Simultaneous Introduction of Trifluoromethyl and $\lambda^5$-Pentafluorosulfanyl Substituents using SF$_5$-C≡C-CF$_3$ as Dienophile

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General remarks
All reagents from commercial suppliers were used without further purification. All solvents were freshly distilled from appropriate drying agents before use. Volatile reagents were transferred using a glass vacuum line system. Reactions were carried out under atmosphere of dry argon. TLC/PTLCs were performed with silica gel 60 F$_{254}$ plates. Column chromatography was carried out using silica gel 60. The NMR spectra were recorded on JEOL ECS 400 in CDCl$_3$; $^1$H-NMR (Me$_4$Si) at 400 MHz, $^{13}$C-NMR (Me$_4$Si) at 100 MHz and $^{19}$F-NMR (CFCl$_3$) at 376 MHz. EI mass spectra were recorded on a MAT 711 (Varian MAT Bremen). ESI mass spectra were recorded on an Agilent 6210 ESI-TOF, Agilent Technologies.
Procedure for the preparation of SF₅-C≡C-CF₃

3,3,3-Trifluoropropyne (22 mmol) and SF₅Br (22 mmol) were condensed into a 100 mL flask equipped with a Young-valve using a glass vacuum line. The valve was closed and the reaction mixture was kept at 80 °C for 2 days. The product was isolated and purified by fractional condensation under vacuum through traps kept at -78 and -196 °C. The product was collected in the -78 °C trap as a mixture of the E and Z alkenes 1a-b in a ratio of 1:2. 1a-b was slowly evaporated under vacuum and passed over KOH pellets in a U-tube kept at 90 °C. The alkyne 2 (2.65 g, 65 %) was collected in the trap kept at -196 °C.

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\begin{align*}
\text{SF}_5 & \\
\mid & \\
\text{CF}_3 & 
\end{align*}
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¹³C NMR (100 MHz, CDCl₃) δC 63.2 (q, ²JCF = 57 Hz, C-CF₃), 83.5 (quintet, ²JCF(eq) = 40 Hz, F₅S-C), 112.9 (q, ¹JCF = 262 Hz, -CF₃); ¹⁹F NMR (376 MHz) δ 80.8 (B₄-part, d, ²JF(eq)F(ax) = 161 Hz, 4F), 68.2 (A-part, 8 lines, 1F), -52.5 (s, CF₃).
$^{13}$C NMR of 2

$^{19}$F NMR of 2
General procedure for the synthesis of 4a-h

Diene 3a-h (1 mmol) was dissolved in dry DCM (3 mL) in a round-bottomed flask equipped with a Young valve. The reaction mixture was then cooled with liquid nitrogen and evacuated using a glass vacuum line system. Subsequently, the alkyne 2 (1.2 mmol) was condensed to the reaction mixture. After allowing to warm to room temperature within 15-20 min the reaction mixture was stirred at ambient temperature. All volatile materials were removed under reduced pressure. The crude product was purified by flash column chromatography using DCM/n-pentane (1:2 v/v) as eluent to obtain pure 4a-h.

4a: solidified oil; Yield (100%); 1H NMR (400 MHz, CDCl3) δH 7.30 (m, 2H), 7.55 (m, 6H), 7.83 (AB, JAB = 8 Hz, 1H, B-part), 7.98 (d, J = 8 Hz, 2H), 8.04 (AB, JAB = 8 Hz, 1H, A-Part), 8.09 (d, J = 8 Hz, 2H); 13C NMR (100 MHz, CDCl3) δC 93.7, 94.8, 120.6 (q, 1JCF = 273 Hz), 123.6, 123.9, 126.9, 128.3, 128.4, 128.8, 129.8, 133.1, 134.2, 146.9 (qquintet, 2JCF = 35 Hz, 3JCF(eq) = 4 Hz), 147.7, 148.4, 173.0 (quintetq, 2JCF(eq) = 18 Hz, 3JCF = 4 Hz); 19F NMR (376 MHz, CDCl3) δF 78.8 (9 lines, A-part), 71.9 (dq, 2JF(eq)F(ax) = 150 Hz, 5JF(eq)F = 12 Hz, B4-part), -57.2 (quintet, 5JFF(eq) = 12 Hz); HRMS (ESI) [M+Na]+ C23H14F8SNa found: 513.0548, calcd: 513.0529.

1H NMR of 4a.
$^{19}$F NMR of 4a

$^{13}$C NMR of 4a
4b: colorless oil; Yield (98%); ¹H NMR (400 MHz, CDCl₃) δH 5.68 (br s, 1H), 5.76 (br s, 1H), 7.27 – 7.30 (ABXY, J_AB = 5 Hz, J_AX = J_BY = 2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δC 84.2 (q, ³JC_F = 3 Hz), 86.5 (quintet, ³JC_F(eq) = 4 Hz), 120.4 (q, ¹JC_F = 269 Hz), 143.2, 143.3, 144.4 (qquintet, ²JC_F = 39 Hz, ³JC_F(eq) = 5 Hz), 169.5 (quintetqd, ³JC_F(eq) = 23 Hz, ³JC_F = 5 Hz, ²JC_F(ax) = 2 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δF 77.5 (9-lines, A-part), 65.6 (dq, ²J_F(eq)F(ax) = 152 Hz, ⁵J_F(eq)F = 10 Hz, B₄-part), -62.8 (quintet, ⁵J_F(eq)F = 10 Hz); HRMS (ESI) [M-H]- C₇H₄F₅SO found: 286.9835, calcd: 286.9837.
$^{13}$C NMR of 4b

$^{19}$F NMR of 4b
4c: colorless oil; Yield (78%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$ 1.80 (quintet, $^5$$J_{HF(eq)}$ = 1 Hz, 3H), 1.85 (q, $^5$$J_{HF}$ = 1 Hz, 3H), 6.96 – 7.00 (AB, $J_{AB}$ = 6 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta_C$ 16.1 (q, $^4$$J_{CF}$ = 2 Hz), 17.1 (quintet, $^4$$J_{CF(eq)}$ = 3 Hz), 92.5 (q, $^3$$J_{CF}$ = 1 Hz), 94.7 (quintet, $^4$$J_{CF(eq)}$ = 2 Hz), 120.7 (q, $^1$$J_{CF}$ = 271 Hz), 147.4, 147.9, 148.2 (quintet, $^2$$J_{CF}$ = 35 Hz, $^3$$J_{CF(eq)}$ = 4 Hz), 171.8 (quintet, $^3$$J_{CF(eq)}$ = 24 Hz, $^3$$J_{CF}$ = 6 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta_F$ 79.6 (9-lines, A-part), 68.5 (dq, $^2$$J_{F(eq)F(ax)}$ = 150 Hz, $^5$$J_{F(eq)F}$ = 10 Hz, B$_4$-part), -62.3 (quintet, $^5$$J_{FF(eq)}$ = 10 Hz); HRMS (ESI) [M+H]$^+$ C$_9$H$_9$F$_8$SO found: 317.4226, calcd: 317.422.
$^{13}$C NMR of 4c

$^{19}$F NMR of 4c
4d: colorless oil; Yield (98% without correction for the dicyclopentadiene impurity); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta_H 2.09\) (d, \(2J_{HH} = 7\) Hz, C-H\(_A\), 1H); 2.37 (dquintet, \(2J_{HH} = 7\) Hz, \(5J_{HF(eq)} = 1\) Hz, C-H\(_B\), 1H), 3.92 (br s, 1H), 4.11 (br s, 1H), 6.97 (m, 2H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta_C 52.4, 56.2\) (quintet, \(3J_{CF(eq)} = 4\) Hz), 71.5, 121.1 (q, \(1J_{CF} = 270\) Hz), 141.9, 142.5, 143.4 (qquintet, \(2J_{CF} = 38\) Hz, \(3J_{CF(eq)} = 5\) Hz), 168.3 (quintetq, \(2J_{CF(eq)} = 15\) Hz, \(3J_{CF} = 5\) Hz); \(^1^9\)F NMR (376 MHz, CDCl\(_3\)) \(\delta_F 80.1\) (A-Part, 9 lines), 64.7 (dq, \(2J_{F(eq)F(ax)} = 151\) Hz, \(5J_{F(eq)} = 10\) Hz, B\(_4\)-Part), -62.9 (quintet, \(5J_{F(eq)} = 10\) Hz); HRMS (EI, 80 eV): [M]** C\(_8\)H\(_6\)F\(_8\)S calcd. 286.0063, found 286.0070.

\(^1\)H NMR of 4d, impurity signals are due to the Diels-Alder dimer of cyclopentadiene (dicyclopentadiene, tricyclo[5,2,1,0\(^2\),6\]deca-3,8-diene).
13C NMR of 4d
19F NMR of 4d

Yellowish oil; Yield (98%); HRMS (EI, 80 eV): [M]+ C13H16F8S; calcd: 356.2126; found: 356.2122.

endo-4e: 1H NMR (400 MHz, CDCl3) δH 1.05 (d, 3JHH = 7 Hz, 3H), 1.34 (q, 4JHF = 2 Hz, 3H), 1.42 (quintet, 4JH(eq) = 3 Hz, 3H), 1.80 (s, 3H, CH3), 1.85 (s, 3H, CH3), 2.52 (qquintet, 3JHH = 6 Hz, 5JH(eq) = 1 Hz, 1H); 13C NMR (100 MHz, CDCl3) δC 9.6, 11.37, 11.38, 12.4 (q, 4JCF = 3 Hz), 14.1 (quintet, 4JCF(eq) = 4 Hz), 63.7, 66.5, 80.5, 121.8 (q, 1JCF = 271 Hz), 141.1, 141.5, 143.0 (qquintet, 2JCF = 34 Hz, 3JCF(eq) = 5 Hz), 168.2 (qquintet, 2JCF(eq) = 16 Hz, 3JCF = 5 Hz, 2JCF(ax) = 2 Hz); 19F NMR (376 MHz, CDCl3) δF 82.4 (quintet, 2JF(ax)F(eq) = 150 Hz), 69.7 (dq, 2JF(eq)F(ax) = 150 Hz, 5JF(eq)F = 14 Hz), -59.7 (quintet, 5JF(eq) = 15 Hz).

exo-4e: 1H NMR (400 MHz, CDCl3) δH 0.76 (d, 3JHH = 7 Hz, 3H), 1.33 (q, 4JHF = 2 Hz, 3H), 1.40 (quintet, 4JH(eq) = 3 Hz, 3H), 1.66 (s, 6H), 2.44 (q, 3JHH = 6 Hz, 1H); 13C NMR (100 MHz, CDCl3) δC 10.0, 10.90, 10.92, 11.8 (q, 4JCF = 3 Hz), 13.6 (quintet, 4JCF(eq) = 4 Hz), 63.8, 66.2, 78.7, 121.9 (q, 1JCF = 271 Hz), 134.2, 137.7, 147.7 (qquintet, 2JCF = 34 Hz, 3JCF(eq) = 5 Hz), 172.3 (qquintet, 2JCF(ax) = 16 Hz, 3JCF = 5 Hz, 2JCF(ax) = 2 Hz); 19F NMR (376 MHz, CDCl3) δF 82.3 (quintet, 2JF(ax)F(eq) = 150 Hz), 70.5 (dq, 2JF(eq)F(ax) = 150 Hz, 5JF(eq)F = 14 Hz), -59.4 (quintet, 5JF(eq) = 15 Hz).
$^1$H NMR of \textbf{4e}

$^1$H NMR of \textbf{4e} indicating the C-H group
$^{19}$F NMR of 4e

$^{13}$C NMR of 4e
$^{19}$F NMR of 4e indicating the -CF$_3$ groups of both regioisomers
4f: Colorless oil; Yield (65% due to incomplete conversion); $^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$
1.501 (s, CH$_3$, 3H), 1.504 (s, CH$_3$, 3H), 4.37 (br s, 1H), 4.55 (br s, 1H), 7.05 (m, 2H); $^{13}$C
NMR (100 MHz, CDCl$_3$) $\delta_C$ 18.2, 18.3, 52.4, 55.7, 101.9, 120.9 (q, $^1$J$_{CF}$ = 270 Hz), 142.0,
142.6, 143.1 (qquintet, $^2$J$_{CF}$ = 36 Hz, $^3$J$_{CF(eq)}$ = 4 Hz), 158.9, 167.6 (quintetq, $^2$J$_{CF(eq)}$ = 18
Hz, $^3$J$_{CF(eq)}$ = 4 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta_F$ 80.2 (9-lines, A-part), 65.2 (dq, $^2$J$_{F(eq)F(ax)}$ = 150
Hz, $^5$J$_{F(eq)F} = 11$ Hz, B$_4$-part), -62.5 (quintet, $^5$J$_{F(eq)}F$ = 11 Hz); HRMS (EI, 80 eV): [M]$^+$
C$_{11}$H$_{10}$F$_8$S; calcd: 326.0375; found: 326.0367.

$^1$H NMR of 4f
4g: yellowish oil; Yield (97%); $^1$H NMR (400 MHz, CDCl3) $\delta_H$ 1.55 (m, 4H), 4.06 (br s, 1H), 4.29 (quintet, $^4$J$_{HF(eq)}$ = 2 Hz, 1H), 6.42 (m, 2H); $^{13}$C NMR (100 MHz, CDCl3) $\delta_C$ 24.0, 24.2, 39.2, 41.7 (quintet, $^3$J$_{CF(eq)}$ = 4 Hz), 120.8 (q, $^1$J$_{CF}$ = 272 Hz), 133.6, 133.8, 134.9 (q quintet, $^2$J$_{CF}$ = 35 Hz, $^3$J$_{CF(eq)}$ = 3 Hz), 158.2 (quintetq, $^3$J$_{CF(eq)}$ = 17 Hz, $^3$J$_{CF}$ = 3 Hz); $^{19}$F NMR (376 MHz, CDCl3) $\delta_F$ 81.4 (9-lines, A-part), 63.7 (dq, $^2$J$_{F(eq)F(ax)}$ = 152 Hz, $^5$J$_{F(eq)F}$ = 10 Hz, B$_4$-part), -61.8 (quintet, $^5$J$_{FF(eq)}$ = 10 Hz); HRMS (EI, 80 eV): [M]+ C$_9$H$_8$F$_8$S; calcd: 300.0219; found: 300.0224.

$^1$H NMR of 4g
$^{13}$C NMR of $4g$

$^{19}$F NMR of $4g$
Diene 3h (1 mmol, 100 mg) was dissolved in dry toluene (2 mL) in a round-bottomed flask with a young valve. The reaction mixture was then cooled with liquid nitrogen and evacuated using a glass vacuum line system. Subsequently, the alkyne 2 (1.2 mmol, 275 mg) was condensed to the reaction mixture and slowly warmed to room temperature within 10 min. After 24 h of stirring at 110°C all volatile materials were removed under reduced pressure. The crude product was purified by fractional condensation under vacuum through traps kept at -30, -78 and -196 °C. The product 4h (yield 37%, 0.41 mmol, 128 mg, due to low conversion) was collected in the -30 °C trap.

4h: Colorless oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$H 0.71 (dd, $^2$J$_{HH}$ = 7 Hz, $^3$J$_{HH}$ = 4 Hz, 1H), 0.74 (dd, $^2$J$_{HH}$ = 7 Hz, $^3$J$_{HH}$ = 4 Hz, 1H) 1.49 (m, 1H), 1.58 (m, 1H), 4.08 (q, $^4$J$_{HF}$ = 2 Hz, 1H), 4.31 (quintet, $^4$J$_{HF(eq)}$ = 2.0 Hz, 1H), 6.11 (m, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$C 17.1, 17.3, 17.6, 41.2 (q, $^3$J$_{CF}$ = 3 Hz), 43.8 (quintet, $^3$J$_{CF(eq)}$ = 3 Hz), 121.4 (q, $^1$J$_{CF}$ = 273 Hz), 129.8, 130.1, 140.1 (quintet, $^2$J$_{CF}$ = 34 Hz, $^3$J$_{CF(eq)}$ = 2 Hz), 164.8 (quintet, $^2$J$_{CF(eq)}$ = 18 Hz, $^3$J$_{CF(eq)}$ = 2 Hz); $^{19}$F NMR (CDCl$_3$, 376 MHz) $\delta$F 81.7 (9 lines, A-part, 1F), 64.6 (dq, $^2$J$_{F(eq)F(ax)}$ = 165 Hz, $^5$J$_{F(eq)F}$ = 14 Hz, 4F, B$_4$-part), -61.7 (quintet, $^5$J$_{F(eq)F}$ = 14 Hz, 3F); HRMS (EI, 80 eV): 312 [M$^+$] $^{10}$C$_{10}$H$_8$F$_8$S; calcd: 312.0219; found: 312.0213.
$^1$H NMR of 4h

$^{13}$C NMR of 4h
$^{1}H-^{13}C$ HMQC of 4h
$2H$-pyran-2-on 3i (1 mmol, 100 mg) was dissolved in dry toluene (2 mL) in a round-bottomed flask equipped with a young valve. The reaction mixture was then cooled with liquid nitrogen and evacuated using a glass vacuum line system. Subsequently, the alkyne 2 (1.2 mmol, 275 mg) was condensed to the reaction mixture and slowly warmed up to room temperature within 10 min. After 48 h of stirring at 120°C all volatile materials were removed under reduced pressure. The crude product was purified by flash column chromatography using $n$-pentane as eluent (Rf = 0.5) affording the pure benzene 4i in 54% (0.56 mmol, 154 mg) yield due to low conversion.

4i: Colorless oil; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.65 (t, $^3$J$_{HH}$ = 7 Hz, 1H), 7.70 (t, $^3$J$_{HH}$ = 7 Hz, 1H), 7.93 (d, $^3$J$_{HH}$ = 8 Hz, 1H), 8.02 (d, $^3$J$_{HH}$ = 8 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$C 122.5 (q, $^1$J$_{CF}$ = 269 Hz), 126.5 (q, $^2$J$_{CF}$ = 33 Hz), 129.2 (q, $^3$J$_{CF}$ = 8 Hz), 129.9 (quintet, $^3$J$_{CF(eq)}$ = 6 Hz) 132.1, 132.5, 151.1 (quintet, $^2$J$_{CF(eq)}$ = 21 Hz); $^{19}$F NMR (CDCl$_3$, 376 MHz) $\delta$F 81.7 (9 lines, A-part, 1F), 68.6 (dq, $^2$J$_{(eq)F(ax)}$ = 149 Hz, $^5$J$_{(eq)F}$ = 18 Hz, 4F, B4-part), -57.9 (quintet, $^5$J$_{(eq)F}$ = 18 Hz, 3F); HRMS (EI, 80 eV): 271 [M$^+$] C$_7$H$_4$F$_8$S; calcd: 271.9906; found: 271.9910.
$^{1}H$ NMR of $4i$

$^{13}C$ NMR of $4i$
$^{19}$F NMR of 4i

$^{1}$H-$^{13}$C HMQC of 4i
$^{19}\text{F}-^{13}\text{C}$ HMQC of 4i

$^{19}\text{F}-^{13}\text{C}$ HMBC of 4i (C-CF$_3$)
$^{19}\text{F}\text{-}^{13}\text{C} \text{HMBC of 4i (C-SF}_5\text{)}$
6. Dark-purple crystals, mp 221-225 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$H 2.25 (s, 6H), 2.77 (s, 6H), 7.33 (m, 2H), 7.61 (dd, $J = 7$ Hz, $J = 4$ Hz, 2H); HRMS (ESI) [M+H]$^+$ C$_{19}$H$_{17}$O found: 261.1269, calcd: 261.1264.
$^1$H NMR after 4h indicating the decomposition of 6 in the solution
The *in situ* prepared compound 6 (2 mmol, 0.5 g) was dissolved in acetic anhydride (5 mL) in a round-bottomed flask equipped with a young valve. The reaction mixture was then cooled with liquid nitrogen and evacuated using a glass vacuum line system. Subsequently, the alkyne 2 (6 mmol, 1.3 g) was condensed to the reaction mixture and slowly warmed up to room temperature. After 24 h of stirring at 80°C the crude mixture was diluted with 50 mL of dichloromethane and extracted with water. The organic layer was dried over Na$_2$SO$_4$ for 1 h, filtered off and concentrated on the rotary evaporator. The crude product was purified by column chromatography using n-pentane as eluent (Rf = 0.3) affording the pure fluoranthene 7 in 75% (1.5 mmol, 0.67 g) yield.

7, Yellowish crystals, Yield (75%), mp = 121-123 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 2.69 (s, 3H), 2.78 (s, 3H), 2.87 (q, $^5$J$_{H-F}$ = 3 Hz, 3H), 2.92 (quintet, $^5$J$_{H-F(eq)}$ = 1 Hz, 3H), 7.37 (d, $^3$J$_{HH}$ = 8 Hz, 2H), 7.37 (d, $^3$J$_{HH}$ = 8 Hz, 2H); $^{13}$C NMR (CDCl$_3$) δ 24.1 (q, $^1$J$_{C-F}$ = 6 Hz), 24.7, 25.5, 25.7 (quintet, $^4$J$_{C-F(eq)}$ = 7 Hz), 124.1 (q, $^1$J$_{C-F}$ = 277 Hz), 128.1, 128.9, 131.7, 132.3, 132.7 (quintet, $^2$J$_{C-F}$ = 28 Hz, $^3$J$_{C-F(eq)}$ = 3 Hz), 133.5, 135.4, 143.4, 153.6 (quintet, $^2$J$_{C-F(eq)}$ = 14 Hz, $^3$J$_{C-F}$ = 4 Hz); $^{19}$F NMR (CDCl$_3$) δ 85.4 (A-part, 8-lines, 1F), 74.2 (dq, B$_4$-part, $^5$J$_{F(eq)}$ = 24 Hz, 1F), -49.7 (quintet, $^5$J$_{F-F(eq)}$ = 25 Hz, 3F); HRMS (EI, 80 eV): 452 [M$^+$] C$_{21}$H$_{16}$F$_8$S found: 452.0854, calcd: 452.0845.
$^{1}H$ NMR of 7

$^{13}C$ NMR of 7