Perfluoroalkylation of Unactivated Alkenes with Acid Anhydrides as the Perfluoroalkyl Source

Shintaro Kawamura and Mikiko Sodeoka


$$\text{(RFCO)}_2\text{O} \quad \text{urea} \cdot \text{H}_2\text{O}_2 \quad \text{Cu, cat. (10 mol%),} \quad \text{CH}_2\text{Cl}_2 \quad \text{CH}_2\text{Cl}_2$$

1b 82% (80:20)
1c-e
1d 71% (82:18)
1e 77% (79:21)
Ar = 4-MeC_6H_4
Ar = 4-FC_6H_4
Ar = 4-MeOC_6H_4

2f 83% (79:21)
2g 49% (81:19)

2h 92% (80:20)
2i 80% (73:27)

2j 93% (71:29)

2k 91% (76:24)

2l 75% (96:4)

2m 48% (NMR yield)

1a 96% (72:28)
1b 80% (72:28)
1c 72% (75:25)

[a] E/Z ratios were determined by $^{19}$F NMR analysis. [b] The reaction was conducted in 0.2 M CH_2Cl_2 at 0°C. [c] 20 mol% of the catalyst was used. [d] Cu(O_2CCF_3)_2 was used instead of [Cu(CH_3CN)_4]PF_6. [e] The crude product was hydrolyzed with Et_3N/SiO_2.
Copper-Mediated Trifluoroacetylation of Arenediazonium Salts with Ethyl Trifluoropyruvate
Wei Wu, Qinli Tian, Taotao Chen, and Zhiqiang Weng

\[
\begin{align*}
\text{R}^+\text{N}_2\text{BF}_4^- + \text{C}_3\text{F}_7\text{O} & \xrightarrow{\text{Cu}_2\text{O} (25 \text{ mol} \%) \text{CH}_2\text{Cl}_2/\text{DMSO} (17:1) \text{RT, 16 h}} \text{R}^+\text{CF}_3
\end{align*}
\]

Perfluoroalkylation of Alkenes by Frustrated Lewis Pairs
Ilona Behrends, Susanne B-hr, and Constantin Czekelius

\[
\begin{align*}
\text{R}_1^+\text{C}_4\text{F}_9 & \xrightarrow{\text{CF}_3(\text{CF}_2)_2\text{CF}_2I, \text{B(C}_6\text{F}_5)_3 (10 \text{ mol} \%) \text{PtBu}_3 (10 \text{ mol} \%) \text{CH}_2\text{Cl}_2, \text{RT}} \text{R}_2^+\text{C}_4\text{F}_9
\end{align*}
\]

Continuous Flow Homolytic Aromatic Substitution with Electrophilic Radicals: A Fast and Scalable Protocol for Trifluoromethylation
Jffilia L. Monteiro, Paula F. Carneiro, Petteri Elsner, Dominique M. Roberge, Peter G. M. Wuts, Katherine C. Kurjan, Bernhard Gutmann, and C. Oliver Kappe

\[
\begin{align*}
a + \text{R-I} + \text{H}_2\text{O}_2 + \text{Me-SO-Me} & \xrightarrow{\text{Fe}^{2+}} \text{R} + \text{Me-I} + \text{H}_2\text{O} + \text{Me-SO-OH}
\end{align*}
\]

b: \( R = \text{CF}_3 \\
c: \( R = \text{C}_4\text{F}_9 \\
d: \( R = \text{CH}_2\text{CN} \\
e: \( R = \text{CH}_2\text{CO}_2\text{Et} \)
Vicinal Difluoroalkylation and Aminosulfonylation of Alkynes Under Photoinduced Conditions
Yuanchao Xiang, Yuewen Li, Yunyan Kuang, and Jie Wu

Journal of the American Chemical Society

PyFluor: A Low-Cost, Stable, and Selective Deoxyfluorination Reagent
Matthew K. Nielsen, Christian R. Ugaz, Wenping Li, and Abigail G. Doyle
J.Am.Chem.Soc., 2015, 137, 9571-9574

F⁻ Nucleophilic Addition Induced Allylic Alkylation
Panpan Tian, Cheng-Qiang Wang, Sai-Hu Cai, Shengjin Song, Lu Ye, Chao Feng, and Teck-Peng Loh
Visible light-promoted activation of unactivated C(sp3)--H bonds and its selective trifluoromethylthiolation
Satobhisha Mukherjee, Biplab Maji, Adrian Tlahuext-Aca, Frank Glorius


\[
\text{Ir-F (1 mol%), PhCO}_2\text{N Bu}_4 (5 mol%), \text{Phth-SCF}_3 (1.5 equiv.)} \\
\text{blue LEDs (5 W), } \lambda_{(\text{max})} = 455 \text{ nm} \\
\text{CH}_3\text{CN (0.2 M), rt.} \\
\text{F}_3\text{CS} \rightarrow \text{96\% single regioisomer}
\]

Nucleophilic Deoxyfluorination of Phenols via Aryl Fluorosulfonate Intermediates
Sydonie D. Schimler, Megan A. Cismesia, Patrick S. Hanley, Robert D. J. Froese, Matthew J. Jansma, Douglas C. Bland, and Melanie S. Sanford


Nucleophilic 1,1-difluoroethylation with fluorinated phosphonium salt
Zuyong Deng, Can Liu, Xian-Liang Zeng, Jin-Hong Lin, and Ji-Chang Xiao

J. Org. Chem., 2016, 81, 12084-12090
Copper-Catalyzed Decarboxylative Difluoroalkylation and Perfluoroalkylation of \( \alpha,\beta \)-Unsaturated Carboxylic Acids
Yin-Long Lai, Dian-Zhao Lin, and Jing-Mei Huang


\[
\text{This work} \quad \text{CuOTf}_2 \cdot \text{toluene (0.05 eq)} + \text{bipy (0.2 eq)} + \text{HPO(OMe)}_2 (2.0 eq), 60^\circ \text{C}
\]

\[
\begin{align*}
\text{COOH} & \quad \text{X-CF}_2\text{-R}^2 \\
\text{R}^1 & = \text{aryl, heterocycle} \\
\text{X} & = \text{Br, I} \\
\text{R}^2 & = \text{COOEt, R}_f
\end{align*}
\]

Visible-Light-Induced Direct Difluoroalkylation of Uracils, Pyridinones, and Coumarins
Chun-Yang He, Jingjing Kong, Xuefei Li, Xiaofei Li, Qiuli Yao, and Fu-Ming Yuan


\[
\begin{align*}
\text{BrCF}_2\text{R} & \quad \text{fac-Ir(ppy)}_3 (0.5 \text{ mol } \%) + \text{K}_2\text{HPO}_4 (2.0 \text{ equiv}) \\
& \quad \text{DMSO, r.t., 24 h, 12 W blue LED}
\end{align*}
\]

\[
\begin{align*}
\text{X} \quad \text{X-CF}_2\text{COOEt} & \quad \text{BrCF}_2\text{R} \\
\text{X} & = \text{NMe, NH, O}
\end{align*}
\]
Organocatalytic Insertion of Isatins into Aryl Difluoronitromethyl Ketones
Ransheng Ding, Pegah R. Bakhshi, and Christian Wolf

*J. Org. Chem.*, 2017, 82, 1273-1280

\[ \text{Ph} \quad \text{F} \quad \text{F} \quad \text{NO}_2 \quad + \quad \text{Bn} \quad \text{N} \quad \text{O} \quad \xrightarrow{\text{Conditions}} \quad \text{Ph} \quad \text{F} \quad \text{F} \quad \text{NO}_2 \quad \xrightarrow{\text{CH}_2\text{Cl}_2, 30 \degree \text{C}} \quad \text{Bn} \quad \text{N} \quad \text{O} \]

**New Journal of Chemistry**

Catalyst Free Synthesis of α-Fluorinated Aroylacyl Imides
Dhanamoorthy Vaithialingam, Duraimurugan Kumaraguru and Siva Ayyanan


\[ \text{R}_1 \quad \text{N} \quad \text{H} \quad \text{C} = \text{O} \quad \xrightarrow{\text{NaF}} \quad \text{R}_1 \quad \text{N} \quad \text{H} \quad \text{C} = \text{O} \quad \text{F} \quad \text{DMSO, 80} \degree \text{C} \]

**Organic Letters**

Cobalt(III)-Catalyzed Regio- and Stereoselective α-Fluoroalkenylation of Arenes with gem-Difluorostyrenes
Lingheng Kong, Xukai Zhou, and Xingwei Li

*Org. Lett.*, 2016, 18, 6320-6323

\[ \text{DG} \quad \text{H} \quad + \quad \text{[CoCp*(MeCN)_3](SbF_6)_2} \quad (5 \text{ mol} \%) \quad 25-70 \degree \text{C} \quad \text{mostly > 80\%} \quad \xrightarrow{25-70 \degree \text{C}} \quad \text{DG}^\prime \quad \text{F} \quad \text{F} \quad \text{Ar} \quad \text{Ar} \] - mild conditions
- redox-neutral
- stereospecific
- functionalizable DGs
- broad scope (43 examples)
C2-Symmetric Chiral Bisoxazolines as Hydrogen-Bond-Acceptor Catalysts in Enantioselective Aldol Reaction of β-Carbonyl Acids with Trifluoroacetaldehyde Hemiacetals

Zhen-Yan Yang, Jun-Liang Zeng, Nan Ren, Wei Meng, Jing Nie, and Jun-An Ma

Org. Lett., 2016, 18, 6364-6367

Perfluoroalkyl Analogues of Diethylaminosulfur Trifluoride: Reagents for Perfluoroalkylthiolation of Active Methylene Compounds under Mild Conditions

Ibrayim Saidalimu, Shugo Suzuki, Takuya Yoshioka, Etsuko Tokunaga, and Norio Shibata

Org. Lett., 2016, 18, 6404-6407

Trichloroisocyanuric Acid Promoted Cascade Cyclization/Trifluoromethylation of Allylic Oximes: Synthesis of Trifluoromethylated Isoxazolines

Weigang Zhang, Yingpeng Su, Ke-Hu Wang, Lili Wu, Bingbing Chang, Ya Shi, Danfeng Huang, and Yulai Hu

Synthesis of Diaziridines and Diazirines via Resin-Bound Sulfonyl Oximes
Irina Protasova, Bekir Bulat, Nicole Jung, and Stefan Bräse

Catalytic Radical Trifluoromethylalkynylation of Unactivated Alkenes
Shaofang Zhou, Tao Song, He Chen, Zhonglin Liu, Haigen Shen, and Chaozhong Li
A highly efficient one-pot trifluoromethylation/cyclization reaction of electron-deficient 1,3-conjugated enynes: modular access to trifluoromethylated furans and 2,3-dihydrofurans
Wei Zhou, Zhenting Yue and Junliang Zhang

Organic Chemistry Frontiers, 2016, 3, 1416-1419

Direct vicinal difunctionalization of alkynes through trifluoromethylation and aminosulfonylation via insertion of sulfur dioxide under catalyst-free conditions
Yuewen Li, Yuanchao Xiang, Zhiming Li and Jie Wu

Organic Chemistry Frontiers, 2016, 3, 1493-1497
Reductive insertion of sulfur dioxide for the synthesis of trifluoromethyl thiolsulphonates through a one-pot reaction of aniline and trifluoromethanesulfanlylamide
Jie Sheng, Yuewen Li and Guanyinsheng Qiu


Tetrahedron Letters

Syntheses of trifluoroethylated unsymmetrical 1,3-diynes by using 1,1-dichloro-2,2,2-trifluoroethane
Jian Zheng, Qing-Yun Chen, Ke Sun, Yangen Huang, Yong Guo,

An efficient method for the synthesis of gem-difluoroolefins
Chun-Ru Cao, Song Ou, Min Jiang, Jin-Tao Liu


\[
\text{Ph} \, \text{C} = \text{O} \quad + \quad 4 \quad \text{F} \quad \text{F} \quad \text{OTMS} \quad \xrightarrow{\text{LDA (2.0 equiv)}} \quad \text{5a} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F}
\]

HMPA:THF = 1:10
-78 °C, 3 h

<table>
<thead>
<tr>
<th>Entry</th>
<th>4</th>
<th>Product</th>
<th>5</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
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<tr>
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<td></td>
<td></td>
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<td>5h</td>
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<td></td>
<td>5i</td>
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<tr>
<td>6</td>
<td></td>
<td></td>
<td>5j</td>
<td>69</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: 1a (1.0 equiv), 4 (10.0 equiv), LDA (2.0 equiv), HMPA:THF = 1:10 (V:V) at −78 °C for 3 h;
<sup>b</sup> Isolated yield.
Generation of trifluoromethyl thiol sulphonate through one-pot reaction of sulfonyl chloride and trifluoromethanesulfanylamides
Yuewen Li, Guanyinsheng Qiu, Hailong Wang, Jie Sheng

R-SO₂Cl (2.0 equiv) + Na₂SO₃ (2.0 equiv)
R-SO₂Na
Wet H₂O, 80 °C

NaHCO₃ (2.0 equiv)

O
S
O
Na

R
S
O
H
Ph

SCF₃

2a

O
S
O
SCF₃

R = aryl, heteoaryl

Tetrahedron

Synthesis of 2-(trifluoromethylthio)-indenones by silver-mediated cascade trifluoromethylthiolation/cyclization of arylpropynones
Yi-Kang Song, Peng-Cheng Qian, Fan Chen *, Chen-Liang Deng, Xing-Guo Zhang
Tetrahedron, 2016, 72, 7589-7593

R
R'

1

+ AgSCF₃

2 equiv K₂S₂O₈
1.5 equiv NaHCO₃
DMSO, 80 °C
**Copper-Catalyzed Cyclization/Oxidation/Aromatization Cascade: Efficient Synthesis of Trifluoromethylated Pyrrolo[2,1-a]isoquinolines**

Lili Tao, Zhiliang Xu, Jing Han, Hongmei Deng, Min Shao, Jie Chen, Hui Zhang, Weiguo Cao

*Synthesis, 2016, 48, 4228-4236*

**Sodium Chloride Catalyzed Regioselective Trifluoromethylthiolation of Furans**

Johannes B. Ernst, Lena Rakers, Frank Glorius

*Synthesis, 2017, 49, 260-268*
One-Pot Synthesis of Trifluoromethylated Iodoisoxazoles via the Reaction of Trifluoroacetohydroximoyl Chloride with Terminal Alkynes and N-Iodosuccinimide

Yuwei Guoa, Xiaojun Wanga, Zhentong Zhu Jianmin Zhang Yongming Wu

Synlett, 2016, 27, 2259-2263

R = aryl, alkyl or thiényl

20 examples up to 81% yield