Recent Advances in the Application of Selectfluor\textsuperscript{TM} F-TEDA-BF\textsubscript{4} as a Versatile Mediator or Catalyst in Organic Synthesis

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Abstract: Selectfluor\textsuperscript{TM} F-TEDA-BF\textsubscript{4} (1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) is not only one of the most efficient and popular reagents for electrophilic fluorination, but as a strong oxidant is also a convenient mediator or catalyst of several “fluorine-free” functionalizations of organic compounds. Its applications as a mediator in transformations of oxidizable functional groups or gold-catalyzed C-C and C-heteroatom oxidative coupling reactions, a catalyst in formation of various heterocyclic rings, a reagent or catalyst of various functionalizations of electron-rich organic compounds (iodination, bromination, chlorination, nitration, thiocyanation, sulfonylation, alkylation, alkoxylation), a catalyst of one-pot-multi-component coupling reactions, a catalyst of regioselective ring opening of epoxides, a deprotection reagent for various protecting groups, and a mediator for stereoselective rearrangement processes of bicyclic compounds are reviewed and discussed.

Keywords: Selectfluor\textsuperscript{TM} F-TEDA-BF\textsubscript{4}; oxidative transformations; coupling reactions; halogenation

1. Introduction

Selective fluorofunctionalisation of organic compounds under mild reaction conditions following an electrophilic reaction process is one of the most important strategic approaches in the organic synthesis of fluoro-substituted organic derivatives, chemicals of wide interest to the basic and applied research
community [1-3]. The group of agents enabling this type of functionalisation are known as “electrophilic fluorinating reagents”, and besides molecular fluorine, include three main groups of reagents; xenon fluorides, fluoroxy compounds and N-F compounds. Organic compounds bearing a reactive N-F bond were introduced as mild reagents for selective introduction of a fluorine atom into organic compounds less than 25 years ago by the efforts of Umemoto’s group, leading to the first isolatable N-fluoroypyridinium salts, their application for fluorofunctionalization of organic compounds, and soon after, also to their commercial production [4,5]. These easily-handled “bench-top” chemicals, usually with optimal stability/reactivity characteristics, have practically revolutionized the common perception of synthesis of site-selective fluoro-substituted organic compounds, and brought this important task in organic synthesis to the status of an ordinary experimental procedure suitable for any organic chemistry laboratory [3,6-8]. The main N-fluoro reagents families are neutral N-fluoro amines or amides, N-fluoroypyridinium salts and quaternary N-fluoro salts, and the most often used members of the last group are the N-fluoro derivatives of 1,4-diazeniabicyclo[2.2.2]octane (triethylendiamine; TEDA), among which 1-chloromethyl-4-fluoro-1,4-diazeniabicyclo[2.2.2]octane bis(tetrafluoroborate) (1, Figure 1) known under the trade name of Selectfluor™ F-TEDA-BF₄ is the most representative and widely used in this series.

**Figure 1.** 1-Chloromethyl-4-fluoro-1,4-diazeniabicyclo[2.2.2]octane bis(tetrafluoroborate)

*Selectfluor F-TEDA-BF₄.*

Since its discovery [9] and academic introduction [10] twenty years ago, Selectfluor™ F-TEDA-BF₄ quickly became one of the most popular reagents for electrophilic fluorination of organic compounds [11-14], not only as an ordinary reagent at the laboratory level, but also as multi-ton scale material produced for several industrial applications [15]. Its thermal stability (up to 195 °C), moderate to high solubility and stability in polar solvents (water, acetonitrile, DMF, methanol, nitromethane, THF) [16], and low toxicity [13,15] are characteristics giving F-TEDA-BF₄ its utility, while its half-wave potential against SCE as high as 0.33 V [17] makes it one of the most powerful oxidants in the N-F compounds series [18] and therefore a convenient moderator of many “other-than-fluorine” functionalizations of organic compounds. The literature data dealing with Selectfluor™ F-TEDA-BF₄ as a fluorinating reagent have been comprehensively surveyed during last 15 years [1,6-8,11-14], while its role in other transformations has been reviewed separately [19]; newer literature and recent advances on this topics are the subject of the present account.
2. Functionalizations of Organic Compounds with Selectfluor F-TEDA-BF$_4$ Other than Fluorine

2.1. Transformations of Oxidizable Functional Groups

In the presence of chemicals having oxidizing power the hydroxyl functional group could often be transformed to various kinds of carbonyl functionality. Primary benzylic alcohols were found to be relatively stable towards 1 since their transformations with 1 in acetonitrile media to moderate amounts of corresponding aldehydes, and further to benzoic acid derivatives, needs long reaction times (15-435 hours) and reflux temperature. It was also established that aromatic aldehydes could be transformed with 1 to benzamides or benzoates after reaction in the presence of amines or alcohols, but again the long reaction time (40-70 hours) required for these functionalisations makes them less attractive [20]. On the other hand, catalytic amounts of molecular iodine enhance the reaction and its efficiency considerably. Benzyl alcohol (2a) and 4-methoxybenzyl alcohol (2b) were thus readily transformed to their aldehydes and further to benzoic acid derivatives (3 and 4) after 2 hours treatment with 1 in MeCN solution in the presence of 5 mol% of I$_2$ under an air atmosphere (Scheme 1), while in the case of the treatment of 2b in aqueous media and in the presence of 55 mol% of iodine, the benzylic hydroxyl group remained unattached and iodo-functionalization of the aromatic ring to 5 took place [21]. Alkyl alcohols could also be readily transformed by 1 to their carbonyl derivatives [22].

![Scheme 1. Reactions of benzylic alcohols with Selectfluor F-TEDA-BF$_2$ 1.](image)

Reactions of phenols with 1 were intensively studied. Phenols substituted by an additional hydroxy substituent at the ortho or para position were readily oxidized to the corresponding quinones when treated by 1 in MeCN [22], while the course of reaction of 2,4,6-trialkyl substituted phenols with 1 was found to be strongly dependent on the structure of the target compounds 6 and the reaction media used (Scheme 2). Reactions in pure MeCN gave fluorinated products, while in the presence of alcohols or water para-quinols or para-quinol ethers 7 were formed in moderate to high yield. The presence of a more acidic nucleophile, such as trifluoroacetic acid (TFA), caused quite different transformations and Ritter-type functionalisation at the 4-benzylic position resulted in the formation of 4-methylacetamido-2,6-dialky substituted phenol derivatives 8, while after ipso attack at position 2, followed by dealkylation and internal cyclisation, alkyl substituted benzoazole derivatives 9 were formed [23,24]. Another oxidative transformation of oxygen containing functional moieties with 1 was found to be the
ring opening of 2,5-diaryl substituted furans 10, resulting in the stereoselective formation of cis-1,2-dibenzoyldione derivatives 11 [25].

Scheme 2. Transformations of 2,4,6-trialkyl substituted phenols and 2,5-diarylfurans with Selectfluor F-TEDA-BF₂ 1.

Sulfur-containing functional groups are usually very sensitive to oxidation. The mild oxidative nature of 1 was efficiently used advantageous in glycoside chemistry in the case of the development of a selective and efficient method for the oxidation of thioglycosides to their corresponding sulfoxide derivatives. A variety of thioglycosides (12, Scheme 3) were thus readily transformed to their sulfinyl derivatives 13 by treatment with a moderate molar excess of 1 in aqueous MeCN (MeCN/H₂O = 20/1) at room temperature for a few minutes [26]. The thiophenolic functionality was found to be more unstable towards 1 than its phenolic analogues and could be readily transformed to disulfides and further to sulfonates [22], and this path was accepted as a methodology for concise synthesis of thiosulfonates. Symmetric aromatic or benzylic disulfides 17 were thus efficiently transformed to thiosulfonates 18 with a 2.5 fold molar excess of 1 in aqueous MeCN [27], while alkyl phenyl sulfides under these reaction conditions with an equimolar amounts of 1 gave selectively the sulfoxide functionality [28].
An amino functional group bonded to an aromatic ring usually cannot survive the presence of 1 and demands protection by acetylation, while primary, secondary or tertiary aliphatic amines can be transformed by 1 to N-fluoro-substituted derivatives, often selectively and in moderate to good yield [14]. On the other hand, amides are relatively stable towards oxidation to imides, and up to now only a few efficient methods for direct preparation of these valuable chemicals are known, but recently the combination of the copper(I) moiety and Selectfluor F-TEDA-BF₄ was introduced as an efficient and selective reagent system for the oxidation of amides to imides [29]. A variety of amides 19 were thus efficiently transformed to their imide derivatives 20 using the combination of 1 (2.5 equiv)/CuBr (1.2 equiv) in MeCN at room temperature (Table 1).

**Table 1.** Oxidation of amides 19 to imides 20 using Selectfluor F-TEDA-BF₄/CuBr tandem. a

| Entry | R     | R¹     | Yield (%) |
|-------|-------|--------|-----------|
| 1     | Ph    | CH₂CH(Me)₂ | 88        |
| 2     | Ph    | Et     | 77        |
| 3     | Ph    | C₂H₄COOMe | 82        |
| 4     | Ph    | Ph     | 84        |
| 5     | Ph    | (CH₂)₃OCOPh | 84        |
| 6     | 4-F-Ph | Et    | 80        |
| 7     | 4-F-Ph | c-C₆H₁₁ | 50        |
| 8     | Me    | Ph     | 83        |
| 9     | n-C₆H₁₃ | CH₂CH(Me)₂ | 79        |

a Reaction conditions: amide 19 (0.25 mmol), Selectfluor F-TEDA-BF₄ (0.625 mmol), CuBr (0.3 mmol added in six portions over 40 min), MeCN (5 mL), r.t., 1 hour.
Hypervalent iodine(III) compounds are valuable and versatile reagents in organic synthesis. It has been demonstrated that various types of aryl hypervalent iodine(III) compounds could be efficiently prepared using Selectfluor F-TEDA-BF₄ starting from the corresponding aryl iodides (21, Scheme 4), or even straightforwardly from arenes 25 following 1 mediated oxidative iodination and further in situ functionalization of aryl iodides. Using one or other approach, a variety of phenyliodine(III)diacetates 22, 26 or phenyliodine(III)ditrifluoromethylacetates 24 were prepared with a 2.6 fold molar excess of 1 in MeCN solution in the presence of acetic or trifluoromethyl acetic acid, while in the presence of TsOH.H₂O, Koser’s reagents 23 were synthesized [30]. The same methodology was applied for the synthesis of chiral hypervalent iodine(III) reagents 28 [31] and 30 [32], and further used for various enantioslective transformations.

Scheme 4. Synthesis of hypervalent iodine(III) compounds using Selectfluor F-TEDA-BF₄.

2.2. Oxidative Halogenation

Halogenation of organic compounds using the oxidative approach mediated by Selectfluor F-TEDA-BF₄ has been introduced in our laboratory [33] and the methodology originally applied for the regioselective iodination of aromatic ethers using molecular iodine. Regioselective iodination at the
Para position took place, while when this position was occupied, regioselective ortho iodofunctionalization took place. Acetonitrile was found to be the best medium for these transformations and 50 mol% of molecular iodine was found to be enough for complete transformation of starting the material. This methodology has been intensively used for efficient and selective iodination of alkyl-substituted benzene derivatives [34], also those sterically hindered [35], as well for iodofunctionalization of arenes in ionic liquids as the reaction media [36].

We have also demonstrated that the regioselectivity of iodination could be regulated by the solvent used. In the case of iodination of substituted aryl-alkyl ketones regioselective functionalization of the aromatic ring took place (32, Scheme 5) when the reactions were performed in MeCN, while regioselective iodination of the side chain (eg. 33) has been found in reactions performed in MeOH [37]. It has been established that the stoichiometry of the process for substrate/I$_2$/F-TEDA-BF$_4$ is 1/0.5/0.6. This MeOH directed and F-TEDA-BF$_4$ mediated iodination methodology was applied for side chain iodination of a variety of acetyl substituted aromatic compounds [38], and indane and tetralone derivatives [39] bearing a strongly activated aromatic ring; these achievements have been reviewed in our previous account [19]. 1-(4-Methoxyphenyl)propan-2-one (34) was further chosen as a model substrate; in MeCN ring iodination forming 35 was established, in MeOH exclusive side-chain methoxy functionalization at the benzylic position took place (36), while in water regioselectivity was lost and a mixture of ring and side-chain functionalized products were observed in the crude reaction mixture [21]. Recently application of the method was successfully demonstrated for the synthesis of euplectin, where by varying the substituents on the euplectin precursor 37, the regioselectivity of the F-TEDA-BF$_4$ mediated iodination could be directed towards aryl ring iodofunctionalization resulting in 38, or to the $\alpha$-to carbonyl position resulting in 39 [40], and for side chain iodination of the protected 2,4-dihydroxy acetophenone derivative 40 to 41, one of precursors in total synthesis of glyceollin I [41].

Selectfluor F-TEDA-BF$_4$ mediated iodination of dimethoxybenzenes (42, Table 2) was studied and the role of reaction media and the relative ratio of reactants on the course of the transformation evaluated. In the case of 1,2- (42a) and 1,4-dimethoxybenzene (42c) equimolar amounts of all three reactants (B) were found to be necessary for high conversion of starting material (entries 1-3 and 8,9 in Table 2), while for the iodofunctionalization of 1,3-dimethoxybenzene 42b to 43b a 0.5 molar amount of iodine and 0.6 molar amount of F-TEDA-BF$_4$ (A) was enough for high yield iodination in all three solvents (entries 4-6). This result was explained by the different nature of the reaction path and a predominantly ionic process was proposed for case A, where iodine has the role of activator of the system and F-TEDA-BF$_4$ the role of activator and regenerator of iodide liberated during the iodination process, while in the case of B, a reaction course through single electron transfer was proposed [21].

Bromination and chlorination of various unsaturated organic compounds mediated by F-TEDA-BF$_4$ have also been demonstrated. Electrophilic bromination or chlorination of benzene derivatives was reported at room temperature using the anionic precursors of bromide or chloride transformed in situ into their electrophilic species by 1 [42]. Acetonitrile was found to be the best choice for the reaction medium, while reactions did not proceed in MeOH. A number of olefins were oxidative brominated using the F-TEDA-BF$_4$/KBr tandem and for different types of substrates, addition, monobromine-substituted, or Hunsdiecker-Borodin reaction products were readily obtained [43].
Scheme 5. Oxidative iodination of organic compounds mediated by Selectfluor F-TEDA-BF₄. The original idea and recent applications.

Table 2. Iodination of dimethoxy benzenes with elemental iodine mediated by F-TEDA-BF₄.
Table 2. Cont.

| Entry | Substrate | Solvent | T/t (°C/h) | Reactants ratio a | Product | Yield (%) b |
|-------|-----------|---------|------------|-------------------|---------|-------------|
| 1     | 42a       | MeCN    | 20/4       | B                 | 43a     | 100(46)     |
| 2     | MeOH      | 20/18   | B          | 43a               | 100(96) |
| 3     | H2O       | 20/22   | B          | 43a               | 32(5)   |
| 4     | 42b       | MeOH    | 20/3       | A                 | 43b     | 100(71)     |
| 5     | H2O       | 20/3    | A          | 43b               | 88(68)  |
| 6     | MeCN      | B       | 0          |                   | 0       |
| 7     | 42c       | MeOH    | B          | 43c               | 60(38)  |
| 8     | H2O       | B       | 93(17)     |                   |         |

a Ratio of 42 / I2 / 1 : A = 1 / 0.5 / 0.6; B = 1 / 1 / 1; b The first value is the conversion of starting material, the values in parentheses are the yield of isolated 43.

2.3. Electrophilic Functionalization of Arenes Using Anionic Precursors other than Halogens

It was demonstrated that various anionic precursors could be oxidized by I to active electrophilic species which efficiently functionalized the benzene ring. As already mentioned, bromide and chloride anions are readily oxidized to their electrophile equivalents and the same was established for thiocyanate (CNS−) and nitrite (NO2−) anions, which were transformed by I into CNS+ and NO2+ species, respectively, and efficiently functionalized electron-rich benzene derivatives [42]. Anions such as ACO− or TfO− were found to be relatively resistant towards oxidation with I, while cyanide, cyanate, methoxide or thiomethoxide anions could not be oxidized with I at all.

2.4. Functionalisation at a Benzylic Carbon Atom

In the transformations described in sections 2.2 and 2.3 F-TEDA-BF4 acts as an oxidant forming electrophilic species from various unreactive sources which afterwards collapse with the electron-rich part of the organic substrates. In this section the opposite situation is described and a variety of examples reviewed where I acted as oxidant for the chosen substrates, thus forming an electron deficient reactive intermediate which reacted with an external nucleophile.

An example of this kind is the versatile derivatisation of a benzylic carbon atom in hexamethylbenzene (HMB, 44). Table 3 summarizes reactions of HMB with F-TEDA-BF4 in the presence of alcohols or potassium salts of perfluoroalkanoic acids in MeCN media. Pentamethylbenzylalkyl ethers (entries 1-9) or esters (entries 10-15) were readily obtained in high to excellent yields. When this reaction was performed in TFA in the presence of various nitriles, Ritter-type benzylic amidation took place and the corresponding pentamethylbenzyl amides (46, Table 4) were formed in high yield [44].

Using appropriate reaction conditions, selective functionalisation of HMB can be obtained in the presence of compounds bearing two different nucleophilic active sites. Reaction in MeCN in the presence of 2-cyanoethanol gave the benzylic ether derivative (47, Scheme 6), while in TFA Ritter transformation took place and benzyl amide derivative 48 was formed.
Table 3. Reactions of hexamethyl benzene 44 with F-TEDA-BF$_4$ 1 in the presence of alcohols or potassium salts of carboxylic acids.$^a$

| Entry | R   | Y   | R$^1$ | Yield (%) | Reference |
|-------|-----|-----|-------|-----------|-----------|
| 1     | H   | O   | i-Pr  | 88        | [44]      |
| 2     | H   | O   | n-hexyl | 90       | [44]      |
| 3     | H   | O   | c-pentyl | 98       | [44]      |
| 4     | H   | O   | Bn    | 75        | [44]      |
| 5     | H   | O   | MeOCH$_2$CH$_2$ | 93       | [44]      |
| 6     | H   | O   | CF$_3$CH$_2$ | 75       | [44]      |
| 7     | H   | O   | CF$_3$CF$_2$CH$_2$ | 70       | [45]      |
| 8     | H   | O   | CF$_3$(CF$_2$)$_2$CH$_2$ | 70       | [45]      |
| 9     | H   | O   | (CF$_3$)$_2$CH | 71       | [45]      |
| 10    | H   | OCO | Me$^b$ | 97        | [44]      |
| 11    | H   | OCO | CF$_3$ | 97        | [45]      |
| 12    | K   | OCO | CF$_3$CF$_2$ | 97       | [45]      |
| 13    | K   | OCO | CF$_3$CF$_2$CF$_2$ | 72       | [45]      |
| 14    | K   | OCO | CF$_3$(CF$_2$)$_2$CF$_2$ | 96       | [45]      |
| 15    | K   | OCO | CF$_3$(CF$_2$)$_2$CF$_2$ | 90       | [45]      |

$^a$ Reaction conditions: HMB (2 mmol), F-TEDA-BF$_4$ (2.2 mmols), 25 mmol of R$^1$OH or 2.4 mmol of KOCOR$^1$, MeCN (20 mL), 55 °C, 1-2 hours. $^b$ Reactions were performed in AcOH or TFA, respectively, as solvent.

Table 4. Ritter-type functionalization of the benzylic position in hexamethylbenzene mediated by F-TEDA-BF$_4$ [44].$^a$

| Entry | R          | Time (h) | Yield |
|-------|------------|----------|-------|
| 1     | Et         | 2        | 82    |
| 2     | n-pentyl   | 3        | 65    |
| 3     | i-Pr       | 2        | 75    |
| 4     | c-Pr       | 1        | 86    |
| 5     | MeOCH$_2$  | 1        | 95    |
| 6     | MeOCOCH$_2$| 1        | 98    |
| 7     | EtOCOCH$_2$| 1        | 84    |
| 8     | Ph         | 1        | 75    |
| 9     | p-COOMe-Ph | 1        | 71    |
| 10    | Bn         | 1        | 90    |
| 11    | C$_6$F$_5$ | 1        | 81    |

$^a$ Reaction conditions: HMB (5 mmol), RCN (15 mmol), F-TEDA-BF$_4$ (5 mmol) TFA (50 mL), 55 °C.
Similarly, cyanoacetic acid as a source of an external nucleophile was activated at its cyanide moiety if TFA was used as solvent and the corresponding benzyl amide 49 was formed, while in MeCN, potassium cyanoacetate acted as a carboxy nucleophile and pentamethylbenzyl cyanoacetate 50 was formed [44].

Scheme 6. F-TEDA-BF$_4$ mediated benzylic functionalisation of hexamethyl benzene in the presence of compounds bearing two different nucleophilic centres.

A quite different course of reaction of HMB with 1 was established in the case when water was used as the external nucleophile. In aqueous MeCN phenyl ring transformation took place, starting with ipso attack of water and further rearrangement of the methyl group as the main process. Primarily formed rearranged 2,3,4,5,6,6-hexamethylcyclohexa-2,4-dienone (52, Scheme 7) was further transformed to 5-hydroxy-2,3,5,6,6-pentamethyl-4-methylene cyclohex-2-en-1-one 53 or 5-fluoro-2,3,5,6,6-pentamethyl-4-methylene cyclohex-2-en-1-one 54; the relative yield of these final products was found to be dependent on the concentration of water in the reaction mixture (Scheme 7). Product 52 was independently obtained in excellent yield by treating hexamethyl Dewar benzene 51 with an aqueous MeCN solution of 1. In the presence of water and alcohol as the second external nucleophile, competition between ring and benzylic functionalisation was observed. In the case of MeOH or EtOH up to 40% of benzylic functionalisation took place thus forming benzyl alkyl ethers, while in the presence of trifluoroethanol or hexafluoro i-propanol product 54 was selectively formed in excellent yield [46].

The reaction of 1,2,4,5-tetramethyl benzene (55, Table 5) with 1 was also studied and the role of solvent and external nucleophile on the course of the transformation established. In MeOH benzylic functionalisation forming benzyl methyl ether derivative 57a (entry 1, Table 5) was the exclusive process, in acetic acid ring attack of the nucleophile forming 2,3,5,6-tetramethylphenyl acetate (58a, entry 2) was found to be predominant process, while in TFA exclusive ring esterification thus forming 2,3,5,6-tetramethylphenyl trifluoroacetate 58b (entry 3) was observed. In reactions performed in MeCN, the nature of the external nucleophile regulated the course of reaction. In the presence of TFA (entry 4) Ritter-type benzylic functionalization to $N$-(2,4,5-trimethylbenzyl)acetamide 56 took place exclusively, in the presence of acetic acid benzylic amidation, benzylic and ring acetoxylation competed, while in the presence of water (entry 6) ipso attack of water followed by methyl group rearrangement and further fluorination or fluoro amidation forming equal amounts of products 59 and
60 was observed [46]. Other isomeric tetra- and trimethyl benzene derivatives were also tested in the presence of 1 and an external nucleophile; the kinetics of the reactions of polymethyl-substituted benzene derivatives with 1 studied and the results obtained supported the assumption that single electron transfer (SET) is the dominant process in these transformations [46].

**Scheme 7.** Transformation of hexamethyl benzene with F-TEDA-BF₄ in the presence of water.

![Scheme 7](image)

**Table 5.** Effect of solvent and external nucleophile on the transformation of 1,2,4,5-tetramethyl benzene with F-TEDA-BF₄.⁴

| Entry | Solvent/nucleophile | 56 | 57 | 58 | 59 | 60 | Yield (%) ⁵ |
|-------|---------------------|----|----|----|----|----|-------------|
| 1     | MeOH / -            |    | 100|    |    |    | 93          |
| 2     | AcOH / -            |    | 29 | 71 |    |    | 85          |
| 3     | TFA / -             |    |    | 100|    |    | 95          |
| 4     | MeCN / TFA c        | 100|    |    |    |    | 82          |
| 5     | MeCN / AcOH         | 27 | 21 | 52 |    |    | 80          |
| 6     | MeCN / H₂O d        |    |    |    | 50 | 50 | 95          |

⁴ Reaction conditions: 1,2,4,5-tetramethyl benzene (1 mmol), F-TEDA-BF₄ (1 mmol), 10 mL of solvent and 10 mmol of nucleophile, 60–120 °C, 1.5–18 hours; ⁵ Total yield of products calculated on starting material; 10 mL of MeCN/TFA = 9/1; ⁶ 2 mmols of 1 was necessary for total conversion of 55.
2.5. Lewis Acid-Type Mediation of Condensation Reactions and Ring Opening of Epoxides

Selectfluor F-TEDA-BF₄ can act as a Lewis acid and this fact was used to advantage in a variety of condensation reactions. Reactions of aryl or alkyl aldehydes (61, Scheme 8) with allylbutylin mediated 62 by 1 in MeCN resulted in the formation of homoallylic alcohols 63, and the analogous reactions in the presence of amines 64 lead to homoallylic amines 65 in good yields with excellent moisture and air tolerance [47].

Scheme 8. Synthesis of homoallylic alcohols or amines and β-acetamido ketones mediated by F-TEDA-BF₄.

An efficient, room temperature process for the stereoselective synthesis of β-amido ketones (68, Scheme 8) employing a one-pot multi-component reaction of benzaldehyde derivatives 66, alkyl phenyl ketone 67, an acid chloride, and a nitrile in the presence of catalytic amounts of F-TEDA-BF₄ was reported [48]. The method offers advantages such as high yield, short reaction time and energy efficiency, high anti-stereoselectivity and a simple work-up protocol.

A synthetic protocol for the preparation of aryl-14H-dibenzo[a,j]xanthene derivatives (71, Scheme 9) through the F-TEDA-BF₄ catalyzed one-pot condensation of substituted benzaldehydes 69 with 2-naphthole 70 under solvent-free conditions was devised and methodology efficiently demonstrated by 14 examples [49]. An efficient procedure for the synthesis of 1,8-dioxo-octahydro-xanthenes 74 through one-pot condensation of 5,5-dimethyl-1,3-cyclohexadione 73 with aryl aldehyde derivatives 72 in the presence of catalytic amounts of 1 was developed and efficiently demonstrated with 19 examples [50]. One-pot condensation of β-ketoesters 76 and substituted phenols 75 catalyzed by 1 resulted in the efficient formation of 2H-chromen-2-one derivatives 77 [51]. Reactions were performed under solvent-free conditions and application of ultrasonic irradiation improved the yields and reduced the reaction times [52].
Scheme 9. F-TEDA-BF$_4$ catalyzed condensation reactions forming oxygen heterocycles.

It was also found that F-TEDA-BF$_4$ efficiently catalyzed the conjugate addition of indoles (78, Scheme 10) with $\alpha,\beta$-unsaturated ketones 79 thus forming Michael adducts 80 under extremely mild reaction conditions and the methodology was confirmed with 14 examples [53]. The same approach was used in the case of reactions of indoles 78 with different aldehydes 81, resulting in the formation of bis(indolyl)methane derivatives 82 and the efficiency of the reaction was improved by MW irradiation under solvent-free conditions [54]. The Biginelli reaction, i.e., one-pot multi-component condensation of aldehyde 83, $\beta$-ketoester 84 and urea or thiourea 85 forming dihydropyrimidinones 86, was considerably improved when 1 was used as the catalyst [55]. Aryl imines formed in situ from aryl aldehydes 87 and aromatic amines 88 underwent smooth [4+2] cycloaddition reactions with cyclic enol ethers 89 such as 3,4-dihydro-2H-pyran or 2,3-dihydrofuran in the presence of 10 mol % 1 in MeCN at room temperature to afford pyrano- and furanotetrahydroquinoline derivatives 90 with high endo-stereoselectivity and high yield [56].

A variety of epoxides (91, 93, Scheme 11) could be efficiently opened regio and stereoselectively with ammonium thiocyanate in the presence of 10 mol% of F-TEDA-BF$_4$ in MeCN at room temperature, affording the corresponding $\beta$-hydroxy thiocyanates 92, in the case of cyclic epoxides with trans stereochemistry 94 [57].

2.6. Deprotection of Functional Groups

An efficient method for cleavage of $p$-methoxybenzylidene (PMP), tetrahydropyranyl (THP) and 1,3 dithiane protecting groups with F-TEDA-BF$_4$ was reported. PMP and THP are very useful protecting groups for diols, but their deprotection usually demands strong acidic or oxidative conditions, and 1,3-dithiane deprotection usually requires harsh conditions, too, which is inconvenient
in the case of multifunctionally derivatized target molecules. It has been shown that 1 can smoothly and efficiently cleave PMP (95, Scheme 12), THP 97 or 1,3-dithiane protected compounds under mild reaction conditions [58].

Scheme 10. F-TEDA-BF₄ catalyzed condensation reactions forming nitrogen heterocycles.

Scheme 11. Regio and stereoselective ring opening of epoxides catalysed by F-TEDA-BF₄.
Scheme 12. Cleavage of PMP, THP, and 1,3-dithiane protecting groups by F-TEDA-BF₄.

A novel microwave-assisted, chemoselective and efficient method for the cleavage of aliphatic and aromatic silyl ethers catalyzed by F-TEDA-BF₄ was reported. A wide range of aliphatic and aromatic tert-butyldimethyl (TBS) protected silyl ethers (100, Scheme 13) were chemoselectively cleaved. In MeCN, MeNO₂ or DMF alkyl silyl ether was deprotected (101), while in MeOH phenolic silyl ether was cleaved (102). In addition, the transetherification of benzylic TBS-protected ethers 103 and etherification of benzyl alcohols 105 in alcoholic solvents resulting in the formation of 104 or 106 was observed [59].

Scheme 13. Chemoselective microwave-assisted deprotection of alkyl and aryl silyl ethers, transetherification and etherification of benzylic hydroxyl groups catalyzed by F-TEDA-BF₄.
2.7. Transformations of Halogen-Substituted Azabicyclic Compounds

Stereoselective synthesis of 5,6-functionalized-2-azabicyclo[2.1.1]hexanes containing 5-anti-fluoro or hydroxyl in one methano bridge have been prepared by the F-TEDA-BF$_4$ mediated rearrangement of derivatives of N-alkoxycarbonyl-6-exo-iodo-2-azabicyclo[2.2.0]hexanes [60]. It was also found that 1 has the ability to act as a nucleofuge for hydrolysis of β-anti-halides in N-alkoxycarbonyl derivatives of 6-anti-Y-7-anti-X-2-azabicyclo[2.2.1]heptanes (107, Table 6) and 4-anti-Y-8-anti-X-6-azabicyclo[3.2.1]octanes (109, Table 7), thus forming hydroxyl substituted derivatives 108 or hydroxyl or oxo-substituted products 110, respectively [61].

Table 6. Hydrolysis of β-halo-N-alkoxycarbonyl-2-azabicyclo[2.2.1]heptanes with F-TEDA-BF$_4$.

| Entry | X  | Y  | W  | Z  | Yield (%) |
|-------|----|----|----|----|-----------|
| 1     | Br | Br | Br | OH | 60        |
| 2     | I  | Cl | I  | OH | 35        |
| 3     | I  | OH | OH | OH | 80        |
| 4     | I  | F  | OH | F  | 86        |

Table 7. F-TEDA-BF$_4$ as a nucleofuge and oxidant of β-halo-N-Aloxycarbonyl-2-azabicyclo[3.2.1]octanes.

| Entry | X  | Y  | W  | Z  | Yield (%) |
|-------|----|----|----|----|-----------|
| 1     | Br | Br | Br | =O | 91        |
| 2     | Br | OH | Br | =O | 99        |
| 3     | I  | Cl | I  | OH | 77        |
| 4     | I  | OH | I  | =O | 20        |

2.8. Functionalization of N-Heterocycles

The direct thiolation of indoles (111, Table 8) with a variety of thiols 112 has been achieved in the presence of F-TEDA-BF$_4$. This versatile and efficient method works for thiolation of 5- or 7-substituted indoles, as well as for 1-substituted (entries 6 and 9) and 2-substituted (entries 5, 12, and 13) indole derivatives with aromatic thiols (entries 1–17), alkyl thiols (entries 18 and 19) and benzyl thiol (entry 20). The reaction protocol is simple; the transformation goes to completion at room temperature within 20–30 minutes, efficiently and selectively forming 3-sulfenylindoles 113 [62].
Table 8. F-TEDA-BF₄ mediated synthesis of 3-sulfenylindoles.

\[
\begin{align*}
\text{R} & \quad \text{R}^1 & \quad \text{R}^2 & \quad \text{R}^3 & \quad \text{Yield} \, [%] \\
1 & \text{H} & \text{H} & \text{H} & \text{Ph} & 96 \\
2 & \text{5-Br} & \text{H} & \text{H} & \text{Ph} & 85 \\
3 & \text{5-OMe} & \text{H} & \text{H} & \text{Ph} & 96 \\
4 & \text{7-Et} & \text{H} & \text{H} & \text{Ph} & 89 \\
5 & \text{H} & \text{H} & \text{Me} & \text{Ph} & 89 \\
6 & \text{H} & \text{Bn} & \text{H} & \text{Ph} & 87 \\
7 & \text{H} & \text{H} & \text{H} & \text{4-Cl-Ph} & 92 \\
8 & \text{5-OMe} & \text{H} & \text{H} & \text{4-Cl-Ph} & 97 \\
9 & \text{H} & \text{Bn} & \text{H} & \text{4-Cl-Ph} & 93 \\
10 & \text{7-Et} & \text{H} & \text{H} & \text{4-Cl-Ph} & 90 \\
11 & \text{7-Et} & \text{H} & \text{H} & \text{4-Me-Ph} & 89 \\
12 & \text{H} & \text{H} & \text{Me} & \text{4-Cl-Ph} & 94 \\
13 & \text{H} & \text{H} & \text{H} & \text{4-Cl-Ph} & 94 \\
14 & \text{5-Br} & \text{H} & \text{H} & \text{4-Me-Ph} & 90 \\
15 & \text{H} & \text{H} & \text{H} & \text{4-NO₂-Ph} & 78 \\
16 & \text{H} & \text{H} & \text{H} & \text{4-Br-Ph} & 87 \\
17 & \text{H} & \text{H} & \text{H} & \text{2-naphthyl} & 85 \\
18 & \text{H} & \text{H} & \text{H} & \text{Et} & 87 \\
19 & \text{5-Br} & \text{H} & \text{H} & \text{n-Bu} & 78 \\
20 & \text{H} & \text{H} & \text{H} & \text{Bn} & 82 \\
\end{align*}
\]

Various substituted indoles 111 have been efficiently thiocyanated under mild and neutral conditions to selectively produce 3-indoylthiocyanates 114 (Table 9) in excellent yield following the reaction of indole derivatives with ammonium thiocyanate in the presence of F-TEDA-BF₄. Mechanistically, the reaction was declared to be the electrophilic substitution of indole derivatives by in situ generated thiocyanogen electrophilic species from 1 and ammonium thiocyanate. Following the same protocol was also successful for thiocyanation of azaindole, carbazole and pyrrole [63].

The tungsten η²-coordinated pyridinium complex 115 (Scheme 14) undergoes a stereoselective dialkoxylation when treated with F-TEDA-BF₄ in alcohol. The alkoxy groups add to the 5- and 6-positions of TpW(NO)(PMe₃)(3,4-η²-methoxypyridine) 115 in a syn fashion. The reaction pathway has been not completely investigated but apparent stabilization by tungsten of the allyl cation intermediate resulting from the electrophilic attack of 1 to the 5,6-double bond on 115, captured by alkoxy anion and further fluorine atom replacement by the alkoxide in a subsequent substitution reaction resulting in the final formation of 116 seems to be a reasonable explanation of the reaction route [64].
Table 9. Thiocyanation of indole derivatives with ammonium thiocyanate using F-TEDA-BF₄.

| Entry | R     | R¹   | R²   | Yield [%] |
|-------|-------|------|------|-----------|
| 1     | H     | H    | H    | 95        |
| 2     | H     | H    | Me   | 92        |
| 3     | 7-Et  | H    | H    | 94        |
| 4     | 5-NO₂ | H    | H    | 93        |
| 5     | 5-CN  | H    | H    | 92        |
| 6     | 5-Br  | H    | H    | 93        |
| 7     | 5-OMe | H    | H    | 96        |
| 8     | H     | H    | Ph   | 89        |
| 9     | H     | Bn   | H    | 94        |
| 10    | H     | Bn   | Ph   | 86        |

Scheme 14. Dimethoxylation of η²-pyridinium complex mediated by F-TEDA-BF₄.

2.9. Gold-Catalyzed and Palladium-Catalyzed Oxidative C-C or C-Heteroatom Bond Formation

Cross-coupling reactions are powerful tools for the rapid construction of organic molecules and one of the most important and valuable approaches in organic synthesis. Various transition metals catalyze these valuable transformations and gold was introduced for this purpose recently [65]. The gold/Selectfluor F-TEDA-BF₄ tandem was recognized as a valuable combination in numerous cross-coupling C-C or C-heteroatom bond formations.

The pioneer work on this area has been done by Zhang and co-workers with the discovery that under oxidative conditions gold catalyzes the coupling of propargyl acetates (117, Table 10) with boronic acids 118 resulting in the formation of α-aryl α,β-enones 119 in moderate to good yields and total E-stereoselectivity [66]. Following the proposed mechanism, reactions start by gold mediated 3,3-rearrangement of propargyl acetates to allenyl acetates and their hydrolysation into the vinyl-Au(I) species which is subsequently oxidized by F-TEDA-BF₄ to furnish Au(III) intermediates; later these undergo transmetallation with boronic acids to give diorganogold derivatives, which after reductive elimination, regenerate the active Au(I) species and deliver the final cross-coupled products 119.
Without the presence of boronic acid derivatives, oxidative dimerization of propargylic acetates was observed [67].

**Table 10.** Gold-catalyzed oxidative cross-coupling of propargyl acetates with boronic acids.

| Entry | R       | R⁺      | Yield (%) |
|-------|---------|---------|-----------|
| 1     | Ph      | n-butyl | H         | 62        |
| 2     | iPr     | n-butyl | H         | 65        |
| 3     | Me      | Ph      | H         | 59        |
| 4     | Me      | MeOCH₂CH₂ | H      | 60        |
| 5     | Me      | cyclohexyl | H       | 68        |
| 6     | cyclohexyl | cyclohexyl | H       | 70        |
| 7     | PhCH₂CH₂ | n-butyl | H         | 70        |
| 8     | 4-Br-Ph | n-butyl | H         | 59        |
| 9     | AcOCH₂CH₂ | n-butyl | H         | 61        |
| 10    | H       | cyclohexyl | H       | 61        |
| 11    | cyclohexyl | n-butyl | 4-Me-Ph  | 72        |
| 12    | cyclohexyl | n-butyl | 4-CO₂Me-Ph | 57        |
| 13    | cyclohexyl | n-butyl | 4-Cl-Ph  | 58        |
| 14    | cyclohexyl | n-butyl | 3-CO₂Me-Ph | 45        |

Analogous reactions were observed when propargyl benzoates (120, Table 11) were treated under similar reaction conditions and 1-benzoylvVinyl ketones 121 were isolated [68]. Intramolecular cross-coupling resulting in carboamination, carboalkoxylation or carbolactonization processes and formation of N- or O-heterocycles (123, Scheme 15) were reported when alkenes bearing a terminal hydroxyl, tosylamido or carboxy group (122) were treated with the gold cat/F-TEDA-BF₄ tandem in the presence of boronic acid [69]. The scope of this reaction was considerably extended using bimetallic gold complexes as catalysts. The best results were obtained in the case of [dpmp(AuBr)₂] catalyst where bis(diphenylphosphine)methane (dpmp) was the ligand part of the bimetallic Au catalyst and a variety of alkenes and boronic acid reactants cross-coupled forming N-heterocycle derivatives [70].

The same group of authors further reported three-component coupling reactions using this valuable methodology. Various combinations of alkenes (125, Scheme 16), boronic acid derivatives 126, and alcohols, carbocyclic acids or even water (127) were treated with catalytic amounts of dpmp(AuBr)₂ bimetallic complex in the presence of F-TEDA-BF₄ and oxyarylation of the double bond took place resulting in compounds 128. The ability to use either alcohols or water as nucleophiles in this gold-catalyzed three-component coupling provided access to a greater diversity of products. In the case of alkene 129 and 2-carboxymethyl boronic acid 130, methoxyarylation producing 131 took place when methanol was used as nucleophile, while in the presence of water, hydroxyarylation, followed by in situ lactone formation 131 was the result of the reaction [71].
Table 11. Gold-catalyzed synthesis of 1-benzoylvinyl ketones from propargylic benzoxides.

| Entry | R          | Yield (%) |
|-------|------------|-----------|
| 1     | cyclohexyl | 76        |
| 2     | Ph         | 66        |
| 3     | cyclopropyl| 56        |
| 4     | BnOCH₂CH₂  | 71        |
| 5     | BzOCH₂CH₂  | 78        |
| 6     | BzCH₂CH₂CH₂| 70        |

Scheme 15. Gold-catalyzed oxidative carboheterofunctionalization of alkenes.

Scheme 16. Gold-catalyzed F-TEDA-BF₄ mediated oxyarylation of alkenes.
The versatility of this methodology was expanded and arylsilicon compounds were taken as transmetallation components. The best results were obtained with phenyltrimethylsilane (133, Table 12) and efficient three-component coupling was accomplished when alkene 129, various alcohols and 133 were treated with the dpmm(AuBr)₂ / F-TEDA-BF₄ tandem, resulting in oxyarylated products 134. As in the case of boronic acid in the presence of methanol, 2-carboxymethyl-trimethylphenylsilane was methoxyarylated to product 131, while the water mediated reaction yielded lactone product 132. In the case when a side chain bearing terminal alkene functionality is bonded at the ortho position of phenyltrimethylsilane reagent (135, Table 13), intramolecular coupling reaction took place resulting in products 136 [72].

Table 12. Gold-catalyzed and F-TEDA-BF₄ mediated three-component oxyarylation of C-C double bond.

| Entry | R   | R¹  | Yield [%] |
|-------|-----|-----|-----------|
| 1     | 4-OAc| Me  | 83        |
| 2     | 4-OTf| Me  | 53        |
| 3     | 4-N(Me)Ts| Me | 66        |
| 4     | 4-Me | Me  | 73        |
| 5     | 4-Br | Me  | 82        |
| 6     | 4-CHO| Me  | 77        |
| 7     | 4-CO₂Me| Me | 68        |
| 8     | 3-CO₂Me| Me | 83        |
| 9     | 2-CH₂CH₂OH| Me | 69        |
| 10    | H    | Me  | 87        |
| 11    | H    | Et  | 83        |
| 12    | H    | i-Pr| 81        |
| 13    | H    | t-Bu| 37        |
| 14    | H    | neopentyl| 64    |
| 15    | H    | cyclopentyl| 68    |
| 16    | H    | 2-methoxyethyl| 86    |
| 17    | H    | H   | 77        |
| 18    | 2-CH₂CH₂OH| H | 55        |

A comparison of gold-catalyzed oxyarylation of terminal alkenes (137, Table 14) using arylsilanes 138a or arylboronic acids 138b as transmetallating reactants was reported. The results collected in Table 14 demonstrate some advantages of the application of arylboronic acids in these reactions but the differences are not so remarkable. The commercially available gold catalyst Ph₃PAuCl was used, making this valuable and versatile transformation even more attractive [73].
Table 13. Gold-catalyzed and F-TEDA-BF₄ mediated intramolecular coupling reactions.

| Entry | R   | R¹  | n | Yield (%) |
|-------|-----|-----|---|-----------|
| 1     | H   | H   | 1 | 66        |
| 2     | H   | Me  | 1 | 73        |
| 3     | H   | Et  | 1 | 70        |
| 4     | H   | H   | 0 | 15        |
| 5     | F   | H   | 1 | 47        |
| 6     | F   | Et  | 1 | 68        |
| 7     | Cl  | H   | 1 | 62        |
| 8     | Cl  | Me  | 1 | 65        |
| 9     | CF₃ | H   | 1 | 51        |
| 10    | CF₃ | Me  | 1 | 59        |
| 11    | Ph  | Me  | 1 | 74        |

Another valuable application of the Au(catalyst)/F-TEDA-BF₄(oxidant) tandem was reported by Gouverneur and co-authors. They developed a novel cascade cyclization cross-coupling process leading to tricyclic dihydroindeno furane-type compounds (141a-e, 143a-c, and 145, Scheme 17) following the Ph₃PAuNTf₂ catalyzed and F-TEDA-BF₄ mediated transformations of t-butyl ester substituted allenates bearing a benzyl functional group on the opposite side of an allenolate moiety (140), or vicinal to a tert-butyl ester group (142). The substrates 140 readily gave products 141a-e, while starting materials 142 gave products 143 a–b. In the case when both relevant allenolate carbon atoms were substituted by a benzyl group, the formation of product 143c was found to be preferential. It has also been established that the transformation is stereospecific, since pure enantiomer 144 gave only enantiomer 145 [74].

The same group of authors developed efficient cascade cyclization-oxidative alkynylation of allenates (146, Scheme 17) with phenyl acetylenes 147, resulting in the formation of 5-butynyl-3-methyl-4-(phenylethynyl)furan-2(5H)-one derivatives 148. The selectivity as well as the efficiency of the transformation decreased if other than a n-butyl group was bonded to alleonate 146, or an alkyl group bonded to the alkynyl substrate 147 [75].

Various arylgold(I) and alkynylgold(I) triphenylphosphane complexes (149, Table 15) were subjected to electrophilic halogenations reagents. Iodo, bromo and chloro reagents gave halogenated products, while reactions with F-TEDA-BF₄ followed exclusively the homocoupling process and corresponding dimeric products 150 were isolated in high yield [76].
Aminooxygenation of unactivated alkenes (151, Scheme 18) were achieved by gold catalysis assisted by F-TEDA-BF$_4$ as an oxidant. In the case when the solvent was 20/1 mixture of MeCN and water ($R^2 = H$), methanol ($R^2 = Me$), or ethanol ($R^2 = Et$) mixtures of piperidine 152 and pyrrolidine derivatives 153 were formed. The formation of piperidine derivatives prevailed. On the other hand, by reducing the amount of water in the reaction mixture to only 2 equivalents and using nitriles as the reaction media, the aminoamidation process took place and 3-amido substituted piperidine derivatives 154 were selectively formed [77].

Table 14. Gold-catalyzed and F-TEDA-BF$_4$ mediated oxyarylation of terminal alkenes using arylsilanes [73] or arylboronic acids [71].

| Entry | Alkene | $R^1$ | $R^2$ | $Z = SiMe_3$ | $Z = B(OH)_2$ |
|-------|--------|-------|-------|--------------|--------------|
| 1     | 137 a  | H     | Me    | 71           | 79           |
| 2     | 137 a  | H     | Et    | 69           | 85           |
| 3     | 137 a  | H     | i-Pr  | 70           | 90           |
| 4     | 137 a  | H     | t-Bu  | -            | 33           |
| 5     | 137 a  | H     | neopentyl | 80       | 91           |
| 6     | 137 a  | H     | c-pentyl | 57      | 85           |
| 7     | 137 a  | H     | Ac    | 79           | 62           |
| 8     | 137 a  | 4-Me  | Me    | 55           | 88           |
| 9     | 137 a  | 2-Me  | Me    | 20           | -            |
| 10    | 137 a  | 4-Br  | Me    | 80           | 90           |
| 11    | 137 a  | 3-F   | Me    | 63           | 79           |
| 12    | 137 a  | 4-CO$_2$Me | Me     | 80       | 83           |
| 13    | 137 b  | 4-Br  | c-pentyl | 51      | 69           |
| 14    | 137 b  | 4-Br  | Ac    | 51           | 51           |
| 15    | 137 b  | H     | H     | 76           | 76           |
| 16    | 137 c  | 4-Br  | c-pentyl | 38      | 76           |
| 17    | 137 c  | 4-Br  | neopentyl | 85     | 73           |
| 18    | 137 c  | H     | H     | 78           | 73           |
| 19    | 137 d  | H     | H     | 75           | 67           |
Recently the Zhang group reported the first oxidative cross-coupling reaction between an aryl C-H bond and an alkyl gold compound generated in situ, combining Au(I)/Au(III) catalysis with C-H functionalization. They have chosen \(N,N\)-diallyl-\(N'\)-phenylurea derivatives (155d-k, Table 16) as substrates, (4-CF\(_3\)-C\(_6\)H\(_4\))\(_3\)P-Au-NTf\(_2\) as the catalyst, and F-TEDA-BF\(_4\) as the oxidant and following an initial aminoauration and subsequent intramolecular [3+2] annulation process isolated tricyclic indoline derivatives 156 in high yield. The efficiency of the reaction was significantly improved by the addition of 30 equivalents of water in TFH as the optimal reaction media and the transformation was successful in the case when the additional allyl group in 155 was replaced by benzyl (entry 1), alkyl (entry 2) or phenyl group (entry 3). On the basis of performed deuterium labeling and kinetic isotope
effect studies along with the isolation of alkyl gold intermediates the reaction mechanism anticipating an electrophilic aromatic substitution for the C-H functionalization and a subsequent inner-sphere concerted reductive elimination for the C\textsubscript{sp2}-C\textsubscript{sp3} bond formation were strongly supported [78].

Table 15. Homocoupling reactions of organogold(I) triphenylphosphane compounds induced by F-TEDA-BF\textsubscript{4}.

| Entry | R          | Yield (%) |
|-------|------------|-----------|
| 1     | Ph         | 90        |
| 2     | 3-nitrophenyl | 91        |
| 3     | 3-methoxyphenyl | 85       |
| 4     | 4-methoxyphenyl | 94       |
| 5     | 2-formylfuran-5-yl | 82       |
| 6     | 3-formylfuran-5-yl | 81       |
| 7     | phenyletynyl | 94        |
| 8     | i-Pr       | 71        |

Scheme 18. Gold-catalyzed and F-TEDA-BF\textsubscript{4} assisted aminoxygenation or aminomimidation of unactivated alkenes.
Table 16. Gold-catalyzed and F-TEDA-BF₄ mediated C-C coupling through C-H functionalization.

| Entry | 155 | R   | R¹  | Yield [%] of 156 |
|-------|-----|-----|-----|-----------------|
| 1     | a   | H   | Bn  | 75              |
| 2     | b   | H   | n-hexyl | 69              |
| 3     | c   | H   | Ph  | 70              |
| 4     | d   | 4-Me | allyl | 72              |
| 5     | e   | 2-Me | allyl | 43              |
| 6     | f   | 3-Me | allyl | 79              |
| 7     | g   | 4-F  | allyl | 70              |
| 8     | h   | 4-OTs | allyl | 67              |
| 9     | i   | 4-CF₃ | allyl | 64              |
| 10    | j   | 4-COOEt | allyl | 84              |
| 11    | k   | 4-Ac | allyl | 75              |

In the same laboratory a straightforward, efficient, and reliable catalyst system for the Sonogashira cross-coupling reaction of terminal alkyne derivatives (157, Scheme 19) with arylboronic acids 158 was developed very recently. The catalyst consisting Ph₃PAuCl and AgBF₄ gave the best results in the presence of F-TEDA-BF₄ as the oxidant and Et₃N as the base and the scope of the method was illustrated by eleven examples of cross-coupling yielding aryl functionalized alkyne derivatives 159 [79].

Scheme 19. Gold-catalyzed F-TEDA-BF₄ mediated Sonogashira-type cross-coupling reactions of terminal alkynes with arylboronic acids.

Palladium-catalyzed directed ortho amidation of aromatic ketones (160, Scheme 20) with both sulfoanamides 161a and amides 161b has been accomplished using different oxidants, including N-F compounds. The efficiency of the formation of the corresponding sulfonamides 162a or amides 162b was moderate to good when F-TEDA-BF₄ mediated the reactions. It has been proposed and supported by X-ray crystallography that the formation of cyclopalladation complexes of aryl ketones and amides are the key intermediates for this valuable transformation. The palladium(II) complex is oxidized to the Pd(IV) moiety, which following reductive elimination, ends in the final ortho amido derivatized product [79].
3. Conclusions and Perspectives

Selectfluor™ F-TEDA-BF₄ is one of the most popular electrophilic fluorination reagents. Besides this, its major role in organic synthesis, it also acts as a reagent or catalyst of many functionalizations of organic compounds other than fluorinations, where its characteristics as an oxidant or a Lewis acid regulate the versatile utility. As a transformer of oxidizable functional groups F-TEDA-BF₄ could be very efficient but from the green chemical point of view its perspectives, except for specific cases, are limited, as well as in the field of oxidative halogenations, where a variety of greener protocols using environmentally more acceptable oxidants, such as H₂O₂ or oxygen, were developed recently, also in our laboratory. On the other hand, F-TEDA-BF₄ possesses unlimited potential as a catalyst or reagent in various condensations and coupling reactions. Up to now reported discoveries illustrate the really amazing possibilities of the organic molecule skeleton building reactions mediated by F-TEDA-BF₄. It seems that many research groups have already recognized this fact, since a considerable number of recent papers reviewed in the present account are dedicated to this matter.

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