Site-Selective C-H bond Carbonylation with CO2 and Cobalt Catalysis

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1. General information: Unless stated otherwise, all reactions were carried out under argon atmosphere in ovendried glassware. Chlorobenzene, α,α,α -trifluorotoluene, 2,2,2-trifluoro acetic acid and o-xylene were purchased from commercial sources namely Spectrochem and Alfa aesar and Merck. Dichloromethane (CaH₂), DMF (CaSO₄), DMSO (CaSO₄), Toluene (Na) were purified by distillation over the indicated drying agents under argon. Flash Column Chromatography was conducted on silica gel (Merck, 100-200 and 230-240 mesh). ¹H and ¹³C NMR were recorded on JEOL (400 and 500 MHz) using CDCl₃ and DMSO-*d*₆ as solvent. Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals used as references and the chemicals shifts converted to TMS scale (CDCl₃: $\delta C = 77$ ppm; residual CHCl₃ in CDCl₃: $\delta H = 7.26$ ppm, DMSO-*d*₆: ¹H NMR shift for residual DMSO-*d*₆ at 2.5 ppm and ¹³C NMR shift at 40 ppm). The abbreviations used for ¹H NMR spectra to indicate the signal multiplicity are s = singlet, d = doublet, t = triplet, q = quartet, quin = quintuplet, m = multiplet, br = broad, dd = double doublet, dt = double triplet, ddd = double double doublet; coupling constant(s) in Hz; integration. ESI-MS was recorded on a Waters-Micromass Quattro Micro triplequadrupole mass spectrometer. GC– MS was used to analyse our samples on a Shimadzu GC 2010 plus and MS 2010SE system. All the reactions were monitored by analytical thin layer chromatography (TLC) using commercial aluminium sheets precoated with silica gel. Unless stated otherwise, all commercially available compounds (Alfa, Aldrich) were used as received.

2. General procedure for preparation of starting materials:

a. 4'-((1,7'-dimethyl-2'-propyl-1H,3'H-2,5'-bibenzo[d]imidazol-3'-yl)methyl)-*N*-(quinolin-8-yl)biphenyl-2carboxamide (6):

Compound 6 was prepared according to the reported literature.¹

To an oven dried 25 mL flask charged with Teflon coated stir bar, Telmisartan (2 mmol) and diisopropylethylamine (DIEA) (3 mmol) were dispersed with CH_2Cl_2 (10 mL). After the suspension turned transparent, HBTU (3 mmol) was added. The solvent was stirred for 2 hours before 8-aminoquinoline (3 mmol) was added, then stirred for another 24 hours at room temperature. After completion of reaction saturated aqueous NaHCO₃ was added to the mixture to quench reaction and then extracted with CH_2Cl_2 (10 mL x 3). Combined organic phase was washed with saturated NaCl (aq) and dried over Na₂SO₄, and then filtered, the solvent was removed in a rotary evaporator. The crude product was purified by flash column chromatography (20% Acetone/Chloroform) on silica gel the desired product was obtained in 48% as white solid. R_f Value = 0.2.



¹**H NMR** (500 MHz, CDCl₃): δ 9.97 (brs, 1H), 8.73 (d, *J* = 7.1 Hz, 1H), 8.44 (dd, *J* = 4.1, 1.5 Hz, 1H), 7.90 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.82 (m, 2H), 7.53-7.45 (m, 3H), 7.42 (m, 2H), 7.39 (m, 2H), 7.31-7.27 (m, 4H), 7.26-7.23 (m, 2H), 6.96 (d, *J* = 8.1 Hz, 2H), 5.21 (s, 2H), 3.66 (s, 3H), 2.73 (s, 3H), 2.62 (t, *J* = 7.6 Hz, 2H), 1.65 (t, *J* = 15.0, 7.5 Hz, 2H), 0.86 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 167.4, 156.1, 154.4, 147.5, 142.9, 142.6, 139.7, 139.3, 138.1, 136.5, 136.0, 135.9, 135.0, 134.8, 134.2, 130.44, 130.43, 129.42, 129.25, 128.8, 127.7, 127.5, 127.0, 126.0, 123.66, 123.61, 122.4, 122.2, 121.4, 121.3, 119.3, 116.0, 109.4, 108.4, 46.6, 31.6, 29.4, 21.4, 16.7, 13.8.

HRMS: $[M+H]^+$ calculated for $C_{42}H_{37}N_6O$: 641.3029, found 641.2827.

b. 5-(2,5-dimethylphenoxy)-2,2-dimethyl-N-(quinolin-8-yl)pentanamide (8):

compound **8** was prepared from modified procedure reported in literature.² Oxalyl chloride (1.5 equiv) was added slowly to a stirred solution of the carboxylic acid (1.1 mmol) in CH₂Cl₂ (30 mL) and DMF (0.1 mL) at 0 °C. The obtained mixture was stirred at 0 °C for 1 h and continued further at room temperature for another 3 h. After 3 h, solvents were evaporated in *vacuo* and the corresponding crude acid chloride was used directly used for the next step without any purification. The solution of acid chloride in dichloromethane (5 mL) was added drop wise to a solution of 8-aminoquinoline (1 mmol) and Et₃N (1.5 equiv) in CH₂Cl₂ (15 mL) at 0 °C and stirring continued at room temperature for 14 h. The completion of the reaction was monitored by TLC and the reaction was quenched with water after dilution with CH₂Cl₂ (10 mL), washed successively with saturated aqueous NaHCO₃ and brine. The organic layer was dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography (5% EtOAc/hexane) on silica gel the desired product was obtained in 90 % as colourless liquid. R_f Value = 0.3.



¹**H NMR** (400 MHz, CDCl₃): δ 10.32 (brs, 1H), 8.83 (m, 2H), 8.16 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.57-7.49 (m, 2H), 7.45 (dd, *J* = 8.1, 4.4 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 7.5 Hz, 1H), 6.59 (s, 1H), 3.97 (t, *J* = 5.6 Hz, 2H), 2.28 (s, 3H), 2.16 (s, 3H), 1.97-1.87 (m, 4H), 1.48 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 176.2, 156.8, 148.1, 138.6, 136.3, 136.2, 134.5, 130.1, 127.8, 127.3, 123.4, 121.4, 121.2, 120.5, 116.1, 111.8, 67.8, 43.5, 37.9, 25.6, 25.1, 21.3, 15.7.

HRMS: $[M+H]^+$ calculated for $C_{24}H_{20}N_2O_2$: 377.2229, found 377.2223.

All sp² and sp³ aminoquinoline amides prepared from the reported literature.^{2, 3, 6}.

3. General procedure (A) for cobalt-catalyzed carbonylation of aminoquinoline aromatic amides:



In an oven-dried Schlenk tube **A** equipped with **a** teflon coated stir bar, 1,2-diphenyl -1,1,2,2-tetra methyl disilane (122 mg, 0.45 mmol, 1.5 equiv), caesium fluoride (71 mg, 0.45 mmol, 1.5 equiv) and DMF (1.0 mL) were added in order under argon atmosphere. Schlenk tube was closed with a screw cap, evacuated and subsequently filled with 1-2 atm of carbon dioxide before keeping in preheated (100 °C) oil bath for 90 min. In an another oven-dried Schlenk tube **B** equipped with a teflon coated stir bar, Co(acac)₂ (15.42 mg, 0.06 mmol, 20 mol%), NaO₂CPh (8.6 mg, 0.6 mmol, 20 mol%), Ag₂CO₃ (206.2 mg, 0.75 mmol, 2.5 equiv), followed by 2-methyl-*N*-(quinolin-8-yl)benzamide (78.6 mg, 0.3 mmol, 1 equiv) in α,α,α -trifluorotoluene (1 mL) was added. Finally Schlenk tube was evacuated. The *in situ* generated CO (CO_{gen}) was in Schlenk tube **A** (Chamber-one) was transferred to vacuumized Schlenk tube **B** (chamber-two), which is connected through small rubber tube. The Schlenk tube **B** was then placed in preheated oil bath at 100 °C for 24 h. After the completion of reaction it was cooled to room temperature and depressurized. Solvents were removed under reduced pressure and the reaction mixture was purified by flash column chromatography (25% EtOAc/Hexane) on silica gel. The desired phthalimide 2 was obtained in 78% (68 mg) as white solid. R_f Value = 0.2.

4-methyl-2-(quinolin-8-yl)isoindoline-1,3-dione (2a): Compound (2a) was prepared according to the general



procedure **A** starting from **1a** (78.6 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (25% EtOAc/Hexane) in 78% (68 mg) yield as white solid. R_f Value = 0.2. The NMR data of **2a** is in accordance with the literature.³ **'H NMR** (500 MHz, CDCl₃): δ 8.86 (dd, J = 4.3, 1.6 Hz, 1H), 8.20 (dd, J = 8.1, 1.7 Hz, 1H),

TH NMR (500 MHz, CDCl₃): δ 8.86 (dd, J = 4.3, 1.6 Hz, 1H), 8.20 (dd, J = 8.1, 1.7 Hz, 1H), 7.94 (m, 1H), 7.82 (d, J = 7.5 Hz, 1H), 7.74 (dd, J = 7.3, 1.2 Hz, 1H), 7.64 (q, J = 7.9 Hz, 2H), 7.53 (d, J = 7.5 Hz, 1H), 7.41 (dd, J = 8.5, 4.4 Hz, 1H), 2.76 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 168.6, 167.9, 150.8, 144.3, 138.4, 136.4, 136.1, 133.6, 132.8, 130.2, 129.9, 129. 4, 129.2, 129.0, 126.0, 121.7, 121.4, 17.6.

2-(quinolin-8-yl)isoindoline-1,3-dione (2b): Compound (2b) was prepared according to the general procedure A



starting from 1b (74.4 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (25% EtOAc/Hexane) in 67% (55.3 mg) yield as white solid. Rf Value = 0.2. The NMR data of **2b** is in accordance with the literature.³ ¹H NMR (400 MHz, CDCl₂): δ 8.84 (dd, J = 4.0, 1.4 Hz, 1H), 8.19 (dd, J = 8.3, 1.7 Hz,

1H), 7.98 (m, 2H), 7.93 (d, J = 8.2, 1.2 Hz, 1H), 7.86-7.40 (m, 3H), 7.65 (t, J = 7.7 Hz, 1H), 7.41 (dd, J = 8.4, 4.1 Hz, 1H). ¹³**C** NMR (100 MHz, CDCl₃): δ 167.9, 150.8, 144.1, 136.1, 134.1, 132.3, 130.1, 129.7, 129.5,

129.2, 126.0, 123.7, 121.8.

5-methyl-2-(quinolin-8-yl)isoindoline-1,3-dione (2c): Compound (2c) was prepared according to the general



procedure A from 1c (78.6 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (25% EtOAc/Hexane) in 68% (59 mg) yield as white solid. Rf Value = 0.2. The NMR data of 2c is in accordance with the literature.³

¹H NMR (400 MHz, CDCl₃): δ 8.85 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.22 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.95 (dd, J = 8.5, 1.7 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.80 (s, 1H), 7.75 (dd, J = 7.1, 1.3 Hz, 1H), 7.67 (t, J = 7.7 Hz, 1H), 7.59 (d, J = 6.9 Hz, 1H), 7.43 (dd, J = 8.6, 4.2 Hz, 1H), 2.56 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 168.1, 167.9, 150.7, 145.4, 144.0, 136.3, 134.7, 132.7, 130.3, 129.8, 129.7, 129.5, 129.2, 126.1, 124.3, 123.7, 121.8, 22.0.

5-tert-butyl-2-(quinolin-8-yl)isoindoline-1,3-dione (2d): Compound (2d) was prepared according to the general



procedure A from 1d (91.2 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (25% EtOAc/Hexane) in 65% (65 mg) yield as white solid. R_f Value = 0.2. The NMR data of 2d is in accordance with the literature.⁴

¹**H NMR** (400 MHz, CDCl₃): δ 8.85 (dd, *J* = 3.8, 1.2 Hz, 1H), 8.20 (dd, *J* = 8.1, 1.9 Hz, 1H), 8.05 (d, J = 1.5 Hz, 1H), 7.95-7.91 (m, 2H), 7.82 (dd, J = 8.0, 1.8 Hz, 1H), 7.74 (dd, J = 7.2, 1.4 Hz, 1H), 7.65 (t, J = 8.3 Hz, 1H), 7.41 (dd, J = 8.2, 4.0 Hz, 1H), 1.42 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ 168.3, 167.9, 158.7, 150.7, 144.2, 136.1, 132.5, 131.1, 130.2, 129.8, 129.6, 129.4, 129.2, 126.0, 123.6, 121.8, 121.0, 35.7, 31.1.

5-methoxy-2-(quinolin-8-yl)isoindoline-1,3-dione (2e): Compound (2e) was prepared according to the general



procedure A from 1e (83.4 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (30% EtOAc/Hexane) in 57% (52 mg) yield as white solid. R_f Value = 0.2. The NMR data of **2e** is in accordance with the literature.³

¹**H NMR** (500 MHz, CDCl₃): δ 8.85 (dd, J = 4.2, 1.6 Hz, 1H), 8.20 (dd, J = 8.3, 1.6 Hz, 1H), 7.94 (dd, J = 8.2, 1.2 Hz, 1H), 7.89 (d, J = 8.9 Hz, 1H), 7.74 (dd, J = 7.3, 1.2 Hz, 1H), 7.66 (t, J = 7.7 Hz, 1H), 7.47 (d, J = 2.3 Hz, 1H), 7.42 (dd, J = 8.2, 4.1 Hz, 1H), 7.24 (dd, *J* = 8.2, 2.3 Hz, 1H), 3.94 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 167.7, 167.6, 164.7, 150.8, 144.2, 136.1, 134.9, 130.2, 129.8, 129.4, 129.2, 126.0, 125.4, 124.2, 121.8, 120.2, 108.2, 56.0.

5-(methylthio)-2-(quinolin-8-yl)isoindoline-1,3-dione (2f): Compound (2f) was prepared according to the



general procedure A from 1f (88 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (30% EtOAc/Hexane) in 32% (31 mg) yield as white solid. R_f Value = 0.2.

¹**H NMR** (400 MHz, CDCl₃): δ 8.86 (s, 1H), 8.22 (d, *J* = 7.4 Hz, 1H), 7.96 (d, *J* = 7.0 Hz, 1H), 7.85 (d, J = 7.0 Hz, 1H), 7.76 (m, 2H), 7.64 (m, 2H), 7.45 (m, 1H), 2.61 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 167.7, 167.6, 150.8, 148.2, 144.2, 136.2, 133.3, 130.4,

130.2, 129.7, 129.5, 129.2, 128.1, 126.1, 123.8, 121.8, 119.6, 15.1. **HRMS**: $[M+H]^+$ calculated for $C_{18}H_{13}N_2O_2S$: 321.0698, found 321.0692. 5-fluoro-2-(quinolin-8-yl)isoindoline-1,3-dione (2g): Compound (2g) was prepared according to the general



Rr

 F_3C

procedure A from 1g (79.8 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (25% EtOAc/Hexane) in 41% (36 mg) yield as white solid. R_f Value = o.2. The NMR data of 2g is in accordance with the literature.⁴

¹**H NMR** (400 MHz, CDCl₃): δ 8.85 (dd, J = 4.2, 1.6 Hz, 1H), 8.23 (dd, J = 8.2, 1.6 Hz, 1H), 8.01-7.96 (m, 2H), 7.75 (dd, J = 7.6, 1.6 Hz, 1H), 7.69-7.65 (m, 2H), 7.49-7.43 (m, 2H).

¹³C NMR (100 MHz, CDCl₂): δ 167.7, 166.6 (d, J = 256.9 Hz), 166.5 (d, J = 2.8 Hz), 150.9, 144.0, 136.2, 135.1 (d, J = 9.6 Hz), 130.1, 129.7, 129.4, 129.2, 128.1 (d, J = 2.9 Hz), 126.2 (d, J = 9.0 Hz), 121.9, 121.3, 121.1, 111.5 (d, J = 24.2 Hz).

5-chloro-2-(quinolin-8-yl)isoindoline-1,3-dione (2h): Compound (2h) was prepared according to the general procedure A from 1h (84.6 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (25% EtOAc/Hexane) in 54% (50 mg) yield as white solid. R_f Value = 0.2. The NMR data of **2h** is in accordance with the literature.⁴

¹**H NMR** (500 MHz, CDCl₃): δ 8.84 (dd, J = 3.8, 1.2 Hz, 1H), 8.23 (dd, J = 7.9, 1.6 Hz, CI 1H), 7.97 (m, 2H), 7.93 (d, J = 7.8 Hz, 1H), 7.78-7.74 (ddd, J = 12.3, 7.7, 1.6 Hz, 2H),

7.67 (m, 1H), 7.44 (d, J = 4.3 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 166.9, 166.6, 150.9, 144.0, 140.8, 136.2, 134.2, 134.0, 130.4,

130.1, 129.7, 129.4, 129.2, 126.1, 125.0, 124.2, 121.9.



¹**H NMR** (400 MHz, CDCl₃): δ 8.84 (dd, *J* = 4.1, 1.4 Hz, 1H), 8.23 (dd, *J* = 8.5, 1.6 Hz, 1H), 8.14 (d, J = 1.9 Hz, 1H), 7.98-7.93 (m, 2H), 7.86 (d, J = 7.7 Hz, 1H), 7.75 (dd, J = 7.3, 1.2 Hz, 1H), 7.67 (t, J = 8.0 Hz, 1H), 7.44 (dd, J = 8.4, 4.0 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 167.1, 166.5, 150.9, 144.0, 137.1, 136.2, 134.0, 130.9, 130.1, 129.7, 129.4, 129.2, 129.0, 127.1, 126.1, 125.2, 121.9.

2-(quinolin-8-yl)-5-(trifluoromethyl)isoindoline-1,3-dione (2j): Compound (2j) was prepared according to the general procedure A from 1j (94.8 mg, 0.3 mmol, 1 equiv) and purified by flash \cap column chromatography (25% EtOAc/Hexane) in 63% (65 mg) yield as white solid. R_f Value = 0.2. The NMR data of 2j is in accordance with the literature.³

> ¹**H NMR** (400 MHz, CDCl₃): δ 8.84 (dd, *J* = 4.0, 1.4 Hz, 1H), 8.28-8.23 (m, 2H), 8.15-8.08 (m, 2H), 7.99 (dd, J = 8.2, 1.4 Hz, 1H), 7.76 (dd, J = 7.2, 1.2 Hz, 1H), 7.69 (t, J = 8.1 Hz, 1H), 7.48 (dd, *J* = 8.2, 4.2 Hz, 1H).

¹³**C NMR** (100 MHz, CDCl₃): δ 165.5, 166.4, 150.9, 143.8, 136.4 (q, *J*_{C-F} = 33.2Hz) 135.2, 133.0, 131.3, 131.2, 130.2, 129.9, 129.2, 129.1, 126.1 (overlapped), 124.4, 122.0 (overlapped), 121.1 q, (J_{C-F} = 4.2 Hz), 29.6.

Methyl-1,3-dioxo-2-(quinolin-8-yl)isoindoline-5-carboxylate (2k): Compound (2k) was prepared according to the general procedure A from 1k (91.8 mg, 0.3 mmol, 1 equiv) and purified by \cap



flash column chromatography (25% EtOAc/Hexane) in 66% (66 mg) yield as white solid. R_f Value = 0.2. ¹**H NMR** (400 MHz, CDCl₃): δ 8.84 (dd, *J* = 4.5, 1.7 Hz, 1H), 8.63 (m, 1H), 8.49

(dd, J = 7.7, 1.3 Hz, 1H), 8.22 (dd, J = 8.4, 1.7 Hz, 1H), 8.06 (d, J = 7.2 Hz, 1H), 7.96 (dd, J = 8.3, 1.6 Hz, 1H), 7.76 (dd, J = 7.0, 1.4 Hz, 1H), 7.67 (m, 1H), 7.43 (dd, *J* = 8.3, 4.3 Hz, 1H), 4.00 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 166.9, 165.2, 150.9, 143.9, 136.2, 135.69, 135.67, 135.5, 132.5, 130.1, 129.8, 129.5, 129.3, 129.2, 126.1, 124.9, 123.8, 121.9, 52.8.

HRMS: $[M+H]^+$ calculated for $C_{10}H_{13}N_2O_4$: 333.0875, found 309.0866.

5-methyl-2-(quinolin-8-yl)isoindoline-1,3-dione (2l): Compound (2l) was prepared according to the general



procedure A from 1 (78.6 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (25% EtOAc/Hexane) in $6_{1\%}$ (53 mg) yield as white solid. R_f Value = 0.2. The NMR data of 2l is in accordance with the literature.³

¹**H NMR** (400 MHz, CDCl₃): δ 8.85 (m, 1H), 8.21 (m, 1H), 7.94 (d, *J* = 7.3 Hz, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.80 (s, 1H), 7.75 (m, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.59 (d, J = 7.3 Hz, 1H), 7.42 (dd, *J* = 8.3, 4.3 Hz, 1H), 2.55 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 168.1, 167.9, 150.8, 145.4, 144.2, 136.1, 134.7, 132.8, 130.2, 129.9, 129.8, 129.4, 129.2, 126.1, 124.3, 123.7, 121.8, 22.0.

5-methoxy-2-(quinolin-8-yl)isoindoline-1,3-dione (2m): Compound (2m) was prepared according to the general



procedure A from 1m (83.4 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (30% EtOAc/Hexane) in 68% (62 mg) yield as white solid. Rf Value = 0.2. The NMR data of 2m is in accordance with the literature.³ ¹**H NMR** (400 MHz, CDCl₃): δ 8.86 (dd, J = 4.0, 1.4 Hz, 1H), 8.22 (dd, J = 8.3, 1.3)

Hz, 1H), 7.95 (m, 1H), 7.90 (d, J = 8.3 Hz, 1H), 7.76-7.65 (m, 2H), 7.48 (d, J = 2.1 Hz, 1H), 7.44 (dd, *J* = 8.2, 4.1 Hz, 1H), 7.22-7.24 (m, 1H), 3.96 (s, 3H).

¹³C NMR (100 MHz, CDCl₂): δ 167.8, 167.7, 164.8, 150.8, 144.2, 136.2, 135.0, 130.2, 129.9, 129.5, 129.2, 126.1, 125.5, 124.3, 121.8, 120.2, 108.2, 56.1.

5-chloro-2-(quinolin-8-yl)isoindoline-1,3-dione (2n): Compound (2n) was prepared according to the general



procedure A from in (84.6 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (25% EtOAc/Hexane) in 53% (49 mg) yield as white solid. R_f Value = 0.2.

¹**H NMR** (500 MHz, CDCl₃): δ 8.85 (dd, J = 4.1, 1.5 Hz, 1H), 8.22 (dd, J = 8.2, 1.5 Hz, 1H), 7.96 (m, 2H), 7.93 (d, J = 8.1 Hz, 1H), 7.78-7.74 (m, 2H), 7.67 (m, 1H), 7.44 (dd, J = 8.2, 4.2 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 166.9, 166.6, 150.9, 144.0, 140.8, 136.1, 134.2, 134.0, 130.4, 130.1, 129.7, 129.4, 129.2, 126.0, 125.0, 124.2, 121.9.

HRMS: $[M+H]^+$ calculated for $C_{17}H_{10}ClN_2O_2$: 309.0431, found 309.0433.

5-bromo-2-(quinolin-8-yl)isoindoline-1,3-dione (20): Compound (20) was prepared according to the general procedure A from 10 (97.8 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (25% EtOAc/Hexane) in 60% (63 mg) yield as white solid. R_f Br Value = 0.2. The NMR data of **20** is in accordance with the literature.³

¹**H NMR** (400 MHz, CDCl₃): δ 8.84 (dd, J = 4.3, 2.0 Hz, 1H), 8.22 (dd, J = 8.0, 1.5 Hz, 1H), 8.14 (d, J = 1.8 Hz, 1H), 7.95 (m, 2H), 7.85 (d, J = 8.0 Hz, 1H), 7.75 (dd, J = 7.4, 1.4 Hz, 1H), 7.67 (m, 1H), 7.44 (dd, *J* = 8.6, 4.4 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 167.0, 166.5, 150.9, 144.0, 137.1, 136.2, 134.0, 130.9, 130.1, 129.7, 129.4, 129.2, 129.0, 127.1, 126.1, 125.2, 121.9.

2-(quinolin-8-yl)-5-(trifluoromethyl)isoindoline-1,3-dione (2p): Compound (2p) was prepared according to the general procedure A from 1p (94.8 mg, 0.3 mmol, 1 equiv) and purified by flash റ column chromatography (25% EtOAc/Hexane) in 58% (60 mg) yield as white

solid. R_f Value = 0.2. The NMR data of **2p** is in accordance with the literature.⁵ ¹**H NMR** (400 MHz, CDCl₃): δ 8.84 (dd, J = 4.1, 1.7 Hz, 1H), 8.27 (s, 1H), 8.22 (dd, J = 8.1, 1.7 Hz, 1H), 8.11 (m, 2H), 7.97 (dd, J = 8.3, 1.3 Hz, 1H), 7.76 (dd, J = 7.7, 1.9 Hz, 1H), 7.68 (m, 1H), 7.44 (dd, *J* = 8.5, 4.2 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 166.5, 166.4, 150.9, 143.8, 136.2, 135.9 (q, J_{C-F} = 33.2 Hz), 135.1, 133.0, 131.29 (d, *J*_{C-F} = 3.7 Hz), 130.1, 129.8, 129.2, 129.1, 126.1, 124.3 (q, *J*_{C-F} = 274 Hz), 122.0, 121.01 (q, *J*_{C-F} = 4.0 Hz), 29.6.

5-nitro-2-(quinolin-8-yl)isoindoline-1,3-dione (2q): Compound (2q) was prepared according to the general



F₃C

procedure A from 1q (87.9 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (25% EtOAc/Hexane) in 42% (40 mg) yield as white solid. R_f Value = 0.2. The NMR data of 2q is in accordance with the literature.³

¹**H NMR** (500 MHz, CDCl₃): δ 8.86 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.81 (d, *J* = 1.7 Hz, 1H), 8.67 (dd, J = 8.2, 1.8 Hz, 1H), 8.26 (dd, J = 8.6, 1.6 Hz, 1H), 8.18 (d, J = 8.0 Hz, 1H), 8.01 (dd, J = 8.3, 1.2 Hz, 1H), 7.78 (dd, J = 7.4, 1.2 Hz, 1H), 7.71 (m, 1H), 7.48 (dd, J =

¹³C NMR (125 MHz, CDCl₃): δ 165.7, 165.5, 151.8, 151.0, 143.6, 136.7, 136.4, 133.7, 130.1, 129.6, 129.3, 128.8, 128.1, 126.2, 125.0, 122.1, 119.2.

4-fluoro-2-(quinolin-8-yl)isoindoline-1,3-dione (2r): Compound (2r) was prepared according to the general



8.4, 4.2 Hz, 1H).

procedure A from ir (79.8 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (25% EtOAc/Hexane) in 69% (61.2 mg) yield as white solid. R_f Value = o.2. The NMR data of 2r is in accordance with the literature.⁴

¹H NMR (500 MHz, CDCl₃): δ 8.84 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.20 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.95 (dd, J = 8.3, 1.5 Hz, 1H), 7.80-7.73 (m, 3H), 7.65 (m, 1H), 7.45-7.41 (m, 2H).

¹³C NMR (125 MHz, CDCl₃): δ 166.73, 166.71, 165.96 (d, *J* = 285 Hz), 156.7, 150.9, 144.0, 136.7 (d, J = 7.6 Hz), 136.1, 134.4, 130.1, 129.7, 129.23 (d, J = 8.7 Hz), 126.0, 122.48 (d, J = 19.7 Hz),

121.9, 119.98 (d, J = 3.3 Hz), 118.17 (d, J = 12.2 Hz).

¹⁹**F NMR** (377 MHz, $CDCl_3$): δ = -112.17.

4-iodo-2-(quinolin-8-yl)isoindoline-1,3-dione (2s): Compound (2s) was prepared according to the general



procedure **A** from **1s** (112 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (25% EtOAc/Hexane) in 71% (86 mg) yield as white solid. R_f Value = 0.2. ¹H **NMR** (500 MHz, CDCl₃): δ 8.86 (dd, J = 4.1, 1.6 Hz, 1H), 8.23 (dd, J = 8.3, 1.6 Hz, 1H), 8.19 (dd, J = 7.9, 0.8 Hz, 1H), 7.99-7.96 (m, 2H), 7.44 (dd, J = 7.2, 1.4 Hz, 1H), 7.69-7.65 (m, 1H), 7.48-7.43 (m, 2H).

¹³**C NMR** (125 MHz, CDCl₃): δ 166.4, 165.9, 150.9, 145.4, 144.1, 136.1, 134.7, 134.2, 132.8, 130.1, 129.7, 129.5, 129.2, 126.0, 123.6, 121.9, 89.2.

HRMS: $[M+H]^+$ calculated for $C_{17}H_{10}IN_2O_2$: 400.9787, found 400.9782.

5-(quinolin-8-yl)-4H-thieno[3,2-c]pyrrole-4,6(5H)-dione (2t): Compound (2t) was prepared according to the



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general procedure **A** from **it** (76.2 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (25% EtOAc/Hexane) in 47% (40 mg) yield as white solid. R_f Value = 0.2. ¹H **NMR** (500 MHz, CDCl₃): δ 8.88 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.22 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.95 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.85 (d, *J* = 4.6 Hz, 1H), 7.75 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.45 (q, *J* = 3.9 Hz, 2H). ¹³C **NMR** (100 MHz, CDCl₃): δ 163.4, 162.3, 150.9, 144.9, 144.4, 141.3, 137.7, 136.1, 130.5, 129.8,

¹³C NMR (100 MHz, CDCl₃): *δ* 163.4, 162.3, 150.9, 144.9, 144.4, 141.3, 137.7, 136.1, 130.5, 129.8, 129.6, 129.2, 126.1, 121.9, 121.6.

HRMS: $[M+H]^+$ calculated for $C_{15}H_0N_2O_2S$: 281.0385, found 281.0486.

2-(quinolin-8-yl)-1*H*-benzo[*e*]isoindole-1,3(2*H*)-dione (2u): Compound (2u) was prepared according to the general procedure **A** from 1u (89.4 mg, o.3 mmol, 1 equiv) and purified by flash column chromatography (25% EtOAc/Hexane) in 41% (40 mg) yield as white solid. R_f Value = 0.2. The NMR data of 2u is in accordance with the literature.⁴

¹**H NMR** (400 MHz, CDCl₃): δ 9.00 (m, 1H), 8.86 (dd, *J* = 3.8, 1.8 Hz, 1H), 8.24-8.20 (m, 2H), 8.00-7.95 (m, 3H), 7.82 (dd, *J* = 7.2, 1.4 Hz, 1H), 7.75-7.65 (m, 3H), 7.42 (dd, *J* = 8.6, 4.2 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 169.1, 168.5, 150.8, 144.4, 136.6, 136.1, 135.1, 131.6, 130.4, 129.8, 129.5, 129.4, 129.2, 128.7, 128.6, 128.2, 127.6, 126.1, 125.1, 121.8, 118.8.

5-Methyl-2-(quinolin-8-yl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide (2v): Compound (2v) was prepared according to the general procedure **A** from 1v (89.4 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (30% EtOAc/Hexane) in 42% (41 mg) yield as white solid. R_f Value = 0.2. The NMR data of 2v is in accordance with the literature.⁶

¹**H NMR** (400 MHz, CDCl₃): δ 8.90 (d, *J* = 4.2, 1H), 8.21 (dd, *J* = 8.2, 1.6 Hz, 1H), 8.01 (m, 3H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.70-7.68 (m, 2H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 1H), 2.56 (s, 3H).

¹³**C NMR** (100 MHz, CDCl₃): δ 159.0, 151.3, 145.7, 144.6, 136.1, 135.45, 135.42, 131.6, 131.0, 129.5, 127.7, 126.5, 126.1, 125.9, 122.1, 121.1, 21.7.

5-Methoxy-2-(quinolin-8-yl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide (2w): Compound (2w) was prepared



according to the general procedure **A** from $\mathbf{1w}$ (94.2 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (40% EtOAc/Hexane) in 55% (56.5 mg) yield as white solid. R_f Value = 0.25. The NMR data of $\mathbf{2w}$ is in accordance with the literature.⁶

¹**H NMR** (400 MHz, CDCl₃): δ 8.93 (dd, J = 4.0, 1.6 Hz, 1H), 8.23 (dd, J = 8.4, 1.7 Hz, 1H), 8.02 (d, J = 7.7 Hz, 2H), 7.91 (d, J = 8.5 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.62 (d, J = 2.4 Hz, 1H), 7.46 (dd, J = 8.4, 4.2 Hz, 1H), 7.37 (dd, J = 8.5, 2.4 Hz, 1H),

3.97 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 164.4, 158.9, 151.4, 144.6, 136.2, 131.6, 131.0, 130.1, 129.8, 129.6, 126.5, 126.2, 122.9, 122.1, 121.8, 108.8, 56.2.

5-(tert-Butyl)-2-(quinolin-8-yl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide (2x): Compound (2x) was prepared



according to the general procedure **A** from **1x** (102 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (30% EtOAc/Hexane) in 36% (40.2 mg) yield as white solid. R_f Value = 0.25. The NMR data of **2x** is in accordance with the literature.⁶

¹**H NMR** (400 MHz, CDCl₃): δ 8.94 (s, 1H), 8.24 (m, 2H), 8.03 (d, *J* = 7.6 Hz, 2H), 7.95 (s, 2H), 7.69 (t, *J* = 7.9 Hz, 1H), 7.48 (m, 1H), 1.43 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ 159.3, 159.0, 151.2, 144.4, 136.5, 135.3, 132.1, 131.8, 131.0,

129.6, 127.6, 126.4, 126.3, 122.7, 122.16, 121.14, 35.8, 31.0.

5,6-Dimethoxy-2-(quinolin-8-yl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide (2y): Compound (2y) was prepared



according to the general procedure **A** from **1y** (103 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (50% EtOAc/Hexane) in 45% (50.2 mg) yield as white solid. R_f Value = 0.25.

¹**H NMR** (500 MHz, CDCl₃): δ 8.92 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.23 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.01 (m, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.57 (s, 1H), 7.45 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.41 (s, 1H), 4.04 (s, 3H), 4.03 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 159.1, 154.6, 153.9, 151.2, 144.6, 136.3, 131.8, 131.2, 130.9, 129.6, 126.7, 126.2, 122.1, 121.0, 106.4, 102.8, 56.8, 56.7.

HRMS: $[M+H]^+$ calculated for $C_{18}H_{15}N_2O_5S$: 371.0702, found 371.0705.

2-(Quinolin-8-yl)-5-(trifluoromethyl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide (2z): Compound (2z) was



prepared according to the general procedure **A** from **1z** (105 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (30% EtOAc/Hexane) in 45% (51 mg) yield as white solid. R_f Value = 0.2. **¹H NMR** (500 MHz, CDCl₃): δ 8.91 (d, J = 2.8 Hz, 1H), 8.49 (s, 1H), 8.26 (m, 1H),

8.18 (m, 2H), 8.04 (m, 2H), 7.70 (t, J = 7.8 Hz, 1H), 7.48 (dd, J = 8.3, 4.2 Hz, 1H).

¹³**C NMR** (125 MHz, CDCl₃): δ 157.4, 151.5, 144.4, 141.1, 136.6 (q, J_{C-F} = 33.9 Hz), 136.2,

131.87 (q, J_{C-F} = 3.3 Hz), 131.5, 131.4, 129.6, 128.6, 126.2, 126.1, 123.2 (q, J_{C-F} = 3.5 Hz), 22.33.

122.8 (q, J_{C-F} = 273.6 Hz), 122.37, 122.33. ¹⁹F NMR (377 MHz, CDCl₃): δ = -62.97.

HRMS: $[M+H]^+$ calculated for $C_{17}H_{10}F_3N_2O_3S$: 379.0364, found 379.0357.

4. Site selective (sp²)C-H bond carbonylation of aminoquinoline amides:

5-(pyrimidin-2-yl)-2-(quinolin-8-yl)isoindoline-1,3-dione (3a): Compound (3a) was prepared according to the



general procedure **A** from **1aa** (97.8 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (30% EtOAc/Hexane) in 75% (79 mg) yield as white solid. R_f Value = 0.25.

¹**H** NMR (400 MHz, CDCl₃): δ 9.11 (s, 1H), 8.94 (m, 1H), 8.87 (d, J = 4.5 Hz, 3H), 8.23 (m, 1H), 8.11 (d, J = 7.6 Hz, 1H), 7.96 (d, J = 7.8 Hz, 1H), 7.79 (m, 1H), 7.68 (t, J = 7.9 Hz, 1H), 7.44 (dd, J = 7.9, 3.9 Hz, 1H), 7.29 (t, J = 4.5 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 167.6, 167.5, 162.7, 157.4, 150.8, 144.1, 143.5, 136.2, 133.85, 133.81, 132.9, 130.2, 129.7, 129.6, 129.2, 126.1, 123.9, 123.7, 121.8, 120.1.

HRMS: $[M+H]^+$ calculated for $C_{21}H_{13}N_4O_2$: 353.1039, found 353.1036.

4-(pyridin-2-yl)-N-(quinolin-8-yl)benzamide (3b): Compound **(3b)** was prepared according to the general procedure **A** from **1ab** (97.2 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (30% EtOAc/Hexane) in 60% (64 mg) yield as white solid. R_f Value = 0.25.

¹**H** NMR (400 MHz, CDCl₃): δ 8.87 (dd, J = 4.2, 1.5 Hz, 1H), 8.78 (d, J = 5.0 Hz, 1H), 8.60 (s, 1H), 8.54 (m, 1H), 8.24 (m, 1H), 8.10 (d, J = 8.1 Hz, 1H), 7.98 (d, J = 7.7 Hz, 1H), 7.87 (m, 2H), 7.79 (m, 1H), 7.69 (t, J = 8.2 Hz, 1H), 7.45 (dd, J = 8.0, 4.0 Hz, 1H), 7.36 (m, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 167.78, 167.74, 155.0, 150.9, 150.0, 145.4, 144.1, 137.1, 136.2, 133.1, 132.7, 132.2, 130.2, 129.7, 129.6, 129.2, 126.1, 124.2, 123.4, 122.1, 121.9, 121.0.

HRMS: $[M+H]^+$ calculated for $C_{22}H_{14}N_3O_2$: 352.1086, found 352.1086.

5-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)-2-(quinolin-8-yl)isoindoline-1,3-dione (3c): Compound (3c) was prepared according to the general procedure **A** from 1ac (94.2 mg, 0.2 mmol, 1 equiv) and purified by flash column chromatography (30% EtOAc/Hexane) in 23% (18 mg) yield as white solid. R_f Value = 0.25.

¹**H NMR** (400 MHz, CDCl₃): δ 8.88 (d, J = 3.7 Hz, 1H), 8.50-8.43 (m, 3H), 8.26 (d, J = 7.8 Hz, 1H), 8.14 (d, J = 8.2 Hz, 1H), 8.00 (m, 2H), 7.80 (d, J = 7.2 Hz, 1H), 7.73-7.66 (m, 2H), 7.47 (dd, J = 8.3, 4.1 Hz, 1H), 7.22 (dd, J = 7.9, 4.8 Hz, 1H), 6.75 (d, J = 3.7 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 167.46, 167.42, 150.9, 147.5, 144.1, 144.0, 143.8, 136.3, 134.1, 133.4, 130.4, 130.0, 129.7, 129.5, 128.3, 127.9, 126.6, 126.2, 125.1, 122.1, 121.9, 117.9, 117.7, 103.9.

HRMS: [M+H]⁺ calculated for C₂₄H₁₅N₄O₂: 391.1195, found 391.1188.

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5-(1H-pyrazol-1-yl)-2-(quinolin-8-yl)isoindoline-1,3-dione (3d): Compound (3d) was prepared according to the



general procedure **A** from **1ad** (94.2 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (30% EtOAc/Hexane) in 51% (53 mg) yield as white solid. R_f Value = 0.25.

¹**H NMR** (400 MHz, CDCl₃): δ 8.86 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.28 (d, *J* = 2.0 Hz, 1H), 8.23 (dd, *J* = 8.3, 2.0 Hz, 2H), 8.09 (d, *J* = 2.3 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.97 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.82 (d, *J* = 1.7 Hz, 1H), 7.78 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.68 (t, *J* = 7.9 Hz, 1H), 7.45 (dd, *J* = 8.1, 4.1 Hz, 1H), 6.57 (t, *J* = 2.3 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 167.19, 167.11, 150.9, 144.7, 144.1, 142.5, 136.2, 134.3, 130.2, 129.7, 129.6, 129.29, 129.23, 127.0, 126.1, 125.4, 123.8, 121.9, 113.4, 109.2.

HRMS: $[M+H]^+$ calculated for $C_{20}H_{13}N_4O_2$: 341.1039, found 341.1031.

2-(quinolin-8-yl)-5-(thiophen-2-yl)isoindoline-1,3-dione (3e): Compound (3e) was prepared according to the



general procedure **A** from **1ae** (99 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (30% EtOAc/Hexane) in 51% (55 mg) yield as white solid. R_f Value = 0.25. **¹H NMR** (500 MHz, CDCl₃): δ 8.87 (dd, J = 4.0, 1.4 Hz, 1H), 8.22 (m, 2H), 7.98

(m, 3H), 7.77 (m, 1H), 7.68 (t, J = 7.9 Hz, 1H), 7.53 (d, J = 3.5 Hz, 1H), 7.44 (m, 2H), 7.16 (m, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 167.7, 167.5, 150.9, 144.1, 142.0, 140.5, 136.2, 133.4, 130.8, 130.3, 130.2, 129.7, 129.6, 129.2, 128.6, 127.2, 126.1, 125.4, 124.5, 121.9, 120.6.

HRMS: $[M+H]^+$ calculated for $C_{21}H_{13}N_2O_2S$: 357.0698, found 357.0694.

2-(quinolin-8-yl)-5-(thiophen-3-yl)isoindoline-1,3-dione (3f): Compound (**3f**) was prepared according to the general procedure **A** from **1af** (99 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (20% FtOAc (Hexane) in 47% (50 mg) yield as white



general procedure **A** from **1af** (99 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (30% EtOAc/Hexane) in 47% (50 mg) yield as white solid. R_f Value = 0.25. **'H NMR** (500 MHz, CDCl₃): δ 8.86 (dd, J = 4.0, 1.6 Hz, 1H), 8.22 (m, 2H), 8.00

H NMR (500 MHz, CDCl_3): δ 8.86 (dd, J = 4.0, 1.6 Hz, 1H), 8.22 (m, 2H), 8.00 (s, 2H), 7.96 (dd, J = 8.2, 1.6 Hz, 1H), 7.77 (dd, J = 7.1, 1.1 Hz, 1H), 7.69 (m, 2H), 7.50-7.47 (m, 2H), 7.44 (dd, J = 8.3, 4.3 Hz, 1H).

S⁻¹³**C NMR** (100 MHz, CDCl₃): δ 167.8, 167.7, 150.8, 144.2, 141.8, 140.2, 136.1, 133.3, 131.6, 130.3, 130.2, 129.7, 129.5, 129.2, 127.2, 126.1, 126.0, 124.4, 122.9, 121.8, 121.4.

HRMS: $[M+H]^+$ calculated for $C_{21}H_{13}N_2O_2S$: 357.0698, found 357.0698.



5-(benzo[*d*]**oxazol-2-yl**)-**2-(quinolin-8-yl)isoindoline-1,3-dione (3g):** Compound (**3g**) was prepared according to the general procedure **A** from **1ag** (73 mg, 0.2 mmol, 1 equiv) and purified by flash column chromatography (30% EtOAc/Hexane) in 54% (42.5 mg) yield as white solid. R_f Value = 0.25.

¹**H NMR** (500 MHz, DMSO-d₆): δ 8.88 (dd, J = 4.1, 1.5 Hz, 1H), 8.73 (m, 1H), 8.63 (s, 1H), 8.55 (dd, J = 8.2, 1.4 Hz, 1H), 8.23 (m, 2H), 7.98 (m, 1H), 7.92 (d, J = 7.7 Hz, 1H), 7.88 (d, J = 7.9 Hz, 1H), 7.82 (t, J = 7.5 Hz, 1H), 7.64 (dd, J = 8.2, 4.0 Hz, 1H), 7.55-7.47 (m, 2H).

¹³C NMR (125 MHz, CDCl₃): δ 167.1, 167.0, 160.9, 151.0, 150.9, 144.1, 141.8, 136.2, 134.1, 133.2, 133.0, 132.8, 130.2, 129.8, 129.5, 129.3, 126.2, 126.1, 125.1, 124.4, 122.8, 122.0, 120.6, 110.9.

HRMS: [M+H]⁺ calculated for C₂₄H₁₄N₃O₃: 392.1035, found 392.1038.

4-(benzo[d]oxazol-2-yl)-2-(quinolin-8-yl)isoindoline-1,3-dione (3h): Compound (3h) was prepared according



to the general procedure **A** from **1ah** (73 mg, 0.2 mmol, 1 equiv) and purified by flash column chromatography (30% EtOAc/Hexane) in 48% (38 mg) yield as white solid. R_f Value = 0.25.

¹**H NMR** (500 MHz, DMSO-d₆): δ 8.87 (dd, J = 3.9, 1.6 Hz, 1H), 8.72 (dd, J = 7.8, 1.4 Hz, 1H), 8.61 (s, 1H), 8.54 (dd, J = 8.3, 1.4 Hz, 1H), 8.22 (m, 2H), 7.79 (dd, J = 7.3, 1.4 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.81 (t, J = 7.6 Hz, 1H), 7.64 (dd, J = 8.2, 4.1 Hz, 1H), 7.54-7.47 (m, 2H).

¹³C NMR (125 MHz, DMSO-d₆): δ 167.3, 167.2, 161.2, 152.0, 151.0, 144.1, 141.9, 137.3, 134.3, 134.0, 133.3, 132.7, 131.3, 130.6, 129.8, 129.3, 127.2, 127.0, 126.0, 125.3, 123.0, 122.2, 121.0, 111.9. HRMS: $[M+H]^+$ calculated for $C_{24}H_{14}N_3O_3$: 392.1035, found 392.1032.

5. General procedure (B) for cobalt-catalyzed carbonylation of sp³(C-H) aliphatic amides:



In an oven-dried Schlenk tube **A** equipped with a teflon coated stir bar, to which 1,2-diphenyl -1,1,2,2-tetramethyldisilane (162 mg, 0.6 mmol, 3 equiv), caesium fluoride (94.8 mg, 0.6 mmol, 3 equiv) and DMF (2.0 mL) were added in order under argon atmosphere. Schlenk tube was closed with a screw cap, evacuated and subsequently filled with 1-2 atm of carbon dioxide before keeping in preheated (110 °C) oil bath for 90 min. In an another oven-dried Schlenk tube **B** equipped with a teflon coated stir bar, Co(acac)₂ (5.1 mg, 0.02 mmol, 10 mol%), NaO₂CPh (43 mg, 0.3 mmol, 1.5 equiv), Ag₂CO₃ (165 mg, 0.6 mmol, 3 equiv), followed by *N*-(quinolin-8-yl)pivalamide (45 mg, 0.2 mmol, 1 equiv) in chlorobenzene (2 mL) was added. Finally Schlenk tube was evacuated. Gas produced in Schlenk tube **A** was transferred to Schlenk tube **B** connected through small rubber tube. The Schlenk tube **B** was placed in preheated oil bath at 160 °C for 30 h. After the completion of reaction it was cooled to room temperature and depressurized. The reaction mixture was diluted with ethyl acetate and then filtered through a short pad of celite. Solvents were removed under reduced pressure and the reaction mixture was purified by flash column chromatography (50% EtOAc/Hexane) on silica gel the desired product was obtained in 68% (35 mg) as white solid. R_f Value = 0.2.

3,3-dimethyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (5a): Compound (5a) was prepared according to the general



procedure **B** from **4a** (45.6 mg, 0.2 mmol, 1 equiv) and purified by flash column chromatography (50% EtOAc/Hexane) in 68% (35 mg) yield as white solid. R_f Value = 0.2. The NMR data of **5a** is in accordance with the literature.²

¹**H** NMR (500 MHz, CDCl₃): δ 8.85 (m, 1H), 8.17 (m, 1H), 7.91 (m, 1H), 7.62 (m, 2H), 7.41 (m, 1H), 2.95 (d, *J* = 18.0 Hz, 1H), 2.82 (d, *J* = 18.0 Hz, 1H), 1.61 (s, 3H), 1.50 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 182.9, 175.6, 150.9, 143.5, 135.9, 130.2, 129.5, 129.3, 129.1, 125.9, 121.8,



3-butyl-3-methyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (5b): Compound (**5b**) was prepared according to the general procedure **B** from **4b** (54 mg, 0.2 mmol, 1 equiv) and purified by flash column chromatography (40% EtOAc/Hexane) in 71% (41.5 mg) yield as pale yellow solid. R_f Value = 0.25. The NMR data of **5b** is in accordance with the literature.²

¹**H NMR** (500 MHz, CDCl₃, a mixture of atropisomers in ratio 1.1:1.0, the minor one is marked with an *): δ 8.85 (ddd, *J* = 11.9, 8.0, 4.3 Hz, 1H), 8.18 (dt, *J* = 8.2, 1.8 Hz, 1H), 7.91 (m, 1H), 7.64-7.58 (m, 2H), 7.44-7.41 (ddd, *J* = 12.6, 8.4, 4.2 Hz, 1H), 2.90 (d, *J* = 18.2 Hz, 1H), 2.84 (d, *J* = 18.2 Hz, 1H), 1.96-1.69 (m, 2H), 1.58 (s, 3H), 1.46-1.37 (m, 4H), 0.97 (q, *J* = 7.2 Hz, 3H); 8.85 (ddd, *J* = 11.9, 8.0, 4.3 Hz, 1H)*, 8.18 (dt, *J* = 8.2, 1.8 Hz, 1H)*, 7.64-7.58 (m, 2H)*, 7.44-7.41 (ddd, *J* = 12.6, 8.4, 4.2 Hz, 1H)*, 3.04 (d, *J* = 18.3 Hz, 1H)*, 2.69 (d, *J* = 18.2 Hz, 1H)*, 1.96-1.69 (m, 2H)*, 1.48 (s, 3H)*, 1.46-1.37 (m, 4H)*, 0.97 (q, *J* = 7.2 Hz, 3H)*.

¹³**C NMR** (100 MHz, CDCl₃): δ 182.6, 176.0, 150.6, 143.4, 136.0, 130.3, 129.54, 129.39, 129.19, 126.0, 121.8, 44.5, 41.5, 38.3, 26.7, 24.4, 22.9, 13.9; 182.5^{*}, 175.9^{*}, 150.7^{*}, 143.4^{*}, 136.3^{*}, 130.1^{*}, 129.59^{*}, 129.3^{*}, 129.15^{*}, 126.1^{*}, 121.8^{*}, 44.6^{*}, 41.6^{*}, 38.1^{*}, 26.7^{*}, 24.7^{*}, 23.0^{*}, 14.0^{*}.

3-isobutyl-3-methyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (5c): Compound (5c) was prepared according to the general procedure **B** from 4c (54 mg, 0.2 mmol, 1 equiv) and purified by flash column chromatography (40% EtOAc/Hexane) in 51% (30.5 mg) yield as pale yellow liquid. R_f Value = 0.2. The NMR data of 5c is in accordance with the literature.²



¹**H NMR** (500 MHz, CDCl₃, a mixture of atropisomers in ratio 1.2:1.0, the minor one is marked with an *): δ 8.87-8.84 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.17 (m, 1H), 7.91 (m, 1H), 7.63-7.58 (m, 2H), 7.43-7.40 (dd, *J* = 4.1, 1.6 H, 1H), 3.01 (d, *J* = 18.2 Hz, 1H), 2.84 (d, *J* = 18.2 Hz, 1H), 1.91-1.86 (m, 1H),

1.85-1.82 (m, 1H), 1.78 (m, 1H), 1.59 (s, 3H), 1.07-1.00 (m, 6H); 8.87-8.84 (dd, J = 4.1, 1.6 Hz, 1H)*, 8.17 (m, 1H)*, 7.91 (m, 1H)*, 7.63-7.58 (m, 2H)*, 7.43-7.40 (dd, J = 4.1, 1.6 H, 1H)*, 3.16 (d, J = 18.1 Hz, 1H)*, 2.69 (d, J = 18.0, Hz, 1H)*, 2.05-2.00 (m, 1H)*, 1.85-1.82 (m, 1H)*, 1.78 (m, 1H)*, 1.48 (s, 3H)*, 1.07-1.00 (m, 6H)*.

¹³C NMR (100 MHz, CDCl₃): δ 182.9, 176.1, 150.6, 143.45, 136.1, 130.2, 129.58, 129.3, 129.1, 126.0, 121.8, 45.9, 44.3, 41.6, 25.6, 25.2, 24.6, 22.9; 182.8*, 175.9*, 150.7*, 143.42*, 136.3*, 130.1*, 129.56*, 129.3*, 129.1*, 126.1*, 121.8*, 45.8*, 44.4*, 42.0*, 25.9*, 25.0*, 24.7*, 23.3*.

3-cyclopentyl-3-methyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (5d): Compound (5d) was prepared according to



the general procedure **B** from **4d** (56.4 mg, 0.2 mmol, 1 equiv) and purified by flash column chromatography (40% EtOAc/Hexane) in 49% (30.5 mg) yield as pale yellow liquid. R_f Value = 0.2. The NMR data of 5d is in accordance with the literature.²

¹H NMR (500 MHz, CDCl₂, a mixture of atropisomers in ratio 1.2:1.0, the minor one is marked with an *): δ 8.86 (ddd, J = 13.8, 9.6, 4.1 Hz, 1H), 8.18 (ddd, J = 12.2, 8.3, 4.0 Hz, 1H), 7.91 (m, 1H), 7.63-7.57 (m, 2H), 7.43 (m, 1H), 2.86 (d, J = 18.3 Hz, 1H), 2.75 (d, J = 18.2 Hz, 1H), 2.48-2.36 (m, 1H), 1.96-1.82 (m, 2H), 1.67 (m, 4H), 1.60 (s, 3H), 1.43-1.32 (m, 2H); 8.86 (ddd, J = 13.8, 9.6, 4.1 Hz, 1H)*, 8.18 (ddd, J = 12.2, 8.3, 4.0 Hz, 1H)*, 7.91 (m, 1H)*, 7.63-7.57 (m, 2H)*, 7.43 (m, 1H)*, 3.00 (d, *J* = 18.3 Hz, 1H)*, 2.60 (d, *J* = 18.2 Hz, 1H)*, 2.48-2.36 (m, 1H)*, 1.96-1.82 (m, 2H)*,

1.67 (m, 4H)*, 1.50 (s, 3H)*, 1.43-1.32 (m, 2H)*.

¹³C NMR (100 MHz, CDCl₃): δ 182.5, 176.2, 150.7, 143.5, 135.9, 130.2, 129.59, 129.3, 129.17, 126.0, 121.9, 46.99, 46.4, 39.0, 27.8, 27.6, 25.6, 25.3, 24.3; 182.5*, 176.1*, 150.9*, 143.5*, 136.0*, 130.4*, 129.51*, 129.2*, 129.14*, 125.9*, 121.8*, 46.99*, 46.1*, 39.4*, 27.9*, 27.7*, 25.9*, 25.5*, 24.4*.

2-(quinolin-8-yl)-2-azaspiro[4.4]nonane-1,3-dione (5e): Compound (5e) was prepared according to the general procedure **B** from **4e** (50.8 mg, 0.2 mmol, 1 equiv) and purified by flash column chromatography (40% EtOAc/Hexane) in 56% (31.5 mg) yield as white solid. R_f Value = 0.2.



The NMR data of **5e** is in accordance with the literature.²

¹**H NMR** (400 MHz, CDCl₃): δ 8.86 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.19 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.92 (q, J = 3.2 Hz, 1H), 7.62 (m, 2H), 7.43 (dd, J = 8.3, 4.2 Hz, 1H), 3.00 (d, J = 18.0 Hz, 1H), 2.85 (d, J = 18.0 Hz, 1H), 2.45-2.38 (m, 1H), 2.34-2.29 (m, 1H), 2.03-1.94 (m, 3H), 1.88-1.78 (m, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 183.0, 176.1, 150.9, 143.5, 136.0, 130.4, 129.5, 129.3, 129.1, 126.0, 121.9, 51.0, 44.2, 39.9, 38.1, 25.4, 25.3.

2-(quinolin-8-yl)-2-azaspiro[4.5]decane-1,3-dione (5f): Compound (5f) was prepared according to the general procedure **B** from $4\mathbf{f}$ (53.6 mg, 0.2 mmol, 1 equiv) and purified by flash column chromatography (40% EtOAc/Hexane) in 51% (30.5 mg) yield as white solid. R_f Value = 0.2. The NMR data of **5f** is in accordance with the literature.²



¹**H NMR** (400 MHz, CDCl₃): δ 8.84 (dd J = 4.1, 1.8 Hz, 1H), 8.17 (dd, J = 8.3, 1.6 Hz, 1H), 7.90 (q, J = 3.2 Hz, 1H), 7.61 (m, 2H), 7.41 (dd, J = 8.1, 4.0 Hz, 1H), 2.98 (d, J = 18.2 Hz, 1H), 2.80 (d, J = 18.2 Hz, 1H), 2.02-1.97 (m, 3H), 1.89-1.85 (m, 2H), 1.74 (m, 2H), 1.46-1.40 (m, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 182.6, 176.0, 150.9, 143.5, 135.9, 130.2, 129.5, 129.3, 129.1, 125.9, 121.8, 45.7, 40.5, 33.6, 33.4, 25.0, 22.2, 22.0.

3-benzyl-3-methyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (5g): Compound (5g) was prepared according to the general procedure B from 4g (60.8 mg, 0.2 mmol, 1 equiv) and purified by flash column



chromatography (30% EtOAc/Hexane) in 70% (46.5 mg) yield as white solid. R_f Value = 0.2. ¹H NMR (500 MHz, CDCl₂, a mixture of atropisomers in ratio 2.6:1.0, the minor one is marked with an *): δ 8.85 (dd, J = 4.2, 1.7 Hz, 1H), 8.16 (dd, J = 8.2, 1.6 Hz, 1H), 7.88 (dd, J = 8.3, 1.2 Hz, 1H), 7.63-7.54 (m, 1H), 7.44-7.27 (m, 6H), 7.16 (dd, J = 7.2, 1.1 Hz, 1H), 3.35 (d, J = 13.5 Hz, 1H), 3.03 (d, J = 18.3 Hz, 1H), 2.83 (d, J = 13.3 Hz, 1H), 2.82 (d, J = 18.3 Hz, 1H), 1.71 (s, 3H); 8.79 (dd, J = 4.1, 1.7 Hz, 1H)*, 8.19 (m, 1H)*, 7.92 (dd, J = 6.1, 3.6 Hz, 1H)*, 7.63-7.54 (m, 1H)*, 7.44-7.27 (m, 6H)*, 7.16 (dd, J = 7.2, 1.1 Hz, 1H)*, 3.14 (d, J = 13.8 Hz, 1H)*, 3.18 (d, J = 18.1 Hz, 1H)*, 2.83 (d, J = 13.3 Hz, 1H)*, 2.57 (d, J = 18.1 Hz, 1H)*, 1.52 (s, 3H)*.

¹³C NMR (125 MHz, CDCl₃): δ 181.8, 175.4, 151.0, 143.59, 136.35, 135.99, 130.6, 130.06, 129.5, 129.22, 129.07, 128.6, 127.3, 125.98, 121.8, 46.0, 43.9, 40.2, 25.6; 182.2*, 175.5*, 150.7*, 143.54*, 136.38*, 135.92*, 130.6*, 130.08*, 129.6*, 129.26*, 129.14*, 128.4*, 126.9*, 125.97*, 121.9*, 45.7*, 43.1*, 40.6*,

24.7*.

HRMS: $[M+H]^+$ calculated for $C_{21}H_{19}N_2O_2$: 331.1447, found 331.1449.

3-(4-bromobenzyl)-3-methyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (5h): Compound (5h) was prepared



according to the general procedure **B** from **4h** (76.4 mg, 0.2 mmol, 1 equiv) and purified by flash column chromatography (40% EtOAc/Hexane) in 42% (34 mg) yield as white solid. R_f Value = 0.25. The NMR data of **5h** is in accordance with the literature.²

¹H NMR (500 MHz, CDCl₂, a mixture of atropisomers in ratio 2.4:1.0, the minor one is marked with an *): δ 8.85 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.18 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.90 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.64-7.57 (m, 1H), 7.51-7.48 (m, 2H), 7.45-7.41 (m, 1H), 7.20 (m, 1H), 7.15 (m, 2H), 3.30 (d, J = 13.4 Hz, 1H), 2.96 (d, J = 18.2 Hz, 1H), 2.81-2.77 (m, 2H), 1.69 (s, 3H); 8.76 (dd, J = 4.1, 1.7 Hz, 1H)*, 8.18 (dd, J = 8.3, 1.6 Hz, 1H)*, 7.93 (m, 1H)*, 7.64-7.57 (m, 1H)*, 7.51-7.48 (m, 2H)*, 7.45-7.41 (m, 1H)*, 7.20 (m, 1H)*, 7.15 (m, 2H)*, 3.36 (d, J = 13.8 Hz, 1H)*, 3.10 (d, J = 18.0 Hz, 1H)*, 2.95 (d, J = 13.6 Hz, 1H)*, 2.60 (d, J = 18.2 Hz, 1H)*, 1.53 (s, 3H)*.

¹³C NMR (125 MHz, CDCl₃): δ 181.6, 175.1, 151.0, 143.5, 136.0, 135.38, 132.2, 131.7, 129.9, 129.6, $129.20, 129.12, 126.0, 121.93, 121.4, 45.9, 43.0, 40.0, 25.7; 181.8^*, 175.2^*, 150.8^*, 143.4^*, 135.9^*, 135.31^*, 131.8^*, 131.5^*, 130.0^*, 131.8^*, 131.5^*, 130.0^*, 131.8^*, 1$ 129.7*, 129.24*, 129.15*, 125.9*, 121.98*, 121.0*, 45.6*, 42.6*, 40.4*, 25.1*.

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3-methyl-3-phenyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (5i): Compound (5i) was prepared according to the general procedure B from 4i (58 mg, 0.2 mmol, 1 equiv) and purified by flash column chromatography (30% EtOAc/Hexane) in 32% (5i)(20.5 mg) of sp³ and 9% (5i') (6 mg) sp² carbonylated product yield. R_f Value = 0.3. The NMR data of **5i** is in accordance with the literature.²

> ¹H NMR (400 MHz, CDCl₂, a mixture of atropisomers in ratio 1.2:1.0, the minor one is marked with an *): δ 8.90 (m, 1H), 8.20 (dt, J = 8.3, 1.5 Hz, 1H), 7.94 (m, 1H), 7.78 (m, 1H), 7.71-7.67 (m, 1H), 7.65-7.62 (m, 1H), 7.58-7.55 (m, 1H), 7.47-7.42 (m, 3H), 7.36-7.31 (m, 1H), 3.42 (d, J = 18.3 Hz, 1H), 3.13 (d, *J* = 18.2 Hz, 1H), 2.02 (s, 3H); 8.90 (m, 1H)*, 8.20 (dt, *J* = 8.3, 1.5 Hz, 1H)*, 7.94 (m, 1H)*, 7.78 (m, 1H)*, 7.71-7.67 (m, 1H)*, 7.65-7.62 (m, 1H)*, 7.58-7.55 (m, 1H)*, 7.47-7.42 (m, 3H)*, 7.36-7.31 (m, 1H)*, 3.38 (d, J = 18.1 Hz, 1H)*, 3.28 (d, J = 18.1 Hz, 1H)*, 1.93 (s, 3H)*.

¹³C NMR (100 MHz, CDCl₃): δ 180.6, 175.4, 150.8, 143.5, 142.1, 136.0, 130.3, 129.77, 129.3, 129.2, 128.9, 127.4, 126.0, 125.8, 121.9, 48.5, 45.5, 24.9; 180.9*, 175.4*, 151.0*, 143.5*, 142.4*, 136.0*, 130.2*, 129.70*, 129.5*, 129.1*, 128.7*, 127.3*, 126.3*, 126.0*, 121.9*, 48.7*, 46.6*, 26.3*.

3-methyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (5j): Compound (5j) was prepared according to the general



procedure B from 4j (42.8 mg, 0.2 mmol, 1 equiv) and purified by flash column chromatography (70% EtOAc/Hexane) in 72% (35 mg) yield as pale yellow solid. R_f Value = 0.2. The NMR data of **5j** is in accordance with the literature.²

¹H NMR (400 MHz, CDCl₃, a mixture of atropisomers in ratio 1.1:1.0, the minor one is marked with an *): δ 8.87 (m, 1H), 8.20 (m, 1H), 7.93 (dt, *J* = 7.5, 2.6 Hz, 1H), 7.62 (m, 2H), 7.44 (m, 1H), 3.35-3.29 (m, 1H), 3.20-3.12 (m, 1H), 2.63-2.57 (m, 1H), 1.51 (d, J = 7.0 Hz, 3H); 8.87 (m, 1H)*, 8.20 (m, 1H)*, 7.93 (dt, *J* = 7.5, 2.6 Hz, 1H)*, 7.62 (m, 2H)*, 7.44 (m, 1H)*, 3.35-3.29 (m, 1H)*, 3.20-3.12 (m, 1H)*, 2.78-2.74 (m, 1H)*, 1.60 (d, *J* = 7.0 Hz, 3H)*.

¹³C NMR (100 MHz, CDCl₃): δ 180.2, 176.0, 150.8, 143.3, 136.1, 130.0, 129.63, 129.3, 129.2, 126.0, 121.9, 37.1, 35.3, 16.7; 180.3*, 176.3*, 150.9*, 143.4*, 136.3*, 130.1*, 129.69*, 129.5*, 129.1*, 126.1*, 121.9*, 37.0*, 35.3*, 17.1*.

3-decyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (5k): Compound (5k) was prepared according to the general



procedure **B** from 4k (68 mg, 0.2 mmol, 1 equiv) and purified by flash column chromatography (50% EtOAc/Hexane) in 42% (30.5 mg) yield as yellow liquid. R_f Value = 0.3.

¹H NMR (500 MHz, CDCl₃, a mixture of atropisomers in ratio 1.1:1.0, the minor one is marked with an *): δ 8.87 (ddd, J = 10.3, 4.2, 1.7 Hz, 1H), 8.21-8.19 (m, 1H), 7.92 (m, 1H), 7.64-7.58 (m, 2H), 7.45-7.42 (m, 1H), 3.24 (m, 1H), 3.09 (m, 1H), 2.65 (m, 1H), 2.14-2.00 (m, 2H), 1.89-1.81 (m, 1H), 1.74-1.67 (m, 1H), 1.63-1.34 (m, 1H), 1.54-1.45 (m, 2H), 1.27 (m, 11H), 0.89 (m, 3H); 8.87 (ddd, J = 10.3, 4.2, 1.7 Hz, 1H)*, 8.21-8.19 (m, 1H)*, 7.92 (m, 1H)*, 7.64-7.58 (m, 2H)*, 7.45-7.42 (m, 1H)*, 3.24 (m, 1H)*, 3.09 (m, 1H)*, 2.82 (m, 1H)*, 2.14-2.00 (m, 2H)*, 1.89-1.81 (m, 1H)*, 1.74-1.67 (m, 1H)*, 1.63-1.34 (m, 1H)*, 1.54-1.45 (m, 2H)*,

1.27 (m, 11H)*, 0.89 (m, 3H)*.

¹³C NMR (100 MHz, CDCl₃): δ 179.7, 176.4, 150.91, 143.3, 136.1, 133.4, 130.0, 129.6, 129.4, 129.3, 128.4, 126.1, 121.99, 40.8, 35.0, 31.8, 31.4, 29.5, 29.41, 29.31, 26.80, 22.6, 14.10; 179.8*, 176.5*, 150.94*, 143.4*, 136.5*, 133.4*, 130.2*, 129.7*, 129.4*, 129.2*, 128.4*, 126.1*, 121.93*, 40.5*, 34.9*, 31.8*, 31.5*, 29.6*, 29.49*, 29.33*, 26.85*, 22.6*, 14.10*. **HRMS**: [M+H]⁺ calculated for C₂₃H₃₁N₂O₂: 367.2386, found 367.2381.

3-tert-butyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (5l): Compound (5l) was prepared according to the general



procedure **B** from 41 (51.2 mg, 0.2 mmol, 1 equiv) and purified by flash column chromatography (50% EtOAc/Hexane) in 56% (32 mg) yield as yellow liquid. R_f Value = 0.3. The NMR data of **5l** is in accordance with the literature.²

¹H NMR (500 MHz, CDCl₂, a mixture of atropisomers in ratio 1.2:1.0, the minor one is marked with an *): δ 8.91-8.82 (m, 1H), 8.19-8.14 (m, 1H), 7.91-7.87 (m, 1H), 7.62-7.54 (m, 2H), 7.44-7.38 (m, 1H), 3.18-3.05 (m, 1H), 2.96-2.77 (m, 2H), 1.17 (s, 9H); 8.8-8.82 (m, 1H)*, 8.19-8.14 (m, 1H)*, 7.91-7.87 (m, 1H)*, 7.62-7.54 (m, 2H)*, 7.44-7.38 (m, 1H)*, 3.18-3.05 (m, 1H)*, 2.96-2.77 (m, 2H)*, 1.23 (s, 9H)*.

¹³C NMR (100 MHz, CDCl₃): δ 177.9, 176.28, 150.8, 143.4, 136.4, 130.0, 129.6, 129.2, 129.03, 126.0, 121.8, 50.3, 33.5, 32.33, 27.2; 178.08*, 176.26*, 150.6*, 143.2*, 135.8*, 130.3*, 129.7*, 129.5*, 129.4*, 125.9*, 121.8*, 50.5*, 33.7*, 32.31*, 27.3*.

3-(quinolin-8-yl)-3-azabicyclo[3.1.0]hexane-2,4-dione (5m): Compound (5m) was prepared according to the



general procedure B from 4m (42.4 mg, 0.2 mmol, 1 equiv) and purified by flash column chromatography (50% EtOAc/Hexane) in 83% (39.6 mg) yield as white solid. Rf Value = 0.3. The NMR data of **5m** is in accordance with the literature.

¹H NMR (400 MHz, CDCl₂, a mixture of atropisomers in ratio 5.1:1.0, the minor one is marked with an *): δ 8.83 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.17 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.89 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.67 (dd, J = 7.1, 1.2 Hz, 1H), 7.63-7.57 (m, 1H), 7.42 (m, 1H), 2.70 (dd, J = 7.7, 3.2 Hz, 2H), 2.45 (q, J = 4.0 Hz, 1H), 1.69 (td, J = 8.2, 4.0 Hz, 1H); 8.92 (dd, J = 4.0, 1.6 Hz, 1H)*, 8.20 (dd, J = 8.3, 1.6 Hz, 1H)*, 7.92 (dd, J = 8.1, 1.2 Hz, 1H)*, 7.67 (dd, J = 7.1, 1.2 Hz, 1H)*, 7.63-7.57 (m, 1H)*, 7.45 (m, 1H)*, 2.78 (dd, J = 8.2, 3.8 Hz, 2H)*, 2.45 (q, J = 4.0 Hz, 1H)*, 1.79-1.75 (m, 1H)*.

¹³C NMR (100 MHz, CDCl₃): δ 174.8, 150.7, 143.3, 136.0, 130.5, 129.9, 129.3, 129.04, 129.01, 126.0, 121.8, 21.3, 20.8, 20.0; 174.7*, 150.8*, 143.3*, 136.5*, 130.5*, 129.9*, 129.2*, 129.4*, 128.9*, 126.0*, 121.9*, 21.3*, 20.9*, 20.0*.

2-(2,5-dioxo-1-(quinolin-8-yl)pyrrolidin-3-yl)isoindoline-1,3-dione (5n): Compound (5n) was prepared



according to the general procedure **B** from 4n (69 mg, 0.2 mmol, 1 equiv) and purified by flash column chromatography (80% EtOAc/Hexane) in 38% (28.4 mg) yield as white solid. R_f Value = 0.25. The NMR data of **5n** is in accordance with the literature.⁷

¹H NMR (400 MHz, CDCl₂, a mixture of atropisomers in ratio 6.2:1.0, the minor one is marked with an *): δ 8.90 (dd, J = 4.1, 1.6 Hz, 1H), 8.23 (m, 1H), 7.97 (dd, J = 8.2, 1.2 Hz, 1H), 7.92 (dd, J = 5.4, 3.0 Hz, 2H), 7.83 (dd, J = 8.3, 1.2 Hz, 1H), 7.79 (dd, J = 5.4, 3.0 Hz, 2H), 7.68 (m, 1H), 7.48 (dd, J = 8.2, 4.2 Hz, 1H), 5.69 (dd, J = 9.9, 5.9 Hz, 1H), 3.54 (dd, J = 18.0, 10.0 Hz, 1H), 3.20 (dd, J = 18.0, 5.8 Hz, 1H); 9.05 (dd, J = 4.0, 1.7 Hz, 1H)*, 8.20 (m, 1H)*, 7.97 (dd, J = 8.2, 1.2 Hz, 1H)*, 7.92 (dd, J = 5.4, 3.0 Hz, 2H)*, 7.83 (dd, J = 8.3, 1.3 Hz, $(H)^*$, 7.79 (dd, J = 5.4, 3.0 Hz, 2H)*, 7.64 (m, 1H)*, 7.48 (dd, J = 8.2, 4.2 Hz, 1H)*, 5.57 (dd, J = 8.2, 4.2 Hz, 3.2 Hz, 3.2 Hz, 3.2J = 9.3, 7.4 Hz, 1H)*, 3.63 (dd, J = 17.3, 7.4 Hz, 1H)*, 3.35 (dd, J = 17.2, 9.3 Hz, 1H)*.

¹³C NMR (100 MHz, CDCl₃, major isomer): δ 173.1, 172.7, 151.4, 151.0, 134.6, 131.7, 131.6, 129.9, 129.8, 129.2, 128.9, 126.2, 125.9, 123.8, 122.0, 47.3, 34.6.

1-(quinolin-8-yl)pyrrolidine-2,5-dione (50): Compound (50) was prepared according to the general procedure B



from **40** (60 mg, 0.3 mmol, 1 equiv) and purified by flash column chromatography (80% EtOAc/Hexane) in 40% (27.6 mg) yield as pale yellow solid. R_f Value = 0.2. The NMR data of **50** is in accordance with the literature.²

¹**H NMR** (500 MHz, CDCl₃): δ 8.86 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.19 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.92 (dd, J = 7.4, 2.3 Hz, 1H), 7.65-7.60 (m, 2H), 7.43 (dd, J = 8.3, 4.2 Hz, 1H), 3.15-3.08 (m, 2H), 3.01-2.94 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 176.8, 150.8, 143.3, 136.2, 130.0, 129.7, 129.4, 129.2, 126.0, 121.9, 28.8.

1-(5-(1H-pyrazol-1-yl)quinolin-8-yl)-3,3-dimethylpyrrolidine-2,5-dione (5p): Compound (5p) was prepared



according to the general procedure B from 4p (58.8 mg, 0.2 mmol, 1 eq) and purified by flash column chromatography (40% EtOAc/Hexane) in 53% (34 mg) yield as white solid. R_f Value = 0.25. ¹**H NMR** (500 MHz, CDCl₃): δ 8.90 (dd, *J* = 4.1, 1.7 Hz, 1H), 8.41 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.88 (d, *J* =

1.4 Hz, 1H), 7.81 (d, J = 2.0 Hz, 1H), 7.67 (q, J = 7.7 Hz, 2H), 7.47 (dd, J = 8.7, 4.1 Hz, 1H), 6.57 (t, J = 2.1 Hz, 1H), 2.97 (d, J = 17.9 Hz, 1H), 2.83 (d, J = 17.8 Hz, 1H), 1.62 (s, 3H), 1.51 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 182.7, 175.5, 151.4, 143.9, 141.7, 138.1, 132.8, 131.4, 130.5, 128.7, 125.0, 122.6, 122.0, 107.3, 44.1, 41.0, 26.1, 25.4.

HRMS: [M+H]⁺ calculated for C₁₈H₁₇N₄O₂: 321.1352, found 321.1353.

1-(5-chloroquinolin-8-yl)-3,3-dimethylpyrrolidine-2,5-dione (5q): Compound (5q) was prepared according to the general procedure **B** from 4q (52.4 mg, 0.2 mmol, 1 equiv) and purified by flash column



chromatography (40% EtOAc/Hexane) in 51% (29.5 mg) yield as white solid. R_f Value = 0.2. ¹H NMR (500 MHz, CDCl₃): δ 8.90 (dd, J = 4.1, 1.6 Hz, 1H), 8.59 (dd, J = 8.6, 1.6 Hz, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.57-7.53 (m, 2H), 2.94 (d, J = 18.0 Hz, 1H), 2.82 (d, J = 18.0 Hz, 1H), 1.60 (s, 3H), 1.50 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 182.7, 175.5, 151.4, 144.0, 133.1, 133.0, 129.4, 129.2, 127.2, 126.1, 122.6, 44.1, 41.0, 26.2, 25.3.

HRMS: [M+H]⁺ calculated for C₁₅H₁₄ClN₂O₂: 289.0744, found 289.0750.

6. A. Late stage C-H bond functionalization:

4-(4-((1,7'-dimethyl-2'-propyl-1H,3'H-2,5'-bibenzo[d]imidazol-3'-yl)methyl)phenyl)-2-(quinolin-8-

yl)isoindoline-1,3-dione (7): Compound 7 was prepared according to the general procedure A at 120 °C for 30 h, from aminoquinoline based Telmisartan 6 (128 mg, 0.2 mmol, 1 equiv) and purified by flash column chromatography (20% Acetone/Chloroform) in 30% (40 mg) yield as white solid. R_f Value = 0.2.

¹**H NMR** (400 MHz, CDCl₃): δ 8.82 (dd, J = 3.8 Hz, 1H), 8.18 (dd, J = 8.2, 1.2 Hz, 1H), 7.97 (d, J = 7.4 Hz, 1H), 7.91 (d, J = 7.9 Hz, 1H), 7.78 (m, 2H), 7.69 (d, J = Hz, 1H), 7.66-7.60 (m, 2H), 7.56 (d, J = 8.1 Hz, 2H), 7.42-7.38 (m, 3H), 7.24-7.18 (m, 3H), 7.11 (d, J = 8.1 Hz, 2H), 5.41 (s, 2H), 3.66 (s, 3H), 2.92 (t, J = 7.7 Hz, 2H), 2.75 (s, 3H), 1.86 (dt, J = 15.0, 7.41 Hz, 2H), 1.03 (t, J = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 167.41, 167.40, 156.5, 154.34, 154.32, 150.9, 144.1, 143.0, 140.5, 136.3, 136.2, 136.1, 136.0, 135.9, 134.7, 134.1, 133.5, 130.26, 130.22, 129.6, 129.5, 129.4, 129.1, 128.0, 127.9, 127.7, 126.9, 126.0, 125.7, 123.8, 122.9, 122.5, 122.4, 121.9, 119.2, 109.5, 109.2, 47.0, 31.8, 29.6, 21.9, 16.8, 14.0.

HRMS: $[M+H]^+$ calculated for $C_{43}H_{35}N_6O_2$: 667.2821, found 667.2827.



5-(2,5-dimethylphenoxy)-2,2-dimethyl-N-(quinolin-8-yl)pentanamide (9):



Compound (9) was prepared according to the general procedure **B** from aminoquinoline derived Gemfibrozil **8** (75.2 mg, 0.2 mmol, 1 equiv) and purified by flash column chromatography (30% EtOAc/Hexane) in 52% (42.6 mg) yield as pale yellow solid. R_f Value = 0.2.

¹H NMR (400 MHz, CDCl₃, a mixture of atropisomers in ratio 1.1:1.0, the minor one is marked

with an *): δ 8.80 (dd, J = 3.9, 1.2 Hz, 1H), 8.18 (m, 1H), 7.92 (m, 1H), 7.63 (m, 2H), 7.42 (m, 1H), 7.06 (d, J = 7.6 Hz, 1H), 6.71 (t, J = 4.8 Hz, 1H), 6.66 (s, 1H), 4.02 (m, 2H), 2.98 (d, J = 17.9 Hz, 1H), 2.91 (d, J = 18.0 Hz, 1H), 2.33 (d, J = 8.2 Hz, 3H), 2.24 (s, 3H), 2.18-2.13 (m, 1H), 2.07-2.01 (m, 2H), 1.98-1.89 (m, 1H), 1.55 (s, 3H); 8.89 (dd, J = 4.0, 1.2 Hz, 1H)*, 8.18 (m, 1H)*, 7.92 (m, 1H)*, 7.63 (m, 2H)*, 7.42 (m, 1H)*, 7.06 (d, J = 7.6 Hz, 1H)*, 6.71 (t, J = 4.8 Hz, 1H)*, 6.66 (s, 1H)*, 4.02 (m, 2H)*, 7.42 (m, 1H)*, 7.06 (d, J = 7.6 Hz, 1H)*, 6.71 (t, J = 4.8 Hz, 1H)*, 6.66 (s, 1H)*, 4.02 (m, 2H)*, 3.10 (d, J = 18.0 Hz, 1H)*, 2.78 (d, J = 18.0 Hz, 1H)*, 2.33 (d, J = 8.2 Hz, 3H)*, 2.24 (s, 3H)*, 2.18-2.13 (m, 1H)*, 1.98-1.89 (m, 1H)*, 1.66 (s, 3H)*.

¹³**C** NMR (100 MHz, CDCl₃): δ 182.2, 175.61, 156.7, 150.6, 143.33, 136.33, 135.8, 130.20, 130.03, 129.4, 129.1, 128.9, 125.84, 123.3, 121.7, 120.6, 111.8, 67.4, 44.1, 41.5, 35.1, 24.62, 24.2, 21.2, 15.7; 182.1*, 175.67*, 156.5*, 150.8*, 143.38*, 136.36*, 136.0*, 130.26*, 130.03*, 129.5*, 129.2*, 129.0*, 125.87*, 123.3*, 121.7*, 120.8*, 111.8*, 67.1*, 44.2*, 41.4*, 34.7*, 24.67*, 24.5*, 21.2*, 15.7*.

 $\textbf{HRMS:} \ [M+H]^{+} \ calculated \ for \ C_{25}H_{27}N_{2}O_{3}{:}\ 403.2022, \ found \ 403.2025.$

6. B. Diversification:

3,3-dimethyl-1-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)pyrrolidine-2,5-dione (10): In an oven-dried Schlenk tube A equipped with a stir bar, 1,2-diphenyl -1,1,2,2-tetramethyldisilane (162 mg, 0.6 mmol, 3 equiv), caesium fluoride (94.8 mg, 0.6 mmol, 3 equiv) and DMF (2.0 mL) were added in order under argon atmosphere. Schlenk tube was closed with a screw cap, evacuated and subsequently filled with 1-2 atm of carbon dioxide before keeping in preheated (110 $^{\circ}$ C) oil bath for 90 min. In an another oven-dried Schlenk tube **B** equipped with a stir bar, Pd(OAc)₂ (4.48 mg, 0.02 mmol, 10 mol%), AgOAc (66.8 mg, 0.4 mmol, 2 equiv), KH₂PO₄ (54.2 mg, 0.4 mmol, 2 equiv), TEMPO (62.4 mg, 0.4 mmol, 2 equiv), followed by N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)pivalamide (63.4 mg, 0.2 mmol, 1 equiv) in hexane (2 mL) was added. Finally Schlenk tube was evacuated. Gas produced in Schlenk tube A was transferred to Schlenk tube B connected through small rubber tube. The Schlenk tube B was then heated at 130 °C for 24 h under vigorous stirring. After the completion of reaction it was cooled to room temperature and depressurized. The reaction mixture was diluted with ethyl acetate and then filtered through a short pad of celite. Solvents were removed under reduced pressure and the reaction mixture was purified by flash column chromatography (5% EtOAc/Hexane) on silica gel obtained desired product in 65% (44.5 mg) as white solid. R_f Value = 0.25. The NMR data of 10 is in accordance with the literature.⁸



¹**H NMR** (500 MHz, CDCl₃): δ 2.85 (s, 2H), 1.49 (s, 6H). ¹³**C NMR** (125 MHz, CDCl₃): δ 179.4, 171.7, 44.0, 41.7, 25.6.

1-ethylindoline-2,3-dione (11): In an oven-dried Schlenk tube **A** equipped with a stir bar, 1,2-diphenyl -1,1,2,2-tetramethyldisilane (243 mg, 0.9 mmol, 3 equiv), caesium fluoride (142 mg, 0.9 mmol, 3 equiv) and DMF (2.0 mL) were added in order under argon atmosphere. Schlenk tube was closed with a screw cap, evacuated and subsequently filled with 1-2 atm of carbon dioxide before keeping in preheated (110 °C) oil bath for 90 min. In an another oven-dried Schlenk tube **B** equipped with a stir bar, $PdCl_2(PPh_3)_2$ (10.53 mg, 0.01 mmol, 5 mol%), $Cu(OPiv)_2$ (159 mg, 0.6 mmol, 2 equiv), DMSO/toluene (0.7 mL/0.7 mL) was added. Subsequently *N*-ethyl anilines (37.8 mg, 0.3 mmol, 1 equiv) was added to reaction and followed by evacuation of Schlenk tube. Gas produced in Schlenk tube **B** connected through small rubber tube. The Schlenk tube **B** was

then heated at 100 °C for 30 h. After the completion of reaction it was cooled to room temperature and depressurized. The reaction mixture was quenched by saturated potassium carbonate solution and extracted with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated in vacuum. The desired products were obtained in 28% yield (30 mg) as whine red solid after purification by flash column chromatography (20% EtOAc/Hexane) on silica gel. R_f Value = 0.2. The NMR data of \mathbf{n} is in accordance with the literature.⁹



¹**H NMR** (400 MHz, CDCl₃): δ 7.59 (m, 2H), 7.11 (t, *J* = 8.1 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 3.78 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 183.6, 157.8, 150.6, 138.3, 125.4, 123.6, 117.6, 109.9, 34.9, 12.4.

4-methyl-2*H*-chromen-2-one (12):



In an oven-dried Schlenk tube **A** equipped with a stir bar, 1,2-diphenyl -1,1,2,2-tetramethyldisilane (122 mg, 0.45 mmol, 1.5 equiv), caesium fluoride (71 mg, 0.45 mmol, 1.5 equiv) and DMF (1.0 mL) were added in order under argon atmosphere. Schlenk tube was closed with a screw cap, evacuated and subsequently filled with 1-2 atm of carbon dioxide before keeping in preheated (110 °C) oil bath for 90 min. In an another oven-dried Schlenk tube **B** equipped with a stir bar, $Cp^*Co(CO)I_2$ (14.2 mg, 0.03 mmol, 10 mol%), Ag_2CO_3 (82.5 mg, 0.3 mmol, 1 equiv), $Cu(OAc)_2 \cdot H_2O$ (59.7 mg, 0.3 mmol, 1 equiv) in o-xylene (1.5 mL) was added. Subsequently 2-(prop-1-en-2-yl)phenol (40 mg, 0.3 mmol, 1 equiv) was also added to reaction vessel and finally Schlenk tube was evacuated. Gas produced in Schlenk tube **A** was transferred to Schlenk tube **B** connected through small rubber tube. The Schlenk tube **B** was placed in preheated oil bath for 24 h at 30 °C. After the completion of reaction it was cooled to room temperature and depressurized. Solvents were removed under reduced pressure and the reaction mixture was purified by flash column chromatography (20% EtOAc/Hexane) on silica gel obtained desired product in 70% yield (34.2 mg) as white solid. R_f Value = 0.2. The NMR data of 12 is in accordance with the literature.¹⁰

¹**H** NMR (400 MHz, CDCl₃): δ 7.57 (d, *J* = 7.6 Hz, 1H), 7.48 (m, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.24 (s, 1H), 2.40 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 160.6, 153.3, 152.3, 131.6, 124.4, 124.1, 119.7, 116.8, 114.9, 18.5.

2,7-dimethyl-9H-xanthen-9-one (13):



In an oven-dried Schlenk tube **A** equipped with a stir bar, 1,2-diphenyl -1,1,2,2-tetramethyldisilane (122 mg, 0.45 mmol, 1.5 equiv), caesium fluoride (71 mg, 0.45 mmol, 1.5 equiv) and DMF (1.0 mL) were added in order under argon atmosphere. Schlenk tube was closed with a screw cap, evacuated and subsequently filled with 1-2 atm of carbon dioxide before keeping in preheated (110 °C) oil bath for 90 min. In an another oven-dried Schlenk tube **B** equipped with a stir bar, Pd(OAc)₂ (3.36 mg, 0.015 mmol, 5 mol%), K₂S₂O₈ (162 mg, 0.6 mmol, 2 equiv), and 4,4'-oxybis(methylbenzene) (59.6 mg, 0.3 mmol, 1 equiv) and TFA (1.5 mL) was added, finally Schlenk tube was evacuated. Gas produced in Schlenk tube **A** was transferred to Schlenk tube **B** connected through small rubber tube. The Schlenk tube **B** was kept in preheated oil bath at 50 °C for 6 h. After the completion of reaction it was cooled to room temperature and depressurized. The reaction was quenched by water and extracted with CH₂Cl₂ three times. The combined organic layers were dried over anhydrous Na₂SO₄ and evaporated in vacuum. The desired products were obtained in 44% (30 mg) as white solid after purification by flash column chromatography (10% EtOAc/Hexane) on silica gel. R_f Value = 0.2. The NMR data of **13** is in accordance with the literature.ⁿ

¹**H NMR** (500 MHz, CDCl₃): δ 8.11 (m, 2H), 7.51 (dd, *J* = 8.7, 2.2 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 2.46 (s, 6H). ¹³**C NMR** (125 MHz, CDCl₃): δ 177.3, 154.3, 135.9, 133.4, 125.9, 121.3, 117.6, 20.8.

6.C. Derivatization of disilaxane:



In an oven-dried Schlenk tube equipped with a Teflon coated stir bar, 1,2-diphenyl -1,1,2,2-tetramethyldisilane (122 mg, 0.45 mmol, 1.5 equiv), caesium fluoride (71 mg, 0.45 mmol, 1.5 equiv) and DMF (1.0 mL) were added in order under argon atmosphere. The Schlenk tube was closed with a screw cap, evacuated and subsequently filled with 1-2 atm of carbon dioxide before keeping in preheated (110 °C) oil bath for 90 min. After the completion of reaction it was cool down to the room temperature and depressurised under argon. To this 4-Iodo toluene (65.4 mg, 0.3 mmol, 1 equiv), Pd(acac)₂ (8.1 mg, 0.01 mmol, 5 mol%), Cu(OAc)₂ (5.43 mg, 0.03 mmol, 10 mol%), 1,10-phenanthroline (5.40 mg, 0.04 mmol, 15 mol%) was added in DMF (1.5 mL). Finally evacuation of schlenk tube followed by subsequent filling with 1-2 atm carbon monoxide gas and kept at 110 °C for 1 h. After completion of reaction, Schlenk tube was depressurized and solvents were removed under reduced pressure and purified by flash column chromatography (100% Hexane) on silica gel obtained desired product in 43% (25.1 mg) as colourless liquid. R_f Value = 0.2.

¹**H NMR** (400 MHz, CDCl₃): δ 7.78 (m, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.56 (m, 1H), 7.46 (t, J = 7.9 Hz, 2H), 7.27 (m, 2H), 2.43 (s, 3H).

¹³**C NMR** (100 MHz, CDCl₃): δ 196.4, 143.1, 137.8, 134.7, 132.0, 130.2, 129.8, 128.8, 128.1, 21.5. **HRMS**: $[M+H]^+$ calculated for C₁₄H₁₃O: 197.0966, found 197.0961.

7. Mechanistic Investigations:

A. ¹³C Labelled experiments:

4-methyl-2-(quinolin-8-yl)isoindoline-1,3-dione (2a): Compound (**2a**) was prepared according to the general procedure **A**, from **1a** (78.6 mg, 0.3 mmol, 1 equiv) but using ¹³C labelled carbon dioxide and then purified by flash column chromatography (25% EtOAc/Hexane) in 58% (51 mg) yield as white solid. R_f Value = 0.2.



¹**H NMR** (400 MHz, CDCl₃): δ 8.86 (dd, J = 3.8, 1.5 Hz, 1H), 8.20 (dd, J = 8.1, 1.5 Hz, 1H), 7.81 (dd, J = 7.2, 3.5 Hz, 1H), 7.93 (dd, J = 8.2, 1.3 Hz, 1H), 7.74 (m, 1H), 7.65 (m, 2H), 7.52 (d, J = 7.7 Hz, 1H), 7.41 (dd, J = 8.2, 4.0 Hz, 1H), 2.75 (s, 3H).

¹³**C NMR** (100 MHz, CDCl₃): δ 168.5, 167.9, 150.8, 144.2, 138.4, 136.4, 136.1, 133.6, 133.0, 130.2, 129.7, 129.4, 129.1, 128.9, 126.0, 121.7, 121.3, 17.6.

HRMS: $[M+H]^+$ calculated for $C_{17}^{13}CH_{13}N_2O_2$: 290.1011, found 290.1013.

3,3-dimethyl-1-(quinolin-8-yl)pyrrolidine-2,5-dione (5a): Compound (**5a**) was prepared according to the general procedure **B**, from **4a** (45.6 mg, 0.2 mmol, 1 equiv) but using ¹³C labelled carbon dioxide and then purified by flash column chromatography (50% EtOAc/Hexane) in 60% (31 mg) yield as white solid. R_f Value = 0.2.



¹**H NMR** (500 MHz, $CDCl_3$): δ 8.86 (dd, J = 4.2, 1.6 Hz, 1H), 8.19 (dd, J = 8.2, 1.5 Hz, 1H), 7.92 (dd, J = 6.2, 3.4 Hz, 1H), 7.62 (m, 2H), 7.43 (dd, J = 8.2, 4.1 Hz, 1H), 2.93 (d, J = 18.1 Hz, 1H), 2.81 (d, J = 18.1 Hz, 1H), 1.61 (s, 3H), 1.50 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 182.9, 175.6, 150.9, 143.6, 136.1, 130.3, 129.6, 129.4, 129.2, 126.0, 121.9, 44.3, 40.9, 26.2, 25.5.

HRMS: $[M+H]^+$ calculated for $C_{14}^{13}CH_{15}N_2O_2$: 256.1167, found 256.1169.

B. Radical quenching experiments:



(i) Radical quenching experiment for benzamide:

In an oven-dried Schlenk tube **A** equipped with a teflon coated stir bar, 1,2-diphenyl -1,1,2,2-tetramethyldisilane (122 mg, 0.45 mmol, 1.5 equiv), caesium fluoride (71 mg, 0.45 mmol, 1.5 equiv) and DMF (1.0 mL) were added in order under argon atmosphere. Schlenk tube was closed with a screw cap, evacuated and subsequently filled with 1-2 atm of carbon dioxide before keeping in preheated (110 °C) oil bath for 90 min. In an another oven-dried Schlenk tube **B** equipped with a teflon coated stir bar, Co(acac)₂ (15.42 mg, 0.06 mmol, 20 mol%), NaO₂CPh (8.6 mg, 0.6 mmol, 20 mol%), Ag₂CO₃ (206.2 mg, 0.75 mmol, 2.5 equiv), followed by 2-methyl-*N*-(quinolin-8-yl)benzamide (78.6 mg, 0.3 mmol, 1 equiv) along with 1 equiv of TEMPO (2,2,6,6-Tetramethyl-piperidin-1-yl)oxyl (46.8 mg, 0.3 mmol, 1 equiv) in α,α,α -trifluorotoluene (1 mL) was added. Finally Schlenk tube was evacuated. Gas produced in Schlenk tube **A** was transferred to Schlenk tube **B** connected through small rubber tube. The Schlenk tube **B** was placed in preheated oil bath for 24 h at 100 °C. After the completion of reaction it was cooled to room temperature and depressurized. Solvents were removed under reduced pressure and the reaction mixture was purified by flash column chromatography (25% EtOAc/Hexane) on silica gel obtained desired product **2a** in 48% (42 mg) as white solid. R_f Value = 0.2.

ii. Radical quenching experiment for pivalamide:

In an oven-dried Schlenk tube **A** equipped with a teflon coated stir bar, 1,2-diphenyl -1,1,2,2-tetramethyldisilane (162 mg, 0.6 mmol, 3 equiv), caesium fluoride (94.8 mg, 0.6 mmol, 3 equiv) and DMF (2.0 mL) were added in order under argon atmosphere. Schlenk tube was closed with a screw cap, evacuated and subsequently filled with 1-2 atm of carbon dioxide before keeping in preheated (110 °C) oil bath for 90 min. In an another oven-dried Schlenk tube **B** equipped with a teflon coated stir bar, $Co(acac)_2$ (5.1 mg, 0.02 mmol, 10 mol%), NaO_2CPh (43 mg, 0.3 mmol, 1.5 equiv), Ag_2CO_3 (165 mg, 0.6 mmol, 3 equiv), followed by *N*-(quinolin-8-yl)pivalamide (45 mg, 0.2 mmol, 1 equiv) along with 1 equiv of TEMPO (2,2,6,6-Tetramethyl-piperidin-1-yl)oxyl (31.2 mg, 0.2 mmol, 1 equiv) in chlorobenzene (2 mL) was added, finally Schlenk tube was evacuated. Gas produced in Schlenk tube **A** was transferred to Schlenk tube **B** connected through small rubber tube. The Schlenk tube **B** was placed in preheated oil bath for 30 h at 160 °C. After the completion of reaction it was cooled to room temperature and depressurized. The reaction mixture was diluted with ethyl acetate and then filtered through a short pad of celite. Solvents were removed under reduced pressure and the reaction mixture was purified by flash column chromatography (50% EtOAc/Hexane) on silica gel obtained desired product in 16% (8.5 mg) as white solid. R_f Value = 0.2.



C. Stoichiometric reactions with benzamide complex:



In an oven-dried Schlenk tube **A** equipped with a teflon coated stir bar, 1,2-diphenyl -1,1,2,2-tetramethyldisilane (28 mg, 0.1 mmol, 1.5 equiv), caesium fluoride (16 mg, 0.1 mmol, 1.5 equiv) and DMF (0.5 mL) were added in order under argon atmosphere. Schlenk tube was closed with a screw cap, evacuated and subsequently filled with 1-2 atm of carbon dioxide before keeping in preheated (110 °C) oil bath for 90 min. In an another oven-dried Schlenk tube **B** equipped with a teflon coated stir bar, Co intermediate¹² (40 mg, 0.06 mmol, 1 equiv) in α,α,α -trifluorotoluene (0.5 ml) was added, finally Schlenk tube was evacuated. Gas produced in Schlenk tube **A** was transferred to Schlenk tube **B** connected through small rubber tube. The Schlenk tube **B** was then heated at 100 °C for 2 h. After the completion of reaction it was cooled to room temperature and depressurized. Solvents were removed under reduced pressure and the reaction mixture was purified by flash column chromatography (25% EtOAc/Hexane) on silica gel obtained desired product **2a** in 43% as white solid along with 31% of recovered starting material (**1a**). R_f Value = 0.2.

D. Kinetic isotopic experiment:

(i) KIE Experiment with benzamide (parallel):



In an oven-dried Schlenk tube **A** equipped with a teflon coated stir bar, 1,2-diphenyl -1,1,2,2-tetramethyldisilane (41 mg, 0.15 mmol, 1.5 equiv), caesium fluoride (23 mg, 0.15 mmol, 1.5 equiv) and DMF (0.5 mL) were added in order under argon atmosphere. Schlenk tube was closed with a screw cap, evacuated and subsequently filled with 1-2 atm of carbon dioxide before keeping in preheated (110 °C) oil bath for 90 min. In an another oven-dried Schlenk tube **B** equipped with a teflon coated stir bar, Co(acac)₂ (5.14 mg, 0.02 mmol, 20 mol%), NaO₂CPh (2.88 mg, 0.02 mmol, 20 mol%), Ag₂CO₃ (68 mg, 0.24 mmol, 2.5 equiv), followed by [**1b**-H₅](24.8 mg, 0.1 mmol, 1 equiv) in α,α,α -trifluoro toluene (0.5 mL) was added. On the other hand, in an another dried Schlenk tube Co(acac)₂ (5.14 mg, 0.02 mmol, 20 mol%), PhCO₂Na (2.88 mg, 0.02 mmol, 20 mol%), Ag₂CO₃ (68 mg, 0.24 mmol, 2.0 mol%), Ag₂CO₃ (68 mg, 0.24 mmol, 2.0 mol%), Ag₂CO₃ (68 mg, 0.24 mg, 0.02 mmol, 20 mol%), Ag₂CO₃ (68 mg, 0.02 mmol, 20 mol%), PhCO₂Na (2.88 mg, 0.02 mmol, 20 mol%), Ag₂CO₃ (68 mg, 0.14 mg, 0.02 mmol, 20 mol%), Ag₂CO₃ (68 mg, 0.14 mg, 0.02 mmol, 20 mol%), PhCO₂Na (2.88 mg, 0.02 mmol, 20 mol%), Ag₂CO₃ (68 mg, 0.24 mmol, 2.5 equiv), followed by [**1b**-D₅](25.3 mg, 0.1 mmol, 1 equiv) in α,α,α -trifluoro toluene (0.5 mL) was added. After that both the Schlenk tubes was

evacuated. Gas produced in Schlenk tube **A** was transferred to Schlenk tubes **B** connected through small rubber tube. The Schlenk tube **B** was placed in preheated oil bath for 10, 20, 30, 40 min and immediately the reaction mixture was diluted with ethyl acetate and then filtered through a small pad of celite. Solvents were removed under reduced pressure and the reaction mixture was purified by flash column chromatography (25% EtOAc/Hexane) on silica gel.¹H NMR was taken using anisole (8 mg) as the internal standard. The $k_{\rm H}/k_{\rm D}$ value for parallel experiment is 1.53±0.47 determined by ¹H NMR spectroscopy by plotting NMR yield *vs* time (min).



(ii) KIE Experiment with aliphatic amide (Parallel):

In an oven-dried Schlenk tube **A** equipped with a teflon coated stir bar, 1,2-diphenyl -1,1,2,2-tetramethyldisilane (82 mg, 0.3 mmol, 3 equiv), caesium fluoride (47 mg, 0.3 mmol, 3 equiv) and DMF (0.5 mL) were added in order under argon atmosphere. Schlenk tube was closed with a screw cap, evacuated and subsequently filled with 1-2 atm of carbon dioxide before keeping in preheated (110 $^{\circ}$ C) oil bath for 90 min. In an another oven-dried Schlenk tube **B** equipped with a teflon coated stir bar, Co(acac)₂ (2.57 mg, 0.01 mmol, 10 mol%), NaO₂CPh (21.6 mg, 0.15 mmol, 1.5 equiv), Ag₂CO₃ (82.5 mg, 0.3 mmol, 3 equiv), followed by [**4e-CH**₃](25.4 mg, 0.1 mmol, 1 equiv) in chlorobenzene (1 mL) was added. On the other hand, in an another dried Schlenk tube Co(acac)₂ (2.57 mg, 0.01 mmol, 1 equiv), followed by [**4e-CD**₃](25.7 mg, 0.1 mmol, 1 equiv), followed by [**4e-CD**₃](25.7 mg, 0.1 mmol, 1 equiv) in chlorobenzene (1 mL) was added. Finally both the Schlenk tubes was evacuated. Gas produced in Schlenk tube **A** was transferred to Schlenk tube **B** connected through small rubber tube. The Schlenk tube **B** was placed in preheated oil bath for 10, 20, 30, 40 min and immediately the reaction mixture was diluted with ethyl acetate and then filtered through a short pad of celite. Solvents were removed under reduced pressure and the reaction mixture was purified by flash column chromatography (50% EtOAc/Hexane) on silica gel.¹H NMR was

taken using anisole (7 mg) as the internal standard. The $k_{\rm H}/k_{\rm D}$ value for parallel experiment is 1.69±0.47 determined by ¹H NMR spectroscopy by plotting NMR yield vs time (min).

Time (min)	10	20	30	40
Yield of 5e (%)	1.96	5.88	11.76	17.64
Yield of [D2]-5e (%)	1.96	3.92	5.88	11.76



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8. NMR Spectra



Figure S1. ¹H & ¹³C NMR spectrum of **6**.



Figure S2. ¹H & ¹³C NMR spectrum of 8.



Figure S3. ¹H & ¹³C NMR spectrum of **2a**.





Figure S4. ¹H & ¹³C NMR spectrum of 2b.



Figure S5. ¹H & ¹³C NMR spectrum of **2c**.





Figure S6. ¹H & ¹³C NMR spectrum of 2d.



Figure S7. ¹H & ¹³C NMR spectrum of **2e**.





Figure S8. ¹H & ¹³C NMR spectrum of 2f.





Figure S9. ¹H & ¹³C NMR spectrum of **2g**.





Figure S10. ¹H & ¹³C NMR spectrum of **2h**.





Figure S11. ¹H & ¹³C NMR spectrum of 2i.



Figure S12. 1 H & 13 C NMR spectrum of 2j.



Figure S13. ¹H & ¹³C NMR spectrum of **2k**.



Figure S14. ¹H & ¹³C NMR spectrum of 2I.


Figure S15. ¹H & ¹³C NMR spectrum of **2m**.





Figure S16. ¹H & ¹³C NMR spectrum of **2n**.





Figure S17. ¹H & ¹³C NMR spectrum of **20**.





Figure S18. ¹H & ¹³C NMR spectrum of **2p**.





Figure S19. ¹H & ¹³C NMR spectrum of **2q**.







Figure S20. 1 H & 13 C & 19 F NMR spectrum of 2r.





Figure S21. ¹H & ¹³C NMR spectrum of 2s.





Figure S22. 1 H & 13 C NMR spectrum of 2t.





Figure S23. ¹H & ¹³C NMR spectrum of 2u.











Figure S25. 1 H & 13 C NMR spectrum of **2w**.











Figure S27. 1 H & 13 C NMR spectrum of 2y.







60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -21

Figure S28. ¹H & ¹³C & ¹⁹FNMR spectrum of 2z.





Figure S29. ¹H & ¹³C NMR spectrum of 3a.





Figure S30. ¹H & ¹³C NMR spectrum of **3b**.





Figure S31. ¹H & ¹³C NMR spectrum of **3c**.





Figure S32. ¹H & ¹³C NMR spectrum of **3d**.



Figure S33. ¹H & ¹³C NMR spectrum of **3e**.





Figure S34. ¹H & ¹³C NMR spectrum of 3f.





Figure S35. ¹H & ¹³C NMR spectrum of 3g.



Figure S36. ¹H & ¹³C NMR spectrum of **3h**.



Figure S37. ¹H & ¹³C NMR spectrum of 5a.



Figure S38. ¹H & ¹³C NMR spectrum of 5b.



Figure S39. ¹H & ¹³C NMR spectrum of 5c.



Figure S40. ¹H & ¹³C NMR spectrum of **5d**.



Figure S41. ¹H & ¹³C NMR spectrum of 5e.



Figure S42. ¹H & ¹³C NMR spectrum of 5f.



Figure S43. ¹H & ¹³C NMR spectrum of 5g.



Figure S44. ¹H & ¹³C NMR spectrum of 5h.



Figure S45. ¹H & ¹³C NMR spectrum of 5i.





Figure S46. ¹H & ¹³C NMR spectrum of 5j.







Figure S47. ¹H & ¹³C NMR spectrum of 5k.





10 (



Figure S49. ¹H & ¹³C NMR spectrum of 5m.




Figure S50. ¹H & ¹³C NMR spectrum of 5n.



Figure S51. ¹H & ¹³C NMR spectrum of 50.



Figure S52. ¹H & ¹³C NMR spectrum of 5p.



Figure S53. 1 H & 13 C NMR spectrum of 5q.



Figure S54. ¹H & ¹³C NMR spectrum of 7.



Figure S55. ¹H & ¹³C NMR spectrum of **9.**



Figure S56. 1 H & 13 C NMR spectrum of 10.



Figure S57. ¹H & ¹³C NMR spectrum of **11.**



Figure S58. ¹H & ¹³C NMR spectrum of **12.**



Figure S59. ¹H & ¹³C NMR spectrum of 13.



Figure S60. ¹H & ¹³C NMR spectrum of **phenyl**(*p***-tolyl)methanone**.



Figure S61. ¹H & ¹³C NMR spectrum of 2a (¹³C labelled experiment).



Figure S62. ¹H & ¹³C NMR spectrum of 5a (¹³C labelled experiment).