

## Supplementary information

### Functionalisation of Homopropargyl Boronic Esters via Hydrozirconation followed by Pd-catalysed Cross-Coupling Reaction

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## General information

All air and moisture sensitive reactions were conducted in dried glassware (>100 °C) under a nitrogen atmosphere if not stated otherwise. Dried solvents were distilled prior to use: THF was distilled from sodium/benzophenone and *N,N*-diisopropylamine was dried over CaH<sub>2</sub> before distillation. All other anhydrous solvents were purchased from *Thermo Scientific* and stored under nitrogen atmosphere over molecular sieves. Pentane and ethyl acetate were distilled prior to use. Column chromatography was performed using the *Büchi Pure C-815 Flash* system with *Teledyne Isco RediSep Rf Silver Silica* normal-phase columns (30-70 µm) with mixtures of cyclohexane and ethyl acetate as eluent. Reverse-phase chromatography was performed using the *Büchi Reveleris Prep* system with *Büchi FlashPure Select C18* 30 µm spherical cartridges with mixtures of water and acetonitrile as eluent. For analytical TLC, the precoated silica-gel plates *Polygram Sil G/UV<sub>254</sub>* by *Macherey-Nagel* were used. Detection was accomplished with UV light ( $\lambda = 254$  nm) and cerium(IV)/ammonium molybdate solution. <sup>1</sup>H-, <sup>13</sup>C- and <sup>19</sup>F-NMR spectra were measured on a *Bruker Advance II* 400 MHz spectrometer (<sup>1</sup>H: 400 MHz, <sup>13</sup>C: 100 MHz, <sup>19</sup>F: 400 MHz), a *Bruker Advance I* 500 MHz spectrometer (<sup>1</sup>H: 500 MHz, <sup>13</sup>C: 125 MHz) or a *Bruker Advance Neo* 500 MHz spectrometer (<sup>1</sup>H: 500 MHz, <sup>13</sup>C: 125 MHz). Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) relative to the internal solvent signal (7.26 ppm for CDCl<sub>3</sub> as NMR solvent) for <sup>1</sup>H- and <sup>13</sup>C-NMR and to a tertiary reference (-61.62 ppm for benzotrifluoride or -75.39 ppm for trifluoroacetic acid) for <sup>19</sup>F-NMR. The peaks were assigned using <sup>1</sup>H,<sup>1</sup>H-COSY, <sup>1</sup>H,<sup>13</sup>C-HSQC and <sup>1</sup>H,<sup>13</sup>C-HMBC spectra. NMR spectra were evaluated using ACD Labs NMR Processor Version 12.01 or *Bruker Top Spin* Version 4.3.0. Mass spectra were recorded with a *Finnigan MAT95* spectrometer (quadrupol) using the CI technique or an *Orbitrap Q* exactive mass spectrometer, equipped with a heated ESI source and a quadrupole-orbitrap coupled mass detector and an *Ultimate3000* HPLC (Thermo Finnigan, San Jose, CA). The MS detection was carried out at a spray voltage of 3.8 kV in positive ionisation mode, a nitrogen sheath gas pressure of 4.0·10<sup>-5</sup> Pa, an auxiliary gas pressure of 1.0·10<sup>-5</sup> Pa and a capillary temperature of 300 °C. All samples were injected by autosampler with an injection volume of 15 µL. A *RP Nucleoshell Phenyle-hexyle*® (50-2, 3.0µm) column (Macherey-Nagel GmbH, Düren, Germany) was used as stationary phase. The solvent system consisted of formic acid 0.1% (A) and acetonitrile with formic acid 0.1% (B). HPLC method: flow rate 600 µL/min. The percentage of B started at an initial of 1%, was kept at 1% for 1.5 min, then rapidly increased to 100 % during 4.0 min, then kept at 100% until 1.5 min and flushed back to the initial 1 %. Xcalibur software was used for data acquisition and plotting. Optical rotations were measured with a *Krüß P8000-T* polarimeter in a thermostat-controlled cuvette (20.0 ± 0.1 °C) using a sodium vapour lamp ( $\lambda = 589$  nm) as radiation source.  $[\alpha]_D^{20}$  values are given in 10<sup>-1</sup> deg·cm<sup>2</sup>·g<sup>-1</sup> and c is given in g·cm<sup>-3</sup>.

## General procedures

### GP-1: Matteson homologation

To a solution of *N,N*-diisopropylamine (1.35 eq.) in anhydrous THF (0.2 ml/mmol) was added *n*-BuLi (1.25 eq., 1.6 M in hexanes) dropwise at a temperature between  $-40\text{ }^{\circ}\text{C}$  and  $-50\text{ }^{\circ}\text{C}$ . The reaction mixture was stirred for 20 min at room temperature. The freshly prepared LDA solution was added slowly at a temperature between  $-40\text{ }^{\circ}\text{C}$  and  $-50\text{ }^{\circ}\text{C}$  to a solution of the boronic ester (1.0 eq.) and anhydrous DCM (3.0 eq.) in anhydrous THF (1.4 ml/mmol).<sup>1</sup> After 10 min of stirring at the same temperature, a solution of  $\text{ZnCl}_2$  (2.0–3.0 eq., flame dried *in vacuo*) in anhydrous THF (0.6 ml/mmol  $\text{ZnCl}_2$ ) was added and the reaction was stirred for 2 h at room temperature before adding the nucleophile solution according to the respective variant.

After completion, saturated  $\text{NH}_4\text{Cl}$  solution was added to the reaction mixture. The biphasic mixture was stirred for 5 min before separating the phases. The aqueous phase was extracted twice with pentane. The combined organic phases were dried over  $\text{Na}_2\text{SO}_4$  and filtered. The solvent was removed under reduced pressure. The crude product was purified by column chromatography.

#### *Variant A*) Substitution with organozinc reagent

Organozinc reagent was prepared by suspending LiCl (1.1 eq., flame dried *in vacuo*) and zinc dust (2.0 eq.) in anhydrous THF (1.0 M) and adding 1,2-dibromoethane (2 mol-%). The reaction mixture is carefully heated with a heat gun to gentle boiling. After cooling to room temperature, trimethylsilyl chloride (5 mol-%) is added and the reaction mixture is again heated with a heat gun to gentle boiling. After cooling to room temperature, a solution of the alkyl bromide (1.0 eq.) in anhydrous THF (1.0 M) was added dropwise. An exothermic reaction could be observed. After 1 h excess zinc dust was allowed to settle and the supernatant solution was directly used in the next step. The concentration of the organozinc solution was determined by iodometric titration.<sup>1</sup>

The reaction mixture resulting from homologation was cooled to  $0\text{ }^{\circ}\text{C}$  and the freshly prepared organozinc solution was added dropwise. The reaction mixture was stirred at room temperature until completion indicated by  $^1\text{H-NMR}$  analysis.

#### *Variant B*) Substitution with Grignard reagent

The reaction mixture was cooled to  $0\text{ }^{\circ}\text{C}$  and the solution of the Grignard reagent (2.5 eq.) was added slowly. The reaction mixture was stirred at room temperature until completion indicated by  $^1\text{H-NMR}$  analysis.

#### *Variant C*) Substitution with sodium alcoholate

To a suspension of sodium hydride (1.3 eq., 60% in mineral oil) in anhydrous THF (0.5 ml/mmol) and anhydrous DMSO (1.3 ml/mmol) was added the respective alcohol (1.4 eq.). the reaction mixture was stirred for 6 – 7 h at room temperature.

The reaction mixture resulting from homologation was cooled to  $0\text{ }^{\circ}\text{C}$  and the alcoholate solution was added slowly. The reaction mixture was stirred at room temperature until completion indicated by  $^1\text{H-NMR}$  analysis.

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<sup>1</sup> The LDA solution should be added very carefully by direct addition to the reaction mixture. If this is done too fast, the reaction mixture turns from non-transparently dark brown to black. In this case, the reaction mixture should be discarded. If done correctly, the reaction mixture turns yellow to orange. When adding the  $\text{ZnCl}_2$  solution, the intensity decreases slightly and returns after 2 h of stirring at room temperature.

### GP-2: Hydrozirconation and Negishi cross-coupling with benzyl halogenides

Boronic ester (1.0 eq.) and Schwartz reagent (1.0 eq.) were suspended in anhydrous THF (0.2 M) in the absence of light. The reaction mixture was stirred for 10 min until the reaction mixture became transparent indicating complete hydrozirconation. Then, Pd(PPh<sub>3</sub>)<sub>4</sub> (3 mol-%) and benzyl halide (1.0 eq.) were added. The reaction mixture was stirred at 60 °C until completion indicated by <sup>1</sup>H-NMR analysis.

After cooling to room temperature, the solvent was removed under reduced pressure. The residue was dissolved in pentane/ethyl acetate (9:1 v/v) and filtered over Celite. The Celite was rinsed with pentane. The solvent was removed under reduced pressure and the residue was purified by column chromatography.

### GP-3: Hydrozirconation and Negishi cross-coupling with aryl iodides

Boronic ester (1.0 eq.) and Schwartz reagent (1.0 eq.) were suspended in anhydrous THF (0.75 M) in the absence of light. The reaction mixture was stirred for 10 min until the reaction mixture became transparent indicating complete hydrozirconation. Then, Pd(PPh<sub>3</sub>)<sub>4</sub> (6.6 mol-%), aryl iodide (2.0 eq.) and a solution of ZnCl<sub>2</sub> (1.3 eq., flame dried *in vacuo*) in anhydrous THF (1.95 M) were added. The reaction mixture was stirred at room temperature until completion indicated by <sup>1</sup>H-NMR analysis.

After completion, water was added to the reaction mixture and the phases were separated. The aqueous phase was extracted three times with Et<sub>2</sub>O. The combined organic phases were washed with water. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The solvent was removed under reduced pressure and the crude product was purified by column chromatography.

### GP-4: Oxidation of boronic esters to alcohols

At 0 °C H<sub>2</sub>O<sub>2</sub> (5.0 eq., 33% in water) and a solution of NaOH (5.0 eq.) in water (2 ml/mmol) were added to a solution of the boronic ester (1.0 eq.) in THF (2 ml/mmol). The reaction mixture was warmed to room temperature and stirred at the same temperature until completion indicated by TLC. The reaction mixture was then washed with brine and the aqueous phase was extracted three times with Et<sub>2</sub>O. The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The solvent was removed under reduced pressure. To improve separation of the alcohol and DICHD, the crude product was diluted in Et<sub>2</sub>O (5 ml/mmol) and methylboronic acid (1.2 eq.) was added with an excess of MgSO<sub>4</sub> and the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography.

### GP-5: Sonogashira cross-coupling

Boronic ester (1.0 eq.), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.1 eq.), CuI (0.2 eq.) and aryl iodide (5.0 eq.) were dissolved in NEt<sub>3</sub> (0.15 M) under an argon atmosphere. The reaction mixture was stirred at room temperature until completion indicated by <sup>1</sup>H-NMR analysis.

The reaction mixture was diluted with pentane and filtered over Celite. The Celite was rinsed with pentane. The solvent was removed under reduced pressure. The crude product was purified by column chromatography.

## Test reactions and optimisations

### Deprotection of alkyne 2

Since the direct introduction of the unprotected propargyl substituent via Matteson homologation was not successful, the TMS protected substituent was used. To afford the terminal alkyne **3**, **2** had to be deprotected first. Fluoride-containing reagents as TBAF or KF are not compatible to the boronic ester functionality because the fluoride rather binds to the boron rather than the silicon leading to at least partial protodeboration.<sup>2,3</sup> The same could be observed when trying deprotection with TBAF (entry 1).<sup>4</sup> The attack on the boronic ester functionality was indicated by the formation of DICHD during the reaction. So, different deprotection conditions were tested. First, deprotection with potassium carbonate (entry 2)<sup>5</sup> was investigated which showed to be the best method despite the relatively long reaction time because of complete conversion and a high isolated yield (87%). When sodium methylate was used as base, no reaction could be observed (entry 3).<sup>6</sup> The conditions in entry 4<sup>7</sup> offered the shortest reaction time but also a low isolated yield.

**Tab. S1.** Tested conditions for the deprotection of alkyne **2**.

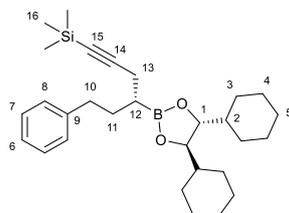
Entry	Reagent	Solvent	Temperature	Time	Commentary
1	TBAF	THF	RT	1 h	Attack on boronic ester
2	K <sub>2</sub> CO <sub>3</sub>	MeOH/Et <sub>2</sub> O 9:1	RT	7 d	Complete conversion
3	NaOMe	MeOH/Et <sub>2</sub> O 9:1	RT	24 h	No reaction
4	AgNO <sub>3</sub> , 2,6-lutidine	THF/H <sub>2</sub> O/EtOH 1:1:1	RT	1 h	Complete conversion, low isolated yield (24%)

## Synthesis of compounds

### **((*R*)-4-((4*R*,5*R*)-4,5-Dicyclohexyl-1,3,2-dioxaborolan-2-yl)-6-phenylhex-1-yn-1-yl)trimethylsilane (**2**)**

According to GP-1, 1.72 ml (1.22 g, 12.1 mmol) *N,N*-diisopropylamine, 6.98 ml (11.2 mmol, 1.6 M) *n*-butyllithium and 1.79 ml anhydrous THF were used for the LDA solution, 2.44 g (17.9 mmol) zinc chloride and 10.7 ml anhydrous THF were used for the ZnCl<sub>2</sub> solution and 3.04 g (8.93 mmol) boronic ester **1**,<sup>8</sup> 1.73 ml (2.28 g, 26.8 mmol) anhydrous DCM and 12.5 ml anhydrous THF were used for the homologation.

The organozinc reagent was prepared according to variant A using 2.10 g (49.5 mmol) LiCl, 5.88 g (90.0 mmol) zinc dust, 78.0 μl (0.90 mmol) 1,2-dibromoethane, 288 μl (2.25 mmol) trimethylsilyl chloride, 45.0 ml anhydrous THF and a solution of 7.35 ml (45.0 mmol) (3-bromoprop-1-yn-1-yl)trimethylsilane in 45.0 ml anhydrous THF. The reaction mixture was worked up after 15 h. After column chromatography (SiO<sub>2</sub>, CyH/EE 0-3%), the product **5** (3.65 g, 7.86 mmol, 88%) was obtained as a colourless oil. R<sub>f</sub> (**2**) = 0.34 (pentane/EE 97:3). [α]<sub>D</sub><sup>20</sup> = +49.4 (c = 1.0, CHCl<sub>3</sub>).



**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.30–7.26 (m, 2 H, 7-H), 7.21–7.16 (m, 3 H, 6-H, 8-H), 3.89–3.86 (m, 2 H, 1-H), 2.66 (m, 2 H, 10-H), 2.46–2.33 (m, 2 H, 13-H), 1.88–1.61 (m, 12 H, 3-Ha, 3-Hb, 4-Ha, 4-Hb, 5-Ha, 11-H), 1.37–0.97 (m, 13 H, 2-H, 3-Hc, 3-Hd, 4-Hc, 4-Hd, 5-Hb, 12-H), 0.14 (s, 9 H, 16-H) ppm.

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): δ = 142.8 (C-9), 128.4 (C-8), 128.2 (C-7), 125.6 (C-6), 107.2 (C-14), 84.7 (C-1), 83.5 (C-15), 43.0 (C-2), 34.9 (C-10), 32.3 (C-11), 28.3 (C-3a), 27.4 (C-3b), 26.5 (C-5), 26.0 (C-4a), 25.9 (C-4b), 21.1 (C-13), 0.2 (C-16) ppm.

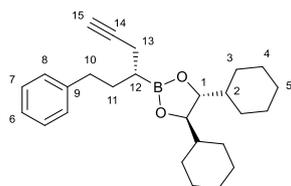
The signal of C-12 could not be detected.

**HRMS** (CI) *m/z* calcd for C<sub>29</sub>H<sub>45</sub>BO<sub>2</sub>Si [M]<sup>+</sup>: 464.3282, found: 464.3312.

### **(4*R*,5*R*)-4,5-Dicyclohexyl-2-((*R*)-1-phenylhex-5-yn-3-yl)-1,3,2-dioxaborolane (**3**)**

To a solution of 2.58 g (5.55 mmol, 1.0 eq.) boronic ester **2** in 76.9 ml methanol/diethyl ether (9:1 v/v, 0.07 M) was added 1.53 g (11.1 mmol, 2.0 eq.) K<sub>2</sub>CO<sub>3</sub>. The reaction mixture was stirred at room temperature for 7 d.

To the reaction mixture, saturated NH<sub>4</sub>Cl solution and diethyl ether were added and the phases were separated. The aqueous phase was extracted twice with diethyl ether. The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO<sub>2</sub>, CyH/EE 0-5%). The product **6** (1.89 g, 4.81 mmol, 87%) was obtained as colourless oil. R<sub>f</sub> (**3**) = 0.30 (pentane/EE 97:3). [α]<sub>D</sub><sup>20</sup> = +49.4 (c = 1.0, CHCl<sub>3</sub>).



**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.29–7.24 (m, 2 H, 7-H), 7.23–7.16 (m, 3 H, 6-H, 8-H), 3.90–3.87 (m, 2 H, 1-H), 2.72–2.60 (m, 2 H, 10-H), 2.41–2.29 (m, 2 H, 13-H), 1.93 (t, *J* = 2.6 Hz, 1 H, 15-H), 1.94–1.66 (m, 12 H, 3-Ha, 3-Hb, 4-Ha, 4-Hb, 5-Ha, 11-H), 1.42–1.00 (m, 13 H, 2-H, 3-Hc, 3-Hd, 4-Hc, 4-Hd, 5-Hb, 12-H) ppm.

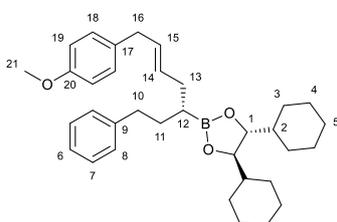
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): δ = 142.7 (C-9), 128.4 (C-8), 128.2 (C-7), 125.6 (C-6), 84.3 (C-14), 85.5 (C-1), 68.6 (C-15), 43.0 (C-2), 35.0 (C-10), 32.4 (C-11), 28.4, 27.5, 26.5, 25.9, 19.8 (C-13) ppm.

The signal of C-12 could not be detected.

**HRMS** (CI) *m/z* calcd for C<sub>26</sub>H<sub>38</sub>BO<sub>2</sub> [M+H]<sup>+</sup>: 393.2965, found: 393.2974.

#### **(4*R*,5*R*)-4,5-dicyclohexyl-2-((*R*,*E*)-7-(4-methoxyphenyl)-1-phenylhept-5-en-3-yl)-1,3,2-dioxaborolane (5h)**

According to GP-2, 113 mg (288 μmol) boronic ester **3**, 82.0 mg (316 μmol, 1.1 eq) Schwartz reagent and 1.44 ml anhydrous THF were used for the hydrozirconation. 10.0 mg (8.63 μmol) Pd(PPh<sub>3</sub>)<sub>4</sub>, 39.2 μl (45.1 mg, 288 μmol) 4-methoxybenzyl chloride and additional 0.58 ml anhydrous THF were used for the Negishi coupling. The reaction was worked up after 24 h. After column chromatography (SiO<sub>2</sub>, CyH/EE 0-5%), the product **5h** (131 mg, 242 μmol, 84%) was obtained as a colourless oil. *R*<sub>f</sub> (**5h**) = 0.32 (pentane/EE 95:5). [α]<sub>D</sub><sup>20</sup> = +17.9 (c = 1.0, CHCl<sub>3</sub>).



**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.28–7.24 (m, 2 H, 7-H), 7.18–7.14 (m, 3 H, 6-H, 8-H), 7.09–7.07 (m, 2 H, 18-H), 6.82–6.80 (m, 2 H, 19-H), 5.59–5.45 (m, 2 H, 14-H, 15-H), 3.25 (d, *J* = 6.0 Hz, 2 H, 16-H), 2.67–2.55 (m, 2 H, 10-H), 2.26–2.12 (m, 2 H, 13-H), 1.82 – 1.59 (m, 12 H, 3-Ha, 3-Hb, 4-Ha, 4-Hb, 5-Ha, 11-H), 1.33 – 0.97 (m, 13 H, 2 H, 3-Hc, 3-Hd, 4-Hc, 4-Hd, 12-H) ppm.

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): δ = 157.8 (C-20), 143.1 (C-9), 133.1 (C-15), 131.0 (C-18), 129.9 (C-14), 129.4 (C-17), 128.4 (C-8), 128.2 (C-7), 125.5 (C-6), 113.7 (C-19), 83.4 (C-1), 55.2 (C-21), 43.1 (C-2), 38.2 (C-16), 35.5 (C-10), 34.0 (C-13), 33.0 (C-11), 28.5 (C-3a), 27.6 (C-3b), 26.5 (C-5), 26.0 (C-4a), 25.9 (C-4b) ppm.

The signal of C-12 could not be detected.

**HRMS** (ESI) *m/z* calcd for C<sub>34</sub>H<sub>48</sub>BO<sub>3</sub> [M+H]<sup>+</sup>: 515.3691, found: 515.3672.

### (*R,E*)-1,7-Diphenylhept-5-en-3-ol (**6a**)

According to GP-2, 104 mg (265  $\mu\text{mol}$ ) boronic ester **3**, 75.0 mg (265  $\mu\text{mol}$ ) Schwartz reagent and 1.32 ml anhydrous THF were used for the hydrozirconation. 9.2 mg  $\text{Pd}(\text{PPh}_3)_4$  (7.94  $\mu\text{mol}$ ), 31.5  $\mu\text{l}$  (45.2 mg, 261  $\mu\text{mol}$ ) benzyl bromide and additional 0.53 ml anhydrous THF were used for the Negishi coupling. The reaction was worked up after 21.5 h. After column chromatography ( $\text{SiO}_2$ , CyH/EE 0-3%), the product **5a** (120 mg, 220  $\mu\text{mol}$ , 83%) was obtained as a colourless oil.

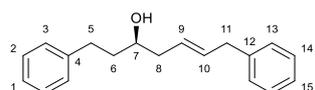
110 mg (226  $\mu\text{mol}$ ) boronic ester **5a** was subjected to oxidation according to GP-5 using 452  $\mu\text{l}$  THF, 103  $\mu\text{l}$  (38.4 mg, 1.13 mmol, 33 %wt) aqueous  $\text{H}_2\text{O}_2$  solution and a solution of 45.2 mg (1.13 mmol) NaOH in 452  $\mu\text{l}$  water. The reaction was worked up after 1 h. To improve chromatographic separation, 16.2 mg (271  $\mu\text{mol}$ ) methylboronic acid and 1.13 ml diethyl ether were used. After column chromatography ( $\text{SiO}_2$ , CyH/EE 0-20%; C18- $\text{SiO}_2$ ,  $\text{H}_2\text{O} \rightarrow \text{MeCN}$ ), the product **6a** (47 mg, 177  $\mu\text{mol}$ , 78%) was obtained as a colourless oil.

#### 1 mmol scale:

According to GP-2, 505 mg (1.29 mmol) boronic ester **3**, 365 mg (1.42 mmol) Schwartz reagent and 6.43 ml anhydrous THF were used for the hydrozirconation. 44.7 mg (39.0  $\mu\text{mol}$ )  $\text{Pd}(\text{PPh}_3)_4$ , 153  $\mu\text{l}$  (220 mg, 1.29 mmol) benzyl bromide and additional 2.57 ml anhydrous THF were used for the Negishi coupling. The reaction was worked up after 16 h. After column chromatography ( $\text{SiO}_2$ , CyH/EE 0-3%), the product **5a** (587 mg, 1.10 mmol, 86%) was obtained as a colourless oil.

549 mg (1.13 mmol) boronic ester **5a** was subjected to oxidation according to GP-4 using 2.26 ml THF, 516  $\mu\text{l}$  (193 mg, 5.66 mmol, 33 %wt) aqueous  $\text{H}_2\text{O}_2$  solution and a solution of 226 mg (5.66 mmol) NaOH in 2.26 ml water. The reaction was worked up after 1 h. To improve chromatographic separation, 81.0 mg (1.36 mmol) methylboronic acid and 5.66 ml diethyl ether were used. After column chromatography ( $\text{SiO}_2$ , CyH/EE 0-20%; C18- $\text{SiO}_2$ ,  $\text{H}_2\text{O} \rightarrow \text{MeCN}$ ), the product **6a** (248 mg, 931  $\mu\text{mol}$ , 82%) was obtained as a colourless oil.

$R_f$  (**6a**) = 0.32 (pentane/EE 8:2).  $[\alpha]_D^{20} = +10.1$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).



$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.30 - 7.24$  (m, 4 H, 2-H, 14-H), 7.19 – 7.15 (m, 6 H, 1-H, 3-H, 13-H, 15-H), 5.74 – 5.67 (m, 1 H, 10-H), 5.54 – 5.47 (m, 1 H, 9-H), 3.67 – 3.61 (m, 1 H, 7-H), 3.36 (d,  $^3J_{11,10} = 6.7$  Hz, 2 H, 11-H), 2.83 – 2.76 (m, 1 H, 5-Ha), 2.71 – 2.63 (m, 1 H, 5-Hb), 2.32 – 2.26 (m, 1 H, 8-Ha), 2.19 – 2.12 (m, 1 H, 8-Hb), 1.80 – 1.74 (m, 2 H, 6-H), 1.63 (br s, 1 H, OH) ppm.

$^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 142.1$  (C-4), 140.4 (C-12), 133.1 (C-10), 128.4 (C-3), 128.4 (C-2, C-13), 128.4 (C-14), 127.2 (C-9), 126.0 (C-15), 125.8 (C-1), 70.2 (C-7), 40.7 (C-8), 39.1 (C-11), 38.4 (C-6), 32.0 (C-5) ppm.

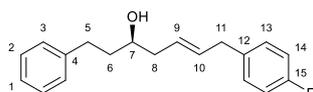
HRMS (CI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{21} [\text{M}-\text{OH}]^+$ : 249.1643, found: 249.1685.

### (*R,E*)-7-(4-Fluorophenyl)-1-phenylhept-5-en-3-ol (**6b**)

According to GP-2, 114 mg (290  $\mu\text{mol}$ ) boronic ester **3**, 82.0 mg (318  $\mu\text{mol}$ ) Schwartz reagent and 1.45 ml anhydrous THF were used for the hydrozirconation. 10.0 mg (8.69  $\mu\text{mol}$ )  $\text{Pd}(\text{PPh}_3)_4$ , 35.8  $\mu\text{l}$  (54.7 mg, 290  $\mu\text{mol}$ ) 4-fluorobenzyl bromide and additional 0.58 ml

anhydrous THF were used for the Negishi coupling. The reaction was worked up after 16 h. After column chromatography (SiO<sub>2</sub>, CyH/EE 0-4%), the product **5b** (131 mg, 229 μmol, 79%) was obtained as a colourless oil.

113 mg (224 μmol) boronic ester **5b** was subjected to oxidation according to GP-4 using 449 μl THF, 102 μl (38.2 mg, 1.12 mmol, 33 %wt) aqueous H<sub>2</sub>O<sub>2</sub> solution and a solution of 44.9 mg (1.12 mmol) NaOH in 449 μl water. The reaction was worked up after 1 h. To improve chromatographic separation, 16.1 mg (269 μmol) methylboronic acid and 1.12 ml diethyl ether were used. After column chromatography (SiO<sub>2</sub>, CyH/EE 0-20%; C18-SiO<sub>2</sub>, H<sub>2</sub>O → MeCN), the product **6b** (50.1 mg, 176 μmol, 78%) was obtained as a colourless oil. R<sub>f</sub> (**6b**) = 0.35 (pentane/EE 8:2). [α]<sub>D</sub><sup>20</sup> = +7.7 (c = 1.0, CHCl<sub>3</sub>).



**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.31–7.27 (m, 2 H, 2-H), 7.20–7.17 (m, 3 H, 1-H, 3-H), 7.14–7.10 (m, 2 H, 13-H), 6.99–6.95 (m, 2 H, 14-H), 5.72–5.65 (m, 1 H, 9-H), 5.54–5.46 (m, 1 H, 10-H), 3.69–3.62 (m, 1 H, 7-H), 3.33 (d, *J* = 6.6 Hz, 2 H, 11-H), 2.84–2.77 (m, 1 H, 5-Ha), 2.72–2.64 (m, 1 H, 5-Hb), 2.33–2.27 (m, 1 H, 8-Ha), 2.20–2.13 (m, 1 H, 8-Hb), 1.81–1.75 (m, 2 H, 6-H), 1.55 (s, 1 H, OH) ppm.

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): δ = 161.4 (d, *J* = 244.3 Hz, C-15), 142.0 (C-4), 136.0 (d, *J* = 2.9 Hz, C-12), 132.9 (C-9), 129.8 (d, *J* = 8.1 Hz, C-13), 128.4 (C-3), 128.4 (C-2), 127.4 (C-10), 125.8 (C-1), 115.2 (d, *J* = 21.3 Hz, C-14), 70.2 (C-7), 40.7 (C-6), 38.4 (C-8), 38.2 (C-11), 32.0 (C-5).

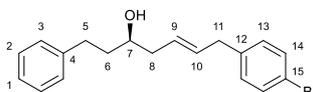
**<sup>19</sup>F-NMR** (400 MHz, CDCl<sub>3</sub>): δ = –117.4 ppm.

**HRMS** (CI) *m/z* calcd for C<sub>19</sub>H<sub>19</sub>FO [M–2H]<sup>+</sup>: 282.1420, found: 282.1384.

### **(*R,E*)-7-(4-Bromophenyl)-1-phenylhept-5-en-3-ol (6c)**

According to GP-2, 112 mg (285 μmol) boronic ester **3**, 73.5 mg (285 μmol) Schwartz reagent and 1.42 ml anhydrous THF were used for the hydrozirconation. 9.9 mg (8.55 μmol) Pd(PPh<sub>3</sub>)<sub>4</sub>, 71.2 mg (285 μmol) 1-bromo-4-(bromomethyl)benzene and additional 0.57 ml anhydrous THF were used for the Negishi coupling. The reaction was worked up after 17 h. After column chromatography (SiO<sub>2</sub>, CyH/EE 0-4%), the product **5c** (125 mg, 197 μmol, 69%) was obtained as a colourless oil.

105 mg (165 μmol) boronic ester **5c** subjected to oxidation according to GP-4 using 331 μl THF 75.0 μl (827 μmol, 33%wt) aqueous H<sub>2</sub>O<sub>2</sub> solution and a solution of 33.1 mg (827 μmol) NaOH in 331 μl water. The reaction was worked up after 1 h. To improve chromatographic separation, 11.9 mg (198 μmol) methylboronic acid and 0.93 ml diethyl ether were used. After column chromatography (SiO<sub>2</sub>, CyH/EE 0-20%; C18-SiO<sub>2</sub>, H<sub>2</sub>O → MeCN), the product **6c** (54.3 mg, 157 μmol, 95%) was obtained as a colourless oil. R<sub>f</sub> (**6c**) = 0.34 (pentane/EE 8:2). [α]<sub>D</sub><sup>20</sup> = +7.2 (c = 1.0, CHCl<sub>3</sub>).



**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.41–7.39 (m, 2 H, 13-H), 7.31–7.17 (m, 2 H, 2-H), 7.21–7.18 (m, 2 H, 1-H, 3-H), 7.05–7.03 (m, 2 H, 14-H), 5.70–5.63 (m, 1 H, 10-H), 5.54–5.47 (m,

1 H, 9-H), 3.69–3.62 (m, 1 H, 7-H), 3.31 (d,  $J = 6.5$  Hz, 11-H), 2.83–2.76 (m, 1 H, 5-Ha), 2.71–2.64 (m, 1 H, 5-Hb), 2.32–2.62 (m, 1 H, 8-Ha), 2.20–2.13 (m, 1 H, 8-Hb), 1.84–1.71 (m, 2 H, 6-H), 1.56 (s, 1 H, OH) ppm.

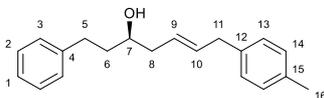
$^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 142.0$  (C-4), 139.4 (C-12), 132.4 (C-10), 131.5 (C-13), 130.2 (C-14), 128.4 (C-2, C-3), 127.8 (C-9), 125.9 (C-1), 119.8 (C-15), 70.2 (C-7), 40.7 (C-8), 38.4 (C-6), 38.4 (C-11), 32.0 (C-5) ppm.

**HRMS** (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{22}^{79}\text{BrO}$   $[\text{M}+\text{H}]^+$ : 345.0849, found: 345.0835.

### **(*R,E*)-1-Phenyl-7-(*p*-tolyl)hept-5-en-3-ol (6d)**

According to GP-2, 111 mg (282  $\mu\text{mol}$ ) boronic ester **3**, 72.7 mg (282  $\mu\text{mol}$ ) Schwartz reagent and 1.41 ml anhydrous THF were used for the hydrozirconation. 9.8 mg  $\text{Pd}(\text{PPh}_3)_4$  (8.46  $\mu\text{mol}$ ), 52.2 mg (282  $\mu\text{mol}$ ) 4-methylbenzyl bromide and additional 0.56 ml anhydrous THF were used for the Negishi coupling. The reaction was worked up after 16 h. After column chromatography ( $\text{SiO}_2$ , CyH/EE 0-3%), the product **5d** (121 mg, 220  $\mu\text{mol}$ , 78%) was obtained as a colourless oil.

104 mg (208  $\mu\text{mol}$ ) boronic ester **5d** was subjected to oxidation according to GP-4 using 416  $\mu\text{l}$  THF, 107  $\mu\text{l}$  (35.3 mg, 1.04 mmol, 33 %wt) aqueous  $\text{H}_2\text{O}_2$  solution and a solution of 41.6 mg (1.04 mmol) NaOH in 416  $\mu\text{l}$  water. The reaction was worked up after 1 h. To improve chromatographic separation, 14.9 mg (249  $\mu\text{mol}$ ) methylboronic acid and 1.04 ml diethyl ether were used. After column chromatography ( $\text{SiO}_2$ , CyH/EE 0-20%; C18- $\text{SiO}_2$ ,  $\text{H}_2\text{O} \rightarrow \text{MeCN}$ ), the product **6d** (39 mg, 137  $\mu\text{mol}$ , 66%) was obtained as a colourless oil.  $R_f$  (**6d**) = 0.36 (pentane/EE 8:2).  $[\alpha]_D^{20} = +7.5$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).



$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.31$ – $7.27$  (m, 2 H, 2-H), 7.21–7.18 (m, 3 H, 1-H, 3-H), 7.12–7.06 (m, 4 H, 13-H, 14-H), 5.75–5.67 (m, 1 H, 10-H), 5.54–5.46 (m, 1 H, 9-H), 3.69–3.62 (m, 1 H, 7-H), 3.34 (d,  $J = 6.7$  Hz, 2 H, 11-H), 2.84–2.77 (m, 1 H, 5-Ha), 2.72–2.65 (m, 1 H, 5-Hb), 2.33 (s, 3 H, 16-H), 2.32–2.27 (m, 1 H, 8-Ha), 2.20–2.12 (m, 1 H, 8-Hb), 1.85–1.72 (m, 2 H, 6-H), 1.63 (br s, 1 H, OH) ppm.

$^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 142.1$  (C-4), 137.3 (C-12), 135.5 (C-15), 133.5 (C-10), 129.1 (C-), 128.4 (C-3), 128.4 (C-), 128.3 (C-2), 126.9 (C-9), 125.8 (C-1), 70.2 (C-7), 40.7 (C-8), 38.7 (C-6), 38.4 (C-11), 32.0 (C-5), 21.0 (C-16) ppm.

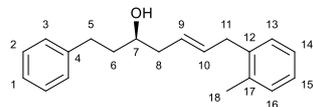
**HRMS** (CI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{23}$   $[\text{M}-\text{OH}]^+$ : 263.1800, found: 263.1843.

### **(*R,E*)-1-Phenyl-7-(*o*-tolyl)hept-5-en-3-ol (6e)**

According to GP-2, 103 mg (261  $\mu\text{mol}$ ) boronic ester **3**, 67.4 mg (261  $\mu\text{mol}$ ) Schwartz reagent and 1.31 ml anhydrous THF were used for the hydrozirconation. 9.1 mg (7.84  $\mu\text{mol}$ )  $\text{Pd}(\text{PPh}_3)_4$ , 35.0  $\mu\text{l}$  (48.3 mg, 261  $\mu\text{mol}$ ) 1-(bromomethyl)-2-methylbenzene and additional 0.52 ml anhydrous THF were used for the Negishi coupling. The reaction was worked up after 15.5 h. After column chromatography ( $\text{SiO}_2$ , CyH/EE 0-3%), the product **5e** (116 mg, 207  $\mu\text{mol}$ , 79%) was obtained as a colourless oil.

90 mg (180  $\mu\text{mol}$ ) boronic ester **5e** was subjected to oxidation according to GP-4 using 361  $\mu\text{l}$  THF, 82.0  $\mu\text{l}$  (902  $\mu\text{mol}$ , 33 %wt) aqueous  $\text{H}_2\text{O}_2$  solution and a solution of 36.1 mg (902  $\mu\text{mol}$ )

NaOH in 361  $\mu$ l water. The reaction was worked up after 1 h. To improve chromatographic separation, 13.0 mg (216  $\mu$ mol) methylboronic acid and 0.90 ml diethyl ether were used. After column chromatography (SiO<sub>2</sub>, CyH/EE 0-20%; C18-SiO<sub>2</sub>, H<sub>2</sub>O  $\rightarrow$  MeCN), the product **6e** (37 mg, 132  $\mu$ mol, 73%) was obtained as a colourless oil.  $R_f$  (**6e**) = 0.36 (pentane/EE 8:2).  $[\alpha]_D^{20} = +11.0$  (c = 1.0, CHCl<sub>3</sub>).



**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.31–7.27 (m, 2 H, 2-H, 7.21–7.13 (m, 7 H, 1-H, 3-H, 13-H, 14-H, 15-H, 16-H), 5.74–5.67 (m, 1 H, 10-H), 5.48–5.40 (m, 1 H, 9-H), 3.67–3.61 (m, 1 H, 7-H), 3.36 (d,  $J$  = 6.4 Hz, 2 H, 11-H), 2.84–2.77 (m, 1 H, 5-Ha), 2.71–2.64 (m, 1 H, 5-Hb), 2.32–2.26 (m, 4 H, 8-Ha, 18-H), 2.20–2.13 (m, 1 H, 8-Hb), 1.81–1.74 (m, 2 H, 6-H), 1.69 (br s, 1 H, OH) ppm.

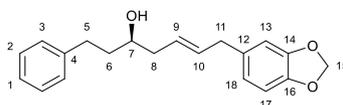
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 142.1 (C-4), 138.5 (C-12), 136.1 (C-17), 132.2 (C-10), 130.1 (C-16), 128.9 (C-13), 128.4 (C-3), 128.3 (C-2), 127.0 (C-9), 126.2 (C-15), 126.0 (C-14), 125.7 (C-1), 70.2 (C-7), 40.7 (C-8), 38.4 (C-6), 36.6 (C-11), 32.0 (C-5), 19.3 (C-18) ppm.

**HRMS** (CI)  $m/z$  calcd for C<sub>20</sub>H<sub>23</sub> [M–OH]<sup>+</sup>: 263.1800, found: 263.1792.

#### **(*R,E*)-7-(Benzo[d][1,3]dioxol-5-yl)-1-phenylhept-5-en-3-ol (6f)**

According to GP-2, 104 mg (265  $\mu$ mol) boronic ester **3**, 68.2 mg (271  $\mu$ mol) Schwartz reagent and 1.32 ml anhydrous THF were used for the hydrozirconation. 9.2 mg (7.94  $\mu$ mol) Pd(PPh<sub>3</sub>)<sub>4</sub>, 34.2  $\mu$ l (265  $\mu$ mol) 5-(chloromethyl)benzo[d][1,3]dioxole and additional 0.53 ml anhydrous THF were used for the Negishi coupling. The reaction was worked up after 16 h. After column chromatography (SiO<sub>2</sub>, CyH/EE 0-4%), the product **5f** (125 mg, 203  $\mu$ mol, 77%) was obtained as a colourless oil.

113 mg (214  $\mu$ mol) boronic ester **5f** subjected to oxidation according to GP-4 using 428  $\mu$ l THF, 98.0  $\mu$ l (1.07 mmol, 33%wt) aqueous H<sub>2</sub>O<sub>2</sub> solution and a solution of 42.8 mg (1.07 mmol) NaOH in 428  $\mu$ l water. The reaction was worked up after 1 h. To improve chromatographic separation, 15.4 mg (159  $\mu$ mol) methylboronic acid and 1.07 ml diethyl ether were used. After column chromatography (SiO<sub>2</sub>, CyH/EE 0-20%; C18-SiO<sub>2</sub>, H<sub>2</sub>O  $\rightarrow$  MeCN), the product **6f** (48.3 mg, 156  $\mu$ mol, 73%) was obtained as a colourless oil.  $R_f$  (**6f**) = 0.29 (pentane/EE 8:2).  $[\alpha]_D^{20} = +5.6$  (c = 1.0, CHCl<sub>3</sub>).



**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.30–7.27 (m, 2 H, 2-H), 7.21–7.17 (m, 3 H, 1-H, 3-H), 6.73 (d,  $J$  = 7.8 Hz, 1 H, 17-H), 6.66 (d,  $J$  = 1.2 Hz, 1 H, 13-H), 6.62 (dd,  $J_1$  = 7.9 Hz, 1.2 Hz, 1 H, 18-H), 5.92 (s, 2 H, 15-H), 5.67 (dt,  $J$  = 15.2 Hz, 6.7 Hz, 1 H, 10-H), 5.49 (dt,  $J$  = 15.3 Hz, 7.3 Hz, 1 H, 9-H), 3.68–3.62 (m, 1 H, 7-H), 3.28 (d,  $J$  = 6.6 Hz, 2 H, 11-H), 2.84–2.77 (m, 1 H, 5-Ha), 2.72–2.64 (m, 1 H, 5-Hb), 2.32–2.26 (m, 1 H, 8-Ha), 2.19–2.12 (m, 1 H, 8-Hb), 1.81–1.74 (m, 2 H, 6-H), 1.58 (s, 1 H, OH) ppm.

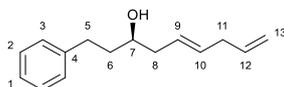
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 147.6 (C-14), 145.8 (C-16), 142.1 (C-4), 134.3 (C-12), 133.3 (C-10), 128.4 (C-3), 128.4 (C-2), 127.1 (C-9), 125.8 (C-1), 121.1 (C-18), 108.9 (C-13), 108.2 (C-17), 100.8 (C-15), 70.2 (C-7), 40.7 (C-8), 38.8 (C-11), 38.4 (C-6), 32.0 (C-5) ppm.

**HRMS** (ESI)  $m/z$  calcd for  $C_{20}H_{22}O_3$   $[M]^+$ : 310.1563, found: 310.1553.

### **(*R,E*)-1-phenylnona-5,8-dien-3-ol (6g)**

According to GP-2, 111 mg (282  $\mu$ mol) boronic ester **3**, 72.8 mg (282  $\mu$ mol) Schwartz reagent and 1.41 ml anhydrous THF were used for the hydrozirconation. 9.8 mg (8.47  $\mu$ mol)  $Pd(PPh_3)_4$ , 24.4  $\mu$ l (34.2 mg, 282  $\mu$ mol) allyl bromide and additional 0.56 ml anhydrous THF were used for the Negishi coupling. The reaction was worked up after 17 h. After column chromatography ( $SiO_2$ , CyH/EE 0-3%), the product **5g** (122 mg, 239  $\mu$ mol, 85%) was obtained as a colourless oil.

86.9 mg (200  $\mu$ mol) boronic ester **5g** was subjected to oxidation according to GP-4 using 400  $\mu$ l THF, 91.0  $\mu$ l (1.00 mmol, 33 %wt) aqueous  $H_2O_2$  solution and a solution of 40.0 mg (1.00 mmol) NaOH in 400  $\mu$ l water. The reaction was worked up after 1 h. To improve chromatographic separation, 14.4 mg (240  $\mu$ mol) methylboronic acid and 1.00 ml diethyl ether were used. After column chromatography ( $SiO_2$ , CyH/EE 0-20%; C18- $SiO_2$ ,  $H_2O \rightarrow MeCN$ ), the product **6g** (31.8 mg, 147  $\mu$ mol, 74%) was obtained as a colourless oil.  $R_f$  (**6g**) = 0.41 (pentane/EE 8:2).  $[\alpha]_D^{20} = +11.0$  ( $c = 1.0$ ,  $CHCl_3$ ).



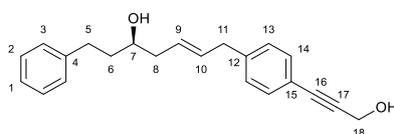
**$^1H$ -NMR** (400 MHz,  $CDCl_3$ ):  $\delta = 7.31$ – $7.27$  (m, 2 H, 2-H),  $7.22$ – $7.17$  (m, 3 H, 1-H, 3-H),  $5.82$  (ddt,  $J = 16.9$  Hz,  $10.3$  Hz,  $6.4$  Hz, 1 H, 12-H),  $5.61$ – $5.54$  (m, 1 H, 10-H),  $5.49$ – $5.42$  (m, 1 H, 9-H),  $5.06$ – $4.99$  (m, 2 H, 13-H),  $3.66$ – $3.60$  (m, 1 H, 7-H),  $2.85$ – $2.77$  (m, 3 H, 5-Ha, 11-H),  $2.72$ – $2.65$  (m, 1 H, 5-Hb),  $2.31$ – $2.25$  (m, 1 H, 8-Ha),  $2.18$ – $2.10$  (m, 1 H, 8-Hb),  $1.81$ – $1.75$  (m, 2 H, 6-H),  $1.61$  (br s, 1 H, OH) ppm.

**$^{13}C$ -NMR** (100 MHz,  $CDCl_3$ ):  $\delta = 142.1$  (C-4),  $136.8$  (C-12),  $132.0$  (C-10),  $128.4$  (C-3),  $128.4$  (C-2),  $127.0$  (C-9),  $125.8$  (C-1),  $115.2$  (C-13),  $70.1$  (C-7),  $40.8$  (C-8),  $38.4$  (C-6),  $36.8$  (C-11),  $32.0$  (C-5) ppm.

**HRMS** (CI)  $m/z$  calcd for  $C_{15}H_{20}O$   $[M]^+$ : 216.1514, found: 216.1525.

### **(*R,E*)-7-(4-(3-Hydroxyprop-1-yn-1-yl)phenyl)-1-phenylhept-5-en-3-ol (6i)**

To a solution of 101 mg (291  $\mu$ mol, 1.0 eq.) aryl bromide **11e** were added 5.60 mg (29  $\mu$ mol, 0.1 eq.) CuI and 52.1  $\mu$ l (49.0 mg, 874  $\mu$ mol, 3.0 eq.) propargyl alcohol, followed by the addition of 16.8 mg (15  $\mu$ mol, 0.05 eq.)  $Pd(PPh_3)_4$ . The reaction mixture was stirred at 80  $^\circ C$  for 24 h. after cooling to room temperature, sat.  $NH_4Cl$  solution was added. The phases were separated and the organic phase was extracted three times with ethyl acetate. The combined organic phases were washed with brine, dried over  $Na_2SO_4$  and filtered. The solvent was removed under reduced pressure. The residue was purified by column chromatography ( $SiO_2$ , CyH/EE 0-40%; C18- $SiO_2$ ,  $H_2O \rightarrow MeCN$ ). The product **6i** (66.2 mg, 207  $\mu$ mol, 71%) was obtained as a yellow oil.  $R_f$  (**6i**) = (pentane/EE).  $[\alpha]_D^{20} = +5.6$  ( $c = 1.0$ ,  $CHCl_3$ ).



**$^1H$ -NMR** (500 MHz,  $CDCl_3$ ):  $\delta = 7.37$ – $7.35$  (m, 2 H, 14-H),  $7.30$ – $7.27$  (m, 2 H, 2-H),  $7.20$ – $7.18$  (m, 3 H, 1-H, 3-H),  $7.13$ – $7.11$  (m, 2 H, 13-H),  $5.71$ – $5.65$  (m, 1 H, 10-H),  $5.54$ – $5.48$  (m,

1 H, 9-H), 4.49 (s, 2 H, 18-H), 3.68–3.63 (m, 1 H, 7-H), 3.35 (d,  $J = 6.6$  Hz, 11-H), 2.83–2.77 (m, 1 H, 5-Ha), 2.71–2.65 (m, 1 H, 5-Hb), 2.32–2.27 (m, 1 H, 8-Ha), 2.20–2.14 (m, 1 H, 8-Hb), 1.83–1.72 (m, 3 H, 6-H, 7-OH), 1.61 (br s, 1 H, 18-OH) ppm.

$^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 142.0$  (C-4), 141.1 (C-12), 132.3 (C-10), 131.8 (C-14), 128.5 (C-3), 128.4 (C-2), 128.4 (C-13), 127.8 (C-9), 125.8 (C-1), 120.2 (C-15), 86.8 (C-17), 85.7 (C-16), 70.2 (C-7), 51.7 (C-18), 40.7 (C-8), 38.9 (C-11), 38.4 (C-6), 32.0 (C-5) ppm.

**HRMS** (ESI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{23}\text{O}_2$   $[\text{M-H}]^-$ : 319.1704, found: 319.1698.

### **(*R,E*)-1,6-Diphenylhex-5-en-3-ol (8a)**

According to GP-3, 104 mg (265  $\mu\text{mol}$ ) boronic ester **3**, 68.4 mg (265  $\mu\text{mol}$ ) Schwartz reagent and 0.35 ml anhydrous THF were used for the hydrozirconation. 20.2 mg (18.0  $\mu\text{mol}$ )  $\text{Pd}(\text{PPh}_3)_4$ , 59.2  $\mu\text{l}$  (108 mg, 531  $\mu\text{mol}$ ) iodobenzene and 47.0 mg (345  $\mu\text{mol}$ )  $\text{ZnCl}_2$  in 0.18 ml anhydrous THF were used for the Negishi coupling. The reaction was worked up after 17.5 h. After column chromatography ( $\text{SiO}_2$ , CyH/EE 0-3%), the product **7a** (105 mg, 207  $\mu\text{mol}$ , 78%) was obtained as a colourless oil.

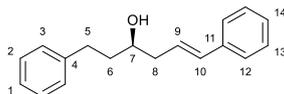
91 mg (167  $\mu\text{mol}$ ) boronic ester **7a** was subjected to oxidation according to GP-4 using 385  $\mu\text{l}$  THF, 88.0  $\mu\text{l}$  (99.0 mg, 962  $\mu\text{mol}$ , 33 %wt) aqueous  $\text{H}_2\text{O}_2$  solution and a solution of 38.5 mg (962  $\mu\text{mol}$ ) NaOH in 385  $\mu\text{l}$  water. The reaction was worked up after 1 h. To improve chromatographic separation, 13.8 mg (231  $\mu\text{mol}$ ) methylboronic acid and 0.96 ml diethyl ether were used. After column chromatography ( $\text{SiO}_2$ , CyH/EE 0-20%; C18- $\text{SiO}_2$ ,  $\text{H}_2\text{O} \rightarrow \text{MeCN}$ ), the product **8a** (39 mg, 153  $\mu\text{mol}$ , 80%) was obtained as a colourless oil.

#### 1 mmol scale:

According to GP-3, 501 mg (1.28 mmol) boronic ester **3**, 330 mg (1.28 mmol) Schwartz reagent and 1.70 ml anhydrous THF were used for the hydrozirconation. 97.0 mg (84.0  $\mu\text{mol}$ )  $\text{Pd}(\text{PPh}_3)_4$ , 285  $\mu\text{l}$  (521 mg, 2.56 mmol) iodobenzene and 226 mg (1.66 mmol)  $\text{ZnCl}_2$  in 0.85 ml anhydrous THF were used for the Negishi coupling. The reaction was worked up after 16 h. After column chromatography ( $\text{SiO}_2$ , CyH/EE 0-3%), the product **7a** (464 mg, 917  $\mu\text{mol}$ , 72%) was obtained as a colourless oil.

459 mg (976  $\mu\text{mol}$ ) boronic ester **7a** was subjected to oxidation according to GP-4 using 1.95 ml THF, 445  $\mu\text{l}$  (503 mg, 4.88 mmol, 33 %wt) aqueous  $\text{H}_2\text{O}_2$  solution and a solution of 195 mg (4.88 mmol) NaOH in 1.95 ml water. The reaction was worked up after 1 h. To improve chromatographic separation, 70.1 mg (1.71 mmol) methylboronic acid and 4.88 ml diethyl ether were used. After column chromatography ( $\text{SiO}_2$ , CyH/EE 0-20%; C18- $\text{SiO}_2$ ,  $\text{H}_2\text{O} \rightarrow \text{MeCN}$ ), the product **8a** (179 mg, 711  $\mu\text{mol}$ , 73%) was obtained as a colourless oil.

$R_f$  (**8a**) = 0.30 (pentane/EE 8:2).  $[\alpha]_D^{20} = +7.9$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).



$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.37$ – $7.35$  (m, 2 H, 12-H), 7.32– $7.27$  (m, 4 H, 2-H, 13-H), 7.24– $7.18$  (m, 4 H, 1-H, 3-H, 14-H), 6.49 (d,  $J = 15.9$  Hz, 10-H), 6.22 (dt,  $J = 15.7$  Hz, 7.6 Hz, 1 H, 9-H), 3.80– $3.72$  (m, 1 H, 7-H), 2.88– $2.81$  (m, 1 H, 5-Ha), 2.76– $2.68$  (m, 1 H, 5-Hb), 2.51– $2.44$  (m, 1 H, 8-Ha), 2.39– $2.31$  (m, 1 H, 8-Hb), 1.87– $1.81$  (m, 2 H, 6-H), 1.64 (d,  $J = 4.3$  Hz, 1 H, OH) ppm.

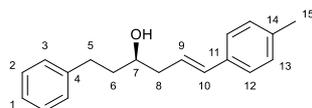
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ = 142.0 (C-4), 137.1 (C-11), 133.4 (C-10), 128.5 (C-13), 128.5 (C-3), 128.4 (C-2), 127.3 (C-14), 126.1 (C-12), 126.0 (C-9), 125.8 (C-1), 70.4 (C-7), 41.3 (C-8), 38.5 (C-6), 32.1 (C-5) ppm.

HRMS (CI) m/z calcd for C<sub>18</sub>H<sub>21</sub>O [M+H]<sup>+</sup>: 253.1592, found: 253.1589.

### (*R,E*)-1-Phenyl-6-(*p*-tolyl)hex-5-en-3-ol (**8b**)

According to GP-3, 107 mg (272 μmol) boronic ester **3**, 73.6 mg (285 μmol) Schwartz reagent and 0.36 ml anhydrous THF were used for the hydrozirconation. 20.7 mg (17.0 μmol) Pd(PPh<sub>3</sub>)<sub>4</sub>, 118 mg (543 μmol) 1-iodo-4-methylbenzene and 48.1 mg (353 μmol) ZnCl<sub>2</sub> in 0.18 ml anhydrous THF were used for the Negishi coupling. The reaction was worked up after 16 h. After column chromatography (SiO<sub>2</sub>, CyH/EE 0-3%), the product **7b** (100 mg, 165 μmol, 61%) was obtained as a colourless oil.

81 mg (167 μmol) boronic ester **7b** was subjected to oxidation according to GP-4 using 334 μl THF, 76.0 μl (834 μmol, 33%wt) aqueous H<sub>2</sub>O<sub>2</sub> solution and a solution of 33.4 mg (834 mmol) NaOH in 334 μl water. The reaction was worked up after 1 h. To improve chromatographic separation, 12.0 mg (185 μmol) methylboronic acid and 0.84 ml diethyl ether were used. After column chromatography (SiO<sub>2</sub>, CyH/EE 0-20%; C18-SiO<sub>2</sub>, H<sub>2</sub>O → MeCN), the product **8b** (41 mg, 153 μmol, 92%) was obtained as a colourless oil. R<sub>f</sub> (**8b**) = 0.39 (pentane/EE 8:2). [α]<sub>D</sub><sup>20</sup> = +6.2 (c = 1.0, CHCl<sub>3</sub>).



<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.30–7.16 (m, 7 H, 1-H, 2-H, 3-H, 12-H), 7.11–7.09 (m, 2 H, 13-H), 6.44 (d, *J* = 15.9 Hz, 1 H, 10-H), 6.15 (dt, *J* = 15.8 Hz, *J* = 7.6 Hz, 1 H, 9-H), 3.77–3.70 (m, 1 H, 7-H), 2.86–2.79 (m, 1 H, 5-Ha), 2.74–2.67 (m, 1 H, 5-Hb), 2.48–2.42 (m, 1 H, 8-Ha), 2.36–2.28 (m, 4 H, 8-Hb, 15-H), 1.85–1.79 (m, 2 H, 6-H), 1.64 (d, *J* = 4.2 Hz, 1 H, OH) ppm.

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ = 142.0 (C-4), 137.1 (C-14), 134.3 (C-11), 133.3 (C-10), 129.2 (C-13), 128.5 (C-3), 128.4 (C-2), 126.0 (C-12), 125.8 (C-1), 124.9 (C-9), 70.4 (C-7), 41.3 (C-8), 38.5 (C-6), 32.1 (C-5), 21.1 (C-15) ppm.

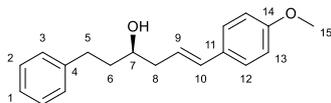
HRMS (CI) m/z calcd for C<sub>19</sub>H<sub>23</sub>O [M+H]<sup>+</sup>: 267.1749, found: 267.1742.

### (*R,E*)-6-(4-Methoxyphenyl)-1-phenylhex-5-en-3-ol (**8c**)

According to GP-3, 103 mg (262 μmol) boronic ester **3**, 67.4 mg (275 μmol) Schwartz reagent and 0.35 ml anhydrous THF were used for the hydrozirconation. 20.0 mg (17.0 μmol) Pd(PPh<sub>3</sub>)<sub>4</sub>, 123 mg (524 μmol) 1-iodo-4-methoxybenzene and 46.4 mg (341 μmol) ZnCl<sub>2</sub> in 0.18 ml anhydrous THF were used for the Negishi coupling. The reaction was worked up after 16 h. After column chromatography (SiO<sub>2</sub>, CyH/EE 0-3%), the product **7c** (107 mg, 190 μmol, 73%) was obtained as a colourless oil.

77 mg (154 μmol) boronic ester **7c** was subjected to oxidation according to GP-4 using 308 μl THF, 70.2 μl (769 μmol, 33%wt) aqueous H<sub>2</sub>O<sub>2</sub> solution and a solution of 30.8 mg (769 μmol) NaOH in 308 μl water. The reaction was worked up after 1 h. To improve chromatographic separation, 11.1 mg (185 μmol) methylboronic acid and 0.77 ml diethyl ether were used. After column chromatography (SiO<sub>2</sub>, CyH/EE 0-20%; C18-SiO<sub>2</sub>, H<sub>2</sub>O → MeCN), the product **8c**

(32 mg, 112  $\mu\text{mol}$ , 73%) was obtained as a colourless oil.  $R_f$  (**8c**) = 0.25 (pentane/EE 8:2).  $[\alpha]_D^{20} = +7.6$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).



**$^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.31\text{--}7.27$  (m, 4 H, 2-H, 12-H), 7.23–7.17 (m, 3 H, 1-H, 3-H), 6.86–6.84 (m, 2 H, 13-H), 6.43 (d,  $J = 15.8$  Hz, 1 H, 10-H), 6.07 (dt,  $J = 15.9$  Hz, 7.3 Hz, 1 H, 9-H), 3.81 (s, 3 H, 15-H), 3.76–3.71 (m, 1 H, 7-H), 2.88–2.80 (m, 1 H, 5-Ha), 2.75–2.68 (m, 1 H, 5-Hb), 2.48–2.42 (m, 1 H, 8-Ha), 2.35–2.28 (m, 1 H, 8-Hb), 1.86–1.80 (m, 2 H, 6-H), 1.66 (d,  $J = 3.5$  Hz, 1 H, OH) ppm.

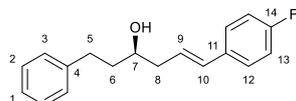
**$^{13}\text{C-NMR}$**  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 159.0$  (C-14), 142.0 (C-4), 132.8 (C-10), 130.0 (C-11), 128.4 (C-3), 128.4 (C-2), 127.2 (C-12), 125.8 (C-1), 123.7 (C-9), 113.9 (C-13), 70.4 (C-7), 55.3 (C-15), 41.3 (C-8), 38.5 (C-6), 32.1 (C-5) ppm.

**HRMS** (CI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{23}\text{O}$   $[\text{M}+\text{H}]^+$ : 267.1749, found: 267.1761.

### **(*R,E*)-6-(4-Fluorophenyl)-1-phenylhex-5-en-3-ol (8d)**

According to GP-3, 106 mg (270  $\mu\text{mol}$ ) boronic ester **3**, 69.6 mg (270  $\mu\text{mol}$ ) Schwartz reagent and 0.36 ml anhydrous THF were used for the hydrozirconation. 20.6 mg (18.0  $\mu\text{mol}$ )  $\text{Pd}(\text{PPh}_3)_4$ , 62.2  $\mu\text{l}$  (540  $\mu\text{mol}$ ) 1-fluoro-4-iodobenzene, 47.8 mg (351  $\mu\text{mol}$ )  $\text{ZnCl}_2$  and additional 0.18 ml anhydrous THF were used for the Negishi coupling. The reaction was worked up after 15 h. After column chromatography ( $\text{SiO}_2$ , CyH/EE 0-3%), the product **7d** (105.9 mg, 186  $\mu\text{mol}$ , 69%) was obtained as a colourless oil.

95.3 mg (195  $\mu\text{mol}$ ) boronic ester **7d** was subjected to oxidation according to GP-4 using 390  $\mu\text{l}$  THF, 89.0  $\mu\text{l}$  (975  $\mu\text{mol}$ , 33%wt) aqueous  $\text{H}_2\text{O}_2$  solution and a solution of 39.0 mg (975  $\mu\text{mol}$ ) NaOH in 390  $\mu\text{l}$  water. The reaction was worked up after 1 h. To improve chromatographic separation, 14.0 mg (234  $\mu\text{mol}$ ) methylboronic acid and 0.98 ml diethyl ether were used. After column chromatography ( $\text{SiO}_2$ , CyH/EE 0-20%; C18- $\text{SiO}_2$ ,  $\text{H}_2\text{O} \rightarrow \text{MeCN}$ ), the product **8d** (33.8 mg, 125  $\mu\text{mol}$ , 64%) was obtained as a colourless oil.  $R_f$  (**8d**) = 0.29 (pentane/EE 8:2).  $[\alpha]_D^{20} = +8.7$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).



**$^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.33\text{--}7.18$  (m, 7 H, 1-H, 2-H, 3-H, 12-H), 7.01–6.99 (m, 2 H, 13-H), 6.44 (d,  $J = 15.8$  Hz, 1 H, 10-H), 6.13 (dt,  $J = 15.5$  Hz,  $J = 7.5$  Hz, 1 H, 9-H), 3.78–3.72 (m, 1 H, 7-H), 2.88–2.80 (m, 1 H, 5-Ha), 2.75–2.68 (m, 1 H, 5-Hb), 2.49–2.43 (m, 1 H, 8-Ha), 2.37–2.30 (m, 1 H, 8-Hb), 1.87–1.81 (m, 2 H, 6-H), 1.62 (br s, 1 H, OH) ppm.

**$^{13}\text{C-NMR}$**  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 162.3$  ( $J = 246.5$  Hz, C-14), 141.9 (C-4), 133.3 ( $J = 3.7$  Hz, C-11), 132.1 (C-10), 128.4 (C-3), 127.5 ( $J = 8.1$  Hz, C-12), 125.8 (C-9), 125.8 (C-1), 115.3 ( $J = 22.0$  Hz, C-13), 70.4 (C-7), 41.2 (C-8), 38.6 (C-6), 32.1 (C-5) ppm.

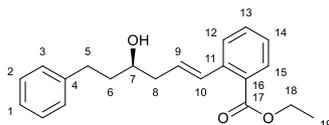
**$^{19}\text{F-NMR}$**  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = -114.8$  ppm.

**HRMS** (CI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{19}\text{FO}$   $[\text{M}]^+$ : 270.1420, found: 270.1375.

### **Ethyl (*R,E*)-2-(4-hydroxy-6-phenylhex-1-en-1-yl)benzoate (8e)**

According to GP-3, 113 mg (288  $\mu\text{mol}$ ) boronic ester **3**, 74.2 mg (288  $\mu\text{mol}$ ) Schwartz reagent and 0.38 ml anhydrous THF were used for the hydrozirconation. 21.9 mg (18.0  $\mu\text{mol}$ ) Pd(PPh<sub>3</sub>)<sub>4</sub>, 159 mg (575  $\mu\text{mol}$ ) ethyl 2-iodobenzoate and 51.0 mg (374  $\mu\text{mol}$ ) ZnCl<sub>2</sub> in 0.19 ml anhydrous THF were used for the Negishi coupling. The reaction was worked up after 17.5 h. After column chromatography (SiO<sub>2</sub>, CyH/EE 0-3%), the product **7e** (148 mg, 254  $\mu\text{mol}$ , 88%) was obtained as a colourless oil.

To a solution of 132 mg (243  $\mu\text{mol}$ , 1.0 eq.) boronic ester **7e** in 486  $\mu\text{l}$  THF were added 111  $\mu\text{mol}$  (41.3 mg, 1.22 mmol, 33%wt, 5.0 eq.) aqueous H<sub>2</sub>O<sub>2</sub> solution and a solution of 129 mg (1.22 mmol, 5.0 eq.) Na<sub>2</sub>CO<sub>3</sub> in 486  $\mu\text{l}$  water at 0 °C. The reaction mixture was warmed to room temperature and stirred for 1h. The reaction mixture was then washed with brine and the aqueous phase was extracted three times with Et<sub>2</sub>O. The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The solvent was removed under reduced pressure. To improve separation of **8e** and DICHD, the crude product was diluted in 1.22 ml Et<sub>2</sub>O and 17.5 mg (292  $\mu\text{mol}$ , 1.2 eq.) methylboronic acid was added with an excess of MgSO<sub>4</sub> and the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO<sub>2</sub>, CyH/EE 0-20%; C18-SiO<sub>2</sub>, H<sub>2</sub>O  $\rightarrow$  MeCN). The product **8e** (45.7 mg, 141  $\mu\text{mol}$ , 58%) was obtained as a colourless oil. R<sub>f</sub>(**8e**) = 0.29 (pentane/EE 8:2). [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +23.5 (c = 1.0, CHCl<sub>3</sub>).



**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.89 (d,  $J$  = 8.1 Hz, 1 H, 15-H), 7.49–7.43 (m, 2 H, 13-H, 14-H), 7.32–7.27 (m, 3 H, 2-H, 12-H), 7.24–7.15 (m, 4 H, 1-H, 3-H, 10-H), 6.03 (ddd,  $J$  = 15.5 Hz, 8.3 Hz, 6.8 Hz, 1 H, 9-H), 4.36 (q,  $J$  = 7.1 Hz, 2 H, 18-H), 3.79–3.73 (m, 1 H, 7-H), 2.90–2.83 (m, 1 H, 5-Ha), 2.77–2.70 (m, 1 H, 5-Hb), 2.52–2.46 (m, 1 H, 8-Ha), 2.39–2.31 (m, 1 H, 8-Hb), 2.30 (s, 1 H, OH), 1.88–1.82 (m, 2 H, 6-H), 1.38 (t,  $J$  = 7.1 Hz, 3 H, 19-H) ppm.

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 167.4 (C-17), 142.2 (C-4), 139.6 (C-11), 133.0 (C-10), 132.0 (C-13), 130.2 (C-15), 128.8 (C-16), 128.5 (C-3, C-9), 128.3 (C-2), 127.6 (C-14), 127.0 (C-12), 125.8 (C-1), 70.1 (C-18), 61.1 (C-7), 41.1 (C-8), 38.6 (C-6), 32.1 (C-5), 14.3 (C-19) ppm.

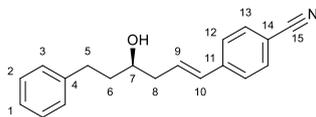
**HRMS** (CI)  $m/z$  calcd for C<sub>21</sub>H<sub>25</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 325.1804, found: 325.1807.

#### **(R,E)-4-(4-Hydroxy-6-phenylhex-1-en-1-yl)benzonitrile (8f)**

According to GP-3, 157 mg (399  $\mu\text{mol}$ ) boronic ester **3**, 103 mg (399  $\mu\text{mol}$ ) Schwartz reagent and 0.53 ml anhydrous THF were used for the hydrozirconation. 30.5 mg (26.0  $\mu\text{mol}$ ) Pd(PPh<sub>3</sub>)<sub>4</sub>, 183 mg (799  $\mu\text{mol}$ ) 4-iodobenzonitrile and 70.8 mg (519  $\mu\text{mol}$ ) ZnCl<sub>2</sub> in 0.27 ml anhydrous THF were used for the Negishi coupling. The reaction was worked up after 15 h. After column chromatography (SiO<sub>2</sub>, CyH/EE 0-3%), the product **7f** (142 mg, 286  $\mu\text{mol}$ , 72%) was obtained as a colourless oil.

To a solution of 117 mg (237  $\mu\text{mol}$ , 1.0 eq.) boronic ester **7f** in 473  $\mu\text{l}$  THF were added 40.1 mg (260  $\mu\text{mol}$ , 1.1 eq.) NaBO<sub>3</sub> · 4 H<sub>2</sub>O and a solution of 10.4 mg (260  $\mu\text{mol}$ , 1.1 eq.) NaOH in 473  $\mu\text{l}$  water at 0 °C. The reaction mixture was warmed to room temperature and stirred for 1h. The reaction mixture was then washed with brine and the aqueous phase was extracted three times with Et<sub>2</sub>O. The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The solvent

was removed under reduced pressure. To improve separation of **7f** and DICHD, the crude product was dissolved in 1.19 ml Et<sub>2</sub>O and 17.0 mg (284 μmol, 1.2 eq.) methylboronic acid was added with an excess of MgSO<sub>4</sub> and the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO<sub>2</sub>, CyH/EE 0-20%; C18-SiO<sub>2</sub>, H<sub>2</sub>O → MeCN). The product **7f** (58.1 mg, 209 μmol, 88%) was obtained as a colourless oil. R<sub>f</sub> (**7f**) = 0.19 (pentane/EE 8:2). [α]<sub>D</sub><sup>20</sup> = +8.4 (c = 1.0, CHCl<sub>3</sub>).



<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.58 (d, *J* = 8.3 Hz, 2 H, 13-H), 7.42 (d, *J* = 8.2 Hz, 12-H), 7.31–7.18 (m, 2 H, 2-H), 7.22–7.18 (m, 3 H, 1-H, 3-H), 6.48 (d, *J* = 16.0 Hz, 1 H, 10-H), 6.39 (dt, *J* = 15.8 Hz, 7.0 Hz, 1 H, 9-H), 3.83–3.76 (m, 1 H, 7-H), 2.87–2.80 (m, 1 H, 5-Ha), 2.75–2.68 (m, 1 H, 5-Hb), 2.53–2.47 (m, 1 H, 8-Ha), 2.43–2.36 (m, 1 H, 8-Hb), 1.87–1.81 (m, 2 H, 6-H), 1.58 (s, 1 H, OH) ppm.

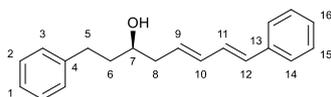
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ = 141.7 (C-4), 141.6 (C-11), 132.4 (C-13), 131.5 (C-10), 130.6 (C-9), 128.5 (C-3), 128.4 (C-2), 126.6 (C-12), 126.0 (C-1), 119.0 (C-15), 110.4 (C-14), 70.4 (C-7), 41.3 (C-8), 38.7 (C-6), 32.0 (C-5) ppm.

HRMS (CI) *m/z* calcd for C<sub>19</sub>H<sub>20</sub>NO [M+H]<sup>+</sup>: 278.1545, found: 278.1577.

#### (*R,5E,7E*)-1,8-diphenylocta-5,7-dien-3-ol (**8g**)

According to GP-3, 101 mg (295 μmol) boronic ester **3**, 66.2 mg (257 μmol) Schwartz reagent and 0.34 ml anhydrous THF were used for the hydrozirconation. 19.6 mg (17.0 μmol) Pd(PPh<sub>3</sub>)<sub>4</sub>, 69.5 μl (118 mg, 514 μmol) (*E*)-(2-iodovinyl)benzene<sup>9</sup> and 45.5 mg (334 μmol) ZnCl<sub>2</sub> in 0.17 ml anhydrous THF were used for the Negishi coupling. The reaction was worked up after 18 h. After column chromatography (SiO<sub>2</sub>, CyH/EE 0-3%), the product **7g** (100 mg, 185 μmol, 72%) was obtained as a yellow oil.

80.8 mg (150 μmol) boronic esters **7g** was subjected to oxidation according to GP-4 using 325 μl THF, 74.2 μl (27.7 mg, 814 μmol, 33%wt) aqueous H<sub>2</sub>O<sub>2</sub> solution and a solution of 32.5 mg (814 μmol) NaOH in 325 μl water. The reaction was worked up after 1 h. To improve chromatographic separation, 11.7 mg (195 μmol) methylboronic acid and 0.82 ml diethyl ether were used. After column chromatography (SiO<sub>2</sub>, CyH/EE 0-20%; C18-SiO<sub>2</sub>, H<sub>2</sub>O → MeCN), the product **8g** (28.1 mg, 101 μmol, 67%) was obtained as a colourless oil. R<sub>f</sub> (**8g**) = 0.31 (pentane/EE 8:2). [α]<sub>D</sub><sup>20</sup> = +1.4 (c = 1.0, CHCl<sub>3</sub>).



<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.39–7.37 (m, 2 H, 14-H), 7.35–7.27 (m, 4 H, 2-H, 15-H), 7.23–7.18 (m, 4 H, 1-H, 3-H, 16-H), 6.76 (dd, *J* = 15.6 Hz, 10.4 Hz, 1 H, 11-H), 6.49 (d, *J* = 15.6 Hz, 1 H, 12-H), 6.30 (dd, *J* = 15.1 Hz, 10.5 Hz, 1 H, 10-H), 5.81 (dt, *J* = 15.2 Hz, 7.6 Hz, 1 H, 9-H), 3.75–3.68 (m, 1 H, 7-H), 2.86–2.79 (m, 1 H, 5-Ha), 2.74–2.67 (m, 1 H, 5-Hb), 2.44–2.38 (m, 1 H, 8-Ha), 2.33–2.25 (m, 1 H, 8-Hb), 1.84–1.78 (m, 2 H, 6-H), 1.59 (d, *J* = 4.3 Hz, 1 H, OH) ppm.

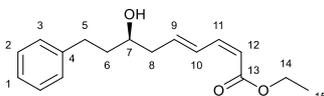
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ = 142.0 (C-4), 137.3 (C-13), 134.0 (C-12), 131.3 (C-11), 130.4 (C-9), 128.7 (C-10), 128.6 (C-15), 128.4 (C-3), 128.4 (C-2), 127.4 (C-16), 126.2 (C-14), 125.9 (C-1), 70.4 (C-7), 41.1 (C-8), 38.5 (C-6), 32.1 (C-5) ppm.

HRMS (ESI) m/z calcd for C<sub>20</sub>H<sub>23</sub>O [M+H]<sup>+</sup>: 279.1743, found: 279.1731.

### Ethyl (*R*,*2Z*,*4E*)-7-hydroxy-9-phenylnona-2,4-dienoate (**8h**)

107 mg (273 μmol, 1.0 eq.) boronic ester **3**, 77.0 mg (273 μmol, 1.1 eq.) Schwartz reagent were suspended in 0.82 ml anhydrous THF at room temperature in the absence of light. The reaction mixture was stirred for 10 min until it became clear. To a solution of 15.8 mg (14.0 μmol, 5 mol-%) Pd(PPh<sub>3</sub>)<sub>4</sub> in 0.55 ml anhydrous THF was added a solution of 41.9 μl (74.0 mg, 327 μmol, 1.2 eq.) ethyl (*Z*)-3-iodoacrylate in 0.55 ml anhydrous THF. The mixture was stirred for 5 min at room temperature before the solution of the freshly prepared vinylzirconium reagent is added. A solution of 74.3 mg (287 μmol, 2.0 eq.) ZnCl<sub>2</sub> in 0.55 ml anhydrous THF was added and the reaction mixture was stirred for 16 h at room temperature. Saturated NH<sub>4</sub>Cl solution is added and the phases were separated. The aqueous phase was extracted three times with diethyl ether. The combined organic phases were washed with saturated NaHCO<sub>3</sub> solution, dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO<sub>2</sub>, CyH/EE 0-3%). The product **7h** (116 mg, 185 μmol, 68%) was obtained as a colourless oil.

To a solution of 99,6 mg (202 μmol, 1.0 eq.) boronic esters **7h** in 404 μl THF were added 34.2 mg (222 μmol, 1.1 eq.) NaBO<sub>3</sub> · 4 H<sub>2</sub>O and 404 μl Sørensen phosphate buffer pH 8 at 0 °C. The reaction mixture was warmed to room temperature and stirred for 5 h. The reaction mixture was then washed with brine and the aqueous phase was extracted three times with Et<sub>2</sub>O. The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The solvent was removed under reduced pressure. To improve separation of **7h** and DICHD, the crude product was dissolved in 1.01 ml Et<sub>2</sub>O and 14.5 mg (243 μmol, 1.2 eq.) methylboronic acid was added with an excess of MgSO<sub>4</sub> and the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO<sub>2</sub>, CyH/EE 0-20%; C18-SiO<sub>2</sub>, H<sub>2</sub>O → MeCN). The product **8h** (38.8 mg, 141 μmol, 89%) was obtained as a colourless oil. R<sub>f</sub> (**8h**) = 0.31 (pentane/EE 8:2). [α]<sub>D</sub><sup>20</sup> = +1.7 (c = 1.0, CHCl<sub>3</sub>).



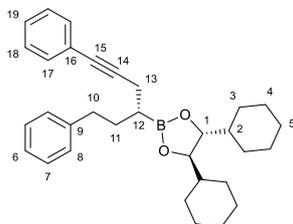
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.49–7.42 (m, 1 H, 10-H), 7.31–7.27 (m, 2 H, 2-H), 7.21–7.17 (m, 3 H, 1-H, 3-H), 6.55 (dd, *J* = 11.3 Hz, 1 H, 11-H), 6.07 (dt, *J* = 15.3 Hz, 7.5 Hz, 1 H, 9-H), 5.61 (d, *J* = 11.4 Hz, 1 H, 12-H), 4.18 (q, *J* = 7.1 Hz, 2 H, 14-H), 3.79–3.72 (m, 1 H, 7-H), 2.85–2.77 (m, 1 H, 5-Ha), 2.73–2.65 (m, 1 H, 5-Hb), 2.48–2.33 (m, 2 H, 8-H), 1.83–1.77 (m, 2 H, 6-H), 1.52 (d, *J* = 4.5 Hz, 1 H, OH), 1.29 (t, *J* = 7.1 Hz, 3 H, 15-H) ppm.

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ = 166.4 (C-13), 144.4 (C-11), 141.8 (C-4), 140.3 (C-9), 129.6 (C-10), 128.4 (C-3), 128.4 (C-2), 125.9 (C-1), 116.7 (C-12), 70.4 (C-7), 60.0 (C-14), 41.1 (C-8), 38.7 (C-6), 32.0 (C-5), 14.3 (C-15) ppm.

HRMS (CI) m/z calcd for C<sub>17</sub>H<sub>21</sub>O<sub>3</sub> [M-H]<sup>+</sup>: 273.1491, found: 273.1490.

**(4*R*,5*R*)-4,5-Dicyclohexyl-2-((*R*)-1,6-diphenylhex-5-yn-3-yl)-1,3,2-dioxaborolane (9a)**

According to GP-5, 150 mg (382  $\mu\text{mol}$ ) boronic ester **3**, 26.8 mg (38.0  $\mu\text{mol}$ )  $\text{PdCl}_2(\text{PPh}_3)_2$ , 14.5 mg (76.0  $\mu\text{mol}$ )  $\text{CuI}$ , 213  $\mu\text{l}$  (389 mg, 1.91 mmol) iodobenzene and 2.54 ml  $\text{NEt}_3$  were used. The reaction mixture was worked up after 16 h. After column chromatography ( $\text{SiO}_2$ ,  $\text{CyH}/\text{EE}$  0-3%), the product **9a** (178 mg, 379  $\mu\text{mol}$ , 99%) was obtained as a yellow oil.  $R_f$  (**9a**) = 0.30 (pentane/EE 97:3).  $[\alpha]_D^{20} = +34.0$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).



**$^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.37\text{--}7.35$  (m, 2 H, 17-H), 7.29–7.16 (m, 8 H, 6-H, 7-H, 8-H, 18-H, 19-H), 3.90–3.87 (m, 2 H, 1-H), 2.72–2.68 (m, 2 H, 10-H), 2.57 (d,  $J = 6.9$  Hz, 2 H, 13-H), 1.94–1.84 (m, 2 H, 11-H), 1.81–1.61 (m, 10 H, 3-Ha, 3-Hb, 4-Ha, 4-Hb, 5-Ha), 1.44–0.95 (m, 13 H, 2-H, 3-Hc, 3-Hd, 4-Hc, 4-Hd, 5-Hb, 12-H) ppm.

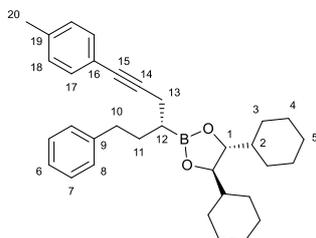
**$^{13}\text{C-NMR}$**  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 142.8$  (C-9), 131.6 (C-17), 128.4 (C-8), 128.3 (C-7), 128.1 (C-19), 127.3 (C-18), 125.6 (C-6), 124.1 (C-16), 90.1 (C-14), 83.5 (C-1), 81.0 (C-15), 43.0 (C-2), 35.1 (C-10), 32.7 (C-11), 28.4 (C-3a), 27.4 (C-3b), 26.4 (C-5), 26.0 (C-4a), 25.9 (C-4b), 20.9 (C-13) ppm.

The signal of C-12 could not be detected.

**HRMS** (CI)  $m/z$  calcd for  $\text{C}_{32}\text{H}_{41}\text{BO}_2$   $[\text{M}]^+$ : 468.3200, found: 468.3208.

**(4*R*,5*R*)-4,5-dicyclohexyl-2-((*R*)-1-phenyl-6-(*p*-tolyl)hex-5-yn-3-yl)-1,3,2-dioxaborolane (9b)**

According to GP-5, 149 mg (379  $\mu\text{mol}$ ) boronic ester **3**, 26.6 mg (36.0  $\mu\text{mol}$ )  $\text{PdCl}_2(\text{PPh}_3)_2$ , 14.4 mg (76.0  $\mu\text{mol}$ )  $\text{CuI}$ , 413 mg (1.90 mmol) 1-iodo-4-methylbenzene and 2.53 ml  $\text{NEt}_3$  were used. The reaction mixture was worked up after 16 h. After column chromatography ( $\text{SiO}_2$ ,  $\text{CyH}/\text{EE}$  0-3%), the product **9b** (183 mg, 379  $\mu\text{mol}$ , 100%) was obtained as a yellow oil.  $R_f$  (**9b**) = 0.29 (pentane/EE 97:3).  $[\alpha]_D^{20} = +33.6$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).



**$^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.29\text{--}7.25$  (m, 4 H, 7-H, 17-H), 7.22–7.15 (m, 3 H, 6-H, 8-H), 7.08–7.06 (m, 2 H, 18-H), 3.90–3.87 (m, 2 H, 1-H), 2.74–2.65 (m, 2 H, 10-H), 2.56 (d,  $J = 6.7$  Hz, 2 H, 13-H), 2.32 (s, 3 H, 20-H), 1.97–1.86 (m, 2 H, 11-H), 1.84–1.61 (m, 10 H, 3-Ha, 3-Hb, 4-Ha, 4-Hb, 5-Ha), 1.43–0.95 (m, 13 H, 2-H, 3-Hc, 3-Hd, 4-Hc, 4-Hd, 5-Hb, 12-H) ppm.

**$^{13}\text{C-NMR}$**  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 142.8$  (C-9), 137.3 (C-19), 131.4 (C-17), 128.8 (C-18), 128.5 (C-8), 128.3 (C-7), 125.6 (C-6), 121.1 (C-16), 89.2 (C-14), 83.5 (C-1), 81.0 (C-15), 43.0 (C-2),

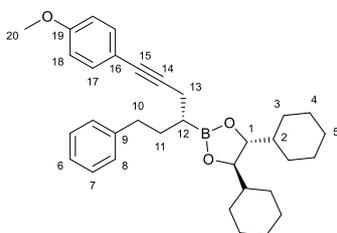
35.1 (C-10), 32.6 (C-11), 28.4 (C-3a), 27.4 (C-3b), 26.4 (C-5), 26.0 (C-4a), 25.9 (C-4b), 21.4 (C-20), 20.9 (C-13) ppm.

The signal of C-12 could not be detected.

**HRMS** (CI)  $m/z$  calcd for  $C_{33}H_{42}BO_2$   $[M-H]^+$ : 481.3278, found: 481.3230.

**(4*R*,5*R*)-4,5-Dicyclohexyl-2-((*R*)-6-(4-methoxyphenyl)-1-phenylhex-5-yn-3-yl)-1,3,2-dioxaborolane (9c)**

According to GP-5, 160 mg (406  $\mu$ mol) boronic ester **3**, 28.5 mg (41.0  $\mu$ mol)  $PdCl_2(PPh_3)_2$ , 15.5 mg (81.0  $\mu$ mol)  $CuI$ , 476 mg (2.03 mmol) 1-iodo-4-methoxybenzene and 2.71 ml  $NEt_3$  were used. The reaction mixture was worked up after 18 h. After column chromatography ( $SiO_2$ , CyH/EE 0-3%), the product **9c** (202 mg, 405  $\mu$ mol, 100%) was obtained as a yellow oil.  $R_f$  (**9c**) = 0.26 (pentane/EE 97:3).  $[\alpha]_D^{20} = +33.3$  ( $c = 1.0$ ,  $CHCl_3$ ).



**$^1H$ -NMR** (400 MHz,  $CDCl_3$ ):  $\delta = 7.31$ – $7.24$  (m, 4 H, 7-H, 17-H),  $7.22$ – $7.16$  (m, 3 H, 6-H, 8-H),  $6.81$ – $6.79$  (m, 2 H, 18-H),  $3.90$ – $3.87$  (m, 2 H, 1-H),  $3.80$  (s, 3 H, 20-H),  $2.73$ – $2.64$  (m, 2 H, 10-H),  $2.55$  (d,  $J = 6.9$  Hz, 13-H),  $1.97$ – $1.84$  (m, 2 H, 11-H),  $1.81$ – $1.61$  (m, 12 H, 3-Ha, 3-Hb, 4-Ha, 4-Hb, 5-Ha, 11-H),  $1.43$ – $0.97$  (m, 13 H, 2-H, 3-Hc, 3-Hd, 4-Hc, 4-Hd, 5-Hb, 12-H) ppm.

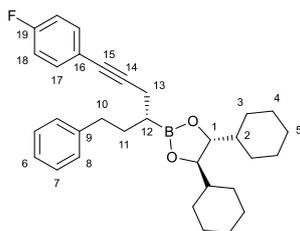
**$^{13}C$ -NMR** (100 MHz,  $CDCl_3$ ):  $\delta = 158.9$  (C-19),  $142.8$  (C-9),  $132.9$  (C-17),  $128.5$  (C-8),  $128.3$  (C-7),  $125.6$  (C-6),  $116.4$  (C-16),  $113.7$  (C-18),  $88.4$  (C-14),  $83.5$  (C-1),  $80.7$  (C-15),  $55.2$  (C-20),  $43.0$  (C-2),  $35.1$  (C-10),  $32.7$  (C-11),  $28.3$  (C-3a),  $27.4$  (C-3b),  $26.4$  (C-5),  $26.0$  (C-4a),  $25.9$  (C-4b),  $20.9$  (C-13) ppm.

The signal of C-12 could not be detected.

**HRMS** (CI)  $m/z$  calcd for  $C_{33}H_{43}BO_3$   $[M]^+$ : 498.3305, found: 498.3277.

**(4*R*,5*R*)-4,5-Dicyclohexyl-2-((*R*)-6-(4-fluorophenyl)-1-phenylhex-5-yn-3-yl)-1,3,2-dioxaborolane (9d)**

According to GP-5, 101 mg (257  $\mu$ mol) boronic ester **3**, 18.0 mg (26.0  $\mu$ mol)  $PdCl_2(PPh_3)_2$ , 9.8 mg (51.0  $\mu$ mol)  $CuI$ , 148  $\mu$ l (285 mg, 1.28 mmol) 1-fluoro-4-iodobenzene and 1.71 ml  $NEt_3$  were used. The reaction mixture was worked up after 18 h. After column chromatography ( $SiO_2$ , CyH/EE 0-3%), the product **9d** (122 mg, 251  $\mu$ mol, 98%) was obtained as a yellow oil.  $R_f$  (**9d**) = 0.33 (pentane/EE 97:3).  $[\alpha]_D^{20} = +32.4$  ( $c = 1.0$ ,  $CHCl_3$ ).



**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.35–7.24 (m, 4 H, 17-H, 7-H), 7.21–7.16 (m, 3 H, 6-H, 8-H), 6.98–6.93 (m, 2 H, 18-H), 3.90–3.87 (m, 2 H, 1-H), 2.74–2.66 (m, 2 H, 10-H), 2.55 (d, *J* = 6.9 Hz, 2 H, 13-H), 1.97–1.84 (m, 2 H, 11-H), 1.83–1.61 (m, 12 H, 3-Ha, 3-Hb, 4-Ha, 4-Hb, 5-Ha, 11-H), 1.44–0.97 (m, 13 H, 2-H, 3-Hc, 3-Hd, 4-Hc, 4-Hd, 5-Hb, 12-H) ppm.

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): δ = 161.9 (*J* = 248.0 Hz, C-19), 142.7 (C-9), 133.3 (*J* = 8.1 Hz, C-17), 128.4 (C-8), 128.3 (C-7), 125.6 (C-6), 120.2 (*J* = 2.9 Hz, C-16), 115.2 (*J* = 22.0 Hz, C-18), 89.7 (C-14), 83.5 (C-1), 79.9 (C-15), 43.0 (C-2), 35.1 (C-10), 32.7 (C-11), 28.3 (C-3a), 27.4 (C-3b), 26.4 (C-5), 26.0 (C-4a), 25.9 (C-4b), 20.8 (C-13) ppm.

The signal of C-12 could not be detected.

**<sup>19</sup>F-NMR** (400 MHz, CDCl<sub>3</sub>): δ = –112.5 ppm.

**HRMS** (CI) *m/z* calcd for C<sub>32</sub>H<sub>40</sub>BFO<sub>2</sub> [M]<sup>+</sup>: 486.3105, found: 486.3109.

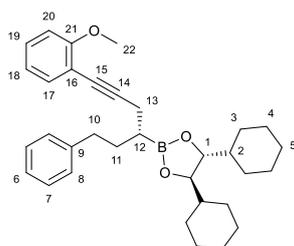
### **(4*R*,5*R*)-4,5-dicyclohexyl-2-((*R*)-6-(2-methoxyphenyl)-1-phenylhex-5-yn-3-yl)-1,3,2-dioxaborolane (9e)**

According to GP-5, 159 mg (406 μmol) boronic ester **3**, 28.5 mg (41.0 μmol) PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 15.5 mg (81.0 μmol) CuI, 476 mg (2.03 mmol) 1-iodo-2-methoxybenzene and 2.71 ml NEt<sub>3</sub> were used. The reaction mixture was worked up after 16 h. After column chromatography (SiO<sub>2</sub>, CyH/EE 0-2%), the product **9e** (202 mg, 405 μmol, 100%) was obtained as a yellow oil.

#### 1 mmol scale

According to GP-5, 492 mg (1.25 mmol) boronic ester **3**, 88.0 mg 125 μmol PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 47.8 mg (251 μmol) CuI, 522, 1.47 g (6.27 mmol) 1-iodo-2-methoxybenzene and 8.36 ml NEt<sub>3</sub> were used. The reaction mixture was worked up after 16 h. After column chromatography (SiO<sub>2</sub>, CyH/EE 0-2%), the product **9e** (546 mg, 1.09 mmol, 87%) was obtained as a yellow oil.

R<sub>f</sub> (**9e**) = 0.36 (pentane/EE 97:3). [α]<sub>D</sub><sup>20</sup> = +37.8 (c = 1.0, CHCl<sub>3</sub>).



**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.34 (dd, *J* = 7.6 Hz, 1.5 Hz, 1 H, 17-H), 7.29–7.15 (m, 6 H, 6-H, 7-H, 8-H, 19-H), 6.88–6.82 (m, 2 H, 18-H, 20-H), 3.89–3.86 (m, 2 H, 1-H), 3.83 (s, 3 H, 22-H), 2.74–2.57 (m, 4 H, 10-H, 13-H), 1.97–1.91 (m, 2 H, 11-H), 1.80–1.60 (m, 10 H, 3-Ha, 3-Hb, 4-Ha, 4-Hb, 5-Ha), 1.46–0.93 (m, 13 H, 2-H, 3-Hc, 3-Hd, 4-Hc, 4-Hd, 5-Hb, 12-H) ppm.

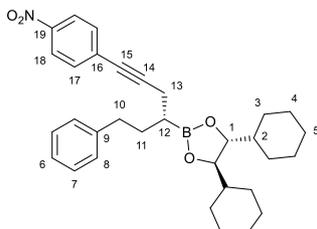
**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): δ = 159.9 (C-21), 142.9 (C-9), 133.6 (C-17), 128.7 (C-19), 128.5 (C-8), 128.2 (C-7), 125.6 (C-6), 120.2 (C-18), 113.3 (C-16), 110.4 (C-20), 94.3 (C-14), 83.5 (C-1), 77.1 (C-15), 55.7 (C-22), 43.0 (C-2), 35.1 (C-10), 32.6 (C-11), 28.4 (C-3a), 27.4 (C-3b), 26.4 (C-5), 26.0 (C-4a), 25.9 (C-4b), 21.1 (C-13) ppm.

The signal of C-12 could not be detected.

**HRMS** (CI) *m/z* calcd for C<sub>33</sub>H<sub>43</sub>BO<sub>3</sub> [M]<sup>+</sup>: 498.3305, found: 498.3317.

**(4*R*,5*R*)-4,5-Dicyclohexyl-2-((*R*)-6-(4-nitrophenyl)-1-phenylhex-5-yn-3-yl)-1,3,2-dioxaborolane (**9f**)**

According to GP-5, 98.7 mg (252  $\mu\text{mol}$ ) boronic ester **3**, 17.7 mg (25.0  $\mu\text{mol}$ )  $\text{PdCl}_2(\text{PPh}_3)_2$ , 9.6 mg (50.0  $\mu\text{mol}$ )  $\text{CuI}$ , 313 mg (1.26 mmol) 1-iodo-4-nitrobenzene and 1.68 ml  $\text{NEt}_3$  were used. The reaction mixture was worked up after 18 h. After column chromatography ( $\text{SiO}_2$ ,  $\text{CyH}/\text{EE}$  0-2%), the product **9f** (119 mg, 232  $\mu\text{mol}$ , 92%) was obtained as a yellow oil.  $R_f$  (**9f**) = 0.24 (pentane/EE 97:3).  $[\alpha]_D^{20} = +24.2$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).



**$^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.15\text{--}8.13$  (m, 2 H, 18-H), 7.49–7.47 (m, 2 H, 17-H), 7.30–7.26 (m, 2 H, 7-H), 7.21–7.17 (m, 3 H, 6-H, 8-H), 3.91–3.88 (m, 2 H, 1-H), 2.73–2.68 (m, 2 H, 10-H), 2.61 (d,  $J = 6.7$  Hz, 2 H, 13-H), 1.95–1.85 (m, 2 H, 11-H), 1.80–1.60 (m, 10 H, 3-Ha, 3-Hb, 4-Ha, 4-Hb, 5-Ha), 1.37–0.96 (m, 13 H, 2-H, 3-Hc, 3-Hd, 4-Hc, 4-Hd, 5-Hb, 12-H) ppm.

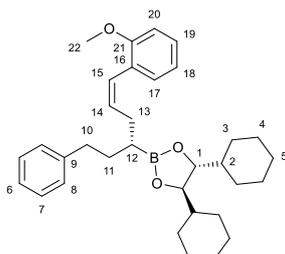
**$^{13}\text{C-NMR}$**  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 146.5$  (C-19), 142.5 (C-9), 132.2 (C-17), 128.4 (C-16), 128.4 (C-8), 128.3 (C-7), 125.8 (C-6), 123.4 (C-18), 96.7 (C-14), 83.6 (C-1), 79.7 (C-15), 43.0 (C-2), 35.0 (C-10), 32.7 (C-11), 28.3 (C-3a), 27.4 (C-3b), 26.4 (C-5), 26.0 (C-4a), 25.9 (C-4b), 21.0 (C-13) ppm.

The signal of C-12 could not be detected.

**HRMS** (CI)  $m/z$  calcd for  $\text{C}_{32}\text{H}_{41}\text{BNO}_4$   $[\text{M}+\text{H}]^+$ : 514.3129, found: 514.3097.

**(4*R*,5*R*)-4,5-Dicyclohexyl-2-((*R*,*Z*)-6-(2-methoxyphenyl)-1-phenylhex-5-en-3-yl)-1,3,2-dioxaborolane (**10e**)**

86.3 mg (173  $\mu\text{mol}$ , 1.0 eq.) boronic ester **9e** and 89 mg (346  $\mu\text{mol}$ , 2.0 eq.) Schwartz reagent were suspended in 1.08 ml anhydrous  $\text{DCM}$  (0.16 M) in the absence of light. The reaction mixture was stirred for 3 h at room temperature until the white precipitate was completely dissolved. Saturated  $\text{NH}_4\text{Cl}$  solution was added and the phases were separated. The aqueous phase was extracted three times with pentane. The combined organic phases were dried over  $\text{Na}_2\text{SO}_4$  and filtered. The solvent was removed under reduced pressure. The crude product was purified by column chromatography ( $\text{SiO}_2$ ,  $\text{CyH}/\text{EE}$  0-3%). The product **10e** (33.7 mg, 67.0  $\mu\text{mol}$ , 39%, 62% brsm) was obtained as a colourless oil.  $R_f$  (**10e**) = 0.26 (pentane/EE 8:2).  $[\alpha]_D^{20} = +31.4$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).



**$^1\text{H-NMR}$**  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.28\text{--}7.19$  (m, 4 H, 7-H, 17-H, 19-H), 7.16–7.12 (m, 3 H, 6-H, 8-H), 6.91 (app t,  $J = 7.4$  Hz, 1 H, 18-H), 6.85 (d,  $J = 8.2$  Hz, 1 H, 20-H), 6.52 (d,  $J = 11.5$  Hz,

1 H, 15-H), 5.74 (dt,  $J = 11.6$  Hz, 7.2 Hz, 1 H, 14-H), 3.87–3.84 (m, 2 H, 1-H), 3.80 (s, 3 H, 22-H), 2.61–2.50 (m, 2 H, 10-H), 2.49–2.35 (m, 2 H, 13-H), 1.82–1.59 (m, 12 H, 3-Ha, 3-Hb, 4-Ha, 4-Hb, 5-Ha, 11-H), 1.32–0.94 (m, 13 H, 2-H, 3-Hc, 3-Hd, 4-Hc, 4-Hd, 5-Hb, 12-H) ppm.

$^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 157.0$  (C-21), 143.1 (C-9), 132.5 (C-14), 130.1 (C-19), 128.4 (C-8), 128.2 (C-7), 127.9 (C-17), 126.5 (C-16), 125.5 (C-6), 124.5 (C-15), 120.0 (C-18), 110.3 (C-20), 83.4 (C-1), 55.3 (C-22), 43.1 (C-2), 35.5 (C-10), 33.1 (C-11), 29.9 (C-13), 28.5 (C-3a), 27.5 (C-3b), 26.4 (C-5), 26.0 (C-4a), 25.9 (C-4b) ppm.

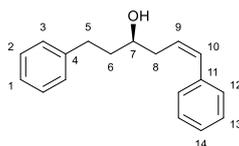
The signal of C-12 could not be detected.

**HRMS** (CI)  $m/z$  calcd for  $\text{C}_{33}\text{H}_{45}\text{BO}_3$   $[\text{M}]^+$ : 500.3462, found: 500.3455.

### **(*R,Z*)-1,6-diphenylhex-5-en-3-ol (11a)**

171 mg (364  $\mu\text{mol}$ , 1.0 eq.) Boronic ester **9a** and 188 mg (728  $\mu\text{mol}$ , 2.0 eq.) Schwartz reagent were suspended in 2.28 ml anhydrous DCM (0.16 M) in the absence of light. The reaction mixture was stirred for 2.5 h at room temperature until the white precipitate was completely dissolved. Saturated  $\text{NH}_4\text{Cl}$  solution was added and the phases were separated. The aqueous phase was extracted three times with pentane. The combined organic phases were dried over  $\text{Na}_2\text{SO}_4$  and filtered. The solvent was removed under reduced pressure. The crude product was purified by column chromatography ( $\text{SiO}_2$ , CyH/EE 0-3%). The product **10a** (152 mg, 322  $\mu\text{mol}$ , 88%) was obtained as a colourless oil.

67.3 mg (143  $\mu\text{mol}$ ) Boronic ester **10a** was subjected to oxidation according to GP-4 using 286  $\mu\text{l}$  THF, 65.2  $\mu\text{l}$  (24.3 mg, 715  $\mu\text{mol}$ , 33%wt) aqueous  $\text{H}_2\text{O}_2$  solution and a solution of 28.6 mg (715  $\mu\text{mol}$ )  $\text{NaOH}$  in 286  $\mu\text{l}$  water. The reaction was worked up after 1 h. To improve chromatographic separation, 10.3 mg (172  $\mu\text{mol}$ ) methylboronic acid and 0.72 ml diethyl ether were used. After column chromatography ( $\text{SiO}_2$ , CyH/EE 0-20%; C18- $\text{SiO}_2$ ,  $\text{H}_2\text{O} \rightarrow \text{MeCN}$ ), the product **11a** (28.1 mg, 111  $\mu\text{mol}$ , 78%) was obtained as a colourless oil.  $R_f$  (**11a**) = 0.34 (pentane/EE 8:2).  $[\alpha]_D^{20} = -0.6$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).



$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.35$ –7.18 (m, 10 H, 1-H, 2-H, 3-H, 12-H, 13-H, 14-H), 6.60 (d,  $J = 11.7$  Hz, 1 H, 10-H), 5.73 (dt,  $J = 11.6$  Hz, 7.4 Hz, 1 H, 9-H), 3.80–3.73 (m, 1 H, 7-H), 2.89–2.48 (m, 4 H, 5-H, 8-H), 1.87–1.76 (m, 2 H, 6-H), 1.54 (d,  $J = 4.2$  Hz, 1 H, OH) ppm.

$^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 141.9$  (C-4), 137.1 (C-11), 131.8 (C-10), 128.7 (C-13), 128.4 (C-2, C-3), 128.2 (C-9), 128.0 (C-12), 126.8 (C-14), 125.8 (C-1), 71.0 (C-7), 38.6 (C-6), 36.5 (C-8), 32.0 (C-5) ppm.

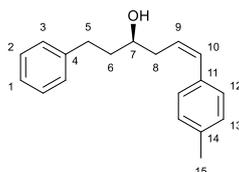
**HRMS** (CI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{19}$   $[\text{M-OH}]^+$ : 235.1487, found: 235.1508.

### **(*R,Z*)-1-Phenyl-6-(*p*-tolyl)hex-5-en-3-ol (11b)**

166 mg (345  $\mu\text{mol}$ , 1.0 eq.) Boronic ester **9b** and 178 mg (689  $\mu\text{mol}$ , 2.0 eq.) Schwartz reagent were suspended in 2.15 ml anhydrous DCM (0.16 M) in the absence of light. The reaction mixture was stirred for 2.5 h at room temperature until the white precipitate was completely dissolved. Saturated  $\text{NH}_4\text{Cl}$  solution was added and the phases were separated. The aqueous

phase was extracted three times with pentane. The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (CyH/EE 0-3%). The product **10b** (141 mg, 290 μmol, 84%) was obtained as a colourless oil.

126 mg (260 μmol) Boronic esters **10b** was subjected to oxidation according to GP-4 using 521 μl THF, 119 μl (44.3 mg, 1.30 mmol, 33%wt) aqueous H<sub>2</sub>O<sub>2</sub> solution and a solution of 52.1 mg (1.30 mmol) NaOH in 521 μl water. The reaction was worked up after 1 h. To improve chromatographic separation, 18.7 mg (313 μmol) methylboronic acid and 1.30 ml diethyl ether were used. After column chromatography (SiO<sub>2</sub>, CyH/EE 0-20%; C18-SiO<sub>2</sub>, H<sub>2</sub>O → MeCN), the product **11b** (53.0 mg, 199 μmol, 76%) was obtained as a colourless oil. R<sub>f</sub> (**11b**) = 0.31 (pentane/EE 8:2). [ $\alpha$ ]<sub>D</sub><sup>20</sup> = -4.4 (c = 1.0, CHCl<sub>3</sub>).



<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.31–7.24 (m, 2 H, 2-H), 7.22–7.09 (m, 7 H, 1-H, 3-H, 12-H, 13-H), 6.56 (d, *J* = 11.7 Hz, 1 H, 10-H), 5.68 (dt, *J* = 11.7 Hz, 7.3 Hz, 1 H, 9-H), 3.79–3.73 (m, 1 H, 7-H), 2.87–2.73 (m, 1 H, 5-Ha), 2.72–2.63 (m, 1 H, 5-Hb), 2.60–2.50 (m, 2 H, 8-H), 2.34 (s, 3 H, 15-H), 1.85–1.78 (m, 2 H, 6-H), 1.60 (br s, 1 H, OH) ppm.

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ = 142.0 (C-4), 136.5 (C-11), 134.3 (C-14), 131.6 (C-10), 128.9 (C-12), 128.7 (C-13), 128.4 (C-3), 128.4 (C-2), 127.3 (C-9), 125.8 (C-1), 71.1 (C-7), 38.6 (C-6), 36.5 (C-8), 32.0 (C-5), 21.2 (C-15) ppm.

HRMS (CI) *m/z* calcd for C<sub>19</sub>H<sub>22</sub>O [M]<sup>+</sup>: 266.1671, found: 266.1664.

### (*R,Z*)-6-(4-methoxyphenyl)-1-phenylhex-5-en-3-ol (**11c**)

187 mg (376 μmol, 1.0 eq.) Boronic ester **9c** and 194 mg (751 μmol, 2.0 eq.) Schwartz reagent were suspended in 2.35 ml anhydrous DCM (0.16 M) in the absence of light. The reaction mixture was stirred for 2.5 h at room temperature until the white precipitate was completely dissolved. Saturated NH<sub>4</sub>Cl solution was added and the phases were separated. The aqueous phase was extracted three times with pentane. The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO<sub>2</sub>, CyH/EE 0-3%). The product **10c** (133 mg, 265 μmol, 71%) was obtained as a colourless oil.

127 mg (254 μmol) Boronic ester **10c** was subjected to oxidation according to GP-4 using 507 μl THF, 116 μl (43.2 mg, 1.27 mmol, 33%wt) aqueous H<sub>2</sub>O<sub>2</sub> solution and a solution of 50.7 mg (1.27 mmol) NaOH in 507 μl water. The reaction was worked up after 1 h. To improve chromatographic separation, 18.2 mg (304 μmol) methylboronic acid and 1.27 ml diethyl ether were used. After column chromatography (SiO<sub>2</sub>, CyH/EE 0-20%; C18-SiO<sub>2</sub>, H<sub>2</sub>O → MeCN), the product **11c** (64.5 mg, 228 μmol, 90%) was obtained as a colourless oil.

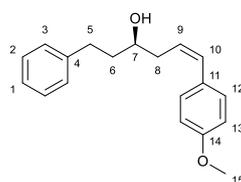
#### 1 mmol scale

527 mg (1.06 mmol, 1.0 eq.) Boronic ester **9c** and 545 mg (2.12 mmol, 2.0 eq.) Schwartz reagent were suspended in 6.61 ml anhydrous DCM (0.16 M) in the absence of light. The reaction mixture was stirred for 2.5 h at room temperature until the white precipitate was

completely dissolved. Saturated NH<sub>4</sub>Cl solution was added and the phases were separated. The aqueous phase was extracted three times with pentane. The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO<sub>2</sub>, CyH/EE 0-3%). The product **10c** (441 mg, 880 μmol, 83%) was obtained as a colourless oil.

426 mg (850 μmol) Boronic ester **10c** was subjected to oxidation according to GP-4 using 1.70 ml THF, 388 μl (438 mg, 4.25 mmol, 33%wt) aqueous H<sub>2</sub>O<sub>2</sub> solution and a solution of 170 mg (4.25 mmol) NaOH in 1.70 ml water. The reaction was worked up after 1 h. To improve chromatographic separation, 61.1 mg (1.02 mmol) methylboronic acid and 4.25 ml diethyl ether were used. After column chromatography (SiO<sub>2</sub>, CyH/EE 0-20%; C18-SiO<sub>2</sub>, H<sub>2</sub>O → MeCN), the product **11c** (202 mg, 716 μmol, 84%) was obtained as a colourless oil.

R<sub>f</sub> (**11c**) = 0.23 (pentane/EE 8:2). [α]<sub>D</sub><sup>20</sup> = -2.4 (c = 1.0, CHCl<sub>3</sub>).



<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.35–7.17 (m, 7 H, 1-H, 2-H, 3-H, 12-H), 6.88–6.86 (m, 2 H, 13-H), 6.53 (d, *J* = 11.6 Hz, 1 H, 10-H), 5.62 (dt, *J* = 11.7 Hz, 7.3 Hz, 1 H, 9-H), 3.81 (s, 3 H, 15-H), 3.79–3.74 (m, 1 H, 7-H), 2.83–2.76 (m, 1 H, 5-H<sub>a</sub>), 2.71–2.63 (m, 1 H, 5-H<sub>b</sub>), 2.60–2.48 (m, 1 H, 8-H), 1.85–1.79 (m, 2 H, 6-H), 1.55 (d, *J* = 4.5 Hz, 1 H, OH) ppm.

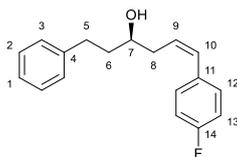
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ = 158.4 (C-14), 142.0 (C-4), 131.2 (C-10), 130.0 (C-12), 129.8 (C-11), 128.5 (C-3), 128.4 (C-2), 128.4 (C-12), 126.4 (C-9), 125.8 (C-1), 113.6 (C-13), 71.1 (C-7), 55.2 (C-15), 38.6 (C-6), 36.5 (C-8), 32.0 (C-5) ppm.

HRMS (CI) *m/z* calcd for C<sub>19</sub>H<sub>21</sub>O [M-H]<sup>+</sup>: 265.1592, found: 265.1600.

#### (*R,Z*)-6-(4-Fluorophenyl)-1-phenylhex-5-en-3-ol (**11d**)

174 mg (358 μmol, 1.0 eq.) Boronic ester **9d** and 185 mg (716 μmol, 2.0 eq.) Schwartz reagent were suspended in 2.24 ml anhydrous DCM (0.16 M) in the absence of light. The reaction mixture was stirred for 2.5 h at room temperature until the white precipitate was completely dissolved. Saturated NH<sub>4</sub>Cl solution was added and the phases were separated. The aqueous phase was extracted three times with pentane. The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO<sub>2</sub>, CyH/EE 0-3%). The product **10d** (153 mg, 313 μmol, 87%) was obtained as a colourless oil.

143 mg (294 μmol) Boronic esters **10d** was subjected to oxidation according to GP-4 using 587 μl THF, 134 μl (49.9 mg, 1.47 mmol, 33%wt) aqueous H<sub>2</sub>O<sub>2</sub> solution and a solution of 58.7 mg (1.47 mmol) NaOH in 587 μl water. The reaction was worked up after 1 h. To improve chromatographic separation, 21.1 mg (352 μmol) methylboronic acid and 1.47 ml diethyl ether were used. After column chromatography (SiO<sub>2</sub>, CyH/EE 0-20%; C18-SiO<sub>2</sub>, H<sub>2</sub>O → MeCN), the product **11d** (60.5 mg, 224 μmol, 76%) was obtained as a colourless oil. R<sub>f</sub> (**11d**) = 0.29 (pentane/EE 8:2). [α]<sub>D</sub><sup>20</sup> = -8.8 (c = 1.0, CHCl<sub>3</sub>).



**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.40–7.18 (m, 7 H, 1-H, 2-H, 3-H, -H), 7.04–6.99 (m, 2 H, -H), 6.54 (d,  $J$  = 11.6 Hz, 10-H), 5.71 (dt,  $J$  = 11.7 Hz, 7.3 Hz, 1H, 9-H), 3.80–3.73 (m, 1 H, 7-H), 2.83–2.74 (m, 1 H, 5-Ha), 2.71–2.63 (m, 1 H, 5-Hb), 2.56–2.45 (m, 2 H, 8-H), 1.84–1.78 (m, 2 H, 6-H), 1.54 (d,  $J$  = 4.2 Hz, 1-H, OH) ppm.

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 161.6 ( $J$  = 246.5 Hz, C-14), 141.8 (C-4), 133.5 ( $J$  = 8.1 Hz, C-12), 130.6 (C-10), 130.3 ( $J$  = 8.1 Hz, C-11), 128.4 (C-3), 128.4 (C-2), 128.0 (C-9), 125.9 (C-1), 115.1 ( $J$  = 21.3 Hz, C-13), 71.0 (C-7), 38.6 (C-6), 36.3 (C-8), 32.0 (C-5) ppm.

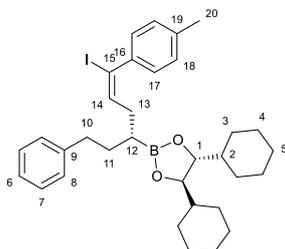
**<sup>19</sup>F-NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = -115.20 ppm.

**HRMS** (CI)  $m/z$  calcd for C<sub>18</sub>H<sub>19</sub>FO [M]<sup>+</sup>: 270.1420, found: 270.1419.

**(4*R*,5*R*)-4,5-Dicyclohexyl-2-((*R,E*)-5-iodo-1-phenyl-6-(*p*-tolyl)hex-5-en-3-yl)-1,3,2-dioxaborolane and (4*R*,5*R*)-4,5-dicyclohexyl-2-((*R,E*)-6-iodo-1-phenyl-6-(*p*-tolyl)hex-5-en-3-yl)-1,3,2-dioxaborolane (**12b** & **13b**)**

132 mg (274  $\mu$ mol, 1.0 eq.) Boronic ester **9b** and 141 mg (584  $\mu$ mol, 2.0 eq.) Schwartz reagent were suspended in 2.42 ml anhydrous DCM in the absence of light. The reaction mixture was stirred for 2.5 h at room temperature until the white precipitate was completely dissolved. Then, a solution of 123 mg (548  $\mu$ mol, 2.0 eq.) *N*-iodosuccinimide in 1.10 ml anhydrous THF was added dropwise and the reaction mixture was stirred for 30 min at room temperature. Pentane and a 1:1 (v/v) mixture of saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and NaHCO<sub>3</sub> solution were added. The phases were separated and the aqueous phase was extracted twice with pentane. The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (cyclohexane/ethyl acetate 0-3%). The products **12b** (89.0 mg, 145  $\mu$ mol, 53%) and **13b** (55.2 mg, 90.0  $\mu$ mol, 33%) were obtained as a colourless oil and as a mixture.  $R_f$  (**12b**) =  $R_f$  (**13b**) = 0.36 (pentane/EE 97:3).  $[\alpha]_D^{20}$  = +32.8 ( $c$  = 1.0, CHCl<sub>3</sub>).

Major regioisomer **12b**:



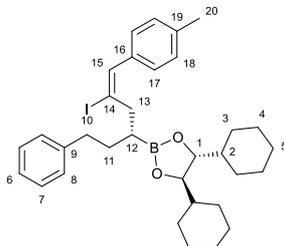
**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.29–7.21 (m, 2 H, 7-H), 7.20–7.05 (m, 7 H, 6-H, 8-H, 17-H, 18-H), 6.47 (t,  $J$  = 7.4 Hz, 1 H, 14-H), 3.86–3.85 (m, 2 H, 1-H), 2.55–2.49 (m, 2 H, 10-H), 2.33 (s, 3 H, 20-H), 2.17–2.13 (m, 2 H, 13-H), 1.81–1.50 (m, 12 H, 3-Ha, 3-Hb, 4-Ha, 4-Hb, 5-Ha, 11-H), 1.33–0.96 (m, 13 H, 2-H, 3-Hc, 3-Hd, 4-Hc, 4-Hd, 5-Hb, 12-H) ppm.

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 143.0 (C-14), 142.6 (C-9), 141.4 (C-18), 137.7 (C-19), 134.9 (C-16), 129.0 (C-17), 128.7 (C-8), 128.2 (C-7), 125.6 (C-6), 95.3 (C-15), 83.5 (C-1), 43.1 (C-

2), 35.3 (C-10), 33.6 (C-13), 32.0 (C-11), 28.5 (C-3a), 27.6 (C-3b), 26.5 (C-5), 26.0 (C-4a), 25.9 (C-4b), 21.2 (C-20) ppm.

The signal of C-12 could not be detected.

Minor regioisomer **13b** (selected signals):



**<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>): δ = 7.20–7.05 (m, 8 H, 6-H, 8-H, 15-H, 17-H, 18-H), 3.82–3.81 (m, 2 H, 1-H), 2.71–2.67 (m, 2 H, 10-H), 2.32 (s, 3 H, 20-H) ppm.

**<sup>13</sup>C-NMR** (100 MHz, CDCl<sub>3</sub>): δ = 142.8 (C-15), 138.9 (C-19), 136.9 (C-16), 110.2 (C-14), 83.5 (C-1) ppm.

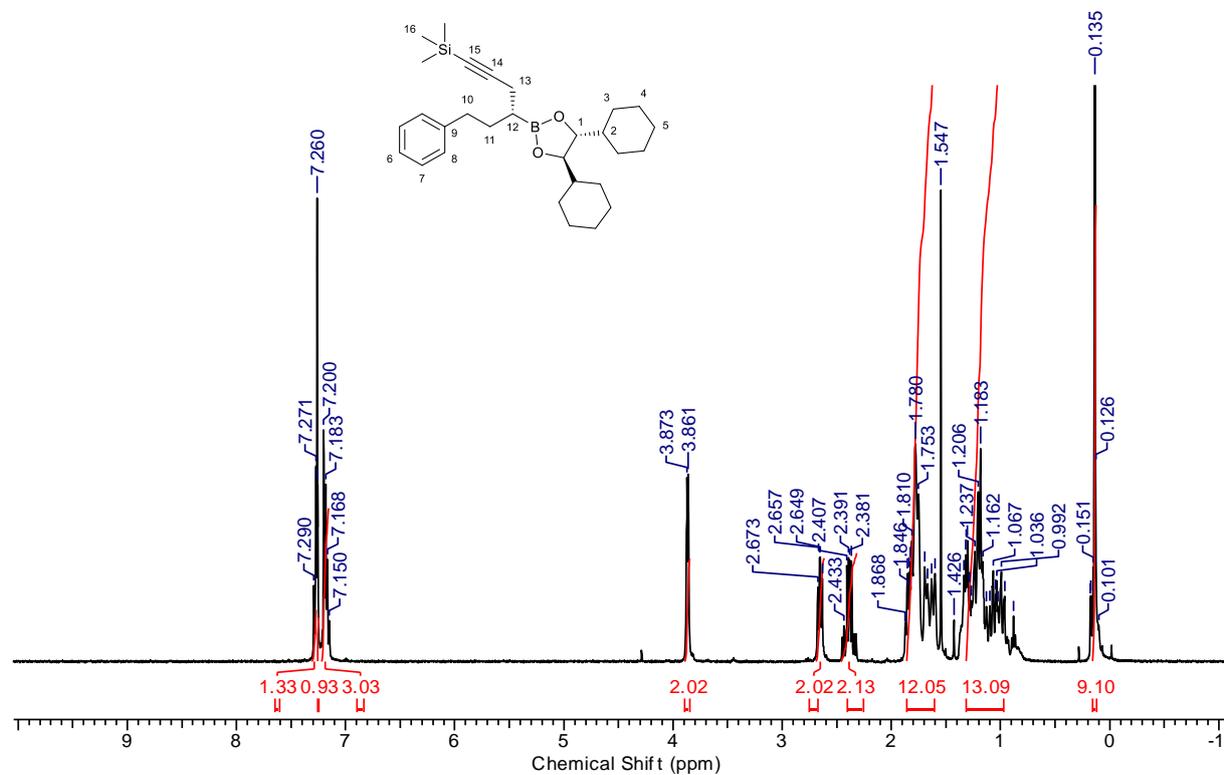
The signal of C-12 could not be detected.

**HRMS** (ESI) *m/z* calcd for C<sub>33</sub>H<sub>45</sub>BO<sub>2</sub> [M+H]<sup>+</sup>: 611.2552, found: 611.2521.

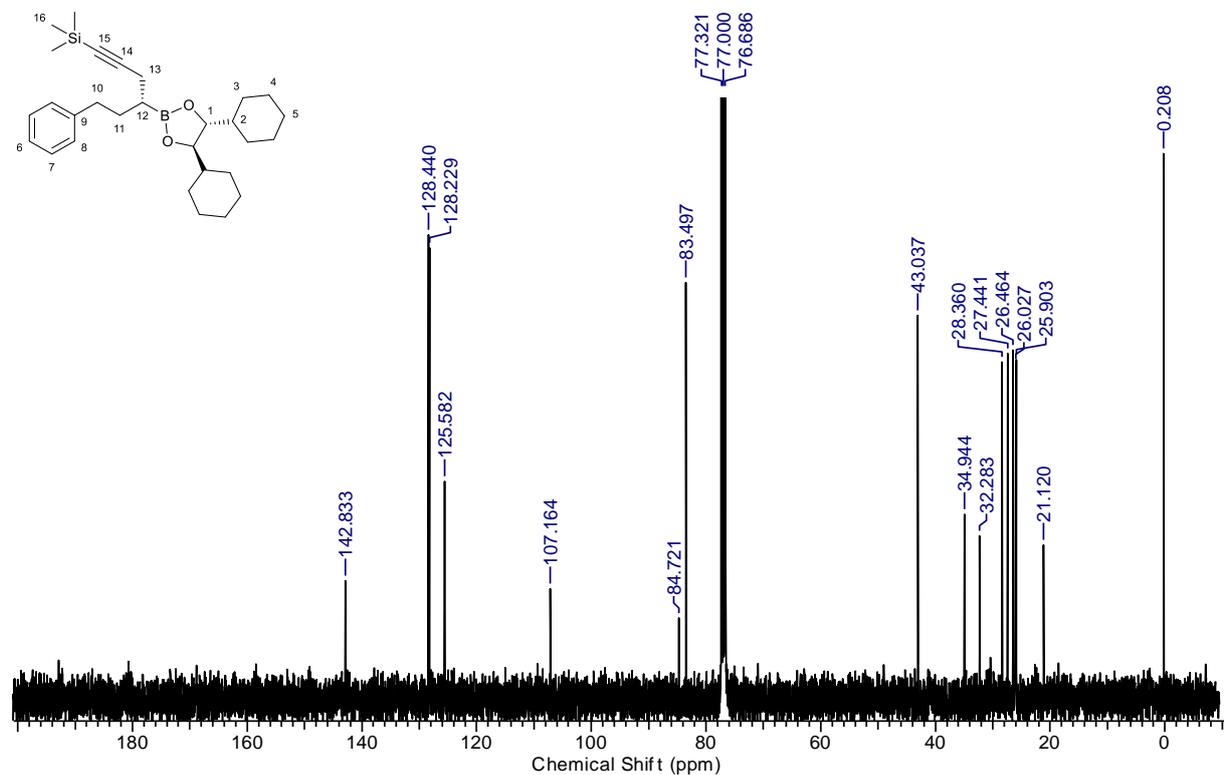
## Copies of NMR spectra

### ((*R*)-4-((4*R*,5*R*)-4,5-Dicyclohexyl-1,3,2-dioxaborolan-2-yl)-6-phenylhex-1-yn-1-yl)trimethylsilane (2)

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):

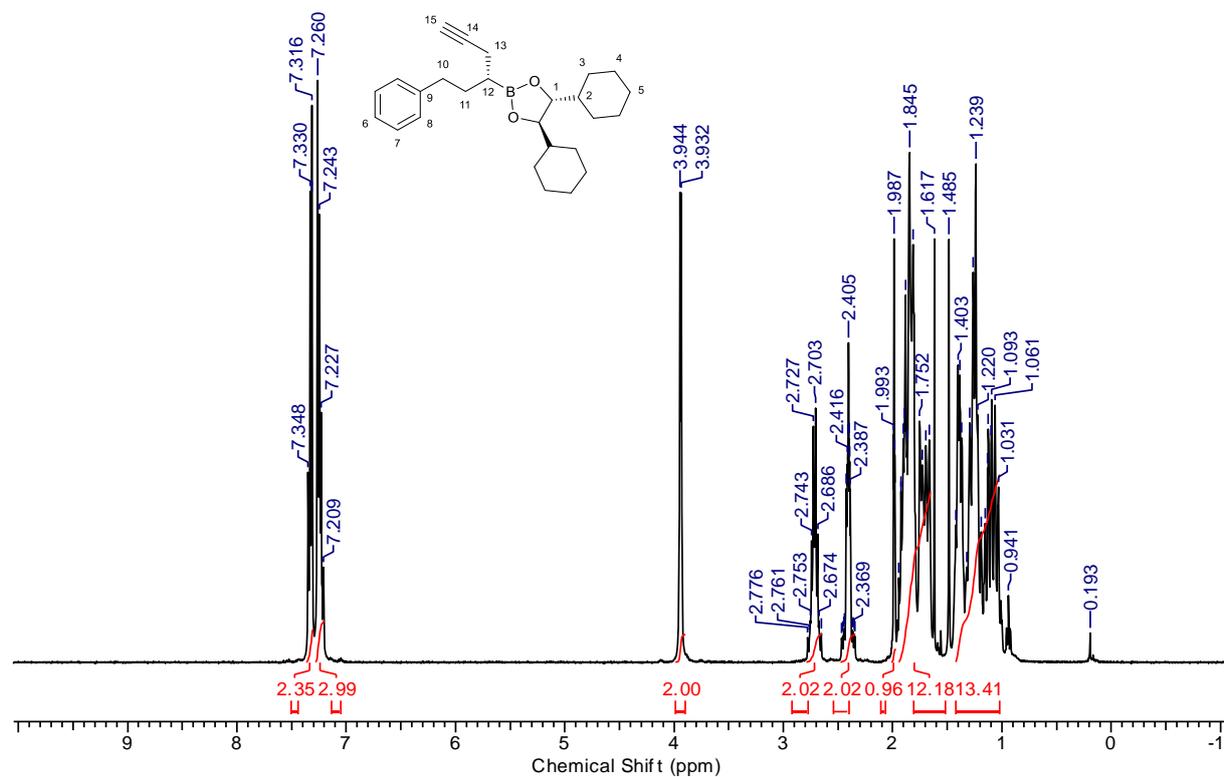


<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):

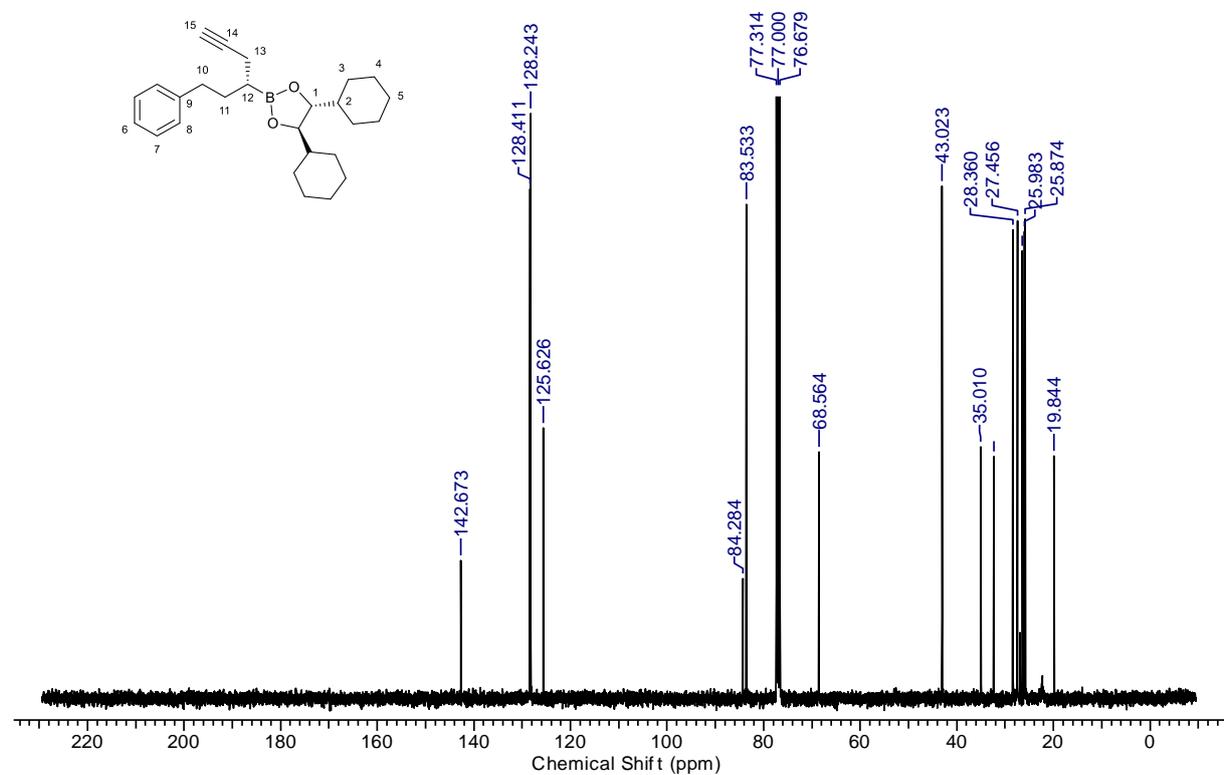


**(4*R*,5*R*)-4,5-Dicyclohexyl-2-((*R*)-1-phenylhex-5-yn-3-yl)-1,3,2-dioxaborolane (3)**

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):

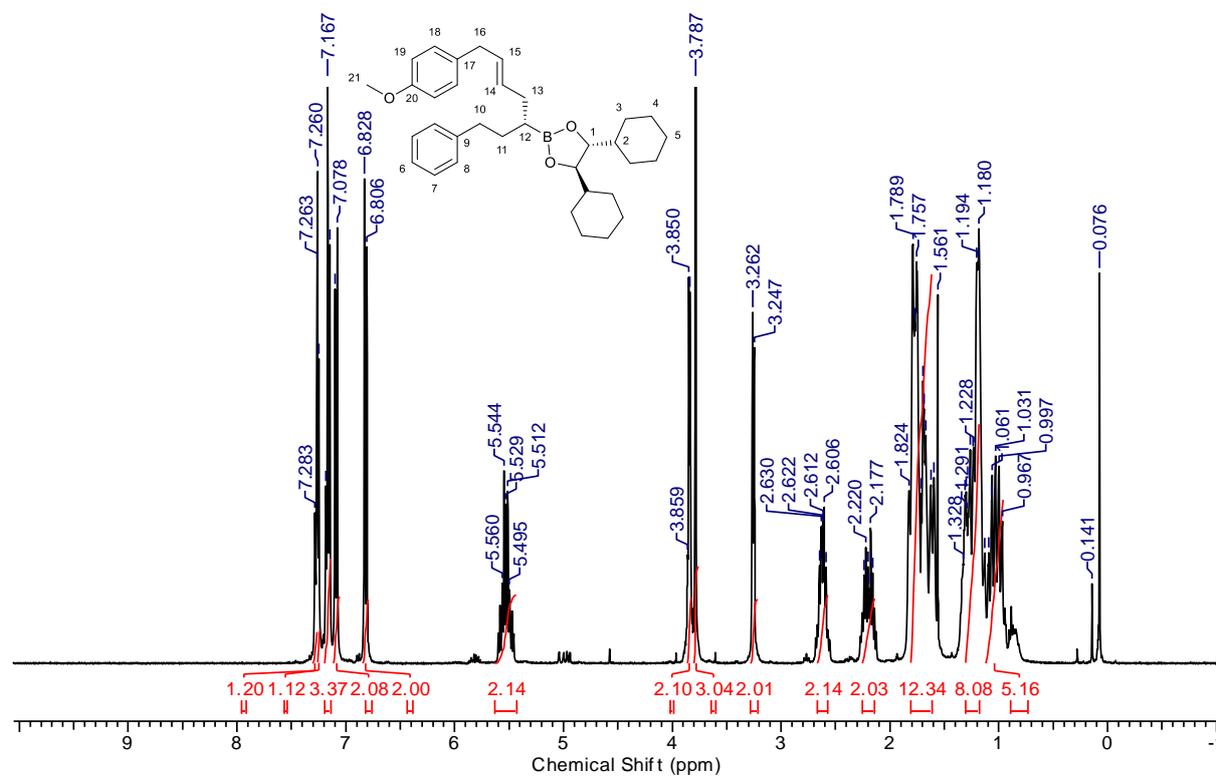


<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):

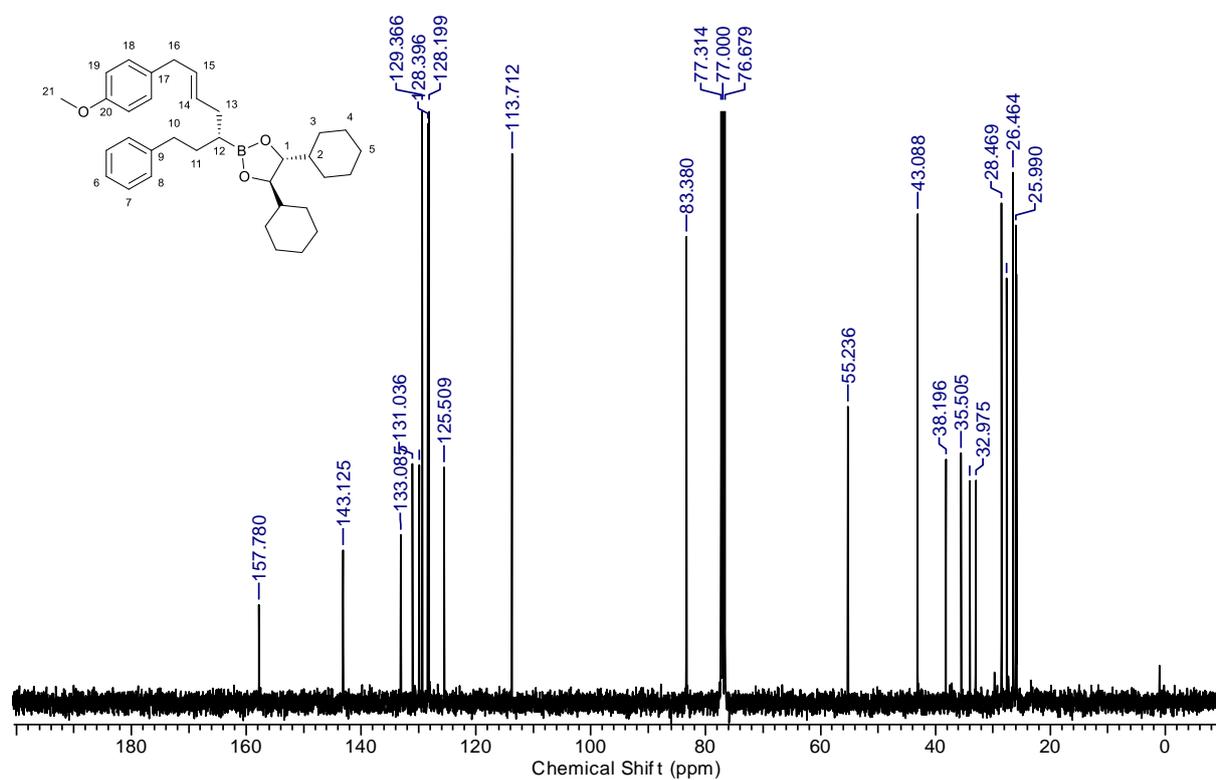


**(4*R*,5*R*)-4,5-dicyclohexyl-2-((*R*,*E*)-7-(4-methoxyphenyl)-1-phenylhept-5-en-3-yl)-1,3,2-dioxaborolane (5h)**

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):

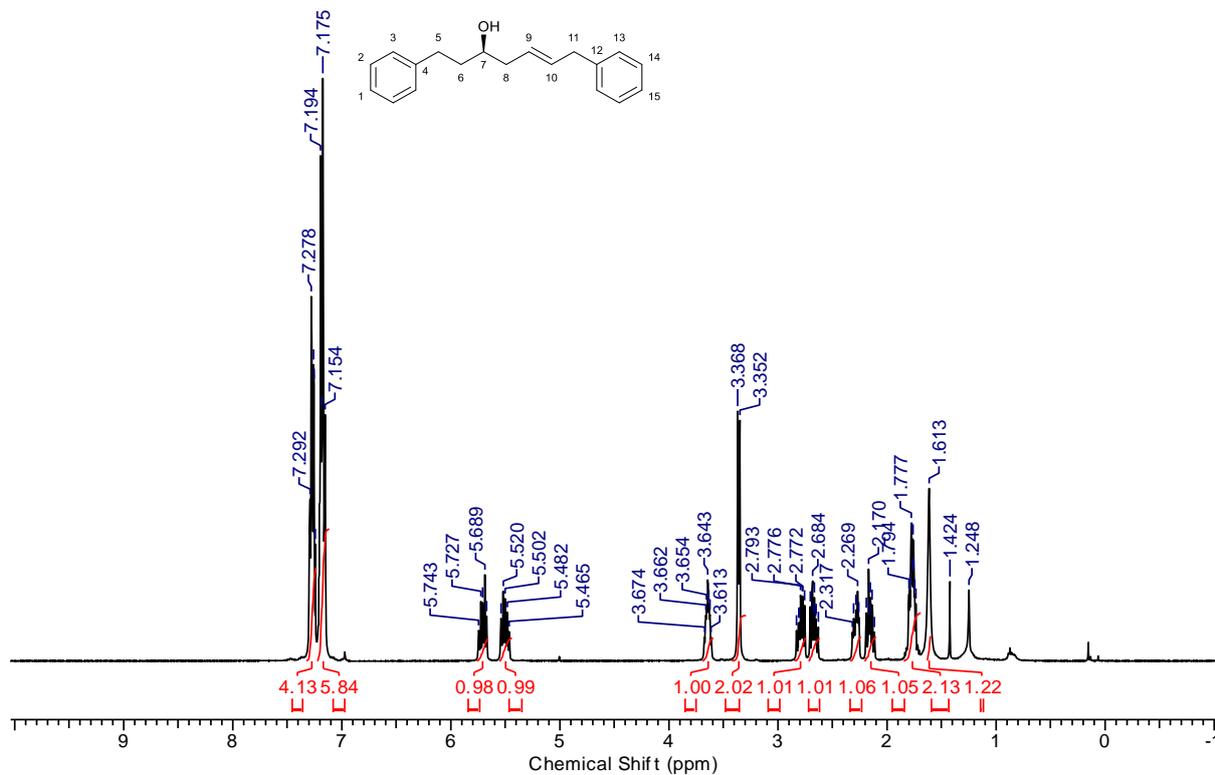


<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):

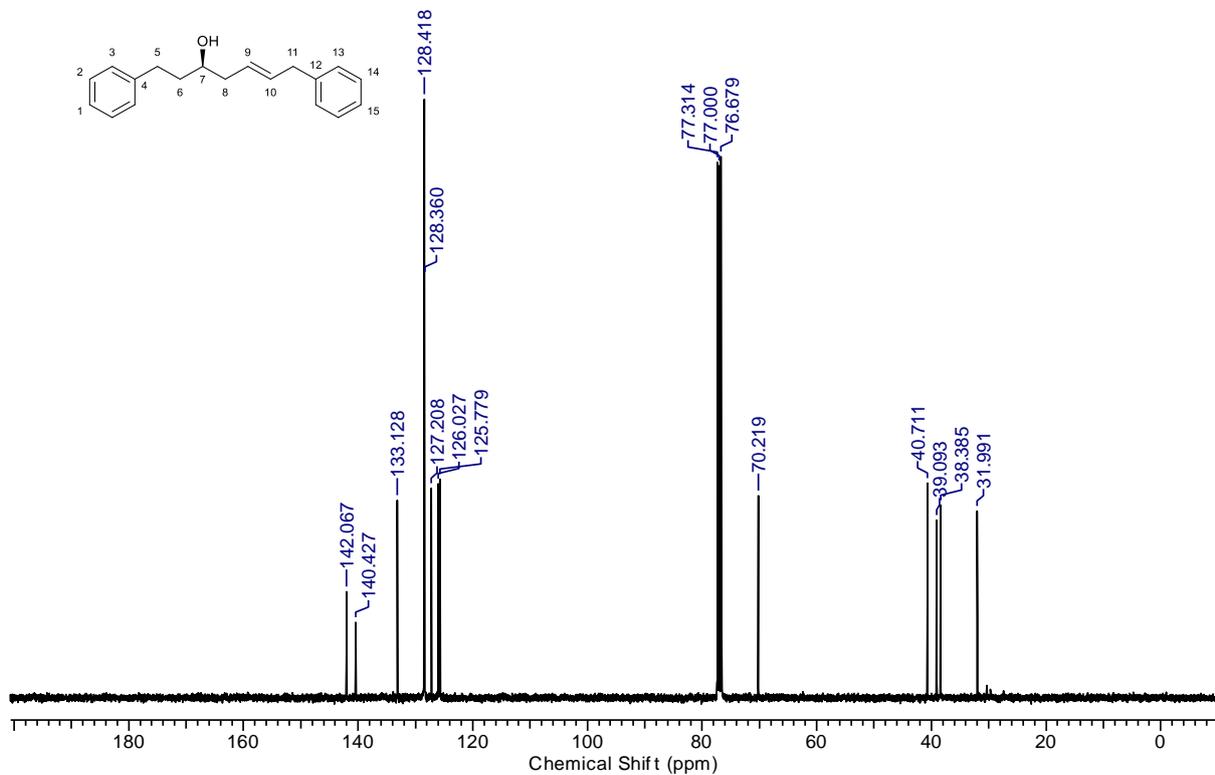


**(*R,E*)-1,7-Diphenylhept-5-en-3-ol (6a)**

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):

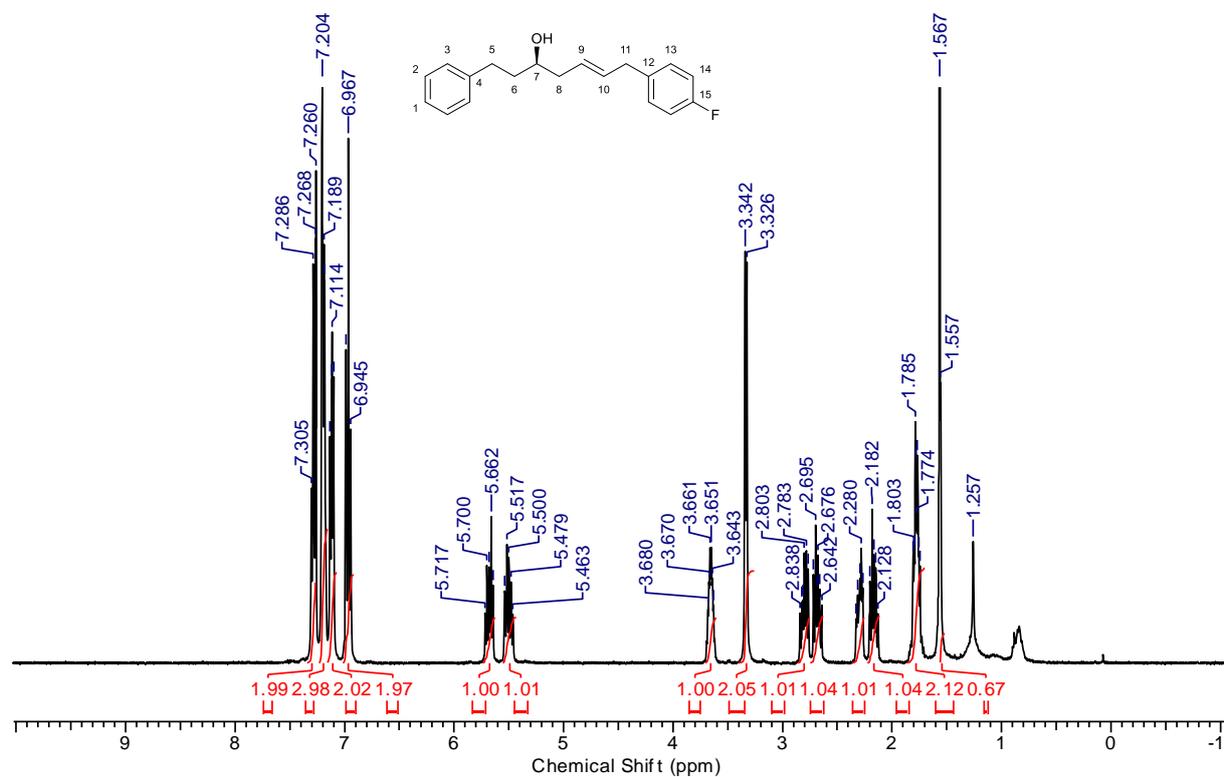


<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):

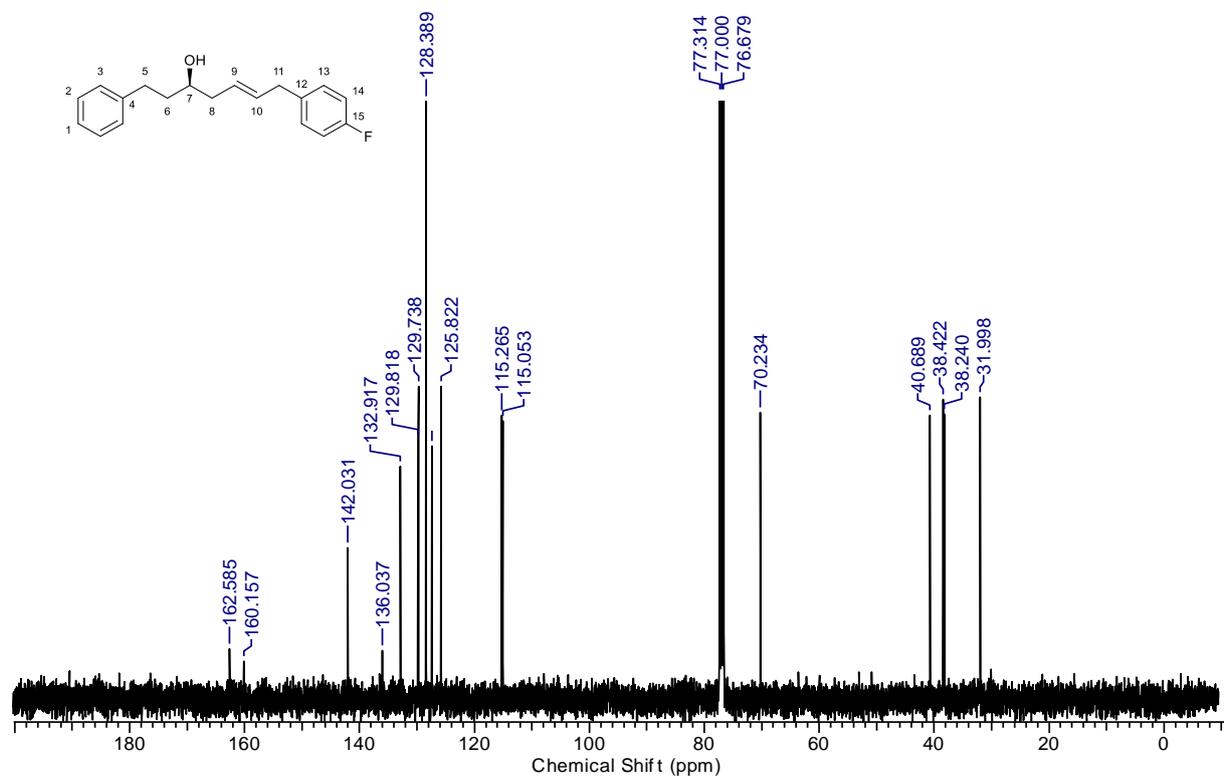


**(*R,E*)-7-(4-Fluorophenyl)-1-phenylhept-5-en-3-ol (6b)**

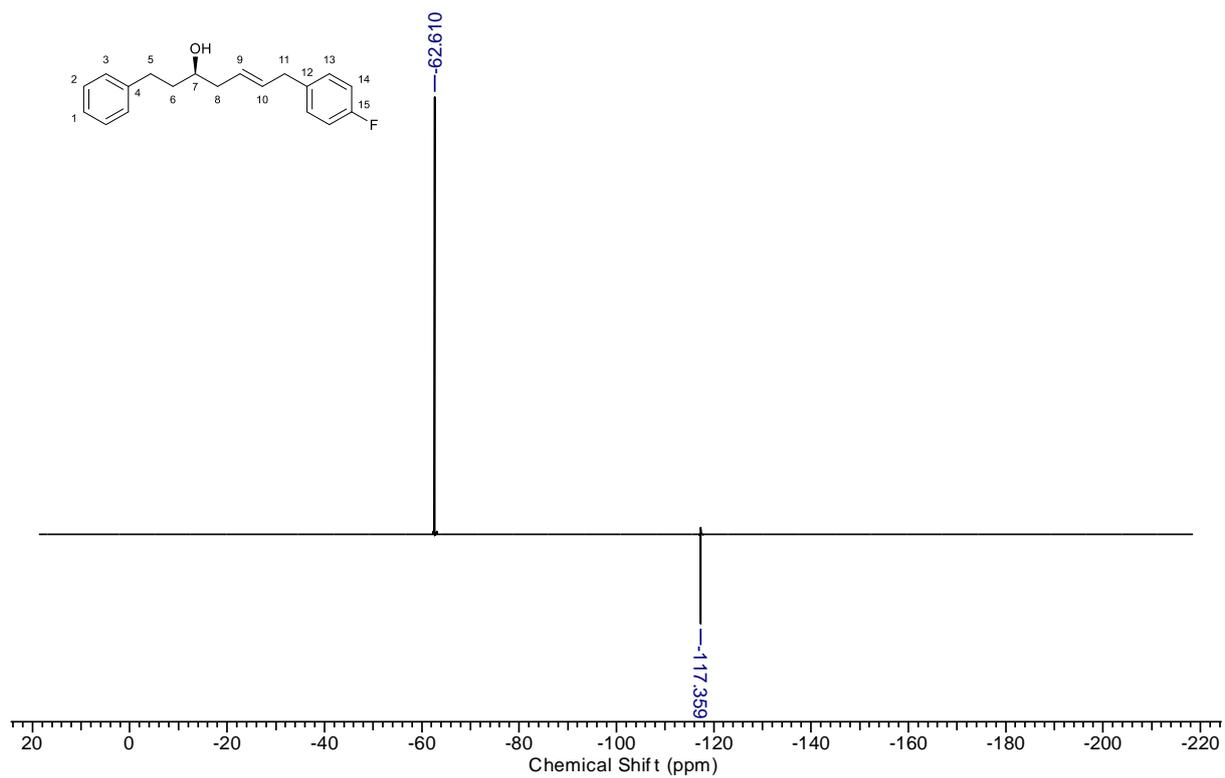
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):



<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):

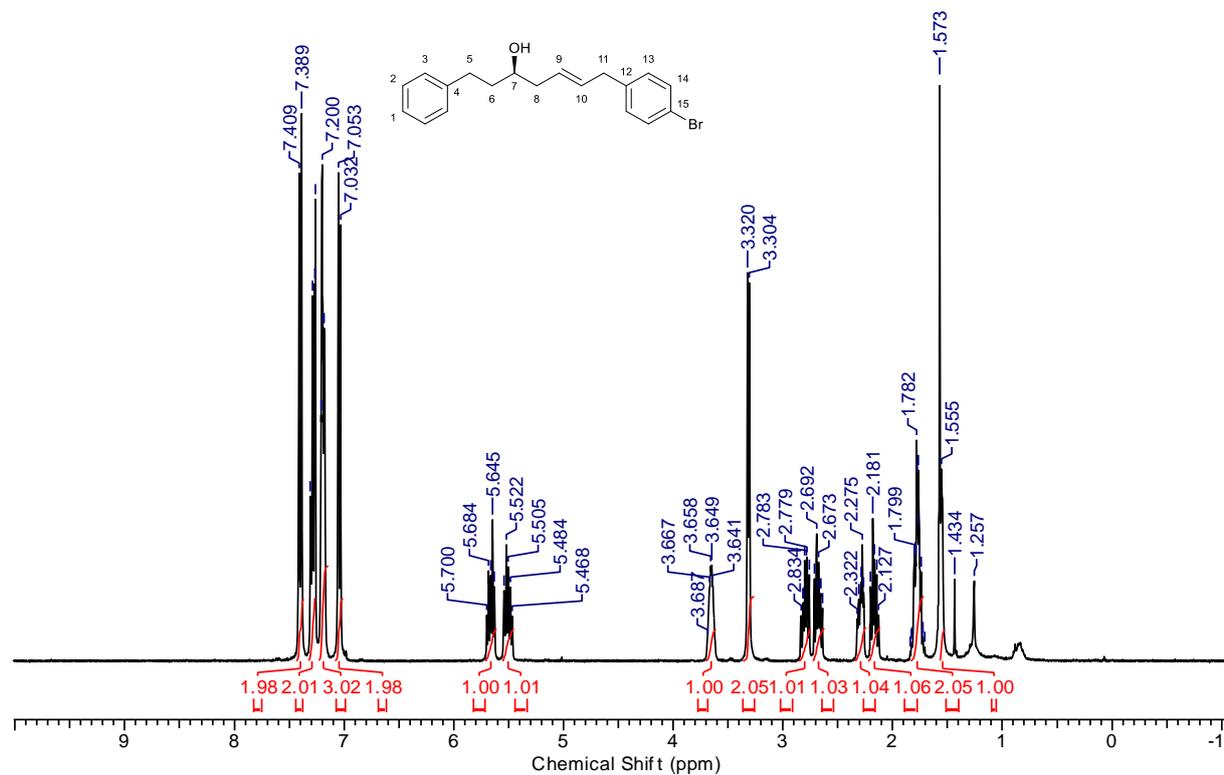


**<sup>19</sup>F-NMR (400 MHz, CDCl<sub>3</sub>):**

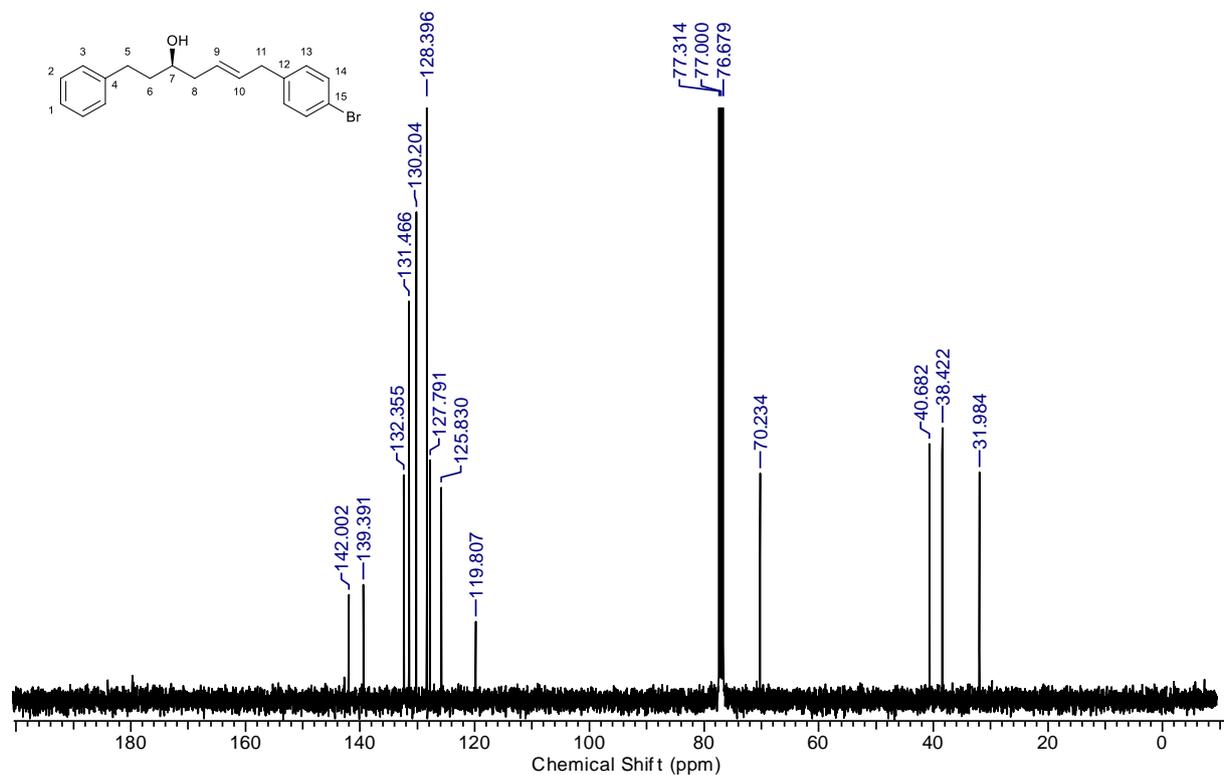


**(*R,E*)-7-(4-Bromophenyl)-1-phenylhept-5-en-3-ol (6c)**

**<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):**

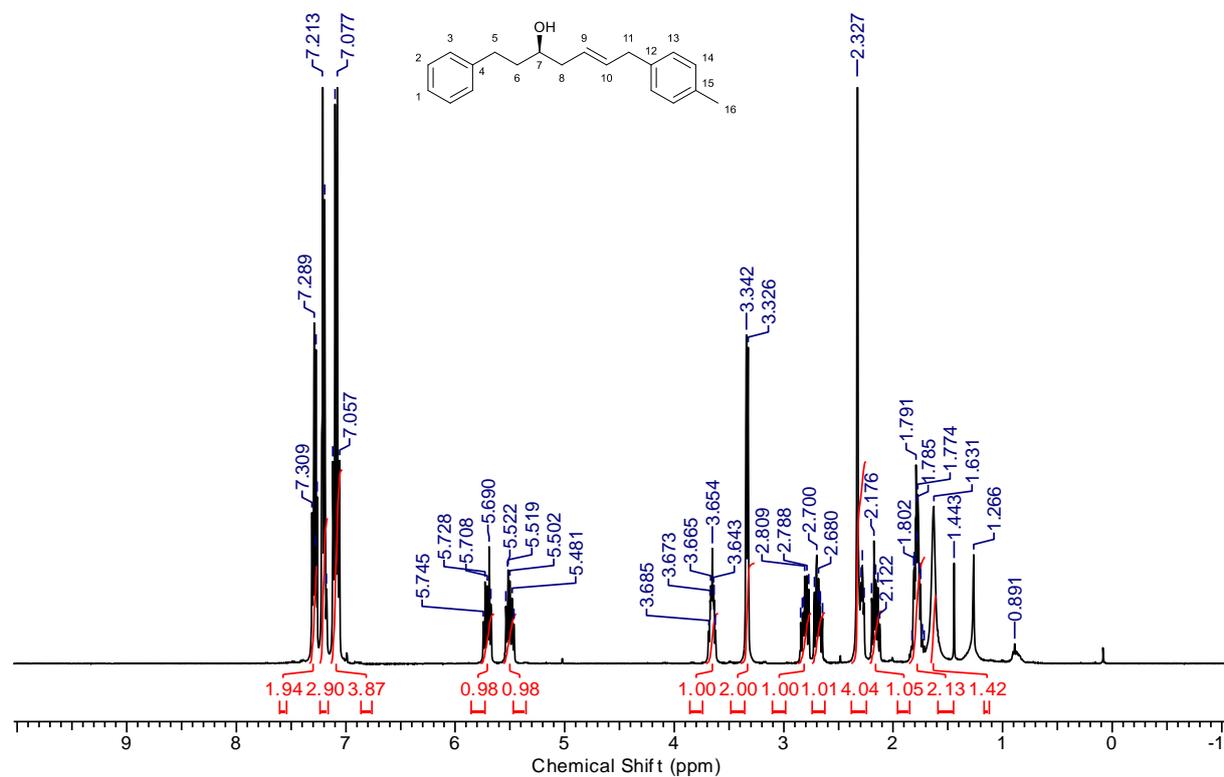


**<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):**

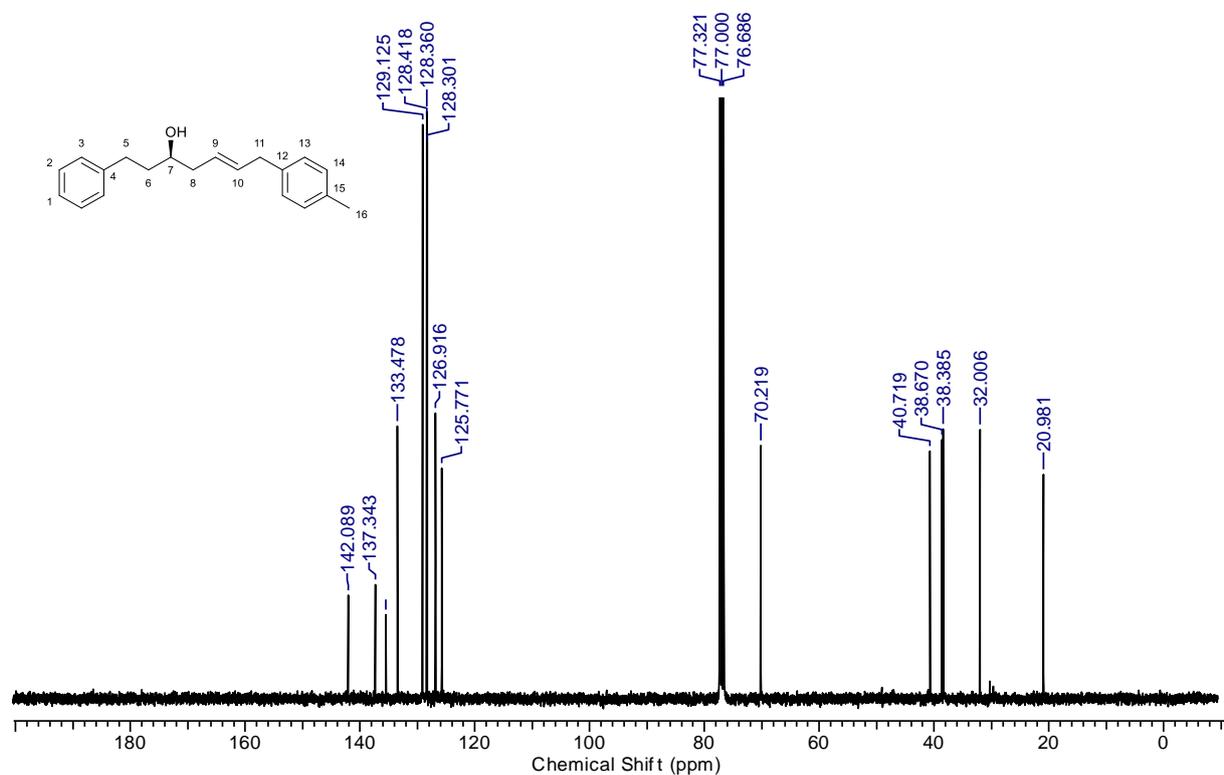


**(*R,E*)-1-Phenyl-7-(*p*-tolyl)hept-5-en-3-ol (6d)**

**<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):**

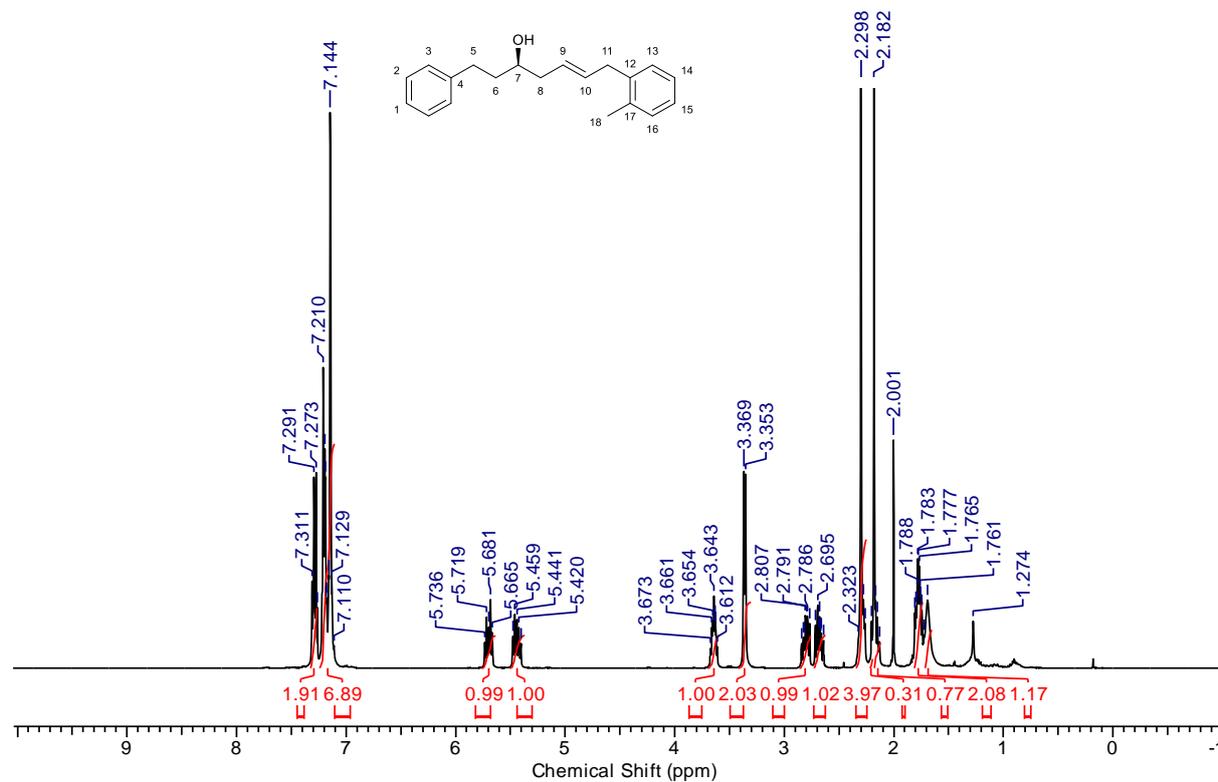


**<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):**

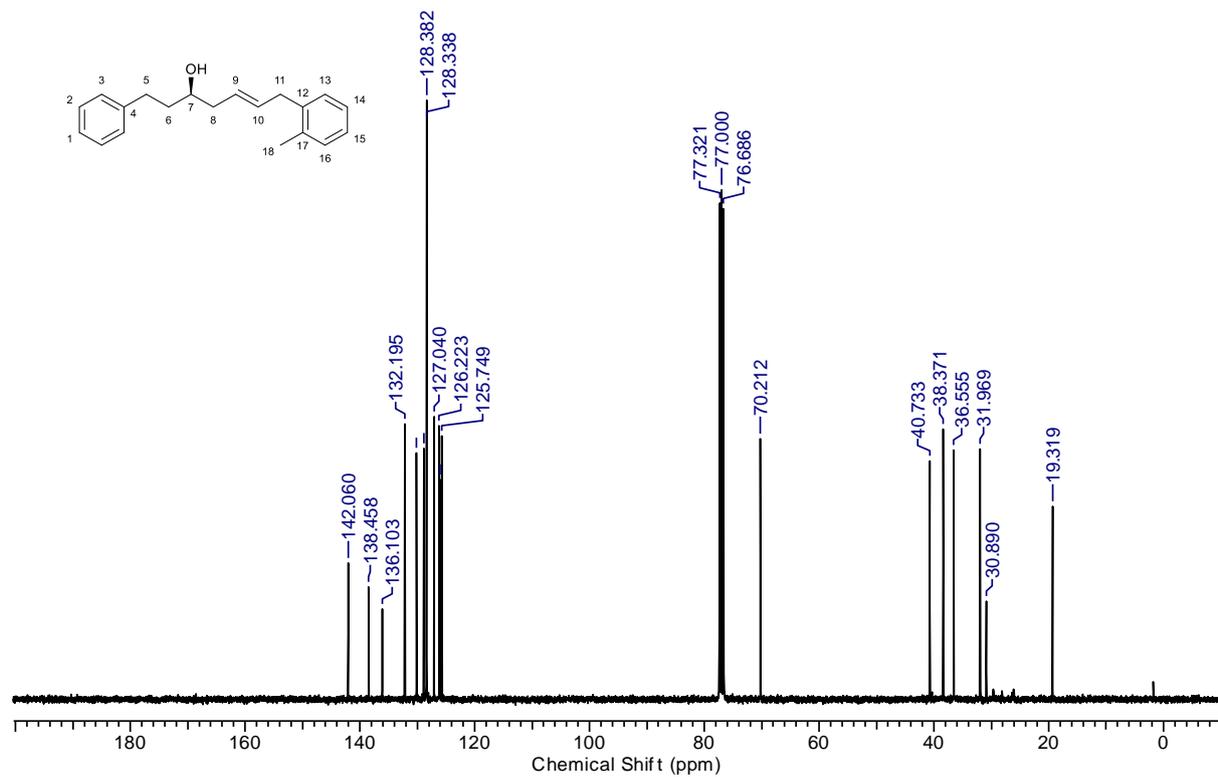


**(*R,E*)-1-Phenyl-7-(*o*-tolyl)hept-5-en-3-ol (6e)**

**<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):**

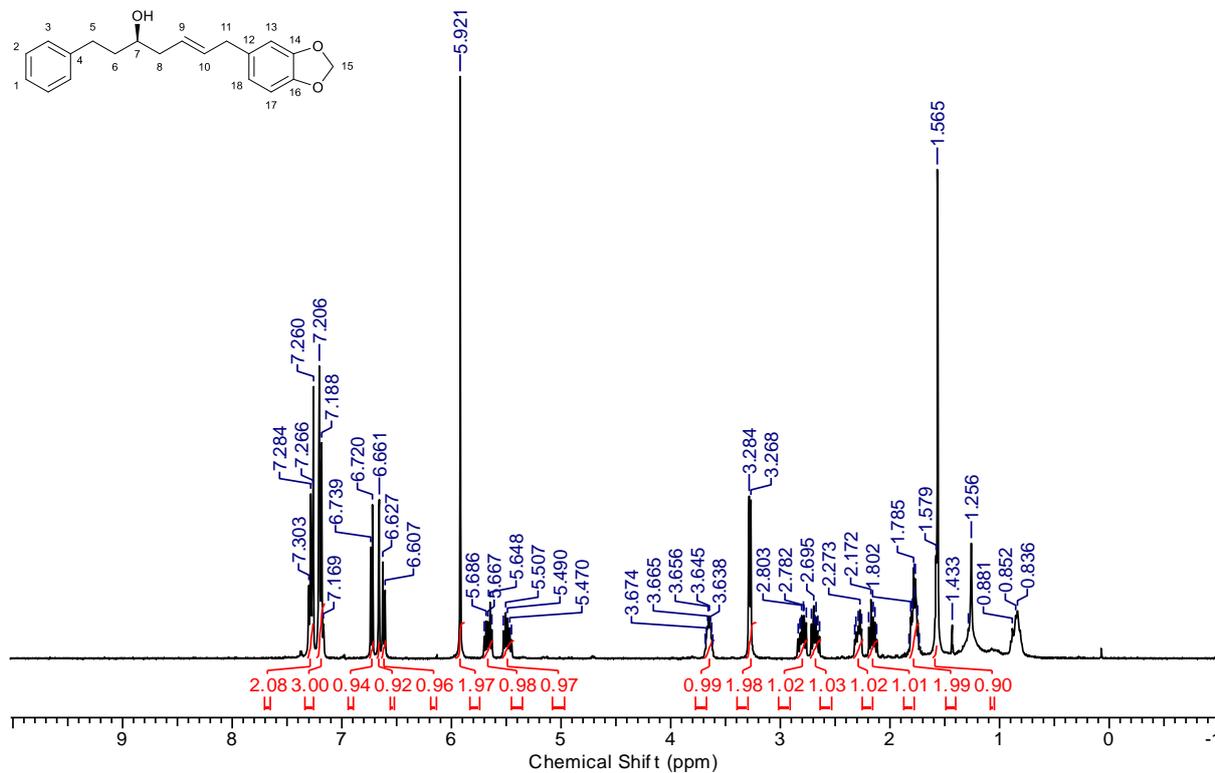


**<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):**

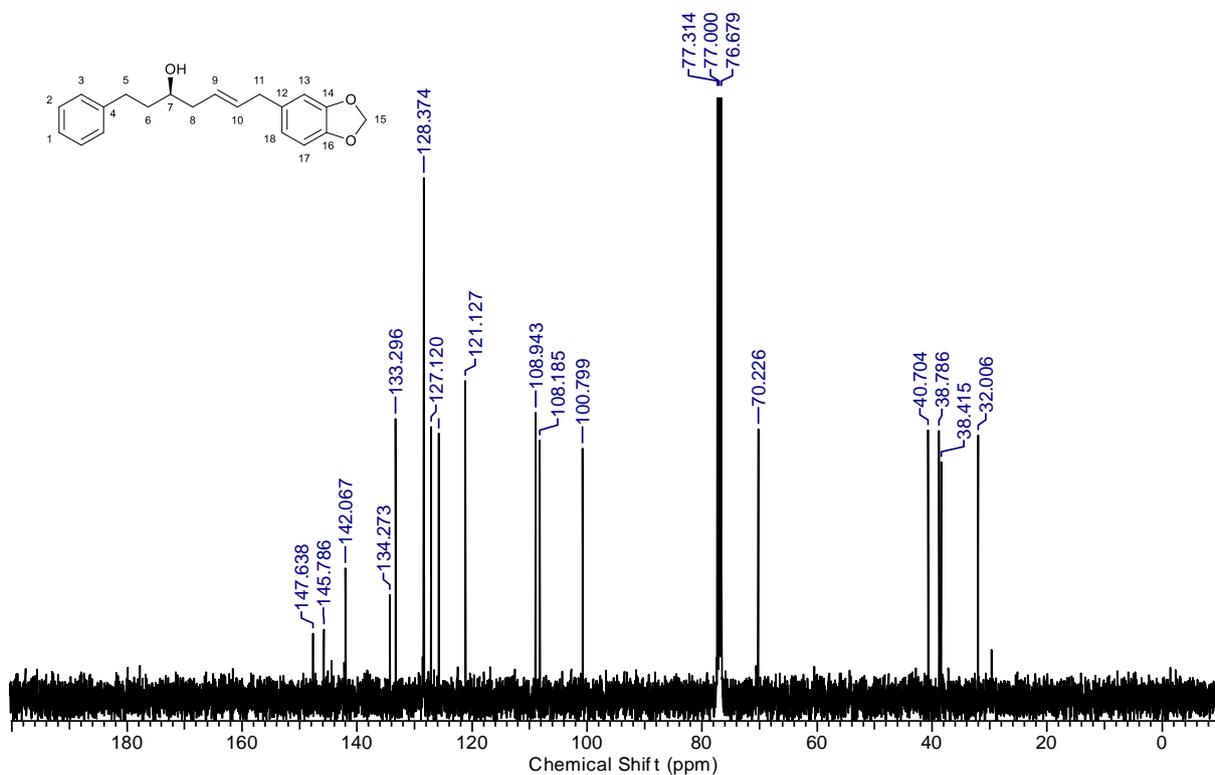


**(*R,E*)-7-(Benzo[d][1,3]dioxol-5-yl)-1-phenylhept-5-en-3-ol (6f)**

**<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):**

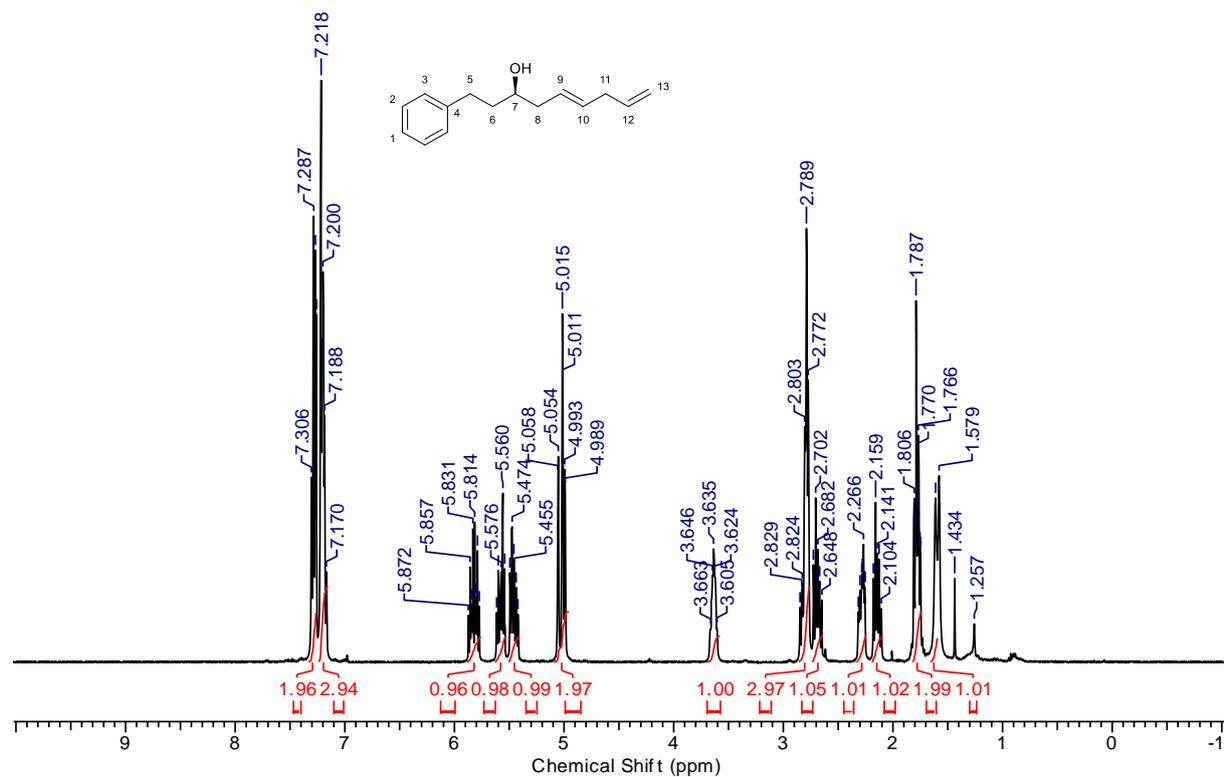


**<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):**

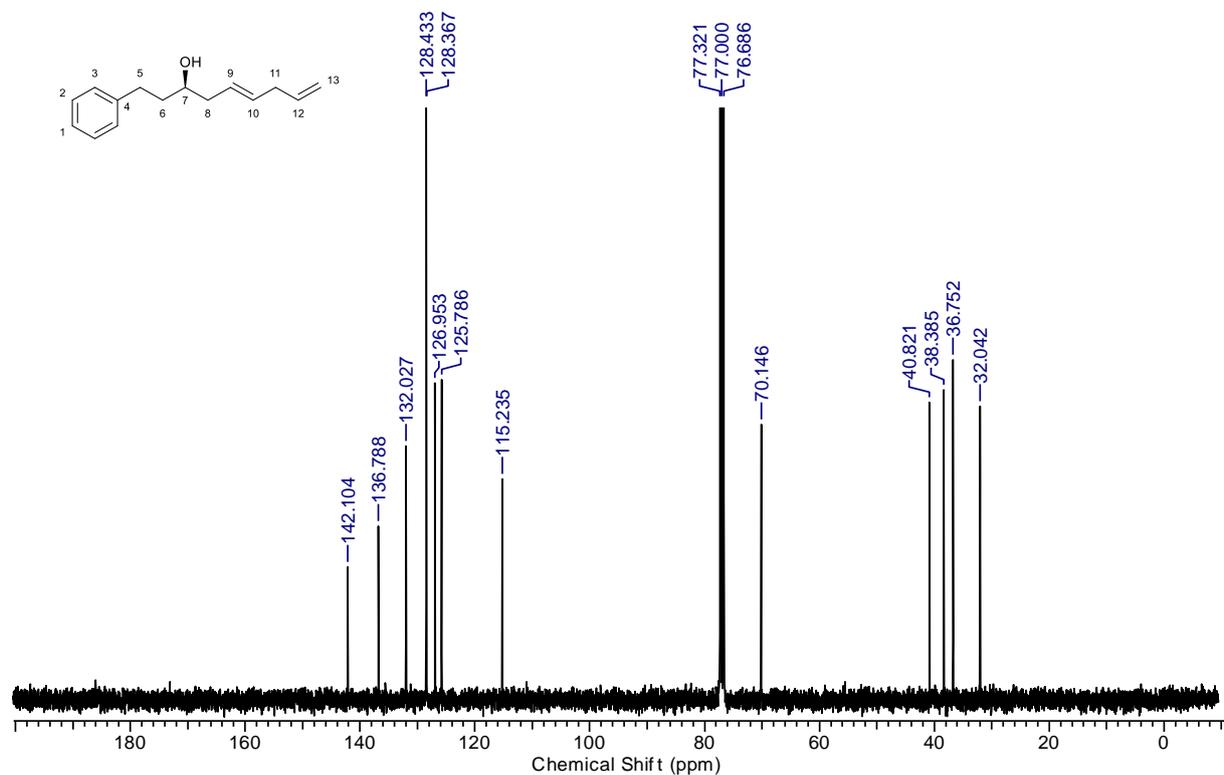


**(*R,E*)-1-phenylnona-5,8-dien-3-ol (6g)**

**<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):**

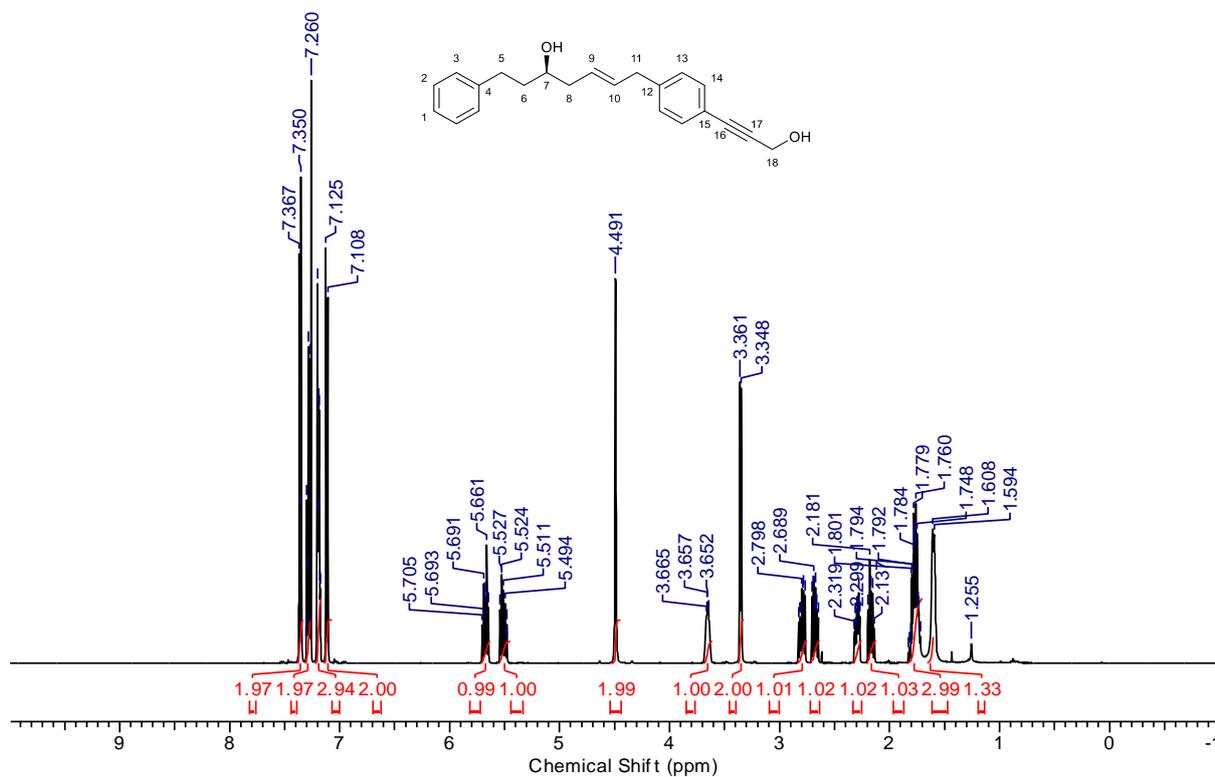


**<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):**

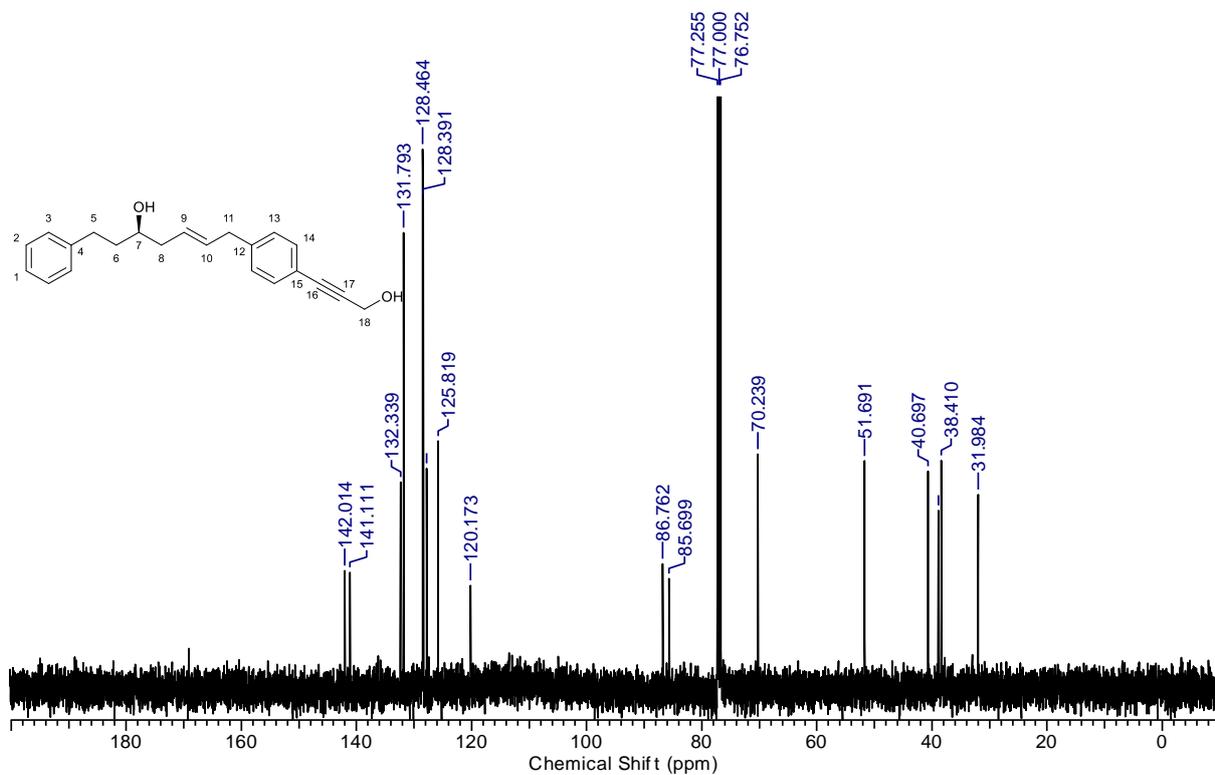


**(*R,E*)-7-(4-(3-Hydroxyprop-1-yn-1-yl)phenyl)-1-phenylhept-5-en-3-ol (6i)**

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):

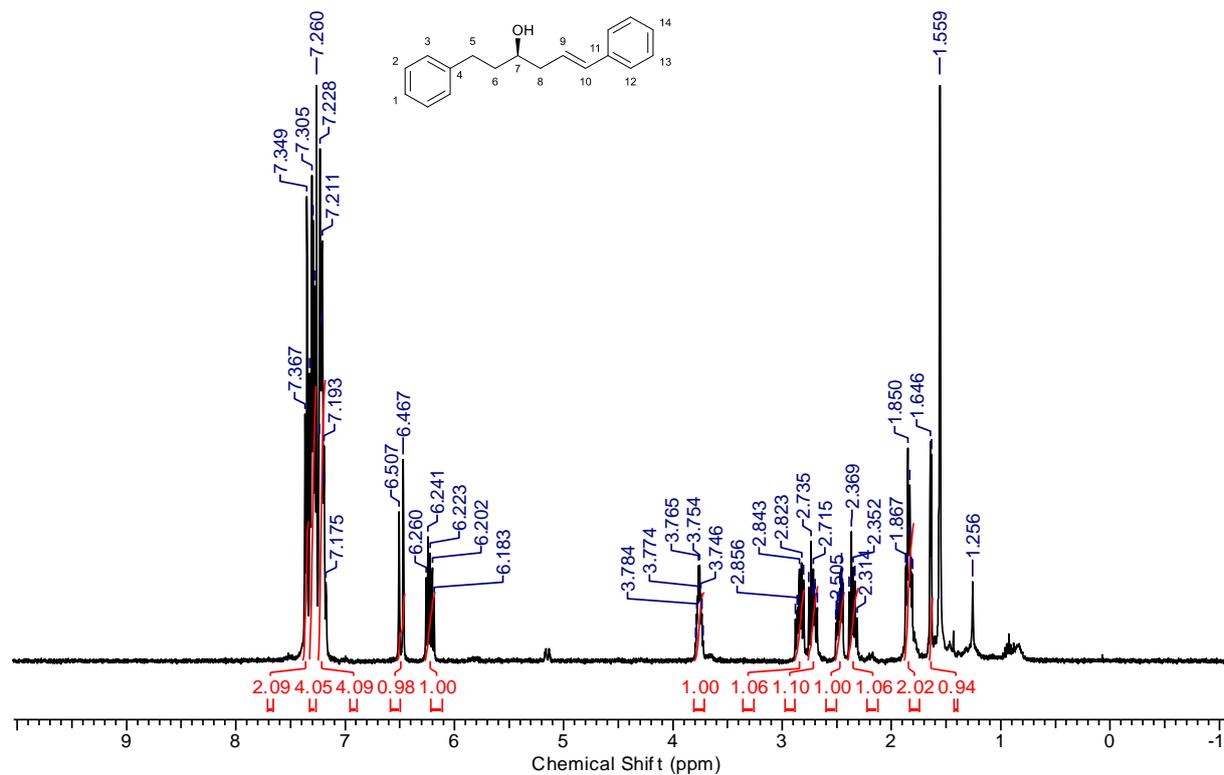


<sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>):

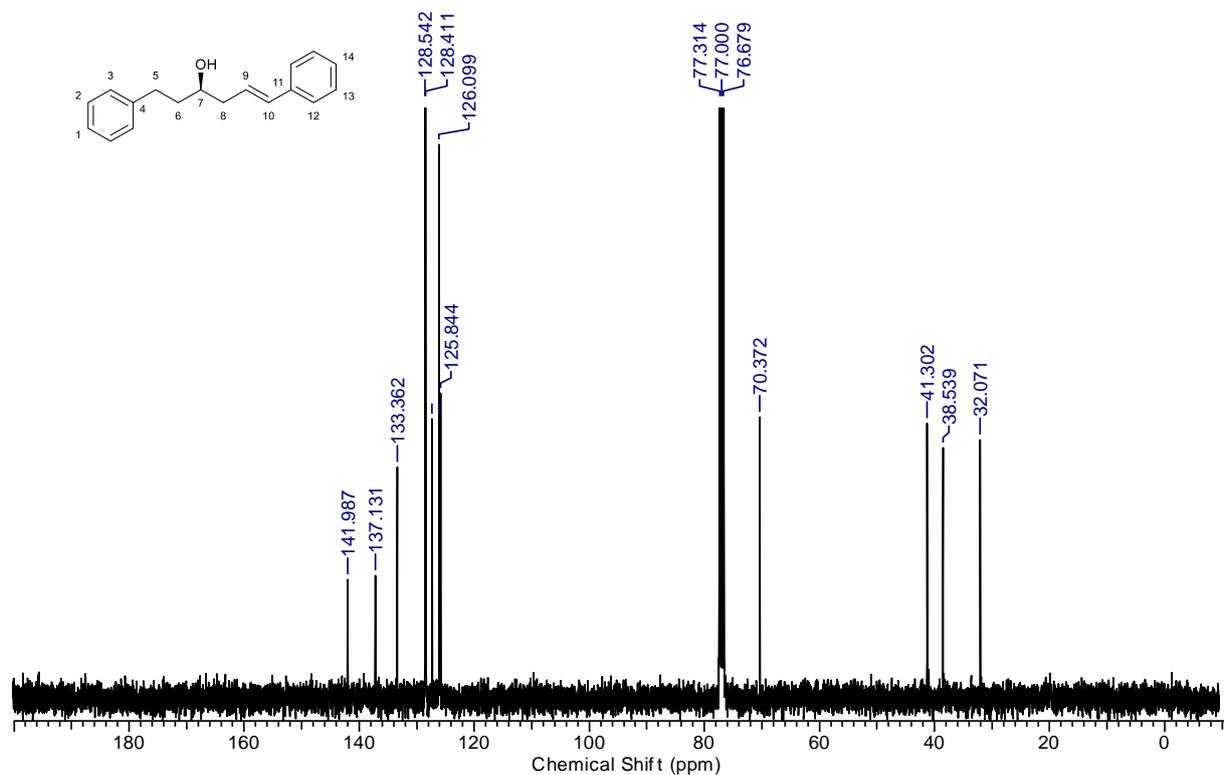


**(*R,E*)-1,6-Diphenylhex-5-en-3-ol (8a)**

**<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):**

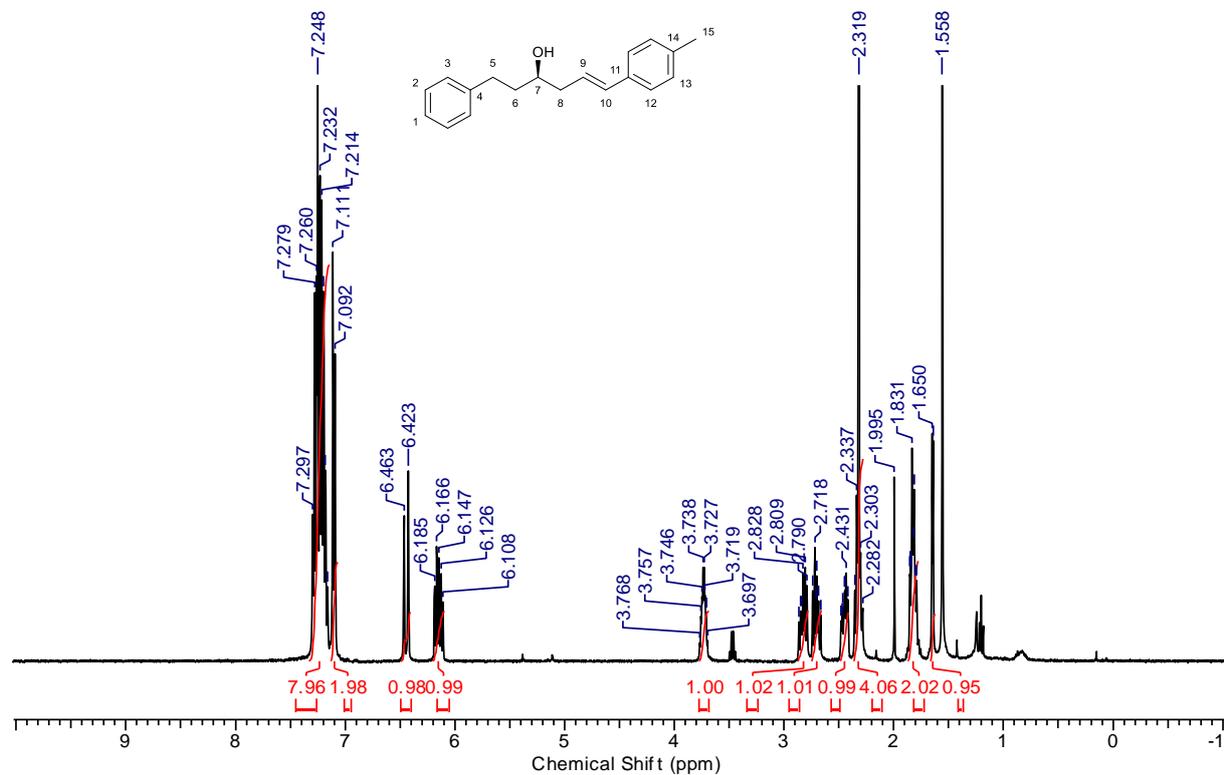


**<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):**

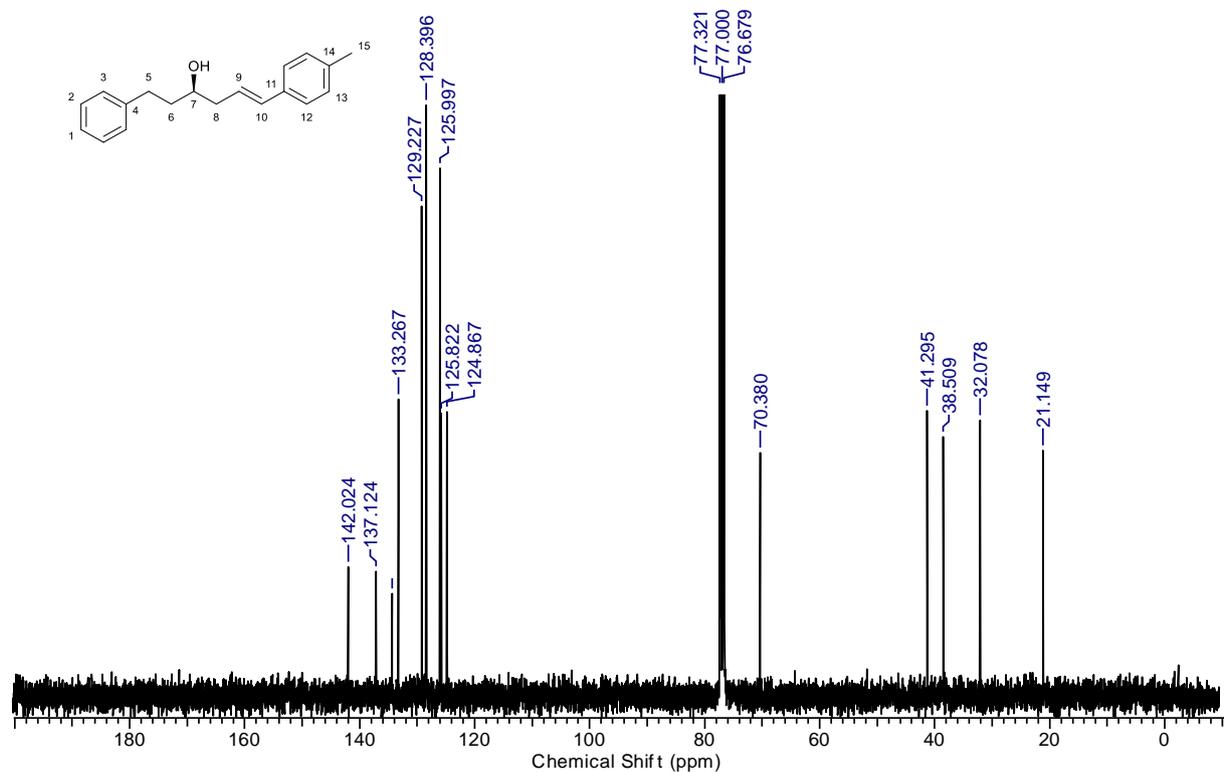


**(*R,E*)-1-Phenyl-6-(*p*-tolyl)hex-5-en-3-ol (**8b**)**

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):

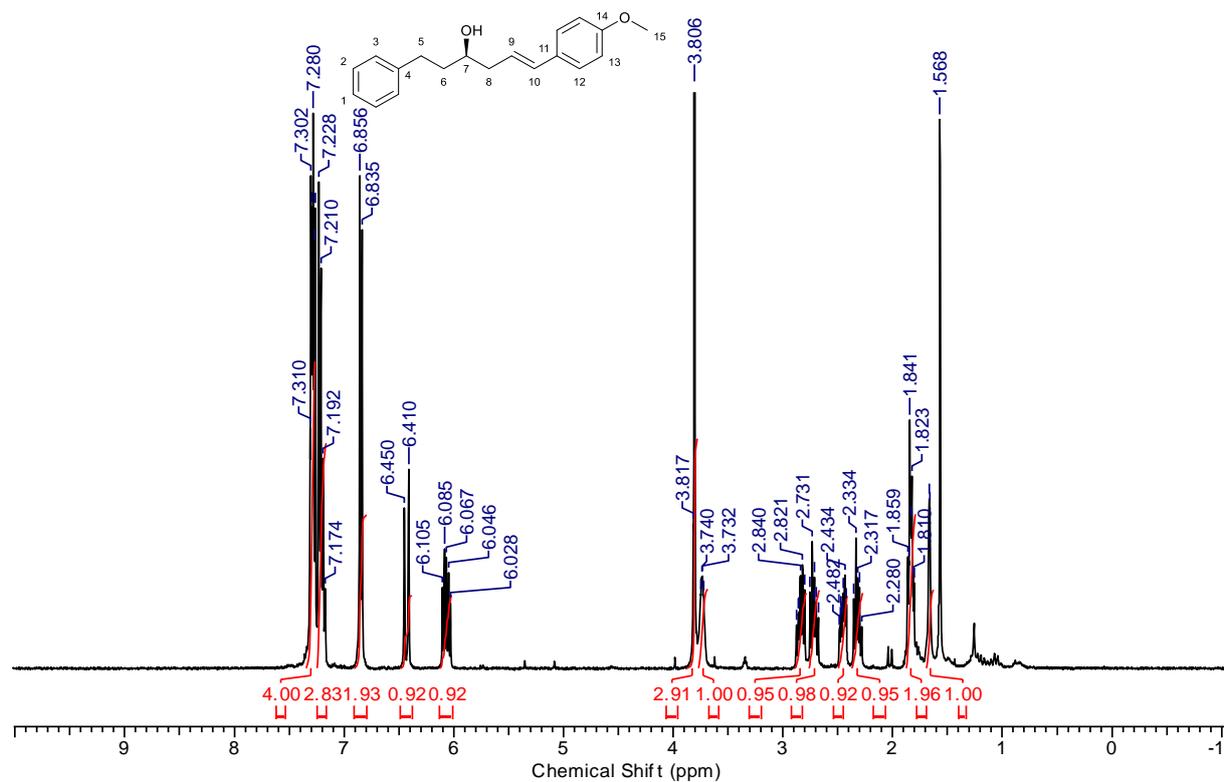


<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):

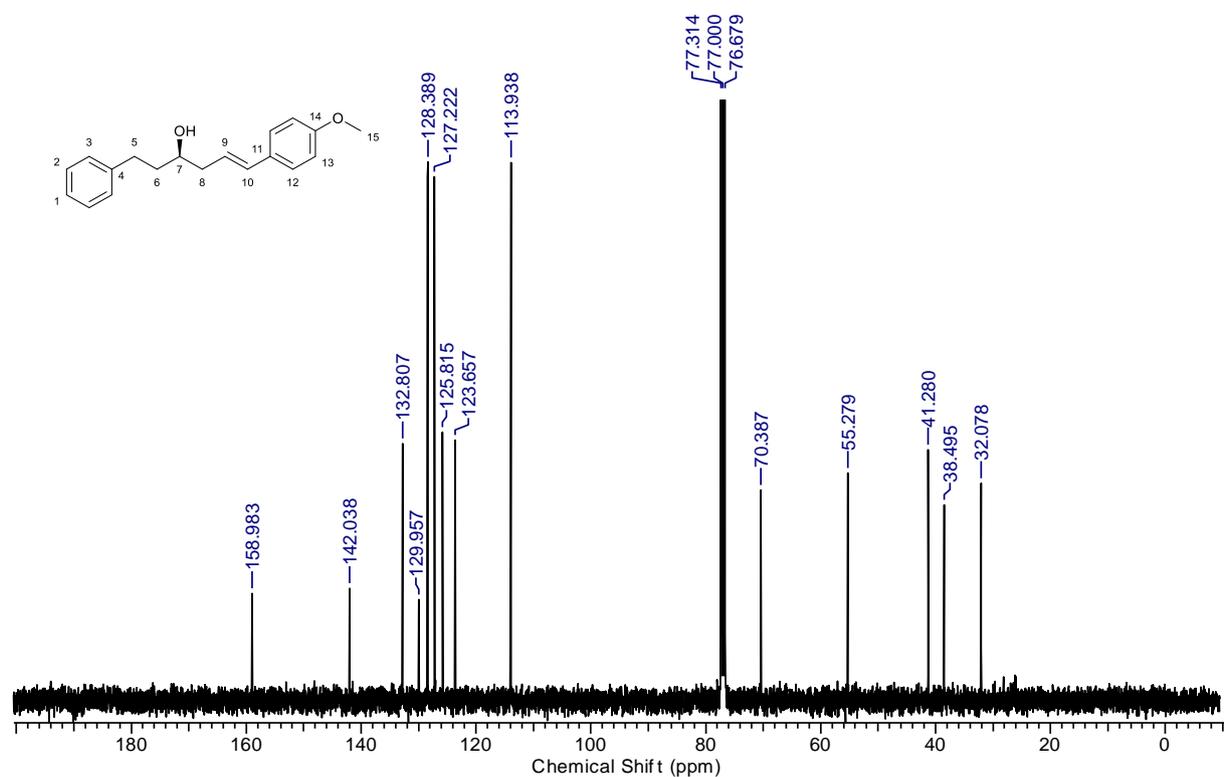


**(*R,E*)-6-(4-Methoxyphenyl)-1-phenylhex-5-en-3-ol (8c)**

**<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):**

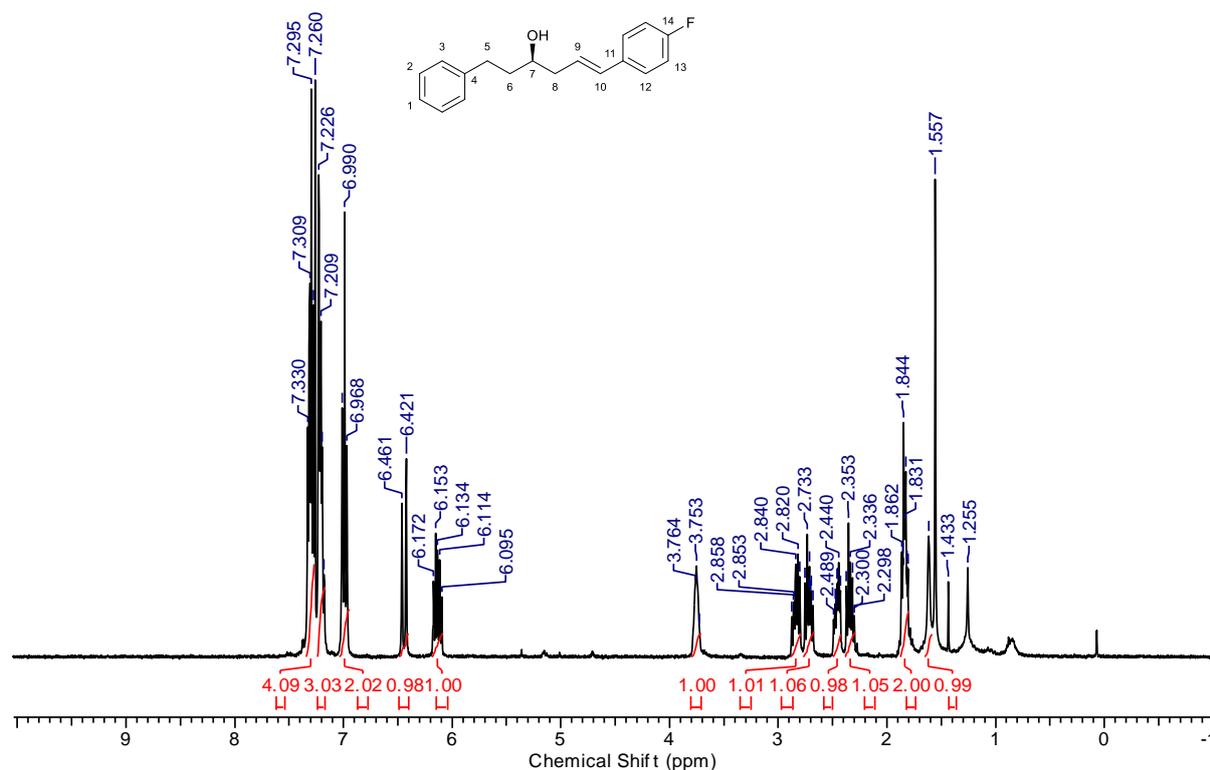


**<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):**

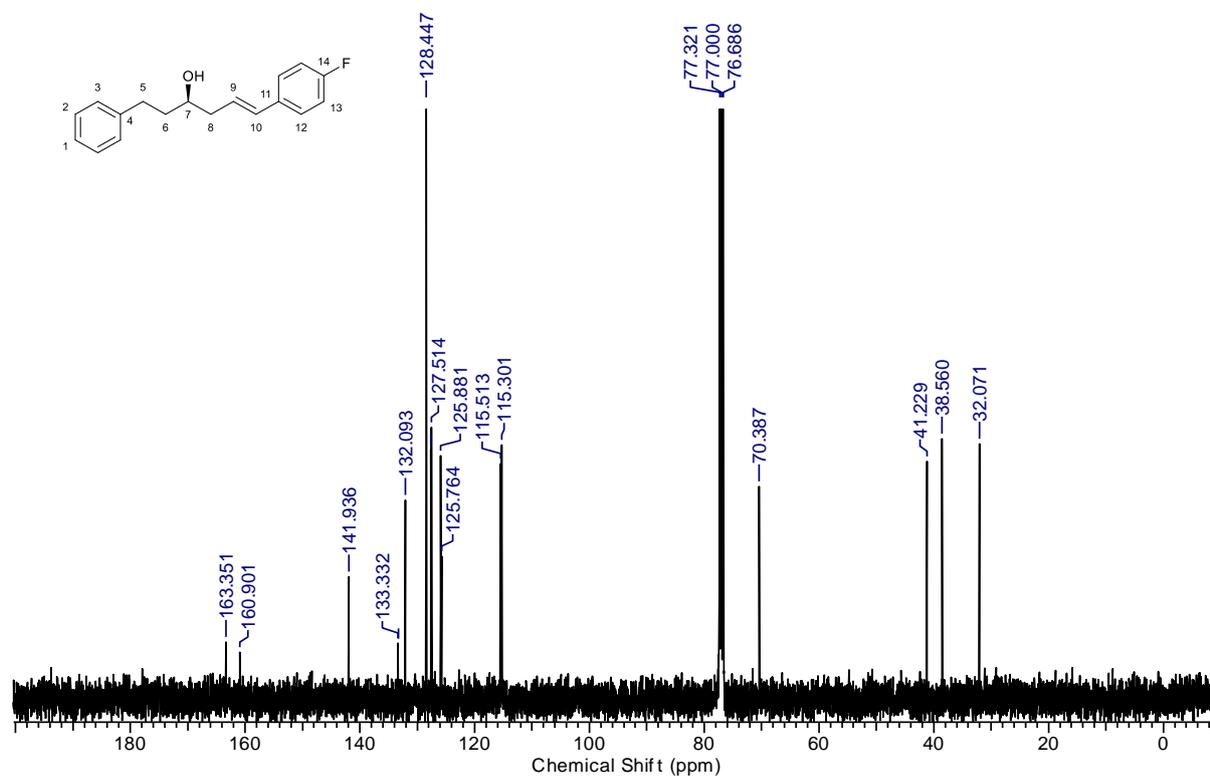


**(*R,E*)-6-(4-Fluorophenyl)-1-phenylhex-5-en-3-ol (8d)**

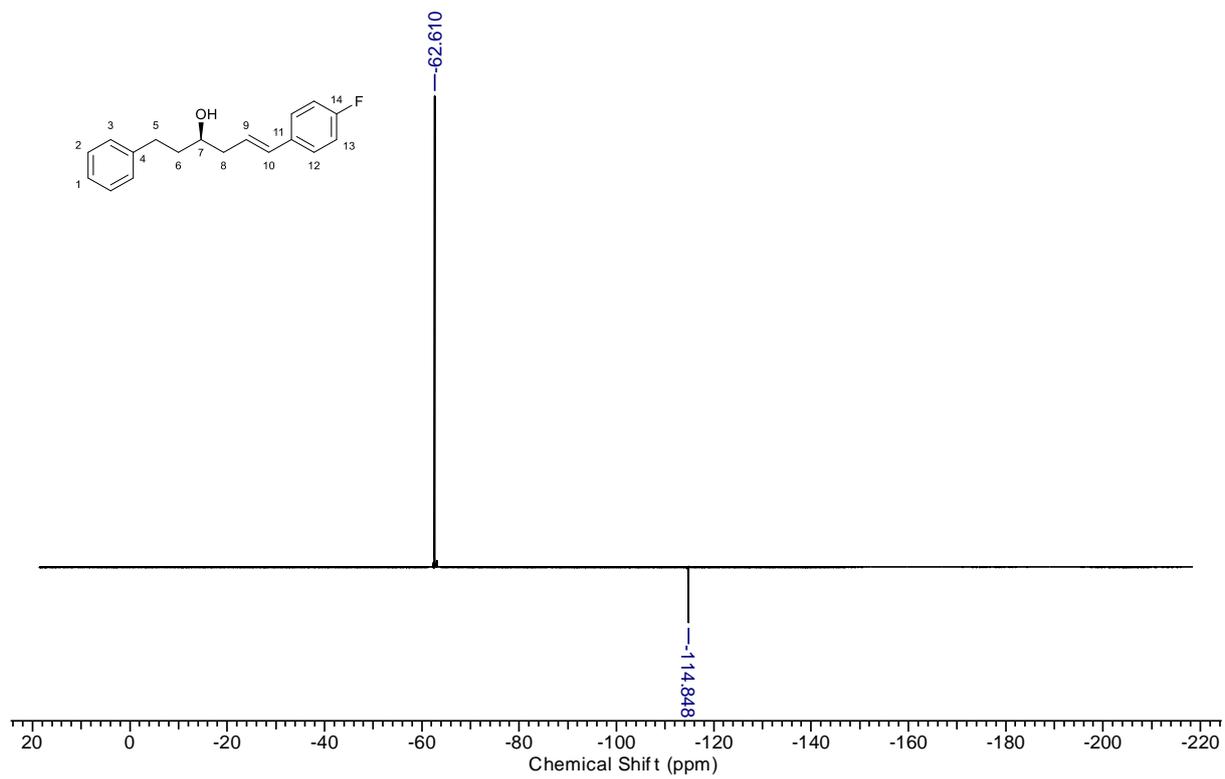
**<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):**



**<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):**

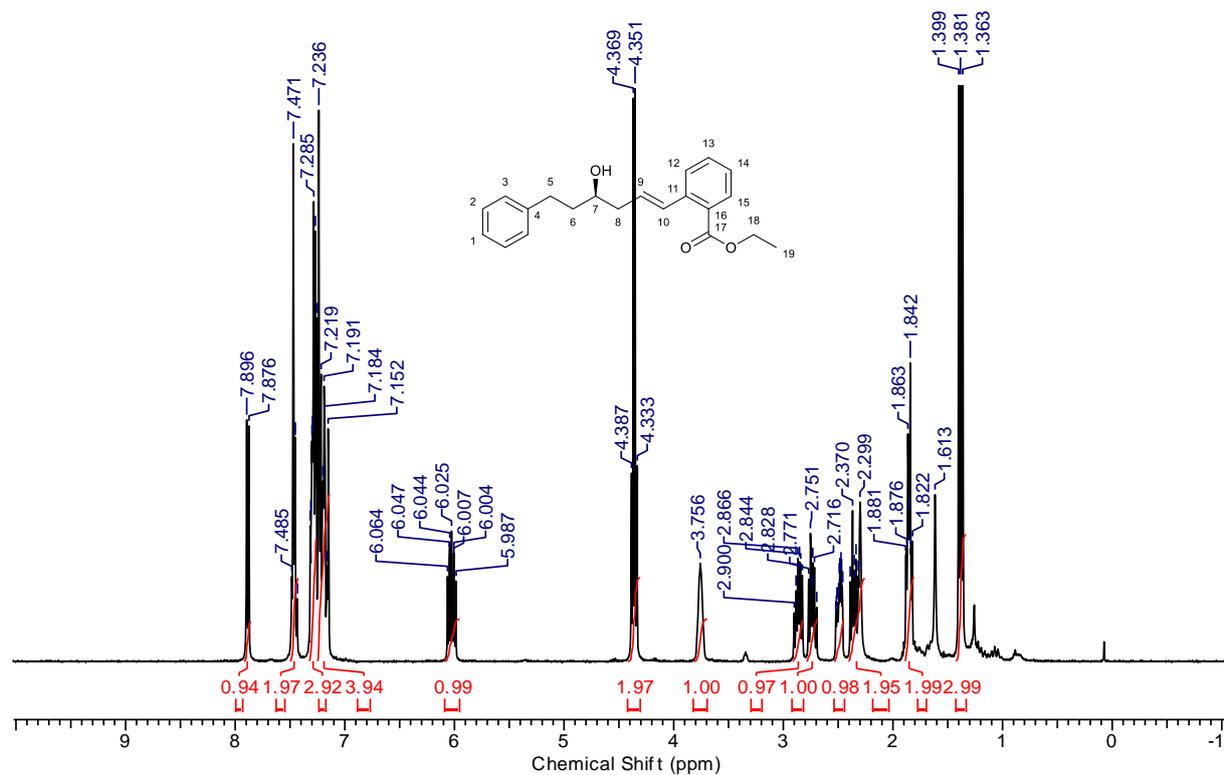


**<sup>19</sup>F-NMR (400 MHz, CDCl<sub>3</sub>):**

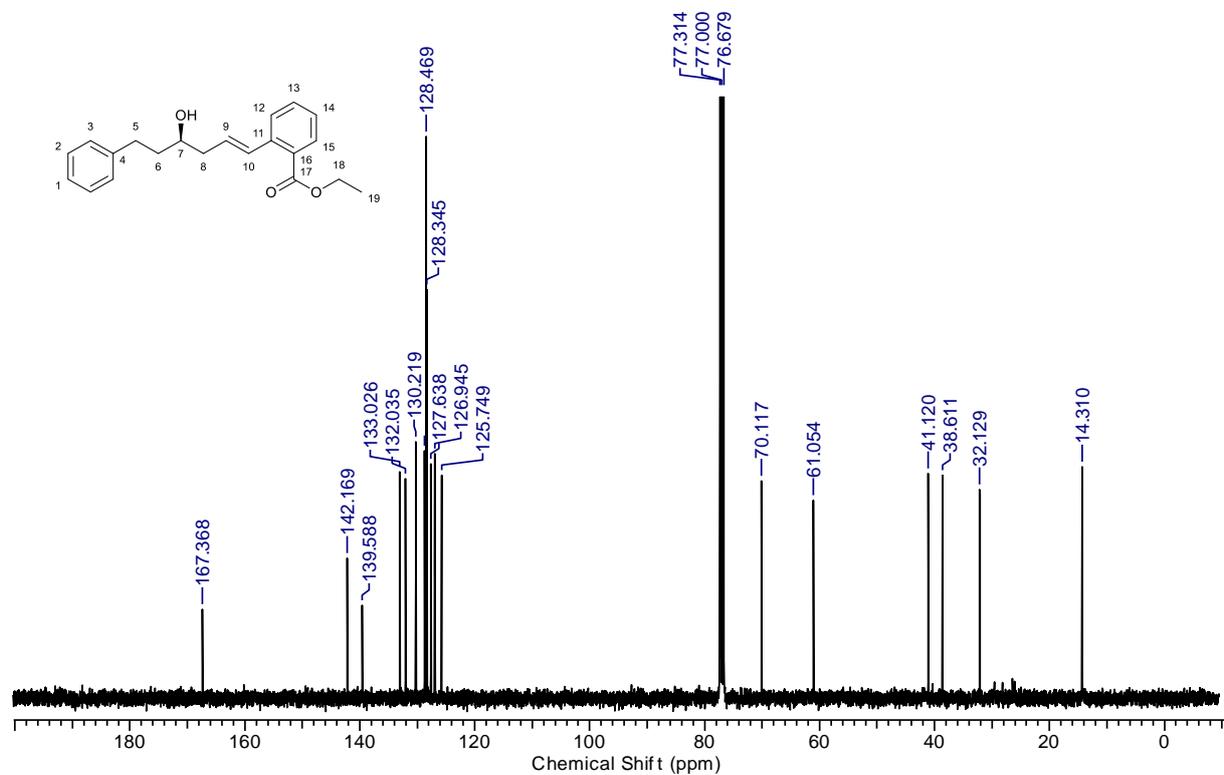


# Ethyl (*R,E*)-2-(4-hydroxy-6-phenylhex-1-en-1-yl)benzoate (**8e**)

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):

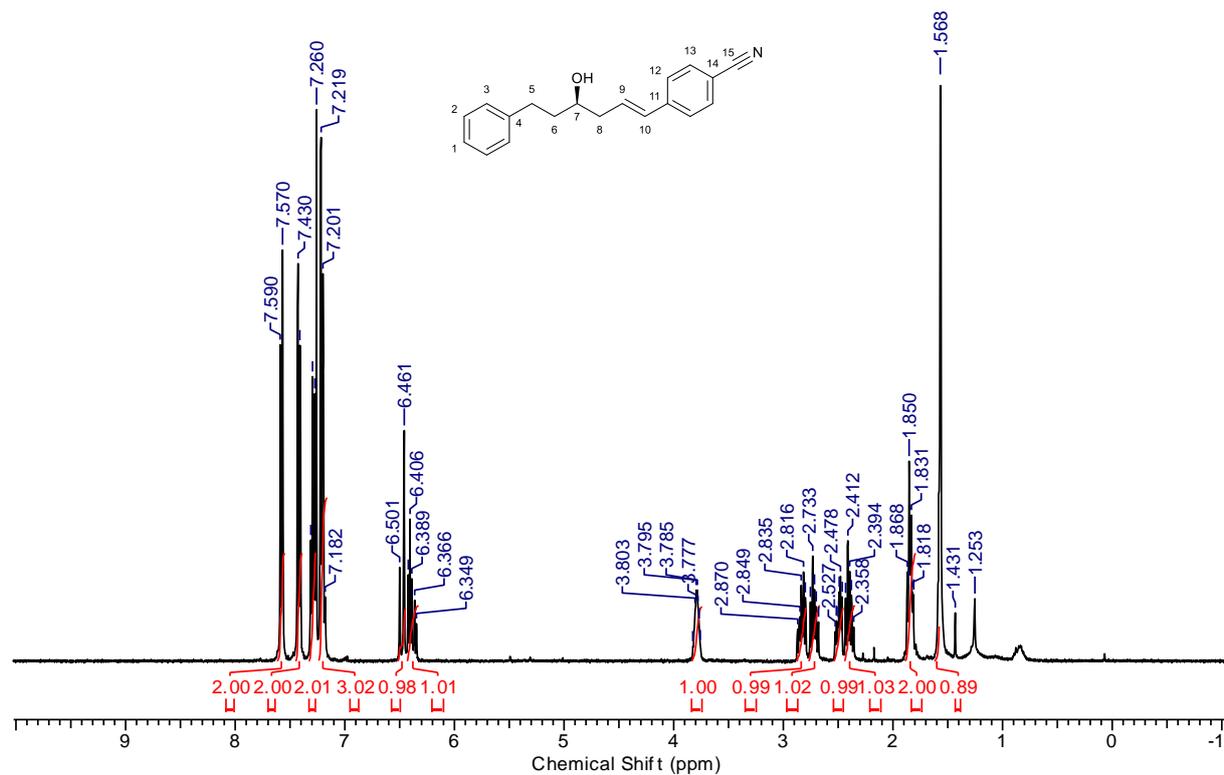


<sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>):

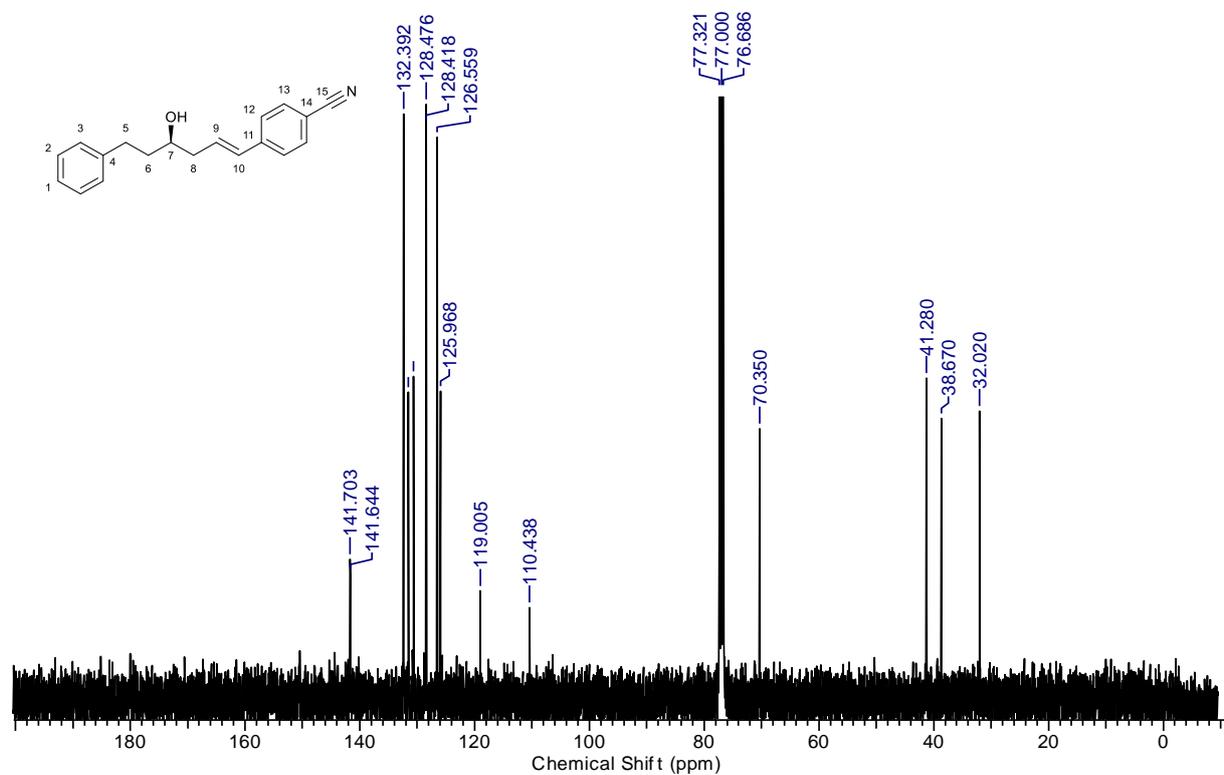


**(*R,E*)-4-(4-Hydroxy-6-phenylhex-1-en-1-yl)benzonitrile (8f)**

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):

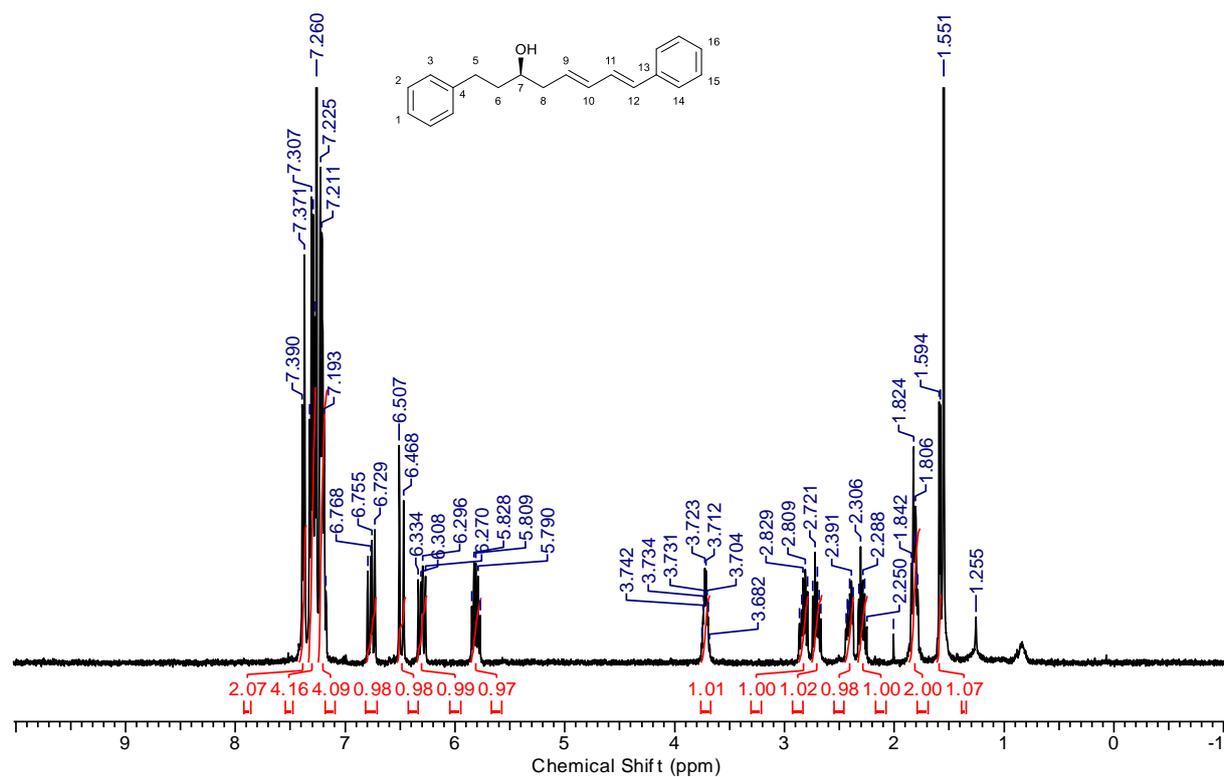


<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):

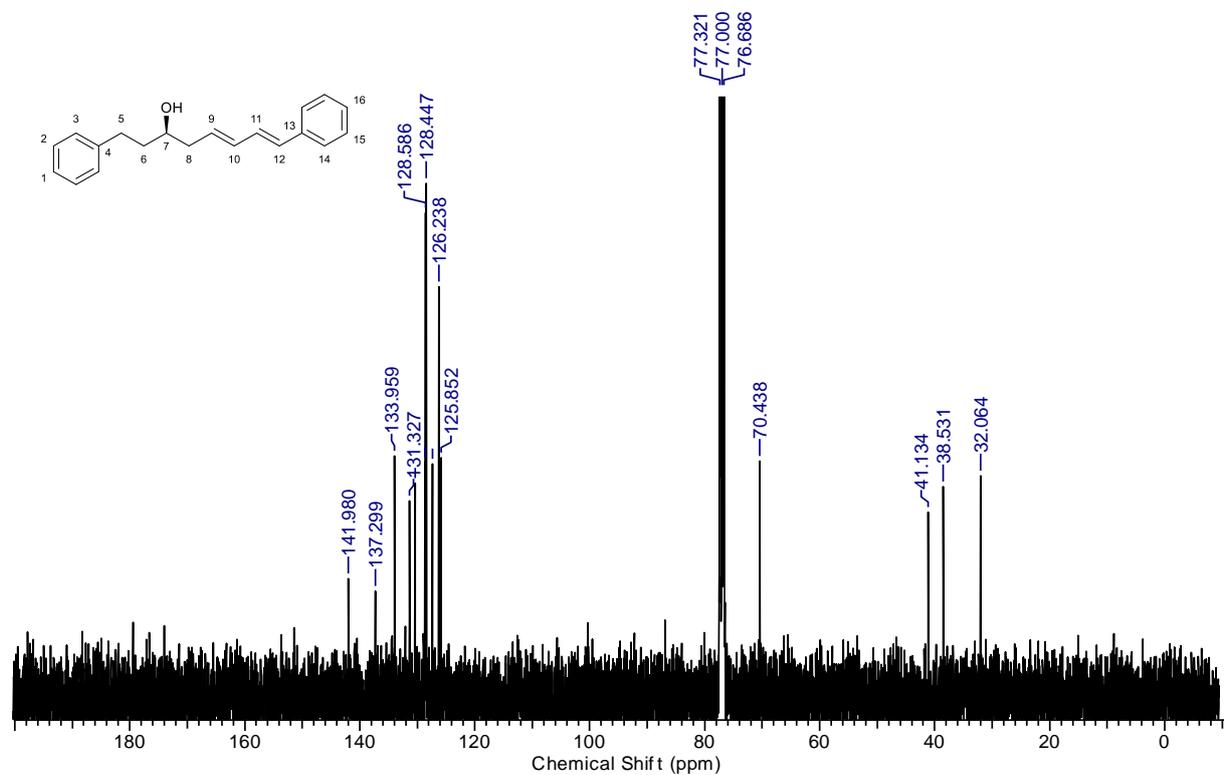


**(*R,5E,7E*)-1,8-diphenylocta-5,7-dien-3-ol (8g)**

**<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):**

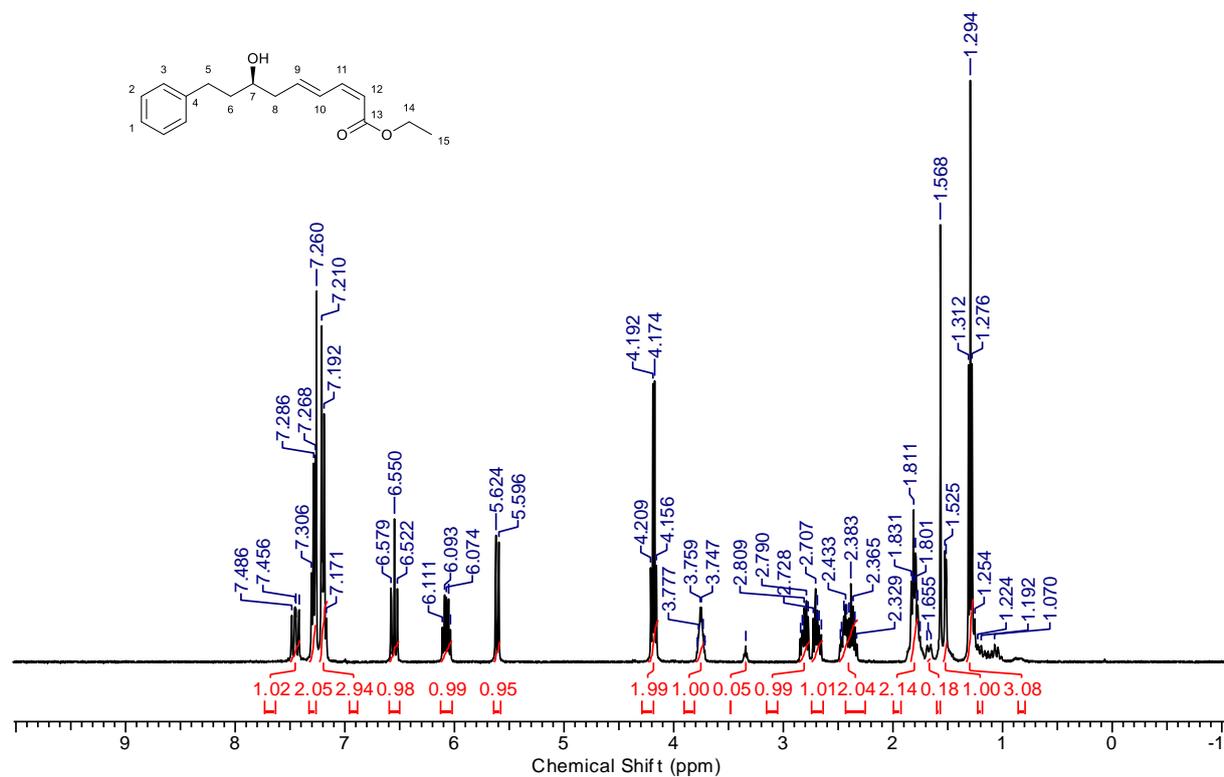


**<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):**

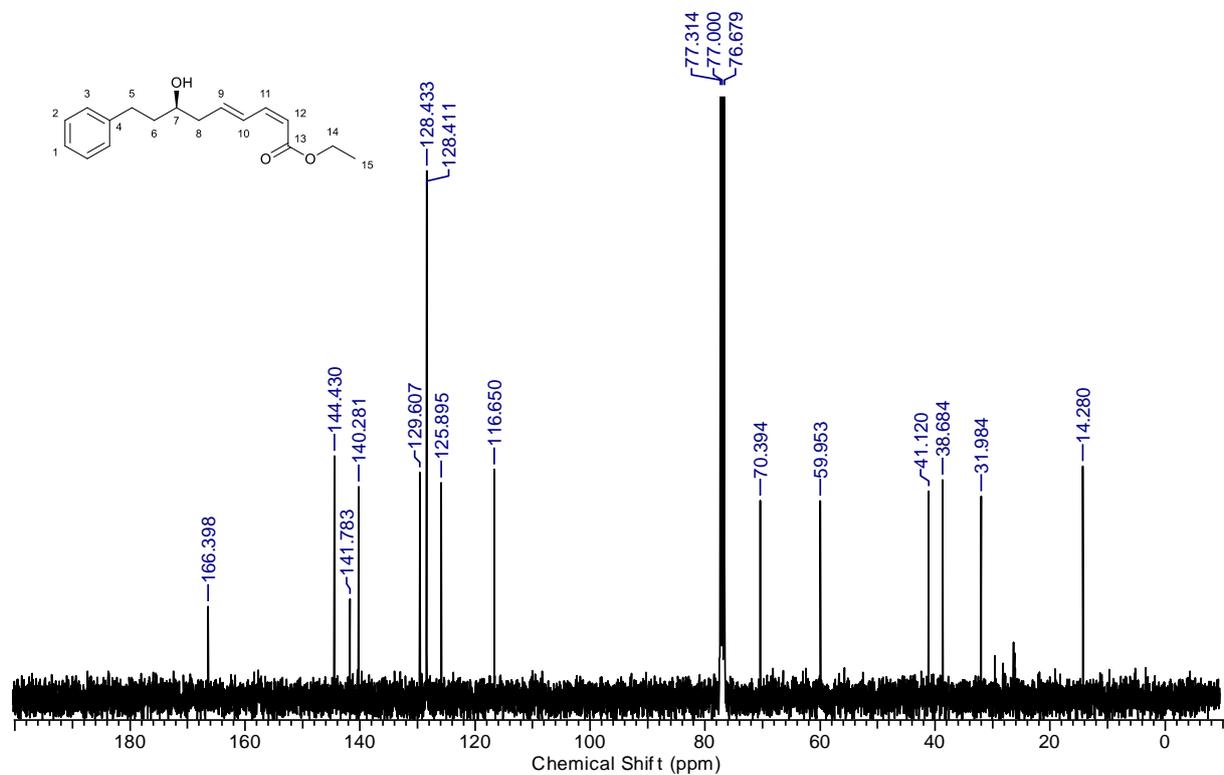


# Ethyl (R,2Z,4E)-7-hydroxy-9-phenylnona-2,4-dienoate (8h)

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):

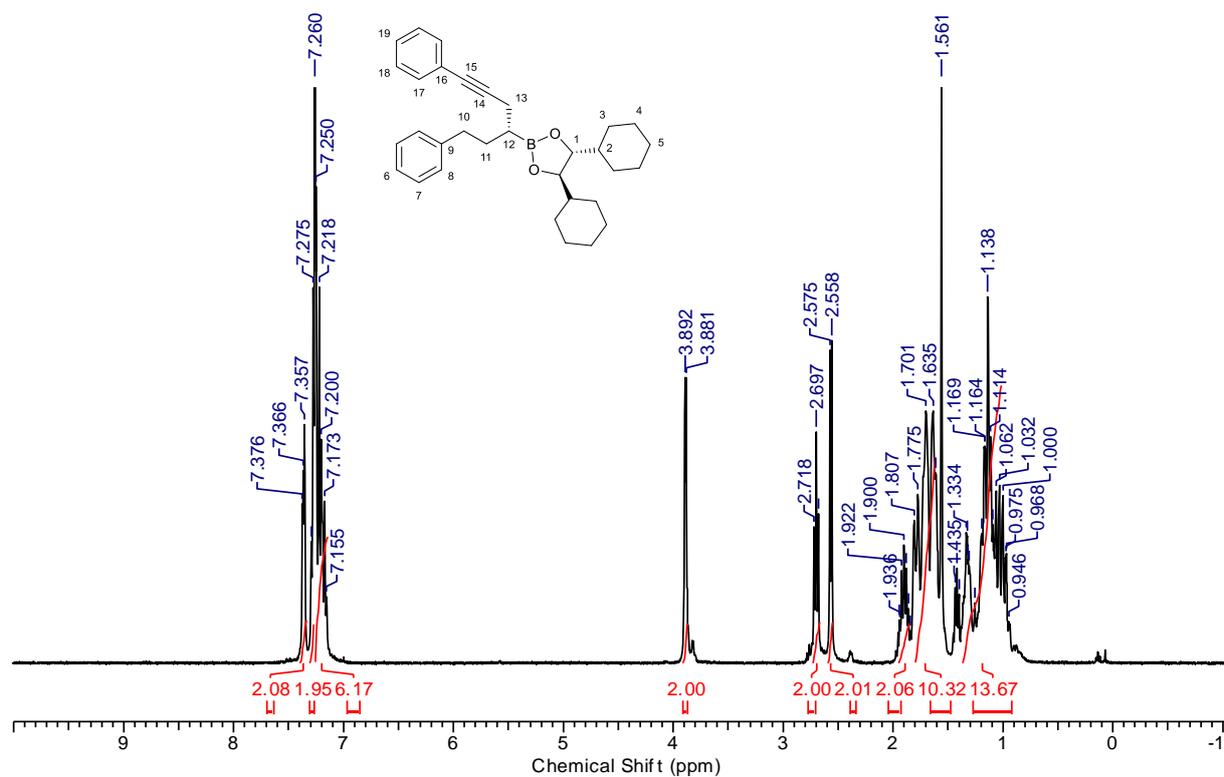


<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):

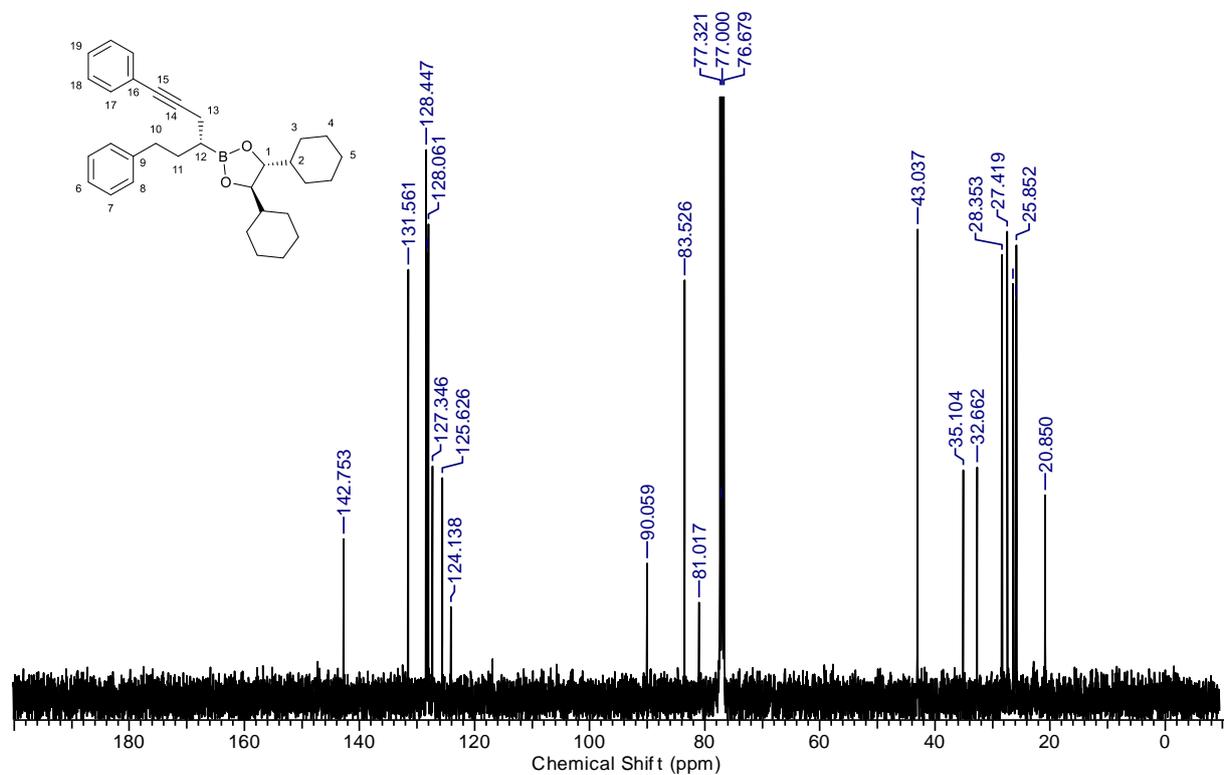


**(4*R*,5*R*)-4,5-Dicyclohexyl-2-((*R*)-1,6-diphenylhex-5-yn-3-yl)-1,3,2-dioxaborolane (9a)**

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):

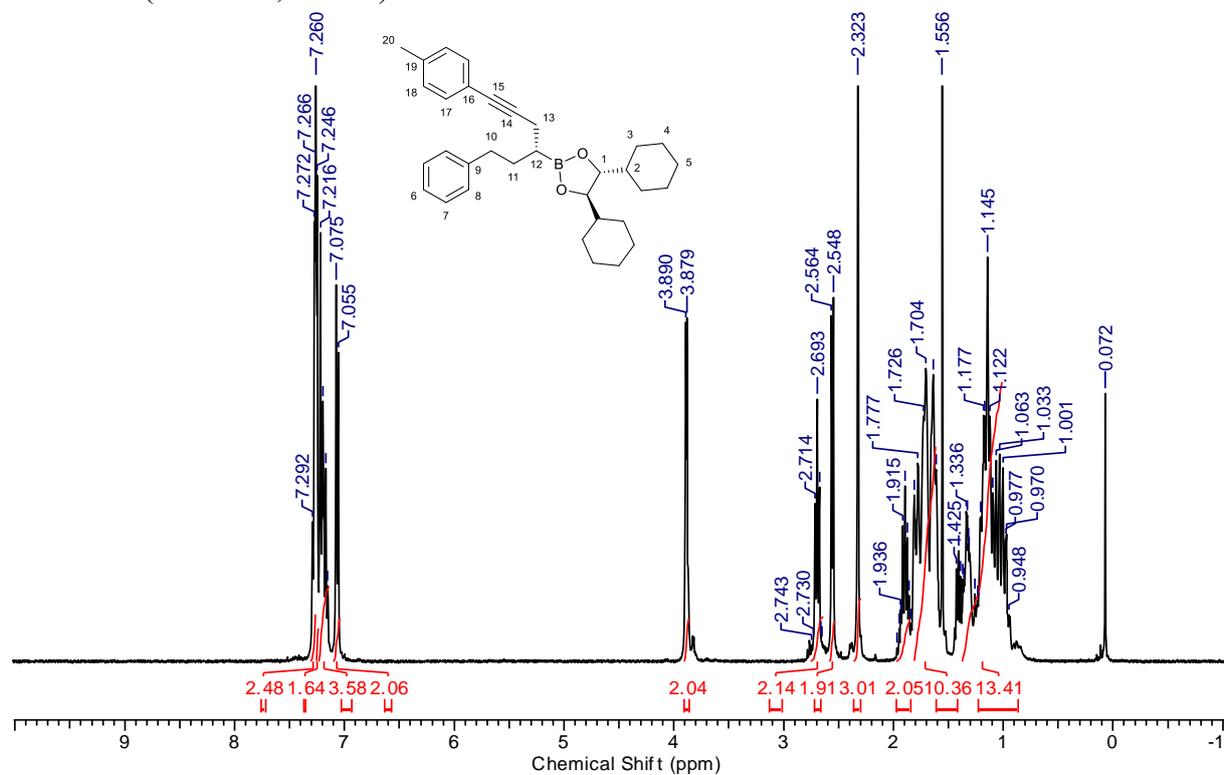


<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):

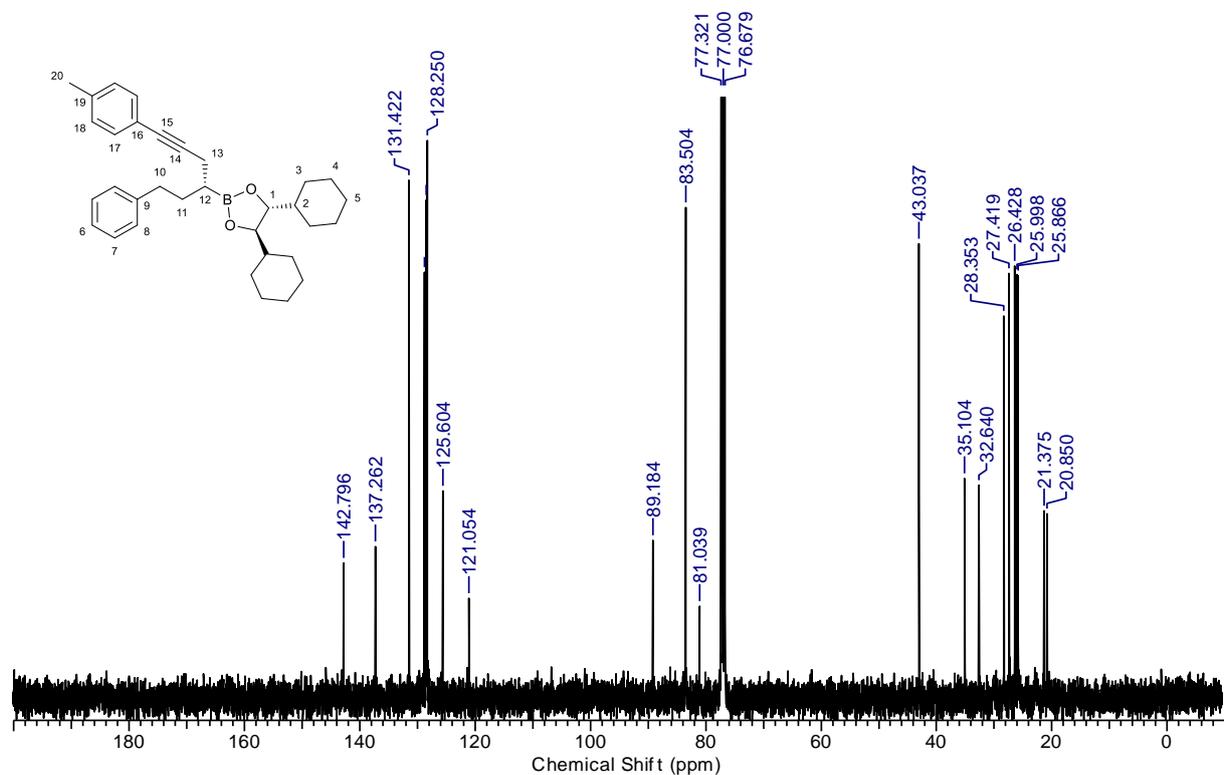


**(4*R*,5*R*)-4,5-dicyclohexyl-2-((*R*)-1-phenyl-6-(*p*-tolyl)hex-5-yn-3-yl)-1,3,2-dioxaborolane (9b)**

**<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):**

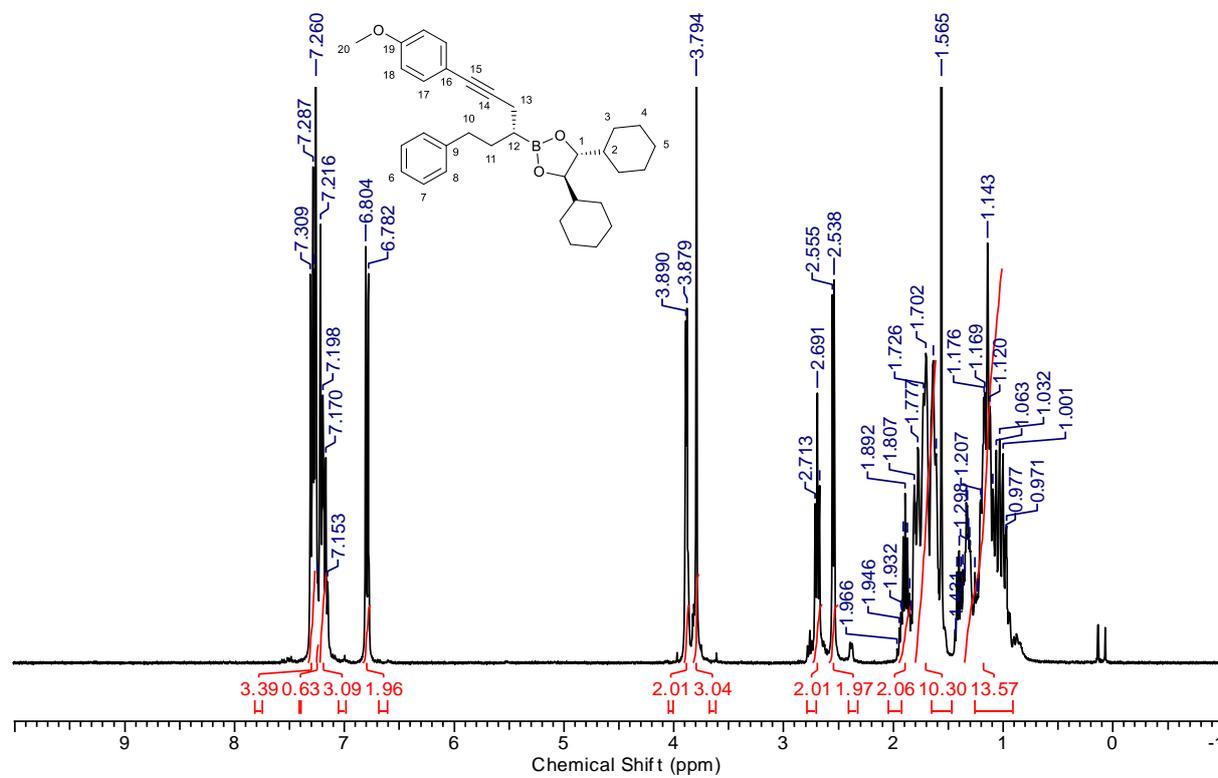


**<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):**

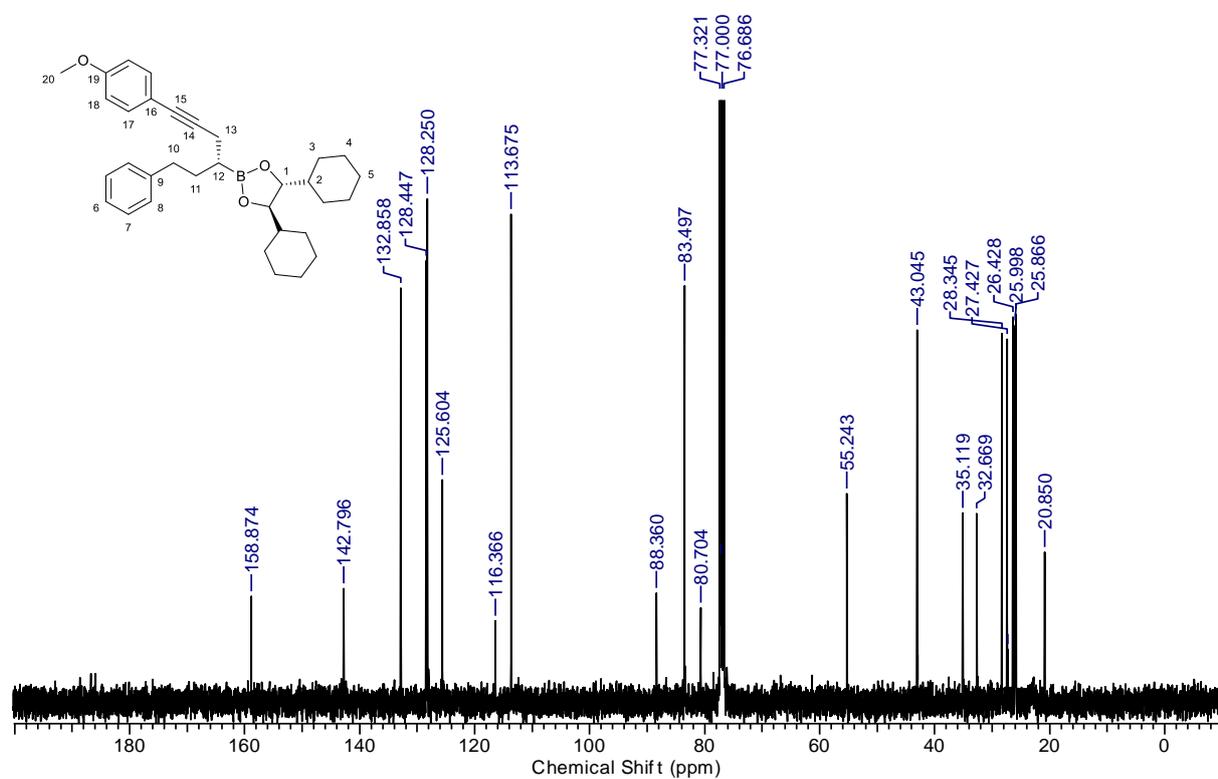


**(4*R*,5*R*)-4,5-Dicyclohexyl-2-((*R*)-6-(4-methoxyphenyl)-1-phenylhex-5-yn-3-yl)-1,3,2-dioxaborolane (9c)**

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):

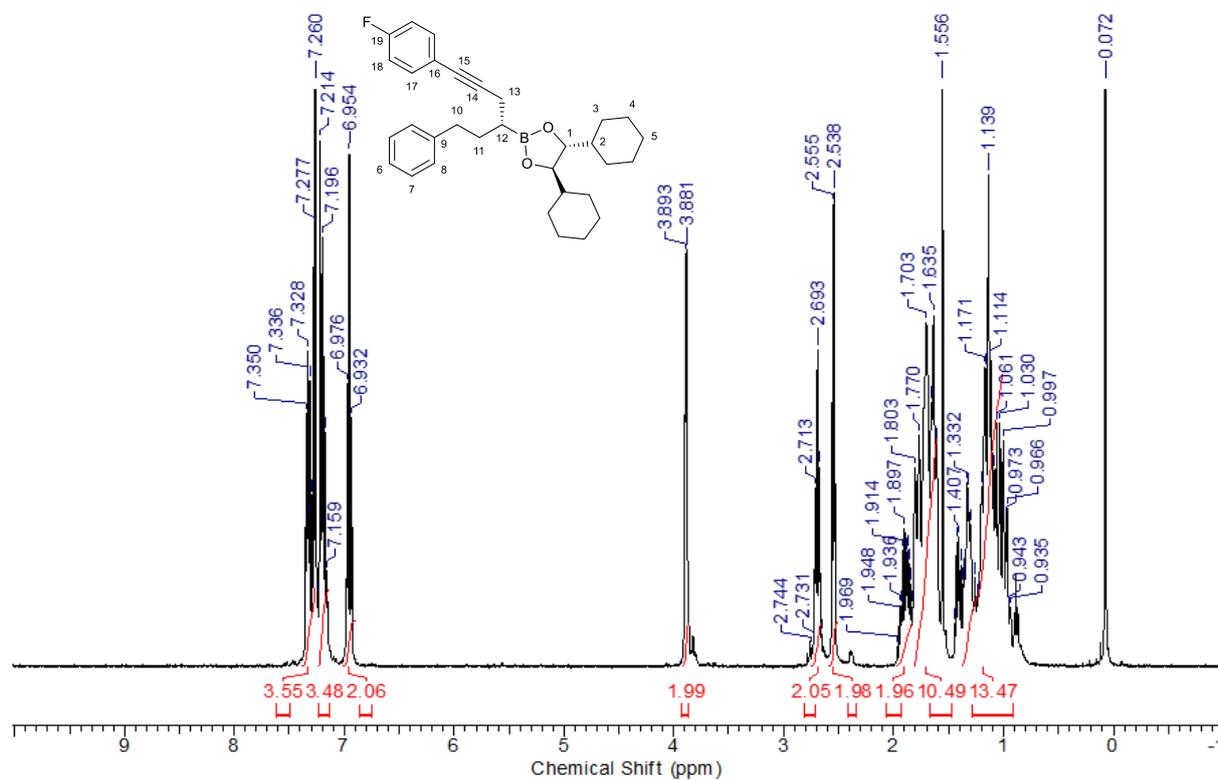


<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):

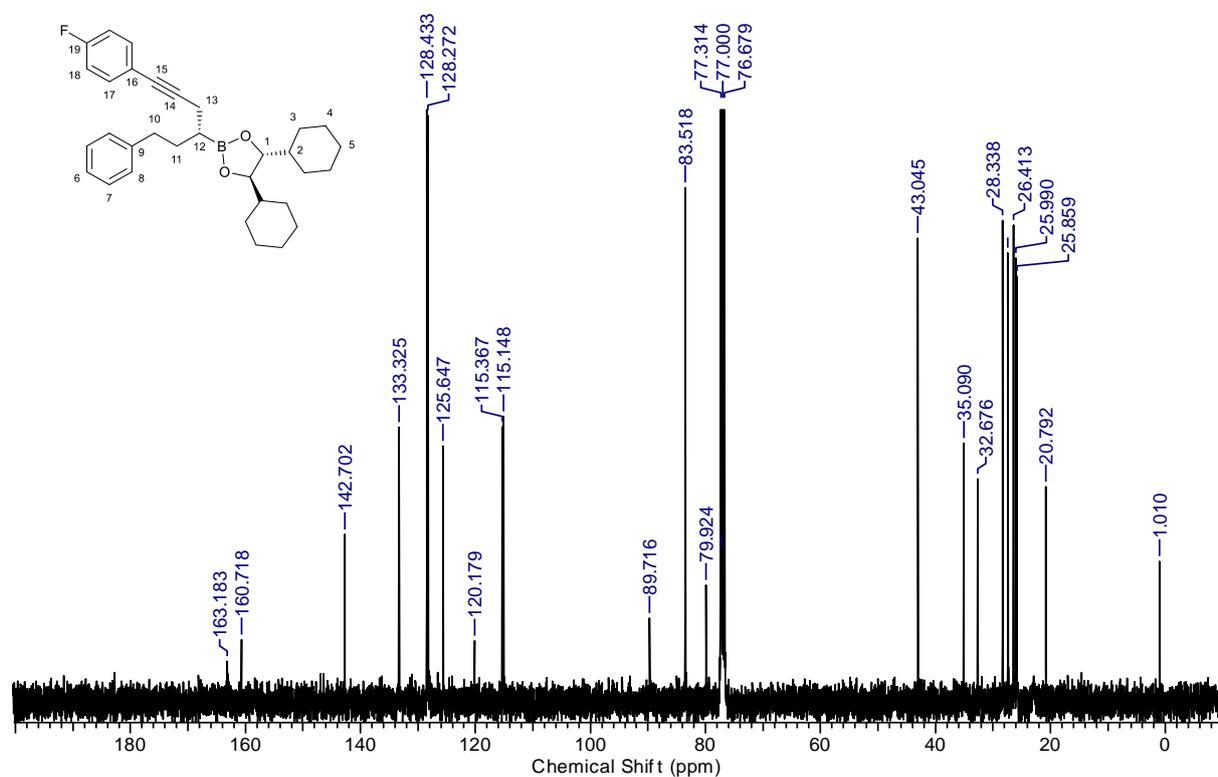


**(4*R*,5*R*)-4,5-Dicyclohexyl-2-((*R*)-6-(4-fluorophenyl)-1-phenylhex-5-yn-3-yl)-1,3,2-dioxaborolane (9d)**

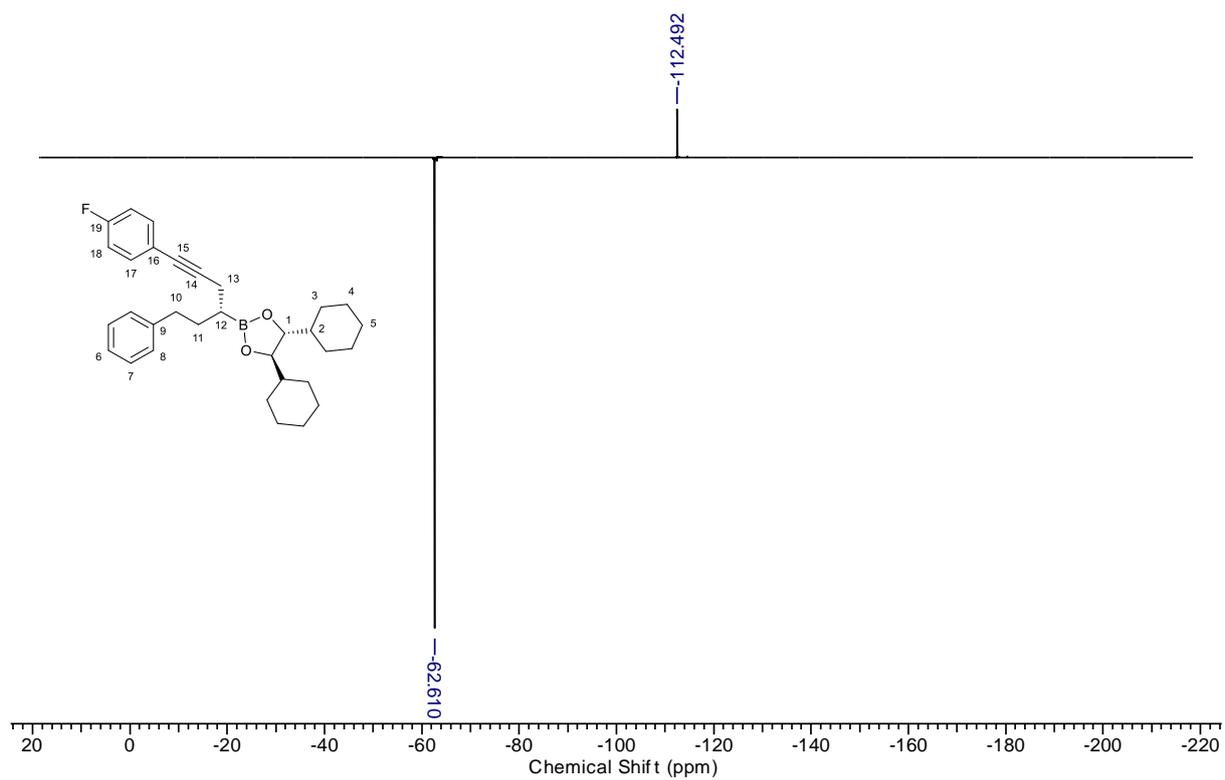
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):



<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):

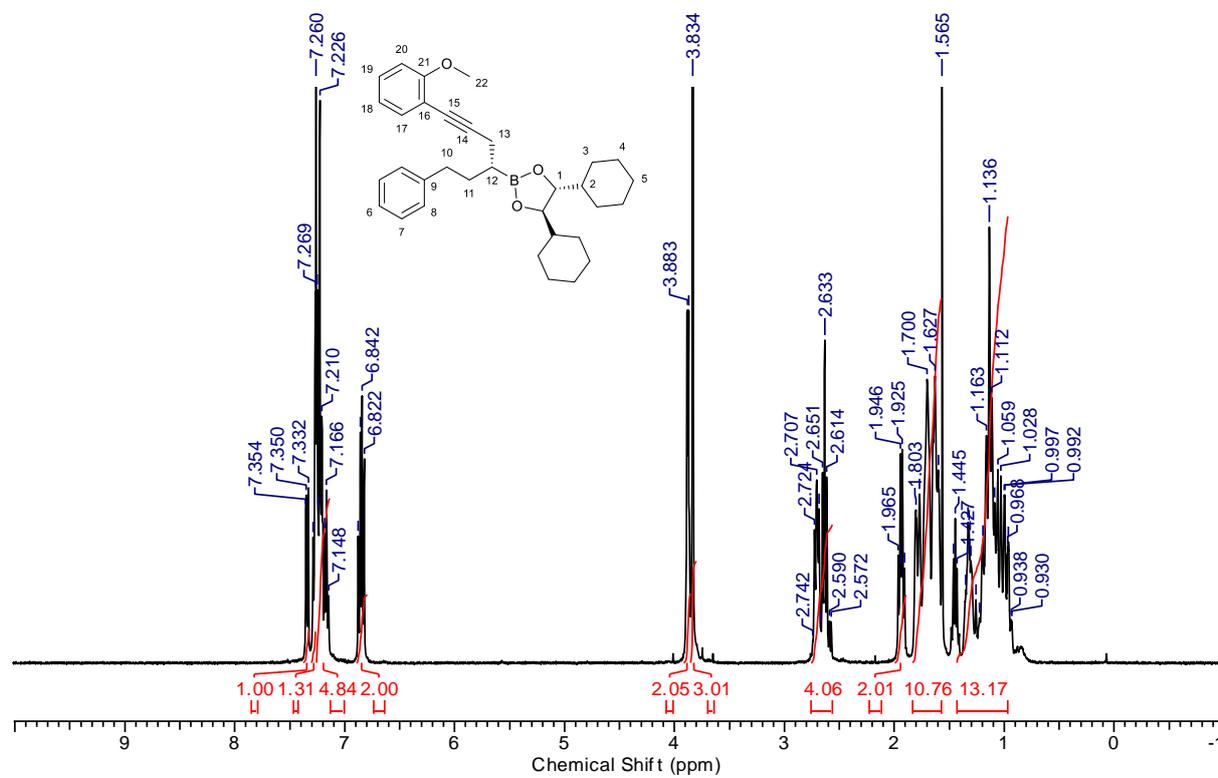


**$^{19}\text{F}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):**

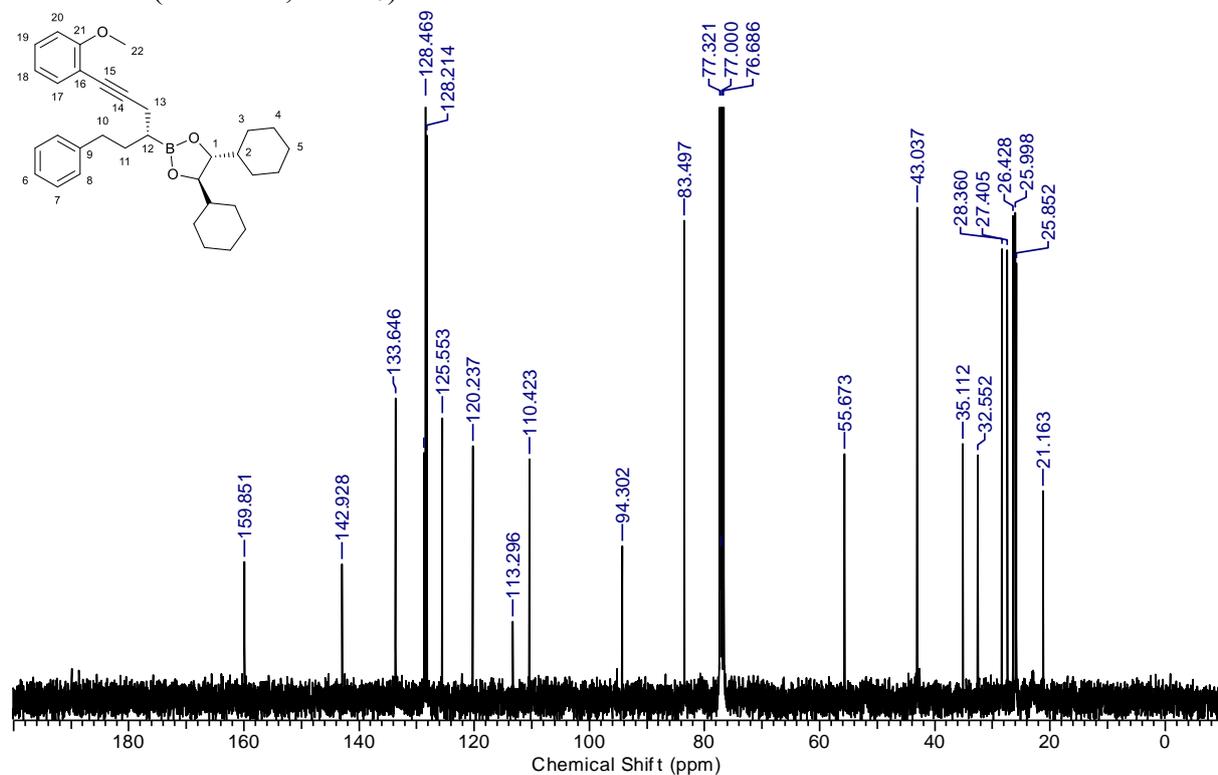


**(4*R*,5*R*)-4,5-dicyclohexyl-2-((*R*)-6-(2-methoxyphenyl)-1-phenylhex-5-yn-3-yl)-1,3,2-dioxaborolane (9e)**

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):

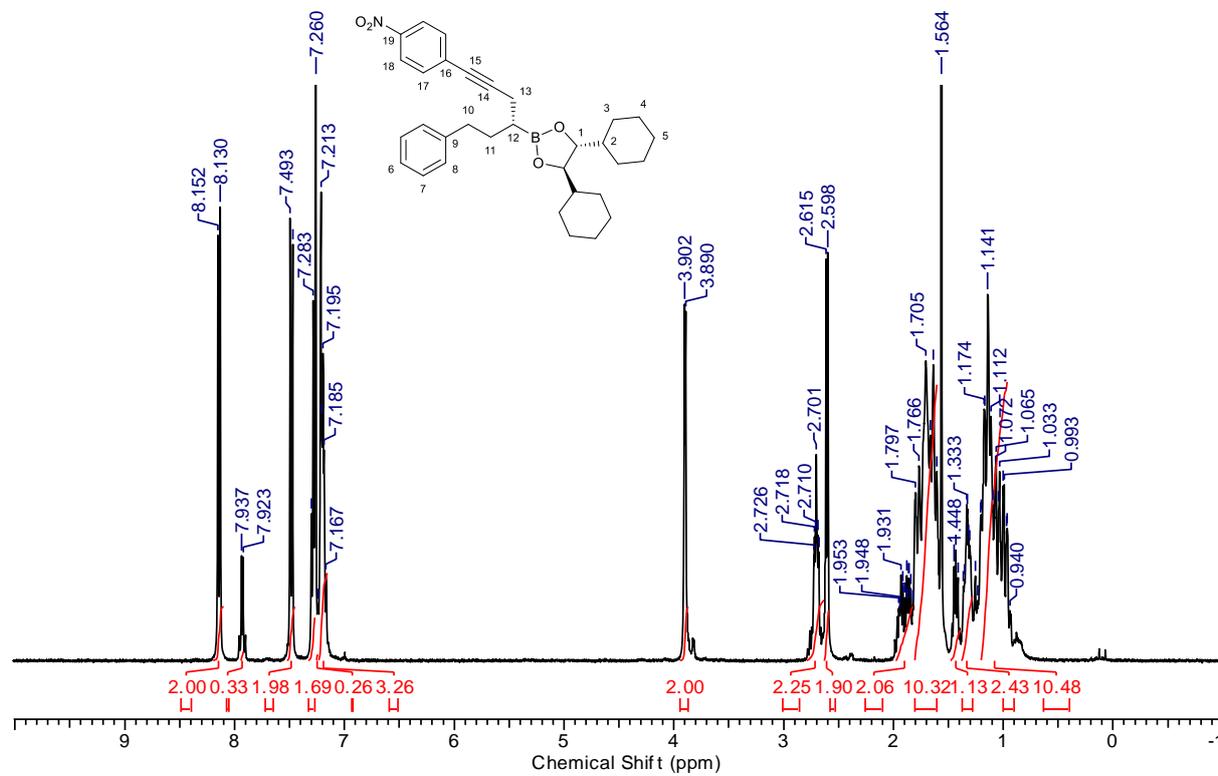


<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):



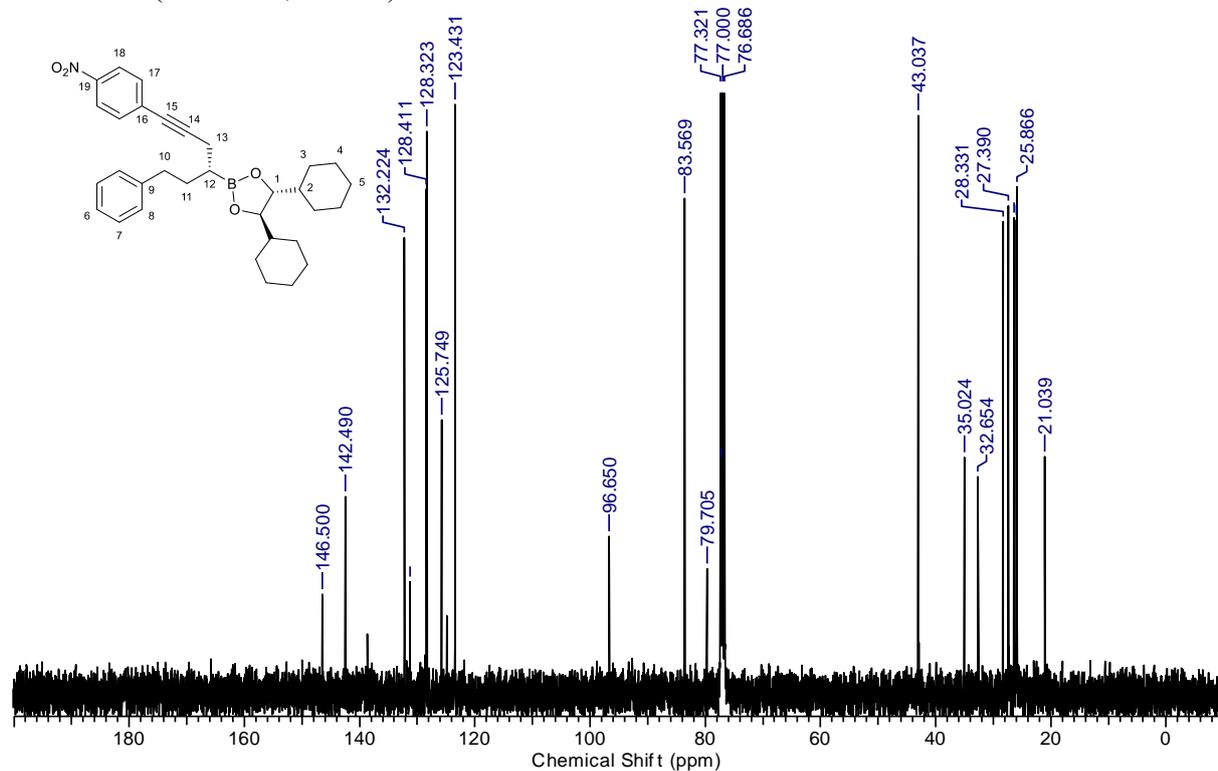
**(4*R*,5*R*)-4,5-Dicyclohexyl-2-((*R*)-6-(4-nitrophenyl)-1-phenylhex-5-yn-3-yl)-1,3,2-dioxaborolane (9f)**

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):



Additional signal arising from 1-iodo-4-nitrobenzene

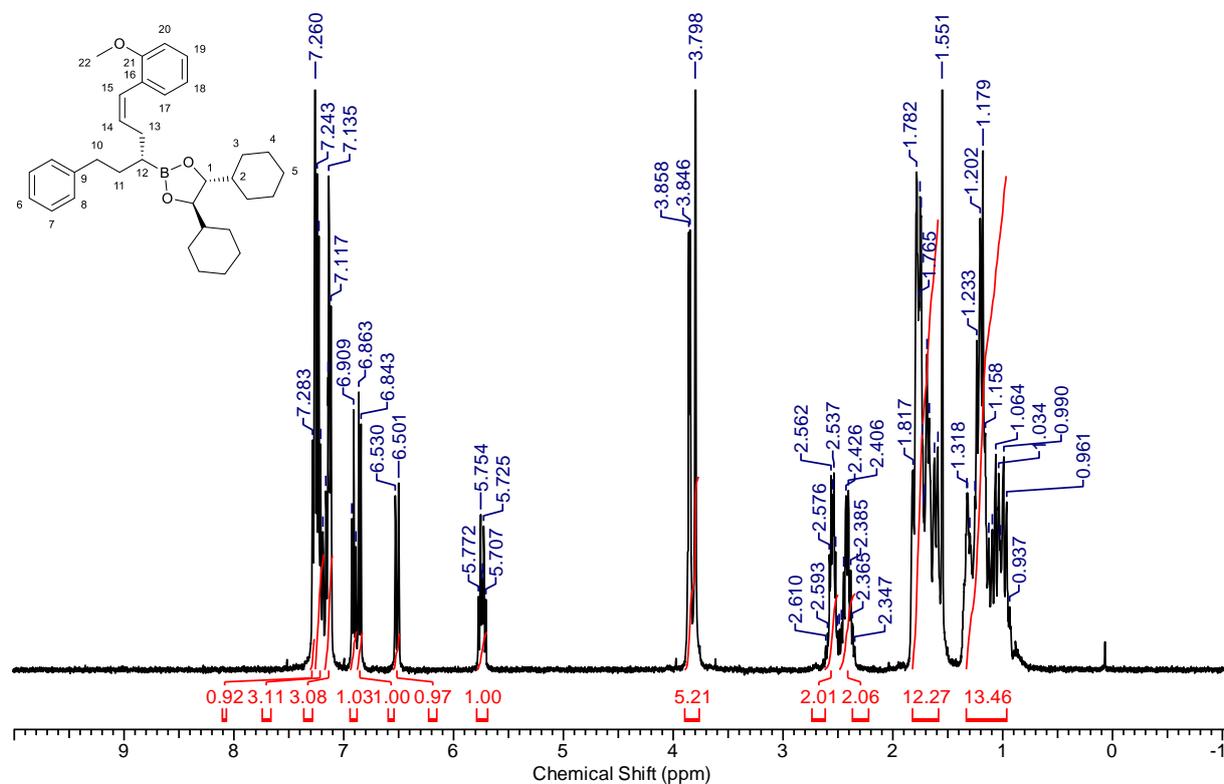
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):



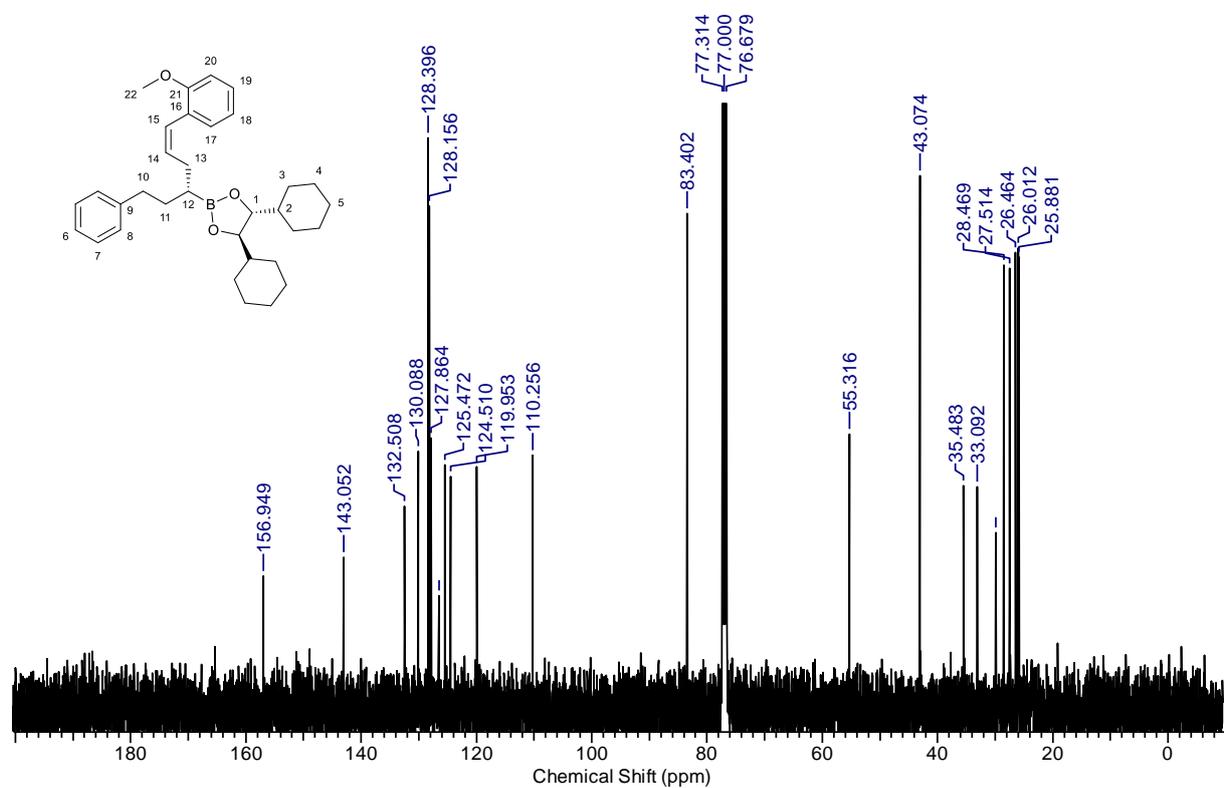
Additional signals arising from 1-iodo-4-nitrobenzene

**(4*R*,5*R*)-4,5-Dicyclohexyl-2-((*R*,*Z*)-6-(2-methoxyphenyl)-1-phenylhex-5-en-3-yl)-1,3,2-dioxaborolane (10e)**

**<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):**

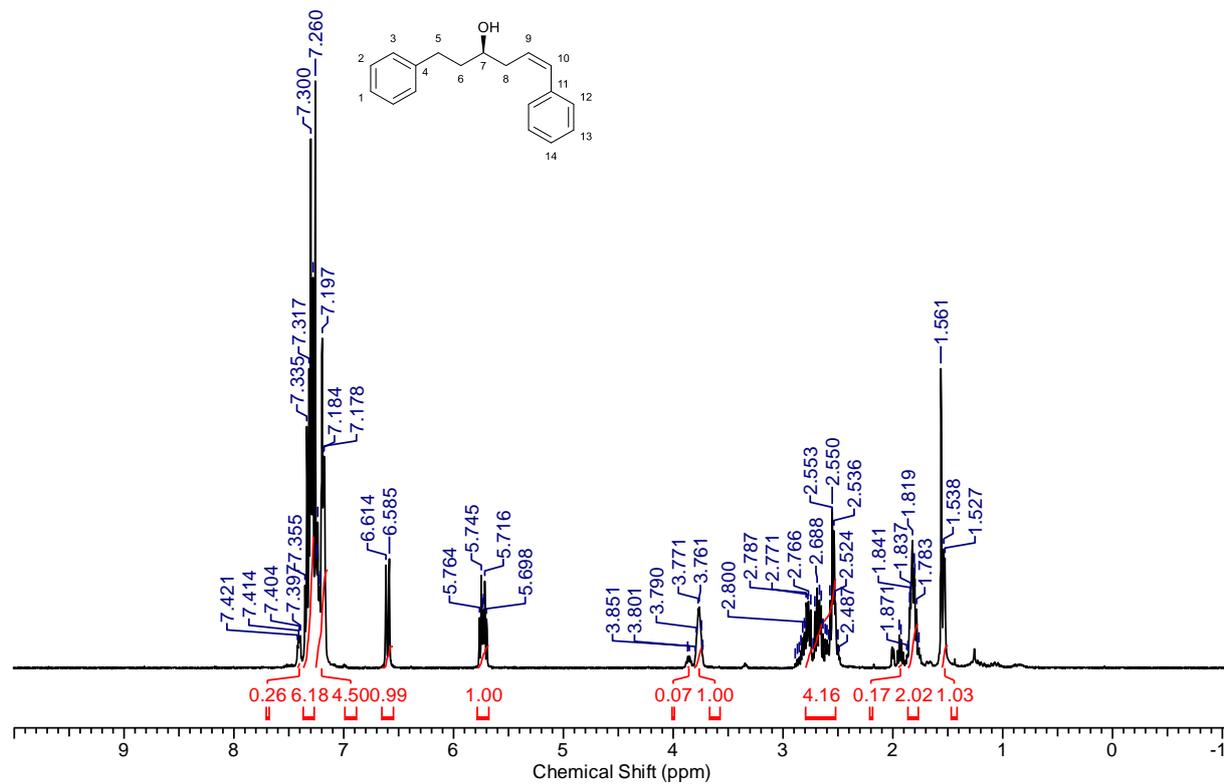


**<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):**

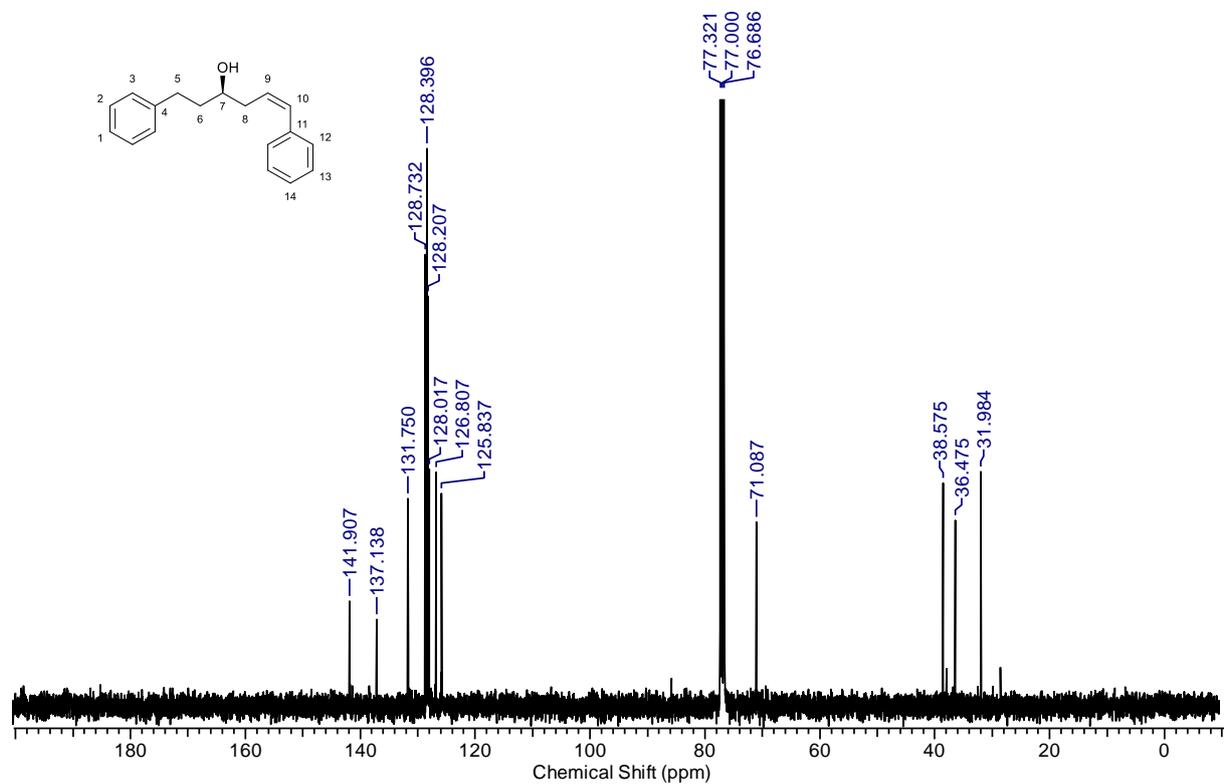


**(*R,Z*)-1,6-diphenylhex-5-en-3-ol (11a)**

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):

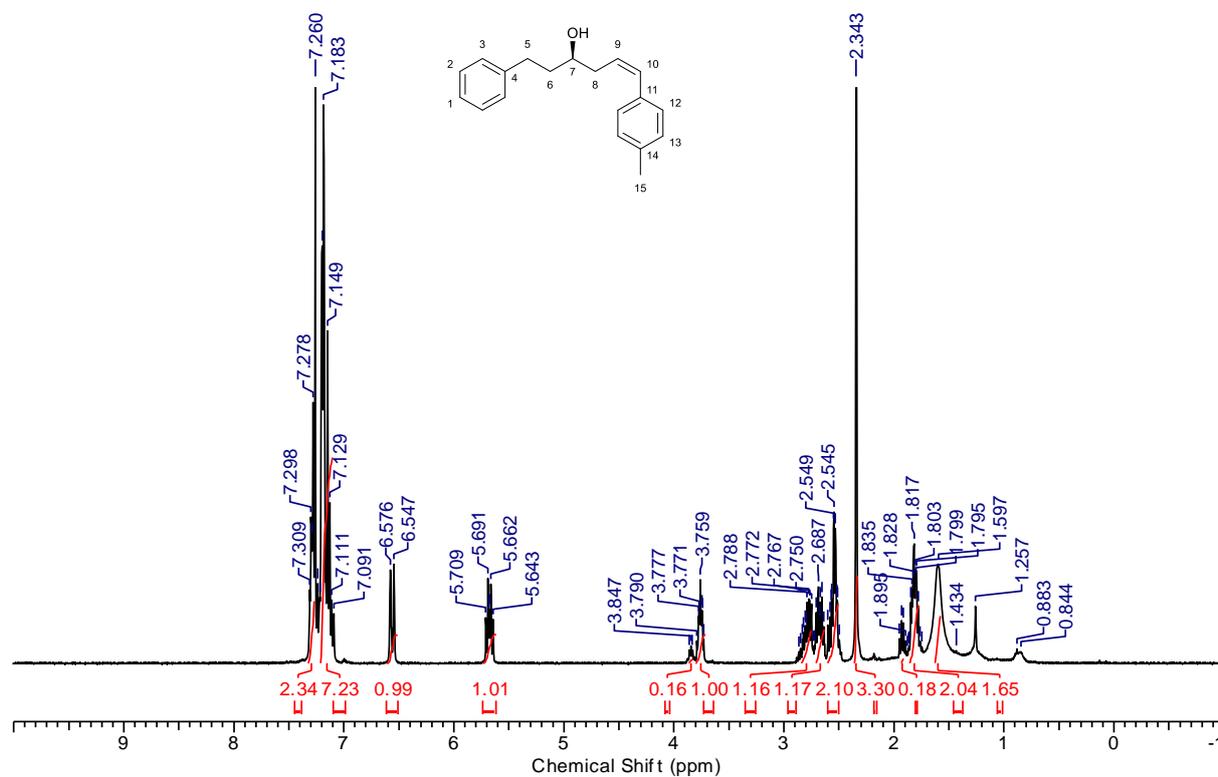


<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):

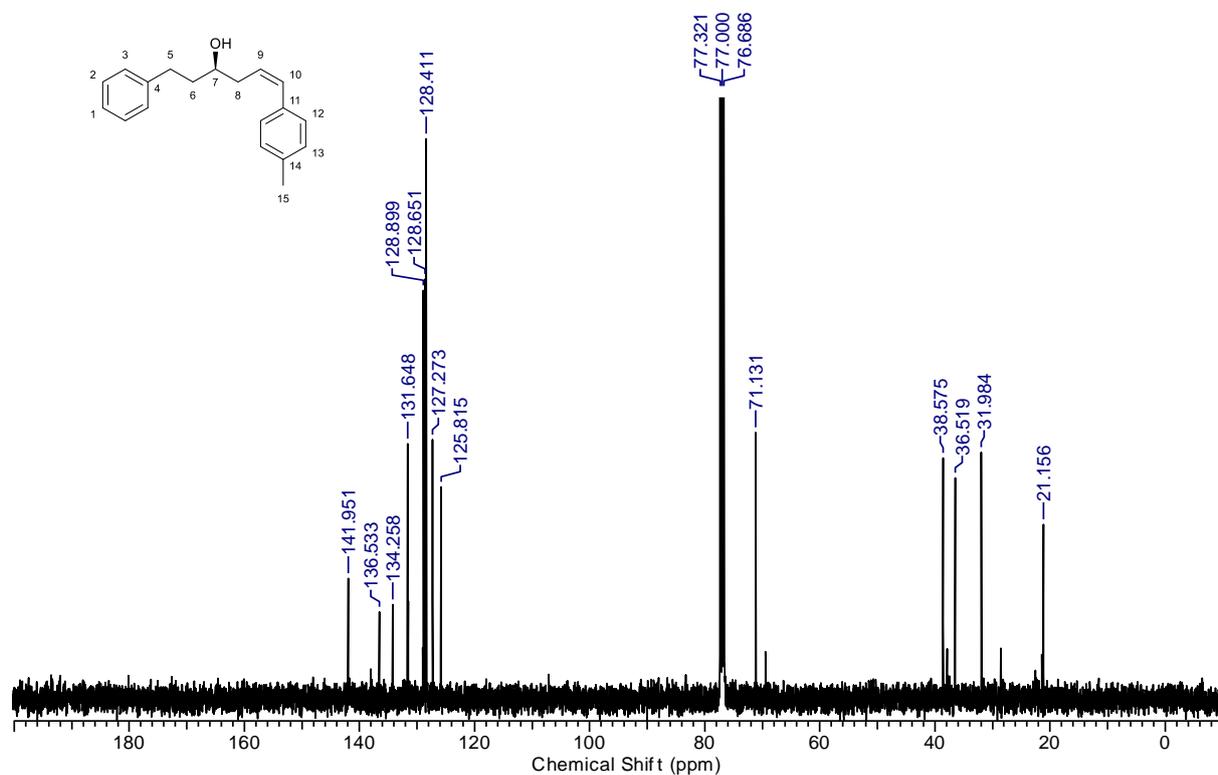


**(*R,Z*)-1-Phenyl-6-(*p*-tolyl)hex-5-en-3-ol (11b)**

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):

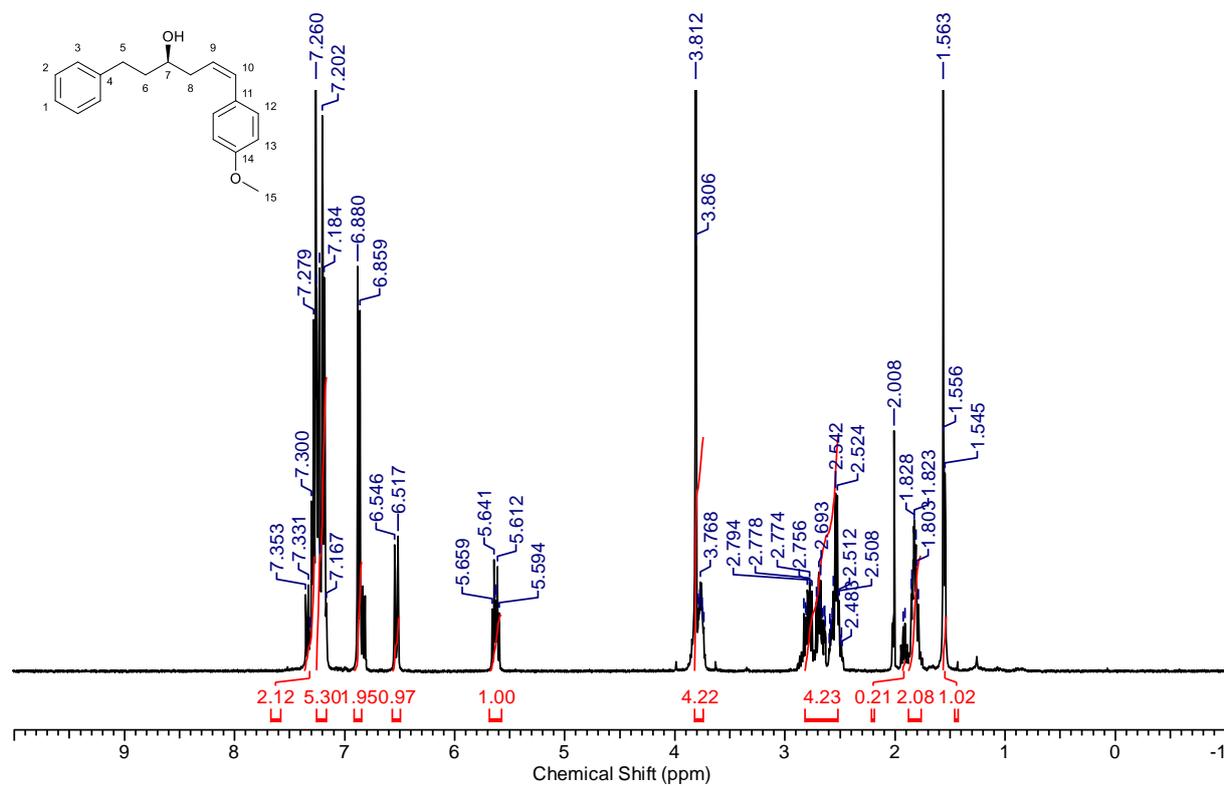


<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):

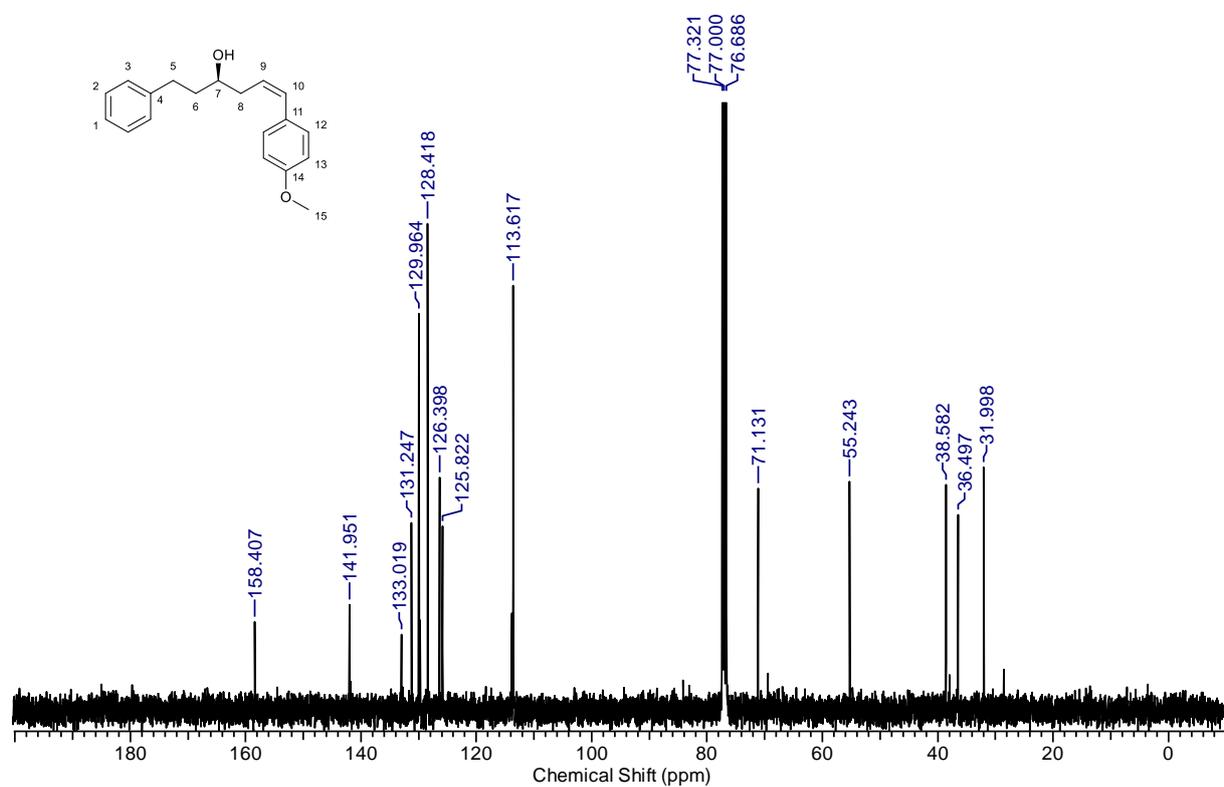


**(*R,Z*)-6-(4-methoxyphenyl)-1-phenylhex-5-en-3-ol (11c)**

**<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):**

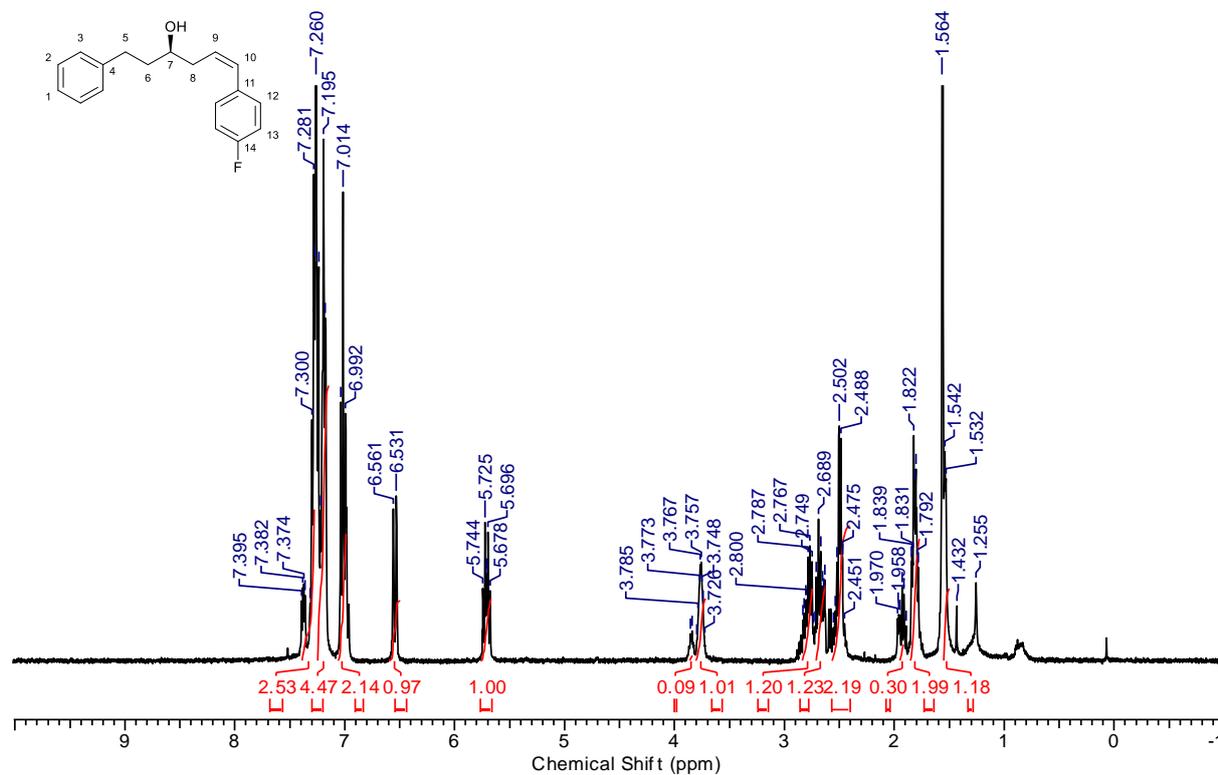


**<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):**

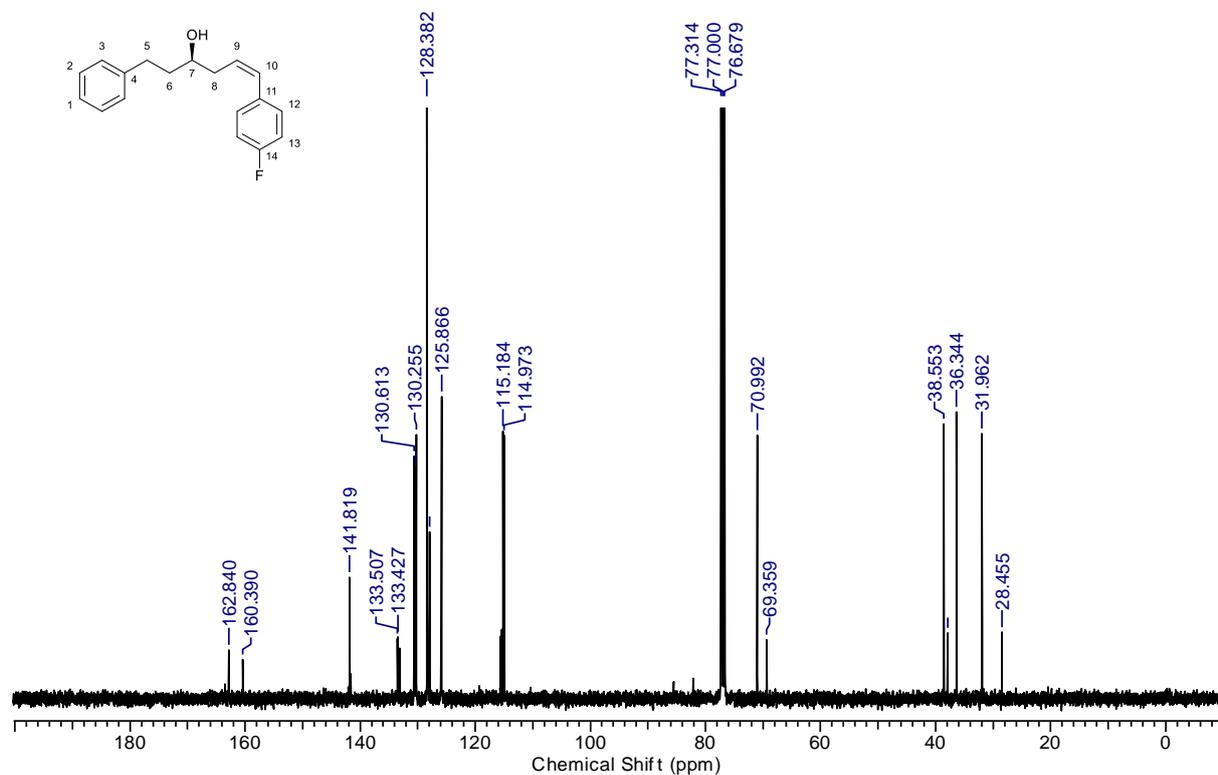


**(*R,Z*)-6-(4-Fluorophenyl)-1-phenylhex-5-en-3-ol (11d)**

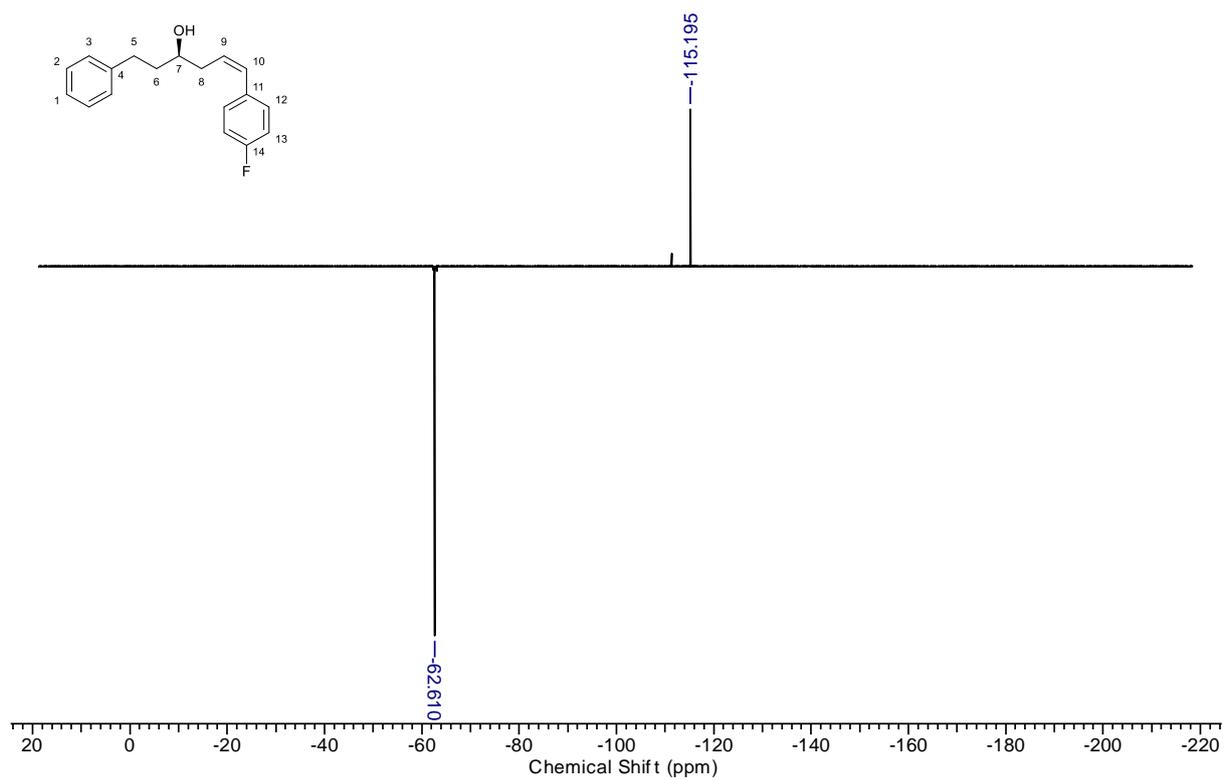
**<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):**



**<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):**

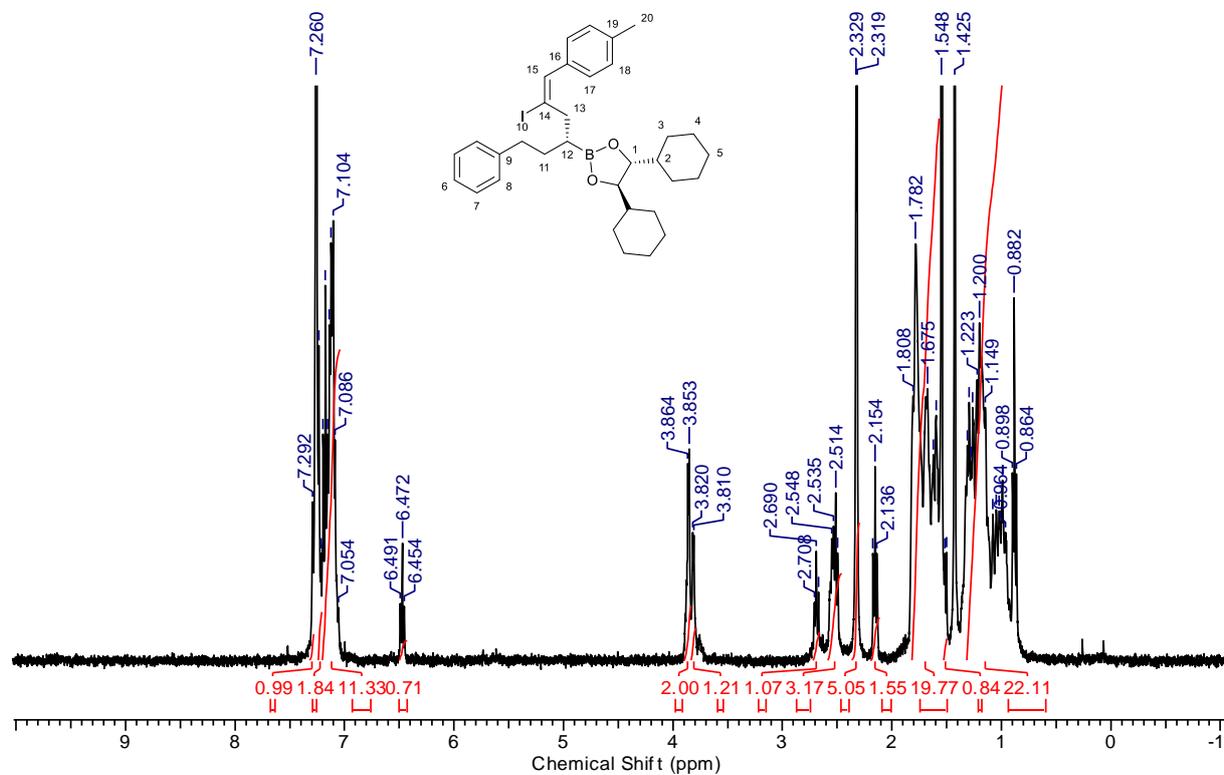


**$^{19}\text{F}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):**

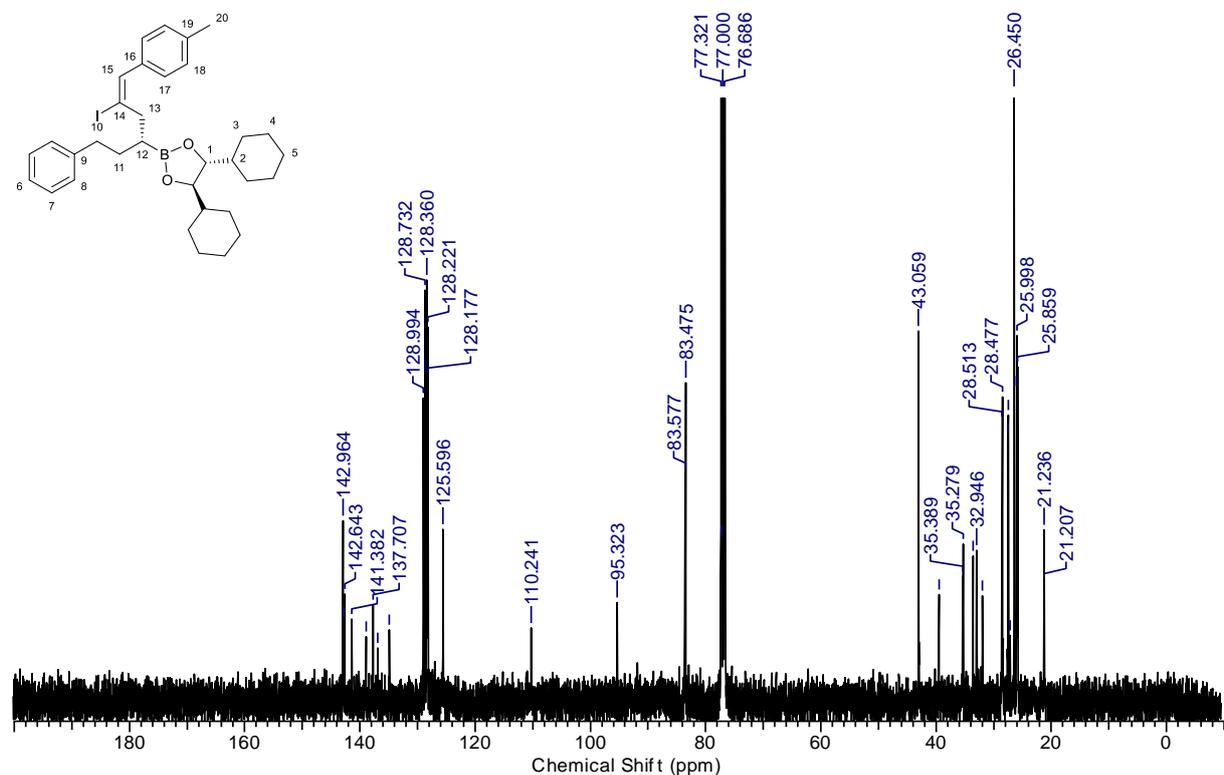


**(4*R*,5*R*)-4,5-Dicyclohexyl-2-((*R*,*E*)-5-iodo-1-phenyl-6-(*p*-tolyl)hex-5-en-3-yl)-1,3,2-dioxaborolane (12b) and (4*R*,5*R*)-4,5-dicyclohexyl-2-((*R*,*E*)-6-iodo-1-phenyl-6-(*p*-tolyl)hex-5-en-3-yl)-1,3,2-dioxaborolane (13b)**

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):



<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):



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