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Preparation of the *E*- and *Z*-heptafluorobutenyl-2-zinc reagent by zinc-induced dehalogenation/metallation of 2,2-dibromo-octafluorobutane

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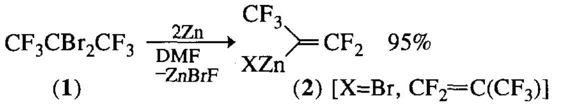
Abstract

The $AlCl_3$-catalyzed isomerization of $CF_3CFBrCFBrCF_3$ afforded $CF_3CF_2CBr_2CF_3$, which upon treatment with 2 equiv. zinc in DMF underwent dehalogenation/metallation to afford a 1:1 mixture of *E*- and *Z*-$CF_3CF{=}C(ZnX)CF_3$ in 96% ^{19}F NMR yield. The zinc reagent exhibited poor thermal stability in DMF and completely decomposed by a β-elimination route in 24 h at 60 °C. However, the zinc reagent prepared from *E*- and *Z*-$CF_3CF{=}ClCF_3$ in triglyme showed enhanced thermal stability and gave *E*- and *Z*-*p*-$NO_2C_6H_4C(CF_3){=}CFCF_3$ in a palladium-catalyzed coupling reaction with *p*-$NO_2C_6H_4I$.

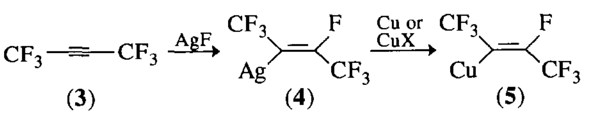
Introduction

We recently reported [1, 2] the zinc-induced metallation/dehalogenation of 2,2-dibromohexafluoropropane (**1**) as a convenient, high-yield route to pentafluoropropenyl-2-zinc (**2**) [eqn. (1)].



(1)

The significance of this work was the introduction of the zinc moiety into the *internal* position of the alkene: the majority of reported fluorinated organometallic reagents have been metallated at the *terminal* position [3]. Addition of silver fluoride to tetrafluoroallene affords pentafluoropropenyl-2-silver [4]. Silver fluoride also adds to hexafluoro-2-butyne (**3**) to generate *E*-$CF_3CF{=}C(Ag)CF_3$ (**4**) [5], which is a precursor to *E*-$CF_3CF{=}C(Cu)CF_3$ (**5**) [6] [eqn. (2)].



(2)

However, the synthetic applicability of these methods is severely limited by the availability and cost of the starting materials. Also, the latter method cannot be utilized to prepare *Z*-$CF_3CF{=}C(Ag)CF_3$. Jiang and Xu have reported the synthesis and palladium-catalyzed coupling reactions of the partially fluorinated internal zinc reagent $CF_3(ZnX)C{=}CH_2$ with aryl [7] and vinyl [8] halides. The present paper describes the preparation of *E*- and *Z*-$CF_3CF{=}C(ZnX)CF_3$ (**9a, b**) by the zinc-induced dehalogenation/metallation of $CF_3CF_2CBr_2CF_3$ (**8**).

Results and discussion

The starting material for this study, $CF_3CF_2CBr_2CF_3$ (**8**), was prepared [9] by the aluminum chloride-catalyzed rearrangement of 2,3-dibromo-octafluorobutane (**7**) [eqn. (3)].

$$\underset{(6)}{CF_3CF{=}CFCF_3} \xrightarrow[h\nu/\Delta \; 76\%]{Br_2} \underset{(7)}{CF_3CFBrCFBrCF_3} \xrightarrow[71\%]{AlCl_3} \underset{(8)}{CF_3CF_2CBr_2CF_3} \qquad (3)$$

Extension of our dehalogenation/metallation methodology to $CF_3CF_2CBr_2CF_3$ (**8**) was directed at three questions: (1) the regiochemistry of elimination in **8**; (2) if the elimination is internal, the stereochemical consequences of this elimination; and (3) the thermal stability and coupling ability of the more hindered internal zinc reagent.

Treatment of **8** with 2 equiv. zinc metal in DMF gave a 1:1 ratio of *E*- and *Z*-$CF_3CF{=}C(ZnX)CF_3$ (**9**) [X = Br, $CF_3CF{=}C(CF_3)$] in 96% yield, as determined by ^{19}F NMR analysis [eqn. (4)].

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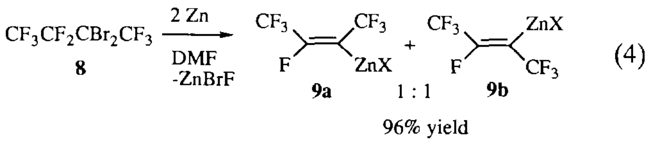
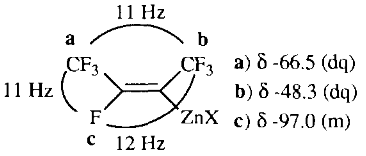


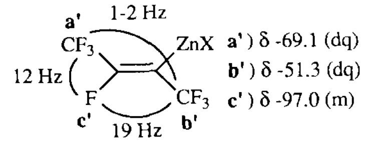
[X = Br, $CF_3CF=C(CF_3)$]

The regiochemistry of the elimination was not unexpected, as we had anticipated that the more thermodynamically stable internal alkene would be formed. Additionally, formation of the 1-butene derivative would have necessitated cleavage of the stronger C−F bond at the more highly fluorinated CF_3 carbon [10].

The stereochemistry of **9a** and **9b** was determined by examination of the ^{19}F NMR coupling constants {$^5J(cis\text{-}CF_3-CF_3) > {}^5J(trans\text{-}CF_3-CF_3)${ [11].
^{19}F NMR spectroscopy

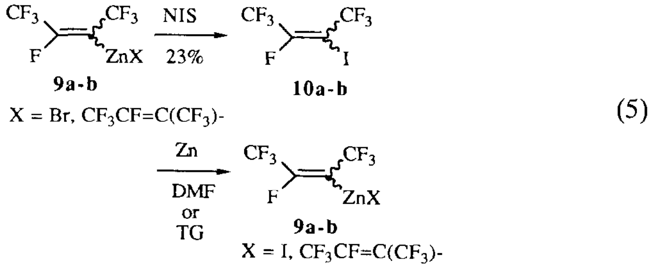


9a



9b

The reaction of $CF_3CBr_2CF_3$ with Zn was studied in a variety of solvents (CH_3CN, THF, Et_2O, dioxan and triglyme), but found to give zinc reagent **2** cleanly only in DMF or *N*,*N*-dimethylacetamide (DMAC) [1, 2]. However, 2-iodopentafluoropropene, available by iodination of **2**, reacted cleanly with zinc in the less polar solvent, triglyme (TG) [1, 2]. Thus, zinc reagent **9a,b** was quenched with *N*-iodosuccinimide (NIS) to afford *E*- and *Z*-$CF_3CF=ClCF_3$ (**10a, b**). (Compound **10a, b** prepared by the addition of CsF/I_2 to **3** was also utilized: *E*-/*Z*-(**10**) = 65:35 [12].) Subsequent reaction of vinyl iodides **10a, b** with zinc proceeded smoothly in TG or DMF solvents [eqn. (5)] [13].



The thermal stability of **9a, b** [X = I, $CF_3CF=C(CF_3)$] in DMF and TG [both prepared as shown in eqn. (5)] was studied. The stability of a 0.30 M sample of **9a, b** in DMF at room temperature was moderate, sustaining only a 25% decrease in molarity after 7 d. However, **9a, b** quickly decomposed at 60 °C (Table 1), affording a solid mixture. We propose that **9a, b** decomposes in DMF by *β*-elimination of ZnXF to generate $CF_3C\equiv CCF_3$ (**3**), which in the presence of fluoride ion polymerizes [14] to poly(hexafluoro-2-butyne) [eqn. (6)]. Consistent with the proposed *β*-elimination pathway was the observation that **9b** (*trans* elimination) decomposed at a faster rate than **9a** (*cis* elimination) [15]. A similar stereochemical observation hs been reported by Normant [3a], who found *trans*-ArCF=CFLi to be stable towards *β*-elimination at temperatures below −5 °C, while the *cis* isomer was only stable below −85 °C.

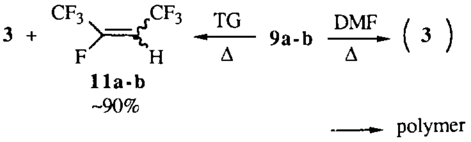
Zinc reagent **9a, b** also exhibited moderate thermal stability in TG at room temperature; a 0.39 M sample showed a 33% decrease in molarity after 7 d. The stability of **9a, b** in TG at elevated temperatures was in sharp contrast to the DMF mixture: a sample of **9a, b** in TG experienced only a 26% decrease in molarity after 38 h at 80 °C (Table 2). It is interesting to note that unlike the DMF solution, the mixture in TG did not solidify after complete thermal decomposition. In fact, thermal decomposition of **9a, b** in TG followed a different pathway, giving **11a, b** as the major products, presumably by hydrogen-atom extraction from the solvent. In this instance, **9a** was found to decompose faster than **9b**. Small amounts of elimination product **3** were also detected [eqn. (6)]. Since DMF is a better donor solvent than TG, *β*-elimination of **9a, b** may be favored in DMF rather than in TG because of the greater carbanion character of **9a, b** in the **9a, b**·DMF complex [2].

TABLE 1. Thermal stability of **9a, b** in DMF at 60 °C

Time (h)	Molarity of **9a, b**	Ratio **9a/9b**
0	0.30	56:44
1	0.27	65:35
8	0.10	74:26
24	0.05	81:19

TABLE 2. Thermal stability of **9a, b** in TG at 80 °C

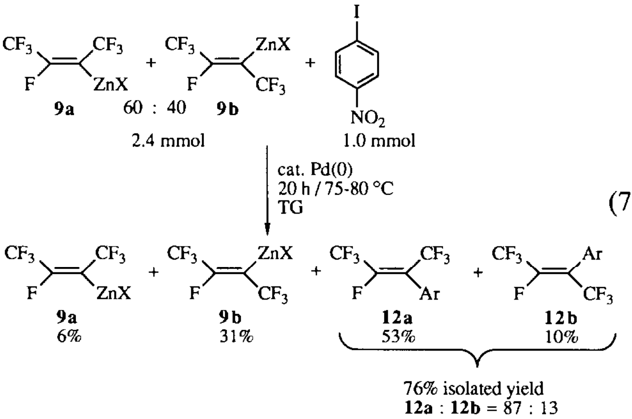
Time (h)	Molarity of **9a, b**	Ratio **9a/9b**
0	0.27	63:37
22	0.22	48:52
38	0.20	41:59
54	0.15	34:66



(6)

Since zinc reagent **2** underwent facile palladium-catalyzed coupling reactions with aryl iodides, a similar reaction with zinc reagent **9a, b** was examined in order to prepare the 2-(aryl)-heptafluoro-2-butenes. These compounds have been prepared by the fluoride-catalyzed isomerization of 2-(aryl)-heptafluoro-1-butenes [16] and by addition/elimination of phenyllithium and octafluoro-2-butene [17a, b].*

As expected from the thermal stability study, zinc reagent **9a, b** in DMF was not useful for the palladium-catalyzed coupling reaction. For example, treatment of **9a, b** in DMF with *p*-iodoanisole and a catalytic amount of $Pd[PPh_3]_4$ under typical [2] coupling conditions (95 °C/17 h) gave a solid reaction mixture, and no coupled product was observed. However, the zinc reagent had adequate stability in TG to react with *p*-iodonitrobenzene [eqn. (7)].



(7)

When a 2.4-fold excess of zinc reagent **9a, b** was employed, **9a** was found to react at a faster rate than **9b**, as evidenced by the 87:13 product distribution of styrene **12a** and **12b**. Presumably **9a** reacts preferentially, because it is less sterically hindred (*cis*-F versus *cis*-CF_3) than **9b**. Utilization of a 4-fold excess of **9a, b** gave a 96:4 ratio of **12a/12b**. The latter mixture of isomers could be photochemically isomerized (254 nm) in pentane or benzene to a 25:75 ratio of **12a/12b**.

Unfortunately, the coupling reaction could not be applied to other substituted aryl iodides. The palladium-catalyzed reaction of **9a, b** in TG with y-C_6H_4I (y = *m*-NO_2,*p*-Br) and 3,5-$(CF_3)_2C_6H_3I$ gave only small amounts of coupled products, even when higher temperatures and longer reaction times were employed. We believe that the nucleophilicity of **9a, b** is repressed relative to other *F*-vinyl zinc reagents due to electronic and steric considerations [2].

In summary, the zinc-induced dehalogenation/metallation of $CF_3CF_2CBr_2CF_3$ was found to proceed regiospecifically, but not stereospecifically, affording *E*- and *Z*-$CF_3CF{=}C(ZnX)CF_3$ in high yield. This zinc reagent had poor thermal stability in DMF, decomposing by a β-elimination route. However, the zinc reagent exhibited better thermal stability in TG, and was utilized for the preparation of *E*- and *Z*-*p*-$NO_2C_6H_4C(CF_3){=}CFCF_3$.

Experimental

All boiling points are uncorrected. All glassware was oven-dried. ^{19}F NMR spectra were recorded on a JEOL FX90Q (83.81 MHz) or Bruker AC-300 (282.44 MHz) spectrometer, and $\{^1H\}^{13}C$ NMR (75.48 MHz) and ^1H NMR (300.17 MHz) spectra were recorded on the AC-300 spectrometer. All samples were taken in $CDCl_3$ solvent unless noted otherwise. All chemical shifts are reported in parts per million (ppm) downfield (positive) of the standard: TMS for ^1H and ^{13}C; $CFCl_3$ for ^{19}F NMR spectroscopy. FT–IR spectra were recorded as CCl_4 solutions and reported in wavenumbers (cm^{-1}). GC–MS spectra were obtained at 70 eV in the electron impact mode. GLPC analyses were performed on a 5% OV-101 column with a thermal conductivity detector. High-resolution mass spectral determinations were made at the University of Iowa Mass Spectrometry Facility or the Midwest Center for Mass Spectrometry, the latter with partial support by the National Science Foundation, Biology Division (Grant No. DIR9017262). Dimethyl formamide (DMF) was distilled at reduced pressure from CaH_2. Triglyme (TG, Grant Chemical) was distilled twice at reduced pressure from sodium benzophenone ketyl. $Pd(PPh_3)_4$ was prepared by Coulson's procedure [18]. Zinc (325 mesh, Aldrich) was activated by washing with dilute HCl, then dried *in vacuo* at room temperature. All other materials were used without further purification. All reagents and aryl iodides were obtained from Aldrich, with the exception of $CF_3CF{=}CFCF_3$ (Matheson) and 3,5-$(CF_3)_2C_6H_3I$ (Fairfield Chemical Co.).

Preparation of $CF_3CFBrCFBrCF_3$ (7) [19]

A 1 l Pyrex tube was charged with octafluoro-2-butene (235.1 g, 1.175 mol) and 183.1 g (1.146 mol) of bromine, and then degassed. The tube was then irradiated with a Blak-Ray® 3000 Å broad-band mercury spot lamp in a fume hood behind a blast shield, with the lamp located 2 in. from the tube in order to warm the solution and induce the bromine and organic layers to mix by convection. After 3.5 d, the lower layer of bromine had been consumed and a pinkish clear solution remained, which was washed with aqueous 2% $NaHSO_3$

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*Traces of addition/elimination products have been reported from the reaction of C_6H_5MgBr with $CF_3CF{=}CFCF_3$ [17b].

(3×300 ml) and H_2O (1×100 ml), dried over $MgSO_4$ and filtered. The crude product was distilled at atmospheric pressure to afford 314.3 g (76% yield) of **7**, b.p. 93–94 °C (GLPC purity 97%). ^{19}F NMR δ: −73.6 (d, 22 Hz, 6F); −127.9 (m, 1F); −129.4 (m, 1F) ppm. ^{13}C NMR δ: 98.9 (dm, 290 Hz, *C*FBr); 119.6 (qdm, 287, 27 Hz, *C*F₃) ppm. FT-IR (CCl_4) (cm^{-1}): 706.12 (m); 779.32 (vw); 810.06 (s); 901.44 (vw); 1119.4 (vw); 1229.1 (vs); 1271.1 (m).

Preparation of $CF_3CF_2CBr_2CF_3$ (8) [9]

A one-neck 100 ml flask, equipped with a Teflon-coated stir-bar and a 1 ft. tap H_2O condenser attached to an N_2-tee, was charged with 20 g (0.15 mol) $AlCl_3$ and 170.9 g (0.4750 mol) $CF_3CFBrCFBrCF_3$. The mixture was stirred and heated with an oil bath to 85–95 °C for 24 h. The reaction mixture was distilled at reduced pressure (50 °C/1.5 mmHg) into a series of two −196 °C traps. The combined distillates were washed with aqueous 10% $NaHSO_3$ (1×100 ml), dried over $MgSO_4$ and filtered. The crude material was distilled at atmospheric pressure, collecting 121.4 g of **8**, b.p. 90–91 °C (71% yield, 100% GLPC purity). ^{19}F NMR (DMF) δ: −69.5 (m, 3F); −75.7 (m, 3F); −106.7 (m, 2F) ppm. ^{13}C NMR δ: 52.0 (qm, 36 Hz); 110.8 (tq, 267 Hz, 36 Hz); 118.2 (qt, 288, 37 Hz); 120.9 (q, 281 Hz) ppm. FT-IR (CCl_4) (cm^{-1}): 713.6 (m); 1195.5 (vs); 1206.9 (vs); 1233.9 (vs); 1317.0 (vs). GC–MS *m/z* (% abundance): 363 (3%, M+1); 361 (6, M+1); 359 (4, M+1); 282 (14); 280 (14); 241 (28); 239 (17); 129 (51); 69 (100). HRMS: Calc. for $C_4F_8{}^{81}Br_2$, 361.8198. Obs., 361.8198.

Preparation of $CF_3CF{=}C(ZnX)CF_3$ (9a, b) from $CF_3CF_2CBr_2CF_3$

A two-neck 25 ml flask, equipped with a Teflon-coated stir-bar, septum and a tap H_2O condenser further attached to an N_2-tee, was charged with Zn (1.03 g, 15.8 mmol) and 5 ml DMF. $CF_3CF_2CBr_2CF_3$ (**8**) (1.82 g, 5.06 mmol) was added slowly via a syringe to the reaction mixture with vigorous stirring. After a 1-min induction period, the reaction mixture turned slightly green then black and an exothermic reaction occurred. Compound **8** was added at a rate to control the exothermic reaction at 60–70 °C. After the addition was complete, the reaction mixture was stirred for 2 h at room temperature. ^{19}F NMR spectral analysis of the reaction mixture with hexafluorobenzene as internal standard showed a 96% NMR yield of a 1:1 mixture of *E*- and *Z*-isomers; the data for these isomers are described in the text. The addition of several drops of 1:1 HCl/H_2O to an NMR sample of **9a, b** afforded **11a, b** and the NMR data are presented in a subsequent section.

Preparation of $CF_3CF{=}CICF_3$ (10a, b)

A three-neck 100 ml flask, equipped with a Teflon-coated magnetic stir-bar, solid addition tube charged with 4.84 g (21.5 mmol) NIS and a septum, was connected to a −196 °C trap linked to a vacuum source. The apparatus was charged with a Schlenk-filtered solution of **9a, b** prepared from 5.32 g (14.8 mmol) **8** and 3.54 g (54.1 mmol) Zn in 20 ml of DMF. The apparatus was evacuated to 1.7 mmHg, then the NIS was slowly added over a 30-min period at a rate to keep the reaction mixture from bubbling into the cold trap. After the addition was complete, the mixture was distilled for an additional 1 h at room temperature, collecting 11.0 g of a slightly yellow liquid. The distillate was washed with H_2O (2×20 ml) and the organic residue (3.1 g) was dried over $MgSO_4$, filtered and distilled to give two fractions, b.p. 60–68 °C (0.24 g, 100% GLPC pure) and b.p. 68–69 °C (0.81 g, 95% GLPC pure), combined yield 23% (lit. b.p. 71.3 °C [12]). ^{19}F NMR *Z*-isomer (49%) δ: −56.1 (qd, 11.6, 10.1 Hz, 3F); −66.0 (qd, 11.6, 8.0 Hz, 3F); −77.9 (qq, 10, 8 hz, 1F) ppm. *E*- Isomer (51%) δ: −58.9 (dq, 24, 1.5 Hz, 3F); −67.1 (dq, 4.3, 1.5 Hz, 3F); −86.9 (qq, 24, 4.3 Hz, 1F) ppm. GC–MS (mixture, 1 peak) *m/z* (% abundance): 308 (100%, M^+); 289 (28); 239 (93); 127 (80); 112 (31); 93 (91); 69 (67).

Preparation of $CF_3CF{=}C(ZnX)CF_3$ (9a, b) from $CF_3CF{=}CICF_3$ (10a, b)

A two-neck 25 ml flask, equipped with a Teflon-coated magnetic stir-bar, septum and a tap H_2O condenser further attached to an Ar-tee, was charged with Zn (0.28 g, 4.3 mmol) and 5 ml TG. After **10a, b** (0.82 g, 2.7 mmol) was added dropwise via a syringe, the solution was stirred for 2 h at room temperature. The ^{19}F NMR spectrum of this solution was similar to that described for **9a, b** in DMF.

Thermal decomposition in TG was studied by heating a sample of **9a, b** in an 80 °C oil bath, with frequent monitoring by ^{19}F NMR spectroscopy (see Table 2). The volatile materials were trapped in a −196 °C trap and determined by ^{19}F NMR spectroscopy to consist of **11a, b** and **3**. Data for *Z*-(**11**): ^{19}F NMR δ: −59.8 (ddq, 17, 7, 1.5 Hz, 3F, *CF₃*CH); −74.4 (dqm, 10, 1.5 Hz, 3F, *CF₃*CF); −117.4 (m, 1F) ppm. ^1H NMR δ: 5.90 (dqm, 27, 7 Hz) ppm. Data for *E*-(**11**): ^{19}F NMR δ: −56.4 (dqd, 11, 9.4, 7.8 Hz, 3F, *CF₃*CH); −69.8 (qdd, 9.4, 7.9, 0.6 Hz, 3F, *CF₃*CF); −113.1 (m, 1F) ppm. ^1H NMR δ: 6.06 (dqm, 17, 7.9 Hz) ppm. The data agreed with a literature report [5] and were identical to those of an authentic sample prepared by hydrolysis of **9a, b**.

Preparation of p-$NO_2C_6H_4C(CF_3)=CFCF_3$ *(12a, b) (nc)*

Zinc reagent **9a, b** was prepared from 0.82 g (2.7 mmol) **10a, b** and 0.28 g (4.3 mmol) Zn in 5 ml of TG and the solution was filtered through a Schlenk funnel under positive Ar pressure. A two-neck 25 ml flask, equipped with an Ar-tee, tap H_2O condenser and Teflon-coated magnetic stir-bar, was charged with 0.10 g (10 mol%) $Pd(PPh_3)_4$ and 0.26 g (1.0 mmol) *p*-$NO_2C_6H_4I$. The apparatus was purged with Ar, then **9a, b** was added via a syringe. After 75–80 °C/20 h, the reaction was judged complete by ^{19}F NMR determination [see eqn. (7)]. The mixture was triturated with pentane (4×10 ml) and the pentane extracts washed with H_2O (3×10 ml), dry-loaded onto a 30 g silica gel column and eluted with 8:2 pentane/CH_2Cl_2. Fractions (100 ml) were collected and analyzed by TLC, those with similar spots being combined. The solvent was removed by rotary evaporation and exposure to vacuum (1 mmHg/ 25 °C/1 min) to give 0.23 g (76%) **12a, b** as a yellow oil. The purity of **12a, b** was determined to be greater than 95% by ^1H, ^{19}F and ^{13}C NMR techniques. Data for **12a**: ^{19}F NMR δ: -57.7 (dq, 10–12, 10–12 Hz, 3F, CF_3CAr); -66.9 (m, 3F CF_3CF); -109.1 (qq, 10, 6 Hz, 1F) ppm. ^1H NMR δ: 8.36 (d, 9 Hz, 1H); 7.56 (d, 9Hz, 1H) ppm. ^{13}C NMR δ: 150.4 (dqq, 43, 4 Hz, CF_3CF); 149.1, 133.2, 130.6, 130.0 (m); 124.3, 121.2 (qd, 273, 12–13 Hz, CF_3CAr); 117.9 (qd, 276, 40 Hz, CF_3CF) ppm. GC–MS *m/z* (% abundance): 303 (85%, M^+); 273 (29); 238 (40); 237 (64); 187 (100); 169 (59); 138 (29); 69 (40). Data for **12b**: ^{19}F NMR δ: -61.0 (d, 25 Hz, 3F, CF_3CAr); -66.4 (d, 7.5 Hz, 3F, CF_3CF); -112.5 (qq, 25, 7.5 Hz, 1F) ppm. ^{13}C and ^1H NMR signals either overlapped or were too weak to observe. GC–MS *m/z* (% abundance): 303 (84%, M^+); 273 (35); 238 (40); 237 (70); 187 (100); 169 (56); 138 (31); 69 (33).

Acknowledgments

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