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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General Remarks: All reactions were carried out under nitrogen atmosphere in a RR98030 12 place Carousel Reaction Station™ 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 Pd$_2$(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. Bromodiienes 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 procedure$^{16}$ 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 $^1$H and 75 or 50.3 MHz for $^{13}$C, with tetramethylsilane as internal standard for $^1$H and the residual solvent signals as standard for $^{13}$C. Chemical shifts are given in ppm. Mass spectra were obtained by EI (70eV).
Preparation of 1-bromodienes 1a and 1b:

\[
\text{CH}_n \quad \text{H} \quad \text{i) Cp}_2\text{Zr(H)}\text{Cl, CH}_2\text{Cl}_2 \\
\text{ii) Br}_2
\]

\[\text{Br}\]

To the stirred suspension of 24 mmol of \(\text{Cp}_2\text{Zr(H)}\text{Cl}\) in 30 ml THF under \(\text{N}_2\) atmosphere, and in a flask protected from the sun light, were added dropwise 20 mmol of the corresponding en-yne dissolved in 10 mL of THF. The mixture was stirred at room temperature overnight. The solution was cooled to 0 °C and then 20 mmol of bromine were added dropwise. After stirring for 10 min, the reaction was quenched with 20 mL of saturated aqueous \(\text{Na}_2\text{S}_2\text{O}_3\) solution. The organics were extracted with diethyl ether (2x30 mL), the organic layers were combined, washed with brine and dried over \(\text{Na}_2\text{SO}_4\). Careful removal of the solvent under reduced pressure (water aspirator for 1a, 50 mbar for 1b) afforded the bromodienes as nearly pure materials, which were further purified by filtration through a short chromatographic column (SiO\(_2\), pentane).

1-\(\{E\}\)-2-bromovinyl]cyclohex-1-ene 1a

It was obtained 1.57 g, 42 % yield.

\[
\text{Br}
\]

HRMS calcd. for \(\text{C}_8\text{H}_{11}\text{Br}\): 186.0044; found: 186.0037; \(^1\text{H NMR (CDCl}_3, 300MHz)\): \(\delta = 1.64 – 1.72\) (m, 4H), 2.10 – 2.15 (m, 4H), 5.80 (s, 1H), 6.15 (d, \(^3\text{J}_\text{trans} = 13.8\text{Hz}, 1\text{H}\)), 6.73 (d, \(^3\text{J}_\text{trans} = 13.7\text{Hz}, 1\text{H}\)); \(^13\text{C NMR (CDCl}_3, 75\text{MHz)\): \(\delta = 22.55\) (CH\(_2\)), 22.64 (CH\(_2\)), 24.61 (CH\(_2\)), 26.23 (CH\(_2\)), 103.06 (CH), 131.28 (CH), 135.11 (C), 141.02 (CH).

1-\(\{E\}\)-2-bromovinyl]cyclopent-1-ene 1b.

It was obtained 1.62 mg, 47 % yield.
HRMS calcd. for C$_7$H$_9$Br: 171.9882; found: 171.9879; $^1$H NMR (CDCl$_3$, 300MHz): $\delta =$ 1.90 – 2.00 (m, 2H), 2.38 – 2.43 (m, 4H), 5.79 (s, 1H), 6.17 (d, $^3$J$_{trans}$ = 13.7Hz, 1H), 6.96 (d, $^3$J$_{trans}$ = 13.9Hz, 1H); $^{13}$C NMR (CDCl$_3$, 75MHz): $\delta =$ 25.41 (CH$_2$), 33.28 (CH$_2$), 35.12 (CH$_2$), 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 C$_{11}$H$_{11}$Br: 222.0039; found: 222.0040; $^1$H NMR (CDCl$_3$, 300MHz): $\delta =$ 2.02 (s, 3H), 6.42 (d, $^3$J$_{trans}$ = 13.7Hz, 1H), 6.56 (s, 1H), 6.96 (d, $^3$J$_{trans}$ = 13.7Hz, 1H), 7.27 – 7.42 (m, 5H, arom. H); $^{13}$C NMR (CDCl$_3$, 75MHz): $\delta =$ 13.58 (CH$_3$), 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-halodiienes 1a-d with secondary amines 2. Synthesis of 1-aminodiienes 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 bromodiienes or 90 °C for chlorodiienes) 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 C_{12}H_{19}ON: 193.1461; found: 193.1460; \(^1\)H NMR (CDCl\(_3\), 300MHz): \(\delta = 1.61 – 1.68\) (m, 4H), 2.09 – 2.12 (m, 4H), 2.87 – 2.93 (m, 4H); 3.72 – 3.77 (m, 4H); 5.26 (d, \(^3\)J\(_{\text{trans}}\) = 14.2 Hz, 1H), 5.48 (s, 1H), 6.03 (d, \(^3\)J\(_{\text{trans}}\) = 14.2 Hz, 1H); \(^1^3\)C NMR (CDCl\(_3\), 75 MHz): \(\delta = 23.05\) (CH\(_2\)), 23.14 (CH\(_2\)), 25.25 (CH\(_2\)), 26.06 (CH\(_2\)), 49.49 (CH\(_2\)), 66.77 (CH\(_2\)), 106.88 (CH), 122.27 (CH), 134.70 (C), 136.82 (CH).

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

HRMS calcd. for C_{15}H_{19}N: 213.1512; found: 213.1514; \(^1\)H NMR (CDCl\(_3\), 300MHz): \(\delta = 1.68 – 1.78\) (m, 4H), 2.19 – 2.26 (m, 4H), 3.23 (s, 3H), 5.55 (d, \(^3\)J\(_{\text{trans}}\) = 14.0 Hz, 1H), 5.62 (s, 1H), 6.87 (d, \(^3\)J\(_{\text{trans}}\) = 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); \(^1^3\)C NMR (CDCl\(_3\), 75MHz): \(\delta = 25.30\) (CH\(_2\)), 25.39 (CH\(_2\)), 27.59 (CH\(_2\)), 28.35 (CH\(_2\)), 37.54 (CH\(_3\)), 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 C_{16}H_{21}N: 227.1668; found: 227.1668; \(^1\)H NMR (CDCl\(_3\), 300MHz): \(\delta = 1.70 – 1.80\) (m, 4H), 2.20 – 2.24 (m, 4H), 2.70 (s, 3H), 4.24 (s, 2H), 5.19 (d, \(^3\)J\(_{\text{trans}}\)=14.0Hz, 1H), 5.51 (s, 1H), 6.47 (d, \(^3\)J\(_{\text{trans}}\)=14.0Hz, 1H), 7.31 – 7.41 (m, 5H, arom.); \(^1^3\)C NMR (CDCl\(_3\), 75MHz): \(\delta = 23.43\) (CH\(_2\)), 23.55 (CH\(_2\)), 25.67 (CH\(_2\)), 26.29
(CH$_2$), 36.84 (CH$_3$), 59.81 (CH$_2$), 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 C$_{11}$H$_{17}$ON: 179.1305; found: 179.1301; $^1$H NMR (CDCl$_3$, 300MHz): $\delta$ = 1.91 – 1.96 (m, 2H), 2.39 – 2.44 (m, 4H), 2.95 (t, $^3$J= 4.8Hz , 4H), 3.76 (t, $^3$J= 4.8Hz, 4H), 5.43 (s, 1H), 5.49 (d, $^3$J$_{trans}$= 13.9Hz, 1H), 6.05 (d, $^3$J$_{trans}$= 13.9Hz, 1H); $^{13}$C NMR (CDCl$_3$, 75MHz): $\delta$ = 23.68 (CH$_2$), 32.06 (CH$_2$), 32.96 (CH$_2$), 49.40 (CH$_2$), 66.84 (CH$_2$), 100.34 (CH), 123.14 (CH), 140.32 (CH), 141.67 (C).

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

HRMS calcd. for C$_{11}$H$_{17}$ON: 199.1355; found: 199.1352; $^1$H NMR (CDCl$_3$, 300MHz): $\delta$ = 2.03 – 2.06 (m, 2H), 2.53 – 2.56 (m, 4H), 3.26 (s, 3H), 5.56 (s, 1H), 5.77 (d, $^3$J$_{trans}$= 13.7Hz, 1H), 6.87 (d, $^3$J$_{trans}$= 13.7Hz, 1H), 7.01 – 7.10 (m, 3H, arom. H), 7.34 – 7.37 (m, 2H, arom. H); $^{13}$C NMR (CDCl$_3$, 75MHz): $\delta$ = 23.19 (CH$_2$), 31.67 (CH$_2$), 32.55 (CH$_2$), 34.97 (CH$_3$), 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 C$_{15}$H$_{19}$ON: 229.1461; found: 229.1465. $^1$H NMR (CDCl$_3$, 300MHz): $\delta$ = 2.06 (s, 3H), 3.04 (t, $^3$J=4.8Hz, 4H), 3.81 (t, $^3$J=4.8Hz, 4H), 5.51 (d, $^3$J$_{trans}$=14.0Hz, 1H), 6.30 (d, $^3$J$_{trans}$=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): $\delta$ = 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

![结构式](image)

HRMS calcd. for C$_{18}$H$_{19}$N: 249.1512; found: 249.1510; $^1$H NMR (CDCl$_3$, 300MHz): $\delta$ = 2.15 (s, 3H), 3.32 (s, 3H), 5.76 (d, $^3$J$_{trans}$=13.8Hz, 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): $\delta$ = 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

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

![结构式](image)

HRMS calcd. for C$_{14}$H$_{17}$ON: 215.1305; found: 215.1294; $^1$H NMR (CDCl$_3$, 300MHz): $\delta$ = 3.02 (s, 4H), 3.75 (s, 4H), 5.42 (t, $^3$J=11.9Hz, 1H), 6.29 (d, $^3$J$_{trans}$=13.8Hz, 1H), 6.76 (dd, $^3$J$_{trans}$=15.0Hz, $^3$J=10.8Hz, 1H), 7.15 – 7.40 (m, 6H); $^{13}$C NMR (CDCl$_3$, 75MHz): $\delta$ = 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

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

![结构式](image)
HRMS calcd. for C_{17}H_{17}N: 235.1355; found: 235.1350; ^1H NMR (CDCl₃, 300MHz): δ = 3.30 (s, 3H), 5.70 (dd, J_{trans}=13.2Hz, J=10.5Hz, 1H), 6.50 (d, J=15.6Hz, 1H), 6.96 (dd, J_{trans}=15.6Hz, J=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 C_{14}H_{25}ON: 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, J=4.9Hz, 4H), 3.72 (t, J=4.8Hz, 4H), 5.22 (dd, J_{trans}=13.7Hz, J=10.2Hz, 1H), 5.38 (dt, J_{trans}=14.5Hz, J=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 C_{17}H_{25}N: 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, J_{trans}=15.0 Hz, J=10.4 Hz, 1H), 6.82 (d, J_{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).