Supporting Information

Metal-Free Radical Trifluoromethylation of (Hetero-)Arenes

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1 Materials and methods

^{1}H NMR spectra were recorded on a BRUKER Avance 300 (300 MHz) or a BRUKER Avance 400 (400 MHz) device as solutions at room temperature. Chemical shifts are expressed in parts per million (ppm, δ), downfield from tetramethylsilane (TMS) and referenced to chloroform (7.26 ppm) as internal standards. All coupling constants are absolute values and *J* values are expressed in Hertz (Hz). The spectra were analyzed according to first order and the descriptions of signals include: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet. **^{13}C NMR** spectra were recorded on a BRUKER Avance 300 (75 MHz), or a BRUKER Avance 400 (100 MHz) device as solutions at room temperature. Chemical shifts are expressed in parts per million (ppm, δ), downfield from tetramethylsilane (TMS) and referenced to $CDCl_3$ (77.0 ppm) as internal standards. The signal structure was analyzed by DEPT and is described as follows: + = primary or tertiary C-atom (positive signal), – = secondary C-atom (negative signal), and C_q = quaternary C-atom (no signal). **^{19}F NMR** spectra were recorded on a BRUKER Avance 400 (376 MHz) as solutions at room temperature without internal reference.

EI-MS (electron ionization mass spectrometry) was performed by using a *Finnigan* MAT 90 (70 eV). The molecular fragments are quoted as the relation between mass and charge (*m/z*), the intensities as a percentaged value relative to the intensity of the base signal (100%). The abbreviation $[M]^+$ refers to the molecule ion.

GC-MS (gas chromatography–mass spectrometry) was performed on an *Agilent* GC-MS (GC 8690N, MS 5975B VL MSD) with an *Agilent* HP-5MS (5%-Phenyl)-methylpolysiloxan column with helium as mobile phase and EI as ionization method.

IR (infrared spectroscopy) data were recorded on FT-IR *Bruker* IFS 88 and are reported as follows: frequency of absorption (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak, br = broad).

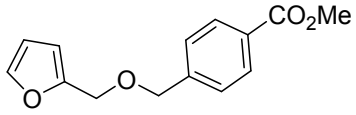
Reactions were monitored by silica gel coated aluminium plates (*Merck*, silica gel 60, F_{254}). Detection was performed by examination under UV light (254 nm) and by staining with molybdato phosphate (5% phosphor molybdic acid in ethanol) or potassium permanganate (0.75% $KMnO_4$ in H_2O). Solvents, reagents and chemicals were purchased from *Sigma-Aldrich*, *ABCR*, and *Fisher Scientific*. Tetrahydrofuran was distilled from sodium/potassium

prior to use. Dichloromethane was purchased from *Acros* over molecular sieves. All reactions involving moisture sensitive reactants were executed under argon atmosphere using oven dried glassware. All other solvents, reagents and chemicals were used as purchased unless stated otherwise.

2 Experimental procedures

Synthesis of substrates

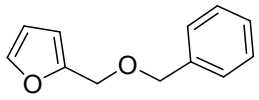
Methyl 4-((furan-2-ylmethoxy)methyl)benzoate (3)



A solution of 2-(hydroxymethyl)furan (0.217 mL, 245 mg, 2.50 mmol, 1.00 equiv.) and tetrabutylammonium iodide (92.3 mg, 0.250 mmol, 0.100 equiv.) in anhydrous THF (25 mL) was treated portionwise with NaH (60% in mineral oil, 200 mg, 5.00 mmol, 2.00 equiv.) at 0 °C. Then methyl 4-(bromomethyl)benzoate (1.43 g, 6.25 mmol, 2.50 equiv.) was added and the mixture was allowed to warm to rt. The reaction mixture was stirred for 15 h at rt., then quenched by addition of H_2O (50 mL), extracted with Et_2O (3 × 50 mL), dried over Na_2SO_4, and the solvent removed under reduced pressure. Column chromatography (cyclohexane/ethyl acetate = 10:1) afforded benzyl ether **3** as a colorless oil (601 mg, 2.44 mmol, 98%).

$\boldsymbol{R_f}$ (cyclohexane/ethyl acetate = 10:1) = 0.29. – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 3.91 (s, 3H, CH_3), 4.52 (s, 2H, CH_2), 4.60 (s, 2H, CH_2), 6.33–6.41 (m, 2H, O_{Fur}CHC*H*C*H*), 7.41 (d, ^3J = 8.3 Hz, 2H, CH_{Ar}), 7.43–7.46 (m, 1H, O_{Fur}C*H*), 8.02 (d, ^3J = 8.3 Hz, 2H, CH_{Ar}) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 52.1 (+, *C*H_3), 64.2 (–, *C*H_2), 71.2 (–, *C*H_2), 109.6 (+, *C*H_{Fur}), 110.3 (+, *C*H_{Fur}), 127.2 (C_q, *C*CO_2Me), 127.4 (+, 2 × *C*H_{Ar}), 129.7 (+, 2 × *C*H_{Ar}), 143.0 (+, O_{Fur}*C*H), 143.2 (C_q, *C*$_{Ar}$), 151.4 (C_q, *C*$_{Fur}$), 167.0 (C_q, *C*O_2Me) ppm. – **IR** (KBr): $\tilde{\nu}$ = 3429 (w), 2952 (m), 2857 (w), 1721 (s), 1614 (m), 1578 (w), 1503 (w), 1436 (m), 1415 (m), 1358 (m), 1280 (s), 1176 (m), 1151 (m), 1108 (s), 1019 (m), 919 (m), 885 (w), 858 (w), 814 (w), 756 (m), 704 (w), 601 (w) cm^{-1}. – **MS** (EI, 70 eV), *m/z* (%): 246 (21) $[M]^+$, 215 (11), 165 (16), 150 (50) $[C_9H_{10}O_2]^+$, 149 (72) $[M - C_9H_9O_2]^+$, 121 (39), 82 (61), $[C_5H_6O]^+$, 81 (100) $[C_5H_5O]^+$. – **HRMS** (EI, $C_{14}H_{14}O_4$): calcd. 246.0887; found: 246.0885.

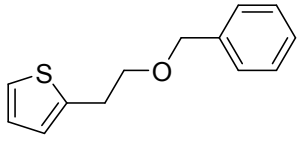
2-((Benzyloxy)methyl)furan (13)[1]



A solution of 2-(hydroxymethyl)furan (0.434 mL, 491 mg, 5.00 mmol, 1.00 equiv.) and tetrabutylammonium iodide (185 mg, 0.500 mmol, 0.100 equiv.) in anhydrous THF (50 mL) was treated portionwise with NaH (60% in mineral oil, 400 mg, 10.0 mmol, 2.00 equiv.) at 0 °C. Then benzyl bromide (1.79 mL, 2.57 g, 15.0 mmol, 3.00 equiv.) was added and the mixture was allowed to warm to rt. The reaction mixture was stirred for 15 h at rt., then quenched by addition of H_2O (50 mL), extracted with Et_2O (3 × 50 mL), dried over Na_2SO_4, and the solvent was removed under reduced pressure. Column chromatography (cyclohexane/ethyl acetate = 10:1) afforded benzyl ether **13** as a colorless oil (856 mg, 4.55 mmol, 91%).

$\boldsymbol{R_f}$ (cyclohexane/ethyl acetate = 10:1) = 0.58. – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 4.54 (s, 2H, CH_2), 4.60 (s, 2H, CH_2), 6.38–6.41 (m, 2H, O_{Fur}CHC*H*C*H*), 7.38–7.43 (m, 5H, CH_{Ph}), 7.47–7.48 (m, 1H, O_{Fur}C*H*) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 63.8 (–, *C*H_2), 71.8 (–, *C*H_2), 109.3 (+, *C*H_{Fur}), 110.2 (+, *C*H_{Fur}), 127.7 (+, *C*H_{Ph}), 127.9 (+, 2 × *C*H_{Ph}), 128.4 (+, 2 × *C*H_{Ph}), 137.8 (C_q, *C*$_{Ph}$), 142.8 (+, O_{Fur}*C*H), 151.7 (C_q, *C*$_{Fur}$) ppm. – **IR** (KBr): $\tilde{\nu}$ = 3443 (vw), 3117 (w), 3064 (w), 3031 (w), 2857 (w), 1712 (m), 1604 (vw), 1499 (w), 1454 (w), 1359 (m), 1269 (w), 1222 (m), 1150 (m), 1070 (m), 1016 (m), 919 (m), 885 (w), 815 (w), 738 (m), 699 (m), 601 (w), 530 (w) cm^{-1}. – **MS** (EI, 70 eV), *m/z* (%): 188 (13) $[M]^+$, 97 (18) $[M - C_7H_7]^+$, 92 (65), 91 (83) $[C_7H_7]^+$, 82 (70), 81 (100) $[M - OBn]^+$. – **HRMS** (EI, $C_{12}H_{12}O_2$): calcd. 188.0832; found: 188.0834. – The analytical data was in accordance with the literature.[1]

2-(2-(Benzyloxy)ethyl)thiophene (starting material for **6**)



A solution of 2-thiopheneethanol (0.278 mL, 321 mg, 2.50 mmol, 1.00 equiv.) and tetrabutylammonium iodide (92.3 mg, 0.250 mmol, 0.100 equiv.) in anhydrous THF (25 mL) was treated portionwise with NaH (60% in mineral oil, 200 mg, 5.00 mmol, 2.00 equiv.) at 0 °C. Then benzyl bromide (0.897 mL, 1.28 g, 7.50 mmol, 3.00 equiv.) was added and the

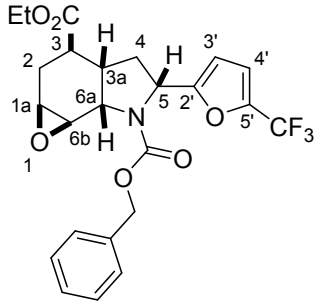
mixture was allowed to warm to rt. The reaction mixture was stirred for 3 d at rt., then quenched by addition of H_2O (50 mL), extracted with Et_2O (3 × 50 mL), dried over Na_2SO_4, and the solvent was removed under reduced pressure. Column chromatography (cyclohexane/ethyl acetate = 50:1) afforded 2-(2-(Benzyloxy)ethyl)thiophene as a yellow oil (546 mg, 2.50 mmol, 99%).

***R*f** (cyclohexane/ethyl acetate = 50:1) = 0.39. – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 3.22 (t, ^3J = 6.8 Hz, 2H, C*H*$_2$CH$_2$O), 3.79 (t, ^3J = 6.8 Hz, 2H, CH$_2$C*H*$_2$O), 4.62 (s, 2H, OC*H*$_2$Ph), 6.92–6.94 (m, 1H, C*H*$_{Thiophene}$), 7.00 (dd, ^3J = 5.1, ^3J = 3.5 Hz, 1H, C*H*$_{Thiophene}$), 7.21 (dd, ^3J =5.1, ^4J = 1.1 Hz, 1H, C*H*$_{Thiophene}$), 7.34–7.46 (m, 5H, C*H*$_{Ph}$) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 30.5 (+, *C*H$_2$CH$_2$O), 70.9 (–, OCH$_2$), 73.0 (–, OCH$_2$), 123.6 (+, *C*H), 125.1 (+, *C*H), 126.6 (+, *C*H), 127.5 (+, *C*H), 127.6 (+, 2 × *C*H), 128.3 (+, 2 × *C*H), 138.2 (C$_q$), 141.2 (C$_q$) ppm. – **IR** (KBr): $\tilde{\nu}$ = 3443 (vw), 3065 (vw), 3030 (vw), 2857 (w), 1496 (vw), 1454 (w), 1361 (w), 1205 (vw), 1101 (m), 1029 (w), 850 (vw), 823 (vw), 736 (w), 696 (w), 605 (vw) cm^{-1}. – **MS** (EI, 70 eV), *m/z* (%): 218 (35) [M]$^+$, 112 (14) [C$_6$H$_8$S]$^+$, 97 (100), 91 (62) [C$_7$H$_7$]$^+$. – **HRMS** (EI, C$_{13}$H$_{14}$OS): calcd. 218.0760; found: 218.0758.

General procedure for the trifluoromethylation, pentafluoroethylation, and heptafluoropropylation of arenes:

A solution of the substrate in dichloromethane was cooled to 0 °C. Then urea–hydrogen peroxide (7.00–10.0 equiv.) was added, followed by dropwise addition (over 10 min) of a fluorinated carboxylic anhydride (6.00–20.0 equiv.). The suspension was stirred at 0 °C until complete consumption of the starting material was observed. The mixture poured into saturated aqueous $NaHCO_3$ solution (25 mL per mmol substrate) and stirred for another 30 min. The phases were separated, the aqueous phase was extracted with dichloromethane, the combined organic layers were dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The yield was analyzed by ^{1}H and/or ^{19}F NMR with an internal standard (^{1}H: mesitylene; ^{19}F: *o*-fluoronitrobenzene) or the crude product was purified by column chromatography.

***rac*-Ethyl (1a*R*,3*S*,3a*R*,5*S*,6a*R*,6b*S*)-5-(5-(trifluoromethyl)furan-2-yl)octahydro-2*H*-oxireno[2,3-*g*]indole-3-carboxylate (2a)**



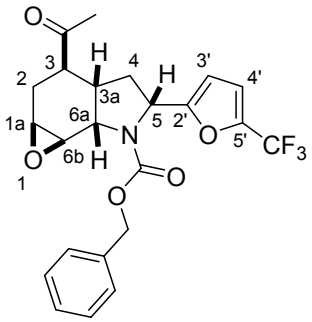
This compound was synthesized according to the **general procedure** using *rac*-1-benzyl 4-ethyl (2*S*,3a*R*,4*S*,7a*S*)-2-(furan-2-yl)-2,3,3a,4,5,7a-hexahydro-1*H*-indole-1,4-dicarboxylate (**1a**, 53.4 mg, 0.135 mmol, 1.00 equiv.)[a], urea–hydrogen peroxide (152 mg, 1.62 mmol, 12.0 equiv.) and TFAA (0.133 mL, 199 mg, 0.945 mmol, 7.00 equiv.) in 2 mL dichloromethane; reaction time: 2.5 h. The product **2a** was obtained after column chromatography (cyclohexane/ethyl acetate = 3:1) as a yellow oil (26.4 mg, 55.1 µmol, 41%).

R_f (cyclohexane/ethyl acetate = 3:1) = 0.22. – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.28 (t, ^3J = 7.1 Hz, 3H, CH_2CH_3), 2.00–2.09 (m, 1H, 4-H_A), 2.15–2.28 (m, 1H, 2-H_A), 2.30 (dt, ^2J = 13.1, ^3J = 7.9 Hz, 1H, 4-H_B), 2.39–2.51 (m, 1H, 3-H), 2.73–2.83 (m, 1H, 2-H_B), 2.88–2.99 (m, 1H, 3a-H), 3.14–3.23 (m, 1H, 6b-H), 3.24–3.29 (m, 1H, 1a-H), 4.19 (q, ^3J = 7.1 Hz, 2H, CH_2CH_3), 4.47–4.63 (m, 1H, 6a-H), 4.86–5.03 (m, 1H, 5-H), 5.03–5.23 (m, 2H, OCH_2), 6.01–6.24 (m, 1H, H_{Fur}), 6.58–6.79 (m, 1H, H_{Fur}), 7.09–7.43 (m, 5H, H_{Ar}) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 14.3 (+, CH_2CH_3), 21.7 (–, C2), 33.3 (–, C4), 34.0 (+, C3a), 35.6 (+, C3), 51.4 (+, C1a), 52.6 (+, C6b), 53.4 (+, C6a), 54.7 (+, C5), 61.1 (–, CH_2CH_3), 67.5 (–, OCH_2), 108.2 (+, CH_{Fur}), 112.5 (+, CH_{Fur}), 119.2 (q, C_q, ^1J = 266.7 Hz, CF_3), 128.1 (+, 2 × CH_{Ar}), 128.3 (+, CH_{Ar}), 128.6 (+, 2 × CH_{Ar}), 136.4 (C_q, C_{Ar}), 154.8 (C_q, NCO_2Bn), 173.1 (C_q, CO_2H) ppm. Both quaternary C atoms of the furyl ring could not be assigned due to low signal intensity. – **^{19}F NMR** (376 MHz, $CDCl_3$): δ = –64.3 ppm. – **IR** (KBr): $\tilde{\nu}$ = 3443 (w), 3134 (w), 2984 (m), 1713 (s), 1614 (m), 1560 (m), 1499 (w), 1454 (m), 1406 (s), 1321 (s), 1178 (s), 1128 (s), 1033 (s), 938 (m), 915 (w), 863 (m), 799 (m), 772 (m), 739 (m), 699 (m), 634 (w) cm^{-1}. – **MS** (EI, 70 eV), *m/z* (%): 479 (1.6) $[M]^+$, 418 (2), 388 (40) $[M – C_7H_7]^+$, 344

[a] For synthesis of **1a** and **1b** see: B. M. Ruff, S. Zhong, M. Nieger, M. Sickert, C. Schneider, S. Bräse, *Eur. J. Org. Chem.* **2011**, 6558–6566.

(8) $[M - C_7H_7 - CO_2]^+$, 270 (4), 254 (9), 252 (6), 91 (100) $[C_7H_7]^+$. – **HRMS** (EI, $C_{24}H_{24}NF_3O_6$): calcd. 479.1555; found: 479.1559.

***rac*- Benzyl (1a*R*,3*S*,3a*R*,5*S*,6a*R*,6b*S*)-3-acetyl-5-(5-(trifluoromethyl)furan-2-yl)octahydro-6*H*-oxireno[2,3-*g*]indole-6-carboxylate (2b)**

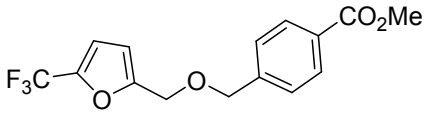


This compound was synthesized according to the **general procedure** using *rac*-benzyl (2*S*,3a*R*,4*S*,7a*S*)-4-acetyl-2-(furan-2-yl)-2,3,3a,4,5,7a-hexahydro-1*H*-indole-1-carboxylate (**1b**, 26.0 mg, 71.2 µmol, 1.00 equiv.)[a], urea–hydrogen peroxide (80.1 mg, 0.852 mmol, 12.0 equiv.) and TFAA (70.0 µL, 104 mg, 0.497 mmol, 7.00 equiv.) in 0.9 mL dichloromethane; reaction time: 3 h. The reaction was quenched with H_2O (3 mL) and stirred for another 1 h. The phases were separated and the aqueous phase was extracted with dichloromethane (3 × 10 mL), the combined organic layers were washed with saturated aqueous $NaHCO_3$, H_2O, and aqueous NaCl solution (10 mL each), dried over Na_2SO_4, and the solvent removed under reduced pressure. The product **2b** was obtained after column chromatography (cyclohexane/ethyl acetate = 2:1) as a colorless oil (15.8 mg, 35.2 µmol, 50%).

$\boldsymbol{R_f}$ (cyclohexane/ethyl acetate = 2:1) = 0.17. – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.99–2.08 (m, 1H, 4-H_A), 2.22 (s, 3H, CH_3), 2.24–2.46 (m, 3H, 2-H_A, 3-H, 4-H_B), 2.70 (d, ^2J = 15.9 Hz, 1H, 2-H_B), 2.98–3.04 (m, 1H, 3a-H), 3.09–3.24 (m, 1H, 6b-H), 3.25–3.32 (m, 1H, 1a-H), 4.43–4.60 (m, 1H, 6a-H), 4.87–5.01 (m, 1H, 5-H), 5.12 (s, 2H, OCH_2), 6.03–6.40 (m, 1H, H_{Fur}), 6.68–6.76 (m, 1H, H_{Fur}), 7.06–7.42 (m, 5H, H_{Ar}) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 21.8 (–, C2), 27.8 (+, CH_3), 32.8 (–, +, C4, C3a), 43.5 (+, C3), 51.1 (+, C1a), 52.6 (+, C6a, C6b), 54.4 (+, C5), 67.4 (–, OCH_2), 107.8 (+, CH_{Fur}), 112.4 (+, CH_{Fur}), 119.0 (q, C_q, ^1J = 269.3 Hz, CF_3), 127.9 (+, 2 × CH_{Ar}), 128.1 (+, CH_{Ar}), 128.5 (+, 2 × CH_{Ar}), 136.1 (C_q, C_{Ar}), 140.7 (q, C_q, ^2J = 43.2 Hz, C5'), 147.7 (C_q, C2'), 154.6 (C_q, NCO_2Bn), 207.6 (C_q,

*C*OCH$_3$) ppm. – **^{19}F NMR** (376 MHz, $CDCl_3$): δ = –63.9 ppm. – **IR** (ATR): $\tilde{\nu}$ = 2952 (w), 1699 (s), 1615 (w), 1560 (w), 1405 (m), 1352 (m), 1318 (m), 1172 (s), 1100 (s), 1019 (m), 965 (m), 938 (w), 906 (w), 872 (w), 796 (m), 771 (w), 737 (m), 697 (m), 628 (vw), 589 (w), 544 (vw), 458 (w) cm^{-1}. – **MS** (EI, 70 eV), *m/z* (%): 449 (9) $[M]^+$, 388 (5), 358 (25) $[M - C_7H_7]^+$, 314 (5) $[M - C_7H_7 - CO_2]^+$, 224 (7), 91 (100) $[C_7H_7]^+$. – **HRMS** (EI, $C_{23}H_{22}NF_3O_5$): calcd. 449.1450; found: 449.1449.

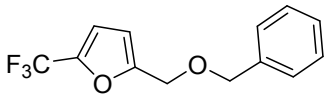
Methyl 4-(((5-(trifluoromethyl)furan-2-yl)methoxy)methyl)benzoate (4)



This compound was synthesized according to the **general procedure** using methyl 4-((furan-2-ylmethoxy)methyl)benzoate (**3**, 49.3 mg, 0.200 mmol, 1.00 equiv.), urea–hydrogen peroxide (188 mg, 2.00 mmol, 10.0 equiv.) and TFAA (0.564 mL, 840 mg, 4.00 mmol, 20.0 equiv.) in 4 mL dichloromethane; reaction time: 1 h. The product **4** was obtained after column chromatography (cyclohexane/ethyl acetate = 10:1) as a colorless liquid (31.0 mg, 98.0 µmol, 49%).

***R*$_f$** (cyclohexane/ethyl acetate = 10:1) = 0.18. – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 3.91 (s, 3H, C*H*$_3$), 4.54 (s, 2H, OC*H*$_2$), 4.63 (s, 2H, OC*H*$_2$), 6.41 (d, ^3J = 3.3 Hz, 1H, CHC*H*CCF$_3$), 6.74–6.77 (m, 1H, C*H*CHCCF$_3$), 7.41 (d, ^3J = 8.1 Hz, 2H, *H*$_{Ph}$), 8.03 (d, ^3J = 8.1 Hz, 2H, *H*$_{Ph}$) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 52.1 (+, *C*H$_3$), 63.9 (–, O*C*H$_2$), 71.8 (–, O*C*H$_2$), 110.0 (+, *C*H$_{Fur}$), 112.3 (+, *C*H$_{Fur}$), 118.9 (q, C$_q$, ^1J = 266.4 Hz, *C*F$_3$), 127.4 (+, 2 × *C*H$_{Ar}$), 129.6 (C$_q$, *C*CO$_2$Me), 129.8 (+, 2 × *C*H$_{Ar}$), 141.9 (q, C$_q$, ^2J = 43.2 Hz, *C*CF$_3$), 142.7 (C$_q$, *C*$_{Ar}$CH$_2$), 154.3 (C$_q$, *C*$_{Fur}$), 166.9 (C$_q$, *C*O$_2$Me) ppm. – **^{19}F NMR** (376 MHz, $CDCl_3$): δ = –64.1 ppm. – **IR** (KBr): $\tilde{\nu}$ = 2955 (w), 1718 (m), 1614 (w), 1566 (w), 1508 (vw), 1436 (w), 1384 (w), 1275 (s), 1175 (s), 1105 (s), 1018 (m), 955 (m), 933 (m), 807 (m), 757 (m), 730 (m), 704 (w), 629 (vw), 552 (w), 504 (w) cm^{-1}. – **MS** (EI, 70 eV), *m/z* (%): 314 (5) $[M]^+$, 283 (5), 149 (46), 133 (50), 99 (100), 82 (78). – **HRMS** (EI, $C_{15}H_{13}F_3O_4$): calcd. 314.0760; found: 314.0759.

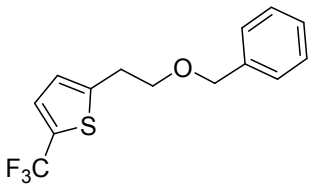
2-((Benzyloxy)methyl)-5-(trifluoromethyl)furan (5)



This compound was synthesized according to the **general procedure** using 2-((benzyloxy)methyl)furan (**13**, 37.6 mg, 0.200 mmol, 1.00 equiv.), urea–hydrogen peroxide (188 mg, 2.00 mmol, 10.0 equiv.) and TFAA (0.564 mL, 840 mg, 4.00 mmol, 20.0 equiv.) in 4 mL dichloromethane; reaction time: 1 h. The product **5** was obtained after column chromatography (cyclohexane/ethyl acetate = 10:1) as a colorless liquid (25.1 mg, 98.0 µmol, 49%).

$\boldsymbol{R_f}$ (cyclohexane/ethyl acetate = 10:1) = 0.40. – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 4.52 (s, 2H, OCH_2), 4.59 (s, 2H, OCH_2), 6.40 (d, ^3J = 3.3 Hz, 1H, CHCHCCF$_3$), 6.74–6.77 (m, 1H, CHCHCCF$_3$), 7.29–7.41 (m, 5H, H_{Ph}) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 63.6 (–, OCH$_2$), 72.5 (–, OCH$_2$), 109.7 (+, CH$_{Fur}$), 112.2 (+, CH$_{Fur}$), 119.0 (q, C$_q$, ^1J = 264.2 Hz, CF$_3$), 127.91 (+, 2 × CH$_{Ar}$), 127.93 (+, CH$_{Ar}$), 128.5 (+, 2 × CH$_{Ar}$), 137.4 (C$_q$, C_{Ar}), 141.8 (q, C$_q$, ^2J = 42.5 Hz, CCF$_3$), 154.7 (C$_q$, C_{Fur}) ppm. – **^{19}F NMR** (376 MHz, $CDCl_3$): δ = –64.0 ppm. – **IR** (KBr): $\tilde{\nu}$ = 3032 (vw), 2860 (vw), 1725 (vw), 1614 (w), 1561 (w), 1497 (vw), 1454 (w), 1384 (w), 1353 (w), 1317 (m), 1175 (m), 1128 (m), 1106 (s), 1072 (m), 1023 (m), 956 (w), 933 (m), 804 (m), 735 (m), 696 (m), 603 (w), 460 (w) cm^{-1}. – **MS** (EI, 70 eV), *m/z* (%): 256 (16) [M]$^+$, 149 (47), [M – OBn]$^+$, 107 (20) [C$_7$H$_7$O]$^+$, 92 (100) [C$_7$H$_8$]$^+$, 91 (89) [C$_7$H$_7$]$^+$. – **HRMS** (EI, C$_{13}$H$_{11}$F$_3$O$_2$): calcd. 256.0706; found: 256.0705.

2-(2-(Benzyloxy)ethyl)-5-(trifluoromethyl)thiophene (6)

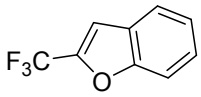


This compound was synthesized according to the **general procedure** using 2-(2-(benzyloxy)ethyl)thiophene (43.7 mg, 0.200 mmol, 1.00 equiv.), urea–hydrogen peroxide (188 mg, 2.00 mmol, 10.0 equiv.) and TFAA (0.564 mL, 840 mg, 4.00 mmol, 20.0 equiv.) in 4 mL dichloromethane; reaction time: 3 h. The yield of **6** was determined to be 24% by analysis with *o*-fluoronitrobenzene as internal standard. A pure sample was obtained after

column chromatography (cyclohexane/ethyl acetate = 50:1) as a colorless liquid (12.6 mg, 44.0 µmol, 22%).

***R*f** (cyclohexane/ethyl acetate = 50:1) = 0.13. – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 3.13 (t, ^{3}J = 6.4 Hz, 2H, CH_2CH_2O), 3.71 (t, ^{3}J = 6.4 Hz, 2H, CH_2CH_2O), 4.56 (s, 2H, OCH_2Ph), 6.80–6.83 (m, 1H, $CH_{Thiophene}$), 7.26–7.39 (m, 6H, $CH_{Thiophene}$, 5 × CH_{Ph}) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 30.7 (–, OCH_2CH_2), 70.0 (–, OCH_2), 73.2 (–, OCH_2), 122.5 (q, C_q, ^{1}J = 268.6 Hz, CF_3), 125.0 (+, $CH_{Thiophene}$), 127.69 (+, 2 × CH_{Ph}), 127.73 (+, CH_{Ph}), 128.3 (q, +, ^{3}J = 3.9 Hz, $CH_{Thiophene}$), 128.4 (+, 2 × CH_{Ph}), 129.3 (q, C_q, ^{2}J = 38.8 Hz, CCF_3), 137.9 (C_q), 146.1 (C_q) ppm. – **^{19}F NMR** (376 MHz, $CDCl_3$): δ = –55.1 ppm. – **IR** (KBr): $\tilde{\nu}$ = 2857 (w), 1553 (w), 1480 (w), 1454 (w), 1358 (w), 1300 (m), 1203 (vw), 1150 (m), 1114 (s), 1059 (m), 999 (m), 808 (w), 736 (m), 696 (m), 623 (w) cm^{-1}. – **MS** (EI, 70 eV), *m/z* (%): 286 (12) $[M]^+$, 256 (12), 165 (8), 91 (100) $[C_7H_7]^+$. – **HRMS** (EI, $C_{14}H_{13}SF_3O$): calcd. 286.0634; found: 286.0632.

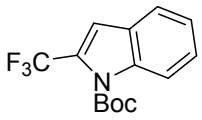
2-(Trifluoromethyl)benzofuran (7)



This compound was synthesized according to the **general procedure** using benzofuran (59.0 mg, 0.500 mmol, 1.00 equiv.), urea–hydrogen peroxide (470 mg, 5.00 mmol, 10.0 equiv.) and TFAA (1.41 mL, 2.10 g, 10.0 mmol, 20.0 equiv.) in 4 mL dichloromethane; reaction time: 2 h. The yield of **7** was determined to be 36% by analysis with *o*-fluoronitrobenzene as internal standard. A pure sample for analysis was obtained after column chromatography (pentane) as a colorless volatile liquid (16.1 mg, 86.5 µmol, 17%).

***R*f** (pentane) = 0.35. – **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.18 (s, 1H, $CHCCF_3$), 7.34 (t, ^{3}J = 7.7 Hz, 1H, H_{Ar}), 7.45 (t, ^{3}J = 7.7 Hz, 1H, H_{Ar}), 7.58 (d, ^{3}J = 8.3 Hz, 1H, H_{Ar}), 7.68 (d, ^{3}J = 7.9 Hz, 1H, H_{Ar}) ppm. – **^{19}F NMR** (376 MHz, $CDCl_3$): δ = –64.8 ppm. – The analytical data was in accordance with the literature.[2]

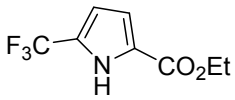
tert-Butyl 2-(trifluoromethyl)-1*H*-indole-1-carboxylate (8)



This compound was synthesized according to the **general procedure** using *tert*-butyl 1*H*-indole-1-carboxylate (43.5 mg, 0.200 mmol, 1.00 equiv.), urea–hydrogen peroxide (188 mg, 2.00 mmol, 10.0 equiv.) and TFAA (0.564 mL, 840 mg, 4.00 mmol, 20.0 equiv.) in 4 mL dichloromethane; reaction time: 1 h. The product **8** was obtained after preparative TLC (cyclohexane/ethyl acetate = 50:1) as a yellow oil (11.2 mg, 39.3 µmol, 20%).

$\boldsymbol{R_f}$ (cyclohexane/ethyl acetate = 50:1) = 0.55. – **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 1.67 (s, 9H, C(CH_3)$_3$, 7.14 (s, 1H, C*H*), 7.29 (t, ^3J = 7.6 Hz, 1H, C*H*), 7.44 (t, ^3J = 7.8 Hz, 1H, C*H*), 7.62 (d, ^3J = 7.7 Hz, 1H, C*H*), 8.28 (d, ^3J = 8.5 Hz, 1H, C*H*) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 27.8 (+, C(CH_3)$_3$), 85.4 (C_q, C(CH_3)$_3$), 113.4 (q, +, ^3J = 4.9 Hz, CHCCF$_3$), 116.0 (+, *C*H), 120.7 (q, C_q, ^1J = 267, CF_3), 122.0 (+, *C*H), 123.5 (+, *C*H), 126.5 (C_q), 126.9 (C_q, q, ^2J = 39.0 Hz, CCF_3), 127.0 (+, *C*H), 137.7 (C_q), 148.6 (C_q) ppm. – **^{19}F NMR** (471 MHz, $CDCl_3$): δ = –58.4 ppm. – The analytical data was in accordance with the literature.[3]

Ethyl 5-(trifluoromethyl)-1*H*-pyrrole-2-carboxylate (9)

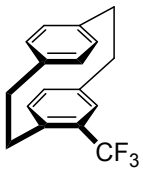


This compound was synthesized according to the **general procedure** using Ethyl 1*H*-pyrrole-2-carboxylate (27.8 mg, 0.200 mmol, 1.00 equiv.), urea–hydrogen peroxide (188 mg, 2.00 mmol, 10.0 equiv.) and TFAA (0.564 mL, 840 mg, 4.00 mmol, 20.0 equiv.) in 4 mL dichloromethane; reaction time: 1 h. The product **9** was obtained after column chromatography (cyclohexane/ethyl acetate = 10:1 → 5:1) as a yellow oil (6.5 mg, 31.4 µmol, 16%).

$\boldsymbol{R_f}$ (cyclohexane/ethyl acetate = 10:1) = 0.24. – **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 1.38 (t, ^3J = 7.1 Hz, 3H, CH_2CH_3), 4.38 (q, ^3J = 7.1 Hz, 2H, CH_2CH_3), 6.57–6.61 (m, 1H, C*H*), 6.86–6.90 (m, 1H, C*H*), 9.98 (bs, 1H, NH) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 14.3 (+, CH_2CH_3), 61.2 (–, CH_2CH_3), 110.9 (q, +, ^3J = 2.7 Hz, CHCCF$_3$), 114.8 (+, *C*H), 120.4 (q, C_q, ^1J = 268.8 Hz, CF_3), 124.4 (q, C_q, ^2J = 40.9 Hz, CCF_3), 125.3 (C_q), 160.7 (C_q, CO_2Et) ppm. –

^{19}F NMR (471 MHz, $CDCl_3$): δ = –60.9 ppm. – The analytical data was in accordance with the literature.[4]

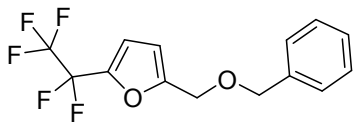
4-Trifluoromethyl[2.2]paracyclophane (10), *mixture with di- and tri-trifluoromethylated products*



This compound was synthesized according to the **general procedure** using [2.2]paracyclophane (41.7 mg, 0.200 mmol, 1.00 equiv.), urea–hydrogen peroxide (188 mg, 2.00 mmol, 10.0 equiv.) and TFAA (0.141 mL, 210 mg, 1.00 mmol, 5.00 equiv.) in 4 mL dichloromethane; reaction time: 50 min. The yield was determined to be 13% by analysis with *o*-fluoronitrobenzene as internal standard. After preparative TLC (cyclohexane/ethyl acetate = 20:1), a yellow solid was isolated (13.4 mg) which, as analyzed by GC-MS, contained of the product **10** (as main product) along with di-trifluoromethyl- and tri-trifluoromethyl[2.2]paracyclophane (mixture of isomers with unknown ratio).

***R*$_f$** (cyclohexane/ethyl acetate = 10:1) = 0.62. – **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 2.94–3.31, 3.41–3.57 (2 × m, 8H, 4 × CH_2), 6.36–6.94 (m, 7H, CH_{Ar}) ppm. – **^{19}F NMR** (376 MHz, $CDCl_3$): δ = –59.6 ppm. – **IR** (ATR):[b] $\tilde{\nu}$ = 2929 (m), 2854 (w), 1596 (w), 1497 (w), 1418 (w), 1323 (m), 1296 (s), 1170 (m), 1140 (s), 1106 (vs), 1049 (s), 959 (w), 946 (w), 915 (m), 900 (m), 854 (m), 808 (w), 794 (m), 736 (m), 722 (m), 695 (w), 669 (m), 649 (m), 612 (m), 514 (m) cm^{-1}. – **GC-MS**: *m/z* = 276 $[M]^+$, 172 $[C_9H_7F_3]^+$, 104 $[C_8H_8]^+$. – **HRMS** (EI, $C_{17}H_{15}F_3$): calcd. 276.1120; found: 276.1122.

2-((Benzyloxy)methyl)-5-(perfluoroethyl)furan (17)

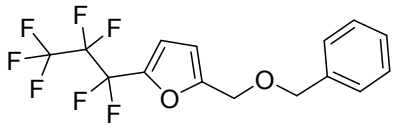


[b] The IR spectrum was measured for the product mixture.

This compound was synthesized according to the **general procedure** using 2-((benzyloxy)methyl)furan (**13**, 37.6 mg, 0.200 mmol, 1.00 equiv.), urea–hydrogen peroxide (188 mg, 2.00 mmol, 10.0 equiv.) and pentafluoropropionic anhydride (**16**, 0.789 mL, 1.24 g, 4.00 mmol, 20.0 equiv.) in 4 mL dichloromethane; reaction time: 1 h. The product **17** was obtained after column chromatography (cyclohexane/ethyl acetate = 20:1) as a yellow liquid (28.2 mg, 92.1 µmol, 46%).

R_f (cyclohexane/ethyl acetate = 10:1) = 0.40. – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 4.53 (s, 2H, OCH_2), 4.58 (s, 2H, OCH_2), 6.44 (d, ^3J = 3.5 Hz, 1H, CHCHCCF_2), 6.80–6.83 (m, 1H, CHCHCCF_2), 7.29–7.39 (m, 5H, H_{Ph}) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 63.6 (–, OCH_2), 72.5 (–, OCH_2), 108.7 (tq, C_q, ^1J = 251.8 Hz, ^2J = 40.3 Hz, CF_2), 110.1 (+, CH_{Fur}), 114.2 (t, +, ^3J = 2.9 Hz, CH_{Fur}), 118.5 (qt, C_q, ^1J = 286.2 Hz, ^2J = 38.1 Hz, CF_3), 127.9 (+, 2 × CH_{Ph}), 128.0 (+, CH_{Ph}), 128.5 (+, 2 × CH_{Ph}), 137.4 (C_q, C_{Ph}), 140.7 (t, C_q, ^2J = 32.2 Hz, CC_2F_5), 155.8 (q, ^4J = 2.2 Hz, C_q, C_{Fur}) ppm. – **^{19}F NMR** (376 MHz, $CDCl_3$): δ = –114.0 (q, ^3J = 3.4 Hz, 2F, CF_2), –84.1 (t, ^3J = 3.4 Hz, 3F, CF_3) ppm. – **IR** (KBr): $\tilde{\nu}$ = 2860 (vw), 1608 (vw), 1555 (vw), 1497 (vw), 1454 (vw), 1335 (w), 1297 (w), 1202 (s), 1149 (m), 1106 (m), 1028 (m), 1014 (m), 955 (w), 903 (m), 803 (w), 744 (m), 697 (m), 602 (w), 458 (w) cm^{-1}. – **MS** (EI, 70 eV), *m/z* (%): 306 (8) $[M]^+$, 200 (15) $[C_7H_5F_5O]^+$, 199 $[M – OBn]^+$, 130 (26), 107 (28) $[C_7H_7O]^+$, 92 (100) $[C_7H_8]^+$, 91 (54) $[C_7H_7]^+$. – **HRMS** (EI, $C_{14}H_{11}F_5O_2$): calcd. 306.0674; found: 306.0675.

2-((Benzyloxy)methyl)-5-(perfluoropropyl)furan (19)

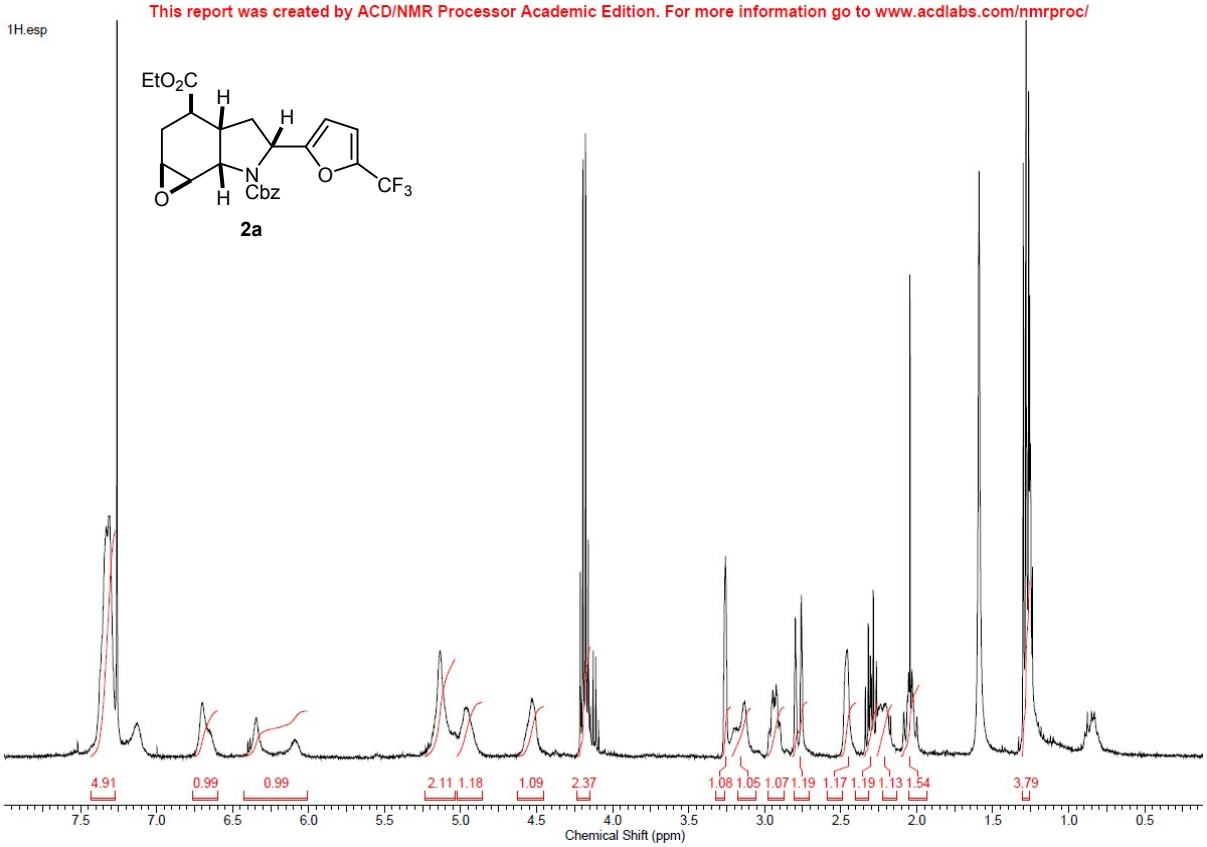


This compound was synthesized according to the **general procedure** using 2-((benzyloxy)methyl)furan (**15**, 37.6 mg, 0.200 mmol, 1.00 equiv.), urea–hydrogen peroxide (188 mg, 2.00 mmol, 10.0 equiv.) and heptafluorobutyric anhydride (**18**, 0.987 mL, 1.64 g, 4.00 mmol, 20.0 equiv.) in 4 mL dichloromethane; reaction time: 1 h. The product **19** was obtained after column chromatography (cyclohexane/ethyl acetate = 20:1) as a yellow liquid (28.6 mg, 80.3 µmol, 40%).

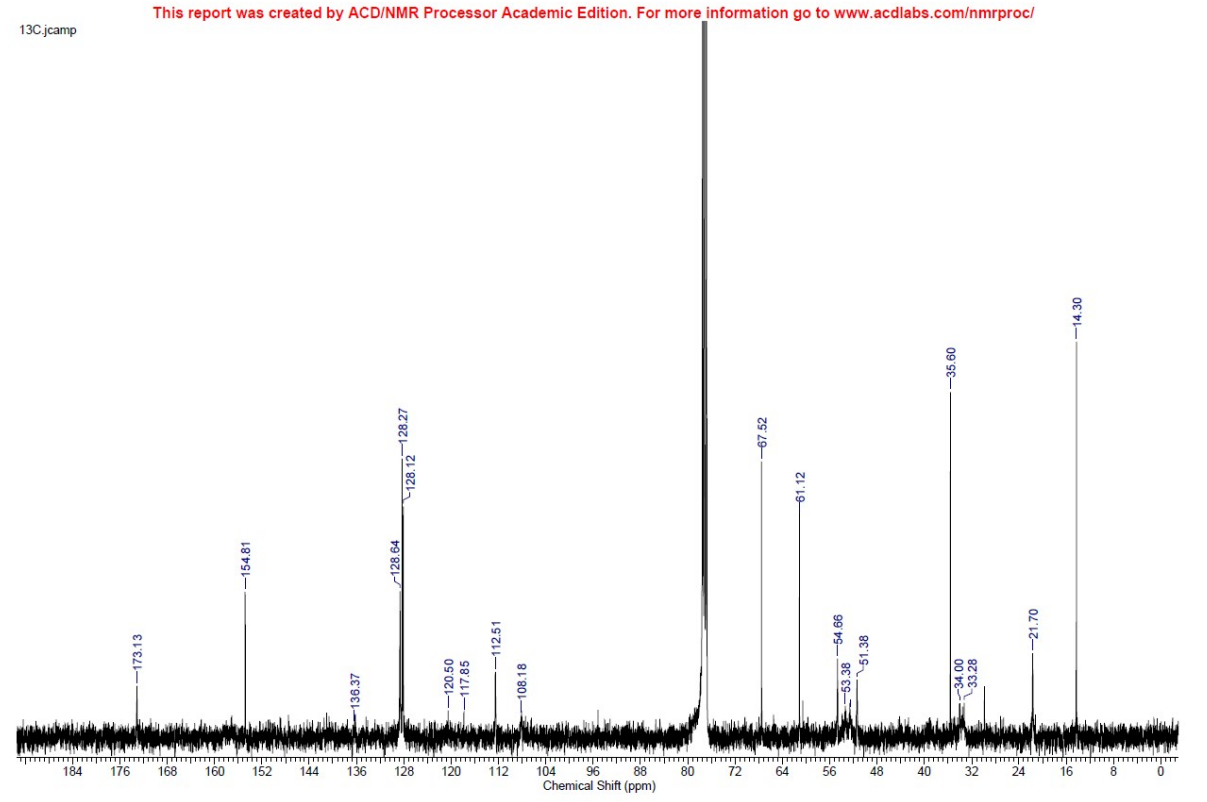
***R*$_f$** (cyclohexane/ethyl acetate = 10:1) = 0.40. – **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 4.53 (s, 2H, OC*H*$_2$), 4.57 (s, 2H, OC*H*$_2$), 6.45 (d, ^3J = 3.3 Hz, 1H, CHC*H*CCF$_2$), 6.81–6.84 (m, 1H, C*H*CHCCF$_2$), 7.29–7.39 (m, 5H, *H*$_{Ph}$) ppm. – **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 63.5 (–, O*C*H$_2$), 72.4 (–, O*C*H$_2$), 110.2 (+, *C*H$_{Fur}$), 114.6 (t, +, ^3J = 3.7 Hz, *C*H$_{Fur}$), 127.9 (+, 2 × *C*H$_{Ph}$), 128.0 (+, *C*H$_{Ph}$), 128.5 (+, 2 × *C*H$_{Ph}$), 137.3 (C$_q$, *C*$_{Ph}$), 140.7 (t, C$_q$, ^2J = 33.7 Hz, *C*C$_3$F$_7$), 155.9 (t, C$_q$, ^4J = 1.5 Hz, *C*$_{Fur}$) ppm.[c] – **^{19}F NMR** (376 MHz, $CDCl_3$): δ = –127.1–(–127.0) (m, 2F, C*F*$_2$), –112.1–(–112.0) (m, 2F, C*F*$_2$), –80.6 (t, ^3J = 9.2 Hz, 3F, C*F*$_3$) ppm. – **IR** (KBr): $\tilde{\nu}$ = 3138 (vw), 2860 (vw), 1607 (vw), 1553 (vw), 1497 (vw), 1454 (vw), 1347 (w), 1266 (w), 1213 (m), 1181 (m), 1145 (w), 1113 (m), 1064 (m), 1024 (w), 963 (w), 889 (w), 869 (vw), 851 (w), 802 (w), 742 (m), 696 (w), 447 (w) cm^{-1}. – **MS** (EI, 70 eV), *m/z* (%): 356 (19) [M]$^+$, 249 (50) [M – OBn]$^+$, 130 (27), 107 (18) [C$_7$H$_7$O]$^+$, 92 (100) [C$_7$H$_8$]$^+$, 91 (88) [C$_7$H$_7$]$^+$. – **HRMS** (EI, C$_{15}$H$_{11}$F$_7$O$_2$): calcd. 356.0642; found: 356.0640.

[c] The signals of the perfluoroalkyl group could not be assigned due to low signal intensity and complex couplings.

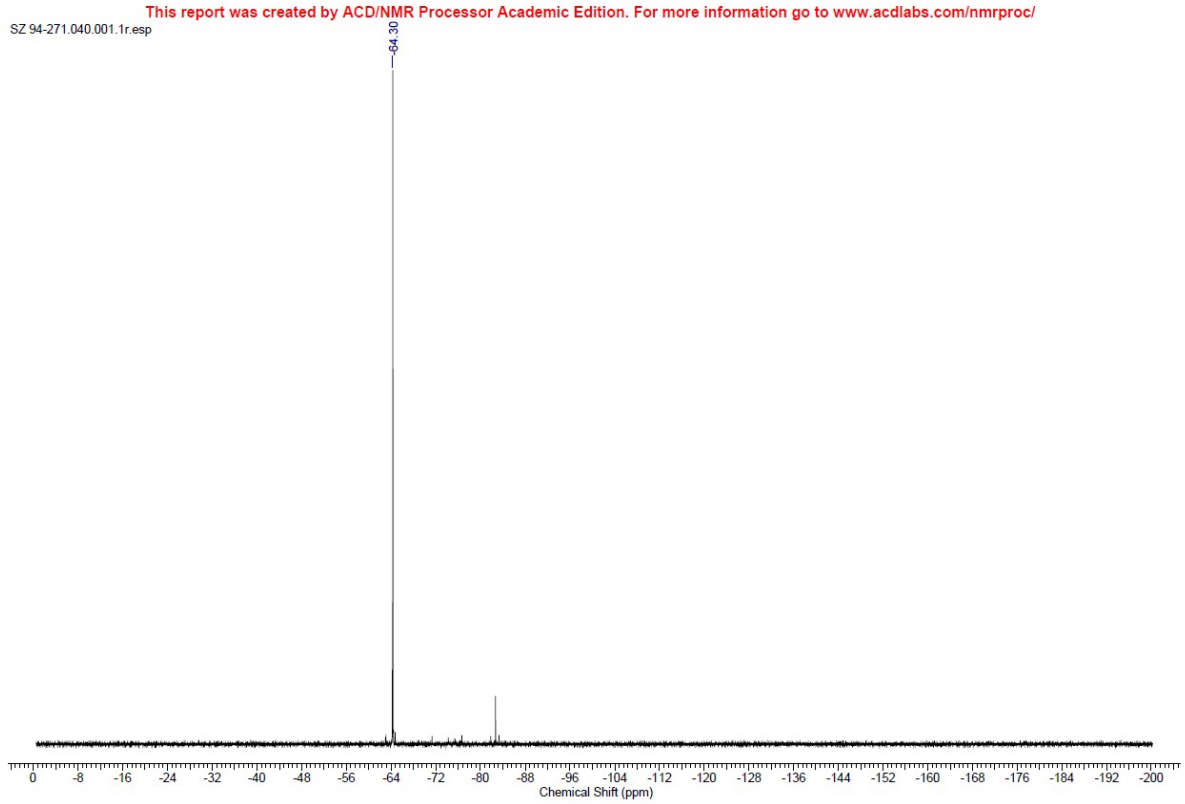
3 NMR spectra of new compounds



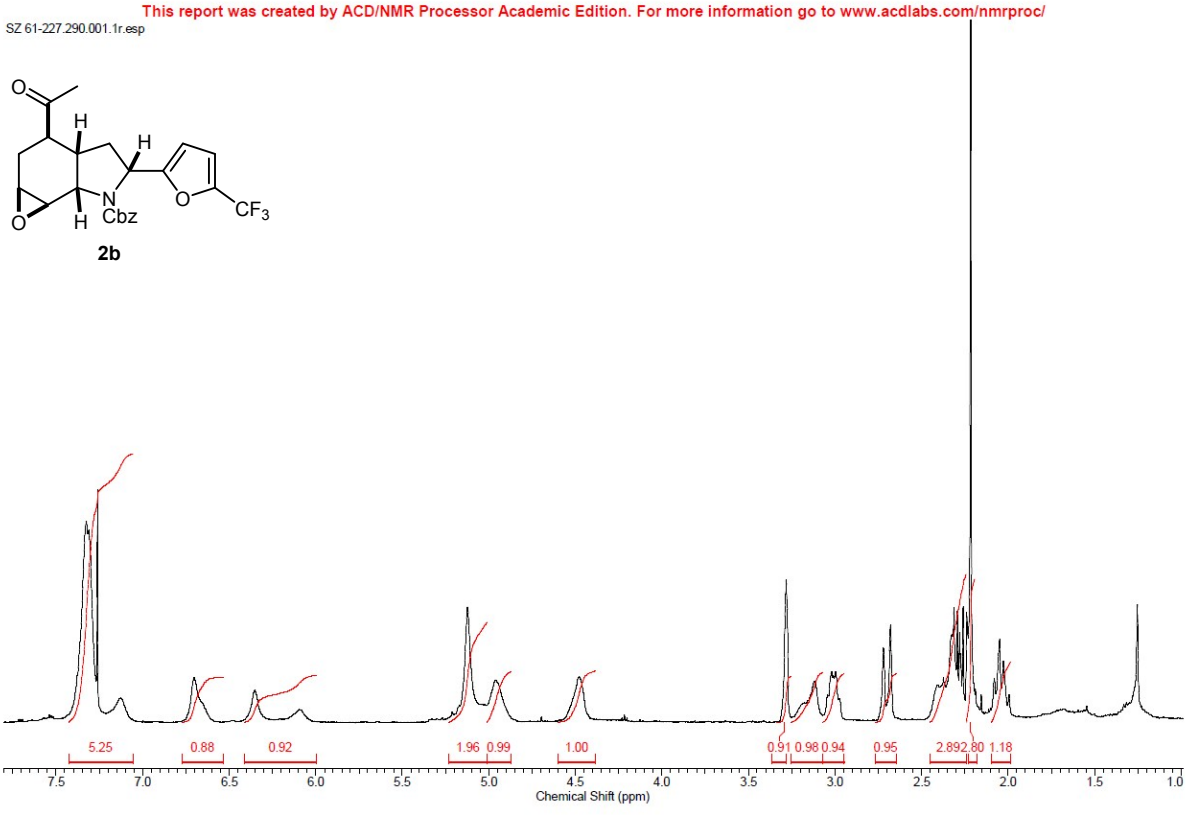
2a, ^{1}H NMR, 400 MHz, $CDCl_3$



2a, ^{13}C NMR, 100 MHz, $CDCl_3$

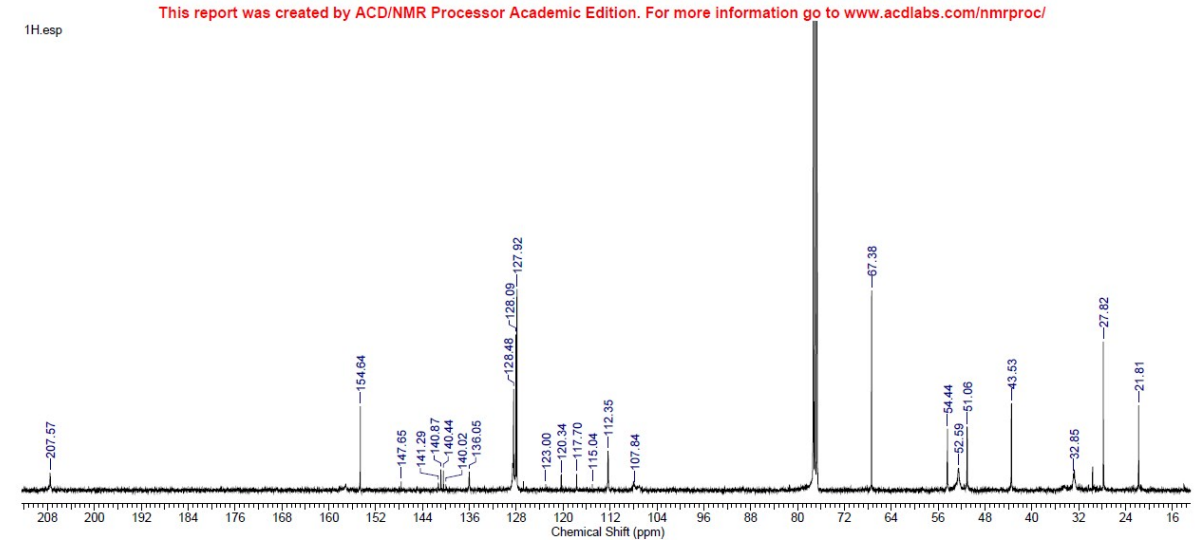


2a, ^{19}F NMR, 376 MHz, $CDCl_3$

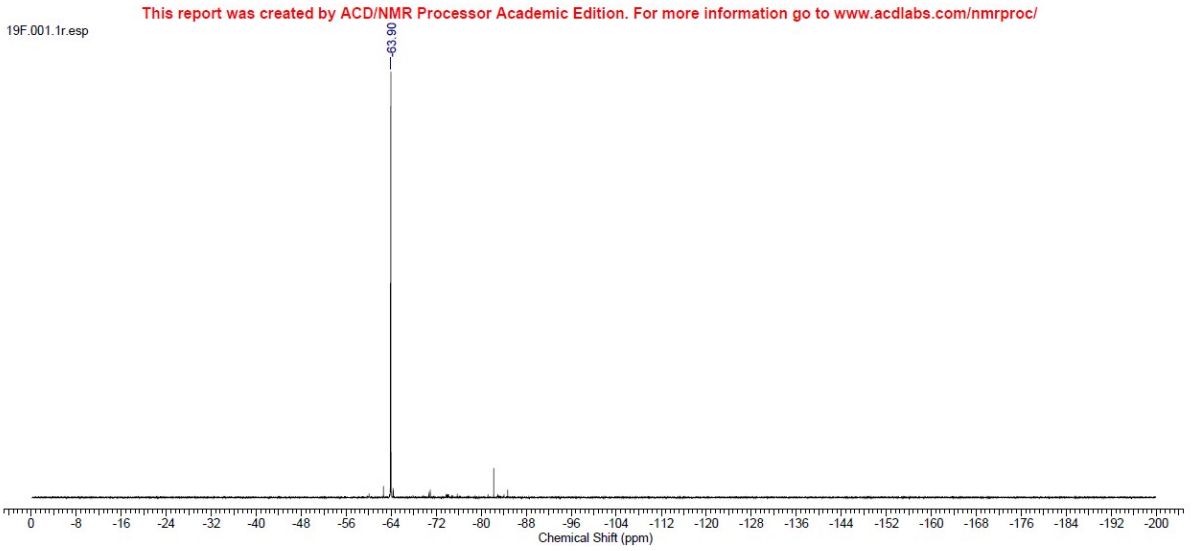


2b

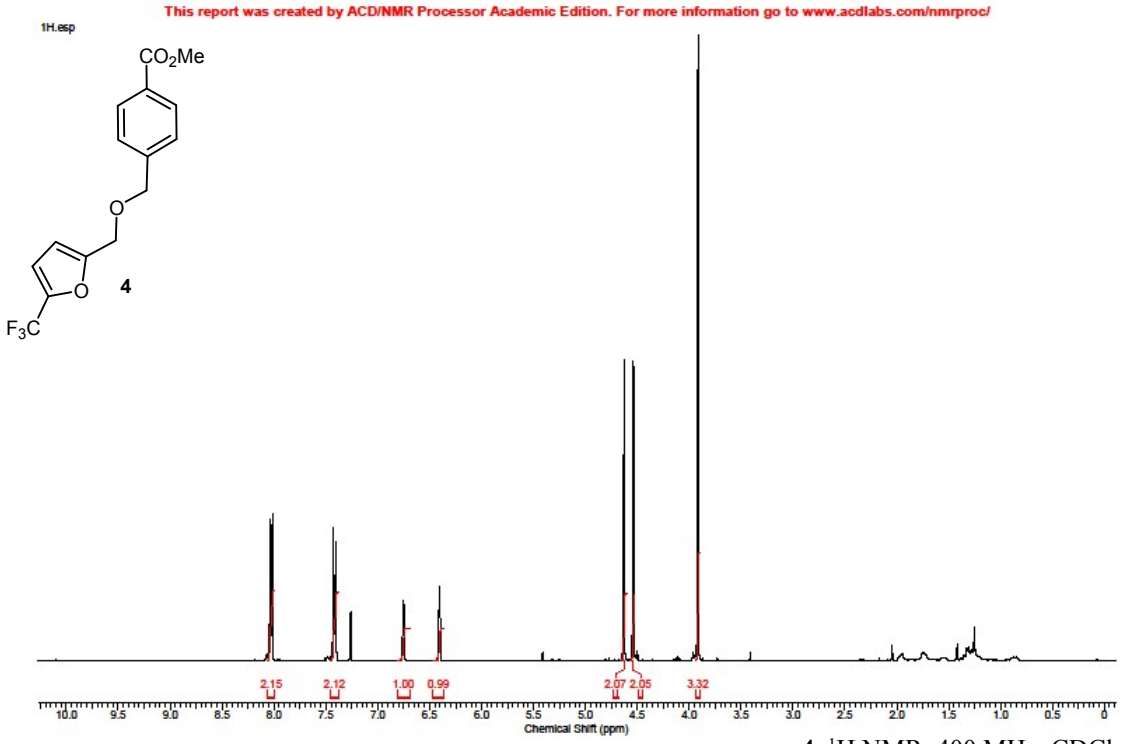
2b, ^{1}H NMR, 400 MHz, $CDCl_3$



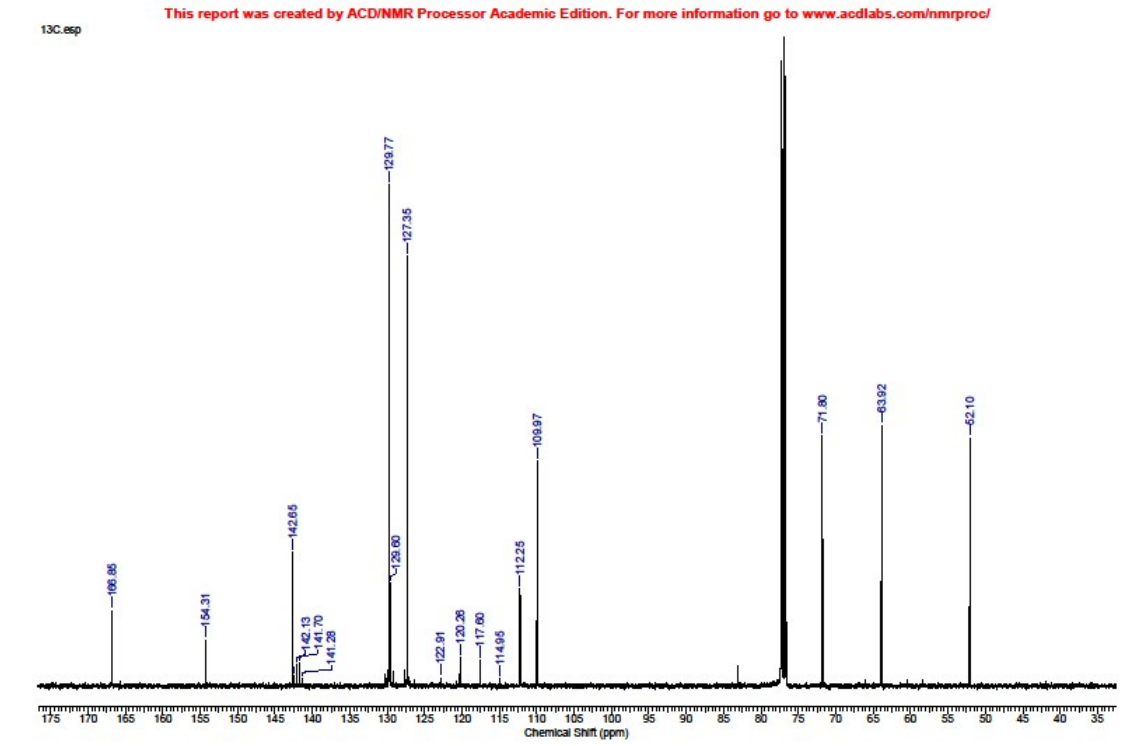
2b, ^{13}C NMR, 100 MHz, $CDCl_3$



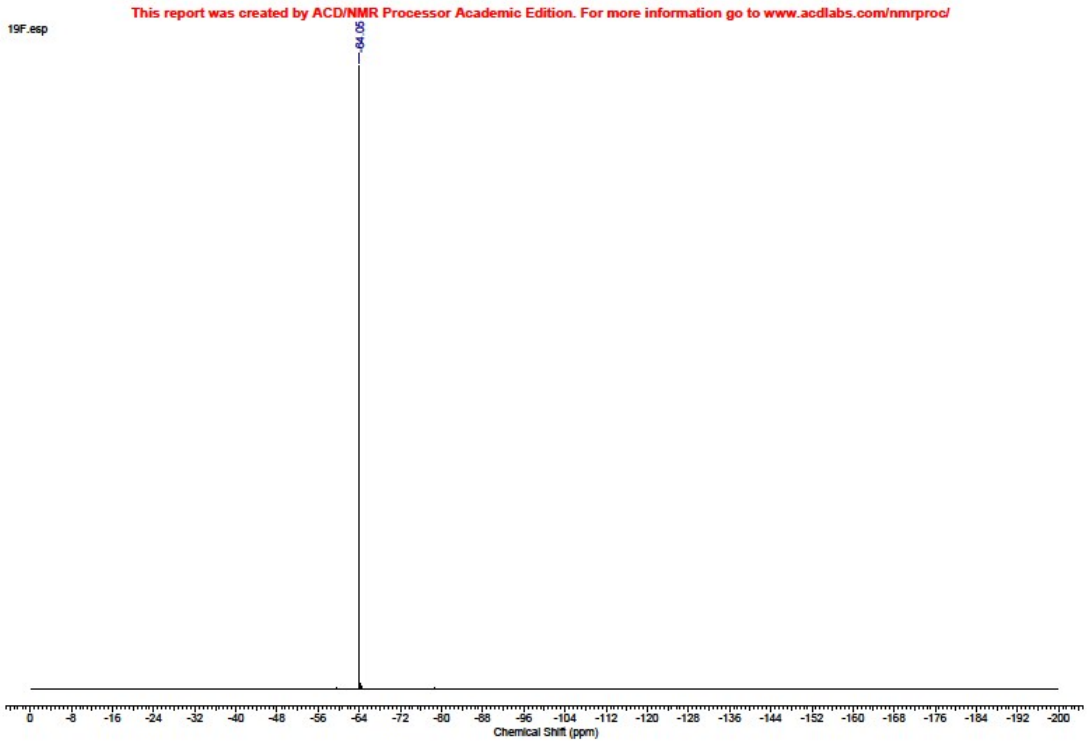
2b, ^{19}F NMR, 376 MHz, $CDCl_3$



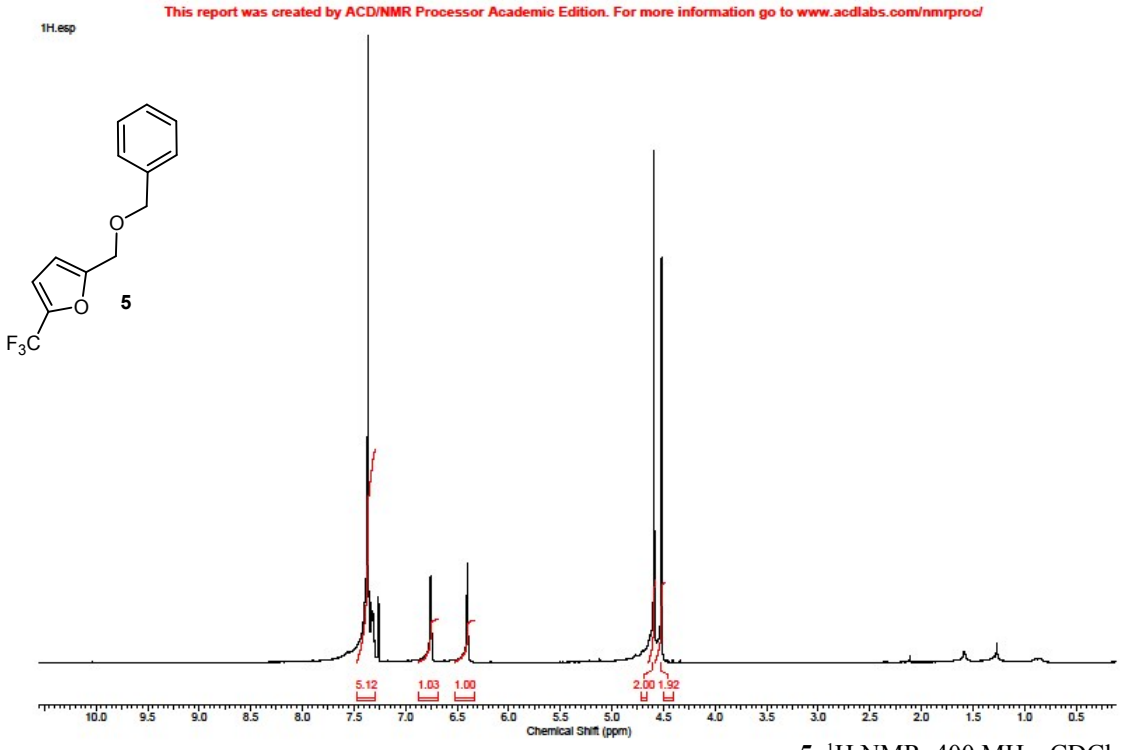
4, ^{1}H NMR, 400 MHz, $CDCl_3$



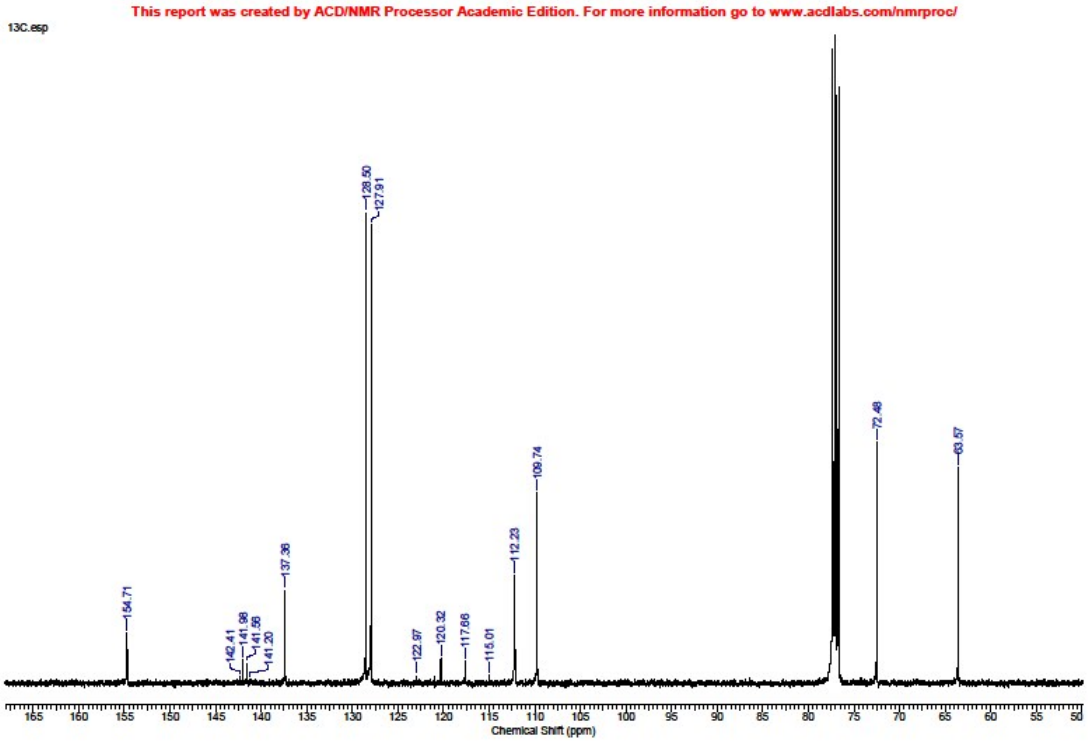
4, ^{13}C NMR, 100 MHz, $CDCl_3$



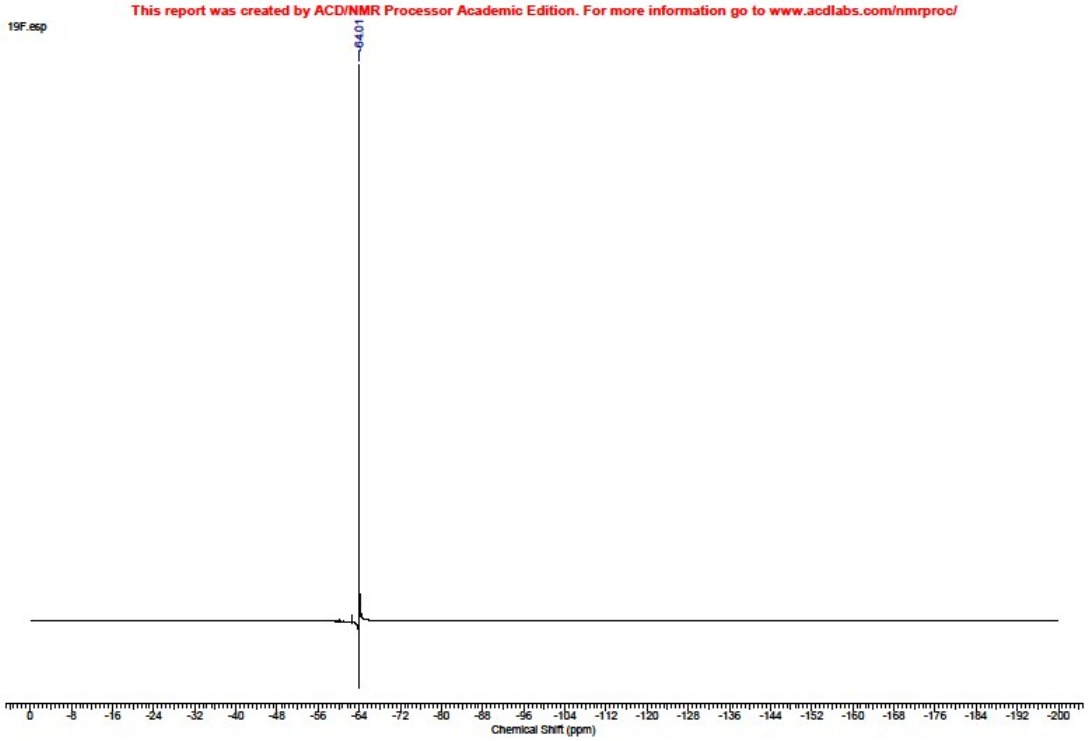
4, ^{19}F NMR, 376 MHz, $CDCl_3$



5, ^{1}H NMR, 400 MHz, $CDCl_3$

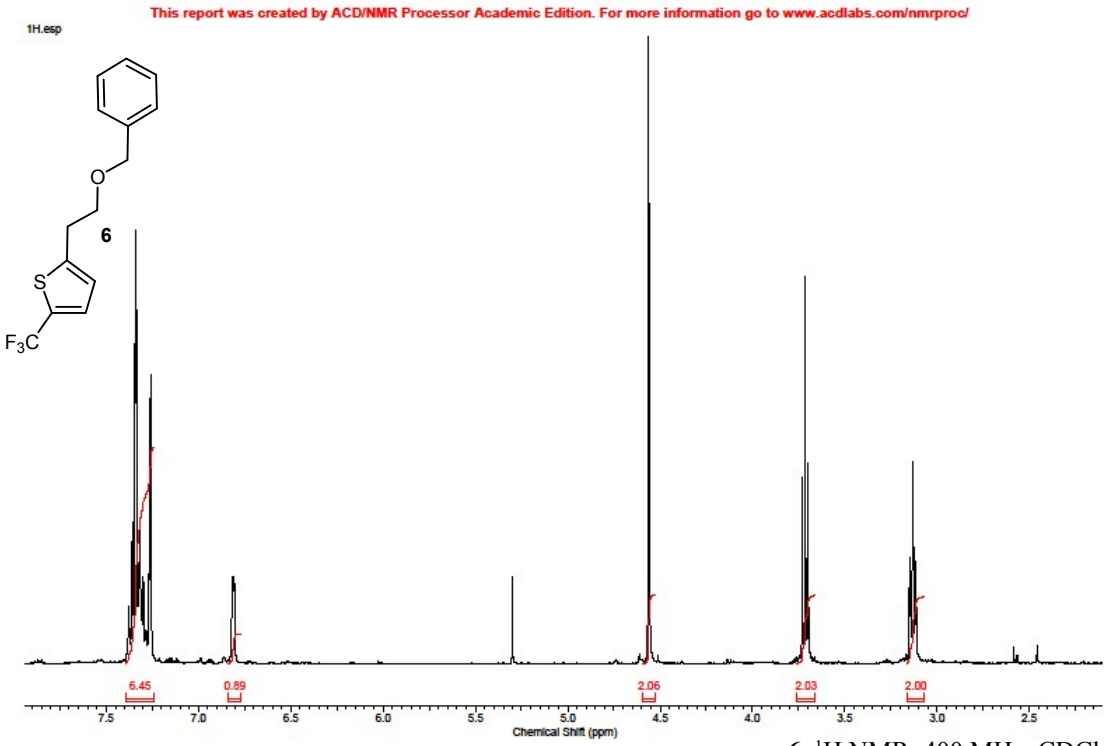


5, ^{13}C NMR, 100 MHz, $CDCl_3$

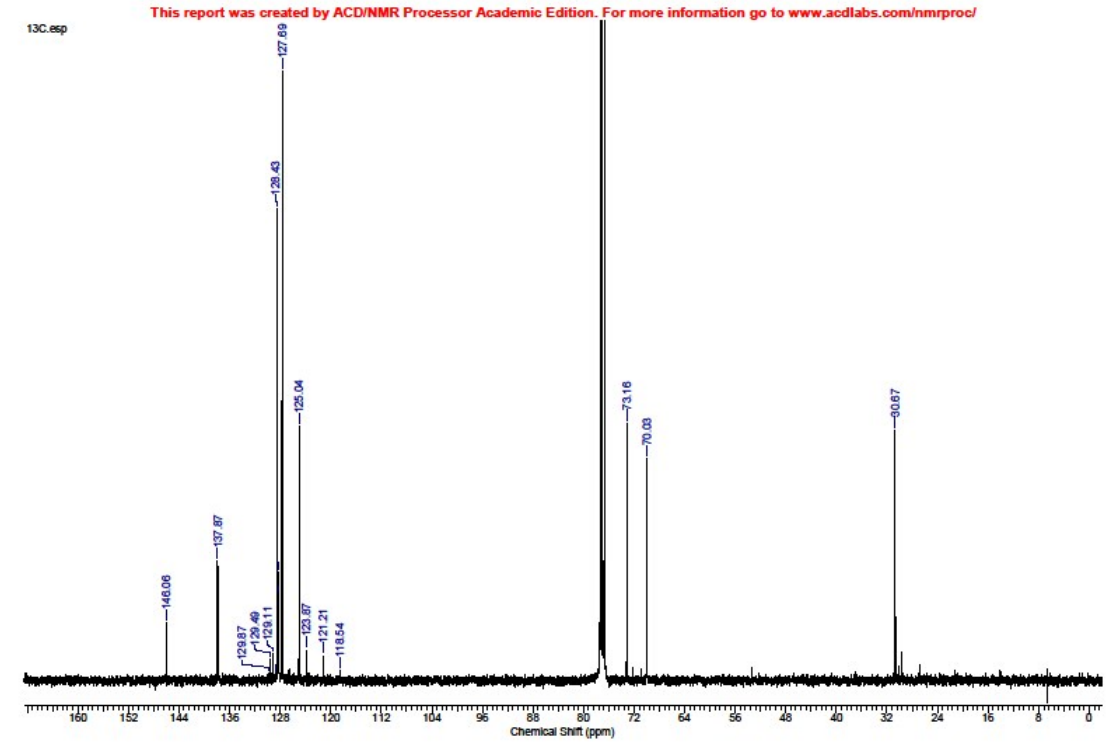


5, ^{19}F NMR, 376 MHz, $CDCl_3$

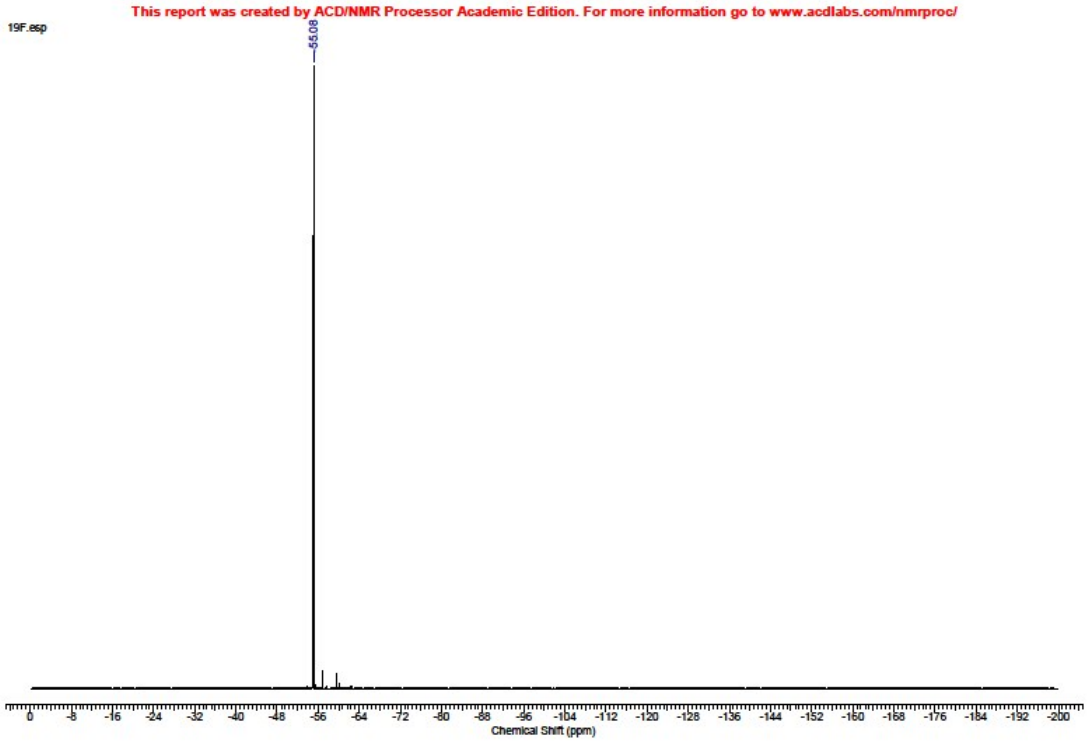
3



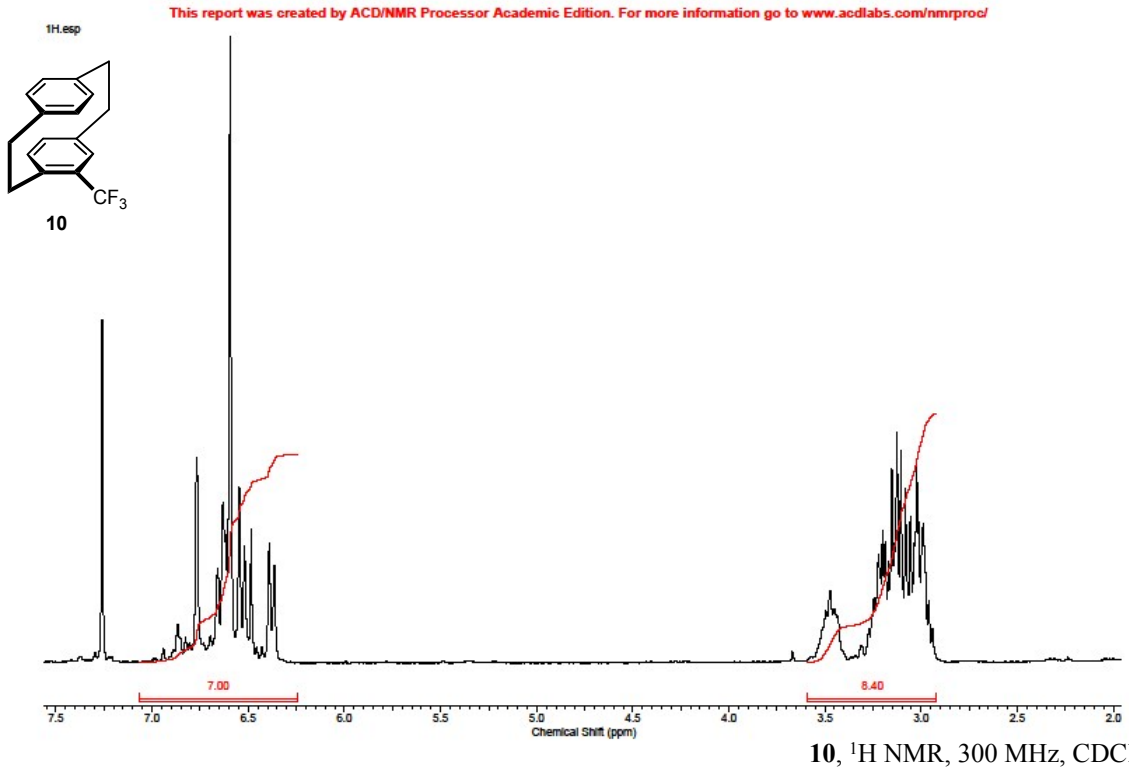
6, ^{1}H NMR, 400 MHz, $CDCl_3$



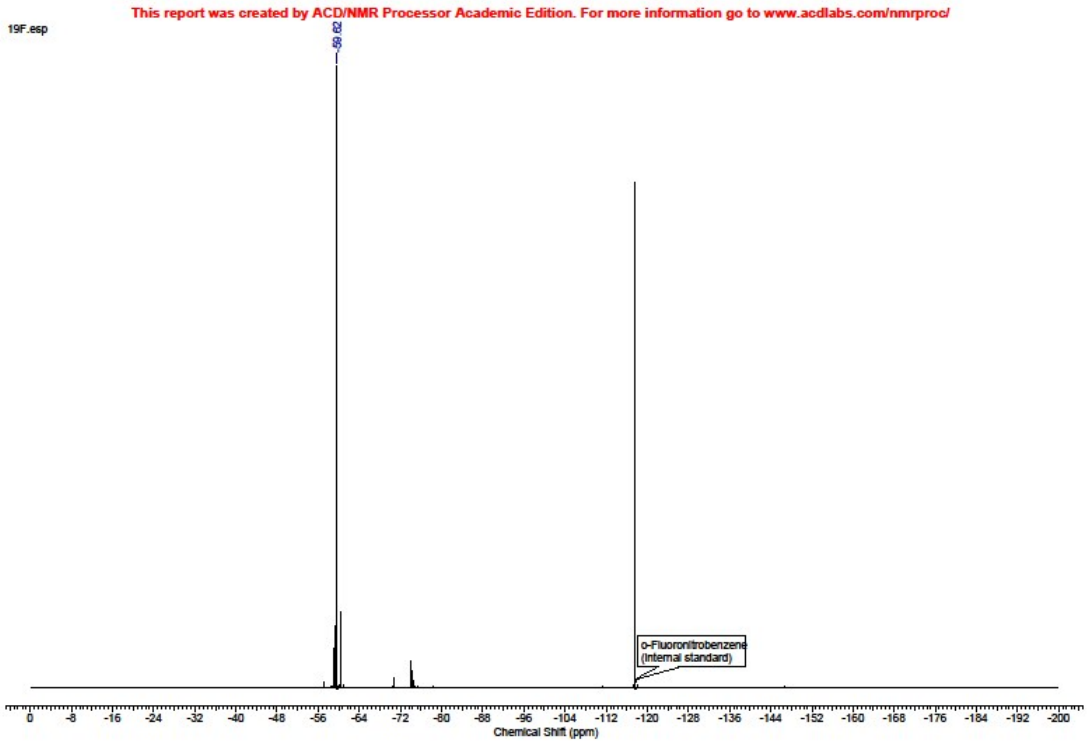
6, ^{13}C NMR, 100 MHz, $CDCl_3$



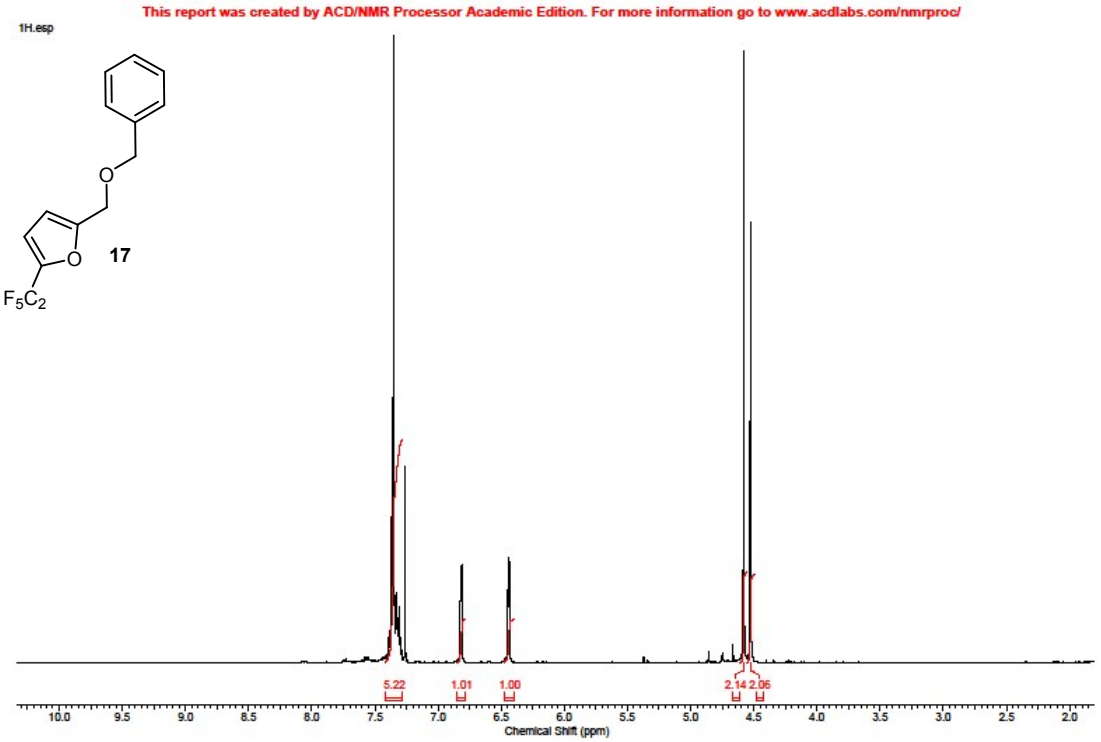
6, ^{19}F NMR, 376 MHz, $CDCl_3$



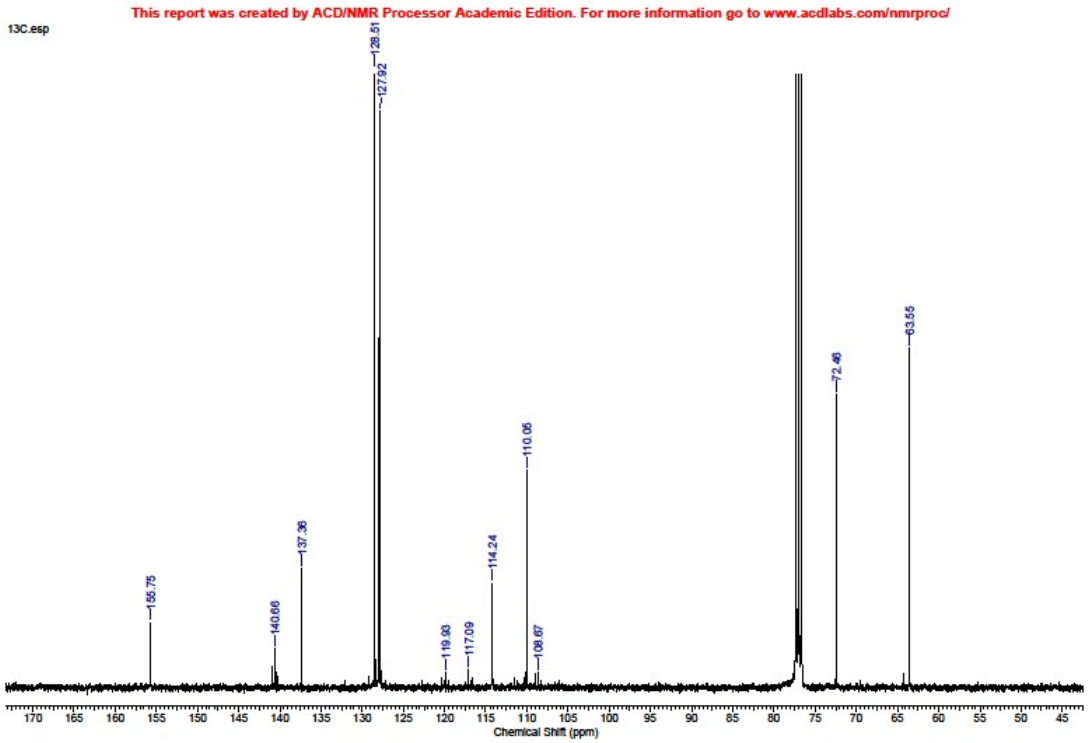
10, ^{1}H NMR, 300 MHz, $CDCl_3$



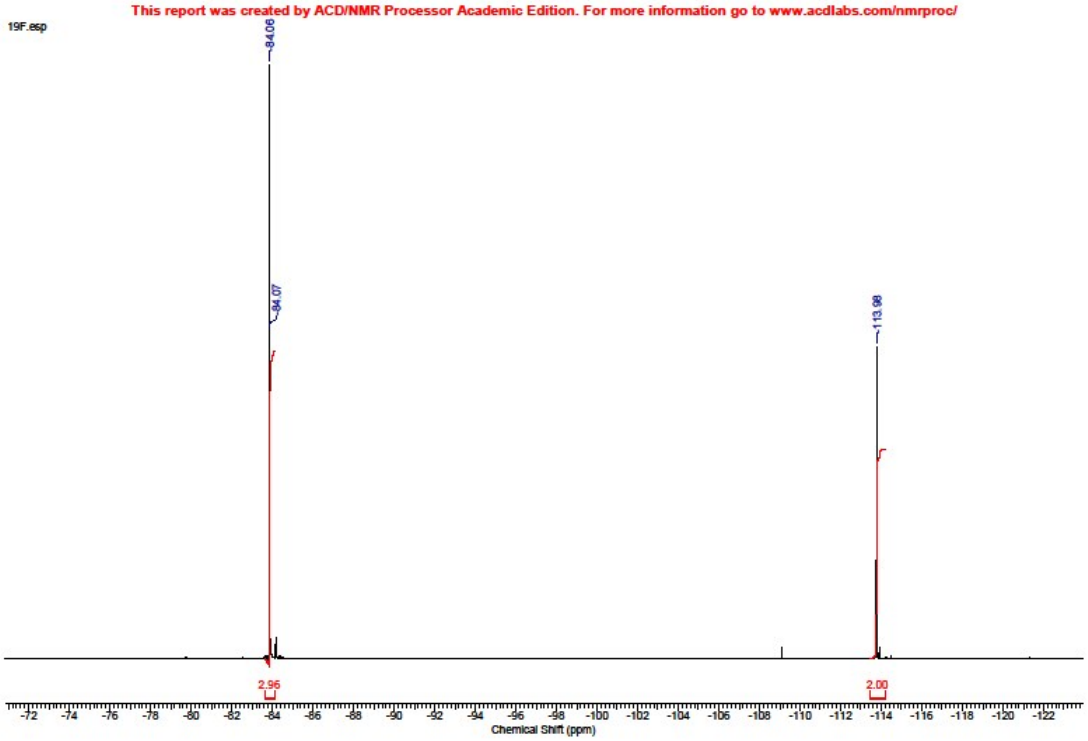
10, ^{19}F NMR, 376 MHz, $CDCl_3$



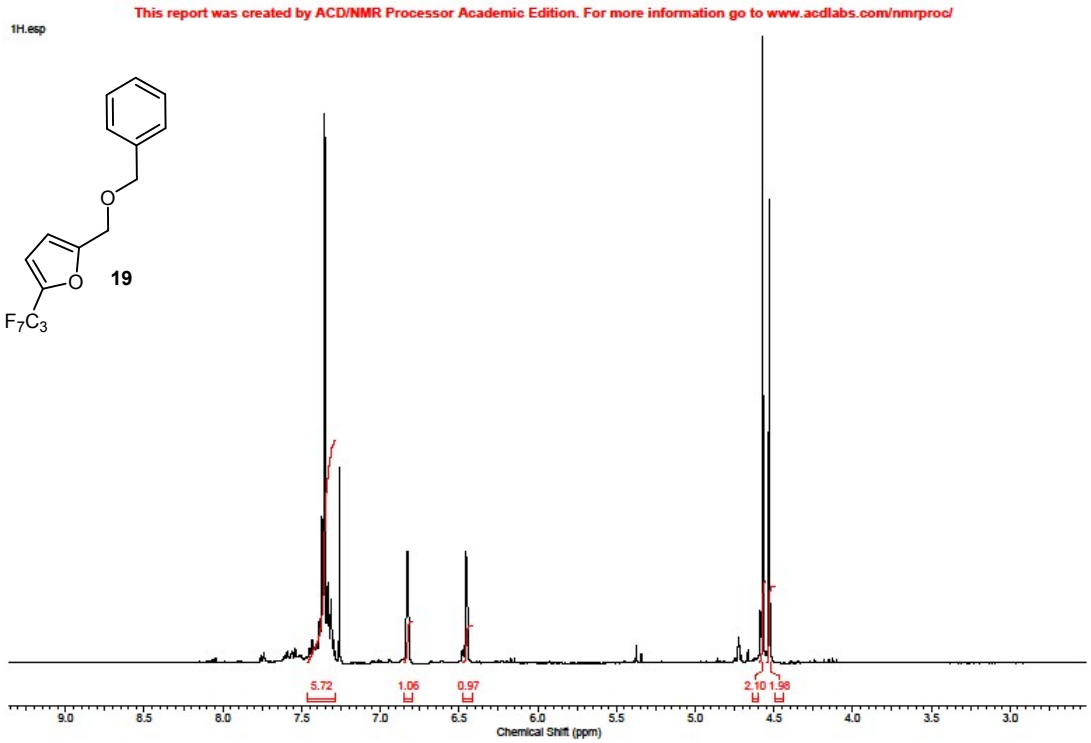
17, ^{1}H NMR, 400 MHz, $CDCl_3$



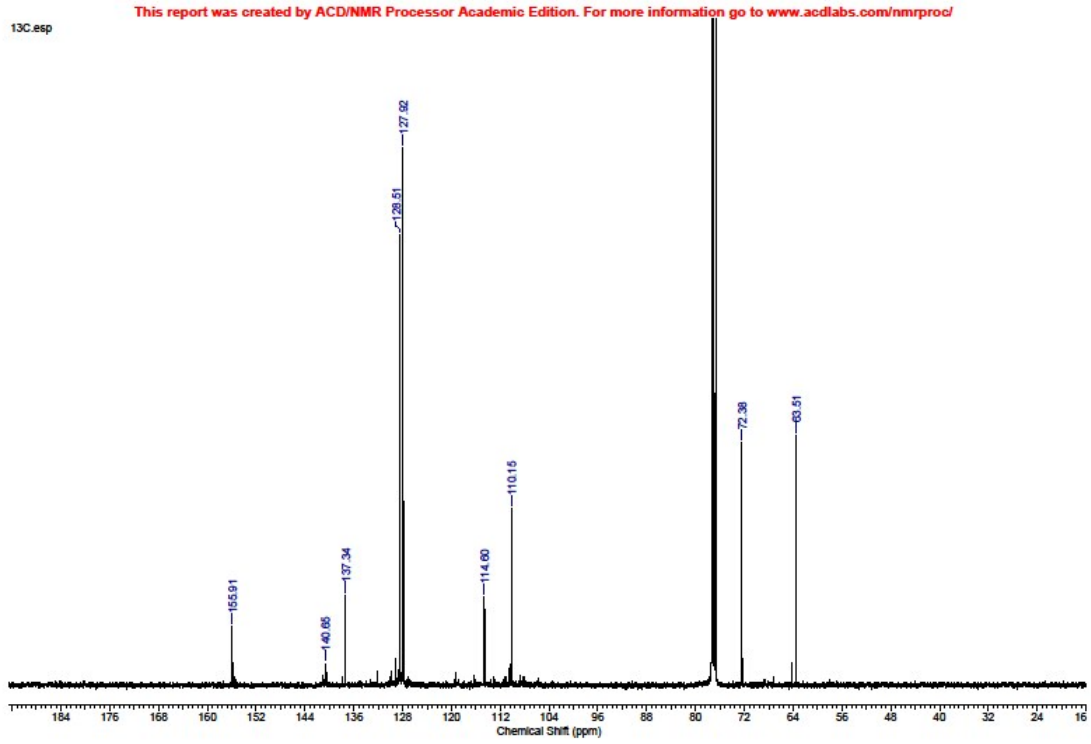
17, ^{13}C NMR, 100 MHz, $CDCl_3$



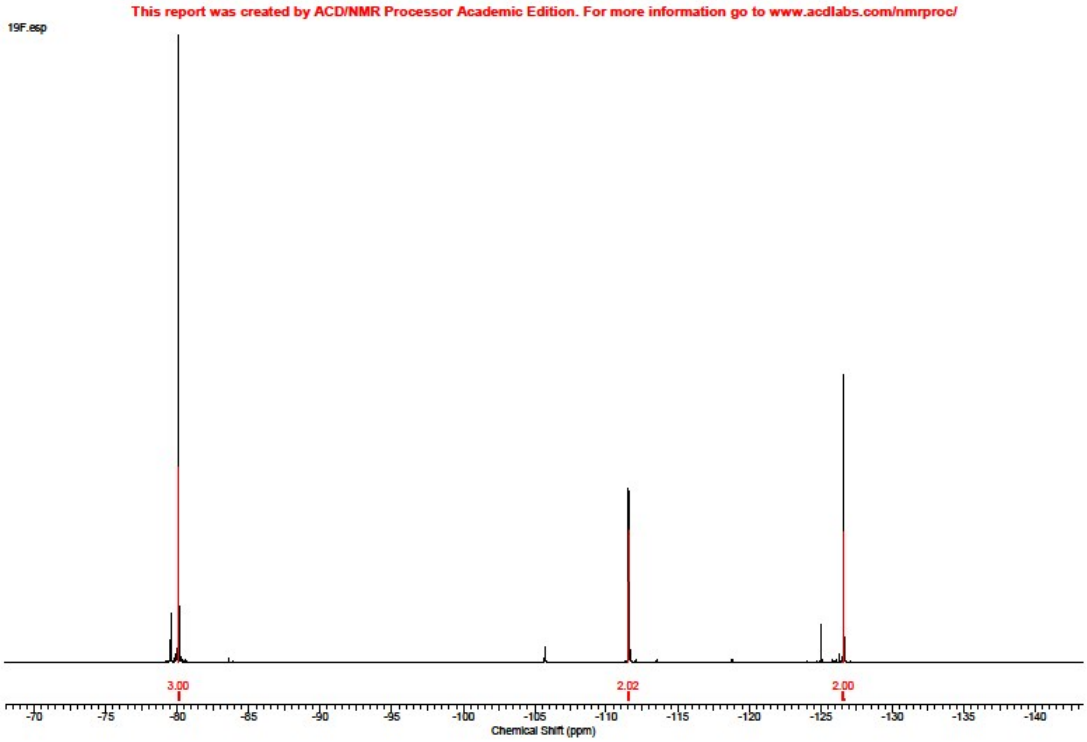
17, ^{19}F NMR, 376 MHz, $CDCl_3$



19, ^{1}H NMR, 400 MHz, $CDCl_3$

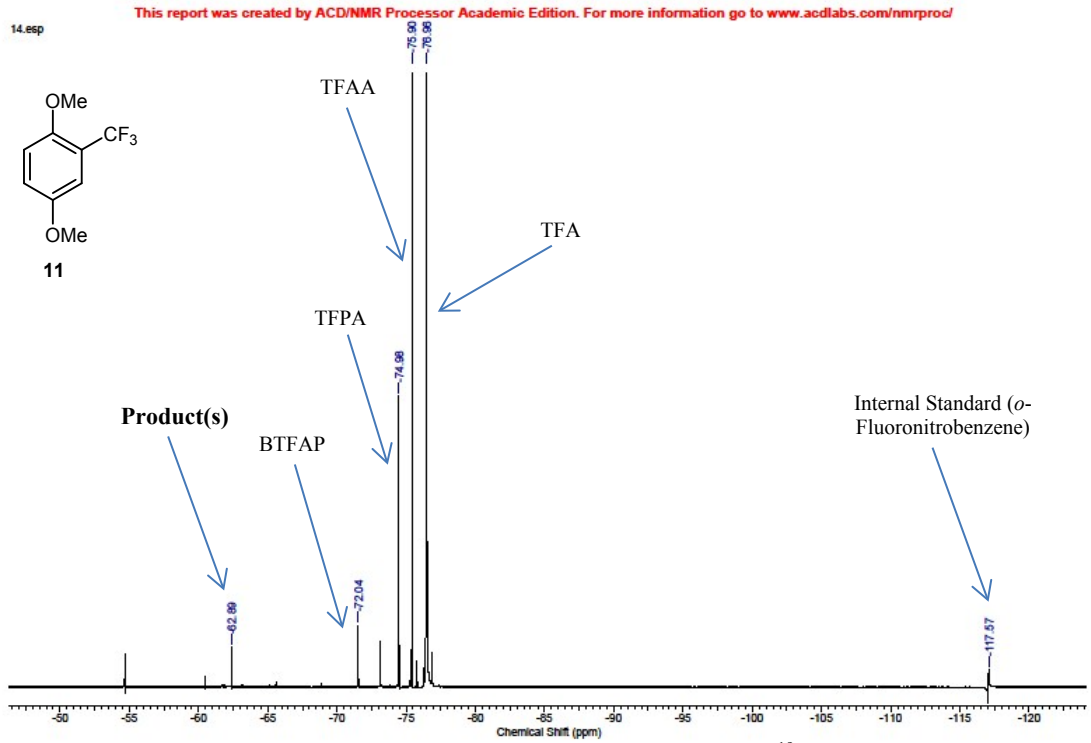


19, ^{13}C NMR, 100 MHz, $CDCl_3$

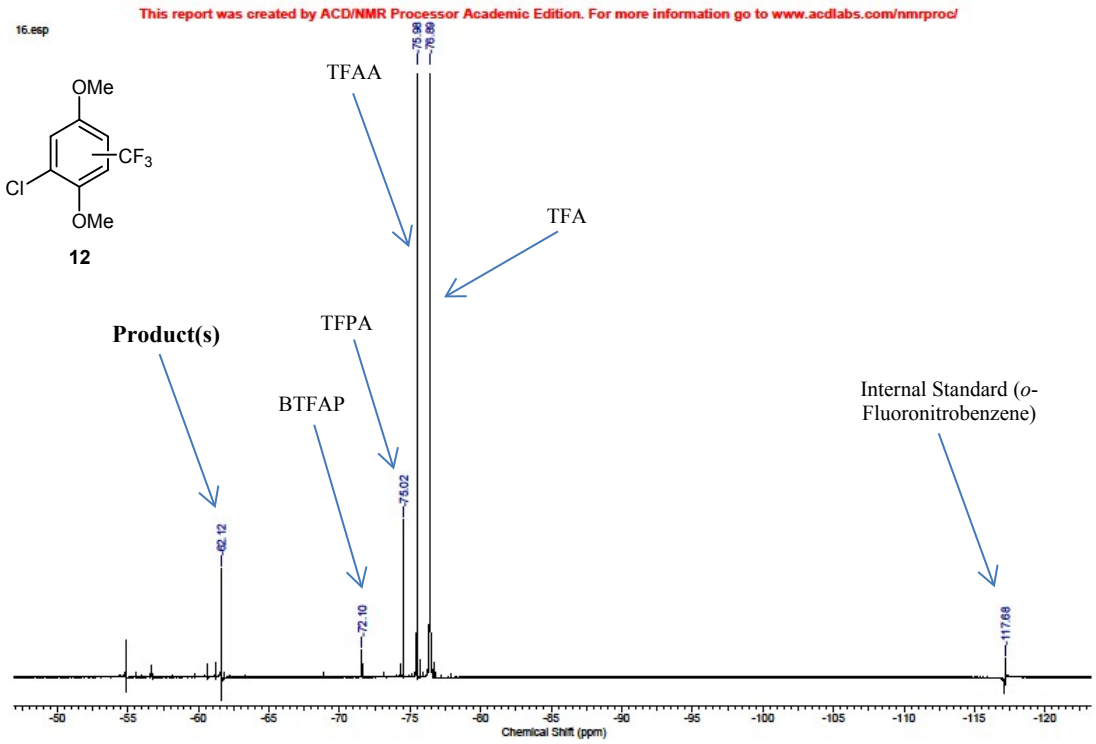


19, ^{19}F NMR, 376 MHz, $CDCl_3$

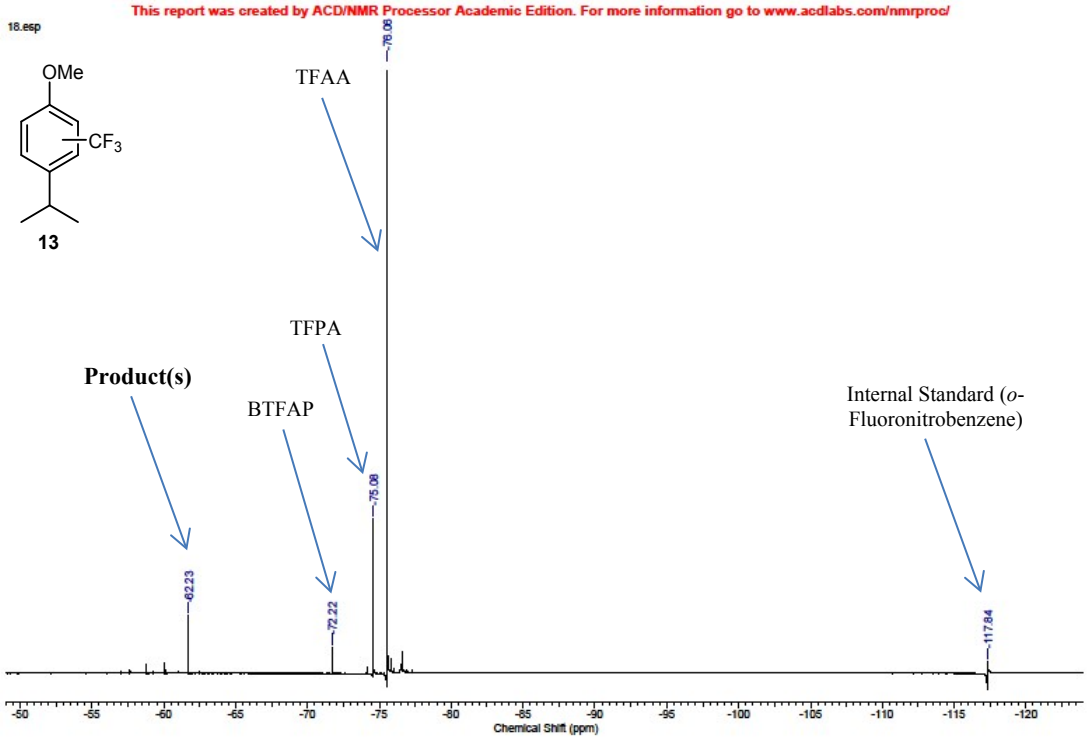
^{19}F NMR spectra of the crude products of **11**, **12**, **13**, and **14**



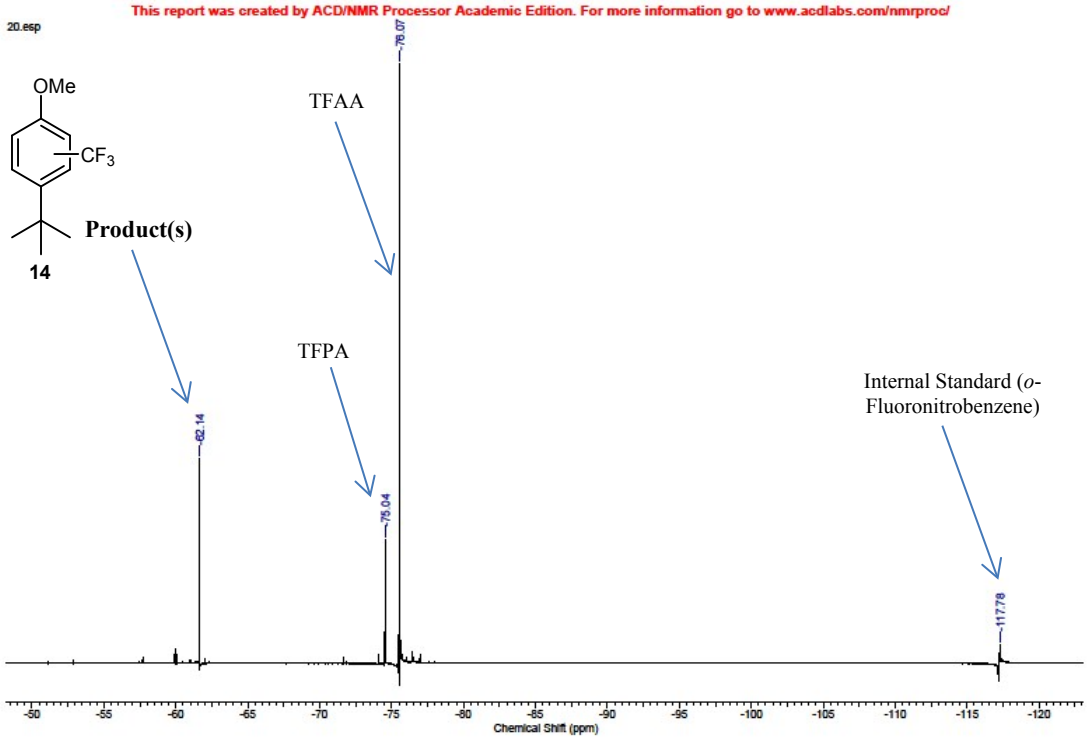
^{19}F NMR, 376 MHz, $CDCl_3$



^{19}F NMR, 376 MHz, $CDCl_3$



^{19}F NMR, 376 MHz, $CDCl_3$



^{19}F NMR, 376 MHz, $CDCl_3$

4 Crystallographic data

Crystal Structure Determinations of 2b

The single-crystal X-ray diffraction studies was carried out on a Bruker-Nonius Kappa-CCD diffractometer at 123(2) K using MoKα radiation (λ = 0.71073 Å). Direct Methods (SHELXS-97)[5] were used for structure solution and refinement was carried out using SHELXL-97[3] (full-matrix least-squares on F^2). Non hydrogen atoms were refined anisotropically, hydrogen atoms were refined using a riding model. Due to the bad quality of the crystals only the constitution and conformation could be determined and the data were not deposited into the Cambridge Database.

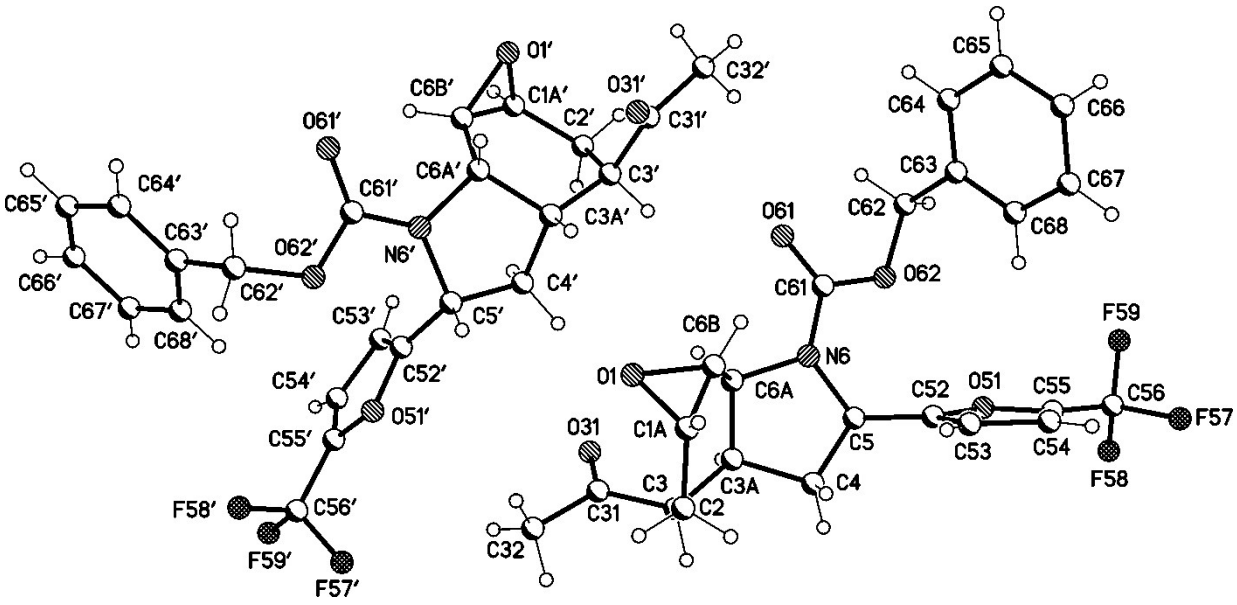


Fig. S1. Molecular structure of **2b**

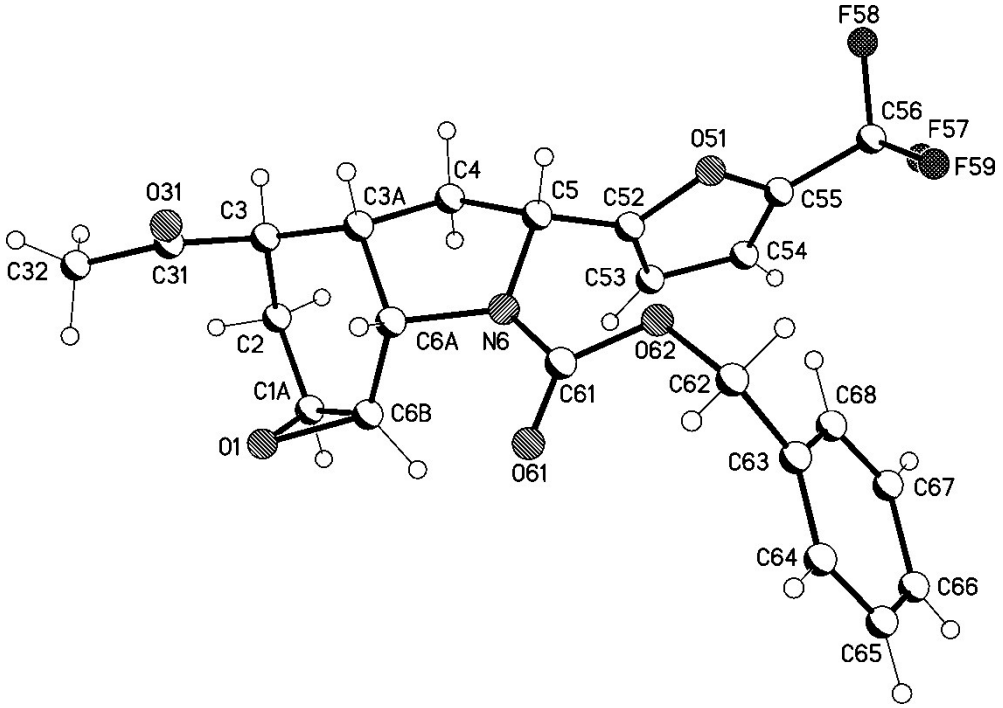


Fig. S2. Molecular structure of **2b** (first crystallographic independent molecule)

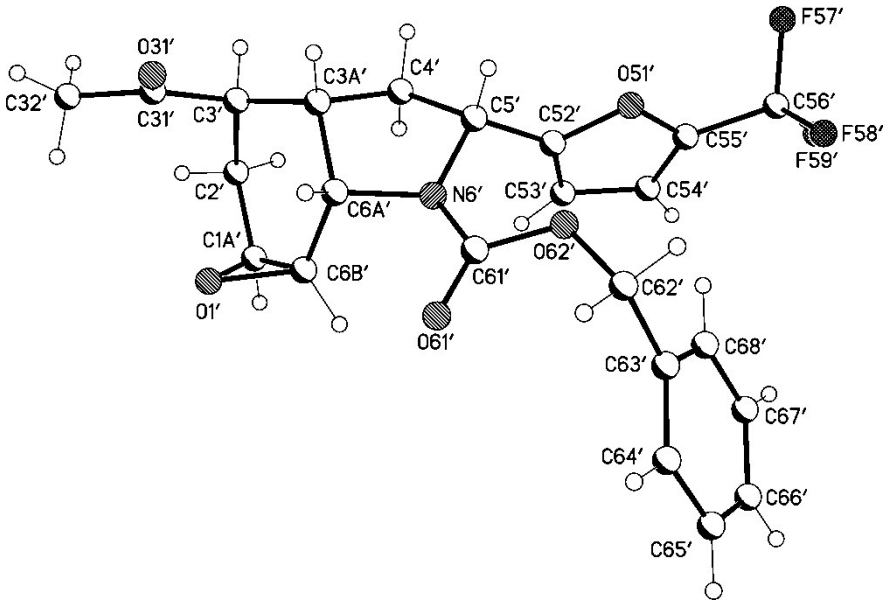


Fig. S3. Molecular structure of **2b** (second crystallographic independent molecule)

Table S 1. Crystal data, data collection and structure refinement details of **2b**

Crystal data

$C_{23}H_{22}F_3NO_5$	$Z = 4$
$M_r = 449.42$	$F(000) = 936$
Triclinic, P-1 (no.2)	$D_x = 1.407$ Mg m^{-3}
$a = 11.058$ (1) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 13.487$ (2) Å	Cell parameters from 70 reflections
$c = 14.414$ (2) Å	$\theta = 2.5–25.0°$
$\alpha = 88.39$ (1)°	$\mu = 0.12$ mm^{-1}
$\beta = 80.91$ (1)°	$T = 123$ K
$\gamma = 89.00$ (1)°	Plates, colourless
$V = 2121.7$ (5) Å^3	0.45 × 0.15 × 0.03 mm

Data collection

Bruker-Nonius KappaCCD diffractometer	4183 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.104$
Graphite monochromator	$\theta_{max} = 25.0°$, $\theta_{min} = 2.9°$
rotation in phi and ω, 2 deg. scans	$h = -13 \rightarrow 13$
24435 measured reflections	$k = -16 \rightarrow 16$
7393 independent reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.148$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.406$	H-atom parameters constrained
$S = 1.39$	$w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
7393 reflections	$(\Delta/\sigma)_{max} = 0.002$
579 parameters	$\Delta\rangle_{max} = 1.59$ e Å^{-3}
998 restraints	$\Delta\rangle_{min} = -0.62$ e Å^{-3}

[1] O. Arjona, F. Iradier, R. M. Manas, J. Plumet, X. Grabuleda, C. Jaime, *Tetrahedron* **1998**, *54*, 9095-9110.
[2] Y. Ye, S. A. Künzi, M. S. Sanford, *Org. Lett.* **2012**, *14*, 4979–4981.
[3] T. Liu, Q. Shen, *Org. Lett.* **2011**, *13*, 2342–2345.
[4] I. S. Kondratov, V. G. Dolovanuk, N. A. Tolmachova, I. I. Gerus, K. Bergander, R. Fröhlich, G. Haufe, *Org. Biomol. Chem.* **2012**, *10*, 8778–8785.
[5] G. M. Sheldrick, *Acta Crystallog*. **2008**, *A64*, 112–122.