Copper(I) Salt Catalyzed Reaction of 1,1,1-Trichloro-2,2,2-trifluoroethane with Trimethylsilyl Enol Ethers. A Convenient Synthesis of β-Chloro-β-(trifluoromethyl) α,β-Unsaturated Carbonyl Compounds

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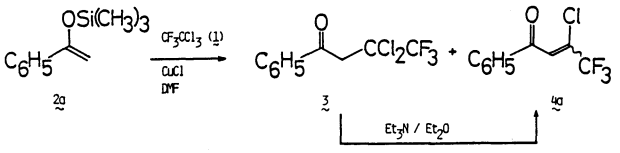
(Received January 23, 1989)

β-Chloro-β-(trifluoromethyl) α,β-unsaturated carbonyl compounds were obtained by the reaction of trimethylsilyl enol ethers with CF_3CCl_3 and CuCl, followed by dehydrochlorination with triethylamine or DBN. Aromatic enol ethers gave moderate to good yields of the chloro(trifluoromethyl)methylene ketone derivatives but aliphatic enol ethers and silyl ketene acetal gave only lower yields.

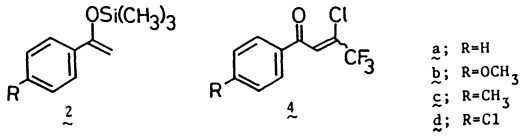
Synthetic methods for the preparation of trifluoromethyl-substituted organic compounds have drawn considerable interest recently because of their remarkable biological activity.[1] As one of versatile and economical reagents, 1,1,1-trichloro-2,2,2-trifluoroethane (**1**) has been utilized extensively to effect polyhaloalkylmetal addition to carbonyl compounds.[2,3] On the other hand, the addition of polyhalocarbons to carbon-carbon double bonds is known to be catalyzed effectively by copper chloride-2-aminoethanol redox system.[4] The successful addition of polyhalocarbons to trimethylsilyl enol ethers catalyzed by copper(I) chloride to afford β-halo α,β-unsaturated ketones has been reported also by Murai et al.[5] In spite of these pioneering works, the scope and limit of the Cu(I) catalyzed addition reaction of polyfluorinated **1** with silyl enol ethers seem to be yet unclarified. We report here the Cu(I) catalyzed addition reaction of **1** with various types of trimethylsilyl enol ethers, that provides a convenient regiospecific route to β-chloro-β-(trifluoromethyl) α,β-unsaturated ketones.[6] These compounds seem to be difficult to prepare regiospecifically by enol chlorination route of 1-trifluoromethyl-1,3-diketones. The reaction of 1-trifluoromethyl-3-aryl- or -3-alkyl-1,3-diketones with thionyl chloride has been reported to afford a regioisomeric mixture of the corresponding enol chlorides or only undesired α-chloromethylene ketone derivatives.[7]

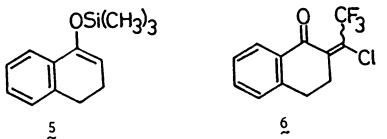
Results and Discussion

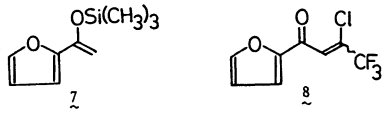
Since dichloromethylenation of acetophenone trimethylsilyl enol ether (**2a**) with CCl_4 in the presence of CuCl was reported by Murai et al.,[5] we examined first the reaction of **2a** with two equivalent of CF_3CCl_3 (**1**). In the presence of a catalytic amount of CuCl (0.1 equivalent), the reaction in DMF (*N*,*N*-dimethylformamide) at 80 °C afforded a mixture of saturated ketone **3** and dehydrochlorinated ketone **4a** (*E* : *Z* ratio was 10 : 90). Since **3** and **4a** were not readily separable, the mixture was treated with triethylamine at room temperature to complete the dehydrochlorination, affording **4a** in 23% yield. The *E* : *Z* ratio of **4a** was 10 : 90 as determined ^{19}F NMR data. A strong anisotropic effect for the carbonyl bond to CF_3 group was observed for *E*-isomer **4a**-*E* (δ 13.56 for **4a**-*E* and 8.65 for **4a**-*Z*, CF_3COOH as an external standard).[8,9]

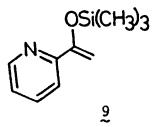


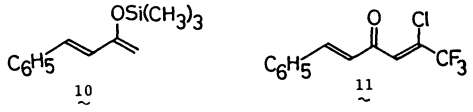
Scheme 1.

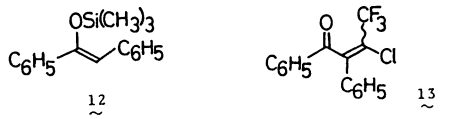


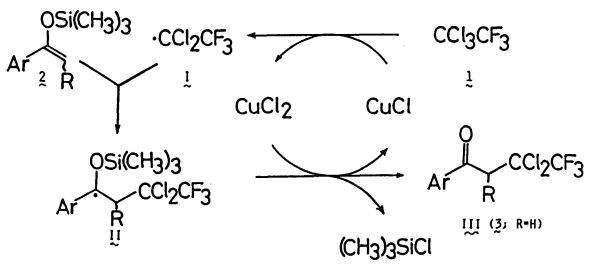












Scheme 2.

As outlined in Scheme 2, the reaction mechanism may involve one-electron transfer from CuCl to CF_3CCl_3 to afford a radical intermediate, $CF_3CCl_2\cdot$ (**I**). Following the addition of the β-position of the electron-rich silyl enol ether **2** to form benzyl radical **II**, oxidative desilylation with Cu(II) cation yields saturated ketone **3**. A partial dehydrochlorination of the primary product **3** under the reaction conditions gives unsaturated ketone **4**.

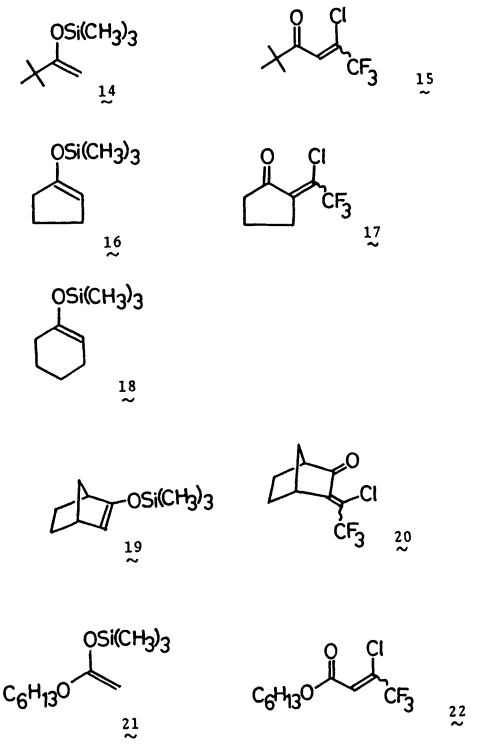
The use of large excess of **1** (20-fold equivalent) as well as equimolar CuCl along with addition of 4A Molecular Sieves to trap liberated HCl[10] raised the yield upon dehydrochlorination with triethylamine to 52%. DMF has been predicted as the most favorable solvent for electron transfer reactions,[11] in fact, no other solvent such as acetonitrile, dioxane, ethanol, nor pyridine gave better results.

Under the reaction conditions mentioned above, various silyl enol ethers were converted into unsaturated ketones with a β-trifluoromethyl group (Table 1).[12]

Table 1. β-Chloro-β-(trifluoromethyl) α,β-Unsaturated Carbonyl Compounds from Trimethylsilyl Enol Ethers and CF_3CCl_3

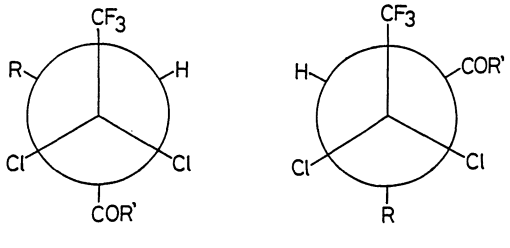
Entry	Silyl enol ether	Product	Reaction time/h	Yield (%)[a]	*Z*:*E*
1	**2a** R=H	**4a**	3	52	90:10
2	**2b** R=OCH_3	**4b**	2	44	92: 8
3	**2c** R=CH_3	**4c**	2	49	93: 7
4	**2d** R=Cl	**4d**	1	55	93: 7
5	**5**	**6**	12	49	30:70
6	**7**	**8**	1	70	97: 3
7	**9**	—	2	0[b]	—
8	**10**	**11**	3	59	>99: 1
9	**12**	**13**	15	14[c]	12:88
10	**14**	**15**	5	12(15)[d]	88:12
11	**16**	**17**	5	21(39)[d]	88:12
12	**18**	—	36	0[e]	—
13	**19**	**20**	7.5	32[c]	58:42
14	**21**	**22**	3	15	79:21

a) Isolated yield. b) A complex mixture was obtained. c) 1,5-Diazabicyclo[4. 3. 0]non-5-ene was used in dehydrochlorination. d) GLC yield determined by addition of adamantane as an internal standard; see Experimental. e) Cyclohexanone was a major product.



Aromatic ketone derivatives **4b—d** and **6** were obtained in moderate yields from the corresponding silyl enol ethers **2b—d** and **5**. Among heterocyclic enol ethers **7** and **9**, **7** gave furyl ketone **8** in 70 % yield, but pyridyl enol ether **9** afforded only a complex mixture due to the side reactions between CuCl and the pyridine moiety. Even in the case of conjugated silyl enol ether **10** which can generate a stable allyl radical intermediate, dienone **11** was obtained in 59% yield. Since $CF_3CCl_2\cdot$ radical is a bulky intermediate, sterically hindered substrates such as the diphenyl derivative **12** are unfortunately less reactive, affording the corresponding enones only in lower yields.

In contrast to aromatic enol ethers, alkyl or alicyclic enol ethers **18** and **21**, except sterically favorable methylene derivative **14** or strained cyclic enol ethers **16** and **19**, were not suitable substrates for this reaction because of the relative instability of the radical intermediates involved. Pinacolone silyl enol ether (**14**) gave *t*-butyl ketone **15** in 15% yield based on GLC. Silyloxycyclopentene (**16**) and silyloxynorbornene (**19**) gave α-[chloro(trifluoromethyl)methylene] ketones **17**



IV V

and **20** in lower yields. However, less strained silyloxycyclohexene (**18**) was unreactive under the reaction conditions except by slow hydrolysis to form cyclohexanone.[13] It is notable that benzo-fused derivative **5** is a suitable substrate in which a cyclohexadiene subunit is involved. Ketene silyl acetal **21** also gave unsaturated ester **22** in a low yield.

In the elimination step, triethylamine was effective in the most cases, but the more basic 1,5-diazabicyclo-[4.3.0]non-5-ene (DBN) was needed to obtain sterically hindered ketones **13** and **20**. The stereoselectivity of the elimination depends on the structure of the saturated intermediate **III** (Scheme 2). The *E*:*Z* isomer ratio was not changed before and after the triethylacetyl compounds, **2a—d**, **7**, **10**, **14**, and **21**, and cyclopentene **16** and **19** gave *Z*-isomers as major products via anti-elimination of HCl from the more stable via anti-elimination of HCl from the more stable conformers **IV** (R=H- or $-CH_2-$) where R'CO- group and CF_3- group are antiperiplanar. However, **5** and **12** gave *E*-isomers as major products. The increased repulsion between α-R group (R=$-CH_2-$ or Ph-) and CF_3 group destabilizes **IV** relative to conformer **V** affording *E*-isomers via anti-dehydrochlorination.[14]

In conclusion, CF_3CCl_3 (**1**) was found to be a convenient trifluoromethyl-containing synthon for methylenation of various silyl enol ethers, with some limitations in the applicable substrates. The resulting chlorinated unsaturated carbonyl compounds have synthetic potential for other transformations to trifluoromethyl-containing organic compounds.[15]

Experimental

All the melting points were taken on a Yanagimoto micromelting point hot stage apparatus and are uncorrected. ^1H NMR spectra were recorded on a JEOL JNM-FX-60 FT NMR spectrometer at 60 MHz and on A JEOL JNM-GX-500 FT NMR spectrometer at 500 MHz in $CDCl_3$. ^{19}F NMR spectra were recorded on a Hitachi R-20 instrument at 56.45 MHz in $CDCl_3$. Chemical shifts were reported in parts per million (δ) relative to Me_4Si as an internal standard for ^1H and to CF_3COOH as an external standard for ^{19}F. IR spectra were obtained on a JASCO IRA-1 spectrometer. Mass spectra (MS) were obtained on a ESCO EMD-05B mass spectrometer at 70 eV. Microanalyses were performed with a Perkin-Elmer 240B elemental analyzer. GLC analyses were carried out by using a Shimadzu GC-14A gas chromatograph on a 2 m packed column with OV-17 as stationary phase. Silyl enol ethers were prepared by ordinary methods; trimethylsilylation of lithium enolate prepared from a ketone or an ester with LDA, or by the reactions of ketones with chlorotrimethylsilane and triethylamine in DMF.

Preparation of β-Chloro-β-(trifluoromethyl) α,β-Unsaturated Ketones. A Typical Method: 3-Chloro-4,4,4-trifluoro-1-phenyl-2-buten-1-one (4a): A mixture of **2a** (192 mg, 1.00 mmol), **1** (3.82 g, 20.0 mmol), CuCl (49 mg, 1.0 mmol), and 4A Molecular Sieves (1.00 g) in anhydrous DMF (2 ml) was refluxed under nitrogen atmosphere for 3 h, and then Molecular Sieves were removed by filtration. To the filtrate was added Et_2O (50 ml) and saturated aqueous NaCl (50 ml). After separation of organic layer, the aqueous layer was extracted with Et_2O. The extracts were combined and dried (Na_2SO_4). After removal of the solvent by distillation, the residue was purified on a short silica gel (Fuji-Davison BW-300) column (1:1 hexane-CH_2Cl_2). The resultant mixture of **3** and **4a** (153 mg) was dissolved in Et_2O (2 ml) and triethylamine (110 mg, 1.00 mmol) was added. The mixture was stirred at room temperature overnight. The solvent was evaporated and the residue was chromatographed on a silica gel column (1:1 hexane-CH_2Cl_2) to give **4a** as pale yellow oil; 120 mg (52%); ^1H NMR ($CDCl_3$) δ=8.0—7.3 (m, 5H) and 7.44 (m, 1H); ^{19}F NMR ($CDCl_3$) δ=13.56 (s, 0.10F) and 8.65 (s, 0.90F); IR(neat) 3060, 1680, 1624, 1602, 1580, 1450, 1276, 1224, 1190, and 1150 cm^{-1}; MS *m/z* (rel intensity) 236(M^++2, 5), 234(M^+, 16), 206(8), 105(100), 77(94), 51(68), and 50(20). Found: C, 51.30; H, 2.48%. Calcd for $C_{10}H_6ClF_3O$: C, 51.20; H, 2.58%.

3-Chloro-4,4,4-trifluoro-1-(4-methoxyphenyl)-2-buten-1-one (4b). As described above, a mixture of **2b** (455 mg, 2.05 mmol), **1** (7.67 g, 40.9 mmol), CuCl (203 mg, 2.05 mmol), 4A Molecular Sieves (2.0 g) in DMF (3 ml) was treated and workup gave **4b** as pale yellow oil; 232 mg (44%); ^1H NMR($CDCl_3$) δ=7.91 (d, 2H, *J*=9.0 Hz), 7.39 (m, 1H), 6.98 (d, 2H, *J*=9.0 Hz), and 3.90 (s,3H); ^{19}F NMR($CDCl_3$) δ=13.70 (s, 0.08F) and 8.88 (s, 0.92F); IR(neat) 3045, 3020, 2970, 2945, 2840, 1678, 1600, 1576, 1514, 1460, 1444, 1422, 1260, 1236, 1184, 1168, and 1150 cm^{-1}; MS *m/z* 266(M^++2, 9), 264(M^+, 27), 236(19), 135(100), 107(19), 92(31), 77(40), 64(25), 63(31), 51(11), and 50(20). Found: C, 50.01; H, 2.96%. Calcd for $C_{11}H_8ClF_3O_2$: C, 49.92; H, 3.05%.

3-Chloro-4,4,4-trifluoro-1-(4-methylphenyl)-2-buten-1-one (4c). As described above, a mixture of **2c** (491 mg, 2.38 mmol), **1** (8.92 g, 47.6 mmol), CuCl (236 mg, 2.38 mmol), and 4A Molecular Sieves (2.38 g) in DMF (2 ml) was treated and workup gave **4c** as pale yellow oil; 237 mg (49%); ^1H NMR($CDCl_3$) δ=7.83 (d, 2H, *J*=8.2 Hz), 7.41 (m, 1H), 7.31 (d, 2H, *J*=8.2 Hz), and 2.44 (s, 3H); ^{19}F NMR($CDCl_3$) δ=14.30 (s, 0.07F) and 8.94 (s, 0.93F); IR(neat) 3050, 1678, 1602, 1576, 1408, 1280, 1270, 1230, 1180, and 1150 cm^{-1}; MS *m/z* 250(M^++2, 7), 248(M^+, 21), 220(10), 119(100), 91(64), 89 (12), 65(39), 63(21), 51(17), and 50(12). Found: C, 53.07; H, 3.26%. Calcd for $C_{11}H_8ClF_3O$: C, 53.14; H, 3.24%.

3-Chloro-4,4,4-trifluoro-1-(4-chlorophenyl)-2-buten-1-one (4d). As described above, a mixture of **2d** (548 mg, 2.41 mmol), **1** (9.02 g, 48.1 mmol), CuCl (238 mg, 2.40 mmol), and 4A Molecular Sieves (2.40 g) in DMF (3 ml) was treated and workup gave **4d** as pale yellow oil; 353 mg (55%); ^1H NMR($CDCl_3$) δ=7.88 (d, 2H, *J*=9.0 Hz), 7.53 (d, 2H, *J*=9.0 Hz), and 7.41 (m, 1H); ^{19}F NMR($CDCl_3$) δ=13.78 (s, 0.07F) and 8.94 (s, 0.93F); IR(neat) 3110, 3080, 1682, 1624, 1596, 1576, 1494, 1402, 1280, 1224, 1190, and 1156 cm^{-1}; MS *m/z* 272(M^++4, 3), 270(M^++2, 20), 268(M^+, 27), 242(12), 240 (19), 157(14), 141(30), 139(100), 113(13), 111(54), 86(35), 84(52), 76(17), 75(70), 74(17), 51(26), and 50(52). Found: C, 44.75; H, 1.76%. Calcd for $C_{10}H_5ClF_3O$: C, 44.64; H, 1.87%.

3,4-Dihydro-2-(1-chloro-2,2,2-trifluoroethylidene)-1(2*H*)-naphthalenone (6). As described above, a mixture of **5** (531 mg, 2.43 mmol), **1** (9.11 g, 48.6 mmol), CuCl (241 mg, 2.43 mmol), and 4A Molecular Sieves (2.40 g) in DMF (3 ml) was treated and workup gave **6** as pale yellow oil; 309 mg (49 %); ^1H NMR (500 MHz)($CDCl_3$) δ=8.096 (dd, 0.70H, *J*=7.9 and

1.2 Hz), 8.036 (dd, 0.30H, J=7.5 and 1.2 Hz), 7.533 (td, 1H, J=7.5 and 1.2 Hz), 7.377 (t, 1H, J=7.5 Hz), and 7.269 (d, J=7.5 Hz); ^{19}F NMR($CDCl_3$) δ=19.09 (s, 0.30F) and 17.83 (s, 0.70F); IR(neat) 3070, 3030, 2980, 2910, 1684, 1600, 1480, 1454, 1432, 1370, 1300, 1268, 1240, 1222, 1206, 1180, 1162, and 1132 cm^{-1}; MS m/z 262(M^++2, 17), 260(M^+, 53), 234(21), 232 (60), 225(20), 197(42), 187(54), 146(16), 128(52), 127(17), 118(37), 91(19), 90(100), 99(78), 88(12), 78(12), 77(32), 76(20), 75(28), 74(15), 73(25), 65(12), 64(37), 63(81), 62(28), 57(12), 51(89), and 50(58). Found: C, 55.24; H, 3.13%. Calcd for $C_{12}H_8ClF_3O$: C, 55.30; H, 3.09%.

3-Chloro-4,4,4-trifluoro-1-(2-furyl)-2-buten-1-one (8). As described above, a mixture of **7** (557 mg, 3.06 mmol), **1** (11.45 g, 61.1 mmol), CuCl (303 mg, 3.06 mmol), and 4A Molecular Sieves (3.01 g) in DMF (2 ml) was treated and workup gave **8** as a pale yellow solid; 447 mg (70%); mp 54—56 °C; ^{1}H NMR($CDCl_3$) δ=7.66 (m, 1H), 7.51 (s, 1H), 7.32 (d, 1H, J=3.7Hz), and 6.61 (dd, 1H, J=3.7 and 1.5 Hz); ^{19}F NMR($CDCl_3$) δ=12.58 (s, 0.03F) and 7.25 (s, 0.97F); IR(KBr) 3280, 3140, 3070, 1672, 1626, 1562, 1466, 1395, 1342, 1290, 1275, 1244, 1206, 1164, and 1150 cm^{-1}; MS m/z 226(M^++2, 10), 224(M^+, 27), 198(10), 196(30), 157(11), 95(100), and 69(25). Found: C, 42.76; H, 1.83%. Calcd for $C_8H_4ClF_3O_2$: C, 42.79; H, 1.80%.

(1*E*,4*Z*)-5-Chloro-6,6,6-trifluoro-1-phenyl-1,4-hexadien-3-one (11). As described above, a mixture of **10** (446 mg, 2.04 mmol), **1** (3.75 g, 20.0 mmol), CuCl (198 mg, 2.00 mmol), and 4A Molecular Sieves (2.00 g) in DMF (3 ml) was treated and workup gave **11** as a pale yellow solid; 314 mg (59%); Mp<30 °C; ^{1}H NMR($CDCl_3$) δ=7.65 (d, 1H, J=16.4 Hz), 7.3—7.9 (m, 5H), 7.17 (m, 1H), and 6.88 (d, 1H, J=16.4Hz); ^{19}F NMR($CDCl_3$) δ=8.79(s); IR(KBr) 3070, 3060, 1660, 1640, 1630, 1600, 1580, 1500, 1456, 1336, 1300, 1274, 1200, 1174, and 1140 cm^{-1}; MS m/z 262(M^++2, 18), 260(M^+, 49), 259(76), 197 (14), 157(10), 131(35), 128(15), 103(74), 102(22), 78(13), 77(100), 76(13), 75(18), 63(32), 51(38), and 50(38). Found: C, 55.20; H, 3.09%. Calcd for $C_{12}H_8ClF_3O$: C, 55.30; H, 3.09%.

3-Chloro-4,4,4-trifluoro-1,2-diphenyl-2-buten-1-one (13). As described above, a mixture of **12** (329 mg, 1.23 mmol), **1** (4.61 g, 24.6 mmol), CuCl (122 mg, 1.23 mmol), and 4A Molecular Sieves (1.23 g) in DMF (2 ml) was treated and after treatment with DBN (153 mg, 1.23 mmol) in Et_2O (3 ml), workup gave **13** as a colorless solid; 55 mg (14%); Mp 43—45 °C; ^{1}H NMR (500 MHz) ($CDCl_3$) δ=8.008 (d, 0.88H, J=7.9 Hz), 7.944 (d, 0.12H, J=7.3 Hz), 7.624 (t, 0.88H, J=7.3 Hz), 7.577 (t, 0.12H, J=7.3 Hz), and 7.45—7.33(m, 5H); ^{19}F NMR($CDCl_3$) δ=16.83 (s, 0.88F) and 14.05 (s, 0.12F); IR(KBr) 3060, 1678, 1598, 1580, 1492, 1450, 1300, 1250, 1184, and 1140 cm^{-1}; MS m/z 312(M^++2, 2), 310(M^+, 5), 106(14), 105(100), 77(50), 51(33), and 50(20). Found: C, 62.10; H, 3.52%. Calcd for $C_{16}H_{10}ClF_3O$: C, 61.85; H, 3.24%.

5-Chloro-6,6,6-trifluoro-2,2-dimethyl-4-hexen-3-one (15). As described above, a mixture of **14** (437 mg, 2.54 mmol), **1** (9.52 g, 50.8 mmol), CuCl (251 mg, 2.54 mmol), and 4A Molecular Sieves (2.5 g) in DMF (3 ml) was treated and workup gave **15** as colorless oil; 65 mg (12%); ^{1}H NMR($CDCl_3$) δ=7.21 (d, 1H, J=0.9 Hz) and 1.20 (s, 9H); ^{19}F NMR($CDCl_3$) δ=12.61 (s, 0.12F) and 7.43 (s, 0.88F); IR(neat) 2970, 2940, 2910, 2860, 1704, 1622, 1474, 1464, 1390, 1364, 1280, 1246, 1180, and 1150 cm^{-1}; MS m/z 157($M^+-C_4H_9$, 3),[16] 101(25), 59(100), 57(63), and 56(50). Found: C, 44.49; H, 4.96%. Calcd for $C_8H_{10}ClF_3O$: C, 44.78; H, 4.70%.

2-(1-Chloro-2,2,2-trifluoroethylidene)cyclopentanone (17). As described above, a mixture of **16** (160 mg, 1.02 mmol), **1** (3.77 g, 20.1 mmol), CuCl (101 mg, 1.02 mmol), and 4A Molecular Sieves (1.03 g) in DMF (2 ml) was treated and workup gave **17** as pale yellow oil; 41 mg (21%); ^{1}H NMR (500 MHz)($CDCl_3$) δ=3.100 (tq, 0.88H, J=7.1 and 3.3 Hz), 2.915 (tq, 0.12H, J=7.5 and 2.8 Hz), 2.551 (t, 0.12H, J=7.8 Hz), 2.479 (t, 0.88H, J=8.0 Hz), and 2.08—1.96 (m, 1H); ^{19}F NMR($CDCl_3$) δ=18.09 (t, 0.12F, J=3 Hz) and 14.19 (t, 0.88F, J=3 Hz); IR(neat) 2960, 2890, 1750, 1636, 1476, 1456, 1296, 1280, 1220, 1200, 1184, 1176, and 1150 cm^{-1}; MS m/z 200(M^++2, 2), 198(M^+, 6), 149(31), 97(10), 85(14), 83(15), 81(11), 73 (18), 71(25), 70(12), 69(25), 67(11), 65(11), 57(67), 56(24), 55(51), 53(11), 51(12), and 41(100). Found: C, 42.27; H, 2.98%. Calcd for $C_7H_6ClF_3O$: C, 42.34; H, 3.05%.

3-(1-Chloro-2,2,2-trifluoroethylidene)bicyclo[2.2.1]-heptan-2-one (20). As described above, a mixture of **19** (435 mg, 2.39 mmol), **1** (8.94 g, 47.7 mmol), CuCl (236 mg, 2.38 mmol), and 4A Molecular Sieves (2.40 g) in DMF (3 ml) was treated and after treatment with DBN (297 mg, 2.39 mmol) in THF (2 ml), workup gave **20** as pale yellow oil; 170 mg (32%); ^{1}H NMR($CDCl_3$) δ=3.5—4.0 (m, 2H), 2.7—3.0 (m, 2H), and 1.3—2.3 (m, 6H); ^{19}F NMR($CDCl_3$) δ=14.32 (s, 0.42F) and 11.99 (s, 0.58F); IR(neat) 2960, 2890, 1750, 1636, 1476, 1456, 1296, 1280, 1220, 1184, 1176, and 1150 cm^{-1}; MS m/z 226(M^++2, 9), 224(M^+, 25), 196(35), 161(79), 141(54), 91(46), 85(13), 79(40), 77(18), 75(25), 69(18), 68 (70), 67(100), 66(79), 63(27), 55(63), 54(13), 53(20), and 51(38). Found: C, 48.12; H, 3.58%. Calcd for $C_9H_8ClF_3O$: C, 48.13; H, 3.59%.

Hexyl 3-Chloro-4,4,4-trifluoro-2-butenoate (22). As described above, a mixture of **21** (131 mg, 0.61 mmol), **1** (2.27 g, 12.1 mmol), CuCl (60 mg, 0.61 mmol), and 4A Molecular Sieves (0.6 g) in DMF (3 ml) was treated and workup gave **22** as pale yellow oil; 24 mg (15%); ^{1}H NMR($CDCl_3$) δ=6.67 (d, 1H, J=0.7 Hz), 4.16 (t, 2H, J=7 Hz), and 1.1—0.7 (m, 11H); ^{19}F NMR ($CDCl_3$) δ=7.48 (s, 0.21F) and 7.13 (s, 0.79F); IR(neat) 3070, 2960, 2930, 2860, 1740, 1658, 1464, 1380, 1320, 1280, 1254, 1186, and 1140 cm^{-1}; MS m/z 223(M^+—Cl, 0.5),[16] 215(0.6), 201(1), 159(25), 157(78), 84(52), 83(18), 69(43), 55(100), and 54(48). Found: C, 46.25; H, 5.61%. Calcd for $C_{10}H_{14}ClF_3O_2$: C, 46.43; H, 5.46%.

Determination of GLC Yields: After the elimination reaction, a comparable amount of adamantane was added to the ethereal solution as an internal standard before the final workup, and then the mixture was analyzed on a GLC by comparison of relative sensitivity with an authentic sample of an *E*- and *Z*-mixture.

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