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# Indium-Mediated Reaction of 3-Bromo-3,3-difluoropropene and Bromodifluoromethylacetylene Derivatives with Aldehydes

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**Abstract**—Aldehydes reacted with 3-bromo-3,3-difluoropropene at the α-position in the presence of indium to afford 1-substituted-2,2-difluorobut-3-en-1-ols. Ketones and other electrophiles are inert under the examined conditions. The reaction of bromodifluoromethylacetylene derivatives with an aldehyde in the presence of indium provided difluorohomopropargylic alcohols. These reactions efficiently proceeded in polar solvents (water, DMF) under mild conditions. 

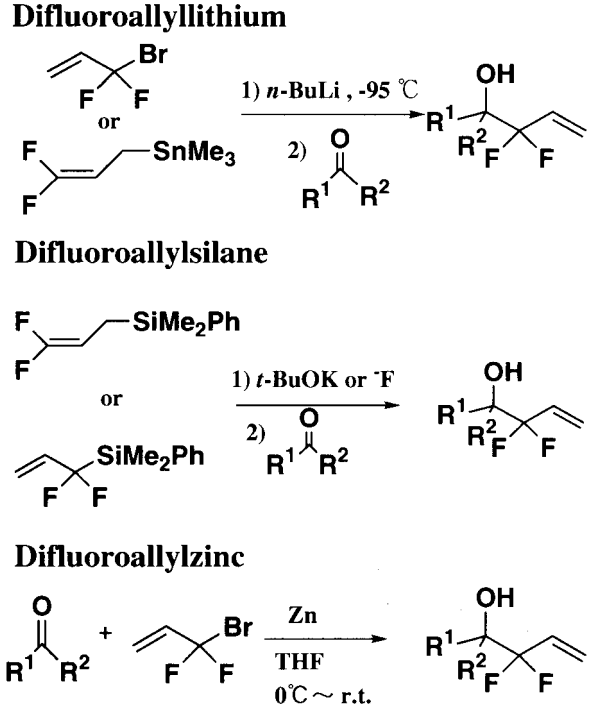
## Introduction

The difluoromethylene moiety ($CF_2$) is a key structural unit in many fluorinated compounds of biological and pharmaceutical significance.[1] This group has been recognized as an isopolar–isosteric substitute for oxygen and used as one strategy for the modification of biologically active compounds.[2–6] Some procedures have been developed to introduce $CF_2$ into organic compounds.[1]

The coupling of the *gem*-difluoroallylic metal species with carbonyl compounds is one of the most important procedures since the resulting *gem*-difluorohomoallyl alcohols have an alkene moiety capable of conversion into other functionalities. Seyferth reported the reaction of carbonyl compounds with (*gem*-difluoroallyl)lithium, available from either the lithium–halogen exchange of 3-bromo-3,3-difluoropropane[7,8] or metal exchange of the (difluoroallyl)trimethyltin[9] with butyllithium at low temperature (−95°C) in tetrahydrofuran gave *gem*-difluorohomoallyl alcohols in moderate to high yields.

Hiyama found that the treatment of (α,α-difluoroallyl)-silane[10] or (γ,γ-difluoroallyl)silane[11,12] with fluoride or with *t*-butoxide in the presence of a carbonyl compound efficiently afforded *gem*-difluorohomoallyl alcohols. Burton reported that aldehydes and ketones reacted with 3-bromo-3,3-difluoropropene in the presence of the acid-washed zinc powder at 0°C to room temperature to afford *gem*-difluorohomoallyl alcohols in moderate yields (Scheme 1).[13,14]

We found that the *gem*-difluoroallylindium generated from 3-bromo-3,3-difluoropropene and indium reacts with aldehydes to afford *gem*-difluorohomoallyl alcohols in high yields under mild conditions, which was described in a preliminary communication.[15] We now report the full details and further results of this reaction.




**Scheme 1.**

*Keywords*: indium and compounds; fluorine and compounds.

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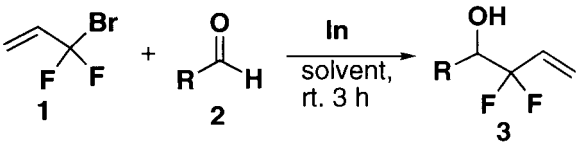
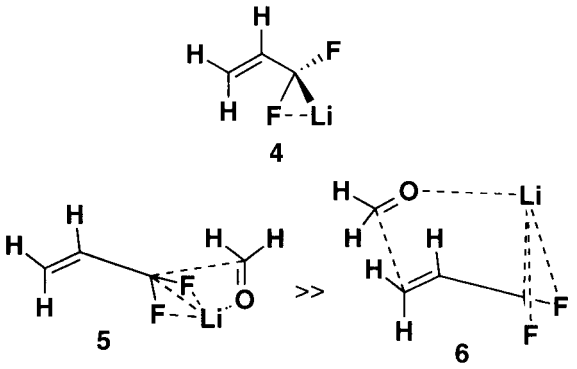



**Scheme 2.**

## Results and Discussion

In the presence of indium, 3-bromo-3,3-difluoropropene (**1**) efficiently reacted with aldehydes (**2**) at room temperature to afford *gem*-difluorohomoallyl alcohols (**3**) (Scheme 2). These results are summarized in Table 1.



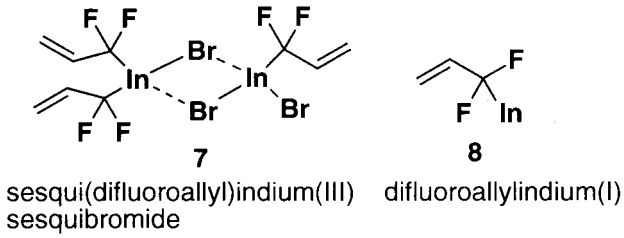

**Scheme 3.**

The products were obtained in high yields in DMF. As in the case of conventional indium-mediated allylations,[16–19] water was also an excellent solvent for this reaction. This result was in sharp contrast to other *gem*-difluoroallylations which are required anhydrous conditions. Tetrahydrofuran was not an effective solvent (entry 3). Only the $CF_2$ terminus of **1** attacked the carbonyl of the aldehydes (α-attack). These results were in contrast with the indium mediated allylations using 1-substituted 3-bromopropenes which attack carbonyls at their γ-position.[20–22]

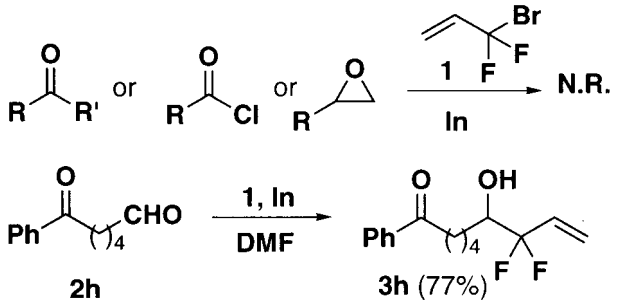
**Table 1.** Indium-mediated difluoroallulation of 3-bromo-3,3-difluoropropene with aldehydes

| Entry | Starting Material | Product | Solvent | Yield (%) |
|---|---|---|---|---|
| 1 | CHO 2a | OH F F 3a | DMF | 99 |
| 2 | | | $H_2O$ | 100 |
| 3 | | | THF | 33 |
| 4 | CHO HO 2b | OH F F HO 3b | DMF | 97 |
| 5 | CHO Br 2c | OH F F Br 3c | DMF | 95 |
| 6 | $CH_3(CH_2)_7CHO$ 2d | OH $CH_3(CH_2)_7$ F F 3d | DMF | 93 |
| 7 | | | $H_2O$ | 100 |
| 8 | CHO 2e | OH F F 3e | DMF | 99 |
| 9 | CHO 2f | OH F F 3f | DMF | 88 |
| 10 | | | $H_2O$ | 100 |
| 11 | Me Ph CHO 2g | Me F F Ph OH 3g | DMF | 87* |

*A single isomer was obtained. The stereochemistry of **3g** has not yet been determined.




**Scheme 4.**




**Scheme 5.**

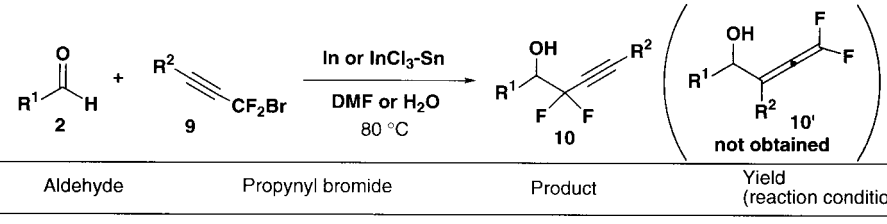
All the other *gem*-difluoroallylic metal species have also been reported to react with carbonyl compounds at the $CF_2$ terminus.[7–14] Tonachini and Canepa investigated difluoroallyllithium for various levels using the ab initio theory, and concluded the structure of **4** to be the most stable.[23] They also calculated the addition reaction of formaldehyde with (1,1-difluoroallyl)lithium, and the α-attack is significantly preferred. The transition structure **5** is 17 kcal/mol higher in energy than **6** (Scheme 3).[24]

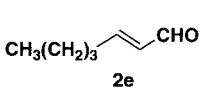
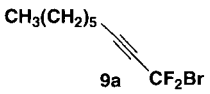
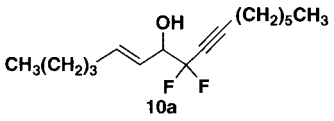
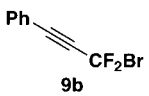
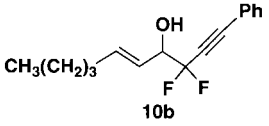
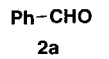
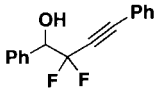
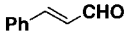
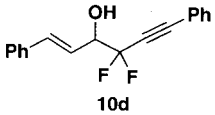
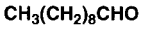
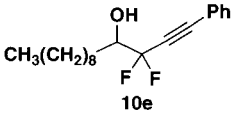
This indium-mediated *gem*-difluoroallylation might proceed through sesqui(difluoroallyl)indium(III) sesquibromide (**7**) or difluoroallylindium(I) (**8**)† as shown in Scheme 3, and they attacked the aldehyde in a way similar to difluoroallyllithium (Scheme 4).

As noted in entries 8–10 of Table 1, the reaction with the α,β-unsaturated aldehydes (**2e**,**f**) exclusively gave the 1,2-adducts (**3e**,**f**). For the aldehyde (**2g**), only one diastereoisomer was obtained.

Interestingly, ketones, acid chlorides and epoxides did not react with **1** under these reaction conditions. For the

**Table 2.**




| Aldehyde | Propynyl bromide | Product | Yield (reaction conditions) |
|---|---|---|---|
|  2e |  9a |  10a | 18% (In/$H_2O$) |
| 2e |  9b |  10b | 28% (In/DMF)<br>38% (In/$H_2O$)<br>46% ($InCl_3$-Sn/$H_2O$) |
|  2a | 9b |  10c | 22% (In/DMF)<br>33% (In/$H_2O$)<br>67% ($InCl_3$-Sn/$H_2O$) |
|  2f | 9b |  10d | 32% (In/$H_2O$)<br>48% ($InCl_3$-Sn/$H_2O$) |
|  2i | 9b |  10e | 27% (In/DMF)<br>61% ($InCl_3$-Sn/$H_2O$) |

† Recently, Chan et al. reported that allyl bromide reacted with indium to afford allylindium(I) in aqueous media.[25]

compound (**2h**) bearing both aldehyde and ketone functionalities, **1** chemoselectively reacted with the aldehyde carbonyl to provide **3h** (Scheme 5).

These results are in contrast with those of the other *gem*-difluoroallylations,[7–14] where little or no difference was observed between the aldehydes and ketones, and also with conventional allylindiums,[16–20] which have been found to react with a wide varaiety of ketones and acid halides.

We then examined the reaction of the bromodifluoromethylacetylene derivatives (**9**) with aldehydes in the presence of indium. The $CF_2$ terminus of **9** attacked the carbonyl of the aldehydes (α-attack) exclusively to give *gem*-difluorohomopropargyl alcohols (**10**). These results are summarized in Table 2.

The allenes (**10′**) were not obtained in all cases.‡ These results are in contrast to the indium-mediated reaction of γ-substituted propargyl bromides with aldehydes which affords allenes.[27] Although the yields of **10** were not high for the reaction using indium metal, **10** was obtained in moderate yields in the reaction using the combination of indium chloride ($InCl_3$) and Sn.[22]

## Conclusion

In the presence of indium, 3-bromo-3,3-difluoropropene chemoselectively reacted with aldehydes to provide *gem*-difluorohomoallyl alcohols. *gem*-Difluorohomopropargyl alcohols were obtained in the reaction of bromodifluoromethylacetylene derivatives with aldehydes in the presence of indium or $InCl_3$–Sn. These reaction efficiently proceeded in polar solvents (water, DMF) under very mild conditions.

## Experimental

The infrared spectra (IR) were measured using a Perkin–Elmer 1600 series FT-IR spectrophotometer. The $^1$H- and $^{19}$F NMR spectra were obtained using a JEOL GX270, Varian Gemini 300 or Varian UNITY plus 500 instrument with tetramethylsilane (for $^1$H) and chlorotrifluoromethane (for $^{19}$F) as the internal standards. The mass spectra (MS) and high-resolution mass spectra (HR-MS) were measured on a JEOL JMS D-200 spectrometer. Column chromatography was performed on silica gel (Merck Kieselgel 60). 3-Bromo-3,3-difluoropropene (**1**) was purchased from Kanto Chemical Co. Bromodifluoromethylacetylene derivatives (**9**) were prepared according to the literature.[28]

### General procedure for the indium-mediated coupling of aldehydes with 1

A suspension consisting of an aldehyde (0.50 mmol), **1** (76 ml, 0.75 mmol), powdered indium (86 mg, 0.75 mmol) and DMF (or water) (5 ml) was stirred for 3 h at room temperature. The reaction mixture was then quenched with 10% HCl and extracted with ether (3×20 ml). The combined organic extract was dried over anhydrous sodium sulfate, filtered, and the solvent was removed in vacuo. The residue was purified using chromatography on silica gel (*n*-hexane–ethyl acetate) to give **3**.

**2,2-Difluoro-1-phenylbut-3-en-1-ol (3a).** The spectral data for this sample were identical with those in the literature.[14]

**2,2-Difluoro-1-(*p*-hydroxyphenyl)but-3-en-1-ol (3b).** A colorless oil. IR (neat) cm$^{-1}$: 3363, 3267; $^1$H NMR ($CDCl_3$) δ: 2.47 (1H, d, *J*=2.7 Hz), 4.83 (1H, td, *J*=10.0, 2.2 Hz), 5.07 (1H, s), 5.46 (1H, d, *J*=10.0 Hz), 5.57 (1H, d, *J*=17.0 Hz), 5.75–5.88 (1H, m), 6.81 (2H, d, *J*=8.2 Hz), 7.27 (2H, d, *J*=8.2 Hz); $^{19}$F NMR ($CDCl_3$) δ: −108.65 (1F, dt, $J_{FF}$=246.0 Hz, $J_{FH}$=10.0 Hz), −110.23 (1F, dt, $J_{FF}$=246.0 Hz, $J_{FH}$=10.0 Hz); MS (*m*/*z*) 200 ($M^+$); HRMS calcd for $C_{10}H_{10}F_2O_2$ ($M^+$): 200.0649, found 200.0630.

**1-(*p*-Bromophenyl)-2,2-difluorobut-3-en-1-ol (3c).** A colorless oil. IR (neat) cm$^{-1}$: 3420; $^1$H NMR ($CDCl_3$) δ: 2.54–2.63 (1H, br), 4.88 (1H, td-like), 5.48 (1H, d, *J*=10.0 Hz), 5.58 (1H, d, *J*=18.0 Hz), 5.74–5.91 (1H, m), 7.29 (2H, d, *J*=8.2 Hz), 7.49 (2H, d, *J*=8.2 Hz); $^{19}$F NMR ($CDCl_3$) δ: −107.85 (1F, dt, $J_{FF}$=246.0 Hz, $J_{FH}$=10.0 Hz), −109.20 (1F, dt, $J_{FF}$=246.0 Hz, $J_{FH}$=10.0 Hz); MS (*m*/*z*) 262 ($M^+$); HRMS calcd for $C_{10}H_9BrF_2O$ ($M^+$): 261.9804, found 261.9808.

**3,3-Difluorododec-1-en-4-ol (3d).** A colorless oil. IR (neat) cm$^{-1}$: 3420; $^1$H NMR ($CDCl_3$) δ: 0.87 (3H, t, *J*=6 Hz), 1.10–1.90 (14H, m), 2.00–2.15 (1H, m), 3.71–3.80 (1H, br), 5.53 (1H, d, *J*=10.0 Hz), 5.70 (1H, d, *J*=17.0 Hz), 5.82–6.06 (1H, m); $^{19}$F NMR ($CDCl_3$) δ: −109.15 (1F, dt, $J_{FF}$=249.0 Hz, $J_{FH}$=10.0 Hz), −112.70 (1F, dt, $J_{FF}$=249.0 Hz, $J_{FH}$=10.0 Hz); MS (*m*/*z*) 220 ($M^+$); HRMS calcd for $C_{12}H_{22}F_2O$ ($M^+$): 220.1639, found 220.1756.

**3,3-Difluorodeca-1,5-dien-4-ol (3e).** A colorless oil. IR (neat) cm$^{-1}$: 3404; $^1$H NMR ($CDCl_3$) δ: 0.89 (3H, t, *J*=7.0 Hz), 1.25–1.43 (4H, m), 2.03–2.12 (3H, m), 4.24–4.27 (1H, br), 5.43–6.04 (5H, m); $^{19}$F NMR ($CDCl_3$) δ: −109.75 (1F, dt, $J_{FF}$=249.0 Hz, $J_{FH}$=10.0 Hz), −111.78 (1F, dt, $J_{FF}$=249.0 Hz, $J_{FH}$=10.0 Hz); MS (*m*/*z*) 190 ($M^+$), 113 ($M^+-CF_2CHCF_2$); HRMS calcd for $C_{10}H_{16}F_2O$ ($M^+$): 190.1169, found 190.1122.

**4,4-Difluoro-1-phenylhexa-1,5-dien-3-ol (3f).** The spectral data for this sample were identical with those in the literature.[14]

**4,4-Difluoro-2-phenylhex-5-en-3-ol (3g).** The spectral data for this sample were identical with those in the literature.[14]

**7,7-Difluoro-6-hydroxy-1-phenylnon-8-en-1-one (3h).** A colorless oil. IR (neat) cm$^{-1}$: 3446, 1684; $^1$H NMR ($CDCl_3$) δ: 1.41–2.17 (7H, m), 3.00 (2H, t, *J*=6.5 Hz), 3.75–3.89 (1H, m), 5.54 (1H, d, *J*=10.0 Hz), 5.72 (1H, d, *J*=18.0 Hz), 5.89–6.07 (1H, m), 7.44–7.97 (5H, m); $^{19}$F NMR ($CDCl_3$) δ: −108.93 (1F, dt, $J_{FF}$=248.0 Hz, $J_{FH}$=10.0 Hz), −112.84 (1F, dt, $J_{FF}$=248.0 Hz, $J_{FH}$=10.0 Hz);

‡ A similar regioselectivity was reported in the zinc-mediated reaction of **9** with aldehydes.[26]

MS (*m/z*) 268 ($M^+$); HRMS calcd for $C_{15}H_{18}F_2O_2$ ($M^+$): 268.1275, found 268.1263.

### General procedure for the indium-mediated coupling of aldehydes with 9

A suspension consisting of an aldehyde (**2**) (0.50 mmol), **9** (0.75 mmol), powdered indium (86 mg, 0.75 mmol) and DMF (or water) (5 ml) was stirred at room temperature for 3 h and then stirred at 80°C for 12 h. The reaction mixture was quenched with 10% HCl and extracted with ether (3×20 ml). The combined organic extract was dried over anhydrous sodium sulfate, filtered, and the solvent was removed in vacuo. The residue was purified using chromatography on silica gel (*n*-hexane–ethyl acetate) to give **10**.

### General procedure for the indium trichloride/tin-mediated coupling of aldehydes with 9

A suspension consisting of an aldehyde (**2**) (0.50 mmol), **9** (0.75 mmol), indium trichloride (147 mg, 0.50 mmol), tin (59 mg, 0.50 mmol) and water (5 ml) was stirred at room temperature for 3 h and then stirred at 80°C for 12 h. The reaction mixture was then quenched with 10% HCl and extracted with ether (3×20 ml). The combined organic extract was dried over anhydrous sodium sulfate, filtered, and the solvent was removed in vacuo. The residue was purified using chromatography on silica gel (*n*-hexane–ethyl acetate) to give **10**.

**8,8-Difluorohexadec-5-en-9-yn-7-ol (10a).** A colorless oil. IR (neat) $cm^{-1}$: 3447, 2929, 2858, 2252; $^1H$ NMR ($CDCl_3$) $\delta$: 0.87–0.92 (6H, t-like), 1.26–1.61 (12H, m), 2.07–2.33 (4H, m), 4.25–4.28 (1H, m), 5.52 (1H, dd, $J$=15.9, 6.6 Hz), 5.92 (1H, dt, $J$=15.9, 6.9 Hz); $^{19}F$ NMR ($CDCl_3$) $\delta$: −93.70 (1F, dq, $J_{FF}$=270.0 Hz, $J_{FH}$=6.2 Hz), −95.20 (1F, dd, $J_{FF}$=270.0 Hz, $J_{FH}$=11.0 Hz); MS (*m/z*) 253 ($M^+-F$); HRMS calcd for $C_{16}H_{26}F_2O$ ($M^+$): 272.1952, found 272.1984.

**3,3-Difluoro-1-phenyldec-5-en-1-yn-4-ol (10b).** A colorless oil. IR (neat) $cm^{-1}$: 3421, 2241; $^1H$ NMR ($CDCl_3$) $\delta$: 0.78–0.83 (3H, m), 1.18–1.36 (6H, m), 4.33 (1H, dd, $J$=16.2, 7.1 Hz), 5.53 (1H, dd, $J$=16.2, 6.8 Hz), 5.86–5.96 (1H, m), 7.36–7.52 (5H, m); $^{19}F$ NMR ($CDCl_3$) $\delta$: −94.81 (1F, dd, $J_{FF}$=273.0 Hz, $J_{FH}$=9.7 Hz), −96.36 (1F, dd, $J_{FF}$=273.0 Hz, $J_{FH}$=9.7 Hz); MS (*m/z*) 264 ($M^+$), 244 ($M^+-HF$); HRMS calcd for $C_{16}H_{18}F_2O$ ($M^+$): 264.1326, found 264.1328.

**2,2-Difluoro-1,4-diphenylbut-3-yn-1-ol (10c).** A colorless oil. IR (neat) $cm^{-1}$: 3446, 3064, 2925, 2242; $^1H$ NMR $\delta$: 2.73 (1H, br), 4.97 (1H, t, $J$=9.2 Hz), 7.22–7.56 (10H, m); $^{19}F$ NMR $\delta$: −92.76 (1F, dd, $J_{FF}$=273.0 Hz, $J_{FH}$=7.4 Hz), −94.23 (1F, dd, $J_{FF}$=273.0 Hz, $J_{FH}$=9.2 Hz); MS (*m/z*): 258 ($M^+$), 238 ($M^+-HF$); HRMS calcd for $C_{16}H_{12}F_2O$ ($M^+$): 258.0856, found 258.0836.

**4,4-Difluoro-1,6-diphenylhex-1-en-5-yn-3-ol (10d).** A colorless oil. IR (neat) $cm^{-1}$: 3649, 2923, 2241; $^1H$ NMR ($CDCl_3$) $\delta$: 4.63 (1H, dd, $J$=16.0, 7.9 Hz), 6.31 (1H, dd, $J$=16.0, 7.9 Hz), 6.87 (1H, d, $J$=16.0 Hz), 7.27–7.50 (10H, m); $^{19}F$ NMR ($CDCl_3$) $\delta$: −94.33 (1F, dd, $J_{FF}$=273.0 Hz, $J_{FH}$=7.9 Hz), −95.54 (1F, dd, $J_{FF}$=273.0 Hz, $J_{FH}$=10.2 Hz); MS (*m/z*) 284 ($M^+$); HRMS calcd for $C_{18}H_{14}F_2O$ ($M^+$): 284.1013, found 284.1025.

**3,3-Difluoro-1-phenyltridec-1-yn-4-ol (10e).** A colorless oil. IR (neat) $cm^{-1}$: 3446, 2925, 2855, 2242; $^1H$ NMR ($CDCl_3$) $\delta$: 0.78–0.83 (3H, m), 1.19–1.76 (16H, m), 3.82 (1H, dd, $J$=17.8, 6.8 Hz), 7.25–7.47 (5H, m); $^{19}F$ NMR ($CDCl_3$) $\delta$: −94.76 (1F, dd, $J_{FF}$=273.0 Hz, $J_{FH}$=10.2 Hz), −96.34 (1F, dd, $J_{FF}$=273.0 Hz, $J_{FH}$=10.2 Hz); MS (*m/z*) 308 ($M^+$); HRMS calcd for $C_{19}H_{26}\cdot F_2O$ ($M^+$): 264.1326, found 264.1328.

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