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Gold Catalysis: Selectivity Problems in Hydroarylations with Pyrroles

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Gold-catalyzed reactions of pyrrole derivatives with methyl vinyl ketone preferentially give rise to doubly substituted products, with an excess of methyl vinyl ketone even triple substitutions can be observed. This is independent of the electronic nature of substituents on the pyrrole ring, even substrates with electron-withdrawing acyl substituents in 1-, 2- or 3-position show this behavior. The NH group of the pyrrole ring may be unprotected, no competing hydroamination is observed. In an intramolecular competition experiment with a furan ring only the pyrrole ring reacted. The constitutions of the highly-substituted pyrroles were proven by NMR spectroscopy and one X-ray structure analysis. Control experiments show that $Yb(OTf)_3$ does not catalyze these reactions, but Ag^+ and H^+ does. Contrary to pyrroles, under similar reaction conditions indoles show a clean monosubstitution reaction.

Introduction

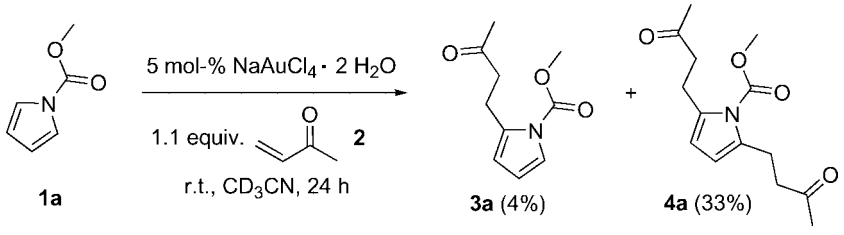
During the last years, gold complexes have proven to possess high catalytic activity for various organic transformations.[1] Gold-catalysed hydroarylation reactions of furans were reported as early as in the year 2000.[2,3] Subsequently, other electron-rich arenes were investigated,[4] among these the only nitrogen-containing heteroarenes were indoles[5–7] and 7-azaindoles.[8]

In most of the examples mentioned above, α,β-unsaturated carbonyl compounds were used. Occasionally, activated alkynes,[4b,9] and even unactivated[10] alkynes were investigated.

Since in the latter case intermolecular reactions[10f] proceeded very slow, we wanted to investigate more reactive electron-rich heterocycles. Here we report our observations when using pyrroles as substrates in gold-catalysed reactions with α,β-unsaturated carbonyl compounds.

Results and Discussion

In order to start with simple substrates, the gold-catalysed addition of different pyrroles to methyl vinyl ketone as one of the simplest Michael acceptors was investigated. We started with the *N*-protected pyrrole **1a**. The reaction proceeded at room temperature, defined prodcuts could be obtained with a catalyst of low activity (5 mol-% of $NaAuCl_4$ in deuterated acetonitrile, see Scheme 1). Even with 1.1 equivalents of **2** only 4% of **3a** could be obtained, most of the product that could be isolated was the doubly alkylated **4a** (33%). The regioselectivity of the reaction is easily deduced by comparison with the ^1H and ^{13}C NMR shifts of the heteroaryl hydrogen and carbon atoms of **3a** and **4a** with the corresponding signals of pyrrole or **1a**. For **3a** only one low-field signal for the α-position to nitrogen is observed (δ = 7.20 ppm), two signals at higher field for the hydrogen atoms in 3- and 4-position (δ = 5.97 and 6.09 ppm). The same applies for the methine-carbon atoms, one signal at lower field (δ = 120.88 ppm) and two signals at higher field (δ = 111.80 and 111.82 ppm). Based on that data a safe signal assignment for **4a** is possible. The ^1H



Scheme 1. Reaction of the protected pyrrole **1a** with **2**.

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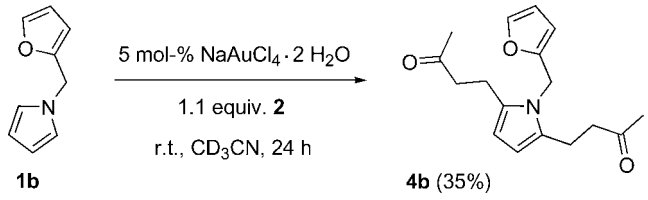
NMR shift at δ = 5.83 ppm and the ^{13}C NMR shift at δ = 110.38 ppm for the aryl-CH groups clearly prove the 2,5-disubstitution.

Next we switched to an alkyl substituent on the pyrrole nitrogen atom, substrate **1b** allowed the intramolecular competition of a pyrrole and a 2-alkylfuran (Scheme 2). Under the same conditions as applied for **1a**, **1b** produced **4b**. Again NMR spectroscopy supports the assumption of a 2,5-disubstituted pyrrole (symmetrical unit, δ_H = 5.79 ppm, and methine group signal at δ = 110.33 ppm in the ^{13}C NMR spectrum), the typical resonances of the 2-substituted furan ring (δ_H = 6.02, 6.27, and 5.79 ppm with the typical coupling constants of the ABC system; the methine group signals at δ = 104.46, 107.17, and 143.18 ppm in the ^{13}C NMR spectrum) are quite similar to the furan resonances in the starting material.

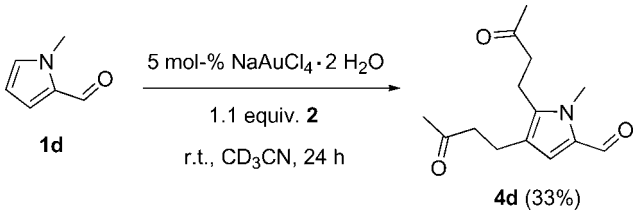


Scheme 2. Reaction of the *N*-alkylpyrrole **1b** with **2**.

Next we placed an acceptor into the 2-position of the pyrrole ring. Unprotected **1c** delivered a small amount of **3c** and again **4c** as the major product (Scheme 3). Here the structure assignment was more difficult. The spectroscopic data for **3c** again supports a 2,5-substituted pyrrole: the shifts δ_H = 5.99 and 6.81 ppm are typical of methine groups and they are similar to a related 5-alkyl-1*H*-pyrrole-2-carbaldehyde (δ = 6.11 and 6.94 ppm).[11] For the latter from an X-ray crystal structure analysis of a product derived from it, the assignment was clearly proved. This is in accordance with the initial product **3c**, the second reaction with **2** is expected to lead to **4c** (attack of the electrophile at the more electron-rich 4-position of **3c**, the 3-postion would be part of an α,β-unsaturated ketone substructure and thus less reactive). The corresponding ^{13}C NMR spectroscopic data for the pyrrole methine groups (δ = 108.62 and 117.41 ppm) in **3c** reflects the great difference of charge density.

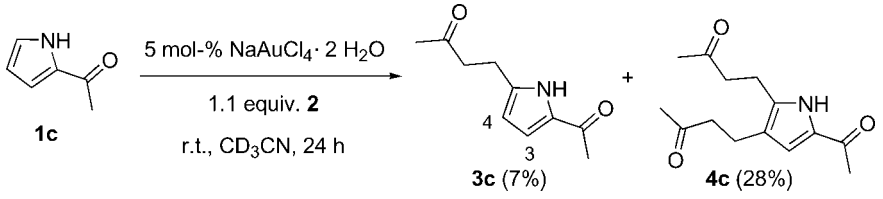
Finally, the structure assignment of **4c** was confirmed by a crystal structure analysis, which unambiguously confirmes the position of the three substitutents on the pyrrole ring (Figure 1).[12] The amino ketone substructure gives rise to the formation of dimers in the solid state by two hydrogen bonds. It is interesting to note, that even in this case of a free NH group no hydroamination like that reported by Arcadi et al. for 7-azaindoles can be observed.[8]

A similar behavior was observed with 1-methyl-1*H*-pyrrole-2-carbaldehyde (**1d**). Here only **4d** could be isolated from the reaction mixture (Scheme 4). The analogy to **4c** (twofold reaction with **2**, δ_H = 5.65 ppm, ^{13}C NMR resonance at δ = 123.36 ppm) allows the assignment in this case.



Scheme 4. Reaction of 1-methyl-1*H*-pyrrole-2-carbaldehyde (**1d**) with **2**.

The last substrate we used was 3-acetyl-1-methyl-1*H*-pyrrole (**1e**). Again the product of a twofold reaction with **2** was observed as the main product when 1.1 equivalents of **2** were used. In **4e** the new side chains can be found in the 2- and 5-position of the pyrrole ring. The chemical shifts clearly indicate this: δ = 6.15 ppm in the ^{1}H and 107.00 ppm in the ^{13}C NMR spectrum for the remaining methine unit



Scheme 3. Reaction of the 2-acetylpyrrole **1c** with **2**.

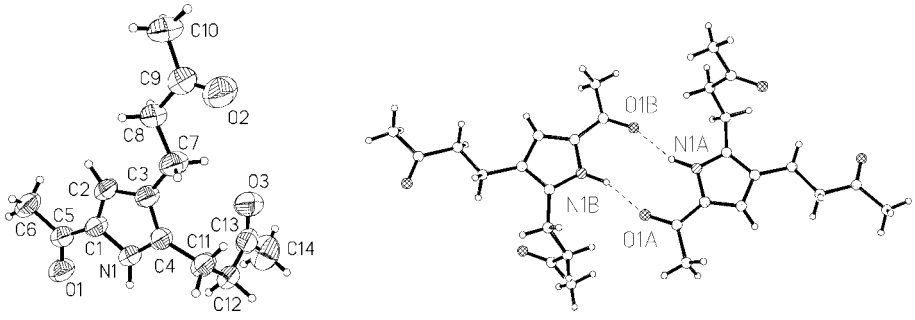
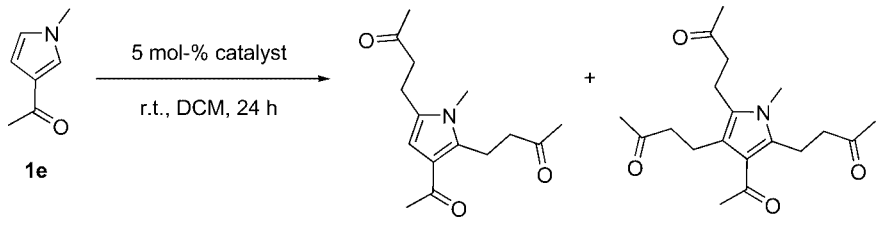


Figure 1. Solid state structure of **4c** and hydrogen-bonded dimers in the crystal.



5 mol-% $NaAuCl_4 \cdot 2\ H_2O$		
1.1 equiv. **2**	**4e** (42%)[a]	not detected
5 mol-% $Ph_3PAuNTf_2$		
1.1 equiv. **2**	**4e** (40%)[a]	**5e** (7%)[a]
2 equiv. **2**	**4e** (51%)[a]	**5e** (12%)[a]
3 equiv. **2**	**4e** (44%)[a]	**5e** (52%)[a]
5 mol-% $AgPF_6$		
1.1 equiv. **2**	**4e** (49%)[a]	**5e** (10%)[a]
5 mol-% *p*-TsOH		
1.1 equiv. **2**	**4e** (49%)[a]	**5e** (7%)[a]

a) yields based on **1e**

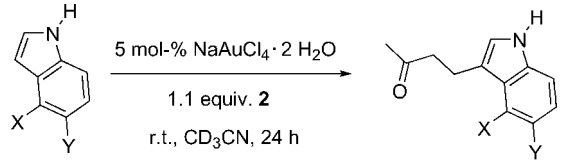
Scheme 5. Reaction of 3-acetyl-1-methyl-1*H*-pyrrole (**1e**) with **2**.

were observed. In the HMBC spectrum, the N-CH_3 signal shows two strong cross-correlations to peaks at δ = 131.15 and 138.59 ppm referring to the quaternary carbon atoms. The signal of the third quaternary pyrrole carbon atom at δ = 119.74 ppm is cross-correlated to the peak of the methyl group of the acetyl substituent. Further support for this assignment comes from the $^1J_{C,H}$ coupling constant observed for the remaining pyrrole hydrogen atom, from the ^{13}C satellites in the proton NMR spectrum a value of 169 Hz was measured, which is in perfect harmony with the literature value of 169 Hz for the 3-position of the pyrrole, while for the 2-position of pyrrole a value of 183 Hz is reported.[13]

Another product observed with Gagosz's[14] gold(I) catalyst, $Ph_3PAuNTf_2$, was the tetrasubstituted compound **5e**. As expected, when more of **2** was used, the amount of **5e** increased, too. Recently it was reported that in some reactions silver(I) catalysts[15] or Brønsted acids[16] can be as effective as gold catalysts. For the pyrroles this is also the case, as shown in Scheme 5 $AgPF_6$ or *p*TsOH lead to results that are comparable to those for gold catalysts. In contrast to these observations, with $Yb(OTf)_3$ no reaction of **1e** and **2** was observed.

All reactions reported here were monitored by ^1H NMR spectroscopy and the mixtures worked up when the conversion of the substrates had stopped. Thus, the yields given are the maximum yields obtainable with 5 mol-% of catalyst.

In order to verify our reaction conditions, we tested two indole derivatives under similar conditions. With **6a** and **6b** good yields of **7a** and **7b** were obtained, clearly demonstrating that the selectivity problems are intrinsic to the pyrrole system. Related selectivity problems (the second gold-catalysed functionalisation being faster than the first one) have already been reported earlier (Scheme 6).[3b,16c]



Scheme 6. Highly selective reactions of indoles.

Conclusions

Gold-catalyzed reactions of pyrroles with methyl vinyl ketone were studied. The high reactivity of the pyrrole ring leads to multiple substitution products, a selective monosubstitution of the pyrrole ring failed, which clearly excludes gold catalysts for the functionalization of pyrroles. This observation is in strong contrast to the behaviour of indoles in corresponding reactions. Both gold(III) and gold(I) pre-catalysts are active, but also silver(I) and Brønsted acids. $Yb(OTf)_3$ does not catalyze these reactions.

Experimental Section

General Procedure: To a solution of pyrrole derivative **1** in [D_3]-acetonitrile (650 μL) was added methyl vinyl ketone (1.1 equiv.). The progress of the reaction was monitored by ^1H NMR spectroscopy. Upon completion, the reaction mixture was concentrated in vacuo and the crude product was purified by column chromatography on silica gel, using a mixture of petroleum ether and ethyl acetate. Products of type **3** and/or **4** and/or **5** were obtained.

3a and 4a: Reaction according to the general procedure with **1a** (100 mg, 800 μmol), **2** (61.7 mg, 880 μmol) and $Na[AuCl_4]\cdot 2H_2O$ (15.9 mg, 40.0 μmol, 5 mol-%). Purification with PE/EE, 4:1, delivered **3a** (6.60 mg, 4%) as a yellow solid and **4a** (38.4 mg, 33%) as a yellow solid. **3a**: M.p. 45 °C. R_f (PE/EE, 2:1) = 0.50. IR (neat): ṽ

= 3108, 2963, 1753, 1714, 1446, 1331, 1204, 1127, 834 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.16 (s, 3 H), 2.76–2.79 (m, 2 H), 3.12–3.16 (m, 2 H), 3.94 (s, 3 H), 5.97 (s, 1 H), 6.09 (t, J = 3.4 Hz, 1 H), 7.20 (dd, J = 3.4 Hz, 1.8 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 22.91 (t), 29.85 (q), 43.04 (t), 53.74 (q), 110.80 (d), 111.82 (d), 120.88 (d), 134.82 (s), 151.23 (s), 212.71 (s) ppm. MS (EI, 70eV): *m/z* (%) = 195 (100) [M^+], 152 (95), 138 (70), 125 (25), 94 (25). HRMS (EI, 70 eV): $C_{10}H_{13}NO_3$: calcd. 195.0895; found: 195.0896. **4a**: M.p. 48 °C. R_f (PE/EE, 2:1) = 0.22. IR (neat): $\tilde{\nu}$ = 2961, 2916, 1745, 1719, 1537, 1433, 1304, 1110, 1030, 779, 600 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.16 (s, 6 H), 2.70–2.76 (m, 4 H), 3.03–3.08 (m, 4 H), 3.93 (s, 3 H), 5.83 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 23.81 (t, 2 C), 29.90 (q, 2 C), 43.22 (t, 2 C), 53.24 (q), 110.38 (d, 2 C), 134.91 (s, 2 C), 152.12 (s), 207.78 (s, 2 C) ppm. MS (EI, 70 eV): *m/z* (%) = 265 (51) [M^+], 222 (10), 208 (48), 164 (100), 132 (21), 106 (34). $C_{14}H_{19}NO_4$ (265.31): calcd. C 63.38, H 7.22, N 5.28; found C 63.60, H 7.29, N 5.16.

4b: Reaction according to the general procedure with **1b** (100 mg, 681 µmol), **2** (52.5 mg, 750 µmol) and $Na[AuCl_4]\cdot 2H_2O$ (14.4 mg, 34.0 µmol, 5 mol-%). Purification with PE/EE, 4:1 delivered **4b** (37.7 mg, 35%) as a yellow solid. **4b**: M.p. 73 °C. R_f (PE/EE, 2:1) = 0.31. IR (neat): $\tilde{\nu}$ = 2906, 1705, 1515, 1432, 1371, 1248, 1014, 755, 737 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.16 (s, 6 H), 2.72–2.76 (m, 4 H), 2.78–2.87 (m, 4 H), 4.98 (s, 2 H), 5.79 (s, 2 H), 6.03 (dd, J = 3.2 Hz, 0.8 Hz, 1 H), 6.27 (dd, J = 3.2 Hz, 1.8 Hz, 1 H), 7.31 (dd, J = 1.8 Hz, 0.8 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 20.40 (t, 2 C), 29.96 (q, 2 C), 42.77 (t, 2 C), 53.40 (t), 104.46 (d, 2 C), 107.17 (d) 110.33 (d), 131.54 (s, 2 C), 143.18 (d), 150.94 (s), 207.75 (s, 2 C) ppm. MS (EI, 70eV): *m/z* (%) = 287 (45) [M^+], 230 (15), 186 (5), 106 (5), 81 (100). HRMS (EI, 70eV): $C_{17}H_{21}NO_3$: calcd. 287.1521; found: 287.1522.

3c and 4c: Reaction according to the general procedure with **1c** (60.0 mg, 550 µmol), **2** (42.4 mg, 605 µmol) and $Na[AuCl_4]\cdot 2H_2O$ (11.1 mg, 27.5 µmol, 5 mol-%). Purification with PE/EE, 3:1 delivered **3c** (7.20 mg, 7%) as a yellow solid and **4c** (39.1 mg, 28%) as a yellow solid [RS 76 (3)]. **3c**: M.p. 74 °C. R_f (PE/EE, 2:1) = 0.23. IR (neat): $\tilde{\nu}$ = 3255, 3129, 2920, 1714, 1603, 1496, 1603, 1496, 1401, 1297, 1159, 822 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.19 (s, 3 H), 2.40 (s, 3 H), 2.77–2.83 (m, 2 H), 2.87–2.92 (m, 2 H), 5.99 (dd, J = 3.7 Hz, 2.6 Hz, 1 H), 6.81 (dd, J = 3.7 Hz, 2.5 Hz, 1 H), 9.54 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 21.51 (t), 25.05 (q), 29.94 (q), 42.95 (t), 108.62 (d), 117.41 (d), 131.43 (s), 139.10 (s), 187.12 (s), 207.61 (s) ppm. MS (EI, 70eV): *m/z* (%) = 179 (91) [M^+], 136 (97), 122 (100), 94 (45). HRMS (EI, 70 eV): $C_{10}H_{13}NO_2$: calcd. 179.0946; found: 179.0947. **4c**: M.p. 101 °C. R_f (PE/EE, 2:1) = 0.13. IR (neat): $\tilde{\nu}$ = 3257, 3127, 2919, 1715, 1604, 1497, 1402, 1365, 1220, 1159, 1065, 869 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 2.15 (s, 3 H), 2.16 (s, 3 H), 2.34 (s, 3 H), 2.64–2.72 (m, 4 H), 2.76–2.77 (m, 2 H), 2.82–2.85 (m, 2 H), 6.63 (d, J = 2.6 Hz, 1 H), 9.47 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 19.27 (t), 19.47 (t), 25.01 (q), 29.93 (q), 30.15 (q), 42.86 (t), 44.58 (t), 116.71 (d), 121.37 (s), 130.23 (s), 135.87 (s), 186.65 (d), 207.75 (s), 207.76 (s) ppm. MS (EI, 70 eV): *m/z* (%) = 249 (22) [M^+], 206 (23), 192 (16), 148 (100), 106 (33). $C_{14}H_{19}NO_3$ (249.31): calcd. C 67.45, H 7.68, N 5.62; found C 67.44, H 7.70, N 5.43.

4d: Reaction according to the general procedure with **1d** (58.4 mg, 535 µmol), **2** (41.2 mg, 589 µmol) and $Na[AuCl_4]\cdot 2H_2O$ (10.8 mg, 27.0 µmol, 5 mol-%). Purification with PE/EE, 2:1 delivered **4d** (24.0 mg, 33%) as a yellow solid. **4d**: M.p. 47 °C. R_f (PE/EE, 2:1) = 0.10. IR (neat): $\tilde{\nu}$ = 2922, 2779, 2703, 1704, 1643, 1347, 1162, 1135, 821 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 2.15 (s, 3 H), 2.16 (s, 3 H), 2.64–2.70 (m, 6 H), 2.85–2.91 (m, 2 H), 3.86 (s, 3 H), 6.65 (s, 1 H), 9.36 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 17.72 (t), 19.47 (t), 29.93 (q), 30.12 (q), 32.47 (q), 41.97 (t), 44.12 (t), 121.79 (s), 123.36 (d), 131.05 (s), 140.05 (s), 178.53 (d), 206.44 (s), 207.82 (s) ppm. MS (EI, 70 eV): *m/z* (%) = 249 (46) [M^+], 206 (15), 192 (46), 148 (100), 120 (42). $C_{14}H_{19}NO_3$ (249.31): calcd. C 67.45, H 7.68, N 5.62; found C 67.45, H 7.65, N 5.39.

4e: Reaction according to the general procedure with **1e** (53.4 mg, 434 µmol), **2** (33.4 mg, 477 µmol) and $Na[AuCl_4]\cdot 2H_2O$ (8.63 mg, 21.7 µmol, 5 mol-%). Purification with PE/EE, 3:1 delivered **4e** (26.3 mg, 42%) as a yellow solid. **4e**: M.p. 54 °C. R_f (PE/EE, 2:1) = 0.16. IR (neat): $\tilde{\nu}$ = 2927, 1713, 1646, 1515, 1412, 1362, 1229, 1164, 937 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.13 (s, 3 H), 2.21 (s, 3 H), 2.36 (s, 3 H), 2.75–2.83 (m, 6 H), 3.09–3.15 (m, 2 H), 3.52 (s, 3 H), 6.15 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 20.17 (t), 20.36 (t), 28.28 (q), 29.82 (q), 30.04 (q), 41.91 (t), 42.41 (t), 53.51 (q), 107.00 (d), 119.74 (s), 131.15 (s), 138.59 (s), 194.23 (s), 207.03 (s), 208.41 (s) ppm. MS (EI, 70eV): *m/z* (%) = 263 (68) [M^+], 220 (66), 206 (100), 162 (65), 136 (60). HRMS (EI, 70eV): $C_{15}H_{21}NO_3$: calcd. 263.1521; found: 263.1522.

5e: Reaction according to the general procedure with **1e** (50.0 mg, 406 µmol), **2** (85.3 mg, 1.22 mmol) and PPh_3AuNTf_2 (15.0 mg, 20.3 µmol). Purification with PE/EE, 1:1 delivered **5e** (70.3 mg, 52%) as a yellow oil and **4e** (47.0 mg, 44%). **5e**: M.p. 94 °C. R_f (PE/EE, 1:5) = 0.17. IR (neat): $\tilde{\nu}$ = 2923, 1701, 1629, 1493, 1472, 1406, 1363, 1161 cm^{-1}. ^1H NMR (CD_2Cl_2, 300 MHz): δ = 2.07 (s, 3 H), 2.10 (s, 3 H), 2.11 (s, 3 H), 2.34 (s, 3 H), 2.52–2.57 (m, 4 H), 2.63–2.68 (m, 2 H), 2.74–2.82 (m, 4 H), 3.00–3.06 (m, 2 H), 3.40 (s, 3 H) ppm. ^{13}C NMR (CD_2Cl_2, 126 MHz): δ = 17.93 (t), 19.88 (t), 20.26 (t), 29.66 (q), 29.76 (q), 29.80 (q), 30.32 (q), 30.45 (q), 42.78 (t), 43.41 (t), 45.55 (t), 118.93 (s), 120.36 (s), 128.94 (s), 137.49 (s), 194.48 (s), 206.98 (s), 207.19 (s), 208.21 (s) ppm. MS (ESI, 70eV): *m/z* (%) = 334 (37) [MH^+], 316 (15), 290 (6), 274 (40), 234 (100). HRMS (ESI) [M + Na^+]: $C_{19}H_{27}NO_4$: calcd. 356.1832; found. 356.1827.

7a: Reaction according to the general procedure with **6a** (56.0 mg, 286 µmol), **2** (22.0 mg, 314 µmol) and $Na[AuCl_4]\cdot 2H_2O$ (5.69 mg, 14.3 µmol, 5 mol-%). Purification with PE/EE, 5:1 delivered **7a** (57.4 mg, 75%) as a colourless solid. **7a**: M.p. 105 °C. R_f (PE/EE, 2:1) = 0.16. IR (neat): $\tilde{\nu}$ = 3356, 3364, 2922, 2886, 2856, 1697, 1432, 1354, 1337, 1182, 1160, 914, 774, 743, 729 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 2.13 (s, 3 H), 2.87 (t, J = 7.4 Hz, 2 H), 3.26 (t, J = 7.4 Hz, 2 H), 6.98 (t, J = 7.8 Hz, 1 H), 7.03 (d, J = 2.2 Hz, 1 H), 7.30–7.34 (m, 2 H), 8.11 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 20.35 (t), 30.12 (q), 45.94 (t), 110.51 (d), 114.12 (s), 116.09 (s), 122.83 (d), 123.71 (d), 123.87 (d), 125.30 (s), 137.64 (s), 208.77 (s) ppm. MS (EI, 70 eV): *m/z* (%) = 267 (42) [$^{81}Br - M^+$], 265 (43) [$^{79}Br - M^+$], 222 (13), 208 (100), 143 (37), 115 (26). $C_{12}H_{12}BrNO$ (266.13): calcd. C 54.16, H 4.54, N 5.26; found C 54.39, H 4.67, N 4.99.

7b: Reaction according to the general procedure with **6b** (70.4 mg, 360 µmol), **2** (27.7 mg, 400 µmol) and $Na[AuCl_4]\cdot 2H_2O$ (7.16 mg, 18.0 µmol, 5 mol-%). Purification with PE/EE, 5:1 delivered **7b** (64.6 mg, 67%) as a colourless solid. **6b**: M.p. 83 °C. R_f (PE/EE, 2:1) = 0.53. ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.17 (s, 3 H), 2.82–2.88 (m, 2 H), 2.99–3.05 (m, 2 H), 7.03 (s, 1 H), 7.26–7.29 (m, 2 H), 7.73 (s, 1 H), 8.05 (s,1 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.12 (t), 30.12 (q), 43.93 (t), 112.62 (d), 112.65 (s), 115.02 (s), 121.35 (d), 122.83 (d), 124.91 (d), 129.02 (s), 134.90 (s), 208.37 (s) ppm. MS (EI, 70 eV): *m/z* (%) = 267 (52) [$^{81}Br - M^+$], 265 (51) [$^{79}Br - M^+$], 222 (21), 208 (100), 143 (50), 129 (28). $C_{12}H_{12}BrNO$ (266.13): calcd. C 54.16, H 4.54, N 5.26; found C 54.03, H 4.59, N 5.04.

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