Supplementary Information 1

Doubleisomerization / cycloisomerization / aromatization of 1-(allyloxy)-2-(cyclopropylmethyl)benzenes to give 2-ethyl-3-isopropylbenzofurans using multitasking single rhodium catalyst

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Contents

General

[1] H-NMR spectra were recorded in $CDCl_3$ at 25 °C unless otherwise noted, at 300, 400 or 500 MHz, with TMS as an internal standard. ^{13}C-NMR spectra were recorded in $CDCl_3$ at 25 °C unless otherwise noted, at 300, 400 or 500MHz with TMS or $CDCl_3$ as an internal standard. ^{19}F NMR spectra were recorded in $CDCl_3$ at 25 °C unless otherwise noted, at 376 MHz, with $C_6H_5CF_3$ as an internal standard.

NOE measurements for structure determination of 2a

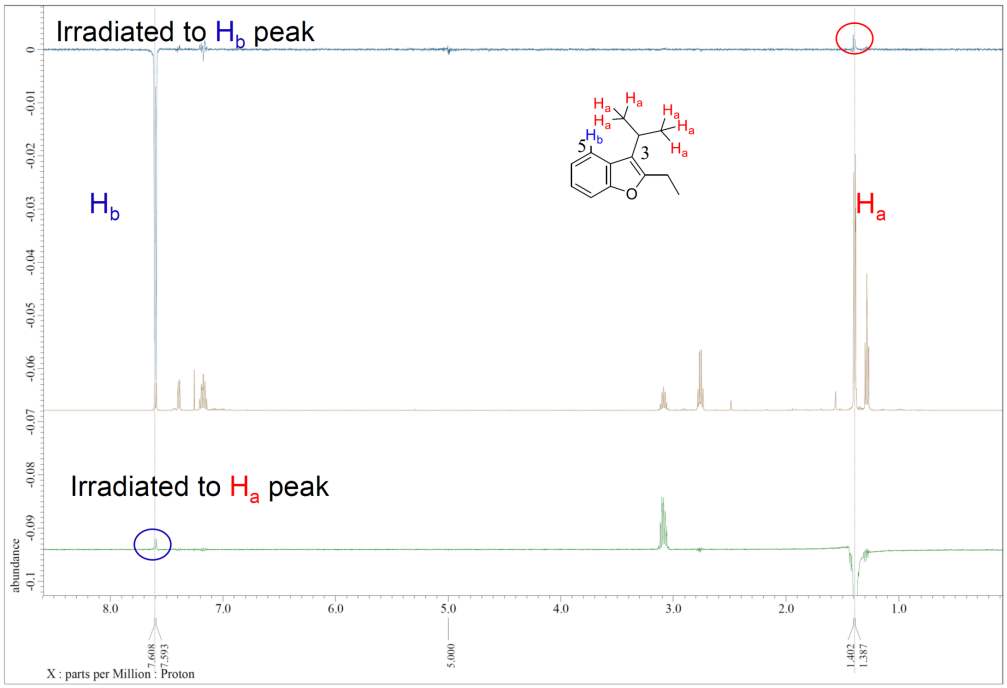
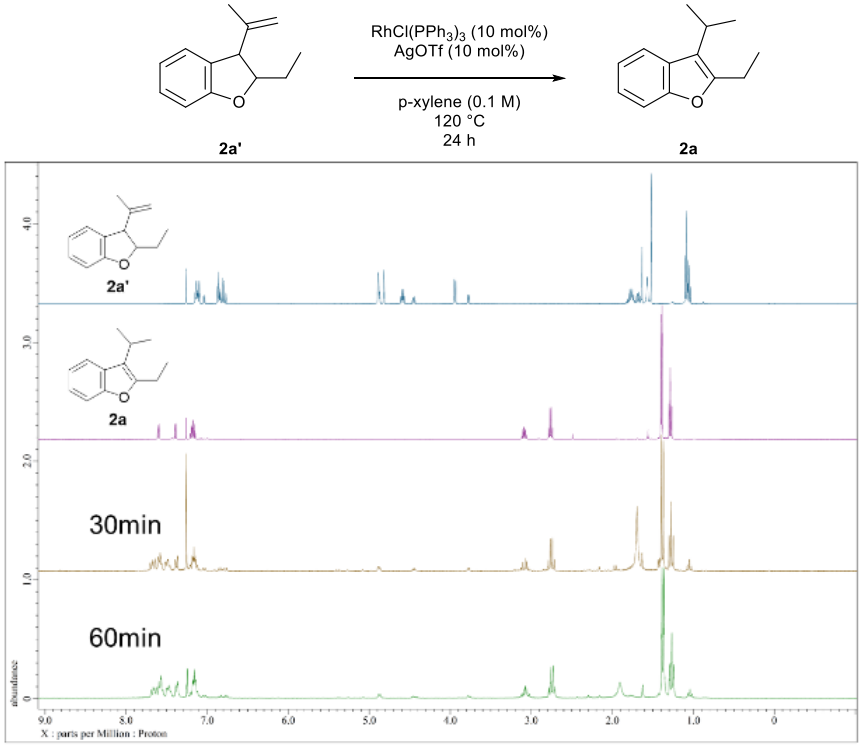


Figure S1. Result of NOE measurement.

To determine the structure of compound **2a**, NOE measurements were performed. First, we irradiated the hydrogen peak of the isopropyl group (H_a). Next, we irradiated the hydrogen peak of the 5-position of benzofuran (H_b). Since there was a correlation between H_a and H_b in both measurements, it was determined that the isopropyl group was substituted at the 3-position of benzofuran.

NMR time-course experiment (conversion from 2a' to 2a)

a) With 10 mol% of $RhCl(PPh_3)_3$ and 10 mol% of AgOTf



b) Without catalyst

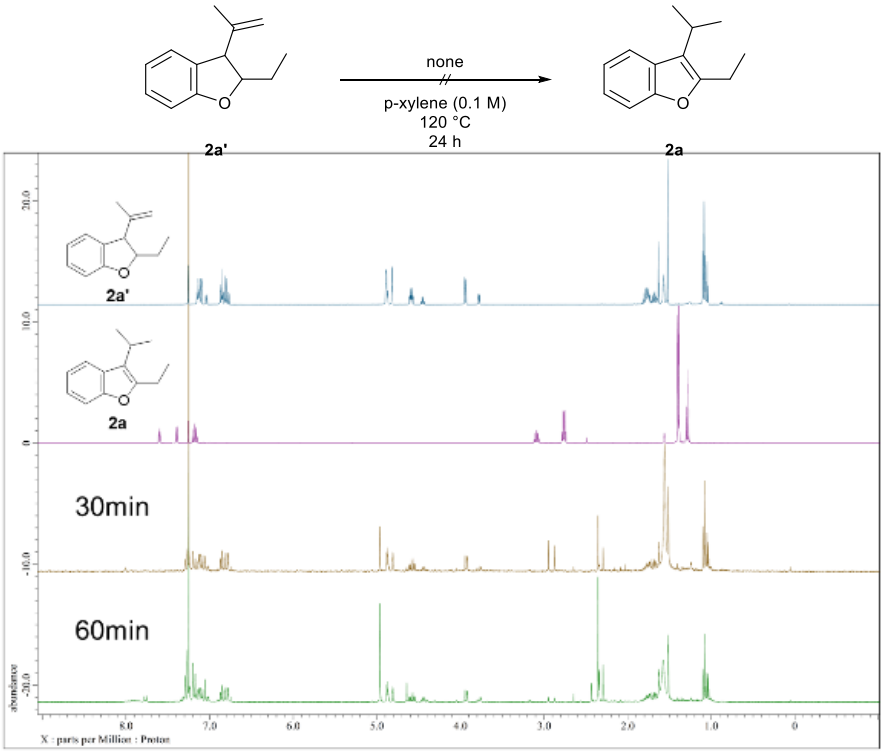
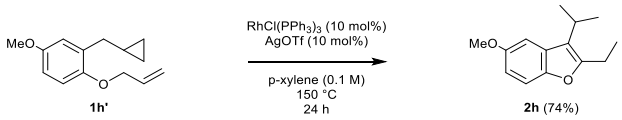


Figure S2 NMR time-course experiment (conversion from **2a'** to **2a**)

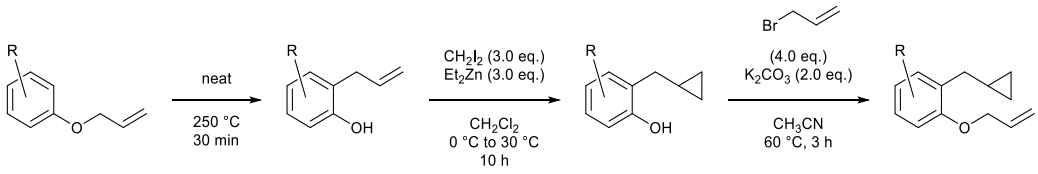
Scheme S1 1.3 mmol scale experiment



To a stirred solution of 1-(allyloxy)-2-(cyclopropylmethyl)benzene **1'** 280 mg 1.3mmol) in *p*-xylene (0.1 M), degassed with N_2 bubbling, was added $RhCl(PPh_3)_3$ (120 mg, 0.13mmol) and AgOTf (33 mg, 0.13 mmol) under an N_2 atmosphere. The reaction mixture was refluxed (120 °C) for 24 h. Then, the mixture was filtered through 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 2-ethyl-3-isopropylbenzofurans **2h** (211 mg 74%).

Preparation of 1a'-1x

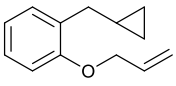
・ Typical procedure A for the preparation of compounds **1a'-1n'**



(Allyloxy)benzene were prepared according to the known literature. [1-4] (Allyloxy)benzenes were 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 separated by column chromatography on silica gel (*n*-hexane/ AcOEt = 10/1) to afford the corresponding allyl phenol. To a round-bottom flask containing allyl phenol and diiodomethane (3.0 eq.) in DCM (0.2M) was slowly added diethyl zinc (3.0 eq, 1.6 M in hexane) at 0 °C. The mixture was stirred at 30 °C for 10 h. Afterwards, sat. NH_4Cl and 1 *N* HCl 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 2-(cyclopropylmethyl)phenol.

To a round-bottom flask containing the above obtained 2-(cyclopropylmethyl)phenol and K_2CO_3 (2.0 eq.) in CH_3CN (0.5 M) was added allyl bromide (4.0 eq.). The reaction mixture was stirred at 60 °C for 3 h. The mixture was filtered through glass filter with AcOEt, and filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel using *n*-hexane/ AcOEt = 20/1) as an eluent to afford 1-(allyloxy)-2-(cyclopropylmethyl)benzene.

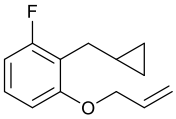
Compound 1a'



Following the typical procedure, A, (allyloxy)benzene [1] (2.86 g, 22.2 mmol) was converted to **1a'** (3.2 g, 80%) after column chromatography on silica gel (*n*-hexane/

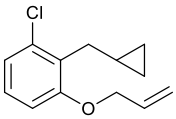
AcOEt = 20/1). Colorless oil.; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.29 (d, *J* = 7.2 Hz, 1H), 7.17 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.91 (dd, *J* = 7.4, 7.4 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 6.13-6.01 (m, 1H), 5.43 (ddt *J* = 17.2, 1.7, 1.4 Hz, 1H), 5.27 (ddt, *J* = 10.5, 1.7, 1.4 Hz, 1H), 4.55 (d, *J* = 5.2 Hz, 2H), 2.57 (d, *J* = 6.9 Hz, 2H), 1.11-0.98 (m, 1H), 0.52-0.46 (m, 2H), 0.19 (td, *J* = 4.8, 4.8 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 156.3, 133.6, 130.9, 129.5, 126.8, 120.5, 116.8, 111.3, 68.6, 34.5, 10.6, 4.6; HRMS (APCI) calcd for $C_{13}H_{17}O$ $(M+H)^+$: 189.1279, found: 189.1275

Compound 1b'



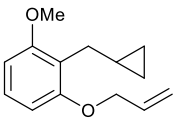
Following the typical procedure A, 1-(allyloxy)-3-fluorobenzene [2] (2.42 g, 16 mmol) was converted to **1b'** (730 mg, 25%) after column chromatography on silica gel (*n*-hexane/ AcOEt = 20/1). Colorless oil.; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.12-7.08 (m, 1H), 6.70-6.57 (m, 2H), 6.10-6.01 (m, 1H), 5.43 (ddt, *J* = 17.4, 1.8, 1.8 Hz, 1H), 5.28 (ddt, *J* = 10.5, 1.4, 1.4 Hz, 1H), 4.56 (ddd, *J* = 3.2, 1.5, 1.5 Hz, 2H), 2.62-2.60 (m, 2H), 1.07-1.00 (m, 1H), 0.41-0.37 (m, 2H), 0.25-0.21 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 161.7 ($^{1}J_{CF}$ = 242.5 Hz), 157.6 ($^{3}J_{CF}$ = 9.6 Hz), 133.2, 126.9 ($^{3}J_{CF}$ = 10.5 Hz), 118.2 ($^{2}J_{CF}$ = 19.2 Hz), 117.1, 107.9 ($^{2}J_{CF}$ = 23.0 Hz), 107.2, 69.1, 27.0, 10.9, 4.5; ^{19}F-NMR (376 MHz, $CDCl_3$) δ: −117.7; HRMS (APCI) calcd for $C_{13}H_{16}FO$ $(M+H)^+$: 207.1185, found: 207.1178

Compound 1c'



Following the typical procedure A, 1-(allyloxy)-3-chlorobenzene [3] (1.70 g, 10.1 mmol) was converted to **1c'** (540 mg, 24%) after column chromatography on silica gel (*n*-hexane/AcOEt = 20/1). Colorless oil.; ^{1} H-NMR (300 MHz, $CDCl_3$) δ: 7.07 (dd, *J* = 8.1 8.1 Hz, 1H), 6.98 (dd, *J* = 7.9, 1.0 Hz, 1H), 6.75 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.11-5.98 (m, 1H), 5.42 (ddt *J* = 17.5, 1.7, 1.4 Hz, 1H), 5.28 (ddt *J* = 10.7, 1.7, 1.4 Hz, 1H), 4.54 (ddd, *J* = 3.3, 1.7, 1.7 Hz, 2H), 2.77 (d, *J* = 6.9 Hz, 2H), 1.16-1.03 (m, 1H), 0.42-0.34 (m, 2H), 0.32-0.27 (m, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 157.4, 134.9, 133.1, 129.3, 127.0, 121.8, 117.2, 110.0, 69.0, 31.1, 10.4, 4.3; HRMS (APCI) calcd for $C_{13}H_{16}ClO$ $(M+H)^+$: 223.0890, found: 223.0884

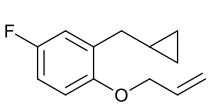
Compound 1d'



Following the typical procedure A, 1-(allyloxy)-3-methoxybenzene [3] (1.70 g, 10.4 mmol) was converted to **1d'** (720 mg, 32%) after column chromatography on silica gel (*n*-hexane/AcOEt = 10/1). Colorless oil.; ^{1} H-NMR (500 MHz, $CDCl_3$) δ: 7.11 (dd, *J* = 8.3, 8.3 Hz 1H), 6.56 (d, *J* = 8.6 Hz, 1H), 6.53 (d, *J* = 8.0 Hz, 1H), 6.09-6.02 (m, 1H), 5.42 (ddt, *J* = 17.4, 1.4, 1.4 Hz, 1H), 5.25 (ddt, *J* = 10.5, 1.4, 1.4 Hz, 1H), 4.54 (dd, *J* = 3.2, 1.7, 1.7 Hz, 2H), 3.81 (s, 3H), 2.62 (d, *J* = 6.3 Hz, 2H), 1.07-0.99 (m, 1H), 0.36-0.32 (m, 2H), 0.23 (td, *J* = 5.3, 3.8 Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 158.4, 157.2, 133.7, 126.6, 119.1, 116.7, 104.9, 103.8, 68.9, 55.6, 27.2, 10.9, 4.4; HRMS

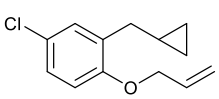
(APCI) calcd for $C_{14}H_{19}O_2$ $(M+H)^+$: 219.1385, found: 219.1378

Compound 1e'



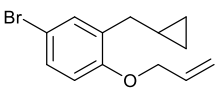
Following the typical procedure A, 1-(allyloxy)-4-fluorobenzene [2] (1.3 g, 8.5 mmol) was converted to **1e'** (820 mg, 46%) after column chromatography on silica gel (*n*-hexane/AcOEt = 20/1). Colorless oil.; [1] H-NMR (300 MHz, $CDCl_3$) δ: 7.05 (dd, *J* = 9.3, 3.1 Hz, 1H), 6.83 (ddd, *J* = 8.6, 8.3, 3.1 Hz, 1H), 6.74 (dd *J* = 9.0, 4.8 Hz, 1H), 6.05 (m, 1H), 5.41 (ddt, *J* = 17.2, 1.7, 1.7 Hz, 1H), 5.27 (ddt, *J* = 10.7, 1.4, 1.4 Hz, 1H), 4.50 (d, *J* = 4.8 Hz, 2H), 2.54 (d, *J* = 6.9 Hz, 2H), 1.06-0.96 (m, 1H), 0.52 (m, 2H), 0.19 (td *J* = 5.2, 4.8 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 157.1 ($^1J_{CF}$ = 237.7 Hz), 152.3 ($^4J_{CF}$ = 1.9 Hz), 133.4, 132.9 ($^3J_{CF}$ = 6.7 Hz), 117.1, 116.1 ($^2J_{CF}$ = 23.0 Hz), 112.3 ($^2J_{CF}$ = 23.0 Hz), 112.1 ($^3J_{CF}$ = 8.6 Hz), 69.3, 34.2, 10.1, 4.6; ^{19}F-NMR (376 MHz, $CDCl_3$) −124.7; HRMS (APCI) calcd for $C_{13}H_{16}FO$ $(M+H)^+$: 207.1185, found: 207.1178

Compound 1f'



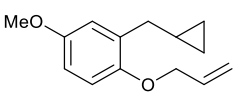
Following the typical procedure A, 1-(allyloxy)-4-chlorobenzene [4] (1.13 g, 6.7 mmol) was converted to **1f'** (735 mg, 53%) after column chromatography on silica gel (*n*-hexane/AcOEt = 20/1). Colorless oil.; [1] H-NMR (300 MHz, $CDCl_3$) δ: 7.27 (d, *J* = 4.1 Hz, 1H), 7.11 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.74 (d, *J* = 8.7 Hz, 1H), 6.04 (m, 1H), 5.41 (dd, *J* = 17.4, 1.4 Hz, 1H), 5.28 (dd, *J* = 10.5, 1.4 Hz, 1H), 4.52 (d, *J* = 4.6 Hz, 2H), 2.53 (d, *J* = 6.9 Hz, 2H), 1.05-0.95 (m, 1H), 0.52 (m, 2H), 0.19 (td, *J* = 5.0, 4.9 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): 154.8, 133.1, 132.9, 129.3, 126.4, 125.3, 117.2, 112.4, 68.9, 34.2, 10.2, 4.7; HRMS (APCI) calcd for $C_{13}H_{16}ClO$ $(M+H)^+$: 223.0890, found: 223.0883

Compound 1g'



Following the typical procedure A, 1-(allyloxy)-4-bromobenzene [5] (1.05 g, 5.3 mmol) was converted to **1g'** (821 mg, 58%) after column chromatography on silica gel (*n*-hexane/AcOEt = 20/1). Colorless oil.; [1] H-NMR (500 MHz, $CDCl_3$) δ: 7.40 (d, *J* = 2.9 Hz, 1H), 7.25 (dd, *J* = 9.2, 1.7 Hz, 1H), 6.69 (d, *J* = 8.6 Hz, 1H), 6.07-6.00 (m, 1H), 5.40 (ddt, *J* = 17.2, 1.7, 1.7 Hz, 1H), 5.28 (ddt, *J* = 10.3, 1.7, 1.7 Hz, 1H), 4.51 (d, *J* = 5.2 Hz, 2H), 2.52 (d, *J* = 6.9 Hz, 2H), 0.53-0.50 (m, 2H), 0.19 (td, *J* = 5.2, 4.6 Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): 155.4, 133.3, 133.1, 132.1, 129.4, 117.2, 112.9, 112.8, 68.8, 34.2, 10.2, 4.7; HRMS (APCI) calcd for $C_{13}H_{16}BrO$ $(M+H)^+$: 267.0385, found: 267.0378

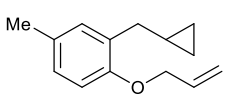
Compound 1h'



Following the typical procedure A, 1-(allyloxy)-4-methoxybenzene [4] (1.32 g, 8.0 mmol) was converted to **1h'** (746 mg, 43%) after column chromatography on silica

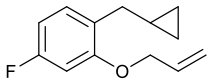
gel (*n*-hexane/AcOEt = 10/1). Colorless oil.; [1] H-NMR (300 MHz, $CDCl_3$) δ: 6.91 (d, *J* = 3.1 Hz, 1H), 6.77 (d, *J* = 8.9 Hz, 1H), 6.68 (dd, *J* = 8.9, 3.1 Hz, 1H), 6.12-5.99 (m, 1H), 5.41 (ddt *J* = 17.2, 1.7, 1.7 Hz, 1H), 5.25 (ddt *J* = 10.7, 1.7, 1.4 Hz, 1H), 4.49 (ddd, *J* = 3.3, 1.7, 1.7 Hz, 2H), 3.78 (s, 3H), 2.54 (d, *J* = 6.9 Hz, 2H), 1.09-0.96 (m, 1H), 0.53-0.47 (m, 2H), 0.20 (td, *J* = 5.2, 4.0 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): 153.6, 150.6, 133.9, 132.4, 116.8, 116.1, 112.4, 110.4, 69.5, 55.6, 34.5, 10.5, 4.6; HRMS (APCI) calcd for $C_{14}H_{19}O_2$ $(M+H)^+$: 219.1385, found: 219.1378

Compound 1i'



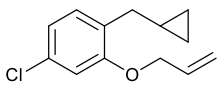
Following the typical procedure A, 1-(allyloxy)-4-methylbenzene [4] (800 mg, 5.4 mmol) was converted to **1i'** (451 mg, 41%) after column chromatography on silica gel (*n*-hexane/AcOEt = 20/1). Colorless oil.; [1] H-NMR (400 MHz, $CDCl_3$) δ: 7.09 (d, *J* = 1.8 Hz, 1H), 6.96 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 6.00-6.12 (1H), 5.41 (ddt, *J* = 17.4, 1.8, 1.4 Hz, 1H), 5.25 (ddt, *J* = 10.5, 1.8, 1.4 Hz, 1H), 4.52 (ddd, *J* = 3.3, 1.7, 1.7 Hz, 2H), 2.53 (d, *J* = 6.9 Hz, 2H), 2.29 (s, 3H), 1.08-0.98 (m, 1H), 0.50-0.46 (m, 2H), 0.19 (td, *J* = 5.0 Hz, 4.6 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): 154.2, 133.8, 130.7, 130.4, 129.6, 127.0, 116.7, 111.4, 68.8, 34.5, 20.6, 10.7, 4.7; HRMS (APCI) calcd for $C_{14}H_{19}O$ $(M+H)^+$: 203.1436, found: 203.1430

Compound 1j'



Following the typical procedure A, 1-(allyloxy)-3-fluorobenzene [2] (2.42 g, 16 mmol) was converted to **1j'** (966 mg, 30%) after column chromatography on silica gel (*n*-hexane/AcOEt = 20/1). Colorless oil.; [1] H-NMR (400 MHz, $CDCl_3$) δ: 7.20 (dd *J* = 7.8, 7.8 Hz, 1H), 6.65-6.55 (m, 2H), 6.05 (m, 1H), 5.43 (ddt, *J* = 17.4, 1.8, 1.4 Hz, 1H), 5.29 (dd, *J* = 11.7, 1.4 Hz, 1H), 4.52 (d, *J* = 5.0 Hz, 2H), 2.51 (d, *J* = 6.9 Hz, 2H), 1.03-0.96 (m, 1H), 0.48 (m, 2H), 0.17 (td, *J* = 5.0 Hz, 4.6 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): 161.9 ($^1J_{CF}$ = 242.3 Hz), 157.0 ($^3J_{CF}$ = 8.6 Hz), 132.9, 129.8 ($^3J_{CF}$ = 9.6 Hz), 126.4 ($^4J_{CF}$ = 2.9 Hz), 117.3, 106.4 ($^2J_{CF}$ = 21.1 Hz), 99.6 ($^2J_{CF}$ = 24.9 Hz), 68.8, 33.9, 10.6, 4.6; ^{19}F-NMR (376 MHz, $CDCl_3$): −115.7 MHz; HRMS (APCI) calcd for $C_{13}H_{16}FO$ $(M+H)^+$: 207.1185, found: 207.1179

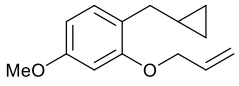
Compound 1k'



Following the typical procedure A, 1-(allyloxy)-3-chlorobenzene [3] (1.70 g, 10.1 mmol) was converted to **1k'** (782 mg, 31%) after column chromatography on silica gel (*n*-hexane/AcOEt = 20/1). Colorless oil.; [1] H-NMR (300 MHz, $CDCl_3$) δ: 7.19 (d, *J* = 8.3 Hz, 1H), 6.88 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.80 (d, *J* = 2.1 Hz, 1H), 6.10-5.98 (m, 1H), 5.42 (ddt, *J* = 17.2, 1.7, 1.4 Hz, 1H), 5.29 (ddt, *J* = 10.5, 1.4, 1.4 Hz, 1H), 4.51 (ddd, *J* = 3.3, 1.5, 1.5 Hz, 2H), 2.51 (d, *J* = 6.7 Hz, 2H), 1.06-0.93 (m, 1H), 0.51-0.45 (m, 2H), 0.17 (td, *J* = 5.2 Hz, 4.5 Hz, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): 156.8, 132.9, 131.9, 130.2, 129.4, 120.4, 117.3, 111.9, 68.8, 34.0, 10.4, 4.6; HRMS (APCI) calcd for $C_{13}H_{16}ClO$

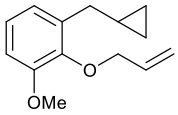
$(M+H)^+$: 223.0890, found: 223.0882

Compound 1l'



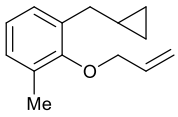
Following the typical procedure A, 1-(allyloxy)-3-methoxybenzene [4] (1.3 g, 7.92 mmol) was converted to **1l'** (920 mg, 53%) after column chromatography on silica gel (*n*-hexane/AcOEt = 20/1). Colorless oil.; [1] H-NMR (400 MHz, $CDCl_3$) δ: 7.17 (d, *J* = 7.8 Hz, 1H), 6.50-6.44 (m, 2H), 6.11-6.01 (m, 1H), 5.43 ddt, *J* = 17.4, 1.4, 1.4 Hz, H), 5.27 (ddt, *J* = 10.5, 1.4, 1.4 Hz, 1H), 4.5 5-4.51 (m, 2H), 3.82-3.75 (m, 3H), 2.55-2.49 (m, 2H), 1.06-0.96 (m, 1H), 0.52-0.44 (m, 2H), 0.17 (td, *J* = 5.0 Hz, 4.6 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): 158.9, 157.1, 133.4, 129.7, 123.3, 117.0, 104.0, 99.5, 68.6, 55.3, 33.8, 10.8, 4.6; HRMS (APCI) calcd for $C_{14}H_{19}O_2$ $(M+H)^+$: 219.1385, found: 219.1377

Compound 1m'



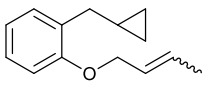
Following the typical procedure A, 1-(allyloxy)-2-methoxybenzene [4] (1.3 g, 7.92 mmol) was converted to **1m'** (920 mg, 53%) after column chromatography on silica gel (*n*-hexane/AcOEt = 20/1). Colorless oil.; [1] H-NMR (400 MHz, $CDCl_3$) δ: 7.01 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.93 (dd, *J* = 7.3, 1.4 Hz, 1H), 6.79 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.15-6.05 (m, 1H), 5.38 (dd, *J* = 16.9, 1.8 Hz, 1H), 5.22 (dd, *J* = 10.3, 1.6 Hz, 1H), 4.48 (ddd, 6.0, 1.4, 1.4 Hz), 3.85 (s, 3H), 2.56 (d, *J* = 7.3 Hz, 2H), 1.05-0.95 (m, 1H), 0.51-0.47 (m, 2H), 0.20 (td, *J* = 5.5, 3.7 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): 152.6, 145.7, 136.2, 134.5, 123.7, 121.6, 117.0, 110.0, 73.6, 55.7, 34.4, 11.2, 4.7; HRMS (APCI) calcd for $C_{14}H_{19}O_2$ $(M+H)^+$: 219.1385, found: 219.1378

Compound 1n'



Following the typical procedure A, 1-(allyloxy)-2-methylmbenzene [4] (1.3 g, 8.77 mmol) was converted to **1n'** (1.0 g, 58%) after column chromatography on silica gel (*n*-hexane/AcOEt = 20:1). Colorless oil.; [1] H-NMR (400 MHz, $CDCl_3$) δ: 7.22 (d, *J* = 7.3 Hz, 1H), 7.06-6.97 (m, 2H), 6.16-6.06 (m, 1H), 5.44 (dd, *J* = 17.4, 1.4 Hz, 1H), 5.26 (d, *J* = 10.5 Hz, 1H), 4.30 (d, *J* = 5.5 Hz, 2H), 2.57 (d, *J* = 6.9 Hz, 2H), 2.30 (s, 3H), 1.06-0.96 (m, 1H), 0.52 (m, 2H), 0.21 (td, *J* = 5.0, 4.6 Hz , 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): 155.5, 135.2, 134.1, 130.9, 129.0, 127.4, 123.9, 116.9, 73.4, 34.3, 16.5, 11.1, 4.8; HRMS (APCI) calcd for $C_{14}H_{19}O$ $(M+H)^+$: 203.1436, found: 203.1429

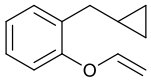
Compound 1o



To a solution of 2-(cyclopropylmethyl)phenol (750 mg, 5.1 mmol), which is an intermediate in the preparation of **1a'**, and K_2CO_3 (1.4 g, 2.0 eq.) in CH_3CN (10 mL, 0.5 M), crotyl chloride (2.0 mL, 4.0 eq.) was added. The reaction mixture was stirred at 60 °C for 10 h The mixture was filtered through glass filter with AcOEt, and filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (*n*-hexane/ AcOEt = 20/1) to afford

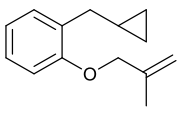
1-(but-2-en-1-yloxy)-2-(cyclopropylmethyl)benzene (**1o)** (960mg, 94%). Colorless oil (*E*:*Z* = 4:1).; ^{1} H-NMR (400 MHz, $CDCl_3$) δ: 7.28 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.16 (ddd, *J* = 7.7, 7.7, 1.6 Hz, 1H), 6.90 (ddd, *J* = 7.6, 7.6, 1.0 Hz, 1H), 6.85 (dd, *J* = 7.6, 7.6 Hz, 1H), 5.90-5.67 (m, 2H), 4.61-4.46 (m, 2H), 2.55 (d, *J* = 6.9 Hz, 2H), 1.77-1.72 (m, 3H), 1.10-0.97 (m, 1H), 0.52-0.45 (m, 2H), 0.19 (td, *J* = 5.0, 4.8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): 156.5, 130.9, 129.4, 129.4, 127.9, 126.8, 126.5, 126.2, 120.3, 111.3, 111.2, 68.6, 63.8, 34.4, 17.9, 10.5, 4.7; HRMS (APCI) calcd for $C_{14}H_{19}O$ $(M+H)^+$: 203.1436, found: 203.1428

Compound 1p



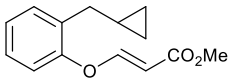
To a solution of 2-(cyclopropylmethyl)phenol (750 mg, 5.1 mmol), which is an intermediate in the preparation of **1a'**, and K_2CO_3 (1.4 g, 2.0 eq.) in CH_3CN (10 mL, 0.5 M), dibrormoethane (1.8 mL, 4.0 eq.) was added. The solution was stirred at 60 °C for 10 h. The mixture was filtered through glass filter with ethyl acetate, and filtrate was concentrated under reduced pressure. The clued residue was dissolved in THF (25 mL) and *t*-BuOK (860 mg, 1.5eq.) was added. The mixture was filtered through glass filter with AcOEt, and filtrate was concentrated under reduced pressure. The clued residue was purified by column chromatography on silica gel (*n*-hexane/ AcOEt = 20/1) to afford 1-(cyclopropylmethyl)-2-(vinyloxy)benzene (**1p)** (712 mg, 81 %). Colorless oil.; ^{1} H-NMR (400 MHz, $CDCl_3$) δ: 7.34 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.19 (ddd, *J* = 7.8, 7.8, 1.8 Hz, 1H), 7.06 (ddd, *J* = 7.4, 7.4, 1.2 Hz, 1H), 6.95 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.62 (dd, *J* = 14.0, 6.2 Hz, 1H), 4.64 (dd, *J* = 14.0, 1.6 Hz, 1H), 4.37 (dd, *J* = 6.2, 1.6 Hz, 1H), 2.55 (d, *J* = 6.9 Hz, 2H), 1.06-0.96 (m, 1H), 0.52-0.48 (m, 2H), 0.20 (td, *J* = 5.3, 4.3 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): 154.4, 149.1, 132.4, 130.0, 127.1, 123.4, 116.8, 93.9, 34.2, 10.8, 4.7; HRMS (APCI) calcd for $C_{12}H_{15}O$ $(M+H)^+$: 175.1123, found: 175.1117

Compound 1q



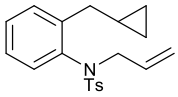
To a solution of 2-(cyclopropylmethyl)phenol (750 mg, 5.1 mmol), which is an intermediate in the preparation of **1a'**, and K_2CO_3 (1.4 g, 2.0 eq.) in CH_3CN (10 mL, 0.5 M), 3-chloro-2-methylpropene (988 μL, 2.0 eq.) was added. The reaction mixture was stirred at 60 °C for 10 h. The mixture was filtered through glass filter with AcOEt, and filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (*n*-hexane/AcOEt = 20/1) to afford 1-(cyclopropylmethyl)-2-((2-methylallyl)oxy)benzene (**1q)** (935 mg, 91%). Colorless oil.; ^{1} H-NMR (400 MHz, $CDCl_3$) δ: 7.29 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.16 (ddd, *J* = 7.8, 7.8, 1.6 Hz, 1H), 6.91 (ddd, *J* = 7.4, 7.4, 0.8 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 5.11 (s, 1H), 4.98 (s, 1H), 4.43 (s, 2H), 2.58 (d, *J* = 6.9 Hz, 2H), 1.84 (s, 3H), 1.10-0.99 (m, 1H), 0.52-0.46 (m, 2H), 0.19 (td, *J* = 5.2, 4.4Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): 156.4, 141.2, 130.8, 129.5, 126.8, 120.4, 112.1, 111.1, 71.4, 34.4, 19.5, 10.5, 4.6; HRMS (APCI) calcd for $C_{14}H_{19}O$ $(M+H)^+$: 203.1436, found: 203.1429

Compound 1r



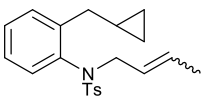
To a stirred solution of 2-(cyclopropylmethyl)phenol (760 mg, 5.1 mmol), which is an intermediate in the preparation of **1a'**, in THF (5.1 mL, 0.1 M) was added DABCO (57.5 mg, 10 mol%) and methyl propiolate (474 mg, 1.05 equiv). The mixture was stirred at ambient temperature for 2 h. The mixture was diluted with AcOEt and washed with water and brine. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (*n*-hexane/AcOEt = 10 /1) to give compound **1r** (869 mg, 73%). Colorless oil.; ^{1}H-NMR (300 MHz, $CDCl_3$); 7.78 (d, *J* = 12.4 Hz, 1H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.27-7.22 (m, 1H), 7.19-7.14 (m, 1H), 7.00 (d, *J* = 7.9 Hz, 1H), 5.44 (d, *J* = 12.4 Hz, 1H), 3.72 (s, 3H), 2.52 (d, *J* = 6.9 Hz, 2H), 1.01-0.90 (m, 1H), 0.54-0.48 (m, 2H), 0.19 (td, *J* = 4.8 Hz, 4.1 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): 167.8, 160.2, 153.5, 132.9, 130.4, 127.5, 125.3, 118.2, 100.9, 51.3, 34.2, 10.7, 4.7; HRMS (APCI) calcd for $C_{14}H_{17}O_3$ $(M+H)^+$: 233.1178, found: 233.1171

Compound 1s



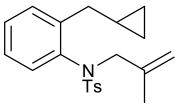
Following the typical procedure A, *N*-(2-allylphenyl)-4-methylbenzenesulfonamide [6] (1.1 g, 3.8 mmol) was converted to **1s** (1.2 g, 89%) after column chromatography on silica gel (*n*-hexane/AcOEt = 10 /1). Colorless oil.; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.62-7.55 (m, 3H), 7.27 (m, 3H), 7.03 (ddd, *J* = 7.6, 7.6, 1.3 Hz, 1H), 6.52 (dd, *J* = 7.9, 1.0 Hz, 1H), 5.79-5.65 (m, 1H), 5.00-4.92 (m, 2H), 4.30 (dd, *J* = 14.1, 5.8 Hz, 1H), 3.83 (dd, *J* = 13.9, 7.7 Hz, 1H), 2.79-2.63 (m, 2H), 2.40-2.49 (3H), 1.02-0.94 (m, 1H), 0.58-0.54 (m, 2H), 0.26-0.19 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): 144.0, 143.4, 137.4, 135.9, 132.4, 129.5, 129.4, 128.4, 128.0, 127.9, 126.0, 119.4, 54.9, 35.2, 21.6, 10.4, 5.1, 4.9; HRMS (APCI) calcd for $C_{20}H_{24}NO_2S$ $(M+H)^+$: 342.1528, found: 342.1521

Compound 1t



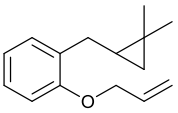
To a solution of *N*-(2-allylphenyl)-4-methylbenzenesulfonamide (750 mg, 5.1 mmol), which is an intermediate in the preparation of **1s**, and K_2CO_3 (1.4 g, 2.0 eq.) in CH_3CN (10 mL, 0.5 M), crotyl chloride (2.0 mL, 4.0 eq.) was added. The reaction mixture was stirred at 60 °C for 10 h The mixture was filtered through glass filter with AcOEt, and filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (*n*-hexane/ AcOEt = 20/1) to afford 1-(but-2-en-1-yloxy)-2-(cyclopropylmethyl)benzene (**1t)** (960mg, 94%). White solid (*E*:*Z* = 4:1).; m.p.: 66-67 °C.; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.61-7.55 (m, 3H), 7.29-7.24 (m, 3H), 7.03 (ddd, *J* = 7.7, 7.7, 1.5 Hz, 1H), 6.53 (m, 1H), 5.50-5.30 (m, 2H), 4.32-4.21 (m, 1H), 3.97-3.74 (m, 1H), 2.70 (m, 2H), 2.44 (m, 3H), 1.52-1.37 (m, 3H), 1.02-0.94 (m, 1H), 0.60-0.51 (m, 2H), 0.27-0.14 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): 144.1, 143.3, 137.5, 136.2, 135.9, 130.8, 129.4, 129.4, 129.3, 128.2, 128.0, 127.6, 126.0, 125.0, 123.9, 54.2, 48.1, 35.2, 21.6, 17.6, 12.6, 10.4, 5.1, 4.9; HRMS (APCI) calcd for $C_{21}H_{26}NO_2S$ $(M+H)^+$: 356.1684, found: 356.1682

Compound 1u



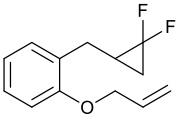
To a solution of *N*-(2-allylphenyl)-4-methylbenzenesulfonamide (750 mg, 5.1 mmol), which is an intermediate in the preparation of **1s**, and K_2CO_3 (1.4 g, 2.0 eq.) in CH_3CN (10 mL, 0.5 M), 3-chloro-2-methylpropene (988 μL, 2.0 eq.) was added. The reaction mixture was stirred at 60 °C for 10 h. The mixture was filtered through glass filter with AcOEt, and filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (*n*-hexane/AcOEt = 20/1) to afford 1-(cyclopropylmethyl)-2-((2-methylallyl)oxy)benzene (**1u)** (935 mg, 91%). White solid.; m.p.: 94-96 °C.; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.65 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.54 (ddd, *J* = 8.5, 8.5, 1.8 Hz, 2H), 7.29-7.24 (m, 3H), 7.05 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 6.57 (dd, *J* = 7.8, 1.4 Hz, 1H), 4.71 (s, 1H), 4.54 (s, 1H), 4.24 (d, *J* = 13.7 Hz, 1H), 3.73 (d, *J* = 13.3 Hz, 1H), 2.69 (m, 2H), 2.44 (s, 3H), 1.80 (s, 3H), 0.99-0.91 (m, 1H), 0.60-0.54 (m, 2H), 0.28-0.16 (m, 2H); ^{13}C-NMR (100 MHz, CD_3OD): 144.0, 143.8, 139.9, 137.6, 135.6, 129.3, 129.1, 128.0, 127.8, 127.8, 125.9, 115.3, 58.2, 34.8, 20.2, 19.5, 10.1, 4.4, 4.0; HRMS (APCI) calcd for $C_{21}H_{26}NO_2S$ $(M+H)^+$: 356.1684, found: 356.1682

Compound 1v



Following the typical procedure A, 2-(3-methylbut-2-en-1-yl)phenol[7] (1.1 g, 3.8 mmol) was converted to **1v** (1.2 g, 89%) after column chromatography on silica gel (*n*-hexane/AcOEt = 10 :1). Colorless oil.; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.28 (d, *J* = 7.4 Hz, 1H), 7.16 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.92 (d, *J* = 14.9 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.07 (m, 1H), 5.43 (dd, *J* = 17.5, 1.4 Hz, 1H), 5.27 (dd, *J* = 10.6, 1.4 Hz, 1H), 4.55 (d, *J* = 5.2 Hz, 2H), 2.72-2.63 (m, 2H), 1.09 (d, *J* = 4.0 Hz, 6H), 0.84 (dt, *J* = 14.5, 6.7 Hz, 1H), 0.46 (q, *J* = 4.2 Hz, 1H), 0.09 (t, *J* = 4.9 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$); 156.2, 133.6, 131.4, 129.0, 126.6, 120.5, 116.8, 111.1, 68.6, 29.4, 27.5, 23.7, 20.0, 19.7, 15.7; HRMS (APCI) calcd for $C_{15}H_{21}O$ $(M+H)^+$: 217.1592, found: 217.1589

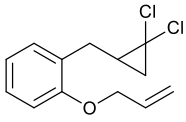
Compound 1w



To a round-bottom flask containing 2-((2,2-difluorocyclopropyl)methyl)phenol[8] (296 mg, 1.6 mmol) and K_2CO_3 (444 mg, 3.2 mmol) in CH_3CN (3.2 mL) was added allyl bromide (1.4 mL, 6.4 mmol). The reaction mixture was stirred at 60 °C for 3 h. The mixture was filtered through glass filter with AcOEt, and filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (*n*-hexane/AcOEt = 10/1) to afford **1w** (330 mg, 93%). Colorless oil.; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.23-7.16 (m, 2H), 6.95-6.89 (m, 1H), 6.85 (d, J = 8.3 Hz, 1H), 6.13-6.01 (m, 1H), 5.42 (ddt, *J* = 17.5, 1.7, 1.4 Hz, 1H), 5.28 (ddt, *J* = 10.7, 1.4, 1.4 Hz, 1H), 4.56 (td, *J* = 3.3, 1.5 Hz, 2H), 2.81 (dd, *J* = 7.0, 2.0 Hz, 2H), 1.96-1.80 (m, 1H), 1.45-1.34 (m, 1H), 1.11-1.01 (m, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 156.3, 133.4, 129.6, 128.3, 127.6, 120.7, 117.1 (t, $^1J_{CF}$ = 284 Hz), 111.4, 68.6, 27.4, 27.4, 22.3 (t, $^2J_{FC}$ = 11 Hz), 16.2 (t, $^2J_{FC}$ = 11 Hz); ^{19}F-NMR (376 MHz,

$CDCl_3$): -128.6 (dd, $^2J_{FF}$ = 157 Hz, $^3J_{HF}$ = 17.4 Hz), -144.7 (dd, $^2J_{FF}$ = 148 Hz, $^3J_{HF}$ = 17.4 Hz); HRMS (APCI) calcd for $C_{13}H_{15}F_2O$ $(M+H)^+$: 225.1091, found: 225.1088

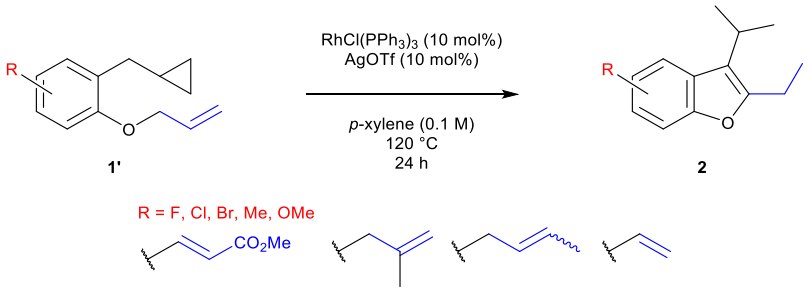
Compound 1x



To a round-bottom flask containing 2-((2,2-dichlorocyclopropyl)methyl)phenol[9] (312 mg, 1.44 mmol) and K_2CO_3 (695 mg, 2.9 mmol) in CH_3CN (2.9 mL) was added allyl bromide (1.4 mL, 5.8 mmol). The reaction mixture was stirred at 60 °C for 3 h. The mixture was filtered through glass filter with AcOEt, and filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (*n*-hexane/ AcOEt = 10/1) as an eluent to afford **1x** (340 mg, 92%)**.** Colorless oil.; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.27 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.22 (ddd, *J* = 7.8, 7.8, 1.8 Hz, 1H), 6.94 (ddd, *J* = 7.6, 7.6 Hz, 1.1 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.12-6.03 (m, 1H), 5.42 (ddt *J* = 16.9, 1.8, 1.4 Hz, 1H), 5.29 (ddt *J* = 10.5, 1.8, 1.4 Hz, 1H), 4.57 (td, *J* = 3.3, 1.7 Hz, 2H), 2.99-2.84 (m, 2H), 2.00-1.92 (m, 1H), 1.61 (dd, *J* = 10.5, 6.9 Hz, 1H), 1.25 (t, *J* = 7.3 Hz, 1H) : ^{13}C-NMR (100 MHz, $CDCl_3$): 156.3, 133.3, 129.7, 128.0, 127.6, 120.7, 117.2, 111.3, 68.6, 61.7, 30.7, 30.3, 26.7; HRMS (APCI) calcd for $C_{13}H_{15}Cl_2O$ $(M+H)^+$: 257.0500, found: 257.0499

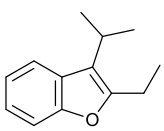
Preparation of 2a-2u

・Typical procedure B for the preparation of compounds **2a-2u**



To a stirred solution of 1-(allyloxy)-2-(cyclopropylmethyl)benzene **1'** (1.0 eq.) in *p*-xylene (0.1 M), degassed with N_2 bubbling, was added $RhCl(PPh_3)_3$ (10 mol%) and AgOTf (10 mol%) under an N_2 atmosphere. The reaction mixture was refluxed (120 °C) for 24 h. Then, the mixture was filtered through 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 2-ethyl-3-isopropylbenzofurans **2**.

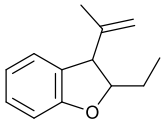
Compound 2a



Following the typical procedure B, **1a'** (30.0 mg, 0.159 mmol) was converted to **2a** (26.4 mg, 88%) after flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 10/1). Colorless oil.; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.62-7.59 (m, 1H), 7.41-7.39 (m, 1H),

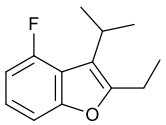
7.22-7.15 (m, 2H), 3.13-3.06 (m, 1H), 2.77 (q, J = 7.5 Hz, 2H), 1.40 (d, J = 7.3 Hz, 6H), 1.29 (t, J = 7.5 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 154.2, 154.0, 128.4, 122.7, 121.6, 120.1, 119.1, 110.8, 25.3, 22.5, 20.0, 13.5, 13.4; HRMS (APCI) calcd for $C_{13}H_{17}O$ $(M+H)^+$: 189.1279, found: 189.1279

Compound 2a'



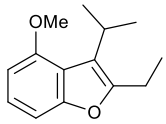
From the typical procedure B, the temperature condition was lowered to 100 °C and the reaction was stopped after 12 h, **1a'** (30.0 mg, 0.159 mmol) was converted to **2a** (26.7 mg, 89%) after flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 10/1). Colorless oil (erythro/threo = 7/3).; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.15-7.03 (m, 2H), 6.87-6.76 (m, 2H), 4.89-4.82 (m, 2H), 4.61-4.43 (m, 1H), 3.95-3.77 (m, 1H), 1.83-1.65 (m, 2H), 1.63 (s, 1H), 1.50-1.55 (2H), 1.10-1.03 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 159.7, 144.7, 143.4, 130.1, 128.9, 128.4, 125.5, 124.9, 120.5, 120.2, 114.0, 113.3, 109.6, 109.3, 88.4, 88.3, 56.2, 52.9, 28.6, 23.6, 21.0, 18.9, 11.3, 9.7; HRMS (APCI) calcd for $C_{13}H_{17}O$ $(M+H)^+$: 189.1279, found: 189.1276

Compound 2b



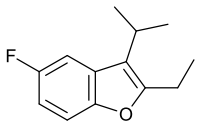
Following the typical procedure B, **1b'** (30.0 mg, 0.145 mmol) was converted to **2b** (19.8 mg, 66%) after flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 10/1). Colorless oil.; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.20-7.09 (m, 2H), 6.89-6.83 (m, 1H), 3.17-3.06 (m, 1H), 2.76 (q, J = 7.6 Hz, 2H), 1.33 (dd, J = 7.1, 1.2 Hz, 6H), 1.28 (t, J = 7.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 156.3 ($^4J_{CF}$ = 2.4 Hz), 155.3 ($^1J_{CF}$ = 235.1 Hz), 154.1, 123.4 ($^3J_{CF}$ = 7.2 Hz), 118.7 ($^3J_{CF}$ = 4.8 Hz) , 116.8 ($^2J_{CF}$ = 20.4 Hz), 108.1 ($^2J_{CF}$ = 21.6 Hz) , 106.9 ($^3J_{CF}$ = 3.6 Hz), 24.9, 22.6 ($^4J_{CF}$ = 3.6 Hz), 20.0, 13.4; ^{19}F-NMR (283 MHz, $CDCl_3$): –119.1; HRMS (APCI) calcd for $C_{13}H_{14}FO$ $(M–H)^–$: 205.1029, found: 205.1024

Compound 2d



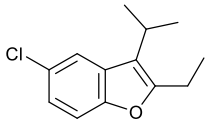
Following the typical procedure B, **1d'** (30.0 mg, 0.137mmol) was converted to **2d** (25.2 mg, 84%) after flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 5/1). Pale-yellow oil.; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.11 (dd, J = 8.1 Hz, 8.1 Hz, 1H), 7.01 (d, J = 8.3 Hz, 1H), 6.61 (d, J = 7.9 Hz, 1H), 3.92 (s, 3H), 3.25-3.16 (m, 1H), 2.74 (q, J = 7.5 Hz, 2H), 1.32 (d, J = 6.9 Hz, 6H), 1.24 (t, J = 7.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 155.5, 153.5, 153.0, 123.5, 119.8, 118.2, 104.0, 102.9, 55.1, 25.2, 22.8, 20.3, 13.6; HRMS (APCI) calcd for $C_{14}H_{17}O_2$ $(M–H)^–$: 217.1229, found: 217.1223

Compound 2e



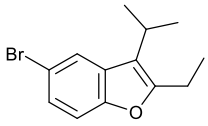
Following the typical procedure B, **1e'** (30.0 mg, 0.145 mmol) was converted to **2e** (25.8 mg, 86%) after flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 10/1). Colorless oil.; 7.28 (m, 2H), 7.23 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.89 (ddd, *J* = 9.1, 9.1 Hz, 2.6 Hz, 1H), 3.09-3.00 (m, 1H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.36 (d, *J* = 7.2 Hz, 6H), 1.27 (t, *J* = 7.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 158.5 ($^1J_{CF}$ = 235.8 Hz), 156.2, 150.3, 129.1 ($^3J_{CF}$ = 10.5 Hz), 119.5 ($^4J_{CF}$ = 3.8 Hz), 111.1 ($^3J_{CF}$ = 9.6 Hz), 110.0 ($^2J_{CF}$ = 25.9 Hz), 105.8 ($^2J_{CF}$ = 24.9 Hz), 25.2, 22.3, 20.1, 13.2; ^{19}F-NMR (376 MHz, $CDCl_3$) δ: –22.9; HRMS (APCI) calcd for $C_{13}H_{14}FO$ $(M–H)^–$: 205.1029, found: 205.1023

Compound 2f



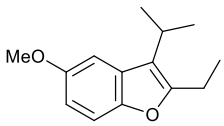
Following the typical procedure B, **1f'** (30.0 mg, 0.135 mmol) was converted to **2f** (22.8 mg, 76%) after flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 10/1). Colorless oil.; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.54 (d, *J* = 2.3 Hz, 1H), 7.29 (d, *J* = 8.6 Hz, 1H), 7.13 (dd, *J* = 8.6, 2.3 Hz, 1H), 3.09-3.00 (m, 1H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.36 (d, *J* = 7.4 Hz, 6H), 1.27 (t, *J* = 7.7 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 156.0, 152.6, 129.9, 127.2, 122.9, 119.8, 119.1, 111.8, 25.3, 22.5, 20.2, 13.3; HRMS (APCI) calcd for $C_{13}H_{16}ClO$ $(M+H)^+$: 223.0890, found: 223.0885

Compound 2g



Following the typical procedure B, **1g'** (30.0 mg, 0.135 mmol) was converted to **2g** (17.7 mg, 59%) after flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 10/1). Colorless oil.; ^{1}H-NMR; 7.69 (d, *J* = 1.0 Hz, 1H), 7.29-7.22 (m, 2H), 3.09-2.99 (m, 1H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.36 (d, *J* = 7.2 Hz, 6H), 1.27 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 155.7, 152.8, 130.5, 125.4, 122.7, 118.9, 114.7, 112.2, 25.1, 22.4, 20.0, 13.2; HRMS (APCI) calcd for $C_{13}H_{14}BrO$ $(M–H)^–$: 265.0228, found: 265.0224

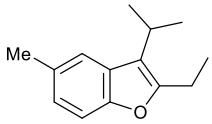
Compound 2h



Following the typical procedure B, **1h'** (30.0 mg, 0.137 mmol) was converted to **2h** (24.0 mg, 80%) after flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 10/1). Colorless oil.; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.26 (s, 1H), 7.06 (d, *J* = 2.8 Hz, 1H), 6.79 (dd, *J* = 8.8, 2.6 Hz, 1H), 3.85 (s, 3H), 3.10-3.01 (m, 1H), 2.73 (q, *J* = 7.5 Hz, 2H), 1.37 (d, *J* = 6.9 Hz, 6H), 1.26 (t, *J* = 7.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 155.4, 155.1, 149.2, 129.1, 119.3, 111.1, 110.5, 103.8, 56.2, 25.3, 22.5, 20.3, 13.4; HRMS (APCI) calcd for $C_{14}H_{17}O_2$ $(M–H)^–$: 217.1229,

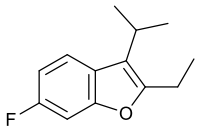
found: 217.1224

Compound 2i



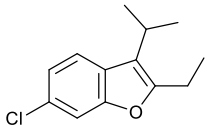
Following the typical procedure B, **1i'** (30.0 mg, 0.148 mmol) was converted to **2i** (22.5 mg, 75%) after flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 10/1). Colorless oil.; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.37 (s, 1H), 7.25 (d, *J* = 8.3 Hz, 1H), 6.99 (dd, *J* = 8.3, 1.4 Hz, 1H), 3.10-3.01 (m, 1H), 2.73 (q, *J* = 7.6 Hz, 2H), 2.43 (s, 3H), 1.38 (d, *J* = 7.2 Hz, 6H), 1.26 (t, *J* = 7.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 154.4, 152.5, 131.0, 128.6, 123.9, 120.2, 118.9, 110.4, 25.4, 22.6, 21.6, 20.2, 13.5; HRMS (APCI) calcd for $C_{14}H_{17}O$ $(M–H)^–$: 201.1279, found: 201.1275

Compound 2j



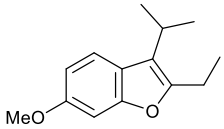
Following the typical procedure B, **1j'** (30.0 mg, 0.145 mmol) was converted to **2j** (27.3 mg, 91%) after flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 10/1). Colorless oil.; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.47 (dd, *J* = 8.6, 5.5 Hz, 1H), 7.10 (dd, *J* = 9.3, 2.4 Hz, 1H), 6.95-6.88 (m, 1H), 3.10-3.01 (m, 1H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.37 (d, *J* = 6.9 Hz, 6H), 1.27 (t, *J* = 7.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 160.0 ($^1J_{CF}$ = 240.6 Hz), 154.9, 154.0 ($^3J_{CF}$ = 13.4 Hz), 124.6, 120.1 ($^3J_{CF}$ = 9.6 Hz), 118.9, 109.6 ($^2J_{CF}$ = 24.0 Hz), 98.6 ($^2J_{CF}$ = 25.9 Hz), 25.2, 22.5, 20.0, 13.3; ^{19}F-NMR (376 MHz, $CDCl_3$) δ: –120.6; HRMS (APCI) calcd for $C_{13}H_{14}FO$ $(M–H)^–$: 205.1029, found: 205.1023

Compound 2k



Following the typical procedure B, **1k'** (30.0 mg, 0.135 mmol) was converted to **2k** (24.0 mg, 80%) after flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 10/1). Colorless oil.; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.47 (d, *J* = 8.3 Hz, 1H), 7.38 (d, *J* = 1.7 Hz, 1H), 7.13 (dd, *J* = 8.4, 1.9 Hz, 1H), 3.10-3.01 (m, 1H), 2.74 (q, *J* = 7.5 Hz, 2H), 1.36 (d, *J* = 7.2 Hz, 6H), 1.27 (t, *J* = 7.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 155.1, 154.2, 128.5, 127.1, 122.2, 120.5, 119.1, 111.3, 25.2, 22.5, 20.0, 13.2; HRMS (APCI) calcd for $C_{13}H_{14}ClO$ $(M–H)^–$: 221.0733, found: 221.0728

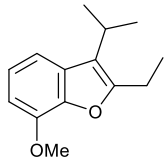
Compound 2l



Following the typical procedure B, **1l'** (30.0 mg, 0.137 mmol) was converted to **2l** (27.9 mg, 93%) after flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 5/1). Colorless oil.; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.44 (d, *J* = 8.6 Hz, 1H), 6.95 (d, *J* = 2.3 Hz, 1H), 6.80 (dd, *J* = 8.6, 2.3 Hz, 1H), 3.83 (s, 3H), 3.06-3.01 (m, 1H), 2.72 (q, *J* = 7.4 Hz, 2H), 1.36 (d, *J* = 6.9 Hz, 6H), 1.26 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 156.9, 154.9, 153.2,

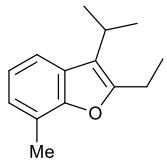
121.8, 120.1, 118.9, 110.2, 95.9, 55.7, 25.3, 22.6, 20.0, 13.4; HRMS (APCI) calcd for $C_{14}H_{17}O_2$ $(M–H)^–$: 217.1229, found: 217.1224

Compound 2m



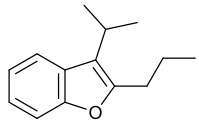
Following the typical procedure B, **1m'** (30.0 mg, 0.137 mmol) was converted to **2m** (25.5 mg, 85%) after flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 5/1). Colorless oil.; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.19 (d, *J* = 7.9 Hz, 1H), 7.08 (dd, *J* = 7.9 Hz, 7.9 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 3.98 (s, 3H), 3.10-3.01 (m, 1H), 2.77 (q, *J* = 7.5 Hz, 2H), 1.36 (d, *J* = 6.9 Hz, 6H), 1.27 (t, *J* = 7.4 Hz, 3H); ^{13}C -NMR (125 MHz, C_6D_6) δ 154.3, 146.1, 144.2, 130.6, 122.7, 119.7, 113.0, 106.0, 55.5, 25.6, 22.6, 20.2, 13.5; HRMS (APCI) calcd for $C_{14}H_{19}O_2$ $(M+H)^+$: 219.1385, found: 219.1381

Compound 2n



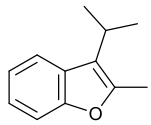
Following the typical procedure B, **1n'** (30.0 mg, 0.148 mmol) was converted to **2n** (25.5 mg, 77%) after flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 10/1). Colorless oil.; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.42 (d, *J* = 8.0 Hz, 1H), 7.06 (dd, *J* = 7.4 Hz, 7.4 Hz, 1H), 6.99 (d, *J* = 6.9 Hz, 1H), 3.10-3.04 (m, 1H), 2.76 (q, *J* = 7.6 Hz, 2H), 2.48 (s, 3H), 1.38 (d, *J* = 6.9 Hz, 6H), 1.28 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 153.9, 153.0, 127.8, 123.7, 121.6, 121.0, 119.3, 117.6, 25.3, 22.6, 20.1, 15.0, 13.5; HRMS (APCI) calcd for $C_{14}H_{17}O$ $(M–H)^–$: 201.1279, found: 201.1274

Compound 2o



Following the typical procedure B, **1o** (30.0 mg, 0.148 mmol) was converted to **2o** (26.1 mg, 87%) after flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 10/1). Colorless oil.; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.61-7.59 (m, 1H), 7.38 (dd, *J* = 6.7, 2.6 Hz, 1H), 7.21-7.13 (m, 2H), 3.12-3.03 (m, 1H), 2.71 (t, *J* = 7.4 Hz, 2H), 1.73 (td, *J* = 14.8, 7.2 Hz, 2H), 1.39 (d, *J* = 6.9 Hz, 6H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 154.1, 152.9, 128.3, 122.7, 121.6, 120.1, 120.0, 110.8, 28.5, 25.4, 22.5, 21.9, 13.8; HRMS (APCI) calcd for $C_{14}H_{17}O$ $(M–H)^–$: 201.1279, found: 201.1275

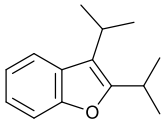
Compound 2p



Following the typical procedure B, **1o** (30.0 mg, 0.172 mmol) was converted to **2o** (24.0 mg, 80%) after flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 10/1). Colorless oil.; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.58 (dd, *J* = 5.7, 3.3 Hz, 1H), 7.38-7.34 (m, 1H), 7.21-7.12 (m, 2H), 3.12-3.03 (m, 1H), 2.40 (s, 3H), 1.38 (d, *J* = 7.2 Hz, 6H); ^{13}C-NMR (100 MHz, C_6D_6) δ: 154.5, 148.9, 128.6, 123.0, 121.9, 120.0, 119.8, 110.9, 25.4, 22.1, 11.8; HRMS (APCI) calcd for

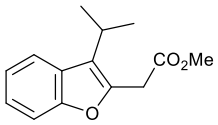
$C_{12}H_{13}O$ $(M–H)^-$: 173.0966, found: 173.0961

Compound 2q



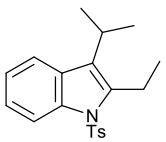
Following the typical procedure B, **1q** (30.0 mg, 0.148 mmol) was converted to **2q** (27.0 mg, 90%) after flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 10/1). Colorless oil.; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.61-7.58 (m, 1H), 7.40 (dd, *J* = 7.1, 2.2 Hz, 1H), 7.21-7.12 (m, 2H), 3.25-3.06 (m, 2H), 1.39 (d, *J* = 7.2 Hz, 6H), 1.32 (d, *J* = 6.9 Hz, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 157.2, 154.0, 128.4, 122.6, 121.5, 120.2, 117.9, 110.9, 26.4, 25.2, 22.6, 21.5; HRMS (APCI) calcd for $C_{14}H_{17}O$ $(M–H)^-$: 201.1279, found: 201.1274

Compound 2r



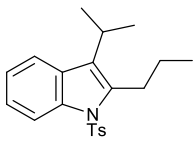
Following the typical procedure B, **1r** (30.0 mg, 0.129 mmol) was converted to **2r** (27.9 mg, 93%) after flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 10/1). Colorless oil.; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.62 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.41 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.23-7.15 (m, 2H), 3.79 (s, 2H), 3.71 (s, 3H), 3.12-3.03 (m, 1H), 1.39 (d, *J* = 7.2 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 169.6, 154.4, 144.4, 127.8, 123.7, 122.9, 122.0, 120.5, 111.2, 52.4, 32.9, 25.5, 22.2; HRMS (APCI) calcd for $C_{14}H_{17}O_3$ $(M+H)^+$: 233.1178, found: 233.1172

Compound 2s



Following the typical procedure B, **1s** (30.0 mg, 0.088 mmol) was converted to **2s** (19.2 mg, 64%) after flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 10/1). White solid.; m.p.: 122-123 °C.; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.20 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7.3 Hz, 2H), 7.23-7.15 (m, 4H), 3.17-3.10 (m, 1H), 3.02 (q, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 1.35 (d, *J* = 6.9 Hz, 6H), 1.25 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 144.3, 137.6, 137.1, 136.2, 129.6, 129.3, 126.1, 125.9, 123.5, 122.8, 120.0, 115.3, 25.9, 22.1, 21.5, 19.7, 15.8; HRMS (APCI) calcd for $C_{20}H_{24}NO_2S$ (M+H): 342.1528, found: 342.1528

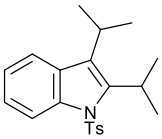
Compound 2t



Following the typical procedure B, **1t** (30.0 mg, 0.088 mmol) was converted to **2t** (15.0 mg, 50%) after flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 10/1). White solid.; m.p.: 116-117 °C.; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 8.19 (dd, *J* = 7.2, 1.7 Hz, 1H), 7.59 (dd, *J* = 6.7, 1.9 Hz, 1H), 7.54 (ddd, *J* = 8.5, 8.5, 1.9 Hz, 2H), 7.21 (dd, *J* = 7.1, 1.5 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 3.17-3.07 (m, 1H), 2.95 (t, *J* = 7.7 Hz, 2H), 2.32 (s, 3H), 1.69 (td, *J* = 15.0, 7.5 Hz, 2H), 1.34 (d, *J* = 7.2 Hz, 6H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 144.2, 137.1, 136.2, 136.1, 129.6, 129.3, 126.6, 126.1, 123.4, 122.8, 120.1, 115.4, 28.2, 26.0, 24.3, 22.1,

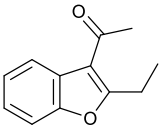
21.5, 14.1; HRMS (APCI) calcd for $C_{21}H_{26}NO_2S$ (M+H): 356.1684, found: 356.1685.

Compound 2u



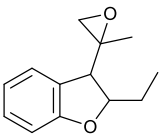
Following the typical procedure B, **1u** (30.0 mg, 0.088 mmol) was converted to **2u** (12.3 mg, 41%) after flash column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 10/1). White solid.; m.p.: 108-109 °C.; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.28 (dd, *J* = 8.7, 0.9 Hz, 1H), 7.63 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.56 (dd, *J* = 8.4, 8.4, 1.9 Hz, 2H), 7.23 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.21-7.17 (m, 3H), 4.01-3.90 (m, 1H), 3.43-3.33 (m, 1H), 2.36 (s, 3H), 1.37 (d, *J* = 6.9 Hz, 6H), 1.21 (d, *J* = 6.9 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 144.3, 140.9, 137.4, 137.1, 129.7, 129.2, 126.2, 126.2, 123.4, 122.5, 120.5, 115.7, 26.1, 25.6, 21.8, 21.6, 21.5; HRMS (APCI) calcd for $C_{21}H_{26}NO_2S$ (M+H): 356.1684, found: 356.1685.

Compound 4



To a solution of **2a'** (37.8m mg, 0.201 mmol) and 2,6-lutidine (43 mg, 0.402 mmol) in H_2O/1,4-dioxane = 1/3 (3 mL) was added potassium osmate(VI) dihydrate (3.7 mg, 0.01 mmol) and sodium periodate (172 mg, 0.803 mmol) at 0 °C. The mixture was stirred at 0 °C for 1 h. The mixture was diluted with AcOEt and the organic layer was washed with sat. $Na_2S_2O_3$ aq. and brine, dried over Na_2SO_4, filtered, and concentrated. The obtained residue was purified by column chromatography on silica gel (*n*-hexane/AcOEt = 10/1) to give the corresponding ketone (32 mg, 0.16 mmol, 82%). A solution of ketone and DDQ (42 mg, 0.19 mmol) in 0.8 mL of toluene was stirred at 100 °C for 24 h. Then the resulting reaction mixture was cooled to room temperature, filtered, and s concentrated. The resulting residue was purified by column chromatography on silica gel (*n*-hexane/AcOEt = 1/:1) to give **4** (23 mg, 73%). Colorless oil.; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.93-7.89 (m, 1H), 7.48-7.43 (m, 1H), 7.34-7.28 (m, 2H), 3.18 (q, *J* = 7.6 Hz, 2H), 2.65 (s, 3H), 1.36 (t, *J* = 7.6 Hz, 3H); ^{13}C-NMR (100 MHz, C_6D_6) δ: 192.8, 167.1, 154.0, 126.7, 124.5, 124.1, 122.0, 117.0, 111.2, 30.8, 22.4, 11.9; HRMS (APCI) calcd for $C_{12}H_{13}O_2$ $(M+H)^+$: 189.0916, found: 189.0910

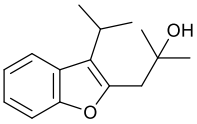
Compound 5



A solution of **2a'** (20 mg, 0.11 mmol) and $NaHCO_3$ (45 mg, 0.53 mmol) in DCM (1.1 mL) was treated with *m*-CPBA (822 mg, 0.13 mmol) at 0°C. After stirring for 2 h, the reaction mixture was quenched with 10% $Na_2S_2O_4$ aqueous solution (1 mL). The aqueous phase was extracted with diethyl ether (5 mL × 3). The combined ether phase was washed with saturated $NaHCO_3$ (2 mL × 3) and brine (2 mL × 1), dried with anhydrous Na_2SO_4, concentrated under vacuum to give the residue, purified by silica gel column chromatography (*n*-hexane/AcOEt, 10/1→3/1). **5** (17 mg, 0.11 mmol, 80% yield) as a colorless oil.; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.36 (dd *J* = 7.6, 0.7 Hz, 1H), 7.19 (ddd, *J* = 7.7, 7.7 Hz, 1.4 Hz, 1H), 6.92 (ddd, *J* = 7.4 Hz, 7.4 Hz, 1.0 Hz, 1H), 6.82

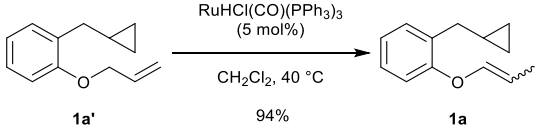
(d, J = 7.6 Hz, 1H), 4.60-4.53 (m, 1H), 2.87 (d, J = 8.3 Hz, 1H), 2.78-2.74 (m, 2H), 2.08-1.82 (m, 2H), 1.19 (t, J = 7.4 Hz, 3H), 1.01 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ:159.3, 129.0, 128.4, 125.9, 120.9, 109.5, 87.5, 57.1, 54.0, 52.4, 23.8, 18.5, 11.7; HRMS (APCI) calcd for $C_{13}H_{17}O_2$ $(M+H)^+$: 205.1229, found: 205.1225

Compound 6

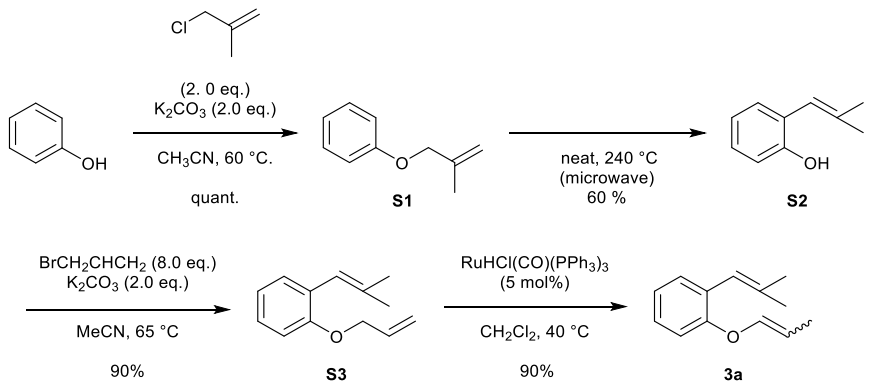


To a round-bottom flask containing **2r** (23.2 mg, 0.099 mmol) in Et_2O (0.3 M) was slowly added methylmagnesium bromide (133 μL, 3.0 M in Et_2O) at 0 ℃. The mixture was stirred at ambient temperature for 2 h. The obtained residue was purified by flash column chromatography on silica gel (*n*-hexane/AcOEt = 8/1) to give compound **6** (18.6 mg, 80%) as a colorless oil.; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.66 (dd, J = 6.9, 2.4 Hz, 1H), 7.42 (dd, J = 7.1, 1.9 Hz, 1H), 7.23-7.16 (m, 2H), 3.13-3.04 (m, 1H), 2.93 (s, 2H), 1.89 (br s, 1H), 1.40 (d, J = 6.9 Hz, 6H), 1.31 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 154.4, 149.4, 127.6, 123.3, 122.7, 121.9, 120.6, 111.1, 71.2, 40.2, 29.4, 25.6, 22.4; HRMS (APCI) calcd for $C_{15}H_{19}O$ $(M–OH)^–$: 215.1436, found: 215.1433

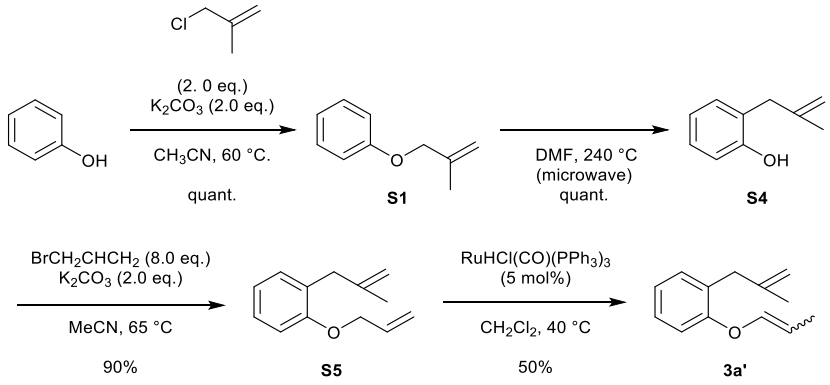
・Preparation of standard compound **1a**, **3a** and **3a'** for NMR experiment.



To a solution of **1a'** in CH_2Cl_2, RuHCl(CO)PPh_3 (5 mol%) was added and the reaction mixture was stirred at 40 °C for 1 h. After removal of the solvent, the residue was purified by column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 10/1) to afford **1a** (*E*/*Z* = 1/4).; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.31 (dd, J = 7.3, 1.4 Hz, 1H), 7.18 (ddd, J = 7.8, 7.8, 1.4 Hz, 1H), 7.00 (ddd, J = 7.4, 7.4, 1.2 Hz, 1H), 6.92 (dd, J = 8.2, 0.9 Hz, 1H), 6.40-6.34 (m, 1H), 5.34-4.82 (m, 1H), 2.57 (m, 2H), 1.73 (d, J = 6.9 Hz, 3H), 1.66 (dd, J = 6.8, 1.9 Hz, 0H), 1.08-1.00 (m, 1H), 0.52-0.48 (m, 2H), 0.23-0.19 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 155.3, 142.7, 141.3, 131.5, 129.9, 129.8, 127.0, 126.9, 122.5, 122.3, 115.3, 114.5, 107.4, 106.8, 34.4, 34.3, 12.3, 10.8, 10.7, 9.4, 4.8, 4.6; HRMS (APCI) calcd for $C_{13}H_{17}O$ (M+H): 189.1279, found: 189.1276



To a solution of phenol and K_2CO_3 in CH_3CN, 3-chloro-2-methylpropene was added and the reaction mixture was stirred at 60 °C for 8 h. The mixture was filtered through glass filter with AcOEt, and filtrate was concentrated under reduced pressure. The crude residue was put in a vial (Anton Paar). The sealed vial was then heated at 240 °C under microwave irradiation for 30 min. After cooling to room temperature, the residue was separated by column chromatography on silica gel (*n*-hexane/ AcOEt = 10/1) to afford **S2.** To a round-bottom flask containing **S2** and K_2CO_3 (2.0 eq.) in CH_3CN (0.5 M) was added allyl bromide (4.0 eq.). The reaction mixture was stirred at 60 °C for 3 h. The mixture was filtered through glass filter with AcOEt, and filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (*n*-hexane/ AcOEt = 20/1) to afford **S3**. To a solution of **S3** in CH_2Cl_2, RuHCl(CO)PPh_3 (5 mol%) was added and the reaction mixture was stirred at 40 °C for 1 h. After removal of the solvent, the residue was purified by column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 10/1) to afford **3a** (*E*/*Z* = 3/2). Colorless oil. ; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.24-7.21 (m, 1H), 7.17 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.01 (dd, *J* = 7.4, 7.4 Hz, 1H), 6.95-6.92 (m, 1H), 6.38-6.29 (m, 2H), 5.37-4.83 (m, 1H), 1.93 (dd, *J* = 4.6, 1.1 Hz, 3H), 1.81 (dd, *J* = 6.9, 1.1 Hz, 3H), 1.73 (dd, *J* = 6.9, 1.7 Hz, 2H), 1.66 (dd, *J* = 6.9, 1.7 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 154.9, 154.8, 142.5, 141.4, 136.1, 136.0, 130.6, 130.5, 128.4, 128.4, 127.2, 122.0, 121.9, 119.9, 115.4, 114.9, 107.8, 107.0, 26.6, 19.6, 12.3, 9.4; HRMS (APCI) calcd for $C_{13}H_{17}O$ (M+H): 189.1279, found: 189.1276



To a solution of phenol and K_2CO_3 in CH_3CN, 3-chloro-2-methylpropene was added and the reaction mixture was stirred at 60 °C for 8 h. The mixture was filtered through glass filter with AcOEt, and filtrate was concentrated under reduced pressure. The crude residue was dissolved in DMF and put in a vial (Anton

Paar). The sealed vial was then heated at 240 °C under microwave irradiation for 30 min. After cooling to room temperature, the residue was separated by column chromatography on silica gel (*n*-hexane/ AcOEt = 10/1) to afford **S4.** To a round-bottom flask containing **S4** and K_2CO_3 (2.0 eq.) in CH_3CN (0.5 M) was added allyl bromide (4.0 eq.). The reaction mixture was stirred at 60 °C for 3 h. The mixture was filtered through glass filter with AcOEt, and filtrate was concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (*n*-hexane/ AcOEt = 20/1) to afford **S5**. To a solution of **S5** in CH_2Cl_2, $RuHCl(CO)PPh_3$ (5 mol%) was added and the reaction mixture was stirred at 40 °C for 1 h. After removal of the solvent, the residue was purified by column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 10/1) to afford **3a'** (*E*/*Z* = 4/1). Colorless oil; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.20-7.15 (m, 2H), 7.01-6.91 (m, 2H), 6.39-6.33 (m, 1H), 5.34-4.82 (m, 1H), 4.79-4.65 (m, 2H), 3.37 (d, *J* = 13.4 Hz, 2H), 1.73-1.63 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 155.5, 144.7, 142.7, 141.3, 130.6, 129.2, 127.4, 122.5, 122.3, 115.7, 114.7, 111.5, 107.3, 106.7, 37.9, 37.7, 22.4, 12.3, 9.4; HRMS (APCI) calcd for $C_{13}H_{17}O$ (M+H): 189.1279, found: 189.1275

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・ Typical procedure A for the preparation of compounds **1a'-1n'**

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Methyl 2,2-Difluoro-2-(fluorosulfonyl)acetate, a Difluorocarbene Reagent with Reactivity Comparable to That of Trimethylsilyl 2,2- Difluoro-2-(fluorosulfonyl)acetate (TFDA). *J. Org. Chem.* **2012**, *77*, 5461-5464.
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