Supporting Information

*An Additive-Free Pd-Catalyzed α-Allylation of Imine Containing Heterocycles*

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General information

All commercially available reagents and solvents were purchased from Alfa Aesar, ABCR, Acros Organics, Sigma-Aldrich, Fisher Scientific, Roth, or VWR, and were used without further purification except otherwise noted. When it was required, non-dry solvents were distilled before use. All experiments were carried out using standard Schlenk technique, if not otherwise stated. Solvents were dried and/or degassed with common methods and afterwards stored under inert gas atmosphere (argon or N₂) over molecular sieves. DCM was distilled over P₂O₅ and then over CaH₂ under an argon atmosphere and stored over 4 Å molecular sieves in a brown 1000 mL Schlenk bottle. THF was dried over Na under refluxing conditions and an argon atmosphere until benzophenone indicated its dryness by turning into deep blue color. The dry THF was stored over 4 Å molecular sieves in a brown 1000 mL Schlenk bottle under argon atmosphere.

When high vacuum was declared in experimental procedures, typically a vacuum of 10⁻²·10⁻³ mbar was applied. All reactions were stirred with Teflon-coated magnetic stirring bars. Molecular sieves (Sigma-Aldrich, beads with 8-12 mesh) were activated in a round-bottom flask with a gas-inlet adapter by heating them in a heating mantle for approximately 16 h under high vacuum until complete dryness was obtained. These activated molecular sieves were stored at room temperature under an argon atmosphere.

Temperatures were measured externally if not otherwise stated. When working at a temperature of 0 °C, an ice-water bath served as the cooling medium. Reactions, which were carried out at higher temperatures than room temperature, were heated in a silicon oil bath on a heating plate (RCT basic IKAMAG® safety control, 0-1500 rpm) equipped with an external temperature controller.

Analytical thin layer chromatography (TLC) was carried out on Merck TLC silica gel 60 F254 aluminum sheets and spots were visualized by UV light (λ = 254 and/or 366 nm) and/or by staining with potassium permanganate (0.3 g KMnO₄, 20 g K₂CO₃, 5 mL 5% aqueous NaOH in 300 mL H₂O) or cerium ammonium molybdate (2.0 g Ce(SO₄)₂, 50.0 g (NH₄)₂MoO₄ and 50 mL conc. H₂SO₄ in 400 mL water) (CAM). Stains were developed by heating the TLC plates. Preparative thin layer chromatography (prep. TLC) was carried out on Analtech silica gel 75 Blue Hen Drive (20×20 cm) on glass plates, which were visualized by UV light (λ = 254). Flash column chromatography was performed with silica gel 0.035-0.070 mm, 60 Å (Acros Organics). A 50 to 100 fold excess of silica gel was used with respect to the amount of crude product, depending on the separation problem. The dimensions of the column were selected in such a way that the required amount of silica gel formed a pad between 10-25 cm. The column was equilibrated first with the solvent or solvent mixture, and the crude product diluted in the eluent was applied onto the top of the silica pad. If the crude product was insoluble in the eluent, then the sample was dissolved in an appropriate solvent (EtOAc or DCM), and the equal amount of silica gel was added to the solution, followed by removal of the solvent under reduced pressure. The solid was then directly loaded onto the top of the silica column. The mobile phase was forced through the column using a rubber bulb pump. Basic silica gel was prepared according to the procedure by Nagy et al.⁸ 100 g commercially available silica gel 0.035-0.070 mm, 60 Å (Acros Organics) were stirred in 1 L saturated aqueous sodium hydrogen carbonate solution for 2 h. The gel was then filtered and washed with deionized water (3×200 mL) and acetone (3×200 mL). The washed basic silica was ultimately dried in a compartment drier for 1 d at 100 °C.

GC-MS analyses were carried out on an Agilent Technologies 7890A GC system equipped with a 5975C mass selective detector (inert MSD with Triple Axis Detector system, EI, 70 eV). Samples were injected by employing autosampler 7683B in a split mode 1/25 (inlet temperature: 250 °C; injection volume: 0.1 μL) and separated on an Agilent Technologies J&W GC HP-5MS capillary column (30 m x 0.2 mm x 0.25 μm) at a constant helium flow rate (He 5.0 (Air Liquide), 1.000 mL/min, average velocity 36.5 cm/sec). A general gradient temperature method was used (initial temperature: 50 °C for 1 min, linear increase to 300 °C (40 °C.min⁻¹), hold for 1 min, 1 min post-run at 300 °C, detecting range: 50.0-550.0 amu, solvent delay of 2.80 min).

¹H-, ¹³C-NMR spectra were recorded on a Bruker AVANCE III 300 spectrometer (¹H: 300.36 MHz; ¹³C: 75.53 MHz). Chemical shifts were referenced to the residual proton and carbon signal of the deuterated solvent, respectively (DMSO-d₆: δ = 2.50 ppm (¹H), 39.52 ppm (¹³C); CDCl₃: δ = 7.26 ppm (¹H), 77.16 ppm (¹³C)). Signal multiplicities are abbreviated as s (singlet), bs (broad singlet), d (doublet), dd (doublet of doublet), t
(triplet), q (quadruplet), p (pentet) and m (multiplet). Additionally, quarternary carbon atoms are designated as C_q. Deuterated solvents for nuclear resonance spectroscopy were purchased from euriso top®.

High Resolution Mass Spectrometry (HRMS) was performed on an Agilent Technologies 7890A (G3440A) GC system equipped with an Agilent Technologies J&W GC-column DB-5MS (length: 30 m; inner-diameter: 0.250 mm; film: 0.25 μm) at a constant helium flow. The GC was coupled to a Waters GCT Premier Micromass. For Direct Inlet (DI-EI) the Waters GCT Premier Micromass unit was used.

Melting points were measured on a Mel-Temp® melting point apparatus (Electrothermal) with an integrated microscopical support in open capillary tubes and were not corrected. The temperature was measured with a mercury-in-glass thermometer.
**Substrate Synthesis**

**General procedure for the synthesis of thiazolines:**

The synthesis of thiazolines was performed according to the work of C. Fuganti et al.[a] In a 80 mL Schlenk tube 1.01 g (44 mmol, 1.0 equiv) sodium were carefully added to ice cooled abs. EtOH (20 mL). After complete dissolution of the sodium 5.00 g (44 mmol, 1.0 equiv) cystamine hydrochloride were added portionwise at 0 °C to the NaOEt solution. Then the nitrile substrate and 2.00 g (26 mmol, 0.6 equiv) NH₄OAc were added slowly and heated under reflux for 17 h. The reaction mixture was concentrated under reduced pressure, diluted with 40 mL Et₂O and washed with brine (1×20 mL) and water (1×20 mL). The organic phase was dried over Na₂SO₄ and concentrated under reduced pressure to give the desired thiazolines. Further purification was not necessary.

**2-Benzyl-4,5-dihydrothiazole**

![Diagram of 2-Benzyl-4,5-dihydrothiazole]

2-Benzyl-4,5-dihydrothiazole was synthesized according to the general procedure for the synthesis of thiazolines with 5.16 mL (45 mmol, 1.0 equiv) 2-phenylacetonitrile.

Yield: 7.03 g (39.7 mmol, 90%) yellowish liquid.

$^1$H-NMR (300.36 MHz, CDCl₃): $\delta$ = 7.34 – 7.17 (m, 5H, C₆-10), 4.20 (t, $^3J_{H,H}$ = 8.4 Hz, 2H, C1), 3.79 (s, 2H, C₄), 3.22 (t, $^3J_{H,H}$ = 8.4 Hz, 2H, C₂).

$^{13}$C-NMR (75.53 MHz, CDCl₃): $\delta$ = 171.0 (C₃), 136.1 (C₅), 129.2 (CH, C₆+10), 128.7 (CH, C₇+9), 127.2 (CH, C₈), 64.5 (CH₂, C₁), 40.8 (CH₂, C₄), 34.1 (CH₂, C₂).

**2-Propyl-4,5-dihydrothiazole**

![Diagram of 2-Propyl-4,5-dihydrothiazole]

2-Propyl-4,5-dihydrothiazole was synthesized according to the general procedure for the synthesis of thiazolines with 3.85 mL (44 mmol, 1.0 equiv) butyronitrile.

Yield: 3.62 g (28.01 mmol, 64%) colorless liquid.

$^1$H-NMR (300.36 MHz, CDCl₃): $\delta$ = 4.21 (t, $^3J_{H,H}$ = 8.3 Hz, 2H, C₁), 3.27 (t, $^3J_{H,H}$ = 8.4 Hz, 2H, C₂), 2.49 (t, $^3J_{H,H}$ = 7.5 Hz, 2H, C₄), 1.75 – 1.57 (m, 2H, C₅), 0.96 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, C₆).

$^{13}$C-NMR (75.53 MHz, CDCl₃): $\delta$ = δ 172.1 (C₃), 64.5 (CH₂, C₁), 36.4 (CH₂, C₂), 33.8 (CH₂, C₄), 21.0 (CH₂, C₅), 13.8 (CH₃, C₆).

**2-Ethyl-4,5-dihydrothiazole**

![Diagram of 2-Ethyl-4,5-dihydrothiazole]

2-Ethyl-4,5-dihydrothiazole was synthesized according to the general procedure for the synthesis of thiazolines with 11.5 mL (132 mmol, 3.0 equiv) propionitrile.

Yield: 3.65 g (31.68 mmol, 72%) pale yellow liquid.
\[^{1}\text{H}-\text{NMR} (300.36 \text{ MHz, CDCl}}_3): \delta = 4.21 (t, J = 8.3 \text{ Hz, 2H, C1}), 3.27 (t, ^{3}J_{\text{HH}} = 8.3 \text{ Hz, 2H, C2}), 2.52 (q, ^{3}J_{\text{HH}} = 7.5 \text{ Hz, 2H, C4}), 1.21 (t, ^{3}J_{\text{HH}} = 7.5 \text{ Hz, 3H, C5}).\]

\[^{13}\text{C}-\text{NMR} (75.53 \text{ MHz, CDCl}}_3): \delta = 173.1 (\text{C}, \text{C3}), 64.6 (\text{CH}_2, \text{C1}), 33.9 (\text{CH}_2, \text{C2}), 27.9 (\text{CH}_2, \text{C4}), 11.9 (\text{CH}_3, \text{C5}).\]

**2-Benzyl-4,4-dimethyl-4,5-dihydrooxazole (4)**

![Diagram of 2-Benzyl-4,4-dimethyl-4,5-dihydrooxazole (4)]

3.10 g (8.54 mmol, 0.2 equiv) of Zn(OTf)$_2$ were weighed into a three-neck round bottom flask equipped with a reflux condenser. Zn(OTf)$_2$ was heated under vacuum and flushed with nitrogen after cooling. This was performed three times. 40 mL abs. toluene were added followed by 4.9 mL (42.68 mmol, 1.0 equiv) 2-phenylacetonitrile and 4.57 g (51.22 mmol, 1.2 equiv) 2-amino-2-methylpropan-1-ol. The reaction mixture was heated under reflux for 4 d. After cooling to rt 40 mL toluene were added to dilute the reaction mixture. The organic phase was washed with H$_2$O (2×100 mL) and then concentrated on a rotary evaporator. The product could be obtained in excellent purity (≥99% product, GC-MS) after drying in oil pump vacuum for several hours.

Yield: 6.92 g (36.56 mmol, 85%) yellowish oil.

\[^{1}\text{H}-\text{NMR} (300.36 \text{ MHz, CDCl}}_3): \delta = 7.38 – 7.17 (m, 5H, C8-12), 3.90 (s, 2H, C2), 3.59 (s, 2H, C6), 1.27 (s, 6H, C3+4).\]

\[^{13}\text{C}-\text{NMR} (75.53 \text{ MHz, CDCl}}_3): \delta = 164.3 (\text{C}, \text{C5}), 135.4 (\text{C}, \text{C7}), 128.8 (\text{CH}, \text{C8+12}), 128.7 (\text{CH}, \text{C9+11}), 127.0 (\text{CH}, \text{C10}), 79.4 (\text{CH}_2, \text{C2}), 67.1 (\text{C}, \text{C1}), 35.0 (\text{CH}_2, \text{C6}), 28.4 (2x\text{CH}_3, \text{C3+4}).\]

**2-Benzyl-5,6-dihydro-4H-1,3-oxazine**

![Diagram of 2-Benzyl-5,6-dihydro-4H-1,3-oxazine]

An 80 mL Schlenk tube was charged with 620 mg (1.71 mmol, 0.2 equiv.) Zn(OTf)$_2$ and evacuated under heat three times. 849 µL (11.10 mmol, 1.3 equiv.) 3-aminopropan-1-ol, 979 µL (8.54 mmol, 1.0 equiv.) phenylacetonitrile, and 15 mL chlorobenzene were added at rt. A reflux condenser with a bubbler was attached and the reaction mixture was heated to 130 °C for 36 h. The homogenous mixture was then cooled to rt and diluted in 100 mL ethyl acetate. The organic phase was washed with H$_2$O (2×100 mL), dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The final product could be purified via Kugelrohr distillation.

Yield: 320 mg (1.83 mmol, 21%) colorless liquid.

b.p.: 125 °C (0.85 mbar).

\[^{1}\text{H}-\text{NMR} (300.36 \text{ MHz, CDCl}}_3): \delta = 7.37 – 7.13 (m, 5H, C7-11), 4.09 (t, J = 5.4 \text{ Hz, 2H, C1}), 3.41 (s, 2H, C5), 3.35 (t, J = 5.8 \text{ Hz, 2H, C3}), 1.85 – 1.74 (m, 2H, C2).\]

\[^{13}\text{C}-\text{NMR} (75.53 \text{ MHz, CDCl}}_3): \delta = 159.2 (\text{C}, \text{C4}), 136.9 (\text{C}, \text{C6}), 129.0 (\text{CH}, \text{C8+10}), 128.5 (\text{CH}, \text{C7+11}), 126.7 (\text{CH}, \text{C9}), 65.2 (\text{CH}_2, \text{C1}), 42.7 (\text{CH}_2, \text{C3}), 42.5 (\text{CH}_2, \text{C5}), 21.8 (\text{CH}_2, \text{C2}).\]
1,2-Dimethyl-1H-benzo[d]imidazole

![Structure](image)

The synthesis of 1,2-dimethyl-1H-benzo[d]imidazole was performed according to the work of Oisaki. A 100 mL round bottom flask was charged with 1.00 g (7.57 mmol, 1.0 equiv) 2-methyl-1H-benzo[d]imidazole, 3.14 g (22.71 mmol, 3.0 equiv) of K₂CO₃ and 30 mL ethanol. The reaction mixture was cooled to 0 °C in an ice-bath and 947 µL (15.14 mmol, 2.0 equiv) methyl iodide were added. The reaction mixture was stirred at 40 °C for 16 h. The pale yellow solution was diluted with 100 mL dichloromethane. The organic phase was washed with brine (3×50 mL), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The product was purified via column chromatography (SiO₂, dichloromethane/methanol 50/1).

Yield: 805 mg (5.51 mmol, 73%) colorless oil. Rf: 0.33 (dichloromethane/methanol 20/1).

m.p.: 55-60 °C.

³¹H-NMR (300.36 MHz, DMSO-d₆): δ = 7.46 – 7.34 (m, 2H, C2+5), 7.07 (m, 2H, C1+6), 3.63 (s, 3H, C9), 2.43 (s, 3H, C8).

¹³C-NMR (75.53 MHz, DMSO-d₆): δ = 152.1 (C₇, C7), 142.2 (C₈, C4), 135.8 (C₉, C3), 121.2 (CH, C6), 121.0 (CH, C1), 118.0 (CH, C5), 109.6 (CH, C2), 29.6 (CH₃, C9), 13.4 (CH₃, C8).

1-Benzyl-2-methyl-1H-benzo[d]imidazole

![Structure](image)

The synthesis of this compound was performed according to the work of Yamamoto. To a solution of 1.19 g (9.00 mmol, 1.0 equiv) 2-methyl-1H-benzo[d]imidazole in 15 mL methanol in a 50 mL round bottom flask were added 2.76 mL (23.98 mmol, 2.7 equiv) benzyl chloride at rt. The reaction was heated under reflux for 24 h. After cooling to rt the reaction mixture was diluted with 70 mL chloroform and washed with sat. NaHCO₃ (1×100 mL). The organic phase was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product (3.2 g) was taken up onto 3 g silica gel and purified via column chromatography (SiO₂, ethyl acetate/methanol 100/1).

Yield: 1.24 g (5.58 mmol, 62%) colorless oil. Rf: 0.23 (ethyl acetate).

³¹H-NMR (300.36 MHz, CDCl₃): δ = 7.77 (d, J = 7.0 Hz, 1H, C5), 7.39 – 7.19 (m, 6H, aromatic), 7.09 (d, J = 6.2 Hz, 2H, aromatic), 5.36 (s, 2H, C9), 2.61 (s, 3H, C8).

¹³C-NMR (75.53 MHz, CDCl₃): δ = 152.0 (C₇, C7), 142.9 (C₈, C4), 136.0 (C₉, C3), 135.6 (C₉, C10), 129.1 (CH, C12+14), 128.0 (CH, C11+15), 126.4 (CH, C13), 122.4 (CH, C6), 122.1 (CH, C1), 119.3 (CH, C5), 109.5 (CH, C2), 47.2 (CH₃, C9), 14.2 (CH₃, C8).
**tert-Butyl 2-methyl-1H-benzo[d]imidazole-1-carboxylate (27)**

The synthesis of 27 was performed according to the work of Mendiola.\(^c\) In a 100 mL round bottom flask 2.00 g (15.13 mmol, 1.0 equiv) 2-methyl-1H-benzo[d]imidazole, 6.30 mL (45.40 mmol, 3.0 equiv) Et\(_3\)N and 92 mg (1.53 mmol, 0.1 equiv) DMAP were dissolved in 20 mL dichloromethane. The yellow reaction mixture was cooled to 0 °C in an ice bath and 3.30 g (30.26 mmol, 2.0 equiv) di-tert-butyl dicarbonate were added. After stirring for 24 h at rt the reaction mixture was transferred into 100 mL H\(_2\)O. The aqueous phase was then washed with dichloromethane (3×100 mL). The organic phase was dried over Na\(_2\)SO\(_4\), filtered, and concentrated under reduced pressure. The product was purified via column chromatography (SiO\(_2\), cyclohexane/ethyl acetate (20/1 to 1/1)).

Yield: 3.40 g (14.64 mmol, 97\%) white crystals.

R\(_f\): 0.30 (cyclohexane/ethyl acetate 4/1).

m.p.: 74 °C.

\(^1\)H-NMR (300.36 MHz, CDCl\(_3\)): \(\delta = 7.90\) (dd, \(J_{HH} = 6.3, 2.8\) Hz, 1H, C2), 7.65 (dd, \(J_{HH} = 6.3, 2.7\) Hz, 1H, C5), 7.35 – 7.23 (m, 2H, C1+6), 2.82 (s, 3H, C8), 1.71 (s, 9H, C11-13).

\(^{13}\)C-NMR (75.53 MHz, CDCl\(_3\)): \(\delta = 153.3\) (C\(_q\), C9), 149.2 (C\(_q\), C7), 142.2 (C\(_q\), C4), 133.1 (C\(_q\), C3), 124.3 (CH, C1+6), 119.4 (CH, C5), 114.9 (CH, C2), 85.5 (C\(_q\), C10), 28.3 (3×CH\(_3\), C11-13), 18.6 (CH\(_3\), C8).

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**2-Methyl-1-tosyl-1H-benzo[d]imidazole (28)**

In a 100 mL round bottom flask 1.00 g (7.57 mmol, 1.00 equiv.) methyl benzimidazole and 1.16 mL (8.33 mmol, 1.10 equiv.) Et\(_3\)N were added to 30 mL dichloromethane. The white suspension was cooled to 0 °C in an ice bath and 1.52 g (7.95 mmol, 1.05 equiv.) 4-methylbenzenesulfonyl chloride were added. The reaction mixture was allowed to stir at rt for 20 h. The organic phase was then washed with H\(_2\)O (2×50 mL), dried over Na\(_2\)SO\(_4\), filtered, and concentrated under reduced pressure. The crude product was purified via flash column chromatography (100 g SiO\(_2\), cyclohexane/ethyl acetate (1/1)).

Yield: 1.89 g (6.58 mmol, 87%) white powder.

R\(_f\): 0.47 (cyclohexane/ethyl acetate 1/1).

m.p.: 119-123 °C.

\(^1\)H-NMR (300.36 MHz, CDCl\(_3\)): \(\delta = 8.03 – 7.94\) (m, 1H, C2), 7.77 (d, \(J = 8.2\) Hz, 2H, C10+14), 7.64 – 7.53 (m, 1H, C5), 7.36 – 7.18 (m, 4H, C1+6+11+13), 2.77 (s, 3H, C8), 2.35 (s, 3H, C15).

\(^{13}\)C-NMR (75.53 MHz, CDCl\(_3\)): \(\delta = 151.5\) (C\(_q\), C7), 146.2 (C\(_q\), C12), 141.9 (C\(_q\), C4), 135.6 (C\(_q\), C9), 133.3 (C\(_q\), C3), 130.4 (CH, C11+13), 126.9 (CH, C10+14), 124.9 (CH, C1), 124.8 (CH, C6), 119.8 (CH, C5), 113.6 (CH, C2), 21.8 (CH\(_3\),C15), 17.0 (CH\(_3\), C8).
1-Allyl-2-methyl-1H-benzo[d]imidazole (33)

In a flame dried 80 mL Schlenk tube 13 mg (0.058 mmol, 0.01 equiv) Pd(OAc)$_2$ and 46 mg (0.174 mmol, 0.03 equiv) triphenylphosphone were dissolved in 10 mL abs. THF. After stirring the yellow solution for 10 min at rt 689 µL (6.387 mmol, 1.1 equiv.) allyl acetate and 767 mg (5.806 mmol, 1.0 equiv.) 2-methyl-1H-benzo[d]imidazole were added. The suspension was first stirred at rt for 3 h and then heated to 70 °C for 16 h for the completion of the reaction. The solvent was removed under reduced pressure and the crude product was purified via flash column chromatography (150 g SiO$_2$, cyclohexane/ethyl acetate 1/6).

Yield: 877 mg (5.09 mmol, 88%) yellowish oil.

R$_f$: 0.17 (cyclohexane/ethyl acetate 1/1).

$^1$H-NMR (300.36 MHz, CDCl$_3$): $\delta = 7.76 - 7.66$ (m, 1H, C2), 7.30 – 7.19 (m, 3H, C1+C4-6), 5.94 (m, 1H, C10), 5.21 (d, $^2J_{HH} = 10.3$ Hz, 1H, C11-cis), 4.95 (d, $^2J_{HH} = 17.1$ Hz, 1H, C11-trans), 4.71 (dd, $^2J_{HH} = 2.9$, 1.8 Hz, 2H, C9), 2.59 (s, 3H, C8).

$^{13}$C-NMR (75.53 MHz, CDCl$_3$): $\delta = 151.7$ (C_q, C7), 142.5 (C_q, C4), 135.2 (C_q, C3), 131.7 (CH, C10), 122.3 (CH, C5), 122.1 (CH, C1), 119.2 (CH, C5), 117.4 (CH$_2$, C11), 109.3 (CH, C2), 45.9 (CH$_2$, C9), 13.8 (CH$_3$, C8).
General procedure for the synthesis of dihydroisoquinolines:

In a 250 mL one neck round bottom flask 3.00 g (24.7 mmol, 1.00 equiv.) phenylethylamine and 5.22 mL (37.1 mmol, 1.50 equiv.) triethylamine were dissolved in 70 mL abs. dichloromethane. The reaction mixture was cooled in an ice bath to 0 °C and a solution of 24.7 mmol (1.00 equiv.) of the corresponding acyl chloride in 40 mL dichloromethane were added dropwise via a dropping funnel within 30 min and stirred for 19 h at rt. The reaction mixture was washed with 1 M HCl (1x100 mL) and saturated NaHCO₃ solution (1x100 mL). The organic layer was dried over Na₂SO₄, filtered, washed with dichloromethane (1x20 mL), and the solvent was removed under reduced pressure to give a white solid in quantitative yield, which was used in the following step without further purification. 1.2 g (7.3 mmol, 1.00 equiv.) of the crude product were weighed into a 100 mL one neck round bottom flask and an excess (5 g) polyphosphoric acid (PPA) was added. The suspension was heated to 180 °C under vigorous stirring. After stirring for 16 h the black suspension was cooled to rt and 25 mL water were added slowly. A pH of 10 was adjusted with 10 M NaOH. Subsequently, the reaction mixture was extracted with EtOAc (3x25 mL). The combined organic layers were washed with brine (1x100 mL), dried over Na₂SO₄, filtered, and concentrated in vacuum. The black residue was distilled under reduced pressure to give the desired product.

1-Methyl-3,4-dihydroisoquinoline

Yield: 0.81 g (5.6 mmol, 76%), colorless oil.

b.p.: 75 °C (0.79 mbar).

$^1$H-NMR (300.36 MHz, CDCl₃): δ = 7.47 (d, $^3$J_HH = 7.6 Hz, 1H, C₃), 7.39 – 7.24 (m, 2H, C₁-2), 7.17 (d, $^3$J_HH = 6.9 Hz, 1H, C₆), 3.66 (t, $^3$J_HH = 7.4, 1.3 Hz, 2H, C₉), 2.78 – 2.61 (m, 2H, C₁₀), 2.38 (s, 3H, C₈).

$^{13}$C-NMR (75.53 MHz, CDCl₃): δ = 164.3 (Cₗ, C₇), 137.4 (Cₗ, C₅), 130.6 (Cₗ, C₄), 129.6 (CH, C₆), 127.5 (CH, C₂), 126.9 (CH, C₁), 125.3 (CH, C₃), 47.0 (CH₂, C₉), 26.1 (CH₃, C₈), 23.4 (CH₂, C₁₀).

1-Ethyl-3,4-dihydroisoquinoline

Yield: 1.41 g (8.8 mmol, 79%), colorless oil.

b.p.: 93 °C (0.84 mbar).

$^1$H-NMR (300.36 MHz, CDCl₃): δ = 7.63 – 7.05 (m, 4H, C₁-3+6), 3.67 (t, $^3$J_HH = 7.4 Hz, 2H, C₁₀), 2.82 – 2.62 (m, 4H, C₈+9), 1.22 (t, $^3$J_HH = 7.4 Hz, 3H, C₁₁).

$^{13}$C-NMR (75.53 MHz, CDCl₃): δ = 168.0 (Cₗ, C₇), 137.9 (Cₗ, C₅), 130.3 (CH, C₁), 129.1 (Cₗ, C₄), 127.6 (CH, C₆), 126.9 (CH, C₂), 124.9 (CH, C₃), 46.9 (CH₂, C₈), 28.9 (CH₂, C₁₀), 26.3 (CH₃, C₉), 11.3 (CH₃, C₁₁).
1-Benzyl-3,4-dihydroisoquinoline

Yield: 2.58 g (11.6 mmol, 48%), yellow oil.
b.p.: 148 °C (0.45 mbar).

\[ ^1H-NMR \ (300.36 \text{ MHz, CDCl}_3): \delta = 7.45 \ (d, \ J_{HH} = 7.6 \text{ Hz, } 1H, C1), \ 7.35 - 7.22 \ (m, \ 5H, C11-16), \ 7.22 - 7.13 \ (m, \ 3H, C2+3+6), \ 4.08 \ (s, \ 2H, C10), \ 3.80 - 3.73 \ (m, \ 2H, C8), \ 2.76 - 2.67 \ (m, \ 2H, C9). \]

\[ ^13C-NMR \ (75.53 \text{ MHz, CDCl}_3): \delta = 166.1 \ (C \equiv C, C7), \ 138.2 \ (C \equiv C, C11), \ 138.1 \ (C \equiv C, C5), \ 130.6 \ (C \equiv C, C4), \ 128.9 \ (CH, \ C3), \ 128.8 \ (CH, \ C12+16), \ 128.7 \ (CH, \ C13+15), \ 127.7 \ (CH, \ C6), \ 127.0 \ (CH, \ C2), \ 126.5 \ (CH, \ C1), \ 125.9 \ (CH, \ C13), \ 47.3 \ (CH_2, \ C10), \ 43.1 \ (CH_2, \ C8), \ 26.3 \ (CH_2, \ C9). \]

3-Methyl-1-phenyl-4,5-dihydro-1H-pyrazole (22)

55 mg (0.15 mmol, 0.05 equiv.) Zn(OTf)_2 were weighed into a 80 mL Schlenk tube and the solid was evacuated under heat (heat gun). After cooling to rt and purging with argon 8 mL toluene, 228 µL (3.00 mmol, 1.00 equiv.) but-3-yn-1-ol and 387 µL (3.90 mmol, 1.30 equiv.) phenylhydrazine were added sequentially. The reaction was then heated to 120 °C for 23 h. After cooling to rt the reaction mixture was transferred into a round bottom flask and the remaining volatiles were removed under reduced pressure. The crude material was purified via flash column chromatography (75 g SiO_2, cyclohexane/ethyl acetate 20/19).

Yield: 410 mg (2.56 mmol, 86%) yellow-orange crystals.

R_f: 0.32 (cyclohexane/ethyl acetate 9/1).
m.p.: 65-70 °C.

\[ ^1H-NMR \ (300.36 \text{ MHz, CDCl}_3): \delta = 7.26 \ (t, \ J_{HH} = 7.9 \text{ Hz, } 1H, C7 + C9), \ 7.01 \ (d, \ J_{HH} = 7.8 \text{ Hz, } 1H, C6 + C10), \ 6.81 \ (t, \ J_{HH} = 7.3 \text{ Hz, } 1H, C8), \ 3.67 \ (t, \ J_{HH} = 10.0 \text{ Hz, } 1H, C1), \ 2.83 \ (t, \ J_{HH} = 10.0 \text{ Hz, } 1H, C2), \ 2.08 \ (s, \ 1H, C4). \]

\[ ^13C-NMR \ (75.53 \text{ MHz, CDCl}_3): \delta = 151.1 \ (C \equiv C, C3), \ 147.2 \ (C \equiv C, C5), \ 129.2 \ (CH, \ C7 + C9), \ 118.8 \ (CH, \ C8), \ 113.0 \ (CH, \ C6 + C10), \ 48.7 \ (CH_2, \ C1), \ 36.5 \ (CH_2, \ C2), \ 16.2 \ (CH_3, \ C4). \]

2-Phenyl-4,5-dihydrothiazole (42)

The synthesis of 2-phenyl-4,5-dihydrothiazole was performed according to the work of Trose.[e] 4.41g (38.79 mmol, 2.0 equiv) cysteamine hydrochloride and 155 mg (3.88 mmol, 0.2 equiv) NaOH were weighed into a 50 mL round bottom flask. 2.00 mL (19.39 mmol, 1.0 equiv) benzonitrile were added and the reaction mixture was...
heated to 80 °C for 2 h. The reaction mixture was then cooled to rt, taken up in 40 mL ethyl acetate and washed with H$_2$O (1×150 mL). The aqueous phase was extracted with ethyl acetate (3×100 mL). The combined organic phase was dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure to give product, which was used without further purification.

Yield: 2.83 g (17.34 mmol, 89%) pale yellow liquid.

$^1$H-NMR (300.36 MHz, CDCl$_3$) $\delta$ = 7.84 (d, $^3J_{HH} = 6.6$ Hz, 2H, C1+5), 7.51 – 7.35 (m, 3H, C2+4), 4.46 (t, $^3J_{HH} = 8.3$ Hz, 2H, C9), 3.42 (t, $^3J_{HH} = 8.3$ Hz, 2H, C8).

$^{13}$C-NMR (75.53 MHz, CDCl$_3$) $\delta$ = 168.6 (Cq, C7), 133.4 (Cq, C6), 131.2 (CH, C3), 128.6 (CH, C1+5), 128.5 (CH, C2+4), 65.4 (CH$_2$, C9), 33.8 (CH$_2$, C8).

**Cyclohex-2-en-1-yl acetate (39)**

In a 100 mL round bottom flask 2.0 mL (20.38 mmol, 1.0equiv.) cyclohex-2-en-1-ol, 8.5 mL (61.1 mmol, 3.0equiv.) triethylamine and 498 mg (4.08 mmol, 0.2equiv.) DMAP were dissolved in 40 mL abs. dichloromethane. The solution was cooled to 0 °C in an ice bath and 2.32 mL (24.46 mmol, 1.2equiv.) acetic anhydride were added. Subsequently, the reaction was allowed to warm to rt and stirred for 3 h. The organic phase was transferred into a separation funnel and washed with sat. NaHCO$_3$ (2×60 mL) and H$_2$O (2×60 mL), dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The final product was purified via flash column chromatography (125 g SiO$_2$, cyclohexane/ethyl acetate 9/1).

Yield: 2.07 g (14.77 mmol, 73%) pale yellow liquid.

R$_f$: 0.49 (cyclohexane/ethyl acetate 6/1).

$^1$H-NMR (300.36 MHz, CDCl$_3$): $\delta$ = 5.94 (m, 1H, C4), 5.74 – 5.64 (m, 1H, C5), 5.25 (m, 1H, C6), 2.05 (s, 3H, C8), 2.09 – 1.56 (m, 6H, C1-3).

$^{13}$C-NMR (75.53 MHz, CDCl$_3$): $\delta$ = 170.9 (Cq, C7), 132.8 (CH, C5), 125.9 (CH, C4), 68.2 (CH, C6), 28.4 (CH$_2$, C1), 25.0 (CH$_2$, C3), 21.6 (CH$_2$, C8), 19.0 (CH$_2$, C2).

**Cinnamyl methyl carbonate (43)**

4.30 g (32.1 mmol, 1.15 equiv.) cinnamylalcohol and 4.52 g (40.0 mmol, 1.32 equiv.) DMAP were dissolved in 100 mL dichloromethane in a 250 mL three neck round bottom flask. The colorless solution was cooled to 0 °C in an ice bath and 2.16 mL (28.0 mmol, 1.00 equiv) methyl chloroformate were added slowly via a syringe. The white suspension was allowed to warm to rt and was stirred for 15 h until additional 250 mL dichloromethane were added. The organic phase was then washed with H$_2$O (2×200 mL), dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The yellow, liquid crude material was purified via flash column chromatography (500 g SiO$_2$, cyclohexane/ethylacetate 20/1 to 10/1).

Yield: 5.29 g (27.52 mmol, 98%) colorless liquid.

R$_f$: 0.39 (cyclohexane/ethyl acetate 5/1).

$^1$H-NMR (300.36 MHz, CDCl$_3$): $\delta$ = 7.38 – 7.15 (m, 5H, C1-6), 6.63 (d, $^3J_{HH} = 15.9$ Hz, 1H, C7), 6.23 (dt, $^3J_{HH} = 15.8$, 6.4 Hz, 1H, C8), 4.73 (d, $^3J_{HH} = 6.3$ Hz, 2H, C9), 3.74 (s, 3H, C11).
$^{13}$C-NMR (75.53 MHz, CDCl$_3$): $\delta = 155.8$ (C$_q$, C10), 136.2 (C$_q$, C1), 134.9 (CH, C2), 128.7 (CH, aromatic), 128.3 (CH, C5), 126.8 (CH, aromatic), 122.6 (CH, C8), 68.5 (CH$_2$, C9), 54.9 (CH$_3$, C11).
General procedure for the allylation of substrates:

7.3 mg (0.02 mmol, 2 mol%) \([\eta^1\text{-C}_3\text{H}_5\text{PdCl}]_2\) and 23.1 mg (0.04 mmol, 4 mol%) Xantphos-ligand were weighed into a dried Schlenk-tube and evacuated once again. 1 mL DMSO (abs.) was added and the catalyst solution was stirred for 5-10 min at 60 °C. Internal standard (mesitylene, 139 µL, 1.00 mmol), 107.9 µL (1.00 mmol, 1.0 equiv) allyl acetate and substrate (1.00 mmol, 1.0 equiv) were added sequentially to the reaction mixture. After complete consumption of the substrate was indicated via GC-MS the reaction mixture was either directly loaded onto the preconditioned silica or alox column and then purified via column chromatography or dissolved in 3 mL CH₂Cl₂ and then purified via preparative TLC.

8-Allyl-2,3,4,6,7,8-hexahydropyrrolo[1,2-a]pyrimidine (3)

This compound was synthesized according to the general procedure starting from 1,5-diazabicyclo[4.3.0]non-5-ene in 1 h reaction time. For the synthesis of this compound 113.6 µL (1.00 mmol, 1.0 equiv.) allylmethylcarbonate were used instead of allyl acetate. This compound was purified via flash column chromatography (50 g alox, dichloromethane/methanol 50/1 to dichloromethane/methanol 10/1).

Yield: 90 mg (0.55 mmol, 55%) yellowish oil.

R<sub>f</sub>: 0.17 (alox: dichloromethane/methanol 10/1).

<sup>1</sup>H-NMR (300.36 MHz, CDCl₃): δ = 5.79 (m, 1H, C9), 5.16 – 4.94 (m, 2H, C10), 3.39 – 3.26 (m, 2H, C1), 3.25 – 3.09 (m, 4H, C3+4), 2.59 (m, 2H, C8), 2.20 – 1.96 (m, 2H, C5), 1.84 – 1.69 (m, 2H, C2), 1.68 – 1.52 (m, 1H, C6).

<sup>13</sup>C-NMR (75.53 MHz, CDCl₃): δ = 162.4 (C<sub>q</sub>, C7), 136.5 (CH, C9), 116.5 (CH₂, C10), 49.9 (CH₂, C4), 44.00 (CH₂, C1), 43.4 (CH₃, C3), 42.1 (CH₂, C1), 36.9 (CH, C6), 26.0 (CH₂, C8), 21.0 (CH₂, C2).

HRMS: calcd for C₁₀H₁₆N₂ [M⁺] 164.1313, found 164.1307.

4,4-Dimethyl-2-(1-phenylbut-3-en-1-yl)-4,5-dihydrooxazole (5)

This compound was synthesized according to the general procedure starting from 2-benzyl-4,4-dimethyl-4,5-dihydrooxazole in 1 h reaction time. This compound was purified via flash column chromatography (40 g SiO₂, cyclohexane/ethyl acetate 50/1 to 10/1).

Yield: 204 mg (0.89 mmol, 89%) pale yellow oil.

R<sub>f</sub>: 0.28 (cyclohexane/ethyl acetate 3/2).

<sup>1</sup>H-NMR (300.36 MHz, CDCl₃): δ = 7.35 – 7.14 (m, 5H, C11-15), 5.69 (m, 1H, C6), 4.97 (m, 2H, C7), 3.86 – 3.74 (m, 2H, C2), 3.57 (t, J = 7.9 Hz, 1H, C4), 2.84 – 2.42 (m, 2H, C5), 1.21 (d, J = 1.6 Hz, 6H, C8+9).
**4,4-Dimethyl-2-(pent-4-en-2-yl)-4,5-dihydrooxazole (6)**

This compound was synthesized according to the general procedure starting from 2-ethyl-4,4-dimethyl-4,5-dihydrooxazole in 1 h reaction time. This compound was purified via flash column chromatography (40 g SiO₂, cyclohexane/ethyl acetate 50/1 to 10/1).

Yield: 129 mg (0.77 mmol, 77%) colorless liquid.

**Rf**: 0.29 (cyclohexane/ethyl acetate 5/1).

**¹H-NMR (300.36 MHz, CDCl₃)**: δ = 5.76 (m, 1H, C6), 5.03 (m, 2H, C7), 3.88 (s, 2H, C2), 2.52 (dd, ³J_HH = 13.9, 6.9 Hz, 1H, C4), 2.45 – 2.13 (m, 2H, C5), 1.25 (s, 6H, C9+10), 1.17 (d, ³J_HH = 6.9 Hz, 3H, C8).

**¹³C-NMR (75.53 MHz, CDCl₃)**: δ = 169.0 (C₄, C3), 135.9 (CH, C6), 116.7 (CH₂, C7), 79.0 (CH₂, C2), 66.9 (C₄, C1), 38.6 (CH, C4), 33.4 (CH₂, C5), 28.6 (CH₃, C9+10), 17.4 (CH₃, C8).

**HRMS**: calc for C₁₉H₁₉NO [M+H]⁺ 229.1467, found 229.1473.

**2-(But-3-en-1-yl)-1-methyl-1H-benzo[d]imidazole (7)**

The reaction for this compound was performed with 0.50 mmol 1,2-dimethyl-1H-benzo[d]imidazole and stirred for 1h. The final product was purified via flash column chromatography (20 g SiO₂, cyclohexane/ethyl acetate 3/1 to 1/3).

Yield: 45 mg (0.24 mmol, 48%) pale yellow oil.

**Rf**: 0.31 (cyclohexane/ethyl acetate 1/1).

**¹H-NMR (300.36 MHz, CDCl₃)**: δ = 7.73 (dd, J = 6.0, 2.7 Hz, 1H, C-2), 7.34 – 7.18 (m, 3H, C-1+C-5-6), 5.94 (ddt, J = 16.8, 10.2, 6.6 Hz, 2H, C-10), 5.19 – 5.00 (m, 2H, C-11), 3.72 (s, 3H, C-12), 2.97 (dd, J = 8.9, 6.7 Hz, 2H, C-8), 2.70 – 2.57 (m, 2H, C-9).

**¹³C-NMR (75.53 MHz, CDCl₃)**: δ = 154.7 (C₄, C-7), 142.7 (C₄, C-4), 137.1 (CH, C-10), 135.9 (C₄, C-3), 122.2 (CH, C-1 or -6), 121.9 (CH, C-1 or -6), 119.3 (CH, C-5), 116.0 (CH₂, C-11), 109.0 (CH, C-2), 31.7 (CH₂, C-9), 29.9 (CH₃, C-12), 27.2 (CH₂, C-8).

**HRMS**: calc for C₁₃H₁₄N₂ [M]⁺ 186.1157, found 186.1151.
1-Benzyl-2-(but-3-en-1-yl)-1H-benzo[d]imidazole (8)

This compound was synthesized according to the general procedure starting from 1-benzyl-2-methyl-1\textit{H}-benzo[d]imidazole in 1 h reaction time and then purified via flash column chromatography (50 g SiO\textsubscript{2}, cyclohexane/ethyl acetate 10/1 to 3/1).

Yield: 230 mg (0.88 mmol, 88\% pale yellow oil.

R\textsubscript{f}: 0.21 (cyclohexane/ethyl acetate 3/1).

\[^1\text{H}-\text{NMR}\ (300.36 \text{ MHz, CDCl}\textsubscript{3}): \delta = 7.77 (d, J = 7.4 \text{ Hz}, 1H, C-3), 7.38 – 7.14 (m, 6H, C-1+2+6+15-17), 7.04 (d, J = 5.6 \text{ Hz}, 2H, C-14+18), 5.89 \text{ (dtd, } J = 16.8, 10.2, 6.5 \text{ Hz}, 1H, C-10), 5.35 \text{ (s, 2H, C-12)}, 5.11 – 4.94 \text{ (m, 2H, C-11)}, 3.00 – 2.86 \text{ (m, 2H, C-8)}, 2.60 \text{ (m, 2H, C-9)}.\]

\[^{13}\text{C}-\text{NMR}\ (75.53 \text{ MHz, CDCl}\textsubscript{3}): \delta = 154.8 \text{ (C\textsubscript{q}, C-7), 142.8 (C\textsubscript{q}, C-5), 137.1 (CH, C-10), 136.1 (C\textsubscript{q}, C-13), 135.6 (C\textsubscript{q}, C-4), 129.1 (CH, C-15+17), 128.1 (CH, C-1), 126.3 (CH, C-14+18), 122.5 (CH, C-2), 122.2 (CH\textsubscript{2}, C-16), 119.5 (CH, C-6), 115.9 (CH\textsubscript{2}, C-11), 109.6 (CH, C-3), 47.1 (CH\textsubscript{2}, C-12), 31.7 (CH\textsubscript{2}, C-9), 27.3 (CH\textsubscript{2}, C-8).}\]

HRMS: calcd for C\textsubscript{19}H\textsubscript{18}N\textsubscript{2} [M\textsuperscript{+}] 262.1470, found 262.1465.

1-Allyl-2-(but-3-en-1-yl)-1H-benzo[d]imidazole – 1 eqiv. allylacetate (9)

This compound was synthesized according to the general procedure starting from 1-allyl-2-methyl-1\textit{H}-benzo[d]imidazole in 1 h reaction time and then was purified via flash column chromatography (40 g SiO\textsubscript{2}, cyclohexane/ethyl acetate 9/1).

Yield: 140 mg (0.66 mmol, 66\% pale yellow oil.

R\textsubscript{f}: 0.49 (cyclohexane/ethyl acetate 2/3).

\[^1\text{H}-\text{NMR}\ (300.36 \text{ MHz, CDCl}\textsubscript{3}): \delta = 7.79 – 7.70 \text{ (m, 1H, C2), 7.31 – 7.17} \text{ (m, 3H, C1+C5-6), 5.93 \text{ (dd, } J = 8.2, 6.6, 4.2 \text{ Hz}, 2H, C10+13), 5.26 – 4.89 \text{ (m, 4H, C11+14)}, 4.78 – 4.68 \text{ (m, 2H, C12)}, 2.94 \text{ (dd, } J = 9.0, 6.6 \text{ Hz}, 2H, C8), 2.66 \text{ (dd, } J = 14.8, 7.1 \text{ Hz, 2H, C9}).\]

\[^{13}\text{C}-\text{NMR}\ (75.53 \text{ MHz, CDCl}\textsubscript{3}): \delta = 154.5 \text{ (C\textsubscript{q}, C-7), 142.5 (C\textsubscript{q}, C-4), 137.1 (CH, C-13), 135.1 (C\textsubscript{q}, C-3), 131.9 (CH, C-10), 122.4 (CH, C-1), 122.2 (CH\textsubscript{2}, C-6), 119.4 (CH, C-5), 117.5 (CH\textsubscript{3}, C-11), 115.9 (CH\textsubscript{3}, C-14), 109.5 (CH, C-2), 45.8 (CH\textsubscript{2}, C-12), 31.8 (CH\textsubscript{2}, C-9), 27.0 (CH\textsubscript{2}, C-8).\]

HRMS: calcd for C\textsubscript{19}H\textsubscript{18}N\textsubscript{2} [M-H]\textsuperscript{+} 211.1235, found 211.1236.
1- Allyl-2-(but-3-en-1-yl)-1H-benzo[d]imidazole – 2 eqv. allylacetaet (10)

This compound was synthesized according to the general procedure starting from 2-methyl-1H-benzo[d]imidazole and 215.8 µL (2.00 mmol, 2.00 equiv.) allyl acetate in 1 h reaction time. This compound was purified via flash column chromatography (40 g SiO₂, cyclohexane/ethyl acetate 9/1 to 3/1).

Yield: 136 mg (0.64 mmol, 64%) pale yellow oil.

Rf: 0.49 (cyclohexane/ethyl acetate 2/3).

1H-NMR (300.36 MHz, CDCl₃): δ = 7.78 – 7.70 (m, 1H, C-2), 7.30 – 7.18 (m, 3H, C1+C5-6), 6.02 – 5.84 (m, 2H, C10+13), 5.08 (m, 4H, C11+14), 4.81 – 4.70 (m, 2H, C12), 2.98 – 2.87 (m, 2H, C8), 2.66 (dd, J = 14.9, 7.1 Hz, 2H, C9).

13C-NMR (75.53 MHz, CDCl₃): δ = 154.5 (Cq, C-7), 142.8 (Cq, C-4), 137.2 (CH, C-13), 135.2 (Cq, C-3), 132.0 (CH, C-10), 122.3 (CH, C-1), 122.0 (CH, C-6), 119.4 (CH, C-5), 117.5 (CH₂, C-11), 115.9 (CH₂, C-14), 109.5 (CH, C-2), 45.8 (CH₂, C-12), 31.8 (CH₂, C-9), 27.1 (CH₂, C-8).

1-Allyl-2-(1-phenylbut-3-en-1-yl)-4,5-dihydro-1H-imidazole (11)

This compound was synthesized according to the general procedure starting from 2-benzyl-4,5-dihydro-1H-imidazole in 1 h reaction time. This compound was purified via flash column chromatography (40 g SiO₂, dichloromethane/methanol 20/1 to dichloromethane/methanol/ammonia(aq.) 20/1/0.1).

Yield: 179 mg (0.75 mmol, 75%) yellowish oil.

Rf: 0.28 (dichloromethane/methanol/ammonia(aq.) 20/1/0.1).

1H-NMR (300.36 MHz, CDCl₃): δ = 7.35 - 7.15 (m, 5H, C1-6), 5.80 – 5.60 (m, 1H, C15), 5.41 (m, 1H, C9), 5.11 – 4.84 (m, 4H, C10+16), 3.85 – 3.65 (m, 2H, C14), 3.68 – 3.52 (m, 1H, C7), 3.50 – 3.40 (m, 2H, C12), 3.35 – 3.10 (m, 2H, C13), 2.90 - 2.80 (m, 1H, C8), 2.57 - 2.43 (m, 1H, C8).

13C-NMR (75.53 MHz, CDCl₃): δ = 167.4 (Cq, C11), 140.3 (Cq, C1), 136.5 (CH, C8), 133.7 (CH, C15), 128.8 (CH, C3+5), 128.2 (Cq, C2+6), 127.2 (CH, C4), 117.3 (CH₂, C16), 116.5 (CH₂, C10), 51.9 (CH₂, C12), 50.1 (CH₂, C14), 49.1 (CH₂, C13), 44.6 (CH, C7), 39.7 (CH₂, C8).

HRMS: calcd for C24H30N₂ [M]+ 240.1626, found 240.1617.
2-(1-Phenylbut-3-en-1-yl)-4,5-dihydrothiazole (12)

This compound was synthesized according to the general procedure starting from 2-benzyl-4,5-dihydrothiazole in 1 h reaction time. This compound was purified via flash column chromatography (40 g SiO₂, cyclohexane/ethyl acetate 10/1).

Yield: 208 mg (0.96 mmol, 96%) yellowish liquid.

Rf: 0.26 (cyclohexane/ethyl acetate 10/1).

1H-NMR (300.36 MHz, CDCl₃): δ = 7.37 – 7.16 (m, 5H, C1-6), 5.67 (ddt, J = 17.0, 10.1, 6.8 Hz, 1H, C9), 5.08 – 4.87 (m, 2H, C11), 4.20 (t, J = 8.3 Hz, 2H, C12), 3.79 (t, J = 7.7 Hz, 1H, C7), 3.17 (tt, J = 8.5, 4.3 Hz, 2H, C13), 2.85 (dt, J = 14.2, 7.1 Hz, 1H, C9), 2.61 (ddd, J = 14.5, 7.9, 6.9 Hz, 1H, C9).

13C-NMR (75.53 MHz, CDCl₃): δ = 173.8 (Cq, Cq), 140.1 (Cq, C-1), 135.8 (CH, C-10), 128.7 (CH, C-3+5), 128.3 (CH, C-2+6), 127.4 (CH, C-4), 116.9 (CH₂, C-11), 64.6 (CH₂, C-12), 50.8 (CH, C-7), 38.5 (CH₂, C-13), 33.6 (CH₂, C-9).

HRMS: calcd for C₁₃H₁₅NS [M-H]+ 217.0925, found 217.0931.

2-(Hex-5-en-3-yl)-4,5-dihydrothiazole (13)

This compound was synthesized according to the general procedure starting from 2-propyl-4,5-dihydrothiazole in 1 h reaction time. This compound was purified via flash column chromatography (40 g SiO₂, cyclohexane/ethyl acetate 50/1 to 20/1).

Yield: 137 mg (0.81 mmol, 81%) pale yellow liquid.

Rf: 0.33 (cyclohexane/ethyl acetate 5/1).

1H-NMR (300.36 MHz, CDCl₃): δ = 5.75 (m, 1H, C7), 5.03 (m, 2H, C9), 4.20 (t, J₁HLH = 8.3 Hz, 2H, C1), 3.23 (t, J₂HLH = 8.3 Hz, 2H, C2), 2.74 – 2.52 (m, 1H, C4), 2.44 – 2.17 (m, 2H, C5), 1.70 – 1.49 (m, 2H, C6), 0.91 (t, J₃HLH = 7.4 Hz, 3H, C8).

13C-NMR (75.53 MHz, CDCl₃): δ = 175.5 (Cq, C-3), 135.9 (CH, C-7), 116.6 (CH₂, C9), 64.2 (CH₂, C1), 46.4 (CH, C4), 38.0 (CH₂, C2), 33.1 (CH, C5), 26.5 (CH₂, C6), 11.7 (CH₃, C8).

HRMS: calcd for C₉H₁₅NS [M]+ 169.0925, found 169.0922.
2-(Pent-4-en-2-yl)-4,5-dihydrothiazole (14)

\[
\begin{array}{c}
\text{N} \\
\text{S} \\
\text{1} \\
\text{2} \\
\text{3} \\
\text{4} \\
\text{5} \\
\text{6} \\
\text{7} \\
\text{8} \\
\end{array}
\]

This compound was synthesized according to the general procedure starting from 2-ethyl-4,5-dihydrothiazole in 1 h reaction time. This compound was purified via preparative TLC with cyclohexane/ethyl acetate (5/1).

Yield: 112 mg (0.72 mmol, 72%) pale yellow liquid.

Rf: 0.33 (cyclohexane/ethyl acetate 5/1).

\(^1\)H-NMR (300.36 MHz, CDCl\(_3\)): \(\delta = 5.76\) (m, 1H, C6), 5.05 (m, 2H, C7), 4.20 (t, \(\beta J_{HH} = 8.3\) Hz, 2H, C1), 3.24 (t, \(\beta J_{HH} = 8.3\) Hz, 2H, C2), 2.76 (m, 1H, C4), 2.52 – 2.14 (m, 2H, C5), 1.20 (d, \(\beta J_{HH} = 6.9\) Hz, 3H, C8).

\(^{13}\)C-NMR (75.53 MHz, CDCl\(_3\)): \(\delta = 176.4\) (Cq, C3), 135.9 (CH, C6), 116.9 (CH\(_2\), C7), 64.4 (CH\(_2\), C1), 39.7 (CH\(_2\), C2), 33.3 (CH, C4), 18.7 (CH\(_3\), C8).

HRMS: calcd for C\(_8\)H\(_{13}\)NS [M+H]\(^+\) 155.0769, found 155.0768.

2-(Hepta-1,6-dien-4-yl)-4,5-dihydrothiazole (15)

\[
\begin{array}{c}
\text{N} \\
\text{S} \\
\text{1} \\
\text{2} \\
\text{3} \\
\text{4} \\
\text{5} \\
\text{6} \\
\text{7} \\
\text{8} \\
\text{9} \\
\text{10} \\
\end{array}
\]

This compound was synthesized according to the general procedure starting from 2-methyl-4,5-dihydrothiazole in 1 h reaction time. This compound was purified via preparative TLC with cyclohexane/ethyl acetate (2/1).

Yield: 180 mg (0.99 mmol, 99%) pale yellow oil.

Rf: 0.75 (cyclohexane/ethyl acetate 5/1).

\(^1\)H-NMR (300.36 MHz, CDCl\(_3\)): \(\delta = 5.84 - 5.64\) (m, 2H, C6+9), 5.05 (m, 2H, C7+10), 4.19 (t, \(\beta J_{HH} = 8.3\) Hz, 2H, C1), 3.23 (t, \(\beta J_{HH} = 8.3\) Hz, 2H, C2), 2.76 (p, \(\beta J_{HH} = 7.0\) Hz, 1H, C4), 2.44 – 2.24 (m, 4H, C5+8).

\(^{13}\)C-NMR (75.53 MHz, CDCl\(_3\)): \(\delta = 174.6\) (Cq, C3), 135.6 (CH, C6+9), 117.0 (CH\(_2\), C7+10), 64.4 (CH\(_2\), C1), 44.4 (CH, C4), 37.5 (CH\(_2\), C2), 33.4 (CH\(_2\), C5+8).

HRMS: calcd for C\(_{10}\)H\(_{16}\)NS [M+H]\(^+\) 182.1003, found 182.0995.

2-(Hepta-1,6-dien-4-yl)-3,3-dimethyl-3H-indole (16)

\[
\begin{array}{c}
\text{N} \\
\text{1} \\
\text{2} \\
\text{3} \\
\text{4} \\
\text{5} \\
\text{6} \\
\text{7} \\
\text{8} \\
\text{9} \\
\text{10} \\
\text{11} \\
\text{12} \\
\text{13} \\
\text{14} \\
\text{15} \\
\text{16} \\
\end{array}
\]

This compound was synthesized according to the general procedure starting from 2,3,3-trimethyl-3H-indole in 1 h reaction time. This compound was purified via preparative TLC using cyclohexane/ethyl acetate 8/1 as eluent.
Yield: 82 mg (0.34 mmol, 34%) yellow oil.

Rf: 0.28 (cyclohexane/ethyl acetate 10/1).

1H-NMR (300.36 MHz, CDCl3): δ = 7.61 (d, 3JH-H = 7.6 Hz, 1H, C-2), 7.37 – 7.16 (m, 3H, C-1+4+5), 5.88 – 5.70 (m, 2H, C-14+15), 5.04 (dd, 3JH-H = 23.4, 13.5 Hz, 4H, C-16+17), 2.79 (p, 3JH-H = 6.8 Hz, 1H, C-11), 2.50 (ddq, 3JH-H = 20.7, 13.8, 6.9 Hz, 4H, C-12+13), 1.30 (s, 6H, C-9+10).

13C-NMR (75.53 MHz, CDCl3): δ = 192.8 (Cq, C8), 153.9 (Cq, C3), 145.3 (Cq, C4), 136.4 (CH, C14+15), 127.7 (CH, C6), 125.3 (CH, C1), 121.3 (CH, C2), 120.3 (CH, C5), 117.1 (CH2, C16+17), 54.2 (Cq, C7), 39.4 (CH, C11), 38.7 (CH2, C12+13), 23.0 (CH3, C9+10).

HRMS: calcd for C17H23N [M]+ 239.1674, found 239.1675.

1-(But-3-en-1-yl)-3,4-dihydroisoquinoline (17)

This compound was synthesized according to the general procedure starting from 1-methyl-3,4-dihydroisoquinoline in 1 h reaction time. This compound was purified via flash column chromatography (40 g SiO2, cyclohexane/ethyl acetate 20/1 to 5/1).

Yield: 99 mg (0.53 mmol, 53%) pale yellow oil.

Rf: 0.20 (cyclohexane/ethyl acetate 3/1).

1H-NMR (300.36 MHz, CDCl3): δ = 7.49 (d, 3JH-H = 7.1 Hz, 1H, C2), 7.39 – 7.25 (m, 2H, C1+6), 7.19 (d, 3JH-H = 6.9 Hz, 1H, C5), 5.91 (ddt, 3JH-H = 13.2, 10.2, 6.6 Hz, 1H, C13), 5.01 (dd, 3JH-H = 18.9, 13.8 Hz, 2H, C14), 3.67 (t, 3JH-H = 7.3 Hz, 2H, C9), 2.87 – 2.75 (m, 2H, C10), 2.72 – 2.63 (m, 2H, C11), 2.42 (dd, 3JH-H = 14.8, 7.0 Hz, 2H, C12), 2.09 (s, 1H).

13C-NMR (75.53 MHz, CDCl3): δ = 166.8 (Cq, C7), 138.1 (CH, C13), 138.0 (Cq, C4), 130.6 (CH, C6), 129.2 (Cq, C3), 127.7 (CH, C5), 127.0 (CH, C1), 125.1 (CH, C2), 115.0 (CH2, C14), 47.0 (CH2, C9), 35.2 (CH2, C11), 31.3 (CH2, C12), 26.3 (CH3, C10).

HRMS: calcd for C18H21N [M-H]+ 184.1125, found 184.1122.

1-(Hepta-1,6-dien-4-yl)-3,4-dihydroisoquinoline (18)

This compound was synthesized according to the general procedure starting from 1-methyl-3,4-dihydroisoquinoline in 1 h reaction time. This compound was purified via flash column chromatography (40 g SiO2, cyclohexane/ethyl acetate 20/1 to 5/1).

Yield: 35 mg (0.16 mmol, 16%) pale yellow oil.

Rf: 0.53 (cyclohexane/ethyl acetate 3/1).
**1-H-NMR (300.36 MHz, CDCl$_3$):** $\delta = 7.50$ (d, $^{3}J_{HH} = 6.8$ Hz, 1H, C2), 7.39 – 7.24 (m, 2H, C1+6), 7.19 (d, $^{3}J_{HH} = 6.7$ Hz, 1H, C5), 5.78 (dq, $^{2}J_{HH} = 9.9$, 7.2 Hz, 2H, C13+14), 5.09 – 4.86 (m, 4H, C15+16), 3.76 – 3.61 (m, 2H, C8), 3.27 – 3.14 (m, 1H, C10), 2.71 – 2.58 (m, 2H, C9), 2.42 (m, 4H, C11+12), 1.85 (s, 1H).

**13C-NMR (75.53 MHz, CDCl$_3$):** $\delta =$ 169.2 (C$_q$ C7), 138.3 (C$_q$ C4), 136.8 (CH, C13+14), 130.4 (CH, C6), 129.8 (C$_q$ C3), 127.7 (CH, C5), 127.0 (CH, C1), 124.7 (CH, C2), 116.3 (CH$_2$, C15+16), 46.9 (CH$_2$, C8), 42.0 (CH, C10), 37.6 (CH$_2$, C11+12), 26.6 (CH$_2$, C9).

HRMS: calcd for C$_{16}$H$_{18}$N [M-H]$^{-}$ 224.1439, found 224.1439.

### 1-(Pent-4-en-2-yl)-3,4-dihydroisoquinoline (19)

This compound was synthesized according to the general procedure starting from 1-ethyl-3,4-dihydroisoquinoline in 1 h reaction time. This compound was purified via flash column chromatography (40 g SiO$_2$, cyclohexane/ethyl acetate 50/1 to 5/1).

Yield: 151 mg (0.76 mmol, 76%) pale yellow oil.

R$_f$: 0.37 (cyclohexane/ethyl acetate 5/1).

**1-H-NMR (300.36 MHz, CDCl$_3$):** $\delta =$ 7.51 (d, $^{3}J_{HH} = 6.8$ Hz, 1H, C3), 7.40 – 7.24 (m, 2H, C1+2), 7.19 (d, $^{3}J_{HH} = 6.4$ Hz, 1H, C6), 5.92 – 5.73 (m, 1H, C13), 5.00 (m, 2H, C14), 3.78 – 3.55 (m, 2H, C8), 3.20 (m, 1H, C11), 2.65 (t, $J = 7.3$ Hz, 2H, C9), 2.58 – 2.44 (m, 1H, C12), 2.26 – 2.12 (m, 1H, C12), 1.20 (d, $^{3}J_{HH} = 6.8$ Hz, 3H, C10).

**13C-NMR (75.53 MHz, CDCl$_3$):** $\delta =$ 170.5 (C$_q$ C7), 138.4 (C$_q$ C5), 137.2 (C$_q$ C4), 130.3 (CH, C13), 129.2 (CH, C1), 127.8 (CH, C6), 127.0 (CH, C2), 124.7 (CH, C3), 116.1 (CH$_2$, C14), 47.0 (CH$_2$, C8), 39.5 (CH$_2$, C12), 36.9 (CH, C11), 26.5 (CH$_2$, C9), 18.6 (CH$_3$, C10).

HRMS: calcd for C$_{13}$H$_{17}$N [M-H]$^{-}$ 199.1361, found 199.1354.

### 1-(1-Phenylbut-3-en-1-yl)-3,4-dihydroisoquinoline (20)

This compound was synthesized according to the general procedure starting from 1-benzyl-3,4-dihydroisoquinoline in 1 h reaction time. This compound was purified via flash column chromatography (40 g SiO$_2$, cyclohexane/ethyl acetate 50/1 to 10/1).

Yield: 219 mg (0.84 mmol, 84%) pale yellow oil.

R$_f$: 0.42 (cyclohexane/ethyl acetate 10/1).
**1H-NMR (300.36 MHz, CDCl₃):** δ = 7.50 – 7.05 (m, 8H, C1-6+12-16), 5.88 – 5.69 (m, 1H, 18), 4.95 (dd, J₁H,HH = 18.0, 14.2 Hz, 2H, C19), 4.24 (t, J₁H,HH = 7.3 Hz, 1H, C10), 3.79 (t, J₁H,HH = 7.2 Hz, 2H, C8), 2.94 (m, 1H, C17), 2.75 – 2.51 (m, 3H, C9+C17).

**13C-NMR (75.53 MHz, CDCl₃):** δ = 167.2 (C₇, C7), 142.3 (C₉, C11), 138.3 (C₉, C4), 137.4 (CH, C18), 130.3 (CH, aromatic), 129.6 (C₉, C3), 128.7 (CH, aromatic), 128.2 (CH, aromatic), 127.6 (CH, aromatic), 126.9 (CH, aromatic), 126.7 (CH, aromatic), 125.3 (CH, aromatic), 116.0 (CH₂, C19), 50.2 (CH₂, C8), 47.1 (CH, C10), 39.7 (CH₂, C17), 26.4 (CH₂, C9).

**HRMS:** calcd for C₁₃H₁₇N [M-H]⁺ 260.1439, found 260.1440.

2-(1-Phenylbut-3-en-1-yl)-5,6-dihydro-4H-1,3-oxazine (21)

This compound was synthesized according to the general procedure starting from 2-benzyl-5,6-dihydro-4H-1,3-oxazine in 1 h reaction time. This compound was purified via flash column chromatography (40 g basic SiO₂, cyclohexane/ethyl acetate 20/1 to 3/1).

Yield: 155 mg (0.84 mmol, 72%) pale yellow oil.

Rᵣ: 0.28 (cyclohexane/ethyl acetate 3/2).

**1H-NMR (300.36 MHz, CDCl₃):** δ = 7.36 – 7.12 (m, 5H, C10-14), 5.71 (m, 1H, C7), 4.96 (m, 2H, C8), 4.06 (s, 2H, C1), 3.37 (m, 2H, C3), 2.78 – 2.34 (m, 2H, C6), 1.85 – 1.72 (m, 2H, C2), 1.68 (m, 1H, C5).

**13C-NMR (75.53 MHz, CDCl₃):** δ = 160.7 (C₇, C4), 141.2 (C₉, C9), 136.5 (CH, C7), 128.5 (CH, C11+13), 128.0 (CH, C10+14), 126.9 (CH, C12), 116.3 (CH₂, C8), 65.2 (CH₂, C1), 52.0 (CH₂, C3), 42.4 (CH₂, C2), 37.7 (CH, C5), 22.0 (CH₂, C6).

**HRMS:** calcd for C₁₃H₁₇NO [M⁺] 215.1310, found 215.1314.

2-(But-3-en-1-yl)-1H-benzo[d]imidazole (32)

7.3 mg (0.02 mmol, 2 mol%) [(η³-C₅H₅)PdCl]₂ and 23.1 mg (0.04 mmol, 4 mol%) of Xantphos were weighed into a dried Schlenk-tube and evacuated once again. 1 mL DMSO (abs.) was added and the catalyst solution was stirred for 5-10 min at 60 °C. 107.9 µL (1.00 mmol, 1.0 equiv) allyl acetate and 132 mg (1.00 mmol, 1.0 equiv) 2-methyl-1H-benzo[d]imidazole were added sequentially to the reaction mixture. After complete consumption of the substrate was indicated after 6 h via GC-MS the reaction mixture was cooled to rt and 259 µL (2.10 mmol, 2.1 equiv.) phenylsilane were slowly added to the reaction mixture and stirred for 1 h. The black reaction mixture was then directly loaded onto 40 g of silica and purified via column chromatography (cyclohexane/ethyl acetate 1/1 to 1/3).

Yield:105 mg (0.61 mmol 61%) white solid.

Rᵣ: 0.32 (cyclohexane/ethyl acetate 1/3).
m.p.: 142-145 °C.

$^1$H-NMR (300.36 MHz, CDCl$_3$): $\delta$ = 7.55 (s, 2H, C4+5), 7.31 – 7.17 (m, 2H, C3+6), 5.89 (m, 1H, C10), 5.07 (m, 2H, 11), 3.06 (t, $^3J_{HH}$ = 7.5 Hz, 2H, C8), 2.63 (m, 2H, C9).

$^{13}$C-NMR (75.53 MHz, CDCl$_3$): $\delta$ = 154.5 (C$q$, C7), 137.0 (C$q$+CH, C1+2+10), 122.4 (C$q$, 4+5), 116.4 (CH+CH$_2$, 3+6+11), 32.2 (CH$_2$, C9), 28.9 (CH$_2$, C8).

HRMS: calcd for C$_{11}$H$_{12}$N$_2$ [M$^+$] 172.1001, found 172.0992.

2-(1-Phenylhept-3-en-1-yl)-4,5-dihydrothiazole (36)

158.4 µL (1.00 mmol, 1.00 equiv.) trans-2-hexenyl acetate were used instead of allyl acetate. The reaction was stirred for 6 h. This compound was purified via flash column chromatography (50 g SiO$_2$, cyclohexane/ethyl acetate 25/1 to 10/1).

Yield: 213 mg (0.82 mmol, 82%) pale yellow oil (9/1 E/Z mixture).

R$_f$: 0.35 (cyclohexane/ethyl acetate 10/1).

$^1$H-NMR (300.36 MHz, CDCl$_3$): $\delta$ = 7.40 – 7.17 (m, 5H, C12-16), 5.51 – 5.22 (m, 2H, C6+7), 4.24 (t, $^3J_{HH}$ = 8.3 Hz, 2H, C1), 3.81 (t, $^3J_{HH}$ = 7.7 Hz, 1H, C4), 3.21 (t, $^3J_{HH}$ = 8.2 Hz, 2H, C2), 2.82 (dt, $^3J_{HH}$ = 14.1, 7.0 Hz, 1H, C5), 2.59 (dt, $^3J_{HH}$ = 14.1, 7.2 Hz, 1H, C5), 1.92 (dd, $^3J_{HH}$ = 13.9, 6.9 Hz, 2H, C8), 1.36 – 1.20 (m, 2H, C9), 0.83 (dt, $^3J_{HH}$ = 14.7, 7.3 Hz, 3H, C10).

$^{13}$C-NMR (75.53 MHz, CDCl$_3$): $\delta$ = 174.3 (C$q$, C3), 140.3 (C$q$, C11), 133.1 (CH, C7, E), 132.0 (CH, C7, Z), 128.6 (CH, C-aromatic), 128.3 (CH, C-aromatic), 127.4 (CH, C6), 127.3 (CH, C6), 127.1 (CH, aromatic), 126.5 (CH, C-aromatic), 64.5 (CH$_2$, C1), 51.3 (CH, C4), 37.5 (CH$_2$, C2), 34.7 (CH$_2$, C5), 33.6 (CH$_2$, C5), 33.6 (CH$_2$, C8), 32.2 (CH$_2$, C8), 29.6 (CH$_2$, C5), 22.8 (CH$_2$, C9), 22.7 (CH$_2$, C9), 13.9 (CH$_3$, C10), 13.6 (CH$_3$, C10).

HRMS: calcd for C$_{16}$H$_{21}$NS [M$^+$] 259.1395, found 259.1400.

(E)-2-(1,4-Diphenylbut-3-en-1-yl)-4,5-dihydrothiazole (38)

166.7 µL (1.00 mmol, 1.00 equiv.) cinnamyl acetate were used instead of allyl acetate. The reaction was stirred for 6 h. This compound was purified via flash column chromatography (50 g SiO$_2$, cyclohexane/ethyl acetate 15/1 to 7/1).

Yield: 124 mg (0.42 mmol, 42%) pale yellow oil.
Rf: 0.23 (cyclohexane/ethyl acetate 9/1).

\(^1\)H-NMR (300.36 MHz, CDCl\(_3\)): \(\delta = 7.44 - 7.11\) (m, 10H), 6.42 (d, \(J = 15.8\) Hz, 1H, C-13), 6.18 - 6.03 (m, 1H, C-12), 4.26 (t, \(J = 8.0\) Hz, 2H, C-1), 3.91 (t, \(J = 7.5\) Hz, 1H, C-4), 3.22 (m, 2H, C-2), 3.06 (dt, \(J = 14.3, 7.3\) Hz, 1H, C-11), 2.81 (dt, \(J = 14.4, 7.4\) Hz, 1H, C-11).

\(^{13}\)C-NMR (75.53 MHz, CDCl\(_3\)): \(\delta = 173.6\) (C, C-3), 140.2 (C, C-5), 137.7 (C, C-14), 132.1 (CH, aromatic), 128.8 (CH, aromatic), 128.6 (CH, aromatic), 128.3 (CH, aromatic), 127.6 (CH, aromatic), 127.5 (CH, C-8), 127.2 (CH, C-12), 126.3 (CH, aromatic), 64.7 (CH\(_2\), C-1), 51.2 (CH, C-4), 37.9 (CH\(_2\), C-2), 33.7 (CH\(_2\), C-11).

HRMS: calcd for C\(_{19}\)H\(_{19}\)NS [M]\(^+\) 293.1238, found 293.1232.

3-Cinnamyl-2-methoxy-2-phenylthiazolidine (45)

Yield: 75 mg (0.24 mmol 12%) pale yellow oil.

Rf: 0.32 (cyclohexane/ethyl acetate 10/1).

\(^1\)H-NMR (300.36 MHz, CDCl\(_3\)): \(\delta = 7.40 - 7.11\) (m, 10H, C 1-6+13-18), 6.28 (d, \(J_{HH} = 15.7\) Hz, 1H, C12), 6.13 - 6.00 (m, 1H, C11), 3.75 (s, 1H, C19), 3.45 (t, \(J_{HH} = 7.0\) Hz, 2H, C9), 3.18 (d, \(J_{HH} = 7.2\) Hz, 2H, C10), 2.63 (t, \(J_{HH} = 7.0\) Hz, 2H, C8).

\(^{13}\)C-NMR (75.53 MHz, CDCl\(_3\)): \(\delta = 162.1\) (C, C7), 136.9 (C, C6), 132.4 (C, C13), 132.1 (CH, C12), 129.6 (CH, C-aromatic), 128.7 (CH, C-aromatic), 128.5 (CH, C-aromatic), 128.0 (CH, C-aromatic), 127.6 (CH, C-aromatic), 126.4 (CH, C-aromatic), 126.3 (CH, C11), 53.3 (CH\(_2\), C19), 50.3 (CH\(_2\), C9), 34.7 (CH\(_2\), C10), 32.9 (CH\(_2\), C8).

HRMS: calcd for C\(_{19}\)H\(_{21}\)NOS [M]\(^+\) 311.1344, found 311.1349.
Table 1: Optimization for the Pd-catalyzed additive free allylation.

| Entry | Ligand | LG | temperature | conversion $^b$ |
|-------|--------|----|-------------|-----------------|
| 1     | ![DPEPhos](image) | Br | 80 °C       | 0%              |
| 2     | DPEPhos | OH | 80 °C       | 0%              |
| 3     | DPEPhos | OCO$_2$Me | 80 °C | 65%           |
| 4     | DPEPhos | OAc | 80 °C | 77%           |
| 5     | DPEPhos | OAc | 60 °C | 72%           |
| 6     | ![P(OPh)$_3$](image) | OAc | 60 °C | 10%           |
| 7     | ![P(O-Tol)$_3$](image) | OAc | 60 °C | 0%            |
| 8     | ![P(C$_6$F$_5$)$_3$](image) | OAc | 60 °C | 0%            |
| 9     | P$^b$Bu$_3$ | OAc | 60 °C | 0%            |
| 10    | PPh$_3$  | OAc | 60 °C | 0%            |
| 11    | PCy$_3$  | OAc | 60 °C | 0%            |
|   | Chemical Structure | Ligand | Solvent | Temperature | Yield |
|---|-------------------|--------|---------|-------------|-------|
| 12 | ![XPhos](image) | OAc | 60 °C | 0% |
| 13 | ![SPhos](image) | OAc | 60 °C | 0% |
| 14 | ![DPPM](image) | OAc | 60 °C | 2% |
| 15 | ![DPPE](image) | OAc | 60 °C | 3% |
| 16 | ![BINAP](image) | OAc | 60 °C | 0% |
| 17 | ![DPPP](image) | OAc | 60 °C | 0% |
| 18 | ![DPPB](image) | OAc | 60 °C | 0% |
| 19 | ![(-)-DIOP](image) | OAc | 60 °C | 0% |
| 20 | ![DPPF](image) | OAc | 60 °C | 9% |
| 21 | ![XantPhos](image) | OAc | 60 °C | 99% |
| 22 | ![Trost ligand](image) | OAc | 60 °C | 0% |
| 23 | ![Helmchen PHOX ligand](image) | OAc | 60 °C | 0% |
|   | ![Structure of Feringa DSM MonoPhos](image) | OAc | 60 °C | 80%<sup>c</sup> |
|---|---|---|---|---|
| 24 | | | | |
| 25 | ![Structure of S,S-Reetz D-Diphosphonite](image) | OAc | 60 °C | 0% |
| 26 | ![Structure of S,S-Reetz X-Diphosphonite](image) | OAc | 60 °C | 0% |

<sup>a</sup>The screening was performed with 2 mol% (C<sub>3</sub>H<sub>5</sub>PdCl), 4 mol% bidentate or 8 mol% monodentate ligand, 1.0 equiv (0.5 mmol) allylreagent and 1.0 equiv (0.5 mmol) substrate at 80 °C in toluene (0.2 M).<sup>b</sup>Conversion was monitored via GC-MS with nonane (0.5 mmol) as internal standard after 18h.<sup>c</sup>This reaction was performed in a 1.0 M DMSO solution and only a racemic mixture of 5 could be observed via chiral GC-FID after 18h.
Table 2. Solvent Screening for the optimization of the allylation.*

| Entry | Solvent   | Product |
|-------|-----------|---------|
| 1     | 1,4 dioxane | 0%      |
| 2     | THF       | 0%      |
| 3     | DME       | 91%     |
| 4     | 1,2 dichloroethane | 80% |
| 5     | DMF       | 85%     |
| 6     | CH₃CN     | 56%     |
| 7     | DMSO      | 99%     |
| 8     | iPrOH     | 40%     |
| 9     | DMSO      | 99%     |

*Reactions were performed with 2 mol% (C₆H₅PdCl)₂, 4 mol% xantphos, 1.0 equiv (0.5 mmol) allylacetate and 1.0 equiv (0.5 mmol) xy at 60 °C, in solvent (0.2 M). Conversion was monitored via GC-MS with mesitylene (0.5 mmol) as internal standard after 6h. The reaction was performed in a 1.0 M solution and conversion was monitored after 1h.
Literature:

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NMR-Spectra

2-Benzyl-4,5-dihydrothiazole
2-Ethyl-4,5-dihydrothiazole
2-Propyl-4,5-dihydrothiazole
2-Benzyl-4,4-dimethyl-4,5-dihydrooxazole
1,2-Dimethyl-1H-benzo[d]imidazole
1-Benzyl-2-methyl-1H-benzo[d]imidazole
1-Allyl-2-methyl-1H-benzo[d]imidazole (33)
Tert-butyl 2-methyl-1H-benzo[d]imidazole-1-carboxylate (27)
2-Methyl-1-tosyl-1H-benzo[d]imidazole (28)
1-Methyl-3,4-dihydroisoquinoline
1-Ethyl-3,4-dihydroisoquinoline
1-Benzyl-3,4-dihydroisoquinoline
3-Methyl-1-phenyl-4,5-dihydro-1H-pyrazole (22)
2-Phenyl-4,5-dihydrothiazole (42)
Cyclohex-2-en-1-yl acetate (39)
Cinnamyl methyl carbonate (43)
8-Allyl-2,3,4,6,7,8-hexahydropyrrolo[1,2-\textit{a}]pyrimidine (3)
4,4-Dimethyl-2-(1-phenylbut-3-en-1-yl)-4,5-dihydrooxazole (5)
4,4-Dimethyl-2-(pent-4-en-2-yl)-4,5-dihydrooxazole (6)
2-(But-3-en-1-yl)-1-methyl-1H-benzo[d]imidazole (7)
1-Benzyl-2-(but-3-en-1-yl)-1H-benzo[d]imidazole (8)
1-Allyl-2-(but-3-en-1-yl)-1H-benzo[d]imidazole (9)
1-Allyl-2-(1-phenylbut-3-en-1-yl)-4,5-dihydro-1H-imidazole (11)
2-(1-Phenylbut-3-en-1-yl)-4,5-dihydrothiazole (12)
2-(Hex-5-en-3-yl)-4,5-dihydrothiazole (13)
2-(Pent-4-en-2-yl)-4,5-dihydrothiazole (14)
2-(Hepta-1,6-dien-4-yl)-4,5-dihydrothiazole (15)
2-(Hepta-1,6-dien-4-yl)-3,3-dimethyl-3\textit{H}-indole (16)
1-(But-3-en-1-yl)-3,4-dihydroisoquinoline (17)
1-(Hepta-1,6-dien-4-yl)-3,4-dihydroisoquinoline (18)
1-(Pent-4-en-2-yl)-3,4-dihydroisoquinoline (19)
1-(1-phenylbut-3-en-1-yl)-3,4-dihydroisoquinoline (20)
2-(1-Phenylbut-3-en-1-yl)-5,6-dihydro-4\(H\)-1,3-oxazine (21)
2-(But-3-en-1-yl)-1H-benzo[d]imidazole (32)
2-(1-Phenylhept-3-en-1-yl)-4,5-dihydrothiazole (36)
(E)-2-(1,4-diphenylbut-3-en-1-yl)-4,5-dihydrothiazole (38)
3-Cinnamyl-2-methoxy-2-phenylthiazolidine (45)