A Novel Fluoride Ion Mediated Olefination of Electron-Deficient Aryl Ketones by Alkanesulfonyl Halides

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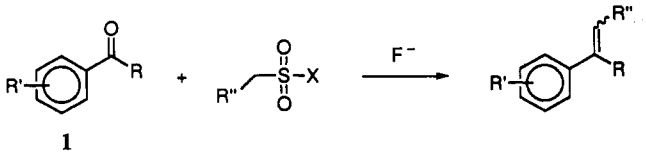
Alkali metal fluorides are well known in the literature to behave as bases, and this property has been utilized to effect a variety of organic transformations.[1] In the course of research efforts aimed at the synthesis of new fluoroalkylarenes for evaluation as potential monomers and intermediates for advanced tribological systems, we discovered a novel fluoride ion mediated olefination of electron-deficient aryl ketones, resulting in arylalkenes. This transformation involves reaction of an aryl ketone **1** in the presence of fluoride ion with an alkanesulfonyl halide having an α-hydrogen (Scheme 1). The use of fluoride ion as a base to effect Knoevenagel[1] or Wittig-type[2] olefination reactions has been reported. However, to our knowledge alkanesulfonyl halides having α-hydrogens have never been reported to react with carbonyl compounds in the presence of fluoride ion, or any other base for that matter, in such a manner as to result in olefination. This reaction is somewhat related to the elimination reactions of β-hydroxy sulfones to give olefins.[3] Taking into consideration that a variety of alkanesulfonyl halides are available commercially at relatively low cost, this novel reaction could potentially offer an economical alternative to conventional olefination reactions. We report herein some preliminary results regarding the scope and limitations of this transformation, including some mechanistic considerations.

Discussion and Results

The reaction described herein involves heating together an aryl ketone, an alkanesulfonyl halide having an α-hydrogen, and a fluoride ion source (e.g., KF) in a solvent such as DMF. We have not yet optimized the conditions for this transformation, but have found that excess amounts of fluoride and alkanesulfonyl halide relative to the aryl ketone are required and have typically employed these reactants in a relative molar ratio of 4:2.5:1, respectively. Best yields were obtained using spray-dried KF as the fluoride ion source. However, we have not carried out a formal evaluation of other available fluoride ion sources. Also, a catalytic amount of 18-crown-6 was found to enhance the reaction. DMF was used as solvent in most cases, although a few runs conducted in 1-methyl-2-pyrrolidinone (NMP) and 1,3-dimethyl-2-imidazolidinone (DMI) gave comparable results. We have found that this reaction works particularly well with aryl perfluoroalkyl ketones, as is shown with compounds **1a-1d** (Table 1, entries 1-5). Thus, when the reaction was performed with MsCl at 110 °C, these compounds were transformed to the corresponding α-(perfluoroalkyl)styrenes **2-6** readily and cleanly in very high isolated yields. Compound **1e**, carrying a CF_2Cl group adjacent to the carbonyl, also underwent this transformation in relatively high yield (Table 1, entry 6), but this was accompanied by halide exchange. An identical run on **1e** with prolonged heating (Table 1, entry 7) gave only compound **2**. While these data indicated that styrene product **7** undergoes halide exchange during the course of the reaction, it was evident that starting material **1e** does as well, since HPLC and GC/MS monitoring during the course of the reaction revealed the presence of **1a**.

Scheme 1



1

It appears that this transformation does not work well with unactivated ketones. For instance, acetophenone **1f** did not undergo olefination with MsCl at 110 °C, and at 153 °C (refluxing DMF) only 19% yield of α-methylstyrene (**8**) was obtained (Table 1, entries 8 and 9). However, compound **1g**, bearing a *m*-CF_3 substituent, did undergo olefination to the corresponding styrene **9** in reasonably good yield. Nitro- and chloroacetophenones **1h-1k** gave moderate to poor yields of the corresponding styrenes **10-13** (Table 1, entries 11-14). The reaction also appears to be sluggish with benzophenones, particularly in the absence of electron-withdrawing groups. Thus, benzophenone (**1m**) was practically unreactive even at 170 °C, whereas *m,m'*-bis(trifluoromethyl)benzophenone (**1n**) did afford the corresponding product **15** in 39% yield (Table 1, entries 15-17).

A few alkanesulfonyl halides other than MsCl were also investigated. Thus, $ClCH_2SO_2Cl$ reacted with **1a** to give **16** in excellent yield (Table 1, entry 18), with an *E:Z* isomeric ratio of approximately 54:46 by GC. The isomers were not separated, but their identity was determined by comparison of the ^{19}F NMR spectrum of the mixture with published ^{19}F NMR spectra of the individual *E*- and *Z*-isomers.[4] The reaction of $PhCH_2SO_2Cl$ with **1a** afforded stilbene **17** in moderate yield (Table 1, entry 19), with an *E:Z* isomeric ratio of approximately 84:16 by GC. The identity of the isomers in this case was determined by comparison of the ^{19}F NMR spectrum of the mixture with the ^{19}F NMR spectrum of an authentic sample (*E:Z* = 86:14) prepared by the Wittig reaction of benzyltriphenylphosphonium chloride and **1a** following the published procedure of Ruban et al.[2] Using $PhCH_2SO_2F$ (Table 1, entry 20) instead of $PhCH_2SO_2Cl$ in the reaction with **1a** resulted in a significantly higher yield of **17**, yet with an identical isomer ratio.

The mechanism of this reaction is not fully understood at this time. We initially suspected that the origin of the new olefinic carbon was the DMF solvent, but this was quickly rejected after conducting the reaction in DMF-d_7 and observing no deuterium incorporation into the

(1) For reviews see: Clark, J. H. *Chem. Rev.* **1980**, *80*, 429-452. Yakobson, G. G.; Akhmetova, N. E. *Synthesis* **1983**, 169-184.
(2) See, for instance: Ruban, G.; Zobel, D.; Kossmehl, G.; Nuck, R. *Chem. Ber.* **1980**, *113*, 3384-3388.
(3) Julia, M.; Paris, J. M. *Tetrahedron Lett.* **1973**, 4833. Kocienski, P. J. *Chem. Ind.* **1981**, 548.
(4) Morken, P. A.; Bachand, P. C.; Swenson, D. C.; Burton, D. J. *J. Am. Chem. Soc.* **1993**, *115*, 5430.

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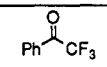
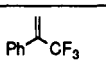
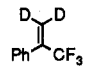
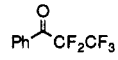
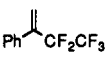
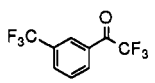
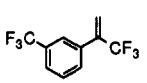
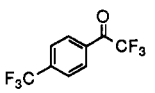
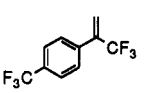
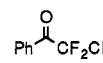
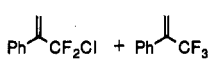
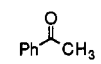
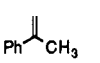
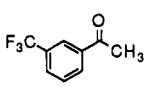
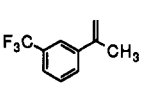
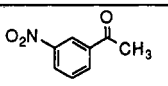
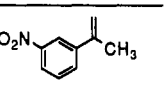
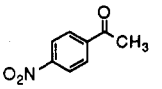
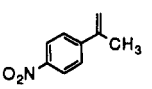
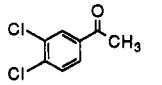
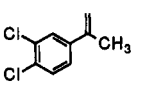
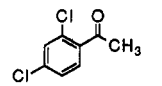
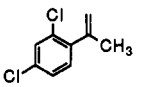
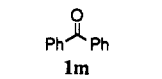
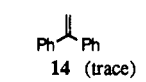
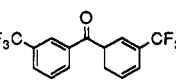
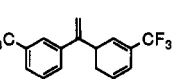
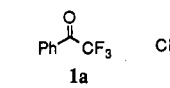
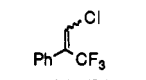
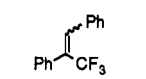
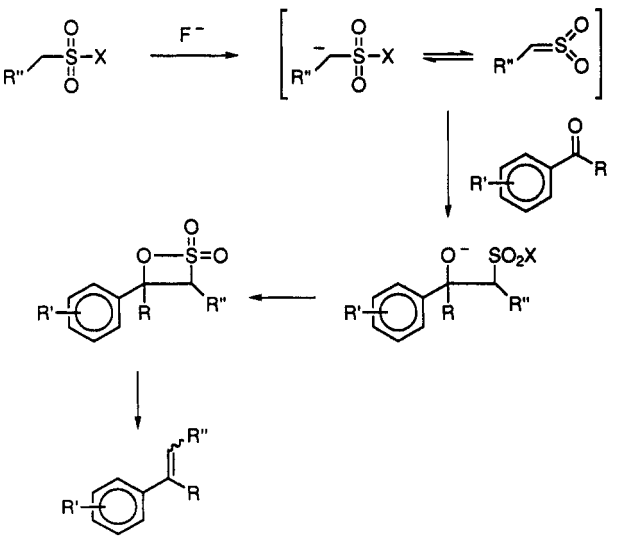
Table 1. Reactions of Aryl Ketones with Alkanesulfonyl Halides and KF in DMF

entry	ketone	sulfonyl halide	temp (°C)	time (h)	product (yield,[a] %)
1.	 **1a**	CH_3SO_2Cl	110	5	 **2** (92)
2.		CD_3SO_2Cl	110	5	 **3** (92)
3.	 **1b**	CH_3SO_2Cl	110	5	 **4** (94)
4.	 **1c**		110	5	 **5** (90)
5.	 **1d**		110	5	 **6** (91)
6.	 **1e**		110	5	 **7** (64) **2** (23)
7.			110	24	**2** (82)
8.	 **1f**		110	24	 **8** (trace)
9.			153	24	**8** (19)
10.	 **1g**		153	20	 **9** (58)
11.	 **1h**		153	20	 **10** (30)
12.	 **1i**		153	20	 **11** (37)
13.	 **1j**		153	20	 **12** (46)
14.	 **1k**		153	20	 **13** (39)
15.	 **1m**		153	48	 **14** (trace)
16.			170[b]	48	**14** (3)
17.	 **1n**		153	24	 **15** (39)
18.	 **1a**	$ClCH_2SO_2Cl$	153	20	 **16** (84)[c]
19.		$PhCH_2SO_2Cl$	153	20	 **17** (48)[d]
20.		$PhCH_2SO_2F$	153	20	**17** (68)

[a] Isolated (unoptimized). [b] 1-Methyl-2-pyrrolidinone used as solvent. [c] *E*:*Z* ≈ 54:46 (by GC). [d] *E*:*Z* ≈ 84:16 (by GC).

product. A complementary experiment using MsCl-d_3 (Table 1, entry 2) indicated that the sulfonyl α-carbon becomes the new olefinic carbon in the product. This was confirmed by subsequent experiments (Table 1, entries 18–20). Consequently, we consider the mechanism of Scheme 2 to be plausible. This proposed mechanism entails deprotonation of the alkanesulfonyl halide by F^- to give a carbanion or sulfene[5] intermediate, which undergoes nucleophilic addition to the ketone to give a β-sultone, followed by elimination of SO_3 (e.g., as DMF·SO_3). A mechanism similar to this has been invoked by Corey et al. in the olefination of aldehydes and ketones with α-lithio sulfinamides, which involves the thermolysis of the intermediate β-hydroxy sulfinamides with loss of SO_2.[6] Furthermore, alkanesulfonyl halides have been reported to react with electrophilic (usually highly halogenated) aldehydes and ketones in the presence of Et_3N to give β-sultones.[7] It is of interest to mention that while carrying out the experiment of Table 1, entry 19, we

Scheme 2



observed (by HPLC and GC/MS) at an early stage the emergence of $PhCH_2SO_2F$ during the course of the reaction. This might be indicative of an initial displacement by F^- on the sulfonyl chloride moiety to give the corresponding sulfonyl fluoride. Consequently, it is possible that RCH_2SO_2F is the actual reactive species in the new olefination reaction, which could explain the need for

(5) For reviews on sulfene chemistry see: (a) King, J. F.; Rajendra, R. In *The Chemistry of Sulfonic Acids, Esters and Their Derivatives*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1991; pp 697–766. (b) Opitz, G. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 107–123.

(6) Corey, E. J.; Durst, T. *J. Am. Chem. Soc.* **1966**, *88*, 5656. Corey, E. J.; Durst, T. *J. Am. Chem. Soc.* **1968**, *90*, 5548 and 5553.

(7) Truce, W. E.; Liu, L. K. *Chem. Ind. (London)* **1969**, 457. Truce, W. E.; Liu, L. K. *Tetrahedron Lett.* **1970**, 517. Norell, J. R. *J. Chem. Soc., Chem. Commun.* **1969**, 1291. Borrmann, D.; Wegler, R. *Chem. Ber.* **1966**, *99*, 1245. King, J. F. *Acc. Chem. Res.* **1975**, *8*, 10.

excess KF, since an additional equivalent of F^- is consumed during the halogen-exchange process. Another observation that might implicate RCH_2SO_2F as the actual reactive species is the fact that use of $PhCH_2SO_2F$ instead of $PhCH_2SO_2Cl$ (Table 1, entries 19 and 20) leads to significantly higher yield of product. It is interesting to note that the new transformation is essentially clean; typically, the high-yield reactions lead to almost pure product, whereas the low-yield reactions give mixtures of alkene and starting ketone.

In summary, we have described herein a novel olefination reaction between alkanesulfonyl halides having an α-hydrogen and aryl ketones in the presence of fluoride ion. This transformation works best with electron-deficient aryl ketones, especially perfluoroalkyl aryl ketones. We believe that this transformation may also be extended to other reactive carbonyl systems such as aldehydes. Indeed, preliminary GC/MS data on a few microscale experiments with aryl aldehydes have shown formation of the corresponding styrenes. Taking into consideration the commercial availability of a variety of relatively inexpensive alkanesulfonyl halides, this novel reaction could potentially offer an economical alternative to conventional olefination reactions, especially for the synthesis of perfluoroalkyl-substituted specialty chemicals, monomers, and biologically active molecules.

Experimental Section

General. All reactions were performed under an atmosphere of nitrogen in oven-dried glassware. Anhydrous, high-purity DMF and 1-methyl-2-pyrrolidinone (NMP), and all of the aryl ketones and alkanesulfonyl halides, were obtained from commercial sources and used as obtained. Spray-dried KF (99%, Aldrich) was used. All reactions were monitored by HPLC on an HP 1090 instrument (ODS-Hypersil column; HP) and by GC/MS on an HP 5890 gas chromatograph (20-m DB-5 capillary column; J & W) interfaced with an HP 5989A MS engine detector. ^1H, ^{13}C, and ^{19}F NMR spectra were obtained in $CDCl_3$ on a Varian VXR300 instrument operating at 299.96, 75.43, and 282.20 MHz, respectively. Chemical shifts for ^1H and ^{13}C NMR spectra are reported in ppm downfield from TMS. Chemical shifts for ^{19}F NMR spectra are reported in ppm upfield from $CFCl_3$, using C_6F_6 as an internal standard (−162.9 ppm relative to $CFCl_3$). Flash column chromatography[8] was performed on silica gel 60 (230–400 mesh, Merck). Elemental analyses and high-resolution mass spectral measurements were performed by the Analytical Sciences Laboratory, Dow Chemical Co. CAUTION: The following reactions might involve the generation of SO_3 and HF and should be conducted in an efficient fume hood.

Typical Procedure for the Reaction of Aryl Ketones with Alkanesulfonyl Halides and KF. 2-Phenyl-3,3,3-trifluoropropene (2). A *mechanically* stirred mixture of **1a** (25 g, 0.14 mol), KF (33 g, 0.57 mol), 18-crown-6 (1.9 g, 7.2 mmol), and DMF (100 mL) was treated with MsCl (28 mL, 0.36 mol) dropwise over 5 min. The temperature was then raised gradually, resulting in a mildly exothermic reaction at around 70–80 °C. The mixture was subsequently heated at 110 °C. The reaction was essentially complete after 3 h, but heating at 110 °C was continued for a total of 5 h. Workup consisted of partitioning the mixture between H_2O (200 mL) and pentane (300 mL), washing the pentane phase with saturated aqueous $NaHCO_3$ solution, drying ($MgSO_4$), and removal of most of the pentane by rotary evaporation at 40–50 °C and atmospheric pressure. Purification of the residual oil by short path fractional distillation afforded 22.7 g (92%) of compound **2** as a colorless oil: bp 150–153 °C (1 atm) (lit.[9] bp 148–151 °C). This compound has been reported several times in the literature,[9,10] but with incomplete NMR spectral characterization. ^1H NMR δ 5.70 (q, J_{HCCCF} = 1.7 Hz, 1 H), 5.91 (q, J_{HCCCF} = 1.4 Hz, 1 H), 7.38 (m, 5 H); ^{13}C NMR δ 120.38 (q, J_{CCCF} = 5.7 Hz), 123.59 (q, J_{CF} = 273.9 Hz), 127.55, 128.69, 129.09, 133.88, 139.43 (q, J_{CCF} = 30.3 Hz); ^{19}F NMR δ −65.64 (s); HRMS calcd for $C_9H_7F_3$ 172.0500, found 172.0501.

1,1-Dideuterio-2-phenyl-3,3,3-trifluoropropene (3). CD_3SO_2Cl was prepared from CD_3SO_3D (Cambridge Isotope Laboratories) and $SOCl_2$.[11] Reaction of CD_3SO_2Cl and **1a** as described in the general procedure above afforded, after purification by flash column chromatography (pentane–CH_2Cl_2 (5:1)), compound **3** as a colorless oil, identical by GC, HPLC, and TLC to compound **2** above. Also, compound **3** gave NMR spectral data identical to those of **2** above, with the following exceptions: ^1H NMR signals at 5.70 and 5.91 absent, as expected; ^{13}C NMR signal at 120.38 complex m (=CD_2), as expected. MS *m/e* 174 (M^+).

3,3,4,4,4-Pentafluoro-2-phenyl-1-butene (4): colorless oil, purified by fractional distillation, bp 154–157 °C (1 atm); ^1H NMR δ 5.72 (t, J_{HCCCF} = 1.6 Hz, 1 H), 5.97 (t, J_{HCCCF} = 1.5 Hz, 1 H), 7.34 (m, 5 H); ^{13}C NMR δ 113.25 (tq, J_1 = 254.5 Hz, J_2 = 37.9 Hz), 119.34 (qt, J_1 = 286.7 Hz, J_2 = 38.3 Hz), 124.61 (t, J_{CCCF} = 8.4 Hz), 128.52, 128.74, 129.01, 135.11, 139.00 (t, J_{CCF} = 19.8 Hz); ^{19}F NMR δ −113.97 (s), −83.64 (s); HRMS calcd for $C_{10}H_7F_5$ 222.0478, found 222.0463.

2-[3-(Trifluoromethyl)phenyl]-3,3,3-trifluoropropene (5). Known compound,[9,10b] isolated as a colorless oil after purification by fractional distillation: bp 156–158 °C (1 atm) (lit.[9] bp 157–158 °C); ^1H NMR δ 5.83 (q, J_{HCCCF} = 1.6 Hz, 1 H), 6.05 (q, J_{HCCCF} = 1.4 Hz, 1 H), 7.59 (m, 4 H), which is in agreement with the literature.[10b] The ^{13}C NMR and ^{19}F NMR spectra of this compound have not been reported in the literature. ^{13}C NMR δ 121.96 (q, J_{CCCF} = 5.6 Hz), 123.32 (q, J_{CF} = 273.7 Hz), 124.14 (q, J_{CF} = 272.2 Hz), 124.59 (q, J_{CCCF} = 3.6 Hz), 125.96 (q, J_{CCCF} = 3.7 Hz), 129.37, 130.96, 131.60 (q, J_{CCF} = 32.5 Hz), 134.80, 138.48 (q, J_{CCF} = 30.8 Hz); ^{19}F NMR δ −65.91 (s), −63.81 (s).

2-(4-Trifluoromethylphenyl)-3,3,3-trifluoropropene (6): colorless oil, purified by flash column chromatography (pentane–CH_2Cl_2, 5:1); ^1H NMR δ 5.83 (q, J_{HCCCF} = 1.6 Hz, 1 H), 6.03 (q, J_{HCCCF} = 1.4 Hz, 1 H), 7.59 (m, 4 H); ^{13}C NMR δ 122.15 (q, J_{CCCF} = 5.6 Hz), 123.35 (q, J_{CF} = 273.7 Hz), 124.23 (q, J_{CF} = 271.9 Hz), 125.81 (q, J_{CCCF} = 3.6 Hz), 128.124, 131.52 (q, J_{CCF} = 32.8 Hz), 137.48, 138.57 (q, J_{CCF} = 30.7 Hz); ^{19}F NMR δ −65.74 (s), −63.85 (s). Anal. Calcd for $C_{10}H_6F_6$: C, 50.01; H, 2.52. Found: C, 49.94; H, 2.48.

2-[3-(Trifluoromethyl)phenyl]propene (9). Known compound,[12,13] isolated as a colorless oil after purification by flash column chromatography (pentane–CH_2Cl_2, 5:1): ^1H NMR δ 2.15 (s, 3 H), 5.16 (s, 1 H), 5.40 (s, 1 H), 7.40 (m, 1 H), 7.48 (m, 1 H), 7.60 (m, 1 H), 7.69 (s, 1 H), which is in agreement with the literature;[13] ^{19}F NMR δ −63.70 (s).

2-(3-Nitrophenyl)propene (10). Known compound,[14] isolated as a faintly yellowish oil after purification by flash column chromatography (CH_2Cl_2). Although this compound has been reported several times in the literature, no NMR characterization has been published: ^1H NMR δ 2.21 (s, 3 H), 5.24 (s, 1 H), 5.49 (s, 1 H), 7.48 (m, 1 H), 7.77 (m, 1 H), 8.09 (m, 1 H), 8.27 (m, 1 H); ^{13}C NMR δ 21.54, 115.04, 120.34, 122.11, 129.18, 131.41, 141.29, 142.92, 138.52.

2-(4-Nitrophenyl)propene (11). Known compound,[14a,15] obtained as a yellow solid after purification by recrystallization

(8) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(9) Tarrant, P.; Taylor, R. E. *J. Org. Chem.* **1959**, *24*, 238.
(10) (a) Jiang, B.; Xu, Y. *J. Org. Chem.* **1991**, *56*, 7336. (b) Ito, H.; Renaldo, A. F.; Ueda, M. *Macromolecules* **1989**, *22*, 45. (c) Ueda, M.; Ito, H. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 89. (d) Koshy, K. M.; Roy, D.; Tidwell, T. T. *J. Am. Chem Soc.* **1979**, *101*, 357.
(11) Hearst, P. J.; Noller, R. C. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 571.
(12) Bachman, G. B.; Lewis, L. L. *J. Am. Chem Soc.* **1947**, *69*, 2022.
(13) Richardson, W. H.; Stiggall-Estberg, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 4173.
(14) (a) Okamoto, Y.; Brown, H. C. *J. Am. Chem. Soc.* **1957**, *79*, 1909. (b) Kornblum, N.; Davies, T. M.; Earl, G. W.; Holy, N. L.; Manthey, J. W.; Musser, M. T.; Swiger, R. T. *J. Am. Chem. Soc.* **1968**, *90*, 6219. (c) Morris, L. R. U. S. Patent 3,336,401, Aug 15, 1967, to Dow Chemical Co.; *Chem. Abstr.* **1967**, *67*, 108431p.
(15) (a) Hall, R. H.; Jordaan, A.; Lourens, G. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 38. (b) Brubacher, G.; Suter, E. *Helv. Chim. Acta* **1950**, *33*, 256. (c) Fraenkel, G.; Geckle, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 2869. (d) Schenk, C.; de Boer, T. J. *Tetrahedron* **1979**, *35*, 147.

from MeOH: mp 50–51 °C (lit.[14a] mp 51–52.5 °C); ^{1}H NMR δ 2.19 (s, 3 H), 5.29 (s, 1 H), 5.52 (s, 1 H), 7.59 (m, 2 H), 8.17 (m, 2 H), which is in agreement with the literature;[13,15a] ^{13}C NMR δ 21.57, 116.33, 123.58, 126.26, 141.66, 147.18, 147.71.

2-(3,4-Dichlorophenyl)propene (12). Known compound,[16] obtained as a colorless oil after purification by flash column chromatography (pentane–CH_2Cl_2, 5:1). Although this compound has been reported several times in the literature, no NMR characterization has been published: ^{1}H NMR δ 2.10 (s, 3 H), 5.13 (s, 1 H), 5.36 (s, 1 H), 7.24–7.51 (m, 3 H); ^{13}C NMR δ 21.59, 114.04, 124.86, 127.60, 130.13, 131.35, 132.48, 141.28, 141.40.

2-(2,4-Dichlorophenyl)propene (13). Known compound,[16a,17] obtained as a colorless oil after purification by flash column chromatography (pentane–CH_2Cl_2, 5:1). Although this compound has been reported several times in the literature, no NMR characterization has been published: ^{1}H NMR δ 2.08 (s, 3 H), 4.96 (s, 1 H), 5.23 (s, 1 H), 7.10–7.36 (m, 3 H); ^{13}C NMR δ 22.75, 116.82, 126.97, 129.47, 130.60, 132.78, 133.34, 141.36, 143.35.

1,1-Bis[3-(trifluoromethyl)phenyl]ethylene (15): faintly yellowish oil, purified by flash column chromatography (pentane–CH_2Cl_2, 5:1); ^{1}H NMR δ 5.59 (s, 2 H), 7.45 (m, 4 H), 7.60 (m, 4 H); ^{13}C NMR δ 117.05, 124.17 (q, J_{CF} = 272.4 Hz), 124.93, 125.00, 129.00, 131.23 (q, J_{CCF} = 31.7 Hz), 131.51, 141.64, 148.00; ^{19}F NMR δ −63.68 (s). Anal. Calcd for $C_{16}H_{10}F_6$: C, 60.77; H, 3.19. Found: C, 60.72; H, 3.24.

1-Chloro-2-phenyl-3,3,3-trifluoropropene (16): colorless oil, purified by flash column chromatography (pentane–CH_2Cl_2, 5:1); unseparated mixture, *E*:*Z* = 54:46; ^{19}F NMR δ −63.69 (s) (*E*-isomer), −58.26 (s) (*Z*-isomer), which is in agreement with the literature.[4] Anal. Calcd for $C_9H_6ClF_3$: C, 52.32; H, 2.93. Found: C, 52.24; H, 2.88.

1,2-Diphenyl-3,3,3-trifluoropropene (17). Obtained as an unseparated mixture of *E*- and *Z*-isomers, both of which are known compounds:[2] faintly yellowish oil, purified by filtration through 2 in. of flash-grade silica gel, eluting with hexane; *E*:*Z* = 84:16; ^{19}F NMR δ −66.89 (s) (*E*-isomer), −57.28 (s) (*Z*-isomer).

(16) (a) Bachman, G. B.; Finholt, R. W. *J. Am. Chem. Soc.* **1948**, *70*, 623. (b) Okumoto, T.; Takeuchi, T. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1717.
(17) Nyquist, R. A. *Appl. Spectrosc.* **1986**, *40*, 196.