A Rapid Approach to 3,5-Disubstituted-1,4-Benzodiazepines via the Photo-Fries Rearrangement of Anilides

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Supplementary material

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General experimental method.

Proton (^1H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts are expressed in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^1H NMR: $\text{CDCl}_3 = 7.25$ ppm, for ^{13}C NMR: $\text{CDCl}_3 = 77.0$. Data are reported as follows: (s = singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublets; dt = doublet of triplets; b = broad). Mass spectra were recorded using an electrospray ion source (ES-MS). HPLC analysis was performed on a C-18 column (250 x 4.60mm, 5 μ , 300 Å; 250 x 10.00mm, 10 μ , 300 Å, respectively).

All the solvents are previously dried following standard procedures. Analytical TLC was performed on silica gel 60 F₂₅₄ plates. Visualization was done under UV or using a KMnO_4 alkaline solution. Flash chromatography was done using an automatic system or 60/230-400 mesh silica gel.

5 Oil. ^1H -NMR (200 MHz, 27°C, CDCl_3): δ 3.73 (s, 3H), 4.23 (s, 2H), 5.95 (bs, 1H), 6.59 (d, $J = 9.0$ Hz, 1H), 6.95 (dd, $J = 9.0$ Hz, $J = 2.6$ Hz, 1H), 7.18-7.38 (m, 6H). ^{13}C -NMR (200 MHz, 27°C, CDCl_3): δ 46.39, 55.92, 114.11, 117.17, 118.70, 123.32, 126.70, 128.55, 129.33, 135.33, 145.61, 149.87, 199.38. ESI-MS: 264 (M+Na), 242 (M+1). Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.85; H, 6.23; N, 5.82.

6 Oil. ^1H -NMR (200 MHz, 27°C, CDCl_3): δ 4.29 (s, 2H), 6.25 (bs, 2H), 6.63-6.74 (m, 2H), 7.20-

7.45 (m, 6H), 7.89 (d, $J = 8.0$ Hz, 1H). ^{13}C -NMR (200 MHz, 27°C , CDCl_3): δ 46.15, 115.79, 117.53, 117.61, 126.85, 128.70, 129.67, 131.73, 134.56, 135.68, 151.13, 200.07. ESI-MS: 234 (M+Na), 212 (M+H). Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{NO}$: C, 79.59; H, 6.20; N, 6.63. Found C, 79.70; H, 6.17; N 6.67.

7: Oil. ^1H -NMR (200 MHz, 27°C , CDCl_3): δ 0.16 (s, 6H), 1.02 (s, 9H), 4.21 (s, 2H), 6.01 (bs, 1H), 6.54 (d, $J = 8.8$ Hz, 1H), 6.87 (dd, $J = 8.8$ Hz, 2.3 Hz, 1H), 7.20-7.38 (m, 6H). ^{13}C -NMR (200 MHz, 27°C , CDCl_3): δ -4.63, 18.03, 25.62, 46.33, 117.31, 118.30, 120.79, 126.56, 127.95, 128.47, 129.16, 135.33, 144.95, 145.76, 199.26. ESI-MS: 364 (M+Na), 342 (M+H). Anal. Calcd for $\text{C}_{20}\text{H}_{27}\text{NO}_2\text{Si}$: C, 70.34; H, 7.97; N, 4.10. Found: C, 70.57; H, 7.95; N, 4.17.

8 Oil. ^1H -NMR (200 MHz, 27°C , CDCl_3): δ 0.87 (t, $J = 6.1$ Hz, 3H), 1.13-1.26 (m, 16H), 1.66-1.73 (m, 2H), 2.89 (t, $J = 7.4$ Hz, 2H), 6.27 (bs, 1H, NH_2), 6.57-6.64 (m, 2H), 7.21 (t, $J = 7.5$ Hz, 1H), 7.71 (d, 1H, $J = 7.5$ Hz, 1H). ^{13}C -NMR (200 MHz, 27°C , CDCl_3): δ 14.01, 22.59, 24.90, 29.27, 29.41, 29.46, 29.55, 31.83, 39.19, 115.53, 117.23, 117.90, 131.86, 133.92, 150.29, 202.95. ESI-MS: 298 (M+Na), 276 (M+1). Anal. Calcd for $\text{C}_{18}\text{H}_{29}\text{NO}$: C, 78.49; H, 10.61; N, 5.09. Found: C, 78.75; H, 10.53; N, 5.09.

9: Mp = 90-92°C. $^1\text{H-NMR}$ (200 MHz, 27°C, CDCl_3): δ 1.38 (s, 9H), 3.75 (s, 3H), 4.24 (s, 2H), 4.24-4.34 (m, 1H), 5.21 (d, 6.6 Hz, 1H), 7.05 (dd, $J = 9.1$ Hz, $J = 2.6$ Hz, 1H), 7.18-7.30 (m, 5H), 7.45 (d, $J = 2.6$ Hz, 1H), 8.66 (d, $J = 9.1$ Hz, 1H), 11.73 (bs, 1H). $^{13}\text{C-NMR}$ (200 MHz, 27°C, CDCl_3): δ 18.74, 28.16, 46.76, 51.44, 55.51, 79.83, 116.11, 120.08, 122.24, 122.57, 126.94, 128.59, 129.29, 134.10, 134.29, 154.29, 155.03, 171.80, 201.22. ESI-MS: 451 (M+K), 435 (M+Na). Anal. Calcd for $\text{C}_{23}\text{H}_{28}\text{N}_2\text{O}_5$: C, 66.97; H, 6.84; N, 6.79. Found: C, 67.37; H, 6.76; N, 6.70;

10: Oil. $^1\text{H-NMR}$ (200 MHz, 27°C, CDCl_3): δ 1.36 (s, 9H), 3.09-3.29 (d, $J = 5.8$ Hz, 2H), 4.25 (s, 2H), 4.10-4.20 (m, 1H), 5.18 (d, $J = 7.5$ Hz, 1H), 7.10-7.45 (m, 11H), 7.51 (t, $J = 8.5$ Hz, 1H), 7.97 (d, $J = 7.8$ Hz, 1H), 8.79 (d, $J = 8.5$ Hz, 1H), 12.06 (bs, 1H). $^{13}\text{C-NMR}$ (200 MHz, 27°C, CDCl_3): δ 28.14, 38.35, 46.54, 58.00, 77.99, 120.83, 121.55, 122.63, 126.76, 126.91, 128.44, 128.50, 128.55, 129.19, 129.35, 134.21, 134.88, 136.35, 140.67, 155.06, 171.03, 201.40. ESI-MS: 481 (M+Na). Anal. Calcd for $\text{C}_{28}\text{H}_{30}\text{N}_2\text{O}_4$: C, 73.34; H, 6.59; N, 6.11. Found: C, 74.11; H, 6.42; N, 6.08.

11: Oil. $^1\text{H-NMR}$ (200 MHz, 27°C , CDCl_3): δ 0.88 (d, $J = 6.7$ Hz, 3H), 0.98 (d, $J = 6.8$ Hz, 3H), 1.38 (s, 9H), 2.25-2.40 (m, 1H), 4.12-4.25 (m, 1H), 4.28 (s, 2H), 5.20 (d, $J = 8.4$ Hz, 1H), 7.08 (t, $J = 7.7$ Hz, 1H), 7.18-7.36 (m, 5H), 7.49 (t, $J = 7.8$ Hz, 1H), 7.99 (d, $J = 8.0$ Hz, 1H), 8.75 (d, $J = 8.2$ Hz, 1H), 12.00 (bs, 1H). $^{13}\text{C-NMR}$ (200 MHz, 27°C , CDCl_3): δ 17.33, 19.26, 28.16, 30.83, 46.61, 60.96, 79.80, 120.87, 121.59, 122.55, 126.91, 128.49, 129.31, 131.11, 134.16, 134.88, 140.71, 155.66, 171.32, 201.69. ESI-MS: 433 (M+Na). Anal. Calcd for $\text{C}_{24}\text{H}_{30}\text{N}_2\text{O}_4$: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.92; H, 7.65; N, 6.73.

12: Oil. $^1\text{H-NMR}$ (200 MHz, 27°C , CDCl_3): δ 0.11 (s, 6H), 0.94 (s, 9H), 1.37 (s, 9H), 1.40 (d, $J = 7.4$ Hz, 3H), 4.20 (s, 2H), 4.20-4.30 (m, 1H), 5.22-5.3 (m, 1H), 6.99 (dd, $J = 9.1$ Hz, 2.7 Hz, 1H), 7.15-7.31 (m, 6H), 8.61 (d, $J = 9.1$ Hz, 1H), 11.78 (bs, 1H). $^{13}\text{C-NMR}$ (200 MHz, 27°C , CDCl_3): δ 4.69, 18.00, 18.64, 25.48, 28.13, 46.81, 51.41, 79.70, 121.82, 122.12, 122.46, 126.67, 126.84, 128.56, 129.10, 134.15, 134.92, 150.20, 154.99, 171.80, 201.08. ESI-MS: 551 (M+K), 535 (M+Na). Anal. Calcd for $\text{C}_{28}\text{H}_{40}\text{N}_2\text{O}_5\text{Si}$: C, 65.59; H, 7.86; N, 5.46; O, 15.60; Si, 5.48. Found: C, 65.11; H, 7.23; N, 5.94; O, 15.21; Si, 5.86.

13: Oil. $^1\text{H-NMR}$ (200 MHz, 27°C , CDCl_3): δ 0.78 (t, $J = 6.7$ Hz, 3H), 0.86 (d, $J = 6.8$ Hz, 3H), 0.95

(d, $J = 6.8$ Hz, 3H), 1.18-1.31 (m, 16H), 1.38 (s, 9H), 1.59-1.66 (m, 2H), 1.18-1.28 (m, 1H), 2.90 (t, $J = 7.2$ Hz, 2H), 4.11-4.23 (m, 1H), 5.20 (d, $J = 8.2$ Hz, 1H), 7.01 (t, $J = 7.8$ Hz, 1H), 7.41 (t, $J = 7.9$ Hz, 1H), 7.82 (d, $J = 7.8$ Hz, 1H), 8.67 (d, $J = 8.7$ Hz, 1H), 12.04 (bs, 1H). ^{13}C -NMR (200 MHz, 27°C , CDCl_3): δ 13.86, 17.30, 19.18, 20.69, 22.45, 23.75, 24.42, 25.19, 28.11, 29.08, 29.26, 29.40, 30.86, 31.69, 39.71, 60.94, 79.54, 120.66, 121.84, 122.39, 130.51, 134.41, 140.21, 155.56, 171.08, 204.52. ESI-MS: 497 (M+Na), 475 (M+H). Anal. Calcd for $\text{C}_{28}\text{H}_{46}\text{N}_2\text{O}_4$: C, 70.85; H, 9.77; N, 5.90. Found: C, 70.32; H, 9.71; N, 6.95.

14: Oil. ^1H -NMR (200 MHz, 27°C , CDCl_3): δ 0.86 (t, $J = 6.1$ Hz, 3H), 1.18-1.38 (m, 16H), 1.43 (s, 9H), 1.60-1.83 (m, 2H), 2.95 (t, $J = 7.3$ Hz, 2H), 4.03 (d, $J = 5.6$ Hz, 2H), 5.50-5.60 (m, 1H), 7.10 (t, $J = 7.2$ Hz, 1H), 7.20-7.43 (m, 5H), 7.50 (t, $J = 7.4$ Hz, 1H), 7.87 (d, $J = 7.8$ Hz, 1H), 8.69 (d, $J = 8.7$ Hz, 1H), 12.15 (bs, 1H). ^{13}C -NMR (200 MHz, 27°C , CDCl_3): δ 14.02, 22.59, 24.55, 28.37, 29.25, 29.42, 29.54, 31.83, 39.89, 45.60, 67.20, 79.46, 120.78, 121.82, 122.66, 128.03, 128.26, 128.38, 130.64, 134.67, 136.20, 140.19, 156.45, 168.28, 204.89. ESI-MS: 455 (M+Na), 433 (M+H). Anal. Calcd for $\text{C}_{25}\text{H}_{40}\text{N}_2\text{O}_4$: C, 69.41; H, 9.32; N, 6.48. Found: C, 69.95; H, 9.33; N, 6.42.

15: Mp = $62-65^\circ\text{C}$. ^1H -NMR (200 MHz, 27°C , CDCl_3): δ 0.85 (t, $J = 5.8$ Hz, 3H), 1.18-1.30 (m, 16H), 1.43 (s, 9H), 1.28-1.55 (m, 6H), 1.67 (t, $J = 6.8$ Hz, 2H), 2.94 (t, $J = 7.3$ Hz, 2H), 3.14 (d, $J = 5.3$ Hz, 2H), 4.22-4.34 (m, 1H), 4.98-5.10 (m, 1H), 5.04 (s, 2H), 5.31-5.41 (m, 1H), 7.08 (t, $J = 7.6$ Hz, 1H), 7.29 (s, 5H), 7.48 (t, $J = 7.8$ Hz, 1H), 7.87 (d, $J = 7.9$ Hz, 1H), 8.71 (d, $J = 8.6$ Hz, 1H), 12.15 (bs, 1H). ^{13}C -NMR (200 MHz, 27°C , CDCl_3): δ 13.96, 22.51, 24.49, 28.20, 29.16, 29.33, 29.46, 31.74, 32.24, 39.79, 40.43, 66.42, 67.75, 79.85, 120.71, 121.86, 122.48, 127.84, 128.29, 130.60, 134.53, 136.53, 140.33, 155.43, 156.39, 171.57, 204.65. ESI-MS: 660 (M+Na). Anal.

Calcd for $C_{37}H_{55}N_3O_6$: C, 69.67; H, 8.69; N, 6.59. Found: C, 69.34; H, 8.72; N, 6.63.

16: Oil. $^1\text{H-NMR}$ (200 MHz, 27°C , CDCl_3): δ 1.63 (d, $J = 6.5$ Hz, 3H), 3.62 (q, $J = 6.5$ Hz, 1H), 3.68 (s, 3H), 3.98-4.13 (AB system, 2H), 4.13 (d, $J = 14.6$ Hz, 1H), 6.87-6.98 (m, 3H), 7.07-7.17 (m, 5H), 9.10 (bs, 1H). $^{13}\text{C-NMR}$ (200 MHz, 27°C , CDCl_3): δ 16.59, 45.29, 55.46, 57.91, 111.60, 118.18, 122.63, 126.54, 128.52, 129.09, 130.77, 134.75, 137.06, 155.46, 168.97, 172.70. ESI-MS: 333 (M+K), 317 (M+Na), 295 (M+H). Anal. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.97; H, 6.11; N, 9.43.

17: Mp = $181-184^\circ\text{C}$. $^1\text{H-NMR}$ (200 MHz, 27°C , CDCl_3): δ 3.55 (AB system, 2H), 3.95-4.05 (m, 1H), 4.47 (AB system, 2H), 7.07-7.32 (m, 11H), 7.41 (d, $J = 7.9$ Hz, 1H), 7.56-7.66 (m, 2H), 10.58 (bs, 1H). $^{13}\text{C-NMR}$ (200 MHz, 27°C , CDCl_3): δ 35.09, 43.61, 63.27, 121.80, 124.47, 126.58, 127.11, 128.47, 128.66, 128.77, 128.97, 129.28, 129.52, 130.58, 133.53, 135.04, 138.22, 169.84, 170.05. ESI-MS: 341 (M+H). Anal. Calcd for $C_{23}H_{20}N_2O$: C, 81.15; H, 5.92; N, 8.23. Found: C, 81.73; H, 5.91; N, 8.21.

18: Mp = 152-155°C. $^1\text{H-NMR}$ (200 MHz, 27°C, CDCl_3): δ 1.01 (d, J = 6.6 Hz, 3H), 1.11 (d, J = 6.6 Hz, 3H), 2.50-2.70 (m, 1H), 3.07 (d, J = 9.5 Hz, 1H), 4.10 (d, J = 14.7 Hz, 1H), 4.23 (d, J = 14.7 Hz, 1H), 7.05-7.20 (m, 7H), 7.39 (t, J = 7.6 Hz, 1H), 7.56 (d, J = 7.9 Hz, 1H), 9.10 (bs, 1H). $^{13}\text{C-NMR}$ (200 MHz, 27°C, CDCl_3): δ 19.07, 20.11, 28.39, 45.03, 68.73, 121.33, 123.76, 126.50, 128.15, 128.47, 128.64, 130.40, 131.50, 137.03, 137.48, 169.90, 170.63. ESI-MS: 293 (M+H). Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}$: C, 78.05; H, 6.89; N, 9.58. Found: C, 78.41; H, 6.384; N, 9.57.

19 : Mp = 239-242°C. $^1\text{H-NMR}$ (200 MHz, 27°C, CD_3OD): δ 1.56 (d, J = 6.4 Hz, 3H), 3.66 (q, J = 6.4 Hz, 1H), 3.92 (d, J = 14.3 Hz, 1H), 4.22 (d, J = 14.3 Hz, 1H), 6.87-7.15 (m, 8H). $^{13}\text{C-NMR}$ (200 MHz, 27°C, CD_3OD): δ 15.34, 43.60, 57.47, 113.06, 119.32, 122.35, 126.21, 128.11, 128.55, 130.31, 133.90, 136.69, 153.50, 170.91, 171.88. ESI-MS: 313 (M+Na), 281 (M+H). Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.56; H, 5.71; N, 10.03.

20: Mp = 67-69°C. $^1\text{H-NMR}$ (200 MHz, 27°C, CDCl_3): δ 0.84 (t, J = 6.2 Hz, 3H), 0.97 (d, J = 6.6 Hz, 3H), 0.99 (d, J = 6.6 Hz, 3H), 1.14-1.36 (m, 16H), 1.43-1.63 (m, 2H), 2.59 (q, J = 6.6 Hz, 1H), 2.73 (t, J = 7.3 Hz, 2H), 2.93 (d, J = 9.1 Hz, 1H), 7.10 (t, J = 7.9 Hz, 1H), 7.19 (d, J = 7.2 Hz, 1H), 7.42 (t, J = 7.3 Hz, 1H), 7.55 (d, J = 7.6 Hz, 1H), 9.05 (bs, 1H). $^{13}\text{C-NMR}$ (200 MHz, 27°C, CDCl_3): δ 14.12, 17.52, 19.04, 20.18, 20.85, 22.68, 23.90, 27.68, 28.73, 29.37, 29.50, 29.58, 31.90, 38.84, 68.63, 121.26, 123.81, 128.03, 128.76, 130.91, 137.14, 170.89, 171.31. ESI-MS: 357 (M+H), 379 (M+Na). Anal. Calcd for $\text{C}_{23}\text{H}_{36}\text{N}_2\text{O}$: C, 77.48; H, 10.18; N, 7.86. Found: C, 77.96; H, 10.16; N, 7.83.

21: Mp = 62-65°C. $^1\text{H-NMR}$ (200 MHz, 27°C, CDCl_3): δ 0.82 (t, J = 6.2 Hz, 3H), 1.10-1.40 (m, 8H), 1.44-1.51 (m, 2H), 2.74 (t, J = 7.6 Hz, 2H), 4.07 (s, 2H), 7.10-7.20 (m, 2H), 7.41 (t, J = 7.8 Hz, 1H), 7.52 (d, J = 7.8 Hz, 1H), 9.67 (bs, 1H). $^{13}\text{C-NMR}$ (200 MHz, 27°C, CDCl_3): δ 14.01, 22.56, 24.87, 25.57, 27.38, 29.20, 29.37, 29.49, 31.80, 33.82, 38.85, 55.70, 121.30, 123.84, 127.94, 128.17, 131.18, 137.47, 172.35, 173.77. ESI-MS: 337 (M+Na), 315 (M+H). Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{N}_2\text{O}$: C, 76.39; H, 9.62; N, 8.91. Found: C, 76.97; H, 9.55; N, 8.94.

22: Oil. $^1\text{H-NMR}$ (200 MHz, 27°C, CDCl_3): δ 0.75-0.90 (m, 3H), 1.00-1.80 (m, 24H), 2.60-3.20 (m, 4H), 3.40-3.70 (m, 1H), 5.09 (s, 2H), 7.10-8.0 (m, 9H), 10.80 (bs, 2H). $^{13}\text{C-NMR}$ (200 MHz, 27°C, CDCl_3): 14.02, 22.15, 22.61, 24.60, 25.79, 26.41, 28.56, 28.85, 29.17, 31.84, 36.19, 39.24, 59.34, 71.9, 121.47, 123.21, 125.34, 125.4, 129.1, 129.5, 129.7, 135.8, 136.63, 139.39, 159.7, 161.69, 168.87. ESI-MS: 520 (M+H). Anal. Calcd for $\text{C}_{32}\text{H}_{45}\text{N}_3\text{O}_3$: C, 73.95; H, 8.73; N, 8.09. Found: C, 73.14; H, 8.75; N, 8.02.

28 Oil. $^1\text{H-NMR}$ (200 MHz, 27°C , CDCl_3): δ 0.75 (d, $J = 6.8$ Hz, 3H), 1.00 (d, $J = 6.8$ Hz, 3H), 1.43 (s, 9H), 2.04-2.22 (m, 1H), 5.08-5.18 (m, 1H), 5.42-5.52 (m, 1H), 6.62-6.69 (m, 2H), 7.26 (t, $J = 7.9$ Hz, 1H), 7.73 (d, $J = 7.9$ Hz, 1H). $^{13}\text{C-NMR}$ (200 MHz, 27°C , CDCl_3): δ 16.56, 20.11, 28.34, 32.38, 59.04, 79.41, 116.16, 117.54, 131.12, 134.79, 155.95, 188.43, 201.17. ESI-MS: 315 (M+Na). Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_3$: C, 65.73; H, 8.27; N, 9.58. Found: C, 65.85; H, 8.20; N, 9.62.

29: Oil. $^1\text{H-NMR}$ (200 MHz, 27°C , CDCl_3): δ 0.13 (s, 6H), 0.93 (s, 9H), 1.35 (d, $J = 7.1$ Hz, 3H), 1.41 (s, 9H), 5.10-5.20 (m, 1H), 5.61 (d, $J = 6.5$ Hz, 1H), 6.53 (d, $J = 8.8$ Hz, 1H), 6.83 (dd, $J = 8.8$ Hz, $J = 2.3$ Hz, 1H), 7.09 (d, $J = 2.3$ Hz, 1H). $^{13}\text{C-NMR}$ (200 MHz, 27°C , CDCl_3): δ -4.56, 18.02, 20.50, 25.62, 28.29, 50.76, 79.34, 114.67, 118.50, 119.83, 128.61, 146.23, 146.27, 154.98, 200.03. ESI-MS: 417 (M+Na), 395 (M+H). Anal. Calcd for $\text{C}_{20}\text{H}_{34}\text{N}_2\text{O}_4\text{Si}$: C, 60.88; H, 8.69; N, 7.10. Found: C, 61.67; H, 8.74; N, 7.16.

30 Oil. $^1\text{H-NMR}$ (200 MHz, 27°C , CDCl_3): δ 1.38 (s, 9H), 1.41 (d, $J = 7.5$ Hz, 3H), 3.75 (s, 3H), 4.24 (s, 2H), 4.25-4.32 (m, 1H), 5.21 (d, $J = 6.6$ Hz, 1H), 7.05 (dd, $J = 9.1$ Hz, $J = 2.6$ Hz, 1H), 7.18-7.30 (m, 5H), 7.45 (d, $J = 2.6$ Hz, 1H), 8.66 (d, $J = 9.1$ Hz, 1H), 11.73 (bs, 1H). $^{13}\text{C-NMR}$ (200 MHz, 27°C , CDCl_3): δ 18.74, 28.16, 46.76, 51.44, 55.51, 79.83, 116.11, 120.08, 122.24, 122.57, 126.94, 128.59, 129.29, 134.10, 134.29, 154.29, 155.03, 171.80, 201.22. ESI-MS: 451 (M+K), 435

(M+Na). Anal. Calcd for C₂₄H₂₉N₃O₆: C, 63.28; H, 6.42; N, 9.22; Found: C, 63.45; H, 6.43; N, 9.27.

31: Oil. ¹H-NMR (200 MHz, 27°C, CDCl₃): δ 1.31 (d, *J* = 6 Hz, 3H), 1.43 (s, 9H), 1.47 (d, *J* = 7.3 Hz, 3H), 4.30-4.50 (m, 1H), 5.12 (s, 2H), 5.20-5.35 (m, 1H), 5.40-5.52 (m, 1H), 5.12-5.32 (m, 1H), 7.11 (t, *J* = 7.9 Hz, 1H), 7.23-7.43 (m, 5H), 7.49 (t, *J* = 7.0 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 8.66 (d, *J* = 8.3 Hz, 1H), 11.72 (bs, 1H). ¹³C-NMR (200 MHz, 27°C, CDCl₃): δ 18.52, 19.75, 28.22, 51.40, 52.08, 66.94, 79.87, 119.89, 122.94, 124.12, 127.80, 128.32, 128.67, 130.42, 135.19, 136.00, 140.60, 155.02, 155.81, 171.75, 203.45. ESI-MS: 492 (M+Na). Anal. Calcd for C₂₅H₃₁N₃O₆: C, 63.95; H, 6.65; N, 8.95. Found: C, 64.34; H, 6.61; N, 9.00.

32: Oil. ¹H-NMR (200 MHz, 27°C, CDCl₃): δ 0.84 (d, *J* = 6.9 Hz, 3H), 0.91 (d, *J* = 6.9 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 3H), 1.40 (s, 9H), 2.19-2.39 (m, 1H), 4.19-4.32 (m, 1H), 5.10 (s, 2H), 5.25-5.40 (m, 1H), 5.43-5.58 (m, 1H), 5.66 (d, *J* = 8.3 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.23-7.38 (m, 5H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.88 (dd, *J* = 7.5 Hz, *J* = 3.8 Hz, 1H), 8.66 (d, *J* = 8.3 Hz, 1H), 11.63 (d, *J* = 3.8 Hz, 1H). ¹³C-NMR (200 MHz, 27°C, CDCl₃): δ 17.42, 19.16, 20.72, 28.17, 30.87, 51.36, 61.57, 66.95, 79.82, 119.77, 121.25, 122.97, 127.90, 128.29, 130.44, 135.16, 135.24, 136.14, 140.59, 155.05, 156.32, 170.73, 203.53. ESI-MS: 498 (M+H). Anal. Calcd for C₂₇H₃₅N₃O₆: C, 65.17; H, 7.09; N, 8.44. Found: C, 65.55; H, 7.12; N, 8.46.

35: Oil. $^1\text{H-NMR}$ (200 MHz, 27°C , CDCl_3): δ 0.86 (d, $J = 7.2$ Hz, 3H), 0.93 (d, $J = 7.2$ Hz, 3H), 1.42 (s, 9H), 1.46 (d, $J = 7.3$ Hz, 3H), 1.88-2.12 (m, 1H), 4.25-4.45 (m, 1H), 5.11 (s, 2H), 5.13-5.42 (m, 2H), 5.60-5.75 (m, 1H), 7.13 (t, $J = 7.5$ Hz, 1H), 7.20-7.40 (m, 5H), 7.53 (t, $J = 7.7$ Hz, 1H), 7.92 (d, $J = 7.3$ Hz, 1H), 8.65 (d, $J = 8.4$ Hz, 1H), 11.69 (bs, 1H). $^{13}\text{C-NMR}$ (200 MHz, 27°C , CDCl_3): δ 17.17, 19.85, 20.75, 28.22, 31.90, 51.99, 59.83, 66.97, 79.84, 120.95, 121.19, 123.05, 127.91, 128.00, 128.37, 130.70, 135.19, 136.15, 140.47, 155.79, 171.71, 203.69. ESI-MS: 520 ($\text{M}+\text{Na}$). Anal. Calcd for $\text{C}_{27}\text{H}_{35}\text{N}_3\text{O}_6$: C, 65.17; H, 7.09; N, 8.44. Found: C, 65.76; H, 7.11; N, 8.42.

36: Oil. $^1\text{H-NMR}$ (200 MHz, 27°C , CDCl_3): δ 0.84 (d, $J = 6.9$ Hz, 3H), 0.91 (d, $J = 6.9$ Hz, 3H), 0.98 (d, $J = 6.1$ Hz, 3H), 1.42 (s, 9H), 1.98-2.18 (m, 1H), 2.20-2.38 (m, 1H), 4.20-4.30 (m, 1H), 5.09 (s, 2H), 5.22-5.30 (m, 1H), 5.60-5.70 (m, 1H), 7.12 (t, $J = 7.6$ Hz, 1H), 7.22-7.41 (m, 5H), 7.51 (t, $J = 7.9$ Hz, 1H), 7.95 (d, $J = 7.1$ Hz, 1H), 8.66 (d, $J = 8.4$ Hz, 1H), 11.64 (bs, 1H). $^{13}\text{C-NMR}$ (200 MHz, 27°C , CDCl_3): δ 17.40, 19.83, 20.74, 28.13, 30.91, 31.84, 59.78, 61.64, 66.94, 79.75, 120.87, 121.10, 122.97, 127.90, 128.27, 130.70, 135.19, 136.10, 140.05, 140.88, 155.75, 156.33, 170.64, 203.67. ESI-MS: 548 ($\text{M}+\text{Na}$). Anal. Calcd for $\text{C}_{29}\text{H}_{39}\text{N}_3\text{O}_6$: C, 66.26; H, 7.48; N, 7.99. Found: C, 66.56; H, 7.42; N, 7.93.

37: Oil. $^1\text{H-NMR}$ (200 MHz, 27°C , CDCl_3): δ 0.88 (d, $J = 7.1$ Hz, 3H), 0.94 (d, $J = 7.1$ Hz, 3H), 1.44 (s, 9H), 1.90-2.00 (m, 1H), 2.86-3.20 (m, 2H), 3.58-3.72 (m, 1H), 4.58-4.80 (m, 1H), 5.08 (s,

2H), 5.20-5.37 (m, 1H), 5.55-5.67 (m, 1H), 6.90-7.32 (m, 11 H), 7.54 (t, $J = 7.8$ Hz, 1H), 7.92 (d, $J = 7.8$ Hz), 8.62 (t, $J = 7.5$ Hz, 1H), 11.70 (bs, 1H). ^{13}C -NMR (200 MHz, 27°C , CDCl_3): δ 16.51, 19.87, 28.20, 32.37, 38.88, 54.87, 59.66, 66.99, 79.76, 120.75, 121.15, 123.07, 126.98, 127.91, 128.02, 128.35, 128.55, 128.59, 129.10, 130.73, 135.23, 135.85, 140.18, 155.72, 156.38, 170.38, 203.51. ESI-MS: 596 ($\text{M}+\text{Na}$). Anal. Calcd for $\text{C}_{33}\text{H}_{39}\text{N}_3\text{O}_6$: C, 69.09; H, 6.85; N, 7.32. Found: C, 69.43; H, 6.80; N, 7.29.

38: Oil. ^1H -NMR (200 MHz, 27°C , CDCl_3): δ 0.17 (s, 6H), 0.96 (s, 9H), 1.31 (d, $J = 6.7$ Hz, 3H), 1.42 (s, 9H), 2.78 (dd, $J = 7.1$ Hz, $J = 4.7$ Hz, 1H), 3.17 (dd, $J = 7.1$ Hz, $J = 4.7$ Hz, 1H), 3.62 (s, 3H), 4.60-4.73 (m, 1H), 5.09-5.28 (m, 3H), 5.41-5.52 (m, 1H), 6.18 (d, 1H, $J = 8.4$ Hz, 1H), 7.02 (dd, $J = 9.0$ Hz, 1H), 7.29-7.42 (m, 6H), 8.50 (d, $J = 9.0$ Hz, 1H), 11.65 (bs, 1H). ^{13}C -NMR (200 MHz, 27°C , CDCl_3): δ -4.56, 18.03, 19.93, 25.51, 28.24, 35.60, 51.43, 51.86, 52.25, 67.26, 79.72, 120.06, 121.25, 122.53, 126.87, 127.86, 128.02, 128.38, 134.32, 136.05, 150.87, 154.86, 156.00, 169.26, 171.72, 202.46. ESI-MS: 680 ($\text{M}+\text{Na}$). Anal. Calcd for $\text{C}_{33}\text{H}_{47}\text{N}_3\text{O}_9\text{Si}$: C, 60.25; H, 7.20; N, 6.39. Found: C, 59.64; H, 7.59; N, 6.74.

39: Oil. ^1H -NMR (200 MHz, 27°C , CDCl_3): δ 1.13 (d, $J = 6.8$ Hz, 3H), 1.43 (s, 9H), 3.76 (d, $J = 11.0$, 1H), 4.48 (d, $J = 11.0$, 1H), 4.96 (t, $J = 6.7$ Hz, 1H), 5.94 (d, $J = 5.9$ Hz, 1H), 7.14 (d, $J = 8.0$ Hz, 1H), 7.22 (t, $J = 7.6$ Hz, 1H), 7.47 (t, $J = 7.4$ Hz, 1H), 7.69 (d, $J = 7.7$ Hz, 1H), 9.38 (bs, 1H). ^{13}C -NMR (200 MHz, 27°C , CDCl_3): δ 20.38, 28.17, 50.69, 54.99, 78.17, 121.09, 124.16, 125.47, 128.00, 131.77, 137.79, 155.06, 171.74, 172.85. ESI-MS: 326 ($\text{M}+\text{Na}$), 304 ($\text{M}+\text{H}$). Anal. Calcd for

C₁₆H₂₁N₃O₃: C, 63.35; H, 6.98; N, 13.85. Found: C, 63.87; H, 6.85; N, 13.86.

41: Mp = 151-154°C. ¹H-NMR (200 MHz, 27°C, CDCl₃): δ 0.84 (d, *J* = 6.6 Hz, 3H), 0.97 (d, *J* = 6.9 Hz, 3H), 1.04 (d, *J* = 6.9 Hz, 3H), 1.43 (s, 9H), 2.56 (q, *J* = 6.9 Hz, 1H), 2.94 (d, *J* = 8.9 Hz, 1H), 4.87-5.02 (m, 1H), 5.91 (d, *J* = 7.1 Hz, 1H), 7.15 (t, *J* = 7.9 Hz, 1H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 1H), 9.44 (bs, 1H). ¹³C-NMR (200 MHz, 27°C, CDCl₃): δ 17.43, 18.79, 20.11, 28.36, 40.95, 50.75, 68.00, 79.21, 121.18, 124.10, 126.15, 127.88, 131.53, 137.73, 155.52, 170.42, 171.38. ESI-MS: 384 (M+K), 368 (M+Na), 346 (M+H). Anal. Calcd for C₁₉H₂₇N₃O₃: C, 66.06; H, 7.88; N, 12.16. Found: C, 66.71; H, 7.85; N, 11.09.

42: Mp = 182-185°C. ¹H-NMR (200 MHz, 27°C, CDCl₃): δ : 0.88 (d, *J* = 6.9 Hz, 3H), 1.47 (s, 9H), 3.39-3.51 (m, 2H), 3.58-3.68 (m, 1H), 4.90-4.98 (m, 1H), 6.08 (d, *J* = 5.8 Hz, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 7.13-7.30 (m, 6H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 9.25 (bs, 1H). ¹³C-NMR (200 MHz, 27°C, CDCl₃): δ 18.79, 28.29, 37.15, 50.65, 65.94, 79.58, 121.97, 124.58, 126.47, 128.26, 128.43, 128.47, 129.34, 130.64, 136.73, 138.21, 155.93, 171.63, 174.56. ESI-MS: 432 (M+K), 416 (M+Na), 394 (M+H). Anal. Calcd for C₂₃H₂₇N₃O₃: C, 70.21; H, 6.92; N, 10.68. Found: C, 70.82; H, 6.86; N, 10.58.

43 Mp = 217-220°C. ^1H -NMR (200 MHz, 27°C, CDCl_3): δ 0.61 (d, J = 6.8 Hz, 3H), 0.73 (d, J = 6.8 Hz, 3H), 1.41 (s, 9H), 1.87-1.98 (m, 1H), 3.64 (d, J = 11.0 Hz, 1H), 4.48 (d, J = 11.0 Hz, 1H), 4.77-4.87 (m, 1H), 5.74 (d, J = 8.2 Hz, 1H), 7.02 (d, J = 7.9 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.73 (d, J = 7.7 Hz, 1H), 8.40 (bs, 1H). ^{13}C -NMR (200 MHz, 27°C, CDCl_3): δ 17.14, 19.59, 28.39, 33.03, 55.43, 59.54, 79.28, 120.99, 124.40, 127.23, 128.64, 131.67, 137.19, 155.01, 171.83, 172.36. ESI-MS: 354 (M+Na), 332 (M+H). Anal. Calcd for $\text{C}_{18}\text{H}_{25}\text{N}_3\text{O}_3$: C, 65.23; H, 7.60; N, 12.68. Found: C, 65.47; H, 7.54; N, 12.59.

44 as a mixture of rotamers: ^1H -NMR (200 MHz, 27°C, CDCl_3): δ .57 (d, J = 6.8 Hz, 3H), 0.72 (d, J = 6.8 Hz, 3H), 0.94 (d, J = 6.6 Hz, 3H), 1.01 (d, J = 6.6 Hz, 3H), 1.29 (s, 9H), 1.44 (s, 9H), 1.52 (d, J = 6.5 Hz, 3H), 1.59 (d, J = 6.5 Hz, 3H), 2.20-2.40 (m, 1H), 3.55 (q, J = 6.6 Hz, 1H), 3.62-3.77 (m, 1H), 4.57-4.67 (m, 1H), 4.78 (dd, J = 8.3 Hz, J = 4.8 Hz, 1H), 4.97-5.10 (m, 1H), 5.71 (d, J = 8.3 Hz, 1H), 7.07-7.20 (m, 6H), 7.36-7.47 (m, 4H), 7.61 (d, J = 7.7 Hz, 1H), 7.73 (d, J = 7.7 Hz, 1H), 9.44 (bs, 1H), 9.52 (bs, 1H). ^{13}C -NMR (200 MHz, 27°C, CDCl_3): 16.49, 17.20, 19.48, 20.29, 28.15, 28.37, 32.12, 32.97, 57.49, 58.14, 59.42, 79.15, 121.13, 121.18, 123.81, 124.07, 127.59, 127.91, 128.28, 131.39, 131.55, 137.25, 155.52, 156.13, 172.93, 173.22. ESI-MS: 368 (M+Na), 346 (M+H). Anal. Calcd for $\text{C}_{19}\text{H}_{27}\text{N}_3\text{O}_3$: C, 66.06; H, 7.88; N, 12.16. Found: C, 66.72; H, 7.84; N, 12.14.

45: Oil. $^1\text{H-NMR}$ (200 MHz, 27°C , CDCl_3): δ 0.72 (d, $J = 6.8$ Hz, 3H), 0.87 (d, $J = 6.9$ Hz, 3H), 0.98 (d, $J = 6.8$ Hz, 3H), 1.03 (d, $J = 6.9$ Hz, 3H), 1.44 (s, 9H), 1.70 (q, $J = 6.8$ Hz, 1H), 2.58 (q, $J = 6.9$ Hz, 1H), 2.94 (d, $J = 9.0$ Hz, 1H), 4.78 (t, $J = 4.6$ Hz, 1H), 5.69 (d, $J = 8.2$ Hz, 1H), 7.08 (d, 8.0 Hz, 1H), 7.22 (t, $J = 7.7$ Hz, 1H), 7.46 (t, $J = 7.8$ Hz, 1H), 7.79 (d, $J = 7.6$ Hz, 1H), 9.00 (bs, 1H). $^{13}\text{C-NMR}$ (200 MHz, 27°C , CDCl_3): δ 17.24, 19.64, 20.11, 20.83, 28.40, 32.66, 40.91, 59.68, 67.97, 79.23, 121.12, 124.24, 127.48, 128.49, 131.58, 137.12, 156.47, 170.50, 171.26. ESI-MS: 412 (M+K), 396 (M+Na), 374 (M+H). Anal. Calcd for $\text{C}_{21}\text{H}_{31}\text{N}_3\text{O}_3$: C, 67.53; H, 8.37; N, 11.25. Found: C, 67.12; H, 8.36; N, 11.17.

46: Oil. $^1\text{H-NMR}$ (200 MHz, 27°C , CDCl_3): δ 0.58 (d, $J = 6.6$ Hz, 3H), 0.75 (d, $J = 6.6$ Hz, 3H), 1.47 (s, 9H), 1.62-1.82 (m, 1H), 3.45-3.55 (m, 2H), 3.60-3.67 (m, 1H), 4.68-4.85 (m, 1H), 5.81 (d, $J = 7.3$ Hz, 1H), 7.07 (d, $J = 7.9$ Hz, 1H), 7.14-7.32 (m, 6H), 7.46 (t, $J = 7.6$ Hz, 1H), 7.71 (d, $J = 7.6$ Hz, 1H), 9.15 (bs, 1H). $^{13}\text{C-NMR}$ (200 MHz, 27°C , CDCl_3): δ 17.14, 19.59, 28.45, 33.12, 40.92, 59.38, 63.65, 79.14, 121.24, 124.34, 126.16, 127.27, 128.16, 128.59, 129.76, 131.61, 137.02, 138.90, 156.12, 162.17, 171.84. ESI-MS: 444 (M+Na), 422 (M+H). Anal. Calcd for $\text{C}_{25}\text{H}_{31}\text{N}_3\text{O}_3$: C, 71.23; H, 7.41; N, 9.97. Found: C, 70.95; H, 7.49; N, 9.90.

47: Oil. $^1\text{H-NMR}$ (200 MHz, 27°C , CDCl_3): δ 0.18 (s, 6H), 0.95 (s, 9H), 1.31 (s, 9H), 1.43 (d, J = 6.5 Hz, 3H), 3.00 (dd, J = 16.7 Hz, J = 6.7 Hz, 1H), 3.27 (dd, J = 16.7 Hz, J = 7.5 Hz, 1H), 3.64 (s, 3H), 4.05 (t, J = 7.3 Hz, 1H), 4.70-4.90 (m, 1H), 5.09 (d, J = 8.8 Hz, 1H), 6.87-7.10 (m, 3H), 9.34 (bs, 1H). $^{13}\text{C-NMR}$ (200 MHz, 27°C , CDCl_3): δ -4.47, 18.08, 20.90, 25.54, 28.21, 36.05, 51.51, 59.39, 60.27, 79.37, 117.59, 122.81, 123.92, 128.08, 130.98, 151.84, 154.76, 170.69, 172.16, 191.72. ESI-MS: 528 ($\text{M}+\text{Na}$), 506 ($\text{M}+\text{H}$). Anal. Calcd for $\text{C}_{25}\text{H}_{39}\text{N}_3\text{O}_6\text{Si}$: C, 59.38; H, 7.77; N, 8.31. Found: C, 59.70; H, 7.74; N, 8.34.

49: Mp = $174\text{-}177^\circ\text{C}$. $^1\text{H-NMR}$ (200 MHz, 27°C , CDCl_3): δ 0.19 (s, 6H), 0.97 (s, 9H), 1.32 (s, 3H), 1.44 (s, 9H), 2.89 (dd, J = 14.8 Hz, J = 4.6 Hz, 1H), 3.14 (dd, J = 14.8 Hz, J = 7.6 Hz, 1H), 3.98-4.10 (m, 1H), 4.34-4.43 (m, 2H), 4.70-4.85 (m, 1H), 5.80 (d, J = 6.7 Hz, 1H), 6.74 (bs, 1H), 6.89-7.04 (m, 3H), 8.98 (bs, 1H). $^{13}\text{C-NMR}$ (200 MHz, 27°C , CDCl_3): δ -4.47, 18.11, 20.93, 25.58, 28.42, 38.30, 43.42, 51.53, 60.31, 79.33, 122.71, 124.24, 127.00, 127.22, 127.58, 127.60, 128.53, 131.37, 138.37, 152.19, 155.08, 161.13, 170.93, 171.30. ESI-MS: 603 ($\text{M}+\text{Na}$), 581 ($\text{M}+\text{H}$). Anal. Calcd for $\text{C}_{31}\text{H}_{44}\text{N}_4\text{O}_5\text{Si}$: C, 64.11; H, 7.64; N, 9.65. Found: C, 64.75; H, 7.53; N, 9.61.

50: Mp = 69-72°C. $^1\text{H-NMR}$ (200 MHz, 27°C, CDCl_3): δ 1.27 (d, J = 6.0 Hz, 3H), 1.41 (s, 9H), 3.14 (dd, J = 16.4 Hz, J = 7.5 Hz, 1H), 3.29 (dd, J = 16.4 Hz, J = 6.9 Hz, 1H), 3.58 (s, 3H), 4.10 (t, J = 7.1 Hz, 1H), 5.51 (t, J = 6.5 Hz, 1H), 7.04 (d, J = 8.7 Hz, 1H), 7.09 (dd, J = 8.7 Hz, J = 2.1 Hz, 1H), 7.43 (d, J = 2.1 Hz, 1H), 7.44 (t, J = 7.3 Hz, 1H), 7.50 (d, J = 7.3 Hz, 2H), 7.81 (d, J = 7.3 Hz, 2H), 8.30 (bs, 1H), 8.95 (bs, 1H), 9.50 (bs, 1H). $^{13}\text{C-NMR}$ (200 MHz, 27°C, CDCl_3): δ 20.02, 36.02, 50.02, 51.84, 58.90, 113.09, 123.32, 125.52, 127.08, 128.83, 130.06, 130.31, 132.04, 133.78, 154.51, 167.77, 170.48, 171.00, 172.11. ESI-MS: 418 (M+Na), 396 (M+H), 394 (M-H). Anal. Calcd for $\text{C}_{21}\text{H}_{21}\text{N}_3\text{O}_5$: C, 63.79; H, 5.35; N, 10.63. Found: C, 64.05; H, 5.36; N, 10.62.