Bimodal photocatalytic behaviour of a Zinc β-diketiminate: Application to trifluoromethylation reaction

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1.0 General information

1.1 Materials:

All reactions were carried out using air sensitive manipulations and glove box unless otherwise mentioned. Arenes, heteroarenes and trifluoromethylsulfonylchloride were obtained from Sigma Aldrich and used without further purification. DMSO-D6, CD_3CN and $CDCl_3$ were purchased from Euroisotope. All chemicals were used as obtained. Acetonitrile was refluxed over calcium hydride and collected via vacuum distillation. Solvents were degassed using three freeze-pump-thaw cycles for reactions and spectroscopic measurements.

1.2 Physical Measurements.

Emission spectra were collected by Fluoromax-4 (Horiba Jobin Yvon, NJ) Spectro fluorophotometer. The analyte solution was placed in quartz cuvettes equipped with screw cap having the path length of 10 mm. Collected data were plotted using Originpro8.

^{1}H NMR spectra were recorded on a Bruker 400 MHz instrument. ^{13}C NMR and ^{19}F NMR spectra were recorded on the same instrument at frequencies of 101 MHz and 376 MHz, respectively. Chemical shifts (δ) are expressed in ppm. Abbreviations for signal couplings are: s, singlet; d, doublet; t, triplet; m, multiplets.

Cyclic Voltammetry experiments were performed on a Keithley 2450 potentiostat. For the measurement, three electrode system was used that consisted of a glassy carbon working electrode, a Pt-wire as counter electrode, and an Ag/Ag^+ (3 M KCl) as the reference electrode. 0.1 M solution of tetrabutyl ammonium hexafluorophosphate was prepared in dichloromethane and used as the electrolyte.

UV/Vis/NIR spectra were recorded with a J&M TIDAS spectrophotometer. Spectroelectrochemical measurements were carried out in an optically transparent thin-layer electrochemical (OTTLE) cell[S1] (CaF_2 windows) with a platinum-mesh working electrode (100 mesh woven from 0.064 mm diameter wire; 99.99% (metals basis)), a platinum-mesh counter electrode, and a silver-foil pseudo-reference electrode. Anhydrous and degassed dichloromethane ($H_2O \leq 0.005\%$, puriss., Sigma Aldrich) distilled from CaH_2 was used as the solvent. A 0.1 M *n*-Bu_4PF_6 solution in dichloromethane was used as electrolyte.

EPR spectra at X-band frequency (ca. 9.5 GHz) were obtained with a Magnettech MS-5000 benchtop EPR spectrometer equipped with a rectangular TE 102 cavity. The measurements were carried out in synthetic quartz glass tubes. For EPR spectroelectrochemistry, a three-electrode setup was employed using two Teflon coated platinum wires (0.005” bare, 0.008” coated) as working (or a Teflon coated gold wire (0.003” bare, 0.0055” coated) as working electrode) and platinum as counter electrode and a Teflon-coated silver wire (0.005” bare, 0.007” coated) as pseudoreference electrode. The low temperature EPR-experiment was performed at -50 °C under constant flow of liquid nitrogen.

2.0 Cyclic voltammetry and calculation of excited-state potential.

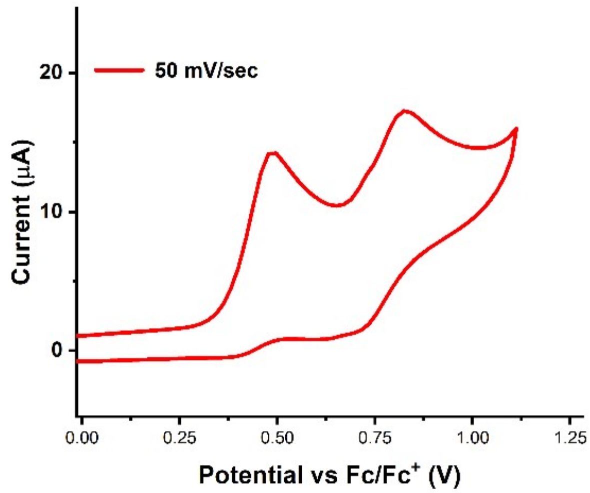


Fig S1. Oxidation wave of **1**, measured in dry and degassed DCM where 0.1 M solution of tetrabutyl-ammonium hexafluorophosphate salt was used as an electrolyte. The full diagram with reduction wave was earlier shown in our previous work.[S2]

Excited state potential calculation: The excited state oxidation potential for catalyst **1** was calculated using equation 1,

$$E^*_{ox} = E_{ox} - E_{00} \quad \text{(eq. 1)}$$

where, E^*_{ox} represents oxidation potential of excited state, E_{ox} represents oxidation potential of ground state and E_{00} represents the difference in energy between the zeroth vibrational states of the ground and excited states. E_{00} was obtained from the intersection point of normalized absorption and emission spectra as 3.01 V.

3. 0 Molecular orbital visualization

Computational Details:

All calculations were carried out using Density Functional Theory as implemented in the Gaussian09[S3] quantum chemistry programs. The geometries of stationary points were optimized with M06-2X functional.[S4] We used double-ζ basis set with the relativistic effective core potential of Hay and Wadt (LANL2DZ) for the zinc atom and 6-31G* basis set for other elements (H, C, O and N). The geometries were optimized without any symmetry constraints. Harmonic force constants were computed at the optimized geometries to characterize the stationary points as minima. The molecular orbitals and spin density were visualized by Gaussview.

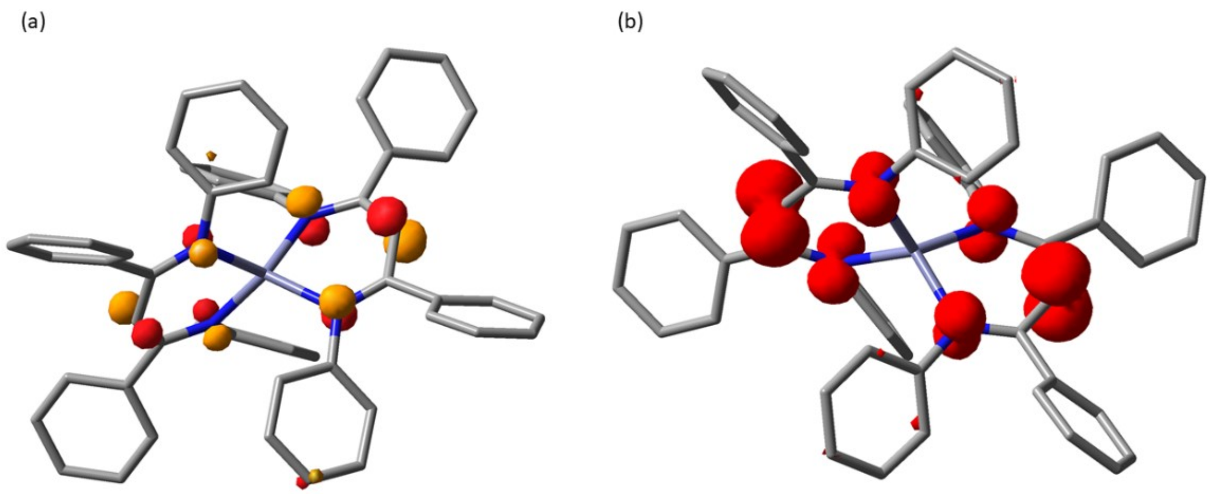


Fig S2. (a) SOMO for one electron oxidized **1** where the iso value was set to 0.06 (e bohr^{-3})$^{1/2}$, (b) Spin density distribution for two-electron-oxidized **1** calculated using the M06-2X/6-31G* level of theory. The isodensity plot for excess α-spin was set to 0.006 (e bohr^{-3})$^{1/2}$.

4.0 Stern-Volmer experiment

Preparation of sample: In a nitrogen filled glove box, 10^{-3} M solution of catalyst **1** was prepared in 10 mL of dry and degassed MeCN. Double dilution was done to give10^{-8} M stock solution in 10 mL MeCN. Different quencher concentrations of CF_3SO_2Cl (0.001 M–0.005 M) were prepared and used. The fluorescence measurement was performed in a 10 mm, 4 mL screw-cap quartz cuvette. Emission intensity was recorded for each solution at excitation maxima 370 nm. Integrated fluorescence intensities were plotted against absolute quencher concentration using Stern-Volmer equation (equation 2),

$$\frac{Io}{I} = 1 + K[Q] = 1 + k_q\tau[Q] \quad \text{(eq. 2)}$$

where, I_o = fluorescence intensity of in absence of quencher, I = fluorescence intensity in the presence of quencher and [Q] is the concentration of quencher, K = Stern-Volmer constant which is the product of average radiative lifetime (τ) and quenching rate constant (k_q). Average excited-state lifetime was calculated using equation 3,

$$\tau = \frac{\sum_{i=1}^{n} \alpha_i \tau_i^2}{\sum_{i=1}^{n} \alpha_i \tau_i} \quad \text{(eq. 3)}$$

[S5]

where α_i and τ_i denote the amplitude fractions and lifetimes, respectively, and n is the number of lifetime components. For catalyst **1**, with amplitude fractions $\alpha_1 = 9.81 \times 10^{-02}$, $\alpha_2 = 9.42 \times 10^{-02}$

α_3 = 1.81 × 10^{-02} and their respective lifetime contribution; τ_1 = 4.98 ns, τ_2 = 1.81 ns, τ_3 = 13.6 ns. The average lifetime was found to be 6.75 × 10^{-09} sec.

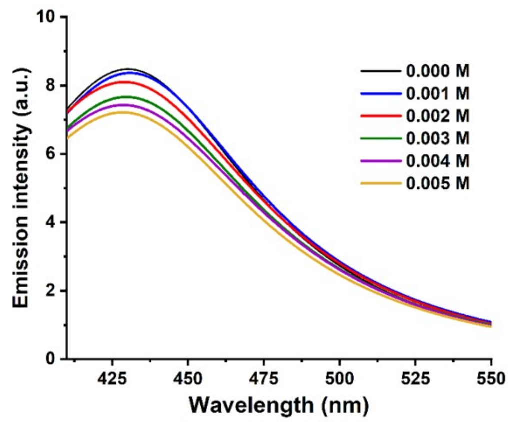
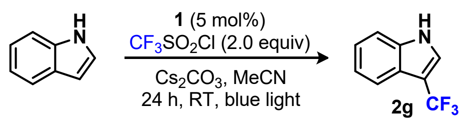


Fig S3. Fluorescence-quenching of **1** upon excitation at 370 nm in MeCN in the presence of CF_3SO_2Cl as quencher.

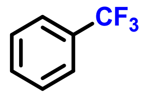
5.0 Reaction conditions for trifluoro-methylated compounds.



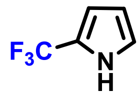
Workup procedure (A) for volatile products: A flame-dried screw-cap vial equipped with magnetic bead was packed with substrate (1 equiv), CF_3SO_2Cl (2 equiv), Cs_2CO_3 (0.5 equiv) and **1** (5 mol%) in MeCN (0.5 mL) in glove box and irradiated with blue light (12 W, positioned 10 cm from reaction tube). After 24 hours, 4-fluoroacetohphenone (1 equiv), 0.5 mL MeCN-D_3 was added to the reaction mixture and ^{19}F NMR was recorded for *in situ* NMR yields. Due to the volatile nature and wide availability of the product, no purification was attempted on this reaction mixture. The fluorine signals of the product were identical to those of a commercially available sample.

Workup procedure (B) for non-volatile products: A flame-dried sealed tube equipped with magnetic bead was packed with substrate (1 equiv), CF_3SO_2Cl (2 equiv), Cs_2CO_3 (1 equiv) and **1** (5 mol%) in MeCN (2 mL) in glove box and irradiated with blue light (12 W, positioned 10 cm from reaction tube). After 24 hours, acetonitrile was removed under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: EtOAc/hexanes) to afford the corresponding product.

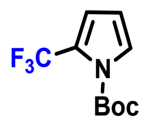
4.0 Spectroscopic characterization of products from trifluoromethylation reactions catalyzed by 1.



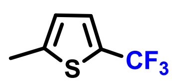
(trifluoromethyl)benzene (2a): Reaction procedure (A) was followed with benzene (100 µL, excess), CF_3SO_2Cl (50 µL, 1.5 mmol), Cs_2CO_3 (50 mg, 0.15 mmol)) and **1** (6.1mg, 5 mol%) and a reaction time of 24 hours. 4-fluoroacetophenone was added to the reaction mixture and analyzed directly by ^{19}F NMR (74 % yield) and is in accordance with literature.[S6] The product is volatile in nature and no further attempt was made for its isolation. ^{19}F NMR (376 MHz, CD_3CN) δ -63.59.



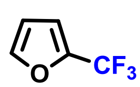
2-(trifluoromethyl)-1H-pyrrole (2b): Reaction procedure (A) was followed with pyrrole (11 µL, 0.15 mmol), CF_3SO_2Cl (32 µL, 0.30 mmol), Cs_2CO_3 (24 mg, 0.07 mmol)) and **1** (6.1mg, 5 mol%) and a reaction time of 24 hours was provided. 4-fluoroacetophenone was added to the reaction mixture and analyzed directly by ^{19}F NMR (40% yield) and is in accordance with literature[S6]. The product is volatile in nature and no further attempt was made for their isolation. ^{19}F NMR (376 MHz, CD_3CN) δ -59.98.



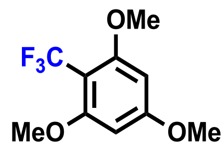
tert-butyl-2-(trifluoromethyl)-1H-pyrrole-1-carboxylate (2c): Reaction procedure (A) was followed with N-boc-pyrole (32 µL, 0.15 mmol), CF_3SO_2Cl (23 µL, 0.30 mmol), Cs_2CO_3 (24 mg, 0.07 mmol)) and **1** (6.1mg, 5 mol%) and a reaction time of 24 hours. 4-fluoroacetophenone was added to the reaction mixture was analyzed directly by ^{19}F NMR (83% yield) and is in accordance with literature [S6]. The product is volatile in nature and no further attempt was made for their isolation. ^{19}F NMR (376 MHz, CD_3CN) δ -58.99.



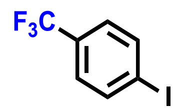
2-methyl-5-(trifluoromethyl)thiophene (2d): Reaction procedure (A) was followed with 2-methyl thiophene (15 µL, 0.15 mmol), CF_3SO_2Cl (32 µL, 0.30 mmol), Cs_2CO_3 (24 mg, 0.07 mmol)) and **1** (6.1 mg, 5 mol%) and a reaction time of 24 hours. 4-fluoroacetophenone (50 mg, 0.36 mmol) was added to the reaction mixture and analyzed directly by ^{19}F NMR (32% yield) and is in accordance with reported literature [S6].
^{19}F NMR (376 MHz, CD_3CN) δ -55.30.



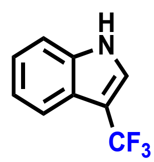
2-(trifluoromethyl)furan (2e): Reaction procedure (A) was followed with furan (14 µL, 0.2 mmol), CF_3SO_2Cl (31 µL, 0.4 mmol), Cs_2CO_3 (43 mg, 0.1 mmol)) and **1** (8 mg, 5 mol%) and a reaction time of 24 hours. 4-fluoroacetophenone was added to the reaction mixture and analyzed directly by ^{19}F NMR (20% yield).
^{19}F NMR (376 MHz, CD_3CN) δ -65.73.



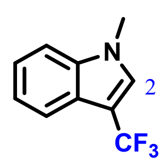
1,3,5-trimethoxy-2-(trifluoromethyl)benzene (2f). Reaction procedure (B) was followed with trimethoxybenzene (168 mg, 1.0 mmol), CF_3SO_2Cl (215 µL, 2.0 mmol), Cs_2CO_3 (330 mg, 1 mmol) and **1** (20 mg, 5 mol%). The product was isolated as colourless oil (225 mg, 96% ; mono: bis trifluoromethylated = 94.4% : 5.6%). Analytical data matches literature-reported product[S7].
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18 (s, 2H), 3.88 (s, 6H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.62, 160.54, 124.47 (q, J = 274.72 Hz), 100.47 (q, J = 32.32 Hz), 91.33, 56.36 (d, J = 3.03 Hz), 55.5 (d, J = 3.03 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -54.13.



1-iodo-4-(trifluoromethyl)benzene (2g): Reaction procedure (B) was followed with iodobenzene (102 mg, 0.5 mmol), CF_3SO_2Cl (107 µL, 1.0 mmol), Cs_2CO_3 (163 mg, 0.5 mmol) and **1** (20 mg, 5 mol%). The product was isolated as colourless oil (132 mg, 98%). Analytical data matches literature reported product [S8].
^{1}H NMR (400 MHz, CDCl3) δ 7.34 – 7.20 (m, 2H), 6.50 (t, J = 8.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.02, 134.41, 132.51 (q, J= 32.32 Hz), 130.53, 124.62 (q, J= 4.04 Hz), 123.08 (q, J = 273.71 Hz), 93.98. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.89.

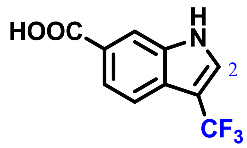


3-(trifluoromethyl)-1H-indole (2h): Reaction procedure (B) was followed with indole (58.5 mg, 0.5 mmol), CF_3SO_2Cl (107 µL, 1.0 mmol), Cs_2CO_3 (82 mg, 0.25 mmol)) and **1** (20 mg, 5 mol%). Product was isolated as white solid (84 mg, 61%) which turns brown overtime. Analytical data matches literature reported product.[S9]
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.69 – 7.64 (m, 1H), 7.37 (dd, J = 7.9, 1.0 Hz, 1H), 7.29 – 7.20 (m, 2H), 7.17 (d, J = 2.6 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.66.

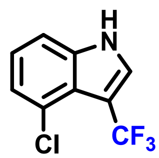


1-methyl-3-(trifluoromethyl)-indole (2i): Reaction procedure (B) was followed with N-methyl indole (65 mg, 0.5 mmol), CF_3SO_2Cl (107 µL, 1.0 mmol), Cs_2CO_3 (82 mg, 0.25 mmol)) and **1** (20 mg, 5 mol%). Product was isolated as pale-yellow oil (73 mg, 74 %, r.r. = 96.2% : 3.8%). Analytical data matches literature-reported product.[S10]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.1 Hz, 1H), 7.45 – 7.33 (m, 2H), 7.28 – 7.22 (m, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.74, 125.89, 124.70, 121.77 (d, J = 35.35 Hz), 121.37, 121.405 (q, J = 269.67 Hz), 120.03, 110.06, 108.28 (q, J = 3.03 Hz), 31.5 (d, J = 3.03 Hz).

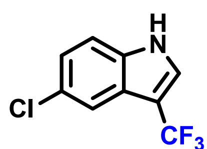
^{19}F NMR (376 MHz, $CDCl_3$) δ -56.76.



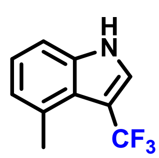
3-(trifluoromethyl)-1H-indole-6-carboxylic acid (2j): Reaction procedure (B) was followed with 6-carboxylic acid indole (40 mg, 0.25 mmol), CF_3SO_2Cl (54 µL, 0.5 mmol), Cs_2CO_3 (40 mg, 0.13 mmol)) and **1** (10 mg, 5 mol%). Product was isolated as white solid (30.9 mg, 54%, r.r. = 85.5% : 14.5%).
^1H NMR (400 MHz, DMSO-d_6) δ 12.68 (s, 1H), 11.74 (s, 1H), 8.06 (s, 1H), 7.78 – 7.52 (m, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.98, 134.25, 129.98 (d, J = 217 Hz), 127.59, 126.03, 124.55, 120.59, 116.87, 114.29, 103.55. ^{19}F NMR (376 MHz, DMSO-d_6) δ -56.81.



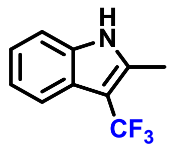
4-chloro-3-(trifluoromethyl)-1H-indole (2k): Reaction procedure (B) was followed with 4-chloro indole (38 mg, 0.25 mmol), CF_3SO_2Cl (54 µL, 0.5 mmol), Cs_2CO_3 (42 mg, 0.13 mmol)) and **1** (10 mg, 5 mol%). The product was isolated as white solid (32 mg, 60%).
^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.80 (d, J = 1.9 Hz, 1H), 7.36 (dd, J = 8.7, 1.9 Hz, 1H), 7.28 (s, 1H), 7.21 (d, J = 2.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.69, 129.24, 129.03 (q, J = 74.7 Hz), 127.14, 120.49 (q, J = 269.7 Hz), 122.35, 115.16, 113.78, 107.46 (q, J = 3.30 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.80.



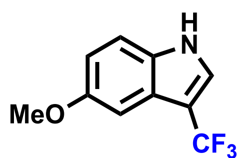
5-chloro-3-(trifluoromethyl)-1H-indole (2l): Reaction procedure (B) was followed with 5-chloro indole (38 mg, 0.25 mmol), CF_3SO_2Cl (54 µL, 0.5 mmol), Cs_2CO_3 (42 mg, 0.13 mmol)) and **1** (0 mg, 5 mol%). Product was isolated as white solid (27 mg, 52%).
^1H NMR (400 MHz, DMSO) δ 11.57 (s, 1H), 7.58 (dd, J = 6.0, 2.3 Hz, 2H), 7.46 – 7.22 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 133.68, 128.04 (d, J = 256.54 Hz), 126.76, 126.28, 124.89, 124.20, 119.28, 114.37, 112.35, 102.54. ^{19}F NMR (376 MHz, DMSO) δ -59.00.



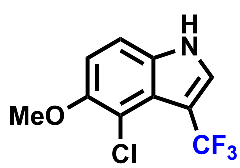
4-methyl-3-(trifluoromethyl)-1H-indole (2m): Reaction procedure (B) was followed with 4-methyl indole (33 mg, 0.25 mmol), CF_3SO_2Cl (54 µL, 0.5 mmol), Cs_2CO_3 (42 mg, 0.13 mmol)) and **1** (10 mg, 5 mol%). The product was isolated white solid. (38 mg, 71 %).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.19 (d, *J* = 2.6 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.1 Hz, 1H), 2.49 (s, 3H). 13C NMR (101 MHz, $CDCl_3$) δ 134.63, 127.75 (d, J = 236.34 Hz), 125.08, 123.72, 120.78, 120.73, 120.66, 116.12, 107.14, 16.34, 16.32. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.42.



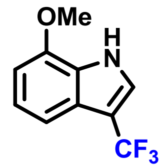
2-methyl-3-(trifluoromethyl)-1H-indole (2n): Reaction procedure (B) was followed with 2-methyl indole (66 mg, 0.5 mmol), CF_3SO_2Cl (110 µL, 1.0 mmol), Cs_2CO_3 (84 mg, 0.25 mmol)) and **1** (20 mg, 5 mol%). Product was isolated as white solid (40 mg, 54 %). Analytical data matches literature reported product.[S11]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.53 (dd, *J* = 5.9, 3.0 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.20 – 7.13 (m, 2H), 2.43 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.94.



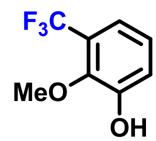
5-methoxy-3-(trifluoromethyl)-1H-indole (2o): Reaction procedure (B) was followed with 5-methoxy indole (37 mg, 0.25 mmol), CF_3SO_2Cl (54 µL, 0. mmol), Cs_2CO_3 (42 mg, 0.13 mmol)) and **1** (10 mg, 5 mol%). The product was isolated as white solid (26 mg, 48%).
^{11}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.24 (d, *J* = 8.8 Hz, 1H), 7.13 (d, *J* = 2.7 Hz, 1H), 7.07 (d, *J* = 2.3 Hz, 1H), 6.92 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.88, 130.07, 127.36 (d, J = 295.93 Hz) 125.87, 121.55, 114.08, 112.57, 106.20, 99.34, 55.93 (d, J = 3.03 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.10.



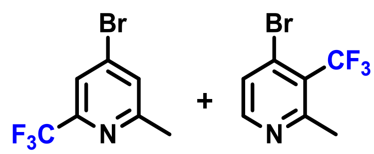
4-chloro-5-methoxy-3-(trifluoromethyl)-1H-indole (2p): Reaction procedure (B) was followed with 4-chloro-5-methoxy-1H-indole (45 mg, 0.25 mmol), CF_3SO_2Cl (54 µL, 0.5 mmol), Cs_2CO_3 (42 mg, 0.13 mmol)) and **1** (10 mg, 5 mol%). The product was isolated as brown solid (40 mg, 71%) which darkens to black overtime.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.30 (d, *J* = 8.7 Hz, 1H), 7.07 – 7.01 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.64, 129.11, 126.08, 120.81 (d, J = 270.68 Hz), 117.69, 114.01, 113.27, 112.01, 99.68, 55.89 (d, J = 4.04 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.78.



7-methoxy-3-(trifluoromethyl)-1H-indole (2q): Reaction procedure (B) was followed with 7-methoxy indole (37 mg, 0.25 mmol), CF_3SO_2Cl (54 µL, 0.5 mmol), Cs_2CO_3 (42 mg, 0.13 mmol)) and **1** (10 mg, 5 mol%). The product was isolated as pale brown solid (30 mg, 55%).
^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.30 (d, J = 8.7 Hz, 1H), 7.03 (d, J = 9.0 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.65, 129.46, 129.13, 126.09, 121.26 (d, J = 39.39 Hz), 120.83 (d, J = 269.67 Hz), 117.68, 113.27, 99.71, 55.89 (d, J = 4.04 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.78.



2-methoxy-3-(trifluoromethyl)phenol (2r): Reaction procedure (B) was followed with 2-methoxyphenol (32 mg, 0.25 mmol), CF_3SO_2Cl (54 µL, 0.5 mmol), Cs_2CO_3 (42 mg, 0.13 mmol)) and **1** (10 mg, 5 mol%). The product was isolated as pale brown solid (24 mg, 50%).
^1H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.28 (d, J = 8.0 Hz, 1H), 7.18 (t, J = 8.0 Hz, 1H), 6.78 (d, J = 7.7 Hz, 1H), 3.98 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.42, 126.80, 125.22, 122.41, 120.84 (q, J = 269.57 Hz), 111.83, 104.92, 55.69 (d, J = 4.04 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.67.



2s **2s'**

2s : 2s' = 63.4 % : 36.6 %

4-bromo-2-methyl-6-(trifluoromethyl)pyridine (2s): Reaction procedure (B) was followed with 4-bromo-2-methyl-pyridine (86 mg, 0.5 mmol), CF_3SO_2Cl (107 µL, 1.0 mmol), Cs_2CO_3 (81 mg, 0.25 mmol)) and **1** (20 mg, 5 mol%). Product was isolated as colourless oil (132 mg, 98%, r.r.: 63.4 % : 36.6 %)
^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 5.4 Hz, 1H), 7.29 (s, 1H), 7.21 (dd, J = 5.4 Hz, 1H), 6.73 (s, 1H), 2.47 (s, 3H), 2.20 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.01, 149.89, 137.85, 133.21, 127.02, 126.78, 124.34, 24.28, 21.33. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.34, -63.43.

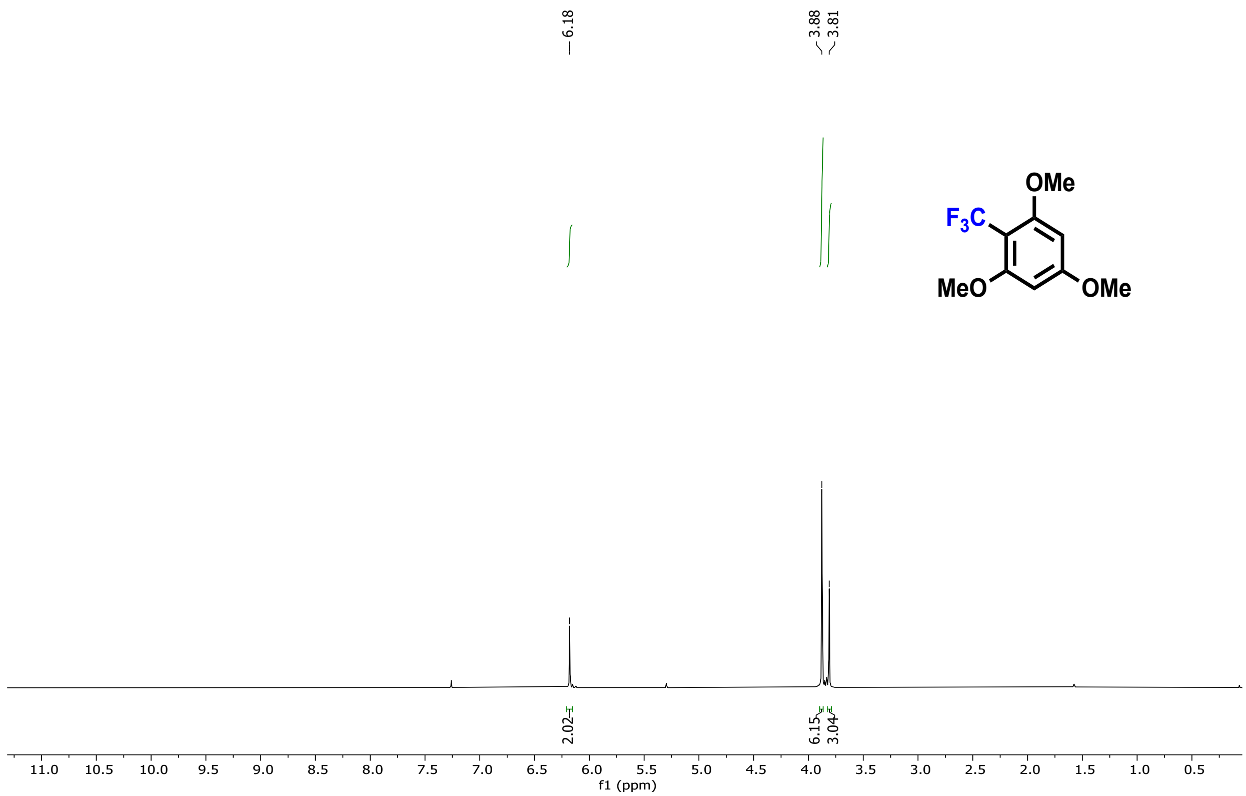


Fig S4. ^{1}H NMR spectrum of **2f** recorded in $CDCl_3$, solvent residual peak is at 7.26 ppm.

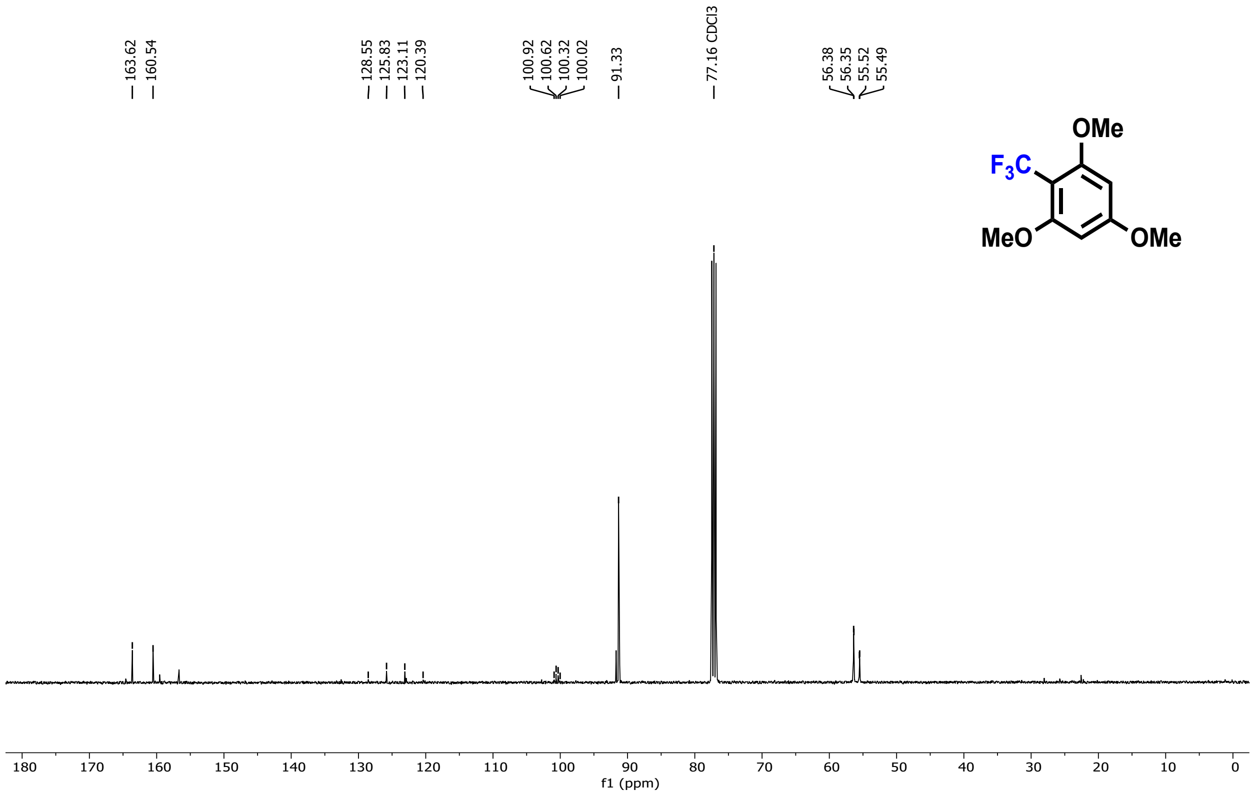


Fig S5. ^{13}C NMR spectrum of **2f** recorded in $CDCl_3$, solvent residual peak is at 77.16 ppm.

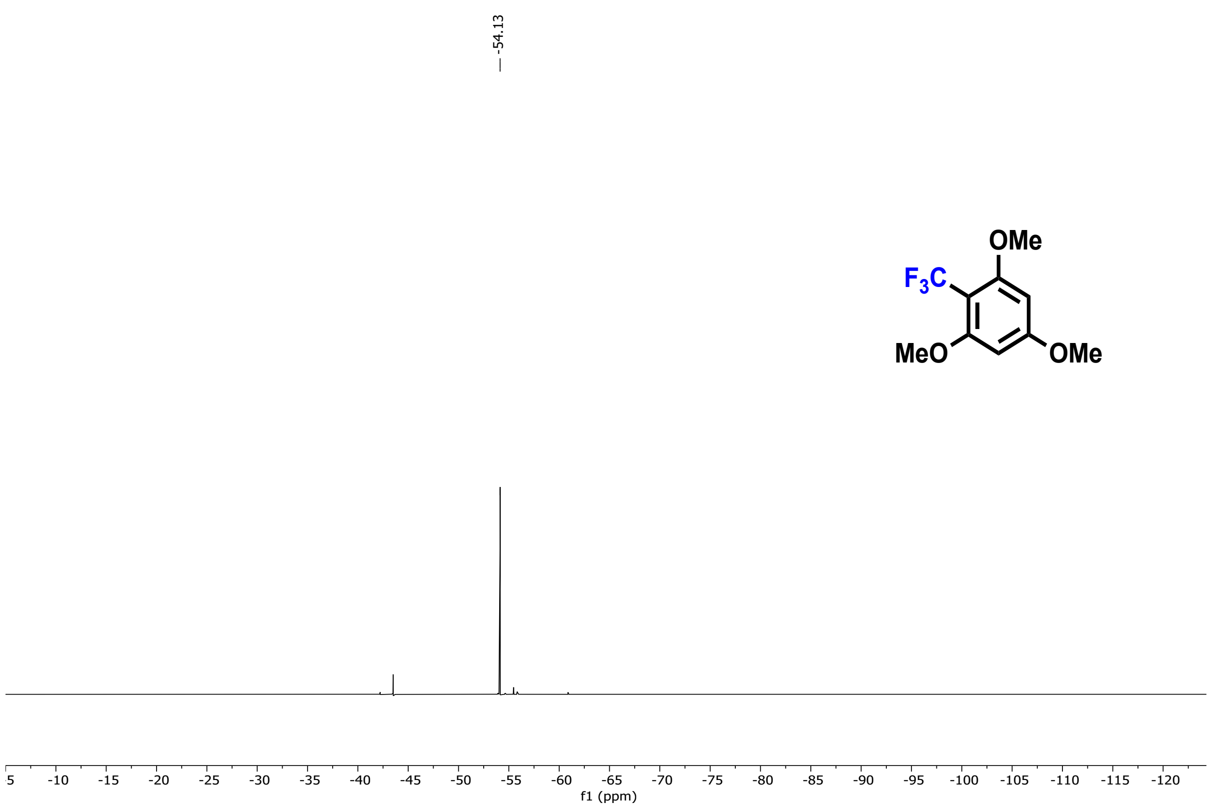


Fig S6. ^{19}F NMR spectrum of **2f** recorded in $CDCl_3$.

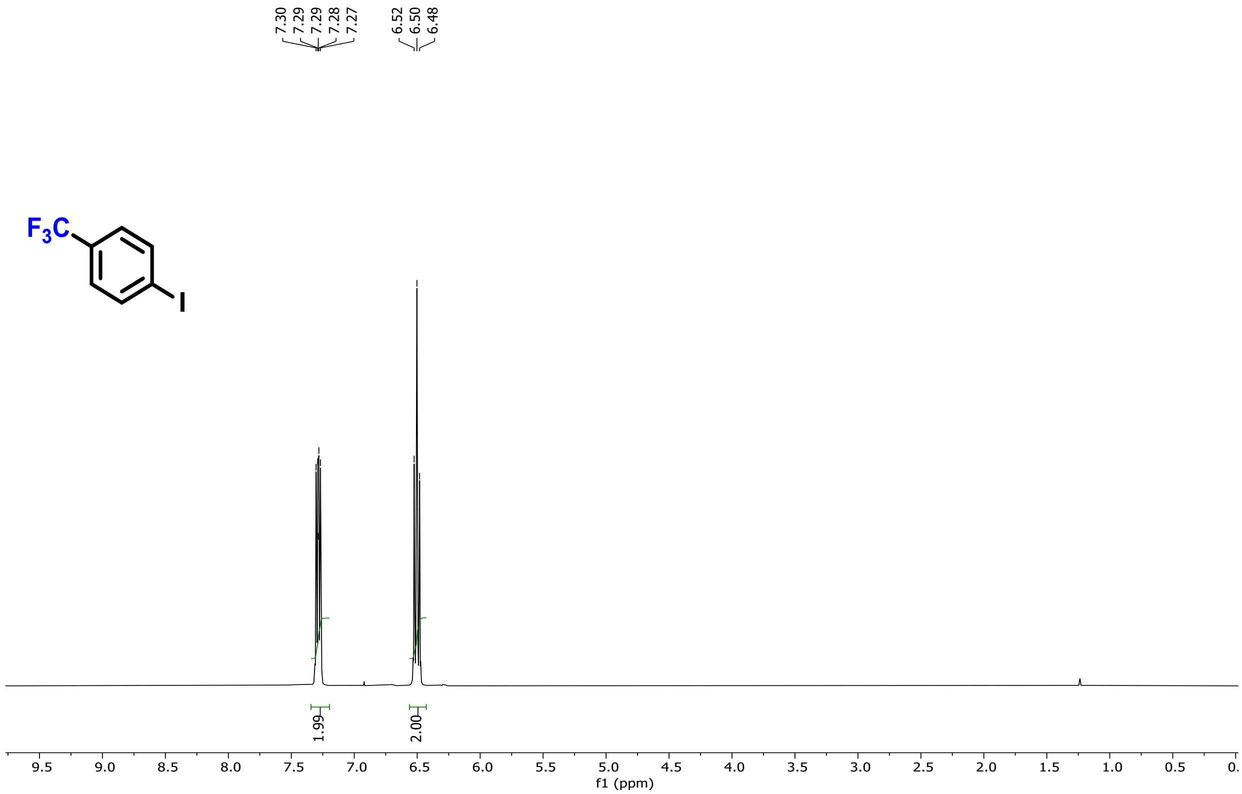


Fig S7. ^{1}H NMR spectrum of **2g** recorded in $CDCl_3$, solvent residual peak is at 7.26 ppm.

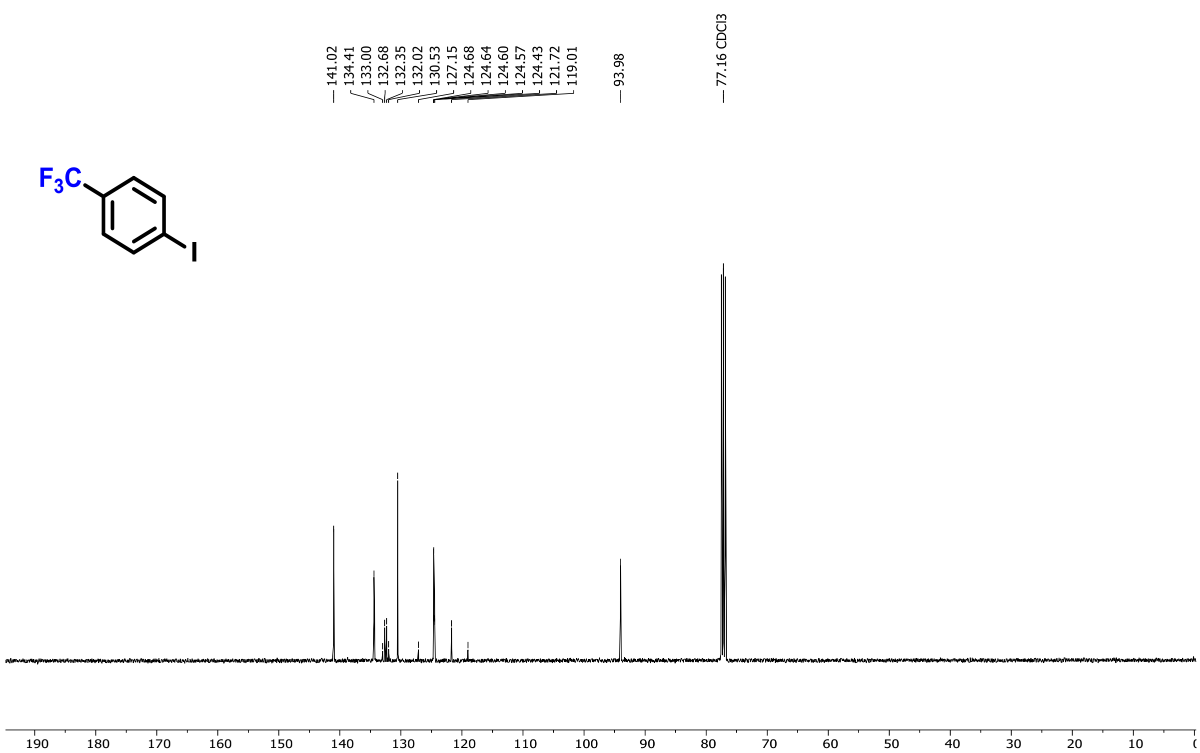


Fig S8. ^{13}C NMR spectrum of **2g** recorded in $CDCl_3$, solvent residual peak is at 77.16 ppm.

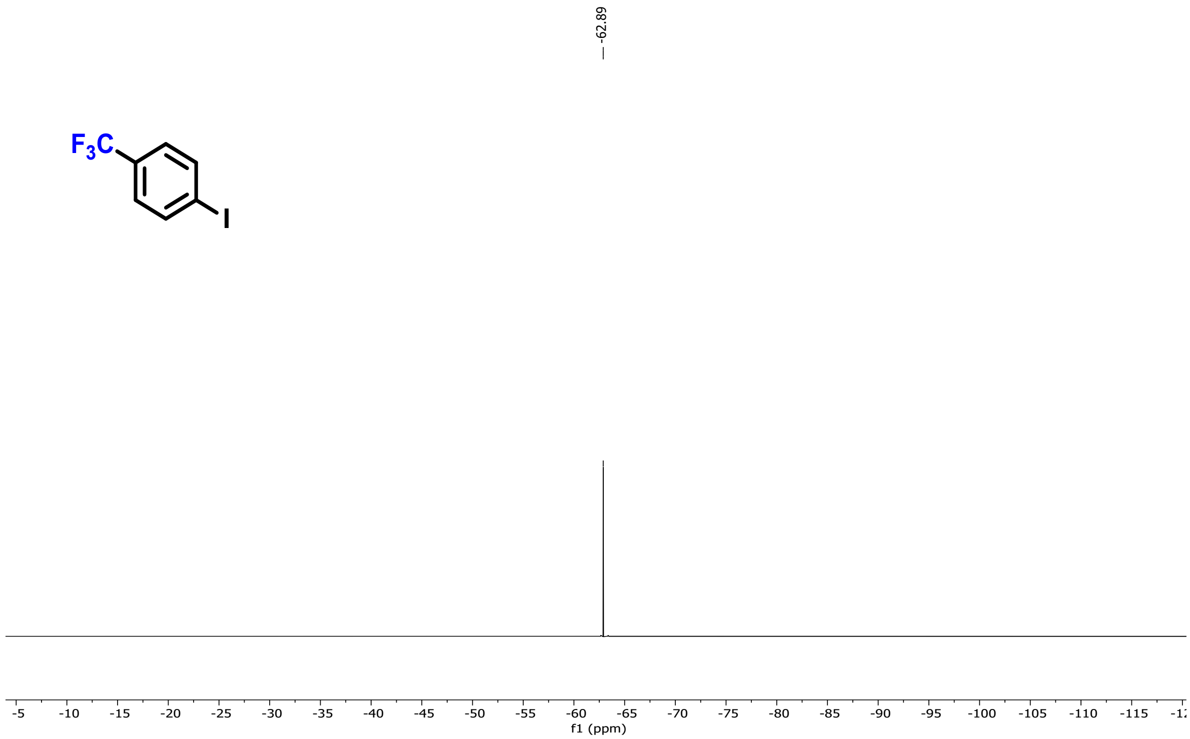


Fig S9. ^{19}F NMR spectrum of **2g** recorded in $CDCl_3$

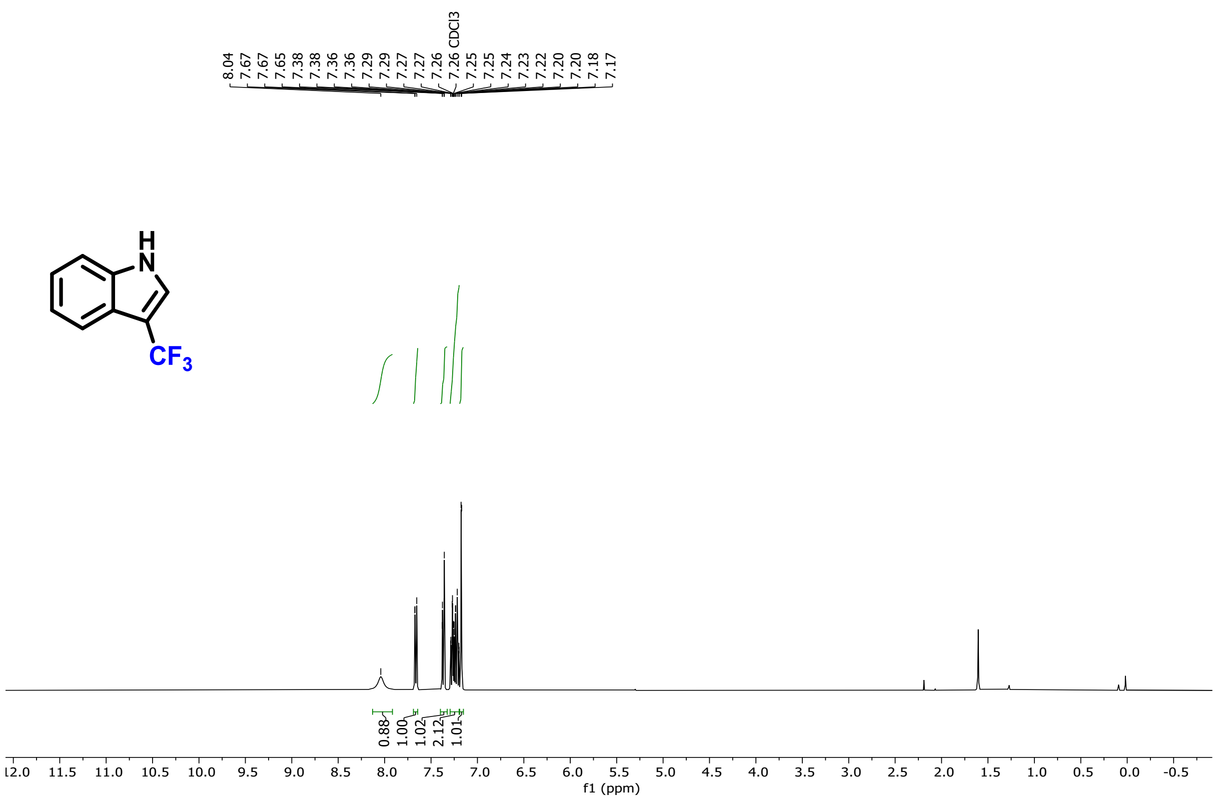


Fig S10. ^{1}H NMR spectrum of **2h** recorded in $CDCl_3$, solvent residual peak is at 7.26 ppm.

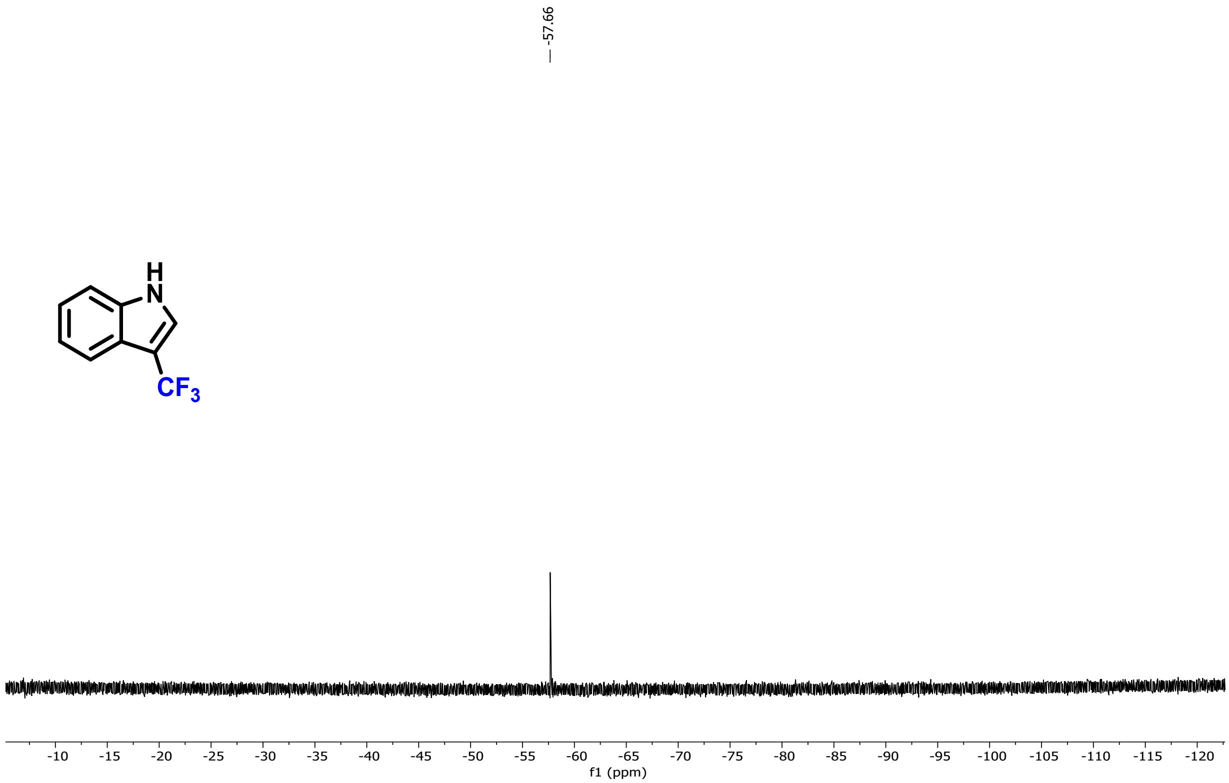


Fig S11. ^{19}F NMR spectrum of **2h** recorded in $CDCl_3$

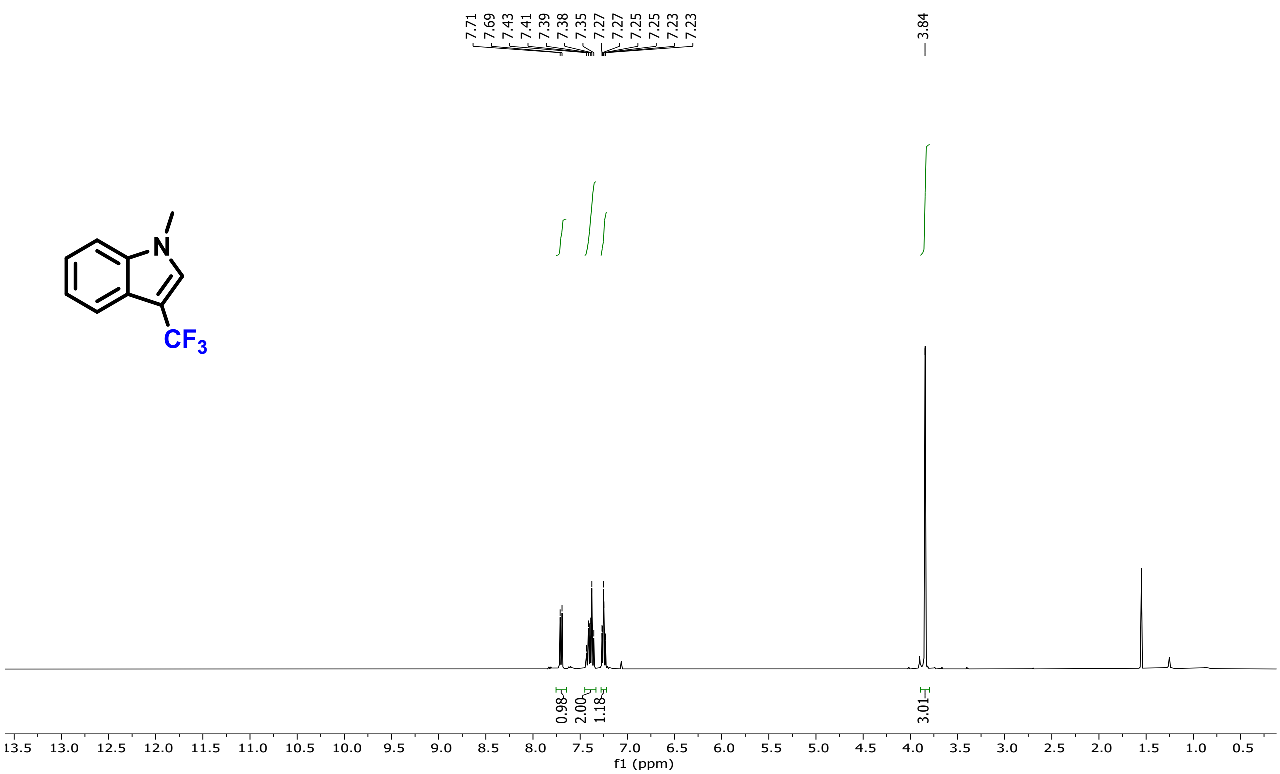


Fig S12. ^{1}H NMR spectrum of **2i** recorded in $CDCl_3$, solvent residual peak is at 7.26 ppm

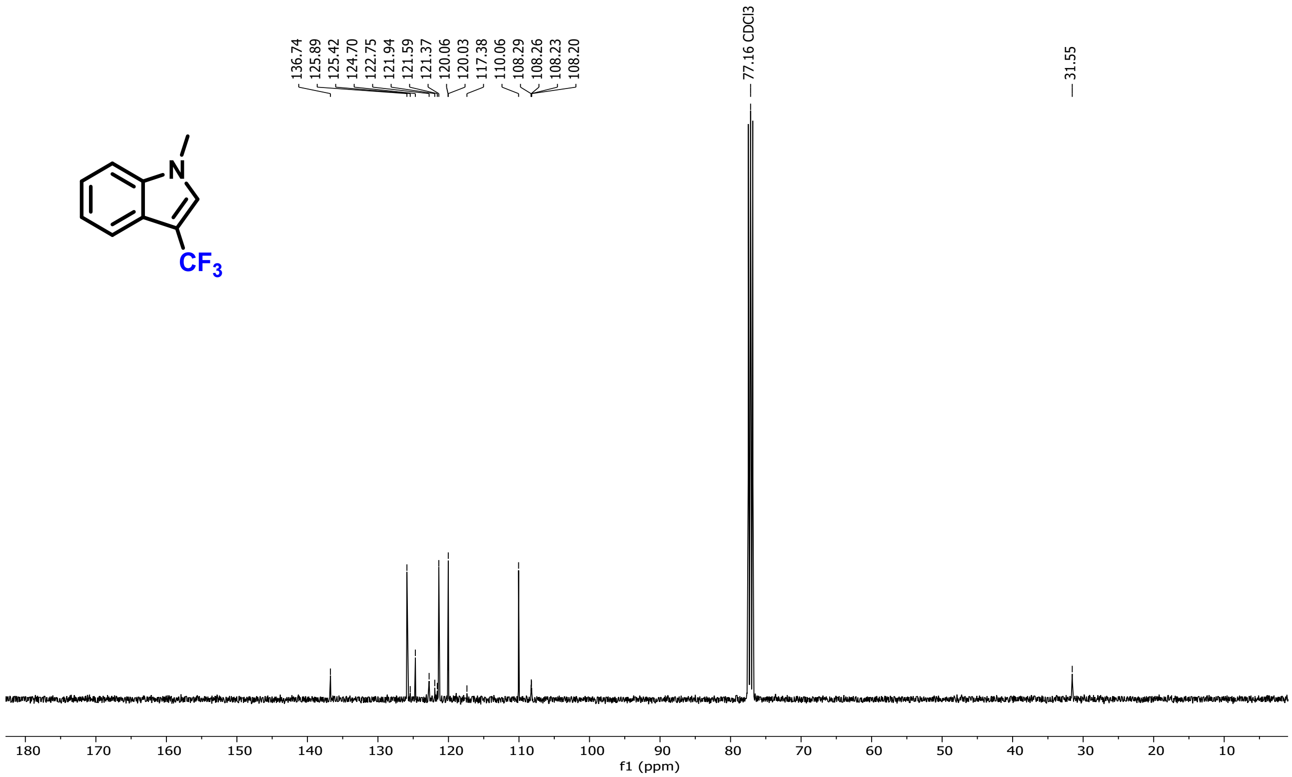


Fig S13. ^{13}C NMR spectrum of **2i** recorded in $CDCl_3$, solvent residual peak is at 77.16 ppm.

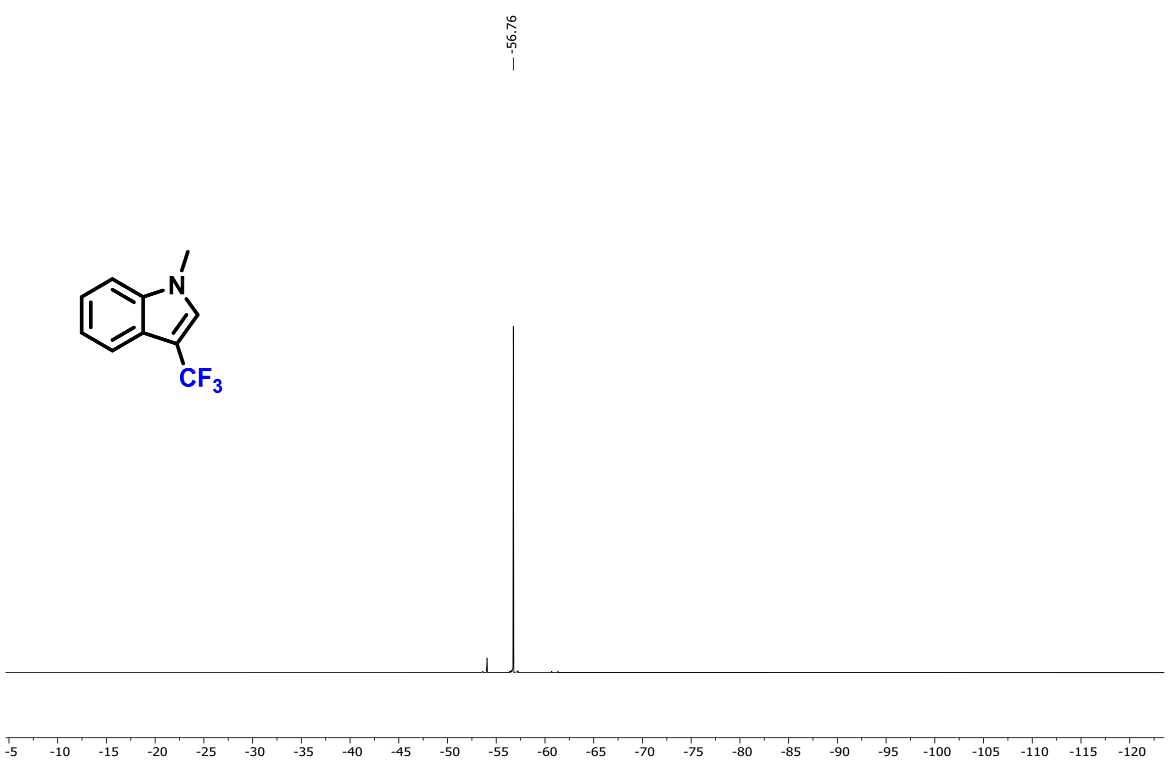


Fig S14. ^{19}F NMR spectrum of **2i** recorded in $CDCl_3$

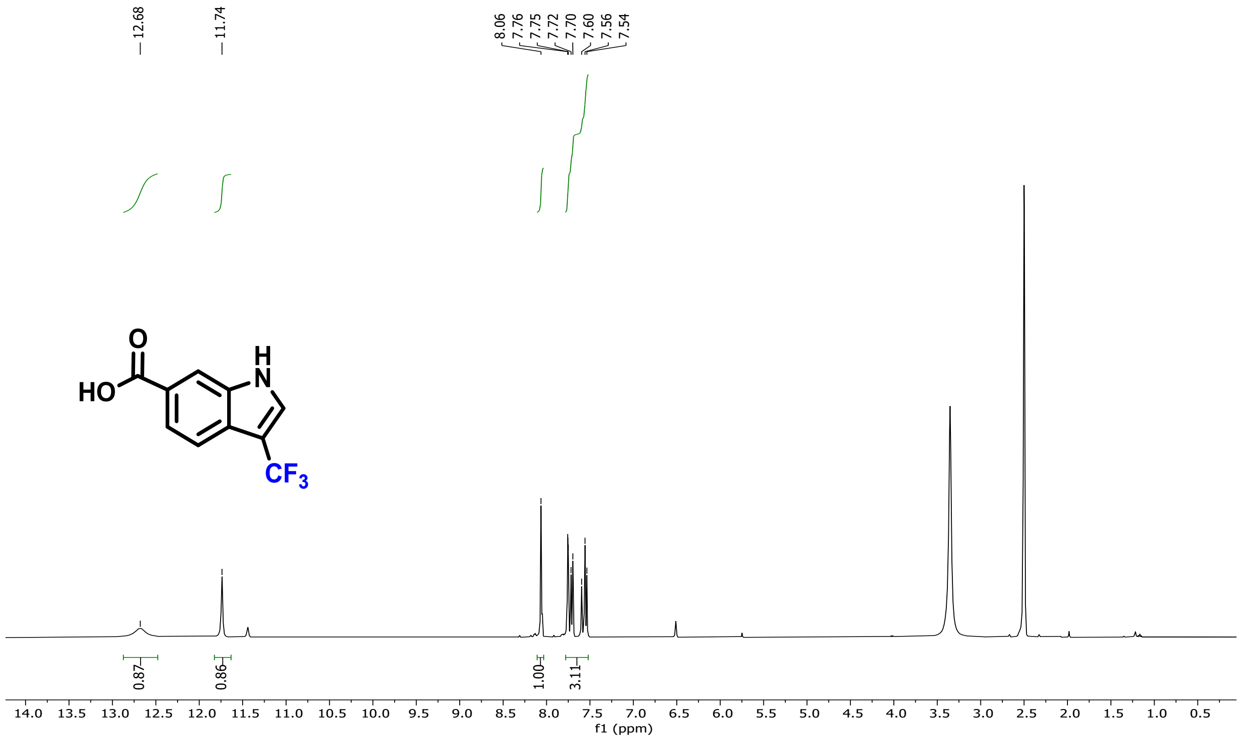


Fig S15. [1]H NMR spectrum of **2j** recorded in DMSO-D6, solvent residual peak is at 2.50 ppm**.**

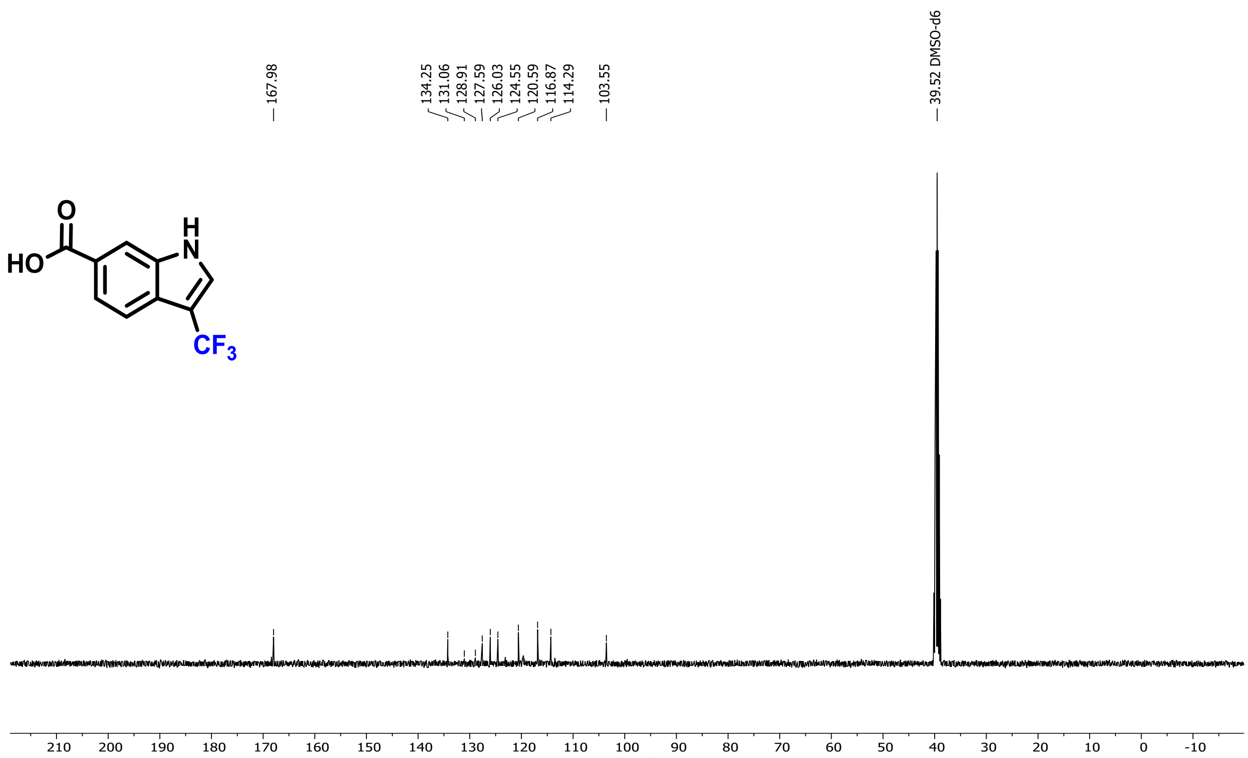


Fig S16. [13]C NMR spectrum of **2j** recorded in DMSO-D6, solvent residual peak is at 39.5 ppm.

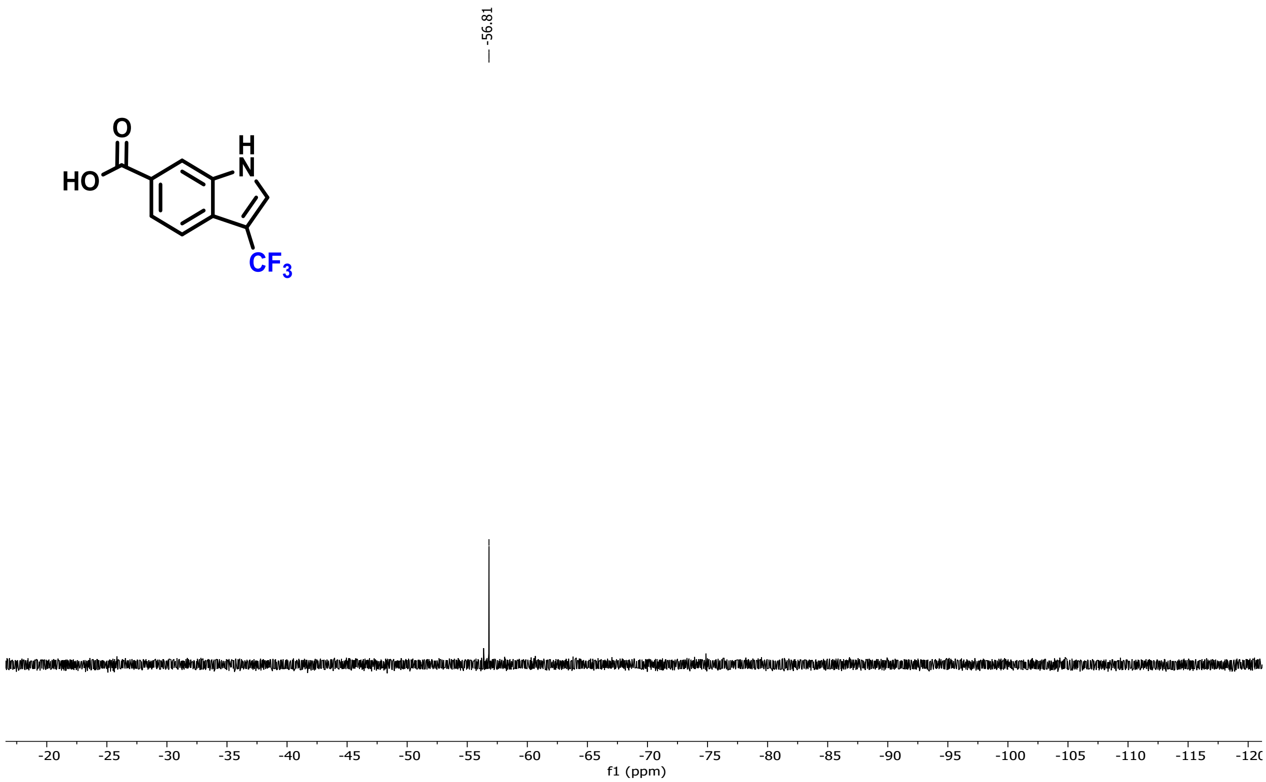


Fig S17. [19]F NMR spectrum of **2j** recorded in DMSO-D6

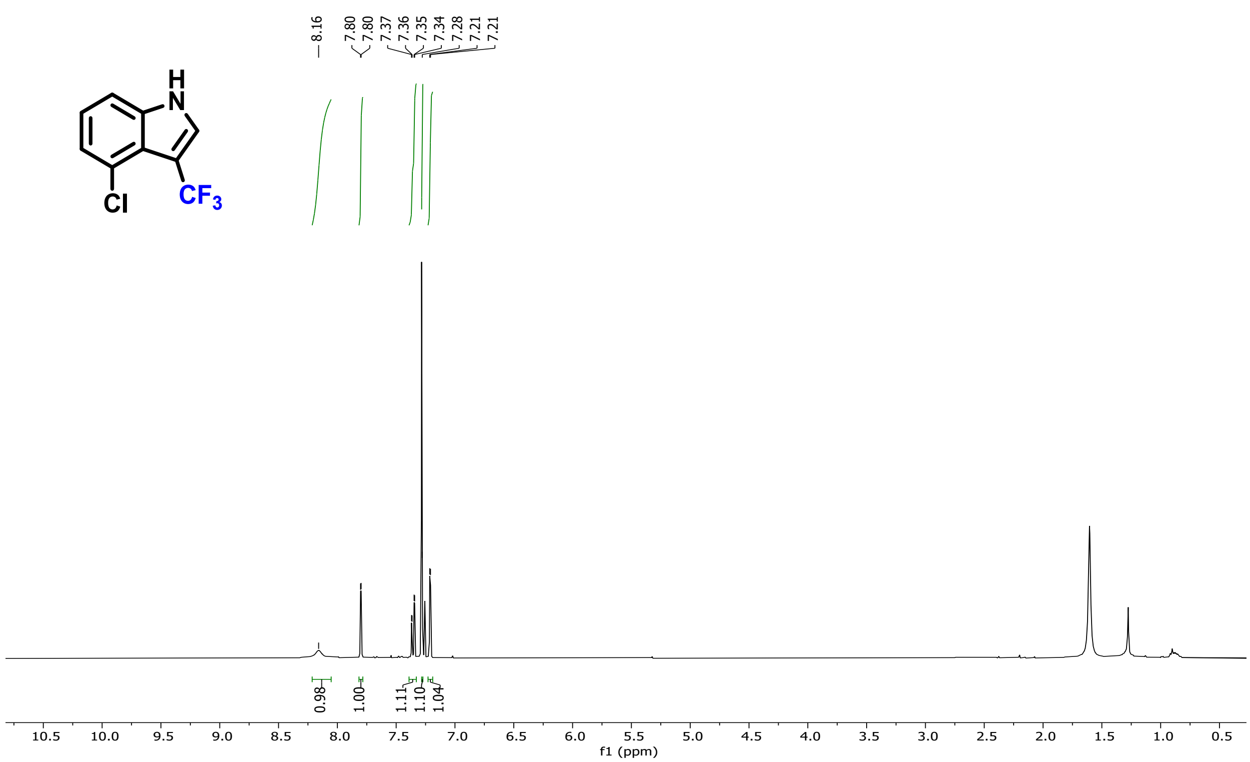


Fig S18. ^{1}H NMR spectrum of **2k** recorded in $CDCl_3$, solvent residual peak is at 7.26 ppm**.**

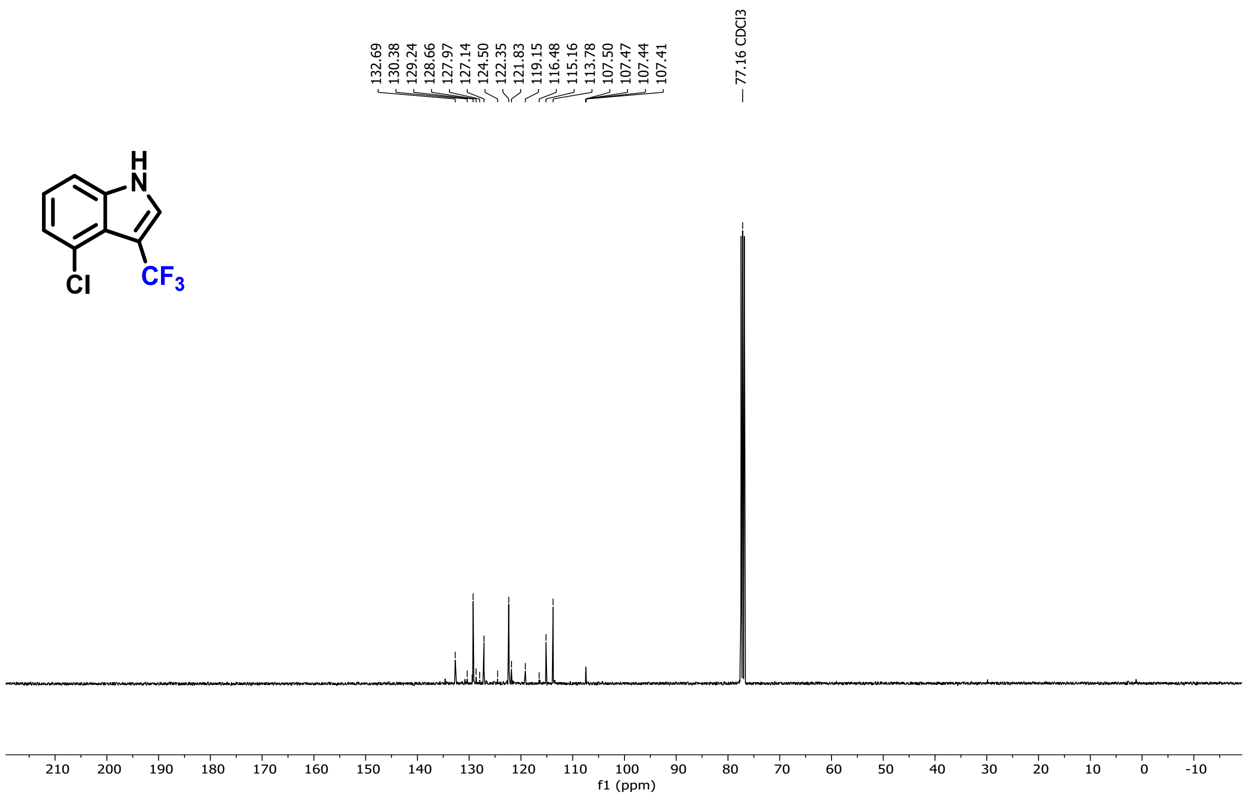


Fig S19. ^{13}C NMR spectrum of **2k** recorded in $CDCl_3$, solvent residual peak is at 77.16 ppm

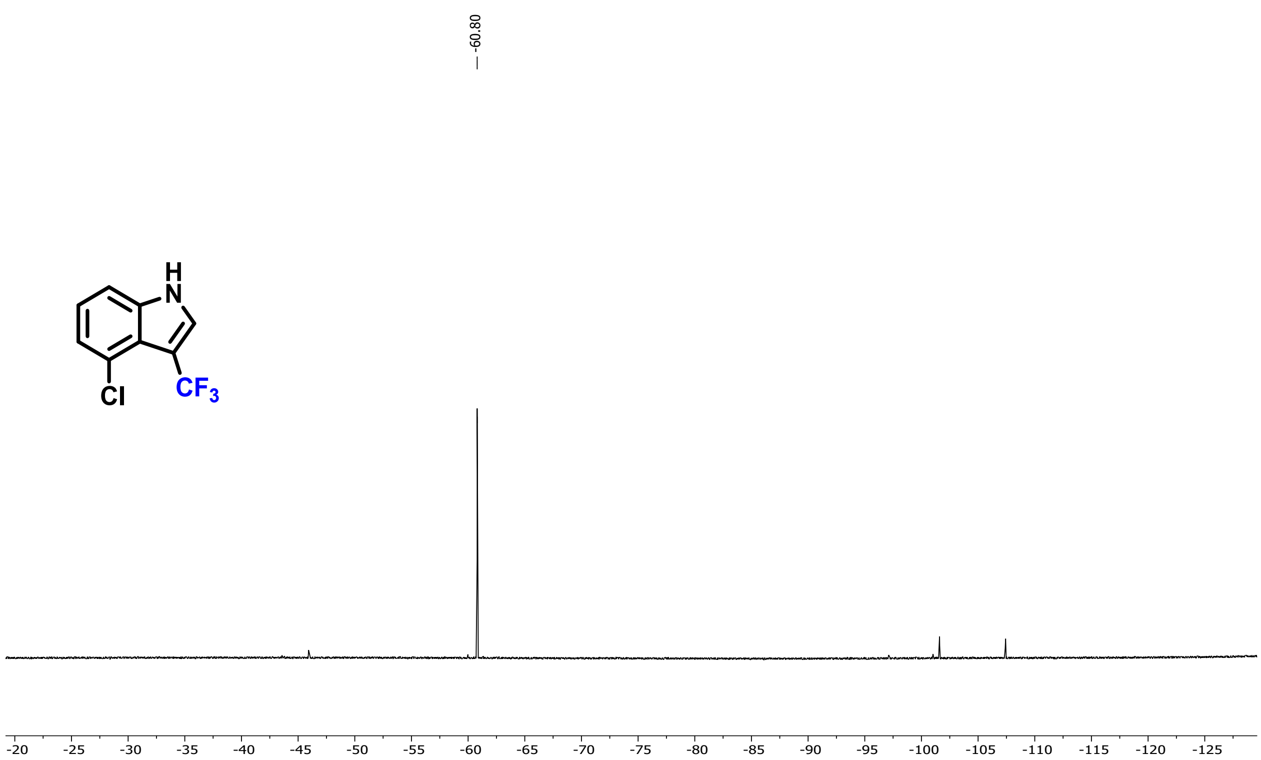


Fig S20. ^{19}F NMR spectrum of **2k** recorded in $CDCl_3$.

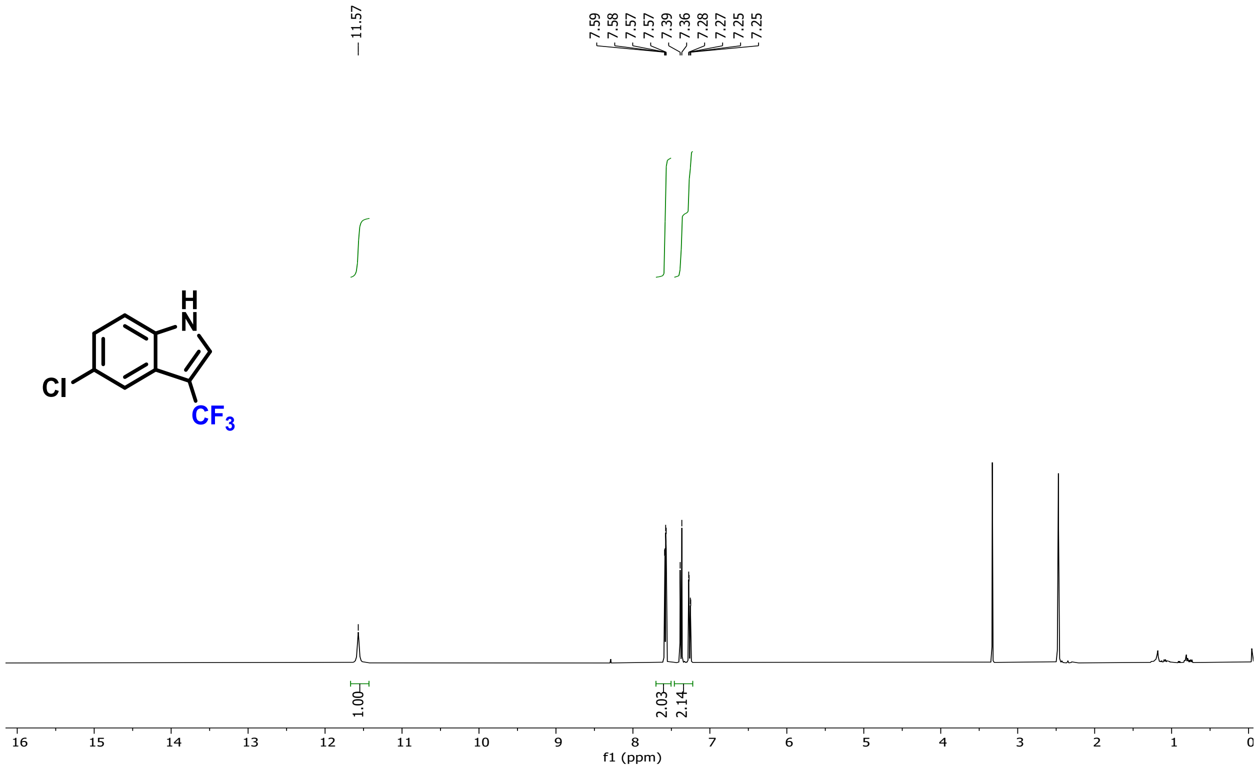


Fig S21. ^{1}H NMR spectrum of **2l** recorded in DMSO-d_6, solvent residual peak is at 2.50 ppm**.**

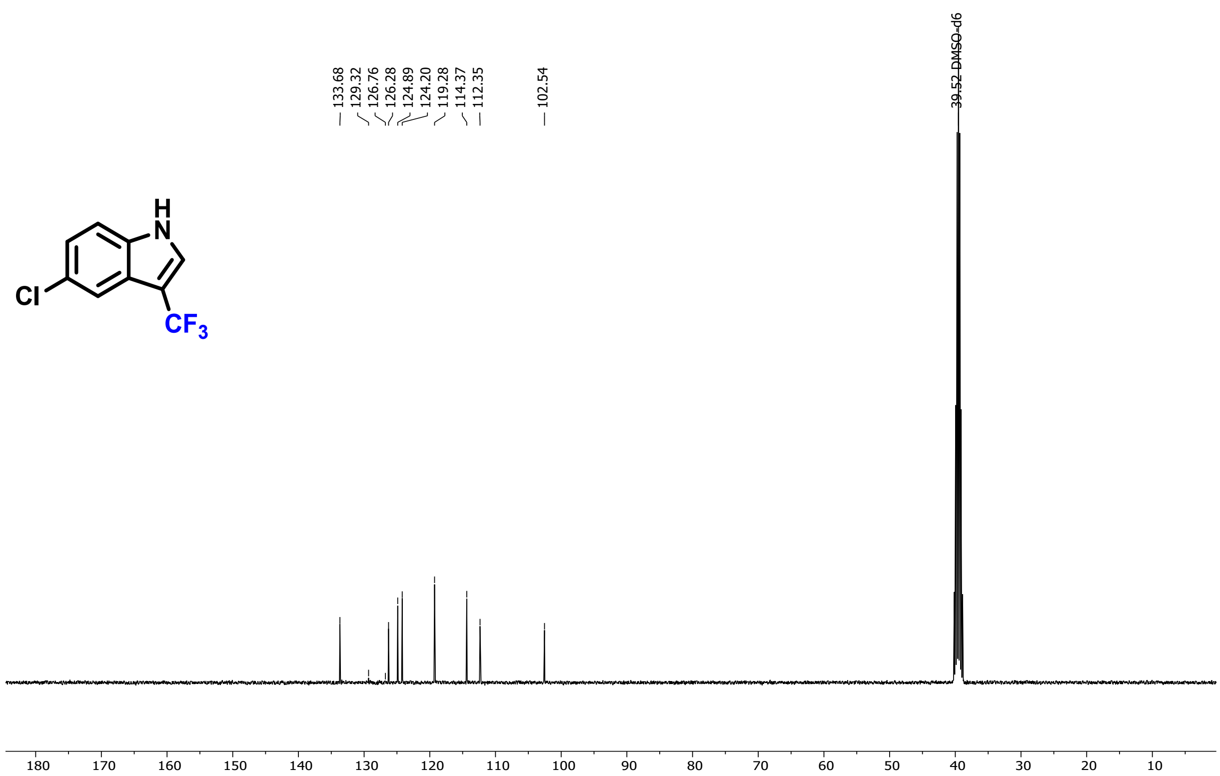


Fig S22. ^{13}C NMR spectrum of **2l** recorded in DMSO-d_6, solvent residual peak is at 39.5 ppm.

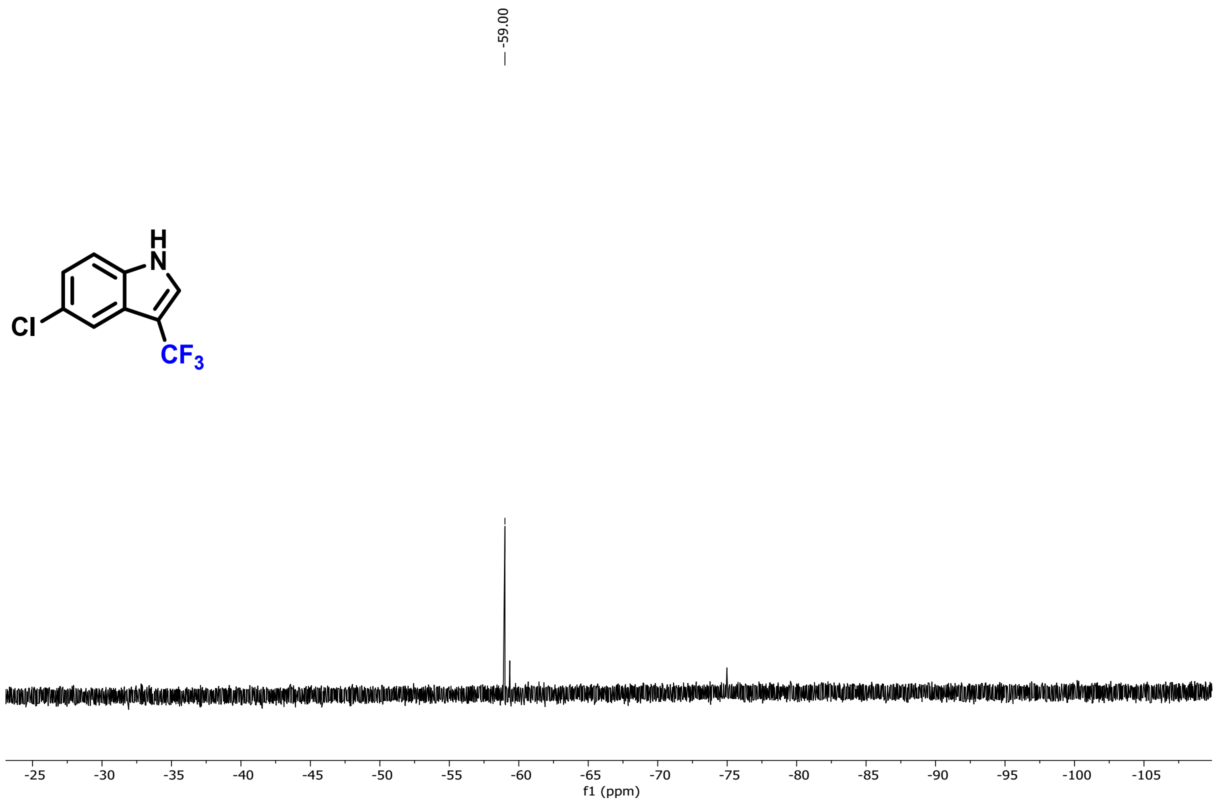


Fig S23. ^{19}F NMR spectrum of **2l** recorded in DMSO-d_6.

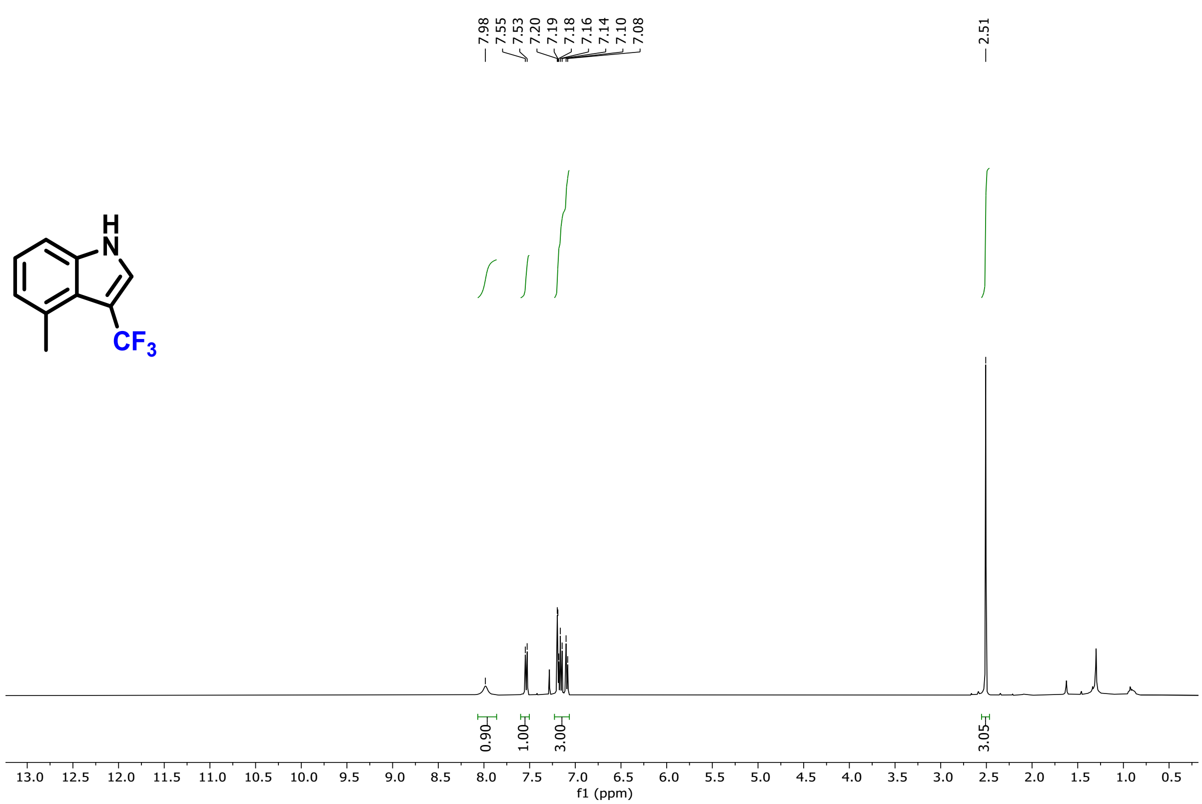


Fig S24. ^{1}H NMR spectrum of **2m** recorded in $CDCl_3$, solvent residual peak is at 7.26 ppm

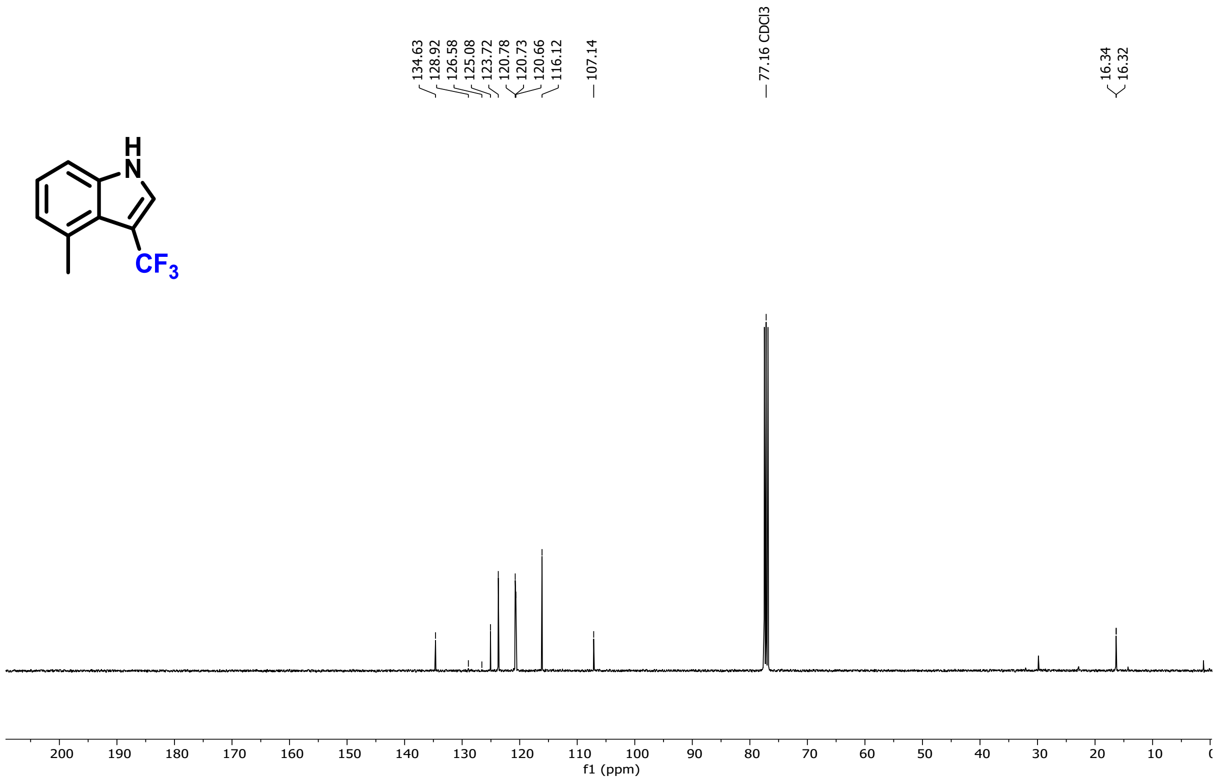


Fig S25. ^{13}C NMR spectrum of **2m** recorded in $CDCl_3$, solvent residual peak is at 77.16 ppm.

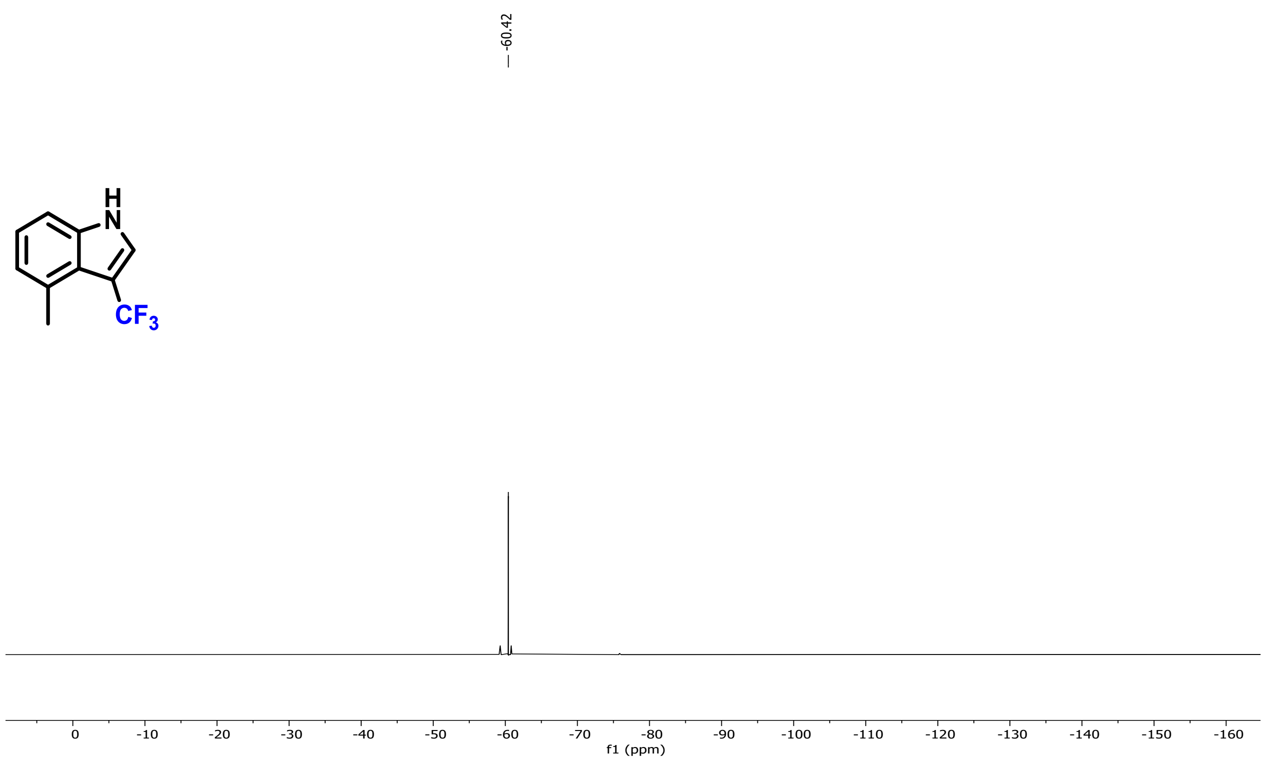


Fig S26. ^{19}F NMR spectrum of **2m** recorded in $CDCl_3$

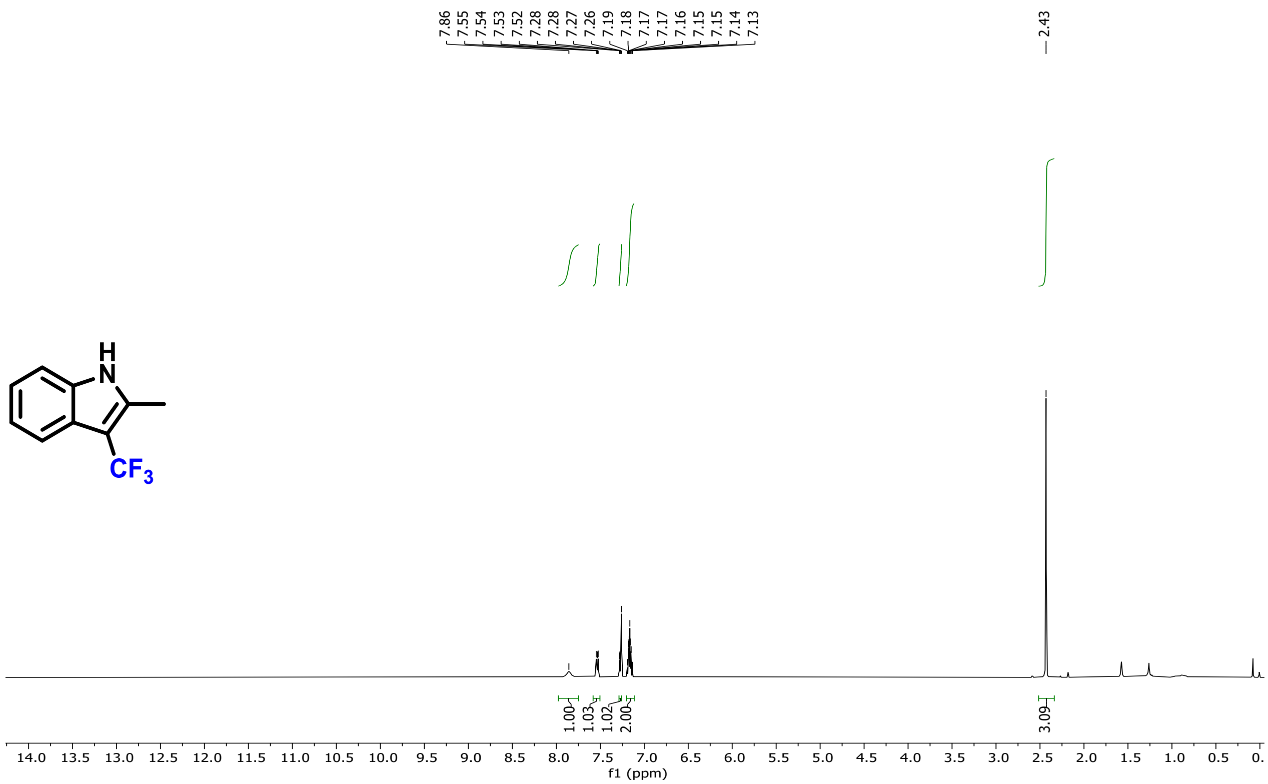


Fig S27. ^{1}H NMR spectrum of **2n** recorded in $CDCl_3$, solvent residual peak is at 7.26 ppm

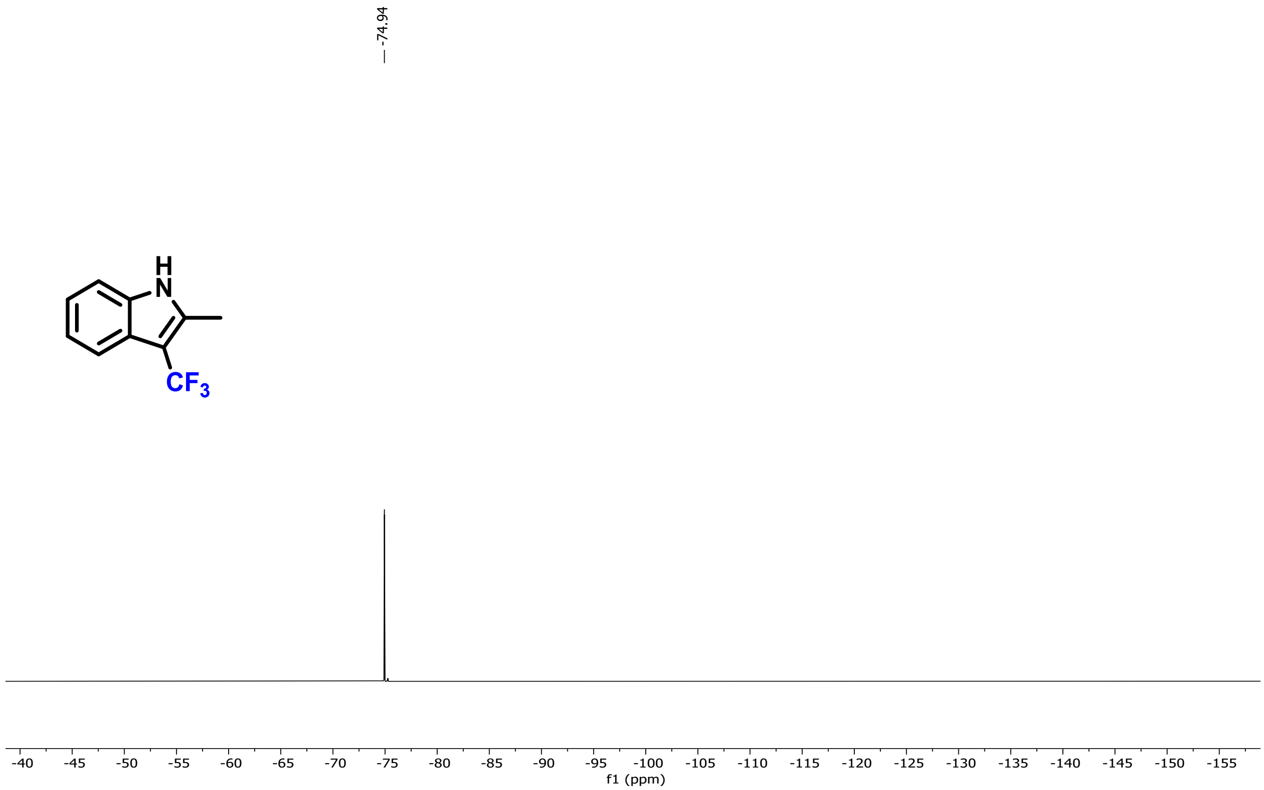


Fig S28. ^{19}F NMR spectrum of **2n** recorded in $CDCl_3$

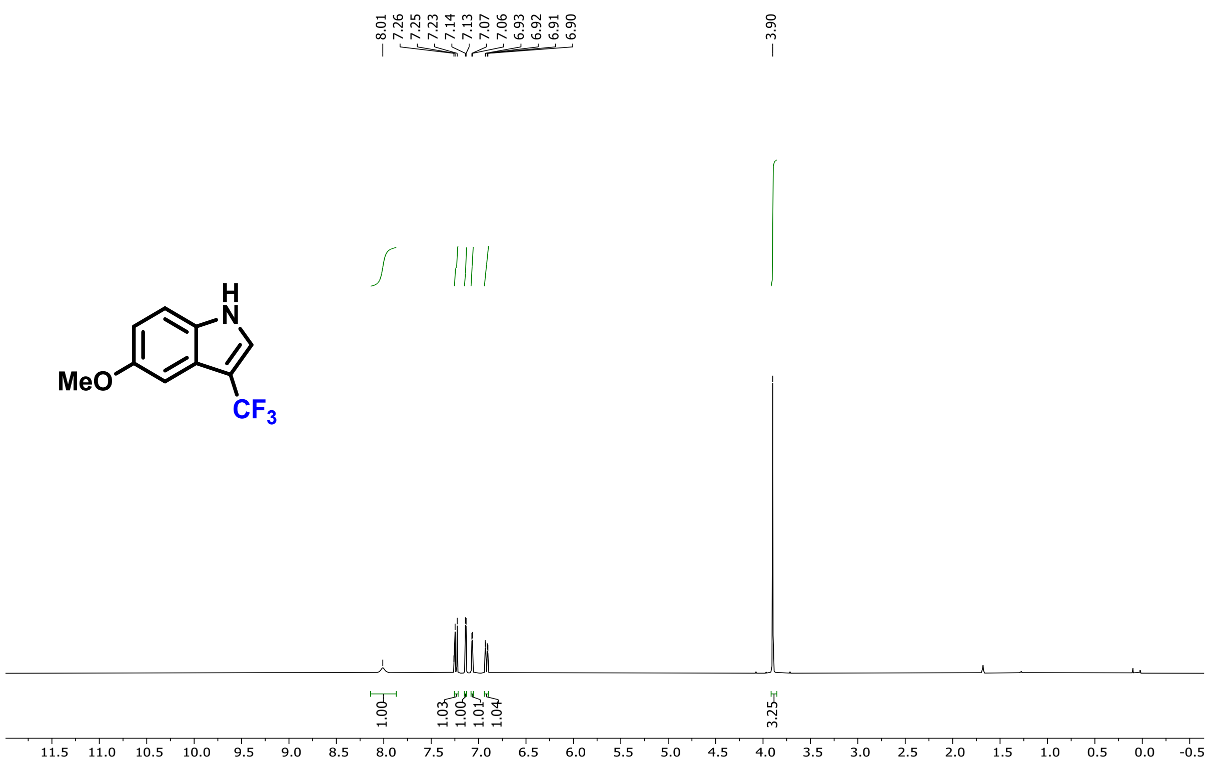


Fig S29. ^{1}H NMR spectrum of **2o** recorded in $CDCl_3$, solvent residual peak is at 7.26 ppm

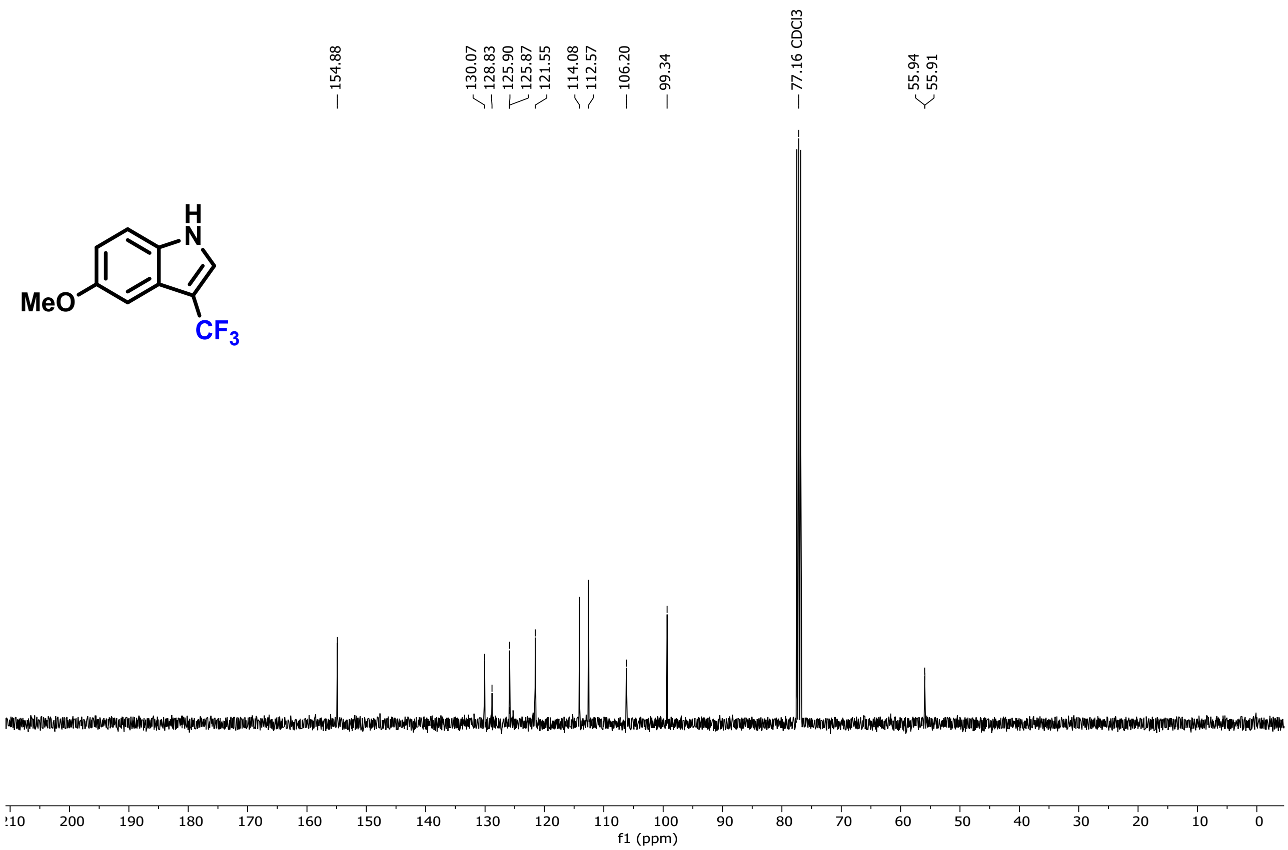


Fig S30. ^{13}C NMR spectrum of **2o** recorded in $CDCl_3$, solvent residual peak is at 77.16 ppm.

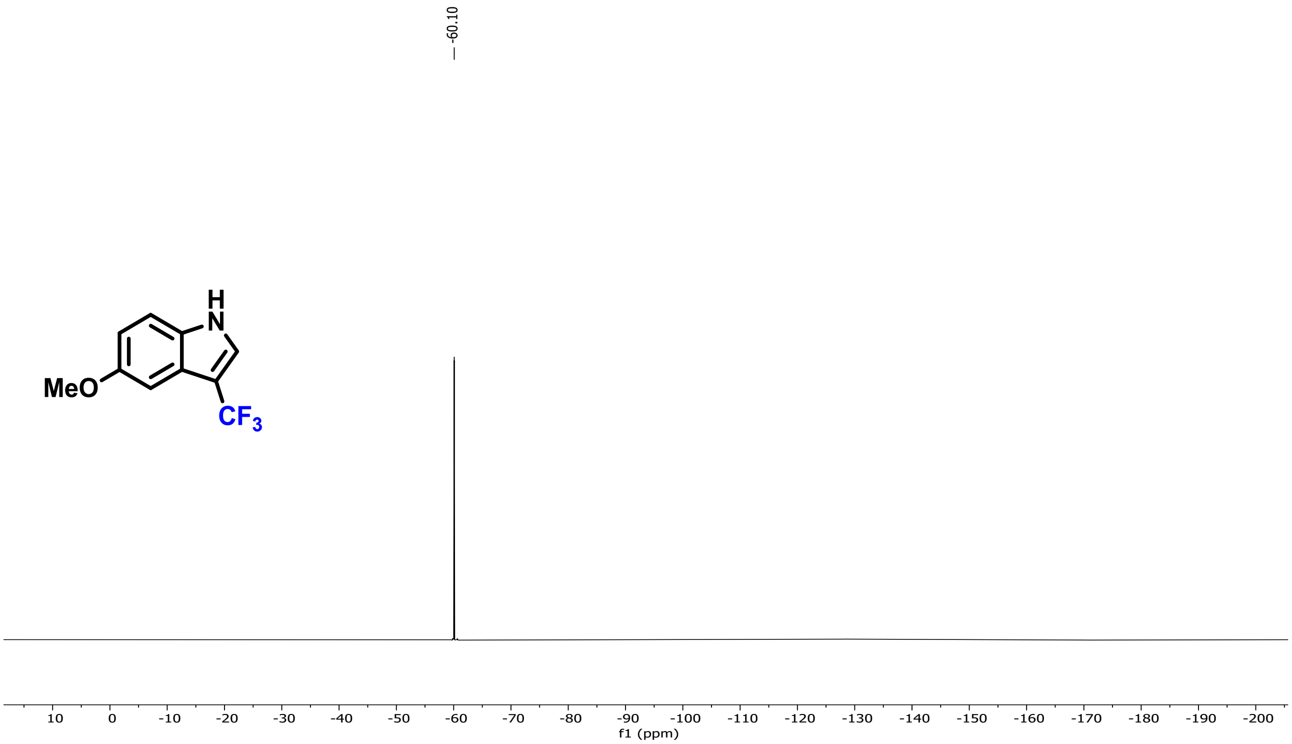


Fig S31. ^{19}F NMR spectrum of **2o** recorded in $CDCl_3$

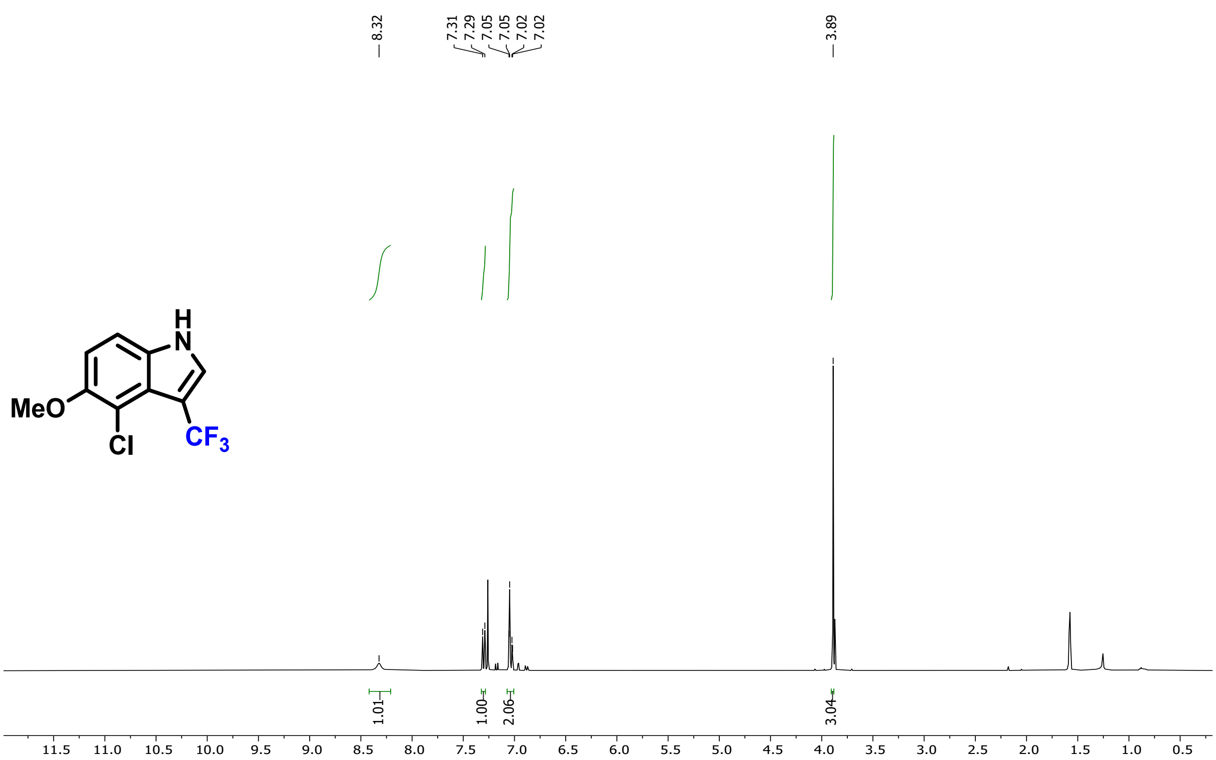


Fig S32. ^{1}H NMR spectrum of **2p** recorded in $CDCl_3$, solvent residual peak is at 7.26 ppm

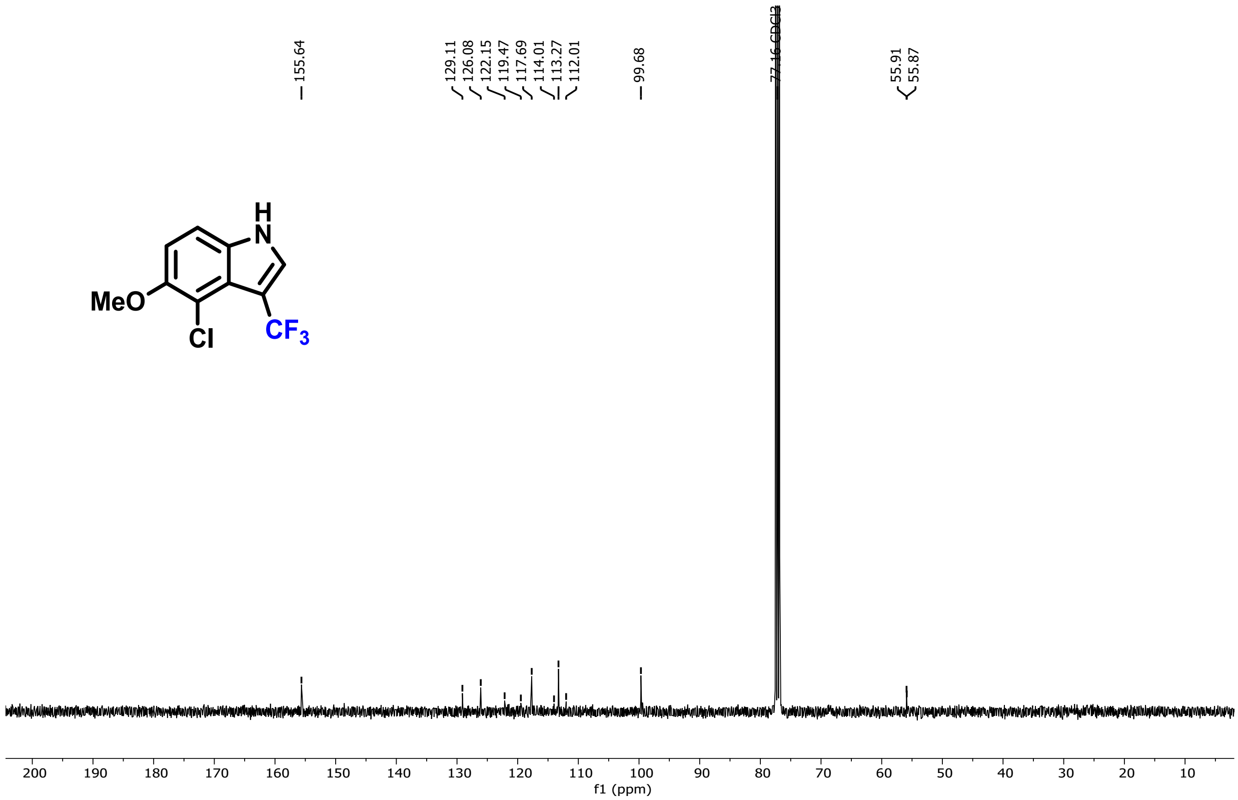


Fig S33. ^{13}C NMR spectrum of **2p** recorded in $CDCl_3$, solvent residual peak is at 77.16 ppm.

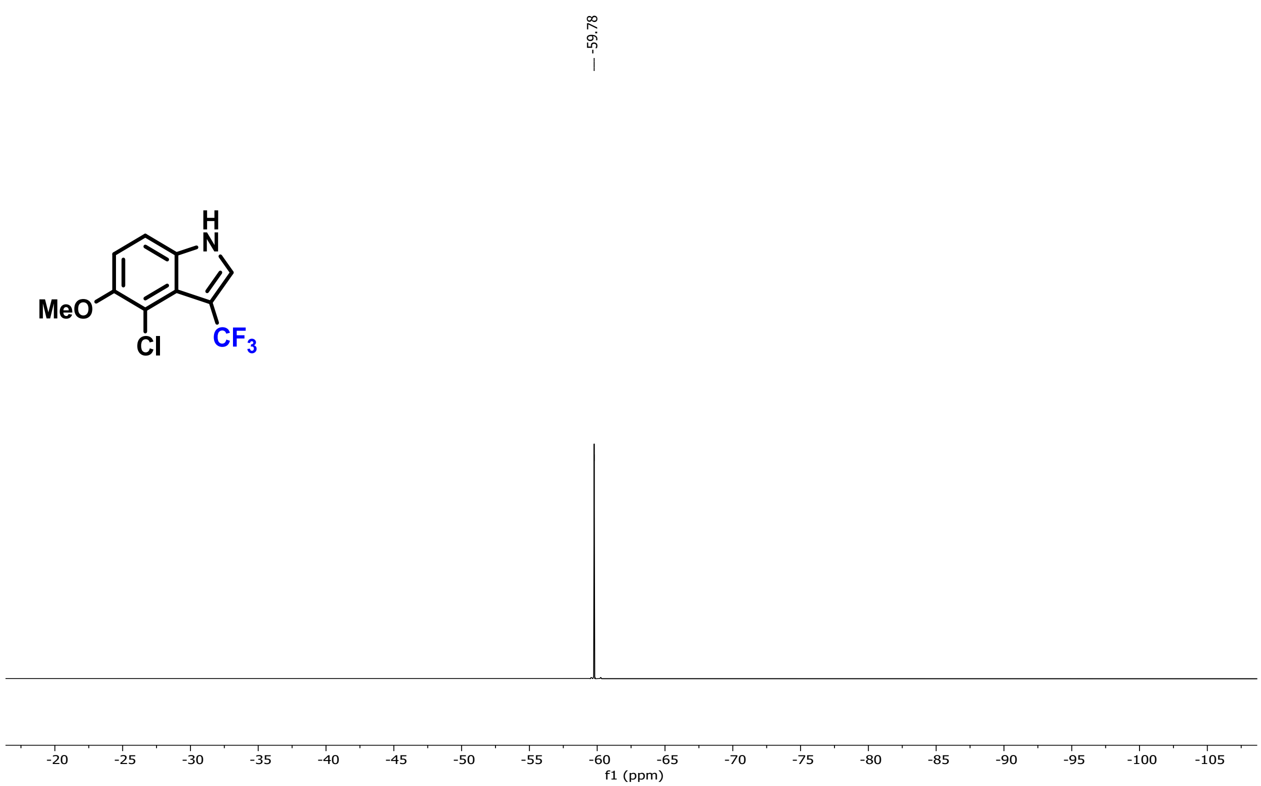


Fig S34. ^{19}F NMR spectrum of **2p** recorded in $CDCl_3$

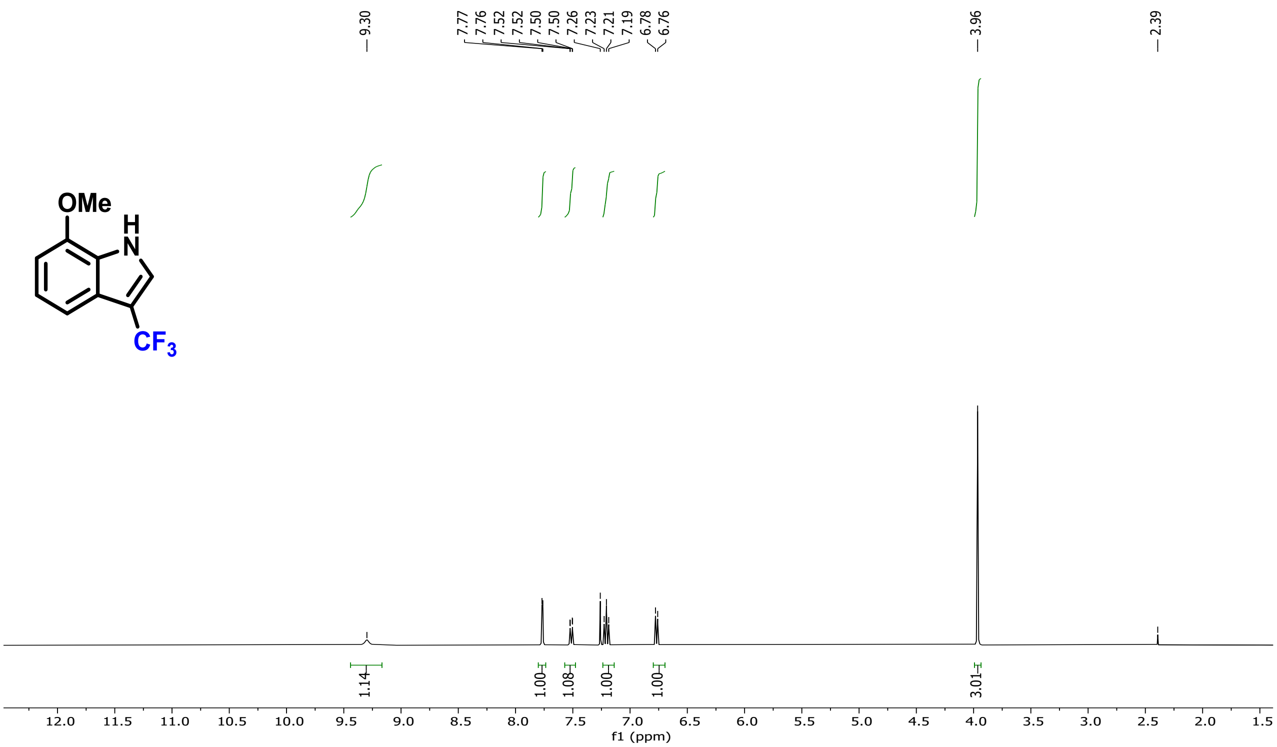


Fig S35. ^{1}H NMR spectrum of **2q** recorded in $CDCl_3$, solvent residual peak is at 7.26 ppm

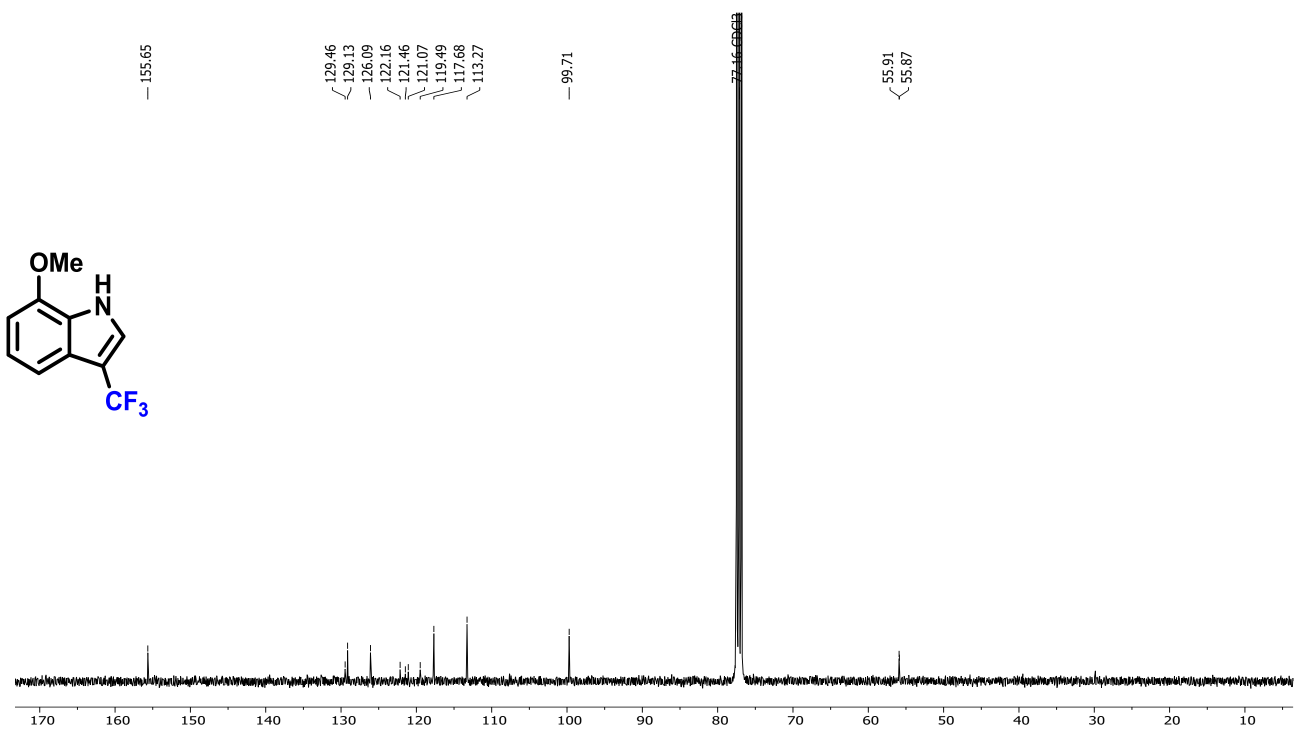


Fig S36. ^{13}C NMR spectrum of **2q** recorded in $CDCl_3$, solvent residual peak is at 77.16 ppm.

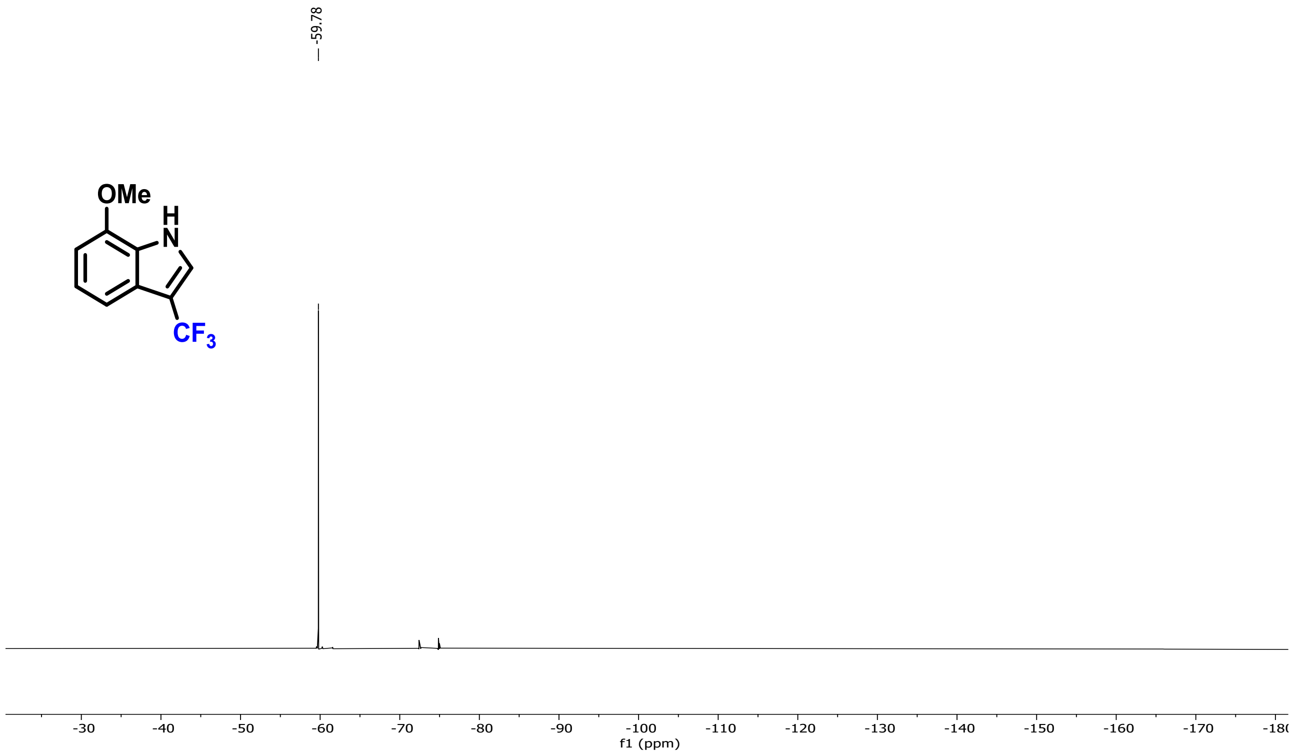


Fig S37. ^{19}F NMR spectrum of **2q** recorded in $CDCl_3$

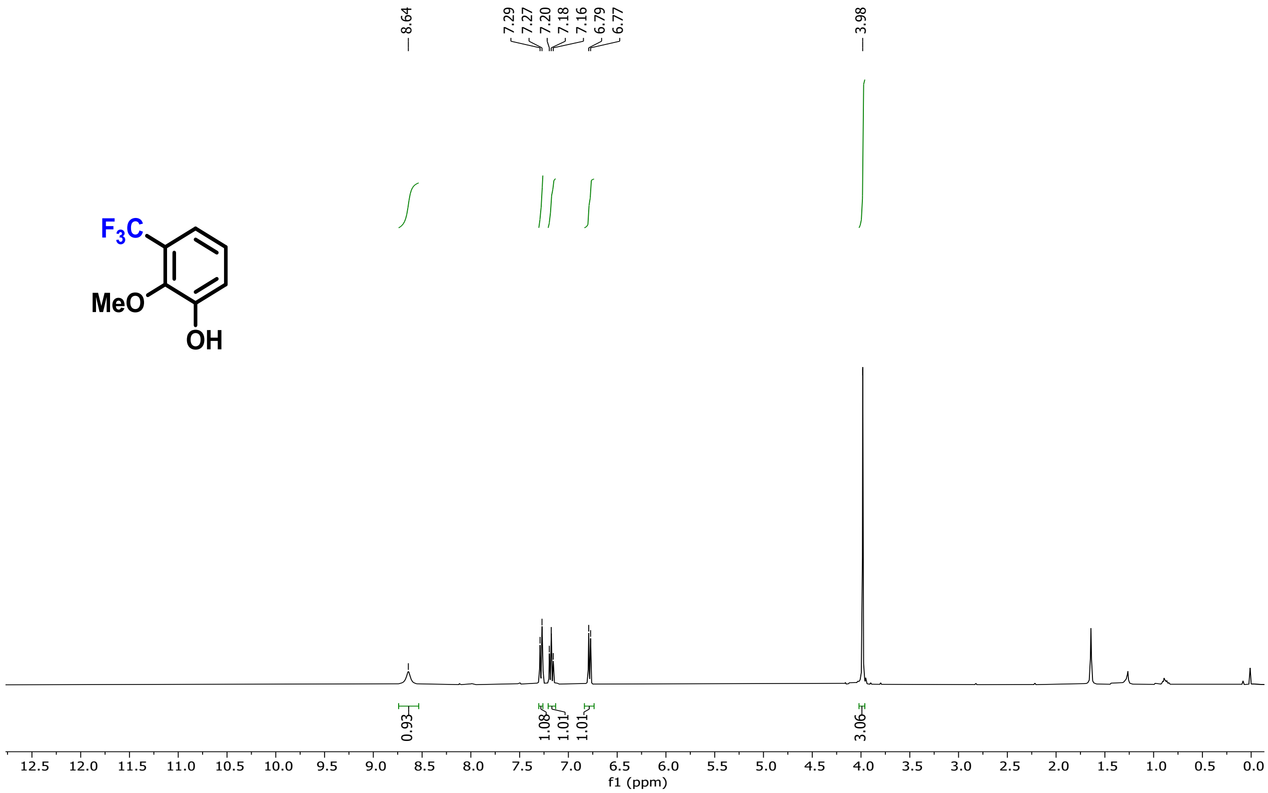


Fig S38. ^{1}H NMR spectrum of **2r** recorded in $CDCl_3$, solvent residual peak is at 7.26 ppm

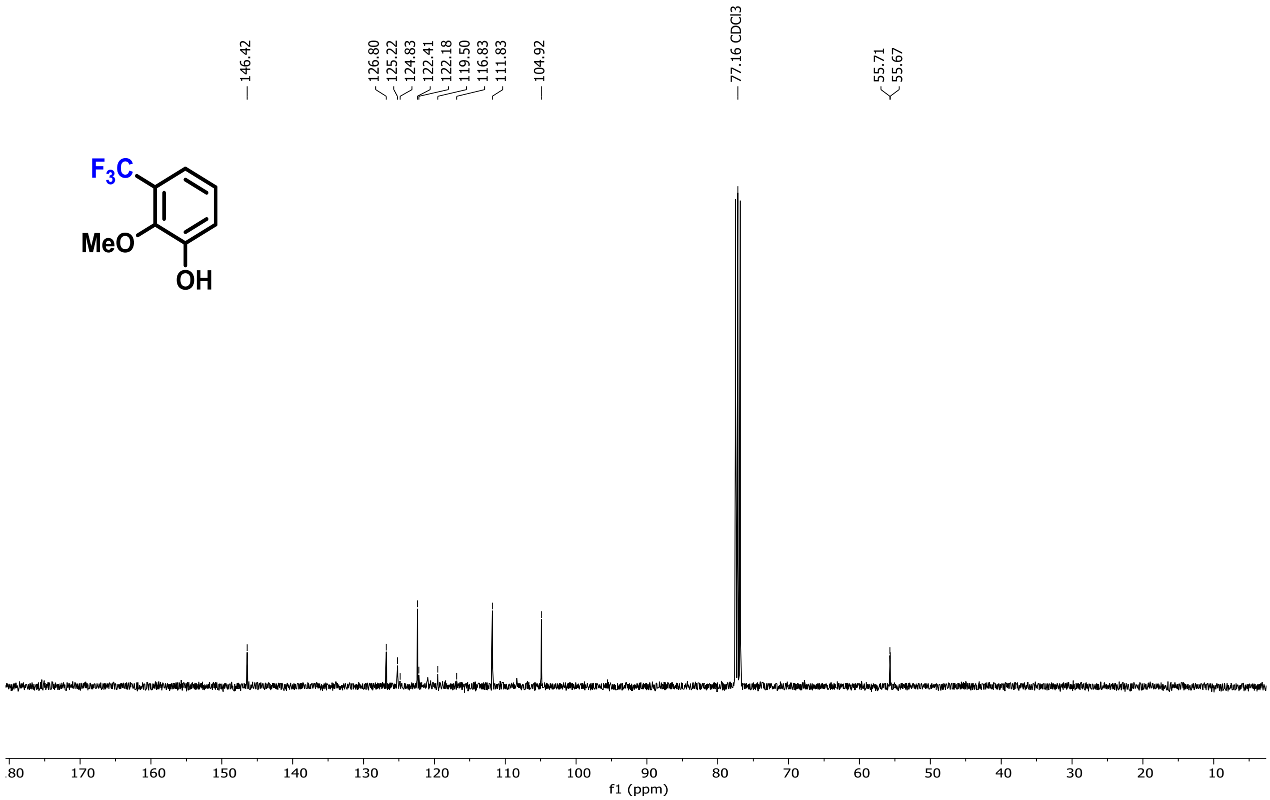


Fig S39. ^{13}C NMR spectrum of **2r** recorded in $CDCl_3$, solvent residual peak is at 77.16 ppm.

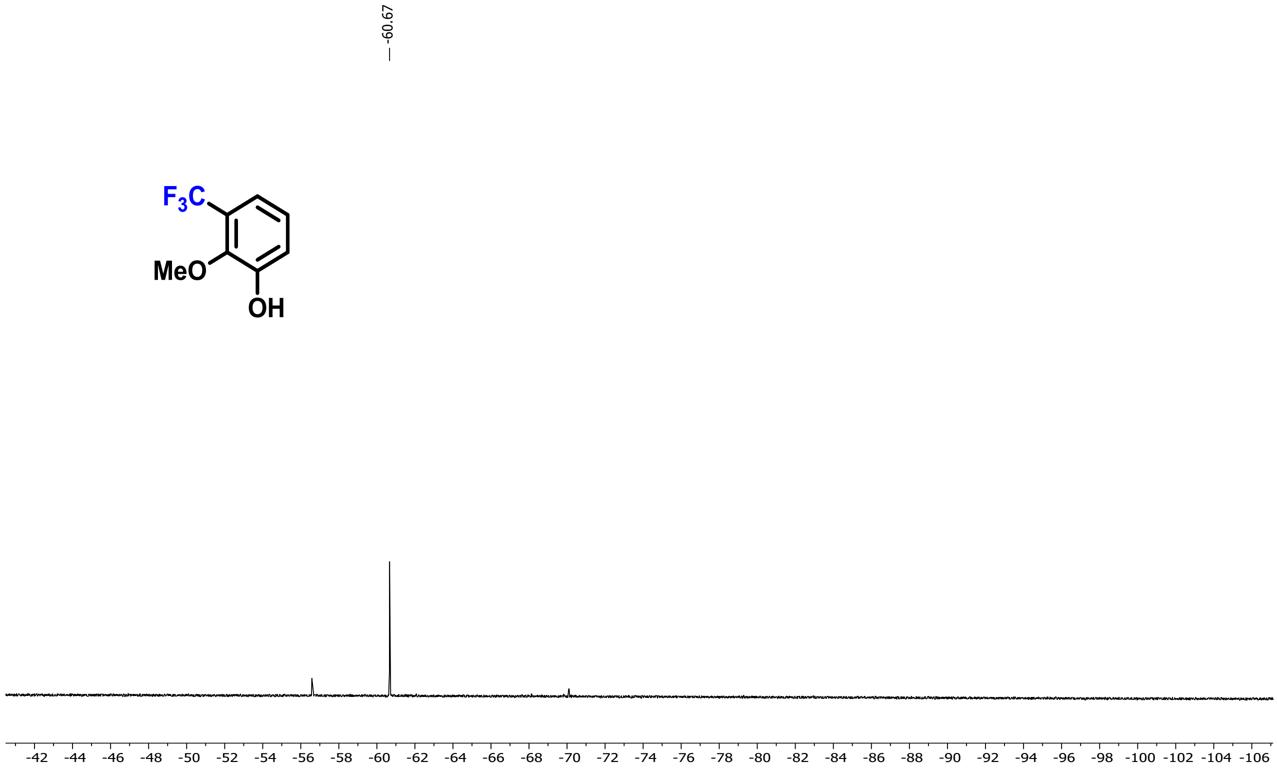


Fig S40. ^{19}F NMR spectrum of **2r** recorded in $CDCl_3$

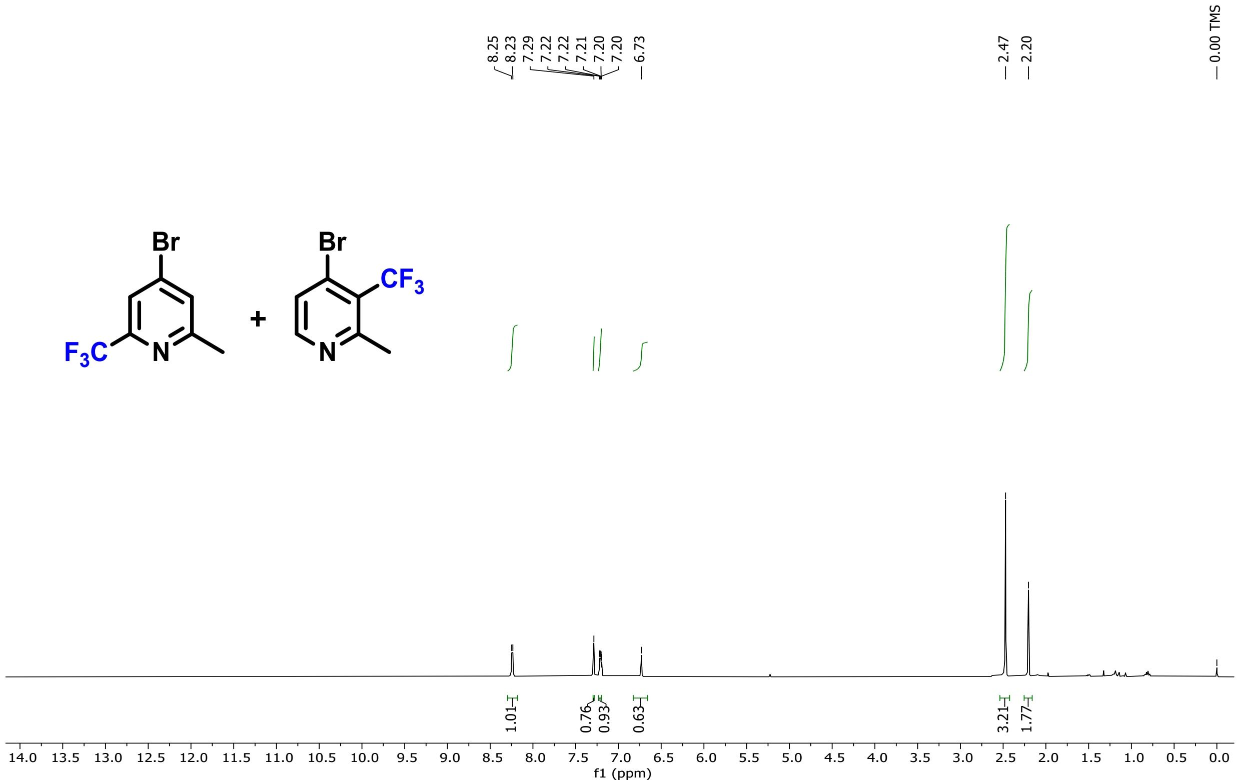


Fig S41. ^{1}H NMR spectrum of **2s** recorded in $CDCl_3$, solvent residual peak is at 7.26 ppm

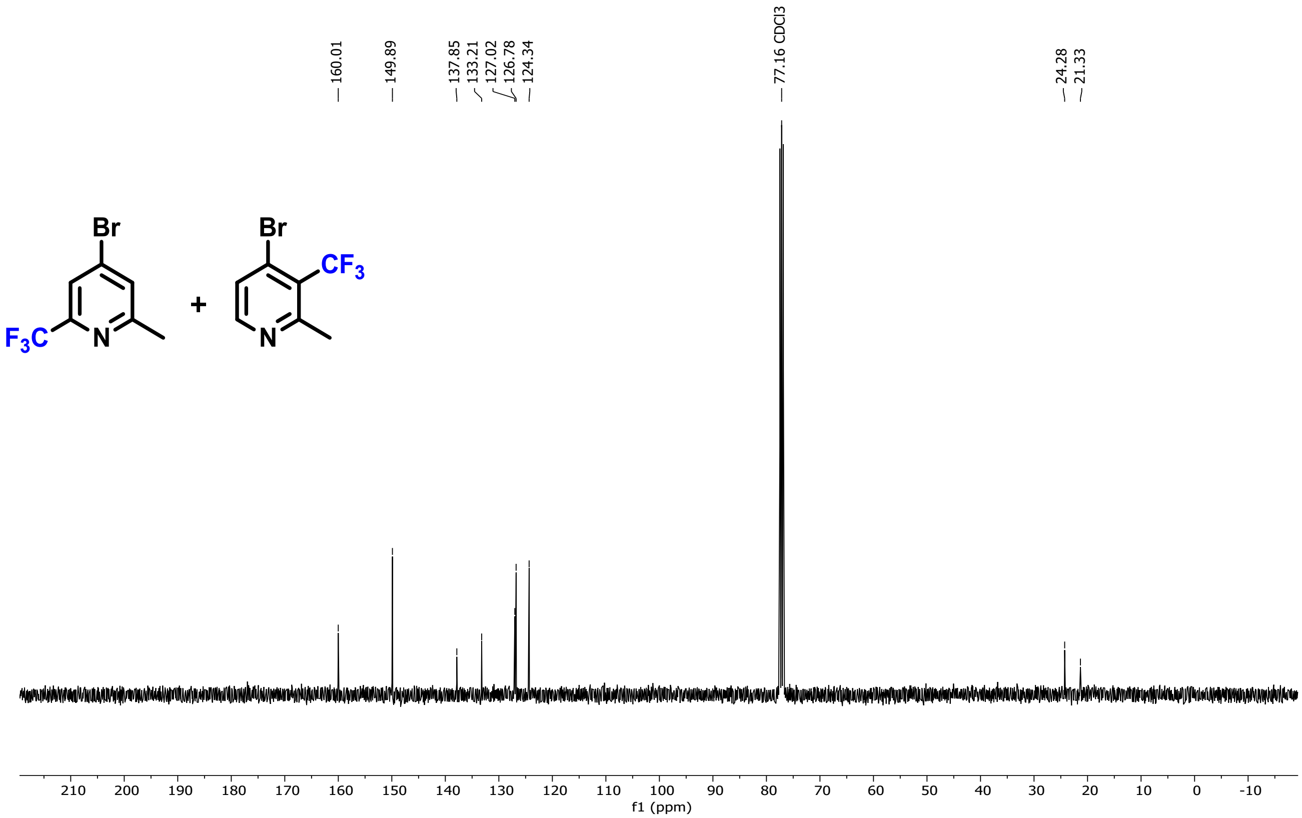


Figure S42. ^{13}C NMR spectrum of **2s** recorded in $CDCl_3$, solvent residual peak is at 77.16 ppm

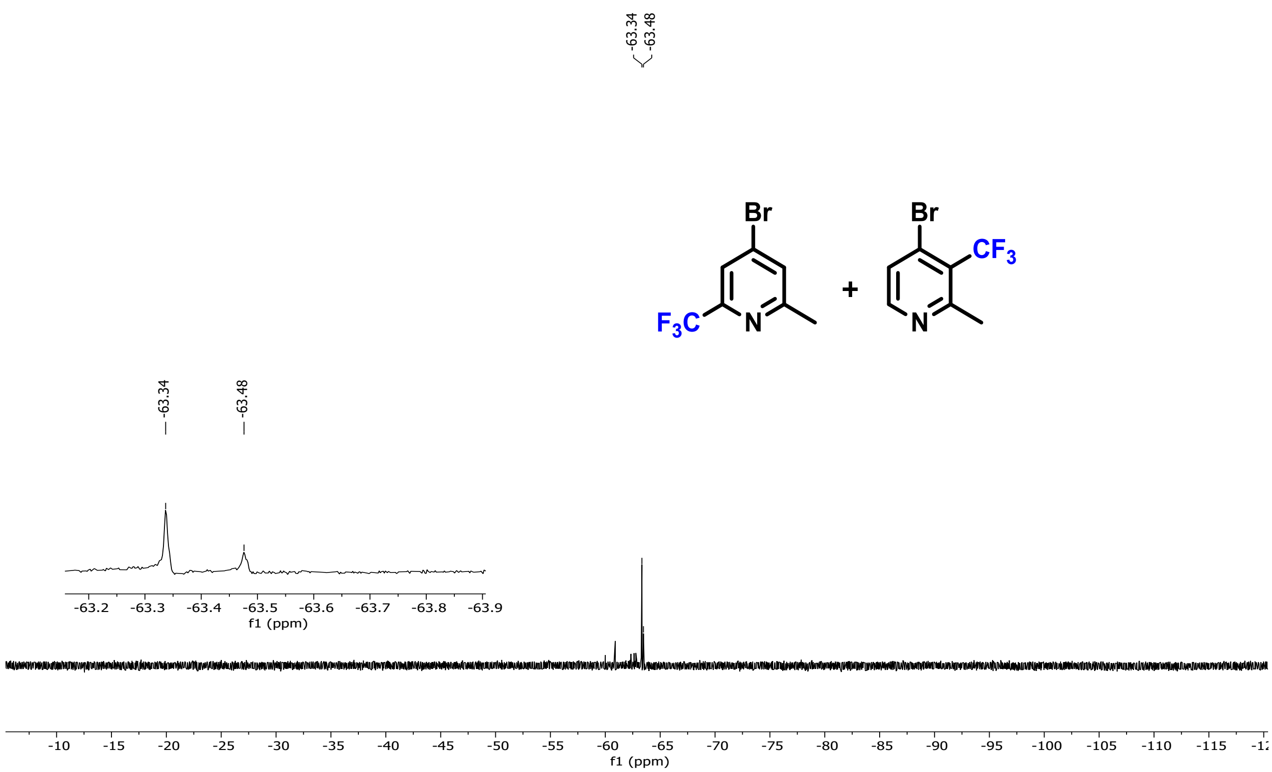


Fig S43. ^{19}F NMR spectrum of **2s** recorded in $CDCl_3$

7.0 Coordinates of optimized geometries

^{Ph,Ph}NacNac$^-$

-1 1

N	0.86741100	0.35513700	1.48441800
N	0.92873200	0.33981200	-1.44661400
C	1.58070800	0.11167900	-2.63712500
C	-0.40833300	0.14908000	1.26522500
C	-1.40260700	0.01668300	2.39915300
C	1.36405900	-1.01209100	-3.46645300
H	0.59808300	-1.72776500	-3.18178400
C	-0.35900200	0.15879200	-1.27875400
C	-1.00288700	0.11713800	-0.01927200
H	-2.08681300	0.11360200	-0.03991300
C	1.48004400	0.13143100	2.69656200
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C	-1.35773600	0.88829000	3.49299000
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C	2.93456400	-0.27466700	5.10175600
H	3.48961400	-0.43015500	6.02239200
C	-3.22898600	-0.92919700	-3.55710500
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C	-2.08777900	0.91977200	-4.58965400
H	-1.98453600	1.62635500	-5.40876400
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1

0 1

Zn	0.00000100	-0.00000200	-0.15269700
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C	0.18767100	-3.93581000	-1.41770900
H	-0.73530300	-4.35713600	-1.03223300
C	-2.01094500	-1.86734100	-1.28437900
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$1^{2.+}$ (as triplet)

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C -2.85790700 -0.28522700 0.70165500

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H	-3.92413500	-3.78234600	-0.65359400
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H	-4.71378200	-2.06553700	1.56809900
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H	-6.80380200	-1.57423500	2.79250400
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C	2.32124400	-2.51984800	-2.99023100
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C	1.42137100	-0.94054700	2.19709700
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H	5.87267700	-2.61934200	2.71097500
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C	3.83442000	4.72616300	-3.91274700
H	4.28861100	5.43887000	-4.59288400
C	-2.31511300	3.90866800	-2.87338000

H -3.13143300 4.49184600 -3.28532800

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