1,2-Didehydro-3- and -4-(trifluoromethoxy)benzene: The "Aryne" Route to 1- and 2-(Trifluoromethoxy)naphthalenes

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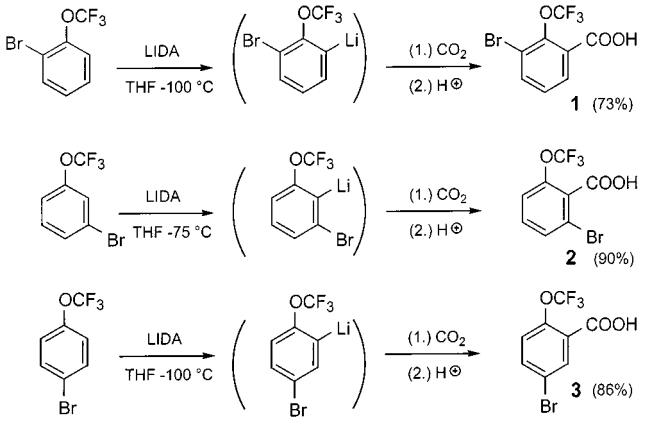
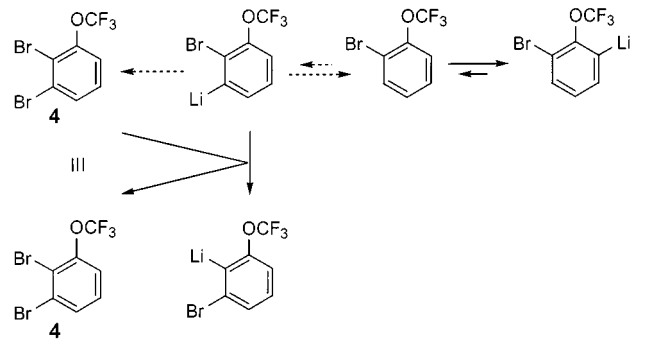
Upon treatment of 1-bromo-2-(trifluoromethoxy)benzene with lithium diisopropylamide (LIDA) at –100 °C, 3-bromo-2-(trifluoromethoxy)phenyllithium is generated. It can be trapped as such, but isomerizes to afford 2-bromo-6-(trifluoromethoxy)phenyllithium when the temperature is raised to –75 °C. The latter intermediate can be directly obtained from 1-bromo-3-(trifluoromethoxy)benzene. 1-Bromo-4-(trifluoromethoxy)benzene gives 5-bromo-2-(trifluoromethoxy)-phenyllithium at –100 °C, but at –75 °C it slowly eliminates lithium bromide, thus setting free 1,2-dehydro-4-(trifluoromethoxy)benzene. In the same way, 1,2-dehydro-3-(trifluoromethoxy)benzene can be generated from 1-bromo-3-(trifluoromethoxy)benzene. Both "arynes" can be intercepted in situ with furan. The resulting [4+2] cycloadducts can be reduced with zinc powder, giving 1- and 2-(trifluoromethoxy)naphthalenes, they may be submitted to acid-catalyzed isomerization to produce trifluoromethoxy-1-naphthols, or they may be brominated to afford *vic*-dibromo derivatives. Base-promoted dehydrobromination of the latter compounds produces 2- or 3-bromo-1,4-epoxy-1,4-dihydro-5- or –6-(trifluoromethoxy)naphthalenes, which undergo regioselective ring-opening in acidic media and halogen/metal exchange when treated with butyllithium.

5-Bromo-2,2-difluoro-1,3-benzodioxole has been reported to undergo smooth deprotonation at the doubly activated 4-position upon treatment with lithium 2,2,6,6-tetramethylpiperidide (LITMP) in tetrahydrofuran (THF) at −75 °C and, upon carboxylation, to afford the corresponding acid in 76% yield.[1] Under these circumstances, it was reasonable to predict analogous behavior in the structurally related 1-bromo-3-(trifluoromethoxy)benzene. When this compound was treated consecutively with lithium diisopropylamide (LIDA) and dry ice, the carboxylic acid **2** was indeed formed, again in high yield (90%). The isomers 1-bromo-2-(trifluoromethoxy)benzene and 1-bromo-4-(trifluoromethoxy)benzene could be submitted to the same deprotonation/carboxylation sequence (although the lithiation had to be performed at −100 °C in these cases) to obtain pure acids **1** (73%) and **3** (74%; at −75 °C: 86%), respectively.



Obviously, the trifluoromethoxy substituent activates its immediate vicinity more powerfully than the bromine atom, a notoriously weak[2] neighboring group, does. When the reaction sequence was performed at −75 °C, however, the organometallic intermediate initially derived from 1-bromo-2-(trifluoromethoxy)benzene was found to isomerize to the less basic 2-bromo-6-(trifluoromethoxy)phenyllithium (71% of acid **2** after 45 min). Apparently, amide-promoted deprotonations become reversible under such conditions, and lithiation at the site adjacent to bromine begins to compete with the otherwise exclusive attack next to the trifluoromethoxy group. 2-Bromo-3-(trifluoromethoxy)phenyllithium, the new organometallic intermediate thus generated, cannot be intercepted as such, since it immediately isomerizes by positional permutation of its bromine and lithium substituents. The crucial step is presumably a halogen/metal exchange between 2-bromo-3-(trifluoromethoxy)phenyllithium and trace amounts of incidentally formed 1,2-dibromo-3-(trifluoromethoxy)benzene (**4**). Analogous mech-



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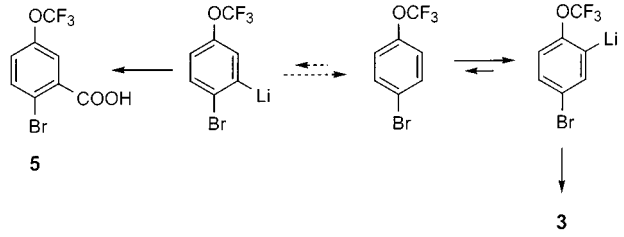
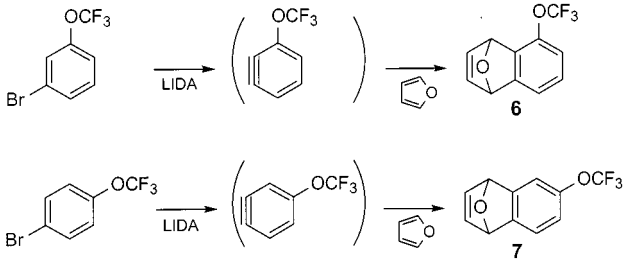
anisms have been invoked to explain similar halogen migrations in the arene and pyridine series.[3,4]

At −75 °C, the *para* isomer also produces minute quantities of a more basic species, *i.e.*, 2-bromo-5-(trifluoromethoxy)phenyllithium, at the expense of the thermodynamically more stable 5-bromo-2-(trifluoromethoxy)-phenyllithium, as equilibration becomes possible. Upon carboxylation, a 99:1 mixture of 5-bromo-2-(trifluoromethoxy)benzoic acid (**3**) and its regioisomer 2-bromo-5-(trifluoromethoxy)benzoic acid[5] (**5**) were detected by gas chromatography (after esterification of the acids with diazomethane).

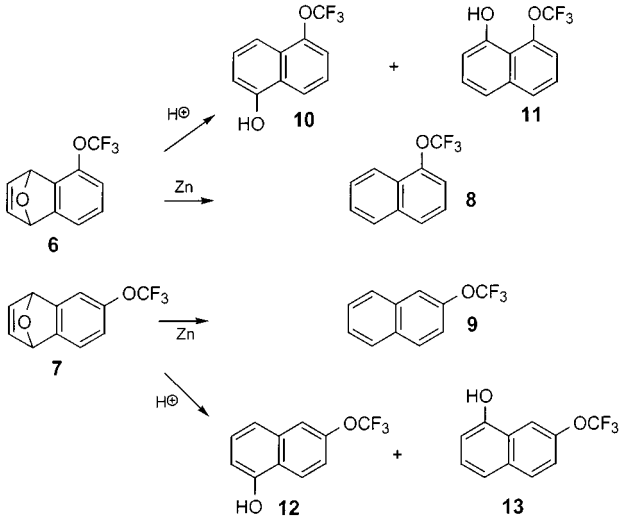


The 2-bromo-5- and -6-(trifluoromethoxy)phenyllithium intermediates eliminate lithium halide at around −60 °C and −30 °C, respectively. The 1,2-didehydro(trifluoromethoxy)benzenes thus liberated could be effectively trapped with furan by Diels−Alder cycloaddition.[6−14] 1-Bromo-3- or -4-(trifluoromethoxy)benzene were added to a solution of LIDA in tetrahydrofuran and furan (approximately equal volumes) at −75 °C and the temperature was allowed to come to +25 °C over the course of 2 h. The 1,4-dihydro-1,4-epoxy-5- and -6-(trifluoromethoxy)naphthalenes (**6** and **7**) were isolated upon distillation in 74% and 70% yields, respectively.

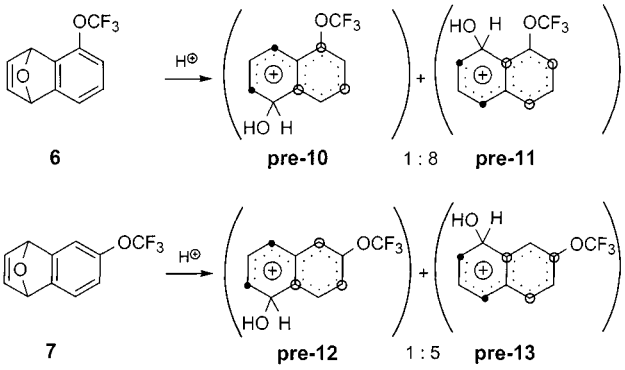


The two 7-oxabenzobicyclo[2.2.1]heptenes **6** and **7** were reduced with zinc dust in acetic acid to 1- and 2-(trifluoromethoxy)naphthalene (**8** and **9**). When heated in the presence of hydrogen chloride, the Diels−Alder cycloadducts **6** and **7** isomerized to pairs of hydroxy(trifluoromethoxy)-naphthalenes **10** and **11** or **12** and **13**, in 1:8 and 1:5 ratios, respectively.

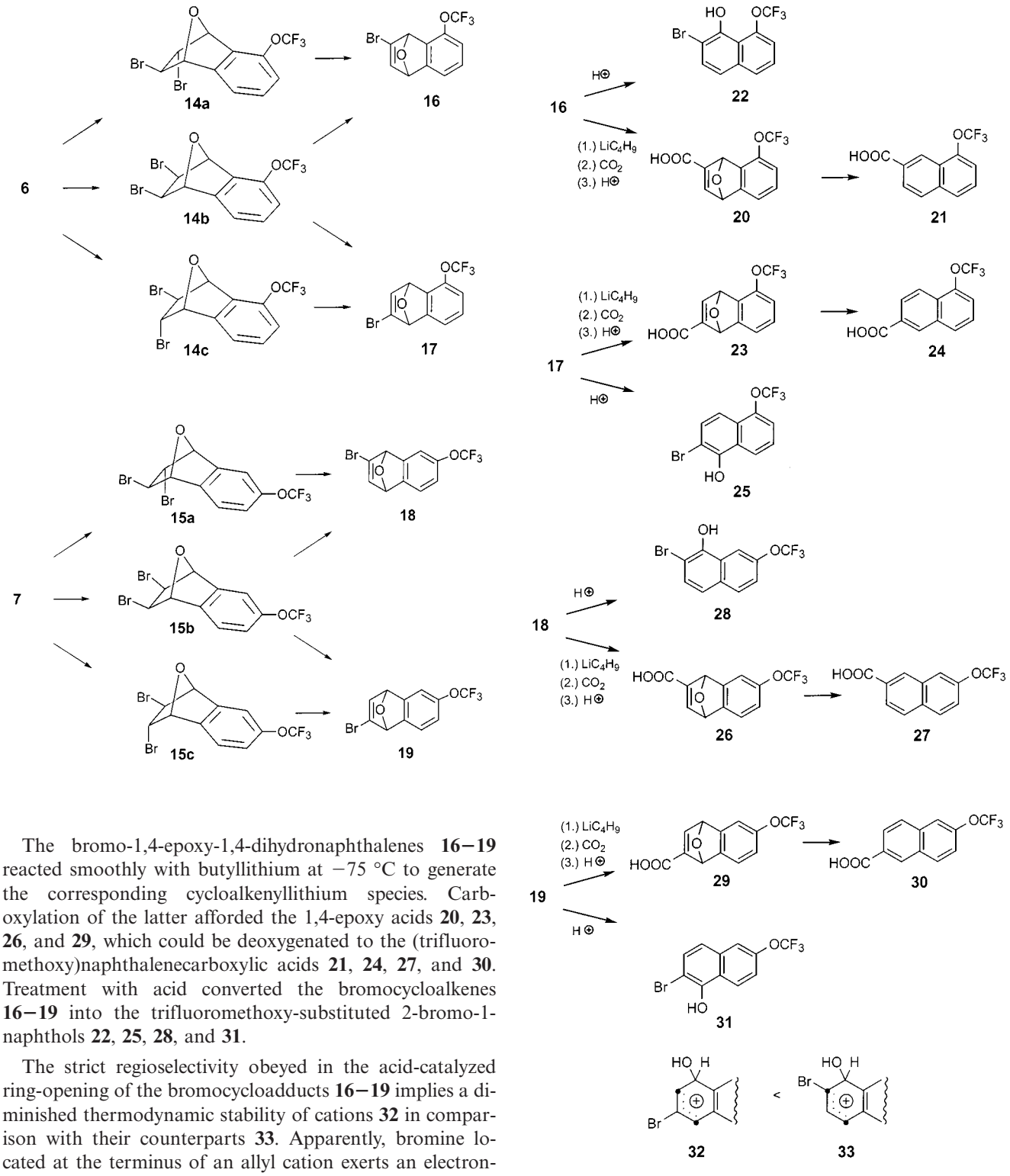
The regiochemical outcome of the acid-catalyzed opening of the 1,4-epoxy bridge in adducts **6** and **7** was surprising. The cations **pre-10** − **pre-13** can safely be assumed to act as the crucial intermediates. If both rings were participating in the resonance stabilization through charge delocalization, the electron-withdrawing trifluoromethoxy substituent would be better accommodated at an antinodal position. On this basis,



the ions **pre-10** and **pre-13** should be preferentially formed at the expense of their counterparts **pre-11** and **pre-12**. This expectation is fulfilled in the 1-trifluoromethoxy series, but is at variance with the findings in the 2-trifluoromethoxy series. A tentative explanation of the observed regiopreferences can be developed if one restricts the area of charge delocalization to just an allyl unit (considering only the area between the solid dots). Then the allyl cation is attached either to an *ortho* or a *meta* or a *para* position with respect to the trifluoromethoxy substituent. The shorter the distance, the greater the destabilizing effect this electronegative group exerts on the allyl cation.



When brominated under the conditions applied by Balcı et al.[15] to benzonorbornene, each of the cycloadducts **6** and **7** provided three stereoisomers (**14a−c** and **15a−c**). These were separated by chromatography and fractional crystallization. The potassium *tert*-butoxide-promoted elimination of hydrogen bromide converted the stereoisomer **14a** into the regioisomer **16** and the stereoisomer **14c** into the regioisomer **17**. The *exo-syn*-elimination mode being favored for obvious reasons, the *cis*-dibromide **14b** reacted only sluggishly to afford a 1:1 mixture of **16** and **17**. In the same way, the dibromo derivatives **15a** and **15c** selectively gave the bromo-1,4-epoxy-1,4-dihydro-6-(trifluoromethoxy)naphthalene isomers **18** and **19**, respectively, whereas intermediate **15b** produced a 1:1 mixture of **18** and **19**.



The bromo-1,4-epoxy-1,4-dihydronaphthalenes **16**–**19** reacted smoothly with butyllithium at −75 °C to generate the corresponding cycloalkenyllithium species. Carboxylation of the latter afforded the 1,4-epoxy acids **20**, **23**, **26**, and **29**, which could be deoxygenated to the (trifluoromethoxy)naphthalenecarboxylic acids **21**, **24**, **27**, and **30**. Treatment with acid converted the bromocycloalkenes **16**–**19** into the trifluoromethoxy-substituted 2-bromo-1-naphthols **22**, **25**, **28**, and **31**.

The strict regioselectivity obeyed in the acid-catalyzed ring-opening of the bromocycloadducts **16**–**19** implies a diminished thermodynamic stability of cations **32** in comparison with their counterparts **33**. Apparently, bromine located at the terminus of an allyl cation exerts an electron-donating resonance effect that outweighs its electron-withdrawing inductive effect, whereas the halogen acts exclusively in the latter fashion when attached to the nodal position.

Resonance stabilization of methyl, allyl, and benzyl cations bearing α-fluoro and α-chloro substituents is well documented.[16–27] Data relating to α-bromoalkyl cations[28–29] are scarce, and nonexistent as far as 1-bromoallyl cations are concerned.[30]

Experimental Section

For standard laboratory practice and abbreviations, see previous publications from this laboratory (e.g., refs.[31–32]). – ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz (or 600 MHz, if marked by an asterisk) and at 101 MHz, respectively, by using samples dissolved in deuteriochloroform.

Bromo(trifluoromethoxy)benzoic Acids

3-Bromo-2-(trifluoromethoxy)benzoic Acid (1): Butyllithium (25 mmol) in hexanes (15 mL) and diisopropylamine (3.5 mL, 2.5 g, 25 mmol) in tetrahydrofuran (50 mL) were mixed at 0 °C. The solution was then cooled to −100 °C, and 1-bromo-2-(trifluoromethoxy)benzene (3.8 mL, 6.0 g, 25 mmol) was added. After 2 h at −100 °C, the mixture was poured onto an excess of freshly crushed dry ice. After evaporation of the volatiles, the residue was dissolved in a 1 M aqueous solution (50 mL) of sodium hydroxide, washed with diethyl ether (2 × 15 mL), and acidified with concentrated hydrochloric acid (7 mL) to pH 1. Upon extraction with diethyl ether (3 × 30 mL) a 95:5 mixture, according to gas chromatographic analysis (30 m, DB-1701, 100 °C; 30 m DB-210, 120 °C), of product **1** and its isomer **2** was obtained. Concentration and recrystallization from a 1:5 (v/v) mixture of ethyl acetate and hexanes afforded the pure acid **1** as colorless cubes; m.p. 123−124 °C; yield 5.2 g (73%). − ^{1}H NMR: **δ** = 7.99 (dd, *J* = 7.8, 1.6 Hz, 1 H), 7.89 (dd, *J* = 8.0, 1.7 Hz, 1 H), 7.33 (t, *J* = 7.8 Hz, 1 H). − ^{13}C NMR: δ = 169.6, 147.5, 138.6, 131.3, 128.4, 126.9, 120.3 (q, *J* = 259.7 Hz), 119.4. − $C_8H_4BrF_3O_3$ (285.02): calcd. C 33.71, H 1.42; found C 33.88, H 1.38.

When the lithiation reaction was carried out at −75 °C, a 4:96 ratio of acids **1** and **2** in 71% yield resulted.

2-Bromo-6-(trifluoromethoxy)benzoic Acid (2): An analogous reaction performed at −75 °C and using 1-bromo-3-(trifluoromethoxy)benzene (3.7 mL, 6.0 g, 25 mmol) as the substrate, gave pure acid **2**; colorless needles; m.p. 70−71 °C (from ethyl acetate/hexanes); yield 6.4 g (90%). − ^{1}H NMR: δ = 7.57 (dd, *J* = 7.4, 1.2 Hz, 1 H), 7.3 (m, 2 H). − ^{13}C NMR: δ = 168.5, 146.4, 131.8, 131.1, 128.8, 120.3, 120.2 (q, *J* = 259.6 Hz), 119.2. − $C_8H_4BrF_3O_3$ (285.02): calcd. C 33.71, H 1.42; found C 33.86, H 1.14.

5-Bromo-2-(trifluoromethoxy)benzoic Acid (3): When the reaction and workup conditions described above were applied to 1-bromo-4-(trifluoromethoxy)benzene (3.7 mL, 6.0 g, 25 mmol), the acid **3** and its isomer **5** were formed in a 99:1 ratio (gas chromatography: 30 m, DB-1701, 100 °C; 30 m, DB-210, 100 °C); colorless needles; m.p. 92−93 °C (from hexanes); yield 6.1 g (86%). − ^{1}H NMR: δ = 8.24 (d, *J* = 2.5 Hz, 1 H), 7.75 (dd, *J* = 8.9, 2.4 Hz, 1 H), 7.27 (d, *J* = 8.7 Hz, 1 H). − ^{13}C NMR: δ = 168.1, 147.4, 137.5, 135.6, 125.1, 124.4, 120.4 (q, *J* = 260.2 Hz), 120.3. − $C_8H_4BrF_3O_3$ (285.02): calcd. C 33.71, H 1.42; found C 33.71, H 1.63.

A reduction in the lithiation temperature to −100 °C produced acid **3** uncontaminated by any isomer.

2-Bromo-5-(trifluoromethoxy)benzoic Acid (5): A 9:1 mixture of acids **3** and **5** was isolated in 88% yield (6.3 g) after 1-bromo-4-(trifluoromethoxy)benzene (25 mmol) in tetrahydrofuran (50 mL) had been allowed to react for 2 h at −75 °C with lithium 2,2,6,6-tetramethylpiperidide (25 mmol, from 2,2,6,6-tetramethylpiperidine and a 1.6 M solution of butyllithium in hexanes) followed by quenching with dry ice. The by-product was identified, after esterification with diazomethane, by gas chromatographic comparison (30 m, DB-1701, 100 °C; 30 m, DB-210, 100 °C; 30 m, DB-WAX, 100 °C) with an authentic sample. The latter was prepared as follows: *tert*-butyl 4-(trifluoromethoxy)phenylcarbamate [6.9 g, 25 mmol; prepared from 4-(trifluoromethoxy)aniline and di-*tert*-butyl dicarbonate] was added to a precooled solution of *sec*-butyllithium (50 mmol) in tetrahydrofuran (50 mL) and hexanes (30 mL). After 2 h at −75 °C, the mixture was poured onto an excess of freshly crushed dry ice. Extraction and crystallization afforded **2-(*tert*-butoxycarbonyl)amino-5-(trifluoromethoxy)benzoic acid** [colorless needles; m.p. 181−183 °C (from hexanes). − ^{1}H NMR (D_3CCOCD_3): δ = 8.59 (d, *J* = 9.1 Hz, 1 H), 7.96 (d, *J* = 2.6 Hz, 1 H), 7.60 (dm, *J* = 9.2 Hz, 1 H), 1.53 (s, 9 H). − ^{13}C NMR (D_3CCOCD_3): δ = 168.0, 152.2, 141.7, 136.6, 127.4, 123.6, 120.3 (q, *J* = 260.1 Hz), 119.8, 115.3, 80.4, 27.4 (3C)]. Deprotection of the latter compound with trifluoroacetic acid in dichloromethane at 25 °C over 2 h afforded **2-amino-5-(trifluoromethoxy)benzoic acid** [colorless needles, m.p. 137−138 °C (from water). − ^{1}H NMR: δ = 7.79 (d, *J* = 2.4 Hz, 1 H), 7.20 (dd, *J* = 9.0, 2.6 Hz, 1 H), 6.66 (d, *J* = 9.0 Hz, 1 H). − ^{13}C NMR: δ =171.6, 149.8, 138.8, 129.0, 124.4, 120.4 (q, *J* = 262.0 Hz), 117.7, 108.9. − $C_8H_6F_3NO_3$ (221.14): calcd. C 43.45, H 2.73; found C 43.29, H 2.92; yield 4.3 g (96%)]. Some of the deprotected compound (1.1 g, 5.0 mmol) was dissolved in 48% aqueous hydrobromic acid (10 mL). Under ice cooling, sodium nitrite (0.35 g, 5.0 mmol) was introduced portionwise (spatula tip quantities) over the course of 2 min, followed by cupric bromide (1.1 g, 5.0 mmol). The mixture was heated to 75 °C for 15 min, diluted with water (10 mL), and extracted with diethyl ether (3 × 15 mL). The combined organic layers were dried and the solvents evaporated. Upon recrystallization of the residue from hexanes, product **5** was obtained in the form of colorless needles; m.p. 70−71 °C; yield 1.2 g (84%). − ^{1}H NMR: δ = 7.87 (d, *J* = 2.5 Hz, 1 H), 7.76 (d, *J* = 8.7 Hz, 1 H), 7.29 (dd, *J* = 8.8, 2.5 Hz, 1 H). − ^{13}C NMR: δ =169.3, 148.0, 136.3, 131.6, 126.0, 124.9, 120.4, 120.3 (q, *J* = 259.6 Hz). − $C_8H_4BrF_3O_3$ (285.02): calcd. C 33.71, H 1.42; found C 33.29, H 1.58.

1,4-Epoxy-1,4-dihydro(trifluoromethoxy)naphthalenes, (Trifluoromethoxy)naphthalenes, and (Trifluoromethoxy)naphthols

1,4-Epoxy-1,4-dihydro-5-(trifluoromethoxy)naphthalene (6): At −75 °C, precooled diisopropylamine (28 mL, 20 g, 0.20 mol) in tetrahydrofuran (0.20 L), furan (0.20 L), and 1-bromo-3-(trifluoromethoxy)benzene (29 mL, 48 g, 0.20 mol) were added consecutively to butyllithium (0.20 mol) in hexanes (0.10 L). The mixture was allowed to warm up, reaching +25 °C over 2 h. It was washed with 1 M hydrochloric acid (2 × 0.10 L) and dried. Upon distillation, a colorless liquid was collected; b.p. 91−93 °C/2 Torr; n_D^{20} 1.4808; yield 33.6 g (74%). − ^{1}H NMR: **δ** = 7.18 (d, *J* = 7.0 Hz, 1 H), 7.0 (m, 3 H), 6.82 (dt, *J* = 8.3, 0.9 Hz, 1 H), 5.91 (br. s, 1 H), 5.74 (br. s, 1 H). − ^{13}C NMR: δ = 152.3, 143.3, 142.3, 141.1, 140.0, 127.2, 120.4 (q, *J* = 259.5 Hz), 119.2, 119.0, 82.5, 80.2. − $C_{11}H_7F_3O_2$ (288.17): calcd. C 57.90, H 3.09; found C 57.97, H 3.11.

1,4-Epoxy-1,4-dihydro-6-(trifluoromethoxy)naphthalene (7): In exactly the same way, 1-bromo-4-(trifluoromethoxy)benzene (29 mL, 48 g, 0.20 mol) gave the isomer **7**; colorless liquid; b.p. 87−89 °C/1 Torr; n_D^{20} 1.4816; yield 31.8 g (70%). − ^{1}H NMR: δ = 7.18 (d, *J* = 7.8 Hz, 1 H), 7.09 (s, 1 H), 7.1 (m, 2 H), 6.80 (dq, *J* = 7.7, 1.0 Hz, 1 H), 5.68 (br. s, 2 H). − ^{13}C NMR: δ = 151.6, 147.5, 146.4, 143.1, 142.7, 120.5, 120.4 (q, *J* = 259.7 Hz), 117.1, 114.5, 82.2, 82.1. − $C_{11}H_7F_3O_2$ (228.17): calcd. C 57.90, H 3.09; found C 57.73, H 3.19.

1-(Trifluoromethoxy)naphthalene (8): A solution of the cycloadduct **6** (11.4 g, 50 mmol) in acetic acid (0.10 L) and in the presence of a large excess of zinc (33 g, 0.50 mol) was heated under reflux (at ≈ 120 °C) for 20 h. The solvents were evaporated to dryness and the residue extracted with diethyl ether (4 × 50 mL). Distillation afforded a colorless liquid; b.p. 55−56 °C/3 Torr; n_D^{20} 1.5123; yield 7.5 g (71%). − ^{1}H NMR: δ = 8.18 (d, *J* = 8.5 Hz, 1 H), 7.91 (d, *J* = 8.2 Hz, 1 H), 7.78 (d, *J* = 8.0 Hz, 1 H), 7.6 (m, 2 H), 7.44 (t, *J* = 7.8 Hz, 1 H), 7.37 (d, *J* = 7.8 Hz, 1 H). − ^{1}H NMR*: δ = 8.17 (d, *J* = 8.3 Hz, 1 H), 7.90 (d, *J* = 8.1 Hz, 1 H), 7.79 (d, *J* = 8.1 Hz, 1 H), 7.6 (m, 2 H), 7.46 (t, *J* = 7.8 Hz, 1 H), 7.39 (dm, *J* =

7.7 Hz, 1 H). − ^{13}C NMR: δ = 145.2, 134.7, 127.8, 126.9 (2C), 126.8, 125.1, 122.2, 121.4, 120.3 (q, *J* = 259.8 Hz), 116.4. − $C_{11}H_7F_3O$ (212.17): calcd. C 62.27, H 3.33; found C 62.04, H 3.21.

2-(Trifluoromethoxy)naphthalene (9): This compound was prepared analogously, from the isomeric cycloadduct **7** (11.4 g, 50 mmol); colorless liquid; b.p. 58−60 °C/3 Torr; n_D^{20} 1.5085; yield 7.7 g (73%). − ^{1}H NMR: δ = 7.9 (m, 3 H), 7.64 (s, 1 H), 7.5 (m, 2 H), 7.31 (dd, *J* = 9.0, 1.6 Hz, 1 H). − ^{1}H NMR*: δ = 7.9 (m, 2 H), 7.83 (d, *J* = 8.0 Hz, 1 H), 7.65 (s, 1 H), 7.5 (m, 2 H), 7.32 (dd, *J* = 9.0, 1.6 Hz, 1 H). − ^{13}C NMR: δ = 146.8, 133.5, 131.7, 130.0, 127.8 (2C), 127.0, 126.3, 120.3 (q, *J* = 258.0 Hz), 120.1, 118.1. − $C_{11}H_7F_3O$ (212.17): calcd. C 62.27, H 3.33; found C 62.17, H 2.96.

5-(Trifluoromethoxy)-1-naphthol (10) and 8-(Trifluoromethoxy)-1-naphthol (11): 1,4-Epoxy-1,4-dihydro-5-(trifluoromethoxy)naphthalene (**6**; 5.7 g, 25 mmol) was dissolved in methanol (40 mL) containing concentrated (32%) hydrochloric acid (10 mL). After 2 h heating under reflux (≈ 75 °C), the solution was evaporated to dryness and the residue was distilled; b.p. 92−93 °C/4 Torr; yield 5.3 g (93%). The 1:8 regioisomeric mixture was separated by preparative gas chromatography (3 m, 10% SE-30, 70 → 200 °C [10 °C/min]). − **Compound 10**: m.p. 107−108 °C. − ^{1}H NMR: δ = 8.21 (d, *J* = 8.0 Hz, 1 H), 7.70 (d, *J* = 8.5 Hz, 1 H), 7.48 (t, *J* = 8.1 Hz, 1 H), 7.4 (m, 2 H), 6.89 (d, *J* = 7.6 Hz, 1 H). − ^{1}H NMR* : δ = 8.19 (d, *J* = 8.2 Hz, 1 H), 7.71 (d, *J* = 8.5 Hz, 1 H), 7.46 (t, *J* = 8.0 Hz, 1 H), 7.42 (t, *J* = 8.1 Hz, 1 H), 7.40 (dm, *J* = 8.2 Hz, 1 H), 6.90 (dd, *J* = 7.4, 0.8 Hz, 1 H), 5.39 (br. s, 1 H). − ^{13}C NMR: δ = 151.4, 145.1, 128.4, 127.0, 125.9, 124.4, 120.9 (q, *J* = 259.6 Hz), 120.8, 117.1, 114.2, 109.6. − **Compound 11**: m.p. 48−49 °C. − ^{1}H NMR: δ = 7.75 (dd, *J* = 8.2, 1.1 Hz, 1 H), 7.43 (d, *J* = 4.3 Hz, 2 H), 7.4 (m, 2 H), 7.29 (d, *J* = 7.7 Hz, 1 H), 7.03 (quint, *J* = 4.4 Hz, 1 H). − ^{1}H NMR*: δ = 7.75 (dd, *J* = 8.2, 1.1 Hz, 1 H), 7.43 (d, *J* = 4.3 Hz, 2 H), 7.38 (t, *J* = 7.8 Hz, 1 H), 7.34 (br. s, 1 H), 7.29 (d, *J* = 7.6 Hz, 1 H), 7.02 (quint, *J* = 4.4 Hz, 1 H). − ^{13}C NMR: δ = 151.9, 145.1, 136.9, 128.1, 127.6, 125.0, 120.5 (q, *J* = 259.2 Hz), 120.2, 116.1, 115.2, 112.7. − $C_{11}H_7F_3O_2$ (228.17): calcd. C 57.90, H 3.09; found C 57.77, H 3.29.

6-(Trifluoromethoxy)-1-naphthol (12) and 7-(Trifluoromethoxy)-1-naphthol (13): These compounds were prepared analogously, from 1,4-epoxy-1,4-dihydro-6-(trifluoromethoxy)naphthalene (**9**; 5.7 g, 25 mmol), yield 5.0 g (88%). The 1:5 regioisomeric mixture (30 m, DB-1701, 100 °C, 30 m DB-210, 100 °C) was again separated by preparative gas chromatography (3 m, 10% SE-30, 70 → 200 °C [10 °C/min]). − **Compound 12**: m.p. 80−82 °C. − ^{1}H NMR: δ = 8.27 (d, *J* = 9.0 Hz, 1 H), 7.64 (s, 1 H), 7.43 (d, *J* = 8.3 Hz, 1 H), 7.4 (m, 2 H), 6.83 (dd, *J* = 7.2, 1.0 Hz, 1 H). − ^{1}H NMR*: δ = 8.25 (d, *J* = 9.1 Hz, 1 H), 7.63 (s, 1 H), 7.41 (d, *J* = 8.4 Hz, 1 H), 7.35 (t, *J* = 7.9 Hz, 1 H), 7.32 (d, *J* = 9.3 Hz, 1 H), 6.82 (dd, *J* = 7.3, 0.8 Hz, 1 H), 5.40 (br. s, 1 H). − ^{13}C NMR: δ = 151.6, 147.5, 135.1, 127.4, 124.3, 122.7, 120.6 (q, *J* = 256.5 Hz), 120.3, 119.2, 117.6, 108.8. − **Compound 13:** m.p. 77−78 °C. − ^{1}H NMR: δ = 8.06 (s, 1 H), 7.85 (d, *J* = 8.7 Hz, 1 H), 7.47 (d, *J* = 8.1 Hz, 1 H), 7.4 (m, 2 H), 6.88 (d, *J* = 7.3 Hz, 1 H). − ^{1}H NMR*: δ = 8.04 (s, 1 H), 7.83 (d, *J* = 8.9 Hz, 1 H), 7.46 (d, *J* = 8.3 Hz, 1 H), 7.34 (d, *J* = 8.9 Hz, 1 H), 7.31 (t, *J* = 7.9 Hz, 1 H), 6.85 (d, *J* = 7.5 Hz, 1 H), 5.55 (br. s, 1 H). − ^{13}C NMR: δ = 151.2, 146.5, 136.4, 129.7, 126.2, 124.5, 120.7, 120.5 (q, *J* = 260.1 Hz), 120.4, 112.8, 109.4. − $C_{11}H_7F_3O_2$ (228.17): calcd. C 57.90, H 3.09; found C 58.02, H 3.24.

2,3-Dibromo-1,4-epoxy-1,2,3,4-tetrahydro(trifluoromethoxy)-naphthalenes, Bromo-1,4-epoxy-1,4-dihydro(trifluoromethoxy)naphthalenes, and Bromo(trifluoromethoxy)naphthols

2,3-Dibromo-1,4-epoxy-1,2,3,4-tetrahydro-5-(trifluoromethoxy)-naphthalenes (14): A solution of 1,4-epoxy-1,4-dihydro-5-(trifluoromethoxy)naphthalene (**6**; 11.4 g, 50 mmol) in tetrachloromethane (0.33 L) was heated to gentle reflux (≈ 80 °C) while bromine (2.6 mL, 8.0 g, 50 mmol) in tetrachloromethane (20 mL) was added dropwise over the course of 2 min. The heating was continued for 3 min. According to gas chromatographic analysis (30 m, DB-1701, 180 °C; 30m DB-210, 180 °C), three products had formed, in the approximate ratio of 3:3:4. Elution with a 1:8 (v/v) mixture of ethyl acetate and hexanes from silica gel (0.35 L) gave two fractions. The first one (11.1 g, 57%) contained two compounds, one of which (**14c**) crystallized from ethanol (10 mL) as colorless prisms and the other of which (**14a**) subsequently crystallized from hexanes as colorless platelets. A third isomer (**14b**) was isolated from the second fraction (5.8 g, 30%) by crystallization from hexanes in the form of colorless needles. − **Compound 14a**: m.p. 86−87 °C, yield 4.0 g (21%). − ^{1}H NMR: δ = 7.35 (dd, *J* = 8.0, 7.4 Hz,1 H), 7.29 (d, *J* = 7.3 Hz, 1 H), 7.18 (d, J = 8.1 Hz, 1 H), 5.69 (d, *J* = 4.5 Hz, 1 H), 5.48 (s, 1 H), 4.52 (dd, *J* = 4.7, 2.5 Hz, 1 H), 3.81 (d, *J* = 2.6 Hz, 1 H). − ^{13}C NMR: δ = 144.5, 144.4, 133.7, 130.4, 119.5, 118.2, 120.4 (q, *J* = 258.9 Hz), 87.2, 81.2, 52.3, 49.9. − **Compound 14b**: m.p. 116−117 °C, yield 5.6 g (29%). − ^{1}H NMR: δ = 7.3 (m, 2 H), 7.12 (d, *J* = 7.2 Hz, 1 H), 5.68 (s, 1 H), 5.55 (s, 1 H), 4.25 (s, 1 H). − ^{13}C NMR: δ = 145.7, 142.0, 134.9, 130.7, 121.5, 120.5 (q, *J* = 260.0 Hz), 119.2, 88.0, 85.5, 51.2, 50.7. − **Compound 14c**: m.p. 74−75 °C, yield 6.3 (32%). − ^{1}H NMR: δ = 7.4 (m, 2 H), 7.18 (d, *J* = 7.1 Hz, 1 H), 5.65 (s, 1 H), 5.50 (d, *J* = 4.7 Hz, 1 H), 4.55 (dd, *J* = 4.6, 2.5 Hz, 1 H), 3.83 (d, *J* = 2.6 Hz, 1 H). − ^{13}C NMR: δ = 144.5, 143.0, 133.8, 129.8, 122.1, 121.2, 120.5 (q, *J* = 259.2 Hz), 84.6, 83.3, 51.7, 49.9. − $C_{11}H_7Br_2F_3O_2$ (387.99): calcd. C 34.05, H 1.82; found C 34.07, H 1.92.

2,3-Dibromo-1,4-epoxy-1,2,3,4-tetrahydro-6-(trifluoromethoxy)-naphthalenes (15): Analogous bromination of compound **7** (11.4 g, 50 mmol) gave a 1:1:1 mixture of three products (30 m, DB-1701, 180 °C, 30 m, DB-Wax, 150 °C). Column chromatography (see above) afforded a first fraction (9.4 g, 48%) from which isomer **15c** was separated as colorless prisms by fractional crystallization from ethanol, followed on subsequent recrystallization from hexanes by isomer **15a**, again as colorless prisms, and a second fraction (5.0 g, 26%) from which isomer **15b** was obtained as colorless cubes by crystallization from hexanes. − **Compound 15a**: m.p. 79−81 °C. − ^{1}H NMR: δ = 7.38 (d, *J* = 8.0 Hz, 1 H), 7.27 (s, 1 H), 7.18 (dm, *J* = 8.2 Hz, 1 H), 5.49 (s, 1 H), 5.45 (d, *J* = 4.6 Hz, 1 H), 4.55 (dd, *J* = 4.6, 2.5 Hz, 1 H), 3.80 (d, *J* = 2.5 Hz, 1 H). − ^{13}C NMR: δ = 149.2, 140.0, 139.1, 121.1, 120.9, 120.3 (q, *J* = 259.9 Hz), 116.9, 86.6, 82.9, 52.4, 50.0. − **Compound 15b**: m.p. 103−105 °C, yield 4.5 g (23%). − ^{1}H NMR: δ = 7.37 (d, *J* = 8.2 Hz, 1 H), 7.23 (s, 1 H), 7.11 (dm, *J* = 8.2, 1.0 Hz, 1 H), 5.52 (d, *J* = 0.9 Hz, 2 H), 4.23 (s, 2 H). − ^{13}C NMR: δ = 144.9, 142.9, 141.1, 121.7, 120.9, 120.4 (q, *J* = 260.2 Hz), 114.0, 87.5, 87.3, 51.3, 51.2. − **Compound 15c**: m.p. 71−72 °C. − ^{1}H NMR: δ = 7.44 (d, *J* = 8.1 Hz, 1 H), 7.25 (s, 1 H), 7.19 (dm, *J* = 8.2 Hz, 1 H), 5.49 (s, 1 H), 5.45 (d, *J* = 4.6 Hz, 1 H), 4.55 (dd, *J* = 4.6, 2.5 Hz, 1 H), 3.82 (d, *J* = 2.6 Hz, 1 H). − ^{13}C NMR: δ = 148.9, 143.6, 139.9, 124.5, 120.4 (q, *J* = 260.4 Hz), 120.3, 113.4, 86.8, 82.7, 52.2, 50.2. − $C_{11}H_7Br_2F_3O_2$ (387.99): calcd. C 34.05, H 1.82; found C 33.98, H 1.85.

3-Bromo-1,4-epoxy-1,4-dihydro-5-(trifluoromethoxy)naphthalene (16): Compound **14a** (7.8 g, 20 mmol), to which the 2-*exo*,3-*endo* configuration was assigned on the basis of its NMR spectrum (see above), was dissolved in tetrahydrofuran (40 mL) and treated with potassium *tert*-butoxide (2.2 g, 20 mmol) over 2 h at 50 °C. Upon distillation, a colorless liquid was collected; b.p. 99−101 °C/4 Torr; n_D^{20} 1.5123; yield 5.4 g (88%). − ^{1}H NMR: δ = 7.21 (d, *J* = 7.0 Hz, 1 H), 7.10 (dd, *J* = 8.3, 7.0 Hz, 1 H), 7.01 (d, *J* = 2.1 Hz, 1 H),

6.92 (dq, J = 8.5, 0.8 Hz, 1 H), 5.76 (m, 1 H), 5.71 (s, 1 H). − ^{13}C NMR: δ = 151.0, 142.6, 139.9, 138.8, 136.0, 128.2, 120.4 (q, J = 258.6 Hz), 119.2, 118.8, 84.6, 84.4. − $C_{11}H_6BrF_3O_2$ (307.07): calcd. C 43.03, H 1.97; found C 43.22, H 1.98.

2-Bromo-1,4-epoxy-1,4-dihydro-5-(trifluoromethoxy)naphthalene (17): Starting with isomer **14c** (7.8 g, 20 mmol), to which the 2-*endo*,3-*exo* configuration was assigned, compound **17** was obtained after distillation as a colorless liquid; b.p. 95−97 °C/4 Torr; n_D^{20} 1.5095; yield 5.8 g (94%). − ^{1}H NMR: δ = 7.33 (d, J = 7.3 Hz, 1 H), 7.09 (dd, J = 8.3, 7.0 Hz, 1 H), 6.95 (d, J = 1.9 Hz, 1 H), 6.91 (dt, J = 8.2, 0.8 Hz, 1 H), 5.93 (s, 1 H), 5.51 (d, J = 1.0 Hz, 1 H). − ^{13}C NMR: δ = 150.2, 141.8, 139.7, 138.9, 136.7, 127.6, 120.4 (q, J = 257.8 Hz), 120.2, 119.6, 87.1, 82.1. − $C_{11}H_6BrF_3O_2$ (307.07): calcd. C 43.03, H 1.97; found C 43.28, H 2.14.

The reaction between isomer **14b** (7.8 g, 20 mmol) and potassium *tert*-butoxide required 20 h to attain completion. The elimination products **16** and **17** were obtained as a 53:47 mixture (30 m, DB-1701, 150 °C; 30 m, DB-210, 150 °C). The two isomers (together 5.7 g, 97%) could be quantitatively separated by column chromatography, using a 1:7 mixture of ethyl acetate and hexanes.

3-Bromo- and 2-Bromo-1,4-epoxy-1,4-dihydro-6-(trifluoromethoxy)-naphthalene (18 and 19): A 1:1 mixture of compound **15a** and **15c** (9.7 g, 25 mmol), to which the 2-*exo*,3-*endo* and 2-*endo*,3-*exo* configurations, respectively, were assigned, was allowed to react with potassium *tert*-butoxide (2.8 g, 25 mmol) over 2 h at 50 °C. On elution with a 1:7 (v/v) mixture of ethyl acetate and hexanes from a column filled with silica gel (0.25 L), a perfect separation of the two regioisomers (formed in a 1:1 ratio; gas chromatography: 30 m, DB-1701, 150 °C; 30 m, DB-210, 150 °C) was achieved. − **Compound 18**: b.p. 97−99 °C/4 Torr; n_D^{20} 1.5060; yield 3.4 g (44%). − ^{1}H NMR: δ = 7.26 (s, 1 H), 7.24 (d, J = 7.8 Hz, 1 H), 7.00 (d, J = 2.2 Hz, 1 H), 6.92 (dm, J = 7.8 Hz, 1 H), 5.77 (br. s, 1 H), 5.48 (s, 1 H). − ^{13}C NMR: δ = 149.6, 146.6, 146.1, 139.8, 136.4, 120.4 (q, J = 256.8 Hz), 120.5, 118.1, 115.1, 86.7, 84.0. − **Compound 19**: b.p. 97−99 °C/4 Torr; n_D^{20} 1.5131; yield 3.2 g (42%). − ^{1}H NMR: δ = 7.36 (d, J = 7.8 Hz, 1 H), 7.13 (s, 1 H), 6.97 (d, J = 2.0 Hz, 1 H), 6.88 (dm, J = 7.8 Hz, 1 H), 5.74 (br. s, 1 H), 5.47 (s, 1 H). − ^{13}C NMR: δ = 150.5, 147.4, 145.8, 139.6, 137.3, 121.6, 120.7 (q, J = 258.4 Hz), 117.8, 114.7, 86.9, 84.4. − Both products **18** and **19** proved to be too unstable to be dispatched to an outside analytical service.

Regioisomer **15b** of the dibromo compound (7.8 g, 20 mmol) required treatment with potassium *tert*-butoxide (2.2 g, 20 mmol) in tetrahydrofuran over 20 h at 50 °C to afford a 1:1 mixture of the elimination products **18** and **19**; total yield 4.7 g (76%).

1,4-Epoxy-1,4-dihydro(trifluoromethoxy)-2-naphthoic Acids, Trifluoromethoxy-2-naphthoic Acids, and 2-Bromo(trifluoromethoxy)-1-naphthols

1,4-Epoxy-1,4-dihydro-8-trifluoromethoxy-2-naphthoic Acid (20): 2-Bromo-1,4-epoxy-1,4-dihydro-8-(trifluoromethoxy)naphthalene (**16**; 4.6 g, 15 mmol) in tetrahydrofuran (30 mL) was treated at −75 °C with butyllithium (15 mmol) in cyclohexane (10 mL). After 15 min the reaction mixture was poured onto an excess of freshly crushed dry ice. The solvents were evaporated and the residue was dissolved in a 1 M aqueous solution of sodium hydroxide (30 mL). The alkaline phase was washed with diethyl ether (2 × 15 mL), acidified to pH 1, and extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried and the solvents evaporated. The remaining solid material was recrystallized from hexanes (10 mL) to afford colorless prisms; m.p. 127−129 °C (dec.); yield 3.1 g (76%). − ^{1}H NMR: δ = 7.90 (d, J = 1.9 Hz, 1 H), 7.26 (d, J = 7.6 Hz, 1 H), 7.09 (t, J = 7.7 Hz, 1 H), 6.93 (d, J = 7.9 Hz, 1 H), 6.12 (s, 1 H), 5.89 (br. s, 1 H). − ^{13}C NMR: δ = 166.5, 154.9, 149.7, 148.5, 148.3, 139.6, 128.0, 120.6 (q, J = 259.4 Hz), 119.7, 119.5, 83.7, 79.7. − $C_{12}H_7F_3O_4$ (272.18): calcd. C 52.95, H 2.59; found C 52.54, H 2.48.

1,4-Epoxy-1,4-dihydro-5-trifluoromethoxy-2-naphthoic Acid (23): This compound was prepared analogously, from 2-bromo-1,4-epoxy-1,4-dihydro-5-(trifluoromethoxy)naphthalene (**17**; 4.6 g, 15 mmol); colorless needles; m.p. 149−150 °C (dec.; from hexanes); yield 3.5 g (86%). − ^{1}H NMR: δ = 7.83 (d, J = 1.2 Hz, 1 H), 7.36 (d, J = 7.0 Hz, 1 H), 7.10 (dd, J = 8.3, 6.9 Hz, 1 H), 6.90 (d, J = 8.4 Hz, 1 H), 6.07 (s, 1 H), 5.94 (s, 1 H). − ^{13}C NMR: δ = 167.6, 154.2, 150.9, 149.1, 142.6, 138.4, 128.3, 120.6 (q, J = 258.3 Hz), 119.8 (2C), 82.1, 81.5. − $C_{12}H_7F_3O_4$ (272.18): calcd. C 52.95, H 2.59; found C 52.75, H 2.36.

1,4-Epoxy-1,4-dihydro-7-trifluoromethoxy-2-naphthoic Acid (26): This compound was prepared analogously, from 2-bromo-1,4-epoxy-1,4-dihydro-7-(trifluoromethoxy)naphthalene (**18**; 4.6 g, 15 mmol); colorless cubes; m.p. 108−110 °C (dec.; from hexanes); yield 3.4 g (83%). − ^{1}H NMR: δ = 7.86 (d, J = 2.0 Hz, 1 H), 7.30 (d, J = 7.8 Hz, 1 H), 7.28 (s, 1 H), 6.89 (dm, J = 7.8 Hz, 1 H), 5.91 (s, 1 H), 5.88 (br. s, 1 H). − ^{13}C NMR: δ = 168.0, 155.4, 150.3, 148.5, 147.1, 144.6, 121.7, 120.6 (q, J = 258.5 Hz), 117.9, 115.3, 83.2, 81.8. − $C_{12}H_7F_3O_4$ (272.18): calcd. C 52.95, H 2.59; found C 52.44, H 2.31.

1,4-Epoxy-1,4-dihydro-6-trifluoromethoxy-2-naphthoic Acid (29): This compound was prepared analogously, from 2-bromo-1,4-epoxy-1,4-dihydro-6-(trifluoromethoxy)naphthalene (**19**; 4.6 g, 15 mmol); colorless needles; m.p. 139−140 °C (dec.; from hexanes); yield 3.6 g (88%). − ^{1}H NMR: δ = 7.87 (d, J = 1.9 Hz, 1 H), 7.37 (d, J = 7.8 Hz, 1 H), 7.19 (s, 1 H), 6.89 (dq, J = 7.9, 1.0 Hz, 1 H), 5.91 (s, 1 H), 5.86 (br. s, 1 H). − ^{13}C NMR: δ = 167.5, 154.5, 149.0, 148.9, 146.9, 146.3, 121.6, 120.5 (q, J = 260.1 Hz), 118.2, 115.4, 83.4, 81.6. − $C_{12}H_7F_3O_4$ (272.18): calcd. C 52.95, H 2.59; found C 52.63, H 2.55.

8-Trifluoromethoxy-2-naphthoic Acid (21): A large excess of zinc powder (6.6 g, 0.10 mol) was added to a solution of 1,4-epoxy-1,4-dihydro-8-trifluoromethoxy-2-naphthoic acid (**20**; 2.7 g, 10 mmol). After having been heated for 20 h under reflux (≈ 120 °C), the mixture was filtered under suction, diluted with water (0.10 L), and extracted with diethyl ether (3 × 50 mL). The combined organic layers were dried and the solvents evaporated. Upon crystallization from hexanes (10 mL), colorless prisms were obtained, m.p. 177−179 °C, yield 1.8 g (70%). − ^{1}H NMR: δ = 9.00 (s, 1 H), 8.21 (dd, J = 8.7, 1.6 Hz, 1 H), 7.97 (d, J = 8.7 Hz, 1 H), 7.85 (d, J = 8.1 Hz, 1 H), 7.61 (d, J = 7.9 Hz, 1 H), 7.47 (d, J = 7.8 Hz, 1 H). − ^{13}C NMR: δ = 171.1, 146.1, 136.9, 128.3, 128.1, 127.6, 126.6, 126.5, 126.1, 125.6, 120.7 (q, J = 261.1 Hz), 116.9. − $C_{12}H_7F_3O_3$ (256.18): calcd. C 56.26, H 2.75; found C 56.41, H 2.57.

5-Trifluoromethoxy-2-naphthoic Acid (24): This compound was prepared analogously, from 1,4-epoxy-1,4-dihydro-5-trifluoromethoxy-2-naphthoic acid (**23**; 2.7 g, 10 mmol); colorless prisms; m.p. 186−187 °C; yield 2.0 g (78%). − ^{1}H NMR: δ = 8.78 (s, 1 H), 8.26 (m, 2 H), 7.97 (dd, J = 7.8, 1.1 Hz, 1 H), 7.6 (m, 2 H). − ^{13}C NMR: δ = 171.0, 145.1, 133.7, 131.8, 129.3, 128.8, 127.4, 126.5, 126.3, 122.1, 120.7 (q, J = 260.2 Hz), 119.1. − $C_{12}H_7F_3O_3$ (256.18): calcd. C 56.26, H 2.75; found C 56.27, H 2.58.

7-Trifluoromethoxy-2-naphthoic Acid (27): This compound was prepared analogously, from 1,4-epoxy-1,4-dihydro-2-trifluorometh-

oxy-2-naphthoic acid (**26**; 2.7 g, 10 mmol). Colorless prisms were obtained; m.p. 169−170 °C (from hexanes), yield 1.8 g (70%). − ^{1}H NMR: δ = 8.73 (s, 1 H), 8.17 (dd, *J* = 8.6, 1.6 Hz, 1 H), 7.98 (d, *J* = 8.9 Hz, 2 H), 7.83 (s, 1 H), 7.50 (dd, *J* = 8.9, 1.5 Hz, 1 H). − ^{13}C NMR: δ = 170.7, 147.4, 134.1, 132.6, 131.7, 130.0, 128.2, 127.7, 125.9, 122.7, 120.5 (q, *J* = 260.6 Hz), 119.4. − $C_{12}H_7F_3O_3$ (256.18): calcd. C 56.26, H 2.75; found C 55.92, H 2.43.

6-Trifluoromethoxy-2-naphthoic Acid (30): This compound was prepared analogously, from 1,4-epoxy-1,4-dihydro-6-trifluoromethoxy-2-naphthoic acid (**29**; 2.7 g, 10 mmol); colorless cubes; m.p. 210−211 °C (from hexanes); yield 2.2 g (86%). − ^{1}H NMR (D_3CCOCD_3): δ = 8.69 (s, 1 H), 8.17 (dd, *J* = 8.6, 1.6 Hz, 1 H), 8.04 (d, *J* = 9.0 Hz, 1 H), 7.91 (d, *J* = 8.7 Hz, 1 H), 7.72 (s, 1 H), 7.41 (dd, *J* = 8.9, 1.6 Hz, 1 H). − ^{13}C NMR (D_3CCOCD_3): δ = 168.1, 148.4, 135.8, 131.5, 131.1, 130.7, 127.9 (2C), 126.7, 120.6, 120.5 (q, *J* = 260.9 Hz), 117.5. − $C_{12}H_7F_3O_3$ (256.18): calcd. C 56.26, H 2.75; found C 56.34, H 2.60.

2-Bromo-8-trifluoromethoxy-1-naphthol (22): 3-Bromo-1,4-epoxy-1,4-dihydro-5-(trifluoromethoxy)naphthalene (**16**; 3.1 g, 10 mmol) was added to a mixture of methanol (15 mL) and concentrated (32%) hydrochloric acid (5 mL), which was heated to 75 °C for 20 h before being evaporated to dryness. The residue was eluted from silica gel (0.15 L) with hexanes containing 10% of ethyl acetate, giving colorless prisms; m.p. 39−41 °C (from hexanes); yield 2.6 g (85%). − ^{1}H NMR: δ = 7.73 (d, *J* = 8.1 Hz, 1 H), 7.60 (d, *J* = 9.0 Hz, 1 H), 7.45 (t, *J* = 8.0 Hz, 1 H), 7.37 (d, *J* = 7.9 Hz, 1 H), 7.32 (d, *J* = 8.9 Hz, 1 H), 7.18 (s, 1 H). − ^{13}C NMR: δ = 147.9, 144.3, 136.0, 130.8, 127.5, 125.9, 121.0, 120.5 (q, *J* = 262.1 Hz), 118.0, 117.4, 107.2. − $C_{11}H_6BrF_3O_2$ (307.07): calcd. C 43.03, H 1.97; found C 43.10, H 1.86.

2-Bromo-5-trifluoromethoxy-1-naphthol (25): This compound was prepared analogously, from 2-bromo-1,4-epoxy-1,4-dihydro-5-(trifluoromethoxy)naphthalene (**17**; 3.1 g, 10 mmol); colorless needles (from hexanes); m.p. 84−85 °C; yield 2.9 g (94%). − ^{1}H NMR: δ = 8.18 (d, *J* = 8.2 Hz, 1 H), 7.6 (m, 2 H), 7.50 (t, *J* = 8.1 Hz, 1 H), 7.41 (d, *J* = 7.6 Hz, 1 H), 6.09 (s, 1 H). − ^{13}C NMR: δ = 148.2, 145.0, 129.5, 127.3, 125.7, 125.6, 121.3, 120.4 (q, *J* = 260.6 Hz), 117.4, 114.9, 105.3. − $C_{11}H_6BrF_3O_2$ (307.07): calcd. C 43.03, H 1.97; found C 43.13, H 1.88.

2-Bromo-7-trifluoromethoxy-1-naphthol (28): This compound was prepared analogously, from 2-bromo-1,4-epoxy-1,4-dihydro-7-(trifluoromethoxy)naphthalene (**18**; 3.1 g, 10 mmol); colorless needles (from hexanes); m.p. 69−71 °C; yield 2.9 g (94%). − ^{1}H NMR: δ = 8.05 (s, 1 H), 7.80 (d, *J* = 9.0 Hz, 1 H), 7.51 (d, *J* = 9.0 Hz, 1 H), 7.36 (dd, *J* = 9.0, 2.1 Hz, 1 H), 7.32 (d, *J* = 8.9 Hz, 1 H), 6.11 (br. s, 1 H). − ^{13}C NMR: δ = 148.0, 147.1, 131.9, 129.7, 128.9, 124.6, 120.9 (2C), 120.5 (q, *J* = 258.8 Hz), 113.2, 105.2. − $C_{11}H_6BrF_3O_2$ (307.07): calcd. C 43.03, H 1.97; found C 43.04, H 1.89.

2-Bromo-6-trifluoromethoxy-1-naphthol (31): This compound was prepared analogously, from 2-bromo-1,4-epoxy-1,4-dihydro-6-(trifluoromethoxy)naphthalene (**19**; 3.1 g, 10 mmol); colorless needles (from hexanes); m.p. 73−74 °C; yield 2.8 g (91%). − ^{1}H NMR: δ = 8.28 (d, *J* = 9.2 Hz, 1 H), 7.62 (s, 1 H), 7.54 (d, *J* = 8.9 Hz, 1 H), 7.36 (d, *J* = 9.1 Hz, 1 H), 7.30 (d, *J* = 8.9 Hz, 1 H), 6.02 (s, 1 H). − ^{13}C NMR: δ = 148.3, 142.9, 129.9, 124.8, 124.6, 122.6, 121.0, 120.5 (q, *J* = 260.7 Hz), 120.1, 117.6, 104.3. − $C_{11}H_6BrF_3O_2$ (307.07): calcd. C 43.03, H 1.97; found C 43.19, H 1.78.

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