Supporting Information

Silyl radical mediated cross-electrophile coupling of \(N\)-acyl-imides with alkyl bromides under photoredox/nickel dual catalysis

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I. General methods

All reactions were performed under an inert atmosphere of argon. Reaction glassware was oven-dried prior to use. $^1$H, and $^{13}$C spectra were recorded on Bruker Avance 300 or 400 spectrometers at 298K. Chemical shifts (δ) are expressed in parts per million. $^1$H and $^{13}$C{$^1$H} NMR spectra were recorded with reference to the solvent resonances (for CDCl$_3$, δ$_H$ at 7.26 ppm, δ$_C$ at 77.16 ppm). Crude reaction products were identified using $^1$H NMR and GC/MS analysis. NMR yields were determined by adding dibromomethane as an internal standard to the crude reaction mixtures and by integration of crude $^1$H NMR spectra. The following abbreviations and their combinations are used: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet. GC-MS analyses were performed using Shimadzu GC-2010 Gas Chromatograph coupled to a GCMS-QP2010S mass spectrometer using helium as the carrier gas at a flow rate of 1.19 mL/min and an initial oven temperature of 70 °C. The column used was a Zebron 5ms (30 m length, 0.25 mm diameter and 0.25 μm thickness). The injector temperature was 250 °C. The detector temperature was 250 °C. For runs with the initial oven temperature of 70 °C, temperature was increased with a 9 °C/min ramp after 70 °C hold for 1 min to a final temperature of 240 °C, then hold at 240 °C for 8 min (split mode of injection, total run time of 27.89 min). The high-resolution mass spectra were recorded by direct introduction in a positive and negative ion mode on a hybrid quadrupole time-of-flight mass spectrometer (MicroTOFQ-II, Bruker Daltonics, Bremen) with an Electrospray Ionization (ESI) ion source. The solutions were infused at 180µL/h. The mass range of the analysis was 50-1000 m/z and the calibration was done with sodium formate. Flash chromatographies were performed using silica gel 60 Å (40-63μm). TLC analyses were carried out on pre-coated TLC-sheets ALUGRAM Xtra SIL G/UV$_{254}$. The plates were visualized using a 254 nm ultraviolet lamp.
II. Chemicals, catalysts and starting materials.

Reagents and anhydrous solvents were purchased at the highest grade and used as received. The catalysts [Ir(dF(CF₃)ppy)₂dtbbpy]PF₆¹ and [Ni(dtbbpy)(H₂O)₄]Cl₂² were prepared according to reported procedures. Alkyl halides used in this study are commercially available compounds, except for 6-bromofucose diacetonide 2j which was prepared following a literature protocol.³

*N-(Acyl)piperidine-2,6-diones and N-(acyl)pyrrolidine-2,5-diones (1) are known compounds for the most part (Scheme 1) and were obtained according to literature procedures⁴⁻⁹ from reaction of the corresponding acyl chlorides with glutarimide or succinimide, respectively.

**Scheme S1.** Structures of imides.
1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl)pyrrolidine-2,5-dione (1e) has been prepared in one step from the corresponding carboxylic acid as follows:

An oven dried 500 mL round bottom flask equipped with a magnetic stirrer was charged with 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid (1 equiv; 4.03 mmol; 1.0 g) and dimethylformamide (0.2 equiv; 0.81 mmol; 62 μL) in dry dichloromethane (20 mL). The solution was stirred at 0 ºC and oxalyl chloride (1.1 equiv; 4.43 mmol; 380 μL) in 5 mL of dry dichloromethane was added dropwise. After complete addition, the reaction mixture was stirred at room temperature for 3 hours. A second oven dried 500 mL round bottom flask equipped with a magnetic stirrer was charged with succinimide (1.1 equiv; 4.43 mmol; 440 mg), DMAP (0.2 equiv; 0.81 mmol; 100 mg) and triethylamine (1.2 equiv; 4.84 mmol; 680 μL) in dry dichloromethane (20 mL). The solution was stirred at 0 ºC, and freshly prepared acyl chloride was added dropwise. After complete addition, the reaction mixture was stirred at room temperature overnight. Reaction was followed by TLC until completion, then Et₂O was added to precipitate salts. The filtrate was washed with HCl 1M (1 x 100 mL) and brine (2 x 100 mL), dried with MgSO₄ and recrystallized from CH₂Cl₂ with cyclohexane. 1e was isolated as a white solid (0.280 g; 25%).

\[ ^1H \text{NMR (300 MHz, CDCl}_3\] δ 7.91-7.88 (m, 2H), 7.80-7.78 (m, 2H), 2.89 (s, 4H), 1.33 (s, 12H). \[ ^{13}C \text{NMR (100 MHz, CDCl}_3\] δ 174.7, 168.0, 135.1, 133.5, 129.6, 84.5, 29.1, 24.9. HRMS (ESI) m/z: [M + H]⁺ Calcd. for C₁₇H₂₁BNO₅ 330.1507; Found 330.1506.
III. Scope of alkyl ketones 3.

General procedure: A 10 mL scintillation vial (with screw cap) equipped with a magnetic stirbar was charged with \([\text{Ir(dF(CF}_3)pypy)_2\text{dtbbpy}]\text{PF}_6\) (1 mol%; 0.005 mmol; 5.6 mg), \([\text{Ni(dtbbpy)}(\text{H}_2\text{O})_4]\text{Cl}_2\) (3 mol%; 0.015 mmol; 7.05 mg), sodium carbonate (1 equiv; 0.5 mmol; 53 mg), tris(trimethylsilyl)ilane (1 equiv; 0.5 mmol; 154 μL), the selected pyrrolidine-2,5-dione (1 equiv; 0.5 mmol; 101 mg) and bromoalkane (1.5 equiv; 0.75 mmol) in dry solvent (5 mL). The vial was sparged with argon and capped, and the reaction mixture was stirred at room temperature under Blue LED irradiation for the allotted time. The mixture was then filtered through Celite® using dichloromethane as eluent to remove solid residues. The volatiles were then removed from the filtrate under vacuum to yield a crude residue which was purified by flash chromatography (silica gel, appropriate mixture of cyclohexane/ethyl acetate) to afford the corresponding ketone.

Conditions and lighting set-ups:

Conditions A: The reaction was run in acetone for 18-24 h under the irradiation of two 40W blue LED Kessil® lamps (A160WE Tuna Blue, 455 nm) used at 100% color and light intensity, and placed 2-3 cm away from the reaction vial with an external cooling fan that maintains the temperature below 33°C (Fig 1A).

Conditions B: The reaction was run in ethyl acetate for 24-72 h under the irradiation of a 450 nm EvoluChem™ 30W blue LED lamp with a built-in fan switched on (P303-30-1 450 nm) using the EvoluChem™ device on a stirrer plate (Fig 1B).

Figure S1. Reaction set-ups
Phenyl(tetrahydro-2H-pyran-4-yl)methanone (3a): Known compound,\textsuperscript{10} prepared according to general conditions A (18h), and purified by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 9:1) to give a colorless oil (0.056 g; 59%).

\textbf{\textsuperscript{1}H\textit{ NMR}} (300 MHz, CDCl\textsubscript{3}) δ 7.95-7.94 (m, 2H), 7.59-7.55 (m, 1H), 7.50-7.46 (m, 2H), 4.08-4.03 (m, 2H), 3.59-3.46 (m, 3H), 1.94-1.77 (m, 4H). \textbf{\textsuperscript{13}C\textit{ NMR}} (75 MHz, CDCl\textsubscript{3}) δ 202.0, 136.0, 133.2, 128.9, 128.4, 67.5, 42.7, 29.2. \textbf{MS (EI) m/z:} [M]\textsuperscript{+} 198.

1-(t-Butoxycarbonyl)-4-(benzoyl)piperidine (3b): Known compound,\textsuperscript{11} prepared according to general conditions B (48h), and purified by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 9:1) to give a white solid (0.100 g; 69%).

\textbf{\textsuperscript{1}H\textit{ NMR}} (300 MHz, CDCl\textsubscript{3}) δ 7.96-7.90 (m, 2H), 7.60-7.53 (m, 1H), 7.51-7.43 (m, 2H), 4.16 (dt, \textit{J} = 13.3, 3.6 Hz, 2H), 3.40 (tt, \textit{J} = 11.0, 3.8 Hz, 1H), 2.94-2.85 (m, 2H), 1.90-1.80 (m, 2H), 1.76-1.63 (m, 2H), 1.46 (s, 9H). \textbf{\textsuperscript{13}C\textit{ NMR}} (75 MHz, CDCl\textsubscript{3}) δ 202.0, 154.7, 135.9, 133.1, 128.8, 128.3, 79.6, 43.5, 43.3, 28.5, 28.4. \textbf{MS (EI) m/z:} [M]\textsuperscript{+} 289.

Cyclohexylphenylmethanone (3c): Known compound,\textsuperscript{12} prepared according to general conditions A (18h), and purified by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 9:1) to give a white solid (0.060 g; 53%).

\textbf{\textsuperscript{1}H\textit{ NMR}} (300 MHz, CDCl\textsubscript{3}) δ 7.95-7.93 (m, 2H), 7.56-7.52 (m, 1H), 7.48-7.45 (m, 2H), 3.30-3.21 (m, 1H) 1.92-1.83 (m, 4H), 1.76-1.72 (m, 1H), 1.58-1.25 (m, 5H). \textbf{\textsuperscript{13}C\textit{ NMR}} (100 MHz, CDCl\textsubscript{3}) δ 204.0, 136.5, 132.8, 128.7, 128.4, 45.8, 29.6, 26.0. \textbf{MS (EI) m/z:} [M]\textsuperscript{+} 188.

1,4-Diphenylbutan-1-one (3d): Known compound,\textsuperscript{13} prepared according to general conditions A, and purified by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 8:2) to give a clear oil (0.063 g; 56%). \textbf{\textsuperscript{1}H\textit{ NMR}} (300 MHz, CDCl\textsubscript{3}) δ 7.94-7.91 (m, 2H), 7.58-7.52 (m, 1H), 7.48-7.42 (m, 2H), 7.33-7.27 (m, 2H), 7.23-7.18 (m, 3H), 2.99 (t, \textit{J} = 7.3 Hz, 2H), 2.73 (t, \textit{J} = 7.85 Hz, 2H), 2.14-2.05 (m, 2H). \textbf{\textsuperscript{13}C\textit{ NMR}} (100 MHz, CDCl\textsubscript{3}) δ 200.2, 141.8, 137.1, 133.1, 128.7, 128.6, 128.5, 128.1, 126.1, 37.8, 35.3, 25.8. \textbf{MS (EI) m/z:} [M]\textsuperscript{+} 224.
1,2-Diphenylethanone (3e): Known compound, prepared according to general conditions A (18h). Flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 8:2) gave a yellow solid (0.021 g; 21%) contaminated with c.a. 15 mol% of (TMS)₃SiH. ¹H NMR (300 MHz, CDCl₃) δ 8.03-8.01 (m, 2H), 7.59-7.54 (m, 1H), 7.49-7.44 (m, 2H), 7.36-7.31 (m, 2H), 7.28-7.25 (m, 3H), 4.29 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 197.8, 136.8, 134.7, 133.3, 129.6, 128.9, 128.8, 128.7, 127.0, 45.7. **MS (EI) m/z:** [M]+ 196.

Ethyl 5-oxo-5-phenylpentanoate (3f): Known compound, prepared according to general conditions A (18h), and purified by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 8:2) to give a white solid (0.056 g; 51%). ¹H NMR (300 MHz, CDCl₃) δ 7.97-7.95 (m, 2H), 7.58-7.53 (m, 1H), 7.48-7.43 (m, 2H), 4.15 (q, J = 7.16 Hz, 2H), 2.43 (t, J = 7.14 Hz, 2H), 2.07 (quint, J = 7.17 Hz, 2H), 1.25 (t, J = 7.16 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 199.6, 173.4, 136.9, 133.2, 128.7, 128.1, 60.5, 37.6, 33.5, 19.5, 14.5. **MS (EI) m/z:** [M]+ 220.

8-Oxo-8-phenyloctanenitrile (3g): Unknown compound, prepared according to general conditions A (18h), and purified by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 8:2) to give a yellow oil (0.073 g; 68%). ¹H NMR (300 MHz, CDCl₃) δ 7.97-7.94 (m, 2H), 7.59-7.54 (m, 1H), 7.49-7.44 (m, 2H), 2.98 (t, J = 7.13 Hz, 2H), 2.35 (t, J = 7.01 Hz, 2H), 1.77-1.66 (m, 4H), 1.54-1.42 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 200.2, 137.1, 133.1, 128.7, 128.2, 119.9, 38.4, 28.7, 28.6, 25.5, 24.0, 17.2. **HRMS (ESI) m/z:** [M + Na]+ Calcd. for C₁₄H₁₇NNaO 238.1198; Found 238.1202.

7,7,7-Trifluoro-1-phenyleptan-1-one (3h): Known compound, prepared according to general conditions A (18h), and purified by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 8:2) to give a white sticky solid (0.077 g; 63%). ¹H NMR (300 MHz, CDCl₃) δ 7.97-7.95 (m, 2H), 7.59-7.54 (m, 1H), 7.49-7.44 (m, 2H), 2.99 (t, J = 9.0 Hz, 2H), 2.18-2.01 (m, 2H), 1.83-1.73 (m, 2H), 1.67-1.57 (m, 2H), 1.51-1.44 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 200.1, 137.1, 133.2, 128.8, 128.2, 127.3 (q, J = 275.0 Hz), 38.3, 33.7 (q, J = 28.0 Hz), 28.5, 23.9, 22.0. ¹⁹F NMR (282.2 MHz, CDCl₃) δ -66.4. **MS (EI) m/z:** [M]+ 224.
3,3-Dimethoxy-1-phenylpropan-1-one (3i): Known compound,\textsuperscript{16} prepared according to general conditions B (48h), and purified by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 7:3) to give a clear oil (0.042 g; 43%). \( ^1H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.97-7.94 (m, 2H), 7.59-7.54 (m, 1H), 7.49-7.44 (m, 2H), 5.01 (t, \(J = 3.0\) Hz, 1H), 3.41 (s, 6H), 3.28 (d, \(J = 3.0\) Hz, 2H). \( ^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 197.1, 137.2, 133.4, 128.8, 128.4, 102.4, 54.3, 42.7. HRMS (EI) m/z: [M + H]\(^+\) Calcd. for C\(_{11}\)H\(_{15}\)O\(_3\) 194.0937; Found 194.0929.

1-Phenyl-2-((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)ethan-1-one (3j): Unknown compound, prepared according to general conditions A (18h), and purified by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 1:1) to give a brown oil (0.035 g; 40%). \( ^1H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.00-7.98 (m, 2H), 7.59-7.53 (m, 1H), 7.48-7.43 (m, 2H), 5.51 (d, \(J = 6.0\) Hz, 1H), 4.67-4.64 (m, 1H), 4.55-4.50 (m, 1H), 4.38-4.31 (m, 2H), 3.43-3.25 (m, 2H), 1.60 (s, 3H), 1.48 (s, 3H), 1.34 (s, 6H). \( ^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 197.6, 137.1, 133.3, 128.7, 128.3, 109.3, 109.0, 96.6, 72.6, 71.0, 70.6, 64.4, 39.5, 26.2, 26.2, 25.2, 24.6. HRMS (EI) m/z: [M + H]\(^+\) Calcd. for C\(_{19}\)H\(_{24}\)NaO\(_6\) 371.1465; Found 371.1458.

1-(4-Methoxyphenyl)oct-7-en-1-one (3k): Unknown compound, prepared according to general conditions B (24h), and purified by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 8:2) to give a clear oil (0.071 g; 61%). \( ^1H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.96 – 7.91 (m, 2H), 6.95-6.90 (m, 2H), 5.81 (ddt, \(J = 16.9, 10.2, 6.7\) Hz, 1H), 5.03 – 4.91 (m, 2H), 3.86 (s, 3H), 2.93 – 2.88 (m, 2H), 2.10 – 2.03 (m, 2H), 1.78-1.68 (m, 2H), 1.49-1.36 (m, 4H); \( ^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 199.2, 163.4, 138.9, 130.4, 130.2, 114.4, 113.7, 55.5, 38.3, 33.7, 29.0, 28.8, 24.5. HRMS (ESI) m/z: [M + H]\(^+\) calcd. for C\(_{15}\)H\(_{21}\)O\(_2\) 233.1541; Found 233.1536.
1-(4-Methoxyphenyl)hept-6-en-1-one (3l) and 2-cyclopentyl-1-(4-methoxyphenyl)ethan-1-one (3l') were obtained as a mixture using general conditions B (24h). $^1$H NMR of crude reaction using dibromomethane as an internal standard indicated a 2:3 ratio of products 3l/3l'. Purification by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 9:1) gave 0.072 g (66%) of a 1:1 mixture of both compounds as a clear oil:

$$\text{3l: Known compound.}$$

$$^1\text{H NMR (300 MHz, CDCl}_3\text{)} \delta 7.96-7.93 \text{ (m, 2H), 6.94-6.91 (m, 2H), 5.88-5.75 (m, 1H), 5.04-4.98 (m, 2H), 3.87 (s, 3H), 2.92 (t, } J = 7.5 \text{ Hz, 2H), 2.14-2.07 (m, 2H), 1.77-1.70 (m, 2H), 1.50-1.43 \text{ (m, 2H).}$$

$$^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 199.2, 163.4, 138.7, 130.5, 114.7, 113.8, 55.6, 38.2, 33.8, 28.8, 24.2. \text{ MS (EI) m/z: [M]+ 218.}$$

$$\text{3l': Known compound.}$$

$$^1\text{H NMR (300 MHz, CDCl}_3\text{)} \delta 7.96-7.93 \text{ (m, 2H), 6.94-6.91 (m, 2H), 3.87 (s, 3H), 2.92 (t, } J = 7.5 \text{ Hz, 2H), 2.42-2.32 (m, 1H), 1.91-1.82 \text{ (m, 2H), 1.64-1.55 (m, 4H), 1.23-1.14 \text{ (m, 2H).}$$

$$^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 199.1, 163.5, 130.4, 113.8, 55.6, 44.6, 36.5, 32.9, 25.1. \text{ MS (EI) m/z: [M]+ 218.}$$

(4-Methoxyphenyl)(tetrahydro-2H-pyran-4-yl)methanone (3m): Known compound, prepared according to general conditions B (24h), and purified by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 8:2) to give a light yellow solid (0.081 g; 74%). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.94 (d, $ J = 8.9 \text{ Hz, 2H), 6.94 (d, } J = 8.9 \text{ Hz, 2H), 4.03 (dd, } J = 11.62, 4.02, \text{ 2.80 Hz, 2H), 3.87 (s, 3H), 3.55 (td, } J = 11.57, 2.46 \text{ Hz, 2H), 3.49-3.40 (m, 1H), 1.96-1.82 \text{ (m, 2H), 1.78-1.73 (m, 2H).}$$

$$^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 200.5, 163.6, 130.7, 128.8, 114.0, 67.5, 55.62, 42.4, 29.4. \text{ MS (EI) m/z: [M]+ 220.}$$

Cyclohexyl(4-methoxyphenyl)methanone (3n): Known compound, prepared according to general conditions B (24h), and purified by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 8:2) to give a clear oil (0.055 g; 50%). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.94 (d, $ J = 8.9 \text{ Hz, 2H), 6.94 (d, } J = 8.9 \text{ Hz, 2H), 3.86 (s, 3H), 3.25-3.18 (m, 1H), 1.87-1.71 \text{ (m, 5H), 1.56-1.24 (m, 5H).}$$

$$^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 202.6, 163.3, 130.6, 129.4, 113.8, 55.6, 45.4, 29.7, 26.1, 26.0. \text{ MS (EI) m/z: [M]+ 218.}$$
(4-Fluorophenyl)(tetrahydro-2H-pyran-4-yl)methanone (3o): Unknown compound, prepared according to general conditions B (48h), and purified by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 8:2) to give a white solid (0.068 g; 65%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.00-7.95 (m, 2H), 7.17-7.11 (m, 2H), 4.05 (ddd, $J$ = 11.6, 4.1, 2.4 Hz, 2H), 3.55 (td, $J$ = 11.5, 2.7 Hz, 2H), 3.49-3.40 (m, 1H), 1.95-1.74 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 200.3, 165.8 (d, $^2$J$_{CF}$ = 255.26 Hz), 132.3 (d, $^2$J$_{CF}$ = 2.86 Hz), 131.0 (d, $^3$J$_{CF}$ = 9.15 Hz), 116.0 (d, $^3$J$_{CF}$ = 22.17 Hz), 67.4, 42.7, 29.2. $^{19}$F NMR (282.2 MHz, CDCl$_3$) $\delta$ -107.09. HRMS (ESI) m/z: [M + H]$^+$ Calcd. for C$_{12}$H$_{14}$FO$_2$ 209.0972; Found 209.0975.

(4-(Trifluoromethyl)phenyl)(tetrahydro-2H-pyran-4-yl)methanone (3p): Unknown compound, prepared according to general conditions B (48h), and purified by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 8:2) to give a white solid (0.072 g; 56%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.05-8.02 (m, 2H), 7.76-7.73 (m, 2H), 4.06 (ddd, $J$ = 11.6, 4.0, 2.6 Hz, 2H), 3.61-3.44 (m, 3H), 1.95-1.76 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 200.9, 138.7, 134.4 (q, $^2$J$_{CF}$ = 32.7 Hz), 128.7, 125.90 (q, $^3$J$_{CF}$ = 3.7 Hz), 123.6 (q, $^3$J$_{CF}$ = 272.7 Hz), 67.2, 43.0, 28.9. $^{19}$F NMR (282.2 MHz, CDCl$_3$) $\delta$ -63.15. HRMS (ESI) m/z: [M + Na]$^+$ Calcd. for C$_{13}$H$_{13}$F$_3$NaO$_2$ 281.0766; Found 281.0762.

(Tetrahydro-2H-pyran-4-yl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (3q): Unknown compound, prepared according to general conditions A (18h), and purified by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 8:2) to give a yellow solid (0.109 g; 69%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.90 (s, 4H), 4.08-4.02 (m, 2H), 3.61-3.45 (m, 3H), 1.94-1.75 (m, 4H), 1.36 (s, 12H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 202.3, 137.9, 135.2, 127.4, 84.4, 67.4, 42.9, 29.2, 25.0. HRMS (ESI) m/z: [M + H]$^+$ Calcd. for C$_{18}$H$_{26}$BO$_4$ 317.1919; Found 317.1922.

(Tetrahydro-2H-pyran-4-yl)(o-tolyl)methanone (3r): Unknown compound, prepared according to general conditions B (72h), and purified by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 9:1) to give a clear oil (0.051 g; 50%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.39-7.36 (m, 1H), 7.26-7.21 (m, 1H), 7.14-7.10 (m, 2H), 3.93-3.87 (m, 2H), 3.41-3.32 (m, 2H), 3.20-3.09 (m, 1H), 2.30 (s, 3H), 1.75-1.62 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 206.5, 138.0, 137.6, 131.9, 130.9, 127.3, 125.7, 67.4, 45.7, 28.6, 20.8. HRMS (ESI) m/z: [M + H]$^+$ Calcd. for C$_{13}$H$_{17}$O$_2$ 205.1223; Found 205.1221.
Naphthalen-2-yl(tetrahydro-2H-pyran-4-yl)methanone (3s): Known compound, prepared according to general conditions A (18h), and purified by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 9:1) to give a beige solid (0.071 g; 59%). \(^{1}H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.46 (s, 1H), 8.03-7.96 (m, 2H), 7.92-7.87 (m, 2H), 7.63-7.53 (m, 2H), 4.11-4.07 (m, 2H), 3.70-3.58 (m, 3H), 2.02-1.83 (m, 4H). \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 201.9, 135.7, 133.2, 132.7, 129.8, 129.6, 128.8, 128.6, 127.9, 127.0, 124.3, 67.5, 42.8, 29.3. MS (EI) m/z: [M]\(^+\) 240.

Oxan-4-yl-(4-phenylphenyl)methanone (3t): Unknown compound, prepared according to general conditions B (24h, acetone as solvent), and purified by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 9:1) to give a beige solid (0.088 g; 66%). \(^{1}H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.05-8.01 (m, 2H), 7.72-7.68 (m, 2H), 7.65-7.61 (m, 2H), 7.51-7.38 (m, 3H), 4.08 (ddd, \(J = 11.5, 4.1, 2.4\) Hz, 2H), 3.63-3.49 (m, 3H), 1.99-1.79 (m, 4H). \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 201.4, 145.8, 139.8, 134.5, 129.0, 128.9, 128.3, 127.4, 127.3, 67.4, 42.7, 29.2. HRMS (ESI) m/z: [M + H]\(^+\) Calcd. for C\(_{18}\)H\(_{19}\)O\(_{2}\) 267.1385; Found 267.1380.

3-Phenyl-1-(tetrahydro-2H-pyran-4-yl)propan-1-one (3u): Known compound, prepared according to general conditions A (18h), and purified by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 8:2) to give a clear oil (0.079 g; 72%). \(^{1}H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.31-7.26 (m, 2H), 7.22-7.16 (m, 3H), 4.00-3.96 (m, 2H), 3.40 (dt, \(J = 10.79\) Hz, \(J = 2.86\) Hz, 2H), 2.90 (t, \(J = 7.28\) Hz, 2H), 2.80 (t, \(J = 7.23\) Hz, 2H), 2.56-2.46 (m, 1H), 1.76-1.59 (m, 4H). \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 210.9, 141.0, 128.4, 128.2, 126.0, 67.1, 47.6, 41.9, 29.6, 27.9. MS (EI) m/z: [M]\(^+\) 218.

Cyclohexyl(tetrahydro-2H-pyran-4-yl)methanone (3v): Known compound, prepared according to general conditions A (18h), and purified by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 9:1) to give a clear oil (0.048 g; 49%). \(^{1}H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 4.02-3.98 (m, 2H), 3.47-3.38 (m, 2H), 2.72-2.65 (m, 1H), 2.54-2.46 (m, 1H), 1.80-1.76 (m, 4H), 1.70-1.66 (m, 4H), 1.40-1.22 (m, 6H). \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 215.1, 67.5, 48.9, 46.0, 28.8, 28.4, 26.0, 25.8. MS (EI) m/z: [M]\(^+\) 196.
Adamantan-1-yl(tetrahydro-2H-pyran-4-yl)methanone (3w): Unknown compound, prepared according to general conditions A (18 h), and purified by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 9:1) to give a clear oil (0.085 g; 68%). ¹H NMR (300 MHz, CDCl₃) δ 4.01-3.97 (m, 2H), 3.43 (td, J = 12.07 Hz, J = 1.78 Hz, 2H), 3.11 (tt, J = 11.58 Hz, J = 3.79 Hz, 1H), 2.09-2.02 (m, 3H), 1.82-1.67 (m, 14H), 1.47-1.42 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 216.4, 67.4, 47.1, 41.0, 37.8, 36.7, 29.5, 27.9. HRMS (ESI) m/z: [M + H]⁺ Calcd. for C₁₆H₂₅O₂ 249.1849; Found 249.1850.

2,2-Difluoro-2-phenyl-1-(tetrahydro-2H-pyran-4-yl)ethan-1-one (3x): Unknown compound, prepared from N-acyl-glutarimide derivative 1l according to general conditions A (18 h), and purified by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 9:1) to give an orange oil (0.041 g; 34%). ¹H NMR (300 MHz, CDCl₃) δ 7.55-7.43 (m, 5H), 3.98-3.94 (m, 2H), 3.45-3.36 (m, 2H) 3.17-3.07 (m, 1H), 1.80-1.59 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 201.2 (t, ²Jₖ-F = 31.0 Hz), 132.1 (t, ²Jₖ-F = 20.0 Hz), 131.2, 129.0, 125.7 (t, ³Jₖ-F = 6.0 Hz), 116.3 (t, ³Jₖ-F = 253.0 Hz), 67.0, 42.4, 28.3. ¹⁹F NMR (282.2 MHz, CDCl₃) δ -105.6. HRMS (ESI) m/z: [M + Na]⁺ Calcd. for C₁₃H₁₃F₂NaO₂ 263.0854; Found 263.0857.
IV. Scaled-up procedure

A 25 mL Schlenk tube equipped with a magnetic stirbar was charged with [Ir(dF(CF\textsubscript{3})ppy\textsubscript{2})dtbbpy]PF\textsubscript{6} (1 mol%; 0.015 mmol; 17 mg), [Ni(dtbbpy)(H\textsubscript{2}O)\textsubscript{4}]Cl\textsubscript{2} (3 mol%; 0.045 mmol; 22 mg), sodium carbonate (1 equiv; 1.5 mmol; 159 mg), tris(trimethylsilyl)silane (1 equiv; 1.5 mmol; 462 µL), 1-benzoylpyrrolidine-2,5-dione (1 equiv; 1.5 mmol; 306 mg) and 4-bromo tetrahydropyran (1.5 equiv; 2.25 mmol, 252 µL) in dry acetone (15 mL). The Schlenk tube was sparged with argon and capped, and the reaction mixture was stirred at room temperature under Blue LED irradiation overnight, in conditions A. The mixture was then filtered through Celite® using dichloromethane as eluent to remove solid residues. The volatiles were then removed from the filtrate under vacuum to yield a crude residue which was purified by flash chromatography (cyclohexane/ethyl acetate, gradient 1:0 to 9:1) to afford cyclohexyl(phenyl)methanone as a yellow oil (0.150 g; 49%).

V. Preparation of silylated succinimide 4

1-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)pyrrolidine-2,5-dione (4) is an unknown compound and was prepared using a literature procedure.\textsuperscript{23} To a 50 mL round bottom flask equipped with a stirrer bar, chlorotris(trimethylsilyl)silane (1 equiv, 2 mmol, 0.6 g) and succinimide (1 equiv, 2 mmol, 0.2 g) were added in triethylamine (2 mL) and stirred for 10 minutes. Then the mixture was heated at 100 °C (oil bath) for 4 hours. The reaction mixture was then allowed to reach room temperature. Hexane (2 mL) was added, a precipitate formed which was filtered off, and the filtrate was concentrated in vacuo. This operation was repeated once again to give the desired product as a white solid (0.641 g, 93%). \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) δ 2.70 (s, 4H), 0.23 (s, 27H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 183.2, 30.9, 1.5. HRMS (ESI): calcd for C\textsubscript{13}H\textsubscript{32}NO\textsubscript{2}Si\textsubscript{4} (M+H): 346.1505; Found: 346.1508.
VI. References


VII. NMR spectra of starting materials and products
$\text{\textsuperscript{1}H NMR, CDCl}_3, 300 \text{ MHz}$

$\text{\textsuperscript{13}C NMR, CDCl}_3, 101 \text{ MHz}$
$3b$

$^1H$ NMR, CDCl$_3$, 300 MHz

$3b$

$^{13}C$ NMR, CDCl$_3$, 101 MHz
$^{1}$H NMR, CDCl$_3$, 300 MHz

$^{13}$C NMR, CDCl$_3$, 101 MHz
$^{1}$H NMR, CDCl$_3$, 300 MHz

$^{13}$C NMR, CDCl$_3$, 101 MHz
$^{1}$H NMR, CDCl$_3$, 300 MHz

$^{13}$C NMR, CDCl$_3$, 101 MHz
$^1$H NMR, CDCl$_3$, 300 MHz

$^{13}$C NMR, CDCl$_3$, 101 MHz
$^1$H NMR, CDCl$_3$, 300 MHz

$^{13}$C NMR, CDCl$_3$, 101 MHz
$^{19}$F NMR, CDCl$_3$, 282.2 MHz
$^{1}H$ NMR, CDCl$_3$, 300 MHz

$^{13}C$ NMR, CDCl$_3$, 101 MHz
$^{1}H$ NMR, CDCl$_3$, 300 MHz

$^{13}C$ NMR, CDCl$_3$, 101 MHz
$^{1}H$ NMR, CDCl$_3$, 300 MHz

$^{13}C$ NMR, CDCl$_3$, 101 MHz
$^{19}$F NMR, CDCl$_3$, 282.2 MHz

$^1$H NMR, CDCl$_3$, 300 MHz
$^1$H NMR, CDCl$_3$, 300 MHz

$^{13}$C NMR, CDCl$_3$, 101 MHz
$^1$H NMR, CDCl$_3$, 300 MHz

$^{13}$C NMR, CDCl$_3$, 101 MHz
$^1$H NMR, CDCl$_3$, 300 MHz

$^{13}$C NMR, CDCl$_3$, 101 MHz
$^{1}H$ NMR, CDCl$_3$, 300 MHz

$^{13}C$ NMR, CDCl$_3$, 101 MHz
3w

$^1$H NMR, CDCl$_3$, 300 MHz

3w

$^{13}$C NMR, CDCl$_3$, 101 MHz
$^1$H NMR, CDCl$_3$, 300 MHz

$^{13}$C NMR, CDCl$_3$, 101 MHz
$^{19}$F NMR, CDCl$_3$, 282.2 MHz

$3\times$
$^{1}H$ NMR, CDCl$_3$, 300 MHz

$^{13}C$ NMR, CDCl$_3$, 101 MHz