# Reactivity of the Nitrogen–Silicon Bond. Pyridines and Furo[2,3-*b*][1,4]diazepines from 4-Amino-1-azabutadienes via 1,2-Dihydro-1,3,2-diazasilines

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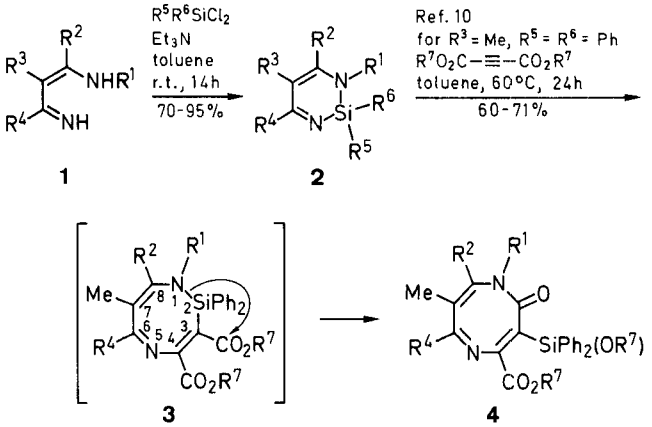
1,2-Dihydro-1,3,2-diazasilines **2** are prepared from 4-amino-1-azadienes **1** and react with dialkyl acetylenedicarboxylates to produce six- and seven-membered heterocycles depending on the substitution pattern of **1**. Highly functionalized pyridine-2-carboxylates **5** and 8,8a-dihydro-2*H*-furo[2,3-*b*][1,4]diazepin-2-ones **11** are formed starting from azadienes **1** with $R^3$ = H and $R^2$ = $R^3$ = H, respectively. On heating diazepines **11** undergo ring-contraction to alkyl 4-hydroxy-5-(iminomethyl)pyridine-2-carboxylates **13** which can be hydrolyzed to the corresponding 5-formyl-4-hydroxypyridine-2-carboxylates **14**.

For a long time organosilicon compounds have been recognized as highly useful reagents or intermediates in organic chemistry.[2,3] On the other hand, the reactivity of the nitrogen–silicon bond has mostly been exploited in the last years;[3] thus, aminosilanes[4] and silyl imines[5,6] represent species of great potential in organic synthesis. Moreover, heterocycles containing the nitrogen–silicon–nitrogen (N–Si–N) moiety (e.g., diazasilolidines[7]) have been reported to yield macrocyclic systems by reaction with electrophiles. However, routes to 1,3,2-diazasilacycloalkanes are very limited in number[8] and reports concerning synthesis of the 1,2-dihydro derivatives of diazasilines remain unknown.

We have for a number of years been involved in the synthesis of new six-membered heterocycles with the N–X–N grouping (X = P, S) from readily available 4-amino-1-azabutadienes.[9] It became interesting to investigate the preparation of the analogous silicon-containing systems and to study their reactivity. Thus, the preliminary results[10] showed that substituted 1,2-dihydro-1,3,2-diazasilines **2** were formed very easily by stirring at room temperature azadienes **1**, dichlorosilane derivatives and triethylamine (molar ratio 1:1:2); more important, we found that the reactivity of heterocycles **2** ($R^3$ = Me) dramatically changed, compared to that of their precursors **1**, when treated with acetylenedicarboxylic acid esters[10,11] and heterocumulenes.[12] In fact, 1,5-diazocin-2(1*H*)-ones **4** – a new class of eight-membered heterocycles – were obtained in good yields in the former case (Scheme 1).[10]

The reaction seems to involve the insertion intermediate **3**, which rearranges to **4** through attack of the enamine nitrogen into the ester attached to C-3 (1,4-attack). The structure of compounds **4** was confirmed by X-ray analysis.[10] At this point, we realized that formation of seven-membered heterocycles involving nitrogen–carbon bond forming reaction between N-1 and the ester group linked to C-3 (1,5-attack) should be feasible and geometrically more favorable (1,4-versus 1,5-attack); we thought that the nature of the transition state in the rearrangement step leading to **4** might be determined primarily from steric interactions since the intermediate **3** is highly substituted. We report here that six- and seven-membered nitrogen heterocycles are selectively




**Scheme 1**

formed by reaction of 1-azabutadienes **1** having $R^2$ = Ar, $R^3$ = H and $R^2$ = $R^3$ = H, respectively, via their diazasiline derivatives **2**.

Compounds **2** were prepared by treating at room temperature azadienes **1** with the corresponding dichlorosilane reagent in the presence of two molar equivalents of triethylamine (see Scheme 1). After stirring overnight triethylammonium chloride was filtered off and compounds **2a–m** were isolated under nitrogen by washing with hexane and purified by recrystallization from hexane/chloroform. Because of their low stability, heterocycles **2n–s** were not isolated but used in the next step (Scheme 1, Table 1).

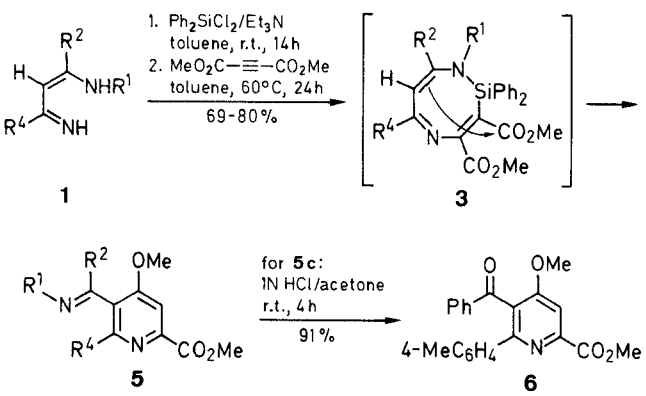
Once we synthesized 1,5-diazocines **4** from azadienes **1** with $R^3$ = Me via heterocycles **2**, we next studied the behavior of diazasilines with lower degree of substitution, e.g., diazasilines **2a–d** ($R^3$ = H), towards acetylenedicarboxylates. Treatment of a solution of **2a–d** in toluene, generated in situ from **1** and dichlorodiphenylsilane (see experimental section), with the corresponding acetylenic ester at 60 °C for 24 hours resulted, after acidic work-up, in the formation of highly functionalized pyridine-2-carboxylates **5** (Scheme 2); compounds **5** were purified by column chromatography (silica gel; toluene/diethyl ether, 2:1) and recrystallized from hexane/chloroform (Scheme 2, Table 3). Further, pyridine **5c** was hydrolyzed to the 5-acyl derivative **6** by stirring with 1 N hydrochloric acid in acetone. On the light of our previous findings,[10,13] the initial formation of the silicon-containing intermediate **3** followed by attack of the unsubstituted $C_\beta$-enamine carbon into the ester group bonded to C-8 (1,6-attack) and loss of diphenylsilicon oxide accounts well for the formation of a methyl 5-(iminobenzyl)-4-methoxypyridine-2-carboxylate **5**. The 2-methoxy-4-methoxycarbonyl regioisomeric structure **7** (Scheme 3), which would result from addition of the enamine $C_\beta$–H of **2** ($R^3$ = H)

**Table 1.** 1,3,2-Diazasilines **2** Prepared

| Product[a,b] | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | $R^6$ | Yield (%)[c] | mp[d] (°C) |
|---|---|---|---|---|---|---|---|---|
| **2a** | Ph | Ph | H | Ph | Ph | Ph | 90 | 250–253 |
| **2b** | 4-$MeC_6H_4$ | Ph | H | Ph | Ph | Ph | 81 | 230–233 |
| **2c** | 4-$MeC_6H_4$ | Ph | H | 4-$MeC_6H_4$ | Ph | Ph | 78 | 263–265 |
| **2d** | 4-$MeC_6H_4$ | Ph | H | *c*-$C_6H_{11}$ | Ph | Ph | 88 | 212–215 |
| **2e** | Ph | Ph | Me | Ph | Ph | Ph | 95 | 260–262 |
| **2f** | Ph | Ph | Me | 4-$MeC_6H_4$ | Ph | Ph | 93 | 169–171 |
| **2g** | 4-$MeC_6H_4$ | Ph | Me | Ph | Ph | Ph | 91 | 237–239 |
| **2h** | 4-$MeC_6H_4$ | Ph | Me | 4-$MeC_6H_4$ | Ph | Ph | 89 | 160–162 |
| **2i** | Ph | Ph | Me | *c*-$C_6H_{11}$ | Ph | Ph | 90 | 133–135 |
| **2j** | Ph | 4-$ClC_6H_4$ | Me | 4-$MeC_6H_4$ | Ph | Ph | 83 | 195–197 |
| **2k** | Ph | Ph | H | 4-$MeC_6H_4$ | Ph | Me | 70 | 137–140 |
| **2l** | Ph | Ph | Me | Ph | Ph | Me | 77 | 190–192 |
| **2m** | Ph | 4-$ClC_6H_4$ | Me | 4-$MeC_6H_4$ | Ph | Me | 72 | 170–173 |
| **2n** | *c*-$C_6H_{11}$ | H | H | 4-$MeC_6H_4$ | Ph | Ph | | |
| **2o** | *c*-$C_6H_{11}$ | H | H | Ph | Ph | Ph | | |
| **2p** | *c*-$C_6H_{11}$ | H | H | 4-$MeOC_6H_4$ | Ph | Ph | | |
| **2q** | *c*-$C_6H_{11}$ | H | H | 4-pyridyl | Ph | Ph | | |
| **2r** | Bu | H | H | 4-$MeC_6H_4$ | Ph | Ph | | |
| **2s** | Bu | H | H | 4-$MeOC_6H_4$ | Ph | Ph | | |

[a] No satisfactory MS spectral data and microanalyses were obtained.
[b] Compounds **2n–s** were not isolated.
[c] Yield of products isolated after washing with hexane.
[d] Recrystallization from hexane/$Et_2O$.

to the acetylenic triple bond and subsequent intramolecular insertion into the nitrogen–silicon bond, was ruled out on the basis of its alternative synthesis; thus, pyridone **8**, prepared from **1** and dimethyl acetylenedicarboxylate,[14] was *O*-methylated[15] with iodomethane/silver carbonate to give compound **7** ($R^1$ = 4-$MeC_6H_4$, $R^2$ = Ph, $R^4$ = 4-$MeC_6H_4$) which did not match the spectral data of pyridine **5c** (Scheme 3).




| 5 | $R^1$ | $R^2$ | $R^4$ | 5 | $R^1$ | $R^2$ | $R^4$ |
|---|---|---|---|---|---|---|---|
| **a** | Ph | Ph | Ph | **c** | 4-$MeC_6H_4$ | Ph | 4-$MeC_6H_4$ |
| **b** | 4-$MeC_6H_4$ | Ph | Ph | **d** | 4-$MeC_6H_4$ | Ph | *c*-$C_6H_{11}$ |

**Scheme 2**

At this point we turned our attention to the reaction of acetylenic diesters with aminoazadienes **1** in which both $C_\alpha$- and $C_\beta$-enamine carbon atoms are unsubstituted ($R^2$ = $R^3$ = H).[16] Thus, azadienes **1** were reacted with dichlorodiphenylsilane in toluene at room temperature

**Table 2.** NMR Data for 1,3,2-Diazasilines **2**

| Product | $^1H$ NMR (solvent[a]/TMS), $\delta$ | $^{13}C$ NMR (solvent[b]/TMS) $\delta$ |
|---|---|---|
| **2a** | 5.7 (s, 1H), 6.7–7.8 (m, 25$H_{arom}$) | 94.3 (d), 121.4 (d), 124.7 (d), 126.2–135.5 ($C_{arom}$), 167.5 (s), 175.2 (s) |
| **2b** | 2.1 (s, 3H), 5.8 (s, 1H), 6.8–7.3 (m, 24$H_{arom}$) | 20.7 (q), 93.4 (d), 124.0 (d), 127.5–136.4 ($C_{arom}$), 167.1 (s), 174.4 (s) |
| **2c** | 2.0 (s, 3H), 2.2 (s, 3H), 5.8 (s, 1H), 6.7–7.3 (m, 23$H_{arom}$) | 20.7 (q), 20.9 (q), 93.3 (d), 123.9 (d), 128.1–136.5 ($C_{arom}$), 141.6 (s), 166.8 (s), 174.2 (s) |
| **2d** | 0.9–2.2 (m, 10H), 2.3 (s, 3H), 3.4 (m, 1H), 5.1 (s, 1H), 6.5 (m, 2$H_{arom}$), 6.8 (m, 2$H_{arom}$), 7.1–7.9 (m, 15$H_{arom}$) | 20.5 (q), 25.7 (t), 26.1 (t), 31.2 (t), 42.2 (d), 96.1 (d), 122.4 (d), 127.7–135.1 ($C_{arom}$), 140.0 (s), 147.3 (s), 166.7 (s), 167.6 (s), 179.5 (s) |
| **2e** | 2.0 (s, 3H), 6.8–7.5 (m, 25$H_{arom}$) | 18.6 (q), 104.1 (s), 121.8 (d), 124.4 (d), 127.9–131.5 ($C_{arom}$), 135.4 (s), 135.5 (s), 140.4 (s), 166.0 (s), 176.3 (s) |
| **2f** | 2.0 (s, 3H), 2.5 (s, 3H), 6.9–8.0 (m, 24$H_{arom}$) | 18.3 (q), 21.1 (q), 102.0 (s), 122.4 (d), 127.0–135.5 ($C_{arom}$), 150.9 (s), 156.8 (s), 172.6 (s) |
| **2g** | 2.0 (s, 3H), 2.3 (s, 3H), 6.8–7.5 (m, 24$H_{arom}$) | 18.3 (q), 20.5 (q), 103.3 (s), 122.1 (d), 127.8–134.2 ($C_{arom}$), 135.6 (s), 136.0 (s), 137.8 (s), 167.0 (s), 175.5 (s) |
| **2h** | 1.9 (s, 3H), 2.0 (s, 3H), 2.1 (s, 3H), 6.6–7.5 (m, 23$H_{arom}$) | 18.9 (q), 20.5 (q), 20.9 (q), 103.3 (s), 122.6 (d), 127.4–132.7 ($C_{arom}$), 133.8 (s), 135.6 (s), 141.2 (s), 165.9 (s), 176.0 (s) |
| **2i** | 1.0–1.6 (m, 10H), 1.8 (s, 3H), 2.0 (s, 3H), 2.1 (m, 1H), 6.6–7.3 (m, 19$H_{arom}$) | 18.4 (q), 20.5 (q), 24.6 (t), 26.0 (t), 30.6 (t), 44.3 (d), 103.4 (s), 122.4 (d), 127.4–134.0 ($C_{arom}$), 136.5 (s), 138.0 (s), 164.1 (s), 184.1 (s) |
| **2j** | 1.9 (s, 3H), 2.1 (s, 3H), 6.7–7.5 (m, 23$H_{arom}$) | 18.6 (q), 21.0 (q), 103.5 (s), 122.0 (d), 124.1 (d), 127.6–135.3 ($C_{arom}$), 136.7 (s), 141.2 (s), 164.3 (s), 174.0 (s) |
| **2k** | 1.1 (s, 3H), 2.4 (s, 3H), 6.3 (s, 1H), 6.8–8.3 (m, 19$H_{arom}$) | 4.1 (q), 21.4 (q), 100.3 (d), 127.4–133.6 ($C_{arom}$), 135.5 (s), 140.0 (s), 145.0 (s), 168.9 (s), 170.3 (s) |
| **2l** | 1.0 (s, 3H), 1.7 (s, 3H), 6.7–7.8 (m, 20$H_{arom}$) | 4.5 (q), 18.8 (q), 105.1 (s), 122.0 (d), 124.6 (d), 127.1–134.6 ($C_{arom}$), 139.5 (s), 169.8 (s), 174.6 (s) |
| **2m** | 0.8 (s, 3H), 1.7 (s, 3H), 2.3 (s, 3H), 6.7–7.8 (m, 18$H_{arom}$) | 4.2 (q), 19.3 (q), 20.9 (q), 109.4 (s), 122.7 (d), 124.9 (d), 126.8–134.7 ($C_{arom}$), 137.3 (s), 139.7 (s), 141.9 (s), 156.9 (s), 178.2 (s) |

[a] The solvents used were: $CDCl_3$ for **2d, f, i, k, l, m**; DMSO-$d_6$ for **2a, b, c, e, g, h, j**.
[b] The solvents used were: $CDCl_3$ for **2d, i, k, l, m**; DMSO-$d_6$ for **2a, b, c, e, f, g, h, j**.

to produce diazasilines **2n–s** which were not isolated; their toluene solutions were then heated with alkyl acetylenedicarboxylates at 60°C to give, after acidic work-up, the silicon substituted fused heterocycles **10**. Although compounds **10** were characterized spectroscopically (see experimental section) they were weakly stable and were therefore, without purification, subjected to protodesilylation with trifluoroacetic acid[17] to yield furodiazepinones **11** in moderate to good overall yield from

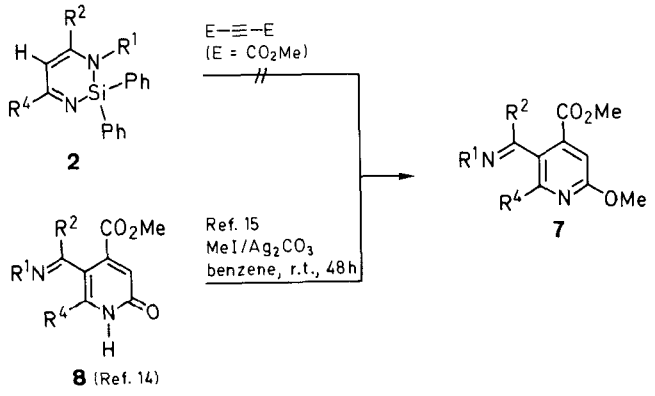
**Table 3.** Pyridines **5** Prepared

| Product | Yield (%)[a] | mp[b] (°C) | Molecular Formula[c] | IR (KBr) $\nu$ ($cm^{-1}$) | MS (70 eV) $m/z$ (%) |
|---|---|---|---|---|---|
| **5a** | 72 | 165–167 | $C_{27}H_{22}N_2O_3$ (422.5) | 1724, 1660 | 422 ($M^+$, 100), 421 (60), 391 (40), 119 (35), 77 (34) |
| **5b** | 69 | 135–137 | $C_{28}H_{24}N_2O_3$ (436.5) | 1720, 1670 | 436 ($M^+$, 100), 453 (46), 405 (30), 377 (22), 133 (20) |
| **5c** | 76 | 147–148 | $C_{29}H_{26}N_2O_3$ (450.5) | 1720, 1670 | 450 ($M^+$, 100), 449 (50), 419 (29), 391 (24), 133 (20) |
| **5d** | 80 | 181–182 | $C_{28}H_{30}N_2O_3$ (442.6) | 1730, 1680 | 442 ($M^+$, 47), 427 (100), 355 (26), 91 (28) |

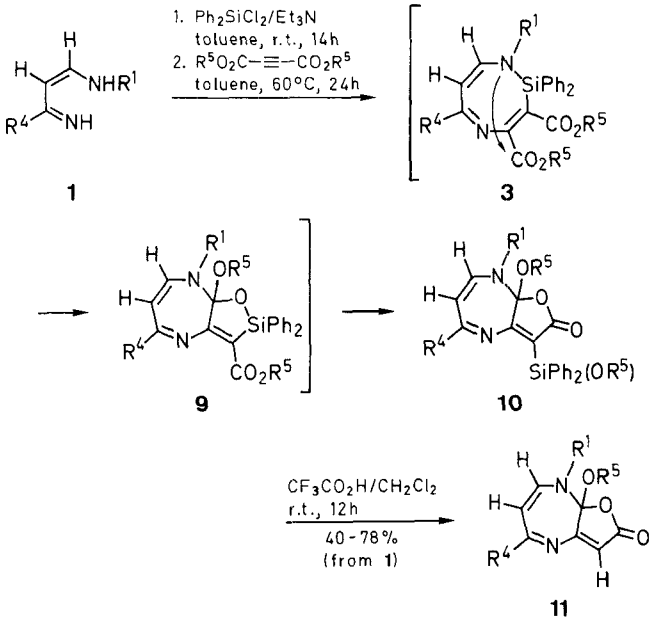
[a] Yield of products isolated after column chromatography.
[b] Recrystallization from hexane/$CHCl_3$.
[c] Satisfactory microanalyses obtained: C ±0.38, H ±0.19, N ±0.23.

**Table 4.** NMR Data for Pyridines **5**

| Product | $^1$H NMR ($CDCl_3$/TMS) $\delta$ | $^{13}$C NMR ($CDCl_3$/TMS) $\delta$ |
|---|---|---|
| **5a** | 3.6 (s, 3H), 3.9 (s, 3H), 6.7–7.6 (m, 16$H_{arom}$) | 52.0 (q), 54.1 (q), 121.0 (d), 121.6 (d), 122.6 (d), 127.0–129.5 ($C_{arom}$), 137.5 (s), 137.9 (s), 147.8 (s), 149.9 (s), 157.2 (s), 157.6 (s), 167.2 (s) |
| **5b** | 2.1 (s, 3H), 3.6 (s, 3H), 4.0 (s, 3H), 6.7–7.7 (m, 15$H_{arom}$) | 20.5 (q), 52.1 (q), 54.0 (q), 120.9 (d), 121.5 (d), 127.1–129.9 ($C_{arom}$), 130.2 (s), 131.8 (s), 134.1 (s), 137.5 (s), 137.9 (s), 145.1 (s), 150.2 (s), 157.2 (s), 157.4 (s), 167.2 (s) |
| **5c** | 2.1 (s, 3H), 2.3 (s, 3H), 3.6 (s, 3H), 4.0 (s, 3H), 6.8–7.6 (m, 14$H_{arom}$) | 20.4 (q), 20.9 (q), 51.9 (q), 53.9 (q), 120.4 (d), 121.4 (d), 125.9–129.1 ($C_{arom}$), 131.3 (s), 134.1 (s), 134.3 (s), 138.0 (s), 139.6 (s), 145.1 (s), 149.7 (s), 150.1 (s), 157.1 (s), 157.5 (s), 167.2 (s) |
| **5d** | 1.1–1.8 (m, 10H), 2.2 (s, 3H), 2.7 (m, 1H), 3.6 (s, 3H), 4.0 (s, 3H), 6.7–7.5 (m, 10$H_{arom}$) | 20.6 (q), 25.7 (t), 26.2 (t), 32.1 (t), 45.8 (d), 52.1 (q), 54.1 (q), 121.7 (d), 127.7–130.3 ($C_{arom}$), 131.8 (s), 134.3 (s), 138.3 (s), 145.1 (s), 149.2 (s), 167.1 (s) |




**Scheme 3**




| **11** | $R^1$ | $R^4$ | $R^5$ | **11** | $R^1$ | $R^4$ | $R^5$ |
|---|---|---|---|---|---|---|---|
| **a** | $c$-$C_6H_{11}$ | 4-$MeC_6H_4$ | Me | **f** | $c$-$C_6H_{11}$ | Ph | Me |
| **b** | Bu | 4-$MeC_6H_4$ | Me | **g** | $c$-$C_6H_{11}$ | 4-pyridyl | Me |
| **c** | $c$-$C_6H_{11}$ | 4-$MeOC_6H_4$ | Me | **h** | $c$-$C_6H_{11}$ | 4-$MeC_6H_4$ | Et |
| **d** | Bu | 4-$MeOC_6H_4$ | Me | **i** | $c$-$C_6H_{11}$ | Ph | Et |
| **e** | $c$-$C_6H_{11}$ | 4-$MeOC_6H_4$ | Et | | | | |

**Scheme 4**

**Table 5.** Furodiazepines **11** Prepared

| Product | Yield (%)[a] | mp[b] (°C) | Molecular Formula[c] | IR (KBr)[d] $\nu$ ($cm^{-1}$) | MS (70 eV) $m/z$ (%) |
|---|---|---|---|---|---|
| **11a** | 75 | 145–147 | $C_{21}H_{24}N_2O_3$ (352.2) | 1762, 1635 | 352 ($M^+$, 5), 293 (95), 211 (63), 115 (47), 55 (100), 41 (56) |
| **11b** | 72 | oil | $C_{19}H_{22}N_2O_3$ (326.2) | 1767, 1626 | – |
| **11c** | 72 | 164–166 | $C_{21}H_{24}N_2O_4$ (368.2) | 1750, 1620, 1605 | 368 ($M^+$, 7), 309 (100), 227 (64), 55 (24) |
| **11d** | 74 | oil | $C_{19}H_{22}N_2O_4$ (342.2) | 1762, 1626, 1602 | – |
| **11e** | 66 | 114–116 | $C_{22}H_{26}N_2O_4$ (382.2) | 1750, 1620, 1600 | 382 ($M^+$, 5), 309 (100), 227 (65), 55 (19) |
| **11f** | 73 | 144–146 | $C_{20}H_{22}N_2O_3$ (338.2) | 1760, 1620 | 338 ($M^+$, 7), 279 (100), 197 (34), 55 (23) |
| **11g** | 40 | 164–166 | $C_{19}H_{21}N_3O_3$ (339.2) | 1760, 1625 | 339 ($M^+$, 5), 280 (100), 198 (85), 156 (30), 55 (38) |
| **11h** | 70 | 108–110 | $C_{22}H_{26}N_2O_3$ (366.2) | 1745, 1610 | 366 ($M^+$, 4), 293 (100), 211 (68), 115 (19), 55 (24) |
| **11i** | 78 | 115–117 | $C_{21}H_{24}N_2O_3$ (352.2) | 1750, 1620 | 352 ($M^+$, 5), 279 (100), 197 (54), 103 (22), 55 (76), 41 (73) |

[a] Yields of products isolated after column chromatography.
[b] Recrystallization from hexane/$CHCl_3$.
[c] Satisfactory microanalyses obtained: C ±0.32, H ±0.15, N ±0.18
[d] IR of compounds **11b, d** were recorded on neat samples.

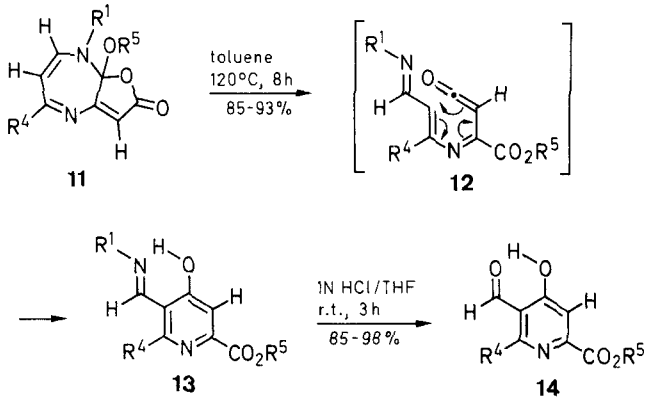
**Table 6.** NMR Data for Furodiazepines **11**

| Product | $^1$H NMR ($CDCl_3$/TMS) $\delta$, $J$ (Hz) | $^{13}$C NMR ($CDCl_3$/TMS) $\delta$ |
|---|---|---|
| **11a** | 1.1–1.9 (m, 9H), 2.2 (m, 1H), 2.4 (s, 3H), 3.2 (s, 3H), 4.1 (m, 1H), 5.6 (s, 1H), 5.7 (d, 1H, $J$ = 9.9), 6.8 (d, 1H, $J$ = 9.9), 7.2 (d, 2H, $J$ = 8.1), 7.8 (d, 2H, $J$ = 8.1) | 21.5 (q), 25.1 (t), 25.6 (t), 26.0 (t), 33.3 (t), 34.3 (t), 49.4 (d), 60.2 (q), 95.3 (d), 100.8 (d), 108.0 (s), 128.1 (d), 129.0 (d), 136.6 (s), 140.2 (d), 141.2 (s), 161.2 (s), 165.6 (s), 168.9 (s) |
| **11b** | 0.9 (t, 3H, $J$ = 7.3), 1.3 (m, 2H), 1.6 (m, 2H), 2.4 (s, 3H), 3.2 (s, 3H), 3.6 (m, 1H), 3.8 (m, 1H), 5.6 (s, 1H), 5.7 (d, 1H, $J$ = 9.6), 6.7 (d, 1H, $J$ = 9.6), 7.2 (d, 2H, $J$ = 8.1), 7.8 (d, 2H, $J$ = 8.1) | 13.5 (q), 19.6 (t), 21.2 (q), 32.7 (t), 49.4 (q), 54.0 (t), 95.5 (d), 100.0 (d), 107.1 (s), 128.0 (d), 129.0 (d), 136.7 (s), 141.2 (s), 144.1 (d), 160.6 (s), 165.8 (s), 169.0 (s) |
| **11c** | 1.1–1.9 (m, 9H), 2.2 (m, 1H), 3.2 (s, 3H), 3.9 (s, 3H), 4.1 (m, 1H), 5.6 (s, 1H), 5.7 (d, 1H, $J$ = 9.9), 6.8 (d, 1H, $J$ = 9.9), 6.9 (d, 2H, $J$ = 8.8), 7.9 (d, 2H, $J$ = 8.8) | 25.2 (t), 25.6 (t), 26.1 (t), 33.3 (t), 34.3 (t), 49.4 (d), 55.3 (q), 60.2 (q), 95.0 (d), 100.4 (d), 108.1 (s), 113.6 (d), 129.9 (d), 131.7 (s), 140.1 (d), 161.0 (s), 161.9 (s), 164.9 (s), 169.0 (s) |
| **11d** | 0.9 (t, 3H, $J$ = 7.4), 1.3 (m, 2H), 1.6 (m, 2H), 3.2 (s, 3H), 3.6 (m, 1H), 3.8 (m, 1H), 3.9 (s, 3H), 5.6 (s, 1H), 5.7 (d, 1H, $J$ = 9.6), 6.6 (d, 1H, $J$ = 9.6), 6.9 (d, 2H, $J$ = 9.0), 7.9 (d, 2H, $J$ = 9.0) | 13.5 (q), 19.6 (t), 32.7 (t), 49.4 (q), 53.9 (t), 55.2 (q), 95.2 (d), 99.6 (d), 107.1 (s), 113.6 (d), 129.8 (d), 131.8 (s), 143.8 (d), 160.7 (s), 162.0 (s), 165.1 (s), 169.1 (s) |
| **11e** | 1.1 (t, 3H, $J$ = 7.0), 1.3–1.9 (m, 9H), 2.2 (m, 1H), 3.5 (q, 2H, $J$ = 7.0), 3.9 (s, 3H), 4.1 (m, 1H), 5.6 (s, 1H), 5.7 (d, 1H, $J$ = 9.9), 6.8 (d, 1H, $J$ = 9.9), 6.9 (d, 2H, $J$ = 9.0), 7.9 (d, 2H, $J$ = 9.0) | 14.7 (q), 25.1 (t), 25.6 (t), 26.0 (t), 33.3 (t), 34.2 (t), 55.3 (q), 58.2 (t), 60.2 (d), 95.0 (d), 100.0 (d), 107.8 (s), 113.6 (d), 129.8 (d), 131.8 (s), 140.2 (d), 161.8 (s), 164.9 (s), 169.1 (s) |
| **11f** | 1.1–1.9 (m, 9H), 2.2 (m, 1H), 3.2 (s, 3H), 4.1 (m, 1H), 5.65 (s, 1H), 5.7 (d, 1H, $J$ = 9.9), 6.8 (d, 1H, $J$ = 9.9), 7.4 (m, 3H), 7.9 (m, 2H) | 25.1 (t), 25.5 (t), 26.0 (t), 33.3 (t), 34.3 (t), 49.4 (q), 60.3 (d), 95.4 (d), 101.2 (d), 108.0 (s), 128.0 (d), 128.3 (d), 130.7 (d), 139.3 (s), 140.4 (d), 161.0 (s), 165.8 (s), 168.7 (s) |
| **11g** | 1.1–1.9 (m, 9H), 2.1 (m, 1H), 3.2 (s, 3H), 4.1 (m, 1H), 5.7 (d, 1H, $J$ = 9.7), 5.75 (s, 1H), 6.9 (d, 1H, $J$ = 9.7), 7.7 (d, 2H, $J$ = 6.1), 8.7 (d, 2H, $J$ = 6.1) | 24.9 (t), 25.4 (t), 25.9 (t), 33.3 (t), 34.1 (t), 49.3 (q), 60.7 (d), 94.6 (d), 102.1 (d), 107.8 (s), 121.6 (d), 141.4 (d), 146.2 (s), 150.0 (d), 160.4 (s), 163.3 (s), 168.0 (s) |
| **11h** | 1.0 (t, 3H, $J$ = 7.0), 1.2–1.9 (m, 9H), 2.2 (m, 1H), 2.4 (s, 3H), 3.5 (q, 2H, $J$ = 7.0), 4.1 (m, 1H), 5.6 (s, 1H), 5.7 (d, 1H, $J$ = 9.7), 6.8 (d, 1H, $J$ = 9.7), 7.2 (d, 2H, $J$ = 8.1), 7.8 (d, 2H, $J$ = 8.1) | 14.5 (q), 21.0 (q), 25.0 (t), 25.3 (t), 25.9 (t), 33.2 (t), 34.1 (t), 58.1 (t), 60.5 (d), 95.2 (d), 100.5 (d), 108.3 (s), 128.1 (d), 129.2 (d), 137.6 (s), 141.4 (d), 141.8 (s), 162.0 (s), 166.1 (s), 169.4 (s) |
| **11i** | 1.0 (t, 3H, $J$ = 7.0), 1.2–1.9 (m, 9H), 2.2 (m, 1H), 3.5 (q, 2H, $J$ = 7.0), 4.1 (m, 1H), 5.6 (s, 1H), 5.7 (d, 1H, $J$ = 9.6), 6.8 (d, 1H, $J$ = 9.6), 7.4 (m, 3H), 7.9 (m, 2H) | 14.7 (q), 25.1 (t), 25.6 (t), 26.0 (t), 33.3 (t), 34.2 (t), 58.2 (t), 60.4 (d), 95.5 (d), 100.7 (d), 107.7 (s), 127.9 (d), 128.3 (d), 130.6 (d), 139.5 (s), 140.5 (d), 161.6 (s), 165.9 (s), 168.9 (s) |

azadienes **1** (Scheme 4, Table 5). In the formation of heterocycles **10**, rearrangement of the intermediate **3** must involve nucleophilic attack of the enamine nitrogen on the carbonyl carbon attached to the $C_\beta$-vinylsilane carbon C-4 (1,5-attack) to give the intermediate **9**; subsequent lactone formation and silicon group removal would account for the process.

Then the thermal behavior of fused diazepines **11** was studied and found that an unusual carbon–carbon bond formation took place; thus, heating a deoxygenated toluene solution of **11** at 120 °C in a sealed tube led to $C_2$–$C_6$ bond formation to give highly functionalized pyridine-2-carboxylates **13** in yields higher than 85%. Compounds **13** were in turn hydrolyzed to 5-formylpyridine-2-carboxylates **14** (Scheme 5, Table 7).[18] One way to explain this thermal **11** → **13** conversion could be by assuming two pericyclic processes; thus, an [8 + 2]-cycloreversion of **11** would give rise to the ketene intermediate **12**, which would undergo electrocyclic ring closure and tautomerization to pyridine **13**.

In summary, the reaction of diazasilines **2** ($R^3$ = H) with dimethyl acetylenedicarboxylate represents a very short, high yield procedure for preparing multifunctionalized pyridines **5** from [3 + 3] atom fragments;[19] it must be pointed out that the regioisomeric pyridines **7** can be synthesized from azadienes **1** themselves.[14] Compounds **11**, which can be regarded as 1,4-diazepines with a fused butenolide ring, are members of a class of heterocycles which has not been previously described, to the best of our knowledge. 1,4-Benzodiazepines have




| 13 | $R^1$ | $R^4$ | $R^5$ | 14 | $R^4$ | $R^5$ |
|---|---|---|---|---|---|---|
| **a** | *c*-$C_6H_{11}$ | 4-$MeC_6H_4$ | Me | **a** | 4-$MeC_6H_4$ | Me |
| **b** | Bu | 4-$MeC_6H_4$ | Me | **b** | 4-$MeOC_6H_4$ | Me |
| **c** | *c*-$C_6H_{11}$ | 4-$MeOC_6H_4$ | Me | **c** | 4-$MeOC_6H_4$ | Et |
| **d** | Bu | 4-$MeOC_6H_4$ | Me | **d** | Ph | Me |
| **e** | *c*-$C_6H_{11}$ | 4-$MeOC_6H_4$ | Et | **e** | Ph | Et |
| **f** | *c*-$C_6H_{11}$ | Ph | Me | | | |

***Scheme 5***

been studied intensively, but recent attention has concentrated on the synthesis of analogues having heterocycles in place of the benzene ring because of their biological and pharmacological properties.[20] Our approach starts with the easily available azadienes **1** ($R^2$ = $R^3$ = H) and provides an efficient, simple entry to furo[2,3-*b*]diazepines. Lastly, it is remarkable that simply by

**Table 7.** Pyridines **13** and **14** Prepared

| Product | Yield (%)[a] | mp[b] (°C) | Molecular Formula[c] | IR (KBr) $\nu$ ($cm^{-1}$) | MS (70 eV) $m/z$ (%) |
|---|---|---|---|---|---|
| **13a** | 93 | 137–139 | $C_{21}H_{24}N_2O_3$ (352.2) | 3440, 1730, 1625 | 352 ($M^+$, 34), 351 (100), 269 (41), 55 (66) |
| **13b** | 91 | 91–93 | $C_{19}H_{22}N_2O_3$ (326.2) | 3440, 1735, 1620 | – |
| **13c** | 91 | 179–181 | $C_{21}H_{24}N_2O_4$ (368.2) | 3440, 1732, 1628 | 368 ($M^+$, 30), 367 (100), 285 (46) |
| **13d** | 88 | 113–115 | $C_{19}H_{22}N_2O_4$ (342.2) | 3440, 1734, 1630 | – |
| **13e** | 89 | 106–108 | $C_{22}H_{26}N_2O_4$ (382.2) | 3440, 1722, 1638 | 382 ($M^+$, 29), 381 (86), 310 (100), 55 (31) |
| **13f** | 85 | 140–142 | $C_{20}H_{22}N_2O_3$ (338.2) | 3440, 1738, 1635 | 338 ($M^+$, 40), 337 (100), 280 (30), 255 (62), 55 (32) |
| **14a** | 98 | 141–142 | $C_{15}H_{13}NO_4$ (271.1) | 3450, 1753, 1647 | 271 ($M^+$, 29), 213 (44), 185 (100), 91 (59) |
| **14b** | 95 | 141–143 | $C_{15}H_{13}NO_5$ (287.1) | 3470, 1748, 1642 | – |
| **14c** | 93 | 124–126 | $C_{16}H_{15}NO_5$ (301.1) | 3440, 1734, 1637 | – |
| **14d** | 95 | 164–166 | $C_{14}H_{11}NO_4$ (257.1) | 3420, 1720, 1661 | – |
| **14e** | 85[d] | 119–121 | $C_{15}H_{13}NO_4$ (271.1) | 3450, 1737, 1636 | – |

[a] Yields of products isolated after column chromatography (compounds **13**) or after washing with hexane (compounds **14**).
[b] Recrystallization from hexane/$CHCl_3$.
[c] Satisfactory microanalyses obtained: C ±0.35, H ±0.22, N ±0.20.
[d] Overall yield from **11i**.

using appropriately substituted 4-amino-1-azabutadienes **1**, this reaction enables us to obtain selectively six-, seven-, or eight-membered heterocycles.

All reactions were run under $N_2$ atmosphere. IR spectra were recorded on a Pye-Unicam or a Perkin-Elmer 1720-X infrared spectrophotometer. NMR spectra were recorded with Varian FT-80A and Bruker AC 300 instruments (solutions in $CDCl_3$ unless otherwise stated, TMS as reference). Mass spectra were obtained using a Hewlett-Packard 5930 A spectrometer (EI: 70 eV). Melting points were determined with a Büchi-Tottoli apparatus and are uncorrected. Microanalyses were obtained using a Perkin-Elmer 240 B analyser.

**1,2-Dihydro-1,3,2-diazasilines 2; General Procedure:**
To a solution of **1**[21] (5 mmol) and $Et_3N$ (1.21 g, 12 mmol) in toluene (40 mL) was slowly added a solution of substituted dichlorosilane (6 mmol) in toluene (20 mL). The mixture was stirred overnight (14 h) at r.t. and then the salt was filtered off. The solvent was removed at reduced pressure to give a yellow solid which was washed with hexane (yield: 70–95%) and recrystallized from hexane/$Et_2O$ (Table 1).

**Methyl 5-[α-(Arylimino)benzyl]-4-methoxypyridine-2-carboxylates 5; General Procedure:**
To a solution of **1** ($R^3$ = H) (5 mmol) and $Et_3N$ (1.21 g, 12 mmol) in toluene (40 mL) was slowly added at solution of dichlorodiphenylsilane (1.52 g, 6 mmol) in toluene (20 mL). The mixture was stirred overnight (14 h) at r.t. and the salt was filtered off. The filtrate was heated with dimethyl acetylenedicarboxylate (0.85 g, 6 mmol) at 60 °C for 24 h. Then, the resulting mixture was cooled back, poured into ice-cooled 2N $H_2SO_4$ (40 mL) and extracted with $Et_2O$ (3 × 20 mL); the organic layer was washed with $H_2O$ (2 × 15 mL) and dried ($Na_2SO_4$). The solvents were evaporated at reduced pressure and the residue purified by chromatography on silica gel, using toluene/$Et_2O$ (2:1) (yield: 69–80%). Analytical samples were obtained by recrystallization from hexane/$CHCl_3$ (Table 3).

**Methyl 5-Benzoyl-4-methoxy-6-(4-methylphenyl)pyridine-2-carboxylate (6):**
A solution of pyridine **5c** (0.45 g, 1 mmol) in acetone (5 mL) was stirred with 1N HCl (5 mL) at r.t. for 4 h. Then $H_2O$ (10 mL) was added, the resulting mixture extracted with $CH_2Cl_2$ (3 × 15 mL) and dried ($Na_2SO_4$). Removal of the solvents at reduced pressure gave **6** as a pure solid (0.329 g, yield: 91%), which was recrystallized from hexane/$CHCl_3$; mp 107–109 °C.

$C_{22}H_{19}NO_4$ (361.4) calc. C 73.12 H 5.30 N 3.87
found 73.39 5.47 3.95

IR (KBr): $\nu$ = 1725 $cm^{-1}$.

$^1H$ NMR: $\delta$ = 2.2 (s, 3H), 3.6 (s, 3H), 3.9 (s, 3H), 7.1 (d, 2H, $J$ = 12.5 Hz), 7.4 (m, 5H), 7.8 (s, 1H), 7.9 (d, 2H, $J$ = 7.9 Hz).

$^{13}C$ NMR: $\delta$ = 21.3 (q), 52.5 (q), 53.1 (q), 123.2 (d),127.1 (d), 128.0 (d), 128.2 (s), 128.6 (d), 128.9 (d), 129.6 (d), 134.7 (s), 137.3 (s), 140.1 (s), 146.1 (s), 149.8 (s), 157.8 (s), 165.7 (s), 167.8 (s).

MS: $m/z$ = 361 ($M^+$, 41), 302 (15), 245 (100), 149 (12).

**8,8a-Dihydro-2*H*-furo[2,3-*b*][1,4]diazepin-2-ones 10 and 11; General Procedure:**
To a solution of **1** ($R^2$ = $R^3$ = H) (5 mmol) and $Et_3N$ (1.21 g, 12 mmol) in toluene (40 mL) was slowly added a solution of dichlorodiphenylsilane (1.51 g, 6 mmol) in toluene (20 mL). The mixture was stirred overnight (14 h) at r.t. and the salt was filtered off. The filtrate was heated with the acetylenedicarboxylate (6 mmol) at 60 °C for 24 h. Then, the resulting mixture was cooled back, poured into ice-cooled 2N $H_2SO_4$ (40 mL) and extracted with $Et_2O$ (3 × 20 mL); the organic layer was washed with $H_2O$ (2 × 15 mL) and dried ($Na_2SO_4$). The solvents were evaporated at reduced pressure to give **10** as an unstable orange solid. Spectral analyses were taken on compound **10** ($R^1$ = $c$-$C_6H_{11}$; $R^4$ = 4-$MeC_6H_4$; $R^5$ = Me):

$^1H$ NMR: $\delta$ = 1.1–2.2 (m, 10H), 2.3 (s, 3H), 3.2 (s, 3H), 3.7 (s, 3H), 4.1 (m, 1H), 5.7 (d, 1H, $J$ = 9.8 Hz), 6.9 (d, 1H, $J$ = 9.8 Hz), 7.0–7.8 (m, 14 $H_{arom}$).

$^{13}C$ NMR: $\delta$ = 21.3 (q), 25.2 (t), 25.6 (t), 26.0 (t), 33.4 (t), 34.2 (t), 49.4 (q), 52.0 (q), 60.3 (d), 95.6 (d), 100.7 (s), 107.9 (s), 127.6 (d), 127.7 (d), 128.1 (d), 128.5 (d), 128.7 (d), 129.2 (d), 129.8 (d), 129.9 (d), 133.8 (s), 134.1 (s), 134.5 (d), 134.9 (d), 135.1 (d), 136.3 (s), 140.4 (d), 164.1 (s), 166.0 (s), 168.4 (s), 171.3 (s).

MS: $m/z$ = 564 ($M^+$, 4), 487 (70), 390 (28), 55 (100).

The crude compounds **10** obtained above were treated with $CF_3CO_2H$ (0.6 mL, 7.8 mmol) in $CH_2Cl_2$ at r.t. for 12 h. The resulting mixture was diluted with $H_2O$ (20 mL), extracted with $CH_2Cl_2$ (3 × 20 mL) and dried ($Na_2SO_4$). The organic layer was evaporated under reduced pressure and the residue subjected to chromatography on silical gel, using hexane/EtOAc (4:1) (overall yield from **1**: 40–78%). Analytical samples were obtained by recrystallization from hexane/$CHCl_3$ (Table 5).

**Alkyl 4-Hydroxy-5-(iminomethyl)pyridine-2-carboxylates 13; General Procedure:**
A deoxygenated solution of diazepine **11** (0.5 mmol) in toluene (5 mL) was heated in a sealed tube at 120 °C for 8 h. Then, toluene was removed under vacuum and the resulting crude chromatographed on silica gel, using hexane/EtOAc (2:1) to furnish pyridine **13** (yield: 85–93%). Analytical samples were obtained by recrystallization from hexane/$CHCl_3$ (Table 7).

**Alkyl 5-Formyl-4-hydroxypyridine-2-carboxylates 14 by Hydrolysis of 13; General Procedure:**
A solution of **13** (0.5 mmol) in THF (20 mL) was stirred with 1N HCl (2 mL) at r.t. for 3 h. Then $H_2O$ (10 mL) was added, the resulting mixture extracted with $CH_2Cl_2$ (3 × 15 mL) and dried ($Na_2SO_4$). Removal of the solvents at reduced pressure gave

**Table 8.** NMR Data for Pyridines **13** and **14**

| Product | $^1$H NMR ($CDCl_3$/TMS) $\delta$, $J$ (Hz) | $^{13}$C NMR ($CDCl_3$/TMS) $\delta$ |
|---|---|---|
| **13a** | 1.2–1.9 (m, 10H), 2.3 (s, 3H), 3.3 (m, 1H), 3.9 (s, 3H), 7.2 (d, 2H, $J$ = 7.9), 7.4 (d, 2H, $J$ = 7.9), 7.5 (s, 1H), 8.3 (s, 1H), 15.8 (br s, OH) | 21.0 (q), 23.8 (t), 24.8 (t), 33.2 (t), 52.6 (q), 63.2 (d), 113.4 (s), 116.3 (d), 128.9 (d), 129.6 (d), 134.8 (s), 138.9 (s), 149.0 (s), 162.0 (d), 163.8 (s), 165.9 (s), 175.4 (s) |
| **13b** | 0.9 (t, 3H, $J$ = 7.3), 1.4 (m, 2H), 1.7 (m, 2H), 2.4 (s, 3H), 3.5 (t, 2H, $J$ = 6.9), 3.9 (s, 3H), 7.2 (d, 2H, $J$ = 8.0), 7.4 (d, 2H, $J$ = 8.0), 7.5 (s, 1H), 8.3 (s, 1H), 15.3 (br s, OH) | 13.4 (q), 19.8 (t), 21.2 (q), 32.0 (t), 52.8 (q), 55.2 (t), 113.6 (s), 116.1 (d), 129.0 (d), 129.7 (d), 135.9 (s), 139.1 (s), 149.2 (s), 163.7 (s), 164.2 (d), 166.0 (s), 175.0 (s) |
| **13c** | 1.2–1.9 (m, 10H), 3.3 (m, 1H), 3.9 (s, 3H), 4.0 (s, 3H), 7.0 (d, 2H, $J$ = 8.8), 7.5 (d, 2H, $J$ = 8.8), 7.5 (s, 1H), 8.4 (s, 1H), 15.5 (br s, OH) | 23.7 (t), 24.7 (t), 33.1 (t), 52.4 (q), 55.0 (q), 63.0 (d), 113.2 (s), 113.6 (d), 116.0 (d), 130.1 (s), 131.0 (d), 148.9 (s), 160.1 (s), 161.9 (d), 163.3 (s), 165.8 (s), 175.5 (s) |
| **13d** | 1.0 (t, 3H, $J$ = 7.3), 1.4 (m, 2H), 1.7 (m, 2H), 3.5 (t, 2H, $J$ = 6.9), 3.8 (s, 3H), 3.9 (s, 3H), 7.0 (d, 2H, $J$ = 8.5), 7.45 (d, 2H, $J$ = 8.5), 7.5 (s, 1H), 8.3 (s, 1H), 15.6 (br s, OH) | 13.4 (q), 19.8 (t), 32.0 (t), 52.7 (q), 55.2 (t), 55.3 (q), 113.5 (s), 113.8 (d), 115.9 (d), 130.3 (s), 131.2 (d), 149.2 (s), 160.4 (s), 163.4 (s), 164.2 (d), 166.0 (s), 175.1 (s) |
| **13e** | 1.2–2.0 (m, 10H), 1.4 (t, 3H, $J$ = 7.1), 3.3 (m, 1H), 3.9 (s, 3H), 4.4 (q, 2H, $J$ = 7.1), 7.0 (d, 2H, $J$ = 8.8), 7.5 (s, 1H), 7.55 (d, 2H, $J$ = 8.8), 8.4 (s, 1H), 15.1 (br s, OH) | 14.1 (q), 23.9 (t), 24.9 (t), 33.4 (t), 55.3 (q), 61.6 (t), 63.4 (d), 113.4 (s), 113.7 (d), 115.9 (d), 130.4 (s), 131.3 (d), 149.5 (s), 160.3 (s), 162.0 (d), 163.4 (s), 165.5 (s), 175.5 (s) |
| **13f** | 1.2–1.9 (m, 10H), 3.3 (m, 1H), 3.9 (s, 3H), 7.4 (m, 5H), 7.5 (s, 1H), 8.3 (s, 1H), 15.3 (br s, OH) | 23.9 (t), 24.9 (t), 33.3 (t), 52.8 (q), 63.5 (d), 113.6 (s), 116.6 (d), 128.4 (d), 129.0 (d), 129.8 (d), 137.9 (s), 149.1 (s), 161.9 (d), 163.8 (s), 166.0 (s), 175.5 (s) |
| **14a** | 2.4 (s, 3H), 4.0 (s, 3H), 7.3 (d, 2H, $J$ = 7.5), 7.5 (d, 2H, $J$ = 7.5), 7.7 (s, 1H), 10.0 (s, 1H), 12.6 (br s, OH) | 21.3 (q), 53.1 (q), 113.3 (d), 116.4 (s), 129.4 (d), 130.4 (d), 133.3 (s), 140.4 (s), 152.1 (s), 164.8 (s), 165.2 (s), 169.4 (s), 197.2 (d) |
| **14b** | 3.9 (s, 3H), 4.0 (s, 3H), 7.0 (d, 2H, $J$ = 8.6), 7.5 (d, 2H, $J$ = 8.6), 7.6 (s, 1H), 10.0 (s, 1H), 12.5 (br s, OH) | 53.0 (q), 55.3 (q), 112.7 (d), 114.1 (d), 116.1 (s), 128.5 (s), 131.9 (d), 151.9 (s), 161.2 (s), 164.6 (s), 169.3 (s), 197.0 (d) |
| **14c** | 1.4 (t, 3H, $J$ = 7.1), 3.9 (s, 3H), 4.5 (q, 2H, $J$ = 7.1), 7.0 (d, 2H, $J$ = 8.6), 7.5 (d, 2H, $J$ = 8.6), 7.6 (s, 1H), 10.0 (s, 1H), 12.3 (br s, OH) | 14.0 (q), 55.2 (q), 62.1 (t), 112.5 (d), 114.0 (d), 115.9 (s), 128.5 (s), 132.0 (d), 152.3 (s), 161.2 (s), 164.0 (s), 164.4 (s), 169.3 (s), 197.0 (d) |
| **14d** | 4.0 (s, 3H), 7.5 (m, 3H), 7.6 (m, 2H), 7.7 (s, 1H), 10.0 (s, 1H), 12.8 (br s, OH) | 53.2 (q), 113.5 (d), 119.2 (s), 128.7 (d), 130.0 (d), 130.4 (d), 136.5 (s), 152.2 (s), 164.7 (s), 165.2 (s), 169.4 (s), 197.1 (d) |
| **14e** | 1.5 (t, 3H, $J$ = 7.1), 4.5 (q, 2H, $J$ = 7.1), 7.5 (m, 3H), 7.6 (m, 2H), 7.7 (s, 1H), 10.0 (s, 1H), 12.5 (br s, OH) | 14.1 (q), 62.3 (t), 113.5 (d), 116.4 (s), 128.6 (d), 130.0 (d), 130.4 (d), 136.1 (s), 152.3 (s), 164.0 (s), 164.8 (s), 169.5 (s), 197.0 (d) |

pyridines **14** as pure solids, which were washed with hexane (yield: 85–98%) and further recrystallized from hexane/$CHCl_3$ (Table 7).

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