Supporting Information

Long-Range Isomerisation / Cyclopropane Isomerisation / Cycloisomerisation / Aromatisation Reactions Using Multifunctional Rhodium Catalysts

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Contents

1. 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%) and Ethyl acetate (anhydrous, ≥99.0%) were purchased from Nacalai tesque. Solvents were dehydrated by MS4A.

^{1}H, ^{13}C, ^{19}F NMR spectra were measured by JEOL ECS 300, JEOL JNM-ECS 400 or JEOL JNMLA 500 spectrometers. ^{1}H NMR spectra are reported as follows: chemical shift in ppm relative to the chemical shift for $CDCl_3$ at 7.26 ppm, acetone-d_6 at 2.04 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet,

sext = sextet, sept = septet, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra are reported as follows: chemical shift in ppm relative to the chemical shift of triplet for $CDCl_3$ at 77 ppm, septet for acetone-d_6 at 29.8 ppm, septet for acetonitrile-d_3 at 1.3 ppm, quintet for CD_2Cl_2 at 53.8 ppm. ^{19}F NMR spectra are reported as follows: chemical shift in ppm relative as internal standard to the chemical shift of singlet for (trifluoromethyl)benzene at -62.8 ppm.

Column chromatography on SiO_2 was performed with Fuji-silysia CHROMATOREX (PSQ100B, spherical, 100 μm or PSQ60B, spherical, 60 μm) and Kanto Chemical Silica Gel 60 (spherical, 63–210 μm or spherical, 40–50 μm).

MALDI-MS spectra were recorded with JMS-S3000 (JEOL).

ESI-MS and APCI-MS spectra were recorded on an Orbitrap XL (Thermo Fisher Scientific).

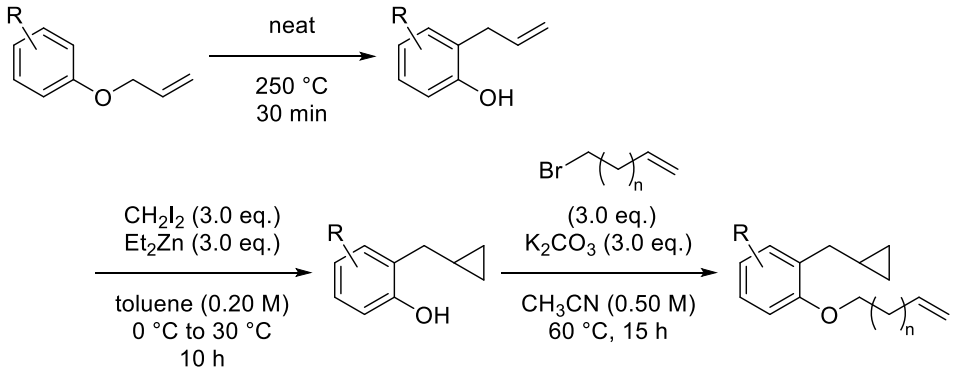
DART-MS spectra were recorded on an LTQ XL (Thermo Fisher Scientific).

Microwave heating reactions were carried out using a microwave generator (Anton Paar, Monowave 300).

2. Preparation of 1, 2, 3, 8 and 9

2-1. Preparation of substrate **1**

Substrates **1** were synthesized with reference to the reported procedure[1].



Typical procedure A: The reaction mixture of the cyclopropanation reaction was directly purified by silica gel column chromatography.

Allyloxybenzenes were synthesized following reported procedures.[2–5] An allyloxybenzene was put in a vial (Anton Paar). The sealed vial was then heated at 250 °C

under microwave irradiation for 30 min. After cooling to room temperature, the residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc = 10/1) to afford the corresponding 2-allylphenol.

To a round-bottom flask containing the 2-allylphenol and diiodomethane (3.0 eq.) in toluene (0.2 M) was slowly added diethyl zinc (3.0 eq, 1.09 M in hexane) at 0 °C. The mixture was stirred at 30 °C for 10 h. Saturated NH_4Cl aq. and 1 M HCl aq. were added to quench the reaction. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. After evaporation, the residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc = 10/1) to afford the corresponding 2-cyclopropylmethylphenol.

To a round-bottom flask containing the above obtained 2-cyclopropylmethylphenol and K_2CO_3 (3.0 eq.) in CH_3CN (0.5 M) was added the corresponding alkyl bromide (3.0 eq.). The reaction mixture was stirred at 60 °C for 15 h. The mixture was filtered through a glass filter, washed with EtOAc, and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on flash silica gel (*n*-hexane) to afford **1a**–**1h, 1j**–**1p** ,**1s**, **1u** and **1v**.

Typical procedure B: After the cyclopropanation reaction and before purification, dihydroxylation of the remaining substrate was performed.

Allyloxybenzenes were synthesized following reported procedures. [2–5] An allyloxybenzene was put in a vial (Anton Paar). The sealed vial was then heated at 250 °C under microwave irradiation for 30 min. After cooling to room temperature, the residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc = 10/1) to afford the corresponding 2-allylphenol.

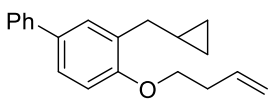
To a round-bottom flask containing the 2-allylphenol and diiodomethane (3.0 eq.) in toluene (0.2 M) was slowly added diethyl zinc (3.0 eq, 1.09 M in hexane) at 0 °C. The mixture was stirred at 30 °C for 10 h. Saturated NH_4Cl aq. and 1 M HCl aq. were added to quench the reaction. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. After evaporation, the residue was filtered by short silica gel column chromatography.

Subsequently, dihydroxylation of the remaining alkenes in the crude mixture was conducted to facilitate the isolation of the corresponding 2-cyclopropylmethylphenol. The concentrated crude material was dissolved into acetone/water = 1/1 (0.20 M),

OsO_4K_2•H_2O (1.0 mol%) and NMO (1.0 eq.) were added. The resulting mixture was stirred at room temperature for 15 h and subsequently concentrated in vacuo to remove acetone. The mixture was extracted three times with EtOAc, and combined organic layers were washed with brine, dried over anhydrous Na_2SO_4. After evaporation, the residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc = 10/1) to afford the corresponding 2-cyclopropylmethylphenol.

To a round-bottom flask containing the above obtained 2-cyclopropylmethylphenol and K_2CO_3 (3.0 eq.) in CH_3CN (0.5 M) was added the corresponding alkyl bromide (3.0 eq.). The reaction mixture was stirred at 60 °C for 15 h. The mixture was filtered through a glass filter, washed with EtOAc, and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on flash silica gel (*n*-hexane) to afford **1i**, **1q**, **1r** and **1t**.

Compound **1a**



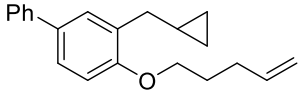
Following the typical procedure A, 1-allyloxy-4-phenylbenzene[2] (4.31 g, 20.5 mmol) was converted to **1a** (2.56 g, 45%) after column chromatography on flash silica gel (*n*-hexane). A colorless oil.

^{1}H NMR (301 MHz, $CDCl_3$) δ: 7.59–7.54(m, 2H), 7.52 (d, J = 2.3 Hz, 1H), 7.44–7.37 (m, 3H), 7.30 (m, 1H), 6.90 (d, J = 8.7 Hz, 1H), 5.94 (m, 1H), 5.22–5.09 (m, 2H), 4.07 (t, J = 6.4 Hz, 2H), 2.62–2.55 (m, 4H), 1.08 (m, 1H), 0.51 (ddd, J = 8.0, 5.7, 4.1 Hz, 2H), 0.22 (ddd, J = 6.0, 4.6, 4.6 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 156.2, 141.2, 134.7, 133.3, 131.1, 128.6, 128.4, 126.8, 126.5, 125.5, 117.0, 111.1, 67.2, 34.6, 33.9, 10.6, 4.7.

HRMS (MALDI) *m/z* calcd for $C_{20}H_{22}O$ ($[M]^+$): 278.1665, found 278.1667.

Compound **1b**



To a round-bottom flask containing 2-(cyclopropylmethyl)-4-phenylphenol (400 mg, 1.78 mmol) and K_2CO_3 (493 mg, 3.57 mmol, 2.0 eq.) in CH_3CN (3.6 mL, 0.50 M) was added 5-bromopent-1-ene (843 μL, 1.40 mmol, 4.0 eq.). The reaction mixture was stirred at 60 °C for 15 h. The mixture was filtered through a glass filter, washed with EtOAc, and the filtrate was concentrated under reduced pressure. The crude residue was purified by

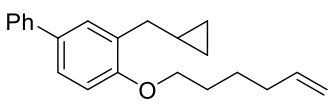
column chromatography on flash silica gel (*n*-hexane) to afford **1b** (442 mg, 85%). A colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.59–7.55 (m, 2H), 7.53 (d, J = 2.3 Hz, 1H), 7.44–7.38 (m, 3H), 7.30 (m, 1H), 6.90 (d, J = 8.4 Hz, 1H), 5.89 (m, 1H), 5.11–5.00 (m, 2H), 4.03 (t, J = 6.3 Hz, 2H), 2.61 (d, J = 6.9 Hz, 2H), 2.32–2.26 (m, 2H), 1.97–1.90 (m, 2H), 1.09 (m, 1H), 0.52 (ddd, J = 8.0, 5.6, 4.2 Hz, 2H), 0.25–0.21 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 156.3, 141.3, 137.9, 133.2, 131.0, 128.6, 128.4, 126.8, 126.5, 125.5, 115.2, 111.0, 67.1, 34.6, 30.3, 28.6, 10.6, 4.7.

HRMS (MALDI) *m*/*z* calcd for $C_{21}H_{24}O$ ($[M]^+$): 292.1822, found 292.1826.

Compound **1c**



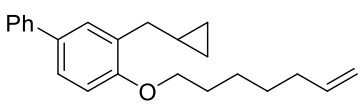
To a round-bottom flask containing 2-(cyclopropylmethyl)-4-phenylphenol (350 mg, 1.56 mmol) and K_2CO_3 (431 mg, 3.12 mmol, 2.0 eq.) in CH_3CN (3.1 mL, 0.50 M) was added 6-bromohex-1-ene (190 μL, 1.4 mmol, 0.90 eq.). The reaction mixture was stirred at 60 °C for 15 h. The mixture was filtered through a glass filter, washed with EtOAc, and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on flash silica gel (*n*-hexane) to afford **1c** (335 mg, 70%). A colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59–7.51 (m, 3H), 7.45 –7.38 (m, 3H), 7.30 (m, 1H), 6.90 (d, J = 8.7 Hz, 1H), 5.85 (m, 1H), 5.09–4.96 (m, 2H), 4.02 (t, J = 6.4 Hz, 2H), 2.60 (d, J = 6.9 Hz, 2H), 2.19–2.11 (m, 2H), 1.89–1.80 (m, 2H), 1.61 (tt, J = 7.3, 7.3 Hz, 2H), 1.08 (m, 1H), 0.55–0.48 (m, 2H), 0.22 (ddd, J = 6.0, 4.6, 4.6 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 156.4, 141.3, 138.6, 133.1, 131.0, 128.6, 128.4, 126.8, 126.4, 125.5, 114.7, 111.0, 67.7, 34.6, 33.4, 28.8, 25.4, 10.6, 4.7.

HRMS (MALDI) *m*/*z* calcd for $C_{22}H_{26}O$ ($[M]^+$): 306.1978, found 306.1979.

Compound **1d**



To a round-bottom flask containing 2-(cyclopropylmethyl)-4-phenylphenol (350 mg, 1.56 mmol) and K_2CO_3 (431 mg, 3.12 mmol, 2.0 eq.) in CH_3CN (3.1 mL, 0.50 M) was added 7-bromohept-1-ene (290 μL, 1.87 mmol, 0.90 eq.). The reaction mixture was stirred at 60 °C for 15 h. The mixture was filtered through a glass

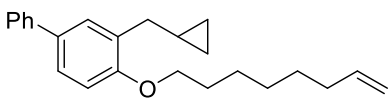
filter, washed with EtOAc, and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on flash silica gel (*n*-hexane) to afford **1d** (427 mg, 85%). A colorless oil.

^{1}H NMR (301 MHz, $CDCl_3$) δ: 7.61–7.51 (m, 3H), 7.44–7.38 (m, 3H), 7.29 (m, 1H), 6.89 (d, J = 8.6 Hz, 1H), 5.83 (m, 1H), 5.06–4.94 (m, 2H), 4.01 (t, J = 6.4 Hz, 2H), 2.60 (d, J = 6.9 Hz, 2H), 2.14–2.07 (m, 2H), 1.83 (tt, J = 6.5, 6.5 Hz, 2H), 1.54–1.48 (m, 4H), 1.08 (m, 1H), 0.54–0.48 (m, 2H), 0.25–0.20 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 156.4, 141.3, 138.8, 133.1, 131.0, 128.6, 128.4, 126.8, 126.4, 125.5, 114.4, 111.0, 67.8, 34.6, 33.7, 29.2, 28.6, 25.7, 10.6, 4.7.

HRMS (MALDI) *m*/*z* calcd for $C_{23}H_{28}O$ ($[M]^+$): 320.2135, found 320.2134.

Compound **1e**



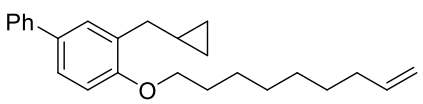
To a round-bottom flask containing 2-(cyclopropylmethyl)-4-phenylphenol (340 mg, 1.69 mmol) and K_2CO_3 (418 mg, 3.39 mmol, 2.0 eq.) in CH_3CN (3.0 mL, 0.50 M) was added 8-bromooct-1-ene (304 μL, 2.03 mmol, 1.2 eq.). The reaction mixture was stirred at 60 °C for 15 h. The mixture was filtered through a glass filter, washed with EtOAc, and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on flash silica gel (*n*-hexane) to afford **1e** (376 mg, 75%). A colorless oil.

^{1}H NMR (301 MHz, $CDCl_3$) δ: 7.59–7.50 (m, 3H), 7.45–7.37 (m, 3H), 7.30 (m, 1H), 6.90 (d, J = 8.6 Hz, 1H), 5.83 (m, 1H), 5.05–4.92 (m, 2H), 4.00 (t, J = 6.4 Hz, 2H), 2.60 (d, J = 6.9 Hz, 2H), 2.12–2.03 (m, 2H), 1.88–1.77 (m, 2H), 1.56–1.36 (m, 6H), 1.07 (m, 1H), 0.55–0.47 (m, 2H), 0.22 (ddd, J = 5.9, 4.8 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, Acetonitrile-d_3) δ: 157.5, 141.8, 140.1, 133.6, 131.8, 129.7, 129.1, 127.5, 127.4, 126.4, 114.8, 112.4, 68.8, 35.3, 34.4, 30.0, 29.6, 29.5, 26.7, 11.7, 5.1.

HRMS (MALDI) *m*/*z* calcd for $C_{24}H_{30}O$ ($[M]^+$): 334.2291, found 334.2290.

Compound **1f**



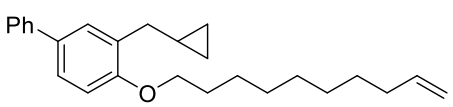
To a round-bottom flask containing 2-(cyclopropylmethyl)-4-phenylphenol (350 mg, 1.56 mmol) and K_2CO_3 (431 mg, 3.12 mmol, 2.0 eq.) in CH_3CN (3.1 mL, 0.50 M) was added 9-bromonon-1-ene (257 µL, 1.40 mmol, 0.90 eq.). The reaction mixture was stirred at 60 °C for 15 h. The mixture was filtered through a glass filter, washed with EtOAc, and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on flash silica gel (*n*-hexane) to afford **1f** (357 mg, 73%). A colorless oil.

^{1}H NMR (301 MHz, $CDCl_3$) δ: 7.60–7.54 (m, 2H), 7.52 (d, J = 2.4 Hz, 1H), 7.46–7.37 (m, 3H), 7.30 (m, 1H), 6.90 (d, J = 8.6 Hz, 1H), 5.83 (m, 1H), 5.06–4.92 (m, 2H), 4.01 (t, J = 6.5 Hz, 2H), 2.61 (d, J = 6.9 Hz, 2H), 2.07 (dt, J = 6.9, 6.9 Hz, 2H), 1.83 (tt, J = 6.5, 6.5 Hz, 2H), 1.56–1.30 (m, 8H), 1.09 (m, 1H), 0.52 (ddd, J = 7.9, 5.6, 4.1 Hz, 2H), 0.23 (ddd, J = 5.6, 4.8, 4.8 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 156.5, 141.3, 139.1, 133.1, 131.0, 128.6, 128.3, 126.8, 126.4, 125.5, 114.2, 111.0, 67.9, 34.6, 33.8, 29.3, 29.2, 29.0, 28.8, 26.1, 10.6, 4.7.

HRMS (MALDI) *m*/*z* calcd for $C_{25}H_{32}O$ ($[M]^+$): 348.2448, found 348.2444.

Compound **1g**



To a round-bottom flask containing 2-(cyclopropylmethyl)-4-phenylphenol (300 mg, 1.34 mmol) and K_2CO_3 (370 mg, 2.67 mmol, 2.0 eq.) in CH_3CN (2.7 mL, 0.50 M) was added 10-bromodec-1-ene (240 µL, 1.20 mmol, 0.90 eq.). The reaction mixture was stirred at 60 °C for 15 h. The mixture was filtered through a glass filter, washed with EtOAc, and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on flash silica gel (*n*-hexane) to afford **1g** (386 mg, 80%). A colorless oil.

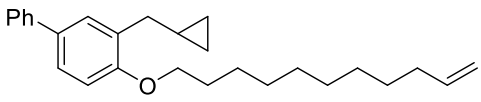
^{1}H NMR (301 MHz, $CDCl_3$) δ: 7.59–7.54 (m, 2H), 7.52 (d, J = 2.4 Hz, 1H), 7.45–7.37 (m, 3H), 7.31 (m, 1H), 6.90 (d, J = 8.3 Hz, 1H), 5.82 (m, 1H), 5.04–4.90 (m, 2H), 4.00 (t, J = 6.5 Hz, 2H), 2.60 (d, J = 6.9 Hz, 2H), 2.05 (dt, J = 7.2, 7.2 Hz, 2H), 1.82 (tt, J = 6.5, 6.5 Hz, 2H), 1.53–1.28 (m, 10H), 1.08 (m, 1H), 0.51 (ddd, J = 7.9, 5.8, 4.1 Hz, 2H), 0.22 (ddd, J = 5.6, 4.1, 4.1 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 156.5, 141.3, 139.2, 133.1, 131.0, 128.6, 128.3,

126.8, 126.4, 125.5, 114.1, 111.0, 67.9, 34.6, 33.8, 29.4, 29.35, 29.30, 29.1, 28.9, 26.1, 10.6, 4.7.

HRMS (MALDI) *m*/*z* calcd for $C_{26}H_{34}O$ ([M]$^+$): 362.2604, found 362.2602.

Compound **1h**



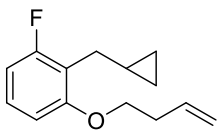
To a round-bottom flask containing 2-(cyclopropylmethyl)-4-phenylphenol (300 mg, 1.33 mmol) and K_2CO_3 (372 mg, 2.67 mmol, 2.0 eq.) in CH_3CN (2.7 mL, 0.50 M) was added 11-bromoundec-1-ene (347 µL, 1.60 mmol, 0.90 eq.). The reaction mixture was stirred at 60 °C for 15 h. The mixture was filtered through a glass filter, washed with EtOAc, and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on flash silica gel (*n*-hexane) to afford **1h** (360 mg, 72%). A colorless oil.

^{1}H NMR (301 MHz, $CDCl_3$) δ: 7.59–7.54 (m, 2H), 7.52 (d, J = 2.4 Hz, 1H), 7.54–7.37 (m, 3H), 7.30 (m, 1H), 6.90 (d, J = 8.3 Hz, 1H), 5.82 (m, 1H), 5.04–4.90 (m, 2H), 4.00 (t, J = 6.5 Hz, 2H), 2.60 (d, J = 6.9 Hz, 2H), 2.05 (dt, J = 6.8, 6.8 Hz, 2H), 1.82 (tt, J = 6.5, 6.5 Hz, 2H), 1.53–1.25 (m, 12H), 1.08 (m, 1H), 0.51 (ddd, J = 7.9, 5.9, 4.5 Hz, 2H), 0.22 (ddd, J = 5.9, 4.5, 4.5 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 156.5, 141.3, 139.2, 133.1, 131.0, 128.6, 128.3, 126.8, 126.4, 125.5, 114.1, 111.0, 67.9, 34.6, 33.8, 29.5, 29.4, 29.3 (overlapped), 29.1, 28.9, 26.2, 10.6, 4.7.

HRMS (MALDI) *m*/*z* calcd for $C_{28}H_{36}O$ ([M]$^+$): 376.2761, found 376.2775.

Compound **1i**



Following the typical procedure B, 1-allyloxy-3-fluorobenzene[3] (5.33 g, 35.0 mmol) was converted to **1i** (184 mg, 2.4%) after column chromatography on flash silica gel (*n*-hexane). A colorless oil

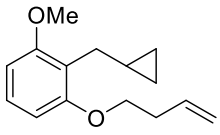
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.09 (m, 1H), 6.70–6.61 (m, 2H), 5.91 (m, 1H), 5.21–5.08 (m, 2H), 4.02 (t, J = 6.5 Hz, 2H), 2.61–2.53 (m, 4H), 1.02 (m, 1H), 0.38 (ddd, J = 8.1, 5.1, 4.2 Hz, 2H), 0.25–0.19 (m, 2H).

^{13}C{^{1}H, ^{19}F} NMR (126 MHz, $CDCl_3$) δ: 161.7, 158.0, 134.5, 126.9, 118.1, 117.1, 107.7, 106.7, 67.6, 33.8, 27.0, 10.9, 4.5.

^{19}F NMR (471 MHz, $CDCl_3$) δ: -117.3.

HRMS (ESI) *m*/*z* calcd for $C_{14}H_{17}FNaO$ ($[M+Na]^+$): 243.1156, found 243.1153.

Compound **1j**



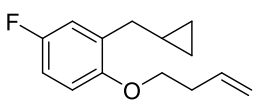
Following the typical procedure A, 1-allyloxy-3-methoxybenzene[3] (2.73 g, 16.6 mmol) was converted to **1j** (200 mg, 5.2%) after column chromatography on flash silica gel (*n*-hexane/EtOAc = 10/1). A colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.11 (dd, J = 8.2, 8.2 Hz, 1H), 6.56–6.51 (m, 2H), 5.92 (m, 1H), 5.20–5.07 (m, 2H), 4.01 (t, J = 6.6 Hz, 2H), 3.81 (s, 3H), 2.61–2.51 (m, 4H), 1.01 (m, 1H), 1.07–0.96 (m, 2H), 0.24–0.19 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 158.4, 157.5, 134.8, 126.6, 119.0, 116.9, 104.5, 103.6, 67.4, 55.6, 34.0, 27.2, 10.8, 4.4.

HRMS (ESI) *m*/*z* calcd for $C_{15}H_{21}O_2$ ($[M+H]^+$): 233.1536, found 233.1535.

Compaund **1k**



Following the typical procedure A, 1-allyloxy-4-fluorobenzene[3] (522 mg, 3.43 mmol) was converted to **1k** (273 mg, 36%) after column chromatography on flash silica gel (*n*-hexane). A colorless oil

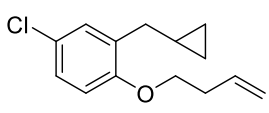
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.03 (dd, J = 3.2 Hz, $J_{H\text{-}F}$ = 9.2 Hz, 1H), 6.83 (ddd, J = 8.7, 3.2 Hz, $J_{H\text{-}F}$ = 8.7 Hz, 1H), 6.73 (dd, J = 8.7 Hz, $J_{H\text{-}F}$ = 4.6 Hz, 1H), 5.91 (m, 1H), 5.20–5.07 (m, 2H), 3.97 (t, J = 6.4 Hz, 2H), 2.58–2.48 (m, 4H), 0.99 (m, 1H), 0.51 (ddd, J = 7.8, 6.0, 4.6 Hz, 2H), 0.18 (ddd, J = 6.0, 4.6, 4.6 Hz, 2H).

^{13}C{^{1}H, ^{19}F} NMR (126 MHz, $CDCl_3$) δ: 157.0, 152.6, 134.6, 132.8, 117.0, 116.1, 112.3, 111.7, 67.8, 34.2, 33.9, 10.2, 4.6.

^{19}F NMR (471 MHz, $CDCl_3$) δ: -124.5.

HRMS (ESI) *m*/*z* calcd for $C_{14}H_{17}FNaO$ ($[M+Na]^+$): 243.1156, found 243.1151.

Compound **1l**



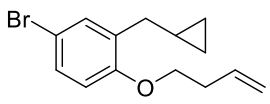
Following the typical procedure A, 1-allyloxy-4-chlorobenzene[4] (810 mg, 4.80 mmol) was converted to **1l** (351 mg, 31%) after column chromatography on flash silica gel (*n*-hexane). A colorless oil

^{1}H NMR (301 MHz, $CDCl_3$) δ: 7.25 (d, J = 2.4 Hz, 1H), 7.11 (dd, J = 8.6, 2.4 Hz, 1H), 6.73 (d, J = 8.6 Hz, 1H), 5.90 (m, 1H), 5.21–5.07 (m, 2H), 3.98 (t, J = 6.5 Hz, 2H), 2.59–2.46 (m, 4H), 0.99 (m, 1H), 0.51 (ddd, J = 7.8, 6.0, 4.5 Hz, 2H), 0.18 (ddd, J = 5.9, 4.8, 4.8 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 155.2, 134.5, 132.8, 129.2, 126.4, 125.1, 117.1, 112.0, 67.4, 34.2, 33.7, 10.2, 4.7.

HRMS (ESI) *m*/*z* calcd for $C_{14}H_{17}ClNaO$ ($[M+Na]^+$): 259.0860, found 259.0855.

Compound **1m**



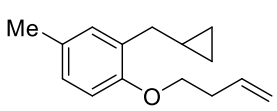
Following the typical procedure A, 1-allyloxy-4-bromobenzene[2] (786 mg, 3.69 mmol) was converted to **1m** (288 mg, 28%) after column chromatography on flash silica gel (*n*-hexane). A colorless oil

^{1}H NMR (500 MHz, Acetone-d_6) δ: 7.39 (d, J = 2.6 Hz, 1H), 7.29 (dd, J = 8.6, 2.6 Hz, 1H), 6.89 (d, J = 8.6 Hz, 1H), 5.93 (m, 1H), 5.19–5.04 (m, 2H), 4.05 (t, J = 6.4 Hz, 2H), 2.57–2.51 (m, 2H), 2.49 (d, J = 6.9 Hz, 2H), 1.02 (m, 1H), 0.45 (ddd, J = 8.7, 5.7, 4.3 Hz, 2H), 0.17 (ddd, J = 6.0, 4.4, 4.4 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, Acetone-d_6) δ: 156.8, 135.7, 134.1, 132.8, 130.4, 117.2, 113.9, 112.8, 68.1, 34.8, 34.4, 11.1, 5.0.

HRMS (ESI) *m*/*z* calcd for $C_{14}H_{17}BrNaO$ ($[M+Na]^+$): 303.0355, found 303.0357.

Compound **1n**



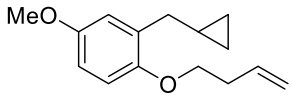
Following the typical procedure A, 1-allyloxy-4-methylbenzene[3] (387 mg, 2.61 mmol) was converted to **1n** (169 mg, 30%) after column chromatography on flash silica gel (*n*-hexane). A colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.07 (d, J = 1.8 Hz, 1H), 6.95 (dd, J = 8.2, 1.8 Hz, 1H), 6.73 (d, J = 8.2 Hz, 1H), 5.92 (m, 1H), 5.19–5.06 (m, 2H), 3.99 (t, J = 6.6 Hz, 2H), 2.57–2.51 (m, 2H), 2.50 (d, J = 6.9 Hz, 2H) 2.28 (s, 3H), 1.01 (m, 1H), 0.47 (ddd, J = 7.8, 5.7, 4.1 Hz, 2H), 0.18 (ddd, J = 6.0, 4.6, 4.6 Hz, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 154.5, 134.8, 130.6, 130.3, 129.4, 127.0, 116.8, 111.0, 67.3, 34.4, 33.9, 20.6, 10.7, 4.7.

HRMS (MALDI) *m*/*z* calcd for $C_{15}H_{20}O$ ($[M]^+$): 216.1509, found 216.1516.

Compound **1o**



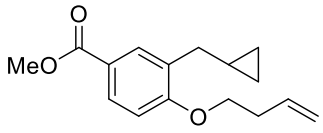
Following the typical procedure A, 1-allyloxy-4-methoxybenzene[3] (1.30 g, 7.96 mmol) was converted to **1o** (120 mg, 6.5%) after column chromatography on flash silica gel (*n*-hexane/EtOAc = 50/1). A colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.89 (d, J = 3.2 Hz, 1H), 6.76 (d, J = 8.7 Hz, 1H), 6.68 (dd, J = 8.7, 3.2 Hz, 1H), 5.92 (m, 1H), 5.20–5.07 (m, 2H), 3.96 (t, J = 6.4 Hz, 2H), 3.77 (s, 3H), 2.57–2.49 (m, 4H), 1.01 (m, 1H), 0.49 (ddd, J = 7.9, 6.0, 4.1 Hz, 2H), 0.19 (ddd, J = 6.0, 4.6, 4.6 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 153.4, 150.8, 134.8, 132.3, 116.8, 116.1, 112.0, 110.4, 67.9, 55.6, 34.4, 34.0, 10.5, 4.6.

HRMS (MALDI) *m*/*z* calcd for $C_{15}H_{20}O_2$ ($[M]^+$): 232.1458, found 232.1452.

Compound **1p**



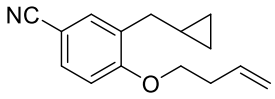
Following the typical procedure A, methyl 4-(allyloxy)benzoate[5] (507 mg, 2.63 mmol) was converted to **1p** (295 mg, 43%) after column chromatography on flash silica gel (*n*-hexane/EtOAc = 10/1). A colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, J = 1.8 Hz, 1H), 7.89 (dd, J = 8.2, 1.8 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H), 5.91 (m, 1H), 5.21–5.09 (m, 2H), 4.07 (t, J = 6.6 Hz, 2H), 3.88 (s, 3H), 2.61–2.51 (m, 4H), 1.04 (m, 1H), 0.50 (ddd, J = 7.8, 5.5, 4.6 Hz, 2H), 0.21–0.16 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 167.2, 160.4, 134.3, 130.9, 130.7, 129.4, 122.0, 117.2, 110.1, 67.2, 51.8, 34.4, 33.6, 10.3, 4.7.

HRMS (ESI) *m*/*z* calcd for $C_{16}H_{20}NaO_3$ ($[M+Na]^+$): 283.1305, found 283.1306.

Compound **1q**



Following the typical procedure B, 3-allyl-4-hydroxybenzonitrile[3] (541 mg, 3.40mmol) was converted to **1q** (252 mg, 33%) after column chromatography on flash silica gel (*n*-hexane/EtOAc = 10/1). A colorless oil

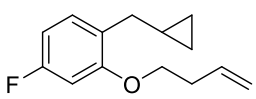
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, J = 2.3 Hz, 1H), 7.49 (dd, J = 8.2, 2.3 Hz, 1H),

6.84 (d, J = 8.2 Hz, 1H), 5.89 (m, 1H), 5.21–5.09 (m, 2H), 4.05 (t, J = 6.4 Hz, 2H), 2.61–2.53 (m, 2H), 2.50 (d, J = 6.9 Hz, 2H), 0.98 (m, 1H), 0.53 (ddd, J = 7.8, 6.0, 4.6 Hz, 2H), 0.17 (ddd, J = 6.0, 4.6, 4.6 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 159.9, 133.9, 132.8, 132.2, 131.8, 119.7, 117.4, 110.8, 103.3, 67.4, 33.9, 33.4, 9.8, 4.7.

HRMS (ESI) *m*/*z* calcd for $C_{15}H_{18}NO$ ($[M+H]^+$): 228.1383, found 228.1384.

Compound **1r**



Following the typical procedure B, 1-allyloxy-3-fluorobenzene[3] (2.45 g, 16.1 mmol) was converted to **1r** (253 mg, 7.1%) after column chromatography on flash silica gel (*n*-hexane). A colorless oil

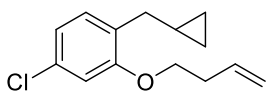
^{1}H NMR (301 MHz, $CDCl_3$) δ: 7.19 (dd, J = 7.6, 7.6 Hz, 1H), 6.62–6.53 (m, 2H), 5.91 (m, 1H), 5.22–5.08 (m, 2H), 3.98 (t, J = 6.5 Hz, 2H), 2.61–2.51 (m, 2H), 2.47 (d, J = 6.9 Hz, 2H), 0.99 (m, 1H), 0.48 (ddd, J = 7.9, 5.9, 4.5 Hz, 2H), 0.16 (ddd, J = 5.9, 4.5, 4.5 Hz, 2H).

^{13}C{^{1}H, ^{19}F} NMR (126 MHz, $CDCl_3$) δ: 162.0, 157.4, 134.4, 129.8, 126.3, 117.1, 106.2, 99.2, 67.3, 33.9, 33.6, 10.6, 4.6.

^{19}F NMR (471 MHz, $CDCl_3$) δ: -120.1.

HRMS (ESI) *m*/*z* calcd for $C_{14}H_{17}FNaO$ ($[M+Na]^+$): 243.1156, found 243.1154.

Compound **1s**



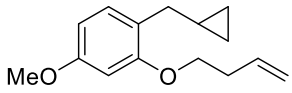
Following the typical procedure A, 1-allyloxy-3-chlorobenzene[4] (872 mg, 5.17 mmol) was converted to **1s** (155 mg, 13%) after column chromatography on flash silica gel (*n*-hexane). A colorless oil

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.18 (d, J = 8.0 Hz, 1H), 6.87 (dd, J = 8.0, 2.0 Hz, 1H), 6.80 (d, J = 2.0 Hz, 1H), 5.90 (m, 1H), 5.20–5.09 (m, 2H), 3.99 (t, J = 6.5 Hz, 2H), 2.58–2.53 (m, 2H), 2.47 (d, J = 6.9 Hz, 2H), 0.98 (m, 1H), 0.48 (ddd, J = 8.0, 5.8, 4.4 Hz, 2H), 0.18–0.14 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 157.1, 134.4, 132.0, 130.1, 129.3, 120.2, 117.1, 111.5, 67.3, 34.0, 33.6, 10.4, 4.6.

HRMS (APCI) *m*/*z* calcd for $C_{14}H_{18}ClO$ ($[M+H]^+$): 237.1041, found 237.1037.

Compound **1t**



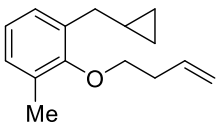
Following the typical procedure B, 1-allyloxy-3-methoxybenzene[3] (3.05 g, 18.6 mmol) was converted to **1t** (98 mg, 2.3%) after column chromatography on flash silica gel (*n*-hexane/EtOAc = 10/1). A colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.16 (d, J = 8.7 Hz, 1H), 6.46–6.41 (m, 2H), 5.92 (m, 1H), 5.20–5.07 (m, 2H), 3.99 (t, J = 6.4 Hz, 2H), 3.79 (s, 3H), 2.59–2.52 (m, 2H), 2.46 (d, J = 6.9 Hz, 2H), 0.99 (m, 1H), 0.46 (ddd, J = 8.0, 5.5, 4.1 Hz, 2H), 0.19–0.13 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 158.9, 157.4, 134.7, 129.6, 123.2, 116.9, 103.7, 99.0, 67.1, 55.3, 33.8, 33.8, 10.8, 4.6.

HRMS (ESI) *m*/*z* calcd for $C_{15}H_{21}O_2$ ($[M+H]^+$): 233.1536, found 233.1533.

Compound **1u**



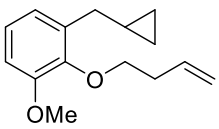
Following the typical procedure A, 1-allyloxy-2-methylbenzene[4] (1.71 g, 10.4 mmol) was converted to **1u** (99.3 mg, 4.3%) after column chromatography on flash silica gel (*n*-hexane). A colorless oil

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.21 (m, 1H), 7.03 (m, 1H), 6.98 (dd, J = 7.4, 7.4 Hz, 1H), 5.96 (m, 1H), 5.21–5.09 (m, 2H), 3.80 (t, J = 6.8 Hz, 2H), 2.60–2.53 (m, 4H), 2.29 (s, 3H), 1.01 (m, 1H), 0.52 (ddd, J = 8.0, 5.7, 4.3 Hz, 2H), 0.23–0.19 (m, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 155.4, 135.1, 134.8, 130.9, 129.0, 127.4, 123.8, 116.9, 71.8, 34.8, 34.2, 16.4, 11.1, 4.8.

HRMS (ESI) *m*/*z* calcd for $C_{15}H_{21}O$ ($[M+H]^+$): 217.1587, found 217.1583.

Compound **1v**



Following the typical procedure A, 1-allyloxy-2-methoxybenzene[4] (230 mg, 1.40 mmol) was converted to **1v** (94.4 mg, 29%) after column chromatography on flash silica gel (*n*-hexane/EtOAc = 40/1). A colorless oil

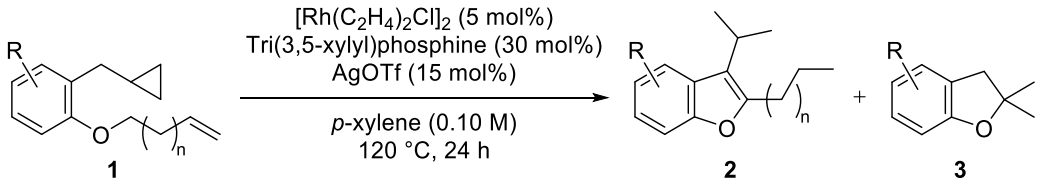
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.00 (t, J = 7.9 Hz, 1H), 6.93 (dd, J = 7.9, 1.6 Hz, 1H), 6.78 (dd, J = 7.9, 1.6 Hz, 1H), 5.90 (m, 1H), 5.20–5.07 (m, 2H), 3.99 (t, J = 6.8 Hz, 2H), 3.85 (s, 3H), 2.57–2.52 (m, 4H), 1.00 (m, 1H), 0.49 (ddd, J = 8.0, 5.8, 4.4 Hz, 2H), 0.21 (ddd, J = 5.8, 4.4, 4.4 Hz, 2H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ: 152.6, 145.9, 136.2, 135.1, 123.6, 121.6, 116.6, 110.0, 72.0, 55.6, 34.8, 34.2, 11.2, 4.7.

HRMS (ESI) *m/z* calcd for $C_{15}H_{21}O_2$ ($[M+H]^+$): 233.1536, found 233.1532.

2-2. Preparation of benzofurans **2** and dihydrobenzofurans **3**

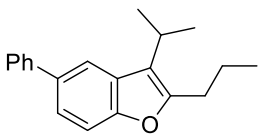
Typical procedure C



In a glovebox, to an oven-dried test tube was added $[Rh(C_2H_4)_2Cl]_2$ (5 mol%), tri(3,5-xylyl)phosphine (30 mol%) and anhydrous *p*-xylene (0.10 M). The resulting solution was stirred for 30 min at room temperature, then AgOTf (15 mol%) was added and the reaction mixture was stirred for 15 min at room temperature.

Next, **1** (1.0 eq.) was added to the mixture, the reaction vessel was sealed, then removed from the glovebox and heated at 120 °C. After stirring at the same temperature for 24 h, the mixture was cooled to room temperature and filtered by short silica gel column chromatography. The filtrate was concentrated in vacuo. The obtained residue was purified by column chromatography on silica gel to give corresponding benzofuran **2** and dihydrobenzofuran **3**.

Compound **2a**



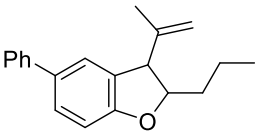
Following the typical procedure C, **1a** (27.8 mg, 0.100 mmol) was converted to **2a** (22.5 mg, 81%) after column chromatography on silica gel (*n*-hexane/EtOAc = 100/1). A colorless oil.

^1H NMR (500 MHz, $CDCl_3$) δ: 7.78 (dd, J = 1.7, 0.6 Hz, 1H), 7.65–7.61 (m, 2H), 7.49–7.44 (m, 3H), 7.42 (dd, J = 8.5, 1.7 Hz, 1H), 7.35 (m, 1H), 3.12 (sept, J = 7.0 Hz, 1H), 2.74 (t, J = 7.4 Hz, 2H), 1.76 (tq, J = 7.4, 7.4 Hz, 2H), 1.44 (d, J = 7.0 Hz, 6H), 0.99 (t, J = 7.4 Hz, 3H).

$^{13}C\{^1H\}$ NMR (76 MHz, $CDCl_3$) δ: 153.8, 153.7, 142.2, 135.4, 128.8, 128.7, 127.5, 126.7, 122.4, 120.2, 118.8, 110.9, 28.5, 25.4, 22.6, 21.9, 13.7.

HRMS (MALDI) *m/z* calcd for $C_{20}H_{22}O$ ($[M]^+$): 278.1665, found 278.1662.

Compound **2a'**



In a glovebox, to an oven-dried test tube was added $[Rh(C_2H_4)_2Cl]_2$ (3.89 mg, 5 mol%), tris-2,4,6-trimethylphenylphosphine (23.3 mg, 30 mol%) and anhydrous *p*-xylene (2.0 mL, 0.10 M). The resulting solution was stirred for 30 min at room temperature, then AgOTf (7.71 mg, 15 mol%) was added and the reaction mixture was stirred for 15 min at room temperature.

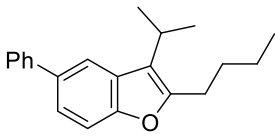
Next, **8a** (0.200 mmol, 55.7 mg, 1.0 eq.) was added to the mixture, the reaction vessel was sealed, then removed from the glovebox and heated at 110 °C. After stirring at the same temperature for 9 h, the mixture was cooled to room temperature and filtered by short silica gel column chromatography. The filtrate was concentrated in vacuo. The obtained residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc = 50/1) to give **2a'** (26.3 mg, 47%, *cis*/*trans* = 1/2)

A colorless oil.

mixture of *cis*-**2a'** and *trans*-**2a'** (*cis*/*trans* = 1/2) : **^{1}H NMR** (500 MHz, Acetone-d_6) δ: 7.58–7.54 (m, 2H), 7.45–7.25 (m, 5H), 6.84 (d, J = 8.3 Hz, 0.33H, *cis* isomer), 6.81 (d, J = 8.3 Hz, 0.56H, trans isomer), 4.98–4.87 (m, 2H), 4.76 (td, J = 8.5, 4.1 Hz, 0.33H, *cis* isomer), 4.59 (td, J = 7.3, 5.0 Hz, 0.63H, trans isomer), 4.07 (d, J = 8.5 Hz, 0.34H, *cis* isomer), 3.88 (d, J = 7.3 Hz, 0.66H, trans isomer), 1.81-1.46 (m, 7H), 1.00–0.95 (m, 3H). **^{13}C{^{1}H} NMR** (126 MHz, Acetone-d_6) δ: 160.5, 160.4, 145.6, 144.5, 142.0, 134.7, 134.4, 132.0, 130.8, 129.6, 128.2, 128.1, 127.3, 127.3, 127.3, 124.8, 124.2, 114.6, 113.9, 110.4, 110.3, 88.2, 87.7, 57.3, 53.7, 38.7, 33.4, 21.4, 20.7, 19.3, 19.2, 14.3, 14.2.

HRMS (APCI) *m*/*z* calcd for $C_{20}H_{23}O$ ($[M+H]^+$): 279.1743, found 279.1737.

Compound **2b**



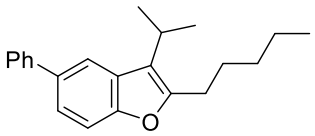
Following the typical procedure C, **1b** (29.2 mg, 0.100 mmol) was converted to **2b** (21.7 mg, 74%) after column chromatography on silica gel (*n*-hexane/EtOAc = 100/1). A colorless oil.

^{1}H NMR (301 MHz, $CDCl_3$) δ: 7.78 (d, J = 1.4 Hz, 1H), 7.66–7.59 (m, 2H), 7.50–7.39 (m, 4H), 7.38–7.31 (m, 1H), 3.12 (sept, J = 7.0 Hz, 1H), 2.76 (t, J = 7.4 Hz, 2H), 1.77–1.63 (m, 2H), 1.47–1.33 (m, 8H), 0.96 (t, J = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 153.9, 153.8, 142.2, 135.4, 128.8, 128.7, 127.5, 126.7, 122.4, 120.0, 118.8, 110.9, 30.7, 26.3, 25.4, 22.6, 22.3, 13.9.

HRMS (ESI) *m*/*z* calcd for $C_{21}H_{24}NaO$ ([M+Na]$^+$): 315.1719, found 315.1716.

Compound **2c**



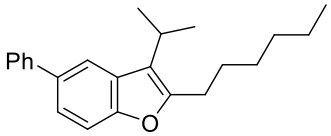
Following the typical procedure C, **1c** (30.7 mg, 0.100 mmol) was converted to **2c** (23.4 mg, 76%) after column chromatography on silica gel (*n*-hexane/EtOAc = 100/1). A colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.78 (m, 1H), 7.65–7.61 (m, 2H), 7.49–7.44 (m, 3H), 7.42 (dd, J = 8.5, 1.7 Hz, 1H), 7.35 (m, 1H), 3.12 (sept, J = 7.0 Hz, 1H), 2.76 (t, J = 7.5 Hz, 2H), 1.74 (tt, J = 7.5 Hz, 2H), 1.44 (d, J = 7.0 Hz, 6H), 1.40–1.35 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 153.9, 153.8, 142.2, 135.4, 128.8, 128.7, 127.5, 126.7, 122.4, 120.0, 118.8, 110.9, 31.4, 28.3, 26.5, 25.4, 22.6, 22.4, 14.0.

HRMS (ESI) *m*/*z* calcd for $C_{22}H_{27}O$ ([M+H]$^+$): 307.2056, found 307.2053.

Compound **2d**



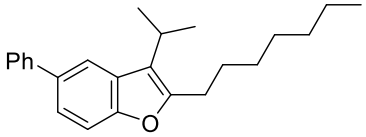
Following the typical procedure C, **1d** (32.1 mg, 0.100 mmol) was converted to **2d** (21.9 mg, 68%) after column chromatography on silica gel (*n*-hexane/EtOAc = 100/1). A colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, J = 0.9 Hz, 1H), 7.64 (dd, J = 8.2, 0.9 Hz, 2H), 7.50–7.44 (m, 3H), 7.43 (dd, J = 8.7, 1.8 Hz, 1H), 7.36 (m, 1H), 3.13 (sept, J = 7.0 Hz, 1H), 2.77 (t, J = 7.4 Hz, 2H), 1.72 (tt, J = 7.4 Hz, 2H), 1.45 (d, J = 7.1 Hz, 6H), 1.42–1.28 (m, 6H), 0.91 (t, J = 7.0 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 153.9, 153.8, 142.2, 135.4, 128.8, 128.7, 127.5, 126.7, 122.4, 120.0, 118.8, 110.9, 31.6, 28.9, 28.6, 26.6, 25.4, 22.60, 22.56, 14.1.

HRMS (ESI) *m*/*z* calcd for $C_{23}H_{28}NaO$ ([M+Na]$^+$): 343.2032, found 343.2029.

Compound **2e**



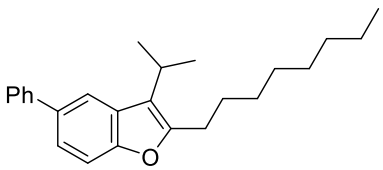
Following the typical procedure C, **1e** (33.5 mg, 0.100 mmol) was converted to **2e** (20.5 mg, 61%) after column chromatography on silica gel (*n*-hexane/EtOAc = 100/1). A colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (m, 1H), 7.63 (dd, J = 8.4, 1.0, 2H), 7.50–7.44 (m, 3H), 7.42 (dd, J = 8.7, 1.8 Hz, 1H), 7.35 (m, 1H), 3.12 (sept, J = 7.0 Hz, 1H), 2.76 (t, J = 7.3 Hz, 2H), 1.72 (tt, J = 7.3, 7.3 Hz, 2H), 1.44 (d, J = 7.0 Hz, 6H), 1.41–1.25 (m, 8H), 0.90 (t, J = 6.9 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 153.9, 153.8, 142.2, 135.4, 128.8, 128.7, 127.5, 126.7, 122.4, 120.0, 118.8, 110.9, 31.8, 29.2, 29.1, 28.6, 26.6, 25.4, 22.7, 22.6, 14.1.

HRMS (ESI) *m*/*z* calcd for $C_{24}H_{31}O$ ($[M+H]^+$): 335.2369, found 335.2363.

Compound **2f**



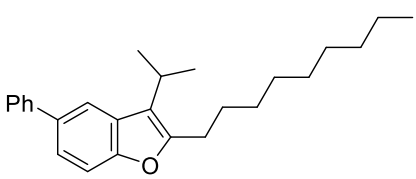
Following the typical procedure C, **1f** (34.9 mg, 0.100 mmol) was converted to **2f** (23.2 mg, 67%) after column chromatography on silica gel (*n*-hexane/EtOAc = 100/1). A colorless oil.

^{1}H NMR (301 MHz, $CDCl_3$) δ: 7.78 (m, 1H), 7.66–7.61 (m, 2H), 7.50–7.40 (m, 4H), 7.35 (m, 1H), 3.12 (sept, J = 7.0 Hz, 1H), 2.76 (t, J = 7.4 Hz, 2H), 1.73 (tt, J = 7.4 Hz, 2H), 1.44 (d, J = 7.0 Hz, 6H), 1.41–1.19 (m, 10H), 0.90 (t, J = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ: 154.5, 154.1, 142.4, 135.6, 129.3, 129.0, 127.7, 127.0, 122.6, 120.4, 119.1, 111.1, 32.2, 29.7, 29.60, 29.56, 28.9, 26.8, 25.8, 23.0, 22.6, 14.2.

HRMS (ESI) *m*/*z* calcd for $C_{25}H_{32}NaO$ ($[M+Na]^+$): 371.2345, found 371.2339.

Compound **2g**



Following the typical procedure C, **1g** (36.3 mg, 0.100 mmol) was converted to **2g** (17.5 mg, 48%) after column chromatography on silica gel (*n*-hexane/EtOAc = 100/1). A colorless oil.

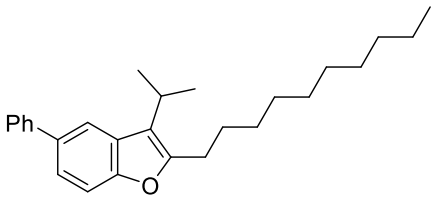
^{1}H NMR (301 MHz, $CDCl_3$) δ: 7.77 (m, 1H), 7.64–7.59 (m, 2H), 7.50–7.39 (m, 4H), 7.35 (m, 1H), 3.12 (sept, J = 7.0 Hz, 1H), 2.75 (t, J = 7.4 Hz, 2H), 1.72 (tt, J = 7.4 Hz,

2H), 1.44 (d, J = 7.0 Hz, 6H), 1.40–1.22 (m, 12H), 0.89 (t, J = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 153.9, 153.8, 142.2, 135.4, 128.8, 128.7, 127.5, 126.7, 122.4, 120.0, 118.8, 110.9, 31.9, 29.5, 29.4, 29.3, 29.2, 28.6, 26.6, 25.4, 22.7, 22.6, 14.1.

HRMS (ESI) *m*/*z* calcd for $C_{26}H_{34}NaO$ ($[M+Na]^+$): 385.2502, found 385.2499.

Compound **2h**



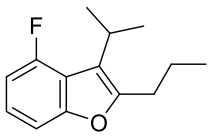
Following the typical procedure C, **1h** (37.7 mg, 0.100 mmol) was converted to **2h** (14.8 mg, 39%) after column chromatography on silica gel (*n*-hexane/EtOAc = 100/1). A colorless oil.

^{1}H NMR (301 MHz, $CDCl_3$) δ: 7.77 (m, 1H), 7.65–7.59 (m, 2H), 7.49–7.41 (m, 4H), 7.34 (m, 1H), 3.11 (sept, J = 7.0 Hz, 1H), 2.75 (t, J = 7.2 Hz, 2H), 1.71 (tt, J = 7.2, 2H), 1.43 (d, J = 7.0 Hz, 6H), 1.40–1.22 (m, 14H), 0.89 (t, J = 6.9 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 153.9, 153.8, 142.2, 135.4, 128.8, 128.7, 127.5, 126.6, 122.4, 120.0, 118.8, 110.9, 31.9, 29.59, 29.56, 29.4, 29.3, 29.2, 28.6, 26.6, 25.4, 22.7, 22.6, 14.1.

HRMS (ESI) *m*/*z* calcd for $C_{27}H_{36}NaO$ ($[M+Na]^+$): 399.2658, found 399.2649.

Compound **2i**



Following the typical procedure C, **1i** (22.0 mg, 0.100 mmol) was converted to **2i** (11.0 mg, 50%) after column chromatography on silica gel (*n*-hexane/EtOAc = 100/1). A colorless oil.

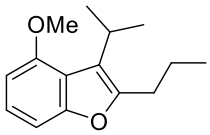
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.18 (dd, J = 8.0, 1.0 Hz, 1H), 7.13 (ddd, J = 8.0, 8.0 Hz, $J_{H\text{-}F}$ = 5.2 Hz, 1H), 6.87 (ddd, J = 8.0, 1.0 Hz, $J_{H\text{-}F}$ = 10.6 Hz, 1H), 3.10 (m, 1H), 2.72 (t, J = 7.4 Hz, 2H), 1.72 (tq, J = 7.4, 7.4 Hz, 2H), 1.34 (dd, J = 7.0 Hz, $J_{H\text{-}F}$ = 1.3 Hz, 6H), 0.97 (t, J = 7.4 Hz, 3H).

^{13}C{^{1}H, ^{19}F} NMR (126 MHz, $CDCl_3$) δ: 156.3, 155.3, 152.9, 123.4, 119.6, 116.7, 108.1, 106.9, 28.4, 24.9, 22.6, 21.9, 13.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ: -113.1

HRMS (APCI) *m*/*z* calcd for $C_{14}H_{18}FO$ ($[M+H]^+$): 221.1336, found 221.1331.

Compound **2j**



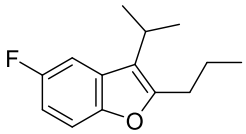
Following the typical procedure C, **1j** (23.2 mg, 0.100 mmol) was converted to **2j** (13.3 mg, 57%) after column chromatography on silica gel (*n*-hexane/EtOAc = 30/1). A colorless oil.

^{1}H NMR (301 MHz, $CDCl_3$) δ: 7.14 (dd, J = 8.0, 8.0 Hz, 1H), 7.03 (dd, J = 8.0, 0.80 Hz, 1H), 6.64 (dd, J = 8.0, 0.80 Hz, 1H), 3.94 (s, 3H), 3.18 (sept, J = 7.0 Hz, 1H), 2.72 (t, J = 7.4 Hz, 2H), 1.71 (tq, J = 7.4, 7.4 Hz, 2H), 1.34 (d, J = 7.0 Hz, 6H), 0.96 (t, J = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 155.6, 153.4, 151.7, 123.5, 120.7, 118.1, 104.0, 102.8, 55.1, 28.6, 25.2, 22.8, 22.1, 13.7.

HRMS (ESI) *m*/*z* calcd for $C_{15}H_{20}NaO_2$ ($[M+Na]^+$): 255.1356, found 255.1351.

Compound **2k**



Following the typical procedure C, **1k** (22.0 mg, 0.100 mmol) was converted to **2k** (16.5 mg, 75%) after column chromatography on silica gel (*n*-hexane/EtOAc = 100/1). A colorless oil.

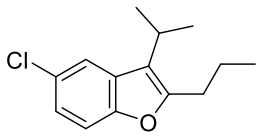
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.28 (dd, J = 9.0 Hz, $J_{H\text{-}F}$ = 4.2 Hz, 1H), 7.24 (dd, J = 2.6 Hz, $J_{H\text{-}F}$ = 9.2 Hz, 1H), 6.89 (ddd, J = 9.0, 2.6 Hz, $J_{H\text{-}F}$ = 9.0 Hz, 1H), 3.04 (sept, J = 7.0 Hz, 1H), 2.70 (t, J = 7.4 Hz, 2H), 1.73 (tq, J = 7.4, 7.4 Hz, 2H), 1.36 (d, J = 7.0 Hz, 6H), 0.97 (t, J = 7.4 Hz, 3H).

^{13}C{^{1}H, ^{19}F} NMR (126 MHz, $CDCl_3$) δ: 158.5, 154.9, 150.3, 129.0, 120.4, 111.1, 110.0, 105.8, 28.5, 25.2, 22.3, 21.8, 13.8.

^{19}F NMR (471 MHz, $CDCl_3$) δ: -122.4.

HRMS (ESI) *m*/*z* calcd for $C_{14}H_{17}FNaO$ ($[M+Na]^+$): 243.1156, found 243.1142.

Compound **2l**



Following the typical procedure C, **1l** (23.7 mg, 0.100 mmol) was converted to **2l** (13.0 mg, 55%) after column chromatography on silica gel (*n*-hexane). A colorless oil.

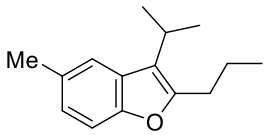
^{1}H NMR (301 MHz, $CDCl_3$) δ: 7.55 (d, J = 2.1 Hz, 1H), 7.28 (d, J = 8.6 Hz, 1H), 7.14 (dd, J = 8.6, 2.1 Hz, 1H), 3.04 (sept, J = 7.0 Hz, 1H), 2.70 (t, J = 7.2 Hz, 2H), 1.72 (tq, J = 7.2, 7.2 Hz, 2H), 1.37 (d, J = 7.0 Hz, 6H), 0.96 (t, J = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 154.6, 152.5, 129.7, 127.1, 122.7, 119.9, 119.7,

111.7, 28.5, 25.2, 22.4, 21.8, 13.7.

HRMS (APCI) *m*/*z* calcd for $C_{14}H_{18}ClO$ ($[M+H]^+$): 237.1041, found 237.1036.

Compound **2n**



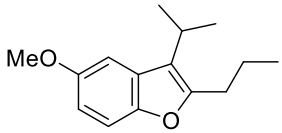
Following the typical procedure C, **1n** (21.6 mg, 0.100 mmol) was converted to **2n** (18.4 mg, 85%) after column chromatography on silica gel (*n*-hexane/EtOAc = 100/1). A colorless oil.

^{1}H NMR (301 MHz, Acetone-d_6) δ: 7.45 (d, J = 1.2 Hz, 1H), 7.24 (d, J = 8.3 Hz, 1H), 6.99 (dd, J = 8.3, 1.2 Hz, 1H), 3.11 (sept, J = 7.1 Hz, 1H), 2.71 (t, J = 7.3 Hz, 2H), 2.39 (s, 3H), 1.69 (tq, J = 7.3, 7.3 Hz, 2H), 1.36 (d, J = 7.1 Hz, 6H), 0.94 (t, J = 7.3 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 153.0, 152.5, 130.9, 128.4, 123.8, 120.1, 119.8, 110.3, 28.5, 25.4, 22.5, 21.9, 21.5, 13.7.

HRMS (ESI) *m*/*z* calcd for $C_{15}H_{20}NaO$ ($[M+Na]^+$): 239.1406, found 239.1402.

Compound **2o**



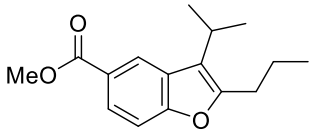
Following the typical procedure C, **1o** (23.2 mg, 0.100 mmol) was converted to **2o** (16.2 mg, 70%) after column chromatography on silica gel (*n*-hexane/EtOAc = 50/1). A colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.28 (d, J = 8.9 Hz, 1H), 7.07 (d, J = 2.6 Hz, 1H), 6.80 (dd, J = 8.9, 2.6 Hz, 1H), 3.86 (s, 3H), 3.05 (sept, J = 7.0 Hz, 1H), 2.69 (t, J = 7.4 Hz, 2H), 1.72 (tq, J = 7.4, 7.4 Hz, 2H), 1.38 (d, J = 7.0 Hz, 6H), 0.96 (t, J = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 155.0, 154.0, 149.1, 128.8, 120.0, 111.0, 110.4, 103.8, 56.0, 28.6, 25.3, 22.4, 21.9, 13.7.

HRMS (MALDI) *m*/*z* calcd for $C_{15}H_{20}O_2$ ($[M]^+$): 232.1458, found 232.1451.

Compound **2p**



Following the typical procedure C, **1p** (26.0 mg, 0.100 mmol) was converted to **2p** (17.0 mg, 64%) after column chromatography on silica gel (*n*-hexane/EtOAc = 30/1). A colorless oil.

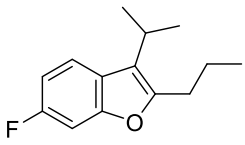
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (d, J = 1.4 Hz, 1H), 7.93 (dd, J = 8.7, 1.4 Hz, 1H), 7.39 (d, J = 8.7 Hz, 1H), 3.93, (s, 3H), 3.09 (sept, J = 6.9 Hz, 1H), 2.72 (t, J = 7.3 Hz,

2H), 1.74 (tq, J = 7.3, 7.3 Hz, 2H), 1.41 (d, J = 6.9 Hz, 6H), 0.97 (t, J = 7.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 167.6, 156.9, 154.4, 128.3, 124.7, 123.9, 122.4, 120.6, 110.6, 52.0, 28.5, 25.2, 22.5, 21.8, 13.7.

HRMS (ESI) *m*/*z* calcd for $C_{16}H_{21}O_3$ ($[M+H]^+$): 261.1485, found 261.1483.

Compound **2r**



Following the typical procedure C, **1r** (22.0 mg, 0.100 mmol) was converted to **2r** (15.3 mg, 70%) after column chromatography on silica gel (*n*-hexane/EtOAc = 100/1). A colorless oil.

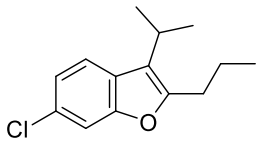
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.48 (dd, J = 8.6 Hz, $J_{H\text{-}F}$ = 5.4 Hz, 1H), 7.10 (dd, J = 2.3 Hz, $J_{H\text{-}F}$ = 9.2 Hz, 1H), 6.92 (ddd, J = 8.6, 2.3 Hz, $J_{H\text{-}F}$ = 9.6 Hz, 1H), 3.05 (sept, J = 7.0 Hz, 1H), 2.69 (t, J = 7.4 Hz, 2H), 1.72 (tq, J = 7.4, 7.4 Hz, 2H), 1.37 (d, J = 7.0 Hz, 6H), 0.96 (t, J = 7.4 Hz, 3H).

^{13}C{^{1}H, ^{19}F} NMR (126 MHz, $CDCl_3$) δ: 160.0, 154.1, 153.5, 124.5, 120.1, 119.8, 109.6, 98.6, 28.4, 25.3, 22.5, 21.8, 13.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ: -120.1.

HRMS (APCI) *m*/*z* calcd for $C_{14}H_{18}FO$ ($[M+H]^+$): 221.1336, found 221.1336.

Compound **2s**



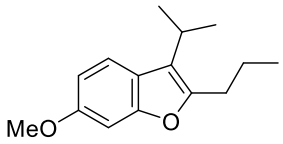
Following the typical procedure C, **1s** (23.7 mg, 0.100 mmol) was converted to **2s** (12.1 mg, 51%) after column chromatography on silica gel (*n*-hexane/EtOAc = 100/1). A colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.48 (d, J = 8.3 Hz, 1H), 7.38 (d, J = 1.9 Hz, 1H), 7.14 (dd, J = 8.3, 1.9 Hz, 1H), 3.05 (sept, J = 7.0 Hz, 1H), 2.69 (t, J = 7.4 Hz, 2H), 1.71 (tq, J = 7.4, 7.4 Hz, 2H), 1.36 (d, J = 7.0 Hz, 6H), 0.96 (t, J = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 154.3, 153.8, 128.5, 127.0, 122.2, 120.5, 120.0, 111.4, 28.4, 25.2, 22.5, 21.8, 13.7.

HRMS (APCI) *m*/*z* calcd for $C_{14}H_{18}ClO$ ($[M+H]^+$): 237.1041, found 237.1038.

Compound **2t**



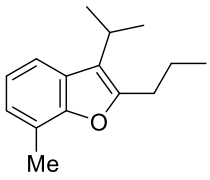
Following the typical procedure C, **1t** (23.2 mg, 0.100 mmol) was converted to **2t** (16.3 mg, 70%) after column chromatography on silica gel (*n*-hexane/EtOAc = 100/1). A colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (d, J = 8.7 Hz, 1H), 6.96 (d, J = 2.3 Hz, 1H), 6.81 (dd, J = 8.7, 2.3 Hz, 1H), 3.84 (s, 3H), 3.03 (sept, J = 7.0 Hz, 1H), 2.67 (t, J = 7.4 Hz, 2H), 1.71 (tq, J = 7.4, 7.4 Hz, 2H), 1.37 (d, J = 7.0 Hz, 6H), 0.96 (t, J = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 156.8, 155.0, 151.8, 121.6, 120.2, 119.8, 110.2, 95.9, 55.7, 28.4, 25.4, 22.6, 22.0, 13.7.

HRMS (ESI) *m*/*z* calcd for $C_{15}H_{21}O_2$ ($[M+H]^+$): 233.1536, found 233.1534.

Compound **2u**



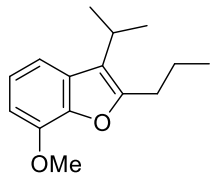
Following the typical procedure C, **1u** (21.6 mg, 0.100 mmol) was converted to **2u** (17.2 mg, 80%) after column chromatography on silica gel (*n*-hexane/EtOAc = 100/1). A colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45 (d, J = 7.6 Hz, 1H), 7.08 (dd, J = 7.6, 7.6 Hz, 1H), 7.00 (d, J = 7.6 Hz, 1H), 3.08 (sept, J = 7.0 Hz, 1H), 2.73 (t, J = 7.4 Hz, 2H), 2.49 (s, 3H), 1.75 (tq, J = 7.4, 7.4 Hz, 2H), 1.39 (d, J = 7.0 Hz, 6H), 0.99 (t, J = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 153.0, 152.6, 127.7, 123.6, 121.6, 121.0, 120.2, 1107.6, 28.5, 25.4, 22.5, 22.0, 15.0, 13.8.

HRMS (ESI) *m*/*z* calcd for $C_{15}H_{21}O$ ($[M+H]^+$): 217.1587, found 217.1585.

Compound **2v**



Following the typical procedure C, **1v** (23.2 mg, 0.100 mmol) was converted to **2v** (12.6 mg, 54%) after column chromatography on silica gel (*n*-hexane/EtOAc = 100/1). A colorless oil.

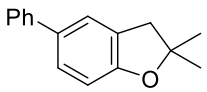
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.21 (dd, J = 7.9, 0.9 Hz, 1H), 7.09 (dd, J = 7.9, 7.9 Hz, 1H), 6.73 (dd, J = 7.9, 0.9 Hz, 1H), 3.99 (s, 3H), 3.06 (sept, J = 7.0 Hz, 1H), 2.73 (t, J = 7.5 Hz, 2H), 1.74 (tq, J = 7.5, 7.5 Hz, 2H), 1.38 (d, J = 7.0 Hz, 6H), 0.96 (t, J = 7.5 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 153.1, 145.1, 143.2, 130.0, 122.2, 120.4, 112.7,

105.0, 55.9, 28.5, 25.4, 22.5, 22.1, 13.7.

HRMS (ESI) *m*/*z* calcd for $C_{15}H_{21}O_2$ ([M+H]$^+$): 233.1536, found 233.1537.

Compound **3a**



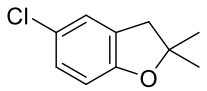
Following the typical procedure C, **1a** (27.8 mg, 0.100 mmol) was converted to **3a** (3.4 mg, 15%) after column chromatography on silica gel (*n*-hexane/EtOAc = 100/1). A colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.54–7.51 (m, 2H), 7.42–7.33 (m, 4H), 7.29 (m, 1H), 6.80 (d, J = 8.2 Hz, 1H), 3.08 (s, 2H), 1.52 (s, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 158.5, 141.4, 133.5, 128.6, 127.8, 127.1, 126.7, 126.4, 124.0, 109.6, 87.1, 42.8, 28.2.

HRMS (APCI) *m*/*z* calcd for $C_{16}H_{17}O$ ([M+H]$^+$): 225.1274, found 225.1269.

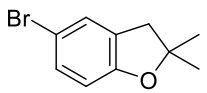
Compound **3l**[6]



Following the typical procedure C, **1l** (23.7 mg, 0.100 mmol) was converted to **3l** (2.3 mg, 14%) after column chromatography on silica gel (*n*-hexane/EtOAc = 50/1). A colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.09 (s, 1H), 7.05 (d, J = 8.2 Hz, 1H), 6.63 (d, J = 8.2 Hz, 1H), 2.99 (s, 2H), 1.46 (s, 6H).

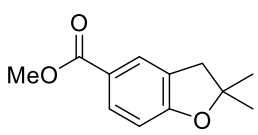
Compound **3m**[7]



Following the typical procedure C, **1m** (28.1 mg, 0.100 mmol) was converted to **3m** (10.4 mg, 46%) after column chromatography on silica gel (*n*-hexane/EtOAc = 50/1). A colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23 (s, 1H), 7.19 (d, J = 8.7 Hz, 1H), 6.60 (d, J = 8.7 Hz, 1H), 2.99 (s, 2H), 1.46 (s, 6H).

Compound **3p**



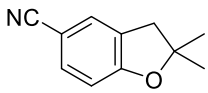
Following the typical procedure C, **1p** (26.0 mg, 0.100 mmol) was converted to **3p** (5.5 mg, 26%) after column chromatography on silica gel (*n*-hexane/EtOAc = 30/1). A colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.88–7.83 (m, 2H), 6.73 (d, J = 8.3 Hz, 1H), 3.87 (s, 3H), 3.03 (s, 2H), 1.49 (s, 6H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 167.1, 162.9, 131.1, 127.5, 127.0, 122.1, 109.2, 88.4, 51.8, 42.2, 28.2.

HRMS (ESI) *m*/*z* calcd for $C_{12}H_{15}O_3$ ($[M+H]^+$): 207.1016, found 207.1013.

Compound **3q**



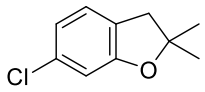
Following the typical procedure C, **1q** (22.7 mg, 0.100 mmol) was converted to **3q** (9.23 mg, 53%) after column chromatography on silica gel (*n*-hexane/EtOAc = 30/1). A colorless oil.

^1H NMR (400 MHz, $CDCl_3$) δ: 7.45–7.39 (m, 2H), 6.76 (d, J = 8.2 Hz, 1H), 3.03 (s, 2H), 1.49 (s, 6H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ: 162.5, 133.6, 129.1, 128.6, 119.7, 110.4, 103.1, 88.8, 42.0, 28.1.

HRMS (ESI) *m*/*z* calcd for $C_{11}H_{12}NO$ ($[M+H]^+$): 174.0913, found 174.0910.

Compound **3s**



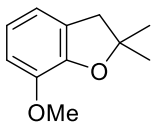
Following the typical procedure C, **1s** (23.7 mg, 0.100 mmol) was converted to **3s** (3.6 mg, 20%) after column chromatography on silica gel (*n*-hexane/EtOAc = 100/1). A colorless oil.

^1H NMR (500 MHz, $CDCl_3$) δ: 7.02 (d, J = 7.9 Hz, 1H), 6.79 (dd, J = 7.9, 1.9 Hz, 1H), 6.71 (d, J = 1.9 Hz, 1H), 2.96 (s, 2H), 1.47 (s, 6H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ: 159.7, 133.2, 125.8, 125.6, 120.0, 110.2, 88.0, 42.3, 28.1.

HRMS (DART) *m*/*z* calcd for $C_{10}H_{12}ClO$ ($[M+H]^+$): 183.0571, found 183.0568.

Compound **3v**



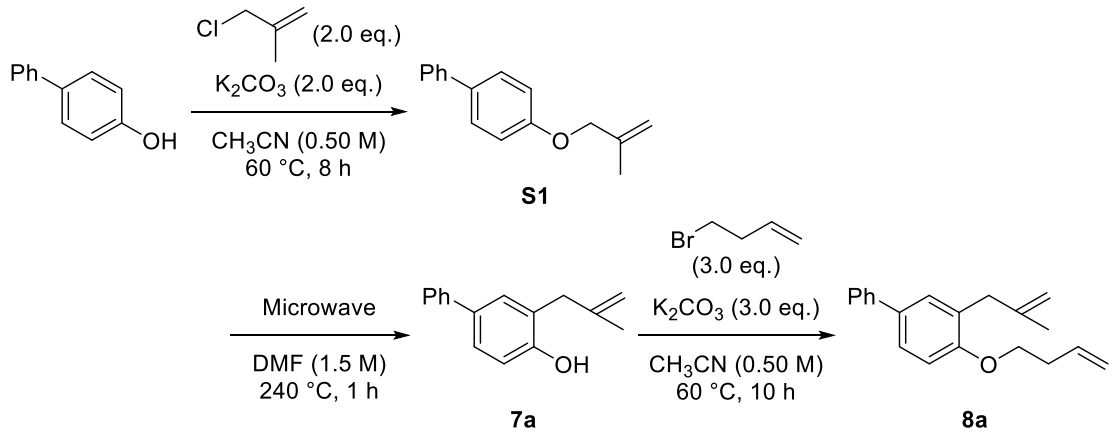
Following the typical procedure C, **1v** (23.2 mg, 0.100 mmol) was converted to **3v** (6.7 mg, 37%) after column chromatography on silica gel (*n*-hexane/EtOAc = 50/1). A colorless oil.

^1H NMR (400 MHz, $CDCl_3$) δ: 6.82–6.71 (m, 3H), 3.87 (s, 3H), 3.04 (s, 2H), 1.51 (s, 6H).

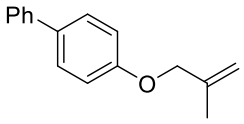
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 147.1, 144.6, 127.9, 120.3, 117.3, 110.5, 87.4, 55.7, 43.3, 28.2.

HRMS (ESI) *m*/*z* calcd for $C_{11}H_{15}O_2$ ($[M+H]^+$): 179.1067, found 179.1063.

2-3. Preparation of compound **7a** and **8a** for control experiment



Compound **S1**



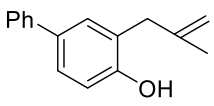
To a round-bottom flask containing 4-phenylphenol (1.00 g, 5.88 mmol, 1.0 eq.) and K_2CO_3 (1.62 g, 11.8 mmol, 2.0 eq.) in CH_3CN (12 mL, 0.50 M) was added 3-chloro-2-methylpropene (1.14 mL, 11.8 mmol, 2.0 eq.). The reaction mixture was stirred at 60 °C for 8 h. The mixture was filtered through a glass filter and washed with EtOAc. The filtrate was concentrated under reduced pressure to afford **S1** (1.30 g, quant.). A white powder. m.p. 70–71 °C.

^{1}H NMR (301 MHz, $CDCl_3$) δ: 7.58–7.48 (m, 4H), 7.45–7.37 (m, 2H), 7.30 (m, 1H), 7.03–6.96 (m, 2H), 5.12 (s, 1H), 5.01 (s, 1H), 4.48 (s, 2H), 1.86 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 158.3, 140.84, 140.77, 133.8, 128.7, 128.1, 126.7, 126.6, 115.0, 112.8, 71.7, 19.4.

HRMS (ESI) *m/z* calcd for $C_{16}H_{17}O$ ($[M+H]^+$): 225.1274, found 225.1275.

Compound **7a**



To a vial (Anton Paar) containing **S1** (500 mg, 2.23 mmol, 1.0 eq.) was added DMF (1.5 mL, 1.5 M). The sealed vial was then heated at 240 °C under microwave irradiation for 1 h. After cooling to room temperature, the mixture was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc = 10/1) to afford **7a** (460 mg, 92%). A yellow oil.

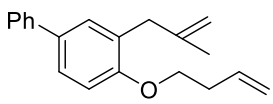
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.59–7.54 (m, 2H), 7.45–7.38 (m, 3H), 7.35 (d, J = 2.1

Hz, 1H), 7.31 (m, 1H), 6.92 (d, J = 8.2 Hz, 1H), 5.25 (s, 1H), 4.97 (s, 1H), 4.93 (s, 1H), 3.46 (s, 2H), 1.79 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 154.3, 144.5, 140.8, 133.9, 129.7, 128.7, 126.70, 126.67, 126.6, 125.0, 116.4, 112.6, 40.1, 22.1.

HRMS (ESI) *m*/*z* calcd for $C_{16}H_{16}NaO$ ([M+Na]$^+$): 247.1093, found 247.1086.

Compound **8a**



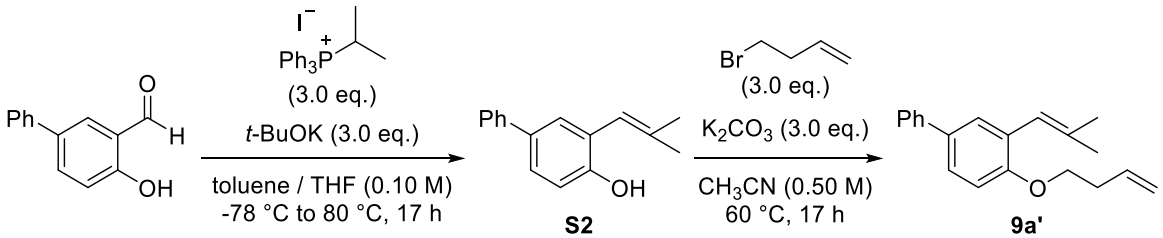
To a round-bottom flask containing **7a** (200 mg, 0.892 mmol, 1.0 eq.) and K_2CO_3 (370 mg, 2.67 mmol, 3.0 eq.) in CH_3CN (1.8 mL, 0.50 M) was added 4-bromobut-1-ene (0.27 mL, 2.67 mmol, 3.0 eq.). The reaction mixture was stirred at 60 °C for 10 h. The mixture was filtered through a glass filter, washed with EtOAc, and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (*n*-hexane) to afford **8a** (183 mg, 74%). A colorless oil.

^{1}H NMR (301 MHz, $CDCl_3$) δ: 7.59–7.51 (m, 2H), 7.46–7.36 (m, 4H), 7.40 (m, 1H), 6.91 (d, J = 8.3 Hz, 1H), 5.94 (m, 1H), 5.24–5.08 (m, 2H), 4.80 (s, 1H), 4.72 (s, 1H), 4.06 (t, J = 6.5 Hz, 2H), 3.40 (s, 2H), 2.63–2.53 (m, 2H), 1.75 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 156.5, 144.8, 141.0, 134.7, 133.3, 129.1, 128.8, 128.6, 126.7, 126.5, 125.8, 116.9, 111.6, 111.5, 67.5, 38.0, 33.9, 22.5.

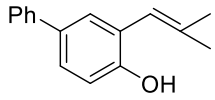
HRMS (ESI) *m*/*z* calcd for $C_{20}H_{22}NaO$ ([M+Na]$^+$): 301.1563, found 301.1556.

2-4. Preparation of compound **9a** and **9a'** for NMR experiment



5-phenyl-2-hydroxybenzaldehyde was synthesized following reported procedure.[8]

Compound **S2**



This method was based on the reported procedure.[9]

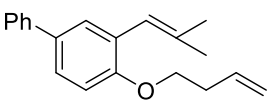
To a round-bottom flask equipped with reflux condenser containing isopropyltriphenylphosphonium iodide (654 mg, 1.51 mmol, 3.0 eq.) in toluene (10 mL), *t*-BuOK (170 mg, 1.51 mmol, 3.0 eq.) in THF (2.5 mL) was added and stirred for 1 h at 50 °C. After some minutes the suspension became a dark red solution. Then, this suspension cooled to -78 °C and 5-phenyl-2-hydroxybenzaldehyde (100 mg, 0.504 mmol, 1.0 eq.) in toluene (2.5 mL) was added to the mixture and stirred at 80 °C for 17 h. Afterwards, sat. NH_4Cl was added to quench the reaction. The organic compounds were extracted with Et_2O. 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/EtOAc = 10/1) to afford **S2** (94.0 mg, 83%). A colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.58–7.53 (m, 2H), 7.44–7.39 (m, 3H), 7.33–7.28 (m, 2H), 6.98 (d, J = 8.3 Hz, 1H), 6.19 (s, 1H), 5.11 (s, 1H), 1.98 (s, 3H), 1.75 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 152.4, 141.0, 140.9, 133.3, 128.7, 128.5, 126.9, 126.7, 126.6, 124.9, 118.6, 115.2, 25.8, 19.5.

HRMS (ESI) *m*/*z* calcd for $C_{16}H_{16}NaO$ ([M+Na]$^+$): 247.1093, found 247.1086.

Compound **9a'**



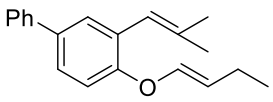
To a round-bottom flask containing **S2** (90.0 mg, 0.401 mmol, 1.0 eq.) and K_2CO_3 (166 mg, 1.20 mmol, 3.0 eq.) in CH_3CN (0.8 mL, 0.50 M) was added 4-bromobut-1-ene (0.12 mL, 1.20 mmol, 3.0 eq.). The reaction mixture was stirred at 60 °C for 17 h. The mixture was filtered through a glass filter, washed with EtOAc, and the filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (*n*-hexane) to afford **9a'** (86.9 mg, 78%). A colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.60–7.55 (m, 2H), 7.48–7.39 (m, 4H), 7.31 (m, 1H), 6.94 (d, J = 8.4 Hz, 1H), 6.38 (s, 1H), 5.95 (m, 1H), 5.23–5.11 (m, 2H), 4.08 (t, J = 6.7 Hz, 2H), 2.64–2.57 (m, 2H), 1.96 (s, 3H), 1.89 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 155.9, 141.1, 135.6, 134.6, 133.1, 129.2, 128.7, 128.1, 126.7, 126.5, 125.8, 120.5, 117.0, 111.9, 67.7, 33.8, 26.7, 19.8.

HRMS (ESI) *m*/*z* calcd for $C_{20}H_{22}NaO$ ([M+Na]$^+$): 301.1563, found 301.1554.

Compound **9a**



In a glovebox, to an oven-dried test tube was added $[Rh(C_2H_4)_2Cl]_2$ (3.89 mg, 5 mol%), tri(3,5-xylyl)phosphine (20.8 mg, 30 mol%) and anhydrous *p*-xylene (2.0 mL, 0.10 M). The resulting solution was stirred for 30 min at room temperature, then AgOTf (7.71 mg, 15 mol%) was added and the reaction mixture was stirred for 15 min at room temperature. Next, **1a** (0.200 mmol, 55.7 mg, 1.0 eq.) was added to the mixture, the reaction vessel was sealed, then removed from the glovebox and heated at 80 °C. After stirring at the same temperature for 8 h, the mixture was cooled to room temperature and filtered by short silica gel column chromatography. The filtrate was concentrated in vacuo. The obtained residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc = 100/1) to give corresponding benzofuran (*E*)-**9a** (4.3 mg, 8%) and mixture of (*E*)-**9a** and (*Z*)-**9a** (4.0 mg, 7%, *E*/*Z* = 1/10). A colorless oil.

(*E*)-**9a** : **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.58–7.54 (m, 2H), 7.47–7.39 (m, 4H), 7.32 (m, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.41 (dt, *J* = 12.2, 1.4 Hz, 1H), 6.35 (s, 1H), 5.41 (dt, *J* = 12.2, 7.3 Hz, 1H), 2.08 (ddq, *J* = 7.3, 7.3, 1.4 Hz, 2H), 1.95 (d, *J* = 1.4 Hz, 3H), 1.87 (d, *J* = 1.3 Hz, 3H), 1.06 (t, *J* = 7.3 Hz, 3H).

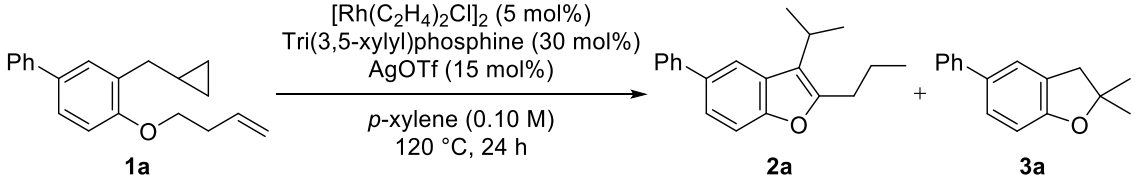
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 154.4, 141.5, 140.9, 136.5, 135.0, 129.4, 128.7, 128.6, 126.9, 126.8, 125.9, 120.0, 115.6, 115.2, 26.6, 20.8, 19.8, 14.6.

HRMS (ESI) *m*/*z* calcd for $C_{20}H_{22}NaO$ ($[M+Na]^+$): 301.1563, found 301.1556.

mixture of (*E*)-**9a** and (*Z*)-**9a** (*E*/*Z* = 1/10): **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.58–7.54 (m, 2H), 7.47–7.38 (m, 4H), 7.42 (m, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.41 (dt, *J* = 12.2, 1.4 Hz, 0.18H, (*E*)-isomer), 6.37 (s, 1H), 6.32 (dt, *J* = 6.0, 1.5 Hz, 1H, (*Z*)-isomer), 5.41 (dt, *J* = 12.2, 7.3 Hz, 0.10H, (*E*)-isomer), 4.85 (dt, *J* = 7.3, 6.0 Hz, 1H, (*Z*)-isomer), 2.26 (ddq, *J* = 7.3, 7.3, 1.5 Hz, 2H, (*Z*)-isomer), 2.08 (ddq, *J* = 7.3, 7.3, 1.4 Hz, 0.26H, (*E*)-isomer), 1.96 (d, *J* = 1.3 Hz, 3H), 1.87 (d, *J* = 1.3 Hz, 3H), 1.05 (t, *J* = 7.6 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 154.4, 141.5, 140.9, 136.5, 135.0, 129.4, 128.7, 128.6, 126.9, 126.8, 125.9, 120.0, 115.6, 115.2, 26.6, 20.8, 19.8, 14.6.

3. Gram scale reaction



In a glovebox, to an oven-dried 100-mL round-bottom flask was added $[Rh(C_2H_4)_2Cl]_2$ (69.9 mg, 5 mol%), tri(3,5-xylyl)phosphine (373 mg, 30 mol%) and anhydrous *p*-xylene (36 mL, 0.10 M). The resulting solution was stirred for 30 min at room temperature, then AgOTf (138 mg, 15 mol%) was added and the reaction mixture was stirred for 15 min at room temperature.

Next, **1a** (3.59 mmol, 1.00 g, 1.0 eq.) was added to the mixture, the reaction vessel was sealed, then removed from the glovebox and heated at 120 °C. After stirring at the same temperature for 24 h, the mixture was cooled to room temperature and filtered by short silica gel column chromatography. The filtrate was concentrated in vacuo. The obtained residue was purified by column chromatography on silica gel (*n*-hexane/EtOAc = 100/1) to give corresponding benzofuran **2a** (0.832 g, 83%) and dihydrobenzofuran **3a** (0.174 g, 17%).

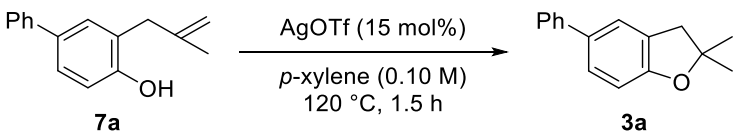
4. Control experiment

4-1. Experiment of **Table 6**

This control experiment was performed according to Typical Procedure C, except for the reaction time and the substrate used. In this control experiment, compound **4**[2] was used as the substrate, and the reaction time was set to 17 h. The crude product was analyzed by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

4-2. Experiment of **Table 7**

Typical procedure D (entry 6)



In a glovebox, to an oven-dried test tube was added **7a** (0.100 mmol, 22.4 mg, 1.0 eq.), AgOTf (3.85 mg, 15 mol%) and anhydrous *p*-xylene (0.10 M). The reaction vessel was

sealed, then removed from the glovebox and heated at 120 °C. After stirring at the same temperature for 1.5 h, the mixture was cooled to room temperature and filtered by short silica gel column chromatography. The filtrate was concentrated in vacuo. The crude product was analyzed by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard, giving **3a** in 68% yield.

References

1. Y. Sato, T. Matsuzaki, T. Takehara, M. Sako, T. Suzuki, M. Arisawa, *Chem. Commun*. 2022, **58**, 415–418.

2. Y. Niki, K. Mitsudo, E. Sato, S. Suga, *Org. Lett*. 2024, **26**, 11111–11116.

3. A. L. Pincock, J. A. Pincock, R. Stefanova, *J. Am. Chem. Soc*. 2002, **124**, 9768–9778.

4. Y. L. Lin, J. Y. Cheng, Y. H. Chu, *Tetrahedron* 2007, **63**, 10949–10957.

5. M. Scheepstra, S. A. Andrei, M. Y. Unver, A. K. H. Hirsch, S. Leysen, C. Ottmann, L. Brunsveld, L. G. Milroy, *Angew. Chem. Int. Ed.* 2017, **56**, 5480–5484.

6. X. Wang, Y. Lu, H. X. Dai, J. Q. Yu, *J. Am. Chem. Soc.* 2010, **132**, 12203–12205.

7. G. Zhao, B. Wang, W. Yang, H. Ren, *Eur. J. Org. Chem*. 2012, **2012**, 6236–6247.

8. B. C. Raju, A. K. Tiwari, J. A. Kumar, A. Z. Ali, S. B. Agawane, G. Saidachary, K. Madhusudana, *Med. Chem*. 2010, **18***,* 358–365.

9. M. Peters, M. Trobe, H. Tan, R. Kleineweischede, R. Breinbauer, *Chem. Eur. J.* 2013, **19**, 2442–2449.