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Synthesis of 2-(polyfluoromethyl)pyrimido[1,2-*a*]benzimidazole-4-carbaldehydes derivatives

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General remarks

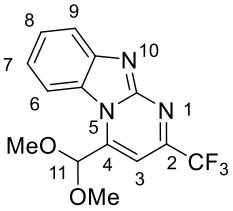
^1H (400, 500 MHz), ^{19}F (376, 470 MHz), ^{13}C (126 MHz) and ^{15}N (50 MHz) NMR spectra were recorded on a Bruker DRX-400 and AVANCE-500 spectrometers with TMS and C_6F_6 as the internal standards. The complete assignment of ^1H, ^{13}C and ^{15}N signals was based on 2D ^1H-^1H NOESY, ^1H-^{13}C HSQC / HMBC and ^1H-^{15}N HMBC experiments. Mass spectrometry was performed using a Bruker maXis Impact HD spectrometer. Melting points were determined on a Stuart Melting Point SMP3 apparatus with open capillaries and are uncorrected. Elemental analysis was carried out on a Eurovector EA 3000 automated analyzer. Reactions were monitored by thin layer chromatography (TLC) with Sorbfil/UV_{254} pre-coated silica gel plate. All reagents and solvents were commercially available and used without further purification. Starting 1-polyfluoromethyl-4,4-dimethoxybutane-2,4-diones **1a,b** were prepared according to the procedure described in our previous work [D. L. Chizhov, D. V. Belyaev, D. S. Yachevskii, G. L. Rusinov, O. N. Chupakhin and V. N. Charushin, *J. Fluorine Chem.*, 2017, **199**, 39].

Reaction of 1-polyfluoromethyl-4,4-dimethoxybutane-2,4-diones 1 with 2-aminobenzimidazole (general procedure).

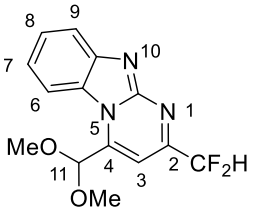
A solution of 1-polyfluoroalkyl-4,4-dimethoxybutane-2,4-dione **1** (1 mmol) and 2-amino-benzimidazole (1.05 mmol, 0.140 g) in an appropriate solvent (10 ml) (see Table 1 in the main text) was refluxed for 6 h. The solvent was evaporated, and the residue was dried *in vacuo*. The crude product was purified by column chromatography on silica gel using $CHCl_3$ as the eluent to collect a mixture of compounds **2** and **3**. R_f **2a** = 0.45; R_f **3a** = 0.4; R_f **2b** = 0.42; R_f **3b** = 0.27. The total yields are listed in Table 1 of the main text.

Regioselective synthesis of 2-R^F-pyrimido[1,2-*a*]benzimidazole-4-carbaldehyde dimethyl acetals 2a,b in the presence of $B(OEt)_3$.

A solution of 1-polyfluoroalkyl-4,4-dimethoxybutane-2,4-dion **1** (1 mmol), 2-amino-benzimidazole (1.05 mmol, 0.140 g) and $B(OEt)_3$ (3 mmol, 0.438 g) in acetonitrile (30 ml) was refluxed for 6 h. The mixture was cooled and diluted with water (100 ml). The resulting precipitate was filtered off, washed with water (3x10 ml) and dried in air. The crude product was crystallized from hexane.



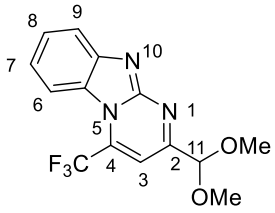
2-Trifluoromethyl-4-(dimethoxymethyl)pyrimido[1,2-a]benzimidazole 2a, (0.21 g) 66%, yellow powder, m.p. 141-142 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.48 (s, 6H, 2*OCH_3), 6.13 (s, 1H, H^{11}), 7.49 (ddd, 1H, H^7, *J* 8.6, 7.2, 1.1 Hz), 7.52 (s, 1H, H^3), 7.63 (ddd, 1H, H^8, *J* 8.2, 7.2, 1.0 Hz), 8.05 (d, 1H, H^9, *J* 8.2 Hz), 8.27 (d, 1H, H^6, *J* 8.6 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ: 92.87 (s, CF_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 53.22 (s, OCH_3), 96.63 (C^{11}), 101.51 (q, C^3, $^3J_{CF}$ 1.5 Hz), 116.68 (C^6), 120.26 (q, CF_3, $^1J_{CF}$ 276.1 Hz), 120.56 (C^9), 123.70 (C^7), 126.58 (C^{5a}), 127.33 (C^8), 144.80 (C^{9a}), 148.30 (C^4), 149.14 (C^{10a}), 151.46 (q, C^2, $^2J_{CF}$ 37.2 Hz). ^{15}N NMR (50 MHz, $CDCl_3$) δ: 171.9 (N^5), 223.1 (N^{10}), 274.5 (N^1). Found, %: C, 54.11, H, 3.87, N, 13.43, F, 18.22. Calculated for $C_{14}H_{12}F_3N_3O_2$: C, 54.02, H, 3.89, N, 13.50, F, 18.31.



2-Difluoromethyl-4-(dimethoxymethyl)pyrimido[1,2-*a*]benzimidazole 2b, (0.25 g) 86%, yellow powder, m.p. 128-130.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.47 (s, 6H, 2*OCH_3), 6.08 (s, 1H, H^{11}), 6.68 (t, 1H, HCF_2, $^2J_{HF}$ 54.7 Hz), 7.47 (ddd, 1H, H^7, *J* 8.6, 7.2, 1.3 Hz), 7.50 (s, 1H, H^3), 7.62 (ddd, 1H, H^8, *J* 8.3, 7.2, 1.1 Hz), 8.06 (d, 1H, H^9, ^3J 8.3 Hz), 8.26 (d, 1H, H^6, ^3J 8.6 Hz). ^{19}F NMR

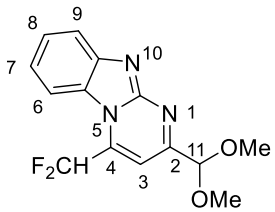
(470 MHz, $CDCl_3$) δ: 45.90 (d, HCF_2, $^2J_{FH}$ 54.7 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 53.14 (s, OCH_3), 96.93 (C^{11}), 101.18 (C^3), 113.55 (t, HCF_2, $^1J_{CF}$ 242.0 Hz), 116.48 (C^6), 120.76 (C^9), 123.16 (C^7), 126.75 (C^8), 126.88 (C^{5a}), 145.29 (C^{9a}), 147.61 (C^4), 150.01 (C^{10a}), 156.43 (t, C^2, $^2J_{CF}$ 28.5 Hz). ^{15}N NMR (50 MHz, $CDCl_3$) δ: 170.4 (N^5), 224.5 (N^{10}), 276.4 (N^1). Found, %: C, 57.01, H, 4.40, N, 14.29, F, 12.73. Calculated for $C_{14}H_{13}F_2N_3O_2$: C, 57.34, H, 4.47, N, 14.33, F, 12.96.

Preparation of 4-R^F-pyrimido[1,2-*a*]benzimidazole-2-carbaldehyde dimethyl acetals 3a,b. Compound **1** (2.5 mmol) and 2-aminobenzimidazole (2.63 mmol, 0.35 g) were refluxed in trifluoroethanol (10 ml) for 6 h. The mixture was evaporated to dryness and twice chromatographed (silica gel, eluent $CHCl_3$).



4-Trifluoromethyl-2-(dimethoxymethyl)pyrimido[1,2-*a*]-benzimidazole 3a, (0.07 g) 9%, yellow powder. ^1H NMR (500 MHz, $CDCl_3$) δ: 3.58 (s, 6H, 2*OCH_3), 5.33 (s, 1H, H^{11}), 7.56 (ddd, 1H, H^7, *J* 8.6, 7.2, 1.3 Hz), 7.65 (s, 1H, H^3), 7.69 (ddd, 1H, H^8, *J* 8.3, 7.2, 0.9 Hz), 8.11 (dm, 1H, H^6, *J* 8.6 Hz), 8.17 (d, 1H, H^9, *J* 8.3 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ: 94.68 (d, CF_3, J_{FH} 2.2 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 55.45 (s, OCH_3), 103.51 (q, C^3, $^3J_{CF}$ 5.3 Hz), 104.57 (C^{11}), 114.31 (q, C^6, $^5J_{CF}$ 5.9 Hz), 119.69 (q, CF_3, $^1J_{CF}$ 274.2 Hz), 120.98 (C^9), 123.96 (C^7), 125.90 (C^{5a}), 127.07 (C^8), 135.46 (q, C^4, $^2J_{CF}$ 37.9 Hz), 144.34 (C^{9a}), 149.58 (C^{10a}), 162.70 (C^2). ^{15}N NMR (50 MHz, $CDCl_3$) δ: 160.1 (N^5), 224.1 (N^{10}), 284.6 (N^1).

Additionally 0.36 g (46 %) of (**2a** + **3a)** mixture was isolated. Overall yield is ~55 %.

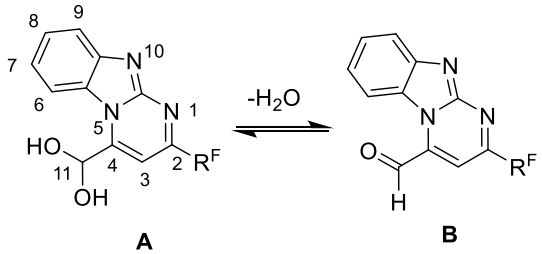


4-Difluoromethyl-2-(dimethoxymethyl)pyrimido[1,2-*a*]benzimidazole 3b, (0.26 g) 36%, yellow powder, m.p. 149-152 °C. ^1H NMR (500 MHz, $CDCl_3$) δ: 3.55 (s, 6H, 2*OCH_3), 5.30 (s, 1H, H^{11}), 7.24 (t, 1H, HCF_2, $^2J_{HF}$ 52.6 Hz), 7.43 (s, 1H, H^3), 7.46 (ddd, 1H, H^7, *J* 8.5, 7.3, 1.1 Hz), 7.60 (t, 1H, H^8, *J* 7.7 Hz), 8.01 (d, 1H, H^6, *J* 8.5 Hz), 8.04 (d, 1H, H^9, *J* 8.3 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ: 40.86 (d, HCF_2, $^2J_{FH}$ 52.4 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 55.30 (s, OCH_3), 102.99 (t, C^3, $^3J_{CF}$ 7.7 Hz), 104.70 (s, C^{11}), 109.84 (t, HCF_2, $^1J_{CF}$ 243.0 Hz), 114.25 (t, C^6, $^5J_{CF}$ 4.7 Hz), 120.90 (C^9), 123.40 (C^7), 126.22 (C^{5a}), 126.65 (C^8), 140.26 (t, C^4, $^2J_{CF}$ 25.6 Hz), 144.58 (C^{9a}), 149.80 (C^{10a}), 162.91 (C^2). ^{15}N NMR (50 MHz, $CDCl_3$) δ: 163.8 (N^5), 224.1 (N^{10}), 281.3 (N^1). Found, %: C, 57.23, H, 4.37, N, 14.35, F, 13.05. Calculated for $C_{14}H_{13}F_2N_3O_2$: C, 57.34, H, 4.47, N, 14.33, F, 12.96.

Additionally 0.40 g (54 %) of (**2b** + **3b**) mixture was isolated. Overall yield is ~90 %.

Hydrolysis of acetals 2 to hydrates 4

Acetal **2** (1.0 mmol) was dissolved in MeOH (~1-2 ml), and hydrochloric acid (5% water solution, 15 ml) was added. The resulting mixture was boiled evaporating the solvent approximately by half in volume. The mixture was diluted with water (30 ml) and neutralized with $NaHCO_3$ (pH ~6-7). The precipitate was filtered off, washed with water (3x20 ml) and dried in air.



2-Trifluoromethyl-4-(dihydroxymethyl)pyrimido[1,2-*a*]benzimidazole 4a, 0.16 g, 55%, greenish yellow powder. Ratio **A:B** 94:6

Major (**A)** ^{1}H NMR (400 MHz, DMSO-d_6) δ: 6.57 (t, 1H, H^{11}, *J* 6.8 Hz), 7.55 (t, 1H, H^7, *J* 7.8 Hz), 7.60 (s, 1H, H^3), 7.61 (d, 2*OH, 2H, *J* 6.8 Hz), 7.68 (t, 1H, H^8, *J* 7.6 Hz), 8.01 (d, 1H, H^9, *J* 8.2 Hz), 8.48 (d, 1H, H^6, *J* 8.6 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ: 94.76 (s, CF_3).

Minor (**B**) ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.08 (d, 1H, H^9, *J* 7.8 Hz), 8.22 (s, 1H, H^3), 8.69 (d, 1H, H^6, *J* 8.6 Hz), 10.41 (s, 1H, H^{11}). Other signals are overlapped. ^{19}F NMR (376 MHz, DMSO-d6) δ: 94.97 (s, CF_3). HRMS (+ESI): m/z calculated for $C_{12}H_8F_3N_3O_2$: 283.0569 $[M]^+$, found 266.0538 $[M\text{-}H_2O]^+$

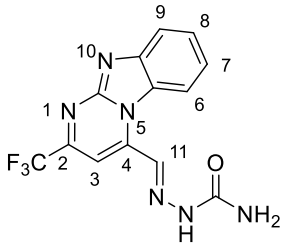
2-Difluoromethyl-4-(dihydroxymethyl)pyrimido[1,2-*a*]benzimidazole 4b, 0.13 g, 50%, greenish yellow powder. Ratio **A:B** 90:10

Major (**A**). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 6.55 (t, 1H, H^{11}, *J* 6.8 Hz) 7.13 (t, 1H, HCF_2, $^2J_{HF}$ 54.2 Hz), 7.49 (t, 1H, H^7, *J* 8.0 Hz), 7.51 (s, 1H, H^3), 7.54 (d, 2H, 2*OH, *J* 6.8 Hz), 7.63 ((t, 1H, H^8, *J* 7.5 Hz), 7.96 (d, 1H, H^9, *J* 8.0 Hz), 8.44 (d, 1H, H^6, *J* 8.5 Hz). ^{19}F NMR (376 MHz, DMSO-d6) δ: 45.97 (d, HCF_2, $^2J_{FH}$ 54.2 Hz).

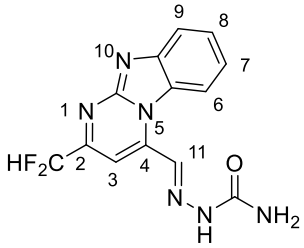
Minor (**B**). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.23 (t, 1H, HCF_2, $^2J_{HF}$ 54.0 Hz), 8.02 (s, 1H, H^3), 8.65 (d, 1H, H^6, *J* 8.5 Hz), 10.40 (s, 1H, H^{11}). Other signals are overlapped. ^{19}F NMR (376 MHz, DMSO-d_6) δ: 44.60 (d, HCF_2, $^2J_{FH}$ 53.9 Hz). HRMS (+ESI): HRMS (+ESI): m/z calculated for $C_{12}H_9F_2N_3O_2$: 265.0663 $[M]^+$, found 248.0628 $[M\text{-}H_2O]^+$

Reactions of 2-(R^F)- 4-(dihydroxymethyl)pyrimido[1,2-*a*]benzimidazoles 4a,b with semicarbazide hydrochloride

A mixture of compound **4** (1 mmol) and semicarbazide hydrochloride (1.1 mmol, 0.12 g) in AcOH (3 ml) was refluxed for 1 h. Then AcONa (2 mmol, 0.16 g) was added, and the mixture was refluxed for more 30 min, cooled to r.t. and diluted with water (50 ml). The precipitate was filtered off, washed with water (3x20 ml) and dried in air.



2-(Trifluoromethyl)pyrimido[1,2-*a*]benzimidazole-4-carbaldehyde semicarbazone 5a, 0.25g, 78%, dark red powder, m.p. 220 °C (decomp.) ^{1}H NMR (500 MHz, DMSO-d_6) δ: 7.0 and 7.4 (both br. s, each 1H, NH_2) 7.56 (t, 1H, H^7, *J* 7.7 Hz), 7.69 (t, 1H, H^8, *J* 7.7 Hz), 8.00 (d, 1H, H^9, *J* 8.2 Hz), 8.32 (s, 1H, H^3), 8.37 (d, 1H, H^6, *J* 8.5 Hz), 9.06 (s, 1H, H^{11}), 11.29 (s, 1H, NH). ^{19}F NMR (470 MHz, DMSO-d_6) δ: 95.31 (s, CF_3). ^{13}C NMR (126 MHz, DMSO-d_6) δ: 98.16 (C^3), 116.54 (C^6), 119.71 (C^9), 120.71 (q, CF_3, $^1J_{CF}$ 275.7 Hz), 122.88 (C^7), 127.02 (C^8), 128.99 ($C^{1'}$), 144.58 (C^4), 148.19 (C^{9a}), 149.40 (C^{10a}), 149.99 (q, C^2, $^2J_{CF}$ 34.9 Hz), 155.58 (C=O). HRMS (+ESI): m/z calculated for $C_{13}H_9F_3N_6O$: 322.0790 $[M]^+$, found 323.0863 $[M+H]^+$



2-(Difluoromethyl)pyrimido[1,2-*a*]benzimidazole-4-carbaldehyde semicarbazone 5b, 0.25 g, 82%, %, dark red powder, m.p.>220 °C (decomp.) ^{1}H NMR (500 MHz, DMSO-d_6) δ: 6.7 – 7.4 (br.s, 2H, NH_2), 7.05 (t, 1H, HCF_2, $^2J_{HF}$ 54.3 Hz) 7.50 (t, 1H, H^7, *J* 7.8 Hz), 7.64 (t, 1H, H^8, *J* 7.6 Hz), 7.97 (d, 1H, H^9, *J* 8.2 Hz), 8.11 (s, 1H, H^3), 8.32 (d, 1H, H^6, *J* 8.5 Hz), 9.02 (s, 1H, H^{11}), 11.19 (s, 1H, NH). ^{19}F NMR (470 MHz, DMSO-d_6) δ: 45.66 (d, HCF_2, $^2J_{FH}$ 54.3 Hz). ^{13}C NMR (126 MHz, DMSO-d_6) δ: 98.33 (C^3), 113.24 (t, HCF_2, $^1J_{CF}$ 240.7 Hz), 116.22 (C^6), 119.87 (C^9), 122.32 (C^7), 126.39 (C^8), 127.09 (C^{5a}), 129.49 (C^{11}), 144.99 (C^4), 147.03 (C^{9a}), 150.10 (C^{10a}), 155.68 (C=O), 156.01 (t, C^2, $^2J_{CF}$ 26.4 Hz). HRMS (+ESI): m/z calculated for $C_{13}H_{10}F_2N_6O$: 304.0884 $[M]^+$, found 305.0957 $[M+H]^+$

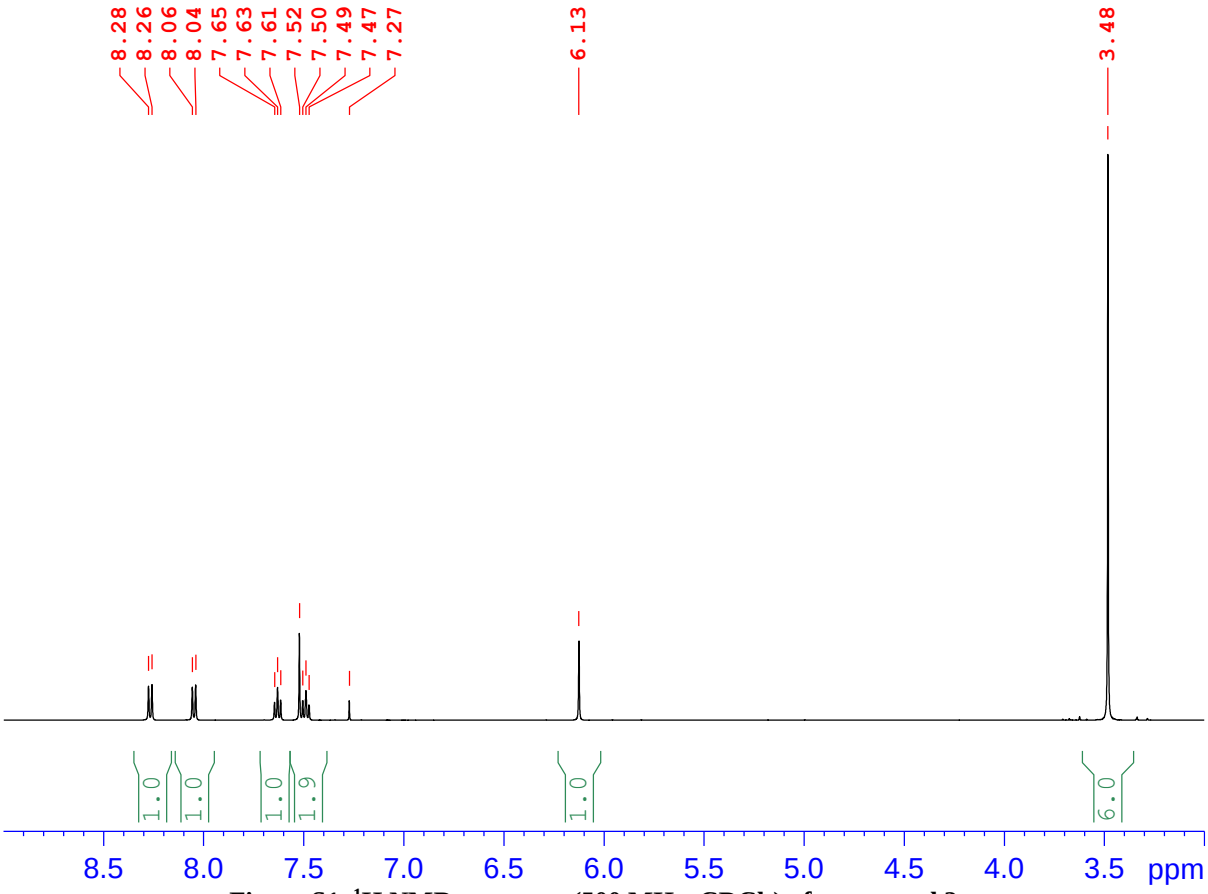


Figure S1. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound 2a.

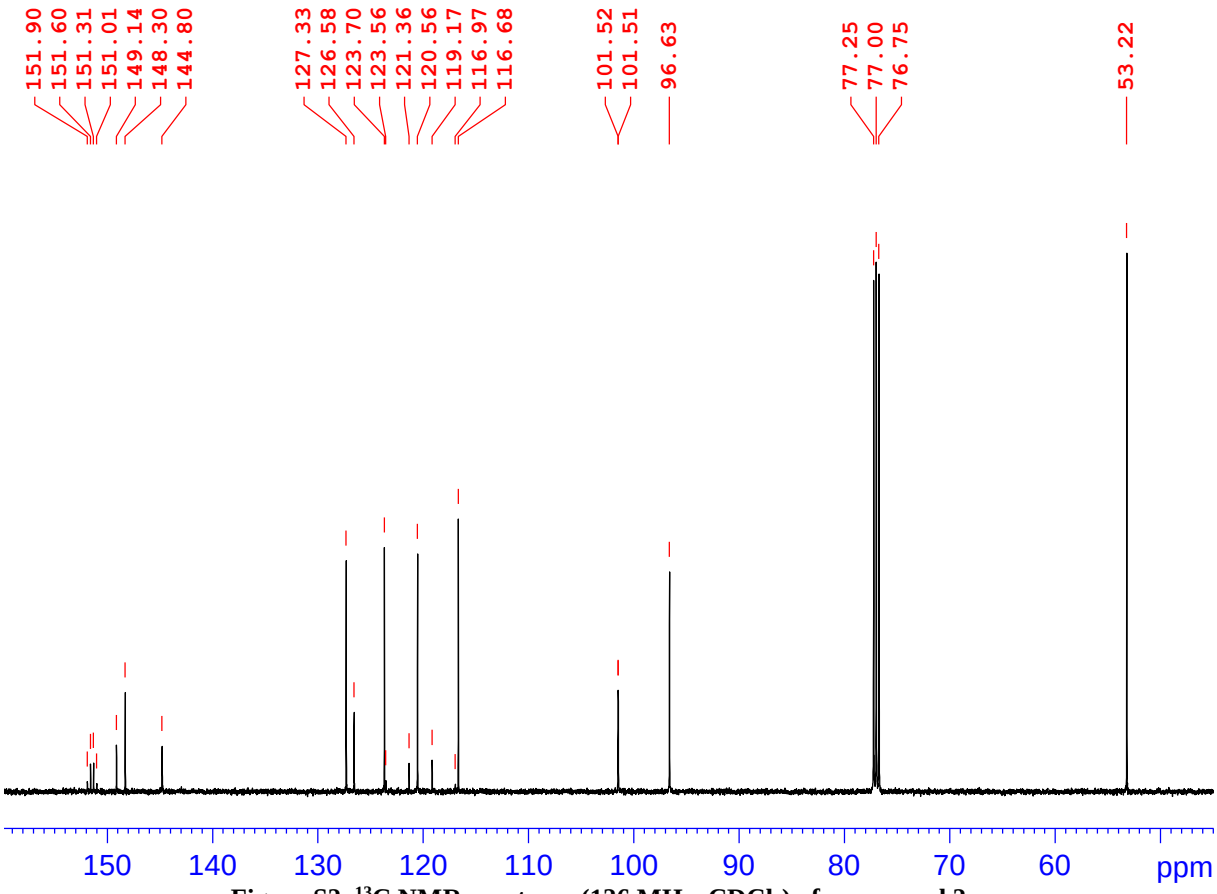


Figure S2. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound 2a.

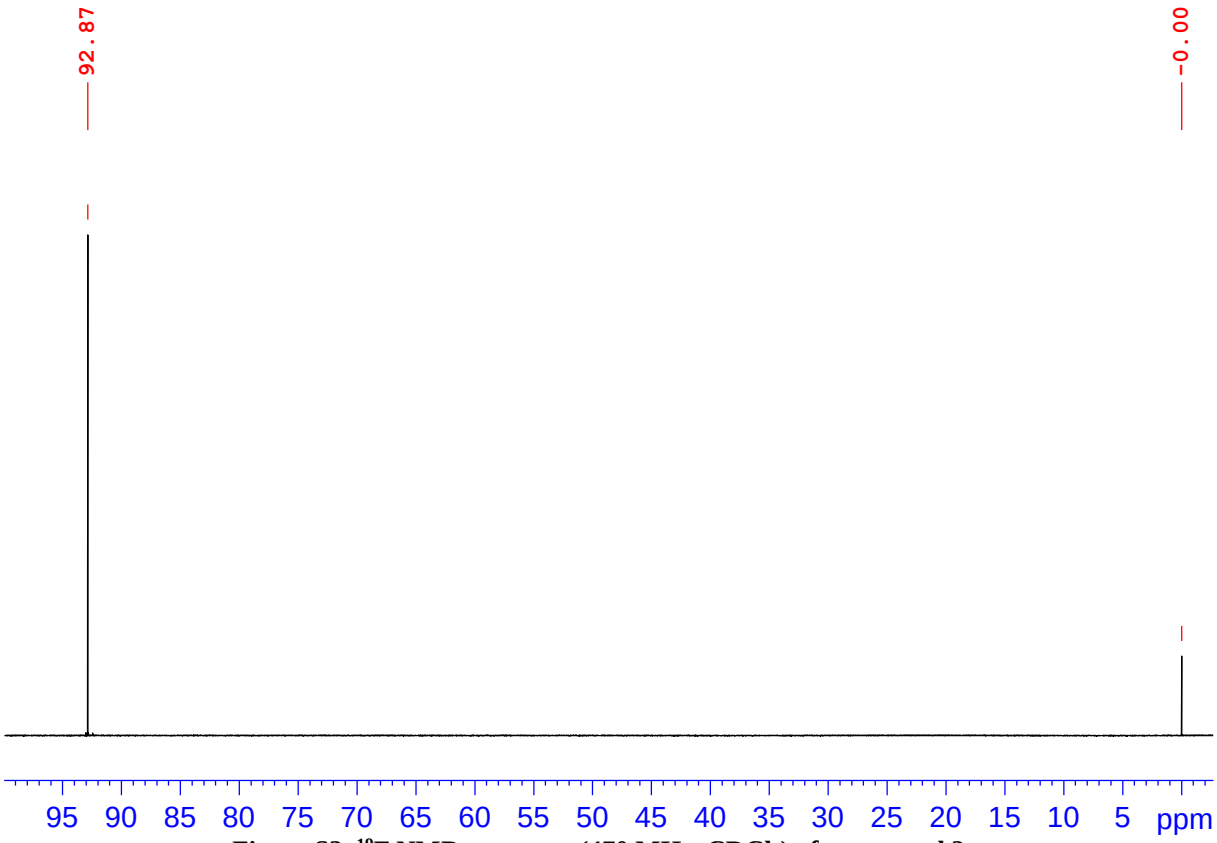


Figure S3. ^{19}F NMR spectrum (470 MHz, $CDCl_3$) of compound 2a.

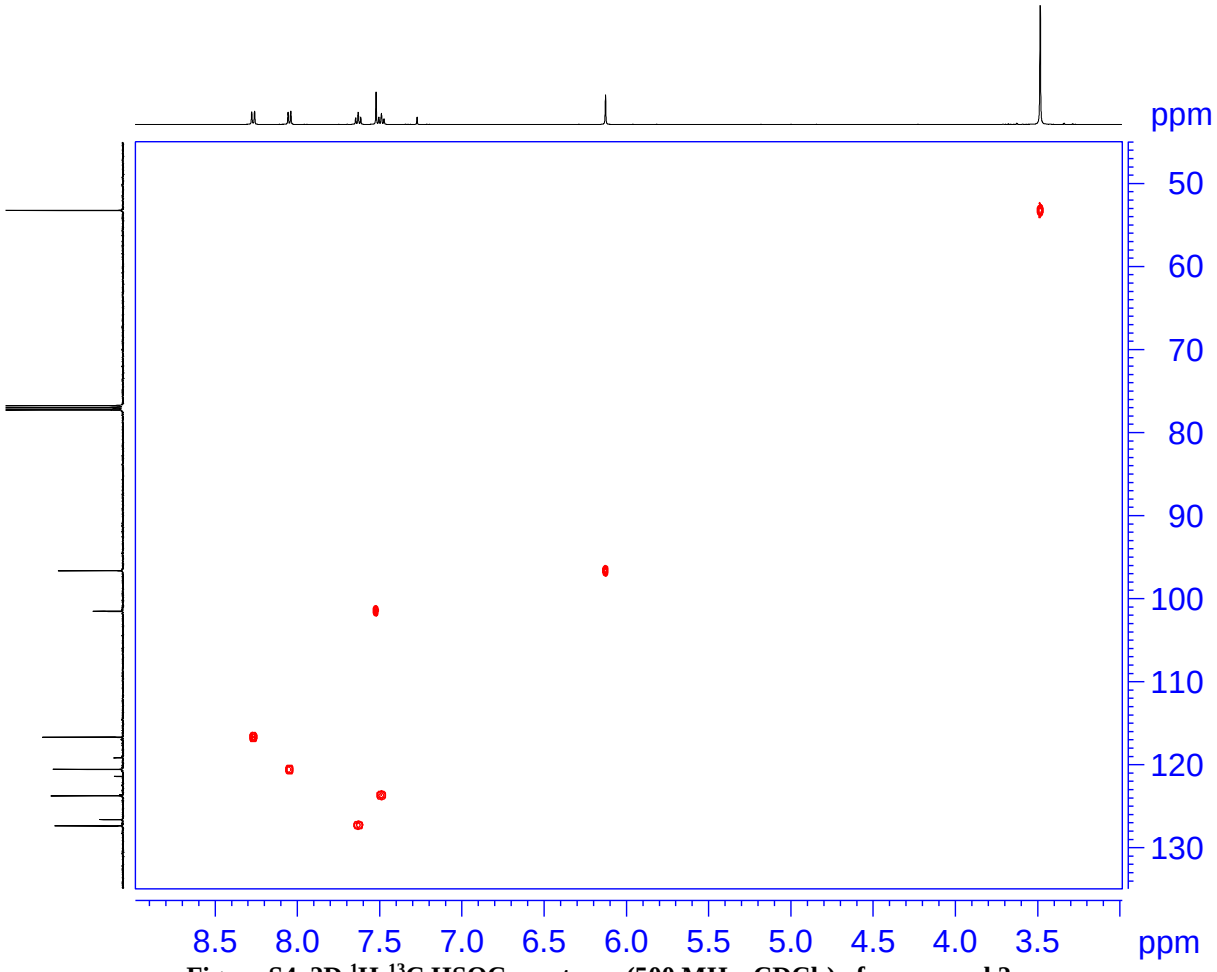


Figure S4. 2D ^{1}H-^{13}C HSQC spectrum (500 MHz, $CDCl_3$) of compound 2a.

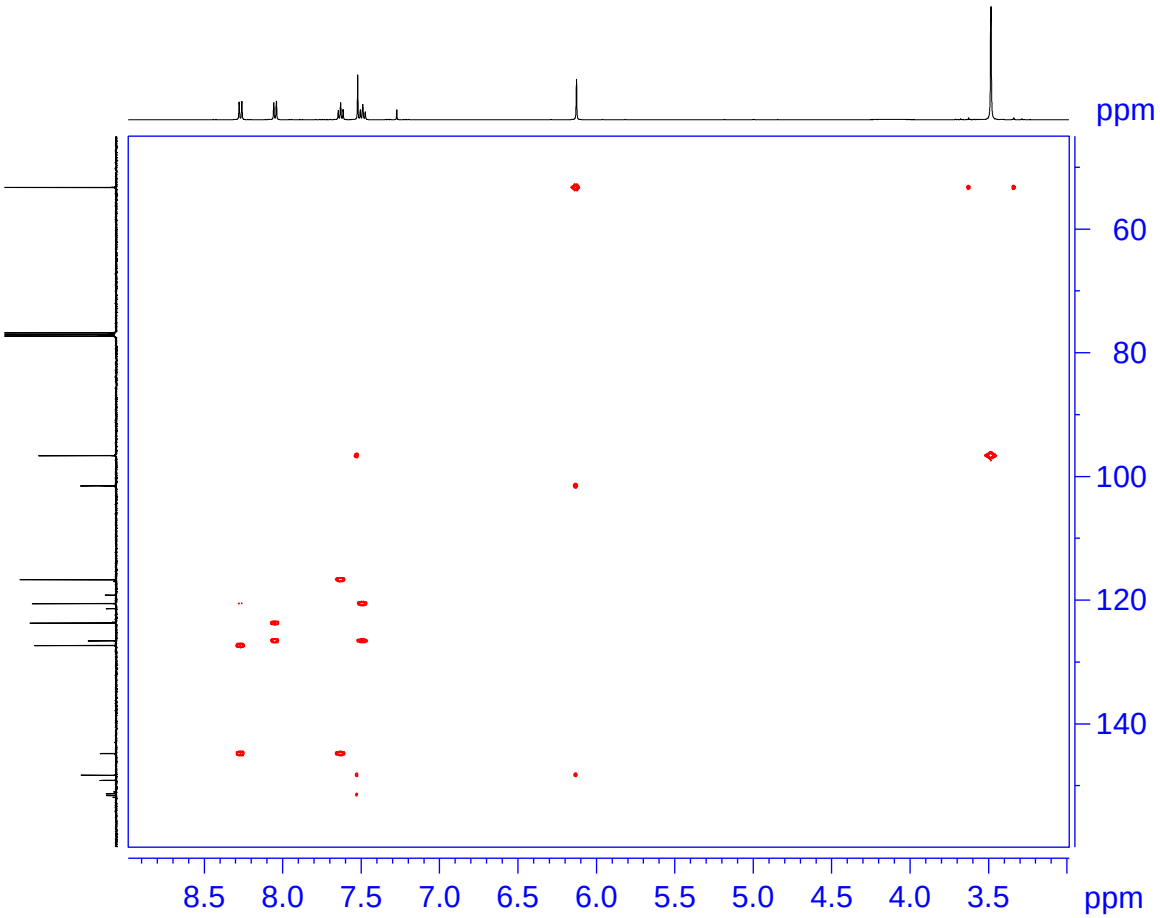


Figure S5. 2D ^{1}H-^{13}C HMBC spectrum (500 MHz, $CDCl_3$) of compound 2a.

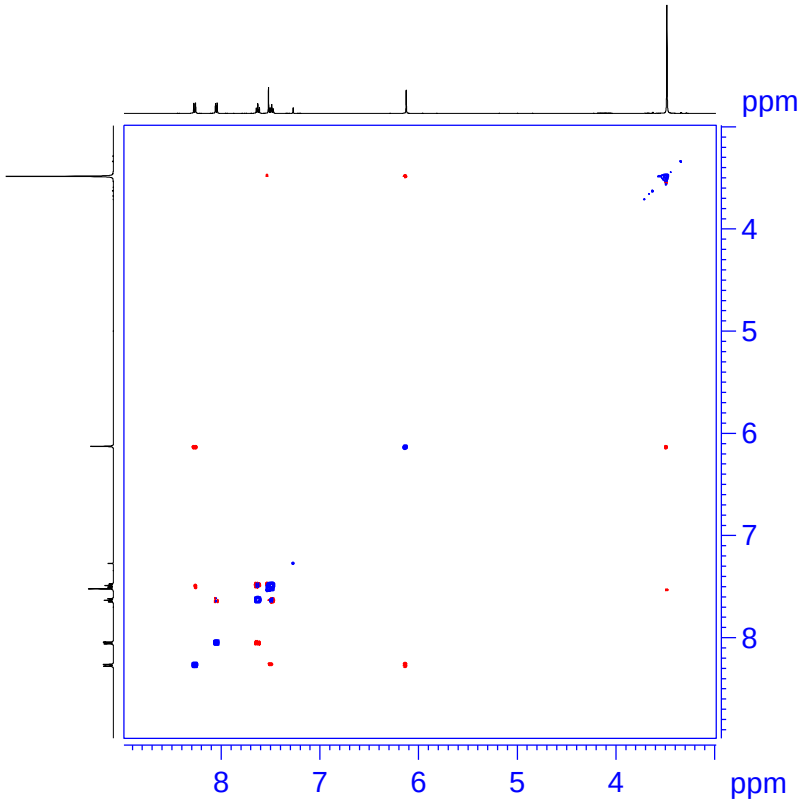


Figure S6. 2D ^{1}H-^{1}H NOESY spectrum (500 MHz, $CDCl_3$) of compound 2a.

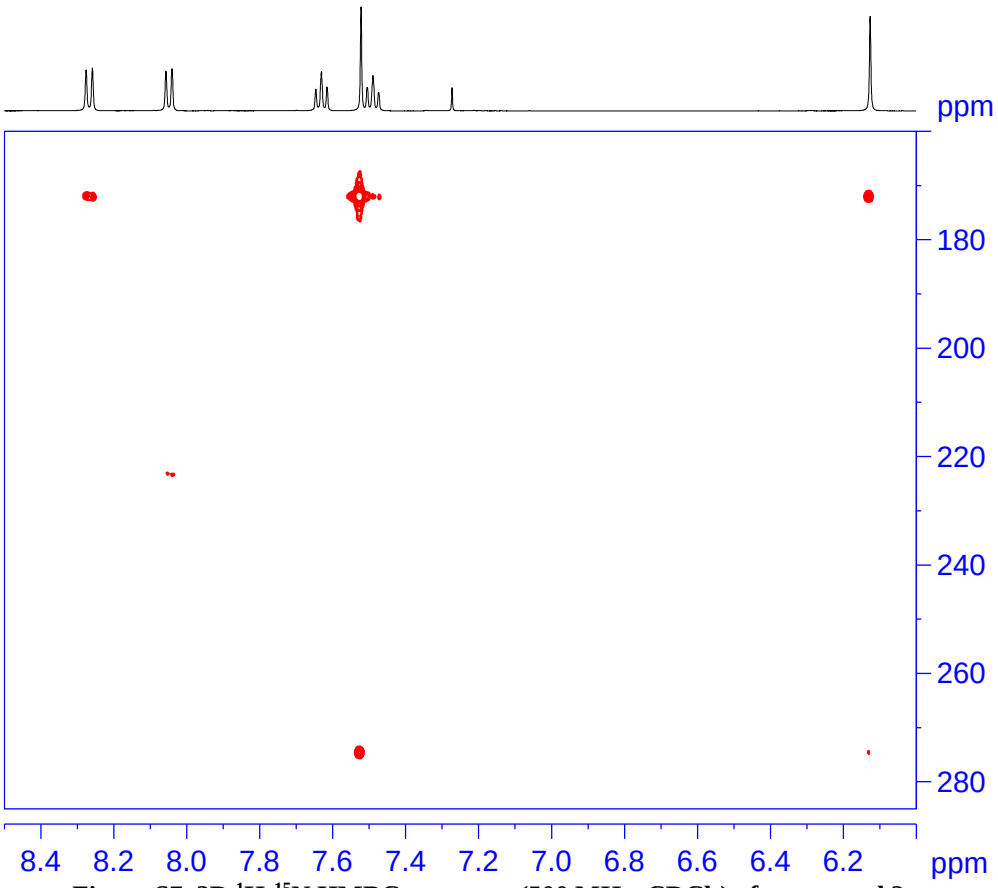


Figure S7. 2D ^{1}H-^{15}N HMBC spectrum (500 MHz, $CDCl_3$) of compound 2a.

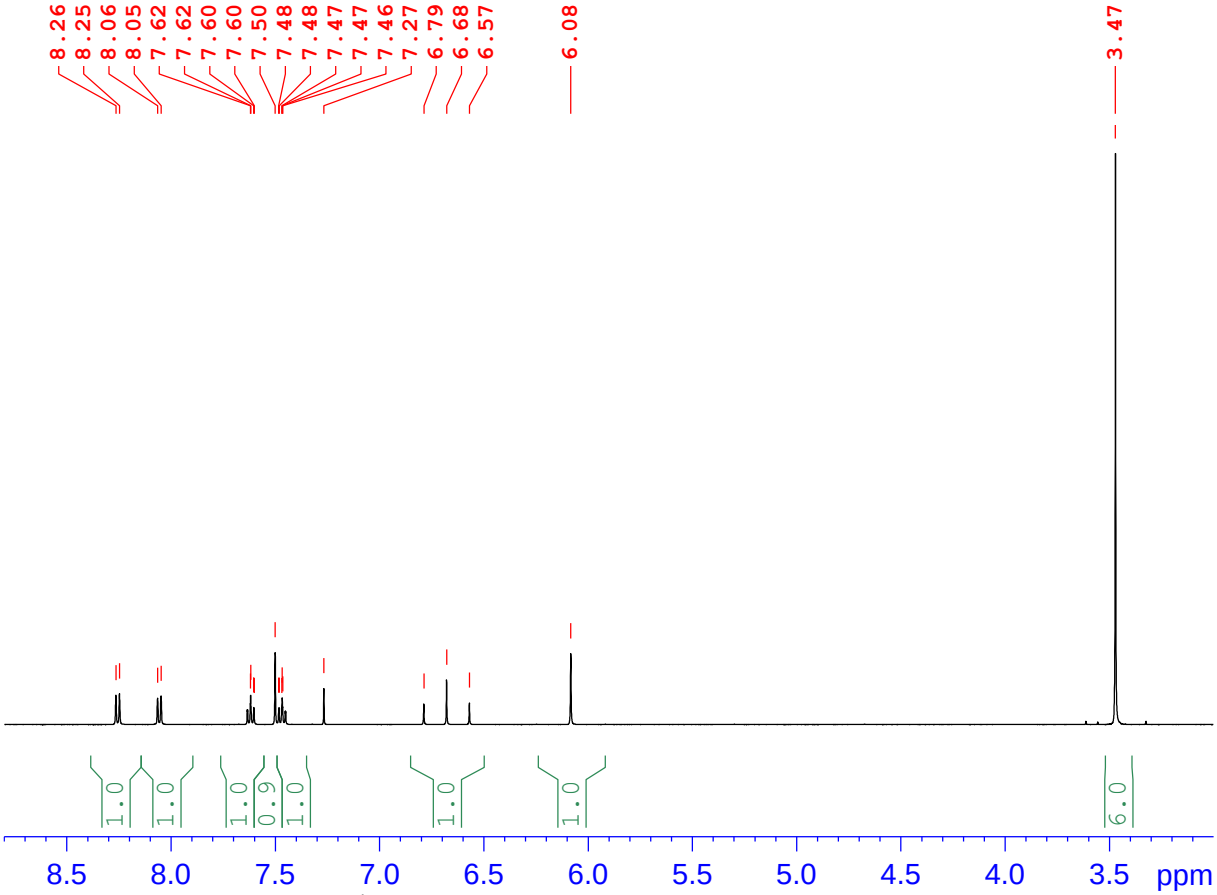


Figure S8. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound 2b.

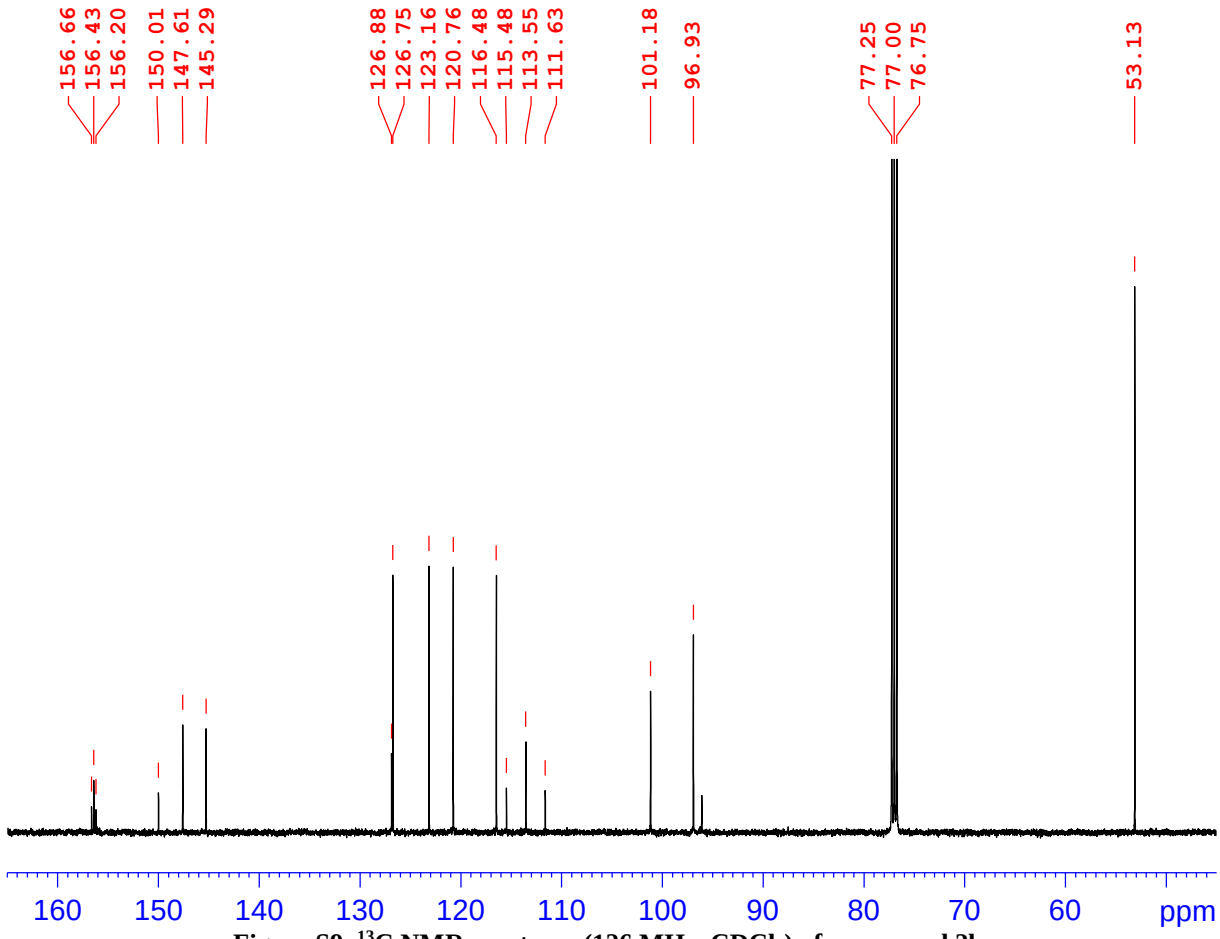


Figure S9. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound 2b.

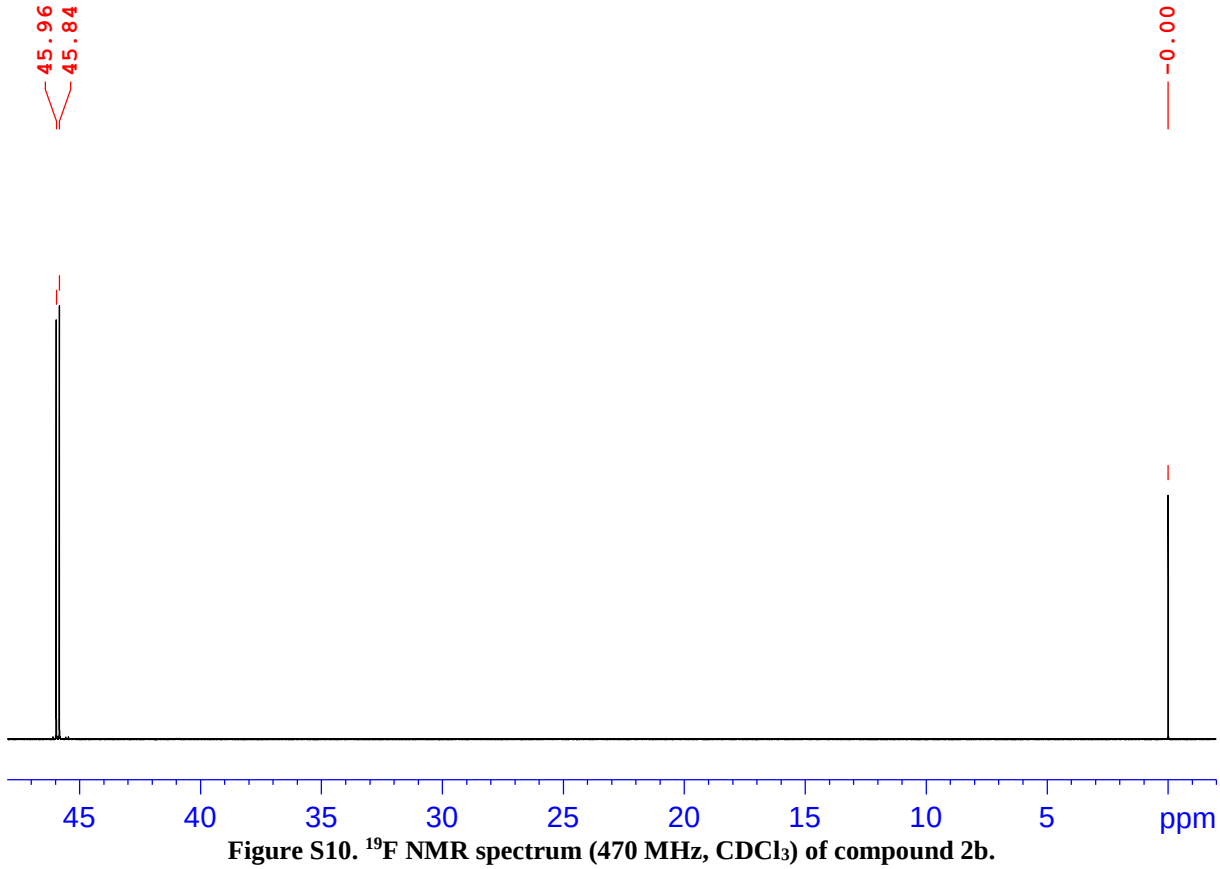


Figure S10. ^{19}F NMR spectrum (470 MHz, $CDCl_3$) of compound 2b.

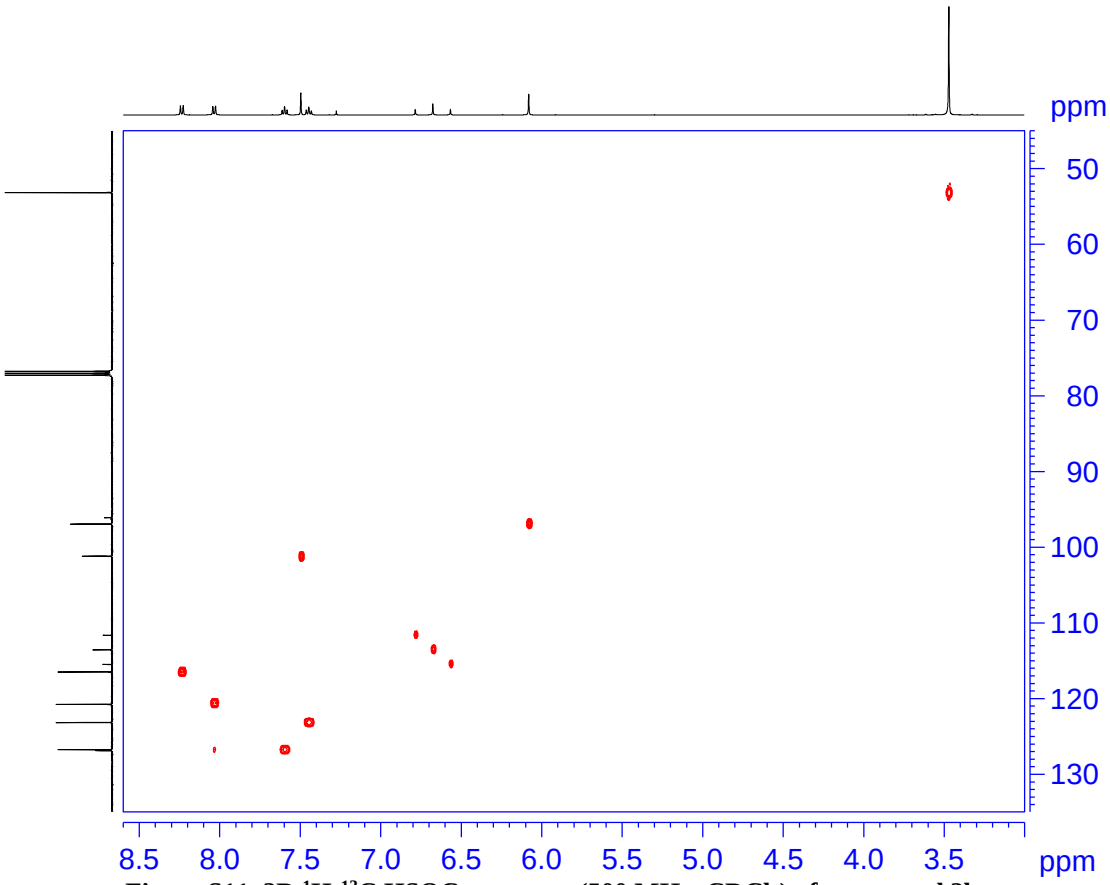


Figure S11. 2D ^{1}H-^{13}C HSQC spectrum (500 MHz, $CDCl_3$) of compound 2b.

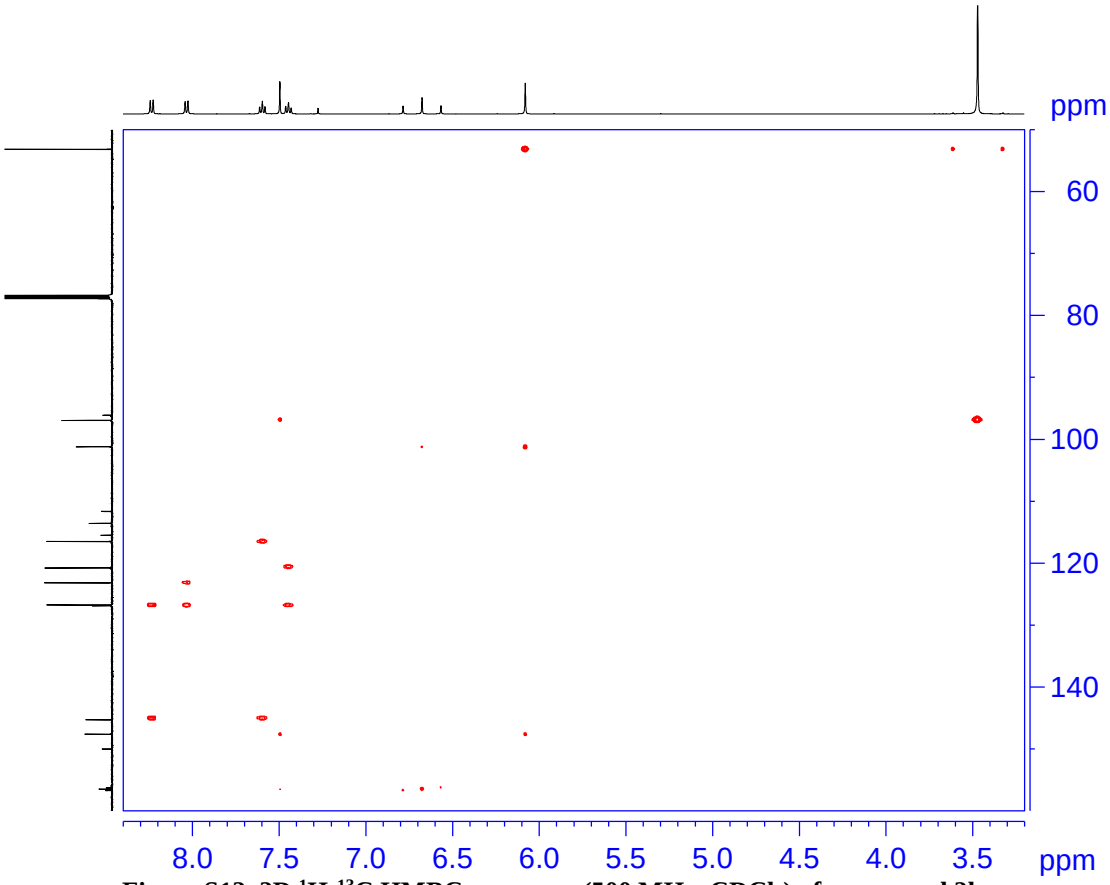


Figure S12. 2D ^{1}H-^{13}C HMBC spectrum (500 MHz, $CDCl_3$) of compound 2b.

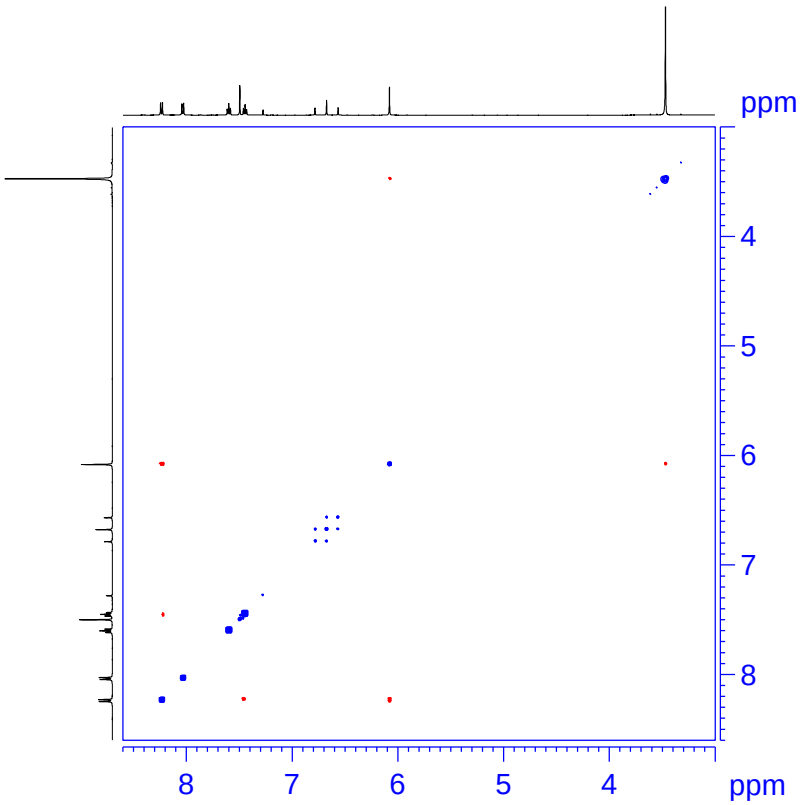


Figure S13. 2D ^{1}H-^{1}H NOESY spectrum (500 MHz, $CDCl_3$) of compound 2b.

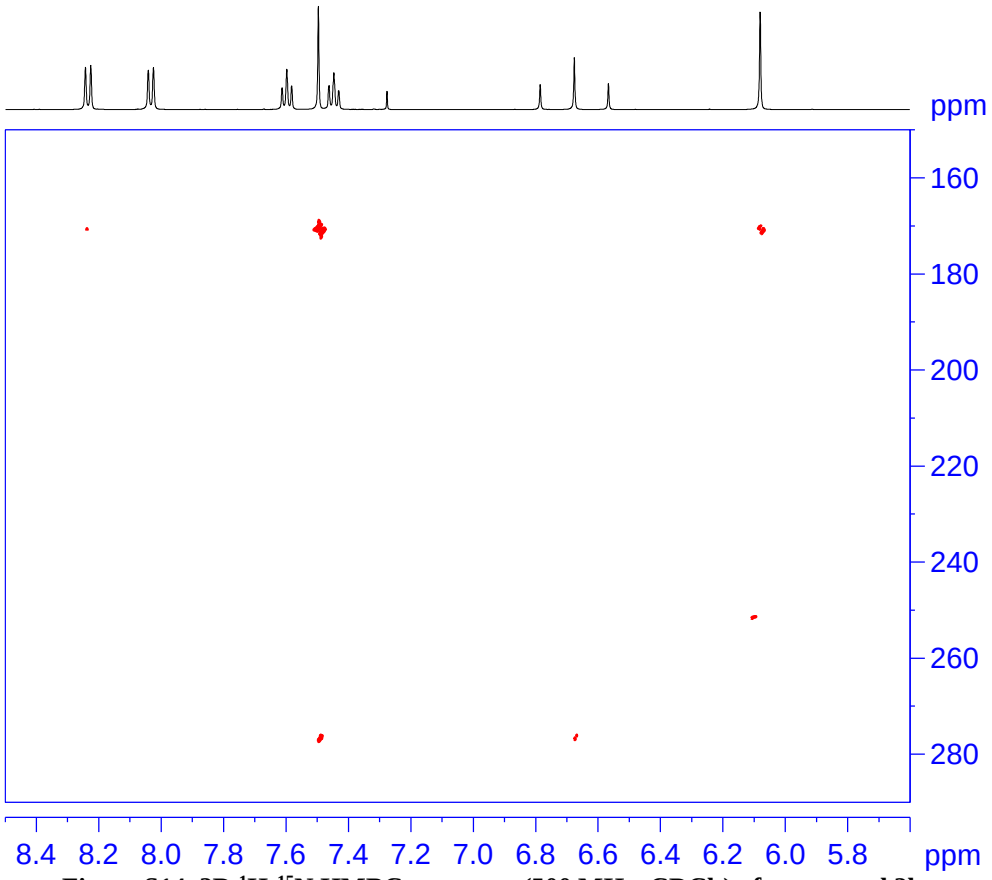


Figure S14. 2D ^{1}H-^{15}N HMBC spectrum (500 MHz, $CDCl_3$) of compound 2b.

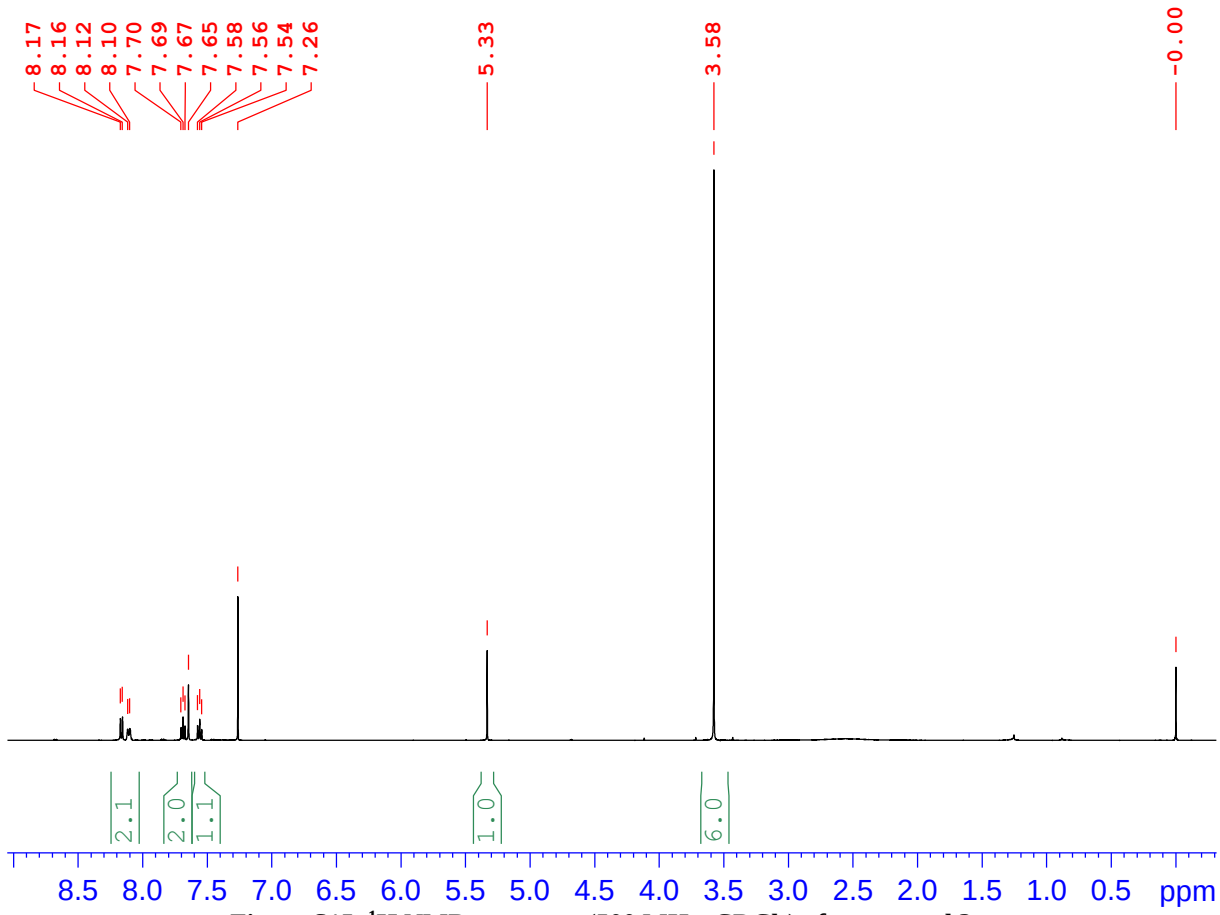


Figure S15. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound 3a.

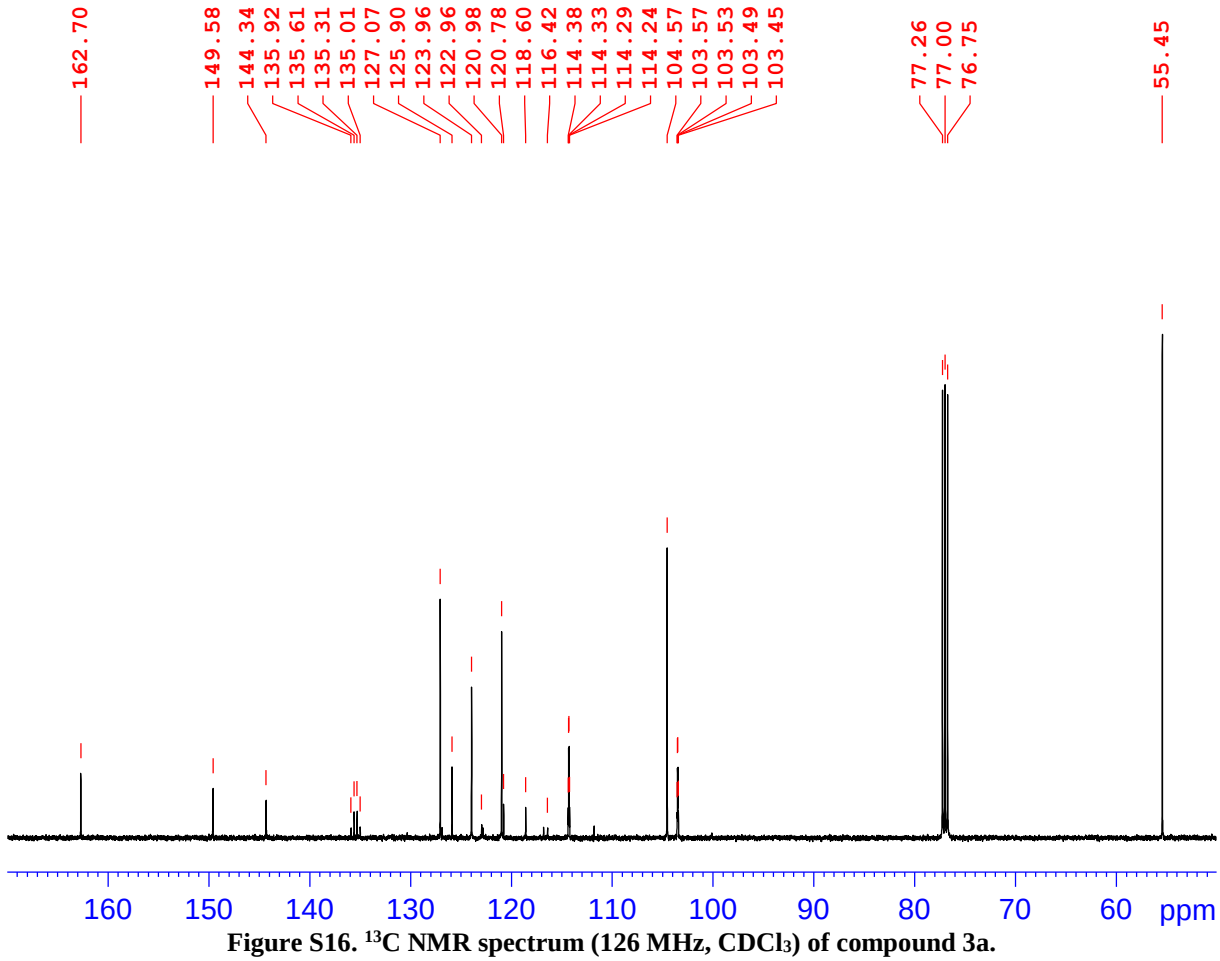


Figure S16. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound 3a.

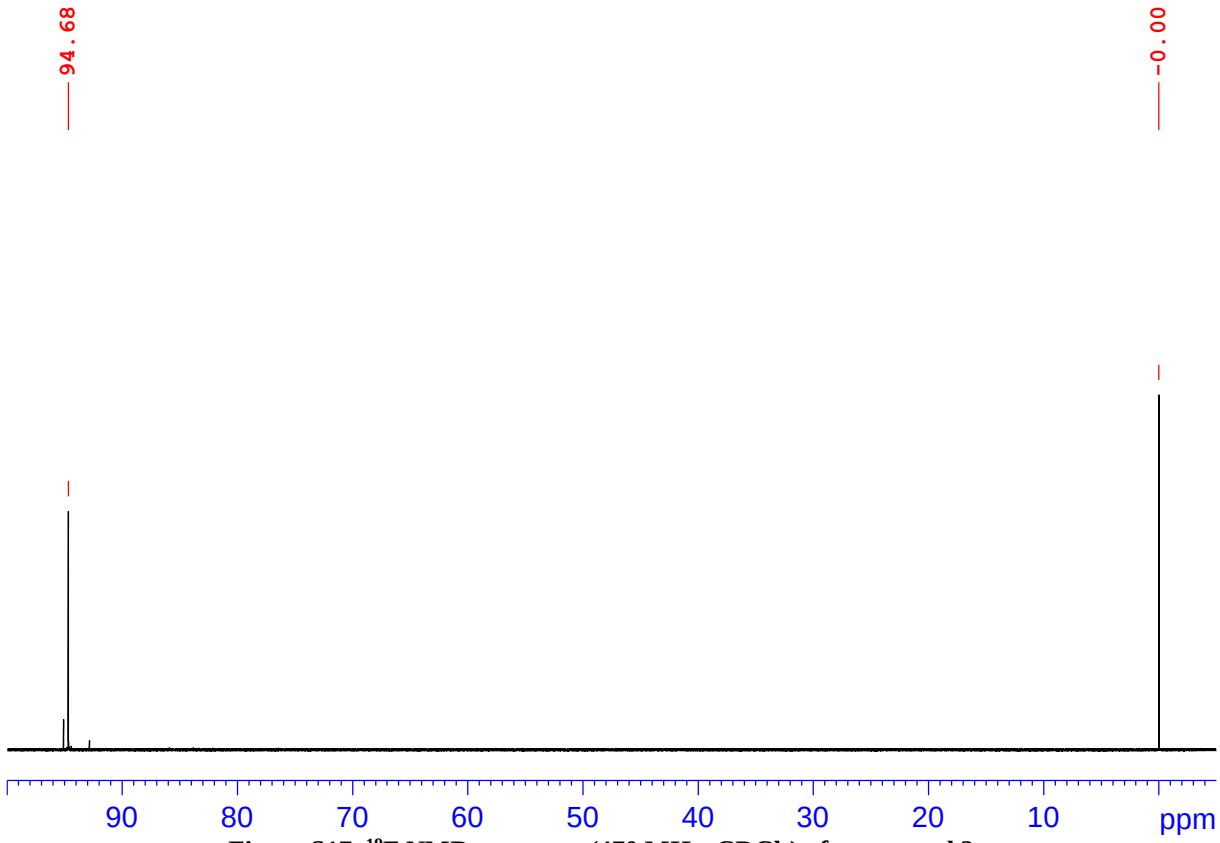


Figure S17. ^{19}F NMR spectrum (470 MHz, $CDCl_3$) of compound 3a.

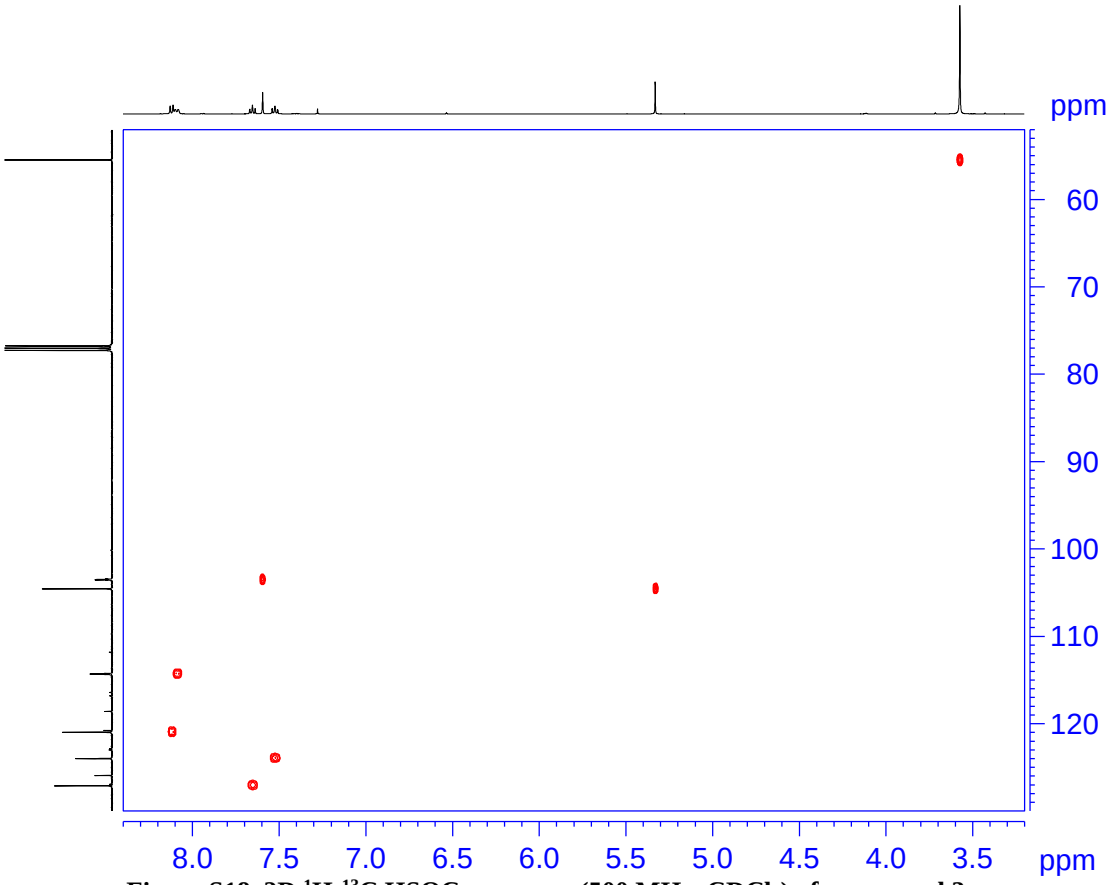


Figure S18. 2D ^{1}H-^{13}C HSQC spectrum (500 MHz, $CDCl_3$) of compound 3a.

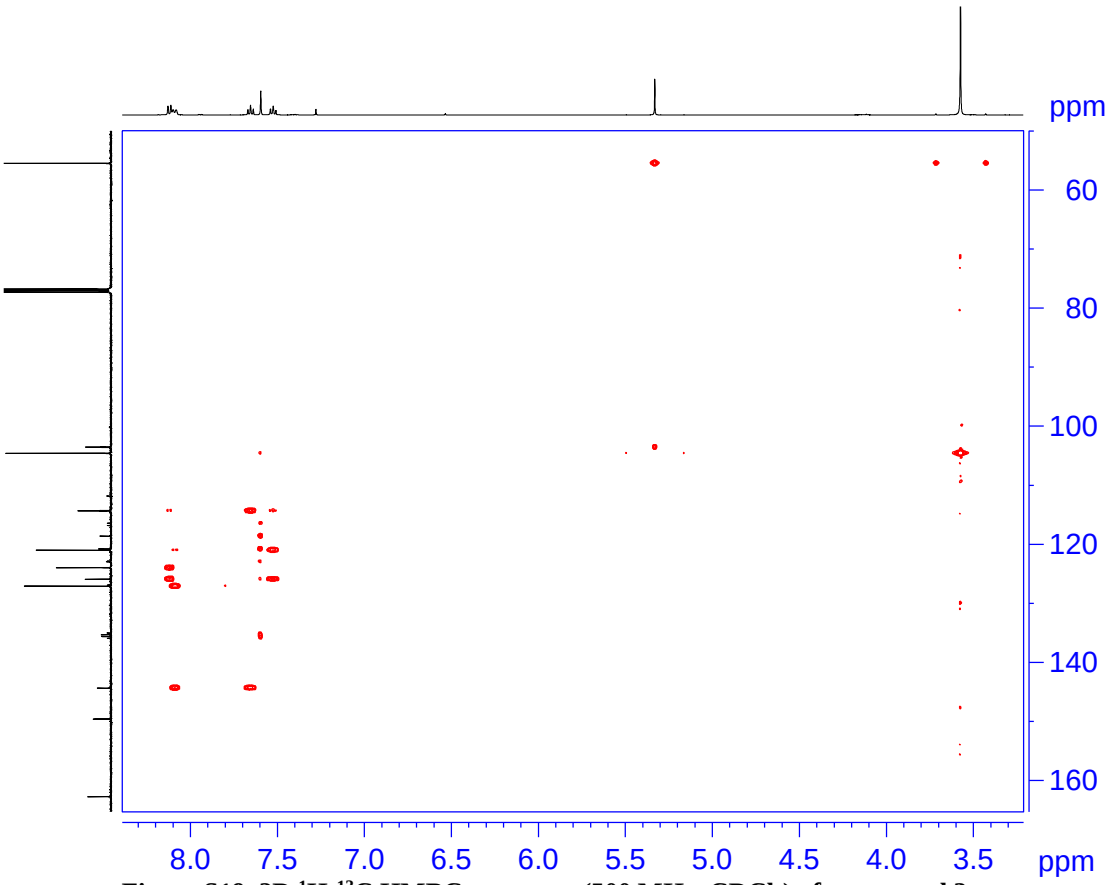


Figure S19. 2D ^{1}H-^{13}C HMBC spectrum (500 MHz, $CDCl_3$) of compound 3a.

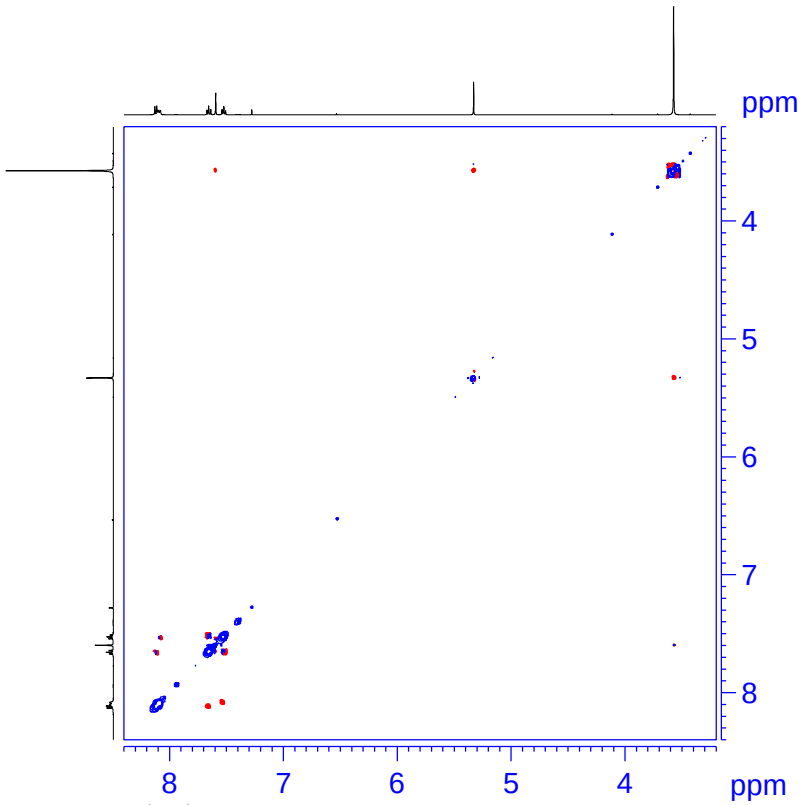


Figure S20. 2D ^{1}H-^{1}H NOESY spectrum (500 MHz, $CDCl_3$) of compound 3a.

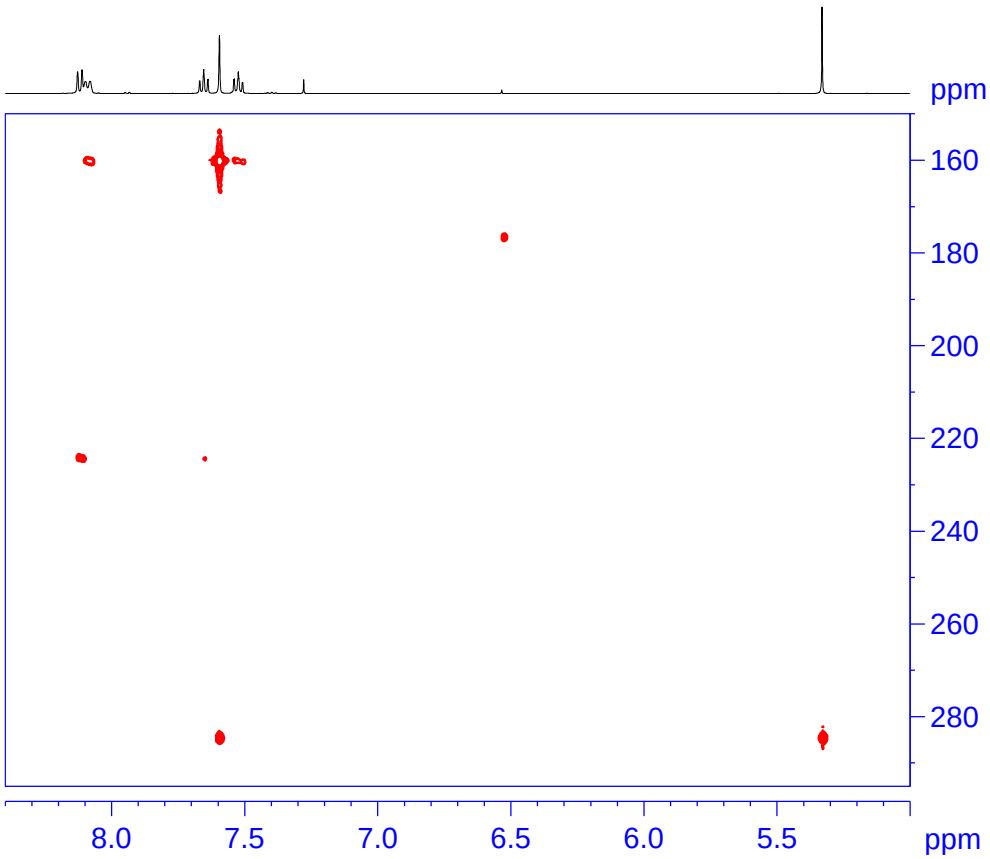


Figure S21. 2D ^{1}H-^{15}N HMBC spectrum (500 MHz, $CDCl_3$) of compound 3a.

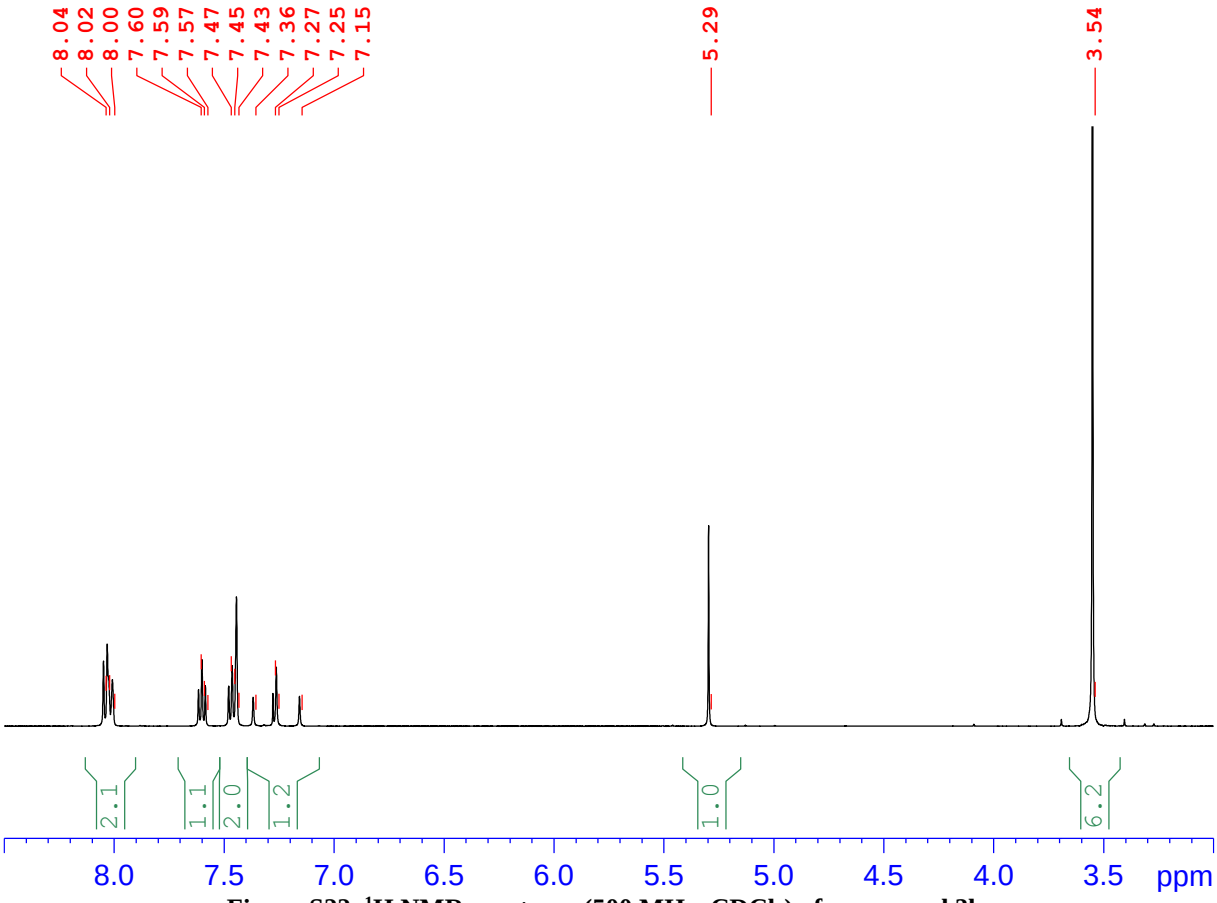


Figure S22. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound 3b.

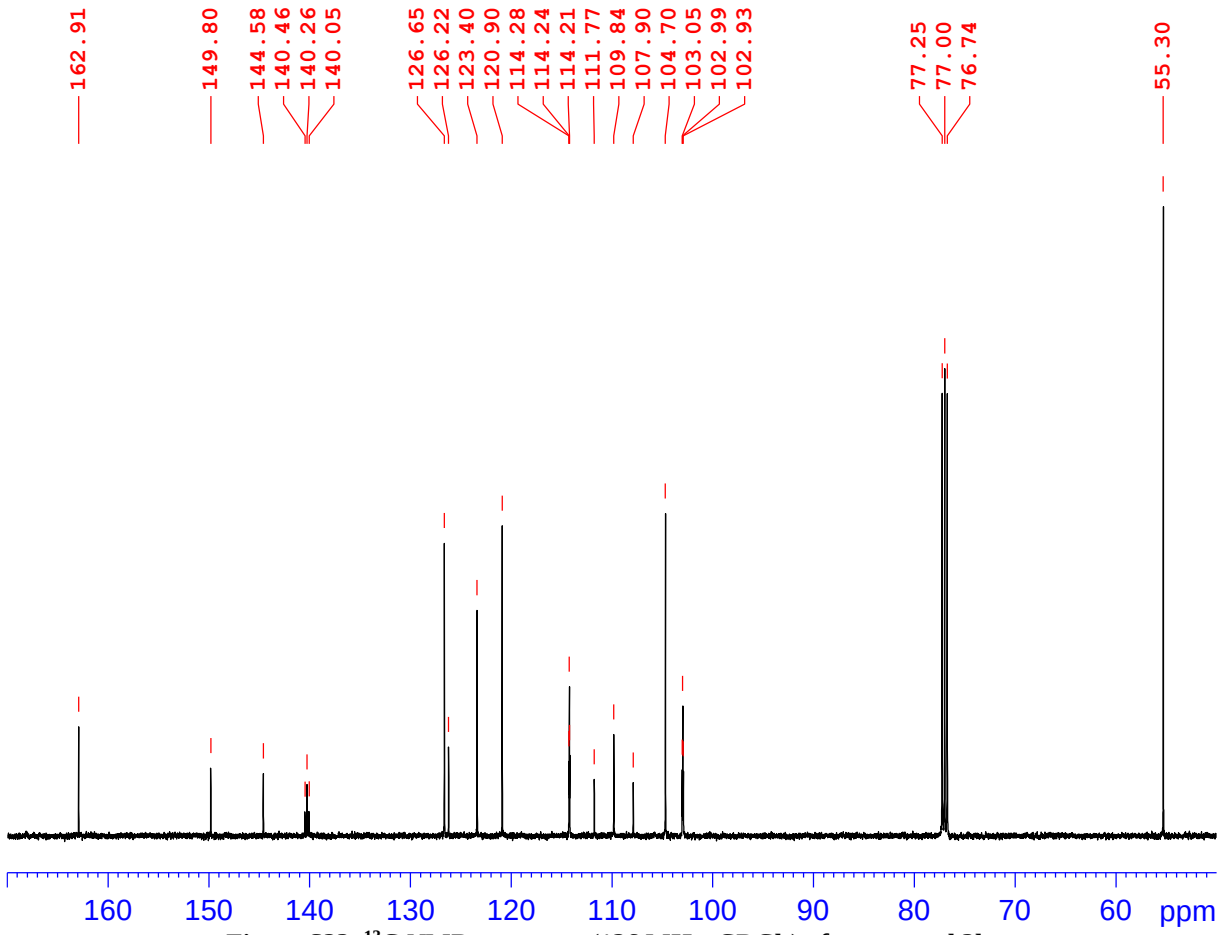


Figure S23. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound 3b.

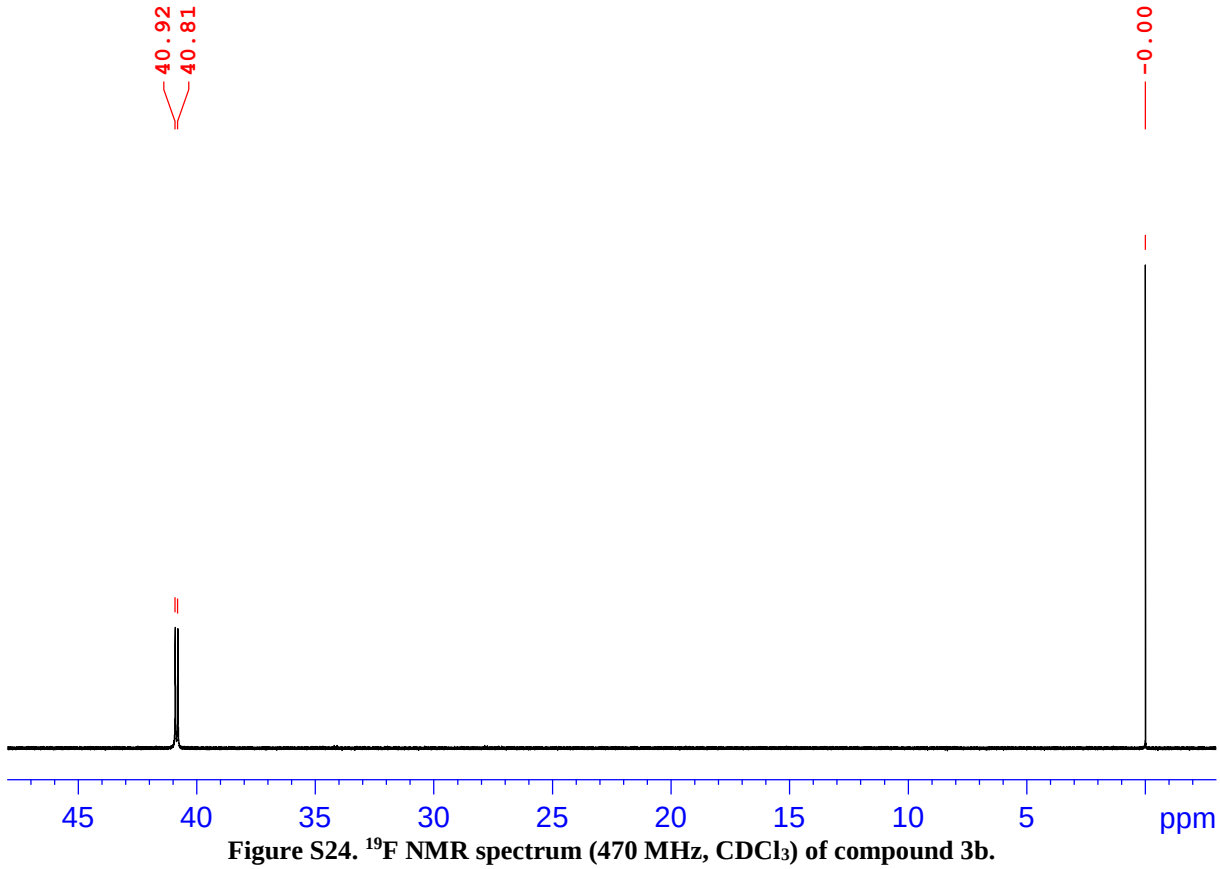


Figure S24. ^{19}F NMR spectrum (470 MHz, $CDCl_3$) of compound 3b.

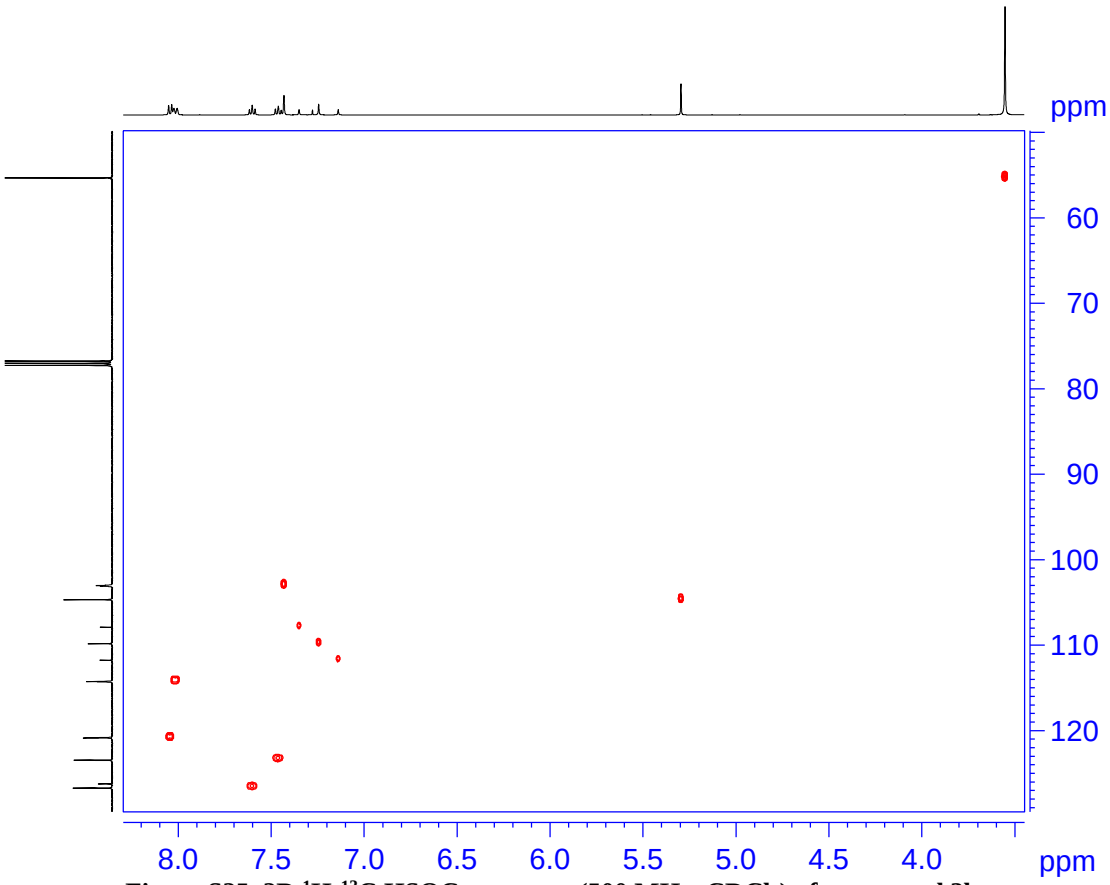


Figure S25. 2D ^{1}H-^{13}C HSQC spectrum (500 MHz, $CDCl_3$) of compound 3b.

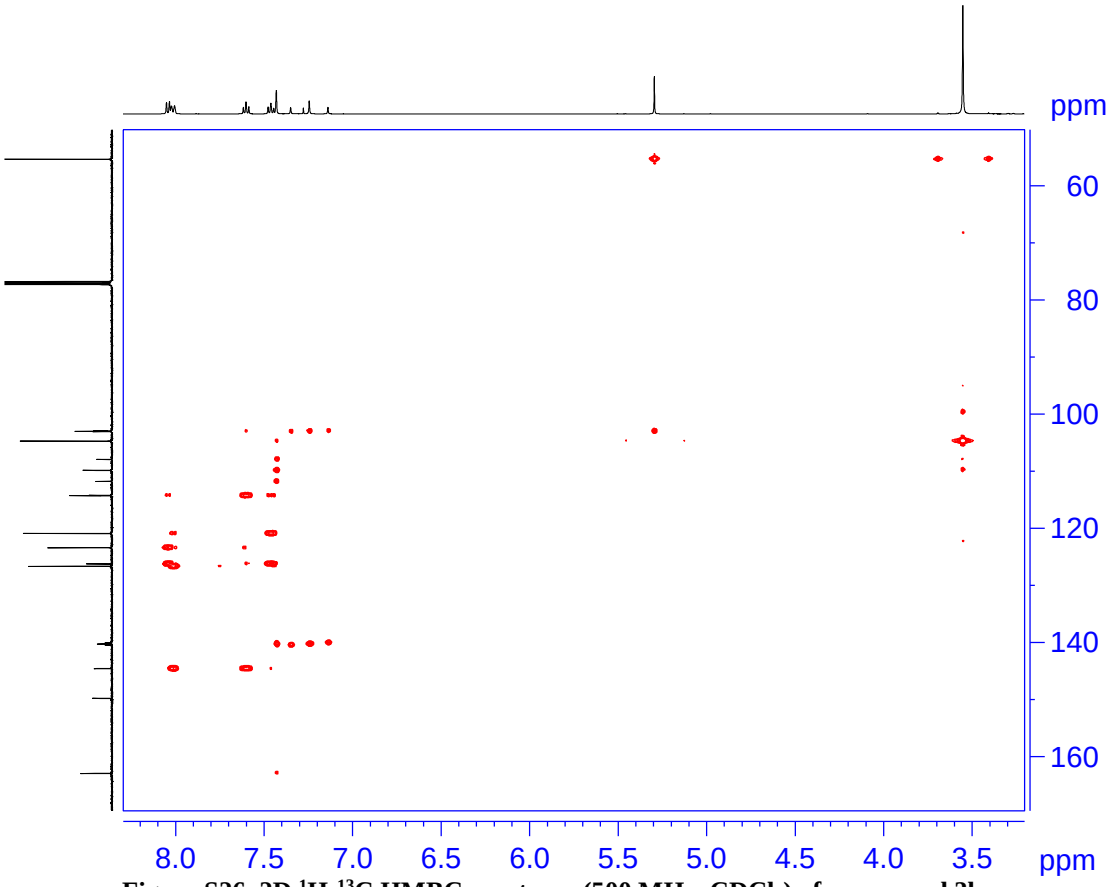


Figure S26. 2D ^{1}H-^{13}C HMBC spectrum (500 MHz, $CDCl_3$) of compound 3b.

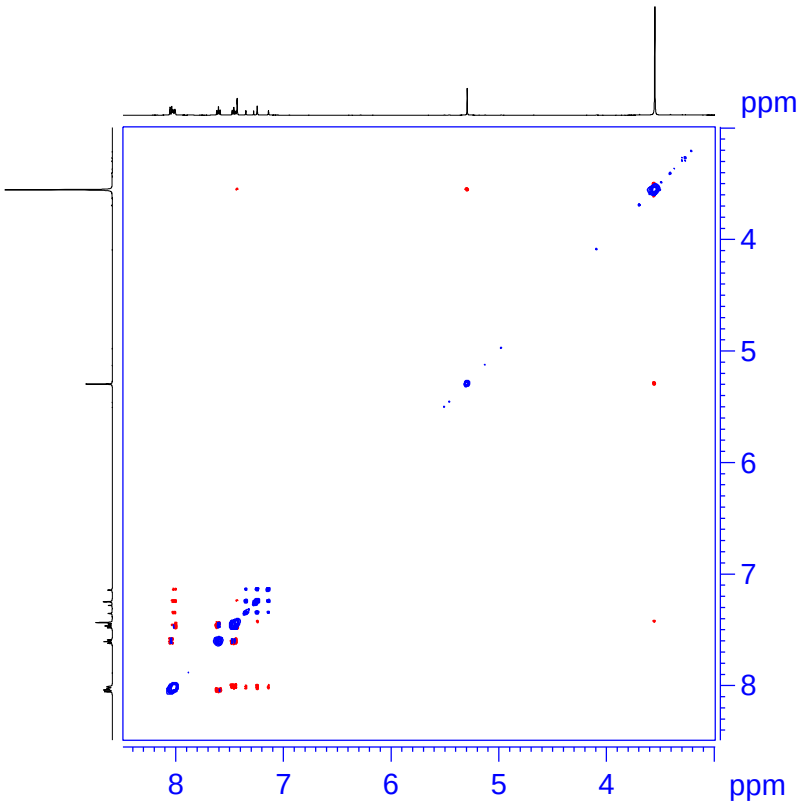


Figure S27. 2D ^{1}H-^{1}H NOESY spectrum (500 MHz, $CDCl_3$) of compound 3b.

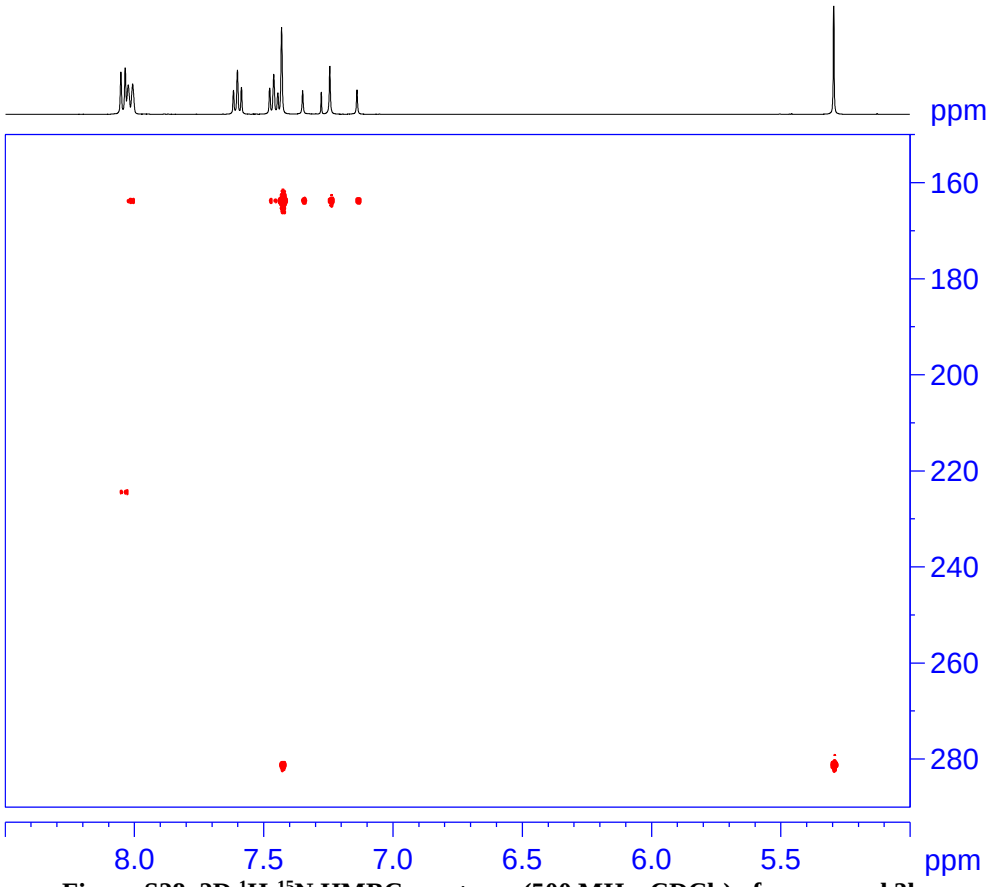


Figure S28. 2D ^{1}H-^{15}N HMBC spectrum (500 MHz, $CDCl_3$) of compound 3b.

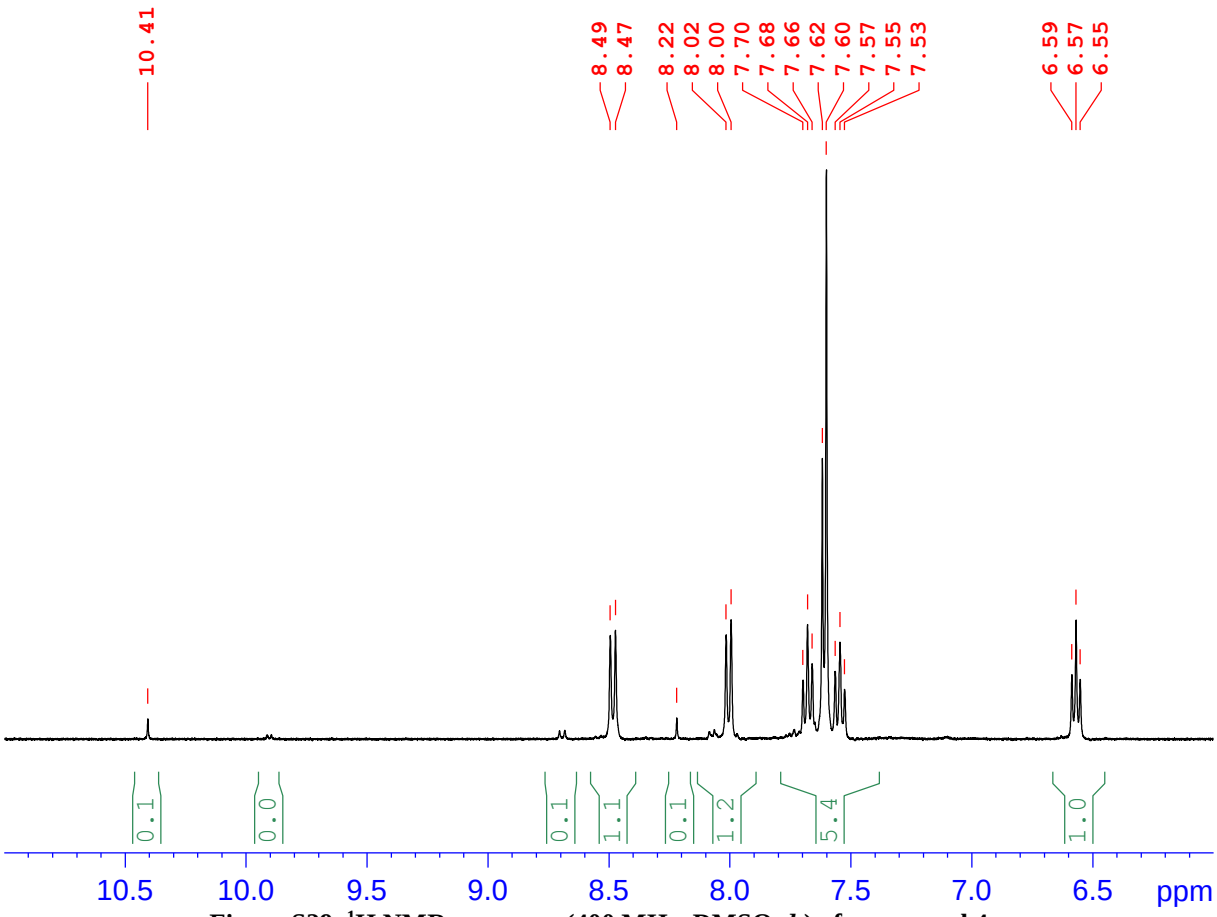


Figure S29. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound 4a.

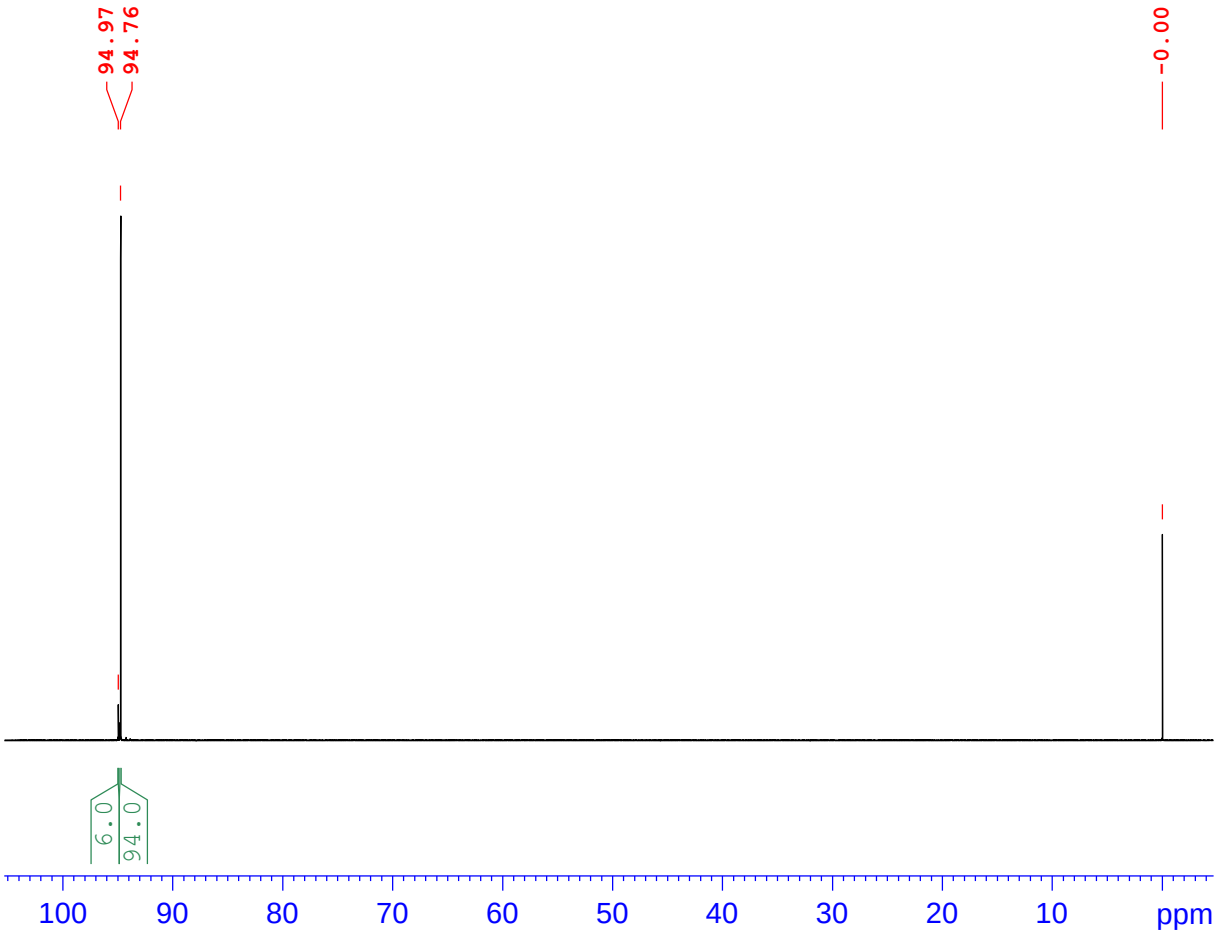


Figure S30. ^{19}F NMR spectrum (376 MHz, DMSO-d_6) of compound 4a.

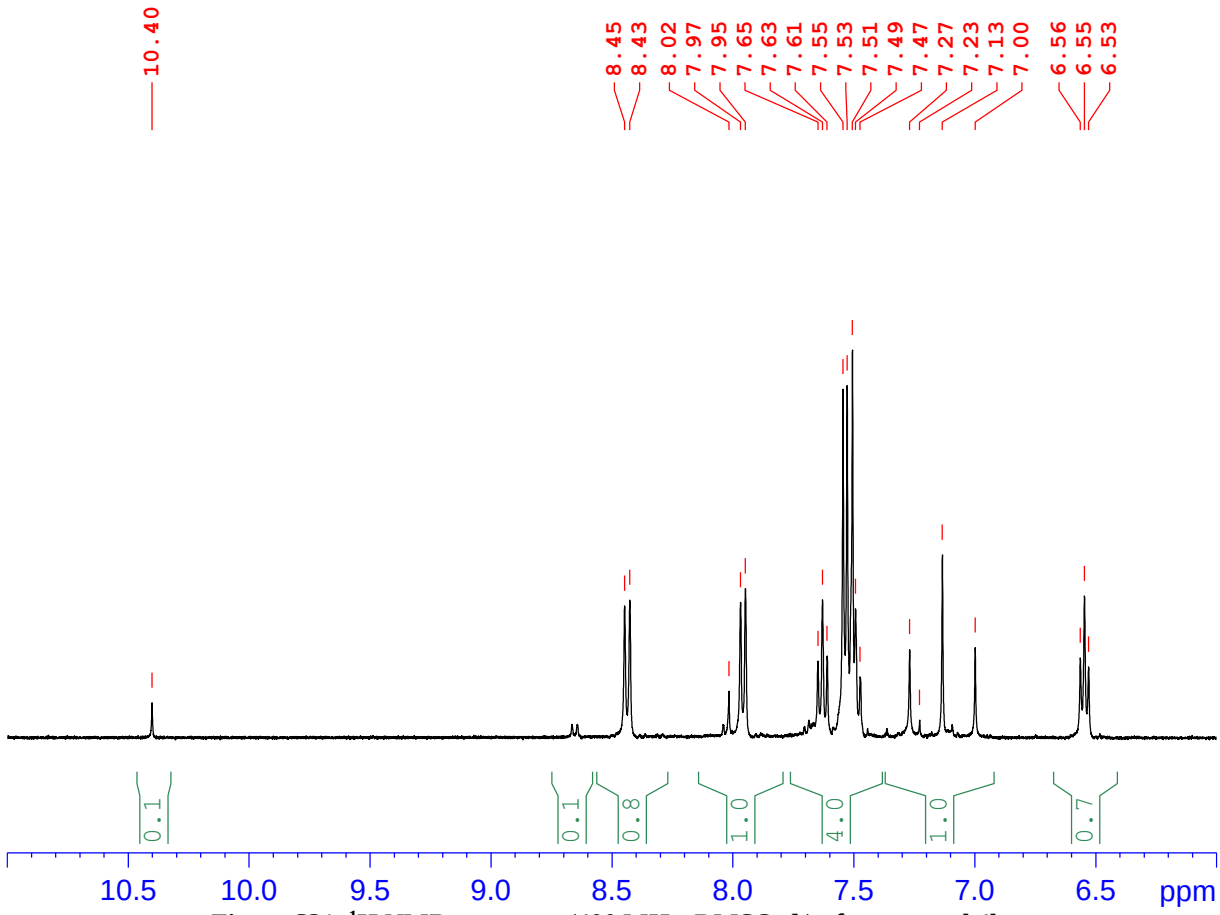


Figure S31. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound 4b.

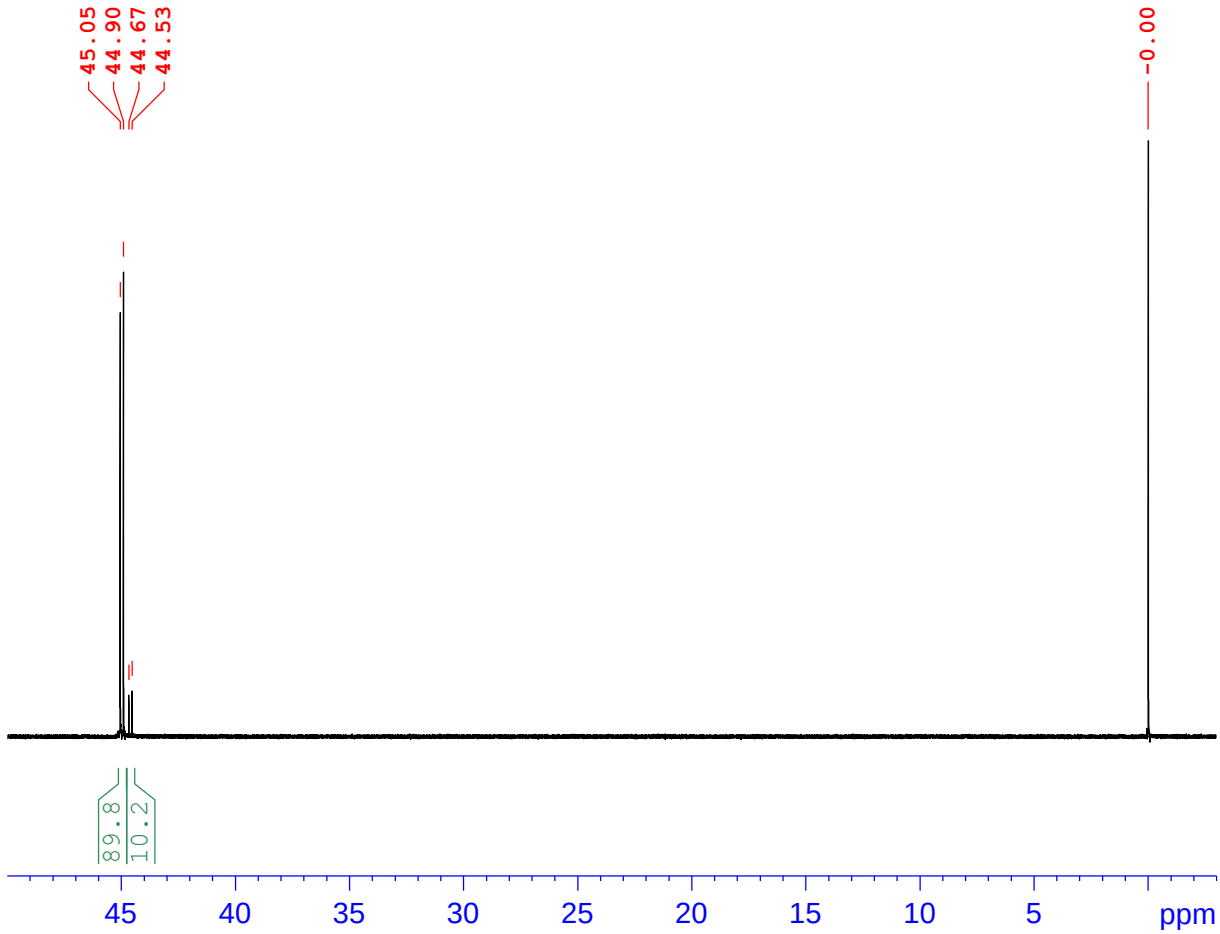


Figure S32. ^{19}F NMR spectrum (376 MHz, DMSO-d_6) of compound 4b.

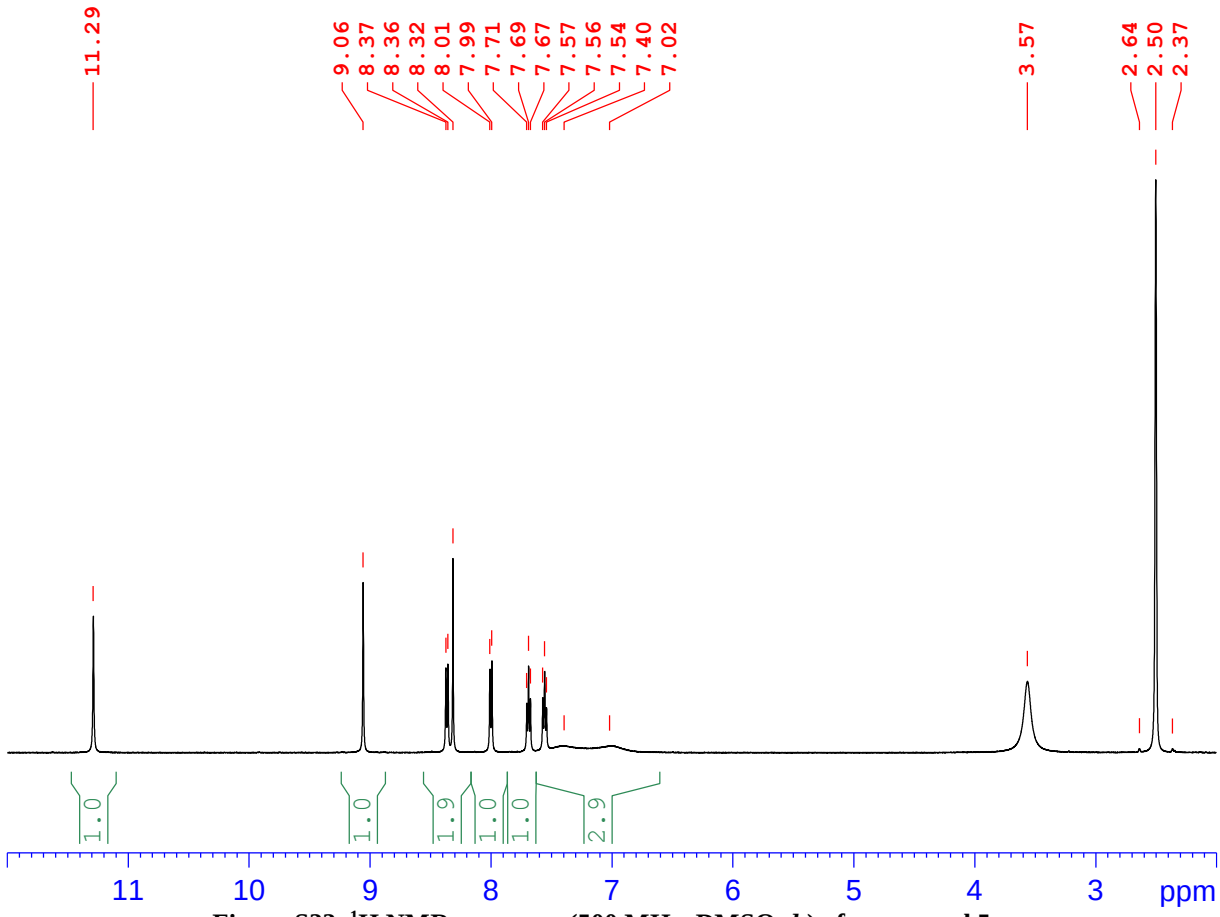


Figure S33. ^{1}H NMR spectrum (500 MHz, DMSO-*d*$_6$) of compound 5a.

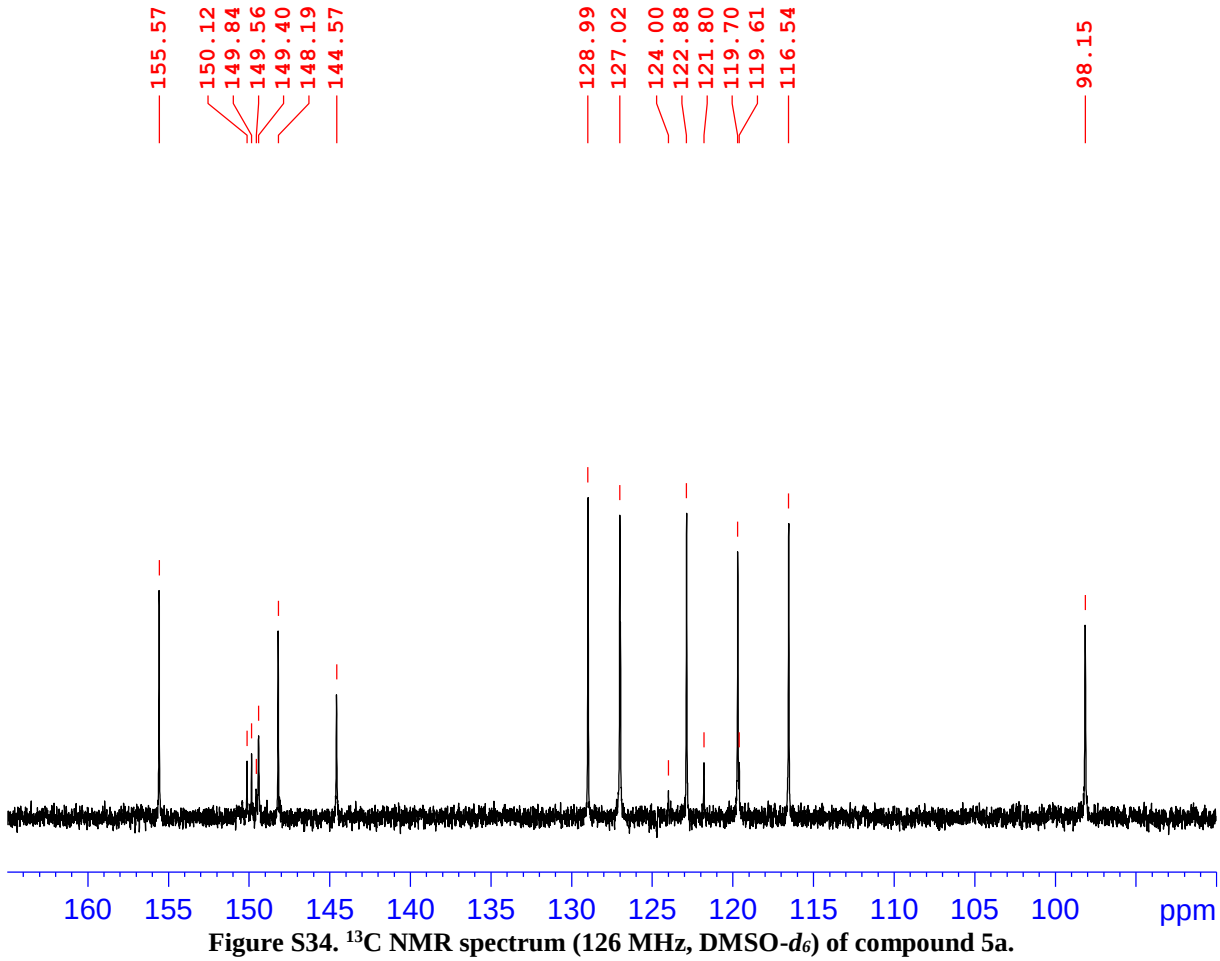


Figure S34. ^{13}C NMR spectrum (126 MHz, DMSO-*d*$_6$) of compound 5a.

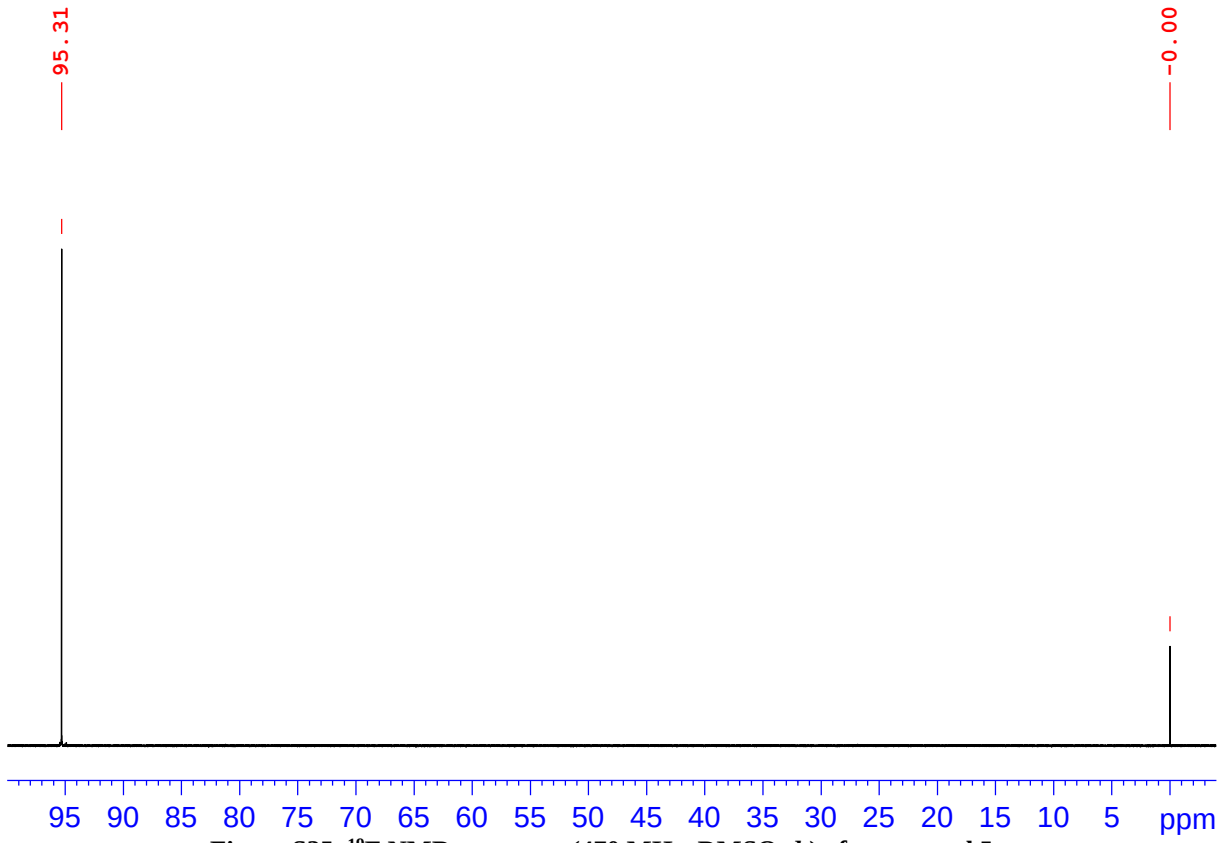


Figure S35. ^{19}F NMR spectrum (470 MHz, DMSO-*d*$_6$) of compound 5a.

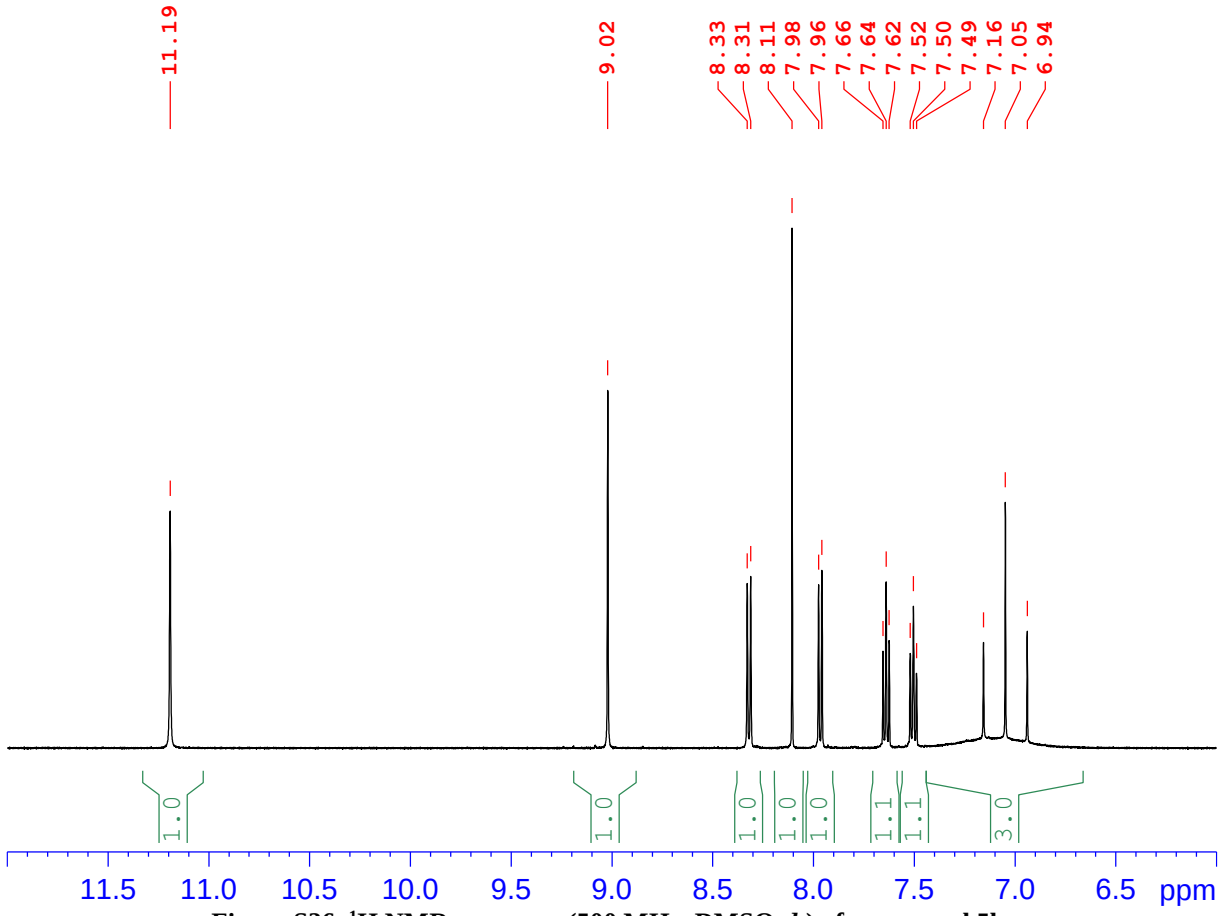


Figure S36. ^{1}H NMR spectrum (500 MHz, DMSO-*d*$_6$) of compound 5b.

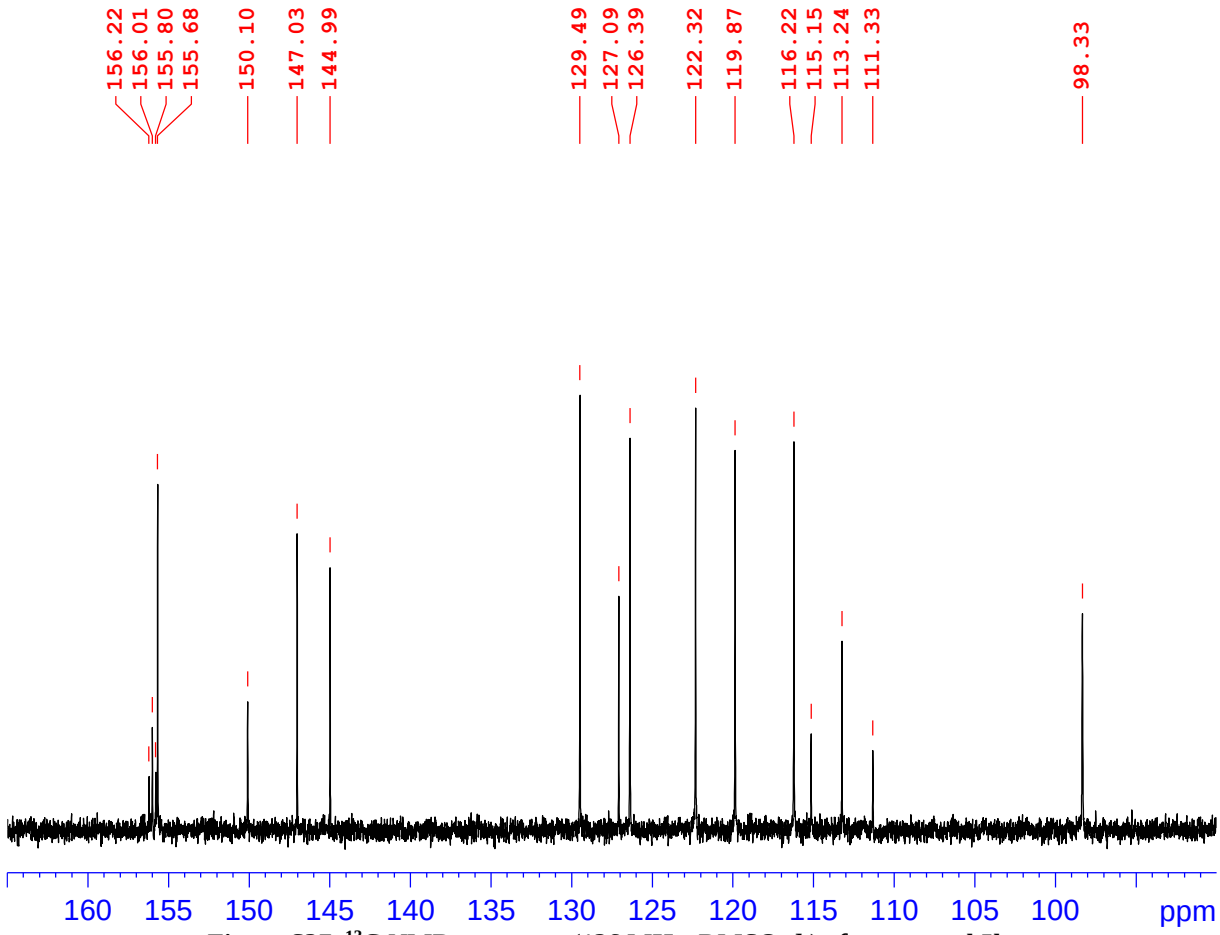


Figure S37. ^{13}C NMR spectrum (126 MHz, DMSO-*d*$_6$) of compound 5b.

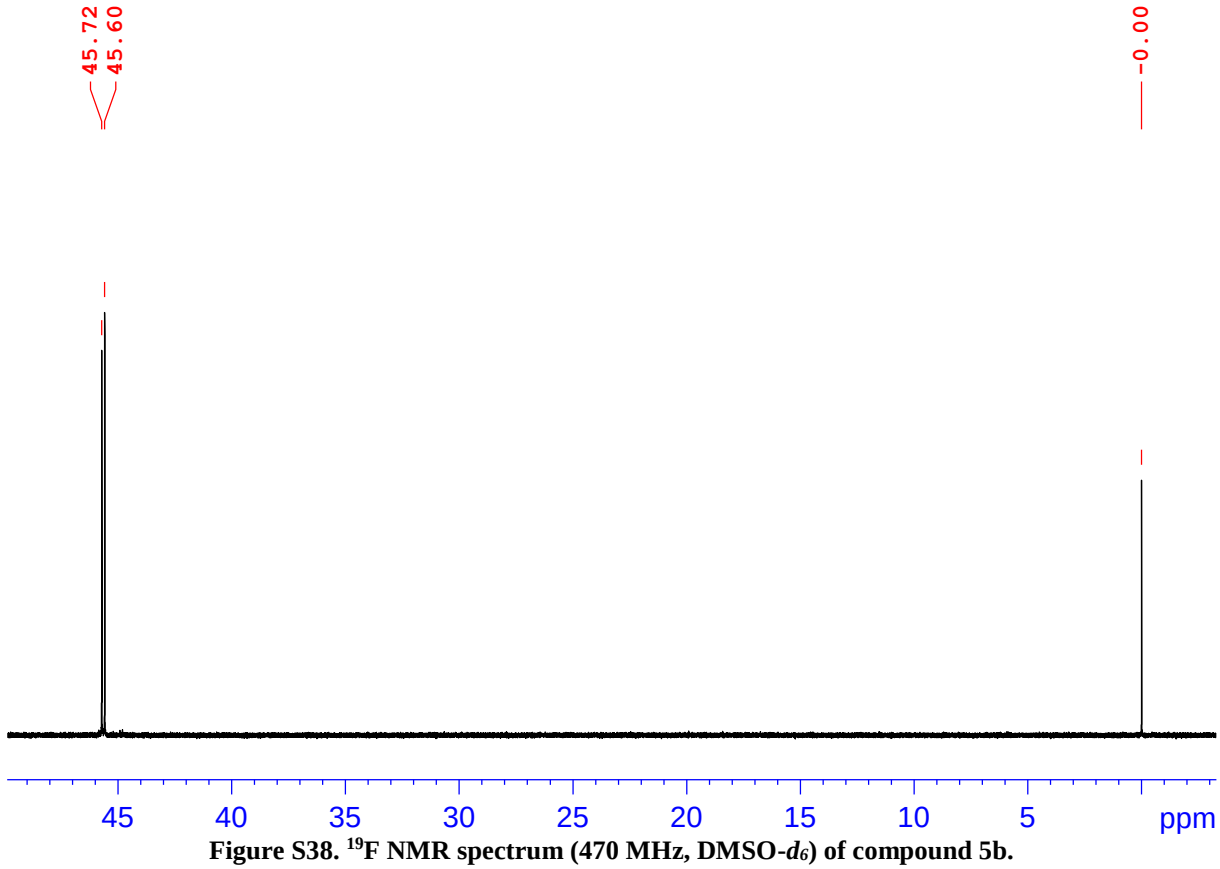


Figure S38. ^{19}F NMR spectrum (470 MHz, DMSO-*d*$_6$) of compound 5b.