Supporting Information

Cu Photoredox Catalysts Supported by a 4,6-Disubstituted-2,2'-Bipyridine Ligand: Application in Chlorotrifluoromethylation of Alkenes

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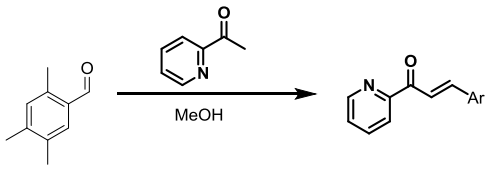
General

All chemicals were purchased from commercial suppliers and used without further purification. The substrates methyl 4-vinylbenzoate[1], methyl 3-vinylbenzoate[2], N,N-diallyl-4-methylbenzenesulfonamide[3], (R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl 4-vinylbenzoate[4] and (8R,9S,13S,14S)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one[5] were prepared according to literature procedure.

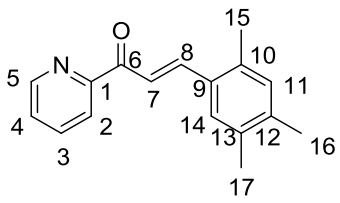
All photoredox reactions were carried under an N_2 atmosphere using standard glovebox techniques and NMR spectra of known compounds agree with reports. The light source was a homemade device (similar to reported devices[6]) from the mechanical and electrical workshop of EPFL (*vide infra*).

Solvents were purified using a two-column solid-state purification system (Innovative Technology, NJ, USA) and transferred to the glovebox without exposure to air. NMR spectra were recorded on a Bruker Avance 400 Spectrometer. ^{1}H and $^{13}C\{^{1}H\}$ chemical shifts were referenced internally to residual solvent peaks relative to TMS (δ = 0 ppm), ^{19}F chemical shifts were externally referenced to $CFCl_3$ (δ = 0 ppm) and $^{31}P\{^{1}H\}$ chemical shifts were referenced externally to 85% H_3PO_4 in H_2O (δ = 0 ppm). Signals were assigned, where indicated, with help of 2D-NMR NOESY, COSY; HMBC and HSQC experiments. High resolution mass spectra, X-ray structures and elemental analyses were determined by the respective EPFL facilities. X-ray quality crystals were grown by slow diffusion of Et_2O in DCM. UV/Vis spectra were recorded on a Varian Cary 50 Bio UV-Visible Spectrometer. Emission spectra were recorded on a Perkin Elmer LS 50 B Luminescence Spectrometer, TCSPC experiments were carried out with a Fluorolog HORIBA Jobin Yvon TCSPC system and a pulsed diode light source. Lifetimes were determined by fitting the data to exponential decays using Matlab®. Degassed samples were prepared in the glovebox and measured in a macro fluorescence cuvette with screw cap from MSScientific. Thin films were obtained by spin coating 0.3 mL of the Cu(I) compound (5E-3M, DCM) and PMMA (20 mg/ml) on a 1.5 cm x1.5 cm glass plate (400 rpm, 30 s). Cyclic voltammograms were measured using a Metrohm Autolab potentiostat with a three electrode setup (glassy carbon (0.07cm^2 surface area) as working electrode, a platinum wire as counter electrode and a $Ag/AgNO_3$ (0.01M) reference electrode) in DCM (0.1mM) and with [*n*-Bu_4N][PF_6] (0.1M) as supporting electrolyte. All redox potentials were internally referenced to $Fc^{0/+}$.

Ligand Synthesis



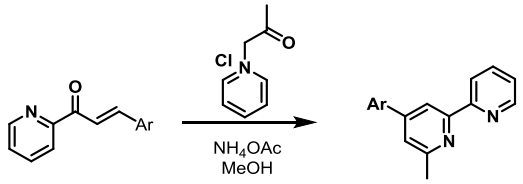
Aryl aldehyde (1.17 g, 8 mmol, 1.0eq) and 2-acetylpyridine (0.97g, 8 mmol, 1eq) were dissolved in MeOH (25 mL). A solution of NaOH (aq, 2M, 10mol%) was added to the mixture at 0°C and the resulting solution was stirred at rt overnight. The resulting suspension was filtered, washed with water and dried to yield the pure product as a pale yellow powder (1.57g, 6.2 mmol, 79%).



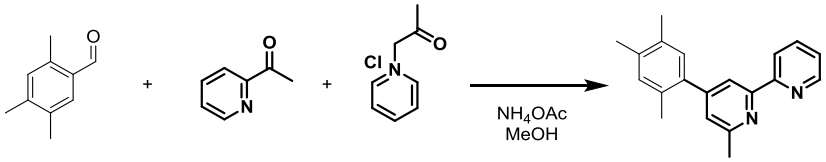
^{1}H NMR (400 MHz, CD_2Cl_2) δ/ppm 2.26 (s, 3H, H^{16}), 2.28 (s, 3H, H^{17}), 2.44 (s, 3H, H^{15}), 7.02 (s, 1H, H^{11}), 7.50 (ddd, 1H, $^{3}J_{H,H}$ = 7.54 Hz, 4.75 Hz, $^{4}J_{H,H}$ = 1.23 Hz, H^{4}), 7.63 (s, 1H, H^{14}), 7.89 ("t"d, 1H, $^{3}J_{H,H}$ = 7.76 Hz. $^{4}J_{H,H}$ = 1.73 Hz, H^{3}), 8.15 (ddd, 1H, $^{3}J_{H,H}$ = 7.85 Hz, $^{4}J_{H,H}$ = 1.23 Hz, $^{5}J_{H,H}$ = 0.93 Hz, H^{2}), 8.18 (d, 1H, $^{3}J_{H,H}$ = 15.97 Hz, H^{7}), 8.21 (d, 1H, $^{3}J_{H,H}$ = 15.97 Hz, H^{8}), 8.74 (ddd, 1H, $^{3}J_{H,H}$ = 4.75 Hz, $^{4}J_{H,H}$ = 1.73 Hz, $^{5}J_{H,H}$ = 0.93 Hz, H^{5}).

^{13}C{^{1}H} NMR (100.62 MHz, CD_2Cl_2) δ/ppm 19.55 (C^{16+17}), 20.01 (C^{15}), 121.04 (C^{7}), 123.20 (C^{2}), 127.34 (C^{4}), 128.24 (C^{14}), 131.93 (C^{9}), 132.79 (C^{11}), 135.17 (C^{13}), 136.75 (C^{10}), 137.57 (C^{3}), 140.34 (C^{12}), 142.51 (C^{8}), 149.45 (C^{5}), 155.15 (C^{1}), 189.82 (C^{6}).

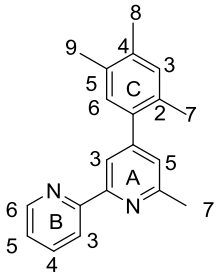
HR MS: *m/z* 252.1388 $[L\text{-}H]^{+}$ (calc. 252.1383).



To a solution of the chalcone (1.0 g, 3.98 mmol, 1eq) and pyridinium salt (0.683 g, 3.98 mmol, 1eq) in MeOH (50 mL) was added NH_4OAc (4.6 g, 59.7 mmol, 15eq) and refluxed overnight. The resulting mixture was cooled to rt. Water (20 mL) was added and the mixture was extracted with DCM (3x20 mL). The organic layers were dried and the solvent removed under reduced pressure. The crude product was purified by column chromatography (2:1, hexane:EtOAc) to yield the pure product as a white solid (0.196 g, 0.679 mmol, 17%).



Aryl aldehyde (3.0 g, 20 mmol, 1eq) and 2-acetylpyridine (2.46 g, 20 mmol, 1eq) were dissolved in MeOH (50 mL) and the mixture was stirred at rt. A solution of NaOH (aq, 2M, 10 mol%) was added dropwise and the resulting mixture stirred for 4h. The pyridinium salt (4.17g, 24 mmol, 1.2eq), NH_4OAc (8g, 0.1 mol, 5 eq) and MeOH (50 mL) were added to the solution and the mixture was refluxed overnight. The solution was cooled to rt and the solvent was removed under reduced pressure. Water (20 mL) was added to the crude mixture and extracted with DCM (3 x 20 mL). The combined organic layers were dried over $MgSO_4$, filtered and purified by column chromatography (5:1, hexane:EtOAc) to yield the product as a white solid (2.43 g, 8.4 mmol, 42%).



^{1}H NMR (400 MHz, CD_2Cl_2) δ/ppm 2.26 (s, 3H, H^{C7}), 2.27 (s, 3H, H^{C9}), 2.28 (s, 3H, H^{C8}),2.64 (s, 3H, H^{A7}), 7.06 (s, 1H, H^{C6}), 7.07 (s, 1H, H^{C3}), 7.14 (d, 1H, $^{4}J_{H,H}$ = 1.11 Hz, H^{A5}), 7.30 (ddd, 1H, $^{3}J_{H,H}$ = 7.50 Hz, 4.77 Hz, $^{4}J_{H,H}$ = 1.20 Hz, H^{B5}), 7.82 (ddd, 1H, $^{3}J_{H,H}$ = 7.99 Hz, 7.50 Hz, $^{4}J_{H,H}$ = 1.80 Hz, H^{B4}), 8.18 (d, 1H, $^{4}J_{H,H}$ = 1.11 Hz, H^{A3}), 8.47 (d"t", 1H, $^{3}J_{H,H}$ = 7.99 Hz, $^{4/5}J_{H,H}$ = 1.01 Hz, H^{B3}), 8.63 (ddd, 1H, $^{3}J_{H,H}$ = 4.77 Hz, $^{4}J_{H,H}$ = 1.80 Hz, $^{5}J_{H,H}$ = 0.90 Hz, H^{B6}).

^{13}C{^{1}H} NMR (100.62 MHz, CD_2Cl_2) δ/ppm 19.45 (C^{C9}), 19.67 (C^{C8}), 20.04 (C^{C7}), 24.93 (C^{A7}), 119.17 (H^{A3}), 121.50 (C^{B3}), 124.04 (C^{B5}), 124.38 (C^{A5}), 131.01 (C^{C6}),

132.39 (C^{C3}), 132.75 (C^{C2}), 134.72 (C^{C5}), 137.15 (C^{C4}), 137.25 (C^{B4}), 137.70 (C^{C1}), 149.67 (C^{B6}), 151.58 (C^{A4}), 155.89 (C^{A2}), 157.14 (C^{B2}), 158.22 (C^{A6}).

HR MS: *m/z* 289.1705[L-H]$^+$ (calc. 289.1699).

Complexation

[Cu(N^N)(Xantphos)][PF_6] (**5**)

Xantphos (1.0 eq) and the N^N ligand (1.0 eq.) were dissolved in DCM and stirred at room temperature for 30 minutes. The solution was then added to a solution of [$Cu(MeCN)_4$][PF_6] (1.0eq.) in DCM which was previously stirred at room temperature for 30 minutes as well. The colorless solutions turned immediately bright red and over time turned yellow. After stirring at room temperature for 1h, the solution was filtered, the solvent was removed under reduced pressure to obtain the product as a yellow powder (98%). If needed the powder was purified by slow diffusion of Et_2O in DCM to yield the product as yellow crystals (80-100%). CCDC- 1850075 contain the supplementary crystallographic data for **5**. These data can be obtained free of charge from *The Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

[Cu(N^N)(POP)][PF_6] (**6**)

POP (1.0eq) and the [$Cu(MeCN)_4$][PF_6] (1.0eq.) were dissolved in DCM and the solution was stirred at room temperature for 30 minutes. A solution of the N^N ligand (1.0 eq.) in DCM was then added to the solution. The colorless solutions turned immediately bright red and turned yellow over time. After stirring at room temperature for 1h, the solution was filtered, the solvent was removed under reduced pressure to obtain the product as a yellow powder (98%). If needed the powder was purified by slow diffusion of Et_2O in DCM to yield the product as yellow crystals (80-100%). CCDC- 1850076 contain the supplementary crystallographic data for **6**. These data can be obtained free of charge from *The Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

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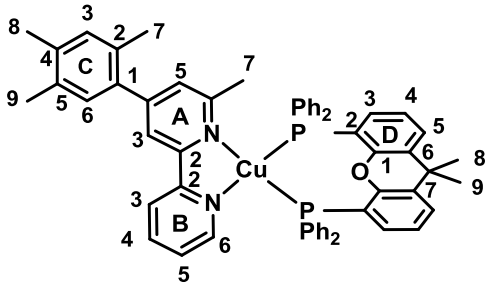

Ph rings in PPh_2 units are labeled E and E'.

^{1}H NMR (400 MHz, Acetone-d6, ppm): δ = 1.70 (s, 3H, $H^{D8/9}$), 1.89 (s, 3H, $H^{D8/9}$), 2.09 (s, 3H, H^{A7}), 2.30 (s, 3H, H^{C8}), 2.31 (s, 3H, H^{C7}), 2.32 (s, 3H, H^{C9}), 6.66-6.72 (m, 2H, H^{D3}), 6.95-7.02 (m, 4H, $H^{E2/E'2}$), 7.14-7.24 (m, 10H, $H^{E3/E'3+E2/E'2+C3+C6}$), 7.25-7.31 (m, 6H, $H^{E3/E'3+D4}$), 7.32-7.43 (m, 4H, $H^{E4+E'4}$), 7.48 (d, 1H, $^4J_{H,H}$ = 0.95 Hz, H^{A5}), 7.50 (ddd, 1H, $^3J_{H,H}$ = 7.49 Hz, 5.20 Hz, $^4J_{H,H}$ = 0.89 Hz, H^{B5}), 7.86 (dd, 2H, $^4J_{H,H}$ = 7.83 Hz, $^4J_{H,H}$ = 1.38 Hz, H^{D5}), 8.09 ("t"d, 1H, $^3J_{H,H}$ = 8.14 Hz, $^4J_{H,H}$ = 1.55 Hz, H^{B4}), 8.39 (d, 1H, $^4J_{H,H}$ = 0.95 Hz, H^{A3}), 8.54 (br. d, 1H, $J_{H,H}$ = 4.80 Hz, H^{B6}), 8.64 (br. d, 1H, $J_{H,H}$ = 8.17 Hz, H^{B3}).

^{13}C{^{1}H} NMR (100.62 MHz, Acetone-d6, ppm): δ = 19.22 ($C^{C7/C8/C9}$), 19.44 ($C^{C7/C8/C9}$), 19.91 ($C^{C7/C8/C9}$), 26.27 (C^{A7}), 26.56 ($C^{D8/D9}$), 30.31 ($C^{D8/D9}$), 36.94 (C^{D7}), 121.55 (t, $^1J_{C,P}$ = 13.68 Hz, C^{D2}), 121.60 (C^{A3}), 124.00 (C^{B3}), 126.28 (t, $^3J_{C,P}$ = 2.38 Hz, C^{D4}), 127.01 (C^{B5}), 127.33 (C^{A5}), 128.56 (C^{D5}), 129.74 (t, $^3J_{C,P}$ = 4.71 Hz, $C^{E3/E'3}$), 129.87 (t, $^3J_{C,P}$ = 4.72 Hz, $C^{E3/E'3}$), 130.97 ($C^{E4/E'4}$), 131.10 ($C^{E4/E'4}$), 131.33 (C^{C3}), 131.55 (C^{D3}), 132.60 (t, $^1J_{C,P}$ = 17.57 Hz, $C^{E1/E'1}$), 132.68 (t, $^1J_{C,P}$ = 16.40 Hz, $C^{E1/E'1}$), 133.05 (C^{C6}), 133.07 ($C^{C2/C4/C5}$), 133.53 (t, $^2J_{C,P}$ = 7.84 Hz, $C^{E2/E'2}$), 133.93 (t, $^2J_{C,P}$ = 8.03 Hz, $C^{E2/E'2}$), 134.98 (t, $^3J_{C,P}$ = 1.48 Hz,

C^{D6}), 135.32 (C^{C1}), 136.22 (C^{A4}), 138.51 ($C^{C2/C4/C5}$), 139.81 (C^{B4}), 149.91 (C^{B6}), 152.29 (C^{A2}), 153.51 (C^{B2}), 153.97 ($C^{C2/C4/C5}$), 155.85 (t, $^2J_{C,P}$ = 6.21 Hz, C^{D1}), 159.02 (C^{A6}).

^{19}F NMR (376.46 MHz, Acetone-d6, ppm): δ = -72.68 (d, $^1J_{F,P}$ = 707.35 Hz).

^{31}P NMR (161.97 MHz, Acetone-d6, ppm): δ = -13.10 (br. s, FWHM = 170.81 Hz), -144.24 (sept, $^1J_{P,F}$ = 707.35 Hz).

HR MS: *m/z* 929.2858 $[M\text{-}PF_6]^+$ (calc. 929.2851).

Elemental analysis: found C 66.00, H 4.72, N 2.53: **A** requires C 65.89, H 4.87, N 2.60%.

UV-Vis (MeCN, 2.5E-5 mol l^{-1}): λ/nm (ε/l $mol^{-1}cm^{-1}$) 245 (40399), 273 (32467), 371 (2679).

Emission: PMMA thin film (λ_{ex} = 400 nm): λ_{em}^{max} = 553 nm, solution (MeCN, 2.5E-5M, λ_{ex} = 410 nm): λ_{em}^{max} = 611 nm.

Cyclic Voltammetry (DCM Vs $Fc^{0/+}$, [*n*-Bu_4N][PF_6] supporting eletrolyte, scan rate = 0.1 V s^{-1}): *V* 0.90 (qr, ox), 0.79 (qr, red).

TCSPC: 4.77 μs (PMMA thin film, λ_{ex} = 405 nm, λ_{em} = 550 nm, τ_1 (α_1) = 2.15 (0.4256), τ_2 (α_2) = 6.662 (0.5918), R-squared = 0.9994), 0.72 μs (degassed DCM, 1E-3M, λ_{ex} = 350 nm, λ_{em} = 581 nm, R-squared = 0.9683), 0.73 μs (degassed DCM, 1E-3M, λ_{ex} = 390 nm, λ_{em} = 581 nm, R-squared = 0.9965), 0.28 μs (DCM, 1E-3M, λ_{ex} = 350 nm, λ_{em} = 586 nm, R-squared = 0.9648), 0.29 μs (DCM, 1E-3M, λ_{ex} = 390 nm, λ_{em} = 586 nm, R-squared = 0.9965).

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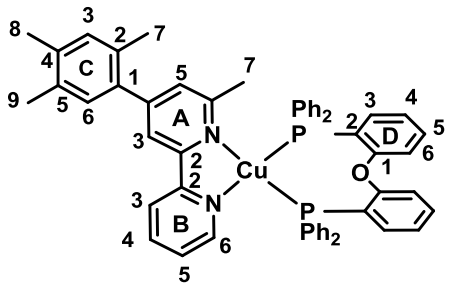


Ph rings in PPh_2 units are labeled E and E'.

^{1}H NMR (400 MHz, Acetone-d6, ppm): δ = 2.29 (s, 3H, $H^{C7/C8/C9}$), 2.30 (s, 6H, $H^{C7/C8/C9}$), 2.41 (s, 3H, H^{A7}), 6.69-6.96 (m, 2H, H^{D3}), 7.11-7.21 (m, 14H, $H^{C3+C6+D4+D6+E2+E'2}$), 7.26-7.33 (m, 8H, $H^{E3+E'3}$), 7.36-7.48 (m, 8H, $H^{A5+B5+D5+E4+E'4}$), 8.06 ("t"d, 1H, $^3J_{H,H}$ = 7.70 Hz, $^4J_{H,H}$ = 1.09 Hz, H^{B4}), 8.33 (d, 1H, $^4J_{H,H}$ = 0.98 Hz, H^{A3}), 8.61 (d, 1H, $^3J_{H,H}$ = 8.27 Hz, H^{B3}), 8.68 (br. d, 1H, $^3J_{H,H}$ = 4.97 Hz, H^{B6}).

^{13}C{^{1}H} NMR (100.62 MHz, Acetone-d6, ppm): δ = 19.22 ($C^{C7/C8/C9}$), 19.43 ($C^{C7/C8/C9}$), 19.90 ($C^{C7/C8/C9}$), 26.46 (C^{A7}), 121.25 ($C^{C3/C6}$), 121.42 (C^{A3}), 123.75 (C^{B3}), 125.13 (t, $^1J_{C,P}$ = 14.51 Hz, C^{D2}), 126.07 (t, $^3J_{C,P}$ = 2.02 Hz, C^{D4}), 126.60 (C^{B5}), 127.30 (C^{A5}), 129.75 (t, $^3J_{C,P}$ = 8.07 Hz, $C^{E3+E'3}$), 131.01 ($C^{E4+E'4}$), 131.30 ($C^{C3/C6}$), 132.13 (t, $^1J_{C,P}$ = 18.49 Hz, C^{E1}), 133.00 (C^{D6}), 133.06 ($C^{C2/C4/C5}$), 133.20 (C^{D5}), 133.81 (t, $^2J_{C,P}$ = 8.07 Hz, $C^{E2/E'2}$), 134.02 (t, $^2J_{C,P}$ = 7.34 Hz, $C^{E2/E'2}$), 134.96 (C^{D3}), 135.26 ($C^{C2/C4/C5}$), 136.29 (C^{C1}), 137.38 (C^{A4}), 138.40 ($C^{C2/C4/C5}$), 139.58 (C^{B4}), 150.28 (C^{B6}), 152.49 (C^{A2}), 153.70 (C^{B2}), 158.95 (t, $^2J_{C,P}$ = 5.99 Hz, C^{D1}), 159.47 (C^{A6}).

^{19}F NMR (376.46 MHz, Acetone-d6, ppm): δ = -72.69 (d, $^1J_{F,P}$ = 707.34 Hz, [PF_6]).

^{31}P NMR (161.97 MHz, Acetone-d6, ppm): δ = -12.82 (br. s, FWHM = 180.77 Hz), -144.25 (sept, $^1J_{P,F}$ = 707.34 Hz, [PF_6]).

HR MS: *m/z* 889.2534 $[M\text{-}PF_6]^+$ (calc. 889.2538).

Elemental analysis: found C 63.42, H 5.30, N 2.40: **B** · 0.02DCM · 0.5H_2O · 0.5Et_2O requires C 63.63, H 4.99, N 2.55%.

UV-Vis (MeCN, 2.5E-5 mol l^{-1}): λ/nm (ε/l $mol^{-1}cm^{-1}$) 245 (22914), 289 (15333), 372 (1240).

Emission: thin film (λ_{ex} = 400 nm): λ_{em}^{max} = 547 nm, solution (MeCN, 2.5E-5M, λ_{ex} = 410 nm): λ_{em}^{max} = 613 nm).

Cyclic Voltammetry (DCM Vs $Fc^{0/+}$, [*n*-Bu_4N][PF_6] supporting eletrolyte, scan rate = 0.1 V s^{-1}): *V* 0.81 (qr, ox), 0.72 (qr, red).

TCSPC: 4.53 µs (PMMA thin film, λ_{ex} = 405 nm, λ_{em} = 550 nm, τ_1 (α_1) = 2.153 µs (0.491), τ_2 (α_2) = 6.732 µs (0.532), R-squared = 0.9984), 0.39 µs (degassed DCM, 1E-3M, λ_{ex} = 350 nm, λ_{em} = 581 nm, R-squared = 0.9679), 0.43 µs (degassed DCM, 1E-3M, λ_{ex} = 390 nm, λ_{em} = 581 nm, R-squared = 0.9981), 0.22 µs (DCM, 1E-3M, λ_{ex} = 350 nm, λ_{em} = 581 nm, R-squared = 0.9944), 0.19 µs (DCM, 1E-3M, λ_{ex} = 390 nm, λ_{em} = 581 nm, R-squared = 0.9617).

Experimental Procedure for Photoredox Catalysis

General procedure A (GP A)

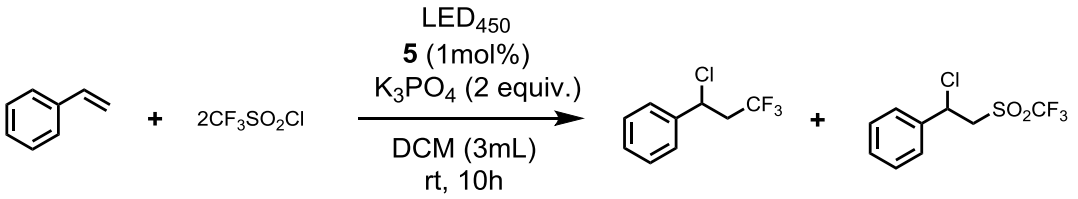
A Schlenk flask (10 mL) was charged with a magnetic stirring bar, catalyst **5** (5.4 mg, 0.5mol%) and K_2CO_3 (276 mg, 2.0 mmol, 2eq.). The Schlenk flask was then transferred into a glovebox where DCM (5 mL), substrate (1.0 mmol) and CF_3SO_2Cl (1.2-2.0eq.) were added. The reaction mixture was then irradiated with a blue LED (λ_{max} = 450 nm) from a distance of ca. 1 cm and stirred at 40°C for 3-5 hours. After completion of the reaction, the flask was transferred out of the glovebox and ca 500 mg neutral Alox was added to the solution. The mixture was then stirred at rt for 5-10 minutes to obtain the vinyl-product of the respective 1-chloro-2-(trifluoromethyl)sulfone compounds. Afterwards, the mixture was filtered, the solvent was removed under reduced pressure and the crude mixture was purified by column chromatography. NMR spectra of known compounds agree with literature values and new compounds were further characterized by HR MS and/or elemental analysis.

General procedure B (GP B)

A Schlenk flask (10mL) was charged with a magnetic stirring bar, catalyst **5** (5.4 mg, 0.5mol%) and K_2CO_3 (276 mg, 2.0 mmol, 2eq.). The flask was then transferred into a glovebox where DCM (5 mL), substrate (1.0 mmol) and CF_3SO_2Cl (1.2-2.0eq.) were added. The reaction mixture was then irradiated with a blue LED (λ_{max} = 450 nm) from a distance of ca. 1 cm and stirred at 40°C for 3-5 hours. After completion of the reaction, the Schlenk flask was transferred out of the glovebox, the solution was filtered, the solvent was removed under reduced pressure and the crude mixture was purified by column chromatography. NMR spectra of known compounds agree with literature values and novel compounds were further characterized by HR MS and/or elemental analysis.

Optimization

In order to optimize the reaction conditions, parameters were changed as described and the conversion of styrene was analyzed via the ratio of starting material to product in the ^{1}H NMR spectra. To verify the ^{1}H NMR conversions, the most promising conditions were further purified acc. to **GP A** to get the obtained yields.

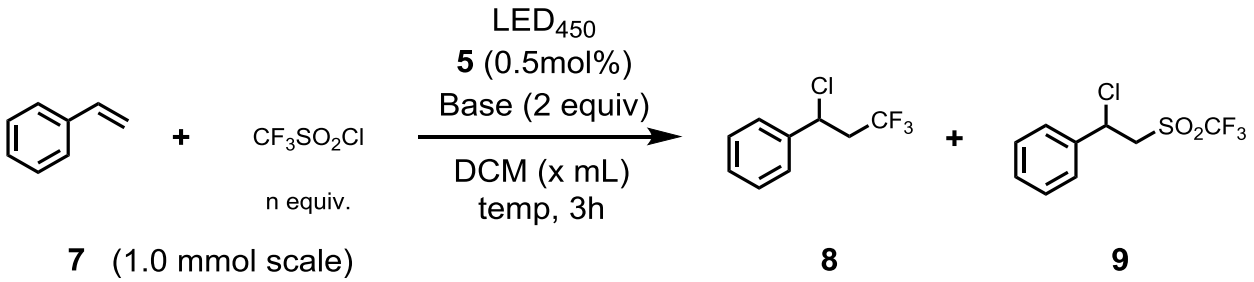


7 (0.5 mmol scale) **8** **9**

Light	[Cu]	N_2	Base	
+	+	+	+	**Quantitative conversion**
+	+	+	-	**~34% conversion**
+	+	-	+	**no reaction**
+	-	+	+	**no reaction**
-	+	+	+	**no reaction**

Figure S1. Control reactions with initial non-optimized conditions.

Table S1. Optimization of base and solvent.

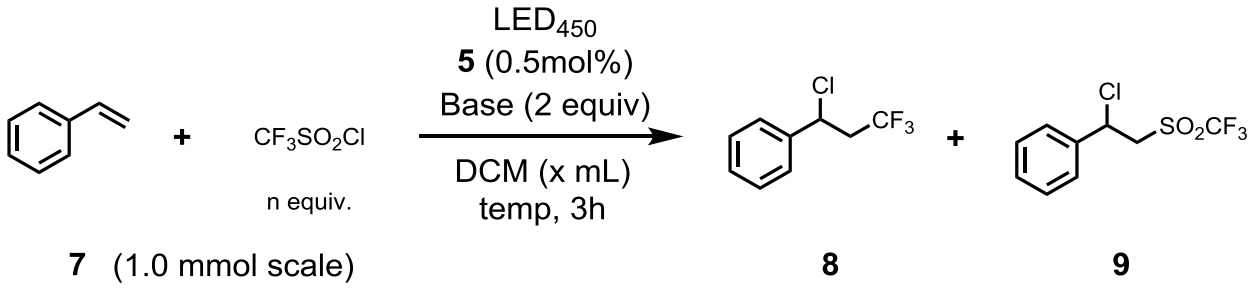


7 (1.0 mmol scale) **8** **9**

Entry	PC	Base	n	x	Temp (°C)	conversion (%)[a]	8/9[b]
1	**5**	HNa_2PO_4	2	3	r.t.	6	n.d.[c]
2	**5**	$HNaCO_3$	2	3	r.t.	95	4:1
3[d]	**5**	K_2CO_3	2	3	r.t.	trace amounts	n.d.
4[e]	**5**	K_2CO_3	2	3	r.t.	5	n.d.
5[f]	**5**	K_2CO_3	2	3	r.t.	58	14:1
6[g]	**5**	K_2CO_3	2	3	r.t.	4	n.d.

[a]According to ^{1}H NMR integrals of products (**8**+**9**) and reagent (**7**). [b]According to ^{1}H NMR integrals of **8** and **9**. [c]n.d. = not determined. [d]1 equivalent of base. [e]MeCN as solvent. [f]THF as solvent. [g]DMF as solvent.

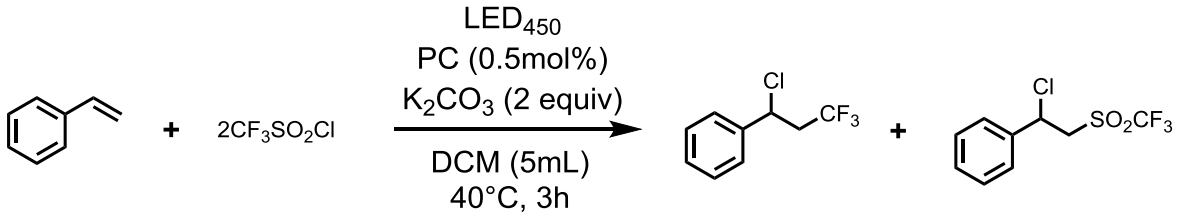
Table S2. Optimization of concentration and temperature.



Entry	PC	Base	n	x	Temp (°C)	conversion (%)[a]	8/9[b]
1	**5**	K_2CO_3	2	10	r.t.	trace amounts	n.d.[c]
2	**5**	K_2CO_3	2	5	r.t.	100	9:1
3	**5**	K_2CO_3	2	1	r.t.	trace amounts	n.d.
4[d]	**5**	K_2CO_3	2	1	r.t.	100	2:1
5[e]	**5**	K_2CO_3	2	3	r.t.	trace amounts	n.d.
6[f]	**5**	K_2CO_3	2	3	<10°C	trace amounts	n.d.

[a]According to ^{1}H NMR integrals of products (**8**+**9**) and reagent (**7**). [b]According to ^{1}H NMR integrals of **8** and **9**. [c]n.d. = not determined. [d]4 equivalent of CF_3SO_2Cl. [e]0.1mol% of **5**. [f]24h instead of 3h.

Table S3. Screening of commercially available photosensitizers.



7 (1.0 mmol scale) **8** **9**

Entry	PC	conversion (%)[a]	8/9[b]
1	**Eosin**	n.r.[c]	n.d.[d]
2	**Eosin B**	n.r.	n.d.
3	**Eosin Y**	trace amounts	n.d.
4	**$Ir(ppy)_3$**	26	n.d.
5	**$Ir(ppy)_2(dtbbpy)PF_6$**	n.r.	n.d.
6	**$Ir(dF\text{-}CF_3\text{-}ppy)_2(dtbbpy)PF_6$**	n.r	n.d.
7	**$Ru(phen)_3Cl_2 \bullet xH_2O$**	n.r	n.d.
8	**$Ru(bpy)_3Cl_2 \bullet 6H_2O$**	n.r	n.d.
9	**$Cu(dap)_2Cl$**	20	n.d.
10	**$[Cu(MeCN)_4]PF_6$**	n.r	n.d.
11	**AIBN (10mol%)**	n.r	n.d.

[a]According to ^{1}H NMR integrals of products (**8**+**9**) and reagent (**7**). [b]According to ^{1}H NMR integrals of **8** and **9**. [c]n.r. = no reaction. [d]n.d. = not determined.

Photophysical Data

Cyclic Voltammetry

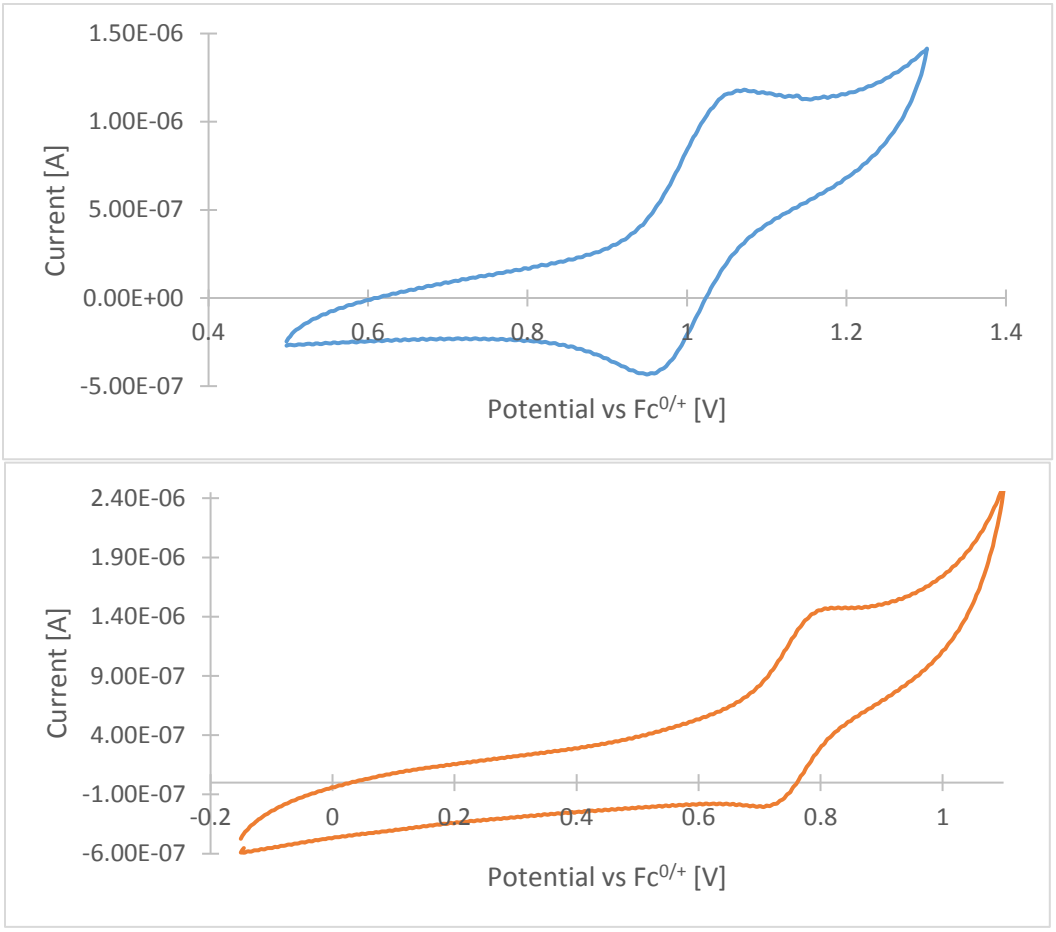


Figure S2. Cyclic voltammograms of **5** (top) and **6** (bottom).

Table S4. Redox potentials of **5** and **6** and comparison with $[Cu(bpy)(P\text{^}P)]^+$.

	E_{ox} [V][a]	E_{red} [V][a]	E_{ox}-E_{red} [mV]	$E_{1/2}$ [V][a]	$E_{1/2}$ [V][b]
5	0.9	0.79	110	0.85	1.23
6	0.81	0.72	90	0.77	1.15
[Cu(**bpy**)(**xantphos**)]$^{+}$[c]	0.82	0.71	110	0.76	1.14
[Cu(**bpy**)(**POP**)]$^{+}$[c]	0.78	0.67	110	0.72	1.1

[a] vs $Fc^{0/+}$. [b] vs SCE.[7] [c]Data from Ref 8.

TCSPC

Table S5. Excited state lifetime data for **5** and **6**. The decays were fitted to $y = y_0 + \sum \alpha_i * \exp(-(x - x_0)/\tau_i)$ and $\tau_{ave} = \sum \alpha_i * \tau_i / \sum \alpha_i$ with R^2 values >0.96.

5	λ_{ex}, λ_{em} [nm]	τ_1 (α_1) [us]	τ_2 (α_2) [us]	τ_{ave} [us]	R^2
Thin Film	405, 550	6.662 (0.5918)	2.15 (0.4258)	4.77	0.9994
N_2-purged DCM[a]	350, 581	0.7154	-	-	0.9683
	390, 581	0.7254	-	-	0.9965
aerated DCM[a]	350, 586	0.283	-	-	0.9648
	390, 586	0.2918	-	-	0.9965
6					
Thin Film	405, 550	6.732 (0.532)	2.153 (0.491)	4.53	0.9984
N_2-purged DCM[a]	350, 581	0.3924	-	-	0.9679
	390, 581	0.4332	-	-	0.9981
aerated DCM[a]	350, 581	0.2177	-	-	0.9944

[a]Concentration of 1E-3M.

Table S6. Summary of photophysical properties of **5**, **6** and comparable common photoredox catalysts.

	$[M^n]^*/M^{n+1}$ [V vs SCE][a]	M^{n+1}/M^n [V vs SCE]	τ_{ave} [ns]	Referecnce
5 [b]	-0.96	1.17[c]	720 4'770[e]	-
6 [b]	-1.08	1.1[c]	410 4'530[e]	-
$[Cu(dap)_2]^+$	-1.43	0.62[b]	270[c] 130[d] 560[e]	[9]
$[Ru(II)(phen)_3]^{2+}$ [d]	-0.87	1.26	500	[10]
$[Ru(II)(bpy)_3]^{2+}$ [d]	-0.81	1.29	950	[9]
$[Ir(III)(ppy)_2(dtbpy)]^+$ [d]	-0.96	1.21	557	[10]

[a]Estimated via Rehm-Weller equation. [b]Measured in DCM. [c] Measured vs Fc and converted to SCE.[11] [d]Measured in MeCN. [e]Measured as PMMA thin film.

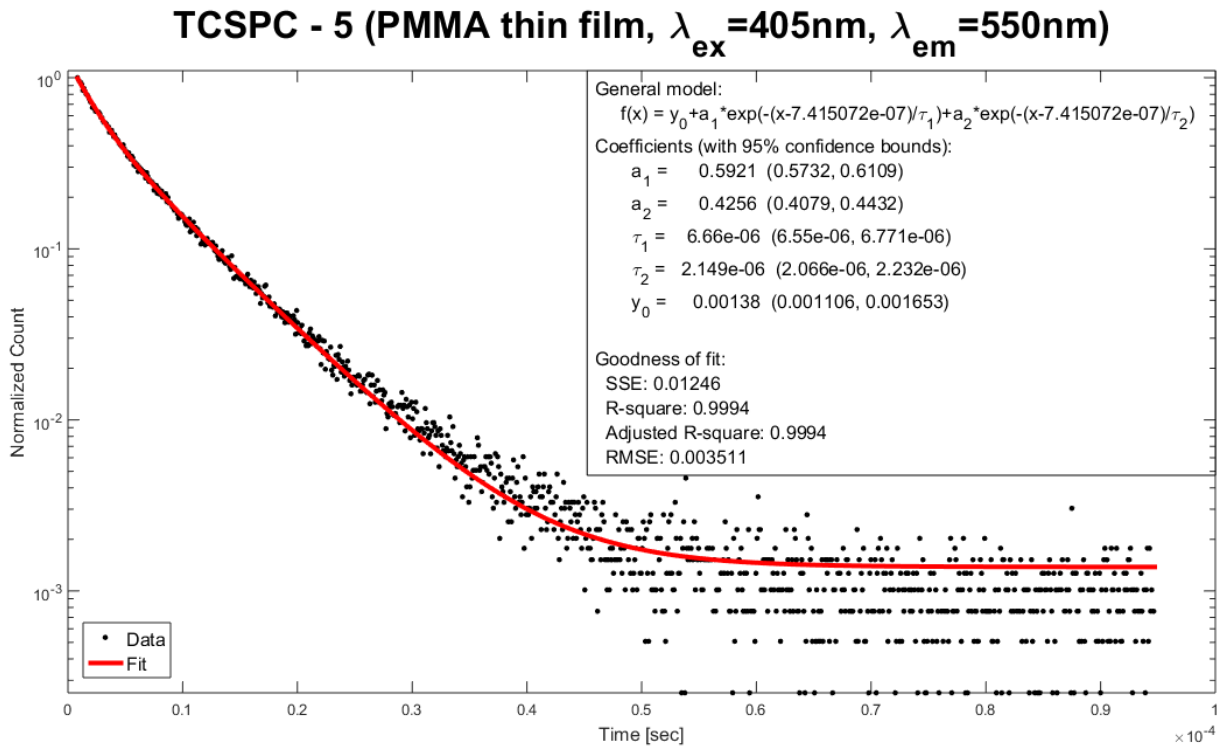


Figure S3. TCSPC measurement of **5** as PMMA thin film fitted to a biexponential decay.

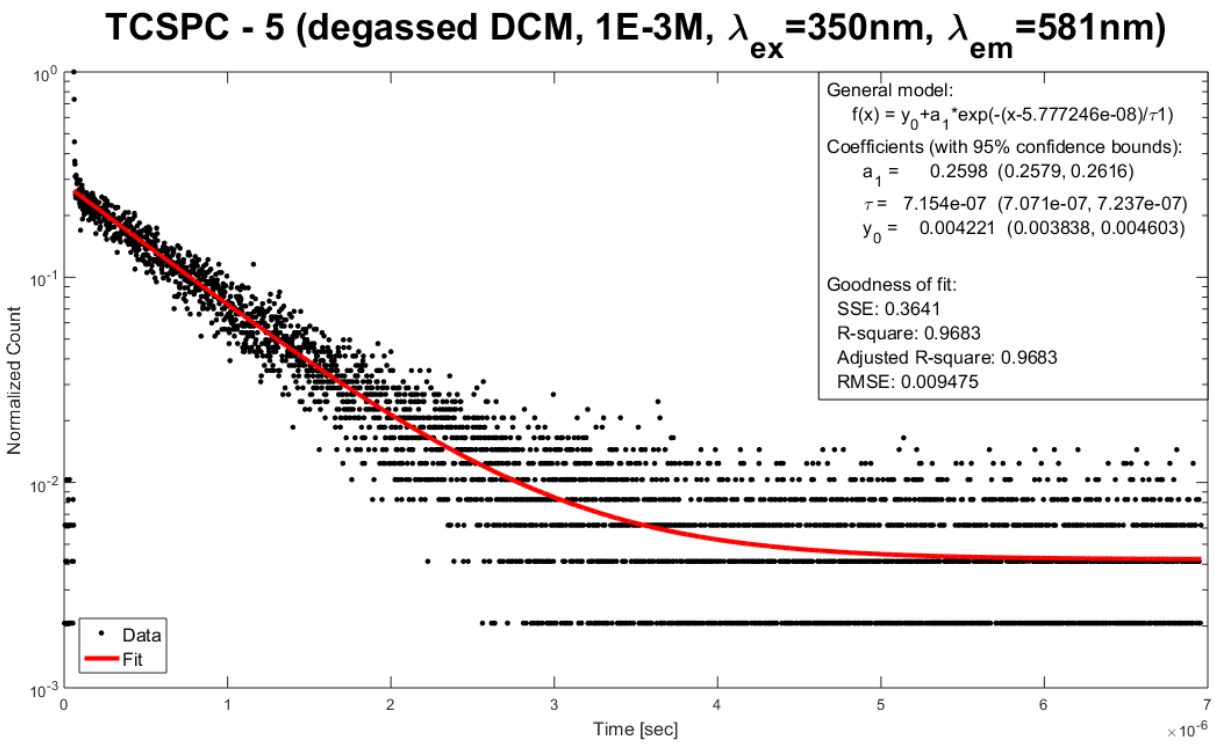


Figure S4. TCSPC measurement of **5** as degassed solution in DCM fitted to a monoexponential decay.

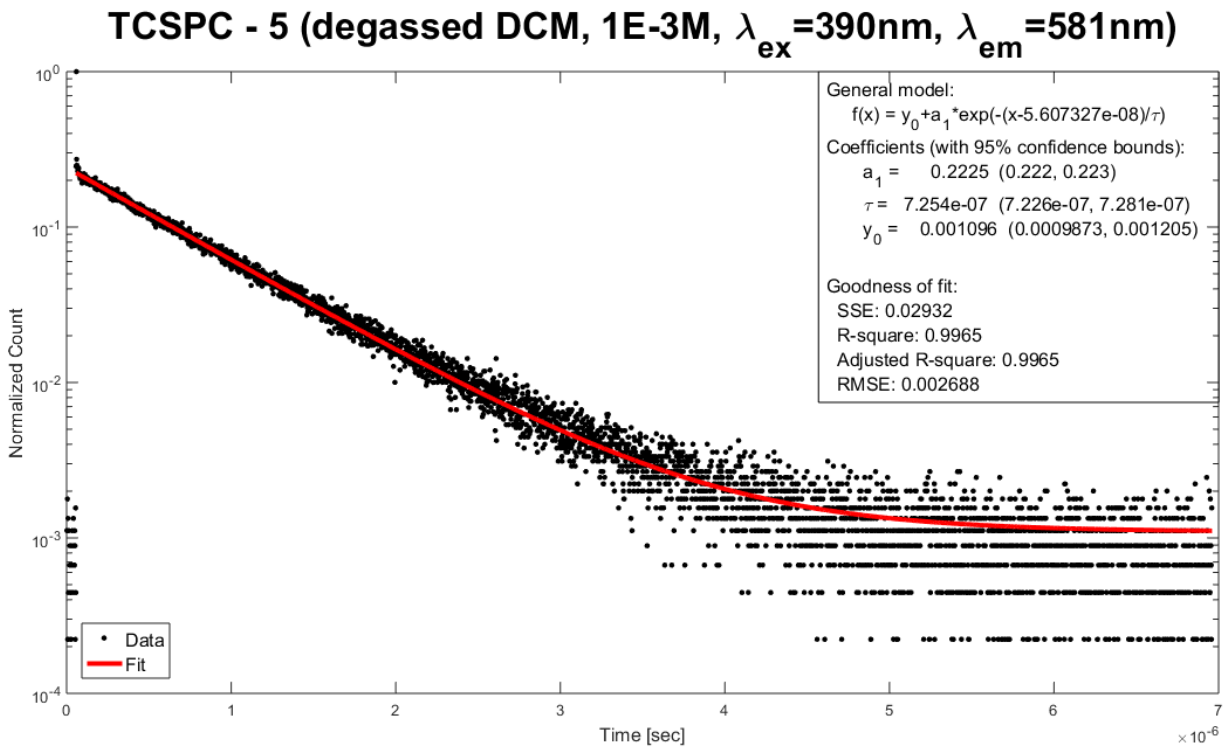


Figure S5. TCSPC measurement of **5** as degassed solution in DCM fitted to a monoexponential decay.

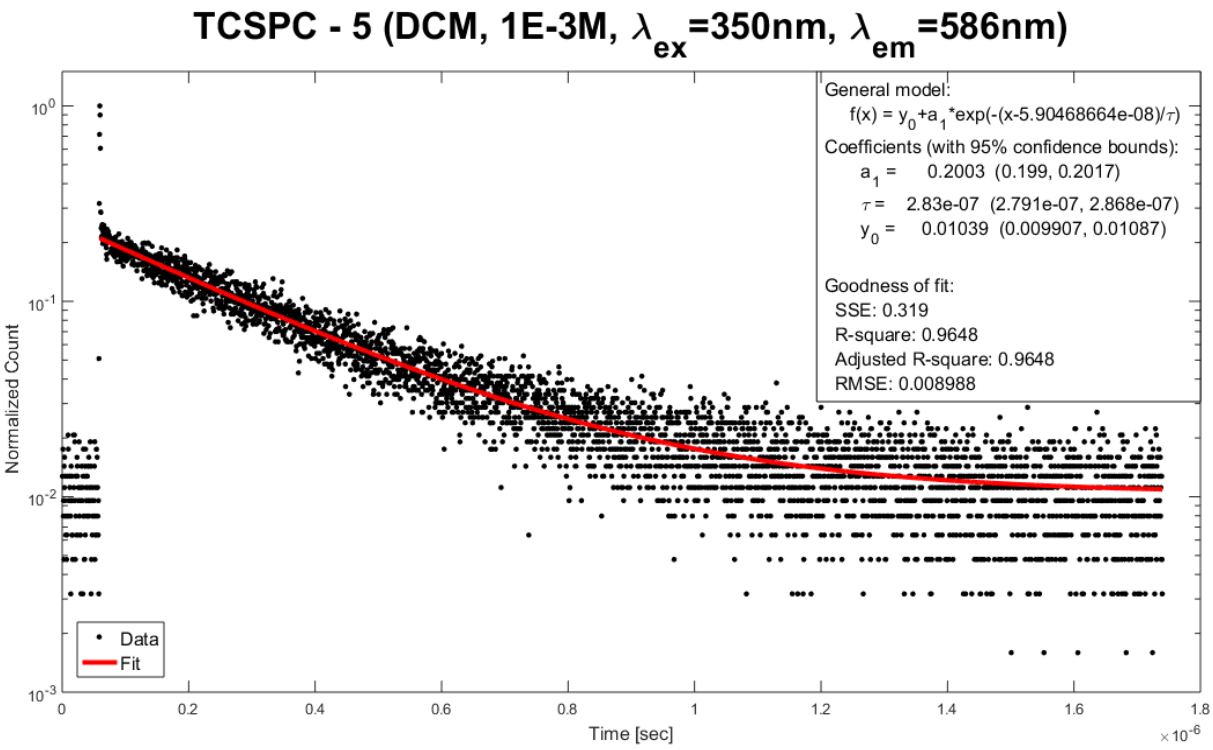


Figure S6. TCSPC measurement of **5** as solution in DCM fitted to a monoexponential decay.

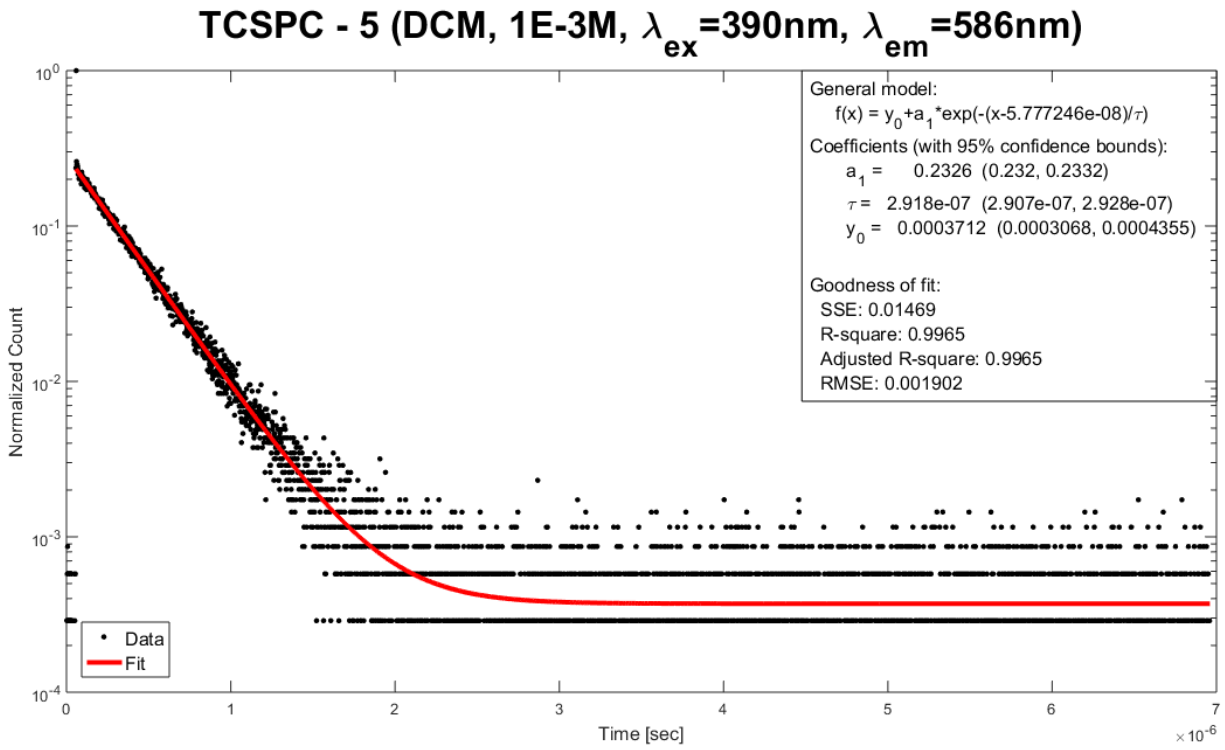


Figure S7. TCSPC measurement of **5** as solution in DCM fitted to a monoexponential decay.

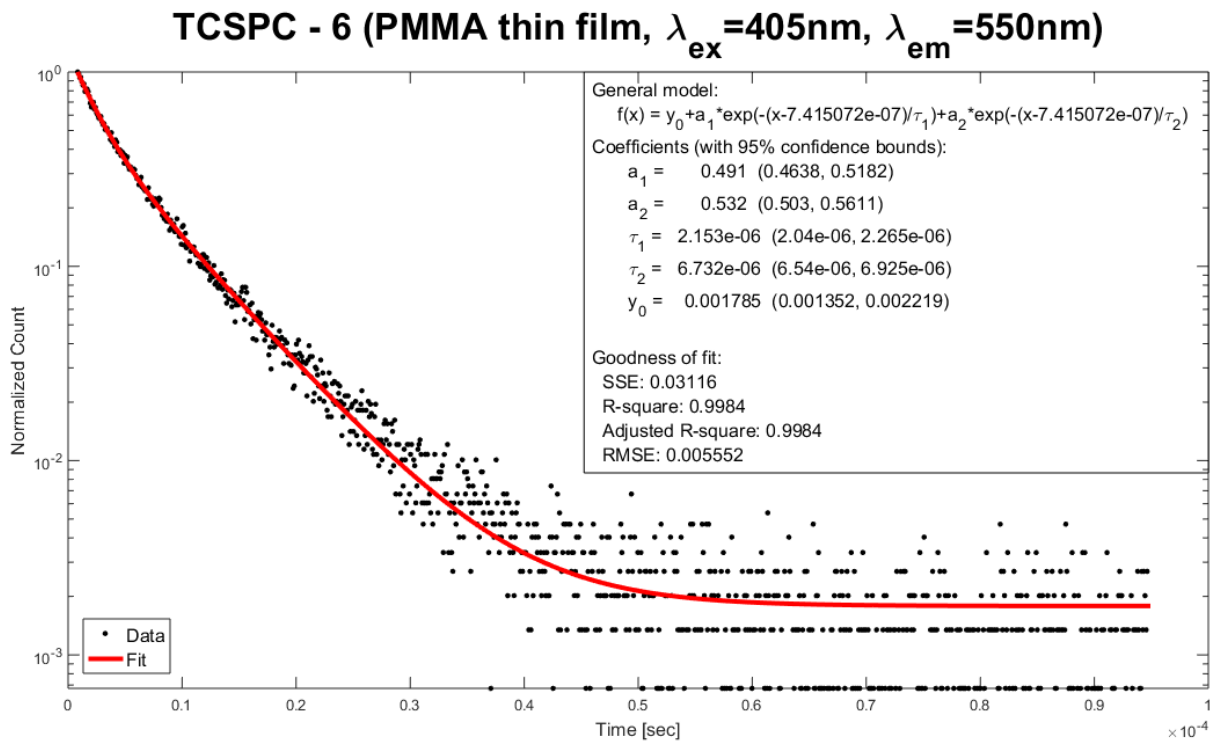


Figure S8. TCSPC measurement of **6** as PMMA thin film fitted to a biexponential decay.

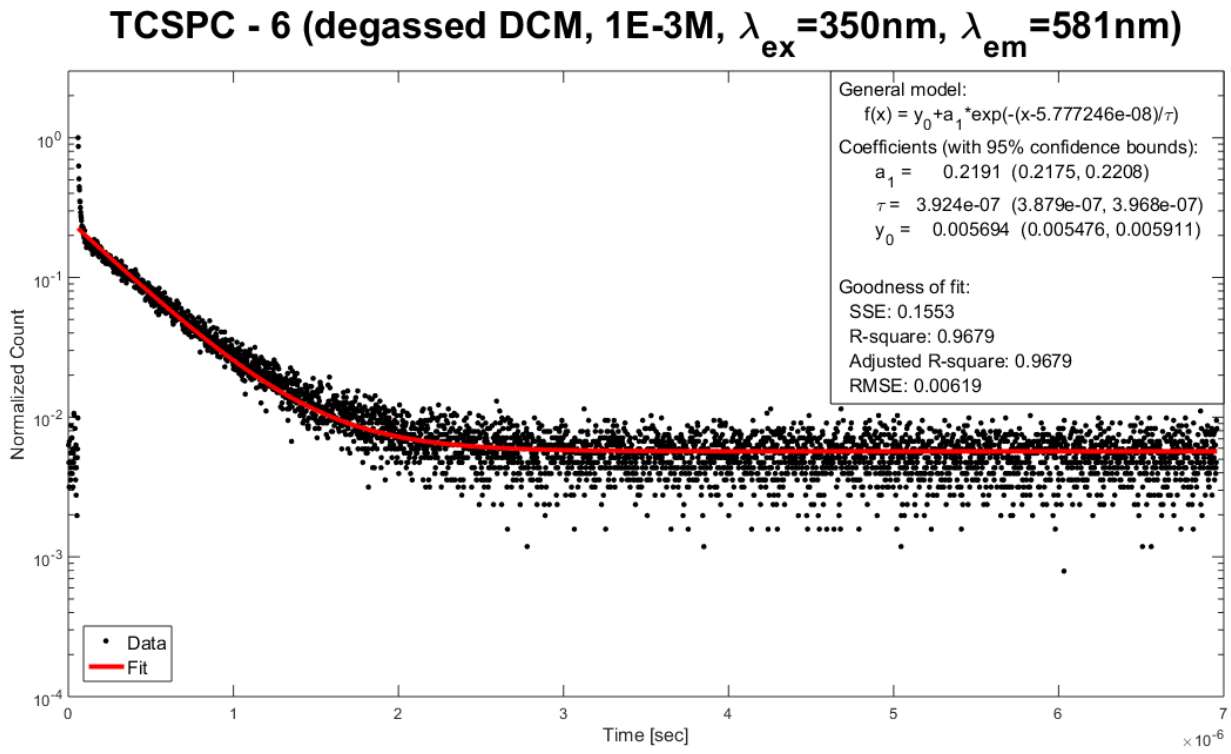


Figure S9. TCSPC measurement of **6** as degassed solution in DCM fitted to a monoexponential decay.

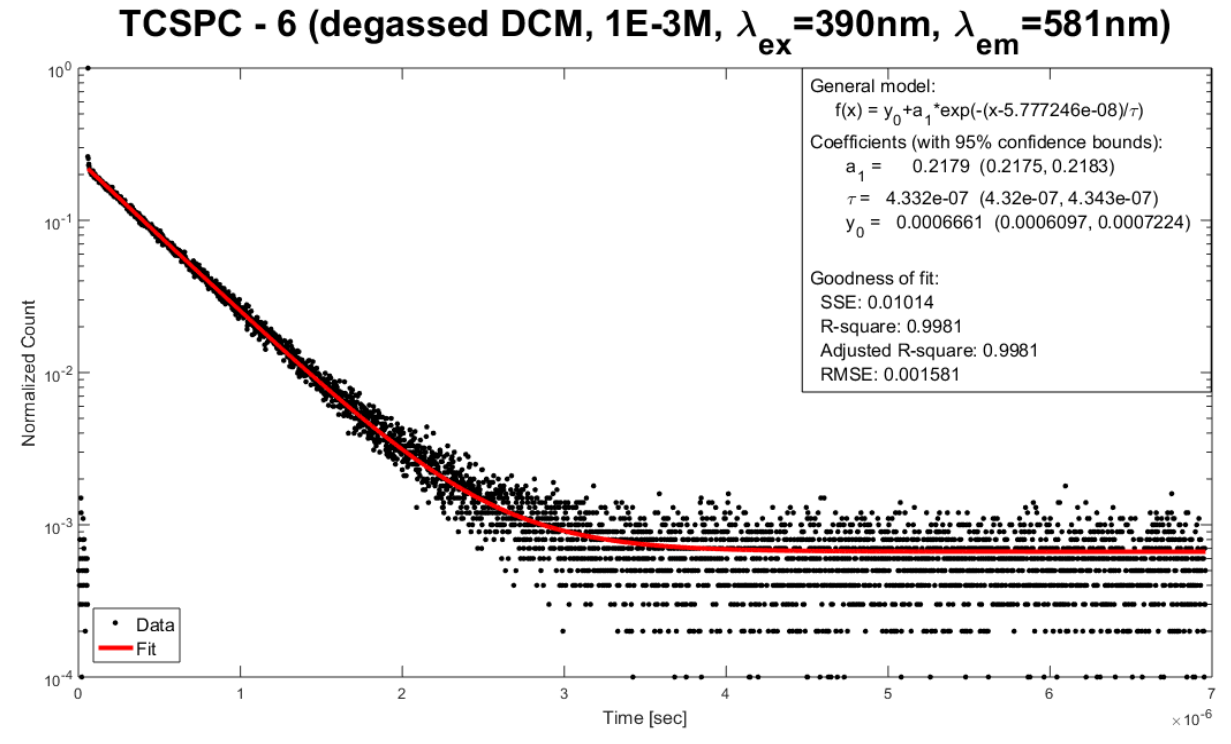


Figure S10. TCSPC measurement of **6** as degassed solution in DCM fitted to a monoexponential decay.

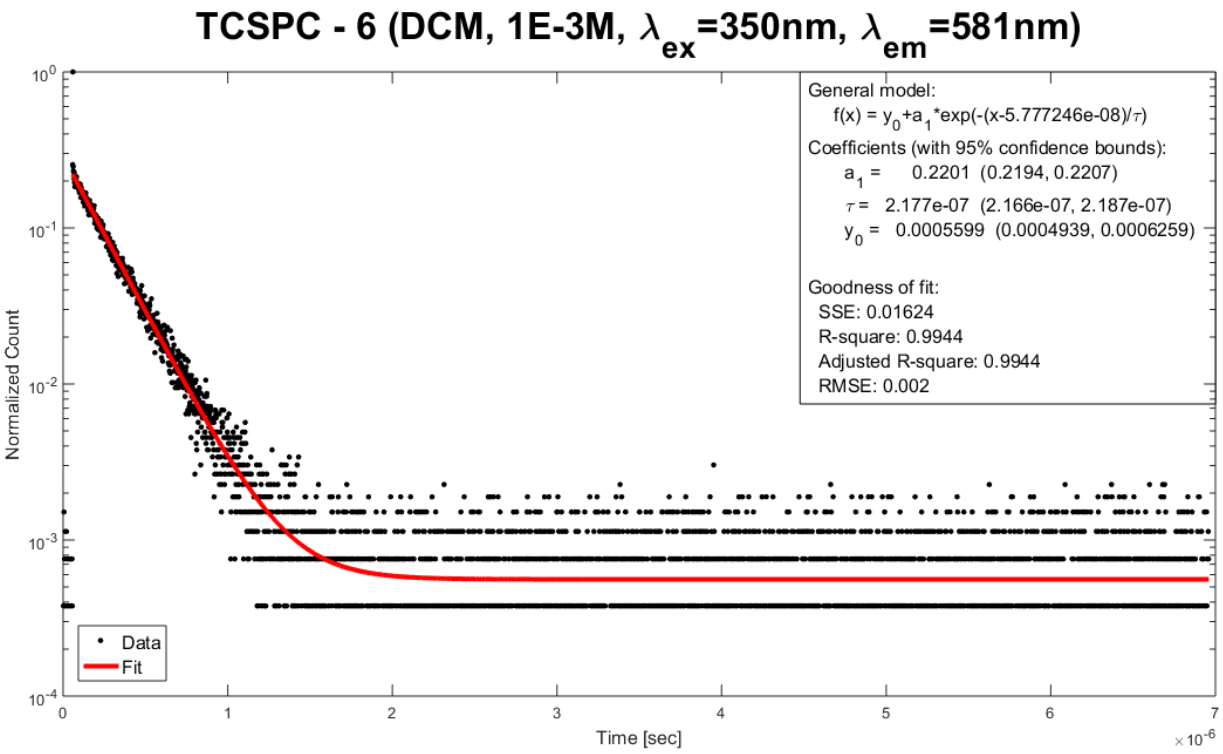


Figure S11. TCSPC measurement of **6** as solution in DCM fitted to a monoexponential decay.

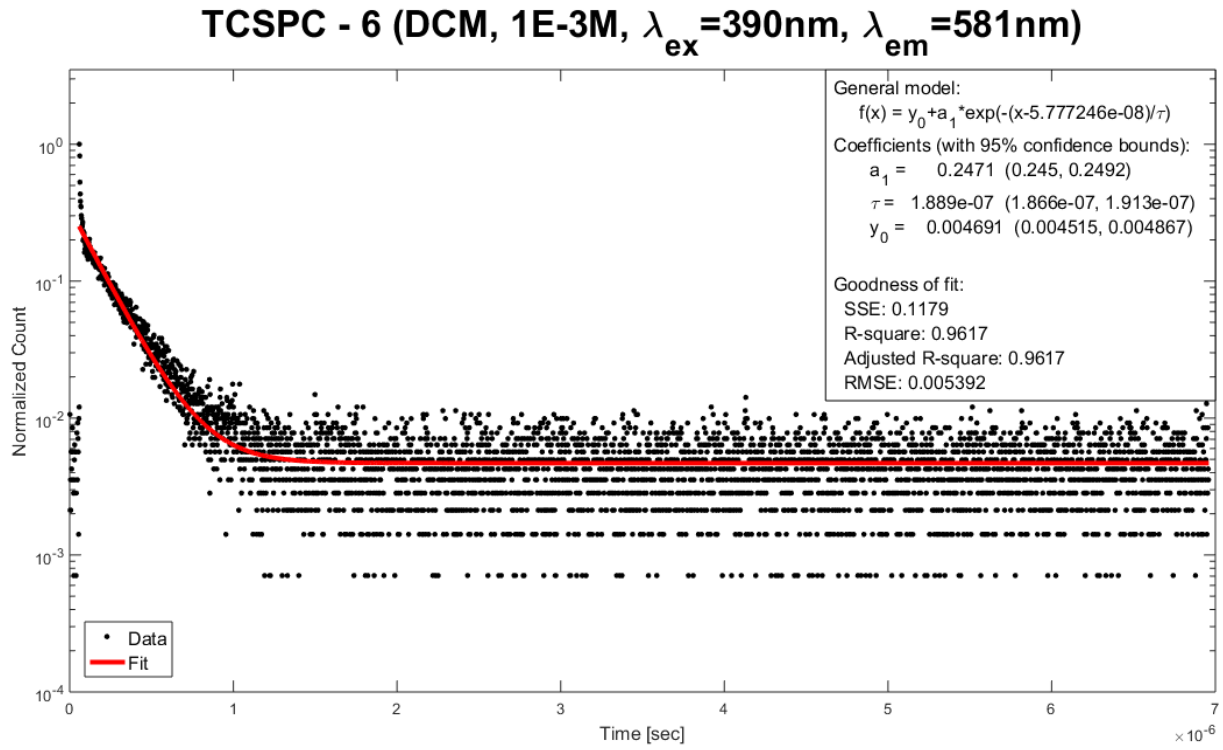
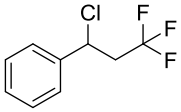


Figure S12. TCSPC measurement of **6** as solution in DCM fitted to a monoexponential decay.

Substrate Characterization



8a - (1-chloro-3,3,3-trifluoropropyl)benzene[12-13]

Reaction conditions: GP A, 3h, 1.2eq CF_3SO_2Cl

Colorless oil

Yield: 82%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.80-3.12 (m, 2H), 5.12 (t, $^3J_{H,H}$ = 7.00 Hz), 7.33-7.46 (m, 5H).

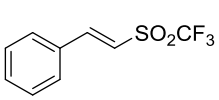
^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -64.05 (t, $^3J_{F,H}$ = 9.73 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 43.93 (q, $^2J_{C,F}$ = 28.47 Hz), 54.92 (q, $^3J_{C,F}$ = 3.08 Hz), 124.9 (q, $^1J_{C,F}$ = 277.95 Hz), 126.92, 129.11, 129.20, 139.88.

HR-MS: *m/z* calcd for $C_9H_8F_3$ 173.0578, found 173.0576; calcd for C_8H_8Cl 139.0315, found 139.0313.

EA: Found C 53.72, H 4.76; $C_9H_8ClF_3 \cdot 0.16$Hex requires C 53.87, H 4.67%.

R_f (10/1, hexane/ethyl acetate): 0.76



10a - (*E*)-(2-((trifluoromethyl)sulfonyl)vinyl)benzene[14]

Reaction conditions: GP A, 3h, 1.2eq CF_3SO_2Cl

White solid

Yield: 9%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 6.84 (d, $^3J_{H,H}$ = 15.49 Hz, 1H), 7.47-7.65 (m, 5H), 7.90 (d, $^3J_{H,H}$ = 15.49 Hz, 1H).

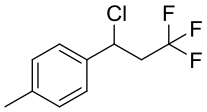
^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -78.74

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 116.78, 119.85 (q, $^1J_{C,F}$ = 324.70 Hz), 129.62, 129.68, 131.32, 133.36, 153.95.

HR-MS: *m/z* $[M+H]^+$ calcd for $C_9H_8F_3O_2S$ 237.0192, found 237.0195.

EA: Found C 45.99, H 2.99; $C_9H_7SO_2F_3$ requires C 45.76, H 2.99%.

R_f (10/1, hexane/ethyl acetate): 0.26



8b - 1-(1-chloro-3,3,3-trifluoropropyl)-4-methylbenzene

Reaction conditions: GP A, 4h, 1.2eq CF_3SO_2Cl

Colorless oil

Yield: 74%

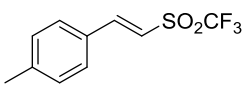
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.79-3.11 (m, 2H), 5.11 (t, $^3J_{H,H}$ = 7.02 Hz, 1H), 7.14-7.24 (m, 2H), 7.28-7.34 (m, 2H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -64.05 (t, $^3J_{F,H}$ = 9.79 Hz).

$^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 27.07, 43.88 (q, $^2J_{C,F}$ = 28.23 Hz), 54.91 (q, $^3J_{C,F}$ = 3.60 Hz), 124.94 (q, $^1J_{C,F}$ = 277.39 Hz), 126.82, 129.75, 136.98, 139.20.

EA: Found C 52.64, H 4.21; $C_{10}H_{10}ClF_3 \cdot 0.1DCM$ requires C 52.49, H 4.45%.

R_f (10/1, hexane/ethyl acetate): 0.7



10b - (*E*)-1-methyl-4-(2-((trifluoromethyl)sulfonyl)vinyl)benzene[15]

Reaction conditions: GP A, 4h, 1.2eq CF_3SO_2Cl

White solid

Yield: 18%

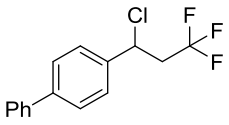
^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.44 (s, 3H), 6.76 (d, $^3J_{H,H}$ = 15.45 Hz, 1H), 7.28-7.34 (m, 2H), 7.47-7.53 (m, 2H), 7.86 (d, $^3J_{H,H}$ = 15.45 Hz).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -78.84.

$^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 21.89, 115.29, 128.68, 129.76, 130.34, 144.54, 153.96.

HR-MS: *m/z* $[M\text{-}Na]^+$ calcd for $C_{10}H_9F_3O_2SNa$ 273.0168, found 273.0166.

R_f (10/1, hexane/ethyl acetate): 0.35



8c - 4-(1-chloro-3,3,3-trifluoropropyl)-1,1'-biphenyl[12]

Reaction conditions: GP A, 4h, 1.2eq CF_3SO_2Cl

White solid

Yield: 78%

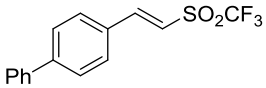
^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.86-3.14 (m, 2H), 5.18 (t, $^3J_{H,H}$ = 7.00 Hz, 1H), 7.38 (t, $^3J_{H,H}$ = 7.30 Hz, 1H), 7.42-7.52 (m, 2H), 7.55-7.68 (m, 2H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -63.98 (t, $^3J_{F,H}$ = 9.96 Hz).

$^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, ppm): δ = 43.87 (q, $^2J_{C,F}$ = 28.26 Hz), 54.72 (q, $^3J_{C,F}$ = 5.22 Hz) 124.91 (q, $^1J_{C,F}$ = 276.74 Hz), 127.27, 127.38, 127.82, 127.86, 129.01, 138.76, 140.34, 142.19.

HR-MS: *m/z* $[M]^{\cdot+}$ calcd for $C_{15}H_{12}ClF_3$ 284.0574, found 284.0582.

R_f (10/1, hexane/ethyl acetate): 0.56



10c - (*E*)-4-(2-((trifluoromethyl)sulfonyl)vinyl)-1,1'-biphenyl

Reaction conditions: GP A, 4h, 1.2eq CF_3SO_2Cl

White solid

Yield: 12%

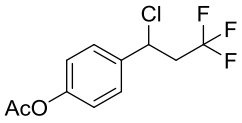
^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 6.85 (d, $^3J_{H,H}$ = 15.41 Hz, 1H), 7.39-7.54 (m, 3H), 7.60-7.66 (m, 2H), 7.66-7.78 (m, 4H), 7.93 (d, $^3J_{H,H}$ = 15.49 Hz, 1H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -78.72.

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 116.22, 127.32, 128.16, 128.72, 129.22, 130.13, 130.25, 139.48, 146.20, 153.45.

HR-MS: *m/z* $[M]^{\cdot+}$ calcd fo $C_{15}H_{11}F_3O_2S$ 312.0426, found 312.0432.

R_f (10/1, hexane/ethyl acetate): 0.37



8d - 4-(1-chloro-3,3,3-trifluoropropyl)phenyl acetate[12-13, 16]

Reaction conditions: GP B, 5h, 1.2eq CF_3SO_2Cl

White solid

Yield: 62%

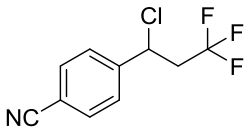
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.30 (s, 3H), 2.77-3.09 (m, 2H), 5.12 (t, $^{3}J_{H,H}$ = 6.44 Hz, 1H), 7.12 (d, $^{3}J_{H,H}$ = 7.84 Hz, 2H), 7.84 (d, $^{3}J_{H,H}$ = 7.41 Hz, 2H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -64.02 (t, $^{3}J_{F,H}$ = 9.68 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 21.21, 43.95 (q, $^{2}J_{C,F}$ = 28.40 Hz), 54.24 (q, $^{3}J_{C,F}$ = 3.34 Hz), 122.26, 124.83 (q, $^{1}J_{C,F}$ = 278.20 Hz), 128.10, 137.35, 151.09, 169.27.

HR-MS: *m/z* calcd for $C_{11}H_{10}ClF_3O_2Na$ 289.0219, found 289.0219.

EA: Found C 48.85, H 3.80; $C_{11}H_{10}ClF_3O_2 \cdot 0.19H_2O$ requires C 48.92, H 3.87%.



8e - 4-(1-chloro-3,3,3-trifluoropropyl)benzonitrile[12-13]

Reaction conditions: GP B, 5h, 1.2eq CF_3SO_2Cl

Colorless oil

Yield: 83%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.75-3.08 (m, 2H), 5.12 (t, $^{3}J_{H,H}$ = 7.10 Hz, 1H), 7.45-7.57 (m, 2H), 7.65-7.75 (m, 2H).

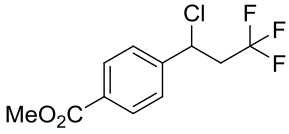
^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -63.86 (t, $^{3}J_{F,H}$ = 9.68 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 43.69 (q, $^{2}J_{C,F}$ = 28.78 Hz), 53.72 (q, $^{3}J_{C,F}$ = 3.60 Hz), 113.25, 118.18, 124.52 (q, $^{1}J_{C,F}$ = 277.43 Hz), 127.88, 132.96, 144.53.

HR-MS: *m/z* calcd for $C_{10}H_8ClF_3N$ 234.0292, found 234.0296.

EA: Found C 51.50, H 2.90, N 6.09; $C_{10}H_7ClF_3N$ requires C 51.41, H 3.02, N 6.00%.

R_f (10/1, hexane/ethyl acetate): 0.26



8f - Methyl 4-(1-chloro-3,3,3-trifluoropropyl)benzoate[12-13]

Reaction conditions: GP B, 4h, 1.2eq CF_3SO_2Cl

Colorless oil

Yield: 60%

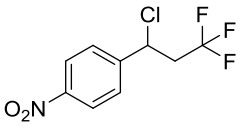
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.76-3.10 (m, 2H), 3.92 (s, 3H), 5.14 (t, $^{3}J_{H,H}$ = 6.98 Hz, 1H), 7.47 (d, $^{3}J_{H,H}$ = 8.08 Hz, 2H), 8.06 (d, $^{3}J_{H,H}$ = 8.12 Hz, 2H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -63.96 (t, $^{3}J_{F,H}$ = 9.70 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 43.75 (q, $^{2}J_{C,F}$ = 28.71 Hz), 52.42, 54.13 (q, $^{3}J_{C,F}$ = 3.60 Hz), 124.70 (q, $^{1}J_{C,F}$ = 278.07 Hz), 127.06, 130.96, 144.38, 166.44.

HR-MS: *m/z* calcd for $C_{11}H_{11}ClF_3O_2$ 267.0394, found 267.0399.

R_f (10/1, hexane/ethyl acetate): 0.28.



8g - 1-(1-chloro-3,3,3-trifluoropropyl)-4-nitrobenzene[12]

Reaction conditions: GP B, 4h, 1.2eq CF_3SO_2Cl

Off-white solid

Yield: 89%

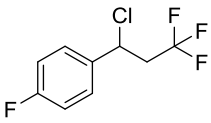
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.80-3.12 (m, 2H), 5.18 (t, $^{3}J_{H,H}$ = 7.10 Hz, 1H), 7.60 (d, $^{3}J_{H,H}$ = 8.40 Hz, 2H), 8.26 (d, $^{3}J_{H,H}$ = 8.40 Hz, 1H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -63.82 (t, $^{3}J_{F,H}$ = 9.70 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 43.76 (q, $^{2}J_{C,F}$ = 28.77 Hz), 43.36 (q, $^{3}J_{C,F}$ = 3.60 Hz), 124.41, 124.49 (q, $^{1}J_{C,F}$ = 278.06 Hz), 128.16, 146.32, 148.31.

HR-MS: *m/z* calcd for $C_9H_8ClF_3NO_2$ 254.0190, found 254.0194.

EA: Found C 42.70, H 2.71, N 5.65; $C_9H_7ClF_3NO_2$ requires C 42.62, H 2.78, N 5.52%.



8h - 1-(1-chloro-3,3,3-trifluoropropyl)-4-fluorobenzene

Reaction conditions: GP A, 4h, 1.2eq CF_3SO_2Cl

Colorless oil

Yield: 78%

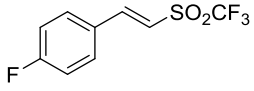
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.77-3.09 (m, 2H), 5.11 (t, $^{3}J_{H,H}$ = 7.10 Hz, 1H), 7.08 (t, $^{3}J_{H,H/F}$ = 8.58 Hz, 2H), 7.32-7.43 (m, 2H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -64.01 (t, $^{3}J_{F,H}$ = 9.81 Hz), -112.12 (m).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 44.03 (q, $^{2}J_{C,F}$ = 28.40 Hz), 54.18 (q, $^{3}J_{C,F}$ = 3.09 Hz), 116.11 (d, $^{2}J_{C,F}$ = 22.09 Hz), 124.75 (q, $^{1}J_{C,F}$ = 277.86 Hz), 128.83 (d, $^{3}J_{C,F}$ = 8.43 Hz), 135.74 (d, $^{4}J_{C,F}$ = 3.49 Hz), 162.97 (d, $^{1}J_{C,F}$ = 248.84 Hz).

EA: Found C 47.74, H 3.10; $C_9H_7ClF_4$ requires C 47.70, H 3.11%.

R_f (10/1, hexane/ethyl acetate): 0.51.



10d - (*E*)-1-fluoro-4-(2-((trifluoromethyl)sulfonyl)vinyl)benzene

Reaction conditions: GP A, 4h, 1.2eq CF_3SO_2Cl

White solid

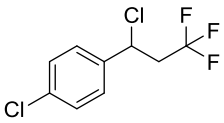
Yield: 13%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 6.75 (d, $^{3}J_{H,H}$ = 15.49 Hz), 7.19 (t, $^{3}J_{H,H/F}$ = 8.48 Hz), 7.62 (dd, $^{3}J_{H,H}$ = 8.62 Hz, $^{4}J_{H,F}$ = 5.26 Hz), 7.85 (d, $^{3}J_{H,H}$ = 15.49 Hz).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -78.69, -103.82 (m).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 116.49, 117.06 (d, $^{2}J_{C,F}$ = 22.37 Hz), 1127.66 (d, $^{4}J_{C,F}$ = 3.62 Hz), 132.00 (d, $^{3}J_{C,F}$ = 9.23 Hz), 152.46, 165.73 (d, $^{1}J_{C,F}$ = 256.64 Hz).

EA: Found C 44.85, H 2.87; $C_9H_7F_4SO_2 \cdot 0.15$Hex requires C 44.51, H 3.06 %.



8i - 1-chloro-4-(1-chloro-3,3,3-trifluoropropyl)benzene[12-13, 16-17]

Reaction conditions: GP A, 4h, 1.2eq CF_3SO_2Cl

Colorless oil

Yield: 76%

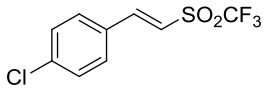
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.76-3.11 (m, 2H), 5.10 (t, $^{3}J_{H,H}$ = 7.06 Hz, 1H), 7.28-7.43 (m, 4H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -63.96 (t, $^{3}J_{F,H}$ = 9.64 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 43.88 (q, $^{2}J_{C,F}$ = 28.50 Hz), 54.10 (q, $^{3}J_{C,F}$ = 3.38 Hz), 124.72 (q, $^{1}J_{C,F}$ = 277.67 Hz), 128.36, 129.34, 135.11, 138.31.

HR-MS: *m/z* $[ArCHCH_2CF_3]^+$ calcd for $C_9H_7ClF_3$ 207.0183, found 207.0186.

R_f (10/1, hexane/ethyl acetate): 0.51



10e - (*E*)-1-chloro-4-(2-((trifluoromethyl)sulfonyl)vinyl)benzene

Reaction conditions: GP A, 4h, 1.2eq CF_3SO_2Cl

White solid

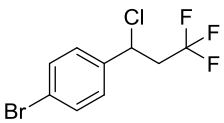
Yield: 7%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 6.81 (d, $^{3}J_{H,H}$ = 15.49 Hz, 1H), 7.47 (d, $^{3}J_{H,H}$ = 8.44 Hz, 2H), 7.54 (d, $^{3}J_{H,H}$ = 8.48 Hz, 2H), 7.84 (d, $^{3}J_{H,H}$ = 15.49 Hz, 1H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -78.61.

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 117.42, 129.74, 130.04, 130.80, 139.75, 152.32.

HR-MS: *m/z* = calcd for $C_9H_6ClF_3O_2SNa$ 292.9621, found 292.9628.



8j - 1-bromo-4-(1-chloro-3,3,3-trifluoropropyl)benzene[13]

Reaction conditions: GP B, 5h, 2eq CF_3SO_2Cl

Colorless oil

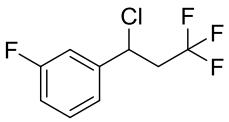
Yield: 75%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.76-3.06 (m, 2H), 5.07 (t, $^{3}J_{H,H}$ = 7.08 Hz, 1H), 7.26-7.31 (m, 2H), 7.46-7.56 (m, 2H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -63.95 (t, $^{3}J_{F,H}$ = 9.77 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 43.83 (q, $^{2}J_{C,F}$ = 28.38 Hz), 54.14 (q, $^{3}J_{C,F}$ = 3.34 Hz), 123.25, 124.70 (q, $^{1}J_{C,F}$ = 278.19 Hz), 128.64, 132.31, 138.81.

EA: Found C 37.50, H 2.40; $C_9H_7BrClF_3$ requires C 37.60, H 2.45%.



8k - 1-(1-chloro-3,3,3-trifluoropropyl)-3-fluorobenzene

Reaction conditions: GP B, 4h, 1.2eq CF_3SO_2Cl

Colorless oil

Yield: 73%

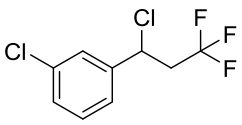
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.77-3.09 (m, 2H), 5.10 (t, $^{3}J_{H,H}$ = 7.00 Hz, 1H), 7.07 (tdd, $^{3}J_{H,H/F}$ = 8.38 Hz, *J* = 2.55 Hz, *J* = 0.93 Hz, 1H), 7.14 (dt, *J* = 9.28 Hz, *J* = 2.06 Hz, 1H), 7.17-7.21 (m, 1H), 7.37 (td, *J* = 7.99 Hz, *J* = 5.82 Hz, 1H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -64.05 (t, $^{3}J_{F,H}$ = 9.90 Hz), -111.58 (dt, $^{3}J_{F,H}$ = 9.20 Hz, $^{4}J_{H,H}$ = 6.14 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 43.91 (q, $^{2}J_{C,F}$ = 28.58 Hz), 54.04(q, $^{3}J_{C,F}$ = 1.80 Hz), 114.14 (d, $^{2}J_{C,F}$ = 22.85 Hz), 116.28 (d, $^{2}J_{C,F}$ = 21.36 Hz), 122.65 (d, $^{4}J_{C,F}$ = 3.10 Hz), 124.73 (q, $^{1}J_{C,F}$ = 278.01 Hz), 130.75 (d, $^{3}J_{C,F}$ = 8.44 Hz), 142.16 (d, $^{2}J_{C,F}$ = 7.36 Hz), 162.99 (d, $^{1}J_{C,F}$ = 247.64 Hz).

EA: Found C 46.29, H 3.09; $C_9H_7ClF_4 \cdot 0.32H_2O$ requires C 46.52, H 3.31%.

R_f (10/1, hexane/ethyl acetate): 0.54.



8l - 1-chloro-3-(1-chloro-3,3,3-trifluoropropyl)benzene

Reaction conditions: GP B, 4h, 1.2eq CF_3SO_2Cl

Colorless oil

Yield: 86%

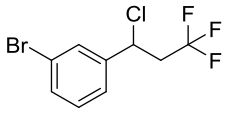
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.76-3.09 (m, 2H), 5.06 (t, $^{3}J_{H,H}$ = 7.02 Hz, 1H), 7.27-7.37 (m, 3H), 7.41 (s, 1H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -64.00 (t, $^{3}J_{F,H}$ = 9.86 Hz)

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 43.85 (q, $^{2}J_{C,F}$ = 28.60 Hz), 53.99 (q, $^{3}J_{C,F}$ = 3.34 Hz), 124.72 (q, $^{1}J_{C,F}$ = 278.10 Hz), 125.16, 127.24, 129.42, 130.40, 134.98, 141.71.

EA: Found C 45.52, H 3.09; $C_9H_7Cl_2F_3 \cdot 0.07$Hex requires C 45.42, H 3.23%.

R_f (10/1, hexane/ethyl acetate): 0.27



8m - 1-bromo-3-(1-chloro-3,3,3-trifluoropropyl)benzene[13]

Reaction conditions: GP B, 5h, 2eq CF_3SO_2Cl

Colorless oil

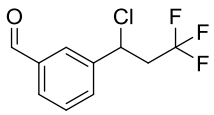
Yield: 73%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.76-3.06 (m, 2H), 5.05 (t, $^{3}J_{H,H}$ = 7.04 Hz, 1H), 7.26 (t, $^{3}J_{H,H}$ = 7.80 Hz, 1H), 7.33 (dt, $^{3}J_{H,H}$ = 7.70 Hz, $^{4}J_{H,H}$ = 2.30 Hz, 1H), 7.49 (ddd, $^{3}J_{H,H}$ = 7.83 Hz, $^{4}J_{H,H}$ = 1.83 Hz, 1.19 Hz, 1H), 7.56 (t, $^{4}J_{H,H}$ = 1.78 Hz, 1H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -63.99 (t, $^{3}J_{F,H}$ = 9.61 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 43.86 (q, $^{2}J_{C,F}$ = 28.60 Hz), 53.92 (q, $^{3}J_{C,F}$ = 3.34 Hz), 123.01, 124.71 (q, $^{1}J_{C,F}$ = 277.95 Hz), 125.63, 130.13, 130.66, 132.36, 141.93.

EA: Found C 38.05, H 2.41; $C_9H_7BrClF_3 \cdot 0.02$Hex requires C 37.87, H 2.54%.



8n - 3-(1-chloro-3,3,3-trifluoropropyl)benzaldehyde

Reaction conditions: GP B, 5h, 2eq CF_3SO_2Cl

Colorless oil

Yield: 64%

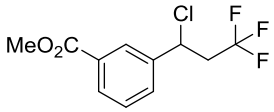
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.81-3.14 (m, 2H), 5.19 (t, $^{3}J_{H,H}$ = 7.08 Hz, 1H), 7.58 (t, $^{3}J_{H,H}$ = 7.64 Hz, 1H), 7.68 (d, $^{3}J_{H,H}$ = 7.76 Hz, 1H), 7.88 (d, $^{3}J_{H,H}$ = 7.52 Hz, 1H), 7.93 (s, 1H), 10.04 (s, 1H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -63.89 (t, 9.75 Hz).

^{13}C NMR (100.6 MHz, $CDCl_3$, ppm): δ = 43.81 (q, $^{2}J_{C,F}$ = 28.59 Hz), 54.03 (q, $^{3}J_{C,F}$ = 3.34 Hz), 124.67 (q, $^{1}J_{C,F}$ = 277.96 Hz), 127.68, 129.95, 130.76, 132.88, 137.13, 141.02, 191.54.

HR-MS: *m/z* calcd for $C_{10}H_9ClF_3O$ 237.0289, found 237.0293.

EA: Found C 50.88, H 3.55; $C_{10}H_8ClF_3O$ C 50.76, H 3.41%.



8o - methyl 3-(1-chloro-3,3,3-trifluoropropyl)benzoate

Reaction conditions: GP B, 4h, 2eq CF_3SO_2Cl

Colorless oil

Yield: 87%

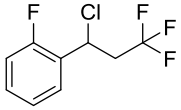
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.82-3.12 (m, 2H), 3.94 (s, 3H), 5.16 (t, $^{3}J_{H,H}$ = 7.06 Hz, 1H), 7.48 (t, $^{3}J_{H,H}$ = 7.74 Hz, 1H), 7.60 (d, $^{3}J_{H,H}$ = 7.72 Hz, 1H), 8.03 (d, $^{3}J_{H,H}$ = 7.76 Hz, 1H), 8.08 (s, 1H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -63.94 (t, $^{3}J_{F,H}$ = 9.90 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 43.80 (q, $^{2}J_{C,F}$ = 28.60 Hz), 54.26 (q, $^{3}J_{C,F}$ = 3.34 Hz), 124.75 (q, $^{1}J_{C,F}$ = 277.85 Hz), 128.12, 129.30, 130.36, 131.15, 131.43, 140.28, 166.45.

HR-MS: *m/z* calcd for $C_{11}H_{11}ClF_3O_2$ 267.0394, found 267.0399.

EA: Found C 49.63, H 3.49; $C_{11}H_{10}ClF_3O_2$ requires C 49.55, H 3.78%.



8p - 1-(1-chloro-3,3,3-trifluoropropyl)-2-fluorobenzene

Reaction conditions: GP B, 4h, 1.2eq CF_3SO_2Cl

Colorless oil

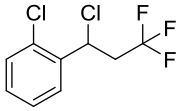
Yield: 85%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.76-3.14 (m, 2H), 5.42 (t, 7.04 Hz, 1H), 7.04-7.14 (m, 1H), 7.15-7.23 (m, 1H), 7.30-7.39 (m, 1H), 7.43-7.50 (m, 1H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -64.42 (t, $^{3}J_{F,H}$ = 9.94 Hz, 3F), -117.14 – -117.23 (m, 1F).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 42.77 (dq, $^{2}J_{C,F}$ = 28.56 Hz, $^{4}J_{C,F}$ = 1.69 Hz), 48.43 (dq, $^{3}J_{C,F}$ = 3.72 Hz, 3.42 Hz), 116.21 (d, $^{2}J_{C,F}$ = 21.66 Hz), 124.85 (q, $^{1}J_{C,F}$ = 277.69 Hz), 124.85 (d, $^{3}J_{C,F}$ = 3.61 Hz), 126.92 (d, $^{2}J_{C,F}$ = 12.48 Hz), 128.72 (d, $^{4}J_{C,F}$ = 2.95 Hz), 130.95 (d, $^{3}J_{C,F}$ = 8.50 Hz), 159.73 (d, $^{1}J_{C,F}$ = 249.24 Hz).

EA: Found C 47.56, H 3.17; $C_9H_7ClF_4$ requires C 47.70, H 3.11%.



8q - 1-chloro-2-(1-chloro-3,3,3-trifluoropropyl)benzene

Reaction conditions: GP B, 5h, 2eq CF_3SO_2Cl

Colorless oil

Yield: 66%

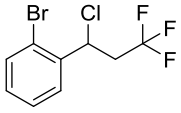
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.75-3.08 (m, 2H), 5.68 (dd, $^{3}J_{H,H}$ = 7.58 Hz, 6.10 Hz, 1H), 7.29 (dt, $^{3}J_{H,H}$ = 7.60 Hz, $^{4}J_{H,H}$ = 1.72 Hz, 1H), 7.35 (dt, $^{3}J_{H,H}$ = 7.52 Hz, $^{4}J_{H,H}$ = 1.36 Hz, 1H), 7.40 (dd, $^{3}J_{H,H}$ = 7.82 Hz, $^{4}J_{H,H}$ = 1.38 Hz, 1H), 7.59 (dd, $^{3}J_{H,H}$ = 7.72 HZ, $^{4}J_{H,H}$ = 1.60 Hz, 1H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -64.18 (t, $^{3}J_{F,H}$ = 9.64 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 42.87 (q, $^{2}J_{C,F}$ = 28.88 Hz), 50.86 (q, $^{3}J_{C,F}$ = 3.60 Hz), 124.87 (q, $^{1}J_{C,F}$ = 278.10 Hz), 127.75, 128.62, 130.10, 130.20, 132.49, 137.15.

HR-MS: *m/z* calcd for $C_9H_7ClF_3$ 207.0183, found 207.0183.

EA: Found C 44.58, H 3.01; $C_9H_7Cl_2F_3$ requires C 44.47, H 2.90%.



8r - 1-bromo-2-(1-chloro-3,3,3-trifluoropropyl)benzene[12-13, 16]

Reaction conditions: GP B, 5h, 2eq CF_3SO_2Cl

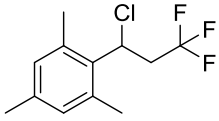
Colourless oil

Yield: 73%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.80-2.99 (m, 2H), 5.67 (dd, $^{3}J_{H,H}$ = 7.60 Hz, 6.08 Hz, 1H), 7.21 (ddd, $^{3}J_{H,H}$ = 7.97 Hz, 7.43 Hz, $^{4}J_{H,H}$ = 1.63 Hz, 1H), 7.39 (dt, $^{3}J_{H,H}$ = 7.65 Hz, $^{4}J_{H,H}$ = 1.10 Hz, 1H), 7.59 (dd, $^{3}J_{H,H}$ = 6.48 Hz, $^{4}J_{H,H}$ = 1.48 Hz, 1H), 7.61 (dd, $^{3}J_{H,H}$ = 6.32 Hz, $^{4}J_{H,H}$ = 1.44 Hz, 1H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -64.05 (t, $^{3}J_{F,H}$ = 9.85 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 42.98 (q, $^{2}J_{C,F}$ = 28.82 Hz), 5344 (q, $^{3}J_{C,F}$ = 3.60 Hz), 122.63, 124.83 (q, $^{1}J_{C,F}$ = 278.07 Hz), 128.41, 128.75, 130.45, 133.38, 138.81.



8s - 2-(1-chloro-3,3,3-trifluoropropyl)-1,3,5-trimethylbenzene

Reaction conditions: GP B, 4h, 1.2eq CF_3SO_2Cl

Colourless oil

Yield: 89%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.27 (s, 3H), 2.39 (s, 3H), 2.54 (s, 3H), 2.99 (ddq, $^{2}J_{H,H}$ = 15.45 Hz, $^{3}J_{H,H}$ = 5.38 Hz, $^{3}J_{H,F}$ = 10.31 Hz, 1H), 3.08-3.27 (m, 1H), 5.67 (t, $^{3}J_{H,H}$ = 6.62 Hz, 1H), 6.76-6.98 (m, 2H).

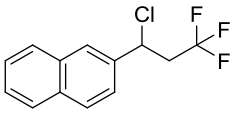
^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -65.45 (t, $^{3}J_{F,H}$ = 10.22 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 20.49, 20.88, 20.95, 42.03 (q, $^{2}J_{C,F}$ = 28.02 Hz), 50.51 (q, $^{3}J_{C,F}$ = 3.34 Hz), 125.51 (q, $^{1}J_{C,F}$ = 277.72 Hz), 129.54, 131.83, 132.76, 135.68, 137.44, 138.68.

HR-MS: *m/z* calcd for $C_{12}H_{14}ClF_3$ 250.0731, found 250.0736.

EA: Found C 57.45, H 5.94; $C_{12}H_{14}ClF_3$ requires C 57.49, H 5.63%.

R_f (10/1, hexane/ethyl acetate): 0.74.



8t - 2-(1-chloro-3,3,3-trifluoropropyl)naphthalene[13, 16]

Reaction conditions: GP A, 4h, 1.2eq CF_3SO_2Cl

Colorless oil

Yield: 76%

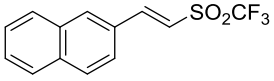
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.92-3.18 (m, 2H), 5.30 (t, $^{3}J_{H,H}$ = 7.00 Hz, 1H), 7.48-7.57 (m, 3H), 7.78-7.93 (m, 4H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -63.96 (t, $^{3}J_{F,H}$ = 9.94 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 43.83 (q, $^{2}J_{C,F}$ = 28.47 Hz), 55.29 (q, $^{3}J_{C,F}$ = 3.49 Hz), 124.02, 124.90 (q, $^{1}J_{C,F}$ = 277.10 Hz), 126.31, 126.91, 127.03, 127.92, 128.29, 129.33, 133.11, 133.54, 136.96.

HR-MS: *m/z* calcd for $C_{13}H_{10}ClF_3$ 258.0418, found 258.0423.

EA: Found C 60.46ss, H 3.85; $C_{13}H_{10}ClF_3$ requires C 60.36, H 3.90%.



10f - *(E)*-2-(2-((trifluoromethyl)sulfonyl)vinyl)naphthalene

Reaction conditions: GP A, 4h, 1.2eq CF_3SO_2Cl

Yellow solid

Yield: 18%

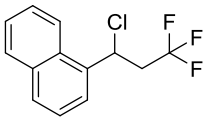
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 6.91 (d, $^{3}J_{H,H}$ = 15.41 Hz, 1H), 7.55-7.68 (m, 3H), 7.87-7.95 (m, 3H), 8.05 (d, $^{3}J_{H,H}$ = 15.57 Hz, 1H), 8.07 (s, 1H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -78.70.

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 116.51, 123.32, 127.63, 128.13, 128.78, 129.10, 129.32 ,129.67, 133.09, 133.37, 135.54, 153.96.

HR-MS: *m/z* calcd for $C_{13}H_9SO_2F_3$ 286.0270, found 286.0274.

EA: Found C 56.54, H 3.70; $C_{13}H_9SO_2F_3 \cdot 0.2Hex$ requires C 56.20, H 3.92%.



8u - 1-(1-chloro-3,3,3-trifluoropropyl)naphthalene

Reaction conditions: GP A, 5h, 1.2eq CF_3SO_2Cl

Colorless oil

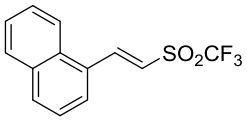
Yield: 61%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.0-3.32 (m, 2H), 5.95 (br s, 1H), 7.51 (t, $^3J_{H,H}$ = 7.74 Hz, 1H), 7.56 (t, $^3J_{F,H}$ = 7.44 Hz, 1H), 7.64 (ddd, $^3J_{H,H}$ = 8.56 Hz, 6.85 Hz, $^4J_{H,H}$ = 1.43 Hz, 1H), 7.69 (d, $^3J_{H,H}$ = 7.11 Hz, 1H), 7.89 (d, $^3J_{H,H}$ = 8.20 Hz, 1H), 7.93 (d, $^3J_{H,H}$ = 8.16 Hz, 1H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -64.22 (br s, FWHM = 28.56 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 43.08 (q, $^2J_{C,F}$ = 28.51 Hz), 122.55, 125.04, 125.30 (q, $^1J_{C,F}$ = 278.10 Hz), 125.41, 126.31, 127.17, 129.45, 129.91, 130.03, 134.15, 135.12.

HR-MS: *m/z* calcd for $C_{13}H_{10}ClF_3$ 258.0423, found 258.0423.



10g - *(E)*-1-(2-((trifluoromethyl)sulfonyl)vinyl)naphthalene

Reaction conditions: GP A, 5h, 1.2eq CF_3SO_2Cl

White solid

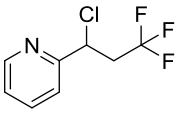
Yield: 5%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 6.96 (d, $^3J_{H,H}$ = 15.29 Hz, 1H), 7.57 (t, $^3J_{H,H}$ = 7.74 Hz, 1H), 7.61 (t, $^3J_{H,H}$ = 7.48 Hz, 1H), 7.68 (t, $^3J_{H,H}$ = 7.16 Hz, 1H), 7.85 (d, $^3J_{H,H}$ = 7.20 Hz, 1H), 7.94 (d, $^3J_{H,H}$ = 7.12 Hz, 1H), 8.06 (d, $^3J_{H,H}$ = 8.20 Hz, 1H), 8.14 (d, $^3J_{H,H}$ = 8.40 Hz, 1H), 8.75, (d, $^3J_{H,H}$ = 15.29 Hz, 1H)

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -78.58.

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 118.81, 121.54, 122.69, 125.49, 127.13, 127.17, 128.31, 129.29, 131.48, 133.78, 133.90, 151.01.

HR-MS: *m/z* calcd for $C_{13}H_9F_3O_2S$ 286.0275, found 286.0276.



8v - 2-(1-chloro-3,3,3-trifluoropropyl)pyridine[13]

Reaction conditions: GP B, 4h, 1.2eq CF_3SO_2Cl

Yellow oil

Yield: 76%

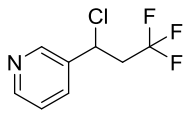
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.00 (ddq, $^2J_{H,H}$ = 15.36 Hz, $^3J_{H,H}$ = 7.29 Hz, $^3J_{H,F}$ = 9.97 Hz, 1H), 3.30 (ddq, $^2J_{H,H}$ = 15.31 Hz, $^3J_{H,H}$ = 6.19 Hz, $^3J_{H,F}$ = 10.18 Hz, 1H), 5.19 (t, $^3J_{H,H}$ = 6.78 Hz, 1H), 7.27 (ddd, $^3J_{H,H}$ = 7.57 Hz, 4.81 Hz, $^4J_{H,H}$ = 1.09 Hz, 1H), 7.44 (d, $^3J_{H,H}$ = 7.84 Hz, 1H), 7.73 (td, $^3J_{H,H}$ = 7.72 Hz, $^4J_{H,H}$ = 1.80 Hz, 1H), 8.26 (ddd, $^3J_{H,H}$ = 4.77 Hz, $^4J_{H,H}$ = 1.59 Hz, $^5J_{H,H}$ = 0.79 Hz, 1H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -64.01 (t, $^3J_{F,H}$ = 10.15 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 41.45 (q, $^2J_{C,F}$ = 28.71 Hz), 54.86 (q, $^3J_{C,F}$ = 3.28 Hz), 122.38, 123.81, 125.30 (q, $^1J_{C,F}$ = 277.57 Hz), 137.40, 149.82, 157.54.

HR-MS: *m/z* calcd for $C_8H_7ClF_3N$ 210.0297, found 210.0307.

EA: Found C 46.09, H 3.65, N 6.05; $C_8H_7ClF_3N \cdot 0.15Hex \cdot 0.1DCM$ requires C 46.09, H 3.82, N 6.18%.



8w - 3-(1-chloro-3,3,3-trifluoropropyl)pyridine

Reaction conditions: GP B, 4h, 1.2eq CF_3SO_2Cl

Yellow oil

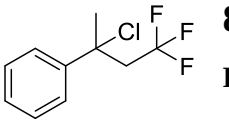
Yield: 79%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.73-3.14 (m, 2H), 5.14 (t, $^3J_{H,H}$ = 7.12 Hz, 1H), 7.35 (dd, $^3J_{H,H}$ = 7.76 Hz, 4.84 Hz, 1H), 7.75 (d, $^3J_{H,H}$ = 7.92 Hz, 1H), 8.50-8.72 (m, 2H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -63.88 (t, $^3J_{F,H}$ = 9.64 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 43.70 (q, $^2J_{C,F}$ = 28.68 Hz), 52.18 (q, $^3J_{C,F}$ = 3.52 Hz), 123.93, 124.59 (q, $^1J_{C,F}$ = 278.07 Hz), 134.53, 135.54, 148.37, 150.56.

EA: Found C 45.64, H 3.09, N 6.81; $C_8H_7ClF_3N$ requires C 45.84, H 3.37, N 6.68%.



8x - (2-chloro-4,4,4-trifluorobutan-2-yl)benzene

Reaction conditions: GP B, 4h, 2eq CF_3SO_2Cl

Colorless oil

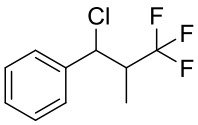
Yield: 67%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.16 (s, 3H), 2.95-3.20 (m, 2H), 7.29-7.35 (m, 1H), 7.35-7.44 (m, 2H), 7.53-7.63 (m, 2H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -60.69 (t, $^3J_{F,H}$ = 10.18 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 30.39, 40.62 (q, $^2J_{C,F}$ = 27.45 Hz), 66.72, 124.65 (q, $^1J_{C,F}$ = 273.84 Hz), 125.99, 128.37, 128.55, 143.31.

EA: Found C 53.07, H 4.25; $C_{10}H_{10}ClF_3 \cdot 0.05DCM$ requires C 53.20, H 4.49%.



8y - (1-chloro-3,3,3-trifluoro-2-methylpropyl)benzene[16]

Reaction conditions: GP B, 4h, 3eq CF_3SO_2Cl

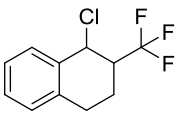
Colorless oil

Yield: 34%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.11 (d, $^3J_{H,H}$ = 7.08 Hz, 3H, dia2), 1.28 (d, $^3J_{H,H}$ = 6.92 Hz, 3H, dia1), 2.63-2.83 (m, 1H, dia1), 2.87-3.04 (m, 1H, dia2), 5.11 (d, $^3J_{H,H}$ = 6.48 Hz, 1H, dia2), 5.27 (d, $^3J_{H,H}$ = 4.04 Hz, 1H, dia1), 7.29-7.47 (m, 5H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -68.83 (d, $^3J_{F,H}$ = 8.21 Hz, dia2), -69.96 (d, $^3J_{F,H}$ = 8.36 Hz, dia1).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 8.96 (q, $^3J_{C,F}$ = 2.31 Hz, dia1), 10.40 (q, $^3J_{C,F}$ = 2.57 Hz, dia2), 46.21 (q, $^2J_{C,F}$ = 25.69 Hz), 59.76 (q, $^3J_{C,F}$ = 2.83 Hz, dia2), 60.50 (q, $^3J_{C,F}$ = 2.83 Hz, dia1), 126.64 (q, $^1J_{C,F}$ = 281.00 Hz), 127.24 (dia1), 128.11 (dia2), 128.62 (dia1), 128.73, 138.09 (dia2), 139.29 (dia1).



8z - 1-chloro-2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalene

Reaction conditions: GP B, 4h, 1.2eq CF_3SO_2Cl

Colorless oil

Yield: 70%

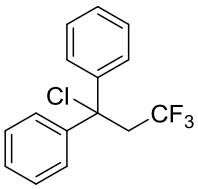
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.98 (ddt, $^{2}J_{H,H}$ = 13.59 Hz, $^{3}J_{H,H}$ = 6.83 Hz, $^{3}J_{H,H}$ = 6.79 Hz, 1H), 2.41 (ddt, $^{1}J_{H,H}$ = 12.77 Hz, $^{3}J_{H,H}$ = 6.55 Hz, $^{3}J_{H,H}$ = 6.27 Hz, 1H), 2.85-2.99 (m, 2H), 3.00-3.15 (m, 1H), 5.37 (d, $^{3}J_{H,H}$ = 4.24 Hz, 1H), 7.08-7.18 (m, 1H), 7.21-7.26 (m, 2H), 7.40-7.47 (m, 1H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -69.66 (d, $^{3}J_{F,H}$ = 9.22 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 20.02 (q, $^{3}J_{C,F}$ = 2.31 Hz), 26.06, 47.44 (q, $^{2}J_{C,F}$ = 26.20 Hz), 54.20 (q, $^{3}J_{C,F}$ = 2.53 Hz), 126.66 (q, $^{1}J_{C,F}$ = 281.14 Hz), 126.95, 128.71, 128.89, 130.41, 134.29, 136.25.

HR-MS: *m/z* = calcd for $C_{11}H_{10}F_3$ 199.0729, found 199.0730.

EA: Found C 56.59, H 4.24; $C_{11}H_{10}ClF_3$ requires C 56.31, H 4.30%.



8aa - (1-chloro-3,3,3-trifluoropropane-1,1-diyl)dibenzene

Reaction conditions: GP B, 4h, 2eq CF_3SO_2Cl

Colorless oil

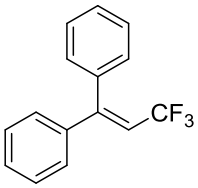
Yield: 21%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.19 (q, $^{3}J_{H,F}$ = 10.34 Hz, 2H), 7.19-7.25 (m, 2H), 7.28-7.35 (m, 4H), 7.36-7.43 (m, 4H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -58.20 (t, $^{3}J_{F,H}$ = 10.26 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 45.08 (q, $^{2}J_{C,F}$ = 25.47 Hz), 75.80 (q, $^{3}J_{C,F}$ = 2.06 Hz), 125.68, 125.85 (q, $^{1}J_{C,F}$ = 278.71 Hz), 127.68, 128.55, 145.25.

HR-MS: *m/z* = calcd for $C_{15}H_{12}F_3$ 249.0886, found 249.0882.



8aa' - (3,3,3-trifluoroprop-1-ene-1,1-diyl)dibenzene[18]

Reaction conditions: GP B, 4h, 2eq CF_3SO_2Cl

Viscous yellow oil

Yield: 56%

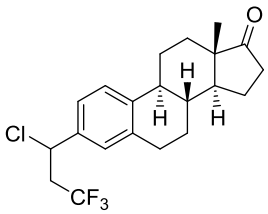
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 6.13 (q, $^{3}J_{H,F}$ = 8.27 Hz, 1H), 7.21-7.28 (m, 4H), 7.29-7.41 (m, 4H).

3.19 (q, $^{3}J_{H,F}$ = 10.34 Hz, 2H), 7.19-7.25 (m, 2H), 7.28-7.35 (m, 4H), 7.36-7.43 (m, 4H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -55.59 (d, $^{3}J_{F,H}$ = 8.21 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 115.58 (q, $^{2}J_{C,F}$ = 33.89 Hz), 123.26 (q, $^{1}J_{C,F}$ = 272.03 Hz), 128.10, 128.17, 128.61, 128.90, 129.25 (q, $^{4}J_{C,F}$ = 1.58 Hz), 129.53, 137.40, 140.27, 152.61 (q, $^{3}J_{C,F}$ = 5.75 Hz).

HR-MS: *m/z* = calcd for $C_{15}H_{11}F_3$ 248.0807, found 248.0801.



8ab - 3-(1-Chloro-3,3,3-trifluoropropyl)estrone[12]

Reaction conditions: GP A, 4h, 1.2eq CF_3SO_2Cl

Colorless oil

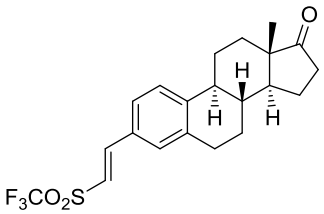
Yield: 43%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.92 (s, 3H), 1.40-1.69 (m, 6H), 1.93-2.21 (m, 4H), 2.26-2.37 (m, 1H), 2.37-2.46 (m, 1H), 2.51 (dd, *J* = 18.67 Hz, 8.70 Hz, 1H), 2.80-3.07 (m, 4H), 5.07 (t, $^3J_{H,H}$ = 6.94 Hz, 1H), 7.12 (s, 1H), 7.17 (d, $^3J_{H,H}$ = 8.00 Hz, 1H), 7.31 (d, $^3J_{H,H}$ = 8.04 Hz, 1H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -64.02 (t, $^3J_{F,H}$ = 9.83 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 13.92, 21.68, 25.73, 26.44, 29.44 (d, 1.50 Hz), 31.67, 35.92, 43.70 (qd, $^2J_{C,F}$ = 29.20 Hz, *J* = 2.61 Hz), 44.47, 48.02, 50.60, 54.78 (q, $^3J_{C,F}$ = 3.14 Hz), 124.14 (d, *J* = 6.07 Hz), 124.94 (q, $^1J_{C,F}$ = 277.92 Hz), 126.12 (d, *J* = 2.51 Hz), 127.41 (d, *J* = 6.55 Hz), 137.33 (d, *J* = 1.54 Hz), 137.38 (d, *J* = 1.54 Hz), 140.95, 220.68.

10h - (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-((*E*)-2-((trifluoromethyl)sulfonyl)vinyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one



Reaction conditions: GP A, 4h, 1.2eq CF_3SO_2Cl

Viscous oil

Yield: 13%

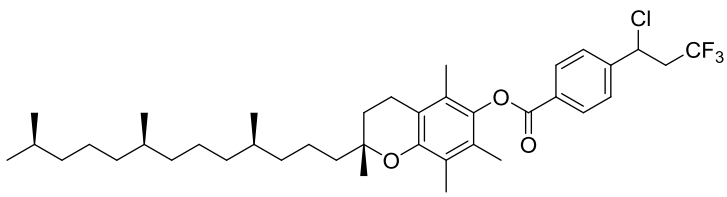
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.92 (s, 3H), 1.40-1.55 (m, 3H), 1.57-1.73 (m, 3H), 1.94-2.02 (m, 1H), 2.05-2.21 (m, 3H), 2.28-2.40 (m, 1H), 2.40-2.47 (m, 1H), 2.52 (dd, *J* = 18.66 Hz, 8.62 Hz, 1H), 6.77 (d, $^3J_{H,H}$ = 15.45 Hz, 1H), 7.33 (s, 1H), 7.35-7.45 (m, 2H), 7.82 (d, $^3J_{H,H}$ = 15.45 Hz, 1H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -78.88.

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 13.89, 21.67, 25.64, 26.21, 29.26, 31.60, 35.88, 37.86, 44.86, 47.95, 50.58, 115.46, 119.88 (q, $^1J_{C,F}$ = 324.96 Hz), 126.65, 127.03, 128.89, 130.39, 138.11, 146.19, 153.97, 220.43.

HR-MS: *m/z* calcd for $C_{21}H_{24}F_3SO_3^+$ 413.1393, found 413.1395.

EA: Found C 59.11, H 5.45; $C_{21}H_{23}F_3O_3S \cdot 0.15CDCl_3$ requires C 59.01, H 5.38%.



8ac - (*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl 4-(1-chloro-3,3,3-trifluoropropyl)benzoate

Reaction conditions: GP B, 4h, 2eq CF_3SO_2Cl

Yellow viscous oil

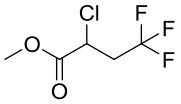
Yield: 84%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.84-0.90 (m, 12H), 1.03-1.18 (m, 6H), 1.20-1.33 (m, 11H), 1.35-1.48 (m, 4H), 1.50-1.62 (m, 3H), 1.74-1.90 (m, 2H), 2.02 (s, 3H), 2.06, (s, 3H), 2.13 (s, 3H), 2.63 (t, *J* = 6.54 Hz, 2H), 2.80-3.15 (m, 2H), 5.10 (t, $^{3}J_{H,H}$ = 7.02 Hz, 1H), 7.57 (d, $^{3}J_{H,H}$ = 8.08 Hz, 2H), 8.28 (d, $^{3}J_{H,H}$ = 8.08 Hz, 2H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -63.90 (t, $^{3}J_{F,H}$ = 9.81 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 12.00, 12.35, 13.20, 19.82, 19.90, 20.79, 21.18, 22,79, 22.87, 23.84, 24.34, 24.61, 24.96, 28.13, 31.04-31.55 (m), 32.85, 32.96, 37.44, 37.61, 39.53, 39.79, 40.57, 43.77 (q, 28.55 Hz), 54.14 (q, 3.34 Hz), 75.29, 117.69, 123.36, 124.73 (q, 277.92 Hz), 125.19, 126.95, 127.29, 130.48, 130.99, 140.67, 144.9, 149.73, 164.52.

HR-MS: *m/z* calcd for $C_{39}H_{56}ClF_3O_3Na$ 687.3762, found 687.3747.



8ad - Methyl 2-chloro-4,4,4-trifluorobutanoate

Reaction conditions: GP B, 5h, 1.2eq CF_3SO_2Cl

Colorless oil

Yield: 59%

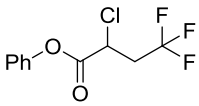
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.62-2.84 (m, 1H), 2.94-3.16 (m, 1H), 3.85 (s, 3H), 4.49 (t, $^{3}J_{H,H}$ = 6.76 Hz, 1H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -64.60 (t, $^{3}J_{F,H}$ = 9.94 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 39.25 (q, $^{2}J_{C,F}$ = 29.80 Hz), 48.84 (q, $^{3}J_{C,F}$ = 3.08 Hz), 53.72, 124.70 (q, $^{1}J_{C,F}$ = 279.49 Hz), 168.35.

HR-MS: *m/z* calcd for $C_5H_7ClF_3O_2$ 191.0087, found 191.0087.

EA: Found C 31.84, H 3.24; $C_5H_6ClF_3O_2$ requires C 31.52, H 3.17%.



8ae - Phenyl 2-chloro-4,4,4-trifluorobutanoate[19]

Reaction conditions: GP B, 4h, 2eq CF_3SO_2Cl

Colorless oil

Yield: 84%

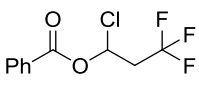
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.76-2.94 (m, 1H), 3.09-3.26 (m, 1H), 4.70 (t, $^{3}J_{H,H}$ = 6.82 Hz, 1H), 7.13 (d, $^{3}J_{H,H}$ = 7.96 Hz, 1H), 7.29 (t, $^{3}J_{H,H}$ = 7.40 Hz, 2H), 7.42 (t, $^{3}J_{H,H}$ = 7.82 Hz, 2H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -64.36 (t, $^{3}J_{F,H}$ = 9.73 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 39.24 (q, $^{2}J_{C,F}$ = 29.86 Hz), 49.01 (q, $^{3}J_{C,F}$ = 3.34 Hz), 121.04, 124.79 (q, $^{1}J_{C,F}$ = 281.03 Hz), 126.82, 129.82, 150.29, 164.44.

HR-MS: *m/z* calcd for $C_{10}H_9ClF_3O_2$ 253.0238, found 253.0242.

EA: Found C 47.64, H 3.21; $C_{10}H_8ClF_3O_2$ requires C 47.55, H 3.19%.



8af - 1-chloro-3,3,3-trifluoropropyl benzoate

Reaction conditions: GP B, 5h, 2eq CF_3SO_2Cl

Colorless oil

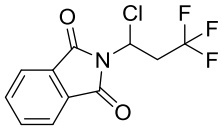
Yield: 77%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.91-3.08 (m, 1H), 3.09-3.27 (m, 1H), 6.94 (dd, $^{3}J_{H,H}$ = 8.36, 3.68 Hz, 1H), 7.50 (t, $^{3}J_{H,H}$ = 7.72 Hz, 2H), 7.65 (t, $^{3}J_{H,H}$ = 7.42 Hz, 1H), 8.08 (d, $^{3}J_{H,H}$ = 7.56 Hz, 2H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -63.83 (t, $^{3}J_{F,H}$ = 9.77 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 47.77 (q, $^{2}J_{C,F}$ = 29.44 Hz), 77.17 (q, $^{3}J_{C,F}$ = 4.37 Hz), 124.00 (q, $^{1}J_{C,F}$ = 277.59 Hz), 128.25, 128.84, 130.28, 134.37, 163.70.

HR-MS: *m/z* calcd for $C_{10}H_9ClF_3O_2$ 253.0238, found 253.0239.



8ag - 2-(1-chloro-3,3,3-trifluoropropyl)isoindoline-1,3-dione

Reaction conditions: GP B, 4h, 2eq CF_3SO_2Cl

Yellow solid

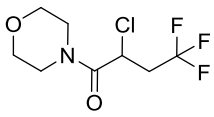
Yield: 98%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.02-3.26 (m, 1H), 3.73-3.94 (m, 1H), 6.39 (dd, $^{3}J_{H,H}$ = 9.46, 5.14 Hz, 1H), 7.71-7.86 (m, 2H), 7.88-7.97 (m, 2H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -65.16 (t, $^{3}J_{F,H}$ = 9.85 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 39.74 (q, $^{2}J_{C,H}$ = 29.29 Hz), 56.19 (q, $^{3}J_{C,H}$ = 4.11 Hz), 124.21 (1, $^{1}J_{C,H}$ = 277.95 Hz), 124.32, 131.50, 135.13, 165.87.

HR-MS: *m/z* calcd for $C_{11}H_8ClF_3NO_2$ 278.0190, found 278.0198.



8ah - 2-chloro-4,4,4-trifluoro-1-morpholinobutan-1-one

Reaction conditions: GP B, 4h, 2eq CF_3SO_2Cl

White solid

Yield: 79%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.72-2.88 (m, 1H), 3.17 (ddq, $^{2}J_{H,H}$ = 15.56 Hz, $^{3}J_{H,H}$ = 5.31 Hz, $^{3}J_{H,F}$ = 10.39 Hz, 1H), 3.47-3.58 (m, 2H), 3.61-3.85 (m, 6H), 4.61 (t, $^{3}J_{H,H}$ = 6.46 Hz, 1H).

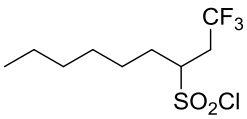
^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -64.10 (t, $^{3}J_{F,H}$ = 10.20 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 38.34 (q, $^{2}J_{C,F}$ = 29.18 Hz), 43.11, 45.66 (q, $^{3}J_{C,F}$ = 3.17 Hz), 46.67, 66.52, 66.72, 125.35 (q, $^{1}J_{C,F}$ = 277.36 Hz), 165.28.

HR-MS: *m/z* calcd for $C_8H_{12}ClF_3NO_2$ 246.0503, found 246.0508.

EA: Found C 40.04, H 4.68, N 5.49; $C_8H_{11}ClF_3NO_2 \cdot 0.15EtOAc$ requires C 39.91, H 4.75, N 5.41%.

CCDC 1850074 contain(s) the supplementary crystallographic data for **8ah**. These data can be obtained free of charge from *The Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.



8ap - 1,1,1-trifluorononane-3-sulfonyl chloride[20]

Reaction conditions: GP B, 4h, 2eq CF_3SO_2Cl

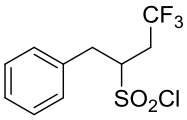
Colorless oil

Yield: 62% (0.5mol% **5**), 74% (1.0mol% **5**).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 0.83-0.9 (m, 3H), 1.23-1.38 (m, 6H), 1.93-2.06 (m, 1H), 2.13-2.25 (m, 1H), 2.49-2.69 (m, 1H), 3.00-3.17 (m, 1H), 3.66-3.84 (m, 1H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -63.73 (t, $^{3}J_{F,H}$ = 10.05 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 14.09, 22.58, 26.06, 28.92, 30.57, 31.38, 34.81 (q, $^{2}J_{C,F}$ = 30.79 Hz), 70.14 (q, $^{3}J_{C,F}$ = 1.73 Hz), 125.08 (q, $^{1}J_{C,F}$ = 276.89 Hz).



8aq - 4,4,4-trifluoro-1-phenylbutane-2-sulfonyl chloride[20]

Reaction conditions: GP B, 4h, 2eq CF_3SO_2Cl

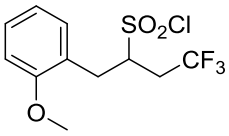
Colorless oil

Yield: 50% (0.5mol% **5**), 61% (1.0mol% **5**).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.57-2.74 (m, 1H), 22.95-3.13 (m, 1H), 3.26 (dd, $^{2}J_{H,H}$ = 14.78 Hz, $^{3}J_{H,H}$ = 6.66 Hz, 1H), 3.57 (dd, $^{2}J_{H,H}$ = 14.81 Hz, $^{3}J_{H,H}$ = 5.24 Hz), 4.01-4.11 (m, 1H), 7.27-7.43 (m, 5H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -63.46 (t, $^{3}J_{F,H}$ = 10.02 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 34.11 (q, $^{2}J_{C,F}$ = 31.15 Hz), 36.31, 71.07 (q, $^{3}J_{C,F}$ = 2.62 Hz), 124.86 (q, $^{1}J_{C,F}$ = 277.13 Hz), 128.17, 129.23, 129.60, 133.99.



8ar - 4,4,4-trifluoro-1-(2-methoxyphenyl)butane-2-sulfonyl chloride[20]

Reaction conditions: GP B, 4h, 2eq CF_3SO_2Cl

Colorless oil

Yield: 40%

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 2.49-2.66 (m, 1H), 2.95-3.11 (m, 1H), 3.17 (dd, $^{2}J_{H,H}$ = 14.07 Hz, $^{3}J_{H,H}$ = 7.86 Hz, 1H), 3.57 (dd, $^{2}J_{H,H}$ = 14.11 Hz, $^{3}J_{H,H}$ = 5.94 Hz, 1H), 3.87 (s, 3H), 4.30-4.41 (m, 1H), 6.86-6.99 (m, 2H), 7.18 (dd, $^{3}J_{H,H}$ = 7.40 Hz, $^{4}J_{H,H}$ = 1.32 Hz, 1H), 7.18 (dd, $^{3}J_{H,H}$ = 7.40 Hz, $^{4}J_{H,H}$ = 1.32 Hz, 1H), 7.31 (dt, $^{3}J_{H,H}$ = 7.87 Hz, $^{4}J_{H,H}$ = 1.58 Hz, 1H).

^{19}F NMR (376.3 MHz, $CDCl_3$, ppm): δ = -64.22 (t, $^{3}J_{F,H}$ = 10.20 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, ppm): δ = 33.10, 34.36 (q, $^{2}J_{C,F}$ = 31.19 Hz), 55.43, 68.64 (q, $^{3}J_{C,F}$ = 2.59 Hz), 110.68, 121.01, 122.38, 124.90 (q, $^{1}J_{C,F}$ = 278.38 Hz), 129.75, 131.73, 157.70.

LED Light Source

LED: OSRAM SSL LD CQ7P-2U3U-W5-1

Heatsink: Fischer Elektronik SK 189 50 SA

Power supply: Archimede elettronica QLT PLP 303 (max 700mA / 12VDC)

The LED was mounted on a stack of copper and Kapton sheets, which made a structure as shown below. This was achieved by taking a copper sheet and applying first a layer of 50um Kapton tape, cutting a slot for the thermal pad, and then adding small squares of 50um copper tape on top. This was cut to make the right shapes for the LED pads, leaving the middle open for the thermal pad. Thermal calculations indicate that with this configuration, the LED die should reach no more than 20-30°C above the heatsink temperature with the LED running at 700mA.

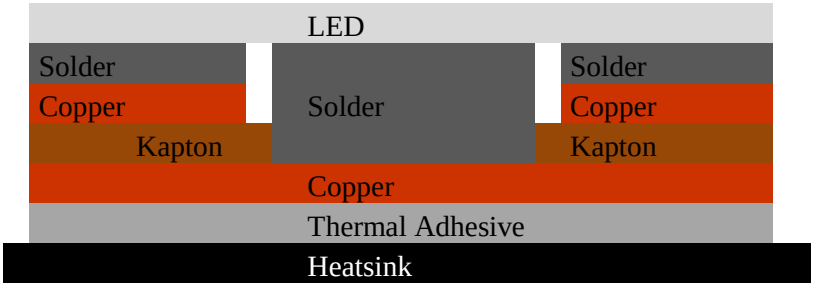


Figure S13. Schematic structure of the LED mounted to a heatsink.

Below, the assembly can be seen before the LEDs were mounted on the left and with the LEDs mounted on the right. The soldering was done in a soldering oven with solder paste. Being small, the LEDs had a tendency to float up on the solder paste during reflow, which was not ideal from a thermal point of view. Because of this, all LEDs were re-touched afterwards with a soldering iron, pushing down on the LED with tweezers to ensure that it sat as close as possible to the copper base.

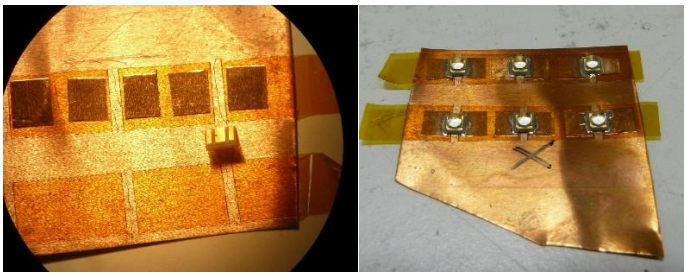


Figure S14. Assembly of the LEDs on a copper sheet before mounting to the heatsink.

After assembly the individual LEDs were cut out with scissors and glued to the heatsink with arctic silver thermal adhesive. The cord of the power supply was also glued to the heatsink with instant adhesive (cyanoacrylate) to provide some strain relief, as the copper pads of the copper and kapton stack are fragile and can be quite easily pulled off. Small wires were used to connect to these pads to reduce stress.

Figure S15. Finished lighting source without (top) and with (bottom) aluminium housing.

When all was assembled, the LED die temperature was verified using a pulsed method whereby the LED temperature is allowed to equilibrate and then the LED current is quickly pulsed from high to low (in this case from 700mA to 10mA) and the forward voltage is measured, before the LED die starts to cool. This value can then be compared to a calibration curve of the 10mA forward voltage vs temperature to indicate the LED temperature. These LEDs have a thermal time constant of around 5ms so if the forward voltage is measured within 100us of switching a reasonably accurate value for the die temperature at 700mA can be obtained.

These tests showed that the LED die was only 9°C warmer than the heatsink at 700mA. However, the LED lens became very hot (105°C when open, 135°C with the aluminum housing mounted). Introducing a small flow of air to the inside of the aluminum block brought the lens temperature down dramatically (from 135°C to 80°C) so a small fan was added to the side to provide some air cooling to the LED lens to prevent overheating. The first series of LEDs did not have this secondary cooling and the lenses all became yellowed with time, presumably due to overheating.

In case it is necessary to repair or replace the LED or power supply, an exacto knife or razor can be used to separate the copper base of the LED assembly from the heat sink. The same can be done with the power cord.

Figure S16. Picture of the final reaction setup. The light appears purple but is blue in reality. The discrepancy was due to the camera.

Potential Design Improvements

The copper/kapton stack approach was used for this application because the LED that we wanted to be used could not be bought already mounted to an aluminum starboard and we wanted to avoid having a custom aluminum LED substrate produced. However, after producing 10 devices as described, we realized that bare aluminium starboards with the right LED footprint were available on the market (i.e. Bergquist 804087). For increased robustness and ease of production, future devices will be mounted with these starboards instead of the above described copper/kapton stack.

Aluminium Housing

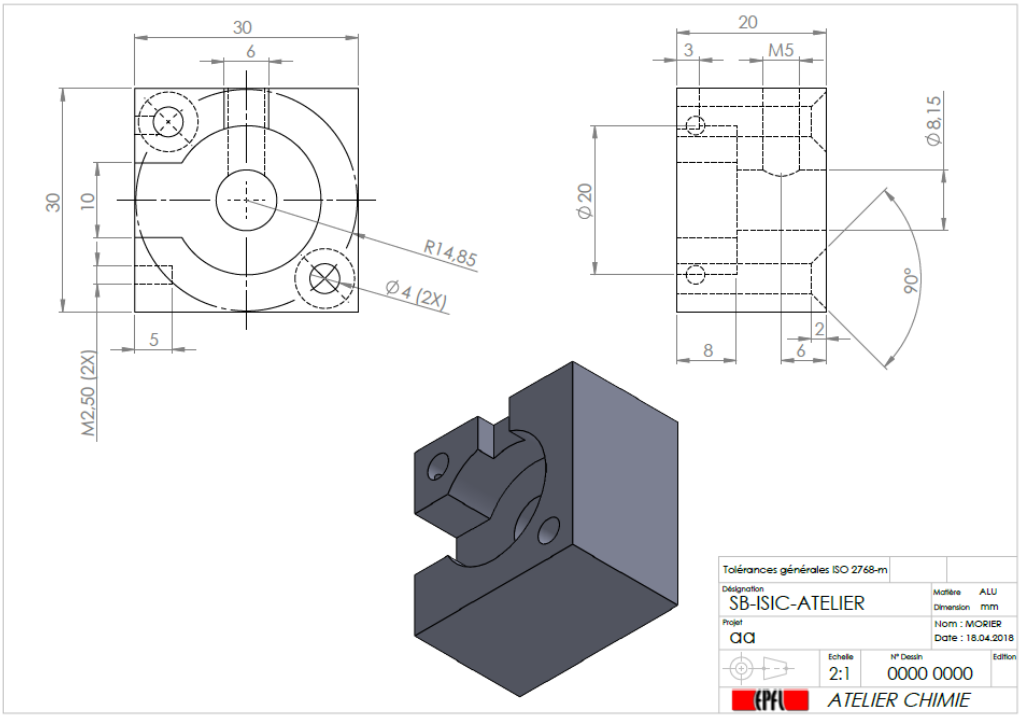


Figure S17. Scheme of the aluminium housing with dimensions.

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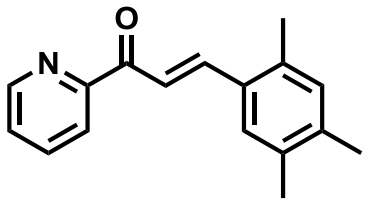
NMR Spectra of New Compounds



4-1 -

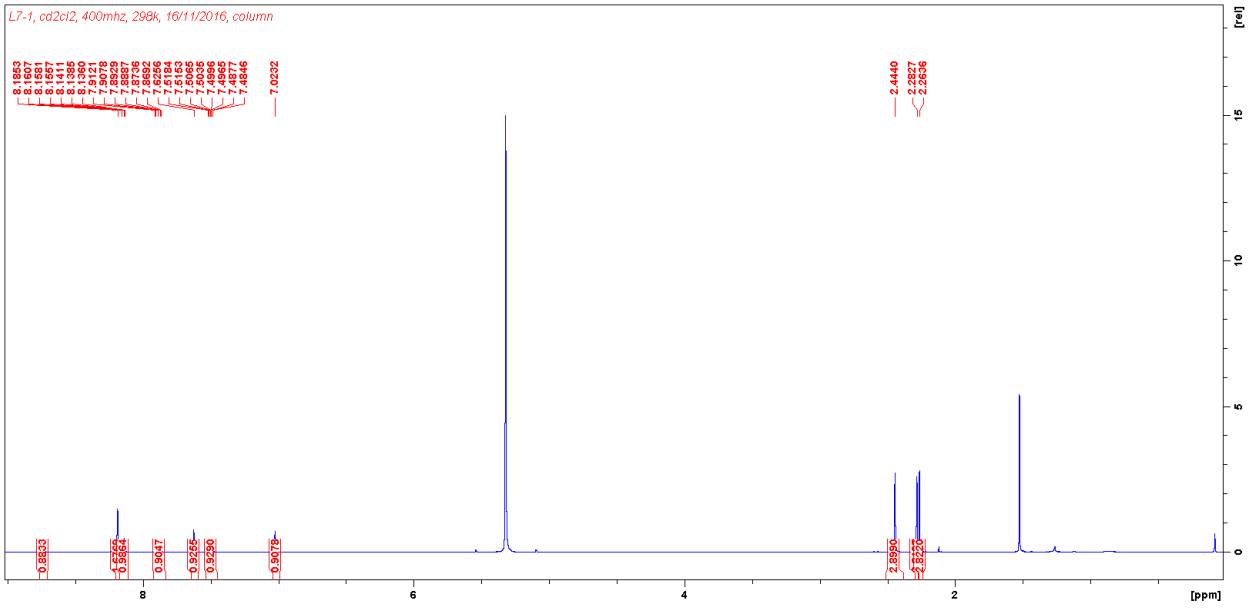


Figure S18. ^{1}H NMR spectrum of **4-1** in deuterated DCM.

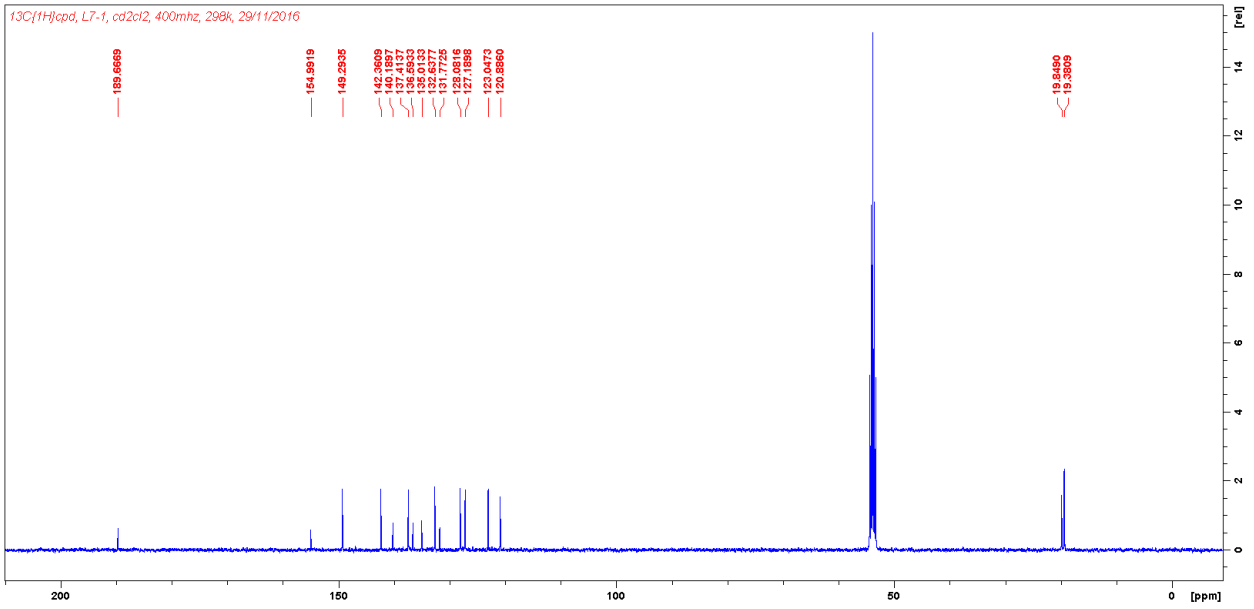


Figure S19. ^{13}C{^{1}H} NMR spectrum of **4-1** in deuterated DCM.

4 -

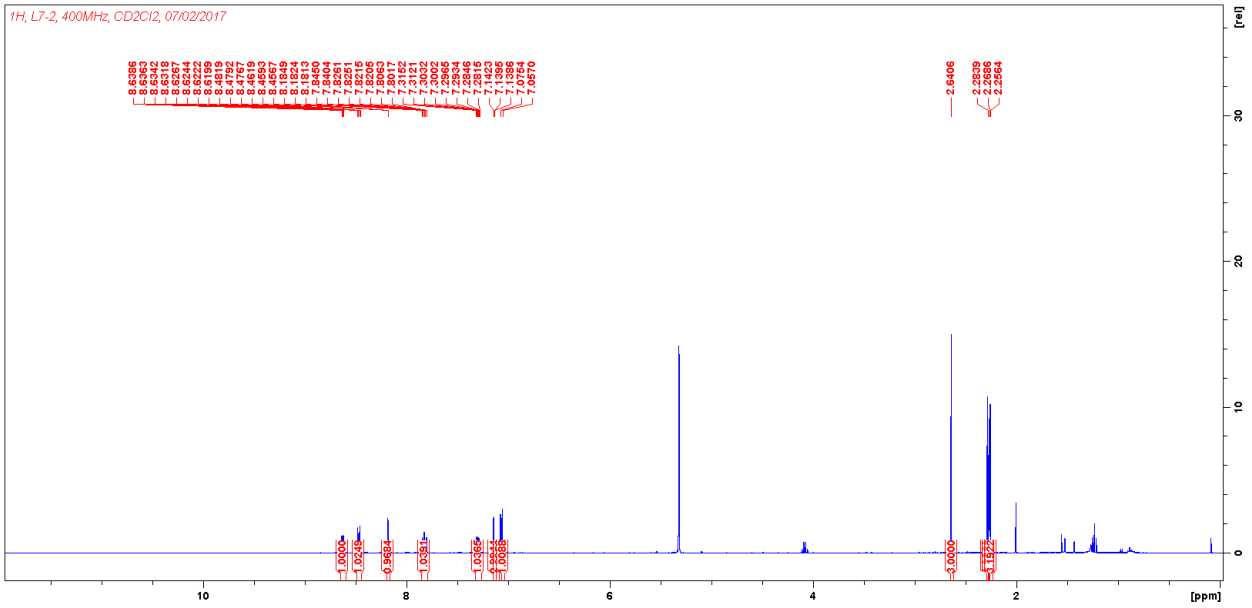


Figure S20. ^{1}H NMR spectrum of **4** in deuterated DCM.

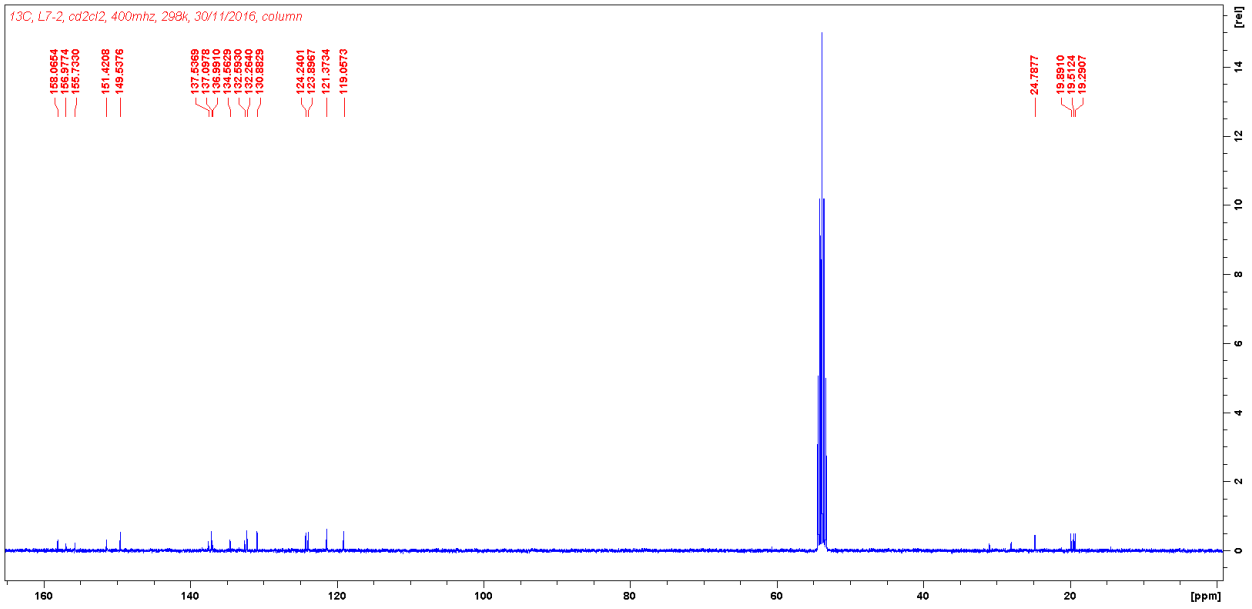
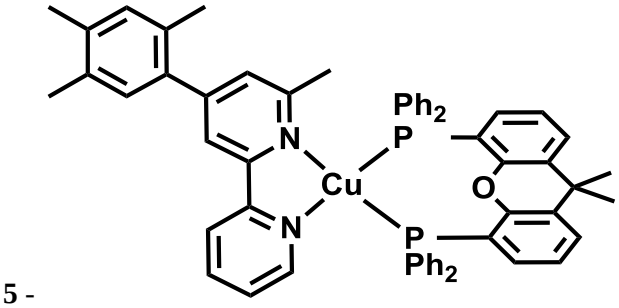


Figure S21. ^{13}C{^{1}H} NMR spectrum of **4** in deuterated DCM.

5 -



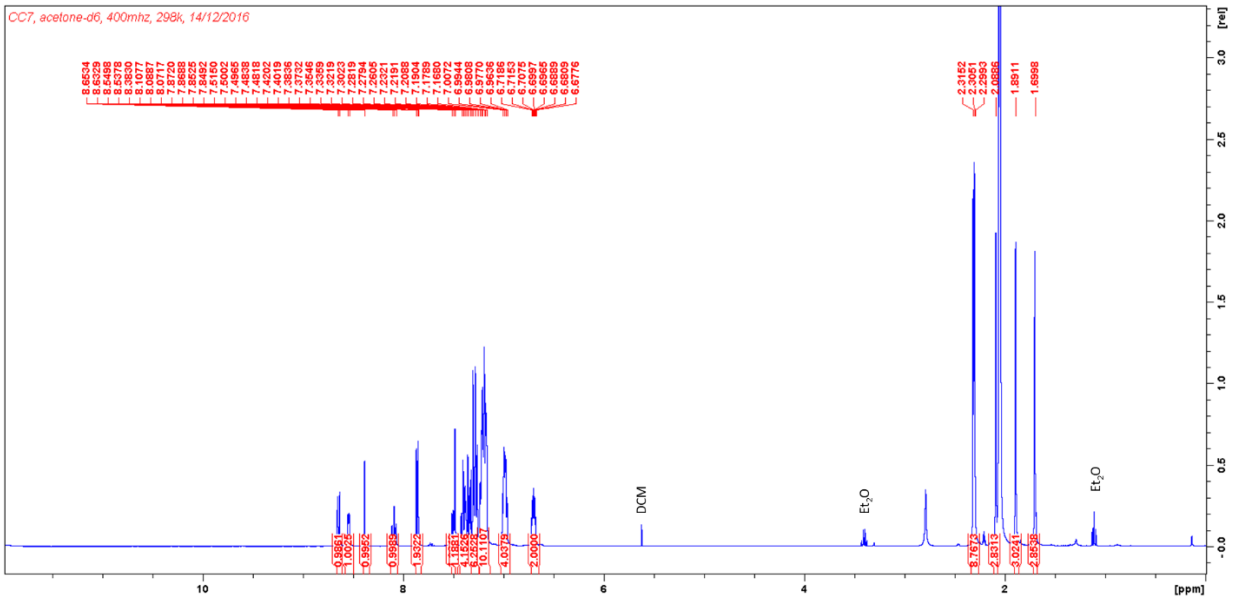


Figure S22. ^{1}H NMR spectrum of **5** in deuterated acetone. Residual solvent peaks from the purification process are denoted.

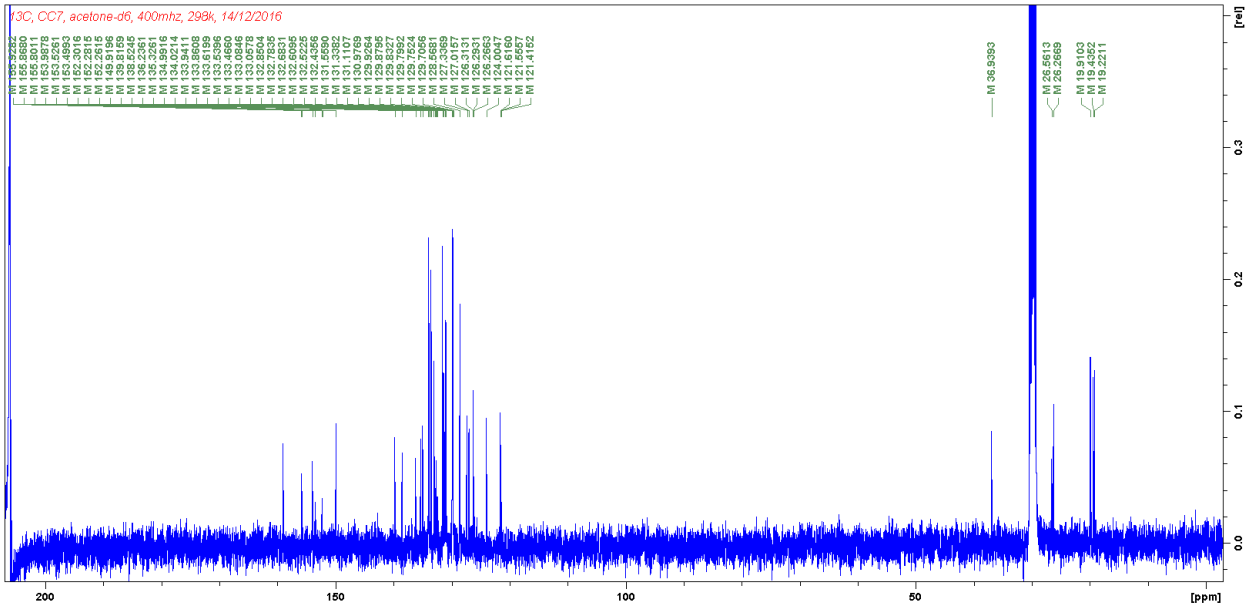


Figure S23. ^{13}C{^{1}H} NMR spectrum of **5** in deuterated acetone.

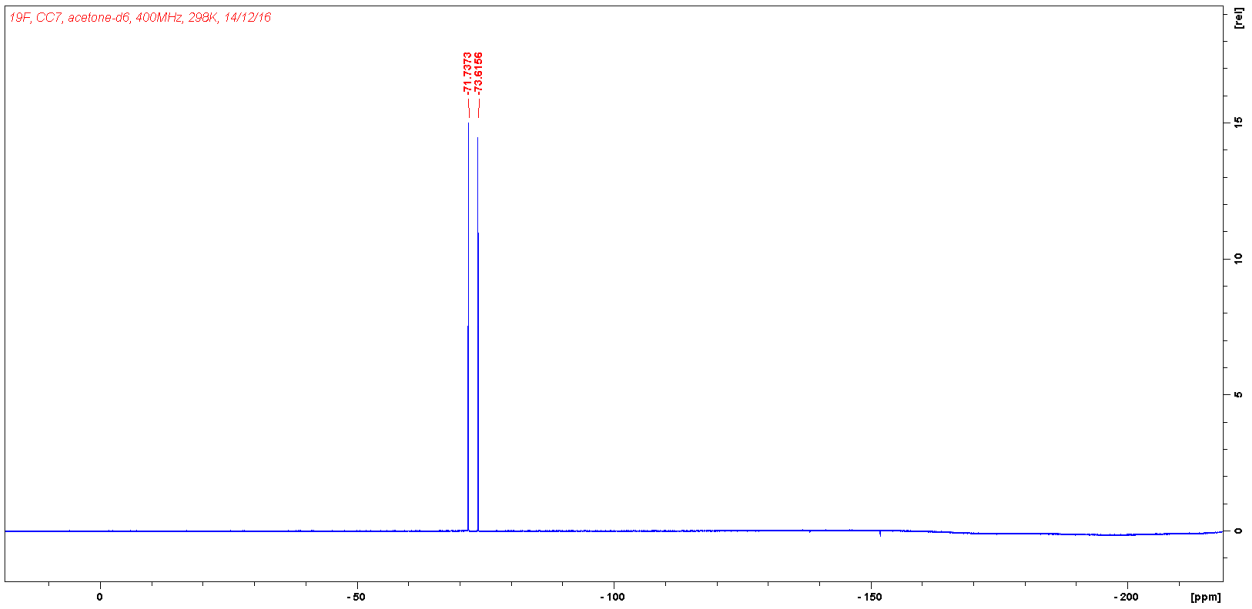


Figure S24. ^{19}F NMR spectrum of **5** in deuterated acetone.

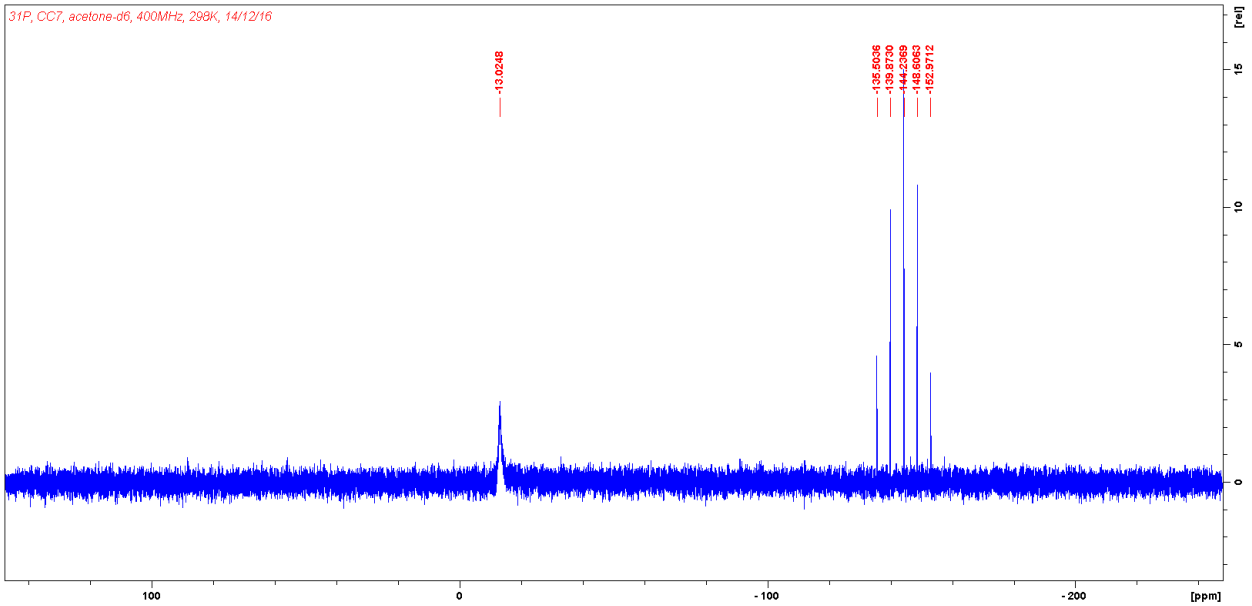
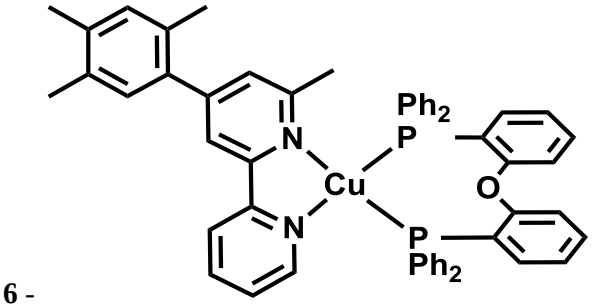


Figure S25. ^{31}P NMR spectrum of **5** in deuterated acetone.

6 -



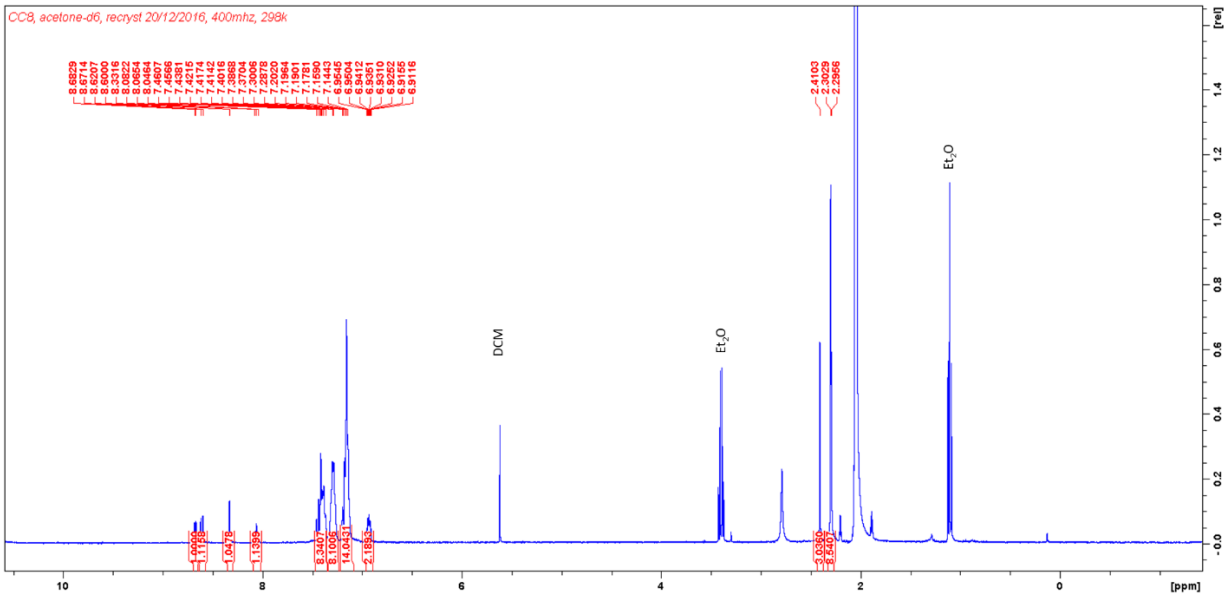


Figure S26. ^{1}H NMR spectrum of **6** in deuterated acetone. Residual solvent peaks from the purification process are denoted.

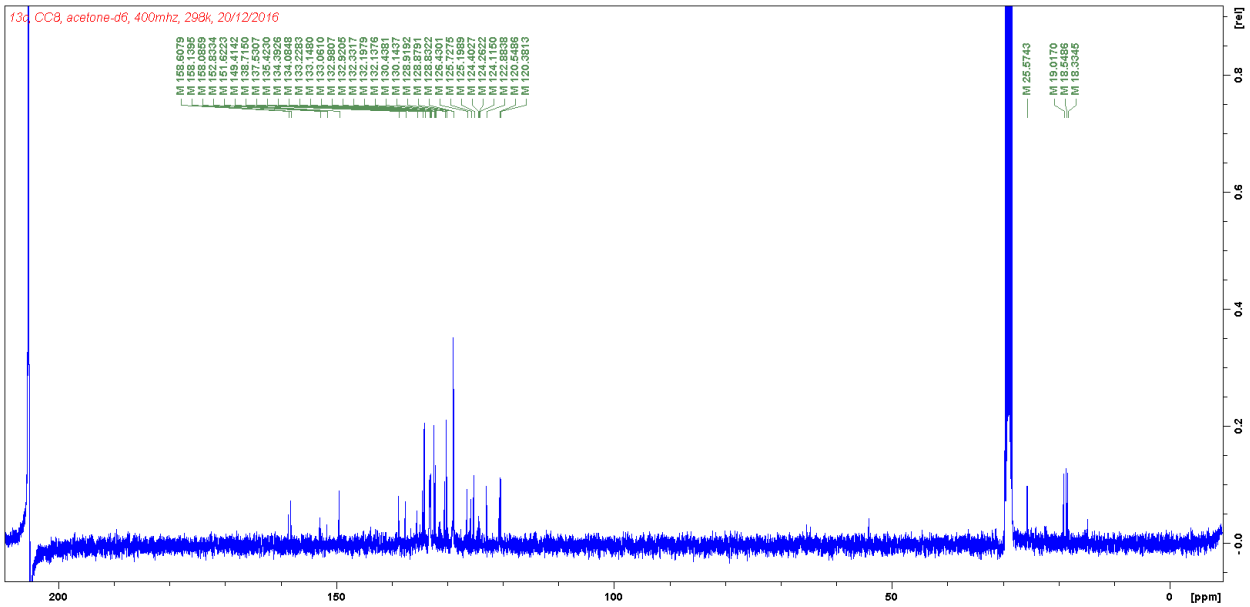


Figure S27. ^{13}C{^{1}H} NMR spectrum of **6** in deuterated acetone.

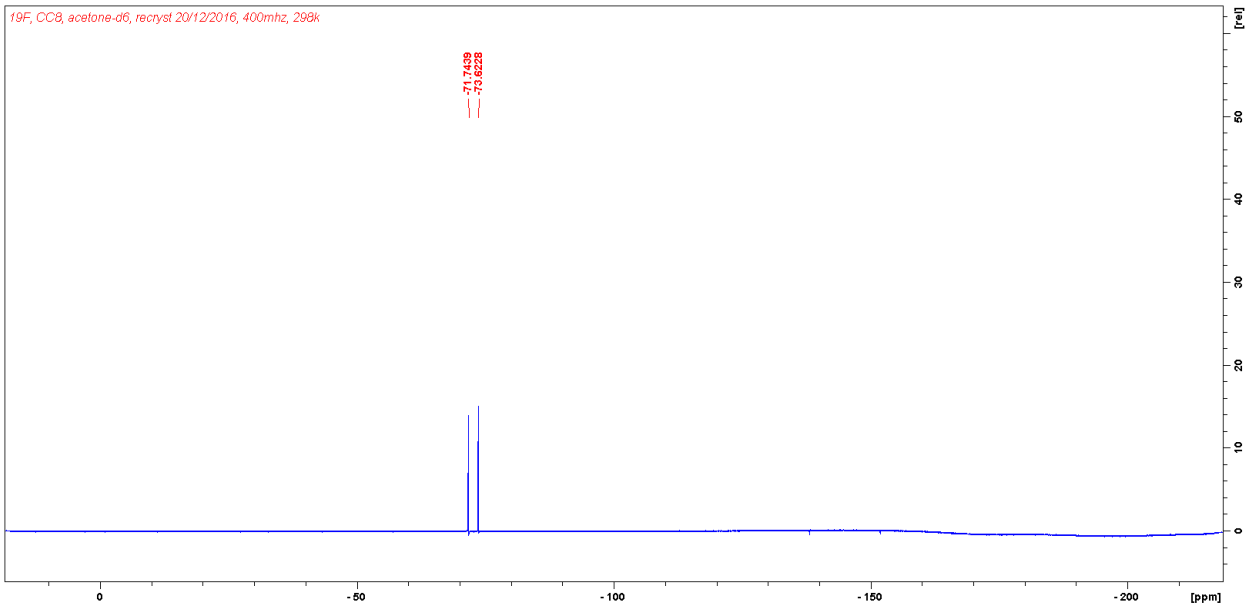


Figure S28. ^{19}F NMR spectrum of **6** in deuterated acetone.

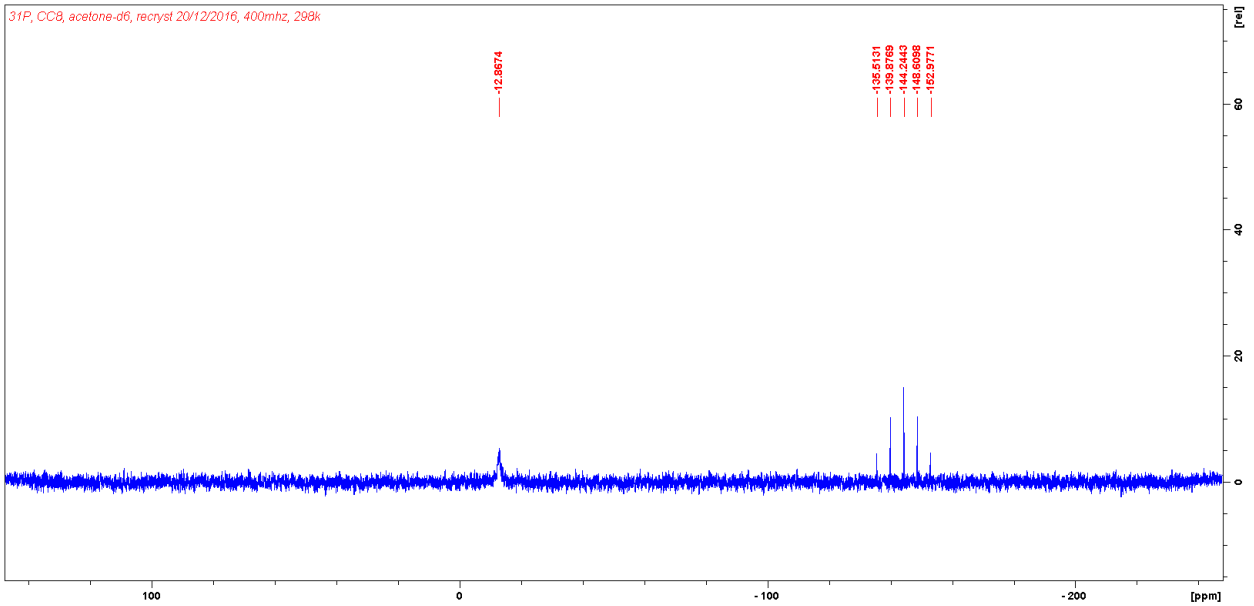


Figure S29. ^{31}P NMR spectrum of **6** in deuterated acetone.

8b -

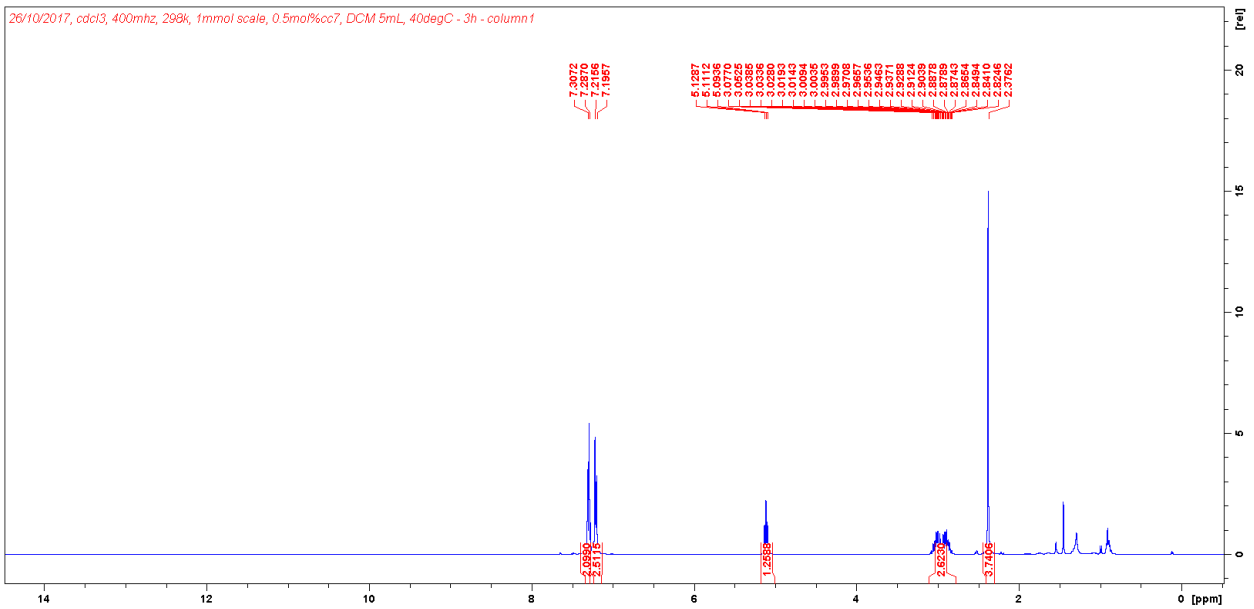


Figure S30. ^{1}H NMR spectrum of **8b** in deuterated chloroform.

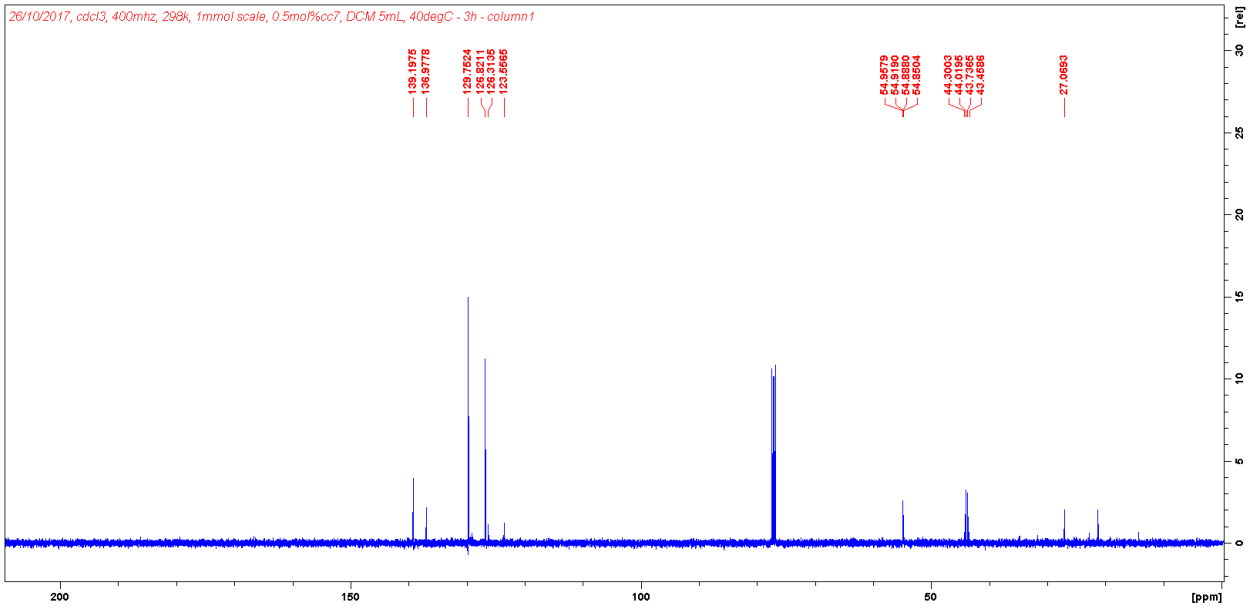


Figure S31. ^{13}C{^{1}H} NMR spectrum of **8b** in deuterated chloroform.

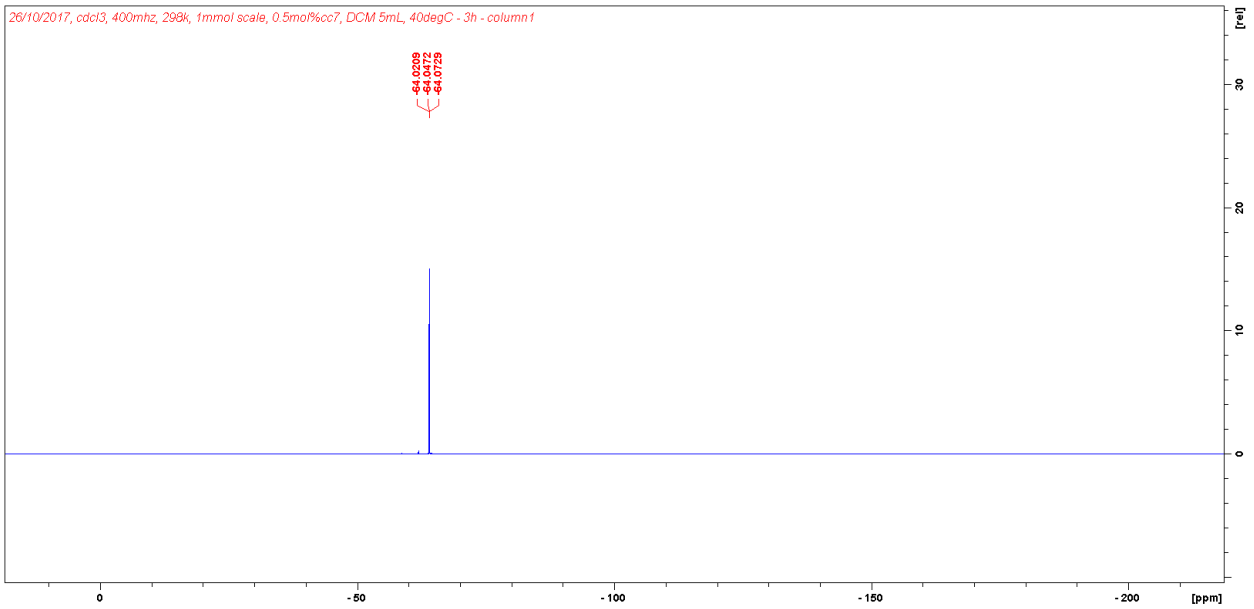
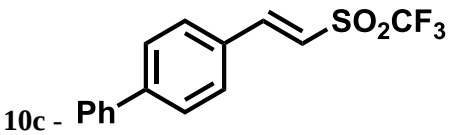


Figure S32. ^{19}F NMR spectrum of **8b** in deuterated chloroform.



10c -

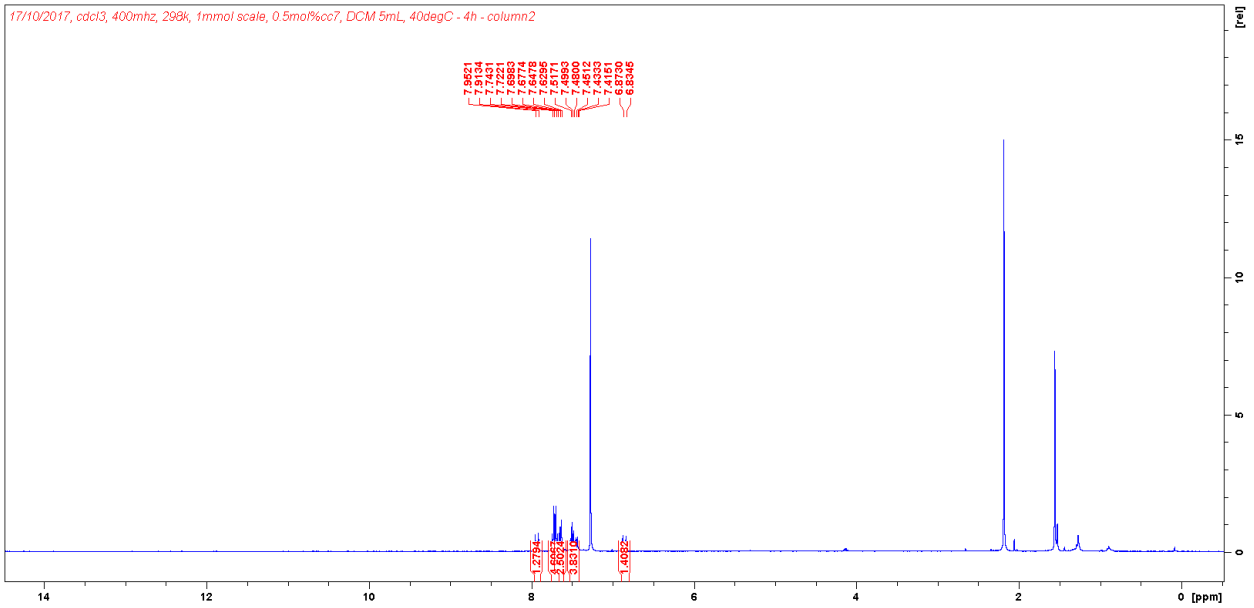


Figure S33. ^{1}H NMR spectrum of **10c** in deuterated chloroform.

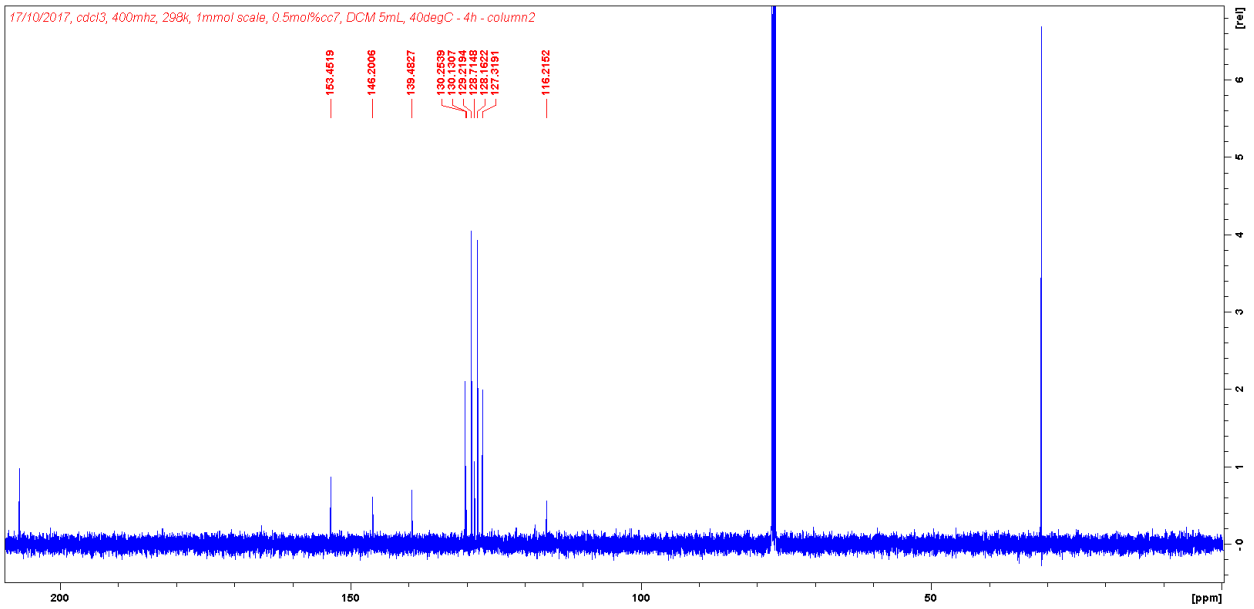


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of **10c** in deuterated chloroform.

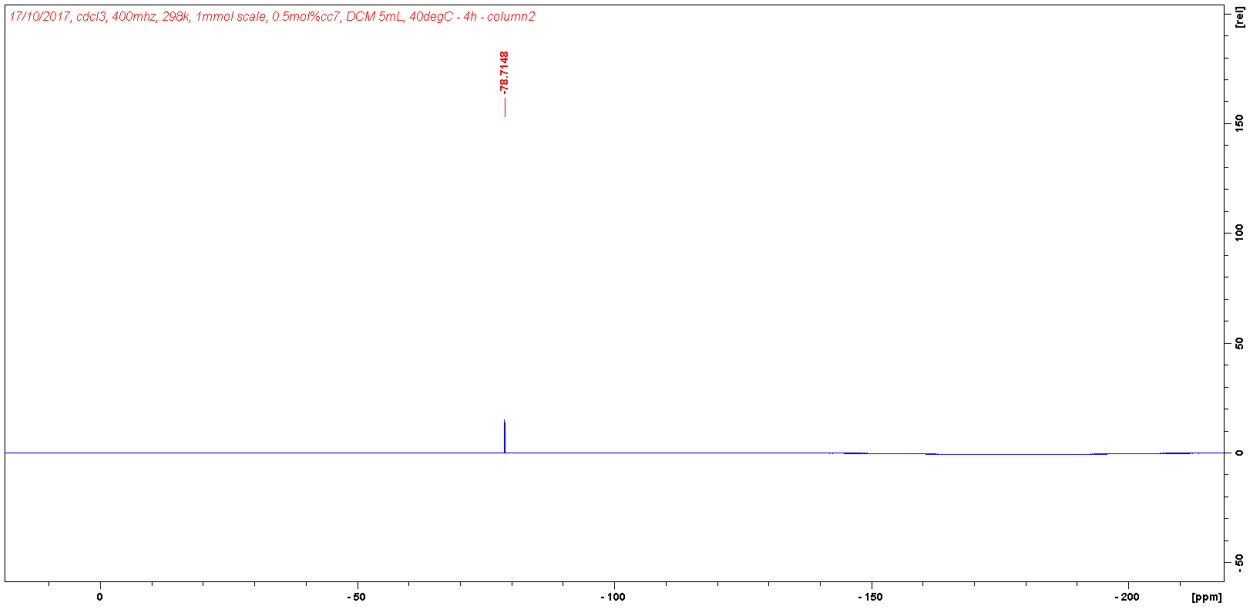
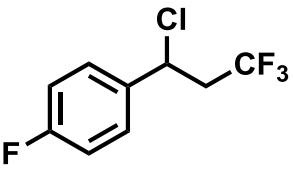


Figure S35. ^{19}F NMR spectrum of **10c** in deuterated chloroform.

8h -



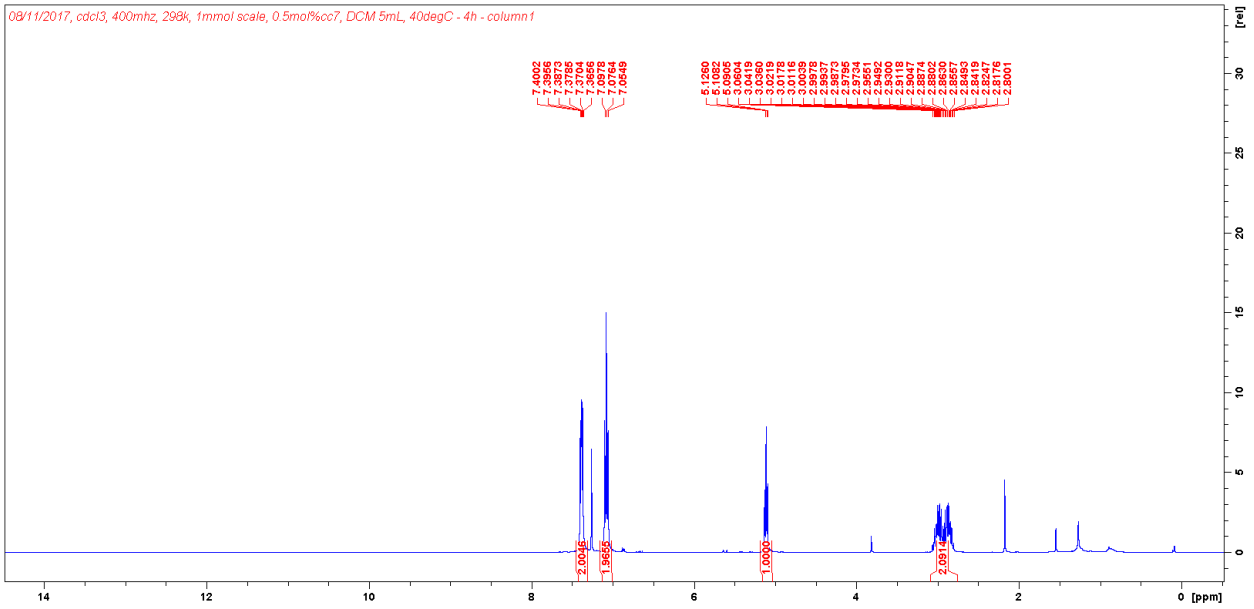


Figure S36. ^{1}H NMR spectrum of **8h** in deuterated chloroform.

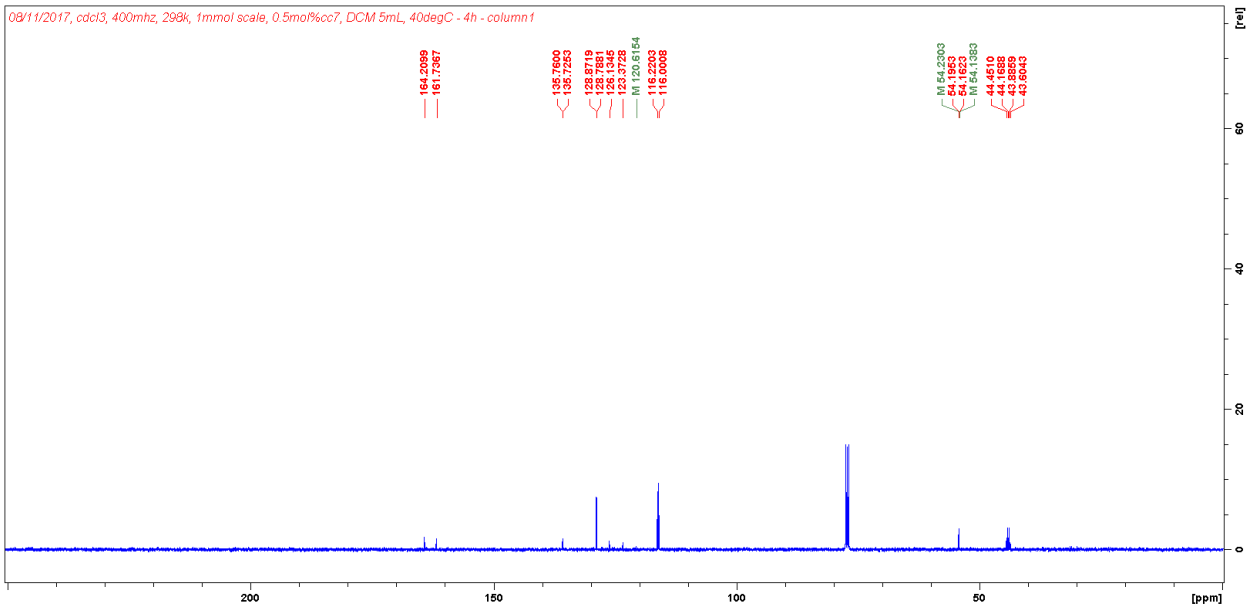


Figure S37. ^{13}C{^{1}H} NMR spectrum of **8h** in deuterated chloroform.

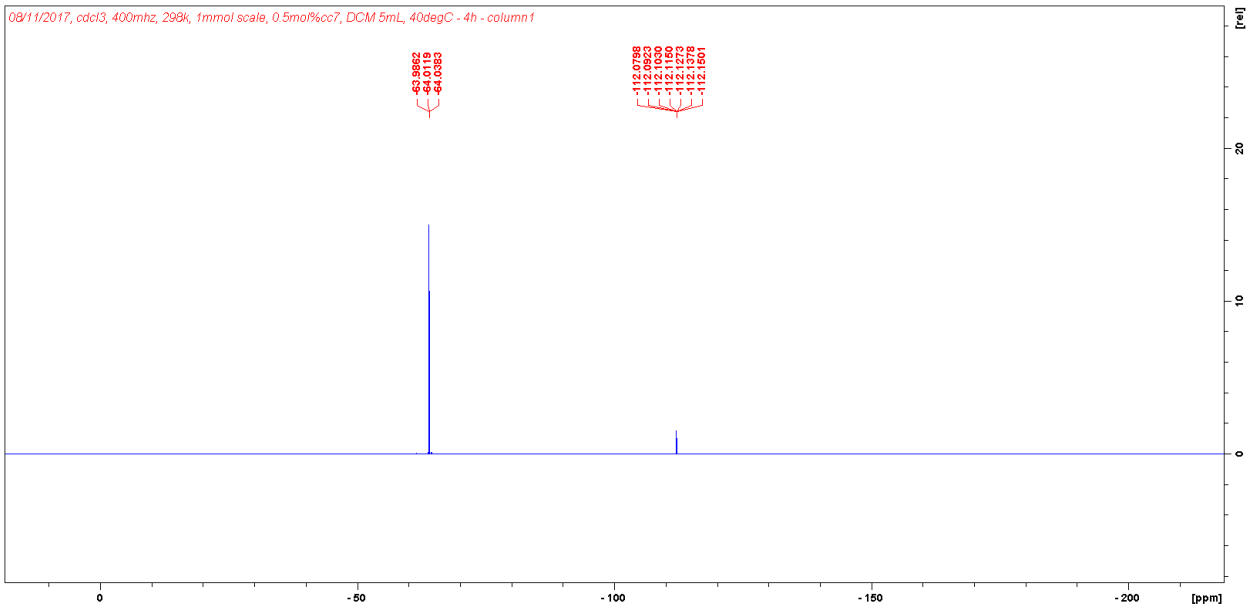


Figure S38. ^{19}F NMR spectrum of **8h** in deuterated chloroform.

10d -

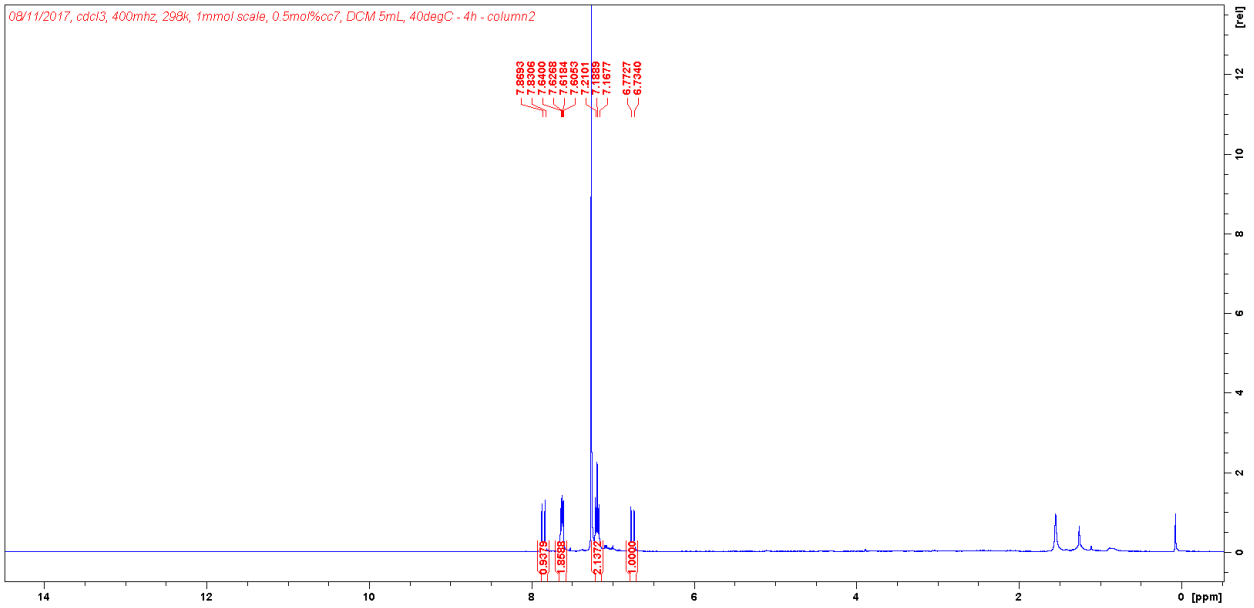


Figure S39. ^{1}H NMR spectrum of **10d** in deuterated chloroform.

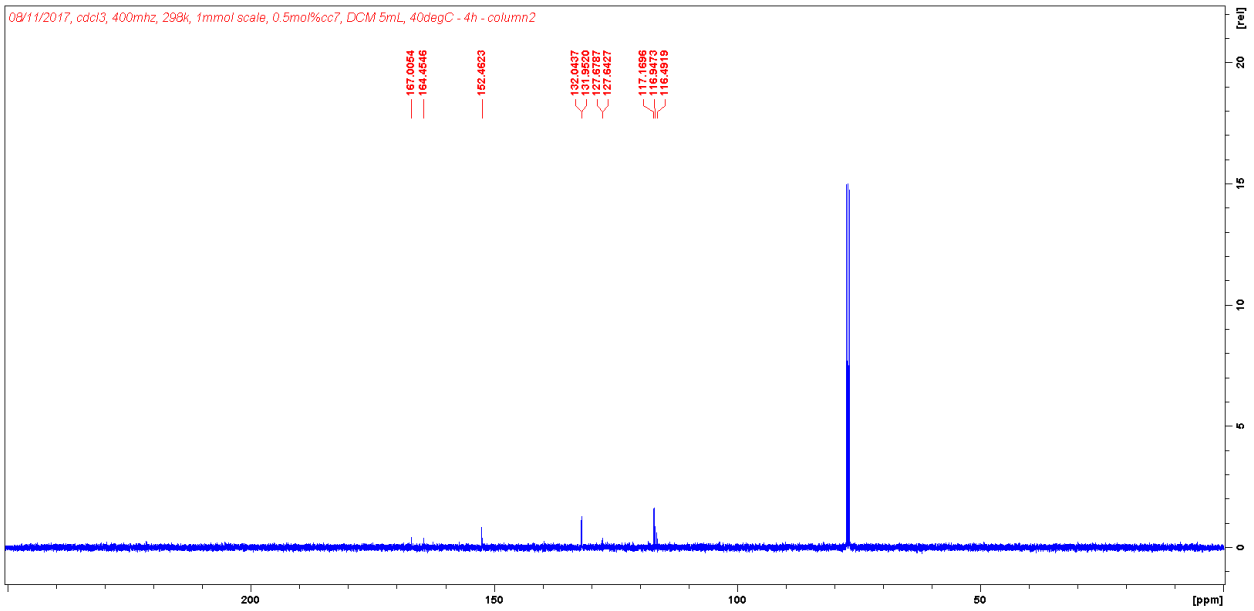


Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum of **10d** in deuterated chloroform.

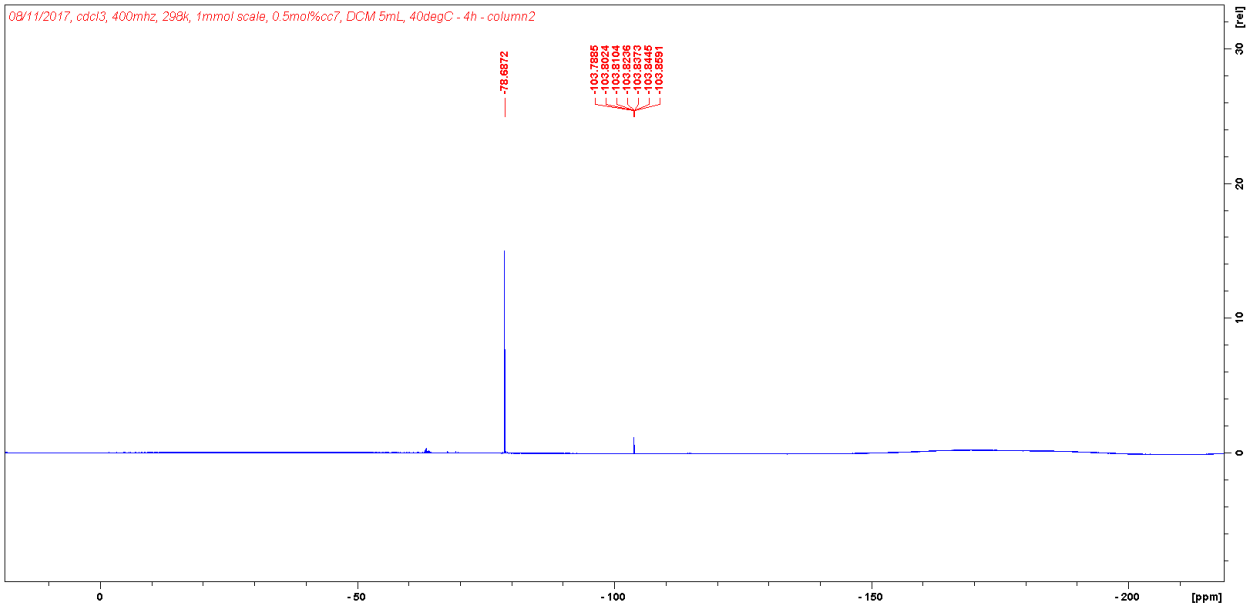
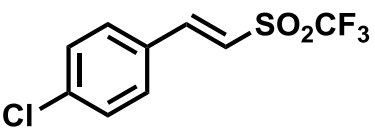


Figure S41. ^{19}F NMR spectrum of **10d** in deuterated chloroform.

10e -



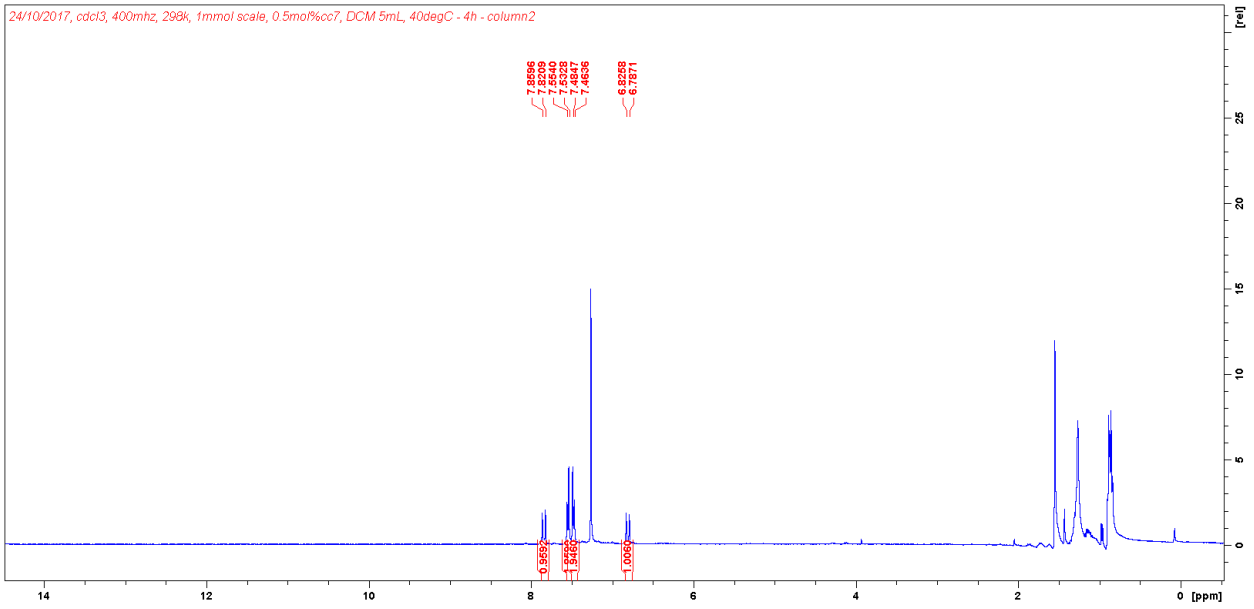


Figure S42. ^{1}H NMR spectrum of **10e** in deuterated chloroform.

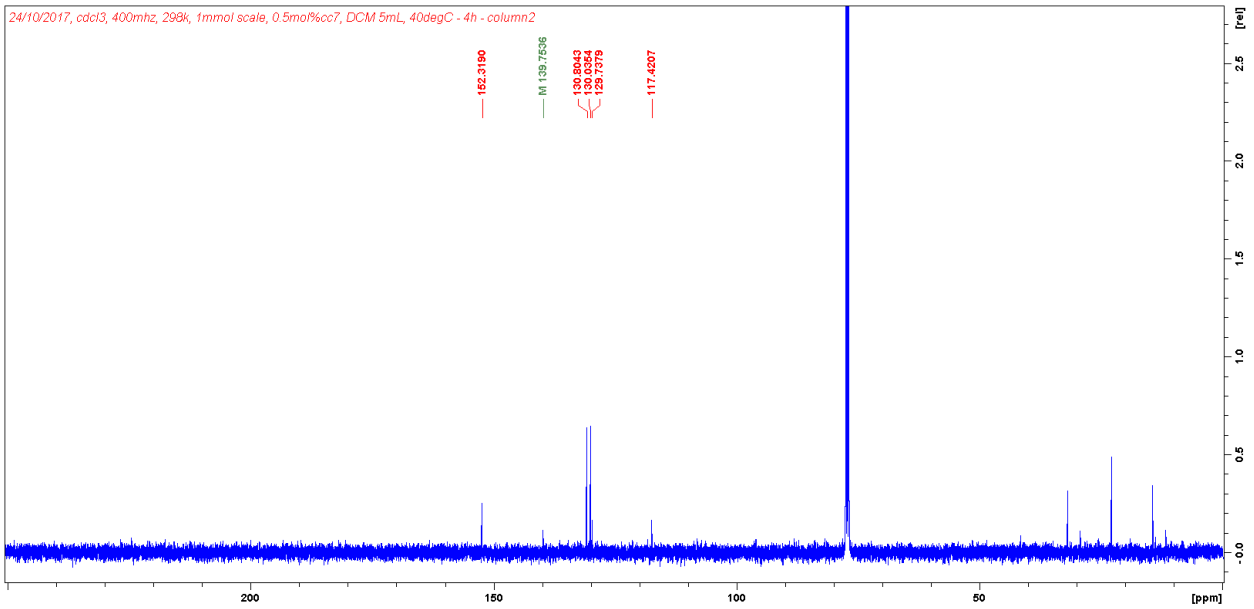


Figure S43. ^{13}C{^{1}H} NMR spectrum of **10e** in deuterated chloroform.

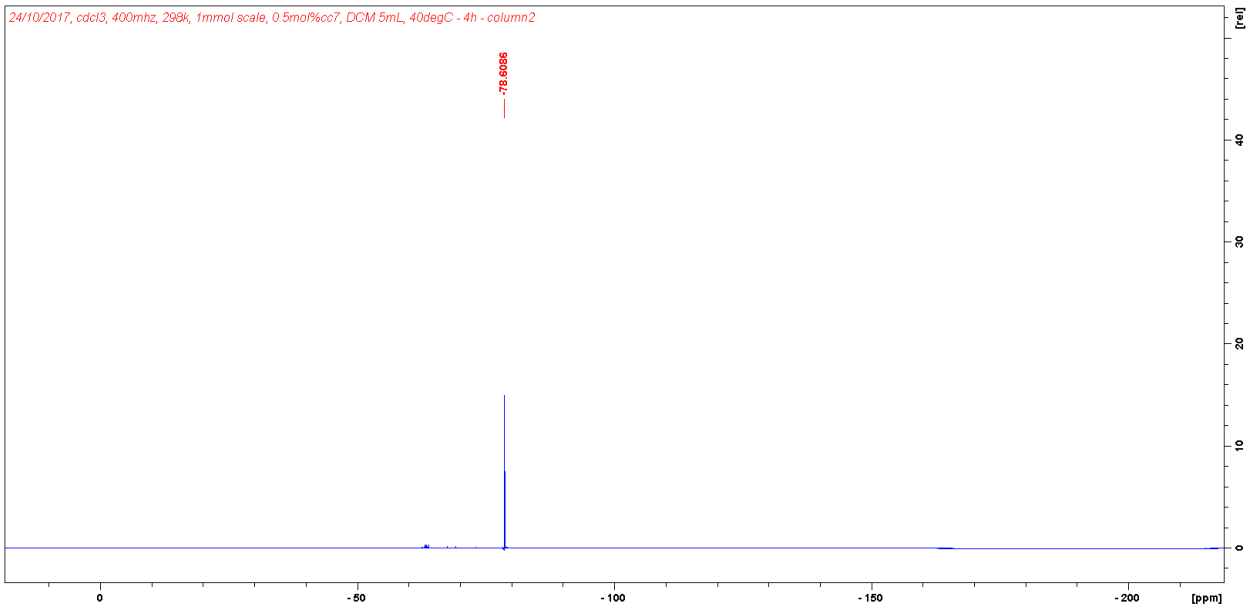
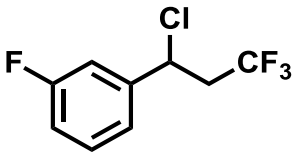


Figure S44. ^{19}F NMR spectrum of **10e** in deuterated chloroform.

8k -



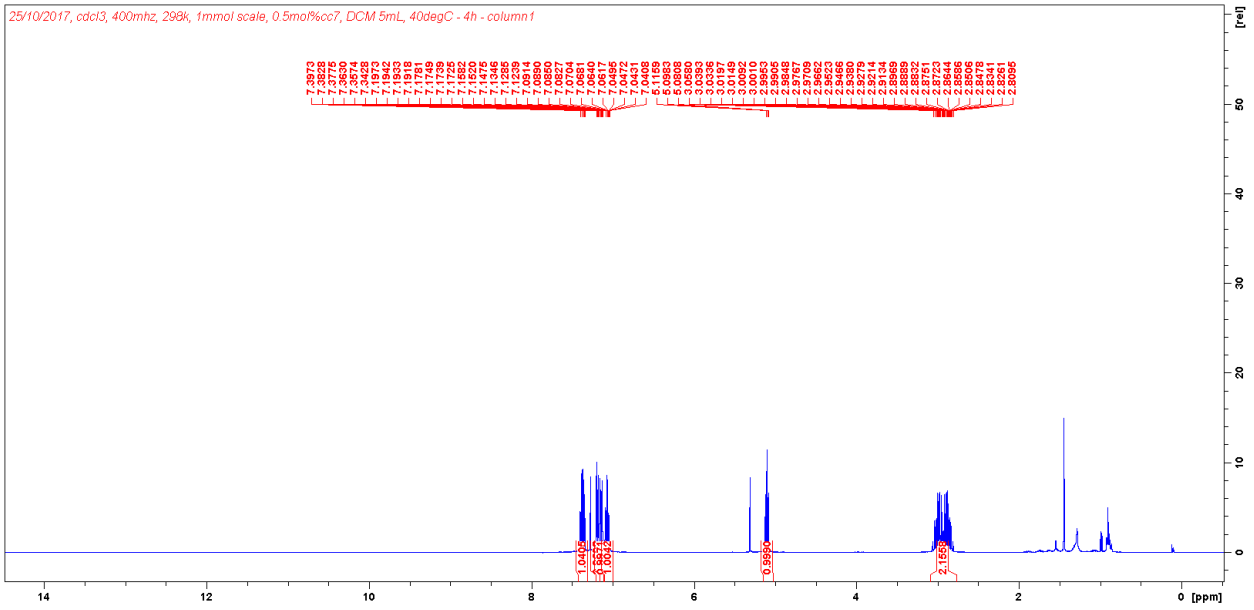


Figure S45. ^{1}H NMR spectrum of **8k** in deuterated chloroform.

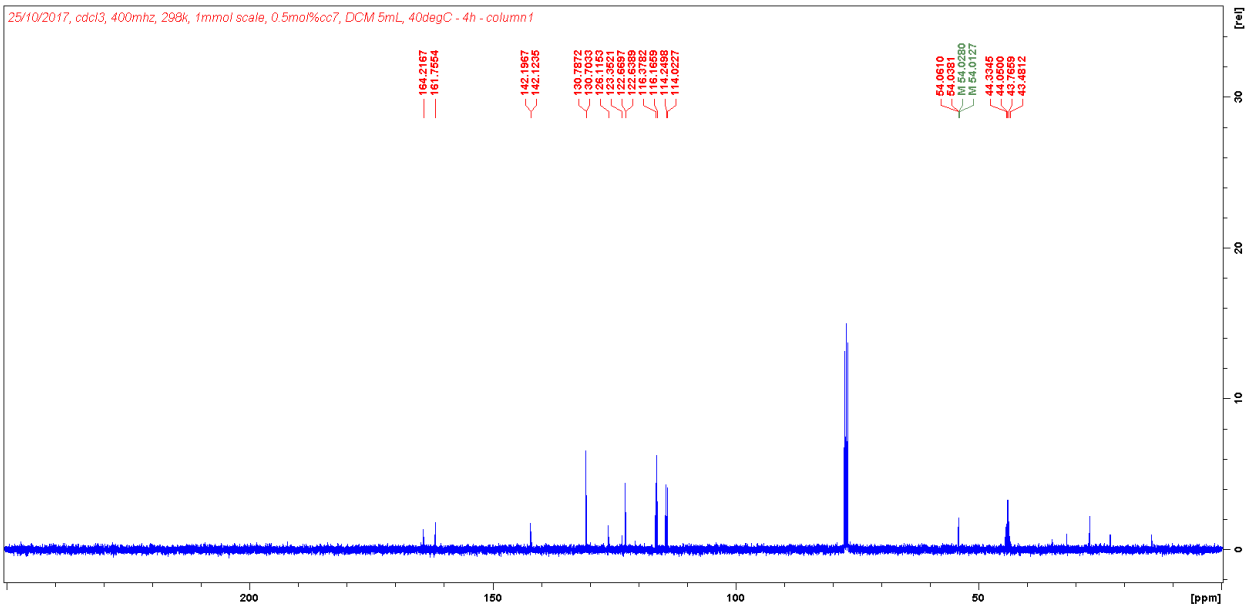


Figure S46. $^{13}C\{^{1}H\}$ NMR spectrum of **8k** in deuterated chloroform.

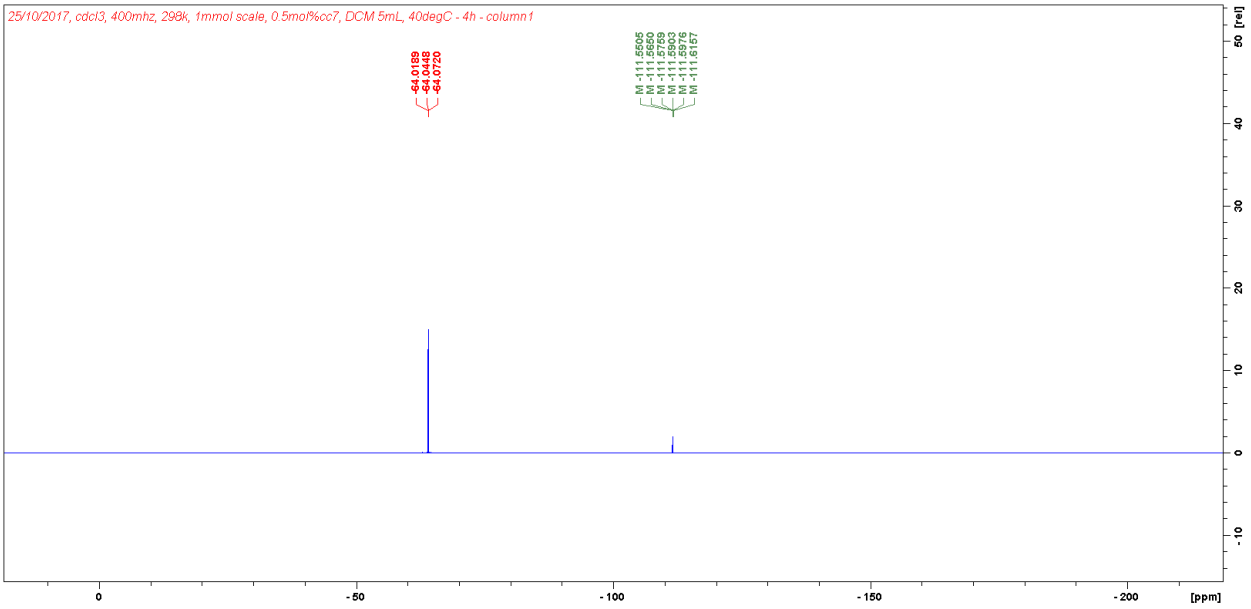


Figure S47. ^{19}F NMR spectrum of **8k** in deuterated chloroform.

8l -

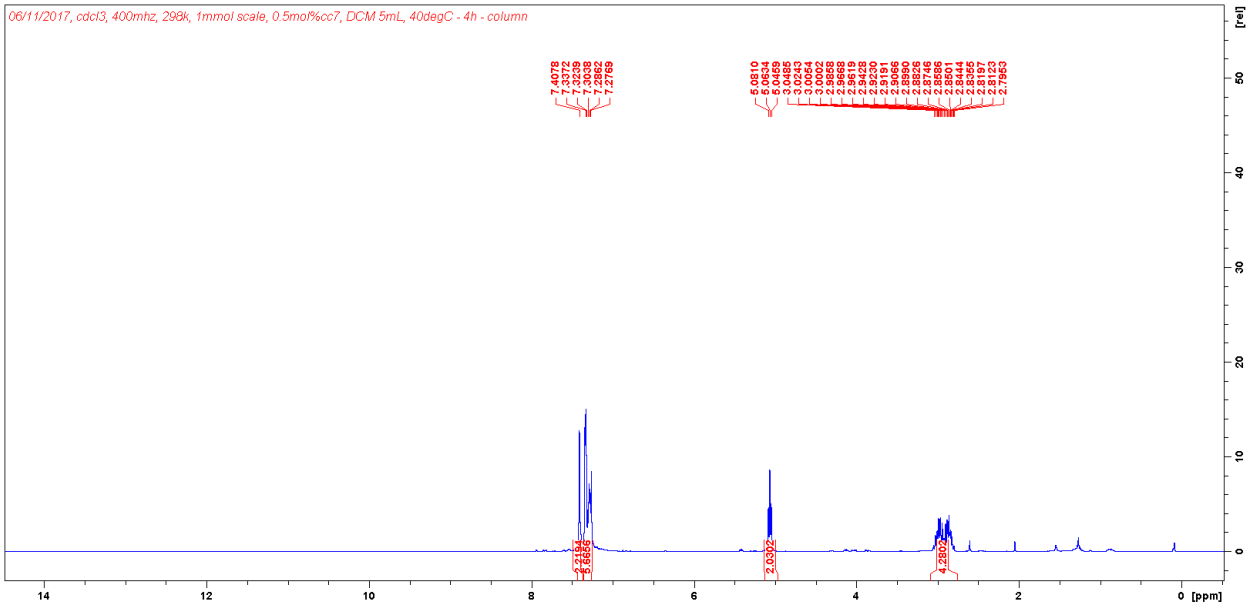


Figure S48. ^{1}H NMR spectrum of **8l** in deuterated chloroform.

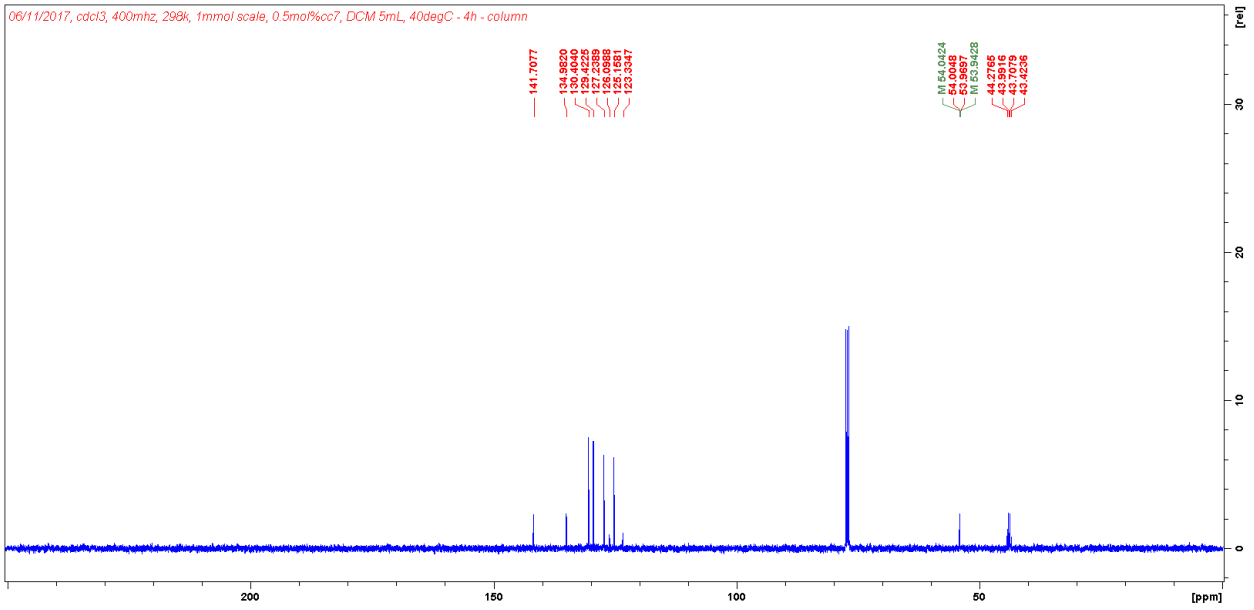


Figure S49. ^{13}C{^{1}H} NMR spectrum of **8l** in deuterated chloroform.

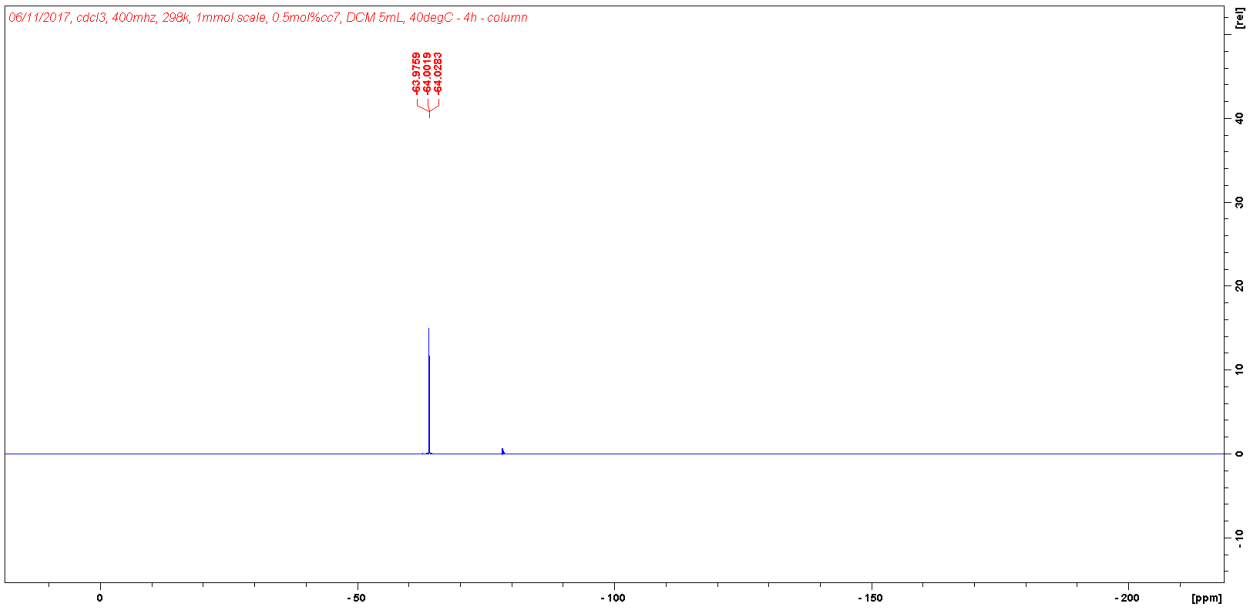
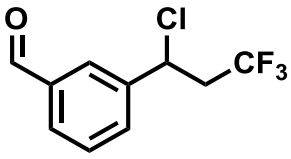


Figure S50. ^{19}F NMR spectrum of **8l** in deuterated chloroform.

8n -



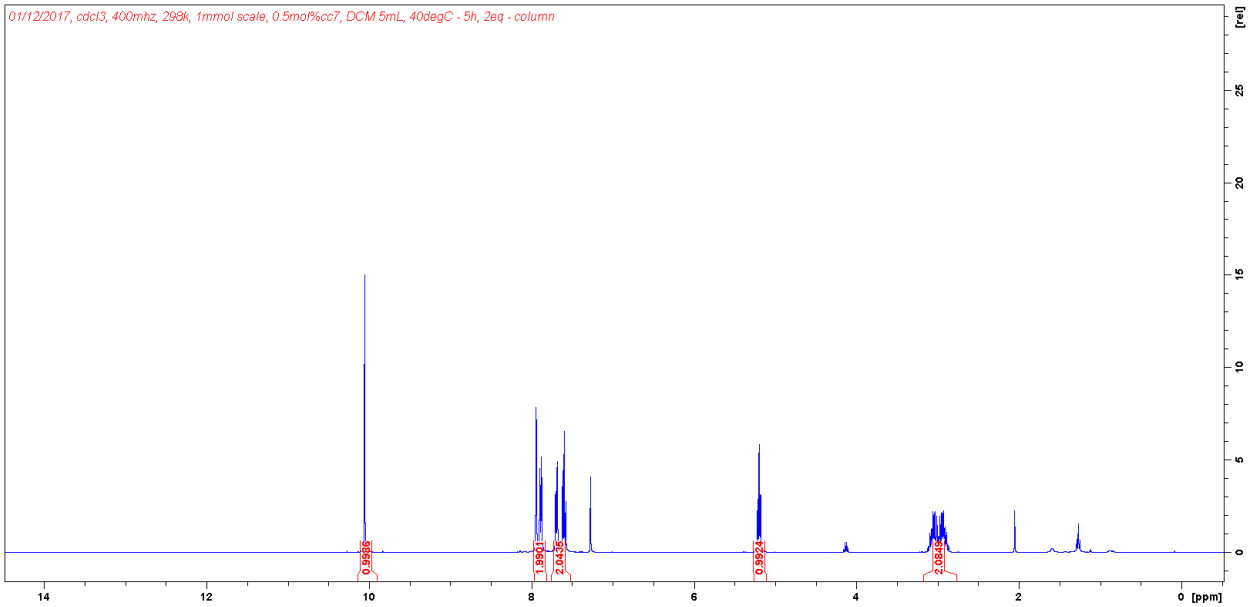


Figure S51. ^{1}H NMR spectrum of **8n** in deuterated chloroform.

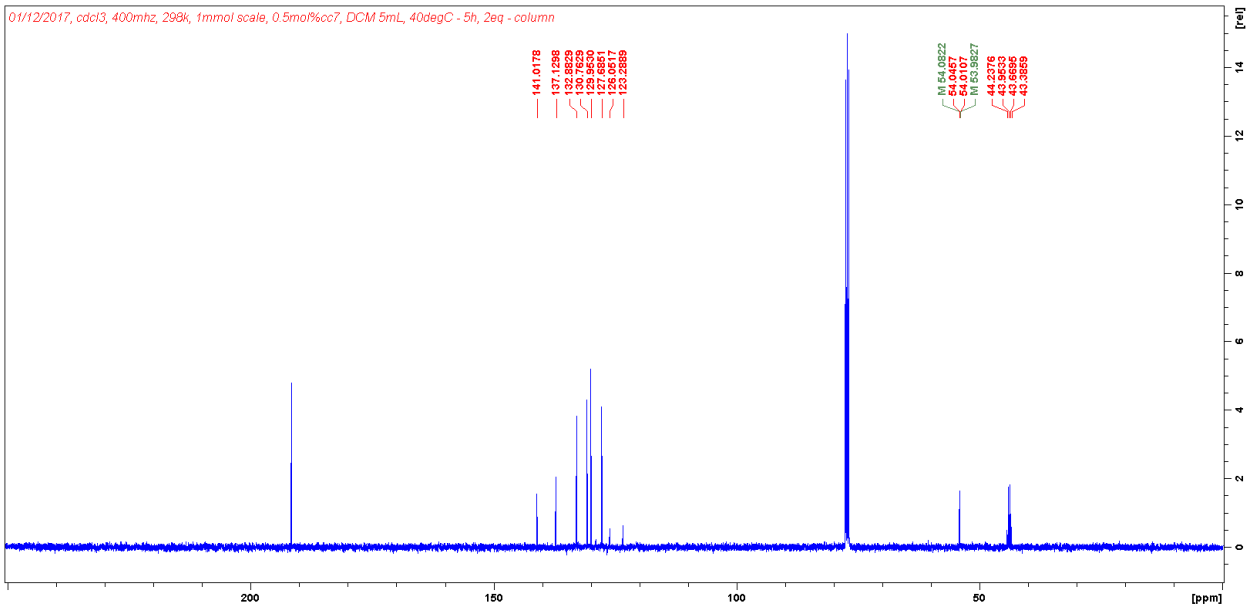


Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum of **8n** in deuterated chloroform.

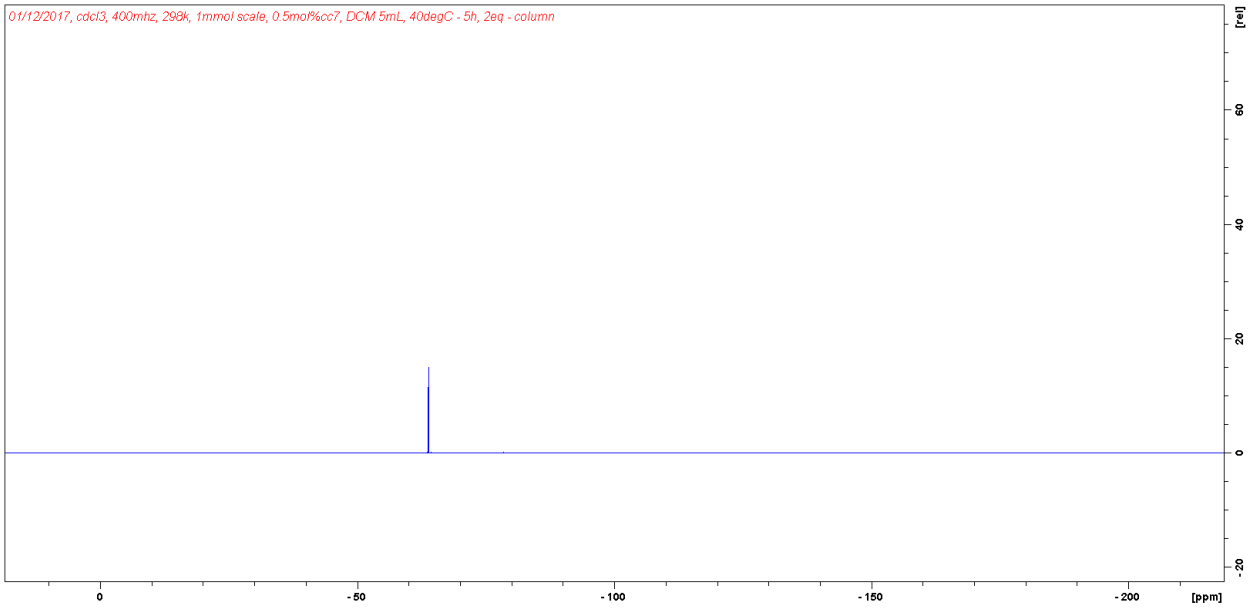


Figure S53. ^{19}F NMR spectrum of **8n** in deuterated chloroform.

8o -

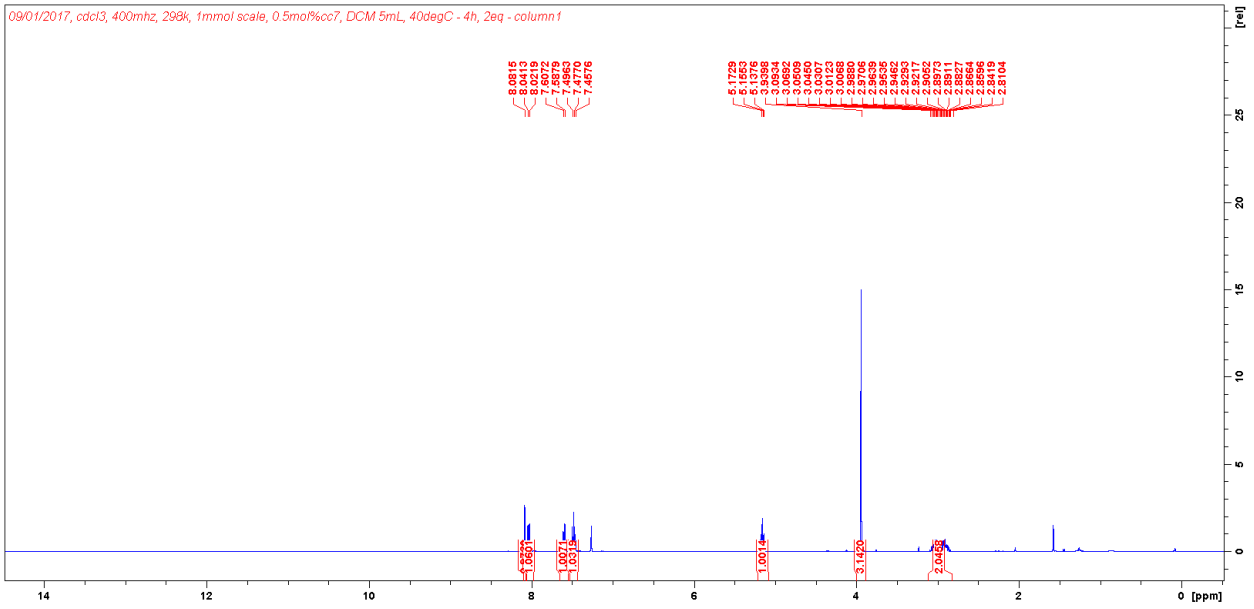


Figure S54. ^{1}H NMR spectrum of **8o** in deuterated chloroform.

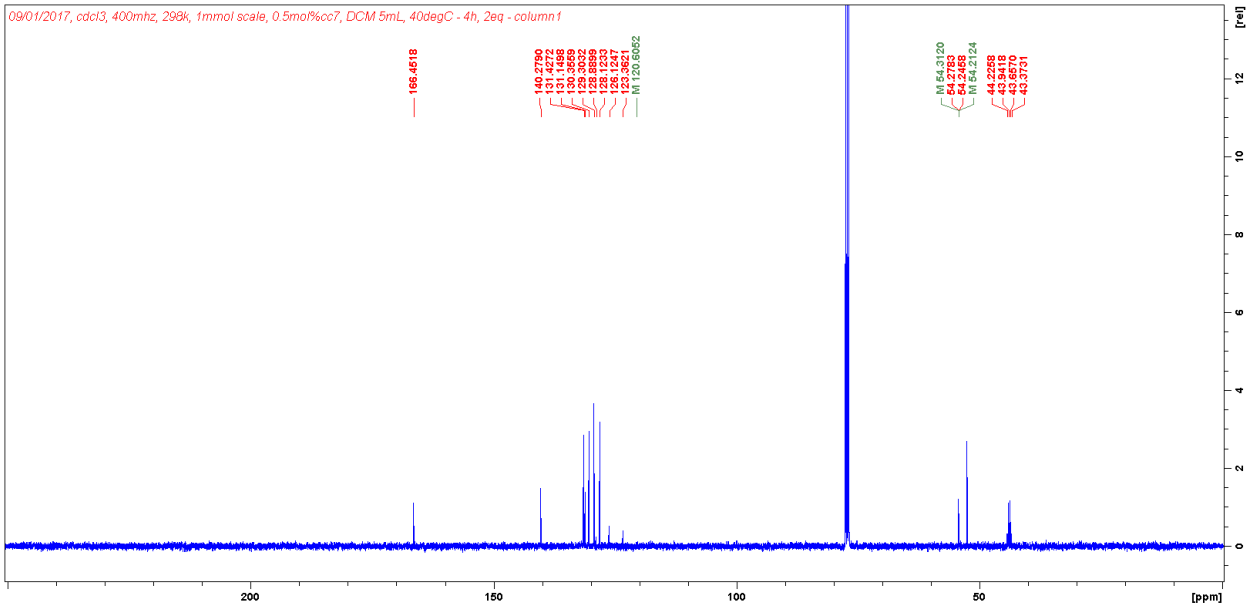


Figure S55. ^{13}C{^{1}H} NMR spectrum of **8o** in deuterated chloroform.

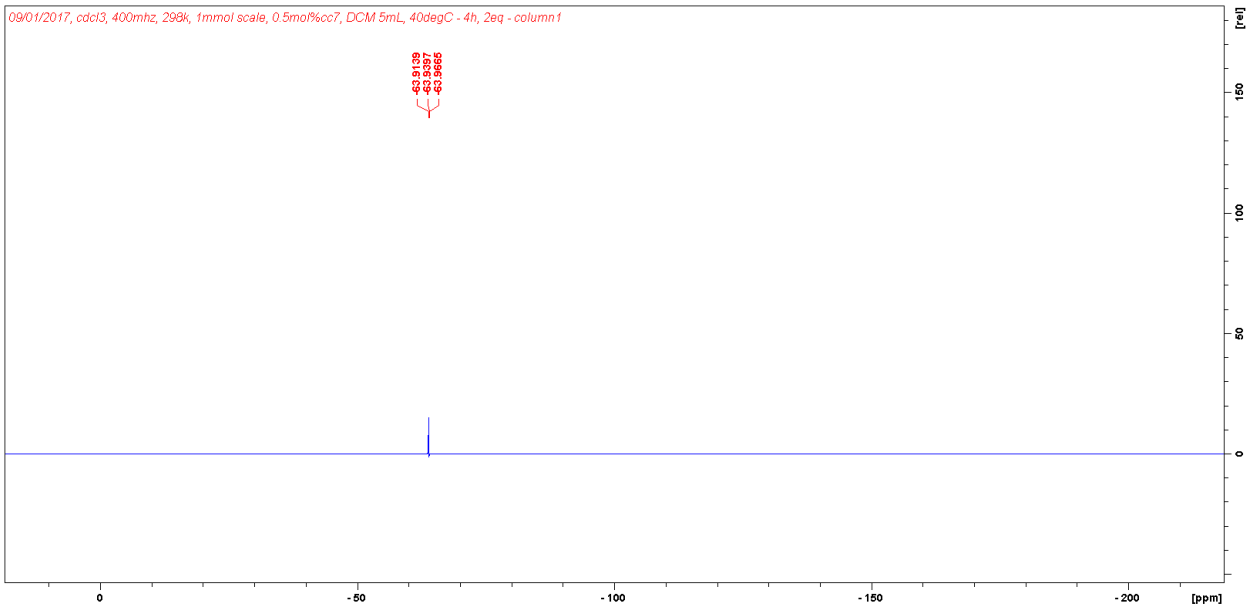


Figure S56. ^{19}F NMR spectrum of **8o** in deuterated chloroform.

8p -

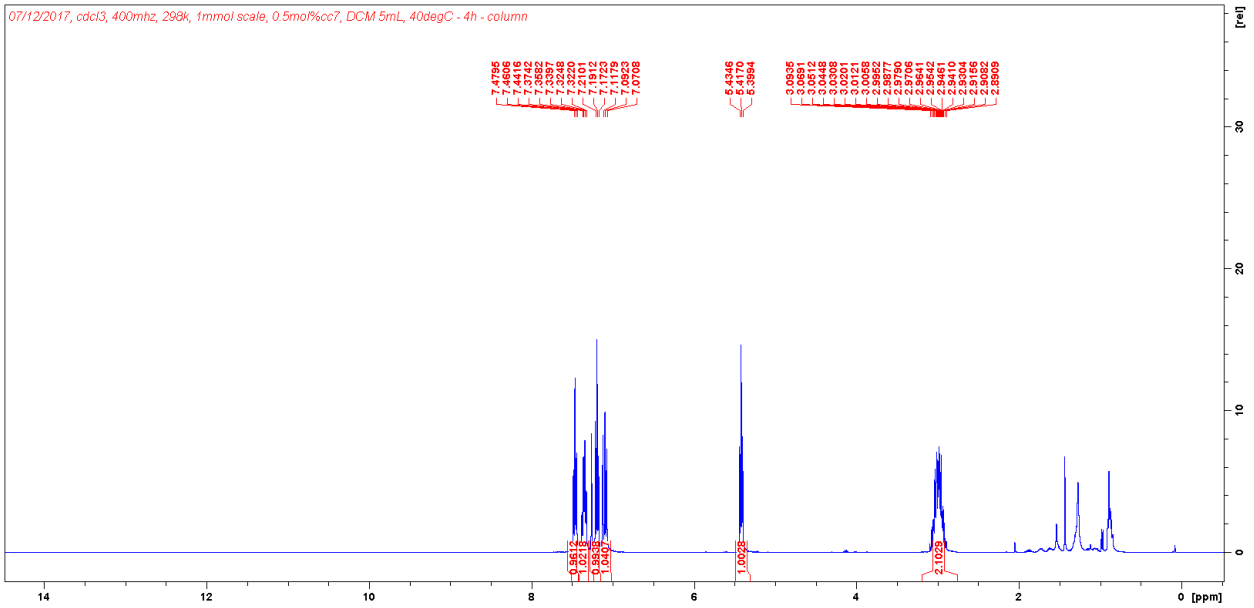


Figure S57. ^{1}H NMR spectrum of **8p** in deuterated chloroform.

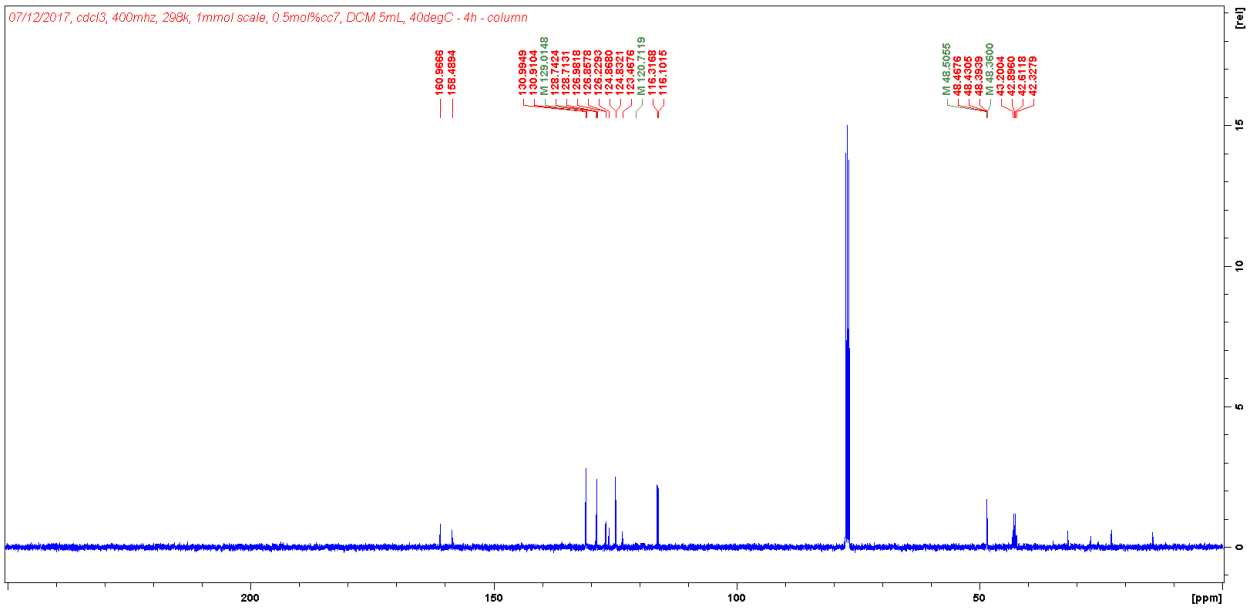


Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum of **8p** in deuterated chloroform.

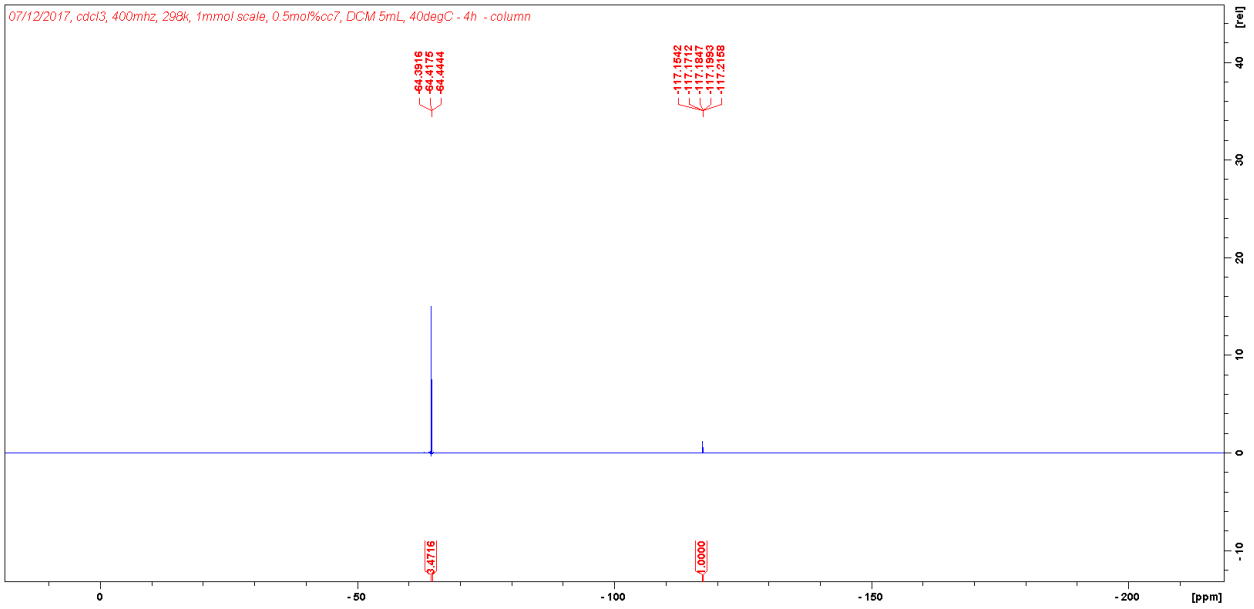


Figure S59. ^{19}F NMR spectrum of **8p** in deuterated chloroform.

8q -

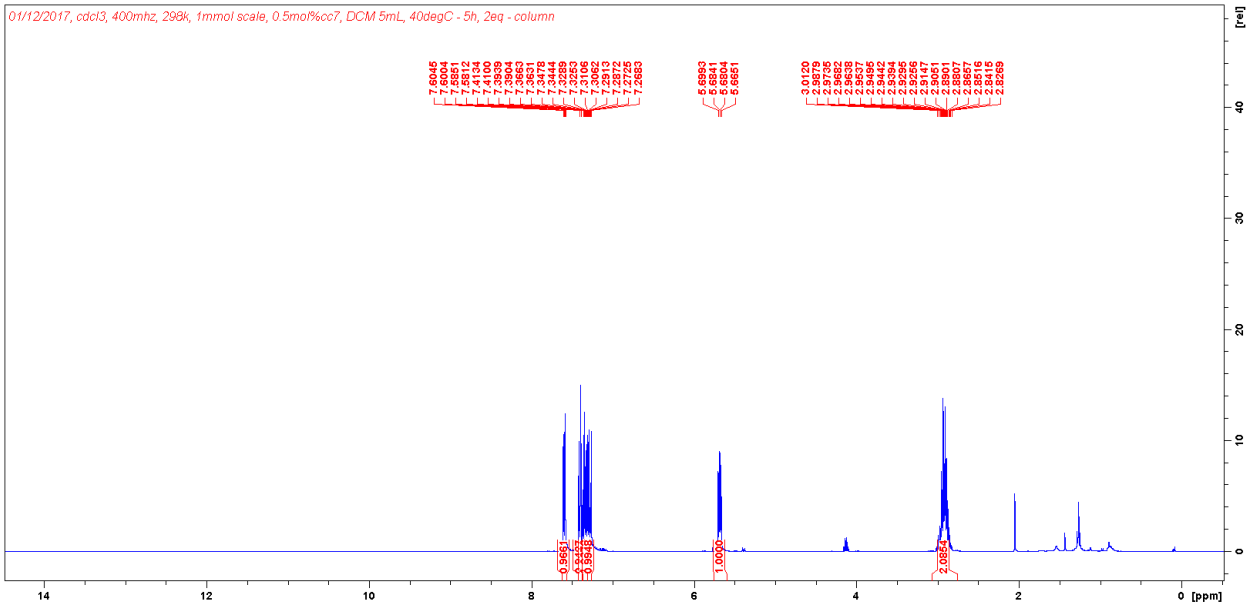


Figure S60. ^{1}H NMR spectrum of **8q** in deuterated chloroform.

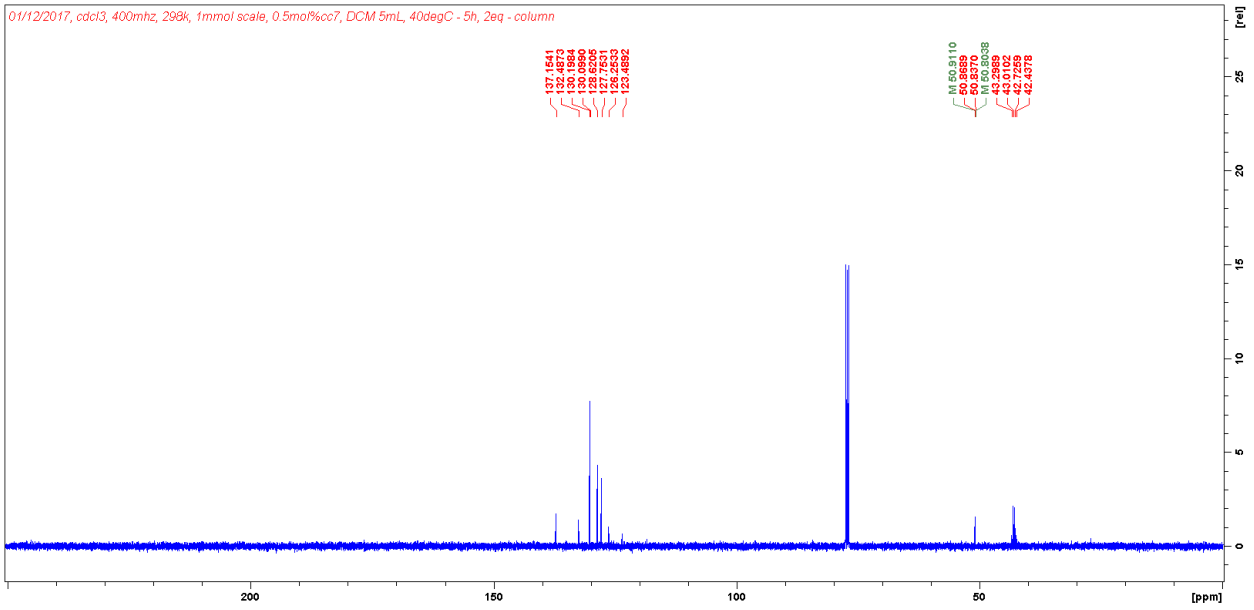


Figure S61. ^{13}C{^{1}H} NMR spectrum of **8q** in deuterated chloroform.

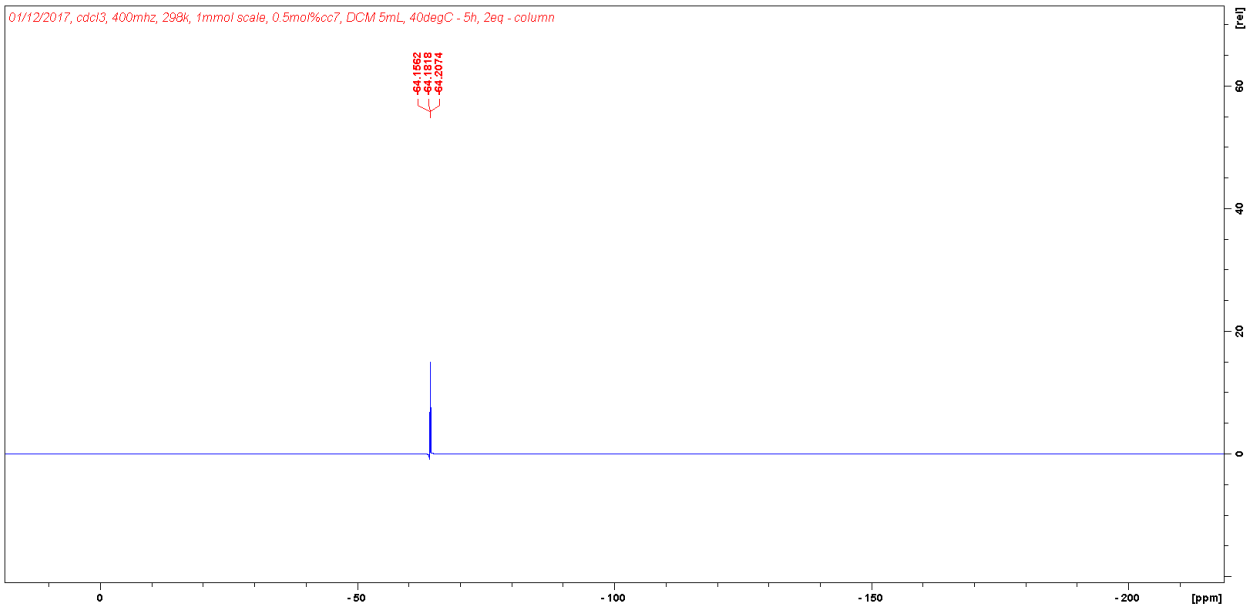


Figure S62. ^{19}F NMR spectrum of **8q** in deuterated chloroform.

8s -

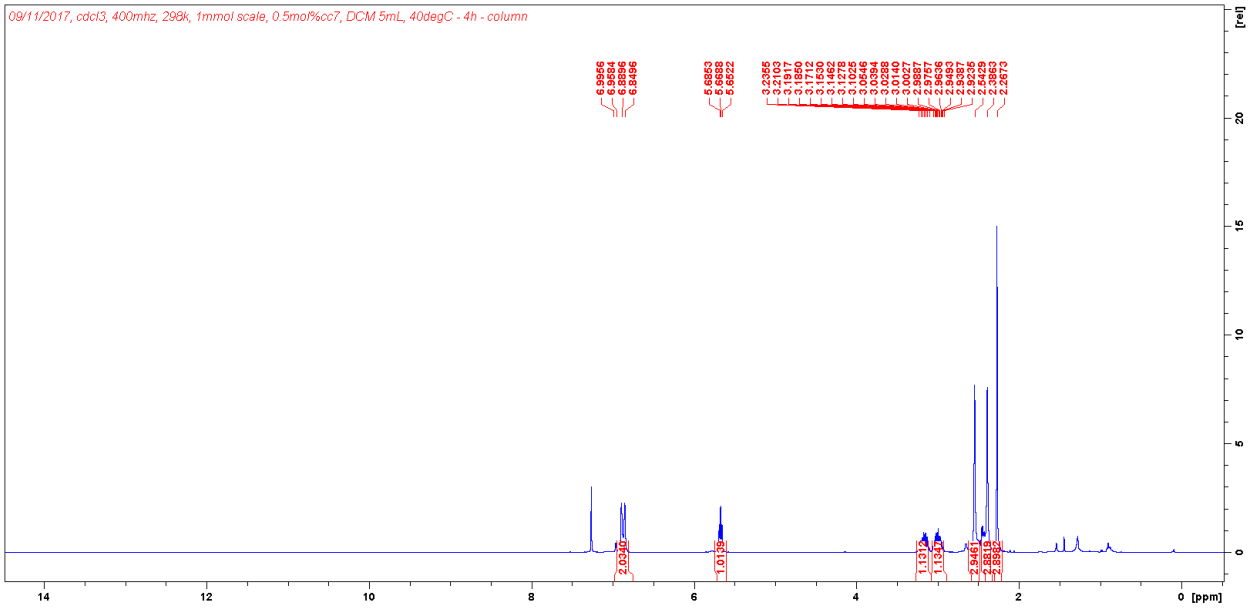


Figure S63. ^{1}H NMR spectrum of **8s** in deuterated chloroform.

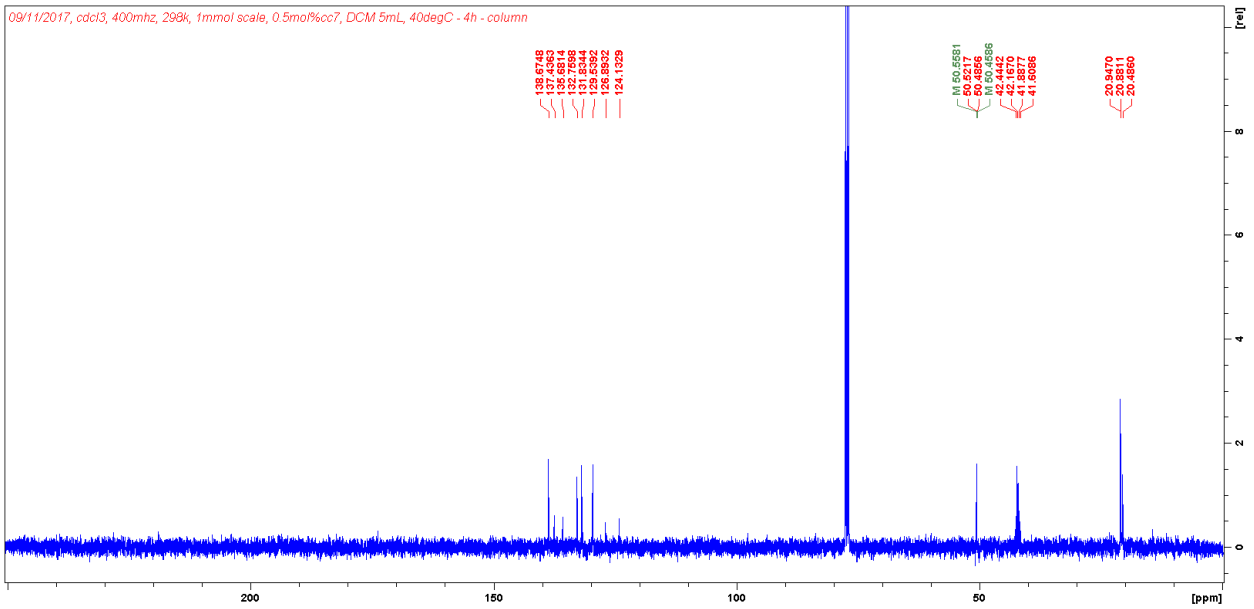


Figure S64. $^{13}C\{^{1}H\}$ NMR spectrum of **8s** in deuterated chloroform.

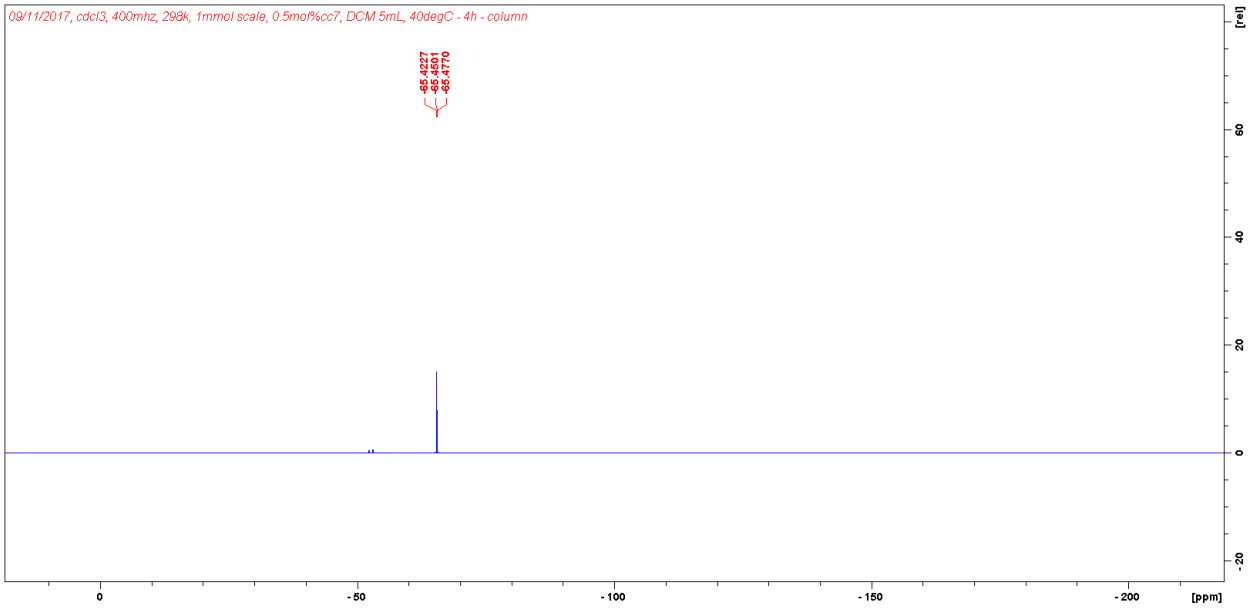


Figure S65. ^{19}F NMR spectrum of **8s** in deuterated chloroform.

10f -

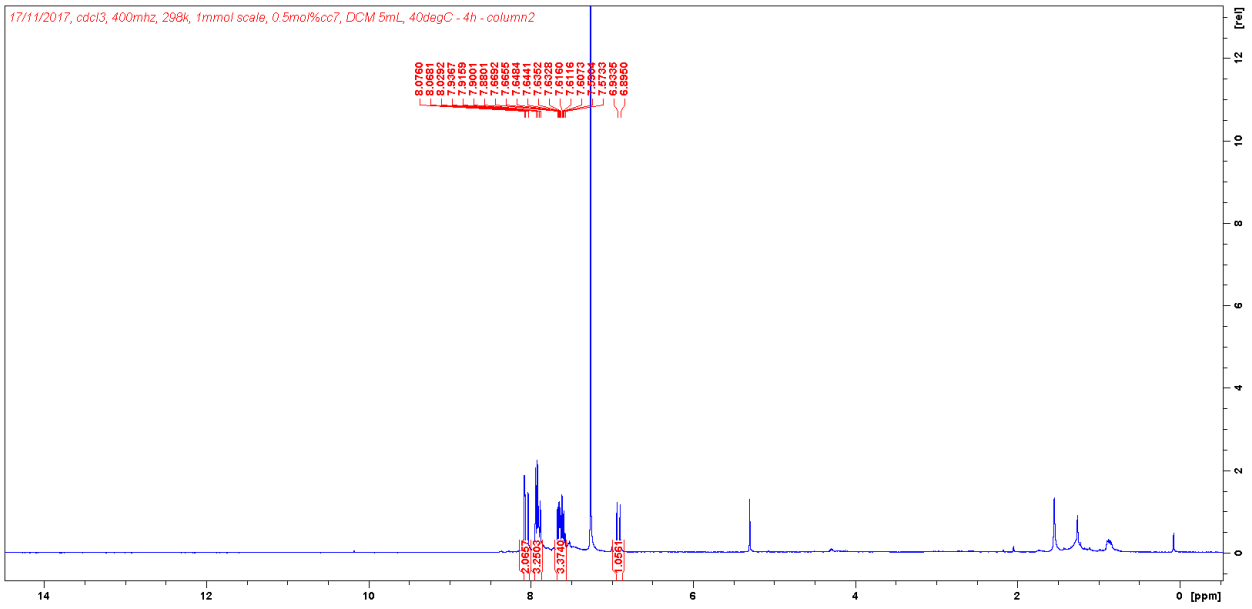


Figure S66. ^{1}H NMR spectrum of **10f** in deuterated chloroform.

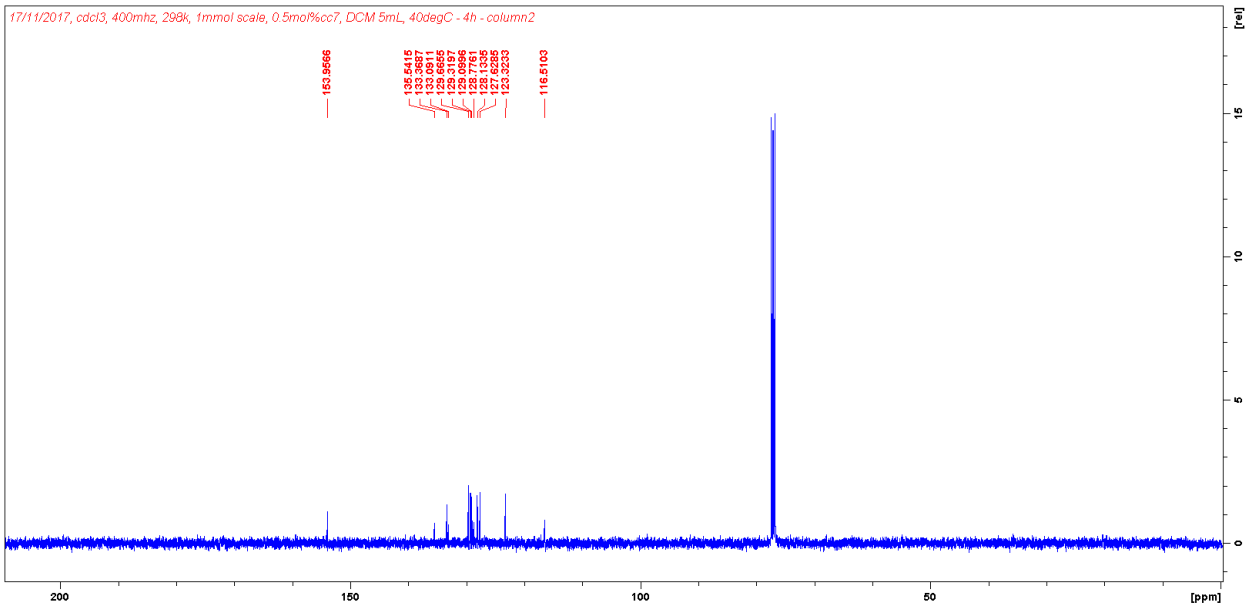


Figure S67. ^{13}C{^{1}H} NMR spectrum of **10f** in deuterated chloroform.

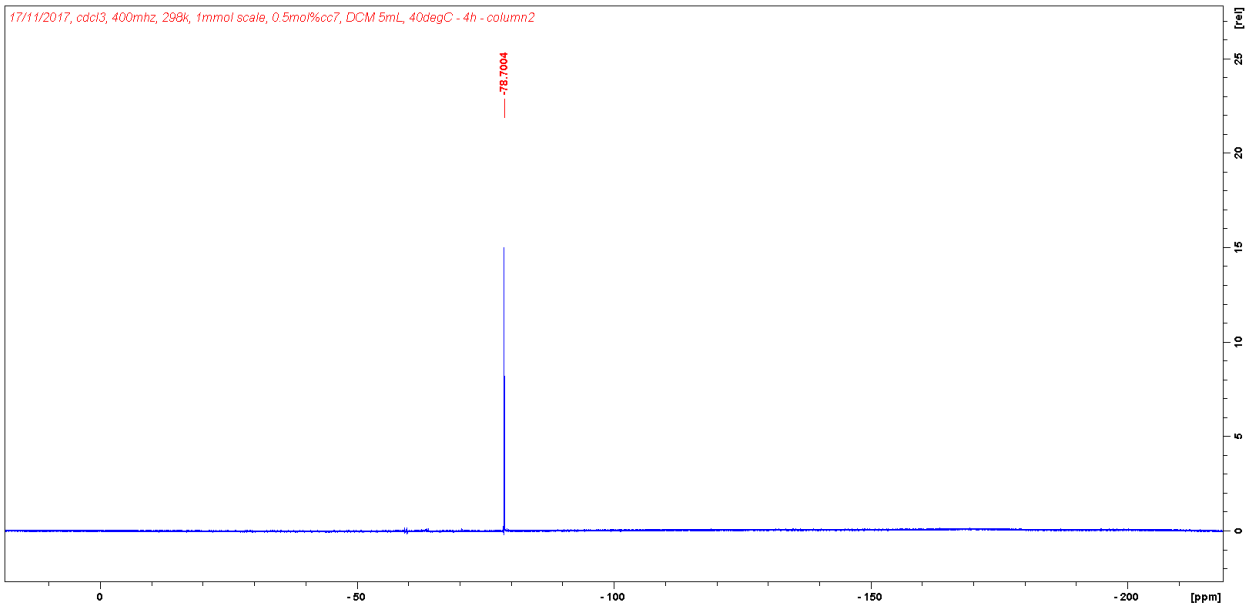
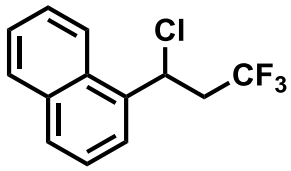


Figure S68. ^{19}F NMR spectrum of **10f** in deuterated chloroform.

8u -



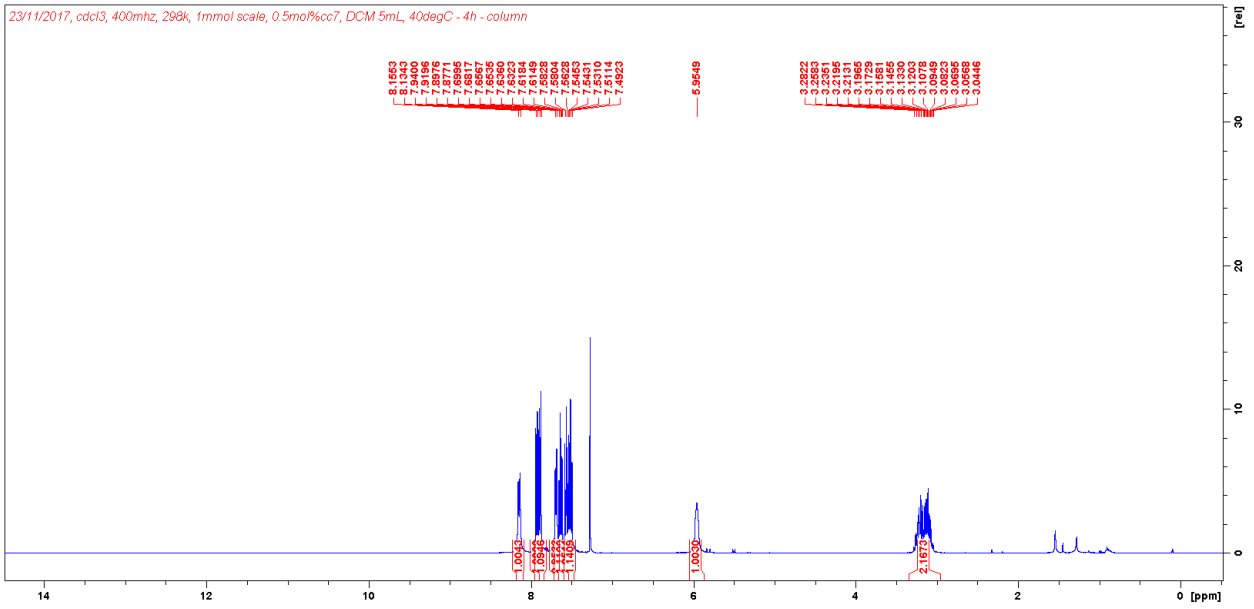


Figure S69. ^{1}H NMR spectrum of **8u** in deuterated chloroform.

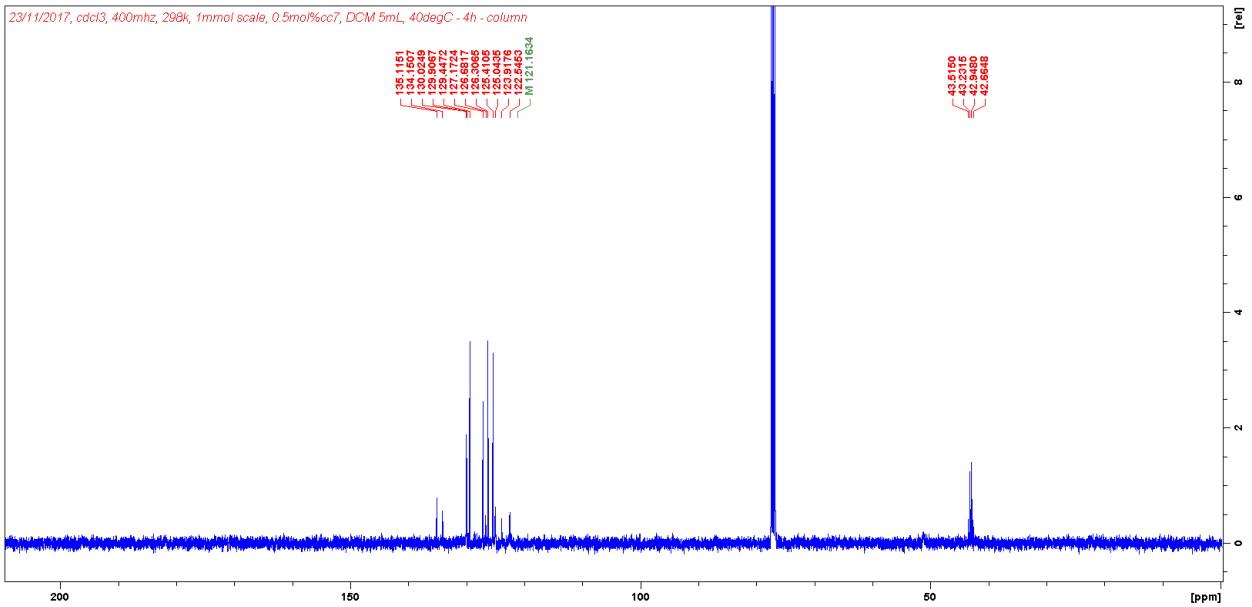


Figure S70. $^{13}C\{^{1}H\}$ NMR spectrum of **8u** in deuterated chloroform.

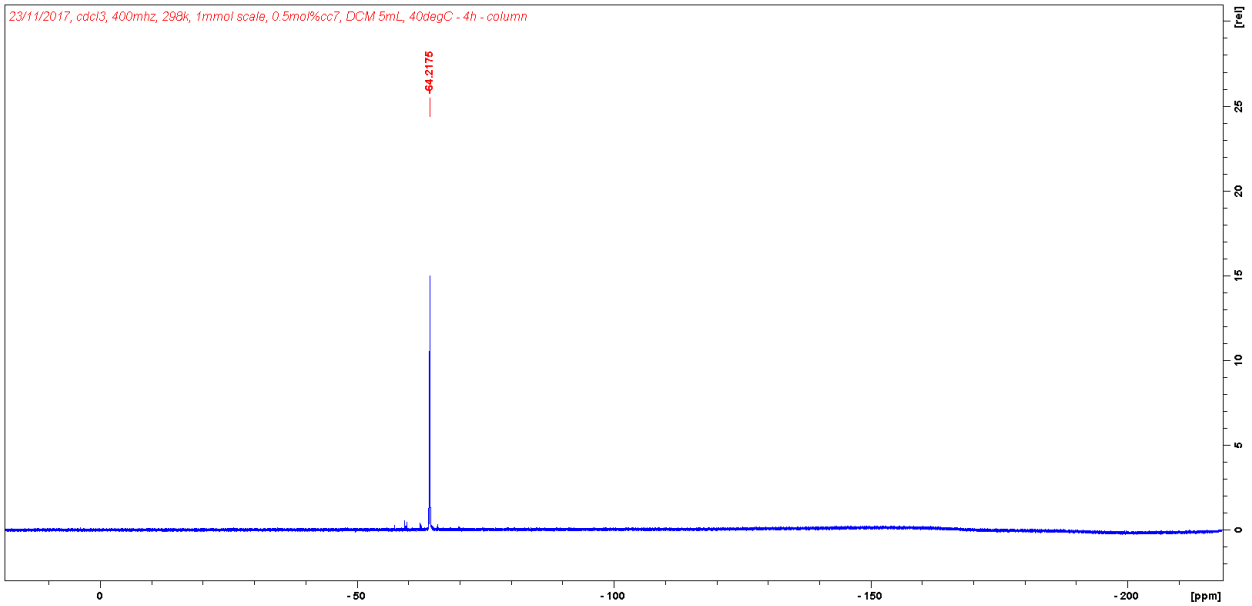
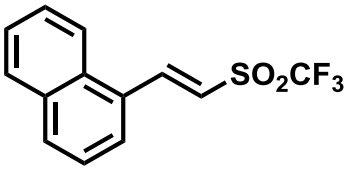


Figure S71. ^{19}F NMR spectrum of **8u** in deuterated chloroform.

10g -



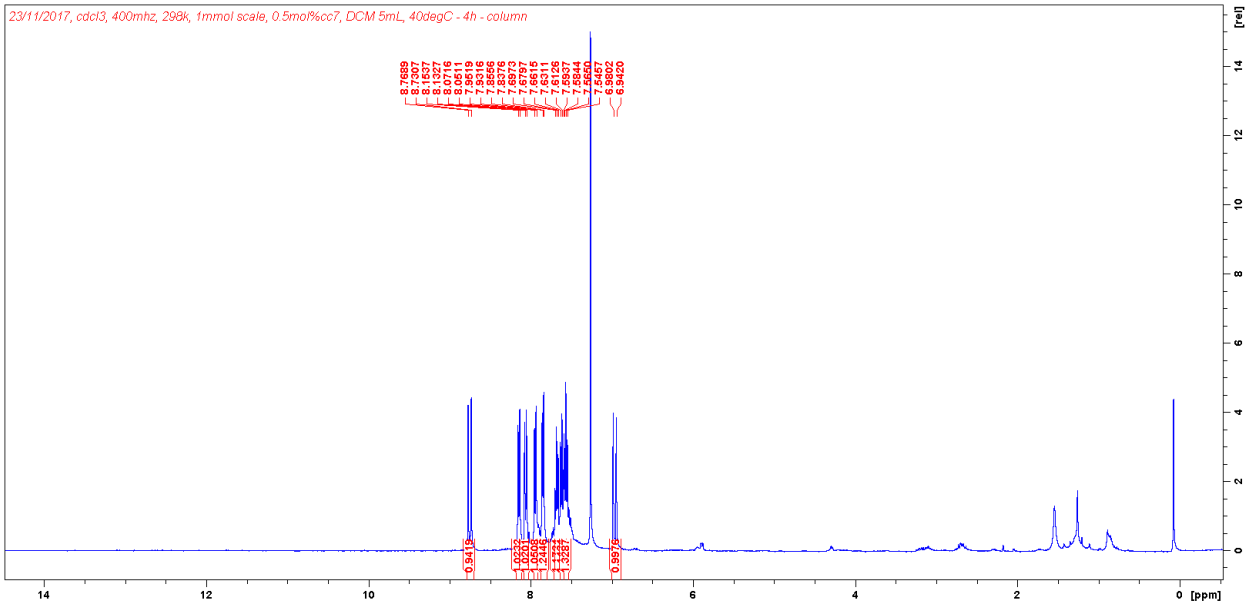


Figure S72. ^{1}H NMR spectrum of **10g** in deuterated chloroform.

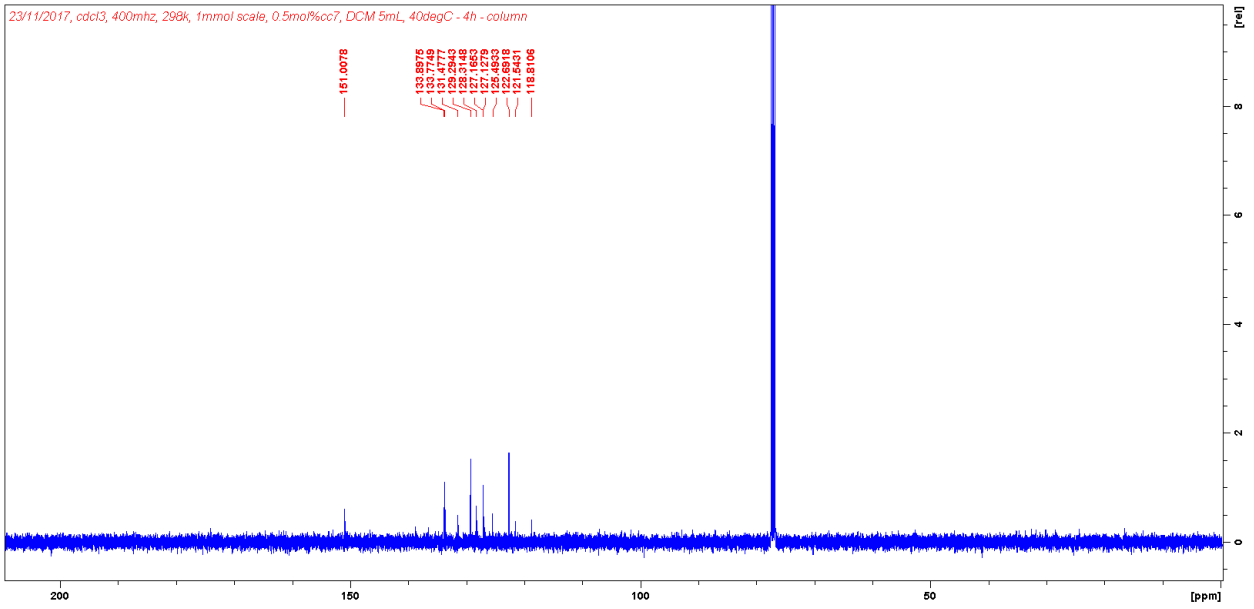


Figure S73. ^{13}C{^{1}H} NMR spectrum of **10g** in deuterated chloroform.

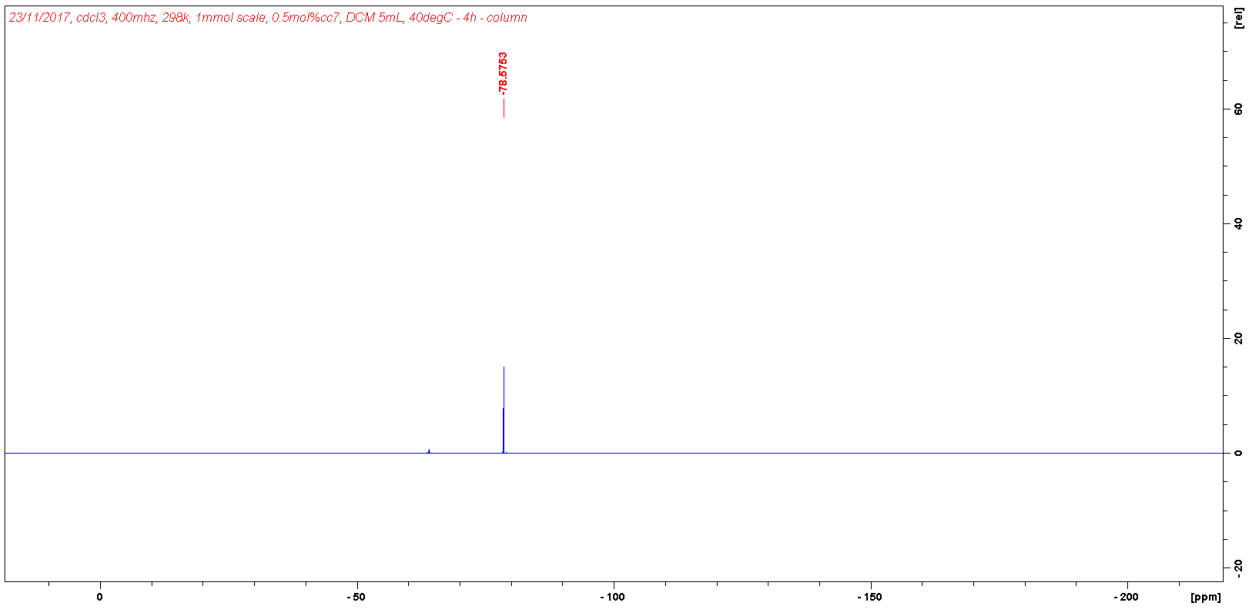
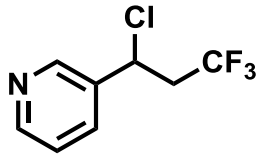


Figure S74. ^{19}F NMR spectrum of **10g** in deuterated chloroform.

8w -



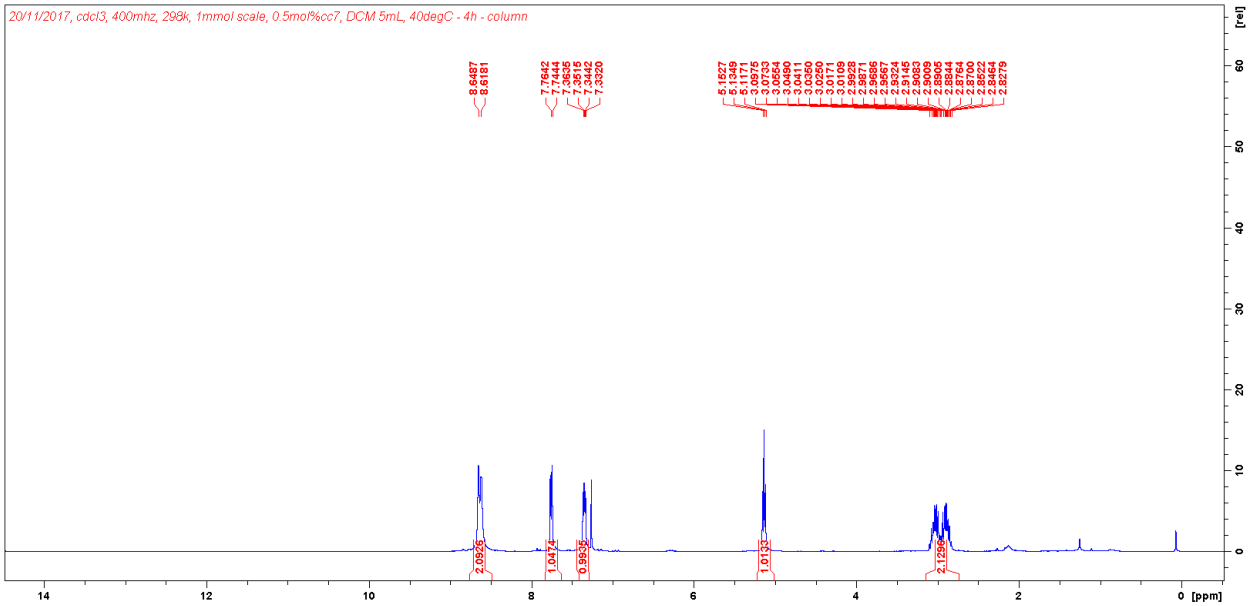


Figure S75. ^{1}H NMR spectrum of **8w** in deuterated chloroform.

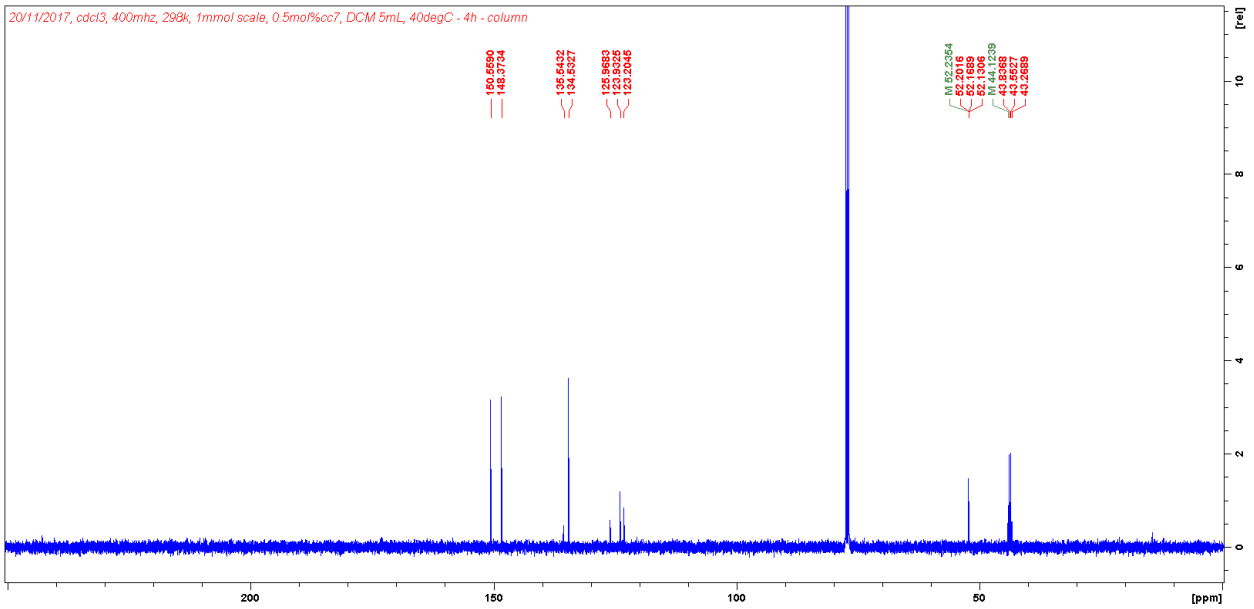


Figure S76. $^{13}C\{^{1}H\}$ NMR spectrum of **8w** in deuterated chloroform.

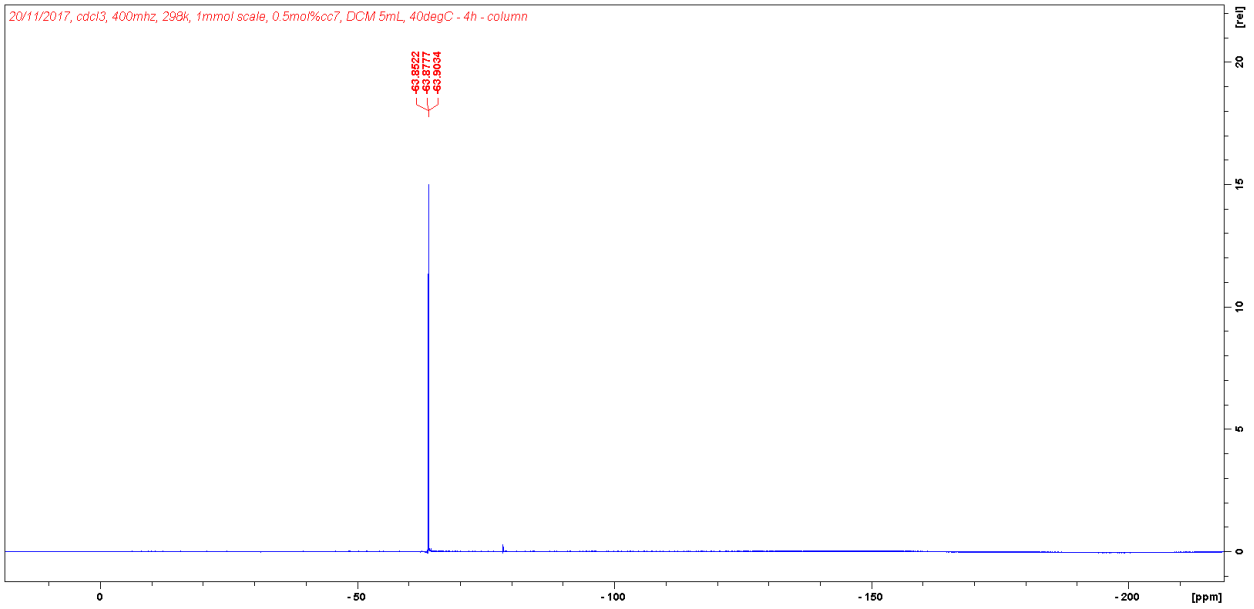


Figure S77. ^{19}F NMR spectrum of **8w** in deuterated chloroform.

8z -

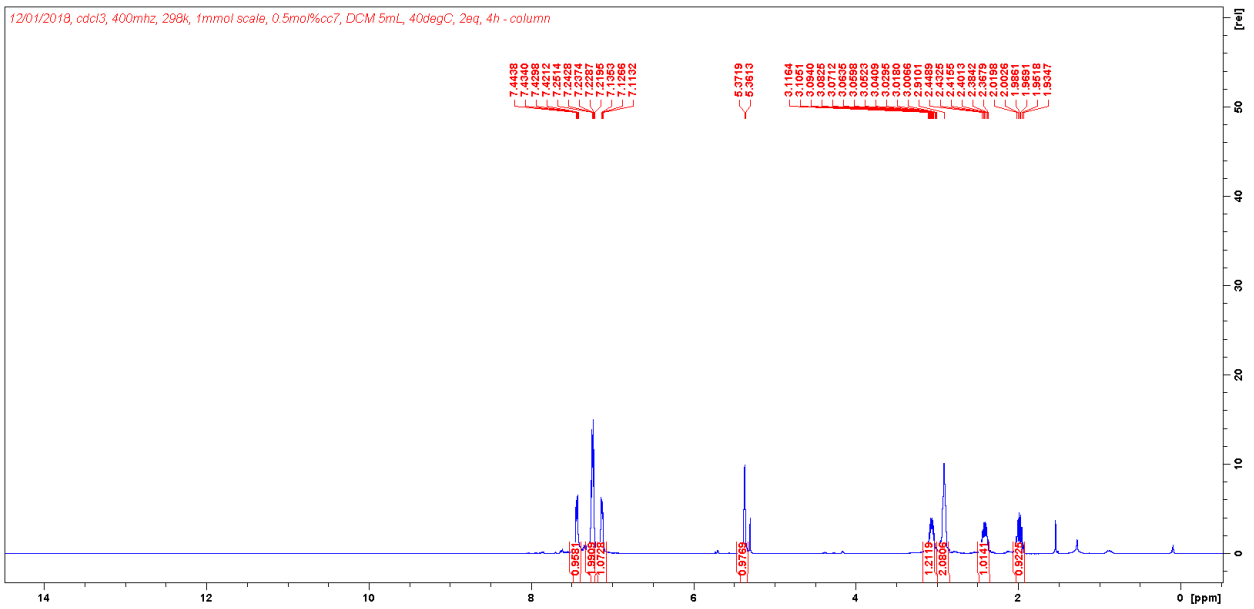


Figure S78. ^{1}H NMR spectrum of **8z** in deuterated chloroform.

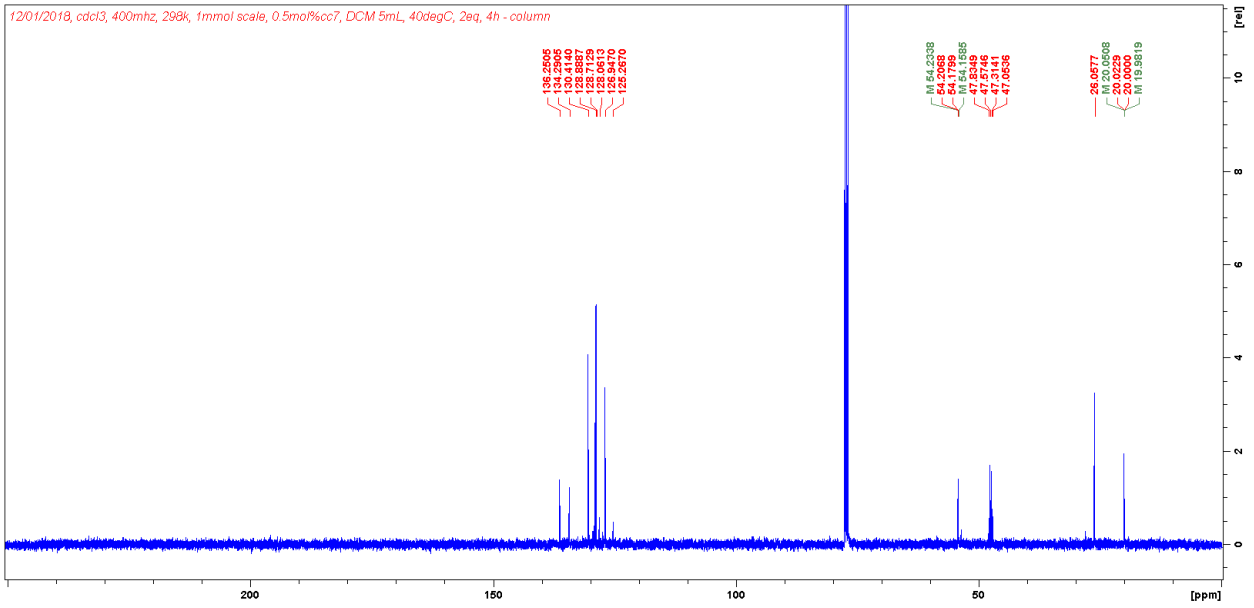


Figure S79. ^{13}C{^{1}H} NMR spectrum of **8z** in deuterated chloroform.

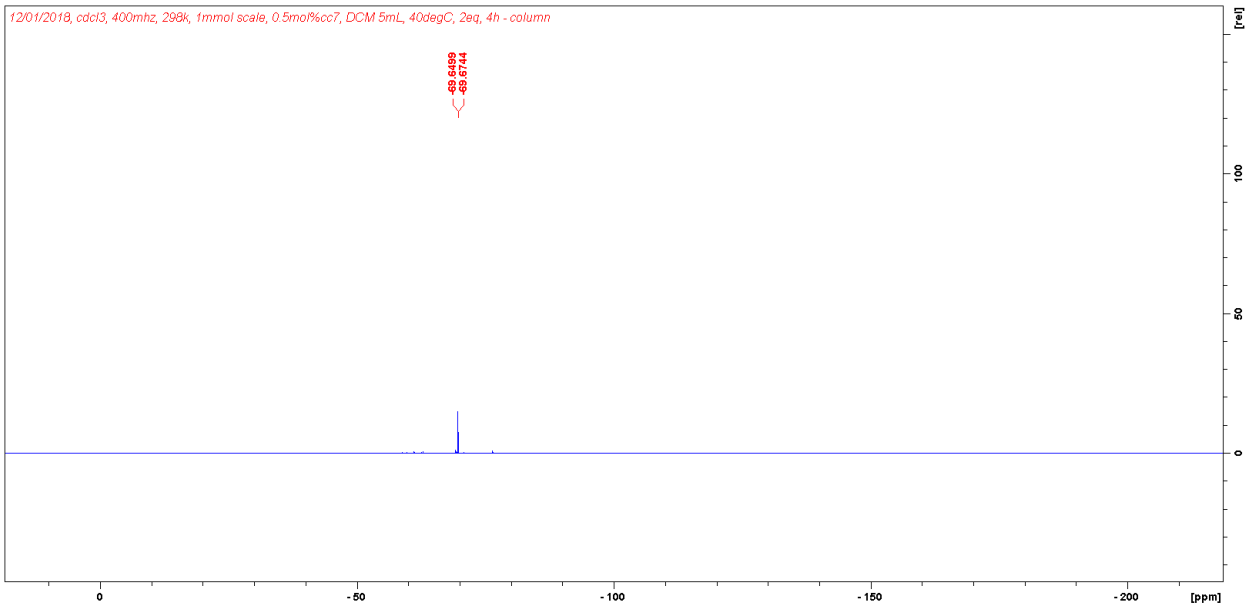


Figure S80. ^{19}F NMR spectrum of **8z** in deuterated chloroform.

8aa -

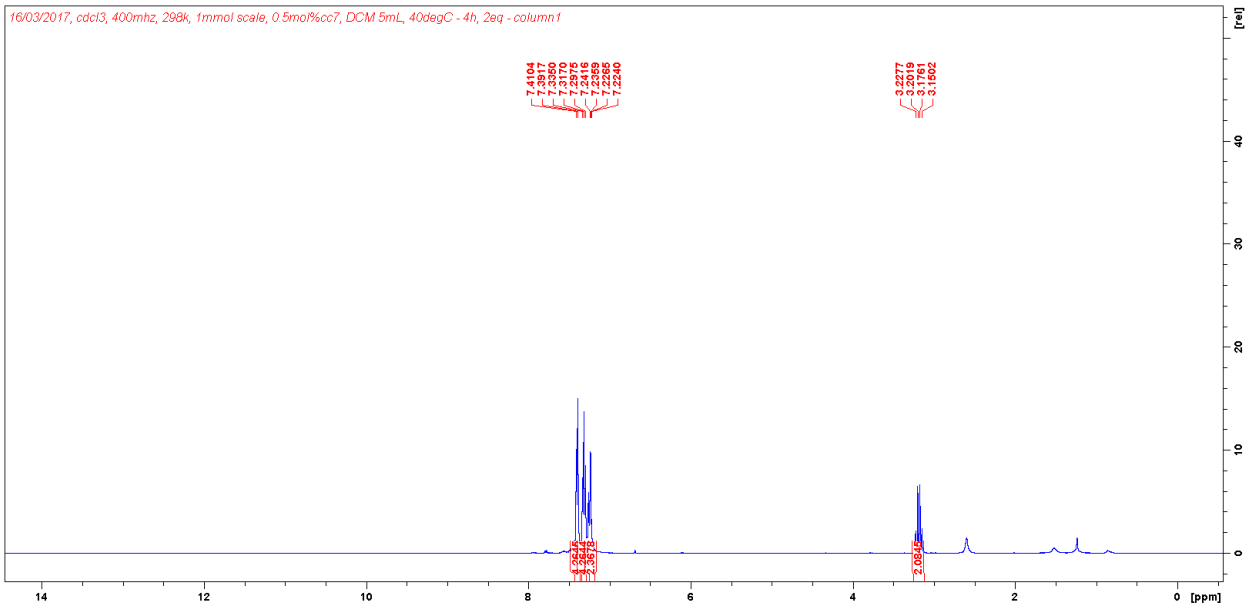


Figure S81. ^{1}H NMR spectrum of **8aa** in deuterated chloroform.

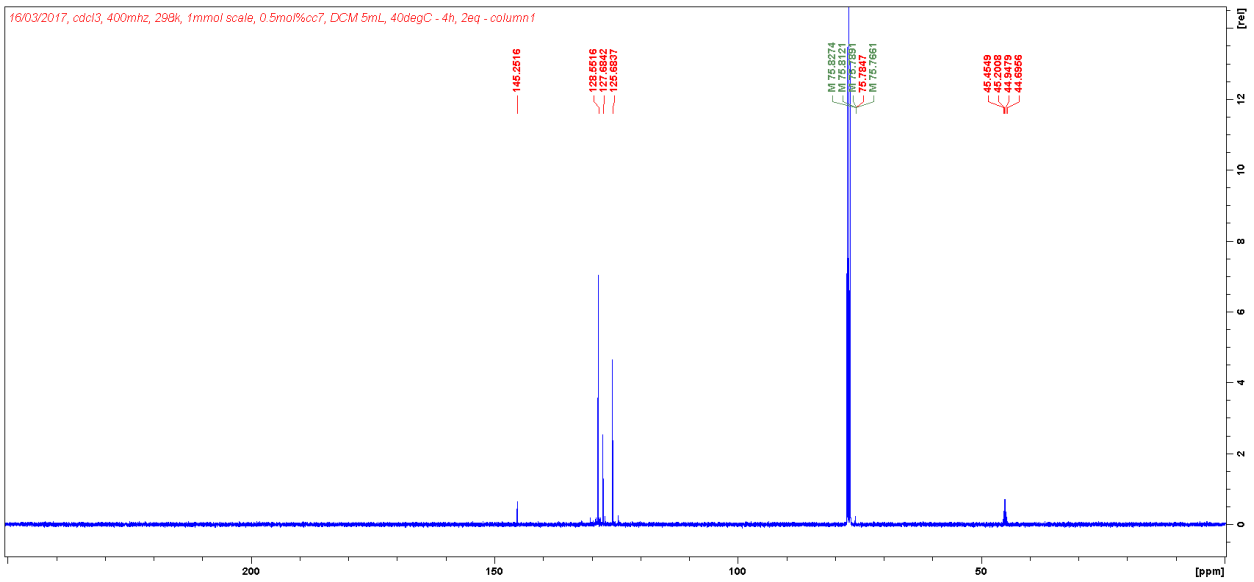


Figure S82. $^{13}C\{^{1}H\}$ NMR spectrum of **8aa** in deuterated chloroform.

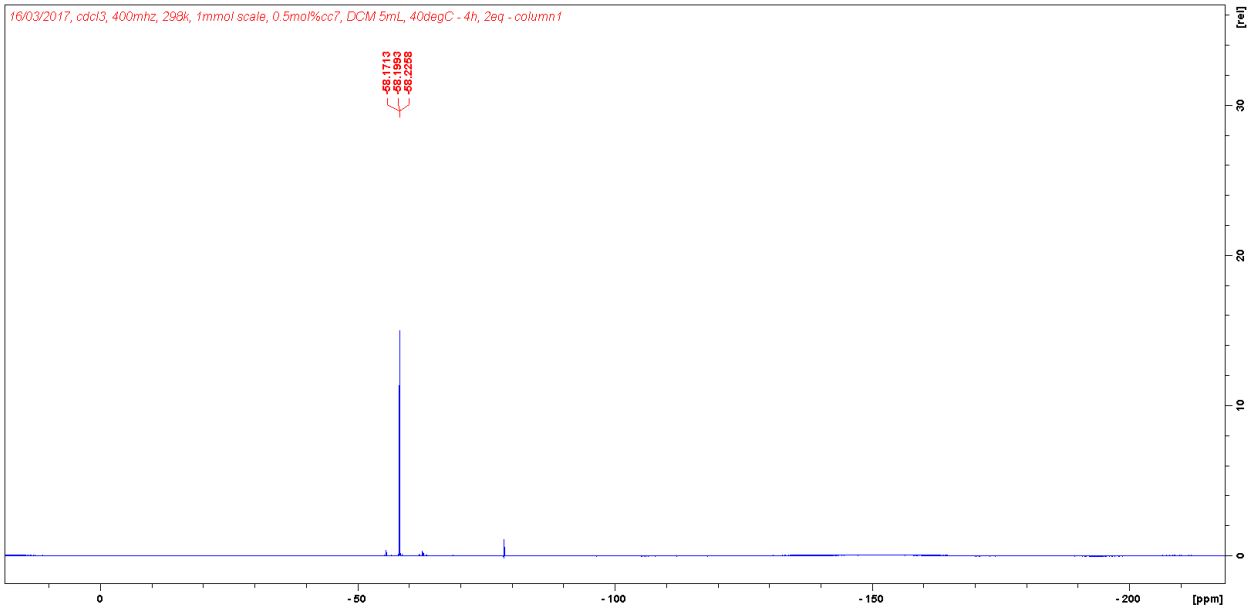
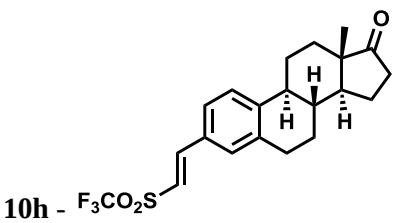


Figure S83. ^{19}F NMR spectrum of **8aa** in deuterated chloroform.



10h - F_3CO_2S

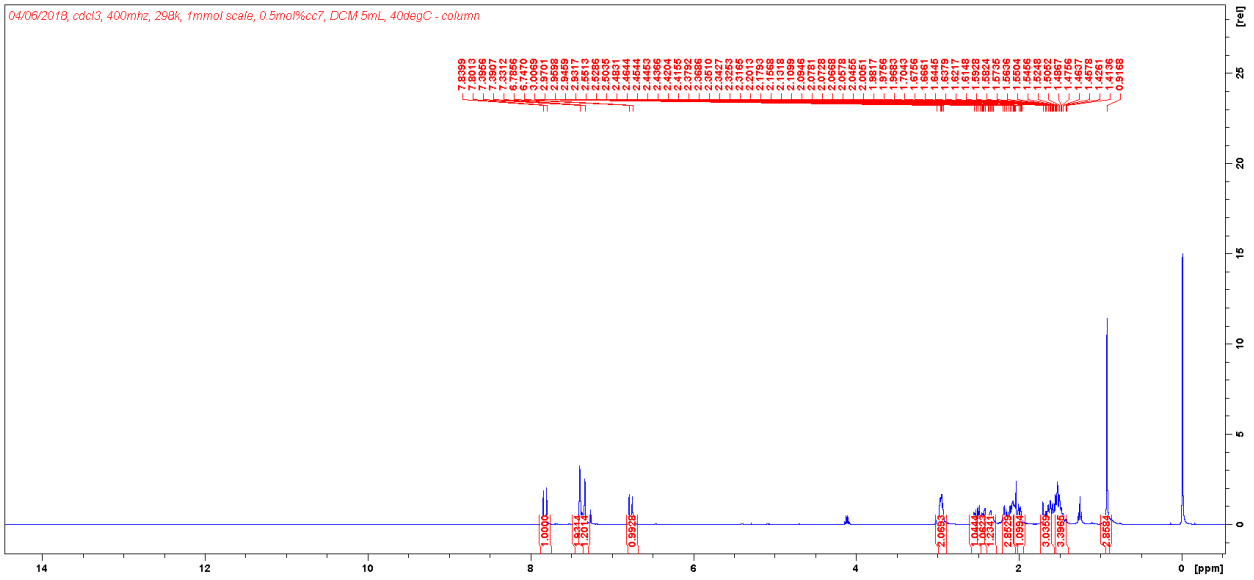


Figure S84. ^{1}H NMR spectrum of **10h** in deuterated chloroform.

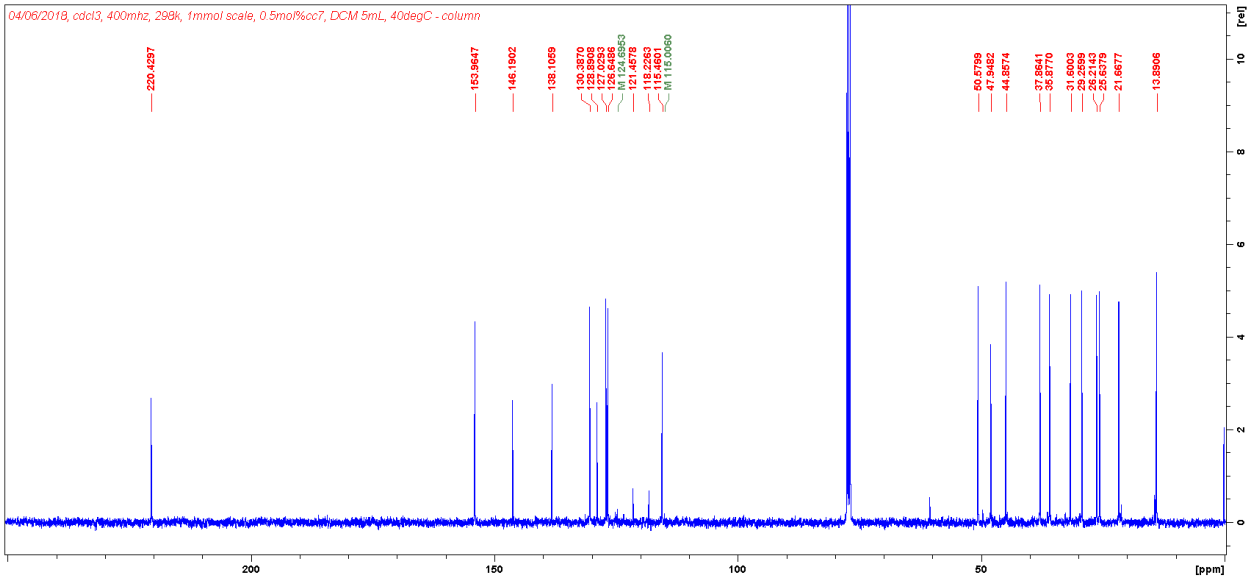


Figure S85. $^{13}C\{^{1}H\}$ NMR spectrum of **10h** in deuterated chloroform.

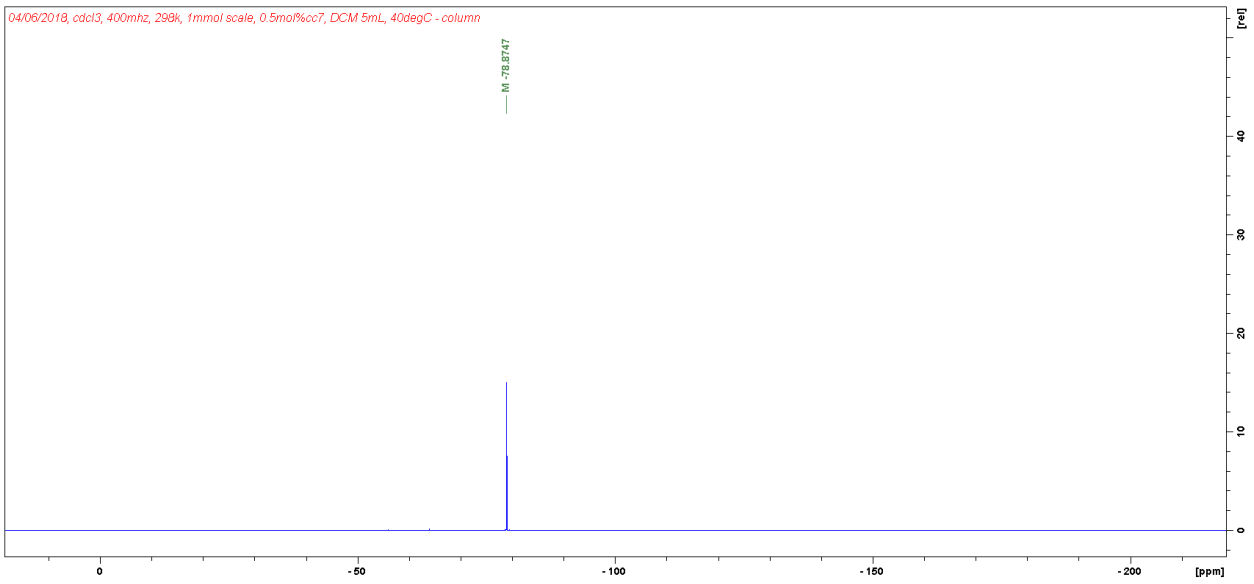
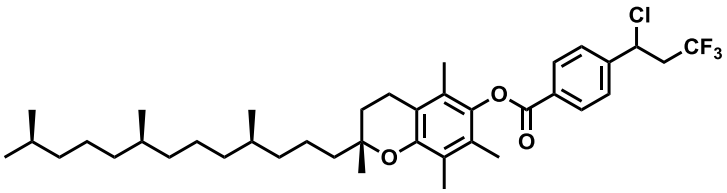


Figure S86. ^{19}F NMR spectrum of **10h** in deuterated chloroform.

8ac -



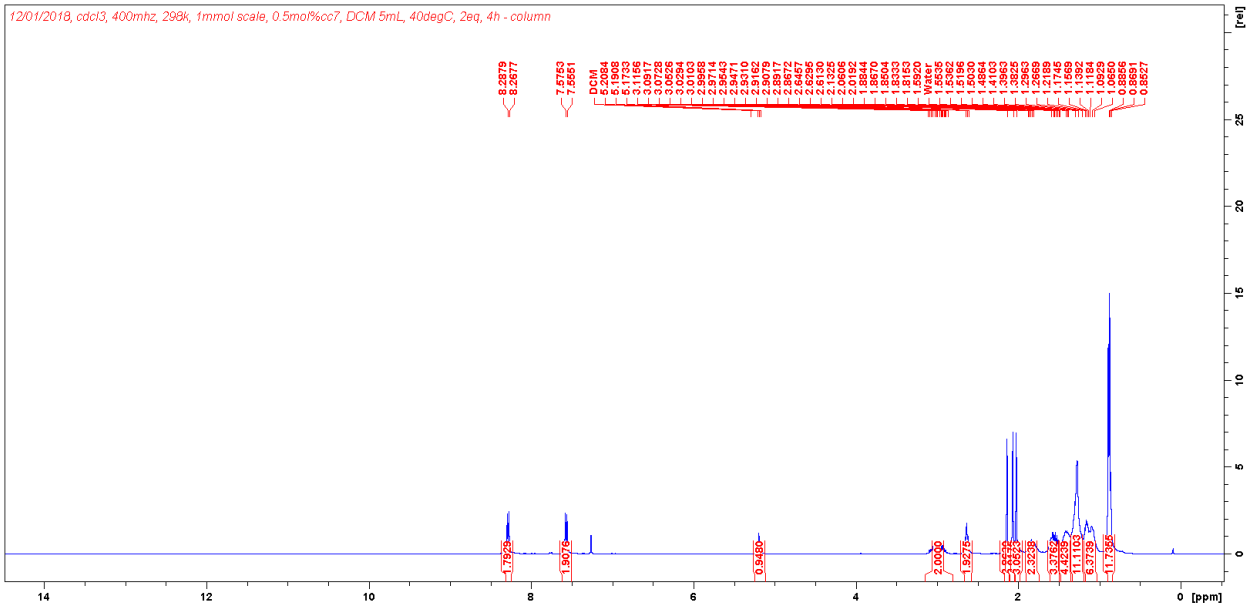


Figure S87. ^{1}H NMR spectrum of **8ac** in deuterated chloroform.

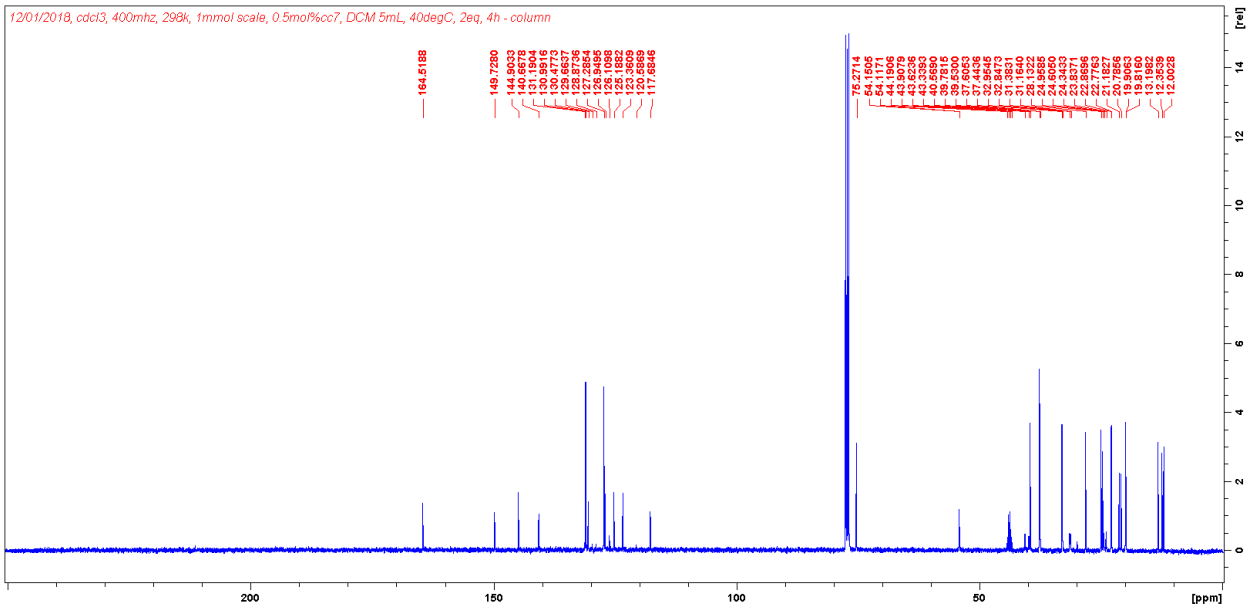


Figure S88. $^{13}C\{^{1}H\}$ NMR spectrum of **8ac** in deuterated chloroform.

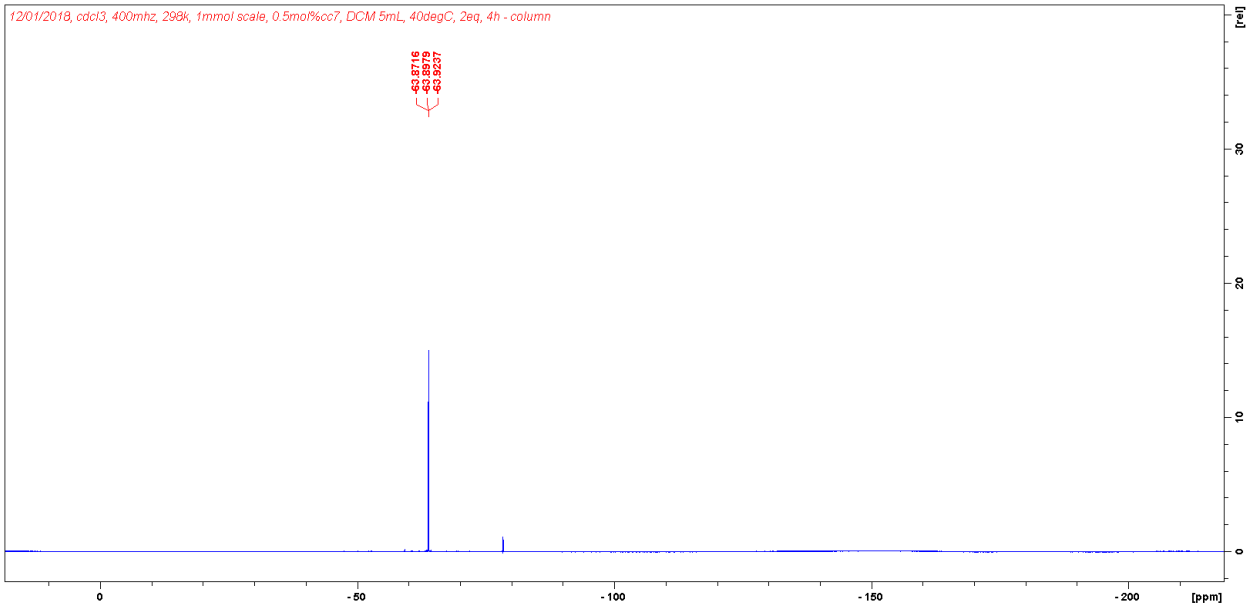


Figure S89. ^{19}F NMR spectrum of **8ac** in deuterated chloroform.

8ad -

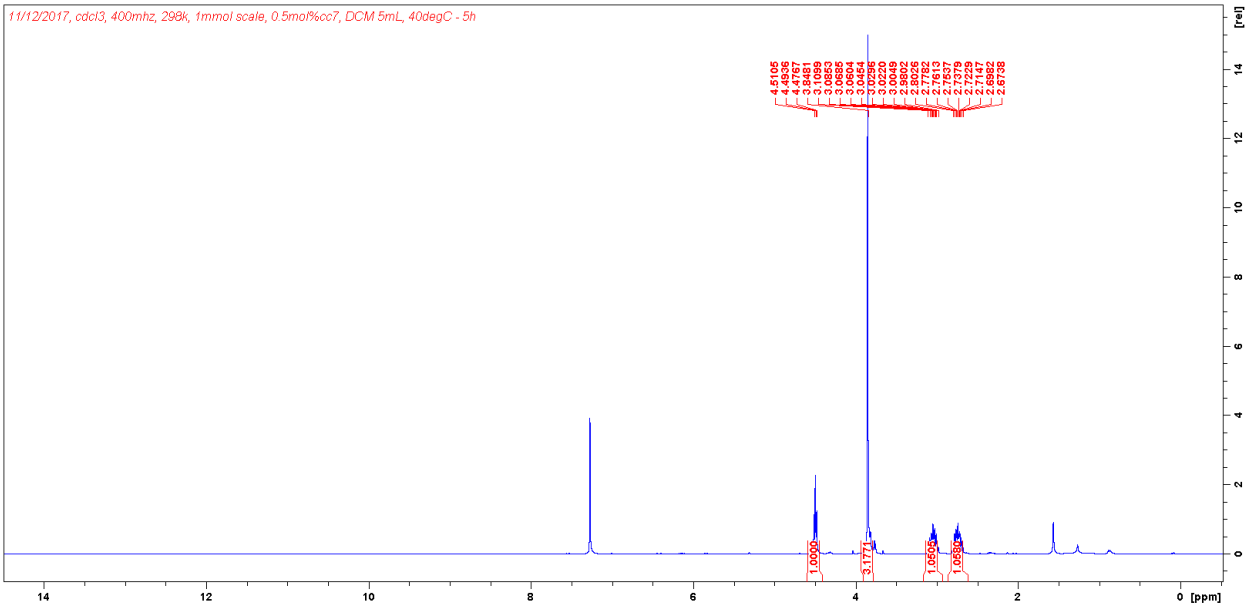


Figure S90. ^{1}H NMR spectrum of **8ad** in deuterated chloroform.

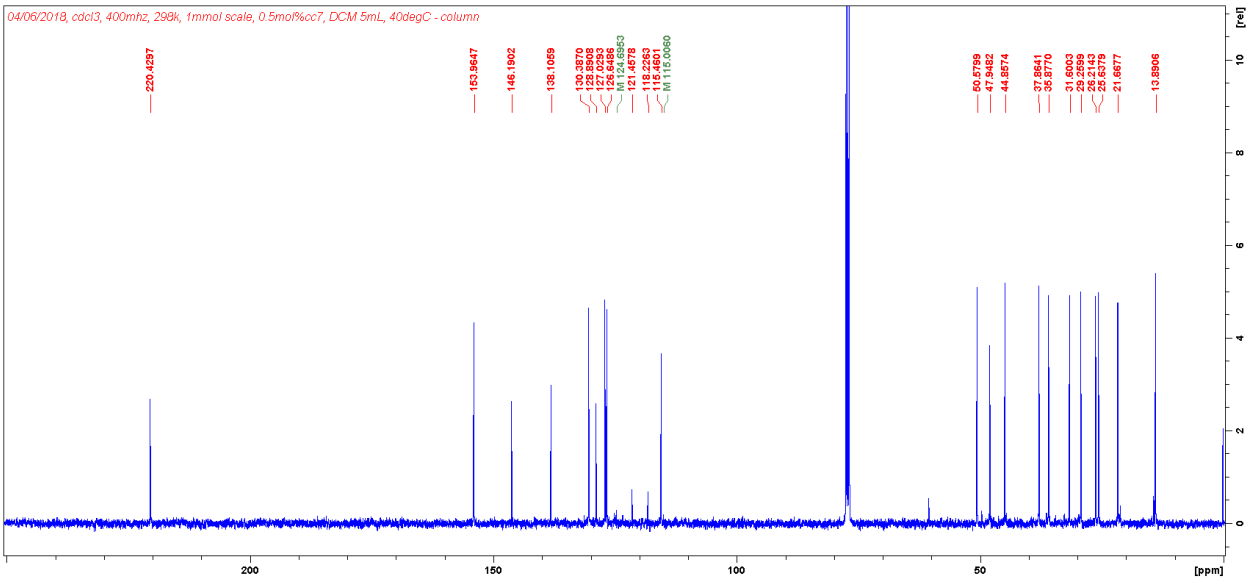


Figure S91. ^{13}C{^{1}H} NMR spectrum of **8ad** in deuterated chloroform.

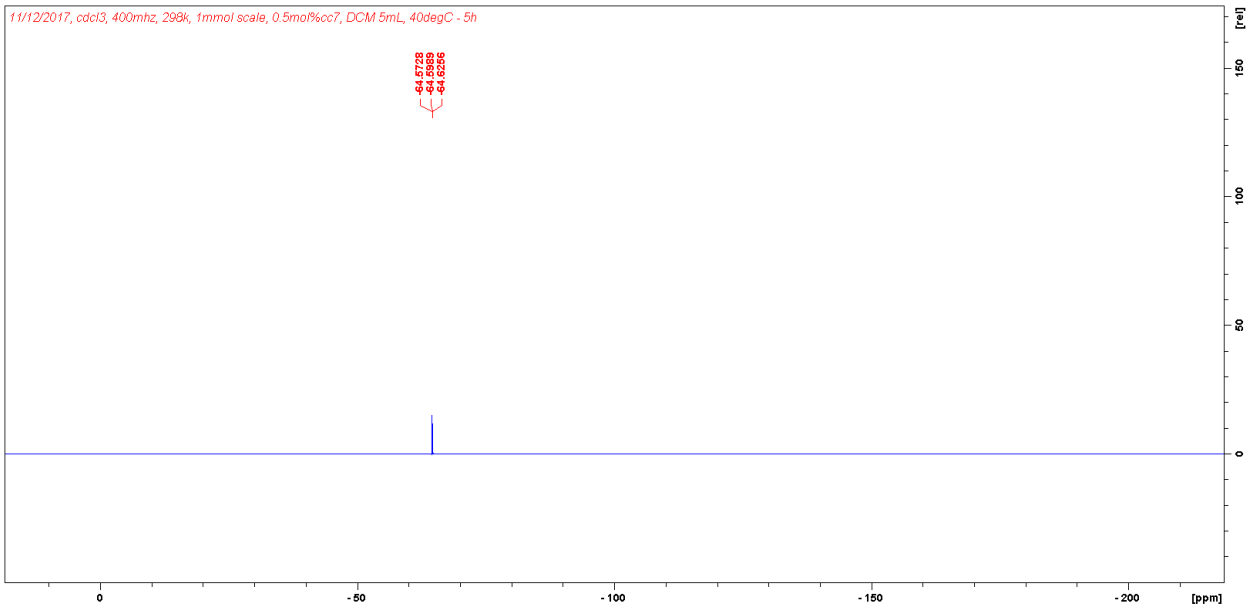


Figure S92. ^{19}F NMR spectrum of **8ad** in deuterated chloroform.

8af -

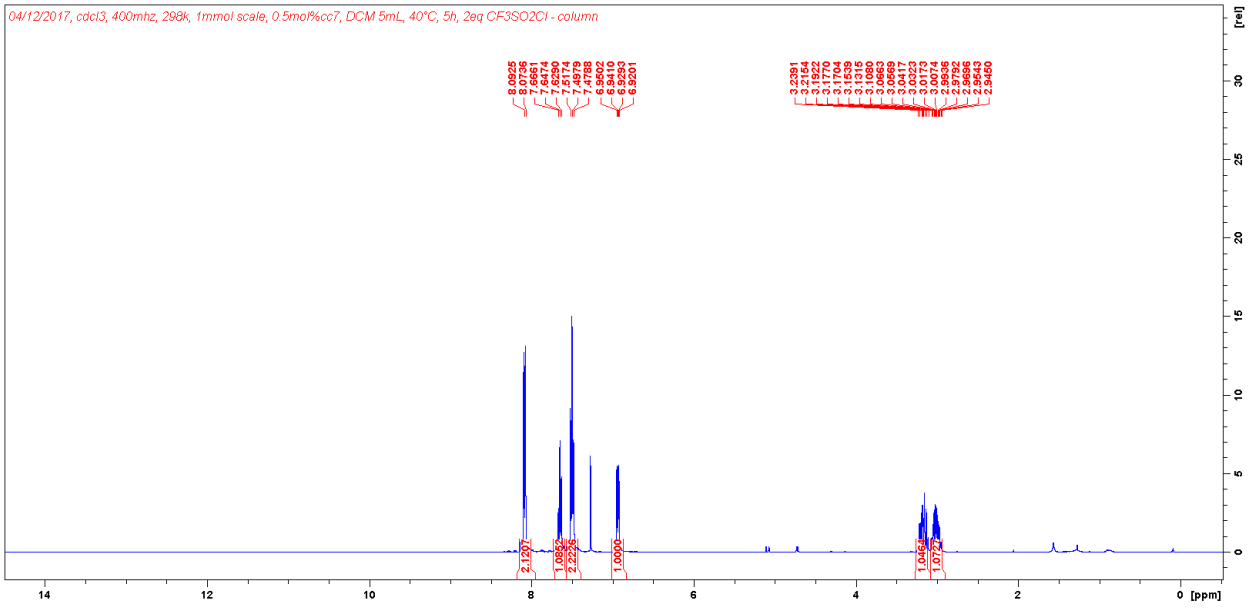


Figure S93. ^{1}H NMR spectrum of **8af** in deuterated chloroform.

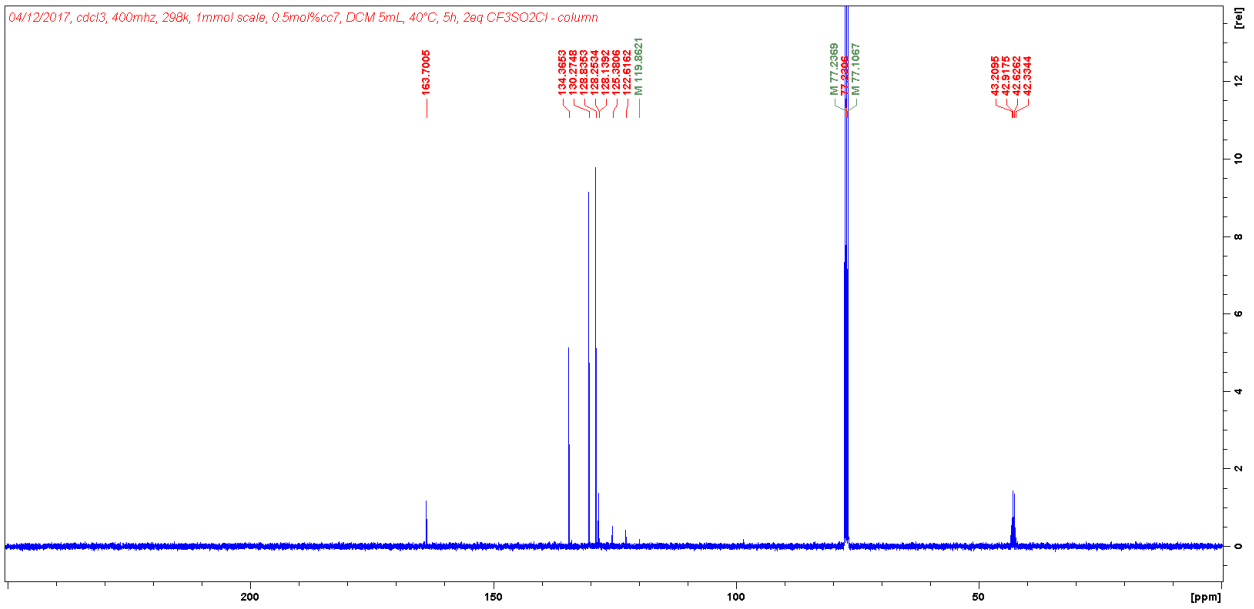


Figure S94. $^{13}C\{^{1}H\}$ NMR spectrum of **8af** in deuterated chloroform.

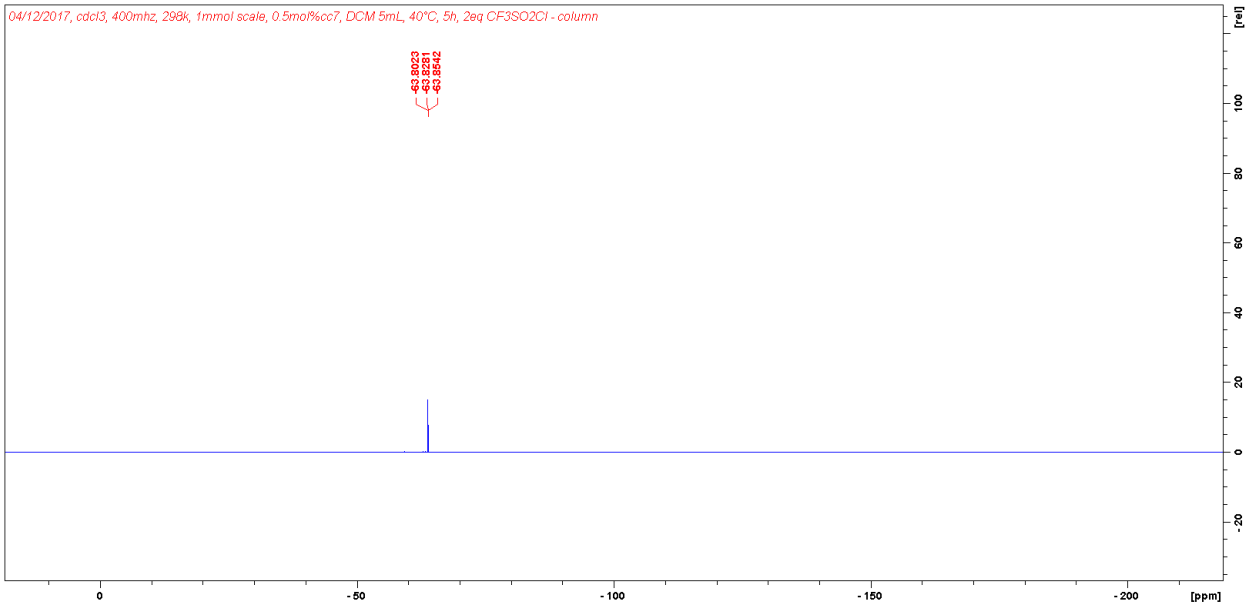


Figure S95. ^{19}F NMR spectrum of **8af** in deuterated chloroform.

8ag -

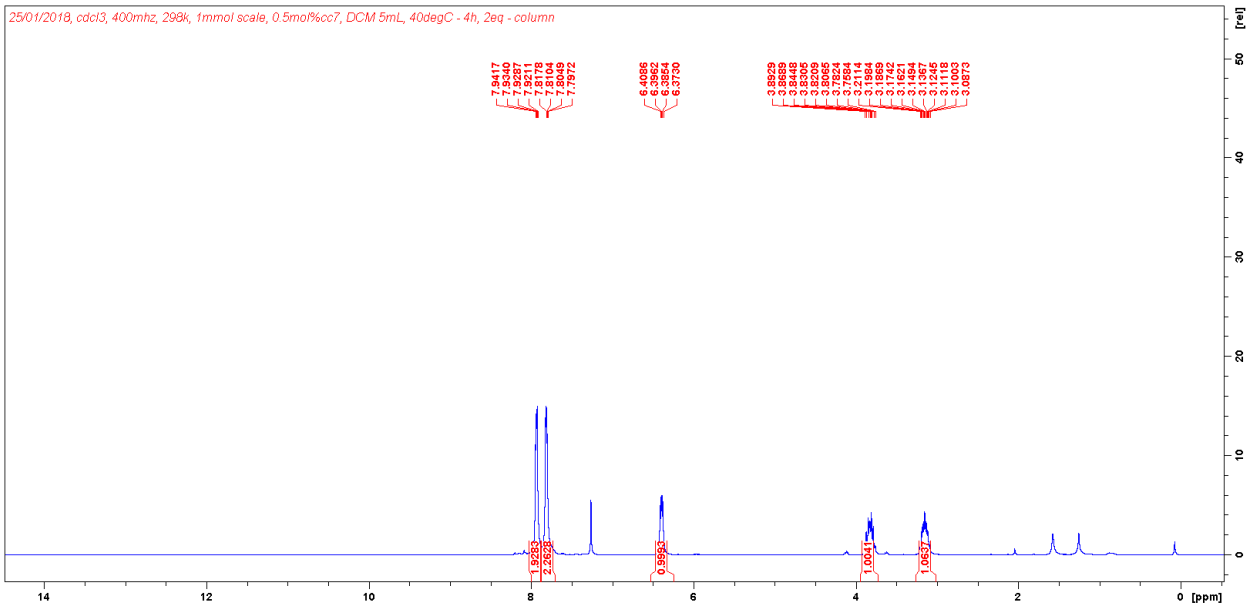


Figure S96. ^{1}H NMR spectrum of **8ag** in deuterated chloroform.

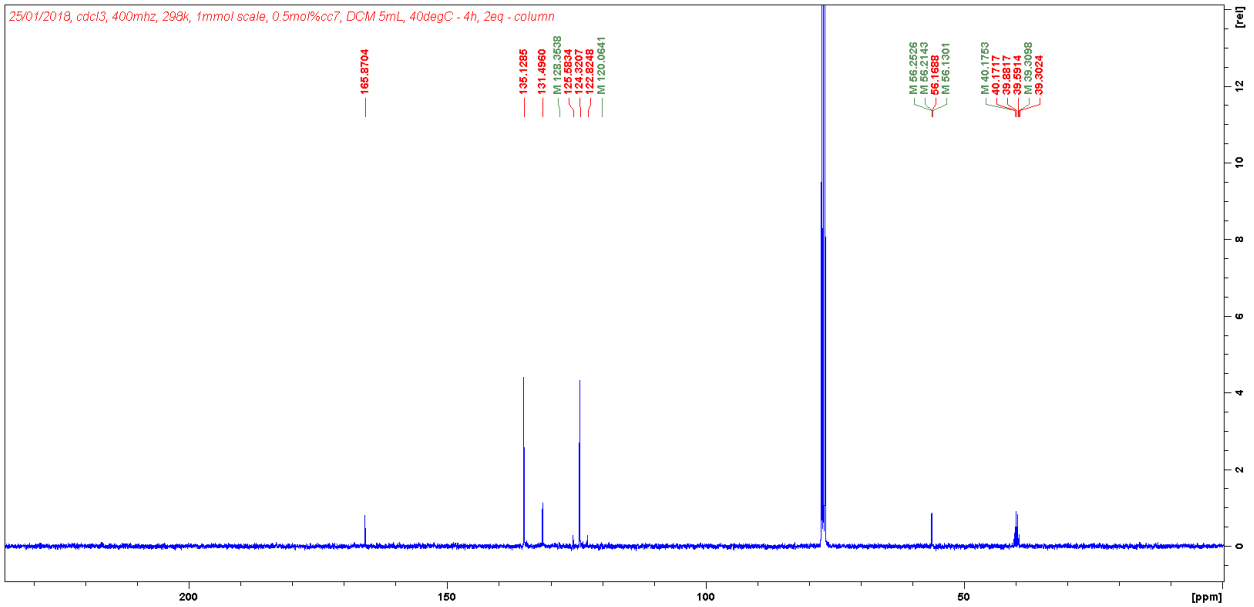


Figure S97. ^{13}C{^{1}H} NMR spectrum of **8ag** in deuterated chloroform.

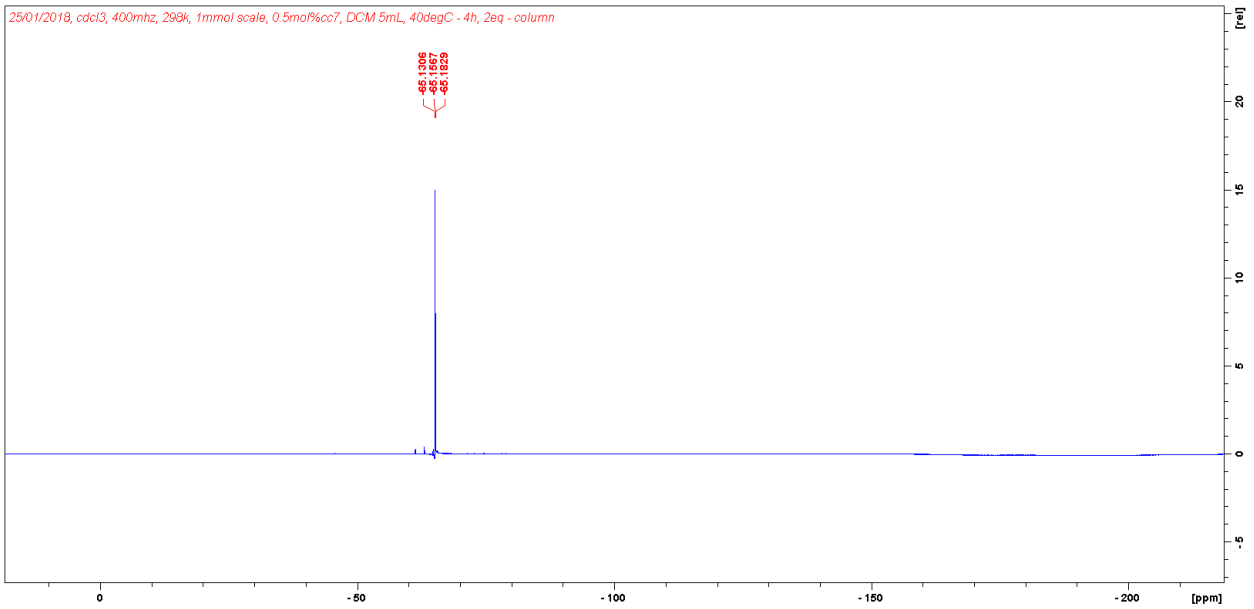
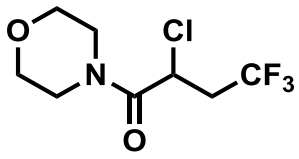


Figure S98. ^{19}F NMR spectrum of **8ag** in deuterated chloroform.

8ah -



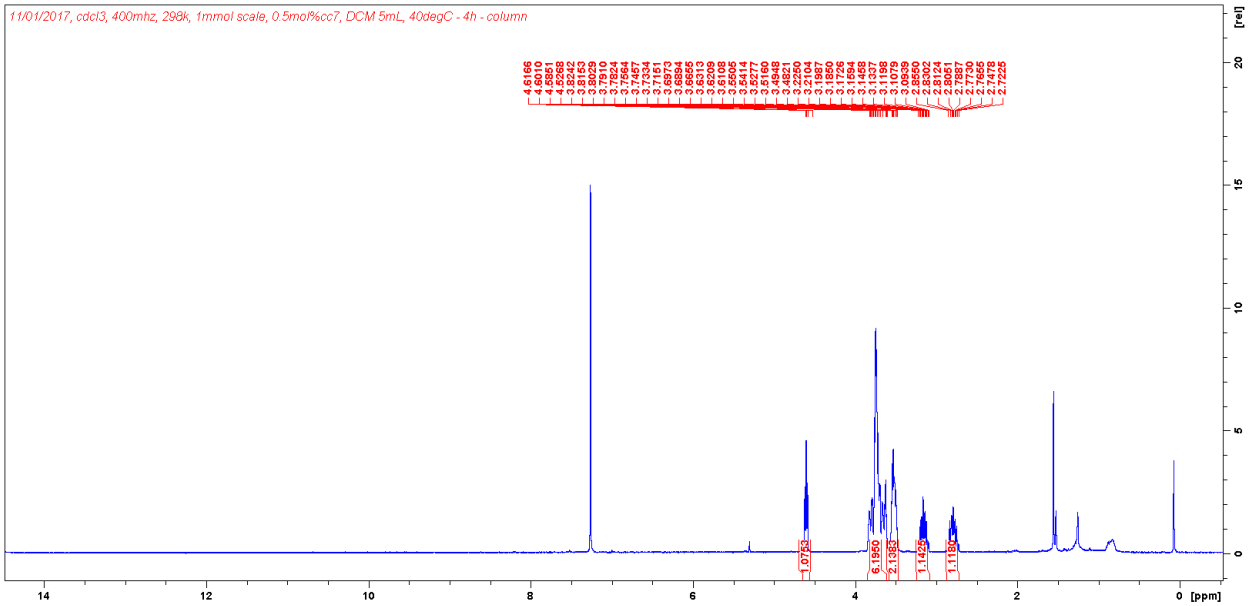


Figure S99. ^{1}H NMR spectrum of **8ah** in deuterated chloroform.

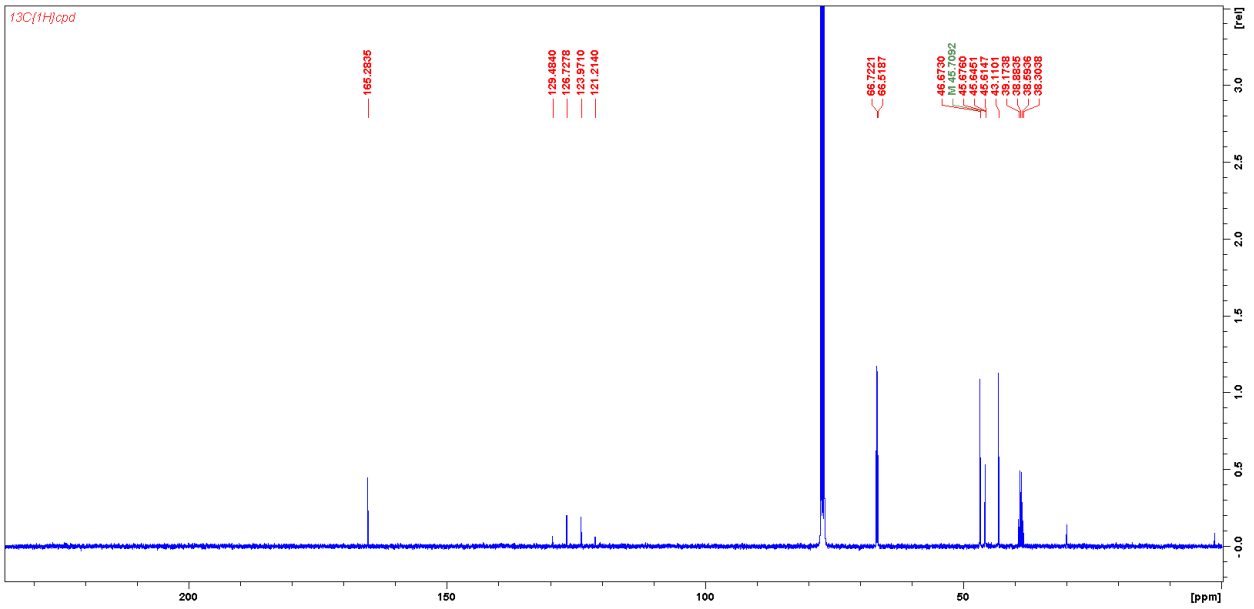


Figure S100. $^{13}C\{^{1}H\}$ NMR spectrum of **8ah** in deuterated chloroform.

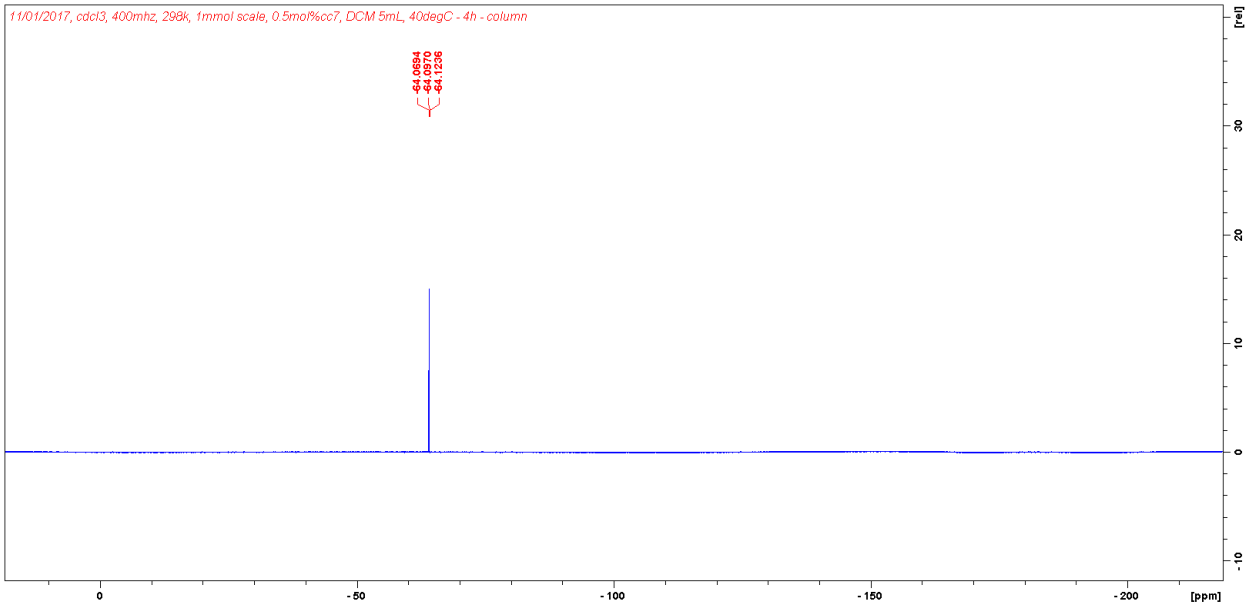


Figure S101. ^{19}F NMR spectrum of **8ah** in deuterated chloroform.