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Supporting Information

Acridine Photocatalysis Enables Tricomponent Direct Decarboxylative Amine Construction

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Materials and experimental details

Materials: Acetonitrile was dried over 3Å molecular sieves and thoroughly degassed under the atmosphere of argon before use. Anhydrous *p*-toluenesulfonic acid was prepared by heating the monohydrate under vacuum at 70 °C for 4 h. 4Å Molecular sieves were dried under vacuum at 120 °C for 3 h before use. All other chemicals were used as commercially available.

Experimental equipment: The photoinduced reactions were conducted in borosilicate glass test-tubes (8 mL capacity, Duran) fitted with GL14 screw-caps placed in a test-tube rack on a magnetic stir plate that was flanked by two 400 nm 36W LED lights ($\lambda_{max} = 400$ nm, 2.6 mW/cm²). The temperature in the test-tube rack was maintained at 25–27 °C with an air flow from a compressed air line. Eight parallel reactions arranged in two rows of four tubes were typically carried out in one test-tube rack.

Purification: Column chromatography was performed using CombiFlash Rf-200 (Teledyne-Isco) automated flash chromatography system, as well as manually. Thin layer chromatography was carried out on silica gel-coated glass plates (Merck Kieselgel 60 F254). Plates were visualized under ultraviolet light (254 nm) and using a potassium permanganate stain.

Characterization: ¹H, ¹³C, ¹¹B, and ¹⁹F NMR spectra were recorded at 500 MHz (¹H), 125 MHz (¹³C), 202 MHz (³¹ P), 470.5 MHz (¹⁹F), and 160.4 MHz (¹¹B) on Bruker AVANCE III 500 instruments in CDCl₃ or other specified deuterated solvents with and without tetramethylsilane (TMS) as an internal standard at 25 °C, unless specified

otherwise. Chemical shifts (δ) are reported in parts per million (ppm) from tetramethylsilane (¹H and ¹³C), BF₃·OEt₂ (¹¹B), and CFCl₃ (¹⁹F). Coupling constants (*J*) are in Hz. Proton multiplicity is assigned using the following abbreviations: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint.), septet (sept.), heptet (hept.), multiplet (m), broad (br).



Irradiance was measured with a UVV420 radiometer at a distance of 2 cm from the light source. Infrared measurements were carried out neat on a Bruker Vector 22 FT-IR spectrometer fitted with a Specac diamond attenuated total reflectance (ATR) module.

General procedure for the photo-induced three component amine construction (GP1).

To a 8 mL test-tube equipped with a stir bar, Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine A1 (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (0.2 mmol), aniline (0.24 mmol, 1.2 equiv.), carboxylic acid (0.26 mmol, 1.3 equiv.), and anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%) were added, followed by acetonitrile (2 mL). The test-tube was capped, and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel to give the amine product.

Additional experimental studies

Table S1. Catalyst Performance in the Acridine-Catalyzed Direct Decarboxylative Tricomponent Amine Construction.^{*a*}

	PC (8 mol%) TSOH (8 mol%) TSOH (8 mol%) Cu(MeCN) ₄ BF ₄ (8 mol%) MeCN, 4Å MS	HN HN 4a
Entry	Photocatalyst	Yield, %
1	Eosin Y at 450 nm	0
2	Eosin Y at 420 nm	0
3	Eosin Y at 400 nm	0
4	Eosin Y disodium salt at 450 nm	0
5	4CzIPN at 450 nm	0
6	4CzIPN at 420 nm	0
7	4CzIPN at 400 nm	0
8	[Acr-Mes] ⁺ (BF ₄) ⁻ at 400 nm	0
9	[Acr-Mes] ⁺ (BF ₄) ⁻ at 450 nm	0^b
10	Ir(ppy)3 at 450 nm	0^b

11	Ir(ppy)2(pq) at 450 nm	0^b
12	(Ir[dF(CF3)ppy]2(dtbpy))PF6 at 450 nm	0^b
13	Ru(bpm)2Cl2 at 450 nm	0^b
14	Ru(<i>p</i> -CF ₃ -bpy) ₃ (BF ₄) ₂ at 450 nm	0^b

^{*a*} Reaction conditions: aldehyde **1** (0.2 mmol), aniline **2** (0.24 mmol), carboxylic acid **3** (0.2 mmol), acridine **A1** (8 mol%), Cu(MeCN)₄BF₄ (8 mol%), TsOH (8 mol%), MeCN (2 mL), 4Å molecular sieves (60 mg), LED light (400 nm), 30 h. Yield was determined by ¹H NMR spectroscopy with 1,4-dimethoxybenzene as an internal standard. ^{*b*} 2 mol% photocatalyst was used. 1,2,3,5-Tetrakis-(carbazol-9-yl)-4,6-dicyanobenzene, [Acr-Mes]⁺(BF₄)⁻: 10-Phenyl-9-(2,4,6-trimethylphenyl)acridinium tetrafluoro-borate, Ir(ppy)₃: Tris(2-phenylpyridine)iridium(III), Ir(ppy)₂(pq): bis(2-phenylpyridine)(2-phenyl-qui-noline)iridium(III), (Ir[dF(CF₃)ppy]₂(dtbpy))PF₆: [4,4'-Bis(1,1-dimethylethyl)-2,2'-bipyridine-*N1,N1'*]-bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-C]Iridium(III) hexafluorophosphate, Ru(bpm)₂Cl₂: Tris(2,2'-bipyrimide)-ruthenium(II) dichloride, Ru(*p*-CF₃-bpy)₃(BF₄)₂: Tris(2,2'-(*p*CF₃)bi-pyridine)ruthenium(II) tetrafluoroborate.

Radical trapping studies with TEMPO



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), benzaldehyde (21.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), cyclohexanecarboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), TEMPO (62.5 mg, 0.4 mmol or 93.75 mg, 0.6 mmol) and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 20 h. The reaction mixture was then diluted with ethyl acetate (15 mL), and washed with a saturated solution of EDTA disodium salt (5 mL). The organic layer was collected, dried over anhydrous sodium sulfate, concentrated, and a ¹H NMR spectrum was recorded with 1,3,5-trimethoxybenezene as an internal standard.

Kinetics of the imine formation



A solution of benzaldehyde (5.3 mg, 0.05 mmol), aniline (4.7 mg, 0.05 mmol), a catalyst or additive (0.004 mmol, 0.7 mg for anhydrous *p*-toluenesulfonic acid; or 0.004 mmol, 1.3 mg for Cu(MeCN)BF₄; or 0.05 mmol, 6.4 mg for acid **3**; one experiment was also carried out without a catalyst or additive) in acetonitrile- d_3 (0.5 mL) was monitored by ¹H NMR spectroscopy at rt.

Amine products

N-(Cyclohexyl(phenyl)methyl)aniline (4a)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **4a** (50.4 mg, 95%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 7.31 (4 H, d, *J* = 4.4 Hz), 7.23 (1 H, dt, *J* = 8.7, 4.2 Hz), 7.13 – 7.04 (2 H, m), 6.63 (1 H, t, *J* = 7.3 Hz), 6.53 (2 H, d, *J* = 8.0 Hz), 4.14 (1 H, d, *J* = 6.3 Hz), 2.06 – 1.86 (1 H, m), 1.83 – 1.61 (4 H, m), 1.60 – 1.53 (1 H, m), 1.28 – 0.98 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 129.2, 128.3, 127.4, 126.9, 117.1, 113.4, 63.6, 45.0, 30.3, 29.6, 26.5, 26.5 ppm – IR: 2921, 2850, 1601, 1503, 1319, 748, 702 cm⁻¹. – HRMS: calcd for C₁₉H₂₃N: 266.1903, found 266.1904 [M+H⁺].

N-(Cyclohexyl(phenyl)methyl)-4-methylaniline (4b)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (25.7 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **4b** (50.2 mg, 90%) as a white solid (m.p. 76 °C).

¹ H NMR (500 MHz, CDCl₃): 7.30 (4 H, d, J = 4.3 Hz), 7.21 (1 H, ddd, J = 8.5, 5.1, 3.6 Hz), 7.03 – 6.76 (2 H, m), 6.44 (2 H, d, J = 8.4 Hz), 4.10 (2 H, d, J = 6.2 Hz), 2.18 (3 H, s), 1.90 (1 H, dt, J = 13.3, 3.0 Hz), 1.83 – 1.48 (5 H, m), 1.36 – 0.84 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 145.7, 143.0, 129.7, 128.3, 127.4, 126.8, 126.1, 113.4, 63.8, 45.1, 30.4, 29.6, 26.6, 26.5, 26.5, 20.4 ppm – IR: 2925, 1740, 1365, 1218 cm⁻¹. – HRMS: calcd for C₂₀H₂₅N: 280.2060, found 280.2058 [M+H⁺].

N-(Cyclohexyl(phenyl)methyl)-3,4,5-trimethylaniline (4c)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (32.4 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **4c** (55.3 mg, 90%) as a white solid (m.p. 75 °C).

¹ H NMR (500 MHz, CDCl₃): 7.35 – 7.29 (4 H, m), 7.23 (1 H, tt, *J* = 5.7, 3.1 Hz), 6.26 (2 H, s), 4.12 (1 H, d, *J* = 6.3 Hz), 3.96 (1 H, s), 2.16 (6 H, s), 2.04 (3 H, s), 1.91 (1 H, dt, *J* = 12.2, 3.2 Hz), 1.84 – 1.72 (2 H, m), 1.67 (2 H, tdd, *J* = 11.8, 5.7, 2.7 Hz), 1.59 – 1.50 (1 H, m), 1.29 – 1.03 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 145.5, 143.3, 137.1, 128.3, 127.3, 126.7, 123.5, 112.8, 63.5, 45.1, 30.5, 29.5, 26.6, 26.5, 26.5, 20.9, 14.4 ppm – IR: 2924, 1739, 1365, 1217 cm⁻¹. – HRMS: calcd for C₂₂H₂₉N: 308.2373, found 308.2372 [M+H⁺].

N-(Cyclohexyl(phenyl)methyl)-2,3-dihydro-1H-inden-5-amine (4d)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (31.9 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **4d** (59.2 mg, 97%) as a colourless oil.

¹H NMR (300 MHz, CDCl₃): 7.36 – 7.28 (4 H, m), 7.22 (1 H, ddt, *J* = 5.5, 4.4, 3.6 Hz), 6.93 (1 H, d, *J* = 8.0 Hz), 6.44 (1 H, d, *J* = 2.3 Hz), 6.32 (1 H, dd, *J* = 8.1, 2.3 Hz), 4.11 (2 H, d, *J* = 6.1 Hz), 2.75 (4 H, td, *J* = 7.5, 6.5, 3.1 Hz), 2.11 – 1.83 (3 H, m), 1.83 – 1.45 (5 H, m), 1.33 – 0.96 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃):146.8, 145.3, 143.2, 132.7, 128.3, 127.3, 126.7, 124.7, 111.5, 109.4, 63.9,

45.1, 33.2, 32.0, 30.4, 29.5, 26.6, 26.5, 26.5, 25.8 ppm – IR: 2924, 2849, 1739, 1499, 1217, 702 cm⁻¹. – HRMS: calcd for C₂₂H₂₇N: 306.2216, found 306.2216 [M+H⁺].

N-(Cyclohexyl(phenyl)methyl)-4-fluoroaniline (4e)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (26.6 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) to give product **4e** (47.5 mg, 84%) as a colourless oil.

F ¹H NMR (500 MHz, CDCl₃): 7.37 – 7.27 (4 H, m), 7.27 – 7.21 (1 H, m), 6.91 – 6.68 (2 H, m), 6.49 – 6.38 (2 H, m), 4.07 (2 H, d, J = 6.2 Hz), 1.92 (1 H, ddd, J = 13.0, 3.5, 1.8 Hz), 1.85 – 1.72 (2 H, m), 1.71
– 1.62 (2 H, m), 1.60 – 1.51 (1 H, m), 1.34 – 1.00 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 155.63 (d, J = 234.3 Hz), 144.26, 142.57, 128.35, 127.36, 126.96, 115.56 (d, J = 22.3 Hz), 114.02 (d, J = 7.4 Hz),

64.22, 45.05, 30.33, 29.65, 26.55, 26.51, 26.47 ppm. – ¹⁹F NMR (376 MHz, CDCl₃) δ -128.8 ppm. – IR: 2925, 2852, 1508, 1218, 817, 702 cm⁻¹. – HRMS: calcd for C₁₉H₂₂FN: 284.1809, found 284.1805 [M+H⁺].

4-Chloro-N-(Cyclohexyl(phenyl)methyl)aniline (4f)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (30.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **4f** (50.4 mg, 84%) as a white solid (m.p. 105 °C).

HN

^{CI} ¹ H NMR (500 MHz, CDCl₃): 7.34 – 7.19 (5 H, m), 6.99 (d, J = 8.7 Hz, 2 H), 6.40 (2 H, d, J = 8.4 Hz), 4.17 (1 H, s), 4.06 (1 H, d, J = 6.3 Hz), 1.88 (1 H, d, J = 12.9 Hz), 1.81 – 1.68 (2 H, m), 1.65 (2 H, dd, J = 9.2, 5.7 Hz), 1.52 (2 H, d, J = 13.8 Hz), 1.29 – 0.94 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 129.0, 128.4, 127.3, 127.0, 114.4, 63.7, 45.0, 30.3, 29.6, 26.5, 26.5, 26.4 ppm – IR: 2925, 2851, 1738,

1498, 1217, 703 cm⁻¹. – HRMS: calcd for C₁₉H₂₂ClN: 300.1514, found 300.1514 [M+H⁺].

3-Bromo-N-(Cyclohexyl(phenyl)methyl)aniline (4g)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (41.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **4g** (60.5 mg, 88%) as a colourless oil.

^{Br} ¹ H NMR (500 MHz, CDCl₃): 7.34 – 7.28 (2 H, m), 7.27 – 7.19 (3 H, m), 6.89 (1 H, t, *J* = 8.0 Hz), 6.74 – 6.69 (1 H, m), 6.66 (1 H, t, *J* = 2.1 Hz), 6.38 (1 H, ddd, *J* = 8.2, 2.3, 0.9 Hz), 4.22 (1 H, s), 4.07 (1 H, d, *J* = 6.4 Hz), 1.88 (1 H, ddt, *J* = 12.9, 3.5, 1.8 Hz), 1.81 – 1.68 (2 H, m), 1.64 (2 H, dddd, *J* = 14.9, 11.7, 6.4, 3.3 Hz), 1.51 (1 H, ddt, *J* = 13.0, 3.5, 1.8 Hz), 1.27 – 0.97 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 149.2, 142.1, 130.5, 128.4, 127.2, 127.1, 123.1, 119.9, 116.1, 111.8, 63.4, 44.9, 30.3, 29.6, 26.5, 26.4, 26.4 ppm – IR: 2921, 2849, 1593, 1480, 985, 702, 681 cm⁻¹. – HRMS: calcd for C₁₉H₂₂BrN: 344.1008, found 344.1002 [M+H⁺].

N-(Cyclohexyl(phenyl)methyl)-3-iodoaniline (4h)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (52.6 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **4h** (62.6 mg, 80%) as a colourless oil.

¹ H NMR (500 MHz, CDCl₃): δ 7.35 – 7.28 (2 H, m), 7.27 – 7.19 (3 H, m), 6.98 – 6.85 (2 H, m), 6.79 – 6.70 (1 H, m), 6.45 – 6.38 (1 H, m), 4.17 (1 H, s), 4.06 (1 H, d, *J* = 6.4 Hz), 1.88 (1H, d, *J* = 13.1 Hz), 1.74 (2 H, dd, *J* = 25.4, 12.3 Hz), 1.64 (2 H, dddd, *J* = 11.8, 8.6, 5.9, 3.2 Hz), 1.58 – 1.44 (1 H, m), 1.34 – 0.96 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 149.1, 142.1, 130.6, 128.4, 127.2, 127.1, 125.9, 122.2, 112.3, 95.1, 63.3, 44.9, 30.3, 29.6, 26.5, 26.4, 26.4 ppm – IR: 2924, 2850, 1738, 1365, 1217 cm⁻¹. – HRMS: calcd for C₁₉H₂₂IN: 392.0807, found 392.0866 [M+H⁺].

N-(Cyclohexyl(phenyl)methyl)-2-methoxyaniline (4i)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **4i** (47.2 mg, 80%) as a colourless oil.

MeO
¹H NMR (500 MHz, CDCl₃): 7.31 (4 H, q, J = 4.0, 2.9 Hz), 7.21 (1 H, tq, J = 5.5, 2.6 Hz), 6.76 (1 H, dd, HN, J = 7.8, 1.4 Hz), 6.68 (1 H, td, J = 7.7, 1.4 Hz), 6.58 (1 H, td, J = 7.7, 1.6 Hz), 6.33 (1 H, dd, J = 7.9, 1.6 Hz), 4.83 (1 H, s), 4.12 (1 H, d, J = 6.2 Hz), 3.91 (3 H, s), 2.01 – 1.87 (1 H, m), 1.83 – 1.62 (4 H, m), 1.62 – 1.49 (1 H, m), 1.33 – 1.00 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 146.8, 143.0, 137.8, 128.2, 127.4, 126.8, 121.3, 116.0, 110.8, 109.4, 63.4, 55.7, 45.0, 30.4, 29.6, 26.6, 26.5 ppm – IR: 2924, 2851, 1602, 1510, 1454, 1221, 1028, 702 cm⁻¹. – HRMS: calcd for C₂₀H₂₅NO: 296.2009, found 296.2004 [M+H⁺].

N-(Cyclohexyl(phenyl)methyl)-3-(methylthio)aniline (4j)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (33.4 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **4j** (44.8 mg, 72%) as a colourless oil.

¹ H NMR (500 MHz, CDCl₃): 7.34 – 7.26 (4 H, m), 7.24 – 7.19 (1 H, m), 6.97 (1 H, t, *J* = 7.9 Hz), 6.65
- 6.47 (1 H, m), 6.40 (1 H, s), 6.28 (1 H, dd, *J* = 8.2, 2.3 Hz), 4.19 (1 H, s), 4.11 (1 H, d, *J* = 6.4 Hz), 2.34
(3 H, s), 1.97 – 1.86 (1 H, m), 1.84 – 1.59 (4 H, m), 1.53 (1 H, ddd, *J* = 13.7, 5.3, 2.8 Hz), 1.36 – 0.94 (5
H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 148.2, 142.5, 139.0, 129.4, 128.4, 127.3, 126.9, 115.3, 111.1, 110.4, 63.5, 44.9, 30.3, 29.6, 26.5, 26.5, 26.4, 15.7 ppm – IR: 2920, 2850, 1738, 1590, 1217, 702 cm⁻¹. – HRMS: calcd for C₂₀H₂₅NS: 312.1780, found 312.1780 [M+H⁺].

N-(Cyclohexyl(phenyl)methyl)-3-(trifluoromethoxy)aniline (4k)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (42.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **4k** (51.0 mg, 73%) as a colourless oil.

OCF₃ ¹ H NMR (500 MHz, CDCl₃): 7.41 – 7.15 (5 H, m), 7.02 (1 H, t, *J* = 8.2 Hz), 6.45 – 6.41 (1 H, m), 6.39 (1 H, dd, *J* = 8.2, 2.2 Hz), 6.32 (1 H, s), 4.30 (1 H, s), 4.08 (1 H, d, *J* = 6.4 Hz), 2.00 – 1.86 (1 H, m), 1.82 – 1.60 (4 H, m), 1.57 – 1.47 (1 H, m), 1.33 – 0.94 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 197.5, 150.4, 149.2, 142.0, 130.0, 128.5, 127.3, 127.1, 111.5, 108.8, 105.5, 63.6, 44.9, 30.3, 29.7, 26.5, 26.4, 26.4 ppm. – ¹⁹F NMR (376MHz, CDCl₃) δ -57.5 ppm. – IR: 2928, 2853, 1738, 1615, 1217, 1157 cm⁻¹. – HRMS: calcd for C₂₀H₂₂FNO: 350.1726, found 350.1726 [M+H⁺].





According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (40.6 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **41** (64.8 mg, 95%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 7.48 (2 H, d, *J* = 7.7 Hz), 7.34 (8 H, dd, *J* = 14.0, 4.6 Hz), 7.23 (2 H, dq, *J* = 7.4, 3.7, 3.0 Hz), 6.58 (2 H, d, *J* = 8.2 Hz), 4.27 (1 H, s), 4.17 (1 H, d, *J* = 6.3 Hz), 1.97 – 1.88 (1 H, m), 1.85 – 1.63 (4 H, m), 1.56 (1 H, dd, *J* = 15.8, 3.8 Hz), 1.32 – 0.97 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃):147.2, 142.6, 141.3, 129.9, 128.6, 128.3, 127.8, 127.2, 126.8, 126.2, 125.9, 113.4, 63.4, 44.9, 30.3, 29.5, 26.4, 26.4, ppm – IR: 2925, 2851, 1738, 1612, 1217, 700 cm⁻¹.

HRMS: calcd for C25H27N: 342.2216, found 342.2216 [M+H+].

HN

N-(Cyclohexyl(phenyl)methyl)-[1,1'-biphenyl]-2-amine (4m)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (40.6 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **4m** (42.9 mg, 96%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 7.49 (3 H, d, *J* = 7.0 Hz), 7.42 – 7.34 (1 H, m), 7.27 (3 H, dd, *J* = 14.2, 6.8 Hz), 7.20 (3 H, dd, *J* = 14.2, 7.2 Hz), 7.09 – 6.98 (2 H, m), 6.66 (1 H, t, *J* = 7.4 Hz), 6.40 (1 H, d, *J* = 8.2 Hz), 4.44 (1 H, s), 4.12 (1 H, d, *J* = 5.9 Hz), 1.71 – 1.47 (5 H, m), 1.43 (1 H, d, *J* = 13.2 Hz), 1.19 – 0.73 (5 H, m). ppm. – ¹³C NMR (125 MHz, CDCl₃): 142.7, 139.8, 130.1, 129.6, 129.0, 128.6, 128.3, 127.4, 127.3, 126.8, 116.6, 111.5, 63.5, 45.0, 30.6, 29.1, 26.5, 26.4 ppm – IR: 2924, 2851, 1738, 1508, 1217, 702 cm⁻¹. – HRMS: calcd for C₂₅H₂₇N: 342.2216, found 342.2216 [M+H⁺].

N-(Cyclohexyl(phenyl)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (4n)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (52.6 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **4n** (70.4 mg, 90%) as a white solid (m.p. 110 °C).

¹H NMR (500 MHz, CDCl₃): 7.29 (4 H, d, *J* = 4.3 Hz), 7.20 (1 H, p, *J* = 4.3 Hz), 7.11 (1 H, d, *J* = 2.5 Hz), 7.08 –



Bpin
7.03 (2 H, m), 6.49 (1 H, dt, J = 5.8, 3.1 Hz), 4.36 – 4.04 (2 H, m), 1.87 (1 H, dd, J = 12.6, 3.3 Hz),
1.74 (2 H, tdd, J = 15.6, 5.6, 2.8 Hz), 1.65 (2 H, dddd, J = 14.7, 12.3, 6.0, 2.9 Hz), 1.59 – 1.50 (1 H, m), 1.34 (12 H, d, J = 3.7 Hz), 1.27 – 0.98 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 147.2,
142.8, 128.7, 128.3, 127.3, 126.8, 123.3, 120.6, 115.0, 83.7, 63.2, 45.1, 30.5, 29.3, 26.6, 26.5, 25.0, 24.9 ppm. – ¹¹B NMR (128 MHz, CDCl₃) δ 30.8 ppm. – IR: 2925, 2852, 1738, 1361, 1144, 704 cm⁻

¹. – HRMS: calcd for C₂₅H₃₄BNO₂: 392.2755, found 392.2755 [M+H⁺].

N-(Cyclohexyl(phenyl)methyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (40)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol%), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (52.6 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **40** (50.8 mg, 91%) as a white solid (m.p. 95 °C).

^{Bpin 1} H NMR (500 MHz, CDCl₃): 7.53 (2 H, d, J = 8.4 Hz), 7.32 – 7.23 (4 H, m), 7.23 – 7.15 (1 H, m), 6.48 (2 H, d, J = 8.3 Hz), 4.36 (1 H, s), 4.18 (1 H, d, J = 6.3 Hz), 1.88 (1 H, dt, J = 13.0, 3.3 Hz), 1.81 – 1.62 (4 H, m), 1.57 – 1.48 (1 H, m), 1.28 (12 H, d, J = 2.6 Hz), 1.25 – 1.00 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 150.3, 142.3, 136.3, 128.3, 127.3, 126.9, 112.4, 83.2, 62.9, 44.9, 30.4, 29.5,

26.5, 26.5, 26.4, 25.0, 24.9 ppm. – ¹¹B NMR (128 MHz, CDCl₃) δ 31.3 ppm. – IR: 2926, 2851, 1738, 1360, 705 cm⁻¹. – HRMS: calcd for C₂₅H₃₄BNO₂: 392.2755, found 392.2756 [M+H⁺].

N-(Cyclohexyl(phenyl)methyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (4p)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (52.6 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **4p** (35.7 mg, 60%) as a colourless oil.

pinB
¹ H NMR (300 MHz, CDCl₃): 7.62 (1 H, dd, J = 7.4, 1.8 Hz), 7.38 – 7.27 (3 H, m), 7.25 – 7.16 (1 H, m), 7.09 (1 H, ddd, J = 8.7, 7.2, 1.8 Hz), 6.61 (1 H, d, J = 5.5 Hz), 6.53 (1 H, td, J = 7.3, 0.9 Hz), 6.21 (1 H, d, J = 8.3 Hz), 4.21 (1 H, t, J = 5.1 Hz), 1.91 – 1.62 (6 H, m), 1.41 (12 H, d, J = 2.2 Hz), 1.35 – 1.05 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 154.4, 143.2, 137.0, 133.1, 128.2, 127.3, 126.6, 115.2, 110.6, 83.6, 63.0, 45.6, 30.8, 28.1, 26.8, 26.7, 25.2, 25.1 ppm. – ¹¹B NMR (128 MHz, CDCl₃) & 31.0 ppm. – IR: 2925, 1738, 1453, 1360, 1217, 1143 cm⁻¹. – HRMS: calcd for C₂₅H₃₄BNO₂: 392.2755, found 392.2755 [M+H⁺].

HN

N-(Cyclohexyl(phenyl)methyl)benzo[d]thiazol-6-amine (4q)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol%), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (36.0 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 10 v/v) to give product **4q** (38.6 mg, 60%) as a colourless oil.

^S ¹H NMR (500 MHz, CDCl₃): 8.81 (1 H, s), 7.58 (1 H, d, *J* = 8.6 Hz), 7.36 – 7.25 (4 H, m), 7.24 – 7.16 (1 H, m), 7.14 (1 H, d, *J* = 2.3 Hz), 6.77 (1 H, dd, *J* = 8.6, 2.3 Hz), 4.20 (1 H, d, *J* = 6.3 Hz), 1.94 (1 H, dt, *J* = 14.2, 2.5 Hz), 1.83 – 1.62 (3 H, m), 1.61 – 1.46 (1 H, m), 1.31 – 0.97 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 154.9, 154.3, 147.2, 142.2, 128.4, 127.4, 127.0, 122.0, 121.8, 115.1, 105.5, 63.9, 44.9, 30.3, 29.7, 26.5, 26.5, 26.4 ppm – IR: 2925, 1738, 1365, 1217, 702 cm⁻¹. – HRMS: calcd for C₂₀H₂₂N₂S: 323.1576, found 323.1571 [M+H⁺].

N-(Cyclohexyl(phenyl)methyl)-3-(oxazol-4-yl)aniline (4r)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (38.4 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 10 v/v) to give product **4r** (43.2 mg, 65%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 7.85 (1 H, s), 7.35 – 7.27 (4 H, m), 7.25 – 7.17 (2 H, m), 7.09 (1 H, J = 7.9 Hz), 6.89 (1 H, dt, J = 7.7, 1.1 Hz), 6.80 (1 H, t, J = 2.0 Hz), 6.47 (1 H, dd, J = 8.1, 2.4 Hz), 4.15 (1 H, d, J = 6.4 Hz), 1.99 – 1.88 (1 H, m), 1.84 – 1.61 (4 H, m), 1.54 (1 H, dd, J = 12.5, 3.6 Hz), 1.37 – 0.95 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 152.2, 150.3, 148.2, 142.4, 129.8, 128.5,

128.4, 127.3, 127.0, 121.3, 113.6, 113.4, 109.1, 63.6, 45.0, 30.3, 29.7, 26.5, 26.5, 26.4 ppm – IR: 2926, 2852, 1738, 1365, 1217, 703 cm⁻¹. – HRMS: calcd for C₂₂H₂₄N₂O: 333.1961, found 333.1956 [M+H⁺].

N-(Cyclohexyl(o-tolyl)methyl)aniline (5a)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (24.0 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **5a** (50.2 mg, 90%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 7.36 – 7.29 (1 H, m), 7.21 – 7.11 (3 H, m), 7.13 – 7.06 (2 H, m), 6.63 (1 HN H, t, *J* = 7.4 Hz), 6.51 – 6.45 (2 H, m), 4.42 (1 H, d, *J* = 6.1 Hz), 4.14 (1 H, s), 2.49 (3 H, s), 2.00 – 1.90 (1 H, m), 1.87 – 1.55 (5 H, m), 1.36 – 1.06 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 148.0, 141.0, 135.3, 130.6, 129.2, 126.5, 126.4, 126.1, 117.0, 113.0, 59.3, 44.4, 30.8, 28.9, 26.7, 26.6, 19.7 ppm – IR:

2925, 2850, 1738, 1600, 1500, 1365, 1216 cm⁻¹. - HRMS: calcd for C₂₀H₂₅N: 280.2060, found 280.2061 [M+H⁺].

N-(Cyclohexyl(*m*-tolyl)methyl)aniline (5b)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol%), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **5b** (53.6 mg, 96%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 7.18 (1 H, t, *J* = 7.4 Hz), 7.12 – 7.04 (4 H, m), 7.02 (1 H, d, *J* = 7.5 Hz), 6.61 (1 H, t, *J* = 7.3 Hz), 6.51 (2 H, d, *J* = 7.9 Hz), 4.20 – 4.10 (1 H, m), 4.08 (1 H, d, *J* = 6.3 Hz), 2.34 (3 H, s), 1.90 (1 H, d, *J* = 12.4 Hz), 1.82 – 1.69 (2 H, m), 1.66 (2 H, dq, *J* = 9.2, 2.9 Hz), 1.58 – 1.45 (1 H, m), 1.30 – 0.96 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 148.0, 142.8, 137.8, 129.2, 128.1, 128.0, 127.6, 124.5, 117.0, 113.3, 63.6, 45.1, 30.5, 29.6, 26.6, 26.5, 26.5, 21.7 ppm – IR: 2923, 2851, 1738, 1601, 1504, 1365, 1217 cm⁻¹. – HRMS: calcd for C₂₀H₂₅N: 280.2060, found 280.2053 [M+H⁺].

N-((4-(tert-Butyl)phenyl)(cyclohexyl)methyl)aniline (5c)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (32.4 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **5c** (63.6 mg, 99%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): δ 7.31 (2 H, d, *J* = 8.3 Hz), 7.21 (2 H, d, *J* = 8.3 Hz), 7.09 (2 H, dd, *J* = 8.6, 7.3 Hz), 6.66 – 6.59 (1 H, m), 6.56 – 6.51 (2 H, m), 4.15 (1 H, s), 4.11 (1 H, d, *J* = 6.4 Hz), 1.92 (1 H, dt, *J* = 12.7, 1.8 Hz), 1.83 – 1.60 (4 H, m), 1.55 (1 H, ddd, *J* = 14.6, 4.6, 2.2 Hz), 1.32 (9 H, s), 1.27 – 0.98 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 149.5, 148.1, 139.6, 129.2, 126.9, 125.2, 116.9, 113.2, 63.1, 45.0, 34.5, 31.6, 30.4, 29.6, 26.6, 26.5, 26.5 ppm – IR: 2922, 2850, 1738, 1600, 1502, 1319, 1217, 747, 691 cm⁻¹. – HRMS: calcd for C₂₃H₃₁N: 322.2529, found 322.2524 [M+H⁺].

N-(Cyclohexyl(2-fluorophenyl)methyl)aniline (5d)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (24.8 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) to give product **5d** (48.1 mg, 85%) as a colourless oil.

¹ H NMR (500 MHz, CDCl₃): 7.35 – 7.24 (1 H, m), 7.18 (1 H, tdd, *J* = 7.5, 5.3, 1.8 Hz), 7.12 – 6.98 (4 H, m), 6.63 (1 H, dd, *J* = 7.9, 6.7 Hz), 6.56 – 6.52 (2 H, m), 4.48 (1 H, d, *J* = 7.2 Hz), 4.26 – 3.98 (1 H, m), 2.13 – 1.90 (1 H, m), 1.83 – 1.62 (4 H, m), 1.58 – 1.43 (1 H, m), 1.33 – 0.99 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 161.01 (d, *J* = 244.4 Hz), 147.43, 129.71, 129.14, 128.65 (d, *J* = 5.1 Hz), 128.19 (d, *J* = 8.3 Hz), 124.04 (d, *J* = 3.5 Hz), 117.18, 115.39, 115.21, 112.99, 57.02, 43.85, 29.98, 29.75, 26.42, 26.27 ppm. – ¹⁹F NMR (376 MHz, CDCl₃) δ -118.8 (m) ppm. – IR: 2923, 2850, 1738, 1601, 1504, 1217, 749, 692 cm⁻¹. – HRMS: calcd for C19H22FN: 284.1809, found 284.1802 [M+H⁺].

N-((4-Chlorophenyl)(cyclohexyl)methyl)aniline (5e)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (28.0 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **5e** (49.8 mg, 83%) as a white solid (m.p. 65 °C).

¹ H NMR (500 MHz, CDCl₃): 7.34 – 7.19 (4 H, m), 7.09 (2 H, dd, *J* = 8.6, 7.2 Hz), 6.72 – 6.60 (1 H, m), 6.48 (2 H, d, *J* = 7.9 Hz), 4.14 (1 H, br), 4.11 (1 H, d, *J* = 6.1 Hz), 1.87 (1 H, dd, *J* = 13.4, 2.6 Hz), 1.83 – 1.72 (2 H, m), 1.71 – 1.48 (3 H, m), 1.31 – 0.98 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 132.5, 129.2, 128.7, 128.5, 117.4, 113.3, 63.0, 45.0, 30.2, 29.5, 26.5, 26.5, 26.4 ppm. – IR: 2925, 2851,

1601, 1504, 1152 cm⁻¹. - HRMS: calcd for C19H22ClN: 300.1514, found 300.1505 [M+H⁺].

N-(Cyclohexyl(4-methoxyphenyl)methyl)aniline (5f)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol%), 4Å molecular sieves (60 mg), aldehyde (27.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **5f** (56.0 mg, 95%) as a colourless oil.

¹ H NMR (500 MHz, CDCl₃): 7.22 (2 H, d, *J* = 8.7 Hz), 7.08 (2 H, dd, *J* = 8.6, 7.2 Hz), 6.85 (2 H, d, *J* = 8.7 Hz), 6.65 – 6.58 (1 H, m), 6.54 – 6.49 (2 H, m), 4.13 (1 H, s), 4.09 (1 H, d, *J* = 6.3 Hz), 3.79 (3 H, s), 1.91 (1 H, ddd, *J* = 13.0, 3.6, 1.9 Hz), 1.81 – 1.71 (2 H, m), 1.70 – 1.59 (2 H, m), 1.56 (1 H, ddt, *J* = 12.9, 3.4, 1.7 Hz), 1.29 – 0.98 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 158.5, 148.0, 134.7, 129.1, 128.4, 128.3, 117.0, 113.8, 113.7, 113.4, 62.9, 55.3, 45.1, 30.2, 29.7, 26.6, 26.5, 26.5 ppm. – IR: 2924, 2850,1739, 1601, 1505, 1243, 1034, 692 cm⁻¹. – HRMS: calcd for C₂₀H₂₅NO: 296.2009, found 296.2010 [M+H⁺].

N-(Cyclohexyl(3,4,5-trimethoxyphenyl)methyl)aniline (5g)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (39.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **5g** (66.7 mg, 94%) as a white solid (m.p. 111 °C).

¹ H NMR (500 MHz, CDCl₃): 7.08 (2 H, dd, J = 8.6, 7.2 Hz), 6.67 – 6.59 (1 H, m), 6.52 (4 H, d, J = 6.5 Hz), 4.08 (1 H, br), 4.00 (1 H, d, J = 6.2 Hz), 3.83 (9 H, d, J = 3.8 Hz), 1.88 (1 H, dd, J = 12.8, ^{MeO} MeO MHz, CDCl₃): 153.2, 148.0, 138.7, 136.7, 129.2, 117.2, 113.4, 104.1, 64.2, 60.9, 56.2, 45.2, 30.5, 29.6, 26.5, 26.5 ppm – IR: 2923, 1738, 1592, 1502, 1231, 1124, 749, 693 cm⁻¹. – HRMS: calcd for

C22H29NO3: 356.2220, found 356.2208 [M+H+].





According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol%), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (32.6 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **5h** (63.1 mg, 98%) as a colourless oil.

¹ H NMR (500 MHz, CDCl₃): 7.41 (2 H, d, *J* = 8.5 Hz), 7.33 (1 H, s), 7.23 (2 H, d, *J* = 8.5 Hz), 7.05 (2 H, dd, *J* = 8.6, 7.2 Hz), 6.66 – 6.55 (1 H, m), 6.52 – 6.44 (2 H, m), 4.20 (1 H, s), 4.08 (1 H, d, *J* = 6.2 Hz), 2.13 (3 H, s), 1.91 – 1.82 (1 H, m), 1.81 – 1.68 (2 H, m), 1.63 (2 H, dddd, *J* = 20.5, 11.6, 4.8, 2.4 Hz), 1.57 – 1.49 (1 H, m), 1.31 – 0.91 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 168.4, 147.8, 138.7, 136.6, 129.2, 127.9, 119.9, 117.1, 113.3, 63.1, 45.0, 30.2, 29.6, 26.5, 26.5, 26.4, 24.6 ppm – IR:

2925, 1668, 1601, 1505, 1316, 749 cm⁻¹. – HRMS: calcd for C₂₁H₂₆N₂O: 323.2118, found 323.2111 [M+H⁺].

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N-(Cyclohexyl(4-(trifluoromethyl)phenyl)methyl)aniline (5i)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (34.8 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 10 v/v) to give product **5i** (50.0 mg, 75%) as a colourless oil.

¹ H NMR (500 MHz, CDCl₃): 7.56 (2 H, d, J = 8.0 Hz), 7.42 (2 H, d, J = 8.0 Hz), 7.07 (2 H, t, J = 7.9Hz), 6.64 (1 H, t, J = 7.3 Hz), 6.46 (2 H, d, J = 7.9 Hz), 4.19 (1 H, d, J = 6.0 Hz), 1.92 – 1.81 (1 H, m), 1.81 – 1.70 (2 H, m), 1.71 – 1.64 (2 H, m), 1.55 (1 H, dd, J = 12.8, 3.6 Hz), 1.31 – 0.99 (5H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 147.3 (d, J = 35.1 Hz), 129.3, 127.7, 125.4 (d, J = 3.9 Hz), 117.5, 113.3, 63.3, 44.9, 30.3, 29.4, 26.4, 26.4 ppm. – ¹⁹F NMR (376 MHz, CDCl₃) δ -62.3 ppm. – IR: 2927, 2853, 1738, 1602, 1325, 1217, 1067 cm⁻¹. – HRMS: calcd for C₂₀H₂₂F₃N: 334.1777, found 334.1777 [M+H⁺].

N-(Cyclohexyl(naphthalen-2-yl)methyl)aniline (5j)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (31.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **5j** (57.3 mg, 91%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 7.89 – 7.76 (3 H, m), 7.74 (1 H, d, *J* = 1.6 Hz), 7.51 – 7.35 (3 H, m), 7.04 (2 H, dd, *J* = 8.6, 7.2 Hz), 6.59 (1 H, t, *J* = 7.3 Hz), 6.54 (2 H, d, *J* = 8.0 Hz), 4.28 (1 H, d, *J* = 6.2 Hz), 1.93 (1 H, d, *J* = 12.3 Hz), 1.84 – 1.47 (5 H, m), 1.33 – 1.00 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 133.4, 132.9, 129.2, 128.1, 128.0, 127.8, 126.2, 126.0, 125.6, 125.5, 117.2, 113.4, 63.8, 45.1, 30.5, 29.7, 26.5, 26.5 ppm – IR: 2924, 1738, 1601, 1503, 1365, 1228, 747, 691 cm⁻¹. – HRMS: calcd for C₂₃H₂₅N: 316.2060, found 316.2048 [M+H⁺].

N-(Cyclohexyl(naphthalen-1-yl)methyl)aniline (5k)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (31.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **5k** (57.3 mg, 91%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 8.21 (1 H, d, *J* = 8.4 Hz), 7.92 (1 H, dd, *J* = 8.1, 1.4 Hz), 7.74 (1 H, d, *J* = 8.1 Hz), 7.63 – 7.49 (3 H, m), 7.40 (1 H, t, *J* = 7.7 Hz), 7.02 (2 H, dd, *J* = 8.6, 7.2 Hz), 6.59 (1 H, dd, *J* = 7.9, 6.7 Hz), 6.47 (2 H, d, *J* = 8.0 Hz), 5.05 (1 H, d, *J* = 5.0 Hz), 4.32 (1 H, s), 1.90 (1 H, ddt, *J* = 11.6, 8.6, 4.3 Hz), 1.84 – 1.72 (3 H, m), 1.71 – 1.59 (2 H, m), 1.38 (1 H, qd, *J* = 12.4, 3.4 Hz), 1.27 – 1.05 (4 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 147.9, 138.2, 134.2, 131.5, 129.4, 129.2, 127.4, 126.0, 125.6, 125.4,

124.1, 122.9, 117.1, 113.2, 58.8, 44.4, 31.4, 28.4, 26.8, 26.6 ppm – IR: 2925, 2850, 1738, 1601, 1365, 1217 cm⁻¹. – HRMS: calcd for $C_{23}H_{25}N$: 316.2060, found 316.2061 [M+H⁺].

N-(Cyclohexyl(pyridin-4-yl)methyl)aniline (51)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.4 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 10 v/v) to give product **XX** (48.9 mg, 92%) as a white solid (m.p. 65 °C).

¹ H NMR (500 MHz, CDCl₃): 8.62 – 8.40 (2 H, m), 7.38 – 7.16 (2 H, m), 7.07 (2 H, dd, *J* = 8.6, 7.2 Hz), 6.64 (1 H, t, *J* = 7.4 Hz), 6.53 – 6.36 (2 H, m), 4.16 (1 H, s), 4.13 (1 H, t, *J* = 4.5 Hz), 1.87 – 1.71 (3 H, m), 1.67 (2 H, dp, *J* = 11.8, 3.1 Hz), 1.61 – 1.49 (1 H, m), 1.29 – 1.01 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 152.2, 149.8, 147.2, 129.3, 122.7, 117.7, 113.2, 62.7, 44.5, 30.2, 29.1, 26.4 ppm – IR: 2925, 2851, 1738, 1599, 1365, 1216, 693 cm⁻¹. – HRMS: calcd for C₁₈H₂₂N₂: 267.1856, found 267.1851 [M+H⁺].

N-(Cyclohexyl(6-methylpyridin-2-yl)methyl)aniline (5m)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (24.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 10 v/v) to give product **5m** (53.8 mg, 96%) as a white solid (m.p. 66 °C).

¹H NMR (500 MHz, CDCl₃): 7.44 (1 H, t, J = 7.7 Hz), 7.13 – 7.06 (2 H, m), 7.03 (1 H, d, J = 7.7 Hz), 6.96 (1 H, d, J = 7.6 Hz), 6.66 – 6.59 (1 H, m), 6.59 – 6.54 (2 H, m), 5.07 – 4.40 (1 H, m), 4.25 (1 H, t, J = 5.4 Hz), 1.95 – 1.60 (6 H, m), 1.58 – 1.46 (1 H, m), 1.32 – 0.98 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 161.4, 157.9, 148.1, 136.3, 129.2, 121.4, 119.0, 117.0, 113.4, 64.3, 43.8, 30.5, 29.0, 26.6, 26.5,

26.4, 24.8 ppm – IR: 2924, 2850, 1738, 1602, 1365, 1217 cm⁻¹. – HRMS: calcd for C₁₉H₂₄N₂: 281.2012, found 281.2007 [M+H⁺].

N-(Benzofuran-2-yl(cyclohexyl)methyl)aniline (5n)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (29.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) to give product **5n** (43.3 mg, 71%) as a white solid (m.p. 90 °C).

¹H NMR (500 MHz, CDCl₃): 7.50 – 7.41 (2 H, m), 7.23 (1 H, td, *J* = 7.7, 1.5 Hz), 7.18 (1 H, t, *J* = 7.4 Hz), 7.13 (2 H, dd, *J* = 8.5, 7.2 Hz), 6.68 (1 H, t, *J* = 7.3 Hz), 6.64 (2 H, d, *J* = 8.0 Hz), 6.53 (1 H, s), 4.39 (1 H, d, *J* = 6.3 Hz), 4.09 (1 H, s), 1.96 (2 H, dt, *J* = 11.1, 3.3 Hz), 1.86 – 1.71 (2 H, m), 1.71 – 1.57 (2 H, m), 1.36 – 1.08 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 158.4, 154.8, 147.5, 129.3, 128.5, 123.6, 122.7, 120.8, 117.8, 113.5, 111.2, 103.9, 57.7, 42.6, 30.0, 29.6, 26.5, 26.4, 26.3 ppm – IR: 2926, 1738, 1365, 1216

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tert-Butyl 5-(Cyclohexyl(phenylamino)methyl)-1H-indole-1-carboxylate (50)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (49.0 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 5 v/v) to give product **50** (66.2 mg, 82%) as a white solid.

¹ H NMR (500 MHz, CDCl₃): 8.05 (1 H, d, *J* = 8.1 Hz), 7.57 (1 H, d, *J* = 3.7 Hz), 7.48 (1 H, d, *J* = 1.7 Hz), 7.32 – 7.18 (1 H, m), 7.04 (2 H, dd, *J* = 8.6, 7.3 Hz), 6.59 (1 H, d, *J* = 7.3 Hz), 6.54 – 6.49 (3 H, m), 4.20 (1 H, d, *J* = 6.2 Hz), 1.92 (1 H, d, *J* = 12.8 Hz), 1.66 (12H, m), 1.60 – 1.46 (2 H, m), 1.33 – 0.94 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 149.9, 148.0, 137.2, 134.4, 130.7, 129.1, 126.2, 123.8, 119.6, 117.0, 114.9, 113.4, 107.5, 83.7, 63.6, 45.4, 30.4, 29.8, 28.3, 26.6,

26.5 ppm – IR: 2925, 2851, 1731, 1601, 1353, 1162, 692 cm⁻¹. – HRMS: calcd for C₂₆H₃₂N₂O₂: 405.2537, found 405.2536 [M+H⁺].





According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (37.4 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **5p** (56.7 mg, 82%) as a white solid.

¹H NMR (500 MHz, CDCl₃): 8.35 (1 H, d, *J* = 8.5 Hz), 7.49 (1 H, d, *J* = 1.6 Hz), 7.38 (1 H, d, *J* = 3.7 Hz), 7.30 (1 H, dd, *J* = 8.5, 1.7 Hz), 7.04 (2 H, dd, *J* = 8.6, 7.2 Hz), 6.66 – 6.56 (2 H, m), 6.52 (2 H, d, *J* = 7.9 Hz), 4.21 (1 H, d, *J* = 6.2 Hz), 2.61 (3 H, s), 1.91 (1 H, d, *J* = 12.6 Hz), 1.81 – 1.60 (4 H, m), 1.55 (1 H, dt, *J* = 12.9, 3.2 Hz), 1.35 – 0.97 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 168.6, 147.9, 138.3, 134.8, 130.6, 129.2, 125.5, 124.8, 119.4, 117.1, 116.3, 113.4, 109.4, 63.6, 45.3, 30.4, 29.7, 26.6, 26.5, 26.5, 24.0 ppm – IR: 2926, 1738, 1365, 1217 cm⁻¹. – HRMS: calcd for C₂₃H₂₆N₂O: 347.2118, found 347.2114 [M+H⁺].

N-(1-Phenylpentyl)aniline (6a)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (26.5 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **6a** (21.7 mg, 46%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 7.43 – 7.27 (4 H, m), 7.25 – 7.18 (1 H, m), 7.08 (2 H, dd, *J* = 8.6, 7.3 Hz), 6.68 – 6.56 (1 H, m), 6.56 – 6.41 (2 H, m), 4.29 (1 H, t, *J* = 6.8 Hz), 4.08 (1 H, s), 1.94 – 1.70 (2 H, m), 1.47 – 1.22 (3 H, m), 0.89 (3 H, t, *J* = 7.0 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 147.6, 144.5, 129.2, 128.7, 127.0, 126.5, 117.2, 113.3, 58.4, 38.9, 28.7, 22.7, 14.1 ppm – IR: 2928, 1738, 1601, 1504, 1217 cm⁻

¹. - HRMS: calcd for C₁₇H₂₁N: 240.1747, found 240.1747 [M+H⁺].

N-(2-Methyl-1-phenylpropyl)aniline (6b)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (22.9 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **6b** (44.1 mg, 98%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 7.36 – 7.28 (4 H, m), 7.22 (1 H, ddd, *J* = 8.7, 4.8, 3.4 Hz), 7.08 (2 H, dd, *J* = 8.6, 7.2 Hz), 6.62 (1 H, tt, *J* = 7.3, 1.2 Hz), 6.55 – 6.49 (2 H, m), 4.14 (2 H, d, *J* = 5.9 Hz), 2.05 (1 H, dq, *J* = 13.4, 6.7 Hz), 1.00 (3 H, d, *J* = 6.8 Hz), 0.94 (3 H, d, *J* = 6.9 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 147.8, 142.7, 129.2, 128.3, 127.3, 126.9, 117.1, 113.4, 63.9, 35.0, 19.9, 18.8 ppm – IR: 2970, 1738, 1365, 1217 cm³ – HRMS: calcd for Cyclus N: 226 1590, found 226 1586 [M+H⁺]

1365, 1217 cm⁻¹. – HRMS: calcd for C₁₆H₁₉N: 226.1590, found 226.1586 [M+H⁺].

N-(1-Phenyl-2-propylpentyl)aniline (6c)



According to GP1, the reaction was carried out with Cu(MeCN)BF4 (5.0 mg, 0.016 mmol, 8 mol%), acridine A1 (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (37.4 mg, 0.26 mmol, 1.3 equiv.), anhydrous p-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **6c** (46.6 mg, 83%) as a colourless oil.

> ¹H NMR (500 MHz, CDCl₃): 7.30 (4 H, d, J = 4.3 Hz), 7.21 (1 H, h, J = 4.4, 3.9 Hz), 7.08 (2 H, dd, *J* = 8.6, 7.2 Hz), 6.67 – 6.59 (1 H, m), 6.53 – 6.45 (2 H, m), 4.43 (1 H, d, *J* = 4.6 Hz), 4.08 (1 H, s), 1.77 (1 H, tt, J = 7.5, 2.8 Hz), 1.48 – 1.04 (7 H, m), 0.90 (3 H, t, J = 7.0 Hz), 0.81 (3 H, t, J = 6.7 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 147.9, 143.0, 129.2, 128.3, 127.2, 126.6, 117.0, 113.2, 59.6,

44.8, 33.4, 31.4, 20.8, 20.8, 14.5, 14.4 ppm – IR: 2955, 1739, 1504, 1217 cm⁻¹. – HRMS: calcd for C₂₀H₂₇N: 282.2216, found 282.2213 [M+H+].

N-(2-Hexyl-1-phenyldecyl)aniline (6d)



According to GP1, the reaction was carried out with Cu(MeCN)BF4 (5.0 mg, 0.016 mmol, 8 mol%), acridine A1 (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (66.6 mg, 0.26 mmol, 1.3 equiv.), anhydrous p-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **6d** (62.9 mg, 1:1 dr, 80%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 7.33 (4 H, d, *J* = 4.4 Hz), 7.24 (1 H, dq, *J* = 8.6, 4.2 Hz), 7.11 (2 H, dd, J = 8.5, 7.2 Hz), 6.65 (1 H, t, J = 7.4 Hz), 6.52 (2 H, d, J = 7.9 Hz), 4.45 (1 H, d, J = 4.5 Hz), 4.10 (1 H, s), 1.75 (1 H, q, J = 6.1, 5.3 Hz), 1.50 – 1.11 (24 H, m), 0.99 – 0.80 (6 H, m) ppm. - 13C NMR (125 MHz, CDCl3): 147.9, 143.0, 129.2, 128.3, 127.2, 126.6, 117.0, 113.3, 59.6, 45.3, 32.0, 32.0, 31.8, 31.1, 30.0, 29.9, 29.7, 29.6, 29.5, 29.4, 29.4, 29.1, 27.7, 27.6, 22.8, 22.7, 14.3, 14.2 ppm – IR: 2922, 2852,

1601, 1503, 1317, 701 cm⁻¹. – HRMS: calcd for C₂₈H₄₃N: 394.3468, found 394.3468 [M+H⁺].

HN

HN

N-(Cyclobutyl(phenyl)methyl)aniline (6e)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (26.0 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **6e** (38.4 mg, 81%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 7.38 – 7.28 (4 H, m), 7.27 – 7.18 (1 H, m), 7.08 (2 H, dd, *J* = 8.6, 7.2 Hz), 6.67 – 6.60 (1 H, m), 6.57 – 6.48 (2 H, m), 4.19 (1 H, d, *J* = 9.1 Hz), 4.03 (1 H, s), 2.65 – 2.47 (1 H, m), 2.25 – 2.08 (1 H, m), 2.01 – 1.73 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 147.8, 142.6, 129.2, 128.5, 127.0, 126.7, 117.3, 113.5, 63.9, 42.7, 26.2, 25.6, 17.7 ppm – IR: 2970, 1739, 1601, 1482, 1217, 701 cm⁻¹. – HRMS: calcd for C₁₇H₁₉N: 238.1590, found 238.1591 [M+H⁺].

N-(Cyclopentyl(phenyl)methyl)aniline (6f)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (29.6 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **6f** (42.7 mg, 85%) as a colourless oil.

¹ H NMR (500 MHz, CDCl₃): δ 7.39 – 7.33 (2 H, m), 7.30 (2 H, dd, J = 8.4, 6.8 Hz), 7.25 – 7.17 (1 H, m), 7.12 – 7.01 (2 H, m), 6.62 (1 H, tt, J = 7.3, 1.2 Hz), 6.56 – 6.49 (2 H, m), 4.20 (1 H, s), 4.10 (1 H, d, J = 8.4 Hz), 2.33 – 2.05 (1 H, m), 2.01 – 1.83 (1 H, m), 1.78 – 1.56 (3 H, m), 1.57 – 1.38 (3 H, m), 1.37 – 1.22 (1 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 147.8, 144.1, 129.2, 128.4, 127.1, 126.9, 117.1, 113.4, 63.2, 47.9, 30.3, 30.1, 25.4, 25.3 ppm – IR: 2951, 1739, 1602, 1365, 1217 cm⁻¹. – HRMS: calcd for C₁₈H₂₁N: 252.1747,

found 252.1747 [M+H+].

N-(Cycloheptyl(phenyl)methyl)aniline (6g)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (36.9 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **6g** (49.1 mg, 88%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 7.37 – 7.27 (4 H, m), 7.26 – 7.19 (1 H, m), 7.09 (2 H, dd, *J* = 8.6, 7.2 Hz), 6.63 (1 H, t, *J* = 7.3 Hz), 6.55 – 6.47 (2 H, m), 4.25 (1 H, d, *J* = 5.4 Hz), 4.11 (1 H, s), 1.92 (1 H, dtt, *J* = 9.2, 6.9, 2.7 Hz), 1.81 (1 H, ddd, *J* = 10.8, 7.8, 4.1 Hz), 1.76 – 1.65 (3 H, m), 1.64 – 1.29 (8 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃):148.0, 143.0, 129.2, 128.3, 127.3, 126.8, 117.0, 113.3, 63.8, 46.5, 32.4,

29.5, 28.4, 28.1, 27.1 ppm – IR: 2921, 1738, 1503, 1217, 701 cm⁻¹. – HRMS: calcd for C₂₀H₂₅N: 280.2060, found 280.2060 [M+H⁺].

N-(Phenyl(tetrahydro-2H-pyran-4-yl)methyl)aniline (6h)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.8 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 5 v/v) to give product **6h** (51.3 mg, 96%) as a white solid (m.p. 85 °C).

¹ H NMR (500 MHz, CDCl₃): 7.36 – 7.28 (4 H, m), 7.24 (1 H, ddt, J = 10.9, 5.7, 2.6 Hz), 7.09 (2 H, dd, J = 8.6, 7.2 Hz), 6.69 – 6.61 (1 H, m), 6.57 – 6.50 (2 H, m), 4.15 (2 H, d, J = 7.0 Hz), 4.03 (1 H, ddd, J = 11.5, 4.9, 1.6 Hz), 3.96 (1 H, ddd, J = 11.6, 4.8, 1.8 Hz), 3.35 (2 H, dtd, J = 24.1, 11.9, 2.3 Hz), 2.02 – 1.74 (2 H, m), 1.61 – 1.41 (2 H, m), 1.39 – 1.25 (1 H, m). ppm. – ¹³C NMR (125 MHz, CDCl₃): 147.5,

141.9, 129.2, 128.5, 127.2, 117.4, 113.4, 68.1, 68.0, 63.1, 42.4, 30.4, 29.9 ppm – IR: 2940, 1725, 1576, 1237, 824 cm⁻¹. – HRMS: calcd for C₁₈H₂₁NO: 268.1696, found 268.1689 [M+H⁺].

N-(2,2-Dimethyl-1-phenylpropyl)aniline (6i)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (26.5 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **6i** (47.3 mg, 99%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 7.34 – 7.25 (4 H, m), 7.24 – 7.16 (1 H, m), 7.05 (2 H, dd, *J* = 8.6, 7.2 Hz), 6.63 – 6.55 (1 H, m), 6.49 (2 H, dd, *J* = 8.7, 1.1 Hz), 4.27 (1 H, s), 4.05 (1 H, s), 1.01 (9 H, s) ppm. – ¹³C NMR (125 MHz, CDCl₃):147.9, 141.3, 129.2, 128.6, 127.8, 126.9, 117.0, 113.3, 67.3, 35.1, 27.2 ppm – IR: 2969, 1739, 1504, 1366, 1217 cm⁻¹. – HRMS: calcd for C₁₇H₂₁N: 240.1747, found 240.1747 [M+H⁺].

N-(2,2-Dimethyl-1-phenylbutyl)aniline (6j)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (30.2 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **6j** (41.6 mg, 82%) as a colourless oil.

¹ H NMR (500 MHz, CDCl₃): 7.37 – 7.26 (4 H, m), 7.26 – 7.19 (1 H, m), 7.10 – 7.03 (2 H, m), 6.61 (1 H, tt, *J* = 7.2, 1.1 Hz), 6.54 – 6.47 (2 H, m), 4.29 (1 H, s), 4.15 (1 H, s), 1.59 – 1.33 (2 H, m), 0.97 (3 H, s), 0.95 – 0.89 (6 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 147.8, 141.2, 129.1, 128.8, 127.8, 126.9, 117.0, 113.2, 65.2, 37.6, 32.4, 24.0, 23.3, 8.4 ppm – IR: 2964, 1601, 1504, 1318 cm⁻¹. – HRMS: calcd for C₁₈H₂₃N: 254.1903, found 254.1904 [M+H⁺].

N-((1-Methylcyclohexyl)(phenyl)methyl)aniline (6k)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol%), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (36.9 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **6k** (51.9 mg, 93%) as a colourless oil.

¹ H NMR (500 MHz, CDCl₃): 7.36 – 7.24 (4 H, m), 7.25 – 7.18 (1 H, m), 7.09 – 7.02 (2 H, m), 6.59 (1 H, t, *J* = 7.3 Hz), 6.50 (2 H, d, *J* = 8.0 Hz), 4.31 (1 H, s), 4.15 (1 H, s), 1.73 – 1.51 (4 H, m), 1.53 – 1.37 (4 H, m), 1.33 – 1.15 (2 H, m), 0.96 (3 H, s) ppm. – ¹³C NMR (125 MHz, CDCl₃): 148.0, 140.9, 129.2, 128.9, 127.8, 126.9, 116.9, 113.2, 66.9, 37.6, 35.7, 35.3, 26.4, 22.1, 21.9, 19.6 ppm – IR: 2923, 1738, 1399, 1501, 1318, 1217, 702 cm⁻¹. – HRMS: calcd for C₂₀H₂₅N: 280.2060, found 280.2054 [M+H⁺].



N-((4-Methyltetrahydro-2H-pyran-4-yl)(phenyl)methyl)aniline (61)

According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol%), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (37.4 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 5 v/v) to give product **61** (50.6 mg, 90%) as a white solid (m.p. 126 °C).

¹H NMR (500 MHz, CDCl₃): 7.35 – 7.26 (4 H, m), 7.23 (1 H, ddt, *J* = 8.4, 5.4, 2.3 Hz), 7.07 (2 H, dd, *J* = 8.6, 7.2 Hz), 6.68 – 6.57 (1 H, m), 6.55 – 6.49 (2 H, m), 4.28 (1 H, s), 4.15 (1 H, s), 3.85 (2 H, dddd, *J* = 12.2, 9.6, 4.8, 3.1 Hz), 3.59 (2 H, dtd, *J* = 26.1, 11.7, 2.5 Hz), 1.82 (2 H, dddd, J = 23.5, 13.5, 11.5, 4.8 Hz), 1.57 (1 H, dd, J = 13.6, 2.6 Hz), 1.08 (4 H, s) ppm. – ¹³C NMR (125 MHz, CDCl₃): 147.6, 139.8, 129.2, 128.8, 128.0, 127.2, 117.4, 113.4, 67.5, 64.0, 63.7, 35.7, 35.5, 18.0 ppm – IR: 2970, 1738, 1365, 1229 cm⁻¹. –

HRMS: calcd for C19H23NO: 282.1852, found 282.1846 [M+H+].

N-((Hexahydro-2,5-methanopentalen-3a(1H)-yl)(phenyl)methyl)aniline (6m)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (43.2 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **6m** (45.4 mg, 75%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 7.36 (2 H, d, *J* = 7.0 Hz), 7.31 – 7.24 (2 H, m), 7.24 – 7.17 (1 H, m), 7.05 (2 H, dd, *J* = 8.6, 7.2 Hz), 6.60 (1 H, t, *J* = 7.3 Hz), 6.49 (2 H, d, *J* = 7.9 Hz), 4.31 (2 H, s), 2.44 (1 H, t, *J* = 6.7 Hz), 2.25 (1 H, s), 2.19 (1 H, s), 1.86 (1 H, d, *J* = 11.3 Hz), 1.80 (1 H, dt, *J* = 10.8, 2.1 Hz), 1.74 (1 H, dtd, *J* = 10.3, 3.7, 1.7 Hz), 1.68 – 1.44 (6 H, m), 1.37 (1 H, dd, *J* = 10.9, 3.0 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 129.2, 128.1, 127.8, 126.9, 117.1, 113.5, 64.5, 54.1, 47.8, 45.2, 44.8, 44.1, 41.5, 37.3, 37.3, 35.6 ppm – IR: 2970, 1738, 1365, 1229, 1217 cm⁻¹. – HRMS: calcd for C₂₂H₂₅N: 304.2060, found 304.2054 [M+H⁺].

N-(((1s,3s)-Adamantan-1-yl)(phenyl)methyl)aniline (6n)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (46.8 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **6n** (39.9 mg, 63%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): δ 7.36 – 7.14 (5 H, m), 7.03 (2 H, dd, *J* = 8.6, 7.2 Hz), 6.57 (1 H, t, *J* = 7.3 Hz), 6.49 (2 H, d, *J* = 8.0 Hz), 4.37 (1 H, s), 3.87 (1 H, s), 2.06 – 1.93 (3 H, m), 1.70 (3 H, ddd, *J* = 16.3, 12.4, 6.2 Hz), 1.63 – 1.46 (6 H, m). ppm. – ¹³C NMR (125 MHz, CDCl₃): 140.4, 129.1, 128.8, 127.7, 126.9, 116.9, 113.3, 68.1, 39.4, 37.1, 36.6, 28.6 ppm – IR: 2902, 1738, 1502, 1365, 1217, 702 cm⁻¹. – HRMS: calcd for C₂₃H₂₇N: 318.2216, found 318.2218 [M+H⁺].

Ethyl 2-((4-methoxyphenyl)amino)hexanoate (7a)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (26.5 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **7a** (49.8 mg, 94%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 6.76 (2 H, d, *J* = 8.9 Hz), 6.60 (2 H, d, *J* = 8.9 Hz), 4.25 – 4.11 (2 H, m), 3.95 (1 H, t, *J* = 6.6 Hz), 3.84 (1 H, s), 3.73 (3 H, s), 1.95 – 1.62 (2 H, m), 1.51 – 1.30 (4 OMe H, m), 1.23 (3 H, t, *J* = 7.1 Hz), 0.91 (3 H, t, *J* = 7.1 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 174.7, 152.8, 141.3, 115.2, 115.0, 60.9, 58.0, 55.8, 33.1, 27.9, 22.6, 14.4, 14.0 ppm – IR: 2956, 1732, 1514, 1237, 1035 cm⁻¹. – HRMS: calcd for C15H23NO3: 266.1751, found 266.1751 [M+H⁺].

Ethyl 2-((4-methoxyphenyl)amino)-5-methylhexanoate (7b)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol%), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (30.2 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **7b** (54.7 mg, 98%) as a colourless oil.

58.2, 55.8, 34.8, 31.3, 28.0, 22.6, 22.5, 14.4 ppm – IR: 2969, 1738, 1514, 1366, 1217, 1036 cm⁻¹. – HRMS: calcd for C₁₆H₂₅NO₃: 280.1907, found 280.1907 [M+H⁺].

Ethyl 2-((4-methoxyphenyl)amino)undecanoate (7c)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (44.7 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **7c** (63.6 mg, 95%) as a colourless oil.

¹ H NMR (500 MHz, CDCl₃): 6.81 – 6.72 (2 H, m), 6.66 – 6.56 (2 H, m), 4.16 (2 H, qd, J =7.2, 0.9 Hz), 3.95 (1 H, t, J = 6.5 Hz), 3.84 (1 H, s), 3.73 (3 H, s), 1.75 (2 H, dddt, J = 26.7, 13.3, 9.6, 6.8 Hz), 1.42 (2 H, dddd, J = 12.9, 9.7, 6.6, 4.5 Hz), 1.38 – 1.18 (15 H, m), 0.88 (3 H, t, J = 6.9 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 174.7, 152.8, 141.3, 115.2, 115.0, 60.9,

58.0, 55.8, 33.4, 32.0, 29.6, 29.5, 29.5, 29.4, 25.7, 22.8, 14.4, 14.2 ppm – IR: 2925, 1738, 1514, 1366, 1217 cm⁻¹. – HRMS: calcd for C₂₀H₃₃NO₃: 336.2533, found 336.2523 [M+H⁺].





According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (36.9 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 10 v/v) to give product **7d** (59.8 mg, 98%) as a colourless oil.

¹ H NMR (500 MHz, CDCl₃): 6.78 (2 H, d, *J* = 8.9 Hz), 6.62 (2 H, d, *J* = 8.9 Hz), 4.19 (2 H, qd, *J* = 7.2, 2.1 Hz), 4.00 (1 H, dd, *J* = 7.8, 5.4 Hz), 3.74 (3 H, s), 2.43 – 2.19 (2 H, m), 2.17 – OMe 2.05 (1 H, m), 1.94 (1 H, dddd, *J* = 13.5, 10.3, 7.7, 5.8 Hz), 1.25 (3 H, t, *J* = 7.1 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 173.5, 153.3, 140.6, 115.7, 115.1, 79.8 – 74.0 (m), 61.6, 57.0, 55.8, 30.4 (q, *J* = 29.3 Hz), 25.8, 14.3 ppm. – ¹⁹F NMR (376 MHz, CDCl₃) δ -66.3 ppm. – IR: 1732, 1515, 1241, 1136, 1031 cm⁻¹. – HRMS: calcd for C₁₄H₁₈F₃NO₃: 306.1312, found 306.1312 [M+H⁺].

Ethyl 2-((4-methoxyphenyl)amino)-4,4,4-triphenylbutanoate (7e)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (78.5 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **7e** (55.8 mg, 60%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 7.37 – 7.28 (5 H, m), 7.22 (3 H, dd, *J* = 5.1, 2.0 Hz), 7.16 – 7.09 (3 H, m), 7.06 (2 H, dd, *J* = 8.2, 6.7 Hz), 6.77 – 6.70 (4 H, m), 6.53 (2 H, d, *J* = 8.9 Hz), 4.80 (1 ^{OMe} H, s), 3.94 – 3.74 (3 H, m), 3.73 (4 H, s), 3.61 (1 H, d, *J* = 12.8 Hz), 0.88 (3 H, t, *J* = 7.1 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 172.6, 152.9, 143.8, 143.5, 140.7, 137.4, 131.3, 130.1,

129.8, 127.7, 127.6, 127.4, 127.0, 126.7, 126.4, 115.5, 114.9, 60.8, 60.7, 55.8, 44.8, 13.9 ppm – IR: 1721, 1512, 1446, 1245, 1035, 704 cm⁻¹. – HRMS: calcd for C₃₁H₃₁NO₃: 466.2377, found 466.2377 [M+H⁺].

Ethyl 3-(4-chlorophenyl)-2-((4-methoxyphenyl)amino)propanoate (7f)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (44.2 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 15 v/v) to give product **7f** (64.6 mg, 97%) as a colourless oil.

¹ H NMR (500 MHz, CDCl₃): 7.26 (2 H, d, *J* = 8.4 Hz), 7.12 (2 H, d, *J* = 8.4 Hz), 6.77 (2 H, d, *J* = 8.9 Hz), 6.58 (2 H, d, *J* = 8.9 Hz), 4.24 (1 H, t, *J* = 6.3 Hz), 4.11 (2 H, qd, *J* = 7.1, 2.4 Hz), OMe 3.74 (3 H, s), 3.24 – 2.95 (2 H, m), 1.17 (3 H, t, *J* = 7.1 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 173.3, 153.0, 140.4, 135.2, 132.9, 130.8, 128.7, 115.5, 115.0, 61.3, 59.0, 55.8, 38.2, 14.3

ppm – IR: 1732, 1514, 1239, 1091 cm⁻¹. – HRMS: calcd for C18H20ClNO3: 334.1204, found 334.1204 [M+H⁺].

Ph

Ph

Ethyl 4-(4-fluorophenyl)-2-((4-methoxyphenyl)amino)butanoate (7g)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (43.7 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **7g** (64.9 mg, 98%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 7.15 (2 H, dd, J = 8.5, 5.5 Hz), 6.98 (2 H, t, J = 8.7 Hz), 6.76 (2 H, d, J = 9.0 Hz), 6.58 (2 H, d, J = 8.9 Hz), 4.16 (2 H, q, J = 7.1 Hz), 3.95 (1 H, dd, J = 7.4, 5.7 O^{Me} Hz), 3.74 (3 H, s), 2.76 (2 H, t, J = 7.8 Hz), 2.12 (1 H, dtd, J = 13.7, 8.0, 5.7 Hz), 2.00 (1 H, dq, J = 13.7, 7.5 Hz), 1.24 (3 H, t, J = 7.1 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 174.4, 161.6 (d, J = 244.2 Hz), 153.0, 141.0, 136.7 (d, J = 3.4 Hz), 130.0 (d, J = 7.9 Hz), 115.4, 115.3, 115.0,

61.2, 57.3, 55.8, 35.0, 31.2, 14.4 ppm. – ¹⁹F NMR (376 MHz, CDCl₃) δ -117.2 (tt, J = 9.3, 5.4 Hz) ppm. – IR: 1731, 1511, 1239, 1037 cm⁻¹. – HRMS: calcd for C₁₉H₂₂FNO₃: 332.1656, found 332.1656 [M+H⁺].

Ethyl 2-((4-methoxyphenyl)amino)-5-phenylpentanoate (7h)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (42.6 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **7h** (59.5 mg, 91%) as a colourless oil.

⁰ H NMR (500 MHz, CDCl₃): 7.31 – 7.25 (2 H, m), 7.22 – 7.13 (3 H, m), 6.76 (2 H, d, *J* = 8.9 Hz), 6.59 (2 H, d, *J* = 8.9 Hz), 4.15 (2 H, q, *J* = 7.1 Hz), 4.05 – 3.90 (1 H, m), 3.74 (3 H, s), 2.66 (2 H, td, *J* = 6.8, 2.8 Hz), 1.85 (1 H, ddd, *J* = 9.7, 5.4, 2.2 Hz), 1.82 – 1.70 (3 H, m), 1.22 (3 H, t, *J* = 7.1 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 174.5, 152.9, 141.9, 141.1, 128.5, 128.5, 126.0, 115.3, 115.0, 61.1, 57.9, 55.8, 35.6, 32.8, 27.5, 14.4 ppm – IR: 2935, 1732, 1514, 1237,

1036, 821 cm⁻¹. – HRMS: calcd for C₂₀H₂₅NO₃: 328.1907, found 328.1906 [M+H⁺].

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Ethyl 2-((4-methoxyphenyl)amino)-6-phenylhexanoate (7i)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol%), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (46.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **7i** (64.1 mg, 94%) as a colourless oil.



¹H NMR (500 MHz, CDCl₃): 7.34 – 7.24 (2 H, m), 7.22 – 7.14 (3 H, m), 6.77 (2 H, d, *J* = 8.9 Hz), 6.60 (2 H, d, *J* = 8.9 Hz), 4.15 (2 H, q, *J* = 7.1 Hz), 3.96 (1 H, t, *J* = 6.5 Hz), 3.84 (1 H, s), 3.74 (3 H, s), 2.74 – 2.53 (2 H, m), 1.81 (2 H, ddq, *J* = 31.2, 9.3, 6.8 Hz), 1.67 (2 H, q, *J* = 7.7 Hz), 1.57 – 1.39 (2 H, m), 1.22 (3 H, t, *J* = 7.1 Hz) ppm. – ¹³C NMR

(125 MHz, CDCl₃): 174.6, 152.8, 142.4, 141.2, 128.5, 128.4, 125.9, 115.2, 115.0, 61.0, 57.9, 55.8, 35.8, 33.2, 31.3, 25.4, 14.4 ppm – IR: 2936, 1732, 1514, 1238, 1036 cm⁻¹. – HRMS: calcd for C₂₁H₂₇NO₃: 342.2064, found 342.2063 [M+H⁺].

Ethyl 2-cyclopentyl-2-((4-methoxyphenyl)amino)acetate (7j)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (29.6 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **7j** (54.8 mg, 99%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 6.75 (2 H, d, *J* = 8.9 Hz), 6.61 (2 H, d, *J* = 8.9 Hz), 4.20 – 4.04 (2 H, m), 3.85 (1 H, s), 3.77 (1 H, d, *J* = 7.9 Hz), 3.73 (3 H, s), 2.20 (1 H, p, *J* = 8.1 Hz), 1.83 (1 H, OMe dtd, *J* = 14.5, 7.6, 4.4 Hz), 1.77 – 1.52 (5 H, m), 1.46 (2 H, dddd, *J* = 15.5, 12.6, 8.8, 7.0 Hz), 1.22 (3 H, t, *J* = 7.1 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 174.6, 152.8, 141.6, 115.2, 114.9, 62.3, 60.8, 55.8, 43.3, 29.6, 29.2, 25.5, 25.3, 14.4 ppm – IR: 2969, 1737, 1514, 1366, 1230, 1035 cm⁻¹. – HRMS: calcd for C₁₆H₂₃NO₃: 278.1751, found 278.1750 [M+H⁺].

Ethyl 2-cyclohexyl-2-((4-methoxyphenyl)amino)acetate (7k)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **7k** (57.0 mg, 98%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 6.75 (2 H, d, *J* = 8.9 Hz), 6.60 (2 H, d, *J* = 9.0 Hz), 4.15 (2 H, qd, *J* = 7.1, 1.2 Hz), 3.86 (1 H, s), 3.76 (1 H, d, *J* = 6.1 Hz), 3.73 (3 H, s), 1.93 – 1.83 (1 H, m), 1.82 – 1.57 (5 H, m), 1.42 – 1.03 (8 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 174.1, 152.7, 141.8, 115.3, 115.0, 63.5, 60.8, 55.8, 41.4, 29.8, 29.3, 26.3, 26.2, 26.2, 14.4 ppm – IR: 2925, 2851, 1729,

1512, 1239, 1036, 821 cm⁻¹. - HRMS: calcd for C17H25NO3: 292.1907, found 292.1904 [M+H⁺].

Ethyl 2-cycloheptyl-2-((4-methoxyphenyl)amino)acetate (71)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (36.9 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **71** (59.2 mg, 97%) as a colourless oil.



¹ H NMR (500 MHz, CDCl₃): 6.82 – 6.70 (2 H, m), 6.66 – 6.56 (2 H, m), 4.15 (2 H, qd, *J* = 7.1, 4.2 Hz), 3.88 (1 H, s), 3.79 (1 H, d, *J* = 5.8 Hz), 3.73 (3 H, s), 2.00 – 1.88 (1 H, m), 1.89 – 1.80
^{OMe} (1 H, m), 1.79 – 1.63 (3 H, m), 1.64 – 1.36 (8 H, m), 1.23 (3 H, t, *J* = 7.1 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 174.2, 152.7, 141.7, 115.3, 115.0, 63.8, 60.8, 55.8, 42.8, 31.3, 30.1, 28.6, 28.0,

26.8, 26.7, 14.4 ppm – IR: 2926, 1732, 1514, 1238, 1036 cm⁻¹. – HRMS: calcd for C₁₈H₂₇NO₃: 306.2064, found 306.2064 [M+H⁺].

Ethyl 2-cyclobutyl-2-((4-methoxyphenyl)amino)acetate (7m)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (26.0 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **7m** (40.0 mg, 76%) as a colourless oil.

¹ H NMR (500 MHz, CDCl₃): 6.76 (2 H, d, *J* = 8.9 Hz), 6.60 (2 H, d, *J* = 8.9 Hz), 4.14 (2 H, p, *J* = 7.1 Hz), 3.88 (1 H, d, *J* = 8.1 Hz), 3.78 (1 H, s), 3.73 (3 H, s), 2.65 (1 H, q, *J* = 8.2 Hz), 2.22 ^{OMe} – 1.73 (6 H, m), 1.22 (3 H, t, *J* = 7.1 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 173.8, 152.8, 141.6, 115.2, 115.0, 62.5, 60.9, 55.8, 38.5, 25.7, 24.9, 18.2, 14.5 ppm – IR: 2970, 1738, 1514, 1230 cm⁻¹. – HRMS: calcd

for C15H21NO3: 264.1594, found 264.1589 [M+H+].

Ethyl 2-((4-methoxyphenyl)amino)-2-(tetrahydro-2H-pyran-4-yl)acetate (7n)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.8 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **7n** (53.3 mg, 91%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 6.79 – 6.73 (2 H, m), 6.61 (2 H, dd, *J* = 9.0, 0.9 Hz), 4.16 (2 H, qd, *J* = 7.2, 1.0 Hz), 4.07 – 3.95 (2 H, m), 3.79 (1 H, d, *J* = 6.7 Hz), 3.73 (3 H, d, *J* = 1.1 Hz), OMe 3.46 – 3.32 (2 H, m), 1.95 (1 H, dtd, *J* = 11.5, 7.2, 3.3 Hz), 1.84 – 1.72 (1 H, m), 1.69 – 1.45 (3 H, m), 1.23 (3 H, td, *J* = 7.1, 1.0 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 173.6, 153.0, 141.3,

115.5, 115.0, 68.0, 67.7, 63.0, 61.1, 55.8, 38.8, 29.6, 29.5, 14.4 ppm – IR: 2948, 1732, 1514, 1239, 1033 cm⁻¹. – HRMS: calcd for C₁₆H₂₃NO₄: 294.1700, found 294.1692 [M+H⁺].

Ethyl (4-methoxyphenyl)valinate (70)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (22.9 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **70** (42.2 mg, 84%) as a colourless oil.

¹ H NMR (500 MHz, CDCl₃): 6.76 (2 H, d, *J* = 8.9 Hz), 6.61 (2 H, d, *J* = 8.9 Hz), 4.16 (2 H, qt, *J* = 7.2, 3.9 Hz), 3.87 (1 H, s), 3.73 (3 H, s), 2.09 (1 H, dq, *J* = 13.4, 6.7 Hz), 1.23 (3 H, t, *J* = 7.1 ^{OMe} Hz), 1.03 (6 H, dd, *J* = 10.2, 6.8 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 174.1, 152.8, 141.7,

115.4, 115.0, 64.0, 60.9, 55.9, 31.7, 19.3, 18.8, 14.4 ppm – IR: 2963, 1732, 1514, 1234, 1035, 821 cm⁻¹. – HRMS: calcd for C₁₄H₂₁NO₃: 252.1594, found 252.1593 [M+H⁺].

Ethyl 2-((4-methoxyphenyl)amino)-3-propylhexanoate (7p)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (37.4 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **7p** (56.5 mg, 92%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 6.76 (d, *J* = 8.9 Hz, 2 H), 6.60 (d, *J* = 9.0 Hz, 2 H), 4.15 (qq, *J* = 10.8, 7.1 Hz, 2 H), 3.97 (d, *J* = 5.0 Hz, 1 H), 3.82 (s, 1 H), 3.73 (s, 3 H), 1.84 (q, *J* = 4.9 Hz, 1 OMe H), 1.55 – 1.25 (m, 8 H), 1.23 (t, *J* = 7.1 Hz, 3 H), 0.98 – 0.83 (m, 6 H) ppm. – ¹³C NMR (125 MHz, CDCl₃): 174.4, 152.8, 141.8, 115.4, 115.0, 60.8, 60.5, 55.8, 40.9, 32.9, 32.3, 20.5, 20.4,

14.4, 14.4 ppm – IR: 2956, 1732, 1513, 1240, 1036, 820 cm⁻¹. – HRMS: calcd for $C_{18}H_{29}NO_3$: 308.2220, found 308.2220 [M+H⁺].

Ethyl 3-hexyl-2-((4-methoxyphenyl)amino)decanoate (7q)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (62.9 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **7q** (80.4 mg, 1:1 dr, 99%) as a colourless oil.



¹ H NMR (500 MHz, CDCl₃): 6.76 (2 H, d, *J* = 8.9 Hz), 6.60 (2 H, d, *J* = 8.9 Hz), 4.30 – 4.04 (2 H, m), 3.97 (1 H, d, *J* = 4.9 Hz), 3.86 – 3.77 (1 H, m), 3.73 (3 H, s), 1.80 (1 H, q, *J* = 5.7 Hz), 1.44 (2 H, td, *J* = 5.1, 4.7, 2.5 Hz), 1.40 – 1.16 (23 H, m), 0.88 (6 H, td, *J* = 6.9, 1.8 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 174.4, 152.8, 141.8, 115.4, 115.0,

60.8, 60.5, 55.9, 41.4, 32.0, 31.9, 31.9, 30.6, 30.0, 30.0, 29.7, 29.6, 29.4, 27.3, 27.2, 22.8, 22.8, 14.4, 14.2, 14.2 ppm – IR: 2926, 1738, 1365, 1217 cm⁻¹. – HRMS: calcd for C₂₆H₄₅NO₃: 372.1594, found 372.1596 [M+H⁺].

Ethyl 2-(2,3-dihydro-1H-inden-2-yl)-2-((4-methoxyphenyl)amino)acetate (7r)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (42.1 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **7r** (48.8 mg, 75%) as a white solid (m.p. 49 °C).

¹H NMR (500 MHz, CDCl₃): 7.23 – 7.09 (4 H, m), 6.77 (2 H, d, *J* = 8.9 Hz), 6.63 (2 H, d, *J* = 9.0 Hz), 4.13 (2 H, p, *J* = 7.0 Hz), 4.00 (2 H, d, *J* = 7.6 Hz), 3.74 (3 H, s), 3.13 (1 H, dd, *J* = 15.9, ^{OMe} 8.1 Hz), 3.06 – 2.94 (3 H, m), 2.89 (1 H, p, *J* = 7.8 Hz), 1.22 (3 H, t, *J* = 7.1 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 174.0, 153.0, 142.4, 142.2, 141.2, 126.6, 124.6, 115.4, 115.0, 61.8, 61.1, 55.9, 42.8, 36.3, 35.8, 14.4 ppm – IR: 1732, 1514, 1238, 1037 cm⁻¹. – HRMS: calcd for

C20H23NO3: 326.1751, found 326.1751 [M+H+].
Ethyl 2-((4-methoxyphenyl)amino)-3,3-dimethylbutanoate (7s)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (26.5 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **7s** (52.5 mg, 99%) as a colourless oil.

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67.2, 60.6, 55.8, 34.4, 26.9, 14.4 ppm – IR: 2970, 1737, 1514, 1366, 1230, 1036 cm⁻¹. – HRMS: calcd for C₁₅H₂₃NO₃: 266.1751, found 266.1751 [M+H⁺].

Ethyl 2-((4-methoxyphenyl)amino)-3,3-dimethylpentanoate (7t)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (30.2 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **7t** (51.9 mg, 93%) as a colourless oil.

¹ H NMR (500 MHz, CDCl₃): 6.76 (2 H, d, *J* = 9.0 Hz), 6.63 (2 H, d, *J* = 8.9 Hz), 4.27 – 4.02 (2 H, m), 3.93 – 3.83 (1 H, m), 3.73 (4 H, s), 1.55 – 1.34 (2 H, m), 1.21 (3 H, t, *J* = 7.1 Hz), 1.01 OMe (3 H, s), 0.99 (3 H, s), 0.91 (3 H, t, *J* = 7.5 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 173.9, 152.9, 141.9, 115.7, 114.9, 65.4, 60.6, 55.8, 37.0, 32.3, 23.5, 23.2, 14.4, 8.3 ppm – IR: 2970, 1738, 1514, 1365, 1217 cm⁻¹. – HRMS: calcd for C₁₆H₂₅NO₃: 280.1907, found 280.1908 [M+H⁺].

Ethyl 2-((4-methoxyphenyl)amino)-2-(1-methylcyclohexyl)acetate (7u)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (36.9 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **7u** (58.0 mg, 95%) as a colourless oil.



¹ H NMR (500 MHz, CDCl₃): 6.75 (2 H, d, *J* = 8.9 Hz), 6.64 (2 H, d, *J* = 8.9 Hz), 4.12 (2 H, qd, *J* = 7.1, 4.7 Hz), 3.94 – 3.85 (1 H, m), 3.82 (1 H, s), 3.73 (3 H, s), 1.73 – 1.40 (8 H, m), 1.31 ^{OMe} (2 H, dt, *J* = 13.2, 4.7 Hz), 1.21 (3 H, t, *J* = 7.1 Hz), 1.03 (3 H, s). ppm. – ¹³C NMR (125 MHz, CDCl₃): 173.8, 152.9, 142.1, 115.8, 115.0, 66.2, 60.6, 55.9, 37.1, 35.1, 26.3, 22.0, 21.8, 20.6,

14.5 ppm – IR: 2928, 1735, 1513, 1366, 1232, 1037 cm⁻¹. – HRMS: calcd for C₁₈H₂₇NO₃: 306.2064, found 306.2062 [M+H⁺].

Ethyl 2-((4-methoxyphenyl)amino)-2-(4-methyltetrahydro-2H-pyran-4-yl)acetate (7v)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (37.4 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 5 v/v) to give product **7v** (55.3 mg, 90%) as a colourless oil.

¹ H NMR (500 MHz, CDCl₃): 6.80 – 6.72 (2 H, m), 6.68 – 6.60 (2 H, m), 4.22 – 4.07 (2 H, m), 3.90 (1 H, s), 3.81 (3 H, tt, *J* = 16.2, 4.3 Hz), 3.73 (3 H, d, *J* = 2.2 Hz), 3.70 – 3.58 (2 H, m), 1.88 (1 H, ddd, *J* = 14.3, 10.4, 4.4 Hz), 1.77 (1 H, ddd, *J* = 14.3, 10.2, 4.4 Hz), 1.59 – 1.48 (1 H, m), 1.31 (1 H, dq, *J* = 13.5, 2.2 Hz), 1.22 (3 H, t, *J* = 7.1 Hz), 1.14 (3 H, s) ppm. – ¹³C NMR (125

MHz, CDCl₃): 173.1, 153.1, 141.7, 116.0, 115.0, 66.7, 63.9, 63.6, 60.8, 55.8, 35.2, 35.1, 35.0, 19.2, 14.4 ppm – IR: 2939, 1728, 1514, 1234, 1037 cm⁻¹. – HRMS: calcd for C₁₇H₂₅NO₄: 308.1856, found 308.1854 [M+H⁺].

Ethyl 2-((4-methoxyphenyl)amino)-2-(1-phenylcyclohexyl)acetate (7w)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (53.0 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **7w** (60.2 mg, 82%) as a white solid (m.p. 98 °C).

⁰ ¹ H NMR (500 MHz, CDCl₃): 7.40 – 7.34 (4 H, m), 7.31 – 7.20 (1 H, m), 6.79 – 6.67 (2 H, m), 6.59 – 6.51 (2 H, m), 3.99 – 3.81 (3 H, m), 3.72 (3 H, s), 3.68 (1 H, s), 2.65 – 2.49 (1 H, m), 2.45 ^{OMe} – 2.29 (1 H, m), 2.05 – 1.87 (1 H, m), 1.83 – 1.50 (4 H, m), 1.42 – 1.22 (3 H, m), 1.01 (3 H, t, J = 7.1 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 172.7, 152.9, 141.8, 140.9, 128.4, 128.2, 126.5,

115.9, 114.9, 68.4, 60.5, 55.8, 45.8, 39.0, 33.4, 33.0, 26.5, 22.2, 14.1 ppm – IR: 2935, 1737, 1512, 1366, 1217 cm⁻¹. – HRMS: calcd for C₂₃H₂₉NO₃: 368.2220, found 368.2220 [M+H⁺].

Ethyl 2-((4-methoxyphenyl)amino)-3-methyl-3-phenylbutanoate (7x)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (42.6 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **7x** (49.7 mg, 76%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 7.45 – 7.39 (2 H, m), 7.33 (2 H, dd, *J* = 8.6, 6.9 Hz), 7.27 – 7.20 (1 H, m), 6.72 (2 H, d, *J* = 8.9 Hz), 6.55 (2 H, d, *J* = 8.9 Hz), 4.04 (1 H, s), 3.93 (2 H, qd, *J* = 7.2, ⁰Me 1.3 Hz), 3.84 – 3.78 (1 H, m), 3.72 (3 H, s), 1.53 (3 H, s), 1.50 (3 H, s), 1.00 (3 H, t, *J* = 7.1 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃)173.2, 153.0, 145.7, 141.7, 128.2, 126.7, 126.6, 115.9, 114.9, 67.9, 60.6, 55.8, 41.5, 25.7, 25.3, 14.1 ppm – IR: 2975, 1727, 1512, 1239, 1032, 700 cm⁻¹. – HRMS: calcd for C₂₀H₂₅NO₃: 328.1907, found 328.1907 [M+H⁺].

Ethyl 2-((3r,5r,7r)-adamantan-1-yl)-2-((4-methoxyphenyl)amino)acetate (7y)



According to GP1, the reaction was carried out with Cu(MeCN)BF4 (5.0 mg, 0.016 mmol, 8 mol%), acridine A1 (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg,

0.24 mmol, 1.2 equiv.), carboxylic acid (46.8 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **7y** (55.6 mg, 81%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 6.75 (2 H, d, *J* = 8.9 Hz), 6.63 (2 H, d, *J* = 8.9 Hz), 4.13 (2 H, q, *J* = 7.2 Hz), 3.92 (1 H, s), 3.73 (3 H, s), 3.53 (1 H, d, *J* = 4.7 Hz), 2.06 – 1.98 (3 H, m), 1.82 (3 ^{OMe} H, dt, *J* = 12.3, 2.7 Hz), 1.73 (3 H, dt, *J* = 12.4, 2.7 Hz), 1.69 – 1.63 (3 H, m), 1.58 (3 H, dq, *J* = 12.3, 2.6 Hz), 1.23 (3 H, t, *J* = 7.1 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 173.3, 152.8, 142.1,

115.6, 114.9, 68.1, 60.5, 55.8, 39.2, 37.0, 37.0, 36.3, 28.5, 14.5 ppm – IR: 2901, 2848, 1728, 1513, 1240, 1037 cm⁻¹. – HRMS: calcd for C₂₁H₂₉NO₃: 344.2220, found 344.2216 [M+H⁺].

Isopropyl 2-cyclohexyl-2-((4-methoxyphenyl)amino)acetate (7z)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (17.6 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (33.3 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **7z** (54.3 mg, 89%) as a white solid (m.p. 93 °C).

¹H NMR (500 MHz, CDCl₃): 6.75 (2 H, d, *J* = 8.9 Hz), 6.60 (2 H, d, *J* = 8.9 Hz), 5.02 (1 H, p, *J* = 6.3 Hz), 3.87 (1 H, d, *J* = 12.1 Hz), 3.73 (4 H, s), 2.00 – 1.84 (1 H, m), 1.82 – 1.56 (5 H, m), ⁰Me 1.44 – 1.07 (11 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 173.6, 152.7, 141.9, 115.3, 114.9, 68.4, 63.5, 55.9, 41.4, 29.8, 29.4, 26.4, 26.3, 26.2, 22.0, 22.0 ppm – IR: 2928, 1728, 1514, 1239,

1106 cm⁻¹. - HRMS: calcd for C18H27NO3: 306.2064, found 306.2056 [M+H⁺].

Benzyl 2-cyclohexyl-2-((4-methoxyphenyl)amino)acetate (7za)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (27.2 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was

then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **7za (**57.9 mg, 82%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃): 7.33 (3 H, td, *J* = 4.7, 2.2 Hz), 7.29 – 7.21 (2 H, m), 6.75 (2 H, d, *J* = 8.9 Hz), 6.60 (2 H, d, *J* = 8.9 Hz), 5.13 (2 H, d, *J* = 2.2 Hz), 3.85 (2 H, t, *J* = 10.0 Me Hz), 3.74 (3 H, s), 1.91 – 1.81 (1 H, m), 1.80 – 1.72 (3 H, m), 1.71 – 1.61 (2 H, m), 1.33 – 1.06 (5 H, m) ppm. – ¹³C NMR (125 MHz, CDCl₃): 174.1, 152.8, 141.7, 135.8, 128.6, 128.4,

115.4, 115.0, 66.6, 63.6, 55.8, 41.4, 29.8, 29.3, 26.3, 26.2 ppm – IR: 2927, 1734, 1514, 1239, 821 cm⁻¹. – HRMS: calcd for C₂₂H₂₇NO₃: 354.2064, found 354.2063 [M+H⁺].

N-(5-(2,5-Dimethylphenoxy)-2,2-dimethyl-1-phenylpentyl)aniline (8a)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (21.2 mg, 0.2 mmol), aniline (22.3 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (65.0 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **8a** (75.1 mg, 97%) as a colourless oil.

¹ H NMR (500 MHz, CDCl₃): 7.35 – 7.24 (4 H, m), 7.24 – 7.17 (1 H, m), 7.04 (2 H, dd, *J* = 8.6, 7.2 Hz), 7.00 (1 H, d, *J* = 7.4 Hz), 6.65 (1 H, d, *J* = 7.4 Hz), 6.62 – 6.55 (2 H, m), 6.49 (2 H, d, *J* = 7.9 Hz), 4.16 (1 H, s), 3.99 – 3.82 (2 H, m), 2.29 (3 H, s), 2.15 (3 H, s), 1.94 – 1.72 (2 H, m), 1.69 – 1.42 (2 H, m), 1.01 (3 H, s), 0.96 (3 H, s) ppm. – ¹³C NMR (125 MHz,

CDCl₃): 157.1, 136.6, 130.4, 129.2, 128.8, 127.9, 127.0, 123.7, 120.8, 117.2, 113.4, 112.1, 68.5, 37.4, 36.4, 24.7, 24.3, 23.9, 21.5, 15.9 ppm – IR: 2951, 1738, 1600, 1504, 1205, 1152, 704 cm⁻¹. – HRMS: calcd for C₂₇H₃₃NO: 388.2635, found 388.2637 [M+H⁺].





According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol%), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (65.0 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was

then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 20 v/v) to give product **8b** (79.3 mg, 96%) as a colourless oil.



¹H NMR (500 MHz, CDCl₃): 7.02 (1 H, d, *J* = 7.4 Hz), 6.78 (2 H, d, *J* = 8.9 Hz), 6.70 – 6.63 (3 H, m), 6.63 (1 H, d, *J* = 1.5 Hz), 4.15 (2 H, qd, *J* = 7.1, 3.1 Hz), 3.95 (3 H, t, *J* = 6.4 Hz), 3.83 – 3.77 (1 H, m), 3.75 (3 H, s), 2.32 (3 H, s), 2.19 (3 H, s), 2.03 – 1.76 (2 H, m), 1.71 – 1.50 (2 H, m), 1.23 (3 H, t, *J* = 7.1 Hz), 1.10 (3 H, s), 1.08 (3 H, s) ppm. – ¹³C NMR (125 MHz, CDCl₃): 173.7, 157.1, 153.0, 141.8, 136.6, 130.4, 123.7, 120.8,

115.9, 114.9, 112.1, 68.4, 65.8, 60.7, 55.8, 36.8, 36.2, 24.2, 24.1, 23.7, 21.5, 15.9, 14.4 ppm – IR: 2919, 1728, 1511, 1366, 1234 cm⁻¹. – HRMS: calcd for C₂₅H₃₅NO₄: 414.2639, found 414.2639 [M+H⁺].

Ethyl 2-((4-methoxyphenyl)amino)-3-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)propanoate (8c)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (69.7 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 10 v/v) to give product **8c** (79.3 mg, 92%) as a colourless oil.

¹ H NMR (500 MHz, CDCl₃): 8.06 (1 H, d, *J* = 2.4 Hz), 7.89 (1 H, dd, *J* = 7.7, 1.4 Hz), 7.55 (1 H, td, *J* = 7.4, 1.4 Hz), 7.47 (1 H, td, *J* = 7.6, 1.3 Hz), 7.35 (1 H, dd, *J* = 7.5, 1.2 Hz), 7.31 (1 OMe H, dd, *J* = 8.4, 2.4 Hz), 6.98 (1 H, d, *J* = 8.4 Hz), 6.76 (1 H, d, *J* = 9.0 Hz), 6.60 (2 H, d, *J* = 8.9 Hz), 5.17 (2 H, s), 4.27 (1 H, t, *J* = 6.3 Hz), 4.15 (2 H, qd, *J* = 7.1, 1.4 Hz), 3.73 (3 H, s), 3.11 (2 H, qd, *J* = 13.7, 6.2 Hz), 1.21 (3 H, t, *J* = 7.1 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 191.0, 173.3, 160.5, 152.9, 140.5, 136.6, 135.7, 132.9, 132.5, 130.5, 129.6, 129.3, 127.9, 125.2,

120.9, 115.5, 115.0, 73.7, 61.3, 59.0, 55.8, 37.9, 14.3 ppm – IR: 2932, 1732, 1647, 1513, 1300, 1240, 823 cm⁻¹. – HRMS: calcd for C₂₆H₂₅NO₅: 432.1805, found 432.1805 [M+H⁺].

Ethyl 3-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)-2-((4-methoxyphenyl)amino)propanoate

(8d)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol%), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (93.1 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 8 v/v) to give product **8d** (96.9 mg, 93%) as a colourless oil.



¹ H NMR (500 MHz, CDCl₃): 7.57 (2 H, d, J = 8.1 Hz), 7.49 – 7.40 (2 H, m), 6.96 (1 H, d, J = 2.5 Hz), 6.93 (1 H, d, J = 9.0 Hz), 6.73 (2 H, d, J = 8.9 Hz), 6.68 (1 H, dd, J = 9.0, ^{DMe} 2.5 Hz), 6.54 (2 H, d, J = 8.9 Hz), 4.30 (1 H, t, J = 6.4 Hz), 4.17 – 3.99 (2 H, m), 3.80 (3 H, s), 3.72 (3 H, s), 3.30 – 3.08 (2 H, m), 2.29 (3 H, s), 1.14 (3 H, t, J = 7.1 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 173.7, 168.4, 156.1, 152.9, 140.7, 139.3, 135.8, 134.1, 131.3, 131.2, 131.0, 129.2, 115.1, 115.0, 114.9, 111.6, 101.4, 61.4, 57.9, 55.8, 28.4, 14.2, 13.7 ppm

– IR: 1732, 1682, 1513, 1477, 1316, 1237, 1037, 824 cm⁻¹. – HRMS: calcd for C₂₉H₂₉ClN₂O₅: 521.1838, found 521.1838 [M+H⁺].

(3R,7R,8R,9R,10S,13R,14R,17R)-17-((2R)-6-Ethoxy-5-((4-methoxyphenyl)amino)-6-oxohexan-2-yl)-8,10,13trimethylhexadecahydro-1*H*-cyclopenta[a]phenanthrene-3,7-diyl diacetate (8e)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (127.4 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 3 v/v) to give product **8e** (118.8 mg, 1:1 dr, 91%) as a colourless oil. [α]²⁰D = + 3.5 (c = 1.0, CH₂Cl₂).



¹H NMR (500 MHz, CDCl₃): 6.75 (2 H, d, *J* = 8.9 Hz), 6.58 (2 H, dd, *J* = 8.9, 1.5 Hz), 4.87 (1 H, d, *J* = 3.1 Hz), 4.58 (1 H, tt, *J* = 11.4, 4.5 Hz), 4.25 – 4.07 (2 H, m), 3.96 – 3.85 (1 H, m), 3.72 (3 H, s), 2.05 (3 H, s), 2.02 (3 H, s), 2.00 – 1.90 (2 H, m), 1.90 – 1.75 (4 H, m), 1.74 – 1.63 (2 H, m), 1.63 – 1.52 (3 H, m), 1.45 (5 H, dddd, *J* = 23.4, 12.1, 8.9, 5.4 Hz), 1.38 – 0.99 (12 H, m), 0.95 – 0.86

(6 H, m), 0.63 (3 H d, *J* = 5.8 Hz,) ppm. – ¹³C NMR (125 MHz, CDCl₃): 174.7, 174.6, 170.7, 170.5, 152.8, 141.2, 141.1, 115.3, 115.0, 74.3, 71.4, 61.0, 58.4, 55.8, 55.8, 50.5, 42.8, 41.1, 39.6, 38.0, 35.6, 35.5, 35.0, 34.9, 34.8, 34.2, 31.8, 31.7, 31.4, 29.8, 29.8, 28.2, 28.1, 26.9, 23.7, 22.8, 21.7, 21.6, 20.8, 18.7, 14.4, 11.8 ppm – IR: 2940, 1732, 1513, 1246, 1025, 758 cm⁻¹. – HRMS: calcd for C₃₈H₅₇NO7: 640.4208, found 640.4209 [M+H⁺].

1-Cyclohexyl 5-ethyl (2S)-2-((tert-butoxycarbonyl)amino)-4-((4-methoxyphenyl)amino)pentanedioate (8f)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (81.9 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 2 v/v) to give product **8f** (80.3 mg, 2:1 dr, 84%) as a white solid (m.p. 79 °C). [α]²⁰_D = 0 (c = 0.5, CH₂Cl₂).

¹ H NMR (500 MHz, CDCl₃, rotamers): 6.79 – 6.70 (3 H, m), 6.63 (3 H, dd, *J* = 8.9, 4.1 Hz), 5.22 (1.5 H, dd, *J* = 15.3, 9.5 Hz), 4.78 (1.5 H, dq, *J* = 9.0, 4.4 Hz), 4.50 (1 H, q, *J* = 4.7 OMe Hz), 4.35 (0.5 H, d, *J* = 7.0 Hz), 4.27 (0.5 H, s), 4.26 – 4.07 (0.5 H, m), 3.72 (4.5 H, s), 2.66 (1.5 H, ddd, *J* = 25.0, 15.9, 6.8 Hz), 2.53 (1.5 H, ddd, *J* = 15.8, 5.9, 2.8 Hz), 1.89 – 1.77 (3 H, m), 1.76 – 1.60 (3 H, m), 1.56 – 1.30 (22.5 H, m), 1.25 (4.5 H, dt, *J* = 10.3, 7.1 Hz) ppm.

- ¹³C NMR (125 MHz, CDCl₃): 172.4, 172.3, 170.7, 155.3, 153.3, 153.1, 141.3, 123.7, 116.0, 115.7, 115.0, 114.9, 114.6, 79.8, 77.4, 77.2, 76.9, 73.4, 73.4, 61.8, 61.6, 61.2, 61.1, 55.8, 55.8, 50.1, 49.8, 37.0, 36.3, 31.6, 31.6, 28.4, 28.4, 25.4, 23.8, 14.3, 14.2 ppm - IR: 2936, 1720, 1512, 1237, 1170, 1038 cm⁻¹. - HRMS: calcd for C₂₅H₃₈N₂O₇: 479.2752, found 479.2755 [M+H⁺].

1-Benzyl 6-ethyl (2S)-2-(((benzyloxy)carbonyl)amino)-5-((4-methoxyphenyl)amino)hexanedioate (8g)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (96.5 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 2 v/v) to give product **8g** (91.8 mg, 1:1 dr, 86%) as a colourless oil. [α]²⁰_D = 0 (c = 0.5, CH₂Cl₂).

¹ H NMR (500 MHz, CDCl₃): 7.33 (10 H, dq, J = 10.0, 4.8, 4.3 Hz), 6.74 (2 H, d, J = 8.9 Hz), 6.57 (2 H, t, J = 8.1 Hz), 5.41 (1 H, dd, J = 29.9, 8.2 Hz), 5.27 – 4.99 (4 H, m), 4.47 (1 H, q, J = 6.9 Hz), 4.20 – 4.05 (2 H, m), 3.93 (1 H, dt, J = 16.0, 5.2 Hz), 3.73 (3 H, d, J = 1.5 Hz), 2.02 (1 H, dt, J = 15.7, 5.2 Hz), 1.94 – 1.75 (2 H, m), 1.66 (1 H, dt, J = 11.3, 8.1 Hz), 1.19 (3 H, td, J = 7.1, 5.0 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 173.9, 172.0, 153.1, 140.9, 140.7, 136.3, 135.3,

 $128.8, 128.7, 128.5, 128.4, 128.2, 115.6, 115.0, 67.5, 67.5, 67.2, 62.7, 61.3, 57.6, 55.8, 53.8, 29.2, 29.2, 29.0, 28.8, 14.3, ppm - IR: 1724, 1513, 1239, 1183, 1029, 699 \, {\rm cm}^{-1}$ - HRMS: calcd for C₃₀H₃₄N₂O₇: 535.2439, found 535.2439 [M+H⁺].

1-Ethyl 6-((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydrobenzo[1,2-d:3,4-d']bis([1,3]dioxole)-3a(4H)-yl) 2-((4-methoxyphenyl)amino)hexanedioate (8h)



According to GP1, the reaction was carried out with Cu(MeCN)BF₄ (5.0 mg, 0.016 mmol, 8 mol%), acridine **A1** (4.7 mg, 0.016 mmol, 8 mol %), 4Å molecular sieves (60 mg), aldehyde (14.8 mg, 0.2 mmol), aniline (29.5 mg, 0.24 mmol, 1.2 equiv.), carboxylic acid (90.1 mg, 0.26 mmol, 1.3 equiv.), anhydrous *p*-toluenesulfonic acid (2.8 mg, 0.016 mmol, 8 mol%), and acetonitrile (2 mL). The test-tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at at room temperature for 30 h. The reaction mixture was then concentrated under reduced pressure, and the remaining material was purified by flash chromatography on silica gel (EtOAc/hexane, 1 : 1 v/v) to give product **8h** (96.9 mg, 1:1 dr, 93%) as a colourless oil. [α]²⁰_D = - 0.60 (c = 1.0, CH₂Cl₂).

¹ H NMR (500 MHz, CDCl₃): 6.75 (2 H, d, *J* = 8.9 Hz), 6.58 (2 H, d, *J* = 8.9 Hz), 4.59 (1 H, dt, *J* = 7.9, 2.4 Hz), 4.40 (1 H, dd, *J* = 11.7, 8.2 Hz), 4.28 (1 H, dd, *J* = 2.6, 1.8 Hz), 4.23 (1 H, dt, *J* = 8.0, 1.8 Hz), 4.15 (2 H, qd, *J* = 7.1, 0.9 Hz), 4.04 (1 H, dd, *J* = 11.7, 8.9 Hz), 3.95 (1 H, dt, *J* = 6.1, 3.1 Hz), 3.90 (1 H, dt, *J* = 12.9, 2.0 Hz), 3.80 – 3.70 (5 H, m), 2.46 – 2.36 (2 H, m), 1.94 – 1.70 (4 H, m), 1.53 (3 H, s), 1.48 (3 H, s), 1.38 (3 H, s), 1.34 (3 H, d, *J* = 1.6 Hz), 1.23 (3 H, t, *J* = 7.1 Hz) ppm. – ¹³C NMR (125 MHz, CDCl₃): 174.2, 172.5, 152.9, 141.1, 116.7, 115.3,

115.0, 114.9, 109.3, 108.8, 101.6, 70.9, 70.7, 70.2, 65.5, 65.5, 61.4, 61.2, 57.7, 55.8, 33.7, 32.5, 26.6, 26.0, 25.3, 24.2, 21.2, 21.1, 14.4 ppm – IR: 2987, 2935, 1736, 1514, 1250, 1209, 1071, 823 cm⁻¹. – HRMS: calcd for C₂₆H₃₇NO₁₀: 538.2647, found 538.2635 [M+H⁺].

Computational studies

Calculations were performed using computational resources at the Texas Advanced Computing Centers (TACC) hosted by The University of Texas at Austin and the Advanced Cyberinfrastructure Coordination Ecosystem: Services and Support (ACCESS). DFT optimization, vibrational analysis, and IRC calculations were conducted with Gaussian 16 (rA.03).¹ Energy decomposition analysis was performed for the optimized transition state structures using the second generation energy decomposition analysis using absolutely localized molecular orbitals (ALMO-EDA2)² and complementary occupied virtual orbital pairs (COVP) methods in Q-chem 6.0.³ Visualizations and monitoring of calculations were performed using Chemcraft.⁴ Images were rendered using CYLview2.0⁵ and VMD 1.9.3.⁶ Spin density information was collected from the optimized geometry check file and later rendered in VMD using an isovalue of 0.05. The contribution of each atom to the spin density was evaluated using NBOpro7.⁷ Calculations related to effective oxidation states (EOS) and intrinsic bonding orbitals (IBOs) were performed with IboView.⁸

Details of computational methods

Ground state minima and transition states were optimized without constraints using PW6B95 density functional approximation with D3BJ dispersion correction and Def2-TZVP basis set in acetonitrile using the SMD solvation model. Optimizations were performed with "tight" convergence criteria and an ultrafine grid. Frequency calculations at the same level of theory were used to confirm the nature of the stationary points. Geometries with no imaginary frequencies were deemed minima, whereas those with exactly one imaginary frequency along the chemical path of interest were deemed transition states. An IRC calculation was performed for each transition state to further corroborate the transition state connected reactants and products. A cut-off frequency of 50 cm⁻¹ was applied for all structures to correct for potential errors associated with low magnitude vibrational frequencies, in addition to aa 1M concentration correction, via GoodVibes.⁹ Single point calculations were performed at the M06-L-D3/def2-TZVPPD level of theory in acetonitrile using the SMD solvation model.

Distortion/Interaction-Activation Strain Analysis

A distortion/interaction-activation strain model analysis¹⁰ was performed on **TS1**, **TS2**, and **TS3** at the M06-L–D3/Def2-TZVPPD/SMD(MeCN) level of theory from the previously optimized geometries. A detailed discussion of distortion/interaction-activation strain analysis can be found in our previous work.¹¹ Fragment definitions were created for each transition state (Figure S1), with the red fragment representing the imine analogues (Fragment **F1**) and the green fragment representing the radical structure (Fragment **F2**). The results of distortion/interaction-activation strain analysis are provided in Figure S2.



Figure S1. Fragment definition for distortion/interaction-activation strain analysis. The imine fragment is highlighted green (**F1**), and the radical fragment is highlighted red (**F2**).



Figure S2. Results of distortion/interaction-activation strain analysis in kcal/mol for TS1, TS2, and TS3.

Energy Decomposition Analysis via ALMO-EDA2

The second generation Absolutely Localized Molecular Orbital Energy Decomposition Analysis (ALMO-EDA2) method of Head-Gordon and co-workers was employed to gain quantitative insight into the intermolecular forces governing the interaction energies of the previously optimized transition state structures. ALMO-EDA2 calculations were performed at the M06-L–D3/def2-TZVPPD/SMD(MeCN) level of theory in Q-Chem 6.0 using the optimized geometries at the same level of theory. The results of ALMO-EDA2 are visualized in Figure SY1 and tabulated in Table S2.

Structure	prep	ΔEPauli	ΔEElec	ΔΕст	ΔE_{Disp}	ΔEPol	ΔEsolv	Total ∆ E ‡ int
TS1	0	56.4	-23.1	-19.7	-15.6	-3.7	1.2	-4.4
TS2	0	56.8	-25.3	-27.2	-17.6	-3.9	1.9	-15.2
TS3	0	57.1	-24.6	-20.5	-18.3	-4.0	1.8	-8.4

Table S2. Energy decomposition analysis of TS1, TS2, and TS3, kcal/mol.



Figure S3. Energy decomposition analysis for **TS3** with respect to **TS1**, $\Delta\Delta E^{\ddagger}$, = ΔE^{\ddagger} TS2 - ΔE^{\ddagger} TS1, kcal/mol.

Complementary occupied-virtual orbital pairs (COVP) analysis

The complementary occupied-virtual orbital pairs (COVP) analysis was employed in tandem with ALMO-EDA2. This method provides insight into the donor/acceptor orbital interactions that contribute to the ΔE_{CT}^{\neq} term. The images were generated in VMD using an isovalue of ±0.01 from for the two COVPs that contributed the most to the charge transfer term. The donor orbitals are represented with an opaque surface while acceptor orbitals are represented by transparent surface. The results for **TS1**, **TS2**, and **TS3** are presented in Figures S4-S6.



Figure S4. The most significant COVPs for TS1 and their energy contribution in kcal/mol.



Figure S5. The most significant COVPs for TS2 and their energy contribution in kcal/mol.



Figure S6. The most significant COVPs for TS3 and their energy contribution in kcal/mol.

Effective oxidation state analysis

Calculations were performed on structures **11** and **12** to determine the effective oxidation states (EOS)¹² of the metal center and ligands (Figures S7 and S8). Each complex was partitioned into fragments and the electronic population of each fragment was evaluated using intrinsic bonding orbitals (IBOs).¹³ Wavefunctions for IBO analysis were performed at the PBE0/Def2-SVP level of theory on the optimized geometries collected from G16.



Fragment	Partial Charge	Partial Spin
Imine	-0.03	0.80
Copper	0.83	0.18
MeCN (blue)	0.07	0.01
MeCN (yellow)	0.06	0.00
MeCN (purple)	0.07	0.01

Figure S7. Fragment definitions used in EOS analysis for **11** and the partial charge and partial spin of each fragment.



Figure S8. Fragment definitions used in EOS analysis for **12** and the partial charge and partial spin of each fragment.

Marcus theory calculations

The following equations, derived from Marcus-Hush Theory,¹⁴ can approximate the SET process:

$$\Delta G_{ET}^{\ddagger} = \Delta G_0^{\ddagger} \left(1 + \frac{\Delta G_r}{4\Delta G_0} \right)^2$$
$$\Delta G_0^{\square} = \frac{\lambda}{4}$$
$$\lambda_0^{\square} = \left(332 \frac{kcal}{mol} \right) \left(\frac{1}{2a_1} + \frac{1}{2a_2} + \frac{1}{R} \right) \left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon} \right)$$

The intrinsic barrier, ΔG_0^{\ddagger} , is estimated by first determining the reorganization energy, λ . As the inner reorganization is expected to have a small contribution to λ , the reorganization energy is approximated by the

outer reorganization energy, $\lambda_0^{\square} \approx \lambda$. The a₁ term is the sphere radius of the donor species; a₂ is the sphere radius of the acceptor species; ϵ_{op} is the square of the refractive index of solvent acetonitrile; ϵ is the dielectric constant of the solvent reported from G16; and *R* is the inter-center distance between the donor and acceptor.



Non-covalent interaction analysis

The independent gradient model (IGM)¹⁵ was employed to detect non-covalent interactions present in **TS1** and **TS2**. Cube files were generated on MultiWFN¹⁶ from the optimized PW6B95-D3BJ/Def2-TZVP/SMD(MeCN) geometries. The files were then exported to VMD for visualization using an isovalue of 0.01 (Figure S9).



Figure S9. Independent gradient model for TS1 and TS2.

Optimized geometries

R• E(UPW6B95D3) = -235.607139049 E(UM06L) = -235.269087994

	Charge = 0	Multiplicity = 2	
С	-2.1776123781	-0.9994810159	0.1290995819
С	-0.6632243592	-0.8883624349	-0.0404584075
С	-0.2265618794	0.5657087826	-0.1163686307
С	-0.6588117321	1.3310170887	1.1238744905
С	-2.1732306264	1.2595702528	1.3144597423
С	-2.6769466577	-0.1307692864	1.2208076543



Η	0.8541734547	0.6270476685	-0.2376024278
Η	-0.1728971437	-1.3630587080	0.8110816041
Η	-0.3499875986	-1.4295412345	-0.9320150410
Η	-2.6437542826	-0.6964764339	-0.8208834379
Η	-2.4730925050	-2.0349234266	0.2900292428
Η	-0.1683470822	0.8984361208	1.9974865926
Η	-0.3420848552	2.3710640342	1.0618866758
Η	-2.4654523026	1.7166898181	2.2583857813
Η	-2.6387223001	1.8706539655	0.5261118785
Η	-3.5709400117	-0.4112445218	1.7588996788
Η	-0.6710148300	1.0301171806	-0.9998849681

RCO₂H

E(RPW6B95D3) = -425.153611424 E(RM06L) = -424.569853863

	Charge = 0	Multiplicity = 1	
С	-2.4068217162	-1.3075391786	0.0136961514
С	-0.8880224908	-1.3309663493	0.0687342457
С	-0.3305400829	0.0929928070	0.0345139268
С	-0.9000351083	0.9173226041	1.1914182682
С	-2.4186428231	0.9360384826	1.1328366289
С	-2.9878098266	-0.4731506636	1.1435325536
Η	-0.5743404487	-1.8262241265	0.9908971867
Η	-0.4819396761	-1.9088873142	-0.7595298855
Η	-2.7210875110	-0.8885927969	-0.9439183039
Η	-2.7907004750	-2.3252942980	0.0558691483
Η	-0.5885257021	0.4795773910	2.1424068431
Η	-0.5009596453	1.9294839668	1.1575856357
Η	-2.8098401766	1.5109787329	1.9703813494
Η	-2.7335673323	1.4472376720	0.2213859832
Η	-2.7497306575	-0.9478192870	2.0977148563
Η	-4.0734670563	-0.4412729765	1.0679220081
Η	-0.6249780638	0.5606942107	-0.9027917454
С	1.1729244071	0.1043393851	0.0376193357
0	1.7735277003	-0.4596764635	1.0990404950
Η	1.1167167549	-0.8032287091	1.7186937108
0	1.8559755701	0.5785255210	-0.8295109621



Cu^IL₃* E(RPW6B95D3) = -2040.27052865 E(RM06L) = -2038.82910189

	Charge = 1	Multiplicity = 1	
Cu	0.1830660908	-0.0620514084	-0.1116717420
Ν	0.0275021135	0.1102921371	1.8535775356
Ν	1.9507609554	-0.1017328752	-0.9762612575
Ν	-1.4821453647	-0.0635087200	-1.1946238023
С	-0.0674816884	0.1991134216	2.9899472512
С	-2.4371970155	-0.0307898517	-1.8231260680
С	2.9833442282	-0.1410055158	-1.4666513286
С	-3.6374004273	0.0121039133	-2.6151761705
Н	-3.9164544440	1.0473538460	-2.7904182375
Н	-3.4619605814	-0.4813370971	-3.5669484673
Н	-4.4401556325	-0.4938570159	-2.0865261365
С	-0.1874311156	0.3081416750	4.4193587247
Н	-1.0720213993	0.8882062703	4.6665800016
Н	-0.2753579405	-0.6855517762	4.8496812406
Н	0.6934161047	0.7998890753	4.8221003408
С	4.2828606029	-0.1938466026	-2.0814520318
Н	4.9450146583	0.5147422579	-1.5920114525
Н	4.6883439755	-1.1966621894	-1.9799985175
Н	4.1977386489	0.0569487245	-3.1349606724



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E(RPW6B95D3) = -557.711544033 E(RM06L) = -556.890262700

	Charge = 0	Multiplicity = 1	
С	-1.5494837499	0.0656027264	0.5013483670
С	-0.3122088336	0.6837737241	0.5284134556
С	-0.1639421406	1.9867435047	0.0638285418
С	-1.2761433859	2.6656808651	-0.4310537587
С	-2.5088109477	2.0474604961	-0.4588495233
С	-2.6487481096	0.7465401402	0.0072950878
Η	-1.6556561079	-0.9448757592	0.8643254950
Η	0.5510915984	0.1599593282	0.9122769632
Η	-1.1585632677	3.6758825521	-0.7906811164
Н	-3.3672505326	2.5762637469	-0.8435387039



Η	-3.6153914250	0.2673050671	-0.0158356758
С	1.1576913991	2.6002198313	0.1128156317
Η	1.9525263175	1.9732510326	0.5204974179
Ν	1.3872431482	3.7785777490	-0.3008377517
С	2.6718094086	4.3167161991	-0.1693383239
С	3.1373708374	5.1515110073	-1.1815496509
С	3.4752908693	4.0902077700	0.9468689184
С	4.3973725472	5.7132500808	-1.1002496087
Η	2.5014465933	5.3410475249	-2.0328570013
С	4.7289841284	4.6686567522	1.0292401563
Η	3.1034831750	3.4832698669	1.7583308120
С	5.1993933763	5.4746398314	0.0050859042
Н	4.7515911702	6.3471960816	-1.8987425219
Н	5.3385041611	4.4942043239	1.9029177904
Н	6.1774267505	5.9248509376	0.0743730752

E(UPW6B95D3) = -793.354110699 E(UM06L) = -792.192071306

	Charge = 0	Multiplicity = 2	
С	-2.1158165680	1.8011550543	0.9384445596
С	-0.8354113427	2.2336954312	0.6323451525
С	-0.1764747506	1.7492232553	-0.4888469674
С	-0.8250769567	0.8255384375	-1.2990407285
С	-2.1036687254	0.3925679494	-0.9959194786
С	-2.7545411777	0.8796417071	0.1266717306
Η	-2.6144439340	2.1870714619	1.8147394918
Η	-0.3457267438	2.9534029462	1.2699485205
Η	-0.3222854757	0.4483230683	-2.1782714444
Η	-2.5947972061	-0.3215467683	-1.6395372792
Η	-3.7531679970	0.5459921015	0.3635465858
С	1.2395520880	2.1631797815	-0.8382010688
Ν	1.6165000334	3.4125432285	-0.2265817122
С	1.1044777482	4.5484535913	-0.7139559585
С	1.5228673443	5.7528152785	-0.0927370326
С	0.1776423952	4.6485876976	-1.7846847215
С	1.0526299272	6.9716323048	-0.5131339656
Η	2.2257919121	5.6764552562	0.7226783718
С	-0.2856991600	5.8762109506	-2.1914329308





Η	-0.1735680152	3.7579485692	-2.2787206430
С	0.1445856805	7.0428558885	-1.5653830757
Н	1.3860148518	7.8755063595	-0.0271329674
Η	-0.9928368386	5.9366178228	-3.0046437120
Н	-0.2269738426	8.0001934320	-1.8959005821
С	2.2477801718	1.0695119442	-0.4486533138
С	3.6325137459	1.4037806093	-0.9851355710
С	2.3049648811	0.8140879974	1.0502149367
Η	1.9079011987	0.1523807948	-0.9367805615
С	4.6432430364	0.3204088207	-0.6464369933
Η	3.9547273375	2.3512056818	-0.5479687966
Н	3.5810754291	1.5546197462	-2.0640823791
С	3.3145376222	-0.2716408690	1.3898471948
Η	2.5855208649	1.7410678347	1.5526772492
Н	1.3193059760	0.5372963868	1.4219324307
С	4.6944063339	0.0689147890	0.8517864534
Η	5.6285728654	0.5967453403	-1.0199292201
Η	4.3611851429	-0.6046223482	-1.1543341821
Η	3.3535680689	-0.4205799412	2.4682602401
Η	2.9846388881	-1.2169744765	0.9530785303
Η	5.3987916246	-0.7305111356	1.0786651127
Η	5.0619158491	0.9673146997	1.3527208318
Η	1.2839321969	2.2507216503	-1.9287562863

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E(UPW6B95D3) = -793.820666855 E(UM06L) = -792.659887658

	Charge = 1	Multiplicity = 2	
С	-3.3540634029	0.2306919735	0.0748805786
С	-2.2229507927	1.0048577964	0.2649322514
С	-1.3212204459	1.1919930193	-0.7732401360
С	-1.5687971421	0.6019891822	-2.0039397041
С	-2.6964701374	-0.1779248659	-2.1925232261
С	-3.5920381665	-0.3648521201	-1.1528942220
Н	-4.0504185290	0.0926417311	0.8876234319
Н	-2.0438310207	1.4668433469	1.2245119316
Η	-0.8759518868	0.7609069695	-2.8172616598
Н	-2.8791967262	-0.6322390141	-3.1541483264
Н	-4.4754742756	-0.9665985226	-1.3004738263



С	-0.0617050812	2.0083597824	-0.5916731882
Ν	-0.3076615744	3.1650072441	0.2578832082
С	-1.0111040812	4.2469424154	-0.0560631401
С	-1.1330126532	5.2743276301	0.9180000941
С	-1.6375375356	4.3925015814	-1.3201632139
С	-1.8540263198	6.3965395665	0.6318248728
Η	-0.6489461685	5.1419191292	1.8735111480
С	-2.3527443672	5.5257903468	-1.5796692238
Η	-1.5484092762	3.6158607344	-2.0604284993
С	-2.4678260551	6.5311401791	-0.6147162129
Н	-1.9502597238	7.1787986759	1.3668638457
Η	-2.8336270866	5.6477402339	-2.5364993338
Н	-3.0364677379	7.4198252283	-0.8373385602
С	1.1330565526	1.2319464904	-0.0211212104
С	0.8585020736	0.5576855346	1.3161474183
С	1.6430515566	0.2087689673	-1.0259437349
Н	1.9229172168	1.9737050755	0.1260105744
С	2.1184535951	-0.1127706327	1.8426180391
Н	0.0817137285	-0.1957647958	1.1818433311
Н	0.4829868659	1.2693635418	2.0527250414
С	2.8995710731	-0.4744845850	-0.5106412289
Н	0.8688158687	-0.5412738587	-1.1955475327
Η	1.8354576647	0.6924506600	-1.9832027355
С	2.6568210055	-1.1227963077	0.8424397423
Η	1.9092597863	-0.5961439553	2.7953487660
Η	2.8779106517	0.6483436765	2.0320288922
Н	3.2393672183	-1.2159161992	-1.2318916630
Η	3.6963855145	0.2660273527	-0.4175606534
Η	3.5753489360	-1.5725358669	1.2163615601
Η	1.9314714797	-1.9308008673	0.7267599634
Η	0.2344602251	2.3886505088	-1.5679469680
Н	0.1007031739	3.1472520173	1.1844715091

E(UPW6B95D3) = -2833.64514467 E(UM06L) = -2831.04770164

Charge = 1 Multiplicity = 2 C -2.3006840456 1.4595849831 -0.0972308384 C -0.9650021595 1.7981248174 0.0293353195



S57

С	0.0014147278	1.1623330757	-0.7399295927
С	-0.3970807302	0.1860837887	-1.6417652007
С	-1.7326226947	-0.1578312302	-1.7684907577
С	-2.6891237270	0.4785982634	-0.9955852555
Η	-3.0403842037	1.9631328635	0.5065462580
Η	-0.6673313847	2.5655355186	0.7281081918
Η	0.3470509340	-0.3015208683	-2.2550094796
Η	-2.0260682654	-0.9179226292	-2.4764700851
Η	-3.7312134584	0.2166739490	-1.0962799608
С	1.4692725475	1.4994177284	-0.5869921170
Ν	1.6653803272	2.9267575326	-0.3614330501
С	1.1936363456	3.7764624667	-1.3237079677
С	1.0197090086	5.1318962748	-0.9842424788
С	0.8696274512	3.3815988610	-2.6369828454
С	0.5562271037	6.0428036781	-1.9049412229
Η	1.2278087149	5.4381376309	0.0296740666
С	0.4211806978	4.3058697458	-3.5541286968
Η	0.9947631352	2.3574386076	-2.9442347417
С	0.2582366355	5.6383892746	-3.1993104466
Η	0.4187561261	7.0728116384	-1.6142865562
Η	0.1943066995	3.9860016969	-4.5594993667
Η	-0.1026145209	6.3523137148	-3.9230053356
С	2.1544407417	0.6722179898	0.5087260119
С	1.4983164081	0.7814466083	1.8781046677
С	2.2903779811	-0.7915522419	0.1161889204
Η	3.1639267102	1.0806662979	0.5871452492
С	2.2949433644	0.0230445983	2.9281220911
Η	0.4929806671	0.3605383651	1.8252377791
Η	1.3895045527	1.8280004605	2.1644317248
С	3.0989007133	-1.5541916260	1.1543541826
Η	1.2984805001	-1.2399752599	0.0346039709
Η	2.7575070895	-0.8718528185	-0.8657523514
С	2.4707755217	-1.4345321434	2.5336584988
Η	1.7997720987	0.0964595341	3.8955591439
Η	3.2765922473	0.4859653505	3.0398632754
Η	3.1860272831	-2.6010204681	0.8667832970
Η	4.1128075864	-1.1483144382	1.1854815456
Η	3.0766218415	-1.9573171036	3.2727640168
Η	1.4934568742	-1.9219578378	2.5227440391
Н	1.9643578455	1.2275144070	-1.5239099723



Cu	2.7834957755	3.6665950070	1.0580070966
Ν	4.0086309696	5.2455298803	0.1411805617
С	5.3381612235	7.0401883023	-1.1602128297
Η	4.6457451831	7.7623024848	-1.5835833724
Η	6.0246475756	7.5484053160	-0.4893244467
Η	5.8997996249	6.5677990216	-1.9609054190
С	4.6014673882	6.0389577102	-0.4323445726
С	1.8787363686	5.0649793925	3.7539170237
С	1.4733790464	5.6787941781	4.9907592875
Η	1.5851583170	4.9648606688	5.8019316926
Η	2.0950544972	6.5478672390	5.1859360268
Η	0.4338179026	5.9856371045	4.9199708269
Ν	2.2007980376	4.5758859819	2.7717411751
Ν	4.5496511750	2.7662167600	1.8346646284
С	6.6841297585	1.5945323633	2.6985823403
Η	6.8266574728	1.8194772478	3.7515832553
Η	6.5726905823	0.5211879388	2.5700597541
Η	7.5473140658	1.9378173117	2.1356918275
С	5.4989977446	2.2563470347	2.2185772133

E(UPW6B95D3) = -2464.80142037 E(UM06L) = -2462.77989777

	Charge = 1	Multiplicity = 2	
Cu	2.9037974988	4.1063133521	1.0434026300
Ν	4.3194981055	4.2971059883	-0.3622854973
С	6.2268121622	4.6501548671	-2.0590715329
Η	6.0401039454	5.5602255487	-2.6223133704
Η	7.1692597497	4.7369299359	-1.5259506914
Η	6.2674298970	3.8032093385	-2.7382669428
С	5.1635286341	4.4513101548	-1.1145637829
С	0.8848807849	4.6670956440	3.3922266556
С	0.0421896932	4.9461578528	4.5211494926
Н	0.3970246082	4.3835316504	5.3801925047
Н	0.0805206321	6.0092770653	4.7418214035
Н	-0.9793339073	4.6577180484	4.2908331313
Ν	1.5591464734	4.4479173805	2.4981031740
0	4.2080227576	3.6213353261	2.3643187076
С	4.7319965606	4.6599888976	2.9193883902



Ο	4.4760900899	5.8099128379	2.5759723754
С	5.6644550150	4.3647520475	4.0727090973
С	6.9254720967	5.2158682542	4.0171383017
С	4.9194181645	4.6041263721	5.3879022112
Η	5.9384314140	3.3114938035	4.0218960825
С	7.8251483426	4.9354851545	5.2100118096
Η	6.6326807799	6.2658762841	4.0129021296
Η	7.4590403694	5.0293245063	3.0855681872
С	5.8175505895	4.3240951381	6.5814701009
Η	4.5908344229	5.6444675488	5.4128999654
Н	4.0252893189	3.9825762157	5.4273619540
С	7.0876737904	5.1571816445	6.5209022165
Η	8.7120197974	5.5659833105	5.1631525353
Н	8.1711928247	3.9006821487	5.1640188233
Н	5.2772581178	4.5217276523	7.5063516308
Н	6.0819754014	3.2647090330	6.5894408940
Н	7.7351525662	4.9200101609	7.3640170602
Н	6.8261231956	6.2138476847	6.6093849490
Ν	1.4431191066	4.0831835123	-0.3573124210
С	-0.4334095024	4.0806636457	-2.1239750009
Н	-0.6670032132	5.1058891714	-2.3974055410
Н	-0.1007321773	3.5355462261	-3.0027797767
Η	-1.3165808306	3.6032350677	-1.7092874230
С	0.6127276340	4.0812575989	-1.1403237264

E(RPW6B95D3) = -2464.96147156 E(RM06L) = -2462.93602524

	Charge = 0 N	Multiplicity = 1	
Cu	2.9468609971	4.8439322009	0.9346779466
Ν	3.8691207345	5.8379602860	-0.5668708219
С	5.1437725646	7.1112599062	-2.4209419712
Н	4.4706424007	7.8032235641	-2.9189944778
Н	5.9675641671	7.6650114858	-1.9796335956
Η	5.5342650438	6.4034564966	-3.1465928305
С	4.4323401042	6.4018112966	-1.3887397427
С	0.8726088678	6.7471931194	2.4157075617
С	-0.0141062839	7.6195251798	3.1425717346
Н	0.2375545394	7.5956157595	4.1990520907



Н	0.0889679816	8.6353057703	2.7716374053
Н	-1.0407457468	7.2905171158	3.0096293167
Ν	1.5807139318	6.0548729849	1.8415138356
0	4.1767732327	3.9171448994	2.3004063405
С	4.8535404838	4.6578284415	3.0793682186
0	4.9041874891	5.8938359130	3.0369006005
С	5.6355835205	3.9314409702	4.1695535681
С	7.0767924391	4.4153875890	4.2592429163
С	4.9375113707	4.1206941172	5.5155458330
Η	5.6329769402	2.8675921491	3.9300461988
С	7.8328378746	3.7161782257	5.3778624657
Η	7.0632486072	5.4910287167	4.4378158536
Η	7.5817757454	4.2588597216	3.3056289039
С	5.6868981876	3.4216148753	6.6381033949
Η	4.8827666414	5.1908947918	5.7237537515
Η	3.9129170076	3.7531521665	5.4566743078
С	7.1291419627	3.8965674649	6.7135517277
Η	8.8536503679	4.0932030275	5.4343034686
Η	7.9039927364	2.6494792095	5.1531132221
Η	5.1816986094	3.5906864315	7.5886917327
Η	5.6737077239	2.3437819591	6.4614978898
Η	7.6633505376	3.3637391304	7.4995221567
Η	7.1422122146	4.9550011179	6.9834485701
Ν	1.8825699149	3.2806555312	0.0981493266
С	0.5687818265	1.2866884884	-0.8936781898
Η	-0.3218269948	1.6513453093	-1.3974811678
Η	1.1943055735	0.7574231435	-1.6068798249
Η	0.2791097805	0.6084241972	-0.0962479529
С	1.3007418142	2.3978333172	-0.3409090567

E(RPW6B95D3) = -558.168370985 E(RM06L) = -557.349825518

	Charge = 1 N	Multiplicity = 1	
С	-1.6863279772	0.1795027215	0.7048763965
С	-0.4530852050	0.7899743952	0.7923187110
С	-0.2144012830	1.9933434985	0.1224973507
С	-1.2336857469	2.5794742773	-0.6365604944
С	-2.4605107392	1.9639646841	-0.7178825106



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С	-2.6880211020	0.7663198044	-0.0494740479
Н	-1.8678612808	-0.7484391139	1.2227413098
Н	0.3395436349	0.3477987290	1.3764510606
Н	-1.0766334284	3.5111726877	-1.1578261475
Н	-3.2483506956	2.4137484257	-1.3003681903
Н	-3.6547977884	0.2925717032	-0.1192125685
С	1.0909152502	2.5549376828	0.2732463831
Н	1.7888131247	2.0261116498	0.9034998505
Ν	1.5049460120	3.6424514241	-0.2827841133
С	2.7703502658	4.2574761065	-0.1614971812
С	2.9936213157	5.3685011975	-0.9594825611
С	3.7462635701	3.7940048707	0.7076507671
С	4.2110175569	6.0181974846	-0.8975366888
Н	2.2137971496	5.7141594266	-1.6213135933
С	4.9583899897	4.4528612514	0.7583931945
Н	3.5760413813	2.9416049759	1.3436991598
С	5.1966620843	5.5607276458	-0.0407971775
Н	4.3860793852	6.8814143580	-1.5195061930
Н	5.7218069891	4.0982545585	1.4324516228
Н	6.1475987285	6.0669264735	0.0094858553
Η	0.8681961307	4.1386776631	-0.8964282015

E(RPW6B95D3) = -2597.99433093 E(RM06L) = -2595.73210614

	Charge = 1	Multiplicity = 1	
С	-1.3063185872	4.2725562884	-2.6726916665
С	-1.6059356240	5.4883918659	-2.0761768740
С	-2.4336557852	5.5301110510	-0.9664172387
С	-2.9520698012	4.3571828874	-0.4529409685
С	-2.6294868786	3.1275809216	-1.0256789144
С	-1.8118486828	3.0976338493	-2.1529953178
С	-3.1949014225	1.9430908748	-0.3993785705
Ν	-2.7600118031	0.7479496785	-0.5035994732
Cu	-1.0842654295	-0.0718338419	-1.4963564374
С	-3.5076856543	-0.2567176470	0.1571034734
С	-4.8746518544	-0.3833396918	-0.0532169120
С	-5.5812963634	-1.3858197434	0.5891546915
С	-4.9337023167	-2.2569727207	1.4480518583



С	-3.5692816686	-2.1252742099	1.6588337617
С	-2.8544638358	-1.1374519501	1.0090361625
Ν	0.5729890516	1.0455413943	-1.1180180582
С	1.4500864955	1.7386009595	-0.8737166722
С	2.5460186692	2.6211225740	-0.5693749606
С	-2.2065655878	-0.4482743986	-6.0031873577
С	-1.8398166866	-0.3199753205	-4.6167502836
Ν	-1.5487126956	-0.2139896783	-3.5149830373
Ν	-0.6085671124	-2.0355736447	-1.1217549769
С	-0.3608276484	-3.1418436521	-0.9663178385
С	-0.0556003123	-4.5344669397	-0.7643996046
Н	-0.6795798571	4.2426363849	-3.5505293122
Н	-1.2045342669	6.4027673365	-2.4851664215
Η	-2.6791449671	6.4746717046	-0.5068065676
Η	-3.6061049008	4.3817351683	0.4062279083
Η	-1.5899924296	2.1609900670	-2.6347720837
Н	-4.0531950821	2.1337361716	0.2422350854
Η	-5.3708012720	0.2890516256	-0.7364529612
Н	-6.6411154574	-1.4864649921	0.4121138500
Η	-5.4861830982	-3.0380100406	1.9467023224
Η	-3.0581250494	-2.7981430339	2.3301752519
Η	-1.7918059071	-1.0302137540	1.1603177266
Н	3.4277108988	2.0374377129	-0.3207906574
Η	2.7581147236	3.2457722364	-1.4325364489
Н	2.2801423407	3.2509473388	0.2748989009
Η	-2.7521720568	-1.3758231201	-6.1512370220
Н	-2.8349588592	0.3898226970	-6.2908684810
Η	-1.3107162256	-0.4548606090	-6.6174181339
Η	0.9995309149	-4.6465855827	-0.5318614510
Η	-0.6497764080	-4.9192988785	0.0597701192
Н	-0.2873748019	-5.0923472412	-1.6672480417

4a

E(RPW6B95D3) = -794.007962980 E(RM06L) = -792.842152861

	Charge = 0 1	Multiplicity = 1	
С	-3.3643277888	0.1896690979	0.0032922531
С	-2.2546304760	0.9869407412	0.2277811364
С	-1.3159549754	1.1906419420	-0.7735507200



С	-1.5167197359	0.5896756898	-2.0089121820
С	-2.6231679035	-0.2104177514	-2.2376135730
С	-3.5514630762	-0.4139879831	-1.2295844268
Н	-4.0866654551	0.0418820463	0.7919368181
Н	-2.1138553915	1.4653962231	1.1852525085
Н	-0.8002623273	0.7595496993	-2.8001863296
Н	-2.7649110909	-0.6681026899	-3.2049830068
Н	-4.4188432198	-1.0314300358	-1.4064303085
С	-0.0835798736	2.0378099070	-0.5398810797
Ν	-0.3407681535	3.1297472729	0.3686972882
С	-1.0363067578	4.2544810810	0.0143652398
С	-1.0485745253	5.3575474103	0.8788950616
С	-1.7592596887	4.3444235890	-1.1791844393
С	-1.7568727184	6.4963988697	0.5615546849
Η	-0.4899006734	5.3021557922	1.8024954657
С	-2.4681090157	5.4954932534	-1.4821076780
Η	-1.7716549819	3.5163586137	-1.8686467191
С	-2.4781468848	6.5798665945	-0.6229264337
Η	-1.7453825724	7.3311391066	1.2467549792
Η	-3.0193486552	5.5380962748	-2.4099278589
Η	-3.0332166685	7.4717640865	-0.8672670324
С	1.1106396809	1.2289731097	-0.0062200867
С	0.8447631283	0.5428976375	1.3279887426
С	1.6188809449	0.2114546689	-1.0163153703
Η	1.9080875045	1.9623041370	0.1488150937
С	2.1034021836	-0.1359574339	1.8464491895
Η	0.0644967848	-0.2076560196	1.1915518173
Η	0.4717990127	1.2552310556	2.0633602437
С	2.8810351933	-0.4708635937	-0.5122086745
Η	0.8491574598	-0.5435587275	-1.1849037179
Η	1.8029199966	0.6975763979	-1.9744660686
С	2.6440995927	-1.1338685131	0.8351990491
Η	1.8966542520	-0.6312228553	2.7941678387
Η	2.8636930058	0.6224944624	2.0449893558
Η	3.2253143566	-1.2040910831	-1.2402261981
Η	3.6745484334	0.2727261997	-0.4123367796
Η	3.5645904246	-1.5856717710	1.2026434226
Η	1.9208830014	-1.9429624112	0.7119472914
Η	0.2195873975	2.4346178845	-1.5143727166
Н	0.3198871062	3.2472482139	1.1160131405

HA E(UPW6B95D3) = -1248.55343885 E(UM06L) = -1247.02164538

	Charge = 0 1	Multiplicity = 2	
С	-4.4316167967	-1.2280411041	0.1058875838
С	-3.0443969755	-1.2012160362	0.0369868141
С	-2.3382696759	0.0250783153	0.0424775019
С	-3.1009908511	1.2044555509	0.1014645520
С	-4.4757712470	1.1710884296	0.1681286433
С	-5.1464139308	-0.0479881129	0.1739236362
Η	-4.9360880738	-2.1831830429	0.1022342459
Η	-2.5892435151	2.1539138313	0.0922246001
Η	-5.0325362511	2.0941424103	0.2139160242
Η	-6.2234522311	-0.0770548360	0.2271541168
С	-0.9201047506	0.0091498111	-0.0265796987
С	-0.9709599700	-2.4337310224	-0.1274281556
С	-0.2288375803	-1.2277193818	-0.1171548091
С	-0.3337346344	-3.6647919579	-0.2149450768
С	1.0442540699	-3.7312688368	-0.2848860433
Η	1.5309204327	-4.6915415942	-0.3530623606
С	1.7968554594	-2.5616872718	-0.2612599548
Η	2.8737496977	-2.6111694589	-0.3060380641
С	1.1723221067	-1.3373662099	-0.1767885599
Η	1.7642394190	-0.4366063147	-0.1522828336
Ν	-2.3342712511	-2.3672996257	-0.0438146265
Η	-2.8485628660	-3.2329116882	-0.0510441695
С	-0.1646518113	1.2746781123	-0.0475544492
С	-0.0421788118	2.1010593364	1.0658544959
С	0.4705103269	1.6915809040	-1.2159882344
С	0.6591308685	3.2925416915	1.0259219038
С	1.1783154954	2.8764477746	-1.2745714555
Η	0.3948843003	1.0640659541	-2.0911115653
С	1.2698069017	3.6814334843	-0.1513480815
Η	0.7287514287	3.9021313211	1.9122495173
Η	1.6546416397	3.1725850882	-2.1960497436
Η	1.8183604480	4.6096244537	-0.1851415741
Cl	-0.7646838419	1.6281669095	2.5740347057
Н	-0.9334768417	-4.5629591391	-0.2250355462



A E(RPW6B95D3) = -1247.95790632 E(RM06L) = -1246.42602246

	Charge = 0 1	Multiplicity = 1	
С	-4.4223305096	-1.2388980687	0.0635864388
С	-3.0041214315	-1.2316999433	0.0043056749
С	-2.3236240654	0.0250940315	0.0098257032
С	-3.0903338559	1.2177303137	0.0680311225
С	-4.4459190482	1.1686551099	0.1250950180
С	-5.1197855884	-0.0759541040	0.1238190344
Η	-4.9195040251	-2.1965583994	0.0588310683
Η	-2.5795952579	2.1678997823	0.0650269067
Η	-5.0189576792	2.0815529048	0.1696467481
Η	-6.1978146784	-0.0934835241	0.1692851429
С	-0.9285313373	0.0213665927	-0.0447367803
С	-1.0363066122	-2.4003388567	-0.1087830043
С	-0.2568238673	-1.2009383488	-0.1028593262
С	-0.3644903238	-3.6494567976	-0.1694559825
С	0.9908632316	-3.7069726590	-0.2124041785
Η	1.4906618021	-4.6623088026	-0.2571410698
С	1.7627424812	-2.5210242334	-0.1936814926
Η	2.8390949199	-2.5888049840	-0.2196549113
С	1.1587196675	-1.3062701356	-0.1406412721
Η	1.7499845401	-0.4047285617	-0.1226404836
Ν	-2.3668721136	-2.3999906339	-0.0561566776
С	-0.1722021737	1.2933951252	-0.0643870887
С	0.0130932847	2.0655557904	1.0753615751
С	0.3822046940	1.7522543990	-1.2543104028
С	0.7186264972	3.2541415389	1.0430017283
С	1.0866221470	2.9399809579	-1.3042943726
Η	0.2491259914	1.1619056556	-2.1478271094
С	1.2542984483	3.6914684249	-0.1538122362
Η	0.8461464145	3.8256243010	1.9479139851
Η	1.5038170279	3.2771365401	-2.2399068758
Η	1.8041933262	4.6189623073	-0.1818645712
Cl	-0.6391032291	1.5323886377	2.5938011693
Н	-0.9688704507	-4.5433499939	-0.1772933358



HA+ E(UPW6B95D3) = -1248.41967033 E(RM06L) = -1246.89103525

	Charge = 1	Multiplicity = 1	
С	-4.4277023678	-1.2398803970	0.0877830797
С	-3.0270595859	-1.2082857450	0.0219575475
С	-2.3237973136	0.0225622322	0.0279852441
С	-3.0804373277	1.2178946905	0.0874116286
С	-4.4367031516	1.1733231813	0.1514860339
С	-5.1126623838	-0.0649360542	0.1544266406
Η	-4.9325063728	-2.1932913361	0.0834219900
Η	-2.5638251752	2.1633216164	0.0753299126
Η	-5.0065210507	2.0871600751	0.1961779796
Η	-6.1898393519	-0.0793410283	0.2056696238
С	-0.9246979121	0.0050461875	-0.0347003002
С	-0.9870494541	-2.4199163890	-0.1211369426
С	-0.2401063747	-1.2141267795	-0.1076101989
С	-0.3457986840	-3.6648040773	-0.1995099712
С	1.0141787615	-3.7060617099	-0.2532366593
Η	1.5151602225	-4.6592296439	-0.3128534838
С	1.7804538976	-2.5223974778	-0.2248451749
Η	2.8558713917	-2.5875753465	-0.2572714943
С	1.1728455743	-1.3093643793	-0.1531868964
Η	1.7563904461	-0.4045319161	-0.1259637149
Ν	-2.3277856946	-2.3539806469	-0.0533281763
Η	-2.8440776874	-3.2251240575	-0.0618366742
С	-0.1667051616	1.2734425957	-0.0553975843
С	-0.0085785534	2.0589069578	1.0791328555
С	0.4141729151	1.7047145998	-1.2425005513
С	0.7008786686	3.2440768553	1.0411138672
С	1.1180131234	2.8920259692	-1.2945679065
Η	0.3010479326	1.0979497857	-2.1274386055
С	1.2606187228	3.6606250965	-0.1521949489
Η	0.8134839752	3.8286963739	1.9394314487
Η	1.5563258478	3.2139192694	-2.2255992750
Η	1.8127140281	4.5865531652	-0.1833404352
Cl	-0.6875280916	1.5416094650	2.5889360144
Η	-0.9422778126	-4.5633741323	-0.2133698727



TS1 E(UPW6B95D3) = -793.316671142 E(UM06L) = -792.158874675

	Charge = 0 N	Aultiplicity = 2	
С	-1.6548108251	0.2075919823	0.0702238756
С	-0.4204291779	0.7757328129	0.3326649208
С	-0.2171416107	2.1402759699	0.1577731172
С	-1.2765459134	2.9299522670	-0.2811651164
С	-2.5104287498	2.3639798242	-0.5354328875
С	-2.7043403282	1.0005079988	-0.3621165365
Н	-1.7973614350	-0.8537340965	0.2048193342
Н	0.3994776076	0.1604345244	0.6736556819
Н	-1.1196261791	3.9886327505	-0.4176344263
Н	-3.3268408495	2.9855969481	-0.8705560223
Н	-3.6690170395	0.5607310123	-0.5637733854
С	1.1105166067	2.7078702209	0.4249783711
Η	1.8465327204	2.0019464634	0.8074236575
Ν	1.4592837006	3.8357356354	-0.1204734548
С	2.7866440841	4.2331807679	-0.1221721359
С	3.0473555617	5.6034112655	-0.2148094032
С	3.8755638885	3.3540904584	-0.0841372600
С	4.3423503915	6.0819070757	-0.2253100622
Н	2.2085678949	6.2814893017	-0.2622575336
С	5.1691467681	3.8390681323	-0.1069146585
Η	3.7079569513	2.2886956703	-0.0622396340
С	5.4135224609	5.2028617746	-0.1674978128
Η	4.5183737739	7.1454337164	-0.2834295820
Η	5.9959020947	3.1448413358	-0.0849738882
Η	6.4263142885	5.5742650187	-0.1848982543
С	0.4559896200	1.9285123396	3.2942427618
С	0.4635473202	2.1422937309	4.8159980946
С	1.7608908172	2.7890738901	5.2689719685
С	2.0018439024	4.1007213481	4.5418045695
С	2.0001847116	3.8896355793	3.0203940591
С	0.7417363726	3.2164846640	2.6128236393
Н	1.7404005264	2.9552326965	6.3451955119
Η	-0.3758907953	2.7829337063	5.0894465931
Η	0.3122628455	1.1853751402	5.3136990210
Η	1.2337976323	1.2008869113	3.0481184300



Η	-0.4971389739	1.5131494278	2.9802133571
Η	1.2170015669	4.8111752185	4.8050766548
Η	2.9501496459	4.5433821951	4.8431597679
Η	2.1273147973	4.8388999907	2.5079273231
Η	2.8540604386	3.2578502444	2.7632293710
Η	-0.1053852929	3.8535893406	2.3936231571
Н	2.5912441801	2.1090657458	5.0677088156

TS2

E(UPW6B95D3) = -793.783111322 E(UM06L) = -792.627108644

Charge = 1 Multiplicity = 2

	_		
С	-1.7881853312	1.2273677443	1.8347925235
С	-0.5397393548	1.4038746673	1.2754876595
С	0.0536775224	2.6673721523	1.2553264609
С	-0.6353179886	3.7531644776	1.8011142545
С	-1.8845444833	3.5699559700	2.3561447644
С	-2.4619713569	2.3089701207	2.3793014966
Н	-2.2370082096	0.2467599275	1.8466948258
Н	-0.0083534802	0.5664970454	0.8493474515
Н	-0.2035766280	4.7423799309	1.8114112943
Н	-2.4086179384	4.4122083504	2.7793526962
Н	-3.4368726873	2.1716825086	2.8203822940
С	1.3727742008	2.7785411607	0.6795316795
Н	1.7854694548	1.8987756192	0.2149807510
Ν	1.8819709418	3.9482105187	0.3229614928
С	3.0847353582	4.1816472916	-0.3471598518
С	3.4689514389	5.5065615361	-0.5261191864
С	3.8841285685	3.1502863657	-0.8264023580
С	4.6470787158	5.7969506119	-1.1826781683
Н	2.8391599510	6.2982048344	-0.1478068854
С	5.0620341979	3.4566305177	-1.4803574045
Η	3.5999257312	2.1188590544	-0.6987018273
С	5.4497848169	4.7740683189	-1.6620669271
Η	4.9390744535	6.8263384924	-1.3185102624
Н	5.6805184281	2.6545759543	-1.8514268963
Η	6.3708722847	5.0017493989	-2.1747677335
С	2.4883403595	3.2903012643	3.4696986290
С	1.9550130041	2.7703357672	4.7978016045



0.8442127583	1.7644021060	4.5626606600
1.3861432046	0.5134769441	3.8865055612
2.3982062554	0.8019646390	2.7681564083
2.6869048674	2.2184949415	2.4645010280
0.3701966524	1.4894071753	5.5024884920
2.7629685619	2.2937418083	5.3540290700
1.6051347456	3.6074496216	5.3968925974
1.7979729282	4.0434312633	3.0758187954
3.4320580084	3.8224452847	3.5993069685
1.8752429470	-0.1024157997	4.6386767038
0.5642317023	-0.0779945177	3.4920086326
3.3730739980	0.3758036842	3.0372591833
2.1370679358	0.2798521693	1.8469058097
3.4788783596	2.3738099856	1.7451923817
0.0725666510	2.2242055959	3.9460305689
1.3945064542	4.7829914971	0.6147217623
	0.8442127583 1.3861432046 2.3982062554 2.6869048674 0.3701966524 2.7629685619 1.6051347456 1.7979729282 3.4320580084 1.8752429470 0.5642317023 3.3730739980 2.1370679358 3.4788783596 0.0725666510 1.3945064542	0.84421275831.76440210601.38614320460.51347694412.39820625540.80196463902.68690486742.21849494150.37019665241.48940717532.76296856192.29374180831.60513474563.60744962161.79797292824.04343126333.43205800843.82244528471.8752429470-0.10241579970.5642317023-0.07799451773.37307399800.37580368422.13706793580.27985216933.47887835962.37380998560.07256665102.22420559591.39450645424.782914971

TS3

E(UPW6B95D3) = -2833.60793761 E(UM06L) = -2831.01007754

	Charge = 1	Multiplicity = 2	
С	3.9935392749	2.3316884472	-3.6902013886
С	3.0733732232	2.6513363927	-2.7096524629
С	2.2398021560	1.6705305462	-2.1805001133
С	2.3324823002	0.3713668987	-2.6743843371
С	3.2597651450	0.0499615242	-3.6478690027
С	4.0955526623	1.0304578908	-4.1574683394
Η	4.6323350151	3.1020050338	-4.0945992245
Н	2.9921978480	3.6672843539	-2.3600147568
Η	1.6725689622	-0.3886539571	-2.2822922475
Η	3.3274251663	-0.9635543386	-4.0120001973
Η	4.8163312325	0.7846585258	-4.9220480205
С	1.2275568033	1.9438164283	-1.1614696642
Ν	1.3534141782	2.8676598818	-0.2443646743
С	0.3476472243	2.9277221888	0.7355932301
С	-0.1888728228	1.7903799683	1.3360365492
С	-0.1113491970	4.1812086463	1.1334450100
С	-1.1690156707	1.9115084160	2.3046180341
Н	0.1846685388	0.8145024252	1.0666919463



С	-1.1004123421	4.2949210199	2.0909671109
Η	0.3220920287	5.0586664026	0.6773743178
С	-1.6346956541	3.1604362237	2.6824372948
Η	-1.5650446386	1.0230396898	2.7724699571
Η	-1.4519921333	5.2734989267	2.3805076666
Η	-2.3996142436	3.2496593817	3.4380733085
С	-0.4297041997	2.8094504819	-2.4667937017
С	-0.0721944819	4.2308562091	-2.6788271289
С	-0.5330954581	1.9872682465	-3.6949845348
Η	-1.1431748989	2.6034782139	-1.6779957108
С	-1.1156005113	4.8700003653	-3.6089474364
Η	0.9032457260	4.2970947589	-3.1652025887
Η	-0.0146775050	4.7729392660	-1.7389985395
С	-1.5886569181	2.6192414984	-4.6185863115
Η	0.4215527885	1.9921686170	-4.2243696357
Η	-0.7878778880	0.9538127767	-3.4708743407
С	-1.2507578422	4.0747393110	-4.8969515866
Η	-0.8298064102	5.9001479645	-3.8180115640
Η	-2.0781993416	4.9010900280	-3.0970606624
Η	-1.6424249314	2.0503051458	-5.5456034315
Η	-2.5680026896	2.5553609040	-4.1430781496
Η	-2.0142142681	4.5205111596	-5.5330175673
Η	-0.3094817435	4.1232316829	-5.4482301899
Η	0.5122119395	1.1418335250	-1.0098630615
Cu	2.9273023495	4.1732388292	0.1568559424
Ν	2.6996473333	5.8676864956	-0.9717872605
С	2.0280421616	7.6979761541	-2.6680901205
Η	2.7421956550	8.5161160343	-2.6421003252
Η	2.0100742521	7.2665951344	-3.6652424851
Η	1.0395476834	8.0742315824	-2.4200210313
С	2.4101498214	6.6865940023	-1.7174407220
С	2.7155515596	4.8668619364	3.2788119084
С	2.5363954247	5.1157975907	4.6856323054
Η	1.4742914405	5.1597786637	4.9110785885
Η	2.9934753270	4.3141161689	5.2585299299
Η	3.0019436860	6.0603228528	4.9521589731
Ν	2.8438248090	4.6660311068	2.1595548166
Ν	4.7893208695	3.3797720228	-0.0954979657
С	7.0105955734	2.1863228976	-0.6592691650
Η	7.8367005965	2.8889918438	-0.5982989485

TsO	-		
С	5.7777366462	2.8552095521	-0.3349239336
Η	6.9476825368	1.7896457729	-1.6691578222
Н	7.1782798513	1.3708442882	0.0382944604

E(RPW6B95D3) = -896.143503551 E(RM06L) = -895.134743536

	Charge = -1	Multiplicity = 1	
С	-0.3922939448	0.7337995954	-0.1405138736
С	0.9890706195	0.7543427365	-0.0762706533
С	1.6596113066	1.9566526072	0.0824864476
С	0.9353863508	3.1329110779	0.1792824369
С	-0.4468044242	3.1041032024	0.1144157117
С	-1.1338447341	1.9064698636	-0.0447574797
Η	-0.9059279667	-0.2088421759	-0.2649444683
Η	1.5533639592	-0.1628882156	-0.1423018138
Η	1.4575688846	4.0676065244	0.3118301456
Η	-1.0032971605	4.0272644441	0.1907437314
S	3.4405107633	1.9920476295	0.0989145287
С	-2.6291405800	1.8744005848	-0.0803154557
Η	-3.0354606890	2.8194985796	-0.4303264204
Η	-2.9913805809	1.0801024857	-0.7279362045
Η	-3.0357285934	1.6922352838	0.9144824804
0	3.8432769505	0.7302247877	0.7009877002
0	3.7962929041	3.1588310498	0.8918235791
0	3.8260179350	2.1092669389	-1.3012123922

TsOH

E(RPW6B95D3) = -896.589700974 E(RM06L) = -895.584096480

	Charge = 0 1	Multiplicity = 1	
С	-0.3956036135	0.7226967162	-0.1212523724
С	0.9830576341	0.7322566547	-0.0452989063
С	1.6384994689	1.9427521608	0.1078758116
С	0.9350203869	3.1343523685	0.1870719884
С	-0.4420230568	3.1041350361	0.1097571134
С	-1.1277040553	1.9025067379	-0.0436474963
Н	-0.9133714124	-0.2168716310	-0.2413116995
Н	1.5438621704	-0.1867380352	-0.0989372610


Η	1.4592932195	4.0680748947	0.3119305792
Н	-0.9972044799	4.0279307682	0.1704904012
S	3.3840788318	1.9736132456	0.1833128981
С	-2.6198518017	1.8783223966	-0.0942286492
Η	-3.0138626317	2.7913890096	-0.5313875782
Η	-2.9803821036	1.0284471440	-0.6664985804
Η	-3.0302089117	1.7941158263	0.9119346279
0	3.8613572348	0.6724166032	0.5324393012
0	3.8123668595	3.1207747599	0.9126665677
0	3.8298980965	2.2778515646	-1.3085289878
Н	3.7527126743	1.4781921190	-1.8538918577

X-Ray crystallogrophic data

N-(Cyclohexyl(phenyl)methyl)-4-methylaniline (4b)

Bond precision:		C-C = 0.0015 A		Wavelength=1.54184	
Cell:	a=5.64642(5)	b=20.4	2415(18)	c=13.59672(11)	
	alpha=90	beta=9	2.2646(7)	gamma=90	
Temperatur	e: 100 K				
	(Calculated		Reported	
Volume	1	566.79(2)		1566.79(2)	
Space group	ŀ	P 21/n		P 1 21/n 1	
Hall group	-	P 2yn		-P 2yn	
Moiety form	ula C	C20 H25 N		C20 H25 N	
Sum formul	a (C20 H25 N		C20 H25 N	
Mr	2	279.41		279.41	
Dx,g cm-3	1	.184		1.185	
Z	4	Ł		4	
Mu (mm-1)	С	0.507		0.507	
F000	6	508.0		608.0	
F000'	6	609.48			
h,k,lmax	7	7,25,17		7,25,17	
Nref	3	3296		3256	
Tmin,Tmax	С).928,0.978		0.465,1.000	
Tmin'	C	0.881			
Correction n	nethod= # Repor	rted T Limits: Tm	in=0.465 Tmax=	=1.000 AbsCorr = GAUSSIAN	
Data completeness= 0.988		Theta(max)= 7	76.664		
R(reflections)= 0.0389(3003)				wR2(reflections)= 0.1021(3256)	
S = 1.041		Npar= 192			



N-(Cyclohexyl(pyridin-4-yl)methyl)aniline (51) CCDC 2340502

Bond precision:		C-C = 0.0024 A		V	Vavelength=1.54184
Cell:	a=9.2584(2)		b=9.9261(2)	c=11.8278(3)	
	alpha=93.448	3(2)	beta=90.414(2)	gamma=96.639	0(2)
Temperature:	100 K				
		Calculated	l		Reported
Volume		1077.62(4)			1077.62(4)
Space group		P -1			P -1
Hall group		-P 1			-P 1
Moiety formul	a	C18 H22 N2, C7 H12 O2			C7 H12 O2, C18 H22 N2
Sum formula		C25 H34 N	J2 O2		C25 H34 N2 O2
Mr		394.54			394.54
Dx,g cm-3		1.216			1.216
Z		2			2
Mu (mm-1)		0.598			0.598
F000		428.0			428.0
F000'		429.16			
h,k,lmax		11,12,14			11,12,14
Nref		4534			4297
Tmin,Tmax		0.934,0.958	3		0.667,1.000
Tmin'		0.909			
Correction method= # Reported T Limits: Tmin=0.667 Tmax=1.000 AbsCorr = GAUSSIAN					
Data completeness= 0.948			Theta(max)=	76.849	
R(reflections)= 0.0521(3797		wR2(re		wR2(refl	ections)= 0.1297(4297)
S = 1.022		Npar	= 296		



N-(Benzofuran-2-yl(cyclohexyl)methyl)aniline (5n)

Bond precision:		C-C = 0.0019 A		Wavelength=1.54184	
Cell:	a=5.71447(11)	b=17.9506(3)	c=16.3618(3)	
	alpha=90		beta=99.380(2)	gamma=90	
Temperature:	100 K				
		Calculated	l		Reported
Volume		1655.92(5)			1655.93(6)
Space group		P 21/n			P 1 21/n 1
Hall group		-P 2yn			-P 2yn
Moiety formul	a	C21 H23 N O			C21 H23 N O
Sum formula		C21 H23 N	10		C21 H23 N O
Mr		305.40			305.40
Dx,g cm-3		1.225			1.225
Z		4			4
Mu (mm-1)		0.575			0.575
F000		656.0			656.0
F000'		657.75			
h,k,lmax		7,22,20			7,22,20
Nref		3495			3206
Tmin,Tmax		0.917,0.960)		0.536,1.000
Tmin'		0.901			
Correction method= # Reported T Limits: Tmin=0.536 Tmax=1.000 AbsCorr = GAUSSIAN					
Data completeness= 0.917		Theta(max)=	= 76.736		
R(reflections)= 0.0409(2778)			wR2(ref	lections)= 0.1053(3206)	
S = 1.051		Npar	= 208		



N-(Phenyl(tetrahydro-2H-pyran-4-yl)methyl)aniline (6h)

Bond precision:		C-C = 0.0015 A		Wavelength=1.54184	
Cell:	a=9.75307(9)		b=16.23315(13)	c=18.76027(18)	
	alpha=90		beta=90	gamma=90	
Temperature:	100 K				
		Calculated	1		Reported
Volume		2970.18(5)			2970.18(5)
Space group		Pbca			Pbca
Hall group		-P 2ac 2ab			-P 2ac 2ab
Moiety formul	la	C18 H21 N	10		C18 H21 N O
Sum formula		C18 H21 N	10		C18 H21 N O
Mr		267.36			267.36
Dx,g cm-3		1.196			1.196
Z		8			8
Mu (mm-1)		0.568			0.568
F000		1152.0			1152.0
F000'		1155.08			
h,k,lmax		12,20,23			12,19,23
Nref		3107			3000
Tmin,Tmax		0.949,0.959)		0.547,1.000
Tmin'		0.887			
Correction method= # Reported T Limits: Tmin=0.547 Tmax=1.000 AbsCorr = GAUSSIAN					
Data completeness= 0.966		Theta(max)=	= 76.115		
R(reflections)= 0.0348(2725)			wR2(reflections)= 0.0928(3000)		
S = 1.019		Npai	= 185		



Ethyl 2-((4-methoxyphenyl)amino)-2-(1-phenylcyclohexyl)acetate (7w)

Bond precision:		C-C = 0.0044 A		V	Vavelength=1.54184
Cell:	a=8.8935(2)		b=14.9861(4)	c=16.6162(3)	
	alpha=112.73	39(2)	beta=90.306(2)	gamma=103.67	6(2)
Temperature:	100 K				
		Calculated	1		Reported
Volume		1972.96(9)			1972.96(8)
Space group		P -1			P -1
Hall group		-P 1			-P 1
Moiety formul	a	C23 H29 N	J O3		C23 H29 N O3
Sum formula		C23 H29 N	J O3		C23 H29 N O3
Mr		367.47			367.47
Dx,g cm-3		1.237			1.237
Ζ		4			4
Mu (mm-1)		0.643			0.643
F000		792.0			792.0
F000'		794.27			
h,k,lmax		11,18,21			11,18,20
Nref		8377			8018
Tmin,Tmax		0.916,0.944	ł		0.648,1.000
Tmin'		0.873			
Correction method= # Reported T Limits: Tmin=0.648 Tmax=1.000 AbsCorr = GAUSSIAN					
Data completeness= 0.957		Theta(max)=	= 77.326		
R(reflections)= 0.0783(6789)			wR2(refle	ections)= 0.1732(8018)	
S = 1.073		Npai	= 497		



NMR Spectroscopic data

N-(Cyclohexyl(phenyl)methyl)aniline (4a)



N-(Cyclohexyl(phenyl)methyl)aniline (4a)







N-(Cyclohexyl(phenyl)methyl)-4-methylaniline (4b)





N-(Cyclohexyl(phenyl)methyl)-3,4,5-trimethylaniline (4c)





N-(Cyclohexyl(phenyl)methyl)-2,3-dihydro-1H-inden-5-amine (4d)



N-(Cyclohexyl(phenyl)methyl)-4-fluoroaniline (4e)







4-Chloro-N-(cyclohexyl(phenyl)methyl)aniline (4f)



3-Bromo-N-(cyclohexyl(phenyl)methyl)aniline (4g)









N-(Cyclohexyl(phenyl)methyl)-3-iodoaniline (4h)



N-(Cyclohexyl(phenyl)methyl)-2-methoxyaniline (4i)







N-(Cyclohexyl(phenyl)methyl)-3-(methylthio)aniline (4j)





N-(Cyclohexyl(phenyl)methyl)-3-(trifluoromethoxy)aniline (4k)





N-(Cyclohexyl(phenyl)methyl)-[1,1'-biphenyl]-4-amine (41)









N-(Cyclohexyl(phenyl)methyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (4n)



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N-(Cyclohexyl(phenyl)methyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (40)




N-(Cyclohexyl(phenyl)methyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (4p)





N-(Cyclohexyl(phenyl)methyl)benzo[d]thiazol-6-amine (4q)





N-(Cyclohexyl(phenyl)methyl)-3-(oxazol-4-yl)aniline (4r)



N-(cyclohexyl(*o*-tolyl)methyl)aniline (5a)







N-(Cyclohexyl(*m*-tolyl)methyl)aniline (5b)







N-((4-(tert-butyl)phenyl)(cyclohexyl)methyl)aniline (5c)





N-(Cyclohexyl(2-fluorophenyl)methyl)aniline (5d)







N-((4-Chlorophenyl)(cyclohexyl)methyl)aniline (5e)







N-(Cyclohexyl(4-methoxyphenyl)methyl)aniline (5f)





N-(cyclohexyl(3,4,5-trimethoxyphenyl)methyl)aniline (5g)





N-(4-(Cyclohexyl(phenylamino)methyl)phenyl)acetamide (5h)









N-(Cyclohexyl(naphthalen-2-yl)methyl)aniline (5j)



N-(Cyclohexyl(naphthalen-1-yl)methyl)aniline (5k)







N-(Cyclohexyl(pyridin-4-yl)methyl)aniline (51)







N-(Cyclohexyl(6-methylpyridin-2-yl)methyl)aniline (5m)





N-(Benzofuran-2-yl(cyclohexyl)methyl)aniline (5n)

N-(Benzofuran-2-yl(cyclohexyl)methyl)aniline (5n)





tert-butyl 5-(cyclohexyl(phenylamino)methyl)-1H-indole-1-carboxylate (50)



tert-butyl 5-(cyclohexyl(phenylamino)methyl)-1H-indole-1-carboxylate (50)


1-(5-(Cyclohexyl(phenylamino)methyl)-1*H*-indol-1-yl)ethan-1-one (5p)



N-(1-Phenylpentyl)aniline (6a)









N-(2-Methyl-1-phenylpropyl)aniline (6b)



N-(1-Phenyl-2-propylpentyl)aniline (6c)







N-(2-Hexyl-1-phenyldecyl)aniline (6d)



N-(Cyclobutyl(phenyl)methyl)aniline (6e)





N-(Cyclopentyl(phenyl)methyl)aniline (6f)





N-(Cycloheptyl(phenyl)methyl)aniline (6g)





N-(Phenyl(tetrahydro-2H-pyran-4-yl)methyl)aniline (6h)



N-(Phenyl(tetrahydro-2H-pyran-4-yl)methyl)aniline (6h)



N-(2,2-Dimethyl-1-phenylpropyl)aniline (6i)













N-((1-Methylcyclohexyl)(phenyl)methyl)aniline (6k)





N-((4-Methyltetrahydro-2H-pyran-4-yl)(phenyl)methyl)aniline (6l)





N-((Hexahydro-2,5-methanopentalen-3a(1H)-yl)(phenyl)methyl)aniline (6m)





N-(((1s,3s)-Adamantan-1-yl)(phenyl)methyl)aniline (6n)

N-(((1s,3s)-Adamantan-1-yl)(phenyl)methyl)aniline (6n)











Ethyl 2-((4-methoxyphenyl)amino)-5-methylhexanoate (7b)





Ethyl 2-((4-methoxyphenyl)amino)undecanoate (7c)

Ethyl 2-((4-methoxyphenyl)amino)undecanoate (7c)




Ethyl 5,5,5-trifluoro-2-((4-methoxyphenyl)amino)pentanoate (7d)





Ethyl 2-((4-methoxyphenyl)amino)-4,4,4-triphenylbutanoate (7e)





Ethyl 3-(4-chlorophenyl)-2-((4-methoxyphenyl)amino)propanoate (7f)





Ethyl 4-(4-fluorophenyl)-2-((4-methoxyphenyl)amino)butanoate (7g)





Ethyl 2-((4-methoxyphenyl)amino)-5-phenylpentanoate (7h)





Ethyl 2-((4-methoxyphenyl)amino)-6-phenylhexanoate (7i)





Ethyl 2-cyclopentyl-2-((4-methoxyphenyl)amino)acetate (7j)





Ethyl 2-cyclohexyl-2-((4-methoxyphenyl)amino)acetate (7k)





Ethyl 2-cycloheptyl-2-((4-methoxyphenyl)amino)acetate (71)



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Ethyl 2-cyclobutyl-2-((4-methoxyphenyl)amino)acetate (7m)





Ethyl 2-((4-methoxyphenyl)amino)-2-(tetrahydro-2H-pyran-4-yl)acetate (7n)





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Ethyl (4-methoxyphenyl)valinate (70)





Ethyl 2-((4-methoxyphenyl)amino)-3-propylhexanoate (7p)





Ethyl 3-hexyl-2-((4-methoxyphenyl)amino)decanoate (7q)





Ethyl 2-(2,3-dihydro-1H-inden-2-yl)-2-((4-methoxyphenyl)amino)acetate (7r)





Ethyl 2-((4-methoxyphenyl)amino)-3,3-dimethylbutanoate (7s)











Ethyl 2-((4-methoxyphenyl)amino)-2-(1-methylcyclohexyl)acetate (7u)




Ethyl 2-((4-methoxyphenyl)amino)-2-(4-methyltetrahydro-2*H*-pyran-4-yl)acetate (7v)





Ethyl 2-((4-methoxyphenyl)amino)-2-(1-phenylcyclohexyl)acetate (7w)





Ethyl 2-((4-methoxyphenyl)amino)-3-methyl-3-phenylbutanoate (7x)









Ethyl 2-((3,5,7)-adamantan-1-yl)-2-((4-methoxyphenyl)amino)acetate (7y)



Isopropyl 2-cyclohexyl-2-((4-methoxyphenyl)amino)acetate (7z)





Benzyl 2-cyclohexyl-2-((4-methoxyphenyl)amino)acetate (7za)





N-(5-(2,5-Dimethylphenoxy)-2,2-dimethyl-1-phenylpentyl)aniline (8a)







Ethyl 6-(2,5-dimethylphenoxy)-2-((4-methoxyphenyl)amino)-3,3-dimethylhexanoate (8b)





Ethyl 2-((4-methoxyphenyl)amino)-3-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)propanoate (8c)





Ethyl 3-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)-2-((4-methoxyphenyl)amino)propanoate (8d)





(3*R*,7*R*,8*R*,9*R*,10*S*,13*R*,14*R*,17*R*)-17-((2*R*)-6-Ethoxy-5-((4-methoxyphenyl)amino)-6-oxohexan-2-yl)-8,10,13-trimethylhexadecahydro-1H-cyclopenta[*a*]phenanthrene-3,7-diyl diacetate (8e)



(3*R*,7*R*,8*R*,9*R*,10*S*,13*R*,14*R*,17*R*)-17-((2*R*)-6-Ethoxy-5-((4-methoxyphenyl)amino)-6-oxohexan-2-yl)-8,10,13-trimethylhexadecahydro-1H-cyclopenta[*a*]phenanthrene-3,7-diyl diacetate (8e)



1-Cyclohexyl 5-ethyl (2S)-2-((tert-butoxycarbonyl)amino)-4-((4-methoxyphenyl)amino)pentanedioate (8f)



1-Cyclohexyl 5-ethyl (2S)-2-((tert-butoxycarbonyl)amino)-4-((4-methoxyphenyl)amino)pentanedioate (8f)



1-Benzyl 6-ethyl (2S)-2-(((benzyloxy)carbonyl)amino)-5-((4-methoxyphenyl)amino)hexanedioate (8g)



1-Benzyl 6-ethyl (2S)-2-(((benzyloxy)carbonyl)amino)-5-((4-methoxyphenyl)amino)hexanedioate (8g)



1-Ethyl 6-((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydrobenzo[1,2-*d*:3,4-*d*']bis([1,3]dioxole)-3a(4*H*)-yl) 2-((4-methoxyphenyl)amino)hexanedioate (8h)



1-Ethyl 6-((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydrobenzo[1,2-*d*:3,4-*d*']bis([1,3]dioxole)-3a(4*H*)-yl) 2-((4-methoxyphenyl)amino)hexanedioate (8h)

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