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Gold catalysis: benzanellation versus alkylidenecyclopentenone synthesis

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ABSTRACT

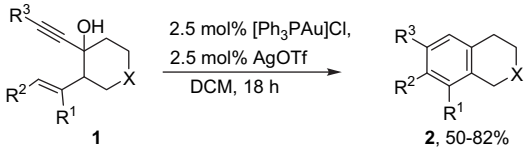
A series of different furan-yn-ols were prepared by a three-step sequence. Their reaction with Gagosz's catalyst $Ph_3PAuNTf_2$ depends strongly on the substitution pattern of the substrate and the quality of the leaving group. Benzofurans, alkylidenecyclopentenones or Meyer–Schuster type products can be obtained. Improving the leaving group quality leads to the preferred formation of benzofurans.

1. Introduction

Homogeneous gold-catalysed reactions have become a highly active research area in the last decade.[1] In addition to the methodology work, in the last years a continuously increasing number of applications in total synthesis was published.[2]

The anellation of electron-rich arenes by intramolecular hydroarylation reactions of alkynes is known to be catalysed by Ru, Pd, Ag and even main group metals like Ga and In.[1d,3] The reaction has recently been reported in inspiring work of Nishizawa et al.[4] to be catalysed even by Hg. Taking into account the superior ability of gold to activate alkynes, it is not surprising that a number of gold-catalysed hydroarylation reactions have also been published in the past years.[5]

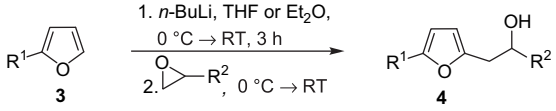
In beautiful work, Barriault et al. demonstrated that a benzoanellation can be achieved by the gold-catalysed conversion of enyn-ols **1** to deliver the products **2** (Scheme 1).[6] In the course of the reaction water is eliminated, which once more demonstrates the good water-tolerance of the gold-catalysts.[7] Here we report our results on the reaction of furan-yn-ols in benzoanellation reactions.



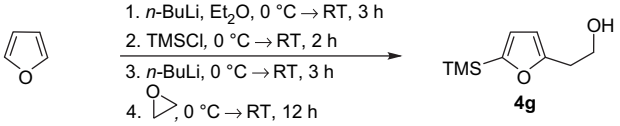
Scheme 1. Barriault's gold-catalysed benzoanellation.

2. Results and discussion

For the synthesis of the catalysis substrates, we started from furans **3**. Metallation in 2-position by *n*-BuLi and opening of epoxides delivers the alcohols **4** (Scheme 2). The conversions of 2-methylfuran **3f–g** (entries 4–6 and 8) provided better yields than the reactions with 2-(trimethylsilyl)furan (entry 7) or furan (entries 1–3). In the case of this silylated furan a one-pot procedure starting from furan and avoiding the work-up of the volatile TMS/furan could be used (Scheme 3). The yield depended on the oxirane, too. The observed reactivity for R^2 was H>Me>Ph. The allylglycidyl ether used for the preparation of **4i** gave an excellent conversion. The use of ethylene oxide was problematic (entries 1, 4 and 7), this unsubstituted oxirane



Scheme 2. Ring-opening of oxiranes by lithiated furans.



Scheme 3. One-pot synthesis of 2-(5-(trimethylsilyl)furan-2-yl)ethanol **4g**.

Table 1
Synthesis of furanalcohols **3**

Entry	Furan	R^1	R^2 in the epoxide	Reaction time	Yield
1	**3a**	H	H	12 h	51%
2	**3b**	H	Me	3 d	41%
3	**3c**	H	Ph	12 h	34%
4	**3d**	Me	H	12 h	68%
5	**3e**	Me	Me	12 h	82%
6	**3f**	Me	Ph	12 h	32%
7	**3g**	TMS	H	12 h	56% over two steps (Scheme 3)
8	**3i**	Me	CH_2Oallyl	8 h	97%

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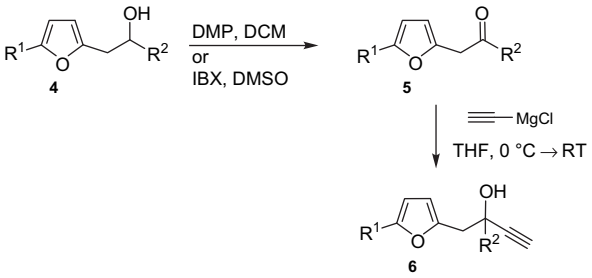
is a gas, which was condensed into the solution with the help of an acetone/dry ice condenser. An excess was problematic, as the alcoholate formed can attack the next epoxide, leading to oligomerisation products with a polyether structure. We had to weigh the pressure bottle in intervals during the reaction (Table 1).

The next step was the oxidation of the alcohols **4** to the aldehydes **5** (Scheme 4). As shown in Table 2, the yields are quite good (entries 2, 3 and 5–7). The subsequent addition of the acetylenic Grignard compound shows lower yields for the ketones (entries 2, 3, 5 and 6), for the aldehydes better yields were obtained (entries 1, 4 and 7). In general, one must keep in mind that the α-arylcarbonyl compounds are difficult substrates in such addition reactions of organometallic compounds, they easily form enolates. Another substrate for the investigation was the tosylated propargylic alcohol **7**, conveniently obtained from **6d** (Scheme 5).

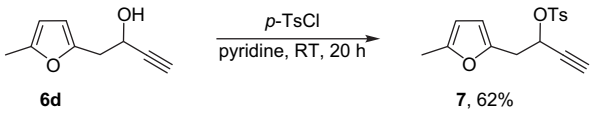


Scheme 4. Oxidation and ethynyl Grignard addition delivers the propargylic alcohols **6**.

Table 2
Synthesis of furan-yn-ols **46**

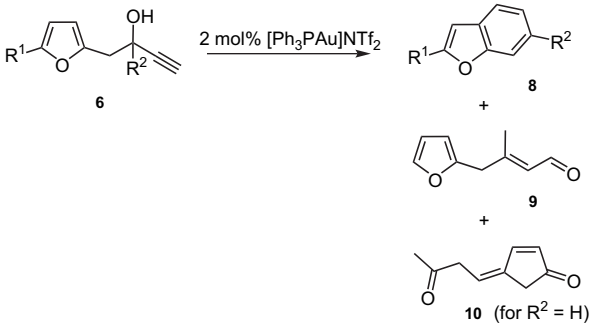
Entry	Compound	Yield (%)	Compound	Yield (%)
1	**5a**	Quantitative	**6a**	61
2	**5b**	71	**6b**	43
3	**5c**	70	**6c**	28
4	**5d**	68	**6d**	62
5	**5e**	92	**6e**	57
6	**5f**	98	**6f**	54
7	**5g**	97[a]	**6g**	72

[a] IBX was used as the oxidant.



Scheme 5. Tosylation of the alcohol **6d**.

From the subsequent conversions we learned that the gold-catalysed conversion of the substrates **6** can lead to three different product-types, the benzofuran **8**, Meyer–Schuster type rearrangement product **9** or the alkylidenecyclopentenone **10** (Scheme 6 Table 3).



Scheme 6.

The monosubstituted furans **6a–c** could only be converted to benzofurans in low yields (Table 3, entries 1–3). The reactions are unselective, but the products could easily be separated from the unknown by-products of higher polarity, probably oligomers/polymers. The volatility of **8a** reduced the yield after removal of the solvent of the chromatography, too.

In the case of **6b** (entry 2), the α,β-unsaturated aldehyde **9b** could be isolated as a side-product, which was obtained as an (*E*/*Z*)-mixture. Compound **9b** is the product of then known gold-catalysed Meyer–Schuster rearrangement.[8]

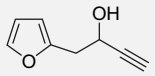
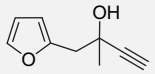
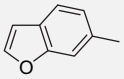
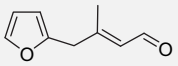
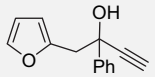
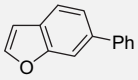
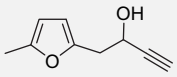
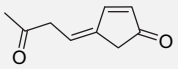
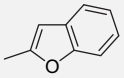
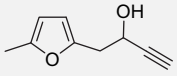
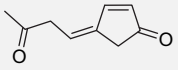
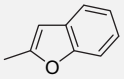
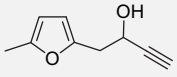
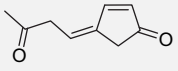
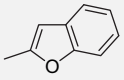
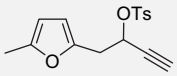
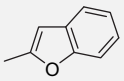
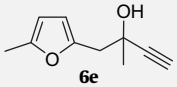
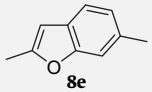
With one methyl group as a donor substituent in 5-position of the furan, which increases the nucleophilicity of the furan ring, much higher yields could be obtained (entries 4–9). For the secondary propargylic alcohol **6d**, depending on the solvent, the product **10d** could be obtained in yields between 50% and 70%. In addition 9–27% of the benzofuran **8d** was isolated. Acid does not influence the product ratio as tested by the addition of 5 mol % of *p*-toluenesulfonic acid (entry 6).

A better leaving group, as exemplified by the tosylate **7**, leads to an almost quantitative conversion to the benzofuran **8d** (entry 7). One additional substituent R^2 in propargylic position also delivered good yields in the cyclisation of the tertiary alcohols **6e** and **6f** (entries 8 and 9).

In DCM the TMS-substituted furan **6g** with a gold(I) catalyst provided 2-TMS-benzofuran **8g**, the desilylated benzofuran **8a** and desilylated starting material **6a** (entry 10). Changing to benzene as solvent leads to a slower reaction, but at the same time less desilylation was observed and 50% of **8g** could be isolated (entry 11). On the other hand, $AuCl_3$ was very efficient in the desilylation, the second product being the benzoanellation (22% yield, entry 12).

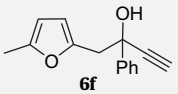
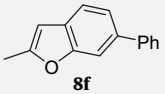
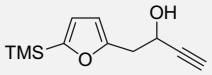
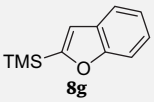
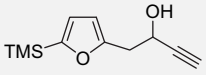
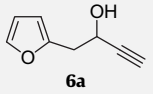
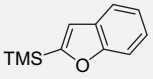
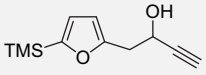
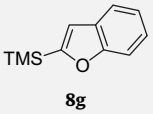
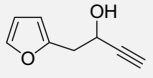
Possible pathways to these products are shown in Scheme 7. The usual electrophilic activation of the alkyne by the cationic gold(I) species in **11** initiates an electrophilic attack to the furan ring. Due to the shorter tether, the *exo-dig* attack to the 2-position of the furan ring is not as efficient as in the phenol synthesis,[5e,g,7b,9] a 6-*endo-dig* should be preferred, leading to intermediate **A**. Re-aromatisation of the furan ring and proto-deauration then would deliver intermediate **B**. Now the elimination of water (R^3=H) will readily form the benzoid aromatic ring in **8**.

Table 3
Gold-catalysed conversion of **6**

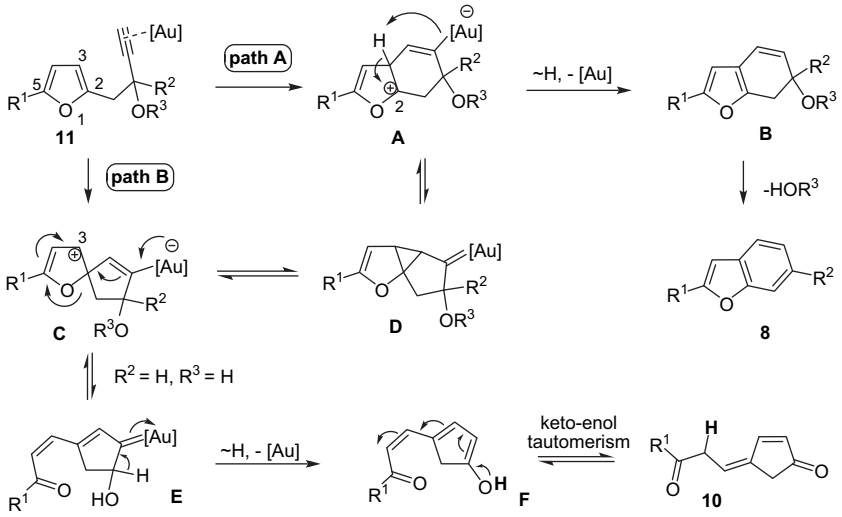
Entry	Compound	Conditions	Products	Yield (%)
1	 **6a**	2 mol % $[Ph_3PAu]NTf_2$, DCM, 1 d	 **8a**	53[a]
2	 **6b**	2 mol % $[Ph_3PAu]NTf_2$, DCM, 1 d	 **8b**	48
			 **9b** (*E*/*Z*-mixture)	17
3	 **6c**	2 mol % $[Ph_3PAu]NTf_2$, DCM, 1 d	 **8c**	56
4	 **6d**	2 mol % $[Ph_3PAu]NTf_2$, DCM, 15 min	 **10** (*E*/*Z*-mixture)	70
			 **8d**	9
5	 **6d**	2 mol % $[Ph_3PAu]NTf_2$, $CDCl_3$, 5 min	 **10d**	57
			 **8d**	26
6	 **6d**	2 mol % $[Ph_3PAu]NTf_2$, 5 mol % *p*-TsOH, $CDCl_3$, 5 min	 **10d**	55
			 **8d**	29
7	 **7**	2 mol % $[Ph_3PAu]NTf_2$, $CDCl_3$, 1 h	 **8d**	95
8	 **6e**	2 mol % $[Ph_3PAu]NTf_2$, DCM, 1 h	 **8e**	65

(*continued on next page*)

Table 3 (*continued*)

Entry	Compound	Conditions	Products	Yield (%)
9	 **6f**	2 mol % $[Ph_3PAu]NTf_2$, DCM, 1 d	 **8f**	70
10	 **6g**	2 mol % $[Ph_3PAu]NTf_2$, DCM, 3 h	 **8g**	25
			 **8a**	25
11	 **6g**	2 mol % $[Ph_3PAu]NTf_2$, benzene, 12 h	 **6a**	35
			 **8g**	50
12	 **6g**	5 mol % $AuCl_3$, DCM, 12 h	 **8g**	22
			 **6a**	75

[a] Volatile product.



Scheme 7. Reaction pathway for the formation of **6** and **10**.

Alternatively, a 5-*endo-dig* cyclisation would deliver intermediate **C**, and the presence of a donor in R^1 seems to be crucial for that pathway, which becomes obvious if one compares the conversion of **6a** and **6d**. Now fragmentation of the ring leads to vinyl carbenoid **E**,[10] then elimination of a proton, proto-deauration and enol–keto tautomerism of **F** delivers product **10**.

Most remarkably, the influence of the leaving group as shown by substrate **7**. The complete switch in selectivity suggests that a late step is selectivity determining and that the earlier intermediates interconvert rapidly. There might even be a link between intermediate **A** and the three-membered **D**, which then opens to deliver **C**.

3. Conclusion

Due to the shorter tether of only two atoms, in the reactions of the furan-yn substrates not the usual phenols but either, in analogy to Barriault's results, benzofurans **8** or alkylidenecyclopentenones **10** can be obtained. The product ratio can be influenced by the leaving group quality, thus suggesting a fast equilibrium between the different intermediates. In addition, monosubstituted furans deliver the products of a Meyer–Schuster type rearrangement of the propargylic alcohol.

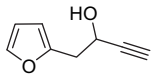
4. Experimental

4.1. General procedure for the synthesis of β-ethynyl-β-hydroxyfurans

To a solution of furans **3** in THF was added *n*-BuLi (1.6 M solution in hexane) at 0 °C under inert gas atmosphere. Then the solution was allowed to warm to room temperature and stirred for 3 h at room temperature. The solution was again cooled to 0 °C and the epoxide was added dropwise. After complete conversion (TLC control) the solution was quenched with aq NH_4Cl and extracted with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and the solvent was removed in vacuo. Purification by column chromatography or fractional distillation afforded the alcohol **4**.

The alcohol **4** was solved in DCM and DMP was added at 0 °C. Subsequently, the solution was allowed to warm to room temperature or was refluxed. After complete conversion (TLC control), the mixture was concentrated in vacuo and the residue was purified by column chromatography.

Then to a solution of ethynylmagnesium chloride (0.6 M solution in THF/toluene, 1.5–2.0 equiv) in THF or diethyl ether was added a solution of **5** in THF at 0 °C under inert gas atmosphere and warmed to room temperature. After 1 h the solution was quenched with aq NH_4Cl until the residue had dissolved. The mixture was extracted with diethyl ether, the combined organic layers were washed with brine and dried over Na_2SO_4. The concentrated residue was purified by column chromatography.

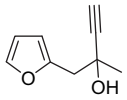


6a

*4.1.1. 1-(Furan-2-yl)but-3-yn-2-ol (**6a**).* According to the general procedure for the preparation of β-ethynyl-β-hydroxyfurans (4.77 g, 70 mmol) furan was dissolved in THF (100 mL), deprotonated with *n*-BuLi (43.8 mL, 1.6 M solution in hexane, 70.0 mmol). Then ethylene oxide (3.39 g, 77.0 mmol) was condensed into this solution by an acetone/dry ice condenser and the mixture was stirred for 8 h at room temperature. After purification by column chromatography (silica gel, PE/EA, 2:1) alcohol **4a** was obtained as yellow oil (3.97 g, 35.4 mmol, 51%). R_f (PE/EA, 1:1)=0.48. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.88 (br s, 1H), 2.90 (t, J=6.3 Hz, 2H), 3.86 (t, J=6.3 Hz, 2H), 6.11 (dd, J=3.2 Hz, J=0.9 Hz, 1H), 6.31 (dd, J=3.2 Hz, J=1.9 Hz, 1H), 7.34 (dd, J=1.9 Hz, J=0.9 Hz, 1H).[11]

To a solution of the alcohol **4a** (2.00 g, 17.8 mmol) in DCM (100 mL) was added DMP (9.63 g, 19.6 mmol). The raw product of **5a** was obtained as a yellow oil (1.96 g, 17.8 mmol, 100%). R_f (PE/EA, 4:1)=0.33. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=3.72 (d, J=2.1 Hz, 1H), 6.25 (ddt, J=3.2, 0.8, 0.8 Hz, 1H), 6.38 (dd, J=3.2, 1.9 Hz, 1H), 9.72 (t, J=2.1 Hz, 1H). $C_6H_6O_2$ (110.11).[12]

To a solution of ethynylmagnesium chloride (22.7 mL, 0.6 M solution in THF/toluene, 13.6 mmol) in THF (20 mL) was added a solution of **5a** (1.00 g, 9.08 mmol) in THF (20 mL). Purification by column chromatography (silica gel, PE/EA, 8:1) afforded **6a** (750 mg, 5.51 mmol, 61%) as a brown oil. R_f (PE/EA, 4:1)=0.20. IR (neat) ν=3361 cm^{-1}, 3289, 1220, 1505, 1145, 1031, 1013, 731, 641. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=2.14 (br s, 1H), 2.48 (d, J=2.1 Hz, 1H), 3.05 (dd, J=15.0, 6.7 Hz, 1H), 3.11 (dd, J=15.0, 5.7 Hz, 1H), 4.62–4.70 (m, 1H), 6.21 (ddt, J=3.2, 0.9, 0.8 Hz, 1H), 6.33 (dd, J=3.2, 1.9 Hz, 1H), 7.37 (dd, J=1.9, 0.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=35.93 (t), 60.44 (d), 72.89 (d), 83.02 (s), 107.28 (d), 109.80 (d), 141.37 (d), 150.13 (s). MS (ESI): m/z (%): 159 (100) $[M+Na]^+$, 135 (27). HRMS (ESI): $[C_8H_8O_2+Na]^+$: calcd 159.0417, found 159.0411.

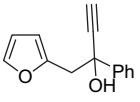


6b

*4.1.2. 1-(Furan-2-yl)-2-methylbut-3-yn-2-ol (**6b**).* According to the general procedure of the preparation of β-ethynyl-β-hydroxyfurans (2.00 g, 29.4 mmol) furan was dissolved in THF (40 mL) and deprotonated with *n*-BuLi (19.3 mL, 1.6 M solution in hexane, 30.9 mmol). Then propylene oxide (1.62 g, 27.9 mmol) was added dropwise and the mixture stirred for 3 d. Purification by column chromatography (silica gel, PE/EA, 4:1) afforded **4b** (1.45 g, 11.6 mmol, 41%) as an orange oil. R_f (PE/EA, 4:1)=0.17. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=1.24 (d, J=6.2 Hz, 3H), 1.96 (br s, 1H), 2.74 (dd, J=14.9, 7.6 Hz 1H), 2.81 (dd, J=14.9, 4.7 Hz, 1H), 4.05–4.12 (m, 1H), 6.10 (d, J=3.2 Hz, 1H), 6.31 (dd, J=3.2, 1.9 Hz, 1H), 7.34 (dd, J=1.9, 0.9 Hz, 1H).[13]

To a solution of the alcohol **4b** (1.45 g, 11.6 mmol) in DCM (80 mL) was added DMP (5.41 g, 12.8 mmol). Column chromatography (silica gel, PE/EA, 2:1) afforded 1.02 g (8.30 mmol, 71%) of the ketone **5b** as a yellow oil. R_f (PE/EA, 10:1)=0.16. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=2.16 (s, 3H), 3.71 (s, 2H), 6.20 (ddd, J=3.2, 0.8, 0.8 Hz, 2H), 6.35 (dd, J=3.2, 1.9 Hz, 1H), 7.37 (dd, J=1.9, 0.8 Hz, 1H).[14]

To a solution of ethynylmagnesium chloride (13.1 mL, 0.6 M solution in THF/toluene, 7.88 mmol) was added a solution of **5b** (511 mg, 4.15 mmol) in THF (50 mL). Column chromatography (silica gel, PE/EA, 10:1) afforded **6b** (270 mg, 1.81 mmol, 43%) as a yellow oil. R_f (PE/EA, 4:1)=0.25. IR (neat): ν=3410 cm^{-1}, 3291, 2985, 2931, 1503, 1146, 1011, 943, 731, 645. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.54 (s, 3H), 2.43 (br s, 1H), 2.44 (s, 1H), 3.01 (d, J=14.8 Hz, 1H), 3.08 (d, J=14.8 Hz, 1H), 6.25 (ddd, J=3.2, 0.9, 0.7 Hz, 1H), 6.35(dd, J=3.2, 1.9 Hz, 1H), 7.38 (d, J=1.9, 0.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ=29.18 (q), 42.07 (t), 67.28 (s), 71.80 (d), 86.80 (s), 108.58 (d), 110.43 (d), 142.07 (d), 150.95 (s). MS (EI, 70 eV): m/z (%): 150 (14) $[M]^+$, 82 (100), 69 (41). HRMS (ESI): $[C_9H_{10}O_2+Na]^+$: calcd 173.0573, found 173.0571.



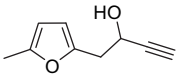
6c

*4.1.3. 1-(Furan-2-yl)-2-phenylbut-3-yn-2-ol (**6c**).* According to the general procedure of the preparation of β-ethynyl-β-hydroxyfurans (2.00 g, 29.4 mmol) furan was dissolved in THF (40 mL) and deprotonated with *n*-BuLi (19.3 mL, 1.6 M solution in hexane, 30.9 mmol). Then styrene oxide (3.35 g, 27.9 mmol) in THF (40 mL) was added and the mixture stirred for 3 d. Purification by column chromatography (silica gel, PE/EA, 10:1) afforded **4c** (1.78 g, 9.48 mmol, 34%) as a yellow oil. R_f (PE/EA, 10:1)=0.07. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=2.27 (d, J=2.8 Hz, 1H), 3.04 (d, J=6.6 Hz, 2H), 4.99 (td, J=6.6, 2.8 Hz, 1H), 6.07 (ddt, J=3.2, 0.8 Hz, J=0.8 Hz, 1H),

6.30 (dd, J=3.2, 1.9 Hz, 1H), 7.26–7.79 (m, 1H), 7.32–7.37 (m, 5H). $C_{12}H_{12}O_2$ (188.22): calcd C 76.57, H 6.43; found C 76.48, H 6.55.[15]

To a solution of the alcohol **4c** (1.79 g, 9.48 mmol) in DCM (60 mL) was added DMP (4.42 g, 10.4 mmol). Column chromatography (silica gel, PE/EA, 2:1) afforded 1.22 g (6.60 mmol, 70%) of **5c** as yellow acicular crystals. R_f (PE/EA, 10:1)=0.23. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=4.30 (s, 2H), 6.24 (ddt, J=3.2, 0.9, 0.8 Hz, 1H), 6.33 (dd, J=3.2, 1.9 Hz, 1H), 7.37 (d, J=1.90 Hz, 0.90 Hz, 1H), 7.44–7.48 (m, 2H), 7.55–7.58 (m, 1H), 7.99–8.02 (m, 2H).[16]

To a solution of ethynylmagnesium chloride (14.6 mL, 0.6 M solution in THF/toluene, 8.75 mmol) in THF (60 mL) was added a solution of **5c** (858 mg, 4.61 mmol) in THF (30 mL). Purification by column chromatography (silica gel, PE/EA, 10:1) afforded an orange oil of **6c** (282 mg, 1.33 mmol, 28%). R_f (PE/EA, 10:1)=0.30. IR (neat): ν=3540 cm^{-1}, 3288, 1501, 1448, 1146, 1011, 670. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=2.66 (s, 1H), 2.87 (br s, 1H), 3.25 (s, 1H), 6.15 (ddt, J=3.2, 0.8, 0.8 Hz, 1H), 6.32 (dd, J=3.2, 1.9 Hz, 1H), 7.29–7.33 (m, 1H), 7.35–7.38 (m, 3H), 7.61–7.64 (m, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ=44.29 (t), 72.24 (d), 74.58 (s), 85.39 (s), 108.89 (d), 110.41 (d), 125.28 (d, 2C), 127.99 (d), 128.23 (d, 2C), 142.06 (d), 143.04 (s), 150.45 (s). MS (EI, 70 eV): m/z (%): (7) $[M]^+$, 131 (88), 82 (100), 53 (53). MS (ESI): m/z (%): 235 (100) $[M+Na]^+$. HRMS (ESI): $[C_{14}H_{12}O_2+Na]^+$: calcd 235.0730, found 235.0726.

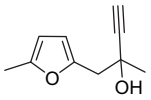


6d

*4.1.4. 1-(5-Methylfuran-2-yl)but-3-yn-2-ol (**6d**).* According to the general procedure of the preparation of β-ethynyl-β-hydroxyfurans 2-methylfuran (10.0 g, 122 mmol) was dissolved in THF (100 mL) and deprotonated with *n*-BuLi (76.1 mL, 1.6 M solution in hexane, 122 mmol). Then ethylene oxide (5.37 g, 122 mmol) was condensed by an acetone/dry ice condenser into the solution and stirred for 8 h at room temperature. Fractional vacuum distillation (bp 69 °C, 1 mbar) afforded the alcohol **4d** (10.5 g, 83.3 mmol, 68%) as a colourless liquid. Bp 69 °C (1 mbar). IR (neat): ν=3324 cm^{-1}, 2921, 2884, 1569, 1443, 1218, 1044, 783, 648. ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.68 (br s, 1H), 2.25 (d, J=1.0 Hz, 1H), 2.84 (t, J=6.2 Hz, 2H), 3.84 (t, J=6.2, 2H), 5.86 (dq, J=3.0, 1.0 Hz, 1H), 5.97 (d, J=3.0 Hz, 1H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=13.65 (q), 31.78 (t), 61.33 (t), 106.17 (d), 107.40 (d), 150.96 (s), 151.26 (s). MS (EI, 70 eV): m/z (%): 126 (21) $[M]^+$, 95 (100), 43 (15). HRMS (EI): $C_7H_{10}O_2$: calcd 126.0681, found 126.0681.

To a solution of the alcohol **4d** (500 mg, 3.96 mmol) in DCM (30 mL) was added DMP (1.86 g, 4.36 mmol). Column chromatography (silica gel, PE/EA, 10:1) afforded 334 mg (2.68 mmol, 68%) of **5d** as a yellow, volatile liquid. R_f (PE/EA, 10:1)=0.18. IR (neat): ν=2922 cm^{-1}, 2928, 2730, 1726, 1566, 1388, 1219, 1022, 942, 785, 618. ^{1}H NMR ($CDCl_3$, 250 MHz): δ=2.27–2.28 (m, 3H), 3.64–3.66 (m, 2H), 5.93–5.95 (m, 1H), 6.11 (d, J=3.0 Hz, 1H), 9.70 (t, J=2.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ=13.49 (q), 42.98 (t), 106.62 (d), 109.52 (d), 144.30 (s), 152.43 (s), 197.26 (s). MS (ESI): m/z (%): 125 (67) $[M+H]^+$, 123 (79), 109 (79), 95 (100). HRMS (ESI): $[C_7H_8O_2+H]^+$: calcd 125.0597, found 125.0594.

To a solution of ethynylmagnesium chloride (6.22 mL, 0.6 M solution in THF/toluene, 3.73 mmol) in Et_2O (20 mL) was added **5d** (858 mg, 4.61 mmol). Purification by column chromatography (silica gel, PE/EA, 6:1) afforded a yellowish liquid of **6d** (232 mg, 1.54 mmol, 62%). R_f (PE/EA, 6:1)=0.17. IR (neat): ν=3283 cm^{-1}, 1711, 1568, 1217, 1030, 787, 657. ^{1}H NMR ($CDCl_3$, 250 MHz): δ=2.22 (br d, J=5.1 Hz, 1H), 2.26–2.27 (m, 3H), 2.47 (d, J=2.1 Hz, 1H), 2.97 (dd, J=14.9, 6.8 Hz, 1H), 3.05 (dd, J=14.9, 5.6 Hz, 1H), 4.59–4.67 (m), 5.89 (dq, J=3.0, 1.1 Hz, 1H), 6.07 (d, J=3.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ=13.55 (q), 36.70 (t), 61.12 (d), 73.35 (d), 83.81 (s), 106.25 (d), 108.66 (d), 148.81 (s), 151.59 (s). MS (ESI): m/z (%): 173 (100) $[M+Na]^+$, 149 (44), 133 (90), 105 (88), 103 (46). HRMS (ESI): $[C_9H_{10}O_2+Na]^+$: calcd 173.0573, found 173.0572.

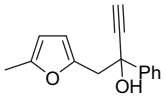


6e

*4.1.5. 2-Methyl-1-(5-methylfuran-2-yl)but-3-yn-2-ol (**6e**).* According to the general procedure of the preparation of β-ethynyl-β-hydroxyfurans 2-methylfuran (2.00 g, 24.4 mmol) was dissolved in THF (20 mL) and deprotonated with *n*-BuLi (16.0 mL, 1.6 M solution in hexane, 25.6 mmol). Then propylene oxide (1.41 g, 24.4 mmol) was added dropwise and the mixture stirred for 2 d. Purification by column chromatography (silica gel, PE/EA, 4:1) afforded **4e** (2.82 g, 20.1 mmol, 82%) as a yellow liquid. R_f (PE/EA, 4:1)=0.23. ^{1}H NMR: ($CDCl_3$, 300 MHz): δ=1.24 (d, J=6.2 Hz, 3H), 1.86–1.88 (m, 1OH), 2.26 (s, 3H), 2.66 (dd, J=14.8, 7.8 Hz, 1H), 2.77 (dd, J=14.8, 4.4 Hz, 1H), 4.00–4.12 (m, 1H), 5.86–5.89 (m, 1H), 5.98 (d, J=3.0 Hz, 1H). $C_8H_{12}O_2$ (140.18).

To a solution of the alcohol **4e** (1.00 g, 7.13 mmol) in DCM (40 mL) was added DMP (3.33 g, 7.85 mmol). Column chromatography (silica gel, PE/EA, 6:1) afforded 905 mg (6.55 mmol, 92%) of the ketone **5e** as a yellow liquid. R_f (PE/EA, 6:1)=0.28. ^{1}H NMR: ($CDCl_3$, 300 MHz):δ=2.17 (s, 3H), 2.27 (s, 3H), 3.65 (s, 2H), 5.91–5.93 (m, 1H), 6.06 (d, J=3.0 Hz, 1H). $C_8H_{10}O_2$ (138.16).

To a solution of ethynylmagnesium chloride (13.0 mL, 0.6 M solution in THF/toluene, 7.78 mmol) in THF (20 mL) was added a solution of **5e** (895 mg, 6.48 mmol) in THF (20 mL). Purification by column chromatography (silica gel, PE/EA, 8:1) afforded a yellow liquid of **6e** (600 mg, 3.65 mmol, 57%). R_f (PE/EA, 8:1)=0.13. IR (neat): ν=3373 cm^{-1}, 3290, 2985, 2929, 1563, 1365, 1208, 1114, 1068, 938, 788, 643. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=1.54 (s, 3H), 2.27 (d, J=1.0 Hz, 3H), 2.43 (s, 1H), 2.51 (br s, 1H), 2.95 (d, J=14.8 Hz, 1H), 3.02 (d, J=14.8 Hz, 1H), 5.91 (dq, J=3.0, 1.0 Hz, 1H), 6.11 (d, J=3.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ=13.61 (q), 29.12 (q), 42.16 (t), 67.24 (s), 71.64 (d), 86.92 (s), 106.30 (d), 109.36 (d), 149.00 (s), 151.69 (s). MS (ESI): m/z (%): 187 (100) $[M+Na]^+$. HRMS (ESI): $[C_{10}H_{12}O2+Na]^+$: calcd 187.0730, found 187.0737.

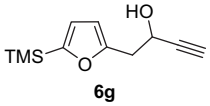


6f

*4.1.6. 1-(5-Methylfuran-2-yl)-2-phenylbut-3-yn-2-ol (**6f**).* According to the general procedure of the preparation of β-ethynyl-β-hydroxyfurans 2-methylfuran (2.00 g, 24.4 mmol) was dissolved in THF (40 mL) and deprotonated with *n*-BuLi (16.0 mL, 1.6 M solution in hexane, 25.6 mmol). Then styrene oxide (2.79 mL, 2.93 g, 24.4 mmol) was added dropwise and the mixture stirred for 2 d. Purification by column chromatography (silica gel, PE/EA, 10:1) afforded **4f** (1.50 g, 7.42 mmol, 32%) as a yellow oil. R_f (PE/EA, 10:1)=0.14. ^{1}H NMR: ($CDCl_3$, 300 MHz):δ=2.27–2.28 (m, 3H+OH), 2.90–3.04 (m, 2H), 4.94–4.99 (m, 1H), 5.88 (d, J=3.0 Hz, 1H), 5.97 (d, J=3.0 Hz, 1H), 7.26–7.41 (m, 5H).

To a solution of the alcohol **4f** (1.50 g, 7.42 mmol) in DCM (50 mL) was added DMP (3.46 g, 8.16 mmol). Column chromatography (silica gel, PE/EA, 10:1) afforded 1.46 g (7.29 mmol, 98%) of the ketone **5f** as a yellow oil. R_f (PE/EA, 4:1)=0.42. ^{1}H NMR: ($CDCl_3$, 300 MHz): δ=2.26 (s, 3H), 4.26 (s, 2H), 5.91 (d, J=3.0 Hz, 1H), 6.09 (d, J=3.0 Hz, 1H), 7.43–7.51 (m, 2H), 7.54–7.61 (m, 1H), 7.99–8.04 (m, 2H).

To a solution of ethynylmagnesium chloride (9.00 mL, 0.6 M solution in THF/toluene, 5.40 mmol) in THF (30 mL) was added a solution of **5f** (565 mg, 2.82 mmol) in THF (15 mL). Purification by column chromatography (silica gel, PE/EA, 10:1) afforded an orange oil of **6f** (347 mg, 1.54 mmol, 54%). R_f (PE/EA, 10:1)=0.14. IR (neat): ν=3532 cm^{-1}, 3286, 2922, 2360, 1562, 1448, 1216, 1021, 967. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ=2.14 (d, J=1.0 Hz, 3H), 2.62 (s, 1H), 2.91 (br s, 1H), 3.06 (d, J=14.8 Hz, 1H), 3.10 (d, J=14.8 Hz, 1H), 5.81 (dq, J=3.1, 1.0 Hz, 1H), 5.94 (d, J=3.1 Hz, 1H), 7.20–7.24 (m, 1H), 7.26–7.30 (m, 2H), 7.51–7.54 (m, 2H). ^{13}C NMR (CD_2Cl_2, 126 MHz): δ=13.67 (q), 44.78 (t), 72.50 (s), 74.55 (d), 86.06 (s), 106.62 (d), 110.05 (d), 125.69 (d, 2C), 128.24 (d), 128.52 (d, 2C), 143.77 (s), 149.03 (s), 152.12 (s). MS (EI, 70 eV): m/z (%): 226 (13) [M]$^+$, 131 (26), 95 (100), 53 (28). $C_{15}H_{14}O_2$ (226.27): calcd C 79.62, H 6.24; found C 79.54, H 6.35.

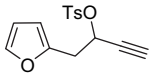


6g

*4.1.7. 1-(5-Trimethylsilanyl-furan-2-yl)-but-3-yn-2-ol (**6g**).* To a cooled solution of furan (3.40 g, 50.0 mmol) in diethyl ether (150 mL) was added *n*-BuLi (34.4 mL, 1.6 M solution in hexane, 55.0 mmol) at 0 °C under inert gas atmosphere. The solution was allowed to warm to room temperature and stirred for 3 h. Then TMSCl (5.34 g, 50 mmol) was added dropwise at 0 °C and the solution was stirred for further 3 h at room temperature. Subsequently, the solution was again cooled to 0 °C and *n*-BuLi (31.3 mL, 1.6 M solution in hexane, 50.0 mmol) was added a second time. After stirring for 3 h at room temperature ethylene oxide (2.42 g, 55.0 mmol) was condensed by an acetone/dry ice condenser into the solution and the solution was stirred for further 12 h at room temperature. The mixture was quenched with aq NH_4Cl, then extracted with diethyl ether and the combined organic layers were dried over Na_2SO_4. Fractional vacuum distillation (bp 103–104 °C/1 mbar) afforded the alcohol **4g** (5.14 g, 27.9 mmol, 56% over two steps) as a yellow liquid. Bp 103–104 °C/1 mbar. R_f (PE/EA, 4:1)=0.23. IR (neat): ν=3347 cm^{-1}, 2957, 2362, 1449, 1249, 1046, 1007, 928, 835, 755. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=0.24 (s, 9H), 1.79 (br t, J=5.8 Hz, 1 OH), 2.93 (t, J=6.3 Hz, 2H), 3.88 (td, J=6.3, 5.8 Hz, 2H), 6.09 (d, J=3.1 Hz, 1H), 6.54 (d, J=3.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=0.00 (q, 3C), 33.34 (t), 62.69 (t), 108.08 (d), 122.04 (d), 158.62 (s), 160.94 (s). MS (EI, 70 eV): m/z (%): 184 (55) [M]$^+$, 169 (31), 153 (94), 75 (100). HRMS (ESI): [$C_9H_{16}O_2$+Na]$^+$: calcd 207.0812, found 207.0818.

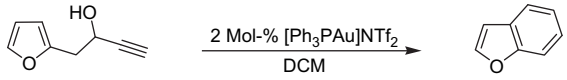
To a solution of the alcohol **4g** (552 mg, 3.00 mmol) in a mixture of DMSO (20 mL) and DCM (20 mL) was added IBX (1.01 g, 3.60 mmol) and stirred for 2 h at 35 °C. Then the mixture was filtered over silica gel and rinsed with diethyl ether. The combined organic layers were washed with water and brine and dried over $MgSO_4$. Column chromatography (silica gel, PE/EA, 6:1) afforded 466 mg (2.56 mmol, 85%) of the ketone **5g** as a yellow, volatile liquid. R_f (PE/EA, 4:1)=0.50. IR (neat): ν=2958 cm^{-1}, 1731, 1249, 1116, 1014, 929, 835, 789, 754. ^{1}H NMR ($CDCl_3$, 250 MHz): δ=0.25 (s, 9H), 3.75 (ddd, J=2.3, 0.8, 0.4 Hz, 2H), 6.23 (dt, J=3.1, 0.8 Hz, 1H), 6.59 (dt, J=3.1, 0.4 Hz, 1H), 9.73 (t, J=2.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ=−1.64 (q, 3C), 43.11 (t), 108.62 (d), 120.75 (d), 150.33 (s), 160.87 (s), 197.12 (d). MS (EI, 70 eV): m/z (%): 182 (27) [M]$^+$, 153 (100), 111 (20), 75 (51). HRMS (ESI): [$C_9H_{14}O_2Si$+H]$^+$: calcd 183.0836, found 183.0827.

To a solution of ethynylmagnesium chloride (8.23 mL, 0.6 M solution in THF/toluene, 4.94 mmol) in THF (20 mL) was added dropwise **5g** (600 mg, 3.29 mmol). Purification by column chromatography (silica gel, PE/EA, 6:1) afforded **6g** (542 mg, 2.60 mmol, 79%) as a yellow liquid. R_f (PE/EA, 4:1)=0.35. IR (neat): ν=3292 cm^{-1}, 2958, 2363, 1492, 1249, 1033, 926, 836. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=0.25 (s, 9H), 2.16 (br s, 1OH), 2.47 (d, J=2.1 Hz, 1H), 3.08 (dd, J=15.0, 6.4 Hz, 1H), 3.14 (dd, J=15.0, 5.5 Hz, 1H), 4.64–4.69 (m, 1H), 6.19 (d, J=3.1 Hz, 1H), 6.55 (d, J=3.1 Hz). ^{13}C NMR ($CDCl_3$, 126 MHz): δ=−1.62 (q), 36.79 (t), 61.05 (d), 73.35 (d), 83.72 (s), 107.89 (s), 120.47 (s), 154.83 (s), 159.95 (s). MS (EI, 70 eV): m/z (%): 208 (16) [M]$^+$, 153 (100), 111 (18), 75 (40). $C_{11}H_{16}O_2Si$ (208.26): calcd C 63.31, H 7.76; found C 63.41, H 7.74.

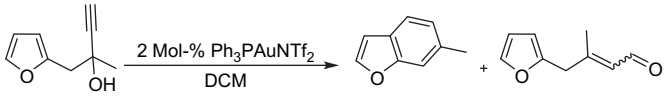


7

*4.1.8. 1-(5-Methylfuran-2-yl)but-3-yn-2-yl 4-toluenesulfonate (**7**).* To a stirred solution of **6d** (108 mg, 719 μmol) in dry pyridine (2.0 mL) was added *p*-toluenesulfonyl chloride (206 mg, 1.08 mmol). After 20 h at room temperature, the solution was quenched with water and stirred for another 30 min. The mixture was extracted with diethyl ether, the combined organic layers were washed with aq NH_4Cl and water and dried over $MgSO_4$. Purification by column chromatography (silica gel, PE/EA, 6:1) afforded **7** (136 mg, 447 μmol, 62%) as a pale yellow solid. Mp 57–58 °C. R_f (PE/EA, 6:1)=0.24. IR (neat): ν=3284 cm^{-1}, 2923, 1597, 1568, 1365, 1174, 892, 663, 567. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=2.22 (d, J=1.0 Hz, 3H), 2.44 (s, 3H), 2.46 (d, J=2.1 Hz, 1H), 3.07 (dd, J=15.2, 6.4 Hz, 1H), 3.14 (dd, J=15.2, 7.3 Hz, 1H), 5.23 (ddd, J=7.3, 6.4, 2.1 Hz, 1H), 5.83 (dq, J=3.1, 1.0 Hz, 1H), 6.02 (d, J=3.1 Hz, 1H), 7.28–7.30 (m, 2H), 7.73–7.75 (m, 2H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ=13.47 (q), 21.67 (q), 34.93 (t), 68.98 (d), 76.60 (d), 78.61 (s), 106.25 (d), 109.24 (d), 128.06 (d, 2C), 129.62 (d, 2C), 133.54 (s), 144.77 (s), 146.53 (s), 151.65 (s). MS (ESI): m/z (%): 327 (100) [M+Na]$^+$, 133 (55), 105 (21). HRMS (ESI): [$C_{16}H_{16}O_4S$+Na]$^+$: calcd 327.0662, found 327.0657.



*4.1.9. Benzofuran (**8a**).* To a solution of **6a** (100 mg, 734 μmol) in DCM (5 mL) was added PPh_3AuNTf_2 (10.8 mg, 14.6 μmol, 2 mol %) and stirred for 2 h at room temperature. Then the solvent was removed in vacuo. Purification of the residue by column chromatography (silica gel, gradient elution with pentane to pentane/EA, 4:1) afforded **8a** (46.7 mg, 394 μmol, 53%) as a colourless oil. R_f (PE/EA, 4:1)=0.55. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=6.77 (dd, J=2.2, 1.0 Hz, 1H), 7.21–7.33 (m, 2H), 7.51 ('d', J=8.1 Hz, 1H), 7.60 ('d', J=7.3 Hz, 1H). This compound has been reported earlier.[17]



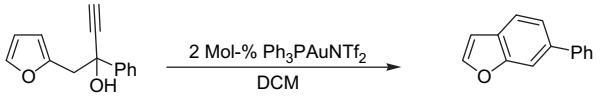
*4.1.10. 6-Methylbenzofuran (**8b**) and (E/Z)-4-(furan-2-yl)-3-methylbut-2-enal (**9b**).* To a solution of **6b** (108 mg, 724 μmol) in DCM (5 mL) was added PPh_3AuNTf_2 (10.7 mg, 14.5 μmol, 2 mol %) and stirred for 1 d at room temperature. Then the solvent was removed in vacuo. Purification of the residue by column chromatography (silica gel, gradient elution with PE to PE/EA, 4:1) afforded **8b** (45.9 mg, 347 μmol, 48%) as a colourless oil and a yellowish oil of **9b** (17.7 mg, 117 μmol, 17%) as a mixture of (*E*/*Z*)-isomers in a ratio of 69:31.

*4.1.10.1. Compound **8b**.* R_f (PE/EA, 4:1)=0.61. IR (neat): ν=3027 cm^{-1}, 2923, 2856, 1493, 1452, 1265, 1128, 1028, 806, 697. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=2.47 (s, 3H), 6.71 (dd, J=2.2, 1.0 Hz, 1H), 7.06 (d, J=7.9 Hz, 1H), 7.30–7.32 (m, 1H), 7.47 (d, J=7.9 Hz, 1H), 7.55 (d, J=2.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ=21.64 (q), 106.34 (d), 111.59 (d), 120.58 (d), 124.15 (d), 124.83 (s), 134.42 (s), 144.33 (d),

155.37 (s). MS (EI, 70 eV): *m*/*z* (%): 132 (100) $[M]^+$, 104 (20), 77 (22), 51 (23). HRMS (EI): C_9H_8O: calcd 132.0575, found 132.0576. This compound has been reported earlier.[18]

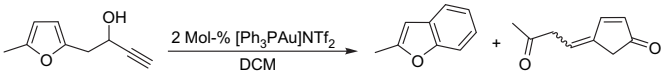
4.1.10.2. Major diastereomer of ***9b****.* R_f (PE/EA, 4:1)=0.31. IR (neat): ν=2921 cm^{-1}, 2855, 1673, 647. ^1H NMR ($CDCl_3$, 500 MHz): δ=2.17 (d, *J*=1.3 Hz, 3H), 3.52 (s, 2H), 5.89 (dq, *J*=7.9, 1.3 Hz, 1H), 6.14 (d, *J*=3.2 Hz, 1H), 6.33 (dd, *J*=3.2, 1.9 Hz, 1H), 7.35 (dd, *J*=1.9, 0.9 Hz, 1H), 10.0 (d, *J*=7.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ=17.32 (q), 38.90 (t), 107.83 (d), 110.49 (d), 128.49 (d), 142.13 (d), 150.53 (s), 159.26 (s), 191.20 (d). MS (EI, 70 eV): *m*/*z* (%): 150 (100) $[M]^+$, 121 (66), 82 (64). HRMS (ESI): $[C_9H_{10}O_2+Na]^+$: calcd 173.0573, found 173.0570.

4.1.10.3. Minor diastereomer of ***9b****.* ^1H NMR ($CDCl_3$, 500 MHz): δ=1.98 (d, *J*=1.3 Hz, 3H), 3.90 (s, 2H), 5.99 (d, *J*=7.9 Hz, 1H), 6.11 (d, *J*=3.2 Hz, 1H), 6.32 (dd, *J*=3.2, 1.9 Hz, 1H), 7.34 (dd, *J*=1.9, 0.9 Hz, 1H), 10.6 (d, *J*=7.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ=25.00 (q), 31.24 (t), 107.16 (d), 110.54 (d), 129.26 (d), 142.09 (d), 150.78 (s), 158.40 (s), 190.79 (d).



*4.1.11. 6-Phenylbenzofuran (****8c****).* To a solution of **6c** (200 mg, 942 μmol) in DCM (10 mL) was added PPh_3AuNTf_2 (13.9 mg, 18.8 μmol, 2 mol %) and stirred for 1 d at room temperature. Then the solvent was removed in vacuo. Purification of the residue by column chromatography (silica gel, PE/EA, 10:1) afforded **8c** (101 mg, 522 μmol, 56%) as a yellow oil, which shows a strong fluorescence in UV light.

R_f (PE/EA, 4:1)=0.52. IR (neat): ν=3059 cm^{-1}, 3032, 2926, 2361, 2340, 1474, 1297, 1028, 768, 670. ^1H NMR ($CDCl_3$, 500 MHz): δ=6.80 (d, *J*=2.2, 1.0 Hz, 1H), 7.34–7.37 (m, 1H), 7.44–7.48 (m, 2H), 7.50 (dd, *J*=8.0, 1.6 Hz, 1H), 7.63–7.66 (m, 4H), 7.73–7.73 (m, 1H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ=106.46 (d), 109.93 (d), 121.23 (d), 122.41 (d), 126.59 (s), 127.15 (d), 127.40 (d, 2C), 128.28 (d, 2C), 138.02 (s), 141.33 (s), 145.47 (d), 155.59 (s). MS (EI, 70 eV): *m*/*z* (%): 194 (100) $[M]^+$, 165 (34). HRMS (EI): $C_{14}H_{10}O$: calcd 194.0732, found 194.0743. This compound has been reported earlier, but not completely been characterised.[19]

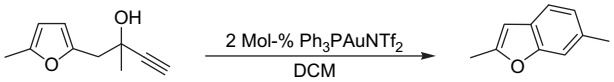


*4.1.12. 2-Methylbenzofuran (****8d****) and 4-[3-oxo-but-(Z)-ylidene]-cyclopent-2-enone (****10d****).* To a solution of **6d** (120 mg, 799 μmol) in DCM (10 mL) was added PPh_3AuNTf_2 (11.8 mg, 16.0 μmol, 2 mol %) and stirred for 15 min at room temperature. Then the solvent was removed in vacuo. Purification of the residue by column chromatography (silica gel, gradient elution with PE to PE/EA, 1:1) afforded **8d** (10 mg, 75.8 μmol, 9%) as a colourless oil and a colourless solid of **10d** (84 mg, 559 μmol, 70%) as a mixture of *E*/*Z*-isomers in a ratio of 69:31.

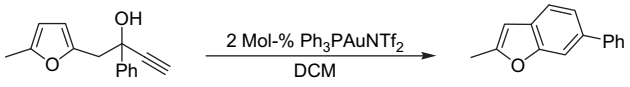
4.1.12.1. Compound ***8d****.* R_f (PE, 100%)=0.18. ^1H NMR ($CDCl_3$, 300 MHz): δ=2.45 (d, *J*=1.1 Hz, 3H), 6.36 (dq, *J*=1.1, 1.0 Hz, 1H), 7.14–7.22 (m, 2H), 7.38–7.42 (m, 1H), 7.44–7.48 (m, 1H). C_9H_8O (132.2). This compound has been reported earlier.[20]

4.1.12.2. Major diastereomer of ***10d****.* R_f (PE/EA, 1:1)=0.18. IR (neat): ν=2916 cm^{-1}, 1697, 1536, 1351, 1153, 812. ^1H NMR (Acetone-d_6, 500 MHz): δ=2.16 (s, 3H), 2.88–2.89 (m, 2H), 3.43 (d, *J*=7.4 Hz, 2H), 6.04 (t, *J*=7.4 Hz, 1H), 6.19 (d, *J*=5.5 Hz, 1H), 7.90 (d, *J*=5.5 Hz, 1H). ^{13}C NMR (acetone-d_6, 126 MHz): δ=29.81 (q), 37.47 (t), 44.51 (t), 123.25 (d), 134.30 (d), 141.18 (s), 160.31 (d), 204.88 (s), 205.23 (s). MS (ESI): *m*/*z* (%): 173 (100) $[M+Na]^+$, 151 (53) $[M+H]^+$, 133 (49), 123 (20), 109 (93). HRMS (ESI): $[C_9H_{10}O_2+Na]^+$: calcd 173.0573, found 173.0571.

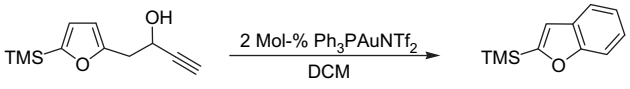
4.1.12.3. Minor diastereomer of ***10d****.* ^1H NMR (acetone-d_6, 500 MHz): δ=2.17 (s, 3H), 2.92–2.93 (m, 2H), 3.61 (d, *J*=7.7 Hz, 2H), 5.85 (t, *J*=7.7 Hz, 1H), 6.27 (dd, *J*=5.7, 1.8 Hz, 1H), 8.20 (d, *J*=5.7 Hz, 1H). ^{13}C NMR (acetone-d_6, 126 MHz): δ=29.66 (q), 40.25 (t), 43.01 (t), 121.82 (d), 135.63 (d), 139.41 (d), 154.89 (s), 205.16 (s), 205.68 (s).



*4.1.13. 2,6-Dimethylbenzofuran (****8e****).* To a solution of **6e** (164 mg, 1.00 mmol) in DCM (5 mL) was added PPh_3AuNTf_2 (14.8 mg, 20.0 μmol, 2 mol %) and stirred for 1 h at room temperature. Then the solvent was removed in vacuo. Purification of the residue by column chromatography (silica gel, PE/EA, 10:1) afforded **8e** (107 mg, 732 μmol, 65%) as a colourless oil. R_f (PE, 100%)=0.18. IR (neat): ν=3029 cm^{-1}, 2921, 1608, 1489, 1427, 1294, 1266, 1117, 955, 810, 598. ^1H NMR ($CDCl_3$, 300 MHz): δ=2.42 (d, *J*=1.1 Hz, 3H), 2.44 (s, 3H), 6.30 (dq, *J*=1.1, 1.0 Hz, 1H), 6.99 (d, *J*=7.9 Hz, 1H), 7.19–7.21 (m, 1H), 7.32 (d, *J*=7.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ=14.05 (q), 21.59 (q), 102.31 (d), 110.94 (d), 119.49 (d), 123.70 (d), 126.60 (d), 133.10 (s), 154.71 (s), 155.15 (s). MS (EI, 70 eV): *m*/*z* (%): 146 (100) $[M]^+$. HRMS (EI): $C_{10}H_{10}O$: calcd 146.0732, found 146.0715. $C_{10}H_{10}O$ (146.2): calcd C 81.17, H 6.81; found C 81.57, H 7.19.



*4.1.14. 2-Methyl-6-phenylbenzofuran (****8f****).* To a solution of **6f** (340 mg, 1.50 mmol) in DCM (10 mL) was added PPh_3AuNTf_2 (22.2 mg, 30.0 μmol, 2 mol %) and stirred for 1 d at room temperature. Then the solvent was removed in vacuo. Purification of the residue by column chromatography (silica gel, PE/EA, 10:1) afforded **8f** (219 mg, 1.05 mmol, 64%) as a colourless oil. R_f (PE, 100%)=0.13. IR (neat): ν=3031 cm^{-1}, 2920, 1600, 1472, 1420, 1292, 946, 824, 759, 696. ^1H NMR ($CDCl_3$, 500 MHz): δ=2.47 (d, *J*=1.0 Hz, 3H), 6.38 (dq, *J*=1.0, 1.0 Hz, 1H), 7.31–7.35 (m, 1H), 7.42–7.46 (m, 3H), 7.50 (d, *J*=8.0 Hz, 1H), 7.61–7.61 (m, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ=14.18 (q), 102.47 (d), 109.20 (d), 120.10 (d), 122.02 (d), 126.92 (d), 127.92 (d, 2C), 128.43 (d), 128.77 (d, 2C), 136.77 (s), 141.55 (s), 155.38 (s), 156.09 (s). MS (EI, 70 eV): *m*/*z* (%): 208 (100) $[M]^+$. $C_{15}H_{12}O$ (208.26): calcd C 86.51, H 5.81; found C 86.28, H 6.14.



*4.1.15. 2-Methyl-6-phenylbenzofuran (****8g****).* To a solution of **6g** (50 mg, 240 μmol) in DCM (2 mL) was added PPh_3AuNTf_2 (3.5 mg, 4.80 μmol, 2 mol %) and stirred for 12 h at room temperature. Then the solvent was removed in vacuo. Purification of the residue by column chromatography (silica gel, petrol ether) afforded **8g** (23 mg, 121 μmol, 50%) as a colourless oil. R_f (PE/EE, 4:1)=0.91. IR (neat): ν=3066 cm^{-1}, 2959, 1251, 1066, 921, 841, 746. ^1H NMR ($CDCl_3$, 500 MHz): δ=0.35 (s, 9H), 6.95 (d, *J*=1.0 Hz, 1H), 7.19 (dd, *J*=7.6, 7.2 Hz, 1H), 7.26 (dd, *J*=8.3, 7.2 Hz, 1H), 7.50 (d, *J*=8.4 Hz, 1H), 7.57 (d, *J*=7.5 Hz, 1H). MS (EI, 70 eV): *m*/*z* (%): 190 (47) $[M]^+$, 175 (100). HRMS

(EI): $C_{11}H_{14}OSi$: calcd 190.0814, found 190.0812. This compound has been reported earlier, but not completely been characterised.[21]

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