Supplementary Information 1

Multi-task Rhodium-Catalyzed Remote C(sp^3)–H Functionalization Reactions of Acyclic Dienes to Yield Benzene-fused Heterocycles

Yuta Sato[a], Momoko Nagafuchi[a], Masaharu Takatsuki[a], Tsuyoshi Matsuzaki[b], Takeyuki Suzuki[b], Makoto Sako[a], Mitsuhiro Arisawa*[a]

[a] Y. Sato, M. Nagafuchi, M. Takatsuki, M. Arisawa

Graduate Schoolof Pharmaceutical Sciences, Osaka University, 1-6, Yamada-oka, Suita, Osaka 565-0871(Japan)

[b] T. Matsuzaki, T. Suzuki

Comprehensive Analysis Center, SANKEN, Osaka University, 8-1, Mihogaoka, Ibaraki, Osaka 567-0047

Contents

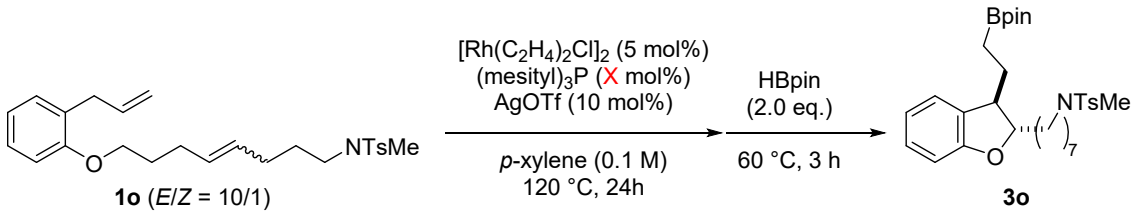
General information

All reactions involving air-sensitive materials were carried out in pre-dried glassware under a nitrogen atmosphere working in a nitrogen-filled glove box (MBRAUN Co., Ltd., LABstar). All solvents were reagent grade. Toluene (anhydrous, ≥99.0%), *p*-xylene (anhydrous, ≥98.0%), ethyl acetate (anhydrous, ≥99.0%) and dichloromethane (anhydrous, ≥98.0%) were purchased from Nacalai tesque. THF (anhydrous, ≥99.5%, Stabilizer Free) was purchased from KANTO CHEMICAL Co., Inc. Solvents were dehydrated by MS3A, MS4A, or MS5A.

^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra were recorded on JEOL JNM-ECS 400, JEOL ECS 300, or JEOL JNM-LA 500 spectrometers. ^{1}H-NMR spectra were recorded using an internal deuterium lock at ambient temperature on a JEOL 500, 400 or 300 MHz spectrometer. Internal reference of δ H 7.26 was used for $CDCl_3$, δ H 3.30 for CD_3OD. Data are presented as follows: chemical shift (in ppm on the δ scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (*J*/Hz) and integration. Resonances that are either partially or fully obscured are denoted obscured (obs.). ^{13}C-NMR spectra were recorded at 125, 100 or 75 MHz using $CDCl_3$ (δ C 77.0) or CD_3OD (δ C 49.0) as the internal reference. Column chromatography was performed with silica gel 60N (spherical, neutral, 63-210 μm, Kanto Chemical Co., Inc.), flash silica gel 60 (spherical, neutral, 40-50 μm, Kanto Chemical Co., Inc.) unless otherwise noted. ESI-MS and APCI-MS analysis were performed on an Orbitrap XL (THERMO). Microwave heating reactions were carried out using a microwave generator (Anton Paar, Monowave 300). All calculations were carried with the Gaussian 16 program package. Single point energies were calculated at the RB3PW91-D3BJ level using the SDD basis set for Rh and the 6-311++G** basis set for H, C, O and P in *p*-xylene solvent (i-pcm model). Dispersion correction with Becke−Johnson damping (with EmpiricalDispersion = GD3BJ keyword) was also used to calculate the cycloisomerization step, and the results were consistent with those calculated with zero-damping.

Optimization of reaction conditions

Optimization of ligand loading

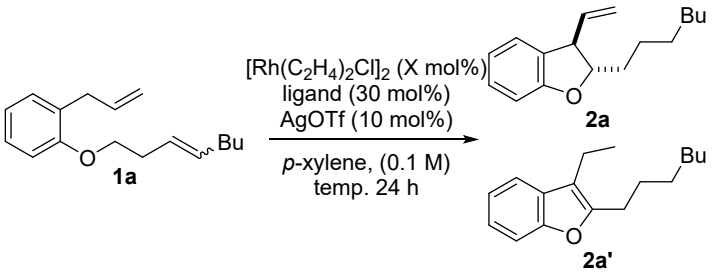


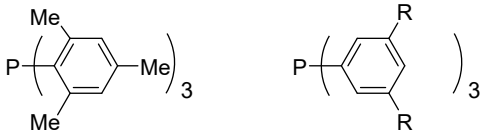
1o (*E*/*Z* = 10/1) **3o**

entry	X	yield (%)
1	10	12[a]
2	20	37[a]
3	30	50[b]

a NMR yield. b) isolated yield.

Results of studies with other ligands





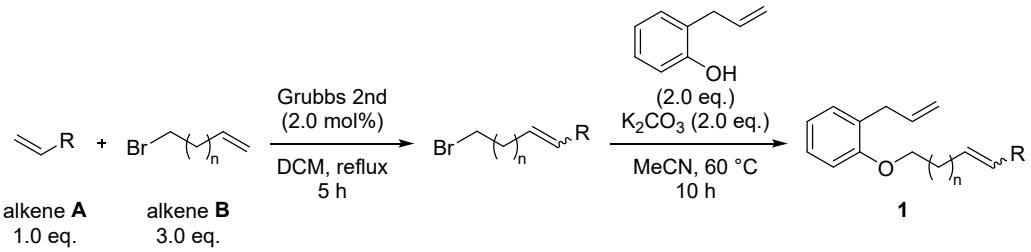
L3 **LS1** : R = Me
LS2 : R = *t*-Bu

entry	X	ligand	**2a** (%)[a]	**2a'** (%)[a]
1	5	**L3**	82	17
2	4	**L3**	53	3
3	3	**L3**	73	9
4	5	**LS1**	0	0
5	5	**LS2**	0	0

a) NMR yield (1,3,5-trimethoxybenzene was used as an internal standard.)

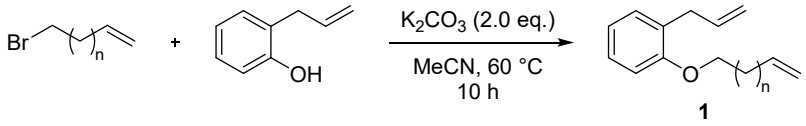
Preparation of 1a-1ag

Typical procedure A



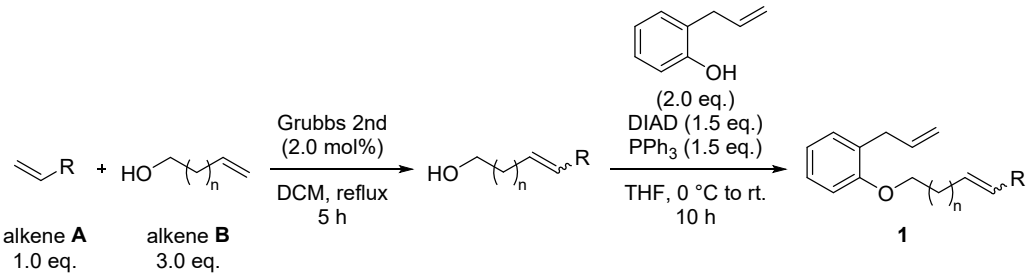
To a round-bottom flask, alkene **A** (1.0 eq.), alkene **B** (3.0 eq.) and DCM (0.5 M) were added. Then, Grubbs 2nd (2 mol%) was added to the mixture and stirred for 5 h with heating under reflux. After removal of the solvent, the residue was purified by column chromatography on silica gel to afford the corresponding alkenyl bromide.

To a round-bottom flask containing the alkenyl bromide and K_2CO_3 (2.0 eq.) in CH_3CN (0.5 M) was added 2-allylphenol (2.0 eq.). The reaction mixture was stirred at 60 °C for 10 h. The mixture was filtered through a glass filter with AcOEt, and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel using *n*-hexane/ AcOEt as an eluent to afford products.



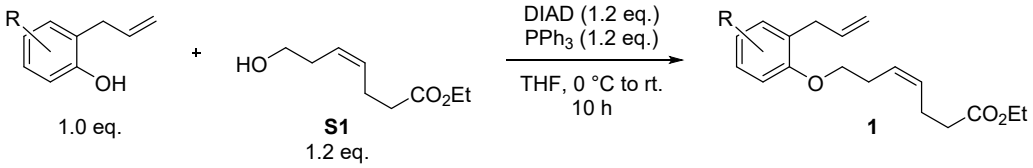
Typical procedure B

To a round-bottom flask containing an alkenyl bromide and K_2CO_3 (2.0 eq.) in CH_3CN (0.5 M) was added 2-allylphenol (2.0 eq.). The reaction mixture was stirred at 60 °C for 10 h. The mixture was filtered through a glass filter with AcOEt, and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel using *n*-hexane/ AcOEt as an eluent to afford products.



Typical procedure C

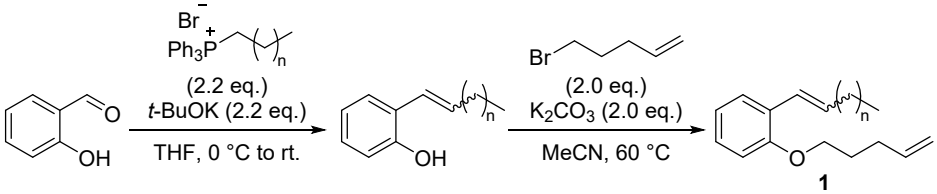
To a round-bottom flask, alkene **A** (1.0 eq.), alkene **B** (3.0 eq.) and DCM (0.5 M) were added. Then, Grubbs 2nd (2 mol%) was added to the reaction mixture and stirred for 5 h with heating under reflux. After removal of the solvent, the residue was purified by column chromatography on silica gel to afford the corresponding alkenyl alcohol. To a round-bottom flask containing the alkenyl alcohol (1.0 eq.), 2-allylphenol (2.0 eq.), PPh_3 (1.5 eq.) and THF (4.7 mL), DIAD (1.5 eq.) were added and stirred for 10 h, at room temperature. The reaction mixture was concentrated *in vacuo* and obtained residue was purified by column chromatography on silica gel (*n*-hexane/ AcOEt) to afford products.



Typical procedure D

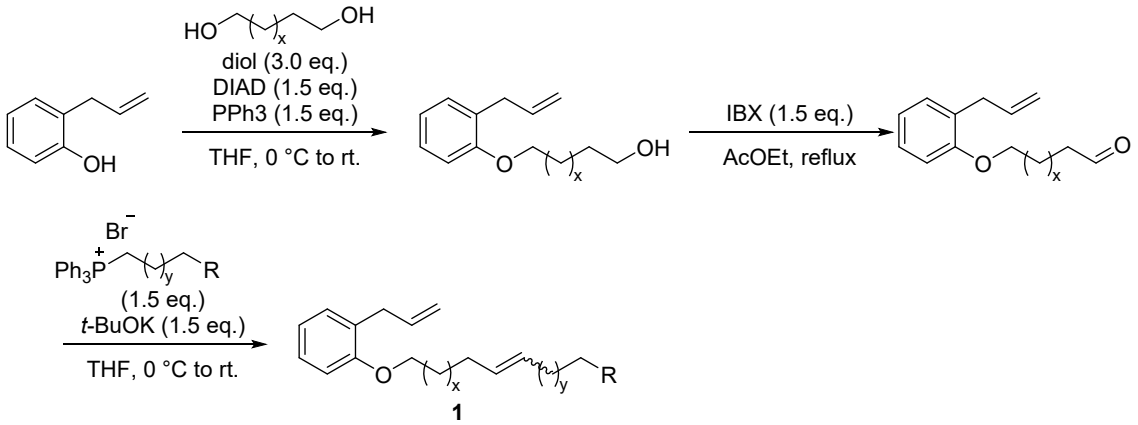
To a round-bottom flask containing a 2-allylphenol derivative (prepared according to the known literature, [1,2] 1.0 eq.), **S1** (1.2 eq. prepared by known method[3]), PPh_3 (1.2 eq.) and THF (0.5 M), DIAD (1.2 eq.) was added and stirred for 10 h, at room temperature. The reaction mixture was concentrated *in vacuo* and obtained residue was purified by column chromatography on silica gel (*n*-hexane/ AcOEt) to afford products.

Typical procedure E



To a round-bottom flask containing a phosphonium salt (2.2 eq.) in THF (0.4 M), *t*-BuOK (2.2 eq.) was added and stirred for 1 h at room temperature. Then, this suspension cooled to 0 °C and salicylaldehyde (1.0 eq.) in THF (1M) was added to the mixture and stirred at room temperature for 6 h. Afterwards, sat. NH_4Cl was added to quench the reaction. The organic compounds were extracted with AcOEt. The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4. After evaporation, the residue was purified by column chromatography on silica gel (*n*-hexane/ AcOEt = 10/1) to afford a 2-(vinyl)phenol derivative. Next, to a round-bottom flask containing the 2-(vinyl)phenol derivative and K_2CO_3 in MeCN (0.5 M), 5-bromo-1-pentene (2.0 eq.) was added and stirred at 60 °C for 10 h. The mixture was filtered through the glass filter with AcOEt and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel using *n*-hexane/ AcOEt as an eluent to afford products.

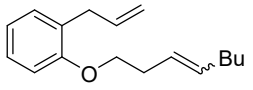
Typical procedure F



1

To a round-bottom flask containing 2-allyphenol (1.0 eq.), a corresponding diol (3.0 eq.) and PPh_3 (1.5 eq.) in THF (0.3 M) was added DIAD (1.5 eq.) at 0 °C and stirred for 10 h, at room temperture. The reaction mixture was concentrated *in vacuo* and obtained residue was purified by column chromatography on silica gel (*n*-hexane/ AcOEt) to afford corresponding alcohol. To a round-bottom flask containing the alcohol in AcOEt (0.1 M), IBX (1.6 g, 5.6 mmol) was added. The reaction mixture was stirred for 5 h with heating under reflux. The mixture was filtered through a glass filter with AcOEt, and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel using *n*-hexane/ AcOEt = 6/1 as an eluent to afford corresponding aldehyde. To a suspension of a corresponding phosphonium salt (1.5 eq.) in THF (0.2 M), *t*-BuOK (1.5 eq.)) was slowly added and stirred for 30 min. Then, reaction mixture was cooled to 0 °C and the solution of the aldehyde (1 M in THF) was added to the mixture and stirred for 3 h at room temperature. Afterwards, sat. NH_4Cl was added to quench the reaction and extracted with AcOEt. The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4. After evaporation, the residue was purified by column chromatography on silica gel (*n*-hexane/ AcOEt = 20/1) to afford products.

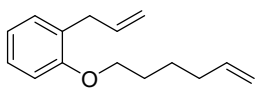
Compound **1a**



Using Alkene **A** = 1-hexene, **B** = 4-bromo-1-butene. Following the typical procedure A 1-Hexene (300 mg, 3.7 mmol) was converted to **1a** (*E*/*Z* = 9/1, 560 mg, 64%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30/1). A colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$, *E*/*Z* mixture) δ: 7.18-7.13 (m, 2H), 6.88 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.04-5.95 (m, 1H), 5.60-5.48 (m, 1.8H, *E* isomer), 5.47-5.40 (m, 0.2H *Z* isomer), 5.08-5.01 (m, 2H), 3.97 (t, *J* = 6.6 Hz, 2H), 3.39 (d, *J* = 6.9 Hz, 2H), 2.55 (q, *J* = 6.7 Hz, 0.2H, *Z*

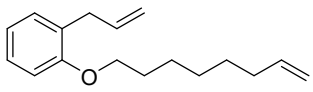
isomer), 2.48 (q, J = 6.5 Hz, 1.8H, *E* isomer), 2.09 (q, *J* = 6.7 Hz, 0.2H, *Z* isomer), 2.01 (q, J = 6.4 Hz, 1.8H, *E* isomer), 1.37-1.28 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$, *E*/*Z* mixture); 156.6, 137.1, 133.2, 132.5, 129.7, 128.8, 127.2, 125.7, 125.0, 120.3, 115.2, 111.2, 67.8, 67.6, 34.5, 32.7, 32.3, 31.8, 31.6, 27.6, 27.1, 22.3, 22.2, 14.0; HRMS (APCI) calcd for $C_{17}H_{25}O$ $(M+H)^+$: 245.1905, found: 245.1894.

Compound **1b**



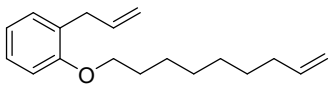
Following the typical procedure B, 6-bromo-1-hexene (400 mg, 2.5 mmol) was converted to **1b** (480 mg, 90%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.20 - 7.09 (m, 2H), 6.88 (dd, *J* = 7.3 Hz, 7.3 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.06-5.92 (m, 1H), 5.90-5.77 (m, 1H), 5.10-4.94 (m, 4H), 3.97 (t, *J* = 6.4 Hz, 2H), 3.39 (d, *J* = 6.9 Hz, 2H), 2.20-2.06 (m, 2H), 1.87-1.76 (m, 2H), 1.65-1.54 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ 156.7, 138.6, 137.1, 129.7, 128.8, 127.2, 120.3, 115.3, 114.7, 111.1, 67.6, 34.4, 33.4, 28.8, 25.4; HRMS (APCI) calcd for $C_{15}H_{21}O$ $(M+H)^+$: 217.1592, found: 217.1586.

Compound **1c**



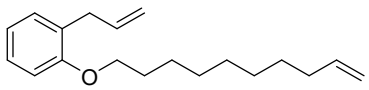
Following the typical procedure B, 8-bromo-1-octene (400 mg, 2.1 mmol) was converted to **1c** (487 mg, 95%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30/1). A colorless oil.; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.19-7.12 (m, 2H), 6.90-6.86 (m, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.04-5.94 (m, 1H), 5.87-5.77 (m, 1H), 5.09-4.92 (m, 4H), 3.95 (t, *J* = 6.4 Hz, 2H), 3.39 (d, *J* = 6.9 Hz, 2H), 2.09-2.04 (m, 2H), 1.83-1.76 (m, 2H), 1.52-1.33 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ 156.7, 139.1, 137.1, 129.7, 128.8, 127.2, 120.2, 115.2, 114.3, 111.1, 67.8, 34.5, 33.7, 29.3, 28.8 (overlapped), 26.0; HRMS (APCI) calcd for $C_{17}H_{25}$ $(M+H)^+$: 245.1905, found: 245.1899.

Compound **1d**



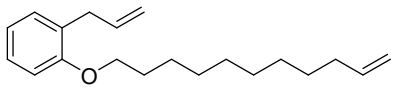
Following the typical procedure B, 9-bromo-1-nonene (400 mg, 2.0 mmol) was converted to **1d** (482 mg, 96%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.19-7.12 (m, 2H), 6.90-6.86 (m, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.04-5.94 (m, 1H), 5.87-5.77 (m, 1H), 5.09-4.92 (m, 4H), 3.95 (t, *J* = 6.4 Hz, 2H), 3.39 (d, *J* = 6.9 Hz, 2H), 2.09-2.04 (m, 2H), 1.83-1.76 (m, 2H), 1.52-1.33 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ 156.7, 139.1, 137.1, 129.6, 128.7, 127.2, 120.2, 115.2, 114.2, 111.1, 67.8, 34.5, 33.8, 29.3, 29.2, 29.0, 28.8, 26.1; HRMS (APCI) calcd for $C_{18}H_{27}O$ $(M+H)^+$: 259.2062, found: 259.2054 .

Compound **1e**



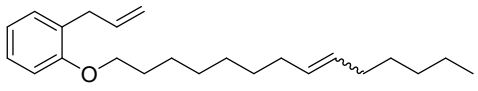
Following the typical procedure B, 10-bromo-1-decene (400 mg, 1.8 mmol) was converted to **1e** (436 mg, 88%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.19-7.13 (m, 2H), 6.87 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.04-5.94 (m, 1H), 5.87-5.76 (m, 1H), 5.09-4.92 (m, 4H), 3.95 (t, *J* = 6.4 Hz, 2H), 3.39 (d, *J* = 6.9 Hz, 2H), 2.07-2.02 (m, 2H), 1.82-1.75 (m, 2H), 1.51-1.26 (m, 10H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ 156.7, 139.2, 137.1, 129.7, 128.8, 127.2, 120.2, 115.2, 114.1, 111.1, 67.9, 34.5, 33.8, 29.4, 29.35, 29.31, 29.1, 28.9, 26.1; HRMS (APCI) calcd for $C_{19}H_{29}O$ $(M+H)^+$: 273.2218, found: 273.2210.

Compound **1f**



Following the typical procedure B, 11-bromo-1-undecene (400 mg, 1.8 mmol) was converted to **1f** (383 mg, 78%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.20-7.14 (m, 2H), 6.89 (dd, *J* = 7.3, 7.3, 0.9 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.06-5.96 (m, 1H), 5.88-5.78 (m, 1H), 5.10-4.92 (m, 4H), 3.96 (t, *J* = 6.4 Hz, 2H), 3.40 (d, *J* = 6.4 Hz, 2H), 2.05 (q, *J* = 7.0 Hz, 2H), 1.83-1.76 (m, 2H), 1.52-1.45 (m, 2H), 1.43-1.31 (m, 10H); ^{13}C-NMR (125 MHz, $CDCl_3$); δ 156.7, 139.2, 137.1, 129.6, 128.7, 127.2, 120.2, 115.2, 114.1, 111.1, 67.8, 34.5, 33.8, 29.5, 29.4, 29.3 (overlapped), 29.1, 28.9, 26.1; HRMS (APCI) calcd for $C_{20}H_{31}O$ $(M+H)^+$: 287.2375, found: 287.2361.

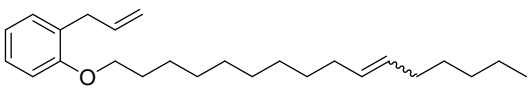
Compound **1g**



Using 1,8-octanediol and hexyltriphenylphosphonium bromide. Following the typical procedure F, 2-allylphenol, (500 mg, 3.7 mmol) was converted to **1g** (980 mg, 51%, *E*/*Z* = 1/5.6) after column chromatography on silica gel (*n*-hexane/AcOEt = 30/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, *E*/*Z* mixture) δ: 7.19-7.13 (m, 2H), 6.88 (ddd, *J* = 7.3, 7.3, 0.9 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.04-5.94 (m, 1H), 5.40-5.38 (m, 0.3H, *E* isomer), 5.37-5.31 (m, 1.7H, *Z* isomer), 5.09-5.00 (m, 2H), 4.02-3.94 (m, 2H), 3.39 (d, J = 6.4 Hz, 2H), 2.03-1.97 (m, 4H), 1.82-1.75 (m, 2H), 1.49-1.44 (m, 2H), 1.40-1.23 (m, 12H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, *E*/*Z* mixture); 156.8, 137.2, 130.6, 130.3, 130.1, 129.9, 129.8, 128.9, 127.3, 120.3, 115.3, 111.2, 68.0, 34.6, 32.7, 31.6, 29.8, 29.7, 29.5, 29.4, 29.4, 29.3, 29.2, 27.3, 26.2, 22.7, 14.2;

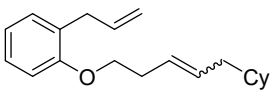
HRMS (APCI) calcd for $C_{23}H_{37}O$ $(M+H)^+$: 329.2844, found: 329.2837.

Compound **1h**



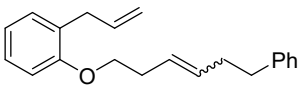
Using 1,10-decaneediol and hexyltriphenylphosphonium bromide. Following the typical procedure F, 2-allylphenol, (500 mg, 3.7 mmol) was converted to **1h** (990 mg, 75%, *E*/*Z* = 1/6.7) after column chromatography on silica gel (*n*-hexane/AcOEt = 30/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, *E*/*Z* mixture) δ: 7.18-7.12 (m, 2H), 6.87 (dd, *J* = 10.1 Hz, 10.1 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.04-5.94 (m, 1H), 5.40-5.38 (m, 0.26H、*E* isomer), 5.36-5.31 (m, 1.74H, *Z* isomer), 5.09-5.00 (m, 2H), 3.95 (t, *J* = 6.4 Hz, 2H), 3.39 (d, *J* = 6.9 Hz, 2H), 2.04-1.96 (m, 4H), 1.82-1.75 (m, 2H), 1.51-1.43 (m, 2H), 1.35-1.25 (m, 16H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, *E*/*Z* mixture); 156.7, 137.1, 129.9, 129.9, 129.6, 128.8, 127.2, 120.2, 115.2, 111.1, 67.9, 34.5, 32.6, 31.5, 31.4, 29.8, 29.6, 29.5, 29.4, 29.4, 29.3, 29.1, 27.2, 26.2, 22.6, 14.1; HRMS (APCI) calcd for $C_{25}H_{41}O$ $(M+H)^+$: 357.3157, found: 357.3149.

Compound **1i**



Using alkene **A** = allylcyclohexane, **B** = 4-bromo-1-butene. Following the typical procedure A, allylcyclohexane (1.95 g, 15.7 mmol) was converted to **1i** (820 mg, 18%, *E*/*Z* = 4.7/1) after column chromatography on silica gel (*n*-hexane/AcOEt = 30/1). A colorless oil; ^{1} H-NMR (400 MHz, $CDCl_3$, *E*/*Z* mixture) δ: 7.18-7.12 (m, 2H), 6.87 (dd, *J* = 10.2 Hz, 10.2 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 6.04-5.93 (m, 1H), 5.58-5.48 (m, 1.65H, *E* isomer), 5.46-5.41 (m, 0.35H, *Z* isomer), 5.08-5.00 (m, 2H), 3.98-3.94 (m, 2H), 3.38 (d, *J* = 6.9 Hz, 2H), 2.55-2.45 (m, 2H), 1.97 (t, *J* = 6.4 Hz, 0.35H, *Z* iomer), 1.90 (t, *J* = 6.6 Hz, 1.65H, *E* isomer), 1.70-1.61 (m, 5H), 1.32-1.06 (m, 4H), 0.95-0.81 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, *E*/*Z* mixture); 156.7, 137.2, 131.8, 131.1, 129.8, 129.0, 127.3, 126.9, 125.7, 120.5, 120.4, 115.4, 111.4, 67.9, 67.7, 40.8, 38.3, 38.1, 35.3, 34.5, 33.3, 33.2, 32.9, 27.7, 26.7, 26.5; HRMS (APCI) calcd for $C_{20}H_{29}O$ $(M+H)^+$: 285.2218, found: 285.2211.

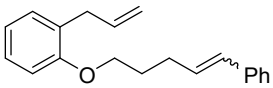
Compound **1j**



Using 1,3-propanediol and triphenyl(3-phenylpropyl)phosphonium bromide. Following the typical procedure F, 2-allylphenol (1.0 g, 7.45 mmol) was converted to **1j** (823 mg, 38%, *E*/*Z* = 1/4) after column chromatography on silica gel (*n*-hexane/AcOEt = 30/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, *E*/*Z*

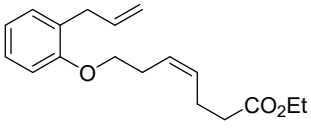
mixture) δ: 7.29-7.26 (m, 2H), 7.20-7.12 (m, 5H), 6.90-6.86 (m, 1H), 6.83-6.77 (m, 1H), 6.04-5.93 (m, 1H), 5.65-5.57 (m, 0.4H, *E* isomer), 5.56-5.47 (m, 1.6H, *Z* isomer), 5.08-5.00 (m, 2H), 3.95 (t, *J* = 6.6 Hz, 0.4 H, *E* isomer), 3.86 (t, *J* = 6.6 Hz, 1.6H, *Z* isomer), 3.42-3.37 (m, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.50-2.29 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$, *E*/*Z* mixture); δ 156.6, 142.0, 137.2, 132.2, 131.2, 129.8, 128.9, 128.6, 128.4, 127.3, 126.7, 126.1, 125.9, 125.9, 120.5, 115.4, 111.4, 67.8, 67.5, 36.0, 35.9, 34.6, 34.6, 34.5, 32.8, 29.4, 27.7; HRMS (APCI) calcd for $C_{21}H_{25}O$ $(M+H)^+$: 293.1905, found: 293.1891.

Compound **1k**



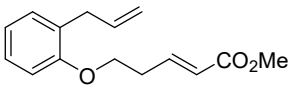
Using alkene **A** = stylene, **B** = 5-bromo-1-butene. Following the typical procedure C, stylene (700 mg, 6.72 mmol) was converted to **1k** (802 mg, 43%, *E*/*Z* = 4.6/1) after column chromatography on silica gel (*n*-hexane/AcOEt = 30/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, *E*/*Z* mixture) δ: 7.72-7.62 (m, 4H), 7.58-7.49 (m, 3H), 7.15-7.29 (2H), 6.88 (d, *J* = 12 Hz, 0.18H, *Z* isomer), 6.78 (d, *J* = 16 Hz, 0.82H, *E* isomer), 6.71-6.58 (m, 1H), 6.41-6.30 (m, 1H), 5.45-5.34 (m, 2H), 4.44 (t, *J* = 6.5 Hz, 0.36H, *Z* isomer), 4.37 (t, *J* = 6.2 Hz, 1.64H, *E* isomer), 3.77 (d, *J* = 6.6 Hz, 2H), 3.09-3.04 (m, 0.36H, *Z* isomer), 2.81-2.75 (m, 1.64H, *E* isomer), 2.37-2.30 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, *E*/*Z* mixture); δ 156.6, 156.0, 137.6, 137.4, 137.1, 132.1, 130.5, 129.8, 129.7, 128.7, 128.5, 127.3, 127.1, 126.9, 126.4, 126.0, 125.9, 120.5, 120.4, 115.3, 115.3, 111.2, 111.1, 77.3, 77.0, 76.7, 75.2, 67.4, 67.0, 34.5, 33.1, 29.6, 29.1; HRMS (APCI) calcd for $C_{20}H_{223}O$ $(M+H)^+$: 279.1749, found: 279.1741.

Compound **1l**



Following the typical procedure D, 2-allylphenol (512 mg, 3.82 mmol) was converted to **1l** (823 mg, 75%) after column chromatography on silica gel (*n*-hexane/AcOEt = 15/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, only *Z* isomer) δ: 7.19-7.12 (m, 2H), 6.88 (dd, *J* = 7.3 Hz, 7.3 Hz 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.04-5.94 (m, 1H), 5.59-5.46 (m, 2H), 5.08-5.00 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.97 (t, *J* = 6.6 Hz, 2H), 3.38 (d, *J* = 6.9 Hz, 2H), 2.58 (dt, *J* = 6.4 Hz, 6.4 Hz, 2H), 2.45-2.35 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, only *Z* isomer); δ 173.1, 156.5, 137.0, 129.9, 129.7, 128.8, 127.2, 126.8, 120.5, 115.3, 111.2, 67.4, 60.3, 34.4, 34.2, 27.5, 22.9, 14.2; HRMS (APCI) calcd for $C_{18}H_{25}O_3$ $(M+H)^+$: 289.1804, found: 289.1796.

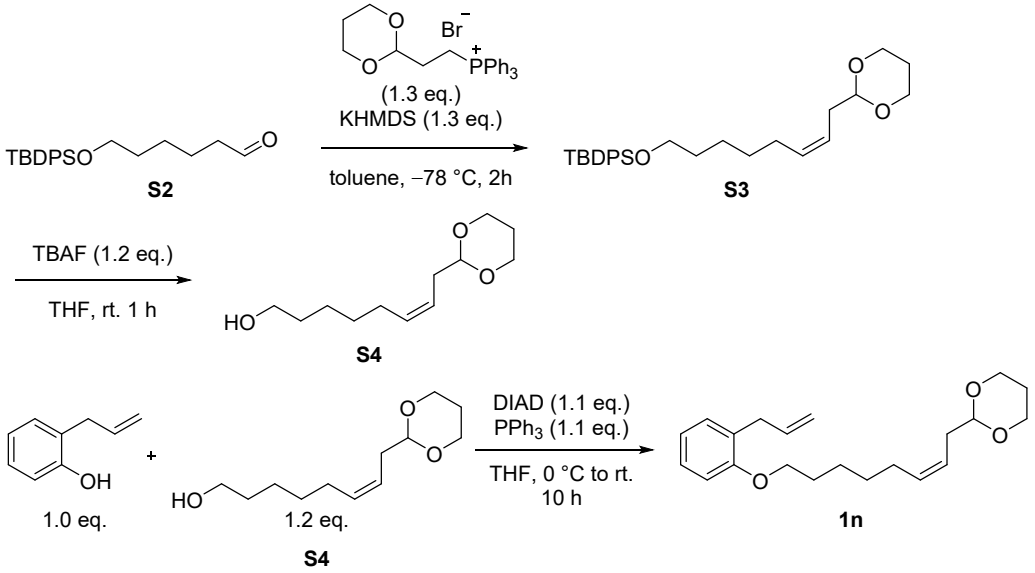
Compound **1m**



Using alkene **A** = methyl acrylate, **B** = 4-bromo-1-butene Following the typical procedure D, methyl acrylate (500 mg, 5.81 mmol) was converted to

1m (947 g, 66%, only *E* isomer) after column chromatography on silica gel (*n*-hexane/AcOEt = 4/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, only *E* isomer) δ: 7.20-7.13 (m, 2H), 7.10-7.03 (m, 1H), 6.91 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.01-5.91 (m, 2H), 5.07-5.01 (m, 2H), 4.09 (t, *J* = 6.4 Hz, 2H), 3.74 (s, 3H), 3.37 (d, *J* = 6.4 Hz, 2H), 2.73-2.68 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, only *E* isomer); δ 166.7, 156.1, 145.2, 136.9, 129.9, 128.8, 127.3, 123.0, 120.8, 115.4, 111.1, 65.9, 51.5, 34.4, 32.2; HRMS (APCI) calcd for $C_{15}H_{19}O_3$ $(M+H)^+$: 247.1334, found: 247.1326.

Preparation of compound **1n**



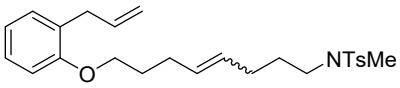
S2 was prepared according to the known literature.[4] To a suspension of 2-(1,3-dioxan-2-yl)ethyltriphenylphosphonium bromide (3.0 g, 6.6 mmol, 1.3 eq.) in toluene (25 mL), KHMDS (11 mL, 0.6 M in toluene, 6.6 mmol, 1.3 eq.) was slowly added and stirred for 30 min. Then, solution of **S2** (1.8 g, 5.1mmol, 0.2 M in toluene) was slowly added to the reaction mixture and stirred for 3 h. Afterwards, sat. NH_4Cl was added to quench the reaction and extracted with AcOEt. The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4. After evaporation, the residue was purified by column chromatography on silica gel (*n*-hexane/ AcOEt = 10/1) to afford **S3** (1.4 g, 63%).

To a round-bottom flask containing **S3** in THF (0.2 M), TBAF (1 M in THF, 3.9 mL, 3.9 mmol, 1.2 eq.) was added and stirred for 1 h at room temperature. The mixture was concentrated *in vacuo* and obtained residue was purified by column chromatography on silica gel (*n*-hexane/ AcOEt = 3/1) to afford **S4** (676 mg, quant.).

To a round-bottom flask containing 2-allylphenol (250 mg, 1.86 mmol), **S4** (439 mg, 2.05 mmol, 1.1 eq.) and PPh_3 (538 mg, 2.05 mmol, 1.1 eq.) in THF (4.7 mL) was added DIAD (402 μL, 2.05 mmol, 1.1 eq.) and stirred for 10 h at room temperature. The reaction mixture was concentrated *in vacuo* and obtained residue was purified by column chromatography on silica gel (*n*-hexane/ AcOEt = 15/1) to afford **1n** (450 mg, 73%). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, only *Z* isomer) δ: 7.19-7.12 (m, 2H), 6.88 (ddd, *J*

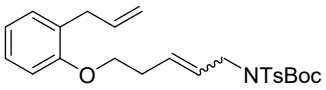
= 7.4, 7.4, 1.1 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.04-5.94 (m, 1H), 5.57-5.40 (m, 2H), 5.09-5.01 (m, 2H), 4.54 (t, *J* = 5.3 Hz, 1H), 4.13-4.09 (m, 2H), 3.95 (t, *J* = 6.4 Hz, 2H), 3.79-3.73 (m, 2H), 3.39 (d, *J* = 6.4 Hz, 2H), 2.40-2.36 (m, 2H), 2.15-2.03 (m, 3H), 1.83-1.76 (m, 2H), 1.53-1.39 (m, 4H), 1.36-1.30 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$ *Z* isomer); δ 156.7, 137.1, 132.4, 129.7, 128.8, 127.2, 123.1, 120.2, 115.3, 111.1, 101.9, 67.8, 67.0, 34.4, 33.5, 29.2 (overlapped), 27.3, 25.8, 25.7; HRMS (APCI) calcd for $C_{21}H_{31}O_3$ $(M+H)^+$: 331.2273, found: 331.2266.

Compound **1o**



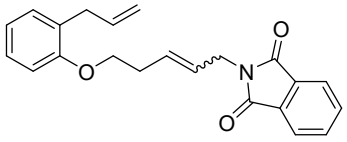
Using alkene **A** = *N*,4-dimethyl-*N*-(pent-4-en-1-yl)benzenesulfonamide,[5] **B** = 5-bromo-1-pentene Following the typical procedure A 1,1-Dimethylethyl *N*,4-dimethyl-*N*-(pent-4-en-1-yl)benzenesulfonamide (1.0 g, 3.95 mmol) was converted to **1o** (1.25 g, 74% *E*/*Z* = 4.8/1) after column chromatography on silica gel (*n*-hexane/AcOEt = 4/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, *E*/*Z* mixture) δ: 7.66 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.18-7.11 (m, 2H), 6.90-6.86 (m, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.04-5.94 (m, 1H), 5.56-5.42 (m, 1.6 ㄱ H, *E* isomer), 5.40-5.39 (m, 033H, *Z* isomer), 5.09-5.01 (m, 2H), 3.96 (t, *J* = 6.4 Hz, 2H), 3.39 (d, *J* = 6.4 Hz, 2H), 2.96 (t, *J* = 7.1 Hz, 2H), 2.69 (s, 3H), 2.42-2.42 (m, 3H), 2.26-2.23 (m, 033H, *Z* isomer), 2.22-2.17 (m, 1.67H, *E* isomer), 2.09-2.01 (m, 2H), 1.89-1.82 (m, 2H), 1.63-1.51 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$ *E*/*Z* mixture); δ 156.6, 143.2, 137.1, 134.5, 130.3, 129.7, 129.7, 129.6, 129.3, 129.2, 128.7, 128.6, 127.4, 127.2, 120.3, 115.3, 111.1, 67.0, 66.9, 49.7, 49.6, 34.6, 34.4, 31.6, 31.2, 29.4, 29.2, 29.1, 29.0, 27.6, 27.4, 24.2, 23.7, 21.5; HRMS (APCI) calcd for $C_{25}H_{34}NO_3S$ $(M+H)^+$: 428.2259, found: 428.2248.

Compound **1p**



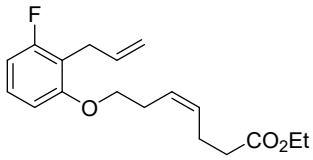
Using alkene **A** = 1,1-Dimethylethyl *N*-[(4-methylphenyl)sulfonyl]-*N*-2-propen-1-ylcarbamate,[6] **B** = 4-bromo-1-butanol Following the typical procedure C 1,1-Dimethylethyl *N*-[(4-methylphenyl)sulfonyl]-*N*-2-propen-1-ylcarbamate (.0 g, 6.42 mmol) was converted to **1p** (899 mg, 30% *E*/*Z* = 4/1) after column chromatography on silica gel (*n*-hexane/AcOEt = 4/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, *E*/*Z* mixture) δ: 7.79-7.76 (m, 2H), 7.29-7.12 (m, 5H), 6.92-6.82 (m, 2H), 6.05-5.65 (m, 3H), 5.09-5.01 (m, 2H), 4.54 (d, *J* = 6.9 Hz, 0.4H, *Z* isomer), 4.42 (d, *J* = 6.0 Hz, 1.6H, *E* isomer), 4.05-3.97 (m, 2H), 3.4 (d, *J* = 6.4 Hz, 0.4H, *Z* isomer), 3.35 (d, *J* = 6.4 Hz, 1.6H, *E* isomer), 2.73 (q, *J* = 6.4 Hz, 0.4H), 2.57 (q, *J* = 6.6 Hz, 1.6H, *E* isomer), 2.43 (s, 0.6H, *Z* isomer), 2.39 (s, 2.4H, *E* isomer), 1.33 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$ *E*/*Z* mixture); δ 156.4, 150.7, 144.0, 137.2, 136.9, 130.9, 129.7, 129.6, 129.2, 129.1, 128.9, 128.0, 127.9, 127.8, 127.4, 127.2, 127.0, 120.5, 115.4, 111.2, 84.1, 67.1, 48.2, 43.6, 34.4, 32.3, 27.9, 27.6, 21.6; HRMS (ESI) calcd for $C_{26}H_{33}NO_5SNa$ $(M+Na)^+$: 494.1977, found: 494.1963.

Compound **1q**



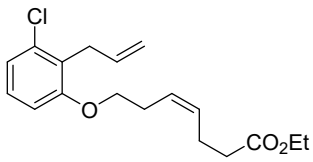
Using alkene **A** = 2-allylisoindoline-1,3-dione,[7] **B** = 4-bromo-1-butanol. Following the typical procedure C 2-allylisoindoline-1,3-dione (1.0 g, 5.34 mmol) was converted to **1q** (1.15 g, 62% *E*/*Z* = 3.5/1) after column chromatography on silica gel (*n*-hexane/AcOEt = 11/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, *E*/*Z* mixture) δ: 7.86-7.84 (m, 2H), 7.73-7.70 (m, 2H), 7.17-7.10 (m, 2H), 6.87 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 5.98-5.81 (m,1.84H, *E* isomer), 5.80-5.75 (0.16H, *Z* isomer), 5.72-5.65 (m, 1H), 5.02-4.95 (m, 2H), 4.37 (d, *J* = 6.9 Hz, 0.16H, *Z* isomer), 4.27 (d, *J* = 6.4 Hz, 1.84H, *E* isomer), 4.07 (t, *J* = 6.4 Hz, 0.16H, *Z* isomer), 3.98 (t, *J* = 6.4 Hz, 1.84H, *E* isomer), 3.38 (d, *J* = 6.0 Hz, 0.16H, *Z* isomer), 3.32 (d, *J* = 6.4 Hz,1.84H, *E* isomer), 2.81 (q, *J* = 6.6 Hz, 0.16H, *Z* isomer), 2.52 (q, J = 6.6 Hz, 1.84H, *E* isomer); ^{13}C-NMR (100 MHz, $CDCl_3$ *E* isomer); δ 167.9, 156.3, 137.0, 133.9, 132.1, 130.6, 129.7, 128.8, 127.2, 125.7, 123.3, 120.5, 115.2, 111.2, 66.9, 39.4, 34.4, 32.2; HRMS (APCI) calcd for $C_{22}H_{22}NO_3$ $(M+H)^+$: 348.1600, found: 348.1592.

Compound **1r**



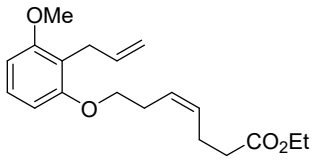
Following the typical procedure D, 2-allyl-3-fluorophenol[1] (200 mg, 1.31 mmol) was converted to **1r** (324 mg, 80%) after column chromatography on silica gel (*n*-hexane/AcOEt =15/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, only *Z* isomer) δ: 7.14-7.03 (m, 1H), 6.68-6.61 (m, 2H), 5.98-5.88 (m, 1H), 5.57-5.47 (m, 2H), 5.06-4.95 (m, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.97 (t, *J* = 6.6 Hz, 2H), 3.40 (d, *J* = 6.2 Hz, 2H), 2.57 (dt, *J* = 6.4 Hz, 6.0 Hz, 2H), 2.45-2.35 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, only *Z* isomer); 173.2, 161.7 ($^{1}J_{CF}$ = 243.5 Hz), 157.9 ($^{3}J_{CF}$ = 8.6 Hz), 135.9, 130.2, 127.4 ($^{3}J_{CF}$ = 10.5 Hz), 126.7, 115.0, 107.9 ($^{2}J_{CF}$ = 23.0 Hz), 107.1 ($^{4}J_{CF}$ = 2.9 Hz), 102.2 ($^{2}J_{CF}$ = 25.9 Hz), 68.0, 60.5, 34.3, 27.5, 27.0, 23.0, 14.3; ^{19}F-NMR (376 MHz, $CDCl_3$) −117.4; HRMS (APCI) calcd for $C_{18}H_{24}FO_3$ $(M+H)^+$: 307.1709, found: 307.1702.

Compound **1s**



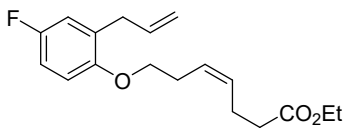
Following the typical procedure D, 2-allyl-5-chlorophenol[1] (200 mg, 1.2 mmol) was converted to **1s** (327 mg, 85%) after column chromatography on silica gel (*n*-hexane/AcOEt = 15/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, only *Z* isomer) δ: 7.08 (dd, *J* = 7.9, 7.9 Hz, 1H), 6.97 (d, *J* = 7.9, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 5.96-5.86 (m, 1H), 5.57-5.47 (m, 2H), 5.05-4.97 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.96 (t, *J* = 6.6 Hz, 2H), 3.54 (d, *J* = 6.4 Hz, 2H), 2.59 (t, *J* = 6.9 Hz, 1H), 2.57 (t, *J* = 6.4 Hz, 1H), 2.44-2.35 (m, 4H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, only *Z* isomer); δ 173.1, 157.6, 135.1, 135.0, 130.1, 127.4, 126.8, 126.5, 121.6, 115.2, 109.7, 67.9, 60.4, 34.2, 31.3, 27.4, 22.9, 14.2; HRMS (APCI) calcd for $C_{18}H_{24}ClO_3$ $(M+H)^+$: 323.1414, found: 323.1406.

Compound **1t**



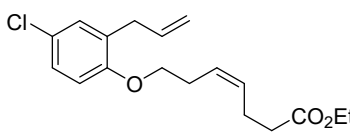
Following the typical procedure D, 2-allyl-3-methoxyphenol[1] (200 mg, 1.2 mmol) was converted to **1t** (304 mg, 78%) after column chromatography on silica gel (*n*-hexane/AcOEt = 15/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, only *Z* isomer) δ: 7.12 (dd, *J* = 8.2, 8.2 Hz, 1H), 6.54 (d, *J* = 8.2 Hz, 1H), 6.52 (d, *J* = 8.2 Hz, 1H), 5.98-5.88 (m, 1H), 5.58-5.45 (m, 2H), 5.01-4.89 (m, 2H), 4.16-4.11 (m, 2H), 3.98-3.94 (m, 2H), 3.81 (s, 3H), 3.41 (d, *J* = 6.4 Hz, 2H), 2.56 (dt, *J* = 6.9 Hz, 6.4 Hz, 2H), 2.45-2.35 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, only *Z* isomer); δ 173.1, 158.2, 157.4, 136.9, 129.8, 127.0, 126.9, 116.8, 114.0, 104.8, 103.8, 67.8, 60.4, 55.8, 34.2, 27.6, 27.3, 22.9, 14.2; HRMS (APCI) calcd for $C_{19}H_{27}O_4$ $(M+H)^+$: 319.1909, found: 319.1900.

Compound **1u**



Following the typical procedure , 2-allyl-4-fluorophenol[1] (253 mg, 1.7 mmol) was converted to **1u** (341 mg, 67%) after column chromatography on silica gel (*n*-hexane/AcOEt = 15/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, only *Z* isomer) δ: 6.88-6.81 (m, 2H), 6.76-6.71 (m, 1H), 5.99-5.89 (m, 1H), 5.57-5.47 (m, 2H), 5.10-5.05 (m, 2H), 4.13 (q, J = 7.2 Hz, 2H), 3.93 (t, *J* = 6.6 Hz, 2H), 3.35 (d, *J* = 6.9 Hz, 2H), 2.56 (dt, *J* = 6.4 Hz, 6.4 Hz, 2H), 2.45-2.35 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, only *Z* isomer); δ 173.1, 157.0 ($^{1}J_{CF}$ = 237.7 Hz), 152.6 ($^{4}J_{CF}$ = 1.9 Hz), 136.2, 130.7 ($^{3}J_{CF}$ = 6.7 Hz), 130.0, 126.7, 116.4 ($^{2}J_{CF}$ = 23.0 Hz), 116.1, 112.8 ($^{2}J_{CF}$ = 22.0 Hz), 112.1 ($^{3}J_{CF}$ = 7.7 Hz), 68.1, 60.4, 34.2 (2C, over lapped), 27.5, 22.9, 14.2; ^{19}F-NMR (376 MHz, $CDCl_3$, only *Z* isomer) −124.0; HRMS (APCI) calcd for $C_{18}H_{24}FO_3$ $(M+H)^+$: 307.1709, found: 307.1701.

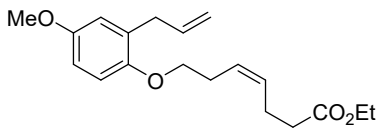
Compound **1v**



Following the typical procedure D, 2-allyl-4-chlorophenol[1] (203 mg, 1.2 mmol) was converted to **1v** (261 mg, 67%) after column chromatography on silica gel (*n*-hexane/AcOEt = 15/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, only *Z* isomer) δ: 7.13-7.10 (m, 2H), 6.74 (d, *J* = 8.7 Hz, 1H), 5.99-5.89 (m, 1H), 5.56-5.48 (m, 2H), 5.10-5.04 (m, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.94 (t, *J* = 6.6 Hz, 2H), 3.33 (d, *J* = 6.9 Hz, 2H), 2.57 (dt, *J* = 6.4 Hz, 6.0 Hz, 2H), 2.45-2.35 (m, 4H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR (100

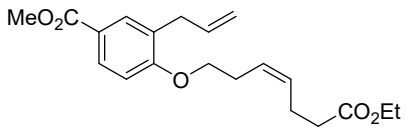
MHz, $CDCl_3$, only *Z* isomer); δ 1173.1, 155.1, 136.1, 130.7, 130.1, 129.5, 126.8, 126.5, 125.2, 116.1, 112.3, 67.8, 60.4, 34.2, 34.1, 27.4, 22.9, 14.2; HRMS (APCI) calcd for $C_{18}H_{24}ClO_3$ $(M+H)^+$: 323.1414, found: 323.1407.

Compound **1w**



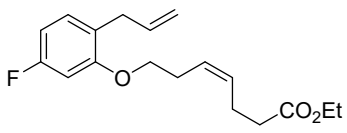
Following the typical procedure D, 2-allyl-4-methoxyphenol[1] (198 mg, 1.2 mmol) was converted to **1w (**224 mg, 62%) after column chromatography on silica gel (*n*-hexane/AcOEt = 15/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, only *Z* isomer) δ: 6.77 (d, *J* = 8.7 Hz, 1H), 6.73-6.67 (m, 2H), 6.02-5.92 (m, 1H), 5.58-5.46 (m, 2H), 5.10-5.02 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.92 (t, *J* = 6.6 Hz, 2H), 3.75 (s, 3H), 3.36 (d, *J* = 6.9 Hz, 2H), 2.55 (dt, *J* = 6.6 Hz, 6.4 Hz, 2H), 2.46-2.35 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, only *Z* isomer); δ 173.1, 153.6, 150.7, 136.8, 130.2, 129.8, 126.9, 116.0, 115.6, 112.6, 111.3, 68.3, 60.4, 55.6, 34.4, 34.2, 27.6, 22.9, 14.2; HRMS (APCI) calcd for $C_{19}H_{27}O_4$ $(M+H)^+$: 319.1909, found: 319.1896.

Compound **1x**



Following the typical procedure D, methyl 3-allyl-4-hydroxybenzoate[2] (198 mg, 1.2 mmol) was converted to **1x (**293 mg, 81%) after column chromatography on silica gel (*n*-hexane/AcOEt = 10/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, only *Z* isomer) δ: 7.89 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.82 (d, *J* = 2.3 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 1H), 6.02-5.92 (m, 1H), 5.57-5.48 (m, 2H), 5.10-5.03 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 4.03 (t, *J* = 6.6 Hz, 2H), 3.87 (s, 3H), 3.38 (d, *J* = 6.4 Hz, 2H), 2.62-2.57 (m, 2H), 2.43-2.35 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, only *Z* isomer); δ 173.0, 167.0, 160.3, 136.2, 131.2, 130.3, 129.7, 128.7, 126.3, 122.1, 115.9, 110.3, 67.5, 60.4, 51.8, 34.3, 34.1, 27.3, 22.9, 14.2; HRMS (APCI) calcd for $C_{20}H_{27}O_5$ $(M+H)^+$: 347.1858, found: 347.1851.

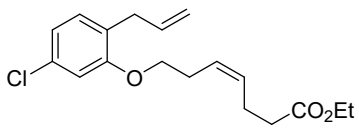
Compound **1y**



Following the typical procedure D, 2-allyl-5-fluorophenol[1] (200 mg, 1.58 mmol) was converted to **1y** (335 mg, 83%) after column chromatography on silica gel (*n*-hexane/AcOEt = 15/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, only *Z* isomer) δ: 7.08-7.04 (m, 1H), 6.61-6.55 (m, 2H), 6.00-5.90 (m, 1H), 5.59-5.44 (m, 2H), 5.07-5.01 (m, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.95 (t, *J* = 6.6 Hz, 2H), 3.32 (d, *J* = 6.9 Hz, 2H), 2.59 (dt, *J* = 6.4 Hz, 6.0 Hz,2H), 2.46-2.36 (m, 4H), 1.27(t, *J* = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, only *Z* isomer); δ 173.1, 162.2 ($^1J_{CF}$ = 242.5 Hz), 157.3 ($^3J_{CF}$ = 9.6 Hz), 136.8, 130.2, 130.1 ($^3J_{CF}$

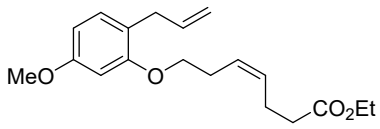
= 8.6 Hz), 126.4, 124.3 ($^4J_{CF}$ = 2.9 Hz), 115.4, 106.5 ($^2J_{CF}$ = 20.1 Hz), 99.4 ($^2J_{CF}$ = 25.0 Hz), 67.6, 60.4, 34.2, 33.8, 27.3, 22.9, 14.2; ^{19}F-NMR (376 MHz, $CDCl_3$, only *Z* isomer) −114.4; HRMS (APCI) calcd for $C_{18}H_{24}FO_3$ $(M+H)^+$: 307.1709, found: 307.1699.

Compound **1z**



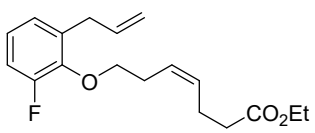
Following the typical procedure D, 2-allyl-3-chlorophenol[1] (200 mg, 1.2 mmol) was converted to **1z** (312 mg, 82%) after column chromatography on silica gel (*n*-hexane/AcOEt = 15/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, only *Z* isomer) δ: 7.04 (d, *J* = 7.9 Hz, 1H), 6.86 (dd, *J* = 7.9, 2.2 Hz, 1H), 6.81 (d, *J* = 2.2 Hz, 1H), 5.98-5.88 (m, 1H), 5.56-5.47 (m, 2H), 5.07-5.01 (m, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.95 (t, *J* = 6.6 Hz, 2H), 3.32 (d, *J* = 6.4 Hz, 2H), 2.57 (dt, *J* = 6.4 Hz, 6.0 Hz, 2H), 2.43-2.35 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, only *Z* isomer); δ 173.1, 157.0, 136.4, 132.3, 130.4, 130.2, 127.3, 126.4, 120.3, 115.7, 111.8, 67.6, 60.4, 34.2, 33.9, 27.3, 22.9, 14.2; HRMS (APCI) calcd for $C_{18}H_{24}ClO_3$ $(M+H)^+$: 323.1414, found: 323.1408.

Compound **1aa**



Following the typical procedure D, 2-allyl-5-methoxyphenol[1] (200 mg, 1.2 mmol) was converted to **1aa** (270 mg, 70%) after column chromatography on silica gel (*n*-hexane/AcOEt = 15/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, only *Z* isomer) δ: 7.02 (d, *J* = 8.7 Hz, 1H), 6.44-6.41 (m, 2H), 6.01-5.91 (m, 1H), 5.58-5.46 (m, 2H), 5.06-4.98 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.94 (t, *J* = 6.6 Hz, 2H), 3.78 (s, 3H), 3.30 (d, *J* = 6.4 Hz, 2H), 2.58 (t, *J* = 6.4 Hz, 1H), 2.55 (t, *J* = 6.4 Hz, 1H), 2.43-2.35 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, only *Z* isomer); δ 173.1, 159.2, 157.3, 137.4, 129.9, 129.9, 126.7, 121.2, 114.9, 104.1, 99.2, 67.4, 60.4, 55.3, 34.2, 33.8, 27.4, 22.9, 14.2; HRMS (APCI) calcd for $C_{19}H_{27}O_4$ $(M+H)^+$: 319.1909, found: 319.1901.

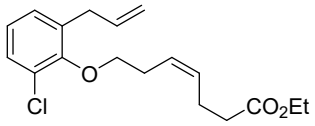
Compound **1ab**



Following the typical procedure D, 2-allyl-6-fluorophenol[1] (200 mg, 1.3 mmol) was converted to **1ab** (300 mg, 75%) after column chromatography on silica gel (*n*-hexane/AcOEt = 15/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, only *Z* isomer) δ: 6.96-6.90 (m, 3H), 6.00-5.90 (m, 1H), 5.58-5.47 (m, 2H), 5.08-5.02 (m, 2H), 4.13

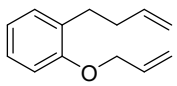
(q, J = 7.1 Hz, 2H), 4.04 (t, J = 6.9 Hz, 2H), 3.41 (d, J = 6.4 Hz, 2H), 2.56 (t, J = 6.9 Hz, 1H), 2.53 (t, J = 6.4 Hz, 1H), 2.43-2.34 (m, 4H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, only Z isomer); 173.1, 155.6 ($^1J_{CF}$ = 246.3 Hz), 144.5 ($^3J_{CF}$ = 10.5 Hz), 136.8, 134.9, 130.1, 126. 6, 125.1 ($^4J_{CF}$ = 2.9 Hz), 123.3 ($^3J_{CF}$ = 8.6 Hz), 115.8, 114.7 ($^2J_{CF}$ = 19.2 Hz), 73.0 ($^4J_{CF}$ = 5.8 Hz), 60.3, 34.2, 34.0 ($^4J_{CF}$ = 1.9 Hz), 28.4, 22.9, 14.2; ^{19}F-NMR (376 MHz, $CDCl_3$, only Z isomer) −130.1; HRMS (APCI) calcd for $C_{18}H_{24}FO_3$ $(M+H)^+$: 307.1709, found: 307.1702.

Compound **11ac**



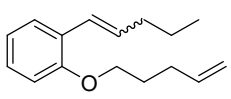
Following the typical procedure D, 2-allyl-6-chlorophenol[1] (200 mg, 1.2 mmol) was converted to **11ac** (258 mg, 67%) after column chromatography on silica gel (*n*-hexane/AcOEt = 15/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, only Z isomer) δ: 7.23 (dd, J = 7.8, 1.7 Hz, 1H), 7.08 (dd, J = 7.8, 1.7 Hz, 1H), 6.98 (dd, J = 7.8, 7.8 Hz, 1H), 6.00-5.90 (m, 1H), 5.63-5.48 (m, 2H), 5.10-5.03 (m, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.93 (t, J = 6.9 Hz, 2H), 3.44 (d, J = 6.4 Hz, 2H), 2.62 (t, J = 6.9 Hz, H), 2.59 (t, J = 6.9 Hz, 1H), 2.44-2.36 (m, 4H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, only Z isomer); δ 173.1, 153.0, 136.7, 135.3, 130.1, 128.8, 128.4, 128.0, 126.5, 124.6, 116.2, 72.6, 60.3, 34.2, 34.2, 28.2, 22.9, 14.2; HRMS (APCI) calcd for $C_{18}H_{24}ClO_3$ $(M+H)^+$: 323.1414, found: 323.1406.

Preparation of **1ad**



To a round-bottom flask containing 2-(3-buten-1-yl)phenol (300 mg, 2.0 mmol, prepared by known method[8]), and K_2CO_3 (560 mg, 4.1 mmol, 2.0 eq.) in CH_3CN (4.1 mmL, 0.5 M) was added allyl bromide (980 mg, 8.1 mmol, 4.0 eq.). The reaction mixture was stirred at 60 °C for 3 h. The mixture was filtered through a glass filter with AcOEt and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel using *n*-hexane/ AcOEt = 6/1) as an eluent to afford **1ae**. A colorless oil.; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.19-7.15 (m, 2H), 6.90 (dd, J = 7.3, 7.3 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 6.13-6.04 (m, 1H), 5.96-5.86 (m, 1H), 5.45 (d, J = 18.8 Hz, 1H), 5.29 (d, J = 11.4 Hz, 1H), 5.06 (d, J = 17.4 Hz, 1H), 4.98 (d, J = 10.1 Hz, 1H), 4.56 (d, J = 5.0 Hz, 2H), 2.76 (t, J = 7.8 Hz, 2H), 2.39 (dt, J = 7.8, 6.9 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ 156.4, 138.7, 133.5, 130.5, 129.9, 126.9, 120.5, 116.7, 114.5, 111.5, 68.5, 33.9, 30.0; HRMS (APCI) calcd for $C_{13}H_{17}O$ $(M+H)^+$: 189.1279, found: 189.1273.

Compound **11ae**

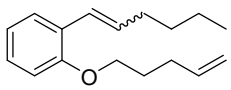


Using butyltriphenylphosphonium bromide. Following the typical procedure E, salicylaldehyde (400 mg, 3.3 mmol) was converted to **1ae** (602 mg, 85%) after column chromatography on silica gel (*n*-hexane/AcOEt = 15/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, E/Z = 1/1.2) δ: 7.42 (dd, J = 7.6, 1.6 Hz, 0.46H, E isomer), 7.26 (dd, J = 7.3, 1.4

Hz, 0.54H *Z* isomer), 7.22-7.13 (m, 1H), 6.93-6.83 (m, 2H), 6.72 (d, *J* = 15.8 Hz, 0.46H, *E* isomer), 6.55 (d, J = 11.9 Hz, 0.54H, *Z* isomer), 6.24 (dt, *J* = 15.8, 6.9 Hz, 0.46H, *E* isomer), 5.93-5.81 (m, 1H), 5.70 (dt, *J* = 11.9, 7.3 Hz, 0.54H, *Z* isomer), 5.10-4.98 (m, 2H), 4.01-3.97 (m, 2H), 2.31-2.19 (m, 4H), 1.96-1.87 (m, 2H), 1.55-1.42 (m, 2H), 0.98-0.91 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, *E*/*Z* mixture); δ 156.5, 155.7, 137.9, 132.5, 131.5, 130.0, 127.8, 127.7, 126.9, 126.4, 124.5, 124.2, 120.5, 119.8, 115.1, 115.1, 111.9, 111.6, 67.5, 67.4, 35.6, 30.8, 30.3, 30.2, 28.5, 28.4, 23.2, 22.7, 13.9, 13.8; HRMS (APCI) calcd for $C_{15}H_{21}O$ $(M+H)^+$: 231.1749, found: 231.1741.

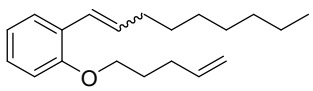
mass

Compound **1af**



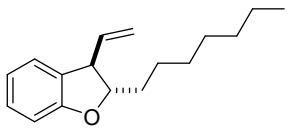
Using pentyltriphenylphosphonium bromide. Following the typical procedure E, salicylaldehyde (400 mg, 3.3 mmol) was converted to **1af** (630 mg, 90%) after column chromatography on silica gel (*n*-hexane/AcOEt = 15/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, *E*/*Z* = 2.4/1) δ: 7.42 (dd, *J* = 7.8, 1.8 Hz, 0.71H, *E* isomer), 7.26 (dd, *J* = 7.3, 1.8 Hz, 0.29H, *Z* isomer), 7.22-7.13 (m, 1H), 6.93-6.83 (m, 2H), 6.71 (d, *J* = 16.0 Hz, 0.71H, *E* isomer), 6.54 (d, *J* = 11.7 Hz, 0.29H, *Z* isomer), 6.24 (dt, *J* = 16.0, 6.9 Hz, 0.71H, *E* isomer), 5.93-5.81 (m, 1H), 5.70 (dt, *J* = 11.7, 7.3 Hz, 0.29H, *Z* isomer), 5.11-4.98 (m, 2H), 4.01-3.97 (m, 2H), 2.31-2.21 (m, 4H), 1.97-1.87 (m, 2H), 1.51-1.30 (m, 4H), 0.95-0.87 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, *E*/*Z* mixture); δ 156.4, 155.7, 137.9, 132.7, 131.7, 129.9, 127.8, 127.6, 127.1, 126.9, 126.3, 124.3, 124.0, 120.5, 119.8, 115.1, 111.9, 111.6, 67.5, 67.4, 33.2, 32.2, 31.6, 30.3, 30.2, 28.5, 28.4, 22.4, 22.3, 14.0; HRMS (APCI) calcd for $C_{17}H_{25}O$ $(M+H)^+$: 245.1905, found: 245.1897.

Compound **1ag**



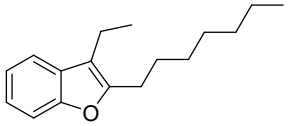
Using octyltriphenylphosphonium bromide. Following the typical procedure H, salicylaldehyde (400 mg, 3.3 mmol) was converted to **1ag** (602 mg, 85%) after column chromatography on silica gel (*n*-hexane/AcOEt = 15/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$, *E*/*Z* = 3/2) δ: 7.41 (dd, *J* = 7.6, 1.6 Hz, 0.6H, *E* isomer), 7.24 (d, *J* = 7.6, 1.4 Hz, 0.4H, *Z* isomer), 7.21-7.12 (m, 1H), 6.93-6.82 (m, 2H), 6.70 (d, *J* = 16.0 Hz, 0.6H, *E* isomer), 6.53 (d, *J* = 11.4 Hz, 0.4H, *Z* isomer), 6.23 (dt, *J* = 16.0, 7.0 Hz, 0.6H, *E* isomer), 5.93-5.81 (m, 1H), 5.69 (dt, *J* = 11.4, 7.3 Hz, 0.4H, *Z* isomer), 5.10-4.98 (m, 2H), 4.01-3.96 (m, 2H), 2.30-2.19 (m, 4H), 1.96-1.86 (m, 2H), 1.50-1.25 (m, 10H), 0.90-0.85 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, *E*/*Z* mixture); δ 156.4, 155.7, 137.9, 132.7, 131.8, 129.9, 127.8, 127.6, 127.1, 126.9, 126.4, 124.3, 124.0, 120.5, 119.8, 115.1, 111.9, 111.6, 67.5, 67.4, 33.5, 31.9, 30.3, 30.2, 30.0, 29.5, 29.3, 29.2, 28.7, 28.5, 28.4, 22.7, 14.1; HRMS (APCI) calcd for $C_{20}H_{31}O$ $(M+H)^+$: 287.2375, found: 287.2366.

Preparation of **2a**



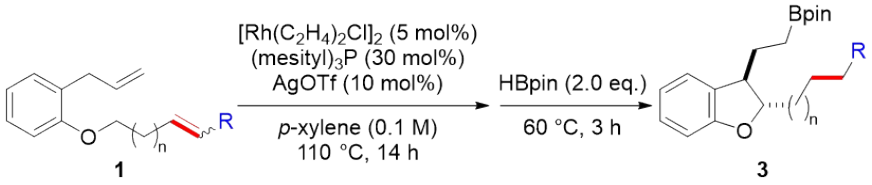
In a glovebox, to an oven-dried 10-mL vial were added $[Rh(C_2H_4)_2Cl]_2$ (3.98 mg 10.2 μmol, 5 mol%), trimesityl phosphine (23.8 mg, 61.4 μmol, 30 mol%) and anhydrous *p*-xylene (2.1 mL, 0.1 M). The resulting solution was stirred for 30 min at ambient temperature, then AgOTf (5.26mg, 20.1 μmol 10 mol%) was added and the reaction mixture was stirred for 30 min. Next, diene **1a** (50 mg, 0.205 mmol, 1.0 eq.) was added and the reaction mixture was sealed, removed from the glovebox and heated at 110 °C for 24 h. After being cooled to room temperature, the reaction mixture was filtered by short silica gel column chromatography (*n*-hexane/AcOEt = 30/1) and concentrated in vacuo to remove the solvent. The obtained residue was purified by flash column chromatography on silica gel to give corresponding 2,3-dihydrobenzofuran **2a** (41.2 mg, 82%). A colorless oil; ^{1}H-NMR (500 MHz, CD_3OD) δ 7.07 (dd, *J* = 7.4, 7.4 Hz 1H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.80 (dd, *J* = 7.4, 7.4 Hz, 1H), 6.68 (d, *J* = 7.4 Hz, 1H), 5.85-5.79 (m, 1H), 5.22-5.14 (m, 2H), 4.37-4.33 (m, 1H), 3.67 (dd, *J* = 80., 8.0 Hz, 1H), 1.84-1.73 (m, 2H), 1.53-1.45 (m, 2H), 1.38-1.25 (m, 8H), 0.96-0.83 (m, 3H); ^{13}C-NMR (125 MHz, CD_3OD); δ 160.7, 139.5, 130.8, 129.5, 125.8, 121.4, 117.3, 110.3, 89.9, 54.6, 35.9, 33.0, 30.6, 30.4, 26.7, 23.7, 14.5; HRMS (APCI) calcd for $C_{17}H_{25}O$ $(M+H)^+$: 245.1905, found: 245.1895.

Preparation of **2a'**



In a glovebox, to an oven-dried 10-mL vial,were added $[Rh(C_2H_4)_2Cl]_2$ (3.98 mg 10.2 μmol, 5 mol%), tri(*o*-tolyl) phosphine (18.7.8 mg, 61.4 μmol, 30 mol%) and anhydrous *p*-xylene (2.1 mL, 0.1 M). The resulting solution was stirred for 30 min at ambient temperature, then AgOTf (5.26mg, 20.1 μmol 10 mol%) was added and the reaction mixture was stirred for 30 min. Next, diene **1a** (50 mg, 0.205 mmol, 1.0 eq.) was added and the reaction mixture was sealed, removed from the glovebox and heated at 110 °C for 24 h. After being cooled to room temperature, the reaction mixture was filtered by short silica gel column chromatography (*n*-hexane/AcOEt = 30/1) and concentrated in vacuo to remove the solvent. The obtained residue was purified by flash column chromatography on silica gel to give corresponding 2,3-dihydrobenzofuran **2a'** (31.6 mg, 63%). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ 7.46-7.44 (m, 1H), 7.33-7.30 (m, 1H), 7.18-7.11 (m, 2H), 2.72 (t, *J* = 7.3 Hz, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.73-1.66 (m, 2H), 1.35-1.27 (m, 8H), 1.22 (t, *J* = 7.6 Hz, 3H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR (125 MHz, CD_3OD); δ 155.5, 155.0, 130.6, 124.0, 123.0, 119.8, 117.1, 111.4, 32.9, 30.2, 30.2, 29.5, 27.0, 23.7, 17.7, 15.2, 14.4; HRMS (APCI) calcd for $C_{17}H_{25}O$ $(M+H)^+$: 245.1905, found: 245.1893.

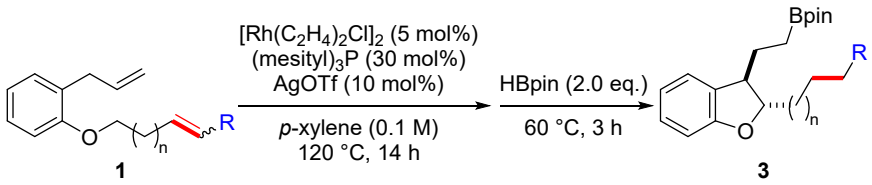
Preparation of 3a, 3b, 3d-3l, 3n-3ag



Typical procedure G

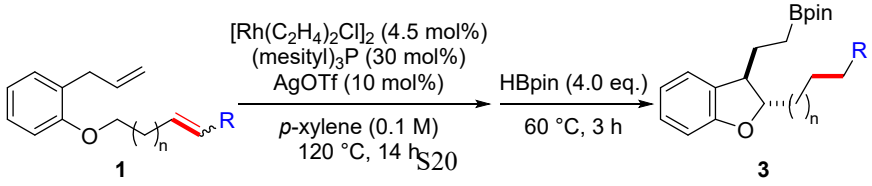
In a glovebox, to an oven-dried 10-mL vial were added $[Rh(C_2H_4)_2Cl]_2$ (5 mol%), trimesitylphosphine (30 mol%) and anhydrous *p*-xylene (0.1 M). The resulting solution was stirred for 30 min at ambient temperature, then AgOTf (10 mol%) was added and the reaction mixture was stirred for 30 min. Next, diene **1** (1.0 eq.) was added and the reaction mixture was sealed, removed from the glovebox and heated at 110 °C for 14 h. Finally, HBin (2.0 eq.) was added to the reaction mixture and stirred at 60 °C for 3 h. After being cooled to room temperature, the reaction mixture was filtered by short silica gel column chromatography and the filtrate was concentrated in vacuo to remove the solvent. The obtained residue was purified by flash column chromatography on silica gel to give corresponding 2,3-dihydrobenzofuran **3**.

Typical procedure H



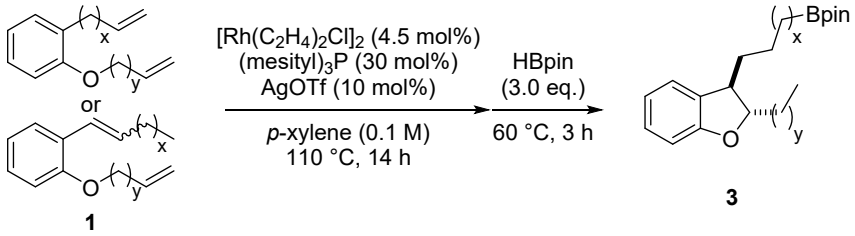
In a glovebox, to an oven-dried 10-mL vial were added $[Rh(C_2H_4)_2Cl]_2$ (5 mol%), trimesityl phosphine (30 mol%) and anhydrous *p*-xylene (0.1 M). The resulting solution was stirred for 30 min at ambient temperature, then AgOTf (10 mol%) was added and the reaction mixture was stirred for 30 min. Next, diene **1** (1.0 eq.) was added and the reaction mixture was sealed, removed from the glovebox and heated at 120 °C for 14 h. Finally, HBpin (2.0 eq.) was added to the reaction mixture and stirred at 60 °C for 3 h. After being cooled to room temperature, the reaction mixture was filtered by short silica gel column chromatography and concentrated in vacuo to remove the solvent. The obtained residue was purified by flash column chromatography on silica gel to give corresponding 2,3-dihydrobenzofuran **3**.

Typical procedure I



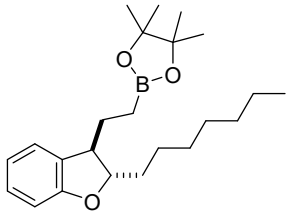
In a glovebox, to an oven-dried 10-mL vial were added $[Rh(C_2H_4)_2Cl]_2$ (4.5 mol%), trimesitylphosphine (30 mol%) and anhydrous *p*-xylene (0.1 M). The resulting solution was stirred for 30 min at ambient temperature, then AgOTf (10 mol%) was added and the reaction mixture was stirred for 30 min. Next, diene **1** (1.0 eq.) was added and the reaction mixture was sealed, removed from the glovebox and heated at 120 °C for 14 h. Finally, HBpin (4.0 eq.) was added to the reaction mixture and stirred at 60 °C for 3 h. After being cooled to room temperature, the reaction mixture was filtered by short silica gel column chromatography and the filtrate was concentrated in vacuo to remove the solvent. The obtained residue was purified by flash column chromatography on silica gel to give corresponding 2,3-dihydrobenzofuran **3**.

Typical procedure J



In a glovebox, to an oven-dried 10-mL vial were added $[Rh(C_2H_4)_2Cl]_2$ (4.5 mol%), trimesitylphosphine (30 mol%) and anhydrous *p*-xylene (0.1 M). The resulting solution was stirred for 30 min at ambient temperature, then AgOTf (10 mol%) was added and the reaction mixture was stirred for 30 min. Next, diene **1** (1.0 eq.) was added and the reaction mixture was sealed, removed from the glovebox and heated at 110 °C for 14 h. Finally, HBin (3.0 eq.) was added to the reaction mixture and stirred at 60 °C for 3 h. After being cooled to room temperature, the reaction mixture was filtered by short silica gel column chromatography and the filtrate was concentrated in vacuo to remove the solvent. The obtained residue was purified by flash column chromatography on silica gel to give corresponding 2,3-dihydrobenzofuran **3**.

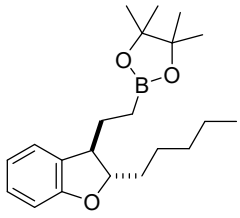
Compound **3a**



Following the typical procedure G, **1a** (30.0 mg, 0.123 mmol) was converted to **3a** (36.9 mg, 81%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30/1). A colorless oil. **2a'** was a byproduct of this reaction and could be separated by column chromatography using this eluent.; ^{1}H-NMR (400 MHz, CD_3OD) δ: 7.13 (d, *J* = 7.3 Hz, 1H), 7.06-7.02 (m, 1H), 6.80-6.76 (m, 1H), 6.66 (d, *J* = 8.2 Hz, 1H), 4.36-4.32 (m, 1H), 3.00-2.96 (m, 1H), 1.81-1.28 (m, 14H), 1.23 (s, 12H), 0.89 (t, *J* = 6.9 Hz, 3H), 0.80 (t, *J* = 8.2 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ 159.2, 130.7, 127.8, 124.4, 119.8, 108.9, 88.3, 83.2, 48.9, 36.0, 31.7, 29.4, 29.2, 29.1, 25.1, 24.0, 24.0, 22.4, 13.2; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; HRMS (APCI) calcd for $C_{23}H_{38}BO_3$ $(M+H)^+$: 373.2914, found: 373.2906.

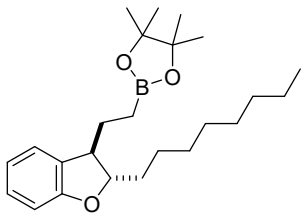
Following the typical procedure J, **1c** (30.0 mg, 0.123 mmol) was also converted to **3a** (31.8 mg, 70%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30 :1).

Compound **3b**



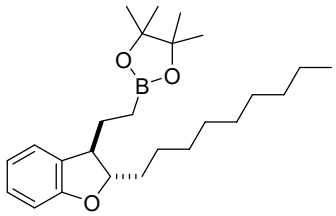
Following the typical procedure G, **1b** (30.0 mg, 0.139 mmol) was converted to **3b** (37.9 mg, 80%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30/1). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ: 7.09 (d, *J* = 7.3 Hz, 1H), 7.03-6.99 (m, 1H), 6.76-6.72 (m, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 4.32-4.28 (m, 1H), 2.94 (dt, *J* = 7.3, 5.5 Hz, 1H), 1.77-1.27 (m, 10H), 1.17 (s, 12H), 0.87 (t, *J* = 7.1 Hz, 3H), 0.75 (t, *J* = 8.0 Hz, 2H); ^{13}C-NMR (100 MHz, CD_3OD); δ 159.2, 130.7, 127.7, 124.4, 119.7, 108.8, 88.3, 83.1, 48.9, 35.9, 31.6, 29.2, 24.8, 23.9, 23.9, 22.4, 13.1; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; HRMS (APCI) calcd for $C_{21}H_{34}BO_3$ $(M+H)^+$: 345.2601, found: 345.2591.

Compound **3d**



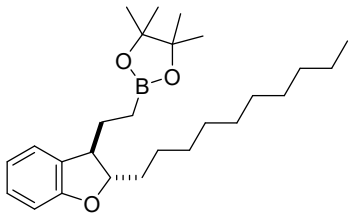
Following the typical procedure G, **1d** (30.0 mg, 0.139 mmol) was converted to **3d** (37.9 mg, 80%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30/1). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ: 7.05-7.01 ddd, *J* = 8.0, 8.0, 0.9 Hz, 1H), 6.76 (ddd, *J* = 7.4, 7.4, 0.9 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 4.33 (dt, *J* = 7.4, 5.2 Hz, 1H), 2.97 (dt, *J* = 7.4, 5.5 Hz, 1H), 1.79-1.28 (m, 16H), 1.22-1.20 (m, 12H), 0.87 (t, *J* = 6.9 Hz, 3H), 0.78 (t, *J* = 8.0 Hz, 2H); ^{13}C-NMR (100 MHz, CD_3OD); δ 160.6, 132.0, 129.1, 125.7, 121.1, 110.1, 89.6, 84.5, 50.2, 37.3, 33.1, 30.7, 30.6, 30.4 (overlapped), 26.4, 25.2, 25.2, 23.7, 14.5; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; HRMS (APCI) calcd for $C_{24}H_{40}BO_3$ $(M+H)^+$: 387.3071, found: 387.3062.

Compound **3e**



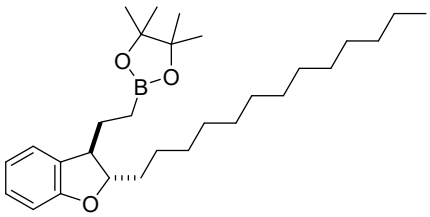
Following the typical procedure G, **1e** (30.0 mg, 0.110 mmol) was converted to **3e** (26.9 mg, 61%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30/1). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ: 7.13 (d, *J* = 7.3 Hz, 1H), 7.05 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.80-6.77 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 4.34 (dt, *J* = 7.4, 5.3 Hz, 1H), 2.99 (dt , *J* = 7.4, 5.3 Hz, 1H), 1.81-1.26 (m, 18H), 1.24 (d, *J* = 1.6 Hz, 12H), 0.85-0.92 (3H), 0.75-0.83 (2H); ^{13}C-NMR (100 MHz, CD_3OD); δ 160.6, 132.0, 129.1, 125.7, 121.1, 110.1, 89.6, 84.5, 50.2, 37.3, 33.1, 30.72, 30.70 (overlapped), 30.6, 30.5, 26.4, 25.2, 25.2, 23.8, 14.5; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; HRMS (APCI) calcd for $C_{25}H_{42}BO_3$ $(M+H)^+$: 401.3227, found: 401.3218.

Compound **3f**



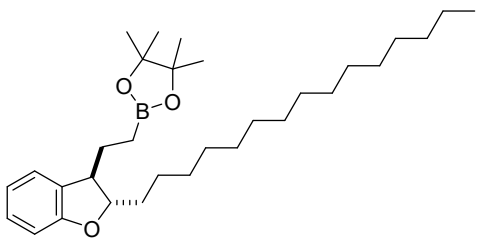
Following the typical procedure G, **1f** (30.0 mg, 0.104 mmol) was converted to **3f** (25 mg, 59%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30/1). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ: 7.13 (d, *J* = 7.3 Hz, 1H), 7.07-7.02 (m, 1H), 6.80-6.76 (m, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 4.35 (dt , *J* = 7.4, 5.0 Hz, 1H), 2.99 (dt , *J* = 7.4, 5.5 Hz, 1H), 1.80-1.25 (m, 20H), 1.24 (d, *J* = 1.6 Hz, 12H), 0.85-0.92 (3H), 0.75-0.83 (2H); ^{13}C-NMR (100 MHz, CD_3OD); δ 160.6, 132.0, 129.1, 125.7, 121.1, 110.1, 89.6, 84.5, 50.2, 37.3, 33.1, 30.7, 30.7, 30.7, 30.6, 30.5, 30.5, 26.4, 25.2, 25.2, 23.8, 14.5; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; HRMS (APCI) calcd for $C_{26}H_{44}BO_3$ $(M+H)^+$: 415.3384, found: 415.3369.

Compound **3g**



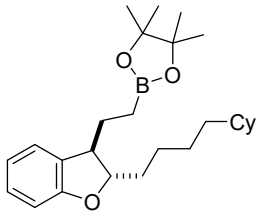
Following the typical procedure G, **1g** (40.0 mg, 0.122 mmol) was converted to **3g** (27.9 mg, 50%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30/1). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ: 7.13 (d, *J* = 7.4 Hz, 1H), 7.05 (ddd, *J* = 7.8, 7.8, 0.8 Hz, 1H), 6.78 (ddd, *J* = 7.4, 7.4, 0.8 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 4.34 (dt, *J* = 7.3, 5.2 Hz, 1H), 2.99 (dt, *J* = 7.3, 5.6 Hz, 1H), 1.87-1.38 (m, 26H), 1.23-1.22 (m, 12H), 0.89 (t, *J* = 6.7 Hz, 3H), 0.80 (t, *J* = 8.0 Hz, 2H); ^{13}C-NMR (100 MHz, CD_3OD); δ 160.6, 132.0, 129.1, 125.7, 121.1, 110.1, 89.6, 84.5, 50.2, 37.3, 33.1, 30.8 (overlapped), 30.7 (overlapped), 30.6, 30.5, 26.4, 25.23 (overlapped), 25.22 (overlapped), 25.1, 23.8, 14.5; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.6; HRMS (APCI) calcd for $C_{29}H_{50}BO_3$ $(M+H)^+$: 457.3853, found: 457.3843.

Compound **3h**



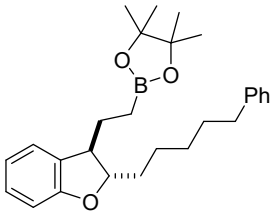
Following the typical procedure G, **1h** (40.0 mg, 0.112 mmol) was converted to **3h** (14.9 mg, 39%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30/1). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ: 7.12 (d, *J* = 7.6 Hz, 1H), 7.05-7.01 (m, 1H), 6.77 (ddd, *J* = 7.6, 7.6, 1.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 4.33 (dt , *J* = 7.3, 5.3 Hz, 1H), 2.97 (dt, *J* = 7.3, 5.6 Hz, 1H), 1.79-1.26 (m, 30H), 1.22-1.20 (m, 12H), 0.87 (t, *J* = 6.9 Hz, 3H), 0.80-0.76 (m, 2H); ^{13}C-NMR (100 MHz, CD_3OD); δ 160.6, 132.0, 129.1, 125.7, 121.1, 110.1, 89.6, 84.5, 50.2, 37.3, 33.1, 30.80 (overlapped), 30.78 (overlapped), 30.69 (overlapped), 30.67 (overlapped), 30.6, 30.5, 26.4, 25.2, 25.2, 23.8, 14.5; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; HRMS (APCI) calcd for $C_{31}H_{54}BO_3$ $(M+H)^+$: 485.4166, found: 485.4142.

Compound **3i**



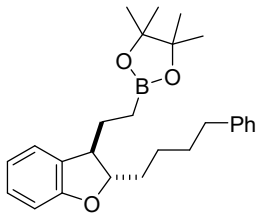
Following the typical procedure H, **1i** (30.0 mg, 0.105 mmol) was converted to **3i** (30.6 mg, 70%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30/1). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ: 7.13 (d, *J* = 7.5 Hz, 1H), 7.04 (dd, *J* = 7.5, 7.5, 1.0 Hz, 1H), 6.78 (dd, *J* = 7.5, 7.5, 1.0 Hz, 1H), 6.66 (d, *J* = 7.5 Hz, 1H), 4.34 (dt, J = 7.5, 5.2 Hz, 1H), 2.98 (dt, *J* = 7.5, 5.7 Hz, 1H), 1.80-1.31 (m, 12H), 1.28-1.10 (m, 19H), 0.88-0.76 (m, 4H); ^{13}C-NMR (100 MHz, CD_3OD); δ 160.6, 132.0, 129.1, 125.7, 121.1, 110.1, 89.6, 84.5, 50.2, 39.0, 38.7, 37.3, 34.6, 30.6, 27.9, 27.8, 27.5, 26.7, 25.2, 25.2; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; HRMS (APCI) calcd for $C_{26}H_{42}BO_3$ $(M+H)^+$: 413.3227, found: 413.3212.

Compound **3j**



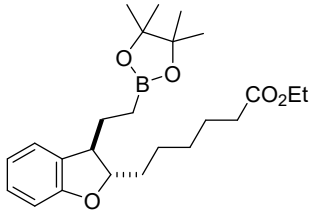
Following the typical procedure H, **1j** (30.0 mg, 0.103 mmol) was converted to **3j** (17.6 mg, 41%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30/1). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ: 7.22 (dd, *J* = 7.3, 7.3 Hz, 2H), 7.15-7.10 (m, 4H), 7.07-7.03 (m, 1H), 6.81-6.76 (m, 1H), 6.65 (d, *J* = 8.2 Hz, 1H), 4.33 (dt, *J* = 7.5, 5.0 Hz, 1H), 2.97 (dt, *J* = 7.5, 5.5 Hz, 1H), 2.59 (t, *J* = 7.6 Hz, 2H), 1.85-1.31 (m, 10H), 1.26-1.22 (m, 12H), 0.79 (t, *J* = 8.0 Hz, 2H); ^{13}C-NMR (100 MHz, CD_3OD); 160.6, 143.9, 132.0, 129.4, 129.3, 129.1, 126.6, 125.7, 121.1, 110.1, 89.5, 84.5, 50.2, 37.2, 36.8, 32.7, 30.5, 30.2, 26.2, 25.2, 25.2; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; HRMS (APCI) calcd for $C_{27}H_{38}BO_3$ $(M+H)^+$: 421.2914, found: 421.2897.

Compound **3k**



Following the typical procedure H, **1k** (30.0 mg, 0.108 mmol) was converted to **3k** (14.5 mg, 33%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30/1). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ: 7.25-7.21 (m, 2H), 7.17-7.10 (m, 4H), 7.07-7.03 (m, 1H), 6.78 (ddd, *J* = 7.4, 7.4, 0.9 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 4.33 (dt, J = 7.4, 5.0 Hz, 1H), 2.97 (dt, *J* = 7.4, 5.6 Hz, 1H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.82-1.38 (m, 8H), 1.23-1.20 (m, 12H), 0.78 (t, *J* = 7.4 Hz, 2H); ^{13}C-NMR (100 MHz, CD_3OD); 160.6, 143.7, 132.0, 129.4, 129.3, 129.1, 126.7, 125.7, 121.1, 110.1, 89.5, 84.5, 50.2, 37.1, 36.8, 32.7, 30.5, 26.1, 25.2, 25.2; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; HRMS (APCI) calcd for $C_{26}H_{36}BO_3$ $(M+H)^+$: 407.2758, found: 407.2747.

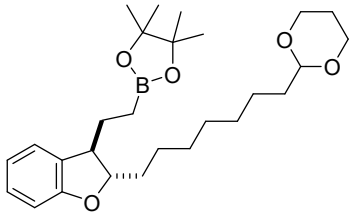
Compound **3l**



Following the typical procedure H, **1l** (30.0 mg, 0.115 mmol) was converted to **3l** (33.7 mg, 75%) after column chromatography on silica gel (*n*-

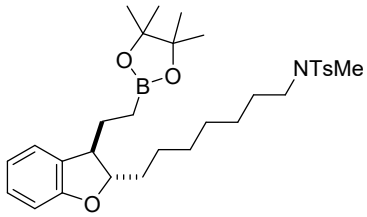
hexane/AcOEt = 15/1). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ: 7.13 (d, *J* = 7.3 Hz, 1H), 7.05 (dd, *J* = 8.2, 8.2 Hz, 1H), 6.78 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.66 (d, *J* = 8.2 Hz, 1H), 4.35 (dt, *J* = 7.3, 5.0 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 2.99 (dt, *J* = 7.8, 5.5 Hz, 1H), 2.30 (t, *J* = 7.3 Hz, 2H), 1.81-1.33 (m, 10H), 1.24-1.19 (m, 15H), 0.81-0.77 (m, 2H); ^{13}C-NMR (100 MHz, CD_3OD); 175.5, 160.5, 132.0, 129.1, 125.7, 121.1, 110.1, 89.4, 84.5, 61.4, 50.2, 37.1, 35.0, 30.5, 30.1, 26.1, 26.0, 25.2, 25.2, 14.6; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; HRMS (APCI) calcd for $C_{24}H_{38}BO_5$ $(M+H)^+$: 417.2812, found: 417.2798.

Compound **3n**



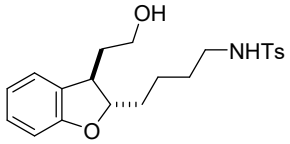
Following the typical procedure H, **1n** (30.0 mg, 0.0908 mmol) was converted to **3n** (25.9 mg, 62%) after column chromatography on silica gel (*n*-hexane/AcOEt = 15/1). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ: 7.13 (d, *J* = 7.3 Hz, 1H), 7.05 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.78 (ddd, *J* = 7.3, 7.3, 0.9 Hz, 1H), 6.66 (d, *J* = 7.3 Hz, 1H), 4.52 (t, *J* = 5.3 Hz, 1H), 4.34 (dt, *J* = 7.5, 5.0 Hz, 1H), 4.05-4.01 (m, 2H), 3.79-3.73 (m, 2H), 2.99 (dt , *J* = 7.5, 5.5 Hz, 1H), 2.03-1.32 (m, 18H), 1.24-1.22 (m, 12H), 0.80 (t, *J* = 8.0 Hz, 2H); ^{13}C-NMR (100 MHz, CD_3OD); 160.6, 132.0, 129.1, 125.7, 121.1, 110.1, 103.6, 89.6, 84.5, 67.9, 50.2, 37.3, 36.2, 30.6 (over lapped), 30.5, 27.0, 26.4, 25.2 (over lapped), 25.2, 25.0; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; HRMS (APCI) calcd for $C_{27}H_{44}BO_5$ $(M+H)^+$: 459.3282, found: 459.3266.

Compound **3o**



Following the typical procedure H, **1o** (50.0 mg, 0.117 mmol) was converted to **3o** (32.5 mg, 50%) after column chromatography on silica gel (*n*-hexane/AcOEt = 6/1). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ: 7.65 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 7.4 Hz, 1H), 7.05 (ddd, *J* = 7.9, 7.9, 0.9 Hz, 1H), 6.79 (ddd, *J* = 7.4, 7.4, 0.9 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 1H), 4.35 (dt, *J* = 7.4, 5.1 Hz, 1H), 3.01-2.94 (m, 3H), 2.67 (s, 3H), 2.42 (s, 3H), 1.26-1.88 (14H), 1.23 (s, 12H), 0.80 (t, *J* = 8.6 Hz, 2H); ^{13}C-NMR (100 MHz, CD_3OD); 159.2, 143.6, 134.5, 130.7, 129.5, 127.7, 127.2, 124.4, 119.7, 108.8, 88.2, 83.2, 49.8, 48.9, 35.9, 33.7, 29.2, 29.2, 28.8, 27.1, 26.1, 25.0, 23.9, 23.9, 20.1; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.1; HRMS (APCI) calcd for $C_{31}H_{47}BNO_5S$ $(M+H)^+$: 556.3268, found: 556.3263.

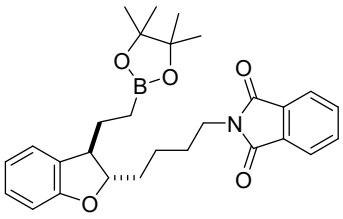
Compound **3p'**



Following the typical procedure H, **1p** (50.0 mg, 0.106 mmol) was converted to **3p.** Next, to **3p** in THF/H_2O (0.4 mL each), sodium perborate tetrahydrate (48.9 mg, 0.318 mmol) was added and stirred at room temperature. After 4 h,

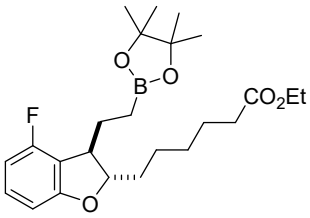
the mixture was extracted three times with Et_2O. The combined organic phases were washed with brine, quickly dried over Na_2SO_4, filtered, and concentrated. Purification of the crude material by silica gel column chromatography (*n*-hexane/AcOEt = 15/1) gave **3p'** (26.4 mg, 63%). A colorless oil; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.73 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.15-7.10 (m, 2H), 6.84 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 4.51 (br, s, 1H), 4.42 (dt, *J* = 7.5, 5.2 Hz, 1H), 3.82-3.75 (m, 2H), 3.21(dt, *J* = 8.0, 5.2 Hz, 1H), 2.97-2.94 (m, 2H), 2.41 (s, 3H), 2.01-1.95 (m, 1H), 1.86-1.79 (m, 1H), 1.69-1.43 (m, 7H); ^{13}C-NMR (125 MHz, $CDCl_3$); 159.0, 143.4, 136.9, 130.3, 129.7, 128.3, 127.1, 124.5, 120.3, 109.5, 88.4, 60.2, 44.1, 42.9, 37.7, 34.9, 29.2, 22.2, 21.5; HRMS (APCI) calcd for $C_{21}H_{28}NO_4S$ $(M+H)^+$: 390.1739, found: 390.1724.

Compound **3q**



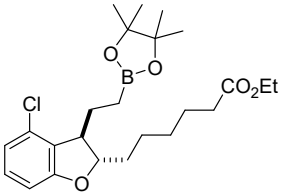
Following the typical procedure H, **1q** (100.0 mg, 0.289 mmol) was converted to **3q** (98.7 mg, 68%) after column chromatography on silica gel (*n*-hexane/AcOEt = 6/1). A colorless oil.; ^{1}H-NMR (400 MHz, CD_3OD) δ: 7.84-7.76 (m, 4H), 7.11 (d, *J* = 7.4 Hz, 1H), 7.02 (ddd, *J* = 7.8. 7.8, 0.9 Hz, 1H), 6.76 (ddd, *J* = 7.4, 7.4, 0.9 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 4.34 (dt, *J* = 7.2, 5.4 Hz, 1H), 3.67 (t, *J* = 7.1 Hz, 2H), 2.97 (dt, *J* = 7.2, 5.6 Hz, 1H), 1.79-1.38 (m, 8H), 1.24-1.19 (m, 12H), 0.78 (t, *J* = 8.0 Hz, 2H); ^{13}C-NMR (100 MHz, CD_3OD); 169.8, 160.5, 135.3, 133.4, 131.9, 129.1, 125.6, 124.1, 121.1, 110.2, 89.3, 84.5, 50.2, 38.6, 36.7, 30.4, 29.4, 25.2, 23.8; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; HRMS (APCI) calcd for $C_{28}H_{35}BNO_5$ $(M+H)^+$: 476.2608, found: 476.2603.

Compound **3r**



Following the typical procedure I, **1r** (35.0 mg, 0.114 mmol) was converted to **3r** (40.0 mg, 81%) after column chromatography on silica gel (*n*-hexane/AcOEt = 15/1). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ: 7.10-7.04 (m, 1H), 6.54-6.49 (m, 2H), 4.46 (dt, *J* = 7.8, 4.6 Hz, 1H), 4.10 (q, *J* = 7.0 Hz, 2H), 3.22 (dt, *J* = 7.8, 4.6 Hz, 1H), 2.31 (t, *J* = 7.3 Hz, 2H), 1.89-1.33 (m, 10H), 1.25-1.19 (m, 15H), 0.74 (t, *J* = 8.0 Hz, 2H); ^{13}C-NMR (100 MHz, CD_3OD); δ 175.5, 163.0 ($^3J_{CF}$ = 8.6 Hz), 161.4 ($^1J_{CF}$ = 241.5 Hz), 130.8 ($^3J_{CF}$ = 8.6 Hz), 117.9 ($^2J_{CF}$ = 21.1 Hz), 108.0 ($^2J_{CF}$ = 21.1 Hz), 106.5 ($^4J_{CF}$ = 2.9 Hz), 90.0, 84.5, 61.4, 48.4, 36.9, 35.0, 30.0, 29.2, 25.9 (overlapped), 25.2, 25.2, 14.6; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; ^{19}F-NMR (376 MHz, CD_3OD) −120.4; HRMS (APCI) calcd for $C_{24}H_{37}BFO_5$ $(M+H)^+$: 435.2718, found: 435.2704.

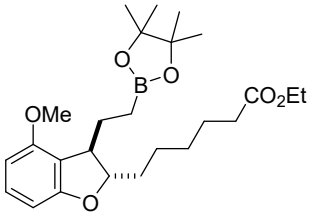
Compound **3s**



Following the typical procedure I, **1s** (35.0 mg, 0.108 mmol) was converted to

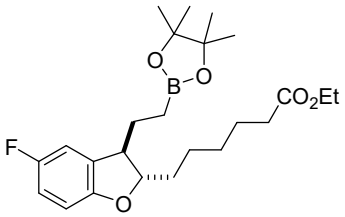
3s (24.3 mg, 50%) after column chromatography on silica gel (*n*-hexane/AcOEt = 15/1). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.01 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 4.50-4.46 (m, 1H), 4.11 (q, *J* = 7.0 Hz, 2H), 3.09 (dt, *J* = 8.7, 3.2 Hz, 1H), 2.28 (t, *J* = 7.3 Hz, 2H), 2.02-1.30 (m, 10H), 1.26-1.21 (m, 15H), 0.75 (t, *J* = 8.5 Hz, 2H); ^{13}C-NMR (125 MHz, CD_3OD); δ 175.5, 161.7, 131.9, 130.7, 129.6, 121.6, 109.1, 88.9, 84.5, 61.4, 50.1, 36.8, 35.0, 30.0, 27.9, 25.9, 25.8, 25.2, 25.2, 14.6; ^{11}B-NMR (160 MHz, $CDCl_3$) δ 33.0; HRMS (APCI) calcd for $C_{24}H_{37}BClO_5$ $(M+H)^+$: 451.2423, found: 451.2403.

Compound **3t**



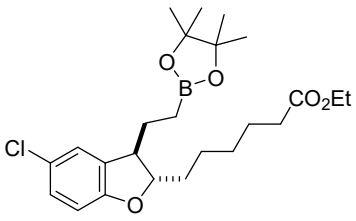
Following the typical procedure I **1t** (30.0 mg, 0.942 mmol) was converted to **3t** (29.1 mg, 69%) after column chromatography on silica gel (*n*-hexane/AcOEt = 15/1). A colorless oil; ^{1}H-NMR (500 MHz, CD_3OD) δ: 7.02 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.42 (d, *J* = 8.0 Hz, 1H), 6.31 (d, *J* = 8.0 Hz, 1H), 4.35 (dt, *J* = 7.3, 5.0 Hz, 1H), 4.09 (q, *J* = 7.3 Hz, 2H), 3.79 (s, 3H), 3.07 (dt, *J* = 7.3, 5.5 Hz, 1H), 2.29 (t, *J* = 7.4 Hz, 2H), 1.89-1.82 (m, 1H), 1.64-1.32 (m, 9H), 1.25-1.20 (m, 15H), 0.68 (t, *J* = 8.3 Hz, 2H); ^{13}C-NMR (125 MHz, CD_3OD); δ 175.5, 161.7, 158.6, 130.3, 118.0, 103.8, 103.6, 89.3, 84.4, 61.4, 55.7, 48.8, 37.0, 35.0, 30.1, 28.6, 26.0, 25.9, 25.2 (overlapped), 14.6; ^{11}B-NMR (160 MHz, CD_3OD) δ 33.0; HRMS (APCI) calcd for $C_{25}H_{40}BO_6$ $(M+H)^+$: 447.2918, found: 447.2902.

Compound **3u**



Following the typical procedure I, **1u** (35.0 mg, 0.114 mmol) was converted to **3u** (28.8 mg, 58%) after column chromatography on silica gel (*n*-hexane/AcOEt = 15/1). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ: 6.90-6.87 (m, 1H), 6.80-6.75 (m, 1H), 6.62-6.59 (m, 1H), 4.39 (dt, *J* = 7.4, 5.0 Hz, 1H), 4.10 (q, *J* = 7.0 Hz, 2H), 3.01 (dt, *J* = 7.4, 6.0 Hz, 1H), 2.31 (t, *J* = 7.3 Hz, 2H), 1.81-1.35 (m, 10H), 1.28-1.19 (m, 15H), 0.81-0.77 (m, 2H); ^{13}C-NMR (100 MHz, CD_3OD); δ 175.5, 164.7 ($^{1}J_{CF}$ = 241.5 Hz), 161.9 ($^{3}J_{CF}$ = 13.4 Hz), 127.9 ($^{4}J_{CF}$ = 2.9 Hz), 126.1 ($^{3}J_{CF}$ = 10.5 Hz), 107.3 ($^{2}J_{CF}$ = 23.0 Hz), 98.3 ($^{2}J_{CF}$ = 26.8 Hz), 91.1, 84.5, 61.4, 49.5, 37.0, 35.0, 30.6, 30.0, 26.0, 26.0, 25.2, 25.2, 14.6; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; ^{19}F-NMR (471 MHz, $CDCl_3$) −125.1; HRMS (APCI) calcd for $C_{24}H_{37}BFO_5$ $(M+H)^+$: 435.2718, found: 435.2709.

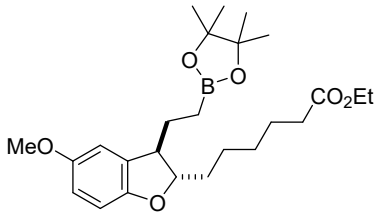
Compound **3v**



Following the typical procedure I, **1v** (35.0 mg, 0.108 mmol) was converted to **3v** (34.3 mg, 70%) after column chromatography on silica gel (*n*-hexane/AcOEt = 15/1). Colorless oil; ^{1}H-NMR (400 MHz,

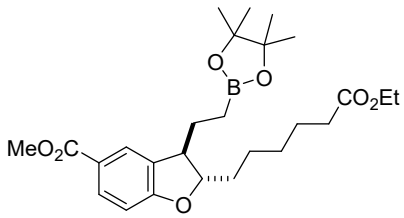
CD_3OD) δ: 7.12 (d, J = 1.9 Hz, 1H), 7.04 (dd, J = 8.7, 1.9 Hz, 1H), 6.64 (d, J = 8.7 Hz, 1H), 4.41 (dt, J = 7.3, 5.5 Hz, 1H), 4.10 (q, J = 7.0 Hz, 2H), 3.02 (dt, J = 7.3, 5.5 Hz, 1H), 2.31 (t, J = 7.3 Hz, 2H), 1.81-1.33 (m, 10H), 1.24-1.20 (m, 15H), 0.84-0.72 (m, 2H); ^{13}C-NMR (100 MHz, CD_3OD); δ 175.5, 159.4, 134.3, 128.9, 125.8, 125.6, 111.3, 90.3, 84.6, 61.4, 50.1, 36.9, 35.0, 30.2, 30.0, 26.0, 25.9, 25.2, 25.2, 14.6; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; HRMS (APCI) calcd for $C_{24}H_{37}BClO_5$ $(M+H)^+$: 451.2423, found: 451.2403.

Compound **3w**



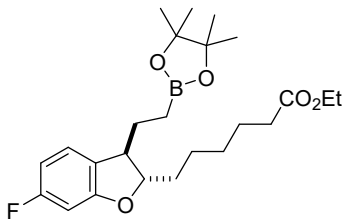
Following the typical procedure I **1w** (30.0 mg, 3.73 mmol) was converted to **3w** (28.6 mg, 68%) after column chromatography on silica gel (*n*-hexane/AcOEt = 15/1). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ: 6.74 (d, J = 2.7 Hz, 1H), 6.63 (dd, J = 8.6, 2.7 Hz, 1H), 6.56 (d, J = 8.6 Hz, 1H), 4.33 (dt, J = 7.5, 5.0 Hz, 1H), 4.10 (q, J = 7.2 Hz, 2H), 3.71 (s, 3H), 2.96 (dt, J = 7.5, 5.5 Hz, 1H), 2.30 (t, J = 7.6 Hz, 2H), 1.81-1.34 (m, 10H), 1.25-1.19 (m, 15H), 0.80 (t, J = 8.0 Hz, 2H); ^{13}C-NMR (100 MHz, CD_3OD); δ 174.2, 154.1, 153.3, 131.6, 112.8, 110.6, 108.7, 88.3, 83.2, 60.1, 55.1, 49.3, 35.7, 33.7, 28.9, 28.7, 24.8, 24.6, 23.9, 23.8, 13.2; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; HRMS (APCI) calcd for $C_{25}H_{40}BO_6$ $(M+H)^+$: 447.2918, found: 447.2919
.

Compound **3x**



Following the typical procedure I, **1x** (40.0 mg, 0.115 mmol) was converted to **3x** (35.2 mg, 64%) after column chromatography on silica gel (*n*-hexane/AcOEt = 10/1). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ: 7.84-7.81 (m, 2H), 6.74 (d, J = 8.7 Hz, 1H), 4.50 (dt, J = 7.3, 5.0 Hz, 1H), 4.10 (q, J = 7.2 Hz, 2H), 3.85 (s, 3H), 3.06 (dt, J = 7.3, 5.5 Hz, 1H), 2.31 (t, J = 7.6 Hz, 2H), 1.85-1.36 (m, 10H), 1.24-1.19 (m, 15H), 0.83-0.78 (m, 2H); ^{13}C-NMR (100 MHz, CD_3OD); δ 175.5, 168.7, 165.1, 132.8, 132.3, 127.6, 123.3, 110.1, 91.1, 84.6, 61.4, 52.3, 49.4, 37.0, 35.0, 30.4, 30.0, 25.9, 25.9, 25.2, 25.2, 14.6; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; HRMS (APCI) calcd for $C_{26}H_{40}BO_7$ $(M+H)^+$: 475.2867, found: 475.2850.

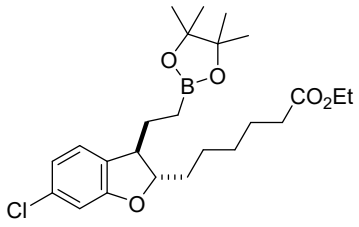
Compound **3y**



Following the typical procedure I, **1y** (40.0 mg, 0.131 mmol) was converted to **3y** (27.1 mg, 50%) after column chromatography on silica gel (*n*-hexane/AcOEt = 15/1). A colorless oil; ^{1}H-NMR (400 MHz,

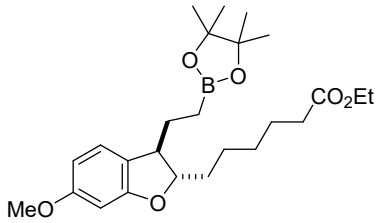
CD_3OD) δ: 7.11-7.07 (m, 1H), 6.53-6.48 (m, 1H), 6.43-6.40 (m, 1H), 4.43 (dt, J = 7.1, 5.5 Hz, 1H), 4.10 (q, J = 7.2 Hz, 2H), 2.96 (dt, J = 7.1, 6.0 Hz, 1H), 2.31 (t, J = 7.6 Hz, 2H), 1.79-1.33 (m, 10H), 1.25-1.21 (m, 15H), 0.80-0.76 (m, 2H); ^{13}C-NMR (100 MHz, CD_3OD); δ 175.5, 164.7 ($^1J_{CF}$ = 241.5 Hz), 161.9 ($^3J_{CF}$ = 13.4 Hz), 127.9 ($^4J_{CF}$ = 2.9 Hz), 126.1 ($^3J_{CF}$ = 10.5 Hz), 107.3 ($^2J_{CF}$ = 23.0 Hz), 98.3 ($^2J_{CF}$ = 26.8 Hz), 91.1, 84.5, 61.4, 49.5, 37.0, 35.0, 30.6, 30.0, 26.0, 26.0, 25.2, 25.2, 14.6; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; ^{19}F-NMR (376 MHz, CD_3OD) −116.7; HRMS (APCI) calcd for $C_{24}H_{37B}FO_5$ $(M+H)^+$: 435.2718, found: 435.2700.

Compound **3z**



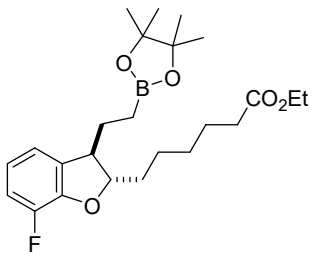
Following the typical procedure I, **1z** (35.0 mg, 0.108 mmol) was converted to **3z** (34.1 mg, 70%) after column chromatography on silica gel (*n*-hexane/AcOEt = 15/1). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ: 7.04 (d, J = 7.6 Hz, 1H), 6.78 (dd, J = 7.6, 1.8 Hz, 1H), 6.71 (d, J = 1.8 Hz, 1H), 4.41 (dt, J = 7.8, 5.0 Hz, 1H), 4.12 (q, J = 7.2 Hz, 2H), 2.92 (dd, J = 7.3, 5.5 Hz, 1H), 2.29 (t, J = 7.6 Hz, 2H), 1.81-1.31 (m, 10H), 1.27-1.23 (m, 15H), 0.87-0.78 (m, 2H); ^{13}C-NMR (100 MHz, CD_3OD); δ 175.5, 161.6, 134.4, 131.2, 126.5, 121.1, 110.7, 90.7, 84.5, 61.4, 49.6, 37.0, 35.0, 30.4, 30.0, 26.0, 25.9, 25.2, 25.2, 14.6; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; HRMS (APCI) calcd for $C_{24}H_{37}BClO_5$ $(M+H)^+$: 451.2423, found: 451.2403.

Compound **3aa**



Following the typical procedure I, **1aa** (30.0 mg, 0.942 mmol) was converted to **3aa** (17.1 mg, 41%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30 :1). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ: 7.00 (d, J = 8.2 Hz, 1H), 6.36 (dd, J = 8.2, 2.1 Hz, 1H), 6.27 (d, J = 2.1 Hz, 1H), 4.35 (dt, J = 7.3, 5.0 Hz, 1H), 4.10 (q, J = 7.0 Hz, 2H), 3.72 (s, 3H), 2.91 (dt, J = 7.3, 5.5 Hz, 1H), 2.31 (t, J = 7.6 Hz, 2H), 1.76-1.35 (m, 10H), 1.25-1.21 (m, 15H), 0.78 (t, J = 8.0 Hz, 2H); ^{13}C-NMR (100 MHz, CD_3OD); δ 175.5, 162.0, 161.8, 125.7, 124.0, 106.6, 96.8, 90.5, 84.5, 61.4, 55.8, 49.6, 37.1, 35.0, 30.7, 30.1, 26.1, 26.0, 25.2, 25.2, 14.6; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; HRMS (APCI) calcd for $C_{25}H_{40}BO_6$ $(M+H)^+$: 447.2918, found: 447.2920.

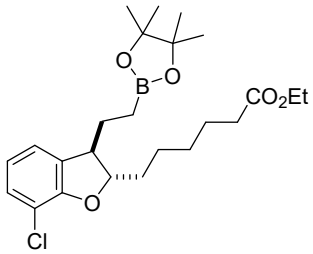
Compound **3ab**



Following the typical procedure I **1ab** (40.0 mg, 0.131 mmol) was converted to **3ab** (30.1 mg, 55%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30 :1). A colorless oil; ^{1}H-NMR (400 MHz,

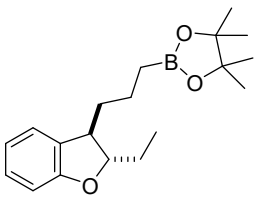
CD_3OD) δ: 6.95 (d, J = 7.3 Hz, 1H), 6.90-6.85 (m, 1H), 6.79-6.74 (m, 1H), 4.49 (dt, J = 7.3, 5.5 Hz, 1H), 4.10 (q, J = 7.2 Hz, 2H), 3.07 (dt, J = 7.3, 5.5 Hz, 1H), 2.31 (t, J = 7.3 Hz, 2H), 1.81-1.35 (m, 10H), 1.25-1.21 (m, 15H), 0.82-0.77 (m, 2H); ^{13}C-NMR (100 MHz, CD_3OD); δ 175.5, 148.9 ($^1J_{CF}$ = 243.4 Hz), 146.9 ($^3J_{CF}$ = 10.5 Hz), 136.0 ($^4J_{CF}$ = 2.9 Hz), 121.7 ($^3J_{CF}$ = 5.6 Hz), 121.2, 116.0 ($^2J_{CF}$ = 17.3 Hz), 91.2, 84.5, 61.4, 50.6, 36.9, 35.0, 30.3, 30.0, 26.0, 25.9, 25.2, 25.2, 14.6; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; ^{19}F-NMR (376 MHz, CD_3OD) −141.2; HRMS (APCI) calcd for $C_{24}H_{37}BFO_5$ $(M+H)^+$: 435.2718, found: 435.2704.

Compound **3ac**



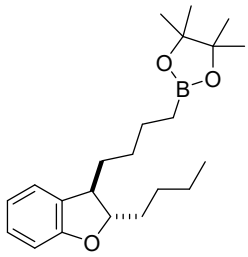
Following the typical procedure I, **1ac** (35.0 mg, 0.108 mmol) was converted to **3ac** (29.4 mg, 60%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30 :1). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ 7.09-7.07 (m, 2H), 6.78 (dd, J = 7.8, 7.8 Hz, 1H), 4.48 (dt, J = 7.3, 7.1 Hz, 1H), 4.10 (q, J = 7.2 Hz, 2H), 3.12-3.07 (m, 1H), 2.31 (t, J = 7.3 Hz, 2H), 1.82-1.34 (m, 10H), 1.25-1.21 (m, 15H), 0.82-0.77 (m, 2H); ^{13}C-NMR (100 MHz, CD_3OD); δ δ 175.6, 156.4, 134.1, 129.3, 124.2, 122.2, 115.8, 90.5, 84.5, 61.4, 50.8, 36.9, 35.0, 30.4, 30.0, 25.9 (overlapped), 25.2, 25.2, 14.6; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; HRMS (APCI) calcd for $C_{24}H_{37}BClO_5$ $(M+H)^+$: 451.2423, found: 451.2404.

Compound **3ad**



Following the typical procedure J, **1ad** (40.0 mg, 0.212 mmol) was converted to **3ad** (58.0 mg, 86%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30 :1). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ 7.11 (d, J = 7.4 Hz, 1H), 7.06-7.02 (m, 1H), 6.77 (ddd, J = 7.4, 7.4, 0.9 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 4.29 (dt, J = 6.4, 5.7 Hz, 1H), 3.01 (dt, J =6.4, 5.9 Hz, 1H), 1.69-1.42 (m, 6H), 1.22 (s, 12H), 1.00 (t, J = 7.4 Hz, 3H), 0.79-0.75 (m, 2H); ^{13}C-NMR (100 MHz, CD_3OD); δ 160.5, 132.2, 129.0, 125.5, 121.1, 110.1, 91.1, 84.3, 48.1, 39.1, 30.0 (over lapped), 25.2, 22.2, 10.0; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; HRMS (APCI) calcd for $C_{19}H_30BO_3$ $(M+H)^+$: 317.2288, found: 317.2281.

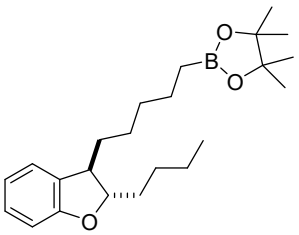
Compound **3ae**



Following the typical procedure J, **1ae** (30.0 mg, 0.130 mmol) was converted to **3ae** (36.5 mg, 78%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30 :1). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ 7.12 (d, J = 7.4 Hz, 1H),

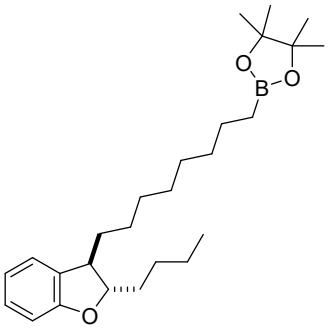
7.06-7.02 (m, 1H), 6.77 (ddd, *J* = 7.4, 7.4, 0.9 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 4.33 (dt, *J* = 7.5, 5.1 Hz, 1H), 2.99 (dt, *J* = 7.5, 5.7 Hz, 1H), 1.71-1.34 (m, 12H), 1.21 (s, 12H), 0.94-0.91 (m, 3H), 0.76-0.73 (m, 2H); ^{13}C-NMR (100 MHz, CD_3OD); δ 160.5, 132.2, 129.0, 125.6, 121.1, 110.1, 89.9, 84.3, 48.6, 37.0, 36.3, 30.2, 28.8 (over lapped), 25.2, 25.1, 23.7, 14.4; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; HRMS (APCI) calcd for $C_{22}H_{36}BO_3$ $(M+H)^+$: 359.2758, found: 359.2749.

Compound **3af**



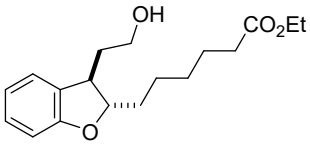
Following the typical procedure J, **1af** (50.0 mg, 0.204 mmol) was converted to **3af** ((53.7 mg, 71%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30 :1). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ 7.12 (d, *J* = 7.4 Hz, 1H), 7.05 (dd, *J* = 7.7, 7.7 Hz, 1H), 6.78 (dd, *J* = 7.4, 7.4 Hz, 1H), 6.66 (d, J = 7.7 Hz, 1H), 4.34 (dt, *J* = 7.4, 5.2 Hz, 1H), 3.01 (dt, *J* = 7.4, 5.7 Hz, 1H), 1.71-1.34 (m, 14H), 1.22 (s, 12H), 0.93 (t, J = 7.1 Hz, 3H), 0.72 (t, J = 7.3 Hz, 2H); ^{13}C-NMR (100 MHz, CD_3OD); δ 160.5, 132.2, 129.0, 125.6, 121.1, 110.1, 89.9, 84.3, 48.5, 37.0, 36.4, 33.3, 28.8, 27.6, 25.2 (over lapped), 24.9, 23.7, 14.4; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.1; HRMS (APCI) calcd for $C_{23}H_{38}BO_3$ $(M+H)^+$: 373.2914, found: 373.2903.

Compound **3ag**



Following the typical procedure M, **1ag** (50.0 mg, 0.175 mmol) was converted to **3ag** (35.9 mg, 50%) after column chromatography on silica gel (*n*-hexane/AcOEt = 30 :1). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ 7.12 (d, *J* = 7.4 Hz, 1H), 7.07-7.03 (dd, *J* = 7.9, 7.9 Hz, 1H), 6.78 (ddd, *J* = 7.4, 7.4, 0.8 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 1H), 4.35 (dt, *J* = 7.5, 5.2 Hz, 1H), 3.01 (dt, *J* = 7.5, 5.6 Hz, 1H), 1.69-1.28 (m, 20H), 1.22 (s, 12H), 0.93 (t, *J* = 7.1 Hz, 3H), 0.71 (t, *J* = 7.5 Hz, 2H); ^{13}C-NMR (100 MHz, CD_3OD); δ 160.5, 132.2, 129.0, 125.6, 121.1, 110.1, 89.9, 84.2, 48.3, 37.0, 36.5, 33.3, 30.7, 30.5, 30.4, 28.7, 27.8, 25.2 (overlapped), 25.0, 23.7, 14.4; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; HRMS (APCI) calcd for $C_{26}H_{44}BO_3$ $(M+H)^+$: 415.3384, found: 415.3384.

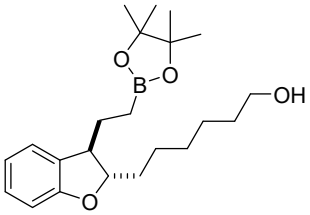
Preparation of compound **4**



To a vigorously stirred solution of **3l** (22.0 mg, 0.053 mmol) in THF/H_2O (0.4 mL each) at room temperature was added sodium perborate tetrahydrate (24.4 mg, 0.159 mmol, 3.0 eq.). After stirring for 4 h, the

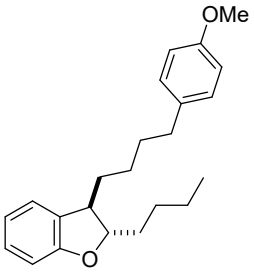
mixture was extracted three times with Et_2O. The combined organic portions were washed with brine, quickly dried over Na_2SO_4, filtered, and concentrated. Purification of the crude material by silica gel column chromatography (*n*-hexane/AcOEt = 4/1) gave **4** (14.6 mg, 0.048 mmol, 90%). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.16-7.10 (m, 2H), 6.84 (ddd, *J* = 7.3, 7.3, 0.9 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 4.45 (dt, *J* = 7.5, 5.0 Hz, 1H), 4.12 (q, *J* = 7.0 Hz, 2H), 3.80-3.76 (m, 2H), 3.22 (dt, *J* = 7.5, 6.0 Hz, 1H), 2.30 (t, *J* = 7.6 Hz, 2H), 2.02-1.83 (m, 2H), 1.77-1.34 (m, 7H), 1.28-1.23 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ 173.9, 159.1, 130.3, 128.2, 124.6, 120.1, 109.5, 88.7, 60.2, 44.1, 37.8, 35.5, 34.2, 28.9, 25.0, 24.8, 24.8, 14.2; HRMS (APCI) calcd for $C_{18}H_{27}O_4$ $(M+H)^+$: 307.1909, found: 307.1898.

Preparation of compound **5**



To a stirred solution of **3l** (30.0 mg, 0.072 mmol) in THF at –78 °C, was dropwised diisobutylaluminium hydride (0.99M, 109 μL, 0.108 mmol, 1.5 eq.). After stirring for 3 h, the mixture was quenched by MeOH and sat. potassium sodium (+)-tertrate aq. and extracted three times with AcOEt. The combined organic phase was washed with brine, quickly dried over Na_2SO_4, filtered, and concentrated. Purification of the crude material by silica gel column chromatography (*n*-hexane/AcOEt = 15/1) gave **5** (23.7 mg, 88%). A colorless oil; ^{1}H-NMR (400 MHz, CD_3OD) δ: δ 7.13 (d, *J* = 7.7 Hz, 1H), 7.05 (dd, *J* = 7.7, 7.7 Hz, 1H), 6.78 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 4.47 (dt, *J* = 7.3, 5.1 Hz, 1H), 3.53 (t, *J* = 6.6 Hz, 2H), 2.99 (dt, *J* = 7.3, 5.6 Hz, 1H), 1.81-1.37 (m, 12H), 1.24-1.23 (m, 12H), 0.81-0.78 (m, 2H); ^{13}C-NMR (100 MHz, CD_3OD); δ 160.6, 132.0, 129.1, 125.7, 121.1, 110.1, 99.9, 89.6, 84.5, 50.2, 37.8, 37.2, 30.5, 30.5, 26.4, 25.8, 25.2, 25.2; ^{11}B-NMR (128 MHz, CD_3OD) δ 33.0; HRMS (APCI) calcd for $C_{22}H_{36}O_4$ $(M+H)^+$: 375.2707, found: 375.2723.

Preparation of compound **6**

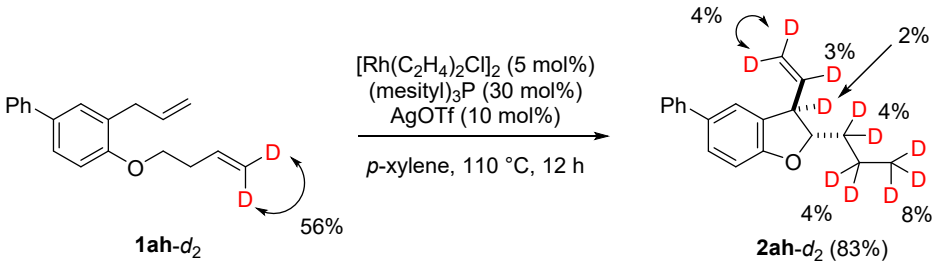


To a 10-mL vial containing **3ae** (40.0 mg, 0.107 mmol), RuPhos (3.01 mg, 6 mol%), 1-bromo-4-methoxybenzene)60.3 mg, 3.0 eq.) and *t*-BuONa (31.0 mg, 3.0 eq.) in Toluene/H_2O (10/1), was added Pd_2dba_3 (2.95 mg, 3 mol%) and stirred at 80 °C for 16 h. After being cooled to room temperature, the reaction mixture was filtered by short silica gel column chromatography and concentrated in vacuo to remove the solvent. The obtained residue was purified by flash column chromatography on silica gel (*n*-hexane/AcOEt = 15/1) to give **6** (33.2 mg, 87%). A colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.13-7.08 (m, 4H), 6.85-6.81 (m, 3H), 6.76 (d, *J* = 8.2 Hz, 1H), 4.36 (dt, *J* = 7.6, 5.0 Hz, 1H), 3.79 (s, 3H), 3.01 (dt, *J* = 7.6, 5.5 Hz, 1H), 2.57 (t, *J* = 7.6 Hz, 2H), 1.77-1.55 (m, 6H), 1.53-1.29 (m, 6H), 0.92 (t, *J* = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ 159.2, 157.7, 134.5, 131.0, 129.2, 128.0, 124.5, 119.9, 113.7, 109.4, 88.9, 55.2, 47.2, 35.8, 35.2, 34.8, 31.8, 27.5, 26.4, 22.6, 14.0; HRMS (APCI) calcd for $C_{23}H_{31}O_2$ $(M+H)^+$: 339.2324, found: 339.2316.

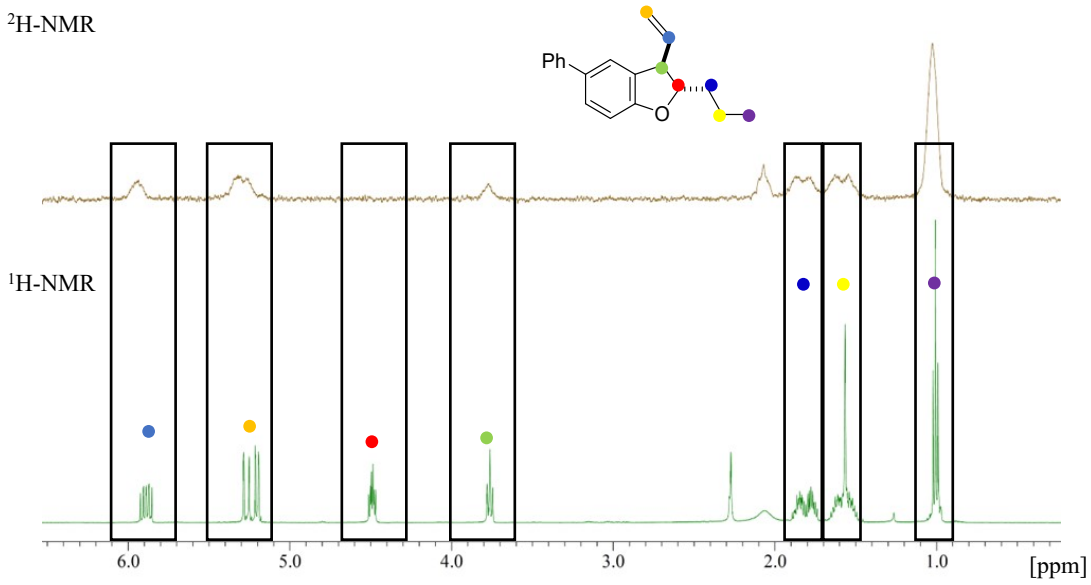
Deuterium labeling experiment (^{2}H-NMR)

In a glovebox, to an oven-dried 10-mL vial were added $[Rh(C_2H_4)_2Cl]_2$ (5 mol%), trimesitylphosphine (30 mol%) and anhydrous *p*-xylene (0.1 M). The resulting solution was stirred for 30 min at ambient temperature, then AgOTf (10 mol%) was added and the reaction mixture was stirred for 30 min. Next, diene **1**-*d* (1.0 eq.) was added, and the reaction mixture was sealed, removed from the glovebox and heated at 110 °C for 24 h. After being cooled to room temperature, the reaction mixture was filtered by short silica gel column chromatography (*n*-hexane/AcOEt = 10/1) and the filtrate was concentrated in vacuo to remove the solvent. The obtained residue was purified by flash column chromatography (*n*-hexane/AcOEt = 30/1) on silica gel to give corresponding 2,3-dihydrobenzofuran **2**-*d*. The resulting **2**-*d* was dissolved in CHCl3 and CDCl3 was added as an internal standard. Then, ^{2}H-NMR spectrum of the mixture was measured.

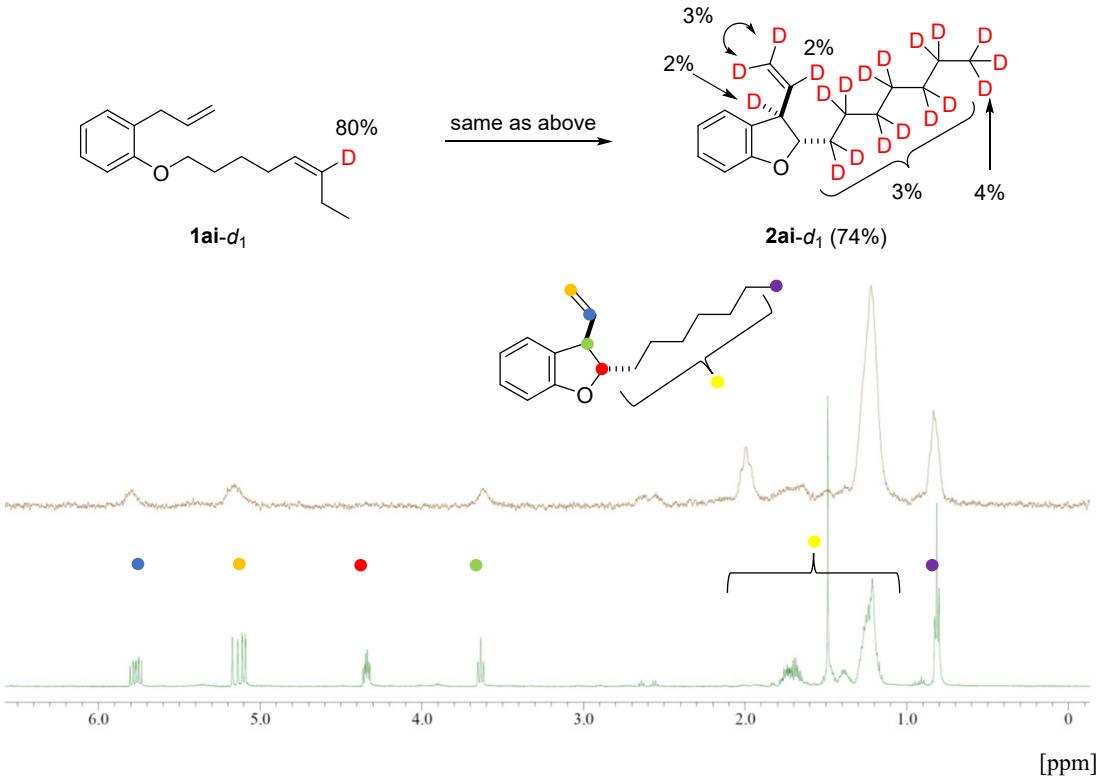
- **1ah**-d_2 to **2ah**-d_2



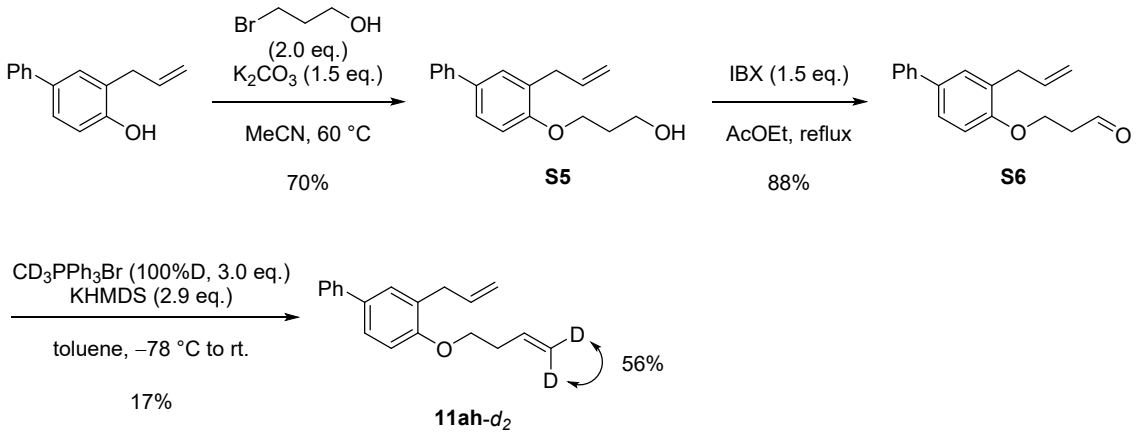
1ah-d_2 **2ah**-d_2 (83%)



• **1ai**-d_1 to **2ai**-d_1



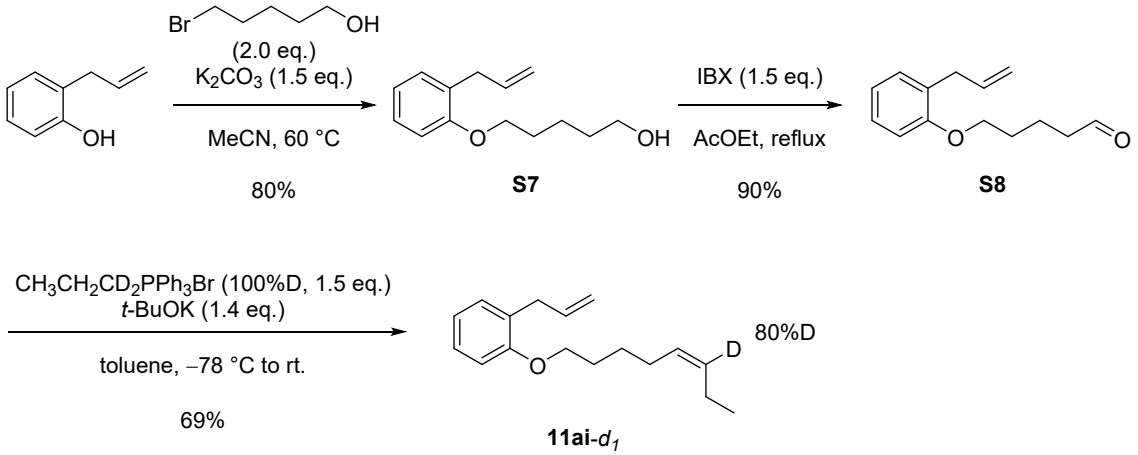
Preparation of **1ah**-d_2



3-Allyl-[1,1'-biphenyl]-4-ol was prepared according to the known literature.[9] To a round-bottom flask containing 3-bromopropan-1-ol (2.6 g, 19.0 mmol, 2.0 eq.) and K_2CO_3 (1.97 g 14.3 mmol, 1.5 eq.) in CH_3CN (0.5 M) was added 3-allyl-[1,1'-biphenyl]-4-ol (2.0 g, 9.5 mmol). The reaction mixture was stirred at 60 °C for 10 h. The mixture was filtered through a glass filter with AcOEt and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel using *n*-hexane/ AcOEt = 3/1 as an eluent to afford **S5** (1.98 g, 7.4 mmol, 78%). To a round-bottom

flask containing **S5** (1.0 g, 3.7 mmol) in AcOEt (0.1 M) was added IBX (1.6 g, 5.6 mmol). The reaction mixture was stirred for 5 h with heating under reflux. The mixture was filtered through a glass filter with AcOEt and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel using *n*-hexane/ AcOEt = 6/1 as an eluent to afford **S6** (620 mg, 3.3 mmol, 88%). To a suspension of (methyl-d_3)triphenylphosphonium bromide (prepared by known method[10], 100%D, 1.3 g, 3.5 mmol, 1.5 eq.) in toluene (12 mL), KHMDS (0.6 M in toluene, 3.3 mL, 1.4 eq.)) was slowly added and stirred for 30 min. Then, reaction mixture was cooled to –78 °C and the solution of **S6** (12 mL in toluene) was slowly added to the reaction mixture and stirred for 3 h. Afterwards, sat. NH_4Cl was added to quench the reaction and extracted with AcOEt. The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4. After evaporation, the residue was purified by column chromatography on silica gel (*n*-hexane/ AcOEt = 20/1) to afford **1ah**-d_2 (108 mg, 17%). A colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.56-7.52 (m, 2H), 7.43-7.38 (m, 4H), 7.31-7.28 (m, 1H), 6.86-6.95 (1H), 6.07-5.90 (m, 2H), 5.22-5.03 (m, 2.88H), 4.07 (t, J = 6.5 Hz, 2H), 3.45 (d, J = 6.9 Hz, 2H), 2.58 (dt, J = 6.5, 6.5 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ 156.1, 141.0, 136.9, 134.7, 133.5, 129.1, 128.6, 128.6, 126.7, 126.5, 125.8, 117.0, 115.6, 111.4, 67.4, 34.6, 33.8; HRMS (APCI) calcd for $C_{19}H_{19}D_2O$ $(M+H)^+$: 267.1718, found: 267.1704.

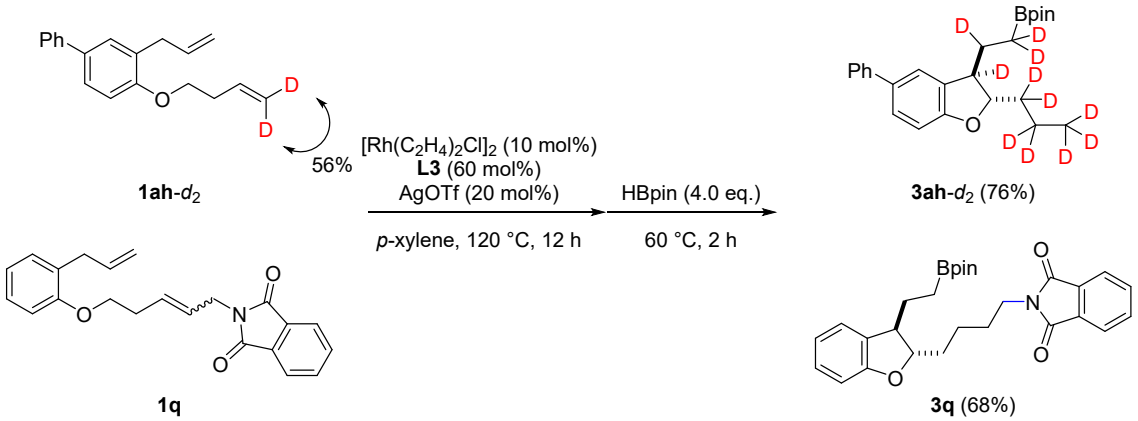
Preparation of **11ai**-d_1



To a round-bottom flask containing 5-bromopentan-1-ol (2.8 g, 16.8 mmol 1.5 eq.) and K_2CO_3 (2.3 g 16.8 mmol, 1.5 eq.) in CH_3CN (22.4 mL, 0.5 M) was added 2-allylphenol (1.5 g, 11.2 mmol). The reaction mixture was stirred at 60 °C for 10 h. The mixture was filtered through a glass filter with AcOEt and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel using *n*-hexane/ AcOEt = 3/1 as an eluent to afford **S7** (1.98 g, 11.2 mmol, 80%). To a round-bottom flask containing **S7** (1.0 g, 4.5 mmol) in AcOEt (0.1 M) was added IBX (2.5 g, 9.1 mmol). The reaction mixture was stirred for 5 h with heating under reflux. The mixture was filtered

through a glass filter with AcOEt, and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel using *n*-hexane/ AcOEt (6/1) as an eluent to afford **S8** (892 mg, 4.1 mmol, 90%). To a suspension of triphenyl(propyl-1,1-d_2)phosphonium bromide (prepared by known method[10], 100%D, 799 mg, 2.1 mmol, 1.5 eq.) in THF (12 mL), *t*-BuOK (232 mg, 2.1 mmol, 1.5eq.) was added and stirred for 30 min. Then, reaction mixture was cooled to 0 °C and **S8** (300 mg, 1.4 mmol) was added to the reaction mixture and warm up to rt. The reaction mixtures stirred for 3 h. Afterwards, sat. NH_4Cl was added to quench the reaction and extracted with AcOEt. The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4. After evaporation, the residue was purified by column chromatography on silica gel (*n*-hexane/ AcOEt = 20/1) to afford **11aj**-d_1 (181 mg, 69%). A colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.19-7.13 (m, 2H), 6.90-6.82 (m, 2H), 6.04-5.94 (m, 1H), 5.43-5.32 (m, 1.2H), 5.09-5.01 (m, 2H), 3.97 (t, *J* = 6.4 Hz, 2H), 3.39 (d, *J* = 6.4 Hz, 2H), 2.14-2.02 (m, 4H), 1.85-1.77 (m, 2H), 1.59-1.51 (m, 2H), 0.97 (t, *J* = 7.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ 156.7, 137.1, 132.1, 129.7, 128.8, 128.6, 127.2, 120.2, 115.3, 111.1, 67.7, 34.4, 29.0, 26.8, 26.3, 20.4, 14.3; HRMS (APCI) calcd for $C_{17}H_{24}DO$ $(M+H)^+$: 246.1968, found: 246.1957.

Crossover experiment

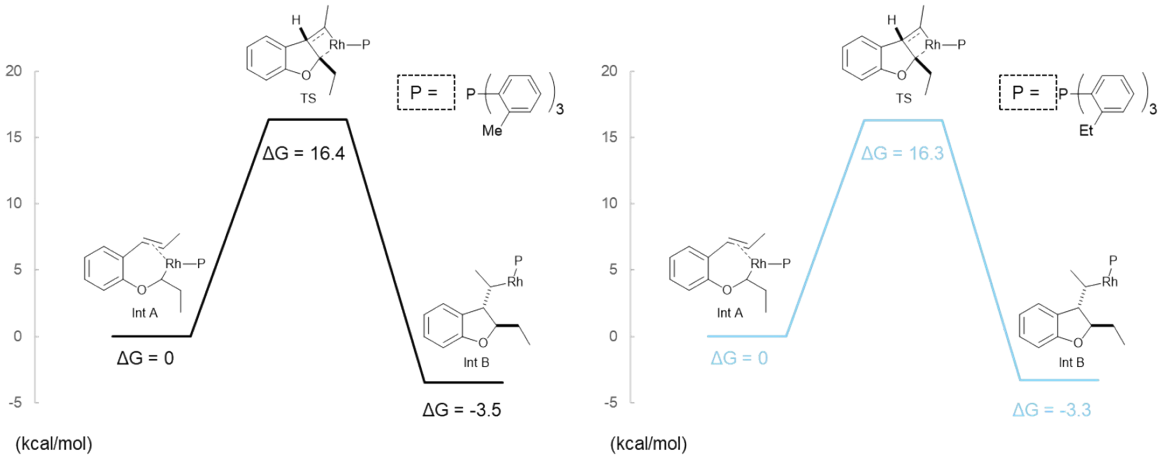


Only trace amounts of deuterium incorporation into **3q** were observed. This result suggested that the intermolecular transfer of rhodium hydride may be slow.

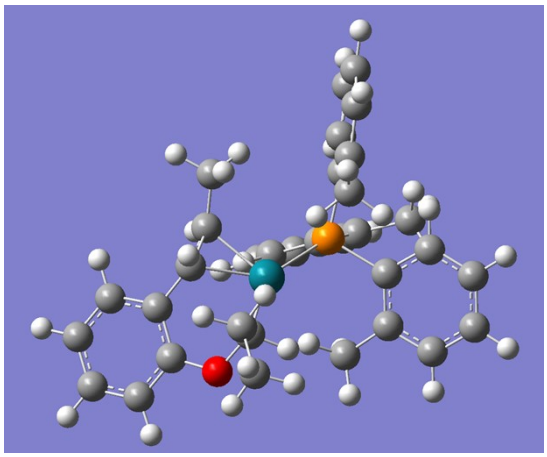
Computational studies

All calculations were carried with the Gaussian 16 program package.[11] Geometry optimizations were performed using density functional theory (DFT) with the RB3PW91-GD3BJ functional, and the basis sets SDD (for Rh) and 6-311++G(d,p) (for the other atoms) with the PCM solvation model in *p*-xylene. Harmonic vibrational analyses were performed at the same level of theory with the geometry optimization to confirm no imaginary vibration was observed for the optimized structure, and only a single imaginary vibration was observed for the transition state. Intrinsic reaction coordinate (IRC) method was used to track minimum energy paths from transition states to the corresponding local minima.

L1 with Me groups and **L2** with Et groups were compared to examine the influence of the substituent of the ligand. The cycloisomerization step was compared because chain walking proceeded in both cases using **L1** and **L2**, but cycloisomerization did not proceed in the case of **L2**. The calculation results showed no significant difference in the transition state energies.



Int A (**L1**)



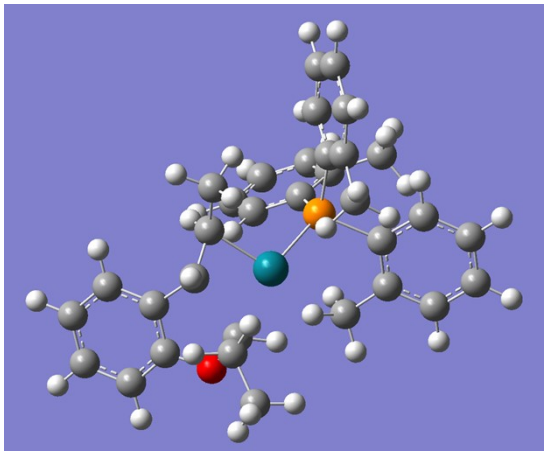
EE + Thermal Free Energy Correction = -1805.865416 Hartree

charge = 0, spin = 1

C	-5.490953	2.445526	0.375067
C	-5.921649	1.807101	-0.792343
C	-5.26917	0.664708	-1.245119
C	-4.182652	0.146368	-0.529137
C	-3.73828	0.761634	0.65965
C	-4.411537	1.920355	1.082657
O	-3.545557	-0.923823	-1.088594
C	-0.777588	0.760838	3.15461
C	-2.534341	-1.595229	-0.338298
C	-3.133933	-2.7142	0.50883
C	-3.776324	-3.832436	-0.329073
Rh	-0.967359	-0.454559	0.267572
P	1.358811	0.123374	-0.008696
H	-5.996083	3.33806	0.733735
H	-6.76434	2.201549	-1.354277
H	-5.575302	0.1623	-2.157824
H	-4.078524	2.403241	1.998432
H	0.286695	1.013247	3.122719
H	-1.249011	1.423536	3.897276
H	-0.869879	-0.267299	3.520614
H	-1.859328	-2.036148	-1.114388
H	-3.887595	-2.293526	1.186348
H	-2.33599	-3.129653	1.138
H	-4.205217	-4.608428	0.315665
H	-3.036407	-4.311368	-0.982797
H	-4.575224	-3.433034	-0.961876
C	-2.611779	0.196797	1.453109
H	-2.886434	-0.606438	2.139513
C	-1.447689	0.934427	1.806773
H	-1.371819	1.946462	1.40464
C	2.418987	-0.03886	1.505091
C	3.22215	1.038509	1.917178
C	2.313051	-1.178759	2.347759
C	3.943962	0.998452	3.109888
H	3.277162	1.930279	1.302433
C	3.058205	-1.198531	3.535518
C	3.869536	-0.132291	3.9201
H	4.556821	1.847925	3.398809
H	2.983016	-2.072103	4.178893
H	4.426677	-0.181925	4.851851
C	1.780226	1.776383	-0.751245
C	3.025484	2.154424	-1.318896
C	0.715229	2.693615	-0.770278
C	3.141443	3.445532	-1.855466
C	0.854576	3.971178	-1.311655
H	-0.244243	2.380343	-0.372082
C	2.079414	4.349438	-1.855525
H	4.094104	3.74352	-2.28733
H	0.011086	4.655892	-1.310822
H	2.211824	5.33991	-2.283042
C	2.026601	-1.103475	-1.241088
C	3.088821	-1.958533	-0.904847
C	1.430512	-1.215099	-2.523685
C	3.559225	-2.922612	-1.795212
H	3.568936	-1.857226	0.063122
C	1.921277	-2.192454	-3.402441

C	2.967591	-3.043924	-3.051511
H	4.38314	-3.569632	-1.506557
H	1.466927	-2.28055	-4.386569
H	3.318261	-3.792742	-3.75668
C	1.416544	-2.35469	2.038793
H	0.406664	-2.012284	1.754702
H	1.790808	-2.954672	1.20109
H	1.331561	-3.012797	2.909494
C	4.231289	1.244297	-1.405554
H	4.413534	0.699837	-0.475713
H	4.109515	0.495261	-2.195993
H	5.128966	1.82712	-1.635498
C	0.326891	-0.300772	-3.011135
H	-0.441662	-0.111976	-2.247768
H	0.723832	0.6813	-3.297364
H	-0.169716	-0.729137	-3.887391

TS (**L1**)

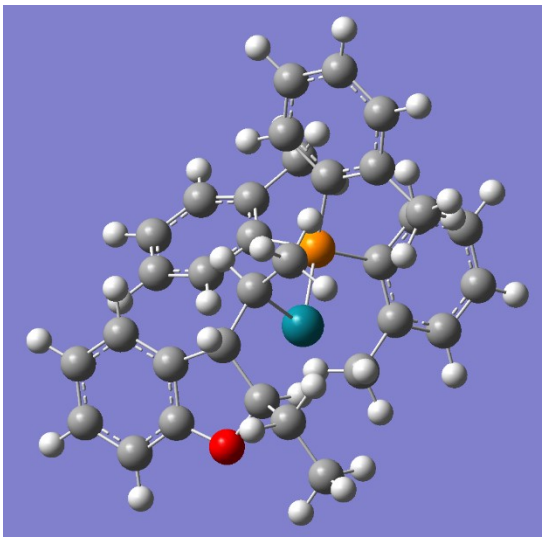


EE + Thermal Free Energy Correction = -1805.839354 Hartree

charge = 0, spin = 1

C	-5.523897	2.357289	0.688735
C	-5.952732	2.005581	-0.596071
C	-5.361795	0.94112	-1.277668
C	-4.340105	0.237158	-0.64257
C	-3.894395	0.563419	0.641559
C	-4.492825	1.641472	1.301654
O	-3.678419	-0.776454	-1.274243
C	-1.033847	0.017531	3.041853
C	-2.844571	-1.515211	-0.394088
C	-3.577127	-2.709219	0.215194
C	-3.987562	-3.750651	-0.834895
Rh	-0.793008	-0.560559	0.034003
P	1.375187	0.085637	-0.009146
H	-5.992196	3.186572	1.2111
H	-6.752263	2.56606	-1.073123
H	-5.674458	0.657556	-2.277673
H	-4.156358	1.913878	2.298894
H	-0.011337	0.379168	3.184547
H	-1.65645	0.467576	3.832104
H	-1.030324	-1.066995	3.19861
H	-2.033122	-1.916779	-1.031726
H	-4.468323	-2.358763	0.752108
H	-2.910459	-3.166862	0.957516
H	-4.520135	-4.58501	-0.364626
H	-3.11046	-4.160982	-1.350508
H	-4.645681	-3.307008	-1.588551
C	-2.784573	-0.278591	1.18543
H	-3.114624	-1.063516	1.86816
C	-1.558856	0.385666	1.66329
H	-1.553639	1.468351	1.496539
C	2.314382	-0.151332	1.578447
C	2.927125	0.95104	2.199111
C	2.290432	-1.396378	2.264597
C	3.541181	0.843069	3.446944
H	2.917189	1.915958	1.704038
C	2.924869	-1.481801	3.512346
C	3.549417	-0.385095	4.104275
H	4.007409	1.715603	3.896712

H	2.912261	-2.435667	4.034842
H	4.02578	-0.489298	5.07561
C	1.697708	1.85633	-0.512153
C	2.945318	2.419422	-0.890067
C	0.549494	2.667045	-0.54754
C	2.975355	3.771432	-1.265207
C	0.603834	4.008242	-0.92586
H	-0.403787	2.213427	-0.293405
C	1.828665	4.564466	-1.285679
H	3.929619	4.208407	-1.550797
H	-0.304218	4.60485	-0.942408
H	1.896578	5.607475	-1.584274
C	2.310129	-0.900105	-1.290504
C	3.449023	-1.645542	-0.945348
C	1.837541	-0.950729	-2.627339
C	4.114225	-2.44111	-1.877465
H	3.83348	-1.591032	0.068163
C	2.522051	-1.757452	-3.548498
C	3.644647	-2.501195	-3.188432
H	4.993555	-3.005301	-1.578103
H	2.16098	-1.796362	-4.573795
H	4.148092	-3.118413	-3.92789
C	1.586181	-2.620398	1.729126
H	0.568203	-2.363363	1.392753
H	2.099757	-3.049591	0.86112
H	1.523465	-3.396327	2.499175
C	4.248634	1.651614	-0.935095
H	4.39637	1.025611	-0.051634
H	4.293046	0.989704	-1.806936
H	5.093179	2.345257	-1.000619
C	0.656642	-0.143383	-3.119506
H	-0.196849	-0.174256	-2.42422
H	0.915462	0.91735	-3.227444
H	0.31773	-0.507291	-4.094734



Int B (**L1**)

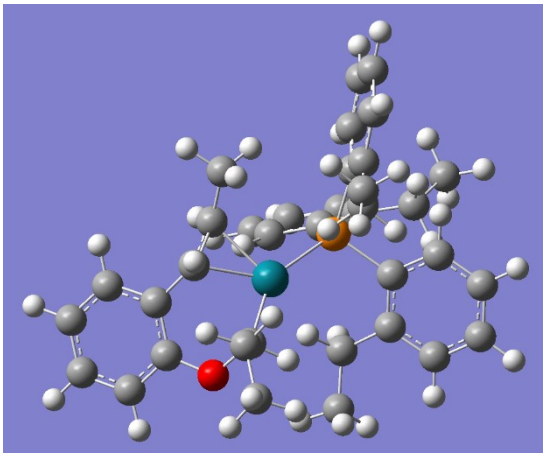
EE + Thermal Free Energy Correction = -1805.871038 Hartree

charge = 0, spin = 1

C	-4.104062	3.037598	0.738551
C	-4.792017	2.853176	-0.464737
C	-4.859592	1.593201	-1.073231
C	-4.217522	0.540763	-0.43213
C	-3.516679	0.701152	0.765052
C	-3.464605	1.955539	1.362224
O	-4.210028	-0.749395	-0.891825
C	-1.098438	-1.852172	2.458882
C	-3.327333	-1.527037	-0.047497
C	-3.981283	-2.870527	0.260883
C	-4.31125	-3.701146	-0.982474
Rh	-0.704932	-0.810628	-0.347519
P	1.324382	0.0632	-0.042008
H	-4.070942	4.021611	1.197972
H	-5.285461	3.697739	-0.938504
H	-5.393995	1.435073	-2.004591
H	-2.932739	2.098573	2.299695
H	-0.037474	-1.826103	2.722374

H	-1.674072	-1.812517	3.400137
H	-1.299408	-2.827383	1.998761
H	-2.424573	-1.758895	-0.684316
H	-4.89395	-2.667555	0.837676
H	-3.305161	-3.428233	0.920609
H	-4.780071	-4.650766	-0.702342
H	-3.403328	-3.93265	-1.553893
H	-4.997698	-3.161814	-1.642049
C	-2.974063	-0.644033	1.203714
H	-3.565569	-1.009279	2.064442
C	-1.467908	-0.684064	1.54099
H	-1.185807	0.255694	2.034259
C	2.229762	-0.33249	1.522652
C	2.452433	0.686754	2.464867
C	2.564482	-1.670236	1.863124
C	3.030117	0.420568	3.705843
H	2.16764	1.706006	2.224617
C	3.152061	-1.910049	3.113519
C	3.391889	-0.885862	4.02862
H	3.193179	1.230857	4.411285
H	3.4135	-2.932921	3.375029
H	3.845456	-1.111589	4.990119
C	1.320913	1.935118	-0.172134
C	2.437222	2.810962	-0.25282
C	0.027381	2.488319	-0.224325
C	2.192862	4.186863	-0.382227
C	-0.189759	3.859719	-0.352888
H	-0.821809	1.81216	-0.168227
C	0.904119	4.716092	-0.435521
H	3.046142	4.858603	-0.443029
H	-1.20664	4.240547	-0.383955
H	0.762969	5.789219	-0.536978
C	2.433706	-0.517935	-1.423474
C	3.81459	-0.695871	-1.256304
C	1.849028	-0.830657	-2.672978
C	4.622332	-1.142057	-2.303559
H	4.264467	-0.500765	-0.288271
C	2.675434	-1.258818	-3.719249
C	4.051252	-1.41075	-3.546255
H	5.688548	-1.279184	-2.144525
H	2.226052	-1.493176	-4.681497
H	4.667692	-1.752965	-4.373208
C	2.290574	-2.844957	0.953236
H	1.282628	-2.778597	0.519819
H	2.995175	-2.888827	0.115047
H	2.370952	-3.785122	1.508381
C	3.882097	2.367592	-0.218212
H	4.079698	1.660123	0.591744
H	4.175398	1.881289	-1.15457
H	4.538809	3.231307	-0.073572
C	0.354681	-0.776166	-2.888112
H	-0.151676	-1.508735	-2.206914
H	-0.067259	0.223208	-2.735278
H	0.081232	-1.101065	-3.897379

Int A (**L2**)



EE + Thermal Free Energy Correction = -1923.728057 Hartree

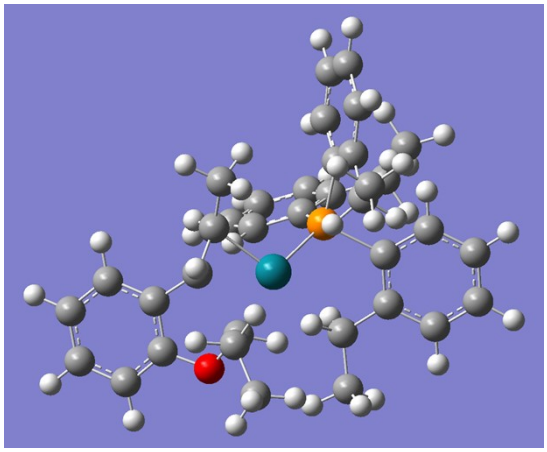
charge = 0, spin = 1

C	-5.520645	-1.687099	-2.195827

C	-5.966657	-2.079712	-0.929809	C	3.635051	2.943883	-2.785008
C	-5.363722	-1.565187	0.213719	H	4.379325	1.175965	-3.777767
C	-4.312101	-0.646904	0.100617	H	2.708016	4.499102	-1.646342
C	-3.85445	-0.221673	-1.163909	H	4.17281	3.641796	-3.421444
C	-4.476825	-0.769676	-2.29843	C	1.697649	-1.736769	-0.756529
O	-3.719821	-0.260121	1.268263	C	2.960294	-2.377339	-0.614287
C	-0.940545	1.685269	-2.854988	C	0.646037	-2.426749	-1.383242
C	-2.744798	0.782743	1.238157	C	3.097649	-3.672881	-1.133885
C	-3.401555	2.14912	1.416519	C	0.8095	-3.715249	-1.891206
C	-4.079362	2.323321	2.785905	H	-0.323281	-1.943358	-1.447713
Rh	-1.13697	0.46765	0.035663	C	2.046755	-4.338655	-1.766616
P	1.219695	-0.044934	-0.137313	H	4.051892	-4.180449	-1.042064
H	-5.987003	-2.085452	-3.092622	H	-0.024295	-4.220367	-2.370781
H	-6.782524	-2.79125	-0.831905	H	2.200708	-5.342984	-2.152918
H	-5.682283	-1.868394	1.206604	C	1.868999	0.006303	1.610537
H	-4.133072	-0.44879	-3.279029	C	2.917344	0.874882	1.952654
H	0.134536	1.534043	-2.990069	C	1.278557	-0.801866	2.6195
H	-1.393766	1.728662	-3.857865	C	3.384148	0.976486	3.262347
H	-1.087866	2.661934	-2.381545	H	3.388908	1.471523	1.178362
H	-2.086923	0.570634	2.117223	C	1.767954	-0.682632	3.928796
H	-4.145696	2.301646	0.624741	C	2.801174	0.195121	4.256824
H	-2.629767	2.917986	1.280694	H	4.196817	1.658606	3.497121
H	-4.548847	3.310539	2.868684	H	1.330804	-1.290791	4.713647
H	-3.351831	2.229073	3.602098	H	3.148338	0.261089	5.284618
H	-4.852603	1.563103	2.935605	C	1.149577	3.147899	0.125622
C	-2.767599	0.787381	-1.297099	H	0.200777	2.57997	0.081179
H	-3.089331	1.827114	-1.212777	H	1.552298	2.942343	1.126078
C	-1.57824	0.573726	-2.047022	C	4.137305	-1.725375	0.098676
H	-1.447956	-0.418234	-2.483578	H	4.16238	-0.661051	-0.150709
C	2.239019	1.167344	-1.105786	H	3.955446	-1.76226	1.180682
C	3.057464	0.698135	-2.146886	C	0.184602	-1.813611	2.305053
C	2.083761	2.5724	-0.926095	H	-0.495263	-1.396559	1.542535
C	3.753354	1.571471	-2.982526	H	0.642044	-2.683931	1.813095
H	3.144755	-0.369155	-2.318302	C	5.52186	-2.320425	-0.188062
C	2.806128	3.426149	-1.771886	H	5.743308	-2.334409	-1.261608

H	6.290706	-1.71578	0.304817
H	5.623646	-3.343287	0.190638
C	-0.661522	-2.29726	3.487582
H	-0.076574	-2.880793	4.207463
H	-1.121506	-1.459745	4.024835
H	-1.467443	-2.94165	3.121927
C	0.837975	4.644339	0.021769
H	1.722945	5.269361	0.189848
H	0.421032	4.905391	-0.957825
H	0.098312	4.918107	0.782033

TS (**L2**)



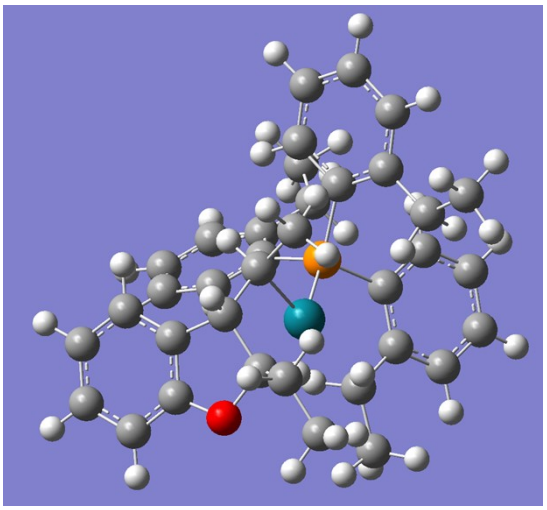
EE + Thermal Free Energy Correction = -1923.702129 Hartree

charge = 0, spin = 1

C	-5.568572	-1.730075	-2.152199
C	-6.00565	-2.22033	-0.916532
C	-5.462288	-1.736561	0.27414
C	-4.47971	-0.750847	0.198367
C	-4.027287	-0.239467	-1.021512
C	-4.577247	-0.747254	-2.2029
O	-3.863274	-0.276597	1.320634
C	-1.217625	1.746109	-2.574292
C	-3.069067	0.872168	1.062919
C	-3.859775	2.164721	1.257292
C	-4.310763	2.370532	2.709868
Rh	-0.978697	0.431181	0.197731
P	1.219739	-0.032374	-0.09898
H	-5.999569	-2.112434	-3.07303
H	-6.774185	-2.987739	-0.878854
H	-5.781963	-2.109379	1.242152
H	-4.234386	-0.365997	-3.161535
H	-0.178669	1.587081	-2.877147
H	-1.821502	1.821369	-3.493243
H	-1.272931	2.712787	-2.060871
H	-2.27349	0.854537	1.832287
H	-4.7376	2.161813	0.597901
H	-3.219717	2.998547	0.941033
H	-4.884837	3.298755	2.808994
H	-3.450112	2.434906	3.387189
H	-4.942316	1.541364	3.04391
C	-2.963418	0.808304	-0.940493
H	-3.336641	1.829583	-1.034179
C	-1.712187	0.610684	-1.692521
H	-1.65354	-0.358565	-2.199551
C	2.133291	1.117567	-1.242407
C	2.789716	0.587449	-2.36583
C	2.046046	2.533048	-1.098859
C	3.391614	1.407229	-3.320629
H	2.823847	-0.487448	-2.505791
C	2.671796	3.33269	-2.065982
C	3.341962	2.788853	-3.162065
H	3.893044	0.963328	-4.176481
H	2.623696	4.412132	-1.968963
H	3.810011	3.446052	-3.890476
C	1.613155	-1.75895	-0.707079
C	2.878586	-2.410386	-0.699963
C	0.488562	-2.460961	-1.173991
C	2.940483	-3.727473	-1.179296

C	0.577201	-3.770259	-1.646313
H	-0.475449	-1.962426	-1.137504
C	1.814774	-4.405223	-1.649265
H	3.89516	-4.242491	-1.187052
H	-0.313531	-4.282188	-2.000321
H	1.912247	-5.425976	-2.010471
C	2.11063	0.07668	1.541721
C	3.222977	0.91871	1.695065
C	1.633102	-0.647886	2.66783
C	3.862898	1.073066	2.924356
H	3.606816	1.454983	0.832983
C	2.294158	-0.477714	3.893242
C	3.391661	0.372206	4.03138
H	4.722012	1.733226	3.009633
H	1.944428	-1.023099	4.763517
H	3.874585	0.479032	4.99929
C	1.275698	3.174964	0.042272
H	0.313069	2.638753	0.1364
H	1.793704	2.979915	0.990216
C	4.144063	-1.745487	-0.175067
H	4.151617	-0.697087	-0.48587
H	4.09875	-1.719331	0.921157
C	0.468072	-1.621043	2.559991
H	-0.314601	-1.183009	1.913949
H	0.800415	-2.509258	2.004229
C	5.474673	-2.381849	-0.596672
H	5.56179	-2.457124	-1.686899
H	6.306239	-1.766843	-0.235943
H	5.609543	-3.385078	-0.177628
C	-0.178855	-2.070638	3.873895
H	0.503331	-2.666542	4.490993
H	-0.516476	-1.2166	4.472856
H	-1.052715	-2.694424	3.658132
C	1.008686	4.67938	-0.068947
H	1.930177	5.272858	-0.036944
H	0.47815	4.931355	-0.994784
H	0.384921	5.004164	0.771284

Int B (**L2**)



EE + Thermal Free Energy Correction = -1923.733395 Hartree

charge = 0, spin = 1

C	4.097478	3.250263	-1.102865
C	4.819618	3.17142	0.09188
C	4.962811	1.954678	0.771196
C	4.36011	0.836085	0.208734
C	3.626679	0.89063	-0.978419
C	3.499408	2.103237	-1.646403
O	4.425936	-0.423144	0.743725
C	1.306504	-1.87009	-2.469187
C	3.565111	-1.291466	-0.032635
C	4.278344	-2.617769	-0.277514
C	4.673617	-3.357187	1.003778
Rh	0.919965	-0.688227	0.289329
P	-1.166115	0.05036	0.000171
H	4.005617	4.202375	-1.61813
H	5.280635	4.065591	0.503165
H	5.524647	1.878447	1.696729

H	2.941079	2.164167	-2.577389	C	-3.559888	-0.798092	1.326491
H	0.240362	-1.911194	-2.709234	C	-1.564903	-0.698616	2.711468
H	1.85962	-1.853258	-3.424621	C	-4.320897	-1.226162	2.415568
H	1.566726	-2.807604	-1.962551	H	-4.036371	-0.69958	0.356437
H	2.688865	-1.528797	0.638309	C	-2.348565	-1.105834	3.798282
H	5.168153	-2.405623	-0.885857	C	-3.713586	-1.364087	3.660708
H	3.617365	-3.245126	-0.88818	H	-5.376895	-1.447614	2.286295
H	5.182828	-4.298096	0.768285	H	-1.885434	-1.240533	4.770032
H	3.789689	-3.597946	1.608095	H	-4.291536	-1.686751	4.522732
H	5.345933	-2.747901	1.615296	C	-1.933806	-2.96099	-0.805337
C	3.142747	-0.502977	-1.324749	H	-0.939245	-2.706465	-0.404745
H	3.734538	-0.889649	-2.175929	H	-2.60564	-2.933839	0.062124
C	1.633766	-0.636763	-1.623611	C	-3.832621	2.203512	0.156019
H	1.29357	0.25894	-2.160336	H	-3.916302	1.381755	-0.56149
C	-2.084599	-0.493892	-1.513672	H	-3.995284	1.749093	1.141022
C	-2.400567	0.46507	-2.490998	C	-0.06178	-0.52098	2.860997
C	-2.332187	-1.869465	-1.785307	H	0.417291	-1.268817	2.170212
C	-2.990991	0.107682	-3.702752	H	0.231446	0.483635	2.531764
H	-2.178245	1.510449	-2.303	C	-4.970704	3.194656	-0.11832
C	-2.937581	-2.198757	-3.00643	H	-4.849628	3.695714	-1.085703
C	-3.27165	-1.232134	-3.95556	H	-5.926657	2.659942	-0.136384
H	-3.22716	0.873161	-4.436969	H	-5.046691	3.9669	0.654977
H	-3.141851	-3.240582	-3.229779	C	0.54085	-0.771034	4.247152
H	-3.737243	-1.531516	-4.890987	H	0.133481	-0.077932	4.992132
C	-1.261976	1.928143	0.023124	H	0.358464	-1.793749	4.595756
C	-2.41716	2.758022	0.102928	H	1.624323	-0.618588	4.209362
C	0.005936	2.537653	-0.011494	C	-1.89904	-4.391163	-1.355399
C	-2.226119	4.147023	0.146197	H	-2.892881	-4.753866	-1.642757
C	0.167931	3.922237	0.030145	H	-1.243095	-4.473285	-2.229648
H	0.881777	1.896149	-0.065502	H	-1.516693	-5.070734	-0.585857
C	-0.959327	4.731409	0.112896				
H	-3.092835	4.796178	0.207004				
H	1.167197	4.346916	-0.004175				
H	-0.86435	5.813878	0.149522				
C	-2.193587	-0.513304	1.454386				

References

1. Sato, Y.; Matsuzaki, T.; Takehara, T.; Sako, M.; Suzuki, T.; Arisawa, M. *Chem. Commun.* **2022**, *58*, 415–418.
2. C. Souris, M. Luparia, F. Frébault, D. Audisio, C. Farès, R. Goddard, N. Maulide, *Chem. Eur. J.* **2013**, *19*, 6566–6570.
3. Porta, A.; Brunoldi, E.; Zanoni, G.; Vidari, G. *Tetrahedron* **2014**, *70*, 1484–1491.
4. Parsutkar, M. M.; Bhunia, S.; Majumder, M.; Lalisse, R. F.; Hadad, C. M.; RajanBabu, T. V. *J. Am. Chem. Soc.* **2023**, *145*, 7462–7481.
5. Qi, X.; Yu, F.; Chen, P.; Liu, G. *Angew. Chem. Int. Ed.* **2017**, *56*, 12692–12696.
6. Terada, Y.; Arisawa, M.; Nishida, A. *Angew. Chem. Int. Ed.* **2004**, *43*, 4063–4067.
7. Zhang, Y.; Torker, S.; Sigrist, M.; Bregović, N.; Dydio, P. *J. Am. Chem. Soc.* **2020**, *142*, 18251–18265.
8. Wang, J. P.; Song, S.; Wu, Y.; Wang, P. *Nat. Commun.* **2022**, *13* 1–10.
9. Xie, W. Bin; Li, Z. *ACS Catal.* **2021**, *11*, 6270–6275.
10. Yamamoto, M.; Oshima, K.; Matsubara, S. *Chem. Lett.* **2004**, *33*, 846–847.
11. Gaussian 16, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.