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Gold-Catalysis: Reactions of Organogold Compounds with Electrophiles

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Different arylgold(I), one alkynylgold(I), and one vinylgold(I) triphenylphosphane complexes were subjected to electrophilic halogenation reagents. With *N*-chlorosuccinimid, *N*-bromosuccinimid, and *N*-iodosuccinimid as well as the Barluenga reagent, selectively halogenated compounds were obtained. Trifluoroacetic acid, as a source of protons, leads to a clean protodeauration. With *N*-fluorobenzenesulfonimide or Selectfluor, exclusively a homocoupling was observed. For the precursor of the vinylgold(I) complex, a similar oxidative coupling could be induced by gold(III) chloride. Reactions with silicon or tin electrophiles failed.

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Introduction

In the past decade, homogeneous gold catalysis has become a powerful tool for organic synthesis and is still experiencing exponential growth.[1] In addition to the innovative advances in methodology and their increasing application in total synthesis,[2] significant insights into the mechanistic details of gold-catalyzed reactions could be gained.[3] Detailed studies of the elemental steps of gold catalysis will help to understand and direct selectivity as well as to develop new reactions.[4]

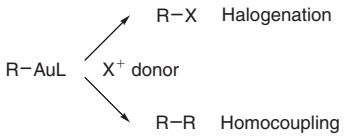
While in many gold-catalyzed reactions the final step is a protodeauration,[5] the reaction with other electrophiles such as halogen$^+$ donors has recently become a topic too.[6] Even palladium(II) compounds were used as electrophiles.[7]

Last year we communicated a homocoupling of organogold compounds by F^+ donors (Scheme 1),[8] which subsequently was extended to a unique heterocoupling of organogold intermediates and boronic acids by Zhang and coworkers.[9] Furthermore, F^+ donors as well as other oxidants have then been used for homocoupling reactions too.[10]

Since F^+ donors and the I^+ donors used in most of the other examples would behave quite different, we now wanted to systematically explore the borderline between the halogenation and the homocoupling pathway.

Results and Discussion

We prepared six different organogold(I) triphenylphosphane complexes **1a**–**1f**[8] and then subjected them to different electrophilic halogenation reagents, namely *N*-chlorosuccinimid, *N*-bromosuccinimid, *N*-iodosuccinimid, and Barluenga's[11] reagent Py_2I^+ BF_4^- (Table 1). The conversions were monitored by in situ ^1H and ^{13}C NMR spectrometry, and due to the detection limits for conversions which appeared to be quantitative by NMR, we listed >95% in the Table 1 . The gold salts were then separated by filtration over silica gel and the product species were analyzed and identified by GC-MS.



Scheme 1. Different pathways in the reaction of organogold compounds with halogen$^+$ donors.

With the nitro-substituted substrate **1a** (entry 1), the corresponding aryl halides **2aa**–**2ac** were exclusively obtained. However, with the unsubstituted phenylgold species **1b**, a reduced yield of only 65% of **2ba** was detected for the less reactive NCS, while the bromination and the iodination proceeded quantitatively to deliver **2bb** and **2bc**, respectively (entry 2). For the methoxy-substituted **1c** as well as for the 2-formylfuran **1d** all conversions were quantitative again, **2ca**–**2cc** and **2da**–**2dc**, respectively, were formed (entries 3 and 4). The 3-formylfuran derivative **1e** failed in the reaction with NCS, **2ea** could not be isolated, all the other halogenations gave excellent conversions to **2eb** and **2ec** (entry 5). Even the alkynylgold complex **1f** reacted smoothly with all the reagents to obtain **2fa**–**2fc** (entry 6). It becomes obvious that NCS is a borderline case, the halogenation pathway with some substrates is feasible, but the chlorination is not general. The treatment with the bromination and iodination reagent, however, seems to be of broad scope, exclusively delivering halogenation products.

In addition to these halogenation reagents, the protodeauration and the deuterodeauration by trifluoroacetic acid was

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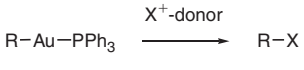
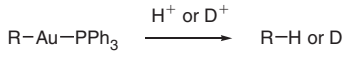
Table 1. Selective halogenation of organogold compounds 1



1 **2**

Entry	Substrate	NCS	NBS	NIS	Barluenga's reagent
1	**1a** R = 3-nitro phenyl	**2aa** X = Cl >95%	**2ab** X = Br >95%	**2ac** X = I >95%	**2ac** X = I >95%
2	**1b** R = phenyl	**2ba** X = Cl 65%	**2bb** X = Br >95%	**2bc** X = I >95%	**2bc** X = I >95%
3	**1c** R = 3-methoxy phenyl	**2ca** X = Cl >95%	**2cb** X = Br >95%	**2cc** X = I >95%	**2cc** X = I >95%
4	**1d** R = 2-formylfuran-5-yl	**2da** X = Cl >95%	**2db** X = Br >95%	**2dc** X = I >95%	**2dc** X = I >95%
5	**1e** R = 3-formyl-5-furan-	–	**2eb** X = Br >95%	**2ec** X = I >95%	**2ec** X = I >95%
6	**1f** R = phenylethynyl	**2fa** X = Cl >95%	**2fb** X = Br >95%	**2fc** X = I >95%	**2fc** X = I >95%

Table 2. Protodemetallation and deuterodemetallation of the substrates 1c and 1f



1 **3**

Entry	Substrate	CF_3COOH	CF_3COOD
3	**1c** R = 3-methoxy phenyl	**3c**-H >95%	**3c**-D >95%
6	**1f** R = phenylethynyl	**3f**-H >95%	**3f**-D >95%

investigated with substrates **1c** and **1f**, which also gave quantitative yields within the detection limits of the NMR experiments (Table 2).

Now we turned towards the fluorination reagents. As in our initial report,[8] we used *N*-fluorobenzenesulfonimide, but as a second reagent we also tested Selectfluor. In addition to substrates **1a**–**1f** from Table 1, the 4-methoxyphenyl compound **1g** and the lactone **1h** were also investigated (Table 3). Indeed, with both reagents only a homocoupling was observed (entries 1–8).[12] The yields vary, but one effect is clear, with Selectfluor usually slightly better yields were obtained. As **1h** possesses a stereogenic centre, the homocoupling leads to a diastereomeric mixture, no stereorecognition was observed.

The mechanistic hypothesis for the homocoupling would be an oxidation of the gold(I) centre by the F^+, the gold(III) species formed then undergoes ligand exchange and reductively eliminates the homocoupling products **4**. In order to investigate this possibility, the allene **5**, the precursors of **1h**, was reacted with one equivalent of gold(III) chloride (Scheme 2). And indeed, a 76% yield of **4h** was obtained, again as a mixture of diastereoisomers. This is in full accordance with our previous observation of an oxidative C–C bond formation and homocoupling by gold(III).[8,13]

Finally, we also investigated Me_3SiCl, Me_3SiOTf, Bu_3SnCl, and Bu_3SnOTf as potential electrophiles for **1c**. These experiments could have indicated the possibility to trap organogold intermediates of catalytic cycles by silicon or tin – the corresponding organosilicon or organotin compounds would have been useful synthetic intermediates. However, no reaction was observed (Scheme 3). One could probably consider such processes to be transmetallation reactions, and silicon and tin are too electropositive for the transfer of the organic moiety from the electronegative gold(I) centre.

Conclusion

The chlorination, bromination, and iodination of these organogold compounds shows that this step might be useful for the synthesis of halo-functionalized products by interception of organogold intermediates in gold-catalyzed reactions. If the substrates of these catalysis reactions do not efficiently and directly cyclize with the halogen donors, this will be of special benefit for synthetic applications. The direct fluorination did not succeed, the observed homocoupling is a useful oxidative dimerization process.

Experimental

General Experimental Procedure: Reaction of Aryl Gold Phosphine Complexes with Electrophiles

A reference spectrum of the aryl gold complexes was recorded first. The electrophiles (*N*-halosuccinimides, trifluoroacetic acid, deutero-trifluoroacetic acid) were then added. The product formation was monitored by NMR spectroscopy. In all the cases, the product was characterized in situ and then purified by filtration over silica gel to remove the gold. The structural assignment was further confirmed by GC-MS analysis.

*Chloro-3-nitro Benzene (**2aa**) (Chart 1)*

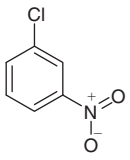
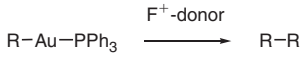
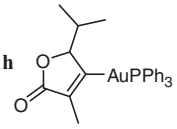


Chart 1.

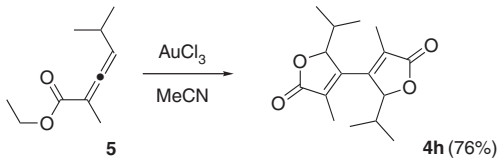
According to the general procedure, in deuterated dichloromethane (500 µL), **1a** (15.02 mg, 258 µmol), *N*-chlorosuccinimide (3.63 mg, 271 µmol) at room temperature. The data matched that of previous literature data.[14–16] Yield (NMR): >95%. δ_H (CD_2Cl_2, 300 MHz) 8.42 (t, *J* 2.03, 1H), 8.21–8.18 (ddd, *J* 1.09, 2.23, 8.23, 1H), 7.93–7.90 (ddd, *J* 1.09, 1.81, 7.77, 1H), 7.63 (t, *J* 8.01, 1H). δ_C (CD_2Cl_2, 75 MHz) 143.94 (s), 134.38 (s), 132.73 (d), 131.16 (d), 123.57 (d), 122.46 (d). *m*/*z* (GC-MS) 157.0 (M^+).

Table 3. Homocoupling induced by F^+ oxidants

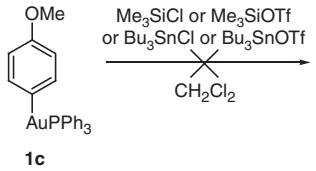


Entry	Substrate	*N*-fluorobenzenesulfonimide	Selectfluor
1	**1a** R = 3-nitro phenyl	**4a** 88%	**4a** 91%
2	**1b** R = phenyl	**4b** 86%	**4b** 90%
3	**1c** R = 3-methoxy phenyl	**4c** 83%	**4c** 85%
4	**1d** R = 2-formylfuran-5-yl	**4d** 77%	**4d** 82%
5	**1e** R = 3-formyl-furan-5-yl	**4e** 78%	**4e** 81%
6	**1f** R = phenylethenyl-	**4f** 91%	**4f** 93%
7	**1g** R = 4-methoxyphenyl	**4g** 87%	**4g** 94%
8	**1h** 	**4h**[A] 69%	**4h**[A] 71%

[A]Obtained as a mixture of diastereoisomers.



Scheme 2. Oxidative coupling of two allenes when using stoichiometric amounts of gold(III) chloride.



Scheme 3. Silicon or tin electrophiles do not react.

*1-Bromo-3-nitro Benzene (**2ab**) (Chart 2)*

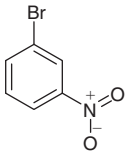


Chart 2.

According to the general procedure, in deuterated dichloromethane (500 µL), **1a** (15.17 mg, 260 µmol), *N*-bromosuccinimide (4.84 mg, 260 µmol) at room temperature. The data matched that of previous literature data.[17] Yield (NMR): >95%. δ_H (CD_2Cl_2, 300 MHz) 8.30 (t, *J* 2.03, 1H), 8.10–8.06 (ddd, *J* 0.94, 2.15, 8.29, 1H), 7.79–7.76 (ddd, *J* 0.95, 1.85, 8.00, 1H), 7.59–7.56 (m, 1H). δ_C (CD_2Cl_2, 75 MHz) 149.26 (s), 138.05 (d), 131.13 (d), 127.02 (d), 123.10 (d), 122.55 (s). *m/z* (GC-MS) 202.9 (M^+).

*1-Iodo-3-nitro Benzene (**2ac**) (Chart 3)*

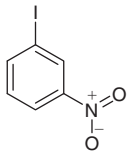


Chart 3.

According to the general procedure, in deuterated dichloromethane (500 µL), **1a** (15.27 mg, 262 µmol), *N*-iodosuccinimide (6.38 mg, 283 µmol) at room temperature. Yield (NMR): >95%. The data matched that of previous literature data.[16,17] δ_H (CD_2Cl_2, 300 MHz) 8.48 (t, *J* 1.94, 1H), 8.13–8.09 (ddd, *J* 0.96, 2.23, 8.23, 1H), 7.99–7.95 (ddd, *J* 1.00, 1.62, 7.88, 1H), 7.22 (t, *J* 8.07, 1H). δ_C (CD_2Cl_2, 75 MHz) 143.95 (d), 132.73 (d), 131.16 (d), 128.83 (s), 123.12 (d), 93.70 (s). *m/z* (GC-MS) 249.0 (M^+).

*1-Iodo-3-nitro Benzene (**2ac**) (Chart 4)*

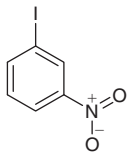


Chart 4.

According to the general procedure, in deuterated dichloromethane (500 µL), **1a** (15.10 mg, 260 µmol), Barluenga's reagent (9.63 mg, 260 µmol) at room temperature. The data matched that of previous literature data.[16,17] Yield (NMR): >95%. δ_H (CD_2Cl_2, 300 MHz) 8.42 (t, *J* 1.99, 1H), 8.21–8.18 (ddd, *J* 0.94, 2.19, 8.22, 1H), 7.93–7.90 (ddd, *J* 1.02, 1.76, 7.76, 1H), 7.62 (t, *J* 8.05, 1H). δ_C (CD_2Cl_2, 75 MHz) 141.14 (s), 138.03 (d), 132.73 (d), 131.16 (d), 123.12 (d), 93.70 (s). *m/z* (GC-MS) 249.0 (M^+).

*Chlorobenzene (**2ba**) (Chart 5)*

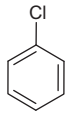


Chart 5.

According to the general procedure, in deuterated benzene (500 µL), **1b** (10.79 mg, 192 µmol), *N*-chlorosuccinimide (2.21 mg, 192 µmol) at room temperature. This data is in accordance to the published data.[14] Yield: 65%. δ_H (CD_2Cl_2, 250 MHz) 7.24–7.19 (m, 5H). *m*/*z* (GC-MS) 112.0 (M^+).

*Bromobenzene (**2bb**) (Chart 6)*

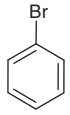


Chart 6.

According to the general procedure, in deuterated benzene (500 µL), **1b** (10.23 mg, 191 µmol), *N*-bromosuccinimide (3.52 mg, 197 µmol) at room temperature. Conversion of the starting material is monitored by ^{1}H NMR spectrometry and EI MS in situ. This data is in accordance to the published data.[14] Yield (NMR): >95%. δ_H (CD_2Cl_2, 250 MHz) 7.33–7.29 (m, 5H). *m*/*z* (HRMS (EI), 70 eV) 154.0938/157.0390 ($M)^+$.

*Iodobenzene (**2bc**) (Chart 7)*

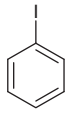


Chart 7.

According to the general procedure, in deuterated benzene (500 µL), **1b** (10.13 mg, 189 µmol), *N*-iodosuccinimide (4.40 mg, 195 µmol) at room temperature. Conversion of the starting material is monitored by ^{1}H NMR spectrometry and EI MS in situ. This data is in accordance to the published data.[14] Yield (NMR): >95%. δ_H (CD_2Cl_2, 250 MHz) 7.39–7.16 (m, 5H). *m*/*z* (HRMS (EI), 70 eV) 204.9730 ($M)^+$.

*Iodobenzene (**2bc**) (Chart 8)*

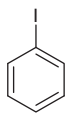


Chart 8.

According to the general procedure, in deuterated benzene (500 µL), **1b** (10.00 mg, 186 µmol), Barluenga's reagent (6.94 mg, 186 µmol) at room temperature. Conversion of the starting material is monitored by ^{1}H NMR spectrometry and EI MS in situ. This data is in accordance to the published data.[14] Yield (NMR): >95%. δ_H (CD_2Cl_2, 250 MHz) 7.39–7.16 (m, 5H). *m*/*z* (HRMS (EI), 70 eV) 204.0587 ($M)^+$.

*1-Chloro-3-methoxybenzene (**2ca**) (Chart 9)*

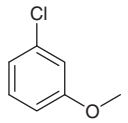


Chart 9.

According to the general procedure, in deuterated chloroform (500 µL), **1c** (15.14 mg, 267 µmol), *N*-chlorosuccinimide (3.57 mg, 267 µmol) at room temperature. Conversion of the starting material is monitored by ^{1}H NMR spectrometry and characterized in situ by NMR spectrometry. The product formed was purified via column chromatography on silica with petrol ether and ethyl acetate as eluents to remove the gold, to measure GC mass. The data matched that of previous literature data.[18] Yield (NMR): >95%. δ_H ($CDCl_3$, 500 MHz) 7.28–7.25 (m, 1H), 7.10–7.09 (m, 1H), 7.04 (t, *J* 1.98, 1H), 6.83–6.81 (m, 1H), 3.78 (s, 3H). δ_C ($CDCl_3$, 125 MHz) 160.30 (s), 129.06 (s), 128.57 (d), 119.72 (d), 112.97 (d), 112.84 (d), 55.33 (q). *m*/*z* (GC-MS) 142.5 $(M)^+$.

*1-Bromo-3-methoxy Benzene (**2cb**) (Chart 10)*

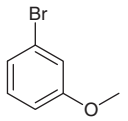


Chart 10.

According to the general procedure, in deuterated chloroform (500 µL), **1c** (15.33 mg, 271 µmol), *N*-bromosuccinimide (4.82 mg, 271 µmol) at room temperature. Conversion of the starting material is monitored by ^{1}H NMR spectrometry and characterized in situ by NMR spectrometry. The product formed was purified via column chromatography on silica with petrol ether and ethyl acetate as eluents to remove the gold, to measure GC mass. The data matched that of previous literature data.[17–19] Yield (NMR): >95%. δ_H ($CDCl_3$, 300 MHz) 7.06 (t, *J* 7.90, 1H), 7.01–6.98 (m, 2H), 6.78–6.74 (ddd, *J* 1.29, 2.47, 7.99, 1H), 3.71 (s, 3H). δ_C ($CDCl_3$, 75 MHz) 160.37 (s), 130.53 (d), 123.76 (d), 122.82 (s), 117.14 (d), 113.08 (d), 55.45 (q). *m*/*z* (GC-MS) 185.9 $(M)^+$.

*1-Iodo-3-methoxybenzene (**2cc**) (Chart 11)*

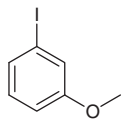


Chart 11.

According to the general procedure, in deuterated chloroform (500 µL), **1c** (15.43 mg, 273 µmol), *N*-iodosuccinimide (6.13 mg, 273 µmol) at room temperature. The data matched that of previous literature data.[15,18] Yield (NMR): >95%. δ_H ($CDCl_3$, 300 MHz) 7.37–7.31 (m, 1H), 7.27–7.26 (m, 1H), 7.01 (t, *J* 8.32, 3H), 6.91–6.86 (ddd, *J* 0.98, 2.47, 8.35, 1H), 3.80 (s, 3H). δ_C ($CDCl_3$, 75 MHz) 159.78 (s), 131.16 (d), 130.22 (d), 123.41 (d), 114.17 (d), 94.00 (s) 55.78 (q). *m*/*z* (GC-MS) 233.9 $(M)^+$.

*1-Iodo-3-methoxybenzene (**2cc**) (Chart 12)*

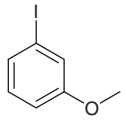


Chart 12.

According to the general procedure, in deuterated chloroform (500 µL), **1c** (15.23 mg, 269 µmol), Barluenga's reagent (10.01 mg, 269 µmol) at room temperature. The data matched that of previous literature data.[14,15,18] Yield (NMR): >95%. δ_H ($CDCl_3$, 500 MHz) 7.12–7.07 (m, 2H), 6.92 (t, *J* 8.05, 1H), 6.80–6.78 (m, 1H), 3.80 (s, 3H). δ_C ($CDCl_3$, 125 MHz) 159.95 (s), 130.76 (d), 129.84 (d), 123.73 (d), 113.91 (d), 94.36 (s), 55.15 (q). *m*/*z* (GC-MS) 233.9 $(M)^+$.

*Methoxybenzene (**3c**-H) (Chart 13)*

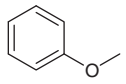


Chart 13.

According to the general procedure, in deuterated chloroform (500 µL), **1c** (15.10 mg, 267 µmol), deuterated trifluoroacetic acid (3.04 mg, 267 µmol) at room temperature. The data matched that of previous literature data.[14,15] Yield (NMR): >95%. δ_H ($CDCl_3$, 250 MHz) 7.00–6.91 (m, 5H), 3.83 (s, 3H).

*Methoxy(3-^{2}H)benzene (**3c**-D) (Chart 14)*

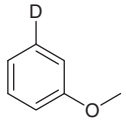


Chart 14.

According to the general procedure, in deuterated chloroform (500 µL), **1c** (15.22 mg, 269 µmol), deuterated trifluoroacetic acid (3.09 mg, 269 µmol) at room temperature. Yield (NMR): >95%. The data matched that of previous literature data.[20] δ_H ($CDCl_3$, 300 MHz) 7.24–7.18 (m, 2H), 6.89–6.82 (m, 3H), 3.73 (s, 3H). δ_C (CD_2Cl_2, 75 MHz) 159.51 (s), 128.23 (d), 127.35 (d), 120.56 (d), 113.90 (d), 113.79 (s), 55.15 (q).

*5-Chlorofuran-2-carbaldehyde (**2da**) (Chart 15)*

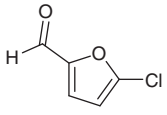


Chart 15.

According to the general procedure, in deuterated chloroform (500 µL), **1d** (10.37 mg, 187 µmol), *N*-chlorosuccinimide (2.50 mg, 187 µmol) at room temperature. The data matched that of previous literature data.[21] Yield (GC): >95%. *m*/*z* (GC-MS) 130.0 $(M)^+$.

*5-Bromofuran-2-carbaldehyde (**2db**) (Chart 16)*

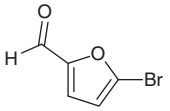


Chart 16.

According to the general procedure, in deuterated chloroform (500 µL), **1d** (10.29 mg, 186 µmol), *N*-bromosuccinimide (3.26 mg, 183 µmol) at room temperature. The data matched that of previous literature data.[14,15] Yield (NMR): >95%. δ_H ($CDCl_3$, 250 MHz) 8.98–8.97 (m, 1H), 6.17–6.15 (m, 1H), 5.63–5.61 (m, 1H). *m*/*z* (GC-MS) 175.0 $(M)^+$.

*5-Iodofuran-2-carbaldehyde (**2dc**) (Chart 17)*

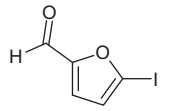


Chart 17.

According to the general procedure, in deuterated chloroform (500 µL), **1d** (10.29 mg, 185 µmol), *N*-iodosuccinimide (4.17 mg, 185 µmol) at room temperature. The data matched that of previous literature data.[21] Yield (GC): >95%. *m*/*z* (GC-MS) 221.9 $(M)^+$.

*5-Iodofuran-2-carbaldehyde (**2dc**) (Chart 18)*

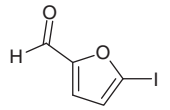


Chart 18.

According to the general procedure, in deuterated chloroform (500 µL), **1d** (10.29 mg, 185 µmol), Barluenga's reagent (7.04 mg, 185 µmol) at room temperature. The data matched that of previous literature data.[14,15] Yield (NMR): >95%. *m*/*z* (GC-MS) 221.9 $(M)^+$.

*5-Chlorofuran-3-carbaldehyde (**2ea**) (Chart 19)*

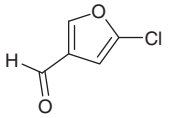


Chart 19.

According to the general procedure, in deuterated chloroform (500 µL), **1e** (10.37 mg, 187 µmol), *N*-chlorosuccinimide (2.50 mg, 187 µmol) at room temperature. The data was matched that of previous literature data.[22] Yield (GC): >95%. *m*/*z* (GC-MS) 130.0 $(M)^+$.

*5-Bromofuran-3-carbaldehyde (**2eb**) (Chart 20)*

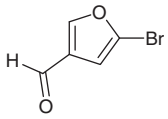


Chart 20.

According to the general procedure, in deuterated chloroform (500 µL), **1e** (10.29 mg, 185 µmol), *N*-bromosuccinimide (3.31 mg, 185 µmol) at room temperature. The Yield (GC): >95%. *m*/*z* (GC-MS) 175.0 $(M)^+$.

*5-Iodofuran-3-carbaldehyde (**2ec**) (Chart 21)*

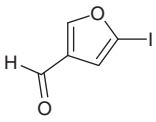


Chart 21.

According to general procedure, in deuterated chloroform (500 µL), **1e** (11.20 mg, 202 µmol), *N*-iodosuccinimide (4.54 mg, 202 µmol) at room temperature. Yield (GC): >95%. *m*/*z* (GC-MS) 221.9 $(M)^+$.

*5-Iodofuran-3-carbaldehyde (**2ec**) (Chart 22)*

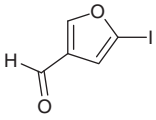


Chart 22.

According to general procedure, in deuterated chloroform (500 µL), **1e** (10.49 mg, 189 µmol), Barluenga's reagent (7.17 mg, 189 µmol) at room temperature. Yield (GC): >95%. *m*/*z* (GC-MS) 221.9 $(M)^+$.

*(Chloroethynyl)benzene (**2fa**) (Chart 23)*

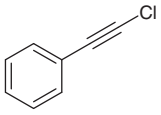


Chart 23.

According to general procedure, in deuterated chloroform (500 µL), **1f** (15.35 mg, 274 µmol), *N*-chlorosuccinimide (3.65 mg, 274 µmol) at room temperature. The data matched that of previous literature data.[14,19] Yield (NMR): >95%. δ_H ($CDCl_3$, 250 MHz) 7.24–7.18 (m, 5H). *m*/*z* (GC-MS) 136.5 $(M)^+$.

*(Bromoethynyl)benzene (**2fb**) (Chart 24)*

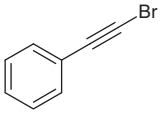


Chart 24.

According to general procedure, in deuterated chloroform (500 µL), **1f** (15.32 mg, 273 µmol), *N*-bromosuccinimide (4.86 mg, 273 µmol) at room temperature. The data matched that of previous literature data.[23] Yield (NMR): >95%. δ_H ($CDCl_3$, 250 MHz) 7.24–7.16 (m, 5H). *m*/*z* (GC-MS) 179.9 $(M)^+$.

*(Iodoethynyl)benzene (**2fc**) (Chart 25)*

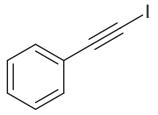


Chart 25.

According to general procedure, in deuterated chloroform (500 µL), **1f** (15.57 mg, 278 µmol), *N*-iodosuccinimide (6.28 mg, 278 µmol) at room temperature. The data matched that of previous literature data.[24] Yield (NMR): >95%. δ_H ($CDCl_3$, 250 MHz) 7.24–7.18 (m, 5H). *m*/*z* (GC-MS) 227.9 $(M)^+$.

*(Iodoethynyl)benzene (**2fc**) (Chart 26)*

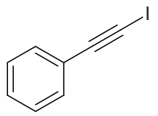


Chart 26.

According to general procedure, in deuterated chloroform (500 µL), **1f** (15.57 mg, 278 µmol), Barluenga's reagent (10.31 mg, 278 µmol) at room temperature. The data matched that of previous literature data.[24] Yield (NMR): >95%. δ_H ($CDCl_3$, 250 MHz) 7.24–7.18 (m, 5H). *m*/*z* (GC-MS) 227.9 $(M)^+$.

*Ethynylbenzene (**3f**-H) (Chart 27)*

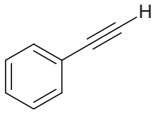


Chart 27.

According to general procedure, in deuterated chloroform (500 µL), **1f** (15.23 mg, 271 µmol), deuterated trifluoroacetic acid (3.09 mg, 271 µmol) at room temperature. The data matched that of previous literature data.[14,15] Yield (NMR): >95%. δ_H ($CDCl_3$, 250 MHz) 7.24–7.19 (m, 5H). *m*/*z* (GC-MS) 102.0 $(M)^+$.

*(^{2}H)ethynylbenzene (**3f**-D) (Chart 28)*

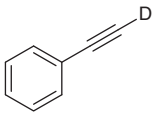


Chart 28.

According to general procedure, in deuterated chloroform (500 µL), **1f** (15.16 mg, 271 µmol), deuterated trifluoroacetic acid (3.12 mg, 271 µmol) at room temperature. The data matched that of previous literature data.[14] Yield (NMR):

>95%. δ_H ($CDCl_3$, 250 MHz) 7.24–7.17 (m, 5H). *m*/*z* (GC-MS) 103.0 $(M)^+$.

*4,4′-Dimethoxy-1,1′-biphenyl (**4g**) (Chart 29)*

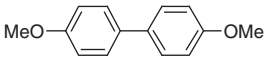


Chart 29.

To Selectfluor (26.0 mg, 74.0 µmol, 1.05 eq) in acetonitrile (5 mL) was added 4-methoxyphenyl(triphenylphosphan)gold (40.0 mg, 71.0 µmol, 1.00 eq) and stirred at room temperature for 1 h. The reaction mixture was adsorbed onto silica and purified by flash column chromatography (20% ethyl acetate in petroleum ether) to give the product as a white solid (8.0 mg, 94%). The NMR data is in accordance with literature data.[24] δ_H ($CDCl_3$, 250 MHz) 7.48 (d, *J* 8.78, 4H), 6.96 (d, *J* 8.79, 4H), 3.85 (s, 6H). *m*/*z* (EI^+) 214 (100%) $[M]^+$. Spectroscopic data match those in the literature.[1]

*4,4′-Dimethyl-2,2′-di(propan-2-yl)-3,3′-bifuran-5,5′(2H,2′H)-dione (**4h**)*

To a solution of ethyl 2,5-dimethylhexa-2,3-dienoate (KG-26) in acetonitrile, one equivalent of gold(III) trichloride was added and the reaction mixture was stirred for 6 h at 80°C. The product formed was purified via column chromatography on silica with petrol ether and ethyl acetate as eluents. Yield: 76% as a mixture of two diastereomers.

Diastereomer 1: δ_H (CD_3CN, 300 MHz) 0.72 (d, *J* 6.89, 3H), 1.15 (d, *J* 6.89, 3H), 1.85 (s, 3H), 1.78 (s, 3H), 2.05 (m, 1H), 4.92 (m, 1H). δ_C (CD_3CN, 75 MHz) 10.37 (q), 14.09 (q), 20.04 (q), 30.08 (d), 86.19 (d), 130.06 (s), 151.82 (s), 173.68 (s).

Diastereomer 2: δ_H (CD_3CN, 300 MHz) 0.64 (d, *J* 6.89, 3H), 1.12 (d, *J* 6.89, 3H), 1.79 (s, 3H), 1.85 (s, 3H), 2.04 (m, 1H), 5.06 (m, 1H). δ_C (CD_3CN, 75 MHz) 11.19 (q), 14.60 (q), 21.16 (q), 31.40 (d), 86.97 (d), 130.80 (s), 152.49 (s), 173.89 (s).

Acknowledgement

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