Supporting Information for:

Substrate-Controlled Regio- and Stereoselective Synthesis of Boron-Substituted 1,4-dienes via Copper-Catalyzed Boryl-Allylation of Alkynes with Allyl Phosphates and Bis(pinacolato)diboron

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Table of Contents

1. Instrumentation and Chemicals **S1**

2. Experimental Procedures **S2**

3. Detailed Investigation on Reaction Conditions and Catalysts. **S4**

4. Preparation of Allyl Phosphates **S7**

5. Typical Procedure for Suzuki-Miyaura Coupling **S17**

6. X-ray Single Crystal Structure of (1*E*,4*E*)-10-4 **S17**

7. Characterization Data for the Products **S19**

8. References **S39**

9. ^{1}H and ^{13}C NMR Spectra

10. NOESY Spectra

1. Instrumentation and Chemicals

1.1 General Procedures

Unless indicated otherwise, all reactions were conducted under an atmosphere of argon using standard vacuum-line techniques. NMR spectra were recorded on Advance Bruker Avance III 500 M (^{1}H: 500 MHz; ^{13}C: 126 MHz) spectrometer. Tetramethylsilane (^{1}H) and $CDCl_3$ (^{13}C) were employed as internal standards. *J* values are given in Hertz. High-resolution mass spectra (EI-HRMS, ESI-HRMS, APCI-HRMS) were recorded on a maXis UHR-TOF HPLC-MS (Bruker Corporation) spectrometers or a LCQ Advantage LC-MS (Thermofinnigan Corporation) spectrometers. Gas chromatographic analyses were conducted on a Shimadzu GC-2014C equipped with a flame ionization detector. HPLC analyses were carried out using Shimadzu LC 20 with UV detector SPD-20A. Silica gel (Qingdao Haiyang Chemical Co., Ltd ZCX-3, spherical, neutral, 50–60 μm) and aluminum oxide (Alfa Aesar, activated, neutral, Brockmann Grade II) were used for column chromatography.

1.2 Materials

Materials were obtained from commercial suppliers and purified by the standard procedure unless otherwise noted. CuCl was purchased from Acros. $Pd(PPh_3)_4$, (±)-Binap and PCy_3 were purchased from Wu Han hsenbruy Chemical Co., Ltd.. PPh_3 was purchased from Aladdin Industrial Inc.. $Pd(dba)_2$ and Sphos were purchased from TianJin Heowns Biochemical Technology Co., Ltd. Bis(pinacolato)diboron (B_2Pin_2, purchased from Dalian AllyChem Co., Ltd.) was recrystallized from n-pentane. IMes·HCl[1], SIPr·HCl[2] and SIMes·HCl[2] were prepared according to the reported procedures. ^{t}BuOK was purchased from Acros and purified by sublimation. THF, dioxane, toluene, DMF, benzene and hexane were purchased from Sinopharm Chemical Reagent Co, Ltd. (SCRC), distilled from sodium metal and degassed via three freeze–pump–thaw cycles before using.

Alkynes:

Phenylacetylene was purchased from Accela ChemBio Co., Ltd..

1-Ethynylcyclohexene was purchased from Sigma.

Diphenylacetylene and 1-Phenyl-1-pentyne were purchased from Alfa Aesar.

Dibutylacetylene and dithylacetylene were purchased from TCI.

Trimethylsilylacetylene was purchased from Energy Chemical Co., Ltd..

4-methylphenylacetylene, 4-methoxyphenylacetylene, 4-(trifluoromethyl)phenylacetylene, 4-bromophenylacetylene, 4-fluorophenylacetylene, 4-chlorophenylacetylene, 3-chlorophenylacetylene and 2-chlorophenylacetylene were prepared according to a similar procedure reported in the literature.[3]

Di-(4-methylphenyl)acetylene, di-(4-methoxyphenyl)acetylene, di-(4-fluorophenyl)acetylene, di-[4-(trifluoromethyl)phenyl]acetylene, di-(4-chlorophenyl)acetylene, di-(3-chlorophenyl)acetylene, di-(2-chlorophenyl)acetylene were prepared according to the reported procedures.[4]

1-Phenyl-1-hexyne, 1-(4-chlorophenyl)-1-hexyne, 1-(4-bromophenyl)-1-hexyne and 1-[4-(trifluoromethyl)phenyl]-1-hexyne were prepared according to a similar procedure reported in the literature.[5]

Chlorophosphates:

Diethyl chlorophosphate, diisopropyl chlorophosphate, di-sec-butyl chlorophosphate and dicyclohexyl chlorophosphate were prepared according to the reported procedures.[6]

Bis(2-ethylhexyl) chlorophosphate was prepared according to the reported procedures.[7]

Allyl alcohols:

Allyl alcohol was purchased from Xiya Reagent Co., Ltd..

Cinnamyl alcohol was purchased from Energy Chemical Co., Ltd..

(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methanol (DIHYDRO CUMINYL ALCOHOL) was purchased from Admas Reagent Co., Ltd..

(*E*)-3,7-dimethylocta-2,6-dien-1-ol (Geraniol) was purchased from TCI.

(*Z*)-1-phenylhex-4-en-3-ol, (*Z*)-1-cyclohexylbut-2-en-1-ol and (*Z*)-hex-4-en-3-ol were prepared according to a similar procedure reported in the literature.[8]

5-phenylpent-1-en-3-ol[9], (*Z*)-4-(benzyloxy)but-2-en-1-ol[10] and (*Z*)-3-phenylprop-2-en-1-ol[11] were prepared according to the reported procedures.

(*Z*)-1-phenylnon-4-en-3-ol, (*Z*)-4-(trimethylsilyl)but-3-en-2-ol, (Z)-6,6-dimethylhept-4-en-3-ol, (*Z*)-non-4-en-3-ol, (*Z*)-4,4-dimethyl-1-phenylpent-1-en-3-ol, (*Z*)-1,5-diphenylpent-1-en-3-ol, (*Z*)-4-phenylbut-3-en-2-ol, (*Z*)-3-(4-methoxyphenyl)prop-2-en-1-ol, (*Z*)-6,6-dimethylhept-4-en-3-ol, (*Z*)-1-cyclohexylhept-2-en-1-ol, (Z)-4,4-dimethylpent-2-en-1-ol, (Z)-3-(o-tolyl)prop-2-en-1-ol and (*Z*)-non-2-en-1-ol were prepared according to a similar procedure in the literature.[11, 12]

Cyclohex-2-en-1-ol[13] and 4,4-dimethylcyclohex-2-en-1-ol[14] were prepared according to the reported procedures.

(*E*)-3-phenylbut-2-en-1-ol and (*E*)-4,4-dimethylpent-2-en-1-ol were prepared according to a similar procedure in the literature.[15]

(*E*)-2-methyl-3-phenylprop-2-en-1-ol was prepared according to the reported procedures.[16]

Halides:

1-chloro-4-iodobenzene and 2-Bromopyridine was purchased from Beijing Ouhe Technology Co., Ltd..

1-chloro-2-iodobenzene and 2-iodo-1,3,5-trimethylbenzene were purchased from Energy Chemical Co., Ltd..

1-bromo-2-methylbenzene was purchased from J&K Scientific Ltd..

(*Z*)-2-bromobut-2-ene was purchased from Aldrich.

(*Z*)-1-bromoprop-1-ene[17] and 1-bromooct-1-yne[18] were prepared according to the reported procedures.

Acetyenic ketones:

Non-4-yn-3-one was prepared according to a similar procedure reported in the literature.[19]

2. Experimental Procedures

2.1 General procedure for the copper(I)-catalyzed γα-(4*E*)-selective synthesis of boron-substituted 1,4-dienes from terminal alkynes, secondary allyl phosphates and bis(pinacolato)diboron. (Table 1 and Table 2)

In air, $B_2(Pin)_2$ was placed in a screw-capped reaction vial. The vial was moved into a glove box. Then,

CuCl, (±)-Binap, KO^{t}Bu and THF were added. The vial was moved out of the glove box and connected to an argon line through a needle. The mixture was stirred for 10 min at room temperature. Terminal alkynes (solid terminal alkynes were dissolved in THF) and allyl phosphates were added dropwise. The mixture was stirred for a specified period of time at room temperature. The reaction mixture was diluted with ethyl acetate and then passed through a Florisil short column (eluent ethyl acetate). After evaporation under reduced pressure, the residue was subjected to silica gel column chromatography to obtain the desired product.

2.2 General procedure for the copper-catalyzed synthesis of boron-substituted 1,4-dienes from symmetrical diaryl alkynes, allyl phosphates and bis(pinacolato)diboron: γ-selective or α-selective. (Table 3, Table 4, Table 7, Scheme 4 and Scheme 5)

In air, $B_2(Pin)_2$ and symmetrical diaryl alkynes were placed in a screw-capped reaction vial. The vial was moved into a glove box. Then, CuCl, ligand, KO^{t}Bu and toluene were added. The vial was moved out of the glove box and connected to an argon line through a needle. The mixture was raised to 65 °C and stirred for 30 min. After the mixture was adjusted to the specified reaction temperature, allyl phosphates were added dropwise and the mixture was stirred for a specified period of time. The reaction mixture was diluted with ethyl acetate and then passed through a Florisil short column (eluent ethyl acetate). After evaporation under reduced pressure, the residue was subjected to silica gel column chromatography to obtain the desired product.

2.3 General procedure for the copper-catalyzed synthesis of boron-substituted 1,4-dienes from dialkylacetylenes, allyl phosphates and bis(pinacolato)diboron. (Scheme 2 and Table 5)

In air, $B_2(Pin)_2$ was placed in a screw-capped reaction vial. The vial was moved into a glove box and CuCl, ligand, KO^{t}Bu and toluene (or DMF) were added. The vial was moved out of the glove box and connected to an argon line through a needle. The mixture was stirred for 10 min at 65 °C. Dialkylacetylenes and allyl phosphates were added dropwise. The mixture was stirred for a specified period of time at 65 °C. The reaction mixture was diluted with ethyl acetate and then passed through a Florisil short column (eluent ethyl acetate). After evaporation under reduced pressure, the residue was subjected to silica gel column chromatography to obtain the desired product.

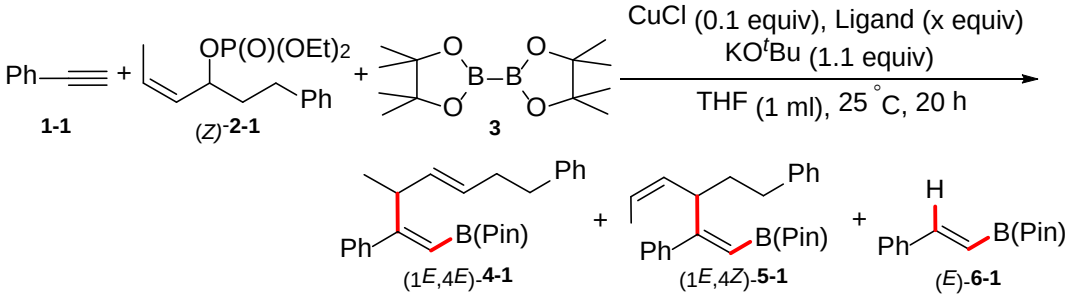
2.4 General procedure for the copper-catalyzed synthesis of boron-substituted 1,4-dienes from arylalkylacetylenes, allyl phosphates and bis(pinacolato)diboron: γ-selective or α-selective. (Table 6, Table 7 and Scheme 3)

In air, $B_2(Pin)_2$ was placed in a screw-capped reaction vial. The vial was moved into a glove box. Then, CuCl, ligand, KO^{t}Bu and DMF (or toluene) were added. The vial was moved out of the glove box and connected to an argon line through a needle. The mixture was raised to the required reaction temperature and stirred for 10 min. Then, aryl alkyl alkynes and allyl phosphates were added dropwise. The reaction mixture was stirred for a specified period of time. The reaction mixture was diluted with ethyl acetate before filtration through a celite plug. The organic solution was washed two times with water and dried over Na_2SO_4. After evaporation under reduced pressure, the residue was subjected to silica gel column chromatography to obtain the desired product.

3. Detailed Investigation on Reaction Conditions and Catalysts

3.1 Reaction optimization for copper(I)-catalyzed γ-(4*E*)-selective synthesis of boron-substituted 1,4-dienes from terminal alkynes, secondary allyl phosphates and bis(pinacolato)diboron.

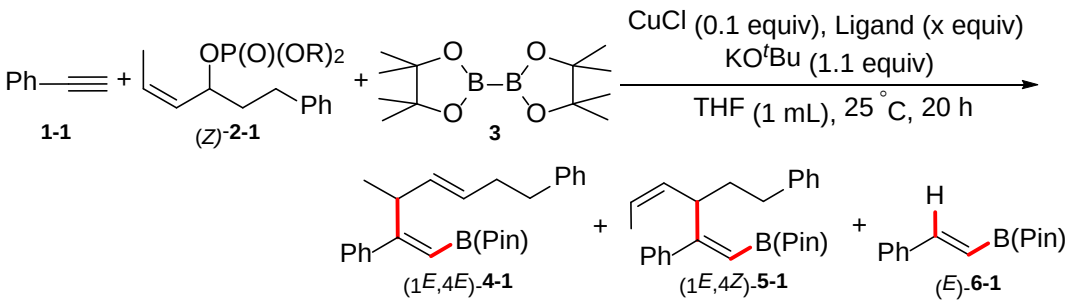
Table S1. Effects of the ligands [a]



entry	ligand	x	yield (%)[b]	**4-1:5-1[c](6-1%)[d]**
1	dppm	0.1	27	-
2	(±)-Binap	0.1	71	94:6(19)
3	$P[N(CH_3)_2]_3$	0.2	77	95:5(27)
4	SIPr·HCl	0.1	71	91:9(7)
5	Xantphos	0.1	45	91:9(35)
6	SIMes·HCl	0.1	61	93:7(32)
7	PCy_3	0.2	80	92:8(12)
8	dppf	0.1	66	92:8(36)
9	$P(^tBu)_3$	0.2	77	92:8(13)
10	PPh_3	0.2	82	91:9(6)
11	IMes·HCl	0.1	66	93:7(15)

[a] Reaction Conditions: **1-1** (0.3 mmol), **2-1** (0.45 mmol), **3** (0.33 mmol), CuCl (0.03 mmol), KO^tBu (0.33 mmol), 25 °C, 20 h, Cy = cyclohexyl. [b] The combined isolated yields of **4-1**, **5-1** and **6-1**. [c] The molar ratio of **4-1** and **5-1** in the isolated product, determined by ^1H NMR. **4-1**, **5-1** and **6-1** can not be separated by column chromatography. [d] The molar percentage of **6-1** in the isolated product, determined by ^1H NMR.

Table S2. Effects of the leaving groups [a]

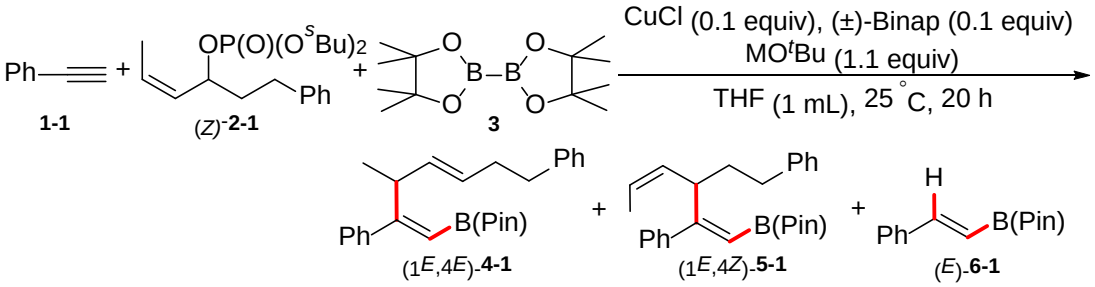


entry	R	ligand	x	yield (%)[b]	**4-1:5-1[c](6-1%)[d]**
1	^{n}Pr	(±)-Binap	0.1	83	>99:<1(7)

2	^{i}Pr	(±)-Binap	0.1	96	>99:<1(7)
3	^{s}Bu	(±)-Binap	0.1	95	>99:<1(3)
4[e]	^{s}Bu	(±)-Binap	0.1	83	94:6(14)
5	Cy	(±)-Binap	0.1	70	97:3(2)
6	2-ethylhexyl	(±)-Binap	0.1	86	>99:<1(3)
7	^{i}Pr	$P[N(CH_3)_2]_3$	0.2	95	>99:<1(15)
8	^{s}Bu	$P[N(CH_3)_2]_3$	0.2	55	>99:<1(14)
9	^{s}Bu	PPh_3	0.2	87	97:3(4)
10	^{s}Bu	PCy_3	0.2	63	80:1(19)

[a] Reaction Conditions: **1-1** (0.3 mmol), **2-1** (0.45 mmol), **3** (0.33 mmol), CuCl (0.03 mmol), KO^{t}Bu (0.33 mmol), 25 °C, 20 h, Cy = cyclohexyl. [b] The combined isolated yields of **4-1**, **5-1** and **6-1**. [c] The molar ratio of **4-1** and **5-1** in the isolated product, determined by ^{1}H NMR. **4-1**, **5-1** and **6-1** can not be separated by column chromatography. [d] The molar percentage of **6-1** in the isolated product, determined by ^{1}H NMR. [e] (*E*)-**2-1** was used instead of (*Z*)-**2-1**, and (1*E*,4*E*)-**5-1** is formed instead of (1*E*,4*Z*)-**5-1**.

Table S3. Effects of the bases and solvents [a]

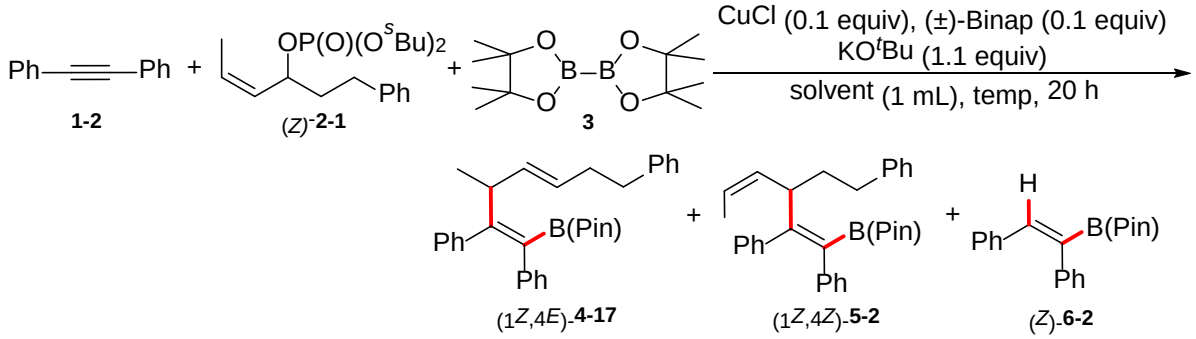


entry	MO^{t}Bu	yield (%)[b]	**4-1:5-1[c](6-1%)[d]**
1	NaO^{t}Bu	70	99:1(30)
2	LiO^{t}Bu	88	98:2(3)
3[e]	KO^{t}Bu	54	99:1(31)

[a] Reaction Conditions: **1-1** (0.3 mmol), **2-1** (0.45 mmol), **3** (0.33 mmol), CuCl (0.03 mmol), (±)-Binap (0.03 mmol), MO^{t}Bu (0.33 mmol), 25 °C, 20 h, Cy = cyclohexyl. [b] The combined isolated yields of **4-1**, **5-1** and **6-1**. [c] The molar ratio of **4-1** and **5-1** in the isolated product, determined by ^{1}H NMR. **4-1**, **5-1** and **6-1** can not be separated by column chromatography. [d] The molar percentage of **6-1** in the isolated product, determined by ^{1}H NMR. [e] The reaction was carried out in toluene.

3.2 Reaction optimization for the copper(I)-catalyzed γ-(4*E*)-selective synthesis of boron-substituted 1,4-dienes from symmetrical diaryl alkynes.

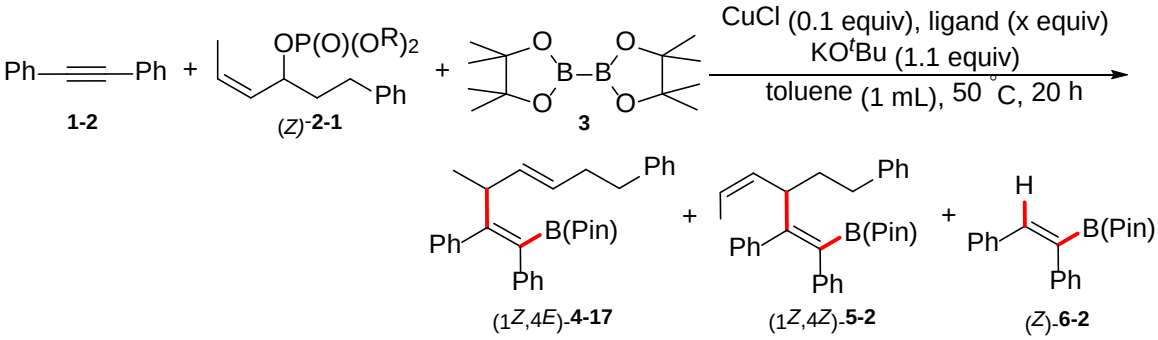
Table S4. Effects of the solvents [a]



entry	solvent	temp (°C)	yield (%)[b]	**4-17:5-2[c](6-2%)[d]**
1	THF	rt	91	48:52(12)
2[e]	toluene/THF	30	80	97:3(7)
3[e]	toluene/THF	40	72	96:4(2)
4	toluene	30	63	96:4(<1)
5	toluene	40	65	96:4(<1)
6	toluene	50	95	99:1(1)
7	benzene	50	74	95:5(5)
8	hexane	50	83	93:7(4)

[a] Reaction Conditions: **1-2** (0.3 mmol), **2-1** (0.45 mmol), **3** (0.33 mmol), CuCl (0.03 mmol), (±)-Binap (0.03 mmol), KO^{t}Bu (0.33 mmol), 20 h. [b] The combined isolated yields of **4-17**, **5-2** and **6-2**. [c] The molar ratio of **4-17** and **5-2** in the isolated product, determined by ^{1}H NMR. **4-17**, **5-2** and **6-2** can not be separated by column chromatography. [d] The molar percentage of **6-2** in the isolated product, determined by ^{1}H NMR. [e] The volume ratio of toluene:THF was 6:1.

Table S5. Effects of the ligands and leaving Groups [a]

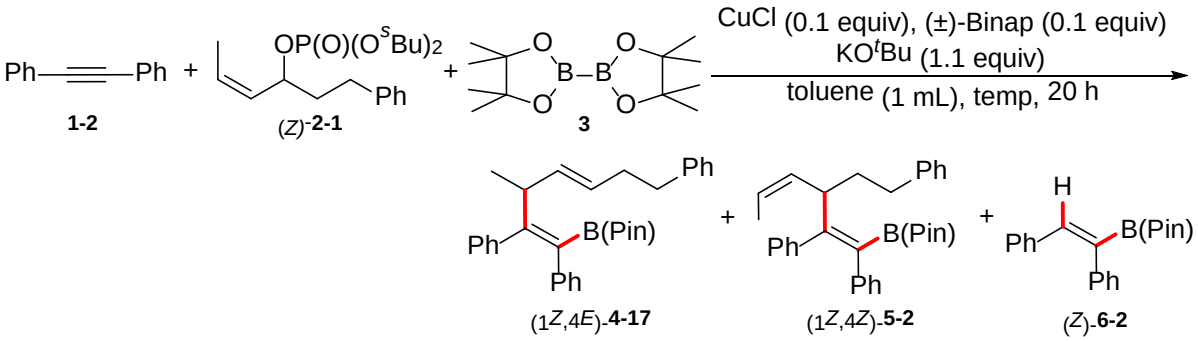


entry	R	ligand	x	yield (%)[b]	**4-17:5-2[c](6-2%)[d]**
1	^{i}Pr	(±)-Binap	0.1	70	98:2(2)
2	2-ethylhexyl	(±)-Binap	0.1	71	98:2(2)
3	Cy	(±)-Binap	0.1	62	99:1(2)
4	^{s}Bu	PPh_3	0.2	80	98:2(2)
5	2-ethylhexyl	PPh_3	0.2	63	99:1(1)

[a] Reaction Conditions: **1-2** (0.3 mmol), **2-1** (0.45 mmol), **3** (0.33 mmol), CuCl (0.03 mmol), KO^{t}Bu (0.33 mmol), 50 °C, 20 h. [b] The combined isolated yields of **4-17**, **5-2** and **6-2**. [c] The molar ratio of **4-17** and **5-2** in the isolated product, determined by ^{1}H NMR. **4-17**, **5-2** and **6-2** can not be separated by column

chromatography. [d] The molar percentage of **6-2** in the isolated product, determined by ^{1}H NMR.

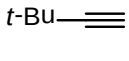
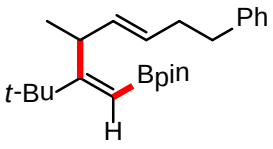
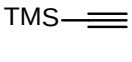
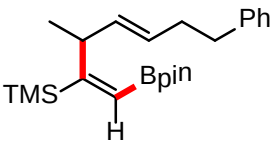
Table S6. Effects of the reaction temperature [a]



entry	temp (°C)	yield (%)[b]	**4-17:5-2[c](6-2%)[d]**
1	65	90	99:1(0)
2	80	87	99:1(2)
3[c]	65	56	94:6(0)

[a] Reaction Conditions: **1-2** (0.3 mmol), **2-1** (0.45 mmol), **3** (0.33 mmol), CuCl (0.03 mmol), KO^{t}Bu (0.33 mmol), 20 h. [b] The combined isolated yields of **4-17**, **5-2** and **6-2**. [c] The molar ratio of **4-17** and **5-2** in the isolated product, determined by ^{1}H NMR. **4-17**, **5-2** and **6-2** cannot be separated by column chromatography. [d] The molar percentage of **6-2** in the isolated product, determined by ^{1}H NMR. [e] (*E*)-**2-1** was used instead of (*Z*)-**2-1** and (1*Z*,4*E*)-**5-2** is produced instead of (1*Z*,4*Z*)-**5-2**.

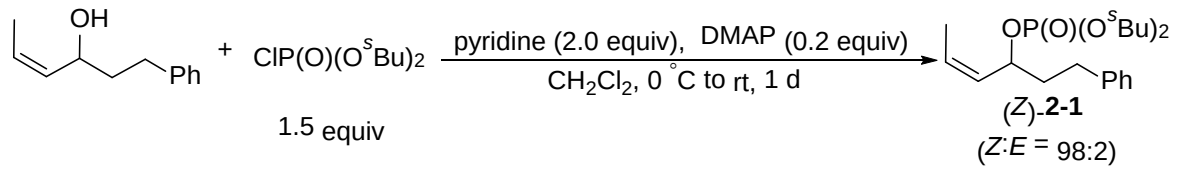
Table S7. The reactions using *tert*-butyl acetylene and trimethylsilyl acetylene with (*Z*)-**2-1**[a]

entry	alkyne	product	yield (%)[b]	γ/α[c]	γ(4*E*):γ(4*Z*)[d]	hydroboration (%)[e]
1			76	34:66	57:43	27
2			68	50:50	77:23	3

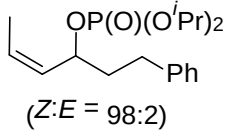
[a] Reaction Conditions: see **Table 2**. [b] Combined isolated yields, containing γ- and α-isomers, and hydroboration product. [c] The molar ratios of γ- and α-regioisoamers, determined by ^{1}H NMR spectroscopy. [d] The ratios are determined by ^{1}H NMR spectroscopy. [e] The molar ratios of hydroboration products in the isolated product, determined by ^{1}H NMR spectroscopy.

4. Preparation of Allyl Phosphates

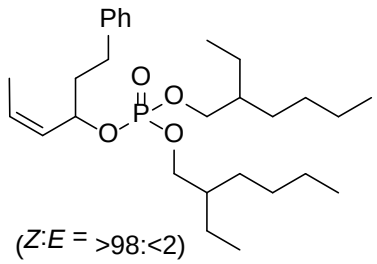
4.1 Synthesis of the Secondary Allyl Phosphates



(*Z*)-**di-sec-butyl (1-phenylhex-4-en-3-yl) phosphate:** In a 25 mL dry two-neck flask equipped with a magnetic bar was added DMAP (2.0 mmol, 0.20 equiv, 244 mg). The flask was then evacuated and back-filled with argon three times. Dry CH_2Cl_2 (10 mL), pyridine (20 mmol, 2.0 equiv, 1.6 mL) and (*Z*)-1-phenylhex-4-en-3-ol (10 mmol, 1.0 equiv, 1.763 g) were added in turn to the flask. The reaction mixture was cooled to 0 °C and then di-sec-butyl chlorophosphate (15 mmol, 1.5 equiv, 3.430 g) was added dropwise. After the reaction was slowly warmed to room temperature through 1 d with stirring, it was quenched with 5% HCl (10 mL) at 0 °C. The organic layer was separated and the water layer was extracted with ether (3 × 15 mL). The combined organic layer was then washed with water (30 mL) and dried with Na_2SO_4. The solution was concentrated in vacuo, which afforded an oil that was purified by silica gel column chromatography (eluent ethyl acetate : hexane = 20:80) and then aluminum oxide flash chromatography (eluent ethyl acetate) to give (*Z*)-**2-1** (3.168 g, 87%) as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.30–7.25 (m, 2H), 7.21–7.19 (m, 3H), 5.66 (dq, *J* = 13.6, 6.9 Hz, 1H), 5.50 (ddd, *J* = 10.9, 9.2, 1.7 Hz, 1H), 5.21–5.13 (m, 1H), 4.49–4.32 (m, 2H), 2.73–2.62 (m, 2H), 2.16–2.04 (m, 1H), 1.93–1.81 (m, 1H), 1.73–1.62 (m, 5H), 1.57 (dt, *J* = 13.3, 6.4 Hz, 2H), 1.36–1.24 (m, 5H), 1.00–0.86 (m, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.48, 129.73 (d, *J* = 3.9 Hz), 128.35, 128.33, 127.72 (d, *J* = 2.0 Hz), 76.67 (d, *J* = 5.8 Hz), 76.57 (d, *J* = 6.5 Hz), 73.73 (d, *J* = 5.5 Hz), 38.04 (d, *J* = 3.5 Hz), 37.98 (d, *J* = 3.8 Hz), 31.09, 30.29, 30.25 (d, *J* = 5.9 Hz), 20.92 (d, *J* = 2.3 Hz), 20.81 (d, *J* = 1.7 Hz), 13.46, 9.40 (d, *J* = 4.2 Hz), 9.35 (d, *J* = 3.8 Hz). **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{20}H_{33}O_4PNa$, 391.2014; found: 391.2013.

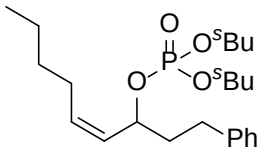


(*Z*)-**diisopropyl (1-phenylhex-4-en-3-yl) phosphate:** Following the general procedure **4.1**, the compound was obtained in 85% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.30–7.24 (m, 2H), 7.22–7.14 (m, 3H), 5.66 (dq, *J* = 11.1, 7.0 Hz, 1H), 5.50 (ddt, *J* = 10.9, 9.2, 1.6 Hz, 1H), 5.19–5.10 (m, 1H), 4.66–4.54 (m, 2H), 2.72–2.63 (m, 2H), 2.15–2.05 (m, 1H), 1.92–1.80 (m, 1H), 1.68 (dd, *J* = 7.0, 1.7 Hz, 3H), 1.35–1.27 (m, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.45, 129.67 (d, *J* = 3.4 Hz), 128.36, 128.33, 127.83, 125.88, 73.72 (d, *J* = 6.1 Hz), 72.05 (d, *J* = 4.2 Hz), 72.01 (d, *J* = 4.3 Hz), 37.97 (d, *J* = 6.4 Hz), 31.10, 23.68 (d, *J* = 5.2 Hz), 23.61 (d, *J* = 4.9 Hz), 13.44. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{18}H_{29}O_4PNa$, 363.1701; found: 363.1694.

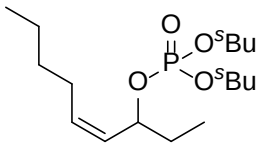


(*Z*)-**bis(2-ethylhexyl) (1-phenylhex-4-en-3-yl) phosphate:** Following the general procedure **4.1**, the compound was obtained in 85% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.31–7.24 (m, 2H), 7.19 (m, 3H), 5.68 (ddt, *J* = 11.5, 7.5, 6.5 Hz, 1H), 5.50 (ddd, *J* = 10.9, 9.2, 1.7 Hz, 1H), 5.23–5.12 (m, 1H), 4.00–3.85 (m, 4H), 2.75–2.62 (m, 2H), 2.10 (ddt, *J* = 13.1, 10.3, 6.5 Hz, 1H), 1.92–1.82 (m, 1H), 1.69 (dd, *J* = 7.0, 1.7 Hz, 3H), 1.55 (tt, *J* = 11.6, 5.7 Hz, 2H), 1.46–1.20 (m, 16H), 0.94–0.82 (m, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.33, 129.49 (d, *J* = 3.2 Hz), 128.35, 128.28, 128.09, 125.88, 73.91 (d, *J* = 5.9 Hz), 69.43 (d, *J* = 5.8 Hz), 69.38 (d, *J* = 6.2 Hz), 40.07 (d, *J* = 4.4 Hz), 40.01 (d, *J* = 4.6 Hz), 37.96 (d, *J* = 6.5 Hz), 31.14, 29.87 (d, *J* = 1.7 Hz), 28.85 (d, *J* = 2.1 Hz), 23.21 (d, *J*

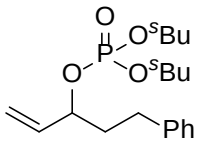
= 1.7 Hz), 22.94, 14.01 (d, *J* = 1.2 Hz), 13.42, 10.88. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{28}H_{49}O_4PNa$, 503.3266; found: 503.3246.


(*Z*:*E* = >99:<1)

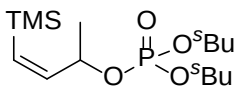
(*Z*)-**di-sec-butyl (1-phenylnon-4-en-3-yl) phosphate:** Following the general procedure **4.1**, the compound was obtained in 75% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.30–7.24 (m, 2H), 7.22–7.14 (m, 3H), 5.56 (dt, *J* = 10.9, 7.4 Hz, 1H), 5.50–5.43 (m, 1H), 5.20–5.12 (m, 1H), 4.47–4.33 (m, 1H), 2.68 (dt, *J* = 10.6, 5.3 Hz, 2H), 2.17–2.02 (m, 3H), 1.93–1.79 (m, 1H), 1.74–1.51 (m, 4H), 1.42–1.19 (m, 10H), 1.01–0.81 (m, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.57, 133.57 (d, *J* = 2.8 Hz), 128.72 (d, *J* = 3.9 Hz), 128.41, 128.38, 125.91, 76.72 (d, *J* = 4.9 Hz), 76.59 (d, *J* = 6.5 Hz), 74.21 (d, *J* = 5.1 Hz), 38.37 (d, *J* = 6.3 Hz), 38.31 (d, *J* = 6.3), 31.7, 31.19, 30.38 (d, *J* = 5.9 Hz), 30.31 (d, *J* = 6.0 Hz), 27.61, 22.40, 21.01 (d, *J* = 3.0 Hz), 20.88 (d, *J* = 2.2 Hz), 13.98, 9.47 (d, *J* = 4.1 Hz), 9.41 (d, *J* = 3.9 Hz). **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{23}H_{39}O_4PNa$, 433.2484; found: 433.2482.


(*Z*)-**2-8**
(*Z*:*E* = >99:<1)

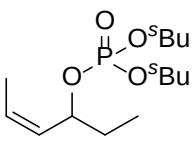
(*Z*)-**di-sec-butyl non-4-en-3-yl phosphate:** Following the general procedure **4.1**, the compound (*Z*)-**2-8** was obtained in 78% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.54 (dt, *J* = 10.9, 7.5 Hz, 1H), 5.39 (t, *J* = 10.1 Hz, 1H), 5.05 (dt, *J* = 14.3, 6.4 Hz, 1H), 4.45–4.32 (m, 2H), 2.19–2.09 (m, 2H), 1.78 (dp, *J* = 13.6, 7.4 Hz, 1H), 1.72–1.51 (m, 5H), 1.43–1.19 (m, 10H), 0.98–0.82 (m, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 133.26 (d, *J* = 5.9 Hz), 128.64 (d, *J* = 4.2 Hz), 76.53 (d, *J* = 5.9 Hz), 76.41 (d, *J* = 6.5 Hz), 75.78 (d, *J* = 5.9 Hz), 31.69 (d, *J* = 1.1 Hz), 30.31 (d, *J* = 6.2 Hz), 30.24 (d, *J* = 6.0 Hz), 29.42 (d, *J* = 2.2 Hz), 27.54 , 22.34 , 20.89 (d, *J* = 3.4 Hz), 20.81 (d, *J* = 2.4 Hz), 13.93 , 9.40 (d, *J* = 3.3 Hz), 9.33 (d, *J* = 3.7 Hz), 9.17 (d, *J* = 3.2 Hz). **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{17}H_{35}O_4PNa$, 357.2171; found: 357.2158.



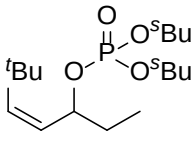
di-sec-butyl (5-phenylpent-1-en-3-yl) phosphate: Following the general procedure **4.1**, the compound was obtained in 73% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.32–7.23 (m, 2H), 7.21–7.15 (m, 3H), 5.88 (ddd, *J* = 17.3, 10.5, 6.9 Hz, 1H), 5.33 (dt, *J* = 17.2, 1.1 Hz, 1H), 5.23 (dt, *J* = 10.5, 1.0 Hz, 1H), 4.80 (p, *J* = 6.6 Hz, 1H), 4.44–4.24 (m, 2H), 2.76–2.63 (m, 2H), 2.10–2.00 (m, 1H), 2.00–1.85 (m, 5H), 1.78–1.65 (m, 4H), 1.62–1.41 (m, 6H), 1.38–1.14 (m, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.41, 136.85 (d, *J* = 3.8 Hz), 128.35, 128.33, 125.86, 117.14, 78.75 (d, *J* = 6.0 Hz), 76.88 (d, *J* = 6.1 Hz), 37.55 (d, *J* = 5.9 Hz), 33.29 (d, *J* = 4.9 Hz), 33.25 (d, *J* = 3.8 Hz), 30.95, 25.12, 23.44. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{19}H_{31}O_4PNa$, 377.1858; found:377.1851.


(*Z*:*E* = 99:1)

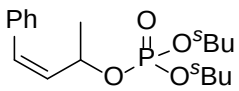
(*Z*)-**di-sec-butyl (4-(trimethylsilyl)but-3-en-2-yl) phosphate:** Following the general procedure **4.1**, the compound was obtained in 62% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.28 (dd, *J* = 15.7, 8.8 Hz, 1H), 5.61 (d, *J* = 14.5 Hz, 1H), 5.13–5.01 (m, 1H), 4.49–4.24 (m, 2H), 1.72–1.51 (m, 4H), 1.38 (d, *J* = 6.4 Hz, 3H), 1.32–1.26 (m, 6H), 0.93 (qd, *J* = 7.2, 2.8 Hz, 6H), 0.16 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 147.47 (d, *J* = 1.8 Hz), 130.68 (d, *J* = 9.6 Hz), 76.67 (d, *J* = 2.5 Hz), 76.58 (d, *J* = 6.2 Hz), 75.10 (d, *J* = 5.9 Hz), 30.31 (d, *J* = 6.7 Hz), 30.22 (d, *J* = 5.1 Hz), 22.99 (d, *J* = 2.0 Hz), 22.95 (d, *J* = 1.9 Hz), 20.95 (d, *J* = 3.1 Hz), 20.86 (d, *J* = 3.3 Hz), 9.43 (d, *J* = 3.8 Hz), 9.35 (d, *J* = 5.2 Hz), 0.09. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{15}H_{33}O_4PSiNa$, 359.1784; found: 359.1774.


(*Z*:*E* = 98:2)

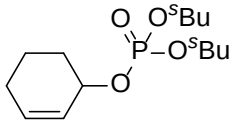
(*Z*)-**di-sec-butyl hex-4-en-3-yl phosphate:** Following the general procedure **4.1**, the compound was obtained in 72% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** 5.70–5.56 (m, 1H), 5.42 (ddd, *J* = 10.9, 9.3, 1.7 Hz, 1H), 5.07 (dp, *J* = 12.7, 6.3 Hz, 1H), 4.46–4.30 (m, 2H), 1.84–1.73 (m, 1H), 1.71 (dd, *J* = 7.0, 1.8 Hz, 3H), 1.68–1.46 (m, 5H), 1.37–1.23 (m, 6H), 1.00–0.85 (m,9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ129.74 (d, *J* = 4.0 Hz), 127.37 (d, *J* = 1.6 Hz), 76.58 (d, *J* = 4.6 Hz), 76.53 (d, *J* = 4.4 Hz), 75.38 (d, *J* = 6.1 Hz), 30.30 (d, *J* = 6.9 Hz), 30.23 (d, *J* = 6.0 Hz), 29.31 (d, *J* = 2.4 Hz), 29.26 (d, *J* = 2.0 Hz), 20.87 (d, *J* = 3.3 Hz), 20.81 (d, *J* = 5.0 Hz), 13.42, 9.35 (d, *J* = 2.2 Hz), 9.30 (d, *J* = 1.6 Hz), 9.07 (d, *J* = 2.9 Hz). **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{14}H_{29}O_4PNa$, 315.1701; found: 315.1698.


(*Z*:*E* = >99:<1)

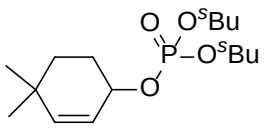
(*Z*)-**di-sec-butyl (6,6-dimethylhept-4-en-3-yl) phosphate:** Following the general procedure **4.1**, the compound was obtained in 47% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.45–5.39 (m, 1H), 5.39–5.31 (m, 1H), 5.20 (ddd, *J* = 11.6, 9.8, 1.6 Hz, 1H), 4.45–4.31 (m, 2H), 1.75 (dq, *J* = 14.8, 7.4 Hz, 1H), 1.72–1.52 (m, 5H), 1.34–1.25 (m, 6H), 1.14 (s, 9H), 0.99–0.89 (m, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.65 (d, *J* = 2.8 Hz), 127.02 (d, *J* = 4.6 Hz), 76.52 (d, *J* = 6.1 Hz), 76.36 (d, *J* = 6.3 Hz), 75.97 (d, *J* = 4.3 Hz), 31.18, 30.33 (d, *J* = 6.0 Hz), 30.24 (d, *J* = 5.8 Hz), 29.97 (d, *J* = 6.2 Hz), 20.95 (d, *J* = 3.3 Hz), 20.79 (d, *J* = 3.2 Hz), 9.41 (d, *J* = 3.4 Hz), 9.35 (d, *J* = 2.2 Hz), 9.31 (d, *J* = 4.6 Hz). **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{17}H_{35}O_4PNa$, 357.2171; found: 357.2158.


(*Z*:*E* = 99:1)

(*Z*)-**di-sec-butyl (4-phenylbut-3-en-2-yl) phosphate:** Following the general procedure **4.1**, the compound was obtained in 74% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.37–7.31 (m, 2H), 7.29–7.23 (m, 3H), 6.51 (d, *J* = 11.8 Hz, 1H), 5.74 (dd, *J* = 11.7, 9.2 Hz, 1H), 5.47–5.36 (m, 1H), 4.43–4.31 (m, 2H), 1.70–1.53 (m, 4H), 1.49 (d, *J* = 6.1 Hz, 3H), 1.28–1.18 (m, 6H), 0.91–0.81 (m, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 136.12, 132.39 (d, *J* = 3.9 Hz), 129.96 (d, *J* = 2.7 Hz), 128.62, 128.36, 127.32, 76.78 (d, *J* = 6.3 Hz, 2C), 71.40 (d, *J* = 6.4 Hz), 30.26 (d, *J* = 5.8 Hz), 30.17 (d, *J* = 5.6 Hz), 22.73 (d, *J* = 3.2 Hz), 20.90 (d, *J* = 3.2 Hz), 20.79 (d, *J* = 3.3 Hz), 9.37 (d, *J* = 2.4 Hz), 9.30 (d, *J* = 2.1 Hz). **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{18}H_{29}O_4PNa$, 363.1701; found: 363.1703.

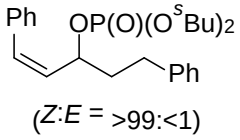


di-sec-butyl cyclohex-2-en-1-yl phosphate: Following the general procedure **4.1**, the compound was obtain in 67% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.88 (d, *J* = 10.1 Hz, 1H), 5.77 (d, *J* = 9.8 Hz, 1H), 4.82 (s, 1H), 4.38 (dt, *J* = 12.5, 6.2 Hz, 2H), 2.10–1.79 (m, 4H), 1.79–1.51 (m, 8H), 1.28 (d, *J* = 6.2 Hz, 6H), 0.91 (t, *J* = 7.5 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 132.18, 126.62 (d, *J* = 4.8 Hz), 76.65 (d, *J* = 6.3 Hz), 71.69 (d, *J* = 6.1 Hz), 30.35 (d, *J* = 5.6 Hz), 30.25 (d, *J* = 6.1 Hz), 29.90 (d, *J* = 3.8 Hz), 24.70, 20.90 (d, *J* = 4.3 Hz), 20.85 (d, *J* = 2.8 Hz), 18.50, 9.43 (d, *J* = 4.9 Hz), 9.36 (d, *J* = 3.2 Hz). **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{14}H_{27}O_4PNa$, 313.1545; found: 313.1530.



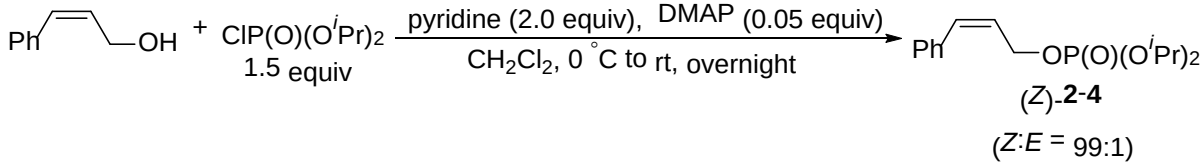
di-sec-butyl (4,4-dimethylcyclohex-2-en-1-yl) phosphate: Following the general procedure **4.1**, the compound was obtained in 70% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.65 (dd, *J* = 10.1, 3.2 Hz, 1H), 5.59 (d, *J* = 10.1 Hz, 1H), 4.85–4.73 (m, 1H), 4.42 (dq, *J* = 12.4, 6.2 Hz, 2H), 2.00–1.96 (m, 1H), 1.90–1.82 (m, 1H), 1.73–1.53 (m, 4H), 1.43 (ddd, *J* = 13.1, 9.1, 3.2 Hz, 1H), 1.32 (dd, *J* = 6.2, 1.6 Hz, 6H),

1.02 (s, 3H), 0.97 (s, 3H), 0.94 (t, *J* = 7.5 Hz, 4H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 142.10 (d, *J* = 2.5 Hz), 124.12 (d, *J* = 2.5 Hz), 76.72 (d, *J* = 7.7 Hz, 2C), 72.01 (d, *J* = 5.1 Hz), 33.11 (d, *J* = 2.0 Hz), 31.69, 30.32 (d, *J* = 2.4 Hz), 30.27 (d, *J* = 2.2 Hz), 28.99 (d, *J* = 2.5 Hz), 28.64 (d, *J* = 2.8 Hz), 27.14 (d, *J* = 3.8 Hz), 20.96 (d, *J* = 3.4 Hz), 20.91 (d, *J* = 3.1 Hz), 9.41 (d, *J* = 3.5 Hz, 2C). **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{16}H_{31}O_4PNa$, 341.1858; found: 341.1844.

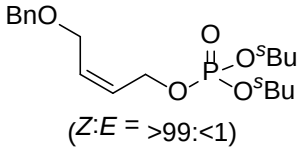


(*Z*)-**di-sec-butyl (1,5-diphenylpent-1-en-3-yl) phosphate:** Following the general procedure **4.1**, the compound was obtained in 51% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.29–7.21 (m, 5H), 7.21–7.17 (m, 3H), 7.15 (d, *J* = 7.7 Hz, 2H), 6.56 (d, *J* = 11.9 Hz, 1H), 5.77 (dd, *J* = 11.8, 9.4 Hz, 1H), 5.42–5.26 (m, 1H), 4.46–4.30 (m, 2H), 2.72 (t, *J* = 7.8 Hz, 2H), 2.20–2.10 (m, 1H), 2.01–1.91 (m, 1H), 1.66–1.44 (m, 4H), 1.29–1.16 (m, 6H), 0.93–0.82 (m, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.31, 136.06 (d, *J* = 2.6 Hz), 131.04 (d, *J* = 3.3 Hz), 128.61, 128.52 (d, *J* = 2.1 Hz), 128.36, 128.34, 127.25, 125.89, 76.85 (d, *J* = 3.6 Hz), 76.80 (d, *J* = 2.8 Hz), 74.10 (d, *J* = 4.3 Hz), 38.25 (d, *J* = 3.4 Hz), 30.98, 30.22 (d, *J* = 3.6 Hz), 30.17 (d, *J* = 2.8 Hz), 20.87 (d, *J* = 2.6 Hz), 20.82 (d, *J* = 3.4 Hz), 9.37 (d, *J* = 2.5 Hz), 9.32 (d, *J* = 2.8 Hz). **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{25}H_{35}O_4PNa$, 453.2171; found: 453.2172.

4.2 Synthesis of the Primary Allyl Phosphates

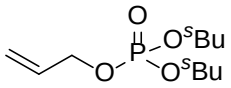


(*Z*)-**diisopropyl (3-phenylallyl) phosphate:** In a 25 mL dry two-neck flask equipped with a magnetic bar was added DMAP (0.5 mmol, 0.05 equiv, 62 mg). The flask was then evacuated and back-filled with argon three times. Dry CH_2Cl_2 (10 mL), pyridine (20 mmol, 2.0 equiv, 1.6 mL) and (*Z*)-3-phenylpropenol (10 mmol, 1.0 equiv, 1.342 g) were added in turn to the flask. The reaction mixture was cooled to 0 °C and then diisopropyl chlorophosphate (15 mmol, 1.5 equiv, 3.010 g) was added dropwise. After the reaction was slowly warmed to room temperature overnight with stirring, it was quenched with 5% HCl (10 mL) at 0 °C. The organic layer was separated and the water layer was extracted with ether (3 × 15 mL). The combined organic layer was then washed with water (30 mL) and dried with Na_2SO_4. After filtration, the solution was concentrated in vacuo, which afforded an oil that was purified by silica gel column chromatography (eluent ethyl acetate : hexane = 30:70) and then aluminum oxide flash chromatography (eluent ethyl acetate) to give the compound **2-4** (2.536 g, 88%) as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.35 (t, *J* = 7.4 Hz, 2H), 7.30–7.25 (m, 1H), 7.20 (d, *J* = 7.3 Hz, 2H), 6.65 (d, *J* = 11.7 Hz, 1H), 5.88 (dt, *J* = 11.8, 6.5 Hz, 1H), 4.79 (ddd, *J* = 7.9, 6.6, 1.6 Hz, 2H), 4.64 (dq, *J* = 12.5, 6.2 Hz, 2H), 1.31 (t, *J* = 6.3 Hz, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 135.78, 132.55, 128.60, 128.27, 127.47, 126.64 (d, *J* = 7.8 Hz), 72.37(d, *J* = 6.0 Hz), 63.72(d, *J* = 5.4 Hz), 23.56 (d, *J* = 2.3 Hz), 23.52 (d, *J* = 2.3 Hz). **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{15}H_{23}O_4PNa$, 321.1232; found: 321.1237.

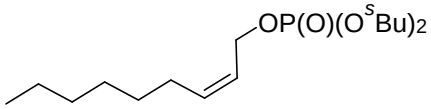


(*Z*)-**4-(benzyloxy)but-2-en-1-yl di-sec-butyl phosphate:** Following the general procedure **4.2**, the compound was obtained in 89% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.34 (d, *J* = 6.3 Hz, 4H), 7.31–7.19 (m, 1H), 5.85–5.73 (m, 2H), 4.64 –4.55 (m, 2H), 4.51 (s, 2H), 4.42 (dq, *J* = 12.3,

6.2 Hz, 2H), 4.11 (d, *J* = 5.0 Hz, 2H), 1.72–1.51 (m, 4H), 1.31 (dd, *J* = 6.2, 4.6 Hz, 6H), 0.93 (td, *J* = 7.5, 3.8 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 137.88, 130.10 (d, *J* = 2.0 Hz), 128.38, 127.74, 127.68, 127.63 (d, *J* = 7.6 Hz), 77.09 (d, *J* = 2.5 Hz), 77.04 (d, *J* = 2.7 Hz), 72.42, 65.65, 62.77 (d, *J* = 5.6 Hz), 30.27 (d, *J* = 3.7 Hz), 30.22 (d, *J* = 3.5 Hz), 20.94 (d, *J* = 3.1 Hz, 2C), 20.90, 9.41 (d, *J* = 3.3 Hz, 2C). **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{19}H_{31}O_5PNa$, 393.1807; found: 393.1801.



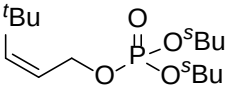
allyl di-sec-butyl phosphate: Following the general procedure **4.2**, the compound was obtained in 75% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.03–5.83 (m, 1H), 5.36 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.23 (dd, *J* = 10.5, 1.2 Hz, 1H), 4.56–4.49 (m, 2H), 4.44 (dtd, *J* = 12.5, 6.3, 4.3 Hz,, 2H), 1.68 (dq, *J* = 14.6, 7.0 Hz, 2H), 1.63–1.53 (m, 2H), 1.32 (dd, *J* = 6.3, 1.9 Hz,6H), 0.95 (td, *J* = 7.4, 1.3 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 132.76 (d, *J* = 7.7 Hz), 117.37 (d, *J* = 2.1 Hz), 76.96 (d, *J* = 3.4 Hz), 76.92 (d, *J* = 3.2 Hz), 67.46 (d, *J* = 5.5 Hz), 30.21 (d, *J* = 2.6 Hz), 30.17 (d, *J* = 2.4 Hz), 20.87 (d, *J* = 3.2 Hz), 20.83 (d, *J* = 3.8 Hz), 9.31 (d, *J* = 3.9 Hz, 2C). **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{11}H_{23}O_4PNa$, 273.1232; found: 273.1217.



(*Z*)-**2-2**

(*Z*:*E* = >99:<1)

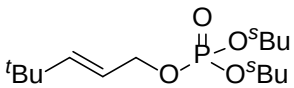
(*Z*)-**di-sec-butyl non-2-en-1-yl phosphate:** Following the general procedure **4.2**, the compound (*Z*)-**2-2** was obtained in 77% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.60 (td, *J* = 11.2, 5.0 Hz, 1H), 4.58 (dq, *J* = 7.4, 4.2, 3.7 Hz, 2H), 4.43 (dq, *J* = 12.4, 6.2 Hz, 1H), 2.08 (q, *J* = 7.1 Hz, 1H), 1.68 (dp, *J* = 14.5, 7.3 Hz, 1H), 1.59 (dp, *J* = 14.6, 7.4 Hz, 1H), 1.40–1.19 (m, 14H), 0.95 (t, *J* = 7.5 Hz, 6H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 134.78, 124.27 (d, *J* = 7.6 Hz), 76.91 (d, *J* = 4.5 Hz), 76.86 (d, *J* = 5.0 Hz), 62.80 (d, *J* = 5.6 Hz), 31.63, 30.29 (d, *J* = 2.3 Hz), 30.24 (d, *J* = 2.2 Hz), 29.31, 28.80, 27.48, 22.54, 20.93 (d, *J* = 3.8 Hz), 20.90 (d, *J* = 3.4 Hz), 14.01, 9.40 (d, *J* = 3.4 Hz, 2C). **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{17}H_{35}O_4PNa$, 357.2171; found: 357.2179.



(*Z*)-**2-3**

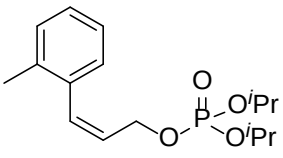
(*Z*:*E* = >99:<1)

(*Z*)-**di-sec-butyl (4,4-dimethylpent-2-en-1-yl) phosphate:** Following the general procedure **4.2**, the compound **2-3** was isolated in 71% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.49 (d, *J* = 12.3 Hz, 1H), 5.42–5.31 (m, 1H), 4.79–4.65 (m, 1H), 4.43 (dq, *J* = 12.1, 6.2 Hz, 2H), 1.76–1.52 (m, 4H), 1.32 (d, *J* = 6.2 Hz, 6H), 1.10 (s, 9H), 0.95 (t, *J* = 7.5 Hz, 6H). **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{15}H_{31}O_4PNa$, 329.1858; found: 329.1849.



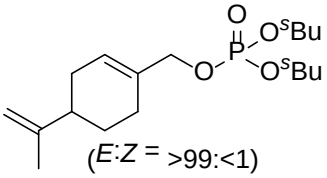
(*E*:*Z* = >99:<1)

(*E*)-**di-sec-butyl (4,4-dimethylpent-2-en-1-yl) phosphate:** Following the general procedure **4.2**, the compound was obtained in 73% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.78 (d, *J* = 15.6 Hz, 1H), 5.50 (dt, *J* = 15.6, 6.2 Hz, 1H), 4.51–4.39 (m, 4H), 1.74–1.54 (m, 4H), 1.32 (d, *J* = 6.2 Hz, 6H), 1.02 (s, 9H), 0.95 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 146.23 (d, *J* = 1.9 Hz), 119.66 (d, *J* = 6.1 Hz), 76.85 (d, *J* = 3.0 Hz), 76.80 (d, *J* = 2.4 Hz), 68.14 (d, *J* = 5.8 Hz), 30.30 (d, *J* = 2.4 Hz), 30.26 (d, *J* = 2.2 Hz), 30.00, 29.20, 20.96 (d, *J* = 1.6 Hz), 20.94 (d, *J* = 1.6 Hz) 9.42 (d, *J* = 3.3 Hz, 2C). **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{15}H_{31}O_4PNa$, 329.1858; found: 329.1847.



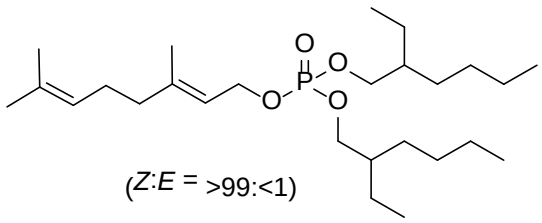
(*Z*:*E* = 99:1)

(*Z*)-**diisopropyl (3-(o-tolyl)allyl) phosphate:** Following the general procedure **4.2**, the compound was obtained in 76% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.23–7.13 (m, 3H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 11.5 Hz, 1H), 5.93 (dt, *J* = 11.5, 6.7 Hz, 1H), 4.67–4.57 (m, 4H), 2.26 (s, 3H), 1.39–1.20 (m, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 136.21, 134.85, 132.08, 129.90, 128.86, 127.76, 126.59 (d, *J* = 7.5 Hz), 125.55, 72.34 (d, *J* = 5.9 Hz), 63.75 (d, *J* = 5.5 Hz), 23.58 (d, *J* = 3.1 Hz), 23.54 (d, *J* = 3.1 Hz), 19.75. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{16}H_{25}O_4PNa$, 335.1388; found: 335.1396.



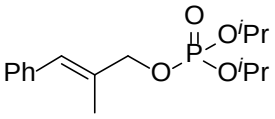
(*E*:*Z* = >99:<1)

di-sec-butyl ((4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl) phosphate: Following the general procedure **4.2**, the compound was obtained in 93% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.78 (s, 1H), 4.72 (d, *J* = 9.8 Hz, 1H), 4.52–4.19 (m, 4H), 2.22–2.05 (m, 4H), 2.02–1.91 (m, 1H), 1.90–1.80 (m, 1H), 1.74 (s, 3H), 1.63 (ddq, *J* = 43.8, 14.0, 7.0 Hz, 1H), 1.48 (ddt, *J* = 18.0, 12.0, 6.0 Hz, 1H), 1.32 (d, *J* = 6.3 Hz, 6H), 0.95 (t, *J* = 7.5 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 149.51, 133.08 (d, *J* = 7.7 Hz), 125.51 (d, *J* = 5.9 Hz), 108.72, 76.88 (d, *J* = 3.5 Hz), 76.84 (d, *J* = 4.7 Hz), 71.01 (d, *J* = 5.9 Hz), 40.78, 30.35, 30.30 (d, *J* = 2.9 Hz), 30.25 (d, *J* = 2.8 Hz), 27.20, 25.89, 20.95 (d, *J* = 3.2 Hz), 20.92 (d, *J* = 3.8 Hz), 20.72, 9.42 (d, *J* = 4.0 Hz, 2C). **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{18}H_{33}O_4PNa$, 367.2014; found: 367.2013.



(*Z*:*E* = >99:<1)

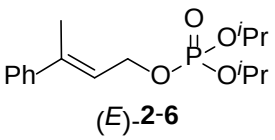
(*E*)-3**,7-dimethylocta-2,6-dien-1-yl bis(2-ethylhexyl) phosphate:** Following the general procedure **4.2**, the compound was obtained in 81% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.46–5.33 (m, 1H), 5.09 (t, *J* = 6.8 Hz, 1H), 4.57 (t, *J* = 7.6 Hz, 2H), 3.98–3.88 (m, 2H), 2.16–1.96 (m, 4H), 1.70 (s, 3H), 1.68 (s, 3H), 1.60 (s, 3H), 1.59–1.51 (m, 2H), 1.47–1.16 (m, 16H), 0.96–0.80 (m, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 142.24, 131.84, 123.64, 119.06, 69.58 (d, *J* = 6.3 Hz), 64.04 (d, *J* = 5.7 Hz), 40.08 (d, *J* = 7.4 Hz), 39.49, 29.87, 28.86, 26.24, 25.64, 23.22, 22.95, 17.64, 16.45, 14.01, 10.88. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{26}H_{51}O_4PNa$, 481.3423; found: 481.3407.



(*E*)-**2-5**

(*E*:*Z* = >99:<1)

(*E*)-**diisopropyl (2-methyl-3-phenylallyl) phosphate:** Following the general procedure **4.2**, the compound **2-5** was obtained in 77% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.34 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.1 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 6.57 (s, 1H), 4.68 (dq, *J* = 12.9, 6.2 Hz, 2H), 4.55 (d, *J* = 6.8 Hz, 2H), 1.93 (s, 3H), 1.35 (dd, *J* = 6.2, 2.5 Hz, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 136.92, 133.06 (d, *J* = 7.5 Hz), 128.85, 128.12, 127.82, 126.74, 72.62 (d, *J* = 5.7 Hz), 72.37 (d, *J* = 5.9 Hz), 23.64 (d, *J* = 5.0 Hz), 15.11. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{16}H_{25}O_4PNa$, 335.1388; found: 335.1382.

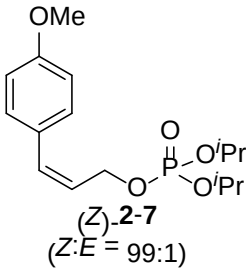


(*E*)-**2-6**

(*E*:*Z* = >99:<1)

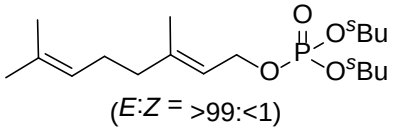
(*E*)-**diisopropyl (3-phenylbut-2-en-1-yl) phosphate:** Following the general procedure **4.2**, the compound **2-6** was obtained in 83% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.40 (d, *J* = 5.1 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.30–7.24 (m, 1H), 5.95 (td, *J* = 6.8, 1.3 Hz, 1H), 4.74 (t, *J* = 7.4 Hz, 2H), 4.66

(dq, *J* = 12.5, 6.2 Hz, 2H), 2.10 (s, 3H), 1.34 (dd, *J* = 6.2, 2.3 Hz, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 142.42, 139.77, 128.25, 127.50, 125.80, 122.19 (d, *J* = 7.3 Hz), 72.32 (d, *J* = 5.9 Hz), 23.64 (d, *J* = 5.0 Hz), 16.18. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{16}H_{25}O_4PNa$, 335.1388; found: 335.1385.



(*Z*)-**2-7**
(*Z*:*E* = 99:1)

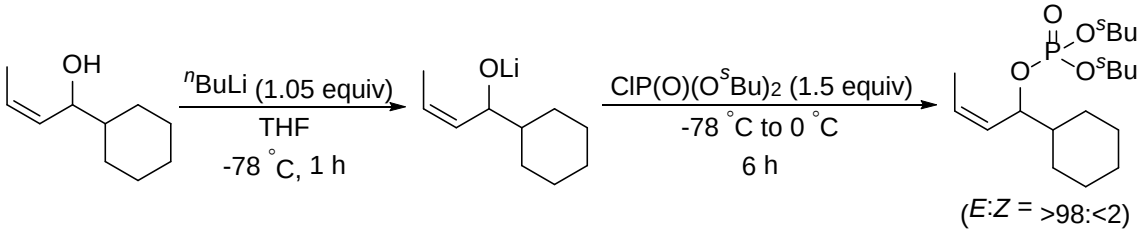
(*Z*)-**diisopropyl (3-(4-methoxyphenyl)allyl) phosphate：** Following the general procedure described for (*Z*)-**2-7**, the compound (*Z*)-**2-7** was obtained in 82% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.15 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.59 (d, *J* = 11.6 Hz, 1H), 5.78 (dt, *J* = 11.7, 6.5 Hz, 1H), 4.82–4.75 (m, 2H), 4.69–4.59 (m, 2H), 3.82 (s, 3H), 1.32 (t, *J* = 5.8 Hz, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 158.99, 132.20, 130.02, 129.31, 124.94 (d, *J* = 7.9 Hz), 113.75, 72.40 (d, *J* = 6.0 Hz), 63.91 (d, *J* = 5.5 Hz), 55.23, 23.62 (d, *J* = 1.5 Hz), 23.58 (d, *J* = 2.0 Hz). **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{16}H_{25}O_5PNa$, 351.1338; found: 351.1334.



(*E*:*Z* = >99:<1)

(*E*)-**di-sec-butyl (3,7-dimethylocta-2,6-dien-1-yl) phosphate:** Following the general procedure **4.2**, the compound was obtained in 78% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.40 (t, *J* = 6.9 Hz, 1H), 5.09 (t, *J* = 6.7 Hz, 1H), 4.55 (dq, *J* = 7.2, 4.0 Hz, 3H), 4.42 (dq, *J* = 12.2, 6.2 Hz, 2H), 2.17–1.99 (m, 4H), 1.75–1.63 (m, 8H), 1.62–1.54 (m, 5H), 1.32 (d, *J* = 6.2 Hz, 6H), 0.94 (t, *J* = 7.4 Hz, 5H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.71, 131.79, 123.67, 119.32 (d, *J* = 7.3 Hz), 76.83 (d, *J* = 2.1 Hz), 76.80 (d, *J* = 1.6 Hz), 63.83 (d, *J* = 5.7 Hz), 39.44, 30.32 (d, *J* = 2.4 Hz), 30.27 (d, *J* = 2.2 Hz), 26.20, 25.64, 20.94(d, *J* = 2.6 Hz), 20.91(d, *J* = 3.3 Hz), 17.64, 16.43, 9.42 (d, *J* = 4.5 Hz, 2C). **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{18}H_{35}O_4PNa$, 369.2171; found: 369.2168.

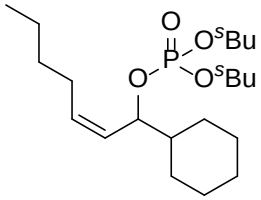
4.3 Synthesis of the Secondary Allyl Phosphates bearing *α-tert*-butyl and α-cyclohexyl



(*E*:*Z* = >98:<2)

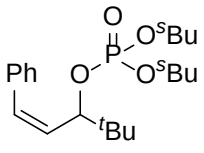
(*Z*)-**di-sec-butyl (1-cyclohexylbut-2-en-1-yl) phosphate:** To a solution of (*Z*)-1-cyclohexylbut-2-en-1-ol (10 mmol, 1.0 equiv, 1.542 g) in anhydrous THF (20 mL) under a nitrogen atmosphere, was added ^{n}BuLi (4.2 mL, 2.5 M in hexane, 10.5 mmol, 1.05 equiv) at -78 °C. The mixture was stirred for 30 min at -78 °C, then for 30 min at 0 °C before addition of di-sec-butyl chlorophosphate (15 mmol, 3.430 g, 1.5 equiv) at -78 °C. The solution was allowed to warm to rt over 6 h. The mixture was quenched with NH_4Cl aqueous solution (20 mL). The organic phase was separated and the aqueous layer was extracted with Et_2O (3 x 30 mL). The combined organic layers were dried with Na_2SO_4, concentrated under reduced pressure, and purified by silica gel column chromatography (eluent ethyl acetate : hexane = 10:90) and then aluminum oxide flash chromatography (eluent ethyl acetate) to give the compound (2.486 g, 65%) as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.72–5.59 (m, 1H), 5.44 (ddd, *J* = 11.1, 9.5, 1.7 Hz, 1H), 4.91 (dq, *J* = 14.0, 6.9 Hz, 1H), 4.48–4.31 (m, 2H), 1.89–1.79 (m, 1H), 1.77–1.49 (m, 13H), 1.35–1.08 (m, 10H), 1.07–0.85 (m, 8H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 128.47 (d, *J* = 2.7 Hz), 127.72 (d, *J* = 2.9 Hz), 78.04 (d, *J* = 4.4 Hz), 76.40 (d, *J* = 4.4 Hz), 76.29 (d, *J* = 6.3 Hz), 43.28 (d, *J* = 2.9 Hz), 30.29 (d, *J* = 5.2 Hz), 30.20 (d, *J* =

5.0 Hz), 28.46 (d, *J* = 2.0 Hz), 27.66, 26.37, 25.92, 25.82, 20.86 (d, *J* = 3.2 Hz), 20.76 (d, *J* = 3.1 Hz), 13.54, 9.32 (d, *J* = 1.9 Hz), 9.26 (d, *J* = 2.2 Hz). **ESI-HRMS (m/z):** [M+Na]+ calcd for $C_{18}H_{35}O_4PNa$, 369.2171; found: 369.2161.



(*E*:*Z* = >99:<1)

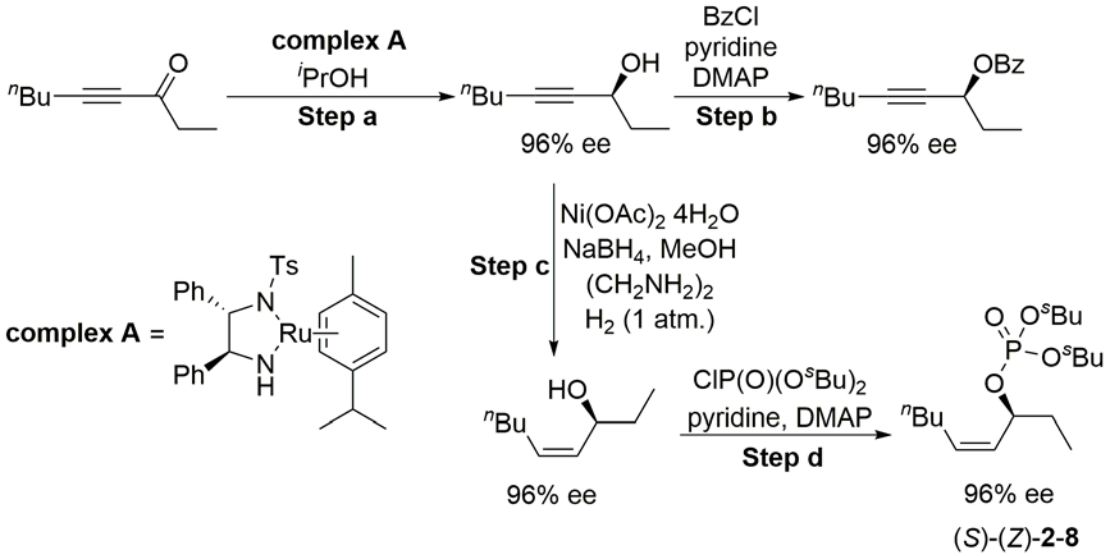
(*Z*)-**di-sec-butyl (1-cyclohexylhept-2-en-1-yl) phosphate:** Following the general procedure **4.3**, the compound was obtained in 63% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.56 (dt, *J* = 11.1, 7.4 Hz, 1H), 5.39 (t, *J* = 10.3 Hz, 1H), 4.99–4.79 (m, 1H), 4.55–4.21 (m, 2H), 2.19–2.02 (m, 2H), 1.84 (d, *J* = 12.6 Hz, 1H), 1.79–1.49 (m, 8H), 1.42–1.09 (m, 14H), 1.06–0.81 (m, 11H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 133.84 (d, *J* = 5.1 Hz), 127.24 (d, *J* = 2.6 Hz), 78.53 (d, *J* = 3.4 Hz), 76.41 (d, *J* = 6.3 Hz), 76.26 (d, *J* = 6.2 Hz), 43.34 (d, *J* = 3.1 Hz), 31.70, 30.29 (d, *J* = 6.3 Hz), 30.23 (d, *J* = 6.0 Hz), 28.52 (d, *J* = 1.5 Hz), 27.83, 27.67, 26.39, 25.99, 25.88, 22.41, 20.92 (d, *J* = 2.7 Hz), 20.76 (d, *J* = 3.5 Hz), 13.96, 9.38 (d, *J* = 3.0 Hz), 9.32 (d, *J* = 4.5 Hz). **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{21}H_{41}O_4PNa$, 411.2640; found: 411.2640.



(*E*:*Z* = 99:1)

(*Z*)-**di-sec-butyl (4,4-dimethyl-1-phenylpent-1-en-3-yl) phosphate:** Following the general procedure **4.3**, the compound was obtained in 55% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.46 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 12.0 Hz, 1H), 5.77–5.64 (m, 1H), 5.10–5.00 (m, 1H), 4.50–4.36 (m, 2H), 1.76–1.61 (m, 4H), 1.35–1.23 (m, 6H), 0.98–0.89 (m, 6H), 0.88 (d, *J* = 2.2 Hz, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 136.70, 132.60 (d, *J* = 1.0 Hz), 132.54 (d, *J* = 2.3 Hz), 128.57, 128.30, 126.95, 81.30 (d, *J* = 7.0 Hz), 76.60 (d, *J* = 5.6 Hz), 76.51 (d, *J* = 6.2 Hz), 36.07 (d, *J* = 3.0 Hz), 30.31 (d, *J* = 6.4 Hz), 30.21 (d, *J* = 6.0 Hz), 25.49 (d, *J* = 1.4 Hz), 20.93 (d, *J* = 3.5 Hz), 20.77 (d, *J* = 3.1 Hz), 9.37 (d, *J* = 3.2 Hz), 9.32 (d, *J* = 3.0 Hz). **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{21}H_{35}O_4PNa$, 405.2171; found: 405.2162.

4.4 Synthesis of the Chiral Allyl Phosphates (*S*)-(*Z*)-2-8:



Step a: The compound was synthesized with the similar procedure reported in the literature.[19] In a glove box **complex A** (0.1 mmol, 0.01 equiv, 60.0 mg) (**complex A** was prepared according to the reported procedures[20]) was added to a round bottomed flask, followed by the addition of freshly distilled 2-propanol

(50 mL). After addition of non-4-yn-3-one (10.0 mmol, 1.0 equiv, 1.383 g) the reaction mixture was stirred for 20 h at 28 °C. The reaction mixture was then passed through a 10 cm long silica column and the column was washed with ethyl acetate. After removal of the solvent under reduced pressure the crude product was purified by silica gel column chromatography (eluent ethyl acetate : hexane = 10:90) to give (*S*)-**non-4-yn-3-ol** (1.206 g, 86%) as a colorless oil.

Step b: In a screw-capped reaction vial equipped with a magnetic bar was added DMAP (0.04 mmol, 0.2 equiv, 4.9 mg). The flask was then evacuated and back-filled with argon three times. Dry CH_2Cl_2 (0.5 mL), pyridine (0.4 mmol, 2.0 equiv, 33 μL) and (*S*)-**non-4-yn-3-ol** (0.2 mmol, 1.0 equiv, 28.1 mg) were added in turn to the flask. The reaction mixture was cooled to 0 °C and then benzoyl chloride (0.4 mmol, 2.0 equiv, 56.3 mg) was added dropwise. After the mixture was slowly warmed to room temperature overnight with stirring, it was quenched with 5% HCl (10 mL) at 0 °C. The organic layer was separated and the water layer was extracted with ether (3 × 2 mL). The combined organic layer was dried with Na_2SO_4 and concentrated in vacuo, which afforded an oil that was purified by silica gel column chromatography (eluent ethyl acetate : hexane = 3:97) to give (*S*)-**non-4-yn-3-yl benzoate** (40.6 mg, 83%) as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.08 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 5.56 (tt, *J* = 6.3, 1.9 Hz, 1H), 2.22 (td, *J* = 7.1, 1.9 Hz, 2H), 1.90 (p, *J* = 7.2 Hz, 2H), 1.50 (dt, *J* = 14.7, 6.8 Hz, 2H), 1.40 (dq, *J* = 14.1, 7.1 Hz, 2H), 1.08 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.65, 132.94, 130.20, 129.70, 128.28, 86.37, 77.37, 66.21, 30.57, 28.51, 21.89, 18.40, 13.58, 9.49. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{16}H_{20}O_2Na$, 267.1361; found: 267.1357. The ee value of (*S*)-**non-4-yn-3-yl benzoate** was determined by HPLC analysis (CHIRALCEL® AD-H DAICEL CHIRAL TECHNOLOGIES CO., LTD., 0.1% 2-PrOH/Hexane, 0.5 mL/min, S isomer t_R = 19.5 min, R isomer t_R = 20.6 min, UV detection at 220 nm, 40 °C).

Step c: The compound was synthesized with the similar procedure reported in the literature.[11] $NaBH_4$ (1.25 mmol, 0.25 equiv, 47.4 mg) was added portionwise to a stirred solution of $Ni(OAc)_2{\cdot}4H_2O$ (1.30 mmol, 0.26 equiv, 247.7 mg) in MeOH (15 mL) at 0 °C and the resultant black mixture was stirred and allowed to warm to rt over 15 min. $(CH_2NH_2)_2$ (175 μL, 2.6 mmol) and a solution of (*S*)-**non-4-yn-3-ol** (5.0 mmol, 1.0 equiv, 0.701 g) in MeOH (5 mL) were added sequentially and the resultant suspension was vigorously stirred under H_2 (1 atm.). The progress of hydrogenation was closely monitored by GC analysis. Once completed (about 8 h), the reaction mixture was filtered through Celite® (eluent ethyl acetate) and the filtrate was concentrated in vacuo. Ethyl acetate (30 mL) was then added to the residue and the resultant pink suspension was filtered through Celite® (eluent ethyl acetate) and the filtrate was concentrated in vacuo. The crude product was purified by silica gel column chromatography (eluent ethyl acetate : hexane = 10:90) to give (*S*)-(*Z*)-**non-4-en-3-ol** (0.641 g, 90%) as a colorless oil.

Step d: In a 25 mL dry two-neck flask equipped with a magnetic bar was added DMAP (0.8 mmol, 0.2 equiv, 97.8 mg). The flask was then evacuated and back-filled with argon three times. Dry CH_2Cl_2 (6 mL), pyridine (8 mmol, 2.0 equiv, 0.65 mL) and (*S*)-(*Z*)-**non-4-en-3-ol** (4 mmol, 1.0equiv, 0.569 g) were added in turn to the flask. The reaction mixture was cooled to 0 °C and then di-sec-butyl chlorophosphate (6 mmol, 1.5 equiv, 1.370 g) was added dropwise. After the reaction mixture was slowly warmed to room temperature overnight with stirring, it was quenched with 5% HCl (6 mL) at 0 °C. The organic layer was separated and the water layer was extracted with ether (3 × 10 mL). The combined organic layer was then washed with water (15 mL) and dried with Na_2SO_4. After filtration, the solution was concentrated in vacuo,

which afforded an oil that was purified by silica gel column chromatography (eluent ethyl acetate : hexane = 20:80) and then aluminum oxide flash chromatography (eluent ethyl acetate) to give (*S*)-(*Z*)-**2-8** (1.030 g, 77%) as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.54 (dt, *J* = 10.9, 7.4 Hz, 1H), 5.39 (t, *J* = 10.1 Hz, 1H), 5.05 (dt, *J* = 13.5, 6.3 Hz, 1H), 4.45–4.32 (m, 2H), 2.20–2.05 (m, *J* = 7.4 Hz, 2H), 1.77 (dq, *J* = 13.5, 7.4, 6.8 Hz, 1H), 1.72–1.51 (m, 5H), 1.41–1.23 (m, 10H), 0.97–0.83 (m, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 133.27 (d, *J* = 6.1 Hz), 128.61 (d, *J* = 4.2 Hz), 76.52 (d, *J* = 6.1 Hz), 76.40 (d, *J* = 6.7 Hz), 75.76 (d, *J* = 6.0 Hz), 31.68 (d, *J* = 1.3 Hz), 30.30 (d, *J* = 6.5 Hz), 30.22 (d, *J* = 6.0 Hz), 29.43 (d, *J* = 3.8 Hz), 27.54 , 22.34, 20.92 (d, *J* = 3.5 Hz), 20.81 (d, *J* = 2.5 Hz), 13.94, 9.41 (d, *J* = 3.3 Hz), 9.34 (d, *J* = 3.8 Hz), 9.18 (d, *J* = 3.3 Hz). **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{17}H_{35}O_4PNa$, 357.2171; found: 357.2169.

5. Typical Procedure for Suzuki-Miyaura Coupling of boron-substituted 1,4-dienes with halides (Table 8)

Method I: $Pd(PPh_3)_4$ Catalyzed Cross Coupling Reactions

To a screw-capped reaction vial were added boron-substituted 1,4-dienes (0.10 mmol) and $Pd(PPh_3)_4$ (11.6 mg, 0.1 equiv, 0.01 mmol). The flask was evacuated and backfilled with argon three times. Then, dioxane (1 mL), halides (0.15 mmol, 1.5 equiv, solid halides were dissolved in dioxane) and 2 M NaOH aq. (100 μL, 2.0 equiv 0.2 mmol) were added in this order, and the resulting mixture was stirred at the specified temperature for 20 h. After the reaction, the mixture was filtrated through a pad of Celite (eluent ethyl acetate) and all volatiles were removed in vacuo. The products were purified with silica gel column chromatography.

Method II: $Pd(dba)_2$/Sphos Catalyzed Cross Coupling Reactions

To a screw-capped reaction vial were added boron-substituted 1,4-dienes (0.10 mmol), $Pd(dba)_2$ (5.8 mg, 0.1 equiv, 0.01 mmol) and Sphos (4.1 mg, 0.1 equiv, 0.01 mmol). The flask was evacuated and backfilled with argon three times. Then, dioxane (1 mL), halides (0.15 mmol, 1.5 equiv, solid halides were dissolved in dioxane) and 2 M NaOH aq. (100 μL, 2.0 equiv, 0.2 mmol) were added in this order, and the resulting mixture was stirred at the specified temperature for 20 h. After the reaction, the mixture was filtrated through a pad of Celite (eluent ethyl acetate) and all volatiles were removed in vacuo. The products were purified with silica gel column chromatography.

6. X-ray Single Crystal Structure of (1*E*,4*E*)-10-4

The single crystal sample was sealed in a thin-walled glass capillary. Data collections were performed at 296 K on a Bruker SMART APEX II diffractometer with a CCD area detector using graphite-monochromated Mo Kα radiation (λ= 0.71069 Å). The structures were solved by a direct method and refined by full-matrix least-square refinement on F2. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located on the calculated positions and not refined. All calculations were performed using the Crystal Structure software package.

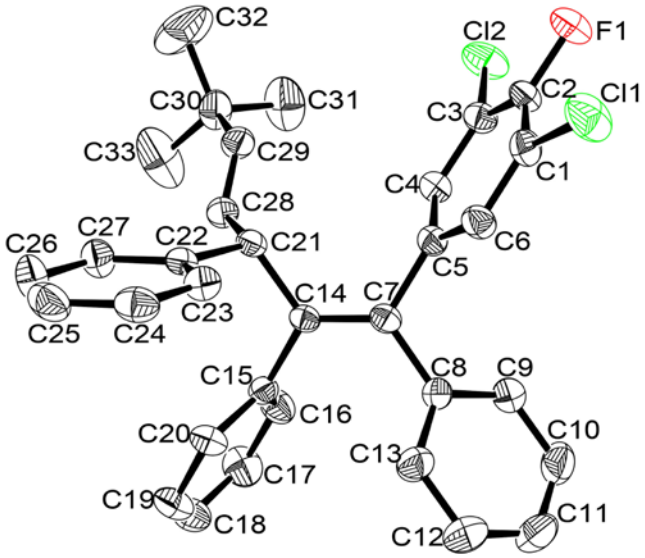


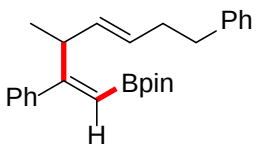
Figure S1. The X-ray crystal structure of (1*E*,4*E*)-**10-4** shows that the two double bonds are in 1*E* and 4*E* congfiguration. The hydrogen atoms are omitted for clearity.

Table S8. Crystal data and structure refinement for (1*E*,4*E*)-**10-4**.

Identification code	**10-4**
Empirical formula	$C_{33}H_{29}Cl_2F$
Formula weight	515.46
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 9.5553(11) Å, b = 27.755(3) Å, c = 10.9004(13) Å, α = 90°, β = 105.431(2)° γ = 90°
Volume	2786.7(6) $Å^3$
Z, Calculated density	4, 1.229 Mg/m^3
Absorption coefficient	0.259 mm^{-1}
F(000)	1080
Crystal size	0.26 x 0.21 x 0.17 mm
Theta range for data collection	2.33 to 25.00 deg.
Limiting indices	-11<=h<=11, -32<=k<=32, -12<=l<=5
Reflections collected / unique	14151 / 4890 [R(int) = 0.0415]
Completeness to theta = 25.00	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9573 and 0.9357
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4890 / 0 / 325
Goodness-of-fit on F^2	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0456, wR2 = 0.1018
R indices (all data)	R1 = 0.0842, wR2 = 0.1148
Largest diff. peak and hole	0.187 and -0.255 e. $Å^{-3}$

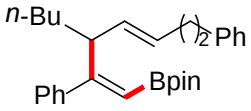
7. Characterization Data for the Products

In ^{13}C NMR spectral, signals of carbon that directly connect to boron were not detected because of quadrupolar relaxation.



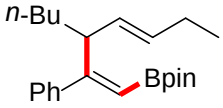
(1*E*,4*E*)-**4-1**
(γ:α = >99:<1)

Following the general procedure **2.1** described above, the compound **4-1** was isolated in 95% yield as a pale yellow solid. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 86–87 °C). **^{1}H NMR (500 MHz, CDCl3)** δ 7.30–7.20 (m, 7H), 7.19–7.13 (m, 3H), 5.63 (dd, *J* = 15.5, 5.9 Hz, 1H), 5.58–5.49 (m, 1H), 5.36 (s, 1H), 4.14 (p, *J* = 6.1 Hz, 1H), 2.74–2.56 (m, 2H), 2.35 (q, *J* = 6.8 Hz, 2H), 1.30 (d, *J* = 1.5 Hz, 12H), 1.08 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 167.29, 143.64, 142.09, 135.28, 128.45, 128.37, 128.22, 127.58, 127.44, 126.88, 125.68, 82.96, 40.80, 35.97, 34.48, 24.91, 24.78, 19.20. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{26}H_{33}BO_2Na$, 411.2472; found: 411.2489.



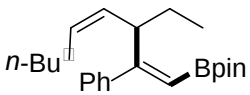
(1*E*,4*E*)-4-2
(γ:α = >99:<1)

Following the general procedure **2.1** described above, the compound **4-2** was isolated in 75% yield as a pale yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.29–7.20 (m, 7H), 7.19–7.13 (m, 3H), 5.65–5.50 (m, 2H), 5.37 (s, 1H), 3.96 (q, *J* = 6.5, 5.9 Hz, 1H), 2.68 (t, *J* = 7.7 Hz, 2H), 2.35 (q, *J* = 6.9 Hz, 2H), 1.44–1.38 (m, 2H), 1.30 (d, *J* = 1.2 Hz, 12H), 1.27–1.13 (m, 4H), 0.82 (t, *J* = 6.2 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.65, 143.87, 142.10, 134.14, 129.45, 128.46, 128.20, 127.64, 127.43, 126.83, 125.65, 82.91, 46.99, 35.96, 34.52, 33.03, 29.65, 24.88, 24.83, 22.42, 14.05. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{29}H_{39}BO_2Na$, 453.2941; found: 453.2950.



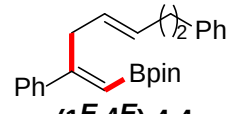
(1*E*,4*E*)-4-3
(γ:α = 91:9)

Following the general procedure **2.1** described above, the compound **4-3** was isolated in 79% yield as a pale yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.30–7.20 (m, 5H), 5.58 (dt, *J* = 15.6, 6.0 Hz, 1H), 5.51 (dd, *J* = 16.0, 7.5 Hz, 1H), 5.37 (s, 1H), 3.97 (q, *J* = 7.2 Hz, 1H), 2.04 (p, *J* = 7.4 Hz, 2H), 1.43 (q, *J* = 6.4 Hz, 2H), 1.30 (d, *J* = 2.3 Hz, 12H), 1.27–1.16 (m, 4H), 0.98 (t, *J* = 7.5 Hz, 3H), 0.83 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ166.81, 143.93, 132.38, 131.93, 127.66, 127.39, 126.81, 82.89, 46.88, 33.06, 29.68, 25.72, 24.86, 24.81, 22.45, 14.06, 13.83. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{23}H_{35}BO_2Na$, 377.2628; found: 377.2617.



(1*E*,4*Z*)-5 (9%)

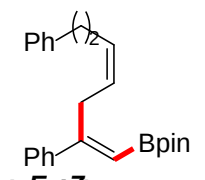
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.29 (s), 5.25–5.18 (m), 4.27–4.19 (m), 2.25–2.11 (m), 1.26 (s).



(1*E*,4*E*)-4-4
(4*E*:4*Z* = 95:5)
(γ:α = >99:<1)

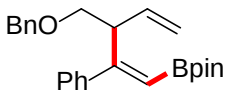
Following the general procedure **2.1** described above, the compound **4-4** was isolated in 77% yield as a pale yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.46 (d, *J* = 7.3 Hz, 2H), 7.33–7.26 (m, 3H), 7.25–7.20 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 6.9 Hz, 2H), 5.72 (s, 1H), 5.58–5.49 (m, 1H), 5.48–5.40 (m, 1H), 3.60 (d, *J* = 6.2 Hz, 1H), 2.61–2.52 (m, 2H), 2.24 (q, *J* = 7.2 Hz, 2H), 1.30 (s, 12H). **^{13}C NMR**

(126 MHz, $CDCl_3$) δ 160.63, 142.95, 142.03, 130.58, 129.19, 128.41, 128.15, 128.08, 127.77, 126.45, 125.59, 82.94, 36.65, 35.93, 34.39, 24.84. **EI-HRMS (m/z):** $[M]^+$ calcd for $C_{25}H_{31}BO_2$, 374.2417; found: 374.2422.



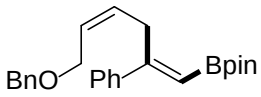
(1*E*,4*Z*)-4-4 (5%)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.65 (s), 5.39–5.28 (m), 3.66 (d, *J* = 6.5 Hz), 1.27 (s).



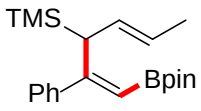
(*E*)-4-5
(γ:α = 92:8)

Following the general procedure **2.1** described above, the compound **4-5** was isolated in 50% yield as a pale yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.36–7.21 (m, 10H), 5.98 (ddd, *J* = 17.2, 10.4, 6.7 Hz, 1H), 5.53 (s, 1H), 5.22 (dt, *J* = 17.3, 1.6 Hz, 1H), 5.12 (dt, *J* = 10.4, 1.6 Hz, 1H), 4.54–4.40 (m, 3H), 3.65–3.50 (m, 2H), 1.29 (d, *J* = 2.9 Hz, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 163.00, 138.58, 138.48, 128.81, 128.20, 127.64, 127.54, 127.49, 127.14, 83.08, 72.41, 71.72, 48.00, 24.91, 24.77. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{25}H_{31}BO_3Na$, 413.2264; found: 413.2278.



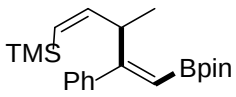
(*E*)-5 (8%)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.66 (s), 3.71 (d, *J* = 6.2 Hz).



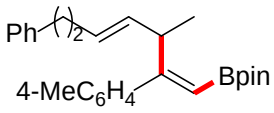
(1*E*,4*E*)-4-6
(γ:α = 85:15)

Following the general procedure **2.1** described above, the compound **4-6** was isolated in 82% yield as a pale yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.30–7.14 (m, 5H), 5.53–5.42 (m, 1H), 5.36 (dd, *J* = 15.0, 6.4 Hz, 1H), 5.14 (s, 1H), 4.02 (d, *J* = 10.2 Hz, 1H), 1.60 (d, *J* = 6.2 Hz, 3H), 1.26 (s, 12H), -0.04 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.31, 144.88, 129.67, 127.56, 127.45, 126.84, 123.03, 82.70, 43.24, 24.94, 18.01, -1.93. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{21}H_{33}BO_2SiNa$, 379.2241; found: 379.2235.



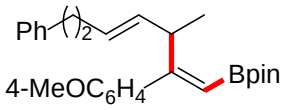
(1*E*,4*Z*)-5 (15%)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.23 (s), 4.28 (dq, J = 10.3, 7.0 Hz).



(1*E*,4*E*)-4-7
(γ:α = 99:1)

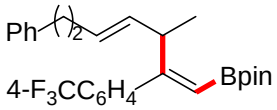
Following the general procedure **2.1** described above, the compound **4-7** was isolated in 75% yield as a pale yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.27 (t, *J* = 7.5 Hz, 2H), 7.18 (m, 3H), 7.15–7.11 (m, 2H), 7.04 (d, *J* = 7.5 Hz, 2H), 5.71–5.61 (m, 1H), 5.55 (dt, *J* = 15.3, 6.5 Hz, 1H), 5.37 (s, 1H), 4.18–4.07 (m, 1H), 2.68 (t, *J* = 7.8 Hz, 2H), 2.43–2.00 (m, 5H), 1.29 (s, 142H), 1.08 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 167.22, 142.12, 140.64, 136.56, 135.40, 128.44, 128.24, 128.21, 128.17, 127.49, 125.66, 82.90, 40.73, 35.98, 34.50, 24.90, 24.77, 21.11, 19.21. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{27}H_{35}BO_2$, 425.2628; found: 452.2607.



(1*E*,4*E*)-4-8

(γ:α = >99:<1)

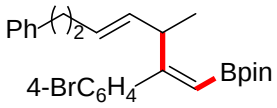
Following the general procedure **2.1** described above, the compound **4-8** was isolated in 74% yield as a pale yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.27 (t, *J* = 7.5 Hz, 2H), 7.22–7.15 (m, 5H), 6.77 (d, *J* = 8.7 Hz, 2H), 5.72–5.62 (m, 1H), 5.55 (dt, *J* = 15.3, 6.5 Hz, 1H), 5.37 (s, 1H), 4.20–4.08 (m, 1H), 3.79 (s, 3H), 2.75–2.61 (m, 2H), 2.36 (q, *J* = 7.1 Hz, 2H), 1.29 (s, 12H), 1.09 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.71, 158.66, 142.09, 135.96, 135.49, 130.88, 128.72, 128.44, 128.21, 125.66, 112.82, 82.87, 55.12, 40.62, 35.96, 34.47, 24.89, 24.75, 19.15. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{27}H_{35}BO_3Na$, 441.2577; found: 441.2572.



(1*E*,4*E*)-4-9

(γ:α = >99:<1)

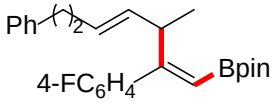
Following the general procedure **2.1** described above, the compound **4-9** was isolated in 57% yield as a pale yellow solid. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 85–86 °C). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.47 (d, *J* = 8.1 Hz, 2H), 7.30–7.22 (m, 4H), 7.20–7.13 (m, 3H), 5.62–5.48 (m, 2H), 5.36 (s, 1H), 4.14 (dt, *J* = 7.3, 3.4 Hz, 1H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.42–2.27 (m, 2H), 1.30 (s, 12H), 1.05 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.70, 147.18, 141.90, 134.75, 128.91, (q, *J* = 32.8 Hz), 128.79, 128.45, 128.26, 127.88, 126.40 (q, *J* = 270.9 Hz), 125.76, 124.44 (q, *J* = 3.7 Hz), 83.18, 40.60, 35.87, 34.33, 24.90, 24.77, 18.96. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{27}H_{32}BF_3O_2Na$, 479.2345; found: 479.2356.



(1*E*,4*E*)-4-10

(γ:α = >99:<1)

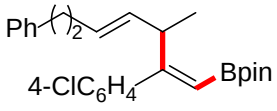
Following the general procedure **2.1** described above, the compound **4-10** was isolated in 83% yield as a pale yellow solid. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 96–97 °C). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 8.7 Hz, 3H), 7.06 (d, *J* = 8.3 Hz, 1H), 5.62–5.47 (m, *J* = 6.0, 5.5 Hz, 2H), 5.34 (s, 1H), 4.12 (p, *J* = 6.8 Hz, 1H), 2.68 (t, *J* = 7.7 Hz, 2H), 2.39–2.28 (m, 2H), 1.29 (s, 12H), 1.05 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.86, 142.36, 141.88, 134.88, 130.55, 129.24, 128.65, 128.41, 128.21, 125.70, 120.96, 83.02, 40.45, 35.83, 34.34, 24.86, 24.72, 18.95. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{26}H_{32}BBrO_2Na$, 489.1577; found: 489.1584.



(1*E*,4*E*)-4-11

(γ:α = >99:<1)

Following the general procedure **2.1** described above, the compound **4-11** was isolated in 77% yield as a pale yellow solid. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 68–69 °C). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.27 (t, *J* = 7.6 Hz, 2H), 7.20–7.11 (m, 3H), 6.90 (t, *J* = 8.8 Hz, 2H), 5.65–5.47 (m, 1H), 5.33 (s, 1H), 4.13 (p, *J* = 6.7 Hz, 1H), 2.68 (t, *J* = 7.7 Hz, 2H), 2.36 (q, *J* = 6.4, 5.9 Hz, 2H), 1.30 (d, *J* = 1.8 Hz, 12H), 1.06 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.11, 161.94 (d, *J* = 245.6 Hz), 141.95, 139.47 (d, *J* = 3.4 Hz), 135.07, 129.13 (d, *J* = 7.7 Hz), 128.54, 128.43, 128.23, 125.70, 114.26 (d, *J* = 21.1 Hz), 83.00, 40.59, 35.88, 34.38, 24.88, 24.74, 18.99. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{26}H_{32}BFO_2Na$, 429.2377; found: 429.2392.

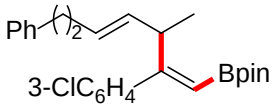


(1*E*,4*E*)-4-12

(γ:α = >99:<1)

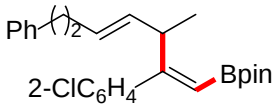
Following the general procedure **2.1** described above, the compound **4-12** was isolated in 43% yield as a pale yellow solid. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 83–84 °C). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.27 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 8.4 Hz, 5H),

7.12 (d, *J* = 8.5 Hz, 2H), 5.55 (qq, *J* = 11.9, 6.1, 5.5 Hz, 1H), 5.34 (s, 1H), 4.12 (q, *J* = 6.8 Hz, 1H), 2.68 (t, *J* = 7.7 Hz, 2H), 2.43–2.29 (m, 2H), 1.29 (d, *J* = 1.6 Hz, 12H), 1.05 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.90, 141.94, 134.95, 132.77, 128.92, 128.66, 128.44, 128.24, 127.63, 125.72, 83.06, 40.54, 35.88, 34.37, 24.89, 24.76, 18.99. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{26}H_{32}BClO_2Na$, 445.2082; found: 445.2073.



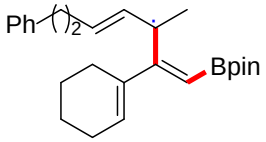
(1*E*,4*E*)-4-13
(γ:α = >99:<1)

Following the general procedure **2.1** described above, the compound **4-13** was isolated in 61% yield as a pale yellow oil. The title compound decomposed partially during the isolation process. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.31–7.23 (m, 3H), 7.22–7.12 (m, 5H), 7.07 (d, *J* = 7.6 Hz, 1H), 5.65–5.47 (m, 1H), 5.35 (s, 1H), 4.17–4.07 (m, 1H), 2.68 (t, *J* = 7.7 Hz, 2H), 2.40–2.30 (m, 2H), 1.30 (d, 12H), 1.07 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.62, 145.38, 142.01, 134.79, 133.29, 129.46, 128.80, 128.73, 128.43, 128.24, 127.75, 126.95, 125.71, 83.10, 40.61, 35.96, 34.50, 24.89, 24.76, 19.00. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{26}H_{32}BClO_2Na$, 445.2082; found: 445.2081.



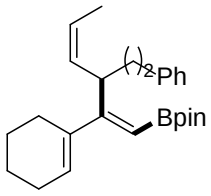
(1*E*,4*E*)-4-14
(γ:α = >99:<1)

Following the general procedure **2.1** described above, the compound **4-14** was isolated in 64% yield as a pale yellow oil. The title compound decomposed partially during the isolation process. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.34 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.29–7.23 (m, 2H), 7.19–7.08 (m, 5H), 6.95 (dd, *J* = 7.5, 1.7 Hz, 1H), 5.54–5.40 (m, 2H), 5.21 (s, 1H), 4.07 (p, *J* = 6.7 Hz, 1H), 2.64 (td, *J* = 7.3, 2.2 Hz, 2H), 2.34–2.25 (m, 2H), 1.31 (s, 12H), 1.06 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.02, 142.10, 134.43, 132.24, 129.84, 129.46, 129.36, 128.44, 128.41, 128.21, 127.69, 125.66, 125.34, 83.06, 41.99, 35.88, 34.45, 24.93, 24.84, 18.79. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{26}H_{32}BClO_2Na$, 445.2082; found: 445.2078.



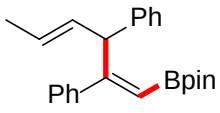
(1*E*,4*E*)-4-15
(γ:α = 89:11)

Following the general procedure **2.1** described above, the compound **4-15** was isolated in 84% yield as a pale yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.30–7.23 (m, 2H), 7.22–7.10 (m, 3H), 5.73 (t, *J* = 3.7 Hz, 1H), 5.65 (dd, *J* = 15.4, 6.0 Hz, 1H), 5.48 (dtd, *J* = 11.8, 6.6, 3.2 Hz, 1H), 3.91 (p, *J* = 5.9 Hz, 1H), 2.71–2.60 (m, 2H), 2.31 (q, *J* = 6.8 Hz, 2H), 2.14–1.84 (m, 4H), 1.64–1.49 (m, 4H), 1.26–1.25 (d, 12H), 1.17 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 169.35, 142.22, 139.39, 135.83, 128.42, 128.18, 127.44, 125.62, 125.54, 82.70, 40.17, 36.08, 34.51, 28.69, 25.52, 24.83, 24.78, 22.96, 22.05, 19.57. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{26}H_{37}BO_2Na$, 415.2785; found: 415.2772.



(1*E*,4*Z*)-5 (11%)

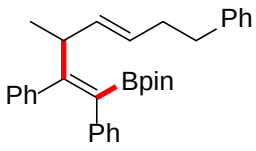
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.23 (s), 4.18 (q, *J* = 7.9 Hz).



(1*E*,4*E*)-4-16

(γ:α = >99:<1)

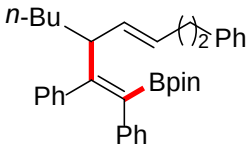
Following the general procedure **2.1** described above, the compound **4-16** was isolated in 95% yield as a pale yellow solid. It could be further purified by recrystallization from methanol to obtain colorless crystals (m.p. 102–103 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.3 Hz, 2H), 7.29–7.24 (m, 2H), 7.20–7.10 (m, 4H), 7.05–7.00 (m, 2H), 5.79 (ddd, *J* = 15.1, 8.7, 1.4 Hz, 1H), 5.69 (dq, *J* = 15.4, 6.4 Hz, 1H), 5.64 (s, 1H), 5.52 (d, *J* = 8.7 Hz, 1H), 1.71 (d, *J* = 7.4 Hz, 3H), 1.28 (d, *J* = 5.2 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.10, 143.31, 142.91, 131.12, 128.04, 127.89, 127.83, 127.70, 127.51, 127.14, 125.78, 83.10, 52.17, 24.85, 24.79, 18.12. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{24}H_{29}BO_2Na$, 383.2159; found: 383.2146.



(1*Z*,4*E*)-**4-17**

(γ:α = 99:1)

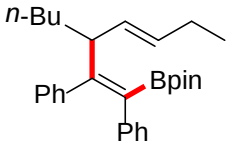
Following the general procedure **2.2** described above, the compound **4-17** was isolated in 95% yield as a white solid. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 90–91 °C). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.27 (t, *J* = 7.5 Hz, 2H), 7.21–7.14 (m, 3H), 7.07–7.02 (m, 3H), 7.00 (t, *J* = 7.3 Hz, 2H), 6.95–6.88 (m 3H), 6.85 (dd, *J* = 6.9, 2.5 Hz, 2H), 5.60–5.49 (m, 2H), 3.71 (p, *J* = 6.5 Hz, 1H), 2.68 (q, *J* = 7.3 Hz, 2H), 2.44–2.28 (m, 2H), 1.31 (d, *J* = 3.9 Hz, 12H), 1.06 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 155.90, 142.05, 141.07, 139.54, 134.50, 129.90, 129.29, 128.69, 128.47, 128.21, 127.24, 126.91, 125.86, 125.66, 125.07, 83.63, 43.88, 35.96, 34.46, 24.69, 19.07. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{32}H_{37}BO_2Na$, 487.2785; found: 487.2798.



(1*Z*,4*E*)-4-18

(γ:α = 99:1)

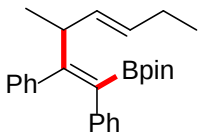
Following the general procedure **2.2** described above, the compound **4-18** was isolated in 82% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.31–7.23 (m, 2H), 7.21–7.15 (m, 3H), 7.07–7.02 (m, 3H), 7.02–6.96 (m, 2H), 6.95–6.88 (m, 3H), 6.87–6.80 (m, 2H), 5.60 (dt, *J* = 14.2, 6.7 Hz, 1H), 5.36 (dd, *J* = 15.4, 7.9 Hz, 1H), 3.46 (q, *J* = 7.1, 6.6 Hz, 1H), 2.78–2.62 (m, 2H), 2.37 (q, *J* = 7.2 Hz, 2H), 1.49–1.41 (m, 1H), 1.33–1.23 (m, 17H), 0.92–0.77 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 155.33, 142.08, 141.10, 139.80, 133.33, 129.98, 129.85, 129.33, 128.52, 128.22, 127.19, 126.92, 125.84, 125.65, 125.01, 83.57, 50.59, 35.98, 34.51, 32.99, 29.67, 24.80, 24.75, 22.59, 14.13. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{35}H_{43}BO_2Na$, 529.3254; found: 529.3242.



(1*Z*,4*E*)-4-19

(γ:α = 98:2)

Following the general procedure **2.2** described above, the compound **4-19** was isolated in 71% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.10–7.03 (m, 3H), 7.00–6.95 (m, 2H), 6.95-6.88 (m, 5H), 5.60 (dt, *J* = 15.2, 6.6 Hz, 1H), 5.34 (dd, *J* = 15.4, 7.8 Hz, 1H), 3.47 (q, *J* = 6.8 Hz, 1H), 2.05 (p, *J* = 7.3 Hz, 2H), 1.51–1.43 (m, 1H), 1.36–1.23 (m, 17H), 0.98 (t, *J* = 7.5 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 155.43, 141.12, 139.88, 132.33, 131.52, 130.02, 129.33, 127.18, 126.88, 125.82, 124.98, 83.56, 50.49, 33.07, 29.71, 25.66, 24.79, 24.73, 22.62, 14.13, 13.83. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{29}H_{39}BO_2Na$, 453.2941; found: 453.2946.

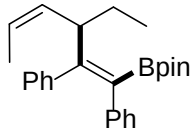


(1*Z*,4*E*)-4-20

(γ:α = 91:9)

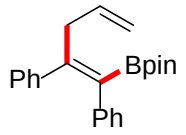
Following the general procedure **2.2** described above, the compound **4-20** was isolated in 74% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.09–7.04 (m, 3H), 6.99 (t, *J* = 7.3 Hz, 2H), 6.95–6.88 (m, 5H), 5.57–5.45 (m, 2H), 3.77–3.66 (m, 1H), 2.10–1.98 (m, 1H), 1.32 (d, *J* = 5.2 Hz, 3H), 1.07 (d, *J* = 6.9 Hz, 12H), 0.98 (t, *J* = 7.5

Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 156.08, 141.12, 139.65, 132.75, 131.23, 129.97, 129.31, 127.24, 126.88, 125.85, 125.05, 83.63, 43.83, 29.68, 25.63, 24.70, 19.18, 13.83. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{26}H_{33}BO_2Na$, 411.2472; found: 411.2475.



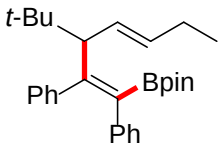
(1*Z*,4*Z*)-5 (9%)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.12–5.06 (m), 3.85–3.79 (m), 1.79 (dd, J = 6.8, 1.8 Hz), 1.31 (d, J = 5.4 Hz).



(*Z*)-4-21

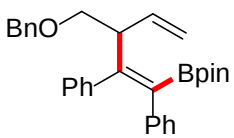
Following the general procedure **2.2** described above, the compound **4-21** was isolated in 53% yield as a pale yellow oil. The title compound decomposed partially during the isolation process. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.11–7.02 (m, 5H), 7.01–6.95 (m, 3H), 6.95–6.91 (m, 2H), 5.81 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1H), 5.06 (dd, *J* = 17.1, 1.7 Hz, 1H), 4.96 (dd, *J* = 10.1, 1.6 Hz, 1H), 3.50 (d, *J* = 6.6 Hz, 2H), 1.32 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 150.88, 142.03, 141.44, 136.47, 129.58, 129.14, 127.49, 127.44, 126.28, 125.28, 115.83, 83.68, 42.87, 24.73. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{23}H_{27}BO_2Na$, 369.2002; found: 369.1990.



(1*Z*,4*E*)-4-22

(γ:α = 99:1)

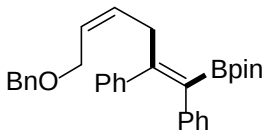
Following the general procedure **2.2** described above, the compound **4-22** was isolated in 94% yield as a white solid (m.p. 97–98 °C). The title compound decomposed partially during the isolation process. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.09–6.94 (m, 7H), 6.94–6.75 (m, 3H), 5.87–5.74 (m, 2H), 3.27 (d, *J* = 8.0 Hz, 1H), 2.22–2.10 (m, 2H), 1.32 (d, *J* = 11.0 Hz, 12H), 1.08 (t, *J* = 7.5 Hz, 3H), 0.80 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 153.12, 141.35, 141.06, 134.16, 130.50, 129.38, 128.68, 127.17, 127.02, 125.80, 124.88, 83.54, 61.73, 34.13, 28.48, 25.84, 24.83, 24.70, 13.81. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{29}H_{39}BO_2Na$, 453.2941; found: 453.2950.



(*Z*)-4-23

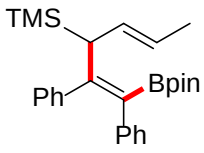
(γ:α = 94:6)

Following the general procedure **2.2** described above, the compound **4-23** was isolated in 53% yield as a pale yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.37–7.29 (m, 4H), 7.30–7.22 (m, 1H), 7.09–7.01 (m, 3H), 7.04–6.96 (m, 2H), 6.97–6.86 (m, 5H), 5.83 (ddd, *J* = 17.4, 10.3, 7.3 Hz, 1H), 5.28 (dt, *J* = 17.3, 1.5 Hz, 1H), 5.16 (dt, *J* = 10.4, 1.4 Hz, 1H), 4.58–4.38 (m, 2H), 4.20 (q, *J* = 7.5 Hz, 1H), 3.54 (dd, *J* = 9.5, 7.6 Hz, 1H), 3.46 (dd, *J* = 9.5, 7.5 Hz, 1H), 1.31 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.66, 141.23, 139.48, 138.69, 137.91, 129.84, 129.32, 128.19, 127.48, 127.27, 127.18, 127.08, 126.08, 125.11, 116.33, 83.67, 72.38, 71.57, 50.39, 24.72. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{31}H_{35}BO_3Na$, 489.2577; found: 489.2563.



(*Z*)-5 (6%)

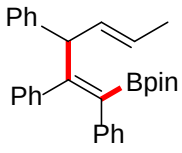
^{1}H NMR (500 MHz, $CDCl_3$ δ 5.65 – 5.48 (m), 3.93 (dd, *J* = 6.0, 1.2 Hz).



(1*Z*,4*E*)-4-24

(γ:α = 99:1)

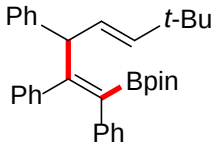
Following the general procedure **2.2** described above, the compound **4-24** was isolated in 93% yield as a white solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.12–7.05 (m, 2H), 7.07–7.00 (m, 1H), 7.01–6.94 (m, 2H), 6.95–6.87 (m, 3H), 6.89–6.83 (m, 2H), 5.54–5.21 (m, 2H), 3.76 (d, *J* = 9.6 Hz, 1H), 1.68 (d, *J* = 4.9 Hz, 3H), 1.31 (s, 12H), 0.01 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 156.34, 142.10, 141.30, 129.74, 129.61, 129.52, 126.99, 126.97, 125.81, 124.56, 123.12, 83.25, 45.71, 24.83, 24.81, 18.09, -2.01. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{27}H_{37}BO_2SiNa$, 455.2554; found: 455.2547.



(1*Z*,4*E*)-4-25

(γ:α = 99:1)

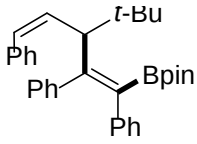
Following the general procedure **2.2** described above, the compound **4-25** was isolated in 75% yield as a pale yellow solid. It could be further purified by recrystallization from methanol to obtain colorless crystals (m.p. 124–125 °C). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.32 (d, *J* = 7.3 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.03–6.88 (m, 8H), 6.52 (d, *J* = 7.0 Hz, 2H), 5.80–5.70 (m, 1H), 5.67 (ddd, *J* = 15.1, 8.6, 1.5 Hz, 1H), 5.04 (d, *J* = 8.6 Hz, 1H), 1.74 (d, *J* = 6.2 Hz, 3H), 1.33 (d, *J* = 4.4 Hz, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 154.31, 142.78, 141.03, 139.56, 130.52, 130.17, 129.41, 128.23, 127.99, 127.39, 127.29, 126.81, 126.02, 125.97, 125.20, 83.83, 55.43, 24.80, 24.72, 18.20. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{30}H_{33}BO_2Na$, 459.2472; found: 459.2466.



(1*Z*,4*E*)-4-26

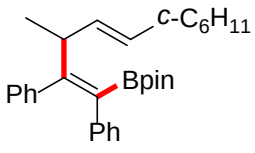
(γ:α = 94:6)

Following the general procedure **2.2** described above, the compound **4-26** was isolated in 63% yield as a pale yellow solid. It could be further purified by recrystallization from methanol to obtain colorless crystals (m.p. 111–112 °C). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.32 (d, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.03–6.87 (m, 8H), 6.54 (d, *J* = 6.8 Hz, 2H), 5.77 (d, *J* = 15.6 Hz, 1H), 5.54 (dd, *J* = 15.6, 8.5 Hz, 1H), 5.08 (d, *J* = 8.5 Hz, 1H), 1.31 (d, *J* = 2.1 Hz, 12H), 1.02 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 154.82, 143.52, 142.96, 141.19, 139.77, 130.14, 129.45, 128.32, 127.90, 127.24, 126.71, 125.92, 125.87, 125.14, 124.69, 83.69, 54.60, 33.19, 29.75, 24.78, 24.71. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{33}H_{39}BO_2Na$, 501.2941; found: 501.2925.



(1*Z*,4*Z*)-5 (6%)

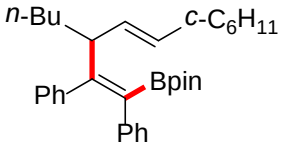
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.79 (d, J = 7.0 Hz, 1H).



(1*Z*,4*E*)-4-27

(γ:α = 99:1)

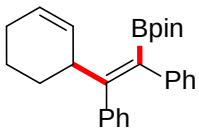
Following the general procedure **2.2** described above, the compound **4-27** was isolated in 62% yield as a pale yellow oil. The title compound decomposed partially during the isolation process. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.14–7.01 (m, 3H), 7.00 (t, *J* = 7.4 Hz, 2H), 6.95–6.86 (m, 5H), 5.52–5.44 (m, 1H), 5.40 (dd, *J* = 15.7, 6.8 Hz, 1H), 3.70 (p, *J* = 6.7 Hz, 1H), 2.01–1.99 (m, 1H), 1.75–1.59 (m, 5H), 1.32 (d, *J* = 5.8 Hz, 12H), 1.30–1.21 (m, 2H), 1.20–1.12 (m, 1H), 1.12–0.99 (m, 5H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 156.23, 141.21, 139.67, 135.58, 131.23, 129.99, 129.34, 127.24, 126.83, 125.82, 125.03, 83.61, 43.59, 40.73, 33.19, 33.03, 26.24, 26.11, 24.70, 19.10. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{30}H_{39}BO_2Na$, 465.2941; found: 465.2963.



(1*Z*,4*E*)-4-28

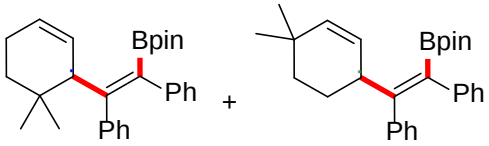
(γ:α = 99:1)

Following the general procedure **2.2** described above, the compound **4-28** was isolated in 73% yield as a pale yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.09–7.02 (m, 3H), 7.00–6.95 (m, 2H), 6.94–6.88 (m, 5H), 5.49 (dd, *J* = 15.6, 6.6 Hz, 1H), 5.29 (dd, *J* = 15.6, 8.7 Hz, 1H), 3.46 (q, *J* = 6.8 Hz, 1H), 2.01–1.91 (m, 1H), 1.77–1.60 (m, 5H), 1.51– 1.41 (m, 1H), 1.35–1.21 (m, 19H), 1.20–1.13 (m, 1H), 1.13–1.01 (m, 2H), 0.87 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 155.62, 141.21, 139.91, 136.70, 130.03, 129.94, 129.34, 127.17, 126.84, 125.79, 124.95, 83.52, 50.28, 40.73, 33.22, 33.01, 29.68, 26.24, 26.11, 26.09, 24.78, 24.72, 22.60, 14.13. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{33}H_{45}BO_2Na$, 507.3411; found: 507.3415.



(*Z*)-4-29

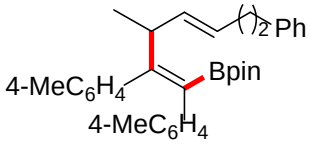
Following the general procedure **2.2** described above, the compound **4-29** was isolated in 91% yield as a white solid. It could be further purified by recrystallization from methanol to obtain white crystals. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.11–7.02 (m, 3H), 7.03–6.99 (m, 2H), 6.99–6.92 (m, 3H), 6.93–6.90 (m, 2H), 5.82 (dt, *J* = 10.0, 1.3 Hz, 1H), 5.73 (ddt, *J* = 10.0, 4.9, 2.7 Hz, 1H), 3.66–3.58 (m, 1H), 1.98–1.82 (m, 3H), 1.71–1.62 (m, 1H), 1.57–1.41 (m, 2H), 1.30 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 155.31, 141.21, 140.61, 130.70, 129.65, 129.32, 128.20, 127.35, 127.09, 125.93, 125.14, 83.67, 45.09, 28.68, 24.73, 24.67, 24.63, 22.06. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{26}H_{31}BO_2Na$, 409.2315; found: 409.2307.



(*Z*)-4-30 **(*Z*)-5-30**

(γ:α = 41:59)

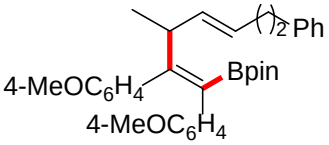
Following the general procedure **2.2** described above, the mixture were isolated in 83% yield as a colorless oil. Then, the mixture were obtained as a white crystal after recrystallization with methanol. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.09–6.86 (m), 5.95 (ddt, *J* = 10.1, 4.3, 2.0 Hz), 5.84 (ddt, *J* = 9.7, 4.6, 2.4 Hz), 5.68 (ddd, *J* = 10.0, 2.5, 1.1 Hz), 5.47 (dd, *J* = 10.1, 2.7 Hz), 3.55 (ddt, *J* = 10.6, 5.6, 2.6 Hz), 3.26–3.14 (m), 2.00–1.87 (m), 1.84–1.65 (m), 1.62–1.46 (m), 1.45–1.14 (m), 0.95 (m), 0.76 (m). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 155.16, 151.54, 141.39, 141.20, 140.51, 138.43, 131.08, 129.64, 129.35, 129.19, 128.07, 127.84, 127.34, 127.30, 127.01, 126.65, 125.96, 125.75, 125.14, 125.01, 83.66, 83.57, 77.25, 77.00, 76.75, 55.65, 45.15, 36.64, 32.62, 31.18, 30.84, 28.79, 28.37, 26.92, 25.50, 24.75, 24.72, 24.57, 22.85. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{28}H_{35}BO_2Na$, 437.2628; found: 437.2625.



(1*Z*,4*E*)-4-31

(γ:α = 98:2)

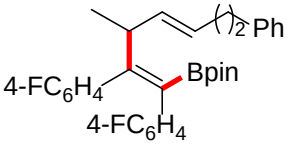
Following the general procedure **2.2** described above, the compound **4-31** was isolated in 65% yield as a pale yellow oil. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 78–79 °C). The title compound decomposed partially during the isolation process. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.31–7.22 (m, 3H), 7.20–7.12 (m, 4H), 6.88 (d, *J* = 7.9 Hz, 2H), 6.84–6.77 (m, 4H), 6.76 (d, *J* = 8.0 Hz, 2H), 5.58–5.46 (m, 1H), 3.64 (p, *J* = 6.6 Hz, 1H), 2.67 (td, *J* = 7.6, 4.8 Hz, 2H), 2.37–2.32 (m, 2H), 2.23 (s, 3H), 2.17 (s, 3H), 1.31 (d, *J* = 4.2 Hz, 12H), 1.04 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 154.98, 142.14, 138.02, 136.59, 135.18, 134.71, 134.33, 129.79, 129.15, 128.50, 128.48, 128.21, 128.09, 127.73, 125.65, 83.57, 44.17, 36.01, 34.50, 24.72, 24.71, 21.13, 21.06, 19.08. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{34}H_{41}BO_2Na$, 515.3098; found: 515.3075.



(1*Z*,4*E*)-4-32

(γ:α = 98:2)

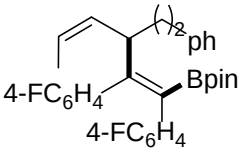
Following the general procedure **2.2** described above, the compound **4-32** was isolated in 80% yield as a white solid. The title compound decomposed partially during the isolation process. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.31–7.23 (m, 3H), 7.21–7.14 (m, 3H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.62 (d, *J* = 8.7 Hz, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 5.61–5.43 (m, 2H), 3.72 (s, 3H), 3.68 (s, 3H), 3.64 (q, *J* = 6.7, 6.2 Hz, 1H), 2.68 (td, *J* = 7.5, 3.9 Hz, 2H), 2.39–2.33 (m, 2H), 1.31 (d, *J* = 4.3 Hz, 12H), 1.04 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 157.60, 156.96, 154.37, 142.09, 134.78, 133.51, 132.06, 130.97, 130.38, 128.47, 128.21, 125.65, 112.80, 112.50, 83.56, 65.53, 54.94, 54.89, 44.13, 35.97, 34.45, 24.70, 19.03. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{34}H_{41}BO_4Na$, 547.2996; found: 547.2995.



(1*Z*,4*E*)-4-33

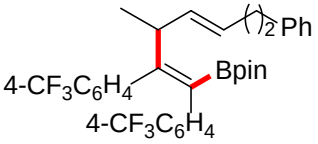
(γ:α = 94:6)

Following the general procedure **2.2** described above, the compound **4-33** was isolated in 95% yield as a pale yellow oil. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 79–80 °C). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.32–7.24 (m, 2H), 7.21–7.14 (m, 3H), 6.82 (dd, *J* = 8.8, 5.6 Hz, 2H), 6.77–6.64 (m, 6H), 5.58–5.43 (m, 1H), 3.72 (p, *J* = 6.9 Hz, 1H), 2.72–2.64 (m, 2H), 2.42–2.29 (m, 2H), 1.30 (d, *J* = 3.2 Hz, 12H), 1.02 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.94 (d, *J* = 66.9 Hz), 160.00 (d, *J* = 66.2 Hz), 155.65, 141.92, 136.86 (d, *J* = 3.4 Hz), 135.20 (d, *J* = 3.5 Hz), 134.24, 131.28 (d, *J* = 7.7 Hz), 130.71 (d, *J* = 7.7 Hz), 129.05, 128.48, 128.25, 125.74, 114.27 (d, *J* = 21.1 Hz), 114.03 (d, *J* = 21.1 Hz), 83.76, 43.57, 35.88, 34.36, 24.68, 18.93. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{32}H_{35}BF_2O_2Na$, 523.2596; found: 523.2601.



(1*Z*,4*E*)-5 (6%)

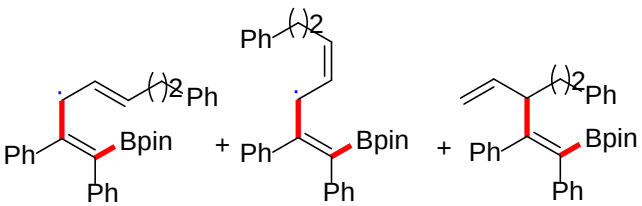
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.16–5.10 (m), 4.03 (td, J = 9.3, 5.6 Hz), 1.79 (dd, J = 6.9, 1.8 Hz).



(1*Z*,4*E*)-4-34

(γ:α = 98:2)

Following the general procedure **2.2** described above, the compound **4-34** was isolated in 82% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.33–7.25 (m, 6H), 7.22–7.15 (m, 3H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 5.58–5.50 (m, 1H), 5.46 (dd, *J* = 15.5, 6.2 Hz, 1H), 3.88–3.76 (m, 1H), 2.69 (tt, *J* = 13.8, 6.7 Hz, 2H), 2.45–2.31 (m, *J* = 7.3 Hz, 2H), 1.31 (d, *J* = 2.5 Hz, 12H), 1.02 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 156.73, 144.62, 142.91, 141.80, 133.70, 129.94, 129.63, 129.43, 128.72 (q, *J* = 32.7 Hz), 128.51 (q, *J* = 32.8 Hz), 128.51, 128.28,126.13 (q, *J* = 272.6 Hz), 125.89 (q, *J* = 272.7 Hz), 125.80, 124.42 (q, *J* = 3.6 Hz), 124.10 (q, *J* = 3.7 Hz), 84.02, 43.33, 35.79, 34.29, 24.67, 18.84. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{34}H_{35}BF_6O_2Na$, 623.2532; found: 623.2529.

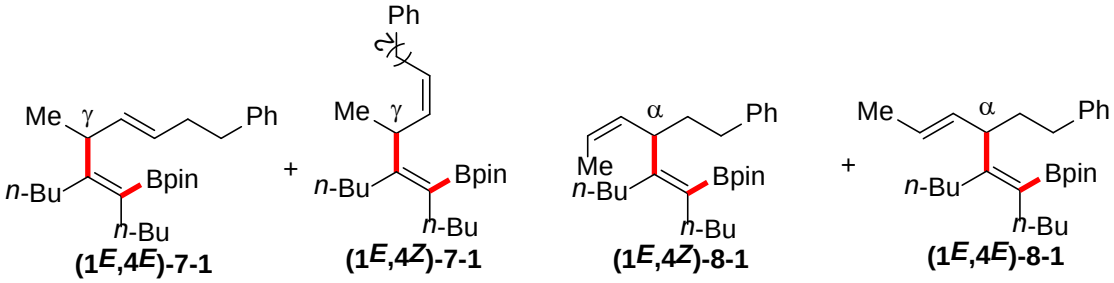


(1*Z*,4*E*)-4-35 **(1*Z*,4*Z*)-4-35** **(*Z*)-5-35**

(25 : 11 : 64)

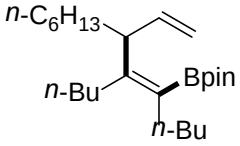
Following the general procedure **2.2** described above, The mixture were isolated in 44% yield as a pale yellow oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.13–7.01 (m), 7.01–6.95 (m), 6.95–6.88 (m), 5.77 (ddd, *J* = 17.2, 10.1, 8.7 Hz), 5.39–5.35 (m), 5.27–5.20 (m), 5.07 (dd, *J* = 10.2, 1.8 Hz, 4H), 3.51 (d, *J* = 5.9 Hz), 3.39

(d, *J* = 5.1 Hz), 3.27 (dd, *J* = 10.4, 8.6 Hz), 1.89–1.74 (m), 1.71–1.51 (m), 1.50–1.42 (m), 1.34–1.28 (m). **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{31}H_{35}BO_2Na$, 473.2628; found: 473.2651.



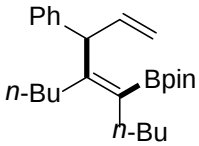
(1*E*,4*E*)-7-1 (28 : **(1*E*,4*Z*)-7-1** 3 : **(1*E*,4*Z*)-8-1** 66 : **(1*E*,4*E*)-8-1** 3)

Following the general procedure **2.3** described above, the mixture were isolated in 52% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.32–7.21 (m), 7.20–7.10 (m), 5.57–5.27 (m), 3.90 (q, *J* = 8.0 Hz), 3.52 (p, *J* = 6.6 Hz), 2.68–2.63 (m), 2.59 (ddd, *J* = 13.8, 10.7, 6.0 Hz), 2.49 (ddd, *J* = 13.8, 10.7, 6.4 Hz), 2.31 (q, *J* = 7.4, 7.0 Hz), 2.15–2.03 (m), 2.00–1.87 (m), 1.78–1.67 (m), 1.65 (d, *J* = 5.0 Hz), 1.41–1.19 (m), 1.06 (d, *J* = 6.9 Hz), 0.89 (dt, *J* = 7.1, 4.2 Hz). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 154.85, 154.79, 143.30, 142.26, 135.34, 133.22, 128.46, 128.38, 128.18, 127.59, 125.62, 125.42, 124.73, 82.77, 82.65, 44.45, 43.21, 37.99, 36.18, 34.60, 34.12, 32.93, 32.85, 32.70, 30.70, 30.64, 29.09, 28.27, 24.98, 24.88, 24.80, 24.77, 23.65, 23.00, 19.02, 14.12, 14.10, 13.87, 13.38. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{28}H_{45}BO_2Na$, 447.3411; found: 447.3402.



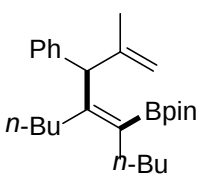
(*E*)-7-2
(γ:α = 99:1)

Following the general procedure **2.3** described above, the compound **7-2** was isolated as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.82 (ddd, J = 17.4, 10.3, 7.3 Hz, 1H), 5.00 (dt, *J* = 17.2, 1.7 Hz, 1H), 4.95 (ddd, *J* = 10.3, 2.1, 1.1 Hz, 1H), 3.39 (q, *J* = 7.3 Hz, 1H), 2.15–2.07 (m, 2H), 2.08–1.89 m, 2H), 1.51–1.15 (m, 30H), 0.92–0.85 (m, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 153.47, 142.14, 113.58, 82.72, 50.85, 32.83, 32.75, 32.65, 31.91, 30.67, 29.42, 28.62, 27.50, 24.86, 24.83, 23.62, 22.98, 22.69, 14.09 (2C), 13.87. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{25}H_{47}BO_2Na$, 413.3567; found: 413.3552.



(*E*)-7-4
(γ:α = 99:1)

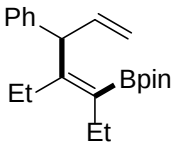
Following the general procedure **2.3** described above, the compound **7-4** was isolated as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.30–7.23 (m, 4H), 7.20–7.13 (m, 1H), 6.24 (ddd, *J* = 17.5, 10.2, 7.4 Hz, 1H), 5.20–5.11 (m, 2H), 4.98 (d, *J* = 7.4 Hz, 1H), 2.20–2.13 (m, 2H), 1.98–1.95 (m, 2H), 1.41–1.29 (m, 7H), 1.27 (s, 12H), 1.20–1.02 (m, 3H), 0.91 (t, *J* = 7.1 Hz, 3H), 0.72 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.47, 143.36, 139.13, 128.14, 127.92, 125.78, 116.14, 82.92, 55.22, 32.64, 32.39, 30.88, 29.95, 24.83, 24.78, 23.36, 23.03, 14.11, 13.66. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{25}H_{39}BO_2Na$, 405.2941; found: 405.2942.



(*E*)-7-5
(γ:α = 95:5)

Following the general procedure **2.3** described above, the compound **7-5** was isolated in 51% yield as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.20 (m, 4H), 7.19–7.14 (m, 1H), 4.98 (s, 1H), 4.85 (s, 1H), 4.72 (s, 1H), 2.21–2.05 (m, 3H), 1.91 (td, *J* = 12.2, 4.5 Hz, 1H), 1.70 (s, 3H), 1.40–1.23 (s, 20H), 0.90 (t, *J* = 5.6 Hz, 3H), 0.63 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.39, 147.04, 141.79, 129.57,

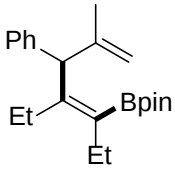
127.81, 125.83, 112.93, 82.82, 58.79, 32.60, 32.05, 31.02, 30.80, 24.81, 24.77, 23.30, 23.08, 23.01, 14.10, 13.53. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{26}H_{41}BO_2Na$, 419.3098; found: 419.3092.



(*E*)-7-7

(γ:α = 99:1)

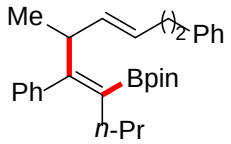
Following the general procedure **2.3** described above, the compound **7-7** was isolated in 43% yield as a colorless oil. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.32–7.23 (m, 4H), 7.20–7.14 (m, 1H), 6.26 (ddd, *J* = 17.1, 10.3, 7.5 Hz, 1H), 5.21–5.13 (m, 1H), 5.03 (d, *J* = 7.5 Hz, 1H), 2.21 (q, J = 7.4 Hz, 2H), 2.00 (q, J = 7.6 Hz, 2H), 1.28 (s, 12H), 1.02 (t, J = 7.5 Hz, 3H), 0.64 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 153.88, 143.34, 139.08, 128.16, 127.95, 125.80, 116.18, 82.95, 55.07, 24.85, 24.81, 24.06, 22.76, 14.90, 14.84. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{21}H_{31}BO_2Na$, 349.2315; found: 349.2311.



(*E*)-7-8

(γ:α = 98:2)

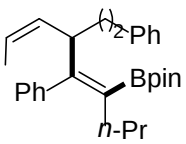
Following the general procedure **2.3** described above, the compound **7-8** was isolated in 35% yield as a colorless oil. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.29–7.23 (m, 4H), 7.19–7.15 (m, 1H), 4.98 (s, 1H), 4.91 (s, 1H), 4.71 (s, 1H), 2.28–2.15 (m, 3H), 2.04–1.94 (m, 1H), 1.71 (s, 3H), 1.28 (s, 12H), 1.01 (t, *J* = 7.5 Hz, 3H), 0.37 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 153.81, 147.06, 141.79, 129.60, 127.87, 125.84, 112.90, 82.86, 58.57, 24.82, 24.80, 24.23, 23.57, 23.07, 14.76, 14.61. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{22}H_{33}BO_2Na$, 363.2472; found: 364.2467.



(1*Z*,4*E*)-$\alpha'\gamma$-1

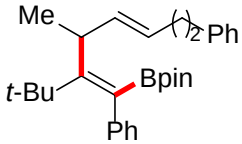
($\alpha'\gamma$:$\alpha'\alpha$:$\beta'\gamma$:$\beta'\alpha$ = 83:12:2:3)

Following the general procedure **2.4** described above, the compound **$\alpha'\gamma$-1** was isolated in 55% yield as a colorless oil. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.30–7.12 (m, 8H), 6.89 (d, *J* = 6.7 Hz, 1H), 5.44–5.31 (m, 2H), 3.75 (p, *J* = 6.7 Hz, 1H), 2.62 (dt, *J* = 13.4, 6.6 Hz, 1H), 2.32–2.22 (m, 2H), 1.81–1.71 (m, 2H), 1.33 (s, 12H), 1.27–1.18 (m, 4H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.71 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 155.85, 142.14, 140.09, 134.89, 129.20, 128.44, 128.16, 127.85, 127.11, 125.84, 125.59, 83.12, 42.77, 36.02, 34.43, 34.32, 24.85, 24.79, 23.39, 19.25, 14.16. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{29}H_{39}BO_2Na$, 453.2941; found: 453.2957.



(1*Z*,4*E*)-$\alpha'\alpha$-1 (12%)

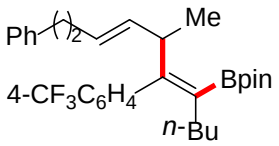
^{1}H NMR (500 MHz, CDCl$_3$) δ 5.00 (ddd, J = 11.1, 9.5, 1.9 Hz), 4.11 (td, J = 9.0, 5.9 Hz), 2.38–2.35 (m).



(1*Z*,4*E*)-$\beta'\gamma$-1

($\alpha'\gamma$:$\alpha'\alpha$:$\beta'\gamma$:$\beta'\alpha$ = 0:0:99:1)

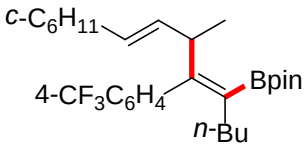
Following the general procedure **2.4** described above, the compound **$\beta'\gamma$-1** was isolated in 57% yield as a colorless oil. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.32–7.23 (m, 2H), 7.23–7.15 (m, 5H), 7.15–7.06 (m, 3H), 5.84 (dd, *J* = 15.4, 5.6 Hz, 1H), 5.52 (dtd, *J* = 15.2, 7.0, 1.7 Hz, 1H), 3.21 (p, *J* = 6.9, 6.4 Hz, 1H), 2.74–2.68 (m, 2H), 2.45–2.31 (m, 2H), 1.38 (d, *J* = 7.2 Hz, 3H), 1.08 (s, 6H), 1.01 (s, 6H), 0.93 (s, 9H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 157.94, 143.59, 142.24, 137.39, 129.21, 128.48, 128.19, 128.00, 127.22, 125.62, 125.15, 83.13, 40.34, 35.97, 34.52, 31.51, 24.52, 24.22, 22.01. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{31}H_{43}BO_2Na$, 467.3098; found: 467.3114.



(1*Z*,4*E*)-α'γ-2

(α'γ:α'α:β'γ:β'α = 85:3:6:6)

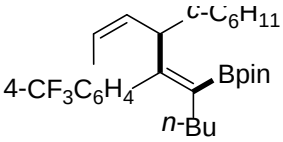
Following the general procedure **2.4** described above, the compound **α'γ-2** was isolated in 94% yield as a colorless oil. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 57–58 °C). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.49 (d, *J* = 7.7 Hz, 2H), 7.30–7.23 (m, 2H), 7.22–7.10 (m, 3H), 6.97 (d, *J* = 7.6 Hz, 2H), 5.46–5.24 (m, 2H), 3.75 (q, *J* = 8.3, 7.1 Hz, 1H), 2.63 (h, *J* = 6.6 Hz, 2H), 2.33–2.25 (m, 2H), 1.79–1.69 (m, 2H), 1.33 (s, 12H), 1.24–1.05 (m, 4H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.73 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 154.07, 144.01, 141.97, 134.36, 129.52, 128.53 (q, *J* = 31.7Hz), 128.47, 128.46, 128.22, 126.49 (q, *J* = 273.4 Hz), 125.69, 124.15 (q, *J* = 3.7 Hz), 83.33, 42.48, 35.93, 34.33, 32.36, 31.92, 24.85, 24.80, 22.55, 19.01, 13.92. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{31}H_{40}BF_3O_2Na$, 535.2971; found: 535.2948.



(1Z,4*E*)-α'γ-3

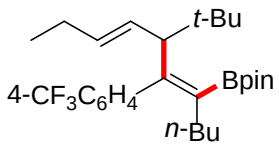
(α'γ:α'α:β'γ:β'α = 91:9:<1:<1)

Following the general procedure **2.4** described above, the compound **α'γ-3** was isolated in 89% yield as a colorless oil. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 62–63 °C). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 5.30–5.20 (m, 2H), 3.79–3.70 (m, 1H), 1.92–1.84 (m, 1H), 1.82–1.56 (m, 7H), 1.34 (s, 12H), 1.28–1.06 (m, 8H), 1.03–0.97 (m, 1H), 0.93 (d, *J* = 6.9 Hz, 3H), 0.73 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 154.32, 144.15, 135.37, 131.00, 129.59, 128.47 (q, *J* = 31.8Hz), 126.50 (q, *J* = 272.2 Hz), 124.07 (q, *J* = 3.6 Hz), 83.30, 42.17, 40.68, 33.18, 33.04, 32.38, 31.95, 26.20, 26.07, 24.85, 24.77, 22.53, 19.00, 13.91. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{29}H_{42}BF_3O_2Na$, 513.3128; found: 513.3134.



(1Z,4*Z*)-α'α-3 (9%)

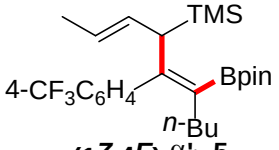
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.66 (dq, J = 11.1, 7.0 Hz, 1H), 4.91 (dt, J = 9.5, 6.9 Hz, 1H), 4.06–3.98 (m).



(1*Z*,4*E*)-α'γ-4

(α'γ:α'α:β'γ:β'α = 99:1:<1:<1)

Following the general procedure **2.4** described above, the compound **α'γ-4** was isolated in 82% yield as a colorless crystal (m.p. 51–52 °C). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 5.30 (d, *J* = 11.9 Hz, 1H), 4.44–4.35 (m, 1H), 4.29 (ddd, *J* = 10.9, 8.7, 5.9 Hz, 1H), 1.77–1.69 (m, 2H), 1.50 (ddd, *J* = 13.3, 7.4, 5.9 Hz, 1H), 1.41–1.33 (m, 1H), 1.32 (d, *J* = 3.4 Hz, 12H), 1.20–1.02 (m, 11H), 1.11–1.02 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H), 0.71 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 155.77, 144.75, 140.15, 131.52, 128.57 (q, *J* = 31.7 Hz), 126.34 (q, *J* = 272.2 Hz), 124.11 (q, *J* = 3.7 Hz), 83.03, 44.64, 32.64, 32.53, 31.83, 31.38, 29.60, 25.03, 24.90, 22.48, 13.92, 11.86. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{28}H_{42}BF_3O_2Na$, 501.3128; found: 501.3135.

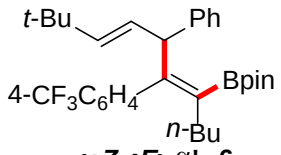


(1*Z*,4*E*)-α'γ-5

(α'γ:α'α:β'γ:β'α = 99:1:<1:<1)

Following the general procedure **2.4** described above, the compound **α'γ-5** was isolated in 49% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 7.2 Hz, 2H), 5.60 (dd, *J* = 13.9, 10.4 Hz, 1H), 5.31 (d, *J* = 14.0 Hz, 1H), 4.22 (dq, *J* = 10.5, 6.8 Hz, 1H), 1.77 (ddd, *J* = 12.9, 9.1, 5.9 Hz, 1H), 1.68 (ddd, *J* = 12.9, 9.0, 6.2

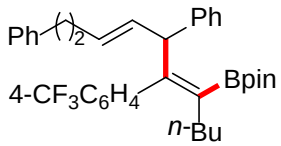
Hz, 1H), 1.32 (d, *J* = 4.1 Hz, 12H), 1.21–1.01 (m, 7H), 0.71 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 157.11, 152.16, 144.75, 128.51 (q, *J* = 31.9 Hz), 127.65, 126.32 (q, *J* = 270.9 Hz), 124.36 (q, *J* = 3.8 Hz), 83.09, 42.97, 32.60, 31.84, 25.17, 24.63, 22.99, 22.47, 13.92, 0.09. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{26}H_{40}BF_3O_2SiNa$, 503.2741; found: 503.2748.



(1*Z*,4*E*)-α'γ-6

(α'γ:α'α:β'γ:β'α = 99:1:<1:<1)

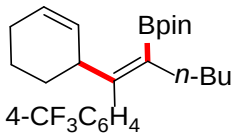
Following the general procedure **2.4** described above, the compound **α'γ-6** was isolated in 65% yield as a white solid. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 113–114 °C). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.37 (d, *J* = 8.1 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 2H), 7.18–7.11 (m, 3H), 6.66 (d, *J* = 8.0 Hz, 2H), 5.69 (d, *J* = 15.5 Hz, 1H), 5.42 (dd, *J* = 15.5, 8.8 Hz, 1H), 5.17 (d, *J* = 8.8 Hz, 1H), 1.83 (ddd, *J* = 13.3, 9.3, 5.9 Hz, 1H), 1.75 (ddd, *J* = 13.2, 9.2, 6.4 Hz, 1H), 1.35 (d, *J* = 2.0 Hz, 12H), 1.25–1.16 (m, 2H), 1.10 (tt, *J* = 13.7, 6.9 Hz, 2H), 1.01 (s, 9H), 0.73 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 153.11, 144.08, 143.40, 142.82, 129.73, 128.20, 127.84, 127.65 (q, *J* = 31.6 Hz), 125.91, 125.45 (q, *J* = 272.1 Hz), 124.34, 123.91 (q, *J* = 3.5 Hz), 83.42, 53.28, 33.18, 32.35, 31.96, 29.74, 24.93, 24.79, 22.48, 13.92. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{32}H_{42}BF_3O_2Na$, 549.3128; found: 549.3102.



(1*Z*,4*E*)-α'γ-7

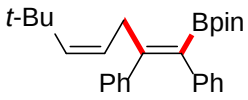
(α'γ:α'α:β'γ:β'α = 99:1:<1:<1)

Following the general procedure **2.4** described above, the compound **α'γ-7** was isolated in 74% yield as a colureless oil. It could be further purified by recrystallization from methanol to obtain white crystals. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.32 (d, *J* = 8.2 Hz, 2H), 7.29–7.23 (m, 3H), 7.22–7.10 (m, 6H), 7.04 (d, *J* = 7.4 Hz, 2H), 6.52 (d, *J* = 6.8 Hz, 2H), 5.69 (dt, *J* = 13.7, 6.7 Hz, 1H), 5.49 (dd, *J* = 15.2, 9.1 Hz, 1H), 5.15 (d, *J* = 9.0 Hz, 1H), 2.70 (t, *J* = 7.4 Hz, 2H), 2.39 (q, *J* = 7.3 Hz, 2H), 1.76 (ttd, *J* = 15.5, 8.6, 7.7, 4.7 Hz, 2H), 1.36 (s, 12H), 1.28–1.17 (m, 2H), 1.10 (tq, *J* = 13.5, 6.2 Hz, 2H), 0.73 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.79, 143.77, 142.45, 141.78, 131.41, 130.18, 129.72, 128.62, 128.37 (q, *J* = 31.4 Hz), 128.26, 128.14, 127.86, 125.96, 125.70, 125.59 (q, *J* = 272.2 Hz), 123.92 (q, *J* = 3.9 Hz), 83.48, 53.82, 35.69, 34.41, 32.34, 31.95, 24.93, 24.86, 22.53, 13.91. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{36}H_{42}BF_3O_2Na$, 597.3128; found: 597.3101.



(*Z*)-α'γ-8

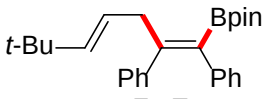
Following the general procedure **2.4** described above, the compound **α'γ-8** was isolated in 93% yield as a white solid. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 117–118 °C). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 5.66–5.56 (m, 2H), 3.64 (dd, *J* = 9.2, 5.0 Hz, 1H), 1.90–1.82 (m, 1H), 1.81–1.70 (m, 4H), 1.60–1.52 (m, 1H), 1.51–1.40 (m, 1H), 1.33 (s, 12H), 1.28–1.17 (m, 3H), 1.17–1.07 (m, 2H), 0.74 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 153.49, 144.93, 130.64, 129.17, 128.21 (q, *J* = 31.9 Hz), 127.95, 126.31 (q, *J* = 273.4 Hz), 124.34 (q, *J* = 3.8 Hz), 83.40, 43.69, 32.28, 32.04, 28.56, 24.82, 24.75, 24.51, 22.53, 21.95, 13.90. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{25}H_{34}BF_3O_2Na$, 457.2502; found: 457.2493.



(1*Z*,4*Z*)-5-3

(α:γ= 98:2)

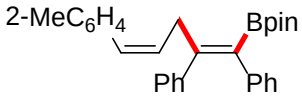
Following the general procedure **2.2** described above, the compound **5-3** was isolated in 71% yield as a pale yellow solid. It could be further purified by recrystallization from methanol. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.12–7.01 (m, 5H), 7.00–6.94 (m, 3H), 6.94–6.90 (m, 2H), 5.26 (dt, *J* = 12.0, 2.0 Hz, 1H), 5.15 (dt, *J* = 12.1, 6.5 Hz, 1H), 3.67 (dd, *J* = 6.5, 2.0 Hz, 2H), 1.31 (s, 12H), 1.04 (s, 9H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 152.79, 142.02, 141.63, 140.18, 129.62, 129.19, 127.44, 127.40, 126.24, 126.21, 125.20, 83.65, 37.23, 33.28, 30.81, 24.73. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{27}H_{35}BO_2Na$, 425.2628; found: 425.2622.



(1*Z*,4*E*)-5-4

(α:γ= 99:1)

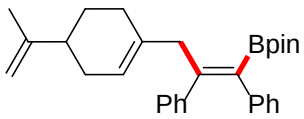
Following the general procedure **2.2** described above, the compound **5-4** was isolated in 68% yield as a pale yellow solid. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 113–114 °C). The title compound decomposed partially during the isolation process. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.09–7.01 (m, 5H), 6.98 (dt, *J* = 8.3, 1.9 Hz, 1H), 6.96–6.91 (m, 4H), 5.40 (d, *J* = 15.6 Hz, 1H), 5.30 (dt, *J* = 15.5, 6.5 Hz, 1H), 3.39 (dd, *J* = 6.6, 1.2 Hz, 2H), 1.32 (s, 12H), 0.89 (s, 9H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 152.09, 143.37, 142.40, 141.57, 129.63, 129.17, 127.37, 127.30, 126.00, 125.18, 122.26, 83.60, 41.74, 32.83, 29.58, 24.75. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{27}H_{35}BO_2Na$, 425.2628; found: 425.2616.



(1*Z*,4*Z*)-5-5

(α:γ= 99:1)

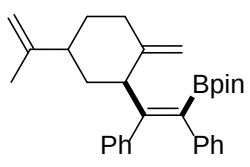
Following the general procedure **2.2** described above, the compound **5-5** was isolated in 51% yield as a pale yellow oil. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 122–123 °C). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.13–7.08 (m, 3H), 7.06–7.01 (m, 6H), 6.99 (d, *J* = 7.2 Hz, 1H), 6.93–6.90 (m, 2H), 6.88 (dd, *J* = 6.6, 3.0 Hz, 2H), 6.37 (d, *J* = 11.4 Hz, 1H), 5.68 (dt, *J* = 11.4, 6.8 Hz, 1H), 3.64 (dd, *J* = 6.8, 1.8 Hz, 2H), 2.09 (s, 3H), 1.19 (s, 12H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 157.96, 153.85, 141.01, 139.51, 138.35, 134.10, 130.17, 129.36, 129.19, 127.30, 126.85, 126.03, 125.23, 116.59, 113.43, 83.80, 55.82, 55.17, 24.75, 24.72. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{30}H_{33}BO_2Na$, 459.2472; found: 459.2456.



(*Z*)-5-6

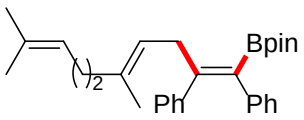
(α:γ= 90:10)

Following the general procedure **2.2** described above, the compound **5-6** was isolated in 69% yield as a colorless oil. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 75–76 °C). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.08–7.01 (m, 5H), 7.00–6.97 (m, 1H), 6.96–6.91 (m, 4H), 5.50–5.37 (m, 1H), 4.66 (s, 3H), 4.63 (s, 3H), 3.37 (t, *J* = 10.1 Hz, 2H), 2.15–1.96 (m, 4H), 1.88–1.73 (m, 2H), 1.69 (s, 3H), 1.45–1.33 (m, 1H), 1.30 (s, 12H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 150.58, 150.08, 142.26, 141.63, 135.20, 129.60, 129.08, 127.40, 127.26, 126.03, 125.21, 122.74, 108.33, 83.55, 46.09, 41.01, 30.83, 28.92, 27.87, 24.72, 24.70, 20.82. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{30}H_{37}BO_2Na$, 463.2785; found: 463.2772.



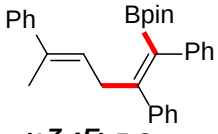
(*Z*)-4 (10%)

^{1}H NMR (500 MHz, CDCl$_3$) δ 5.15 (s), 4.97 (s), 4.83 (s), 4.79 (s), 4.00 (t, J = 7.0 Hz).



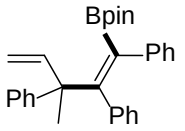
(1*Z*,4*E*)-5-7
(α:γ= 90:10)

Following the general procedure **2.2** described above, the compound **5-7** was isolated in 65% yield as a colorless oil. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 86–87 °C). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.09–7.01 (m, 5H), 7.00–6.91 (m, 5H), 5.14 (t, *J* = 6.8 Hz, 1H), 5.00 (t, *J* = 6.0 Hz, 1H), 3.43 (d, *J* = 7.0 Hz, 2H), 1.94 (dt, *J* = 11.6, 6.3 Hz, 4H), 1.64 (s, 3H), 1.55 (s, 3H), 1.49 (s, 3H), 1.32 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.53, 142.40, 141.63, 135.87, 131.15, 129.64, 129.08, 127.37, 127.36, 126.03, 125.14, 124.32, 122.42, 83.63, 39.72, 37.53, 26.63, 25.66, 24.74, 17.64, 16.13. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{30}H_{39}BO_2Na$, 465.2941; found: 465.2953.



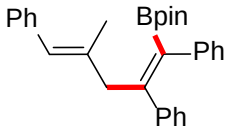
(1*Z*,4*E*)-5-8
(α:γ= 94:6)

Following the general procedure **2.2** described above, the compound **5-8** was isolated in 68% yield as a colorless oil. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 97–98 °C). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.29–7.24 (m, 4H), 7.19–7.15 (m, 1H), 7.08–7.02 (m, 5H), 7.01–6.96 (m, 3H), 6.98–6.92 (m, 2H), 5.76 (td, *J* = 7.1, 1.3 Hz, 1H), 3.66 (d, *J* = 7.1 Hz, 2H), 1.92 (s, 3H), 1.32 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.05, 143.86, 142.28, 141.52, 135.32, 129.63, 129.01, 128.02, 127.52, 127.40, 126.46, 126.29, 126.20, 125.71, 125.24, 83.68, 38.18, 24.75, 16.00.**ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{30}H_{33}BO_2Na$, 459.2472; found: 459.2467.



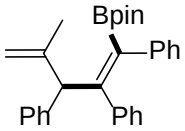
(*Z*)-4 (6%)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.89 (t, J = 7.9 Hz), 3.37 (d, J = 7.5 Hz), 2.01 (s), 1.31 (s).



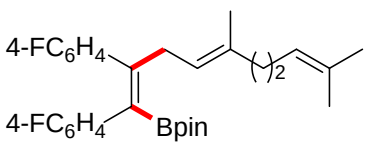
(1*Z*,4*E*)-5-9
(α:γ= 80:20)

Following the general procedure **2.2** described above, the compound **5-9** was isolated in 71% yield as a colorless oil. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 109–110 °C). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.25 (t, *J* = 7.5 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.10–6.95 (m, 12H), 6.26 (s, 1H), 3.60 (s, 2H), 1.86 (s, 3H), 1.31 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 150.57, 141.97, 141.57, 138.57, 136.65, 129.62, 129.11, 128.71, 127.86, 127.44, 127.38, 127.20, 126.16, 125.77, 125.32, 83.65, 48.65, 24.74, 17.79. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{30}H_{33}BO_2Na$, 459.2472; found: 459.2476.



(*Z*)-4 (20%)

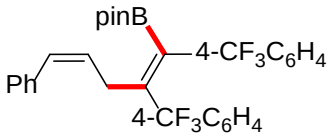
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.06 (d, J = 5.1 Hz), 4.87 (s), 1.89 (s), 1.28 (s).



(1*Z*,4*E*)-5-10
(α:γ= 99:1)

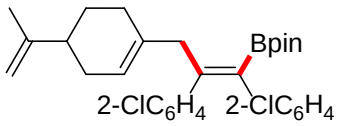
Following the general procedure **2.2** described above, the compound **5-10** was isolated in 62% yield as a pale yellow oil. The title compound decomposed partially during the isolation process. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.92–6.84 (m, 4H), 6.80–6.71 (m, 4H), 5.10 (t, *J* = 7.1 Hz, 1H), 5.00 (t, *J* = 6.7 Hz, 1H), 3.42 (d, *J* = 7.1 Hz, 2H), 1.95 (dt, *J* = 11.1,

6.0 Hz, 4H), 1.64 (s, 3H), 1.56 (s, 3H), 1.49 (s, 3H), 1.31 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.97 (d, *J* = 54.3 Hz), 160.02 (d, *J* = 53.2 Hz), 152.21, 138.08 (d, *J* = 3.5 Hz), 137.35 (d, *J* = 3.4 Hz), 136.22, 131.19, 131.02 (d, *J* = 7.7 Hz), 130.54 (d, *J* = 7.8 Hz), 124.17, 122.01, 114.47 (d, *J* = 4.2 Hz), 114.30 (d, *J* = 4.1 Hz), 83.71, 39.65, 37.32, 26.54, 25.62, 24.68, 17.61, 16.10. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{30}H_{35}BF_2O_2Na$, 501.2753; found: 501.2741.



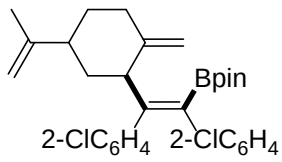
(1*Z*,4*Z*)-5-11
(α:γ= 79:21)

Following the general procedure **2.2** described above, the compound **5-11** was isolated in 60% yield as a pale yellow solid. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 119–120 °C). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.35–7.29 (m, 4H), 7.27 (d, *J* = 13.0 Hz, 3H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 2H), 7.00 (d, *J* = 8.1 Hz, 3H), 6.42 (d, *J* = 11.5 Hz, 1H), 5.58 (dt, *J* = 11.6, 6.8 Hz, 1H), 3.84 (dd, *J* = 6.8, 2.0 Hz, 2H), 1.19 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.18, 144.93, 144.81, 137.12, 130.08, 129.71, 129.39, 129.10 (q, *J* = 31.7 Hz), 128.98, 128.73 (q, *J* = 30.9 Hz), 128.68, 128.11, 126.71, 126.31 (q, *J* = 272.2 Hz), 126.07 (q, *J* = 264.6 Hz), 124.77 (q, *J* = 3.7 Hz), 124.64 (q, *J* = 3.8 Hz), 84.09, 37.53, 24.52. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{31}H_{29}BF_6O_2Na$, 581.2063; found: 581.2038.



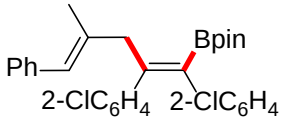
(*Z*)-5-12
(α:γ= 93:7)

Following the general procedure **2.2** described above, the compound **5-12** was isolated in 88% yield as a pale yellow oil. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 91–92 °C). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.06–7.02 (m, 1H), 7.01–6.93 (m, 5H), 6.79–6.72 (m, 2H), 5.40 (s, 1H), 4.68 (s, 1H), 4.63 (s, 1H), 3.43–3.28 (m, 2H), 2.09–1.94 (m, 4H), 1.89–1.74 (m, 2H), 1.70 (s, 3H), 1.44–1.32 (m, 1H), 1.30 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 150.94, 149.83, 143.72, 143.20, 134.58, 133.33, 129.47, 128.77 (2C), 128.69, 127.81, 127.35, 126.51, 125.69, 123.40, 108.47, 83.83, 45.77, 40.91, 30.80, 28.81, 27.79, 24.71, 24.69, 20.82. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{30}H_{35}BCl_2O_2Na$, 531.2005; found: 531.1994.



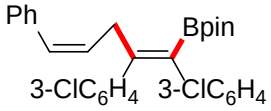
(*Z*)-4 (7%)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.09 (s), 4.98 (s), 4.85 (s), 4.79 (s).



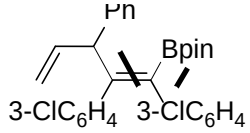
(1*Z*,4*E*)-5-13
(α:γ= 99:1)

Following the general procedure **2.2** described above, the compound **5-13** was isolated in 77% yield as a pale yellow solid. It could be further purified by recrystallization from methanol to obtain white crystals. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.30–7.24 (m, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.4 Hz, 2H), 7.07–7.03 (m, 1H), 7.03–6.96 (m, 5H), 6.82–6.75 (m, 2H), 6.23 (s, 1H), 3.59 (s, 2H), 1.84 (s, 3H), 1.31 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 150.84, 143.40, 143.08, 138.23, 135.85, 133.40, 133.33, 129.45, 128.79, 128.72, 128.67, 127.92, 127.79, 127.71, 127.35, 126.64, 125.97, 125.77, 83.91, 48.22, 24.69, 17.67. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{30}H_{31}BCl_2O_2Na$, 527.1692; found: 527.1695.



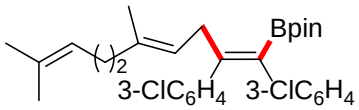
(1*Z*,4*Z*)-5-14
(α:γ= 88:12)

Following the general procedure **2.2** described above, the compound **5-14** was isolated in 73% yield as a pale yellow solid. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 107–108 °C). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 2H), 7.06 (ddd, *J* = 8.0, 2.0, 1.1 Hz, 1H), 7.03–6.97 (m, 3H), 6.96–6.93 (m, 2H), 6.76 (tt, *J* = 6.6, 1.6 Hz, 2H), 6.42 (d, *J* = 11.5 Hz, 1H), 5.59 (dt, *J* = 11.6, 6.7 Hz, 1H), 3.78 (dd, *J* = 6.7, 2.1 Hz, 2H), 1.17 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 151.61, 143.11, 142.94, 137.26, 133.69, 133.38, 129.79, 129.45, 129.37, 128.98, 128.89, 128.83, 128.73, 128.11, 127.75, 127.55, 126.86, 126.65, 125.79, 83.94, 37.55, 24.51. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{29}H_{29}BCl_2O_2Na$, 513.1536; found: 513.1555.



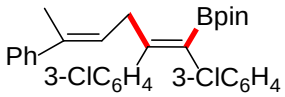
(*Z*)-4 (12%)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.04 (ddd, J = 17.1, 10.0, 8.7 Hz), 5.36 (d, J = 17.0 Hz), 5.25 (dd, J = 10.2, 1.5 Hz), 5.18 (d, J = 8.7 Hz).



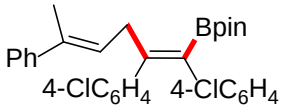
(1*Z*,4*E*)-5-15
(α:γ= 99:1)

Following the general procedure **2.2** described above, the compound **5-15** was isolated in 65% yield as a pale yellow oil. The title compound decomposed partially during the isolation process. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.07–7.03 (m, 1H), 7.02–6.92 (m, 5H), 6.79–6.72 (m, 2H), 5.08 (t, *J* = 7.1 Hz, 1H), 5.01 (t, *J* = 6.1 Hz, 1H), 3.41 (d, *J* = 7.1 Hz, 2H), 2.01–1.90 (m, 1H), 1.65 (s, 3H), 1.57 (s, 3H), 1.49 (s, 3H), 1.32 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.77, 143.87, 143.15, 136.68, 133.37, 133.24, 131.28, 129.49, 128.73, 128.70, 128.67, 127.79, 127.28, 126.46, 125.58, 124.14, 121.54, 83.85, 39.69, 37.11, 26.59, 25.64, 24.67, 17.63, 16.13. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{30}H_{37}BCl_2O_2Na$, 533.2162; found: 533.2147.



(1*Z*,4*E*)-5-16
(α:γ= 99:1)

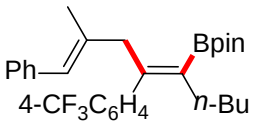
Following the general procedure **2.2** described above, the compound **5-16** was isolated in 79% yield as a pale yellow oil. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 107–108 °C). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.29–7.23 (m, 4H), 7.21–7.17 (m, 1H), 7.06–6.96 (m, 6H), 6.82–6.76 (m, 2H), 5.70 (t, *J* = 7.9 Hz, 1H), 3.64 (d, *J* = 7.2 Hz, 2H), 1.92 (s, 3H), 1.31 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.30, 143.78, 143.69, 143.07, 136.12, 133.55, 133.29, 129.51, 128.93, 128.75, 128.62, 128.09, 127.80, 127.25, 126.67, 126.65, 125.71, 125.69, 125.36, 83.92, 37.77, 24.71, 16.07. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{30}H_{31}BCl_2O_2Na$, 527.1692; found: 527.1680.



(1*Z*,4*E*)-5-17
(α:γ= 97:3)

Following the general procedure **2.2** described above, the compound **5-17** was isolated in 76% yield as a pale yellow solid. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 127–128 °C). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.26 (d, *J* = 4.3 Hz, 4H), 7.20 (q, *J* = 3.6, 2.8 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.69 (t, *J* = 7.1 Hz, 1H), 3.63 (d, *J* = 7.1 Hz, 2H), 1.91 (s, 3H), 1.31 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 151.95, 143.63, 140.45, 139.78, 135.87, 132.27, 131.29, 130.92, 130.26,

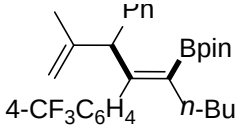
128.10, 127.98, 127.81, 126.66, 125.67, 125.56, 83.89, 37.89, 24.73, 16.05. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{30}H_{31}BCl_2O_2Na$, 527.1692; found: 527.1668.



(1*Z*,4*E*)-5-18

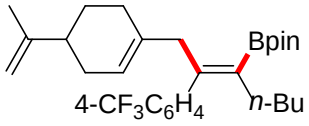
(α'α:α'γ:β'α:β'γ = 93:7:<1:<1)

Following the general procedure **2.4** described above, the compound **5-18** was isolated in 67% yield as a white solid. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 113–114 °C). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.28–7.22 (m, 2H), 7.15 (d, *J* = 8.2 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 3H), 5.98 (s, 1H), 3.45 (s, 2H), 2.03–1.94 (m, 2H), 1.79 (s, 3H), 1.33 (s, 12H), 1.30–1.23 (m, 2H), 1.19–1.13 (m, 2H), 0.76 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 148.62, 146.66, 138.41, 136.02, 128.61, 128.57 (q, *J* = 31.9 Hz), 128.45, 127.92, 127.34, 126.49 (q, *J* = 273.4 Hz), 125.85, 124.64 (q, *J* = 3.7 Hz), 83.39, 48.52, 32.49, 32.28, 24.85, 22.51, 17.46, 13.91. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{29}H_{36}BF_3O_2Na$, 507.2658; found: 507.2660.



(*Z*)-4 (7%)

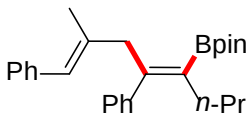
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.12 (s), 5.02 (s), 4.88 (s).



(*Z*)-5-19

(α'α:α'γ:β'α:β'γ = 96:4:<1:<1)

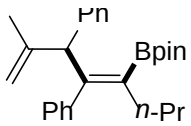
Following the general procedure **2.4** described above, the compound **5-19** was isolated in 87% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 5.17 (s, 1H), 4.68 (s, 1H), 4.64 (s, 1H), 3.27 (d, *J* = 14.0 Hz, 1H), 3.18 (d, *J* = 14.0 Hz, 1H), 2.04–1.73 (m, 7H), 1.69 (s, 3H), 1.32 (s, 12H), 1.27–1.20 (m, 4H), 1.18–1.10 (m, 2H), 0.75 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 150.00, 148.65, 146.86, 134.52, 128.89 (q, *J* = 31.6 Hz), 128.41, 127.54 (q, *J* = 272.2 Hz), 124.53 (q, *J* = 3.6 Hz), 122.99, 108.38, 83.32, 45.94, 41.01, 32.49, 32.18, 30.75, 28.51, 27.85, 24.87, 22.51, 20.82, 13.90. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{29}H_{40}BF_3O_2Na$, 511.2971; found: 511.2976.



(1*Z*,4*E*)-5-20

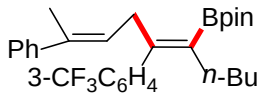
(α'α:α'γ:β'α:β'γ = 94:6:<1:<1)

Following the general procedure **2.4** described above, the compound **5-20** was isolated in 62% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.28–7.22 (m, 4H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.3 Hz, 1H), 7.04 (t, *J* = 6.8 Hz, 4H), 6.00 (s, 1H), 3.45 (s, 2H), 2.06–1.95 (m, 2H), 1.78 (s, 3H), 1.35–1.27 (m, 14H), 0.76 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 150.57, 142.93, 138.81, 136.65, 128.67, 128.09, 127.81, 127.57, 126.96, 126.07, 125.63, 83.17, 48.82, 34.67, 24.87, 23.53, 17.54, 14.08. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{27}H_{35}BO_2Na$, 425.2628; found: 425.2620.



(*Z*)-4 (6%)

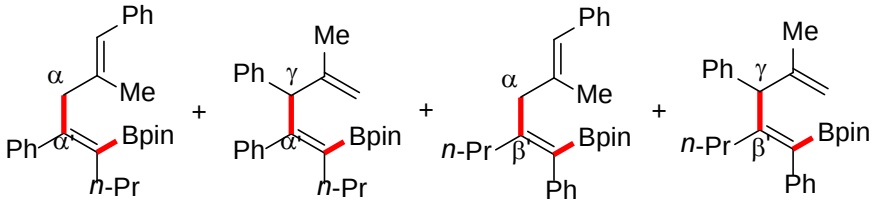
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.12 (s), 4.99 (s), 4.86 (s).



(1*Z*,4*E*)-5-21

(α'α:α'γ:β'α:β'γ = 99:1:<1:<1)

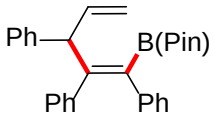
Following the general procedure **2.4** described above, the compound **5-21** was isolated in 62% yield as a pale yellow solid. It could be further purified by recrystallization from methanol to obtain white crystals (m.p. 118–119 °C). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.29–7.22 (m, 4H), 7.22–7.14 (m, 3H), 5.62 (t, *J* = 8.1 Hz, 1H), 3.49 (d, *J* = 7.5 Hz, 2H), 1.97–1.86 (m, 2H), 1.75 (s, 3H), 1.34 (s, 12H), 1.29–1.20 (m, 2H), 1.15 (dq, *J* = 14.2, 7.1 Hz, 2H), 0.75 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 149.89, 147.05, 143.92, 135.59, 128.45, 128.10, 127.43 (q, *J* = 31.9Hz), 126.55, 126.21 (q, *J* = 271.8 Hz), 125.80, 125.66, 124.81 (q, *J* = 3.7 Hz), 83.40, 37.63, 32.54, 32.07, 24.88, 22.53, 15.76, 13.90. **ESI-HRMS (m/z):** [M+Na]$^+$ calcd for $C_{29}H_{36}BF_3O_2Na$, 507.2658; found: 507.2647.



(1*Z*,4*E*)-α'α : (*Z*)-α'γ : (1*Z*,4*E*)-β'α : (*Z*)-β'γ

(57 : 11 : <1 : 5)

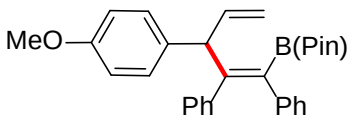
Following the general procedure **2.4** described above, the mixture was isolated in 68% yield as a colorless oil (**Scheme 3**). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.39–7.06 (m), 7.04 (t, *J* = 6.8 Hz), 6.93 (d, *J* = 6.4 Hz), 6.79–6.66 (m), 6.00 (s), 5.12 (s), 5.07 (s), 4.99 (s), 4.89 (s), 4.86 (s), 2.38 (t, *J* = 7.1 Hz), 2.37–2.33 (m), 2.03–1.97 (m), 1.78 (s), 1.74 (s), 1.32 (m), 0.76 (t, *J* = 7.4 Hz), 0.72 (t, *J* = 7.3 Hz).



(*Z*)-**4-36**

(γ:α = 99:1)

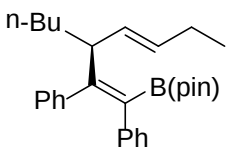
Following the general procedure **2.2** described above, the compound **4-36** was isolated in 77% yield as a pale yellow oil. It could be further purified by recrystallization from methanol to obtain colorless crystals (m.p. 87–88 °C). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.30 (dt, *J* = 15.1, 7.6 Hz, 4H), 7.24–7.17 (m, 1H), 7.05–6.87 (m, 8H), 6.54 (d, *J* = 7.0 Hz, 2H), 6.14–5.99 (m, 1H), 5.35 (d, *J* = 17.0 Hz, 1H), 5.22 (dd, *J* = 10.1, 1.6 Hz, 1H), 5.12 (d, *J* = 8.8 Hz, 1H), 1.32 (d, *J* = 4.2 Hz, 12H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 153.72, 142.06, 141.02, 139.50, 138.09, 130.15, 129.38, 128.25, 128.07, 127.32, 126.87, 126.17, 126.07, 125.27, 116.84, 83.84, 56.50, 24.77, 24.73. **ESI-HRMS (m/z):** [M+Na]$^+$ calcd for $C_{29}H_{31}BO_2Na$, 445.2315; found: 445.2331.



(*Z*)-**4-37**

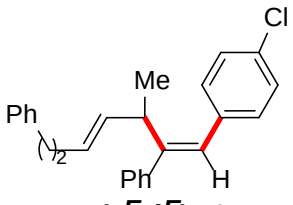
(γ:α = 99:1)

Following the general procedure **2.2** described above, the compound **4-37** was isolated in 69% yield as a pale yellow solid. It could be further purified by recrystallization from methanol to obtain colorless crystals (m.p. 85–86 °C). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.22 (d, *J* = 8.4 Hz, 2H), 7.04–6.89 (m, 8H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.55 (d, *J* = 7.5 Hz, 2H), 6.03 (dt, *J* = 18.7, 9.4 Hz, 1H), 5.33 (d, *J* = 17.0 Hz, 1H), 5.19 (d, *J* = 10.1 Hz, 1H), 5.03 (d, *J* = 8.7 Hz, 1H), 3.81 (s, 3H), 1.33 (d, *J* = 3.8 Hz, 12H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 157.96, 153.85, 141.01, 139.51, 138.35, 134.10, 130.17, 129.36, 129.19, 127.30, 126.85, 126.03, 125.23, 116.59, 113.43, 83.80, 55.82, 55.17, 24.75, 24.72. **ESI-HRMS (m/z):** [M+Na]$^+$ calcd for $C_{30}H_{33}BO_3Na$, 475.2421; found: 475.2417.



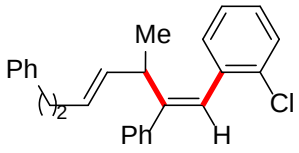
(+)-(1*Z*,4*E*)-**4-19**

Following the general procedure **2.2** described above, the compound (+)-(1*Z*,4*E*)-**4-19** was isolated in 88% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.10 – 7.03 (m, 3H), 7.02 – 6.96 (m, 2H), 6.95 – 6.89 (m, 5H), 5.60 (dt, *J* = 15.1, 6.2 Hz, 1H), 5.33 (dd, *J* = 15.4, 7.8 Hz, 1H), 3.46 (q, *J* = 6.8 Hz, 1H), 2.06 (p, *J* = 7.3 Hz, 2H), 1.52 – 1.42 (m, 1H), 1.39 – 1.23 (m, 17H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 155.40, 141.08, 139.85, 132.34, 131.47, 130.02, 129.32, 127.20, 126.90, 125.83, 124.99, 83.58, 50.53, 33.07, 29.71, 25.67, 24.79, 24.73, 22.63, 14.15, 13.84. **ESI-HRMS (m/z):** $[M+Na]^+$ calcd for $C_{29}H_{39}BO_2Na$, 453.2941; found: 453.2944. $[\alpha]^{19.6}_D$ (deg $cm^3g^{-1}dm^{-1}$) = +55.0 (c = 0.976, CH_2Cl_2). The ee value of (*S*)-(1*Z*,4*E*)-**4kc** was determined by HPLC analysis (CHIRALPAK® AS-RH DAICEL CHIRAL TECHNOLOGIES CO., LTD., 20% H_2O/CH_3CN, 0.5 mL/min, S isomer t_R = 17.18 min, R isomer t_R = 19.15 min, UV detection at 210 nm, 40 °C).



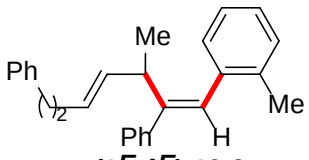
(1*E*,4*E*)-**10-1**

Following the general procedure **5 (Method I)** described above, the compound **10-1** was isolated in 68% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.33–7.22 (m, 11H), 7.21–7.13 (m, 3H), 6.47 (s, 1H), 5.60 (dd, *J* = 15.5, 5.1 Hz, 1H), 5.51 (ddt, *J* = 15.4, 6.5, 1.4 Hz, 1H), 3.74 (p, *J* = 5.7 Hz, 1H), 2.69 (t, *J* = 7.7 Hz, 2H), 2.39 (q, *J* = 7.3 Hz, 2H), 1.03 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 147.04, 141.87, 184.81, 136.12, 134.30, 132.32, 130.10, 129.33, 128.48, 128.45, 128.33, 128.26, 127.94, 127.65, 126.86, 125.76, 37.12, 35.83, 34.34, 19.02. **APCI-HRMS (m/z):** $[M+H]^+$ calcd for $C_{26}H_{26}Cl$, 373.1723; found: 373.1720.



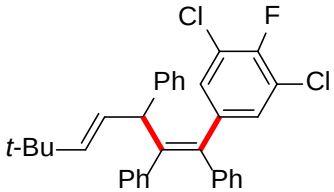
(1*E*,4*E*)-**10-2**

Following the general procedure **5 (Method I)** described above, the compound **10-2** was isolated in 81% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.42 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.38–7.35 (m, 3H), 7.31–7.15 (m, 10H), 6.53 (s, 1H), 5.58 (dd, *J* = 15.5, 5.3 Hz, 1H), 5.47 (dtd, *J* = 15.3, 6.6, 1.6 Hz, 1H), 3.57 (p, *J* = 5.6 Hz, 1H), 2.72–2.64 (m, 2H), 2.40–2.33 (m, 2H), 1.02 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 147.53, 141.88, 141.62, 136.27, 134.37, 134.03, 130.45, 129.31, 129.10, 128.61, 128.46, 128.25, 128.09, 127.65, 126.94, 126.40, 126.28, 125.73, 37.56, 35.84, 34.39, 18.76. **APCI-HRMS (m/z):** $[M+H]^+$ calcd for $C_{26}H_{26}Cl$, 373.1723; found: 373.1712.



(1*E*,4*E*)-**10-3**

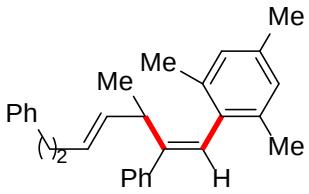
Following the general procedure **5 (Method I)** described above, the compound **10-3** was isolated in 87% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.35–7.13 (m, 14H), 6.46 (s, 1H), 5.54 (dd, *J* = 15.5, 5.7 Hz, 1H), 5.41 (ddt, *J* = 15.3, 6.6, 1.5 Hz, 1H), 3.57 (p, *J* = 5.9 Hz, 1H), 2.69–2.63 (m, 2H), 2.34 (q, *J* = 7.0 Hz, 2H), 2.30 (s, 3H), 1.01 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 146.53, 142.06, 141.93, 137.25, 136.50, 134.62, 129.71, 128.92, 128.66 (3C), 128.45, 128.26, 128.23, 127.61, 126.89, 126.73, 125.71, 125.43, 37.51, 35.89, 34.41, 20.13, 18.87. **APCI-HRMS (m/z):** $[M+H]^+$ calcd for $C_{27}H_{29}$, 353.2269; found: 353.2261.



(1*E*,4*E*)-**10-4**

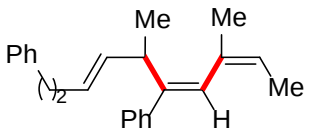
Following the general procedure **5 (Method I)** described above, the compound **10-4** was isolated in 95% yield as a white solid. It could be further purified by recrystallization from methanol to obtain colorless crystals (m.p. 143–144 °C). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.34 (d, *J* = 6.3

Hz, 2H), 7.30–7.24 (m, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.08 (d, *J* = 7.7 Hz, 2H), 7.05–6.95 (m, 6H), 6.88 (dd, *J* = 7.8, 1.7 Hz, 2H), 6.65–6.58 (m, 2H), 5.63 (d, *J* = 15.2 Hz, 1H), 5.47 (dd, *J* = 15.7, 8.8 Hz, 1H), 4.74 (d, *J* = 8.8 Hz, 1H), 1.06 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 153.13 (d, *J* = 250.4 Hz), 144.45, 144.36, 142.51, 141.21, 139.79 (d, *J* = 5.3 Hz), 139.10, 137.61, 130.78, 130.33, 130.25, 128.17, 128.06, 127.60, 127.12, 126.45 (d, *J* = 4.9 Hz), 126.34, 123.69, 122.12 (d, *J* = 17.7 Hz), 51.97, 33.32, 29.63. **APCI-HRMS (m/z):** $[M+H]^+$ calcd for $C_{33}H_{30}Cl_2F$, 515.6378; found: 515.6373.



(1*E*,4*E*)-10-5

Following the general procedure **5 (Method I)** described above, the compound **10-5** was isolated in 93% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.33–7.23 (m, 7H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 2H), 6.90 (s, 2H), 6.22 (s, 1H), 5.43 (dd, *J* = 15.4, 6.6 Hz, 1H), 5.28 (dt, *J* = 14.2, 6.6 Hz, 1H), 3.16 (q, *J* = 6.8 Hz, 1H), 2.62 (t, *J* = 7.7 Hz, 2H), 2.28 (d, *J* = 19.3 Hz, 8H), 2.23 (s, 3H), 0.97 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 146.84, 142.00, 141.95, 135.97, 134.00, 133.98, 129.47, 128.64, 128.42, 128.40, 128.22, 127.94, 127.88, 127.60, 127.06, 126.68, 125.69, 38.49, 35.83, 34.35, 21.02, 20.61, 20.37, 18.38. **APCI-HRMS (m/z):** $[M+H]^+$ calcd for $C_{29}H_{33}$, 381.2582; found: 381.2572.



(2*Z*,4*E*,7*E*)-10-6

Following the general procedure **5 (Method I)** described above, the compound **10-6** was isolated in 91% yield as a colorless oil. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.30–7.21 (m, 7H), 7.21–7.14 (m, 3H), 5.79 (s, 1H), 5.54 (dd, *J* = 15.5, 5.7 Hz, 1H), 5.51–5.43 (m, 1H), 5.40 (q, *J* = 6.7 Hz, 1H), 3.58–3.49 (m, 1H), 2.67 (t, *J* = 7.4 Hz, 2H), 2.34 (q, *J* = 6.6 Hz, 2H), 1.82 (s, 3H), 1.62 (d, *J* = 6.7 Hz, 3H), 1.03 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 145.50, 142.06, 141.99, 134.82, 133.57, 128.58, 128.45, 128.29, 128.22, 128.18, 127.47, 126.48, 125.69, 121.68, 37.85, 35.96, 34.46, 24.27, 18.43, 15.06. **APCI-HRMS (m/z):** $[M+H]^+$ calcd for $C_{24}H_{29}$, 317.2269; found: 317.2263.

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