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Logically organized by functional group

The systematic, logical and consistent organization of the synthetic methods for each functional group enables users to quickly find out which methods are useful for a particular synthesis and which are not.

Thieme Science of Synthesis Results Full text Explore contents E / A NAVIGATION 3.6.13.1 Gold-Catalyzed Coupling Reactions () **General Introduction** Homo- and cross-coupling reactions catalyzed by transition metals are an increasingly important class of carbon-carbon and carbon-heteroatom bond-forming processes. [1] These transformations allow for the efficient coupling of diversely functionalized organic molecules with high selectivity and functional-group tolerance. As exch, coupling reactions have become powerful tools for synthetic chemists with palladium-catalyzed processes, such as the Suzuki-Miyaura, Stille, and Sonogashira reactions, being the subject of the 2010 hobel first in Chemistry. [13] Most coupling reactions proceed via a redox croke where the metal cataly mundergoes a two-electron oxidation to afford an Min-2 species amenable to reductive elimination. Whist palladium is ideally suited to such cycles, other transition metals such as nickel and copper have emerged as afternative catalysts for homo- and cross-coupling reactions, expanding the range of transformations available to synthetic chemists. The use of gold complexes as catalysts for coupling reactions is challenging. Unlike palladium and other late transition metals, gold rarely changes oxidation state during the course of a reaction and most commonly acts as a redox-neutral, carbophilic n-acid, activating multiple bonds toward nucleophilic attack. [4-9] This reactivity as a redox-neutral, carbophilic n-acid, activating multiple bonds toward nucleophilic attack. $^{(4-9)}$ This reactivity can be attributed to the large redox potential of the gold/floploi(III) couple $(8^{6}-4)$ -1.41 V), which is significantly higher than that of palladium(I)($8^{6}-4$ -0.02V). $^{(10)}$ as a result, strongly-oxidizing conditions are required to effect the oxidation of gold[] to gold[III] essential for coupling catalysis. Despite the challenges, several homo- and cross-coupling reactions mediated by gold complexes have been reported in the literature. Isla-14] In this chapter the development of gold-catalyzed coupling reactions proceeding via proposed gold (I)/gold(III) redox cycles under homogeneous conditions will be reviewed. The material is divided into four subcategories according to the type of coupling reaction (homo- or cross-) and the method of oxidation of gold (I) to gold(III). In Sections 3.6.13.1.1 and 3.6.13.1.2, transformations where gold(III) acts as a stoichiometric oxidant and selected examples of some conventional catalytic coupling reactions involving oxidative addition to gold(f) are presented. This is followed in Sections 3.6.13.13 and 3.6.13.14 by a discussion of how the use and cross-coupling reactions. **SAFETY:** Gold complexes are generally mild irritants and care should be taken to avoid contact with eyes or skin, or inhalation of dust particles. Gold(I) chloride and tetrachloroauric acid $(HAuCl_d)$ cause burns and may

Immediately applicable in the lab

Effective and practical experimental procedures can also be implemented quickly and easily in the lab. This enables the chemist to get started immediately with the design and planning of a synthesis.

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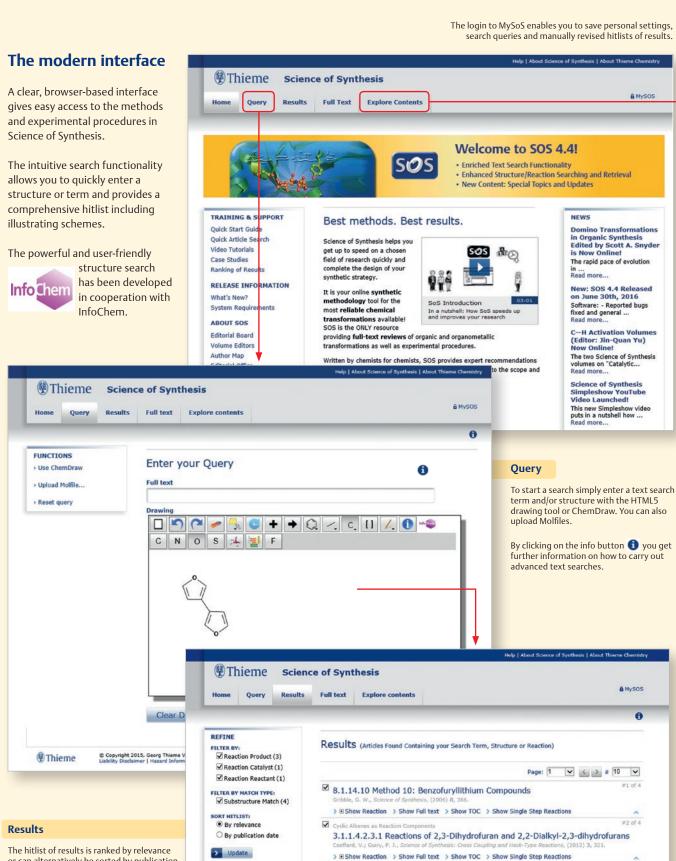
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 $\ensuremath{\overline{\boxtimes}}$ 3.6.13.1.3.3 Method 3: Cyclization–Homocoupling of 2-Alkynylphenols with (Diacetoxylodo)benzene

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☑ 6.1.8.10.2 Variation 2: Preparation of Oligomeric Furans

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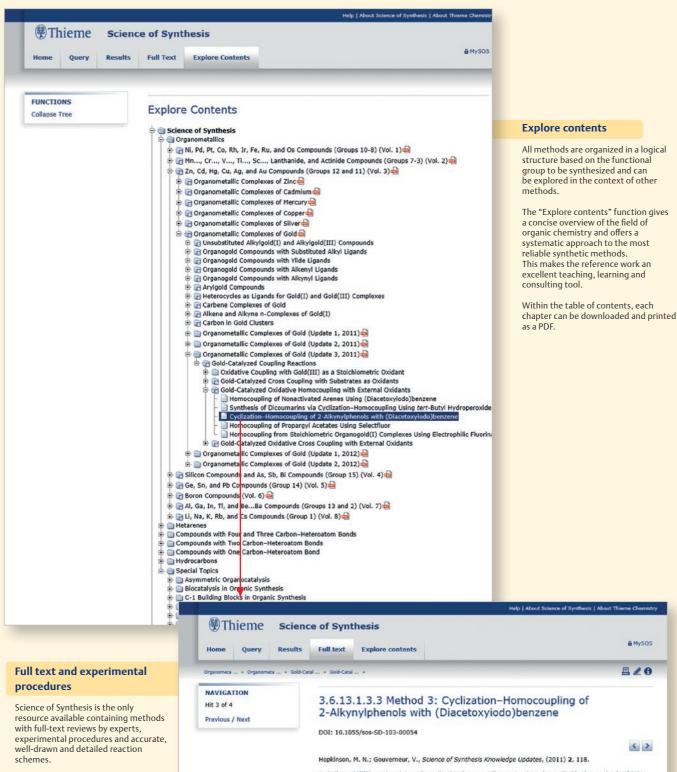
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A similar gold(III)-catalyzed cascade cyclization-homocoupling protocol can be applied in the synthesis of 3,3′-bibenzofurans directly from 2-alkynylphenols (Scheme 17). (69) In this case, (diacetoxylodo)benzene is the most successful oxidant, delivering the dimer 40 in 37% yield from phenol 39 when used with tetrachioroauric acid (10 mol%) in diethyl ether. The low isolated yield of the reaction can be attributed to competitive oxidation of the starting material to quinone derivatives by (diacetoxylodo)benzene.

Scheme 17 Synthesis of a 3,3'-Bibenzofuran from a 2-Alkynylphenol [69]

2,2'-Diphenyl-3,3'-bibenzofuran (40); Typical Procedure: [69]

HAuCl₄ (17.5 mg, 0.05 mmol, 10 mol%) was placed in a predried 20-mL vial equipped with a stirrer bar. Et₂O (10 mL) was added and the mixture was stirred at rt for 5 min. 2-Alkynylphenol 39 (100 mg, 0.5 mmol, 1 equiv) was added, followed, after 5 min, by PhI(OAC)₂ (848 mg, 2.6 mmol, 5 equiv). The mixture was stirred at rt overnight and then filtered and concentrated. The crude product was purified by flash column chromatography (silica gel) or preparative TLC.

References

[69] Auzias, M. G.; Neuburger, M.; Wegner, H. A., Synlett, (2010), 2443.

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