Supporting Information:

Direct N-Cyclopropylation of Secondary Acyclic Amides Promoted by Copper

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I - General experimental methods

All reactions were carried out in Carousel Thermo-Fischer tubes (40 mL). Sand was added in the holes where tubes are inserted until the top of the hole. The temperature was checked by inserting the thermometer in sand. The reaction was stirred at 800 rpm.

Pyridine was distilled under CaH₂ and kept over KOH under nitrogen. Toluene was distilled over Na⁰/benzophenone then kept over Na⁰ under nitrogen. Commercial amides and cesium carbonate (Aldrich, 99.9%) were used without purification. They were crushed, dried at 150 °C for 2 hours then stored in the presence of P₄O₁₀ in a bench-top dessicator under vacuum at room temperature. Pinacolic ester of cyclopropylboronic acid (Borochem, 95+%%) and copper (II) acetate (Alfa Aesar, 99.999% trace metal basis) were used without further purification. Dry air was obtained by passing air through silica gel (200 mL), then molecular sieves (200 mL) and silica gel (200 mL). All the reagents were weighed in the air.

Column chromatography was performed with SDS 60 Å C.C silica gel (35-70 μm). Thin layer chromatography was carried out using Merck silica gel 60 F₂₅₄ plates.

All products were characterized by their NMR, GC/MS spectra. NMR spectra were recorded at 20°C on a Brüker AC 400 MHz working respectively at 400 MHz for \(^1\)H and 100 MHz for \(^{13}\)C. \(^1\)H NMR and \(^{13}\)C NMR spectra were recorded in CDCl₃ (unless otherwise stated). Chemical shifts for \(^1\)H spectra are values from CDCl₃ (δ 7.26) or DMSO (δ 2.50). Chemical shifts for \(^{13}\)C spectra are values from CDCl₃ (δ 77.16) or DMSO (δ 39.52). \(^1\)H NMR spectra are reported as follows: chemical shift (ppm), multiplicity (br: broad; s: singlet; d: doublet; t: triplet; q: quadruplet; m: multiplet), coupling constants (Hz) and integration. Gas chromatography - mass spectra (GC/MS) were recorded on an Agilent Technologies 6890 N instrument with an Agilent 5973 N mass detector (EI) and a HP5-MS 30 m x 0.25 mm capillary apolar column (Stationary phase: 5 % diphenyldimethylpolysiloxane film, 0.25 μm). GC/MS method: Initial temperature: 45°C; Initial time: 2 min; Ramp: 2°C/min until 50°C then 10 °C/min; Final temperature: 250°C; Final time: 10 min. HPLC were recorded on a Shimadzu LC-20AD instrument with Shimadzu SPD-M20A detector and a Supelco analytical apolar column (15 cmx4.6 mm, 5 μm). HPLC method: Gradient: 20% MeCN + 1% TFA, 80% water + 1% TFA to 90% MeCN + 1% TFA, 10% water + 1% TFA in 20 min. HRMS were recorded on a JEOL JMS-DX300 spectrometer (3 keV, xenon) in a m-nitrobenzylalcohol matrix. Melting points were obtained on a Büchi B-540 melting point apparatus and are uncorrected. All the compounds, unless specified, are new and fully described in the characterization section.
II – Typical procedures

II-1 Typical procedure for the preparation of compounds 1b, 1d, 1g-j and 4c

(Procedure A)

Benzoyl chloride (2.4 mmol, 1.2 equiv.) was added to a solution of aniline (2.0 mmol, 1.0 equiv.) and triethylamine (3.0 mmol, 1.5 equiv.) in dichloromethane (2 mL, 1M) at 0 °C under nitrogen. The reaction was run at 40 °C until all the aniline was consumed (TLC). Dichloromethane was added then a saturated aqueous solution of NaHCO₃. The phases were separated and the organic layer was extracted three times with dichloromethane. Organic layers were gathered, washed with brine and the organic phases were separated. Organic phase was dried over MgSO₄, filtered then concentrated. The crude mixture obtained was crystallized using heptanes/ethyl acetate. Solids obtained were filtered, rinsed with heptane and dried under vacuum.

II-2 Typical procedure for the preparation of compound 1c

4-methoxybenzoyl chloride (2.2 mmol, 1.1 equiv.) was added to a suspension of aniline (2.0 mmol, 1.0 equiv.), and sodium dicarbonate (6.0 mmol, 3.0 equiv.) in dichloromethane (12 mL, 0.16 M) at 0 °C under nitrogen. The reaction was run at 40 °C during 1 h. Dichloromethane was added then a saturated aqueous solution of NaHCO₃. The phases were separated and the organic layer was extracted three times with dichloromethane. Organic layers were gathered, washed with brine and the organic phases were separated. Organic phase was dried over MgSO₄, filtered then concentrated. The crude mixture obtained was crystallized using heptanes/ethyl acetate. Solids obtained were filtered, rinsed with heptane and dried under vacuum to furnish pure 1c as white crystals (309 mg, 68%).

II-3 Typical procedure for the preparation of compound 1e

2-chlorobenzoyl chloride (2.2 mmol, 1.1 equiv.) was added to a solution of aniline (2.0 mmol, 1.0 equiv.), pyridine (2.2 mmol, 1.1 equiv.) and DMAP (2.2 mmol, 1.1 equiv.) in dichloromethane (5 mL, 0.4 M) at 0 °C under nitrogen. The reaction was run at 40 °C during 15 h. Dichloromethane was added then a saturated aqueous solution of NaHCO₃. The phases were separated and the organic layer was extracted three times with dichloromethane. Organic layers were gathered, washed with brine and the organic phases were separated. Organic phase was dried over MgSO₄, filtered then concentrated. The crude mixture obtained was crystallized using heptanes/ethyl acetate. Solids obtained were filtered, rinsed with heptane and dried under vacuum to furnish pure 1e as white crystals (374 mg, 81%).

2 Gabbutt, C. D.; Heron, B. M.; Instone, A. C. Heterocycles 2003, 60, 843.
II-4 Typical procedure for the preparation of compound 1f

Benzoyl chloride (2.1 mmol, 1.05 equiv.) was added to a solution of 4-fluoroaniline (2.0 mmol, 1.0 equiv.) and triethylamine (2.1 mmol, 1.05 equiv.) in ethylacetate (5 mL, 0.4 M) at 0 °C under nitrogen. The reaction was run at 40 °C during 4 h. Ethylacetate was added then a saturated aqueous solution of NaHCO₃. The phases were separated and the organic layer was extracted three times with ethylacetate. Organic layers were gathered, washed with brine and the organic phases were separated. Organic phase was dried over MgSO₄, filtered then concentrated. The crude mixture obtained was crystallized using heptanes/ethyl acetate. Solids obtained were filtered, rinsed with heptane and dried under vacuum to furnish pure 1f as beige crystals (228 mg, 53%).

II-5 Typical procedure for the preparation of compounds 3a-j and 5a-j (Procedure B)

An oven-dried (120 °C) Thermo-Fischer tube (Carousel) equipped with a magnetic stirring bar was cool-down under vacuum then back-filled with dry air. Tube was charged with amide (0.2 mmol, 1.0 equiv.), Cu(OAc)₂ (0.2 mmol, 1.0 equiv.) and Cs₂CO₃ (0.1 mmol, 0.5 equiv.). The tube was evacuated then back-filled with dry air three times with stirring (400 rpm). Pyridine (0.6 mmol, 3.0 equiv.) the pinacolic ester of cyclopropylboronic acid (0.4 mmol, 2.0 equiv.) and toluene (0.4 mL, 0.5M) were added (no stirring). The tube was sealed, stirred (800 rpm) and heated to 110 °C for 24 h. After cooling to room temperature, 20 ml of dichloromethane were added. The organic phase was washed twice with water (20 mL). Gathered aqueous phases were extracted with dichloromethane (20 mL) for three times. Organic layers were gathered, dried over MgSO₄, filtered and concentrated under vacuum to furnish the crude product (a small sample of the crude was analyzed by HPLC). The obtained crude was purified by silica gel chromatography using heptanes/ethyl acetate as eluent.

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II- Characterization of compounds 1b-j, 3a-j, 4c and 5a-h

4-fluoro-N-phenylbenzamide (1b) was obtained by procedure A from 4-fluorobenzoyl chloride (2.4 mmol, 1.2 equiv.) and aniline (2.0 mmol, 1.0 equiv.) as white crystals (86 mg, 20%).

$^1H$ NMR (400 MHz, CDCl$_3$) $\delta$: 7.15-7.19 (m, 3H, CH$_{ar}$), 7.36-7.40 (m, 2H, CH$_{ar}$), 7.61-7.63 (m, 2H, CH$_{ar}$), 7.74 (bs, 1H, NH), 7.87-7.91 (m, 2H, CH$_{ar}$); $^{13}C$ NMR (100 MHz, DMSO) 115.2, 115.4, 120.4, 123.7, 128.6, 130.3 and 130.4 (CH$_{ar}$), 131.4 (d), 139.1, 162.8 and 164.4 (C$_q$$_{ar}$), 165.3 (C=O). m.p. 185-187 °C (Lit. 180-181 °C)$^4$; GC/MS: r.t. = 22.1 min., M/Z = 215; HRMS calculated for C$_{13}$H$_{11}$NOF (M+H$^+$) 216.0825, found 216.0828.

4-methoxy-N-phenylbenzamide (1c) (white crystals, 309 mg, 68%).

$^1H$ NMR (400 MHz, CDCl$_3$) $\delta$: 3.87 (s, 3H, OMe), 6.96-6.98 (m, 2H, CH$_{ar}$), 7.12-7.16 (m, 1H, CH$_{ar}$), 7.34-7.38 (m, 2H, CH$_{ar}$), 7.62-7.64 (m, 2H, CH$_{ar}$), 7.76 (bs, 1H, NH), 7.83-7.85 (m, 2H, CH$_{ar}$); $^{13}C$ NMR (100 MHz, CDCl$_3$) $\delta$: 55.6 (CH$_3$), 114.1, 120.3, 124.5, 129.0 and 129.2 (CH$_{ar}$), 127.3, 138.2 and 162.6 (C$_q$$_{ar}$), 165.3 (C=O). m.p. 172-173 °C (Lit. 173-174 °C)$^4$; GC/MS: r.t. = 25.5 min., M/Z = 227; HRMS calculated for C$_{14}$H$_{14}$NO$_2$ (M+H$^+$) 228.1025, found 228.1015.

4-chloro-N-phenylbenzamide (1d) was obtained by procedure A from 4-chlorobenzoyl chloride (2.4 mmol, 1.2 equiv.) and aniline (2.0 mmol, 1.0 equiv.) as beige crystals (139 mg, 30%).

$^1H$ NMR (400 MHz, DMSO) $\delta$: 7.11 (t, J = 8 Hz, 1H, CH$_{ar}$), 7.36 (t, J = 8 Hz, 1H, CH$_{ar}$), 7.61 (d, J = 8 Hz, 2H, CH$_{ar}$), 7.76 (d, J = 8 Hz, 2H, CH$_{ar}$), 7.98 (d, J = 8 Hz, 2H, CH$_{ar}$); $^{13}C$ NMR (100 MHz, DMSO) $\delta$: 120.4, 123.9, 128.5, 128.7 and 129.7 (CH$_{ar}$), 133.7, 136.4 and 139.0 (C$_q$$_{ar}$), 164.5 (C=O). m.p. 197-198 °C (Lit. 199-200 °C)$^4$; GC/MS: r.t. = 25.5 min., M/Z = 231; HRMS calculated for C$_{13}$H$_{11}$NOCl (M+H$^+$) 232.0529, found 232.0521.

2-chloro-N-phenylbenzamide (1e) was obtained by procedure A from 2-chlorobenzoyl chloride (2.4 mmol, 1.2 equiv.) and aniline (2.0 mmol, 1.0 equiv.) as white crystals (374 mg, 81%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.16-7.20 (m, 1H, CH$_{ar}$), 7.36-7.47 (m, 5H, CH$_{ar}$), 7.64-7.66 (m, 2H, CH$_{ar}$), 7.77 (dd, $J = 1.8$ and 7.4 Hz, 1H, CH$_{ar}$), 7.88 (bs, 1H, NH); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 120.3, 124.9, 129.1, 130.2, 130.4 and 131.6 (CH$_{ar}$), 130.7, 135.4 and 137.7 (C$_q$ ar), 164.8 (C=O). m.p. 115-117 °C; GC/MS: r.t. = 22.9 min., M/Z = 231; HRMS calculated for C$_{13}$H$_{11}$NOCl (M+H$^+$) 232.0529, found 232.0521.

$^{N-}(4$-fluorophenyl)benzamide (1f) (beige crystals, 228 mg, 53%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.05-7.09 (m, 2H, CH$_{ar}$), 7.48-7.51 (m, 2H, CH$_{ar}$), 7.54-7.62 (m, 3H, CH$_{ar}$), 7.82 (bs, 1H, NH), 7.85-7.88 (m, 2H, CH$_{ar}$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 115.8, 116.0, 122.2, 122.3, 127.1, 129.0 and 132.1 (CH$_{ar}$), 134.0 and 134.9 (C$_q$ ar), 160.7 (C=O). m.p. 181-183 °C (Lit. 184-185 °C); GC/MS: r.t. = 22.2 min., M/Z = 215; HRMS calculated for C$_{13}$H$_{11}$NOF (M+H$^+$) 216.0825, found 216.0817.

$^{N-}(3$-fluorophenyl)benzamide (1g) was obtained by procedure A from benzyol chloride (2.4 mmol, 1.2 equiv.) and 3-fluoroaniline (2.0 mmol, 1.0 equiv.) as beige oil (344 mg, 80%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.80-7.60 (m, 3H, CH$_{ar}$ and NH), 7.48-7.51 (m, 2H, CH$_{ar}$), 7.54-7.62 (m, 3H, CH$_{ar}$), 7.25-7.19 (m, 2H, CH$_{ar}$), 6.81-6.76 (m, 1H, CH$_{ar}$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 107.6, 111.2, 111.4, 115.3, 127.0, 128.9, 130.2, 132.1, 134.6, 139.4, 161.8, 164.3, 165.7.

$^{N-}(2$-fluorophenyl)benzamide (1h) was obtained by procedure A from benzyol chloride (2.4 mmol, 1.2 equiv.) and 2-fluoroaniline (2.0 mmol, 1.0 equiv.) as white crystals (357 mg, 83%).

$^1$H NMR (400 MHz, CDCl$_3$) δ: 7.07-7.22 (m, 3H, CH$_{ar}$), 7.50-7.60 (m, 3H, CH$_{ar}$), 7.89-7.91 (m, 2H, CH$_{ar}$), 8.07 (s, 1H, NH), 8.48 (dd, J = 1.6 and 8.4 Hz, 1H, CH$_{ar}$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 114.9, 115.0, 121.9, 124.6, 124.8, 129.0 and 132.3 (CH$_{ar}$), 126.6, 126.7, 134.7, 151.7 and 154.0 (C$_q$ ar), 165.6 (C=O). m.p. 112-113 °C (Lit. 108-109 °C)$^6$; GC/MS: r.t. = 20.9 min., M/Z = 215; HRMS calculated for C$_{13}$H$_{11}$NOF (M+H+) 216.0825, found 216.0824.

N-(2-chlorophenyl)benzamide (1i) was obtained by procedure A from benzoyl chloride (2.4 mmol, 1.2 equiv.) and 2-chloroaniline (2.0 mmol, 1.0 equiv.) as white crystals (305 mg, 66%).

$^1$H NMR (400 MHz, CDCl$_3$) δ: 7.09 (td, J = 1.2 and 7.8 Hz, 1H, CH$_{ar}$), 7.32-7.36 (m, 1H, CH$_{ar}$), 7.42 (dd, J = 1.6 and 8.0 Hz, 1H, CH$_{ar}$), 7.51-7.55 (m, 2H, CH$_{ar}$), 7.57-7.61 (m, 1H, CH$_{ar}$), 7.92-7.94 (m, 2H, CH$_{ar}$), 8.46 (bs, 1H, NH), 8.48 (dd, J = 1.6 and 8.2 Hz, 1H, CH$_{ar}$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 121.6, 124.9, 127.2, 128.0, 129.1, 129.2 and 132.3 (CH$_{ar}$), 123.1, 134.8 and 134.9 (C$_q$ ar), 165.4 (C=O). m.p. 103-104 °C; GC/MS: r.t. = 22.1 min., M/Z = 231; HRMS calculated for C$_{13}$H$_{11}$NOCl (M+H+) 232.0529, found 232.0531.

N-(4-methoxyphenyl)benzamide (1j) was obtained by procedure A from benzoyl chloride (2.4 mmol, 1.2 equiv.) and 4-methoxyaniline (2.0 mmol, 1.0 equiv.) as white crystals (313 mg, 69%).

$^1$H NMR (400 MHz, CDCl$_3$) δ: 3.82 (s, 3H, OCH$_3$), 6.90-6.92 (m, 2H, CH$_{ar}$), 7.46-7.50 (m, 2H, CH$_{ar}$), 7.53-7.55 (m, 3H, CH$_{ar}$), 7.74 (s, 1H, NH), 7.85-7.87 (m, 2H, CH$_{ar}$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 55.7 (OCH$_3$), 114.4, 122.2, 127.1, 128.9 and 131.8 (CH$_{ar}$), 131.2 and 135.2 (C$_q$ ar), 156.8 (C=O). m.p. 157-158 °C (Lit. 154-155 °C)$^6$; GC/MS: r.t. = 25.8 min., M/Z = 227; HRMS calculated for C$_{14}$H$_{14}$NO$_2$ (M+H+) 228.1025, found 228.1015.

N-cyclopropyl-N-phenylbenzamide (3a) was obtained by procedure B from commercial benzanilide (0.2 mmol, 1.0 equiv.) as beige oil (44 mg, 93%).

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1H NMR (400 MHz, CDCl₃) δ: 0.49-0.51 (m, 2H, CH₂-propyl), 0.77-0.79 (m, 2H, CH₂-propyl), 3.19-3.23 (m, 1H, CH₃-propyl), 6.94-6.97 (m, 2H, CH₉t), 7.08-7.11 (m, 8H, CH₉t); 13C NMR (100 MHz, CDCl₃) δ: 8.1 (CH₂-propyl), 32.4 (CH₃-propyl), 126.7, 127.7, 128.1, 128.2, 128.8, 129.4 (CH₉t), 136.9, 142.2 (C₉q), 172.1 (C=O); HRMS calculated for C₁₆H₁₅NO (M+H+) 238.1232, found 238.1230.

N-cyclopropyl-4-fluoro-N-phenylbenzamide (3b) was obtained by procedure B from amide 1b (0.2 mmol, 1.0 equiv.) as beige crystals (37 mg, 72%).

1H NMR (400 MHz, CDCl₃) δ: 0.49-0.53 (m, 2H, CH₂-propyl), 0.78-0.83 (m, 2H, CH₂- propyl), 3.17-3.23 (m, 1H, CH₃-propyl), 6.77-6.82 (m, 2H, CH₉t), 6.91-6.96 (m, 2H, CH₉t), 7.09-7.13 (m, 1H, CH₉t), 7.15-7.20 (m, 2H, CH₉t), 7.22-7.28 (m, 2H, CH₉t); 13C NMR (100 MHz, CDCl₃) δ: 8.1 (CH₂- propyl), 32.6 (CH₃-propyl), 114.8, 115.0, 127.0, 128.4, 129.1, 130.7 and 130.8 (CH₉t), 133.0 (d, C-F), 133.1, 142.3 (C₉q), 171.1 (C=O); m.p. 48-49 °C; GC/MS: r.t. = 17.7 min., M/Z = 255; HRMS calculated for C₁₆H₁₄NOF (M+H+) 256.1138, found 256.1129.

N-cyclopropyl-4-methoxy-N-phenylbenzamide (3c) was obtained by procedure B from amide 1c (0.2 mmol, 1.0 equiv.) as beige oil (47 mg, 90%).

1H NMR (400 MHz, CDCl₃) δ: 0.49-0.53 (m, 2H, CH₂- propyl), 0.77-0.83 (m, 2H, CH₂- propyl), 3.15-3.21 (m, 1H, CH₃-propyl), 3.68 (s, 3H, OCH₃), 6.60-6.62 (m, 2H, CH₉t), 6.95-6.97 (m, 2H, CH₉t), 7.07-7.12 (m, 1H, CH₉t), 7.16-7.24 (m, 4H, CH₉t); 13C NMR (100 MHz, CDCl₃) δ: 8.2 (CH₂-propyl), 32.7 (CH₃-propyl), 55.3 (OCH₃), 113.1, 126.7, 128.4, 129.0, and 130.6 (CH₉t), 129.0, 142.9 and 160.6 (C₉q), 171.8 (C=O); GC/MS: r.t. = 13.8 min., M/Z = 267; HRMS calculated for C₁₇H₁₇NO₂ (M+H+) 268.1338, found 268.1335.

4-chloro-N-cyclopropyl-N-phenylbenzamide (3d) was obtained by procedure B from amide 1d (0.2 mmol, 1.0 equiv.) as beige oil (51 mg, 94%).

1H NMR (400 MHz, CDCl₃) δ: 0.48-0.52 (m, 2H, CH₂- propyl), 0.78-0.83 (m, 2H, CH₂- propyl), 3.17-3.23 (m, 1H, CH₃-propyl), 6.91-6.96 (m, 2H, CH₉t), 7.06-7.13 (m, 3H, CH₉t), 7.16-7.21 (m, 4H, CH₉t); 13C NMR (100 MHz,
CDCl₃ δ: 8.1 (CH₂c-propyl), 127.1, 128.1, 128.3, 129.1 and 129.9 (CH₉), 135.5, 135.6 and 142.1 (C₉ar), 171.0 (C=O); GC/MS: r.t. = 14.3 min., M/Z = 271; HRMS calculated for C₁₆H₁₄NOCl (M+H⁺) 272.0842, found 272.0836.

2-chloro-N-cyclopropyl-N-phenylbenzamide (3e) was obtained by procedure B from amide 1e (0.2 mmol, 1.0 equiv.) as beige oil (52 mg, 95%).

¹H NMR (400 MHz, CDCl₃) δ: 0.23-1.08 (m, 4H, CH₂c-propyl), 2.87-3.54 (m, 1H, CHc-propyl), 6.78-7.72 (m, 9H, CH₉);

¹³C NMR (100 MHz, CDCl₃) δ: 7.4 (CH₂c-propyl), 31.2 (CHc-propyl), 126.5, 127.1, 127.9, 128.2, 128.9, 129.1, 129.4 and 129.7 (CH₉), 130.3 and 141.1 (C₉ar), 169.6 (C=O); GC/MS: r.t. = 13.9 min., M/Z = 271; HRMS calculated for C₁₆H₁₄NOCl (M+H⁺) 272.0833, found 272.0836.

N-cyclopropyl-N-(4-fluorophenyl)benzamide (3f) was obtained by procedure B from amide 1f (0.2 mmol, 1.0 equiv.) as beige oil (21 mg, 41%).

¹H NMR (400 MHz, CDCl₃) δ: 0.52-0.57 (m, 2H, CH₂c-propyl), 0.82-0.87 (m, 2H, CH₂c-propyl), 3.22-3.28 (m, 1H, CHc-propyl), 6.91-6.96 (m, 2H, CH₉), 7.00-7.03 (m, 2H, CH₉), 7.20-7.27 (m, 3H, CH₉), 7.29-7.36 (m, 2H, CH₉), 7.29-7.36 (m, 2H, CH₉);

¹³C NMR (100 MHz, CDCl₃) δ: 8.4 (CH₂c-propyl), 32.7 (CHc-propyl), 127.9, 128.1, 129.5, 129.6 and 129.7 (CH₉), 138.4 (C-F), 136.9, 159.9 and 162.3 (C₉), 172.3 (C=O); GC/MS: r.t. = 18.6 min., M/Z = 255; HRMS calculated for C₁₆H₁₄NOF (M+H⁺) 256.1138, found 256.1127.

N-cyclopropyl-N-(3-fluorophenyl)benzamide (3g) was obtained by procedure B from amide 1g (0.2 mmol, 1.0 equiv.) as beige oil (22 mg, 42%).

¹H NMR (400 MHz, CDCl₃) δ: 0.48-0.52 (m, 2H, CH₂c-propyl), 0.78-0.83 (m, 2H, CH₂c-propyl), 3.12-3.17 (m, 1H, CHc-propyl), 6.75-6.84 (m, 3H, CH₉), 7.10-7.24 (m, 4H, CH₉), 7.27-7.29 (m, 2H, CH₉);

¹³C NMR (100 MHz, CDCl₃) δ: 8.9 (CH₂c-propyl), 32.7 (CHc-propyl), 113.6, 113.8, 115.1, 115.3, 123.7, 123.8, 128.0, 128.1, 129.8, 129.9
and 130.0 (CH$_2$), 142.1 (C-F), 136.8, 161.4 and 163.9 (C$_q$ ar), 172.1 (C=O); **GC/MS**: r.t. = 17.1 min., M/Z = 255; **HRMS** calculated for C$_{16}$H$_{14}$NOF (M+H$^+$) 256.1138, found 256.1124.

![Chemical Structure](image)

**N-cyclopropyl-N-(2-fluorophenyl)benzamide (3h)** was obtained by procedure B from amide 1h (0.2 mmol, 1.0 equiv.) as beige crystals (48 mg, 95%).

**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$: 0.56-0.60 (m, 2H, CH$_2$-propyl), 0.78-0.84 (m, 2H, CH$_2$-propyl), 3.25-3.31 (m, 1H, CH$_c$-propyl), 6.99-7.07 (m, 3H, CH$_ar$), 7.15-7.28 (m, 4H, CH$_ar$), 7.37 (br d, $J$ = 7.2 Hz, 2H, CH$_ar$); **$^{13}$C NMR** (100 MHz, CDCl$_3$) $\delta$: 7.7 (CH$_2$-propyl), 32.3 (CH$_c$-propyl), 116.3, 116.5, 124.4, 124.5, 127.7, 127.9, 129.2, 129.3, 129.8 and 130.8 (CH$_ar$), 130.2 (C-F), 136.6, 156.9 and 159.4 (C$_q$ ar), 172.7 (C=O); m.p. 79-80 °C; **GC/MS**: r.t. = 17.0 min., M/Z = 255; **HRMS** calculated for C$_{16}$H$_{14}$NOF (M+H$^+$) 256.1138, found 256.1143.

![Chemical Structure](image)

**N-(2-chlorophenyl)-N-cyclopropyl-benzamide (3i)** was obtained by procedure B from amide 1i (0.2 mmol, 1.0 equiv.) as beige crystals (37 mg, 69%).

**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$: 0.33-1.13 (m, 4H, CH$_2$-propyl), 3.35 (br s, 1H, CH$_c$-propyl), 6.66-8.11 (m, 9H, CH$_ar$); **$^{13}$C NMR** (100 MHz, CDCl$_3$) $\delta$: 127.4, 127.8, 128.9, 129.8 and 130.4 (CH$_ar$), 139.7 (C$_q$ ar), 172.4 (C=O); **GC/MS**: r.t. = 18.4 min., M/Z = 271; **HRMS** calculated for C$_{16}$H$_{14}$NOCl (M+H$^+$) 272.0842, found 272.0836.

![Chemical Structure](image)

**N-cyclopropyl-N-(4-methoxyphenyl)benzamide (3j)** was obtained by procedure B from amide 1j (0.2 mmol, 1.0 equiv.) as white oil (36 mg, 68%).

**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$: 0.53-0.57 (m, 2H, CH$_2$-propyl), 0.80-0.85 (m, 2H, CH$_2$-propyl), 3.26-3.32 (m, 1H, CH$_c$-propyl), 3.75 (s, 3H, OCH$_3$), 6.73-6.76 (m, 2H, CH$_ar$), 6.92-6.94 (m, 2H, CH$_ar$), 7.16-7.24 (m, 3H, CH$_ar$), 7.30-7.32 (m, 2H, CH$_ar$); **$^{13}$C NMR** (100 MHz, CDCl$_3$) $\delta$: 7.7 (CH$_2$-propyl), 32.6 (CH$_c$-propyl), 55.5 (OCH$_3$), 114.2, 127.8, 128.3, 129.4 and 129.6 (CH$_ar$), 135.0, 137.2 and 158.2 (C$_q$ ar), 172.4 (C=O); **GC/MS**: r.t. = 12.6 min., M/Z = 267; **HRMS** calculated for C$_{17}$H$_{17}$NO$_2$ (M+H$^+$) 268.1338, found 268.1320.
N-(pyridine-3-yl)benzamide (4c) was obtained by procedure A from benzoyl chloride (3.6 mmol, 1.2 equiv.) and pyridine-3-amins (3.0 mmol, 1.0 equiv.) as beige powder (339 mg, 57%).

$^1H$ NMR (400 MHz, DMSO-d$_6$) δ: 7.39 (dd, $J = 4.0$ and 8.0 Hz, 1H, CH$_{ar}$), 7.54-7.57 (m, 2H, CH$_{ar}$), 7.60-7.64 (m, 1H, CH$_{ar}$), 7.97-7.99 (m, 1H, CH$_{ar}$), 8.17-8.22 (m, 1H, CH$_{ar}$), 8.31 (dd, $J = 1.2$ and 4.0 Hz, 1H, CH$_{ar}$), 8.92-8.95 (m, 1H, NH); $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ: 19.4 (CH$_3$), 42.3 (CH$_2$Ph), 123.5, 127.3, 127.7, 128.5, 131.9, 142.0 and 144.6 (CH$_{ar}$), 134.4 and 135.8 (C$_q$$_{ar}$), 166.0 (C=O). m.p. 119-120 °C; GC/MS: r.t. = 15.2 min., M/Z = 198; HRMS calculated for C$_{12}$H$_{10}$N$_2$O (M+H+) 199.0871, found 199.0864.

N-cyclopropyl-N-phenylacetamide (5a) was obtained by procedure B from commercial N-phenylbenzamide (0.2 mmol, 1.0 equiv.) as beige oil (35 mg, 78%).

$^1H$ NMR (400 MHz, CDCl$_3$) δ: 0.49 (br s, 2H, CH$_2$$_{c-propyl}$), 0.81 (br s, 2H, CH$_2$$_{c-propyl}$), 2.17 (s, 3H, CH$_3$), 3.16 (br s, 1H, CH$_c$$_{propyl}$), 7.07-7.13 (m, 1H, CH$_{ar}$), 7.28-7.35 (m, 2H, CH$_{ar}$), 7.33-7.42 (m, 1H, CH$_{ar}$), 7.47-7.53 (m, 1H, CH$_{ar}$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 23.6 (CH$_3$), 24.6 (CH$_{c-propyl}$), 29.8 (CH$_{2c-propyl}$), 129.0, 124.2 and 119.9 (CH$_{ar}$), 142.2 (C$_q$$_{ar}$), 168.7 (C=O); GC/MS: r.t. = 12.2 min., M/Z = 175; HRMS calculated for C$_{11}$H$_{13}$NO (M+H+) 176.1075, found 176.1072.

N-cyclopropyl-N-methylbenzamide (5b) was obtained by procedure B from commercial N-methylbenzamide (0.2 mmol, 1.0 equiv.) as beige oil (12 mg, 37%).

$^1H$ NMR (400 MHz, CDCl$_3$) δ: 0.30-0.59 (m, 4H, CH$_2$$_{c-propyl}$), 2.71-2.77 (m, 1H, CH$_c$$_{propyl}$), 3.02 (br s, 3H, CH$_3$), 7.28-7.44 (m, 5H, CH$_{ar}$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 9.7 (CH$_3$), 33.2 (CH$_{c-propyl}$), 35.1 (CH$_{2c-propyl}$), 127.3, 128.0 and 129.5(CH$_{ar}$), 137.3 (C$_q$$_{ar}$), 172.6 (C=O); GC/MS: r.t. = 12.2 min., M/Z = 175; HRMS calculated for C$_{11}$H$_{13}$NO (M+H+) 176.1075, found 176.1084.
**N-cyclopropyl-N-(pyridine-3-yl)benzamide (5c)** was obtained by procedure B from amide 4c (0.2 mmol, 1.0 equiv.) as beige oil (41 mg, 86%).

\[ ^1H \text{NMR} \ (400 \text{ MHz, CDCl}_3) \delta: 0.48-0.52 (m, 2H, CH\_2-propyl), 0.79-0.84 (m, 2H, CH\_2-propyl), 3.15-3.21 (m, 1H, CH\_c-propyl), 7.17-7.30 (m, 6H, CH\_ar), 7.41 (d, J = 8.0 Hz, 1H, CH\_ar), 8.37 (br s, 2H, CH\_ar); ^13C \text{NMR} \ (100 \text{ MHz, CDCl}_3) \delta: 9.2 (CH\_2-propyl), 32.7 (CH\_c-propyl), 128.1, 128.2, 130.0, 147.4 and 148.7 (CH\_ar), 136.4 (C\_q-ar), 172.2 (C=O); \text{GC/MS}: r.t. = 14.6 min., M/Z = 238; \text{HRMS} \text{ calculated for C}_{15}H_{14}N_2O (M+H\+) 239.1184, found 239.1183.

**N-cyclopropyl-2-methyl-N-phenylfuran-3-carboxamide (N-cyclopropyl Fenfuram) (5d)** was obtained by procedure B from commercial Fenfuram (0.2 mmol, 1.0 equiv.) as beige oil (34 mg, 70%).

\[ ^1H \text{NMR} \ (400 \text{ MHz, CDCl}_3) \delta: 0.55-0.59 (m, 2H, CH\_2-propyl), 0.84-0.89 (m, 2H, CH\_2-propyl), 2.49 (s, 3H, Me), 3.19-3.26 (m, 1H, CH\_c-propyl), 5.43 (d, J = 2.0 Hz, CH\_furan), 6.89 (d, J = 2.0 Hz, CH\_furan), 7.17-7.30 (m, 6H, CH\_ar), 7.06-7.08 (m, 2H, CH\_ar), 7.24-7.35 (m, 3H, CH\_ar); ^13C \text{NMR} \ (100 \text{ MHz, CDCl}_3) \delta: 7.7 (CH\_2-propyl), 13.9 (Me), 32.1 (CH\_c-propyl), 110.4 and 139.0 (CH\_furan), 127.3, 128.7 and 129.2 (CH\_ar), 116.6, 142.2 and 157.5 (C\_q-ar), 166.9 (C=O); \text{GC/MS}: r.t. = 16.9 min., M/Z = 241; \text{HRMS} \text{ calculated for C}_{15}H_{15}NO_2 (M+H\+) 242.1181, found 242.1186.

**N-cyclopropyl-N-(3-isopropoxyphenyl)-2-methylbenzamide (N-cyclopropyl Mepronil) (5e)** was obtained by procedure B from commercial Mepronil (0.2 mmol, 1.0 equiv.) as beige oil (44 mg, 70%).

\[ ^1H \text{NMR} \ (400 \text{ MHz, CDCl}_3) \delta: 0.54-0.56 (m, 2H, CH\_2-propyl), 0.80-0.82 (m, 2H, CH\_2-propyl), 1.22 (d, J = 6.0 Hz, 6H, CH(CH\_3)\_2), 2.34 (s, 3H, Me), 3.20 (br s, 1H, CH\_c-propyl), 4.34-4.40 (m, 1H, CH(CH\_3)\_2), 6.53-6.67 (m, 3H, CH\_ar), 6.99-7.13 (m, 5H, CH\_ar); ^13C \text{NMR} \ (100 \text{ MHz, CDCl}_3) \delta: 8.5 (CH\_2-propyl), 19.5 (CH(CH\_3)\_2), 22.0 (CH(CH\_3)\_2), 31.6 (CH\_c-propyl), 70.4 (Me), 114.7, 115.7, 119.9, 125.2, 126.7, 128.6, 129.3 and 130.2 (CH\_ar),
134.3, 137.7, 142.7 and 158.1 (C₉ ar), 172.7 (C=O); **GC/MS**: r.t. = 14.7 min., M/Z = 309; **HRMS** calculated for C₂₀H₂₃NO₂ (M+H⁺) 310.1807, found 310.1794.

1-cyclopropylpyrrolidin-2-one (5f) was obtained by procedure B from commercial pyrrolidin-2-one (0.2 mmol, 1.0 equiv.) as beige oil (23 mg, 93%).

**¹H NMR** (400 MHz, CDCl₃) δ: 0.66-0.70 (m, 2H, CH₅c-propyl), 0.73-0.79 (m, 2H, CH₅c-propyl), 1.93-2.00 (m, 2H, CH₂pyrrol), 2.38 (t, J = 8.4 Hz, 2H, CH₂pyrrol), 2.61-2.66 (m, 1H, CH c-propyl), 3.30 (t, J = 6.8 Hz, 2H, CH₂pyrrol); **¹³C NMR** (100 MHz, CDCl₃) δ: 5.1 (CH₅c-propyl), 25.3 (CH c-propyl), 18.2, 32.0 and 47.7 (CH₂pyrrol); **GC/MS**: r.t. = 14.8 min., M/Z = 125; **HRMS** calculated for C₇H₁₁NO (M+H⁺) 126.0841, found 126.0852.

1-cyclopropyl-3-methylpyridin-2(1H)-one (5g) was obtained by procedure B from commercial 3-methylpyridin-2(1H)-one (0.2 mmol, 1.0 equiv.) as beige oil (27 mg, 90%).

**¹H NMR** (400 MHz, CDCl₃) δ: 0.81-0.85 (m, 2H, CH₅c-propyl), 1.07-1.13 (m, 2H, CH₅c-propyl), 1.93-2.00 (m, 2H, CH₂pyrrol), 2.13 (s, 3H, Me), 3.29-3.36 (m, 1H, CH c-propyl), 6.03 (t, J = 6.8 Hz, 1H, CH₉ ar), 7.15 (d, J = 7.6 Hz, CH₉ ar); **¹³C NMR** (100 MHz, CDCl₃) δ: 6.9 (CH₅c-propyl), 17.2 (Me), 32.4 (CH c-propyl), 105.3, 134.2 and 136.2 (CH₉ ar), 129.7 (C₉ ar), 164.7 (C=O); **GC/MS**: r.t. = 15.3 min., M/Z = 149; **HRMS** calculated for C₉H₁₁NO (M+H⁺) 150.0841, found 150.0834.

1-cyclopropyl-3,4-dihydroquinolin-2(1H)-one (5h) was obtained by procedure B from commercial 3,4-dihydroquinolin-2(1H)-one (0.2 mmol, 1.0 equiv.) as beige crystals (34 mg, 92%).

**¹H NMR** (400 MHz, CDCl₃) δ: 0.56-0.61 (m, 2H, CH₅c-propyl), 1.04-1.09 (m, 2H, CH₅c-propyl), 2.52-2.56 (m, 2H, CH₂quinoline), 2.65-2.75 (m, 3H, CH₂quinoline and CH c-propyl), 6.93 (td, J = 1.2 and 7.2 Hz, 1H, CH₉ ar), 7.06 (br d, J = 7.2 Hz, 1H, CH₉ ar), 7.16-7.24 (m, 2H, CH₉ ar); **¹³C NMR** (100 MHz, CDCl₃) δ: 9.9 (CH₅c-propyl), 25.3 (CH c-propyl), 25.4 and 32.9 (CH₂quinoline), 116.5, 122.9, 127.2 and 127.4 (CH₉ ar), 126.9 and 140.9 (C₉ ar), 172.8 (C=O); m.p. 79-80 °C, **GC/MS**: r.t. = 14.8 min., M/Z = 187; **HRMS** calculated for C₂₀H₂₃NO₂ (M+H⁺) 188.0997, found 188.0989.
IV- $^1$H and $^{13}$C NMR spectra
Electronic Supplementary Material (ESI) for Chemical Communications

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