Stereospecific Isomerization of Allylic Halides via Ion Pairs with Induced NonCovalent Chirality

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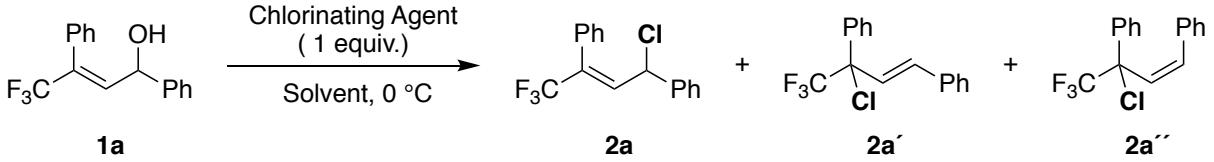
General information

All reagents were utilized without any further purification as obtained from commercial sources. Flash chromatography was performed with 60 Å (35-70 μm) silica gel (GC 60A 35-70 Micron, DAVISIL). Analytical TLC was performed on aluminum plates pre-coated (0-25 mm) with silica gel (Merck, Silica Gel 60 F254). Compounds were detected by exposure to UV light or by revealing the plates in a solution of 5% $KMnO_4$ in water. Melting points were recorded in metal block and are uncorrected. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded at 400 MHz, 100 MHz and 376 MHz respectively on a Bruker Advance spectrometer. Chemical shifts (δ) are shown in ppm, using as a reference the residual peaks of $CDCl_3$ (δ_H 7.26 and δ_C 77.00). Coupling constants (J) are given in Hz. NMR yields were calculated using 1 equiv. of 1,2,4,5-tetrachloronitrobenzene as internal standard. High resolution mass spectra (HRMS) were recorded on Bruker microTOF mass spectrometer using APCI ionization. GCMS were recorded on a Shimadzu GC-2010 Gas Chromatograph with a GCMS-QP2020 Mass Spectrometer. All compounds presented in this project were extremely unstable in all MS instruments. Herein are reported the MS when they were possible to be detected. Enantiomeric excesses were determined using HPLC analysis on an Agilent 1200-series instrument with an autosampler and UV detection and using chiralcel OD-H and OJ-H or chiralpak AD-H columns. Optical rotations were recorded on a RUDOLPH AUTOPOL IV with an automatic polarimeter.

HRMS or MS of compounds **2a-2n**, **3a-3c**, **4a-4c**, **5k**, **6b** and **6c** could not be obtained due to decomposition.
HRMS of compounds **5b-5j**, **5l-5n**, **6a** and **7a-7c** could not be obtained due to decomposition. Observed MS by GCMS of those compounds are here reported.

Optimization studies

Table S1. Regioselective synthesis of γ-trifluoromethylated allylic chlorides.[a]

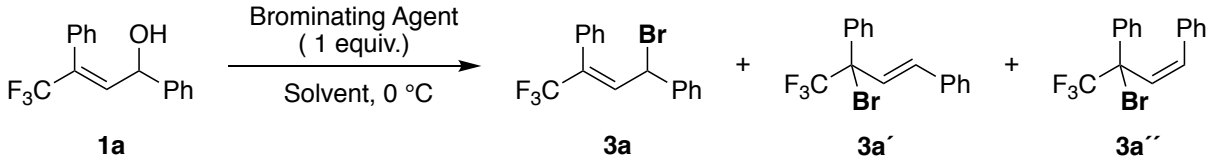


1a **2a** **2a´** **2a´´**

Entry	*Halogenating Agent*	*Solvent*	*Yield (%)*	***2a/2a´/2a´´(%)***
1	$SOCl_2$	THF	78	82/12/6
2	$SOCl_2$	Et_2O	83	76/16/8
3	$SOCl_2$	DCM	83	88/12/-
4	$SOCl_2$	Toluene	-	-
5	$SOCl_2$[b]	DCM	47	80/14/6
6	$SOCl_2$[c]	$CHCl_3$	76	87/13/-
7	PCl_3	DCM	80	96/4/-
8	PCl_5	DCM	50	98/2/-
9	$POCl_3$	DCM	52	12/-/-[d]
10	NCS/PPh_3[e]	DCM	40	94/6/-
11	NCS/PPh_3[e]	THF	67	>99/-/-

[a]Unless otherwise noted, the reaction was performed using 0.1 mmol **1a** and 0.1 mmol of the chlorinated reagent in a 0.1 M solution at 0 °C overnight. [b] with 0.1 mmol of pyridine. [c] with 0.1 mmol of NEt_3.[d] Other unknown product was formed. [e] 0.15 mmol of NCS and PPh_3.

Table S2. Regioselective synthesis of γ-trifluoromethylated allylic bromides.[a]

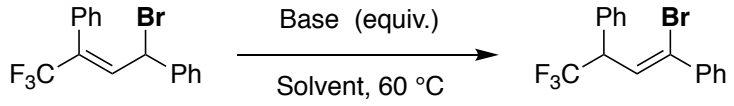


1a **3a** **3a´** **3a´´**

Entry	*Halogenating Agent*	*Solvent*	*Yield (%)*	***3a/3a´/3a´´(%)***
1	PBr_3	THF	93	94/-/6
2	CBr_4/PPh_3	DCM	56	93/-/7
3	NBS/PPh_3	DCM	40	>99/-/-
4	NBS/PPh_3	THF	62	>99/-/-

[a]Unless otherwise noted, the reaction was performed using 0.1 mmol **1a** and 0.1 mmol of the brominating agent in a 0.1 M solution at 0 °C overnight.

Table S3. Base-catalyzed isomerization of γ-trifluoromethylated allylic bromides.[a]

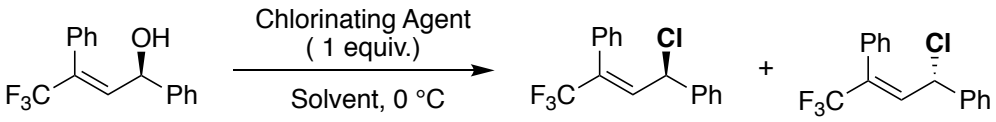


3a **6a**

Entry	*Base (equiv.)*	*Solvent*	*Conv. (%)*[b]	*Yield (%)*[c]
1	NEt_3 (1.0)	Toluene	<5	-[d]
2	Cs_2CO_3 (1.0)	Toluene	<5	-[d]
3	DBU (1.0)	Toluene	75	30[e]
4	TBD (1.0)	Toluene	83	55[e]
5	TBD (0.1)	Toluene	34	nd
6[f]	TBD (0.1)	Toluene	64	nd
7[f]	TBD (0.3)	Toluene	>99	60[e]

[a] The reaction was performed using 0.1 mmol **3a** in a 0.1 M solution overnight. [b] Obtained using ^{19}F NMR spectroscopy. [c] 1,2,4,5-tetrachloronitrobenzene was used as internal standard (IS) [d] >95% of **3a** recovered [e] Decomposition observed. [f] 100 °C instead of 60 °C.

Table S4. Stereospecific synthesis of γ-trifluoromethylated allylic chloride 1a.[a]

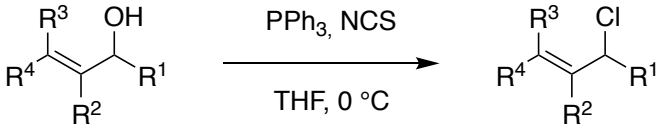


(*R*)–**1a** 98% *ee* (*R*)–**2a** (*S*)–**2a**

Entry	*Chlorinating Agent*	*Solvent*	*(R)–***2a** *(%)*[b]	*(S)–***2a** *(%)*[b]
1	NCS / PPh_3 (1.5 equiv.)	THF	25	75
2	NCS / PPh_3 (1.5 equiv.)	THF, (–20 °C)	25	75
3	**NCS / PPh_3 (1.0 equiv.)**	**THF**	**23**	**77**
4	NCS / PPh_3 (1.0 equiv.)	DCM	37	64
5	NCS / PPh_3 (1.0 equiv.)	Toluene	22	78[c]
6	NCS / PPh_3 (1.0 equiv.)	DMF	*rac.*	
7	NCP[d] / PPh_3 (1.0 equiv.)	THF	29	71
8	NCS / P(*p*-OMePh)$_3$ (1.0 equiv.)	THF	24	76
9	$(COCl)_2$, $POPh_3$ (15 mol%) (1 equiv.)	$CDCl_3$	27	73
10	NCS / PPh_3 / NaCl (1 equiv.)	THF	26	74
11	NCS / PPh_3 / Imidazole (1 equiv.)	THF	26	74

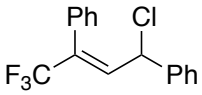
[a] The reaction was performed using 0.1 mmol **(*R*)-1a** in a 0.1 M solution overnight. [b] Obtained using HPLC analysis and chiral columns. [c] 18% Yield.

General procedure for the synthesis of allylic chlorides 2a-2o.[1]



PPh_3 and NCS (1.5 equiv.) were added to a solution of the corresponding allylic alcohol (1 equiv.) in dry THF (0.1 M) at 0 °C. The mixture was warmed to room temperature overnight and petroleum ether (5 mL per mmol of substrate) was added and stirred for 15 min. The resulting suspension was filtered and evaporated under reduced pressure. The resulting residue was purified using silica chromatography employing petroleum ether as eluent and yielding the desired allylic chlorides as pure products.

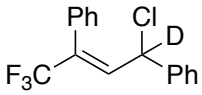
(*E*)-(1-chloro-4,4,4-trifluorobut-2-ene-1,3-diyl)dibenzene (2a)



The title compound was synthesized according to the above procedure using (*E*)-4,4,4-trifluoro-1,3-diphenylbut-2-en-1-ol (1 mmol, 278 mg) as substrate. The final compound was isolated by flash chromatography using petroleum ether as eluent and yielding a colorless oil (199 mg, 67% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.46 (m, 3H), 7.40–7.33 (m, 3H), 7.31–7.29 (m, 4H), 6.77 (dq, *J* = 10.6, 1.5 Hz, 1H), 5.30 (d, *J* = 10.6 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 138.8, 134.4 (q, *J* = 6 Hz), 131.8 (q, *J* = 30 Hz), 130.7, 129.6, 129.2, 129.1, 129.1, 129.0, 127.2, 123.0 (q, *J* = 274 Hz), 57.5. **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 66.51 (s). **HPLC:** CHIRALCEL OJ-H, flow rate 1.0 mL/min, isohexane/isopropanol (90/10) τ_{minor} (*R*) = 4.27 min. τ_{major} (*S*) = 7.21 min. **$[\alpha]_D^{20}$** +10 (c 0.1, $CHCl_3$, *e.r.* 77:23).

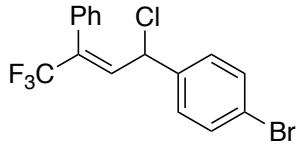
(*E*)-(1-chloro-4,4,4-trifluorobut-2-ene-1,3-diyl-1-*d*)dibenzene (2a-2d)



The title compound was synthesized according to the above procedure using (*E*)-4,4,4-trifluoro-1,3-diphenylbut-2-en-1-d-1-ol (1 mmol, 279 mg) as substrate. The final compound was isolated by flash chromatography using petroleum ether as eluent and yielding a colorless oil (188 mg, 63% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.45 (m, 3H), 7.40–7.29 (m, 7H), 6.76 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 138.8, 134.3 (q, *J* = 6 Hz), 131.8 (q, *J* = 31 Hz), 130.7, 129.6, 129.2, 129.1, 129.0, 127.2, 126.3, 123.0 (q, *J* = 274 Hz), 57.2 (t, *J* = 25 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 66.51 (s).

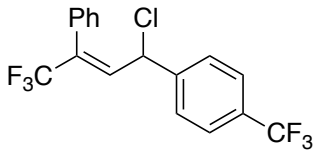
(*E*)-1-Bromo-4-(1-chloro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)benzene (2b)



The title compound was synthesized according to the above procedure using (*E*)-1-(4-bromophenyl)-4,4,4-trifluoro-3-phenylbut-2-en-1-ol (1 mmol, 357 mg) as substrate. The final compound was isolated by flash chromatography using petroleum ether as eluent and yielding a colorless oil (301 mg, 80% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.49 (m, 2H), 7.48–7.45 (m, 3H), 7.30–7.26 (m, 2H), 7.20–7.18 (m, 2H), 6.70 (dq, *J* = 10.6, 1.6 Hz, 1H), 5.25 (d, *J* = 10.6 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 137.9, 133.8 (q, *J* = 6 Hz), 132.4, 132.3 (q, *J* = 30 Hz), 130.5, 129.7, 129.4, 129.0, 128.9, 123.2, 122.9 (q, *J* = 274 Hz), 56.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 66.60 (s). **HPLC:** CHIRALCEL OD-H, flow rate 1.0 mL/min, isohexane/isopropanol (100/0) τ_{minor} (*R*) = 13.05 min. τ_{major} (*S*) = 13.50 min. **$[\alpha]_D^{20}$** +24 (c 0.1, $CHCl_3$, *e.r.* 79:21).

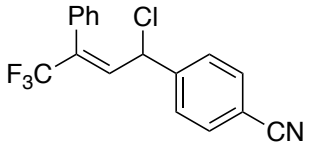
(*E*)-1-(1-chloro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)-4-(trifluoromethyl)benzene (2c)



The title compound was synthesized according to the above procedure using (*E*)-4,4,4-trifluoro-3-phenyl-1-(4-(trifluoromethyl)phenyl)but-2-en-1-ol (1 mmol, 356 mg) as substrate. The final compound was isolated by flash chromatography using petroleum ether as eluent and yielding a colorless oil (296 mg, 81% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.2 Hz, 2H), 7.49–7.47 (m, 3H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.30–7.26 (m, 2H), 6.71 (dq, *J* = 10.5, 1.4 Hz, 1H), 5.33 (d, *J* = 10.5 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 142.7, 133.6 (q, *J* = 6 Hz), 132.9 (q, *J* = 31 Hz), 131.2 (q, *J* = 33 Hz), 130.4, 129.8, 129.4, 129.1, 127.6, 126.2 (q, *J* = 4 Hz), 123.8 (q, *J* = 272 Hz), 122.8 (q, *J* = 274 Hz), 56.5. **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 62.81 (s, 3F), – 66.68 (s, 3F). **HPLC:** CHIRALCEL OD-H, flow rate 0.5 mL/min, isohexane/isopropanol (100/0) τ_{minor} (*R*) = 10.17 min. τ_{major} (*S*) = 10.60 min. **$[\alpha]_D^{20}$** +22 (c 0.1, $CHCl_3$, *e.r.* 94:6).

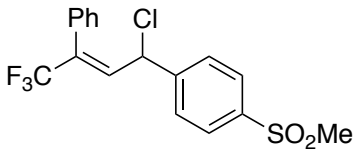
(*E*)-4-(1-chloro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)benzonitrile (2d)



The title compound was synthesized according to the above procedure using ((*E*)-4-(4,4,4-trifluoro-1-hydroxy-3-phenylbut-2-en-1-yl)benzonitrile (1 mmol, 303 mg) as substrate. The final compound was isolated by flash chromatography using petroleum ether as eluent and yielding a colorless oil (229 mg, 71% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.59 (m, 2H), 7.50–7.46 (m, 3H), 7.45–7.40 (m, 2H), 7.30-7.26 (m, 2H), 6.66 (dd, *J* = 10.5, 1.6 Hz, 1H), 5.31 (d, *J* = 10.5 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.7, 133.4 (q, *J* = 31 Hz), 133.1 (q, *J* = 6 Hz), 133.0, 130.3, 129.9, 129.3, 129.2, 128.0, 122.8 (q, *J* = 274 Hz), 125.6, 113.0, 56.3. **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 66.72 (s). **HPLC:** CHIRALCEL AD-H, flow rate 1.0 mL/min, isohexane/isopropanol (95/5) τ_{major} (*S*) = 5.18 min. τ_{minor} (*R*) = 5.44 min. **$[\alpha]_D^{20}$** +38 (c 0.1, $CHCl_3$, *e.r.* 82:18).

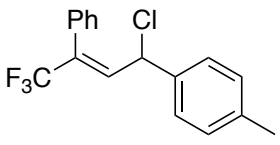
(*E*)-1-(1-chloro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)-4-(methylsulfonyl)benzene (2e)



The title compound was synthesized according to the above procedure using (*E*)-4,4,4-trifluoro-1-(4-(methylsulfonyl)phenyl)-3-phenylbut-2-en-1-ol (1 mmol, 356 mg) as substrate. The final compound was isolated by flash chromatography using petroleum ether as eluent and yielding a colorless oil (296 mg, 79% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–7.87 (m, 2H), 7.61–7.43 (m, 5H), 7.34–7.27 (m, 2H), 6.69 (dd, *J* = 10.5, 1.6 Hz, 1H), 5.35 (d, *J* = 10.5 Hz, 1H), 3.06 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 144.7, 141.2, 133.5, 133.2 (q, *J* = 6 Hz), 130.3, 129.9, 129.4, 129.2, 128.4, 128.3, 122.8 (q, *J* = 271 Hz), 56.2, 44.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 66.71 (s). **HPLC:** CHIRALCEL OD-H, flow rate 1.0 mL/min, isohexane/isopropanol (90/10) τ_{major} (*S*) = 13.48 min. τ_{minor} (*R*) = 14.24 min. **$[\alpha]_D^{20}$** +12 (c 0.1, $CHCl_3$, *e.r.* 87:13).

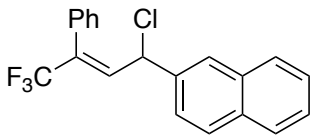
(*E*)-1-(1-chloro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)-4-methylbenzene (2f)



The title compound was synthesized according to the above procedure using (*E*)-4,4,4-trifluoro-3-phenyl-1-(p-tolyl)but-2-en-1-ol (1 mmol, 292 mg) as substrate. The final compound was isolated by flash chromatography using petroleum ether as eluent and yielding a colorless oil (215 mg, 69% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.45 (m, 3H), 7.30–7.28 (m, 2H), 7.22–7.16 (m, 4H), 6.77 (dq, *J* = 10.6, 1.6 Hz, 1H), 5.25 (d, *J* = 10.6 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 139.1, 136.0, 134.5 (q, *J* = 6 Hz), 130.7, 129.8, 129.6, 129.5, 128.9, 127.1, 126.3, 123.1 (q, *J* = 274 Hz), 57.5, 21.3. **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 66.47 (s).

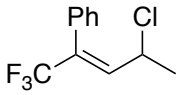
(*E*)-2-(1-chloro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)naphthalene (2g)



The title compound was synthesized according to the above procedure using (*E*)-4,4,4-trifluoro-1-(naphthalen-2-yl)-3-phenylbut-2-en-1-ol (1 mmol, 328 mg) as substrate. The final compound was isolated by flash chromatography using petroleum ether as eluent and yielding a white solid (246 mg, 71% isolated yield) (m.p. = 87–88°C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.81 (m, 3H), 7.71 (s, 1H), 7.53–7.47 (m, 6H), 7.35–7.32 (m, 2H), 6.90 (dq, *J* = 10.6, 1.3 Hz, 1H), 5.48 (d, *J* = 10.6 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 136.1, 134.2 (q, *J* = 6 Hz), 133.5, 133.2, 132.0 (q, *J* = 31 Hz), 130.7, 129.6, 129.3, 129.0, 128.3, 127.9, 127.1, 127.0, 126.9, 126.3, 124.6, 123.0 (q, *J* = 274 Hz), 57.8. **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 66.45 (s). **HPLC:** CHIRALCEL OD-H, flow rate 1.0 mL/min, isohexane/isopropanol (100/0) τ_{minor} (*R*) = 15.23 min. τ_{major} (*S*) = 16.76 min.

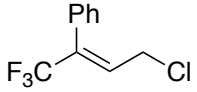
(*E*)-(4-chloro-1,1,1-trifluoropent-2-en-2-yl)benzene (2h)



The title compound was synthesized according to the above procedure using (*E*)-5,5,5-trifluoro-4-phenylpent-3-en-2-ol (1 mmol, 216 mg) as substrate. The final compound was isolated by flash chromatography using petroleum ether as eluent and yielding a colorless oil (169 mg, 69% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.43 (m, 3H), 7.30–7.28 (m, 2H), 6.46 (dd, *J* = 10.4, 1.4 Hz, 1H), 4.39 (dp, *J* = 13.1, 6.6 Hz, 1H), 1.57 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 136.4 (q, *J* = 6 Hz), 131.8 (q, *J* = 30 Hz), 130.9, 129.4, 129.3, 128.9, 123.1 (q, *J* = 274 Hz), 52.1, 25.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 66.56 (s).

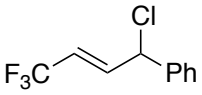
(*E*)-(4-chloro-1,1,1-trifluorobut-2-en-2-yl)benzene (2i)



The title compound was synthesized according to the above procedure using (*E*)-4,4,4-trifluoro-3-phenylbut-2-en-1-ol (1 mmol, 202 mg) as substrate. The final compound was isolated by flash chromatography using petroleum ether as eluent and yielding a colorless oil (177 mg, 80% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.42 (m, 3H), 7.30–7.28 (m, 2H), 6.58-6.54 (m, 1H), 3.95 (dp, *J* = 7.8, 1.5 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 134.7 (q, *J* = 30 Hz), 130.9 (q, *J* = 6 Hz), 130.6, 129.4, 128.9, 125.7, 122.9 (q, *J* = 274 Hz), 39.3. **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 64.52 (s).

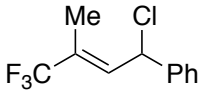
(*E*)-(1-chloro-4,4,4-trifluorobut-2-en-1-yl)benzene (2j)



The title compound was synthesized according to the above procedure using (E)-4,4,4-trifluoro-1-phenylbut-2-en-1-ol (1 mmol, 202 mg) as substrate. The final compound was isolated by flash chromatography using petroleum ether as eluent and yielding a colorless oil (133 mg, 60% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.34 (m, 5H), 6.70–6.64 (m, 1H), 6.00–5.91 (m, 1H), 5.53–5.51 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 138.8 (q, *J* = 6 Hz), 138.2, 129.3, 129.2, 127.6, 122.8 (q, *J* = 270 Hz), 127.1 (q, *J* = 34 Hz), 60.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 64.15 (d, *J* = 6 Hz).

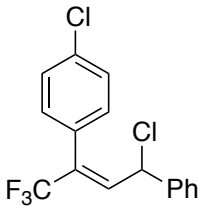
(*E*)-(1-chloro-4,4,4-trifluoro-3-methylbut-2-en-1-yl)benzene (2k)



The title compound was synthesized according to the above procedure using (*E*)-4,4,4-trifluoro-3-methyl-1-phenylbut-2-en-1-ol (1 mmol, 216 mg) as substrate. The final compound was isolated by flash chromatography using petroleum ether as eluent and yielding a colorless oil (167 mg, 71% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.34 (m, 5H), 6.52 (dp, *J* = 9.9, 1.6 Hz, 1H), 5.68 (dd, *J* = 10.0, 1.2 Hz, 1H), 1.96 (d, *J* = 1.5 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 139.2, 132.4 (q, *J* = 6 Hz), 129.2, 129.1, 127.2, 127.1 (q, *J* = 30 Hz), 123.8 (q, *J* = 273 Hz), 56.6, 11.1 (q, *J* = 1 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 70.01 (s). **HPLC:** CHIRALCEL AD-H, flow rate 1.0 mL/min, isohexane/isopropanol (100/0) τ_{minor} (*R*) = 4.71 min. τ_{major} (*S*) = 4.86 min. **$[\alpha]_D^{20}$** +4 (c 0.1, $CHCl_3$, *e.r.* 68:32).

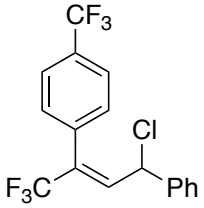
(*E*)-1-chloro-4-(4-chloro-1,1,1-trifluoro-4-phenylbut-2-en-2-yl)benzene (2l)



The title compound was synthesized according to the above procedure using (*E*)-3-(4-chlorophenyl)-4,4,4-trifluoro-1-phenylbut-2-en-1-ol (1 mmol, 313 mg) as substrate. The final compound was isolated by flash chromatography using petroleum ether as eluent and yielding a colorless oil (258 mg, 78% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.44 (m, 2H), 7.42–7.30 (m, 5H), 7.26–7.24 (m, 2H), 6.79 (dd, *J* = 10.7, 1.6 Hz, 1H), 5.25 (d, *J* = 10.7 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 138. 5, 135.9, 134.9 (q, *J* = 6 Hz), 131.0, 129.4, 129.3, 129.2, 129.0, 127.2, 122.8 (q, *J* = 274 Hz), 57.2. **^{19}F NMR (376 MHz, $CDCl_3$)** δ − 66.53 (s).

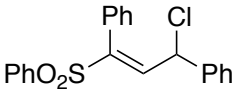
(*E*)-1-(4-Chloro-1,1,1-trifluoro-4-phenylbut-2-en-2-yl)-4-(trifluoromethyl)benzene (2m)



The title compound was synthesized according to the above procedure using (*E*)-4,4,4-trifluoro-1-phenyl-3-(4-(trifluoromethyl)phenyl)but-2-en-1-ol (1 mmol, 346 mg) as substrate. The final compound was isolated by flash chromatography using petroleum ether as eluent and yielding a colorless oil (336 mg, 92% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.42–7.30 (m, 5H), 6.84 (dd, *J* = 10.7, 1.6 Hz, 1H), 5.20 (d, *J* = 10.7 Hz, 1H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 138. 3, 135.3 (q, *J* = 6 Hz), 134.3, 131.9 (q, *J* = 33 Hz), 130.4 (q, *J* = 31 Hz), 130.4, 130.1, 129.3, 127.2, 126.0 (q, *J* = 4 Hz), 123.9 (q, *J* = 272 Hz), 122.7 (q, *J* = 274 Hz), 57.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ − 66.34 (s, 3F), − 62.81 (s, 3F).

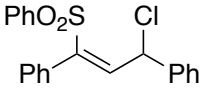
(*E*)-(3-chloro-1-(phenylsulfonyl)prop-1-ene-1,3-diyl)dibenzene ((*E*)-2n)



The title compound was synthesized according to the above procedure using (*E*)-1,3-diphenyl-3-(phenylsulfonyl)prop-2-en-1-ol (1 mmol, 350 mg) as substrate. The final compound was isolated by flash chromatography using petroleum ether as eluent and yielding a colorless oil (185 mg, 50% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.52 (m, 3H), 7.46 (d, *J* = 10.7 Hz, 1H), 7.43–7.29 (m, 10H), 7.06–7.01 (m, 2H), 5.17 (d, *J* = 10.7 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.2, 138.3, 138.1, 138.0, 133.7, 130.4, 129.9, 129.3, 129.2, 129.2, 129.0, 128.8, 128.7, 127.3, 57.6.

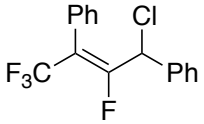
(*Z*)-(3-chloro-1-(phenylsulfonyl)prop-1-ene-1,3-diyl)dibenzene ((*Z*)-2n)



The title compound was synthesized according to the above procedure using (*Z*)-1,3-diphenyl-3-(phenylsulfonyl)prop-2-en-1-ol (1 mmol, 350 mg) as substrate. The final compound was isolated by flash chromatography using petroleum ether as eluent and yielding a colorless oil (233 mg, 63% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.58 (m, 3H), 7.56–7.51 (m, 1H), 7.44–7.36 (m, 5H), 7.34–7.27 (m, 3H), 7.25–7.21 (m, 2H), 7.18–7.15 (m, 2H), 6.45 (d, *J* = 10.8 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 141.9, 140.7, 139.5, 139.0, 134.2, 133.8, 130.2, 129.3, 129.2, 129.04, 129.03, 128.2, 128.1, 127.6, 55.3.

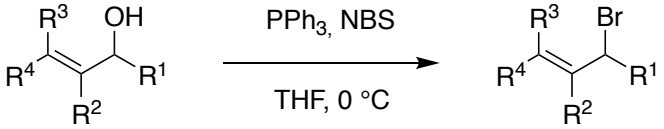
(*Z*)-(1-chloro-2,4,4,4-tetrafluorobut-2-ene-1,3-diyl)dibenzene (2o)



The title compound was synthesized according to the above procedure using (*Z*)-2,4,4,4-tetrafluoro-1,3-diphenylbut-2-en-1-ol (1 mmol, 296 mg) as substrate. The final compound was isolated by flash chromatography using petroleum ether as eluent and yielding a colorless oil (214 mg, 68% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.48 (m, 3H), 7.40–7.35 (m, 7H), 5.37 (d, *J* = 27.2 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.2 (dq, *J* = 281, 3 Hz), 134.9, 130.1 (d, *J* = 3 Hz), 129.8, 129.3, 129.1, 128.8, 127.65, 127.64, 122.1 (d, *J* = 274 Hz), 113.5 (dq, *J* = 33, 10 Hz), 56.0 (d, *J* = 24 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ −59.50 (d, *J* = 24 Hz, 3F), −109.72 (dq, *J* = 26, 24 Hz, 1F).

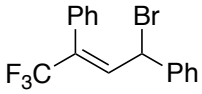
<u>General procedure for the synthesis of allylic bromides 3a-3c</u>



PPh_3 and NBS (1.5 equiv.) were added to a solution of the corresponding allylic alcohol (1 equiv.) in dry THF (0.1 M) at 0 °C. The mixture was warmed to room temperature overnight and petroleum ether (5 mL per mmol of substrate) was added and stirred for 15 min. The resulting suspension was filtered and evaporated under reduced pressure. The final product was

purified using silica chromatography doped with NEt_3 (1%) employing petroleum ether as eluent yielding the desired allylic bromides.

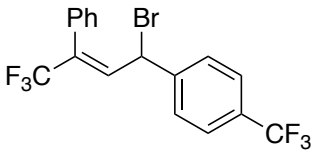
(*E*)-(1-bromo-4,4,4-trifluorobut-2-ene-1,3-diyl)dibenzene (3a)



The title compound was synthesized according to the above procedure using (*E*)-4,4,4-trifluoro-1,3-diphenylbut-2-en-1-ol (1 mmol, 278 mg) as substrate. The final compound was purified using silica chromatography doped with NEt_3 (1%) employing petroleum ether as eluent yielding a yellow oil (211 mg, 62% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.46 (m, 3H), 7.37–7.28 (m, 7H), 6.98 (dq, *J* = 11.0, 1.6 Hz, 1H), 5.41 (d, *J* = 11 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 139.0, 134.3 (q, *J* = 6 Hz), 130.8 (q, *J* = 30 Hz), 129.5, 129.3, 129.2, 129.1, 129.0, 127.6, 126.9, 123.0 (q, *J* = 274 Hz), 47.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 66.41 (s).

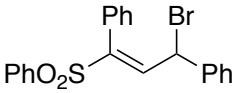
(*E*)-1-(1-bromo-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)-4-(trifluoromethyl)benzene (3b)



The title compound was synthesized according to the above procedure using (*E*)-4,4,4-trifluoro-3-phenyl-1-(4-(trifluoromethyl)phenyl)but-2-en-1-ol (1 mmol, 346 mg) as substrate. The final compound was purified using silica chromatography doped with NEt_3 (1%) employing petroleum ether as eluent yielding a yellow oil (226 mg, 56% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–7.59 (m, 2H), 7.53–7.44 (m, 5H), 7.32–7.27 (m, 2H), 6.93 (dq, *J* = 11.1, 1.6 Hz, 1H), 5.42 (d, *J* = 11.1 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 142.9, 133.5 (q, *J* = 6 Hz), 132.0 (q, *J* = 31 Hz), 131.2 (q, *J* = 33 Hz), 130.4, 129.8, 129.2, 129.1, 128.0, 126.3 (q, *J* = 4 Hz), 123.8 (q, *J* = 272 Hz), 122.9 (q, *J* = 274 Hz), 46.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 66.57 (s, 3F), – 62.84 (s, 3F).

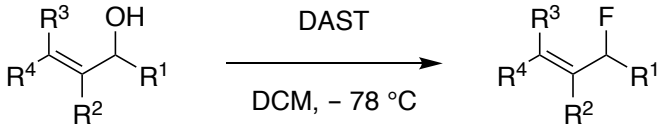
(*E*)-(3-bromo-1-(phenylsulfonyl)prop-1-ene-1,3-diyl)dibenzene (3c)



The title compound was synthesized according to the above procedure using (*E*)-1,3-diphenyl-3-(phenylsulfonyl)prop-2-en-1-ol (1 mmol, 350 mg) as substrate. The final compound was purified using silica chromatography doped with NEt_3 (1%) employing petroleum ether as eluent yielding a yellow oil (155 mg, 35% isolated yield).

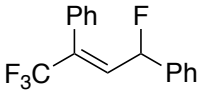
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 11.2 Hz, 1H), 7.60–7.50 (m, 3H), 7.45–7.29 (m, 10H), 7.11–7.01 (m, 2H), 5.28 (d, *J* = 11.3 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 142.2, 138.3, 138.2, 138.2, 133.7, 130.2, 129.8, 129.3, 129.3, 129.2, 129.0, 128.8, 128.7, 127.7, 47.6.

General procedure for the synthesis of allylic fluorides 4a-4c.[2]



To a solution of the corresponding allylic alcohol (1 equiv.) in dry DCM (0.1 M) at -78 °C, DAST (1 equiv.) was added carefully dropwise. The reaction was warmed to room temperature overnight and quenched with a saturated solution of $NaHCO_3$. The mixture was extracted with DCM (3 x 5 mL per mmol of substrate), dried with $MgSO_4$ and the solvent was reduced under vacuum. The final product was purified using silica chromatography employing petroleum ether as eluent.

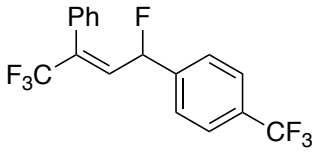
(*E*)-(1-fluoro-4,4,4-trifluorobut-2-ene-1,3-diyl)dibenzene (4a)



The title compound was synthesized according to the above procedure using (*E*)-4,4,4-trifluoro-1,3-diphenylbut-2-en-1-ol (1 mmol, 278 mg) as substrate. The final compound was purified using silica chromatography employing petroleum ether as eluent yielding a yellow oil (126 mg, 45% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.44 (m, 3H), 7.40–7.38 (m, 3H), 7.30–7.24 (m, 4H), 6.70 (tq, *J* = 9.3, 1.5 Hz, 1H), 5.75 (d, *J* = 47.2, 9.3 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 137.8 (d, *J* = 22 Hz), 135.0–134.7 (m), 132.7 (dq, J = 27, 5 Hz), 130.8, 129.7 (d, *J* = 2 Hz), 129.5, 129.3 (d, *J* = 2 Hz), 129.0, 128.8, 126.3 (d, *J* = 5 Hz), 123.0 (q, *J* = 274 Hz), 89.26 (d, *J* = 166 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –66.84 (s, 3F), –166.0 (d, *J* = 47 Hz, 1F).

(*E*)-1-(1,4,4,4-tetrafluoro-3-phenylbut-2-en-1-yl)-4-(trifluoromethyl)benzene (4b)

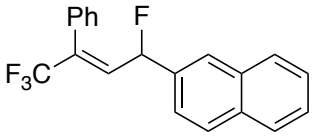


The title compound was synthesized according to the above procedure using (*E*)-4,4,4-trifluoro-3-phenyl-1-(4-(trifluoromethyl)phenyl)but-2-en-1-ol (1 mmol, 346 mg) as substrate. The final compound was purified using silica chromatography employing petroleum ether as eluent yielding a yellow oil (209 mg, 60% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.50–7.49 (m, 3H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.35–7.32 (m, 2H), 6.68 (td, *J* = 9.2 Hz, 1.4 Hz, 1H), 5.86 (dd, *J* = 47.2, 9.2Hz,

1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 141.7 (d, *J* = 22 Hz), 136.6–135.6 (m), 132.0 (dq, *J* = 26, 5 Hz), 131.4 (dq, *J* = 33, 2 Hz), 130.6 (d, *J* = 2 Hz), 129.8, 129.6 (d, *J* = 2 Hz), 129.0, 126.4 (d, *J* = 6 Hz), 126.0 (q, *J* = 4 Hz), 124.0 (d, *J* = 272 Hz), 122.8 (d, *J* = 274 Hz), 88.5 (d, *J* = 168 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –62.84 (s, 3F), –67.07 (d, *J* = 4 Hz, 3F),–170.07 (ddd, *J* = 47, 9, 4 Hz, 1F).

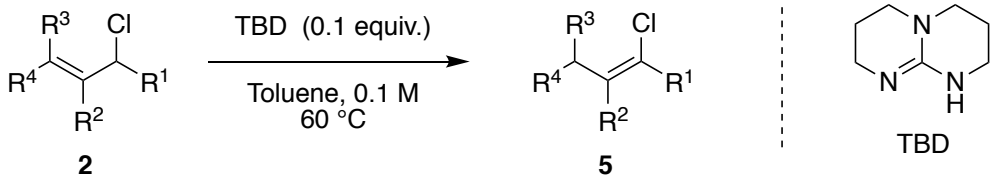
(*E*)-2-(1,4,4,4-tetrafluoro-3-phenylbut-2-en-1-yl)naphthalene (4c)



The title compound was synthesized according to the above procedure using (*E*)-4,4,4-trifluoro-1-(naphthalen-2-yl)-3-phenylbut-2-en-1-ol (1 mmol, 328 mg) as substrate. The final compound was purified using silica chromatography employing petroleum ether as eluent yielding a yellow oil (89 mg, 27% isolated yield).

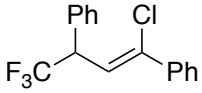
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.83 (m, 3H), 7.68 (s, 1H), 7.55–7.52 (m, 2H), 7.49–7.45 (m, 3H), 7.40–7.38 (m, 1H), 7.34–7.32 (m, 2H), 6.82 (tq, *J* = 9.3, 1.4 Hz, 1H), 5.75 (d, *J* = 47.4, 9.3 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 135.1 (q, *J* = 22 Hz), 133.7, 133.2, 132.8–132.5 (m), 130.8, 129.7, 129.7, 129.6, 129.1, 128.9, 128.3, 127.9, 127.0, 126.8, 125.8 (d, *J* = 7 Hz), 123.5 (d, *J* = 7 Hz), 122.9 (q, *J* = 274 Hz), 89.5 (d, *J* = 166 Hz).

General procedure for the base-catalyzed isomerization of allylic chlorides 2a-2n



The corresponding allylic chloride (0.18 mmol, 1 equiv.) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (2.5 mg, 0.018 mmol, 0.1 equiv.) were placed in a pressure tube and toluene was added (1.8 mL). The mixture was then stirred at 60 °C overnight in an oil bath. The reaction was quenched with H_2O (2 mL) and extracted with EtOAc (3 x 5 mL). The solvent was removed under reduced pressure yielding the desired vinyl chloride.

(*Z*)-(1-chloro-4,4,4-trifluorobut-1-ene-1,3-diyl)dibenzene (5a)

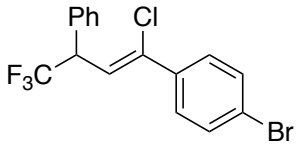


The title compound was synthesized according to the above procedure using (*E*)-(1-chloro-4,4,4-trifluorobut-2-ene-1,3-diyl)dibenzene as substrate. The final compound was isolated as a colorless oil (28 mg, 94% isolated yield). The title compound was also synthesized using (*E*)-(1-chloro-4,4,4-trifluorobut-2-ene-1,3-diyl)dibenzene (1.25 mmol, 371 mg) as substrate using

TBD (0.125 mmol, 17 mg) as catalyst in toluene (0.1 M, 12.5 mL) at 60 °C in an oil bath during 18 h. The reaction was then quenched with H_2O (20 mL) and extracted with EtOAc (3x 30 mL). The organic layers were then combined and the solvent was removed under reduced pressure yielding the title compound in 96% yield (356 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.60 (m, 2H), 7.44–7.37 (m, 8H), 6.52 (d, *J* = 9.0 Hz, 1H), 4.79–4.70 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 138.1, 137.2, 134.1, 129.6, 129.2, 129.0, 128.60, 128.55, 126.9, 126.0 (q, *J* = 280 Hz), 120.3 (q, *J* = 3 Hz), 50.5 (q, *J* = 28 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 69.02 (d, *J* = 9.0 Hz). **HRMS (APCI):** m/z calcd for [$C_{16}H_{12}F_3Cl$]: 296.0574; found: 296.0579. **HPLC:** CHIRALCEL OJ-H, flow rate 1.0 mL/min, isohexane/isopropanol (90/10) τ_{minor} (*R*) = 6.38 min. τ_{major} (*S*) = 7.11 min. **$[\alpha]_D^{20}$** –4 (c 0.1, $CHCl_3$, *e.r.* 76:24).

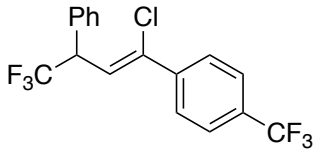
(*Z*)-1-bromo-4-(1-chloro-4,4,4-trifluoro-3-phenylbut-1-en-1-yl)benzene (5b)



The title compound was synthesized according to the above procedure using (*E*)-1-bromo-4-(1-chloro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)benzene as substrate. The final compound was isolated as a colorless oil (31 mg, 82% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.50 (m, 2H), 7.47–7.45 (m, 2H), 7.40–7.36 (m, 5H), 6.49 (d, *J* = 9.0 Hz, 1H), 4.74–4.65 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 137.0, 136.2, 133.8, 131.8, 129.2, 129.1, 128.7, 128.4, 125.9 (q, *J* = 280 Hz), 123.8, 120.9 (q, *J* = 3 Hz), 50.6 (q, *J* = 28 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 69.00 (d, *J* = 9.0 Hz).**GCMS (EI):** for [$C_{16}H_{11}BrClF_3$]; found: 374.0. **HPLC:** CHIRALCEL OJ-H, flow rate 1.0 mL/min, isohexane/isopropanol (90/10) τ_{major} (*S*) = 8.82 min. τ_{minor} (*R*) = 10.37 min. **$[\alpha]_D^{20}$** –6 (c 0.1, $CHCl_3$, *e.r.* 77:23).

(*Z*)-1-(1-chloro-4,4,4-trifluoro-3-phenylbut-1-en-1-yl)-4-(trifluoromethyl)benzene (5c)

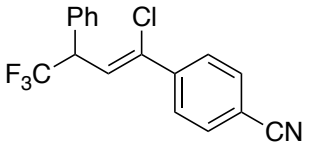


The title compound was synthesized according to the above procedure using (*E*)-1-(1-chloro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)-4-(trifluoromethyl)benzene as substrate. The final compound was isolated as a colorless oil (33 mg, 92% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.3 Hz,2H), 7.41–7.37 (m, 5H), 6.58 (d, *J* = 9.0 Hz, 1H), 4.76–4.67 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 140.5, 136.7, 133.6, 131.5 (q, *J* = 33 Hz), 129.2, 129.1, 128.8, 127.3, 125.8 (q, *J* = 280 Hz), 125.6 (q, *J* = 4 Hz), 123.9 (q, *J* = 272 Hz), 122.5 (q, *J* = 3 Hz), 50.6 (q, *J* = 29 Hz). **^{19}F NMR**

(376 MHz, $CDCl_3$) δ – 62.91 (s, 3F), – 69.00 (d, *J* = 9.0 Hz, 3F). **GCMS (EI):** for [$C_{17}H_{11}ClF_6$]; found: 364.1. **HPLC:** CHIRALCEL OD-H, flow rate 0.5 mL/min, isohexane/isopropanol (100/0) τ_{major} (*S*) = 16.10 min. τ_{minor} (*R*) = 17.73 min. **$[\alpha]_D^{20}$** –8 (c 0.1, $CHCl_3$, *e.r.* 92:8).

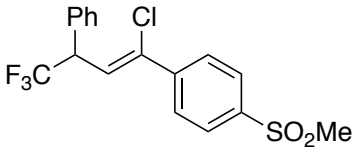
(*Z*)-4-(1-chloro-4,4,4-trifluoro-3-phenylbut-1-en-1-yl)benzonitrile (5d)



The title compound was synthesized according to the above procedure using (*E*)-4-(1-chloro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)benzonitrile as substrate. The final compound was isolated as a colorless oil (28 mg, 88% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 9.0 Hz, 2H), 7.67 (d, *J* = 9.0 Hz, 2H), 7.41–7.38 (m, 5H), 6.61 (d, *J* = 9.0 Hz, 1H), 4.76–4.66 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 141.2, 136.3, 133.4, 132.4, 129.2, 129.1, 128.8, 127.5, 126.8 (q, *J* = 271 Hz), 123.4 (d, *J* = 3 Hz), 118.3, 113.2, 50.7 (q, J = 29 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 69.00 (d, *J* = 9.0 Hz). **GCMS (EI):** for [$C_{17}H_{11}ClF_3N$]; found: 321.1. **HPLC:** CHIRALCEL OD-H, flow rate 1.0 mL/min, isohexane/isopropanol (90/10) τ_{major} (*S*) = 5.81 min. τ_{minor} (*R*) = 6.34 min. **$[\alpha]_D^{20}$** –8 (c 0.1, $CHCl_3$, *e.r.* 81:19).

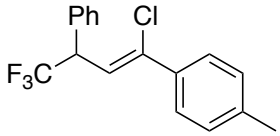
(*Z*)-1-(1-chloro-4,4,4-trifluoro-3-phenylbut-1-en-1-yl)-4-(methylsulfonyl)benzene (5e)



The title compound was synthesized according to the above procedure using (*E*)-1-(1-chloro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)-4-(methylsulfonyl)benzene as substrate. The final compound was isolated as a colorless oil (29 mg, 77% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.0 Hz, 2H), 7.79 (d, *J* = 9.0 Hz, 2H), 7.41–7.38 (m, 5H), 6.64 (d, *J* = 9.3 Hz, 1H), 4.77–4.68 (m, 1H), 3.06 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 142.2, 141.2, 136.2, 133.4, 129.1, 128.8, 128.3, 127.8, 125.7 (q, *J* = 280 Hz), 125.4, 123.6 (q, *J* = 3 Hz), 50.7 (q, *J* = 29 Hz), 44.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 68.90 (d, *J* = 9.0 Hz). **GCMS (EI):** for [$C_{17}H_{14}ClF_3O_2S$]; found: 374.1. **HPLC:** CHIRALCEL OD-H, flow rate 1.0 mL/min, isohexane/isopropanol (80/20) τ_{major} (*S*) = 13.60 min. τ_{minor} (*R*) = 19.01 min. **$[\alpha]_D^{20}$** –4 (c 0.1, $CHCl_3$, *e.r.* 76:24).

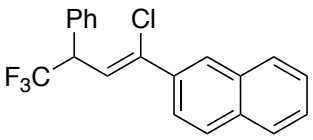
(*Z*)-1-(1-chloro-4,4,4-trifluoro-3-phenylbut-1-en-1-yl)-4-methylbenzene (5f)



The title compound was synthesized according to the above procedure using (*E*)-1-(1-chloro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)-4-methylbenzene as substrate. The final compound was isolated as a colorless oil (25 mg, 80% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.3 Hz, 2H), 7.42–7.35 (m, 5H), 7.18 (d, *J* = 8.3 Hz, 2H), 6.46 (d, *J* = 9.0 Hz, 1H), 4.76–4.67 (m, 1H), 2.37 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 139.7, 138.1, 134.5, 134.2, 129.3, 129.2, 129.0, 128.5, 126.8, 126.0 (q, *J* = 280 Hz), 119.4 (q, *J* = 2 Hz), 50.5 (q, *J* = 28 Hz), 21.3. **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 69.06 (d, *J* = 9.0 Hz). **GCMS (EI):** for [$C_{17}H_{14}ClF_3$]; found: 310.1.

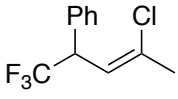
(*Z*)-2-(1-chloro-4,4,4-trifluoro-3-phenylbut-1-en-1-yl)naphthalene (5g)



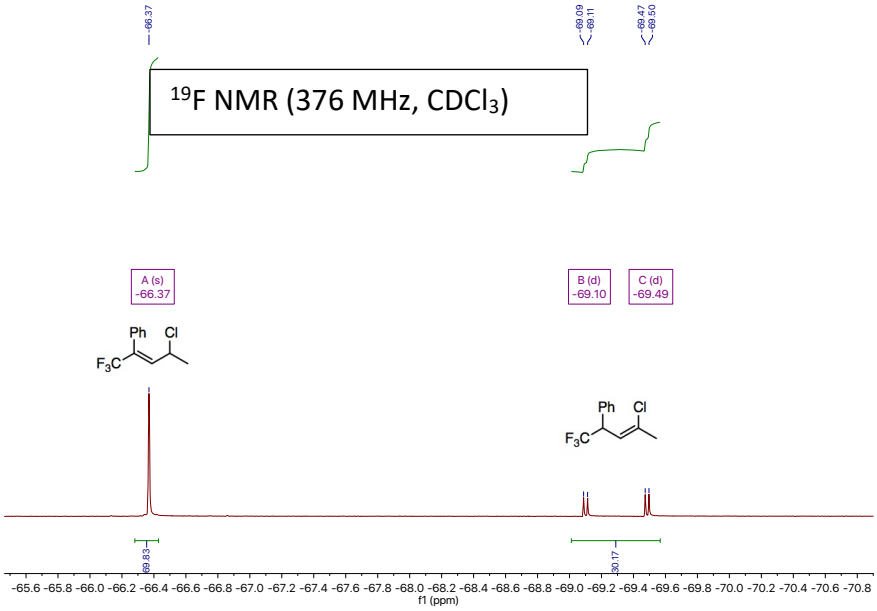
The title compound was synthesized according to the above procedure using (*E*)-2-(1-chloro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)naphthalene as substrate. The final compound was isolated as a white solid (30 mg, 86% isolated yield) (m.p. = 108–109°C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.89–7.82 (m, 3H), 7.70–7.68 (m, 1H), 7.54–7.50 (m, 2H), 7.46–7.37 (m, 5H), 6.64 (d, *J* = 9.0, 1H), 4.83–4.47 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 138.2, 134.4, 134.1, 133.7, 133.0, 129.2, 129.0, 128.7, 128.6, 128.3, 127.7, 127.2, 126.9, 126.8, 126.4 (q, *J* = 280 Hz), 123.9, 120.7 (q, *J* = 3 Hz), 50.7 (q, *J* = 28 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 68.96 (d, *J* = 9 Hz). **GCMS (EI):** for [$C_{20}H_{14}ClF_3$]; found: 346.1. **HPLC:** CHIRALCEL OD-H, flow rate 1.0 mL/min, isohexane/isopropanol (100/0) τ_{minor} (*R*) = 32.77 min. τ_{major} (*S*) = 42.49 min.

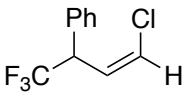
(*Z*)-(4-chloro-1,1,1-trifluoropent-3-en-2-yl)benzene (5h)



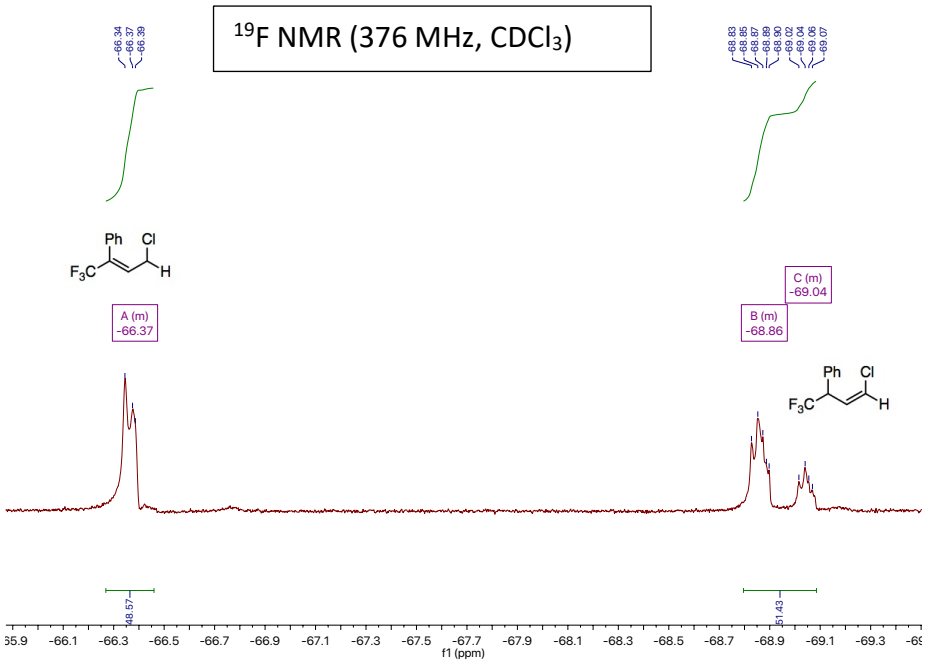
The title compound was synthesized according to the above procedure using (*E*)-(4-chloro-1,1,1-trifluoropent-2-en-2-yl)benzene as substrate. The final compound was not isolated and the conversion to the mixture of *E* and *Z* diastereomers was determined by integration of the CF_3 of both starting material and product by ^{19}F NMR (Shown below). **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 66.37 (s) (Allylic chloride **2h**), – 69.1 (d, *J* = 9.4 Hz) (Vinyl chloride **5h**, *E* or *Z* diastereomer), –69.49 (d, *J* = 8.9 Hz) (Vinyl chloride **5h**, *E* or *Z* diastereomer).



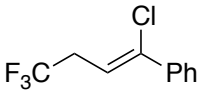
4-chloro-1,1,1-trifluorobut-3-en-2-yl)benzene (5i)



The title compound was synthesized according to the above procedure using (*E*)-(4-chloro-1,1,1-trifluorobut-2-en-2-yl)benzene as substrate. The final compound was not isolated and the conversion to the mixture of *E* and *Z* diastereomers was determined by integration of the CF_3 of both starting material and product by ^{19}F NMR (Shown below). **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 66.34 - – 66.39 (m) (Allylic chloride **2i**), – 68.83 - – 68.90 (m) (Vinyl chloride **5i**, *E* or *Z* diastereomer), – 69.02 - – 69.07 (m) (Vinyl chloride **5i**, *E* or *Z* diastereomer).



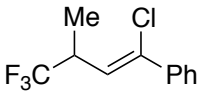
(*Z*)-(1-chloro-4,4,4-trifluorobut-1-en-1-yl)benzene (5j)



The title compound was synthesized according to the above procedure using (*E*)-(1-chloro-4,4,4-trifluorobut-2-en-1-yl)benzene as substrate. The final compound was isolated as a colorless oil (18 mg, 85% isolated yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.61–7.58 (m, 2H), 7.40–7.37 (m, 3H), 6.12 (t, *J* = 6.8 Hz, 1H), 3.25 (qd, *J* = 10.7, 6.8 Hz, 2H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 138.6, 137.2, 129.5, 128.6, 126.8, 125.9 (q, *J* = 277 Hz), 115.2 (q, *J* = 4 Hz), 34.9 (q, *J* = 30 Hz). **^{19}F NMR (376 MHz, CDCl$_3$)** δ –65.61 (t, *J* = 11.0 Hz). **GCMS (EI):** for [$C_{10}H_8ClF_3$]; found: 220.0.

(*Z*)-(1-chloro-4,4,4-trifluoro-3-methylbut-1-en-1-yl)benzene (5k)

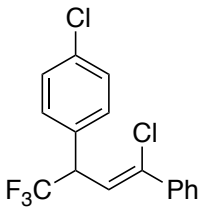


The title compound was synthesized according to the above procedure using (*E*)-(1-chloro-4,4,4-trifluoro-3-methylbut-2-en-1-yl)benzene as substrate. The final compound was isolated as a colorless oil (22 mg, 92% isolated yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.60–7.57 (m, 2H), 7.40–7.36 (m, 3H), 6.05 (d, *J* = 9.0 Hz, 1H), 3.67–3.56 (m, 1H), 1.32 (d, *J* = 7 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 137.3, 132.3, 129.4, 128.6, 127.1 (d, *J* = 279 Hz), 126.8, 122.1 (q, *J* = 3 Hz), 39.7 (q, *J* = 28 Hz), 13.3 (q, *J* = 3 Hz). **^{19}F NMR (376 MHz, CDCl$_3$)** δ –72.24 (d, *J* = 9.0 Hz). **HPLC:** CHIRALCEL

OD-H, flow rate 1.0 mL/min, isohexane/isopropanol (100/0) τ_{major} (*S*) = 6.45 min. τ_{minor} (*R*) = 7.57 min. $[\alpha]_D^{20}$ –3 (c 0.1, $CHCl_3$, *e.r.* 66:34).

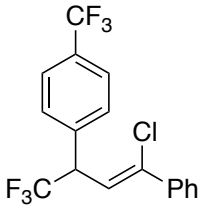
(*Z*)-1-chloro-4-(4-chloro-1,1,1-trifluoro-4-phenylbut-3-en-2-yl)benzene (5l)



The title compound was synthesized according to the above procedure using (*E*)-1-chloro-4-(4-chloro-1,1,1-trifluoro-4-phenylbut-2-en-2-yl)benzene as substrate. The final compound was isolated as a colorless oil (26 mg, 80% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.61 (m, 2H), 7.43–7.36 (m, 7H), 6.54–6.49 (m, 1H), 4.81–4.69 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 138.7, 137.0, 134.6, 132.5, 130.5, 129.7, 129.2, 128.58 (q, *J* = 280 Hz), 128.60, 126.9, 119.7, 50.0 (q, *J* = 29 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –69.11 (d, *J* = 9.0 Hz). **GCMS (EI):** for [$C_{16}H_{11}Cl_2F_3$]; found: 330.1.

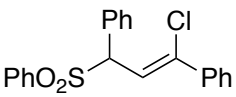
(*Z*)-1-(4-chloro-1,1,1-trifluoro-4-phenylbut-3-en-2-yl)-4-(trifluoromethyl)benzene (5m)



The title compound was synthesized according to the above procedure using (*E*)-1-(4-Chloro-1,1,1-trifluoro-4-phenylbut-2-en-2-yl)-4-(trifluoromethyl)benzene as substrate. The final compound was isolated as a colorless oil (27 mg, 75% isolated yield).

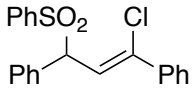
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.63–7.60 (m, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.43–7.38 (m, 3H), 6.51 (d, *J* = 9.0 Hz, 1H), 4.85–3.76 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 139.1, 138.0, 136.9, 130.9 (q, *J* = 33 Hz), 129.8, 129.7, 128.7, 126.9, 126.0 (q, *J* = 4 Hz), 119.3 (q, *J* = 3 Hz), 124.3 (q, *J* = 280 Hz), 124.0 (q, *J* = 272 Hz), 50.4 (q, *J* = 29 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –62.78 (s, 3H), –68.94 (d, *J* = 9.0 Hz). **GCMS (EI):** for [$C_{17}H_{11}ClF_6$]; found: 364.2.

(*Z*)-(1-chloro-3-(phenylsulfonyl)prop-1-ene-1,3-diyl)dibenzene ((*Z*)-5n)



The title compound was synthesized according to the above procedure using (*E*)-(3-chloro-1-(phenylsulfonyl)prop-1-ene-1,3-diyl)dibenzene as substrate. The final compound was isolated as a colorless oil (31 mg, 85% isolated yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.79 (m, 2H), 7.63–7.59 (m, 1H), 7.52–7.43 (m, 6H), 7.38–7.36 (m, 6H), 6.63 (d, *J* = 10.3 Hz, 1H), 5.44 (d, *J* = 10.3 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 139.6, 137.8, 137.0, 134.0, 131.3, 130.1, 129.8, 129.3, 129.28, 129.1, 129.0, 128.6, 126.9, 118.6, 71.6. **GCMS (EI):** for [$C_{21}H_{17}ClO_2S$]; found: 368.2.

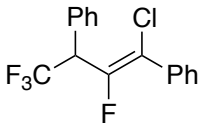
(*E*)-(1-chloro-3-(phenylsulfonyl)prop-1-ene-1,3-diyl)dibenzene ((*E*)-5n)



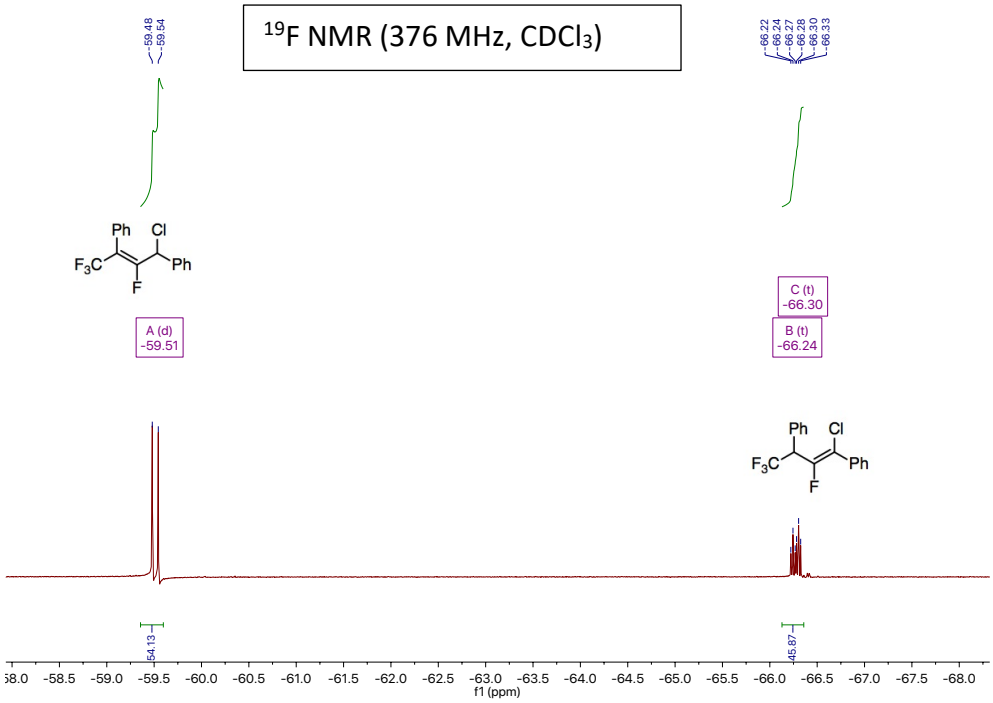
The title compound was synthesized according to the above procedure using (*Z*)-(3-chloro-1-(phenylsulfonyl)prop-1-ene-1,3-diyl)dibenzene as substrate. The final compound was isolated as a colorless oil (30 mg, 80% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.63–7.59 (m, 1H), 7.52–7.47 (m, 4H), 7.45–7.42 (m, 2H), 7.38–7.36 (m, 6H), 6.63 (d, *J* = 10.3 Hz, 1H), 5.43 (d, *J* = 10.3 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 139.5, 137.7, 136.9, 133.9, 131.2, 130.0, 129.7, 129.2, 129.2, 128.9, 128.5, 128.1, 126.8, 118.5, 71.5.

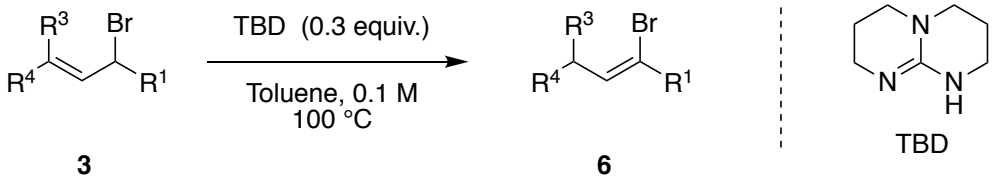
(*E*)-(1-chloro-2,4,4,4-tetrafluorobut-1-ene-1,3-diyl)dibenzene (5o)



The title compound was synthesized according to the above procedure using (*Z*)-(1-chloro-2,4,4,4-tetrafluorobut-2-ene-1,3-diyl)dibenzene as substrate. The final compound was not isolated and the conversion to the mixture of *E* and *Z* diastereomers was determined by integration of the CF_3 of both starting material and product by ^{19}F NMR (Shown below). **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 59.51 (d, J = 23.9 Hz) (Allylic chloride **2h**), – 66.24 (t, J = 8.7 Hz) (Vinyl chloride **5h**, *E* or *Z* diastereomer), –66.30 (t, J = 8.2 Hz) (Vinyl chloride **5h**, *E* or *Z* diastereomer).



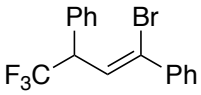
General procedure for the base-catalyzed isomerization of allylic bromides 3a-3c



3 **6**

The corresponding allylic bromide (0.18 mmol, 1 equiv.) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (7.5 mg, 0.054 mmol, 0.3 equiv.) were placed in a pressure tube and toluene was added (1.8 mL). The mixture was then stirred at 100 °C overnight in an oil bath. The reaction was quenched with H_2O (2 mL) and extracted with EtOAc (3 x 5 mL). The solvent was removed under reduced pressure yielding the desired vinyl bromide.

(*Z*)-(1-bromo-4,4,4-trifluorobut-1-ene-1,3-diyl)dibenzene (6a)

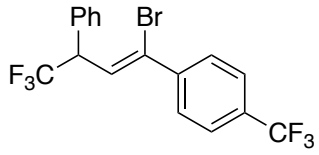


The title compound was synthesized according to the above procedure using (*E*)-(1-bromo-4,4,4-trifluorobut-2-ene-1,3-diyl)dibenzene as substrate. The final compound was isolated as a colorless oil (20 mg, 60% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.53 (m, 2H), 7.40–7.35 (m, 8H), 6.60 (d, *J* = 9.0 Hz, 1H), 4.71–4.62 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 139.1, 133.9, 130.9, 129.5, 129.3, 129.0, 128.6, 128.5, 127.9, 125.9 (q, *J* = 280Hz), 124.2 (q, *J* = 3 Hz), 53.3 (q, *J* = 28Hz). **^{19}F**

NMR (376 MHz, $CDCl_3$) δ – 69.02 (d, *J* = 9.0 Hz). **GCMS (EI):** for [$C_{16}H_{12}BrF_3$]; found: 340.0.

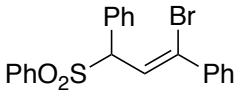
(*Z*)-1-(1-bromo-4,4,4-trifluoro-3-phenylbut-1-en-1-yl)-4-(trifluoromethyl)benzene (6b)



The title compound was synthesized according to the above procedure using (*E*)-1-(1-bromo-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)-4-(trifluoromethyl)benzene as substrate. The final compound was isolated as a colorless oil (31 mg, 76% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.3 Hz,2H), 7.41–7.37 (m, 5H), 6.67 (d, *J* = 9.0 Hz, 1H), 4.71–4.62 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 142.4, 133.5, 132.3 (q, J = 10 Hz), 131.4 (d, *J* = 33 Hz), 129.2, 129.1, 128.8, 128.3, 126.27 (d, *J* = 3 Hz), 125.75 (q, *J* = 280 Hz), 125.59 (q, *J* = 4 Hz), 123.90 (q, *J* = 272 Hz), 53.3 (q, *J* = 29 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –62.79 (s, 3F), –68.87 (d, *J* = 9.0 Hz).

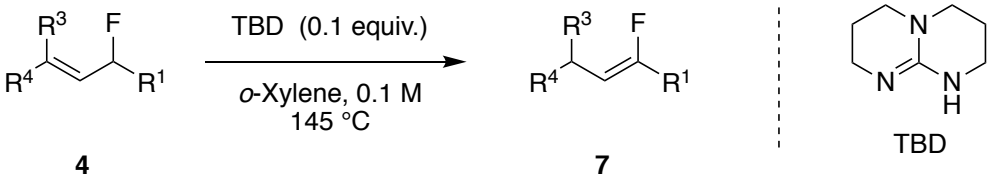
(*Z*)-(1-bromo-3-(phenylsulfonyl)prop-1-ene-1,3-diyl)dibenzene (6c)



The title compound was synthesized according to the above procedure using (*E*)-(3-bromo-1-(phenylsulfonyl)prop-1-ene-1,3-diyl)dibenzene as substrate. The final compound was isolated as a colorless oil (21 mg, 50% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.81 (m, 2H), 7.47–7.42 (m, 4H), 7.38–7.31 (m, 9H), 6.71 (d, *J* = 10.2 Hz, 1H), 5.40 (d, *J* = 10.2 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 138.9, 137.9, 134.0, 132.6, 131.1, 130.1, 129.7, 129.3, 129.1, 129.02, 129.00, 128.6, 127.8, 122.6, 74.3.

General procedure for the base-catalyzed isomerization of allylic fluorides 4a-4c

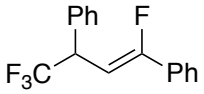


4 **7**

The corresponding allylic fluoride (0.18 mmol, 1 equiv.) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (2.5 mg, 0.018 mmol, 0.1 equiv.) were placed in a pressure tube and *o*-xylene was added (1.8 mL). The mixture was then stirred at 145 °C overnight in an oil

bath. The reaction was quenched with H_2O (2 mL) and extracted with EtOAc (3 x 5 mL). The solvent was removed under reduced pressure yielding the desired vinyl fluoride.

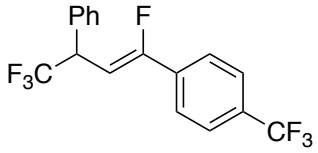
(*Z*)-(1-fluoro-4,4,4-trifluorobut-1-ene-1,3-diyl)dibenzene (7a)



The title compound was synthesized according to the above procedure using (*E*)-(1-fluoro-4,4,4-trifluorobut-2-ene-1,3-diyl)dibenzene as substrate. The final compound was isolated as a colorless oil (17 mg, 60% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.54 (m, 2H), 7.43–7.35 (m, 8H), 5.79 (dd, *J* = 34.0, 10.0 Hz, 1H), 4.71–4.62 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.6 (d, *J* = 254 Hz), 134.7, 131.3 (d, *J* = 28 Hz), 129.9, 129.0, 128.9, 128.80 (q, *J* = 280 Hz), 128.72 (d, *J* = 2 Hz), 128.5, 124.7 (d, *J* = 7 Hz), 99.5 (dd, *J* = 16, 3 Hz), 45.8 (dq, *J* = 29, 6 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –69.56 (dd, *J* = 9.2, 2.5 Hz, 3F), –113.88 (dd, J = 34.60, 2.5 Hz, 1F). **GCMS (EI):** for [$C_{16}H_{12}F_4$]; found: 280.1.

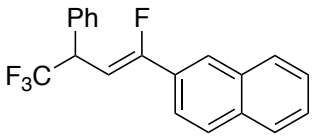
(*Z*)-1-(1-fluoro-4,4,4-trifluoro-3-phenylbut-1-en-1-yl)-4-(trifluoromethyl)benzene (7b)



The title compound was synthesized according to the above procedure using (*E*)-1-(1-chloro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)-4-(trifluoromethyl)benzene as substrate. The final compound was isolated as a colorless oil (19 mg, 55% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.59 (m, 4H), 7.44–7.26 (m, 5H), 5.92 (dd, *J* = 33.2, 10.0 Hz, 1H), 4.74–4.65 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.3 (d, *J* = 254 Hz), 134.6 (d, *J* = 30 Hz), 134.3, 131.7 (q, *J* = 33 Hz), 129.1, 128.9, 128.7, 128.5 (q, *J* = 258 Hz), 125.8–125.7 (m), 125.0 (d, *J* = 7 Hz), 123.9 (q, *J* = 272 Hz), 101.9 (dd, *J* = 16, 3 Hz), 45.9 (dq, *J* = 29, 6 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ – 62.9 (s, 3F), –69.48 (dd, *J* = 9.0, 2.5 Hz, 3F), –114.2 (d, *J* = 35.4, 1F). **GCMS (EI):** for [$C_{17}H_{11}F_7$]; found: 348.1.

(*Z*)-2-(1-fluoro-4,4,4-trifluoro-3-phenylbut-1-en-1-yl)naphthalene (7c)



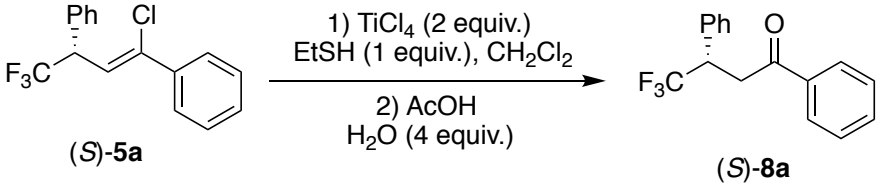
The title compound was synthesized according to the above procedure using (*E*)-2-(1-fluoro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)naphthalene as substrate. The final compound was isolated as a white solid (22 mg, 67% isolated yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.88–7.83 (m, 3H), 7.62 (d, *J* = 9 Hz, 1H), 7.54–7.50 (m, 2H), 7.46 (d, *J* = 8.0, 2H), 7.45–7.36 (m, 3H), 5.92 (dd, *J* = 34.0, 10.0 Hz, 1H), 4.78–4.68 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.6 (d, *J* = 254 Hz), 134.8, 133.8, 133.0, 129.02, 128.96, 128.7, 128.61–128.58 (m), 128.5, 128.30 (q, *J* = 250 Hz), 128.33, 127.8, 127.2, 126.9, 124.4 (d, *J* = 7.0 Hz), 121.9 (d, *J* = 7 Hz), 100.1 (dq, *J* = 16, 3 Hz), 45.9 (dq, *J* = 28, 6 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ –69.47 (dd, *J* = 9.0, 2.4 Hz, 3F), –114.00 (dd, *J* = 34.0, 2.4 Hz, 1F). **GCMS (EI):** for [$C_{20}H_{14}F_4$]; found: 330.1.

Determination of the absolute configuration of 5a

The absolute configuration of **5a** was determined by performing its transformation to the corresponding β-trifluoromethylated ketone. The hydrolysis was accomplished using a modified literature procedure.[3] Vinyl chloride **5a** (1 equiv.) was added to a mixture of EtSH (1 equiv.) and $TiCl_4$ (2 equiv.) in DCM (0.3 M of **5a**) at rt and the reaction was stirred overnight. After that, AcOH (0.3 M of **5a)** and H_2O (4 equiv) were added and the mixture stirred for 3h. The reaction was then quenched with a saturated solution of $NaHCO_3$, extracted with DCM (3 x 5 mL), dried with $MgSO_4$ and the solvent was reduced under vacuum. The final ketone was purified using silica chromatography employing petroleum ether and ethyl acetate as eluents.

The pure final ketone was analysed and the data was compared to that reported in the literature.[4] **HPLC**: CHIRALCEL OD-H, flow rate 1.0 mL/min, isohexane/isopropanol (95/05) τ_{major} (*S*) = 5.0 min. τ_{minor} (*R*) = 6.4 min. and **$[\alpha]_D^{20}$** –12 (c 0.66, $CHCl_3$). It was concluded that the ketone had a (*S*) configuration so the starting material 5a had to have the same (S) configuration. The rest of the vinyl chlorides were assigned by analogy.



Scheme S1. Conversion of (*S*)-**5a** to saturated ketone (*S*)-**8a**.

Mechanistic Investigations: Kinetic Isotope Effect

The Kinetic isotope effect of the TBD-catalyzed isomerization of allylic halides was calculated by performing parallel reactions with non-deuterated allylic chloride **2a** and deuterated compound **2a**-*d*. Individual reactions were run according to the general procedure and stopped at certain times. The resulted KIE was 5.4 ± 0.6 (figure S1 and S2).

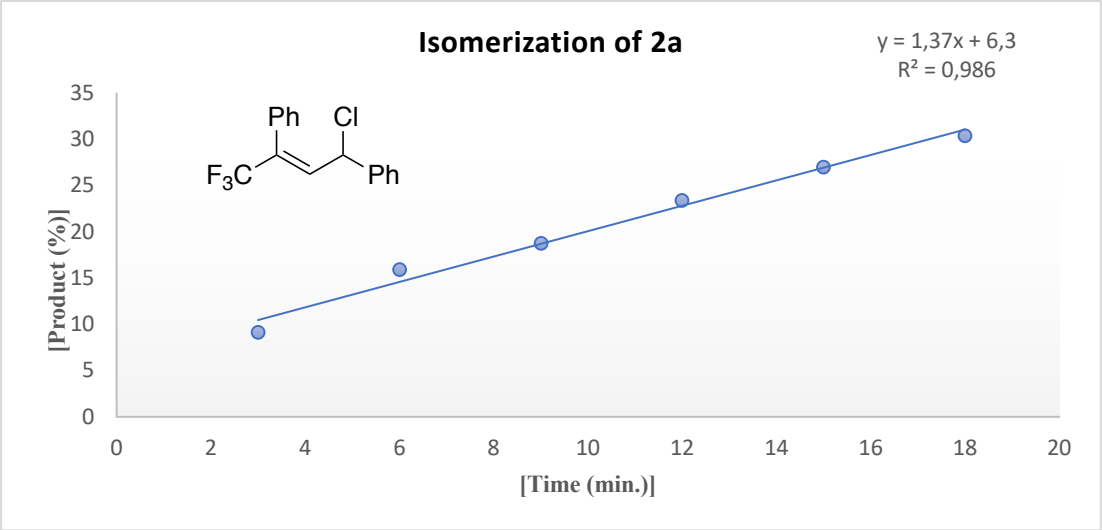


Figure S1. Kinetic profile of the isomerization of allylic halide **2a**.

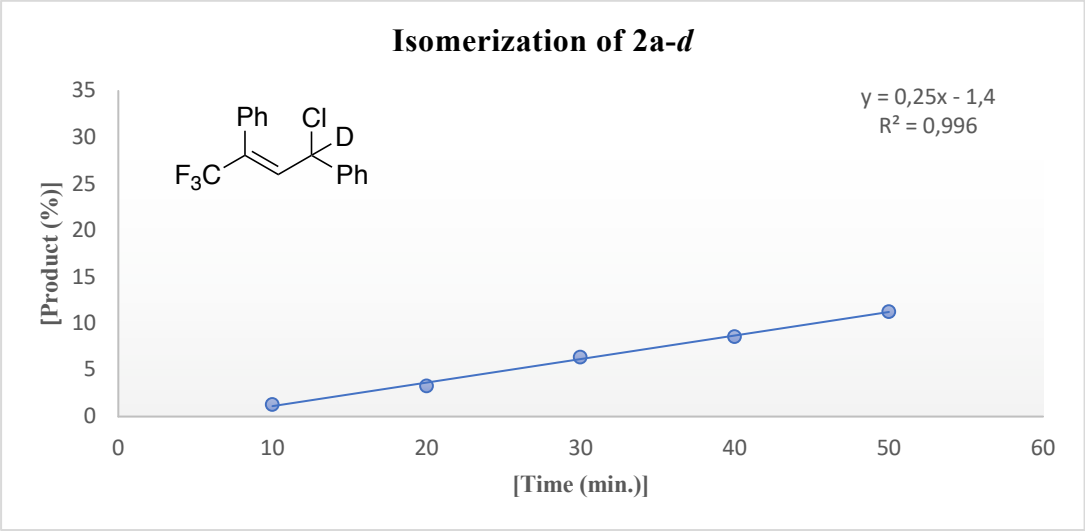


Figure S2. Kinetic profile of the isomerization of allylic halide **2a**-*d*.

(1) (a) Hanessian, S.; Ponpipom, M. M.; Lavalle, P. Procedures for the direct replacement of primary hydroxyl groups in carbohydrates by halogen. *Carbohydr. Res.* **1972**, *24*, 45–56. (b) Jaseer, E. A.; Naidu, A. B.; Kumar, S. S.; Rao, R. K.; Thakur, K, G.; Sekar, G. Highly stereoselective chlorination of β-substituted cyclic alcohols using PPh_3-NCS: factors that control the stereoselectivty. *Chem. Commun.* **2007**, *8*, 867–869.

(2) Pacheco, M. C.; Purser, S.; Gouverneur, V. The Chemistry of Propargylic and Allylic Fluorides. *Chem. Rev.* **2008**, *108*, 1943–1981.

(3) Mukaiyama, T.; Imamoto, T.; Kobayashi, S. A convenient method for the hydrolysis of vinyl chlorides to ketones. *Chemistry letters*, **1973**, *2*, 261–264.

(4) (a) V Bizet, V.; Pannecoucke, X.; Renaud, J.-L., Cahard, D. Ruthenium-Catalyzed Redox Isomerization of Trifluoromethylated Allylic Alcohols: Mechanistic Evidence for an Enantiospeficic Pathway. *Angew. Chem., Int. Ed.* **2012**, *53*, 6467−6470. (b) Martinez-Erro, S.; Sanz-Marco, A.; Bermejo Gómez, A.; Vázquez-Romero, A.; Ahlquist, M. S. G.; Martín-Matute, B. Base-Catalyzed Stereospecific Isomerization of Electron-Deficient Allylic Alcohols and Ethers through Ion-Pairing. *J. Am. Chem. Soc.* **2016**, *138*, 13408–13414.