Supporting Information for

Hydrogen Bond-Promoted Metal-Free Hydroamination of Alkynes

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General information

All reactions were performed in dried 45x14.75 mm screw-cap vials with a magnetic stirring bar under an atmosphere of argon. Ethylene glycol (EG) was used directly from the bottle (using distilled ethylene glycol on 4 Å molecular sieves has no effect on the results). All reagents (alkynes and amines) were purchased from either Sigma-Aldrich, Alfa Aesar or AKSci and purified prior to use (distillation or recrystallization). All reagents were weighed under air. $^1$H and $^{13}$C NMR spectra were recorded on a Varian Inova 400 MHz spectrometer or on a Bruker AC 400 MHz spectrometer in CDCl$_3$. For $^1$H NMR (400 MHz), CHCl$_3$ and TMS served as internal standards ($\delta = 7.27$ and 0 ppm respectively) and data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublet, m = multiplet), coupling constant (in Hz), and integration. For $^{13}$C NMR (100 MHz), CHCl$_3$ was used as internal standard ($\delta = 77.2$ ppm) and spectra were obtained with complete proton decoupling. High-resolution mass spectra (HRMS) were recorded on an Agilent 6210 ESI TOF (time of flight) mass spectrometer or on a JEOL JMS-DX300 mass spectrometer (3 keV, xenon) in a m-nitrobenzylalcohol matrix. Melting points (mp) were recorded on a MEL-TEMP® or on a Büchi B-540 melting point apparatus and are uncorrected.

General procedure for hydroamination of alkynes with amines

A screw-cap vial under atmosphere of argon was charged with ethylene glycol (250 µL, 8.9 equiv) as the solvent, the alkyne (0.5 mmol, 1 equiv) and the amine (1.5 mmol, or 2.5 mmol, see Table 3) at room temperature. The tube was sealed under a positive pressure of argon, stirred and heated to 150 °C for 8 hours. After allowing the reaction to cool to room temperature, the resulting mixture was diluted with ethyl acetate (5 mL) and washed with water (3 x 2 mL) and brine (1 x 2 mL). The combined organic layers were dried over anhydrous MgSO$_4$ and concentrated under reduced pressure (rotary evaporator). The residue was dried under high vacuum to give the desired enamines without any purification. In the case of amines with high boiling points, such as di-$n$-butylamine and di-$n$-pentyamine, the residues were dried by heating to 50 °C under high vacuum.
Additional solvents screened for the hydroamination of phenylacetylene with di-\textit{n}-butylamine

![Reaction diagram]

<table>
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<th>Entry</th>
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<th>2a (equiv)</th>
<th>T (°C)</th>
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<td>135</td>
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</table>

\(^a\) The reaction was stirred for 18 h.

Characterization of compounds 3a–ad

\textbf{(E)-N-Butyl-N-styrylbutyl-1-amine 3a}\(^1\)

Isolated yield = 98%. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.29–7.12 (m, 4H), 6.95–6.90 (m, 1H), 6.76 (d, \(J = 14\) Hz, 1H), 5.95 (d, \(J = 14\) Hz, 1H), 3.75 (t, \(J = 7.4\) Hz, 4H), 1.58–1.51 (m, 4H), 1.38–1.29 (m, 4H), 0.95 (t, \(J = 7.3\) Hz, 6H), \(^1\)^C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 140.4, 138.5, 128.5, 123.0, 122.6, 95.3, 51.4, 30.1, 20.2, 13.9.

\textbf{(E)-N-Pentyl-N-styrylpentan-1-amine 3b}

Isolated yield = 60% (75% when 2.5 mmol of amine is used). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.20–7.14 (m, 4H), 6.95–6.92 (m, 1H), 6.76 (d, \(J = 14\) Hz, 1H), 5.07 (d, \(J = 14\) Hz, 1H), 3.07 (t, \(J = 7.1\) Hz, 4H), 1.60–1.54 (m, 4H), 1.39–1.33 (m, 4H), 1.33–1.28 (m, 4H), 0.92 (t, \(J = 7.2\) Hz, 6H), \(^1\)^C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 140.4, 138.5, 128.5, 123, 122.5, 96.3, 51.7, 29.2, 27.6, 22.5, 14.1. HRMS (ESI-TOF) \(m/z\): 260.2301 (M+H\(^+\)); calc. for C\(_{18}\)H\(_{29}\)N: 260.2300.

\textbf{(E)-N-Propyl-N-styrylpropan-1-amine 3c}\(^2\)

Isolated yield = 96%. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.21–7.14 (m, 4H), 6.93 (tt, \(J = 7.3, 1.4\) Hz, 1H), 6.78 (d, \(J = 14\) Hz, 1H), 5.11 (d, \(J = 14\) Hz, 1H), 3.07 (t, \(J = 7.3\) Hz, 2H), 1.64–1.56 (m, 4H), 0.92 (t, \(J = 7.4\) Hz, 6H), \(^1\)\(^3\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 140.4, 138.6, 128.5, 123.0, 122.6, 95.3, 53.6, 21.2, 11.5.
(E)-N-Ethyl-N-styrylbutan-1-amine 3d

Isolated yield = 80%. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.21–7.13 (m, 4H), 6.94 (tt, $J = 7.2, 1.6$ Hz, 1H), 6.76 (d, $J = 14$ Hz, 1H), 5.13 (d, $J = 14$ Hz, 1H), 3.16 (q, $J = 7.1$ Hz, 2H), 3.08 (t, $J = 7.1$ Hz, 2H), 1.59–1.51 (m, 2H), 1.40–1.30 (m, 2H), 1.15 (t, $J = 7.1$ Hz, 4H), 0.95 (t, $J = 7.3$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 140.3, 138.1, 128.5, 123.1, 122.7, 95.7, 51.2, 45.5, 30.3, 20.2, 14.0, 12.9. HRMS (TOF-ESI) m/z: 204.1752 (M+H$^+$); calc. for C$_{14}$H$_{21}$N: 204.1753.

(E)-1-Styrlpiperidine 3e

Isolated yield = 90%. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.20–7.17 (m, 4H), 7.02–6.98 (m, 1H), 6.66 (d, $J = 14$ Hz, 1H), 5.36 (d, $J = 14$ Hz, 1H), 3.02 (t, $J = 7.2$ Hz, 4H), 1.65–1.57 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 140.3, 139.5, 128.5, 123.8, 123.7, 99.42, 99.4, 49.4, 25.3, 24.3.

(E)-1-Styrylazepane 3f

Isolated yield = 95%. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.19–7.13 (m, 4H), 7.06–6.90 (m, 1H), 6.85 (d, $J = 13.9$ Hz, 1H), 5.08 (d, $J = 13.9$ Hz, 1H), 3.26 (t, $J = 7.1$ Hz, 4H), 1.74–1.72 (m, 4H), 1.59–1.56 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 27.8, 28.6, 51.4, 94.5, 122.5, 123, 128.5, 139.3, 140.3.

(E)-4-Styrylmorpholine 3g

Isolated yield = 98%. mp: 60–65 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.25–7.19 (m, 4H), 7.06–7.02 (m, 1H), 6.61 (d, $J = 14.2$ Hz, 1H), 5.44 (d, $J = 14.1$ Hz, 1H), 3.77 (t, $J = 4$ Hz, 4H), 3.03 (t, $J = 4$ Hz, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 139.6, 138.4, 128.5, 124.4, 124.2, 101.4, 66.4, 48.9.

(E)-1-Methyl-4-styrylpiperazine 3h

Isolated yield = 91%. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.23–7.18 (m, 4H), 7.04–7.01 (m, 1H), 6.65 (d, $J = 14.1$ Hz, 1H), 5.40 (d, $J = 14.1$ Hz, 1H), 3.08 (t, $J = 8$ Hz, 4H), 2.47 (t, $J = 8$ Hz, 4H), 2.33 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 139.4, 138.9, 128.5, 124.1, 124.0, 100.9, 54.5, 48.5, 46.3.
(E)-4-Styrylthiomorpholine 3i

Isolated yield = 80%. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.24–7.17 (m, 4H), 7.02–7.00 (m, 1H), 6.59 (d, $J = 14.1$ Hz, 1H), 5.38 (d, $J = 14.1$ Hz, 1H), 3.43–3.40 (m, 4H), 2.66–2.51 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 139.1, 138.9, 128.5, 128.5, 124.1, 123.9, 100.3, 51.0, 26.4. HRMS (TOF-ESI) $m/z$: 206.1005 (M+H$^+$); calc. for C$_{12}$H$_{15}$NS: 206.1004.

(E)-N-Ethyl-N-(4-methylstyryl)butan-1-amine 3j

Isolated yield = 83%. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.05 (d, $J = 8.3$ Hz, 2H), 7.00 (d, $J = 8$ Hz, 2H), 6.70 (d, $J = 14$ Hz, 1H), 5.12 (d, $J = 14$ Hz, 1H), 3.14 (q, $J = 7.1$ Hz, 2H), 3.06 (dd, $J = 8.3$, 6.5 Hz, 2H), 2.27 (s, 3H), 1.58–1.50 (m, 2H), 1.39–1.30 (m, 2H), 1.13 (t, $J = 7.1$ Hz, 3H), 0.95 (t, $J = 7.3$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 137.4, 132.1, 129.1, 123.1, 95.8, 51.1, 47.9, 45.4, 30.3, 29.7, 20.9, 13.9, 12.9. HRMS (TOF-ESI) $m/z$: 218.1909 (M+H$^+$); calc. for C$_{15}$H$_{23}$N: 218.1908.

(E)-1-Methyl-4-(4-methylstyryl)piperazine 3k

Isolated yield = 81%. mp: 45–50 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.09–7.07 (m, 2H), 7.04–7.02 (m, 2H), 6.71 (d, $J = 14$ Hz, 2H), 5.39 (d, $J = 14$ Hz, 1H), 3.07–3.04 (m, 4H), 2.49–2.46 (m, 4H), 2.33 (s, 3H), 2.28 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 138.8, 135.9, 135.9, 133.6, 129.2, 124.0, 101.1, 84.6, 64.3, 54.5, 20.9.

(E)-N-Ethyl-N-(4-ethylstyryl) butan-1-amine 3l

Isolated yield = 85%. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.09–7.07 (m, 2H), 7.04–7.02 (m, 2H), 6.70 (d, $J = 14$ Hz, 1H), 5.13 (d, $J = 14$ Hz, 1H), 3.14 (q, $J = 7.1$ Hz, 2H), 3.08–3.04 (m, 2H), 2.57 (q, $J = 7.6$ Hz, 2H), 1.58–1.50 (m, 2H), 1.39–1.31 (m, 2H), 1.21 (t, $J = 7.6$ Hz, 3H), 1.13 (t, $J = 7.1$ Hz, 3H), 0.93 (t, $J = 7.3$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 138.7, 137.6, 137.5, 128.0, 123.1, 95.7, 51.1, 45.4, 30.3, 28.4, 20.2, 15.8, 13.9, 12.9. HRMS (TOF-ESI) $m/z$: 232.2067 (M+H$^+$); calc. for C$_{16}$H$_{25}$N: 232.2065.

(E)-N-(4-Ethylstyryl)-N-propylpropan-1-amine 3m

Isolated yield = 75%. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.08–7.01 (m, 4H), 6.71 (d, $J = 14$ Hz, 1H), 5.08 (d, $J = 14$ Hz, 1H), 3.05–3.01 (m, 4H), 2.56 (q, $J = 7.6$ Hz, 2H), 1.62–1.53 (m, 4H), 1.19 (t, $J = 7.6$ Hz, 3H), 0.90 (t, $J = 7.4$ Hz, 6H). $^{13}$C NMR (100
MHz, CDCl$_3$): $\delta$ 138.0, 137.7, 127.9, 123.1, 95.4, 53.6, 28.4, 21.1, 15.8, 11.5. HRMS (TOF-ESI) $m/z$: 232.2066 (M+H$^+$); calc. for C$_{16}$H$_{25}$N: 232.2065.

**E**-1-(4-Ethylstyryl)piperidine 3n

Isolated yield = 88%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.12 (d, $J = 8.2$ Hz, 2H), 7.05 (d, $J = 8.3$ Hz, 2H), 6.61 (d, $J = 14.1$ Hz, 1H), 5.37 (d, $J = 14.1$ Hz, 1H), 3.02–2.99 (m, 4H), 2.59 (q, $J = 7.6$ Hz, 2H), 1.64–1.57 (m, 6H), 1.21 (t, $J = 7.6$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.75, 136.8, 127.9, 123.9, 99.7, 49.7, 28.4, 25.3, 24.3, 15.7. HRMS (TOF-ESI) $m/z$: 216.1760 (M+H$^+$); calc. for C$_{15}$H$_{21}$N: 216.1759.

**E**-1-(4-Ethylstyryl)-4-methylpiperazine 3o

Isolated Yield = 70%. mp: 63–66 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.13 (d, $J = 8.2$ Hz, 2H), 7.05 (d, $J = 8.2$ Hz, 2H), 6.61 (d, $J = 14.1$ Hz, 1H), 5.41 (d, $J = 14.1$ Hz, 1H), 3.08–3.06 (m, 4H), 2.59 (q, $J = 7.6$ Hz, 2H), 2.50–2.48 (m, 4H), 2.23 (s, 3H), 1.21 (t, $J = 7.6$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 140.2, 138.9, 136.2, 128.0, 124.1, 101.2, 54.5, 48.6, 46.3, 28.4, 15.7. HRMS (TOF-ESI) $m/z$: 231.1862 (M+H$^+$); calc. for C$_{15}$H$_{22}$N$_2$: 231.1861.

**N**-(4-Bromostyryl)-**N**-propylpropan-1-amine 3p

Isolated yield = 95%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.26–7.24 (m, 2H), 6.99–6.97 (m, 2H), 6.75 (d, $J = 14$ Hz, 1H), 4.51 (d, $J = 14$ Hz, 1H), 3.06–3.02 (m, 4H), 1.62–1.53 (m, 3H), 0.91 (t, $J = 7.4$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.5, 139.0, 131.3, 124.4, 115.1, 94.0, 93.4, 53.6, 21.2, 11.4. HRMS (TOF-ESI) $m/z$: 282.0856 (M+H$^+$); calc. for C$_{14}$H$_{20}$BrN: 282.0857.

**E**-1-(4-Bromostyryl)piperidine 3q

Isolated yield = 90%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.29–7.27 (m, 2H), 7.04–7.01 (m, 2H), 6.64 (d, $J = 14$ Hz, 1H), 5.25 (d, $J = 14$ Hz, 1H), 3.04–3.01 (m, 4H), 1.59 (t, $J = 7.6$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 138.7, 131.4, 125.2, 116.4, 97.7, 49.6, 25.3, 24.3.
(E)-1-(4-Bromostyryl)-4-methylpiperazine 3r

Isolated yield = 81%. ¹H NMR (400 MHz, CDCl₃): δ 7.31–7.29 (m, 2H), 7.04 (d, J = 8.5 Hz, 2H), 6.63 (d, J = 14.1 Hz, 1H), 5.30 (d, J = 14.1 Hz, 1H), 3.09–3.07 (m, 4H), 2.48–2.45 (m, 4H), 2.33 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 139.8, 138.1, 131.4, 125.4, 116.9, 99.3, 54.4, 48.4, 46.3. mp: 43–45 °C. HRMS (TOF-ESI) m/z: 281.0655 (M+H⁺); calc. for C₁₃H₁₇BrN₂: 281.0653.

(E)-N-(3-Fluorostyryl)-N-propylpropan-1-amine 3s

Isolated yield = 91%. ¹H NMR (400 MHz, CDCl₃): δ 7.13–7.07 (m, 1H), 6.87–6.86 (m, 1H), 6.83–6.79 (m, 2H), 6.78 (d, J = 14 Hz, 1H), 6.61–6.56 (m, 1H), 5.04 (d, J = 13.9 Hz, 1H), 3.07–3.03 (m, 4H), 1.63–1.54 (m, 4H), 0.91 (t, J = 7.4 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 164.7, 142.5 (d, J₈₋₁₉ = 8.4 Hz), 129.6 (d, J₈₋₁₉ = 9.1 Hz), 118.74 (d, J₈₋₁₉ = 2.3 Hz), 109.0, 108.8, 94.2, 53.6, 21.2, 11.4. HRMS (TOF-ESI) m/z: 222.1661 (M+H⁺); calc. for C₁₄H₂₀FN: 222.1659.

(E)-1-(3-Fluorostyryl)-4-methylpiperazine 3t

Isolated yield = 90%. ¹H NMR (400 MHz, CDCl₃): δ 7.17–7.13 (m, 1H), 6.92 (d, J = 7.8 Hz, 1H), 6.86–6.84 (m, 1H), 6.71–6.64 (m, 2H), 5.33 (d, J = 14 Hz, 1H), 3.11–3.08 (m, 4H), 2.48–2.46 (m, 4H), 2.33 (s, 3H), 2.23 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 164.5, 141.5 (d, J₈₋₁₉ = 8.2 Hz), 140.4, 129.7 (d, J₈₋₁₉ = 8.9 Hz), 126.1, 119.7 (d, J₈₋₁₉ = 2.4 Hz), 110.0 (dd, J₈₋₁₉ = 44.1, 21.6 Hz), 99.4, 54.4, 48.4, 46.2. HRMS (TOF-ESI) m/z: 221.1455 (M+H⁺); calc. for C₁₃H₁₇FN₂: 221.1454.

(E)-4-(3,5-bis(Trifluoromethyl)styryl)morpholine 3u

Isolated yield = 93%. ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, J = 14 Hz, 1H), 7.54 (s, 2H), 7.46 (s, 1H), 5.40 (d, J = 14 Hz, 1H), 3.78 (t, J = 4.8 Hz, 4H), 3.13 (t, J = 4.8 Hz, 4H), 13C NMR (100 MHz, CDCl₃): δ 140.2, 140.2, 130.6 (q, J₈₋₁₉ = 32.4 Hz), 124.0, 122.3 (d, J₈₋₁₉ = 3.1 Hz), 121.3, 115.9 (t, J₈₋₁₉ = 4.1 Hz), 96.6, 65.3, 47.6. HRMS (TOF-ESI) m/z: 326.0978 (M+H⁺); calc. for C₁₄H₁₃FN₂O: 326.0980.

(E)-N-Isopropyl-N-(4-nitrostyryl)propan-2-amine 3v

Isolated yield = 97%. ¹H NMR (400 MHz, CDCl₃): δ 1.25 (d, J = 6.8 Hz, 12H), 3.81–3.74 (m, 2H), 5.29 (d, J = 14 Hz, 1H), 7.11 (d, J = 8.8 Hz, 2H),
7.16 (d, J = 14 Hz, 1H), 8.03 (d, J = 9.2 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.7, 136.6, 123.7, 120.6, 93.2, 46.2, 28.7, 20.8. HRMS (TOF-ESI) m/z: 249.1601 (M+H$^+$); calc. for C$_{14}$H$_{20}$N$_2$O$_2$: 249.1603.

(E)-4-(4-Nitrostyryl)morpholine 3

Isolated yield = 95%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.07 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 14 Hz, 1H), 5.40 (d, J = 14 Hz, 1H), 3.78 (t, J = 4.8 Hz, 4H), 3.19 (t, J = 4.8 Hz, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 145.6, 141.9, 123.4, 122.2, 96.9, 65.2, 47.6, 28.7. HRMS (TOF-ESI) m/z: 235.1080 (M+H$^+$); calc. for C$_{12}$H$_{14}$N$_2$O$_3$: 235.1083.

(E)-N-Ethyl-N-(2-(pyridin-3-yl)vinyl)butan-1-amine 3x

Isolated yield = 96%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.36 (d, J = 2.2 Hz, 1H), 8.13 (dd, J = 4.7, 1.4 Hz, 1H), 7.40–7.38 (m, 1H), 7.04 (dd, J = 8, 4.7 Hz, 1H), 6.76 (d, J = 14 Hz, 1H), 5.01 (d, J = 14 Hz, 1H), 3.16 (q, J = 7.1 Hz, 2H), 3.10–3.07 (m, 2H), 1.57–1.50 (m, 2H), 1.38–1.29 (m, 2H), 1.14 (t, J = 7.1 Hz, 3H), 0.94 (t, J = 7.3 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.0, 148.7, 141.9, 135.9, 118.6, 117.0, 94.5, 51.5, 45.8, 30.3, 20.2, 13.9, 13.1. HRMS (TOF-ESI) m/z: 205.1707 (M+H$^+$); calc. for C$_{13}$H$_{20}$N$_2$: 205.1705.

(E)-1-Methyl-4-(2-(pyridin-3-yl)vinyl)piperazine 3y

Isolated yield = 95%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.41 (s, 1H), 8.21 (d, J = 4.6 Hz, 1H), 7.44 (d, J = 8 Hz, 1H), 7.08 (dd, J = 7.8, 4.8 Hz, 2H), 6.67 (d, J = 14.1 Hz, 1H), 5.27 (d, J = 14.1 Hz, 1H), 3.12–3.09 (m, 4H), 2.48–2.45 (m, 4H), 2.32 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.2, 145.0, 140.5, 134.9, 129.9, 123.3, 96.2, 54.4, 48.3, 46.2. HRMS (TOF-ESI) m/z: 204.1502 (M+H$^+$); calc. for C$_{12}$H$_{17}$N$_3$: 204.1501.

(E)-4-(2-(Pyridine-3-yl)vinyl)morpholine 3z

Isolated yield = 95%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.42 (d, J = 2.2 Hz, 1H), 8.25 (dd, J = 4.7, 1.6 Hz, 1H), 7.48–7.45 (m, 1H), 7.13–7.10 (m, 1H), 6.64 (d, J = 14.1 Hz, 1H), 5.33 (d, J = 14.1 Hz, 1H), 3.77–3.75 (m, 4H), 3.08–3.06 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.3, 145.3, 140.7, 134.5, 130.2, 123.3, 96.8, 66.3, 48.7. HRMS (TOF-ESI) m/z: 191.1187 (M+H$^+$); calc. for C$_{11}$H$_{14}$N$_2$O: 191.1185.
(E)-N-Ethyl-N-(2-(pyridine-2-yl)vinyl)butan-1-amine 3aa

Isolated yield = 98%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.29–8.27 (m, 1H), 7.43 (d, $J = 13.4$ Hz, 1H), 6.86–6.83 (m, 1H), 6.74–6.71 (m, 1H), 5.16 (d, $J = 13.4$ Hz, 1H), 1.60–1.52 (m, 2H), 1.37–1.28 (m, 2H), 1.16 (t, $J = 7.1$ Hz, 4H), 0.93 (t, $J = 7.3$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.0, 148.7, 141.9, 135.9, 118.6, 117.0, 94.5, 51.5, 45.8, 30.3, 20.2, 13.9, 13.1. HRMS (TOF-ESI) $m/z$: 205.1706 (M+H$^+$); calc. for C$_{13}$H$_{20}$N$_2$: 205.1705.

(E)-N-Propyl-N-(2-(pyridine-2-yl)vinyl)propan-1-amine 3ab

Isolated yield = 90%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.33 (dd, $J = 4.9, 0.9$ Hz, 1H), 7.45 (d, $J = 13.4$ Hz, 1H), 7.39–7.35 (m, 1H), 6.85 (d, $J = 8.1$ Hz, 1H), 6.74–6.71 (m, 1H), 5.14 (d, $J = 13.4$ Hz, 1H), 3.12–3.09 (m, 4H), 1.65–1.56 (m, 4H), 0.90 (t, $J = 7.4$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.9, 148.6, 142.4, 136.9, 118.6, 116.9, 94.3, 53.7, 21.2, 11.3. HRMS (TOF-ESI) $m/z$: 205.1703 (M+H$^+$); calc. for C$_{13}$H$_{20}$N$_2$: 205.1704.

(E)-1-Methyl-4-(2-(pyridine-2-yl)vinyl)piperazine 3ac

Isolated yield = 97%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.33 (dd, $J = 4.9, 0.9$ Hz, 1H), 7.44–7.40 (m, 1H), 7.33 (d, $J = 13.6$ Hz, 1H), 6.90 (d, $J = 8$ Hz, 1H), 6.84–6.80 (m, 1H), 5.37 (d, $J = 13.6$ Hz, 1H), 3.20–3.18 (m, 4H), 2.46–2.44 (m, 4H), 2.32 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.0, 148.8, 142.7, 136.3, 119.3, 118.2, 98.2, 54.4, 48.2, 46.2.

(E)-4-(2-(Pyridin-2-yl)vinyl)morpholine 3ad

Isolated yield = 98%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.35 (d, $J = 4.8$ Hz, 1H), 7.47–7.41 (m, 1H), 7.30 (d, $J = 13.6$ Hz, 1H), 6.93 (d, $J = 8$ Hz, 1H), 6.85 (dd, $J = 7.4, 4.9$ Hz, 1H), 5.46 (d, $J = 13.6$ Hz, 1H), 3.76–3.73 (m, 4H), 3.16–3.13 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 157.6, 148.9, 142.9, 136.2, 119.5, 118.6, 98.9, 66.3, 48.6.
2D HMQC (Heteronuclear Multiple-Quantum Correlation) (3c):

This spectrum describes the direct C–H coupling for every proton for the molecule 3c.
2D HMBC (Heteronuclear Multiple Bond Correlation) (3c):

This spectrum describes the indirect C–H coupling (2–4 bonds) for every proton for the molecule 3c. Directed C–H bond correlation are suppressed.

The spectrum HMQC and HMBC of the compound 3c allow us to distribute and to assign every proton and carbon for this molecule and also to determine the correlation between them.
Deuterated experiments

1H NMR for the crude deuterated mixture

1H NMR (400 MHz, CDCl3): δ 7.21–7.14 (m, 4H), 6.93 (tt, J = 7.3, 1.4 Hz, 1H), 6.80–6.77 (m, 0.5H), 5.12–5.10 (m, 0.5H), 3.07 (t, J = 7.3 Hz, 2H), 1.56–1.64 (m, 4H), 0.92 (t, J = 7.4 Hz, 6H).

This 1H NMR spectrum of the crude deuterated mixture confirm the presence of all peaks for 3c which means the formation of this molecule. A comparison between this spectrum and the spectrum of 3c shows a difference in the ethylenic protons region. Two new peaks appear between the two doublets of the ethylenic protons. In addition, the integration of these signals does not correspond to one proton each anymore. We believe that those signals correspond to some correlation between the two ethylenic proton H_a and H_b and a deuterium appeared in the molecule resulting from an exchange with the solvent. This observation confirms the formation of 3c’, 3c’’, and 3c’’’. 
$^{13}$C NMR for the crude deuterated mixture

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 140.4 (d), 138.6 (d), 128.5, 123.0 (d), 122.6 (d), 95.4, 95.3, 53.7, 53.6, 21.2, 11.5.

A comparison between this $^{13}$C NMR spectrum and the spectrum of 3c shows the presence of all peaks of 3c and an appearance of new doublets resulting from a correlation between the carbon and the deuterium in the molecule resulting from some exchange with the solvent. This observation also confirms the formation of 3c', 3c'', and 3c'''.

References

Copies of $^1$H and $^{13}$C NMR spectra

$(E)$-N-Butyl-N-styrylbutan-1-amine 3a
(E)-N-Pentyl-N-styrlypentan-1-amine 3b
(E)-N-Propyl-N-styrylpropan-1-amine 3c
(E)-N-Ethyl-N-styrylbutan-1-amine 3d
(E)-1-Styrylpiperidine 3e
(E)-1-Styrylazepane 3f
(E)-4-Styrylmorpholine 3g
(E)-1-Methyl-4-styrylpiperazine 3h
(E)-4-Styrylthiomorpholine 3i
(E)-N-Ethyl-N-(4-methylstyryl)butan-1-amine 3j
(E)-N-Ethyl-N-(4-ethylstyryl) butan-1-amine 3l
(E)-N-(4-Ethylstyryl)-N-propylpropan-1-amine 3m
(E)-1-(4-Ethylstyrly)piperidine 3n
(E)-1-(4-Ethylstyryl)-4-methylpiperazine 3o
(E)-N-(4-Bromostyryl)-N-propylpropan-1-amine 3p
(E)-1-(4-Bromostyryl)piperidine 3q
(E)-1-(4-Bromostyryl)-4-methylpiperazine 3r
(E)-N-(3-Fluorostyryl)-N-propylpropan-1-amine 3s
(E)-1-(3-Fluorostyryl)-4-methylpiperazine 3t
(E)-4-(3,5-Bis(trifluoromethyl)styryl)morpholine 3u
(E)-N-Isopropyl-N-(4-nitrostyryl)propan-2-amine 3v
(E)-4-(4-Nitrostyryl)morpholine 3w
(E)-N-Ethyl-N-(2-(pyridin-3-yl)vinyl)butan-1-amine 3x
(E)-1-Methyl-4-(2-(pyridin-3-yl)vinyl)piperazine 3y
(E)-4-(2-(Pyridine-3-yl)vinyl)morpholine 3z
(E)-N-Ethyl-N-(2-(pyridine-2-yl)vinyl)butan-1-amine 3aa
(E)-N-Propyl-N-(2-(pyridin-2-yl)vinyl)propan-1-amine 3ab
(E)-1-Methyl-4-(2-(pyridin-2-yl)vinyl)piperazine 3ac
(E)-4-(2-(Pyridin-2-yl)vinyl)morpholine 3ad