HETEROCYCLIZATION OF 5-TRIFLUOROACETYLTRICYCLO-[4.3.1.1^{3,8}]UNDECAN-4-ONE TO SOME 6- AND 7-MEMBERED NITROGEN HETEROCYCLES[1] †

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Abstract - Heterocyclization study of 5-trifluoroacetyl[4.3.1.1^{3,8}]undecan-4-one into pyrimidine, pyridine, and 1,4-diazepine derivatives as a route to trifluoromethylated homoadamantane-fused 6- and 7-membered nitrogen heterocycles is reported.

An increasing interest has been paid for several years to the chemistry of organic trifluoromethyl compounds due to their unique physical properties, specific chemical reactivity, and their remarkable potential biological activity.[2] The synthesis of trifluoromethyl heterocycles using a readily available building block with a trifluoromethyl group has often been found to be superior to either selective introduction of a trifluoromethyl group into heterocyclic compounds or conversion of a carboxy group into the trifluoromethyl group.[3] We reported recently heterocyclization of the titled 1,3-diketone, 5-trifluoroacetylhomoadamantan-4-one (**1**), to homoadamantano[4,5]fused 5-membered nitrogen heterocycles.[4] As an extension of our studies on synthesis of heterocycles fused with polycyclic skeletons,[5] we report in this paper heterocyclization of the titled 1,3-diketone to some trifluoromethylated homoadamantano[4,5]fused 6- and 7-membered nitrogen heterocycles.

One of the most promising route to pyrimidine derivatives[6] from 1,3-dicarbonyl compounds is the condensation reaction with amidine function known as the Traube synthesis.[7] On heating a solid mixture of 5-trifluoroacetylhomoadamantan-4-one (**1**) and guanidine carbonate (1.2 equiv.) without solvent at 300 °C for 3 h under argon, the condensation reaction underwent smoothly to afford 2-amino-4-trifluoromethyl-6,7,8,9,10,11-hexahydro-5,9;7,11-dimethano-*5H*-[9]annuleno[*d*]pyrimidine (**2**) in 87% yield (Scheme 1). On acetylation with acetic anhydride in pyridine under reflux for 3 h,[8] **2** afforded mono- and diacetyl derivatives (**3a**) and (**3b**). However, the condensation of **1** with benzamidine hydrochloride was not successful by heating without solvent as above and by heating in refluxing ethanol or xylenes (bp 137-147 °C) for 15 h, suggesting a limit of above method.[9,10] We examined also the Weis and Rosenbach procedure[11] to prepare phenyl pyrimidine derivative (**5**). Heating a mixture of **1**, benzaldehyde and ammonium acetate in DMSO-AcOH (4:1) at 80 °C for 10 h afforded pyrimidine derivative (**5**) in 48 % yield after usual workup

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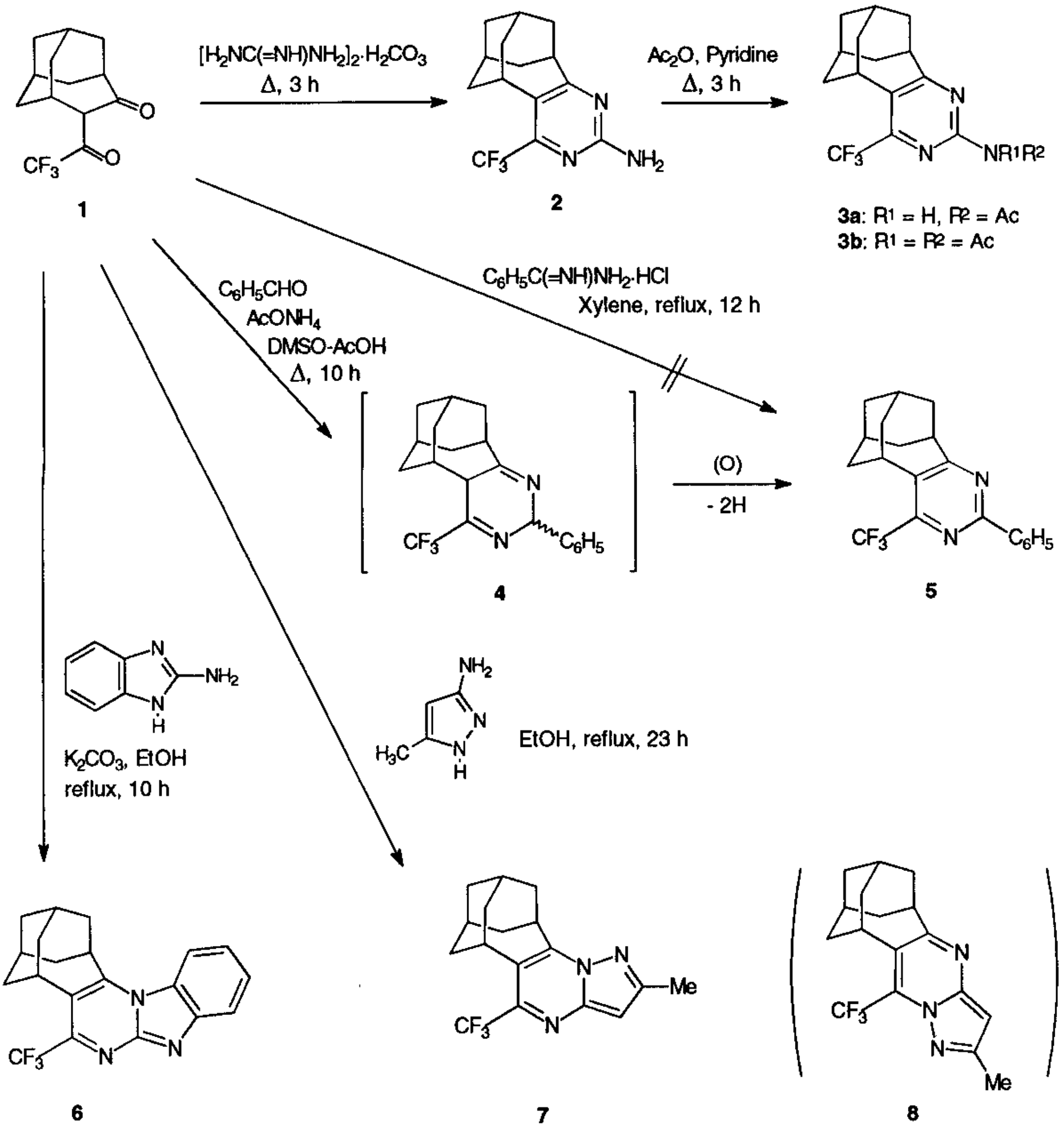
† Dedicated to the memory of the late Professor Yoshio Ban.

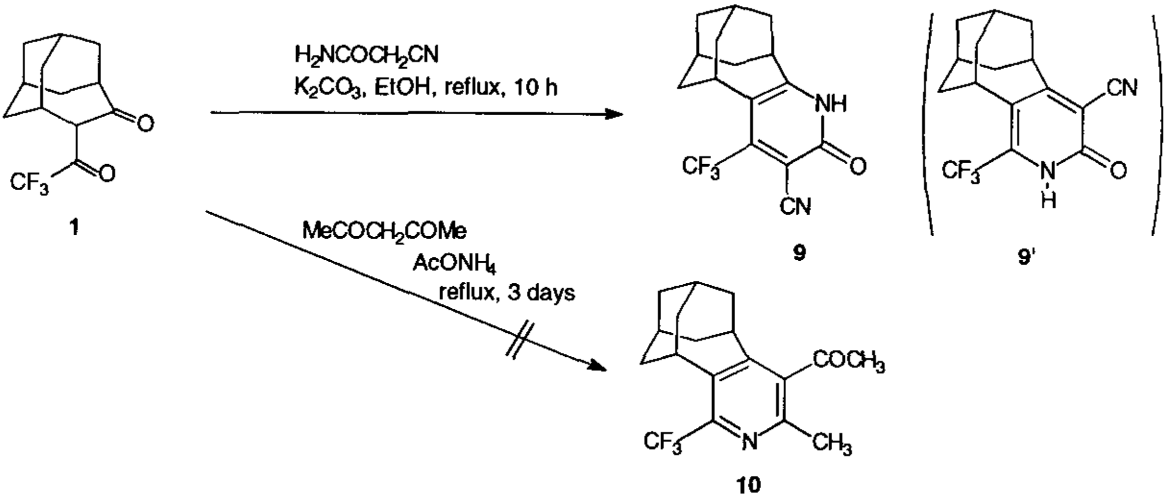
Scheme 1



and chromatography. The given structure was supported by analysis and spectral data. In $CDCl_3$, **5** had characteristic signals at δ 122.29 (q, $^1J_{C,F}$ = 276 Hz, CF_3) and 151.43 (q, $^2J_{C,F}$ = 33 Hz, $=CCF_3$) in ^{13}C nmr spectrum.[12] We examined also condensation reaction of **1** with formamide according to the Bredereck synthesis.[13] However, heating of **1** with formamide at 180-190 °C for 8 h under argon gave only intractable decomposition products. The condensation of **1** with some aminoaza heterocycles afforded fused pyrimidine derivatives albeit the yields were low. Thus heating of **1** with 2-aminobenzimidazole (1.2 equiv.) in ethanol containing potassium carbonate (1.2

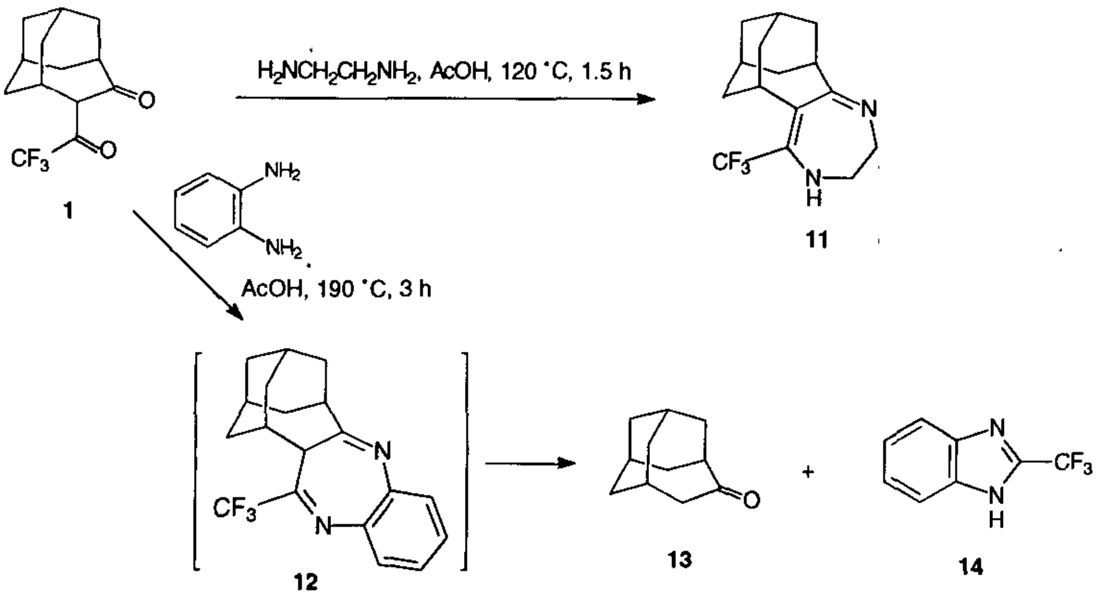
equiv.) under reflux for 10 h afforded fused pyrimidine derivative (**6**) in18 % yield after chromatography. Above reaction without potassium carbonate or in acetic acid under reflux for 10 h gave only 5 and 2% yield of **6**, respectively. Similar condensation of **1** with 3-amino-5-methylpyrazole (1.2 equiv.) in ethanol under reflux for 23 h gave fused pyrimidine (**7**) in 14 % yield, but the reaction in the presence of potassium carbonate afforded **7** only in 6% yield (Scheme 1).

Scheme 2



The condensation reaction underwent regioselectively and regioisomer (**8**) could not be isolated even if it was formed in a trace amount. The condensation of 1,3-diketone with cyanoacetamide is known to give cyanopyridinone ring.[14,15] Heating a mixture of **1**, cyanoacetamide (1.2 equiv.), and potassium carbonate (0.8 equiv.) in ethanol under reflux for 10 h afforded single regioisomer (**9**) in 26% yield (Scheme 2). The 4-trifluoromethylpyridin-2-one structure

Scheme 3



(**9**) was assigned on the basis of the spectral data and of the well established fact that the methylene group of cyanoacetamide tends to react with the most electrophilic carbonyl group.[4,16] The regioisomer (**9'**) was not formed at all. Attempted condensation of **1** with acetylacetone and ammonium acetate did not afford **10**. The condensation reaction of 1,3-dicarbonyl compounds with 1,2-diamines is known as a direct route to dihydro-1,4-diazepine derivatives.[17,18] The reaction of **1** with ethylenediamine (2.0 equiv.) in acetic acid at 120 °C for 1.5 h afforded dihydro-1,4-diazepine derivative (**11**) as a colorless solid in 18% yield (Sceheme 3). However, the condensation of **1** with DAMN (diaminomaleonitrile) in acetic acid under reflux for 15 h, or in ethanol in the presence of phosphorus pentoxide was not successful affording only some decomposition products. The reaction of **1** with *o*-phenylenediamine (1.1 equiv.) in acetic acid at 190 °C for 3 h afforded only homoadamantan-4-one (**13**) and 2-trifluoromethylbenzimidazole (**14**) in 60 and 43 % yields respectively as decomposition products (Scheme 3). The 1,5-benzodiazepine (**12**) seems to be formed but it decomposed via retro-aldol type decomposition as reported for dimethyl analog.[19]

As above 5-acetylhomoadamantan-4-one (**1**) exhibited rather lower reactivity in the heterocyclization reaction to some 6- and 7-membered nitrogen heterocycles probably by the steric factor. However, novel trifluoromethylated homoadamantane-fused pyrimidine and pyridine ring systems can be obatainable from **1** and the conventional reagents.

EXPERIMENTAL

Melting points were taken on a Yanagimoto micro-melting points hot-stage apparatus and are uncorrected. Microanalyses were performed with a Perkin-Elmer 2400S elemental analyzer. ^{1}H and ^{13}C nmr spectra were obtained at 25 °C with a Varian Gemni-200 spectrometer at 200 and 50 MHz respectively for samples in $CDCl_3$ solution with Me_4Si as internal standard. Ir spectra were recorded on a JASCO FT/IR-5300 spectrometer. EI mass spectra were obtained on a ESCO EMD-05B spectrometer at 70 eV. Tlc (Thin layer chromatography) was performed on a Merck Kieselgel 60 F_{254} unless otherwise specified, and/or on Merck Aluminium oxide F_{254}. Flash chromatography was performed with a silica gel column (Fuji-Davison BW-300). All reagents were of commercial quality.

2-Amino-4-trifluoromethyl-6,7,8,9,10,11-hexahydro-5,9;7,11-dimethano-5*H*-[9]annuleno[*d*]pyrimidine (2):
A solid mixture of 5-trifluoroacetylhomoadamantan-4-one (**1**)[4] (260 mg, 1.00 mmol) and guanidine carbonate (216 mg, 1.20 mmol) was heated to melt at 180 °C for 3 h under argon. The cooled mixture was dissolved in dichloromethane and dried (Na_2SO_4). The solvent was removed under reduced pressure to give a solid which was purified by flash chromatography on a silica gel column using 10:1 hexane/AcOEt to afford the product (**2**) as colorless crystals (245 mg, 87%): mp 176-178 °C (AcOEt/hexane); ir(KBr): ν = 3405, 1647, 1577, 1472, 1179, 1121 cm^{-1}; ^{1}H nmr (200 MHz, $CDCl_3$): δ = 1.65-2.20 (m, 12H), 2.80-3.10 (m, 1H), 3.28 (br s, 1H), 5.28 (br s, 2H); ^{13}C nmr (50 MHz, $CDCl_3$): δ = 27.06, 27.77, 29.94, 33.07, 34.72, 37.79, 122.10 (q, *J* = 276 Hz), 127.85, 152.00 (q, *J* = 32 Hz), 160.47, 180.06; ms (EI, 70eV): *m/z* (%) = 283 (M$^+$, 100), 282 (8.9), 267 (11), 255 (6.7), 226 (19), 214 (19). Anal. Calcd for $C_{14}H_{16}N_3F_3$: C, 59.35; H, 5.69; N, 14.83. Found: C, 59.23; H, 5.74; N, 14.72.

Acetylation of 2: 2-Acetylamino-4-trifluoromethyl-6,7,8,9,10,11-hexahydro-5,9;7,11-dimethano-5*H*-[9]annuleno-[*d*]pyrimidine (3a) and 2-(Bisacetylamino)-4-trifluoromethyl-6,7,8,9,10,11-hexahydro-5,9;7,11-dimethano-5*H*-[9]-annuleno[*d*]pyrimidine (3b).
A solution of **2** (69 mg, 0.24 mmol) in acetic anhydride (3 ml, 0.60 mmol) and pyridine (3 ml) was heated to reflux for

3 h. The excess reagent and solvent was removed under reduced pressure to give a solid residue which was purified by flash chromatography on a silica gel column using 50:1 hexane/AcOEt to afford **3a** as a colorless crystal (20 mg, 31.0%) and **3b** as an oil (48 mg, 65%).

3a: mp 183-185 °C (hexane); ir(KBr): ν = 3235, 2919, 1678, 1576, 1499, 1377 cm^{-1}; ^{1}H nmr (200 MHz, $CDCl_3$): δ = 1.57-2.28 (m, 12H), 2.57 (s, 3H), 3.21 (t, *J* = 5.8 Hz, 1H), 3.38 (br s, 1H), 8.07 (br s, 1H); ^{13}C nmr (50 MHz, $CDCl_3$): δ = 25.30, 27.72, 30.27, 32.91, 34.24, 35.12, 43.96, 121.79 (q, *J* = 276 Hz), 133.09, 151.63 (q, *J* = 33 Hz), 154.61, 172.07, 181.86; ms (EI, 70eV): *m/z* (%) = 325 (M$^+$, 35), 310 (10), 306 (2.8), 282 (100), 267 (15). Anal. Calcd for $C_{16}H_{18}N_3OF_3$: C, 59.07; H, 5.58; N, 12.92. Found: C, 58.84; H, 5.65; N, 12.54.

3b: colorless oil; ir(KBr): ν = 2922, 1728, 1561, 1385, 1236, 1194 cm^{-1}; ^{1}H nmr (200 MHz, $CDCl_3$): δ = 1.77-1.98 (m, 6H), 2.01-2.27 (m, 6H), 2.30 (s, 6H), 3.33 (t, *J* = 6.0 Hz, 1H), 3.41-3.57 (m, 1H); ^{13}C nmr (50 MHz, $CDCl_3$): δ = 26.40, 27.69, 30.66, 32.77, 33.68, 34.93, 43.91, 121.46 (q, *J* = 276 Hz), 138.64, 153.19 (q, *J* = 34 Hz), 156.29, 172.43, 183.37; ms (EI, 70eV): *m/z* (%) = 367 (M$^+$, 1.2), 366 (0.4), 348 (0.7), 324 (96), 281 (100, 267 (13). Anal. Calcd for $C_{18}H_{20}N_3O_2F_3$: C, 58.85; H, 5.48; N, 11.43. Found: C, 58.84; H, 5.64; N, 11.26.

2-Phenyl-4-trifluoromethyl-6,7,8,9,10,11-hexahydro-5,9;7,11-dimethano-5*H*-[9]annuleno[*d*]pyrimidine (5):

A mixture of **1** (130 mg, 0.50 mmol), benzaldehyde (0.051 ml, 0.50 mmol), and ammonium acetate (385 mg, 5.00 mmol) in DMSO (4 ml)-AcOH (1 ml) was heated at 80 °C for 10 h. The cooled mixture was diluted with water (20 ml), and extracted with dichloromethane (5 ml x 4) and the combined extracts were washed with water and dried (Na_2SO_4). The solvent was removed under reduced pressure to give a solid which was purified by flash chromatography on a silica gel column using 20:1 hexane/AcOEt to afford the pyrimidine derivative (**5**) as colorless crystals (82 mg, 48 %): mp 141-145 °C (AcOEt/hexane); ir(KBr): ν = 2917, 1562, 1410, 1171, 1123, 700 cm^{-1}; ^{1}H nmr (200 MHz, $CDCl_3$): δ = 1.66-2.28 (m, 12H), 3.35-3.54 (m, 2H), 7.37-7.57 (m, 3H), 8.40-8.53 (m, 2H); ^{13}C nmr (50 MHz, $CDCl_3$): δ = 27.91, 30.62, 33.10, 34.19, 35.29, 44.32, 122.29 (q, *J* = 276 Hz), 128.57, 128.94, 131.18, 136.11. 137.17, 151.43 (q, *J* = 33 Hz), 161.53, 179.73; ms (EI, 70eV): *m/z* (%) = 344 (M$^+$, 100), 343 (8.9), 330 (9.4), 316 (4.7), 275 (50). Anal. Calcd for $C_{20}H_{19}N_3F_3$: C, 69.75; H, 5.56; N, 8.13. Found: C, 69.32; H, 5.85; N, 8.26.

7-Trifluoromethyl-9,10,11,12,13,14-hexahydro-8,12;10,14-dimethano-8*H*-[9]annuleno[4,5]pyrimidino[3,2-*a*]benzimidazole (6):

A mixture of **1** (130 mg, 0.50 mmol), 2-aminobenzimidazole (80 mg, 0.60 mmol), and potassium carbonate (84 mg, 0.60 mmol) in EtOH (4 ml) was heated to reflux for 10 h. The cooled mixture was diluted with water (20 ml), and extracted with dichloromethane (5 ml x 4) and the combined extracts were washed with water and dried (Na_2SO_4). The solvent was removed under reduced pressure to give a solid which was purified by flash chromatography on a silica gel column using 10:1 hexane/AcOEt to afford the benzimidazole derivative (**6**) as a yellowish solid (33 mg, 18 %): mp 195-198 °C (AcOEt/hexane); ir(KBr): ν = 2920, 1501, 1445, 1194, 1113, 735 cm^{-1}; ^{1}H nmr (200 MHz, $CDCl_3$): δ = 1.52-2.60 (m, 12H), 3.57 (t, J = 5.6 Hz, 1H), 4.61 (t, *J* = 5.3 Hz, 1H), 7.51 (ddd, *J* = 42.4, 7.2, 1.2 Hz, 2H), 8.05 (t, *J* = 9.6 Hz, 2H); ^{13}C nmr (50 MHz, $CDCl_3$): δ = 27.73, 30.49, 32.22, 33.82, 34.25, 35.07, 116.21, 121.57 (q, *J* = 276 Hz), 121.74, 122.53, 124.32, 127.04, 127.93, 146.46, 149.28, 150.08 (q, *J* = 33 Hz), 162.03; ms (EI, 70eV): *m/z* (%) = 357 (M$^+$, 100), 356 (2.7), 338 (0.8), 300 (4.8), 288 (11). Anal. Calcd for $C_{20}H_{18}N_3F_3$: C, 67.22; H, 5.08; N, 11.76. Found: C, 67.33; H, 5.04; N, 11.68.

2-Methyl-5-trifluoromethyl-7,8,9,10,11,12-hexahydro-6,10;8,12-dimethano-6*H*-[9]annuleno[*e*]pyrazolo[2,3-*a*]pyrimidine (7):

A mixture of **1** (130 mg, 0.50 mmol) and 3-amino-5-methylpyrazole (58 mg, 0.60 mmol) in EtOH (4 ml) was heated to reflux for 23 h. The solvent was removed under reduced pressure to give a solid which was purified by flash chromatography on a silica gel column using 10:1 hexane/AcOEt to afford the pyrimidine derivative (**7**) as a faintly bluish solid (23 mg, 14 %): mp 151-152 °C (AcOEt/hexane); ir(KBr): ν = 2915, 1514, 1225, 1194, 1138, 934 cm^{-1}; ^{1}H nmr (200 MHz, $CDCl_3$): δ = 1.77-2.30 (m, 12H), 2.54 (d, *J* = 0.6 Hz, 3H), 3.41-3.53 (m, 1H), 4.61-4.74 (m, 1H), 6.61 (s, 1H); ^{13}C nmr (50 MHz, $CDCl_3$): δ = 14.83, 27.85, 30.45 (q, *J* = 3.0 Hz), 31.39, 32.29, 33.38, 35.30, 98.04,122.13 (q, *J* = 276 Hz), 123.80, 143.85 (q, *J* = 33 Hz),146.61, 155.91, 157.15; ms (EI, 70eV): *m/z* (%) = 321 (M$^+$, 100), 320 (8.2), 306 (11), 302 (4.6), 252 (56). Anal. Calcd for $C_{17}H_{18}N_3F_3$: C, 63.54; H, 5.65; N, 13.08. Found: C, 63.69; H, 5.72; N, 12.87.

3-Cyano-4-trifluoromethyl-1,5,6,7,8,9,10,11-octahydro-5,9;7,11-dimethano[9]annuleno[*b*]pyridin-2-one (9): A mixture of **1** (130 mg, 0.50 mmol), 2-cyanoacetamide (51 mg, 0.60 mmol), and potassium carbonate (53 mg, 0.40 mmol) in EtOH (4 ml) was heated to reflux for 10 h. The cooled mixture was diluted with water (20 ml), neutralized by 18% hydrochloric acid, and extracted with dichloromethane (5 ml x 4). The combined extracts were washed with water and dried (Na_2SO_4). The solvent was removed under reduced pressure to give a solid which was purified by flash chromatography on a silica gel column using 2:1 hexane/AcOEt to afford the pyridone derivative (**9**) as a colorless solid (40 mg, 26 %): mp >300 °C (AcOEt/hexane); ir(KBr): ν = 2913, 2230, 1657, 1373, 1146, 953 cm^{-1}; ^{1}H nmr (200 MHz, $CDCl_3$): δ = 1.42-2.34 (m, 12H), 3.03-3.38 (m, 2H), 13.79 (br s, 1H); ^{13}C nmr (50 MHz, $CDCl_3$): δ = 27.31, 31.22, 32.92, 33.98, 34.74, 39.97, 98.48, 113.31, 122.02 (q, *J* = 271 Hz), 125.08, 145.86 (q, *J* = 30 Hz),162.65, 164.43; ms (EI, 70eV): *m/z* (%) = 308 (M$^+$, 100), 307 (4.7), 292 (8.7), 265 (8.0), 239 (17). Anal. Calcd for $C_{16}H_{15}N_2OF_3$: C, 62.33; H, 4.90; N, 9.09. Found: C, 62.46; H, 4.96; N, 9.04.

5-Trifluoromethyl-2,3,4,6,7,8,9,10-octahydro-6,10;8,12-dimethano[9]annuleno[*e*]-1,4-diazepine (11): A mixture of **1** (130 mg, 0.50 mmol) and ethylenediamine (0.066 ml, 1.00 mmol) in acetic acid (0.5 ml) was heated at 120 °C for 1.5 h. The cooled mixture was diluted with water and extracted with dichloromethane (5 ml x 4). The combined extracts were washed with saturated aqueous NaCl and dried (Na_2SO_4). The solvent was removed under reduced pressure to give a solid which was purified by flash chromatography on a silica gel column using 1:1 hexane/AcOEt to afford the diazepine derivative (**11**) as a colorless solid (26 mg, 18 %): mp 152-154 °C (AcOEt/hexane); ir(KBr): ν = 3246, 2909, 1611, 1570, 1520, 1144 cm^{-1}; ^{1}H nmr (200 MHz, $CDCl_3$): δ = 1.53-2.14 (m, 14H), 2.65 (br s, 1H), 3.40-3.56 (m, 2H), 3.90-4.10 (m, 2H); ^{13}C nmr (50 MHz, $CDCl_3$): δ = 27.68, 31.98, 34.04, 35.50, 36.03, 46.60, 51,63, 53.64, 104.69, 121.81 (q, *J* = 280 Hz), 145.91 (q, *J* = 38 Hz),163.71; ms (EI, 70eV): *m/z* (%) = 284 (M$^+$, 100), 283 (31), 265 (8.9), 254 (6.8), 215 (37). Anal. Calcd for $C_{15}H_{19}N_2F_3$: C, 63.37; H, 6.74; N, 9.85. Found: C, 63.53; H, 6.76; N, 9.69.

Reaction of 1 with *o*-Phenylenediamine:
A mixture of **1** (130 mg, 0.50 mmol) and *o*-pehnylenediamine (65 mg, 0.60 mmol) in acetic acid (3.5 ml) was heated at 190 °C for 3 h. The cooled mixture was diluted with water and extracted with dichloromethane (5 ml x 4). The combined extracts,were washed with saturated aqueous NaCl and dried (Na_2SO_4). The solvent was removed under reduced pressure to give a solid which was purified by flash chromatography on a silica gel column using 10:1 hexane/AcOEt to afford homoadamantan-4-one (**13**) as a colorless solid (50 mg, 60 %) and 2-trifluoromethylbenzimidazole (**14**) as a colorless solid (40 mg, 43%). The former product (**13**) was identified by the same Rf values on tlc, ir spectrum with an authentic sample[20] and the latter product (**14**) was characterized by comparison of mp and spectral data (ir, ^{1}H nmr, ms) with the reported values.[21]

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