Supporting Information for

Synthesis of Tetrahydroisoquinolines by Visible-light Mediated 6-exo-trig Cyclization of α-Aminoalkyl Radicals

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**Experimental**

**Materials**

Chemicals were purchased from *Sigma Aldrich* and used without further purification, unless otherwise mentioned. Iridium catalysts were prepared according to literature\(^1\) or purchased from *Sigma Aldrich*. Moisture or air sensitive reactions were conducted in flame-dried glass vessels under argon atmosphere. Dry solvents (MeOH, DMF) were purchased from *Acros Organics*. Dry CH\(_2\)Cl\(_2\) and THF were taken from a MB-SPS-800 apparatus (*M. Braun*).

All solvents were deoxygenized via freeze-pump-thaw procedure prior to use. Dimethylformamide (DMF; 99.8% stored over molecular sieves). Tetrabutylammonium hexafluorophosphate was recrystallized four times from EtOH before use.

**Physical Measurements**

Solution state NMR spectra were recorded at room temperature on a *Bruker AVA 400*, *Bruker AVA 500* or *Bruker AVA 500cryo*. \(^1\)H-NMR spectra were calibrated to the residual solvent signal of chloroform-\(d_1\) (CHCl\(_3\) \(\delta = 7.26\) ppm), benzene-\(d_6\) (C\(_6\)H\(_6\) \(\delta = 7.16\) ppm) or methanol-\(d_4\) (MeOD \(\delta = 3.31\) ppm). \(^1^3\)C-NMR spectra were calibrated to the \(^1^3\)C-D triplet of CDCl\(_3\) (\(\delta = 77.16\) ppm), benzene-\(d_6\) (C\(_6\)H\(_6\) \(\delta = 128.06\) ppm) or methanol-\(d_4\) (MeOD \(\delta = 49.0\) ppm). The following abbreviations for single multiplicities were used: s-singlet, d-doublet, t-triplet, q-quartet, quin-quintet.

HRMS measurements were performed on a Thermo Scientific DFS-HRMS spectrometer (EI, 70 eV), a FinniganLCQ classic (ESI) and a ThermoFinnigan LTQ FT (HRMS-ESI). ESI mass spectra were measured on a Thermo Scientific™ UltiMate™ 3000 HPLC System using loop mode. Electrochemical measurements were carried out with an EmStat\(^{3+}\) potentiostat using a three-electrode cell equipped with glassy carbon working and counter electrode and a Ag/AgNO\(_3\) as reference electrode. Potentials are reported with reference to AgNO\(_3\). Melting points were measured on a Kofler melting point apparatus (Reichert) and are uncorrected. Infrared spectra were recorded on a PerkinElmer IR 4100 spectrometer directly measuring in substance via a total reflection method (ATR). Intensities are assigned as: w = weak, m = medium, s = strong. GC analysis was performed on an Agilent 7890B instrument (FID) with a HP 5 column (30 mm × 320 \(\mu\)m, 0.25 \(\mu\)m).
Single crystal X-Ray Crystallography

Data were collected on an X-ray single crystal diffractometer equipped with a CMOS detector (Bruker Photon-100), a IMS microsource with MoK$_\alpha$ radiation ($\lambda = 0.71073 $ Å) and a Helios mirror optic by using the APEX III software package.$^2$ The measurements were performed on a single crystal coated with perfluorinated ether. The crystal was fixed on top of a microsampler, transferred to the diffractometer and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorentz and polarization effects, scan speed, and background using SAINT.$^3$ Absorption corrections, including odd and even ordered spherical harmonics, were performed using SADABS.$^3$ Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using SHELXL$^4$ in conjunction with SHELXL-2014$^5$. Hydrogen atoms were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogen atoms). If not mentioned otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2-F_c^2)^2$ with SHELXL-97$^6$ weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.$^7$ Images of the crystal structures were generated by PLATON.$^8,9$ CCDC 1915022 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.
Photochemical experiments

All photochemical experiments were carried out using an individually built photoreactor. The interior of the photoreactor is lined with high performance mirrors. The lid and the LED with heat sink are exchangeable. The installed LEDs (10) are Cree XLamp XP-G3 (3 W, Royal blue) lamps with a wavelength distribution of $\lambda = 455 \text{ nm} \pm 10 \text{ nm}$ at a working temperature of 25 °C (for the LED datasheet see: https://www.cree.com/led-components/media/documents/dsXPG3.pdf). The reactor chamber is cooled with two fans from each side for optimal air circulation. The LEDs are mounted on an aluminum heat sink with additional fans on top to guarantee working temperature of 25 °C.

All reaction tubes were flame-dried before usage. The photocatalytic reactions were conducted in 10 mL reactions tubes and are deoxygenated by three freeze-pump-thaw cycles before irradiation.


**Optimization studies**

**Table S1: Optimization studies**

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<th>Yield [%]</th>
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Syntheses

General procedures

General procedure for Wohl-Ziegler bromination reactions GP1

1.00 eq. of the corresponding alkene substrate and 1.20 eq. N-bromosuccinimide (NBS) were dissolved in anhydrous chloroform (ca. 50 mM). 0.05 eq. of dibenzoyl peroxide (DBP) were added to the solution. The reaction mixture was heated to reflux until reaction monitoring by TLC showed full conversion. Afterwards, the reaction mixture was allowed to cool to room temperature, diluted with CH₂Cl₂ and washed with water (3× 10 mL/mmol). The aqueous layer was re-extracted with CH₂Cl₂ (3× 15 mL/mmol). The combined organic layers were washed with brine (1× 20 mL/mmol), dried over Na₂SO₄, filtrated and the solvents were removed under reduced pressure.

General procedure for substrates synthesis GP2

1.00 eq. of the brominated substrate was dissolved in acetone (30 mM) and 5.00 eq. K₂CO₃ were suspended in this solution. 1.10 eq. of the corresponding amine were added dropwise to the mixture which was subsequently heated under reflux (85 °C) over night with continuous stirring. The reaction mixture was allowed to cool to room temperature and remaining K₂CO₃ was removed by filtration at reduced pressure over celite. Residual organic solvents were removed under reduced pressure and the crude product was purified by column chromatography to obtain the desired amine.

General procedure for photocatalytic cyclization reactions GP3

1.00 eq. substrate, 1.00 eq. Cs₂CO₃, 1.00 eq. of H₂O and 0.05 eq. photoredox catalyst [Ir{dF(CF₃)ppy}₂(dtbbpy)]PF₆ [Ir(dF)] were dissolved in dry DMF (ca. 2 ml per 0.10 mmol substrate). The yellow mixture was degassed by repeating three times a freeze-pump-thaw cycle and it was irradiated 14 hours with 30 W blue LED (λ = 455 nm) at room temperature in the previously described photoreactor while continuously stirring under argon atmosphere. After the indicated reaction time, water (ca. 5 ml/0.10 mmol substrate) was added. The phases were separated and the water layer was extracted with diethyl ether (3× ca. 6 mL/0.10 mmol). The organic layers were washed with brine and dried over Na₂SO₄. After filtration, residual solvent was removed under reduced pressure. The crude product was purified by column chromatography to obtain the photoproduct.
Ethyl 2-(2-Benzyl-1,2,3,4-tetrahydroisoquinolin-4-yl) acetate (1a)

According to GP 3 50.9 mg (133 µmol, 1.00 eq.) of substrate 2a, 7.48 mg (6.67 µmol, 0.05 eq) of [Ir(dF)], 2.40 mg (133 µmol, 1.00 eq.) H₂O and 43.5 mg (133 µmol, 1.00 eq.) Cs₂CO₃ in anhydrous dimethylformamide (3.00 mL) were irradiated for 14 hours. After purification by column chromatography (silica, pentane/EtOAc = 20/1) 21.3 mg (69.0 µmol, 52%) of product 1a were isolated as a yellow oil.

**TLC:** Rᵣ = 0.32 (pentane/EtOAc = 20/1), [UV/KMnO₄].

**IR (ATR):** ν (cm⁻¹) = 3060 (w, C-H), 2980 (w, C-H), 2979 (w, C-H), 2731 (vs, C=O), 1494 (w), 1454 (m, C-H), 1370 (m, C-H), 1345 (w, C-N), 1260 (m), 1158 (m, C-O, ester), 135.3 (s, C-8a), 129.1 (d, C-8), 128.4 (d, C-7), 128.4 (d, C-6), 126.7 (d, C-5), 126.5 (d, C-5*), 126.2 (d, C-5), 62.8 (t, C₂H₂), 60.4 (t, C₂H₂), 56.5 (t, C-1), 54.7 (t, C-3), 41.2 (t, C₂H₂), 35.8 (d, C-4), 14.3 (q, C₂H₂).

*Assignment is interconvertible

**HRMS (ESI):** m/z = calc. [M+H]⁺: 310.1802; found: 310.1803.

**GC-MS (El, 70 eV):** tᵣ = 16.9 min m/z (%) = 308 (12), 280 (7) [M–C₃H₇]+, 264 (19) [M–C₂H₅O]⁺, 218 (100) [M–C₂H₃]⁺, 144 (10), 130 (26), 117 (20) [C₆H₅]+, 91 (60) [C₅H₇]⁺.
Methyl-2-(2-benzyl-1,2,3,4-tetrahydroisoquinolin-4-yl) acetate (1b)

According to GP 3 48.8 mg (133 µmol, 1.00 eq.) of substrate 2b, 7.45 mg (6.64 µmol, 0.05 eq) of [Ir(dF)], 2.39 mg (133 µmol, 1.00 eq.) H₂O and 43.3 mg (133 µmol, 1.00 eq.) Cs₂CO₃ in anhydrous dimethylformamide (3.00 mL) were irradiated for 14 hours. After purification by column chromatography (silica, pentane/EtOAc = 20/1) 24.2 mg (82.0 µmol, 62%) of 1b could be isolated as a yellow oil.

TLC: Rᵣ = 0.30 (pentane/EtOAc = 20/1), [UV/KMnO₄].

IR (ATR): v (cm⁻¹) = 2925 (m, C₅-H), 2854 (w, C₆-H), 1735 (s, C=O), 1653 (s, C=C), 1454 (m), 1257 (m), 1166 (m C-O, ester), 749 (m, C₆-H), 700 (m, C₆-H).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.41 – 7.36 (m, 2H, 2 × meta-C₆-H), 7.35 – 7.29 (m, 2H, 2 × ortho-C₆-H), 7.29 – 7.24 (m, 1H, para-C₆-H), 7.18 – 7.10 (m, 3H, H-6, H-7, H-8), 7.00 (d, 3J = 6.5 Hz, 1H, H-5), 3.83 (d, 2J = 14.9 Hz, 1H, CHH-1), 3.74 (d, 2J = 13.1 Hz, 1H, Ph-CHH), 3.63 – 3.56 (m, 4H, CO₂CH₃, Ph-HH), 3.43 (d, 2J = 14.9 Hz, 1H, CHH-1), 3.37 – 3.30 (m, 1H, H-4), 2.93 (dd, 2J = 16.0 Hz, 3J = 9.8 Hz, 1H, CHHCO₂CH₃), 2.85 – 2.78 (m, 1H, H-3), 2.67 – 2.54 (m, 2H, H-3, CHHCO₂CH₃).

¹³C NMR (126 MHz, CDCl₃, 298 K): δ = 173.4 (s, CO₂CH₃), 138.7 (s, CH₂-C₆H), 137.6 (s, C-4a), 135.3 (s, C-8a), 129.1 (d, meta-C₆H₄), 128.4 (d, C-8), 128.4 (d, ortho-C₆H₄), 127.2 (d, para-C₆H₄), 126.7 (d, C-5), 126.5 (d, C-7), 126.3 (d, C-6), 62.8 (t, CH₂-C₆H), 56.5 (t, C-1), 54.5 (t, C-3), 51.6 (q, CO₂CH₃), 41.0 (t, CH₂CO₂CH₃), 35.8 (d, C-4).

HRMS (ESI): m/z = calc. [C₁₉H₂₁NO₂⁺H]⁺: 296.1645; found: 296.1644.

GC-MS (EI, 70 eV): tᵣ = 17.8 min; m/z (%) = 294 (10), 264 (7) [M–OCH₃]⁺, 204 (100) [M–C₂H₇]⁺, 145 (5), 91 (51) [C₇H₇]⁺.

The analytical data obtained matched those reported in the literature.²¹
1-(2-Benzyl-1,2,3,4-tetrahydroisoquinolin-4-yl)propan-2-one (1c)

According to GP 3 51.0 mg (145 µmol, 1.00 eq.) of substrate 2c, 8.14 mg (7.25 µmol, 0.05 eq) of [Ir(dF)], 2.61 mg (145 µmol, 1.00 eq.) H₂O and 47.3 mg (145 µmol, 1.00 eq.) Cs₂CO₃ in anhydrous dimethylformamide (3.00 mL) were irradiated for 14 hours. After purification by column chromatography (silica, pentane/EtOAc = 50/1) 21.0 mg (75.2 µmol, 52%) of 1c were isolated as a yellow oil.

**TLC:** Rᵣ = 0.20 (pentane/EtOAc = 15/1), [UV/KMnO₄].

**IR** (ATR): ᴛ (cm⁻¹) = 3062 (w, C₆H₅-H), 3026 (w C₆H₅-H), 2924 (w, C-H), 1713 (vs, C=O), 1493 (w), 1453 (m, C-H), 1362 (m, C-H), 1258 (w), 1158 (m, C-O), 1094 (w), 1029 (w) 746 (s, C-H).

**¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 7.38 – 7.35 (m, 2H, 2 × meta-C₆H₅-H), 7.35 – 7.30 (m, 2H, 2 × ortho-C₆H₅-H), 7.28 – 7.24 (m, 1H, para-C₆H₅-H), 7.17 – 7.08 (m, 3H, H-6, H-7, H-8), 7.00 (d, 3J = 7.0 Hz, 1H, H-5), 3.84 (d, 2J = 14.9 Hz, 1H, CHH-1), 3.73 (d, 2J = 13.0 Hz, 1H, Ph-CHH), 3.55 (d, 2J = 13.0 Hz, 1H, Ph-CHH), 3.44 (d, 2J = 14.9 Hz, 1H, CHH-1), 3.42 – 3.37 (m, 1H, H-4), 3.15 (dd, 2J = 17.7 Hz, 3J = 9.6 Hz, 1H, CHHCOCH₃), 2.72 (d, 2J = 11.7 Hz, 1H, CHH-3), 2.63 (dd, 2J = 17.7 Hz, 4J = 3.3 Hz, 1H, CHHCOCH₃), 2.54 (dd, 3J = 11.7 Hz, 3J = 3.3 Hz, 1H, CHH-3), 2.01 (s, 3H, CH₃).

**¹³C NMR** (101 MHz, CDCl₃):  δ (ppm) = 208.2 (s, CO), 138.1 (s, CH₂-C₆H₅), 134.6 (s, C-4a), 129.9 (s, C-8a), 129.2 (d, meta-CH₆H₅), 128.4 (d, ortho-CH₆H₅, C-8), 127.3 (d, para-CH₆H₅), 126.7 (d, C-5), 126.6 (d, C-6*), 126.1 (d, C-7*), 62.6 (t, CH₂-C₆H₅), 56.5 (t, C-1), 54.3 (t, C-3), 50.5 (t, CH₂COCH₃), 34.2 (d, C-4), 30.7 (q, CH₃).

*Assignment is interconvertible

**HRMS (ESI):** calc. [C₁₅H₂₁NO+H]⁺: 280.1696; found: 280.1695.

**GC-MS** (El, 70 eV): τᵣ = 16.4 min; m/z (%) = 278 (5), 220 (100) [M–C₃H₇O]⁺, 188 (95) [M–C₇H₉]⁺, 144 (5), 117 (35) [C₆H₅]⁺, 91 (80) [C₇H₇]⁺.
2-(2-Benzyl-1,2,3,4-tetrahydroisoquinolin-4-yl)acetonitrile (1d)

According to GP 3 50.2 mg (150 μmol, 1.00 eq.) of substrate 2d, 8.42 mg (7.50 μmol, 0.05 eq) of [Ir(dF)], 2.70 mg (150 μmol, 1.00 eq.) H₂O and 49.0 mg (150 μmol, 1.00 eq.) Cs₂CO₃ in anhydrous dimethylformamide (3.00 mL) were irradiated for 14 hours. After purification by column chromatography (silica, pentane/EtOAc = 30/1) 16.0 mg (61.0 μmol, 41%) of 1d were isolated as a yellow oil.

**TLC:** Rᵣ = 0.17 (pentane/EtOAc = 15/1), [UV/KMnO₄].

**IR (ATR):** v (cm⁻¹) = 3063 (w, C₆H₅-H), 3028 (w, C₆H₅-H), 2923 (w, C-H), 2806 (w, C-H), 2762 (w, C-H), 2245 (w, C≡N), 1658 (m), 1454 (m, C-H), 1421 (m, C-H), 1369 (m), 1276 (m), 1145 (m, C-N), 1095 (m, C-N), 1028 (m, C-N), 748 (vs, C₆H₅-H), 701 (vs, C₆H₅-H).

**¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 7.40 – 7.33 (m, 4H, 2 × meta-C₆H₅-H, 2 × ortho-C₆H₅-H), 7.32 – 7.27 (m, 1H, para-C₆H₅-H), 7.23 – 7.15 (m, 3H, H-6, H-7, H-8), 7.04 – 6.98 (m, 1H, H-5), 3.85 (d, 2J = 15.1 Hz, 1H, CHH-1), 3.77 – 3.63 (m, 2H, Ph-CH₂), 3.43 (d, 2J = 15.1 Hz, 1H, CHH-1), 3.23 – 3.13 (m, 1H, H-4), 3.01 – 2.98 (m, 1H, CHH-3), 2.89 (dd, 2J = 16.7, 3J = 9.0 Hz, 1H, CHHCN), 2.74 – 2.60 (m, 2H, CHHCN, CHH-3).

**¹³C NMR** (101 MHz, CDCl₃): δ (ppm) = 138.4 (s, CH₂-C₆H₅), 135.5 (s, C-4a), 135.5 (s, C-8a), 129.4 (d, meta-C₆H₅), 128.9 (d, C-8), 128.9 (d, ortho-C₆H₅), 127.9 (d, para-C₆H₅), 127.5 (d, C-5), 127.3 (d, C-6*), 127.1 (d, C-7*), 119.6 (s, CN), 63.1 (t, CH₂-C₆H₅), 56.5 (t, C-1), 54.4 (t, C-3), 36.9 (d, C-4), 24.7 (t, CH₂CN).

*Assignment is interconvertible

**HRMS (ESI):** calc. [C₁₈H₁₈N₂+H⁺]: 263.1543; found: 263.1542.

**GC-MS** (EI, 70 eV): tᵣ = 16.5 min; m/z (%) = 261 (2), 220 (50), 185 (20) [M–C₆H₆]⁺, 171 (90) [M–C₆H₅]⁺, 144 (10), 130 (25), 116 (48), 91 (100) [C₇H₇]⁺.

The analytical data obtained matched those reported in the literature.²¹
Methyl 2-(2-benzyl-7-chloro-1,2,3,4-tetrahydroisoquinolin-4-yl)acetate (1e)

Acoording to GP 3 47.7 mg (119 µmol, 1.00 eq.) of substrate 2e, 6.66 mg (5.93 µmol, 0.05 eq) of [Ir(dF)], 2.14 mg (119 µmol, 1.00 eq.) H₂O and 38.7 mg (119 µmol, 1.00 eq.) Cs₂CO₃ in anhydrous dimethylformamide (3.00 mL) were irradiated for 14 hours. After purification by column chromatography (silica, pentane/EtOAc = 20/1) 26.0 mg (78.8 µmol, 66%) of 1e could be isolated as a yellow oil.

**TLC:** Rᵣ = 0.23 (pentane/EtOAc = 20/1) [UV/KMnO₄].

**IR (ATR):** \( \tilde{\nu} \text{ (cm}^{-1}) = 3026(w) \text{ 2926 (m, C=O), 1486 (m), 1436 (m), 1364 (m), 1259 (m), 1165 (s, C-O, ester), 1086 (w).} \)

**¹H NMR** (400 MHz, CDCl₃): \( \delta \text{ (ppm)} = 7.39 – 7.35 \text{ (m, 2H, 2 × meta-C₈H₅-H), 7.35 – 7.30 \text{ (m, 2H, 2 × ortho-C₈H₅-H), 7.29 – 7.25 \text{ (m, 1H, para-C₈H₅-H), 7.15 – 7.06 \text{ (m, 2H, H-6, H-8), 7.00 – 6.97 \text{ (m, 1H, H-5), 3.82 – 3.70 \text{ (m, 2H, CHH-1, Ph-CHH}), 3.62 – 3.57 \text{ (m, 4H, CO₂CH₃, Ph-CHH), 3.39 \text{ (t, J = 14.9 Hz, 1H, CHH-1), 3.33 – 3.27 \text{ (m, 1H, H-4), 2.88 \text{ (dd, J = 16.1 Hz, J = 9.5 Hz, 1H, CHHCO₂CH₃), 2.81 \text{ (d, J = 10.9 Hz, 1H, CHH-3), 2.62 – 2.53 \text{ (m, 2H, CHH-3, CHHCO₂CH₃).}}} \)

**¹³C NMR** (101 MHz, CDCl₃): \( \delta \text{ (ppm)} = 173.1 \text{ (s, CO₂CH₃), 138.2 \text{ (s, CH₂-C₈H₅), 137.1 \text{ (s, C-8a), 136.0 \text{ (s, C-4a), 131.9 \text{ (s, C-7), 129.8 \text{ (d, C-6), 129.1 \text{ (d, meta-CH₈H₅)}, 128.4 \text{ (d, ortho-CH₈H₅), 127.3 \text{ (d, para-CH₈H₅), 126.7 \text{ (d, C-8), 126.6 \text{ (d, C-5), 62.6 \text{ (t, CH₂-C₈H₅), 56.0 \text{ (t, C-1), 54.3 \text{ (t, C-3), 51.7 \text{ (q, CO₂CH₃), 40.8 \text{ (t, CH₃CO₂CH₃), 35.2 \text{ (d, C-4)}}.} \)

**HRMS (ESI):** m/z = calc. [C₁₉H₂₀³⁵ClNO₂⁺H⁺]: 330.1255 found: 330.1255

**GC-MS** (EI, 70 eV): \( t_R = \text{18.56 min m/z (%) = 328 (5), 298 (5) [M+OCH₃]⁺, 254 (5), 238 (100) [M-C₇H₇]⁺, 164 (10), 91 (33) [C₇H₅]⁺.} \)
Methyl 2-(2-benzyl-7-methoxy-1,2,3,4-tetrahydroisoquinolin-4-yl)acetate (1f)

According to GP 3 52.3 mg (132 µmol, 1.00 eq.) of substrate 2f, 7.38 mg (6.58 µmol, 0.05 eq) of [Ir(dF)], 2.37 mg (132 µmol, 1.00 eq.) H2O and 42.9 mg (132 µmol, 1.00 eq.) Cs2CO3 in anhydrous dimethylformamide (3.00 mL) were irradiated for 14 hours. After purification by column chromatography (silica, pentane/EtOAc = 50/1) 25.0 mg (76.8 µmol, 59%) of 1f could be isolated as a yellow oil.

TLC: \( R_f = 0.23 \) (pentane/EtOAc = 20/1), [UV/KMnO4].

IR (ATR): \( \tilde{\nu} \) (cm\(^{-1}\)) =3026(w) 2926 (m, C\(_{Ar}\)-H), 2852 (w, C\(_{Ar}\)-H), 1735 (s, C=O), 1612 (m, C=C, conjugated), 1503 (s), 1435 (m), 1276 (m), 1246 (s), 1163 (s, C-O, ester), 1099 (w), 1038 (w).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 7.41 – 7.36 (m, 2H, 2 × meta-C\(_{Ph}\)-H), 7.35 – 7.30 (m, 2H, 2 × ortho-C\(_{Ph}\)-H), 7.29 – 7.24 (m, 1H, para-C\(_{Ph}\)-H), 7.07 (d, \(^3\)J = 8.5 Hz, 1H, H-5), 6.73 (dd, \(^3\)J = 8.5 Hz, \(^4\)J = 2.7 Hz, 1H, H-6), 6.52 (d, \(^4\)J = 2.7 Hz, 1H, H-8), 3.82 – 3.69 (m, 5H, OCH\(_3\), CHH-1, Ph-CHH), 3.63 – 3.56 (m, 4H, CO\(_2\)CH\(_3\), Ph-CHH), 3.40 (d, \(^2\)J = 15.0 Hz, 1H, CHH-1), 3.32 – 3.25 (m, 1H, H-4), 2.88 (dd, \(^2\)J = 15.9 Hz, \(^3\)J = 9.6 Hz, 1H, CHHCO\(_2\)CH\(_3\)), 2.83 – 2.77 (m, 1H, CHH-3), 2.64 – 2.55 (m, 2H, CHH-3, CHHCO\(_2\)CH\(_3\)).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 173.5 (s, CO\(_2\)CH\(_3\)), 158.0 (s, C-7), 138.6 (s, CH\(_2\)-C\(_{Ph}\)), 136.4 (s, C-8a), 129.6 (s, C-4a), 129.3 (d, C-8), 129.1 (d, meta-C\(_{Ph}\)), 128.4 (d, ortho-C\(_{Ph}\)), 127.2 (d, para-C\(_{Ph}\)), 113.0 (d, C-6), 111.1 (d, C-5), 62.7 (t, CH\(_2\)-C\(_{Ph}\)), 56.6 (t, C-1), 55.3 (q, OCH\(_3\)), 54.8 (t, C-3), 51.6 (q, CO\(_2\)CH\(_3\)), 41.0 (t, CH\(_2\)CO\(_2\)CH\(_3\)), 35.0 (C-4).

HRMS (ESI): \( m/z \) = calc. [C\(_{20}\)H\(_{23}\)NO\(_3\)+H\(^+\)]: 326.1751 found: 326.1752

GC-MS (EI, 70 eV): \( t_R \) = 19.14 min \( m/z \) (%) = 324 (5), 310 (5) [M–CH\(_3\)]\(^+\), 250 (5), 234 (100) [M–C\(_2\)H\(_5\)]\(^+\), 175.1 (20), 91 (30)[C\(_2\)H\(_3\)]\(^+\).
Methyl 2-(2-isopentyl-1,2,3,4-tetrahydroisoquinolin-4-yl)acetate (1g)

According to GP 3 51.0 mg (146 µmol, 1.00 eq.) of substrate 2g, 8.23 mg (7.34 µmol, 0.05 eq) of [Ir(dF)], 2.64 mg (146 µmol, 1.00 eq.) H₂O and 47.8 mg (146 µmol, 1.00 eq.) Cs₂CO₃ in anhydrous dimethylformamide (3.00 mL) were irradiated for 14 hours. After purification by column chromatography (silica, pentane/EtOAc = 50/1) 16.5 mg (60.0 µmol, 41%) of 1g were isolated as a yellow oil.

TLC: Rᵣ = 0.23 (pentane/EtOAc = 20/1), [UV/KMnO₄].
IR (ATR): ν (cm⁻¹) = 2953 (s, C–H), 2926 (m, C–H), 2868 (w), 2804 (w), 1737 (vs, C=O), 1466 (m, C–H), 1437 (m, C–H), 1360 (m), 1249 (m, C–N), 1165 (s, C–O, ester), 1100 (w), 749 (vs, C₆H₅=H, 1,2-disubst.), 728 (w).

¹H-NMR (400 MHz, CDCl₃): δ (ppm) = 7.17 – 7.09 (m, 3H, H-5, H-6, H-7), 7.05 – 7.00 (m, 1H, H-8), 3.78 (d, ²J = 15.1 Hz, 1H, CHH-1), 3.71 (s, 3H, CO₂CH₃), 3.40 (d, ²J = 15.1 Hz, 1H, CHH-1), 3.36 – 3.30 (m, 1H, H-4), 2.92 – 2.73 (m, 2H, CHH-3, CHHCO₂CH₃), 2.68 – 2.37 (m, 4H, CHHCO₂CH₃, CHH-3, H-1’), 1.66 (h, 6.6 Hz, 1H, H-3’), 1.43 (q, ³J = 7.1 Hz, 2H, H-2’), 0.92 (d, ³J = 6.6 Hz, 6H, H-4’, H-5’).

¹³C-NMR (101 MHz, CDCl₃): δ (ppm) = 173.6 (s, CO), 137.6 (s, C-4a), 135.5 (s, C-8a), 128.3 (d, C-5), 126.7 (d, C-6), 126.5 (d, C-7), 126.2 (d, C-8), 56.8 (t, C-1), 56.5 (t, C-1’), 55.1 (t, CH₃CO₂CH₃), 51.7 (q, CO₂CH₃), 40.9 (t, C-3), 36.2 (t, C-2’), 35.8 (d, C-4), 26.4 (d, C-3’), 22.9 (q, C-4’), 22.8 (q, C-5’).
GC-MS (EI, 70 eV): tᵣ = 14.4 min; m/z (%) = 275 (11) [M⁺], 244 (8) [M–OCH₃]⁺, 218 (100) [M–CO₂CH₃+2H]⁺, 204 (53) [M–C₅H₁₁]⁺, 144 (8), 115 (20), 91 (5) [C₇H₇]⁺.
1-(2-Benzyl-1-methyl-1,2,3,4-tetrahydroisoquinolin-4-yl)-propan-2-one (1h)

According to GP 3 90.4 mg (247 µmol, 1.00 eq.) of substrate 2h, 13.9 mg (12.4 µmol, 0.05 eq) of [Ir(dF)], 4.45 mg (247 µmol, 1.00 eq.) H₂O and 80.6 mg (247 µmol, 1.00 eq.) Cs₂CO₃ in 5.00 ml anhydrous DMF were irradiated for 14 hours. After purification by column chromatography (silica, pentane/EtOAc = 100/1) 41.0 mg (140 µmol, 57%, d.r. = 80/20) of 1h were isolated as a yellow oil.

**IR** (ATR): \(\tilde{\nu} \text{ cm}^{-1} = 3062 \text{ (w, } C\equiv\text{O)}, 1493 \text{ (s)}, 1453 \text{ (m, } C\equiv\text{H), 1363 \text{ (m)}, 1158 \text{ (m, } C-O), 760 \text{ (m, } H \text{-C})\).

**TLC:** \(R_f = 0.21 \text{ (pentane/EtOAc = 15/1), [UV/KMnO}_4\).**

**1H NMR** (400 MHz, CDCl₃): \(\delta \text{ ppm} = 7.38 – 7.34 \text{ (m, } 2H, 2 \times meta-C_{Ph-H}), 7.34 – 7.30 \text{ (m, } 2H, 2 \times ortho-C_{Ph-H}), 7.28 – 7.23 \text{ (m, } 1H, para-C_{Ph-H}), 7.21 – 7.12 \text{ (m, } 3H, H-6,H-7, H-8), 7.10 \text{ (d, } J = 7.3 \text{ Hz, } 1H, H-5), 4.08 \text{ (d, } J = 13.6 \text{ Hz, } 1H, Ph-CHH), 3.74 \text{ (q, } J = 6.0 \text{ Hz, } 1H, H-1), 3.36 \text{ (d, } J = 13.6 \text{ Hz, } 1H, Ph-CHH), 3.34 – 3.29 \text{ (m, } 1H, H-4), 3.04 \text{ (dd, } J = 17.6 \text{ Hz, } 3J = 9.0 \text{ Hz, } 1H, CHHCOCH}_3, 2.80 – 2.71 \text{ (m, } 1H, CHH-3), 2.65 \text{ (dd, } J = 17.6, 3J = 3.9 \text{ Hz, } 1H, CHHCOCH}_3, 2.61 – 2.53 \text{ (m, } 1H, CHH-3), 1.97 \text{ (s, } 3H, COCH}_3, 1.54 \text{ (d, } J = 6.0 \text{ Hz, } 3H, CH}_3).

**13C NMR** (101 MHz, CDCl₃): \(\delta \text{ ppm} = 208.1 \text{ (s, } CO), 140.4 \text{ (s, } CH_2-C_{Ph}), 139.7 \text{ (s, } C-4a), 138.3 \text{ (s, } C-8a), 129.0 \text{ (d, } meta-C_{Ph}), 128.3 \text{ (d, } ortho-C_{Ph}), 128.2 \text{ (d, } C-5), 127.2 \text{ (d, } C-6*), 127.1 \text{ (d, } para-C_{Ph}), 126.2 \text{ (d, } C-7*), 126.1 \text{ (d, } C-8), 58.7 \text{ (t, } CH_2-C_{Ph}), 57.7 \text{ (d, } C-1), 51.0 \text{ (t, } C-3), 49.4 \text{ (t, } CH_2COCH}_3, 33.8 \text{ (d, } C-4), 30.6 \text{ (q, } COCH}_3, 22.0 \text{ (q, } CH}_3).

*Assignment is interconvertible
Minor diastereoisomer

**TLC:** $R_f = 0.17$ (pentane/EtOAc = 15/1), [UV/KMnO$_4$].

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 7.37 – 7.33 (m, 2H, 2 × meta-C$_{\text{Ph}}$-H), 7.33 – 7.28 (m, 2H, 2 × ortho-C$_{\text{Ph}}$-H), 7.26 – 7.22 (m, 1H, para-C$_{\text{Ph}}$-H), 7.16 – 7.11 (m, 2H, H-5, H-8), 7.08 – 7.02 (m, 2H. H-6, H-7), 4.14 (t, $^3J = 6.8$ Hz, 1H, H-1), 3.81 (d, $^2J = 13.0$ Hz, 1H, Ph-CHH), 3.55 (d, $^2J = 13.0$ Hz, 1H, Ph-CHH), 3.09 (dd, $^2J = 17.8$ Hz, $^3J = 10.1$ Hz, 1H, CHHCOCH$_3$), 2.94 (d, $^2J = 12.3$ Hz, 1H, CHH-3), 2.43 (d, $^2J = 17.8$ Hz, 1H, CHHCOCH$_3$), 2.36 (d, $^2J = 12.3$ Hz, 1H, CHH-3), 1.82 (s, 3H, COCH$_3$), 1.28 (d, $^3J = 6.7$ Hz, 3H, CH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ (ppm) = 208.3 (s, CO), 141.5 (s, CH$_2$-C$_{\text{Ph}}$), 139.7 (s, C-4a), 138.1 (s, C-8a), 129.3 (d, meta-CH$_{\text{Ph}}$), 128.8 (d, ortho-CH$_{\text{Ph}}$), 128.3 (d, C-8), 127.3 (d, para-CH$_{\text{Ph}}$), 127.1 (d, C-5*), 126.4 (d, C-6*), 125.9 (d, C-7*), 58.4 (t, CH$_2$-C$_{\text{Ph}}$), 56.7 (d, C-1), 50.7 (d, CH$_2$COCH$_3$), 45.1 (t, C-3), 34.3 (d, C-4), 30.5 (q, COCH$_3$), 14.8 (q, CH$_3$).

*Assignment is interconvertible

HRMS (ESI): calc. [C$_{20}$H$_{23}$NO+H]$^+$: 294.1852; found: 294.1852.

GC-MS (EI, 70 eV): $t_R = 16.8$ min; $m/z$ (%) = 278 (100) [M–CH$_3$]$^+$, 220 (10), 186 (2), 131 (7), 91 (80) [C$_7$H$_7$]$^+$. 
Methyl (Z)-2-(2-benzyl-1-methyl-2,3-dihydroisoquinolin-4(1H)-ylidene)acetate (1i)

According to GP 3 49.0 mg (128 µmol, 1.00 eq.) of substrate 2i, 7.20 mg (6.42 µmol, 0.05 eq) of [Ir(dF)], 2.31 mg (128 µmol, 1.00 eq.) H₂O and 41.8 mg (128 µmol, 1.00 eq.) Cs₂CO₃ in anhydrous dimethylformamide (3.00 mL) were irradiated for 14 hours. After purification by column chromatography (silica, pentane/EtOAc = 50/1) 33.0 mg (107 µmol, 83%, d.r. 82/18) of 1i could be isolated as a yellow oil.

IR (ATR): ʋ (cm⁻¹) = 2949 (w, CAr-H), 2799 (w, C-H), 1734 (vs, C=O), 1492 (w,),1435 (m, C-H), 1364 (m, C-H), 1296 (m), 1157 (s, C-O, ester), 1099 (w, C-N), 764 (m, CAr-H, 1,2-disubst.).

Major diastereoisomer

TLC: Rᵣ = 0.49 (P/EtOAc = 10/1), [UV/KMnO₄].

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.39 – 7.36 (m, 2H, 2 × meta-CPh-H), 7.33 – 7.29 (m, 2H, 2 × ortho-CPh-H), 7.27 –7.22 (m, 1H, para-CPh-H), 7.22 – 7.13 (m, 4H, H-5, H-6, H-7, H-8), 4.10 (d, ²J = 13.6 Hz, 1H, Ph-CH), 3.75 (q, ³J = 6.3 Hz, 1H, H-1), 3.55 (s, 3H, CO₂CH₃), 3.40 (d, ²J = 13.6 Hz, 1H, Ph-CHH), 3.26 (dq, ³J = 9.0 Hz, ³J = 5.0 Hz, 1H, H-4), 2.90 – 2.80 (m, 2H, CHH-3, CHHCO₂CH₃), 2.66 (dd, ²J = 16.0 Hz, ³J = 5.0 Hz, 1H, CHHCO₂CH₃), 2.62 – 2.56 (m, 1H, CHH-3), 1.53 (d, ³J = 6.3 Hz, 3H, CH₃).

¹³C NMR (101 MHz, CDCl₃): δ (ppm) = 173.2 (s, CO), 140.4 (s, C-8a), 139.6 (s, CH₂-CPh), 137.7 (s, C-4a), 128.9 (d, meta-CPh), 128.3 (d, ortho-CPh), 128.1 (d, C-8*), 127.3 (d, C-5*), 127.0 (d, para-CPh), 126.4 (d, C-6**), 126.1 (d, C-7**), 58.9 (t, CH₂-CPh), 57.8 (d, C-1), 51.5 (q, CO₂CH₃), 50.9 (t, C-3), 39.9 (t, CH₂CO₂H₃), 35.1 (d, C-4), 21.9 (q, CH₃).

*/**Assignment is interconvertible
Minor diastereoisomer

**TLC:** $R_f = 0.38$ (pentane/EtOAc = 10/1), [UV/KMnO₄].

**$^1H$ NMR** (400 MHz, CDCl₃): $\delta$ (ppm) = 7.39 – 7.35 (m, 2H, 2 × meta-C₆H₅-H), 7.33 – 7.28 (m, 2H, 2 × ortho-C₆H₅-H), 7.27 – 7.22 (m, 1H, para-C₆H₅-H), 7.17 – 7.09 (m, 3H, H-6, H-7, H-8), 7.06 – 7.00 (m, 1H, H-5), 4.10 (q, $^3J = 6.6$ Hz, 1H, H-1), 3.83 (d, $^3J = 13.1$ Hz, 1H, Ph-CH₂H), 3.63 (d, $^2J = 13.1$ Hz, 1H, Ph-CHH), 3.52 (s, 3H, CO₂CH₃), 3.23 – 3.17 (m, 1H, H-4), 2.88 (dd, $^3J = 16.2$ Hz, $^2J = 10.1$ Hz, 1H, CHH-3), 2.88 (dd, $^3J = 16.2$ Hz, $^2J = 10.1$ Hz, 1H, CHH-3), 2.55 – 2.45 (m, 2H, CH-3, CHHCO₂CH₃), 1.28 (d, $^3J = 6.6$ Hz, 3H, CH₃).

**$^{13}C$ NMR** (101 MHz, CDCl₃): $\delta$ (ppm) = 173.5 (s, CO), 141.4 (s, C-8a), 139.4 (s, CH₂-C₆H₅), 137.5 (s, C-4a), 129.2 (d, meta-CH₃C₆H₅), 128.8 (d, C-8), 128.3 (d, ortho-CH₃C₆H₅), 127.4 (d, para-CH₃C₆H₅), 127.0 (d, C-5), 126.4 (d, C-6*), 126.2 (d, C-7*), 58.4 (t, CH₂-C₆H₅), 56.0 (d, C-1), 51.5 (q, CO₂CH₃), 45.8 (t, C-3), 41.1 (t, CH₂CO₂CH₃), 35.9 (d, C-4), 14.8 (q, CH₃).

*Assignment is interconvertible

**HRMS** (ESI): $m/z = \text{calc.} [C_{20}H_{23}NO_2+H]^+ : 310.1802$ found: 310.1803

**GC-MS** (EI, 70 eV): $t_R = 16.8$ min $m/z$ (%) = 294 (100) [M–CH₃]^+, 278 (5) [M–OCH₃]^+, 218 (5) [M–C₇H₇]^+, 144 (2), 91 (60) [C₇H₇]^+. 
2-(2-Benzyl-1-methyl-1,2,3,4-tetrahydroisoquinolin-4-yl)-acetonitrile (1j)

According to **GP 3** 44.0 mg (126 µmol, 1.00 eq.) of substrate **2j**, 7.08 mg (6.31 µmol, 0.05 eq) of **[Ir(dF)]**, 2.27 mg (126 µmol, 1.00 eq.) H2O and 41.1 mg (126 µmol, 1.00 eq.) Cs2CO3 in anhydrous dimethylformamide (3.00 mL) were irradiated for 14 hours. After purification by column chromatography (silica, pentane/EtOAc = 100/1) 15.0 mg (54.3 µmol, 43%, d.r. = 73/27) of **1j** were isolated as a yellow oil.

**IR** (ATR): \( \tilde{\nu} \) (cm\(^{-1}\)) = 3028 (w, C\(=\)N-H), 2974 (m, C-H), 2804 (w, C-H), 2245 (w, C≡N), 1493 (s) 1453 (s, C-H), 1370 (m), 1326 (w), 1276 (m), 1156 (m, C-N), 1099 (m, C-N), 1028 (m, C-N), 755 (vs, C\(=\)N-H), 70 (vs, C\(=\)N-H).

Major diastereoisomer

**TLC:** \( R_f = 0.26 \) (pentane/EtOAc = 15/1), [UV/KMnO\(_4\)].

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 7.40 – 7.33 (m, 4H, 2 \( \times \) meta-C\(_{Ph}\)-H, 2 \( \times \) ortho-C\(_{Ph}\)-H), 7.32 – 7.23 (m, 2H, para-C\(_{Ph}\)-H, H-5), 7.22 – 7.17 (m, 3H, H-6, H-7, H-8), 4.14 (d, \( ^2J = 13.6 \) Hz, 1H, Ph-CHH), 3.79 (q, \( ^3J = 6.1 \) Hz, 1H, H-1), 3.43 (d, \( ^2J = 13.6 \) Hz, 1H, Ph-CHH), 3.12 – 3.01 (m, 1H, H-4), 2.99 – 2.91 (m, 1H, CHH-3), 2.73 (dd, \( ^3J = 7.0 \) Hz, \( ^4J = 3.3 \) Hz, 2H, CH\(_2\)CN), 2.70 – 2.61 (m, 1H, CHH-3), 1.55 (d, \( ^3J = 6.1 \) Hz, 3H, CH\(_3\)).

**\(^{13}\)C NMR** (101 MHz, CDCl\(_3\)): \( \delta \) (ppm) = 140.3 (s, C-8\(_a\)), 138.9 (s, CH\(_2\)-C\(_{Ph}\)), 135.1 (s, C-4\(_a\)), 128.9 (d, meta-C\(_{Ph}\)), 128.5 (d, ortho-C\(_{Ph}\)), 128.4 (d, C-5\(_*\), C-8\(_*\)), 127.5 (d, para-C\(_{Ph}\)), 127.4 (d, C-6\(_**\)), 126.3 (d, C-7\(_**\)), 119.1 (s, CN), 58.7 (t, CH\(_2\)-C\(_{Ph}\)), 57.8 (d, C-1), 50.8 (t, C-3), 36.0 (d, C-4), 23.5 (t, CH\(_2\)CN), 21.8 (q, CH\(_3\)).

*/**Assignment is interconvertible

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Minor diastereoisomer

**TLC:** $R_f = 0.16$ (pentane/EtOAc = 15/1), [UV/KMnO$_4$].

**$^1$H NMR** (400 MHz, CDCl$_3$): $\delta$ (ppm) = 7.39 – 7.32 (m, 4H, 2 × meta-C$_{\text{Ph}}$-H, 2 × ortho-C$_{\text{Ph}}$-H), 7.31 – 7.26 (m, 1H, para-C$_{\text{Ph}}$-H), 7.23 – 7.15 (m, 3H, H-6, H-7, H-8), 7.07 – 7.02 (m, 1H, H-5), 4.11 (q, $^3J = 6.8$ Hz, 1H, H-1), 3.86 (d, $^2J = 13.1$ Hz, 1H, Ph-CHH), 3.68 (d, $^2J = 13.1$ Hz, 1H, Ph-CHH), 3.09 (dd, $^2J = 12.4$ Hz, $^4J = 3.0$ Hz, 1H, H-3), 3.06 – 3.01 (m, 1H, H-4), 2.78 (dd, $^2J = 16.7$ Hz, $^3J = 9.1$ Hz, 1H, CHHCN), 2.66 (d, $^2J = 12.4$ Hz, 1H, H-3), 2.56 (dd, $^2J = 16.7$ Hz, $^4J = 5.4$ Hz, 1H, CHHCN), 1.27 (d, $^3J = 6.8$ Hz, 3H, CH$_3$).

**$^{13}$C NMR** (101 MHz, CDCl$_3$): $\delta$ (ppm) = 141.3 (s, C-8a), 138.9 (s, CH$_2$-C$_{\text{Ph}}$), 134.9 (s, C-4a), 129.1 (d, 2 × meta-C$_{\text{Ph}}$), 129.0 (d, C-8*), 128.6 (d, 2 × ortho-C$_{\text{Ph}}$), 127.7 (d, C-5), 127.5 (d, para-C$_{\text{Ph}}$), 127.1 (d, C-6*), 126.6 (d, C-7*), 119.4 (d, CN), 58.3 (t, CH$_2$-C$_{\text{Ph}}$), 55.8 (d, C-1), 45.7 (t, C-3), 36.8 (d, C-4), 24.7 (t, CH$_2$CN), 14.6 (q, CH$_3$).

*Assignment is interconvertible

**HRMS** (ESI): calc. [C$_{19}$H$_{20}$N$_2$+H]$^+$: 277.1699; found: 277.1699.

**GC-MS** (EI, 70 eV): $t_R = 17.2$ min; $m/z$ (%) = 261 (100) [M–CH$_3$]$^+$, 220 (5) [M–HCN–CH$_3$]$^+$, 185 (2), 144 (7), 91 (75) [C$_7$H$_7$]$^+$. 
2-(2-Benzyl-1,2,3,4-tetrahydroisoquinolin-4-yl)-1-phenylethan-1-one (1k)

According to GP 3 51.0 mg (123 µmol, 1.00 eq.) of substrate 2k, 6.92 mg (6.16 µmol, 0.05 eq) of [Ir(dF)], 2.22 mg (123 µmol, 1.00 eq.) H2O and 40.2 mg (123 µmol, 1.00 eq.) Cs2CO3 in anhydrous dimethylformamide (3.00 mL) were irradiated for 14 hours. After purification by column chromatography (silica, pentane/EtOAc = 20/1) 23.0 mg (67.4 µmol, 55 %) of 1k could be isolated as a yellow oil.

TLC: Rf = 0.53 (pentane/EtOAc = 10/1) [UV/KMnO4].
IR (ATR): ν (cm⁻¹) = 3062 (w), 2924 (s, C=H), 2854 (w, C=H), 1683 (s, C=O), 1597 (w, C=C), 1494 (m), 1449 (s), 1362 (m), 1205 (m), 1140 (s, C-O), 1104 (m), 1028 (m), 751 (s, C=H), 699 (s).

1H NMR (400 MHz, CDCl3): δ (ppm) = 7.95 (d, 3j = 7.7 Hz, 2H, H-4', H-8'), 7.56 (t, 3j = 7.4 Hz, 1H, H-6'), 7.45 (t, 3j = 7.7 Hz, 2H, H-5', H-7'), 7.34 – 7.28 (m, 2H, CAr-H), 7.21 – 7.11 (m, 6H, CAr-H), 7.02 (d, 3j = 7.2 Hz, 1H, H-5), 3.91 – 3.81 (m, 2H, CHH-1', CHH-1), 3.68 (d, 3j = 13.0 Hz, 1H, Ph-CHH), 3.66 – 3.60 (m, 1H, H-4), 3.59 – 3.52 (m, 1H, Ph-CHH), 3.43 (d, 3j = 15.0 Hz, 1H, CHH-1), 3.08 (d, 3j = 17.3 Hz, 1H, CHH-1'), 2.84 (d, 3j = 11.4 Hz, 1H, CHH-3), 2.60 (d, 3j = 11.4 Hz, 1H, CHH-3).

13C NMR (101 MHz, CDCl3): δ (ppm) = 199.5 (s, CO), 138.5 (s, CH2-CPh), 137.4 (s, C-4a), 135.4 (s, C-8a), 133.1 (d, C-6'), 128.9 (d, CAr), 128.6 (d, C-5', C-7'), 128.6 (s, C-3'), 128.3 (d, CAr), 128.2 (d, C-3', C-8'), 127.1 (d, CAr), 126.7 (d, CAr), 126.6 (d, CAr), 126.1 (d, CAr), 62.8 (t, CH2-CPh), 56.5 (t, C-1), 54.6 (t, C-3), 45.6 (t, C-1'), 34.8 (d, C-4).

HRMS (ESI): m/z = calc. [C24H23NO+H]+: 342.1852 found: 342.1854
GC-MS (EI, 70 eV): tR = 23.29 min m/z (%) = 340 (2), 250 (15) [M−C7H7]+, 221 (100) [M−C8H6O]+, 130 (20), 91 (45) [C9H7]+.
2-Benzyl-4-((phenylsulfonyl)methyl)-1,2,3,4-tetrahydroisoquinoline (1l)

According to GP 3 60.3 mg (134 μmol, 1.00 eq.) of substrate 2l, 7.52 mg (6.70 μmol, 0.05 eq) of [Ir(dF)], 2.42 mg (134 μmol, 1.00 eq.) H₂O and 43.7 mg (134 μmol, 1.00 eq.) Cs₂CO₃ in anhydrous dimethylformamide (3.00 mL) were irradiated for 14 hours. After purification by column chromatography (silica, pentane/EtOAc = 20/1) 18.0 mg (47.7 μmol, 36%) of 1l could be isolated as a yellow oil.

**TLC:** Rᵣ = 0.52 (pentane/EtOAc = 5/1), [UV/KMnO₄].

**IR** (ATR): ν (cm⁻¹) = 3028 (w, C₆H₅-H), 2925 (s, C-H), 2854 (m, C-H), 2808 (w, C-H), 1495 (w), 1447 (m, C-H), 1369 (w), 1305 (vs, S=O), 1147 (vs, S=O), 1087 (s, C-N), 1026 (w), 742 (vs, C₆H₅-H), 721 (w), 701 (w), 689 (w).

**¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 7.90 – 7.78 (m, 2H, H-4’,H-8’), 7.67 – 7.58 (m, 1H, H-6’), 7.57 – 7.50 (m, 2H, H-5’, H-7’), 7.41 – 7.28 (m, 5H, 2 × meta-C₆H₅-H, 2 × ortho-C₆H₅-H, para-C₆H₅-H), 7.17 – 7.06 (m, 2H, H-6, H-7), 7.02 – 6.96 (m, 1H, H-8), 6.96 – 6.90 (m, 1H, H-5), 3.89 (dd, ²J = 14.4, ³J = 9.5 Hz, 1H, CHH-3), 3.78 (d, ²J = 15.1 Hz, 1H, CHH-1), 3.61 (s, 2H, H-1’), 3.45 – 3.43 (m, 1H, H-4), 3.34 (d, ²J = 16.1 Hz, 1H, CHH-1), 3.20 – 3.08 (m, 2H, CHH-3, Ph-CHH), 2.53 (dd, ²J = 11.8 Hz, ⁴J = 2.2 Hz, 1H, Ph-CHH).

**¹³C NMR** (101 MHz, CDCl₃): δ (ppm) = 140.0 (s, C-3’), 138.4 (s, CH₂-C₆H₅), 136.2 (s, C-8a), 135.5 (s, C-4a), 133.7 (d, C-6’), 129.5 (d, C-5’, C-7’), 129.2 (d, ortho-CH₃-C₆H₅), 128.5 (d, meta-CH₃-C₆H₅), 128.1 (d, C-4’, C-8’), 127.4 (d, para-CH₃-C₆H₅), 127.0 (d, C-7), 126.8 (d, C-5, C-6), 62.7 (t, CH₂-C₆H₅), 61.8 (t, C-3), 55.7 (t, C-1), 53.9 (t, C-1’), 34.5 (d, C-4).

**HRMS** (ESI): m/z = calc. [C₂₃H₂₃NO₂S+H]⁺: 378.1522; found: 378.1520.

**GC-MS** (EI, 70 eV): tᵣ = 21.9 min; m/z (%) = 376 (5), 286 (100) [M-C₆H₅]⁺, 236 (54) [M-SO₂Ph]⁺, 144 (19), 117 (54) [C₆H₅]⁺, 91 (59) [C₇H₇]⁺, 77 (9) [C₆H₃]⁺.
Methyl 2-(2-(4-(trifluoromethyl)benzyl)-1,2,3,4-tetrahydroisoquinolin-4-yl)acetate (1m)

According to **GP 3** 53.0 mg (122 µmol, 1.00 eq.) of substrate **2m**, 6.83 mg (6.67 µmol, 0.05 eq) of [Ir(df)], 2.19 mg (122 µmol, 1.00 eq.) H₂O and 39.7 mg (122 µmol, 1.00 eq.) Cs₂CO₃ in 3.00 ml anhydrous DMF were irradiated for 14 hours. After purification by column chromatography (silica, pentane/EtOAc = 20/1) 26.0 mg (71.6 µmol, 59 %) of **1m** could be isolated as a yellow oil.

**TLC**: Rₖ = 0.28 (pentane/EtOAc = 20/1), [UV/KMnO₄].

**IR** (ATR): ν (cm⁻¹) = 2953 (w, C-H), 2925 (w, C-H), 2800 (w, C-H), 2760 (w, C-H), 1735 (s, C=O), 1437 (w, C-H), 1418 (w, C-H), 1325 (vs, CF), 1161 (s, C-O), 1123 (s, CF₃), 1066 (s, CF₃), 1018 (m), 839 (w, C₆H₅-H), 749 (w, C₆H₅-H).

**¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 7.58 (d, 3J = 8.1 Hz, 2H, 2 × meta-C₆H₅-H), 7.50 (d, 3J = 8.1 Hz, 2H, 2 × ortho-C₆H₅-H), 7.15 (d, 3J = 6.8 Hz, 3H, H-6, H-7, H-8), 7.00 (d, 3J = 6.8 Hz, 1H, H-5), 3.84 (d, 2J = 14.9 Hz, 1H, CHH-1), 3.79 (d, 2J = 13.5 Hz, 1H, Ph-CHH), 3.61 (d, 2J = 13.5 Hz, 1H, Ph-CHH), 3.57 (s, 3H, CO₂CH₃), 3.46 (d, 2J = 14.9 Hz, 1H, CHH-1), 3.37 – 3.28 (m, 1H, H-4), 2.91 (dd, 2J = 16.1 Hz, 3J = 10.1 Hz, 1H, CHHCO₂CH₃), 2.77 (d, 2J = 11.7 Hz, 1H, CHH-3), 2.65 – 2.55 (m, 2H, CHH-3, CHHCO₂CH₃).

**¹³C NMR** (101 MHz, CDCl₃): δ (ppm) = 173.3 (s, CO), 142.9 (s, CH₂-C₆H₅), 137.4 (s, C-4a), 134.9 (s, C-8a), 129.7 (s, para-C₆H₅), 129.4 (s, CF₃), 129.3 (d, ortho-C₆H₅), 128.5 (d, C-8), 126.7 (d, C-5), 126.4 (d, C-6*, C-7*), 125.3 (q, 4J = 3.8 Hz, meta-C₆H₅), 62.2 (t, CH₂-C₆H₅), 56.6 (t, C-1), 54.3 (t, C-3), 51.5 (q, CH₃), 40.9 (t, CH₂CO₂CH₃), 35.8 (d, C-4).

*Assignment is interconvertible

**HRMS** (ESI): m/z = calcd [C₂₀H₂₀F₃NO₂]+: 364.1519; found: 364.1517.

**GC-MS** (EI, 70 eV): tᵣ = 16.3 min; m/z (%) = 376 (14), 332 (14) [M-OCH₃]+, 288 (25) [M-C₆H₅]+, 204 (100) [M-C₆H₅F₃]+, 159 (41) [C₆H₆F₃]+, 145 (13), 130 (23).
Ethyl-\((E)-3'\)-[\(\text{benzyl}[(\text{trimethylsilyl})-\text{methyl}]\)-amino]-methyl]-phenyl]-acrylate (2a)

\[
\begin{align*}
\text{O} & \quad \text{TMS} \\
\text{C}_2\text{H}_3\text{NO}_2\text{Si} \\
\text{MW: 381.59 g/mol}
\end{align*}
\]

According to \textbf{GP2}, 3.29 g (12.2 mmol, 1.00 eq.) of amine 8a and 9.00 g (61.1 mmol, 5.00 eq.) \(\text{K}_2\text{CO}_3\) were converted in acetone (150 mL). After purification by column chromatography (silica, pentane/EtOAc = 20/1) 3.76 g (9.85 mmol, 81\%) of 2a were isolated as a yellow oil.

\textbf{TLC:} \(R_f = 0.82\) (pentane/EtOAc = 10/1), [UV/KMnO\(_4\)].

\textbf{IR (ATR):} \(\tilde{\nu} \text{ (cm}^{-1}) = 3063 \text{ (w), } C_{ar}-H, 3028 \text{ (w), } C_{ar}-H, 2955 \text{ (m, } C\text{-H}), 2899 \text{ (w, } C\text{-H}), 2789 \text{ (m, } C\text{-H}), 1714 \text{ (s, } C=O), 1634 \text{ (m, } C=\text{C, conjugated}), 1601 \text{ (w), } 1485 \text{ (w), } 1454 \text{ (m, } C\text{-H}), 1420 \text{ (w, } C\text{-H}), 1366 \text{ (m, } C\text{-H}), 1310 \text{ (s, } C-N), 1273 \text{ (m), } 1249 \text{ (m), } 1174 \text{ (s, } C\text{-O, ester}), 1096 \text{ (w, } C\text{-N}), 1039 \text{ (m), } 980 \text{ (m, } C=\text{C, subst}. \text{ trans}), 856 \text{ (s, } \text{Si-CH}_3), 765 \text{ (m, } \text{Si-CH}_3), 747 \text{ (m, } C_{ar}-H, 1,2\text{-subst.}), 700 \text{ (m, } C_{ar}-H, \text{ monosubst.).}

\textbf{\(^1\)H NMR (400 MHz, CDCl\(_3\))}: \(\delta \text{ (ppm)} = 8.23 \text{ (d, } ^3J = 16.0 \text{ Hz, 1H, } H-3'), 7.49 \text{ (dd, } ^3J = 7.69 \text{ Hz, } ^5J = 1.40 \text{ Hz, 1H, } H-6'), 7.41 \text{ (dd, } ^3J = 7.69 \text{ Hz, } ^5J = 1.40 \text{ Hz, 1H, } H-3'), 7.37 - 7.31 \text{ (m, 2H, } 2 \times \text{ ortho-CH}_3\text{H}), 7.30 - 7.23 \text{ (m, 3H, } 2 \times \text{ meta-CH}_3\text{H-H-4'), 7.23 - 7.16 \text{ (m, 2H, } \text{para-CH}_3\text{H-H-5'), 6.27 \text{ (d, } ^3J = 15.9 \text{ Hz, 1H, H-2), 4.26 \text{ (q, } ^3J = 7.1 \text{ Hz, 2H, } \text{CH}_2\text{CH}_3), 3.52 \text{ (s, 2H, } \text{Ar-CH}_2\text{), 3.45 \text{ (s, 2H, } \text{Ph-CH}_2\text{), 1.85 \text{ (s, 2H, } \text{CH}_3\text{TMS), 1.32 \text{ (t, } ^3J = 7.1 \text{ Hz, 3H, } \text{CH}_2\text{CH}_3\text{), -0.01 \text{ (s, 9H, } \text{Si(CH}_3)_3\text{).}}}

\textbf{\(^{13}\)C NMR (101 MHz, CDCl\(_3\))}: \(\delta \text{ (ppm)} = 167.1 \text{ (s, } C-1), 143.0 \text{ (d, } C-3), 139.9 \text{ (s, } \text{CH}_2\text{-CH}_3\text{), 139.3 \text{ (s, } C-2'), 134.4 \text{ (s, } C-1'), 130.8 \text{ (d, } C-3'), 129.8 \text{ (d, } C-4'), 129.0 \text{ (d, } \text{ortho-CH}_2\text{), 128.4 \text{ (d, } \text{meta-CH}_2\text{), 127.4 \text{ (d, } \text{para-CH}_2\text{), 127.0 \text{ (d, } C-5'), 126.7 \text{ (d, } C-6'), 119.5 \text{ (d, } C-2), 62.8 \text{ (t, } \text{CH}_2\text{-CH}_3\text{), 60.5 \text{ (t, } \text{CH}_2\text{CH}_3\text{), 60.5 \text{ (t, } \text{Ar-CH}_2\text{), 46.4 \text{ (t, } \text{CH}_2\text{TMS), 14.6 \text{ (q, } \text{CH}_2\text{CH}_3\text{), -1.04 \text{ (q, } \text{Si(CH}_3)_3\text{).}})

\textbf{HRMS (ESI)}: m/z = \text{calc. } [\text{C}_{23}\text{H}_{33}\text{NO}_2\text{Si}^+]+: 382.2197; \text{ found: 382.2198.}

\textbf{GC-MS (EI, 70 eV)}: \(t_r = 17.8 \text{ min; } m/z \% = 381 \text{ (10) } [\text{M}]^+, 336 \text{ (7) } [\text{M-C}_2\text{H}_5]^+, 308 \text{ (100) } [\text{M-C}_3\text{H}_5\text{O}_2]^+, 290 \text{ (7) } [\text{M-C}_2\text{H}_4]^+, 189 \text{ (8), 132 \text{ (6, } C_{9}H_{10}N]^+, 117 \text{ (26), 91 \text{ (51) } [C_7H_7]^+, 73 \text{ (6) } [\text{Si(CH}_3)_3]^+.}
Methyl (E)-3-[2’-{(benzylationyletsilylmethyl)amino)methyl]phenyl]acrylate (2b)

According to GP2 378 mg (1.48 mmol, 1.00 eq.) bromide 5b, 0.35 mL (315 mg, 1.63 mmol, 1.10 eq.) amine 8a and 1.02 g (7.40 mmol, 5.00 eq.) K₂CO₃ were converted in acetone (40 mL). After purification by column chromatography (silica, pentane/EtOAc = 20:1) 406 mg (1.10 mmol, 75%) of 2b were isolated as slightly yellow oil.

**TLC:** Rᵢ = 0.56 (pentane/EtOAc = 20:1), [KMnO₄/UV].
**IR** (ATR): \(\tilde{\nu} \text{ (cm}^{-1}) = 3063 \text{ (w, C₆H₅-H)}, 3028 \text{ (w, C₆H₅-H)}, 2951 \text{ (m, C₆H₅-H)}, 2788 \text{ (w, C₆H₅-H)}, 1718 \text{ (vs, C=O)}, 1633 \text{ (m, C=C, conjugated)}, 1435 \text{ (m, C–H)}, 1317 \text{ (s, C–N)}, 1274 \text{ (m), 1249 (m, Si–CH₃)}, 1192 \text{ (m, C–N)}, 1169 \text{ (vs, C–O, ester)}, 1040 \text{ (w), 1016 (w), 979 (m, C=C, disubst. trans)}, 853 \text{ (vs, Si–CH₃)}, 765 \text{ (s, Si–CH₃)}, 747 \text{ (vs, C₆H₅–H, 1,2-disubst.)}, 700 \text{ (s, C₆H₅–H, monosubst.)}.

**¹H NMR** (500 MHz, CDCl₃): \(\delta \text{ (ppm)} = 8.28 \text{ (d, }^3J = 16.0 \text{ Hz, 1H, H-3)}, 7.54 \text{ (d, }^3J = 7.7 \text{ Hz, 1H, H-6‘)}, 7.44 \text{ (d, }^3J = 7.4 \text{ Hz, 1H, H-3‘)}, 7.39 \text{ (d, }^3J = 7.4 \text{ Hz, 2H, 2 × ortho-C₆H₅-H)}, 7.35 – 7.28 \text{ (m, 3H, 2 × meta-C₆H₅-H, H-4‘)}, 7.27 – 7.19 \text{ (m, 2H, para-C₆H₅-H, H-5‘)}, 6.32 \text{ (d, }^3J = 16.0 \text{ Hz, 1H, H-2)}, 3.84 \text{ (s, 3H, CO₂CH₃)}, 3.56 \text{ (s, 2H, Ar-CH₂)}, 3.48 \text{ (s, 2H, Ph-CH₂)}, 1.89 \text{ (s, 2H, CH₂TMS)}, 0.03 \text{ [s, 9H, Si(CH₃)₃]}.

**¹³C NMR** (101 MHz, CDCl₃): \(\delta \text{ (ppm)} = 167.6 \text{ (s, C-1)}, 143.2 \text{ (d, C-3), 139.9 (s, CH₂-C₆H₅)}, 139.3 \text{ (s, C-2‘)}, 134.4 \text{ (s, C-1‘)}, 130.9 \text{ (d, C-3‘)}, 129.9 \text{ (d, C-4‘)}, 129.1 \text{ (d, ortho-CH₆H₅)}, 128.4 \text{ (d, meta-CH₆H₅)}, 127.5 \text{ (d, para-CH₆H₅)}, 127.0 \text{ (d, C-5‘)}, 126.7 \text{ (d, C-6‘)}, 118.9 \text{ (d, C-2)}, 62.8 \text{ (t, CH₂-C₆H₅)}, 60.6 \text{ (t, Ar-CH₂)}, 51.7 \text{ (q, CO₂CH₃)}, 46.4 \text{ (t, CH₂TMS)}, –1.1 [q, Si(CH₃)₃].

**HRMS** (ESI): \(m/z = \text{calc. [C}_{22} \text{H}_{30} \text{NO}_{2} \text{Si+H]}^{+}: 368.2040; \) found: 368.2038.

**GC-MS** (EI, 70 eV): \(tᵣ = 17.5 \text{ min; } m/z \% = 367 \text{ (8) } [\text{M}]^{+}, 336 \text{ (3) } [\text{M-OCH₃}]^{+}, 294 \text{ (100) } [\text{M-Si(CH₃)₃}]^{+}, 276 \text{ (5) } [\text{M-C₆H₅}]^{+}, 131 \text{ (10), 91 (41) } [\text{C₆H₅}]^{+}, 73 \text{ (8) } [\text{Si(CH₃)₃}]^{+}, 59 \text{ (6) } [\text{CO₂CH₃}]^{+}.\)
(E)-4-[2'-(Benzyll((trimethylsilyl)methyl)amino)methyl]phenyl]-but-3-en-2-one (2c)

According to GP2 400 mg (1.67 mmol, 1.00 eq.) bromide 5c, 1.16 g (8.36 mmol, 5.00 eq.) K$_2$CO$_3$ and 0.40 mL (356 mg, 1.84 mmol, 1.10 eq.) N-(trimethylsilylmethyl)benzylamine (8a) were converted in 30 mL acetone. After purification by column chromatography (silica, pentane/EtOAc = 10/1) 447 mg of 2c (1.27 mmol, 76%) was isolated as orange colored oil.

**TLC:** $R_f = 0.51$ (pentane/EtOAc = 10/1), [KMnO$_4$/UV].

**IR** (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3062 (w, C$_{Ar}$-H), 3027 (w, C-H), 2954 (w, C$_{Alk}$-H), 1692 (m), 1672 (s, C=O), 1654 (m), 1609 (m, C=C, conjugated), 1598 (m, C$_{Ar}$=C$_{Ar}$), 1420 (m, C$_{Alk}$-H), 1359 (s), 1248 (s), 1175 (m, C-N), 973 (s, C=C, subst. trans), 853 (vs, Si-CH$_3$), 838 (vs), 750 (vs, C$_{Ar}$-H, 1,2-disubst. trans), 700 (s, C$_{Ar}$-H).

**$^1$H NMR** (400 MHz, CDCl$_3$, 298 K): $\delta$ (ppm) = 8.04 (d, $^3J$ = 16.2 Hz, 1H, H-4), 7.59 – 7.54 (m, 1H, H-3’), 7.47 – 7.41 (m, 1H, H-6’), 7.40 – 7.27 (m, 6H, H-4’, C$_{Ph}$-H), 7.25 – 7.21 (m, 1H, H-5’), 6.58 (d, $^3J$ = 16.2 Hz, 1H, H-3), 3.57 (s, 2H, Ar-CH$_2$), 3.50 (s, 2H, Ph-CH$_2$), 2.36 (s, 3H, COCH$_3$), 1.89 (s, 2H, CH$_2$TMS), 0.03 [s, 9H, Si(CH$_3$)$_3$].

**$^{13}$C NMR** (101 MHz, CDCl$_3$, 298 K): $\delta$ (ppm) = 198.7 (s, C-2), 141.7 (d, C-4), 139.6 (s, CH$_2$-C$_{Ph}$), 139.5 (s, C-2’), 134.4 (s, C-1’), 131.2 (d, C-3’), 130.1 (d, C-4’), 129.2 (d, C$_{Ph}$), 128.5 (d, C$_{Ph}$), 128.3 (d, C-3), 127.6 (d, C$_{Ph}$), 127.2 (d, C-5’), 126.7 (d, C-6’), 63.0 (d, Ar-CH$_2$), 60.7 (d, CH$_2$-C$_{Ph}$), 46.3 (t, CH$_2$TMS), 27.9 (q, COCH$_3$), –1.0 [q, Si(CH$_3$)$_3$].

**HRMS** (ESI): $m/z =$ calc. [C$_{22}$H$_{29}$NOSi+H]$^+$: 352.2091; found: 352.2092.

**GC-MS** (EI, 70 eV): $t_R = 18.0$ min; $m/z$ (%) = 351 (5) [M]$^+$, 308 (2) [M–C$_2$H$_3$O]$^+$, 278 (100) [M–Si(CH$_3$)$_3$]$^+$, 236 (6), 192 (5), 159 (15) , 115 (16), 91 (60) [C$_7$H$_3$]$^+$, 73 (14) [Si(CH$_3$)$_3$]$^+$. 

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25
(E)-3-[2’-{[Benzyl([trimethylsilyl]methyl)amino]methyl}phenyl]acrylonitrile (2d)

According to GP2 300 mg (1.35 mmol, 1.00 eq.) bromide 5d, 0.32 mL (287 mg, 1.49 mmol, 1.10 eq.) amine 8a and 930 mg (6.75 mmol, 5.00 eq.) K₂CO₃ were converted in 25 ml Acetone. After purification by column chromatography (silica, pentane/EtOAc = 10/1) 363 mg (1.08 mmol, 80%) of 2d could be isolated as white solid.

TLC: Rᵣ = 0.82 (pentane/EtOAc = 10/1), [KMnO₄/UV].

IR (ATR): ν (cm⁻¹) = 3069 (w, C=H), 2218 (s, C≡N), 1617 (m, C=C, conjugated), 1485 (m, C₂=C₂, H), 1465 (w, C₁=CH₂), 1228 (m), 1214 (m), 963 (s, C=C, 1,2-disubst. trans), 830 (w, Si-CH₃), 794 (m, Si-CH₃), 760 (vs, C₂-H, 1,2-disubst.), 739 (m, C₂-H, monosubst.).

¹H NMR (400 MHz, CDCl₃, 298 K): δ (ppm) = 7.90 (d, ³J = 16.7 Hz, 1H, H-3), 7.47 – 7.36 (m, 5H, C₂=H), 7.36 – 7.27 (m, 4H, C₂=H), 5.72 (d, ²J = 16.7 Hz, 1H, H-2), 3.48 (s, 2H, Aryl-CH₂), 3.43 (s, 2H, Ph-CH₂), 1.84 (s, 2H, CH₂TMS), 0.01 [s, 9H, Si(CH₃)₃].

¹³C NMR (101 MHz, CDCl₃, 298 K): δ (ppm) = 149.6 (d, C-3), 139.3 (s, CH₂-C₃H₃), 138.9 (s, C-2’), 133.7 (s, C-1’), 131.8 (d, C-3’), 130.5 (d, C-4’), 129.4 (d, ortho-CH₂), 128.8 (d, meta-CH₂), 127.9 (d, para-CH₂), 127.5 (d, C-5’), 125.8 (d, C-6’), 118.5 (s, CN), 96.1 (d, C-2), 63.1 (t, Aryl-CH₂), 60.9 (t, CH₂-C₃H₃), 46.0 (t, CH₂TMS), – 1.1 [q, Si(CH₃)₃].

HRMS (ESI): m/z = calc. [C₂₁H₂₂N₂Si]+: 335.1938; found: 335.1937.

GC-MS (EI, 70 eV): tᵣ = 17.6 min; m/z (%) = 334 (5) [M]+, 319 (9), 261 (100) [M−Si(CH₃)₃]+, 243 (3) [M−C₂H₅]+, 192 (3), 91 (73) [C₂H₇]+, 73 (10) [Si(CH₃)₃]+.
Methyl-(E)-3-(2’-((benzyl((trimethylsilyl)methyl)amino)methyl)-4’-chlorophenyl)acrylate (2e)

According to GP2, 200 mg (0.69 mmol, 1.00 eq.) of bromide 5e, 167 mg (0.86 mmol, 1.10 eq.) of amine 8a and 477 mg (3.54 mmol, 5.00 eq.) K₂CO₃ were converted in acetone (15 mL). After purification by column chromatography (silica, pentane/EtOAc = 50/1) 200 mg (0.49 mmol, 72%) of 2e were isolated as a yellow oil.

TLC: Rᵣ = 0.43 (pentane/EtOAc = 20/1), [UV/KMnO₄].

IR (ATR): ν (cm⁻¹) = 2951 (w, C₆H₅-CH₂), 1721 (vs, C=O), 1634 (m, C=CH, conjugated), 1592 (m), 1435 (m, C-H), 1316 (s, C-N), 1249 (m, ), 1171 (s, C-O, ester), 977 (w, C=C, disubst. trans), 854 (s, Si-CH₃), 700 (m, C₆H₅-H, monosubst).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.14 (d, ³J = 16.0 Hz, 1H, H-3'), 7.49 – 7.43 (m, 2H, H-3', H-6'), 7.40 – 7.36 (m, 2H, 2 × ortho-C₆H₄-H), 7.35 – 7.29 (m, 2H, 2 × meta-C₆H₄-H), 7.26 – 7.19 (m, 2H, H-5', para-C₆H₄-H), 6.28 (d, ³J = 16.0 Hz, 1H, H-2'), 3.83 (s, 3H, CO₂CH₃), 3.62 – 3.40 (m, 4H, Ar-CH₂, Ph-CH₂), 1.90 (s, 2H, CH₂TMS), 0.05 (s, 9H, Si(CH₃)₃).

¹³C NMR (101 MHz, CDCl₃): δ (ppm) = 167.3 (s, C-1), 141.8 (d, C-3, 141.2(s, C-4'), 139.5 (s, CH₂-C₆H₅), 135.8(s, C-2'), 132.7 (s, C-1'), 130.5 (d, C-3'), 129.0 (d, ortho-C₆H₄), 128.5 (d, meta-C₆H₄), 128.0 (d, para-C₆H₄, 127.6 (d, C-5'), 127.2 (d, C-6'), 119.4 (d, C-2), 62.9 (t, CH₂-C₆H₅), 60.0 (t, Ar-CH₂), 51.8 (q, CO₂CH₃), 46.6 (t, CH₂TMS), −1.1 (q, Si(CH₃)₃).

HRMS (ESI): m/z = calc. [C₂₂H₂₈³⁵ClO₂⁺H]^+: 402.1651; found: 402.1652.

m/z = calc. [C₂₂H₂₈³⁷ClO₂⁺H]^+: 404.1621; found: 404.1623.

GC-MS (EI, 70 eV): tᵣ = 19.83 min m/z (%) = 401 (2) [M]^+, 370 (5) [M-OCH₃]^+, 328 (100) [M-Si(CH₃)₃]^+, 281 (2).
Methyl-(E)-3-[2’-{(benzyl[(trimethylsilyl)methyl]amino)methyl}-4’-methoxyphenyl]acrylate (2f)

According to GP2, 250 mg (0.88 mmol, 1.00 eq.) of bromide 5f, 220 mg (1.14 mmol, 1.30 eq.) of amine 8a and 606 mg (4.38 mmol, 5.00 eq.) K₂CO₃ were converted in acetone (20 mL). After purification by column chromatography (silica, pentane/EtOAc = 50/1) 315 mg (0.79 mmol, 90%) of 2f were isolated as a yellow oil.

**TLC:** Rᵣ = 0.65 (pentane/EtOAc = 10/1), [UV/KMnO₄].

**IR (ATR):** ν (cm⁻¹) = 2950 (w, C₆H₅-H), 2837 (w, C₆H₅-H), 1717 (s, C=O), 1602 (s, C=C, conjugated), 1495 (m), 1435 (m), 1258 (s), 1159 (s, C-O, ester), 1041 (m), 854 (s, C-Si).

**¹H NMR** (400 MHz, CDCl₃): δ (ppm) 8.19 (d, ³J = 15.9 Hz, 1H, H-3’), 7.52 (d, ³J = 8.7 Hz, 1H, H-6’), 7.42 – 7.36 (m, 2H, 2 × ortho-C₆H₅-H), 7.34 – 7.27 (m, 2H, 2 × meta-C₆H₅-H), 7.25 – 7.19 (m, 1H, para-C₆H₅-H), 7.07 (d, ³J = 2.7 Hz, 1H, H-3’), 6.78 (dd, ³J = 8.7 Hz, ³J = 2.7 Hz, 1H, H-5’), 6.23 (d, ³J = 15.9 Hz, 1H, H-2), 3.84 (s, 3H, OCH₃), 3.82 (s, 3H, CO₂CH₃), 3.55 (s, 2H, Ar-CH₂), 3.50 (s, 2H, Ph-CH₂), 1.92 (s, 2H, CH₂TMS), 0.04 (s, 9H, Si(CH₃)₃).

**¹³C NMR** (101 MHz, CDCl₃): δ (ppm) = 167.9 (s, C-1), 161.1 (s, C-4’), 142.5 (d, C-3), 141.5 (s, C-2’), 139.9 (s, CH₂-C₆H₅) 129.0 (d, meta-C₆H₅H), 128.4 (d, ortho-C₆H₅H), 128.2 (d, C-6’), 127.0 (d, para-C₆H₅H), 126.7 (s, C-1’), 116.5 (d, C-2), 115.6 (d, C-3’), 113.1 (d, C-5’), 62.8 (t, Ph-CH₂), 60.3 (t, Ar-CH₂), 55.4 (q, OCH₃), 51.6 (q, CO₂CH₃), 46.5 (t, CH₂TMS), −1.0 (q, Si(CH₃)₃).

**HRMS** (ESI): m/z = calc. [C₂₃H₂₃NO₃Si+H]⁺: 398.2146; found: 398.2146.

**GC-MS** (EI, 70 eV): tᵣ = 21.03 min m/z (%): = 397 (5) [M]⁺, 366 (2) [M-OCH₃]⁺, 324 (100) [M-Si(CH₃)₃]⁺, 205 (5) [M-C₆H₁₈NSi]⁺, 145 (20).
Methyl (E)-3-[2-{{isopentyl}((trimethylsilyl)methyl)amino}methyl]phenyl]acrylate (2g)

According to **GP2**, 154 mg (602 µmol, 1.00 eq.) of bromide **5b**, 115 mg (662 µmol, 1.10 eq.) of amine **8b** and 416 mg (3.01 mmol, 5.00 eq.) K₂CO₃ were converted in acetone (20 mL). After purification by column chromatography (silica, pentane/EtOAc = 20/1) 117 mg (336 µmol, 56%) of **2g** were isolated as a yellow oil.

**TLC:** Rᵣ = 0.48 (pentane/EtOAc = 20/1), [UV/KMnO₄].

**IR** (ATR): ʋ (cm⁻¹) = 2953 (m, C–H), 2870 (w, C–H), 2793 (w, C–H), 1721 (vs, C=O), 1634 (m, C=C, conjugated), 1467 (w), 1435 (m), 1366 (w), 1314 (m, C–N), 1272 (m), 1248 (s, Si–CH₃), 1218 (m), 1192 (m, C–N), 1168 (vs, C–O, ester), 1042 (w), 978 (w, C=C, disubst. trans), 852 (vs, Si–CH₃), 765 (s, Si–CH₃), 743 (w, C₆H₅–H, 1,2-disubst.), 700 (w).

**¹H NMR** (400 MHz, CDCl₃):  δ (ppm) = 8.30 (d, ³J = 16.0 Hz, 1H, H-3), 7.56 (d, ³J = 7.4 Hz, 1H, H-6'), 7.36 (d, ³J = 7.1 Hz, 1H, H-3'), 7.33 – 7.28 (m, 1H, H-4'), 7.28 – 7.23 (m, 1H, H-5'), 6.32 (d, ³J = 16.0 Hz, 1H, H-2), 3.80 (s, 3H, CO₂CH₃), 3.58 (s, 2H, Ar-CH₂), 2.40 – 2.32 (m, 2H, H-1''), 1.88 (s, 2H, CH₂TMS), 1.57 – 1.47 (m, 1H, H-3''), 1.43 – 1.38 (m, 2H, H-2''), 0.84 (d, ³J = 6.5 Hz, 6H, 2 × CH₃), –0.01 (s, 9H, Si(CH₃)₃).

**¹³C NMR** (101 MHz, CDCl₃):  δ (ppm) = 167.6 (s, C-1), 143.4 (d, C-3), 139.7 (s, C-2'), 134.5 (s, C-1'), 130.9 (d, C-3'), 129.7 (d, C-4'), 127.4 (d, C-5'), 126.6 (d, C-6'), 118.6 (d, C-2), 60.7 (t, Ar-CH₂), 55.7 (t, C-1''), 51.7 (q, CO₂CH₃), 46.1 (t, CH₂TMS), 35.6 (t, C-2''), 26.5 (d, C-3''), 23.0 (q, 2 × CH₃), –1.2 (q, Si(CH₃)₃).

**HRMS** (ESI): m/z = calc. [C₂₀H₂₃NO₂Si+H]⁺: 348.2353; found: 348.2351.

**GC-MS** (EI, 70 eV):  tᵣ = 15.6 min; m/z (%) = 347 (8) [M]⁺, 332 (3) [M–CH₃]⁺, 316 (3) [M–OCH₃]⁺, 290 (33) [M–C₄H₉]⁺, 274 (100) [M–Si(CH₃)₃]⁺, 218 (15), 175 (5), 131 (12) [C₉H₅N]⁺, 115 (52), 91 (7) [C₇H₇]⁺, 73 (7) [Si(CH₃)₃]⁺, 59 (6) [CO₂CH₃]⁺.
(E)-4-(2''-(1''-(Benzyldimethylsilyl)methylamino)ethyl)phenyl)but-3-en-2-one (2h)

According to GP2 300 mg (1.19 mmol, 1.00 eq.) bromide 5h, 0.28 mL (252 mg, 1.30 mmol, 1.10 eq.) amine 8a and 0.82 g (5.93 mmol, 5.00 eq.) K₂CO₃ were converted in 25 mL Acetone. After purification by column chromatography (silica, pentane/EtOAc = 10/1) 253 mg (0.69 mmol, 58%) of 2h could be isolated as orange oil.

TLC: Rf = 0.46 (pentane/EtOAc = 10/1), [KMnO₄/UV].

IR (ATR): ν (cm⁻¹) = 2953 (m, C₆H₅-H), 1692 (m, C=O), 1672 (vs, C=O), 1607 (s, C₆H₅−C₆H₅), 1452 (w, C₆H₅−H), 1358 (m), 1248 (s), 972 (w, C=O, subst. trans), 856 (vs, Si-CH₃), 749 (s, C₆H₅-H).

¹H NMR (500 MHz, CDCl₃, 298 K): δ (ppm) = 7.94 (d, J = 16.1 Hz, 1H, H-4), 7.54 – 7.46 (m, 2H, 2 × meta-C₆H₅-H), 7.39 – 7.35 (m, 3H, H-5', 2 × ortho-C₆H₅-H), 7.34 – 7.29 (m, 2H, H-4', H-3'), 7.26 – 7.21 (m, 2H, para-C₆H₅-H, H-6'), 6.54 (d, 3J = 16.1 Hz, 1H, H-3), 4.12 (q, 3J = 6.7 Hz, 1H, H-1''), 3.66 – 3.57 (m, 2H, Ph-CH₂), 1.24 (s, 3H, COCH₃), 2.03 (d, 2J = 14.6 Hz, 1H, CHHTMS), 1.95 (d, 2J = 14.7 Hz, 1H, CHHTMS), 1.33 (d, 3J = 6.7 Hz, 3H, H-2''), -0.07 [s, 9H, Si(CH₃)₃].

¹³C NMR (126 MHz, CDCl₃, 298 K): δ (ppm) = 198.7 (s, C-2), 143.6 (s, C-2'), 144.2 (d, C-4), 140.1 (s, CH₂-C₆H₅), 134.5 (s, C-1'), 129.7 (d, para-CH₃), 128.9 (d, ortho-CH₃), 128.8 (d, meta-CH₃), 128.4 (d, C-3), 128.3 (d, C-5'), 127.2 (d, C-3'), 127.2 (d, C-4'), 127.0 (d, C-6'), 58.9 (t, CH₂-C₆H₅), 57.9 (d, C-1’”), 41.8 (t, CH₂TMS), 27.9 (q, COCH₃), 15.5 (q, C-2”’), -1.1 [q, Si(CH₃)₃].

HRMS (ESI): m/z = calc. [C₃₂H₃₃NOSi]+: 366.2248; found: 366.2246.

GC-MS (EI, 70 eV): t₀ = 19.1 min; m/z (%): = 350 (5) [M–CH₃]+, 322 (2) [M–COCH₃]+, 292 (100) [M–Si(CH₃)₃]+, 248 (2), 91 (90) [C₆H₇]+.
Methyl (E)-3-[2’-{1’’-(benzyl[trieptmethyisilyl)methyl]amino)ethyl]phenyl]acrylate (2i)

According to GP2, 0.52 g (1.91 mmol, 1.00 eq.) of bromide 5i, 0.44 mg (2.30 mmol, 1.20 eq.) of amine 8a and 1.32 g (9.57 mmol, 5.00 eq.) K₂CO₃ were converted in acetone (60 mL). After purification by column chromatography (silica, pentane/ETOAc = 50/1) 0.53 mg (1.38 mmol, 72%) of 2i could be isolated as a yellow oil.

**TLC:** Rₖ = 0.53 (pentane/ETOAc = 10/1), [UV/KMnO₄].

**IR (ATR):** \( \tilde{\nu} \) (cm⁻¹) = 2950 (w, C₆H₅-H), 2898 (w, C₆H₅-H), 1719 (s, C=O), 1631 (s, C=C, conjugated), 1435 (m), 1316 (s), 1270 (m), 1169 (s, C-O, ester), 855 (s, C-Si).

**¹H NMR (400 MHz, CDCl₃):** \( \delta \) (ppm) = 8.28 (d, \(^3\)J = 15.9 Hz, 1H, H-3'), 7.51 (d, \(^3\)J = 7.7 Hz, 1H, H-6'), 7.47 - 7.38 (m, 3H, 2 × ortho-C₆H₅-H, H-3'), 7.36 - 7.28 (m, 3H, 2 × meta-C₆H₅-H, H-4'), 7.26 - 7.19 (m, 2H, para-C₆H₅-H, H-5'), 6.29 (d, \(^3\)J = 15.9 Hz, 1H, H-2'), 4.08 (q, \(^3\)J = 6.8 Hz, 1H, H-1’’), 3.83 (s, 3H, CO₂CH₃), 3.66 (d, \(^2\)J = 14.1 Hz, 1H, Ph-CHH), 3.56 (d, \(^2\)J = 14.1 Hz, 1H, Ph-CHH), 1.94 (s, 2H, CH₂TMS), 1.29 (d, \(^3\)J = 6.8 Hz, 3H, H-2’’), \(-0.08 \) (s, 9H, Si(CH₃)₃).

**¹³C NMR (101 MHz, CDCl₃):** \( \delta \) (ppm) = 167.5 (s, C-1), 144.1 (d, C-3), 143.7 (s, C-2’), 140.2 (s, C-CH₂-C₆H₅), 134.5 (s, C-1’), 129.5 (d, C-4’), 129.0 (d, ortho-C₆H₅), 128.3 (d, meta-C₆H₅), 128.3 (d, C-3’), 127.1 (d, C-6’), 127.1 (d, para-C₆H₅), 126.8 (d, C-5’), 119.2 (d, C-2), 59.2 (t, CH₂-C₆H₅), 58.5 (d, C-1’’), 51.7 (q, CO₂CH₃), 42.2 (t, CH₂TMS), 14.5 (q, C-2’’), \(-1.2 \) (q, Si(CH₃)₃).

**HRMS (EI):** m/z = calc. [C₂₅H₃₃NO₂Si+H⁺]: 382.2197; found: 382.2197.

**GC-MS (EI, 70 eV):** \( t_f = 21.03 \) min m/z (%) = 381 (5) [M⁺], 366 (2) [M–CH₃⁺], 308 (95) [M–Si(CH₃)₃⁺], 189 (5), 129 (100) [C₁₀H₉⁺].
3-[2’-(1’”-(Benzyl((trimethylsilyl)methyl)amino)ethyl)phenyl]acrylonitrile (2j)

According to GP2 141 mg (597 µmol, 1.00 eq.) bromide 5j, 139 mg (719 µmol, 1.20 eq.) amine 8a and 413 mg (2.98 mmol, 5.00 eq.) K₂CO₃ were converted in acetone (30 mL). After purification by column chromatography (silica, pentane/EtOAc = 20/1) 150 mg (430 µmol, 71%, 73/27 mixture of E/Z isomers) of 2j were isolated as yellowish oil.

IR (ATR): ð (cm⁻¹) = 3065 (w, C=Ar-H), 3030 (w, C-H, conjugated), 2953 (w, C₆H₅-H), 2216 (m, C=O), 1614 (m, C=C, conjugated), 1599 (m, C₆H₅=C₆H₅), 1452 (m, C₆H₅=CH₂), 1372 (m), 1247 (s), 1122 (w, C=N), 1081 (w), 957 (m, C=C, disubst. trans), 854 (vs, Si-CH₃), 837 (vs), 779 (m, Si-CH₃), 749 (vs, C₆H₅-H, 1,2-disubst.), 703 (s, C₆H₅-H, monosubst.)

E-isomer:

TLC: Rᵣ = 0.71 (pentane/EtOAc = 10/1), [KMnO₄/UV].

¹H NMR (400 MHz, CD₆₂O, 298 K): δ (ppm) = 7.69 (d, 3 JT = 16.6 Hz, 1H, H-3), 7.60 – 7.42 (m, 3H, C₆H₅-H), 7.29 – 7.19 (m, 2H, C₆H₅-H), 7.13 – 7.05 (m, 1H, C₆H₅-H), 7.04 – 6.94 (m, 2H, C₆H₅-H), 6.89 – 6.83 (m, 1H, C₆H₅-H), 5.07 (d, 3 JT = 16.6 Hz, 1H, H-2), 3.77 (q, 3 JT = 6.6 Hz, 1H, H'-1”), 3.66 (d, 2 JT = 13.0 Hz, 1H, Ph-CH₂), 3.21 (d, 2 JT = 13.0 Hz, 1H, Ph-CH₂), 1.71 (d, 2 JT = 10.6 Hz, 1H, CH₂TMS), 1.59 (d, 2 JT = 10.6 Hz, 1H, CH₂TMS), 1.03 (d, 3 JT = 6.6 Hz, 3H, H-2”), -0.14 [s, 9H, Si(CH₃)₃].

¹³C NMR (101 MHz, CD₆₂O, 298 K): δ (ppm) = 149.1 (d, C-3), 142.8 (s, CH₂-C₆H₅), 138.9 (s, C-2’), 134.3 (s, C-1”), 129.8 (d, ortho-CH₂Ph), 129.7 (d, meta-CH₂Ph), 129.3 (d, C₆H₅), 127.2 (d, para-CH₂Ph), 126.1 (d, C₆H₅), 118.4 (s, CN), 96.6 (d, C-2), 59.0 (t, CH₂-C₆H₅), 54.5 (d, C-1”), 39.6 (t, CH₂TMS), 8.2 (q, C-2”), -1.4 [q, Si(CH₃)₃].
(E)-3-[2-{(Benzyl[(trimethylsilyl)methyl]amino)methyl}phenyl]-1-phenylprop-2-en-1-one (2k)

According to GP2, 150 mg (498 µmol, 1.00 eq.) of bromide 5k, 116 mg (598 µmol, 1.20 eq.) of amine 8a and 344 mg (2.49 mmol, 5.00 eq.) K₂CO₃ were converted in acetone (7 mL). After purification by column chromatography (silica, pentane/EtOAc = 20/1) 185 mg (447 µmol, 90%) of 2k were isolated as a yellow oil.

TLC: R₁ = 0.54 (pentane/EtOAc = 10/1), [UV/KMnO₄].

IR (ATR): 𝜈 (cm⁻¹) = 3062, (w, C=H), 2952 (w, C–H), 2788 (w), 1765 (w), 1663 (vs, C=O), 1605 (s, C₆H₅–C₆H₅), 1594 (s, C₆H₅–C₆H₅), 1482 (w, C₆H₅–C₆H₅), 1448 (w, C₆H₅–C₆H₅), 1328 (w), 1247 (m), 1211 (s), 1016 (s), 976 (m, C=C, disubst. trans), 855 (s), 839 (s), 765 (m, Si-CH₃).

¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.34 (d, 3, 3J = 15.6 Hz, 1H, H-3), 8.07 – 8.02 (m, 2H, H-2”, H-6”), 7.69 – 7.65 (m, 1H, C₆H₅–H), 7.62 – 7.57 (m, 1H, C₆H₅–H), 7.55 – 7.48 (m, 3H, H-3”, H-5”, H-3’), 7.42 – 7.34 (m, 4H. H-2, C₆H₅–H), 7.32 – 7.24 (m, 3H, C₆H₅–H), 7.23 – 7.17 (m, 1H, H-6’), 3.60 (s, 2H, Ar-CH₂), 3.50 (s, 2H, Ph-CH₂), 1.91 (s, 2H, CH₂TMS), 0.02 (s, 9H, Si(CH₃)₃).

¹³C NMR (101 MHz, CDCl₃): δ (ppm) = 190.6 (s, C-1), 143.1 (d, C-3), 140.0 (s, C-3’), 139.8 (s, CH₂–C₆H₅), 138.6 (s, C-1”), 135.0 (s, C-1’), 132.8 (d, C₆H₅), 130.8 (d, C₆H₅), 130.1 (d, C₆H₅), 129.1 (d, C₆H₅), 128.8 (d, C₆H₅), 128.7 (d, C₆H₅), 128.4 (d, C₆H₅), 127.4 (d, C₆H₅), 127.0 (d, C₆H₅), 126.7 (d, C₆H₅), 123.5 (d, C-2), 62.8 (t, CH₂–C₆H₅), 60.2 (t, Ar-CH₂), 46.4 (t, CH₂TMS), –1.0 (q, Si(CH₃)₃).

HRMS (ESI): m/z = calc. [C₂₂H₃₄NOSi]+: 414.2248; found: 414.2251.

GC-MS (EI, 70 eV): țᵣ = 24.6 min; m/z (%) = 413 (3) [M]+, 340 (75) [M–Si(CH₃)₃]⁺, 221 (5), 105 (100) [C₇H₅O]+.
(E)-N-Benzyl-N-[2’-{2”-(phenylsulfonyl)vinyl}benzyl]-1-(trimethylsilyl)methanamine (2l)

According to GP2, 102 mg (302 µmol, 1.00 eq.) bromide 5l, 0.07 mL (63.0 mg, 326 µmol, 1.10 eq.) amine 8a and 207 mg (1.50 mmol, 5.00 eq.) K₂CO₃ were converted in of acetone (15 mL). After purification by column chromatography (silica, pentane/EtOAc = 20/1) 128 mg (285 µmol, 95%) of 2l were isolated as slightly yellow oil.

TLC: Rᵥ = 0.33 (n-hexane/EtOAc = 5/1) [UV].
IR (ATR): v (cm⁻¹) = 3061 (w, C=Ar–H), 3029 (w, C=Ar–H), 2953 (w, C–H), 2790 (w, C–H), 1699 (w), 1612 (m, C=C, conjugated), 1447 (m, C–H), 1364 (w), 1307 (s, S=O), 1248 (m, Si–CH₃), 1146 (vs, S=O), 1085 (s, C–N), 972 (w, C=C), 852 (vs, Si–CH₃), 788 (m, Si–CH₃), 748 (vs, C=Ar–H, 1,2-disubst.), 701 (s, C=Ar–H, monosubst.), 688 (s, C=Ar–H, monosubst.).

¹H NMR (500 MHz, CDCl₃): δ (ppm) = 8.30 (d, ³J = 15.3 Hz, 1H, H-1’’’), 7.94 (d, ³J = 7.4 Hz, 2H, H-5’’’), 7.61 (t, ³J = 7.4 Hz, 1H, H-7’’’), 7.54 (t, ³J = 7.4 Hz, 2H, H-6’’’), 7.44 – 7.42 (m, 4H, 2 × meta-Cₘₕ–H, 2 × ortho-Cₘₕ–H), 7.38 – 7.30 (m, 3H, H-3’, H-4’, H-5’), 7.26 – 7.17 (m, 2H, H-6’, para-Cₘₕ–H), 6.76 (d, ³J = 15.3 Hz, 1H, H-2’’’), 3.56 (s, 2H, Ph-CH₂), 3.53 (s, 2H, Ar-CH₂), 1.88 (s, 2H, CH₂TMS), 0.03 (s, 9H, Si(CH₃)₃).

¹³C NMR (126 MHz, CDCl₃): δ (ppm) = 141.1 (s, C-4’’’), 140.6 (d, C-1’’’), 140.0 (s, CH₂-Cₘₕ), 139.5 (s, C-1’), 133.4 (d, C-7’’’), 132.1 (s, C-2’), 131.4 (d, Cₘₕ), 130.8 (d, C-3’), 129.4 (d, C-5’’’), 129.2 (d, ortho-CHₘₕ), 128.6 (d, meta-CHₘₕ), 128.0 (d, C-2’’’), 127.8 (d, C-3’’’), 127.6 (d, Cₘₕ), 127.2 (d, Cₘₕ), 127.0 (d, Cₘₕ), 63.0 (t, Ar-CH₂), 60.6 (t, CH₂-Cₘₕ), 46.3 (t, CH₂TMS), −4.0 (q, Si(CH₃)₃).

HRMS (ESI): m/z = calc. [C₂₆H₃₃NO₂SSi+H]⁺: 450.1918; found: 450.1915.

GC-MS (EI, 70 eV): tᵣ = 22.9 min; m/z (%) = 434 (5) [M–CH₃]⁺, 376 (100) [M–Si(CH₃)₃]⁺, 308 (14) [M–SO₂Ph]⁺, 141 (14) [SO₂Ph]⁺, 115 (10), 91 (72) [C₇H₇]⁺, 73 (18) [Si(CH₃)₃]⁺.
Methyl (E)-3-[2’-{[(4’’-trifluoromethyl)benzyl]((trimethylsilyl)methyl)amino)methyl]phenyl]acrylate (2m)

First N-(4-(trifluoromethyl)benzyl)-1-(trimethylsilyl)methylamine (8c) was synthesized according to a literature procedure. 0.68 mL (0.83 g, 4.76 mmol, 1.20 eq.) 4-(trifluoromethyl)benzylamine and 1.12 g (8.07 mmol, 2.00 eq.) K₂CO₃ were suspended in acetonitrile (40 mL). 0.60 mL (0.86 g, 4.04 mmol, 1.00 eq.) (trimethylsilyl)methyl iodide were added dropwise. After 20 h at 85 °C the mixture was concentrated under reduced pressure. The residue was dissolved in water (25 mL) and extracted with dichloromethane (3 × 25 mL). The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The compound was used without further purification in the next synthesis step. According to GP2, 149 mg (585 µmol, 1.00 eq.) of bromide 5b, 191 mg (732 µmol, 1.25 eq.) N-(4-(trifluoromethyl)benzyl)-1-(trimethylsilyl)methylamine and 405 mg (2.93 mmol, 5.00 eq.) K₂CO₃ were converted in acetone (20 mL). After purification by column chromatography (silica, pentane/EtOAc = 50/1) 83.1 mg (191 µmol, 33%) of 2m could be isolated as slightly yellow oil.

**TLC:** Rᵣ = 0.58 (pentane/EtOAc = 20/1) [UV].

**IR (ATR):** ν (cm⁻¹) = 2952 (w, C–H), 2899 (w, C–H), 2798 (w, C–H), 1719 (s, C=O), 1634 (m, C=C, conjugated), 1485 (w), 1436 (w), 1417 (w), 1324 (vs, C–F), 1275 (m), 1250 (m, Si–CH₃), 1193 (m, C–N), 1165 (vs, C–O, ester), 1123 (vs, CF₃), 1066 (s, CF₃), 1018 (m), 980 (w, C=C, subst. trans), 890 (w), 855 (s, Si–CH₃), 840 (s, Si–CH₃), 823 (m), 765 (m, Si–CH₃), 745 (w, Cα–H, 1,2-disubst.), 700 (w, Cα–H, monosubst.).

**¹H NMR (400 MHz, CDCl₃):** δ (ppm) = 8.27 (d, ³J = 15.9 Hz, 1H, H-3), 7.58 – 7.53 (m, 3H, 2 × meta-C₆H₅, H-6'), 7.49 (d, ³J = 8.0 Hz, 2H, 2 × ortho-C₆H₅, H), 7.42 (d, ³J = 7.4 Hz, 1H, H-3'), 7.33 (t, ³J = 7.4 Hz, 1H, H-4'), 7.26 (t, ³J = 7.4 Hz, 1H, H-5'), 6.33 (d, ³J = 15.9 Hz, 1H, H-2), 3.84 (s, 3H, CO₂CH₃), 3.59 (s, 2H, Ph-CH₂), 3.51 (s, 2H, Ar-CH₂), 1.91 (s, 2H, CH₂TMS), 0.04 (s, 9H, Si(CH₃)₃).
$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ (ppm) = 167.5 (s, C-1), 144.1 (s, C-1’’), 143.0 (d, C-3), 138.8 (s, C-2’’), 134.4 (s, C-1’), 130.9 (d, C-3’), 129.9 (d, C-4’), 129.1 (q, $^{3}J_{C-F} = 31.1$ Hz, C-4’’), 129.1 (d, ortho-CH$_{Ph}$), 127.7 (d, C-5’), 126.8 (d, C-6’), 125.3 (q, $^{3}J_{C-F} = 3.7$ Hz, meta-CH$_{Ph}$), 124.3 (q, $^{1}J_{C-F} = 270$ Hz, CF$_{3}$), 119.1 (d, C-2), 62.3 (t, CH$_{2}$-C$_{Ph}$), 60.8 (t, Ar-CH$_{2}$), 51.8 (q, CO$_{2}$CH$_{3}$), 46.8 (t, CH$_{2}$TMS), $-1.1$ (q, Si(CH$_{3}$)$_{3}$).

HRMS (ESI): $m/z =$ calc. [C$_{23}$H$_{28}$F$_{3}$NO$_{2}$Si+H]$^+$: 436.1914; found: 436.1913.

GC-MS (EI, 70 eV): $t_R = 17.1$ min; $m/z$ (%) = 435 (2) [M]$^+$, 404 (5) [M−OCH$_{3}$]$^+$, 362 (100) [M−Si(CH$_{3}$)$_{3}$]$^+$, 304 (6), 260 (9)$^+$, 175 (9) [C$_{9}$H$_{7}$]$^+$, 159 (20) [C$_{8}$H$_{6}$F$_{3}$]$^+$, 115 (63), 91 (13) [C$_{7}$H$_{7}$]$^+$. 

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2-Ethylbenzaldehyde (3a)

For the synthesis of 2-ethylbenzaldehyde (3a), a literature procedure was adapted. 5.15 mL (7.00 g, 41.6 mmol, 1.00 eq.) 1-bromo-2-ethylbenzene were dissolved in 100 mL anhydrous tetrahydrofuran and cooled to −78 °C. Then 18.1 mL (2.67 g, 1.10 eq.) n-butyllithium solution (2.3 M) in hexane were added slowly. After stirring the mixture at −78 °C for three hours, 3.50 mL (3.32 g, 45.4 mmol, 1.20 eq.) dimethylformamide were added and the solution was stirred for another 30 minutes at −78 °C. The cooling was removed and stirring was continued for 30 minutes. Subsequently an ammonium chloride solution (70 mL) was added, the layers were separated and the organic layer was washed with brine (70 mL). The combined aqueous layers were extracted with ethyl acetate (2 × 100 mL). The combined organic layers were dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure. Purification by column chromatography (silica, pentane/EtOAc = 10/1) gave 4.32 g (32.2 mmol, 85%) of 3a as yellow oil.

**TLC:** Rf = 0.77 (pentane/EtOAc = 10/1), [KMnO₄/UV].

**1H NMR** (400 MHz, CDCl₃, 298 K): δ (ppm) = 10.3 (s, 1H, CHO), 7.83 (dd, 3J = 7.6 Hz, 4J = 1.5 Hz, 1H, H-6), 7.52 (td, 3J = 7.5 Hz, 4J = 1.5 Hz, 1H, H-4), 7.36 (td, 3J = 7.6 Hz, 4J = 1.1 Hz, 1H, H-5), 7.30 (dd, 3J = 7.6 Hz, 4J = 1.1 Hz, 1H, H-3), 3.08 (q, 3J = 7.6 Hz, 2H, CH₂CH₃), 1.28 (t, 3J = 7.6 Hz, 3H, CH₂CH₃).

**13C NMR** (101 MHz, CDCl₃, 298 K): δ (ppm) = 192.5 (d, CHO), 147.2 (s, C-1), 134.1 (d, C-6), 133.7 (s, C-2), 131.9 (d, C-5), 130.4 (d, C-4), 126.5 (d, C-3), 25.9 (t, CH₂CH₃), 16.5 (q, CH₂CH₃).

The analytical data obtained matched those reported in the literature. 12
For the synthesis of 3e, a literature procedure was adapted. A solution of 1.61 mL (1.50 g, 14.9 mmol, 1.00 eq.) N-methylpiperazine in anhydrous benzene (15 mL) was cooled to 0 °C. Then 7.16 mL (1.06 g, 16.5 mmol, 1.10 eq.) of a 2.3 M n-butyllithium in hexane solution were added and the mixture was stirred for one hour at room temperature. 2.00 g (14.2 mmol, 0.94 eq.) of 4-chlorobenzaldehyde were added to the mixture at 0 °C which was then allowed to warm to room temperature. Additional 9.28 mL (1.37 g, 21.3 mmol, 1.42 eq.) n-butyllithium solution (2.3 M) in hexane were transferred to the reaction and the mixture was stored in the freezer for 16 h. 5.31 mL (12.1 g, 85.5 mmol, 6.00 eq.) iodomethane were added to the reaction mixture at −78 °C which was allowed to warm to room temperature. Residual n-butyllithium was hydrolyzed by addition of 1 M HCl-solution (30 ml) and the aqueous layer was extracted with dichloromethane (3 × 20 ml). The combined organic layers were dried over Na₂SO₄ and the solvent were removed under reduced pressure. After purification by column chromatography (silica, pentane/EtOAc = 20/1) 0.68 g (4.40 mmol, 30%) of 3e were isolated as a white solid.

**TLC:** \( R_f = 0.62 \) (pentane/EtOAc = 20/1), [UV/KMnO₄].

**¹H NMR (400 MHz, CDCl₃):** \( \delta \) (ppm) = 10.22 (s, 1H, CHO), 7.73 (d, \(^3J = 8.3\) Hz, 1H, H-6), 7.34 (d, \(^3J = 8.3\) Hz, 1H, H-5), 7.26 (s, 1H, H-2), 2.65 (s, 3H, CH₃).

**¹³C NMR (101 MHz, CDCl₃):** \( \delta \) (ppm) = 191.5 (d, CHO), 142.5 (s, C-1), 140.1 (s, C-4), 133.4 (d, C-6), 132.7 (s, C-3), 131.9 (d, C-5), 126.8 (d, C-2), 19.5 (q, CH₃).

The analytic results match with the literature data.¹⁶
Ethyl (E)-3-(o-tolyl)acrylate (4a)

For the synthesis of 4a, a literature procedure was adapted. 7.00 g (43.2 mmol, 1.00 eq.) 2-methylcinnamic acid was dissolved with 1.50 mL (3.51 g, 23.1 mmol, 1.20 eq.) DBU in anhydrous dimethylformamide (40 mL) and stirred for 15 min at room temperature. 4.16 mL (8.08 g, 51.8 mmol, 1.20 eq.) ethyl iodide was added dropwise and the solution stirred for 48 h at room temperature. The reaction mixture was diluted with diethyl ether (50 mL) and the combined organic layers were washed with 10% aqueous HCl (25 mL), water (20 mL) and brine (50 mL), dried over Na₂SO₄ and the solvents were removed under reduced pressure. After purification by column chromatography (silica, pentane/EtOAc = 10/1) 8.20 g (43.1 mmol, 99%) of 4a were obtained as a yellow oil.

**TLC:** Rₖ = 0.84 (pentane/EtOAc = 10/1), [UV/KMnO₄].

**IR** (ATR): \( \tilde{\nu} \) (cm⁻¹) = 3063 (w, C_ar-H), 2981 (s, C-H), 1709 (vs, C=O), 1633 (m, C=C, conjugated), 1602 (m, C=C, aromat), 1573 (w, C=C, aromat), 1486 (m, C=C, aromat), 1462 (m, C=C, aromat), 1390 (m), 1366 (s), 1312 (s), 1269 (s), 1249 (s), 1220 (s), 1167 (vs, C-O, ester), 1096 (m), 1035 (s), 980 (s, C=C, disubst. trans), 864 (m), 762 (s, CH, aromat), 731 (s, C-H, aromat), 695 (w).

**¹H NMR** (400 MHz, CDCl₃): \( \delta \) (ppm) = 7.98 (d, \( ^3J = 15.9 \) Hz, 1H, H-3), 7.59 – 7.52 (m, 1H, H-6'), 7.33 – 7.23 (m, 1H, H-3'), 7.25 – 7.16 (m, 2H, H-4', H-5'), 6.36 (d, \( ^3J = 15.9 \) Hz, 1H, H-2'), 4.27 (q, \( ^3J = 7.1 \) Hz, 2H, CH₂CH₃), 2.44 (s, 3H, CH₃), 1.35 (t, \( ^3J = 7.1 \) Hz, 3H, CH₂CH₃).

**¹³C NMR** (101 MHz, CDCl₃): \( \delta \) (ppm) = 167.2 (s, C-4), 142.4 (d, C-6), 137.8 (s, C-10a), 133.6 (s, C-6a), 130.9 (d, C-10), 130.1 (d, C-8), 126.5 (d, C-9), 126.5 (d, C-7), 119.5 (d, C-5), 60.6 (t, C-2), 20.0 (q, C-11), 14.5 (q, C-1).

**HRMS** (ESI): \( m/z = \text{calc.} \ [\text{C}_{12}\text{H}_{14}\text{O}_2+\text{H}]^+ :191.1067; \text{found}: 191.1067.\)

**GC-MS** (EI, 70 eV): \( t_r = 11.4 \) min; \( m/z \) (%) = 190 (33) [M]⁺, 175 (11) [M−CH₃]⁺, 145 (100) [M−C₂H₅O]⁺, 115 (81), 91 (25) [C₆H₅]⁺.

The analytical data obtained matched those reported in the literature.
Methyl (E)-3-(o-tolyl)acrylate (4b)

For the synthesis of Methyl (E)-3-(o-tolyl)acrylate (4b), a literature procedure was adapted.\textsuperscript{13} 3.12 g (19.2 mmol, 1.00 eq.) 2-methylcinnamic acid was dissolved with 1.50 mL (3.51 g, 23.1 mmol, 1.20 eq.) 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in anhydrous dimethylformamide (40 mL) and stirred at room temperature for 15 min. 4.00 mL (4.10 g, 28.9 mmol, 1.50 eq.) methyl iodide was added dropwise and the solution stirred at room temperature for 14 h. The reaction mixture was diluted with diethylether (40 mL). The organic layers were washed with 10% aqueous HCl (20 mL), water (2 x 20 mL), brine (20 mL) and dried over Na$_2$SO$_4$. The combined organic layers were removed under reduced pressure. After purification by column chromatography (silica, pentane/EtOAc = 20/1) 2.57 g (14.6 mmol, 76%) of 4b were isolated as colorless oil.

**TLC:** $R_f = 0.62$ (pentane/EtOAc = 10/1), [KMnO$_4$/UV].

**IR (ATR):** $\tilde{\nu}$ (cm$^{-1}$) = 3022 (w, C$_{Ar}$=H), 2951 (s, C–H), 1714 (vs, C=O), 1633 (m, C=C, conjugated), 1602 (w), 1461 (w), 1435 (m, C–H), 1316 (s), 1273 (s), 1220 (m), 1193 (s), 1169 (vs, C–O), 1037 (w), 980 (m, C=C, disubst. trans), 862 (w), 763 (s, C$_{Ar}$=H, 1,2-disubst.), 710 (w).

**$^1$H NMR** (400 MHz, CDCl$_3$): $\delta$ (ppm) = 7.99 (d, $^3J = 15.9$ Hz, 1H, H-3'), 7.58 – 7.48 (m, 1H, H-6'), 7.31 – 7.27 (m, 1H, H-3'), 7.24 – 7.17 (m, 2H, H-4', H-5'), 6.36 (d, $^3J = 15.9$ Hz, 1H, H-2), 3.81 (s, 3H, CO$_2$CH$_3$), 2.44 (s, 3H, CH$_3$).

**$^{13}$C NMR** (126 MHz, CDCl$_3$): $\delta$ (ppm) = 167.7 (s, C-1), 142.7 (d, C-3), 137.8 (s, C-2'), 133.5 (s, C-1'), 130.9 (d, C-4'), 130.2 (d, C-3'), 126.5 (d, C-6'), 126.5 (d, C-5'), 119.0 (d, C-2), 51.9 (q, CO$_2$CH$_3$), 20.0 (q, CH$_3$).

**HRMS** (ESI): $m/z$ = calc. [C$_{11}$H$_{12}$O$_2$+H]$^+$: 177.2225; found: 177.2225.

**GC-MS** (EI, 70 eV): $t_R = 10.7$ min; $m/z$ (%) = 176 (41) [M]$^+$, 161 (32) [M–CH$_3$]$^+$, 145 (100) [M–OCH$_3$]$^+$, 115 (92), 91 (26) [C$_7$H$_7$]$^+$.

The analytical data obtained matched those reported in the literature.\textsuperscript{13}
For the synthesis of 4c a literature procedure was adapted.\textsuperscript{10} 1.94 mL (2.00 g, 16.7 mmol, 1.00 eq.) 2-methylbenzaldehyde were added dropwise to a mixture of acetone (36 mL) and 7.20 mL NaOH solution (20.0 mmol, 1.20 eq., 10\%). The reaction mixture was stirred at room temperature until reaction monitoring by TLC showed only traces of starting material remaining after three hours. The reaction was neutralized using HCl (2 M) and extracted with Et\textsubscript{2}O (3 x 30 mL). The organic layers were dried over Na\textsubscript{2}SO\textsubscript{4}, filtered and the solvent was removed under reduced pressure. Purification by column chromatography (silica, pentane/EtOAc = 10/1→4/1) gave 1.96 g of 4c (12.2 mmol, 74\%) as yellow oil.

**TLC**: $R_t = 0.51$ (pentane/EtOAc = 10/1), [KMnO\textsubscript{4}/UV].

**IR** (ATR): $\tilde{\nu}$ (cm\textsuperscript{-1}) = 1670 (s, C=O), 1646 (s, C=O), 1608 (m, C=C), 1596 (s, C=C), 1484 (m, CH), 1455 (m, CH), 1357 (m, CH\textsubscript{3}), 1209 (brm, C-O-C), 971 (s, C=C trans), 756 (s, C\textsubscript{Ar}-H).

**\textsuperscript{1}H NMR** (400 MHz, CDCl\textsubscript{3}, 298 K): $\delta$ (ppm) = 7.82 (d, $^3J = 16.1$ Hz, 1H, H-4), 7.62 – 7.51 (m, 1H, H-6\'), 7.32 – 7.27 (m, 1H, H-3\'), 7.25 – 7.19 (m, 2H, H-4', H-5\'), 6.65 (d, $^3J = 16.1$ Hz, 1H, H-3), 2.45 (s, 3H, Ar-CH\textsubscript{3}), 2.39 (s, 3H, COCH\textsubscript{3}).

**\textsuperscript{13}C NMR** (101 MHz, CDCl\textsubscript{3}, 298 K): $\delta$ (ppm) = 198.5 (s, C-2), 141.0 (d, C-4), 138.0 (s, C-2\'), 133.5 (s, C-1\'), 131.0 (d, C-4\'), 130.4 (d, C-3\'), 128.3 (d, C-3), 126.6 (d, C-6'), 126.6 (d, C-5'), 28.0 (q, COCH\textsubscript{3}), 19.9 (q, Ar-CH\textsubscript{3}).

**HRMS** (ESI): $m/z$ = calc.[C\textsubscript{11}H\textsubscript{12}O+H]\textsuperscript{+}: 161.0961; found: 161.0961.

**GC-MS** (EI, 70 eV): $t_R = 10.53$ min $m/z$ (%) = 160 (10) [M]\textsuperscript{+}, 145 (100) [M–CH\textsubscript{3}]\textsuperscript{+}, 115 (70) [M–C\textsubscript{2}H\textsubscript{5}O]\textsuperscript{+}, 91 (15) [C\textsubscript{7}H\textsubscript{13}]\textsuperscript{+}.

The analytical data obtained matched those reported in the literature.\textsuperscript{10}
For the synthesis of 4d, a literature procedure was adapted.11 1.10 g (19.6 mmol, 1.18 eq.) powdered KOH were suspended in acetonitrile (10 mL). Then 1.94 mL (2.00 g, 16.7 mmol, 1.00 eq.) 2-methylbenzaldehyde were dissolved in acetonitrile (10 mL) and added to the suspension. The mixture was heated to reflux until reaction monitoring by TLC showed only traces of starting material remaining after 15 min. The red suspension was poured into 100 mL cold water and extracted with CH$_2$Cl$_2$ (3 x 75 mL). The organic layers were dried over Na$_2$SO$_4$, filtered and the solvent was removed under reduced pressure. Purification by column chromatography (silica, pentane/EtOAc = 10/1) gave 1.08 g of 4d (7.56 mmol, 45%, 81/19 mixture of $E$/$Z$ isomers) as off-white crystals.

**M.p.:** 34 °C.

**IR (ATR):** $\tilde{\nu}$ (cm$^{-1}$) =3058 (w, C$_{Ar}$=C$_{Ar}$), 2216 (w), (s, C=N), 1614 (m, C=C), 1599 (m), 1484 (m, C$_{Alk}$=H), 963 (s; C=C, disubst. trans), 749 (vs).

**$E$-isomer:**

**TLC:** $R_t$ = 0.72 (pentane/EtOAc = 10/1), [KMnO$_4$/UV].

**$^1$H NMR (400 MHz, CDCl$_3$, 298 K):** $\delta$ (ppm) = 7.70 (d, $^3$J = 16.6 Hz, 1H, H-3), 7.49 – 7.44 (m, 1H, C$_{Ar}$=H), 7.35 – 7.28 (m, 1H, C$_{Ar}$=H), 7.25 – 7.20 (m, 2H, C$_{Alk}$=H), 5.80 (d, $^3$J = 16.6 Hz, 1H, H-2), 2.41 (s, 3H, CH$_3$).

**$^{13}$C NMR (101 MHz, CDCl$_3$, 298 K):** $\delta$ (ppm) = 148.6 (d, C-3), 137.4 (s, C-1’), 132.7 (s, C-2’), 131.2 (d, C-3’), 131.1 (d, C-4’), 126.7 (d, C-5’), 125.7 (d, C-6’), 118.5 (s, CN), 97.3 (d, C-2), 19.8 (q, CH$_3$).

**$Z$-isomer:**

**TLC:** $R_t$ = 0.62 (pentane/EtOAc = 10/1), [KMnO$_4$/UV].

**$^1$H NMR (400 MHz, CDCl$_3$, 298 K):** $\delta$ (ppm) = 7.92 (dd, $^3$J = 7.5 Hz, $^4$J = 1.4 Hz, 1H, C$_{Ar}$=H), 7.44 – 7.39 (m, 1H, C$_{Ar}$=H), 7.41 (d, $^3$J = 12.0 Hz, 1H, H-3), 7.25 – 7.20 (m, 2H, C$_{Alk}$=H), 5.52 (d, $^3$J = 12.0 Hz, 1H, H-2), 2.35 (s, 3H, CH$_3$).

**$^{13}$C NMR (101 MHz, CDCl$_3$, 298 K):** $\delta$ (ppm) = 147.7 (d, C-3), 137.2 (s, C-1’), 132.8 (s, C-2’), 130.7 (d, C-3’), 130.7 (d, C-4’), 127.8 (d, C-5’), 126.6 (d, C-6’), 117.3 (s, CN), 97.1 (d, C-2), 19.8 (q, CH$_3$).

**HRMS (ESI):** $m/z$ = calc. [C$_{10}$H$_9$N+H]$^+$: 144.0808; found: 144.0809.

**GC-MS (EI, 70 eV):** $t_R$ = 18.0 min; $m/z$ (%) = 143 (75) [M]$^+$, 116 (2) [M–HCN]$^+$, 91 (100) [C$_7$H$_7$]$^+$, 89 (5).
Methyl (E)-3-(4’-chloro-2’-methylphenyl)acrylate (4e)

To a suspension of 142 mg (3.56 mmol, 1.10 eq.) NaH (60 w%) in anhydrous tetrahydrofurane (20 mL) 565 µl (648 mg, 3.56 mmol, 1.10 eq.) trimethylphosphonoacetate were added at 0 °C and the mixture was stirred for 20 minutes at 0 °C. 500 mg (3.23 mmol, 1.00 eq.) of 3e in anhydrous tetrahydrofurane (5 mL) were added to the reaction and the mixture was heated to 80 °C for 16 h. Residual NaH was hydrolyzed with 20 mL water and the mixture was extracted with diethylether (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over Na2SO4 and the solvents were removed under reduced pressure. After purification by column chromatography chromatography (silica, pentane/EtOAc = 20/1) 641 mg (3.09 mmol, 96%) of 4e could be obtained as white powder.

M.p.: 34 °C.

TLC: Rf = 0.56 (pentane/EtOAc = 20/1), [UV/KMnO4].

IR (ATR): ν (cm⁻¹) = 2951 (w, C–H), 1718 (vs, C=O), 1634 (m), 1593 (m), 1481 (m, C=C), 1316 (s), 1194 (m), 1171 (s, C-O, ester), 980 (m, C=C, subst. trans), 818 (w).

1H NMR (400 MHz, CDCl₃): δ (ppm) = 7.89 (d, 3J = 15.9 Hz, 1H, H-2), 7.19 – 7.15 (m, 2H, H-3’, H-5’), 6.34 (d, 3J = 15.9 Hz, 1H, H-2), 3.81 (s, 3H, CO₂CH₃), 2.41 (s, 3H, CH₃).

13C NMR (101 MHz, CDCl₃): δ (ppm) = 167.4 (s, C-1), 141.4 (d, C-3), 139.5 (s, C-2’), 135.8 (s, C-4’), 132.0 (s, C-1’), 130.8 (d, C-5’), 127.8 (d, C-6’), 126.7 (d, C-3’), 119.5 (d, C-2), 51.9 (q, CO₂CH₃), 19.8 (q, CH₃).

HRMS (ESI): m/z = calc. [C₁₁H₁₁ClO₂⁺H]⁺: 211.0520; found: 211.0521.

m/z = calc. [C₁₁H₁₁ClO₂⁺H]⁺: 213.0491; found: 213.0492.

GC-MS (EI, 70 eV): tᵣ = 12.2 min, m/z (%) = 210 (25) [M]⁺, 195 (5) [M–CH₃]⁺, 179 (80) [M–OCH₃]⁺, 150 (30), 115 (100) [M–CO₂CH₃·HCl]⁺, 89 (5).

The analytic results match with the literature data.¹⁷
Methyl-(E)-3-(4'-methoxy-2'-methylphenyl)acrylate (4f)

To a suspension of 0.44 g (10.9 mmol, 1.10 eq.) NaH (60 w%) in anhydrous tetrahydrofurane (100 mL), 1.77 mL (2.00 g, 10.9 mmol, 1.10 eq.) trimethylphosphonooacetate were added at 0 °C and the mixture was stirred for 20 minutes at 0 °C. 1.50 g (9.99 mmol, 1.00 eq.) of 4-methoxy-2-methylbenzaldehyde in anhydrous tetrahydrofurane (20 mL) were added to the reaction and the mixture was heated to 80 °C for 16 h. Residual NaH was hydrolyzed with water (100 mL) and the mixture was extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with brine (150 mL), dried over Na2SO4 and the solvents were removed under reduced pressure. After purification by column chromatography (silica, pentane/EtOAc = 50/1) 2.03 g (9.84 mmol, 99%) of 4f were obtained as colorless viscous oil.

**TLC:** \( R_f = 0.61 \) (pentane/EtOAc = 20/1), [UV/KMnO₄].

**IR (ATR):** \( \tilde{\nu} \left( \text{cm}^{-1} \right) = 2950 \text{ (w, C-H)}, 2839 \text{ (w, C-H)}, 1712 \text{ (s, C=O)}, 1602 \text{ (s, C=C, conjugated)}, 1499 \text{ (m)}, 1435 \text{ (m)}, 1256 \text{ (s)}, 1161 \text{ (s, C-O, ester)}, 1104 \text{ (m)}, 1042 \text{ (m)}, 981 \text{ (w)}, 813 \text{ (w)}. \)

**\(^1\)H NMR (400 MHz, CDCl₃):** \( \delta \) (ppm) 7.93 (d, \( ^3J = 15.8 \text{ Hz}, 1H, H-3' \)), 7.53 (d, \( ^3J = 8.5 \text{ Hz}, 1H, H-3' \)), 6.79 – 6.71 (m, 2H, H-5', H-6'), 6.27 (d, \( ^3J = 15.8 \text{ Hz}, 1H, H-2') \), 3.82 (s, 3H, CO₂CH₃), 3.80 (s, 3H, OCH₃), 2.43 (s, 3H, CH₃).

**\(^{13}\)C NMR (101 MHz, CDCl₃):** \( \delta \) (ppm) = 167.9 (s, C-1), 161.2 (s, C-4'), 142.2 (d, C-3), 139.9 (s, C-2'), 128.1 (d, C-6'), 126.1 (s, C-1'), 116.4 (d, C-2), 116.0 (d, C-5'), 112.3 (d, C-3'), 55.4 (q, CO₂CH₃), 51.7 (q, OCH₃), 20.2 (q, CH₃).

**HRMS (ESI):** \( m/z = \text{calc. } [C_{12}H_{14}O_3]^+ = 207.1016; \text{found: } 207.1016. \)

**GC-MS (EI, 70 eV):** \( t_r = 12.89 \text{ min } m/z \% = 206 \text{ (60) } [M]^+, 191 \text{ (5) } [M-\text{CH}_3]^+, 175 \text{ (100) } [M-\text{OCH}_3]^+, 160 \text{ (5)}, 146 \text{ (20), 131 (15)}. \)

The analytic results match with the literature data.\(^{18}\)
(E)-4-(2’-Ethylphenyl)but-3-en-2-one (4h)

1.00 g (11.2 mmol, 1.00 eq.) 2-ethylbenzaldehyde (3a) was added dropwise to a mixture of acetone (25 mL) and 4.85 mL NaOH solution (13.4 mmol, 1.20 eq., 10%). The reaction mixture was stirred at room temperature until reaction monitoring by TLC showed only traces of starting material remaining after three hours. The reaction was neutralized using HCl (2 M) and extracted with diethyl ether (3 x 20 mL). The organic layer was washed with brine (30 mL) and dried over Na2SO4. After filtration the solvent was removed reduced pressure. Purification by column chromatography (silica, pentane/EtOAc = 10/1) gave 1.37 g (7.85 mmol, 70%) of 4h as yellow solid.

M.p.: 39 °C.

TLC: Rf = 0.59 (pentane/EtOAc = 10/1), [KMnO4/UV].

IR (ATR): v (cm⁻¹) = 3061 (w, C=H), 2956 (m, C=H), 1691 (m, C=C, conjugated), 1669 (vs, C=O), 1609 (s, C=C=C), 1485 (m, C=C=C), 1454 (w, C=C=C), 1358 (m), 1255 (m), 1176 (m), 975 (s, C=H, subst. trans), 760 (s, C=C-H).

¹H NMR (400 MHz, CDCl₃, 298 K): δ (ppm) = 7.87 (d, J = 16.0 Hz, 1H, H-4), 7.60 – 7.56 (m, 1H, H-6’), 7.36 – 7.31 (m, 1H, H-3’), 7.26 – 7.20 (m, 2H, H-3’), 6.66 (d, J = 16.0 Hz, 1H, H-3), 2.80 (q, J = 7.6 Hz, 2H, CH₂CH₃), 2.39 (s, 3H, COCH₃), 1.23 (t, J = 7.6 Hz, 3H, CH₂CH₃).

¹³C NMR (101 MHz, CDCl₃, 298 K): δ (ppm) = 198.5 (s, C=O), 144.2 (s, C=H), 140.8 (d, C-4), 132.8 (s, C-1’), 130.6 (d, C-4’), 129.5 (d, C-3’), 128.4 (d, C-3), 126.7 (d, C-6’), 126.6 (d, C-5’), 28.0 (q, COCH₃), 26.6 (t, CH₂CH₃), 16.0 (q, CH₂CH₃).

HRMS (ESI): m/z = calc. [C₁₂H₁₄O+H]⁺: 175.1117; found: 175.1117.

GC-MS (EI, 70 eV): tᵣ = 11.2 min; m/z (%) = 174 (5) [M]⁺, 159 (15) [M-CH₃]⁺, 145 (100) [M-C₂H₅]⁺, 131 (15) [M-COCH₃]⁺, 115 (20), 91 (10) [C₇H₇]⁺.
Methyl-(E)-3-(2’-ethylphenyl)acrylate (4i)

To a suspension of 0.82 g (20.5 mmol, 1.10 eq.) NaH (60 w%) in anhydrous tetrahydrofurane (250 mL) 3.30 mL (3.73 g, 20.5 mmol, 1.10 eq.) trimethylphosphonoacetat were added at 0 °C and the mixture was stirred at 0 °C for 20 minutes. 2.50 g (18.6 mmol, 1.00 eq.) of 3a in anhydrous tetrahydrofurane (50 mL) were added to the reaction and the mixture was heated to 80 °C for 16 h. Residual NaH was hydrolyzed with 200 mL water and the mixture was extracted with diethylether (3 × 150 mL). The combined organic layers were washed with brine (150 mL), dried over Na2SO4 and the solvents were removed under reduced pressure. After purification by column chromatography (silica, pentane/EtOAc = 50/1) 3.07 g (16.1 mmol, 87%) of 4i were obtained as yellow oil.

**TLC:** Rf = 0.45 (pentane/EtOAc = 20/1), [UV/KMnO4].

**IR (ATR):** v (cm⁻¹) = 3064 (w, C=H), 2967 (w, C=H), 2876 (w, C=H), 1717 (s, C=O), 1632 (m, C=H, conjugated), 1435 (m), 1317 (s), 1170 (s, C=O, ester), 981 (w), 764 (w).

**1H NMR** (400 MHz, CDCl₃): δ (ppm) 8.02 (d, 3J = 15.8 Hz, 1H, H-3), 7.56 (d, 3J = 7.6 Hz, 1H, H-6’), 7.36 – 7.29 (m, 1H, H-3’), 7.25 – 7.18 (m, 2H, H-4’, H-5’), 6.37 (d, 3J = 15.8 Hz, 1H, H-2), 3.82 (s, 3H, CH₃), 2.79 (q, 3J = 7.6 Hz, 2H, CH₂CH₃), 1.22 (t, 3J = 7.6 Hz, 3H, CH₂CH₃).

**13C NMR** (101 MHz, CDCl₃): δ (ppm) = 167.6 (s, C-1), 144.0 (s, C-2’), 142.5 (d, C-3), 132.8, 130.3 (d, C-3’), 129.4 (d, C-5’), 126.5 (d, C-6’), 119.1 (d, C-4’), 51.8 (q, CO₂CH₃), 26.5 (t, CH₂CH₃), 16.0 (q, CH₂CH₃).

*Assignment is interconvertible.

**HRMS (ESI):** m/z = calc. [C₁₂H₁₄O₂+H+]⁺: 191.1067; found: 191.1067.

**GC-MS (EI, 70 eV):** tR = 11.19 min m/z (%) = 190 (25) [M]⁺, 175 (2) [M–CH₃]⁺, 161 (50) [M–C₂H₅]⁺, 130 (100) [M–CO₂CH₃]⁺, 115 (75).

The analytic results match with the literature data.¹⁹
0.99 g (17.6 mmol, 1.18 eq.) potassium hydroxide were suspended in 10 mL acetonitrile and heated to reflux. Then 1.00 g (14.9 mmol, 1.00 eq.) 3a, dissolved in 10 mL acetonitrile was added. The reaction mixture was refluxed until reaction monitoring by TLC showed only traces of starting material remaining after 30 min. The orange suspension was poured into 100 mL cold water and extracted with CH₂Cl₂ (3 ×50 mL). The organic layer was dried over Na₂SO₄, filtered and the solvent was removed in vacuo. After purification by column chromatography (silica, pentane/EtOAc = 50/1) 1.21 g (82/18 mixture of E/Z isomers, 7.66 mmol, 51%) of 4j could be obtained as a yellow oil.

IR (ATR): ν (cm⁻¹) = 3417 (w), 3059 (w, C₆H₅-N), 2968 (m, C₆H₅-CH₂), 2934 (w), 2217 (s, C≡N), 1614 (m, C=C, conjugated), 1600 (m, C₆H₅-C₆H₅), 1483 (m, C₆H₅-C₆H₅), 1453 (m, C₆H₅-C₆H₅), 1265 (w), 1217 (w), 1055 (w), 965 (s, C=C, subst. trans), 786 (w), 752 (s, C₆H₅-N).

E-isomer:

**TLC:** Rₜ = 0.84 (pentane/EtOAc = 10/1), [KMnO₄/UV].

**¹H NMR** (400 MHz, CDCl₃, 298 K): δ (ppm) = 7.74 (d, ³J = 16.5 Hz, 1H, H-3), 7.55 – 7.44 (m, 1H, H-6'), 7.41 – 7.33 (m, 1H, H-3'), 7.26 – 7.21 (m, 2H, H-4', H-5'), 5.82 (d, ³J = 16.5 Hz, 1H, H-2), 2.74 (q, ³J = 7.6 Hz, 2H, CH₂CH₃), 1.22 (t, ³J = 7.6 Hz, 3H, CH₂CH₃).

**¹³C NMR** (101 MHz, CDCl₃, 298 K): δ (ppm) = 148.4 (d, C-3), 143.6 (s, C-2'), 131.9 (s, C-1'), 131.3 (d, C-3'), 129.6 (d, C-4'), 126.7 (d, C-5'), 125.8 (d, C-6'), 118.6 (s, CN), 97.5 (d, C-2), 26.4 (t, CH₂CH₃), 15.9 (q, CH₂CH₃).

Z-Isomer

**TLC:** Rₜ = 0.75 (pentane/EtOAc = 10/1), [KMnO₄/UV].

**¹H NMR** (400 MHz, CDCl₃, 298 K): δ (ppm) = 7.93 – 7.89 (m, 1H, H-6'), 7.55 – 7.44 (m, 1H, H-3), 7.41 – 7.33 (m, 1H, H-3'), 7.33 – 7.28 (m, 2H, H-4', H-5'), 5.53 (d, ³J = 11.9 Hz, 1H, H-2), 2.69 (q, ³J = 7.6 Hz, 2H, CH₂CH₃), 1.21 (t, ³J = 7.6 Hz, 3H, CH₂CH₃).

**¹³C NMR** (101 MHz, CDCl₃, 298 K): δ (ppm) = 147.7 (d, C-3), 143.4 (s, C-2'), 132.1 (s, C-1'), 130.9 (d, C-3'), 129.1 (d, C-4'), 128.1 (d, C-6'), 126.6 (d, C-5'), 117.3 (s, CN), 97.3 (s, C-2), 26.6 (t, CH₂CH₃), 15.6 (q, CH₂CH₃).

**HRMS** (ESI): m/z = calc. [C₁₁H₁1N⁺]: 158.2235; found: 158.2236.

**GC-MS** (EI, 70 eV): tᵣ = 10.6 min; m/z (%) = 157 (83) [M⁺], 142 (30) [M–CH₃]⁺, 129 (41), 115 (100) [M–HCN-CH₃]⁺, 102 (9), 77 (11) [C₆H₅]⁺, 51 (10) [C₆H₅]⁺.
(E)-1-Phenyl-3-(o-tolyl)prop-2-en-1-one (4k)

\[
\begin{align*}
\text{C}_{10}\text{H}_{14}\text{O} & \\
\text{Mw} & 222.28\text{g/mol}
\end{align*}
\]

5.00 mL (5.20 g, 43.3 mmol, 1.00 eq.) 2-methylbenzaldehyde were added dropwise at 0 °C to a mixture of ethanol (50 mL) and 2.60 g (64.9 mmol, 1.50 eq) NaOH in water (15 mL). The reaction mixture was stirred at room temperature for 16 h. The reaction was neutralized with HCl (2 M) and the aqueous layer was extracted with ethylacetate (3 × 50 mL). The combined organic layers were dried over Na₂SO₄, filtrated and the solvent was removed under reduced pressure. After purification by column chromatography (silica, pentane/EtOAc = 20/1) 8.69 g (39.1 mmol, 90%) of 4k were isolated as yellow oil.

**TLC:** \( R_f = 0.61 \) (pentane/EtOAc = 10/1), [UV/KMnO₄].

**IR (ATR):** \( \tilde{\nu} \) (cm⁻¹) = 3058 (w, C=C), 1661 (s, C=O), 1594 (s, C=C, conjugated), 1577 (m, C=C, conjugated), 1447 (w, C-H), 1319 (m, C-H), 1279 (m), 1214 (s), 1015 (s), 977 (m, C=C, disubst. trans).

**¹H NMR** (400 MHz, CDCl₃): \( \delta \) (ppm) = 8.13 (d, \( ^3J = 15.6 \) Hz, 1H, H-3), 8.07 – 8.02 (m, 2H, 2 × ortho-C₆H₄-H), 7.74 – 7.69 (m, 1H, H-3’), 7.63 – 7.56 (m, 1H, para-C₆H₄-H), 7.55 – 7.49 (m, 2H, 2 × meta-C₆H₄-H), 7.47 (d, \( ^3J = 15.6 \) Hz, 1H, H-2), 7.35 – 7.29 (m, 1H, H-5’), 7.28 – 7.22 (m, 2H, H-6’, H-4’), 2.49 (s, 3H, CH₃).

**¹³C NMR** (101 MHz, CDCl₃): \( \delta \) (ppm) = 190.6 (s, C-1), 142.6 (d, C-3), 138.5 (s, C-2’), 138.4 (s, COC₆H₄), 134.1 (s, C-1’), 132.9 (d, para-C₆H₄), 131.1 (d, C-4’), 130.4 (d, C-5’), 128.8 (d, meta-C₆H₄), 128.7 (d, ortho-C₆H₄), 126.6 (d, C-6’), 126.5 (d, C-3’), 123.3 (d, C-2), 20.0 (q, CH₃).

**HRMS (ESI):** m/z = calc. \([\text{C}_16\text{H}_{15}\text{O}+\text{H}]^+\): 223.1117; found: 223.1118.

**GC-MS (EI, 70 eV):** \( t_R = 15.2 \) min; m/z (%) = 222 (25) [M]⁺, 207 (100) [M–CH₂]⁺, 145(10) [M–C₆H₅]⁺, 115 (30), 91 (5) [C₇H₇]⁺.
(E)-1-Methyl-2-[2’-(phenylsulfonyl)vinyl]benzene (4l)

1.00 mL (0.92 g, 7.94 mmol, 1.00 eq.) of 1-ethynyl-2-methylbenzene was added to tetrahydrofuran (25 mL) in a pressure tube. 0.97 mL (1.05 g, 9.52 mmol, 1.20 eq.) benzenethiol, 425 mg (7.94 mmol, 1.00 eq.) NH₄Cl and 0.90 mL H₂O₂ (30% in water) were added successively to the reaction tube. The mixture was stirred at 50 °C for 48 h. The mixture was diluted with water (50 mL) the aqueous layer was separated and extracted with ethylacetate (3 x 20 mL). The organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. After purification by column chromatography (silica, pentane/EtOAc = 5/1) 1.23 g (4.76 mmol, 60%) of 4l were isolated as colorless crystals.

M.p.: 78 °C.

TLC: Rf = 0.56 (pentane/EtOAc = 5/1) [UV].

IR (ATR): ν (cm⁻¹) = 3059 (w, C₆H₅-H), 1613 (w, C=CH, conjugated), 1596 (w), 1446 (m, C-H), 1305 (s, S=O), 1143 (vs, S=O), 1085 (s), 972 (m, C=CH, disubst. trans), 834 (m), 747 (s, C₆H₅-H, 1,2-disubst.), 687 (s, C₆H₅-H, monosubst.).

¹H NMR (500 MHz, CDCl₃): δ (ppm) = 7.97 – 7.94 (m, 3H, C₆H₅-H), 7.66 – 7.53 (m, 3H, C₆H₅-H), 7.46 – 7.42 (m, 1H, C₆H₅-H), 7.30 – 7.28 (m, 1H, C₆H₅-H), 7.24 – 7.16 (m, 2H, C₆H₅-H), 6.79 (d, 3J = 15.3 Hz, 1H, C₆H₅-H), 2.46 (s, 3H, CH₃).

¹³C NMR (126 MHz, CDCl₃): δ (ppm) = 140.8 (s, C-4’), 140.3 (d, C-1’), 138.4 (d, C-2), 133.5 (d, para-CH₂Ph), 131.4 (s, C-1), 131.2 (d, C-4), 131.1 (d, C-3), 129.5 (d, C-2’), 128.2 (d, meta-CH₂Ph), 127.8 (d, C-5), 127.0 (d, ortho-CH₂Ph), 126.6 (d, C-6), 19.9 (q, CH₃).

HRMS (ESI): m/z = calc. [C₁₅H₁₄O₂S⁺]: 259.0787; found: 259.0787.

GC-MS (EI, 70 eV): tᵣ = 17.1 min; m/z (%) = 258 (40) [M⁺], 241 (1), 116 (100) [M–HSO₂Ph]⁺.

The analytical data obtained matched those reported in the literature.¹⁴
Ethyl (E)-3-[2'-{bromomethyl}phenyl] acrylate (5a)

\[
\begin{align*}
\text{C}_12\text{H}_7\text{BrO}_2 \\
\text{Mw: 269.14 g/mol}
\end{align*}
\]

According to GP1, 8.09 g (42.5 mmol, 1.00 eq.) of 4a, 9.71 g (54.5 mmol, 1.20 eq.) NBS and 0.55 g (2.27 mmol, 0.05 eq.) DBP were heated under reflux for 18 h in anhydrous chloroform (200 mL). After purification by column chromatography (silica, pentane/EtOAc = 10/1) 7.96 g (29.6 mmol, 70 %) of 5a were isolated as yellow, viscous oil.

**TLC:** \( R_f = 0.55 \) (pentane/EtOAc = 10/1), [UV/KMnO₄].

**IR** (ATR): \( \tilde{\nu} \) (cm⁻¹) = 3070, (vw, C=Ar-H), 2982 (w, C-H), 1765 (w), 1711 (vs, C=O), 1636 (m, C=C, conjugated), 1601 (w, C=Ar=C=Ar), 1573 (vw, C=Ar=C=Ar), 1487 (w, C=Ar=C=Ar), 1456 (w, C=Ar=C=Ar), 1392 (w), 1367 (w), 1316 (m), 1282 (m), 1253 (m), 1226 (m), 1179 (vs, C-O, ester), 1096 (w), 1035 (m), 977 (m, C=C, disubst. trans), 865 (w), 844 (w), 763 (m, C=Ar-H), 705 (w).

**¹H NMR** (400 MHz, CDCl₃): \( \delta \) (ppm) = 8.06 (d, \(^3J = 15.7\) Hz, 1H, H-3'), 7.64 – 7.54 (m, 1H, H-6'), 7.43 – 7.31 (m, 3H, H-3', H-4', H-5'), 6.44 (d, \(^3J = 15.7\) Hz, 1H, H-2), 4.60 (s, 2H, CH₂Br), 4.29 (q, \(^3J = 7.1\) Hz, 2H, CH₂CH₃), 1.35 (t, \(^3J = 7.1\) Hz, 3H, CH₃CH₂).

**¹³C NMR** (101 MHz, CDCl₃): \( \delta \) (ppm) = 166.8 (s, C-1), 140.6 (d, C-3), 136.7 (s, C-2'), 133.9 (s, C-1'), 130.8 (d, C-5'), 130.4 (d, C-4'), 129.4 (d, C-3'), 127.4 (d, C-6'), 121.2 (d, C-2), 60.8 (t, CH₃CH₂), 30.7 (t, CH₂Br), 14.5 (q, CH₂CH₃).

**HRMS** (ESI): \( \text{m/z = calc. [C}_{12}\text{H}_{13}\text{BrO}_2+H]^+ : 269.0172;\) found: 269.0173.

\( \text{m/z = calc. [C}_{12}\text{H}_{13}\text{BrO}_2+H]^+ : 271.0151;\) found: 271.0152.

**GC-MS** (EI, 70 eV): \( t_r = 13.6 \text{ min}; \text{m/z} \) (%) = 223 (12) [M–C₃H₅O]^+, 189 (83) [M–HBr]^+, 175 (7), 145 (13), 115 (100) [M–C₃H₅O–HBr]^+, 89 (13).

The analytical data obtained matched those reported in the literature. 

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50
Methyl (E)-3-(2’-(bromomethyl)phenyl)acrylate (5b)

According to GP1 2.00 g (11.4 mmol, 1.00 eq.) of 4b, 2.42 g (13.6 mmol, 1.20 eq.) NBS and 140 mg (0.58 mmol, 0.05 eq.) DBP were heated under reflux in anhydrous chloroform (150 mL) for 30 h. After purification by column chromatography (silica, pentane/EtOAc = 20/1) 2.29 g (8.97 mmol, 80 %) of 5b could be isolated as colorless crystals.

M.p.: 82 °C.

TLC: Rf = 0.46 (pentane/EtOAc = 10:1), [KMnO4/UV].

IR (ATR): v (cm\(^{-1}\)) = 3024 (w, C\(_{Ar}\)-H), 2950 (w, C-H), 1714 (vs, C=O), 1634 (m, C=C, conjugated), 1601 (w), 1487 (w), 1435 (m, C\(_{Ar}\)-H), 1320 (s), 1301 (m), 1281 (s), 1254 (m), 1227 (m), 1195 (s), 1173 (vs, C-O, ester), 1037 (w), 1014 (w), 976 (m, C=C, subst. trans), 863 (w), 845 (w), 795 (w), 764 (s, C\(_{Ar}\)-H, 1,2-disubst.), 712 (w).

\(^1H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) (ppm) = 8.07 (d, \(^3J = 15.8\) Hz, 1H, H-3’), 7.62 – 7.56 (m, 1H, H-6’), 7.40 – 7.32 (m, 3H, H-3’, H-4’, H-5’), 6.45 (d, \(^3J = 15.8\) Hz, 1H, H-2’), 4.60 (s, 2H, CH\(_2\)Br), 3.83 (s, 3H, CO\(_2\)CH\(_3\)), 3.07 (t, CH\(_2\)Br).

\(^13C\) NMR (126 MHz, CDCl\(_3\)) \(\delta\) (ppm) = 167.2 (s, C-1), 140.9 (d, C-3), 136.7 (s, C-2’), 133.8 (s, C-1’), 130.8 (d, C-4’), 130.5 (d, C-3’), 129.4 (d, C-6’), 127.4 (d, C-5’), 120.7 (d, C-2), 52.0 (q, CO\(_2\)CH\(_3\)), 30.7 (t, CH\(_2\)Br).

HRMS (ESI): \(m/z = \text{calc. } [C\(_{11}H_{11}\)BrO\(_2\)+H]\(^+\): 255.0015; \text{found: } 255.0015.
\(m/z = \text{calc. } [C\(_{11}H_{11}\)BrO\(_2\)+H]\(^+\): 256.9995; \text{found: } 256.9994.

GC-MS (EI, 70 eV): \(t_k = 13.1\) min; \(m/z\) (%) = 223 (5) [M-CH\(_3\)]\(^+\), 175 (49) [M-HBr]\(^+\), 143 (10), 131 (9), 115 (100) [C\(_3\)H\(_7\)]\(^+\), 91 (13) [C\(_7\)H\(_7\)]\(^+\), 59 (10) [CO\(_2\)CH\(_3\)]\(^+\).

The analytical data obtained matched those reported in the literature.\(^13\)
(E)-4-[2′-(Bromomethyl)phenyl]but-3-en-2-one (5c)

According to GP1 1.00 g (6.24 mmol, 1.00 eq.) of (E)-4-(α-Tolyl)-but-3-en-2-one (4c), 1.33 g (7.49 mmol, 1.20 eq.) NBS and 75.6 mg (310 μmol, 0.05 eq.) DBP were heated under reflux for 16 h in anhydrous chloroform (45 mL). After purification by column chromatography (silica, pentane/EtOAc = 15/1) 494 mg of (2.06 mmol, 57%) 5c was isolated as an off-white solid.

**M.p.:** 43 °C.

**TLC:** Rf = 0.21 (pentane/EtOAc = 15/1), [KMnO₄/UV].

**IR** (ATR): ν (cm⁻¹) = 1690 (m, C=O), 1666 (s, C=C), 1610 (s, C=C), 1596 (s, C=C), 1357 (m, CH₃), 1293 (m), 1254 (s), 1219 (m), 1175 (m), 971 (s, C=C, trans), 748 (vs, C-O), 1565 (w), 1014 (w), 976 (m, C=C, trans), 748 (s, C₆H₅-H).

**¹H-NMR** (400 MHz, CDCl₃, 298 K): δ (ppm) = 7.93 (d, 3 J = 16.1 Hz, 1H, H-3), 7.64 – 7.59 (m, 1H, H-6’), 7.42 – 7.33 (m, 3H, H-3’, H-4’, H-5’), 6.71 (d, 3 J = 16.1 Hz, 1H, H-4), 4.61 (s, 2H, CH₂Br), 2.43 (s, 3H, COCH₃).

**¹³C-NMR** (126 MHz, CDCl₃, 298 K): δ (ppm) = 198.5 (s, C-2), 139.4 (d, C-4), 136.8 (s, C-2’), 134.0 (s, C-1’), 130.9 (d, C-4’), 130.6 (d, C-4’), 129.7 (d, C-3’), 129.6 (d, C-3), 127.4 (d, C-6’), 30.8 (t, Ar-CH₂Br), 27.8 (q, COCH₃).

**HRMS** (ESI): m/z = calc. [C₁₁H₁₁BrO⁺]+: 239.0066; found: 239.0067.

m/z = calc. [C₁₁H₁₁BrO⁺⁺]: 441.0085; found: 441.0047

**GC-MS** (EI, 70 eV): 12.8 min; m/z (%) = 240 (2) [Br⁺], 238 (2) [Br⁺], 223 (3) [M-CH₃⁺], 159 (76) [M-Br⁺], 145 (77), 115 (100) [M-C₃H₅O-Br⁺], 77 (3).
(E)-3-[2-(Bromomethyl)phenyl]acrylonitrile (5d)

According to GP1 490 mg (3.42 mmol, 1.00 eq.) of 3-(o-Tolyl)acrylonitrile (4d) as E/Z-mixture, 731 mg (4.11 mmol, 1.20 eq.) NBS and 41.5 mg (0.17 mmol, 0.05 eq.) DBP were heated under reflux for 18 h in anhydrous chloroform (45 mL). After purification by column chromatography (silica, pentane/EtOAc = 15/1) 525 mg (2.36 mmol, 69%) of 5d was isolated as an off-white solid.

M.p.: 93 °C.

IR (ATR): \( \tilde{\nu} \) (cm\(^{-1}\)) = 3060 (w, C<sub>H</sub>), 2214 (w), (s, C=N), 1615 (m, C=C), 1484 (m, CH<sub>2</sub>), 1212 (m), 965 (s, C=C, subst. trans), 737 (s), 599 (s, C-Br).

TLC: \( R_f = 0.21 \) (pentane/EtOAc = 15/1), [KMnO<sub>4</sub>/UV].

\(^1\)H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): \( \delta \) (ppm) = 7.82 (d, \(^3\)J = 16.4 Hz, 1H, H-3), 7.54 – 7.49 (m, 1H, H-6'), 7.45 – 7.34 (m, 3H, H-3', H-4', H-5'), 5.92 (d, \(^3\)J = 16.4 Hz, 1H, H-2), 4.53 (s, 2H, CH<sub>2</sub>Br).

\(^{13}\)C NMR (101 MHz, CDCl<sub>3</sub>, 298 K): \( \delta \) (ppm) = 147.1 (d, C-3), 136.4 (s, C-1'), 133.0 (s, C-2'), 131.4 (d, C-3'), 131.0 (d, C-4'), 129.7 (d, C-5'), 126.7 (d, C-6'), 118.1 (s, CN), 99.3 (d, C-2), 30.2 (t, CH<sub>2</sub>Br).

HRMS (ESI): \( m/z = \text{calc.} \quad [\text{C}_{10}\text{H}_{8}\text{BrN}+\text{H}+\text{MeCN}]^+ \): 263.0178; found: 263.0179.

GC-MS (El, 70 eV): \( t_R = 18.0 \) min; \( m/z \) (%) = 221 (10), 141 (100) [M−HBr]<sup>+</sup>, 115 (95) [M−HBr−CN]<sup>+</sup>.
Methyl-(E)-3-(2’-(bromomethyl)-4’-chlorophenyl)acrylate (5e)

According to **GP1**, 503 mg (2.39 mmol, 1.00 eq.) of **4e**, 510 mg (2.87 mmol, 1.20 eq.) NBS and 28.9 mg (0.12 mmol, 0.05 eq.) DBP were heated under reflux for 30 h in anhydrous chloroform (150 mL). After purification by column chromatography (silica, pentane/EtOAc = 50/1) 250 mg (0.86 mmol, 36%) of **5e** were isolated as colorless crystals.

**M.p.:** 52 °C.

**TLC:** *R* = 0.43 (pentane/EtOAc = 20/1), [UV/KMnO₄].

**IR** (ATR): *ν* (cm⁻¹) = 2950 (w, C-H), 1717 (vs, C=O), 1636 (m, C=C conjugated), 1593 (m), 1483 (m), 1318 (s), 1276 (m), 1174 (s, C=O, ester), 1109 (m), 900 (w).

**¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 7.97 (d, 3J = 15.8 Hz, 1H, H-3’), 7.52 (d, 3J = 8.4 Hz, 1H, H-6’), 7.39 (d, 4J = 2.0 Hz, 1H, H-3’), 7.31 (dd, 3J = 8.4, 4J = 2.0 Hz, 1H, H-5’), 6.42 (d, 3J = 15.8 Hz, 1H, H-2), 4.52 (s, 2H, CH₂Br), 3.83 (s, 3H, CO₂CH₃).

**¹³C NMR** (101 MHz, CDCl₃): Δ (ppm) = 166.9 (s, C-1), 139.7 (d, C-3), 138.3 (s, C-2’), 136.1 (s, C-4’), 132.3 (s, C-1’), 130.7 (d, C-5’), 129.6 (d, C-6’), 128.7 (d, C-3’), 121.2 (d, C-2), 52.1 (q, CO₂CH₃), 29.5 (t, CH₂Br).

**HRMS** (ESI): *m/z* = calc. [C₁₁H₁₀Br²⁷ClO₂⁺H⁺]: 288.9625; found: 288.9627.

**GC-MS** (EI, 70 eV): *t* = 14.29 min *m/z* (%) = 288 (5) [M]+, 256 (5) [M–OCH₃]+, 209 (50) [M–HBr]+, 179 (10), 149 (50), 130 (10), 115 (100) [M–CO₂CH₃–Cl–Br]+, 89 (5).
Methyl-(E)-3-(2'-(bromomethyl)-4'-methoxyphenyl)acrylate (5f)

According to **GP1**, 750 mg (3.64 mmol, 1.00 eq.) of 4f, 776 mg (4.36 mmol, 1.20 eq.) NBS and 44.0 mg (0.18 mmol, 0.05 eq.) DBP were heated under reflux for 20 h in anhydrous chloroform (100 mL). After purification by column chromatography (silica, pentane/EtOAc = 20/1) 353 mg (1.24 mmol, 34%) of 5f were isolated as colorless crystals.

**M.p.:** 80 °C.

**TLC:** *R* = 0.42 (pentane/EtOAc = 20/1), [UV/KMnO₄].

**IR** (ATR): *v* (cm⁻¹) = 2950 (w, C₆H₅-H), 2841 (w, C₆H₅-H), 1714 (s, C=O), 1603 (s, C=C, conjugated), 1499 (m), 1299 (m), 1262 (s), 1163 (s, C-O, ester), 1035 (m).

**¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 7.99 (d, ³J = 15.8 Hz, 1H, H-3), 7.57 (d, ³J = 8.3 Hz, 1H, H-6'), 6.93 – 6.83 (m, 2H, H-3', H-5'), 6.36 (d, ³J = 15.8 Hz, 1H, H-2), 4.57 (s, 2H, CH₂Br), 3.84 (s, 3H, OCH₃), 3.82 (s, 3H, CO₂CH₃).

**¹³C NMR** (101 MHz, CDCl₃): δ (ppm) = 167.5 (s, C-1), 161.2 (s, C-4'), 140.4 (d, C-3), 138.5 (s, C-2'), 129.0 (d, C-6'), 126.1 (s, C-1'), 118.2 (d, C-2), 115.8 (d, C-3'), 115.3 (d, C-5'), 55.6 (q, OCH₃), 51.9 (q, CO₂CH₃), 30.6 (t, CH₂Br).

**HRMS** (ESI): *m/z* = calc. [C₁₂H₁₉BrO₃⁺H⁺]: 285.0121; found: 285.0122.

**GC-MS** (EI, 70 eV): *t*ᵣ = 14.903 min *m/z* (%) = 253 (5), 205 (90) [M−HBr]^⁺, 175 (5) [M−BrOCH₃]^⁺, 145 (100) [M−HBr−CO₂CH₃]^⁺, 131 (50).
(E)-4-[2’-{1’’-Bromoethyl}phenyl]but-3-en-2-one (5h)

According to GP1 500 mg (2.87 mmol, 1.00 eq.) of 4h, 613 mg (3.44 mmol, 1.20 eq.) NBS and 34.8 mg (0.14 mmol, 0.05 eq.) DBP were heated under reflux for 18 h in anhydrous chloroform (45 mL). After purification by column chromatography (silica, pentane/EtOAc = 10/1) 521 mg (2.06 mmol, 72%) of 5h could be isolated as brown oil.

TLC: Rf = 0.33 (pentane/EtOAc = 10/1), [KMnO₄/UV].
IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 3061 (w, C₆H₅–H), 3021 (w, C₆H₅–H, conjugated), 2967 (m, C₆Al₆–H), 1692 (m, C=C, conjugated), 1670 (vs, C=O), 1609 (s, C₆Al₆=C₆H₅), 1598 (s, C₆Al₆=C₆H₅), 1454 (m, C₆Al₆–H), 1256 (s), 1177 (m), 975 (s, C₆=C, dissubt. trans), 751 (s, C₆=C–H).

¹H NMR (400 MHz, CDCl₃, 298 K): δ (ppm) = 8.04 (d, ³J = 16.0 Hz, 1H, H-4), 7.64 (dd, ³J = 7.9 Hz, ¹J = 1.3 Hz, 1H, H-3'), 7.55 (dd, ³J = 7.7 Hz, ¹J = 1.5 Hz, 1H, H-6'), 7.45 (td, ³J = 7.6 Hz, ¹J = 1.5 Hz, 1H, H-4'), 7.35 (td, ³J = 7.7 Hz, ¹J = 1.3 Hz, 1H, H-5'), 6.67 (d, ³J = 16.0 Hz, 1H, H-3), 5.53 (q, ³J = 6.9 Hz, 1H, CHBr), 2.45 (s, 3H, COCH₃), 2.12 (d, ³J = 6.9 Hz, 3H, CHBrCH₃).

¹³C NMR (101 MHz, CDCl₃, 298 K): δ (ppm) = 198.3 (s, C-2), 141.6 (s, C-2'), 139.8 (d, C-4), 132.9 (s, C-1'), 130.7 (d, C-4'), 130.2 (d, C-3), 128.9 (d, C-5'), 127.5 (d, C-3'), 126.9 (d, C-6'), 44.8 (d, CHBr), 27.9 (q, COCH₃), 26.1 (q, CHBrCH₃).

HRMS (ESI): $m/z$ = calc. [C₁₂H₁₃₇⁹BrO⁺H⁺]: 253.0223; found: 253.0223.

GC-MS (EI, 70 eV): $t_R = 13.1$ min; $m/z$ (%) = 209 (1) [M–COCH₃⁺], 173 (100) [M–HBr⁺], 145 (20) [C₁₀H₈O⁺], 129 (86) [M–COCH₃–HBr⁺], 115 (59), 102 (13) [C₉H₇⁺], 77 (15).
Methyl (E)-3-[2’-(1’’-bromoethyl)phenyl]acrylate (5i)

According to GP1, 1.57 g (8.25 mmol, 1.00 eq.) 4i, 1.76 g (9.90 mmol, 1.20 eq.) NBS and 0.10 g (0.41 mmol, 0.05 eq.) DBP were heated under reflux for 20 h in 200 mL anhydrous chloroform. After purification by column chromatography (silica, pentane/EtOAc = 20/1) 1.89 g (7.01 mmol, 85%) of 5i were isolated as yellow oil.

**TLC:** Rf = 0.65 (pentane/EtOAc = 20/1), [UV/KMnO₄].

**IR (ATR):** ν (cm⁻¹) = 2992 (w, C=H), 2950 (w, C=H), 1717 (s, C=O), 1634 (s, C=C, conjugated), 1435 (m), 1317 (s), 1274 (m), 1172 (s, C-O, ester), 973 (w) 762 (m).

**¹H NMR** (400 MHz, CDCl₃): δ (ppm) = 8.14 (d, J = 15.7 Hz, 1H, H-3’), 7.63 (d, J = 7.8 Hz, 1H, H-6’), 7.50 (d, J = 7.8 Hz, 1H, H-3’), 7.41 (t, J = 7.4 Hz, 1H, H-4’), 7.31 (t, J = 7.4 Hz, 1H, H-5’), 6.38 (d, J = 15.7 Hz, 1H, H-2’), 5.52 (q, J = 6.9 Hz, 1H, CHBrCH₃), 3.83 (s, 3H, CO₂CH₃), 2.07 (d, J = 6.9 Hz, 3H, CHBrCH₃).

**¹³C NMR** (101 MHz, CDCl₃): δ (ppm) = 167.1 (s, C-1), 141.6 (s, C-2’), 141.3 (d, C-3), 132.6 (s, C-1’), 130.5 (d, C-4’), 128.8 (d, C-5’), 127.4 (d, C-3’), 127.0 (d, C-6’), 121.3 (d, C-2), 52.0 (q, CO₂CH₃), 44.6 (d, CHBrCH₃), 26.2 (q, CHBrCH₃).

**HRMS (ESI):** m/z = calc. [C₁₂H₁₃BrO₂]+: 269.0172; found: 269.0173.

3-[2′-(1′-Bromoethyl)phenyl]acrylonitrile (5j)

According to **GP1** 500 mg (3.17 mmol, 1.00 eq.) of 4j, 679 mg (3.82 mmol, 1.20 eq.) NBS and 38.5 mg (0.16 mmol, 0.05 eq.) DBP were heated under reflux for 16 h in anhydrous chloroform (45 mL). After purification by column chromatography (silica, pentane/EtOAc = 20/1) 750 mg (3.17 mmol, quant., 80/20 mixture of E/Z isomers) of 5j were isolated as yellow solid.

**M.p.:** 89 °C.

**IR (ATR):** \( \tilde{\nu} \text{ (cm}^{-1}) = 3060 \text{ (w, } C_{\text{ar}}-H) \), 2981 (w, \( C_{\text{Alkyl}}-H \)), 2219 (s, C≡N), 1616 (m), 1485 (m, \( C_{\text{Ar}}=C_{\text{Ar}} \)), 1452 (m, \( C_{\text{Alkyl}}-H \)), 1378 (m, \( C_{\text{Alkyl}}-H \)), 1222 (m), 1197 (m), 1033 (m), 962 (s, C–C, disubst. trans), 761 (vs, \( C_{\text{Ar}}-H \)), 739 (m, disubst. cis).

**E-isomer**

**TLC:** \( R_{f} = 0.41 \) (pentane/EtOAc = 10/1), [KMnO₄/UV].

**\( ^1H \) NMR** (400 MHz, CDCl₃, 298 K): \( \delta \text{ (ppm)} = 7.92 \text{ (d, } ^3J = 16.4 \text{ Hz, } 1H, \text{ H-3}), 7.63 – 7.59 \text{ (m, } 1H, \text{ H-6′), 7.51 – 7.40 \text{ (m, } 2H, \text{ H-3′, H-4′), 7.39 – 7.31 \text{ (m, } 1H, \text{ H-5′), 5.85 \text{ (d, } ^3J = 16.4 \text{ Hz, } 1H, \text{ H-2), 5.37 \text{ (q, } ^3J = 6.9 \text{ Hz, } 1H, \text{ CHBr), 2.09 \text{ (t, } ^3J = 6.9 \text{ Hz, } 3H, \text{ CHBrCH₃).}} \)

**\( ^13C \) NMR** (126 MHz, CDCl₃, 298 K): \( \delta \text{ (ppm)} = 147.4 \text{ (d, C-3), 140.9 \text{ (s, C-2′), 131.9 \text{ (s, C-1′), 131.3 \text{ (d, C-4′), 128.9 \text{ (d, C-5′), 126.8 \text{ (d, C-3′), 126.7 \text{ (d, C-6′), 117.9 \text{ (s, CN), 99.5 \text{ (d, C-2), 44.0 \text{ (d, CHBr), 25.6 \text{ (q, CHBrCH₃).}}}} \)

**Z-isomer:**

**TLC:** \( R_{f} = 0.34 \) (pentane/EtOAc = 10/1), [KMnO₄/UV].

**\( ^1H \) NMR** (400 MHz, CDCl₃, 298 K): \( \delta \text{ (ppm)} = 7.78 – 7.74 \text{ (m, } 1H, \text{ H-6′), 7.70 \text{ (d, } ^3J = 11.8 \text{ Hz, } 1H, \text{ H-3), 7.50 – 7.40 \text{ (m, } 2H, \text{ H-3′, H-4′), 7.39 – 7.31 \text{ (m, } 1H, \text{ H-5′), 5.67 \text{ (d, } ^3J = 11.8 \text{ Hz, } 1H, \text{ H-2), 5.26 \text{ (q, } ^3J = 6.9 \text{ Hz, } 1H, \text{ CHBr), 2.09 \text{ (t, } ^3J = 6.9 \text{ Hz, } 3H, \text{ CHBrCH₃).}} \)

**\( ^13C \) NMR** (126 MHz, CDCl₃, 298 K): \( \delta \text{ (ppm)} = 147.1 \text{ (d, C-3), 140.7 \text{ (s, C-2′), 131.9 \text{ (s, C-1′), 130.9 \text{ (d, C-4′), 128.8 \text{ (d, C-5′), 126.7 \text{ (d, C-3′), 126.6 \text{ (d, C-6′), 99.6 \text{ (d, C-2), 44.9 \text{ (d, CHBr), 25.5 \text{ (q, CHBrCH₃).}}}} \)

**HRMS (ESI):** \( m/z = \text{calc. } [C_{11}H_{10}^{79}\text{BrN}^{+}]^+: 236.0069; \text{found: } 236.0070. \)

\( m/z = \text{calc. } [C_{11}H_{10}^{81}\text{BrN}^{+}]^+: 238.0049; \text{found: } 238.0051. \)

**GC-MS** (EI, 70 eV): \( t_r = 12.8 \text{ min; } m/z \% = (208 \text{ (1) [M–HCN]}^+, 156 \text{ (100) [M–HBr]}^+, 129 \text{ (92), 115 (36) [M–HCN–CH₃]}^+, 102 (7), 77 (11) [C₆H₅]^{+}, 51 (10) [C₆H₃]^{+}. \)

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Z-isomer:

**TLC:** $R_f = 0.65$ (pentane/EtOAc = 10/1), [KMnO$_4$/UV].

$^1$H NMR (400 MHz, C$_6$D$_6$, 298 K): $\delta$ (ppm) = 8.05 – 8.01 (m, 1H, C$_{Ar}$-H), 7.60 – 7.42 (m, 3H, C$_{Ar}$-H), 7.29 – 7.19 (m, 1H, C$_{Ar}$-H), 7.13 – 7.05 (m, 2H, C$_{Ar}$-H, H-3), 7.04 – 6.94 (m, 2H, C$_{Ar}$-H), 6.89 – 6.83 (m, 1H, C$_{Ar}$-H), 4.75 (d, $^3J = 12.0$ Hz, 1H, H-2), 3.71 (q, $^3J = 6.6$ Hz, 1H, H-1’’), 3.55 (d, $^3J = 13.0$ Hz, 1H, Ph-CHH), 3.21 (d, $^2J = 13.0$ Hz, 1H, Ph-CHH), 1.82 (d, $^2J = 14.6$ Hz, 1H, CHHTMS), 1.67 (d, $^2J = 14.6$ Hz, 1H, CHHTMS), 1.03 (d, $^3J = 6.6$ Hz, 3H, H-2’’), -0.13 [s, 9H, Si(CH$_3$)$_3$].

$^{13}$C NMR (101 MHz, C$_6$D$_6$, 298 K): $\delta$ (ppm) = 148.5 (d, C-3), 142.7 (s, CH$_2$-C$_{Ph}$), 139.5 (s, C-2’’), 134.2 (s, C-1’’), 129.9 (d, ortho-CH$_{Ph}$), 129.7 (d, meta-CH$_{Ph}$), 128.6 (d, C$_{Ar}$), 127.5 (d, para-CH$_{Ph}$), 117.4 (s, CN), 96.0 (d, C-2), 58.5 (t, CH$_2$-C$_{Ph}$), 54.9 (d, C-1’’), 39.9 (t, CH$_2$TMS), 8.7 (q, C-2’’), -1.4 [Si(CH$_3$)$_3$].

**HRMS (ESI):** $m/z = \text{calc. } [C_{22}H_{28}N_{2}Si+H]^+ : 349.2095$; found: 349.2093.

**GC-MS** (EI, 70 eV): $t_R = 18.2$ min; $m/z$ (%) = 348 (8) [M]$^+$, 333 (14) [M−CH$_3$]$^+$, 275 (100) [M−(SiCH$_3$)$_3$]$^+$, 220 (2), 156 (54) [M−C$_{11}$H$_{18}$NSi]$^+$, 120 (81), 91 (71) [C$_7$H$_{13}$]$^+$, 73 (18) [(SiCH$_3$)$_3$]$^+$. 

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(E)-3-[2′-(Bromomethyl)phenyl]-1-phenylprop-2-en-1-one (5k)

According to GP1 1.00 g (4.50 mmol, 1.00 eq.) of 4k, 0.96 g (5.40 mmol, 1.20 eq.) NBS and 0.06 g (0.23 mmol, 0.05 eq.) DBP were heated under reflux for 18 h in anhydrous chloroform (75 mL). After purification by column chromatography (silica, pentane/EtOAc = 50/1) 0.39 g (1.29 mmol, 29%) of 5k were isolated as yellow solid.

**TLC:** $R_f = 0.75$ (pentane/EtOAc = 10/1), [UV/KMnO₄].

**IR (ATR):** $\tilde{\nu}$ (cm⁻¹) = 3062, (vw, CAr-H), 1765 (w), 1663 (s, C=O), 1606 (s, CAr=CAr), 1596 (s, CAr=CAr), 1485 (w, CAr=CAr), 1329 (m), 1216 (s), 1015 (vs), 974 (m, C=C, subst. trans), 756 (m, CArH).

**¹H NMR** (400 MHz, CDCl₃): $\delta$ (ppm) = 8.16 (d, $^3J = 15.6$ Hz, 1H, H-3), 8.09 – 8.03 (m, 2H, 2 × ortho-CPh-H), 7.77 – 7.70 (m, 1H, H-3′), 7.64 – 7.57 (m, 1H, para-CPh-H), 7.56 – 7.49 (m, 3H, 2 × meta-CPh-H, H-2), 7.45 – 7.36 (m, 3H, H-4’, H-5’, H-6’), 4.64 (s, 2H, CH₂Br).

**¹³C NMR** (101 MHz, CDCl₃): $\delta$ (ppm) = 190.5 (s, C-1), 140.8 (d, C-3), 138.1 (s, C-2’), 137.3 (s, COCPh), 134.4 (s, C-1’), 133.1 (d, para-CHPh), 131.0 (d, C-4’), 130.6 (d, C-5’), 129.4 (d, C-3’), 128.8 (d, ortho-CHPh), 128.8 (d, meta-CHPh), 127.6 (d, C-6’), 125.0 (d, C-2), 30.8 (t, CH₂Br).

**HRMS (ESI):** $m/z =$ calc. [C₁₆H₁₃⁷⁹BrO⁺]+: 301.0223; found: 301.0224

$m/z =$ calc. [C₁₆H₁₃⁸¹BrO⁺]+: 303.0202; found: 303.0203.

**GC-MS** (EI, 70 eV): $t_r = 17.4$ min; $m/z$ (%) = 221 (40) [M–HBr]⁺, 207 (95) [M–CH₂Br]⁺, 145 (2), 115 (100) [M–C₆H₅O–HBr]⁺.
(E)-1-(Bromomethyl)-2-(2'-({phenylsulfonyl}vinyl)benzene (5I)

According to GP1, 657 mg (2.54 mmol, 1.00 eq.) of 4I, 550 mg (3.09 mmol, 1.20 eq.) NBS and 30.8 mg (0.13 mmol, 0.05 eq.) DBP were heated under reflux for six days in anhydrous chloroform (45 mL). After purification by column chromatography (silica, pentane/EtOAc = 10/1) 460 mg (1.36 mmol, 54%) of 5I were isolated as colorless crystals.

**M.p.:** 139 °C.

**TLC:** Рт = 0.36 (pentane/EtOAc = 5/1) [UV].

**IR** (ATR): ϋ (cm⁻¹) = 3059 (w, C₆H₃–C₆H₃), 1712 (w), 1616 (w, C=C, conjugated), 1598 (w), 1482 (w), 1447 (m, C–H), 1306 (s, S=O), 1222 (m), 1144 (vs, S=O), 1084 (s), 968 (m, C=C, disubst. trans), 853 (m), 840 (m), 778 (m), 752 (s, C₆H₃–H, 1,2-disubst.), 736 (s), 714 (m), 687 (s, C₆H₃–H, monosubst.).

**₁H NMR** (500 MHz, CDCl₃): δ (ppm) = 8.05 (d, ₃J = 15.2 Hz, 1H, H-1'), 8.02 – 7.96 (m, 2H, 2 × ortho-C₆H₃–H), 7.67 – 7.60 (m, 1H, para-C₆H₃–H), 7.56 (t, ₂J = 7.6 Hz, 2H, 2 × meta-C₆H₃–H), 7.51 – 7.47 (m, 1H, H-3), 7.40 – 7.37 (m, 2H, H-4, H-5), 7.36 – 7.31 (m, 1H, H-6), 6.88 (d, ₃J = 15.2 Hz, 1H, H-2'), 4.60 (s, 2H, CH₂Br).

**₁³C NMR** (126 MHz, CDCl₃): δ (ppm) = 140.4 (s, C-4'), 138.9 (d, C-1'), 137.3 (s, C-1), 133.7 (d, para-C₆H₃–H), 131.9 (s, C-2), 131.3 (d, C-5), 130.9 (d, C-6), 130.1 (d, C-2'), 129.6 (d, meta-C₆H₃–H), 129.5 (d, C-4), 128.0 (d, ortho-C₆H₃–H), 127.9 (d, C-3), 30.4 (t, CH₂Br).


**GC-MS** (EI, 70 eV): tᵣ = 18.4 min; m/z (%) = 257 (39) [M–HBr]⁺, 195 (13), 141 (15) [SO₂Ph]⁺, 115 (100) [C₆H₄]⁺, 77 (27) [C₆H₃]⁺.
Methyl 2-(1-methyl-1,2,3,4-tetrahydroisoquinolin-4-yl)acetate hydrochloride (6)

\[
\begin{align*}
\text{C}_{13}\text{H}_{18}\text{ClNO}_2 \\
\text{Mw: 255.74 g/mol}
\end{align*}
\]

To a reaction mixture of 40.0 mg (129 µmol, 1.00 eq.) 1i (major diastereoisomer) and 0.1 mL of conc. HCl in 1.0 mL methanol 45.9 mg (38.8 µmol, 0.30 eq., 10 w%) Pd/C were added in one portion. The flask atmosphere was exchanged with Hydrogen and the reaction was stirred for 16 hours at room temperature under Hydrogen pressure (1 atm). The suspension was filtered through a celite plug and the organic solvents were removed under reduced pressure. After diffusion crystallization (MeOH/Et₂O) 29.0 mg (113 µmol, 88%) of the ammonium salt 6 were isolated as off-white crystals.

**M.p.:** 159 °C.

**IR** (ATR): \(\tilde{\nu} \text{ (cm}^{-1}\text{)} = 2963 \text{ (bm, NH)}, 2905 \text{ (bm, NH)}, 2766 \text{ (bs, NH)}, 2695\text{(m), 2523 (w), 1735 (s, C=O), 1593 (w, C=C), 1492 (m), 1442 (s), 1385 (m), 1204 (m), 1160 (s, C-O), 1178 (s), 1103 (m), 1016 (m), 775 (s, C₆H₅−H), 751 (s).}

**\(^1\text{H-NMR}\)** (500 MHz, MeOD): \(\delta \text{ (ppm)} = 7.40 - 7.31 \text{ (m, 4H, H-5, H-6, H-7, H-8)}, 4.64 \text{ (q, }^3\text{J = 6.9 Hz, 1H, H-1)}, 3.70 \text{ (s, 3H, CO₂CH₃)}, 3.65 - 3.55 \text{ (m, 3H, H-3, H-4)}, 3.05 - 2.96 \text{ (m, 2H, CH₂CO₂CH₃)}, 1.75 \text{ (d, }^3\text{J = 6.9 Hz, 3H, CH₃}).

**\(^{13}\text{C-NMR}\)** (126 MHz, MeOD): \(\delta \text{ (ppm)} = 173.8 \text{ (s, CO₂CH₃)}, 134.8 \text{ (s, C-8a)}, 134.7 \text{ (s, C-4a)}, 129.6 \text{ (d, C-6)}, 128.8 \text{ (d, C-7)}, 128.6 \text{ (d, C-5)}, 127.5 \text{ (d, C-8)}, 52.6 \text{ (d, C-1)}, 52.5 \text{ (q, CO₂CH₃)}, 43.6 \text{ (t, C-3)}, 38.5 \text{ (t, CH₂CO₂CH₃)}, 32.4 \text{ (d, C-4)}, 19.4 \text{ (q, CH₃)).}

**HRMS** [ESI]: \(m/z = \text{calc. } [\text{C}_{13}\text{H}_{15}\text{ClNO}_2−\text{Cl+H}]^+ : 220.1332 \text{ found: 220.1332.}

**GC-MS** (El, 70 eV): \(t_r = 12.89 \text{ min } m/z \% = 218 \text{ (5) } [\text{M–HCl}]^+, 204 \text{ (100) } [\text{M–Cl–CH₃}]^+, 144 \text{ (40), 130 (55) } [\text{M–Cl–C}_3\text{H}_4\text{O}_2–\text{CH}_3]^+.

62
3-Methyl-N-((trimethylsilyl)methyl)butan-1-amine (8b)

For the synthesis of 3-methyl-N-((trimethylsilyl)methyl)butan-1-amine (8b), a literature procedure was adapted.\(^\text{15}\) 0.46 mL (346 mg, 3.97 mmol, 1.20 eq.) iso-pentylamine and 930 mg (6.73 mmol, 2.00 eq.) K\(_2\)CO\(_3\) were suspended in acetonitrile (40 mL). The mixture was cooled to 0 °C and 0.50 mL (720 mg, 3.36 mmol, 1.00 eq.) (trimethylsilyl)methyl iodide were added dropwise. After 19 h at room temperature, the mixture was concentrated under reduced pressure. The residue dissolved in water (10 mL) and extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over Na\(_2\)SO\(_4\), filtrated and concentrated under reduced pressure. Without further purification 281 mg (1.62 mmol, 49%). of 8b were obtained as clear yellowish oil.

**TLC:** \(R_f = 0.32\) (CH\(_2\)Cl\(_2\)/MeOH = 9/1) [ninhydrin].

**IR (ATR):** \(\tilde{\nu} (\text{cm}^{-1}) = 2955\) (m, C–H), 2871 (w, C–H), 2764 (w), 1647 (w, N–H), 1467 (w), 1384 (w), 1368 (w), 1248 (s, Si–CH\(_3\)), 1126 (w, N–H), 841 (vs, Si–CH\(_3\)), 763 (m, Si–CH\(_3\)), 697 (m).

**\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)):** \(\delta (\text{ppm}) = 2.69 – 2.56\) (m, 2H, H-1), 2.08 (s, 2H, CH\(_2\)TMS), 1.59 (hept, \(^3\)J = 6.7 Hz, 1H, H-3), 1.44 – 1.31 (m, 2H, H-2), 0.89 (d, \(^3\)J = 6.7 Hz, 6H, 2 × CH\(_3\)), 0.05 (s, 9H, Si(CH\(_3\))\(_3\)).

**\(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)):** \(\delta (\text{ppm}) = 52.8\) (t, C-1), 40.4 (t, CH\(_2\)TMS), 38.6 (t, C-2), 26.5 (d, C-3), 22.8 (q, 2 × CH\(_3\)), -2.3 (q, Si(CH\(_3\))\(_3\)).

**HRMS [ESI]:** \(m/z = \text{calc.} [\text{C}_9\text{H}_{23}\text{NSi}+\text{H}]^+: 174.1673; \text{found:} 174.1672.\)

**GC-MS (EI, 70 eV):** \(t_r = 13.7\) min; \(m/z\) (%) = 172 (9), 158 (23) [M–CH\(_3\)]\(^+\), 143 (100) [M–C\(_2\)H\(_6\)]\(^+\), 130 (9) [M–C\(_3\)H\(_7\)]\(^+\), 116 (5) [M–C\(_4\)H\(_5\)]\(^+\), 86 (5) [C\(_3\)H\(_2\)N]\(^+\), 73 (42) [[SiCH\(_3\)]\(_3\)]\(^+\).
Methyl-(E)-3-[2’-((benzyl(methyl)amino)methyl)phenyl]acrylate (10)

![Chemical Structure](image)

According to GP2 360 mg (1.41 mmol, 1.00 eq.) of bromide 5b, 205 mg (1.69 µmol, 1.20 eq.) of benzyl-methyl-amine and 975 mg (7.06 mmol, 5.00 eq.) K₂CO₃ were converted into acetone (20 mL). After purification by column chromatography (silica, pentane/EtOAc = 20/1) 326 mg (1.10 mmol, 78%) of 10 were isolated as a yellow oil.

**TLC:** Rᵣ = 0.62 (pentane/EtOAc = 10/1) [UV/KMnO₄].

**IR (ATR):** ʋ (cm⁻¹) = 3062, (w, C₆H₅-H), 2948 (w, C-H), 2788 (w), 1716 (vs, C=O), 1633 (m, C₆H₅-H), 1434 (w, C₆H₅=C₆H₅), 1316 (m), 1169 (s), 1017 (s), 977 (w, C=C, disubst. trans), 854 (w), 748 (m), 699 (m).

**¹H NMR (400 MHz, CDCl₃):** δ (ppm) = 8.33 (d, J = 16.0 Hz, 1H, H-3'), 7.62 – 7.57 (m, 1H, H-3'), 7.39 – 7.27 (m, 7H, C₆H₅-H), 7.25 – 7.20 (m, 1H, C₆H₅-H), 6.38 (d, J = 16.0 Hz, 1H, H-2), 3.84 (s, 3H, CO₂CH₃), 3.63 (s, 2H, Ar-CH₂), 3.55 (s, 2H, Ph-CH₂), 2.09 (s, 3H, CH₃).

**¹³C NMR (101 MHz, CDCl₃):** δ (ppm) = 167.7 (s, C-1), 143.3 (d, C-3), 139.3 (s, CH₂-C₆H₅), 138.8 (s, C-2'), 134.6 (s, C-1'), 130.9 (d, C₆H₅), 129.8 (d, C₆H₅), 129.1 (d, ortho-CH₃), 128.4 (d, meta-CH₃), 127.8 (d, C₆H₅), 127.1 (d, C₆H₅), 126.8 (d, C₆H₅), 118.7 (d, C-2), 62.6 (t, CH₂-C₆H₅), 60.6 (t, Ar-CH₂), 51.8 (q, CO₂CH₃), 41.7 (q, CH₃).

**HRMS (ESI):** m/z = calc. [C₁₉H₂₁NO₂+H]⁺: 296.1645; found: 296.1644.

**GC-MS (EI, 70 eV):** tᵣ = 16.2 min; m/z (%) = 294 (25), 280 (65) [M–CH₃]⁺, 204 (95) [M–C₆H₅]⁺, 174 (15) [M–C₆H₅NO]⁺, 144 (70), 115 (75), 91 (100) [C₇H₇]⁺,
Molecular Structure

Molecular Structure of 6

A colorless fragment-like specimen of $\text{C}_{13}\text{H}_{18}\text{ClNO}_{2}$, approximate dimensions $0.044$ mm x $0.134$ mm x $0.214$ mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture Duo IMS system equipped with a Helios optic monochromator and a Mo IMS microsource ($\lambda = 0.71073$ Å).

A total of 3434 frames were collected. The total exposure time was 26.12 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 62800 reflections to a maximum $\theta$ angle of 26.73° (0.79 Å resolution), of which 2763 were independent (average redundancy 22.729, completeness = 100.0, $R_{\text{int}}$ = 4.85%, $R_{\text{sig}} = 1.43\%$) and 2599 (94.06%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 15.5693 (9)$ Å, $b = 9.3104(5)$ Å, $c = 9.3874(5)$ Å, $\beta = 106.804(2)^\circ$, volume = $1302.66(12)$ Å$^3$, are based upon the refinement of the XYZ-centroids of 166 reflections above $20 \sigma(I)$ with $5.171^\circ < 2\theta < 45.85^\circ$. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.964. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9420 and 0.9880.

The final anisotropic full-matrix least-squares refinement of $F^2$ with 162 variables converged at $R1 = 4.13\%$, for the observed data and $wR2 = 8.48\%$ for all data. The goodness-of-fit was 1.203. The largest peak in the final difference electron density synthesis was $0.382\ e/\AA^3$ and the largest hole was $-0.226\ e/\AA^3$ with an RMS deviation of $0.050\ e/\AA^3$. On the basis of the final model, the calculated density was $1.304\ g/cm^3$ and $F(000), 544e^\cdot$. 
Figure S1: Molecular structure of 6.

Table S2: Sample and crystal data for 6.

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<th>Identification code</th>
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<tr>
<td>Chemical formula</td>
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<td>Formula weight</td>
<td>255.73</td>
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<td>Temperature</td>
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<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
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<tr>
<td>Crystal size</td>
<td>0.044 x 0.134 x 0.214 mm</td>
</tr>
<tr>
<td>Crystal habit</td>
<td>colorless fragment</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
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<tr>
<td>Space group</td>
<td>P 1 21/c 1</td>
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<td>Unit cell dimensions</td>
<td>a = 15.5693 (9) Å, α = 90°</td>
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<tr>
<td></td>
<td>b = 9.3104 (5) Å, β = 106.804 (2)</td>
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<td></td>
<td>c = 9.3874 (5) Å, γ = 90</td>
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<td>Volume</td>
<td>1302.66 (12) Å³</td>
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<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density</td>
<td>1.304 g/cm³</td>
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<tr>
<td>Absorption</td>
<td>0.284 mm⁻¹</td>
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<td>F (000)</td>
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Table S3: Data collection and structure refinement of 6.

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<th>Description</th>
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<td>Diffractometer</td>
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</tr>
<tr>
<td>Radiation source</td>
<td>IMS microsource, Mo</td>
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<tr>
<td>Theta range for data collection</td>
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<tr>
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<td>Full-matrix least-squares on F²</td>
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<tr>
<td>Refinement program</td>
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<tr>
<td>Function minimized</td>
<td>Σ w (F₀² - Fₐ²)²</td>
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<tr>
<td>Data/ restraints / parameters</td>
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<tr>
<td>Goodness-of-fit on F²</td>
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<tr>
<td>Δ / σ_max</td>
<td>0.001</td>
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<td>Final R indices</td>
<td>2599 data; I&gt;2σ</td>
</tr>
<tr>
<td></td>
<td>All data</td>
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<tr>
<td>Weighting scheme</td>
<td>w = 1/[σ²/F₀²] + (0.0201P)² + 1.3271P</td>
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<td></td>
<td>Where P = (F₀² + 2Fₐ²)/3</td>
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<td>Largest diff. peak and hole</td>
<td>0.382 and -0.226 eÅ⁻³</td>
</tr>
<tr>
<td>R.M.S. deviation from mean</td>
<td>0.050 eÅ⁻³</td>
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</table>
Cyclic Voltammetry

The CV measurements were performed with the corresponding photosubstrates 2, product 1a and 7 (1 mM) in 0.1 M of [N(n-Bu)4]PF6 in MeCN. Glassy carbon electrode was used as working and counter electrode, Ag/AgNO3 (0.01 M in MeCN) as reference electrode, and a scan rate of 100 mV/s. The value of the potential at the inflexion point of each oxidation curve was selected as the oxidation potential of the given substrate or product. 300 mV were added to this value to give the corresponding oxidation potentials (E_{ox}) vs. the Saturated Calomel Electrode (SCE).23

Figure S2: Cyclic voltammogram of 1a.
Figure S3: Cyclic voltammogram of 2a.

Figure S4: Cyclic voltammogram of 2b.
Figure S5: Cyclic voltammogram of 2c.

Figure S6: Cyclic voltammogram of 2d.
**Figure S7:** Cyclic voltammogram of 2e.

**Figure S8:** Cyclic voltammogram of 2f.
**Figure S9:** Cyclic voltammogram of 2g.

**Figure S10:** Cyclic voltammogram of 2h.
Figure S11: Cyclic voltammogram of 2i.

Figure S12: Cyclic voltammogram of 2j.
Figure S13: Cyclic voltammogram of 2k.

Figure S14: Cyclic voltammogram of 2l.
Figure S15: Cyclic voltammogram of 2m.

Figure S16: Cyclic voltammogram of 7.
NMR Spectra

Ethyl-2-(2-benzyl-1,2,3,4-tetrahydroisoquinolin-4-yl) acetate (1a)
Methyl-2-(2-benzyl-1,2,3,4-tetrahydroisoquinolin-4-yl) acetate (1b)
1-(2-Benzyl-1,2,3,4-tetrahydroisoquinolin-4-yl)propan-2-one (1c)
2-(2-Benzyl-1,2,3,4-tetrahydroisoquinolin-4-yl)acetonitrile (1d)
Methyl 2-(2-benzyl-7-chloro-1,2,3,4-tetrahydroisoquinolin-4-yl)acetate (1e)
Methyl 2-(2-benzyl-7-methoxy-1,2,3,4-tetrahydroisoquinolin-4-yl)acetate(1f)
Methyl 2-(2-isopentyl-1,2,3,4-tetrahydroisoquinolin-4-yl)acetate(1g)
1-(2-Benzyl-1-methyl-1,2,3,4-tetrahydroisoquinolin-4-yl)-propan-2-one (major) (1h)
1-(2-Benzyl-1-methyl-1,2,3,4-tetrahydroisoquinolin-4-yl)-propan-2-one (minor)(1h)
Methyl (Z)-2-(2-benzyl-1-methyl-2,3-dihydroisoquinolin-4(1H)-ylidene)acetate (major)(1i)
Methyl (Z)-2-(2-benzyl-1-methyl-2,3-dihydroisoquinolin-4(1H)-ylidene)acetate (minor)(1i)
2-(2-Benzyl-1-methyl-1,2,3,4-tetrahydroisoquinolin-4-yl)-acetonitrile (major)(1j)
2-(2-Benzyl-1-methyl-1,2,3,4-tetrahydroisoquinolin-4-yl)-acetonitrile (minor) (1j)
2-(2-Benzyl-1,2,3,4-tetrahydroisoquinolin-4-yl)-1-phenylethan-1-one (1k)
2-Benzyl-4-((phenylsulfonyl)methyl)-1,2,3,4-tetrahydroisoquinoline (1l)
Methyl 2-(2-(4-(trifluoromethyl)benzyl)-1,2,3,4-tetrahydroisoquinolin-4-yl)acetate (1m)
Ethyl-(E)-3-(2-((benzyl((trimethylsilyl)-methyl)-amino)-methyl)-phenyl)acrylate (2a)
Methyl (E)-3-2-(benzyl((trimethylsilyl)methyl)amino)methylphenyl)acrylate (2b)
(E)-4-((Benzyl((trimethylsilyl)methyl)amino)methyl)phenyl)but-3-en-2-one (2c)
(E)-3-((Benzyl((trimethylsilyl)methyl)amino)methyl)phenyl)acrylonitrile (2d)
Methyl-(E)-3-(2-((benzyl((trimethylsilyl)methyl)amino)methyl)-4-chlorophenyl)acrylate (2e)
Methyl-(E)-3-(2-((benzyl((trimethylsilyl)methyl)amino)methyl)-4-methoxyphenyl)acrylate (2f)
Methyl (E)-3-(2-((isopentyl((trimethylsilyl)methyl)amino)methyl)phenyl)acrylate (2g)
(E)-4-(2-(1-(Benzyl((trimethylsilyl)methyl)amino)ethyl)phenyl)but-3-en-2-one (2h)
Methyl (E)-3-(2-(1-(benzyl((trimethylsilyl)methyl)amino)ethyl)phenyl)acrylate (2i)
3-(2-(1-Benzy(scripsilylsilyl)methyl)amino)ethyl)phenyl)acrylonitrile (2j)
(E)-3-(2-((Benzyl(trimethylsilyl)methyl)amino)methyl)phenyl)-1-phenylprop-2-en-1-one (2k)
(E)-N-Benzyl-N-(2-(2-phenylsulfonyl)vinyl)benzyl)-1-(trimethylsilyl)methanamine (2l)
Methyl (E)-3-((2-((4-(trifluoromethyl)benzyl)((trimethylsilyl)methyl)amino)methyl)phenyl)acrylate (2m)
2-Ethylbenzaldehyde (3a)
4-Chloro-2-methylbenzaldehyde (3e)
Ethyl-(E)-3-(o-tolyl)-acrylate (4a)
Methyl (E)-3-(o-tolyl)acrylate (4b)
(E)-4-(o-Tolyl)but-3-en-2-one (4c)
3-(o-Tolyl)acrylonitrile (4d)
Methyl (E)-3-(4-chloro-2-methylphenyl)acrylate (4e)
Methyl-(E)-3-(4-methoxy-2-methylphenyl)acrylate (4f)
(E)-4-(2-Ethylphenyl)but-3-en-2-one (4h)
Methyl-(E)-3-(2-ethylphenyl)acrylate (4i)
3-(2-Ethylphenyl)acrylonitrile (4j)
(E)-1-Phenyl-3-(o-tolyl)prop-2-en-1-one (4k)
(E)-1-Methyl-2-(2-(phenylsulfonyl)vinyl)benzene (4l)
Ethyl-(E)-3-(2-(bromomethyl)phenyl) acrylate (5a)
Methyl (E)-3-(2-(bromomethyl)phenyl)acrylate (5b)
(E)-4-(2-(Bromomethyl)phenyl)but-3-en-2-one (5c)
(E)-3-(2-(Bromomethyl)phenyl)acrylonitrile (5d)
Methyl (E)-3-(2-(bromomethyl)-4-chlorophenyl)acrylate (5e)
Methyl-(E)-3-(2-(bromomethyl)-4-methoxyphenyl)acrylate (5f)
\[(E)-4-(2-(1-Bromoethyl)phenyl)but-3-en-2-one (5h)\]
Methyl (E)-3-(2-(1-bromoethyl)phenyl)acrylate (5i)
3-(2-(1-Bromoethyl)phenyl)acrylonitrile (5j)
(E)-3-(2-(Bromomethyl)phenyl)-1-phenylprop-2-en-1-one (5k)
(E)-1-(Bromomethyl)-2-(2-(phenylsulfonyl)vinyl)benzene (5l)
Methyl 2-(1-methyl-1,2,3,4-tetrahydroisoquinolin-4-yl)acetate hydrochloride (6)
Methyl-(E)-3-(2-((benzyl(methyl)amino)methyl)phenyl)acrylate (7)
3-Methyl-N-((trimethylsilyl)methyl)butan-1-amine (8b)
References

(1) Monos, T. M.; Sun, A. C.; McAtee, R. C.; Devery III, J. J.; Stephenson, C. R. J. *Org. Chem.* 2016, 81, 6988-6994


