A regioselective synthesis of poly-substituted aryl triflones through self-promoting three component reaction

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1. General and materials
All reactions were carried out under Ar atmosphere. Melting points were uncorrected. 1H and 13C NMR spectra were taken on a 400 MHz spectrometer, and chemical shifts were reported in parts per million (ppm) using CHCl3 (7.26 ppm) in CDCl3 for 1H NMR, and CDCl3 (77.01 ppm) for 13C NMR as an internal standard, respectively. 19F NMR spectra were taken on a 300 MHz spectrometer, and chemical shifts were reported in parts per million using trifluoromethylbenzene (0 ppm) as a standard. Mass spectra were recorded by an electrospray ionization-time of flight (ESI-TOF) mass spectrometer or an EI mass spectrometer. Column chromatography was performed on neutral silica gel (75-150 μm). Medium pressure liquid chromatography (MPLC) was performed using 40 x 300 mm i. d. pre-packed column (silica gel, 50 μm) with UV or RI detector. Tf2CH2 1 was supplied from Central Glass Co. and this material can be also prepared by the Waller’s procedure in the laboratory. 1 Tf2CH2CCHTf2 2 was prepared from Tf2CH2 by the reported procedure. 2 Paraformaldehyde was purchased from Tokyo Chemical Industry, Co.

2. Three component synthesis of gem-bis(triflyl)cyclohexenes
1-Methyl-4,4-bis(trifluoromethylsulfonyl)cyclohex-1-ene (3aa)

To a solution of Tf2CH2 1 (150.1 mg, 0.54 mmol) in acetonitrile (0.4 mL), paraformaldehyde (90% purity, 17.9
mg, 0.54 mmol) and isoprene (107.4 µL, 1.07 mmol) were added at room temperature. After being stirred at the same temperature for 2.5 h, the reaction mixture was evaporated. The resultant residue was purified by column chromatography on neutral silica gel (hexane/EtOAc = 20 : 1) to give the Diels–Alder adduct 3aa in 76% yield (147.2 mg, 0.41 mmol). Likewise, the reaction of Tf₂CH₂ 1 (128.9 mg, 0.46 mmol), paraformaldehyde (90% purity, 15.3 mg, 0.46 mmol) and isoprene (92.2 µL, 0.92 mmol) in 1,2-dichloroethane (1.0 mL) was completed within 13 h at 40 °C to give the adduct 3aa in 84% yield (139.1 mg, 0.39 mmol). Compared to the reaction in acetonitrile, the reaction in 1,2-dichloroethane resulted in the smooth conversion of starting materials without the formation of side products. Colorless oil; IR (neat) ν 3034, 2978, 2923, 2862, 1452, 1385, 1212, 1100 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.74 (3H, s), 2.34 (2H, brt, J = 6.4 Hz), 2.73 (2H, t, J = 6.4 Hz), 3.13 (2H, brs), 5.35-5.38 (1H, m); ¹³C NMR (100 MHz, CDCl₃) δ 22.8, 23.0, 25.6, 25.8, 93.7, 113.4, 120.4 (q, JₑF = 332.9 Hz), 134.6; ¹⁹F NMR (282 Hz, CDCl₃) δ -4.9 (6F, s); MS (ESI-TOF) m/z 383 [M+Na]⁺; HRMS calcd for C₆H₁₀F₆NaO₄S₂ [M+Na]⁺, 382.9822; found, 382.9827. Anal. Calcd for C₆H₁₀F₆NaO₄S₂: C, 30.00; H, 2.80. Found: C, 30.12; H, 2.89.

4,4-Bis(trifluoromethylsulfonyl)cyclohex-1-ene (3ab)

A mixture of Tf₂CH₂ 1 (1.42 g, 5.05 mmol) and paraformaldehyde (90% purity, 252.5 mg, 7.58 mmol) in 1,2-dichloroethane (10 mL) was stirred at 40 °C for 4.5 h under buta-1,3-diene atmosphere. After concentration of the reaction mixture under reduced pressure, column chromatography on neutral silica gel (hexane/EtOAc = 10 : 1) of the resultant residue gave the Diels–Alder adduct 3ab in 99.6% yield (1.74 g, 5.03 mmol). Colorless crystals (Et₂O); Mp. 33.0-33.9 °C; IR (KBr) ν 3050, 2932, 2864, 1442, 1384, 1197, 1104 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.43-2.49 (2H, m), 2.71 (2H, t, J = 6.4 Hz), 3.15 (1H, brs), 5.68-5.72 (1H, m), 5.91-5.94 (1H, m); ¹³C NMR (100 MHz, CDCl₃) δ 20.9, 22.3, 25.4, 93.6, 119.5, 120.4 (q, JₑF = 332.4 Hz), 126.6; ¹⁹F NMR (282 Hz, CDCl₃) δ -4.7 (6F, s); MS (ESI-TOF) m/z 369 [M+Na]⁺; HRMS calcd for C₆H₁₀F₆NaO₄S₂ [M+Na]⁺, 368.9666; found, 368.9649. Anal. Calcd for C₆H₁₀F₆NaO₄S₂: C, 27.75; H, 2.33. Found: C, 27.85; H, 2.47.

1,2-Dimethyl-4,4-bis(trifluoromethylsulfonyl)cyclohex-1-ene (3ac)

According to the synthetic procedure for 3aa, this compound was prepared in 88% yield (149.2 mg, 0.40 mmol) by the reaction of Tf₂CH₂ 1 (127.4 mg, 0.45 mmol), paraformaldehyde (90% purity, 18.2 mg, 0.45 mmol) and 2,3-dimethylbuta-1,3-diene (102.9 µL, 0.91 mmol) in 1,2-dichloroethane (1.0 mL) at 40 °C for 6 h. Colorless oil; IR (neat) ν 2997, 2924, 2865, 1448, 1384, 1200, 1101 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.69 (3H, s), 1.71 (3H, s), 2.31-2.37 (2H, m), 2.67 (2H, t, J = 6.5 Hz), 3.00 (2H, s); ¹³C NMR (100 MHz, CDCl₃) δ 18.5, 18.6, 23.2, 27.1, 30.7, 95.1, 119.0, 120.4 (q, JₑF = 332.5 Hz), 126.7; ¹⁹F NMR (282 Hz, CDCl₃) δ -5.1 (6F, s); MS (ESI-TOF) m/z 397 [M+Na]⁺; HRMS calcd for C₁₀H₁₂F₆NaO₄S₂ [M+Na]⁺, 396.9979; found,
90% purity, 15.2.0 KBr as prepared in 0.0 Hz), 3.42.31.0 C2T2T

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Colorless structure of this compound was confirmed by an X-ray crystallographic analysis (See, Table S1). Anal. Calcd for C19H12F6O3S2: C, 32.09; H, 3.23. Found: C, 32.38; H, 3.30.

3-Methyl-4,4-bis(trifluoromethylsulfonyl)cyclohex-1-ene (3ad)

According to the synthetic procedure for 3aa, this compound was prepared in 81% yield (127.3 mg, 0.35 mmol) by the reaction of Tf2CH2 1 (122.7 mg, 0.44 mmol), paraformaldehyde (90% purity, 21.9 mg, 0.66 mmol) and (E)-penta-1,3-diene (87.8 µL, 0.88 mmol) in 1,2-dichloroethane (2.0 mL) at 40 °C for 8 h. Colorless oil; IR (neat) ν 3047, 2990, 2931, 2868 mmol), paraformaldehyde (100 Hz), 3.42–3.52 (1H, m), 5.51–5.57 (1H, m), 5.79–5.84 (1H, m); 13C NMR (100 MHz, CDCl3) δ 17.8, 21.3, 23.7, 34.3, 99.9, 120.3 (q, JCF = 334.7 Hz), 120.4 (q, JCF = 333.6 Hz), 124.7, 128.0; 19F NMR (282 Hz, CDCl3) δ -4.8 (3F, s), -4.7 (3F, s); MS (ESI-TOF) m/z 383 [M+Na]+; HRMS calcd for C9H10F6NaO3S2 [M+Na]+, 382.9822; found, 382.9859.

3-(Chloromethyl)-4,4-bis(trifluoromethylsulfonyl)cyclohex-1-ene (3ae)

According to the synthetic procedure for 3aa, this compound was prepared in 91% yield (132.1 mg, 0.34 mmol) by the reaction of Tf2CH2 1 (103.3 mg, 0.37 mmol), paraformaldehyde (18.5 mg, 0.55 mmol) and (E)-5-chloropenta-1,3-diene1 (75.6 mg, 0.74 mmol) in 1,2-dichloroethane (1.0 mL) at 40 °C for 6.5 h. Colorless crystals (hexane-EtOAc); Mp. 68.5-72.0 °C; R (KBr) ν 3051, 2932, 1383, 1205, 1102 cm⁻¹; 1H NMR (400 MHz, CDCl3) δ 2.40–2.93 (3H, m), 3.59 (1H, brd, J = 10.6 Hz), 3.73 (1H, t, J = 10.6 Hz), 4.53 (1H, dd, J = 10.6, 2.4 Hz), 5.97–6.04 (2H, m); 13C NMR (100 MHz, CDCl3) 22.1, 24.8, 43.0 (2C), 97.4, 120.1 (q, JCF = 334.6 Hz), 120.3 (q, JCF = 333.6 Hz), 122.7, 126.9; 19F NMR (282 Hz, CDCl3) δ -4.6 (3F, s), -4.5 (3F, s); MS (ESI-TOF) m/z 417 [M+Na]+, 419 [M+2+Na]+; HRMS calcd for C9H9ClF6NaO3S2 [M+Na]+, 416.9466; found, 416.9435. Anal. Calcd for C9H9ClF6O3S2: C, 27.38; H, 2.30. Found: C, 27.38; H, 2.49.

Ethyl 2-(6,6-bis(trifluoromethylsulfonyl)cyclohex-2-enyl)acetate (3af)

According to the synthetic procedure for 3aa, this compound was prepared in 78% yield (1.71 g, 3.97 mmol) by the reaction of Tf2CH2 1 (1.42 g, 5.06 mmol), paraformaldehyde (90% purity, 253 mg, 7.59 mmol) and (E)-ethyl hexa-3,5-dienoate4 (851 mg, 6.07 mmol) in 1,2-dichloroethane (15 mL) at 40 °C for 3 h. The structure of this compound was also confirmed by an X-ray crystallographic analysis (See, Table S1). Colorless crystals (hexane-EtOAc); Mp. 89.0-90.8 °C; IR (KBr) ν 3047, 2987, 2942, 1738, 1379, 1196, 1102 cm⁻¹; 1H NMR (400 MHz, CDCl3) δ 3.73 (2H, m), 2.81 (1H, dt, J = 10.6, 2.4 Hz), 6.04 (2H, m) 419 [M+Na]+, 419 [M+2+Na]+; HRMS calcd for C9H9ClF6O3S2 [M+Na]+, 416.9466; found, 416.9435. Anal. Calcd for C9H9ClF6O3S2: C, 27.38; H, 2.30. Found: C, 27.38; H, 2.49.
1103 cm⁻¹; ¹H NMR (400 MHz, CDCl₃)  δ 1.29 (3H, t, J = 7.2 Hz), 2.38-2.61 (3H, m), 2.77 (1H, dd, J = 16.8, 11.3 Hz), 2.82-2.91 (1H, m), 3.54 (1H, dd, J = 16.8, 1.7 Hz), 3.99 (1H, brd, J = 11.3 Hz), 4.20 (2H, q), 5.51 (1H, dd, J = 10.2, 1.7 Hz), 5.81-5.89 (1H, m); ¹³C NMR (100 MHz, CDCl₃)  δ 14.1, 22.0, 25.0, 34.8, 36.4, 61.4, 97.1, 120.2 (q, Jₑ₋ₓ = 335.1 Hz), 120.3 (q, Jₑ₋ₓ = 334.1 Hz), 125.4, 125.5, 170.6; ¹⁹F NMR (282 Hz, CDCl₃)  δ –4.61 (3F, s), –4.58 (3F, s); MS (ESI-TOF) m/z 433 [M+H⁺]; HRMS calcd for C₁₂H₁₄F₆O₆S₂ [M+H⁺], 433.0214; found, 433.0193. Anal. Calcd for C₁₂H₁₄F₆O₆S₂: C, 33.34; H, 3.26. Found: C, 33.52; H, 3.54.

(1R*, 4R*)-Ethyl 4-methyl-5,5-bis(trifluoromethylsulfonyl)cyclohex-2-enecarboxylate (3aa)

According to the synthetic procedure for 3aa, this compound was prepared in 98% yield (212.7 mg, 0.492 mmol) by the reaction of Tf₂CH₂ 1 (141.1 mg, 0.50 mmol), paraformaldehyde (90% purity, 20.1 mg, 0.60 mmol) and ethyl sorbate (90.1 μL, 0.60 mmol) in 1,2-dichloroethane (0.5 mL) at 40 °C for 2.5 h. The relative stereochemistry was determined by NOESY spectra. Colorless oil; IR (neat) ν 2988, 2951, 1739, 1385, 1196, 1096 cm⁻¹; ¹H NMR (400 MHz, CDCl₃)  δ 1.24 (3H, t, J = 7.1 Hz), 1.38 (3H, d, J = 6.9 Hz), 2.87 (1H, dd, J = 15.0, 11.1 Hz), 2.97 (1H, dd, J = 15.0, 6.3 Hz), 3.44-3.52 (1H, m), 4.16 (2H, q, J = 7.1 Hz), 5.70 (1H, ddd, J = 10.2, 4.8, 2.8 Hz), 5.86 (1H, brd, J = 10.2 Hz); ¹³C NMR (100 MHz, CDCl₃)  δ 14.0, 19.4, 22.7, 31.8, 39.3, 62.0, 101.4, 120.56 (q, Jₑ₋ₓ = 333.9 Hz), 120.62 (q, Jₑ₋ₓ = 334.1 Hz), 123.3, 129.6, 170.5; ¹⁹F NMR (282 Hz, CDCl₃)  δ –4.5 (3F, s), –2.8 (3F, s); MS (ESI-TOF) m/z 433 [M+H⁺]; HRMS calcd for C₁₂H₁₄F₆O₆S₂ [M+H⁺], 433.0214; found, 433.0156. Anal. Calcd for C₁₂H₁₄F₆O₆S₂: C, 33.34; H, 3.26. Found: C, 33.54; H, 3.33.

(1R*, 4R*)-5,5-Bis(trifluoromethylsulfonyl)bicycle[2.2.2]oct-2-ene (3ah)

According to the synthetic procedure for 3aa, this compound was prepared in 60% yield (111.6 mg, 0.30 mmol) by the reaction of Tf₂CH₂ 1 (139.4 mg, 0.50 mmol), paraformaldehyde (90% purity, 33.2 mg, 1.00 mmol) and cyclohexa-1,3-diene (71.2 μL, 0.75 mmol) in 1,2-dichloroethane (2.0 mL) at 80 °C for 8.5 h. Colorless crystals; Mp. 36.0-38.2 °C; IR (KBr) ν 3064, 2958, 2893, 1382, 1192, 1097 cm⁻¹; ¹H NMR (400 MHz, CDCl₃)  δ 1.33-1.38 (2H, m), 1.80-1.83 (1H, m) 2.33-2.40 (2H, m), 2.62 (1H, brd, J = 15.6 Hz), 2.94-3.03 (1H, m), 3.66-3.74 (1H, m), 6.35 (1H, t, J = 7.2 Hz), 6.45 (1H, t, J = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃)  δ 21.3, 23.6, 29.1, 31.6, 33.0, 100.6, 120.3, 120.6 (q, Jₑ₋ₓ = 333.6 Hz), 130.3, 134.8; ¹⁹F NMR (282 Hz, CDCl₃)  δ –4.3 (3F, s), –4.2 (3F, s); MS (ESI-TOF) m/z 395 [M+Na⁺]; HRMS calcd for C₁₀H₁₀F₆NaO₄S₂ [M+Na⁺], 394.9822; found, 394.99843. Anal. Calcd for C₁₀H₁₀F₆NaO₄S₂: C, 32.26; H, 2.71. Found: C, 32.48; H, 2.77.
1-Methyl-5-pentyl-4,4-bis(trifluoromethylsulfonyl)cyclohex-1-ene (3ba)

According to the synthetic procedure for 3aa, this compound was prepared in 88% yield (178.4 mg, 0.41 mmol) by the reaction of Tf₂CH₂ 1 (130.9 mg, 0.47 mmol), hexanal (58.0 µL, 0.47 mmol) and isoprene (94.2 µL, 0.94 mmol) in 1,2-dichloroethane (1.0 mL) at room temperature for 20 h. Colorless oil; IR (neat) ν 2959, 2931, 2962, 1383, 1200, 1099 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.90 (3H, t, J = 6.7 Hz), 1.22-1.40 (5H, m), 1.47-1.58 (1H, m), 1.73 (3H, s), 1.74-1.81 (1H, m), 2.22-2.36 (2H, m), 2.51 (1H, dd, J = 18.1, 6.4 Hz), 2.73-2.85 (1H, m), 3.07 (1H, d, J = 18.5 Hz), 3.18 (1H, dd, J = 18.5, 4.2 Hz), 5.32 (1H, brs); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 22.4 (2C), 27.7, 28.6, 30.8, 31.4, 33.9, 39.9, 100.8, 112.5, 119.9 (q, JCF = 333.1 Hz), 120.4 (q, JCF = 334.8 Hz), 136.2; ¹⁹F NMR (282 Hz, CDCl₃) δ –8.4 (3F, s), –3.9 (3F, s); MS (ESI-TOF) m/z 431 [M+H]⁺; HRMS calcd for C₁₄H₂₁F₂O₄S₂ [M+H]⁺, 431.0785; found, 431.0741.

(2-(3-Methyl-6,6-bis(trifluoromethylsulfonyl)cyclohex-3-enyl)(ethyl)benzene (3ca)

According to the synthetic procedure for 3aa, this compound was prepared in 89% yield (235.1 mg, 0.51 mmol) by the reaction of Tf₂CH₂ 1 (159.1 mg, 0.57 mmol), 3-phenylpropionaldehyde (74.7 µL, 0.57 mmol) and isoprene (114 µL, 1.14 mmol) in 1,2-dichloroethane (1.0 mL) at room temperature for 24 h. Colorless oil; IR (neat) ν 3027, 2920, 1381, 1206, 1100 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.73 (3H, s), 2.03-2.15 (1H, m), 2.36 (1H, d, J = 17.9 Hz), 2.52 (1H, dd, J = 17.9, 6.4 Hz), 2.61-2.92 (4H, m), 3.05 (1H, d, J = 18.2 Hz), 3.16 (1H, dd, J = 18.2, 4.6 Hz), 5.32 (1H, brs), 7.19-7.25 (3H, m), 7.28-7.39 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 22.5, 28.4, 32.2, 33.9, 34.0, 39.1, 100.5 (m), 112.6, 119.9 (q, JCF = 333.3 Hz), 120.3 (q, JCF = 334.8 Hz), 126.4, 128.4, 128.6, 136.1, 140.0; ¹⁹F NMR (282 Hz, CDCl₃) δ –8.3 (3F, s), –3.8 (3F, s); MS (ESI-TOF) m/z 487 [M+Na]⁺; HRMS calcd for C₁₄H₁₈F₅NaO₄S₂ [M+Na]⁺, 487.0448; found, 487.0387.

5-Isobutyl-1-methyl-4,4-bis(trifluoromethylsulfonyl)cyclohex-1-ene (3da)

According to the synthetic procedure for 3aa, this compound was prepared in 89% yield (369.1 mg, 0.89 mmol) by the reaction of Tf₂CH₂ 1 (283.8 mg, 1.01 mmol), 3-methylbutanal (87 mg, 1.01 mmol) and isoprene (200 µL, 2.00 mmol) in 1,2-dichloroethane (2.0 mL) at room temperature for 17 h. Colorless crystals (Et₂O); Mp. 36.0-37.5 °C; IR (KBr) ν 2962, 2874, 1382, 1200, 1098 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.92 (3H, d, J = 6.6 Hz), 0.99 (3H, d, J = 6.5 Hz), 1.72 (3H, s), 1.70-1.84 (2H, m), 2.00-2.09 (1H, m), 2.29 (1H, dd, J = 18.1, 10.4 Hz), 2.47 (1H, dd, J = 18.1, 6.5 Hz), 2.90-3.00 (1H, m), 3.08 (1H, d, J = 18.4 Hz), 3.17 (1H, dd, J = 18.4, 4.3 Hz), 5.32 (1H, brs); ¹³C NMR (100 MHz, CDCl₃) δ 20.4, 22.5, 24.0, 25.6, 28.5, 34.1, 37.8, 39.6, 101.1,
112.4, 119.9 (q, $J_{C,F} = 333.3$ Hz), 120.4 (q, $J_{C,F} = 334.8$ Hz), 136.2; $^{19}$F NMR (282 Hz, CDCl$_3$) $\delta$–8.4 (3F, s), –3.8 (3F, s); MS (ESI-TOF) $m/z$ 439 [M+Na]$^+$; HRMS calcd for C$_{13}$H$_{16}$F$_6$NaO$_5$S$_2$ [M+Na]$^+$, 439.0448; found, 439.0455.

**tert-Butyl((3-methyl-6,6-bis(trifluoromethylsulfonyl)cyclohex-3-enyl)methoxy)diphenylsilane (3ea)**

According to the synthetic procedure for 3aa, this compound was prepared in 78% yield (244.4 mg, 0.39 mmol) by the reaction of Tf$_2$CH$_2$ 1 (139.6 mg, 0.50 mmol), TBDPSOCH$_2$CHO (223.9 mg, 0.75 mmol) and isoprene (100 $\mu$L, 1.0 mmol) in 1,2-dichloroethane (1.0 mL) at room temperature for 20 h. Colorless oil; IR (neat) $\nu$ 3073, 2933, 2859, 1382, 1200, 1103, 702 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.16 (9H, s), 1.76 (3H, s), 2.46 (1H, dd, $J = 18.0, 9.0$ Hz), 2.84 (1H, dd, $J = 18.0, 6.0$ Hz), 3.10–3.28 (3H, m), 4.05 (1H, dd, $J = 10.3, 9.6$ Hz), 4.52 (1H, dd, $J = 10.3, 3.3$ Hz), 5.36 (1H, brs), 7.41–7.53 (6H, m), 7.69–7.77 (4H, m); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 19.3, 22.6, 26.8, 28.0, 31.6, 41.4, 63.1, 99.5, 112.6, 120.0 (q, $J_{C,F} = 333.3$ Hz), 120.4 (q, $J_{C,F} = 334.6$ Hz), 127.8, 129.90 and 129.93, 132.8 and 133.0, 135.5, 135.8; $^{19}$F NMR (282 Hz, CDCl$_3$) $\delta$–7.8 (3F, s), –3.7 (3F, s); MS (ESI-TOF) $m/z$ 651 [M+Na]$^+$; HRMS calcd for C$_{26}$H$_{30}$F$_6$NaO$_5$S$_2$Si [M+Na]$^+$, 651.1106; found, 651.1059.

**1-(3-Methyl-6,6-bis(trifluoromethylsulfonyl)cyclohex-3-enyl)-4-nitrobenzene (3fa)**

According to the synthetic procedure for 3aa, this compound was prepared in 55% yield (187.0 mg, 0.39 mmol) by the reaction of Tf$_2$CH$_2$ 1 (199.5 mg, 0.71 mmol), $\rho$-nitrobenzaldehyde (107.8 mg, 0.71 mmol) and isoprene (142.7 $\mu$L, 1.42 mmol) in 1,2-dichloroethane (1.0 mL) at room temperature for 16 h. Yellow crystals (hexane-EtOAc); Mp. 75.5–76.5 °C; IR (KBr) $\nu$ 3077, 2920, 2859, 1525, 1427, 1371, 1350, 1207, 1095 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.80 (3H, s), 2.70 (1H, dd, $J = 18.5, 6.5$ Hz), 2.80 (1H, dd, $J = 18.5, 6.5$ Hz), 3.34 (2H, s), 4.28 (1H, t, $J = 6.5$ Hz), 5.56 (1H, brs), 7.69 (2H, d, $J = 8.8$ Hz), 8.17 (2H, d, $J = 8.8$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 22.5, 27.0, 36.8, 43.5, 100.3, 113.3, 120.1 (q, $J_{C,F} = 333.9$ Hz), 120.4 (q, $J_{C,F} = 334.0$ Hz), 123.8, 130.9, 135.9, 144.5, 147.9; $^{19}$F NMR (282 Hz, CDCl$_3$) $\delta$–5.7 (3F, s), –4.2 (3F, s); MS (ESI-TOF) $m/z$ 504 [M+Na]$^+$; HRMS calcd for C$_{15}$H$_{13}$F$_6$NO$_5$S$_2$ [M+Na]$^+$, 503.9986; found, 503.9991. Anal. Calcd for C$_{15}$H$_{13}$F$_6$NO$_5$S$_2$: C, 37.43; H, 2.73; N, 2.91. Found: C, 37.48; H, 2.94; N, 3.01.

**1,2-Dimethyl-5-pentyl-4,4-bis(trifluoromethylsulfonyl)cyclohex-1-ene (3bc)**

According to the synthetic procedure for 3aa, this compound was prepared in 87% yield (630 mg, 1.41 mmol)
by the reaction of Tf₂CH₂ 1 (454.7 mg, 1.62 mmol), hexanal (198.2 µL, 1.62 mmol) and 2,3-dimethylbuta-1,3-diene (0.37 mL, 3.24 mmol) in 1,2-dichloroethane (3.0 mL) at room temperature for 16 h. Colorless oil; IR (neat) ν 2928, 2862, 1382, 1198, 1102 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.90 (3H, t, J = 6.7 Hz), 1.22–1.39 (5H, m), 1.45–1.58 (1H, m), 1.67 (3H, s), 1.68 (3H, s), 1.67-1.82 (1H, m), 2.22-2.34 (2H, m), 2.50 (1H, dd, J = 18.0, 6.1 Hz), 2.68-2.77 (1H, m), 2.94 (1H, d, J = 18.2 Hz), 3.05 (1H, d, J = 18.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 18.2, 18.3, 22.4, 27.8, 30.5, 31.4, 33.7, 35.1, 39.9, 102.0, 118.2, 119.9 (q, J_C-F = 333.2 Hz), 120.4 (q, J_C-F = 334.8 Hz), 128.0; ¹⁹F NMR (282 Hz, CDCl₃) δ –9.3 (3F, s), –3.6 (3F, s); MS (ESI-TOF) m/z 467 [M+Na]⁺; HRMS calcd for C₁₃H₂₃F₄NaO₂S₂ [M+Na]⁺, 467.0761; found, 467.0709.

3. Synthesis of poly-substituted aryl triflones

4-Methyl-2-pentyl-1-(trifluoromethylsulfonyl)benzene (5ba)

A solution of 3ba (215.6 mg, 0.50 mmol) in degassed xylene (2.0 mL) was stirred at 140 °C for 4 h. The reaction mixture was directly purified by column chromatography on silica gel (hexane/EtOAc = 20 : 1) to give 1-methyl-5-pentyl-4-(trifluoromethylsulfonyl)cyclohexa-1,3-diene 4ba in 89% yield (132.8 mg, 0.45 mmol). Colorless oil; IR (neat) ν 2960, 2930, 2861, 1450, 1384, 1207, 1100 cm⁻¹; ¹H NMR (400 MHz, CHCl₃) δ 0.87 (3H, t, J = 7.0 Hz), 1.18–1.40 (6H, m), 1.46–1.62 (2H, m), 1.96 (3H, s), 2.36 (1H, dd, J = 18.1, 1.2 Hz), 2.55 (1H, dd, J = 18.1, 8.4 Hz), 2.65–2.75 (1H, m), 5.95–6.02 (1H, m), 7.17 (1H, d, J = 5.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 22.5, 24.2, 25.8, 30.7, 31.5, 31.9, 33.4, 118.3, 120.1 (q, J_C-F = 326.9 Hz), 128.9, 143.3, 149.3; ¹⁹F NMR (282 Hz, CDCl₃) δ –16.0 (3F, s); MS (ESI-TOF) m/z 297 [M+H]⁺; HRMS calcd for C₁₃H₂₃F₄O₂S [M+H]⁺, 297.1136; found, 297.1153.

To a solution of diene 4ba (30.2 mg, 101 µmol) in methylcyclohexane (2.0 mL), activated MnO₂ (Aldrich, azeotropic with toluene, 88.2 mg) was added. After being stirred at 70 °C for 4 h, the mixture was filtered through celite pad. The filtrate was evaporated and purified by column chromatography on silica gel (hexane/EtOAc = 30 : 1) to give aryl triflone 5ba in 80% yield (23.9 mg, 81 µmol). Colorless oil; IR (neat) ν 2958, 2931, 2862, 1601, 1362, 1213, 1152, 1127, 1045, 666 cm⁻¹; ¹H NMR (400 MHz, CD₂CN) δ 0.69 (3H, t, J = 8.0 Hz), 1.08–1.23 (4H, m), 1.38–1.50 (2H, m), 2.22 (3H, s), 2.75 (2H, dd, J = 8.1, 7.8 Hz), 7.14 (d, J = 8.2 Hz), 7.21 (1H, s), 7.73 (1H, d, J = 8.2 Hz); ¹³C NMR (100 MHz, CD₂CN) δ 14.3, 21.7, 23.1, 32.5, 33.1, 34.0, 121.1 (q, J_C-F = 325.9 Hz), 126.5, 129.3, 134.3, 134.7, 148.2, 150.0; ¹⁹F NMR (282 Hz, CDCl₃) δ –15.9 (3F, s); MS (ESI-TOF) m/z 317 [M+Na]⁺; HRMS calcd for C₁₃H₁₃F₄NaO₂S [M+Na]⁺, 317.0799; found, 317.0790.

4-Methyl-2-phenyl-1-(trifluoromethylsulfonyl)benzene (5ca)

According to the synthetic procedure for 5ba, 1-methyl-5-phenylcyclohexa-4-(trifluoromethylsulfonyl)-1,3-diene 4ca was obtained in 95% yield (124.5 mg, 0.38 mmol) by the thermolysis of 3ca (183.5 mg, 0.40
mmol) in degassed xylenes (3.0 mL) for 2 h at 140 °C. Pale yellow oil; IR (neat) v 2929, 1568, 1360, 1211, 1118 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.89-2.08 (2H, m), 2.02 (3H, s), 2.49 (1H, d, J = 18.1 Hz), 2.60-2.72 (2H, m), 2.78 (1H, ddd, J = 13.5, 9.9, 5.8 Hz), 2.84-2.92 (1H, m), 6.09 (1H, brs), 7.20-7.31 (4H, m), 7.31-7.42 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 24.2, 31.8, 32.2, 32.5, 33.5, 118.5, 120.1 (q, J C,F = 326.8 Hz), 126.0, 128.3 (2C), 128.4, 141.2, 143.6, 149.5; ¹⁹F NMR (282 Hz, CDCl₃) δ −15.9 (3F, s); MS (ESI-TOF) m/z 353 [M+Na⁺]; HRMS calcd for C₁₆H₁₃F₃NaO₂S [M+Na⁺], 353.0799; found, 353.0761.

The above cyclohexadiene 4ca (66.1 mg, 0.20 mmol) was oxidized to aryl triflone 5ca in 82% yield (53.9 mg, 0.16 mmol) by treating with activated MnO₂ (Aldrich, azetropic with toluene, 175 mg) in methycyclohexane (2.0 mL) for 4 h at 70 °C. Colorless crystals (Et₂O); Mp. 68.5-70.0 °C; IR (KBr) v 3033, 2926, 1600, 1360, 1200, 1116, 1045, 655 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.49 (1H, s), 3.01 (1H, dd, J = 8.6, 7.9 Hz), 3.33 (1H, dd, J = 8.6, 7.9 Hz), 7.24-7.60 (7H, m), 8.04 (1H, d, J = 8.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 21.7, 36.1, 39.0, 120.1 (q, J C,F = 326.8 Hz), 126.3, 126.4, 128.3, 128.5, 128.6, 133.6, 133.8, 141.0, 145.8, 148.0; ¹⁹F NMR (282 Hz, CDCl₃) δ −15.9 (3F, s); MS (ESI-TOF) m/z 351 [M+Na⁺]; HRMS calcd for C₁₆H₁₂F₃NaO₂S [M+Na⁺], 351.0643; found, 351.0638.

2-Isobutyl-4-methyl-1-(trifluoromethylsulfonyl)benzene (5da)

![Image](https://i.imgur.com/3da.png)

According to the synthetic procedure for 5ba, 5-isobutyl-1-methyl-4-(trifluoromethylsulfonyl)cyclohexa-1,3-diene 4da was obtained in 98% yield (141.9 mg, 0.50 mmol) by thermolysis of 3da (212.4 mg, 0.51 mmol) in degassed xylenes (3.0 mL) for 3 h at 140 °C. Pale yellow oil; IR (neat) v 2959, 2872, 1568, 1359, 1214, 1129 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.89 (6H, d, J = 6.5 Hz), 1.26 (1H, ddd, J = 13.4, 10.1, 3.5 Hz), 1.54 (1H, ddd, J = 13.4, 10.9, 3.9 Hz), 1.56-1.68 (1H, m), 1.95 (3H, s), 2.34 (1H, d, J = 17.9 Hz), 2.52 (1H, dd, J = 17.9, 7.9 Hz), 2.73-2.81 (1H, m), 5.99 (1H, brs), 7.15 (1H, d, J = 5.7 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 20.9, 23.7, 24.3, 24.6, 29.9, 33.1, 38.9, 118.4, 120.1 (q, J C,F = 326.7 Hz), 129.3, 143.2, 149.1; ¹⁹F NMR (282 Hz, CDCl₃) δ −15.9 (3F, s); MS (ESI-TOF) m/z 283 [M+H⁺]; HRMS calcd for C₁₆H₁₃F₃S [M+H⁺], 283.0980; found, 283.0951.

The above cyclohexadiene 4da (54.2 mg, 192 μmol) was oxidized to aryl triflone 5da in 83% yield (44.7 mg, 159 μmol) by treating with activated MnO₂ (Aldrich, azetotropic with toluene, 200 mg) in methycyclohexane (2.0 mL) for 5 h at 70 °C. Colorless crystals (hexane); Mp. 55.0-58.5 °C; IR (neat) v 3054, 2962, 2872, 1600, 1362, 1212, 1128 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.94 (6H, d, J = 6.6 Hz), 1.96-2.09 (1H, m), 2.46 (3H, s), 2.86 (2H, d, J = 7.2 Hz), 7.23 (1H, s), 7.26 (1H, d, J = 8.2 Hz), 7.96 (1H, d, J = 8.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 21.7, 22.2, 30.8, 41.9, 120.0 (q, J C,F = 326.6 Hz), 126.8, 128.0, 133.6, 133.9, 145.9, 147.4; ¹⁹F NMR (282 Hz, CDCl₃) δ −16.0 (3F, s); MS (EI) m/z 280 [M⁺]; Anal. Calcd for C₁₂H₁₅F₃O₂: C, 51.42; H, 5.39. Found: C, 51.50; H, 5.38.
**tert-Butyl(5-methyl-2-(trifluoromethylsulfonyl)benzyl)oxy)diphenylsilane (5ea)**

According to the synthetic procedure for 5ba, tert-butyl(5-methyl-2-(trifluoromethylsulfonyl)cyclohexa-2,4-dienyl)methoxy)diphenylsilane 4ea was obtained in 85% yield (138.8 mg, 0.28 mmol) by thermolysis of 3ea (207.5 mg, 0.33 mmol) in degassed xylene (3.0 mL) for 4 h at 140 °C. Pale yellow oil; IR (neat) ν 3072, 2932, 2859, 1567, 1360, 1214, 1129, 703, 670 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.07 (9H, s), 1.92 (3H, s), 2.54 (1H, dd, J = 18.3, 8.6 Hz), 2.88 (1H, d, J = 18.3 Hz), 2.85-3.02 (1H, m), 3.57 (1H, t, J = 9.7 Hz), 3.78 (1H, dd, J = 9.7, 4.3 Hz), 5.92-5.97 (1H, m), 7.21 (1H, d, J = 5.9 Hz), 7.35-7.47 (6H, m), 7.60-7.66 (4H, m); ¹³C NMR (100 MHz, CDCl₃) δ 19.3, 24.0, 26.8, 31.2, 34.6, 61.9, 118.3, 120.0 (q, J₅₋₇ = 326.7 Hz), 124.4, 127.7, 127.76, 129.77 and 129.80, 133.1 and 133.3, 135.49 and 135.51, 145.5, 150.4; ¹⁹F NMR (282 Hz, CDCl₃) δ –15.8 (3F, s); MS (ESI-TOF) m/z 495 [M+H]⁺; HRMS calcd for C₂₅H₃₆F₅O₃SSi [M+H]⁺, 495.1637; found, 495.1592.

The above cyclohexadiene 4ea (38.6 mg, 78 μmol) was oxidized to aryl triflone 5ea in 80% yield (30.9 mg, 63 μmol) by treating with activated MnO₂ (Aldrich, azeotropic with toluene, 120 mg) in methylcyclohexane (1.0 mL) for 5 h at 70 °C. Colorless oil; IR (neat) ν 3072, 2939, 2859, 1598, 1364, 1214, 1125, 822, 702 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.15 (9H, s), 2.52 (3H, s), 5.20 (2H, s), 7.32 (1H, d, J = 8.1 Hz), 7.35-7.47 (6H, m), 7.64-7.69 (4H, m), 7.88 (1H, d, J = 8.1 Hz), 8.01 (1H, s); ¹³C NMR (100 MHz, CDCl₃) δ 19.4, 22.2, 26.9, 62.1, 119.9 (q, J₅₋₇ = 326.9 Hz), 124.0, 127.8, 128.4, 129.1, 129.9, 132.8, 133.2, 135.4, 144.9, 148.5; ¹⁹F NMR (282 Hz, CDCl₃) δ –16.1 (3F, s); MS (ESI-TOF) m/z 493 [M+H]⁺; HRMS calcd for C₂₅H₃₆F₃O₃SSi [M+H]⁺, 493.1481; found, 493.1529.

**5-Methyl-4′-nitro-2-(trifluoromethylsulfonyl)biphenyl (5fa)**

According to the synthetic procedure for 5ba, 1-(5-methyl-2-(trifluoromethylsulfonyl)cyclohexa-2,4-dienyl)-4-nitrobenzene 4fa was obtained in 98% yield (96.0 mg, 276 μmol) by thermolysis of 3fa (135.2 mg, 281 μmol) in degassed xylene (3.0 mL) for 4 h at 140 °C. Yellow crystals (hexane-Et₂O); Mp. 119–120 °C; IR (KBr) ν 3080, 2935, 1566, 1522, 1348, 1209, 1127, 855 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.87 (3H, s), 2.50 (1H, d, J = 18.3 Hz), 3.12 (1H, dd, J = 10.2 Hz), 4.12 (1H, d, J = 10.2 Hz), 6.13-6.20 (1H, m), 7.40 (2H, d, J = 8.7 Hz), 7.55 (1H, d, J = 5.9 Hz), 8.14 (2H, d, J = 8.7 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 24.0, 36.7, 38.3, 118.9, 119.8 (q, J₅₋₇ = 326.4 Hz), 124.0, 126.2, 127.9, 145.7, 147.41, 147.44, 149.3; ¹⁹F NMR (282 Hz, CDCl₃) δ –15.6 (3F, s); MS (ESI-TOF) m/z 348 [M+H]⁺; HRMS calcd for C₁₅H₁₃F₃NO₃S [M+H]⁺, 348.0517; found, 348.0544.

The above cyclohexadiene 4fa (95.8 mg, 276 μmol) was oxidized to aryl triflone 5fa in 97% yield (93.3 mg, 270 μmol) by treating with activated MnO₂ (Aldrich, azeotropic with toluene, 300 mg) in methylcyclohexane (2.0 mL) for 4 h at 70 °C. Colorless crystals (acetone); Mp. 157.5-159.5 °C; IR (KBr) ν 3113, 2923, 2854, 1593, 1518, 1365, 1347, 1213, 1132 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.54 (3H, s), 7.23 (1H, s), 7.28 (2H, s), 7.35-7.40 (4H, m), 7.80 (1H, d, J = 8.7 Hz), 7.85 (1H, d, J = 5.9 Hz), 8.05 (2H, d, J = 8.7 Hz).
d, \(J = 8.6\) Hz), 7.54 (1H, d, \(J = 8.3\) Hz), 8.11 (1H, d, \(J = 8.3\) Hz), 8.25 (2H, d, \(J = 8.6\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 20.7, 118.6 (q, \(J_{C,F} = 326.9\) Hz), 121.6, 125.4, 129.4, 129.5, 132.5, 132.8, 142.1, 143.4, 146.8, 147.1; \(^{19}\)F NMR (282 Hz, CDCl\(_3\)) \(\delta\) −15.4 (3F, s); MS (ESI-TOF) \(m/z\) 368 [M+Na]\(^+\); HRMS calcd for C\(_{14}\)H\(_{16}\)F\(_3\)NNaO\(_4\)S [M+Na]\(^+\), 368.0180; found, 368.0183.

1,2-Dimethyl-4-pentyl-5-(trifluoromethylsulfonyl)benzene (5bc)

According to the synthetic procedure for 5ba, cyclohexadiene 4bc was obtained in 93% yield (148.2 mg, 0.48 mmol) as an inseparable mixture of 1,2-dimethyl-5-pentyl-4-(trifluoromethylsulfonyl)cyclohexa-1,3-diene and cyclohexa-1,4-diene in a ratio of 12 : 1 by thermolysis of 3be (228.2 mg, 0.51 mmol) in degassed xylene (3.0 mL) for 2 h at 140 °C. Pale yellow oil; IR (neat) \(\nu\) 2954, 2932, 1568, 1360, 1211, 1149, 1118 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.86 (3H, t, \(J = 7.0\) Hz), 1.14-1.37 (6H, m), 1.44-1.54 (2H, m), 1.84 (3H, s), 1.87 (3H, s), 2.33 (1H, d, \(J = 17.1\) Hz), 2.50-2.66 (2H, m), 7.04 (1H, s); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 13.9, 16.7, 20.4, 22.4, 25.9, 30.6, 31.5, 31.9, 34.9, 120.1 (q, \(J_{C,F} = 326.8\) Hz), 124.1, 128.9, 141.2, 147.6; \(^{19}\)F NMR (282 Hz, CDCl\(_3\)) \(\delta\) −15.9 (3F, s); MS (ESI-TOF) \(m/z\) 311 [M+H]\(^+\); HRMS calcd for C\(_{14}\)H\(_{12}\)F\(_3\)O\(_2\)S [M+H]\(^+\), 311.1293; found, 311.1306.

The above cyclohexadiene 4bc (69.4 mg, 224 \(\mu\)mol) was oxidized to aryl triflone 5bc in 81% yield (55.9 mg, 181 \(\mu\)mol) by treating with activated MnO\(_2\) (Aldrich, azeotropic with toluene, 220 mg) in methylcyclohexane (2.0 mL) for 12 h at 70 °C. Colorless oil; IR (neat) \(\nu\) 2956, 2929, 1490, 1215, 1200, 1119 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.91 (3H, t, \(J = 6.8\) Hz), 1.30-1.43 (4H, m), 1.59-1.68 (2H, m), 2.31 (3H, s), 2.35 (3H, s), 2.90-2.98 (2H, m), 7.32 (1H, s), 7.79 (1H, s); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.0, 19.2, 20.1, 22.4, 31.8, 32.3, 33.0, 120.1 (q, \(J_{C,F} = 326.8\) Hz), 126.1, 133.7, 133.8, 136.0, 144.7, 147.6; \(^{19}\)F NMR (282 Hz, CDCl\(_3\)) \(\delta\) −15.9 (3F, s); MS (EI) \(m/z\) 308 [M]\(^+\), 239 [M–CF\(_3\)]\(^+\). Anal. Calcd for C\(_{14}\)H\(_{10}\)F\(_3\)O\(_2\)S: C, 54.53; H, 6.21. Found: C, 54.65; H, 6.31.
4. X-ray crystallographic data of 3af

Crystallographic data for the X-ray crystal structure analysis of 3af has been deposited with Cambridge Crystallographic Data Center (CCDC) as supplementary publication No. CCDC 821320. This data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

ORTEP diagram of 3af

Table S1. Crystal data and structure refinement for 3af.

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5. $^1$H and $^{13}$C NMR spectrum
6. References


