

Supporting Information

Palladium Catalyzed Amination of 1-Bromo- and 1-Chloro-1,3-butadienes: a General Method for the Synthesis of 1-Amino-1,3-butadienes

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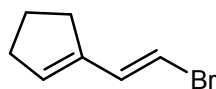
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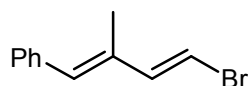
General Remarks: All reactions were carried out under nitrogen atmosphere in a RR98030 12 place Carousel Reaction StationTM from Radleys Discovery Technologies, equipped with gas-tight threaded caps with a valve, cooling reflux head system, and digital temperature controller. Toluene, pentane and hexanes were continuously refluxed and freshly distilled from sodium/benzophenone under nitrogen. Pd(OAc)₂ and Pd₂(dba)₃ were purchased from Strem Chemical co. and used without further purification. All phosphine ligands used are commercially available from Strem or Aldrich and were used without further purification. NaOtBu was purchased from Aldrich chemical co., stored in a flask purged with nitrogen and weighted in the air. Bromodienes **1a** and **1b** were prepared as described in the supplementary material. The synthesis of 1-bromo-3-methyl-4-phenyl-1,3-butadiene **1c** and 1-bromo-4-phenylbutadiene **1d** was adapted from a known procedure¹⁶ and is detailed in the supplementary material. GC analysis were performed with a GC Agilent Technologies 6890N instrument. NMR spectra were recorded at 300 or 200 MHz for ¹H and 75 or 50.3 MHz for ¹³C, with tetramethylsilane as internal standard for ¹H and the residual solvent signals as standard for ¹³C. Chemical shifts are given in ppm. Mass spectra were obtained by EI (70eV).



HRMS calcd. for C₇H₉Br: 171.9882; found: 171.9879; ¹H NMR (CDCl₃, 300MHz): δ = 1.90 – 2.00 (m, 2H), 2.38 – 2.43 (m, 4H), 5.79 (s, 1H), 6.17 (d, ³J_{trans} = 13.7Hz, 1H), 6.96 (d, ³J_{trans} = 13.9Hz, 1H) ; ¹³C NMR (CDCl₃, 75MHz): δ = 25.41 (CH₂), 33.28 (CH₂), 35.12 (CH₂), 108.48 (CH), 134.63 (CH), 136.79 (CH), 143.01 (C).

Preparation of bromodiene 1-((1E,3E)-4-bromo-2-methylbuta-1,3-dienyl)benzene

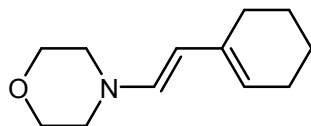
1c: Bromodiene 1c was prepared following the procedure described in S. Abbas, C.J. Hayes, S. Worden, *Tetrahedron Lett.* **2000**, *41*, 3215-3219.



HRMS calcd. for C₁₁H₁₁Br: 222.0039; found: 222.0040; ¹H NMR (CDCl₃, 300MHz): δ = 2.02 (s, 3H), 6.42 (d, ³J_{trans} = 13.7Hz, 1H), 6.56 (s, 1H), 6.96 (d, ³J_{trans} = 13.7Hz, 1H), 7.27 – 7.42 (m, 5H, arom. H); ¹³C NMR (CDCl₃, 75MHz): δ = 13.58 (CH₃), 105.61 (CH), 126.93 (CH), 128.15 (CH), 129.09 (CH), 132.27 (CH), 134.01 (C), 136.91 (C), 142.19 (CH).

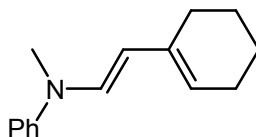
General Procedure for the Cross-coupling of 1-halodienes 1a-d with secondary amines 2. Synthesis of 1-aminodienes 3a-k: A carousel reaction tube under nitrogen atmosphere was charged with XPHOS (0.01 mmol, 1 mol %), tris(dibenzylideneacetone)dipalladium (0) (0.005 mmol, 1 mol %), sodium tert-butoxide (1.4 mmol) and toluene (4 mL). After 1 minute, the halodiene **1** (1 mmol) was added and the reaction mixture was stirred for 2 additional minutes, when the amine **2** (1 mmol) was added. The system was heated (80°C for bromodienes or 90 °C for chlorodienes) with stirring until the starting halide had been completely consumed as judged by GC analysis. The mixture was allowed to cool to room temperature, taken up in dry pentane or hexanes (15 mL), and filtered through celite. The solvents were evaporated under reduced pressure. The residue was redissolved in dry hexanes (15 mL), filtered again through celite, concentrated under reduced pressure and dried under high vacuum to afford a residue which consisted of the essentially pure 1-aminodiene **3**.

4-[(1E)-2-cyclohexenylvinyl]morpholine 3a



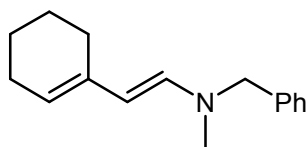
HRMS calcd. for C₁₂H₁₉ON: 193.1461; found: 193.1460; ¹H NMR (CDCl₃, 300MHz): δ = 1.61 – 1.68 (m, 4H), 2.09 – 2.12 (m, 4H), 2.87 – 2.93 (m, 4H); 3.72 – 3.77 (m, 4H); 5.26 (d, ³J_{trans} = 14.2 Hz, 1H), 5.48 (s, 1H), 6.03 (d, ³J_{trans} = 14.2 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz): δ = 23.05 (CH₂), 23.14 (CH₂), 25.25 (CH₂), 26.06 (CH₂), 49.49 (CH₂), 66.77 (CH₂), 106.88 (CH), 122.27 (CH), 134.70 (C), 136.82 (CH).

N-[(1E)-2-cyclohexenylvinyl]-N-methylbenzenamine 3b



HRMS calcd. for C₁₅H₁₉N: 213.1512; found: 213.1514; ¹H NMR (CDCl₃, 300MHz): δ = 1.68 – 1.78 (m, 4H), 2.19 – 2.26 (m, 4H), 3.23 (s, 3H), 5.55 (d, ³J_{trans} = 14.0 Hz, 1H), 5.62 (s, 1H), 6.87 (d, ³J_{trans} = 14.0 Hz, 1H), 6.94 – 6.99 (m, 1H, arom. H), 7.03 – 7.06 (m, 2H, arom. H), 7.31 – 7.36 (m, 2H, arom. H); ¹³C NMR (CDCl₃, 75MHz): δ = 25.30 (CH₂), 25.39 (CH₂), 27.59 (CH₂), 28.35 (CH₂), 37.54 (CH₃), 111.00 (CH), 119.53 (CH), 122.93 (CH), 124.56 (CH) 131.67 (CH) 133.03 (CH), 137.23 (C), 150.34 (C).

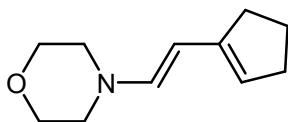
(1E)-N-benzyl-2-cyclohexenyl-N-methylethenamine 3c



HRMS calcd. for C₁₆H₂₁N: 227.1668; found: 227.1668; ¹H NMR (CDCl₃, 300MHz): δ = 1.70 – 1.80 (m, 4H), 2.20 – 2.24 (m, 4H), 2.70 (s, 3H), 4.24 (s, 2H), 5.19 (d, ³J_{trans} = 14.0 Hz, 1H), 5.51 (s, 1H), 6.47 (d, ³J_{trans} = 14.0 Hz, 1H), 7.31 – 7.41 (m, 5H, H arom.); ¹³C NMR (CDCl₃, 75MHz): δ = 23.43 (CH₂), 23.55 (CH₂), 25.67 (CH₂), 26.29

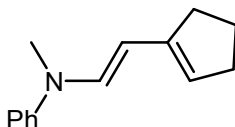
(CH₂), 36.84 (CH₃), 59.81 (CH₂), 103.48 (CH), 119.92 (CH), 127.60 (CH), 127.98 (CH), 128.94 (CH), 135.47 (C), 137.15 (CH), 139.09 (C).

4-[(1E)-2-cyclopentenylvinyl]morpholine 3d



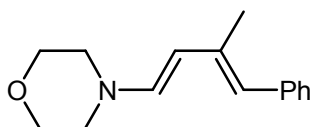
HRMS calcd. for C₁₁H₁₇ON: 179.1305; found: 179.1301; ¹H NMR (CDCl₃, 300MHz): δ = 1.91 – 1.96 (m, 2H), 2.39 – 2.44 (m, 4H), 2.95 (t, ³J = 4.8Hz, 4H), 3.76 (t, ³J = 4.8Hz, 4H), 5.43 (s, 1H), 5.49 (d, ³J_{trans} = 13.9Hz, 1H), 6.05 (d, ³J_{trans} = 13.9Hz, 1H); ¹³C NMR (CDCl₃, 75MHz): δ = 23.68 (CH₂), 32.06 (CH₂), 32.96 (CH₂), 49.40 (CH₂), 66.84 (CH₂), 100.34 (CH), 123.14 (CH), 140.32 (CH), 141.67 (C).

N-((1E)-2-cyclopentenylvinyl)-N-methylbenzenamine 3e



HRMS calcd. for C₁₁H₁₇ON: 199.1355; found: 199.1352; ¹H NMR (CDCl₃, 300MHz): δ = 2.03 – 2.06 (m, 2H), 2.53 – 2.56 (m, 4H), 3.26 (s, 3H), 5.56 (s, 1H), 5.77 (d, ³J_{trans} = 13.7Hz, 1H), 6.87 (d, ³J_{trans} = 13.7Hz, 1H), 7.01 – 7.10 (m, 3H, arom. H), 7.34 – 7.37 (m, 2H, arom. H); ¹³C NMR (CDCl₃, 75MHz): δ = 23.19 (CH₂), 31.67 (CH₂), 32.55 (CH₂), 34.97 (CH₃), 101.85 (CH), 117.19 (CH), 120.71 (CH), 122.80 (CH), 129.11 (CH), 133.95 (CH), 141.47 (C), 147.54 (C).

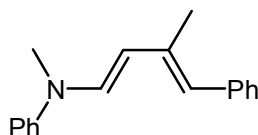
4-[(1E,3E)-3-methyl-4-phenylbuta-1,3-dienyl]morpholine 3f



HRMS calcd. for C₁₅H₁₉ON: 229.1461; found: 229.1465. ¹H NMR (CDCl₃, 300MHz): δ = 2.06 (s, 3H), 3.04 (t, ³J = 4.8Hz, 4H), 3.81 (t, ³J = 4.8Hz, 4H), 5.51 (d, ³J_{trans} = 14.0Hz, 1H), 6.30 (d, ³J_{trans} = 14.0Hz, 1H), 6.36 (s, 1H), 7.19 – 7.22 (m, 1H, arom. H), 7.23 –

7.40 (m, 4H, arom. H); ^{13}C NMR (CDCl_3 , 75MHz): δ = 14.11 (CH_3), 48.92 (CH_2), 66.28 (CH_2), 107.36 (CH), 123.82 (CH), 125.28 (CH), 127.85 (CH), 128.86 (CH), 135.26 (C), 138.76 (C), 139.15 (CH).

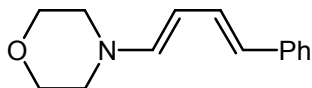
***N*-methyl-*N*-[(1*E*,3*E*)-3-methyl-4-phenylbuta-1,3-dienyl]benzenamine 3g**



HRMS calcd. for $\text{C}_{18}\text{H}_{19}\text{N}$: 249.1512; found: 249.1510; ^1H NMR (CDCl_3 , 300MHz): δ = 2.15 (s, 3H), 3.32 (s, 3H), 5.76 (d, $^3J_{\text{trans}}=13.8\text{Hz}$, 1H), 6.46 (s, 1H), 7.02 – 7.14 (m, 4H), 7.24 – 7.25 (m, 1H), 7.26 – 7.43 (m, 6H); ^{13}C NMR (CDCl_3 , 75MHz): δ = 14.29 (CH_3), 35.33 (CH_3), 109.68 (CH), 117.60 (CH), 121.10 (CH), 124.17 (CH), 125.35 (CH), 127.94 (CH), 128.94 (CH), 129.22 (CH), 133.62 (CH), 135.62 (C), 138.85 (C), 147.70 (C).

4-[(1*E*,3*E*)-4-phenylbuta-1,3-dienyl]morpholine 3h

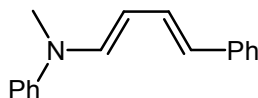
$\text{Pd}(\text{OAc})_2$ 2 mol % and BINAP 4 mol % were used as catalytic system.



HRMS calcd. for $\text{C}_{14}\text{H}_{17}\text{ON}$: 215.1305; found: 215.1294; ^1H NMR (CDCl_3 , 300MHz): δ = 3.02 (s, 4H), 3.75 (s, 4H), 5.42 (t, $^3J=11.9\text{Hz}$, 1H), 6.29 (d, $^3J_{\text{trans}}=13.8\text{Hz}$, 1H), 6.76 (dd, $^3J_{\text{trans}}=15.0\text{Hz}$, $^3J=10.8\text{Hz}$, 1H), 7.15 – 7.40 (m, 6H); ^{13}C NMR (CDCl_3 , 75MHz): δ = 48.53 (CH_2), 66.11 (CH_2), 102.20 (CH), 123.19 (CH), 125.03 (CH), 125.52 (CH), 128.31 (CH), 128.89 (CH), 138.66 (C), 143.29 (CH).

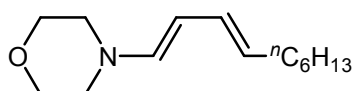
***N*-methyl-*N*-[(1*E*,3*E*)-4-phenylbuta-1,3-dienyl]aniline 3i**

$\text{Pd}(\text{OAc})_2$ 2 mol % and BINAP 4 mol % were used as catalytic system.



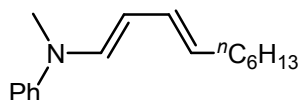
HRMS calcd. for C₁₇H₁₇N: 235.1355; found: 235.1350; ¹H NMR (CDCl₃, 300MHz): δ = 3.30 (s, 3H), 5.70 (dd, ³J_{trans}=13.2Hz, ³J=10.5Hz, 1H), 6.50 (d, ³J=15.6Hz, 1H), 6.96 (dd, ³J_{trans}=15.6Hz, ³J=10.5Hz, 1H), 7.20 – 7.50 (m, 6H); ¹³C NMR (CDCl₃, 75MHz): δ = 35.23 (CH₃), 104.81 (CH), 118.76 (CH), 122.59 (CH), 124.68 (CH), 126.31 (CH), 129.59 (CH), 130.27 (CH), 130.37 (CH), 138.83 (CH), 139.26 (C), 147.55 (C).

4-[(1E,3E)-deca-1,3-dienyl]morpholine 3j



HRMS calcd. for C₁₄H₂₅ON: 223.1931; found: 223.1929; ¹H NMR (CDCl₃, 300MHz): δ = 0.87 – 0.91 (m, 3H), 1.25 – 1.35 (m, 8H), 2.01 – 2.07 (m, 2H), 2.89 (t, ³J=4.9Hz, 4H), 3.72 (t, ³J=4.8Hz, 4H), 5.22 (dd, ³J_{trans}=13.7Hz, ³J=10.2Hz, 1H), 5.38 (dt, ³J_{trans}=14.5Hz, ³J=6.9Hz, 1H), 5.9 – 6.09 (m, 2H); ¹³C NMR (CDCl₃, 75MHz): δ = 14.01 (CH₃), 22.55 (CH₂), 28.81 (CH₂), 29.82 (CH₂), 31.70 (CH₂), 32.76 (CH₂), 48.86 (CH₂), 66.29 (CH₂), 102.93 (CH), 126.39 (CH), 128.76 (CH), 140.82 (CH).

N-[(1E,3E)-deca-1,3-dienyl]-N-methylbenzenamine 3k



HRMS calcd. for C₁₇H₂₅N: 243.1981; found: 223.1980; ¹H NMR (CDCl₃, 300MHz): δ = 0.92 – 0.94 (m, 3H), 1.32 – 1.37 (m, 8H), 2.08 – 2.13 (m, 2H), 3.19 (s, 3H), 5.44 – 5.53 (m, 2H), 6.10 (dd, ³J_{trans}=15.0 Hz, ³J=10.4 Hz, 1H), 6.82 (d, ³J_{trans}= 13.5 Hz, 1H), 6.92 – 7.03 (m, 3H, arom. H), 7.28 – 7.31 (m, 2H, arom. H); ¹³C NMR (CDCl₃, 75 MHz): δ = 14.06 (CH₃), 22.60 (CH₂), 28.86 (CH₂), 29.89 (CH₂), 31.75 (CH₂), 32.87 (CH₂), 35.03 (CH₃), 104.95 (CH), 117.04 (CH), 120.62 (CH), 126.62 (CH), 129.06 (CH), 129.12 (CH), 134.84 (CH), 147.34 (C).