Supporting Information for:

Ligand-Free and Recyclable Palladium(II) Acetate Catalyzes the Decarboxylative Cross-Coupling of Alkynyl Carboxylic Acids with Arylboronic Acids in Aqueous PEG-400

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List of Contents

(A) General ................................................................. 2

(B) Reusable Experimental Procedure .............................................................. 2

(C) Analytical data for 3 ................................................................. 2

(E) Spectra ................................................................. 6
(A) General

All reactions were carried out in air without any protection of inert gases. Starting materials were purchased from common commercial sources and used without further purification. All products were isolated by chromatography on a silica gel (300–400 mesh) using petroleum ether (60 °C–90 °C) and ethyl acetate. $^1$H NMR and $^{13}$C spectra were recorded on a Bruker Avance 400 MHz spectrometer.

(B) Reusable Experimental Procedure

After initial experimentation, the reaction mixture was extracted with petroleum ether/ethyl acetate (10:1), and the Pd(OAc)$_2$/H$_2$O/PEG-400 system was then evaporated in vacuo and cooled, and subjected to a second run of the decarboxylative cross-coupling reaction by charging with 1a (0.3 mmol), 2 (0.5 mmol), Ag$_2$O (1 equiv), base (2 equiv), air, and 4 h at 80 °C.

(C) Analytical data for 3

1-methoxy-4-(2-phenylethynyl)benzene (3a, CAS:7380-78-1)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.52 – 7.49 (m, 2H), 7.46 (d, $J = 8.8$ Hz, 2H), 7.34 – 7.27 (m, 3H), 6.86 (d, $J = 8.8$ Hz, 2H), 3.80 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.6, 133.0, 131.4, 128.3, 127.9, 123.6, 115.3, 114.0, 89.4, 88.0, 55.2.

1-methyl-4-(2-phenylethynyl)benzene (3c, CAS:3287-02-3)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.55 – 7.51 (m, 4H), 7.37 – 7.28 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 131.6, 128.3, 128.2, 123.3, 89.4.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53 – 7.51 (m, 2H), 7.42 (d, $J$ = 8.0 Hz, 2H), 7.36 – 7.30 (m, 3H), 7.15 (d, $J$ = 8.0 Hz, 2H), 2.36 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.4, 131.5, 131.5, 129.1, 128.3, 128.1, 123.5, 120.2, 89.5, 88.7, 21.5.

1-methyl-3-(2-phenylethynyl)benzene (3d, CAS:14635-91-7)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53 – 7.51 (m, 2H), 7.36 (s, 1H), 7.50 – 7.31 (m, 4H), 7.23 (t, $J$ = 7.6 Hz, 1H), 7.13 (d, $J$ = 7.6 Hz, 1H), 2.34 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.0, 132.2, 131.6, 129.1, 128.7, 128.3, 128.2, 128.1, 123.4, 123.0, 89.5, 89.0, 21.2.

1-methyl-2-(2-phenylethynyl)benzene (3e, CAS:14309-60-5)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 – 7.49 (m, 3H), 7.36 – 7.30 (m, 3H), 7.22 (d, $J$ = 4.0 Hz, 2H), 7.18 – 7.14 (m, 1H), 2.51 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.2, 131.8, 131.5, 129.4, 128.3, 128.1, 125.6, 123.5, 123.0, 93.3, 88.3, 20.7.

1-chloro-4-(2-phenylethynyl)benzene (3f, CAS:5172-02-1)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53– 7.50 (m, 2H), 7.46 – 7.43 (m, 2H), 7.36 – 7.29 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 134.2, 132.8, 131.6, 128.7, 128.5, 128.4, 122.9, 121.8, 90.3, 88.2.

1-chloro-3-(2-phenylethynyl)benzene (3g, CAS:51624-34-1)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54 – 7.51 (m, 3H), 7.41 – 7.39 (m, 1H), 7.36 – 7.33(m, 3H), 7.30 – 7.24 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 134.2, 131.7, 131.4, 129.7, 129.5, 128.6, 128.5, 128.4, 125.0, 122.7, 90.5, 87.9.

2-(2-phenylethynyl)naphthalene (3h, CAS:23975-17-9)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.06 (s, 1H), 7.83 – 7.80 (m, 3H), 7.59 – 7.57 (m, 3H), 7.51 – 7.47 (m, 2H), 7.39 – 7.32 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 133.0, 132.8, 131.7, 131.4, 128.4, 128.3, 127.9, 127.8, 126.6, 126.5, 123.3, 120.6, 89.8, 89.7.

1-(2-phenylethynyl)naphthalene (3i, CAS:4044-57-9)
$^1$H NMR (400 MHz, CDCl$_3$) δ 8.45 (d, $J = 8.4$ Hz, 1H), 7.85 – 7.80 (m, 2H), 7.76 – 7.75 (m, 1H), 7.66 – 7.63 (m, 2H), 7.60 – 7.56 (m, 1H), 7.53 – 7.49 (m, 1H), 7.45 – 7.41 (m, 1H), 7.40 – 7.32 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 133.3, 133.2, 131.6, 130.3, 128.7, 128.4, 128.3, 128.2, 126.8, 126.4, 126.2, 125.3, 123.4, 120.9, 94.3, 87.3.

$N, N$-dimethyl-4-(2-phenylethynyl)benzenamine (3j, CAS:14301-08-7)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.50 – 7.48 (m, 2H), 7.40 (d, $J = 8.8$ Hz, 2H), 7.39 – 7.24 (m, 3H), 6.64 (d, $J = 8.8$ Hz, 2H), 2.96 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.1, 132.7, 131.2, 128.2, 127.4, 124.1, 111.8, 110.0, 90.6, 87.3, 40.2.

4-(2-phenylethynyl)pyridine (3k, CAS:13295-94-8)

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.59 (d, $J = 6.0$ Hz, 2H), 7.39 – 7.24 (m, 2H), 7.39 – 7.24 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.7, 131.8, 131.4, 129.2, 128.4, 125.5, 122.0, 93.9, 86.6.

3-(2-phenylethynyl)pyridine (3l, CAS:13238-38-5)

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.77 (d, $J = 1.5$ Hz, 1H), 8.55 – 8.54 (m, 1H), 7.83 – 7.80 (m, 1H), 7.56 – 7.54 (m, 2H), 7.38 – 7.36 (m, 3H), 7.30 – 7.26 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 152.2, 148.5, 138.4, 131.7, 128.8, 128.4, 123.0, 122.5, 120.5, 92.6, 85.9.

1-(hept-1-ynyl)-4-methoxybenzene (3m, CAS:64146-61-8)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 (d, $J = 8.8$ Hz, 2H), 6.80 (d, $J = 8.8$ Hz, 2H), 3.78 (s, 3H), 2.38 (t, $J = 7.2$ Hz, 2H), 1.61 – 1.58 (m, 2H), 1.41 – 1.34 (m, 4H), 0.92 (t, $J = 7.2$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.9, 132.8, 116.3, 113.8, 88.8, 80.2, 55.2, 31.1, 28.6, 22.2, 19.4, 14.0.

1-methoxy-4-(prop-1-ynyl)benzene (3n, CAS:2749-94-2)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 (d, $J = 8.7$ Hz, 2H), 6.81 (d, $J = 8.7$ Hz, 2H), 3.79 (s, 3H), 2.03 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.0, 132.8, 116.2, 113.8, 84.1, 79.4, 55.2, 4.3.

4-(hept-1-ynyl)pyridine (3o, CAS:1393897-16-9)
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.52 (d, $J = 6.0$ Hz, 2H), 7.24 (d, $J = 6.0$ Hz, 2H), 2.42 (t, $J = 7.1$ Hz, 1H), 1.64 – 1.60 (m, 2H), 1.43 – 1.35 (m, 4H), 0.93 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.5, 132.4, 125.7, 96.0, 78.3, 31.0, 28.0, 22.1, 19.4, 13.9.

(E) Spectra

1-methoxy-4-(2-phenylethynyl)benzene (3a)
1-methoxy-4-(2-phenylethynyl)benzene (3a)
1,2-diphenylethyne (3b)
1,2-diphenylethyne (3b)
1-methyl-4-(2-phenylethynyl)benzene (3c)
1-methyl-4-(2-phenylethynyl)benzene (3c)
1-methyl-3-(2-phenylethynyl)benzene (3d)
1-methyl-3-(2-phenylethynyl)benzene (3d)
1-methyl-2-(2-phenylethynyl)benzene (3e)
1-methyl-2-(2-phenylethynyl)benzene (3e)
1-chloro-4-(2-phenylethynyl)benzene (3f)
1-chloro-4-(2-phenylethynyl)benzene (3f)
1-chloro-3-(2-phenylethynyl)benzene (3g)
1-chloro-3-(2-phenylethynyl)benzene (3g)
2-(2-phenylethynyl)naphthalene (3h)
2-(2-phenylethynyl)naphthalene (3h)
1-(2-phenylethynyl)naphthalene (3i)
1-(2-phenylethynyl)naphthalene (3i)
$N, N$-dimethyl-4-(2-phenylethynyl)benzenamine (3j)
N, N-dimethyl-4-(2-phenylethynyl)benzenamine (3j)
4-(2-phenylethynyl)pyridine (3k)
4-(2-phenylethynyl)pyridine (3k)
3-(2-phenylethynyl)pyridine (31)
3-(2-phenylethynyl)pyridine (31)
1-(hept-1-ynyl)-4-methoxybenzene (3m)
1-(hept-1-ynyl)-4-methoxybenzene (3m)
1-methoxy-4-(prop-1-ynyl)benzene (3n)
1-methoxy-4-(prop-1-ynyl)benzene (3n)
4-(hept-1-ynyl)pyridine (3o)
4-(hept-1-ynyl)pyridine (3o)