from Solvias AG under their University Ligand Kit program. Segphos and H_8-BINAP were obtained from Takasago International Corporation. Anhydrous CH_2Cl_2 (No. 27,099-7), $(CH_2Cl)_2$ (No. 28,450-5), and CH_3CN (No. 27,100-4) were obtained from Aldrich and used as received. All reagents were obtained from commercial sources and used as received, unless otherwise indicated. All reactions were carried out under argon or nitrogen in oven-dried glassware, unless otherwise indicated.

Starting Materials: The diynes **1a**,[24] **1b**,[25] **1c**,[26] **1d**,[27] and **1e**[28] and the nitriles **2k**[29] and **2l**[29] were prepared according to literature procedures.

(3-But-2-ynyloxyprop-1-ynyl)benzene (1h): To a stirred suspension of sodium hydride (50% in mineral oil, 0.49 g, 10.3 mmol) in THF (25 mL) was added a THF (25 mL) solution of (3-bromoprop-1-ynyl)benzene[30] (1.00 g, 5.1 mmol) at room temperature, and the resulting mixture was stirred at room temperature for 10 min. 2-Butyn-1-ol (0.40 g, 5.6 mmol) was added, and the resulting mixture was stirred at room temperature for 4 h. The reaction mixture was extracted with diethyl ether. The organic layer was washed with brine, dried with Na_2SO_4, and concentrated. The crude product was purified by silica gel column chromatography (hexane/ethyl acetate, 20:1) and afforded **1h** (0.51 g, 2.8 mmol, 36% yield) as a yellow oil. IR (neat): $\tilde{\nu}$ = 2850, 1440, 1340, 1650, 760, 685 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.40–7.49 (m, 2 H), 7.28–7.35 (m, 3 H), 4.46 (s, 2 H), 4.28 (q, J = 2.4 Hz, 2 H), 1.88 (t, J = 2.4 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 131.7, 128.4, 128.2, 122.5, 86.5, 84.5, 83.1, 74.4, 57.2, 57.1, 3.6 ppm. HRMS (EI): calcd. for $C_{13}H_{12}O$ $[M]^+$ 184.0888; found 184.0859.

Representive Procedure for [2+2+2] Cycloaddition of Alkynes with Nitriles (Table 1, Entry 1): Under Ar, BINAP (7.5 mg, 0.012 mmol) and $[Rh(cod)_2]BF_4$ (4.9 mg, 0.012 mmol) were dissolved in CH_2Cl_2 (2.0 mL), and the mixture was stirred at room temperature for 5 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 0.5 h, the resulting solution was concentrated to dryness and the residue dissolved in CH_2Cl_2 (2.0 mL). To this solution was added dropwise over 1 min a solution of dimethyl 2,2-dibut-2-ynylmalonate (**1a**, 94.5 mg, 0.400 mmol) and ethyl cyanoformate (**2a**, 43.6 mg, 0.440 mmol) in CH_2Cl_2 (1.0 mL) at room temperature. Undissolved substrate was dissolved by addition of CH_2Cl_2 (1.0 mL). The mixture was stirred at room temperature for 3 h. The resulting solution was concentrated and purified by silica gel column chromatography (Et_2O), which furnished pyridine **3aa** (134.1 mg, 0.400 mmol, >99% yield) as a pale yellow solid.

Pyridine 3aa: M.p. 72.0–74.0 °C. IR (neat): $\tilde{\nu}$ = 3350, 2900, 1720, 1420, 1200, 1040, 860, 720 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 4.43 (q, J = 7.2 Hz, 2 H), 3.78 (s, 6 H), 3.60 (s, 4 H), 2.49 (s, 3 H), 2.39 (s, 3 H), 1.41 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 171.5, 166.9, 150.9, 150.0, 146.8, 136.3, 127.7, 61.5, 59.1, 53.2, 39.9, 39.2, 21.8, 15.4, 14.2 ppm. HRMS (EI): calcd. for $C_{17}H_{21}NO_6$ $[M]^+$ 335.1369; found 335.1342.

Pyridine 3ba: Yield 91% (112 mg). Pale yellow oil. IR (neat): $\tilde{\nu}$ = 2850, 1710, 1580, 1430, 1380, 1320, 1190, 1110, 1050 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.43 (q, J = 7.2 Hz, 2 H), 3.36 (s, 6 H), 3.36 (s, 2 H), 3.34 (s, 2 H), 2.83 (s, 4 H), 2.45 (s, 3 H), 2.36 (s, 3 H), 1.41 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 167.2, 152.3, 151.4, 146.0, 138.6, 128.2, 75.9, 61.4, 59.2, 47.3, 38.1, 37.5, 21.8, 15.4, 14.3 ppm. HRMS (EI): calcd. for $C_{17}H_{25}NO_4$ $[M]^+$ 307.1784; found 307.1799.

Pyridine 3ca: Yield >99% (150 mg). Pale yellow solid; m.p. 185–187 °C. IR (neat): $\tilde{\nu}$ = 1710, 1330, 1160, 1050, 820, 690, 660 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.79 (d, J = 8.1 Hz, 2 H), 7.35 (d, J = 8.1 Hz, 2 H), 4.62 (s, 4 H), 4.43 (q, J = 7.2 Hz, 2 H), 2.44 (s, 3 H), 2.43 (s, 3 H), 2.34 (s, 3 H), 1.40 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.2, 149.9, 147.4, 146.5, 144.1, 133.5, 132.8, 130.0, 127.4, 126.5, 61.8, 53.4, 52.8, 21.7, 21.5, 15.4, 14.2 ppm. HRMS (EI): calcd. for $C_{18}H_{21}N_3O_3S$ $[M]^+$ 359.3285; found 359.3295.

Pyridine 3da: Yield >99% (100 mg). Pale yellow oil. IR (neat): $\tilde{\nu}$ = 2850, 1710, 1580, 1430, 1300, 1180, 1050, 900, 730 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.17 (s, 2 H), 5.16 (s, 2 H), 4.46 (q, J = 7.2 Hz, 2 H), 2.62–2.82 (m, 4 H), 1.43 (t, J = 7.5 Hz, 3 H), 1.27 (t, J = 7.5 Hz, 3 H), 1.20 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.8, 153.8, 149.0, 147.3, 134.7, 130.8, 72.5, 72.4, 61.5, 29.2, 23.4, 14.3, 14.1, 12.7 ppm. HRMS (EI): calcd. for $C_{15}H_{19}NO_3$ $[M]^+$ 202.0550; found 202.0526.

Pyridine 3ea:[31] Yield 69% (85 mg). Pale yellow oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.59 (s, 1 H), 8.01 (s, 1 H), 4.47 (q, J = 7.2 Hz, 2 H), 3.78 (s, 6 H), 3.69 (s, 2 H), 3.67 (s, 2 H), 1.44 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 171.1, 165.2, 150.7, 147.1, 145.5, 139.9, 121.2, 61.9, 60.1, 53.3, 40.2, 38.4, 14.3 ppm.

Pyridine 3ab: Yield >99% (147 mg). Pale yellow solid; m.p. 150.0–151.0 °C. IR (neat): $\tilde{\nu}$ = 2900, 1730, 1430, 1260, 1160, 1060, 920, 680 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.82–7.92 (m, 2 H), 7.52–7.62 (m, 1 H), 7.34–7.50 (m, 2 H), 3.81 (s, 6 H), 3.65 (s, 2 H), 3.63 (s, 2 H), 2.46 (s, 3 H), 2.23 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 195.7, 171.6, 153.6, 150.3, 149.6, 136.4, 135.0, 133.3, 130.6, 128.3, 125.8, 59.1, 53.3, 39.8, 39.3, 21.7, 14.7 ppm. HRMS (EI): calcd. for $C_{21}H_{21}NO_5$ $[M-CO_2Me]^+$ 308.1287; found 308.1263.

Pyridine 3ac: Yield 98% (120 mg). Colorless solid; m.p. 100.0–102.0 °C. IR (neat): $\tilde{\nu}$ = 2925, 1730, 1690, 1570, 1420, 1250, 1160, 1060, 930, 680 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.78 (s, 6 H), 3.06 (s, 4 H), 2.67 (s, 3 H), 2.46 (s, 3 H), 2.43 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 202.8, 171.6, 150.8, 150.1, 149.9, 136.6, 127.6, 59.1, 53.2, 39.8, 39.3, 28.5, 21.7, 15.6 ppm. HRMS (EI): calcd. for $C_{16}H_{19}NO_5$ $[M-Ac]^+$ 262.1079; found 262.1050.

Pyridine 3ed: Yield 87% (108 mg). Colorless solid; m.p. 109.0–110.0 °C. IR (neat): $\tilde{\nu}$ = 2950, 1720, 1430, 1260, 1160, 1050, 880, 730, 690 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.53 (s, 1 H), 7.85–7.96 (m, 2 H), 7.58 (s, 1 H), 7.38–7.50 (m, 3 H), 3.78 (s, 6 H), 3.664 (s, 2 H), 3.655 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 171.5, 156.4, 150.4, 145.2, 139.5, 134.6, 128.7, 128.6, 126.9, 116.5, 60.1, 53.2, 40.4, 38.0 ppm. HRMS (EI): calcd. for $C_{18}H_{17}NO_4$ $[M]^+$ 311.1158; found 311.1144.

Pyridine 3ee: Yield 63% (63 mg). Pale yellow solid; m.p. 99.0–100.0 °C. IR (neat): $\tilde{\nu}$ = 1720, 1270, 1150, 870 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.33 (s, 1 H), 7.03 (s, 1 H), 3.76 (s, 6 H), 3.58 (s, 2 H), 3.55 (s, 2 H), 2.51 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 171.5, 156.7, 149.9, 144.6, 133.0, 119.0, 60.1, 53.1, 40.1, 37.9, 24.2 ppm. HRMS (EI): calcd. for $C_{13}H_{15}NO_4$ $[M]^+$ 249.1001; found 249.0972.

Pyridine 3ef:[31] Yield 60% (93 mg). Pale yellow solid; m.p. 152.0–154.0 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.48 (s, 1 H), 8.04 (s, 1 H), 7.92 (d, J = 8.4, 2 H), 7.32 (d, J = 8.4, 2 H), 3.77 (s, 6 H), 3.68 (s, 2 H), 3.64 (s, 2 H), 2.41 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.8, 157.6, 151.9, 146.0, 144.7, 140.0, 136.0, 129.7, 128.8, 118.2, 59.9, 53.3, 40.2, 38.1, 21.6 ppm.

Pyridine 3eg: Yield 35% (39 mg). Pale yellow oil. IR (neat): $\tilde{\nu}$ = 2950, 1730, 1590, 1430, 1260, 1060 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.28 (s, 1 H), 7.06 (s, 1 H), 3.76 (s, 6 H), 3.56 (s, 2 H), 3.53 (s, 2 H), 2.54 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 171.4, 158.2, 149.9, 144.8, 132.1, 116.9, 60.2, 53.2, 40.0, 37.7, 13.6 ppm. HRMS (EI): calcd. for $C_{13}H_{15}NO_4S$ $[M-OMe]^+$ 250.0538; found 250.0518.

Pyridine 3eh:[32] Yield 47% (60 mg). Colorless solid; m.p. 147.0–148.0 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.02 (s, 1 H), 6.53 (s, 1 H), 3.78–3.85 (m, 4 H), 3.75 (s, 6 H), 3.50 (s, 4 H), 3.41–3.48 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 171.6, 159.3, 151.5, 142.9, 126.2, 102.6, 66.7, 65.6, 60.5, 53.0, 48.8, 46.1, 40.4, 37.4 ppm.

Pyridine 3fa: Yield 84% (88 mg). Colorless oil. IR (neat): $\tilde{\nu}$ = 2820, 1700, 1550, 1400, 1290, 1160, 1040, 760 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 4.43 (q, J = 7.2 Hz, 2 H), 2.60–2.85 (m, 8 H), 1.70–1.88 (m, 4 H), 1.40 (t, J = 7.2 Hz, 3 H), 1.24 (t, J = 7.2 Hz, 3 H), 1.18 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.1, 158.7, 146.1, 145.1, 133.6, 132.2, 61.2, 28.0, 26.0, 22.2, 22.1, 21.4, 14.3, 14.2, 12.8 ppm. HRMS (EI): calcd. for $C_{16}H_{23}NO_2$ $[M]^+$ 261.1729; found 261.1760.

Pyridine 3ga: Yield 63% (62 mg). Pale brown oil. IR (neat): $\tilde{\nu}$ = 2900, 1720, 1560, 1420, 1310, 1190, 1050 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 4.44 (q, J = 7.2 Hz, 2 H), 2.80–2.90 (m, 4 H), 2.54 (s, 3 H), 2.34 (s, 3 H), 1.72–1.90 (m, 2 H), 1.47–1.65 (m, 4 H), 1.42 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.1, 152.5, 152.1, 147.0, 138.8, 127.0, 61.5, 31.8, 29.4, 29.1, 26.2, 25.8, 23.2, 15.2, 14.2 ppm. HRMS (EI): calcd. for $C_{15}H_{21}NO_2$ $[M]^+$ 247.1572; found 247.1585.

Pyridine 3ai:[32] Yield 84% (102 mg). Pale yellow solid; m.p. 107–109 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.83 (s, 2 H), 3.78 (s, 6 H), 3.57 (s, 4 H), 2.42 (s, 1 H), 2.27 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 171.6, 151.2, 149.7, 146.5, 134.0, 125.0, 59.4, 53.3, 39.8, 39.0, 24.7, 21.5, 14.7 ppm.

Pyridine 3ei:[33] Yield 73% (80 mg). Pale brown oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.41 (s, 1 H), 7.32 (s, 1 H), 3.90 (s, 2 H), 3.77 (s, 6 H), 3.63 (s, 2 H), 3.62 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 171.2, 151.4, 148.9, 145.5, 135.7, 118.2, 117.1, 60.1, 53.2, 40.2, 37.9, 26.4 ppm.

Pyridine 3ej: Yield 59% (62 mg). Pale yellow solid; m.p. 66.5–68.5 °C. IR (neat): $\tilde{\nu}$ = 3200, 1720, 1420, 1270, 1160, 1060, 920, 890 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.41 (s, 1 H), 7.27 (s, 1 H), 6.79 (dd, J = 10.8, 17.4 Hz, 1 H), 6.12 (d, J = 17.4 Hz, 1 H), 5.44 (d, J = 10.8 Hz, 1 H), 3.77 (s, 6 H), 3.61 (s, 2 H), 3.59 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 171.4, 154.6, 150.0, 145.1,

136.9, 134.9, 117.6, 116.8, 60.2, 53.2, 40.2, 38.1 ppm. HRMS (EI): calcd. for $C_{14}H_{15}NO_4$ $[M]^+$ 261.1001; found 261.0960.

Pyridine 6ha: Yield 74% (84 mg). Pale yellow oil. IR (neat): $\tilde{\nu}$ = 2850, 1720, 1580, 1420, 1320, 1190, 1140, 1060, 1030, 900, 730, 700 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.33–7.46 (m, 3 H), 7.19–7.30 (m, 2 H), 5.20 (s, 2 H), 5.01 (t, J = 2.1 Hz, 2 H), 4.13 (q, J = 7.2 Hz, 2 H), 2.56 (s, 3 H), 0.99 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.8, 150.3, 148.8, 148.0, 136.2, 135.2, 128.9, 128.5, 128.0, 127.9, 73.3, 72.6, 61.4, 22.0, 13.5 ppm. HRMS (EI): calcd. for $C_{17}H_{17}NO_3$ $[M]^+$ 283.1208; found 283.1251.

Pyridine 7ha: Yield 12% (14 mg). Colorless oil. IR (neat): $\tilde{\nu}$ = 1700, 1420, 1200, 1140, 1040, 920, 780, 730, 690 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.70–7.80 (m, 2 H), 7.36–7.55 (m, 3 H), 5.40 (t, J = 2.1 Hz, 2 H), 5.17 (s, 2 H), 4.47 (q, J = 7.2 Hz, 2 H), 2.46 (s, 3 H), 1.45 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.3, 151.1, 149.0, 147.7, 138.3, 134.2, 129.1, 128.7, 127.7, 126.2, 73.9, 72.8, 61.6, 15.7, 14.3 ppm. HRMS (EI): calcd. for $C_{17}H_{17}NO_3$ $[M]^+$ 283.1208; found 283.1137.

Pyridine 6hi: Yield 73% (73 mg). Pale yellow oil. IR (neat): $\tilde{\nu}$ = 2850, 1580, 1420, 1060, 900, 730, 710 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.40–7.53 (m, 3 H), 7.20–7.28 (m, 2 H), 5.17 (s, 2 H), 4.90 (t, J = 2.4 Hz, 2 H), 3.72 (s, 2 H), 2.51 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 150.8, 149.0, 146.4, 135.5, 133.3, 129.3, 128.7, 128.6, 128.3, 73.2, 72.6, 24.5, 22.0 ppm. HRMS (EI): calcd. for $C_{16}H_{14}N_2O$ $[M]^+$ 250.1106; found 250.1098.

Pyridine 9: Yield 71% (123 mg). Pale yellow oil. IR (neat): $\tilde{\nu}$ = 2850, 1710, 1600, 1210 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.75 (s, 1 H), 7.13 (s, 1 H), 4.46 (q, J = 7.2 Hz, 2 H), 2.85 (t, J = 7.8 Hz, 2 H), 2.63 (t, J = 7.8 Hz, 2 H), 1.55–1.85 (m, 4 H), 1.43 (t, J = 7.2 Hz, 3 H), 1.17–1.39 (m, 28 H), 0.88 (t, J = 6.6 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 165.9, 163.0, 152.9, 147.8, 125.9, 122.8, 61.7, 38.4, 35.2, 31.88, 31.86, 30.3, 30.1, 29.58, 29.55, 29.48, 29.45, 29.34, 29.30, 29.27, 29.16, 22.7, 14.3, 14.1 ppm. HRMS (ESI): calcd. for $C_{28}H_{49}NO_2$ $[M + Na]^+$ 454.3661; found 454.3660.

Pyridine 10: Yield 23% (40 mg). Colorless oil. IR (neat): $\tilde{\nu}$ = 2850, 1720, 1590, 1450, 1280, 1200, 1080 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.48 (d, J = 8.1 Hz, 1 H), 7.17 (d, J = 8.1 Hz, 1 H), 4.44 (q, J = 7.2 Hz, 2 H), 2.70–2.85 (m, 4 H), 1.50–1.78 (m, 4 H), 1.42 (t, J = 7.2 Hz, 3 H), 1.15–1.38 (m, 28 H), 0.88 (t, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 167.2, 159.9, 148.2, 138.7, 134.9, 124.4, 61.6, 38.0, 32.3, 31.9, 31.3, 29.9, 29.58, 29.55, 29.52, 29.5, 29.4, 29.3, 22.7, 14.2, 14.1 ppm. HRMS (ESI): calcd. for $C_{28}H_{49}NO_2$ $[M + Na]^+$ 454.3661; found 454.3666.

Pyridine (+)-3ak: Yield 91% (143 mg). Colorless oil. $[\alpha]_D^{25}$ = +29.3 ($CHCl_3$, c = 2.335, 64% *ee*). IR (neat): $\tilde{\nu}$ = 2900, 1720, 1580, 1430, 1260, 1160, 1060, 730, 700 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.32–7.14 (m, 5 H), 4.21 (dd, J = 8.4, 6.9 Hz, 1 H), 3.78 (s, 3 H), 3.77 (s, 3 H), 3.74 (s, 2 H), 3.51 (s, 2 H), 3.36 (dd, J = 13.5, 8.4 Hz, 1 H) 3.22 (dd, J = 13.5, 6.9 Hz, 1 H), 2.47 (s, 3 H), 2.05 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 171.7, 171.5, 151.4, 150.1, 149.4, 137.2, 133.5, 129.1, 128.6, 127.2, 124.3, 120.0, 59.3, 53.24, 53.22, 39.9, 39.1, 39.0, 38.2, 21.7, 14.3 ppm. HRMS (EI): calcd. for $C_{23}H_{24}N_2O_4$ $[M-CO_2Me]^+$ 333.1603; found 333.1589. Chiralpak AD-H, hexane/2-PrOH, 95:5, 1.0 mL/min, retention times: 25.8 min (major isomer) and 27.9 min (minor isomer).

Pyridine (+)-3al: Yield 75% (122 mg). Colorless oil. $[\alpha]_D^{25}$ = +2.4 ($CHCl_3$, c = 9.520, 33% *ee*). IR (neat): $\tilde{\nu}$ = 2900, 1730, 1580, 1430, 1260, 1160, 1060, 740, 700 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.17–7.33 (m, 5 H), 3.79 (s, 3 H), 3.78 (s, 3 H), 3.57 (s, 2 H), 3.54 (s, 2 H), 3.43 (d, J = 13.5 Hz, 1 H), 3.09 (d, J = 13.5 Hz, 1 H), 2.41 (s, 3 H), 2.36 (s, 3 H), 1.74 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 171.73, 171.71, 152.3, 150.5, 149.8, 136.0, 133.1, 130.6, 128.1, 127.1, 125.4, 123.4, 59.2, 53.2, 45.4, 42.8, 40.2, 38.9, 25.7, 21.7, 15.9 ppm. HRMS (EI): calcd. for $C_{24}H_{26}N_2O_4$ $[M]^+$ 406.1893; found 406.1888. Chiralpak AD-H, hexane/2-PrOH, 95:5, 1.0 mL/min, retention times: 10.0 min (major isomer) and 8.9 min (minor isomer).

Supporting Information (see footnote on the first page of this article): ^1H NMR spectra of product pyridines and diyne **1h**.

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