Supporting information for

**Palladium-catalyzed Cross-Coupling of Aryl Electrophiles with
Dimethylalkynylaluminum reagents.**

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Hept-1-ynyl-benzene¹

¹H NMR (400 MHz, CDCl₃) δ 7.41 (m, 2H), 7.27 (m, 3H), 2.42 (t, *J* = 7.1 Hz, 2H), 1.62 (m, 2H), 1.34-1.48 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H).

Hept-1-ynyl-4-methoxy-benzene²

¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 7.4 Hz, 2H), 6.82 (d, *J* = 7.4 Hz, 2H), 3.80 (s, 3H), 2.40 (t, *J* = 7.1 Hz, 2H), 1.61 (m, 2H), 1.34-1.48 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H).

Hept-1-ynyl-3-methoxy-benzene³

¹H NMR (400 MHz, CDCl₃) δ 7.19 (t, *J* = 7.9 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.94 (m, 1H), 6.82 (ddd, *J* = 8.4, 2.6, 0.8 Hz, 1H), 3.80 (s, 3H), 2.40 (t, *J* = 7.1 Hz, 2H), 1.61 (m, 2H), 1.34-1.48 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H).

Hept-1-ynyl-2-methoxy-benzene²

¹H NMR (400 MHz, CDCl₃) δ 7.39 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.24 (td, *J* = 7.5, 1.6 Hz, 1H), 6.88 (m, 2H), 3.88 (s, 3H), 2.47 (t, *J* = 7.1 Hz, 2H), 1.62 (m, 2H), 1.34-1.48 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H).

4-hept-1-ynyl-phenol

Air sensitive oil. ¹H NMR (400 MHz, CDCl₃) δ 7.28 (d, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 8.6 Hz, 2H), 4.96 (br s, 1H), 2.39 (t, *J* = 7.1 Hz, 2H), 1.61 (m, 2H), 1.34-1.48 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 155.0, 133.2, 116.6, 115.4, 89.1, 80.3, 31.2, 28.7, 22.4, 19.4, 14.13 ; IR (cm⁻¹) 3394, 2956, 2931, 2859, 1608.

1-Hept-1-ynyl-2-methyl-benzene²

¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, *J* = 7.3 Hz, 1H), 7.08-7.17 (m, 3H), 2.44 (t, *J* = 7.1 Hz, 2H), 1.62 (m, 2H), 1.34-1.48 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H).

4-Hept-1-ynyl-benzoic acid methyl ester⁴

¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 3.91 (s, 3H), 2.43 (t, *J* = 7.1 Hz, 2H), 1.61 (m, 2H), 1.34-1.48 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H).

2-Hept-1-ynyl-thiophene⁵

¹H NMR (400 MHz, CDCl₃) δ 7.17 (dd, *J* = 5.2, 1.0 Hz, 1H), 7.12 (dd, *J* = 3.5, 0.8 Hz, 1H), 6.94 (dd, *J* = 5.2, 3.5 Hz, 1H), 2.43 (t, *J* = 7.1 Hz, 2H), 1.61 (m, 2H), 1.34-1.48 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H).

2-Hept-1-ynyl-pyridine⁴

¹H NMR (400 MHz, CDCl₃) δ 8.53 (d, *J* = 4.1 Hz, 1H), 7.59 (td, *J* = 7.8, 1.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.16 (ddd, *J* = 7.8, 4.1, 1.8 Hz, 1H), 2.43 (t, *J* = 7.1 Hz, 2H), 1.61 (m, 2H), 1.34-1.48 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H).

3-Hept-1-ynyl-pyridine

Oil. ¹H NMR (400 MHz, CDCl₃) δ 8.62 (br s, 1H), 8.47 (d, *J* = 4.9 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.16 (dd, *J* = 7.8, 4.8 Hz, 1H), 2.42 (t, *J* = 7.1 Hz, 2H), 1.61 (m, 2H), 1.34-1.48 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 152.4, 147.9, 138.4, 122.9, 121.3, 94.2, 77.5, 31.2, 28.3, 22.3, 19.5, 14.1; IR (cm⁻¹) 3029, 2956, 2931, 2859, 2241, 2221, 1560, 1475, 1406 ; HRMS (ES⁺) for C₁₂H₁₆N : calcd.: 174.1283, found: 174.1279.

2,5-Di-hept-1-ynyl-pyridine

Oil. ¹H NMR (400 MHz, CDCl₃) δ 8.54 (d, *J* = 1.3 Hz, 1H), 7.58 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 1H), 2.43 (m, 4H), 1.63 (m, 4H), 1.34-1.48 (m, 8H), 0.92 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 152.4, 142.0, 138.4, 126.0, 119.7, 95.5, 92.7, 80.3, 77.5, 31.2, 28.3, 28.1, 22.3, 19.6, 19.5, 14.0; IR (cm⁻¹) 2931, 2860, 2225, 1468, 1363 ; HRMS (ES⁺) for C₁₂H₁₆N : calcd.: 268.2065, found: 268.2053.

1,3-Dichloro-2-hept-1-ynyl-benzene

Oil. ^1H NMR (400 MHz, CDCl_3) δ 7.29 (t, $J = 8.1$ Hz, 2H), 7.11 (t, $J = 8.1$ Hz, 1H), 2.54 (t, $J = 7.0$ Hz, 2H), 1.68 (m, 2H), 1.47-1.55 (m, 2H), 1.35-1.40 (m, 2H), 0.93 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.2, 128.2, 127.4, 124.0, 102.3, 77.4, 75.13, 28.2, 22.3, 19.9, 14.1; IR (cm^{-1}) 2931, 2859, 2240, 1553, 1446, 1428, 789, 774, 720.

Diphenylacetylene⁶

^1H NMR (400 MHz, CDCl_3) δ 7.56 (m, 4H), 7.39 (m, 6H).

1-Methoxy-4-phenethynyl-benzene⁷

^1H NMR (400 MHz, CDCl_3) δ 7.47-7.53 (m, 4H), 7.27-7.35 (m, 3H), 6.87 (d, $J = 8.8$ Hz, 2H), 3.84 (s, 3H).

2-(4-Methoxy-phenethynyl)-pyridine⁸

^1H NMR (400 MHz, CDCl_3) δ 8.62 (d, $J = 4.8$ Hz, 1H), 7.67 (td, $J = 7.7, 1.8$ Hz, 1H), 7.60 (m, 2H), 7.52 (dd, $J = 7.8, 0.8$ Hz, 1H) 7.36 (m, 3H), 7.24 (m, 1H).

Deca-1,9-diynyl-benzene

Oil. ^1H NMR (400 MHz, CDCl_3) δ 7.40 (m, 2H); 7.28 (m, 3H); 2.42 (t, $J = 7.0$ Hz, 2H), 2.21 (td, $J = 6.9, 2.5$ Hz, 2H), 1.95 (t, $J = 2.5$ Hz, 1H), 1.45-1.63 (m, 8H). δ ^{13}C NMR (100 MHz, CDCl_3) δ 131.7, 128.31, 127.6, 124.2, 90.3, 84.7, 80.8, 68.4, 28.7, 28.5, 19.5, 18.5; IR (cm^{-1}) 3299, 2936, 2858, 2236, 2116, 1598, 1489; HRMS (ES^+ , CoCl_2) for $\text{C}_{20}\text{H}_{20}\text{OCoCl}$ calcd: 304.0416, found: 304.0429.

Deca-1,9-diynyl-4-methoxy-benzene

Oil. ^1H NMR (400 MHz, CDCl_3) δ 7.32 (d, $J = 8.7$ Hz, 2H), 6.81 (d, $J = 8.7$ Hz, 2H), 3.80 (s, 3H), 2.40 (t, $J = 7.0$ Hz, 2H), 2.21 (td, $J = 6.9, 2.5$ Hz, 2H), 1.95 (t, $J = 2.5$ Hz, 1H), 1.55-1.63 (m, 4H), 1.46 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.1, 132.0, 116.3, 113.9, 88.7, 84.7, 80.4, 76.8, 55.3, 28.8, 28.4, 19.4, 18.4; IR (cm^{-1}) 3295, 2934, 2858, 1606, 1508; HRMS (ES^+ , CoCl_2) for $\text{C}_{20}\text{H}_{20}\text{OCoCl}$ calcd: 334.0539, found: 334.0535.

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2-mq

bmw-4crude
CDCl₃

CDCl₃
bm-g

bw-21a
CDCl₃

bw-20 (with 4-Iodophenol)
CDCl₃

bm-7
CDC13

bw-8
CDC13

bw-8
CDCl₃

bw-14 (with 2-bromopyridine)
CDCl₃

bw-13 (with 3-bromopyridine)
CDCl₃

bw-11
CDCl₃

ppm
8.54072
8.54398
7.59390
7.59863
7.57367
7.56839
7.28724
7.26947

bw-12
CDC13

bw-15
CDCl₃

7.57040
7.56409
7.56184
7.55933
7.55065
7.54615
7.38163
7.37320
7.36894
7.36701
7.35978
7.35541
7.26888

ppm

bw-17
CDCl₃

bw-19
CDC13

DM-16
CDC13

S24

bm-22b
CDC13

bw-6 (reac. of p-NO₂PhI)
CDCl₃

bw-18 (homocoupling of phenylacetylene)
CDCl₃