1-Trifluoromethyl Epoxy Ethers. Effect of Hexafluoro-2-propanol on Reactions with Secondary Aromatic Amines: Synthesis of 3-Trifluoromethyl Indole Derivatives

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Trifluoromethyl epoxy ethers **1** and **2** reacted with aromatic amines in hexafluoro-2-propanol at room temperature providing trifluoromethyl indolinols **3** and **4** in excellent isolated yields. 3-Trifluoromethyl indoles **9** and **10** could be prepared by treatment of indolinols with $SOCl_2$.

Trifluoromethyl epoxy ethers, which are versatile and useful building blocks, are easily available in two steps from the inexpensive ethyl trifluoroacetate.[1,2,3] The electron-withdrawing character of the CF_3 group stabilizes epoxy ethers toward proteolysis. This stability allows investigations on the oxirane ring opening with various nucleophiles.[3,4] For instance, oxirane ring opening of these epoxy ethers by nitrogen nucleophiles is a good access to trifluoromethyl α-amino ketones and then to *β*-amino alcohols by stereoselective reduction.[5,6,7]

In particular, we have reported that disubstituted aliphatic amines could react with epoxy ethers **1** and **2**, providing in good yields the corresponding amino ketones.[5] However, until now reaction of epoxy ethers **1** and **2** with less nucleophilic aromatic amines had not been studied. Recently we showed that ring opening of epoxides with thiols and with aromatic amines were facilitated when performed in hexafluoro-2-propanol (HFIP), with no use of metal or Lewis acid catalysis.[8,9] Consequently, we have investigated the reaction of epoxy ethers **1** and **2** with several aromatic secondary amines in HFIP, and we report here the results of this study.

The reaction of the epoxy ether **1** with *N*-methylaniline (1 equiv) was conducted in HFIP as solvent. The reaction was fast and complete at room temperature after only 45 min. However, the expected amino ketone could not be detected, and the new compound **3a** could be isolated in 91% yield, as a 94:6 mixture of diastereoisomers (Scheme 1).

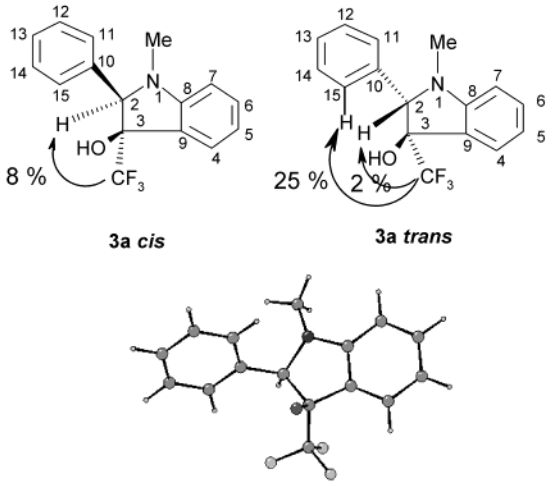
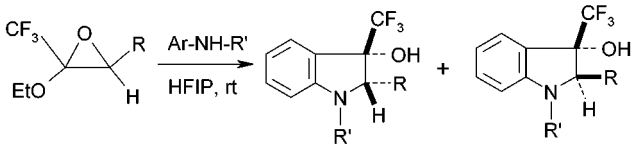


Figure 1. Structure of *cis*-**3a**: NOE experiments and ORTEP stereoplot view of the crystal structure.[10]

Scheme 1. Reaction of Epoxy Ethers 1 and 2 with *N*-Methylaniline



1 R = C_6H_5
2 R = CH_2-CH_2-C_6H_5

3a R = C_6H_5 (91 %) (94:6)
4a R = CH_2-CH_2-C_6H_5 (90 %) (86:14)

a Ar-NH-R' = C_6H_5-NH-Me

Structure of this trifluoromethyl indolinol **3a** has been elucidated by NMR through total assignment of protons and carbons (HMBC, HMQC, COSY). Hetero NOE experiments suggested the cis relationship between the trifluoromethyl group and the proton H-2 for the major diastereoisomer: irradiation of the CF_3 group induced an enhancement of the H-2 signal of 8%, while the same experiment performed on the minor isomer induced a 2% enhancement for H-2 and a 25% enhancement for the ortho proton of the phenyl substituent. The structure of the major cis isomer **3a** has been confirmed by X-ray diffraction (Figure 1).[10]

Under the same conditions, the epoxy ether **2** reacted similarly with *N*-methylaniline to provide the indolinols

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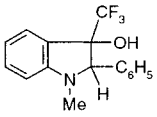
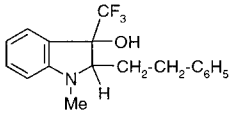
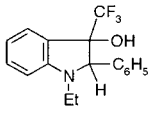
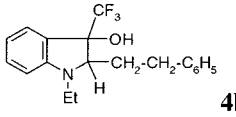
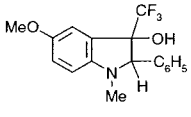
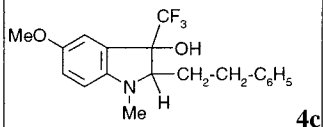
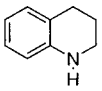
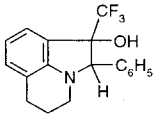
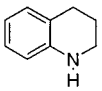
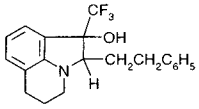
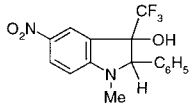
Table 1. Preparation of 3-Trifluoromethyl Indolinols in HFIP at Room Temperature

Epoxy ether	Amine	Time	Compound	% *cis/trans*[a]	Yields[b]
1	C_6H_5-NH-CH_3	45min	 **3a**	94:6	91 %
2	C_6H_5-NH-CH_3	10 h	 **4a**	86:14	90 %
1	C_6H_5-NH-C_2H_5	30min	 **3b**	96:4	98 %
2	C_6H_5-NH-C_2H_5	40 h	 **4b**	89:11	90 %
1	MeO-C_6H_4-NH-Me	5 min	 **3c**	90:10	90 %
2	MeO-C_6H_4-NH-Me	5 h	 **4c**	85:15	89 %
1		20min	 **3d**	96:4	98 %
2		40 h	 **4d**	79:21	90 %
1	NO_2-C_6H_4-NH-Me	16 h	 **3e**	92:8	65 %[c]

[a] This ratio remains unchanged during the reaction. [b] Isolated yields. [c] About 25% of amino alcohols **7e** were also isolated as a mixture 85:15 of two diastereosisomers.

4a (cis/trans: 86/14) in a 90% yield. However, reaction time with **2** was longer than with **1**, 10 h instead of 45 min. This reaction has been then extended to a range of secondary arylamines (Table 1). With *N*-ethylaniline and *N*-methyl-*p*-anisidine, complete conversion occurred at room temperature, leading to the indolinols **3b**,**c** and **4b**,**c** in very high yields (90−98%). With **2** reaction times were longer than with **1** and selectivity toward the cis isomer was slightly lower than with **1**. A cyclic secondary amine, the tetrahydroquinoline, also reacted, leading to the tricyclic compounds **3d** and **4d** (98 and 90%).

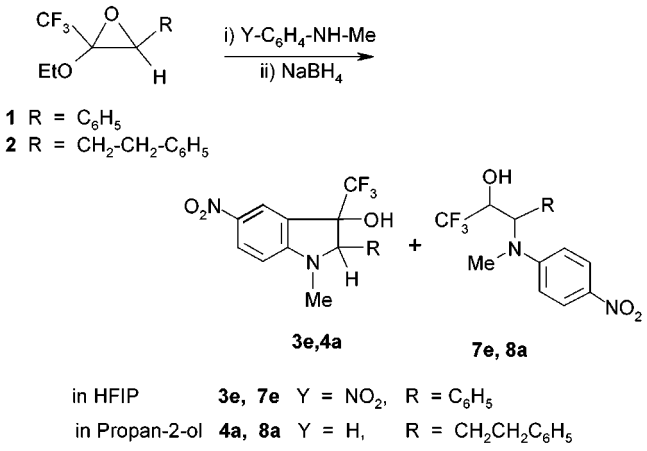
Interestingly, even the poor nucleophilic *N*-methyl-*p*-nitroaniline still reacted with the epoxy ether **1**. However, a long reaction time was required (16 h), and the indolinol **3e** (92/8) was accompanied with 25% of the amino ketone **5e**, which was reduced in situ with $NaBH_4$ into the amino alcohol **7e** as a 85/15 mixture of diastereoisomers (Scheme 2, Table 1). When the reaction was stopped before the complete disappearance of starting material (75% conversion), the ratio ketone/indolinol was 60/40.

These experiments with nitroaniline indicate that the formation of indolinols is a two-step process, the oxirane ring opening by the aromatic amine leading to amino ketones **5** and **6** followed by a cyclization, similar to a Bischler-type reaction (Scheme 3).[11,12]

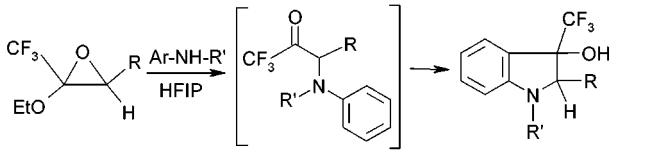
(10) The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Center. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK.

(11) Moody, C. J.; Swann, E. *Synlett* **1998**, 135−136.

Scheme 2. Reactions of Epoxy Ethers 1 and 2 with *N*-Methylanilines



Scheme 3. Two-Step Formation of CF_3-Indolinols



Apart from the reaction with *N*-methyl-*p*-nitroaniline, the intermediate amino ketone could not be detected, even when the reaction was stopped before completion. Consequently, the cyclization step is instantaneous, and the difference of reaction rate between epoxy ethers **1** and **2** is due to the first step: the oxirane ring opening of **1** is greatly facilitated by the activating effect of the phenyl group as exemplified in ring opening reactions of styrene oxide.[9,13]

The high diastereoselectivity of the reaction preponderantly leading to the cis trifluoromethyl indolinol probably results from the geometry of the second step transition state. Due to the steric hindrance of the trifluoromethyl group,[14] conformation **A** of the amino ketones **5** and **6**, leading to the cis isomer, will be greatly favored to the detriment of the conformation **B** (leading to trans compound). (Figure 2).

This second step, as other cyclialkylation reactions generally requires proton or Lewis acid catalysis.[12] It is well-known that cyclialkylation reactions are greatly facilitated by the strong electrophilicity of the carbonyl group of the trifluoromethyl ketones.[15,16] This effect joined to the great nucleophilicity of the aromatic ring, due to the amino-substituent, explains the easiness of the reaction in these very smooth conditions.[17,18] As expected,

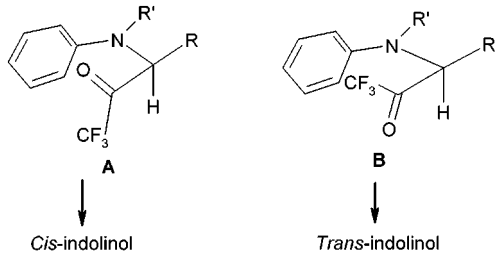


Figure 2. Cyclization transition state of amino ketone **5** and **6**.

when the arylamine is deactivated, as for the *p*-nitro *N*-methylaniline, the rate of cyclization slowed and the intermediate amino ketone could be observed, while with the *N*-methyl-*p*-anisidine the reaction was greatly accelerated. Conversely, the nature of the *N*-substituent did not have any clear effect on reaction rate. However, its presence is required: when treated with aniline under the same conditions, the epoxy ether **1** led to a complex mixture of unidentified products, as already observed in reactions of epoxy ethers with nonaromatic primary amines.[6]

To evaluate the role of HFIP in this cascade process, the reaction has also been performed in 2-propanol at room temperature. As an example, with the less reactive epoxy ether **2**, after 25 h, there was only 25% conversion with a 97/3 mixture of amino ketone **6a** and indolinol **4a**. After 2 days, 42% of **2** were converted into a 88/12 mixture of **6a** and **4a**, and 5 days were required for a complete reaction with the formation of a 50/50 mixture of **6a** and **4a**. After reduction, a mixture of amino alcohols **8a** (96/4) and indolinols **4a** (70/30) was obtained (Scheme 2). This clearly indicates that, as expected,[8,9] the strong ionizing power of HFIP,[19] and its hydrogen bond donor ability[20] activates the epoxy ether ring opening. Moreover, HFIP facilitates also the cyclialkylation reaction, acting probably through strong hydrogen bonding with the carbonyl of the trifluoromethyl amino ketone. This explains the striking difference of cyclization rates in HFIP and 2-propanol.

Trifluoromethyl indolinols **3** and **4** did not undergo aromatization into indoles in the reaction medium, conversely to the Nordlander reaction with nonfluorinated substrates where the intermediate indolinols are not isolated.[11,12] Although tertiary trifluoromethyl alcohols are stable even in acidic conditions, as previously reported in other electrophilic cyclizations,[21,22] benzylic ones are more often prone to elimination or substitution.[15,16,23] In our case, despite the aromatization energy profits, the dehydration into corresponding indoles did not occur. This is the result of the very mild conditions of cyclization.

However, the preparation of 3-trifluoromethyl indoles from corresponding indolinols could be of great interest.

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(15) Bonnet-Delpon, D.; Charpentier-Morize, M.; Jacquot, R. *J. Org. Chem.* **1988**, *53*, 759−762.

(16) Aubert, C.; Bégué, J. P.; Bonnet-Delpon, D.; Mesureur, D. *J. Chem. Soc., Perkin Trans. 1* **1989**, 395−399.

(17) Reaction of epoxy ether **1** and *N*-methyl benzylamine in HFIP provided only the amino ketone; cyclialkylation did not occur.

(18) Sundberg, R. J. In *Indoles, Best Synthetic Series*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Academic Press Publishers: London, 1996; p 42.

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(20) Eberson, L.; Hartshorn, M. P.; Persson, O.; Radner, F. *J. Chem. Soc., Chem. Commun.* **1996**, 2105−2112.

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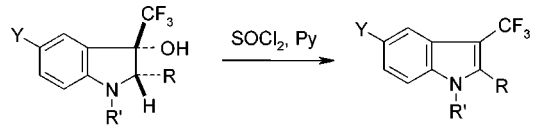
(23) Okada, E.; Tsukushi, N. *Heterocycles* **2000**, *53*, 127−134.

Scheme 4. Preparation of 3-Trifluoromethyl Indoles from Indolinols



3a R = C_6H_5 Y = H **9a** R = C_6H_5 Y = H
4a R = CH_2-CH_2-C_6H_5 Y = H **10a** R = CH_2-CH_2-C_6H_5 Y = H
4c R = CH_2-CH_2-C_6H_5 Y = OMe **10c** R = CH_2-CH_2-C_6H_5 Y = OMe

Indolic structures are present in numerous natural and bioactive compounds,[24] but often suffer from instability due to a great sensitivity to oxidizing conditions, in particular at C-3.[24,25] Presence of the electron-withdrawing trifluoromethyl substituent at this site could disfavor electrophilic processes. There are only a few reported fluoroalkyl indoles in the literature, and most of described approaches are not regioselective and give rise to a mixture of 2- and 3-fluoroalkyl indoles.[26] We thus searched for good conditions for indolinol dehydration. The use of thionyl chloride appeared to allow a clean dehydration. As examples, treatment of indolinols **3a** and **4a**,**c** with thionyl chloride in the presence of pyridine provided in good yields (80%) the 2-substituted-3-trifluoromethyl indoles **9a** and **10a**,**c**, respectively (Scheme 4). These compounds can be easily purified and stored without any particular caution.

In conclusion, this easy and clean reaction of trifluoromethyl epoxy ethers with aromatic amines in HFIP allows the stereoselective preparation of bi- or tricyclic heterocyclic compounds, which can be converted into corresponding 3-trifluoromethyl indoles. 3-Trifluoromethyl indoles were poorly described in the literature,[26] and this new approach is particularly efficient and concise. These results also demonstrate the interest of the use of HFIP as reaction solvent and as replacement of acid catalysis.

Experimental Section

NMR spectra were performed with $CDCl_3$ solutions, on a Varian EM, FH dual probehead, a Bruker AC200, and an ARX 400 spectrometer (^{1}H: 200, or 400 MHz, ^{19}F 188, or 376 MHz; and ^{13}C: 50 or 100 MHz). Chemicals shifts are reported in ppm relative to Me_4Si and $CFCl_3$ (for ^{19}F NMR) as internal standards. In the ^{13}C NMR data, reported signal multiplicities are related to C−F coupling. For the determination of fine coupling constants, an acquisition of 16K data points, a Lorenz-Gauss transformation of the FID and a zero filling to 64K were performed in order to obtain a minimum of resolution of 0.2 Hz/pt (1H) or 0.5 Hz/pt (13c). When indicated, assignments of signals resulted from a complete assignment of the spectrum through HMQC, HMBC experiments performed on a multinuclear probehead equipped with a Z-gradient coil.

General Procedure for Reaction of Epoxy Ethers 1 and 2 with Aromatic Amines. A solution of epoxy ether **1** or **2**[2] (2 mmol) and aromatic amine (1 equiv) in 2.5 mL of HFIP was stirred at room temperature. After disappearance of starting material (monitored by GC), the reaction mixture was evaporated under reduced pressure in order to eliminate solvent and recovered aromatic amine. The residue was purified on SiO_2 chromatography column (petroleum ether/Et_2O: 85/15).

Reaction of *N*-Methylaniline with Epoxy Ether 1: 1-Methyl-2-phenyl-3-(trifluoromethyl)-3-indolinol (3a). From epoxy ether **1** (500 mg, 2.15 mmol) and *N*-methylaniline (0.2 mL), after 45 min and workup, a 94/6 mixture of cis and trans indolinols **3a** was isolated (575 mg, 91%). ^{19}F NMR δ −76.6 and −77.8. Anal. Calcd for $C_{16}H_{14}F_3NO$: C, 65.52; H, 4.81; N 4.78. Found: C, 65.42; H, 4.83; N 4.71.

Separation by SiO_2 chromatography provided pure diastereoisomer *cis*-**3a**:

(2*S,3*S**) 1-Methyl-2-phenyl-3-(trifluoromethyl)-3-indolinol (*cis*-3a)**: 547 mg (87%); mp: 91 °C (Et_2O, hexane); ^{19}F NMR δ −77.8 (s); ^{1}H NMR δ 2.2 (br s, 1 H, OH), 2.75 (s, 3 H, CH_3), 4.7 (s, 1 H, H-2), 6.7 (d, J = 8 Hz, 1 H, H-7), 6.85 (t, ^3J = 7.5 Hz, 1 H, H-5), 7.4 (m, 7 H, arom); ^{13}C NMR δ 33.0, 73.8, 80.0 (q, $^2J_{CF}$ = 28 Hz), 107.8, 118.7, 123.6, 125.1 (q, $^1J_{CF}$ = 283 Hz), 125.3, 128.7, 129.1, 129.5, 131.6, 133.6, 152.9.

(2*S,3*R**)-1-Methyl-2-phenyl-3-(trifluoromethyl)-3-indolinol (*trans*-3a)**: 28 mg (4%); ^{19}F NMR δ −76.6; ^{1}H NMR δ 2.7 (s, 3 H, CH_3), 3.0 (br s, 1 H, OH), 4.5 (s, 1 H, H-2), 6.7 (d, ^3J = 8 Hz, 1 H, H-7), 6.85 (t, ^3J = 7.5 Hz, 1 H, H-5), 7.4 (m, 7 H, arom); ^{13}C NMR δ 34.0, 81.0, 83.0 (q, $^2J_{CF}$ = 28 Hz), 108.3, 118.5, 123.5 (q, $^1J_{CF}$ = 284 Hz), 125.0, 131.5, 132.0, 134.0, 128.8, 129.2, 129.9, 153.0.

Reaction of *N*-Ethylaniline with Epoxy Ether 1: 1-Ethyl-2-phenyl-3-(trifluoromethyl)-3-indolinol (3b). From epoxy ether **1** (500 mg, 2.15 mmol) and *N*-ethylaniline (0.27 mL), after 30 min and workup, a 96/4 mixture of cis and trans indolinols **3b** was isolated (648 mg, 98%). ^{19}F NMR δ −75.9 and −78.3. Anal. Calcd for $C_{17}H_{16}F_3NO$: C, 66.44; H, 5.25; N 4.56. Found: C, 66.27; H, 5.48; N 4.39.

Separation by SiO_2 chromatography provided pure diastereoisomers *cis*- and *trans*-**3b**:

(2*S,3*S**) 1-Ethyl-2-phenyl-3-(trifluoromethyl)-3-indolinol (*cis*-3b)**: 628 mg (95%); mp 75 °C (Et_2O, hexane); ^{19}F NMR δ −77.3 (s); ^{1}H NMR δ 1.04 (t, ^3J = 7 Hz, 3 H, C*H*$_3$), 2.0 (br s, 1 H, O*H*), 3.0 (qd, ^3J = 7 Hz, ^2J = 14.5 Hz, 1 H, H_AH$_B$-CH$_3$), 3.4 (qd, ^3J = 7 Hz, ^2J = 14.5 Hz, 1 H, H$_A$$H_B$-CH$_3$), 4.9 (s, 1 H, H-2), 6.6 (d, J = 8 Hz, 1 H, H-7), 6.8 (t, ^3J = 7.5 Hz, 1 H, H-5), 7.4 (m, 7 H, arom); ^{13}C NMR δ 10.2, 39.4, 70.2, 80.3 (q, $^2J_{CF}$ = 29 Hz, C−CF$_3$), 107.8, 118.2, 123.8, 125.4 (q, $^1J_{CF}$ = 283 Hz), 125.7, 128.8, 129.1, 129.7, 131.7, 133.6, 151.7.

(2*S,3*R**)-1-Ethyl-2-phenyl-3-(trifluoromethyl)-3-indolinol (*trans*-3b)**: 33 mg (4%); mp 111 °C; ^{19}F NMR δ −75.9; ^{1}H NMR δ 1.06 (t, ^3J = 7 Hz, 3 H, C*H*$_3$), 2.9 (br s, 1 H, O*H*), 3.0 (qd, ^3J = 7 Hz, ^2J = 14 Hz, 1 H, H_AH$_B$-CH$_3$), 3.4 (qd, ^3J = 7 Hz, ^2J = 14 Hz, 1 H, H$_A$$H_B$-CH$_3$), 4.8 (s, 1 H, H-2), 6.7 (d, ^3J = 8 Hz, 1 H, H-7), 6.8 (t, ^3J = 7.5 Hz, 1 H, H-5), 7.4 (m, 7 H, arom); ^{13}C NMR δ 10.2, 39.8, 77.5, 83.3 (q, $^2J_{CF}$ = 29 Hz), 108.6, 118.6, 124.5 (q, $^1J_{CF}$ = 285 Hz), 124.7, 125.4, 128.5, 128.7, 131.8, 134.5, 152.2.

Reaction of *N*-Methyl-*p*-anisidine with Epoxy Ether 1: 1-Methyl-5-methoxy-2-phenyl)-3-(trifluoromethyl)-3-indolinol (3c). From epoxy ether **1** (400 mg, 1.72 mmol) and *N*-methyl-*p*-anisidine (236 mg, 1.72 mmol) after 5 min and workup, a 90/10 mixture of cis and trans indolinols **3c** was isolated (500 mg, 90%). ^{19}F NMR δ −76.7 and −77.2. Anal. Calcd for $C_{17}H_{16}F_3NO_2$: C, 63.15; H, 4.99; N 4.33. Found: C, 63.08; H, 4.97; N 4.30.

Separation by SiO_2 chromatography provided pure diastereoisomer *cis*-**3c**:

(2*S,3*S**)-1-Methyl-5-methoxy-2-phenyl)-3-(trifluoromethyl)-3-indolinol (*cis*-3c)**: 467 mg (84%); mp: 105 °C (Et_2O, hexane); ^{19}F NMR δ −77.2 (s); ^{1}H NMR δ 2.1 (s, 1 H, OH), 2.6 (s, 3 H, CH_3), 3.8 (s, 3 H, O−CH_3), 4.5 (s, 1 H, H-2), 6.6 (d, J = 8 Hz, 1 H, H-7), 6.9 (t, ^3J = 8 Hz, 1 H, H-6), 7.0 (br s, H-4), 7.4 (m, 5 H, arom); ^{13}C NMR δ 34.3, 56.3, 74.8, 80.3 (q, $^2J_{CF}$ = 30 Hz), 109.2, 111.2, 118.1, 124.6, 125.2 (q, $^1J_{CF}$ = 284 Hz), 128.9, 129.3, 129.8, 133.4, 147.7, 153.6.

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Reaction of Tetrahydroquinoline with Epoxy Ether 1: 2-Phenyl-3-(trifluoromethyl)-1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-1-ol (3d). From epoxy ether **1** (300 mg, 1.29 mmol) and tetrahydroquinoline (0.16 mL, 1.29 mmol) after 20 min and workup, a 96/4 mixture of cis and trans indolinols **3d** was isolated (407 mg, 98%). ^{19}F NMR δ −76.6 and −76.8. Anal. Calcd for $C_{18}H_{16}F_3NO$: C, 67.70; H, 5.05; N 4.39. Found: C, 67.69; H, 5.19; N 4.30.

Separation by SiO_2 chromatography provided pure diastereoisomers *cis*-**3d** and *trans*-**3d**:

(2*S,3*S**)-2-Phenyl-3-(trifluoromethyl)-1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-1-ol (*cis*-3d)**: yellow oil (379 mg, 92%); ^{19}F NMR δ −76.8 (s); ^{1}H NMR δ 2.2 (m, 1 H, H-5$_{eq}$), 2.3 (qdd, $^3J_{H5_{ax}-H6_{eq}} = 4$ Hz, $^3J_{H5_{ax}-H4_{eq}} = 7$ Hz, $^2J_{H5_{ax}-H5_{eq}} = {}^3J_{H5_{ax}-H4_{ax}} = {}^3J_{H5_{ax}-H6_{ax}} = 11$ Hz, 1 H, H-5$_{ax}$), 2.5 (br s, 1 H, OH), 2.9 (m, 3 H, H-4, H-6$_{ax}$), 3.2 (dt, $^3J_{H6_{eq}-H5_{eq}} = {}^3J_{H6_{eq}-H5_{eq}} = 4.4$ Hz, $^3J_{H6_{eq}-H6_{ax}} = 11$ Hz, 1 H, H-6$_{eq}$), 4.8 (s, 1 H, H-2), 6.9 (t, $^3J = 7.5$ Hz, 1 H, H-8), 7.2 (d, $^3J = 7$ Hz, H-7), 7.4 (d, $^3J = 7$ Hz, H-9), 7.6 (m, 5 H); ^{13}C NMR δ 23.0, 24.5, 44.0, 73.5, 81.7 (q, $^2J_{CF} = 29$ Hz), 119.0, 120.0, 123.0, 123.6, 125.1 (q, $^1J_{CF} = 283$ Hz), 129.1, 130.0, 130.2, 143.0, 149.0.

(2*S,3*R**)-2-Phenyl-3-(trifluoromethyl)-1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-1-ol (*trans*-3d)**: yellow oil (28 mg, 7%); ^{19}F NMR δ −76.6 (s); ^{1}H NMR δ 2.2 (m, 1 H, H-5$_{eq}$), 2.3 (qdd, $^3J_{H5_{ax}-H6_{eq}} = 4$ Hz, $^3J_{H5_{ax}-H4_{eq}} = 7$ Hz, $^2J_{H5_{ax}-H5_{eq}} = {}^3J_{H5_{ax}-H4_{ax}} = {}^3J_{H5_{ax}-H6_{ax}} = 11$ Hz, 1 H, H-5$_{ax}$), 2.5 (br s, 1 H, OH), 2.9 (m, 3 H, H-4, H-6$_{ax}$), 3.1 (dt, $^3J_{H6_{eq}-H5_{eq}} = {}^3J_{H6_{eq}-H5_{eq}} = 3.8$ Hz, $^3J_{H6_{eq}-H6_{ax}} = 10.5$ Hz, 1 H, H-6$_{eq}$), 4.5 (s, 1 H, H-2), 6.7 (t, $^3J = 7.5$ Hz, 1 H, H-8), 7.0 (d, $^3J = 7$ Hz, H-7), 7.1 (d, $^3J = 7$ Hz, H-9), 7.3 (m, 5 H); ^{13}C NMR δ 22.6, 24.2, 45.0, 81.1, 83.7 (q, $^2J_{CF} = 28$ Hz, *C*-CF$_3$), 119.5, 120.9, 122.6, 123.4, 124.4 (q, $^1J_{CF} = 286$ Hz, CF$_3$), 128.5, 128.6, 130.3, 134.2, 150.3.

Reaction of *N*-Methyl-*p*-nitroaniline with Epoxy Ether 1. Epoxy ether **1** (100 mg, 0.43 mmol) and *N*-methyl-*p*-nitroaniline (65 mg, 0.43 mmol) reacted in HFIP (0.43 mL) for 16 h. $NaBH_4$ (16 mg, 1 equiv) was then added. After 1 h, hydrolysis with a few drops of water, drying on $MgSO_4$, and evaporation of solvent provided 141 mg of crude product, as a 74/26 mixture of indolinols **3e** (cis/trans: 92/8) and amino alcohols **7e** (85/15), (^{19}F NMR ($CFCl_3$) δ −75.2 (s) (6%), −75.9 (d, $J = 6.3$ Hz) (22%), −76.2 (d, $J = 6.3$ Hz) (4%), and −79.6 (s) (68%)). Chromatography on SiO_2 (petroleum ether/Et_2O: 65/35) afforded first 88 mg of pure cis indolinol **3e** (60%) and then 44 mg of a mixture of trans indolinol **3e** and amino alcohols **7e**.

(2*S*,* 3*S)-1-Methyl-5-nitro-2-phenyl-3-(trifluoromethyl)-2,3-dihydro-1*H*-indolin-3-ol (*cis*-3e)**: mp 129 °C; ^{19}F NMR δ −79.6, (s); ^{1}H NMR δ 2.7 (s, 3 H, NCH$_3$), 4.9 (s, 1 H, H-2), 5.3 (bs, 1 H, OH), 6.4 (d, $^3J_{H7-H6} = 9.6$ Hz, 1 H, H-7), 7.2−7.4 (m, 5 H, Ph); 8.1 (d, $^3J_{H6-H7} = 9.6$ Hz, 1 H, H-6), 8.2 (s, 1 H, H-4); ^{13}C NMR δ 31.9 (NCH$_3$), 73.8, 79.3 (q, $^2J_{CF} = 30.0$ Hz, C-3), 105.3, 123.0, 123.7, 124.7 (q, $^1J_{CF} = 283$ Hz, CF$_3$), 129.3, 129.5, 129.9, 131.2, 140.0, 156.7. Anal. Calcd for $C_{16}H_{13}F_3N_2O_3$: C, 56.80; H, 3.85; N 8.28. Found: C, 56.82; H, 3.94; N 8.07.

(2*S,3*R**)-1-Methyl-5-nitro-2-phenyl-3-(trifluoromethyl)-2,3-dihydro-1*H*-indolin-3-ol (*trans*-3e)**: ^{19}F NMR δ −75.2, (s); ^{1}H NMR δ 2.9 (s, 3 H, NCH$_3$), 4.6 (bs, 1 H, OH), 4.8 (s, 1 H, H-2), 6.5 (d, $^3J_{H7-H6} = 9.3$ Hz, 1 H, H-7), 7.3−7.4 (m, 5 H, Ph); 8.1 (d, $^3J_{H6-H7} = 9.3$ Hz, 1 H, H-6), 8.3 (s, 1 H, H-4); ^{13}C NMR δ 32.5, 76.7, 81.7 (q, $^2J_{CF} = 30$ Hz, C-3), 110.7, 122.2, 124.6, 126.4, 128.6, 129.2, 132.2, 138.0, 154.1, (CF$_3$ not obsvd).

1,1,1-Trifluoro-3-(methyl-3-nitroanilino)-5-phenyl-pentan-2-ol (major isomer 7e): ^{19}F NMR δ −75.9 (d, $^3J_{FH} = 6.3$ Hz); ^{1}H NMR δ 2.8 (s, 3 H, NCH$_3$), 4.7 (q, $^3J_{H2-H3} = {}^3J_{H2-F} = 6.3$ Hz, 1 H, H-2), 5.2 (bs, 1 H, OH), 5.3 (d, $^3J_{H3-H2} = 6.3$ Hz, 1 H, H-3), 6.8 (d, $^3J_{H6-H7} = {}^3J_{H10-H9} = 9.4$ Hz, 2 H, H-6 and H-10), 7.2−7.3 (m, 5 H, Ph), 8.0 (d, $^3J_{H7-H6} = {}^3J_{H9-H10} = 9.4$ Hz, 2H, H-7 and H-9). ^{13}C NMR ^{1}H δ 34.3, 61.0, 69.4, 112.5, 124.5 (q, $^1J_{CF} = 282$ Hz, CF$_3$), 126.0, 127.5, 128.0, 129.0, 134.8, 138.8, 155.0.

Reaction of *N*-Methylaniline with Epoxy Ether 2: 1-Methyl-2-phenethyl-3-(trifluoromethyl)-3-indolinol (4a). From epoxy ether **2** (500 mg, 1.92 mmol) and *N*-methylaniline (0.21 mL, 1.92 mmol) after 10 h, and workup, a 86/14 mixture of cis and trans indolinols **4a** was isolated (555 mg, 90%). ^{19}F NMR δ −76.5 and −79.1. Anal. Calcd for $C_{18}H_{18}F_3NO$: C, 67.28; H, 5.65; N 4.36. Found: C, 67.21; H, 5.64; N, 4.30.

Separation by SiO_2 chromatography provided pure diastereoisomer *cis*-**4a**:

(2*S,3*S**)-1-Methyl-2-phenethyl-3-(trifluoromethyl)-3-indolinol (*cis*-4a)**: 422 mg (68%); mp 68 °C (Et_2O, hexane); ^{19}F NMR δ −79.1 (s); ^{1}H NMR δ 2.1 (dddd, $^3J = 3.6$ Hz, $^3J = 6.2$ Hz, $^3J = 10.2$, $^2J = 14.5$ Hz, 1 H, C*H*$_A$H$_B$-CH$_2$-C$_6$H$_5$), 2.3 (dddd, $^3J = 7.2$ Hz, $^3J = 5.7$ Hz, $^3J = 10.5$, $^2J = 14.5$ Hz, 1 H, CH$_A$*H*$_B$-CH$_2$-C$_6$H$_5$), 2.4 (br s, 1 H, OH); 2.80 (ddd, $^3J = 6.2$ Hz, $^3J = 10.4$ Hz, $^2J = 13.8$ Hz, 1 H, CH$_2$−C*H*$_A$H$_B$-C$_6$H$_5$), 2.83 (s, 3 H, CH$_3$); 2.9 (ddd, $^3J = 5.5$ Hz, $^3J = 10.7$ Hz, $^2J = 13.8$ Hz, 1 H, CH$_2$−CH$_A$*H*$_B$-C$_6$H$_5$), 3.5 (dd, $^3J = 3.7$ Hz, $^3J = 7.2$ Hz, 1 H-2), 6.6 (d, $J = 8$ Hz, 1 H, H-7), 6.8 (t, $^3J = 7.5$ Hz, 1 H, H-5), 7.3 (m, 7 H, arom); ^{13}C NMR δ 29.6, 32.6, 33.8, 68.2, 80.7 (q, $^2J_{CF} = 30$ Hz), 108.1, 118.2, 124.5, 124.8, 125.1 (q, $^1J_{CF} = 283$ Hz), 125.9, 128.4, 131.8, 142.3, 152.9.

(2*S,3*R**) 1-Methyl-2-phenethyl-3-(trifluoromethyl)-3-indolinol (*trans*-4a)**: 28 mg (12%); ^{19}F NMR δ −76.5; ^{1}H NMR δ 2.3 (q, $^3J = 7.5$ Hz, 2 H, C*H*$_2$−CH$_2$−C$_6$H$_5$); 2.8 (s, 3 H, CH$_3$); 2.9 (ddd, $^2J = 14$ Hz, $^3J = 8.5$ Hz, $^3J = 5.5$ Hz, 1 H, CH$_2$−CH$_A$*H*$_B$−C$_6$H$_5$); 3.1 (ddd, $^2J = 14$ Hz, $^3J = 10.5$ Hz, $^3J = 7.5$ Hz, 1 H, CH$_2$−C*H*$_A$H$_B$−C$_6$H$_5$); 3.3 (dd, $^3J = 6.5$ Hz, $^3J = 5.5$ Hz, 1 H, H$_2$); 6.7 (d, $^3J_{H7-H6} = 8$ Hz, 1 H, H$_7$); 6.9 (t, $^3J = 7.5$ Hz, $^4J = 1$ Hz, 1 H, H$_5$); 7.2−7.4 (m, 7 H, arom); ^{13}C NMR δ 29.3, 32.4, 35.0, 76.4, 82.1 (q, $^2J_{CF} = 30$ Hz), 109.5, 119.2, 124.6, 125.1 (q, $^1J_{CF} = 286$ Hz), 125.6, 126.1, 128.6, 131.5, 141.7, 153.4.

Reaction of *N*-Ethylaniline with Epoxy Ether 2: 1-Ethyl-2-phenethyl-3-(trifluoromethyl)-3-indolinol (4b). From epoxy ether **2** (500 mg, 1.92 mmol) and *N*-ethylaniline (0.24 mL, 1.92 mmol), after 40 h and workup, a 89/11 mixture of cis and trans indolinols **4b** was isolated (555 mg, 90%). ^{19}F NMR δ −76.5 and −79.5. Anal. Calcd for $C_{19}H_{20}F_3NO$: C, 68.05; H, 6.01; N 4.18. Found: C, 68.17; H, 6.12; N 4.12.

Separation by SiO_2 chromatography provided pure diastereoisomer *cis*-**4b**:

(2*S,3*S**)-1-Ethyl-2-phenethyl-3-(trifluoromethyl)-3-indolinol (*cis*-4b)**: 522 mg (81%); mp 67 °C (Et_2O, hexane); ^{19}F NMR δ −79.5 (s); ^{1}H NMR δ 1.08 (t, $^3J = 7$ Hz, 3 H, CH$_3$), 2.1 (dddd, $^3J_{H2-H10b} = 3.4$ Hz, $^3J_{H11b-H10b} = 6.3$ Hz, $^3J_{H11a-H10b} = 10$ Hz, $^2J_{H10a-H10b} = 13$ Hz, 1 H, C*H*$_B$H$_A$-CH$_2$−C$_6$H$_5$), 2.3 (dddd, $^3J_{H2-H10a} = 7.8$ Hz, $^3J_{H11a-H10a} = 6$ Hz, $^3J_{H11b-H10a} = 10$ Hz, $^2J_{H10b-H10a} = 13.8$ Hz, 1 H, C*H*$_A$H$_B$-CH$_2$−C$_6$H$_5$), 2.4 (br s, 1 H, OH); 2.80 (ddd, $^3J_{H10b-H11b} = 6$ Hz, $^3J_{H10a-H11b} = 10.6$ Hz, $^2J_{H11a-H11b} = 13.8$ Hz, 1 H, CH$_2$−CH$_A$*H*$_B$-C$_6$H$_5$), 2.9 (ddd, $^2J_{H11a-H11b} = 13.8$ Hz, $^3J_{H11a-H10b} = 10$ Hz, $^3J_{H11a-H10a} = 6$ Hz, 1 H, CH$_2$−C*H*$_A$H$_B$-C$_6$H$_5$), 3.2 (qd, $^3J = 7$ Hz, $^3J = 14.5$ Hz, 1 H, N-C*H*H−CH$_3$), 3.5 (qd, $^3J = 7$ Hz, $^3J = 14.5$ Hz, 1 H, N-CH*H*-CH$_3$), 3.8 (dd, $^3J = 7.8$ Hz, $^3J = 3.3$ Hz, 1 H, H-2), 6.5 (d, $J = 8$ Hz, 1 H, H-7), 6.8 (m, 1 H, H-5), 7.3 (m, 7 H, arom); ^{13}C NMR δ 10.5, 30.0, 33.0, 39.2, 64.0, 81.3 (q, $^2J_{CF} = 29.5$ Hz), 108.1, 117.5, 124.8 (q, $^4J_{CF} = 2$ Hz), 125.0, 125.3 (q, $^1J_{CF} = 283$ Hz), 126.0, 128.5, 128.6, 131.8, 142.3, 151.4.

Reaction of *N*-Methyl-*p*-anisidine with Epoxy Ether 2: 1-Methyl-2-phenethyl-5-methoxy-3-(trifluoromethyl)-3-indolinol (4c). From epoxy ether **2** (500 mg, 1.92 mmol) and *N*-methyl-*p*-anisidine (263 mg, 1.92 mmol) after 5 h and workup, a 85/15 mixture of cis and trans indolinols **4c** was isolated (599 mg, 89%). ^{19}F NMR δ −76.7 and −78.5. Anal. Calcd for $C_{19}H_{20}F_3NO_2$: C, 64.95; H, 5.74; N 3.99. Found: C, 65.10; H, 5.87; N, 3.89.

Separation by SiO_2 chromatography provided pure diastereoisomer *cis*-**4c**:

(2*S,3*S**)-1-Methyl-2-phenethyl-5-methoxy-3-(trifluoromethyl)-3-indolinol (*cis*-4c)**: 431 mg, 64%); mp 90 °C; ^{19}F NMR δ −78.5 (s); ^{1}H NMR δ 2.1 (dddd, $^3J = 4.2$ Hz, $^3J = 6.5$ Hz, $^3J = 10.5$, $^2J = 14.5$ Hz, 1 H, C*H*$_A$H$_B$-CH$_2$−C$_6$H$_5$), 2.3 (dddd, $^3J = 6.5$ Hz, $^3J = 5.8$ Hz, $^3J = 9.5$, $^2J = 14.5$ Hz, 1 H, CH$_A$*H*$_B$-CH$_2$−C$_6$H$_5$), 2.7 (s, 3 H, N−CH$_3$), 2.80 (ddd, $^3J = 6.2$ Hz, $^3J = 9.5$ Hz, $^2J = 13.9$ Hz, 1 H, CH$_2$−CH$_A$*H*$_B$-C$_6$H$_5$), 2.9 (m, 2 H, O*H*, H-11a), 3.4 (dd, $^3J = 4.2$ Hz, $^3J = 6.5$ Hz, 1 H-2), 3.7 (s, 3 H, OCH$_3$), 6.5 (d, $J = 8.5$ Hz, 1 H, H-7), 6.8 (dd, $^3J = 8.5$ Hz, $^3J = 2.4$ Hz, 1 H, H-6), 6.9 (s, 1 H), 7.3 (m, 5 H); ^{13}C

NMR δ 29.7, 32.9, 35.7, 56.1, 64.4, 80.7 (q, $^2J_{CF}$ = 30 Hz), 110.0, 110.6, 117.9, 125.1 (q, $^1J_{CF}$ = 283 Hz), 126.0, 128.4, 142.2, 147.5, 153.2.

Reaction of Tetrahydroquinoline with Epoxy Ether 2. From epoxy ether **2** (500 mg, 1.92 mmol) and tetrahydroquinoline (0.24 mL, 1.92 mmol) after 40 h and workup, a 79/21 mixture of cis and trans indolinols **4d** was isolated (600 mg, 90%). ^{19}F NMR δ −77.0 and −77.8. Anal. Calcd for $C_{20}H_{20}F_3NO$: C, 69.15; H, 5.80; N 4.03. Found: C, 69.30; H, 5.91; N 4.01.

Separation by SiO_2 chromatography provided pure diastereoisomer *cis*-**4d**:

(2*S,3*S**)-2-Phenethyl-3-(trifluoromethyl)-1,2,5,6-tetrahydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-1-ol (*cis*-4d)**: 493 mg (74%); mp 85 °C; ^{19}F NMR δ −77.8 (s); ^{1}H NMR δ 2.1 (m, 2 H, H-5), 2.15 (dddd, $^3J_{H10b-H2}$ = 4 Hz, $^3J_{H10b-H11b}$ = 6.5 Hz, $^3J_{H10b-H11a}$ = 10.5 Hz, $^2J_{H10a-H10a}$ = 14.5 Hz, 1 H, H-10b), 2.4 (ddt, $^3J_{H10a-11a}$ = $^3J_{H10a-H2}$ = 6.0 Hz, $^3J_{H10a-H11b}$ = 10 Hz, $^2J_{H10a-H10b}$ = 14.6 Hz, 1 H, H-10a), 2.70 (m, 2 H, H-6), 2.7 (td, $^3J_{H_{ax}-5_{eq}}$ = 3.3 Hz, $^3J_{H4_{ax}-H5_{ax}}$ = $^2J_{H4_{ax}-H4_{eq}}$ = 10.5 Hz, 1 H, H-4ax), 2.88 (ddd, $^3J_{H11b-H10b}$ = 6.5 Hz, $^3J_{H11b-H10a}$ = 10.5 Hz, $^3J_{H11a-H11b}$ = 13.8 Hz, 1 H, H-11a), 2.95 (ddd, $^3J_{H11a-H10a}$ = 5.9 Hz, $^3J_{H11a-H10b}$ = 10.5 Hz, $^3JH_{11aH11b}$ = 13.8 Hz, 1 H, H-11b), 3.1 (br s, 1 H, OH), 3.4 (dt, $^3J_{H4_{eq}-H5_{eq}}$ = $^3J_{H4_{eq}-H5_{ax}}$ = 4.2 Hz, $^2J_{H4_{ax}-H4_{eq}}$ = 10.5, 1 H, H-4eq), 3.5 (dd, $^3J_{H2-H10b}$ = 4 Hz, $3J_{H2-H10a}$ = 6 Hz 1 H-2), 6.7 (m, 1 H, H-8), 7.0 (d, ^3J = 7 Hz, H-7), 7.3 (m, 6 H); ^{13}C NMR δ 22.5, 24.0, 28.8, 33.4, 44.9, 68.8, 80.8 (q, $^2J_{CF}$ = 29 Hz, *C*-CF_3), 119.3, 120.7, 121.9, 123.8, 125.3 (q, $^1J_{CF}$ = 283 Hz, CF_3) 126.1, 128.6, 130.3, 142.2, 149.3.

Reaction of *N*-Methylaniline with Epoxy Ether 2 in 2-Propanol. From epoxy ether **2** (500 mg, 1.92 mmol) and *N*-methyl aniline (0.21 mL, 1.92 mmol), in 2.5 mL of 2-propanol, after 5 days of reaction at room temperature, a 50:50 mixture of amino ketone **6a** and of indolinols **4a** was obtained. $NaBH_4$ (175 mg, 4.5 mmol) was added. After 1 h at room temperature, reaction mixture was hydrolyzed with H_2O and extracted (Et_2O). Organic phases were dried ($MgSO_4$) and concentrated. The residue was purified on SiO_2, leading to a 70/30 mixture of cis and trans indolinols **4a** (50%) and a 96/4 mixture of syn and anti amino alcohols **8a** (50%), which were not separated: ^{19}F NMR δ −75.8 (d, $^3J_{FH}$ = 6.2 Hz, 48%), −76.5 (s, 15%), −76.8 (d, $^3J_{FH}$ = 7.2 Hz, 2%), −79.0 (s, 35%).

(2*R*,*3S*)-1,1,1-Trifluoro-3-(methylanilino)-5-phenyl-2-pentanol (8a) (major product)**: IR cm^{-1}: ν_{OH} = 3500, ν_{CH} = 2927, $\nu_{C=C}$ = 1599; ^{19}F NMR δ −75.8 (d, $^3J_{FH}$ = 6.2 Hz); ^{1}H NMR δ 2.0−2.1 (m, 1H, H-4b), 2.2 (dddd, $^3J_{H4a-H5a}$ = 4.7 Hz, $^3J_{H4a-H5b}$ = 9.5 Hz, $^3J_{H4a-H3}$ = 11 Hz, $^2J_{H4a-H4b}$ = 14.2 Hz, 1H, H-4a), 2.4 (ddd, $^3J_{H5b-H4b}$ = 7.3 Hz, $^3J_{H5b-H4a}$ = 9.5 Hz, $^2J_{H5b-H5a}$ = 14 Hz, 1 H, H-5b), 2.6 (ddd, $^3J_{H5a-H4a}$ = 4.7 Hz, $^3J_{H5a-H4b}$ = 9.5 Hz, $^2J_{H5a-H5b}$ = 14 Hz, 1 H, H-5a), 2.9 (s, 3 H, Me), 3.9 (dq, $^3J_{H2-H3}$ = 8.5 Hz, $^3J_{H-F}$ = 6.2 Hz, 1 H, H-2), 4.0 (ddd, $^3J_{H3-H4a}$ = 11 Hz, $^3J_{H3-H2}$ = 8.5 Hz, $^3J_{H3-H4b}$ = 3.6 Hz, 1 H, H-3), 6.9−7.0 (m, 5 H, Ph), 7.2−7.4 (m, 5 H, Ph); ^{13}C NMR δ 29.6, 32.6, 41.1, 60.5, 70.4 (q, $^2J_{CF}$ = 29.7 Hz, C−CF_3), 115.3, 119.7, 125.4 (q, $^1J_{CF}$ = 287.7 Hz, CF_3), 126.2, 128.3, 128.5, 129.5, 140.6, 151.3.

Amino ketone **6a** could be identified before the reduction step:

1,1,1-Trifluoro-3-(methylanilino)-5-phenylpentan-2-one (6a): IR: $\nu_{C=O}$ = 1753 cm^{-1}; ^{19}F NMR δ −76.6 (s); ^{1}H NMR δ: 2.1 (m, 1 H, H-4b), 2.2 (m, 1 H, H-4a), 2.8 (m, 2 H, H-5), 2.9 (s, 3 H, Me), 4.8 (dd, $^3J_{H3-H4a}$ = 7.9 Hz, $^3J_{H3-H4b}$ = 6.5 Hz, 1 H, H-3), 6.7−6.9 (m, 5 H), 7.2 (m, 5H); ^{13}C NMR δ 29.3, 32.5, 33.8, 61.5, 113.5, 118.2, 118.9, 126.3, 128.3, 128.4, 128.5, 129.2, 129.3, 140.0, 149.0, 190.0, (q, ^3J = 30 Hz).

General Procedure for Dehydration of Indolinols into Indoles 9 and 10. To a solution of indolinol (0.34 mmol) in freshly distilled pyridine (0.5 mL) was added thionyl chloride (0.02 mL, 1 equiv), at 0 °C, under Ar. After 1 h at this temperature, excess of reagent was evaporated under vacuum. An aqueous solution 1 M of HCl was added to the residue. After extraction with Et_2O, organic phases were washed (brine), dried ($MgSO_4$), and concentrated. The crude product was purified on SiO_2 to give trifluoromethyl indole **9** or **10**.

1-Methyl-2-phenyl-3-(trifluoromethyl)indole (9a). From indolinol **3a** (100 mg), reaction and workup provided the indole **9a** (75 mg, 80%), mp 74 °C; ^{19}F NMR δ −52.9 (s); ^{1}H NMR δ 3.6 (s, 3 H, CH_3), 7.3 to 7.5 (m, 8 H), 7.8 (dq, $^3J_{H4-F}$ = 1.2 Hz, $^3J_{H4H5}$ = 7.8 Hz, 1 H); ^{13}C NMR δ 30.6, 104.0 (q, $^2J_{CF}$ = 35 Hz), 110.0, 119.6, 121.5, 122.9, 124.3, 124.8 (q, $^1J_{CF}$ = 267 Hz), 128.3, 129.3, 130.0, 130.3, 136.3, 140.8 (q, $^4J_{CF}$ = 3.0 Hz). Anal. Calcd for $C_{16}H_{12}F_3N$: C, 69.81; H, 4.39; N, 5.09. Found: C, 69, 55 H, 4.60; N, 4.80.

1-Methyl-2-phenethyl-3-(trifluoromethyl)indole (10a). From indolinol **4a** (100 mg), reaction and workup provided the indole **10a** as an oil (86 mg, 92%); ^{19}F NMR δ −53.9 (s); ^{1}H NMR δ 2.9 (t, ^3J = 7 Hz, 2 H), 3.2 (t, ^3J = 7 Hz, 2 H), 3.5 (s, 3 H, CH_3), 7.2 (m, 8 H), 7.8 (dq, $^3J_{H4-F}$ = 1.2 Hz, $^3J_{H4-H5}$ = 7.5 Hz, 1 H, H-4); ^{13}C NMR δ 27.5, 29.5, 36.6, 102.0 (q, $^2J_{CF}$ = 36 Hz, *C*-CF_3), 109.7, 119.4, 121.3, 122.4, 124.6, 126.7, 128.6, 128.8, 136.4, 140.6, (CF_3 not obsvd). Anal. Calcd for $C_{18}H_{16}F_3N$: C, 71.28; H, 5.32; N, 4.62. Found: C, 70.89; H, 5.53; N, 4.56.

1-Methyl-2-phenethyl-3-trifluoromethyl-5-methoxyindole (10c). From indolinol **4c** (140 mg), reaction and workup provided the indole **10c** (116 mg, 87%); mp 85 °C; ^{19}F NMR δ −53.9 (s); ^{1}H NMR δ 2.9 (t, ^3J = 7 Hz, 2 H), 3.2 (t, ^3J = 7 Hz, 2 H), 3.4 (s, 3 H, CH_3), 3.9 (s, 3 H, O−CH_3), 6.8 (dd, ^3J = 9 Hz, ^3J = 2.4 Hz, 1 H), 7.2 (m, 7 H); ^{13}C NMR δ 27.6, 29.5, 29.8, 56.0, 95.2, 101.2, 102.2 (q, $^2J_{CF}$ = 35 Hz), 110.4, 112.6, 125.0, 126.6, 128.6, 128.7, 131.5, 140.6, 155.2, (CF_3 not obsvd). Anal. Calcd for $C_{19}H_{18}F_3NO$: C, 68.46; H, 5.44; N, 4.20. Found: C, 68.76; H, 5.67; N, 3.99.

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Supporting Information Available: Crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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