

Supplementary material

Palladium-catalysed direct arylation of heteroarenes using 1-bromophenyl-1,2,3-triazoles as aryl sources

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General: All reactions were performed in Schlenk tubes under argon. Potassium acetate 99+ was used. DMA (99%) was purchased from Acros. Pd(OAc)₂, [Pd(C₃H₅)Cl]₂, 1,4-bis(diphenylphosphino)butane (98%) were purchased from Alfa Aesar. The heteroarenes were used without purification. NMR spectra were recorded on Bruker GPX (400 MHz) spectrometer in CDCl₃ solutions. Chemical shifts are reported in ppm relative to CDCl₃ (¹H: 7.26 and ¹³C: 77.0). Flash chromatography was performed on silica gel (230-400 mesh).

Preparation of the PdCl(C₃H₅)(dppb) catalyst [1]: An oven-dried 40 mL Schlenk tube equipped with a magnetic stirring bar under argon atmosphere, was charged with [Pd(C₃H₅)Cl]₂ (182 mg, 0.5 mmol) and dppb (426 mg, 1 mmol). 10 mL of anhydrous dichloromethane were added, then, the solution was stirred at room temperature for twenty minutes. The solvent was removed in vacuum. The yellow powder was used without purification. ³¹P NMR (81 MHz, CDCl₃) δ = 19.3 (s).

The bromo-substituted 1-aryl-1,2,3-triazoles 1-7 were prepared using a reported procedure [2].

In a typical experiment, the β-dicarbonyl compound (1 mmol), morpholine (0.087 g, 1 mmol) and the bromophenyl azide (1 mmol) were dissolved in Et₂O (2 mL). The reaction mixture was stirred at room temperature for 24 h. Then, the solvent was evaporated and the product was recrystallized in ethanol or purified by silica gel column chromatography (pentane:AcOEt).

General procedure for the synthesis of compounds 8-26: In a typical experiment, the 1-(bromophenyl)-1,2,3-triazole **1-6** (1 mmol), heteroarene (1.5 mmol), KOAc (0.196 g, 2 mmol) and Pd(OAc)₂ (2.2 mg, 0.01 mmol) or PdCl(C₃H₅)(dppb) (6.1 mg, 0.01 mmol) (see table or schemes) were dissolved in DMA (4 mL) under an argon atmosphere. The reaction mixture was stirred at 150 °C for 16 h. Then, the solvent was evaporated and the product was purified by silica gel column chromatography.

Ethyl 1-(4-(2-ethyl-4-methylthiazol-5-yl)phenyl)-5-methyl-1,2,3-triazole-4-carboxylate (8)

From ethyl 1-(4-bromophenyl)-5-methyl-1,2,3-triazole-4-carboxylate **1** (0.310 g, 1 mmol) and 2-ethyl-4-methylthiazole (0.191 g, 1.5 mmol), **8** was obtained in 91% (0.324 g) yield.

¹H NMR (400 MHz, CDCl₃): δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 4.47 (q, *J* = 7.4 Hz, 2H), 3.03 (q, *J* = 7.4 Hz, 2H), 2.65 (s, 3H), 2.51 (s, 3H), 1.45 (t, *J* = 7.4 Hz, 3H), 1.42 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 171.1, 161.7, 148.1, 138.9, 136.8, 134.6, 134.4, 130.2, 129.1, 125.5, 61.1, 26.9, 16.1, 14.4, 14.2, 10.0.

elemental analysis: calcd (%) for C₁₈H₂₀N₄O₂S (356.44): C 60.65, H 5.66; found: C 60.71, H 5.48.

Ethyl 5-methyl-1-(4-(5-methylthiophen-2-yl)phenyl)-1,2,3-triazole-4-carboxylate (9)

From ethyl 1-(4-bromophenyl)-5-methyl-1,2,3-triazole-4-carboxylate **1** (0.310 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), **9** was obtained in 87% (0.284 g) yield.

¹H NMR (400 MHz, CDCl₃): δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 3.5 Hz, 1H), 6.80 (d, *J* = 3.5 Hz, 1H), 4.50 (q, *J* = 7.4 Hz, 2H), 2.64 (s, 3H), 2.56 (s, 3H), 1.48 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 161.8, 141.2, 139.8, 138.8, 136.8, 136.6, 133.8, 126.6, 126.3, 125.7, 124.3, 61.1, 15.5, 14.3, 10.1.

elemental analysis: calcd (%) for C₁₇H₁₇N₃O₂S (327.40): C 62.37, H 5.23; found: C 62.50, H 5.12.

Ethyl 1-(4-(5-acetylthiophen-2-yl)phenyl)-5-methyl-1,2,3-triazole-4-carboxylate (10)

From ethyl 1-(4-bromophenyl)-5-methyl-1,2,3-triazole-4-carboxylate **10** (0.310 g, 1 mmol) and 2-acetylthiophene (0.189 g, 1.5 mmol), **9** was obtained in 85% (0.301 g) yield.

¹H NMR (400 MHz, CDCl₃): δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 3.5 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 3.5 Hz, 1H), 4.48 (q, *J* = 7.4 Hz, 2H), 2.65 (s, 3H), 2.61 (s, 3H), 1.47 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 190.4, 161.6, 150.1, 144.4, 138.7, 136.9, 135.5, 135.1, 133.3, 127.3, 125.9, 125.1, 61.1, 26.7, 14.3, 10.1.

elemental analysis: calcd (%) for C₁₈H₁₇N₃O₃S (355.41): C 60.83, H 4.82; found: C 60.96, H 4.75.

Ethyl 1-(4-(5-cyanothiophen-2-yl)phenyl)-5-methyl-1,2,3-triazole-4-carboxylate (11)

From ethyl 1-(4-bromophenyl)-5-methyl-1,2,3-triazole-4-carboxylate **1** (0.310 g, 1 mmol) and thiophene-2-carbonitrile (0.164 g, 1.5 mmol), **11** was obtained in 87% (0.294 g) yield.

¹H NMR (400 MHz, CDCl₃): δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 3.5 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 3.5 Hz, 1H), 4.50 (q, *J* = 7.4 Hz, 2H), 2.67 (s, 3H), 1.48 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 161.6, 149.3, 138.8, 138.5, 137.1, 136.0, 134.0, 127.6, 126.1, 124.5, 113.9, 109.8, 61.1, 14.4, 10.1.

elemental analysis: calcd (%) for C₁₇H₁₄N₄O₂S (338.39): C 60.34, H 4.17; found: C 60.12, H 4.31.

Ethyl 1-(4-(5-butylfuran-2-yl)phenyl)-5-methyl-1,2,3-triazole-4-carboxylate (12)

From ethyl 1-(4-bromophenyl)-5-methyl-1,2,3-triazole-4-carboxylate **1** (0.310 g, 1 mmol) and 2-*n*-butylfuran (0.186 g, 1.5 mmol), **12** was obtained in 82% (0.289 g) yield.

¹H NMR (400 MHz, CDCl₃): δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 3.2 Hz, 1H), 6.12 (d, *J* = 3.2 Hz, 1H), 4.49 (q, *J* = 7.4 Hz, 2H), 2.72 (t, *J* = 7.4 Hz, 2H), 2.61 (s, 3H), 1.70 (quint., *J* = 7.4 Hz, 2H), 1.53-1.40 (m, 5H), 0.97 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 161.7, 157.7, 150.3, 138.8, 136.7, 133.3, 132.8, 125.5, 124.0, 107.7, 107.3, 61.0, 30.1, 27.8, 22.2, 14.3, 13.7, 10.0.

elemental analysis: calcd (%) for C₂₀H₂₃N₃O₃ (353.42): C 67.97, H 6.56; found: C 68.11, H 6.44.

Ethyl 1-(4-(5-(methoxycarbonyl)furan-2-yl)phenyl)-5-methyl-1,2,3-triazole-4-carboxylate (13)

From ethyl 1-(4-bromophenyl)-5-methyl-1,2,3-triazole-4-carboxylate **1** (0.310 g, 1 mmol) and methyl furan-2-carboxylate (0.189 g, 1.5 mmol), **13** was obtained in 73% (0.259 g) yield.

¹H NMR (400 MHz, CDCl₃): δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 3.6 Hz, 1H), 6.90 (d, *J* = 3.6 Hz, 1H), 4.50 (q, *J* = 7.4 Hz, 2H), 3.97 (s, 3H), 2.66 (s, 3H), 1.48 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 161.7, 159.0, 155.5, 144.5, 138.8, 135.4, 131.1, 125.9, 125.7, 119.9, 108.5, 61.2, 52.0, 14.4, 10.1.

elemental analysis: calcd (%) for C₁₈H₁₇N₃O₅ (355.35): C 60.84, H 4.82; found: C 60.71, H 4.61.

Ethyl 1-(4-(4-(methoxycarbonyl)-5-methylfuran-2-yl)phenyl)-5-methyl-1,2,3-triazole-4-carboxylate (14)

From ethyl 1-(4-bromophenyl)-5-methyl-1,2,3-triazole-4-carboxylate **1** (0.310 g, 1 mmol) and methyl 2-methylfuran-3-carboxylate (0.210 g, 1.5 mmol), **14** was obtained in 83% (0.306 g) yield.

¹H NMR (400 MHz, CDCl₃): δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.03 (s, 1H), 4.48 (q, *J* = 7.4 Hz, 2H), 3.88 (s, 3H), 2.70 (s, 3H), 2.63 (s, 3H), 1.47 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 164.1, 161.7, 159.7, 150.0, 138.8, 136.8, 134.2, 131.6, 125.7, 124.5, 115.5, 107.4, 61.1, 51.5, 14.4, 13.9, 10.0.

elemental analysis: calcd (%) for C₁₉H₁₉N₃O₅ (369.38): C 61.78, H 5.18; found: C 61.90, H 5.24.

Ethyl 1-(4-(5-formyl-1-methyl-pyrrol-2-yl)phenyl)-5-methyl-1,2,3-triazole-4-carboxylate (15)

From ethyl 1-(4-bromophenyl)-5-methyl-1,2,3-triazole-4-carboxylate **1** (0.310 g, 1 mmol) and 1-methylpyrrole-2-carbaldehyde (0.163 g, 1.5 mmol), **15** was obtained in 77% (0.260 g) yield.

¹H NMR (400 MHz, CDCl₃): δ 9.65 (s, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 4.1 Hz, 1H), 6.42 (d, *J* = 4.1 Hz, 1H), 4.50 (q, *J* = 7.4 Hz, 2H), 4.00 (s, 3H), 2.68 (s, 3H), 1.48 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 179.9, 161.7, 142.0, 138.8, 137.0, 135.4, 133.6, 133.0, 130.4, 125.5, 124.3, 111.4, 61.2, 34.5, 14.4; 10.1.

elemental analysis: calcd (%) for C₁₈H₁₈N₄O₃ (338.37): C 63.89, H 5.36; found: C 63.70, H 5.21.

Ethyl 1-(4-(3,5-dimethylisoxazol-4-yl)phenyl)-5-methyl-1,2,3-triazole-4-carboxylate (16)

From ethyl 1-(4-bromophenyl)-5-methyl-1,2,3-triazole-4-carboxylate **1** (0.310 g, 1 mmol) and 3,5-dimethylisoxazole (0.146 g, 1.5 mmol), **16** was obtained in 92% (0.300 g) yield.

¹H NMR (400 MHz, CDCl₃): δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 4.48 (q, *J* = 7.4 Hz, 2H), 2.66 (s, 3H), 2.47 (s, 3H), 2.32 (s, 3H), 1.46 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 165.8, 161.6, 158.3, 138.8, 136.8, 134.6, 132.6, 130.2, 125.7, 115.4, 61.1, 14.3, 11.6, 10.8, 10.0.

elemental analysis: calcd (%) for $C_{17}H_{18}N_4O_3$ (326.36): C 62.57, H 5.56; found: C 62.67, H 5.39.

Ethyl 5-ethyl-1-(4-(2-ethyl-4-methylthiazol-5-yl)phenyl)-1,2,3-triazole-4-carboxylate (17)

From ethyl 1-(4-bromophenyl)-5-ethyl-1,2,3-triazole-4-carboxylate **2** (0.324 g, 1 mmol) and 2-ethyl-4-methylthiazole (0.191 g, 1.5 mmol), **17** was obtained in 90% (0.333 g) yield.

1H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, $J = 8.4$ Hz, 2H), 7.49 (d, $J = 8.4$ Hz, 2H), 4.48 (q, $J = 7.4$ Hz, 2H), 3.10-3.00 (m, 4H), 2.52 (s, 3H), 1.46 (t, $J = 7.4$ Hz, 3H), 1.42 (t, $J = 7.4$ Hz, 3H), 1.22 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 161.6, 148.3, 144.6, 136.3, 135.0, 134.6, 130.3, 129.2, 126.0, 61.2, 27.1, 17.2, 16.3, 14.5, 14.3, 13.4.
elemental analysis: calcd (%) for $C_{19}H_{22}N_4O_2S$ (370.47): C 61.60, H 5.99; found: C 61.41, H 5.87.

Ethyl 1-(4-(2-ethyl-4-methylthiazol-5-yl)phenyl)-5-phenyl-1,2,3-triazole-4-carboxylate (18)

From ethyl 1-(4-bromophenyl)-5-phenyl-1,2,3-triazole-4-carboxylate **3** (0.372 g, 1 mmol) and 2-ethyl-4-methylthiazole (0.191 g, 1.5 mmol), **18** was obtained in 85% (0.355 g) yield.

1H NMR (400 MHz, $CDCl_3$): δ 7.50-7.25 (m, 9H), 4.39 (q, $J = 7.4$ Hz, 2H), 3.01 (q, $J = 7.4$ Hz, 2H), 2.46 (s, 3H), 1.41 (t, $J = 7.4$ Hz, 3H), 1.35 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.0, 160.9, 148.0, 140.7, 137.1, 134.7, 133.9, 130.2, 130.0, 129.7, 129.1, 128.4, 125.7, 125.2, 61.2, 26.9, 16.2, 14.2, 14.1.

elemental analysis: calcd (%) for $C_{23}H_{22}N_4O_2S$ (418.52): C 66.01, H 5.30; found: C 65.89, H 5.21.

ethyl 1-(4-(3,5-dimethylisoxazol-4-yl)phenyl)-5-phenyl-1H-1,2,3-triazole-4-carboxylate (19)

From ethyl 1-(4-bromophenyl)-5-phenyl-1,2,3-triazole-4-carboxylate **3** (0.372 g, 1 mmol) and 3,5-dimethylisoxazole (0.146 g, 1.5 mmol), **19** was obtained in 83% (0.322 g) yield.

1H NMR (400 MHz, $CDCl_3$): δ 7.50-7.33 (m, 7H), 7.29 (d, $J = 8.4$ Hz, 2H), 4.38 (q, $J = 7.4$ Hz, 2H), 2.41 (s, 3H), 2.26 (s, 3H), 1.34 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 160.8, 158.2, 140.7, 137.1, 134.9, 131.9, 130.2, 130.0, 129.7, 128.4, 125.6, 125.4, 115.3, 61.2, 14.1, 11.6, 10.7.

elemental analysis: calcd (%) for $C_{22}H_{20}N_4O_3$ (388.43): C 68.03, H 5.19; found: C 68.10, H 5.04.

Ethyl 1-(3-(2-ethyl-4-methylthiazol-5-yl)phenyl)-5-methyl-1,2,3-triazole-4-carboxylate (20)

From ethyl 1-(3-bromophenyl)-5-methyl-1,2,3-triazole-4-carboxylate **4** (0.310 g, 1 mmol) and 2-ethyl-4-methylthiazole (0.191 g, 1.5 mmol), **20** was obtained in 87% (0.310 g) yield.

1H NMR (400 MHz, $CDCl_3$): δ 7.62-7.56 (m, 2H), 7.48 (s, 1H), 7.39 (d, $J = 8.4$ Hz, 1H), 4.43 (q, $J = 7.4$ Hz, 2H), 2.96 (q, $J = 7.4$ Hz, 2H), 2.61 (s, 3H), 2.46 (s, 3H), 1.42 (t, $J = 7.4$ Hz, 3H), 1.37 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 161.5, 149.0, 140.0, 136.3, 134.3, 132.5, 130.9, 130.0, 129.7, 128.4, 124.7, 61.0, 26.5, 15.3, 14.3, 13.9, 9.3.

elemental analysis: calcd (%) for $C_{18}H_{20}N_4O_2S$ (356.44): C 60.65, H 5.66; found: C 60.47, H 5.41.

Ethyl 5-methyl-1-(3-(5-methylthiophen-2-yl)phenyl)-1,2,3-triazole-4-carboxylate (21)

From ethyl 1-(3-bromophenyl)-5-methyl-1,2,3-triazole-4-carboxylate **4** (0.310 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), **21** was obtained in 81% (0.265 g) yield.

1H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, $J = 8.4$ Hz, 1H), 7.62 (s, 1H), 7.56 (t, $J = 7.8$ Hz, 1H), 7.31 (d, $J = 8.4$ Hz, 1H), 7.20 (d, $J = 3.5$ Hz, 1H), 6.79 (d, $J = 3.5$ Hz, 1H), 4.50 (q, $J = 7.4$ Hz, 2H), 2.64 (s, 3H), 2.55 (s, 3H), 1.48 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7, 141.1, 139.6, 138.9, 136.8, 136.6, 136.0, 130.0, 126.8, 126.5, 124.3, 123.3, 122.2, 61.1, 15.5, 14.4, 10.0.

elemental analysis: calcd (%) for $C_{17}H_{17}N_3O_2S$ (327.40): C 62.37, H 5.23; found: C 62.52, H 5.14.

Ethyl 1-(3-(3,5-dimethylisoxazol-4-yl)phenyl)-5-methyl-1,2,3-triazole-4-carboxylate (22)

From ethyl 1-(3-bromophenyl)-5-methyl-1,2,3-triazole-4-carboxylate **4** (0.310 g, 1 mmol) and 3,5-dimethylisoxazole (0.146 g, 1.5 mmol), **22** was obtained in 92% (0.300 g) yield.

1H NMR (400 MHz, $CDCl_3$): δ 7.66 (t, $J = 7.8$ Hz, 1H), 7.47 (d, $J = 8.4$ Hz, 2H), 7.37 (s, 1H), 4.46 (q, $J = 7.4$ Hz, 2H), 2.64 (s, 3H), 2.44 (s, 3H), 2.30 (s, 3H), 1.44 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 161.5, 158.1, 138.7, 136.8, 135.9, 132.4, 130.5, 130.1, 125.7, 124.2, 115.2, 61.0, 14.3, 11.6, 10.7, 10.0.

elemental analysis: calcd (%) for $C_{17}H_{18}N_4O_3$ (326.36): C 62.57, H 5.56; found: C 62.47, H 5.60.

Ethyl 1-(3-(2-ethyl-4-methylthiazol-5-yl)phenyl)-5-phenyl-1,2,3-triazole-4-carboxylate (23)

From ethyl 1-(3-bromophenyl)-5-phenyl-1,2,3-triazole-4-carboxylate **5** (0.372 g, 1 mmol) and 2-ethyl-4-methylthiazole (0.191 g, 1.5 mmol), **23** was obtained in 94% (0.393 g) yield.

^1H NMR (400 MHz, CDCl_3): δ 7.50-7.25 (m, 9H), 4.37 (q, $J = 7.4$ Hz, 2H), 2.97 (q, $J = 7.4$ Hz, 2H), 2.17 (s, 3H), 1.37 (t, $J = 7.4$ Hz, 3H), 1.32 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 171.1, 160.9, 147.9, 140.8, 137.2, 136.1, 133.9, 130.3, 130.1, 130.0, 129.7, 128.8, 128.6, 125.8, 125.5, 124.0, 61.3, 26.9, 15.8, 14.2, 14.1.

elemental analysis: calcd (%) for $\text{C}_{23}\text{H}_{22}\text{N}_4\text{O}_2\text{S}$ (418.52): C 66.01, H 5.30; found: C 65.87, H 5.22.

Ethyl 1-(2-(2-ethyl-4-methylthiazol-5-yl)phenyl)-5-methyl-1,2,3-triazole-4-carboxylate (**24**)

From ethyl 1-(2-bromophenyl)-5-methyl-1,2,3-triazole-4-carboxylate **6** (0.310 g, 1 mmol) and 2-ethyl-4-methylthiazole (0.191 g, 1.5 mmol), **24** was obtained in 90% (0.320 g) yield.

^1H NMR (400 MHz, CDCl_3): δ 7.65 (t, $J = 7.8$ Hz, 1H), 7.62-7.42 (m, 3H), 4.44 (q, $J = 7.4$ Hz, 2H), 2.94 (q, $J = 7.4$ Hz, 2H), 2.29 (s, 3H), 2.22 (s, 3H), 1.44 (t, $J = 7.4$ Hz, 3H), 1.31 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 173.3, 161.5, 149.0, 140.1, 136.3, 134.3, 132.5, 130.9, 130.0, 129.8, 128.4, 124.7, 61.0, 26.5, 15.3, 14.3, 13.9, 9.3.

elemental analysis: calcd (%) for $\text{C}_{18}\text{H}_{20}\text{N}_4\text{O}_2\text{S}$ (356.44): C 60.65, H 5.66; found: C 60.47, H 5.41.

Ethyl 5-methyl-1-(2-(5-methylthiophen-2-yl)phenyl)-1,2,3-triazole-4-carboxylate (**25**)

From ethyl 1-(2-bromophenyl)-5-methyl-1,2,3-triazole-4-carboxylate **6** (0.310 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), **25** was obtained in 92% (0.301 g) yield.

^1H NMR (400 MHz, CDCl_3): δ 7.69 (d, $J = 8.2$ Hz, 1H), 7.60 (t, $J = 7.8$ Hz, 1H), 7.47 (t, $J = 7.8$ Hz, 1H), 7.37 (d, $J = 8.2$ Hz, 1H), 6.55 (d, $J = 3.5$ Hz, 1H), 6.33 (d, $J = 3.5$ Hz, 1H), 4.45 (q, $J = 7.4$ Hz, 2H), 2.42 (s, 3H), 2.18 (s, 3H), 1.46 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 161.7, 142.1, 140.5, 136.3, 135.1, 132.7, 131.8, 131.1, 130.1, 128.6, 128.1, 126.6, 126.3, 61.0, 15.2, 14.3, 9.0.

elemental analysis: calcd (%) for $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2\text{S}$ (327.40): C 62.37, H 5.23; found: C 62.42, H 5.31.

Ethyl [1,2,3]triazolo[1,5-f]phenanthridine-3-carboxylate (**26**) [3]

From ethyl 1-(2-bromophenyl)-5-phenyl-1,2,3-triazole-4-carboxylate **7** (0.372 g, 1 mmol) **26** was obtained in 85% (0.247 g) yield.

^1H NMR (400 MHz, CDCl_3): δ 9.80 (d, $J = 8.0$ Hz, 1H), 8.93 (d, $J = 8.0$ Hz, 1H), 8.52 (d, $J = 8.0$ Hz, 2H), 7.88-7.68 (m, 4H), 4.63 (q, $J = 7.4$ Hz, 2H), 1.58 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 162.5, 133.7, 132.8, 130.8, 130.6, 129.9, 129.0, 128.9, 128.7, 128.0, 123.5, 122.6, 122.4, 121.4, 117.6, 61.7, 14.4.

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