

Supporting Information

Metal-Free [3 + 2 + 1] Annulation of Allylic Alcohols, Ketones, and Ammonium Acetate: Radical-Involved Synthesis of 2,3-Diarylpyridine Derivatives

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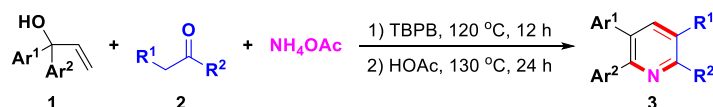
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General information

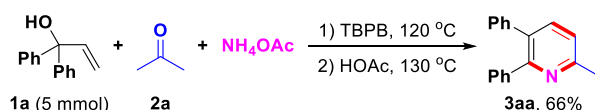
Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out under air atmosphere using undistilled solvent. Melting points were recorded on an Electrothermal digital melting point apparatus. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. ^1H , ^{19}F , and ^{13}C NMR spectra were recorded in CDCl_3 on Bruker Avance or Joel 400 MHz spectrometers. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. High resolution mass spectra (HRMS) were obtained using a commercial apparatus (ESI Source). Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions.

General procedure for the synthesis of pyridines 3



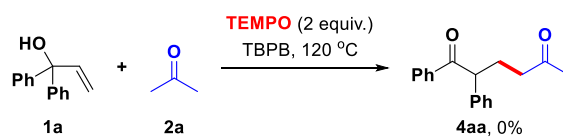
A solution of diaryl allylic alcohol **1** (0.5 mmol), ketone **2** (4 mL), NH_4OAc (154 mg, 2.0 mmol), and *tert*-butylperoxybenzoate (TBPB, 194 mg, 1.0 mmol) was stirred at 120 °C under air for 12 h. Upon completion of the reaction (indicated by TLC), the organic solvent (ketone **2**) was removed under vacuum. HOAc (3 mL) was added to above system, and the mixture was stirred at 130 °C under air for 24 h. The reaction was then quenched by saturated NaHCO_3 solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (100/1 ~ 20/1) as eluent to afford the pure products **3**.

General procedure for the large scale synthesis of pyridine 3aa



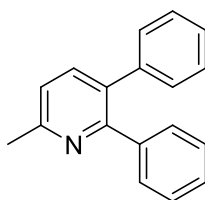
A solution of diaryl allylic alcohol **1a** (1.1 g, 5 mmol), acetone (**2a**, 20 mL), NH_4OAc (1.54 g, 20 mmol), and *tert*-butylperoxybenzoate (TBPB, 1.94 g, 10 mmol) was stirred at 120 °C under air for 12 h. Upon completion of the reaction (indicated by TLC), the organic solvent (acetone) was removed under vacuum. HOAc (30 mL) was added to above system, and the mixture was stirred at 130 °C under air for 24 h. The reaction was then quenched by saturated NaHCO_3 solution (20 mL x 3) and extracted with EtOAc (100 mL x 3). The organic layer was washed with saturated brine twice, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (100/1 ~ 20/1) as eluent to afford the pure product **3aa** (0.8 g, 66% yield).

Mechanistic study

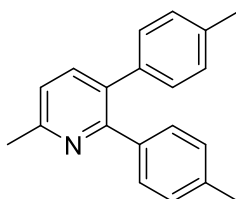


A solution of diaryl allylic alcohol **1a** (105 mg, 0.5 mmol), acetone (**2a**, 4 mL), NH_4OAc (154 mg, 2.0 mmol), *tert*-butylperoxybenzoate (TBPB, 194 mg, 1.0 mmol), and 2,2,6,6-tetramethylpiperidinoxy (TEMPO, 156 mg, 1 mmol) was stirred at 120 °C under air for 12 h. No desired 1,5-dicarbonyl compound **4aa** was observed. **This result suggested that radical intermediate was involved in the reaction.**

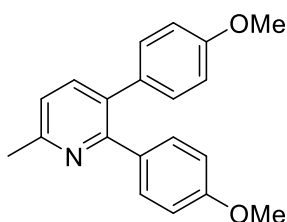
Characterization data for products:



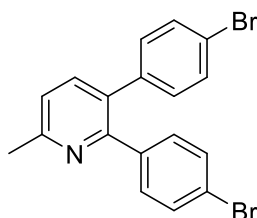
6-Methyl-2,3-diphenylpyridine (3aa): Yield = 71 %. White solid. M.p. 84.0–85.9 °C. ^1H NMR (400MHz, CDCl_3): δ = 7.61 (d, J = 7.8 Hz, 1H), 7.36–7.32 (m, 2H), 7.25–7.17 (m, 7H), 7.16–7.17 (m, 2H), 2.66 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 157.3, 156.7, 140.6, 140.3, 139.0, 133.3, 130.1, 129.8, 128.4, 128.1, 127.8, 127.1, 121.9, 24.6 ppm. HRMS m/z : calcd for $\text{C}_{18}\text{H}_{16}\text{N}$ $[\text{M}+\text{H}]^+$ 246.1277, found: 246.1286.



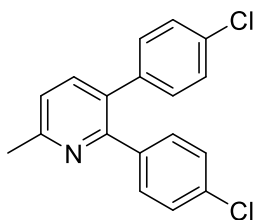
6-Methyl-2,3-di-*p*-tolylpyridine (3ba): Yield = 48 %. White solid. M.p. 105–107 °C. ^1H NMR (400MHz, CDCl_3): δ = 7.57 (d, J = 7.8 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.14 (d, J = 7.8 Hz, 1H), 7.08 – 7.01 (m, 6H), 2.63 (s, 3H), 2.32 (s, 3H), 2.30 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 157.0, 156.6, 138.9, 137.9, 137.5, 137.4, 136.7, 133.0, 130.0, 129.6, 129.1, 128.8, 121.6, 24.6, 21.4, 21.3 ppm. HRMS m/z : calcd for $\text{C}_{20}\text{H}_{20}\text{N}$ $[\text{M}+\text{H}]^+$ 274.1590, found: 274.1598.



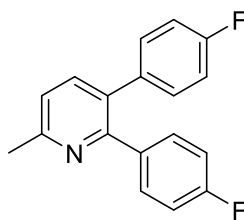
2,3-Bis(4-methoxyphenyl)-6-methylpyridine (3ca): Yield = 55 %. White solid. M.p. 110.0–112.0 °C. ^1H NMR (400MHz, CDCl_3): δ = 7.55 (d, J = 7.8 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.12 (d, J = 7.8 Hz, 1H), 7.10 – 7.05 (m, 2H), 6.83 – 6.75 (m, 4H), 3.79 (s, 3H), 3.77 (s, 3H), 2.63 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 159.3, 158.7, 156.8, 156.2, 138.9, 133.3, 132.8, 132.5, 132.4, 131.4, 130.8, 121.4, 113.9, 55.4, 55.4, 24.6 ppm. HRMS m/z : calcd for $\text{C}_{20}\text{H}_{20}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 306.1489, found: 306.1493.



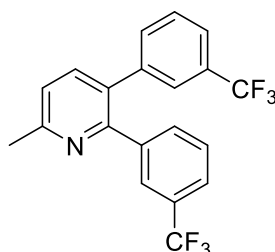
2,3-Bis(4-bromophenyl)-6-methylpyridine (3da): Yield = 60 %. White solid. M.p. 164.9–166.6 °C. ^1H NMR (400MHz, CDCl_3): δ = 7.57 (d, J = 7.9 Hz, 1H), 7.44 – 7.36 (m, 4H), 7.24 – 7.17 (m, 3H), 7.04 – 6.98 (m, 2H), 2.64 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 158.0, 155.3, 139.2, 138.9, 138.9, 132.1, 131.8, 131.8, 131.5, 131.3, 122.5, 122.3, 121.7, 24.6 ppm. HRMS m/z : calcd for $\text{C}_{18}\text{H}_{14}\text{Br}_2\text{N}$ $[\text{M}+\text{H}]^+$ 401.9488, found: 401.9489.



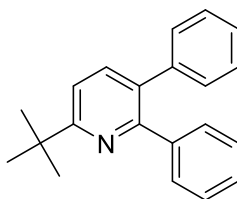
2,3-Bis(4-chlorophenyl)-6-methylpyridine (3ea): Yield = 52 %. White solid. M.p. 159.2–161.4 °C. ^1H NMR (400MHz, CDCl_3): δ = 7.57 (d, J = 7.9 Hz, 1H), 7.29 – 7.26 (m, 3H), 7.25 – 7.18 (m, 4H), 7.10 – 7.04 (m, 2H), 2.65 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 157.9, 155.3, 138.9, 138.8, 138.4, 134.2, 133.5, 132.1, 131.5, 131.0, 128.9, 128.5, 122.3, 24.6 ppm. HRMS m/z : calcd for $\text{C}_{18}\text{H}_{14}\text{Cl}_2\text{N}$ $[\text{M}+\text{H}]^+$ 314.0498, found: 314.0500.



2,3-Bis(4-fluorophenyl)-6-methylpyridine (3fa): Yield = 40 %. White solid. M.p. 58.7–59.8 °C. ^1H NMR (400MHz, CDCl_3): δ = 7.57 (d, J = 7.8 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.18 (d, J = 7.8 Hz, 1H), 7.13 – 7.06 (m, 2H), 7.00 – 6.88 (m, 4H), 2.65 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 162.5 (d, J = 200.3 Hz), 162.4 (d, J = 290.9 Hz), 157.6, 155.6, 138.9, 136.5 (d, J = 3.2 Hz), 136.0 (d, J = 3.4 Hz), 132.2, 131.9 (d, J = 8.2 Hz), 131.3 (d, J = 8.0 Hz), 122.1, 115.5 (d, J = 40.7 Hz), 115.3 (d, J = 40.8 Hz), 24.6 ppm. ^{19}F NMR (376 MHz, $\text{CDCl}_3\text{-}d_6$): δ = -114.28 (s, 1F), -115.18 (s, 1F) ppm. HRMS m/z : calcd for $\text{C}_{18}\text{H}_{14}\text{F}_2\text{N}$ $[\text{M}+\text{H}]^+$ 282.1089, found: 282.1097.

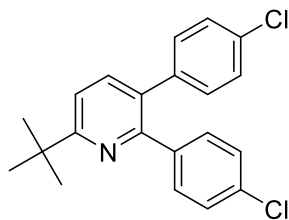


6-Methyl-2,3-bis(3-(trifluoromethyl)phenyl)pyridine (3ga): Yield = 56 %. Colourless liquid. ^1H NMR (400MHz, CDCl_3): δ = 7.66 (d, J = 7.9 Hz, 1H), 7.59 (s, 1H), 7.54 – 7.47 (m, 3H), 7.42 – 7.33 (m, 3H), 7.31 – 7.25 (m, 2H), 2.68 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 158.5, 155.2, 140.7, 140.4, 138.9, 133.4, 133.1, 132.1, 131.0 (d, J = 48.0 Hz), 130.8 (d, J = 48.0 Hz), 129.1, 128.7, 127.2 (m), 126.5 (m), 125.4 (d, J = 9.8 Hz), 124.8 (m), 124.2 (m), 122.7 (d, J = 9.8 Hz), 122.7, 24.6 ppm. ^{19}F NMR (376 MHz, CDCl_3) δ = -62.92, -62.95 ppm. HRMS m/z : calcd for $\text{C}_{20}\text{H}_{14}\text{F}_6\text{N}$ $[\text{M}+\text{H}]^+$ 382.1025, found: 382.1079.

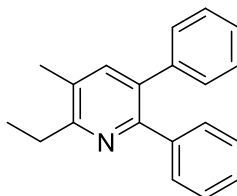


6-(tert-Butyl)-2,3-diphenylpyridine (3ab): Yield = 56 %. White solid. M.p. 112.6–114.0 °C. ^1H

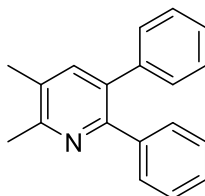
NMR (400MHz, CDCl₃): δ = 7.61 (d, J = 8.0 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.33 (d, J = 8.0 Hz, 1H), 7.27 – 7.19 (m, 6H), 7.19 – 7.14 (m, 2H), 1.44 (s, 9H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 168.0, 155.2, 140.9, 140.8, 138.9, 132.8, 130.5, 129.8, 128.4, 127.8, 127.7, 127.0, 117.4, 37.7, 30.5 ppm. HRMS m/z : calcd for C₂₁H₂₂N [M+H]⁺ 288.1747, found: 288.1753.



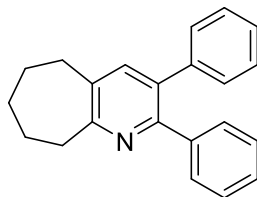
6-(*tert*-Butyl)-2,3-bis(4-chlorophenyl)pyridine (3eb): Yield = 49 %. White solid. M.p. 120.2–122.5 °C. ¹H NMR (400MHz, CDCl₃): δ = 7.58 (d, J = 8.1 Hz, 1H), 7.38 – 7.31 (m, 3H), 7.28 – 7.24 (m, 2H), 7.23 – 7.19 (m, 2H), 7.12 – 7.07 (m, 2H), 1.42 (s, 9H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 168.4, 153.7, 138.9, 138.7, 138.7, 133.8, 133.2, 131.5, 131.4, 130.8, 128.7, 128.0, 117.6, 37.5, 30.2 ppm. HRMS m/z : calcd for C₂₁H₂₀Cl₂N [M+H]⁺ 356.0967, found: 378.0789.



2-Ethyl-3-methyl-5,6-diphenylpyridine (3ac): Yield = 51 %. White solid. M.p. 118.3–119.2 °C. ¹H NMR (400MHz, CDCl₃): δ = 7.43 (s, 1H), 7.38 – 7.33 (m, 2H), 7.25 – 7.19 (m, 6H), 7.17 – 7.13 (m, 2H), 2.95 – 2.86 (m, 2H), 2.38 (s, 3H), 1.36 (t, J = 7.5 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 160.5, 154.0, 140.7, 140.5, 140.3, 133.4, 130.2, 129.8, 129.2, 128.4, 128.0, 127.5, 127.0, 28.7, 18.4, 13.2 ppm. HRMS m/z : calcd for C₂₀H₂₀N [M+H]⁺ 274.1590, found: 274.1590.

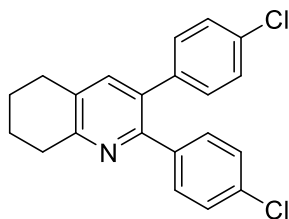


2,3-Dimethyl-5,6-diphenylpyridine (3ad): Yield = 56 %. White solid. M.p. 75.2–78.0 °C. ¹H NMR (400MHz, CDCl₃): δ = 7.44 (s, 1H), 7.36 – 7.31 (m, 2H), 7.25 – 7.18 (m, 6H), 7.16 – 7.12 (m, 2H), 2.60 (s, 3H), 2.35 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 156.0, 154.0, 140.6, 140.3, 139.8, 133.6, 130.1, 130.0, 129.8, 128.4, 128.0, 127.5, 127.0, 22.7, 18.9 ppm. HRMS m/z : calcd for C₁₉H₁₈N [M+H]⁺ 260.1434, found: 260.1423.

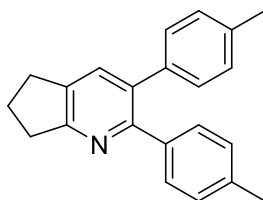


2,3-Diphenyl-6,7,8,9-tetrahydro-5H-cyclohepta[b]pyridine (3ae): Yield = 51 %. White solid. M.p. 117.0–119.5 °C. ¹H NMR (400MHz, CDCl₃): δ = 7.41 (s, 1H), 7.34 (dd, J = 6.6, 3.0 Hz, 2H), 7.26 – 7.19 (m, 6H), 7.18 – 7.14 (m, 2H), 3.19 – 3.10 (m, 2H), 2.90 – 2.80 (m, 2H), 1.97 – 1.87 (m,

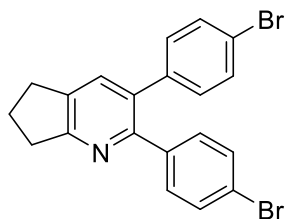
2H), 1.82 – 1.69 (m, 4H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 162.2, 153.5, 140.6, 140.4, 139.3, 136.7, 133.5, 130.2, 129.8, 128.4, 128.0, 127.5, 127.0, 39.5, 35.1, 32.8, 28.3, 26.9 ppm. HRMS m/z : calcd for $\text{C}_{22}\text{H}_{22}\text{N}$ $[\text{M}+\text{H}]^+$ 300.1747, found: 300.1749.



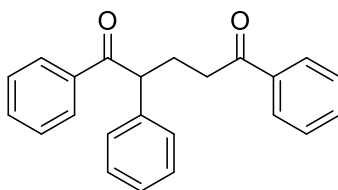
2,3-Bis(4-chlorophenyl)-5,6,7,8-tetrahydroquinoline (3ef): Yield = 75 %. White solid. M.p. 158–169 °C. ^1H NMR (400MHz, CDCl_3): δ = 7.35 (s, 1H), 7.26 – 7.18 (m, 6H), 7.06 (d, J = 8.4 Hz, 2H), 3.00 (t, J = 6.3 Hz, 2H), 2.84 (t, J = 6.2 Hz, 2H), 2.00 – 1.91 (m, 2H), 1.91 – 1.83 (m, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 156.9, 153.0, 139.1, 138.7, 138.4, 133.8, 133.3, 132.2, 131.4, 131.3, 130.9, 128.7, 128.3, 32.6, 28.6, 23.3, 22.8 ppm. HRMS m/z : calcd for $\text{C}_{21}\text{H}_{18}\text{Cl}_2\text{N}$ $[\text{M}+\text{H}]^+$ 354.0811, found: 354.0798.



2,3-Di-*p*-tolyl-6,7-dihydro-5H-cyclopenta[*b*]pyridine (3bg): Yield = 62 %. White solid. M.p. 92–94 °C. ^1H NMR (400MHz, CDCl_3): δ = 7.49 (s, 1H), 7.21 (d, J = 8.0 Hz, 2H), 7.06 – 6.98 (m, 6H), 3.10 (t, J = 7.7 Hz, 2H), 3.00 (t, J = 7.4 Hz, 2H), 2.32 (s, 3H), 2.29 (s, 3H), 2.22 – 2.17 (m, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 164.3, 155.4, 137.9, 137.9, 136.9, 136.3, 135.3, 134.6, 133.4, 129.8, 129.5, 128.9, 128.5, 34.2, 30.5, 23.4, 21.2, 21.1 ppm. HRMS m/z : calcd for $\text{C}_{22}\text{H}_{22}\text{N}$ $[\text{M}+\text{H}]^+$ 300.1747, found: 300.1745.

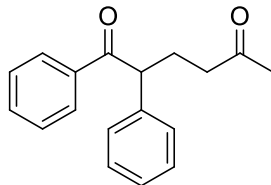


2,3-Bis(4-bromophenyl)-6,7-dihydro-5H-cyclopenta[*b*]pyridine (3dg): Yield = 63 %. White solid. M.p. 145.8–147.0 °C. ^1H NMR (400MHz, CDCl_3): δ = 7.48 (s, 1H), 7.42 – 7.34 (m, 4H), 7.21 – 7.15 (m, 2H), 7.03 – 6.97 (m, 2H), 3.10 (t, J = 7.7 Hz, 2H), 3.01 (t, J = 7.4 Hz, 2H), 2.20 (p, J = 7.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 165.5, 154.2, 139.5, 136.4, 134.6, 132.6, 131.8, 131.8, 131.5, 131.4, 122.1, 121.5, 34.4, 30.7, 23.5 ppm. HRMS m/z : calcd for $\text{C}_{20}\text{H}_{16}\text{Br}_2\text{N}$ $[\text{M}+\text{H}]^+$ 427.9644, found: 427.9640.

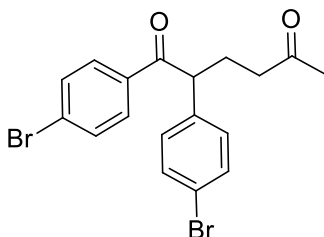


1,2,5-Triphenylpentane-1,5-dione (3ai'): Yield = 37 %. White solid. M.p. 60.5–63.5 °C. ^1H

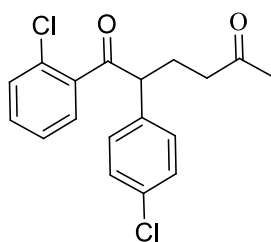
NMR (400MHz, CDCl₃): δ = 8.03 – 7.98 (m, 2H), 7.96 – 7.90 (m, 2H), 7.59 – 7.54 (m, 1H), 7.51 – 7.39 (m, 5H), 7.36 – 7.29 (m, 4H), 7.26 – 7.20 (m, 1H), 4.80 (t, J = 7.3 Hz, 1H), 3.10 – 2.89 (m, 2H), 2.67 – 2.56 (m, 1H), 2.38 – 2.25 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 200.1, 199.8, 139.3, 137.0, 136.8, 133.2, 133.1, 129.2, 128.9, 128.7, 128.7, 128.5, 128.2, 127.4, 52.6, 36.1, 28.4 ppm. HRMS m/z : calcd for C₂₃H₂₁O₂ [M+H]⁺ 329.1536, found: 329.1546.



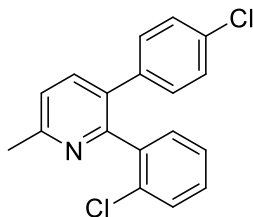
1,2-diphenylhexane-1,5-dione (4aa): Yield = 95 %. White solid. M.p. 60–62 °C. ¹H NMR (400MHz, CDCl₃): δ = 7.98 – 7.92 (m, 2H), 7.50 – 7.44 (m, 1H), 7.41 – 7.35 (m, 2H), 7.32 – 7.26 (m, 4H), 7.23 – 7.18 (m, 1H), 4.69 – 4.61 (m, 1H), 2.46 – 2.34 (m, 3H), 2.17 – 2.10 (m, 1H), 2.08 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 208.7, 199.7, 139.2, 136.8, 133.2, 129.2, 128.9, 128.7, 128.5, 127.4, 52.4, 41.2, 30.2, 27.8 ppm. HRMS m/z : calcd for C₁₈H₁₉O₂ [M+H]⁺ 267.1380, found: 267.1390.



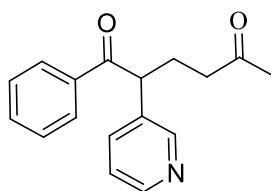
1,2-bis(4-bromophenyl)hexane-1,5-dione (4da): Yield = 84 %. Colorless oil. ¹H NMR (400MHz, CDCl₃): δ = 7.82 – 7.76 (m, 2H), 7.53 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 4.59 (t, J = 7.1 Hz, 1H), 2.43 – 2.39 (m, 2H), 2.38 – 2.30 (m, 1H), 2.09 (s, 3H), 2.08 – 2.00 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 208.4, 198.3, 137.8, 135.2, 132.5, 132.2, 130.4, 130.1, 128.6, 121.7, 51.6, 40.7, 30.3, 27.5 ppm. HRMS m/z : calcd for C₁₈H₁₇Br₂O₂ [M+H]⁺ 422.9590, found: 422.9602.



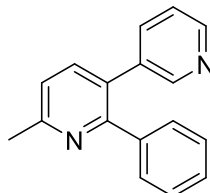
1-(2-Chlorophenyl)-2-(4-chlorophenyl)hexane-1,5-dione (4ia): Yield = 59 %. Colorless oil. ¹H NMR (400MHz, CDCl₃): δ = 7.36 – 7.28 (m, 2H), 7.28 – 7.23 (m, 2H), 7.21 – 7.15 (m, 1H), 7.14 – 7.08 (m, 3H), 4.51 – 4.45 (m, 1H), 2.48 – 2.40 (m, 3H), 2.10 (s, 3H), 2.09 – 2.05 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 208.2, 202.7, 139.4, 136.0, 133.7, 131.7, 130.6, 130.5, 130.2, 129.3, 129.1, 126.9, 56.0, 40.9, 30.2, 26.5 ppm. HRMS m/z : calcd for C₁₈H₁₇Cl₂O₂ [M+H]⁺ 335.0600, found: 335.0619.



2-(2-Chlorophenyl)-3-(4-chlorophenyl)-6-methylpyridine (3ha): Yield = 75 %. White solid. M.p. 64–65.2 °C. ^1H NMR (400MHz, CDCl_3): δ = 7.62 (d, J = 7.9 Hz, 1H), 7.31 – 7.20 (m, 5H), 7.16 (d, J = 8.5 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 2.65 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 157.4, 155.0, 139.5, 138.0, 137.7, 133.4, 133.3, 133.0, 131.7, 130.6, 129.8, 129.5, 128.4, 126.9, 122.9, 24.5 ppm. HRMS m/z : calcd for $\text{C}_{18}\text{H}_{14}\text{Cl}_2\text{N}$ $[\text{M}+\text{H}]^+$ 314.0498, found: 314.0507.



1-Phenyl-2-(pyridin-3-yl)hexane-1,5-dione (4ja): Yield = 64 %. White solid. M.p. 99.3–101.9 °C. ^1H NMR (400MHz, CDCl_3): δ = 8.58 (s, 1H), 8.49 (d, J = 3.6 Hz, 1H), 7.97 (d, J = 7.4 Hz, 2H), 7.64 (d, J = 7.9 Hz, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.24 (dd, J = 7.8, 4.7 Hz, 1H), 4.75 (t, J = 7.0 Hz, 1H), 2.51 – 2.37 (m, 3H), 2.16 – 2.04 (m, 4H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 208.12, 199.10, 150.12, 148.90, 136.28, 135.67, 134.92, 133.61, 128.94, 128.87, 124.12, 49.30, 40.80, 30.22, 27.76 ppm. HRMS m/z : calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 268.1332, found: 268.1340.



6-Methyl-2-phenyl-3,3'-bipyridine (3ja): Yield = 55 %. White solid. M.p. 71.1–72.2 °C. ^1H NMR (400MHz, CDCl_3): δ = 8.55 – 8.41 (m, 2H), 7.63 (d, J = 7.8 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.34 – 7.29 (m, 2H), 7.27 – 7.21 (m, 4H), 7.18 – 7.12 (m, 1H), 2.68 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 158.3, 157.1, 150.2, 148.3, 139.9, 138.8, 137.1, 136.0, 130.1, 129.6, 128.4, 128.2, 123.1, 122.1, 24.7 ppm. HRMS m/z : calcd for $\text{C}_{17}\text{H}_{15}\text{N}_2$ $[\text{M}+\text{H}]^+$ 247.1230, found: 247.1229.

^1H , ^{19}F , and ^{13}C NMR spectra of products:

