Synthesis of Functionalized Pyrroles *via* Gold(I)-Catalyzed *aza*-Claisen type rearrangement

Florin M. Istrate and Fabien Gagosz

Laboratoire de Synthèse Organique, UMR 7652 CNRS / Ecole Polytechnique, 91128 Palaiseau, France.

Supporting Information

General informations p 2

Synthesis of substrates 8a-8c p 2-4

Synthesis of enynes 10a-10l p 4-11

Gold catalyzed formation of pyrroles 9a-c p 11-12

Gold catalyzed formation of pyrroles 11a-l p 12-18

Synthesis of substrates 21,22 and 25 p 18-19

Gold catalyzed formation of pyrroles 23,24 and 27 p 19-21

General Information.

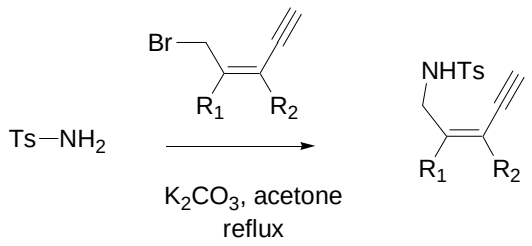
Commercially available reagents were used as received without further purification. Dry THF and hexanes were obtained by distillation from Na/benzophenone, dry diethylether from $CaCl_2$ and then NaH, and dry CH_2Cl_2 from P_2O_5. $CDCl_3$ was distilled from P_2O_5, and stored on 4 Å Linde molecular sieves. All products were purified by flash column chromatography using silica gel SDS 60 C.C. 40-63 or neutral alumina SDS C.C. 50-200. NMR spectra were recorded in $CDCl_3$ (or CD_2Cl_2) with TMS as an internal standard at ambient temperature on a Bruker Avance 400 operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C or on a Bruker 300 operating at 121.5 MHz for ^{31}P. Infrared Absorption spectra were recorded as a solution in CCl_4 with a Perkin-Elmer 1600 Fourier Transform Spectrophotometer. Mass spectra were recorded with a HP 5989B mass spectrometer. High resolution mass spectra were recorded on a JEOL GCmate II spectrometer. Melting points were determined by Reichert microscope apparatus and were uncorrected. $R_3PAuNTf_2$ catalysts were synthesized as previously described.[1]

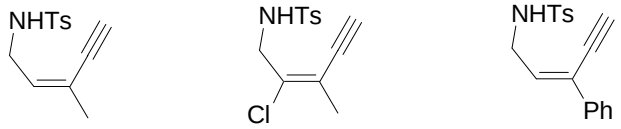
Experimental Section.

Synthesis of substrates 8a-8c.

Substrates **8a-8c** were synthesized by monoallylation of tosylamide following the procedure described by Robin and coworkers.[2] The corresponding allylating agents were synthesized as described in the following scheme.

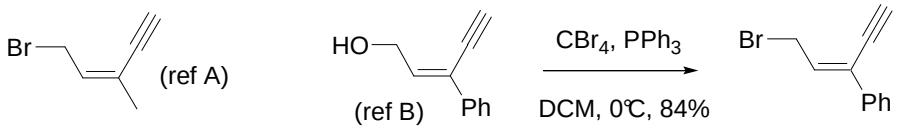
[1] N. Mezailles, L. Ricard, F. Gagosz *Org. Lett.* **2005**, *7*, 4133-4136.
[2] S. Robin, G. Rousseau *Eur. J. Org. Chem.* **2000**, *3007*-3011.

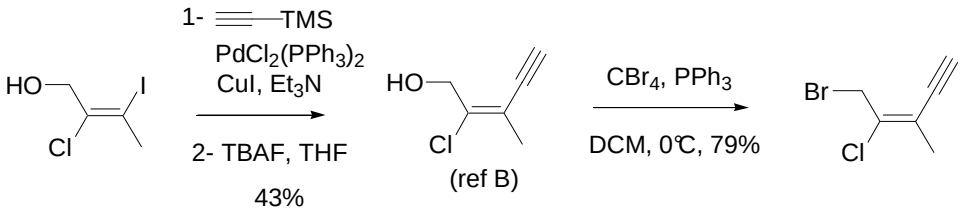




8a 61% **8b** 65% **8c** 71%

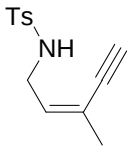
(S. Robin, G. Rousseau *Eur. J. Org. Chem.* **2000**, 3007-3011)





A) B. Gabriele, G. Salerno, A. Fazio, M. R. Bossio, *Tetrahedron Lett.* **2001**, *42*, 1339-1342

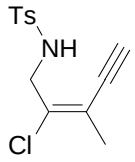
B) B. Gabriele, G. Salerno, E. Lauria, *J. Org. Chem.* **1999**, *64*, 7687 - 7692



8a

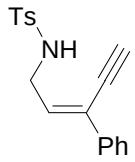
4-Methyl-*N*-((Z)-3-methyl-pent-2-en-4-ynyl)-benzene-sulfonamide (8a). Yield: 61%, pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 5.69 (t, *J* = 6.9 Hz, 1H), 4.83 (t, *J* = 6.0 Hz, 1H), 3.80 (dd, *J* = 6.9, 6.0 Hz, 2H), 3.14 (s, 1H), 2.47 (s, 3H), 1.81 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.5, 136.9, 133.3, 129.7, 127.3, 121.4, 82.9, 81.4, 42.9, 22.7, 21.5. IR (CCl_4) 3395, 3307, 2978, 1406, 1339, 1162, 1095, 1046

cm^{-1}. MS (CI+ NH_3) m/z 284, 267 (MNH_4^+), 250 (MH^+). HR-MS (EI) m/z calcd for $C_{13}H_{15}NO_2S$: 249.0823, found: 249.0819.



8b

***N*-((E)-2-Chloro-3-methyl-pent-2-en-4-ynyl)-4-methyl-benzenesulfonamide (8b).** Yield: 65%, pale yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 5.22 (t, *J* = 6.4 Hz, 1H), 4.19 (d, *J* = 6.4 Hz, 2H), 3.33 (s, 1H), 2.46 (s, 3H), 1.78 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.5, 137.7, 137.0, 129.4, 127.4, 118.5, 84.0, 80.7, 47.5, 21.6, 19.8. IR (CCl_4) 3370, 3296, 3058, 1559, 1416, 1137, 1161 cm^{-1}. MS (CI+ NH_3) m/z 317, 301 (MNH_4^+), 284 (MH^+). HR-MS (EI) m/z calcd for $C_{13}H_{14}ClNO_2S$: 283.0434, found: 283.0425.



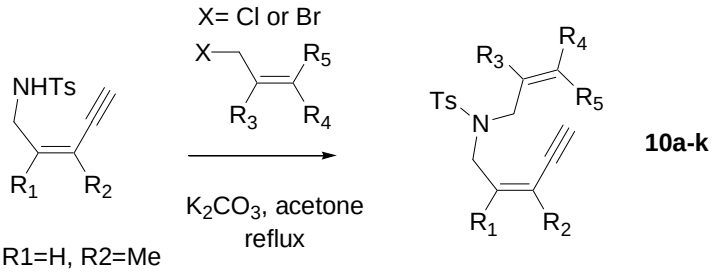
8c

4-Methyl-*N*-((Z)-3-phenyl-pent-2-en-4-ynyl)-benzene-sulfonamide (8c). Yield: 71%, pale yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.35-7.31 (m, 5H), 6.31 (t, *J* = 6.8 Hz, 1H), 5.08 (t, *J* = 5.6 Hz, 1H), 4.08 (dd, *J* = 6.8, 5.6 Hz, 2H), 3.40 (s, 1H), 2.43 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.7, 137.1, 136.2, 133.2, 129.8, 128.5, 128.4, 127.3, 126.0, 125.4, 85.4, 79.4, 43.4, 21.5. IR (CCl_4) 3370, 3296, 3056, 1599, 1410, 1333, 1160 cm^{-1}. MS (CI+ NH_3) m/z 329 (MNH_4^+), 312 (MH^+). HR-MS (EI) m/z calcd for $C_{18}H_{17}NO_2S$: 311.0980, found: 311.0979.

Synthesis of substrates 10a-10l.

Substrates **10a-k** were synthesized allylation of tosylamide following the procedure described by Robin and coworkers, as described in the following

scheme.[3] Substrate **10l** was obtained as by-product (13% yield) in the reaction of formation of **8a** (see above).



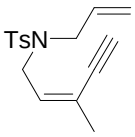
10a-k

8a R1=H, R2=Me

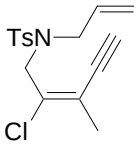
8b R1=Cl, R2=Me

8c R1=Cl, R2=Ph

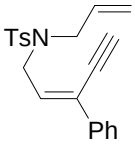
(S. Robin, G. Rousseau *Eur. J. Org. Chem.* **2000**, 3007-3011)



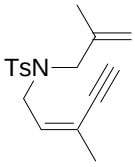
10a 96%



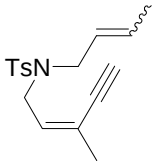
10b 93%



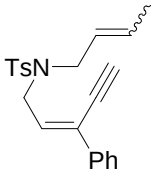
10c 99%



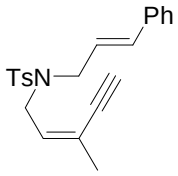
10d 94%



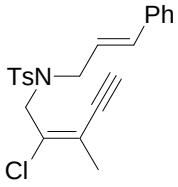
10e 89%
(Z:E=1:3.5)



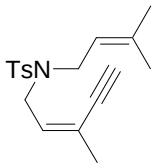
10f 99%
(Z:E=1:2.6)



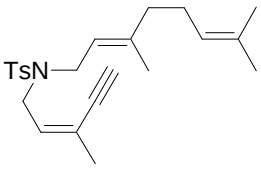
10g 92%



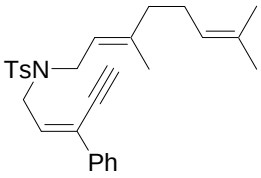
10h 92%



10i 76%

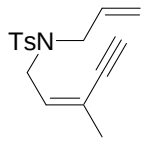


10j 82%



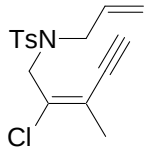
10k 99%

[3] S. Robin, G. Rousseau *Eur. J. Org. Chem.* **2000**, *3007*-3011.



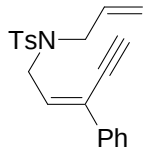
10a

***N*-Allyl-4-methyl-*N*-((Z)-3-methyl-pent-2-en-4-ynyl)-benzenesulfonamide (10a).** Yield: 96%, pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz , 2H), 7.34 (d, *J* = 8.2 Hz , 2H), 5.76-5.66 (m, 2H), 5.24-5.16 (m, 2H), 4.02 (d, *J* = 6.9 Hz , 2H), 3.81 (d, *J* = 6.3 Hz , 2H), 3.16 (s, 1H), 2.47 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.2, 137.3, 133.6, 132.7, 129.7, 127.3, 121.1, 118.8, 82.5, 81.7, 50.2, 46.9, 22.9, 21.6. IR (CCl_4) 3052, 2984, 1242, 1264, 1159 cm^{-1}. MS (CI+ NH_3) m/z 307 (MNH_4^+), 290 (MH^+). HR-MS (EI) m/z calcd for $C_{16}H_{19}NO_2S$: 289.1136, found: 289.1150.



10b

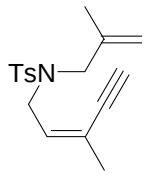
***N*-Allyl-*N*-((E)-2-chloro-3-methyl-pent-2-en-4-ynyl)-4-methyl-benzenesulfonamide (10b).** Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 5.77.5.67 (m, 1H), 5.23-5.14 (m, 2H), 4.39 (s, 2H), 3.84 (d, *J* = 6.4 Hz, 2H), 3.30 (s, 1H), 2.47 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.3, 138.6, 137.3, 132.5, 129.5, 127.4, 119.1, 119.0, 83.2, 51.0, 50.3, 21.6, 20.3. IR (CCl_4) 3306, 2924, 1356, 1163, 1095, 1018 cm^{-1}. MS (CI+ NH_3) m/z 341 (MNH_4^+), 324 (MH^+). HR-MS (EI) m/z calcd for $C_{16}H_{18}ClNO_2S$: 323.0747, found: 323.0756.



10c

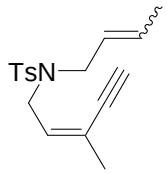
***N*-Allyl-4-methyl-*N*-((Z)-3-phenyl-pent-2-en-4-ynyl)-benzene-sulfonamide (10c).** Yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.53 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.40-7.32 (m, 5H), 6.33 (t, *J* = 6.9 Hz, 1H), 5.82-5.72 (m, 1H), 5.28-5.19 (m, 2H), 4.28 (d, *J* = 6.9 Hz, 2H), 3.89 (d, *J* = 6.3 Hz, 2H), 3.42 (s, 1H), 2.47 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.4, 137.2, 136.5, 133.6, 132.7, 129.8, 128.4, 128.3, 127.3, 126.0, 125.3, 119.1, 85.1, 79.6,

50.7, 47.5, 21.6. IR (CCl_4) 3307, 2982, 1354, 1261, 1162, 1093 cm^{-1}. MS (CI+ NH_3) m/z 369 (MNH_4^+), 352 (MH^+), 224, 196, 158, 141. HR-MS (EI) m/z calcd for $C_{21}H_{21}NO_2S$: 351.1293, found: 351.1292.



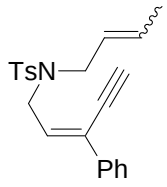
10d

4-Methyl-*N*-(2-methyl-allyl)-*N*-((Z)-3-methyl-pent-2-en-4-ynyl)-benzenesulfonamide (10d). Yield: 94%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 5.62 (t, *J* = 6.7 Hz, 1H), 4.93 (s, 1H), 4.91 (s, 1H), 3.99 (d, *J* = 6.8 Hz, 2H), 3.78 (s, 2H), 3.15 (s, 1H), 2.47 (s, 3H), 1.83 (s, 3H), 1.75 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.2, 140.1, 137.0, 133.4, 129.6, 127.3, 120.9, 114.3, 82.5, 81.6, 53.8, 47.0, 22.8, 21.5, 19.9. IR (CCl_4) 3308, 2979, 1442, 1351, 1261, 1162, 1096 cm^{-1}. MS (CI+ NH_3) m/z 321 (MNH_4^+), 304 (MH^+). HR-MS (EI) m/z calcd for $C_{17}H_{21}NO_2S$: 303.1293, found: 303.1289.



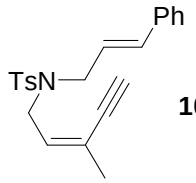
10e

***N*-But-2-enyl-4-methyl-*N*-((Z)-3-methyl-pent-2-en-4-ynyl)-benzenesulfonamide (10e).** Yield: 89%, isolated as a mixture of isomers (Z:E=1:3.5). For the major *E* isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 5.72-5.60 (m, 2H), 5.35-5.29 (m, 1H), 4.00 (d, *J* = 7.0 Hz, 2H), 3.74 (d, *J* = 6.7 Hz, 2H), 3.17 (s, 1H), 2.47 (s, 3H), 1.87 (s, 3H), 1.66 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.2, 137.4, 134.0, 130.7, 129.6, 127.3, 125.2, 120.8, 82.3, 81.8, 49.6, 46.6, 22.9, 21.5, 17.7. For the isomeric mixture: IR (CCl_4) 3308, 2922, 1442, 1350, 1160 cm^{-1}. MS (CI+ NH_3) m/z 321 (MNH_4^+), 304 (MH^+). HR-MS (EI) m/z calcd for $C_{17}H_{21}NO_2S$: 303.1293, found: 303.1283.



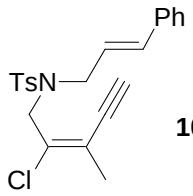
10f

***N*-But-2-enyl-4-methyl-*N*-((Z)-3-phenyl-pent-2-en-4-ynyl)-benzenesulfonamide (10f).** Yield: 99% isolated as a mixture of isomers (Z:E=1:2.6). For the major *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.40-7.34 (m, 5H), 6.32 (t, *J* = 6.8 Hz, 1H), 5.69-5.62 (m, 1H), 5.42-5.36 (m, 1H), 4.26 (d, *J* = 7.0 Hz, 2H), 3.81 (d, *J* = 6.7 Hz, 2H), 3.42 (s, 1H), 2.47 (s, 3H), 1.67 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.3, 137.3, 136.6, 134.0, 131.0, 129.7, 128.5, 128.3, 127.3, 126.0, 125.2, 124.9, 84.9, 79.7, 50.0, 47.2, 21.5, 17.7. For the isomeric mixture: IR (CCl_4) 3307, 2975, 1444, 1353, 1261, 1161, 1093 cm^{-1}. MS (CI+ NH_3) m/z 383 (MNH_4^+), 366 (MH^+). HR-MS (EI) m/z calcd for $C_{22}H_{23}NO_2S$: 365.1449, found: 365.1450.



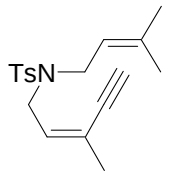
10g

4-Methyl-*N*-((Z)-3-methyl-pent-2-en-4-ynyl)-*N*-((E)-3-phenyl-allyl)-benzenesulfonamide (10g). Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.36-7.27 (m, 7H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.03 (td, *J* = 15.8, 6.8 Hz, 1H), 5.73 (t, *J* = 7.0 Hz, 1H), 4.09 (d, *J* = 7.0 Hz, 2H), 3.98 (d, *J* = 6.8 Hz, 2H), 3.10 (s, 1H), 2.47 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.3, 137.4, 136.5, 134.1, 133.6, 129.7, 128.5, 127.8, 127.3, 126.5, 123.7, 121.4, 82.6, 81.8, 49.6, 46.9, 22.9, 21.6. IR (CCl_4) 3307, 3030, 1597, 1496, 1442, 1351, 1160, 1094 cm^{-1}. MS (CI+ NH_3) m/z 383 (MNH_4^+), 366 (MH^+). HR-MS (EI) m/z calcd for $C_{22}H_{23}NO_2S$: 365.1449, found: 365.1457.



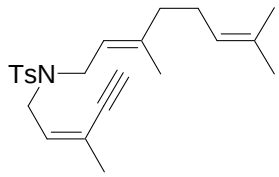
10h

***N*-((E)-2-Chloro-3-methyl-pent-2-en-4-ynyl)-4-methyl-*N*-((E)-3-phenyl-allyl)-benzenesulfonamide (10h).** Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.35-7.25 (m, 7H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.05 (td, *J* = 15.9, 6.8 Hz, 1H), 4.47 (s, 2H), 3.99 (d, *J* = 6.8 Hz, 2H), 3.23 (s, 1H), 2.47 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.4, 138.7, 137.4, 136.4, 134.3, 129.6, 128.5, 127.8, 127.5, 126.5, 123.5, 119.3, 83.9, 81.4, 51.1, 49.7, 21.6, 20.4. IR (CCl_4) 3304, 2924, 1440, 1357, 1261, 1161, 1096 cm^{-1}. MS (CI+ NH_3) m/z 400 (MH^+). HR-MS (EI) m/z calcd for $C_{22}H_{22}ClNO_2S$: 399.1060, found: 399.1047.



10i

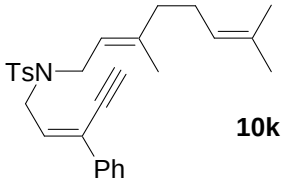
4-Methyl-*N*-(3-methyl-but-2-enyl)-*N*-((Z)-3-methyl-pent-2-en-4-ynyl)-benzenesulfonamide (10i). Yield: 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 5.69 (t, *J* = 6.5 Hz, 1H), 5.06 (bt, *J* = 7.1 Hz, 1H), 4.02 (d, *J* = 6.5 Hz, 2H), 3.80 (d, *J* = 7.1 Hz, 2H), 3.15 (s, 1H), 2.47 (s, 3H), 1.87 (s, 3H), 1.69 (s, 3H), 1.64 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.0, 137.3, 137.0, 134.4, 129.6, 127.3, 120.5, 118.9, 82.3, 81.7, 46.9, 45.3, 25.8, 22.9, 21.6, 17.8. IR (CCl_4) 3308, 2924, 1445, 1348, 1161, 1094 cm^{-1}. MS (CI+ NH_3) m/z 335 (MNH_4^+), 318 (MH^+), 267, 250. HR-MS (EI) m/z calcd for $C_{18}H_{23}NO_2S$: 317.1449, found: 317.1452.



10j

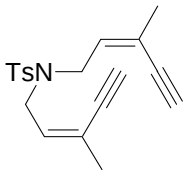
***N*-((E)-3,7-Dimethyl-octa-2,6-dienyl)-4-methyl-*N*-((Z)-3-methyl-pent-2-en-4-ynyl)-benzenesulfonamide (10j).** Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 5.70 (t, *J* =

6.6 Hz, 1H), 5.08-5.03 (m, 2H), 4.02 (d, *J* = 6.6 Hz, 2H), 3.83 (d, *J* = 7.0 Hz, 2H), 3.14 (s, 1H), 2.47 (s, 3H), 2.07-1.96 (m, 4H), 1.87 (s, 3H), 1.71 (s, 3H), 1.62 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.0, 140.4, 137.4, 134.4, 131.7, 129.6, 127.3, 123.9, 120.4, 118.6, 82.4, 81.7, 46.9, 45.3, 39.6, 26.3, 25.7, 22.9, 21.5, 17.7, 16.3. IR (CCl_4) 3308, 2924, 1445, 1349, 1261, 1161, 1094 cm^{-1}. MS (CI+ NH_3) m/z 386 (MH^+). HR-MS (EI) m/z calcd for $C_{23}H_{31}NO_2S$: 385.2075, found: 385.2083.



10k

***N*-((E)-3,7-Dimethyl-octa-2,6-dienyl)-4-methyl-*N*-((Z)-3-phenyl-pent-2-en-4-ynyl)-benzenesulfonamide (10k).** Yield: 99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.53 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.39-7.31 (m, 5H), 6.34 (t, *J* = 6.7 Hz, 1H), 5.14 (t, *J* = 7.0 Hz, 1H), 5.06 (t, *J* = 6.1 Hz, 1H), 4.28 (d, *J* = 6.7 Hz, 2H), 3.90 (d, *J* = 7.0 Hz, 2H), 3.40 (s, 1H), 2.47 (s, 3H), 2.04-1.92 (m, 4H), 1.70 (s, 3H), 1.63 (s, 3H), 1.60 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.3, 140.9, 137.3, 136.6, 134.4, 131.7, 129.7, 128.5, 128.3, 127.3, 126.0, 124.7, 123.8, 118.5, 84.9, 79.6, 47.5, 45.6, 39.6, 26.3, 25.7, 21.5, 17.7, 16.4. IR (CCl_4) 3307, 2979, 1445, 1351, 1261, 1161, 1095 cm^{-1}. MS (CI+ NH_3) m/z 448 (MH^+). HR-MS (EI) m/z calcd for $C_{28}H_{33}NO_2S$: 447.2232, found: 447.2222.



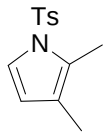
10l

4-Methyl-*N*,*N*-bis-((Z)-3-methyl-pent-2-en-4-ynyl)-benzenesulfonamide (10l). Yield: 13%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 5.69 (t, *J* = 6.7 Hz, 2H), 4.02 (d, *J* = 6.7 Hz, 4H), 3.16 (s, 2H), 2.47 (s, 3H), 1.87 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.3, 136.8, 133.5, 129.7, 127.4, 121.0, 82.6, 81.7, 47.6, 22.9, 21.5. IR (CCl_4)

3308, 2922, 1441, 1351, 1161, 1095 cm^{-1}. MS (CI+ NH_3) m/z 328 (MH^+). HR-MS (EI) m/z calcd for $C_{19}H_{21}NO_2S$: 327.1293, found: 327.1280

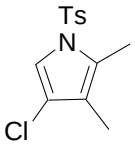
General procedures for the gold(I)-catalyzed formation of pyrroles 9a-c

General procedure: To a solution of the substrate (0.25 mmol, 1eq) in CH_2Cl_2 (0.1M) was added catalyst PPh_3AuNTf_2 (1.9 mg, 1 mol%). The mixture was stirred at rt and monitored periodically by TLC. Upon completion, the mixture was evaporated, loaded onto a silicagel column and chromatographed with the appropriate mixture of petroleum ether and ether to give the to give the pyrrole.



9a

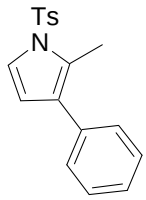
2,3-Dimethyl-1-(toluene-4-sulfonyl)-1*H*-pyrrole (9a). Yield: 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.33 (b, *J* = 8.3 Hz , 2H), 7.26 (d, *J* = 3.3 Hz, 1H), 6.11 (d, *J* = 3.3 Hz , 1H), 2.45 (s, 3H), 2.24 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.5, 136.6, 129.9, 126.8, 126.1, 121.0, 120.7, 113.9, 21.6, 11.3, 10.8. IR (CCl_4) 2924, 1596, 1493, 1371, 1187, 1161, 1094 cm^{-1}. MS (CI+ NH_3) m/z 250 (MH^+), 189. HR-MS (EI) m/z calcd for $C_{13}H_{15}NO_2S$: 249.0823, found: 249.0820.



9b

4-Chloro-2,3-dimethyl-1-(toluene-4-sulfonyl)-1*H*-pyrrole (9b). Yield: 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.35 (b, *J* = 8.3 Hz , 2H), 7.28 (s, 1H), 2.46 (s, 3H), 2.25 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 145.0, 135.9, 130.1, 126.9, 126.4, 119.8, 117.8, 117.0, 21.7, 11.4, 8.9. IR (CCl_4) 2926, 1595, 1376, 1257, 1182, 1158, 1093, 1053 cm^{-1}. MS (CI+

NH_3) m/z 284 (MH^+). HR-MS (EI) m/z calcd for $C_{13}H_{14}ClNO_2S$: 283.0434, found: 283.0439.

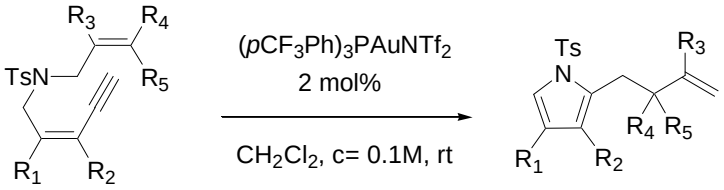


9c

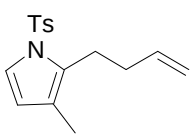
2-Methyl-3-phenyl-1-(toluene-4-sulfonyl)-1*H*-pyrrole (9c). Yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.43-7.28 (m, 7H), 6.42 (s, 1H), 2.47 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.9, 136.4, 135.2, 130.1, 128.6, 128.4, 127.4, 127.0, 126.6, 126.2, 121.4, 112.5, 21.7, 11.9. IR (CCl_4) 2925, 1501, 1373, 1269, 1179, 1022 cm^{-1}. MS (CI+ NH_3) m/z 312 (MH^+). HR-MS (EI) m/z calcd for $C_{18}H_{17}NO_2S$: 311.0980, found: 311.0974.

General procedures for the gold(I)-catalyzed formation of pyrroles 11a-l

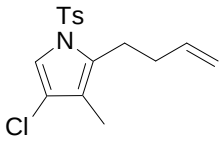
General procedure: To a solution of the substrate (0.25 mmol, 1eq) in CH_2CL_2 (0.1M) was added catalyst **12** (4.7 mg, 2 mol%). The mixture was stirred at rt and monitored periodically by TLC. Upon completion, the mixture was evaporated, loaded onto a silicagel column and chromatographed with the appropriate mixture of petroleum ether and ether to give the to give the pyrrole.



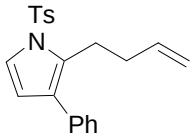
10a-l **11a-l**



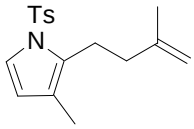
11a 94%



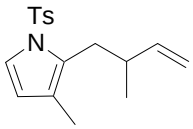
11b 88%



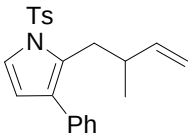
11c 72%



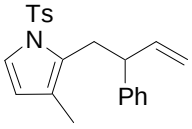
11d 89%



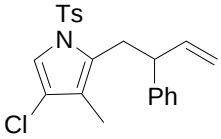
11e 91%



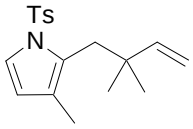
11f 89%



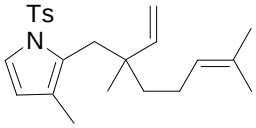
11g 97%



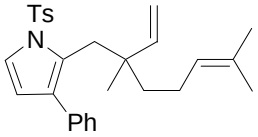
11h 98%



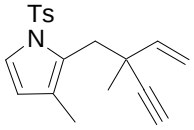
11i 90%



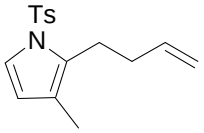
11j 91%



11k 93%

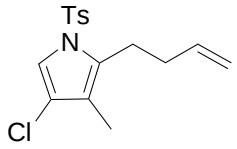


11l 84%



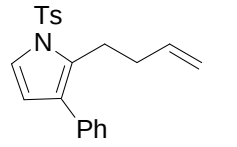
11a

2-But-3-enyl-3-methyl-1-(toluene-4-sulfonyl)-1*H*-pyrrole (11a). Yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz , 2H), 7.31 (d, *J* = 8.2 Hz , 2H), 7.25 (d, *J* = 3.3 Hz , 1H), 6.13 (d, *J* = 3.3 Hz , 1H), 5.88-5.78 (m, 1H), 5.06-4.98 (m, 2H), 2.78-2.74 (m, 2H), 2.44 (s, 3H), 2.26-2.20 (m, 2H), 1.97 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.5, 137.8, 136.9, 130.4, 129.9, 126.6, 121.9, 121.4, 115.0, 114.3, 34.4, 24.9, 21.6, 11.5. IR (CCl_4) 2925, 1639, 1143, 1371, 1183, 1159, 1098 cm^{-1}. MS (CI+ NH_3) m/z 290 (MH^+), 248. HR-MS (EI) m/z calcd for $C_{16}H_{19}NO_2S$: 289.1136, found: 289.1137.



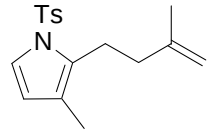
11b

2-But-3-enyl-4-chloro-3-methyl-1-(toluene-4-sulfonyl)-1*H*-pyrrole (11b). Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz , 2H), 7.34 (d, *J* = 8.3 Hz , 2H), 7.27 (s, 1H), 5.87-5.76 (m, 1H), 5.06-4.99 (m, 2H), 2.78-2.74 (m, 2H), 2.45 (s, 3H), 2.25-2.20 (m, 2H), 1.93 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 145.0, 137.4, 136.3, 130.6, 130.1, 126.8, 120.6, 118.1, 117.7, 115.4, 34.2, 25.4, 21.7, 9.0. IR (CCl_4) 2926, 1592, 1376, 1256, 1181, 1095 cm^{-1}. MS (CI+ NH_3) m/z 324 (MH^+), 282. HR-MS (EI) m/z calcd for $C_{16}H_{18}ClNO_2S$: 323.0747, found: 323.0739.



11c

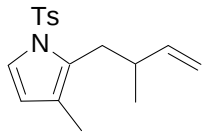
2-But-3-enyl-3-phenyl-1-(toluene-4-sulfonyl)-1*H*-pyrrole (11c). Yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz , 2H), 7.42-7.29 (m, 8H), 6.43 (d, *J* = 3.3 Hz , 1H), 5.82-5.72 (m, 1H), 5.03-4.95 (m, 2H), 2.92-2.88 (m, 2H), 2.46 (s, 3H), 2.36-2.30 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.9, 137.6, 136.7, 135.3, 130.8, 130.0, 128.5, 128.3, 128.1, 126.8, 126.7, 122.3, 115.0, 113.2, 34.9, 25.1, 21.7. IR (CCl_4) 2981, 1501, 1374, 1261, 1180, 1127 cm^{-1}. MS (CI+ NH_3) m/z 352 (MH^+), 310. HR-MS (EI) m/z calcd for $C_{21}H_{21}NO_2S$: 351.1293, found: 351.1283.



11d

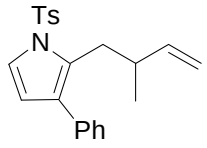
3-Methyl-2-(3-methyl-but-3-enyl)-1-(toluene-4-sulfonyl)-1*H*-pyrrole (11d). Yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz , 2H), 7.31 (d, *J* = 8.3 Hz , 2H), 7.25 (d, *J* = 3.3 Hz , 1H), 6.13 (d, *J* = 3.3 Hz , 1H), 4.77 (s, 1H), 4.72 (s, 1H), 2.81-2.77 (m, 2H), 2.44 (s, 3H), 2.14-2.10 (m, 2H), 1.97 (s, 3H), 1.78 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 145.4, 144.5, 136.9, 130.6, 129.9, 126.6, 121.7, 121.3, 114.2, 110.2, 38.1, 24.0, 22.5, 21.6, 11.3. IR

(CCl_4) 2928, 1446, 1371, 1184, 1127, 1093 cm^{-1}. MS (CI+ NH_3) m/z 321 (MNH_4^+), 304 (MH^+). HR-MS (EI) m/z calcd for $C_{17}H_{21}NO_2S$: 303.1293, found: 303.1285.



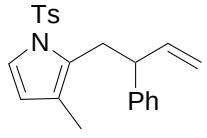
11e

3-Methyl-2-(2-methyl-but-3-enyl)-1-(toluene-4-sulfonyl)-1*H*-pyrrole (11e). Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz , 2H), 7.30 (d, *J* = 8.3 Hz , 2H), 7.24 (d, *J* = 3.3 Hz , 1H), 6.13 (d, *J* = 3.3 Hz , 1H), 5.83-5.74 (m, 1H), 4.96-4.91 (m, 2H), 2.72-2.56 (m, 3H), 2.43 (s, 3H), 1.96 (s, 3H), 0.99 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.4, 143.7, 136.9, 129.9, 129.8, 126.5, 123.0, 121.9, 114.6, 112.8, 38.8, 32.4, 21.6, 19.0, 12.0. IR (CCl_4) 2927, 11740, 1638, 1371, 1183, 1164, 1095 cm^{-1}. MS (CI+ NH_3) m/z 304 (MH^+), 248. HR-MS (EI) m/z calcd for $C_{17}H_{21}NO_2S$: 303.1293, found: 303.1284.



11f

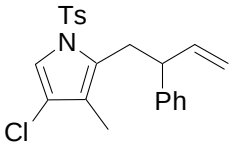
2-(2-Methyl-but-3-enyl)-3-phenyl-1-(toluene-4-sulfonyl)-1*H*-pyrrole (11f). Yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz , 2H), 7.40-7.28 (m, 8H), 6.38 (d, *J* = 3.3 Hz , 1H), 5.56-5.47 (m, 1H), 4.82-4.77 (m, 2H), 2.98-2.82 (m, 2H), 2.58-2.46 (m, 1H), 2.47 (s, 3H), 0.78 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.8, 143.4, 136.8, 135.8, 130.0, 129.9, 128.9, 128.4, 126.7, 126.6, 122.6, 113.7, 112.9, 38.6, 32.3, 21.7, 19.0. IR (CCl_4) 2964, 1501, 1374, 1179, 1135, 1089 cm^{-1}. MS (CI+ NH_3) m/z 366 (MH^+), 310. HR-MS (EI) m/z calcd for $C_{22}H_{23}NO_2S$: 365.1449, found: 365.1448.



11g

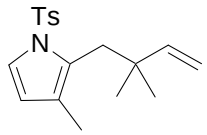
3-Methyl-2-(2-phenyl-but-3-enyl)-1-(toluene-4-sulfonyl)-1*H*-pyrrole (11g). Yield: 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz , 2H), 7.32-7.17 (m, 8H), 6.17-6.07 (m, 1H), 6.04 (d, *J* = 3.3 Hz , 1H), 5.09 (d, *J* =

10.3 Hz, 1H), 5.02 (d, *J* = 17.1 Hz, 1H), 3.79 (q, *J* = 7.5 Hz, 1H), 3.12 (dd, *J* = 14.4, 7.5 Hz, 1H), 2.91 (dd, *J* = 14.4, 7.5 Hz, 1H), 2.43 (s, 3H), 1.56 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.5, 143.7, 140.5, 136.8, 129.9, 128.7, 128.3, 127.9, 126.5, 126.3, 123.9, 122.1, 115.0, 114.6, 50.2, 32.6, 21.6, 11.4. IR (CCl_4) 2926, 1493, 1371, 1250, 1184, 1157, 1106 cm^{-1}. MS (CI+ NH_3) m/z 366 (MH^+), 248. HR-MS (EI) m/z calcd for $C_{22}H_{23}NO_2S$: 365.1449, found: 365.1447.



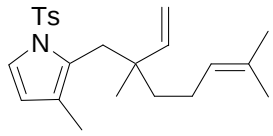
11h

4-Chloro-3-methyl-2-(2-phenyl-but-3-enyl)-1-(toluene-4-sulfonyl)-1*H*-pyrrole (11h). Yield: 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz , 2H), 7.34-7.16 (m, 8H), 6.15-6.06 (m, 1H), 5.10 (d, *J* = 10.3 Hz, 1H), 5.04 (d, *J* = 17.1 Hz, 1H), 3.77 (q, *J* = 7.5 Hz, 1H), 3.14 (dd, *J* = 14.5, 7.5 Hz, 1H), 2.90 (dd, *J* = 14.5, 7.5 Hz, 1H), 2.45 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 145.0, 143.3, 140.1, 136.2, 130.1, 129.0, 128.4, 127.8, 126.7, 126.5, 122.4, 118.3, 118.2, 115.4, 50.1, 33.1, 21.7, 9.0. IR (CCl_4) 2981, 1595, 1376, 1259, 1181, 1095 cm^{-1}. MS (CI+ NH_3) m/z 400 (MH^+), 282. HR-MS (EI) m/z calcd for $C_{22}H_{22}ClNO_2S$: 399.1060, found: 399.1071.



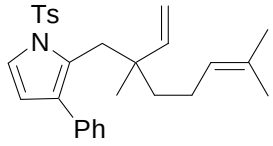
11i

2-(2,2-Dimethyl-but-3-enyl)-3-methyl-1-(toluene-4-sulfonyl)-1*H*-pyrrole (11i). Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.3 Hz , 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 3.3 Hz , 1H), 6.13 (d, *J* = 3.3 Hz , 1H), 6.03-5.96 (m, 1H), 4.94 (dd, *J* = 6.3, 1.2 Hz , 1H), 4.91 (s, 1H), 2.85 (s, 2H), 2.41 (s, 3H), 1.94 (s, 3H), 1.10 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.7, 144.2, 136.7, 129.7, 126.3, 124.8, 123.3, 116.2, 110.2, 39.9, 36.4, 26.8, 21.6, 13.3. IR (CCl_4) 2926, 1372, 1184, 1108 cm^{-1}. MS (CI+ NH_3) m/z 318 (MH^+), 248. HR-MS (EI) m/z calcd for $C_{18}H_{23}NO_2S$: 317.1449, found: 317.1439.



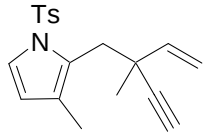
11j

2-(2,6-Dimethyl-2-vinyl-hept-5-enyl)-3-methyl-1-(toluene-4-sulfonyl)-1*H*-pyrrole (11j). Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz , 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 3.3 Hz , 1H), 6.11 (d, *J* = 3.3 Hz , 1H), 5.91 (dd, *J* = 17.5, 10.0 Hz , 1H), 5.14 (t *J* = 7.0 Hz, 1H), 5.00 (dd, *J* = 10.0, 1.4 Hz , 1H), 4.86 (dd, *J* = 17.5, 1.4 Hz, 1H), 2.82-2.90 (m, 2H), 2.41 (s, 3H), 1.99-1.88 (m, 2H), 1.93 (s, 3H), 1.72 (s, 3H), 1.63 (s, 3H), 1.49 (t, *J* = 8.5 Hz, 2H), 1.07 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 146.9, 144.2, 136.7, 130.9, 129.7, 129.5, 126.3, 125.1, 124.9, 123.3, 116.2, 112.1, 43.0, 41.0, 36.5, 25.8, 23.1, 21.6, 21.1, 17.7, 13.4. IR (CCl_4) 2922, 1447, 1372, 1184, 1104 cm^{-1}. MS (CI+ NH_3) m/z 386 (MH^+), 248. HR-MS (EI) m/z calcd for $C_{23}H_{31}NO_2S$: 385.2075, found: 385.2099.



11k

2-(2,6-Dimethyl-2-vinyl-hept-5-enyl)-3-phenyl-1-(toluene-4-sulfonyl)-1*H*-pyrrole (11k). Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz , 2H), 7.38-7.24 (m, 8H), 6.36 (d, *J* = 3.3 Hz, 1H), 5.55 (dd, *J* = 17.4, 10.7 Hz, 1H), 4.97 (t *J* = 7.0 Hz, 1H), 4.74 (dd, *J* = 10.7, 1.4 Hz, 1H), 4.66 (dd, *J* = 17.4, 1.5 Hz, 1H), 3.17 (bs, 2H), 2.44 (s, 3H), 1.83-1.68 (m, 2H), 1.68 (s, 3H), 1.56 (s, 3H), 1.25 (t, *J* = 8.6 Hz, 2H), 0.79 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 146.1, 144.6, 136.8, 136.6, 131.4, 130.8, 129.3, 129.2, 128.3, 126.7, 126.3, 125.0, 123.8, 115.2, 111.8, 43.3, 41.2, 36.0, 25.7, 22.9, 21.6, 20.9, 17.6. IR (CCl_4) 2923, 1374, 1181, 1121, 1089 cm^{-1}. MS (CI+ NH_3) m/z 448 (MH^+). HR-MS (EI) m/z calcd for $C_{28}H_{33}NO_2S$: 447.2232, found: 447.2235.



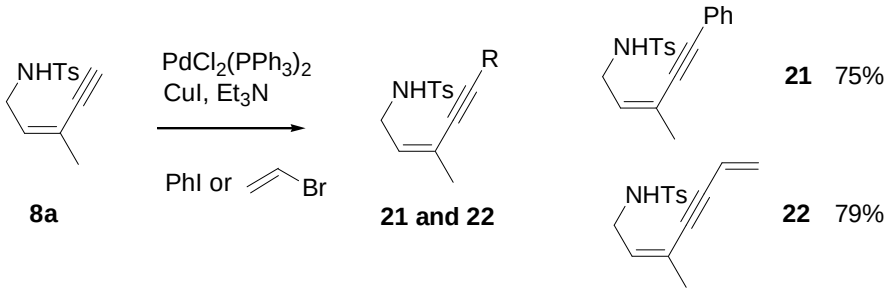
11l

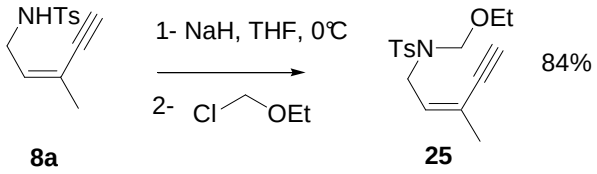
2-(2-Ethynyl-2-methyl-but-3-enyl)-3-methyl-1-(toluene-4-sulfonyl)-1*H*-pyrrole (11l). Yield: 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J*

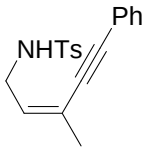
= 8.3 Hz , 2H), 7.26 (d, *J* = 8.3 Hz , 2H), 7.19 (d, *J* = 3.3 Hz, 1H), 6.15 (d, *J* = 3.3 Hz, 1H), 5.97 (dd, *J* = 17.0, 10.1 Hz, 1H), 5.40 (dd, *J* = 17.0, 1.3 Hz, 1H), 5.09 (dd, *J* = 10.1, 1.3 Hz, 1H), 3.18 (bs, 2H), 2.45 (s, 3H), 2.34 (s, 1H), 2.05 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.3, 142.7, 136.7, 129.7, 127.8, 126.2, 126.0, 123.5, 116.3, 113.1, 88.6, 72.2, 40.8, 36.0, 27.4, 21.4, 13.3. IR (CCl_4) 3310, 2928, 1595, 1372, 1260, 1185, 1158, 1114 cm^{-1}. MS (CI+ NH_3) m/z 328 (MH^+). HR-MS (EI) m/z calcd for $C_{19}H_{21}NO_2S$: 327.1293, found: 447.1297.

Synthesis of substrates 21,22 and 25.

Substrates **21, 22** and **25** were synthesized as described in the following scheme.



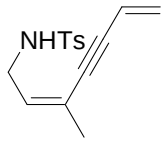




21

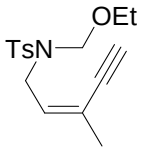
4-Methyl-*N*-((Z)-3-methyl-5-phenyl-pent-2-en-4-ynyl)-benzenesulfonamide (21). Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.23 (m, 5H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.56 (tq, *J* = 1.5, 7.0 Hz, 1H), 4.66 (t, *J* = 6.0 Hz, 1H), 3.75 (t, *J* = 7.0 Hz, 2H), 2.30 (s, 3H), 1.78 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.4, 136.8, 131.5, 131.0, 129.7, 128.5, 128.3, 127.3, 122.9, 122.6, 94.8, 86.8, 43.2, 22.9, 21.5. IR (CCl_4) 3396, 3261, 3059, 2958, 2925, 2861, 1727, 1596, 1489, 1441, 1407, 1341, 1162, 1117, 1093,

1038 cm^{-1}. MS (CI+ NH_3) m/z 343 (MNH_4^+), 326 (MH^+), 309, 276, 261. HR-MS (EI) m/z calcd for $C_{19}H_{19}NO_2S$: 325.1136, found: 325.1137.



22

4-Methyl-*N*-((Z)-3-methyl-hepta-2,6-dien-4-ynyl)-benzenesulfonamide (22). Yield: 79%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.84 (dd, *J* = 11.1, 17.5 Hz, 1H), 5.57 (tq, *J* = 1.3, 7.0 Hz, 1H), 5.54 (dd, *J* = 2.0, 17.5 Hz, 1H), 5.47 (dd, *J* = 2.0, 11.1 Hz, 1H), 5.02 (t, *J* = 6.0 Hz, 1H), 3.75 (t, *J* = 6.1 Hz, 2H), 2.41 (s, 3H), 1.77 (d, *J* = 1.1 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.2, 136.7, 131.4, 129.5, 127.1, 127.0, 122.0, 116.6, 93.3, 87.4, 42.9, 22.7, 21.3. IR (CCl_4) 3396, 3274, 3014, 2956, 2923, 2874, 1597, 1406, 1338, 1162, 1094, 1044 cm^{-1}. MS (CI+ NH_3) m/z 293 (MNH_4^+), 276 (MH^+), 189. HR-MS (EI) m/z calcd for $C_{15}H_{17}NO_2S$: 275.0980, found: 275.0979.

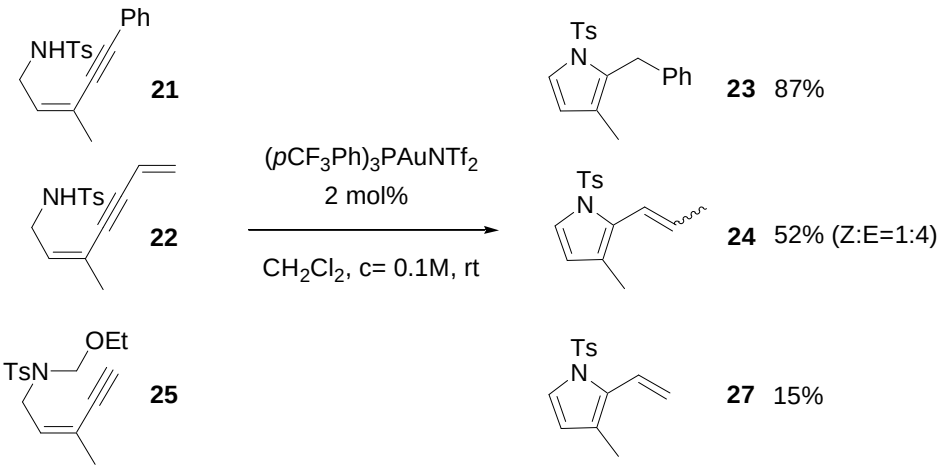


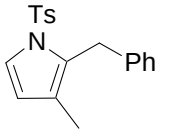
25

***N*-Ethoxymethyl-4-methyl-*N*-((Z)-3-methyl-pent-2-en-4-ynyl)-benzenesulfonamide (25).** Yield: 84%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.60 (tq, *J* = 0.7, 6.3 Hz, 1H), 4.65 (s, 2H), 3.94 (d, *J* = 6.9 Hz, 2H), 3.41 (q, *J* = 7.0 Hz, 2H), 3.05 (s, 1H), 2.34 (s, 3H), 1.75 (d, *J* = 1.3 Hz, 3H), 1.07 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.2, 137.4, 133.4, 129.4, 127.3, 121.0, 82.3, 81.4, 77.7, 63.5, 46.2, 22.8, 21.4, 14.8. IR (CCl_4) 3308, 2977, 2927, 2878, 1445, 1350, 1191, 1162, 1084, 1012 cm^{-1}. MS (CI+ NH_3) m/z 325 (MNH_4^+), 308 (MH^+), 262. HR-MS (EI) m/z calcd for $C_{16}H_{21}NO_3S$: 307.1242, found: 307.1242.

General procedures for the gold(I)-catalyzed formation of pyrroles 23,24 and 27

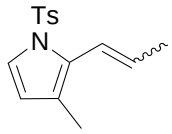
General procedure: To a solution of the substrate (0.25 mmol, 1eq) in CH_2CL_2 (0.1M) was added catalyst **12** (12 mg, 5 mol%). The mixture was stirred at rt and monitored periodically by TLC. Upon completion, the mixture was evaporated, loaded onto a silicagel column and chromatographed with the appropriate mixture of petroleum ether and ether to give the to give the pyrrole.





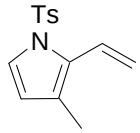
23

2-Benzyl-3-methyl-1-(toluene-4-sulfonyl)-1*H*-pyrrole (23). Yield: 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 3.3 Hz, 1H), 7.11 (m, 3H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.89 (m, 2H), 6.18 (d, *J* = 3.3 Hz, 1H), 4.17 (s, 2H), 2.32 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.0, 138.9, 136.1, 129.5, 128.3, 128.1, 127.9, 126.7, 125.6, 123.3, 121.6, 114.0, 30.0, 21.5, 11.4. IR (CCl_4) 3031, 2958, 2925, 2864, 1742, 1597, 1493, 1452, 1372, 1322, 1260, 1180, 1132, 1093 cm^{-1}. MS (CI+ NH_3) m/z 343 (MNH_4^+), 326 (MH^+). HR-MS (EI) m/z calcd for $C_{19}H_{19}NO_2S$: 325.1136, found: 325.1126.



24

3-Methyl-2-propenyl-1-(toluene-4-sulfonyl)-1*H*-pyrrole (24). Yield: 52%, isolated as a mixture of *cis* and *trans* isomers (*Z*:*E*=1:3.8). For the mixture of isomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H, *E* isomer), 7.63 (d, *J* = 8.1 Hz, 2H, *Z* isomer), 7.27-7.18 (m, 3H), 6.62 (d, *J* = 16.1 Hz, 1H, *E* isomer), 6.38 (d, *J* = 10.9 Hz, 1H, *Z* isomer), 6.12 (d, *J* = 3.3 Hz, 1H, Z isomer), 6.09 (d, *J* = 3.3 Hz, 1H, *E* isomer), 5.82 (dq, *J* = 6.0, 11.1 Hz, 1H, *Z* isomer), 5.64 (dq, *J* = 6.7, 15.9 Hz, 1H, *E* isomer), 2.39 (s, 3H, *E* isomer), 2.38 (s, 3H, *Z* isomer), 2.02 (s, 3H, *E* isomer), 1.87 (dd, *J* = 1.7, 6.6 Hz, 3H, *E* isomer), 1.81 (s, 3H, *Z* isomer), 1.27 (m, 3H, *Z* isomer). For the *Z* isomer: ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.3, 136.1, 130.6, 129.5, 127.2, 127.0, 123.4, 122.0, 119.7, 114.5. For the *E* isomer: ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.5, 136.2, 130.2, 129.6, 129.2, 127.0, 122.4, 120.8, 120.1, 115.2. For the mixture of isomers: IR (CCl_4) 3149, 3033, 2924, 2860, 1596, 1447, 1374, 1190, 1171, 1140, 1099, 1051 cm^{-1}. MS (CI+ NH_3) m/z 276 (MH^+). HR-MS (EI) m/z calcd for $C_{15}H_{17}NO_2S$: 275.0980, found: 275.0977.



27

3-Methyl-1-(toluene-4-sulfonyl)-2-vinyl-1*H*-pyrrole (27). Yield: 15%, isolated in mixture with pyrrole **9a**. Selected data: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.2 Hz, 2H), 7.21-7.13 (m, 3H), 6.93 (dd, J = 11.7, 17.8 Hz, 1H), 6.04 (d, J = 3.3 Hz, 1H), 5.25 (dd, J = 1.5, 11.6 Hz, 1H), 5.12 (dd, J = 1.5, 17.7 Hz, 1H), 2.31 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.7, 136.1, 129.7, 129.1, 126.9, 125.9, 123.9, 121.7, 117.2, 115.4.