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Copper-Catalyzed Carbene Insertion into the Sulfur–Sulfur Bond of RS–SCF_2H/SCF_3 under Mild Conditions

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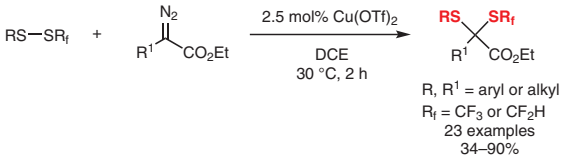

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Abstract A copper-catalyzed carbene insertion into the sulfur–sulfur bond of trifluoromethyl/difluoromethyl/diphenyldisulfides under mild conditions has been developed. Diverse dithioketal derivatives were synthesized in moderate to good yields in an atom-economic process.

Key words copper, carbene, difluoromethylthio, dithioketal

Recently, the trifluoromethylthio group (–SCF_3) and difluoromethylthio group (–SCF_2H) have attracted much attention from both academia and industry, mainly because of their beneficial properties such as high yet tunable lipophilicity (Hansch's hydrophobicity parameter for SCF_3: π = 1.44; SCF_2H: π = 0.68) that are important in fine-tuning the pharmacokinetic and pharmacodynamic properties of lead compound.[1] Moreover, the difluoromethylthio group bears a slightly acidic proton that can act as a hydrogen-bond donor, which could increase the binding strength and selectivity between the lead compound and the host enzyme.[2] Consequently, in the last decade, synthetic methods that could form the C–SCF_3 or C–SCF_2H bonds have been extensively investigated.[3] Nevertheless, new trifluoromethylthiolating/difluoromethylthiolating methods are still urgently needed to strengthen the medicinal chemists' arsenal for new drug discovery.

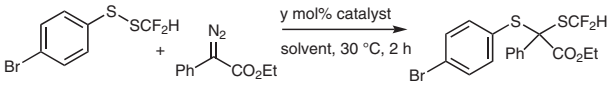
Diazo compounds are readily available, powerful building blocks for the construction of carbon–carbon or carbon–heteroatom bonds.[5] It is well known that a highly reactive intermediate carbene or metal carbenoid can be generated in situ from the diazo compound, which then undergoes a wide range of synthetic transformations including C–H and X–H insertion (X = N, O, S, P, and Si),[6] cyclopropanation[7] and ylide formation.[8] More recently, the metal-catalyzed insertion of carbenoid species into X–Y bonds (X, Y = C, N, O, Si, S, etc.) has emerged as a powerful method for the construction of versatile chemical frameworks.[9] More specifically, insertion of metal carbenoid into the S–S bond for the simultaneous formation of two C–S bonds at one carbon represents an intriguing yet attractive method. In this respect, the Kawamura group reported the first di-insertion reaction of fluorenylidene, which was generated from 9-diazofluorene upon irradiation with a Xenon lamp, into the S–S bond of diaryl disulfides.[10] It was proposed that the reaction proceeded via a double Stevens rearrangement. Shortly after, similar 1,1-insertion of the S–S bond into a carbene was observed by Hamaguchi during their investigation of vinylcarbenoid with cyclic disulfides.[11] In 2016, Bao, Xu and co-workers reported a catalyst-free, donor/acceptor free carbene insertion into a S–S bond of diaryl disulfide.[12] Crossover experiments as well as DFT calculations indicated that the reaction proceeded through a radical pathway. Shortly after, Arunprasath and Sekar reported that the carbene from *N*-tosylhydrazone generated in situ in the presence of a base was able to insert into the S–S bond of diaryl disulfide, although the reaction was proposed to proceed via a sulfonium ylide, followed by 1,2-migration or Stevens rearrangement.[13] Very recently, Song[14] and Xu[15] independently described a rhodium- or copper-catalyzed carbene insertion into the S–S bond of benzenesulfonothioate, although two different mechanisms were proposed.

Inspired by these reports and our interests in the development of efficient methods for the incorporation of fluoroalkylthio groups,[16] we envisaged that the S–S bond of fluoroalkyl-substituted disulfide may undergo insertion upon reaction with carbene to generate fluoroalkylthiolated acetal, which is otherwise difficult to access. Herein, we report our preliminary results on copper-catalyzed carbene insertion into the S–S bond of RS–SCF_2H/SCF_3.

We initially chose the reaction of difluoromethylphenyldisulfide (**1a**) and phenyldiazoacetate (**2a**) as a model system to optimize the reaction conditions (Table 1). Various copper and rhodium catalysts that are commonly used for the generation of metal carbenoid were initially screened and it was found that all of them were able to pro-

mote the reaction to give the desired product in 10–72% yields, although the rhodium catalyst typically showed higher reactivity than the copper catalyst (entries 1–4). Considering that the rhodium complexes were much more expensive than the copper salts, we chose to use $Cu(OTf)_2$ as the catalyst for further optimization. The choice of solvent was crucial for the conversion of the reaction. When the reaction was conducted in non-coordinating less polar solvent such as 1,2-dichloroethane (DCE) or toluene, the reaction occurred in 70–72% yields, whereas the formation of the desired product was not observed using coordinating, more polar solvents such as THF or DMF (Table 1, entries 5, 6, 8, and 9).

Table 1 Optimization of Reaction Conditions for Carbene Insertion into the ArS–SCF_2H Bond[a]



1a **2a** (x equiv) **3a**

Entry	Catalyst	Solvent	x	y	Yield (%)[b]
1	$Rh_2(esp)_2$	DCE	1:1.5	1	64
2	$Rh_2(OAc)_4$	DCE	1:1.5	1	72
3	$Cu(MeCN)_4PF_6$	DCE	1:1.5	10	10
4	$Cu(OTf)_2$	DCE	1:1.5	10	72
5	$Cu(OTf)_2$	toluene	1:1.5	10	70
6	$Cu(OTf)_2$	MeCN	1:1.5	10	50
7	$Cu(OTf)_2$	THF	1:1.5	10	0
8	$Cu(OTf)_2$	DMF	1:1.5	10	0
9	$Cu(OTf)_2$	DCE	1:2	10	80
10	$Cu(OTf)_2$	DCE	1:2.5	10	76
11	$Cu(OTf)_2$	DCE	1:2	10	90[c]
12	$Cu(OTf)_2$	DCE	1:2	5	92[c]
13	$Cu(OTf)_2$	DCE	1:2	2.5	82[c]
14	$Cu(OTf)_2$	DCE	1:2	2.5	90[d]
15	$Cu(OTf)_2$	DCE	1:2	2.5	94[e]

[a] Reaction conditions: compound **1a** (0.10 mmol), diazo compound **2a** (0.12 mmol), catalyst and solvent as indicated, at room temperature for 2.0 h.
[b] Yields were determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.
[c] The diazo compound was added in two portions.
[d] The concentration of compound **1a** was 0.2 M.
[e] The concentration of compound **1a** was 0.5 M.

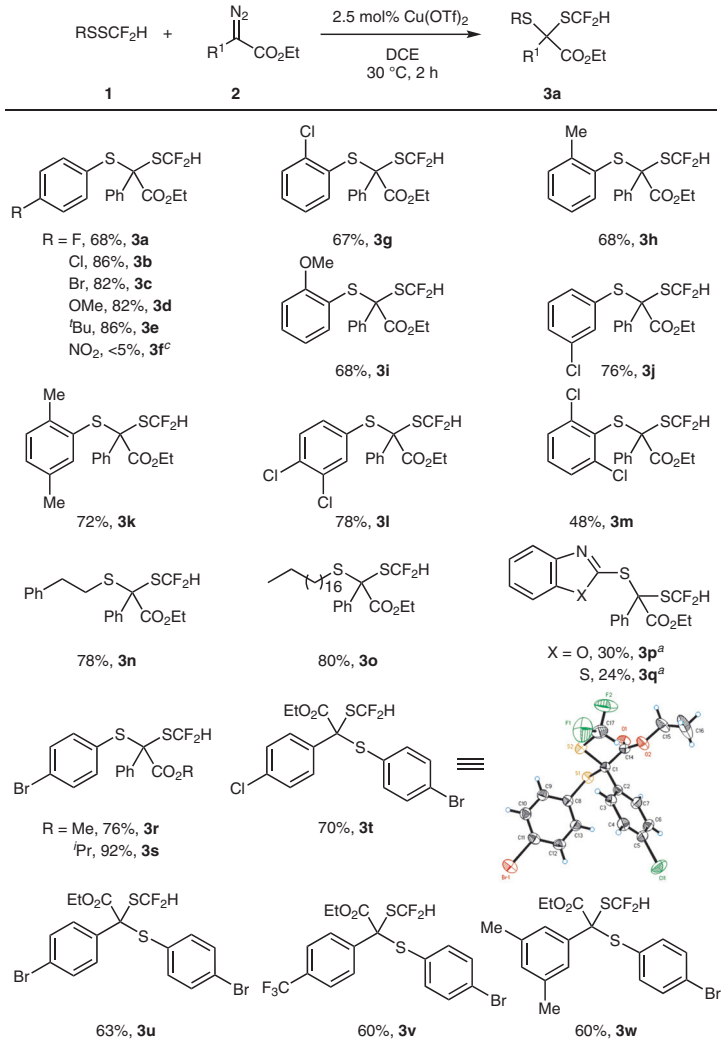
Interestingly, reaction in acetonitrile also occurred in moderate yield, even though acetonitrile is a coordinating polar solvent (Table 1, entry 6). Further adjusting the equivalents of the diazo compound, the loading of the catalyst and the concentration of the reaction mixture led to the optimized conditions that generated the desired product **3a** in 94% yield (entries 9–15).

With the optimized conditions established as indicated in Table 1, entry 15, we next studied the substrate scope. As shown in Scheme 1, vaious difluoromethyl-substituted disulfide were prepared and subjected in the optimized reaction conditions, affording the corresponding products **3a–q** in moderate to high yields. In general, substrates with either electron-withdrawing or electron-donating groups (fluoro, chloro, bromo, ^{t}Bu and methoxyl) at the *para*-position of the phenyl ring were well tolerated, giving the corresponding products in high yields (Scheme 1, 3a–e). Substrates with strong electron-withdrawing group such as nitro at the *para*-position, however, did not react with diazo compound at all, likely due to the low nucleophilicity of the sulfur of the substrate (Scheme 1, 3f). In addition, difluoromethyl-substituted aryldisulfide substrates with different substituents at the *ortho*- or *meta*-position also reacted to give the corresponding products in moderate to good yields (Scheme 1, 3g–m). Furthermore, difluoromethyl-substituted alkyldisulfides also reacted under the standard conditions, leading to the desired product **3n** in 64% yield and **3o** in 80% yield. However, reaction of difluoromethyl-substituted heteroaryldisufide occurred in low yield (Scheme 1, 3p–q). Next, we also investigated the scope of diazo compounds and it was found that methyl or isopropyl phenyldiazoacetates also reacted to give the corresponding products in 76% and 92% yield, respectively (Scheme 1, 3r–s). In addition, reactions of aryldiazoacetate with different functional groups such as Cl, Br, CF_3 also occurred smoothly to give the corresponding products in good yields (Scheme 1, 3t–w). The structure of compound **3t** was confirmed by X-ray diffraction analysis of its single crystals.

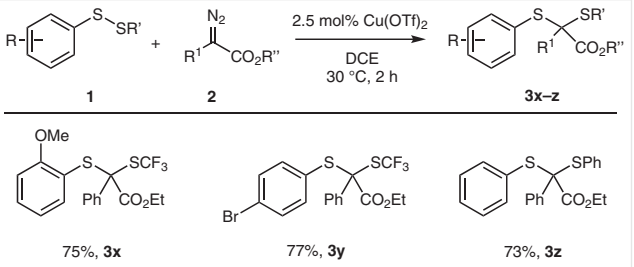
Encouraged by the board scope of the reaction, we next tried to extend the reaction to other substituted disulfides. As summarized in Scheme 2, under the standard conditions, reaction of trifluoromethyl-substituted disulfide also reacted with diazo compound to give the corresponding trifluoromethylthiolated acetal in high yields. For example, reactions of 1-(trifluoromethyl)-2-(2-methoxyphenyl)disulfide or 1-(4-bromophenyl)-2-(difluoromethyl)disulfide with ethyl phenyldiazoacetate afforded the trifluoromethylthiolated acetal **3x** and **3y** in 75% and 77% yields, respectively (Scheme 2). Likewise, diphenyl disulfide also reacted to give the phenylthiolated acetal **3z** in 73% yield (Scheme 2).

Notably, the product of the carbene insertion reaction bears a chiral carbon center, which indicates the possibility of an asymmetric carbene insertion into the S–S bond of the disulfide. In a preliminary screening of chiral diamine ligands, it was found that the highest enantioselectivity of 40% ee could be achieved when **L1** was used as the ligand (Scheme 3). Clearly, further efforts are needed to improve the enantioselectivity of reaction before it becomes applicable.

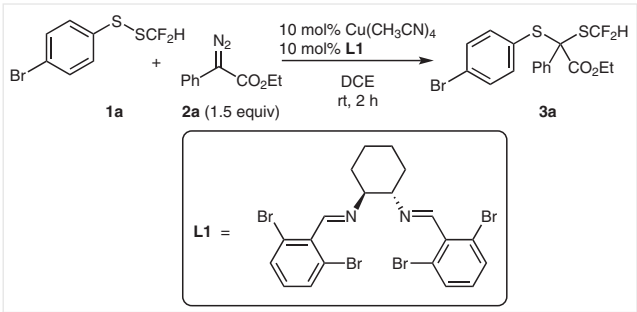
In summary, we have developed a copper-catalyzed carbene insertion reaction between disulfides including trifluoromethyl-/difluoromethyl-/phenyl-substituted disulfides



Scheme 1 Scope of carbene insertion into ArS–SCF_2H bond. *Reagents and conditions*: compound **1a** (0.30 mmol), diazo compound **2a** (0.60 mmol), $Cu(OTf)_2$ (2.5 mol%) in DCE (0.6 mL) at room temperature for 2.0 h; Isolated yields. [a] Yields were determined by ^{19}F NMR spectroscopy using $PhCF_3$ as an internal standard.



Scheme 2 Scope for reaction of ethyl phenyldiazoacetates with substituted disulfides. *Reagents and conditions*: compound **1** (0.30 mmol), diazo compound **2a** (0.60 mmol), $Cu(OTf)_2$ (2.5 mol%) in DCE (0.6 mL) at room temperature for 2.0 h; Isolated yields.



Scheme 3 Copper-catalyzed asymmetric insertion of carbene into the S–S bond of difluoromethyl-substituted disulfide

and diazo compounds under mild conditions.[17] Two new C–S bonds were formed simultaneously at one carbon. Various common functional groups such as fluoride, chloride, bromide, methoxy, trifluoromethyl were compatible. When a chiral ligand was employed, moderate enantioselectivity was observed. Further extension of the scope of the reaction to other types of carbene precursors is under way in our laboratory.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611839.

References

(1) (a) Leo, A.; Hansch, C.; Elkins, D. *Chem. Rev.* **1971**, *71*, 525. (b) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165. (c) Landelle, G.; Panossian, A.; Leroux, F. R. *Curr. Top. Med. Chem.* **2014**, *14*, 941.

(2) Sessler, C. D.; Rahm, M.; Becker, S.; Goldberg, J. M.; Wang, F.; Lippard, S. J. *J. Am. Chem. Soc.* **2017**, *139*, 9325.

(3) Selected recent reviews for trifluoromethylthiolation/difluoromethylthiolation, see: (a) Leroux, F.; Jeschke, P.; Schlosser, M. *Chem. Rev.* **2005**, *105*, 827. (b) Manteau, B.; Pazenok, S.; Vors, J.-P.; Leroux, F. R. *J. Fluorine Chem.* **2010**, *131*, 140. (c) Landelle, G.; Panossian, A.; Pazenok, S.; Vors, J.-P.; Leroux, F. R. *Beilstein J. Org. Chem.* **2013**, *9*, 2476. (d) Ni, C.; Hu, M.; Hu, J. *Chem. Rev.* **2015**, *115*, 765. (e) Xu, X.-H.; Matsuzaki, K.; Shibata, N. *Chem. Rev.* **2015**, *115*, 731. (f) Chachignon, H.; Cahard, D. *Chin. J. Chem.* **2016**, *34*, 445. (g) Xiong, H.-Y.; Pannecoucke, X.; Besset, T. *Chem. Eur. J.* **2016**, *22*, 16734. (h) Zheng, H.; Huang, Y.; Weng, Z. *Tetrahedron Lett.* **2016**, *57*, 1397. (i) Zhang, P.; Lu, L.; Shen, Q. *Acta Chim. Sin.* **2017**, *75*, 744.

(4) Selected recent reviews for transformation of diazo compounds, see: (a) Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1091. (b) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911. (c) Zhu, S.-F.; Zhou, Q.-L. *Nat. Sci. Rev.* **2014**, *1*, 580. (d) Ford, A.; Miel, H.; Ring, A.; Slattery, C. N.; Maguire, A. R.; McKervey, M. A. *Chem. Rev.* **2015**, *115*, 9981. (e) Candeias, N. R.; Paterna, R.; Gois, P. M. P. *Chem. Rev.* **2016**, *116*, 2937. (f) Xia, Y.; Wang, J. *Chem. Soc. Rev.* **2017**, *46*, 2306. (g) Xia, Y.; Qiu, D.; Wang, J. *Chem. Rev.* **2017**, *117*, 13810. (h) Wang, X.; Wang, X.; Wang, J. *Tetrahedron* **2019**, *75*, 949.

(5) Selected examples for the use of diazo substrates in the preparation of trifluoromethylthiolated compounds: (a) Hu, M.; Rong, J.; Miao, W.; Ni, C.; Han, Y.; Hu, J. *Org. Lett.* **2014**, *16*, 2030. (b) Wang, X.; Zhou, Y.; Ji, G.; Wu, G.; Li, M.; Zhang, Y.; Wang, J. *Eur. J. Org. Chem.* **2014**, 3093. (c) Lefebvre, Q.; Fava, E.; Nikolaienko, P.; Rueping, M. *Chem. Commun.* **2014**, *50*, 6617. (d) Matheis, C.; Krause, T.; Bragoni, V.; Goossen, L. J. *Chem. Eur. J.* **2016**, *22*, 12270. (e) Zhang, Z.; Sheng, Z.; Yu, W.; Wu, G.; Zhang, R.; Chu, W.-D.; Zhang, Y.; Wang, J. *Nat. Chem.* **2017**, *9*, 970. (f) Chen, T.; You, Y.; Weng, Z. *J. Fluorine Chem.* **2018**, *216*, 43.

(6) Selected recent reviews for carbene from diazo compound insertion into C–H and X–H bonds, see: (a) Davies, H. M. L.; Hedley, S. J. *Chem. Soc. Rev.* **2007**, *36*, 1109. (b) Doyle, M. P.; Duffy, R.; Ratnikov, M.; Zhou, L. *Chem. Rev.* **2010**, *110*, 704. (c) Zhu, S.-F.; Zhou, Q.-L. *Acc. Chem. Res.* **2012**, *45*, 1365.

(7) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411.

(8) (a) Aggarwal, V.; Winn, C. L. *Acc. Chem. Res.* **2004**, *37*, 611. (b) Zhang, Y.; Wang, J. *Coord. Chem. Rev.* **2010**, *254*, 941.

(9) Selected recent examples of insertion of carbenoid species into X–Y bonds (X, Y = C, N, O, Si, S, etc.), see: (a) Zheng, Y.; Bian, R.; Zhang, X.; Yao, R.; Qiu, L.; Bao, X.; Xu, X. *Eur. J. Org. Chem.* **2016**, 3872. (b) Zhang, H.; Wang, H.; Yang, H.; Fu, H. *Org. Biomol. Chem.* **2015**, *13*, 6149. (c) Li, H.; Wang, L.; Zhang, Y.; Wang, J. *Angew. Chem. Int. Ed.* **2012**, *51*, 2943. (d) Li, H.; Shangguan, X.; Zhang, Z.; Huang, S.; Zhang, Y.; Wang, J. *Org. Lett.* **2014**, *16*, 448. (e) Liu, Z.; Tan, H.; Fu, T.; Xia, Y.; Qiu, D.; Zhang, Y.; Wang, J. *J. Am. Chem. Soc.* **2015**, *137*, 12800. (f) Ganapathy, D.; Sekar, G. *Org. Lett.* **2014**, *16*, 3856. (g) Arunprasath, D.; Muthupandi, P.; Sekar, G. *Org. Lett.* **2015**, *17*, 5448.

(10) Kawamura, Y.; Akitomo, K.; Oe, M.; Horie, T.; Tsukayama, M. *Tetrahedron Lett.* **1997**, *38*, 8989.

(11) Hamagichi, M.; Misumi, T.; Oshima, T. *Tetrahedron Lett.* **1998**, *39*, 7113.

(12) Zheng, Y.; Bian, R.; Zhang, X.; Yao, R.; Qiu, L.; Bao, X.; Xu, X. *Eur. J. Org. Chem.* **2016**, 3872.

(13) Arunprasath, D.; Sekar, G. *Adv. Synth. Catal.* **2017**, *359*, 698.

(14) Rao, C.; Mai, S.; Song, Q. *Chem. Commun.* **2018**, *54*, 5964.

(15) Yuan, H.; Nuligonda, T.; Gao, H.; Tung, C.-H.; Xu, Z. *Org. Chem. Front.* **2018**, *5*, 1371.

(16) (a) Shao, X.-X.; Xu, C.-F.; Lu, L.; Shen, Q. *Acc. Chem. Res.* **2015**, *48*, 1227. (b) Shao, X.-X.; Wang, X.-Q.; Yang, T.; Long, Lu L.; Shen, Q. *Angew. Chem. Int. Ed.* **2013**, *52*, 3457. (c) Wang, X.-Q.; Tao, Y. T.; Xiaolin, C. X.; Shen, Q. *Angew. Chem. Int. Ed.* **2013**, *52*, 12860. (d) Xu, C.-F.; Ma, B.-Q.; Shen, Q. *Angew. Chem. Int. Ed.* **2014**, *53*, 9316. (e) Zhu, D.-H.; Gu, Y.; Lu, L.; Shen, Q. *J. Am. Chem. Soc.* **2015**, *137*, 10547. (f) Wu, J.; Gu, Y.; Leng, X.-B.; Shen, Q. *Angew. Chem. Int. Ed.* **2015**, *54*, 7648. (g) Zhu, D.-H.; Shao, X.-X.; Hong, X.; Lu, L.; Shen, Q. *Angew. Chem. Int. Ed.* **2016**, *55*, 15807.

(17) General procedure for copper-catalyzed carbene insertion of disulfides (**3a–e**, **3g–o**, **3r–z**). In a flame-dried glass tube, under an argon atmosphere, a mixture of disulfide (0.3 mmol) and $Cu(OTf)_2$ (2.7 mg, 0.0075 mmol, 2.5 mol%) was added to DCE (0.6 mL) at room temperature. Diazo compound (0.3 mmol) was then added in one portion. The mixture was stirred for 1 h and then additional diazo compound (0.3 mmol) was added. The mixture was stirred for another 1 h and subsequently filtered through a short plug of Celite and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography (EtOAc/PE) to give the product.

Ethyl 2-((Difluoromethyl)thio)-2-((4-fluorophenyl)thio)-2-phenylacetate (**3a**). R_f = 0.5 (EtOAc/PE, 1:20); yield: 76 mg (68%); yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS): δ = 7.33–7.20 (m, 5 H), 7.17–7.13 (m, 2 H), 6.93 (dd, *J* = 56.2, 54.1 Hz, 1 H), 6.89 (t, *J* = 8.6 Hz, 2 H), 4.35–4.23 (m, 2 H), 1.27 (t, *J* = 7.1 Hz, 3 H). ^{19}F NMR (375 MHz, $CDCl_3$): δ = –92.72 (dd, *J* = 252.6, 56.2 Hz, 1 F), –95.60 (dd, *J* = 252.7, 54.3 Hz, 1 F), –109.87 (s, 1 F). ^{13}C NMR (100.7 MHz, $CDCl_3$): δ = 169.4, 164.2 (d, *J* = 251.6 Hz), 139.6 (d, *J* = 8.8 Hz), 136.3, 128.8, 128.3, 127.6, 124.4 (d, *J* = 3.2 Hz), 122.7 (t, *J* = 269.9 Hz), 115.7 (d, *J* = 21.9 Hz), 70.6, 63.5, 13.7. IR (KBr): ν_{max} = 2984, 1728, 1589, 1489, 1446, 1232,

1067, 1041, 864 cm^{-1}. MS (ESI): *m*/*z* = 390.0 [M + NH_4^+]. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{19}NF_3O_2S_2$ [M + NH_4^+]: 390.0809; found: 390.0803.

Ethyl 2-((4-Cchlorophenyl)thio)-2-((difluoromethyl)thio)-2-phenylacetate (**3b**). R_f = 0.5 (EtOAc/PE, 1:20); yield: 100 mg (86%); yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS): δ = 7.30–7.22 (m, 5 H), 7.16 (d, *J* = 8.4 Hz, 2 H), 7.08 (d, *J* = 8.6 Hz, 2 H), 6.92 (dd, *J* = 56.2, 54.1 Hz, 1 H), 4.34–4.22 (m, 2 H), 1.25 (t, *J* = 7.1 Hz, 3 H). ^{19}F NMR (375 MHz, $CDCl_3$): δ = 92.65 (dd, *J* = 252.7, 56.2 Hz, 1 F), –95.65 (dd, *J* = 252.7, 54.1 Hz, 1 F). ^{13}C NMR (100.7 MHz, $CDCl_3$): δ = 169.3, 138.6, 136.8, 136.3, 128.9, 128.8, 128.4, 127.6, 122.6 (t, *J* = 269.9 Hz), 70.6, 63.5, 13.7. IR (KBr): ν_{max} = 2983, 1728, 1573, 1475, 1301, 1233, 1067, 1042, 796 cm^{-1}. MS (ESI): *m*/*z* = 406.0 [M + NH_4^+]. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{19}NF_2ClO_2S_2$ [M + NH_4^+]: 406.0514; found: 406.0508.

Ethyl 2-((4-Bromophenyl)thio)-2-((difluoromethyl)thio)-2-phenylacetate 3c. R_f = 0.5 (EtOAc/PE, 1:20); yield: 107 mg (82%); yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS): δ = 7.25 (d, *J* = 8.4 Hz, 2 H), 7.23–7.16 (m, 5 H), 6.95 (d, *J* = 8.4 Hz, 2 H), 6.85 (dd, *J* = 56.2, 54.1 Hz, 1 H), 4.28–4.16 (m, 2 H), 1.19 (t, *J* = 7.1 Hz, 3 H). ^{19}F NMR (375 MHz, $CDCl_3$): δ = –92.64 (dd, *J* = 252.7, 56.3 Hz, 1 F), –95.67 (dd, *J* = 252.7, 54.1 Hz, 1 F). ^{13}C NMR (100.7 MHz, $CDCl_3$): δ = 169.3, 138.8, 136.2, 131.7, 128.8, 128.4, 128.1, 127.5, 125.2, 122.6 (t, *J* = 270.1 Hz), 70.5, 65.8, 63.5. IR (KBr): ν_{max} = 2982, 1727, 1473, 1446, 1232, 1068, 1041, 815, 769 cm^{-1}. MS (ESI): *m*/*z* = 449.9 [M + NH_4^+]. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{19}NF_2BrO_2S_2$ [M + NH_4^+]: 450.0009; found: 450.0003