Nickel-Catalyzed Cycloaddition of Alkynes and Isocyanates

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SUPPORTING INFORMATION

General information. Ni(COD)₂ was purchased from Strem and used without further purification. Tri-(n-butyl)-phosphine, tri-(*tert*-butyl)-phosphine, tricyclohexylphosphine and triphenylphosphine were purchased from Aldrich and used without further purification. 1,3-Bis-(2,4,6-trimethylphenyl)-imidazol-2-ylidene (**IMes**), 1,3-bis-(2,6-diisopropylphenyl)-imidazol-2-ylidene (**IPr**), 1,3-dicyclohexylimidazol-2-ylidene (**ICy**), 1,3-di-*tert*-butylimidazol-2-ylidene (**ItBu**), 1,3-diadamantylimidazol-2-ylidene (**IAd**), 1,3-bis-(2,6-diisopropylphenyl)-imidazolin-2-ylidene (**SIPr**) were prepared according to literature procedures.¹ Phenyl isocyanate (**2a**), 4-methoxyphenyl isocyanate (**2b**), α,α,α -trifluoro-*p*-tolyl isocyanate (**2c**), 2,6-dimethylphenyl isocyanate (**2d**), cyclohexyl isocyanate (**2e**) and butyl isocyanate (**2f**) were purchased from Aldrich, dried over phosphorous pentoxide, and degassed prior to use. 3,9-Dodecadiyne (**12**), propargyl ether (**16**) and 3-hexyne, and 2,9-undecadiyne (**22**) were purchased from GFS chemicals, Aldrich and Lancaster, respectively, and were dried over calcium hydride, and degassed prior to use. Diynes 2,2-di-but-2-ynyl-malonic acid dimethyl ester (**1**), 2,2-bis-(4-methyl-pent-2-ynyl)-malonic acid dimethyl ester (**10**),² *N,N*-di-2-butynyl-*p*-toluenesulfonamide (**14**),³ and 2,2-di-prop-2-ynyl-malonic acid dimethyl ester (**18**)⁴ were prepared according to literature procedures.

¹H and ¹³C NMR spectra were recorded on a Varian VXL-300 spectrometer and a Varian VXR-500 spectrometer and referenced to residual protiated solvent (resonances downfield to the standard are reported as positive). All ¹³C NMR spectra were proton decoupled. IR spectra were recorded on a Bruker Tensor 27 spectrometer. Elemental analyses were performed at Midwest Microlab LLC., Indianapolis, IN.

General co-cycloaddition procedure of internal diynes: A toluene solution of Ni(COD)₂ and SIPr was prepared and allowed to equilibrate for at least 6h.² In a glove box, a solution of diyne and isocyanate in toluene was added to an oven-dried vial equipped with a stir bar. To the stirring solution, a solution of Ni(COD)₂ and SIPr was added and the reaction was stirred at room temperature for 30 minutes (or until complete consumption of starting material was observed as judged by GC). The mixture was then concentrated and purified by silica gel column chromatography. This procedure was used for the cycloaddition unless otherwise noted.

2-Butyl-1,4-dimethyl-3-oxo-2,3,5,7-tetrahydro-[2]pyrindine-6,6-dicarboxylic acid dimethyl ester (3): The general procedure was used with diyne **1** (200 mg, 0.85 mmol, 0.1 M), phenyl isocyanate **2a** (100 mg, 0.85 mmol, 0.1 M), Ni(COD)₂ (7.0 mg, 0.025 mmol, 3 mol %), SIPr (9.8 mg, 0.025 mmol, 3 mol %) and 8.5 mL of toluene. The reaction mixture was purified by column chromatography on silica gel (hexane/ethyl acetate 1:2) to afford **3** as a white solid (264 mg, 88 %). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.62-7.52 (m, 3H), 7.25 (d, 7.0 Hz, 2H), 3.90 (s, 6H), 3.58 (s, 2H), 3.50 (s, 2H), 2.17 (s, 3H), 1.96 (s, 3H); ¹³C {¹H} NMR (125 MHz, CDCl₃, ppm): δ 171.8, 164.2, 150.3, 139.7, 136.3, 129.8, 128.6, 128.3, 121.0, 116.7, 59.5, 53.4, 39.6, 37.9, 18.5, 13.4; IR (KBr pellet): 1744, 1666, 1616, 1572; Anal. Calcd for C₂₀H₂₁NO₅: C, 67.59; H, 5.96; N, 3.94, found: C, 67.55; H, 5.99; N, 3.99.

2-(4-Methoxy-phenyl)-1,4-dimethyl-3-oxo-2,3,5,7-tetrahydro-[2]pyrindine-6,6-dicarboxylic acid dimethyl ester (5): The general procedure was used with diyne **1** (100 mg, 0.42 mmol, 0.1 M), 4-

methoxyphenyl isocyanate **2b** (63 mg, 0.42 mmol, 0.1 M), Ni(COD)₂ (3.5 mg, 0.013 mmol, 3 mol %), SIPr (4.9 mg, 0.013 mmol, 3 mol %) and 4.2 mL of toluene. The reaction mixture was purified by column chromatography on silica gel (10% hexanes in ethyl acetate) to afford **5** as a white solid (140 mg, 86 %). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.06 (d, 9.0 Hz, 2H), 6.99 (d, 9.0 Hz, 2H), 3.85 (s, 3H), 3.80 (s, 6H), 3.47 (s, 2H), 3.39 (s, 2H), 2.07 (s, 3H), 1.88 (s, 3H); ¹³C {¹H} NMR (125 MHz, CDCl₃, ppm): δ 171.8, 164.5, 159.5, 150.1, 136.8, 132.4, 129.2, 120.8, 116.5, 115.0, 59.5, 55.7, 53.4, 39.5, 37.9, 18.5, 13.4; IR (KBr pellet): 1730, 1666, 1614, 1574; Anal. Calcd for C₂₁H₂₃NO₆: C, 65.44; H, 6.02; N, 3.63, found: C, 65.39; H, 6.15; N, 3.72.

1,4-Dimethyl-3-oxo-2-(4-trifluoromethyl-phenyl)-2,3,5,7-tetrahydro-[2]pyrindine-6,6-dicarboxylic acid dimethyl ester (6): In a glove box, a solution of diyne **1** (50 mg, 0.21 mmol, 0.1 M) and α,α,α-trifluoro-*p*-tolyl isocyanate **2c** (40 mg, 0.21 mmol, 0.1 M) in toluene (1.3 mL) was added to an oven dried screw-cap vial. The vial was removed from the glove box and heated in an oil bath at 80 °C for several minutes. A solution of Ni(COD)₂ (2.9 mg, 0.011 mmol, 5 mol %) and SIPr (4.1 mg, 0.011 mmol, 5 mol %) in toluene (0.8 mL) was added via syringe and the reaction was heated for 30 minutes. The mixture was then concentrated and purified by chromatography on silica gel (hexane/ethyl acetate 1:2) to afford **6** as a white solid (75 mg, 84 %). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.78 (d, 8.2 Hz, 2H), 7.31 (d, 8.2 Hz, 2H), 3.81 (s, 6H), 3.49 (s, 2H), 3.40 (s, 2H), 2.08 (s, 3H), 1.86 (s, 3H); ¹³C {¹H} NMR (125 MHz, CDCl₃, ppm): δ 171.7, 164.0, 150.8, 142.9, 135.6, 131.0 (q, J²(C,F) = 33.0 Hz), 129.1, 127.0, 124.0 (q, J¹(C,F) = 272.3 Hz), 121.3, 117.2, 59.5, 53.5, 39.6, 37.8, 18.5, 13.4; IR (KBr pellet): 1740, 1671, 1620, 1579; Anal. Calcd for C₂₁H₂₀F₃NO₅: C, 59.57; H, 4.76; N, 3.31, found: C, 59.43; H, 4.87; N, 3.22.

2-(2,6-Dimethyl-phenyl)-1,4-dimethyl-3-oxo-2,3,5,7-tetrahydro-[2]pyrindine-6,6-dicarboxylic acid dimethyl ester (7): The general procedure was used with diyne **1** (50 mg, 0.21 mmol, 0.1 M), 2,6-dimethylphenyl isocyanate **2d** (31 mg, 0.21 mmol, 0.1 M), Ni(COD)₂ (1.7 mg, 0.006 mmol, 3 mol %), SIPr (2.4 mg, 0.006 mmol, 3 mol %) and 4.2 mL of toluene. The reaction was complete after 2 hours as monitored by gas chromatography. The reaction mixture was purified by column chromatography on silica gel (10% hexanes in diethyl ether) to afford **7** as a white solid (67 g, 83 %). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.24-7.13 (m, 3H), 3.80 (6H), 3.51 (s, 2H), 3.42 (s, 2H), 2.08 (s, 3H), 1.99 (s, 6H), 1.76 (s, 3H); ¹³C {¹H} NMR (125 MHz, CDCl₃, ppm): δ 171.8, 162.8, 150.5, 138.0, 135.7, 135.1, 128.8, 128.6, 121.0, 117.0, 59.5, 53.4, 39.6, 37.9, 17.9, 17.1, 13.4; IR (KBr pellet): 1734, 1667, 1614, 1578; Anal. Calcd for C₂₂H₂₅NO₅: C, 68.91; H, 6.57; N, 3.65, found: C, 68.77; H, 6.61; N, 3.62.

2-Cyclohexyl-1,4-dimethyl-3-oxo-2,3,5,7-tetrahydro-[2]pyrindine-6,6-dicarboxylic acid dimethyl ester (8): The general procedure was used with diyne **1** (50 mg, 0.21 mmol, 0.1 M), cyclohexyl isocyanate **2e** (27 mg, 0.21 mmol, 0.1 M), Ni(COD)₂ (1.7 mg, 0.006 mmol, 3 mol %), SIPr (2.4 mg, 0.006 mmol, 3 mol %) and 4.2 mL of toluene. The reaction mixture was purified by column chromatography on silica gel (hexane/diethyl ether 1:1) to afford **8** as a white solid (70 mg, 91 %). ¹H NMR (300 MHz, CDCl₃, ppm): δ 3.90-3.77 (m, 7H), 3.39-3.37 (m, 4H), 2.91-2.88 (m, 2H), 2.26 (s, 3H), 2.00 (s, 3H), 1.88 (m, 2H), 1.62 – 1.58 (m, 3H), 1.30-1.28 (3H); ¹³C {¹H} NMR (125 MHz, CDCl₃, ppm): δ 171.9, 164.5, 148.6, 136.0, 121.9, 117.2, 60.6, 59.4, 53.4, 39.4, 38.6, 28.4, 26.8, 25.4, 18.1, 13.4; IR (KBr pellet): 1742, 1670, 1619, 1582; Anal. Calcd for C₂₀H₂₇NO₅: C, 66.46; H, 7.53; N, 3.88, found: C, 66.63; H, 7.73; N, 3.98.

2-Butyl-1,4-dimethyl-3-oxo-2,3,5,7-tetrahydro-[2]pyrindine-6,6-dicarboxylic acid dimethyl ester (9): The general procedure was used with diyne **1** (50 mg, 0.21 mmol, 0.1 M), butyl isocyanate **2f** (42 mg, 0.21 mmol, 0.1 M), Ni(COD)₂ (1.7 mg, 0.006 mmol, 3 mol %), SIPr (2.4 mg, 0.006 mmol, 3 mol %) and 4.2 mL of toluene. The reaction mixture was purified by column chromatography on silica gel (diethyl ether) to afford **9** as a white solid (67 mg, 94 %). ¹H NMR (300 MHz, CDCl₃, ppm): δ 3.97 (t, 8.0 Hz, 2H), 3.77 (s, 6H), 3.41 (s, 2H), 3.37 (s, 2H), 2.28 (s, 3H), 2.04 (s, 3H), 1.68-1.57 (m, 2H), 1.48-1.35 (m, 2H), 0.96 (t, 7.3 Hz, 3H); ¹³C {¹H} NMR (125 MHz, CDCl₃, ppm): δ 171.8, 163.6, 149.1, 136.0, 120.3, 116.9, 59.4, 53.4, 44.9, 39.5, 38.2, 30.9, 20.6, 17.2, 14.0, 13.6; IR (KBr pellet): 1732, 1664, 1610, 1587; Anal. Calcd for C₁₈H₂₅NO₅: C, 64.46; H, 7.51; N, 4.18, found: C, 64.34; H, 7.63; N, 4.12.

Dimethyl 2-butyl-2,3-dihydro-1,4-diisopropyl-3-oxo-5H-cyclopenta[c]pyridine-6,6(7H)-dicarboxylate (11): The general procedure was used with diyne **10** (47 mg, 0.16 mmol, 0.1 M), butyl isocyanate **2f** (16 mg, 0.16 mmol, 0.1 M), Ni(COD)₂ (2.2 mg, 0.008 mmol, 5 mol %), SIPr (3.1 mg, 0.008 mmol, 5 mol %) and 1.6 mL of toluene. The reaction mixture was purified by column chromatography on silica gel (hexane/ethyl acetate 1:1) to afford **11** as a colorless oil (54 mg, 86%). ¹H NMR (300 MHz, CDCl₃, ppm): δ 4.00 (s, 2H), 3.76 (s, 6H), 3.42 (s, 2H), 3.41 (s, 2H), 3.24-3.12 (m, 2H), 1.64-1.56 (m, 2H), 1.48-1.25 (m, 14H), 0.97 (t, 2.4 Hz, 3H); ¹³C {¹H} NMR (125 MHz, CDCl₃, ppm): δ 171.6, 162.4, 149.2, 146.2, 129.3, 115.5, 60.4, 53.3, 44.6, 38.5, 38.0, 32.0, 30.2, 28.8, 20.5, 20.4, 20.2, 14.0; IR (CHCl₃): 1738, 1651, 1564; Anal. Calcd for C₂₂H₃₃NO₅: C, 67.49; H, 8.50; N, 3.58, found: C, 67.55; H, 8.31; N, 3.61.

2-Cyclohexyl-1,4-diethyl-5,6,7,8-tetrahydro-2H-isoquinolin-3-one (13): The general procedure was used with diyne **12** (200 mg, 1.23 mmol, 0.1 M), cyclohexyl isocyanate **2e** (154 mg, 1.23 mmol, 0.1 M), Ni(COD)₂ (10.2 mg, 0.037 mmol, 3 mol %), SIPr (14.4 mg, 0.037 mmol, 3 mol %) and 12.3 mL of toluene. The reaction mixture was purified by column chromatography on silica gel (hexane/ethyl acetate 3:1) to afford **13** as a white solid (348 mg, 98 %). ¹H NMR (300 MHz, CDCl₃, ppm): δ 3.94 (t, 11.3 Hz, 1H), 3.02 (q, 12.2 Hz, 2H), 2.64-1.90 (m, 8H), 1.90-1.87 (m, 2H), 1.72-1.58 (m, 7H), 1.37-1.26 (m, 3H), 1.18 (t, 7.5 Hz, 3H), 1.06 (t, 7.5 Hz, 3H); ¹³C {¹H} NMR (125 MHz, CDCl₃, ppm): δ 162.6, 145.3, 143.8, 130.1, 113.1, 60.5, 28.8, 27.2, 26.9, 26.4, 25.5, 23.4, 22.6, 22.5, 19.8, 13.0, 12.6; IR (KBr pellet): 1634, 1580, 1568, 1529, 1455; Anal. Calcd for C₁₉H₂₉NO: C, 79.39; H, 10.17; N, 4.87, found: C, 79.32; H, 10.24; N, 4.91.

4,7-Dimethyl-5-phenyl-2-(toluene-4-sulfonyl)-1,2,3,5-tetrahydro-pyrrolo[3,4-c]pyridin-6-one (15): The general procedure was used with diyne **14** (100 mg, 0.36 mmol, 0.1 M), phenyl isocyanate **2a** (43 mg, 0.36 mmol, 0.1 M), Ni(COD)₂ (3.0 mg, 0.011 mmol, 3 mol %), SIPr (4.2 mg, 0.011 mmol, 3 mol %) and 3.6 mL of toluene. The reaction mixture was purified by column chromatography on silica gel (hexane/ethyl acetate 1:4) afford **15** as white solid (112 mg, 78 %). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.80 (d, 8.2 Hz, 2H), 7.51-7.36 (m, 5H), 7.09 (d, 7.0 Hz, 2H), 4.44 (s, 2H), 4.40 (s, 2H), 2.45 (s, 3H), 2.00 (s, 3H), 1.80 (s, 3H); ¹³C {¹H} NMR (125 MHz, CDCl₃, ppm): δ 163.9, 146.2, 144.3, 139.0, 136.3, 133.5, 130.2, 130.0, 129.0, 128.1, 127.9, 120.2, 113.4, 52.5, 51.4, 21.8, 18.5, 13.4; IR (KBr pellet): 1675, 1625, 1582; Anal. Calcd for C₂₂H₂₂N₂O₃S: C, 66.98; H, 5.62; N, 7.10, found: C, 66.75; H, 5.84; N, 6.87.

5-Phenyl-3,5-dihydro-1H-furo[3,4-c]pyridine-6-one (17):⁵ In a glove box, a solution of Ni(COD)₂ (7.0 mg, 0.025 mmol, 5 mol %) and SIPr (9.9 mg, 0.025 mmol, 5 mol %) in toluene (2.1 mL) was added to an oven dried vial. To the stirring solution, a solution of propargyl ether **16** (48 mg, 0.51 mmol, 0.05 M) and phenyl isocyanate **2a** (61 mg, 0.51 mmol, 0.05 M) was added slowly over one minute and the reaction was stirred at room temperature for 30 minutes. The reaction was concentrated and the residue was purified by column chromatography on silica gel (ethyl acetate/hexane 4:1) to afford a yellowish solid (42 mg, 39 %). This solid was dissolved in 5 mL of methanol, stirred with a small amount of charcoal for several minutes, filtered and concentrated. The resulting solid was recrystallized in CH₂Cl₂/hexane to afford **17** as a white solid (34 mg, 31 %). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.51-7.37 (m, 5H), 7.26 (s, 1H), 6.52 (s, 1H), 4.93 (s, 2H), 4.90 (s, 2H); ¹³C {¹H} NMR (125 MHz, CDCl₃, ppm): δ 162.4, 155.3, 141.4, 129.8, 129.6, 128.7, 126.8, 119.1, 112.3, 71.8, 70.0; IR (KBr pellet): 1686, 1616.

3-Oxo-2-phenyl-2,3,5,7-tetrahydro-[2]pyrindine-6,6-dicarboxylic acid dimethyl ester (19):⁵ In a glove box, a solution of Ni(COD)₂ (3.3mg, 0.012 mmol, 5 mol %) and SIPr (4.7 mg, 0.012 mmol, 5 mol %) in toluene (0.95 mL) was added to an oven dried vial. To the stirring solution, phenyl isocyanate **2a** (115 mg, 0.96 mmol, 0.20 M) was added followed by slow addition of a solution of diyne **18** (50 mg, 0.24 mmol, 0.05 M) in toluene (3.8 mL) over one minute and the reaction was stirred at room temperature for 30 minutes. The reaction was concentrated and the residue was purified by column chromatography on silica gel (ethyl acetate) to afford **19** as a white solid (57 mg, 72 %). ¹H NMR (500 MHz, CDCl₃, ppm): δ 7.49-7.35 (m, 5H), 7.18 (s, 1H), 6.51 (s, 1H), 3.79 (s, 6H), 3.48 (d, 1.0 Hz, 2H), 3.38 (d, 0.9 Hz, 2H); ¹³C

$\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , ppm): δ 171.3, 162.5, 155.9, 141.5, 132.0, 129.5, 128.5, 126.9, 119.3, 115.6, 60.8, 53.5, 40.0, 36.7; IR (KBr pellet): 1736, 1682, 1621, 1269.

2-Cyclohexyl-3-oxo-2,3,5,7-tetrahydro-[2]pyrindine-6,6-dicarboxylic acid dimethyl ester (20):⁵ In a glove box, a solution of $\text{Ni}(\text{COD})_2$ (3.3mg, 0.012 mmol, 5 mol %) and SIPr (4.7 mg, 0.012 mmol, 5 mol %) in toluene (0.95 mL) was added to an oven dried vial. To the stirring solution, cyclohexyl isocyanate **2e** (120 mg, 0.96 mmol, 0.20 M) was added followed by slow addition of a solution of diyne **18** (50 mg, 0.24 mmol, 0.05 M) in toluene (3.8 mL) over one minute and the reaction was stirred at room temperature for 30 minutes. The reaction was concentrated and the residue was purified by column chromatography on silica gel (ethyl acetate) to afford **20** as a white solid (62 mg, 77 %). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.17 (s, 1H), 6.41 (s, 1H), 4.91-4.82 (m, 1H), 3.77 (s, 6H), 3.41 (d, 1.1 Hz, 2H), 3.36 (s, 2H), 1.92-1.15 (m, 10H); ^{13}C $\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , ppm): δ 171.4, 162.3, 154.0, 127.5, 119.1, 114.5, 60.8, 53.9, 53.4, 40.0, 37.1, 33.0, 26.0, 25.7; IR (KBr pellet): 1738, 1677, 1596.

2-Benzyl-3-oxo-2,3,5,7-tetrahydro-[2]pyrindine-6,6-dicarboxylic acid dimethyl ester (21):⁵ In a glove box, a solution of $\text{Ni}(\text{COD})_2$ (3.3mg, 0.012 mmol, 5 mol %) and SIPr (4.7 mg, 0.012 mmol, 5 mol %) in toluene (0.95 mL) was added to an oven dried vial. To the stirring solution, a solution of diyne **18** (50 mg, 0.24 mmol, 0.05 M) and benzyl isocyanate **2g** (32 mg, 0.24 mmol, 0.05 M) was added slowly over one minute and the reaction was stirred at room temperature for 30 minutes. The reaction was concentrated and the residue was purified by column chromatography on silica gel (ethyl acetate/hexane 4:1) to afford a yellowish solid (51 mg, 62%), which is pure as observed by ^1H NMR. This solid was dissolved in 5 mL of methanol and stirred with a small amount of charcoal for several minutes. The solution was filtered and concentrated in vacuo to afford **21** as a white solid (50 mg, 61 %). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.31-7.24 (m, 5H), 7.08 (s, 1H), 6.43 (s, 1H), 5.05 (s, 2H), 3.71 (s, 6H), 3.38 (d, 1.2 Hz, 2H), 3.26 (d, 1.0 Hz, 2H); ^{13}C $\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , ppm): δ 171.5, 162.6, 155.3, 136.7, 131.1, 128.9, 128.3, 128.0, 119.5, 114.8, 60.7, 53.3, 52.0, 39.9, 36.7; IR (KBr pellet): 1737, 1672, 1601.

2-Butyl-1,4-dimethyl-2,5,6,7,8,9-hexahydro-cyclohepta[c]pyridine-3-one (23): In a glove box, a solution of $\text{Ni}(\text{COD})_2$ (4.8mg, 0.018 mmol, 5 mol %) and SIPr (6.8 mg, 0.018 mmol, 5 mol %) in toluene (1.4 mL) was added to an oven dried screw-cap vial. The vial was removed from the glove box and heated in an oil bath at 80 °C minutes for several minutes. To the stirring solution, a solution of diyne **22** (52 mg, 0.35 mmol, 0.05 M) and butyl isocyanate **2f** (35 mg, 0.35 mmol, 0.05 M) in toluene (5.6 mL) was added slowly over one minute via syringe. After 30 minutes, the solvent was removed in vacuo and the residue was purified by chromatography on silica gel (hexane/ether 1:5) to afford **23** as a white solid (32 mg, 37 %). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 4.07 (t, 7.9 Hz, 2H), 2.72 (t, 5.2 Hz, 2H), 2.63 (t, 5.2 Hz, 2H), 2.35 (s, 3H), 2.15 (s, 3H), 1.72-1.40 (m, 10H), 0.97 (t, 7.2 Hz, 3H); ^{13}C $\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , ppm): δ 163.0, 151.8, 136.4, 121.9, 120.1, 45.4, 31.0, 30.9, 30.7, 29.0, 28.5, 27.2, 20.6, 16.1, 14.0, 13.1; IR (CHCl_3): 1639, 1588, 1543; Anal. Calcd for $\text{C}_{16}\text{H}_{25}\text{NO}$: C, 77.68; H, 10.19; N, 5.66, found: C, 77.69; H, 10.07; N, 5.58.

3,4,5,6-Tetraethyl-1-phenyl-1H-pyridine-2-one (24):⁶ In a glove box, a solution of 3-hexyne (50 mg, 0.61 mmol, 0.1 M) and phenyl isocyanate **2a** (73 mg, 0.61 mmol, 0.1 M) in toluene (4.7 mL) was added to an oven dried vial. To the stirring solution, a solution of $\text{Ni}(\text{COD})_2$ (5.0 mg, 0.018 mmol, 3 mol %) and SIPr (7.0 mg, 0.018 mmol, 3 mol %) in toluene (1.5 mL) was added. After 30 minutes, the solvent was removed in vacuo and the residue was purified by column chromatography (ether) to give colorless oil. Recrystallization from hexane gave **24** as a white solid (78 mg, 90 %). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.52-7.21 (m, 5H), 2.63-2.57 (m, 4H), 2.49 (q, 7.5 Hz, 2H), 2.36 (q, 7.5 Hz, 2H), 1.21-1.15 (m, 9H), 0.95 (t, 7.5 Hz, 3H); ^{13}C $\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , ppm): δ 163.0, 151.6, 144.3, 140.0, 130.0, 129.4, 128.7, 128.2, 117.7, 23.2, 22.6, 21.0, 20.7, 16.1, 15.0, 14.0, 13.7; IR (KBr pellet): 1642, 1579, 1529; Anal. Calcd for $\text{C}_{19}\text{H}_{25}\text{NO}$: C, 80.52; H, 8.89; N, 4.94, found: C, 80.64, H, 9.28; N, 4.90.

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