Supporting information (23 pages)

Cobalt-catalyzed hydroazidation of olefins: convenient access to alkyl azides

Jérôme Waser, Hisanori Nambu and Erick M. Carreira*

Laboratorium für Organische Chemie, ETH Hönggerberg, CH-8093 Zürich, Switzerland.

carreira@org.chem.ethz.ch

General. All reactions were carried out in oven dried glassware under an atmosphere of argon or nitrogen. For flash chromatography technical grade solvents were used, which were distilled prior to use. Solvents for reactions were analytical grade purchased from Merck or Baker and used without further purifications. All chemicals were purchased from Acros, Aldrich, Fluka, Merck or Lancaster and used as such unless stated otherwise. Tosyl azide and ethylsulfonyl azide were synthesized following a published procedure.¹

Chromatographic purification was performed as flash chromatography using Brunschwig silica 32-63, 60Å, using the solvents indicated as eluent with 0.3-0.5 bar pressure.

TLC was performed on Merck silica gel 60 F₂₅₄ TLC glass plates and visualized with UV light and permanganate stain.

Melting points were measured on a Büchi 510 melting point apparatus using open glass capillaries, the data is uncorrected.

¹H-NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer in chloroform-d, DMSO-d₆ or CD₃OD, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm, the internal DMSO signal at 2.50 ppm or the internal methanol signal at 3.30 ppm as standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration, interpretation).

¹³C-NMR spectra were recorded with ¹H-decoupling on a VARIAN Mercury 75 MHz spectrometer in chloroform-d, DMSO-d₆ or CD₃OD, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm, the internal DMSO signal at 39.5 ppm or the internal methanol signal at 49.0 ppm as standard.

Infrared spectra were recorded on a Perkin Elmer Spectrum RX-I FT-IR spectrophotometer as thin films unless stated otherwise and are reported as cm⁻¹ (w=weak, m=medium, s=strong, sh=shoulder).

Gas chromatographic measurements were performed on a Varian 3300 gas chromatographer using a Supelco fused silica column (length: 30 m, diameter: 0.25 cm, film thickness 0.25 µm), hydrogen as carrier gas and a FID detector.

Mass spectrometric measurements were performed by the mass spectrometry service of the LOC at the ETHZ on a Finnigan TSQ 7000 ESI spectrometer for low resolution measurements and on an IONSPEC Ultima ESI-FT-ICR spectrometer at 4.7 Tesla, on an Ion Spec Ultima HR FT-ICR MS MALDI-FT-ICR MS using the DHB-tl (2,5-Dihydroxy-benzoic acid-two layers) method at 4.7 Tesla or on a EI-HIRES Micromass Autospel-ULTIMA spectrometer at 70 eV for high resolution measurements.

Elemental analysis was performed by the Mikroelementaranalytisches Laboratorium der ETHZ.

Caution: Azides are potentially hazardous compounds and adequate safety measures should be taken. Reaction, especially when involving bigger quantities or heating, should be conducted behind safety shields.

Part A: Catalysts preparation

Potassium{[1-(3,5-di-*tert*-butyl-2-hydroxy-phenyl)-meth-(E)-ylidene]-amino}-diphenyl-acetate (**1**)

Potassium hydroxide (0.5 M in EtOH, 9.3 ml, 4.6 mmol, 1.1 equiv) was added to a suspension of α,α -diphenyl-glycine (Acros, 1.0 g, 4.4 mmol, 1.1 equiv) in ethanol (50 ml) at 23 °C under argon. After 30 min, 3,5-di-*tert*-butyl-salicylaldehyde (1.0 g, 4.4 mmol, 1.0 equiv) was added to the clear colorless solution, and the color changed to intensive yellow. The reaction mixture was stirred at 23 °C for 10 h and the solvent was removed under reduced pressure. The isolated hygroscopic yellow solid was further dried in high vacuo for 8 h to furnish **1** (2.2 g, 4.5 mmol, 100%), which was used without further purifications.

N-salicylidene-2-amino-isobutyrate –derivated cobalt (III) complexes

Procedure A:

Salicylaldehyde (1.06 ml, 10.0 mmol, 2.00 equiv) and 2-amino-isobutyric acid (1.03 g, 10.0 mmol, 2.00 equiv) were added to a solution of sodium hydroxide (0.21 g, 5.0 mmol, 1.0 equiv) in ethanol (10 ml) at 23 °C under N₂. The resulting thick yellow suspension was cooled to 0 °C and cobalt(II) nitrate hexahydrate (1.45 g, 5.0 mmol, 1.0 equiv) was added as a cold (0 °C) solution in ethanol (10 ml) and the suspension turned to orange. After stirring 15 min at 0 °C, hydrogen peroxide (35%, 7 ml) was added dropwise over 20 min, whereas the reaction mixture immediately turned dark red under gas evolution. The reaction mixture was further stirred at 0 °C for 2 h and then warmed to 23 °C over 3 h. The resulting nearly clear dark red solution was filtered, the solvent was removed under reduced pressure and the residues co- evaporated with methanol (2x) and CH₂Cl₂ (2x). The resulting dark red-brown residues were suspended in Et₂O, triturated for 1 h and filtered, the obtained fine dark red-brown powder was dried in high vacuo at 70 °C for 12 h to afford a dark-red brown solid (2.04 g, 4.14 mmol, 83%).

The identity of the isolated compound was established to be a mixture by NMR analysis. Further repeated attempts to purify it via column chromatography or recrystallization were unsuccessful. The catalyst was used without further purifications and several batches furnished reproducible results. No loss of activity was observed after several months when the compound was kept in dessicator at 23 °C.

Procedure B:**Sodium-bis-[N-salicylidene-2-amino-isobutyrate]-cobaltate(III) (5)**

Sodium peroxide (0.47 g, 6.0 mmol, 1.2 equiv) was added slowly over 10 min to a solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.5 g, 5.0 mmol, 1.0 equiv) in water (15 ml), whereas black-green $\text{Co}(\text{OH})_3$ precipitated. The reaction mixture was filtered and the precipitate washed with water (2x7 ml) and ethanol (7 ml). The collected $\text{Co}(\text{OH})_3$ gel in ethanol (10 ml) was added to a suspension of salicylaldehyde (1.1 ml, 10 mmol, 2.0 equiv) and 2-amino-isobutyric acid (1.0 g, 10 mmol, 2.0 equiv) in ethanol (10 ml) and the resulting suspension was refluxed for 18 h. The nearly clear dark red solution was cooled to 23 °C, filtered and the solvent was removed under reduced pressure. After co-evaporating with CH_2Cl_2 (3x), the dark red solid was triturated in Et_2O (50 ml), filtered, washed with Et_2O (50 ml) and dried 6 h in high vacuo at 70 °C. The obtained complex was nearly pure **6**EtOH, but this complex proved much less active for the hydrohydrazination reaction and not active at all for the hydroazidation reaction.

^1H NMR (CD_3OD , 300 MHz) δ 8.65 (s, 2H, imine H), 7.49 (d, J = 8.1 Hz, 2H, Ar H), 7.07-7.01 (m, 2H, Ar H), 6.74 (d, J = 8.7 Hz, 2H, Ar H), 6.58-6.53 (m, 2H, Ar H), 3.48 (q, J = 7.2 Hz, 2H, ethanol- CH_2), 1.88 (s, 6H, CH_3), 1.87 (s, 6H, CH_3), 1.17 (t, J = 7.2 Hz, 3H, ethanol- CH_3);

^{13}C NMR (CD_3OD , 300 MHz) δ 188.1, 165.3, 164.6, 135.4, 134.2, 122.5, 120.5, 115.4, 71.2, 66.5, 29.0, 27.8, 15.2.

IR (KBr pellets) ν 3412 (m), 3051 (w), 2974 (m), 2930 (w), 2870 (w), 1641 (s), 1602 (s), 1555 (m), 1532 (m), 1466 (s), 1450 (s), 1383 (s), 1350 (s), 1321 (m), 1205 (m), 1173 (m), 1146 (m), 1125 (m), 1108 (w), 1030 (w), 994 (w), 962 (w), 901 (m), 845 (w), 803 (w), 752 (m), 735 (m), 706 (w), 656 (w), 624 (w), 587 (w), 556 (w), 533 (w), 514 (w), 464 (w), 407 (w);

HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{22}\text{CoN}_2\text{Na}_2\text{O}_6^+$ ($\text{M}+\text{Na}$): 515.0600, found 515.0608.

Procedure C:**[N-salicylidene-2-amino-isobutyrate]-[2-amino-isobutyrate]-cobalt (III) (6)**

Co(OAc)₂·4H₂O (12.5 g, 50.2 mmol, 1.00 equiv) was added to a suspension of salicylaldehyde (5.2 ml, 50 mmol, 1.0 equiv) and 2-amino-isobutyric acid (5.1g, 50 mmol, 1.0 equiv) in water (50 ml) at 23 °C under argon and the reaction mixture was heated to reflux. After refluxing for 2 h, a thick suspension was obtained. The reaction mixture was filtered, the solid washed with water (60 ml) and dried 12 h in high vacuo.

A small amount of the isolated solid (180 mg, about 0.6 mmol) was then suspended in water (3.5 ml) and ethanol (9 ml) under air and 2-amino-isobutyric acid (70 mg, 0.68 mmol) was added. The reaction mixture was stirred under air at 23 °C and slowly turned to a dark red solution. After 5 h, the dark red solution was filtered and the solvent was removed under reduced pressure. The residues were co-evaporated with CH₂Cl₂ (2x), dissolved in ethanol, filtered, the solvent was removed under reduced pressure and dried 6 h in high vacuo at 80 °C. The complex obtained by this procedure contained mainly **6** as a mixture of isomers (2:1). It shows comparable activity as the complex obtained following procedure A.

¹H NMR (CD₃OD, 300 MHz) δ 8.61 (s, 1H (33%), imine H 1. isomer), 8.30 (s, 1H (66%), imine H 2. isomer), 7.56-7.48 (m, 2H, Ar H), 7.29-7.19 (m, 2H, Ar H), 7.09 (d, *J* = 8.7 Hz, 2H, Ar H), 6.70-6.62 (m, 2H, Ar H), 1.84 (s, 3H (33%), CH₃ 1.isomer), 1.82 (s, 3H (33%), CH₃ 1.isomer), 1.79 (s, 3H (66%), CH₃ 2. isomer), 1.70 (s, 3H (33%), CH₃ 1.isomer), 1.67 (s, 3H (66%), CH₃ 2. isomer), 1.62 (s, 3H (33%), CH₃ 1.isomer), 1.32 (s, 3H (66%), CH₃ 2. isomer), 1.26 (s, 3H (66%), CH₃ 2. isomer);

¹³C NMR (DMSO-*d*₆, 300 MHz) δ 185.5, 184.3, 183.8, 183.2, 166.3, 165.8, 163.8, 163.5, 157.6, 134.7, 134.6, 133.6, 121.9, 121.7, 118.6, 118.2, 114.4, 114.0, 69.6, 69.4, 60.3, 58.2, 29.0, 28.3, 28.2, 27.9, 27.1, 26.6;

IR (KBr pellets) ν 3410 (m), 3242 (m), 3130 (m), 2978 (m), 1661 (s, sh), 1644 (s), 1600 (s), 1546 (s, sh), 1467 (m), 1450 (s), 1387 (s), 1345 (s), 1310 (m), 1205 (m), 1174 (m), 1147 (m), 1128 (w), 1032 (w), 995 (w), 901 (m), 847 (w), 807 (w), 756 (m), 705 (w), 661 (w), 626 (w), 588 (w), 552 (w), 530 (w), 468 (w), 419 (w);

HRMS (MALDI) calcd for C₁₅H₂₀CoN₂O₅⁺ (M+H): 367.0704, found 367.0695.

[N-3,5-di-tert-butyl-salicylidene-2,2-diphenyl-glycinato]- cobalt (III) (**7**)

A solution of Co(NO₃)₂·6H₂O (61 mg, 0.21 mmol, 1.0 equiv) in ethanol (1 ml) was added to a solution of ligand (100 mg, 0.21 mmol, 1.0 equiv) in ethanol (0.5 ml) and CH₂Cl₂ (1.5 ml) at 0 °C under argon, whereas a orange solid precipitated. The reaction mixture was warmed to 23 °C, stirred for 6 h and hydrogen peroxide (43 μl, 0.42 mmol, 2.0 equiv) was added dropwise at 0 °C. After 30 min, the reaction mixture was warmed to 23 °C, stirred for 1.5 h and the dark red solution was filtered. The solvent was removed under reduced pressure, co-evaporated with CH₂Cl₂ (2x), the residues were dissolved in CH₂Cl₂ (10 ml) and filtered. The solvent was removed under reduced pressure and the remaining solid dissolved in Et₂O (20 ml) and filtered. The solvent was removed under reduced pressure and the obtained dark red solid triturated in hexane (30 ml), filtered, washed with hexane (10 ml) and dried 12 h in

high vacuo to afford a dark red solid (84 mg), which appear to be the nearly pure 1:1 complex **7** by ^1H NMR, the coordination sphere of the complex being probably completed with water.

^1H NMR (DMSO- d_6 , 300 MHz) δ 8.03 (s, 1H, imine H), 7.48-7.41 (m, 4H, Ar H), 7.27-7.20 (m, 6H, ArH), 6.87-6.85 (m, 2H, Ar H), 3.53 (br s, 5 to 10H, H_2O), 1.08 (s, 9H, CCH_3), 0.70 (s, 9H, CCH_3);

^{13}C NMR (DMSO- d_6 , 300 MHz) 2 δ 168.9, 163.1, 143.8, 143.1, 140.9, 133.4, 130.0, 129.7, 129.6, 128.4, 127.6, 127.5, 127.0, 126.9, 126.6, 118.9, 82.5, 34.6, 33.2, 31.2, 29.5;

IR (KBr pellets) ν 3390 (m), 2955 (m), 1762 (w), 1635 (s), 1527 (w), 1431 (m), 1385 (s), 1270 (w), 1254 (w), 1200 (w), 1169 (w), 1090 (w), 1049 (w), 1027 (w), 916 (w), 870 (w), 844 (w), 826 (w), 743 (w), 700 (m), 595 (w), 545 (w);

HRMS (MALDI) calcd for $\text{C}_{29}\text{H}_{31}\text{CoNNaO}_3^+$ (M+Na): 523.1528, found 523.1519.

Part B: Hydroazidation reaction of alkenes

(3-Azido-butyl)-benzene 3 (**10**)

General procedure A:

$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (10 mg, 0.030 mmol, 0.060 equiv) and ligand **1** (14 mg, 0.030 mmol, 0.060 equiv) were dissolved in ethanol (2.5 ml) at 23 °C under argon. After 30 min, 4-phenyl-butene (**4**) (75 μl , 0.50 mmol, 1.0 equiv) was added to the homogenous orange solution, followed by tosyl azide (0.23 ml, 1.5 mmol, 3.0 equiv) and *tert*-butyl hydroperoxide (5.5 M in decane, 25 μl , 0.14 mmol, 0.28 equiv). The reaction mixture was stirred until the colour changed to dark orange (10 min) and phenylsilane (0.10 ml, 0.80 mmol, 1.6 equiv) was added dropwise. The resulting brown solution was stirred at 23 °C and the reaction monitored by TLC (AcOEt/hexane 1:40) or by gas chromatography. Gas chromatography showed full conversion (> 99%) after 2 h and a selectivity of 89:11 for the azidation of the alkene compared to simple reduction. After completion the reaction was quenched with H_2O (2 ml). Saturated NaHCO_3 solution (2 ml) and brine (5 ml) were added and the reaction mixture was extracted with AcOEt (3x10 ml). The combined organic layers were dried over Na_2SO_4 , filtered and the solvents were removed under reduced pressure (50 mbar, 40 °C). The isolated product was purified by column chromatography (solvent gradient: pentane, then pentane/ Et_2O 60:1) to afford (3-azido-butyl)-benzene (**10**) (79 mg, 0.45 mmol, 90%) as a colorless liquid.

General procedure B:

$\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (10 mg, 0.030 mmol, 0.060 equiv) and ligand **1** (14 mg, 0.030 mmol, 0.060 equiv) were dissolved in ethanol (2.5 ml) at 23 °C under argon. After 30 min, 4-phenyl-butene (**4**) (75 μl , 0.50 mmol, 1.0 equiv) was added to the homogenous orange solution, followed by tosyl azide (0.23 ml, 1.5 mmol, 3.0 equiv) and *tert*-butyl hydroperoxide (5.5 M in decane, 25 μl , 0.14 mmol, 0.28 equiv). The reaction mixture was stirred until the colour changed to dark

orange (10 min) and tetramethyldisiloxane (0.18 ml, 1.0 mmol, 2.0 equiv, for some substrates: 0.26 ml, 1.5 mmol, 3.0 equiv) was added dropwise. The resulting dark brown solution was stirred at 23 °C and the reaction monitored by TLC (AcOEt/hexane 1:40) or by gas chromatography. Gas chromatography showed full conversion (> 99%) after 3 h and a selectivity of 96:4 for the azidation of the alkene compared to simple reduction. After completion (3 h) the reaction was quenched with H₂O (2 ml). Saturated NaHCO₃ solution (2 ml) and brine (5 ml) were added and the reaction mixture was extracted with AcOEt (3x10 ml). The combined organic layers were dried over Na₂SO₄, filtered and the solvents were removed under reduced pressure (50 mbar, 40 °C). The isolated product was purified by column chromatography (solvent gradient: pentane, then pentane/ Et₂O 60:1) to afford (3-azido-butyl)-benzene (**10**) (75 mg, 0.43 mmol, 86%) as a colorless liquid.

Gas chromatographic measurements:

100 µl of the reaction mixture were diluted with 0.9 ml hexane and filtered through a short silica gel plug (2.5 cm) to remove the catalyst. 2 µl of the obtained solution were injected in the gas chromatographer and the following temperature program was followed:

- 10 min at 60 °C
- to 110 °C with a temperature gradient of 8 °C/min
- 1 min at 110 °C
- to 180 °C with a temperature gradient of 20 °C/min.

Using this procedure, 4-phenyl-butene (**4**) eluted after 12.8 min, 4-phenyl-butane after 13.5 min and (3-azido-butyl)-benzene (**10**) after 23.8 min.

R_f (AcOEt/hexane 1:40) 0.30;

¹H NMR (CDCl₃, 300 MHz) δ 7.37-7.32 (m, 2H, Ar H), 7.27-7.22 (m, 3H, Ar H), 3.52-3.43 (m, 1H, CHN₃), 2.86-2.66 (m, 2H, PhCH₂), 1.92-1.75 (m, 2H, CH₂CHN₃), 1.33 (d, *J* = 6.6 Hz, 3H, CH₃);

¹³C NMR (CDCl₃, 300 MHz) δ 141.1, 128.4, 128.3, 126.0, 57.1, 37.8, 32.2, 19.4;

IR ν 3064 (w), 3028 (m), 2972 (m), 2931 (m), 2862 (w), 2100 (s), 1947 (w), 1881 (w), 1805 (w), 1604 (w), 1496 (m), 1454 (m), 1380 (m), 1330 (m), 1250 (s), 1125 (w), 1047 (w), 1031 (w), 916 (w), 857 (w), 832 (w), 800 (w), 747 (m), 699 (s), 578 (w), 562 (w), 515 (w), 466 (w).

(3-Methyl-but-3-enyl)-naphtalene⁴ (**11**)

A solution of 2-bromomethyl-naphtalene (5.0 g, 23 mmol, 1.0 equiv) in dry Et₂O (25 ml) was added dropwise over 90 min to a solution of allyl magnesium bromide (1 M in Et₂O, 45 ml, 45 mmol, 2.0 equiv) at 0 °C under argon. The reaction mixture was warmed to 23 °C over 14 h, cooled to 0 °C and quenched with saturated NH₄Cl solution (30 ml). After diluting with H₂O (30 ml), the reaction mixture was extracted with Et₂O (3x50 ml), the combined organic layers were washed with brine (30 ml), dried over Na₂SO₄ and the solvent was removed under

reduced pressure. The isolated product was purified by column chromatography (hexane) to afford (3-methyl-but-3-enyl)-naphthalene (**11**) (3.09 g, 16.9 mmol, 73%) as a colorless oil.

R_f (hexane) 0.35;

¹H NMR (CDCl₃, 300 MHz) δ 7.82-7.76 (m, 3H, naphthyl H), 7.63 (d, *J* = 0.6 Hz, 1H, naphthyl H), 7.48-7.39 (m, 3H, naphthyl H), 7.35 (dd, *J* = 8.4, 1.9 Hz, 1H, naphthyl H), 5.95-5.84 (m, 1H, alkene H), 5.11-4.98 (m, 2H, alkene H), 2.91 (t, *J* = 7.5 Hz, 2H, naphthyl-CH₂), 2.51-2.44 (m, 2H, alkene-CH₂);

¹³C NMR (CDCl₃, 300 MHz) δ 139.3, 138.0, 133.6, 132.0, 127.8, 127.6, 127.4, 127.3, 126.4, 125.8, 125.1, 115.0, 35.5, 35.4;

IR ν 3053 (m), 3018 (w), 2977 (w), 2925 (m), 2853 (w), 1912 (w) 1821 (w), 1639 (m), 1600 (m), 1508 (m), 1439 (w), 1365 (w), 1332 (w), 1270 (w), 1169 (w), 1143 (w), 1125 (w), 1017 (w), 996 (w), 959 (w), 911 (s), 853 (s), 815 (s), 745 (s), 648 (w), 617 (w), 475 (s).

(3-Azido-3-methyl-butyl)-naphthalene (**12**)

Azide **12** (80 mg, 0.36 mmol, 72%) was obtained as an oil following the general procedure **A** with (3-methyl-but-3-enyl)-naphthalene (**11**) (89 mg, 0.49 mmol, 1.0 equiv) in 8 h using 6 mol% catalyst after purification by column chromatography (solvent gradient: pentane, then pentane/ Et₂O 60:1).

Azide **12** (76 mg, 0.34 mmol, 69%) and (3-methyl-but-3-enyl)-naphthalene (**11**) (23 mg, 0.13 mmol, 26% recovery) were obtained as oils following the general procedure **B** with (3-methyl-but-3-enyl)-naphthalene (77 mg, 0.53 mmol, 1.0 equiv) and tetramethyldisiloxane (0.18 ml, 1.0 mmol, 2.0 equiv) in 12 h using 6 mol% catalyst after purification by column chromatography (solvent gradient: pentane, then pentane/ Et₂O 60:1).

R_f (AcOEt/hexane 1:40) 0.30;

¹H NMR (CDCl₃, 300 MHz) δ 7.85-7.79 (m, 3H, naphthyl H), 7.65 (s, 1H, naphthyl H), 7.51-7.42 (m, 3H, naphthyl H), 7.35 (dd, *J* = 8.4, 1.9 Hz, 1H, naphthyl H), 3.52-3.45 (m, 1H, CHN₃), 2.99-2.80 (m, 2H, naphthyl-CH₂), 2.00-1.82 (m, 2H, CH₂CHN₃), 1.33 (d, *J* = 6.5 Hz, 3H, CH₃);

¹³C NMR (CDCl₃, 300 MHz) δ 139.0, 133.9, 132.3, 128.4, 127.9, 127.7, 127.4, 126.8, 126.3, 125.6, 57.4, 38.0, 32.7, 19.8;

IR ν 3052 (w), 3019 (w), 2969 (m), 2929 (m), 2861 (w), 2099 (s), 1633 (w), 1600 (w), 1507 (m), 1452 (m), 1379 (m), 1332 (m), 1270 (m), 1246 (m), 1125 (w), 1059 (w), 1018 (w), 960 (w), 891 (w), 854 (m), 818 (s), 746 (s), 650 (w), 621 (w), 560 (w), 477 (m);

MS (EI-HIRES) 182.0974 (M-HN₃), 196.1130 (M-HN₂), 197.1201 (M-N₂), 219.1375 (M-HN₂+Na);

Anal. calcd for C₁₄H₁₅N₃: C, 74.64; H, 6.71; N, 18.65. Found: C, 74.71; H, 6.88; N, 18.37.

5-(2-Azido-propyl)-benzo[1,3]dioxole (13)

Azide **13** (67 mg, 0.33 mmol, 66%) and safrole (9 mg, 0.06 mmol, 11% recovery) were obtained as oils following the general procedure **A** with safrole (74 μ l, 0.50 mmol, 1.0 equiv) in 20 h using 6 mol% catalyst after purification by column chromatography (pentane/Et₂O 120:1).

Azide **13** (64 mg, 0.31 mmol, 62%) and safrole (12 mg, 0.075 mmol, 15% recovery) were obtained as oils following the general procedure **B** with safrole (74 μ l, 0.50 mmol, 1.0 equiv) and tetramethyldisiloxane (0.18 ml, 1.0 mmol, 2.0 equiv) in 20 h using 6 mol% catalyst after purification by column chromatography (pentane/Et₂O 120:1).

R_f (AcOEt/hexane 1:40) 0.25;

¹H NMR (CDCl₃, 300 MHz) δ 6.96-6.63 (m, 3H, Ar H), 5.94 (s, 2H, acetal-H), 3.66-3.60 (m, 1H, CHN₃), 2.77-2.61 (m, 2H, ArCH₂), 1.25 (d, J = 6.6 Hz, 3H, CH₃);

¹³C NMR (CDCl₃, 300 MHz) δ 147.5, 146.2, 131.3, 122.2, 109.5, 108.2, 100.9, 59.2, 42.3, 19.1;

IR ν 2973 (w), 2894 (w), 2105 (s), 1844 (w), 1608 (w), 1503 (s), 1490 (s), 1443 (m), 1379 (w), 1362 (w), 1327 (w), 1250 (s), 1190 (m), 1123 (w), 1100 (w), 1040 (s), 931 (m), 913 (w), 862 (w), 808 (w), 772 (w), 743 (w), 650 (w), 619 (w), 602 (w), 560 (w), 526 (w), 452 (w);

HRMS (EI) calcd for C₁₀H₁₁N₃O₂⁺ (M): 205.0851, found 205.0846;

Anal. calcd for C₁₀H₁₁N₃O₂: C, 58.53; H, 5.40; N, 20.48 Found: C, 58.53; H, 5.52; N, 20.41.

But-3-enyloxy-*tert*-butyl-diphenyl-silane⁵ (14)

tert-Butyldiphenyl-silyl-chloride (3.1 ml, 12 mmol, 1.2 equiv) was added dropwise to a solution of 3-butenol (0.86 ml, 10 mmol, 1.0 equiv) and imidazole (0.82 g, 12 mmol, 1.2 equiv) in dry DMF (15 ml) at 23 °C under argon. After stirring for 20 h, the reaction mixture was quenched with water (30 ml) and extracted with AcOEt (3x30 ml). The combined organic layers were washed with water (4x20 ml) and brine (20 ml), dried over Na₂SO₄ and the solvent was removed under reduced pressure. The isolated product was purified by column chromatography (gradient: hexane, then hexane/ AcOEt 200:1) to afford **14** (3.0 g, 9.8 mmol, 98%) as a colorless oil.

¹H NMR (CDCl₃, 300 MHz) δ 7.70-7.66 (m, 4H, Ar H), 7.45-7.35 (m, 6H, Ar H), 5.89-5.77 (m, 1H, alkene-H), 5.10-4.99 (m, 2H, alkene-H), 3.72 (t, J = 6.5 Hz, 2H, CH₂O), 2.36-2.28 (m, 2H, alkene-CH₂), 1.06 (s, 9H, CH₃);

¹³C NMR (CDCl₃, 300 MHz) δ 135.6, 135.4, 134.0, 129.5, 127.6, 116.4, 63.5, 37.2, 26.8, 19.2;

IR ν 3071 (m), 3050 (w), 3013 (w), 2958 (m), 2930 (m), 2894 (m), 2857 (m), 1958 (w), 1887 (w), 1822 (w), 1641 (w), 1589 (w), 1472 (m), 1462 (w), 1428 (m), 1389 (w), 1361 (w), 1329 (w), 1305 (w), 1263 (w), 1227 (w), 1188 (w), 1111 (s), 1007 (w), 998 (w), 988 (w), 912 (m), 823 (m), 737 (m), 701 (s), 689 (m), 613 (m), 506 (s), 491 (m).

(3-Azido-butoxy)-*tert*-butyl-diphenyl-silane (15)

Azide **15** (127 mg, 0.359 mmol, 73%) and butoxy-*tert*-butyl-diphenyl-silane (25 mg, 0.080 mmol, 16%) were obtained as oils following the general procedure **A** with but-3-enyloxy-*tert*-butyl-diphenyl-silane (**14**) (152 mg, 0.490 mmol, 1.00 equiv) in 3 h using 6 mol% catalyst after purification by column chromatography (solvent gradient: pentane, then pentane/ Et₂O 60:1).

Azide **15** (146 mg, 0.413 mmol, 85%) and butoxy-*tert*-butyl-diphenyl-silane (9 mg, 0.03 mmol, 6%) were obtained as oils following the general procedure **B** with but-3-enyloxy-*tert*-butyl-diphenyl-silane (**14**) (150 mg, 0.483 mmol, 1.00 equiv) and tetramethyldisiloxane (0.26 ml, 1.5 mmol, 3.0 equiv) in 3 h using 6 mol% catalyst after purification by column chromatography (solvent gradient: pentane, then pentane/ Et₂O 60:1).

R_f (AcOEt/hexane 1:40) 0.27;

¹H NMR (CDCl₃, 300 MHz) δ 7.70-7.66 (m, 4H, Ar H), 7.45-7.38 (m, 6H, Ar H), 3.81-3.70 (m, 3H, CH₂O and CHN₃), 1.74-1.67 (m, 2H, CH₂CHN₃), 1.29 (d, J = 6.6 Hz, 3H, CHN₃CH₃), 1.07 (s, 9H, CCH₃);

¹³C NMR (CDCl₃, 300 MHz) δ 135.5, 133.7, 129.7, 127.7, 60.4, 54.8, 38.8, 26.8, 19.6, 19.2;

IR ν 3070 (w), 3049 (w), 2959 (m), 2931 (m), 2878 (m), 2857 (m), 2103 (s), 1959 (w), 1887 (w), 1822 (w), 1657 (w), 1589 (w), 1472 (m), 1462 (w), 1428 (m), 1389 (w), 1361 (w), 1332 (w), 1268 (w), 1188 (w), 1112 (s), 1007 (w), 997 (w), 982 (w), 939 (w), 899 (w), 868 (w), 823 (m), 737 (m), 702 (s), 614 (m), 505 (s), 488 (m);

MS (ESI) 354.3 (M+H), 376.3 (M+Na);

Anal. calcd for C₂₀H₂₇N₃OSi: C, 67.95; H, 7.70; N, 11.89 Found: C, 68.16; H, 7.66; N, 11.91.

Prop-2-enyloxy-*tert*-butyl-diphenyl-silane⁶ (16)

tert-Butyldiphenyl-silyl-chloride (8.4 ml, 32 mmol, 1.1 equiv) was added dropwise to a solution of allyl alcohol (2.0 ml, 29 mmol, 1.0 equiv) and imidazole (2.4 g, 35 mmol, 1.2 equiv) in dry DMF (25 ml) at 23 °C under argon. After stirring for 2 h, the reaction mixture was quenched with water (60 ml) and extracted with Et₂O (3x60 ml). The combined organic layers were washed with water (4x40 ml) and brine (40 ml), dried over Na₂SO₄ and the solvent was removed under reduced pressure. The isolated product was purified by column

chromatography (hexane/ AcOEt 50:1) to afford **16** (8.91 g, 30.0 mmol, 100%) as a colorless oil.

¹H NMR (CDCl₃, 300 MHz) δ 7.71-7.67 (m, 4H, Ar H), 7.46-7.35 (m, 6H, Ar H), 5.98-5.87 (m, 1H, alkene-H), 5.42-5.34 (m, 1H, alkene-H), 5.15-5.09 (m, 1H, alkene-H), 4.22-4.20 (m, 2H, CH₂O), 1.07 (s, 9H, CH₃);

¹³C NMR (CDCl₃, 300 MHz) δ 136.9, 135.4, 133.6, 129.5, 127.5, 113.8, 64.6, 26.9, 19.4;

IR ν 3070 (m), 3050 (w), 3013 (w), 2998 (w), 2958 (m), 2930 (m), 2891 (m), 2857 (s), 1959 (w), 1888 (w), 1824 (w), 1771 (w), 1646 (w), 1589 (w), 1472 (m), 1462 (m), 1427 (s), 1402 (w), 1398 (w), 1378 (w), 1361 (w), 1306 (w), 1288 (w), 1261 (w), 1188 (w), 1134 (m), 1112 (s), 1079 (m), 1035 (m), 1008 (m), 998 (m), 916 (m), 824 (m), 811 (m), 740 (m), 701 (s), 620 (m), 616 (m), 564 (w), 505 (s), 490 (m).

(3-Azido-butoxy)-*tert*-butyl-diphenyl-silane (**17**)

Azide **17** (93 mg, 0.27 mmol, 55%, about 95% purity in ¹H NMR) and propoxy-*tert*-butyl-diphenyl-silane (36 mg, 0.12 mmol, 24%) were obtained as oils following the general procedure **A** with prop-3-enyloxy-*tert*-butyl-diphenyl-silane (**16**) (148 mg, 0.499 mmol, 1.00 equiv) in 2 h using 6 mol% catalyst after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:10, then CH₂Cl₂/hexane 1:5).

Azide **17** (114 mg, 0.34 mmol, 67%, about 90% purity in ¹H NMR), propoxy-*tert*-butyl-diphenyl-silane (7 mg, 0.02 mmol, 4%) and prop-3-enyloxy-*tert*-butyl-diphenyl-silane (**16**) (18 mg, 0.061 mmol, 12% recovery) were obtained as oils following the general procedure **B** with prop-3-enyloxy-*tert*-butyl-diphenyl-silane (**16**) (147 mg, 0.496 mmol, 1.00 equiv) and tetramethyldisiloxane (0.18 ml, 1.0 mmol, 2.0 equiv) in 18 h using 6 mol% catalyst after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:10, then CH₂Cl₂/hexane 1:5).

Analytically pure samples of the desired product were obtained after a second purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:10, then CH₂Cl₂/hexane 1:5).

R_f (AcOEt/hexane 1:40) 0.30;

¹H NMR (CDCl₃, 300 MHz) δ 7.71-7.66 (m, 4H, Ar H), 7.47-7.37 (m, 6H, Ar H), 3.67-3.53 (m, 3H, CH₂O and CHN₃), 1.17 (d, *J* = 6.5 Hz, 3H, CHN₃CH₃), 1.08 (s, 9H, CCH₃);

¹³C NMR (CDCl₃, 300 MHz) δ 135.5, 133.0, 129.7, 127.6, 68.0, 58.9, 26.8, 19.3, 16.0;

IR ν 3070 (w), 3050 (w), 2959 (m), 2931 (m), 2893 (w), 2858 (m), 2123 (s), 2109 (s), 1890 (w), 1824 (w), 1652 (w), 1589 (w), 1472 (w), 1463 (w), 1428 (m), 1390 (w), 1362 (w), 1332 (w), 1271 (m), 1188 (w), 1112 (s), 1022 (w), 1008 (w), 938 (w), 912 (m), 824 (m), 805 (w), 741 (s), 702 (s), 615 (m), 504 (s), 489 (m);

MS (ESI) 339.2 (M), 362.0 (M+Na);

Anal. calcd for C₁₉H₂₅N₃OSi: C, 67.22; H, 7.42; N, 12.38 Found: C, 67.48; H, 7.56; N, 12.29.

(2-Azido-propoxymethyl)-benzene (**18**)

Azide **18** (33 mg, 0.17 mmol, 35%) and allyl-benzyl-ether (14 mg, 0.09 mmol, 19% recovery) were obtained as oils following the general procedure **A** with allyl-benzyl-ether (77 μ l, 0.50 mmol, 1.0 equiv) in 48 h using 6 mol% catalyst after purification by column chromatography (pentane/Et₂O 100:1).

Azide **18** (37 mg, 0.19 mmol, 39%) and allyl-benzyl-ether (16 mg, 0.11 mmol, 22% recovery) were obtained as oils following the general procedure **B** with allyl-benzyl-ether (77 μ l, 0.50 mmol, 1.0 equiv) and tetramethyldisiloxane (0.26 ml, 1.5 mol, 3.0 equiv) in 48 h using 6 mol% catalyst after purification by column chromatography (pentane/Et₂O 100:1).

R_f (AcOEt/hexane 1:40) 0.25;

¹H NMR (CDCl₃, 300 MHz) δ 7.38-7.28 (m, 5H, Ar H), 4.58 (s, 2H, PhCH₂), 3.74-3.68 (m, 1H, CHN₃), 3.54-3.42 (m, 2H, CH₂O), 1.22 (d, J = 6.8 Hz, 3H, CH₃);

¹³C NMR (CDCl₃, 300 MHz) δ 137.7, 128.3, 127.6, 127.5, 73.8, 73.3, 57.0, 16.3;

IR ν 3064 (w), 3030 (w), 2976 (w), 2861 (w), 2124 (s), 2103 (s), 1496 (w), 1453 (w), 1379 (w), 1362 (w), 1330 (w), 1266 (m), 1206 (w), 1102 (m), 1028 (w), 998 (w), 913 (s), 743 (s), 698 (m), 651 (w), 621 (w), 558 (w), 458 (w), 441 (w);

MS (EI-HIRES) 162.0912 (M-HN₂), 163.0947 (M-N₂);

Anal. calcd for C₁₀H₁₃N₃O: C, 62.81; H, 6.85; N, 21.97 Found: C, 63.04; H, 7.00; N, 21.79.

Pent-4-enoic acid benzyl ester⁷ (**19**)

Benzyl bromide (1.3 ml, 12 mmol, 1.2 equiv) was added to a solution of 4-pentanoic acid (1.0 ml, 9.8 mmol, 1.0 equiv) in acetone (20 ml) at 23 °C under Ar. Potassium carbonate (6.8 g, 49 mmol, 5.0 equiv) and tetrabutylammonium iodide (0.24 g, 1.0 mmol, 0.10 equiv) were added and the resulting colorless suspension was stirred for 15 h, filtered and the solvent was removed under reduced pressure. The reaction mixture was then dissolved in AcOEt (40 ml), washed with 2 M HCl (30 ml), saturated NaHCO₃ solution (30 ml) and brine (30 ml), dried over Na₂SO₄ and the solvent was removed under reduced pressure. The isolated product was purified by column chromatography (AcOEt/hexane 30:1) to afford **19** (1.65 g, 8.67 mmol, 88%) as a colorless oil.

¹H NMR (CDCl₃, 300 MHz) δ 7.39-7.33 (m, 5H, Ar H), 5.91-5.78 (m, 1H, alkene-H), 5.14 (s, 2H, PhCH₂), 5.14-5.00 (m, 2H, alkene-H), 2.52-2.39 (m, 4H, CH₂CO and alkene-CH₂);

¹³C NMR (CDCl₃, 300 MHz) δ 172.6, 136.4, 135.8, 128.4, 128.0, 115.4, 66.1, 33.5, 28.9;

IR ν 3067 (w), 3034 (w), 2979 (w), 2959 (w), 1738 (s), 1642 (w), 1608 (w), 1587 (w), 1498 (w), 1455 (m), 1381 (m), 1350 (m), 1257 (m), 1213 (m), 1165 (s), 1115 (w), 1002 (m), 916 (m), 844 (w), 825 (w), 786 (w), 751 (m), 698 (s), 577 (w), 500 (w), 450 (w).

4-Azido-pentanoic acid benzyl ester (**20**)

Azide **20** (86 mg, 0.37 mmol, 75%) was obtained as an oil following the general procedure **A** with pent-4-enoic acid benzyl ester (**19**) (94 mg, 0.49 mmol, 1.0 equiv) in 10 h using 6 mol% catalyst after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:2, then CH₂Cl₂/hexane 1:1).

Azide **20** (90 mg, 0.39 mmol, 77%) was obtained as an oil following the general procedure **B** with pent-4-enoic acid benzyl ester (**19**) (95 mg, 0.50 mmol, 1.0 equiv) and tetramethyldisiloxane (0.18 ml, 1.0 mmol, 2.0 equiv) in 10 h using 6 mol% catalyst after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:2, then CH₂Cl₂/hexane 1:1).

R_f (AcOEt/hexane 1:10) 0.40;

¹H NMR (CDCl₃, 300 MHz) δ 7.42-7.31 (m, 5H, Ar H), 5.14 (s, 2H, PhCH₂), 3.55-3.48 (m, 1H, CHN₃), 2.51-2.42 (m, 2H, CH₂CO), 1.92-1.71 (m, 2H, CH₂CHN₃), 1.29 (d, J = 6.5 Hz, 3H, CH₃);

¹³C NMR (CDCl₃, 300 MHz) δ 172.5, 135.6, 128.4, 128.1, 128.1, 66.3, 57.0, 31.2, 30.8, 19.3;

IR ν 3336 (w), 3066 (w), 3034 (w), 2972 (m), 2102 (s), 1736 (s), 1498 (w), 1455 (m), 1382 (m), 1339 (m), 1269 (s), 1167 (s), 1127 (m), 1028 (m), 965 (m), 913 (w), 868 (w), 739 (m), 697 (m);

MS (EI-HIRES) 204.1027 (M-HN₂), 205.1074 (M-N₂);

Anal. calcd for C₁₂H₁₅N₃O₂: C, 61.79; H, 6.48; N, 18.01 Found: C, 62.04; H, 6.40; N, 17.88.

1-Phenyl-pent-4-en-1-one⁸ (**21**)

A solution of acetophenone (2.6 ml, 22 mmol, 1.0 equiv) in dry THF (8 ml) was added dropwise over 10 min to a suspension of potassium hydride (1.1 g, 27 mmol, 1.2 equiv) in dry THF (45 ml) at 0 °C under Ar. The yellow suspension was stirred at 23 °C for 30 min and BEt₃ (4.0 ml, 28 mmol, 1.2 equiv) was added dropwise at 15 °C over 15 min. After stirring the resulting clear yellow solution at 23 °C for 15 min, allyl bromide (freshly distilled, 2.9 ml, 34 mmol, 1.5 equiv) was added dropwise over 10 min and the resulting suspension was stirred

for 4 h at 23 °C and quenched with a 1:1 mixture of 30% NaOH and 30% H₂O₂ (24 ml) at 0°C over 15 min. The reaction mixture was then diluted with H₂O (40 ml), the layers were separated and the organic layer diluted with Et₂O (100 ml) and washed with water (2x50 ml). The combined water layers were extracted with CH₂Cl₂ (2x50 ml) and the combined organic layers were dried over Na₂SO₄ and the solvents were removed under reduced pressure. The isolated product was purified by column chromatography (AcOEt/hexane 1:30) to afford **21** (2.85 g, 17.8 mmol, 80%) as a colorless oil.

¹H NMR (CDCl₃, 300 MHz) δ 7.97 (d, *J* = 7.2 Hz, 2H, Ar H), 7.59-7.43 (m, 3H, Ar H), 5.98-5.84 (m, 1H, alkene-H), 5.13-4.99 (m, 2H, alkene-H), 3.11-3.06 (m, 2H, CH₂CO), 2.54-2.46 (m, 2H, alkene-CH₂);

¹³C NMR (CDCl₃, 300 MHz) δ 199.1, 137.1, 136.8, 132.9, 128.4, 127.9, 115.2, 37.8, 28.2;

IR ν 3067 (w), 2977 (w), 2922 (w), 2855 (w), 1820 (w), 1687 (s), 1641 (w), 1597 (w), 1580 (w), 1448 (m), 1411 (w), 1361 (w), 1268 (w), 1207 (m), 1180 (w), 1159 (w), 1102 (w), 1076 (w), 1001 (w), 971 (w), 913 (m), 744 (m), 690 (m), 656 (w), 567 (w).

4-Azido-1-phenyl-pentan-1-one (**22**)

Azide **22** (51 mg, 0.25 mmol, 49%) and 1-phenyl-pent-4-en-1-one (**21**) (26 mg, 0.16 mmol, 32% recovery) were obtained as oils following the general procedure **A** with 1-phenyl-pent-4-en-1-one (**21**) (82 mg, 0.51 mmol, 1.0 equiv) in 24 h using 6 mol% catalyst after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:2, then CH₂Cl₂/hexane 1:1).

Azide **22** (46 mg, 0.23 mmol, 46%) and 1-phenyl-pent-4-en-1-one (**21**) (30 mg, 0.19 mmol, 38% recovery) were obtained as oils following the general procedure **B** with 1-phenyl-pent-4-en-1-one (**21**) (79 mg, 0.49 mmol, 1.0 equiv) and tetramethyldisiloxane (0.26 ml, 1.5 mol, 3.0 equiv) in 24 h using 6 mol% catalyst after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:2, then CH₂Cl₂/hexane 1:1).

R_f (AcOEt/hexane 1:10) 0.40;

¹H NMR (CDCl₃, 300 MHz) δ 7.99-7.95 (m, 2H, Ar H), 7.60-7.51 (m, 1H, Ar H), 7.50-7.43 (m, 2H, Ar H), 3.62-3.53 (m, 1H, CHN₃), 3.18-3.00 (m, 2H, CH₂CO), 2.05-1.76 (m, 2H, CH₂CHN₃), 1.34 (d, *J* = 6.5 Hz, 3H, CH₃);

¹³C NMR (CDCl₃, 300 MHz) δ 198.9, 136.6, 133.0, 128.5, 127.9, 57.3, 34.8, 30.4, 19.6;

IR ν 3353 (w), 3062 (w), 2972 (w), 2931 (w), 2105 (s), 1686 (s), 1597 (w), 1580 (w), 1448 (m), 1413 (w), 1381 (w), 1342 (w), 1218 (m), 1208 (m), 1180 (w), 1126 (w), 1071 (w), 1017 (w), 1002 (w), 970 (w), 913 (m), 744 (s), 690 (m), 654 (w), 616 (w), 564 (w), 506 (w);

MS (EI-HIRES) 161.0924 (M-N₃), 175.0989 (M-N₂);

Anal. calcd for C₁₁H₁₃N₃O: C, 65.01; H, 6.45; N, 20.67 Found: C, 64.82; H, 6.59; N, 20.76.

(3-Methyl-but-3-enyl)-benzene⁹ (23)

Methallyl chloride (5.3 ml, 54 mmol, 2.5 equiv) was added slowly (10 min) to a suspension of magnesium turnings (1.3 g, 55 mmol, 2.5 equiv) in dry THF (40 ml) at 15 °C. The resulting suspension was stirred at 23 °C for 2 h and refluxed for 2 h. After cooling to 23 °C, the suspension was decanted and transferred via canula to a 100 ml-Schlenk flask. The solution was titrated (quenched with exact amount of 0.2 M HCl, neutralisation of excess HCl with 0.2 M NaOH over phenolphthalein) and appeared to be 0.6 M (24 mmol Grignard reagent, 1.1 equiv). Benzyl bromide (2.6 ml, 22 mmol, 1.0 equiv) was then added at 0 °C over 3 h via syringe pump and the reaction mixture was refluxed for 3 h, cooled to 0 °C and quenched with saturated NH₄Cl solution (20 ml). After diluting with H₂O (20 ml), the reaction mixture was extracted with Et₂O (3x40 ml), the combined organic layers were washed with brine (20 ml), dried over Na₂SO₄ and the solvent was removed under reduced pressure (50 mbar, 40 °C). The isolated product was purified by column chromatography (pentane) to afford (3-methyl-but-3-enyl)-benzene (**23**) (2.22 g, 15.2 mmol, 69%) as a colorless liquid.

R_f (hexane) 0.60;

¹H NMR (CDCl₃, 300 MHz) δ 7.34-7.18 (m, 5H, Ar H), 4.78-4.75 (m, 2H, alkene H), 2.82-2.76 (m, 2H, PhCH₂), 2.38-2.33 (m, 2H, alkene-CH₂), 1.81 (s, 3H, CH₃);

¹³C NMR (CDCl₃, 300 MHz) δ 145.2, 142.1, 128.2, 125.6, 110.1, 39.7, 34.3, 22.7;

IR ν 3064 (w), 3027 (m), 2968 (m), 2936 (m), 2857 (w), 1800 (w), 1649 (m), 1604 (w), 1495 (m), 1453 (s), 1374 (w), 1078 (w), 1031 (w), 887 (s), 745 (m), 697 (s), 574 (w), 520 (w).

(3-Azido-3-methyl-butyl)-benzene¹ (24)

Azide **24** (81 mg, 0.43 mmol, 86%) was obtained as an oil following the general procedure **A** with (3-methyl-but-3-enyl)-benzene (**23**) (73 mg, 0.50 mmol, 1.0 equiv) in 3 h using 6 mol% catalyst after purification by column chromatography (solvent gradient: pentane, then pentane/ Et₂O 60:1).

Azide **24** (90 mg, 0.48 mmol, 90%) was obtained as an oil following the general procedure **B** with (3-methyl-but-3-enyl)-benzene (**23**) (77 mg, 0.53 mmol, 1.0 equiv) and tetramethyldisiloxane (0.18 ml, 1.0 mmol, 2.0 equiv) in 12 h using 6 mol% catalyst after purification by column chromatography (solvent gradient: pentane, then pentane/ Et₂O 60:1).

R_f (AcOEt/hexane 1:40) 0.30;

¹H NMR (CDCl₃, 300 MHz) δ 7.34-7.20 (m, 5H, Ar H), 2.73-2.67 (m, 2H, PhCH₂), 1.84-1.79 (m, 2H, CH₂CN₃), 1.35 (s, 6H, CH₃);

¹³C NMR (CDCl₃, 300 MHz) δ 141.8, 128.4, 128.3, 125.9, 61.4, 43.5, 30.7, 26.0;

IR ν 3329 (w), 3086 (w), 3062 (w), 3027 (w), 2972 (m), 2099 (s), 1603 (w), 1497 (w), 1454 (m), 1388 (w), 1370 (m), 1255 (s), 1204 (m), 1163 (w), 1124 (w), 1073 (w), 1030 (w), 871 (w), 767 (w), 744 (m), 699 (s), 631 (w), 565 (w), 512 (w).

2-Azido-2,6,6-trimethyl-bicyclo[3.1.1]heptane (25)

Azide **25** (80 mg, 0.45 mmol, 89%, mixture of diastereoisomers: 4:1) was obtained as an oil following the general procedure **A** with β-pinene (78 μl, 0.50 mmol, 1.0 equiv) in 12 h using 6 mol% catalyst after purification by column chromatography (pentane/Et₂O 100:1).

Azide **25** (68 mg, 0.38 mmol, 76%, mixture of diastereoisomers: 4:1) was obtained as an oil following the general procedure **B** with β-pinene (78 μl, 0.50 mmol, 1.0 equiv) in 12 h and tetramethyldisiloxane (0.26 ml, 1.5 mol, 3.0 equiv) in 12 h using 6 mol% catalyst after purification by column chromatography (pentane/Et₂O 100:1).

Caution: As the desired product displayed a very high tendency to co-evaporate with many solvents, the following work-up was substituted to the one described in the general procedure: After completion (12 h) the reaction was quenched with H₂O (2 ml). Saturated NaHCO₃ solution (2 ml) and brine (5 ml) were added and the reaction mixture was extracted with Et₂O (3x10 ml). The combined organic layers were washed with water (3x10 ml) and brine (10 ml), dried over Na₂SO₄, filtered and the solvents were removed under reduced pressure (700 mbar, 40 °C). After column chromatography, the fractions were not fully concentrated and the yield was determined via ¹H NMR.

R_f (AcOEt/hexane 1:40) 0.40;

¹H NMR (CDCl₃, 300 MHz) δ 2.27-2.19 (m, 1H, CH₂ or CH), 1.97-1.64 (m, 7H, CH₂ or CH), 1.42 (s, 3H (80%), CH₃ 1. diastereoisomer), 1.41 (s, 3H (20%), CH₃ 2. diastereoisomer), 1.26 (s, 3H (80%), CH₃ 1. diastereoisomer), 1.23 (s, 3H (20%), CH₃ 2. diastereoisomer), 0.99 (s, 3H, CH₃);

¹³C NMR (CDCl₃, 300 MHz) δ 67.6, 51.5, 40.2, 38.4, 28.9, 28.7, 27.8, 27.3, 25.1, 24.1, 23.4, 23.2;

IR ν 2917 (m), 2099 (s), 1465 (w), 1378 (w), 1252 (m), 1161 (w), 1133 (w), 1095 (w), 1075 (w), 1011 (w), 911 (w), 831 (w);

MS (EI-HIRES) 137.1346 (M-N₃);

Anal. calcd for C₁₀H₁₇N₃: C, 67.00; H, 9.56; N, 23.44 Found: C, 66.95; H, 9.38; N, 23.37.

***tert*-Butyl-(2-methyl-allyloxy)-diphenyl-silane¹⁰ (26)**

tert-Butyldiphenyl-silyl-chloride (3.1 ml, 12 mmol, 1.2 equiv) was added dropwise to a solution of methallyl alcohol (0.85 ml, 10 mmol, 1.0 equiv) and imidazole (0.82 g, 12 mmol, 1.2 equiv) in dry DMF (15 ml) at 23 °C under Ar. After stirring for 15 h, the reaction mixture was quenched with water (30 ml) and extracted with AcOEt (3x30 ml). The combined organic layers were washed with water (4x20 ml) and brine (20 ml), dried over Na₂SO₄ and the solvent was removed under reduced pressure. The isolated product was purified by column chromatography (pentane/Et₂O 100:1) to afford **26** (3.1 g, 9.9 mmol, 99%) as a colorless oil.

¹H NMR (CDCl₃, 300 MHz) δ 7.71-7.68 (m, 4H, Ar H), 7.43-7.35 (m, 6H, Ar H), 5.13 (s, 1H, alkene-H), 4.86 (s, 1H, alkene-H), 4.07 (s, 2H, CH₂O), 1.69 (s, 3H, alkene-CH₃), 1.07 (s, 9H, CCH₃);

¹³C NMR (CDCl₃, 300 MHz) δ 144.0, 135.4, 133.6, 129.5, 127.6, 109.1, 67.3, 26.9, 19.4, 19.1;

IR ν 3071 (w), 3050 (w), 2998 (w), 2959 (m), 2931 (m), 2893 (m), 2857 (m), 1959 (w), 1889 (w), 1822 (w), 1659 (w), 1589 (w), 1486 (w), 1472 (m), 1462 (w), 1428 (m), 1390 (w), 1361 (w), 1306 (w), 1262 (w), 1188 (w), 1112 (s), 1029 (w), 1007 (w), 998 (w), 938 (w), 896 (m), 826 (m), 740 (m), 701 (s), 614 (m), 504 (s), 490 (m), 436 (w).

(2-Azido-2-methyl-propoxy)-*tert*-butyl-diphenyl-silane (27)

Azide **27** (130 mg, 0.368 mmol, 74%) and *tert*-butyl-(2-methyl-allyloxy)-diphenyl-silane (**26**) (31 mg, 0.10 mmol, 20% recovery) were obtained as oils following the general procedure **A** with *tert*-butyl-(2-methyl-allyloxy)-diphenyl-silane (**26**) (156 mg, 0.502 mmol, 1.00 equiv) in 24 h using 6 mol% catalyst after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:10, then CH₂Cl₂/hexane 1:5).

Azide **27** (101 mg, 0.286 mmol, 58%) and *tert*-butyl-(2-methyl-allyloxy)-diphenyl-silane (**26**) (50 mg, 0.16 mmol, 33% recovery) were obtained as oils following the general procedure **B** with *tert*-butyl-(2-methyl-allyloxy)-diphenyl-silane (**26**) (152 mg, 0.490 mmol, 1.00 equiv) and tetramethyldisiloxane (0.26 ml, 1.5 mmol, 3.0 equiv) in 24 h using 6 mol% catalyst after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:10, then CH₂Cl₂/hexane 1:5).

R_f (AcOEt/hexane 1:40) 0.30;

¹H NMR (CDCl₃, 300 MHz) δ 7.70-7.66 (m, 4H, Ar H), 7.45-7.38 (m, 6H, Ar H), 3.51 (s, 2H, CH₂O), 1.25 (s, 6H, CN₃CH₃), 1.09 (s, 9H, CCH₃);

¹³C NMR (CDCl₃, 300 MHz) δ 135.5, 132.9, 129.7, 127.6, 71.5, 61.9, 26.8, 23.1, 19.4;

IR ν 3070 (w), 3050 (w), 2961 (w), 2931 (m), 2895 (w), 2858 (m), 2134 (m), 2098 (s), 2053 (w), 1890 (w), 1824 (w), 1589 (w), 1472 (w), 1428 (m), 1392 (w), 1365 (w), 1265 (m), 1164 (w), 1112 (s), 1007 (w), 998 (w), 913 (w), 866 (w), 825 (m), 773 (w), 741 (m), 702 (s), 614 (m), 504 (m), 489 (m);

MS (ESI) 376.1 (M+Na);

Anal. calcd for $C_{20}H_{27}N_3OSi$: C, 67.95; H, 7.70; N, 11.89 Found: C, 68.16; H, 7.93; N, 11.82.

***tert*-Butyl-(3-methyl-but-2-enyloxy)-diphenyl-silane¹¹ (**28**)**

tert-Butyldiphenyl-silyl-chloride (2.1 ml, 22 mmol, 1.2 equiv) was added dropwise to a solution of 3-methyl-2-butenol (1.0 ml, 10 mmol, 1.0 equiv) in dry CH_2Cl_2 (17 ml) at 23 °C under argon. Triethylamine (freshly distilled, 1.7 ml, 12 mmol, 1.2 equiv) and 4-dimethylamino-pyridine (48 mg, 0.39 mmol, 0.039 equiv) were added. After stirring 48 h at 23 °C the reaction mixture was diluted with CH_2Cl_2 and washed with water (2x50 ml), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The isolated product was purified by column chromatography (AcOEt/hexane 1:100) to afford **28** (2.54 g, 7.83 mmol, 78%) as a colorless oil.

¹H NMR ($CDCl_3$, 300 MHz) δ 7.75-7.71 (m, 4H, Ar H), 7.47-7.37 (m, 6H, Ar H), 5.44-5.38 (m, 1H, alkene-H), 4.23 (d, J = 6.5 Hz, 2H, CH_2O), 1.72 (m, 3H, alkene- CH_3), 1.48 (s, 3H, alkene- CH_3), 1.08 (s, 9H, CCH_3);

¹³C NMR ($CDCl_3$, 300 MHz) δ 135.6, 134.0, 133.8, 129.5, 127.6, 124.2, 61.1, 26.8, 25.7, 19.2, 17.9;

IR ν 3070 (w), 3049 (w), 2960 (m), 2930 (m), 2891 (m), 2857 (m), 2104 (w), 1958 (w), 1888 (w), 1824 (w), 1771 (w), 1722 (w), 1675 (w), 1589 (w), 1487 (w), 1472 (m), 1462 (w), 1446 (w), 1428 (m), 1380 (w), 1361 (w), 1329 (w), 1261 (w), 1189 (w), 1112 (s), 1062 (s), 1028 (m), 1007 (w), 998 (w), 938 (w), 913 (w), 855 (w), 823 (m), 774 (w), 739 (m), 701 (s), 689 (m), 613 (m), 504 (s), 440 (w).

(3-Azido-3-methyl-butoxy)-*tert*-butyl-diphenyl-silane (29**)**

Azide **29** (116 mg, 0.316 mmol, 66%) and *tert*-butyl-(3-methyl-but-2-enyloxy)-diphenyl-silane (**28**) (34 mg, 0.10 mmol, 21% recovery) were obtained as oils following the general procedure **A** with *tert*-butyl-(3-methyl-but-2-enyloxy)-diphenyl-silane (**28**) (157 mg, 0.484 mmol, 1.00 equiv) in 24 h using 6 mol% catalyst after purification by column chromatography (solvent gradient: CH_2Cl_2 /hexane 1:10, then CH_2Cl_2 /hexane 1:5).

Azide **29** (85 mg, 0.23 mmol, 50%) and *tert*-butyl-(3-methyl-but-2-enyloxy)-diphenylsilane (**28**) (74 mg, 0.23 mmol, 50% recovery) were obtained as oils following the general procedure **B** with *tert*-butyl-(3-methyl-but-2-enyloxy)-diphenylsilane (**28**) (150 mg, 0.462 mmol, 1.00 equiv) and tetramethyldisiloxane (0.26 ml, 1.5 mmol, 3.0 equiv) in 24 h using 6 mol% catalyst after purification by column chromatography (solvent gradient: CH₂Cl₂/hexane 1:10, then CH₂Cl₂/hexane 1:5).

R_f (AcOEt/hexane 1:40) 0.30;

¹H NMR (CDCl₃, 300 MHz) δ 7.70-7.67 (m, 4H, Ar H), 7.45-7.37 (m, 6H, Ar H), 3.79 (t, *J* = 6.8 Hz, 2H, CH₂O), 1.81 (t, *J* = 6.8 Hz, 2H, CN₃CH₂), 1.28 (s, 6H, CN₃CH₃), 1.06 (s, 9H, CCH₃);

¹³C NMR (CDCl₃, 300 MHz) δ 135.4, 133.5, 129.6, 127.6, 60.7, 60.3, 43.5, 26.9, 26.6, 19.2;

IR ν 3070 (w), 3050 (w), 2962 (m), 2931 (m), 2887 (m), 2857 (m), 2099 (s), 1889 (w), 1824 (w), 1652 (w), 1589 (w), 1472 (w), 1428 (m), 1389 (w), 1370 (w), 1304 (w), 1260 (m), 1186 (w), 1144 (w), 1112 (s), 1048 (w), 997 (w), 938 (w), 913 (w), 893 (w), 823 (w), 758 (w), 738 (m), 702 (s), 689 (w), 613 (m), 505 (m), 490 (m), 416 (s);

MS (ESI) 362.1 (M-N₂+Na), 390.0 (M+Na);

Anal. calcd for C₂₁H₂₉N₃OSi: C, 68.62; H, 7.95; N, 11.43 Found: C, 68.46; H, 7.74; N, 11.28.

((*E*)-3-Methyl-pent-3-enyl)-benzene¹² (**30**)

A suspension of 3-(diphenyl-phosphinoyl)-3-methyl-5-phenyl-pentan-2-ol (666 mg, 1.76 mmol, 1.00 equiv, diastereomerically pure, synthesized following a published procedure)¹¹ in dry DMF (30 ml) was added to a suspension of sodium hydride (45 mg, 1.8 mmol, 1.0 equiv) in dry DMF (15 ml). After heating the resulting suspension at 50 °C for 1 h, the reaction mixture was cooled to 0 °C, quenched with water (50 ml), diluted with water (20 ml) and brine (70 ml) and extracted with Et₂O (3x100 ml). The combined organic layers were washed with water (4x50 ml) and brine (50 ml), dried over Na₂SO₄ and the solvent was removed under reduced pressure (100 mbar, 40 °C). The isolated product was purified by column chromatography (pentane) to afford **30** (101 mg, 0.631 mmol, 36%) as a colorless liquid.

¹H NMR (CDCl₃, 300 MHz) δ 7.31-7.25 (m, 2H, Ar H), 7.20-7.15 (m, 3H, Ar H), 5.27-5.20 (m, 1H, alkene-H), 2.73-2.68 (m, 2H, PhCH₂), 2.30-2.25 (m, 2H, alkene-CH₂), 1.66 (s, 3H, CH₃), 1.58 (d, *J* = 6.5 Hz, 3H, CH₃);

¹³C NMR (CDCl₃, 300 MHz) δ 142.4, 135.2, 128.3, 128.1, 125.5, 118.7, 41.7, 34.9, 15.9, 13.5;

IR ν 3026 (w), 2922 (m), 2858 (w), 1602 (w), 1496 (w), 1453 (w), 1380 (w), 1030 (w), 913 (m), 807 (w), 743 (s), 697 (s), 516 (w), 451 (w).

(3-Azido-3-methyl-pentyl)-benzene (31)

Following general procedure A:

Co(BF₄)₂·6H₂O (6 mg, 0.02 mmol, 0.06 equiv) and ligand (8 mg, 0.02 mmol, 0.06 equiv) were dissolved in ethanol (1.5 ml) at 23 °C under argon. After 30 min, ((*E*)-3-methyl-pent-3-enyl)-benzene (**30**) (46 mg, 0.29 mmol, 1.0 equiv) was added to the homogenous orange solution, followed by tosylazide (0.14 ml, 0.90 mmol, 3.0 equiv) and *tert*-butyl hydroperoxide (5.5 M in decane, 15 µl, 0.083 mmol, 0.28 equiv). The reaction mixture was stirred until the colour changed to dark orange (10 min) and phenylsilane (60 µl, 0.48 mmol, 1.6 equiv) was added dropwise. The resulting brown solution was stirred at 23 °C and the reaction monitored by TLC (AcOEt/hexane 1:40). After 30 h the reaction was quenched with H₂O (2 ml). Saturated NaHCO₃ solution (2 ml) and brine (5 ml) were added and the reaction mixture was extracted with AcOEt (3x10 ml). The combined organic layers were dried over Na₂SO₄, filtered and the solvents were removed under reduced pressure (50 mbar, 40 °C). The isolated product was purified by column chromatography (solvent gradient: pentane, then pentane/Et₂O 60:1) to afford **31** (39 mg, 0.19 mmol, 66%) as a colorless liquid.

Following general procedure B:

Co(BF₄)₂·6H₂O (6 mg, 0.02 mmol, 0.06 equiv) and ligand (8 mg, 0.02 mmol, 0.06 equiv) were dissolved in ethanol (1.5 ml) at 23 °C under argon. After 30 min, ((*E*)-3-methyl-pent-3-enyl)-benzene (**30**) (46 mg, 0.29 mmol, 1.0 equiv) was added to the homogenous orange solution, followed by tosylazide (0.14 ml, 0.90 mmol, 3.0 equiv) and *tert*-butyl hydroperoxide (5.5 M in decane, 15 µl, 0.083 mmol, 0.28 equiv). The reaction mixture was stirred until the colour changed to dark orange (10 min) and tetramethyldisiloxane (0.16 ml, 0.90 mmol, 3.0 equiv) was added dropwise. The resulting brown solution was stirred at 23 °C and the reaction monitored by TLC (AcOEt/hexane 1:40). After 30 h the reaction was quenched with H₂O (2 ml). Saturated NaHCO₃ solution (2 ml) and brine (5 ml) were added and the reaction mixture was extracted with AcOEt (3x10 ml). The combined organic layers were dried over Na₂SO₄, filtered and the solvents were removed under reduced pressure (50 mbar, 40 °C). The isolated product was purified by column chromatography (solvent gradient: pentane, then pentane/Et₂O 60:1) to afford **31** (28 mg, 0.14 mmol, 48%) as a colorless liquid.

R_f (AcOEt/hexane 1:40) 0.30;

¹H NMR (CDCl₃, 300 MHz) δ 7.33-7.18 (m, 5H, Ar H), 2.69-2.63 (m, 2H, PhCH₂), 1.83-1.76 (m, 2H, CH₂CN₃), 1.63 (q, *J* = 7.5 Hz, 2H, CH₂CH₃), 1.30 (s, 3H, CN₃CH₃), 0.97 (t, *J* = 7.5 Hz, 3H, CH₂CH₃);

¹³C NMR (CDCl₃, 300 MHz) δ 141.8, 128.4, 128.2, 125.8, 64.3, 41.1, 32.1, 30.5, 22.9, 8.5;

IR ν 3063 (w), 3026 (w), 2971 (w), 2939 (w), 2880 (w), 2092 (s), 1603 (w), 1497 (w), 1455 (w), 1381 (w), 1256 (m), 1190 (w), 1136 (w), 1074 (w), 1030 (w), 912 (w), 856 (w), 741 (m), 698 (m), 565 (w), 510 (w), 460 (w), 450 (w);

MS (EI-HIRES) 160.1171 (M-HN₃), 174.1281 (M-HN₂), 175.1343 (M-N₂);

Anal. calcd for C₁₂H₁₇N₃: C, 70.90; H, 8.43; N, 20.67 Found: C, 71.15; H, 8.52; N, 20.76.

Part C: Conversion of azides to amines and triazoles

One-pot reduction of azide:¹³

1-methyl-3-phenyl-propylamine¹⁴ (**8**)

Co(BF₄)₂·6H₂O (10 mg, 0.030 mmol, 0.060 equiv) and ligand (14 mg, 0.030 mmol, 0.060 equiv) were dissolved in ethanol (1.5 ml) at 23 °C under argon. After 30 min, 4-phenyl-butene (**4**) (75 µl, 0.50 mmol, 1.0 equiv) was added to the homogenous orange solution, followed by tosyl azide (0.23 ml, 1.5 mmol, 3.0 equiv) and *tert*-butyl hydroperoxide (5.5 M in decane, 25 µl, 0.14 mmol, 0.28 equiv). The reaction mixture was stirred until the colour changed to dark orange (10 min) and tetramethyldisiloxane (0.18 ml, 1.0 mmol, 2.0 equiv) was added dropwise. The resulting dark brown solution was stirred at 23 °C and the reaction monitored by TLC (AcOEt/hexane 1:40). After 4 h, the reaction mixture was cooled to 0 °C and a black suspension of CuSO₄·5H₂O (12 mg, 0.050 mmol, 0.10 equiv) and NaBH₄ (10 mg, 0.26 mmol, 0.50 equiv) in methanol (1.5 ml) was added. Further NaBH₄ (65 mg, 1.7 mmol, 3.4 equiv) was added in small portions over 45 min at 0 °C. At this point, TLC (AcOEt/hexane 1:40) showed a clean reduction of the excess of tosyl azide, but the alkyl azide was not yet totally reduced. Further NaBH₄ (100 mg, 2.6 mmol, 5.3 equiv) was added in 4 portions over 2 h, whereas TLC showed complete reduction of the alkyl azide. The reaction mixture was allowed to warm to 23 °C over 12 h and filtered over Celite. The Celite was washed with 20 ml methanol and the solvent was removed under reduced pressure (50 mbar, 40 °C). The crude product was diluted with water (10 ml) and 1 M HCl (10 ml) and the mixture was extracted with Et₂O (3x20 ml). NaOH pellets were added to the water layer until the pH was higher than 10, and the mixture was extracted with Et₂O (3x20 ml), the organic layers were dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure (50 mbar, 40 °C) to afford the free amine **8** (56 mg, 0.38 mmol, 76%, > 95% pure according to ¹H NMR) as a slightly yellow oil.

¹H NMR (CDCl₃, 300 MHz) δ 7.31-7.16 (m, 5H, Ar H), 2.96 (brs, 1H, CHNH₂), 2.76-2.58 (m, 2H, PhCH₂), 1.75-1.66 (m, 2H, CH₂CHNH₂), 1.13 (d, *J* = 6.2 Hz, 3H, CH₃);

¹³C NMR (CDCl₃, 300 MHz) δ 142.2, 128.3, 128.2, 125.6, 46.4, 41.8, 32.7, 23.9;

IR ν 3286 (w), 3061 (w), 3025 (m), 2957 (s), 2925 (s), 2858 (m), 1581 (m), 1495 (m), 1454 (s), 1372 (m), 1294 (w), 1155 (w), 1100 (w), 1067 (w), 1030 (w), 907 (w), 817 (w), 747 (m), 699 (s), 579 (w), 518 (w), 471 (w), 450 (w).

One-pot cycloaddition with phenyl acetylene: ¹⁵

1-(1-Methyl-3-phenyl-propyl)-4-phenyl-1H-[1,2,3]triazole (**9**)

Co(BF₄)₂·6H₂O (10 mg, 0.030 mmol, 0.060 equiv) and ligand (14 mg, 0.030 mmol, 0.060 equiv) were dissolved in ethanol (2.5 ml) at 23 °C under argon. After 30 min, 4-phenyl-butene (**5**) (75 µl, 0.50 mmol, 1.0 equiv) was added to the homogenous orange solution, followed by tosyl azide (0.23 ml, 1.5 mmol, 3.0 equiv) and *tert*-butyl hydroperoxide (5.5 M in decane, 25 µl, 0.14 mmol, 0.28 equiv). The reaction mixture was stirred until the colour changed to dark orange (10 min) and tetramethyldisiloxane (0.18 ml, 1.0 mmol, 2.0 equiv) was added dropwise. The resulting dark brown solution was stirred at 23 °C and the reaction monitored by TLC (AcOEt/hexane 1:40). After 4 h, water (2 ml) was added. After further stirring for 30 min, a solution of sodium ascorbate (40 mg, 0.20 mmol, 0.40 equiv) in water (0.1 ml), a solution of CuSO₄·5H₂O (12 mg, 0.050 mmol, 0.10 equiv) in water (0.1 ml) and phenylacetylene (0.28 ml, 2.5 mmol, 5.0 equiv) were added and the heterogenous mixture stirred at 23 °C for 20 h. The reaction mixture was then diluted with water (5 ml) and brine (5 ml), extracted with AcOEt (3x12 ml), the combined organic layers were dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure. The isolated product was purified by column chromatography (solvent gradient: pentane/CH₂Cl₂/Et₂O 50:100:5, then pentane/CH₂Cl₂/Et₂O 50:100:7.5) to afford **11** (83 mg, 0.30 mmol, 60%) as a slightly yellow solid. Analytically pure samples of **11** were obtained after recrystallization from AcOEt/hexane.

R_f (pentane/CH₂Cl₂/ Et₂O 50:100:7.5) 0.30;

Mp 72-73 °C;

¹H NMR (CDCl₃, 300 MHz) δ 7.88-7.84 (m, 2H, Ar H), 7.75 (s, 1H, triazole H), 7.46-7.13 (m, 8H, Ar H), 4.75-4.68 (m, 1H, CHN), 2.57 (t, *J* = 7.6 Hz, 2H, PhCH₂), 2.41-2.14 (m, 2H, CH₂CHN), 1.63 (d, *J* = 6.8 Hz, CH₃);

¹³C NMR (CDCl₃, 300 MHz) δ 147.4, 140.2, 130.6, 128.7, 128.4, 128.3, 127.9, 126.1, 125.5, 117.4, 56.7, 38.7, 32.1, 21.7;

IR ν 3130 (w), 3084 (w), 3061 (w), 3026 (w), 2978 (w), 2935 (w), 2860 (w), 1951 (w), 1883 (w), 1812 (w), 1604 (w), 1580 (w), 1553 (w), 1495 (w), 1482 (m), 1454 (m), 1436 (m), 1383 (w), 1364 (w), 1226 (w), 1180 (w), 1156 (w), 1119 (w), 1074 (m), 1028 (w), 973 (w), 914 (w), 765 (s), 749 (m), 696 (s);

HRMS (EI) calcd for C₁₈H₁₉N₃⁺ (M): 277.1579, found 277.1572;

Anal. calcd for C₁₈H₁₉N₃: C, 77.95; H, 6.90; N, 15.15 Found: C, 77.87; H, 6.93; N, 15.11.

References:

- (1) Ollivier, C.; Renaud, P. *J. Am. Chem. Soc.* **2001**, *123*, 20, 4717.
- (2) The region of the ^{13}C spectra between 125 and 135 ppm was not totally resolved, due probably to hindered rotation of the two phenyl groups of the ligand or/and a potential loss of symmetry occurring during complex formation.
- (3) Ito, M.; Koyakumar, K.; Ohta, T.; Takaya, H. *Synthesis* **1995**, 4, 376.
- (4) Abeywickrema, A. N.; Beckwith, A. L. J.; Gerba, S. *J. Org. Chem.* **1987**, *52*, 18, 4072.
- (5) Berque, I.; Le Menez, P.; Razon, P.; Mahuteau, J.; Ferezou, J. P.; Pancrazi, A.; Ardisson, J.; Brion, J. D. *J. Org. Chem.* **1999**, *64*, 2, 373.
- (6) Saygili, N.; Brown, R. J.; Day, P.; Hoelzl, R.; Kathirgamanathan, P.; Mageean, E. R.; Ozturk, T.; Pilkington, M.; Qayyum, M. M. B.; Turner, S. S.; Vorwerk, L.; Wallis, J. D. *Tetrahedron* **2001**, *57*, 23, 5015.
- (7) Hogg, J. H.; Ollmann, I. R.; Wetterholm, A.; Andberg, M. B.; Haeggstrom, J.; Samuelsson, B.; Wong, C. H. *Chem. Eur. J.* **1998**, *4*, 9, 1698.
- (8) Motorina, I. A.; Fowler, F. W.; Grierson, D. S. *J. Org. Chem.* **1997**, *62*, 7, 2098.
- (9) Hoffmann, R. W.; Haerberlin, E.; Rohde, T. *Synthesis* **2002**, 2, 207.
- (10) Jordine, G.; Bick, S.; Moller, U.; Welzel, P.; Daucher, B.; Maas, G. *Tetrahedron* **1994**, *50*, 1, 139.
- (11) Sen, S. E.; Ewing, G. J. *J. Org. Chem.* **1997**, *62*, 11, 3529.
- (12) Buss, A. D.; Greeves, N.; Mason, R.; Warren, S. *J. Chem. Soc. Perkin Trans. 1* **1987**, 12, 2569.
- (13) Rao, H. S. P.; Siva, P. *Synth. Commun.* **1994**, *24*, 4, 549.
- (14) (a) Miriyala, B.; Bhattacharyya, S.; Williamson, J. S. *Tetrahedron* **2004**, *60*, 7, 1463. (b) Gonzalez-Sabin, J.; Gotor, V.; Rebollo, F. *Tetrahedron: Asymmetry* **2002**, *13*, 12, 1315.
- (15) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem. Int. Ed.* **2002**, *41*, 14, 2596.