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Supporting Information

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Straightforward Synthesis of CF_3-substituted Triarylethenes via Stereoselective Three-fold Cross-coupling Reaction of 1,1-Dibromo-3,3,3-trifluoro-2-tosyloxypropene with Organoboronic Acids

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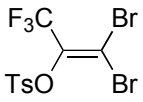
General Information

Melting points were determined using a Yanagimoto Micro Point Apparatus. ^{1}H NMR spectra measured on a Varian Mercury 300 (300 MHz) and 400 (400 MHz) spectrometers. The chemical shifts of ^{1}H NMR are expressed in parts per million downfield relative to the internal tetramethylsilane (δ = 0 ppm) or chloroform (δ = 7.26 ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet, q, quartet; m, multiplet. ^{13}C NMR spectra were measured on a Varian Mercury 300 (75 MHz) and 400 (100 MHz) spectrometers with tetramethylsilane as an internal standard (δ = 0 ppm) or chloroform (δ = 77.0 ppm). ^{19}F NMR spectra were measured on a Varian Mercury 300 (282 MHz) spectrometer with $CFCl_3$ as an internal standard (δ = 0 ppm). Chemical shift values are given in parts per million downfield relative to the internal standard. Infrared spectra (IR) were recorded on a Shimadzu FTIR-8400 spectrometer. GC-MS analyses were performed with a JEOL JMS-700 spectrometer by electron ionization at 70 eV. FAB-MS analyses were performed with a JEOL-HX110A spectrometer. Elemental analyses were carried out with a YANAKO MT2 CHN CORDER machine at Elemental Analysis Center of Kyoto University. TLC analyses were performed by means of Merck Kieselgel 60 F_{254} and column chromatography was carried out using Merck Kieselgel 60 (230-400 mesh). Preparative HPLC was carried out with a Japan Analytical Industry Co., Ltd, LC-908 chromatograph using a JAIGEL-1H and -2H GPC columns. 3,3-Dibromo-1,1,1-trifluoroacetone was purchased from SynQuest Laboratories, Inc. and distilled before use. All boronic acids were purchased from Aldrich and used without any further purification. Toluene and terahydrofuran were passed through two packed columns of neutral alumina and copper oxide under a nitrogen atmosphere before use. All reactions were carried out under an argon atmosphere.

Preparation of 1,1-dibromo-3,3,3-trifluoro-2-tosyloxypropene (1)



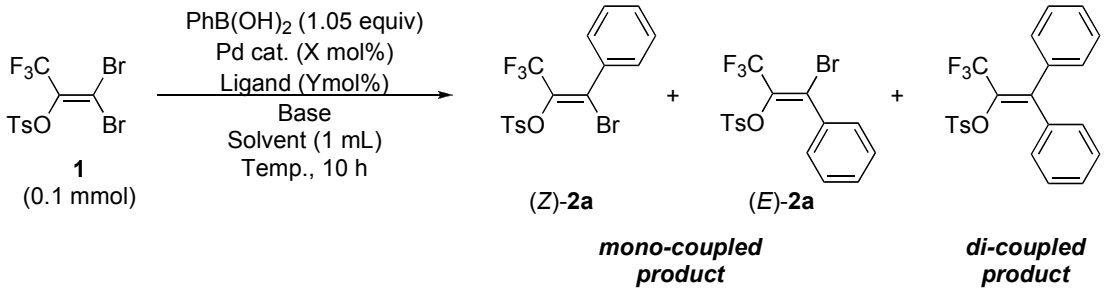
To a two-necked round-bottomed flask (50 mL) equipped with a magnetic stirring bar and a dropping funnel were added *p*-toluenesulfonyl chloride (1.71 g, 9.0 mmol), freshly distilled (57 °C/36 Torr) 3,3-dibromo-1,1,1-trifluoroacetone (1.22 mL, 10 mmol), and CH_2Cl_2 (20 mL) under an argon atmosphere. The solution was cooled to 0 °C and stirred for 10 min before adding Et_3N (1.26 mL, 9.0 mmol) dropwise. The resulting solution was warmed to room temperature and stirred for 3 h. Saturated aq. NH_4Cl (15 mL) was added to the reaction mixture and the aqueous layer was extracted with CH_2Cl_2 (20 mL x 3). The combined organic layer was washed with sat. aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. Recrystallization of the crude product from hexane gave **1** (2.28 g, 60% yield) as a colorless solid.

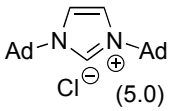
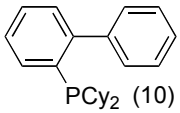
Mp: 64.0–65.5 °C. TLC: R_f 0.50 (hexane/AcOEt 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 (s, 3H), 7.38 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7, 99.7 (q, J = 2.7 Hz), 119.3 (q, J = 275.5 Hz), 128.5, 130.0, 132.8, 137.4 (q, J = 38.2 Hz), 146.5. ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.1 (s). IR (KBr): ν = 2964, 2929, 1596, 1492, 1382, 1296, 1205, 1180, 1141, 1080, 1141, 1080, 906, 819, 719, 692, 678, 559, 543 cm^{-1}. MS (FAB) *m/z*: 427 (2, [M^+ + H] + 4), 425 (5, [M^+ + H] + 2), 423 (2, [M^+ + H]), 407 (5), 405 (9), 403 (5). Anal. Calcd for $C_{10}H_7Br_2F_3O_3S$: C, 28.33; H, 1.66. Found: C, 28.44; H, 1.78.

Cross-coupling reaction of 1 with phenylboronic acid

Representative results on screening of the conditions for the reaction of 1,1-dibromo-3,3,3-trifluoro-2-tosyloxypropene (**1**) with phenylboronic acid was summarized in the following Table.

Table 1. Representative results on the reaction of **1** with $PhB(OH)_2$.

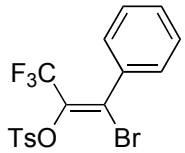


Pd cat. (X mol%)	Ligand (Y mol%)	Base	Solvent	Temp. (°C)	conv. of **1** (%)	**2a** (%) (*Z*/*E*)	***di-coupled*** *product* (%)
$Pd(PPh_3)_4$ (5.0)	none	KOH aq.	THF	r.t.	77	29 (100:0)	17
$Pd(PPh_3)_4$ (5.0)	none	Ag_2CO_3	THF	60	59	19 (100:0)	29
$Pd(PPh_3)_4$ (5.0)	none	KOH aq.	toluene	80	3	0	0
$Pd(PPh_3)_4$ (5.0)	none	Cs_2CO_3 aq.	toluene	60	33	34 (91:9)	0
$Pd(PPh_3)_4$ (5.0)	none	Cs_2CO_3 aq.	toluene	70	56	56 (89:11)	0
$Pd(PPh_3)_4$ (5.0)	none	Cs_2CO_3 aq.	toluene	80	100	99 (89:11)	1
$Pd_2(dba)_3{\cdot}CHCl_3$ (2.5)	 (5.0)	Cs_2CO_3 aq.	1,4-dioxane	80	100	57 (>99:1)	32
$Pd_2(dba)_3{\cdot}CHCl_3$ (2.5)	P(*o*-tolyl)$_3$ (10)	Cs_2CO_3 aq.	toluene	80	53	<10 (>90:10)	43
$Pd_2(dba)_3{\cdot}CHCl_3$ (2.5)	$P(C_6F_5)_3$ (10)	Cs_2CO_3 aq.	toluene	80	41	37 (70:30)	2
$Pd(OAc)_2$ (5.0)	 (10)	Cs_2CO_3 aq.	toluene	80	43	14 (93:7)	23
$Pd(OAc)_2$ (5.0)	P(*t*-Bu)$_3$ (10)	Cs_2CO_3 aq.	toluene	80	13	trace (-)	7
$PdCl_2(PPh_3)_2$ (5.0)	none	Cs_2CO_3 aq.	toluene	80	60	56 (86:14)	4
$PdCl_2(PPh_3)_2$ (5.0)	PPh_3 (5.0)	Cs_2CO_3 aq.	toluene	80	99	99 (90:10)	trace
$PdCl_2(PPh_3)_2$ (5.0)	P(*o*-tolyl)$_3$ (5.0)	Cs_2CO_3 aq.	toluene	80	61	55 (98:2)	6
$PdCl_2(PPh_3)_2$ (5.0)	**P(*m*-tolyl)$_3$ (5.0)**	**Cs_2CO_3 aq.**	**toluene**	**80**	**82**	**81 (94:6)**	**0**
$PdCl_2(PPh_3)_2$ (5.0)	P(*t*-Bu)$_3$ (5.0)	Cs_2CO_3 aq.	toluene	80	100	61 (93:7)	21
$PdCl_2(PPh_3)_2$ (5.0)	PCy_3 (5.0)	Cs_2CO_3 aq.	toluene	80	83	78 (87:13)	5
$PdCl_2(PPh_3)_2$ (5.0)	P(2-$MeOC_6H_4$)$_3$ (5.0)	Cs_2CO_3 aq.	toluene	80	80	69 (91:9)	10

General Procedure for Cross-coupling Reaction of 1 with Arylboronic acids

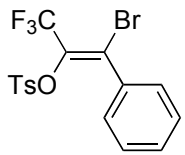
To a Schlenk tube (20 mL) equipped with a magnetic stirring bar were added $PdCl_2(PPh_3)_2$ (18 mg, 25 μmol), P(*m*-tolyl)$_3$ (7.5 mg, 25 μmol), **1** (0.21 g, 0.50 mmol), and arylboronic acid (0.55 mmol). The tube was then capped with a rubber septum, evacuated for 5 min and purged with argon. The evacuation–purge operation was repeated twice. Toluene (5 mL) and 5 M aq. Cs_2CO_3 (0.20 mL, 1.0 mmol) was added to the mixture at room temperature. After stirred at room temperature for 5 min, the solution was heated in an 80 °C oil bath and stirred for 24 h. The reaction was monitored by TLC. Upon completion of the reaction, the mixture was allowed to cool to room temperature, diluted wit EtOAc (5 mL), and filtered through a pad of Florisil. The filtrate was washed with water (10 mL) and the aqueous layer was extracted with EtOAc (15 mL x 3). The combined organic layer was washed with sat. aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel followed by preparative HPLC or recrystallization.

(*Z*)-1-Bromo-3,3,3-trifluoro-1-phenyl-2-tosyloxypropene (2a)



Purification: silica gel column chromatography (hexane/AcOEt 8:1). Yield: 86%, colorless solid. Mp: 90.0–91.9 °C. TLC: R_f 0.45 (hexane/AcOEt 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (s, 3H), 7.37–7.42 (m, 7H), 7.94 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.9, 119.1 (q, *J* = 274.5 Hz), 128.2, 128.3, 129.4 (q, *J* = 3.1 Hz), 129.6, 130.2, 133.2, 134.2 (q, *J* = 36.6 Hz), 134.5, 145.9. ^{19}F NMR (282 MHz, $CDCl_3$): δ –60.5 (s). IR (KBr): ν = 3057, 2029, 1641, 1595, 1492, 1446, 1382, 1301, 1230, 1193, 1180, 1145, 1080, 918, 821, 767, 734, 698, 680, 661, 563, 543, 524 cm^{-1}. MS (FAB) *m/z*: 423 (12, [M^+ + H] + 2), 421 (12, [M^+ + H]), 343 (71), 342 (11), 341 (68). Anal. Calcd for $C_{16}H_{12}BrF_3O_3S$: C, 45.62; H, 2.87. Found: C, 45.36; H, 2.90.

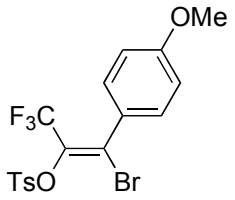
(*E*)-1-Bromo-3,3,3-trifluoro-1-phenyl-2-tosyloxypropene (2a)



Purification: silica gel column chromatography (hexane/AcOEt 8:1). Yield: 8%, colorless solid.

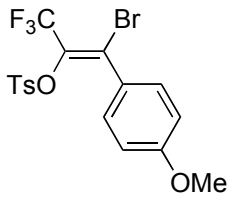
Mp: 87.5–88.6 °C. TLC: R_f 0.35 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 3H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.20–7.27 (m, 5H) 7.40 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 119.8 (q, *J* = 273.7 Hz), 126.1 (q, *J* = 2.4 Hz), 127.9, 129.0, 129.5, 129.7, 131.9, 133.0, 133.5 (q, *J* = 36.2 Hz), 135.0, 145.3. ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.6 (s). IR (KBr): ν = 3058, 2922, 1627, 1596, 1490, 1444, 1386, 1298, 1195, 1184, 1176, 1145, 1074, 910, 767, 707, 692, 557 cm^{-1}. MS (FAB) *m/z*: 423 (15, [M^+ + H] + 2), 421 (15, [M^+ + H]). Anal. Calcd for $C_{16}H_{12}BrF_3O_3S$: C, 45.62; H, 2.87. Found: C, 45.57; H, 2.78.

(*Z*)-1-Bromo-3,3,3-trifluoro-1-(4-methoxyphenyl)-2-tosyloxypropene (2b)



Purification: silica gel column chromatography (hexane/AcOEt 8:1) followed by recrystallization from hexane. Yield: 67%, colorless solid. Mp: 80.0–82.3 °C. TLC: R_f 0.23 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 (s, 3H), 3.84 (s, 3H), 6.89 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8, 55.3, 113.7, 119.2 (q, *J* = 273.8 Hz), 126.6, 128.3, 129.6, 129.8 (q, *J* = 3.1 Hz), 130.1 (d, *J* = 1.5 Hz), 133.2, 133.5 (q, *J* = 36.6 Hz), 145.8, 160.9. ^{19}F NMR (282 MHz, $CDCl_3$): δ –60.3 (s). IR (KBr): ν = 3060, 2937, 1624, 1604, 1512, 1394, 1296, 1267, 1199, 1174, 1145, 1078, 916, 810, 723, 692, 680, 663, 597, 545 cm^{-1}. MS (FAB) *m/z*: 453 (69, [M^+ + H] + 2), 451 (69, [M^+ + H]), 371 (27). Anal. Calcd for $C_{17}H_{14}BrF_3O_4S$: C, 45.25; H, 3.13. Found: C, 45.48; H, 3.10.

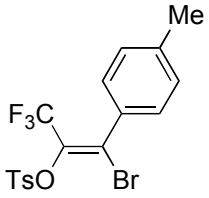
(*E*)-1-Bromo-3,3,3-trifluoro-1-(4-methoxyphenyl)-2-tosyloxypropene (2b)



Purification: silica gel column chromatography (hexane/AcOEt 8:1) followed by HPLC. Yield: 7%, colorless solid. Mp: 87.0–88.6 °C. TLC: R_f 0.21 (hexane/AcOEt 8:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 3H), 3.80 (s, 3H), 6.66 (d, *J* = 9.0 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 9.0 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 55.3, 113.3, 120.0 (q, *J* = 273.0 Hz), 126.2 (q, *J* = 3.0 Hz), 127.0, 127.9, 129.3, 130.8, 132.40, 132.45 (q, *J* = 37.3 Hz),

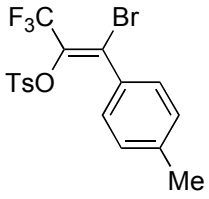
145.2, 160.6. ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.2 (s). IR (KBr): ν = 3062, 2956, 1622, 1604, 1508, 1382, 1303, 1261, 1182, 1157, 1066, 1028, 914, 833, 812, 731, 709, 696, 655, 596, 545, 522 cm^{-1}. MS (FAB) *m/z*: 453 (60, [M$^+$ + H] + 2), 451 (60, [M$^+$ + H]), 371 (2), 297 (100), 295 (100). Anal. Calcd for $C_{17}H_{14}BrF_3O_4S$: C, 45.25; H, 3.13. Found: C, 45.30; H, 3.25.

(*Z*)-1-Bromo-3,3,3-trifluoro-1-(4-tolyl)-2-tosyloxypropene (2c)



Purification: silica gel column chromatography (hexane/AcOEt 8:1) followed by recrystallization from hexane. Yield: 65%, colorless solid. Mp: 91.5–92.7 °C. TLC: R_f 0.28 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 3H), 2.48 (s, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 21.9, 119.1 (q, *J* = 274.4 Hz), 128.35, 128.37, 128.9, 129.6, 129.8 (q, *J* = 3.0 Hz), 131.6, 133.2, 133.9 (q, *J* = 37.4 Hz), 140.6, 145.8. ^{19}F NMR (282 MHz, $CDCl_3$): δ –60.4 (s). IR (KBr): ν = 3060, 2925, 1625, 1606, 1595, 1396, 1294, 1199, 1182, 1149, 1080, 918, 812, 800, 721, 692, 680, 663, 596, 545 cm^{-1}. MS (FAB) *m/z*: 437 (19, [M$^+$ + H] + 2), 435 (19, [M$^+$ + H]), 355 (6). Anal. Calcd for $C_{17}H_{14}BrF_3O_3S$: C, 46.91; H, 3.24. Found: C, 47.02; H, 3.30.

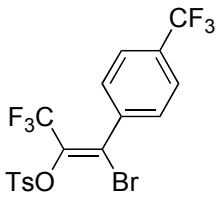
(*E*)-1-Bromo-3,3,3-trifluoro-1-(4-tolyl)-2-tosyloxypropene (2c)



Purification: silica gel column chromatography (hexane/AcOEt 8:1) followed by HPLC. Yield: 8%, colorless solid. Mp: 58.0–58.9 °C. TLC: R_f 0.36 (hexane/AcOEt 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.32 (s, 3H), 2.39 (s, 3H), 6.98 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 21.8, 119.9 (q, *J* = 273.8 Hz), 126.3 (q, *J* = 2.8 Hz), 127.9, 128.6, 129.0, 129.3, 132.1, 132.3, 132.9 (q, *J* = 37.0 Hz), 140.2, 145.2. ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.5 (s). IR (KBr): ν = 3062, 2922, 1622, 1608, 1595, 1386, 1294, 1193, 1180, 1157, 1068, 916, 812, 725, 707, 655, 543, 536 cm^{-1}. MS (FAB) *m/z*: 437 (31, [M$^+$ + H] + 2), 435 (31, [M$^+$ + H]), 355 (30), 281 (30), 221 (38), 207 (36). Anal. Calcd for

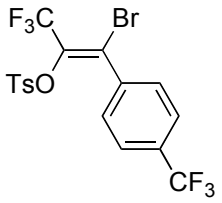
$C_{17}H_{14}BrF_3O_3S$: C, 46.91; H, 3.24. Found: C, 46.75; H, 3.24.

(*Z*)-1-Bromo-3,3,3-trifluoro-2-tosyloxy-1-(4-trifluoromethylphenyl)propene (2d)



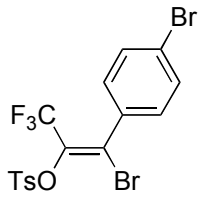
Purification: silica gel column chromatography (hexane/AcOEt 8:1) followed by HPLC. Yield: 77%, colorless solid. Mp: 57.0–58.3 °C. TLC: R_f 0.50 (hexane/AcOEt 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 (s, 3H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.9, 118.9 (q, *J* = 274.5 Hz), 123.3 (q, *J* = 269.9 Hz), 125.4 (q, *J* = 3.8 Hz), 127.2 (q, *J* = 2.3 Hz), 128.3, 128.8 (d, *J* = 1.5 Hz), 129.7, 132.1 (q, *J* = 38.8 Hz), 133.0, 135.2 (q, *J* = 39.3 Hz), 138.1 (d, *J* = 1.8 Hz), 146.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ –60.6 (s, 3F), –63.5 (s, 3F). IR (KBr): ν = 3070, 2931, 1624, 1593, 1396, 1330, 1294, 1201, 1149, 1080, 1066, 923, 850, 812, 727, 667, 642, 555, 547 cm^{-1}. MS (FAB) *m/z*: 491 (8, [M^+ + H] + 2), 489 (8, [M^+ + H]), 423 (30), 422 (100). Anal. Calcd for $C_{17}H_{11}BrF_6O_3S$: C, 41.74; H, 2.27. Found: C, 41.85; H, 2.25.

(*E*)-1-Bromo-3,3,3-trifluoro-2-tosyloxy-1-(4-trifluoromethylphenyl)propene (2d)



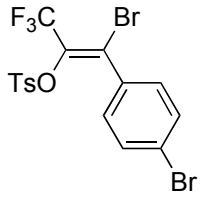
Purification: silica gel column chromatography (hexane/AcOEt 8:1) followed by HPLC. Yield: 12%, colorless oil. TLC: R_f 0.50 (hexane/AcOEt 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.35–7.39 (m, 4H), 7.42 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 119.5 (q, *J* = 274.5 Hz), 122.2 (q, *J* = 265.5 Hz), 124.9 (q, *J* = 3.0 Hz), 126.6 (d, *J* = 1.5 Hz), 127.8, 129.4, 129.6, 131.4 (q, *J* = 32.8 Hz), 132.1, 134.7 (q, *J* = 35.9 Hz), 138.5, 147.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ –63.0 (s, 3F), –63.5 (s, 3F). IR (neat): ν = 3070, 2929, 1616, 1596, 1392, 1325, 1299, 1195, 1180, 1149, 1132, 1068, 923, 835, 813, 731, 711, 657, 561 cm^{-1}. MS (FAB) *m/z*: 491 (8, [M^+ + H] + 2), 489 (8, [M^+ + H]), 471 (19), 469 (19), 427 (16), 425 (16). Anal. Calcd for $C_{17}H_{11}BrF_6O_3S$: C, 41.74; H, 2.27. Found: C, 41.70; H, 2.39.

(*Z*)-1-Bromo-1-(4-bromophenyl)-3,3,3-trifluoro-2-tosyloxypropene (2e)



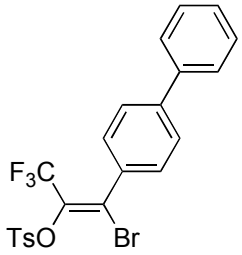
Purification: silica gel column chromatography (hexane/AcOEt 8:1) followed by recrystallization from hexane. Yield: 75%, colorless solid. Mp: 91.5–92.7 °C. TLC: R_f 0.31 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 (s, 3H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.9, 119.0 (q, *J* = 274.5 Hz), 124.8, 128.0 (q, *J* = 2.8 Hz), 128.3, 129.7, 129.9, 131.6, 133.1, 133.4, 134.6 (q, *J* = 37.3 Hz), 146.0. ^{19}F NMR (282 MHz, $CDCl_3$): δ –60.5 (s). IR (KBr): ν = 2960, 2931, 1593, 1583, 1485, 1396, 1290, 1199, 1180, 1147, 1080, 1012, 918, 804, 734 669, 644, 557, 547 cm^{-1}. MS (FAB) *m/z*: 503 (11, [M^+ + H] + 4), 501 (17, [M^+ + H] + 2), 499 (11, [M^+ + H]), 421 (3), 419 (3). Anal. Calcd for $C_{16}H_{11}Br_2F_3O_3S$: C, 38.42; H, 2.22. Found: C, 38.67; H, 2.39.

(*E*)-1-Bromo-1-(4-bromophenyl)-3,3,3-trifluoro-2-tosyloxypropene (2e)



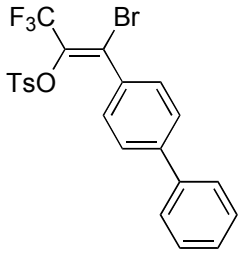
Purification: silica gel column chromatography (hexane/AcOEt 8:1) followed by HPLC. Yield: 10%, colorless solid. Mp: 118.5–119.0 °C. TLC: R_f 0.31 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (s, 3H), 7.11 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.9, 119.7 (q, *J* = 273.8 Hz), 124.3 (q, *J* = 3.0 Hz), 124.6, 127.8, 129.5, 130.5, 131.1, 131.6, 132.4, 133.8, 137.8 (q, *J* = 36.0 Hz), 145.8. ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.9 (s). IR (KBr): ν = 2962, 2925, 1595, 1583, 1483, 1379, 1303, 1288, 1193, 1172, 1149, 1072, 918, 810, 732, 711, 563, 540 cm^{-1}. MS (FAB) *m/z*: 503 (6, [M^+ + H] + 4), 501 (9, [M^+ + H] + 2), 499 (6, [M^+ + H]), 347 (6), 345 (9), 343 (6). Anal. Calcd for $C_{16}H_{11}Br_2F_3O_3S$: C, 38.42; H, 2.22. Found: C, 38.71; H, 2.16.

(*Z*)-1-Bromo-3,3,3-trifluoro-1-(biphenyl-4-yl)-2-tosyloxypropene(2f)



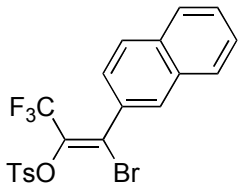
Purification: silica gel column chromatography (hexane/AcOEt 8:1). Yield: 84%, colorless solid. Mp: 135.5–137.7 °C. TLC: R_f 0.35 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.49 (s, 3H), 7.39–7.41 (m, 3H), 7.44–7.48 (m, 4H), 7.59–7.63 (m, 4H), 7.96 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.9, 119.1 (q, *J* = 274.5 Hz), 126.9, 127.0, 127.9, 128.3, 128.7, 128.9, 129.3 (q, *J* = 3.1 Hz), 129.7, 133.2, 133.3, 134.2 (q, *J* = 37.4 Hz), 139.5, 143.0, 145.9. ^{19}F NMR (282 MHz, $CDCl_3$): δ –60.3 (s). IR (KBr): ν = 3066, 3033, 1639, 1595, 1404, 1369, 1298, 1207, 1193, 1176, 1136, 1076, 921, 819, 812, 769, 756, 717, 690, 680, 623, 563 cm^{-1}. MS (FAB) *m/z*: 499 (30, [M^+ + H] + 2), 497 (30, [M^+ + H]), 417 (5), 343 (69), 341 (69). Anal. Calcd for $C_{22}H_{16}BrF_3O_3S$: C, 53.13; H, 3.24. Found: C, 52.86; H, 2.97.

(*E*)-1-Bromo-3,3,3-trifluoro-1-(biphenyl-4-yl)-2-tosyloxypropene (2f)



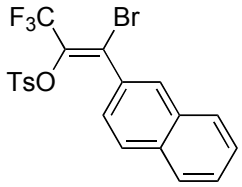
Purification: silica gel column chromatography (hexane/AcOEt 8:1). Yield: 12%, colorless solid. Mp: 129.4–130.2 °C. TLC: R_f 0.28 (hexane/AcOEt 8:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.48 (s, 3H), 7.38–7.48 (m, 7H), 7.59–7.64 (m, 4H), 7.96 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.9, 119.1 (q, *J* = 274.5 Hz), 126.9, 127.0, 127.9, 128.3, 128.7, 128.9 (d, *J* = 1.6 Hz), 129.3 (q, *J* = 3.1 Hz), 129.7, 133.2, 133.3, 134.2 (q, *J* = 36.6 Hz), 139.5, 143.0, 145.9. ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.7 (s). IR (KBr): ν = 3053, 3035, 1647, 1596, 1386, 1303, 1203, 1180, 1132, 1083, 925, 813, 756, 723, 711, 690, 659, 621, 563, 538 cm^{-1}. MS (FAB) *m/z*: 499 (25, [M^+ + H] + 2), 497 (25, [M^+ + H]), 343 (60), 341 (60). Anal. Calcd for $C_{22}H_{16}BrF_3O_3S$: C, 53.13; H, 3.24. Found: C, 53.02; H, 3.14.

(*Z*)-1-Bromo-3,3,3-trifluoro-1-(2-naphthyl)-2-tosyloxypropene (2g)



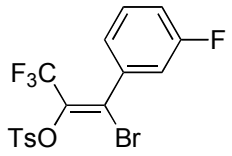
Purification: silica gel column chromatography (hexane/AcOEt 8:1). Yield: 69%, colorless solid. Mp: 78.5–79.0 °C. TLC: R_f 0.31 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.49 (s, 3H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 1H), 7.55–7.57 (m, 2H), 7.85-7.88 (m, 4H), 7.98 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.9, 119.2 (q, *J* = 274.5 Hz), 126.8, 127.60, 127.64, 128.33, 128.34, 128.38, 128.4, 129.6 (q, *J* = 3.1 Hz), 129.7, 131.7, 132.2, 133.2, 133.5, 134. 3 (q, *J* = 37.4 Hz), 145.9. ^{19}F NMR (282 MHz, $CDCl_3$): δ –60.3 (s). IR (KBr): ν = 3060, 2931, 1595, 1380, 1298, 1197, 1178, 1134, 1074, 925, 835, 825, 794, 750, 715, 688, 657, 592, 569, 561 cm^{-1}. MS (FAB) *m/z*: 473 (16, [M^+ + H] + 2), 471 (16, [M^+ + H]), 391 (3), 317 (34), 315 (34). Anal. Calcd for $C_{20}H_{14}BrF_3O_3S$: C, 50.97; H, 2.99. Found: C, 50.96; H, 3.00.

(*E*)-1-Bromo-3,3,3-trifluoro-1-(2-naphthyl)-2-tosyloxypropene (2g)



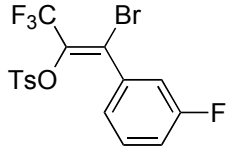
Purification: silica gel column chromatography (hexane/AcOEt 8:1) followed by recrystallization from hexane. Yield: 9%, colorless solid. Mp: 111.6–111.45 °C. TLC: R_f 0.24 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05 (s, 3H), 6.63 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 4.0 Hz, 2H), 7.35 (dd, *J* = 4.0, 2.0 Hz, 1H), 7.47–7.56 (m, 2H), 7.61–7.65 (m, 3H), 7.77 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 119.9 (q, *J* = 273.8 Hz), 125.6, 125.7 (q, *J* = 3.0 Hz), 126.5, 127.3, 127.5, 127.6, 127.7, 128.3, 128.9, 129.4, 132.05, 132.08, 132.3, 133.4, 134.5 (q, *J* = 32.0 Hz), 145.2. ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.7 (s). IR (KBr): ν = 3060, 2923, 1629, 1595, 1386, 1292, 1197, 1174, 1145, 1072, 918, 891, 864, 808, 731, 700, 657, 557, 547 cm^{-1}. MS (FAB) *m/z*: 473 (13, [M^+ + H] + 2), 471 (13, [M^+ + H]), 391 (3), 317 (36), 315 (36). Anal. Calcd for $C_{20}H_{14}BrF_3O_3S$: C, 50.97; H, 2.99. Found: C, 50.98; H, 3.10.

(*Z*)-1-Bromo-3,3,3-trifluoro-1-(3-fluorophenyl)-2-tosyloxypropene (2h)



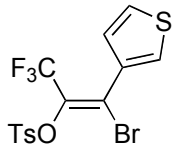
Purification: silica gel column chromatography (hexane/AcOEt 8:1). Yield: 77%, colorless solid. Mp: 61.6–63.2 °C. TLC: R_f 0.32 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 (s, 3H), 7.08–7.15 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.35–7.40 (m, 3H), 7.93 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.9, 115.6 (d, *J* = 24.4 Hz), 117.3 (d, *J* = 20.6 Hz), 119.0 (q, *J* = 274.5 Hz), 124.2 (d, *J* = 1.6 Hz), 127.5 (q, *J* = 3.1 Hz), 128.3, 129.7, 130.0 (d, *J* = 8.4 Hz), 133.1, 134.9 (q, *J* = 37.3 Hz), 136.3 (d, *J* = 7.6 Hz), 146.0, 161.8 (d, *J* = 246.2 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ –60.7 (s, 3F), –112.2 (td, *J* = 9.0, 4.5 Hz, 1F). IR (KBr): ν = 3060, 1647, 1587, 1384, 1303, 1267, 1195, 1180, 1149, 1080, 839, 792, 734, 692, 663, 543 cm^{-1}. MS (FAB) *m/z*: 441 (11, [M^+ + H] + 2), 439 (11, [M^+ + H]), 359 (3), 285 (27), 283 (27). Anal. Calcd for $C_{16}H_{11}BrF_4O_3S$: C, 43.75; H, 2.52. Found: C, 43.74; H, 2.60.

(*E*)-1-Bromo-3,3,3-trifluoro-1-(3-fluorophenyl)-2-tosyloxypropene (2h)



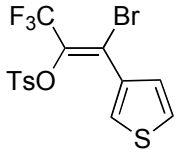
Purification: silica gel column chromatography (hexane/AcOEt 8:1) followed by recrystallization from hexane. Yield: 10%, colorless solid. Mp: 76.2–76.6 °C. TLC: R_f 0.24 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 6.85 (dt, *J* = 9.0, 2.4 Hz, 1H), 6.95 (tdd, *J* = 2.4, 1.2, 0.8 Hz, 1H), 7.09 (t, *J* = 1.2 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.19 (td, *J* = 8.0, 5.6 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 116.3 (d, *J* = 23.6 Hz), 116.8 (d, *J* = 21.4 Hz), 119.6 (q, *J* = 273.7 Hz), 124.8, 128.0, 129.5, 129.6, 129.4 (q, *J* = 2.0 Hz), 131.8, 138.3 (q, *J* = 37.0 Hz), 145.8, 148.4, 161.8 (d, *J* = 245.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ –62.8 (s, 3F), –112.5 (td, *J* = 9.0, 4.5 Hz, 1F). IR (KBr): ν = 3074, 2920, 1625, 1587, 1388, 1296, 1201, 1180, 1143, 1074, 871, 798, 788, 705, 694, 682, 557, 543 cm^{-1}. MS (FAB) *m/z*: 439 (18, [M^+ + H] + 2), 437 (18, [M^+ + H]). Anal. Calcd for $C_{16}H_{11}BrF_4O_3S$: C, 43.75; H, 2.52. Found: C, 43.77; H, 2.68.

(*Z*)-1-Bromo-3,3,3-trifluoro-1-(3-thienyl)-2-tosyloxypropene (2i)



Purification: silica gel column chromatography (hexane/AcOEt 8:1). Yield: 72%, colorless solid. Mp: 82.5–83.0 °C. TLC: R_f 0.20 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.51 (s, 3H), 7.15 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.35 (dd, *J* = 4.8, 2.8 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.51 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.9, 119.2 (q, *J* = 274.5 Hz), 123.9 (q, *J* = 3.5 Hz), 126.2, 127.5 (d, *J* = 2.3 Hz), 127.7, 128.3, 129.7, 133.1, 133.7, 134.1 (d, *J* = 37.4 Hz), 145.9. ^{19}F NMR (282 MHz, $CDCl_3$): δ –60.3 (s). IR (KBr): ν = 3105, 1595, 1394, 1290, 1197, 1182, 1145, 1078, 846, 810, 790, 763, 688, 671, 657, 611, 549 cm^{-1}. MS (FAB) *m/z*: 429 (50, [M^+ + H] + 2), 427 (50, [M^+ + H]), 347 (8), 273 (75), 271 (75). Anal. Calcd for $C_{14}H_{10}BrF_3O_3S_2$: C, 39.36; H, 2.36. Found: C, 39.26; H, 2.19.

(*E*)-1-Bromo-3,3,3-trifluoro-1-(3-thienyl)-2-tosyloxypropene (2i)



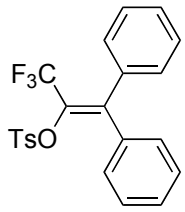
Purification: silica gel column chromatography (hexane/AcOEt 8:1) followed by recrystallization from hexane. Yield: 8%, colorless solid. Mp: 77.3–78.5 °C. TLC: R_f 0.13 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 7.10-7.16 (m, 4H), 7.46 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8, 120.0 (q, *J* = 273.7 Hz), 120.3 (q, *J* = 2.0 Hz), 125.3, 127.9, 128.1, 129.43, 129.44 (q, *J* = 53.0 Hz), 129.6, 131.8, 134.9, 145.6. ^{19}F NMR (282 MHz, $CDCl_3$): δ –61.9 (s). IR (KBr): ν = 3136, 1618, 1593, 1386, 1288, 1203, 1176, 1136, 1072, 802, 790, 707, 698, 675, 650, 632, 561, 542 cm^{-1}. MS (FAB) *m/z*: 429 (8, [M^+ + H] + 2), 427 (8, [M^+ + H]), 273 (8), 271 (8). Anal. Calcd for $C_{14}H_{10}BrF_3O_3S_2$: C, 39.36; H, 2.36. Found: C, 39.21; H, 2.51.

General Procedure for Cross-coupling Reaction of (*Z*)-2 with Arylboronic acids

To a vial tube (5 mL) equipped with a magnetic stirring bar were added $Pd(PPh_3)_4$ (11 mg, 10 μmol) and (*Z*)-**2** (0.20 mmol), and arylboronic acid (0.24 mmol). The vial tube was then capped with a rubber septum, evacuated for 5 min and charged with argon. The evacuation–purge

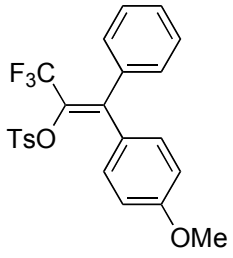
operation was repeated twice. Toluene (2 mL) and 5 M aq. Cs_2CO_3 (0.08 mL, 0.4 mmol) was added to the mixture at room temperature under an argon atmosphere. After stirred at room temperature for 5 min, the solution was heated on the hot plate at 100 °C for 24 h. Upon completion of the reaction, the reaction mixture was allowed to cool to room temperature, diluted wit EtOAc (3 mL), and filtered through a pad of Florisil. To the filtrate was added water (5 mL) and the aqueus layer was extracted with EtOAc (3 mL × 3). The combined organic layer was washed with sat. aq. NaCl (10 mL), dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by preparative TLC.

3,3,3-Trifluoro-1,1-diphenyl-2-tosyloxypropene (3aa)



Purification: preparative TLC (hexane/AcOEt 8:1). Yield: 97%, colorless solid. Mp: 124.0–125.2 °C. TLC: R_f 0.39 (hexane/AcOEt 4:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 3H), 7.00 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.6 Hz, 2H), 7.13-7.26 (m, 5H), 7.32–7.38 (m, 3H), 7.44 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 120.2 (q, *J* = 273.7 Hz), 127.8, 127.9, 128.0, 128.6, 128.9, 129.1, 129.1, 129.3, 129.6, 132.1, 136.3 (q, *J* = 76.3 Hz), 144.0 (q, *J* = 2.5 Hz), 144.9. ^{19}F NMR (282 MHz, $CDCl_3$): δ –59.7 (s). IR (KBr): ν = 3055, 3037, 1633, 1595, 1446, 1367, 1305, 1278, 1195, 1176, 1126, 1056, 777, 769, 738, 729, 717, 702, 655, 617, 559 cm^{-1}. MS (FAB) *m/z*: 419 (41, [M^+ + H]), 418 (4, M^+), 399 (8), 264 (23), 263 (100). Anal. Calcd for $C_{22}H_{17}F_3O_3S$: C, 63.15; H, 4.10. Found: C, 63.21; H, 4.07.

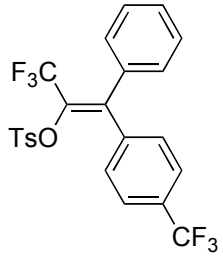
(*Z*)-3,3,3-Trifluoro-1-(4-methoxyphenyl)-1-phenyl-2-tosyloxypropene (3ab)



Purification: preparative TLC (hexane/AcOEt 8:1). Yield: 88%, colorless solid. Mp: 116.6–117.8 °C. TLC: R_f 0.36 (hexane/AcOEt 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.37 (s, 3H), 3.78 (s, 3H), 6.64 (d, *J* = 6.6 Hz, 2H), 6.94 (d, *J* = 6.9 Hz, 2H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.15–7.18

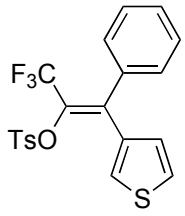
(m, 2H), 7.32–7.36 (m, 3H), 7.49 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 55.2, 113.1, 120.4 (q, J = 273.0 Hz), 127.9, 128.9, 129.1, 129.22, 129.24, 130.1 (q, J = 35.8 Hz), 131.3, 132.4, 136.1, 143.5 (q, J = 1.9 Hz), 144.8, 159.8. ^{19}F NMR (282 MHz, $CDCl_3$): δ –59.4 (s). IR (KBr): ν = 3066, 3008, 2960, 1600, 1510, 1382, 1325, 1305, 1255, 1176, 1163, 1126, 1066, 943, 831, 752, 729, 702, 677, 549 cm^{-1}. MS (FAB) *m/z*: 449 (61, [M^+ + H]), 448 (8, M^+), 294 (55), 293 (100). Anal. Calcd for $C_{23}H_{19}F_3O_4S$: C, 61.60; H, 4.27. Found: C, 61.68; H, 4.32.

(*Z*)-3,3,3-Trifluoro-1-phenyl-2-tosyloxy-1-(4-trifluoromethylphenyl)propene (3ad)



Purification: preparative TLC (hexane/AcOEt 8:1). Yield: 83%, colorless solid. Mp: 110.2–116.5 °C. TLC: R_f 0.35 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 3H), 7.07 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.19 (dd, J = 7.6, 1.6 Hz, 2H), 7.35–7.42 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 119.9 (q, J = 273.7 Hz), 123.5 (q, J = 269.9 Hz), 124.7 (q, J = 3.8 Hz), 127.7, 128.3, 129.0 (d, J = 1.4 Hz), 129.3, 129.4, 129.9, 130.3 (q, J = 32.8 Hz), 132.2 (q, J = 37.0 Hz), 132.2, 135.0, 140.2, 142.3 (q, J = 1.4 Hz), 145.4. ^{19}F NMR (282 MHz, $CDCl_3$): δ –60.2 (s, 3F), –63.3 (s, 3F). IR (KBr): ν = 3049, 3031, 1595, 1409, 1377, 1325, 1193, 1176, 1147, 1112, 1058, 1016, 939, 842, 813, 729, 715, 702, 650, 561 cm^{-1}. MS (FAB) *m/z*: 487 (35, [M^+ + H]), 486 (3, M^+), 467 (29), 331 (100). Anal. Calcd for $C_{23}H_{16}F_6O_3S$: C, 56.79; H, 3.32. Found: C, 56.84; H, 3.30.

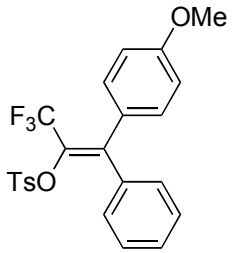
(*Z*)-3,3,3-Trifluoro-1-phenyl-1-(3-thienyl)-2-tosyloxypropene (3ai)



Purification: preparative TLC (hexane/AcOEt 8:1). Yield: 60%, colorless solid. Mp: 112.6–113.3 °C. TLC: R_f 0.17 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3H), 6.93 (dd, J = 3.2 Hz, 1.2 Hz, 1H), 6.97 (dd, J = 5.2, 1.2 Hz, 1H), 7.12 (dd, J = 5.2, 3.2 Hz, 1H),

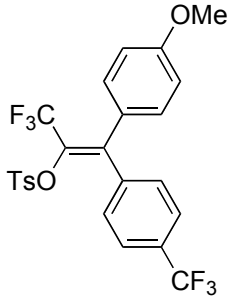
7.15–7.19 (m, 4H), 7.33–7.39 (m, 3H), 7.63 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 120.3 (q, J = 273.7 Hz), 124.7, 127.9, 128.2, 128.5, 128.9, 129.0, 129.1, 129.3, 130.4 (q, J = 35.8 Hz), 131.8, 135.5, 137.1, 138.2 (q, J = 2.9 Hz), 145.3. ^{19}F NMR (282 MHz, $CDCl_3$): δ –58.9 (s). IR (KBr): ν = 3114, 1633, 1596, 1369, 1307, 1265, 1193, 1178, 1157, 1128, 1056, 956, 916, 804, 763, 723, 702, 648, 561 cm^{-1}. MS (FAB) *m/z*: 425 (44, [M^+ + H]), 424 (2, M^+), 270 (23), 269 (100). Anal. Calcd for $C_{20}H_{15}F_3O_3S_2$: C, 56.59; H, 3.56. Found: C, 56.52; H, 3.58.

(*E*)-3,3,3-Trifluoro-1-(4-methoxyphenyl)-1-phenyl-2-tosyloxypropene (3ba)



Purification: preparative TLC (hexane/AcOEt 8:1). Yield: 82%, colorless solid. Mp: 90.2–92.4 °C. TLC: R_f 0.12 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 3H), 3.82 (s, 3H), 6.86 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 7.2 Hz, 2H), 7.08–7.17 (m, 6H), 7.20-7.25 (m, 1H), 7.42 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 55.2, 120.4 (q, J = 273.0 Hz), 127.7, 127.9, 128.2, 128.6, 129.2, 129.8, 130.1 (q, J = 36.0 Hz), 130.7, 132.1, 137.0, 144.0 (q, J = 1.8 Hz), 144.9, 160.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ –59.6 (s). IR (KBr): ν = 3055, 3035, 2976, 1606, 1510, 1363, 1294, 1274, 1247, 1195, 1168, 1122, 1055, 1029, 941, 829, 815, 771, 744, 717, 624, 543 cm^{-1}. MS (FAB) *m/z*: 449 (72, [M^+ + H]), 448 (8, M^+), 429 (8), 294 (52), 293 (100). Anal. Calcd for $C_{23}H_{19}F_3O_4S$: C, 61.60; H, 4.27. Found: C, 61.38; H, 4.40.

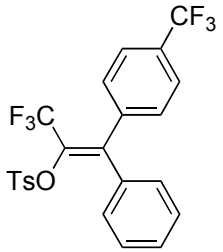
(*E*)-3,3,3-Trifluoro-1-(4-methoxyphenyl)-2-tosyloxy-1-(4-trifluoromethylphenyl)propene (3bd)



Purification: preparative TLC (hexane/AcOEt 8:1). Yield: 70%, colorless solid. Mp: 87.4–89.2 °C. TLC: R_f 0.09 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3H), 3.79 (s, 3H), 6.64 (d, J = 6.8 Hz, 2H), 6.93 (d, J = 6.8 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 7.6 Hz, 2H), 7.35

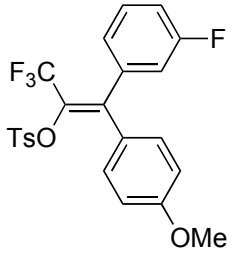
(d, J = 7.6 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 55.3, 113.7, 120.1 (q, J = 272.9 Hz), 123.6 (q, J = 270.2 Hz), 124.6 (q, J = 3.8 Hz), 127.2, 127.7, 129.4, 130.1, 130.3 (q, J = 32.3 Hz), 130.7, 131.4 (q, J = 38.5 Hz), 132.3, 140.6, 142.3 (q, J = 2.7 Hz), 145.3, 160.3. ^{19}F NMR (282 MHz, $CDCl_3$): δ –60.1 (s, 3F), –63.3 (s, 3F). IR (KBr): ν = 3024, 2977, 2939, 1606, 1595, 1512, 1407, 1373, 1326, 1298, 1253, 1197, 1168, 1130, 1110, 1058, 1029, 844, 829, 813, 744, 715, 655, 561 cm^{-1}. MS (FAB) *m/z*: 517 (60, [M^+ + H]), 516 (8, M^+), 497 (14), 362 (69), 361 (100). Anal. Calcd for $C_{24}H_{18}F_6O_4S$: C, 55.81; H, 3.51. Found: C, 56.05; H, 3.69.

(*E*)-3,3,3-Trifluoro-1-phenyl-2-tosyloxy-1-(4-trifluoromethylphenyl)propene (3da)



Purification: preparative TLC (hexane/AcOEt 8:1). Yield: 97%, colorless solid. Mp: 110.0–111.0 °C. TLC: R_f 0.23 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3H), 7.00 (d, J = 7.2 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 7.18 (t, J = 7.2 Hz, 2H), 7.23–7.25 (m, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 120.0 (q, J = 273.8 Hz), 123.6 (q, J = 270.0 Hz), 125.1 (q, J = 3.8 Hz), 127.9, 128.1, 129.0, 129.3, 129.5 (d, J = 2.2 Hz), 129.5, 131.0 (q, J = 32.0 Hz), 131.7 (q, J = 36.6 Hz), 132.1, 136.0, 139.6, 142.5 (q, J = 3.0 Hz), 145.2. ^{19}F NMR (282 MHz, $CDCl_3$): δ –59.9 (s, 3F), –63.3 (3F). IR (KBr): ν = 3043, 1645, 1618, 1595, 1409, 1371, 1325, 1180, 1136, 1118, 1062, 945, 833, 773, 731, 719, 673, 563 cm^{-1}. MS (FAB) *m/z*: 487 (42, [M^+ + H]), 467 (15), 332 (28), 331 (100). Anal. Calcd for $C_{23}H_{16}F_6O_3S$: C, 56.79; H, 3.32. Found: C, 57.07; H, 3.62.

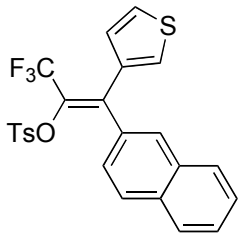
(*E*)-3,3,3-Trifluoro-1-(3-fluorophenyl)-1-(4-methoxyphenyl)-2-tosyloxypropene (3hb)



Purification: preparative TLC (hexane/AcOEt 8:1). Yield: 90%, colorless solid. Mp: 136.0–136.6 °C. TLC: R_f 0.10 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3H),

3.79 (s, 3H), 6.65 (d, *J* = 8.8 Hz, 2H), 6.87 (dt, *J* = 9.2, 2.4 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 7.05–7.08 (m, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.30–7.35 (m, 1H), 7.48 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 55.2, 113.3, 116.0 (d, *J* = 21.4 Hz), 116.3 (d, *J* = 22.1 Hz), 120.2 (q, *J* = 272.9 Hz), 125.1, 128.3, 128.6 (d, *J* = 122.8 Hz), 129.6 (d, *J* = 8.4 Hz), 130.6 (d, *J* = 35.9 Hz), 131.3, 132.4, 138.1 (d, *J* = 7.6 Hz), 142.2 (q, *J* = 1.9 Hz), 144.9, 160.0, 160.8, 163.2. ^{19}F NMR (282 MHz, $CDCl_3$): δ –59.7 (s, 3F), –113.1 (m, 1F). IR (KBr): ν = 3070, 2964, 1600, 1585, 1510, 1487, 1380, 1280, 1255, 1193, 1178, 1132, 1068, 829, 732, 673, 555, 522 cm^{-1}. MS (FAB) *m/z*: 467 (35, [M^+ + H]), 466 (5, M^+), 423 (17), 422 (54), 312 (20), 311 (100). Anal. Calcd for $C_{23}H_{18}F_4O_4S$: C, 59.22; H, 3.89. Found: C, 59.18; H, 3.97.

(*E*)-3,3,3-Trifluoro-1-(2-naphthyl)-1-(3-thienyl)-2-tosyloxypropene (3ig)



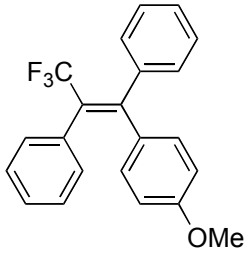
Purification: preparative TLC (hexane/AcOEt 8:1). Yield: 88%, colorless solid. Mp: 124.0–125.3 °C. TLC: R_f 0.13 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.08 (s, 3H), 6.63 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 4.8 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.24 (d, *J* = 9.6 Hz, 2H), 7.28–7.29 (m, 2H), 7.40–7.61 (m, 5H), 7.76 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 120.4 (q, *J* = 272.9 Hz), 125.7, 126.1, 126.5, 126.9, 127.30, 127.34, 127.5, 128.1, 128.41, 128.42, 128.8, 129.6, 130.8 (q, *J* = 42.8 Hz), 132.1, 132.4, 132.9, 133.4, 135.3, 138.5 (q, *J* = 2.1 Hz), 144.8. ^{19}F NMR (282 MHz, $CDCl_3$): δ –59.8 (s). IR (KBr): ν = 3120, 3055, 1620, 1595, 1415, 1384, 1299, 1265, 1191, 1178, 1149, 1122, 1064, 850, 812, 775, 740, 721, 705, 663, 551 cm^{-1}. MS (FAB) *m/z*: 475 (31, [M^+ + H]), 474 (8, M^+), 423 (31), 422 (85), 320 (28), 319 (100). Anal. Calcd for $C_{24}H_{17}F_3O_3S_2$: C, 60.75; H, 3.61. Found: C, 60.52; H, 3.64.

General Procedure for Cross-coupling Reaction of 3 with Arylboronic acids

To a vial (5 mL) equipped with a magnetic stirring bar were added $Pd(OAc)_2$ (0.5 mg, 2 μmol), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (2.5 mg, 5 μmol), **3** (0.10 mmol), and arylboronic acid (0.20 mmol). The vial was then capped with a rubber septum, evacuated for 5 min and purged with argon. The evacuation–purge operation was repeated twice. THF (0.5 mL) and 2 M aq. K_3PO_4 (0.15 mL, 0.3 mmol) was added to the mixture under an argon atmosphere.

After stirred at room temperature for 5 min, the mixture was heated on a hot plate at 80 °C for 2 h. Upon completion of the reaction, the resulting mixture was allowed to cool to room temperature, diluted with Et_2O (5 mL), and filtered through a pad of Florisil. To the filtrate was added water (10 mL), and the aqueous layer was extracted with Et_2O (5 mL x 3). The combined organic layer was washed with sat. aq. NaCl (15 mL), dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by preparative TLC followed by recrystallization from hexane.

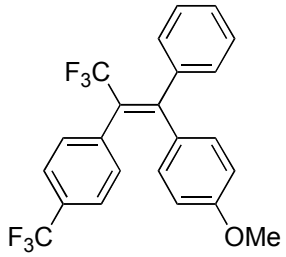
(*E*)-3,3,3-Trifluoro-1-(4-methoxyphenyl)-1,2-diphenylpropene (4aba)



Purification: preparative TLC (hexane/AcOEt 8:1). Yield: 95%.

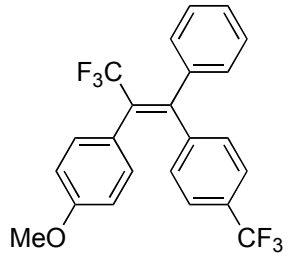
Compound data was identical to those reported in the reference (Liu, X.; Shimizu, M.; Hiyama, T. *Angew. Chem. Int. Ed.* **2004,** *43,* 879).

(*E*)-3,3,3-Trifluoro-1-(4-methoxyphenyl)-1-phenyl-2-(4-trifluoromethylphenyl)propene (4abd)



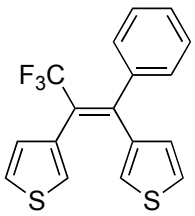
Purification: preparative TLC (hexane/AcOEt 8:1). Yield: 96%, colorless solid. Mp: 104.7–105.3 °C. TLC: R_f 0.42 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.69 (s, 3H), 6.57 (d, *J* = 9.2 Hz, 2H), 6.78 (d, *J* = 9.2 Hz, 2H), 7.28 (dd, *J* = 8.0, 5.6 Hz, 2H), 7.35–7.39 (m, 5H), 7.50 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.1, 109.6, 113.1, 123.2 (q, *J* = 272.4 Hz), 123.8 (q, *J* = 269.9 Hz), 124.8 (q, *J* = 3.8 Hz), 127.8, 127.9, 128.4, 129.6 (q, *J* = 32.0 Hz), 131.2, 131.8, 132.4, 139.1, 140.1, 151.0 (q, *J* = 3.0 Hz), 158.8. ^{19}F NMR (282 MHz, $CDCl_3$): δ –55.7 (s, 3F), –63.1 (s, 3F). IR (KBr): ν = 3058, 3006, 2993, 1602, 1510, 1467, 1444, 1326, 1307, 1261, 1224, 1184, 1166, 1136, 1109, 1068, 1033, 1022, 983, 827, 790, 700, 677, 567 cm^{-1}. MS (FAB) *m/z*: 423 (65, [M^+ + H]), 422 (100, M^+), 403 (18). Anal. Calcd for $C_{23}H_{16}F_6O$: C, 65.40; H, 3.82. Found: C, 65.38; H, 3.86.

(*E*)-3,3,3-Trifluoro-2-(4-methoxyphenyl)-1-phenyl-1-(4-trifluoromethylphenyl)propene (4adb)



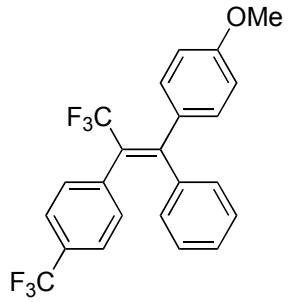
Purification: preparative TLC (hexane/AcOEt 8:1). Yield: 96%, colorless solid. Mp: 71.7–72.4 °C. TLC: R_f 0.44 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77 (s, 3H), 6.75 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H), 7.28 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.34–7.40 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.1, 113.5, 123.2 (q, *J* = 271.7 Hz), 123.7 (q, *J* = 269.9 Hz), 124.6 (q, *J* = 3.9 Hz), 126.2, 128.00, 128.04, 128.3 (d, *J* = 2.2 Hz), 128.9 (q, *J* = 32.8 Hz), 129.8, 130.1 (q, *J* = 27.7 Hz), 132.3, 139.6, 144.6, 148.3 (q, *J* = 3.7 Hz), 159.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ –56.8 (s, 3F), –63.2 (s, 3F). IR (KBr): ν = 2962, 2935, 1614, 1514, 1323, 1294, 1255, 1226, 1168, 1143, 1109, 1064, 1018, 813, 736, 700, 648, 534 cm^{-1}. MS (FAB) *m/z*: 423 (39, [M^+ + H]), 422 (100, M^+), 403 (10), 353 (4), 345 (4). Anal. Calcd for $C_{23}H_{16}F_6O$: C, 65.40; H, 3.82. Found: C, 65.18; H, 3.99.

(*E*)-3,3,3-Trifluoro-1-phenyl-1,2-bis(3-thienyl)propene (4aii)



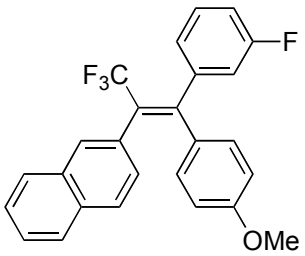
Purification: preparative TLC (hexane/AcOEt 8:1). Yield: 91%, colorless solid. Mp: 52.3–53.0 °C. TLC: R_f 0.50 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.37 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.67 (dd, *J* = 3.2, 1,2 Hz, 1H), 6.96–6.99 (m, 2H), 7.24–7.28 (m, 3H), 7.32–7.37 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 119.6, 120.5 (q, *J* = 272.2 Hz), 124.2, 125.2, 126.0 (q, *J* = 28.2 Hz), 126.4, 127.7, 127.8, 127.9, 128.3, 128.4, 129.8, 134.8 (q, *J* = 1.6 Hz), 140.1, 141.5. ^{19}F NMR (282 MHz, $CDCl_3$): δ –56.5 (s). IR (KBr): ν = 3105, 3093, 1618, 1558, 1442, 1301, 1257, 1222, 1184, 1157, 1112, 1072, 1004, 839, 794, 771, 732, 704, 686, 650, 594 cm^{-1}. MS (FAB) *m/z*: 337 (21, [M^+ + H]), 336 (69, M^+). Anal. Calcd for $C_{17}H_{11}F_3S_2$: C, 60.70; H, 3.30. Found: C, 60.93; H, 3.34.

(*Z*)-3,3,3-Trifluoro-1-(4-methoxyphenyl)-1-phenyl-2-(4-trifluoromethylphenyl)propene (4bad)



Purification: preparative TLC (hexane/AcOEt 8:1). Yield: 95%, colorless solid. Mp: 125.5–126.7 °C. TLC: R_f 0.33 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 3H), 6.87–6.91 (m, 4H), 7.05–7.07 (m, 3H), 7.22 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.2, 113.3, 123.2 (q, *J* = 276.0 Hz), 123.7 (q, *J* = 269.9 Hz), 124.7 (q, *J* = 3.8 Hz), 127.6, 127.7, 129.5, 129.6 (q, *J* = 32.8 Hz), 129.8, 129.9, 131.8, 132.1, 138.9, 140.6, 151.4 (q, *J* = 2.6 Hz), 159.3. ^{19}F NMR (282 MHz, $CDCl_3$): δ –56.2 (s, 3F), –63.4 (s, 3F). IR (KBr): ν = 3003, 2979, 1604, 1573, 1508, 1469, 1325, 1290, 1249, 1178, 1143, 1118, 1066, 1033, 1020, 821, 761, 696, 624, 570 cm^{-1}. MS (FAB) *m/z*: 423 (32, [M^+ + H]), 422 (100, M^+), 403 (5). Anal. Calcd for $C_{23}H_{16}F_6O$: C, 65.40; H, 3.82. Found: C, 65.21; H, 4.07.

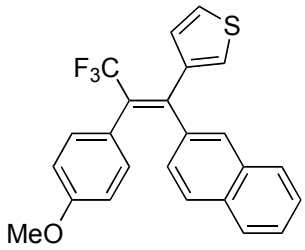
(*Z*)-3,3,3-Trifluoro-1-(3-fluorophenyl)-1-(4-methoxyphenyl)-2-(2-naphthyl)propene (4hbg)



Purification: preparative TLC (hexane/AcOEt 8:1). Yield: 90%, colorless solid. Mp: 120.6–121.7 °C. TLC: R_f 0.30 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.62 (s, 3H), 6.51 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 7.03–7.08 (m, 2H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.31–7.39 (m, 2H), 7.43–7.49 (m, 2H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.74–7.79 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.0, 109.6, 113.1, 114.7 (d, *J* = 20.6 Hz), 115.7 (d, *J* = 23.6 Hz), 123.5 (q, *J* = 273.8 Hz), 124.3, 126.1 (d, *J* = 33.5 Hz), 127.4 (d, *J* = 7.6 Hz), 128.0, 128.5 (q, *J* = 28.2 Hz), 128.9, 129.3 (d, *J* = 8.4 Hz), 130.5, 131.2, 132.2, 132.3, 132.4, 132.7, 142.7 (d, *J* = 7.6 Hz), 148.4-148.6 (m), 158.6, 160.9, 163.3. ^{19}F NMR (282 MHz, $CDCl_3$): δ –55.8 (s, 3F), –113.8 (q, *J* = 9.6 Hz, 1F). IR (KBr): ν = 3058, 3006, 2956, 2837, 1606, 1583, 1510, 1461, 1433, 1319, 1303, 1249, 1166, 1155, 1105, 1029, 831, 817, 794, 765, 750, 522 cm^{-1}. MS (FAB) *m/z*: 423 (50, [M^+ + H]), 422 (100,

M^+), 403 (4), 353 (5). Anal. Calcd for $C_{26}H_{18}F_4O$: C, 73.93; H, 4.30. Found: C, 74.05; H, 4.30.

(*Z*)-3,3,3-Trifluoro-2-(4-methoxyphenyl)-1-(2-naphthyl)-1-(3-thienyl)propene (4igb)



Purification: preparative TLC (hexane/AcOEt 8:1). Yield: 95%, colorless solid. Mp: 137.0–137.9 °C. TLC: R_f 0.25 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.70 (s, 3H), 6.68 (d, *J* = 8.8 Hz, 2H), 6.96 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.03 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.17 (d, *J* = 9.2 Hz, 2H), 7.28 (dd, *J* = 4.8 Hz, 2.8 Hz, 1H), 7.36–7.40 (m, 4H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.1, 113.3, 123.6 (q, *J* = 273.7 Hz), 124.80, 124.83, 125.8, 126.2, 127.00, 127.04, 127.2, 127.3, 128.0, 128.6 (d, *J* = 1.5 Hz), 129.26 (q, *J* = 28.9 Hz), 129.28, 132.1, 132.5, 132.6, 138.3, 140.0, 144.6 (q, *J* = 3.1 Hz), 158.8. ^{19}F NMR (282 MHz, $CDCl_3$): δ –56.6 (s). IR (KBr): ν = 3112, 3007, 1606, 1510, 1465, 1319, 1288, 1249, 1157, 1103, 1028, 1002, 840, 827, 815, 759, 690, 540 cm^{-1}. MS (FAB) *m/z*: 411 (21, [M^+ + H]), 410 (53, M^+). Anal. Calcd for $C_{24}H_{17}F_3OS$: C, 70.23; H, 4.17. Found: C, 70.42; H, 4.14.

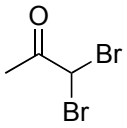
One-pot synthesis of 4aba

To a vial (5 mL) equipped with a magnetic stirring bar were added $PdCl_2(PPh_3)_2$ (7.0 mg, 10 μmol), P(*m*-tolyl)$_3$ (3.0 mg, 10 μmol), **1** (85 mg, 0.20 mmol), and phenylboronic acid (28 mg, 0.22 mmol). The tube was then capped with a rubber septum, evacuated for 5 min. and purged with argon. The evacuation–purge operation was repeated twice. Toluene (2 mL) and 5 M aq. Cs_2CO_3 (0.08 mL, 0.40 mmol) was added to the mixture at room temperature under an argon atmosphere. After stirred at room temperature for 5 min, the mixture was heated on a hot plate at 80 °C for 24 h. Upon completion of the reaction, the mixture was allowed to cool to room temperature. To the vial *p*-methoxyphenylboronic acid (36 mg, 0.24 mmol) and 5 M aq. Cs_2CO_3 (0.08 mL, 0.40 mmol) were added under an argon atmosphere. The resulting mixture was heated again on a hot plate at 100 °C. After 24 h, the reaction mixture was allowed to cool to room temperature. To the vial were added $Pd(OAc)_2$ (2.5 mg, 10 μmol), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (10 mg, 20 μmol), phenylboronic acid (27 mg, 0.40 mmol), THF (1 mL), and 2 M aq. K_3PO_4 (0.30 mL, 0.60 mmol) under an argon atmosphere.

After stirred for 5 min at room temperature, the solution was heated on a hot plate at 80 °C for 12 h. Upon completion of the reaction, the reaction mixture was diluted with EtOAc (5 mL) and filtered through a pad of Florisil. To the filtrate was added water (10 mL), and the aqueous layer was extracted with EtOAc (5 mL x 3). The combined organic layer was washed with sat. aq. NaCl (15 mL), dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by preparative TLC and recrystallization from hexane, giving rise to **4aba** (49 mg, 69% yield).

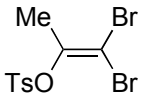
Preparation of 1,1-dibromopropan-2-one

1,1-Dibromopropan-2-one was prepared in 87% yield according to the procedure reported in the literature [Barluenga, J.; Llavona, L.; Concellón, J. M.; Yus, M. *J. Chem. Soc., Perkin Trans. 1* **1991,** 297].



Purification: distillation (70 °C/53 Torr). Colorless liquid. TLC: R_f 0.44 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.57 (s, 3H), 5.75 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.3, 42.9, 194.1. IR (neat): ν = 3016, 2927, 1732, 1703, 1421, 1359, 1245, 1213, 1147, 721, 677, 553 cm^{-1}. MS (EI) *m/z*: 218 (27, $M^+ + 4$), 216 (58, $M^+ + 2$), 214 (27, M^+), 175 (48), 173 (100), 171 (48). Anal. Calcd for $C_3H_4Br_2O$: C, 16.69; H, 1.87. Found: C, 16.94; H, 1.93.

Preparation of 1,1-dibromo-2-tosyloxypropene (5a)

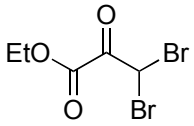


To a solution of 1,1-dibromopropan-2-one (0.65 g, 3.0 mmol) in THF (10 mL) was added lithium hexamethyldisilazide (1.6 M in THF solution, 2.0 mL) dropwise at –78 °C over a period of 10 min. After stirred at –78 °C for 20 min, the solution was added *p*-toluenesulfonic anhydride (1.07 g, 3.3 mmol) in one portion, and stirred at -78 °C for 30 min and then at –50 °C ~ –40 °C for 1h. The mixture was warmed to 0 °C over a period of 30 min before quenching with sat. aq. NH_4Cl. The aqueous layer was extracted with diethyl ether (10 mL x 3). The combined organic layer was washed with sat. aq. NaCl, dried over anhydrous $MgSO_4$, and concentrated in vacuo. Purification of the crude product by silica gel column chromatography (hexane/AcOEt 8:1) followed by recrystallization from hexane gave **5a** (0.34 g, 31% yield) as a colorless solid.

Mp: 53.2–53.9 °C. TLC: R_f 0.34 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.23 (s, 3H),

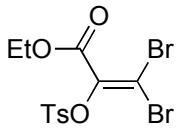
2.48 (s, 3H), 7.38 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.2, 21.9, 87.0, 128.2, 129.7, 133.0, 145.6, 146.3. IR (KBr): ν = 3091, 3070, 1595, 1433, 1371, 1197, 1184, 1168, 1087, 925, 837, 813, 731, 702, 655, 611, 553, 540, 513, 480 cm^{-1}. MS (EI) *m/z*: 372 (3, $M^+ + 4$), 370 (6, $M^+ + 2$), 368 (3, M^+). Anal. Calcd for $C_{10}H_{10}Br_2O_3S$: C, 32.46; H, 2.72. Found: C, 32.54; H, 2.80.

Ethyl 3,3-dibromo-2-oxopropanoate



Compound data was identical to those reported in the literature [Gore, M. P.; Nanjappan, P.; Hoops, G. C.; Woodard, R. W. *J. Org. Chem.* **1990,** *55,* 758].

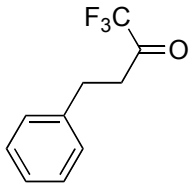
Ethyl 3,3-dibromo-2-tosyloxyacrylate (5b)



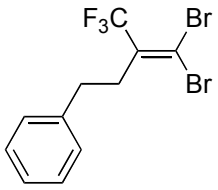
Purification: silica gel column chromatography (hexane/AcOEt 8:1). Yield: 66%, colorless solid. Mp: 44.6–45.2 °C. TLC: R_f 0.22 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (t, J = 7.2 Hz, 3H), 2.48 (s, 3H), 4.25 (q, J = 6.8 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 21.9, 62.7, 100.1, 128.4, 129.7, 132.7, 138.7, 145.9, 159.7. IR (KBr): ν = 2985, 2962, 1735, 1595, 1444, 1384, 1272, 1195, 1174, 1130, 1109, 1085, 1016, 931, 881, 815, 729, 680, 655, 590, 549, 515 cm^{-1}. MS (FAB) *m/z*: 431 (29, $[M^+ + H] + 4$), 429 (82, $[M^+ + H] + 2$), 427 (29, $[M^+ + H]$), 385 (10), 383 (16), 381 (11). Anal. Calcd for $C_{12}H_{12}Br_2O_5S$: C, 33.67; H, 2.83. Found: C, 33.67; H, 2.80.

Preparation of 1,1,1-trifluoro-4-phenylbutan-2-one

1,1,1-Trifluoro-4-phenylbutan-2-one was prepared in 81% yield according to the procedure reported in the literature [Creary, X. *J. Org. Chem.* **1987,** *52,* 5026]. Compound data were identical to those reported in the literature [Singh, R. P.; Cao, G.; Kirchmeier, R. L.; Shreeve, J. M. *J. Org. Chem.* **1999,** *64,* 2873].



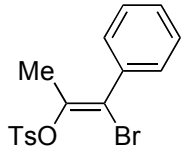
Preparation of 1,1-Dibromo-4-phenyl-2-trifluoromethylbut-1-ene (5c)



To a two-necked round-bottomed flask (500 mL) equipped with a magnetic stirring bar and a dropping funnel were added tetrabromomethane (9.94 g, 30 mmol), triphenylphosphine (15.7 g, 60 mmol), and hexane (200 mL) under an argon atmosphere at 0 °C. To the mixture was added 1,1,1-trifluoro-4-phenylbutan-2-one (2.01 g, 10 mmol) dropwise at 0 °C. The resulting mixture was warmed to room temperature and stirred for 22 h. The reaction mixture was rinsed with hexane and the combined organic layer was washed with sat. aq. NaCl (100 mL x 3), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel followed by GPC to give **5c** (1.15 g, 32% yield) as a colorless oil.

TLC: R_f 0.68 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.70–2.75 (m, 2H), 2.78–2.83 (m, 2H), 7.20–7.25 (m, 3H), 7.29–7.33 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 33.4, 36.8, 98.9 (q, J = 3.6 Hz), 122.5 (q, J = 274.4 Hz), 126.4, 128.2, 128.4, 135.4 (q, J = 29.8 Hz), 139.6. ^{19}F NMR (282 MHz, $CDCl_3$): δ –60.5 (s). IR (neat): ν = 3064, 3028, 2949, 2869, 1600, 1585, 1496, 1456, 1301, 1271, 1163, 1136, 1087, 1070, 819, 808, 796, 748, 698, 640 cm^{-1}. MS (EI) *m/z*: 360 (1, M^+ + 4), 358 (2, M^+ + 2), 356 (1, M^+), 279 (20), 277 (20), 91 (100). Anal. Calcd for $C_{11}H_9Br_2F_3$: C, 36.91; H, 2.53. Found: C, 37.21; H, 2.65.

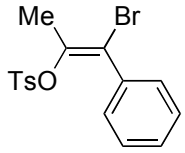
(*Z*)-1-Bromo-1-phenyl-2-tosyloxypropene (6a)



Purification: preparative TLC (hexane/AcOEt 8:1) followed by HPLC. Yield: 48%, colorless solid. Mp: 55.2–56.0 °C. TLC: R_f 0.15 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.08 (s, 3H), 2.47 (s, 3H), 7.27–7.38 (m, 7H), 7.92 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.1,

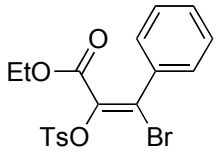
21.8, 113.1, 128.2, 128.3, 128.8, 129.2, 129.5, 133.5, 136.9, 144.1, 145.2. IR (KBr): ν = 3085, 3064, 1658, 1444, 1350, 1197, 1174, 1151, 1089, 927, 866, 819, 761, 742, 692, 650, 597, 542, 522 cm^{-1}. MS (FAB) *m/z*: 369 (10, $[M^+ + H] + 2$), 367 (10, $[M^+ + H]$), 213 (10), 211 (10), 197 (7), 195 (7). Anal. Calcd for $C_{16}H_{15}BrO_3S$: C, 52.33; H, 4.12. Found: C, 52.20; H, 4.04. The *Z*-stereochemistry was confirmed by X-ray diffraction analysis of the single crystal.

(*E*)-1-Bromo-1-phenyl-2-tosyloxypropene (6a)



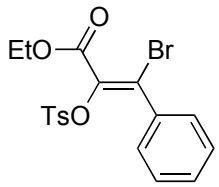
Purification: preparative TLC (hexane/AcOEt 8:1) followed by HPLC. Yield: 22%, colorless oil. TLC: R_f 0.15 (hexane/AcOEt 8:1). ^1H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 3H), 2.44 (s, 3H), 7.02 (d, *J* = 8.4 Hz, 2H), 7.10–7.17 (m, 5H), 7.29 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 21.7, 117.7, 127.5, 127.7, 128.1, 129.23, 129.26, 129.5, 135.9, 142.6, 144.5. IR (neat): ν = 2920, 2850, 1371, 1195, 1180, 1157, 1091, 929, 906, 761, 692, 667 cm^{-1}. MS (FAB) *m/z*: 369 (24, $[M^+ + H] + 2$), 367 (24, $[M^+ + H]$), 197 (39), 195 (39). Anal. Calcd for $C_{16}H_{15}BrO_3S$: C, 52.33; H, 4.12. Found: C, 52.24; H, 4.03.

(*Z*)-Ethyl 3-bromo-3-phenyl-2-tosyloxyacrylate (6b)



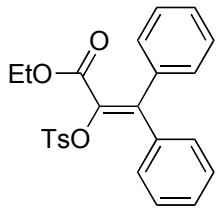
Purification: preparative TLC (hexane/AcOEt 8:1) followed by HPLC. Yield: 55%, colorless solid. Mp: 73.0–73.9 °C. TLC: R_f 0.16 (hexane/AcOEt 8:1). ^1H NMR (400 MHz, $CDCl_3$): δ 0.95 (t, *J* = 7.2 Hz, 3H), 2.48 (s, 3H), 3.98 (q, *J* = 7.2 Hz, 2H), 7.27–7.29 (m, 2H), 7.33–7.39 (m, 5H), 7.93 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.5, 21.9, 62.0, 128.0, 128.3, 128.5, 129.5, 129.6, 129.9, 133.2, 136.5, 136.8, 145.5, 160.4. IR (KBr): ν = 2981, 1730, 1633, 1390, 1284, 1195, 1182, 1130, 1083, 927, 813, 738, 696, 663, 599, 547, 534 cm^{-1}. MS (FAB) *m/z*: 427 (97, $[M^+ + H] + 2$), 425 (83, $[M^+ + H]$), 381 (75), 379 (62). Anal. Calcd for $C_{18}H_{17}BrO_5S$: C, 50.83; H, 4.03. Found: C, 50.63; H, 3.96. The *Z*-stereochemistry was confirmed by X-ray diffraction analysis of the single crystal.

(*E*)-Ethyl 3-bromo-3-phenyl-2-tosyloxyacrylate (6b)



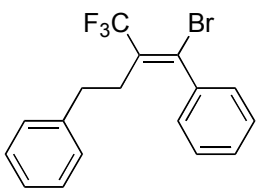
Purification: preparative TLC (hexane/AcOEt 8:1) followed by HPLC. Yield: 2%, colorless oil. TLC: R_f 0.16 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.40 (t, *J* = 7.2 Hz, 3H), 2.39 (s, 3H), 4.36 (q, *J* = 7.2 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.13–7.15 (m, 5H), 7.41 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 21.7, 62.4, 127.6, 127.9, 128.8, 129.2, 129.3, 131.8, 133.6, 134.6, 135.5, 144.9, 161.3. IR (neat): ν = 2981, 2925, 1732, 1596, 1444, 1382, 1259, 1193, 1178, 1105, 1083, 939, 752, 692, 667 cm^{-1}. MS (FAB) *m/z*: 427 (70, [M^+ + H] + 2), 425 (66, [M^+ + H]), 381 (14), 379 (14). Anal. Calcd for $C_{18}H_{17}BrO_5S$: C, 50.83; H, 4.03. Found: C, 50.81; H, 4.07.

Ethyl 3,3-diphenyl-2-tosyloxyacrylate (7b)



Purification: preparative TLC (hexane/AcOEt 8:1) followed by HPLC. Yield: 16%, colorless solid. Mp: 103.4–104.4 °C. TLC: R_f 0.16 (hexane/AcOEt 8:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (t, *J* = 7.2 Hz, 3H), 2.38 (s, 3H), 4.04 (q, *J* = 7.2 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 7.09–7.19 (m, 7H), 7.31–7.33 (m, 3H), 7.55 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6, 21.7, 61.5, 100.8, 127.6, 127.7, 127.9, 128.3, 128.4, 129.1, 129.6, 133.1, 133.5, 136.9, 137.9, 144.5, 144.6, 162.5. IR (KBr): ν = 3032, 2976, 1730, 1595, 1371, 1253, 1191, 1174, 1076, 941, 779, 756, 696, 680, 551 cm^{-1}. MS (FAB) *m/z*: 423 (40, [M^+ + H]), 422 (8, M^+), 378 (27), 377 (100). Anal. Calcd for $C_{24}H_{22}O_5S$: C, 68.23; H, 5.25. Found: C, 68.28; H, 5.19.

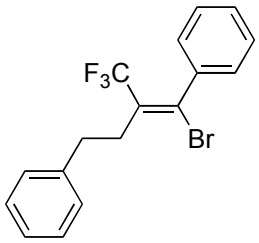
(*Z*)-1-Bromo-1,4-diphenyl-2-trifluoromethy1but-1-ene (6c)



Purification: Preparative TLC (hexane) followed by HPLC. Yield: 12%, colorless solid. Mp:

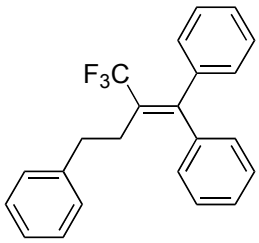
62.8–63.4 °C. TLC: R_f 0.37 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (t, J = 6.8 Hz, 2H), 2.70 (t, J = 6.8 Hz, 2H), 6.90 (m, 2H), 7.03–7.05 (m, 2H), 7.16–7.22 (m, 3H), 7.31–7.34 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 33.5, 35.0, 123.2 (q, J = 273.7 Hz), 126.1, 127.0 (q, J = 3.9 Hz), 127.3, 128.3, 128.4, 128.8, 131.5 (q, J = 28.2 Hz), 139.5, 139.8. ^{19}F NMR (282 MHz, $CDCl_3$): δ –61.0 (s). IR (KBr): ν = 3022, 2937, 2866, 1629, 1602, 1488, 1454, 1444, 1313, 1303, 1271, 1232, 1164, 1136, 1088, 1064, 1021, 871, 761, 752, 700, 586, 488 cm^{-1}. MS (EI) *m/z*: 356 (10, M^+ + 2), 354 (10, M^+), 275 (71), 265 (36), 263 (36). Anal. Calcd for $C_{17}H_{14}BrF_3$: C, 57.48; H, 3.98. Found: C, 57.63; H, 4.08. The *Z*-stereochemistry was confirmed by X-ray diffraction analysis of the single crystal.

(*E*)-1-Bromo-1,4-diphenyl-2-trifluoromethy1but-1-ene (6c)



Purification: Preparative TLC (hexane) followed by HPLC. Yield: 3%, colorless oil. TLC: R_f 0.37 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.84–2.89 (m, 2H), 2.92–2.97 (m, 2H), 7.27–7.51 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 33.8, 35.8, 122.7 (q, J = 274.5 Hz), 126.2, 127.70, 127.72, 127.9, 128.3 (d, J = 2.3 Hz), 128.9, 130.5 (q, J = 28.2 Hz), 133.5 (q, J = 4.6 Hz), 139.4, 140.4. ^{19}F NMR (282 MHz, $CDCl_3$): δ –57.8 (s). IR (neat): ν = 3062, 3028, 1641, 1496, 1456, 1444, 1319, 1271, 1224, 1161, 1122, 1089, 1029, 881, 808, 754, 696, 661, 634, 559 cm^{-1}. MS (EI) *m/z*: 356 (4, M^+ + 2), 354 (4, M^+), 275 (31), 265 (13), 263 (13). Anal. Calcd for $C_{17}H_{14}BrF_3$: C, 57.48; H, 3.98. Found: C, 57.64; H, 4.09.

1,1,4-Triphenyl-2-trifluoromethylbut-1-ene (7c)

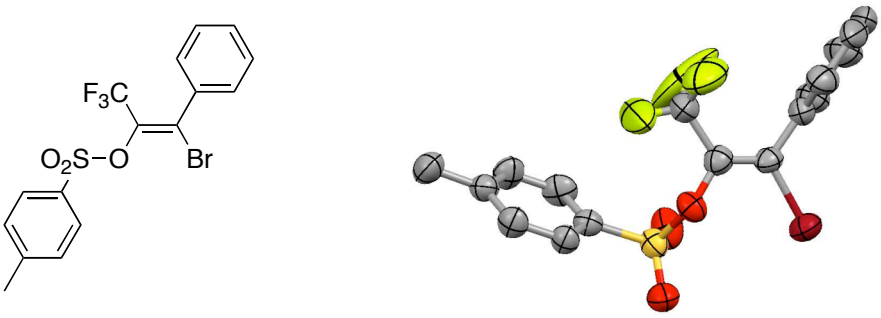


Purification: preparative TLC (hexane/AcOEt 8:1) followed by GPC. Yield: 47%, colorless solid. Mp: 71.9–72.4 °C. TLC: R_f 0.31 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.57–2.61 (m, 2H),

2.79–2.83 (m, 2H), 6.97–7.02 (m, 4H), 7.17–7.32 (m, 11H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.9, 35.3, 124.5 (q, J = 274.5 Hz), 125.8, 127.32, 127.39, 127.6, 127.72, 127.76, 128.1, 128.2, 128.3, 140.5, 140.6, 140.8, 149.4 (q, J = 3.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ –56.4 (s). IR (KBr): ν = 3057, 3028, 2939, 1635, 1595, 1488, 1444, 1326, 1263, 1191, 1168, 1134, 1110, 1060, 1006, 763, 744, 727, 696, 619, 567 cm^{-1}. MS (EI) *m/z*: 352 (9, M^+), 261 (100), 241 (96), 221 (54). Anal. Calcd for $C_{23}H_{19}F_3$: C, 78.39; H, 5.43. Found: C, 78.17; H, 5.48.

Data of X-ray crystallographic analysis:

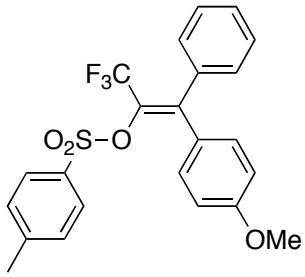
Compound **2a:** The detailed crystallographic data have been deposited at the Cambridge Crystallographic Data Centre and allocated the number CCDC-657359.

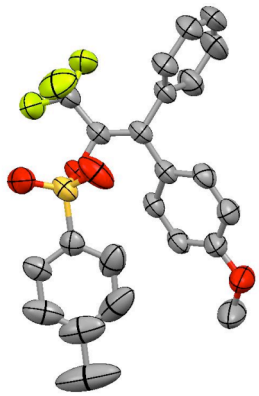


Crystal data and structure refinement for **2a**.

Empirical formula	C16 H12 Br F3 O3 S	
Formula weight	421.23	
Temperature	300(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.9162(17) Å	α = 90°.
	b = 8.3917(15) Å	β = 102.742(3)°.
	c = 20.928(4) Å	γ = 90°.
Volume	1698.6(5) $Å^3$	
Z	4	
Density (calculated)	1.647 Mg/m^3	
Absorption coefficient	2.585 mm^{-1}	
F(000)	840	
Crystal size	0.50 x 0.50 x 0.50 mm^3	
Theta range for data collection	2.00 to 25.50°	
Index ranges	-11<=h<=12, -7<=k<=10, -25<=l<=24	
Reflections collected	8909	
Independent reflections	3158 [R(int) = 0.0584]	
Completeness to theta = 25.50°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	0.3581 and 0.3581	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3158 / 0 / 218	
Goodness-of-fit on F^2	1.123	
Final R indices [I>2sigma(I)]	R1 = 0.0504, wR2 = 0.1553	
R indices (all data)	R1 = 0.0627, wR2 = 0.1608	
Largest diff. peak and hole	0.728 and -0.583 e. $Å^{-3}$	

Compound **3ab**: The detailed crystallographic data have been deposited at the Cambridge Crystallographic Data Centre and allocated the number CCDC-657360.

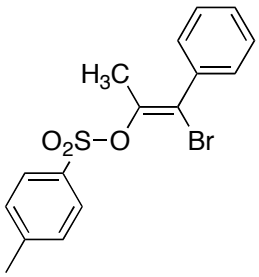


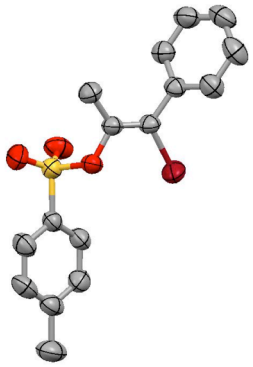


Crystal data and structure refinement for **3ab**.

Empirical formula	C23 H19 F3 O4 S	
Formula weight	448.44	
Temperature	300(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.2200(18) Å	α = 75.867(3)°.
	b = 11.1353(19) Å	β = 70.324(3)°.
	c = 11.260(2) Å	γ = 65.320(3)°.
Volume	1088.3(3) $Å^3$	
Z	2	
Density (calculated)	1.368 Mg/m^3	
Absorption coefficient	0.201 mm^{-1}	
F(000)	464	
Crystal size	0.50 x 0.50 x 0.50 mm^3	
Theta range for data collection	1.94 to 25.98°	
Index ranges	-12<=h<=11, -13<=k<=6, -13<=l<=13	
Reflections collected	6194	
Independent reflections	4182 [R(int) = 0.0146]	
Completeness to theta = 25.98°	97.8 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9062 and 0.9062	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4182 / 48 / 282	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0508, wR2 = 0.1448	
R indices (all data)	R1 = 0.0600, wR2 = 0.1527	
Largest diff. peak and hole	0.245 and -0.301 e. $Å^{-3}$	

Compound (*Z*)-**6a**: The detailed crystallographic data have been deposited at the Cambridge Crystallographic Data Centre and allocated the number CCDC-657361.

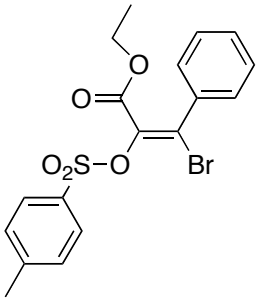


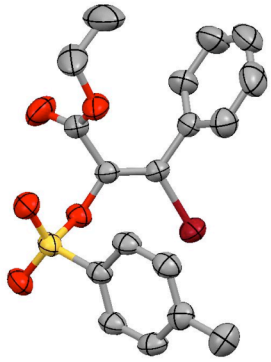


Crystal data and structure refinement for (*Z*)-**6a**.

Empirical formula	C16 H15 Br O3 S	
Formula weight	367.25	
Temperature	300(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 14.5715(18) Å	α = 90°.
	b = 9.2194(11) Å	β = 93.513(2)°.
	c = 12.0161(15) Å	γ = 90°.
Volume	1611.2(3) $Å^3$	
Z	4	
Density (calculated)	1.514 Mg/m^3	
Absorption coefficient	2.687 mm^{-1}	
F(000)	744	
Crystal size	0.50 x 0.50 x 0.50 mm^3	
Theta range for data collection	2.62 to 25.50°	
Index ranges	-17<=h<=17, -10<=k<=11, -14<=l<=10	
Reflections collected	8541	
Independent reflections	2998 [R(int) = 0.0230]	
Completeness to theta = 25.50°	100.0 %	
Absorption correction	SADABS	
Max. and min. transmission	0.3468 and 0.3468	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2998 / 0 / 193	
Goodness-of-fit on F^2	1.052	
Final R indices [I>2sigma(I)]	R1 = 0.0354, wR2 = 0.0940	
R indices (all data)	R1 = 0.0431, wR2 = 0.0980	
Extinction coefficient	0.0217(13)	
Largest diff. peak and hole	0.811 and -0.757 e. $Å^{-3}$	

Compound (*Z*)-**6b**: The detailed crystallographic data have been deposited at the Cambridge Crystallographic Data Centre and allocated the number CCDC-657362.

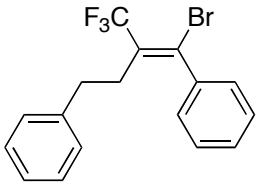


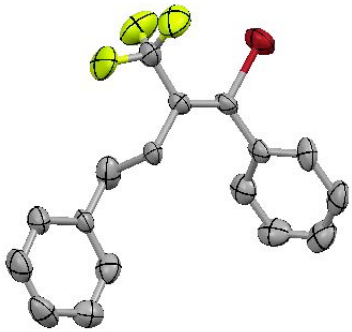


Crystal data and structure refinement for (*Z*)-**6b**.

Empirical formula	C18 H17 Br O5 S	
Formula weight	425.29	
Temperature	300(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 6.1892(9) Å	α = 90°.
	b = 8.2107(11) Å	β = 93.212(2)°.
	c = 36.297(5) Å	γ = 90°.
Volume	1841.6(4) $Å^3$	
Z	4	
Density (calculated)	1.534 Mg/m^3	
Absorption coefficient	2.370 mm^{-1}	
F(000)	864	
Crystal size	0.50 x 0.50 x 0.50 mm^3	
Theta range for data collection	2.25 to 25.50°	
Index ranges	-6<=h<=7, -9<=k<=9, -35<=l<=43	
Reflections collected	9712	
Independent reflections	3428 [R(int) = 0.0564]	
Completeness to theta = 25.50°	99.9 %	
Absorption correction	None	
Max. and min. transmission	0.3837 and 0.3837	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3428 / 0 / 229	
Goodness-of-fit on F^2	0.992	
Final R indices [I>2sigma(I)]	R1 = 0.0358, wR2 = 0.0955	
R indices (all data)	R1 = 0.0435, wR2 = 0.0983	
Extinction coefficient	0.0198(13)	
Largest diff. peak and hole	0.422 and -0.425 e. $Å^{-3}$	

Compound (*Z*)-**6c**: The detailed crystallographic data have been deposited at the Cambridge Crystallographic Data Centre and allocated the number CCDC-657363.





Crystal data and structure refinement for (*Z*)-**6c**.

Empirical formula	C17 H14 Br F3	
Formula weight	355.19	
Temperature	300(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.354(5) Å	α = 90°.
	b = 14.496(7) Å	β = 114.662(8)°.
	c = 10.894(5) Å	γ = 90°.
Volume	1485.9(13) Å^3	
Z	4	
Density (calculated)	1.588 Mg/m^3	
Absorption coefficient	2.789 mm^{-1}	
F(000)	712	
Crystal size	0.50 x 0.40 x 0.30 mm^3	
Theta range for data collection	2.28 to 25.50°.	
Index ranges	-12<=h<=11, -17<=k<=17, -13<=l<=12	
Reflections collected	7420	
Independent reflections	2748 [R(int) = 0.0698]	
Completeness to theta = 25.50∞	99.4 %	
Absorption correction	Empirical	
Max. and min. transmission	0.4884 and 0.3361	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2748 / 0 / 190	
Goodness-of-fit on F2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.1004, wR2 = 0.2375	
R indices (all data)	R1 = 0.1558, wR2 = 0.2608	
Largest diff. peak and hole	2.337 and -1.086 e.Å^{-3}	