Supplementary Information – Experimental Procedures

Arylation of *gem*-Difluoroalkenes Using a Pd/Cu Co-Catalytic System that Avoids β-Fluoride Elimination

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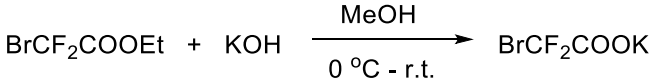
General Information

Unless otherwise noted, all catalytic reactions were carried out in oven-dried 10 mL glassware with PTFE screw-caps under an atmosphere of N_2. Arylsulfonyl chlorides，CuCl (99.99%), anhydrous Li_2CO_3 (99%) were purchased from commercial sources and used without further purification. Anhydrous 1,4-dioxane (99.8%) was purchased from Sigma-Aldrich and used in a glovebox. Other solvents, *N*-methyl pyrrolidone (NMP, anhydrous, 99.5%), 1,2-dichloroethane (DCE, anhydrous, 99+%), toluene (anhydrous, 99.8%), *m*-xylene (anhydrous, ≥ 99%) and DMSO (anhydrous) were purchased from commercial sources and used as received. *N,N*-Dimethylformamide (DMF) was dispensed from a solvent purification system and used in a glovebox. For all difluoroalkene arylation-isomerization reactions, the solid chemicals were weighed under air and solvents were subsequently added under N_2 flow. ^{1}H NMR spectra were recorded on Bruker AVIIIHD 400 MHz spectrometer, Bruker DRX 500 MHz spectrometer and Bruker Avance AVIII 500 MHz spectrometer, ^{19}F NMR spectra were recorded on the same spectrometer. Chemical shifts (δ) were reported in parts per million relative to residual chloroform (7.26 ppm for ^{1}H NMR; 77.0 ppm for ^{13}C NMR). ^{19}F NMR chemical shifts were corrected by using $CFCl_3$ as internal standard, (0.0 ppm). Coupling constants were reported in Hertz. ^{1}H NMR assignment abbreviations were the following: singlet (s), broad singlet (bs), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). ^{13}C NMR spectra were recorded at 126 MHz on a Bruker Avance AVIII 126 MHz spectrometer and reported in ppm. Uncorrected melting points were measured on a Thomas-Hoover melting point apparatus. Infrared radiation (IR) were performed on a Thermo Scientific Nicolet iS5 Fourier Transform Infrared Spectrometer by using commercial Teflon-tape as sample film support. High-resolution mass analysis was performed by atmospheric-pressure chemical ionization (APCI–hexane/PhMe) on a Water Q-Tof Premier™.

Experimental Details

Synthesis of Starting Materials

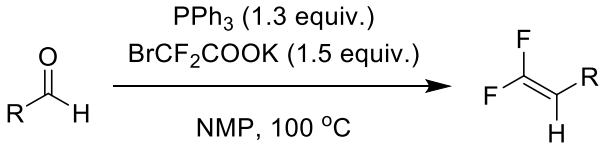
Potassium bromodifluoroacetate ($BrCF_2COOK$):



The product was prepared following a previous literature report.[1] To a 1 L round-bottom flask, ethyl bromodifluoroacetate (101 g, 0.500 mol) and MeOH (300 mL) were added sequentially, and the reaction was stirred in an ice bath (0 °C) for 10 min. KOH (28 g, 0.50 mol) was added portion wise. The reaction was then warmed to room temperature and stirred for another 20 h. Upon completion, the solvent was removed in *vacuo* and the product was kept under vacuum overnight to afford the product as a white powder in 97% yield (103.3 g).

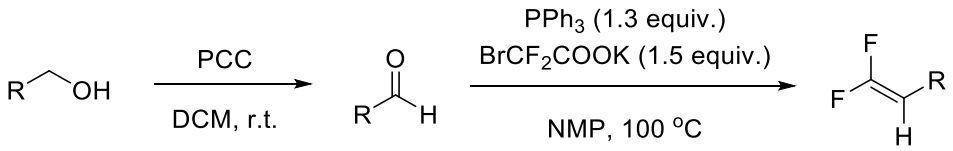
Synthesis of Difluoroalkenes

General Procedure A: Synthesis of Difluoroalkenes from Aldehydes



The corresponding difluoroalkenes were prepared from aldehydes according to a previous literature report[2] with a slight modification. A solution of PPh_3 (13.0 mmol, 1.30 equiv.), aldehyde (0.010 mol, 1.0 equiv.) and NMP (6.0 mL, ≈ 1.8 M) was heated to 100 °C and $BrCF_2COOK$ (15.0 mmol, 1.30 equiv.) was added portionwise over 10 min. The reaction vessel was attached to rubber septum connected to an empty balloon to release pressure. After evolution of gas ceased, the reaction stirred for another 30 min. Upon cooling, Et_2O (30 mL) and H_2O (50 mL) were added to the mixture, followed by H_2O_2 (30% aqueous solution, 10 mL). After stirring for 2–3 h, the mixture was filtered and extracted with Et_2O (50 mL x 3). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The compounds were purified by silica gel column chromatography using Et_2O/pentane as eluent, affording the corresponding difluoroalkenes

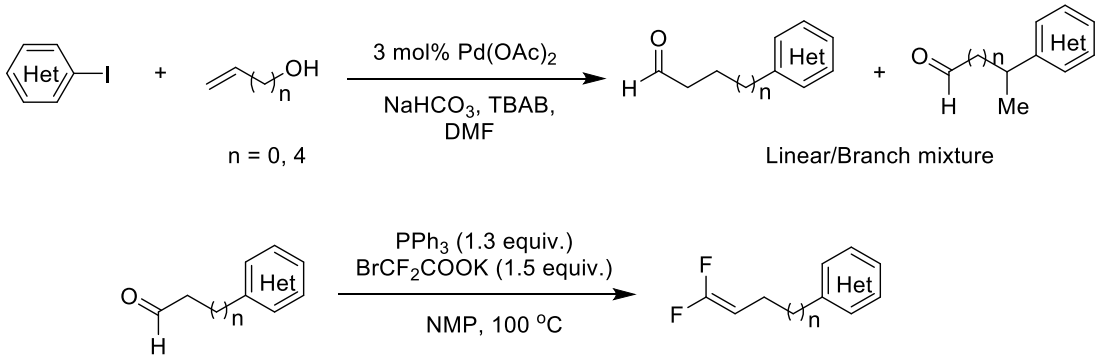
General Procedure B: Synthesis of Difluoroalkenes from Alcohols



A 100 mL round-bottom flask was charged with primary alcohol (5.00 mmol, 1.00 equiv.), pyridinium chlorochromate complex (10.0 mmol, 2.00 equiv.) and DCM (20 mL). The reaction was stirred at room temperature and monitored by TLC. After 3–5 h, the reaction mixture was filtered by a short silica gel column and the crude product was used in the next step without further purification.[2]

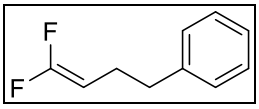
A solution of PPh_3 (1.3 equiv.) and freshly prepared aldehyde (1.0 equiv.) in NMP (≈ 1–1.8 M) was heated to 100 °C, and $BrCF_2COOK$ (1.5 equiv.) was added portionwise over 10 min. The reaction vessel was attached to a rubber septum connected to an empty balloon to release pressure. After evolution of gas ceased, the reaction was stirred for another 30 min. Upon cooling, Et_2O (30 mL) and H_2O (50 mL) were added to the mixture, followed by H_2O_2 (30% aqueous solution, 5 mL). After stirring for 2–3 h, the mixture was filtered and extracted with Et_2O (30 mL x 3). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The compounds were purified by silica gel column chromatography using Et_2O/pentane as eluent, affording the corresponding difluoroalkenes.

General Procedure C: Synthesis of Difluoroalkenes from Aryl Iodides



The aldehydes were prepared according a previous report as linear/branched mixture.[3] An oven-dried 100 mL two-neck flask was charged with (hetero)aryl iodides (0.010 mol, 1.0 equiv.), $Pd(OAc)_2$ (67 mg, 0.30 mmol), $NaHCO_3$ (2.5 g, 0.030 mol), tetrabutylammonium bromide (1.6 g, 5.0 mmol) and DMF (20 mL, 0.5 M), followed by the addition of alcohols (20 mmol, 2.0 equiv.). The mixture was evacuated and backfilled with N_2 (3 times), then stirred in a preheated oil bath at 70 °C for 6 h. Upon completion, the mixture was cooled to room temperature, then washed by Et_2O and H_2O, and dried over Na_2SO_4. The crude mixture was used in the next step without further purification.

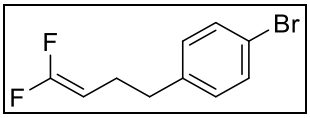
A solution of PPh_3 (1.3 equiv.), freshly prepared aldehyde (1.0 equiv.) in NMP (≈ 1–1.8 M) was heated to 100 °C and $BrCF_2COOK$ (1.5 equiv.) was added portionwise over 10 min. The reaction vessel was attached to a rubber septum connected to an empty balloon to release pressure. After evolution of gas ceased, the reaction stirred for another 30 min. Upon cooling, Et_2O (30 mL) and H_2O (50 mL) were added to the mixture, followed by H_2O_2 (30% aqueous solution, 5 mL). After stirring for 2–3 h, the mixture was filtered and extracted with Et_2O (30 mL x 3). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The compounds were purified by silica gel column chromatography using Et_2O/pentane as eluent, to afford the corresponding difluoroalkenes.



(4,4-difluorobut-3-en-1-yl)benzene [1] **(1a)**

Compound **1a** was prepared according to general procedure A on a 60 mmol scale. 3-Phenylpropionaldehyde (5.20 g, 60.0 mmol) and PPh_3 (20.4 g, 78.0 mmol) were placed in an oven-dried 250 mL two neck round-bottom flask connected to reflux condenser. Anhydrous NMP (≈ 1.7 M solution, 35 mL) was then added to the flask, and the reaction mixture was stirred in a preheated oil bath at 100 °C under N_2 atmosphere for 3–5 minutes until it became a clear solution. To this solution, $BrCF_2COOK$ (90 mmol, 19.2 g) was added portion wise over 20 min, and the reaction was allowed to stir for another 30 min after gas evolution ceased. Upon cooling, Et_2O (100 mL) and H_2O (150 mL) were poured into the mixture, followed by addition of H_2O_2 (30% aqueous solution, 50 mL). After stirring for 2–3 h, the mixture was filtered and extracted with Et_2O (100 mL x 3). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The compounds were purified by silica gel column chromatography using pentane (Rf ≈ 0.8) as eluent, affording **1a** as colorless oil in 53% yield, 5.3 g.

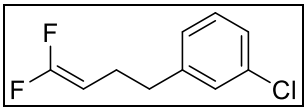
^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (td, J = 8.3, 6.7 Hz, 2H), 7.24–7.14 (m, 3H), 4.14 (dtd, J = 25.5, 7.8, 2.2 Hz, 1H), 2.67 (t, J = 7.6 Hz, 2H), 2.34–2.23 (m, 2H). Spectral data of **1a** matched literature report.[1]



1-bromo-4-(4,4-difluorobut-3-en-1-yl)benzene [4] **(1b)**

Compound **1b** was prepared according to general procedure B on a 5 mmol scale from 3-(4-bromophenyl)propan-1-ol (1.07 g, 1.00 equiv.). Purification by silica gel column chromatography using pentane as eluent (Rf ≈ 0.5) afforded **1b** as colorless oil in 31% yield after two steps, 375 mg.

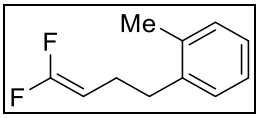
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 4.12 (dtd, *J* = 25.3, 7.8, 2.4 Hz, 1H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.28 (qt, *J* = 7.5, 1.8 Hz, 2H). Spectral data of **1b** matched literature report.[4]



1-chloro-3-(4,4-difluorobut-3-en-1-yl)benzene (1c)

Compound **1c** was prepared according to general procedure B on a 10 mmol scale from 3-(3-chlorophenyl)propan-1-ol (1.70 g, 1.00 equiv.). Purification by silica gel column chromatography using pentane as eluent (Rf ≈ 0.5) afforded **1c** as colorless oil in 41% yield after two steps, 832 mg.

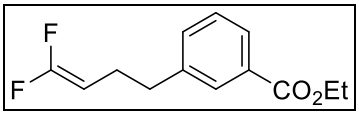
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.16 (m, 3H), 7.06 (dd, *J* = 7.0, 1.6 Hz, 1H), 4.14 (dddd, *J* = 25.3, 8.5, 7.2, 2.2 Hz, 1H), 2.67 (t, *J* = 7.6 Hz, 2H), 2.45–2.21 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –89.00 (dd, *J* = 46.2, 11.1 Hz), –91.09 (ddd, *J* = 46.7, 25.2, 15.8 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.2 (dd, *J* = 287.6, 285.6 Hz), 142.9, 134.2, 129.7, 128.5, 126.6, 126.4, 76.9 (dd, *J* = 34.5, 32.5 Hz), 35.3 (t, *J* = 2.7 Hz), 23.8 (d, *J* = 4.8 Hz); HRMS (ESI, m/z): calcd. for $C_{10}H_{10}ClF_2$ $[M+H]^+$ = 203.0439, found 203.0433. IR (film): 2932, 2865, 1747, 1598, 1573, 1476, 1305, 1216, 1158, 1081, 905, 780 cm^{-1}.



1-(4,4-difluorobut-3-en-1-yl)-2-methylbenzene (1d)

Compound **1d** was prepared according to general procedure B on a 10 mmol scale from 3-(*o*-tolyl)propan-1-ol (1.50 g, 1.00 equiv.). Purification by silica gel column chromatography using pentane as eluent (Rf ≈ 0.5) afforded **1d** as colorless oil in 54% yield after two steps, 982 mg.

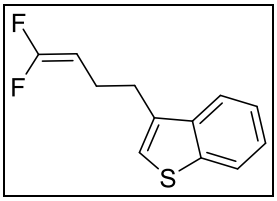
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20–7.08 (m, 4H), 4.21 (dtd, *J* = 25.4, 7.9, 2.5 Hz, 1H), 2.69 (dd, *J* = 9.0, 6.7 Hz, 2H), 2.33 (s, 3H), 2.31–2.22 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –89.54 (dd, *J* = 47.4, 2.3 Hz), –91.66 (dd, *J* = 47.3, 25.4 Hz).^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4 (dd, *J* = 285.2, 287.5 Hz), 139.1, 135.9, 130.3, 128.8, 126.3, 126.0, 77.5 (dd, *J* = 20.8, 21.9 Hz), 33.0 (t, *J* = 2.8 Hz), 22.8 (d, *J* = 4.7 Hz), 19.2; HRMS: (ESI, m/z): calcd. for $C_{11}H_{13}F_2$ $[M+H]^+$ = 183.0985, found 183.0976. IR (film) 2950, 2869, 1747, 1493, 1460, 1308, 1220, 1159, 997, 749 cm^{-1}.



ethyl 3-(4,4-difluorobut-3-en-1-yl)benzoate (1e)

Compound **1e** was prepared according to general procedure C on a 5 mmol scale from ethyl 3-iodobenzoate (1.38g, 1.00 equiv.) and allyl alcohol. Purification by silica gel column chromatography using Et_2O/pentane as eluent (10%, Rf ≈ 0.4) afforded **1e** as colorless oil in 55% yield after two steps, 659 mg.

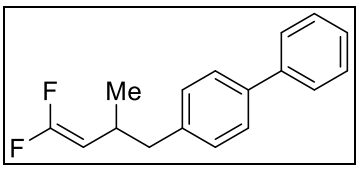
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (td, *J* = 4.7, 1.7 Hz, 1H), 7.87 (d, *J* = 1.7 Hz, 1H), 7.39–7.34 (m, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.14 (dtd, *J* = 25.3, 7.8, 2.5 Hz, 1H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.32 (qt, *J* = 7.5, 1.8 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –88.60 (d, *J* = 46.3 Hz), –90.65 (dd, *J* = 46.3, 25.2 Hz).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 156.4 (dd, *J* = 285.2, 287.5 Hz), 141.1, 132.9, 130.6, 129.4, 128.4, 127.4, 77.0 (t, *J* = 20.6 Hz), 60.9, 35.4 (t, *J* = 2.6 Hz), 23.9 (d, *J* = 4.7 Hz), 14.3. HRMS (ESI, m/z): calcd. for $C_{13}H_{15}F_2O_2$ $[M+H]^+$ = 241.1040, found 241.1031. IR (film): 2983, 1714, 1588, 1445, 1367, 1286, 1106, 751 cm^{-1}.



3-(4,4-difluorobut-3-en-1-yl)benzo[b]thiophene (1f)

Compound **1f** was prepared according to general procedure C on a 4 mmol scale from 3-iodobenzo[b]thiophene (1.04 g, 1.00 equiv.) and allyl alcohol. Purification by silica gel column chromatography using pentane as eluent (Rf ≈ 0.5) afforded **1f** as colorless oil in 30% yield after two steps, 270 mg.

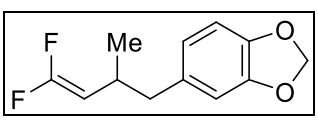
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dq, *J* = 7.6, 1.0 Hz, 1H), 7.74 (dq, *J* = 8.2, 1.0 Hz, 1H), 7.50–7.31 (m, 2H), 7.12 (s, 1H), 4.25 (dtdd, *J* = 25.4, 7.8, 2.4, 1.0 Hz, 1H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.78–2.35 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –88.57 (d, *J* = 46.5 Hz), –90.57 (dd, *J* = 46.4, 25.3 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4 (dd, *J* = 286.6, 287.63 Hz), 140.5, 138.7, 135.3, 124.2, 123.9, 122.9, 121.5, 121.4, 77.5 (t, *J* = 20.6 Hz), 28.4 (t, *J* = 2.8 Hz), 22.0 (d, *J* = 4.6 Hz). HRMS (ESI, m/z): calcd. for $C_{12}H_{11}F_2S$ $[M+H]^+$ = 225.0550, found 225.0536. IR (film): 3069, 2927, 2863, 1732, 1427, 1301, 1162, 1012, 944, 7131 cm^{-1}.



4-(4,4-difluoro-2-methylbut-3-en-1-yl)-1,1'-biphenyl (1g)

Compound **1g** was prepared according to general procedure C on a 10 mmol scale from 4-iodo-1,1'-biphenyl (2.80 g, 1.00 equiv.) and *β*-methyl allyl alcohol. Purification by silica gel column chromatography using pentane as eluent (Rf ≈ 0.5) afforded **1g** as colorless oil in 47% yield for two steps, 1.21 g.

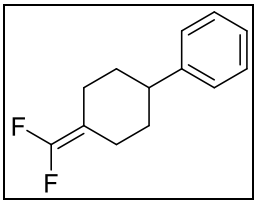
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.41–7.35 (m, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 4.12 (ddd, *J* = 25.4, 9.3, 3.0 Hz, 1H), 2.79–2.72 (m, 1H), 2.71 (m, 2H), 1.12 (d, *J* = 6.7 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –90.19 (dd, *J* = 48.7, 3.0 Hz), –90.95 (dd, *J* = 48.5, 25.4 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8 (dd, *J* = 285.8, 287.4 Hz), 141.0, 139.0, 138.9, 129.5, 128.7, 127.1, 127.0, 126.9, 83.3 (t, *J* = 19.9 Hz), 43.2 (t, *J* = 2.4 Hz), 30.1 (d, *J* = 5.0 Hz), 20.7 (t, *J* = 2.6 Hz). HRMS (ESI, m/z): calcd. for $C_{17}H_{17}F_2$ $[M+H]^+$ = 259.1298, found 259.1289. IR (film): 3028, 2964, 1747, 1599, 1486, 1376, 1293, 1220, 1170, 1008, 973, 761 cm^{-1}.



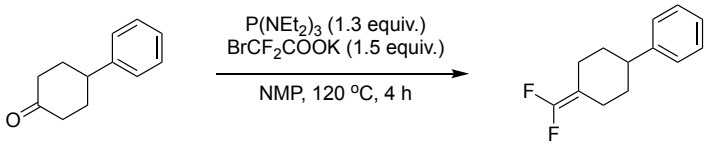
5-(4,4-difluoro-2-methylbut-3-en-1-yl)benzo[d][1,3]dioxole (1h)

Compound **1h** was prepared according to general procedure A on a 20 mmol scale from 3-(benzo[d][1,3]dioxol-5-yl)-2-methylpropanal (3.84 g, 1.00 equiv.). Purification by silica gel column chromatography using

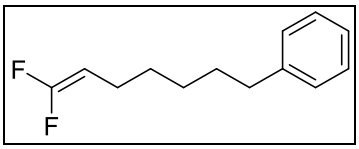
Et_2O/pentane as eluent (2%, Rf ≈ 0.3) afforded **1h** as colorless oil in 51% yield, 2.30 g.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (d, *J* = 7.9 Hz, 1H), 6.64 (d, *J* = 1.7 Hz, 1H), 6.59 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.93 (s, 2H), 4.02 (ddd, *J* = 25.6, 9.4, 3.0 Hz, 1H), 2.64–2.55 (m, 1H), 2.53 (m，2H), 1.03 (d, *J* = 6.6 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –89.68 (dd, *J* = 48.8, 2.9 Hz), –90.58 (dd, *J* = 48.7, 25.6 Hz).^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0 (dd, 285.4, 287.2 Hz), 147.4, 145.8, 133.6, 121.9, 109.4, 107.9, 100.7, 83.3 (t, *J* = 20.0 Hz), 43.3 (t, *J* = 2.4 Hz), 30.3 (d, *J* = 5.0 Hz), 20.6 (t, *J* = 2.5 Hz). HRMS (ESI, m/z): calcd. for $C_{12}H_{12}F_2O_2$ $[M]^+$ = 226.0805, found 226.0800. IR (film): 2964, 1739, 1489, 1441, 1360, 1243, 1040, 930, 806 cm^{-1}.



(4-(difluoromethylene)cyclohexyl)benzene (1i)

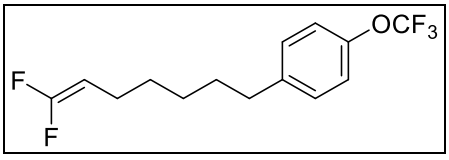


Compound **1i** was prepared according to general procedure A with slight modification on a 20 mmol scale from 4-phenylcyclohexan-1-one (3.48 g, 1.00 equiv.). Purification by silica gel column chromatography using pentane as eluent (Rf ≈ 0.5) afforded **1i** as colorless oil in 19% yield, 791mg.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.33 (m, 3H), 7.25 (ddd, *J* = 7.8, 5.7, 1.7 Hz, 2H), 2.64 (ddt, *J* = 12.1, 8.8, 3.4 Hz, 3H), 2.13–1.86 (m, 4H), 1.56 (qd, *J* = 12.1, 11.4, 3.7 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ –99.02 (t, *J* = 4.5 Hz). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.8 (t, *J* = 280.9 Hz), 146.4, 128.4, 126.7, 126.2, 87.1 (t, *J* = 18.9 Hz), 43.9, 33.7 (t, *J* = 2.1 Hz), 24.5 (t, *J* = 1.8 Hz). HRMS (ESI, m/z): calcd. for $C_{13}H_{14}F_5$ $[M]^+$ = 208.1064, found 208.1057. IR (film): 2968, 2928, 1759, 1452, 1272, 1212, 1158, 1070, 757, 699 cm^{-1}.



(7,7-difluorohept-6-en-1-yl)benzene [5] **(1j)**

Compound **1j** was prepared according to general procedure B on a 6.5 mmol scale from 6-phenylhexan-1-ol (1.16 g, 1.00 equiv.). Purification by silica gel column chromatography using pentane as eluent (Rf ≈ 0.8) afforded **1j** as colorless oil in 63% yield after two steps, 860 mg.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.27 (m, 2H), 7.19 (td, *J* = 5.7, 5.3, 2.8 Hz, 3H), 4.13 (dtd, *J* = 25.6, 7.9, 2.6 Hz, 1H), 2.67–2.54 (m, 2H), 1.98 (tdd, *J* = 7.5, 5.3, 1.9 Hz, 2H), 1.70–1.58 (m, 2H), 1.47–1.33 (m, 4H). Spectral data of **1j** matched literature report.[5]

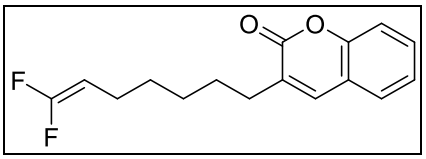


1-(7,7-difluorohept-6-en-1-yl)-4-(trifluoromethoxy)benzene (1k)

Compound **1k** was prepared according to general procedure C on a 10 mmol scale from 1-iodo-4-

(trifluoromethoxy)benzene (2.88 g, 1.00 equiv.) and hex-5-en-1-ol (2.0 g, 2.00 equiv.). Purification by silica gel column chromatography using pentane as eluent (Rf ≈ 0.6) afforded **1k** as colorless oil in 25% yield (containing ≈ 14% branched isomer) after two steps, 735 mg.

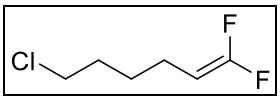
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.6 Hz, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 4.11 (dtd, *J* = 25.5, 7.9, 2.7 Hz, 1H), 2.64–2.51 (m, 2H), 2.06–1.89 (m, 2H), 1.69–1.57 (m, 2H), 1.47–1.32 (m, 4H). ^{19}F NMR (471 MHz, $CDCl_3$) δ –58.45, –90.09 (dd, *J* = 49.4, 2.3 Hz), –92.54 (ddt, *J* = 49.4, 25.7, 2.3 Hz). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.3 (dd, *J* = 286.6, 284.5 Hz), 147.3, 141.3, 129.5, 120.8, 120.5 (q, *J* = 256.4 Hz), 77.7 (t, *J* = 21.2 Hz), 35.2, 31.1, 29.2 (t, *J* = 2.3 Hz), 28.4, 22.0 (d, *J* = 4.0 Hz). HRMS (ESI, m/z): calcd. for $C_{14}H_{15}F_5O$ $[M]^+$ = 294.1043, found 294.1032. IR (film): 2936, 1750, 1509, 1463, 1243, 1019, 811 cm^{-1}.



3-(7,7-difluorohept-6-en-1-yl)-2H-chromen-2-one (1l)

Compound **1l** was prepared according to general procedure C on a 10 mmol scale from 3-iodo-2H-chromen-2-one (2.72 g, 1.00 equiv.) and hex-5-en-1-ol (2.0 g, 2.0 equiv.). Purification by silica gel column chromatography using Et_2O/pentane as eluent (3%, Rf ≈ 0.5) afforded **1l** as colorless oil in 31% yield after two steps, 862 mg.

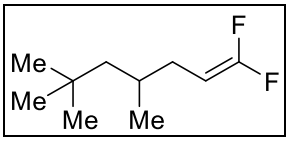
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.39–7.34 (m, 2H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.20–7.13 (m, 1H), 4.05 (dtd, *J* = 25.6, 7.9, 2.7 Hz, 1H), 2.51–2.46 (m, 2H), 1.91 (dt, *J* = 7.6, 1.9 Hz, 2H), 1.69–1.49 (m, 2H), 1.34 (dt, *J* = 7.4, 3.0 Hz, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –89.50 (d, *J* = 48.9 Hz), –91.90 (dd, *J* = 49.0, 25.5 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.7, 155.1 (dd, *J* = 287.0, 284.8 Hz), 153.1, 138.4, 130.5, 129.8, 127.1, 124.2, 119.5, 116.3, 77.8 (t, *J* = 21.3 Hz), 30.8, 29.1 (t, *J* = 2.6 Hz), 28.5, 27.7, 22.0 (d, *J* = 4.2 Hz). HRMS (ESI, m/z): calcd. for $C1_6H_{12}F_2O_2$ $[M+H]^+$ = 279.1197, found 279.1195. IR (film): 2965, 2928, 1749, 1710, 1207, 1151, 758 cm^{-1}.



6-chloro-1,1-difluorohex-1-ene [6] **(1m)**

Compound **1m** was prepared according to general procedure A on a 20 mmol scale from 5-chloropentanal (2.40 g, 1.0 equiv.). Purification by silica gel column chromatography using pentane as eluent (Rf ≈ 0.6) afforded **1m** as colorless oil in 45% yield, 1.40 g.

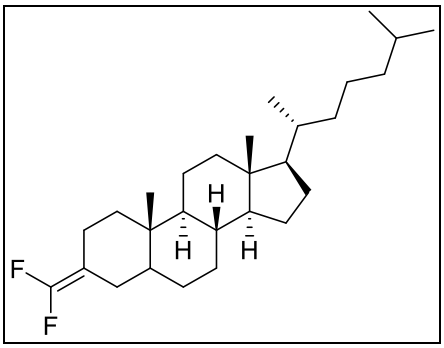
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.13 (dt, *J* = 25.3, 8.1 Hz, 1H), 3.41 (q, *J* = 6.9, 5.4 Hz, 2H), 2.02 (q, *J* = 7.7 Hz, 2H), 1.88 (m, 2H), 1.53 (t, *J* = 7.6 Hz, 2H). HRMS (ESI, m/z): calcd. for $C_6H_{10}ClF_2$ $[M+H]^+$ = 155.0439, found 155.0433.



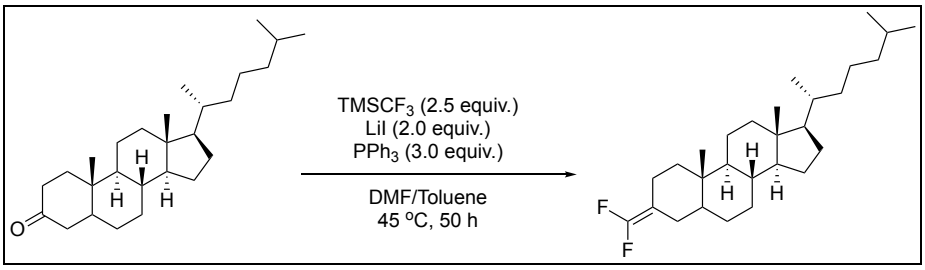
1,1-difluoro-4,6,6-trimethylhept-1-ene (1n)

Compound **1n** was prepared according to general procedure A on a 20 mmol scale from 3,5,5-trimethylhexanal. Purification by silica gel column chromatography using pentane as eluent (Rf ≈ 0.5) afforded **1n** as colorless oil in 84% yield, 2.97 g.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.12 (dtd, *J* = 25.5, 8.0, 2.8 Hz, 1H), 1.95 (dddd, *J* = 14.0, 7.9, 6.0, 1.7 Hz, 1H), 1.82 (dtd, *J* = 14.1, 7.6, 1.7 Hz, 1H), 1.65–1.49 (m, 1H), 1.21 (dd, *J* = 14.0, 3.7 Hz, 1H), 1.05 (dd, *J* = 14.0, 6.4 Hz, 1H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.89 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –89.15 (dd, *J* = 48.6, 2.6 Hz), –91.78 (dd, *J* = 48.7, 25.3 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.6 (dd, *J*= 284.5, 286.8 Hz), 50.2, 31.6, 31.5, 31.0, 29.9, 29.6 (t, *J* = 2.5 Hz), 22.1. HRMS (ESI, m/z): calcd. for $C_{10}H_{18}F_2$ $[M+H]^+$ = 177.1455, found 177.1645. IR (film): 2956, 1743, 1468, 1365, 1250, 1206, 922, 797 cm^{-1}.



(8R,9S,10S,13R,14S,17R)-3-(difluoromethylene)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthrene [7] (1o)

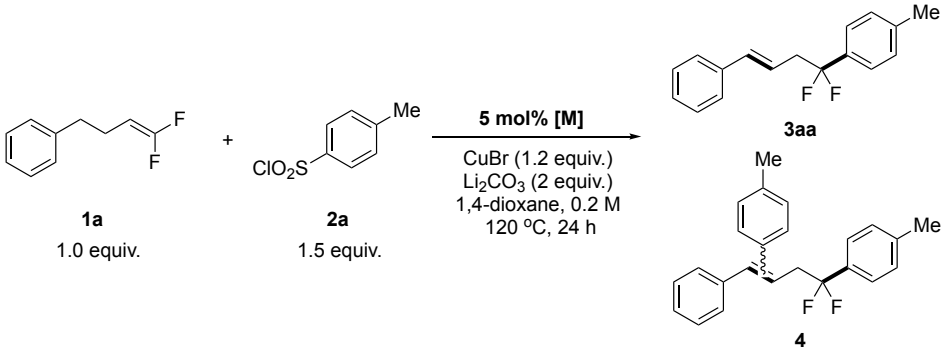


Compound **1o** was prepared according to previous report on 7.8 mmol scale. To an oven-dried 250 ml Schlenk reaction flask, (8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-3H-cyclopenta[a]phenanthren-3-one (3.01 g, 7.80 mmol), PPh_3 (6.13 g, 23.4 mmol), LiI (2.09 g, 15.6 mmol), were added under a stream of N_2. The reaction flask was then transferred in a glovebox, and DMF (anhydrous, 30 mL) and toluene (anhydrous, 70 mL) were added. Subsequently, $TMSCF_3$ (2.77 g, 19.5 mmol) was injected into the reaction flask under N_2 and the flask was stirred in a preheated 45 °C oil bath for 50 h. Upon cooling, the mixture was stirred with a solution of H_2O_2 (30% aqueous, 10 mL) for 3 h, and the reaction was extracted with Et_2O (60 mL x 3) and water (100 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in *vacuo*. Purification by silica gel column chromatography using pentane as eluent (Rf ≈ 0.9) afforded the desired product **1o** as colorless solid in 44 % yield, 1.44 g.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (d, *J* = 14.9 Hz, 2H), 2.03 (d, *J* = 14.7 Hz, 2H), 1.97 (dt, *J* = 12.6, 3.4 Hz, 2H), 1.93–1.42 (m, 7H), 1.42–0.93 (m, 18H), 0.90 (d, *J* = 6.4 Hz, 3H), 0.86 (dd, *J* = 6.7, 1.8 Hz, 6H), 0.82 (d, *J* = 0.6 Hz, 3H), 0.65 (s, 3H). Spectral data of **1o** matched literature report.[7]

Reaction Optimization

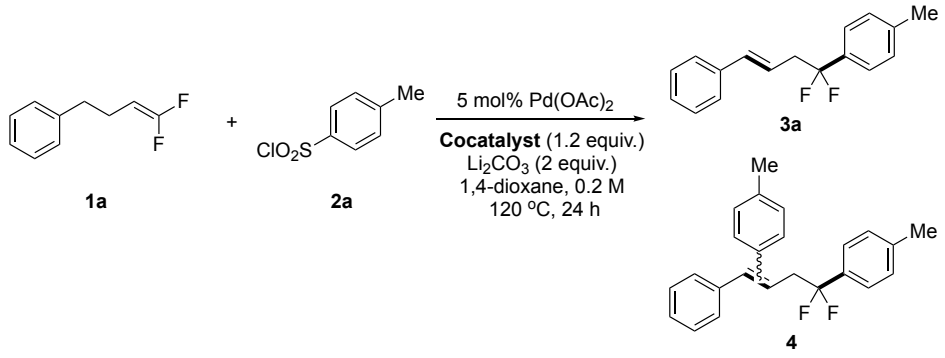
Table S1. Metal Complex Screening [a]



Entry	Catalyst [M]	Conv. (%)	Yield (%) [b]
1	$PdCl_2$	78	38
2	$Pd(OAc)_2$	86	57
3	$Pd(TFA)_2$	83	55
4	$Pd_2(dba)_3$	76	21
5	$PdCl_2(dppf)$	75	45
6	$NiCl_2(dme)$	<5	0
7	$Rh_2(OAc)_4$	<5	0
8	$PdCl_2(PPh_3)_2$	84	49

[a] Conditions: **1a**, 0.10 mmol; **2a**, 0.15 mmol; CuBr, 0.12 mmol; Li_2CO_3, 0.20 mmol; 0.50 mL 1,4-dioxane, N_2, reflux at 120 °C for 24 h. [M] (5 mol%) indicates dimeric [M] (2.5 mol%) and Monomeric [M] (5 mol%). [b] Yields were determined by ^{19}F NMR using 0.10 mmol *α,α,α*-trifluorotoluene as internal standard. 4-Bromotoluene, diarylation products **4** (mixtures) were observed as major byproducts.

Table S2. Co-catalysts and Substrates Ratio Screening [a]

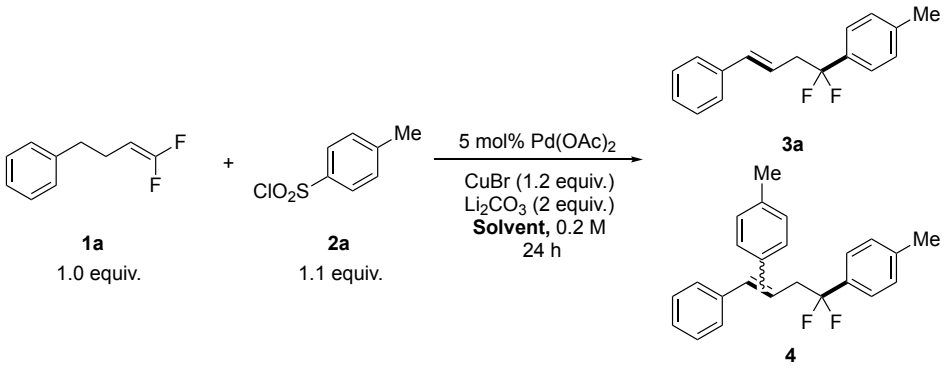


Entry	Cocatalyst	**1a**:**2a**	Conv. (%)	Yield (%) [b]
1	-	1:1.5	78	<5
2	CuI	1:1.5	21	17
3	CuCl	1:1.5	86	58
4	CuCl	1:1.2	89	63
5	CuBr	1:1.2	91	65
6	$CuBr(SMe_2)$	1:1.2	<10	0
7	Cu_2O	1:1.5	70	26
8	CuOAc	1:1.2	71	41

9	$CuBr_2$	1:1.5	25	15
10	Cu(0)	1:1.2	74	48
11	$FeCl_2$	1:1.2	52	<10
12	Ag(OTf)	1:1.2	0	0
13	Ag(TFA)	1:1.2	0	0
14	CuTc	1:1.5	52	32

[a] Conditions: **1a**, 0.10 mmol; $Pd(OAc)_2$, 0.0050 mmol; Li_2CO_3, 0.20 mmol; 0.50 mL 1,4-dioxane, N_2, reflux at 120 °C. [b] Yields was determined by ^{19}F NMR using 0.10 mmol *α,α,α*-trifluorotoluene as internal standard. 4-Bromotoluene, mixture of diarylation products **4** were observed as major byproducts.

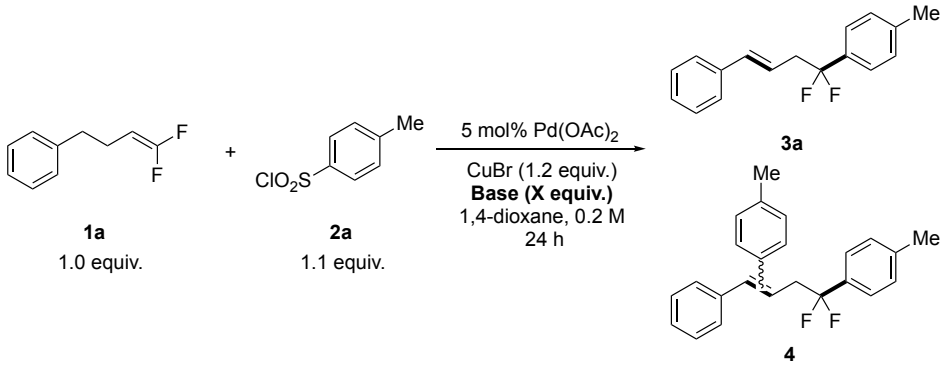
Table S3. Organic Solvent Screening [a]



Entry	Solvent	T (°C)	Conc.(M)	Conv. (%)	Yield (%) [b]
1	1,2-Dichloroethane	110	0.2	21	<5
2	Cyclohexane	110	0.2	15	trace
3	1,2-Dimethoxyethane	110	0.2	43	25
4	Toluene	120	0.2	<10	trace
5	*o*-Xylene	120	0.2	<5	trace
6	DMF	120	0.2	<10	<5
7	DMSO	120	0.2	0	0
8	1,4-Dioxane	120	0.2	84	62
9	Diglyme	120	0.2	56	18
10	Diglyme	130	0.5	97 [c]	20

[a] Conditions: **1a**, 0.10 mmol; **2a**, 0.11 mmol; $Pd(OAc)_2$, 0.0050 mmol; CuBr, 0.12 mmol; Li_2CO_3, 0.20 mmol; 0.50 mL solvent, N_2, reflux for 24 h. [b] Yields was determined by ^{19}F NMR using 0.10 mmol *α,α,α*-trifluorotoluene as internal standard. 4-Bromotoluene, mixture of diarylation products **4** were observed as major byproducts. [c] **1a** was decomposed.

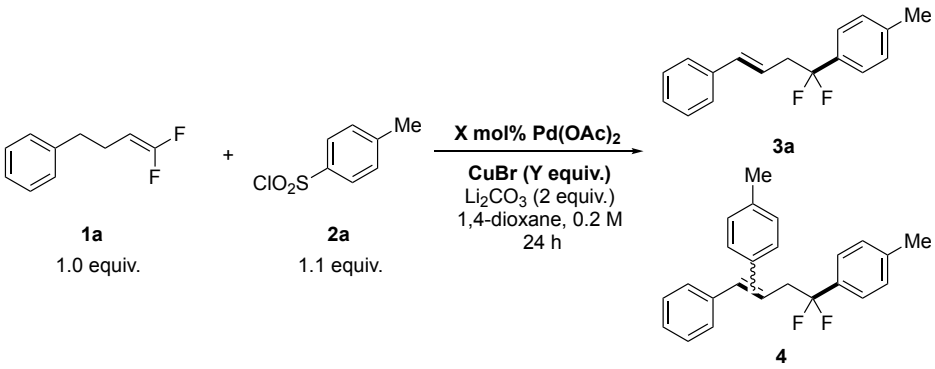
Table S4. Inorganic Base Screening [a]



Entry	Base	Conv. (%)	Yield (%) [b]
1	LiOAc	85	56
2	NaOAc	44	8
3	K_2CO_3	17	5
4	Na_2CO_3	31	7
5	Cs_2CO_3	8	<5
6	Li_2CO_3	87	64
7	K_3PO_4	32	11
8	KH_2PO_4	38	12
9 [c]	0	12	0

[a] Conditions: **1a**, 0.10 mmol; **2a**, 0.11 mmol; $Pd(OAc)_2$, 0.0050 mmol, CuBr, 0.12 mmol; Base, 0.20 mmol; 0.50 mL 1,4-dioxane, N_2, reflux at 120 °C. [b] Yields was determined by ^{19}F NMR using 0.10 mmol *α,α,α*-trifluorotoluene as internal standard. 4-bromotoluene, mixture of diarylation products **4** were observed as major byproducts. [c] No Base.

Table S5. Pd, Cu Loading Screening [a]



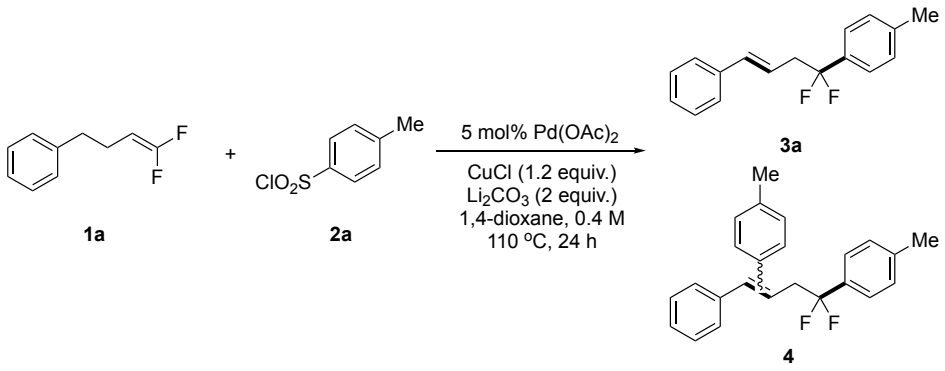
1a
1.0 equiv.

2a
1.1 equiv.

Entry	$Pd(OAc)_2$ (X mol%)	CuBr (Y equiv.)	T (°C)	Conv. (%)	Yield (%) [b]
1	5	0.05	120	70	12
2	5	0.1	120	47	30
3	5	0.5	120	65	39
4	5	0.8	120	76	44
5	5	1.2	120	88	68
6	5	2.0	120	87	56
7	2.5	1.2	120	38	15
8	5	1.2	130	85	67
9	7.5	1.2	120	81	60
10	10	1.2	120	79	61
11	10	1.2	130	88	44
12	5	(CuCl) 1.2	120	89	66
13	5	(CuCl) 1.2	110	93	68
14	5	(CuCl) 1.2	100	35	<10

[a] Conditions: **1a**, 0.10 mmol; **2a**, 0.11 mmol; Li_2CO_3, 0.20 mmol; 0.50 mL 1,4-dioxane, N_2, reflux for 24 h. [b] Yields was determined by ^{19}F NMR using 0.10 mmol *α,α,α*-trifluorotoluene as internal standard. 4-bromotoluene, mixture of diarylation products were observed **4** as major byproducts.

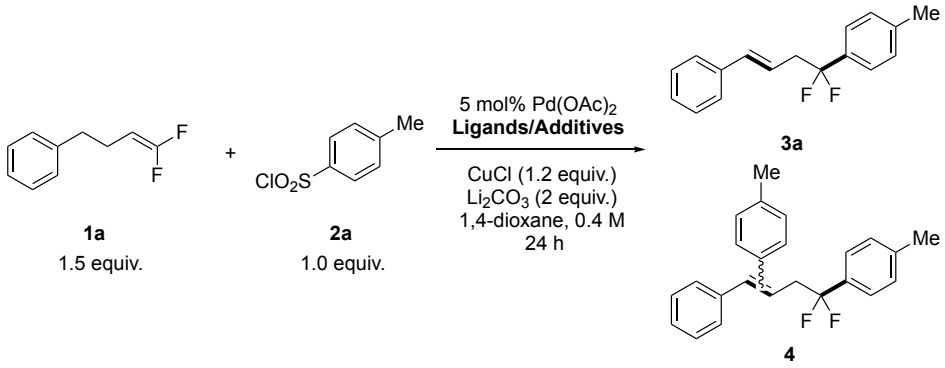
Table S6. Ratio of 1a:2a Screening [a]



Entry	**1a**:**2a**	Conv. (%) [b]	Yield (%) [c]
1	1.5:1	100	72
2	1.6:1	100	73
3	1.75:1	100	73(61)
4	2:1	100	75
5	2.25:1	100	75(63)
6	2.5:1	100	78(63)

[a] Conditions: **2a**, 0.20 mmol; Li_2CO_3, 0.40 mmol; 0.50 mL 1,4-dioxane, N_2, reflux for 24 h. [b] Conversion based on **2a**. [c] Yields was determined by ^{19}F NMR using 0.10 mmol *α,α,α*-trifluorotoluene as internal standard, isolated yields are given in parentheses. Mixture of diarylation products **4** (<20%) were observed as major byproducts.

Table S7. Ligand/Additives and Substrate Ratio Screening [a]



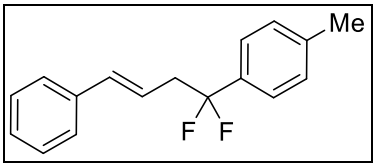
Entry	Ligands/Additives	Loading	**1a**:**2a**	T (°C)	Conv. (%)	Yield (%) [b]
1	P(*o*-Tolyl)$_3$	10 mol%	1.5:1	110	100	48
2	P(*p*-Tolyl)$_3$	10 mol%	1.5:1	110	100	50
3	DPE-Phos	5 mol%	1.5:1	110	100	39
4	Xantphos	5 mol%	1.5:1	110	100	42
5	CyJohnPhos	10 mol%	1.5:1	110	100	41
6	PCy_3	10 mol%	1.5:1	110	100	40
7	SIMes•Cl	10 mol%	1.5:1	110	100	51
8	SIPr•Cl	10 mol%	1.5:1	110	100	51
9	TBAF•3H_2O	20 mol%	2:1	120	100	28
10	$BzEt_3NCl$	20 mol%	2:1	120	100	37
11	2,2′-bipyridine	5 mol%	1:1.2	120	0	0
12	1,10-Phen	5 mol%	1:1.2	120	<	21
13[c]	CuBr	-	1.5:1	110	100	43

14	CuCl	-	1.5:1	110	100	45
15 [d]	SIPr•Cl	10 mol%	2.25:1	120	100	76(72)
16	SIMes•Cl	10 mol%	1.75:1	115	100	51
17	SIPr•Cl	10 mol%	1.75:1	115	100	64

[a] Conditions: **1a**, 0.30 mmol; **2a**, 0.20 mmol; $Pd(OAc)_2$, 0.010 mmol; Li_2CO_3, 0.40 mmol; 0.50 mL 1,4-dioxane, N_2, reflux for 24 h. [b] Yields was determined by GC analysis using 20 μL of dodecane as internal standard. Mixture of diarylation products **4** (<10%) were observed as major byproducts. [c] No ligand or additives. [d] The reaction was performed on 0.50 mmol of **2a** in 1.5 mL of 1,4-dioxane for 21 h, isolated yields are given in parentheses.

General procedure D: Arylation of Difluoroalkenes

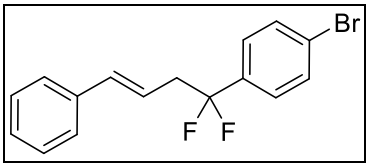
To an oven-dried 10 ml glass reaction tube, $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), Ar-SO_2Cl (0.50 mmol, 1.0 equiv.) and difluoroalkene (1.125 mmol, 2.25 equiv.) were added sequentially. The reaction tube was then transferred in a glovebox, in which anhydrous 1,4-dioxane (1.5 mL) was added. The reaction tube was then sealed under a N_2 atmosphere and stirred in a preheated 120 °C oil bath for 21 h. Upon cooling, the mixture was filtered through a short silica gel column for GC, GC-MS and crude ^{19}F NMR analysis. Then the combined filtrate was concentrated under vacuo and purified by silica gel column chromatography using Et_2O/pentane as eluent to afford the desired products.



(*E*)-1-(1,1-difluoro-4-phenylbut-3-en-1-yl)-4-methylbenzene (3aa)

Compound **3aa** was prepared according to general procedure D using *para*-toluenesulfonyl chloride (95.5 mg, 0.500 mmol), **1a** (189 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using pentane (Rf ≈ 0.3) as eluent afforded **3aa** as a colorless solid in 72% yield, 93 mg. Melting point: 65.0–68.2 °C.

^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.1 Hz, 2H), 7.37–7.34 (m, 2H), 7.33–7.31 (m, 2H), 7.27 (td, J = 3.2, 2.8, 1.4 Hz, 2H), 7.24 (d, J = 1.4 Hz, 1H), 6.51 (dt, J = 15.9, 1.5 Hz, 1H), 6.14 (dt, J = 15.9, 7.3 Hz, 1H), 3.07 (tdd, J = 15.6, 7.3, 1.4 Hz, 2H), 2.41 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –94.60 (t, J = 15.6 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.7 (t, J = 2.1 Hz), 136.9, 135.1, 134.2 (dt, J = 26.7 Hz), 129.0, 128.5, 127.6, 126.3, 124.9 (t, J = 6.4 Hz), 122.0 (t, J = 242.8 Hz), 120.5 (d, J = 5.3 Hz), 43.1 (t, J = 29.4 Hz), 21.2. HRMS (ESI, m/z): calcd. for $C_{17}H_{16}F_2$ $[M]^+$ = 258.1220, found 258.1233. IR (film): 3027, 2917, 1447, 1212, 1151, 1096, 979, 763 cm^{-1}.

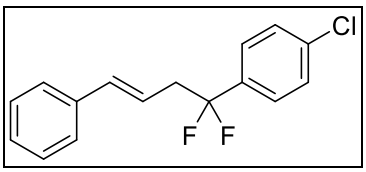


(*E*)-1-bromo-4-(1,1-difluoro-4-phenylbut-3-en-1-yl)benzene (3ab)

Compound **3ab** was prepared according to general procedure D using 4-bromobenzenesulfonyl chloride (128 mg, 0.500 mmol), **1a** (189 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica

gel column chromatography using pentane (Rf ≈ 0.3) as eluent afforded **3ab** as a white solid in 76% yield, 122 mg. Melting point: 83.6–84.8 °C.

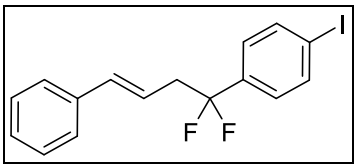
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.7 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.35–7.31 (m, 3H), 7.27–7.25 (m, 1H) 6.46 (d, *J* = 15.9 Hz, 1H), 6.05 (ddd, *J* = 11.0, 10.1, 5.0 Hz, 1H), 3.02 (tdd, *J* = 15.5, 7.3, 1.3 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –95.30 (t, *J* = 15.4 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.6, 136.1 (t, *J* = 27.0 Hz), 135.7, 131.6, 128.6, 127.8, 126.9 (t, *J* = 6.4 Hz), 126.3, 124.2 (t, *J* = 2.7 Hz), 122.5 (t, *J* = 243.5 Hz), 119.6 (t, *J* = 5.6 Hz), 43.0 (t, *J* = 28.6 Hz). HRMS (ESI, m/z): calcd. for $C_{16}H_{13}BrF_2$ $[M]^+$ = 322.0169, found 322.0166. IR (film): 3055, 1912, 1448, 1394, 1249, 1159, 978, 826 cm^{-1}.



(*E*)-1-chloro-4-(1,1-difluoro-4-phenylbut-3-en-1-yl)benzene (3ac)

Compound **3ac** was prepared according to general procedure D using 4-chlorobenzenesulfonyl chloride (106 mg, 0.500 mmol), **1a** (189 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using pentane (Rf ≈ 0.3) as eluent afforded **3ac** as a white solid in 65% yield, 90 mg. Melting point: 78.5–82.0 °C.

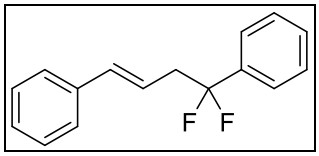
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.39 (m, 4H), 7.35–7.29 (m, 4H), 7.26 (dd, *J* = 6.5, 3.0 Hz, 1H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.08 (dt, *J* = 15.9, 7.3 Hz, 1H), 3.04 (tdd, *J* = 15.4, 7.3, 1.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –95.14 (t, *J* = 15.5 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.6, 135.9 (t, *J* = 2.2 Hz), 135.6, 135.5 (t, *J* = 27.0 Hz), 128.7, 128.6, 127.7, 126.6 (t, *J* = 6.3 Hz), 126.3, 121.5 (t, *J* = 243.6 Hz), 119.8 (t, *J* = 5.5 Hz), 42.9 (d, *J* = 28.9 Hz). HRMS (ESI, m/z): calcd. for $C_{16}H_{13}ClF_2$ $[M]^+$ = 278.0674, found 278.0683. IR (film): 3058, 1493, 1398, 1161, 1093, 1032, 972, 746 cm^{-1}.



(*E*)-1-(1,1-difluoro-4-phenylbut-3-en-1-yl)-4-iodobenzene (3ad)

Compound **3ad** was prepared according to general procedure D using 4-iodobenzenesulfonyl chloride (151 mg, 0.500 mmol), **1a** (189 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using pentane (Rf ≈ 0.3) as eluent afforded **3ad** as a white solid in 63% yield, 117 mg. Melting point: 98.8–103.2 °C.

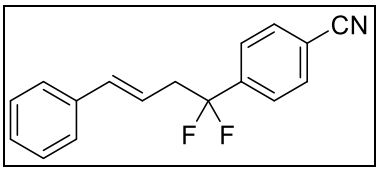
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.39–7.32 (m, 4H), 7.29–7.24 (td, *J* = 8.7, 8.2, 3.5 Hz, 3H), 6.49 (dd, *J* = 15.8, 2.2 Hz, 1H), 6.10 (ddt, *J* = 13.8, 6.5, 2.6 Hz, 1H), 3.04 (tdt, *J* = 15.4, 7.2, 1.7 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –95.59 (t, *J* = 15.4 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.6, 136.6, 136.5 (t, *J* = 27.0 Hz), 135.6, 128.6, 127.7, 126.9 (t, *J* = 6.4 Hz), 126.3, 122.5 (t, *J* = 243.5 Hz), 119.8 (t, *J* = 5.5 Hz), 96.1 (t, *J* = 2.5 Hz), 42.9 (t, *J* = 28.8 Hz). HRMS (ESI, m/z): calcd. for $C_{16}H_{13}IF_2$ $[M]^+$ = 370.0030, found 370.0022. IR (film)：3079, 1912, 1448, 1390, 1158, 1024, 977, 771 cm^{-1}.



(*E*)-(4,4-difluorobut-1-ene-1,4-diyl)dibenzene (3ae)

Compound **3ae** was prepared according to general procedure D using benzenesulfonyl chloride (88 mg, 0.50 mmol), **1a** (189 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using pentane (Rf ≈ 0.3) as eluent afforded **3ae** as a colorless oil in 70% yield, 87 mg.

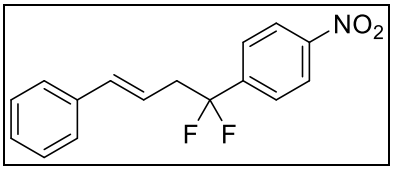
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61–7.56 (m, 2H), 7.52–7.46 (m, 3H), 7.40–7.33 (m, 4H), 7.32–7.23 (m, 1H), 6.54 (d, *J* = 15.9 Hz, 2H), 6.22–6.14 (dt, *J* = 14.8, 7.3 Hz, 1H), 3.12 (tdd, *J* = 15.7, 7.3, 1.5 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –95.34 (t, *J* = 15.7 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.0 (t, *J* = 26.4 Hz), 136.8, 135.3, 129.7 (t, *J* = 2.0 Hz), 128.5, 128.4, 127.6, 126.3, 125.0 (t, *J* = 6.4 Hz), 121.8 (t, *J* = 243.1 Hz), 120.3 (t, *J* = 5.4 Hz), 43.1 (t, *J* = 28.9 Hz). HRMS (ESI, m/z): calcd. for $C_{16}H_{14}F_2$ $[M]^+$ = 244.1064, found 244.1062. IR (film): 3027, 1450, 1318, 1155, 1038, 966, 765 cm^{-1}.



(*E*)-4-(1,1-difluoro-4-phenylbut-3-en-1-yl)benzonitrile (3af)

Compound **3af** was prepared according to general procedure D using 4-cyanobenzenesulfonyl chloride (101 mg, 0.500 mmol), **1a** (189 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using Et_2O/pentane (3%, Rf ≈ 0.3) as eluent afforded **3af** as a colorless solid in 61% yield, 82 mg. Melting point: 78.0–81.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.32–7.28 (m, 4H), 7.26–7.22 (m, 1H), 6.51–6.39 (d, *J* = 15.9 Hz, 1H), 6.03 (ddd, *J* = 15.9, 8.4, 6.2 Hz, 1H), 3.12–2.94 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –96.52 (t, *J* = 15.5 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4 (t, *J* = 27.2 Hz), 136.4, 136.2, 132.3, 128.6, 127.9, 126.3, 126.1 (t, *J* = 6.5 Hz), 121.0 (t, *J* = 244.3 Hz), 119.0 (t, *J* = 5.7 Hz), 118.0, 113.9 (t, *J* = 2.2 Hz), 42.7 (t, *J* = 28.2 Hz). HRMS (ESI, m/z): calcd. for $C_{17}H_{14}F_2N$ $[M+H]^+$ = 270.1094, found 270.1090. IR (film): 3027, 2230, 1405, 1230, 1162, 1041, 969 cm^{-1}

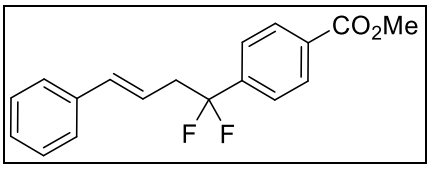


(*E*)-1-(1,1-difluoro-4-phenylbut-3-en-1-yl)-4-nitrobenzene (3ag)

Compound **3ag** was prepared according to general procedure D using 4-nitrobenzenesulfonyl chloride (111 mg, 0.500 mmol), **1a** (189 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.0 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using Et_2O/pentane (5%, Rf ≈ 0.3) as eluent afforded **3ag** as a yellow solid in 63% yield, 92 mg. Melting point: 73.8–76.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 9.1 Hz, 2H), 7.69 (d, *J* = 9.1 Hz, 2H), 7.32–7.29 (m, 3H), 7.28–7.23 (m, 2H), 6.47 (dd, *J* = 15.9, 1.7 Hz, 1H), 6.06 (dt, *J* = 15.8, 7.3 Hz, 1H), 3.08 (tdd, *J* = 15.5, 7.3, 1.3 Hz, 2H).

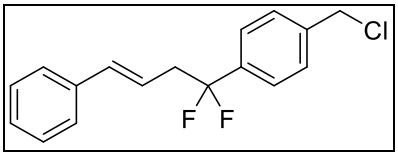
^{19}F NMR (376 MHz, $CDCl_3$) δ –96.12 (t, J = 15.4 Hz).^{13}C NMR (126 MHz, $CDCl_3$) δ 148.8, 143.1 (t, J = 27.2 Hz), 136.3, 136.3, 128.6, 127.9, 126.5 (t, J = 6.3 Hz), 126.3, 123.7, 121.0 (t, J = 244.4 Hz), 118.8 (t, J = 5.6 Hz), 42.8 (t, J = 28.1 Hz). HRMS (ESI, m/z): calcd. for $C_{16}H_{14}F_2NO_2$ $[M+H]^+$ = 290.0093, found 290.0989. IR (film): 3028, 1519, 1352, 1254, 1163, 1040, 748 cm^{-1}.



methyl (*E*)-4-(1,1-difluoro-4-phenylbut-3-en-1-yl)benzoate (3ah)

Compound **3ah** was prepared according to general procedure D using methyl 4-(chlorosulfonyl)benzoate (117.3 mg, 0.500 mmol), **1a** (189 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using Et_2O/pentane (2%, Rf ≈ 0.3) as eluent afforded **3ah** as a white solid in 75% yield, 114 mg. Melting point: 83.8–88.2 °C.

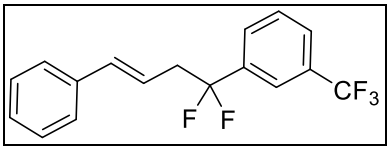
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, J = 8.0, 0.8 Hz, 2H), 7.58–7.55 (d, J = 8.0, 2H), 7.30–7.28 (m, 4H), 7.23 (m, 1H), 6.45 (d, J = 15.7 Hz, 1H), 6.06 (dt, J = 15.9, 7.3 Hz, 1H), 3.94 (s, 3H), 3.05 (tdd, J = 15.5, 7.3, 1.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –96.10 (t, J = 15.6 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 141.3 (t, J = 26.8 Hz), 136.6, 135.7, 131.5, 129.7, 128.5, 127.7, 126.3, 125.3 (t, J = 6.3 Hz), 121.5 (t, J = 243.9 Hz), 119.6 (t, J = 5.5 Hz), 52.3, 42.9 (t, J = 28.4 Hz). HRMS (ESI, m/z): calcd. for $C_{18}H_{17}F_2O_2$ $[M+H]^+$ = 303.1197, found 303.1190. IR (film): 3028, 1713, 1593, 1441, 1407, 1282, 1161, 1039, 774 cm^{-1}.



(*E*)-1-(chloromethyl)-4-(1,1-difluoro-4-phenylbujt-3-en-1-yl)benzene (3ai)

Compound **3ai** was prepared according to general procedure D using 4-(chloromethyl)benzenesulfonyl chloride (112.5 mg, 0.500 mmol), **1a** (189 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using pentane (Rf ≈ 0.3) as eluent afforded **3ai** as a colorless oil in 43% yield, 63 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.35–7.27 (m, 4H), 7.25–7.20 (m, 1H), 6.47 (d, J = 15.9 Hz, 1H), 6.09 (dt, J = 15.8, 7.3 Hz, 1H), 4.60 (s, 2H), 3.04 (tdd, J = 15.7, 7.3, 1.4 Hz, 2H).^{19}F NMR (376 MHz, $CDCl_3$) δ –95.22 (t, J = 15.7 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.0 (t, J = 1.9 Hz), 137.1 (t, J = 26.8 Hz), 136.7, 135.5, 128.6, 128.5, 127.7, 126.3, 125.5 (t, J = 6.4 Hz), 121.6 (t, J = 243.4 Hz), 120.0 (t, J = 5.4 Hz), 45.4, 42.9 (t, J = 28.7 Hz). HRMS (ESI, m/z): calcd. for $C_{17}H_{16}ClF_2$ $[M+H]^+$ = 293.0909, found 293.0896. IR (film): 3036, 2919, 1415, 1209, 1157, 1018, 982, 968, 768 cm^{-1}.

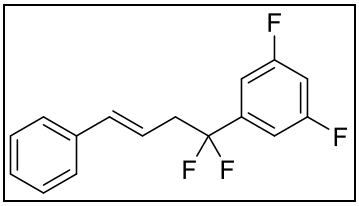


(*E*)-1-(1,1-difluoro-4-phenylbut-3-en-1-yl)-3-(trifluoromethyl)benzene (3aj)

Compound **3aj** was prepared according to general procedure D using 3-(trifluoromethyl)benzenesulfonyl

chloride (1.22 g, 5.00 mmol), **1a** (1.89 g, 11.25 mmol), $Pd(OAc)_2$ (56 mg, 0.25 mmol), SIPr•Cl (213.5 mg, 0.500 mmol), Li_2CO_3 (0.74 g, 10 mmol), CuCl (0.60 g, 6.0 mmol), and 1,4-dioxane (30 mL). Purification by silica gel column chromatography using pentane (Rf ≈ 0.3) as eluent afforded **3aj** as a colorless oil as 59% yield, 921 mg. (Note: reaction performed in a 250 mL Schlenk pressure-flask)

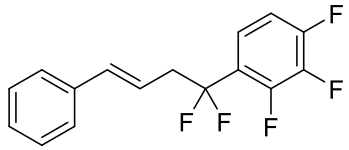
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.73 (t, *J* = 8.7 Hz, 2H), 7.60 (t, *J* = 7.9 Hz, 1H), 7.40–7.32 (m, 4H), 7.31–7.27 (m, 1H), 6.52 (d, *J* = 15.8 Hz, 1H), 6.13 (dt, *J* = 15.8, 7.3 Hz, 1H), 3.10 (tdd, *J* = 15.7, 7.3, 1.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.72, –95.24 (t, *J* = 15.7 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.0 (t, *J* = 27.2 Hz), 136.6, 135.9, 131.2 (q, *J* = 32.9 Hz), 129.1, 128.7 (m), 128.6, 127.8, 126.7 (dq, *J* = 4.0, 2.1 Hz), 126.3, 123.9 (q, *J* = 272.0 Hz), 122.2 (tt, *J* = 7.9, 3.3 Hz), 121.2 (t, *J* = 244.5 Hz), 119.5 (t, *J* = 5.5 Hz), 42.9 (t, *J* = 28.4 Hz). HRMS (ESI, m/z): calcd. for $C_{17}H_{13}F_5$ $[M]^+$ = 312.0937, found 312.0930. IR (film): 2924, 1598, 1329, 1205, 1158, 1072, 700 cm^{-1}.



(*E*)-1-(1,1-difluoro-4-phenylbut-3-en-1-yl)-3,5-difluorobenzene (3ak)

Compound **3ak** was prepared according to general procedure D using 3,5-difluorobenzenesulfonyl chloride (111.3 mg, 0.500 mmol), **1a** (189 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using pentane (Rf ≈ 0.3) as eluent afforded **3ak** as a colorless oil in 75% yield, 105 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.27 (m, 4H), 7.29–7.16 (m, 1H), 7.03 (dt, *J* = 6.0, 2.0 Hz, 2H), 6.88 (tt, *J* = 8.7, 2.4 Hz, 1H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.06 (dt, *J* = 15.8, 7.3 Hz, 1H), 3.02 (tdd, *J* = 15.7, 7.3, 1.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –95.57 (t, *J* = 15.6 Hz), –108.38 (t, *J* = 7.7 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.9 (d, *J* = 12.4 Hz), 161.9 (d, *J* = 12.4 Hz), 136.5, 136.0, 128.6, 127.8, 126.3, 120.6 (tt, *J* = 244.7, 2.9 Hz), 119.2 (t, *J* = 5.5 Hz), 108.7 (dt, *J* = 27.7, 6.7 Hz), 105.3 (dt, *J* = 25.3, 1.5 Hz) 2.6 (t, *J* = 28.2 Hz). HRMS (ESI, m/z): calcd. for $C_{16}H_{12}F_4$ $[M]^+$ = 280.0875, found 280.0872. IR (film): 3028, 1598, 1444, 1347, 1124, 1061, 984, 865, 749 cm^{-1}.

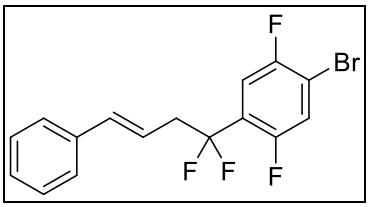


(*E*)-1-(1,1-difluoro-4-phenylbut-3-en-1-yl)-2,3,4-trifluorobenzene (3al)

Compound **3al** was prepared according to general procedure D using 2,3,4-trifluorobenzenesulfonyl chloride (115.3 mg, 0.500 mmol), **1a** (189 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using pentane (Rf ≈ 0.3) as eluent afforded **3al** as a colorless oil in 63% yield, 94 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.30 (m, 4H), 7.29–7.25 (m, 2H), 7.27 (dd, *J* = 3.2, 2.0 Hz, 1H), 7.23 (ddd, *J* = 4.7, 3.4, 2.1 Hz, 1H), 7.01 (tdd, *J* = 9.1, 6.8, 2.1 Hz, 1H), 6.49 (d, *J* = 15.8 Hz, 1H), 6.10–6.00 (m, 1H), 3.15 (td, *J* = 16.1, 7.3 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –92.85 (td, *J* = 16.1, 11.5 Hz), –130.58 (dddd, *J* = 24.0, 12.3, 6.3, 2.8 Hz), –135.40 (dt, *J* = 20.6, 9.8 Hz), –158.83 (tt, *J* = 20.5, 4.4 Hz). ^{13}C NMR (126 MHz,

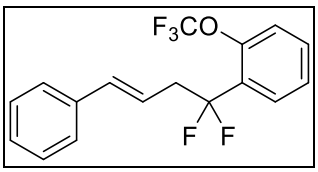
$CDCl_3$) δ 152.1 (dm, *J* = 253.7 Hz), 148.7 (ddd, *J* = 256.0, 11.9, 4.2 Hz), 141.3 (t, *J* = 15.4 Hz), 139.3 (t, *J* = 15.6 Hz), 136.5, 135.92 128.6, 127.8, 126.3, 120.9 (ddd, *J* = 8.4, 4.9, 3.4 Hz), 119.8 (tt, *J* = 245.3, 3.0 Hz), 119.3 (t, *J* = 5.3 Hz), 112.0 (dd, *J* = 17.8, 4.2 Hz), 41.7 (dt, *J* = 27.3, 3.3 Hz). HRMS (ESI, m/z): calcd. for $C_{16}H_{11}F_5$ $[M]^+$ = 298.0781, found 298.0783. IR (film): 3028, 1620, 1517, 1449, 1324, 1228, 1143, 1062, 966, 815 cm^{-1}.



(*E*)-1-bromo-4-(1,1-difluoro-4-phenylbut-3-en-1-yl)-2,5-difluorobenzene (3am)

Compound **3am** was prepared according to general procedure D using 4-bromo-2,5-difluorobenzenesulfonyl chloride (145.7 mg, 0.500 mmol), **1a** (189 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using pentane (3Rf ≈ 0.4) as eluent afforded **3am** as a colorless oil in 57% yield, 102 mg.

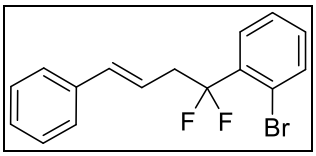
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (ddt, *J* = 9.5, 5.3, 1.0 Hz, 1H), 7.35–7.29 (m, 4H), 7.29–7.25 (m, 1H), 7.25–7.21 (m, 1H), 6.52 (d, *J* = 15.8 Hz, 1H), 6.07 (dtd, *J* = 15.8, 7.4, 1.0 Hz, 1H), 3.23–3.11 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –94.27 (td, *J* = 16.1, 10.9 Hz), –112.16 (ddd, *J* = 15.8, 8.4, 5.5 Hz), –118.76 (dqd, *J* = 16.5, 10.6, 6.2 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.3 (dd, *J* = 245.5, 3.1 Hz), 153.8 (dq, *J* = 252.1, 3.5 Hz), 136.5, 136.0, 128.6, 127.8, 126.3, 121.7, 121.5, 119.5 (td, *J* = 245.4 3.2 Hz), 119.1 (t, *J* = 5.2 Hz), 114.7 (dtd, *J* = 27.0, 8.1, 3.6 Hz), 111.4 (dd, *J* = 23.5, 10.0 Hz), 41.4 (td, *J* = 27.2, 3.8 Hz). HRMS (ESI, m/z): calcd. for $C_{16}H_{12}BrF_4$ $[M+H]^+$ = 359.0058, found 359.0053. IR (film): 3062, 3028, 1621, 1486, 1402, 1313, 1158, 966, 750 $cm^{-1.}$



(*E*)-1-(1,1-difluoro-4-phenylbut-3-en-1-yl)-2-(trifluoromethoxy)benzene (3an)

Compound **3an** was prepared according to general procedure D using 2-(trifluoromethoxy)benzenesulfonyl chloride (130.3 mg, 0.500 mmol), **1a** (189 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using pentane (Rf ≈ 0.4) as eluent afforded **3an** a colorless oil in 76% yield, 125 mg.

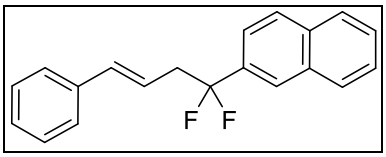
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.49 (td, *J* = 7.8, 1.7 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.36–7.29 (m, 5H), 7.28–7.19 (m, 1H), 6.49 (d, *J* = 15.8 Hz, 1H), 6.09 (dt, *J* = 15.8, 7.3 Hz, 1H), 3.20 (dd, *J* = 7.3, 1.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –56.61 (q, *J* = 2.6 Hz), –94.35 (td, *J* = 16.2, 2.9 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.3 (h, *J* = 2.2 Hz), 136.7, 135.4, 131.5 (t, *J* = 1.8 Hz), 128.8 (t, *J* = 26.6 Hz), 128.5, 127.7 (t, *J* = 8.4 Hz), 127.6, 126.4, 126.3, 120.2 (q, *J* = 259.1 Hz), 120.5 (t, *J* = 245.1 Hz), 120.2 (q, *J* = 2.2 Hz), 119.9 (t, *J* = 5.5 Hz), 41.8 (d, *J* = 27.5 Hz). HRMS (ESI, m/z): calcd. for $C_{17}H_{13}F_5O$ $[M]^+$ = 328.0887, found 328.0886. IR (film): 3028, 2926, 1611, 1495, 1454, 1224, 1036, 966, 763, 692 cm^{-1}.



(*E*)-1-bromo-2-(1,1-difluoro-4-phenylbut-3-en-1-yl)benzene (3ao)

Compound **3ao** was prepared according to general procedure D using 2-bromobenzenesulfonyl chloride (128 mg, 0.500 mmol), **1a** (189 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using pentane (Rf ≈ 0.4) as eluent afforded **3ao** as a colorless oil in 58% yield, 95 mg.

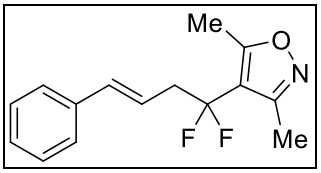
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.53 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.31 (td, *J* = 7.6, 1.2 Hz, 1H), 7.28–7.13 (m, 6H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.04 (dt, *J* = 15.8, 7.3 Hz, 1H), 3.26 (tdd, *J* = 16.3, 7.3, 1.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –94.40 (t, *J* = 16.3 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.8, 135.7 (t, *J* = 25.4 Hz), 135.4, 134.8, 131.2, 128.5, 128.0 (t, *J* = 9.3 Hz), 127.6,127.3, 126.2, 121.4 (t, *J* = 247.3 Hz), 120.0 (t, *J* = 5.1 Hz), 119.5 (t, *J* = 4.1 Hz), 40.9 (t, *J* = 27.0 Hz). HRMS: (ESI, m/z): calcd. for $C_{16}H_{13}BrF_2$ $[M]^+$ = 322.0169, found 322.0172. IR (film) 3027, 1593, 1439, 1301, 1166, 1071, 1030, 966, 750 cm^{-1}.



(*E*)-2-(1,1-difluoro-4-phenylbut-3-en-1-yl)naphthalene (3ap)

Compound **3ap** was prepared according to general procedure D using naphthalene-2-sulfonyl chloride (113.3 mg, 0.500 mmol), **1a** (189 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using pentane (Rf ≈ 0.3) as eluent afforded **3ap** as a white solid in 53% yield, 79 mg. Melting point: 91.0–92.6 °C.

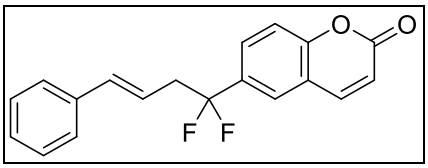
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05–7.98 (s, 1H), 7.95–7.81 (m, 3H), 7.63–7.50 (m, 3H), 7.35–7.27 (m, 4H), 7.25–7.20 (m, 1H), 6.52 (d, *J* = 15.9 Hz, 1H), 6.15 (dt, *J* = 15.9, 7.2 Hz, 1H), 3.16 (tdd, *J* = 15.7, 7.3, 1.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –96.52 (t, *J* = 15.5 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.8, 135.4, 134.3 (t, *J* = 26.4 Hz), 133.7 (t, *J* = 1.6 Hz), 132.6, 128.6, 128.5, 128.4, 127.7, 127.6, 127.1, 126.6, 126.3, 124.8 (t, *J* = 7.3 Hz), 122.3 (t, *J* = 5.9 Hz), 122.0 (t, *J* = 243.4 Hz), 120.3 (t, *J* = 5.5 Hz), 43.2 (t, *J* = 28.9 Hz). HRMS (ESI, m/z): calcd. for $C_{20}H_{16}F_2$ $[M]^+$ = 294.1220, found 294.1217. IR (film): 3058, 2923, 1495, 1314, 1212, 1155, 966, 749 cm^{-1}.



(*E*)-4-(1,1-difluoro-4-phenylbut-3-en-1-yl)-3,5-dimethylisoxazole (3aq)

Compound **3aq** was prepared according to general procedure D using 3,5-dimethylisoxazole-4-sulfonyl chloride (97.8 mg, 0.500 mmol), **1a** (189 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using Et_2O/pentane (3%, Rf ≈ 0.3) as eluent afforded **3aq** as a colorless oil in 40% yield, 53 mg.

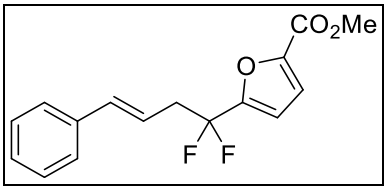
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.29 (m, 4H), 7.28–7.23 (m, 1H), 6.49 (d, *J* = 16.0 Hz, 1H), 6.05 (dt, *J* = 15.8, 7.4 Hz, 1H), 2.98 (tdd, *J* = 15.3, 7.4, 1.4 Hz, 2H), 2.42 (t, *J* = 1.9 Hz, 3H), 2.30 (t, *J* = 1.2 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ –91.01 (t, *J* = 15.3 Hz).^{13}C NMR (151 MHz, $CDCl_3$) δ 167.9 (t, *J* = 4.2 Hz), 157.6 (t, *J* = 2.4 Hz), 136.3, 136.3, 128.6, 127.9, 126.2, 119.9 (t, *J* = 240.5 Hz), 118.9 (t, *J* = 5.4 Hz), 112.1 (t, *J* = 31.4 Hz), 42.7 (t, *J* = 29.0 Hz), 12.2 (t, *J* = 1.9 Hz), 11.1 (t, *J* = 1.9 Hz). HRMS (ESI, m/z): calcd. for $C_{15}H_{16}F_2NO$ $[M+H]^+$ = 264.1200, found 264.1192. IR (film): 2925, 1633, 1455, 1324, 1163, 1031, 969, 750 cm^{-1}.



(*E*)-6-(1,1-difluoro-4-phenylbut-3-en-1-yl)-2H-chromen-2-one (3ar)

Compound **3ar** was prepared according to general procedure D using 2-oxo-2H-chromene-6-sulfonyl chloride (122.3 mg, 0.500 mmol), **1a** (189 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography ethyl acetate/pentane (10%, Rf ≈ 0.3) as eluent afforded **3ar** as a white solid in 48% yield, 76 mg. Melting point: 87.5–90.8 °C.

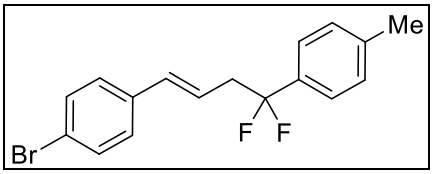
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 9.6 Hz, 1H), 7.65 (m, 1H), 7.63 (s, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.42–7.27 (m, 4H), 7.24 (td, *J* = 4.4, 3.9, 1.6 Hz, 1H), 6.49 (m, 1H), 6.46 (d, *J* = 6.8 Hz, 1H), 6.07 (dt, *J* = 15.9, 7.3 Hz, 1H), 3.07 (tdd, *J* = 15.5, 7.3, 1.4 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –93.96 (t, *J* = 15.6 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 154.6 (t, *J* = 1.9 Hz), 143.0, 136.5, 135.9, 133.2 (t, *J* = 27.3 Hz), 128.6 (t, *J* = 6.0 Hz), 128.6, 127.8, 126.3, 124.9 (t, *J* = 6.8 Hz), 121.2 (t, *J* = 243.8 Hz), 119.5 (t, *J* = 5.6 Hz), 118.3, 117.6, 117.2, 43.0 (t, *J* = 28.8 Hz). HRMS (ESI, m/z): calcd. for $C_{19}H_{15}F_2O_2$ $[M+H]^+$ = 313.1040, found 313.1027. IR (film): 3079, 1731, 1614, 1574, 1377, 1253, 1157, 1093, 968, 765 cm^{-1}.



methyl (*E*)-5-(1,1-difluoro-4-phenylbut-3-en-1-yl)furan-2-carboxylate (3as)

Compound **3as** was prepared according to general procedure D using methyl 5-(chlorosulfonyl)furan-2-carboxylate (112.3 mg, 0.500 mmol), **1a** (189 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography ethyl acetate/pentane (10%, Rf ≈ 0.3) as eluent afforded **3as** as a colorless oil in 50% yield, 73 mg.

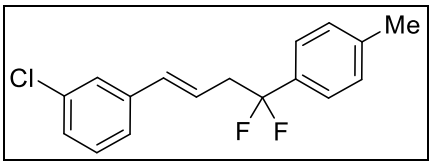
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.30 (m, 4H), 7.28–7.24 (m, 1H), 7.18 (d, *J* = 3.4 Hz, 1H), 6.72 (d, *J* = 3.5 Hz, 1H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.11 (dt, *J* = 15.8, 7.3 Hz, 1H), 3.94 (s, 3H), 3.22 (tdd, *J* = 15.8, 7.3, 1.4 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ –95.82 (t, *J* = 15.8 Hz). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 151.6 (t, *J* = 37.2 Hz), 145.2, 136.6, 136.0, 128.5, 127.8, 126.3, 118.8 (t, *J* = 4.9 Hz), 118.1, 116.7 (t, *J* = 239.5 Hz), 110.9 (t, *J* = 3.0 Hz), 52.2, 40.0 (t, *J* = 26.1 Hz). HRMS (ESI, m/z): calcd. for $C_{16}H_{15}F_2O_3$ $[M+H]^+$ = 293.0989, found 293.0981. IR (film): 2925, 1731, 1435, 1314, 1297, 1158, 1019, 984, 762 cm^{-1}.



(*E*)-1-bromo-4-(4,4-difluoro-4-(p-tolyl)but-1-en-1-yl)benzene (3ba)

Compound **3ba** was prepared according to general procedure D using *para*-toluenesulfonyl chloride (96 mg, 0.50 mmol), **1b** (277.9 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using pentane (Rf ≈ 0.4) as eluent afforded **3ba** as a white solid in 72% yield, 121 mg. Melting point: 87.5–91.8 °C.

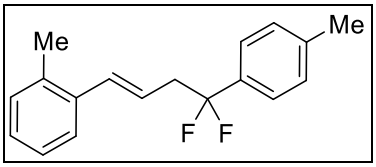
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.40 (d, *J* = 15.9 Hz, 1H), 6.10 (dt, *J* = 15.9, 7.2 Hz, 1H), 3.01 (tdd, *J* = 15.5, 7.2, 1.4 Hz, 2H), 2.38 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –94.67 (t, *J* = 15.6 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.8 (t, *J* = 2.3 Hz), 135.8, 133.9, 131.6, 129.1, 128.7, 127.8, 127.5, 124.9 (t, *J* = 6.4 Hz), 121.8 (t, *J* = 242.6 Hz), 121.4 (t, *J* = 5.4 Hz), 42.9 (t, *J* = 29.3 Hz), 21.2. HRMS (ESI, m/z): calcd. for $C_{17}H_{15}BrF_2$ $[M]^+$ = 336.0325, found 336.0321. IR (film): 2925, 1486, 1275, 1205, 1151, 913, 748 cm^{-1}.



(*E*)-1-chloro-3-(4,4-difluoro-4-(p-tolyl)but-1-en-1-yl)benzene (3ca)

Compound **3ca** was prepared according to general procedure D using *para*-toluenesulfonyl chloride (96 mg, 0.50 mmol), **1c** (227.9 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using pentane (Rf ≈ 0.4) as eluent afforded **3ca** as a colorless oil in 65% yield, 95 mg.

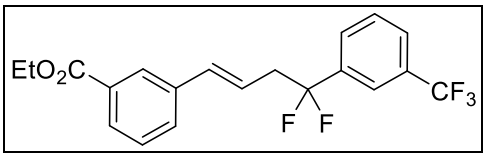
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 1.8 Hz, 1H), 7.23 (dd, *J* = 7.6, 1.4 Hz, 2H), 7.21–7.16 (m, 3H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.12 (dt, *J* = 15.8, 7.3 Hz, 1H), 3.03 (tdd, *J* = 15.6, 7.3, 1.4 Hz, 2H), 2.38 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ –94.50 (t, *J* = 15.5 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.8 (t, *J* = 2.1 Hz), 138.7, 134.5, 134.1 (t, *J* = 26.5 Hz), 133.8, 129.7, 129.1, 127.5, 126.2, 124.9 (t, *J* = 6.4 Hz), 124.5, 122.2 (t, *J* = 5.4 Hz), 121.8 (t, *J* = 245.7 Hz), 43.0 (t, *J* = 29.4 Hz), 21.2. HRMS (ESI, m/z): calcd. for $C_{17}H_{15}ClF_2$ $[M]^+$ = 292.0830, found 292.0823. IR (film) 2923, 1616, 1594, 1475, 1312, 1252, 1158, 1038, 965, 818, 778 cm^{-1}.



(*E*)-1-(4,4-difluoro-4-(p-tolyl)but-1-en-1-yl)-2-methylbenzene (3da)

Compound **3da** was prepared according to general procedure D using *para*-toluenesulfonyl chloride (96 mg, 0.50 mmol), **1d** (204.9 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using pentane (Rf ≈ 0.3) as eluent afforded **3da** as a colorless oil in 63% yield, 86 mg.

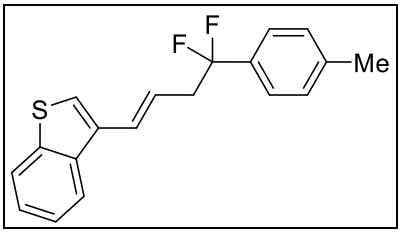
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.36–7.33 (m, 1H), 7.23(d, *J* = 8.0 Hz, 2H), 7.13 (qd, *J* = 4.9, 4.5, 2.6 Hz, 3H), 6.64 (d, *J* = 15.7 Hz, 1H), 5.95 (dt, *J* = 15.7, 7.3 Hz, 1H), 3.06 (tdd, *J* = 15.4, 7.3, 1.4 Hz, 2H), 2.38 (s, 3H), 2.26 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –94.03 (t, *J* = 15.5 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.7 (t, *J* = 1.9 Hz), 136.2, 135.2, 134.1 (t, *J* = 26.8 Hz), 133.3, 130.1, 129.0, 127.5, 126.0, 125.7, 125.0 (t, *J* = 6.4 Hz), 122.1 (t, *J* = 242.5 Hz), 121.9 (t, *J* = 5.5 Hz), 43.2 (t, *J* = 29.1 Hz), 21.2, 19.6. HRMS (ESI, m/z): calcd. for $C_{18}H_{18}F_2$ $[M]^+$ = 272.1377, found 272.1377. IR (film): 3020, 2923, 1616, 1517, 1460, 1309, 1252, 1158, 1036, 966, 749 cm^{-1}.



ethyl (*E*)-3-(4,4-difluoro-4-(3-(trifluoromethyl)phenyl)but-1-en-1-yl)benzoate (3ej)

Compound **3ej** was prepared according to general procedure D using 3-trifluoromethylbenzenesulfonyl chloride (122.3 mg, 0.500 mmol), **1e** (210 mg, 0.875 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using Et_2O/pentane (5%, Rf ≈ 0.3) as eluent afforded **3ej** as a colorless oil in 61% yield, 115 mg.

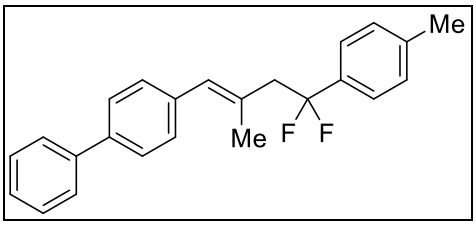
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (t, *J* = 1.8 Hz, 1H), 7.92 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.77 (tt, *J* = 1.8, 0.9 Hz, 1H), 7.71–7.67 (t, *J* = 8.0 Hz, 2H), 7.60–7.54 (t, *J* = 7.8 Hz, 1H), 7.50 (dt, *J* = 7.7, 1.6 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 6.52 (d, *J* = 15.8 Hz, 1H), 6.18 (dt, *J* = 15.9, 7.3 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.07 (tdd, *J* = 15.8, 7.3, 1.3 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.75, –95.31 (t, *J* = 15.7 Hz).^{13}C NMR (151 MHz, $CDCl_3$) δ 166.5, 137.9 (t, *J* = 27.2 Hz), 136.8, 135.1, 131.1 (m), 130.9, 130.5, 129.2, 128.8, 128.6, 128.6 (m), 127.4, 126.8 (m), 124.6 (t, *J* = 261.7 Hz), 122.2 (m), 121.1 (t, *J* = 244.1Hz), 120.8 (t, *J* = 5.0 Hz), 61.1, 42.9 (t, *J* = 28.3 Hz), 14.3. HRMS (ESI, m/z): calcd. for $C_{20}H_{17}F_5O_2$ $[M]^+$ = 384.1149, found 384.1146. IR (film): 2983, 1715, 1446, 1255, 1165, 968, 751 cm^{-1}.



(*E*)-3-(4,4-difluoro-4-(p-tolyl)but-1-en-1-yl)benzo[b]thiophene (3fa)

Compound **3fa** was prepared according to general procedure D using *para*-toluenesulfonyl chloride (96 mg, 0.5 mmol), **1f** (196 mg, 0.875 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using pentane (Rf ≈ 0.2) as eluent afforded **3fa** as a colorless oil in 57% yield, 92 mg.

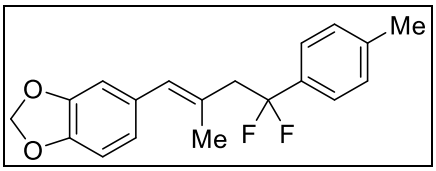
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87–7.82 (m, 1H), 7.81–7.76 (m, 1H), 7.43–7.39 (m, 2H), 7.39–7.34 (m, 3H), 7.25–7.21 (m, 2H), 6.71 (d, *J* = 15.9 Hz, 1H), 6.16 (dt, *J* = 15.9, 7.3 Hz, 1H), 3.10 (tdd, *J* = 15.4, 7.3, 1.4 Hz, 2H), 2.38 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ –94.10 (t, *J* = 15.6 Hz). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.36, 139.77, 137.56, 134.02 (t, *J* = 26.7 Hz), 133.65, 129.06, 127.54, 125.02 (t, *J* = 6.0 Hz), 124.43, 124.21, 122.85, 122.46 (t, *J* = 5.2 Hz), 122.07, 121.98 (t, *J* = 243.1 Hz), 121.91, 43.27 (t, *J* = 29.0 Hz), 21.24. HRMS (ESI, m/z): calcd. for $C_{19}H_{17}F_2S$ $[M+H]^+$ = 315.1019, found 315.1017. IR (film): 3005, 1275, 2, 1204, 1150, 750 cm^{-1}.



(*E*)-4-(4,4-difluoro-2-methyl-4-(p-tolyl)but-1-en-1-yl)-1,1'-biphenyl (3ga)

Compound **3ga** was prepared according to general procedure D using *para*-toluenesulfonyl chloride (96 mg, 0.50 mmol), **1g** (290.6 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). The crude mixture was analyzed by GC and GC-MS (Z/E≈19:1). Purification by silica gel column chromatography using pentane (Rf ≈ 0.3) as eluent afforded **3ga** as the major isomer in 55% yield, colorless oil, 96 mg.

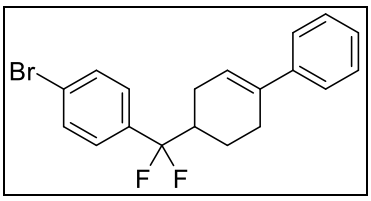
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.36–7.31 (m, 1H), 7.23 (m, 4H), 6.27 (s, 1H), 2.98 (td, *J* = 15.9, 0.9 Hz, 2H), 2.38 (s, 3H), 1.88 (d, *J* = 1.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –93.45 (t, *J* = 15.9 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.8, 139.6, 139.2, 136.7, 134.4 (t, *J* = 26.8 Hz), 130.9, 130.8 (t, *J* = 4.0 Hz), 129.3, 128.9, 128.7, 127.2, 126.9, 126.7, 125.0 (t, *J* = 6.4 Hz), 122.6 (t, *J* = 244.5 Hz), 50.0 (t, *J* = 28.1 Hz), 21.3, 19.3 (t, *J* = 1.9 Hz). HRMS (ESI, m/z): calcd. for $C_{24}H_{22}F_2$ $[M]^+$ = 348.1690, found 348.1674. IR (film): 3028, 2922, 1743, 1486, 1597, 1486, 1325, 1156, 1061, 818, 762 cm^{-1}.



(*E*)-5-(4,4-difluoro-2-methyl-4-(p-tolyl)but-1-en-1-yl)benzo[d][1,3]dioxole (3ha)

Compound **3ha** was prepared according to general procedure D using *para*-toluenesulfonyl chloride (96 mg, 0.50 mmol), **1h** (254.5 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60 mg, 0.60 mmol), and 1,4-dioxane (1.5 mL). The crude mixture was analyzed by GC and GC-MS (Z/E≈18:1). Purification by silica gel column chromatography using Et_2O/pentane (3%, Rf ≈ 0.3) as eluent afforded **3ha** as major isomer in 56% yield, colorless oil, 88 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.76 (d, *J* = 8.0 Hz, 2H), 6.66 (d, *J* = 1.7 Hz, 2H), 6.62 (ddd, *J* = 8.0, 1.7, 0.7 Hz, 1H), 6.14 (s, 1H), 5.94 (s, 2H), 2.93 (td, *J* = 15.8, 0.9 Hz, 2H), 2.38 (s, 3H), 1.81 (d, *J* = 1.3 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ –93.54 (t, *J* = 16.0 Hz). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.3, 146.0, 139.5, 134.4 (t, *J* = 26.7 Hz), 131.8, 130.9, 129.5 (t, *J* = 3.7 Hz), 128.9, 125.0 (t, *J* = 6.2 Hz), 122.6 (t, *J* = 244.4 Hz), 122.5, 109.1, 108.0, 100.9, 49.9 (t, *J* = 27.8 Hz), 21.2, 19.2. HRMS (ESI, m/z): calcd. for $C_{19}H_{19}F_2O_2$ $[M+H]^+$ = 317.1353, found 317.1348. IR (film): 2920, 1617, 1503, 1440, 1323, 1257, 1040, 933, 818 cm^{-1}.

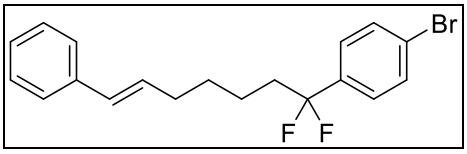


4-((4-bromophenyl)difluoromethyl)-2,3,4,5-tetrahydro-1,1'-biphenyl (3ib)

Compound **3ib** was prepared according to general procedure D using 4-bromobenzenesulfonyl chloride (128 mg, 0.500 mmol), **1i** (182.3 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500

mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60 mg, 0.60 mmol), and 1,4-dioxane (1.5 mL). The crude mixture was analyzed by GC and GC-MS (*d.r.* >95:5). Purification by silica gel column chromatography using pentane (Rf ≈ 0.3) as eluent afforded **3ib** as a white solid in 62% yield, 92 mg. The crystal of **3ib** was obtained by slow evaporation of hexane solution. Melting point: 96.2–99.4 °C.

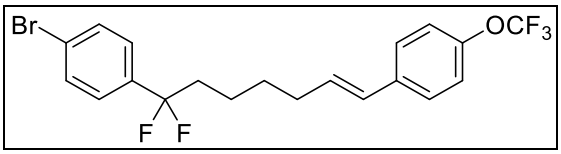
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.44–7.26 (m, 6H), 7.25–7.20 (m, 1H), 6.04 (dt, *J* = 5.1, 2.7 Hz, 1H), 2.60–2.39 (m, 2H), 2.38–2.11 (m, 3H), 2.12–2.00 (m, 1H), 1.67–1.47 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –104.22 (dd, *J* = 92.5, 13.2 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 136.6, 135.4 (t, *J* = 27.5 Hz), 131.5, 128.3, 127.2 (t, *J* = 6.8 Hz), 126.9, 125.0, 124.0 (t, *J* = 2.6 Hz), 123.6 (t, *J* = 245.44 Hz), 122.3, 42.1 (t, *J* = 26.6 Hz), 27.2, 25.6 (t, *J* = 4.6 Hz), 22.3 (t, *J* = 4.2 Hz). HRMS (ESI, m/z): calcd. for $C_{19}H_{17}BrF_2$ $[M]^+$ = 362.0482, found 362.0481. IR (film): 3051, 2931, 2843, 1594, 1494, 1454, 1396, 1323, 1268, 747 cm^{-1}.



(*E*)-1-bromo-4-(1,1-difluoro-7-phenylhept-6-en-1-yl)benzene (3jb)

Compound **3jb** was prepared according to general procedure D using 4-bromobenzenesulfonyl chloride (128 mg, 0.500 mmol), **1j** (184 mg, 0.875 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60 mg, 0.60 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using pentane (Rf ≈ 0.3) as eluent afforded **3jb** as a colorless oil in 42% yield, 76 mg.

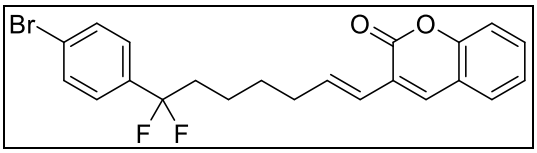
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.36–7.32 (m, 6H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.24–7.18 (m, 1H), 6.37 (dt, *J* = 15.9, 1.5 Hz, 1H), 6.17 (dt, *J* = 15.8, 6.9 Hz, 1H), 2.28–2.19 (m, 2H), 2.17–1.95 (m, 2H), 1.54–1.44 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –95.42 (t, *J* = 16.1 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.6, 136.4 (t, *J* = 27.6 Hz), 131.6, 130.3, 130.1, 128.5, 126.9, 126.7 (t, *J* = 6.5 Hz), 125.9, 123.9 (t, *J* = 2.5 Hz), 122.7 (t, *J* = 242.6 Hz), 38.7 (t, *J* = 27.6 Hz), 32.6, 28.8, 21.9 (t, *J* = 4.2 Hz). HRMS (ESI, m/z): calcd. for $C_{19}H_{19}BrF_2$ $[M]^+$ = 364.0638, found 364.0634. IR (film): 2932, 2359, 2341, 1597, 1491, 1326, 1290, 1171, 826, 744, 692 cm^{-1}.



(*E*)-1-bromo-4-(1,1-difluoro-6-(4-(trifluoromethoxy)phenyl)hex-5-en-1-yl)benzene (3kb)

Compound **3kb** was prepared according to general procedure D using 4-bromobenzenesulfonyl chloride (128 mg, 0.500 mmol), **1k** (257.5 mg, 0.875 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using pentane (Rf ≈ 0.3) as eluent afforded **3kb** as a colorless oil in 53% yield, 119 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.6 Hz, 2H), 7.35–7.30 (m, 4H), 7.14 (dd, *J* = 8.6, 1.1 Hz, 2H), 6.33 (d, *J* = 15.8 Hz, 1H), 6.14 (dt, *J* = 15.8, 6.9 Hz, 1H), 2.19 (td, *J* = 7.0, 1.5 Hz, 2H), 2.15–2.05 (m, 2H), 1.52–1.41 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –58.40, –96.06 (t, *J* = 16.2 Hz). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.0, 136.4, 136.4 (t, *J* = 27.3 Hz), 131.6, 131.2, 128.9, 127.1, 126.7 (t, *J* = 6.1 Hz), 123.9, 122.6 (t, *J* = 301.7 Hz), 121.1, 120.5 (q, *J* = 257.0 Hz), 38.8 (t, *J* = 27.4 Hz), 32.6, 28.7, 21.9 (t, *J* = 3.9 Hz). HRMS (ESI, m/z): calcd. for $C_{20}H_{18}BrF_5O$ $[M]^+$ = 448.0461, found 448.0450. IR (film): 2932, 1598, 1507, 1433, 1397, 1327, 1255, 1103, 1073, 1030, 966, 828 cm^{-1}.

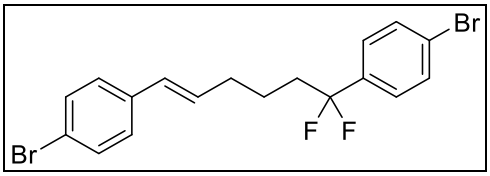


(*E*)-3-(6-(4-bromophenyl)-6,6-difluorohex-1-en-1-yl)-2H-chromen-2-one (3lb)

Compound **3lb** was prepared according to general procedure D using 4-bromobenzenesulfonyl chloride (128 mg, 0.500 mmol), **1l** (243.5 mg, 0.875 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60 mg, 0.60 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using pentane (Rf ≈ 0.3) as eluent afforded **3lb** as a colorless oil in 48% yield, 104 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 7.1 Hz, 2H), 7.36–7.29 (m, 3H), 7.28–7.23 (m, 1H), 6.65 (dt, *J* = 15.9, 7.0 Hz, 1H), 6.39 (d, *J* = 15.9 Hz, 1H), 2.23 (qd, *J* = 7.1, 1.6 Hz, 2H), 2.19–2.06 (m, 2H), 1.52–1.42 (m, 4H). ^{19}F NMR (471 MHz, $CDCl_3$) δ –96.03 (t, *J* = 16.2 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.5, 152.8, 136.4 (t, *J* = 27.3 Hz),136.2, 136.1, 131.6, 130.8, 127.4, 126.7 (t, *J* = 6.5 Hz), 125.1, 124.4, 124.0, 123.9 (t, *J* = 2.1 Hz), 122.6 (t, *J* = 242.7 Hz),119.6, 116.4, 38.7 (t, *J* = 27.4 Hz), 33.2, 28.5, 22.0 (t, *J* = 4.2 Hz). HRMS (ESI, m/z): calcd. for $C_{22}H_{20}BrF_4O_2$ $[M+H]^+$ = 433.0615, found 433.0611. IR (film): 3005, 1723, 1275, 1206, 1150, 1070, 913, 747 cm^{-1}

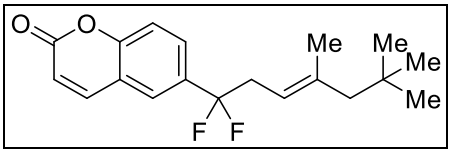
(*E*)-4,4'-(6,6-difluorohex-1-ene-1,6-diyl)bis(bromobenzene) (3mb)



Compound **3mb** was prepared according to general procedure D using 4-bromobenzenesulfonyl chloride (128 mg, 0.500 mmol), **1m** (134.8 mg, 0.875 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60 mg, 0.60 mmol), and 1,4-dioxane (1.5 mL). Purification by silica gel column chromatography using pentane (Rf ≈ 0.3) as eluent afforded **3mb** as a colorless solid in 81% yield, 87 mg. Melting point: 86.2–88.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.30 (dt, *J* = 15.7, 1.5 Hz, 1H), 6.12 (dt, *J* = 15.7, 6.8 Hz, 1H), 2.22 (qd, *J* = 7.3, 1.4 Hz, 2H), 2.18–2.06 (m, 2H), 1.66–1.54 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –95.64 (t, *J* = 16.2 Hz). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.30 (t, *J* = 26.9 Hz), 131.64, 131.64, 131.55, 130.23, 129.67, 127.49, 126.70 (t, *J* = 6.1 Hz), 124.00 (t, *J* = 2.2 Hz), 121.8 (t, *J* = 242.5 Hz), 120.69, 38.38 (t, *J* = 27.5 Hz), 32.30, 22.01 (t, *J* = 3.9 Hz). HRMS (ESI, m/z): calcd. for $C_{18}H_{16}Br_2F_2$ $[M]^+$ = 427.9587, found 427.9589. IR (film):2926, 1597, 1487, 1397, 1175, 1073, 969, 827 cm^{-1}.

(*E*)-6-(1,1-difluoro-4,6,6-trimethylhept-3-en-1-yl)-2H-chromen-2-one (3nr)



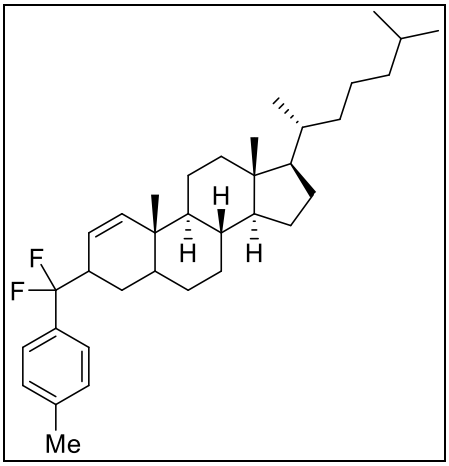
Compound **3nr** was prepared according to general procedure D using 2-oxo-2H-chromene-6-sulfonyl chloride (122 mg, 0.500 mmol), **1n** (198.0 mg, 1.125 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60 mg, 0.60 mmol), and 1,4-dioxane (1.5 mL). The crude mixture

was analyzed by GC and GC-MS (>3 isomers observed, major:minor ≈ 17:1). Purification by silica gel column chromatography using Et_2O/pentane (5%, Rf ≈ 0.3) afforded **3nr** (major isomer) as a colorless oil in 44% yield, 71 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 9.6 Hz, 1H), 7.64–7.58 (m, 2H), 7.36 (d, *J* = 8.5 Hz, 1H), 6.47 (d, *J* = 9.6 Hz, 1H), 5.02 (td, *J* = 7.4, 6.7, 3.3 Hz, 1H), 2.90 (td, *J* = 15.6, 7.4 Hz, 2H), 1.88 (s, 2H), 1.57 (s, *J* = 1.4 Hz, 3H), 0.82 (s, 9H). ^{19}F NMR (471 MHz, $CDCl_3$) δ –93.80 (t, *J* = 15.6 Hz). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.24, 154.58, 143.03, 139.69, 133.87 (t, *J* = 27.7 Hz), 128.72 (t, *J* = 5.8 Hz), 124.98 (t, *J* = 6.5 Hz), 121.92 (t, *J* = 243.7 Hz), 118.42, 117.60 (t, *J* = 5.2 Hz), 117.55, 117.05, 53.49, 38.32 (t, *J* = 28.1 Hz), 31.69, 29.95, 19.12. HRMS (ESI, m/z): calcd. for $C_{19}H_{23}F_2O_2$ $[M+H]^+$ = 321.1666, found 321.1658.

IR (film): 3005, 1737, 1275, 1205, 1150, 764, 750 cm^{-1}.

(8S,9S,10R,13R,14S,17R)-3-(difluoro(p-tolyl)methyl)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-4,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a]phenanthrene (3oa)



Compound **3oa** was prepared according to general procedure D using *p*-toluenesulfonyl chloride (95.6 mg, 0.500 mmol), **1o** (367 mg, 0.875 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), SIPr•Cl (21.3 mg, 0.0500 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60 mg, 0.60 mmol), and 1,4-dioxane (2.0 mL) reflux at 110 °C for 38 h. The crude mixture was analyzed by GC, GC-MS and ^{19}F NMR (d.r. ≈ 3.6:1). Purification by silica gel column chromatography using pentane (Rf ≈ 0.6) afforded **3or** as a white solid in 61% yield as a mixture of stereoisomers, 156 mg. Melting point: 136.2–138.0 °C. The crystal of S isomer was obtained by slow evaporation of hexane solution.

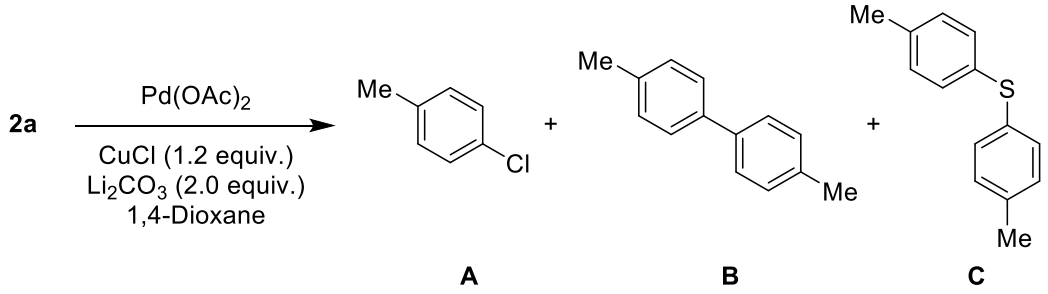
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 6.12 (dd, *J* = 10.4, 2.3 Hz, 1H), 5.40 (dd, *J* = 10.3, 3.6 Hz, 1H), 2.85–2.73 (m, 1H), 2.38 (s, 3H), 1.98 (dt, *J* = 12.6, 3.4 Hz, 1H), 1.80 (ddt, *J* = 13.2, 9.4, 4.9 Hz, 1H), 1.70–1.57 (m, 4H), 1.54–1.45 (m, 1H), 1.40–1.20 (m, 8H), 1.20–1.05 (m, 7H), 1.04–0.96 (m, 3H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 6.6, 2.0 Hz, 6H), 0.77 (s, 3H), 0.77–0.65 (m, 2H), 0.65 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –97.39 (dd, *J* = 240.1, 14.4 Hz), –101.20 (dd, *J* = 240.0, 17.8 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.82, 139.40, 133.64 (t, *J* = 27.1 Hz), 128.70, 125.56 (t, *J* = 6.9 Hz), 123.84 (t, *J* = 246.2 Hz), 120.42 (t, *J* = 5.5 Hz), 56.47, 56.21, 50.65, 42.67, 42.11 (t, *J* = 26.6 Hz), 40.25, 39.93, 39.51, 39.36, 36.97, 36.15, 35.80, 35.56, 31.79, 28.24, 28.02, 28.01, 25.11 (t, *J* = 3.0 Hz), 24.17, 23.84, 22.82, 22.55, 21.25, 21.02, 18.65, 14.44, 12.16. HRMS (ESI, m/z): calcd. for $C_{35}H_{52}F_2$ $[M]^+$ = 510.4037, found 510.4042. IR (film) 3029, 2931, 2867, 1466, 1381, 1209, 1154, 1042, 754 cm^{-1}.

Mechanistic Exploration Experiments

Control Experiments for Activation of *p*-Toluenesulfonyl Chloride (2a)

To an oven-dried 10 ml glass reaction tube, $Pd(OAc)_2$ (2.24–44.8 mg, 5–100 mol%), Li_2CO_3 (29.6 mg, 1.00 mmol), CuCl (24.0 mg, 0.240 mmol), *p*-toluenesulfonyl chloride (**2a**, 38.1 mg, 0.200 mmol) were added according to the variation of reaction parameters presented in Table S8. The reaction tube was then transferred in a glovebox, in which anhydrous 1,4-dioxane (0.50 mL) was added. The reaction tube was then sealed under a N_2 atmosphere and stirred in a preheated 120 °C oil bath for 21 h. Upon cooling, the mixture was filtered through a short silica gel column for GC and GC-MS analysis.

Table S8. Control Experiments of *p*-Toluenesulfonyl Chloride (2a) [a]



A **B** **C**

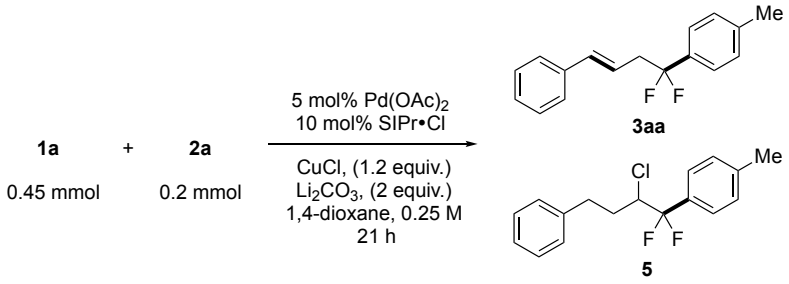
Entry	$Pd(OAc)_2$	CuCl (equiv.)	Li_2CO_3 (equiv.)	Conversion	**A**	**B**	**C**
1	5 mol%	1.2	2.0	100%	37%	41%	20%
2	5 mol%	1.2	0	23%	16%	7%	0
3	5 mol%	0	2.0	40%	13%	25%	0
4	50 mol%	0	2.0	100%	48%	42%	0
5	100 mol%	0	2.0	100%	40%	52%	0
6	5 mol%	0	0	68%	14%	0	0
7	0	1.2	2.0	<2%	0	0	1%

[a] Conditions: **2a**, 0.20 mmol; 0.50 mL 1,4-dioxane, N_2, reflux at 120 °C for 21 h. [b] Yields were evaluated by GC-MS and GC Analysis.

Control Experiments for 3aa Formation from 1a and 2a

To an oven-dried 10 ml glass reaction tube, $Pd(OAc)_2$ (0 or 5 mol%), Li_2CO_3 (0 or 2.0 equiv.), CuCl (0 or 1.2 equiv.), SIPr•Cl (0 or 10 mol%), *p*-toluenesulfonyl chloride (**2a**, 38.1 mg, 0.200 mmol) and difluoroalkene (**1a**, 75.6 mg, 0.450 mmol) were added according to the variation of reaction parameters presented in Table S9. The reaction tube was then transferred in a glovebox, in which anhydrous 1,4-dioxane (0.50 mL) was added. The reaction tube was then sealed under a N_2 atmosphere and stirred in a preheated 120 °C oil bath for 21 h. Upon cooling, the mixture was filtered through a short silica gel column for GC, GC-MS and crude ^{19}F NMR analysis.

Table S9. Control Experiments of 3aa Formation from 1a and 2a [a]

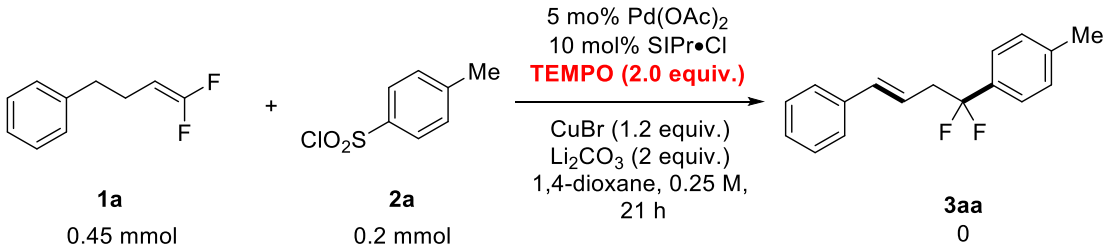


Entry	$Pd(OAc)_2$	SIPr-Cl	CuCl (equiv.)	Li_2CO_3 (equiv.)	Conv. [b]	**3aa** [c]	**5**
1	5 mol%	10 mol%	1.2	2.0	100%	69%	0
2	5 mol%	10 mol%	0	2.0	100%	16%	28%
3	0	10 mol%	1.2	2.0	<3%	0	0
4	5 mol%	10 mol%	1.2	0	100%	-	-
5	5 mol%	0	1.2	2.0	100%	63%	0
6	5 mol%	10 mol%	0	0	15%	0	0
7	0	0	1.2	2.0	<3%	0	0
8	5 mol%	0	0	0	12%	3%	0
9	0	0	1.2	0	<3%	0	0
10	0	10 mol%	1.2	0	<5%	0	0
11	5 mol%	0	0	2.0	40%	20%	13%
12[d]	5 mol%	0	0	2.0	100%	31%	32%

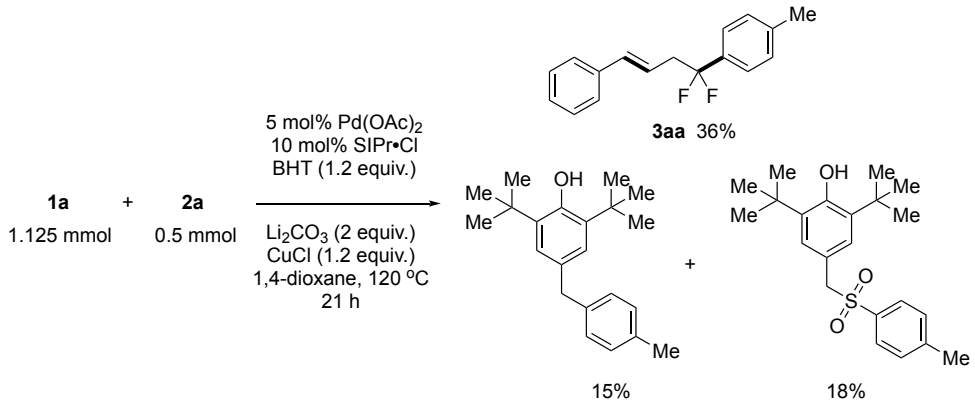
[a] Conditions: **1a**, 0.45 mmol; **2a**, 0.20 mmol; 0.50 mL 1,4-dioxane, N_2, reflux at 120 °C for 21 h. [b] Trace amount of 4-chlorotoluene was observed. [c] Yields was determined by GC analysis using dodecane as internal standard. [d] stoichiometric $Pd(OAc)_2$ (0.2 mmol, 1.0 equiv.) was used.

Radical Scavenger Experiments Study

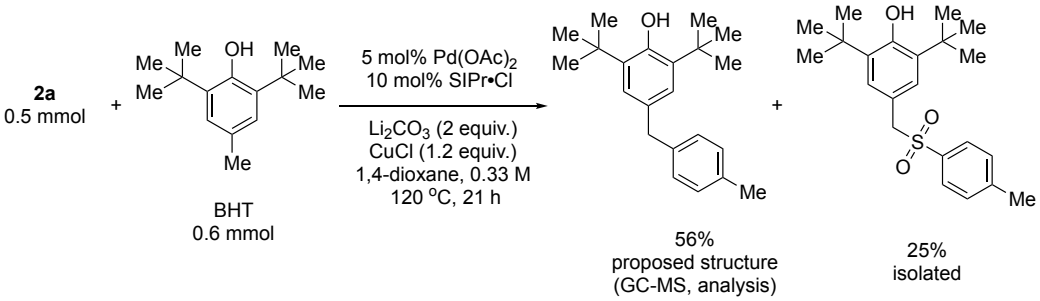
To an oven-dried 10 ml glass reaction tube, $Pd(OAc)_2$ (5 mol%), Li_2CO_3 (2.0 equiv.), CuCl (1.2 equiv.), *p*-toluenesulfonyl chloride (**2a**, 1.0 equiv.) and **1a** were added subsequently. The reaction tube was then charged with radical scavengers (TEMPO, BHT. See Scheme 1–3), followed by addition of anhydrous 1,4-dioxane. The reaction tube was then sealed under a N_2 atmosphere and stirred in a preheated 120 °C oil bath for 21 h. Upon cooling, the mixture was filtered through a short silica gel column for GC (20 μL dodecane was used as internal standard) and GC-MS analysis (See picture 1).



Scheme 1. Full Reaction Using TEMPO as Radical Scavenger

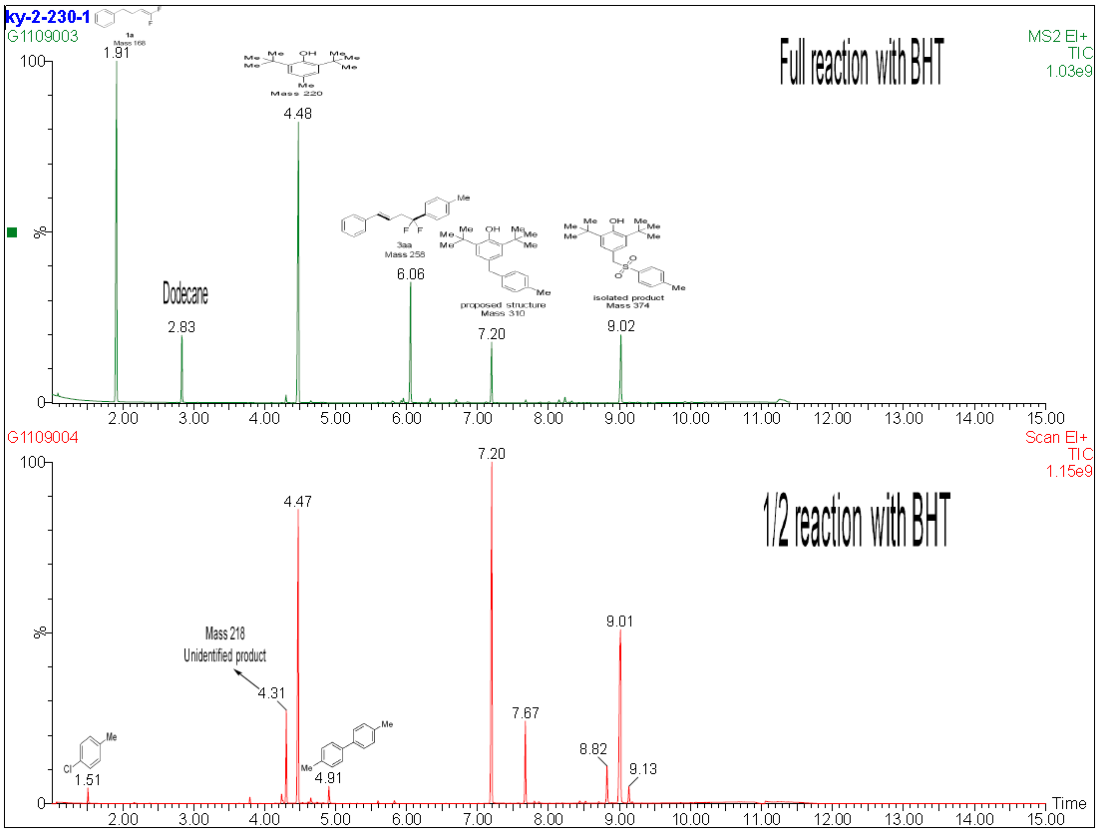


Scheme 2. Full Reaction Using BHT as Radical Scavenger

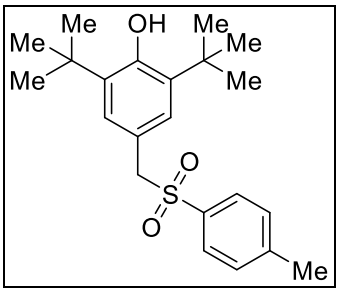


Scheme 3. Half (1/2) Reaction Using BHT as Radical Scavenger

Picture 1. Crude Reaction Mixture Analysis of BHT Radical Scavenger Experiments



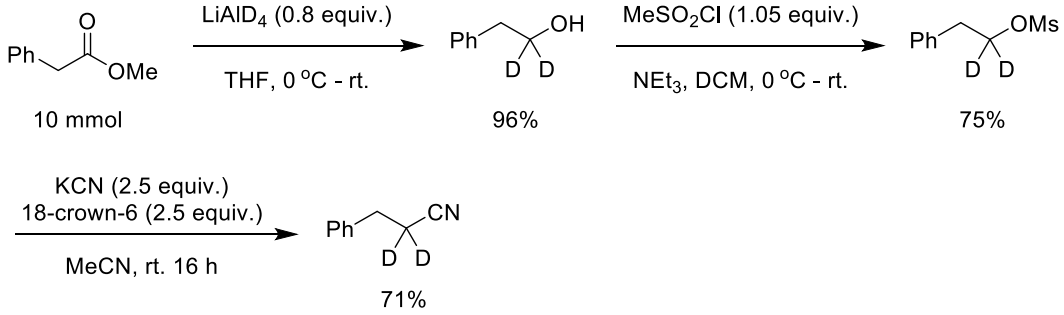
2,6-di-tert-butyl-4-(tosylmethyl)phenol



The compound was prepared according to the procedure mentioned above using *p*-toluenesulfonyl chloride (**2a**, 95.5 mg, 0.500 mmol**)** $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), Li_2CO_3 (74.0 mg, 1.00 mmol), CuCl (60.0 mg, 0.600 mmol), SIPr•Cl (21.3 mg, 0.05 mmol), BHT (132 mg, 0.600 mmol) and 1,4-dioxane (1.5 mL) reflux for 21 h. Upon cooling, the mixture was filtered for GC-MS analysis. Then the combined filtrate was concentrated under vacuo and purified by silica gel column chromatography using EtOAc/Hexane as eluent (15%, Rf ≈ 0.3) to afford the sulfonylation product [2,6-di-tert-butyl-4-(tosylmethyl)phenol] as colorless oil in 25% yield, 47 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.3 Hz, 2H), 6.73 (s, 2H), 5.23 (s, 1H), 4.19 (s, 2H), 2.40 (s, 3H), 1.32 (s, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.17, 144.29, 135.95, 134.92, 129.27, 128.89, 127.65, 118.94, 63.24, 34.10, 30.03, 21.52. HRMS (ESI, m/z): calcd. for $C_{22}H_{30}O_3SNa$ $[M+Na]^+$ = 397.1813, found 397.1375.

Deuterium Scrambling Experiments

3-Phenylpropanenitrile-2,2-d_2[8]



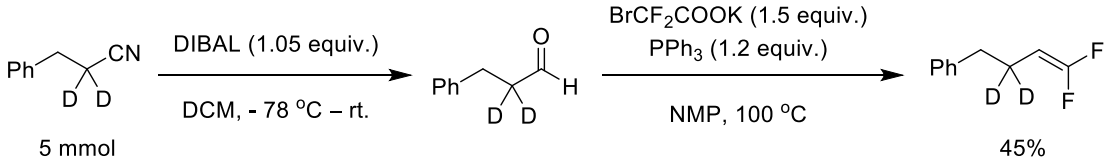
3-Phenylpropanenitrile-2,2-d_2 was prepared according to a previous literature report.[9] To a suspension of $LiAlD_4$ (672 mg, 16.0 mmol, 0.800 equiv.) in THF (32 mL, 0.50 M) at 0 °C was added methyl 2-phenylacetate (3.0 g, 0.020 mol, 1.0 equiv.). The ice bath was maintained for 2 h. Then, the suspension was stirred at 23 °C for 3 h. After cooling to 0 °C, a saturated solution of $NH_4Cl_{(aq.)}$ was added dropwise into the mixture. The resulting precipitate was removed by filtration and washed with Et_2O (50 mL). The filtrate was concentrated under reduced pressure by rotary evaporation to afford the crude alcohol without further purification.

To a solution of the crude alcohol in CH_2Cl_2 (40 mL, 0.5 M) cooled in a 0 °C ice bath, MsCl (24 mmol, 1.2 equiv.), and Et_3N (40 mmol, 2.0 equiv.) were sequentially added dropwise. After addition, the ice bath was removed. The resulting mixture was stirred for 16 h at 23 °C. The mixture was quenched by addition of a saturated solution of $NH_4Cl_{(aq.)}$ (30 mL), and the organic phase was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure by rotary evaporation without further purification.

To a solution of above crude 2-phenylethyl-1,1-d_2 methanesulfonate (1.0 equiv) in MeCN (60. 0 mL) were sequentially added 18-crown-6 (13.2 g, 50.0 mmol, 2.50 equiv.), and KCN (3.0 g, 50 mmol, 2.5 equiv.). The resulting suspension was stirred at 23 °C for 16 h. The mixture was quenched by addition of $NaOH_{(aq.)}$ (0.5 M) solution (50 mL), and then diluted with Et_2O (50 mL). The organic phase was extracted with Et_2O (3 × 30 mL)

and the combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure by rotary evaporation. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 10:1) afforded 3-phenylpropanenitrile-2,2-d_2 as a colorless oil (1.37 g, 51% yield for 3 steps, >97% D).

(4,4-difluorobut-3-en-1-yl-2,2-d2)benzene (1q)

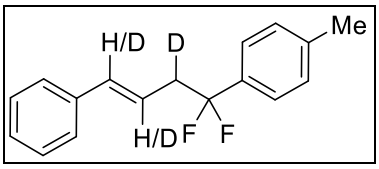


A solution of 3-phenylpropanenitrile-2,2-d_2 (5.0 mmol, 1.0 equiv.) in dry CH_2Cl_2 (20 mL, 0.25 M) was cooled to –70 °C, and DIBAL (1.0 M solution in toluene, 6.0 mmol, 1.2 equiv.) was added dropwise. The resulting mixture was stirred for 3 h, and then it was allowed to stir at 23 °C for 5 h. The mixture was quenched by addition of a saturated solution of $NH_4Cl_{(aq.)}$ (15 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL) and the combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure by rotary evaporation without further purification.

Compound **1q** was prepared according to general procedure A using crude 3-phenylpropanal-2,2-d_2 (0.68 g, 5.0 mmol). Purification by using pentane (Rf ≈ 0.7) as eluent afforded **1q** as a colorless oil in 45% yield after two steps (>97% D), 382 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (dd, J = 8.1, 6.9 Hz, 2H), 7.22 (d, J = 7.3 Hz, 1H), 7.20–7.15 (m, 2H), 4.15 (dt, J = 25.5, 1.2 Hz, 1H), 2.68 (s, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ –89.51 (dd, J = 47.3, 2.4 Hz), –91.60 (dd, J = 47.4, 25.3 Hz). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.38 (t, J = 286.1 Hz), 140.97, 128.45, 128.44, 126.15, 77.25(t, J = 20.4 Hz), 35.52 (t, J = 2.7 Hz), 23.53 (m). HRMS (ESI, m/z): calcd. for $C_{10}H_9D_2F_4$ $[M+H]^+$ = 171.0954, found 171.0946. IR (film): 2923, 1747, 1275, 1205, 1151, 913, 747 cm^{-1}.

D-labelled (*E*)-1-(1,1-difluoro-4-phenylbut-3-en-1-yl)-4-methylbenzene (3qa)



Compound **3qa** was prepared according to general procedure D using *p*-toluenesulfonyl chloride (**2a**, 38.1 mg, 0.200 mmol**), 1q** (68 mg, 0.40 mmol), $Pd(OAc)_2$ (2.2 mg, 0.010 mmol), Li_2CO_3 (29.6 mg, 0.40 mmol), CuCl (24 mg, 0.24 mmol), SIPr•Cl (8.5 mg, 0.020 mmol), and 1,4-dioxane (0.5 mL). Purification by silica gel column chromatography using pentane (Rf ≈ 0.3) as eluent afforded a colorless oil in 57% yield, 30 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 8.0 Hz, 2H), 7.34–7.28 (m, 4H), 7.25–7.21 (m, 3H), 6.59–6.40 (m, 0.82 H), 6.10 (dd, J = 15.9, 7.2 Hz, 0.46 H), 3.01 (t, J = 15.6 Hz, 1.07 H), 2.38 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ –94.67 (d, J = 15.5 Hz). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.70 (t, J = 2.1 Hz), 136.88, 135.04, 134.15 (t, J = 26.5 Hz), 129.03, 128.50, 127.56 (d, J = 1.9 Hz), 126.26, 124.97 (t, J = 6.1 Hz), 121.98 (t, J = 242.7 Hz), 120.43 (dt, J = 18.5, 4.9 Hz), 42.55 (m), 21.24. HRMS (ESI, m/z): calcd. for $C_{17}H_{15}D_2F_2$ $[M+H]^+$ = 261.1424, found 261.1494. IR (film): 2922, 1515, 1446, 1210, 1165, 1076, 817 cm^{-1}.

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