Heterocyclization Reaction of 4-(2-Methylaziridin-1-yl)-3-ureidobenzotrifluorides under Appel's Conditions

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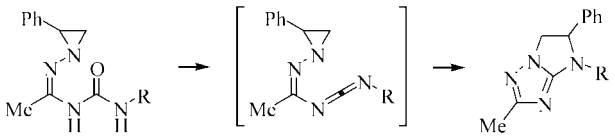
The reaction of 4-(2-methylaziridin-1-yl)-3-ureidobenzotrifluorides **4** with triphenylphosphine, carbon tetrachloride, and triethylamine (Appel's condition) led to the corresponding carbodiimides **5**, which underwent intramolecular cycloaddition reaction with aziridine under the reaction condition to give the benzimidazole-fused heterocycles, 2,3-dihydro-1*H*-imidazo[1,2-*a*]benzimidazoles **8** and 12,13-dihydro-5*H*-benzimidazo[2,3-*b*][1,3]benzodiazepines **9**.

Key Words : Heterocyclization, Urea, Aziridine, Carbodiimide, Appel's conditions

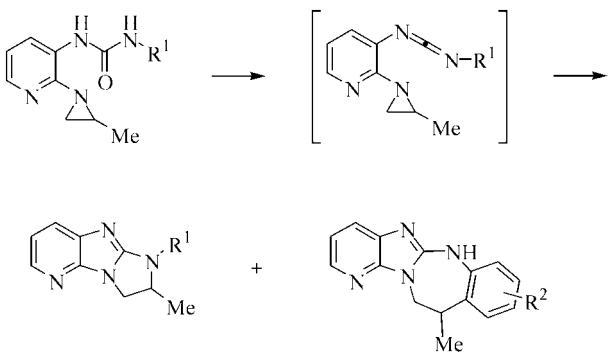
Introduction

2,3-Dihydroimidazo[1,2-*a*]benzimidazole derivatives have been shown to exhibit antihypertensive,[1] antihistamine,[2] antidiabetic,[3] and antiarrhythmic[3] activities and this justifies continuous efforts in developing more general and versatile synthetic methodologies to this class of compounds. Usually they are prepared by the intramolecular substitution reaction of suitable functionalized benzimidazoles having amine moieties.[4]

We have recently reported a new synthesis of 5,6-dihydro-7*H*-imidazo[1,2-*b*][1,2,4]triazoles,[5] 2,3-dihydro-1*H*-imidazo-[2',3':2,3]imidazo[4,5-*b*]pyridines[6] and 12,13-dihydro-5*H*-1,3-benzodiazepino[2',3':2,3]imidazo[4,5-*b*]pyridines[6] involving intramolecular cycloaddition reaction of aziridine and carbodiimide[7] obtained from the corresponding ureas using Appel's dehydration condition[8] as shown in Scheme 1 and Scheme 2. The present paper describes the synthesis of related heterocycles, 2,3-dihydro-1*H*-imidazo[1,2-*a*]benzimidazoles **8** and hitherto unknown 12,13-dihydro-5*H*-benzimidazo[2,3-*b*][1,3]benzodiazepines **9** by the similar manner (Scheme 3).



Scheme 1



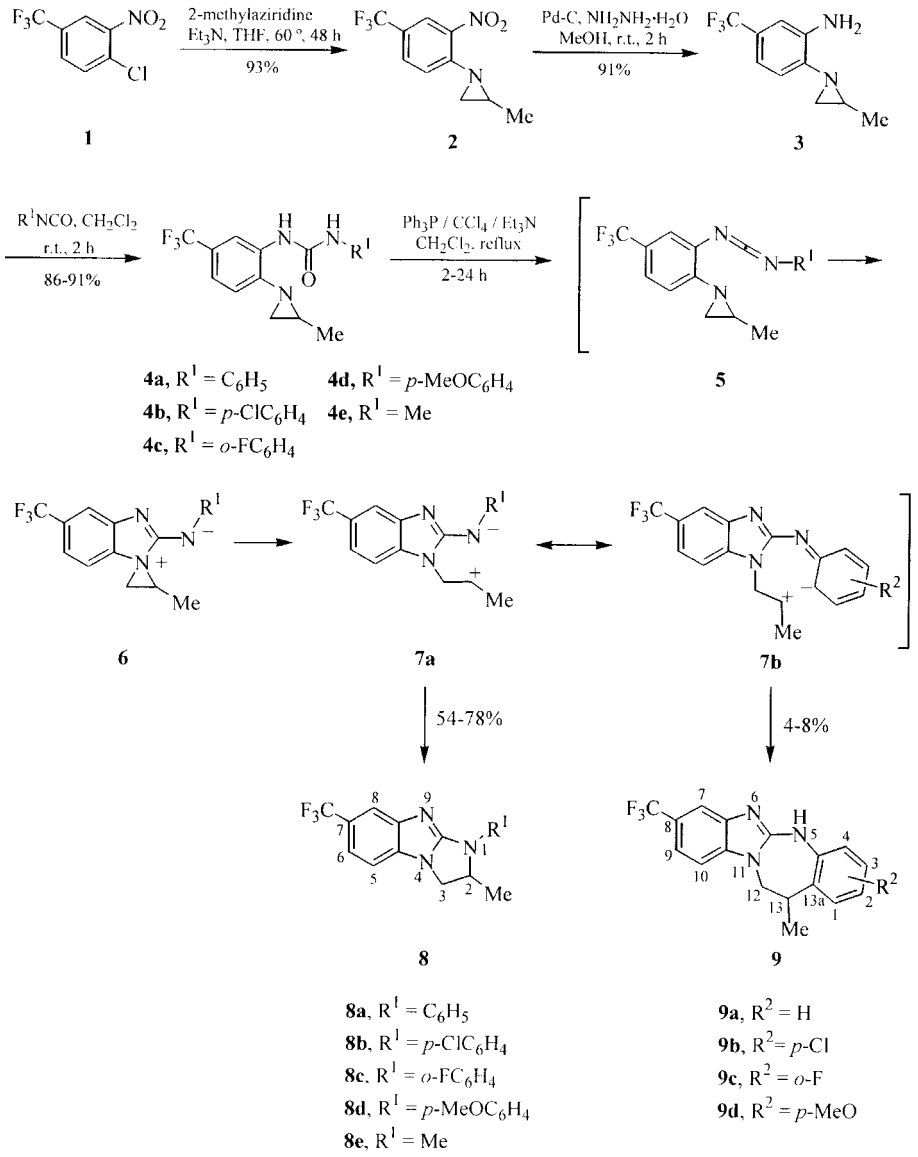
Scheme 2

Results and Discussion

The four-step synthetic approach to **8** and **9** required linking an aziridine moiety to a phenyl ring followed by reduction of the nitro group, urea formation and cyclization under Appel's condition to the benzimidazole-fused heterocylces **8** and **9** as shown in Scheme 3. Thus, 4-chloro-3-nitrobenzotrifluoride (**1**) was reacted with 2-methylaziridine in the presence of triethylamine in tetrahydrofuran at 60 ºC for 48 h to give 4-(2-methylaziridin-1-yl)-3-nitrobenzotrifluoride (**2**) in 93% yield. Reduction of the nitro group of **2** with 5% palladium on charcoal in hydrazine hydrate at room temperature for 2 h afforded aniline **3** in 91% yield. Treatment of the aniline **3** with isocyanates in dichloromethane at room temperature gave the ureas **4** in 86-91% yields. Reaction of ureas **4** with triphenylphosphine, carbon tetrachloride, and triethylamine in refluxing dichloromethane for 2-24 h afforded 2,3-dihydro-1*H*-imidazo[1,2-*a*]benzimidazoles **8** (54-78%) as a major product and 12,13-dihydro-5*H*-benzimidazo[2,3-*b*][1,3]benzodiazepines **9** (4-8%) as a minor one. In the case of *N*-methyl urea **4e**, a single product **8e** (74%) was isolated as a HCl salt.

A suitable mechanism for the formation of **8** and **9** is depicted in Scheme 3. Although the isolation of carbodiimides **5** was unsuccessful under the reaction conditions, an intramolecular cycloaddition reaction of aziridinyl carbodiimides **5** may give the zwitterionic aziridinium ions **6** followed by aziridine ring opening to afford the resonance-stabilized zwitterionic intermediates **7a-b** and subsequent ring closure to give **8** and **9** after rearomatization. Presumably the low yields of the minor products **9** might be explained by the small contribution of resonance form **7b** due to the loss of resonance energy of benzene ring.

The structures **8** and **9** were assigned on the basis of spectroscopic data. Compound **8a**, for instance, had the molecular formula of $C_{17}H_{14}F_3N_3$, as indicated by mass spectra (M^+ 317) as a base peak. In the ^{1}H NMR spectrum of



4a, $R^1 = C_6H_5$ **4d**, $R^1 = p\text{-}MeOC_6H_4$
4b, $R^1 = p\text{-}ClC_6H_4$ **4e**, $R^1 = Me$
4c, $R^1 = o\text{-}FC_6H_4$

8a, $R^1 = C_6H_5$
8b, $R^1 = p\text{-}ClC_6H_4$
8c, $R^1 = o\text{-}FC_6H_4$
8d, $R^1 = p\text{-}MeOC_6H_4$
8e, $R^1 = Me$

9a, $R^2 = H$
9b, $R^2 = p\text{-}Cl$
9c, $R^2 = o\text{-}F$
9d, $R^2 = p\text{-}MeO$

Scheme 3

8a, the signals from the two C3 hydrogens appear as two doublet of doublets at 4.26 (J = 15.6 and 7.3 Hz) and 4.36 ppm (J = 15.6 and 4.5 Hz), which arise as a result of coupling of the nonequivalent geminal hydrogens with one another and of each of them with the C2 hydrogen. The signal corresponding to the C2 hydrogen appears as a complex multiplet at 4.48 ppm, which arises from coupling with the C3 hydrogen atoms and the C2 methyl group. The ^{13}C NMR showed fifteen absorption peaks and its infrared spectrum showed no absorption in the region near 3400 cm^{-1}. Compound **9a** had the molecular formula of $C_{17}H_{14}F_3N_3$, as indicated by mass spectra (M^+ 317) as a base peak again. Comparison of the ^1H NMR signals for the CH_2 (δ 4.03, dd, J = 9.5 and 5.8 Hz and δ 4.60, dd, J = 9.5 and 8.9 Hz) and CH (δ 4.76, m) groups with those of **8a** showed different coupling constant (15.6 vs 9.5). Unfortunately, no N-H proton was observed distinctly. The ^{13}C NMR exhibited seventeen absorption peaks including peak at δ = 133.0 assignable to the bridged carbon (C13a), and its infrared spectrum showed absorption for NH band (3409 cm^{-1}).

In conclusion, using 4-(2-methylaziridin-1-yl)-3-ureidobenzotrifluoride **4** in the new synthesis of benzimidazole-fused heterocycles *via* intramolecular cycloaddition reaction under Appel's conditions was achieved again.

Experimental Section

All reagents and solvents were reagent grade or were purified by standard methods before use and the reactions were routinely carried out under an inert atmosphere. Silica gel 60 (70-230 mesh ASTM) used for column chromatography was supplied by E. Merck. Analytical thin layer chromatography (tlc) was performed on silica gel with fluorescent indicator coated on aluminium sheets. Melting points were taken using an Electrothermal melting point apparatus and are uncorrected. Microanalyses were obtained using a Carlo Erba EA 1180 element analyzer. Mass spectra were obtained using a ThermoQuest Polaris Q mass spectro-

meter operating at 70 eV. Infrared spectra were recorded on a Nicolet Magna 550 FTIR spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on a Gemini 300 spectrometer using deuterochloroform. All chemical shifts are reported in parts per million (δ) relative to tetramethylsilane.

4-Chloro-3-nitrobenzotrifluoride and 2-methylaziridine were purchased from Aldrich Chemical Company.

4-(2-Methylaziridin-1-yl)-3-nitrobenzotrifluoride (2). To a solution of 2-methlaziridine (3.71 g, 65 mmol) and Et_3N (10.1 g, 100 mmol) in 60 mL of THF was added 4-chloro-3-nitrobenzotrifluoride (**1**, 9.02 g, 40 mmol) and the mixture was stirred at 60 °C for 48 h. The solvent was removed on a rotavapor and the residue was partitioned between water (20 mL) and CH_2Cl_2 (100 mL). The organic layer was removed after drying over $MgSO_4$ and the residue was crystallized with hexane to give 9.16 g (93%) of **2**, mp 65 °C; IR (KBr) 1634, 1565, 1534, 1328, 1277, 1153, 1126, 912, 846 cm^{-1}; ^{1}H NMR δ 1.45 (d, 3H, J = 5.5 Hz), 2.25 (d, 1H, J = 6.1 Hz), 2.32 (d, 1H, J = 3.7 Hz), 2.50 (m, 1H), 7.21 (d, 1H, J = 8.5 Hz), 7.68 (d, 1H, J = 8.5 Hz), 8.22 (s, 1H); MS (*m/z*, %) 246 (M$^+$, 7), 174 (17), 145 (25), 127 (11), 105 (100).

Anal. Calcd. for $C_{10}H_9F_3N_2O_2$: C, 48.79; H, 3.68; N, 11.38. Found: C, 48.51; H, 3.55; N, 11.20.

3-Amino-4-(2-methylaziridin-1-yl)benzotrifluoride (3). To a stirred solution of **2** (2.95 g, 12 mmol) and 5% palladium on charcoal (0.50 g, 2.4 mmol) in 40 mL of MeOH was added 98% hydrazine monohydrate (2.0 g, 40 mmol) in 10 mL of MeOH dropwise manner over 1 h at r.t. The mixture was stirred for additional 1 h at r.t., and filtered over celite. The filtrate was evaporated *in vacuo* and the residue was partitioned between water (10 mL) and CH_2Cl_2 (50 mL). The organic layer was removed after drying over $MgSO_4$ and the residue was crystallized with hexane to give 2.36 g (91%) of **3**, mp 124-125 °C; IR (KBr) 3285, 3149, 1619, 1495, 1436, 1405, 1335, 1277, 1203, 1161, 1110, 1075, 1013, 889, 823, 792, 722, 702 cm^{-1}; ^{1}H NMR δ 1.40 (d, 3H, J = 4.2 Hz), 2.08-2.12 (m, 3H), 5.52 (s, 2H), 6.81 (d, 1H, J = 8.2 Hz), 7.10 (d, 1H, J = 7.0 Hz), 7.43 (s, 1H); MS (*m/z*, %) 216 (M$^+$, 22), 201 (15), 187 (100), 167 (28).

Anal. Calcd. for $C_{10}H_{11}F_3N_2$: C, 55.55; H, 5.13; N, 12.96. Found: C, 55.33; H, 4.88; N, 12.67.

4-(2-Methylaziridin-1-yl)-3-ureidobenzotrifluoride 4. *General Procedure*: To a stirred solution of **3** (2.16 g, 10 mmol) in 20 mL of CH_2Cl_2 was added the isocyanate (9.5 mmol) in 10 mL of CH_2Cl_2 dropwise manner at r.t. After stirring for 2 h at ambient temperature, the solvent was removed on a rotavapor. The residue was crystallized from hexane to give **4**.

The yield, physical and spectral data of **4** are as follows:

4a: 90%, mp 160-161 °C; ^{1}H NMR δ 1.22 (d, 1H, J = 5.2 Hz), 2.06 (d, 1H, J =3.7 Hz), 2.10 (d, 1H, J = 6.1 Hz), 2.23 (m, 1H), 6.89 (d, 1H, J = 8.2 Hz), 7.13-7.34 (m, 6H), 7.68 (s, 1H), 7.80 (s, 1H), 8.29 (s, 1H).

Anal. Calcd. for $C_{17}H_{16}F_3N_3O$: C, 60.88; H, 4.81; N, 12.53. Found: C, 60.55; H, 4.75; N, 12.30.

4b: 86%, mp 138-139 °C; ^{1}H NMR δ 1.39 (d, 3H, J = 5.5 Hz), 2.21 (d, 1H, J = 3.4 Hz), 2.39 (m, 2H), 6.97 (d, 1H, J = 8.5 Hz), 7.26-7.47 (m, 5H), 7.74 (s, 1H), 8.21 (s, 1H), 9.53 (s, 1H).

Anal. Calcd. for $C_{17}H_{15}ClF_3N_3O$: C, 55.22; H, 4.09; N, 11.36. Found: C, 55.11; H, 3.82; N, 11.05.

4c: 88%, mp 139-140 °C; ^{1}H NMR δ 1.40 (d, 3H, J = 5.2 Hz), 2.22 (s, 1H), 2.40 (m, 2H), 6.95-7.16 (m, 4H), 7.41-7.44 (m, 1H), 7.74 (s, 1H), 8.19-8.24 (m, 1H), 8.46 (s, 1H), 9.60 (s, 1H).

Anal. Calcd. for $C_{17}H_{15}F_4N_3O$: C, 57.79; H, 4.28; N, 11.89. Found: C, 57.68; H, 4.07; N, 11.67.

4d: 90%, mp 145-146 °C; ^{1}H NMR δ 1.41 (d, 3H, J = 5.9 Hz), 2.22 (d, 1H, J = 3.4 Hz), 2.38 (m, 2H), 3.80 (s, 3H), 6.87-7.01 (m, 3H), 7.40-7.46 (m, 3H), 7.78 (s, 1H), 8.10 (s, 1H), 9.24 (s, 1H).

Anal. Calcd. for $C_{18}H_{18}F_3N_3O_2$: C, 59.17; H, 4.97; N, 11.50. Found: C, 58.81; H, 4.71; N, 11.22.

4e: 91%, mp 138-139 °C; ^{1}H NMR δ 1.35 (d, 3H, J = 4.9 Hz), 2.13 (d, 1H, J = 3.7 Hz), 2.28-2.35 (m, 2H), 2.89 (d, 3H, J = 4.9 Hz), 6.12 (br s, 1H), 6.92 (d, 1H, J = 8.2 Hz), 7.38 (d, 1H, J = 8.5 Hz), 7.64 (s, 1H), 9.12 (s, 1H).

Anal. Calcd. for $C_{12}H_{14}F_3N_3O$: C, 52.75; H, 5.16; N, 15.38. Found: C, 52.60; H, 4.97; N, 15.05.

2,3-Dihydro-1*H*-imidazo[1,2-*a*]benzimidazoles 8 and 12,13-Dihydro-5*H*-benzimidazo[2,3-*b*][1,3]benzodiazepine 9. *General Procedure*: To a stirred solution of the appropriate urea **4** (2 mmol) in 50 mL of CH_2Cl_2 was added Ph_3P (1.80 g, 6.8 mmol), CCl_4 (1.4 mL, 14 mmol), and Et_3N (0.9 mL, 6.8 mmol). The mixture was heated to reflux temperature for 2-24 h. After cooling to room temperature the reaction mixture was partitioned between water (20 mL) and CH_2Cl_2 (50 mL). The solvent was removed after drying over $MgSO_4$ and the residue was chromatographed on silica gel column, eluted with hexane-EtOAc 4 : 1 to give the products **8** and **9**.

The reaction time, yield, phsical and spectral data of **8** and **9** are as follows:

8a: 24 h, 70%, mp 148-150 °C; IR (KBr) 1611, 1561, 1530, 1499, 1440, 1374, 1320, 1242, 1161, 1110 cm^{-1}; ^{1}H NMR δ 1.66 (d, 3H, J = 6.4 Hz), 4.26 (dd, 1H, J = 15.6 and 7.3 Hz), 4.33 (dd, 1H, J = 15.6 and 4.5 Hz), 4.48 (m, 1H), 7.04-7.54 (m, 7H), 7.84 (s, 1H); ^{13}C NMR δ 22.6, 50.9, 56.2, 107.4, 114.7, 117.9, 118.8, 124.3, 124.7, 124.8, (d, J_{CF} = 262 Hz), 129.2, 136.0, 139.2, 141.7, 151.5; MS (*m/z*, %) 317 (M$^+$, 100), 316 (35), 302 (80), 276 (20), 117 (16).

Anal. Calcd. for $C_{17}H_{14}F_3N_3$: C, 64.35; H, 4.45; N, 13.24. Found: C, 64.10; H, 4.31; N, 13.02.

9a: 24 h, 6%, mp 166-168 °C; IR (KBr) 3409, 1697, 1634, 1561, 1495, 1436, 1320, 1114 cm^{-1}; ^{1}H NMR δ 1.68 (d, 3H, J = 6.1 Hz), 4.03 (dd, 1H, J = 9.5 and 5.8 Hz), 4.60 (dd, 1H, J = 9.5 and 8.9 Hz), 4.76 (m, 1H), 7.04-7.44 (m, 4H), 7.68-7.71 (m, 2H), 7.81 (s, 1H); ^{13}C NMR δ 19.8, 48.7, 58.6, 107.2, 114.8, 115.4, 115.7, 117.6, 122.1, 123.9, 125.0 (d, J_{CF} = 272 Hz), 129.2, 129.4, 133.0 (C13a), 139.5, 148.0, 157.3; MS (*m/z*, %) 317 (M$^+$, 100), 302 (95), 276 (15), 213 (10).

Anal. Calcd. for $C_{17}H_{14}F_3N_3$: C, 64.35; H, 4.45; N, 13.24. Found: C, 64.16; H, 4.09; N, 13.39.

8b: 24 h, 54%, mp 155-156 °C; IR (KBr) 1607, 1549, 1526, 1487, 1444, 1413, 1328, 1254, 1168, 1126, 1056 cm^{-1}; ^1H NMR δ 1.69 (d, 3H, J = 6.7 Hz), 4.26 (dd, 1H, J = 15.9 and 7.6 Hz), 4.36 (dd, 1H, J = 15.9 and 3.9 Hz), 4.50 (m, 1H), 7.14-7.51 (m, 6H), 7.83 (s, 1H); ^{13}C NMR δ 22.8, 51.1, 56.5, 107.7, 114.9, 118.1, 120.2, 124.5, 124.8 (d, J_{CF} = 272 Hz), 125.0, 128.0, 129.2, 136.0, 138.0, 151.2; MS (*m/z*, %) 353 (37), 351 (M^+, 100), 338 (15), 336 (51), 301 (18), 275 (50), 226 (15), 151 (26).

Anal. Calcd. for $C_{17}H_{13}ClF_3N_3$: C, 58.05; H, 3.73; N, 11.95. Found: C, 57.75; H, 3.49; N, 11.71.

9b: 24 h, 8%, mp 168-171 °C; IR (KBr) 3405, 1708, 1615, 1553, 1495, 1324, 1165, 1118 cm^{-1}; ^1H NMR δ 1.62 (d, 3H, J = 6.4 Hz), 4.11 (dd, 1H, J = 7.9 and 5.9 Hz), 4.27 (dd, 1H, J = 7.9 and 5.5 Hz), 4.44 (m, 1H), 6.99-7.67 (m, 6H); ^{13}C NMR δ 19.8, 48.8, 58.6, 107.4, 115.1, 116.6, 117.9, 118.4, 124.9 (d, J_{CF} = 272 Hz), 127.0, 127.5, 129.2, 133.0, 136.8 (C13a), 138.1, 147.6, 147.8; MS (*m/z*, %) 353 (32), 351 (M^+, 100), 338 (16), 336 (52), 301 (16), 275 (39), 151 (19).

Anal. Calcd. for $C_{17}H_{13}ClF_3N_3$: C, 58.05; H, 3.73; N, 11.95. Found: C, 57.79; H, 3.50; N, 11.68.

8c: 5 h, 77%, mp 125-127 °C; IR (KBr) 1619, 1553, 1518, 1452, 1382, 1328, 1250, 1168, 1133, 1052 cm^{-1}; ^1H NMR δ 1.70 (d, 3H, J = 6.7 Hz), 4.31 (dd, 1H, J = 15.8 and 7.9 Hz), 4.36 (dd, 1H, J = 15.8 and 4.3 Hz), 4.50 (m, 1H), 7.00-7.43 (m, 5H), 7.87 (s, 1H), 8.37 (m, 1H); ^{13}C NMR δ 22.6, 51.0, 56.1, 107.7, 114.8, 117.9, 119.4, 119.9, 122.8, 124.3, 124.6, 124.8, (d, J_{CF} = 272 Hz), 127.6, 130.2, 135.9, 141.5, 152.4 (d, J_{CF} = 247 Hz); MS (*m/z*, %) 335 (M^+, 100), 320 (58), 294 (15), 226 (14).

Anal. Calcd. for $C_{17}H_{13}F_4N_3$: C, 60.90; H, 3.91; N, 12.53. Found: C, 60.72; H, 3.78; N, 12.35.

9c: 5 h, 4%, oil; IR (KBr) 3378, 1728, 1642, 1557, 1499, 1332, 1157, 1114 cm^{-1}; ^1H NMR δ 1.41 (d, 3H, J = 6.4 Hz), 3.90 (dd, 1H, J =9.5 and 5.7 Hz), 4.42 (dd, 1H, J = 9.5 and 8.5 Hz), 5.11 (m, 1H), 7.01-7.47 (m, 5H), 7.71 (s, 1H); ^{13}C NMR δ 19.3, 47.9, 61.5, 107.3, 111.2, 114.6, 116.7, 117.5, 119.7, 123.7 (d, J_{CF} = 272 Hz), 125.1, 126.5, 127.2, 134.1 (C13a), 147.6, 156.2 (d, J_{CF} = 248 Hz), 159.3; MS (*m/z*, %) 335 (M^+, 100), 320 (50), 316 (15), 294 (11), 226 (13).

Anal. Calcd. for $C_{17}H_{13}F_4N_3$: C, 60.90; H, 3.91; N, 12.53. Found: C, 60.63; H, 3.75; N, 12.20.

8d: 24 h, 78%, mp 157-158 °C; IR (KBr) 1615, 1561, 1510, 1444, 1374, 1332, 1238, 1161, 1114, 1065, 1040 cm^{-1}; ^1H NMR δ 1.67 (d, 3H, J = 6.7 Hz), 3.81 (s, 3H), 4.26 (dd, 1H, J = 15.9 and 7.6 Hz), 4.32 (dd, 1H, J = 15.9 and 3.7 Hz), 4.50 (m, 1H), 6.91-6.94 (m, 2H), 7.12-7.15 (m, 1H), 7.36-7.45 (m, 3H), 7.81 (s, 1H); ^{13}C NMR δ 22.7, 50.8, 55.5, 55.9, 107.4, 114.5, 117.6, 121.8, 124.2, 124.7, 124.9 (d, J_{CF} = 271 Hz), 132.3, 136.3, 141.8, 152.7, 156.1; MS (*m/z*, %) 347 (M^+, 100), 332 (59), 147 (35).

Anal. Calcd. for $C_{18}H_{16}F_3N_3O$: C, 62.24; H, 4.64; N, 12.10. Found: C, 61.93; H, 4.78; N, 11.88.

9d: 24 h, 8%, oil; IR (KBr) 3400, 1700, 1634, 1561, 1514, 1433, 1316, 1242, 1153, 1114, 1044 cm^{-1}; ^1H NMR δ 1.53 (d, 3H, J = 6.1 Hz), 3.81 (s, 3H), 3.90 (dd, 1H, J = 9.5 and 4.9 Hz), 4.40 (dd, 1H, J = 9.2 and 8.8 Hz), 4.98 (m, 1H), 6.96-7.33 (m, 3H), 7.54-7.61 (m, 2H), 7.74 (s, 1H); ^{13}C NMR δ 19.3, 47.6, 55.6, 59.9, 107.0, 114.7, 117.4, 119.7, 120.6, 123.7, 124.1, 125.1 (d, J_{CF} = 272 Hz), 131.3, 134.0, 136.9 (C13a), 147.8, 155.9, 158.8; MS (*m/z*, %) 347 (M^+, 100), 332 (60), 281 (35), 207 (40), 147 (35).

Anal. Calcd. for $C_{18}H_{16}F_3N_3O$: C, 62.24; H, 4.64; N, 12.10. Found: C, 61.91; H, 4.40; N, 11.75.

8e (HCl salt): 2 h, 74%, mp 129-130 °C; IR (KBr) 3196, 1631, 1607, 1588, 1448, 1413, 1378, 1316, 1285, 1141, 1110, 1048, 873, 803 cm^{-1}; ^1H NMR δ 1.61 (d, 3H, J = 6.7 Hz), 3.16 (s, 3H, J = 4.9 Hz), 4.14 (m, 2H), 4.40 (m, 1H), 4.64 (br s, 1H), 7.06 (d, 1H, J = 8.2 Hz), 7.32 (d, 1H, J = 8.2 Hz), 7.75 (s, 1H); ^{13}C NMR δ 22.7, 30.1, 50.6, 55.5, 107.0, 113.8, 117.0, 124.1, 124.9 (d, J_{CF} = 271 Hz), 136.9, 142.2, 156.4; MS (*m/z*, %) 293 (26), 291 (M^+, 79), 256 (100), 228 (29), 215 (42), 187 (41).

Anal. Calcd. for $C_{12}H_{13}ClF_2N_3$: C, 49.41; H, 4.49; N, 14.41. Found: C, 49.11; H, 4.28; N, 14.14.

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