Supporting Information

Synthesis of *E*-Alkyl Alkenes from Terminal Alkynes via Ni-Catalyzed Cross-Coupling of Alkyl Halides with B-Alkenyl-9-Borabicyclo[3.3.1]nonanes

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1. General Considerations.

1.1 Chemicals and Reagents.

All manipulations were carried out under an inert $N_{2(g)}$ atmosphere using standard Schlenk or glovebox techniques. Solvents were purified using a two-column solid-state purification system (Innovative Technology, NJ, USA) and transferred to the glove box without exposure to air. Deuterated solvents were purchased from Aldrich, and were degassed and stored over activated 3 Å molecular sieves. Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification. The complex **1** was prepared according to literature procedure.¹

The following known starting materials (alkyl halides and terminal alkynes) were commercially available and used without further purifications:

(i) Alkyl Halides:



The following known starting materials (alkyl halides and terminal alkynes) were prepared according to the literature procedures: ²⁻¹⁹

(i) Alkyl Halides:



1.2 Physical Methods.

¹H and ¹³C spectra were recorded at room temperature on a Bruker Avance 400 spectrometer. ¹H NMR and ¹³C{¹H} chemical shifts were reported in part per million (ppm) relative to residual solvent (CDCl₃) as determined relative to TMS ($\delta = 0.00$ ppm). ¹H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants, and integration. All GC analyses were performed on a Perkin-Elmer Clarus 400 GC system with a FID detector. GC-MS measurements were conducted on an Agilent Technologies 7890A GC system equipped with a 5975C MS detector. HRMS measurements (ESI and APPI) were conducted at the EPFL ISIC Mass Spectrometry Service using two hybrid Fourier transform mass spectrometers (10 T linear trap quadrupole Fourier transform ion cyclotron resonance mass spectrometer, LTQ FT-ICR MS, and LTQ Orbitrap Elite FTMS, both Thermo Scientific, Bremen, Germany) and two quadrupole time-of-flight mass spectrometers (6530 Accurate-Mass qTOF LC/MS from Agilent Technologies, Santa Clara, CA, USA and Xevo G2-S qTOF MS from Waters Corporation, Milford, MA, USA).

Unless something else is specified, all the column chromatography used to purify the products were done on silica gel.

2. Optimization of the NiCl₂.dme Procedure.

In a 10 mL sealed glass vial and under $N_{2(g)}$, catalyst (5 mol %), Ligand (10 mol%), base (1.2 equiv) were added, followed by the addition of 1-bromo-4-phenylbutane **3b** (0.2 mmol, 43 mg), alkenyl-(9-BBN) **2a** (1.4 equiv, 65 mg) and solvent (1 mL). The mixture was stirred for 24 h under N₂ at the temperatures listed in Table S1. *n*-Decane (60 µL) was then added to the reaction mixture as an internal standard and the reaction mixture was diluted in diethyl ether. An aliquote was taken up and filtered through a short pad of silica and the solution was analyzed by GC to give the yield of the product.

| \ ^ | ∧ ∧ .(9-BBN) | | ∽∽Br | catalyst (5 mol %) ligand (10 mol %) | | | | |
|-------------------|----------------------------|-------------------------|---------|--|----|-------|--------------------------|--|
| 2a (1.4 equiv) | | 3b (0.2 mmol) | | 1.2 equiv base 2 equiv <i>t</i> -amylOH solvent, <i>t</i> , 24 h | | | J | |
| Entry | Catalyst | Ligand | Base | Solvent | t | Conv. | Yield $\binom{0}{2}^{a}$ | |
| 1 | NiCl ₂ ·dme | L_1 | KOt-Bu | 1,4-dioxane | rt | 85 | 53 | |
| 2 | NiCl ₂ ·dme | L ₁ | NaOt-Bu | 1,4-dioxane | rt | 77 | 59 ^b | |
| 3 | $NiCl_2 \cdot (PPh_3)_2$ | L_1 | NaOt-Bu | 1,4-dioxane | rt | 73 | 51 | |
| 4 | NiBr ₂ ·diglyme | L ₁ | NaOt-Bu | 1,4-dioxane | rt | 63 | 21 | |
| 5 | NiCl ₂ ·dme | L_2 | NaOt-Bu | 1,4-dioxane | rt | 77 | 27 | |
| 6 | NiCl ₂ ·dme | L_3 | NaOt-Bu | 1,4-dioxane | rt | > 99 | 57 ^b | |
| 7 | NiCl ₂ ·dme | L_4 | NaOt-Bu | 1,4-dioxane | rt | 58 | 6 | |
| 8 | NiCl ₂ ·dme | L_5 | NaOt-Bu | 1,4-dioxane | rt | 67 | 24 | |

Table S1. Screening results for the NiCl₂.dme procedure.

| 9 | NiCl ₂ ·dme | L ₆ | NaOt-Bu | 1,4-dioxane rt | | 94 | 47 |
|----|----------------------------|----------------|---------|------------------|----------------|------|-----------------|
| 10 | NiCl ₂ ·dme | L ₇ | NaOt-Bu | 1,4-dioxane | rt | > 99 | 25 |
| 11 | NiCl ₂ ·dme | - | NaOt-Bu | 1,4-dioxane | 1,4-dioxane rt | | 0 |
| 12 | NiBr ₂ ·dme | L ₃ | NaOt-Bu | 1,4-dioxane | rt | > 99 | 43 |
| 13 | NiBr ₂ ·diglyme | L ₃ | NaOt-Bu | 1,4-dioxane | rt | 61 | 44 |
| 14 | NiCl ₂ | L ₃ | NaOt-Bu | 1,4-dioxane | rt | 34 | 10 |
| 15 | NiBr ₂ | L ₃ | NaOt-Bu | 1,4-dioxane | rt | 39 | 20 |
| 16 | NiCl ₂ ·dme | L ₃ | NaOt-Bu | THF | rt | > 99 | 42 |
| 17 | NiCl ₂ ·dme | L ₃ | NaOt-Bu | 1,4-dioxane | 40 | > 99 | 77 ^c |
| 18 | NiCl ₂ ·dme | L ₃ | NaOt-Bu | 1,4-dioxane | 60 | > 99 | 68 |
| 19 | NiCl ₂ ·dme | L ₃ | NaOt-Bu | 1,4-dioxane | 80 | > 99 | 50 |
| 20 | NiCl ₂ ·dme | L ₃ | NaOt-Bu | DMF | rt | - | 0 |
| 21 | NiCl ₂ ·dme | L ₃ | NaOt-Bu | MeCN | rt | 82 | 29 |
| 22 | NiCl ₂ ·dme | L ₃ | NaOt-Bu | <i>t</i> -amylOH | rt | 92 | 34 |
| 23 | - | L ₃ | NaOt-Bu | 1,4-dioxane | rt | - | 0 |
| 24 | NiCl ₂ ·dme | L ₃ | - | 1,4-dioxane | rt | - | 0 |
| 25 | NiCl ₂ ·dme | L_8 | NaOt-Bu | 1,4-dioxane | rt | 85 | 71 |
| 26 | CuCl ₂ | L ₃ | NaOt-Bu | 1,4-dioxane | rt | - | 0 |
| 27 | CuBr ₂ | L ₃ | NaOt-Bu | 1,4-dioxane | rt | - | 0 |
| 28 | CuCl | L ₃ | NaOt-Bu | 1,4-dioxane | rt | - | 0 |
| 29 | FeCl ₂ | L ₃ | NaOt-Bu | 1,4-dioxane | rt | - | 0 |
| 30 | FeCl ₃ | L ₃ | NaOt-Bu | 1,4-dioxane | rt | - | 0 |
| 31 | CoBr ₂ | L ₃ | NaOt-Bu | 1,4-dioxane | rt | - | 0 |

^a GC Yield. ^b No Product was formed without *t*-amylOH ^c Yield was 75% when the reaction was performed with the 1-iodo-4-phenylbutane





 L_2















3. Optimization of the *Nickamine* Procedure.

In a 10 mL sealed glass vial and under $N_{2(g)}$, catalyst **1** (5 mol %, 0.01 mmol, 3.5 mg) and base (0-2.0 equiv) were added, followed by the addition of 1-iodo-4-phenylbutane **3a** (0.2 mmol, 52 mg), alkenyl-(9-BBN) **2a** (1.4 equiv, 65 mg) and 1,4-dioxane (1 mL). The mixture was stirred for 24 h under N₂ at the temperatures listed in Table S2. *n*-Decane (60 µL) was then added to the reaction mixture as an internal standard and the reaction mixture was diluted in diethyl ether. An aliquote was taken up and filtered through a short pad of silica and the solution was analyzed by GC to give the yield of the product.

Table S2. Screening results for the Nickamine procedure.



| Entry | Alkyl Halide | Base (1.6 equiv) | t (°C) Conv. (%) | | Yield (%) ^a |
|-------|--------------|---------------------------------|------------------|------|------------------------|
| 1 | 3 a | NaOH | 80 | > 99 | 44 |
| 2 | 3 a | КОН | 80 | > 99 | 21 |
| 3 | 3 a | LiOH | 80 | 96 | 14 |
| 4 | 3 a | NaOMe | 80 | > 99 | 65 |
| 5 | 3a KOMe | | 80 | > 99 | 62 |
| 6 | 3 a | LiOMe | 80 | > 99 | 22 |
| 7 | 3 a | NaOt-Bu | 80 | > 99 | 7 |
| 8 | 3 a | NaOEt | 80 | > 99 | 0 |
| 9 | 3 a | KOEt | 80 | > 99 | 3 |
| 10 | 3 a | Na ₂ CO ₃ | 80 > 99 | | 0 |
| 11 | 3 a | K ₃ PO ₄ | 80 | - | 0 |
| 12 | 3 a | NaOMe | rt | - | 0 |
| 13 | 3 a | NaOMe | 40 | - | 0^{b} |
| 14 | 3 a | NaOMe | 60 | > 99 | 80 |
| 15 | 3 a | NaOMe (1 equiv) | 60 | > 99 | 61 |
| 16 | 3 a | NaOMe (1.2 equiv) | 60 | > 99 | 57 |
| 17 | 3 a | NaOMe (1.4 equiv) | 60 | > 99 | 55 |
| 18 | 3 a | NaOMe (1.8 equiv) | 60 | 82 | 13 |
| 19 | 3 a | NaOMe (2 equiv) | 60 | - | 0 |
| 20 | 3 b | NaOMe | 60 | > 99 | 59 |
| 21 | 3 b | NaOMe | 80 | > 99 | 76 |
| 23 | 3 c | NaOMe | 80 | > 99 | 35 |
| 24 | <u>3c</u> | NaOMe | 100 | > 99 | 82 |

^a GC Yield. ^b Yield was 42% when 2 equiv of *t*-amyl alcohol were added.

4. Optimization of the *one-pot* Procedure

Step a)

In a 10 mL sealed glass vial and under N_{2(g)}, (9-BBN)-H (0.5 M in THF, 0.24 mmol, 0.48 mL) was added dropwise to 1-hexyne (2 equiv., 0.4 mmol, 46 μ L) in 1 mL of solvent at 0 °C. After addition, reaction mixture was stirred for 5 min at 0 °C then was warmed to room temperature and stirred for 2 h.

Step b)

The resulting alkenyl-(9-BBN) was added (with or without 1 ml of fresh solvent) to a 10 mL sealed glass vial containing NaOMe (1.6 equiv, 0.32 mmol, 17 mg), catalyst **1** (5 mol %, 0.01 mmol, 3.5 mg) and 1-iodo-4-phenylbutane **3a** (0.2 mmol, 52 mg) under a N₂ atmosphere. The mixture was heated at 60 °C under stirring for 24 h. *n*-Decane (60 μ L) was then added to the reaction mixture as an internal standard and the reaction mixture was diluted in diethyl ether. An aliquote was taken up and filtered through a short pad of silica and the solution was analyzed by GC to give the yield of the product.

Table S3. Results of one-pot reactions.



| Entry | Solvent a) | Evaporation after step a) | "Fresh" Solvent b) | Conv. (%) | Yield (%) ^a |
|-------|-------------|--------------------------------------|----------------------------|-----------|------------------------|
| 1 | THF | Yes | 1,4-dioxane | > 99 | 70 ^b |
| 2 | THF | No | No | 56 | 4 |
| 3 | THF | No | 1,4-dioxane | 83 | 22 |
| 4 | 1,4-dioxane | No | No | 80 | 26 |

^aGC Yield. ^b Isolated Yield.

5. Stereospecificity of the Reaction.

5.1 (*E*)-configuration of the formed Products.

The diastereoselectivity of the (*E*)-9-(hex-1-en-1-yl)-9-borabicyclo[3.3.1]nonane was determined by ¹H NMR analysis (Figure S1). The analysis was based on the magnitude of *J* coupling of the signal corresponding to the vinylic protons of the product (chemical shift between 6 and 7 ppm). Literature gives for the *J* coupling of hydrogens situated *cis* a value $J_{cis} = 10$ Hz and for the *J* coupling of hydrogens situated *trans* a value $J_{trans} = 16$ Hz (Table S4).²⁰ Within a set of isomers *cis* coupling is always smaller than *trans* coupling. For our synthesized 9-(hex-1-en-1-yl)-9-borabicyclo[3.3.1]nonane, *J* coupling between the two vicinal protons was J = 17.2 Hz. We can conclude without any doubts that only the (*E*)-isomer was formed during the hydroboration of the 1-hexyne with the (9-BBN)-H.



Table S4. J coupling constant for H situated around a double bond.²⁰

The diastereoselectivity of the cross-coupling products is shown with the 2-(non-4-en-1-yl)furan taken as an example (Figure S2). We then determined the diastereoselectivity of each synthesized products in the same manner.

As shown in the Figure S2, *J* coupling between the two vicinal protons was J = 16.8 Hz. As a consequence, we could estimate that only the (*E*)-isomer product was formed during the cross-coupling reaction.



Figure S3 shows a zoom in the vinylic area chemical shift for this product ($\delta = 5.6 - 5.2$ Hz). The shape of the peak corresponds to the predicted splitting pattern for proton H_a.



Figure S3. Zoom in the vinylic area of the ¹H NMR spectrum for the (*E*)-2-(non-4-en-1-yl)furan and predicted splitting pattern for proton H_a .

5.2 Stereospecificity.

To prove the stereospecificity of the reaction, the (*Z*)-9-(hex-1-en-1-yl)-9-borabicyclo[3.3.1]nonane was synthesized from the *cis*-1-iodo-1-hexene²¹ according to a procedure followed by Brown and coworkers.²² The *J* coupling between the two vicinal protons was J = 13.6 Hz for the synthesized 9-(hex-1-en-1-yl)-9-borabicyclo[3.3.1]nonane (Figure S4). This *J* coupling corresponds to a typical value for vicinal *cis* protons of an olefin.



The cross-coupling between this crude (Z)-9-(hex-1-en-1-yl)-9-borabicyclo[3.3.1]nonane and the 2-(3-iodopropyl)furan was then performed to obtain the corresponding cross-coupling product in 71% yield.



As shown in the Figure S5, *J* coupling between the two vicinal protons was J = 13.6 Hz. As a consequence, we could estimate that only the (*Z*)-isomer product was formed during the cross-coupling reaction.



Figure S5. ¹H NMR spectrum of the (Z)-2-(non-4-en-1-yl)furan.

Figure S6 shows a zoom in the vinylic area chemical shift for this product ($\delta = 5.5 - 5.3$ Hz). The shape of the peak corresponds to the predicted splitting pattern for proton H_a.



Figure S6. Zoom in the vinylic area of the ¹H NMR spectrum for the (*Z*)-2-(non-4-en-1-yl)furan and predicted splitting pattern for proton H_a .

As the (*E*)-isomer products are formed from alkenyl-(9-BBN) reagents with (*E*)-configuration and the (*Z*)-isomer products from alkenyl-(9-BBN) reagents with (*Z*)-configuration, we can conclude that this Suzuki-Miyaura cross-coupling reaction catalyzed by the *Nickamine* is stereospecific.

6. General Procedure for Experiments.

6.1 Synthesis of (*E*)-9-(hex-1-en-1-yl)-9-borabicyclo[3.3.1]nonane 2b.²³

(9-BBN)-H (0.5 M in THF, 50 mmol, 100 mL) was added dropwise to the 1-hexyne (2 equiv, 100 mmol, 11.6 mL) at 0 °C under a nitrogen atmosphere. After addition, reaction mixture was stirred for 5 min at 0 °C then was warmed to room temperature and stirred for 2 h. The solvent was removed under reduced pressure. The crude product was then purified by distillation under reduced pressure to provide the pure product **2b** as a pale yellow oil (7.19 g, 70%). B.p. 93-96°C/0.2 mbar (lit B.p. 72-74/0.003 mmHg).

Procedure for the synthesis of the (*E*)-9-(oct-1-en-1-yl)-9-borabicyclo[3.3.1]nonane **2a** was identical using 1-octyne (2 equiv, 40 mmol, 5.96 mL) and (9-BBN)-H (0.5 M in THF, 20 mmol, 40 mL). The crude product was then purified by distillation under reduced pressure to provide the pure product **2a** as a pale yellow oil (3.26 g, 70%). B.p. 147-149°C/0.2 mbar

6.2 Typical Procedure for the Alkyl-Alkenyl Cross-Coupling Reactions.

To a solution of NaOMe (1.6 equiv, 0.8 mmol, 43 mg) and catalyst **1** (5 mol %, 0.025 mmol, 8.7 mg) in dry 1,4-dioxane (1 mL) were added the alkyl halide (0.5 mmol) and the alkenyl-(9-BBN) (1.4 equiv, 0.7 mmol, 143 mg) under a N₂ atmosphere. The mixture was heated under stirring for 24 h. Temperature of heating was 60 °C for alkyl iodide, 80 °C for alkyl bromide and 100 °C for alkyl chloride. The solution was then diluted in Et₂O (10 mL), filtered through a short pad of silica gel which was washed with Et₂O (3 × 10 mL), and concentrated to dryness under reduced pressure. The residue was purified by column chromatography to give the coupling products **4** or **5** (Schemes 3 and 4).

6.3 Typical Procedure for the *one-pot* Synthesis.

(9-BBN)-H (0.5 M in THF, 0.6 mmol, 1.2 mL) was added dropwise to the alkyne (2 equiv, 1 mmol) at 0 °C under a nitrogen atmosphere. After addition, reaction mixture was stirred for 5 min at 0 °C then was warmed to room temperature and stirred for 2 h. The solvent was removed under reduced pressure and the resulting alkenyl-(9-BBN) was added with 1 ml of 1,4-dioxane to a 10 mL sealed glass vial containing NaOMe (1.6 equiv, 0.8 mmol, 43 mg), catalyst 1 (5 mol %, 0.025 mmol, 8.7 mg) and the alkyl halide (0.5 mmol) under a N₂ atmosphere. The mixture was heated under stirring for 24 h. Temperature of heating was 60 °C for alkyl iodide, 80 °C for alkyl bromide and 100 °C for alkyl chloride. The solution was then diluted in Et₂O (10 mL), filtered through a short pad of silica gel which was washed with Et₂O (3 × 10 mL), and concentrated to dryness under reduced pressure. The residue was purified by column chromatography to give the coupling products **6** (Scheme 5).

For products **6i**, **6j** and **6k**, the reaction mixture was stirred for 2 h at 0 °C and then for 1 h at room temperature during the hydroboration step.

6.4 Procedures for the total Synthesis of the (±)-Recifeiolide.



To a solution of 4-pentyn-2-ol (22 mmol, 1.87 g) and imidazole (1.5 equiv, 33 mmol, 2.25 g) in DCM (150 mL) was added the *tert*-butyldimethylsilyl chloride (1.3 equiv, 28.6 mmol, 4.31 g), resulting in the immediate formation of a white solid. The reaction mixture was stirred at room temperature for 3 h. It was then filtered through a short pad of silica, washed with an aqueous solution of HCl 1M (100 mL), a saturated aqueous solution of NaHCO₃ (100 mL) and brine (100 mL). The organic phase was dried over anhydrous Na₂SO₄ and evaporated to afford the pure product **7a** as a colorless oil (3.40 g, Yield 77%).



(9-BBN)-H (0.5 M in THF, 2.8 mmol, 5.6 mL) was added dropwise to the *tert*butyldimethyl(pent-4-yn-2-yloxy)silane **7a** (1.4 equiv, 2.8 mmol, 555 mg) at 0 °C under a nitrogen atmosphere. After addition, reaction mixture was stirred for 2 h at 0 °C then was warmed to room temperature and stirred for 1 h. The solvent was removed under reduced pressure. To the resulting alkenyl-(9-BBN) were added with 4 ml of 1,4-dioxane NaOMe (1.6 equiv, 3.2 mmol, 173 mg), catalyst **1** (5 mol %, 0.1 mmol, 35 mg) and the ethyl 7bromoheptanoate (2 mmol, 474 mg) under a N₂ atmosphere. The mixture was stirred for 24 h at 80 °C. The solution was then diluted in Et₂O (10 mL), filtered through a short pad of silica gel which was washed with Et₂O (3 × 10 mL), and concentrated to dryness under reduced pressure. The residue was purified by column chromatography (Hexane/Ethyl acetate 95:5) to give the ethyl (*E*)-11-((tert-butyldimethylsilyl)oxy)dodec-8-enoate **7b** as a pure product (555 mg, Yield 78%).



Under a N₂ atmosphere, the tetrabutylammonium fluoride TBAF (1 equiv, 1 M in THF, 1 mL) was added dropwise to a cooled solution of the ethyl (*E*)-11-((tert-butyldimethylsilyl)oxy) dodec-8-enoate **7b** (356 mg, 1 mmol) at 0 °C in 5 mL of dry THF. The reaction mixture was then stirred at room temperature overnight under a N₂ atmosphere. 10 mL of a saturated solution of NH₄Cl were added and the product was extracted with Et₂O (3×10 mL). Organic phases were dried over anhydrous Na₂SO₄ and evaporated. The crude product was purified by column chromatography (Hexane/Ethyl acetate 5:5) to afford the pure product **7b'** (208 mg, Yield 86%).



The ethyl (*E*)-11-hydroxydodec-8-enoate **7b'** (128 mg, 0.53 mmol) and the potassium hydroxide (20 equiv, 10.6 mmol, 595 mg) were dissolved in methanol (2 mL) and water (2 mL). The reaction mixture was stirred at 80 °C for 1 h. 10 mL of water were added, and a solution of HCl 1 M was added dropwise to the cooled reaction mixture until pH = 2. The product was extracted with Et₂O (3 × 20 mL), dried over anhydrous Na₂SO₄ and evaporated to give the pure compound **7c** (108 mg, Yield 96%).



(±)-Recifeiolide

The (\pm) -Recifeiolide was synthesized according to the following procedure:²⁴

To the carboxylic acid **7c** (1 equiv, 0.5 mmol, 108 mg) and trimethylamine (10 equiv, 5 mmol, 0.7 mL) in dry toluene (4 mL) was added a solution of 2,4,6-trichlorobenzoyl chloride (1 equiv, 0.5 mmol, 78 μ L) in dry toluene (5 mL). The reaction mixture was stirred for 5 h at room temperature, then filtered and the filtrate was diluted in with dry toluene (150 mL). This solution was added dropwise over 2 h to a solution of 4-(*N*,*N*-dimethylamino)pyridine in dry toluene (50 mL). After being stirred overnight at room temperature, the reaction mixture was evaporated, diluted in 30 mL of Et₂O, washed with a saturated aqueous solution of NH₄Cl (30 mL), water (2 × 30 mL), dried over anhydrous Na₂SO₄ and evaporated. The crude compound was purified by column chromatography (Hexane/Ethyl acetate 9:1) to obtain the pure (±)-Recifeiolide as a colorless oil (69 mg, Yield 70%).

7. Comparison with other existing Cross-Coupling Reactions.

The Ni-catalyzed alkenyl-alkyl cross-coupling reactions developed by Fu and Molander were tested with a selected substrate, the 6-bromo-*N*,*N*-diethylhexanamide, to compare their efficiency.

Fu's procedure:²⁵



Inside a glovebox, Ni(cod)₂ (4 mol %, 0.02 mmol, 5.5 mg), bathophenanthroline (8 mol %, 0.04 mmol, 13.3 mg), KOt-Bu (1.6 equiv, 0.8 mmol, 90 mg) and the (*E*)-9-(hex-1-en-1-yl)-9-borabicyclo[3.3.1]nonane (1.2 equiv, 0.6 mmol, 122 mg) were added wit 1 mL of *s*-butanol to a long vial equipped with a stir bar. Reaction mixture was stirred at room temperature for 10 min, then the 6-bromo-*N*,*N*-diethylhexanamide was added (0.5 mmol, 125 mg). The vial was removed from the glovebox and the reaction mixture was stirred at 60 °C for 5h. The solution was then diluted in Et₂O (10 mL), filtered through a short pad of silica, washed with Et₂O (3×10 mL), and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel with a mixture of hexane/ethyl acetate (8:2) to give the coupling product (12 mg, Yield 9%).

Molander's procedure:²⁶



Inside a glovebox, NiBr₂·glyme (10 mol %, 0.05 mmol, 15.4 mg), bathophenanthroline (10 mol %, 0.05 mmol, 16.6 mg), NaHMDS (3 equiv, 1.5 mmol, 275 mg) and the (*E*)-9-(hex-1-en-1-yl)-9-borabicyclo[3.3.1]nonane (1.05 equiv, 0.525 mmol, 107 mg) were added into a long vial equipped with a stir bar. CPME (1 mL) and *t*-BuOH (1 mL) were added via syringe. The mixture was stirred for 30 min at room temperature, and the 6-bromo-*N*,*N*-diethylhexanamide (0.5 mmol, 125 mg) was added to the resulting solution. The reaction in the sealed vial was stirred at 60 °C overnight outside the glovebox, then passed through a short plug of silica, which was washed thoroughly with CH₂Cl₂ (~10 mL) and EtOAc (~5 mL). The filtrate was concentrated under reduced pressure, then purified by column chromatography on silica gel with a mixture of hexane/ethyl acetate (8:2) to afford the coupling product (17 mg, Yield 13%).

8. Hg experiments.

NiCl₂·dme Test



Following the general NiCl₂·dme procedure (See Table S1), when the reaction of 1-iodo-4phenylbutane with the (*E*)-9-(hex-1-en-1-yl)-(9-BBN) was conducted in the presence of 100 equivalent of Hg (relative to the catalyst) at 40 °C, (*E*)-dec-5-en-1-ylbenzene was produced in a 16% yield. In the same conditions but without Hg, the yield was 75%.

Nickamine Test



Following the general *Nickamine* procedure (See Table S2), when the reaction of 1-iodo-4phenylbutane with the (*E*)-9-(hex-1-en-1-yl)-(9-BBN) was conducted in the presence of 100 equivalent of Hg (relative to the catalyst), (*E*)-dec-5-en-1-ylbenzene was produced in a 70% yield, nearly identical to the coupling in the absence of Hg (80% yield). This suggests that heterogeneous metal particles are not responsible for the catalysis.

9. Characterization of the new Products.

2a :

Colorless oil; Yield after distillation: 70% (3.26 g);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 6.94-6.72 (m, 1H), 6.22 (d, J = 17.3 Hz, 1H), 2.37-2.15 (m, 2H), 1.98-1.61 (m, 12H), 1.61-1.41 (m, 2H), 1.41-1.02 (m, 8H), 1.02-0.71 (t, J = 6.8 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 156.5, 134.3, 36.3, 33.9, 33.6, 31.9, 29.2, 28.6, 23.7, 23.4, 22.8, 14.3;

Product was not detected by ESI, APCI and APPI.

Colorless oil; Yield after distillation: 70% (7.19 g);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 6.83 (dt, J = 17.2, 6.2 Hz, 1H), 6.23 (d, J = 17.2 Hz, 1H), 2.46-2.10 (m, 2H), 2.10-1.57 (m, 12H), 1.57-1.43 (m, 2H), 1.36 (dd, J = 14.6, 7.3 Hz, 2H), 1.32-1.07 (m, 2H), 0.92 (t, J = 7.1 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 156.4, 134.4, 36.0, 33.9, 30.8, 30.1, 23.7, 22.6, 14.1; Product was not detected by ESI, APCI and APPI.

4a :

Colorless oil; solvent for chromatography: hexane; 91 mg (84%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.43-6.85 (m, 5H), 5.51-5.15 (m, 2H), 2.63 (t, J = 7.6 Hz, 2H), 2.11-1.87 (m, 4H), 1.63 (m, 2H), 1.53-1.13 (m, 6H), 0.91 (t, J = 7.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 143.0, 130.8, 130.1, 128.5, 128.4, 125.7, 36.0, 32.6, 32.4, 32.0, 31.1, 29.4, 22.4, 14.1;

HRMS (APPI) for $(M^{+\bullet}: C_{16}H_{24}^{+\bullet})$, calculated: 216.1878, found: 216.1873.



Yellow oil; solvent for chromatography: hexane/ethyl acetate (9:1); 84 mg (56%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.83 (d, J = 8.4 Hz, 2H), 7.77-7.59 (m, 2H), 5.40 (m, 2H), 3.68 (t, J = 7.2 Hz, 2H), 2.04 (m, 2H), 1.92 (m, 2H), 1.74 (m, 2H), 1.35-1.16 (m, 8H), 0.86 (t, J = 6.6 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 168.5, 133.9, 132.3, 131.6, 128.6, 123.2, 37.8, 32.6, 31.8, 30.0, 29.5, 28.9, 28.4, 22.7, 14.2;

HRMS (ESI) for $([M+H]^+: C_{19}H_{26}NO_2^+)$, calculated: 300.1964, found: 300.1968.

Yellow oil; solvent for chromatography: hexane/ethyl acetate (9:1); 105mg (90%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 6.96 (d, J = 4.0 Hz, 1H), 6.84 (d, J = 4.0 Hz, 1H), 6.11 (m, 1H), 5.39 (m, 2H), 4.29 (t, J = 7.1 Hz, 2H), 2.43 (s, 3H), 2.03-1.87 (m, 4H), 1.87-1.70 (m, 2H), 1.36-0.99 (m, 4H), 0.88 (t, J = 6.8 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 147.0, 131.6, 130.4, 129.0, 120.4, 107.9, 49.4, 32.4, 31.9, 31.2, 29.6, 27.5, 22.3, 14.1;

HRMS (ESI) for $([M+H]^+: C_{15}H_{24}NO^+)$, calculated: 234.1858, found: 234.1861.



Yellow oil; solvent for chromatography: hexane/ethyl acetate (9:1); 102 mg (62%); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.18 (d, *J* = 6.9 Hz, 1H), 7.82 (s, 1H), 7.36 (dd, *J* = 6.9, 2.3 Hz, 1H), 7.32-7.24 (m, 2H), 5.40 (m, 2H), 4.14 (t, *J* = 6.9 Hz, 2H), 3.91 (s, 3H), 2.07-1.85 (m, 6H), 1.43-1.12 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 165.7, 136.6, 134.4, 132.6, 128.1, 126.8, 122.7, 121.9, 121.8, 110.2, 107.0, 51.1, 46.3, 32.7, 31.9, 29.7, 29.6, 29.0, 22.8, 14.3;

HRMS (ESI) for ([M+H]⁺: C₂₁H₃₀NO₂⁺), calculated: 328.2277, found: 328.2276.

Yellow oil; solvent for chromatography: hexane/ethyl acetate (98:2); 77 mg (80%); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.36-7.27 (m, 1H), 6.30-6.26 (m, 1H), 6.02-5.91 (m, 1H), 5.57-5.21 (m, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 2.13-1.89 (m, 4H), 1.72 (m, 2H), 1.42-1.21 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 156.5, 140.8, 131.4, 129.5, 110.2, 104.8, 32.4, 32.1, 31.9, 28.0, 27.5, 22.4, 14.1;

HRMS (ESI) for $([M+H]^+: C_{13}H_{21}O^+)$, calculated: 193.1592, found: 193.1594.



Yellow oil; solvent for chromatography: hexane/ethyl acetate (9:1); 98 mg (63%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 5.50-5.19 (m, 2H), 4.20-3.92 (m, 2H), 2.80-2.50 (m, 2H), 1.94 (dd, J = 24.2, 6.6 Hz, 4H), 1.63 (d, J = 13.3 Hz, 1H), 1.44 (s, 9H), 1.40-1.15 (m, 10H), 1.15-0.98 (m, 2H), 0.87 (t, J = 6.6 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 155.1, 132.5, 127.7, 79.3, 39.8, 36.6, 32.8, 32.0, 31.9, 29.9, 29.7, 29.0, 28.6, 22.8, 14.2;

HRMS (ESI) for $([M+Na]^+: C_{19}H_{35}NO_2Na^+)$, calculated: 332.2566, found: 332.2568.

4i: Ph Ph NC

Yellow oil; solvent for chromatography: hexane/ethyl acetate (95:5); 139 mg (84%); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.44-7.23 (m, 10H), 5.34 (m, 2H), 2.36 (t, *J* = 8.8 Hz, 2H), 2.06-1.80 (m, 4H), 1.50-1.37 (m, 4H), 1.37-1.20 (m, 4H), 0.88 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 140.5, 131.1, 129.6, 129.0, 127.9, 127.0, 122.6, 51.9, 39.7, 32.4, 32.3, 31.9, 29.6, 25.2, 22.3, 14.1;

HRMS (ESI) for ($[M+H]^+$: $C_{24}H_{30}N^+$), calculated: 332.2378, found: 332.2376.

4j : N

Yellow oil; solvent for chromatography: hexane/ethyl acetate (95:5); 81 mg (90%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 5.46-5.30 (m, 2H), 2.33 (t, *J* = 7.2 Hz, 2H), 2.09-1.89 (m, 4H), 1.65 (m, 2H), 1.52-1.17 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 131.2, 129.6, 120.0, 32.4, 32.3, 31.9, 28.8, 28.2, 25.4, 22.3, 17.3, 14.1;

HRMS (APPI) for $(M^{+\bullet}: C_{12}H_{21}N^{+\bullet})$, calculated: 179.1669, found: 179.1664.

Yellow oil; solvent for chromatography: hexane/ethyl acetate (95:5); 84 mg (72%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.29 (dt, J = 13.2, 6.5 Hz, 4H), 7.16 (t, J = 7.1 Hz, 1H), 5.40 (m, 2H), 2.91 (t, J = 7.4 Hz, 2H), 2.12 (m, 2H), 1.98 (m, 2H), 1.70 (p, J = 7.3 Hz, 2H), 1.30 (dt, J = 12.7, 6.5 Hz, 4H), 0.89 (t, J = 7.2 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 137.0, 131.9, 129.0, 129.0, 128.8, 125.8, 33.0, 32.4, 31.9, 31.7, 29.1, 22.3, 14.1;

HRMS (ESI) for $([M+H]^+: C_{15}H_{23}S^+)$, calculated: 235.1521, found: 235.1517.

Yellow oil; solvent for chromatography: hexane/ethyl acetate (95:5); 106 mg (91%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 6.98-6.72 (m, 4H), 5.58 (dt, *J* = 13.5, 6.6 Hz, 1H), 5.46 (dt, *J* = 14.3, 6.8 Hz, 1H), 4.23 (d, *J* = 11.2 Hz, 1H), 4.13 (m, 1H), 3.88 (dd, *J* = 11.2, 7.7 Hz, 1H), 2.57-2.38 (m, 1H), 2.32 (dt, *J* = 14.1, 7.2 Hz, 1H), 2.03 (m, 2H), 1.32 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 143.6, 143.4, 135.0, 123.6, 121.6, 121.3, 117.4, 117.1, 72.9, 67.6, 34.6, 32.4, 31.6, 22.3, 14.1;

HRMS (APPI) for $(M^{+\bullet}: C_{15}H_{20}O_2^{+\bullet})$, calculated: 232.1458, found: 232.1451.

Yellow oil; solvent for chromatography: hexane/ethyl acetate (9:1); 87 mg (88%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 5.37 (m, 2H), 4.50 (t, J = 5.2 Hz, 1H), 4.09 (dd, J = 10.9, 4.9 Hz, 2H), 3.81-3.55 (m, 2H), 2.12-1.81 (m, 4H), 1.75-1.50 (m, 2H), 1.39-1.06 (m, 6H), 0.87 (t, J = 7.2 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 131.1, 129.2, 102.0, 67.0, 35.2, 32.4, 31.9, 27.2, 26.0, 22.3, 14.1;

HRMS (APPI) for $([M+H]^+: C_{12}H_{23}O_2^+)$, calculated: 199.1693, found: 199.1691.

4n :

Yellow oil; solvent for chromatography: hexane/ethyl acetate (95:5); 109 mg (94%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.37-7.21 (m, 2H), 7.00-6.82 (m, 3H), 5.64-5.19 (m, 2H), 3.97 (t, *J* = 6.5 Hz, 2H), 2.26-1.90 (m, 4H), 1.80 (dt, *J* = 14.8, 7.0 Hz, 2H), 1.55 (dt, *J* = 14.5, 7.3 Hz, 2H), 1.43-1.12 (m, 4H), 0.91 (t, *J* = 6.2 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 159.2, 131.1, 129.8, 129.5, 120.6, 114.6, 67.9, 32.4, 31.9, 28.9, 26.2, 22.4, 14.1;

HRMS (APPI) for $(M^{+\bullet}: C_{16}H_{24}O^{+\bullet})$, calculated: 232.1822, found: 232.1455.

40 : 0 Et₂N

Blue oil; solvent for chromatography: hexane/ethyl acetate (7:3); 112 mg (88%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 5.48-5.19 (m, 2H), 3.31 (m, 4H), 2.27 (t, *J* = 7.6 Hz, 2H), 2.05-1.80 (m, 4H), 1.73-1.50 (m, 2H), 1.47-1.21 (m, 8H), 1.12 (dt, *J* = 24.8, 7.0 Hz, 6H), 0.88 (t, *J* = 6.4 Hz, 3H).;

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 172.4, 130.6, 130.2, 42.1, 40.1, 33.3, 32.6, 32.4, 31.9, 29.6, 29.2, 25.5, 22.3, 14.5, 14.1, 13.2;

HRMS (ESI) for ($[M+H]^+$: C₁₆H₃₂NO⁺), calculated: 254.2484, found: 254.2489.

Yellow oil; solvent for chromatography: hexane; 131 mg (90%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.13 (d, J = 7.8 Hz, 2H), 7.59-7.33 (m, 4H), 7.33-7.05 (m, 2H), 5.65-5.22 (m, 2H), 4.32 (t, J = 7.2 Hz, 2H), 2.22-1.79 (m, 6H), 1.46-1.17 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 140.5, 131.9, 128.8, 125.7, 122.9, 120.5, 118.8, 108.8, 42.5, 32.4, 31.9, 30.2, 28.7, 22.4, 14.1;

HRMS (ESI) for $([M+H]^+: C_{21}H_{26}N^+)$, calculated: 292.2065, found: 292.2072.

4q :

Yellow oil; solvent for chromatography: hexane/ethyl acetate (15:1); 78 mg (76%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.49-7.14 (m, 2H), 7.04-6.66 (m, 3H), 5.70-5.34 (m, 2H), 3.98 (t, *J* = 6.8 Hz, 2H), 2.50 (m, 2H), 2.12-1.93 (m, 2H), 1.49-1.20 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 159.1, 133.5, 129.5, 125.5, 120.7, 114.7, 67.8, 32.7, 32.5, 31.7, 22.3, 14.1;

HRMS (APPI) for $([M+H]^+: C_{14}H_{21}O^+)$, calculated: 205.1587, found: 205.1582.

4r: 0,0

Orange oil; solvent for chromatography: hexane/ethyl acetate (8:2); 86 mg (80%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 5.57-5.23 (m, 2H), 3.93 (dt, *J* = 8.4, 4.3 Hz, 4H), 2.18-1.87 (m, 4H), 1.75-1.54 (m, 2H), 1.54-1.02 (m, 9H), 0.88 (t, *J* = 7.2 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 131.0, 129.9, 124.6, 64.7, 38.8, 32.8, 32.4, 31.9, 24.2, 23.9, 22.3, 14.1;

HRMS (APPI) for $(M^{+\bullet}: C_{13}H_{24}O_2^{+\bullet})$, calculated: 212.1771, found: 212.1775.

5a :

Colorless oil; solvent for chromatography: hexane; 59 mg (71%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 5.49-5.15 (m, 2H), 2.11-1.92 (m, 2H), 1.92-1.79 (m, 1H), 1.79-1.58 (m, 4H), 1.41-1.11 (m, 8H), 1.11-0.96 (m, 2H) 0.89 (t, *J* = 6.8 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 136.5, 127.8, 40.9, 33.5, 32.5, 32.1, 26.4, 26.3, 22.3, 14.1;

HRMS (APPI) for $(M^{+\bullet}: C_{12}H_{22}^{+\bullet})$, calculated: 166.1716, found: 166.1713.



Yellow oil; solvent for chromatography: hexane/ethyl acetate (9:1); 112 mg (92%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.54-7.14 (m, 5H), 5.42 (m, 2H), 4.37 (d, J = 11.2 Hz, 1H), 4.20 (dd, J = 11.2, 4.2 Hz, 1H), 3.65 (t, J = 11.8 Hz, 1H), 2.48-2.25 (m, 1H), 2.07-1.96 (m, 2H), 1.91 (d, J = 13.3 Hz, 1H), 1.68 (d, J = 13.0 Hz, 1H), 1.44-1.13 (m, 6H), 0.91 (t, J = 6.8 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 143.2, 134.3, 129.2, 128.4, 127.4, 125.9, 79.7, 68.4, 40.7, 38.8, 32.5, 32.4, 31.8, 22.3, 14.1;

HRMS (APPI) for $(M^{+\bullet}: C_{17}H_{24}O^{+\bullet})$, calculated: 244.1777, found: 244.1803.

5f: 0

Yellow oil; solvent for chromatography: hexane/ethyl acetate (15:1); 58 mg (69%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 5.51-5.21 (m, 2H), 3.94 (d, J = 9.5 Hz, 2H), 3.39 (t, J = 11.6 Hz, 2H), 2.23-2.07 (m, 1H), 1.98 (d, J = 6.0 Hz, 2H), 1.58 (d, J = 12.7 Hz, 2H), 1.51-1.36 (m, 2H), 1.36-1.12 (m, 4H), 0.88 (t, J = 6.2 Hz, 3H).;

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 134.5, 129.0, 68.0, 38.0, 33.1, 32.4, 31.9, 22.3, 14.1; HRMS (ESI) for ($[M+H]^+$: C₁₁H₂₁O⁺), calculated: 169.1592, found: 169.1601.

5g :

Colorless oil; solvent for chromatography: hexane; 60 mg (79%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 5.49-5.18 (m, 2H), 2.50-2.28 (m, 1H), 2.08-1.84 (m, 2H), 1.81-1.40 (m, 6H), 1.40-1.06 (m, 6H), 0.88 (t, *J* = 6.5 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 135.1, 128.5, 43.5, 33.4, 32.4, 32.0, 25.3, 22.4, 14.1; HRMS (APPI) for ($M^{+\bullet}$: C₁₁H₂₀^{+•}), calculated: 152.1560, found: 152.1556.

5h :

Yellow oil; solvent for chromatography: hexane; 85 mg (85%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.34-7.07 (m, 4H), 5.58 (m, 2H), 3.24-2.99 (m, 3H), 2.87-2.62 (m, 2H), 2.17-1.89 (m, 2H), 1.47-1.23 (m, 4H), 0.95 (t, *J* = 6.5 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 143.5, 133.8, 130.0, 126.2, 124.4, 43.7, 39.9, 32.4, 31.9, 22.4, 14.1;

HRMS (APPI) for $(M^{+\bullet}: C_{15}H_{20}^{+\bullet})$, calculated: 200.1565, found: 200.1571.

Yellow oil; solvent for chromatography: hexane/ethyl acetate (9:1); 76 mg (64%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 5.53-5.12 (m, 2H), 4.22-3.97 (m, 2H), 2.38-2.18 (m, 1H), 2.01-1.86 (m, 4H), 1.84-1.74 (m, 1H), 1.69 (d, *J* = 13.5 Hz, 1H), 1.53 (d, *J* = 39.0 Hz, 2H), 1.26 (m, 10H), 0.86 (t, *J* = 3.4 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 176.1, 135.2, 128.7, 60.2, 43.4, 40.2, 35.5, 32.5, 32.4, 31.9, 28.7, 25.4, 22.3, 14.4, 14.1;

HRMS (ESI) for $([M+H]^+: C_{15}H_{27}O_2^+)$, calculated: 239.2011, found: 239.2012.

Yellow oil; solvent for chromatography: hexane/ethyl acetate (8:2); 97 mg (76%); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 5.50 (m, 1H), 5.41-5.18 (m, 1H), 3.59-3.34 (m, 2H), 3.25 (dd, J = 14.4, 7.8 Hz, 1H), 3.09-2.84 (m, 1H), 2.79-2.54 (m, 1H), 2.04-1.82 (m, 3H), 1.62 (d, J = 10.9 Hz, 1H), 1.46 (s, 9H), 1.36-1.12 (m, 4H), 0.87 (t, J = 9.3 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 154.7, 131.7, 130.0, 79.1, 51.5, 45.8, 42.2, 32.6, 32.3, 31.7, 28.7, 22.3, 14.1;

HRMS (ESI) for ([M+Na]⁺: C₁₅H₂₇NO₂Na⁺), calculated: 276.1939, found: 276.1941.

5k :

Yellow oil; solvent for chromatography: hexane/ethyl acetate (8:2); 88 mg (73%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 5.52 (m, 2H), 4.04 (t, J = 8.2 Hz, 2H), 3.79-3.55 (m, 2H), 3.22-2.98 (m, 1H), 2.00 (m, 2H), 1.41 (s, 9H), 1.36-1.07 (m, 4H), 0.88 (t, J = 6.3 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 156.5, 132.3, 130.6, 79.3, 55.0, 32.2, 31.6, 31.5, 28.5, 22.3, 14.0;

HRMS (ESI) for $([M+H]^+: C_{14}H_{26}NO_2^+)$, calculated: 240.1964, found: 240.0685.

5m :

Colorless oil; solvent for chromatography: hexane; 86 mg (80%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.48-6.96 (m, 5H), 5.38 (m, 2H), 2.62 (m, 2H), 2.14 (m, 1H), 2.05 (m, 2H), 1.62 (m, 2H), 1.48-1.21 (m, 4H), 1.04 (d, *J* = 6.7 Hz, 3H), 0.95 (t, *J* = 7.0 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 143.2, 136.0, 139.4, 128.6, 128.4, 125.7, 39.1, 36.6, 33.9, 32.4, 32.0, 22.3, 21.2, 14.1;

HRMS (APPI) for $(M^{+\bullet}: C_{16}H_{24}^{+\bullet})$, calculated: 216.1873, found: 216.1869.

Colorless oil; solvent for chromatography: hexane; 81 mg (69%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.58-7.25 (m, 5H), 7.25-7.02 (m, 4H), 6.40 (d, J = 15.8 Hz, 1H), 6.32-6.06 (m, 1H), 2.66 (t, J = 7.6 Hz, 2H), 2.27 (m, 2H), 1.85-1.62 (m, 2H), 1.55 (t, J = 7.3 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 142.8, 138.0, 131.0, 130.0, 128.6, 128.5, 128.4, 126.9, 126.0, 125.8, 36.0, 33.0, 31.2, 29.1;

HRMS (APPI) for $(M^{+\bullet}: C_{18}H_{20}^{+\bullet})$, calculated: 236.1560, found: 236.1559.

Yellow oil; solvent for chromatography: hexane/ethyl acetate (8:2); 42 mg (41%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.30 (d, J = 0.8 Hz, 1H), 6.28 (t, J = 2.4 Hz, 1H), 5.97 (d, J = 2.4 Hz, 1H), 5.43 (m, 2H), 2.61 (t, J = 7.5 Hz, 2H), 2.32 (t, J = 7.2 Hz, 2H), 2.15 (m, 2H), 2.05 (m, 2H), 1.71 (m, 4H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 156.2, 140.9, 132.4, 128.2, 119.8, 110.2, 104.9, 32.0, 31.4, 27.8, 27.5, 25.2, 16.4;

HRMS (ESI) for $([M+H]^+: C_{13}H_{18}NO^+)$, calculated: 204.1388, found: 204.1392.



Yellow oil; solvent for chromatography: hexane/ethyl acetate (8:2); 86 mg (80%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.30 (dt, J = 15.3, 7.5 Hz, 4H), 7.17 (t, J = 6.9 Hz, 1H), 5.44 (m, 2H), 3.52 (t, J = 6.4 Hz, 2H), 2.91 (t, J = 7.3 Hz, 2H), 2.30-2.00 (m, 4H), 1.83 (m, 2H), 1.77-1.58 (m, 2H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 136.9, 130.6, 129.5, 129.1, 129.0, 125.9, 44.5, 33.0, 32.3, 31.6, 29.7, 28.9;

HRMS (ESI) for $([M+H]^+: C_{14}H_{20}ClS^+)$, calculated: 255.0974, found: 255.0975.



Yellow oil; solvent for chromatography: hexane/ethyl acetate (8:2); yield: 90 mg (51 %); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.54 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 6.41 (d, *J* = 16.1 Hz, 1H), 6.25 (dd, *J* = 16.0, 6.8 Hz, 1H), 4.26-3.94 (m, 2H), 2.86-2.69 (m, 2H), 2.46-2.36 (m, 1H), 2.36-2.25 (m, 1H), 1.96-1.82 (m, 1H), 1.76 (d, *J* = 14.4 Hz, 2H), 1.47 (s, 9H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 155.0, 137.2, 127.5, 126.3, 125.6, 125.5, 79.6, 42.1, 39.6, 31.7, 28.6;

HRMS (ESI) for ([M+Na]⁺: C₁₉H₂₄F₃NO₂Na⁺), calculated: 378.1657, found: 378.1654.



Slightly yellow oil; solvent for chromatography: hexane/ethyl acetate (95:5); yield: 90 mg (54%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 6.97 (d, J = 3.8 Hz, 1H), 6.83 (s, 1H), 6.20-6.09 (m, 1H), 6.03 (dt, J = 18.8, 6.2 Hz, 1H), 5.54 (d, J = 18.8 Hz, 1H), 4.31 (t, J = 7.1 Hz, 2H), 2.43 (s, 3H), 2.19-2.09 (m, 2H), 1.89-1.78 (m, 2H), 1.33-1.21 (m, 2H), 1.02 (d, J = 4.1 Hz, 21H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 188.3, 148.1, 130.4, 124.8, 120.4, 108.0, 49.4, 34.3, 30.6, 27.5, 18.8, 11.0;

HRMS (ESI) for ([M+H]⁺: C₂₀H₃₆NOSi⁺), calculated: 334.2566, found: 334.2566.

6g : OTBDMS

Colorless oil; solvent for chromatography: hexane/ethyl acetate (95:5); yield: 103 mg (61%); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.29 (dd, J = 8.1, 5.7 Hz, 2H), 6.97 (t, J = 8.6 Hz, 2H), 6.33 (d, J = 15.8 Hz, 1H), 6.23-6.01 (m, 1H), 3.61 (t, J = 6.5 Hz, 2H), 2.19 (m, 2H), 1.63-1.40 (m, 4H), 1.40-1.28 (m, 4H), 0.89 (s, 9H), 0.05 (s, 6H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 160.8, 131.1, 128.7, 127.4, 115.5, 115.3, 63.4, 33.1, 33.0, 29.5, 29.2, 26.1, 25.9, -5.1;

HRMS (ESI) for ([M+H]⁺: C₂₀H₃₄FOSi^{+•}), calculated: 337.2363, found: 337.2363.

6h :

Yellow oil; solvent for chromatography: hexane/ethyl acetate (95:5); yield: 91 mg (72%); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.32-7.26 (m, 4H), 7.23-7.16 (m, 3H), 6.97-6.86 (m, 3H), 5.69-5.48 (m, 2H), 3.96 (t, *J* = 6.8 Hz, 2H), 2.75-2.65 (m, 2H), 2.49 (m, 2H), 2.36 (m, 2H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 159.1, 142.1, 132.4, 129.5, 128.6, 128.4, 126.5, 125.9, 120.7, 114.7, 67.7, 36.1, 34.6, 32.7;

HRMS (APPI) for $(M^{+\bullet}: C_{18}H_{20}O^{+\bullet})$, calculated: 252.1509, found: 252.1514.

Yellow oil; solvent for chromatography: hexane/ethyl acetate (8:2); yield: 77 mg (55%); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.11 (d, *J* = 6.1 Hz, 1H), 6.91 (m, 1H), 6.78 (d, *J* = 2.8 Hz, 1H), 5.56-5.41 (m, 2H), 4.57 (s, 1H), 3.98-3.80 (m, 1H), 3.72 (m, 1H), 3.63-3.42 (m, 2H), 2.88 (t, *J* = 7.4 Hz, 2H), 2.42-2.25 (m, 2H), 2.22-2.01 (m, 2H), 1.86-1.53 (m, 8H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 145.0, 131.0, 129.3, 126.7, 124.2, 123.0, 99.0, 67.1, 62.4, 34.8, 30.9, 30.2, 29.6, 29.3, 25.6, 19.8;

HRMS (ESI) for $([M+Na]^+: C_{16}H_{24}O_2SNa^+)$, calculated: 303.1395, found: 303.1396.

Yellow oil; solvent for chromatography: hexane/ethyl acetate (9:1); yield: 76 mg (50%); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.25 (d, *J* = 8.4 Hz, 2H), 6.89-6.71 (m, 2H), 6.30 (d, *J* = 15.6 Hz, 1H), 6.05 (m, 1H), 3.78 (s, 3H), 3.31 (m, 4H), 2.38-2.24 (m, 2H), 2.18 (m, 2H), 1.65 (dt, *J* = 15.0, 7.5 Hz, 2H), 1.57-1.42 (m, 2H), 1.42-1.30 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 172.4, 158.7, 130.8, 129.3, 128.9, 127.1, 114.0, 55.4, 42.1, 33.2, 33.0, 29.5, 29.2, 25.5, 14.3;

HRMS (ESI) for $([M+H]^+: C_{19}H_{30}NO_2^+)$, calculated: 304.2277, found: 304.2278.



Yellow oil; solvent for chromatography: hexane/ethyl acetate (6:4); yield: 100 mg (57%); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.28 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.36 (d, *J* = 15.6 Hz, 1H), 6.17 (dd, *J* = 14.8, 7.7 Hz, 1H), 4.73-4.48 (m, 1H), 4.11 (m, 2H), 3.76 (t, *J* = 11.5 Hz, 2H), 3.23 (s, 3H), 2.30 (m, 2H), 1.84 (d, *J* = 5.7 Hz, 2H), 1.76 (d, *J* = 7.6 Hz, 2H), 1.43 (s, 9H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 154.9, 142.6, 135.0, 129.9, 129.7, 126.2, 125.5, 101.7, 80.4, 67.0, 34.9, 32.2, 28.5, 26.3, 22.1;

HRMS (ESI) for ([M+Na]⁺: C₂₀H₂₉NO₄Na⁺), calculated: 370.1994, found: 370.1991.

7a : 🗼

Coloress oil; pure product; 3.40 g (77%); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 4.04-3.85 (m, 1H), 2.41-2.13 (m, 2H), 1.96 (d, *J* = 2.4 Hz, 1H), 1.23 (d, *J* = 6.0 Hz, 3H), 0.89 (s, 9H), 0.07 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 82.1, 69.8, 67.7, 29.5, 26.0, 23.4, 18.3, -4.6; Product was not detected by ESI, APCI and APPI. 7b:

Orange oil; solvent for chromatography: hexane/ethyl acetate (95:5); 555 mg (78%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 5.38 (m, 2H), 4.11 (m, 2H), 3.77 (dt, J = 12.1, 6.0 Hz, 1H), 2.28 (m, 2H), 2.20-2.09 (m, 1H), 2.05 (dd, J = 13.1, 7.0 Hz, 1H), 2.01-1.90 (m, 2H), 1.67-1.52 (m, 2H), 1.32-1.20 (m, 9H), 1.09 (d, J = 6.0 Hz, 3H), 0.87 (s, 9H), 0.03 (s, 6H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 174.0, 132.6, 127.1, 69.0, 60.3, 43.2, 34.5, 34.2, 32.7, 29.4, 29.1, 28.9, 26.0, 25.1, 23.5, 14.4, -4.6;

HRMS (ESI) for $([M+H]^+: C_{20}H_{40}O_3SiNa^+)$, calculated: 379.2644, found: 379.2635.

7b':

Yellow oil; solvent for chromatography: hexane/ethyl acetate (5:5); 208 mg (86%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 5.43 (m, 2H), 4.09 (m, 2H), 3.82-3.68 (m, 1H), 2.26 (m, 3H), 2.10 (m, 2H), 2.00-1.95 (m, 1H), 1.62-1.56 (m, 2H), 1.29-1.19 (m, 9H), 1.15 (d, *J* = 6.1 Hz, 3H).;

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 174.4, 134.4, 126.1, 67.3, 60.3, 42.6, 34.1, 32.6, 29.3, 29.0, 28.8, 25.0, 22.7, 14.3;

HRMS (ESI) for $([M+Na]^+: C_{14}H_{26}O_3Na^+)$, calculated: 265.1780, found: 265.1785.

7c: ∬

Yellow oil; pure product; 108 mg (96%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) δ 5.44 (m, 2H), 3.79 (h, *J* = 6.1 Hz, 1H), 2.32 (dd, *J* = 9.1, 5.6 Hz, 3H), 2.20-2.07 (m, 2H), 2.00 (m, 1H), 1.62 (h, J = 7.0 Hz, 2H), 1.31 (dd, *J* = 21.1, 13.2 Hz, 6H), 1.22-1.13 (m, 3H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 179.3, 134.5, 126.0, 67.6, 42.5, 34.1, 32.6, 29.2, 28.9, 28.8, 24.7, 22.6;

HRMS (ESI) for ([M-H]⁻: C₁₂H₂₁O₃⁻), calculated: 213.1491, found: 213.1493.



Colorless oil; solvent for chromatography: hexane/ethyl acetate (9:1); 69 mg (70%);

¹H NMR (400 MHz, CDCl₃) δ (ppm) 5.40-5.21 (m, 2H), 5.21-5.00 (m, 1H), 2.44-2.22 (m, 4H), 2.14 (m, 2H), 2.07-1.89 (m, 1H), 1.80 (m, 1H), 1.56-1.42 (m, 4H), 1.24 (d, J = 6.4 Hz, 3H), 1.14 (m, 2H);

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 173.6, 133.6, 127.2, 68.7, 41.1, 33.1, 30.4, 25.1, 24.8, 24.3, 23.3, 20.7;

HRMS (ESI) for ([M-H]⁻: C₁₂H₁₉O₂⁻), calculated: 195.1385, found: 195.1385.

10. References.

- ¹ Ren, P.; Vechorkin, O.; Csok, Z.; Salihu, I.; Scopelliti, R.; Hu, X. L. Dalton Trans. **2011**, 40, 8906-8911.
- ² Gómez, G., Rivera, H.; García, I.; Estévez, L.; Fall, Y. *Tetrahedron Lett.* **2005**, *46*, 5819-5822.

³ Zhou, J.; Fu, G. C. J. Am. Chem. Soc. 2003, 125, 12527-12530.

⁴ Smith, S. M.; Takacs, J. M. J. Am. Chem. Soc. 2010, 132, 1740-1741.

⁵ Artis, D. R.; Cho, I.-S.; Jaime-Figueroa, S.; Muchowski, J. M. J. Org. Chem. **1994**, *59*, 2456-2466.

⁶ Fernández-Salas, J. A.; Maestro, M. C.; Rodríguez-Fernández, M. M.; García-Ruano, J. L.; Alonso, I. Org. Lett. **2013**, 15, 1658-1661.

⁷ Pletnev, A. A.; Larock, R. C. J. Org. Chem. 2002, 67, 9428-9438.

⁸ Zhou, X.-T.; Carter, R. G. Angew. Chem. Int. Ed. 2006, 45, 1787-1790.

⁹ Kubota, H.; Kakefuda, A.; Watanabe, T.; Ishii, N.; Wada, K.; Masuda, N.; Sakamoto, S.; Tsukamoto, S.-I. J. Med. Chem. 2003, 46, 4728-4740.

¹⁰ Clarisse, D.; Pelotier, B.; Piva, O.; Fache, F. Chem. Commun. 2012, 48, 157-159.

¹¹ Corley, E. G.; Conrad, K.; Murry, J. A.; Savarin, C.; Holko, J.; Boice, G. J. Org. Chem. 2004, 69, 5120-5123.

¹² Dai, Y.; Wu, F.; Zang, Z.; You, H.; Gong, H. Chem. Eur. J. 2012, 18, 808-812.

¹³ Owen, L. N.; Robins, P. A. J. Chem. Soc. **1949**, 326-333.

¹⁴ Larouche-Gauthier, R.; Elford, T. G.; Aggarwal, V. K. J. Am. Chem. Soc. 2011, 133, 16794-16797.

¹⁵ Ruggli, P.; Girod, E. *Helvetica Chimica Acta* **1944**, *27*, 1464-1478.

¹⁶ Ornstein, P. L.; Bleisch, T. J.; Arnold, M. B.; Wright, R. A.; Johnson, B. G.; Schoepp, D. D. J. Med. Chem. **1998**, *41*, 346-357.

¹⁷ González-Bobes, F.; Fu, G. C. J. Am. Chem. Soc. 2006, 128, 5360-5361.

¹⁸ Hofmann, T.; Altmann, K.-H. Synlett. 2008, 10, 1500-1504.

¹⁹ Yokoyama, A.; Maruyama, T.; Tagami, K.; Masu, H.; Katagiri, K.; Azumaya, I.; Yokozawa, T. *Org. Lett.* **2008**, *10*, 3207-3210.

²⁰ Vollhardt, K. P. C.; Schore, N. E. In *Organic chemistry : structure and function*; Freeman, W. H. and Company: New York, 5th ed., **2007**; Chapter 11.

²¹ Brown, H. C.; Subrahmanya, C.; Hamaoka, T.; Ravindran, N.; Bowman, D. H.; Misumi, S.; Unni, M. K.; Somayaji, V.; Bhat, N. G. *J. Org. Chem.* **1989**, *54*, 6068-6075.

²² Brown, H. C.; Bhat, N. G.; Rajagopalan, S. Organometallics 1986, 5, 816-818.

²³ (a) Fang, G. Y.; Aggarwal, V. K. Angew. Chem. Int. Ed. **2007**, 46, 359-362. (b) Brown, H. C.; Kulkarni, S. U. J. Organomet. Chem. **1979**, 168, 281-293.

²⁴ Okuma, K.; Himbayashi, S.-i.; Ono, M.; Shioji, K.; Matsuyama, H.; Bestmann, H. J. *Tetrahedron* **1998**, *54*, 4243-4250.

²⁵ Zhou, J. S.; Fu, G. C. J. Am. Chem. Soc. 2004, 126, 1340-1341.

²⁶ Molander, G. A.; Argintaru, O. A. Org. Lett. **2014**, *16*, 1904-1907.



¹H and ¹³C NMR spectra of (*E*)-9-(hex-1-en-1-yl)-9-borabicyclo[3.3.1]nonane



¹H and ¹³C NMR spectra of (*E*)-9-(oct-1-en-1-yl)-9-borabicyclo[3.3.1]nonane



¹H and ¹³C NMR spectra of (*E*)-dec-5-en-1-ylbenzene



¹H and ¹³C NMR spectra of (*E*)-2-(undec-4-en-1-yl)isoindoline-1,3-dione



¹H and ¹³C NMR spectra of (*E*)-1-(1-(non-4-en-1-yl)-1*H*-pyrrol-2-yl)ethan-1-one



¹H and ¹³C NMR spectra of methyl (*E*)-1-(undec-4-en-1-yl)-1*H*-indole-3-carboxylate



¹H and ¹³C NMR spectra of (*E*)-2-(non-4-en-1-yl)furan



¹H and ¹³C NMR spectra of *tert*-butyl (*E*)-4-(non-2-en-1-yl)piperidine-1-carboxylate



¹H and ¹³C NMR spectra of (*E*)-2,2-diphenyldodec-7-enenitrile



¹H and ¹³C NMR spectra of (*E*)-dodec-7-enenitrile



¹H and ¹³C NMR spectra of (*E*)-non-4-en-1-yl(phenyl)sulfane



¹H and ¹³C NMR spectra of (*E*)-2-(hept-2-en-1-yl)-2,3-dihydrobenzo[*b*][1,4]dioxine



¹H and ¹³C NMR spectra of (*E*)-2-(oct-3-en-1-yl)-1,3-dioxane



¹H and ¹³C NMR spectra of (*E*)-(dec-5-en-1-yloxy)benzene



¹H and ¹³C NMR spectra of (*E*)-*N*,*N*-diethyldodec-7-enamide



¹H and ¹³C NMR spectra of (*E*)-9-(non-4-en-1-yl)-9*H*-carbazole



¹H and ¹³C NMR spectra of (*E*)-(oct-3-en-1-yloxy)benzene



¹H and ¹³C NMR spectra of (*E*)-2-methyl-2-(non-4-en-1-yl)-1,3-dioxolane



¹H and ¹³C NMR spectra of (*E*)-hex-1-en-1-ylcyclohexane



¹H and ¹³C NMR spectra of (*E*)-4-(hex-1-en-1-yl)-2-phenyltetrahydro-2*H*-pyran



¹H and ¹³C NMR spectra of (*E*)-4-(hex-1-en-1-yl)tetrahydro-2*H*-pyran



¹H and ¹³C NMR spectra of (*E*)-hex-1-en-1-ylcyclopentane



¹H and ¹³C NMR spectra of (*E*)-2-(hex-1-en-1-yl)-2,3-dihydro-1*H*-indene



¹H and ¹³C NMR spectra of ethyl (*E*)- 3-(hex-1-en-1-yl)cyclohexane-1-carboxylate



¹H and ¹³C NMR spectra of *tert*-butyl (*E*)-3-(hex-1-en-1-yl)pyrrolidine-1-carboxylate



¹H and ¹³C NMR spectra of *tert*-butyl (*E*)-3-(hex-1-en-1-yl)azetidine-1-carboxylate



¹H and ¹³C NMR spectra of (*E*)-(3-methylnon-4-en-1-yl)benzene



¹H and ¹³C NMR spectra of (*E*)-hex-1-ene-1,6-diyldibenzene



¹H and ¹³C NMR spectra of (*E*)-9-(furan-2-yl)non-5-enenitrile



¹H and ¹³C NMR spectra of (*E*)-(8-chlorooct-4-en-1-yl)(phenyl)sulfane



 $^{1}\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of *tert*-butyl (*E*)-4-(4-(trifluoromethyl)styryl)piperidine-1-carboxylate



¹H and ¹³C NMR spectra of (*E*)-1-(1-(5-(triisopropylsilyl)pent-4-en-1-yl)-1*H*-pyrrol-2-yl)ethan-1-one



¹H and ¹³C NMR spectra of (*E*)-*tert*-butyl((8-(4-fluorophenyl)oct-7-en-1-yl)oxy) dimethylsilane



¹H and ¹³C NMR spectra of (E)-(6-phenoxyhex-3-en-1-yl)benzene

TD5034.1.fid 5.53 5.48 5.45 -4.57 2.90 2.88 2.86 -1100 7.11 6.99 6.99 6.78 6.78 -1000 -900 SrS 5 -800 515 -700 -600 S O O -500 6i 400 -300 -200 -100 -0 0.96 191 0.71 1.11 - 22 --1.76-2.16 8.71-6.18 2.06 --100 4.5 4.0 f1 (ppm) 5 7.5 7.0 6.5 5.5 3.5 3.0 2.5 2.0 1.0 0.5 0.0 8.0 6.0 5.0 1.5 TD5034.4.fid 34.77 30.88 30.21 29.60 25.62 77.48 77.16 76.84 ---67.08 ---62.41 -1300 -1200 1100 -1000 -900 -800 -700 -600 -500 -400 -300 -200 -100 -0 --100 50 150 140 130 120 110 100 90 80 f1 (ppm) 70 60 50 40 30 20 10 Ó

 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of (E)-2-((7-(thiophen-2-yl)hept-4-en-1-yl)oxy)tetrahydro-2H-pyran



¹H and ¹³C NMR spectra of (*E*)-*N*,*N*-diethyl-8-(4-methoxyphenyl)oct-7-enamide



¹H and ¹³C NMR spectra of *tert*-butyl (E)-(4-(4-(1,3-dioxan-2-yl)but-1-en-1-yl)phenyl)(methyl)carbamate



¹H and ¹³C NMR spectra of *tert*-butyldimethyl(pent-4-yn-2-yloxy)silane



¹H and ¹³C NMR spectra of ethyl (*E*)-11-((*tert*-butyldimethylsilyl)oxy)dodec-8-enoate



¹H and ¹³C NMR spectra of ethyl (E)-11-hydroxydodec-8-enoate



¹H and ¹³C NMR spectra of (*E*)-11-hydroxydodec-8-enoic acid

1H and ^{13}C NMR spectra of (±)-Recifeiolide

