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Diborane as a reducing agent : Part VIII†—Reduction of trifluoroacetylindoles to trifluoroethyl- and hydroxytrifluoroethylindoles and novel dimeric 2-trifluoro-1[1′-(3′-alkylindolino)]ethylboranes

Kshetra M Biswas*, Rabindra N Dhara, (Mrs) Haimanti Mallik, (Mrs) Arunima Sinha-Chaudhuri, (Mrs) Sumita Halder, (Miss) Aparna Saha, Pranay De & Anindya S Brahmachari
Department of Chemistry, University College of Science, University of Calcutta, 92, Acharya Prafulla Chandra Road, Calcutta 700 009, India
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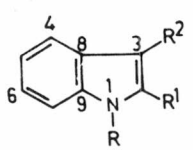
Reduction of the trifluoroacetylindoles **1-5** with diborane affords the hydroxytrifluoroethylindoles **7-10** (20-70%), the trifluoroethylindoles **6** and **11** (8.4-18.5%) and the unique and dimeric indolinotrifluoroethylboranes **16**, **17a** and **17b** (0.6-12%). This appears to be the first report on the formation of alkylboranes in the reduction of a carbonyl chromophore. The existence of indolinoalkylboranes in the form of the dimers **16**, **17a** and **17b** is confirmed by ^{11}B NMR and mass spectra, which show molecular ions for both the monomers and the dimers. Compound **5** does not form dimers corresponding to **16** and **17**,probably due to the electron-withdrawing effect of its phenyl group. The results have been discussed in relation to the mechanisms of diborane reduction and the origin of different products.

Reduction of indole-1-carbonyl compounds with diborane or other reducing agents is not always successful and is also not well-established[1,2]. Earlier, we have reported the reduction of indole-1-carboxaldehydes and indole-1-ketones with diborane and obtained interesting results[1-3]. So far as we are aware, there is only one report in literature on the reduction of a trifluoroacetylindole, viz. the sodium borohydride reduction of 5-cyano-3-trifluoroacetylindole to 5-cyano-3-hydroxytrifluoroethylindole in only 22% yield[4], although trifluoroacetylindoles are known in the literature since 1954[5]. 1-Trifluoroacetylindoles are labile to both alkali[6] and mineral acids[7-9]. Diborane is known to possess acidic character and electrophilic reducing properties[10,11]. Therefore, we considered it worthwhile to study the reduction of a number of 1-, 2- and 3-trifluoroacetylindoles, specially because the donor properties of the carbonyl oxygen of a trifluoroacetyl group towards the Lewis and diborane is greatly diminished by the electron-withdrawing ability of the three fluorine substituents[12,13]. We selected the trifluoroacetylindoles **1-5** as our model compounds for this purpose. Our results are presented herein.

The trifluoroacetylindoles **1-3** were prepared by the method of Biswas and Jackson[14] and characterised by comparing their ^{1}H, ^{19}F and ^{13}C NMR spectral data. The other two, **4** and **5**, were prepared from the corresponding indoles by treatment with trifluoroacetic anhydride (TFAA). Reduction of **1-5** was carried out with diborane, generated externally from sodium borohydride and boron trifluoride etherate. The hydroxytrifluoroethylindoles **7**, **8** and **10** were obtained from **1**, **2** and **5**, respectively, together with a small



1, R, R^1=H, R^2=$COCF_3$
2, R=H, R^1=$COCF_3$, R^2=Me
3, R=$COCF_3$, R^1=H, R^2=Me
4, R=$COCF_3$, R^1=H, R^2=Et
5, R=$COCF_3$, R^1=H, R^2=Ph
6, R, R^1=H, R^2=CH_2CF_3
7, R, R^1=H, R^2=$CH(OH)CF_3$
8, R=H, R^1=$CH(OH)CF_3$, R^2=Me
9, R=$CH(OH)CF_3$, R^1=H, R^2=Me
10, R=$CH(OH)CF_3$, R^1=H, R^2=Ph
11, R=CH_2CF_3, R^1=H, R^2=Et

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amount of **6** from **1**. A similar, rather unstable, hydroxytrifluoroethylindole **9** was also obtained from **3** along with a unique indolinotrifluoroethylborane as the dimer **16**. Another dimeric indolinotrifluoroethylborane was also encountered probably in two diastereoisomeric forms **17a** and **17b** from **4**. A probable 1-hydroxytrifluoroethylindole corresponding to **9** and **10** could not be obtained from **4**, probably because of its unstable nature. However, we obtained **11**, though in poor yield. The dimers **16**, **17a** and **17b** appeared to be quite stable and did not undergo any change in refluxing methanol. But the 1-hydroxytrifluoroethylindoles **9** and **10** showed a tendency to undergo mainly retrograde aldol-type reaction under such conditions.

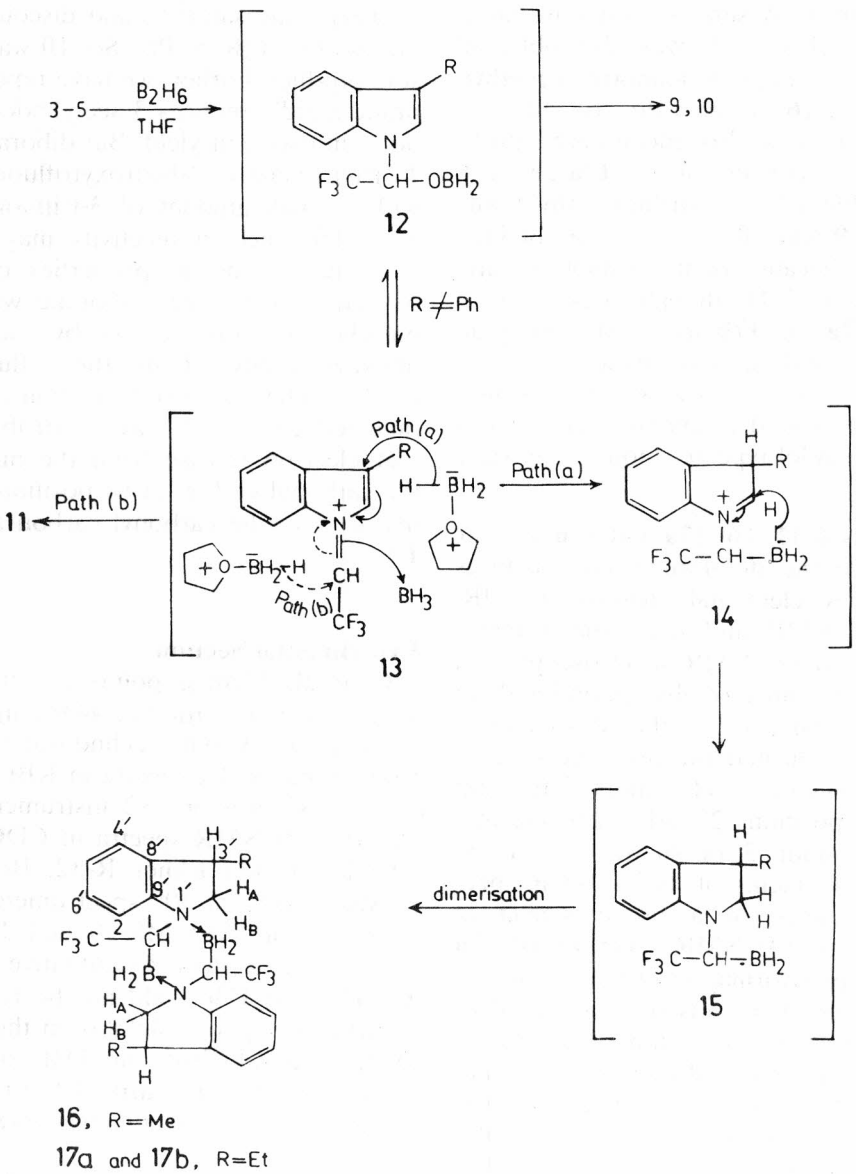
All the products **6-11**, **16**, **17a** and **17b**, appear to be unreported in the literature. Their structures were confirmed by elemental analysis, and IR, UV, ^{1}H and ^{13}C NMR and mass spectrometry and also by ^{19}F and ^{11}B NMR spectroscopy in a few cases. The appearance of absorption bands in the region 2300-2450 cm^{-1} in the IR spectra of **16**, **17a** and **17b** indicated the presence of B-H bonds in their molecules[15]. The inter-relationship of the protons at positions 2′ and 3′ and the methyl protons at position 3′ of **16** was established by decoupling experiments of its ^{1}H NMR spectrum. The appearance of a broad singlet at $\delta - 7.33$ ppm in the ^{11}B NMR spectrum of **17a** indicated the complex formation of boron with nitrogen and also that there was only one kind of boron in the molecule[16]. The dimeric nature of **16**, **17a** and **17b** was indicated by their high melting points (208-260°) and confirmed by their mass spectra. These spectra showed the molecular ions of **16**, **17a** and **17b** at m/z 454 (17%), 482 (28%) and 482 (3%), respectively. The spectra also exhibited the presence of the molecular ions of the monomers of **16**, **17a** and **17b** at m/z 227 (54%), 241 (35%) and 241 (4%), respectively.

The origin of the products **9**, **10**, **11**, **16** and **17** from **3-5** may be rationalised by the reaction mechanism suggested in Scheme I. No dimeric product corresponding to **16** and **17** was formed in the reduction of **5**, probably due to the failure of the alkoxyborane intermediate **12** (R = Ph) to undergo equilibration. The alkyl groups at position 3 of **12** (R = Me/Et) increase electron density on the nitrogen atom and encourage their equilibration to generate the intermediate **13** (R = Me/Et). But the phenyl group of **12** (R = Ph) cannot increase electron density on the nitrogen atom as effectively as an alkyl group, rather it decreases the same[2,17], and discourages its equilibration to **13** (R = Ph). So, **10** was formed as the sole product. Earlier, we have reported[18] that diborane rapidly reduces 3-acetylindoles to 3-ethylindoles in excellent yield. But diborane reduction of **1** gave mainly 3-hydroxytrifluoroethylindole **7** with a small amount of 3-trifluoroethylindole **6**. This difference in reactivity may be due to the fact that the donor properties of the carbonyl oxygen of **1** towards diborane was probably diminished to some extent by the electron-withdrawing ability of its three fluorine substituents[12,13]. The exclusive formation of **8** in the diborane reduction of **2** may be attributed to the fact that electron release from the nitrogen atom to the carbonyl carbon at its position 2 is less effective than to the carbonyl carbon at position 3 of **1**[18].

Experimental Section

General. Melting points are uncorrected. UV spectra were recorded in 99.9% methanol or 95% ethanol on a Varian Technotron Series 634 spectrophotometer, IR spectra in KBr or as thin films on a Perkin Elmer 782 instrument and ^{1}H, ^{13}C, ^{19}F and ^{11}B NMR spectra in $CDCl_3$ on a Varian CFT-20, Perkin Elmer R-32, Bruker AM-300L or Varian Gemini 300 spectrometer. Mass spectra were run on AEI MS-30 and Jeol JMS D300 mass spectrometers. Quantitative UV spectra of **16**, **17a** and **17b** could not be recorded because of their very poor solubility in the usual solvents. Diglyme, tetrahydrofuran (THF) and boron trifluoride etherate were purified[19] just before use. Pet. ether indicates the fraction b.p. 60-80°C.

Preparation of 4 and 5 by trifluoroacetylation: General procedure. To an ice-cold solution of the appropriate indole (8 mmoles) in dry ether (20 mL), was added with stirring a solution of freshly prepared TFAA (2.25 mL, 3.346 g, 15.9 mmoles) in dry ether (7 mL) in a dry nitrogen atmosphere over 15 min. The reaction mixure was left overnight at room temperature and then evaporated to dryness under reduced pressure. The residue was taken up in ethyl acetate, washed successively with 1% sodium hydrogen carbonate solution and water. The ethyl acetate solution was dried (anhydrous sodium sulphate), evaporated and chromatographed on a silica gel (60-120 mesh) column. The compound **4** was eluted with pet. ether and **5** with pet. ether-benzene (19:1). Most of their characterisation data are recorded in Table I and the rest are as folows:



Scheme I

3-Ethyl-1-trifluoroacetylindole (4): Solidified as colourless needles at low temperature and melted at room temperature; IR: 1755, 1745, 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$): δ 1.35 (3H, t, J=7.5 Hz, CH_2-CH_3), 2.80 (2H, q, J=7.5 Hz, CH_2-CH_3), 7.25 (1H, q, J=2 Hz, 2-H), 7.4-7.5 (3H, m, 4,5,6-H), 8.50 (1H, m, 7-H).

3-Phenyl-1-trifluoroacetylindole (5): Colourless needles from pet. ether-benzene; IR: 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) : δ 7.41-7.86 (9H, m, Ar-H), 8.43-8.58 (1H, m, H-7).

Diborane reduction of the trifluoroacetylindoles (1-5): General Procedure. Diborane (7.5 mmoles), generated externally by the slow addition of a solution of sodium borohydride (425 mg, 11.25 mmoles) in dry diglyme (12 mL) to a cold solution of boron trifluoride etherate (2.13 g, 1.846 mL, 15.01 mmoles) in dry diglyme (6 mL) with stirring over 35 min, was passed into an ice-cold solution of each of the trifluoroacetylindoles **1-5** (3 mmoles) in dry tetrahydrofuran (30-60 mL) with a slow stream of oxygen-free dry nitrogen. The apparatus was initially flushed with dry nitrogen, and after completion of the addition, the generator flask was heated at 60-65° for 2 hr to

Table I—Physical and some spectral data of trifluoroacetylation and diborane reduction products

Compd	Yield (%)	m.p. °C	Mol. formula	Found (%) (Calc.) C	H	N	λ_{max} nm (log ε)	Mass spectra EI, m/z (%)
4	37	Colourless oil	$C_{12}H_{10}F_3NO$	59.86 (59.75	4.12 4.18	5.93 5.81)	230(4.50),260(3.60), 282(3.75),289(3.75), 296(3.70)	241(100,M^+),144 (45, M − $COCF_3$)
5	63	126	$C_{16}H_{10}F_3NO$	66.20 (66.44	3.60 3.48	4.93 4.84)	235(4.01),270(4.18)	289(100,M^+), 192 (89,M-$COCF_3$),165 (25,M − $COCF_3$ − HCN)
6	8.4	59-60	$C_{10}H_8F_3N$	60.50 (60.31	3.98 4.05	7.17 7.03)	219(4.48),272(3.82)	—
7	70	110	$C_{10}H_8F_3NO$	56.10 (55.82	3.61 3.75	6.43 6.51)	218(4.42),271(3.89), 277(3.88),288(3.78)	215(53,M^+),198(10, M − OH),146(100,M − CF_3), 117(100,M − CF_3CHO)
8	40	110	$C_{11}H_{10}F_3NO$	57.48 (57.65	4.46 4.39	6.21 6.11)	231(3.87),276(3.87), 283(3.88)	229(100,M^+),212(12, M − OH),160(100,M − CF_3), 130(58,M − CF_3CHOH)
9	20	Colourless oil	$C_{11}H_{10}F_3NO$	57.84 (57.65	4.26 4.39	6.19 6.11)	233,273,280,291	229(16,M^+),131(73, M-CF_3CHO),130(100, M − CF_3CHO − H)
10	25	115	$C_{16}H_{12}F_3NO$	66.15 (65.98	4.01 4.15	4.93 4.81)	224(4.40),267(3.58)	—
11	18.5	52	$C_{12}H_{12}F_3N$	63.61 (63.43	5.14 5.32	6.26 6.16)	223(4.23),275(3.47), 282(3.48),293(3.37)	227(65,M^+),212 (100, M-CH_3), 144 (5,M − CH_2CF_3)
16	12	252(d)	$C_{22}H_{26}B_2F_6N_2$	58.47 (58.19	5.51 5.77	6.02 6.17)	259,265,272	454(16.9,M^+),227 (54.2,monomer),195 (89.2,monomer-BH_2F), 180(50.6,monomer − BH_2F-CH_3), 144 (32.5), 130(100)
17a	5	260	$C_{24}H_{30}B_2F_6N_2$	59.70 (59.79	6.07 6.27	6.06 5.81)	260,266,273	482(28,M^+),241(35, monomer(,209(100, monomer-BH_2F),180(48, monomer-BH_2F-CH_2CH_3)
17b	0.6	208	$C_{24}H_{30}B_2F_6N_2$	59.53 (59.79	6.35 6.27	5.93 5.81)	259,265,272	482(3,M^+),241(4, monomer),228(100, monomer-BH_2),209(16, monomer-BH_2F)

drive out the residual diborane into the reaction vessel. The reaction mixture was allowed to stand overnight at the room temperature. The progress of the reaction was monitored by TLC over silica gel, and the excess diborane destroyed carefully with methanol (10 mL). After addition of a further 20 mL of methanol, the mixture was refluxed for 2 hr, evaporated to dryness on a rotary evaporator and the residue extracted with chloroform (4 × 25 mL). The combined extract was washed successively with 5% sodium hydrogen carbonate solution (2 × 15 mL) and water (3 × 15 mL), dried (anhydrous sodium sulphate) and the solvent removed on a rotary evaporator. The residue was chromatographed on a column of silica gel (60-120 mesh or 100-200 mesh). Elution of the column with pet. ether-benzene (1:1) furnished the trifluoroethylindoles **6** and **11**. Further elution of the column with benzene afforded the hydroxytrifluoroethylindoles **7-10**. In the case of **3**, the product **16** separated out as a colourless crystalline solid upon concentration of the chloroform extract. It was collected by filtration and the residue obtained after evaporation of the filtrate was chromatographed as mentioned above. In the case of **4**, the crude product obtained after evaporation of the solvent from the chloroform extract was reextracted with warm pet. ether. The pet. ether extract was dried (anhydrous sodium sulphate), concentrated and cooled to give **17a**. The residue which did not dissolve in warm pet. ether and that obtained after removal of the solvent from the mother liquor of **17a** were combined together and chromatographed on silica gel. Elution of the column with pet. ether afforded **11** and then with a mixture of pet. ether and ethyl acetate

furnished **17b**. Most of the characterisation data of the products are furnished in Table I and the rest are recorded below:

3-Trifluoroethylindole (6): Colourless needles from pet. ether; IR 3380 cm^{-1} (N−H), ^1H NMR ($CDCl_3$): δ 3.54 (2H, q, J = 11.2 Hz, 3−CH_2CF$_3$), 7.13-7.27 (3H, m, Ar-H), 7.37-7.41 (1H, m, H-7), 7.60-7.64 (1H, m, H-4), 8.10 (1H, br s, exchangeable with D_2O, NH); ^{19}F NMR ($CDCl_3$) : δ −65.20 (3F, t, J = 10 Hz, 3−CH$_2$F$_3$).

3-Hydroxytrifluoroethylindole (7): Colourless prisms from chloroform-pet. ether; IR: 3200- 3540 cm^{-1} (OH and NH); ^1H NMR ($CDCl_3$) : δ 2.40 (1H, d, J = 6 Hz, exchangeable with D_2O, 3-CHOHCF$_3$), 5.34 (1H, quintet, J = 6 Hz, 3-CHOHCF$_3$), 7.17-7.42 (4H, m, Ar-H), 7.69-7.81 (1H, m, H-4), 8.23 (1H, br s, exchangeable with D_2O, NH); ^{13}C NMR ($CDCl_3$) : δ 67.57 (3−CHOHCF$_3$), 111.36 (C-7), 119.27 (C-4), 120.59 (C-6), 122.90 (C-5), 123.53 (C-2), 126.45 (C-3), 132.08 (C-8), 136.03 (C-9); ^{19}F NMR ($CDCl_3$) : δ −77.62 (3F, d, J = 9 Hz, 3−CHOHCF_3).

3-Methyl-2-hydroxytrifluoroethylindole (8): Colourless needles from pet. ether; ^1H NMR ($CDCl_3$) : δ 2.29 (3H, s, 3−CH$_3$), 2.76 (1H, br s, exchangeable with D_2O, 2−CHOHCF$_3$), 5.29 (1H, q, J = 6 Hz, 2−CHOHCF$_3$), 7.09-7.43 (3H, m, Ar-H), 7.59-7.69 (1H, m, H-4) and 8.30 (1H, br s, exchangeable with D_2O, NH); ^{13}C NMR ($CDCl_3$) : δ 8.19 (3−CH$_3$), 65.83 (2−CHOHCF$_3$); 111.09 (C-7), 112.10 (C-3), 119.12 (C-4), 119.58 (C-6), 123.20 (C-5), 128.12 (C-8), 131.15 (C-2), 135.77 (C-9).

3-Methyl-1-hydroxytrifluoroethylindole (9): IR: 3400-3500 cm^{-1} (OH); ^1H NMR ($CDCl_3$): δ 2.29 (3H, s, 3-CH$_3$), 3.06 (1H, br s, exchangeable with D_2O, 1-CHOHCF$_3$), 6.0 (1H, q, J = 4.9 Hz, 1−CHOHCF$_3$), 7.13 (1H, s, H-2), 7.16-7.39 (3H, m, Ar-H), 7.52-7.66 (1H, m, H-7); ^{13}C NMR ($CDCl_3$) : δ 9.41 (3−CH$_3$), 76.06 (1−CHOHCF$_3$), 109.20 (C-7), 113.77 (C-3), 119.23 (C-4), 120.21 (C-6), 121.59 (C-2), 122.50 (C-5), 129.52 (C-8), 136.12 (C-9).

3-Phenyl-1-hydroxytrifluoroethylindole (10): Colourless needles from petroleum ether; IR: 3560 cm^{-1} (OH); ^1H NMR ($CDCl_3$) : δ 3.61 (1H, d, J = 5.1 Hz, exchangeable with D_2O, 1−CHOHCF$_3$), 6.14 (1H, quintet, J = 5.1 Hz, 1−CHOHCF$_3$), 7.11-7.74 (9H, m, Ar-H), 7.84-7.97 (1H, m, H-7); ^{13}C NMR ($CDCl_3$): δ 109.85 (C-7), 119.97 (C-4), 120.18 (C-6), 121.31 (C-5), 121.78 (C-3), 123.04 (C-2), 126.52 (C-8), 126.90 (C-4'), 127.51 (C-2' and 6'), 128.75 (C-3' and 5'), 134.27 (C-1'), 136.37 (C-9), 76.03 (1−CHOHCF$_3$).

3-Ethyl-1-trifluoroethylindole (11): Colourless micro-needles from petroleum ether; ^1H NMR ($CDCl_3$) : δ 1.37 (3H, t, J = 7.5 Hz, 3−CH$_2$CH_3), 2.82 (2H, q, J = 7.5 Hz, 3−CH_2CH$_3$), 4.59 (2H, q, J = 8.67 Hz, 1−CH_2CF$_3$), 6.89 (1H, s, H-2), 7.18-7.67 (4H, m, Ar-H); ^{13}C NMR ($CDCl_3$) : δ 14.08 (3−CH$_2$CH$_3$), 18.04 (3−CH$_2$CH$_3$), 47.55 (1−CH$_2$CF$_3$), 119.80 (C-3), 124.44 (C-2), 108.85 (C-7), 119.25 (C-4), 119.59 (C-5), 122.43 (C-6), 128.18 (C-8), 137.08 (C-9).

Dimeric 2,2,2-trifluoro-1-[1'-(3'-methylindolino)]ethylborane (16): Colourless micro-needles from ethyl acetate-pet. ether; IR:2450 (sh), 2420, 2300 cm^{-1} (BH); ^1H NMR ($CDCl_3$): δ 1.48 (6H, d, J = 8 Hz, 3' and 3''−CH$_3$), 3.38 (2H, t, J= 11 Hz, 2' and 2''−H$_A$), 3.67 (2H, diffused sextet, J~8 Hz, 3' and 3''−H), 4.06 (2H, quintet, J = 9 Hz, 2×CHCF$_3$), 4.35 (2H, dd, J = 11 and 8 Hz, 2' and 2''−H$_B$), 7.2-7.4 (8H, m, Ar-H); ^{13}C NMR ($CDCl_3$) : δ 17.21 (3-CH$_3$), 33.66 (C-3), 61.65 (C-2), 77.73 (1-CHCF$_3$), 117.30 (C-7), 123.82 (C-5), 127.35 (C-4 and C-6), 136.88 (C-8), 150-59, (C-9); $[\alpha]_D^{25°}$ (0.00° (methanol).

Dimeric2,2,2-trifluoro-1-(1'-(3'-ethylindolino)]-ethylborane (17a): While needles from pet. ether; ^1H NMR ($CDCl_3$): δ 1.09 (6H, t,J= 7.22 Hz, 3' and3''-CH$_2$CH_3), 1.63-1.72 (4H, quintet,J= 6.84 and 7.81 Hz, 3' and 3''-CH_2CH$_3$), 2.03-2.09 (4H, m, 2×BH$_2$), 3.48 (2H, q, J= 10.26 Hz,2' and 2''-H$_A$), 3.50-3.56 (2H, m, 3' and 3''H), 3.99 (2H, quintet, J= 8.5 Hz,2×CHCF$_3$), 4.25 (2H, q,J= 10.26 Hz, 2' and 2''-H$_B$), 7.05-7.32(8H, m, Ar-H); ^{13}C NMR ($CDCl_3$): δ 11.48(3-CH$_2$CH$_3$), 25.62(3-CH$_2$CH$_3$), 40.49(C-3), 59.69 (C-2), 95-28 (1-CHCF$_3$), 117.84 (C-7), 124.15 (C-5), 127.38 (C-4), 127.50 (C-6),135-90 (C-8), 151.29 (C-9); optical rotations:, $[\alpha]_D^{29°}$ 0.00° (methanol).

Dimeric 2,2,2-trifluoro-1-[1'-(3'-ethylindolino)]-ethylborane (17b): While micro-needles from a mixture of ethyl acetate and pet.ether; IR: 2440, 2300 cm^{-1} (BH), NMR ($CDCl_3$): δ 1.15 (6H, t, J= 7 Hz, 3' and (3'-CH$_2$CH_3), 1.58-1.63 (4H, diffused quintet, J = 7.5 Hz, 3' and 3''-CH_2CH$_3$), 1.98-2.18 (4H,

m, $2\times BH_2$), 3.42-3.62 (4H, m, 2′ and 2″-H_A and 3′ and 3″-H), 4.05 (2H, diffused quintet, J ~ 8 Hz, $2\times CHCF_3$), 4.30 (2H, q, J = 10 Hz, 2′ and 2″-H_B), 7.26-7.31 (8H, m, Ar-H); ^{13}C NMR ($CDCl_3$) : δ 11.5(3-CH_2-CH_3), 25.75 (3-CH_2CH_3), 40.30 (C-3), 59.50 (C-2), 95.21 (1-$CHCF_3$), 117.88 (C-7), 124.18 (C-5), 127.35 (C-4), 127.56 (C-6), 135.80 (C-8), 151.28 (C-9); $[\alpha]_D^{25°}$ 0.00° (methanol).

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