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Two-Step Synthesis of (γ,γ-Difluoroallyl)carbonyl Compounds via Addition of 1,1,2-Trichloro-2,2-difluoroethyl Radical to Silyl Enol Ethers Followed by Reductive Dechlorination

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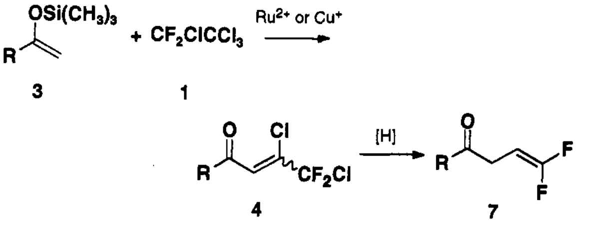
Ru(II)- or Cu(I)-induced radical reaction of $CF_2ClCCl_2^{\bullet}$ radical (**2**), regioselectively derived from CF_2ClCCl_3, to trimethylsilyl enol ethers and a ketene silyl acetal yields (β,β,γ-trichloro-γ,γ-difluoropropyl)carbonyl compounds **5** as the intermediates. Spontaneous dehydrochlorination affords [β-chloro-β-(chlorodifluoromethyl)vinyl]carbonyl compounds **4**. Reductive dechlorination of **4** with zinc gave γ,γ-difluoroallyl ketones **7a–e** and an ester **7f**. In some cases, Ni(0)-catalyzed reduction with zinc is superior than the simple hydrodechlorination.

Fluorine-containing olefins are important synthetic intermediates for the biologically active compounds.[1] We have recently reported the transition metal induced synthesis of trifluoromethylated unsaturated carbonyl compounds.[2] In the reaction, $CF_3CCl_2^{\bullet}$ radical is generated from CF_3CCl_3 by single electron transfer from a Cu(I) or Ru(II) salt and is used as the reactive intermediate for the addition to trimethylsilyl enol ethers to give trifluoromethylated electron-deficient olefins. This type of radical addition to olefins is general for other chlorofluorocarbons, although the reactivity is dependent on the number of fluorine atoms in the substrates and the position of the chlorine substituents.[3] We report here a two-step preparation method of the ω,ω-difluoroallyl ketones and an ester via the addition reaction of trimethylsilyl enol ethers and $CF_2ClCCl_2^{\bullet}$ radical that is regioselectively derived from CF_2ClCCl_3, followed by reductive hydrodechlorination of the addition products (eq 1).



(1)

Transition Metal Induced Radical Reaction of CF_2ClCCl_3 and Silyl Enol Ethers. Previous observation by Burton and Kehoe on the reaction of $CF_2ClCFCl_2$ with Cu(I) salts indicates that single electron transfer from a transition metal salt to polychloropolyfluoroethane selectively gives the more α-chlorinated carbon radicals.[4] On the basis of this fact, the selective generation of $CF_2ClCCl_2^{\bullet}$ radical (**2**) from CF_2ClCCl_3 (**1**) with more effective Ru(II) catalyst[5] is expected. The reaction of **1** with the trimethylsilyl enol ether of acetophenone (**3a**) with a catalytic amount of Ru(II) chloride tristriphenylphosphine complex in DMF at 100 °C in a sealed tube gave a product **4a** (45%), which was formed by dehydrochlorination of the primary addition–desilylation product **5a**, as an *E*/*Z* mixture (0.04:0.96; determined by the ^{19}F NMR spectrum). This spontaneous elimination of hydrogen chloride has been also observed in the radical addition of carbon tetrachloride to **3a**.[6] The regioselectivity of addition of the $CF_2ClCCl_2^{\bullet}$ radical (**2**) was supported by the ^{19}F NMR spectrum in which the resonances of the chlorodifluoromethyl groups appeared at δ −56.8 (s)[7] for the major *Z*-isomer and at δ −52.5 (s) for the minor *E*-isomer. The byproduct of this reaction was acetophenone which was derived from the hydrolytic decomposition of the starting material **3a** by generated hydrogen chloride. To absorb the formed hydrogen chloride, the reaction was concluded in the presence of molecular sieves 4A, and the yield of **4a** improved up to 80% (Scheme I).

Several examples of the reaction are summarized in Table I. In moderate to somewhat low yields, the addition–dehydrochlorination products **4** were obtained from both aromatic and aliphatic silyl enol ethers **3**. The lower yield of the phenylethenyl product is attributed to the highly acid-sensitive nature of the ether **3b**. Use of 2 molar equiv of cuprous chloride instead of the ruthenium salt improved the yield of **4b** from 18% to 40%. Usually, the Ru(II) catalyst is superior to Cu(I) for the reduction–oxidation radical procss.[5] However, in this case, use of a large amount of cuprous chloride avoids the hydrolytic decomposition of the silyl enol ether **3b**. Although the yields of cyclic compounds **4c** and **4e**, in which the reaction centers are secondary, are relatively low, the less hindered open-chain silyl enol ether **3d** and ketene silyl acetal **3f** gave the corresponding products **4d** and **4f** in better yields.

The *E*/*Z* ratios of unsaturated ketones **4** were tentatively determined by the ^{19}F NMR spectra, in which the chlorodifluoromethyl fluorine atoms of the *E*-isomers are

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[1] (a) Welch, J. T. *Tetrahedron* **1987**, *43*, 3123. (b) McDonald, I. A.; Lacoste, J. M.; Bey, P.; Palfreyman, M. G.; Ziena, M. *J. Med. Chem.* **1985**, *28*, 186. (c) Motherwell, W. B.; Tozer, M. J.; Ross, B. C. *J. Chem. Soc., Chem. Commun.* **1989**, 1437.

[2] (a) Okano, T.; Uekawa, T.; Eguchi, S. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2575. (b) Okano, T.; Uekawa, T.; Sawaki, S.; Eguchi, S. *Synlett* **1990**, 403.

[3] (a) Burton, D. J.; Kehoe, L. T. *J. Org. Chem.* **1970**, *35*, 1339. (b) Matsumoto, H.; Nakano, T.; Nagai, Y. *Tetrahedron Lett.* **1973**, 5147. (c) Bentley, P. D.; Cheetham, R.; Huff, R. K.; Pascoe, R.; Sayle, J. D. *Pestic. Sci.* **1980**, *11*, 156. (d) Kamigata, N.; Fukushima, T.; Terakawa, Y.; Yoshida, M.; Sawada, H. *J. Chem. Soc., Perkin Trans. 1* **1991**, 627.

[4] Burton, D. J.; Kehoe, L. T. *J. Org. Chem.* **1971**, *36*, 2596.

[5] Nagashima, H.; Wakamatsu, H.; Ozaki, N.; Ishii, T.; Watanabe, M.; Tajima, T.; Itoh, K. *J. Org. Chem.* **1992**, *57*, 1682.

[6] Murai, S.; Kuroki, Y.; Aya, T.; Sonoda, N.; Tsutsumi, S. *J. Chem. Soc., Chem. Commun.* **1972**, 741.

[7] The small H–F couplings (<3 Hz) are not observed due to the wide range of the spectrum width (240 ppm) of the ^{19}F NMR spectra, even though the small H–F couplings are observed in the ^{1}H NMR spectra, e.g., $J_{\text{H-F}}$ = 0.5 Hz in **4a**.

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Scheme I

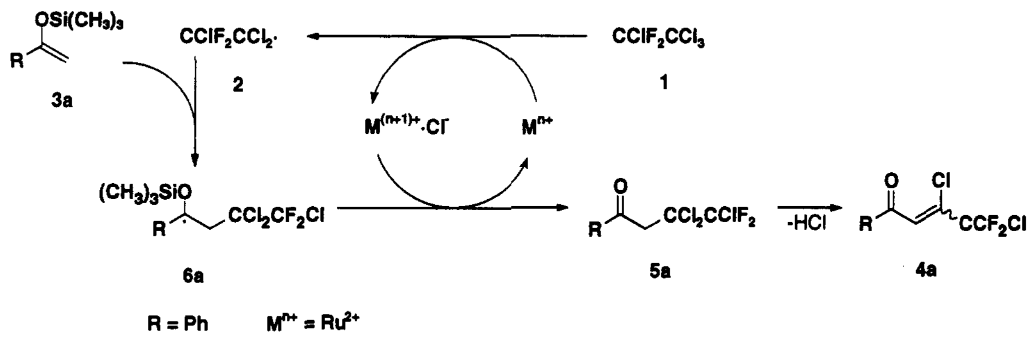
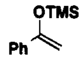
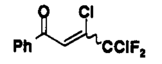
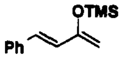
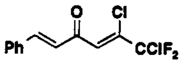
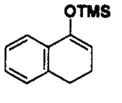
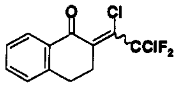
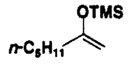
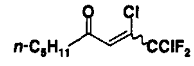
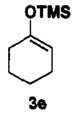
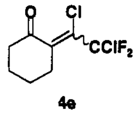
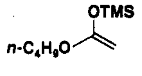
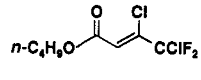


Table I. Reaction of Silyl Enol Ethers with CF$_2$ClCCl$_3$ (2) in DMF at 100 °C

silyl enol ether	product	reaction time (h)	yield (%)	*Z*:*E* ratio[d]
 3a	 4a	15[a] 13[b]	45 80	96:4
 3b	 4b	13[b] 13[c]	12 40	>99:1
 3c	 4c	15[b]	53	90:10
 3d	 4d	13[b]	53	90:10
 3e	 4e	14[b]	26	83:17
 3f	 4f	14[b]	64	>99:1

[a] RuCl$_2$(Ph$_3$P)$_3$ (5 mol %) was used as the catalyst. [b] RuCl$_2$(Ph$_3$P)$_3$ (5 mol %) was used as the catalyst with molecular sieves 4A. [c] CuCl (200 mol %) was used as the catalyst. [d] *Z*:*E* product ratios were determined by ^{19}F NMR spectra.

Table II. ^{1}H–^{1}H, ^{1}H–^{19}F, and ^{19}F–^{19}F Couplings in 7a

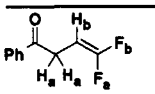
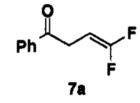
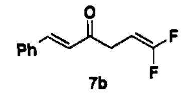
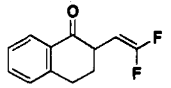
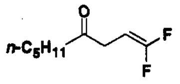
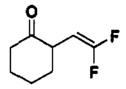
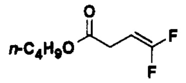
	$J_{H_a\text{-}H_b}$ = 7.2 Hz		
	$J_{H_a\text{-}F_a}$ = 1.8 Hz	$J_{H_b\text{-}F_a}$ = 25.0 Hz	
	$J_{H_a\text{-}F_b}$ = 1.8 Hz	$J_{H_b\text{-}F_b}$ = 1.8 Hz	$J_{F_a\text{-}F_b}$ = 45 Hz

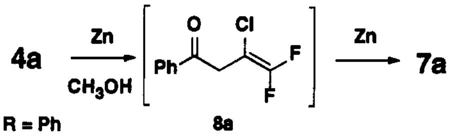
Table III. Reductive Dechlorination of β-Chloro-β-(chlorodifluoromethyl)-α,β-unsaturated Carbonyl Compounds

substrate	product	reaction time (h)	yield (%)
4a	 7a	9.0[a] 10.0[b] 6.0[c] 1.0[d]	5 8[e] 67 49
4b	 7b	2.5[c]	34
4c	 7c	1.0[c] 1.0[d]	41 59
4d	 7d	2.5[c] 1.0[d]	58 20
4e	 7e	2.0[c] 1.0[d]	43 29
4f	 7f	7.0[d]	32

[a] Zn/THF/reflux. [b] Zn–sonication/CH$_3$OH/rt. [c] Zn–sonication/ZnCl$_2$/CH$_3$OH/rt. [d] NiCl$_2$/PPh$_3$/Zn/NaI/DMF–H$_2$O/60 °C. [e] Monochloride 8a (3%) was isolated as a byproduct.

deshielded by the carbonyl group. This stereoselectivity is controlled by the relative bulkiness of the acyl group and hydrogen or the alkyl group attached to the C(2) atom of 5.[2]

Reductive Dechlorination of Dichlorodifluoro Compounds 4. We are interested in the synthetic utility of the neighboring chlorine substituents in the addition products 4, and dechlorination with zinc dust was examined. The reaction of 4a with zinc dust in refluxing THF gave difluoroallyl ketone 7a (5% yield) which was isolated from the complex reaction mixture by chromatographic separation. A complex A$_2$BXY coupling in the ^{1}H NMR spectrum (Table II) clearly shows the difluoroallyl ketone structure. When the solvent was changed to methanol, 7a (8%) and monochloride 8a (3%) were obtained. Finally, difluoroallyl ketone 7a was best obtained by addition of a catalytic amount of zinc chloride and sonication (67%) (eq 2). The dechlorinated difluoroallene was not detected in the reaction mixture. Isolation of chloride 8a suggests the intermediacy of zinc dienolate which was formed by metalation of 4a. The slower second reaction of 8a with zinc gives 7a.

 (2)

In Table III, the yields of the reaction of other dichlorides 4 with zinc are summarized. The longer reaction time to complete the conversion of the monochloride 8 into dechlorinated 7 causes loss of products 7 because of decomposition and/or polymerization, and the yields are relatively low as in the case of 7b. The above-mentioned dechlorination method could not be applied to ester **4f** because of the low reactivity and contamination of the ester-exchanged products. Dechlorination of ester **4f** was performed by Ni(0)-catalyzed reduction (32%) with zinc, nickel chloride, triphenylphosphine, and sodium iodide in aqueous DMF.[8] Since the mechanism of this reaction involves favorable insertion of Ni(0) into a C(sp^2)–Cl bond, monochloride **8f** was not observed during the reaction by GLC analysis. Application of this method to ketones **4**, however, decreased the yields of **7** except **7c**, which was obtained in 59% yield.

In summary, the Ru(II)- or Cu(I)-induced addition of 1,1,2-trichloro-2,2-difluoroethyl radical to silyl enol ethers and ketene silyl acetal followed by reductive dechlorination provides a novel and facile method for the synthesis of (γ,γ-difluoroallyl)carbonyl compounds. This new functional group is difficult to obtain in any other approach and may become a new building block for the synthesis of biologically active fluorinated compounds.

Experimental Section

^{1}H NMR spectra of $CDCl_3$ solutions were recorded at 200 MHz with $Si(CH_3)_4$ as an internal standard. ^{19}F NMR spectra of $CDCl_3$ solutions were recorded at 84.67 MHz. Chemical shifts in the ^{19}F NMR spectra were reported in ppm (δ) relative to internal $CFCl_3$. Trimethylsilyl enol ethers **3a–f** were prepared by usual procedures; lithium enolates derived from the corresponding ketones and butyl acetate with LDA were treated with chlorotrimethylsilane in THF at −78 °C.

General Procedure for Preparation of [β-Chloro-β-(chlorodifluoromethyl)vinyl]carbonyl Compounds 4. A mixture of trimethylsilyl enol ether **3** (5 mmol), CF_2ClCCl_3 (**1**)[9] (20 mmol), and $RuCl_2(PPh_3)_3$ (0.25 mmol) in DMF (2 mL) and 1/16-in. pellets of molecular sieves 4A (2 g) was heated at 100 °C under Ar atmosphere in a sealed glass tube for a given time in Table I. The reaction mixture was poured onto ice–water and extracted with hexane. The hexane solution was dried over Na_2SO_4, and then the solvent was removed at reduced pressure. The crude product **4** was purified by silica gel column chromatography eluted with hexane-CH_2Cl_2 (2:1–1:1).

3,4-Dichloro-4,4-difluoro-1-phenyl-2-buten-1-one (4a) was obtained from **3a** (1.26 g, 5 mmol), **1** (4.1 g, 10 mmol), and $RuCl_2(PPh_3)_3$ (240 mg, 0.25 mmol) as a pale yellow oil (1.00 g, 80%): IR (neat film) 3050, 1680, 1597, 1451, 1319, 1229, 1136, 1012 cm^{-1}; ^{1}H NMR δ 7.98–7.49 (m, 5 H), 7.41 (t, 1 H, J = 0.5 Hz); ^{19}F NMR δ −52.5 (s, 0.04 F; *E*-isomer), −56.8 (s, 0.96 F; *Z*-isomer); MS *m/z* 252 (64, M$^+$ + 2), 250 (93, M$^+$), 187 (100), 189 (36). Anal. Calcd for $C_{10}H_6Cl_2F_2O$: C, 47.84, H, 2.41. Found: C, 48.14, H, 2.33.

5,6-Dichloro-6,6-difluoro-1-phenyl-1,4-hexadien-3-one (4b) was obtained from **3b** (218 mg, 1 mmol), **1** (611 mg, 3 mmol), and $RuCl_2(PPh_3)_3$ (48 mg, 0.05 mmol) as a pale yellow oil (33 mg, 12%) and also with CuCl catalyst as follows: A mixture of **3b** (218 mg, 1 mmol), **1** (611 mg, 3 mmol), and cuprous chloride (198 mg, 2 mmol) in DMF (2 mL) was heated at 100 °C under Ar atmosphere in a sealed glass tube. Chromatography as above gave pure **4b** (110 mg, 40%): IR (neat film) 3059, 1663, 1622, 1599, 1576, 1335, 1215, 1136, 1100, 1013 cm^{-1}; ^{1}H NMR δ 7.63–7.55 (m, 2 H), 7.628 (d, 1 H, J = 16.2 Hz), 7.49–7.38 (m, 3H), 7.13 (t, 1 H, J = 0.5 Hz), 6.91 (d, 1 H, J = 16.2 Hz); ^{19}F NMR δ −56.9 (s); MS *m/z* 280 (44, M$^+$ + 4), 278 (82, M$^+$ + 2), 276 (100, M$^+$). Anal. Calcd for $C_{12}H_8Cl_2F_2O$: C, 52.01, H, 2.92. Found: C, 52.09, H, 3.00.

3,4-Dihydro-2-(1,2-dichloro-2,2-difluoroethylidene)naphthalen-1-one (4c) was obtained from **3c** (655 mg, 3 mmol), **1** (1.83 mg, 9 mmol), and $RuCl_2(PPh_3)_3$ (144 mg, 0.15 mmol) as a pale yellow oil: IR (neat film) 3071, 2936, 1686, 1601, 1456, 1294, 1229, 1194, 1127, 1007 cm^{-1}; ^{1}H NMR δ 8.07 (ddd, 1 H, J = 13.6, 7.6, 1.4 Hz), 7.54 (td, 1 H, J = 7.6, 1.4 Hz), 7.37 (tt, 1 H, J = 7.6, 1.4 Hz), 7.28 (dd, 1 H, J = 7.6, 0.7 Hz), 3.178 (s, 1.52 H; *Z*-isomer), 3.154 (s, 2.48 H; *E*-isomer); ^{19}F NMR δ −47.1 (s, 0.38 F; *Z*-isomer), −49.3 (s, 0.62 F; *E*-isomer); MS *m/z* 278 (20, M$^+$ + 2), 276 (30, M$^+$), 215 (37), 213 (100). Anal. Calcd for $C_{12}H_8Cl_2F_2O$: C, 52.01, H, 2.92. Found: C, 51.95, H, 2.81.

1,2-Dichloro-1,1-difluoro-2-nonen-4-one (4d) was obtained from **3d** (671 mg, 3.6 mmol), **1** (2.6 g, 12.8 mmol), and $RuCl_2(PPh_3)_3$ (173 mg, 0.18 mmol) as a colorless oil (465 mg, 53%): IR (neat film) 2961, 2934, 2874, 1713, 1620, 1466, 1217, 1140, 1072, 1012 cm^{-1}; ^{1}H NMR δ 6.87 (s, 1 H), 2.66 (t, 2 H, J = 7.3 Hz), 1.73–1.55 (m, 2 H), 1.50–1.20 (m, 4 H), 0.91 (t, 2 H, J = 6.5 Hz); ^{19}F NMR δ −47.4 (s, 0.10 F; *E*-isomer), −50.0 (s, 0.90 F; *Z*-isomer); MS *m/z* 202 (34), 200 (100). Anal. Calcd for $C_9H_{12}Cl_2F_2O$: C, 44.10, H, 4.94. Found: C, 43.87, H, 4.97.

2-(1,2-Dichloro-2,2-difluoroethylidene)cyclohexan-1-one (4e) was obtained from **3e** (511 mg, 3 mmol), **1** (1.83 mg, 9 mmol), and $RuCl_2(PPh_3)_3$ (144 mg, 0.15 mmol) as a colorless oil (181 mg, 26%): IR (neat film) 2949, 2868, 1715, 1632, 1447, 1273, 1209, 1142, 1119, 1003 cm^{-1}; ^{1}H NMR δ 2.78 (tt, 2 H, J = 6.2, 0.6 Hz), 2.59 (t, 2 H), 2.09–1.82 (m, 4 H); ^{19}F NMR δ −52.6 (s, 0.05 F; *E*-isomer), −57.1 (s, 0.95 F; *Z*-isomer); MS *m/z* 190 (67), 188 (100). Anal. Calcd for $C_8H_8Cl_2F_2O$: C, 41.95, H, 3.53. Found: C, 42.13, H, 3.46.

Butyl 3,4-dichloro-4,4-difluoro-2-butenoate (4f) was obtained from **3f** (1.11 g, 5.9 mmol), **1** (5.4 g, 26.4 mmol), and $RuCl_2(PPh_3)_3$ (253 mg, 0.264 mmol) as a colorless oil (928 mg, 64%): IR (neat film) 2965, 1738, 1645, 1466, 1314, 1219, 1186, 1140, 1019 cm^{-1}; ^{1}H NMR δ 6.71 (s, 1 H), 4.24 (t, 2 H, J = 6.5 Hz), 1.77–1.56 (m, 2 H), 1.52–1.32 (m, 2 H), 0.96 (t, 3 H, J = 7.3 Hz); ^{19}F NMR δ −57.4 (s); MS *m/z* 248 (2, M$^+$ + 2), 246 (3, M$^+$), 172 (100), 174 (61). Anal. Calcd for $C_8H_{10}Cl_2F_2O_2$: C, 38.89, H, 4.09. Found: C, 39.11, H, 3.87.

Dechlorination of Products 4. Method A. A mixture of **4**, 3 molar equiv of zinc dust, and 10 molar equiv of zinc chloride in methanol was sonicated by a 35-W ultrasonic cleaner (45 KHz) at room temperature for the period shown in Table II. After filtration of the reaction mixture, the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography and/or preparative TLC (hexane–CH_2Cl_2 (4:1–1:1)).

Method B. A solution of **4** in DMF was added dropwise into a mixture of $NiCl_2 \cdot 6H_2O$ (10 mol %), triphenylphosphine (57 mol %), NaI (67 mol %), and zinc (3 molar equiv) in degassed DMF–H_2O (25:1; 1–3 mL), which was preheated at 60 °C for 30 min. The mixture was heated at 60 °C for the period given in Table II. The reaction mixture was filtered, diluted with water, (30 mL), and then extracted with pentane. The pentane solution was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was chromatographed on a silica gel column.

4,4-Difluoro-1-phenyl-3-buten-1-one (7a) was prepared from **4a** (628 mg, 2.5 mmol), zinc dust (490 mg, 7.5 mmol), and $ZnCl_2$ (35 mg, 0.25 mmol) as a colorless oil (307 mg, 68%). Ketone **7a** was also prepared by method B from **4a** (502 mg, 2 mmol), $NiCl_2 \cdot 6H_2O$ (48 mg, 0.2 mmol), PPh_3 (299 mg, 1.14 mmol), NaI (201 mg, 1.34 mmol), zinc dust (392 mg, 6 mmol), and aqueous DMF (4% H_2O, 3 mL): 178 mg, 49%; IR (neat film) 1753, 1692, 1599, 1451, 1358, 1300, 1215, 1177 cm^{-1}; ^{1}H NMR δ 8.10–7.93 (m, 2 H), 7.66–7.44 (m, 3 H), 4.64 (dtd, 1 H, J = 25.0, 7.2, 1.8 Hz), 3.72 (dt, 2 H, J = 7.2, 1.8 Hz); ^{19}F NMR δ −87.0 (d, 1 F, J = 45 Hz), −89.3 (dd, 1 F, J = 45, 25 Hz); MS *m/z* 146 (100), 132 (37), 130 (60). Anal. Calcd for $C_{10}H_8F_2O$: C, 65.92, H, 4.44. Found: C, 65.92, H, 4.44.

3-Chloro-4,4-difluoro-1-phenyl-3-buten-1-one (8a) was isolated as a component of the reaction mixture with **7a** of a reaction as follows: A mixture of **4a** (619 mg, 2.47 mmol) and zinc dust (161 mg, 2.47 mmol) in methanol (10 mL) was refluxed for 14 h. After removal of the solvent under reduced pressure at room temperature, the residue was distilled on a Kugelrohr distillation apparatus (150 °C/0.3 mm). Chromatographic separation of the collected volatile products gave **7a** (36 mg, 8%) and **8a** (16 mg, 3%) as pale yellow oils. **8a**: IR (neat film) 3065, 2922, 1757, 1696, 1451, 1337, 1289, 1219, 1026 cm^{-1}; ^{1}H NMR δ 8.02–7.92 (m, 2 H), 7.68–7.43 (m, 3 H), 3.97 (dd, 2 H, J = 2.8, 2.2 Hz); ^{19}F NMR δ −87.6 (d, 1 F, J = 42 Hz), −93.0 (d, 1 F, J = 42 Hz); MS *m/z*

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[8] (a) Colon, I. *J. Org. Chem.* **1982**, *47*, 2622. (b) Yang, Z.-Y.; Burton, D. J. *J. Org. Chem.* **1992**, *57*, 5144.

[9] Okuhara, K. *J. Org. Chem.* **1976**, *41*, 1487.

218 (M$^+$ + 2, 24), 216 (M$^+$, 22), 184 (100). Anal. Calcd for $C_{10}H_7ClF_2O$: C, 55.44, H, 3.26. Found: C, 55.41, H, 3.54.

6,6-Difluoro-1-phenyl-1,5-hexadien-3-one (7b) was obtained from **4b** (358 mg, 1.3 mmol), zinc dust (255 mg, 3.9 mmol), zinc chloride (18 mg, 0.13 mmol), and methanol (8 mL) as a pale yellow oil: 92 mg, 34%; IR (neat film) 3030, 2926, 1753, 1676, 1612, 1495, 1451, 1358, 1329, 1292, 1171, 1151 cm^{-1}; ^{1}H NMR δ 7.620 (d, 1 H, *J* = 16.0 Hz), 7.60–7.52 (m, 2 H), 7.45–7.40 (m, 3 H), 6.77 (d, 1 H, *J* = 16.0 Hz), 4.56 (dtd, 1 H, *J* = 25.0, 7.4, 1.8 Hz), 3.40 (dt, 2 H, *J* = 7.4, 1.8 Hz); ^{19}F NMR δ −86.9 (d, 1 F, *J* = 42 Hz), −89.2 (dd, 1 F, *J* = 42, 25 Hz); MS *m/z* 208 (M$^+$, 18), 207 (100), 158 (43), 145 (18). Anal. Calcd for $C_{12}H_{10}F_2O$: C, 69.22, H, 4.84. Found: C, 68.93, H, 5.13.

1,2,3,4-Tetrahydro-2-(2,2-difluoroethenyl)-1-naphthalenone (7c) was obtained from **7c** (277 mg, 1.00 mmol), zinc dust (196 mg, 3 mmol), zinc chloride (14 mg, 0.1 mmol), and methanol (8 mL) as a pale yellow oil by method A (86 mg, 41%). Ketone **7d** was also obtained from **4d** (271 mg, 0.98 mmol), $NiCl_2{\cdot}6H_2O$ (48 mg, 0.2 mmol), PPh_3 (299 mg, 1.14 mmol), NaI (201 mg, 1.34 mmol), and zinc dust (392 mg, 6.0 mmol) by method B as a colorless oil: 122 mg, 59%; IR (neat film) 3069, 2940, 1750, 1688, 1603, 1456, 1308, 1275, 1229, 1181 cm^{-1}; ^{1}H NMR δ 8.03 (ddd, 1 H, *J* = 7.8, 1.4, 0.4 Hz), 7.50 (td, 1 H, *J* = 7.8, 1.4 Hz), 7.39–7.19 (m, 2 H), 4.55 (dddt, 1 H, *J* = 12.8, 8.8, 4.4, 1.2), 3.27–2.85 (m, 2 H), 2.31 (dq, 1 H, *J* = 13.2, 4.4 Hz), 2.07 (tdd, 1 H, *J* = 13.2, 11.4, 4.8 Hz); ^{19}F NMR δ −86.9 (d, 1 F, *J* = 42 Hz), −89.3 (dd, 1 F, *J* = 42, 25 Hz); MS (*m/z*) 208 (30, M$^+$), 207 (10), 118 (100). Anal. Calcd for $C_{12}H_{10}F_2O$: C, 69.22, H, 4.85. Found: C, 68.82, H, 5.13.

1,1-Difluoro-1-nonen-4-one (7d) was obtained from **4d** (490 mg, 2 mmol), zinc dust (392 mg, 6.0 mmol), and $ZnCl_2$ (27 mg, 0.2 mmol) as a colorless oil: 181 mg, 58%. Ketone **7e** was also obtained from **4e** (238 mg, 0.97 mmol), $NiCl_2{\cdot}6H_2O$ (46 mg, 0.19 mmol), PPh_3 (290 mg, 1.10 mmol), NaI (195 mg, 1.10 mmol), and zinc dust (380 mg, 5.8 mmol) by method B as a colorless oil: 34 mg, 20%; IR (neat film) 2961, 2934, 2874, 2865, 1753, 1723, 1466, 1414, 1350, 1296, 1194, 1128, 930 cm^{-1}; ^{1}H NMR δ 4.44 (dtd, 1 H, *J* = 25.4, 7.4, 1.8 Hz), 3.11 (dt, 2 H, *J* = 7.4, 1.8 Hz), 2.44 (t, 2 H, *J* = 7.4 Hz), 1.67–1.52 (m, 2 H), 1.35–1.23 (m, 4 H), 0.89 (t, 3 H, *J* = 6.8 Hz); ^{19}F NMR δ −87.2 (d, 1 F, *J* = 42 Hz), −89.5 (dd, 1 F, *J* = 42, 25 Hz); MS (*m/z*) 113 (72), 111 (16), 100 (44), 99 (100). Anal. Calcd for $C_9H_{14}F_2O$: C, 61.35, H, 8.01. Found: C, 61.41, H, 7.94.

2-(2,2-Difluoroethenyl)cyclohexanone (7c) was obtained from **4e** (294 mg, 1.28 mmol), zinc dust (252 mg, 3.85 mmol), and $ZnCl_2$ (18 mg, 0.13 mmol) as a pale yellow oil: 89 mg, 43%. Ketone **7f** was also obtained from **4f** (229 mg, 1.00 mmol), $NiCl_2{\cdot}6H_2O$ (48 mg, 0.2 mmol), PPh_3 (299 mg, 1.14 mmol), NaI (201 mg, 1.34 mmol), and zinc dust (392 mg, 6.0 mmol) by method B as a colorless oil: 46 mg, 29%; IR (neat film) 2944, 2866, 1750, 1715, 1451, 1329, 1296, 1279, 1181 cm^{-1}; ^{1}H NMR δ 4.49 (ddd, 1 H, *J* = 26.4, 9.0, 2.4 Hz), 3.26–3.11 (m, 1 H), 2.55–2.04 (m, 4 H), 2.02–1.51 (m, 4 H); ^{19}F NMR δ −87.5 (d, 1 F, *J* = 44 Hz), −89.6 (dd, 1 F, *J* = 44, 27 Hz); MS (*m/z*) 160 (23, M$^+$), 111 (86), 103 (89), 98 (100), 97 (95). Anal. Calcd for $C_8H_{10}F_2O$: C, 60.00, H, 6.29. Found: C, 60.21, H, 6.07.

Butyl 4,4-difluoro-3-butenoate (7f) was obtained from **4f** (510 mg, 2.0 mmol), $NiCl_2{\cdot}6H_2O$ (95 mg, 0.4 mmol), PPh_3 (598 mg, 2.28 mmol), NaI (402 mg, 2.68 mmol), and zinc dust (784 mg, 12 mmol) as a colorless oil: 113 mg, 32%; IR (neat film) 2965, 2936, 2876, 1755, 1736, 1310, 1171 cm^{-1}; ^{1}H NMR δ 4.43 (dtd, 1 H, *J* = 24.8, 7.6, 1.8 Hz), 4.16 (t, 2 H, *J* = 6.6 Hz), 3.03 (dt, 2 H, *J* = 7.6, 1.8 Hz), 1.68–1.25 (m, 4 H), 0.94 (t, 3 H, *J* = 7.2 Hz); ^{19}F NMR δ −87.4 (d, 1 F, *J* = 42 Hz), −89.6 (dd, 1 F, *J* = 42, 25 Hz); MS (*m/z*) 149 (100), 97 (60). Anal. Calcd for $C_8H_{12}F_2O_2$: C, 53.93, H, 6.79. Found: C, 54.10, H, 6.56.