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Solvent-free synthesis of functionalized 5-imino-2,5-dihydrofurans from isocyanides, activated acetylenes and alkyl cyanoformates

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For **4b**: Pale yellow oil; yield: 0.31 g (85%); IR (KBr) (ν_{max}/cm^{-1}): 2923, 2849, 2250, 1726, 1692, 1280; ^{1}H NMR: δ_H 1.23-1.80 (10 H, m, 5 CH_2), 1.36 (3 H, t, $^3J_{HH}$ = 7.2 Hz, Me), 1.39 (3 H, t, $^3J_{HH}$ = 7.2 Hz, Me), 3.68 (1 H, m, CHN), 3.70 (3 H, s, MeO), 4.35 (2 H, q, $^3J_{HH}$ = 7.2 Hz, CH_2O), 4.42 (2 H, q, $^3J_{HH}$ = 7.2 Hz, CH_2O); ^{13}C NMR: δ_C 14.4 (Me), 15.2 (Me), 24.7 (CH_2), 24.8 (CH_2), 25.9 (CH_2), 33.5 (CH_2), 33.6 (CH_2), 55.3 (MeO), 57.6 (CHN), 63.1 (CH_2O), 63.3 (CH_2O), 99.3 (C), 112.5 (CN), 136.5 (C), 140.0 (C), 149.9, 158.9 and 160.1 (C=N and 2 C=O); MS (EI, 70 eV): *m*/*z* (%) 364 (M^+, 100), 338 (36), 267 (51), 193 (19), 73 (12), 31 (8). Found (%): C, 59.5; H, 6.7; N, 7.8. Calc. for $C_{18}H_{24}N_2O_6$ (%): C, 59.33; H, 6.64; N, 7.69.

For **4c**: Pale yellow oil; yield: 0.32 g (87%); IR (KBr) (ν_{max}/cm^{-1}): 2948, 2850, 2243, 1735, 1690, 1260. ^{1}H NMR: δ_H 0.97 (9H, s, CMe_3), 1.38 (6H, s, 2 Me), 1.63 (2 H, s, CH_2), 3.70 (3 H, s, MeO), 3.93 (3 H, s, MeO), 3.92 (3 H, s, MeO); ^{13}C NMR: δ_C 30.1 (Me), 30.3 (Me), 31.9 (3 C*Me*$_3$), 32.3 (*C*Me$_3$), 53.6 (MeO), 53.7 (MeO), 55.2 (MeO), 55.9 (*C*Me$_2$), 60.1 (CH_2), 99.7 (C), 112.5 (CN), 135.3 (C), 141.8 (C), 146.4, 159.4 and 161.2 (C=N and 2 C=O); MS (EI, 70 eV): *m*/*z* (%) 366 (M^+, 100), 340 (20), 293 (35), 182 (20), 59 (10). Found (%): C, 59.2; H, 7.1; N, 7.7. Calc. for $C_{18}H_{26}N_2O_6$ (%): C, 59.00; H, 7.15; N, 7.65.

For **4d**: Pale yellow oil; yield: 0.35 g (90%); IR (KBr) (ν_{max}/cm^{-1}): 2929, 2848, 2240, 1739, 1684, 1269; ^{1}H NMR: δ_H 0.98 (9H, s, CMe_3), 1.34 (3 H, t, $^3J_{HH}$ = 7.0 Hz, Me), 1.37 (6H, s, 2 Me), 1.64 (2 H, s, CH_2), 1.39 (3 H, t, $^3J_{HH}$ = 7.0 Hz, Me), 3.70 (3 H, s, MeO), 4.32–4.42 (m, 2 CH_2O); ^{13}C NMR: δ_C 14.1 (Me), 14.3 (Me), 30.2 (Me), 30.3 (Me), 31.9 (3 C*Me*$_3$), 32.4 (*C*Me$_3$), 53.6 (MeO), 55.8 (*C*Me$_2$), 60.1 (CH_2), 62.7 (CH_2O), 62.9 (CH_2O), 99.5 (C), 112.6 (CN), 135.8 (C), 142.9 (C), 146.9, 158.5 and 161.9 (C=N and 2 C=O); MS (EI, 70 eV): *m*/*z* (%) 394 (M^+, 100), 368 (15), 267 (41), 193 (15), 73 (9). Found (%): C, 61.1; H, 7.8; N, 7.2. Calc. for $C_{20}H_{30}N_2O_6$ (%): C, 60.90; H, 7.67; N, 7.10.

For **4e**: Yellow oil; yield: 0.30 g (85%); IR (KBr) (ν_{max}/cm^{-1}): 2984, 2855, 2240, 1716, 1665, 1260; ^{1}H NMR: δ_H 2.13 (6 H, s, 2 Me), 3.66 (3 H, s, MeO), 3.96 (3 H, s, MeO), 4.04 (3 H, s, MeO), 6.97–7.08 (3 H, m, C_6H_3); ^{13}C NMR: δ_C 18.4 (2 Me), 53.9 (MeO), 54.7 (MeO), 55.7 (MeO), 99.8 (C), 112.0 (CN), 125.0 (CH_{para}), 127.7 (2 C), 128.1 (2 CH_{meta}), 138.0 (C_{ipso}), 139.0 (C), 143.0 (C), 150.4, 159.0 and 160.5 (C=N and 2 C=O); MS (EI, 70 eV): *m*/*z* (%) 358 (M^+, 100), 332 (35), 239 (26), 182 (21), 77 (70). Found (%): C, 60.1; H, 5.1; N, 7.7. Calc. for $C_{18}H_{18}N_2O_6$ (%): C, 60.33; H, 5.06; N, 7.82.

For **4f**: Yellow oil; yield: 0.32 g (85%); IR (KBr) (ν_{max}/cm^{-1}): 2930, 2845, 2245, 1757, 1717, 1280; ^{1}H NMR: δ_H 1.36 (3 H, t, $^3J_{HH}$ = 7.2 Hz, Me), 1.43 (3 H, t, $^3J_{HH}$ = 7.2 Hz, Me), 2.13 (6 H, s, 2 Me), 3.66 (3 H, s, MeO), 4.40 (2 H, q, $^3J_{HH}$ = 7.2 Hz, CH_2O), 4.49 (2 H, q, $^3J_{HH}$ = 7.2 Hz, CH_2O), 6.97–7.07 (3 H, m, C_6H_3); ^{13}C NMR: δ_C 14.3 (Me), 14.4 (Me), 18.4 (2 Me), 55.8 (MeO), 63.4 (CH_2O), 65.6 (CH_2O), 100.1 (C), 111.9 (CN), 125.0 (CH_{para}), 127.6 (2 C), 128.2 (2 CH_{meta}), 138.2 (C_{ipso}), 139.1 (C), 142.9 (C), 150.4, 158.6 and 160.2 (C=N and 2 C=O); MS (EI, 70 eV): *m*/*z* (%) 386 (M^+, 100), 386 (25), 267 (15), 196 (46), 77 (35). Found (%): C, 62.0; H, 5.8; N, 7.3. Calc. for $C_{20}H_{22}N_2O_6$ (%): C, 62.17; H, 5.74; N, 7.25.

For **4g**: Pale yellow oil; yield: 0.33 g (95%); IR (KBr) (ν_{max}/cm^{-1}): 2933, 2860, 2248, 1743, 1700, 1286; ^{1}H NMR: δ_H 1.23-1.84 (10 H, m, 5 CH_2), 1.34 (3 H, t, $^3J_{HH}$ = 6.9 Hz, Me), 3.63 (1 H, m, CHN), 3.92 (3 H, s, MeO), 3.97 (3 H, s, MeO), 4.03 [2 H, (AB)X_3 system, J_{AX} = J_{BX} = 6.9 Hz, J_{AB} = 14.1 Hz, $\Delta\nu_{AB}$ = 20.2 Hz, CH_2O]; ^{13}C NMR: δ_C 15.2 (Me), 24.7 (CH_2), 24.8 (CH_2), 25.9 (CH_2), 33.4 (CH_2), 33.5 (CH_2), 53.7 (MeO), 53.8 (MeO), 57.8 (CHN), 64.7 (CH_2O), 99.0 (C), 112.7 (CN), 136.9 (C), 140.1 (C), 150.1, 153.4 and 161.1 (C=N and 2 C=O); MS (EI, 70 eV): *m*/*z* (%) 350 (M^+, 100), 324 (23), 253 (43), 193 (9). Found (%): C, 58.0; H, 6.4; N, 8.1. Calc. for $C_{17}H_{22}N_2O_6$ (%): C, 58.28; H, 6.33; N, 8.00.

For **4h**: Pale yellow oil; yield: 0.35 g (93%); IR (KBr) (ν_{max}/cm^{-1}): 2966, 2853, 2245, 1735, 1715, 1262; ^{1}H NMR: δ_H 1.21-1.84 (10 H, m, 5 CH_2), 1.33 (3 H, t, $^3J_{HH}$ = 7.1 Hz, Me), 1.35 (3 H, t, $^3J_{HH}$ = 7.2 Hz, Me), 1.38 (3 H, t, $^3J_{HH}$ = 7.2 Hz, Me), 3.67 (1 H, m, CHN), 4.18 [2 H, (AB)X_3 system, J_{AX} = J_{BX} = 7.1 Hz, J_{AB} = 9.1 Hz, $\Delta\nu_{AB}$ = 21.9 Hz, CH_2O], 4.36 (2 H, q, $^3J_{HH}$ = 7.2 Hz, CH_2O), 4.42 (2 H, q, $^3J_{HH}$ = 7.2 Hz, CH_2O); ^{13}C NMR: δ_C = 14.3 (Me), 14.4 (Me), 15.2 (Me), 24.7 (CH_2), 24.8 (CH_2), 25.9 (CH_2), 33.5 (CH_2), 33.6 (CH_2), 57.6 (CHN), 63.0 (CH_2O), 63.2 (CH_2O), 64.7 (CH_2O), 99.1 (C), 112.8 (CN), 136.8 (C), 139.9 (C), 150.2, 158.9 and 160.6 (C=N and 2 C=O); MS (EI, 70 eV): *m*/*z* (%) 378 (M^+, 100), 352 (27), 281 (55), 210 (18), 73 (10). Found (%): C, 60.5; H, 6.9; N, 7.5. Calc. for $C_{19}H_{26}N_2O_6$ (%): C, 60.30; H, 6.93; N, 7.40.

For **4i**: Pale yellow oil; yield: 0.34 g (90%); IR (KBr) (ν_{max}/cm^{-1}): 2930, 2845, 2248, 1715, 1695, 1281; ^{1}H NMR: δ_H 0.97 (9 H, s, CMe_3), 1.34 (3 H, t, $^3J_{HH}$ = 7.5 Hz, Me), 1.37 (6 H, s, 2 Me), 1.63 (2 H, s, CH_2), 3.91 (3 H, s, MeO), 3.93 (3 H, s, MeO), 4.18 [2 H, (AB)X_3 system, $J_{AX} = J_{BX}$ = 7.5 Hz, J_{AB} = 11.4 Hz, $\Delta\nu_{AB}$ = 17.3 Hz, CH_2O]; ^{13}C NMR: δ_C 15.1 (Me), 30.2 (Me), 30.3 (Me), 31.9 (C*Me*$_3$), 32.1 (*C*Me$_3$), 53.6 (MeO), 53.7 (MeO), 55.8 (*C*Me$_2$), 60.0 (CH_2), 64.7 (CH_2O), 99.2 (C), 112.8 (CN), 135.9 (C), 141.6 (C), 146.7, 159.4 and 161.3 (C=N and 2 C=O); MS (EI, 70 eV): *m*/*z* (%) 380 (M^+, 100), 354 (18), 253 (36), 193 (10), 59 (11), 45 (9). Found (%): C, 59.7; H, 7.5; N, 7.4. Calc. for $C_{19}H_{28}N_2O_6$ (%): C, 59.98; H, 7.42; N, 7.36.

For **4j**: Pale yellow oil; yield: 0.36 g (88%); IR (KBr) (ν_{max}/cm^{-1}): 2924, 2855, 2240, 1735, 1675, 1249; ^{1}H NMR: δ_H = 0.97 (9 H, s, CMe_3), 1.30–1.41 (15 H, m, 5 Me), 1.63 (2 H, s, CH_2), 4.18 [2 H, (AB)X_3 system, $J_{AX} = J_{BX}$ = 7.1 Hz, J_{AB} = 15.8 Hz, $\Delta\nu_{AB}$ = 22.8 Hz, CH_2O], 4.32–4.42 (4 H, m, 2 CH_2O); ^{13}C NMR: δ_C 14.1 (Me), 14.3 (Me), 14.4 (Me), 30.2 (Me), 30.3 (Me), 31.9 (C*Me*$_3$), 32.3 (*C*Me$_3$), 55.8 (*C*Me$_2$), 60.0 (CH_2), 62.8 (CH_2O), 63.0 (CH_2O), 64.6 (CH_2O), 99.3 (C), 115.4 (CN), 141.3 (C), 146.9 (C), 148.9, 158.9 and 160.9 (C=N and 2 C=O); MS (EI, 70 eV): *m*/*z* (%) 408 (M^+, 100), 382 (35), 281 (50), 210 (13), 73 (15), 45 (10). Found (%): C, 62.1; H, 6.8; N, 7.2. Calc. for $C_{21}H_{32}N_2O_6$ (%): C, 61.75; H, 6.86; N, 7.10.

For **4k**: Yellow oil; yield: 0.33 g (88%); IR (KBr) (ν_{max}/cm^{-1}): 2920, 2846, 2240, 1713, 1627, 1274; ^{1}H NMR: δ_H = 1.34 (3 H, t, $^3J_{HH}$ = 7.5 Hz, Me), 2.17 (6 H, s, 2 Me), 3.91 (3 H, s, MeO), 3.93 (3 H, s, MeO), 4.35 [2 H, (AB)X_3 system, $J_{AX} = J_{BX}$ = 7.5 Hz, J_{AB} = 12.7 Hz, $\Delta\nu_{AB}$ = 21.2 Hz, CH_2O], 6.96–7.07 (3 H, m, C_6H_3); ^{13}C NMR: δ_C 15.1 (Me), 18.4 (2 Me), 53.9 (MeO), 54.7 (MeO), 65.5 (CH_2O), 99.5 (C), 112.1 (CN), 125.0 (CH_{para}), 127.5 (2 C), 128.1 (2 CH_{meta}), 136.0 (C_{ipso}), 138.9 (C), 143.0 (C), 150.5, 159.0 and 160.7 (C=N and 2 C=O); MS (EI, 70 eV): *m*/*z* (%) 372 (M^+, 100), 346 (22), 253 (44), 193 (18), 77 (30). Found (%): C, 61.0; H, 5.2; N, 7.6. Calc. for $C_{19}H_{20}N_2O_6$ (%): C, 61.28; H, 5.41; N, 7.52.

For **4l**: Yellow oil; yield: 0.36 g (91%); IR (KBr) (ν_{max}/cm^{-1}): 2935, 2865, 2240, 1721, 1635, 1248; ^{1}H NMR: δ_H 1.27 (3 H, t, $^3J_{HH}$ = 7.2 Hz, Me), 1.37 (3 H, t, $^3J_{HH}$ = 7.2 Hz, Me), 1.41 (3 H, t, $^3J_{HH}$ = 7.2 Hz, Me), 2.17 (6 H, s, 2 Me), 3.97 [2 H, (AB)X_3 system, $J_{AX} = J_{BX}$ = 7.2 Hz, J_{AB} = 15.0 Hz, $\Delta\nu_{AB}$ = 17.5 Hz, CH_2O], 4.41 (2 H, q, $^3J_{HH}$ = 7.2 Hz, CH_2O), 4.50 (2 H, q, $^3J_{HH}$ = 7.2 Hz, CH_2O), 6.96–7.07 (3 H, m, C_6H_3); ^{13}C NMR: δ_C = 13.9 (Me), 14.1 (Me), 15.1 (Me), 18.3 (2 Me), 63.3 (CH_2O), 63.5 (CH_2O), 65.4 (CH_2O), 99.4 (C), 112.4 (CN), 124.9 (CH_{para}), 127.7 (2 C), 128.0 (2 CH_{meta}), 138.1 (C_{ipso}), 138.7 (C), 143.3 (C), 150.6, 158.8 and 160.8 (C=N and 2 C=O); MS (EI, 70 eV): *m*/*z* (%) 400 (M^+, 100), 374 (28), 281 (39), 210 (15), 77 (56). Found (%): C, 62.7; H, 5.9; N, 7.1. Calc. for $C_{21}H_{24}N_2O_6$ (%): C, 62.99; H, 6.04; N, 7.00.