Supporting Materials to

**A Copper and Amine Free Sonogashira Reaction Employing
Aminophosphines as Ligands**

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General: All reactions and manipulations were conducted under nitrogen atmosphere using standard Schlenk techniques. Column chromatography was performed using EM Silica gel 60 (300-400 mesh) or Al₂O₃. ¹H NMR, ¹³C NMR and ³¹P NMR were recorded on a 300 MHz spectrometer. Chemical shifts were reported in ppm downfield from tetramethylsilane with the solvent resonance as the internal standard.

3aa 4-Phenylethynylanisole¹

¹H NMR (300 MHz, CDCl₃): δ 7.54-7.47 (m, 4H), 7.35-7.26 (m, 3H), 6.89 (d, *J* = 8.7 Hz, 2H), 3.84 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 159.8, 133.0, 131.6, 128.5, 128.3, 123.6, 115.3, 114.2, 89.3, 88.0, 55.3.

3ab Phenyl-*p*-tolyl-acetylene²

¹H NMR (300 MHz, CDCl₃): δ 7.56-7.49 (m, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.38-7.35 (m, 3H), 7.19 (d, *J* = 8.4 Hz, 2H), 2.38 (s, 3H). ¹³CNMR (75 MHz, CDCl₃): δ 138.3, 131.5, 131.4, 129.0, 128.3, 128.0, 123.4, 120.1, 89.5, 88.7, 21.5.

3ac Diphenylethyne³

¹H NMR (300 MHz, CDCl₃): δ 7.56-7.51 (m, 4H), 7.35-7.32 (m, 6H). ¹³CNMR (75 MHz, CDCl₃): δ 131.6, 128.3, 128.2, 123.2, 89.3.

¹ Muthiah, C.; Kumar, K. P.; Kumaraswamy, S.; Swamy, K. C. *Tetrahedron* **1998**, 54, 14315-14326.

² Katritzky, A. R.; Abdel-Fattah, A. A.; Wane, M. *J. Org. Chem.* **2002**, 67, 7526–7529.

³ Ibrahim, Y. A.; Al-Awadi, N. A.; Kaul, K. *Tetrahedron* **2001**, 57, 7377-7382.

3ad 1,3-Dimethyl-2-phenylethynylbenzene⁴

¹H NMR (300 MHz, CDCl₃): δ 7.66-7.16 (m, 8H), 2.62 (s, 6H). ¹³CNMR (75 MHz, CDCl₃): δ 140.2, 131.3, 128.3, 128.0, 127.7, 126.7, 123.8, 122.9, 97.8, 87.1, 21.1.

3ae Phenyl-*o*-tolyl-acetylene⁵

¹H NMR (300 MHz, CDCl₃): δ 7.58-7.51 (m, 3H), 7.38-7.37 (m, 3H), 7.35-7.25 (m, 3H), 2.54 (s, 3H). ¹³CNMR (75 MHz, CDCl₃): δ 140.2, 131.8, 131.5, 129.4, 128.3, 128.3, 128.1, 125.6, 123.5, 123.0, 92.9, 88.3, 20.7.

3af Phenylethynyl-naphthalene⁶

¹H NMR (300 MHz, CDCl₃): δ 8.47-8.45 (m, 1H), 7.90-7.76 (m, 3H), 7.68-7.26 (m, 8H). ¹³CNMR (75 MHz, CDCl₃): 133.2, 133.1, 131.6, 130.3, 128.4, 128.4, 128.3, 128.2, 126.7, 126.4, 126.2, 125.3, 123.3, 120.8, 94.3, 87.5.

3ai 3-Phenylethynyl-pyridine⁷

⁴ Cao, D.; Schollmeyer, D.; Meier, H. *Eur. J. Org. Chem.* **1999**, 4, 791-796.

⁵ Mouries, V.; Waschbuesch, R.; Carran, J.; Savignac, P. *Synthesis* **1998**, 271-274.

⁶ Katritzky, A. R.; Abdel-Fattah, A. A.; Wane, M. *J. Org. Chem.* **2002**, 67, 7526-7529.

⁷ Mori, Y.; Seki, M. *J. Org. Chem.* **2003**, 68, 1571 - 1574.

^1H NMR (300 MHz, CDCl_3): δ 8.55-8.53 (m, 1H), 8.78-8.53 (m, 1H), 7.82-7.78 (m, 1H), 7.75-7.53 (m, 2H), 7.39-7.35 (m, 3H), 7.29-7.25 (m, 1H).

^{13}C NMR (75 MHz, CDCl_3): 152.2, 148.5, 138.4, 131.6, 128.7, 128.4, 123.0, 122.4, 120.4, 92.6, 85.9.

3ba 1-(1-Hexynyl)-4-methoxybenzene⁸

^1H NMR (300 MHz, CDCl_3): δ 7.33 (d, J = 8.7 Hz, 2H), 6.81 (d, J = 8.7 Hz, 2H), 3.78 (s, 3H), 2.39 (t, J = 7.2 Hz, 2H), 1.58-1.48 (m, 4H), 0.94 (t, J = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 158.9, 132.8, 116.2, 113.7, 88.7, 80.2, 55.2, 30.9, 22.0, 19.1, 13.7.

3bb 1-(4-Methylphenyl)-1-hexyne⁹

^1H NMR (300 MHz, CDCl_3): δ 7.26 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 2.39 (t, J = 7.2 Hz, 2H), 2.33 (s, 3H), 1.58-1.48 (m, 4H), 0.94 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 137.3, 131.3, 128.9, 120.9, 89.5, 80.5, 30.9, 22.0, 21.4, 19.1, 13.7.

3bc 1-Phenyl-hex-1-yne¹⁰

^1H NMR (300 MHz, CDCl_3): δ 7.41-7.37 (m, 2H), 7.28-7.25 (m, 3H), 2.41 (t, J = 6.9 Hz, 2H), 1.58-1.46 (m, 4H), 0.95 (t, J = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 131.5,

⁸ Crisp, G. T.; Turner, P. D.; Stephens, K. A. *J. Organomet. Chem.* **1998**, 570, 219-224.

⁹ Katritzky, A. R.; Wang, J.; Karodia, N.; Li, J. *J. Org. Chem.* **1997**, 62, 4142-4147.

¹⁰ Sato, H.; Isono, N.; Miyoshi, I.; Mori, M. *Tetrahedron* **1996**, 52, 8143-8158.

128.1, 127.4, 124.0, 90.4, 80.5, 30.8, 22.0, 19.1, 13.7.

3bh 1-(4'-acetyl)phenylhex-1-yne¹¹

¹H NMR (300 MHz, CDCl₃): δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.7 Hz, 2H), 2.53 (s, 3H), 2.39 (t, *J* = 7.2 Hz, 2H), 1.59-1.43 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃): 197.2, 135.4, 131.5, 129.0, 128.0, 94.2, 80.0, 30.5, 26.4, 21.9, 19.1, 13.5.

3bi 3-(1-Hexynyl) pyridine¹²

¹H NMR (300 MHz, CDCl₃): δ 8.49-8.47 (m, 1H), 8.78-8.53 (m, 1H), 7.68-7.65 (m, 1H), 7.27-7.19 (m, 1H), 2.43 (t, *J* = 7.2 Hz, 2H), 1.63-1.47 (m, 4H), 0.96 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃): 152.2, 147.7, 138.3, 122.8, 121.1, 94.0, 77.2, 30.5, 21.9, 19.0, 13.5.

3cb 2-(4-Methyl-phenyl)ethynyl-naphthalene¹³

¹H NMR (300 MHz, CDCl₃): δ 8.53 (d, *J* = 9.0 Hz, 1H), 7.90-7.81 (m, 3H), 7.67-7.47 (m, 5H), 7.26 (d, *J* = 9.0 Hz, 2H), 2.44 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 138.5, 133.2, 133.1, 131.5, 130.2, 129.2, 128.5, 128.2, 126.7, 126.3, 126.0, 125.2, 121.0, 120.3, 94.5, 86.9, 21.5.

¹¹ Molander, G. A.; Katona, B. W.; Machrouhi, F. *J. Org. Chem.* **2002**, 67, 8416 - 8423.

¹² Novak, Z.; Szabo, A.; Repasi, J.; Kotschy, A. *J. Org. Chem.* **2003**, 68, 3327 - 3329.

¹³ Crisp, G. T.; Turner, P. D.; Stephens, K. A. *J. Organomet. Chem.* **1998**, 570, 219-224.

3dc 1-Phenyl-3-benzyloxy-1-propyne¹⁴

¹H NMR (300 MHz, CDCl₃): δ 7.46-7.30 (m, 10H), 4.67 (s, 2H), 4.39 (s, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 137.4, 131.7, 128.4, 128.3, 128.12, 128.10, 127.8, 122.6, 86.4, 85.0, 71.6, 57.9.

3ec Cyclohex-1-enyl-phenylacetylene¹⁵

¹H NMR (300 MHz, CDCl₃): δ 7.43-7.39 (m, 2H), 7.29-7.24 (m, 3H), 6.22-6.19 (m, 1H), 2.24-2.14 (m, 2H), 2.13-2.10 (m, 2H), 1.68-1.57 (m, 4H). ¹³C NMR (75 MHz, CDCl₃): δ 135.1, 131.4, 128.2, 127.6, 123.7, 120.7, 91.2, 86.7, 29.2, 25.7, 22.3, 21.5.

3ej Methyl 2-(2-cyclohexenyl-1-ethynyl)benzoate¹⁶

¹H NMR (300 MHz, CDCl₃): δ 7.93-7.90 (m, 1H), 7.54-7.51 (m, 1H), 7.45-7.42 (m, 1H), 7.33-7.30 (m, 1H), 6.28-6.26 (m, 1H), 3.92 (s, 3H), 2.28-2.24 (m, 2H), 2.16-2.14 (m, 2H), 1.70-1.61 (m, 4H).

¹³C NMR (75 MHz, CDCl₃): 166.7, 135.9, 133.7, 131.44, 131.42, 130.2, 127.2, 124.1, 120.8, 96.3, 85.6, 51.9, 28.9, 25.7, 22.2, 21.4.

3ib Trimethyl-p-tolyethynyl-silane¹⁷

¹⁴ Studemann, T.; Ibrahim-Ouail, M.; Knochel, P. *Tetrahedron* **1998**, *54*, 1299-1316..

¹⁵ Stille, J. K.; Simpson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2138-2152.

¹⁶ Padwa, A.; Austin, D. J.; Gareau, Y.; Kassir, J. M.; Xu, S. L. *J. Amer. Chem. Soc.* **1993**, *115*, 2637-2647.

¹⁷ Paquette, L. A.; Fristad, W. E.; Dime, D. S.; Bailey, T. R. *J. Org. Chem.* **1980**, *45*, 3017-3028.

^1H NMR (300 MHz, CDCl_3): δ 7.39 (d, $J = 8.1$ Hz, 2H), 7.11 (d, $J = 8.1$ Hz, 2H), 2.36 (s, 3H) 0.28 (s, 9H).

^{13}C NMR (75 MHz, CDCl_3): 138.5, 131.8, 128.9, 120.0, 105.3, 93.2, 21.5, 0.

3ic 1-Phenyl-2-(trimethylsilyl)acetylene ¹⁸

^1H NMR (300 MHz, CDCl_3): δ 7.51-7.49 (m, 2H), 8.33-7.31 (m, 3H), 0.30 (s, 9H).

^{13}C NMR (75 MHz, CDCl_3): 131.9, 128.5, 128.2, 123.1, 105.1, 94.0, 0.

3fc 1,3-Diphenyl-propyne ¹⁹

^1H NMR (300 MHz, CDCl_3): δ 7.45-7.25 (m, 10H), 3.81 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 136.7, 131.6, 128.5, 128.2, 127.9, 127.8, 126.6, 123.6, 87.5, 82.6, 25.7.

3ga 4-(4-Methoxy-phenyl)-2-methyl-but-3-yn-2-ol ²⁰

^1H NMR (300 MHz, CDCl_3): δ 7.34 (d, $J = 9.0$ Hz, 2H), 6.81 (d, $J = 9.0$ Hz, 2H), 3.79 (s, 3H), 2.17 (s, br, 1H), 1.60 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3): δ 159.3, 132.9, 114.7, 113.7, 92.4, 81.8, 65.4, 55.1, 31.4.

3gb 2-Methyl-4-*p*-tolyl-but-3-yn-2-ol ²¹

^1H NMR (300 MHz, CDCl_3): δ 7.32 (d, $J = 8.1$ Hz, 2H), 7.11 (d, $J = 7.8$ Hz, 2H), 2.35 (s,

¹⁸ Erdelyi, M.; Gogoll, A. *J. Org. Chem.* **2001**, 66, 4165 - 4169.

¹⁹ Obynochnyi, A. A.; Anisimov, B. N.; Prostakov, N. S. *Russ. J. Org. Chem.* **1993**, 29, 1919-1920.

²⁰ Markert, C.; Bannwarth, W. *Helv. Chim. Acta.* **2002**, 85, 1877-1882.

²¹ Pourjavadi, A.; Marandi, G. B. *J. Chem. Res. (S)*. **2002**, 552-555.

3H), 2.28 (s, br, 1H), 1.63 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3): δ 138.2, 131.5, 129.0, 119.5, 93.0, 82.1, 65.6, 31.5, 21.4.

3gc 2-Methyl-4-phenyl-but-3-yn-2-ol²²

^1H NMR (300 MHz, CDCl_3): δ 7.42-7.39 (m, 2H), 7.30-7.28 (m, 3H), 2.40 (s, br, 1H), 1.62 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3): δ 131.6, 128.19, 128.19, 122.7, 94.0, 82.1, 62.6, 31.4.

3hc 3-Methoxy-3-methyl-but-1-ynyl)-benzene²³

^1H NMR (300 MHz, CDCl_3): δ 7.52-7.41 (m, 2H), 7.30-7.28 (m, 3H), 3.43 (s, 3H), 1.54 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3): δ 131.6, 128.2, 128.1, 122.8, 90.9, 84.2, 70.8, 51.6, 28.3.

4gf 1-Naphthlenylacetylene²⁴

^1H NMR (300 MHz, CDCl_3): δ 8.42 (d, $J=8.1$ Hz, 1H), 7.87 (d, $J=8.1$ Hz, 2H), 7.80-7.76 (m, 1H), 7.62-7.54 (m, 2H), 7.46-7.42 (m, 1H), 3.52 (s, 1H).

^{13}C NMR (75 MHz, CDCl_3): 133.4, 133.0, 131.2, 129.2, 128.2, 126.9, 126.4, 126.0, 125.0, 119.7, 82.0, 81.7.

²² (a) Yu, W.-Y.; Alper, H. *J. Org. Chem.* **1997**, 62, 5684-5687. (b) Bigi, F.; Carloni, S.; Maggi, R.; Muchetti, C.; Sartori, G. *J. Org. Chem.* **1997**, 62, 7024-7027.

²³ Mahrwald, R.; Quint, S.; Scholtis, S. *Tetrahedron* **2002**, 58, 9847-9852.

²⁴ (a) Okamoto, Y.; Chellappa, K. L.; Kundu, S. K. *J. Org. Chem.* **1972**, 37, 3185-3187. (b) Neenan, T. X.; Whitesides, G. M. *J. Org. Chem.* **1988**, 53, 2489-2496. (c) Butler, I. R.; Soucy-Breau, C. *Can. J. Chem.* **1991**, 69, 1117-1123.

L1 CNMR

131.032
130.760
127.505
127.446
126.506
126.481

77.430
77.003
76.579

47.835
47.683

24.543
24.462
24.356
24.258

S9

L1 PNMR

60.205

S10

L1 HNMR

S11

L2 CNMR

S12

L2 HNMR

S13

L2 PNMR

S14

3aa CNMR

3a HNMR

3ab CNMR

3ab HNMR

3ac CNMR

7.577
7.566
7.562
7.550
7.544
7.372
7.366
7.356
7.349

3ac HNMR

S20

3ad CNMR

3ae CNMR

3ae HNMR

3af CNMR

3af HNMR

3ai CNMR

3ai HNMR

3ba CNMR

3ba HNMR

7.337
7.311
7.125
7.099

2.455
2.432
2.408
2.356

1.620
1.595
1.572
1.546
1.521
1.497
1.004
0.980
0.957

3bb HNMR

3bb CNMR

3bc CNMR

3bc HNMR

3bd CNMR

3bd HNMR

3bh CNMR

3bh HNMR

3bi CNMR

3bi HNMR

3cb CNMR

3cb HNMR

3dc CNMR

S43

7.458
7.445
7.381
7.359
7.333
7.322
7.314
7.306
7.303
7.300

4.673
4.397

3dc HNMR

9/31

1.94 2.00

3ec CNMR

7.464
7.455
7.438
7.318
7.300

6.244
6.238
6.234

2.257
2.179
2.170
2.160
1.724
1.712
1.705
1.691
1.686
1.670
1.654
1.635
1.618

3ec HNMR

3ej CNMR

3ej HNMR

3fc CNMR

3fc HNMR

7.454
7.444
7.433
7.426
7.414
7.412
7.387
7.341
7.333
7.317
7.285
7.274
7.272
7.260
7.252

3.805

9.33

2.00

10

8

6

4

2

0

PPM

S50

3ga HNMR

3gb CNMR

S53

3gb HNMR

3gc CNMR

131.576
128.188
122.645

82.064
77.421
77.000
76.577

65.557

31.434

S55

3gc HNMR

3gf CNMR

S57

3gf HNMR

S59

3gg HNMR in d6-acetone

3hc CNMR

3hc HNMR

3ib CNMR

3ib HNMR

3ic CNMR

3ic HNMR

4gc CNMR

7.533
7.527
7.519
7.517
7.509
7.502
7.368
7.359
7.356
7.353
7.345
7.335
7.330

3.095

4gc HNMR

S68