Supporting Information for:

**Solvent- and catalyst-free, quantitative protection of hydroxyl, thiol, carboxylic acid, amide and heterocyclic amino functional groups**

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Tetrahydro-2H-pyran-2-yl benzoate. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.08 (dd, 2H, $^3$$J$ = 7.0 Hz, $^3$$J$ = 1.4 Hz, CH-phenyl), 7.56 (t, 1H, $^3$$J$ = 7.3 Hz, CH-phenyl), 7.44 (t, 2H, $^3$$J$ = 8.0 Hz, CH-phenyl), 6.25 (m, 1H, CH-THP), 3.96−4.02 (m, 1H, CH$_2$O-THP), 3.73−3.77 (m, 1H, CH$_2$O-THP). 1.53−1.92 (m, 6H, CH$_2$-THP) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 165.2, 133.2, 130.4, 129.8, 128.5, 93.2, 63.3, 29.4, 25.1, 18.7 ppm.

Tetrahydro-2H-pyran-2-yl stearate. $^1$H NMR (400 MHz, CDCl$_3$): δ 5.95 (s, 1H, CH-THP), 3.85−3.91 (m, 1H, CH$_2$O-THP), 3.64−3.68 (m, 1H, CH$_2$O-THP). 2.33 (t, 2H, $^3$$J$ = 7.6 Hz, C(O)CH$_2$), 1.75−1.85 (m, 2H, C(O)CH$_2$CH$_2$), 1.50−1.70 (m, 6H, CH$_2$-THP), 1.21−1.28 (m, 28H, C(O)CH$_2$CH$_2$(CH$_2$)$_{14}$CH$_3$). 0.86 (t, 3H, $^3$$J$ = 7.0 Hz, C(O)CH$_2$CH$_2$(CH$_2$)$_{14}$CH$_3$) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 172.7, 92.5, 63.4, 34.6, 32.0, 29.7, 29.6, 29.5, 29.4, 29.35, 29.31, 29.21, 25.0, 24.9, 22.7, 18.8, 14.2 ppm. HRMS (ESI-TOF) m/z: [M + Na]$^+$ caleld for C$_{39}$H$_{44}$NaO$_3$ 391.3182; found 391.3176.

2-(Phenylthio)tetrahydro-2H-pyran. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.48 (d, 2H, $^3$$J$ = 7.2 Hz, CH-phenyl), 7.20−7.30 (m, 3H, CH-phenyl), 5.21 (t, 1H, $^3$$J$ = 5.2 Hz, CH-THP), 4.16−4.20 (m, 1H, CH$_2$O-THP), 3.57−3.60 (m, 1H, CH$_2$O-THP). 2.00−2.05 (m, 1H, CH$_2$-THP), 1.81−1.86 (m, 2H, CH$_2$-THP), 1.62 (m, 3H, CH$_2$-THP) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 135.5, 130.8, 128.8, 126.7, 85.2, 64.5, 31.6, 25.6, 21.7 ppm.

1(2)-(Tetrahydro-2H-pyran-2-yl)-1(2)H-1,2,3-benzotriazole. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.05 (d, 1H, $^3$$J$ = 8.4 Hz, CH-phenyl), 7.87−7.90 (m, 2H, CH-phenyl), 7.73 (d, 1H, $^3$$J$ = 8.8 Hz, CH-phenyl), 7.47 (t, 1H, $^3$$J$ = 6.8 Hz, CH-phenyl), 7.34−7.44 (m, 2H, CH-phenyl), 6.02 (dd, 1H, $^3$$J$ = 8.4 Hz, $^3$$J$ = 3.2 Hz, CH-THP), 3.90−3.95 (m, 1H, CH$_2$O-THP), 3.74−3.82 (m, 1H, CH$_2$O-THP), 2.56−2.65 (m, 1H, CH$_2$-THP), 2.16−2.24 (m, 2H, CH$_2$-THP), 1.71−1.88 (m, 3H, CH$_2$-THP) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 146.3, 144.2, 132.5, 127.6, 127.0, 124.4, 119.8, 118.6, 111.2, 90.8, 85.8, 67.6, 67.0, 30.0, 29.4, 24.9, 24.8, 21.7, 21.5 ppm.

1(2)-(Tetrahydro-2H-pyran-2-yl)-1(2)H-1,2,3-triazole. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.69 (s, 1H, 4-H-triazole), 7.62 (s, 1H, 5-H-triazole), 7.58 (s, 2H, 4-H-triazole and 5-H-triazole), 5.62−5.66 (m, 1H, CH-THP), 3.88−3.94 (m, 1H, CH$_2$O-THP), 3.61−3.67 (m, 1H, CH$_2$O-THP), 2.28−2.40 (m, 1H, CH$_2$-THP), 1.92−2.10 (m, 2H, CH$_2$-THP), 1.53−1.68 (m, 3H, CH$_2$-THP) ppm.

4-Nitro-1-(tetrahydro-2H-pyran-2-yl)-1H-pyrazole. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.35 (s, 1H, 5-H-pz), 8.08 (s, 1H, 3-H-pz), 5.39 (dd, 1H, $^3$$J$ = 9.2 Hz, $^3$$J$ = 2.6 Hz, CH-THP), 4.05−4.09 (m, 1H, CH$_2$O-THP), 3.69−3.75 (m, 1H, CH$_2$O-THP), 2.11−2.17 (m, 1H, CH$_2$-THP), 1.64−2.04 (m, 5H, CH$_2$-THP) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 135.6, 127.1, 88.5, 67.9, 30.7, 24.8, 21.8 ppm. HRMS (ESI-TOF) m/z: [M + Na]$^+$ caleld for C$_{8}$H$_{11}$N$_{3}$NaO$_3$ 220.0692; found 220.0711.

2-Phenoxynitro-tetrahydro-2H-pyran. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.27−7.31 (m, 2H, CH-phenyl), 7.06−7.08 (m, 2H, CH-phenyl). 5.44 (t, 1H, $^3$$J$ = 3.3 Hz, CH-THP), 3.91−3.94 (m, 1H, CH$_2$O-THP), 3.60−3.63 (m, 1H, CH$_2$O-THP), 1.99−2.03 (m, 1H, CH$_2$-THP), 1.80−1.90 (m, 2H, CH$_2$-THP), 1.50−1.78 (m, 3H, CH$_2$-THP) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 157.1, 129.2, 121.4, 116.4, 96.2, 61.8, 30.4, 25.3, 18.8 ppm.

1(2)-(Tetrahydro-2H-pyran-2-yl)-1(2)H-1,2,4-triazole. $^1$H NMR (400 MHz, CDCl$_3$): 8.21 (s, 1H, 5-H-triazole), 8.08 (s, 2H, 3-H-triazole and 5-H-triazole), 7.87 (s, 1H, 3-H-triazole), 5.38
(dd, 1H, \(^3J = 8.8\) Hz, \(^3J = 4.4\) Hz, CH-THP), 3.95–3.99 (m, 1H, CH\(_2\)-O-THP), 3.58–3.65 (m, 1H, CH\(_2\)-O-THP), 1.88–2.05 (m, 3H, CH\(_2\)-THP), 1.52–1.64 (m, 3H, CH\(_2\)-THP) ppm.

2-(Decylthio)tetrahydro-2H-pyran. \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 4.90–4.83 (m, 1H, CH-THP), 4.04–4.09 (m, 1H, CH\(_2\)-O-THP), 3.45–3.51(m, 1H, CH\(_2\)-O-THP), 2.43–2.7 (m, 2H, SCH\(_2\)), 1.52–1.95 (m, 6H, CH\(_2\)-THP), 1.20–1.40 (m, 16H, CH\(_2\)(CH\(_2\))\(_4\)CH\(_2\)), 0.85 (t, 3H, \(^3J = 6.6\) Hz, CH\(_2\)) ppm. \(^13\)C NMR (100 MHz, CDCl\(_3\)): δ 94.7, 64.7, 31.9, 31.5, 30.4, 30.0, 29.64, 29.61, 29.40, 29.3, 29, 25.7, 22.7, 21.9, 14.2 ppm.

4-Chloro-1-(tetrahydro-2H-pyran-2-yl)-1H-pyrazole. \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.61 (s, 1H, 3-H-pz), 7.48 (s, 1H, 3-H-pz), 5.31–5.33 (m, 1H, CH-THP), 3.99–4.02 (m, 1H, CH\(_2\)-O-THP), 3.64–3.69 (m, 1H, CH\(_2\)-O-THP), 1.99–2.09 (m, 3H, CH\(_2\)-THP), 1.59–1.65 (m, 3H, CH\(_2\)-THP) ppm.

1-(Tetrahydro-2H-pyran-2-yl)-1H-benzimidazole. \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 8.06 (s, 1H, CH-imidazole), 7.77–7.79 (m, 1H, CH-phenyl), 7.50–7.52 (m, 1H, CH-phenyl), 7.26–7.31 (m, 2H, CH-phenyl), 5.48 (dd, 1H, \(^3J = 9.6\) Hz, \(^3J = 2.0\) Hz, CH-THP), 4.10–4.12 (m, 1H, CH\(_2\)-O-THP), 3.71–3.77 (m, 1H, CH\(_2\)-O-THP), 2.08–2.21 (m, 3H, CH\(_2\)-THP), 1.68–1.81 (m, 3H, CH\(_2\)-THP) ppm.

3,5-Diphenyl-1-(tetrahydro-2H-pyran-2-yl)-1H-pyrazole. \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.88 (d, 2H, \(^3J = 8.4\) Hz, CH-phenyl), 7.58 (d, 2H, \(^3J = 8.0\) Hz, CH-phenyl), 7.27–7.5 (m, 6H, CH-phenyl), 6.64 (s, 1H, 4-H-pz), 5.22 (dd, 1H, \(^3J = 10.2\) Hz, \(^3J = 2.2\) Hz, CH-THP), 4.16–4.18 (m, 1H, CH\(_2\)-O-THP), 3.62 (t, 1H, \(^3J = 11.7\) Hz, CH\(_2\)-O-THP), 2.65–2.74 (m, 1H, CH\(_2\)-THP), 2.07–2.10 (m, 1H, CH\(_2\)-THP), 1.54–1.88 (m, 4H, CH\(_2\)-THP) ppm. \(^13\)C NMR (100 MHz, CDCl\(_3\)): δ 151.2, 145.6, 133.5, 130.6, 129.1, 128.8, 127.8, 126.0, 103.9, 84.5, 67.7, 30.3, 24.7, 22.2 ppm. HRMS (ESI-TOF) m/z: [M + Na]\(^+\) calc for C\(_8\)H\(_{11}\)ClN\(_2\)NaO 209.0452; found 209.0454.

1-(Tetrahydro-2H-pyran-2-yl)-1(2H)-indazole. \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 8.15 (s, 1H, 5-H-pz), 8.03 (s, 1H, 3-H-pz), 7.71–7.73 (m, 1H, CH-phenyl), 7.58–7.6 (m, 1H, CH-phenyl), 7.37–7.41 (m, 1H, CH-phenyl), 7.52 (dd, 1H, \(^3J = 9.6\) Hz, \(^3J = 2.4\) Hz, CH-THP), 4.01–4.05 (m, 1H, CH\(_2\)-O-THP), 3.72–3.78 (m, 1H, CH\(_2\)-O-THP), 2.54–2.63 (m, 1H, CH\(_2\)-THP), 2.06–2.18 (m, 2H, CH\(_2\)-THP), 1.50–1.82 (m, 3H, CH\(_2\)-THP) ppm.

1-(Tetrahydro-2H-pyran-2-yl)-1H-imidazole. \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.57 (d, 1H, \(^3J = 2.4\) Hz, 5-H-pz), 7.52 (d, 1H, \(^3J = 1.6\) Hz, 3-H-pz), 6.26 (t, 1H, \(^3J = 2\) Hz, 4-H-pz), 5.36 (dd, 1H, \(^3J = 0.6\) Hz, \(^3J = 2.4\) Hz, CH-THP), 4.00–4.04 (m, 1H, CH\(_2\)-O-THP), 3.63–3.69 (m, 1H, CH\(_2\)-O-THP), 1.97–2.13 (m, 3H, CH\(_2\)-THP), 1.48–1.69 (m, 3H, CH\(_2\)-THP) ppm.
(m, 3H, CH2-THP), 1.48–1.66 (m, 3H, CH2-THP) ppm. $^{13}$C NMR (100 MHz, CDCl3): δ 135.6, 129.1, 117.0, 100.8, 67.9, 31.5, 24.8, 22.5 ppm.

3(5)-Methyl-1-(tetrahydro-2H-pyran-2-yl)-1H-pyrazole. $^1$H NMR (400 MHz, CDCl3): δ 7.45 (d, 1H, $^3$J = 2.2 Hz, 5-H-pz), 7.42 (s, 1H, 3-H-pz), 6.05 (d, 1H, $^3$J = 2.2 Hz, 4-H-pz), 6.02 (d, 1H, $^3$J = 0.8 Hz, 4-H-pz), 5.25 (td, 1H, $^3$J = 7.7 Hz, $^3$J = 2.2 Hz, CH-THP), 3.63–3.69 (m, 1H, CH2O-THP), 3.60–3.63 (m, 1H, CH2O-THP), 2.41–2.50 (m, 1H, CH2-THP), 2.32 (s, 3H, CH3), 2.27 (s, 3H, CH3), 2.05–2.12 (m, 1H, CH2-THP), 1.92–2.03 (m, 2H, CH2-THP), 1.51–1.71 (m, 3H, CH2-THP) ppm. $^{13}$C NMR (100 MHz, CDCl3): δ 149.2, 139.1, 139.0, 128.4, 106.2, 105.8, 87.5, 84.4, 68.1, 67.8, 30.5, 29.4, 25.1, 25.0, 22.88, 22.82, 13.7, 10.98 ppm.

4-Octyl-1-(tetrahydro-2H-pyran-2-yl)-1H-pyrazole. $^1$H NMR (400 MHz, CDCl3): δ 7.36 (s, 2H, 3-H-pz and 5-H-pz), 5.30 (dd, 1H, $^3$J = 10.0 Hz, $^3$J = 2.4 Hz, CH-THP), 4.02–4.06 (m, 1H, CH2O-THP), 3.63–3.70 (m, 1H, CH2O-THP), 2.42 (t, 2H, $^3$J = 11.6 Hz, CH2(CH2)6CH3), 2.00–2.12 (m, 3H, CH2-THP), 1.49–1.72 (m, 5H, CH2-THP, CH2C(CH2)5CH3), 1.24–1.30 (m, 10H, CH2CH2(CH2)5CH3), 0.86 (t, 3H, $^3$J = 6.8 Hz, (CH2)7CH3) ppm. $^{13}$C NMR (100 MHz, CDCl3): δ 139.5, 125.6, 122.6, 87.6, 67.9, 32.0, 30.9, 30.5, 29.4, 25.1, 24.3, 22.8, 14.2 ppm. HRMS (ESI-TOF) m/z: [M + Na]+ calcd for C16H28N2NaO 287.2093; found 287.2083.

3,5-Dimethyl-1-(tetrahydro-2H-pyran-2-yl)-1H-pyrazole. $^1$H NMR (400 MHz, CDCl3): δ 5.79 (s, 1H, 4-H-pz), 5.11 (dd, 1H, $^3$J = 10.0 Hz, $^3$J = 2.0 Hz, CH-THP), 3.99–4.04 (m, 1H, CH2O-THP), 3.56–3.62 (td, 1H, $^3$J = 11.6 Hz, $^3$J = 2.8 Hz, CH2O-THP), 2.36–2.46 (m, 1H, CH2-THP), 2.24 (s, 3H, CH3), 2.18 (s, 3H, CH3), 2.01–2.05 (m, 1H, CH2-THP ), 1.84–1.89 (m, 1H, CH2-THP), 1.49–1.72 (m. 3H, CH2-THP) ppm. $^{13}$C NMR (100 MHz, CDCl3): δ 148.4, 139.9, 106.3, 84.4, 68.1, 29.7, 25.1, 23.2, 13.7, 10.9 ppm. HRMS (ESI-TOF) m/z: [M + Na]+ calcd for C10H16N2NaO 203.1154; found 203.1178.

N-(Tetrahydro-2H-pyran-2-yl)benzamide. $^1$H NMR (400 MHz, CDCl3): δ 7.76–7.81 (m, 2H, CH-phenyl), 7.41–7.53 (m, 3H, CH-phenyl), 6.60 (br, 1H, $^3$J = 7.3 Hz, NH), 5.30 (t, 1H, $^3$J = 8.4 Hz, CH-THP), 4.01 (d, 1H, $^3$J = 11.0 Hz, CH2O-THP), 3.63–3.69 (m, 1H, CH2O-THP), 1.41–1.95 (m, 6H, CH2-THP) ppm. $^{13}$C NMR (100 MHz, CDCl3): δ 166.8, 131.8, 129.2, 127.2, 127, 78.4, 66.2, 29.9, 22.0 ppm.

2-Butoxytetrahydro-2H-pyran. $^1$H NMR (400 MHz, CDCl3): δ 4.52 (m, 1H, CH-THP), 3.80–3.83 (m, 1H, CH2O-THP), 3.65–3.75 (m, 1H, OCH2), 3.45–3.51(m, 1H, CH2O-THP), 3.33–3.40 (m, 1H, OCH2), 1.48–1.90 (m, 8H, CH2-THP, OCH2CH2), 1.30–1.40 (m, 2H, CH2CH2CH3), 0.88 (t, 3H, $^3$J = 7.7 Hz, CH3) ppm. $^{13}$C NMR (100 MHz, CDCl3): δ 98.9, 67.4, 62.3, 31.9, 30.8, 25.6, 19.7, 19.5, 14.0 ppm.
Figure S1. $^1$H NMR spectrum of tetrahydro-2H-pyran-2-yl benzoate.

Figure S2. $^1$H NMR spectrum of tetrahydro-2H-pyran-2-yl stearate.
Figure S3. $^{13}$C NMR spectrum of tetrahydro-2$H$-pyran-2-yl stearate.

Figure S4. $^1$H NMR spectrum of 2-(phenylthio)tetrahydro-2$H$-pyran.
**Figure S5.** $^1$H NMR spectrum of 1-(tetrahydro-2H-pyran-2-yl)-1H-1,2,3-benzotriazole (82%) and 2-(tetrahydro-2H-pyran-2-yl)-2H-1,2,3-benzotriazole (18%).

**Figure S6.** $^1$H NMR spectrum of 1-(tetrahydro-2H-pyran-2-yl)-1H-1,2,3-triazole (22%) and 2-(tetrahydro-2H-pyran-2-yl)-2H-1,2,3-triazole (78%).
Figure S7. $^1$H NMR spectrum of 4-nitro-1-(tetrahydro-2$H$-pyran-2-yl)-1$H$-pyrazole.

Figure S8. $^1$H NMR spectrum of 2-phenoxytetrahydro-2$H$-pyran.
Figure S9. $^1$H NMR spectrum of 1-(tetrahydro-2H-pyran-2-yl)-1H-1,2,4-triazole (87%) and 4-(tetrahydro-2H-pyran-2-yl)-4H-1,2,4-triazole (13%).

Figure S10. $^1$H NMR spectrum of 2-(decylthio)tetrahydro-2H-pyran.
Figure S11. $^1$HNMR spectrum of 4-chloro-1-(tetrahydro-$2H$-pyran-2-yl)-$1H$-pyrazole (100%).

Figure S12. $^{13}$C NMR spectrum of 4-chloro-1-(tetrahydro-$2H$-pyran-2-yl)-$1H$-pyrazole.
Figure S13. $^1$H NMR spectrum of 4-bromo-1-(tetrahydro-2$H$-pyran-2-yl)-1$H$-pyrazole.

Figure S14. $^1$H NMR spectrum of 1-(tetrahydro-2$H$-pyran-2-yl)-1$H$-benzimidazole.
**Figure S15.** $^1$HNMR spectrum of 3,5-diphenyl-1-(tetrahydro-2H-pyran-2-yl)-1H-pyrazole.

**Figure S16.** $^{13}$C NMR spectrum of 3,5-diphenyl-1-(tetrahydro-2H-pyran-2-yl)-1H-pyrazole.
Figure S17. $^1$H NMR spectrum of 1-(tetrahydro-2H-pyran-2-yl)-1H-indazole (5%) and 2-(tetrahydro-2H-pyran-2-yl)-2H-indazole (95%).

Figure S18. $^1$H NMR spectrum of 1-(tetrahydro-2H-pyran-2-yl)-1H-pyrazole.
Figure S19. $^1$H NMR spectrum of 1-(tetrahydro-2H-pyran-2-yl)-1H-imidazole.

Figure S20. $^1$H NMR spectrum of 3(5)-methyl-1-(tetrahydro-2H-pyran-2-yl)-1H-pyrazole.
Figure S21. $^1$H NMR spectrum of 4-octyl-1-(tetrahydro-2H-pyran-2-yl)-1H-pyrazole.

Figure S22. $^{13}$C NMR spectrum of 4-octyl-1-(tetrahydro-2H-pyran-2-yl)-1H-pyrazole.
Figure S23. $^1$H NMR spectrum of 3,5-dimethyl-1-(tetrahydro-2H-pyran-2-yl)-1H-pyrazole.

Figure S24. $^{13}$C NMR spectrum of 3,5-dimethyl-1-(tetrahydro-2H-pyran-2-yl)-1H-pyrazole.
Figure S25. $^1$H NMR spectrum of N-(tetrahydro-2H-pyran-2-yl)benzamide.

![NMR spectrum](image)