Supporting Information
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Synthesis of Tetrasubstituted Furans via Sequential Pd(OAc)$_2$/Zn(OTf)$_2$ Catalyzed Oxidation and Cyclization of Aromatic Alkynes with Molecular Oxygen

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Supporting Information

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A. General method

$^1$H and $^{13}$C NMR spectra were recorded on BRUKER DRX-400 spectrometer using CDCl$_3$ as solvent and TMS as an internal standard. Mass spectra were obtained with a SHIMADZU model GCMS-QP5000 spectrometer.

B. General Procedure for Substrate 1a-1f

The reaction was carried out in a HF-15 autoclave. Pd(OAc)$_2$ (4.49 mg, 0.02 mmol), Zn(OTf)$_2$ (98.3 mg, 0.3 mmol), MeOH (3 mL), alkyne (1 mmol) were added into a 15 mL autoclave in sequence. O$_2$ were pumped into the autoclave by a cooling pump to reach the desired pressure, then the autoclave was heated by oil bath under magnetic stirring for the desired reaction time. After the reaction finished, the autoclave was allowed to cool to 0 °C. Residual O$_2$ was vented and the surplus was filtrated and condensed under reduced pressure. The product was purified by chromatography on a silica gel column using light petroleum ether/CH$_2$Cl$_2$ as eluent.

C. Analytical data for 2a-2f, 3e

![Diagram of 2,3,4,5-Tetraphenylfuran](image1)

**2,3,4,5-Tetraphenylfuran**

mp 171–172 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.13–7.16 (m, 4 H), 7.20–7.26 (m, 12 H), 7.49–7.51 (m, 4 H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 125.1, 125.8, 127.1, 127.3, 128.3, 128.5, 130.4, 130.9, 133.1, 147.7 ppm; MS (EI, 70 eV) m/z (%): 372 (M$^+$, 100), 267 (34), 165 (19), 77 (11).

![Diagram of 2,3,4,5-Tetra-p-tolylfuran](image2)

**2,3,4,5-Tetra-p-tolylfuran**

mp 186–187 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 2.30 (s, 12 H), 7.02 (s, 8 H), 7.04 (d, J = 8.0 Hz, 4 H), 7.37 (d, J = 8.4 Hz, 4 H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 21.3, 29.7, 124.3, 125.8, 128.4, 128.7, 129.0, 130.2, 130.3, 136.5, 136.9, 147.5 ppm; MS (EI, 70 eV) m/z (%): 372 (M$^+$, 100), 267 (34), 165 (19), 77 (11).
eV) m/z (%): 428 (M⁺, 100), 309 (29), 119 (73), 91 (28).

2,3,4,5-Tetrakis(4-methoxyphenyl)furan

mp 206–208 °C ¹H NMR (CDCl₃, 400 MHz) δ 3.78 (s, 12 H), 6.77 (d, J = 6.4 Hz, 4 H), 6.79 (d, J = 7.2 Hz, 4 H), 7.04 (d, J = 8.8 Hz, 4 H), 7.42 (d, J = 9.2 Hz, 4 H); ¹³C NMR (CDCl₃, 100 MHz) δ 125.1, 125.8, 127.1, 127.3, 128.3, 128.5, 130.4, 130.9, 133.1, 147.7 ppm; MS (EI, 70 eV) m/z (%): 492 (M⁺, 28), 318 (100), 275 (31), 135 (47).

2,3,4,5-Tetrakis(4-fluorophenyl)furan

¹H NMR (CDCl₃, 400 MHz) δ 6.93 (m, 8 H), 7.05–7.08 (m, 4 H), 7.41–7.44 (m, 4 H); ¹³C NMR (CDCl₃, 100 MHz) δ 115.6 (t, J = 80 Hz), 123.5, 126.7, 127.6, 127.7, 128.6, 131.9, 147.1, 160.9, 163.4 ppm; MS (EI, 70 eV) m/z (%): 444 (M⁺, 100), 321 (73), 123 (69), 95 (55).

2,3,4,5-Tetrakis(4-(trifluoromethyl)phenyl)furan

mp 195–197 °C; ¹H NMR (CDCl₃, 400 MHz) δ 7.24 6 (d, J = 8.0 Hz, 4 H), 7.55–7.57 (m, 12 H); ¹³C NMR (CDCl₃, 100 MHz) δ 119.9, 122.6, 125.1, 125.3, 125.7, 125.9, 126.2, 127.3, 128.0, 129.0, 129.8, 129.9, 130.1, 130.5, 133.0, 135.6, 148.0 ppm; MS (EI, 70 eV) m/z (%): 644(M⁺, 46), 471 (13), 173 (100), 145 (33).
**2,3,4,5-Tetram-tolylfuran**

mp 100–102 °C ¹H NMR (CDCl₃, 400 MHz) δ2.17 (s, 6 H), 2.27 (s, 6 H), 6.91–7.22 (m, 12 H), 7.62–7.66 (m, 4 H); ¹³C NMR (CDCl₃, 100 MHz) δ 21.3, 29.7, 123.0, 127.0, 127.6, 127.9, 128.1, 129.0, 129.2, 130.1, 130.2, 133.7, 135.3, 136.4, 137.9, 138.14, 144.2 ppm; MS (EI, 70 eV) m/z (%): 428 (M⁺, 100), 309 (21), 119 (65), 91 (18).

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**2,3,4,5-Tetram-tolylfuran**

mp 100–102 °C ¹H NMR (CDCl₃, 400 MHz) δ2.17 (s, 6 H), 2.27 (s, 6 H), 6.91–7.22 (m, 12 H), 7.62–7.66 (m, 4 H); ¹³C NMR (CDCl₃, 100 MHz) δ 21.3, 29.7, 123.0, 127.0, 127.6, 127.9, 128.1, 129.0, 129.2, 130.1, 130.2, 133.7, 135.3, 136.4, 137.9, 138.14, 144.2 ppm; MS (EI, 70 eV) m/z (%): 428 (M⁺, 100), 309 (21), 119 (65), 91 (18).

**Z)-1,2,3,4-Tetraphenylbut-2-ene-1,4-dione**

mp 216–217 °C; ¹H NMR (CDCl₃, 400 MHz) δ 7.14–7.40 (m, 16 H), 7.82–7.84 (m, 4 H); ¹³C NMR (CDCl₃, 100 MHz) δ 128.3, 128.4, 128.5, 128.6, 129.8, 130.0, 133.0, 135.2, 136.3, 144.6, 196.9 ppm; MS (EI, 70 eV) m/z (%): 388 (M⁺, 12), 178 (9), 105 (100), 77 (43).

**D. Procedure for cyclization of 1,4-dione (A):**

The reaction was carried out in a HF-15 autoclave. Pd(OAc)₂ (4.49 mg, 0.02 mmol), Zn(OTf)₂ (98.3 mg, 0.3 mmol), MeOH (3 mL), 1,4-dione (A) (388 mg, 1 mmol) were added into a 15 mL autoclave in sequence. O₂ were pumped into the autoclave by a cooling pump to reach the desired pressure, then the autoclave was heated by oil bath under magnetic stirring for the desired reaction time. After the reaction finished, the autoclave was allowed to cool to 0 °C. O₂ was vented and the surplus was filtrated and condensed under reduced pressure. The product was purified by chromatography on a silica gel column using light petroleum ether/CH₂Cl₂ as eluent to give 2a in 72 % yield.

**E. References in Supporting Information**


F. NMR spectra

$^1$H NMR spectrum of sample Az-3-30-1

$^{13}$C NMR spectrum of sample Az-9-1
1H NMR spectrum of sample Az-9-18-4

13C NMR spectrum of sample Az-9-18-4
1H NMR spectrum of sample Az-9-10-3

13C NMR spectrum of sample Az-9-10-3