

Electronic Supporting Information

Ultra-small Luminescent Copper Nanoclusters Catalyzed C-S Cross Coupling Reactions: Effect of Ligand Substituents in Modulating Catalytic Efficiency

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Experimental Section



Fig. S1: Digital photograph of the gram scale synthesized CuNCs@2MB

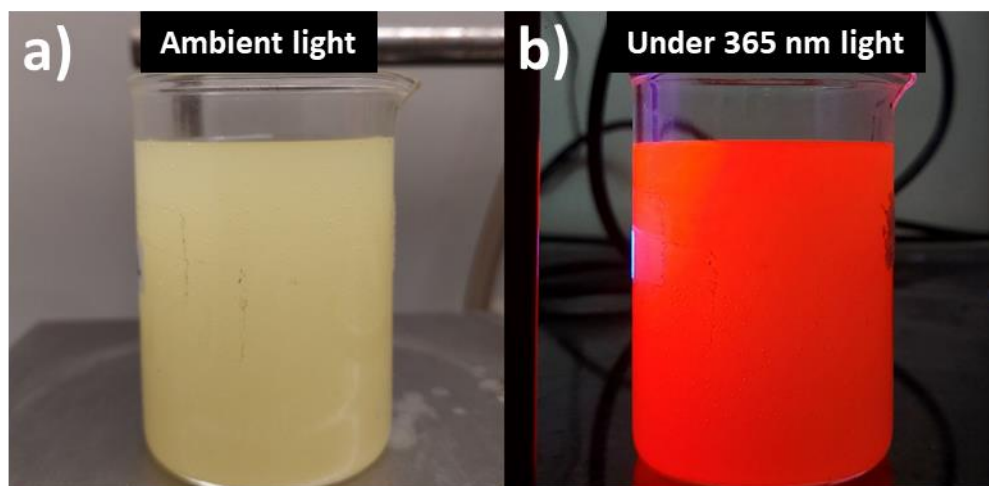


Fig. S2: Dispersed solution images of CuNCs@2MB under daylight and 365 nm light

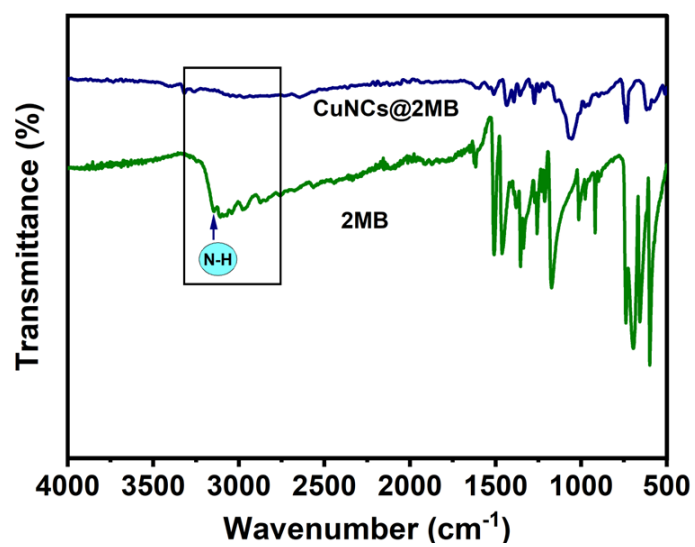


Fig. S3: ATR-FTIR spectra of 2MB and CuNCs@2MB

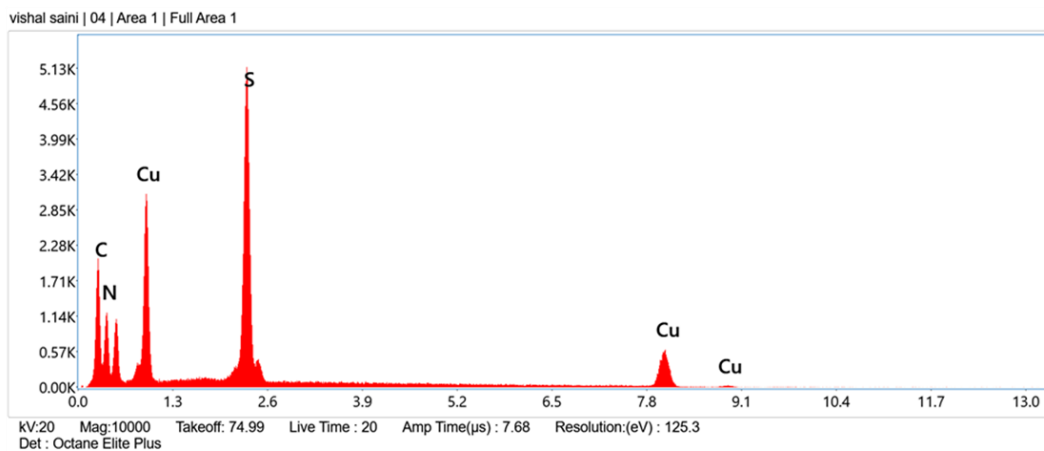


Fig. S4: EDX spectra of CuNCs@2MB

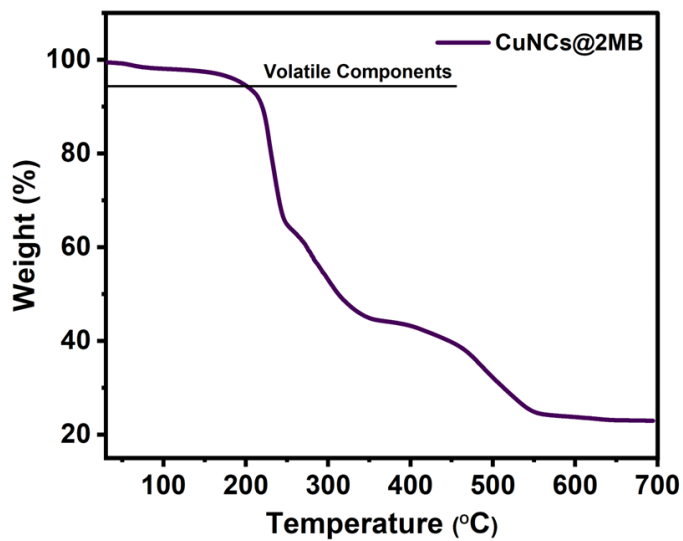
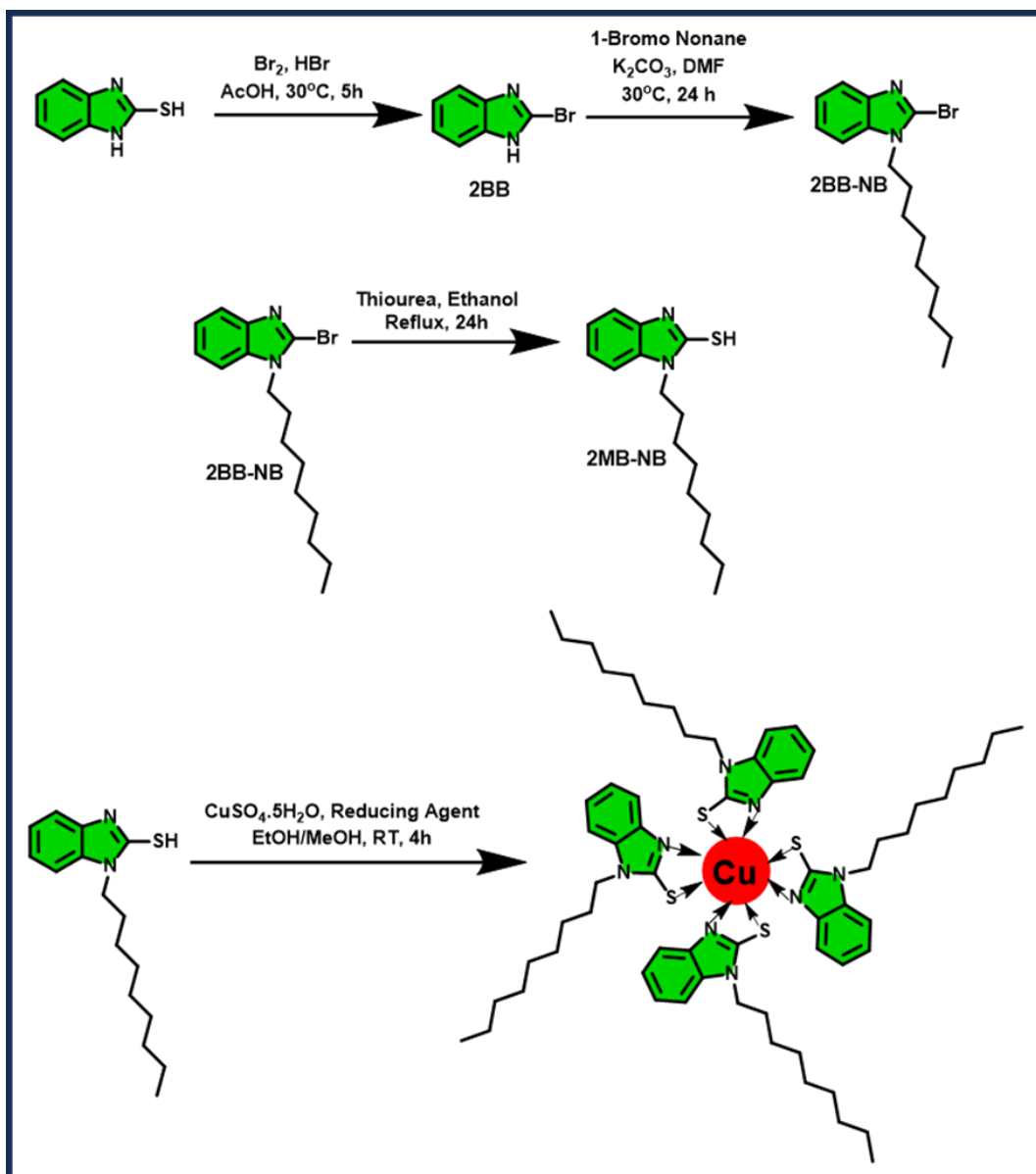


Fig. S5: Thermogravimetric analysis (TGA) of the CuNCs@2MB



Scheme S1: Synthesis of ligand 2MB-NB and red luminescent CuNCs@2MB-NB.

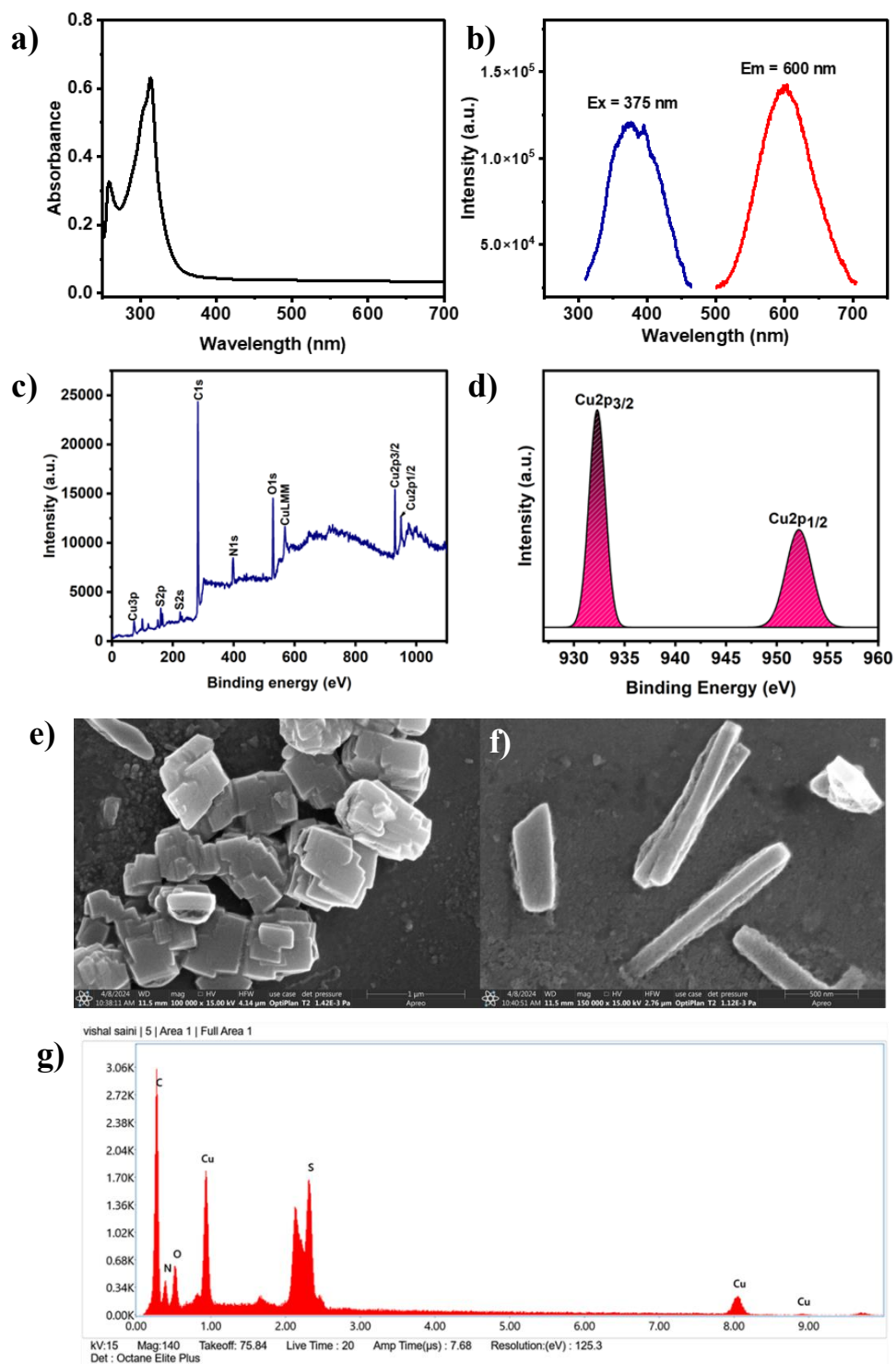


Fig. S6: Characterisations for copper nanoclusters CuNCs@2MB-NB; a) UV-vis spectrum; b) Fluorescence spectrum; c) XPS spectrum and d) Cu2p spectrum of NCs; e) & f); FE-SEM spectra of CuNCs; g) EDX spectra

Synthetic procedure of ligand precursors, ligand and copper nanoclusters (CuNCs@2MB-NB)

(a) Synthesis of 2-Bromobenzimidazole (2BB)¹

To a solution of 2-mercapto-benzimidazole (5 g, 33.28 mmol) in acetic acid (50 mL), add HBr (5 mL) and then bromine (6 mL) drop by drop to the solution. After 5-10 minutes of constant stirring at RT, add 100 mL of acetic acid to the mixture. After 4.5 hours of constant stirring, a thick orange mixture was produced. Then, this thick orange mixture was diluted with 100 mL of water. The product was precipitated out by adding sodium hydroxide until the pH reached 4. The resulting white ppt was filtered, washed with water, and dried for further use.

(b) Synthesis of 2BB-NB

To a solution of 2-Bromobenzimidazole (100 mg, 0.5 mmol) and nonyl bromide (0.095 mL, 0.5 mmol) in a minimum amount of dimethyl formamide (DMF), add potassium carbonate (103.65 mg, 0.75 mmol). The crude product was obtained after constant stirring at room temperature for 24 hours. The oily product was then extracted in the DCM layer, dried over sodium sulphate, and then evaporated to get the oily crude mixture. Column chromatography was performed with DCM to extract the product. An oily compound was obtained. Yield-93%.

¹H-NMR (500 MHz, CDCl₃) δ 7.71 – 7.68 (m, 1H), 7.33 – 7.30 (m, 1H), 7.28 – 7.25 (m, *J* = 1.4 Hz, 1H), 7.25 – 7.21 (m, *J* = 1.5 Hz, 1H), 4.19 – 4.14 (m, *J* = 1.5 Hz, 2H), 1.84 – 1.76 (p, *J* = 7.4 Hz, 2H), 1.38 – 1.30 (m, *J* = 11.9 Hz, 3H), 1.24 (s, 9H), 0.86 (t, 3H); ¹³C-NMR (126 MHz, CDCl₃) δ 143.28, 135.53, 130.07, 123.08, 122.51, 119.49, 109.58, 45.64, 31.88, 29.80, 29.49, 29.27, 26.81, 22.72, 14.19. HRMS (ESI): calculated for [M+H]⁺ *m/z* = 323.1123, found: 323.1119

(c) Synthesis of 2MB-NB

To a solution of 2 BB-NB (180 mg, 0.55 mmol) in ethanol, add thiourea (84.76 mg, 1.1136 mmol). The crude product was obtained after refluxing the reaction for 24 hours at 78 °C. Then the ethanol from the product was evaporated. The oily product was then extracted with a workup of water, and the DCM layer was dried over sodium sulfate and then evaporated to get the oily crude mixture. Column chromatography was performed with DCM to extract the oily product. Then this oily product was washed with n-pentane to get the solid product. Yield-84%.

¹H-NMR (500 MHz, DMSO-*d*₆) δ 12.70 (s, 1H), 7.38 – 7.34 (m, 1H), 7.17 – 7.13 (m, 3H), 4.19 – 4.14 (m, 2H), 1.65 (m, 2H, *J* = 7.3 Hz), 1.25 (m, 4H, *J* = 4.2 Hz), 1.18 (m, 8H, *J* = 4.7 Hz), 0.80 (t, 3H, *J* = 9.4, 4.5 Hz). ¹³C-NMR (126 MHz, DMSO-*d*₆) δ 168.54, 133.02, 131.23, 123.30, 122.73, 110.10, 43.52, 31.76, 29.29, 29.12, 27.90, 26.59, 22.60, 14.48. HRMS (ESI): calculated for [M+H]⁺ *m/z* = 277.1738, found: 277.1734

(d) Synthesis of copper nanocluster (CuNCs@2MB-NB)

8.98 mg (0.036 mmol) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was dissolved in 3 mL of methanol. Then, 2MB-NB (10 mg, 0.036 mmol) ethanol solution was added under stirring. After adding the ligand solution to the reaction mixture, it was left to stand for constant stirring at room temperature for half an hour. After half an hour, hydrazine hydrate (18 mg, 0.36 mmol) was added to the reaction mixture, and the mixture was stirred continuously at room temperature for 4 hours. A yellow precipitate could be isolated *via* centrifugation and repeated washing with methanol. The precipitate was vacuum-dried and stored at room temperature for further studies.

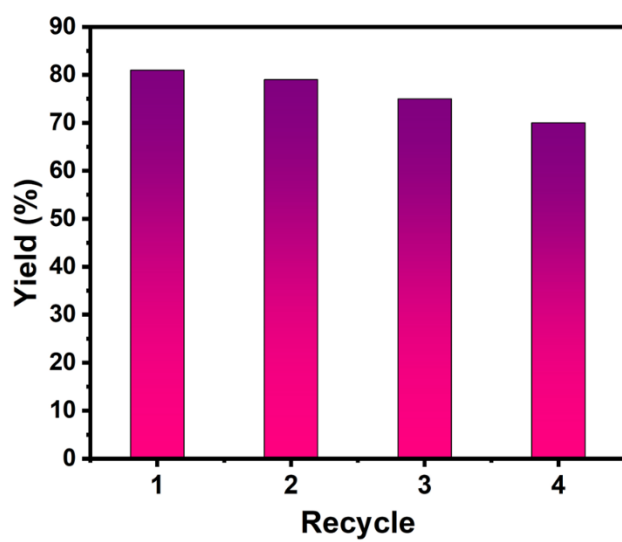


Fig. S7: Recyclability test of CuNCs@2MB

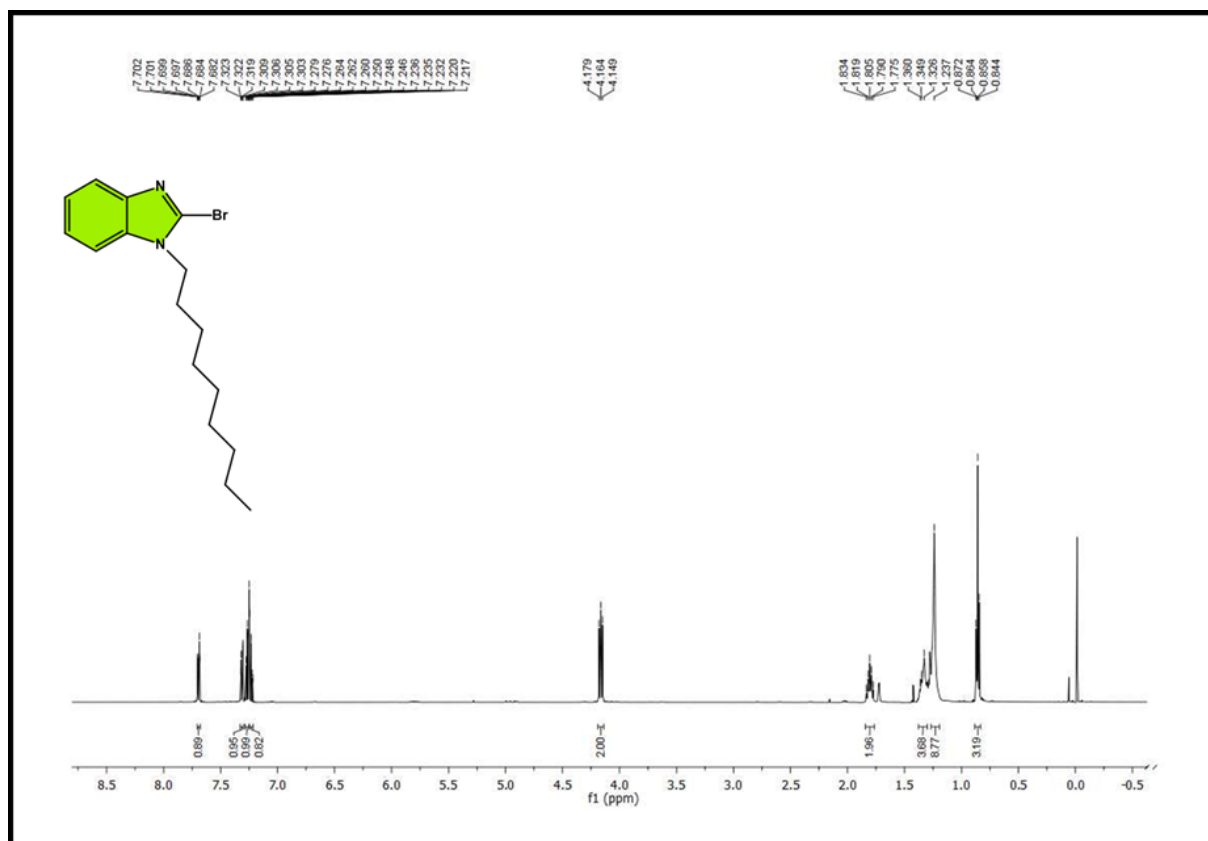


Fig. S8: ^1H NMR spectra of 2BB-NB (CDCl_3)

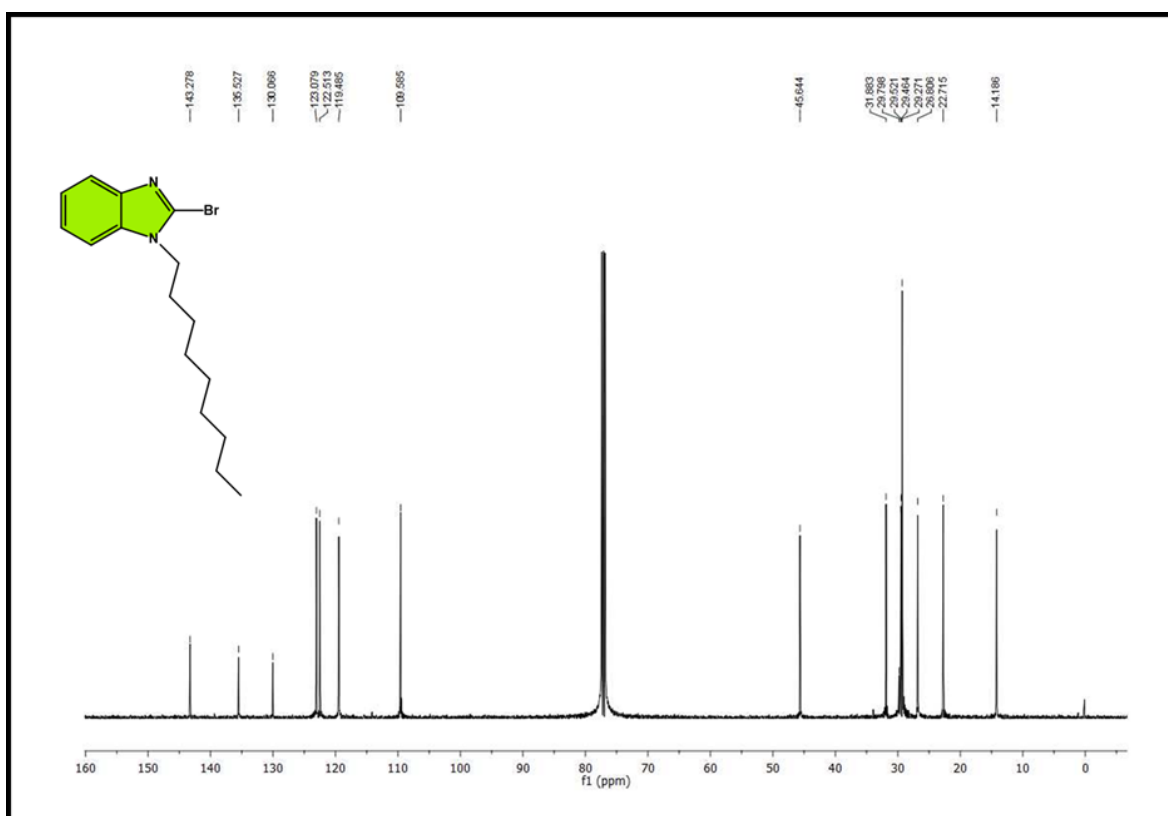


Fig.S9: ^{13}C NMR spectra of 2BB-NB (CDCl_3)

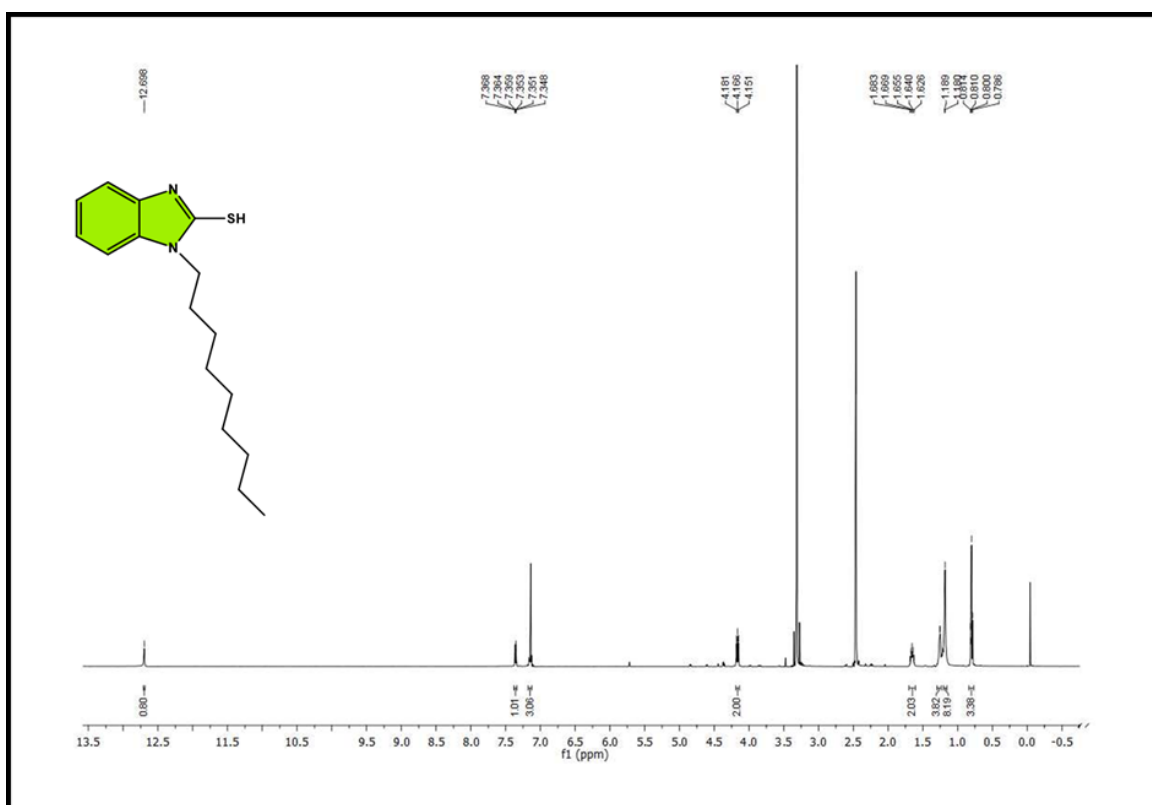


Fig.S10: ¹H NMR spectra of 2MB-NB (DMSO-d₆)

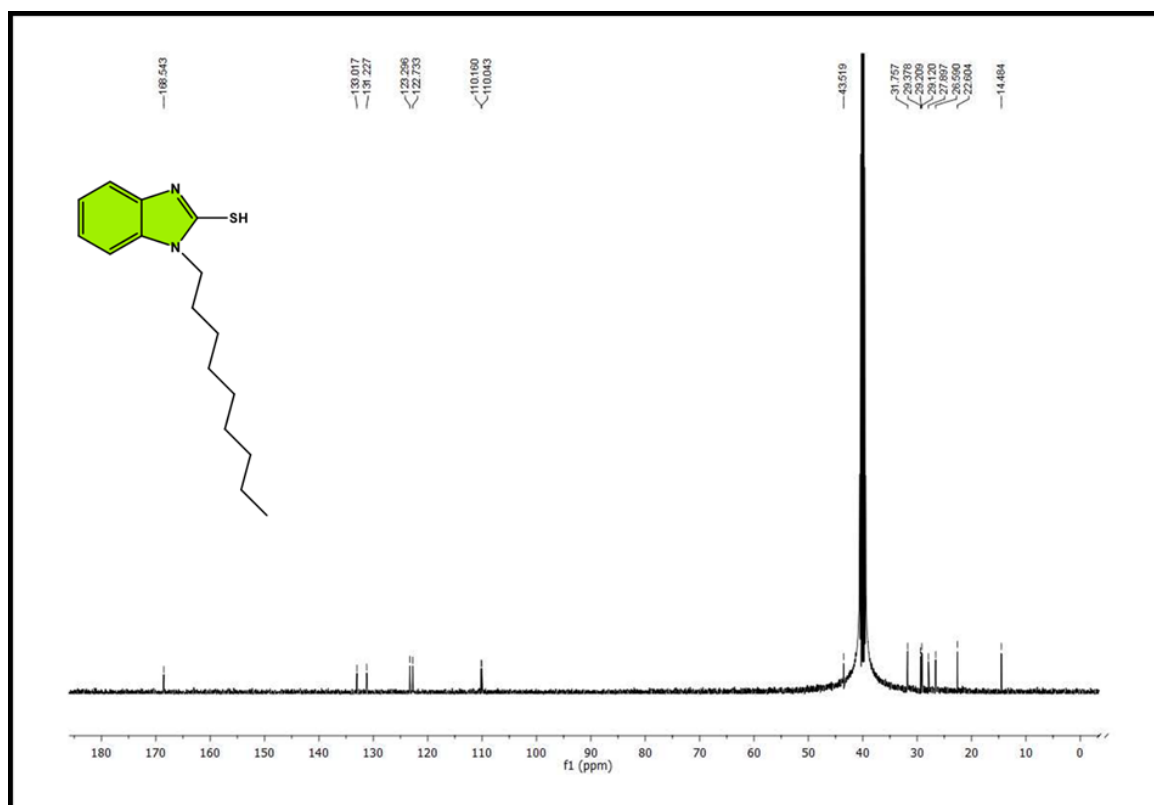


Fig.S11: ¹³C NMR spectra of 2MB-NB (DMSO-d₆)

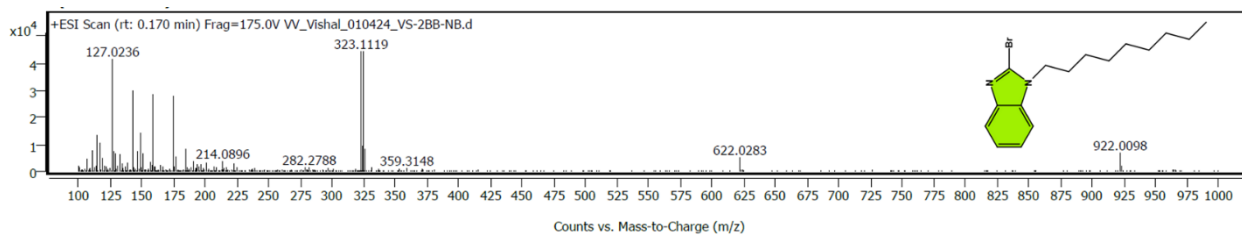


Fig.S12: HRMS spectra of 2BB-NB

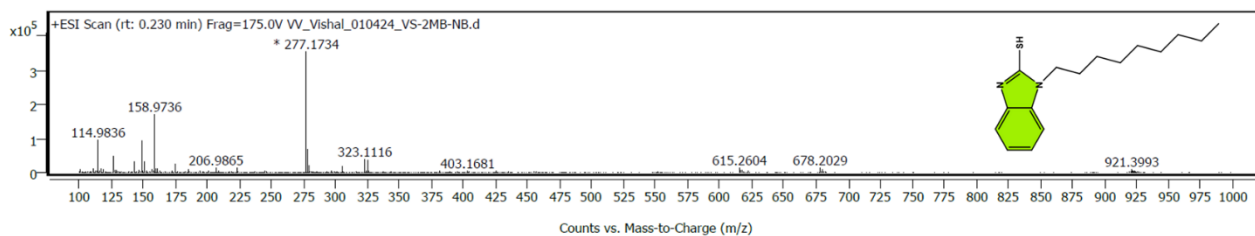


Fig.S13: HRMS spectra of 2MB-NB

NMR Spectra of substrates

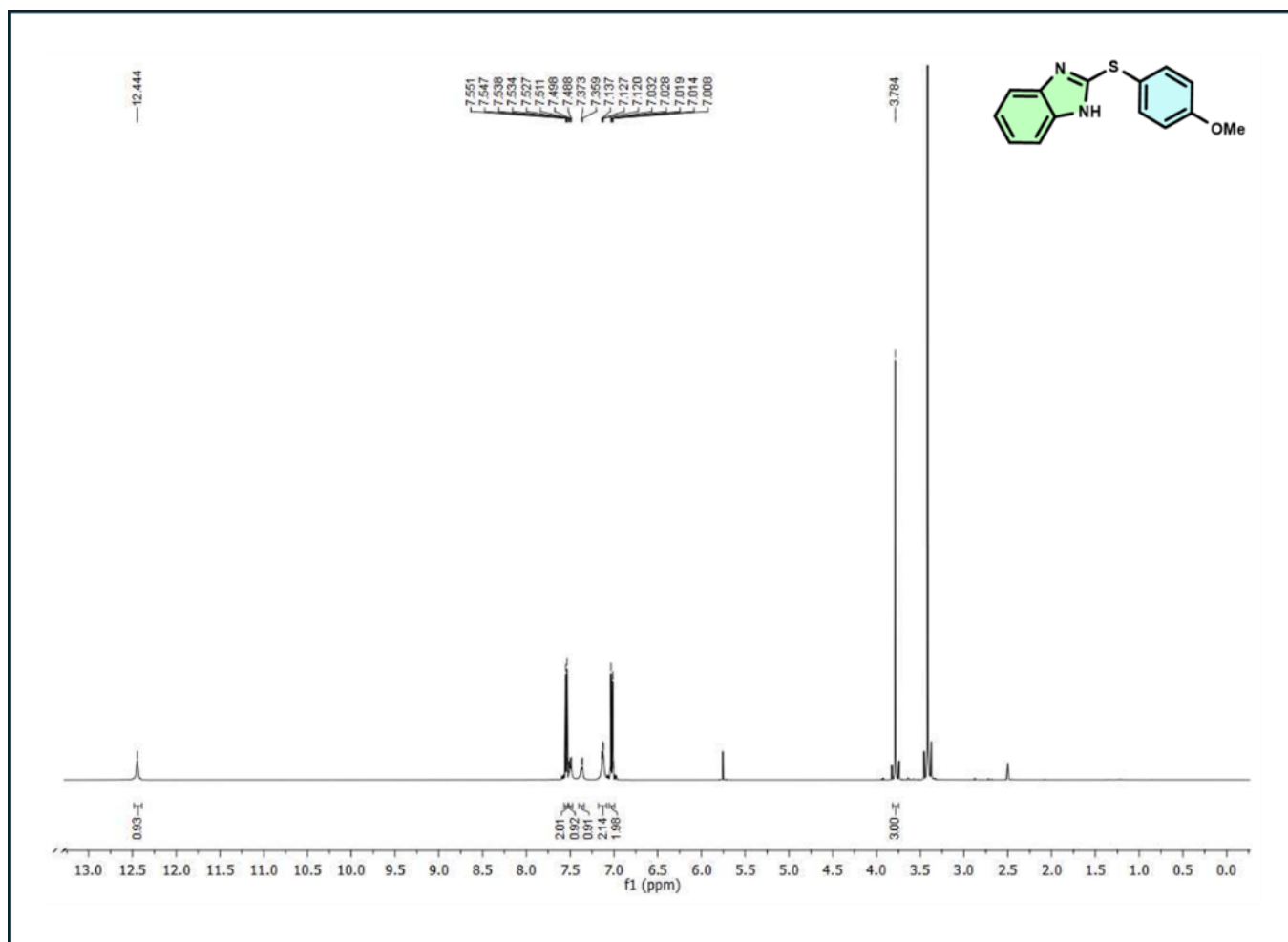


Fig. S14: ^1H NMR spectra of **3a** (DMSO-d_6)

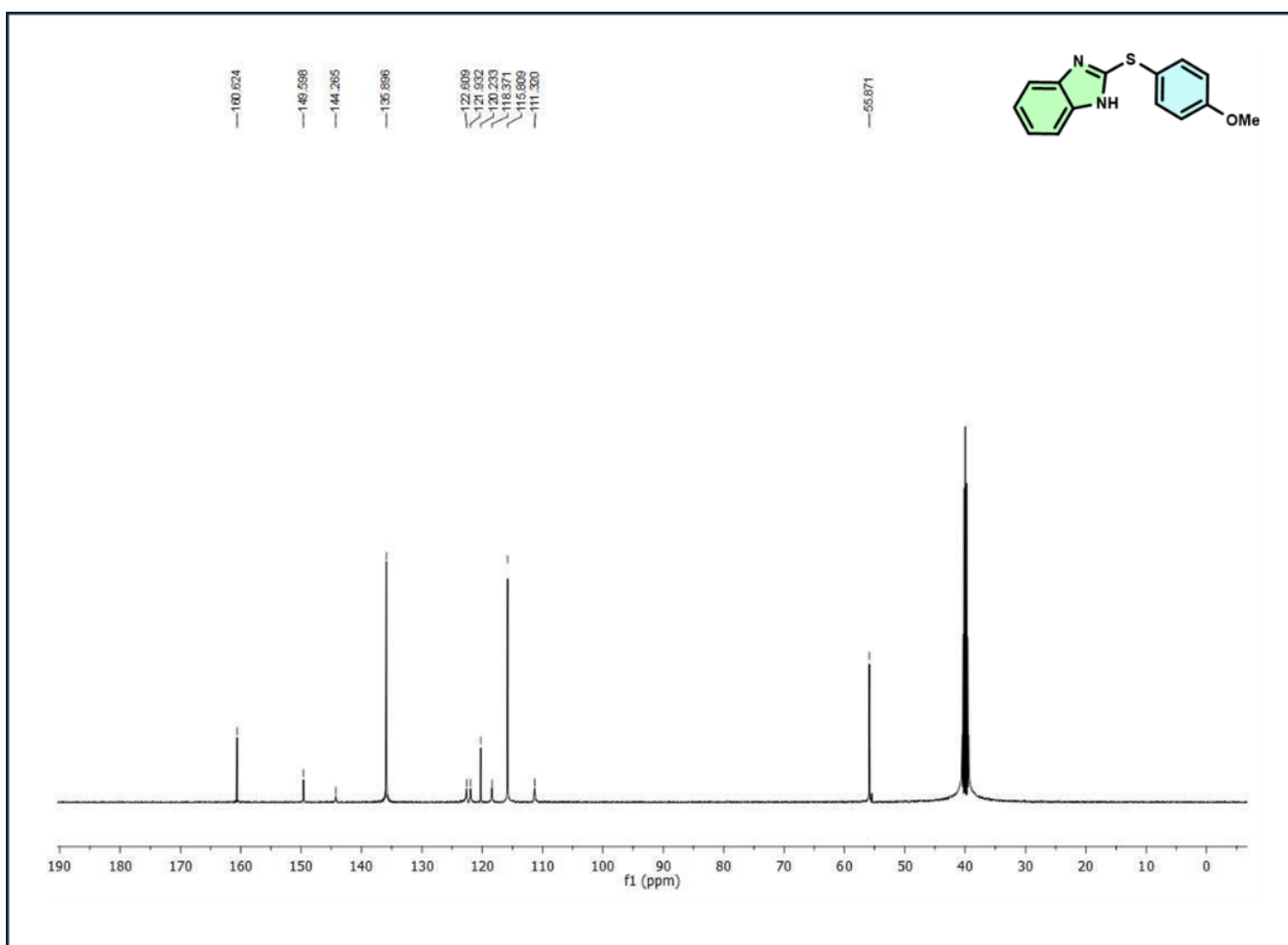


Fig. S15: ¹³C NMR spectra of **3a** (DMSO-d₆)

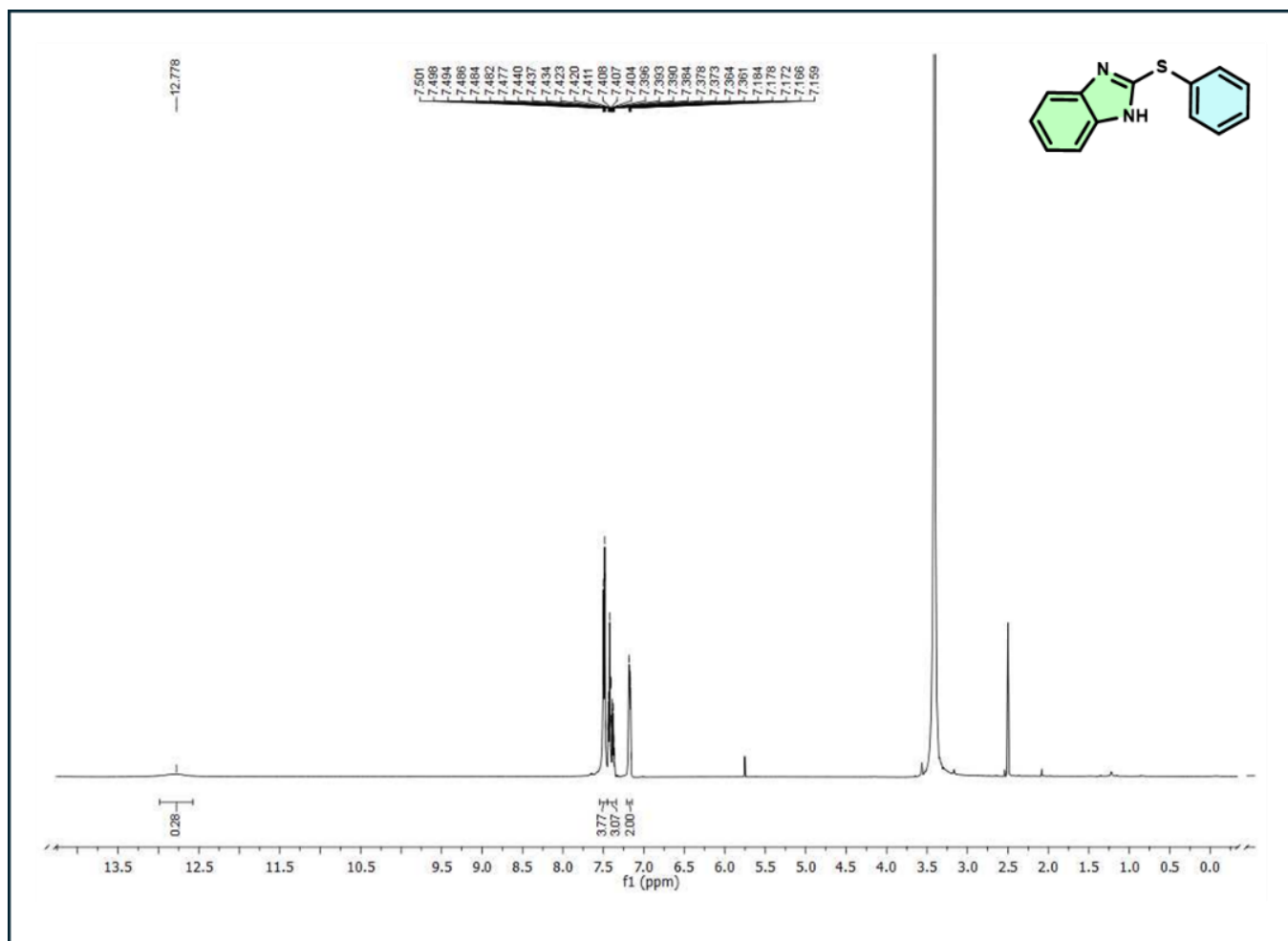


Fig. S16: ^1H NMR spectra of **3b** (DMSO- d_6)

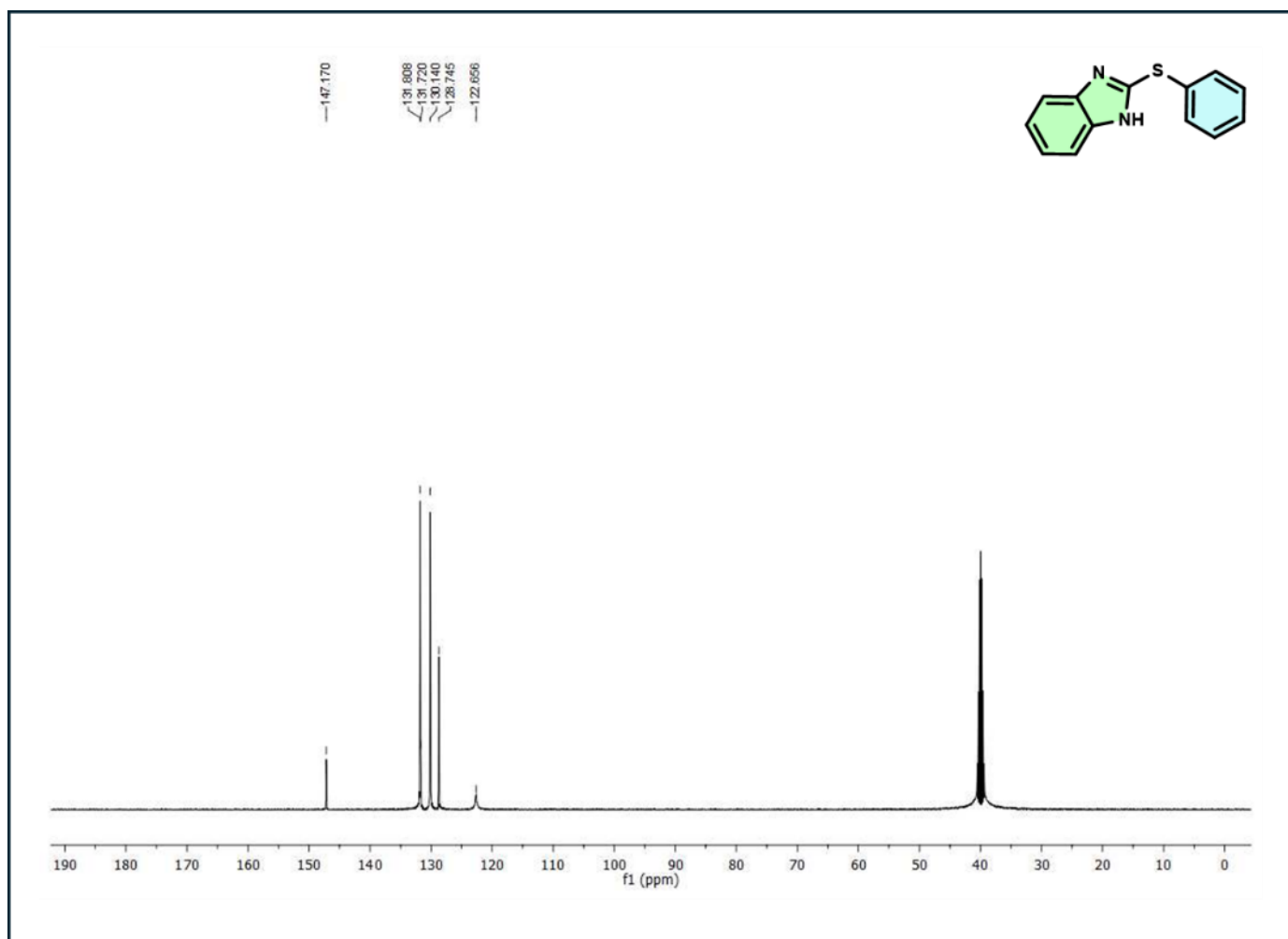


Fig. S17: ^{13}C NMR spectra of **3b** (DMSO- d_6)

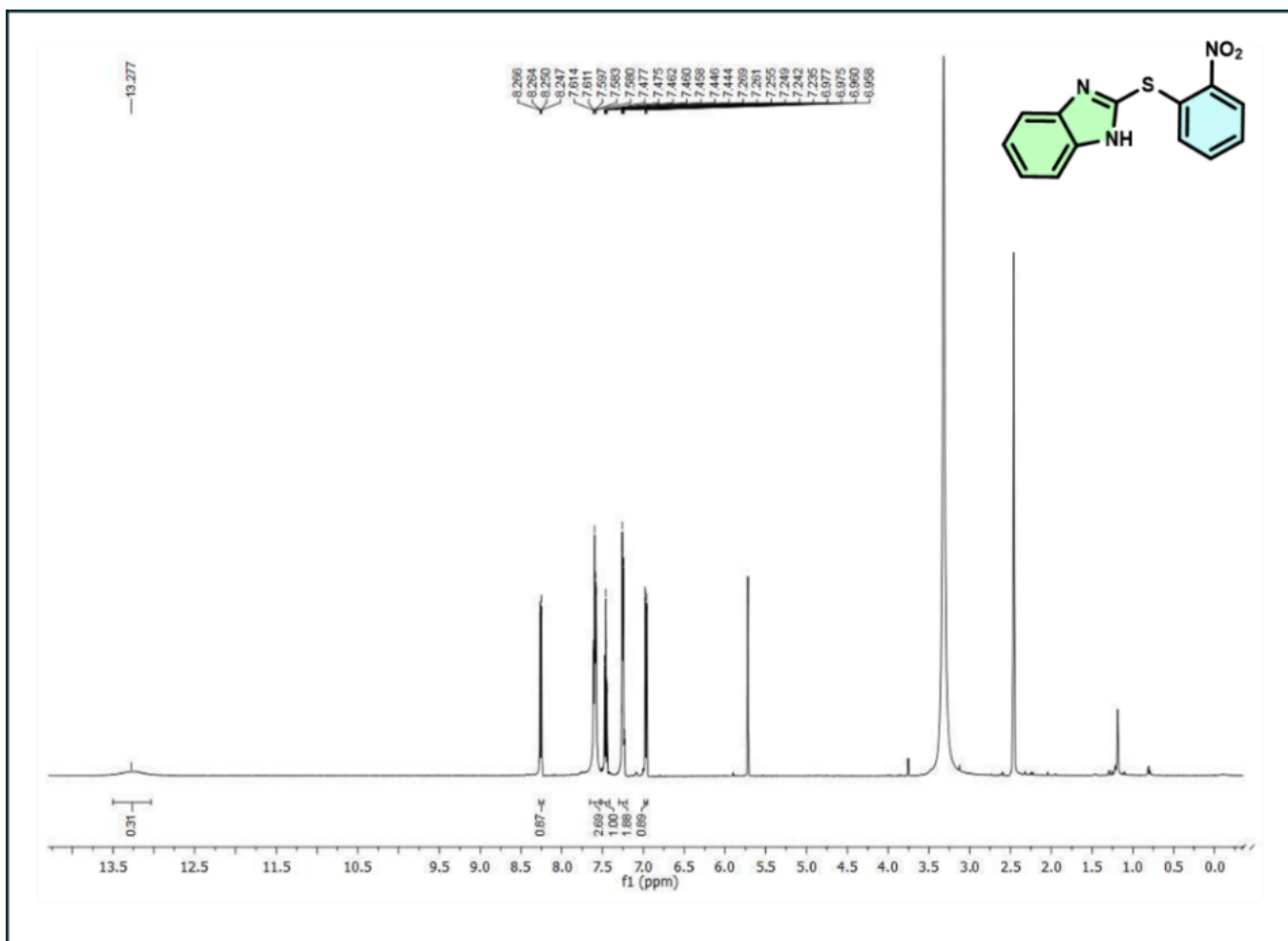


Fig. S18: ^1H NMR spectra of **3c** (DMSO-d_6)

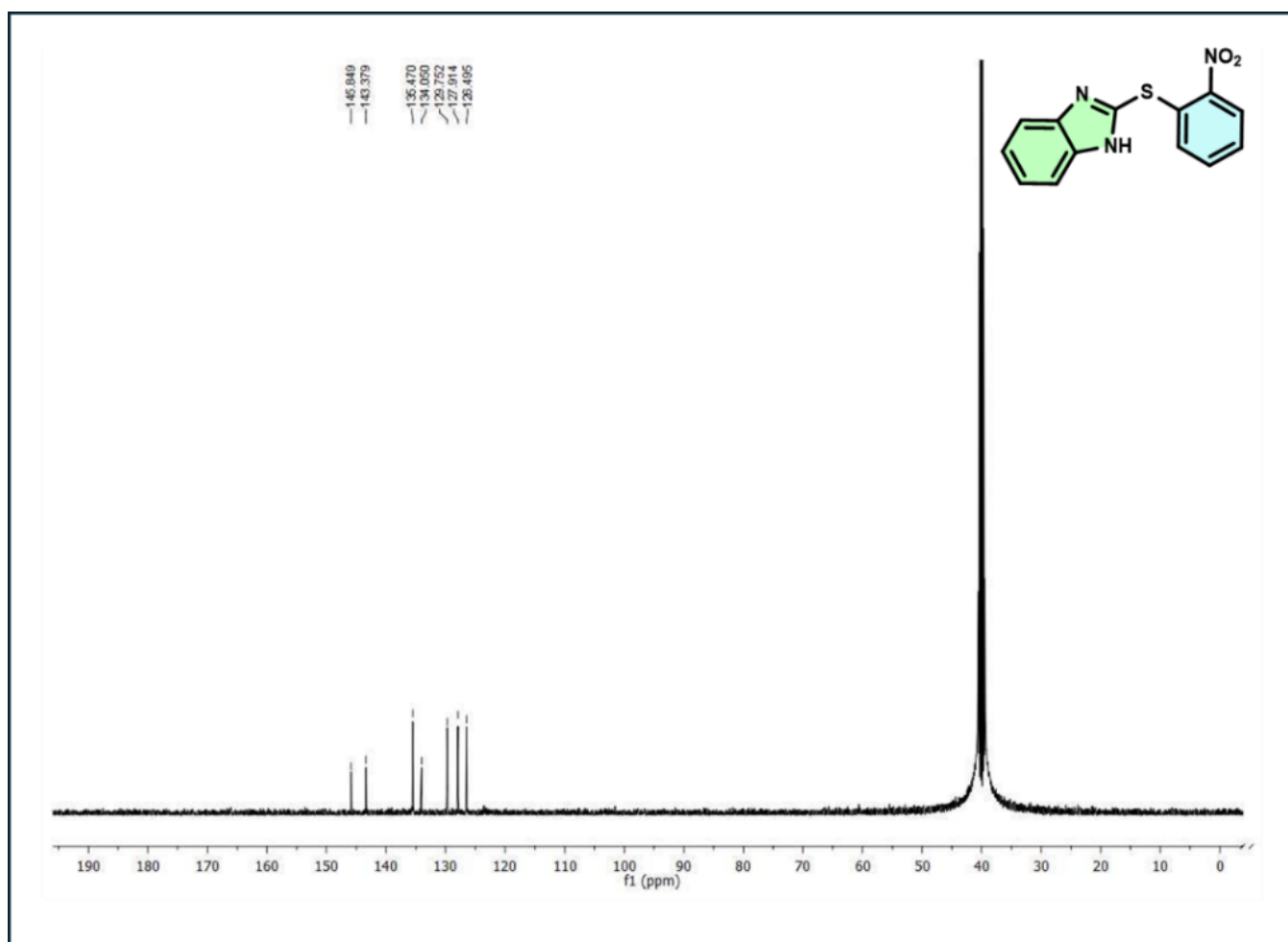


Fig. S19: ^{13}C NMR spectra of **3c** (DMSO-d_6)

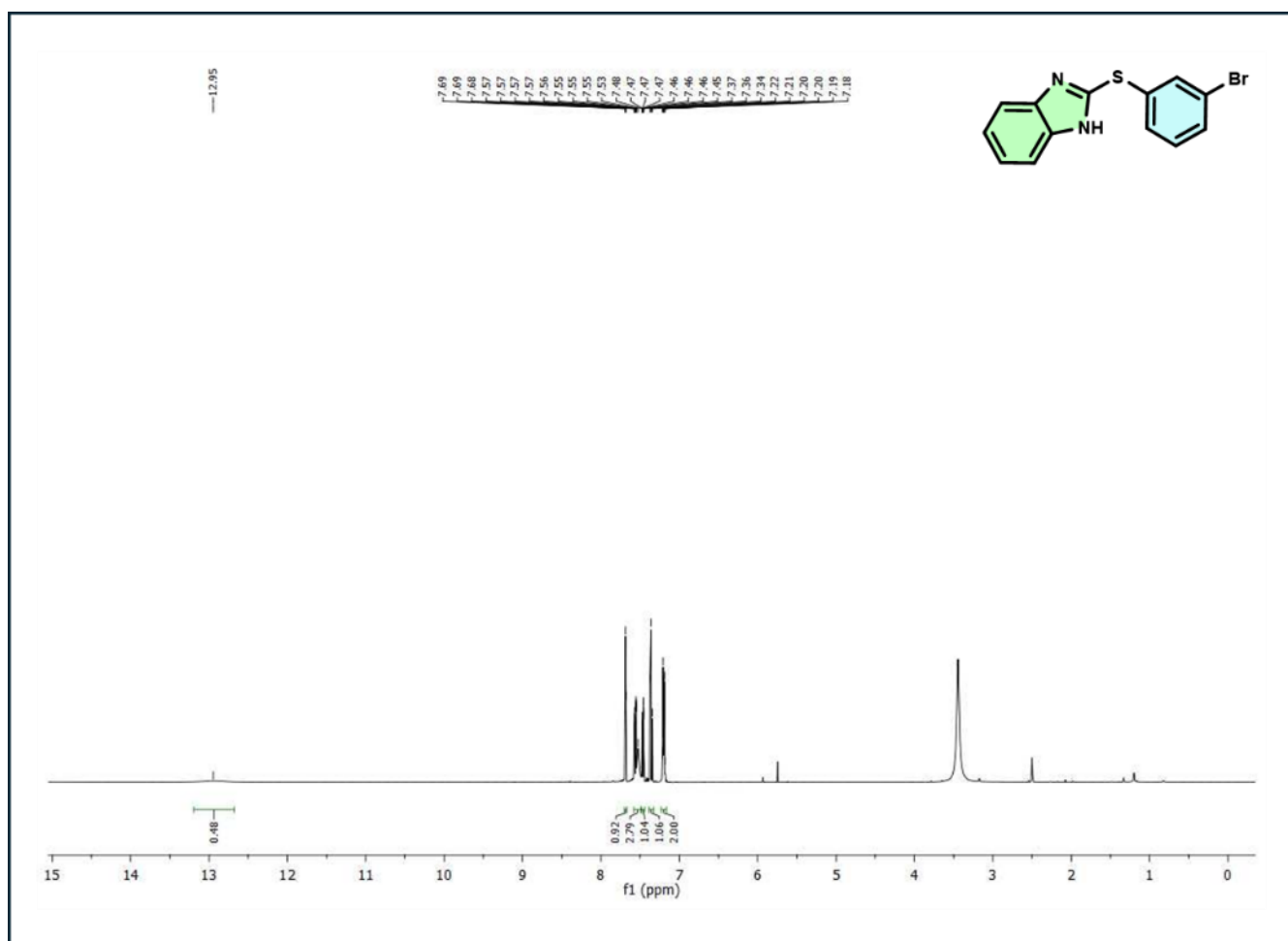


Fig. S20: ^1H NMR spectra of 3d (DMSO- d_6)

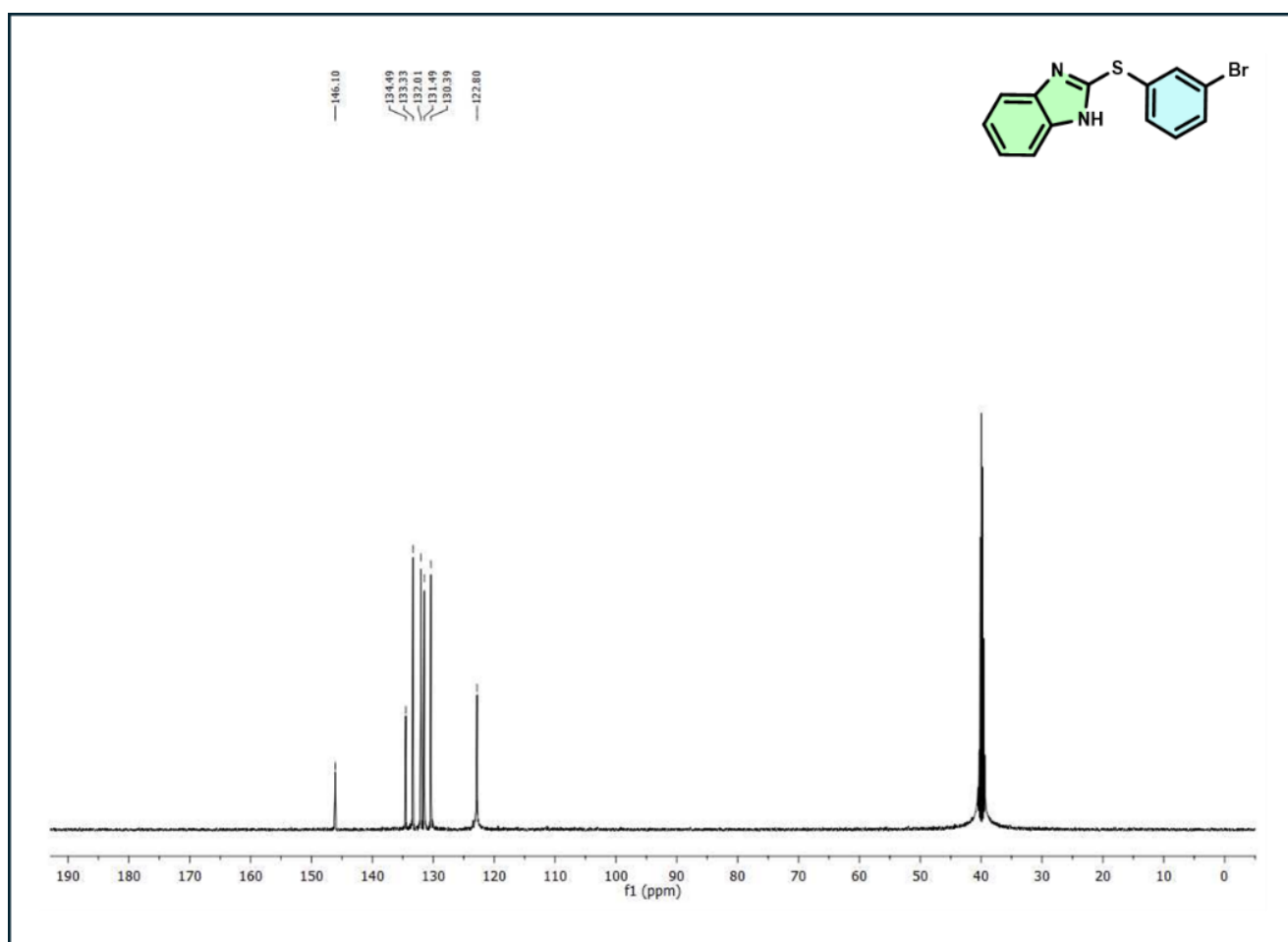


Fig. S21 ^{13}C NMR spectra of **3d** (DMSO-d_6)

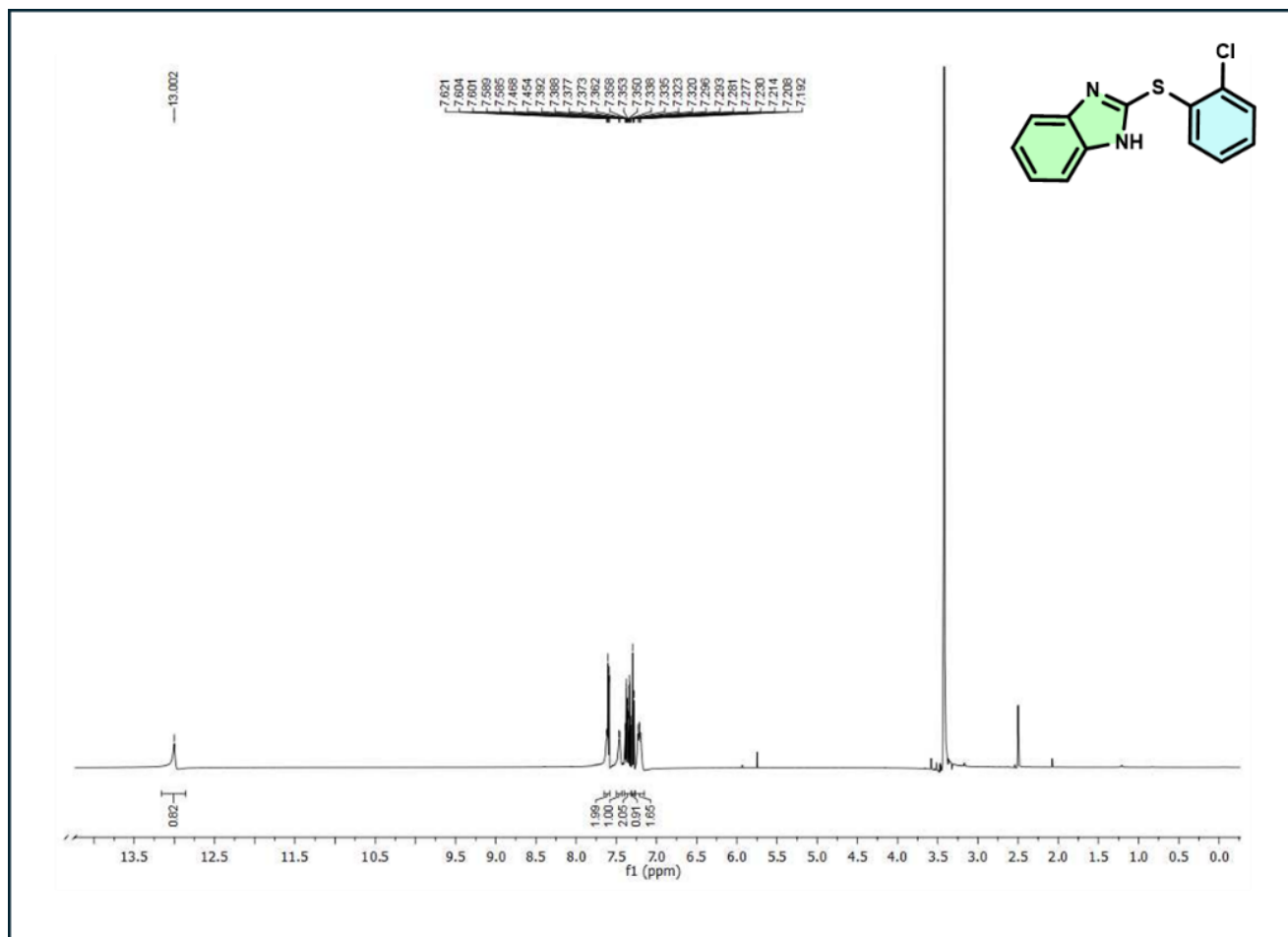


Fig. S22: ¹H NMR spectra of **3e** (DMSO-d₆)

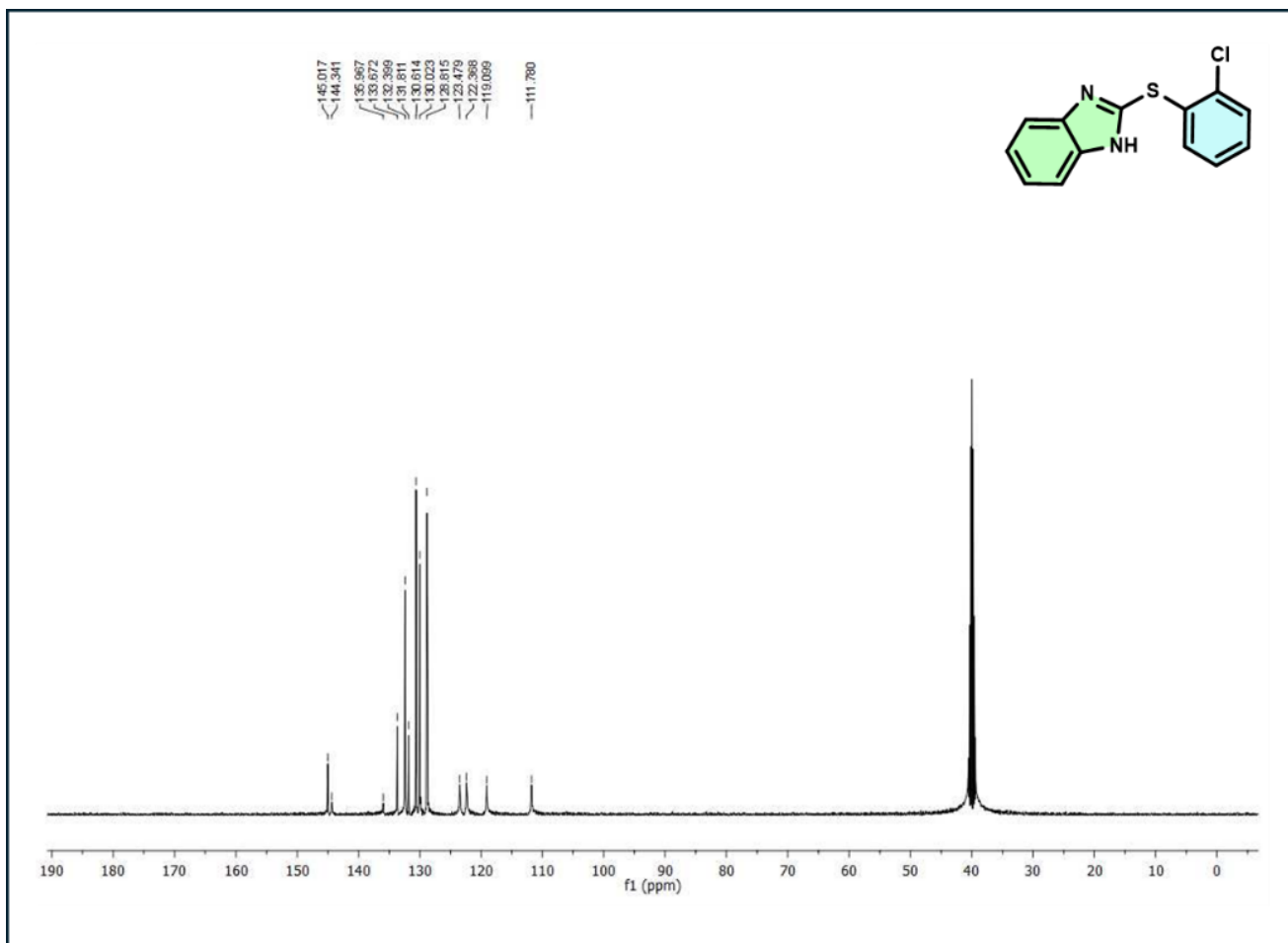


Fig. S23: ^{13}C NMR spectra of **3e** (DMSO-d_6)

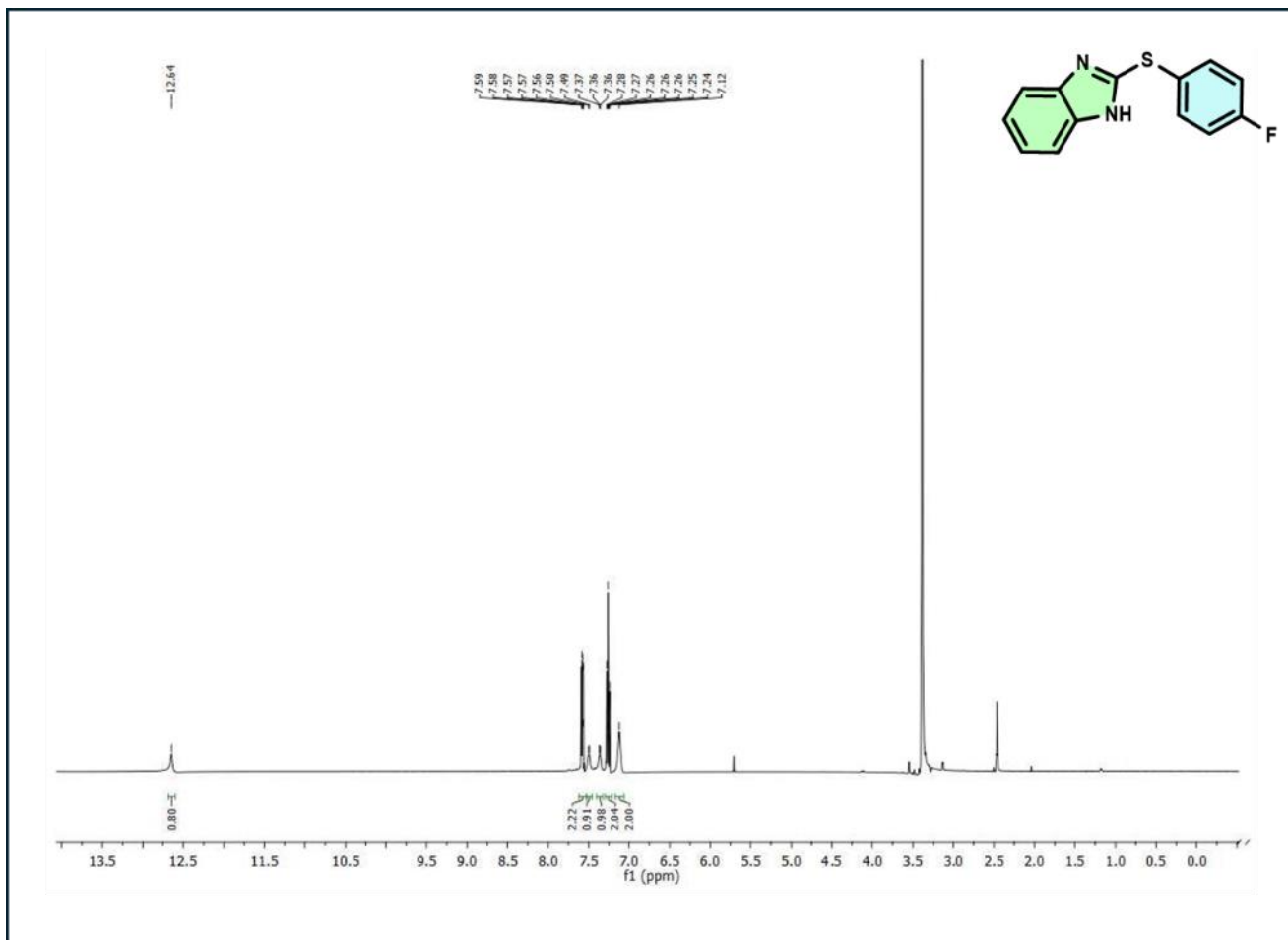


Fig. S24: ^1H NMR spectra of **3f** (DMSO- d_6)

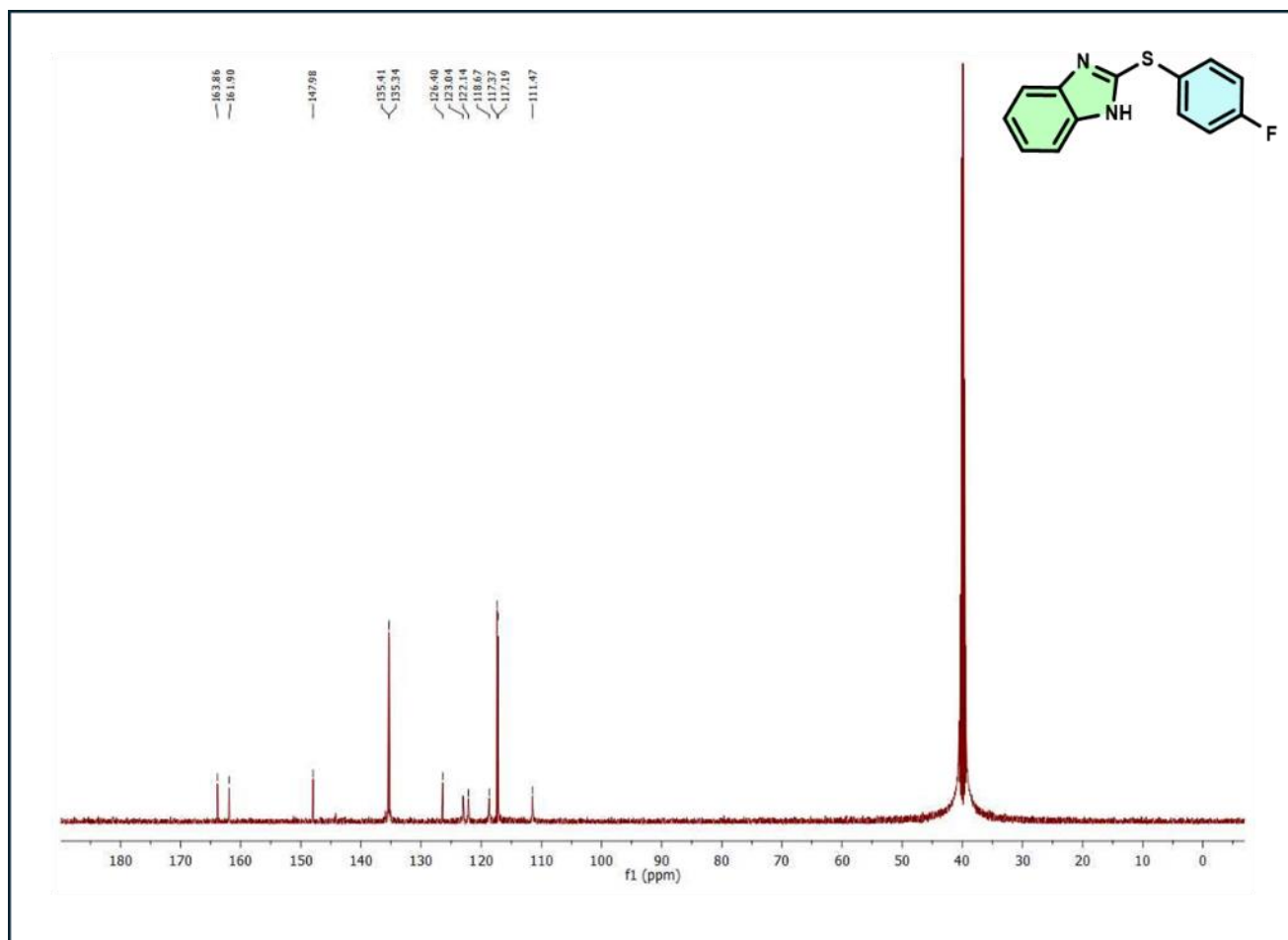


Fig. S25: ^{13}C NMR spectra of **3f** (DMSO-d_6)

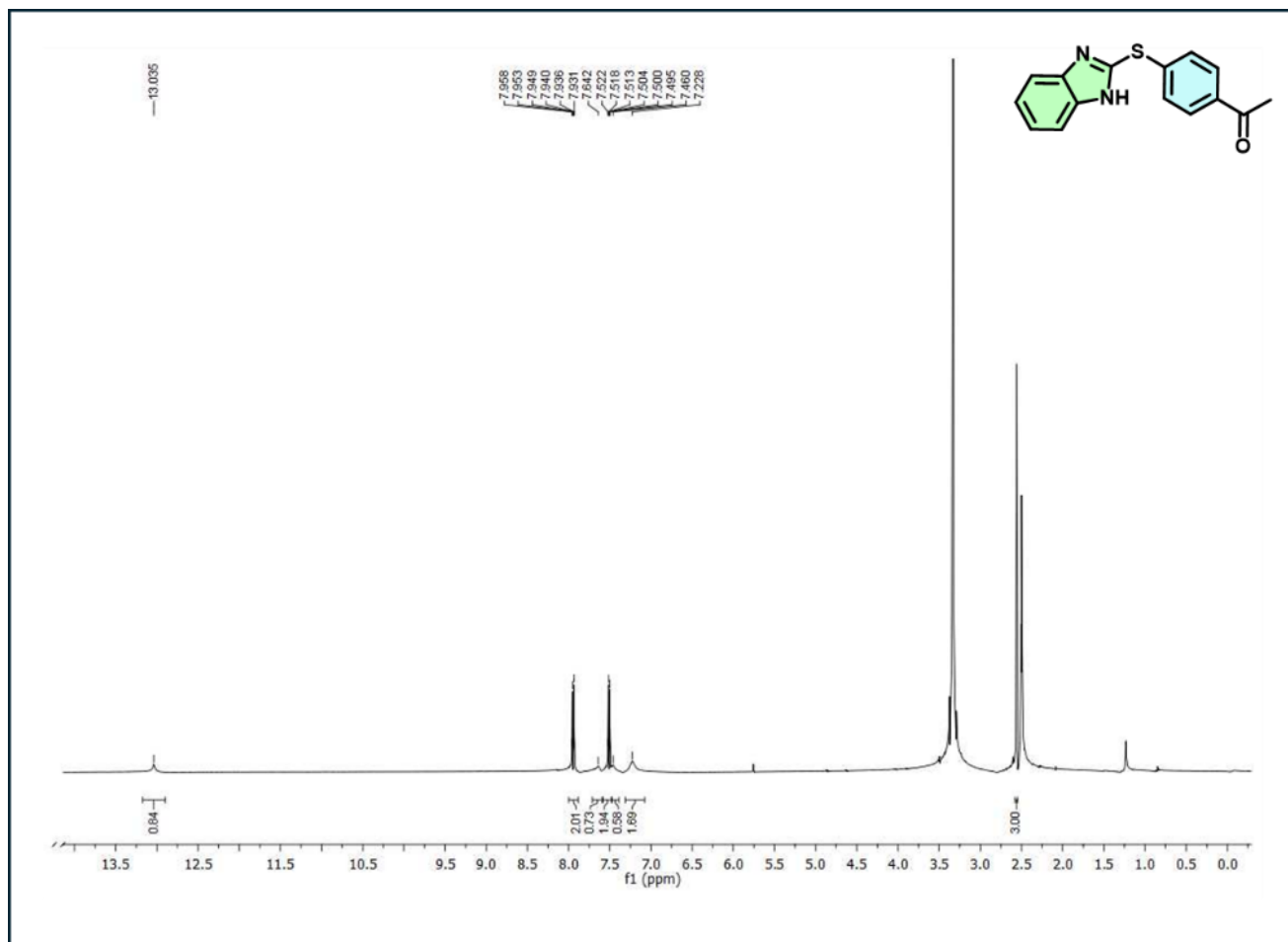


Fig. S26: ¹H NMR spectra of **3g** (DMSO-d₆)

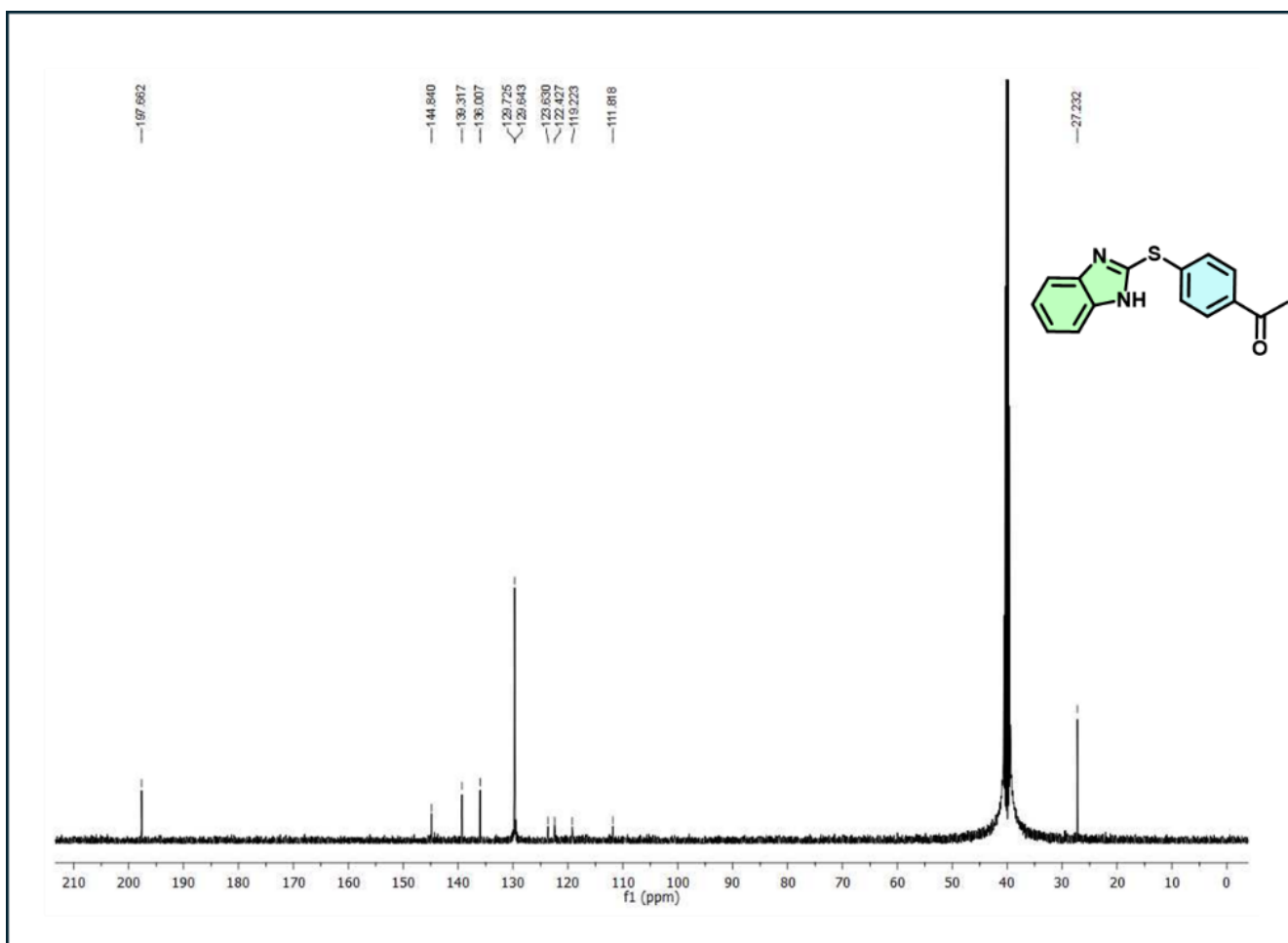


Fig. S27: ^{13}C NMR spectra of **3g** (DMSO-d_6)

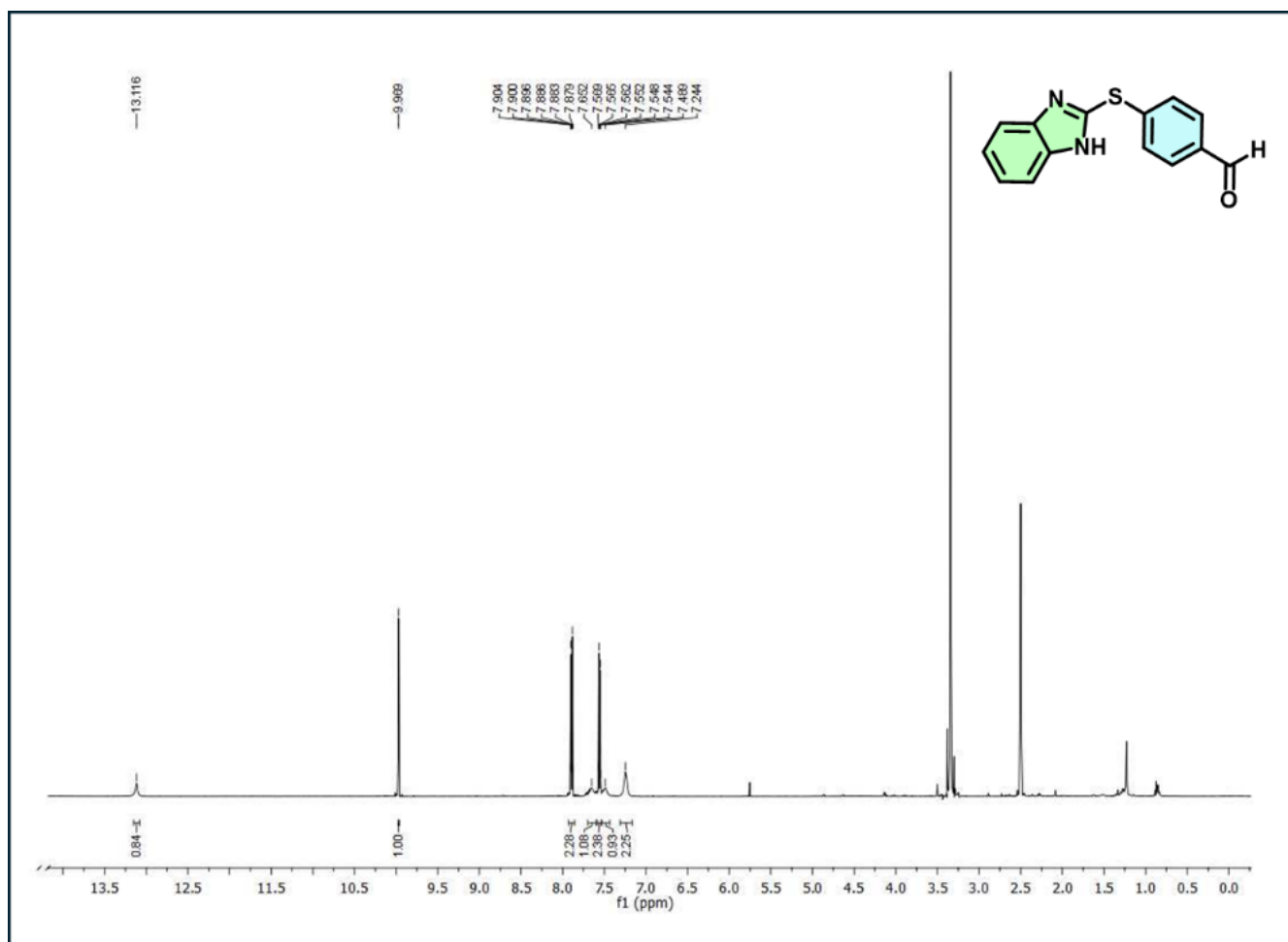


Fig. S28: ^1H NMR spectra of **3h** (DMSO-d_6)

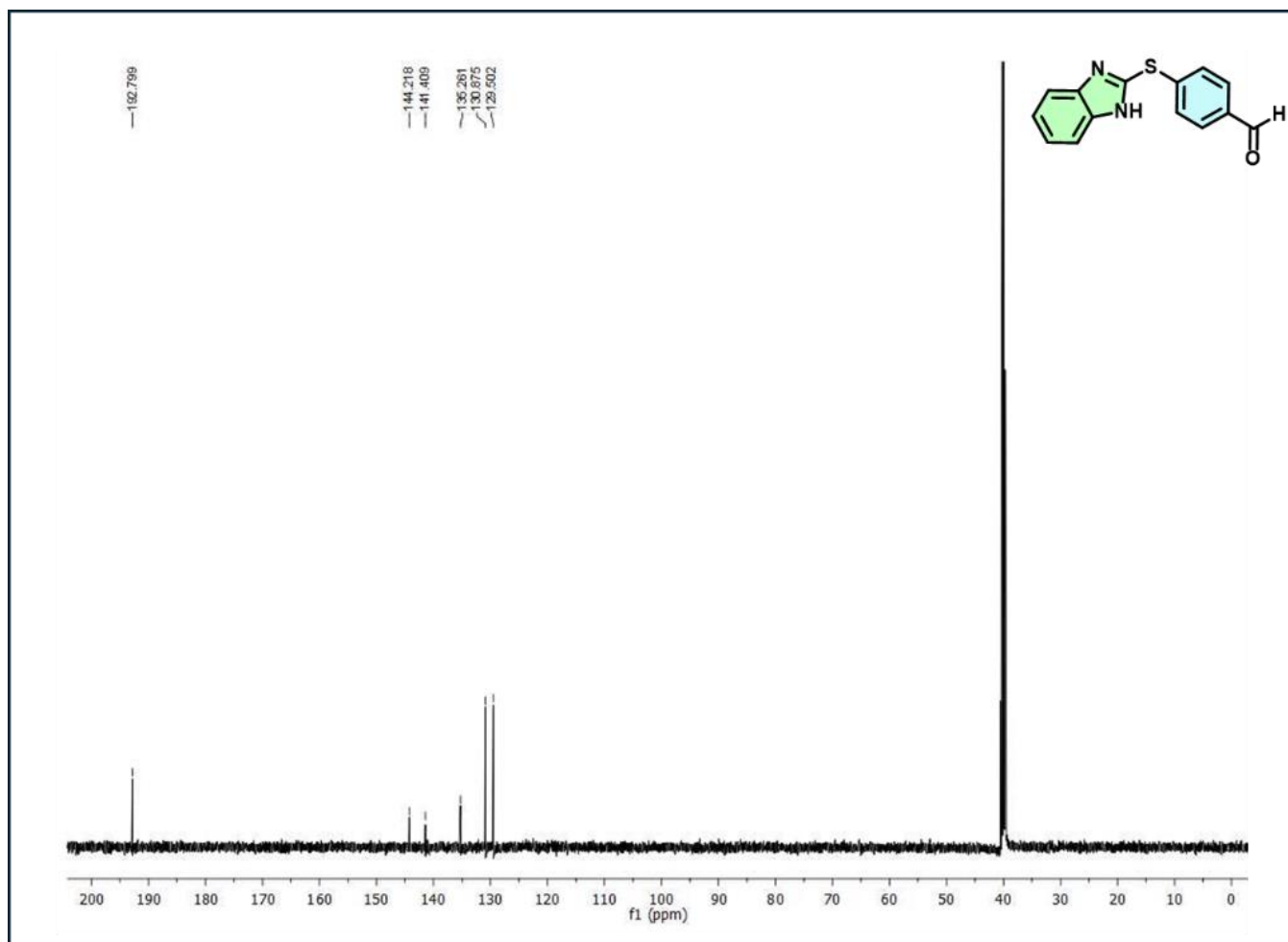


Fig. S29: ^{13}C NMR spectra of **3h** (DMSO-d_6)

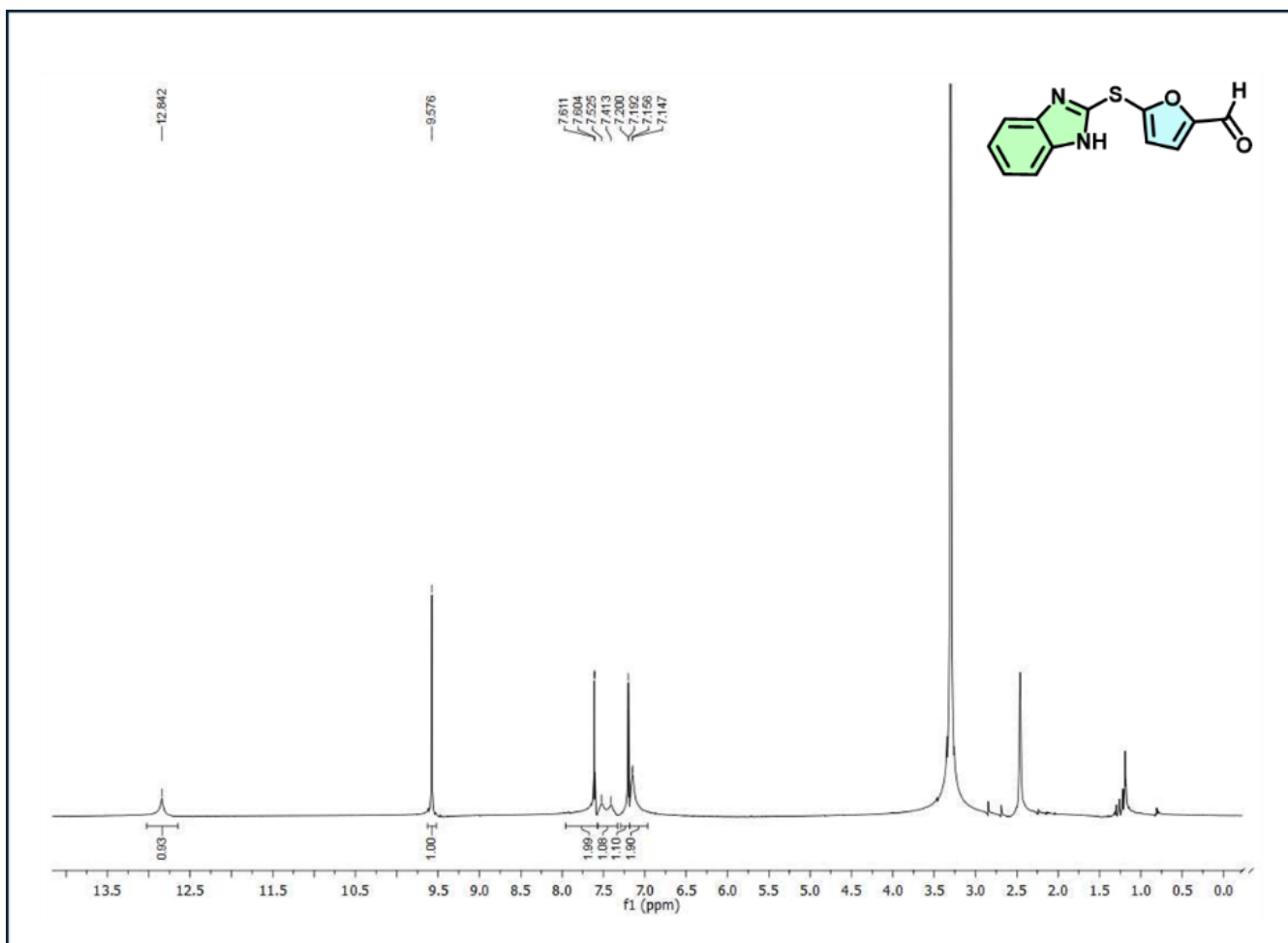


Fig. S30: ¹H NMR spectra of **3i** (DMSO-d₆)

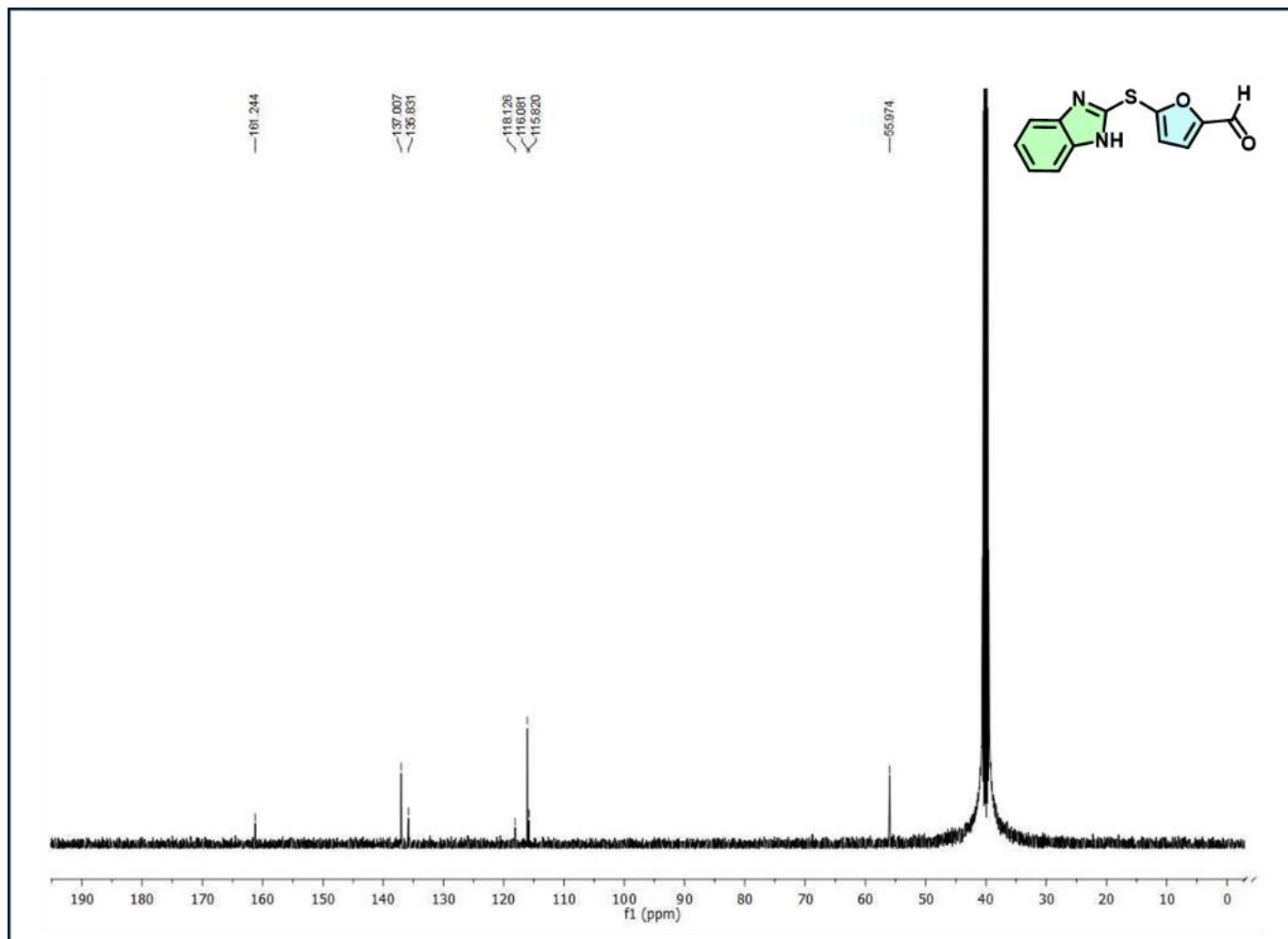


Fig. S31: ^{13}C NMR spectra of **3i** (DMSO-d_6)

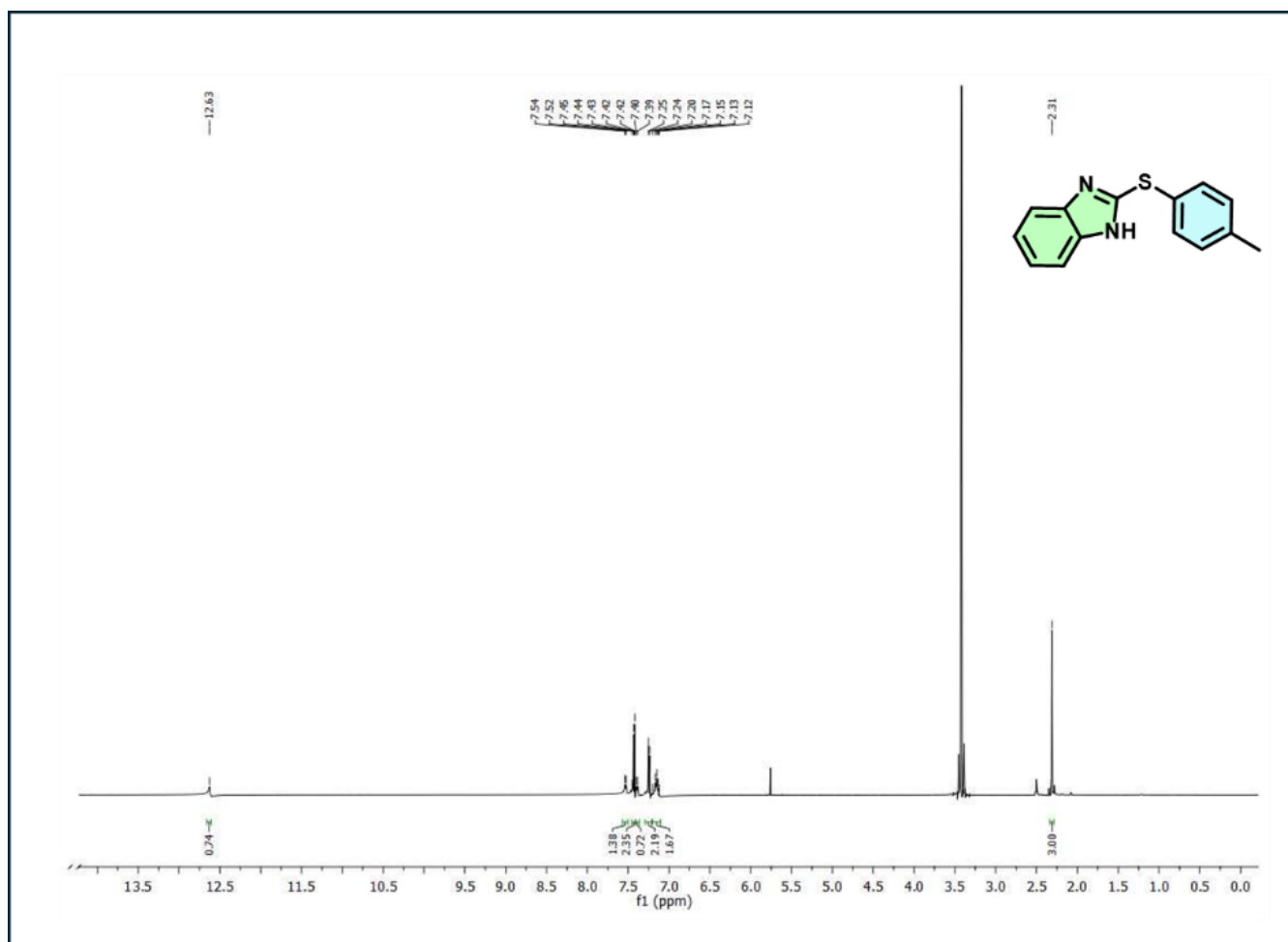


Fig. S32: ^1H NMR spectra of **3j** (DMSO-d_6)

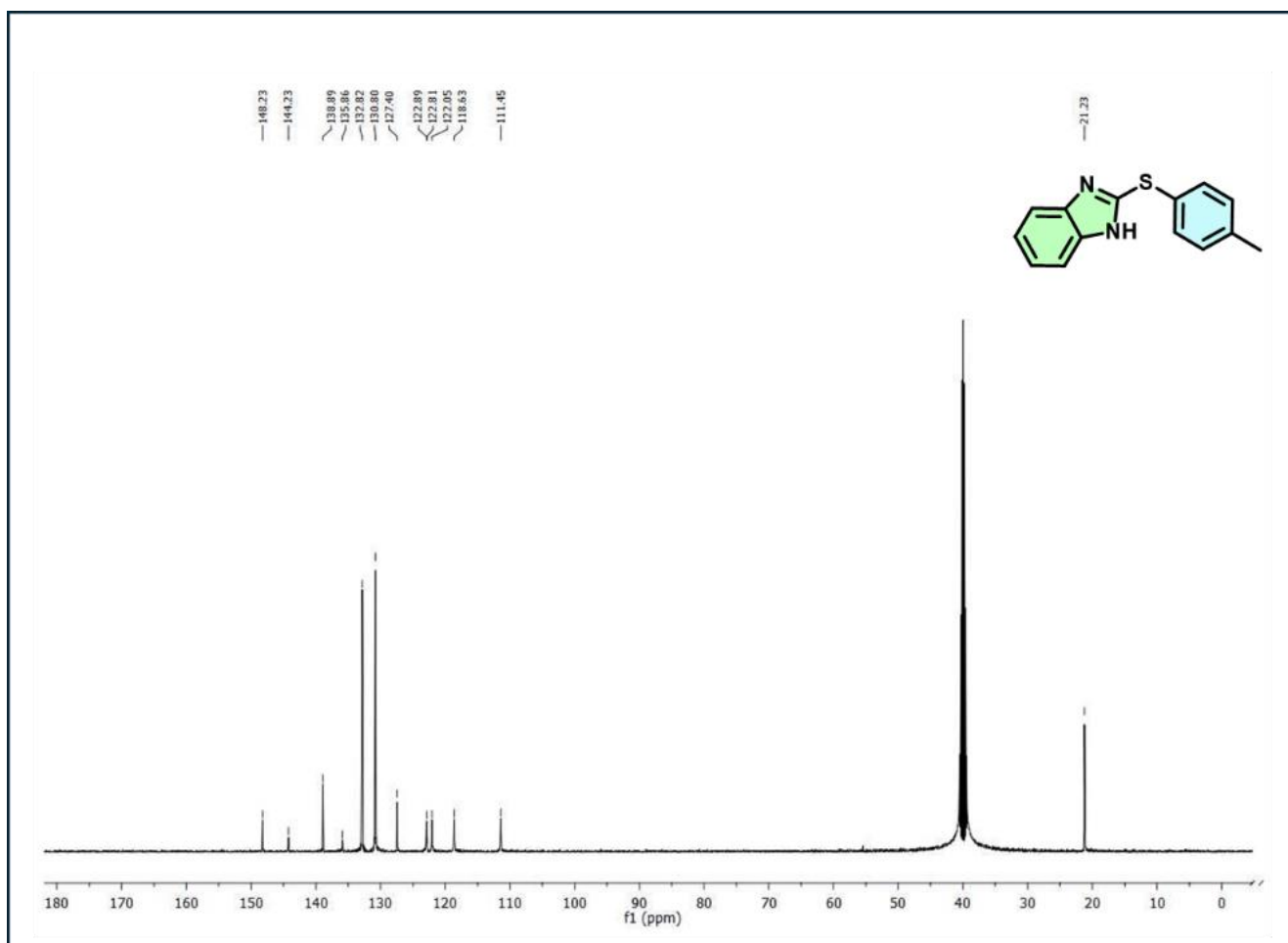


Fig. S33: ¹³C NMR spectra of **3j** (DMSO-d₆)

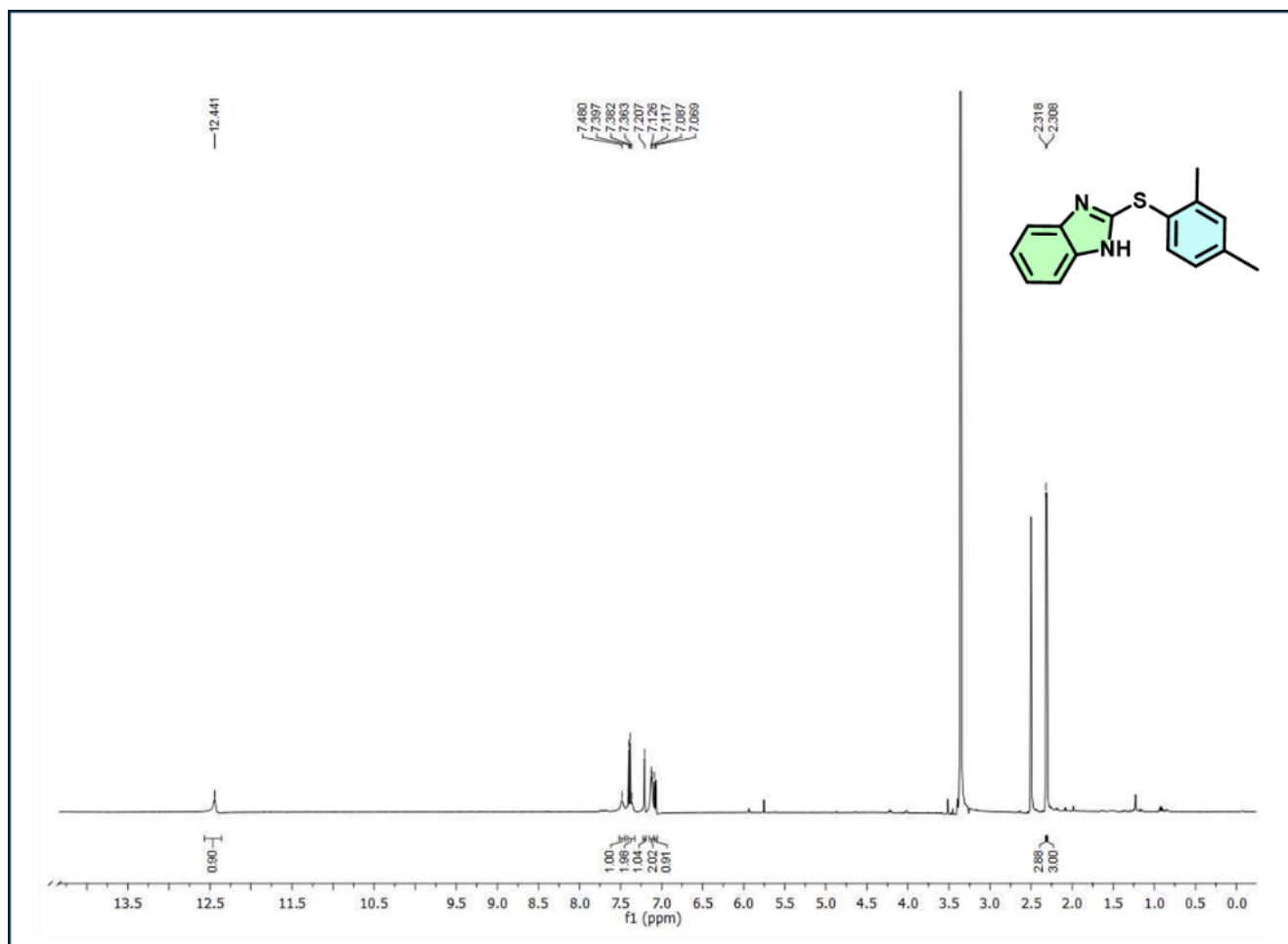


Fig. S34: ^1H NMR spectra of **3k** (DMSO-d_6)

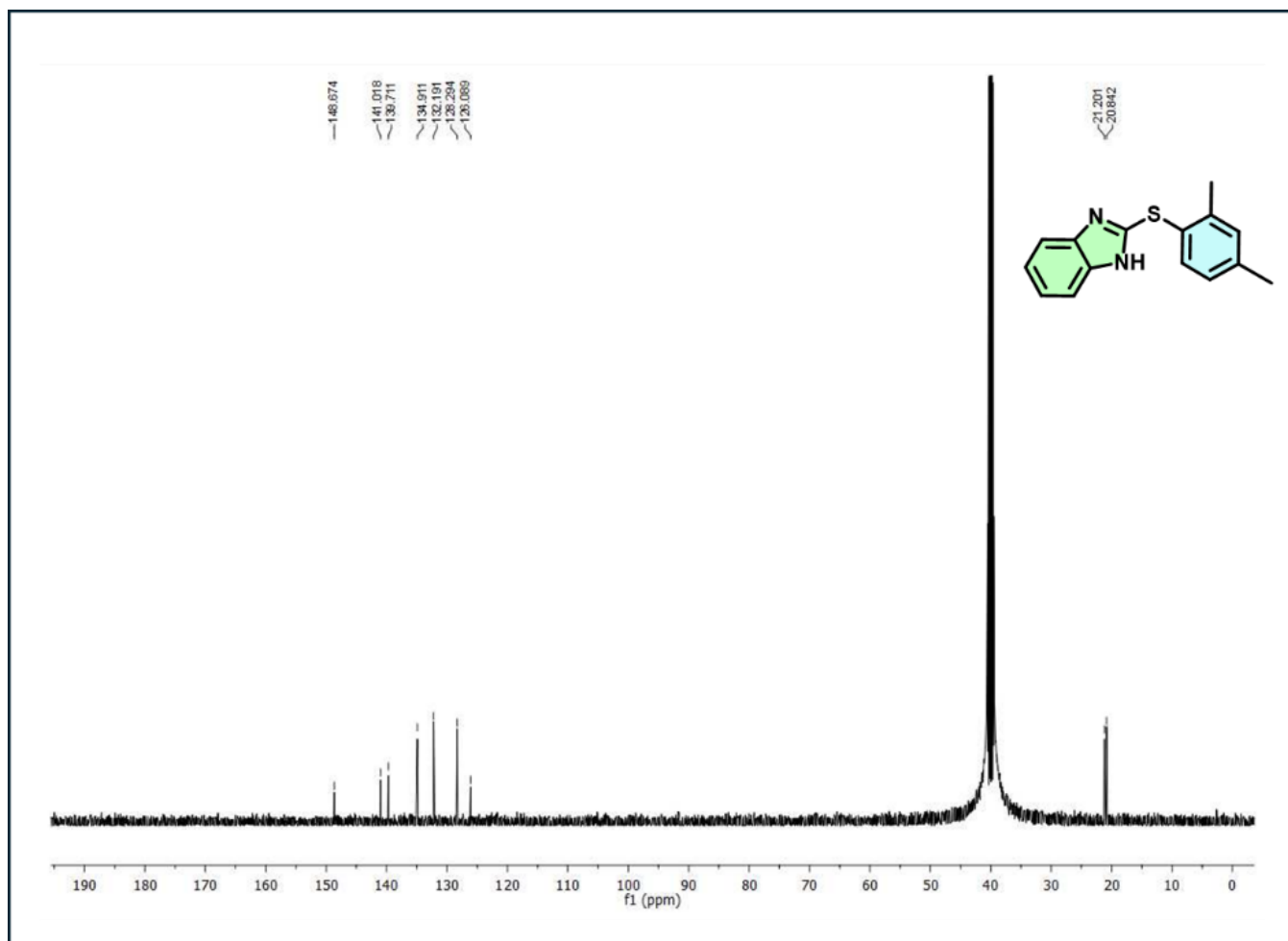


Fig. S35: ^{13}C NMR spectra of **3k** (DMSO-d_6)

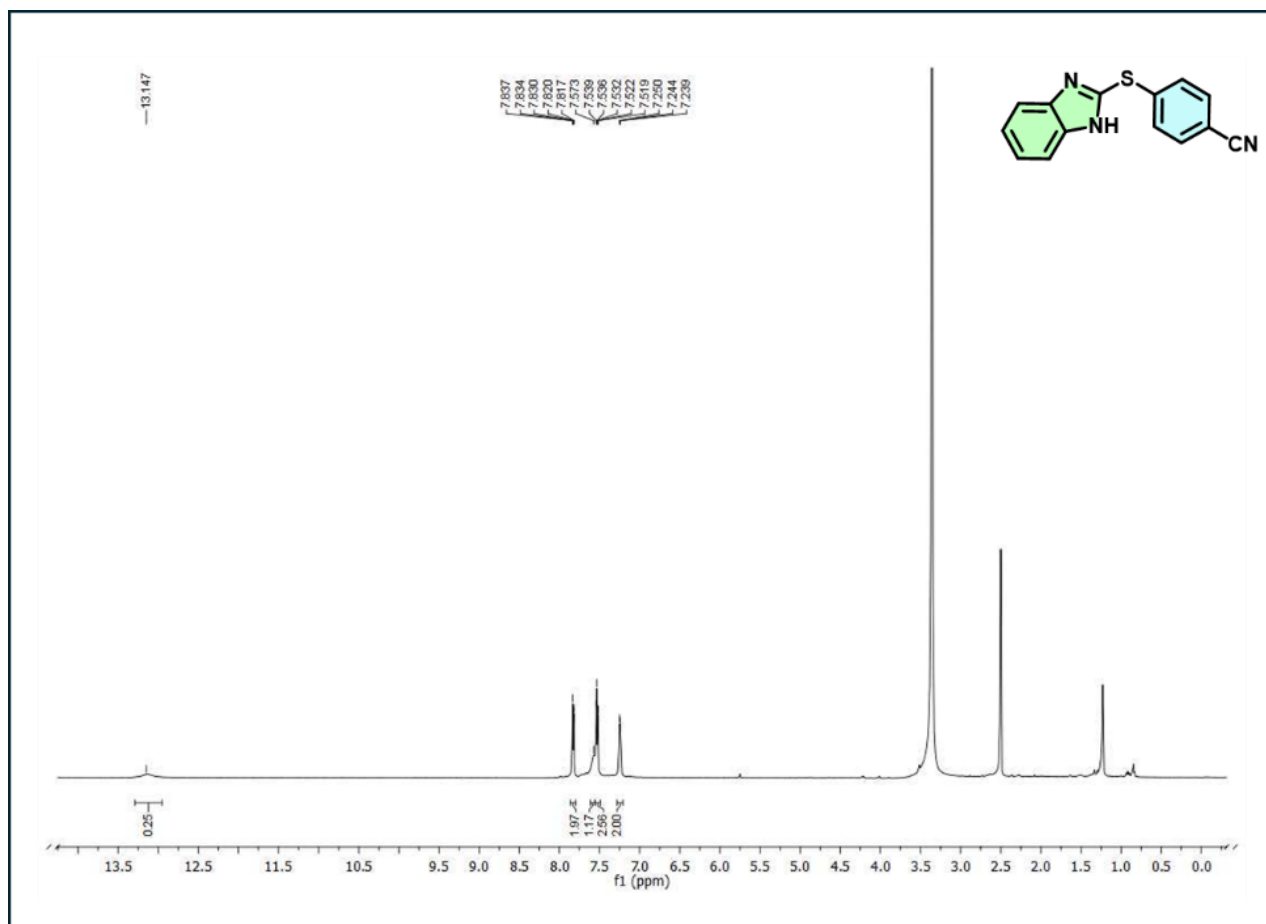


Fig. S36: ¹H NMR spectra of **3I** (DMSO-d₆)

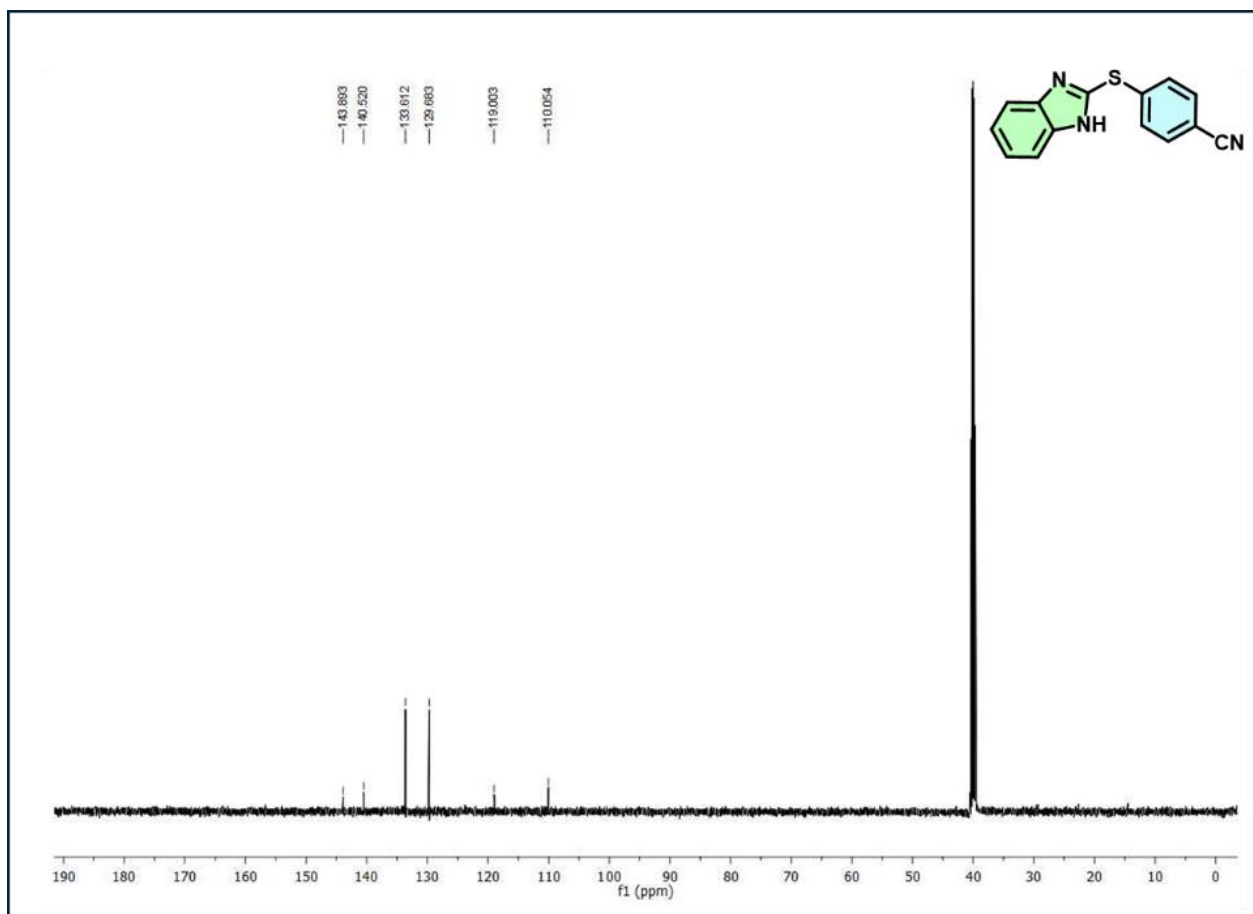


Fig. S37: ^{13}C NMR spectra of **3I** (DMSO-d_6)

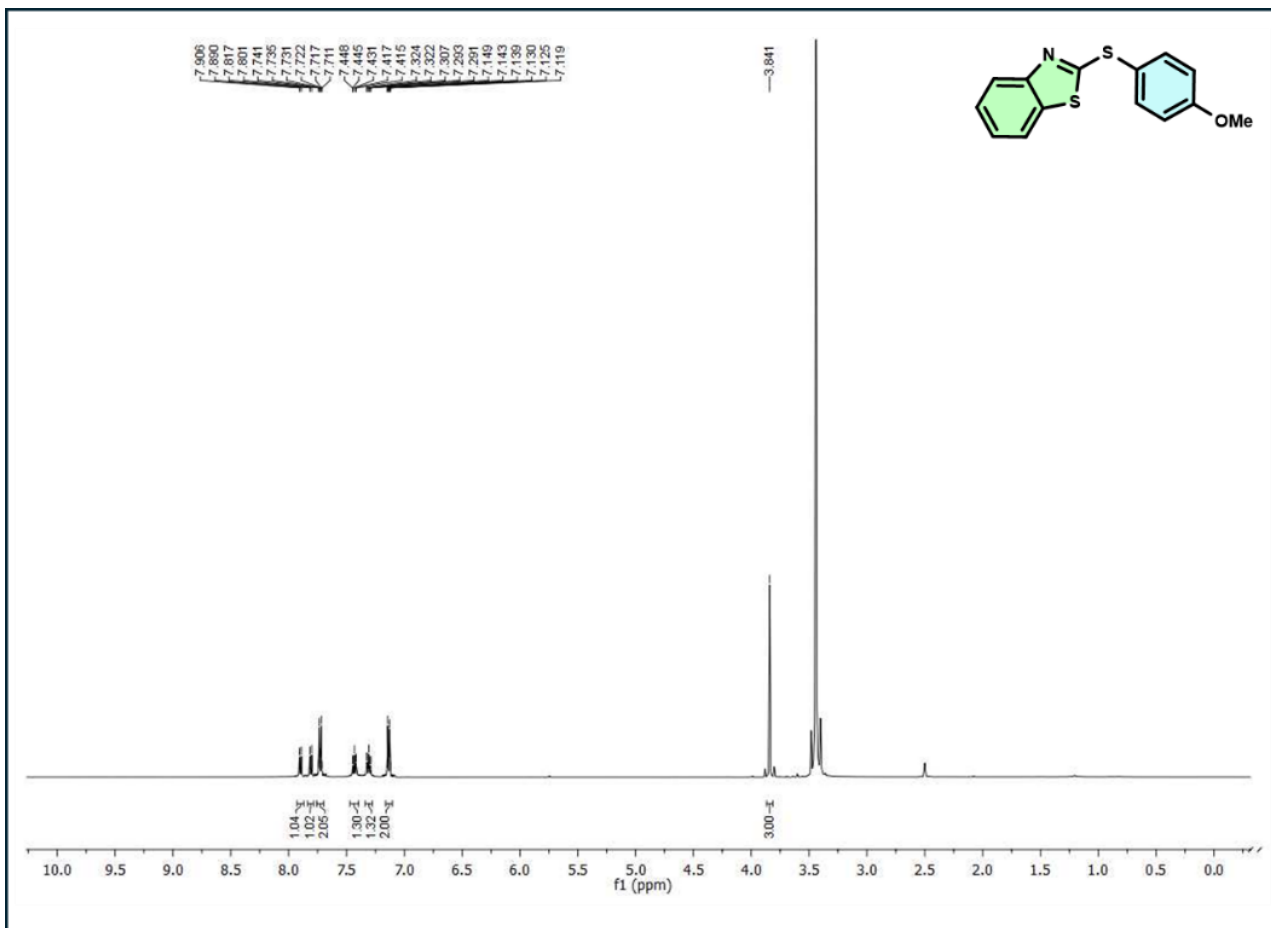


Fig. S38: ¹H NMR spectra of **3m** (DMSO-d₆)

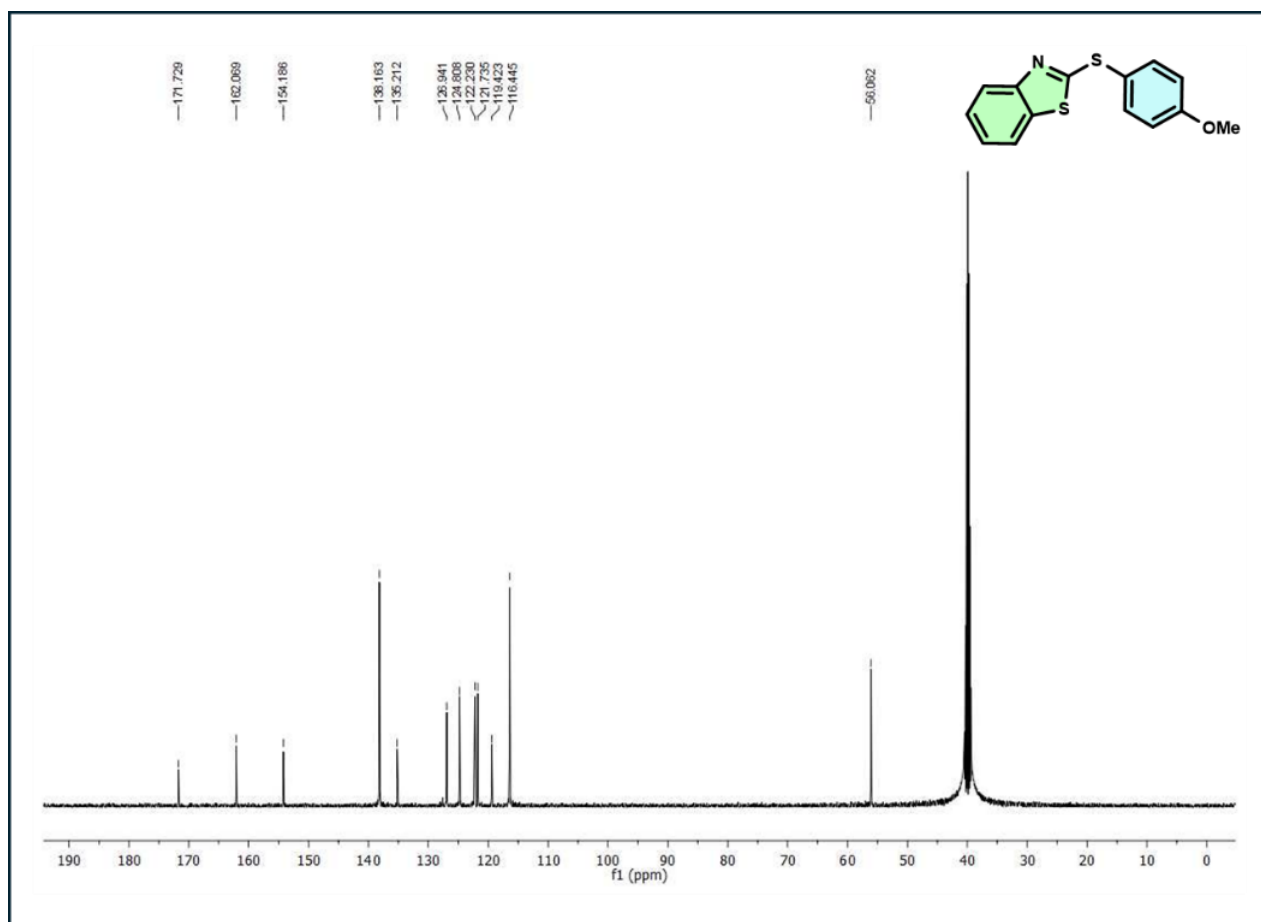


Fig. S39: ^{13}C NMR spectra of **3m** (DMSO-d_6)

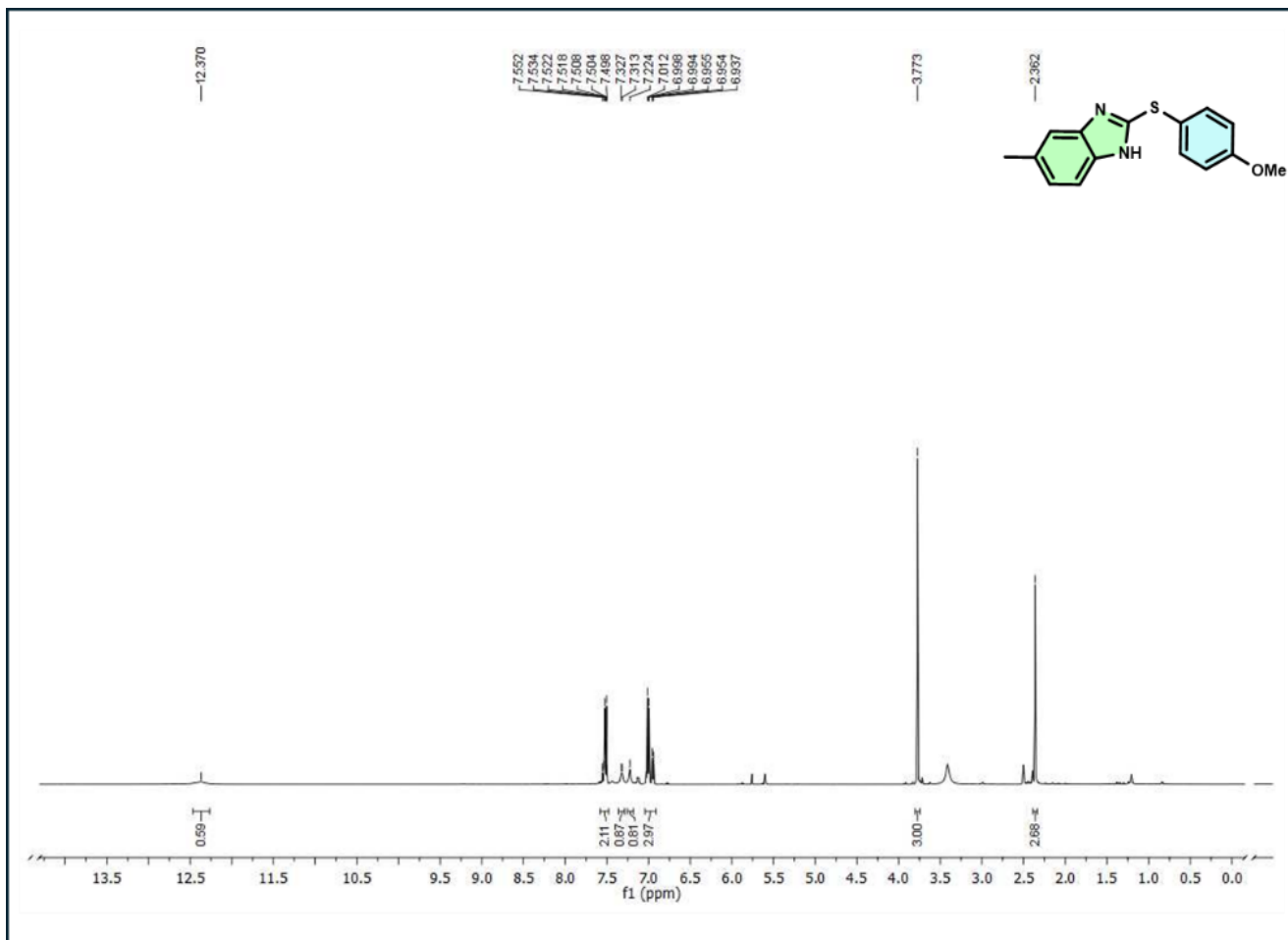


Fig. S40: ^1H NMR spectra of **3n** (DMSO-d_6)

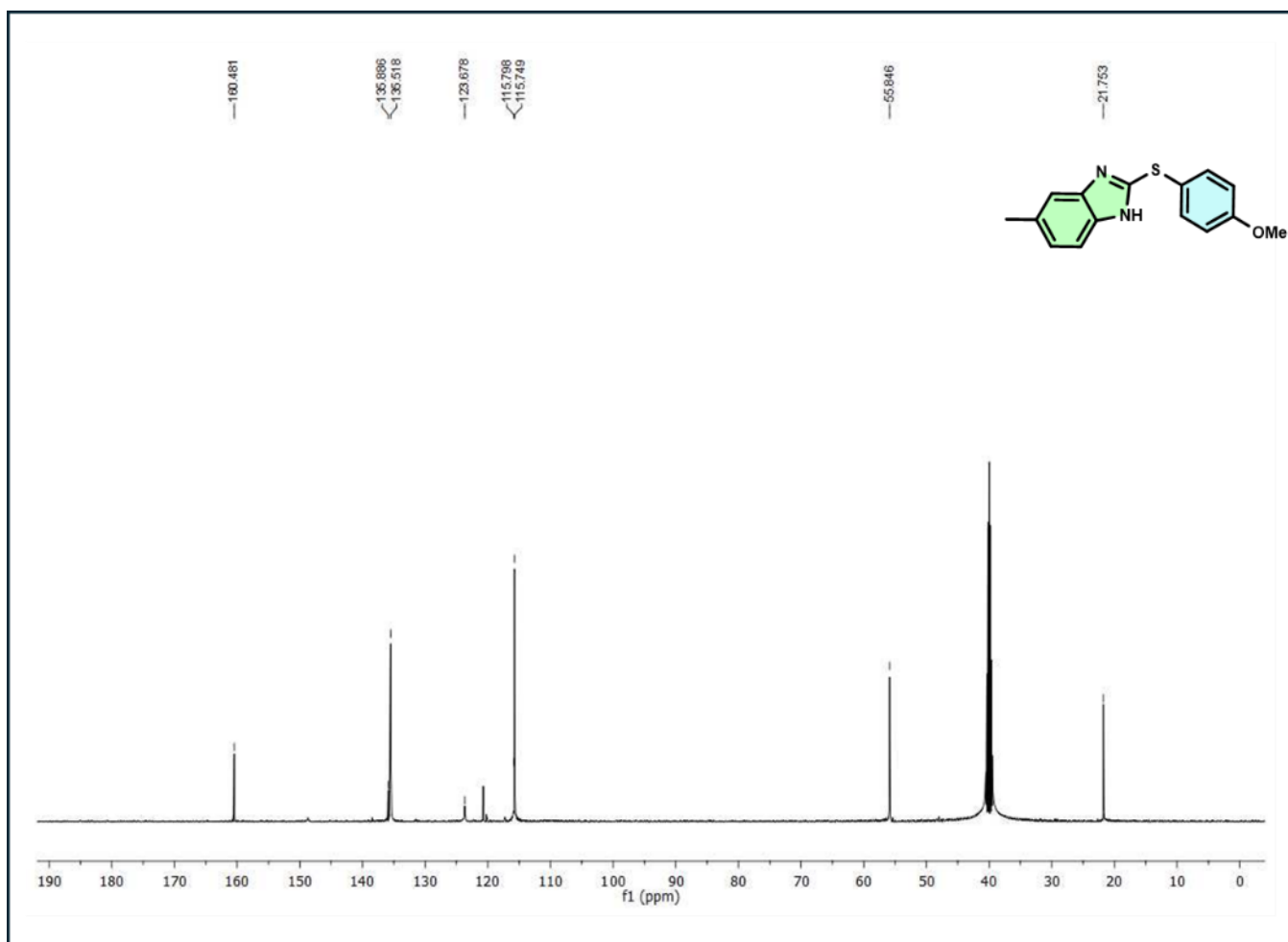


Fig. S41: ^{13}C NMR spectra of **3n** (DMSO- d_6)

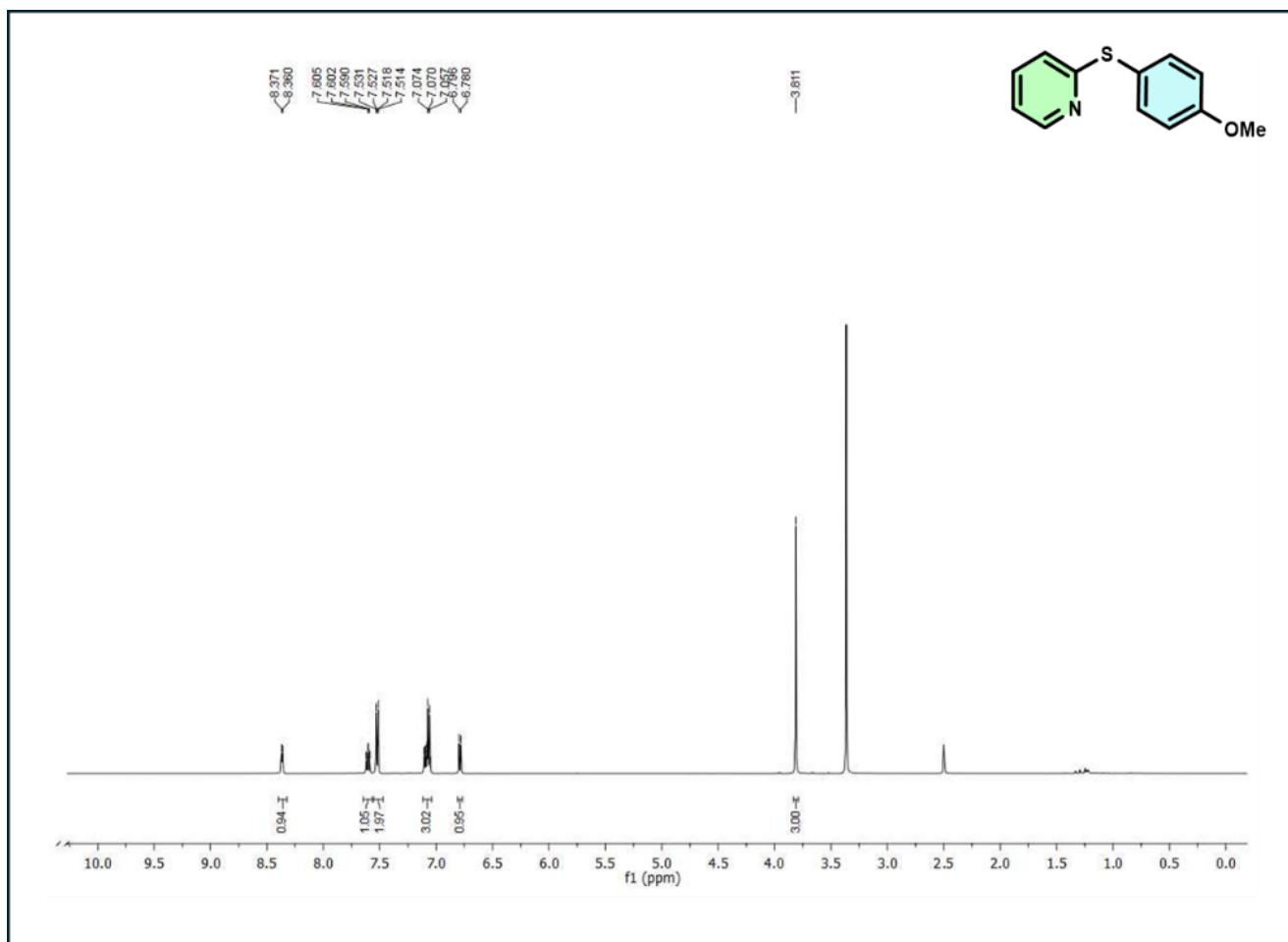


Fig. S42: ^1H NMR spectra of **30** (DMSO-d_6)

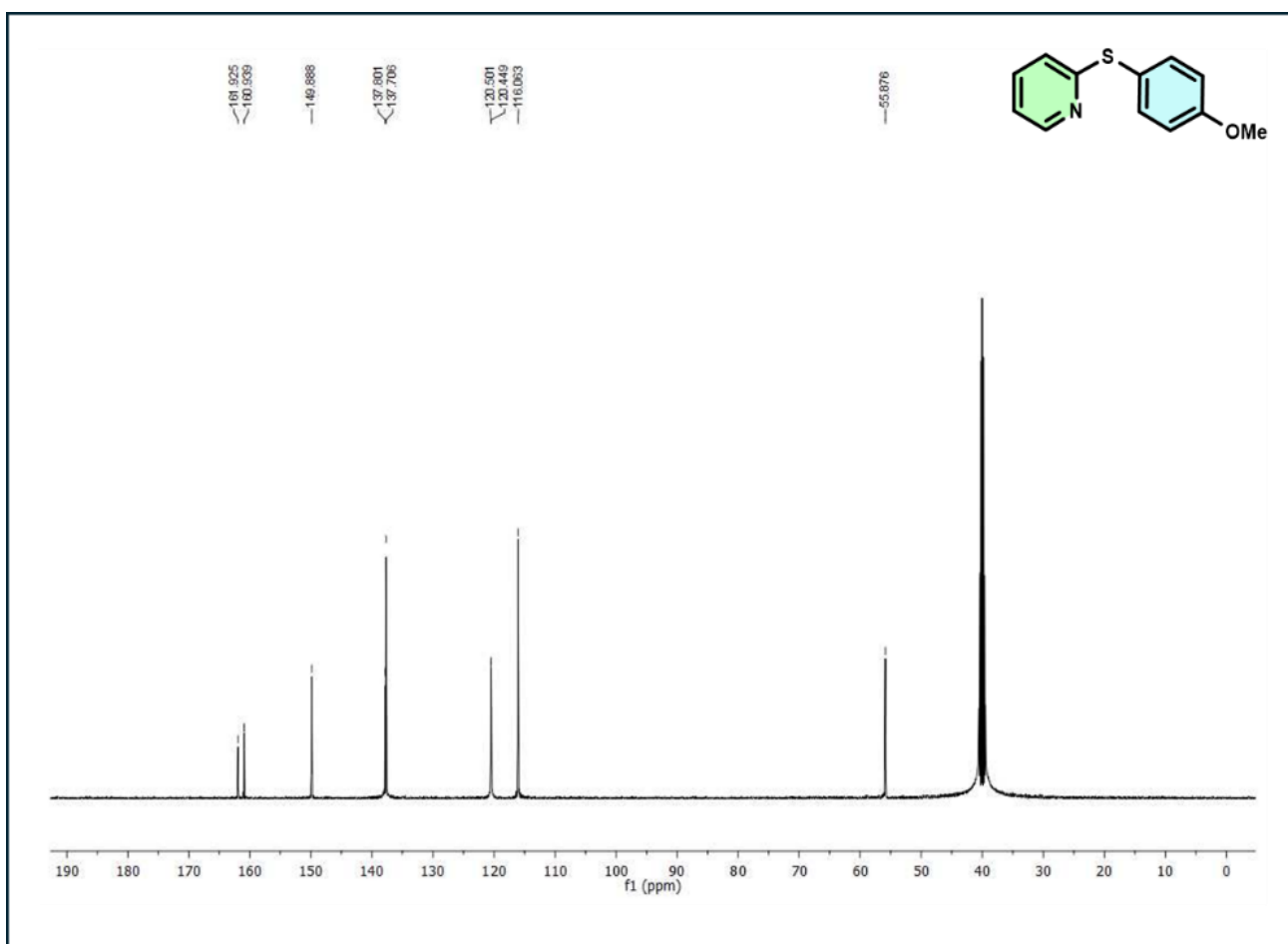


Fig. S43: ^{13}C NMR spectra of **3o** (DMSO-d_6)

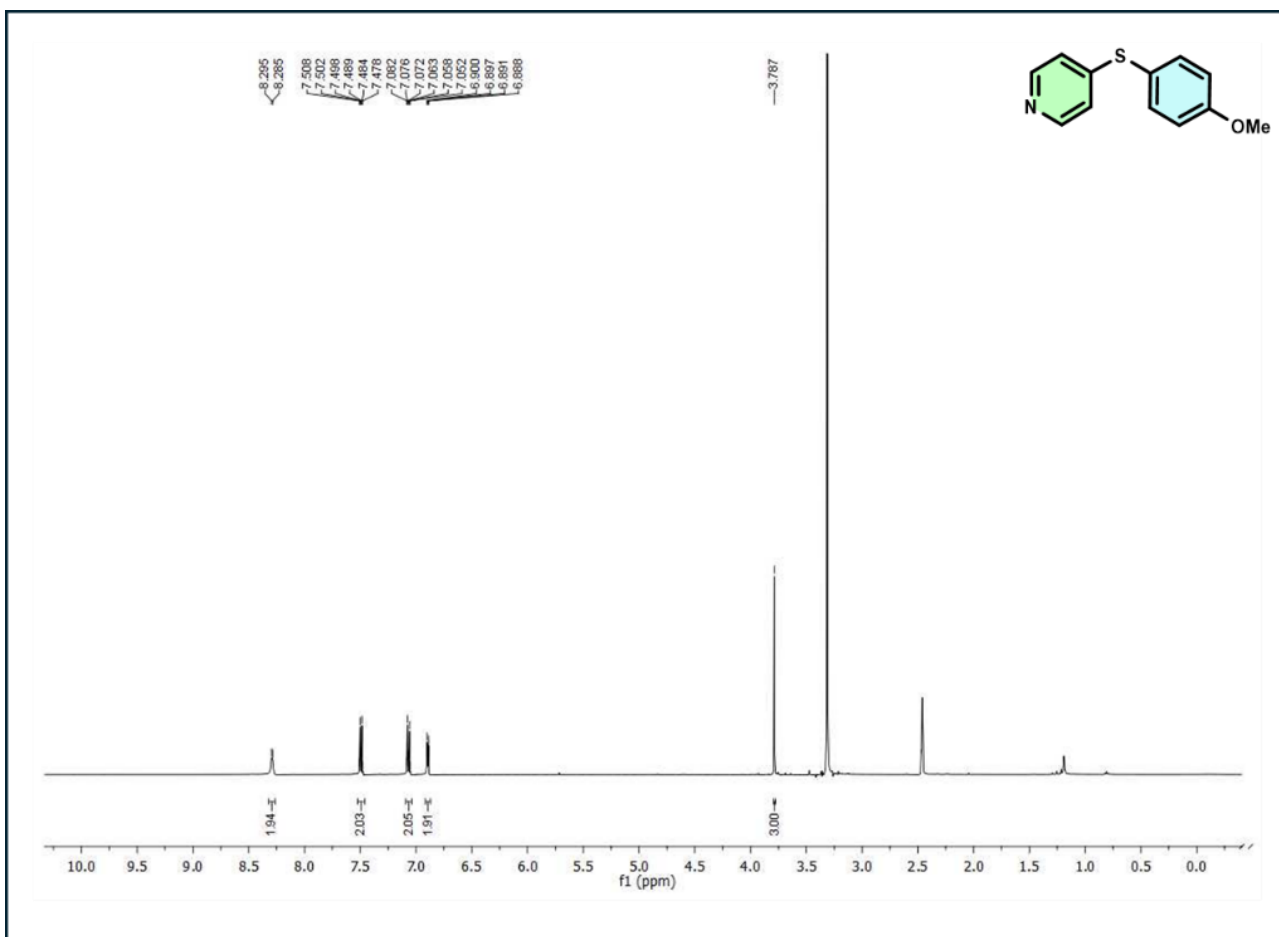


Fig. S44: ¹H NMR spectra of **3p** (DMSO-d₆)

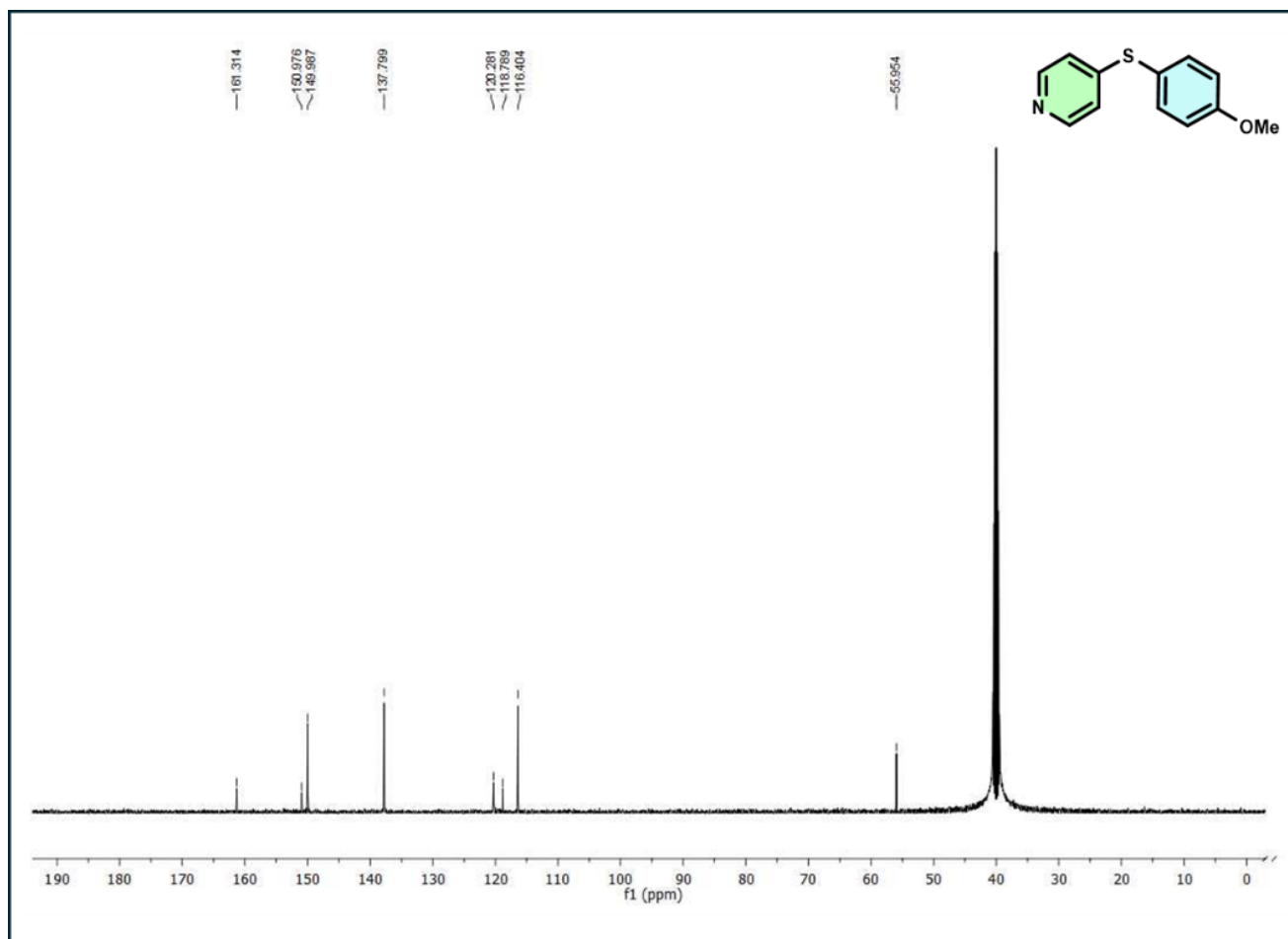


Fig. S45: ^{13}C NMR spectra of **3p** (DMSO- d_6)

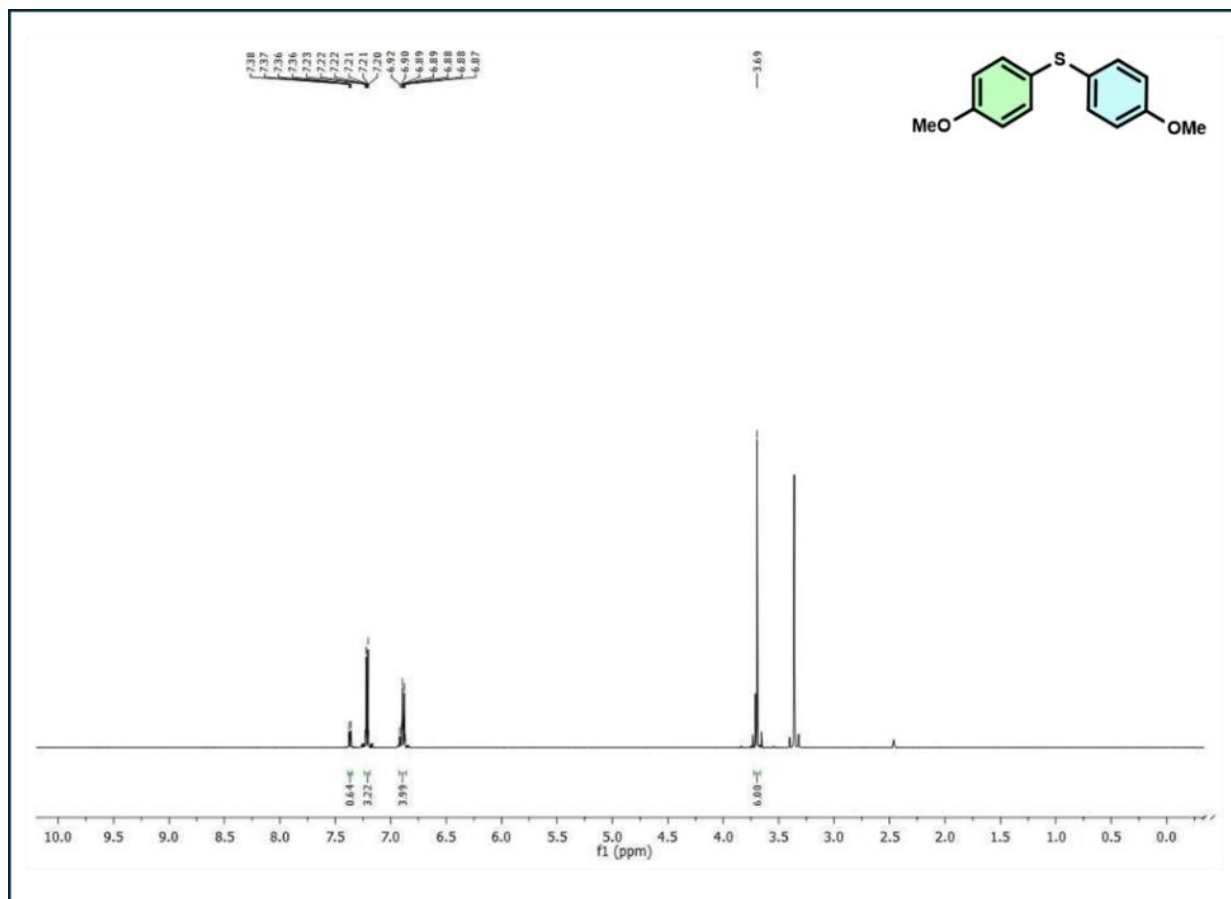


Fig. S46: ^1H NMR spectra of **3q** (DMSO- d_6)

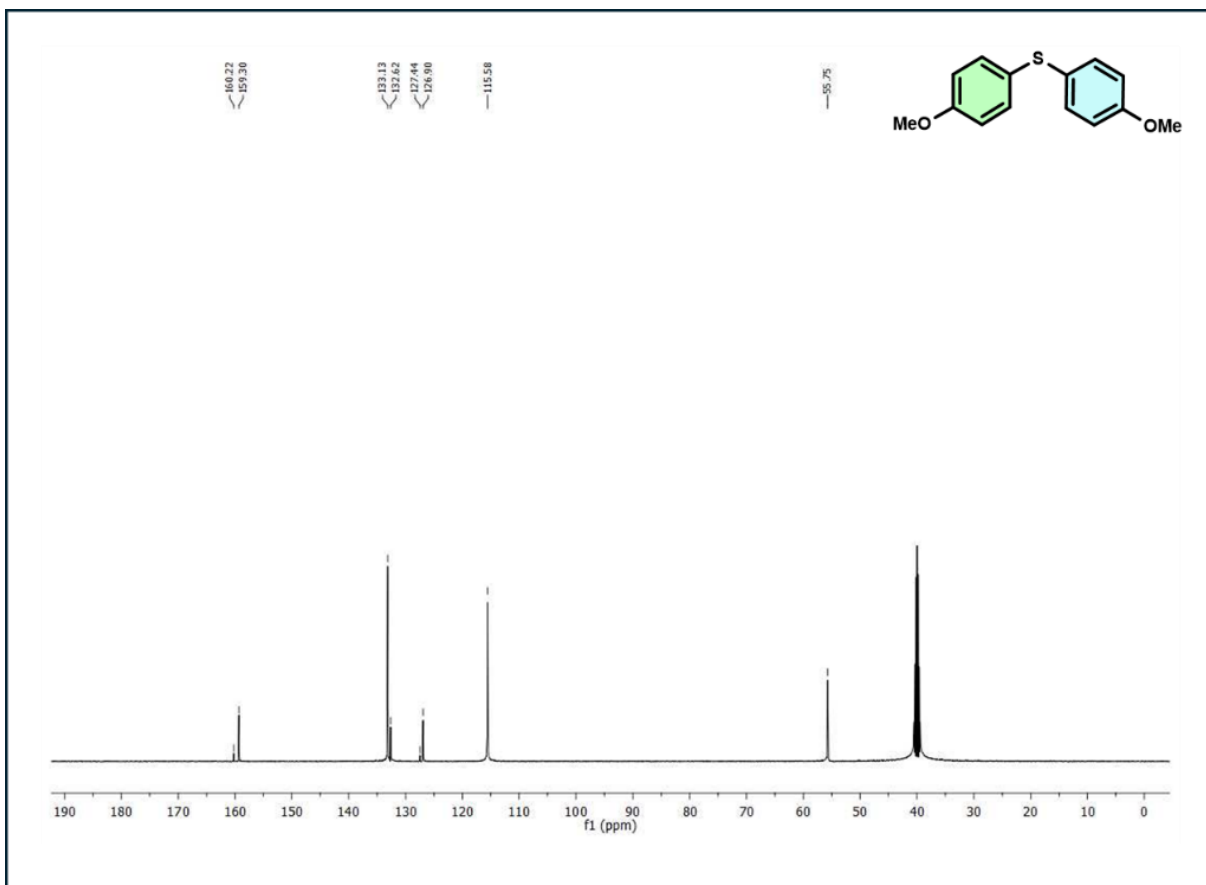


Fig. S47: ¹³C NMR spectra of **3q** (DMSO-d₆)

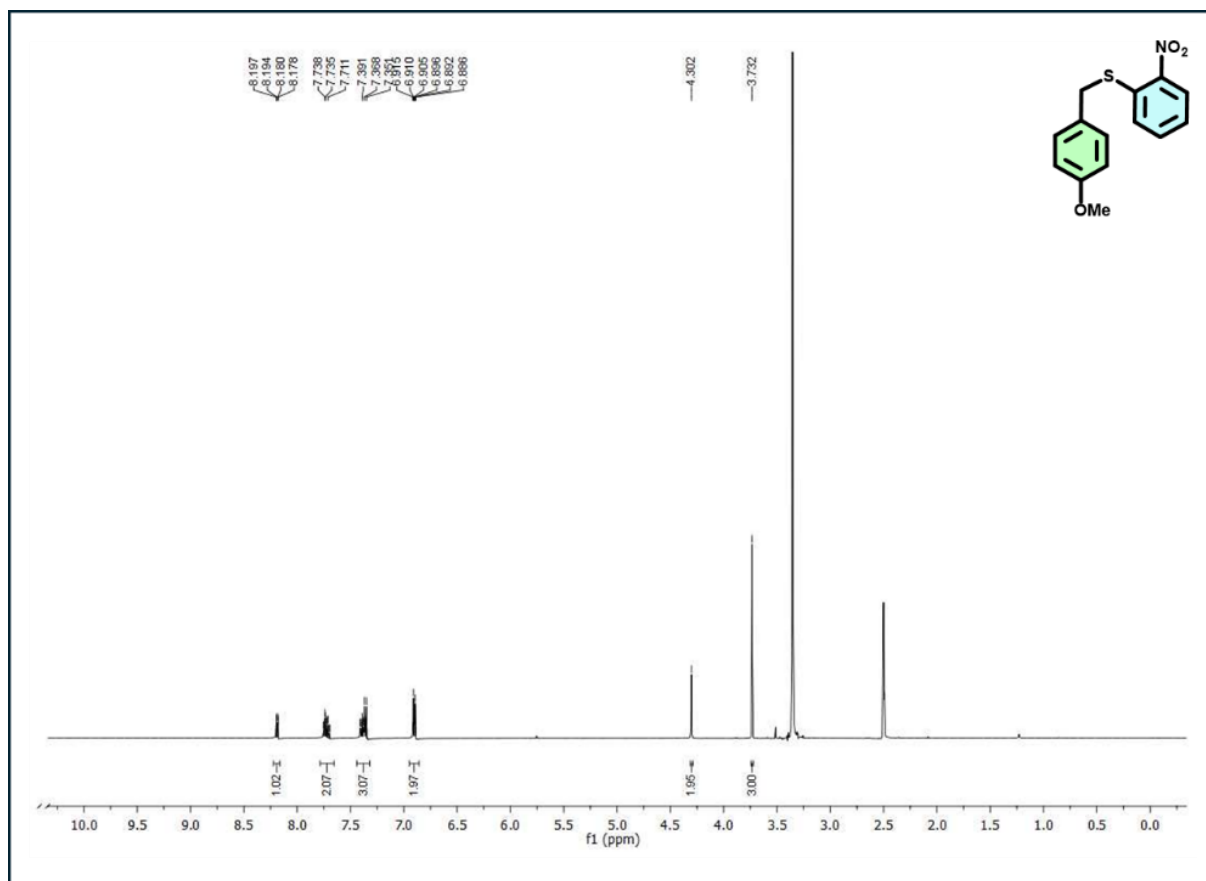


Fig. S48: ^1H NMR spectra of **3r** (DMSO-d_6)

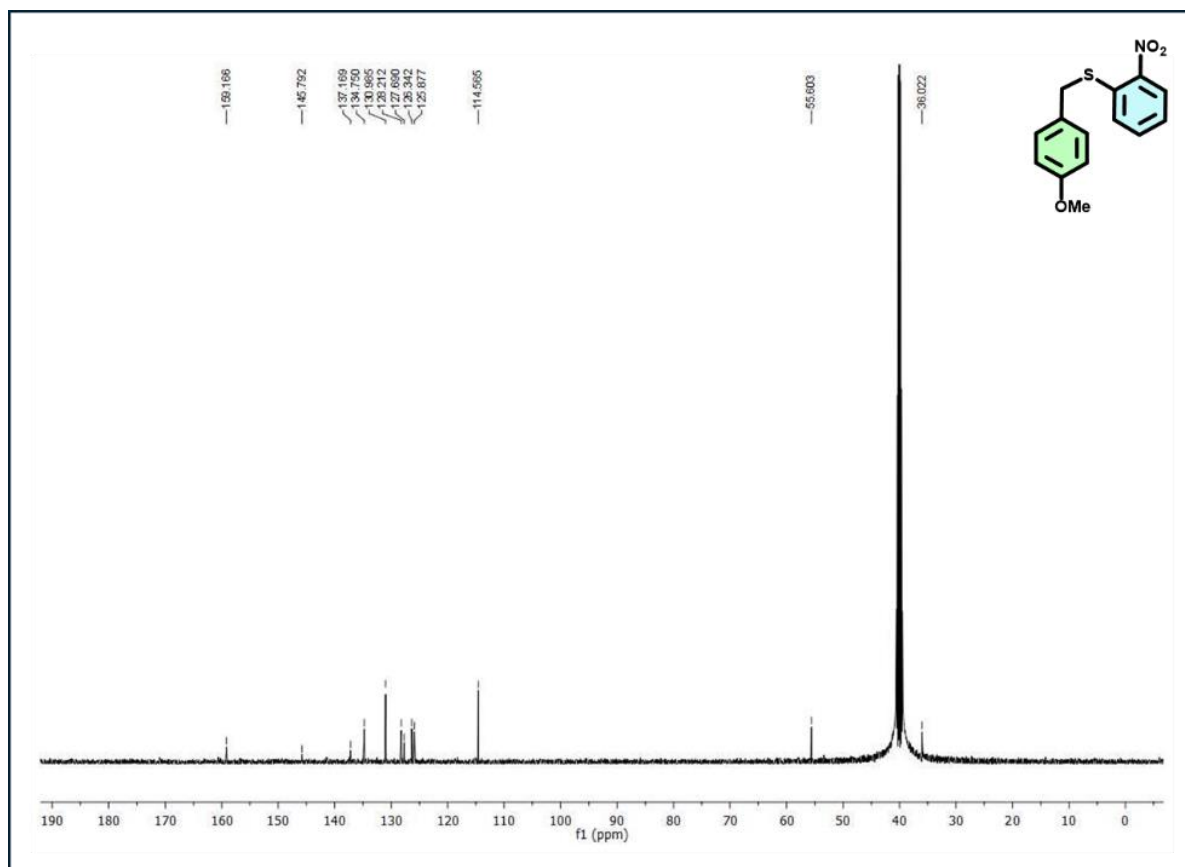


Fig. S49: ^{13}C NMR spectra of **3r** (DMSO-d_6)

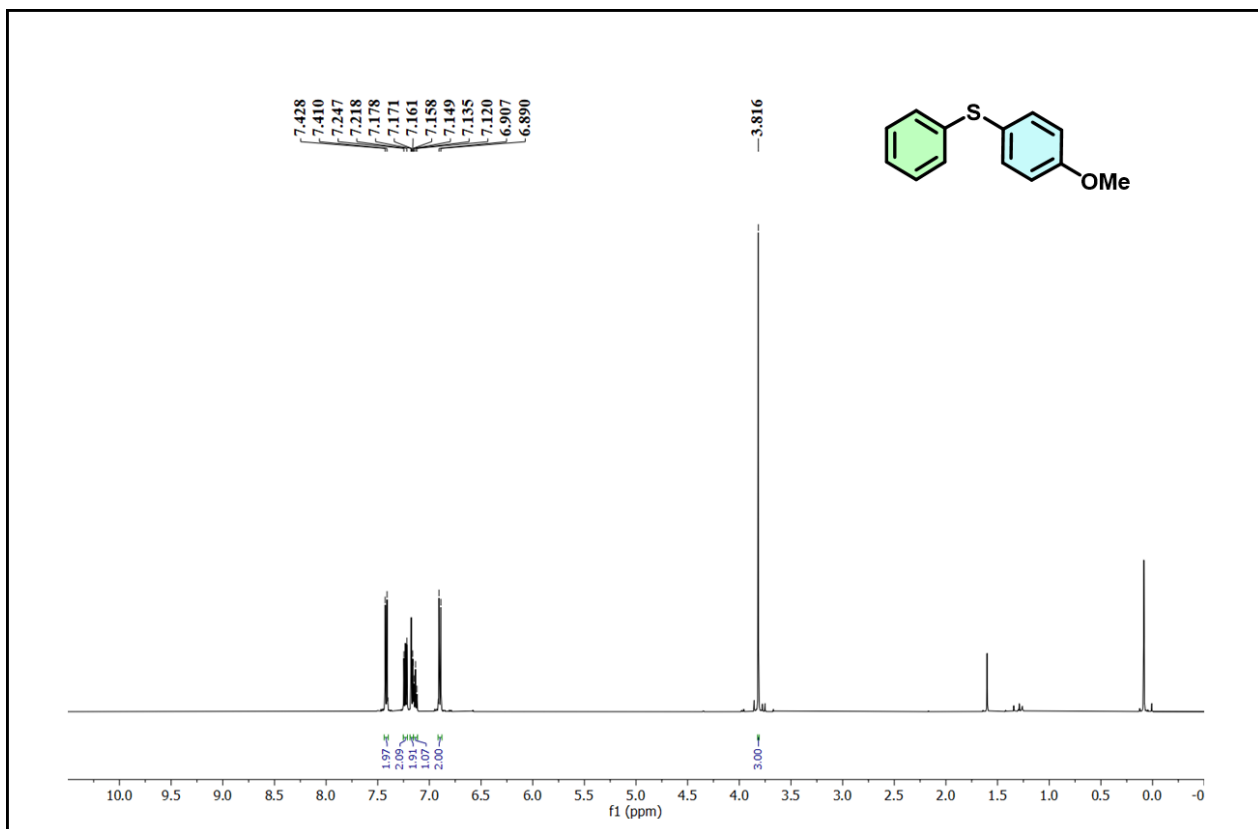


Fig. S50: ¹H NMR spectra of 3s (CDCl₃)

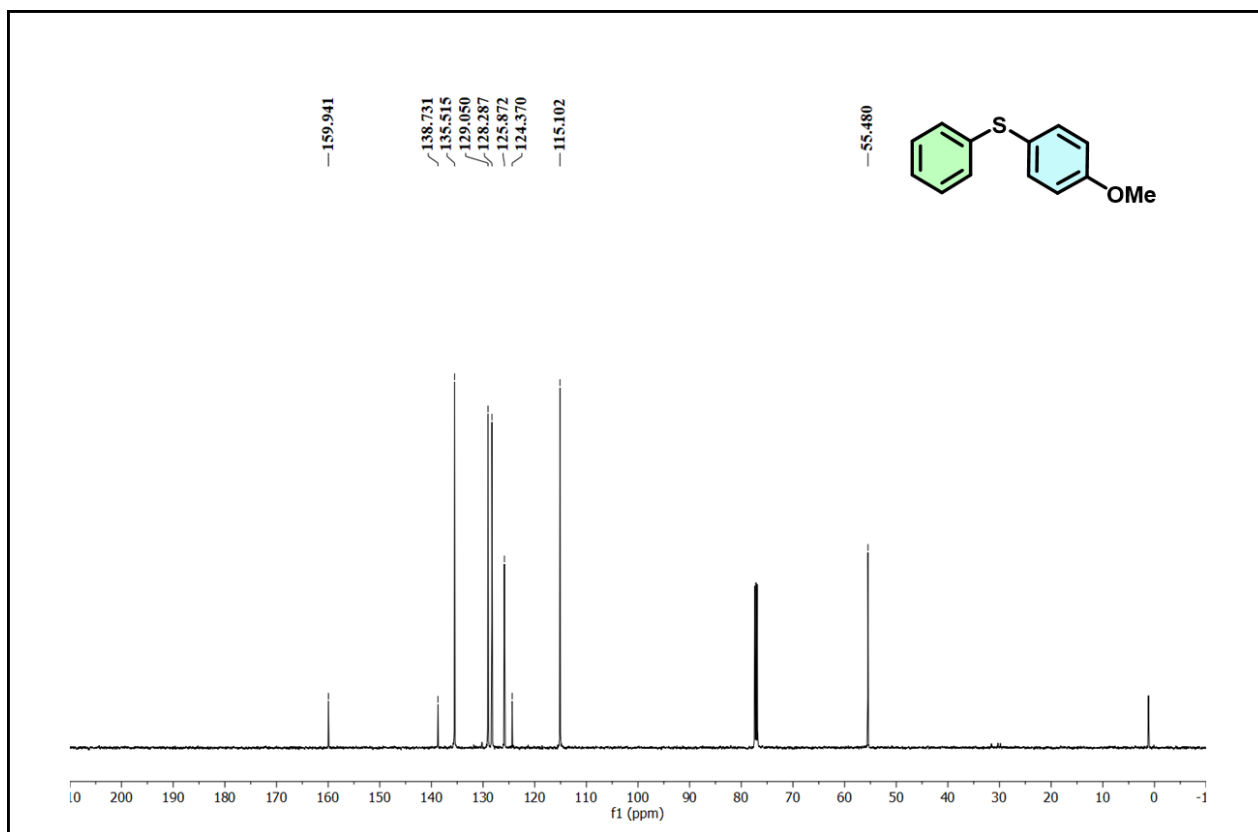


Fig. S51: ^{13}C NMR spectra of **3s** (CDCl_3)

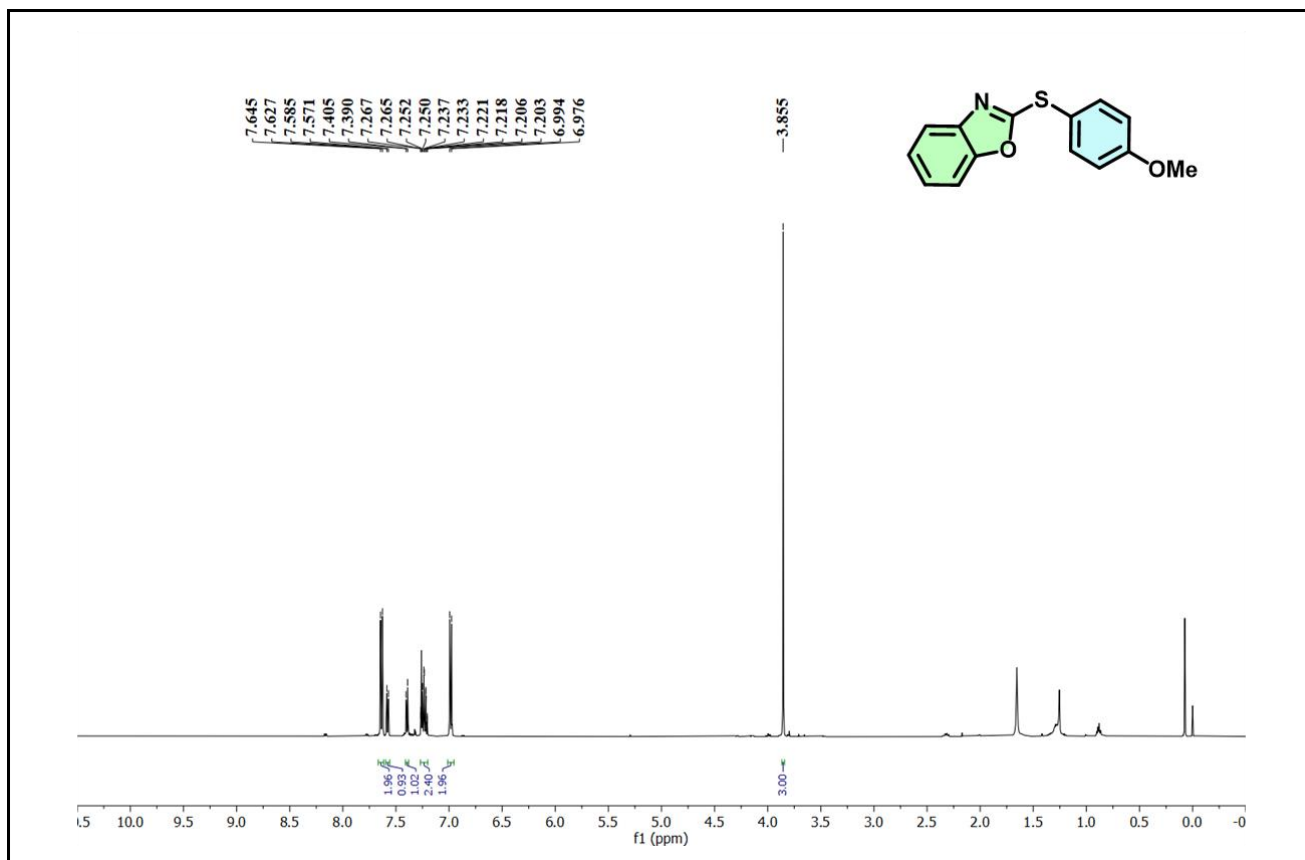


Fig. S52: ¹H NMR spectra of **3t** (CDCl₃)

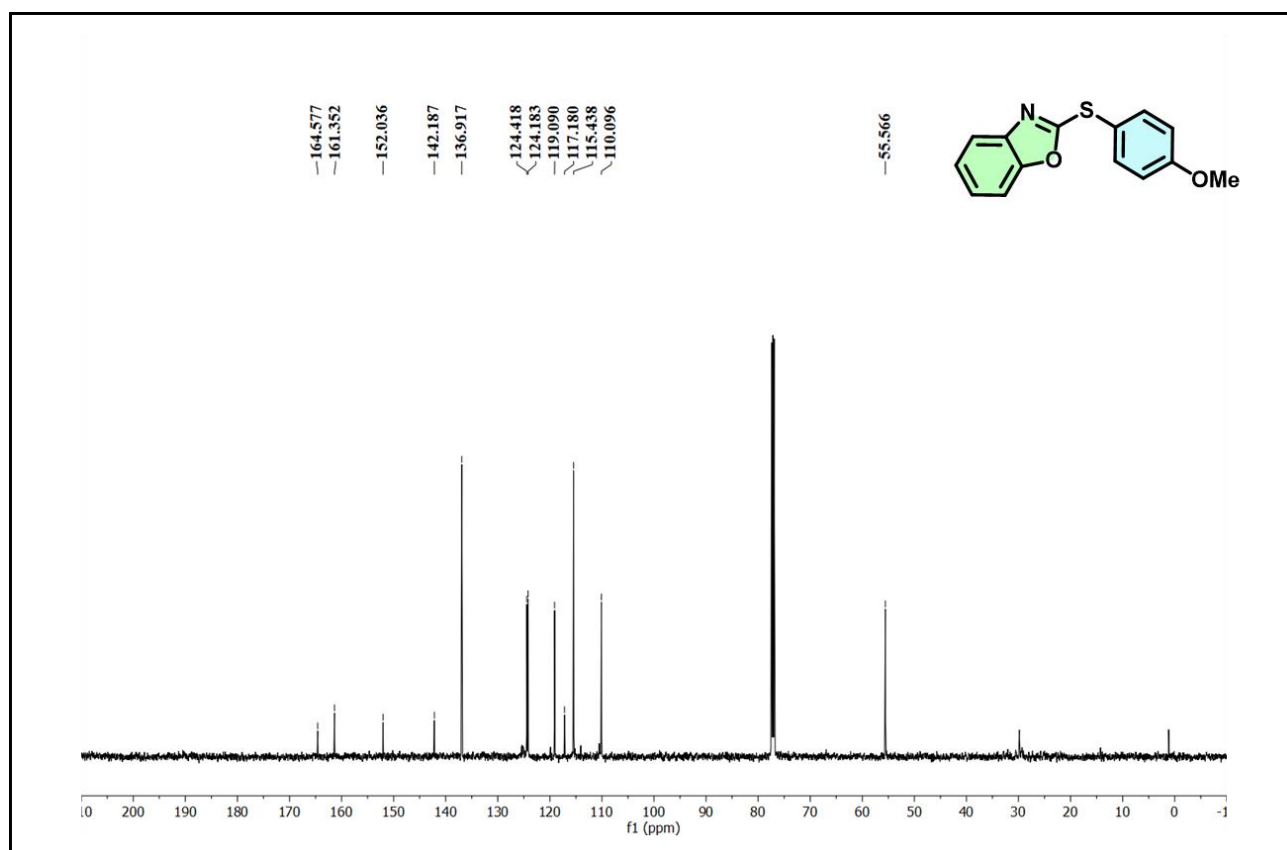


Fig. S53: ¹³C NMR spectra of **3t** (CDCl₃)

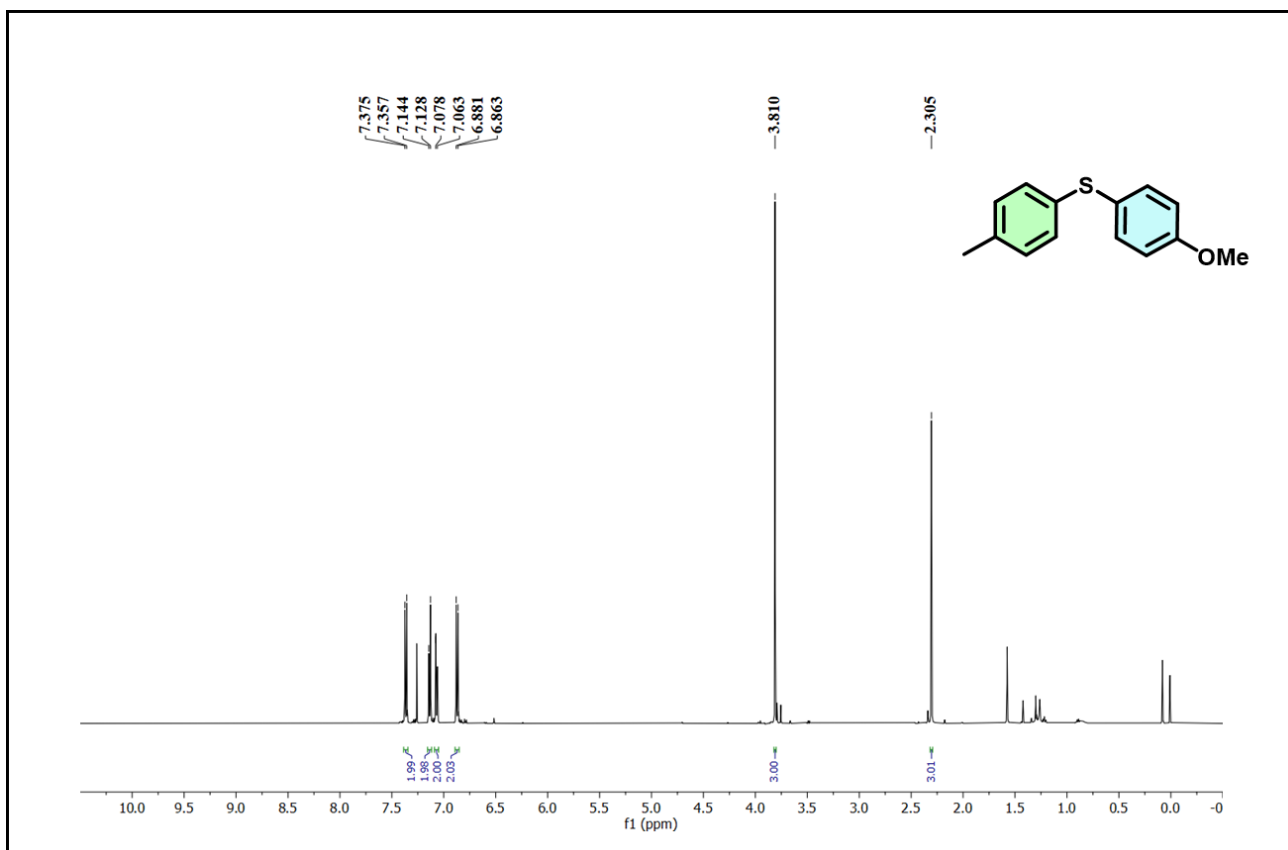


Fig. S54: ^1H NMR spectra of **3u** (CDCl_3)

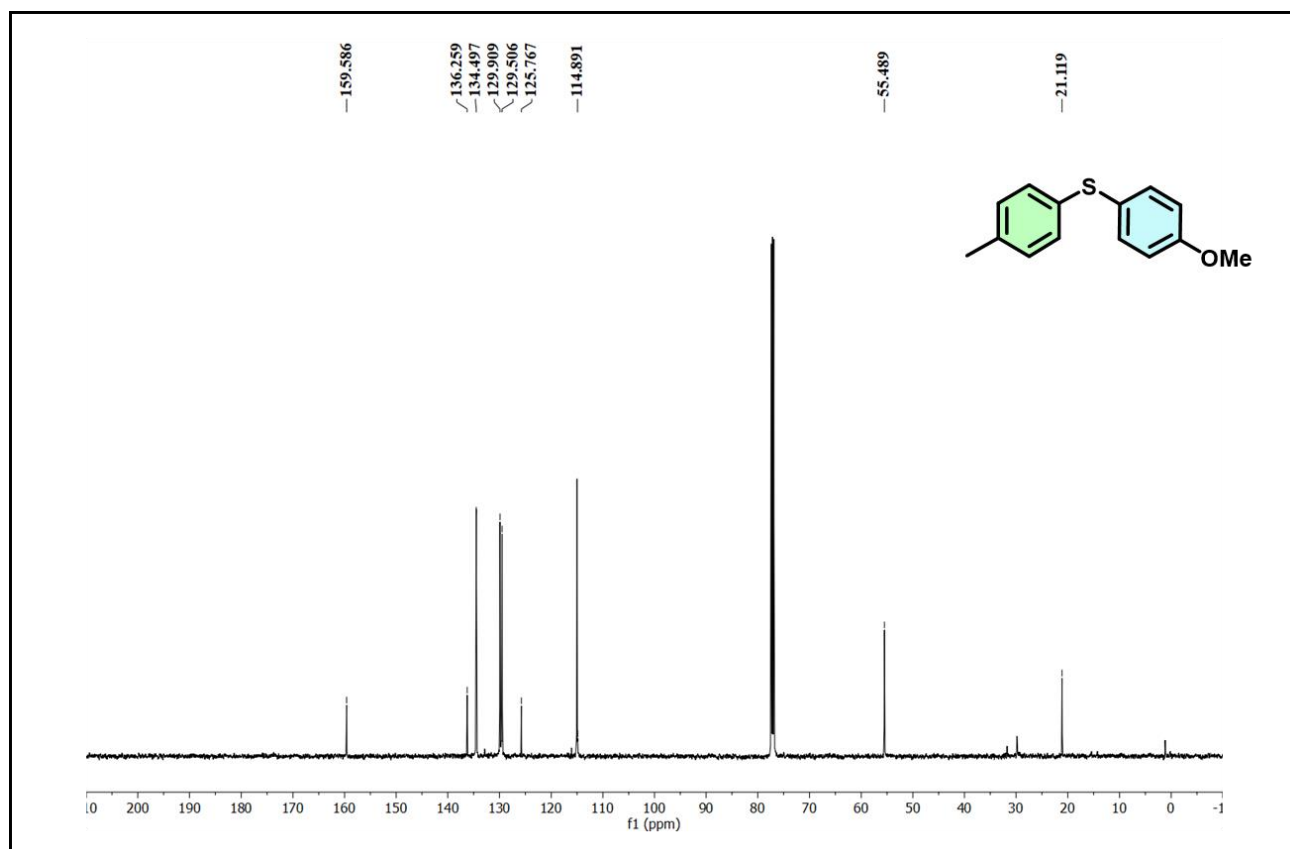


Fig. S55: ^{13}C NMR spectra of **3u** (CDCl_3)

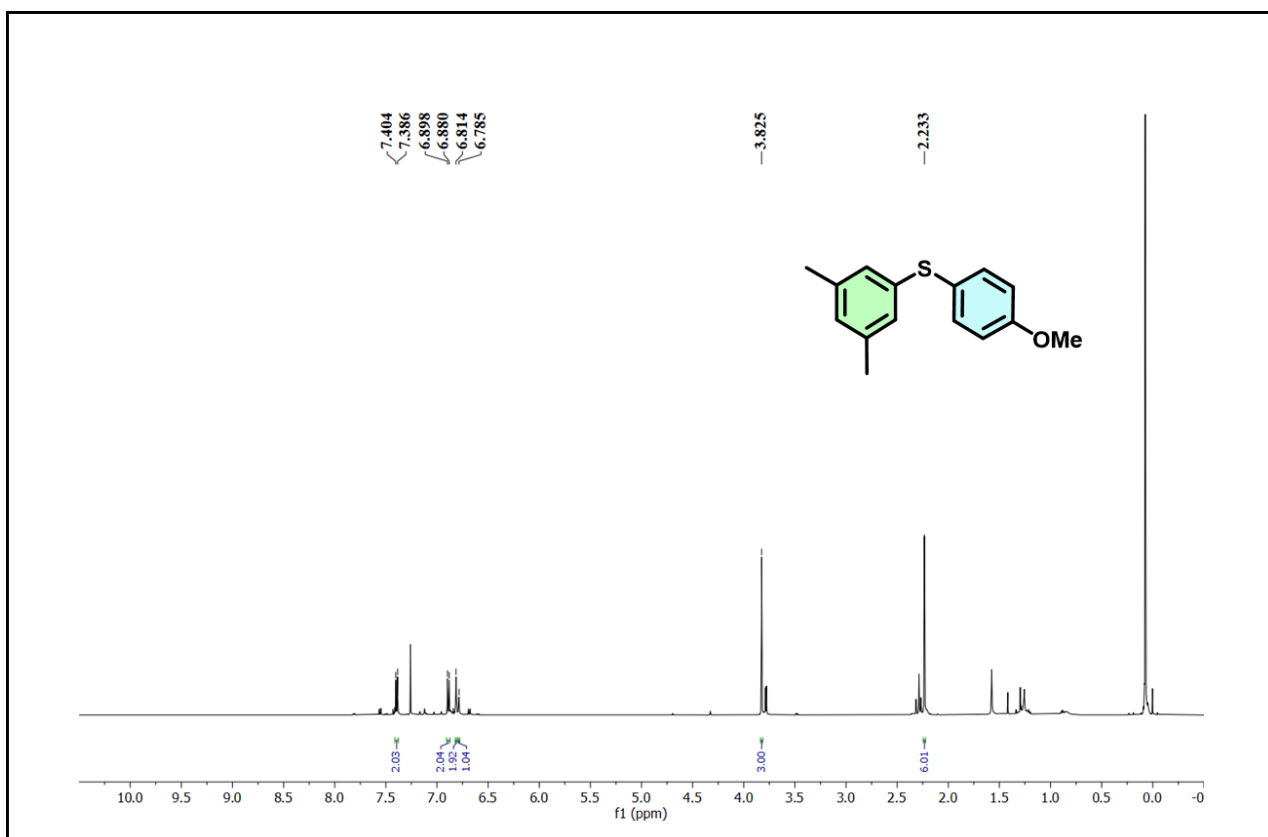


Fig. S56: ¹H NMR spectra of **3v** (CDCl₃)

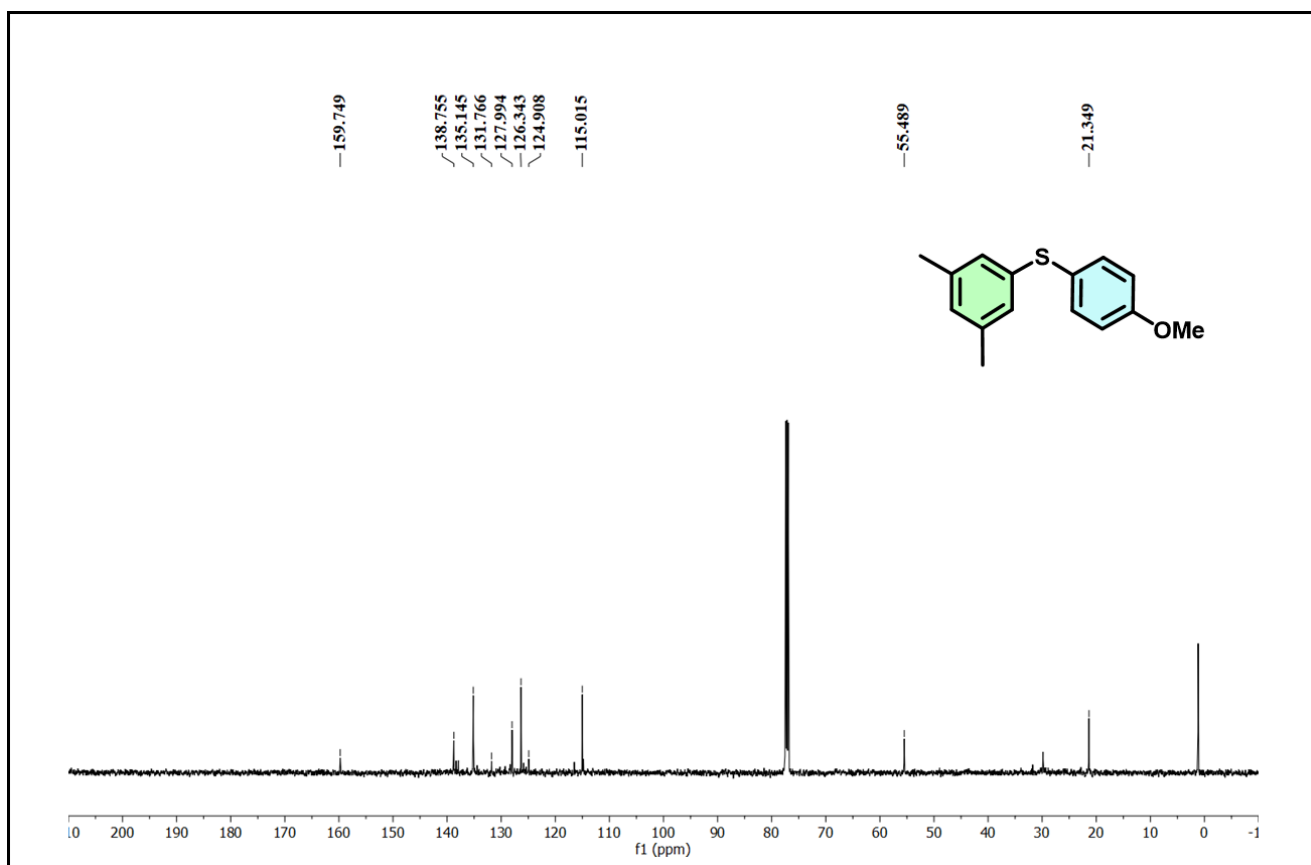


Fig. S57: ^{13}C NMR spectra of **3v** (CDCl_3)

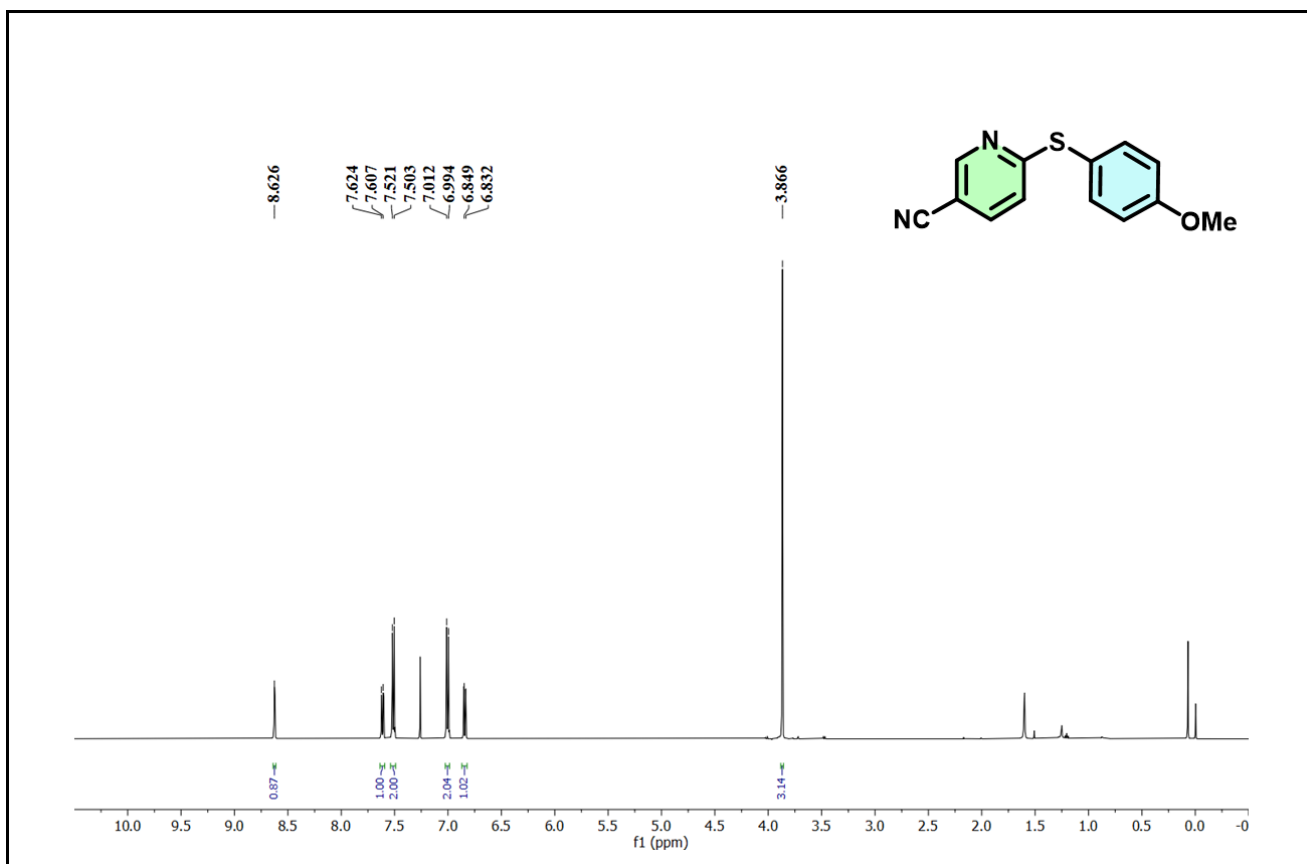


Fig. S58: ^1H NMR spectra of **3w** (CDCl_3)

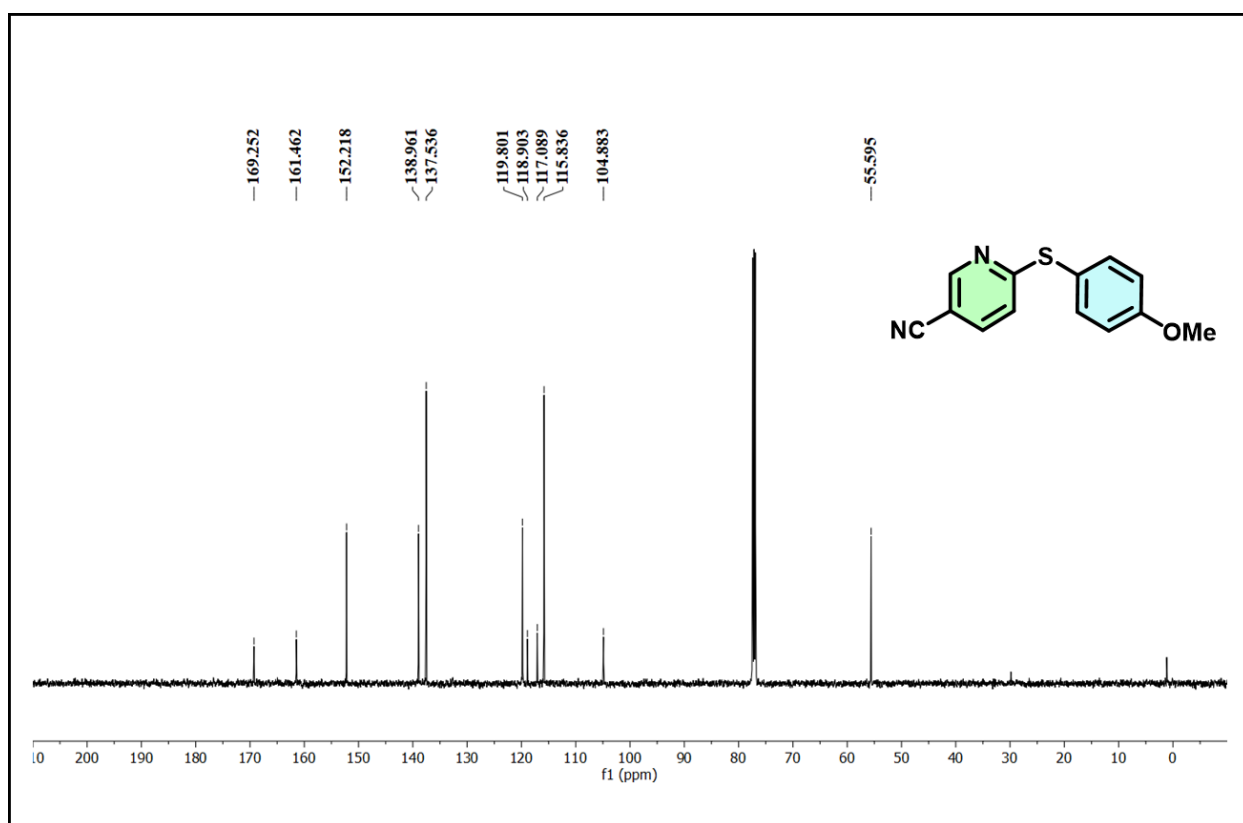


Fig. S59: ^{13}C NMR spectra of **3w** (CDCl_3)

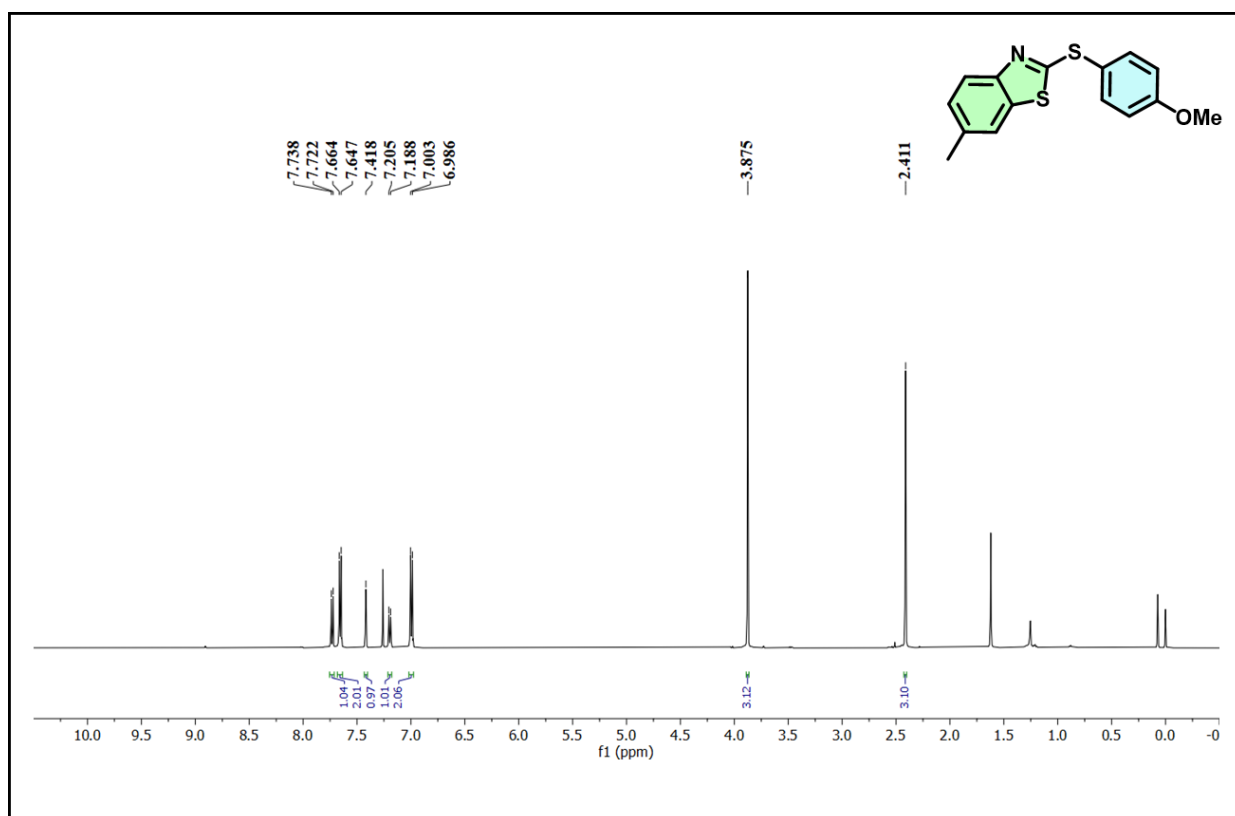


Fig. S60: ^1H NMR spectra of **3x** (CDCl_3)

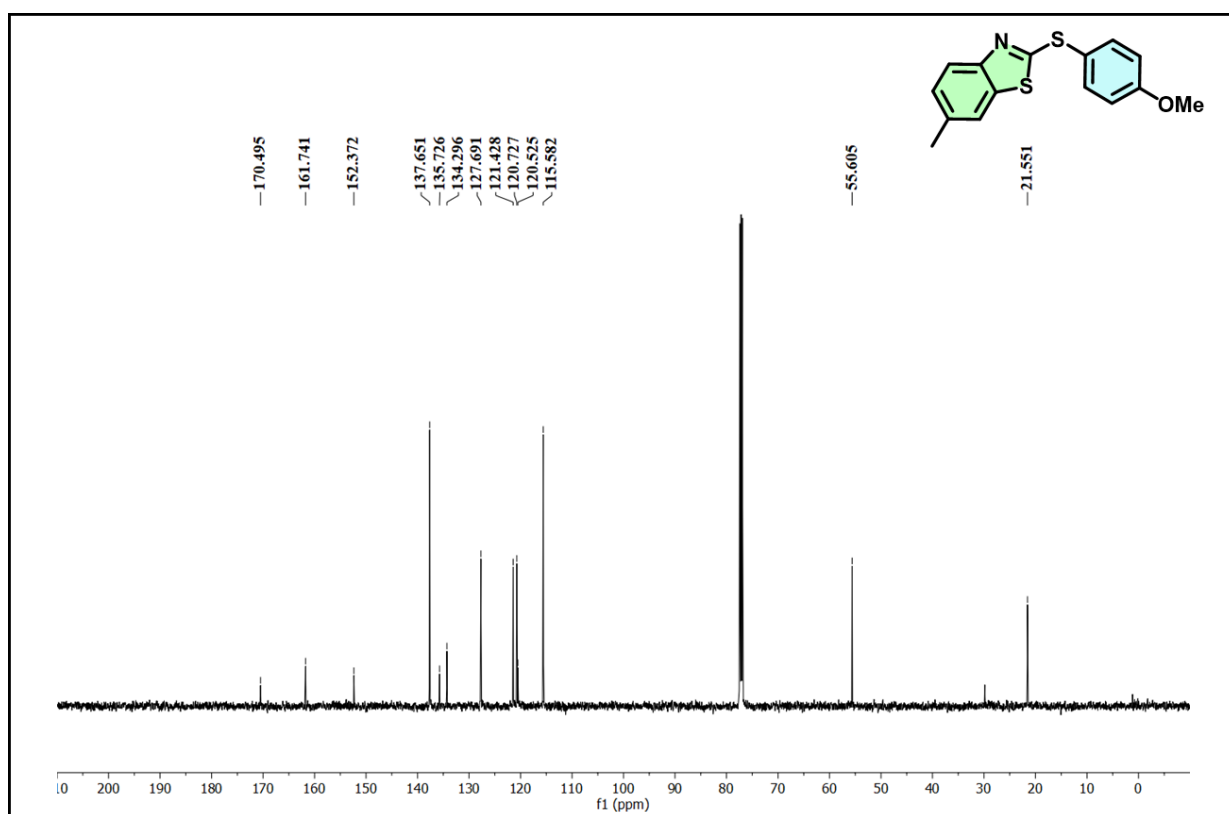


Fig. S61: ^{13}C NMR spectra of **3x** (CDCl_3)

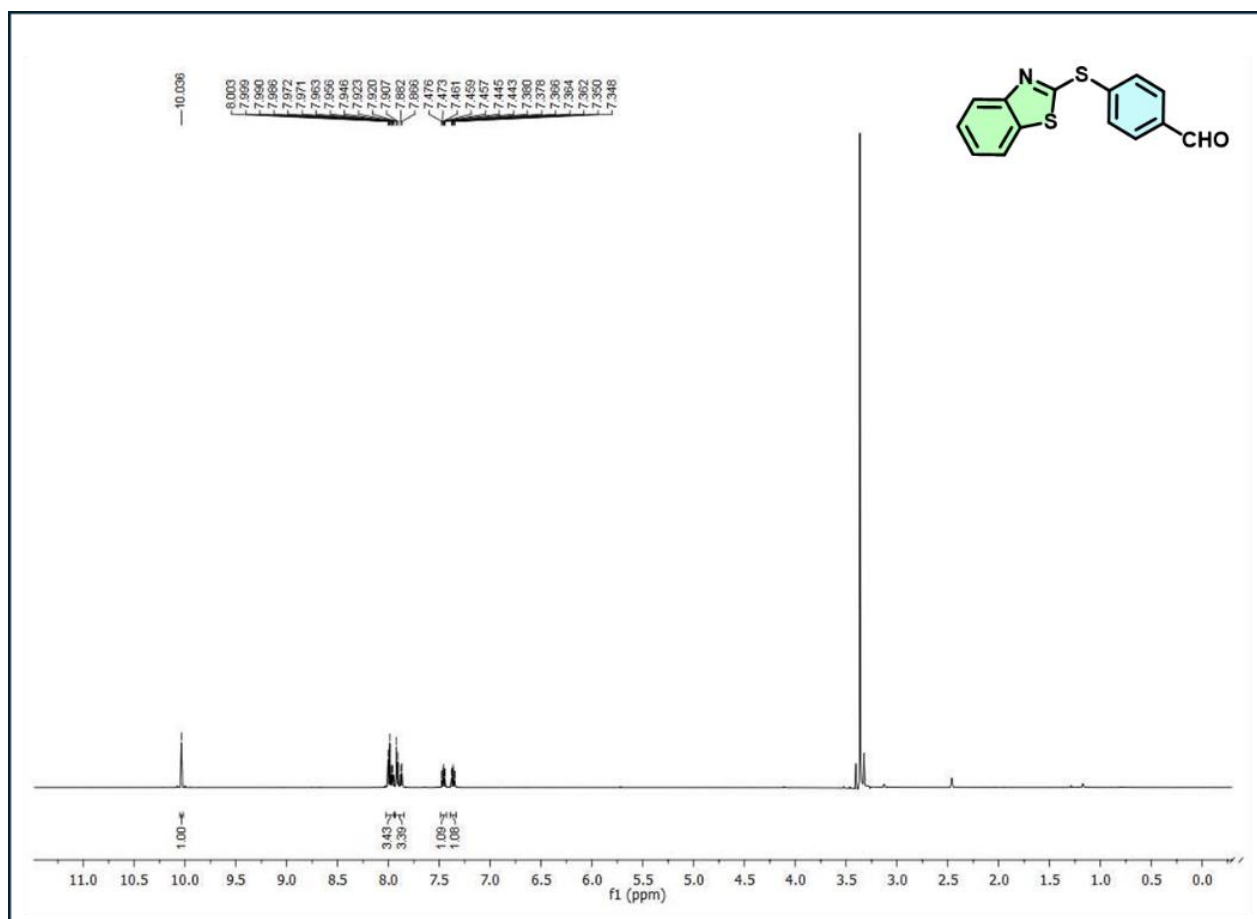


Fig. S62: ^1H NMR spectra of **3i** (DMSO- d_6)

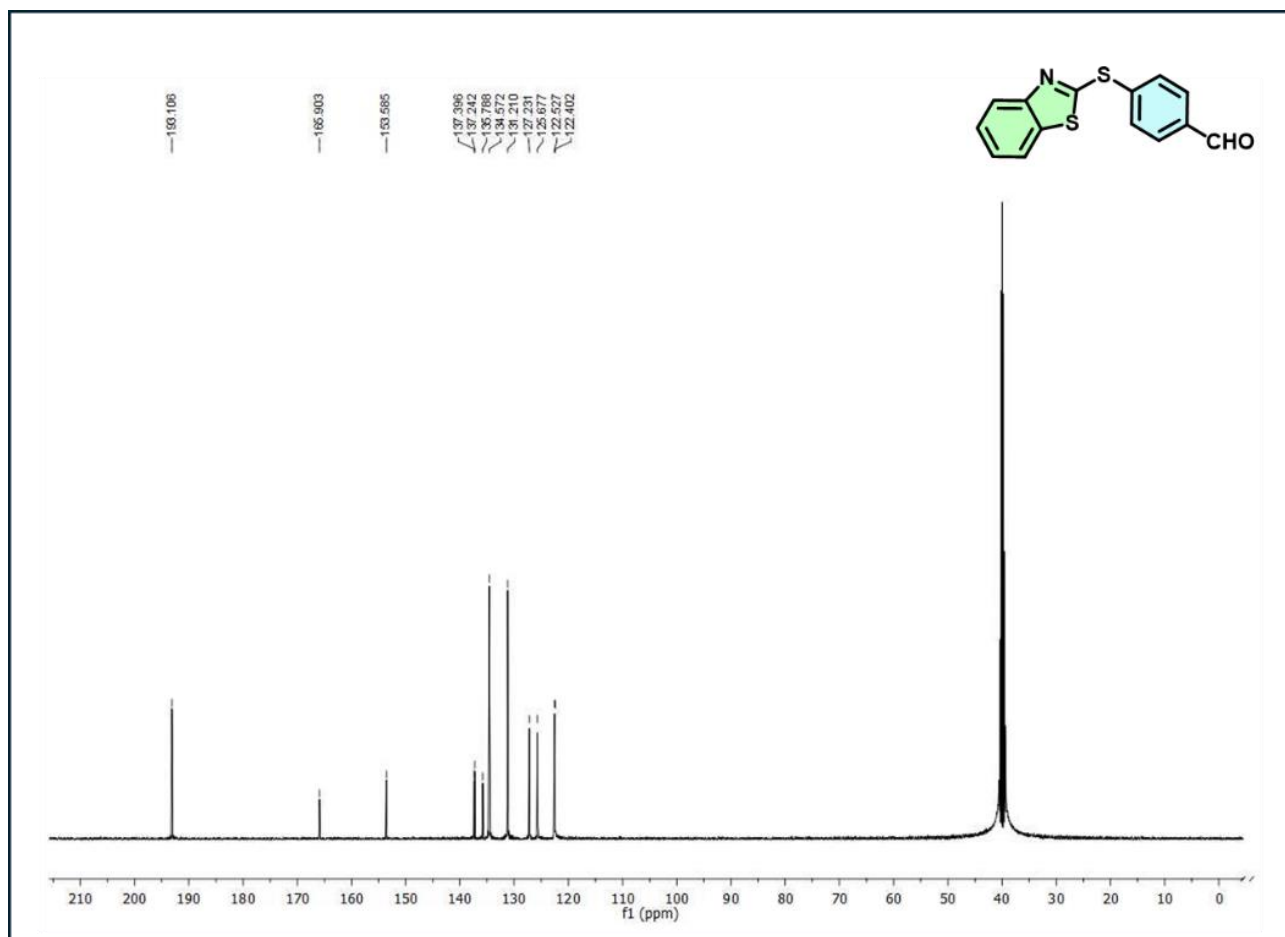


Fig. S63: ^{13}C NMR spectra of **3i** (DMSO-d_6)

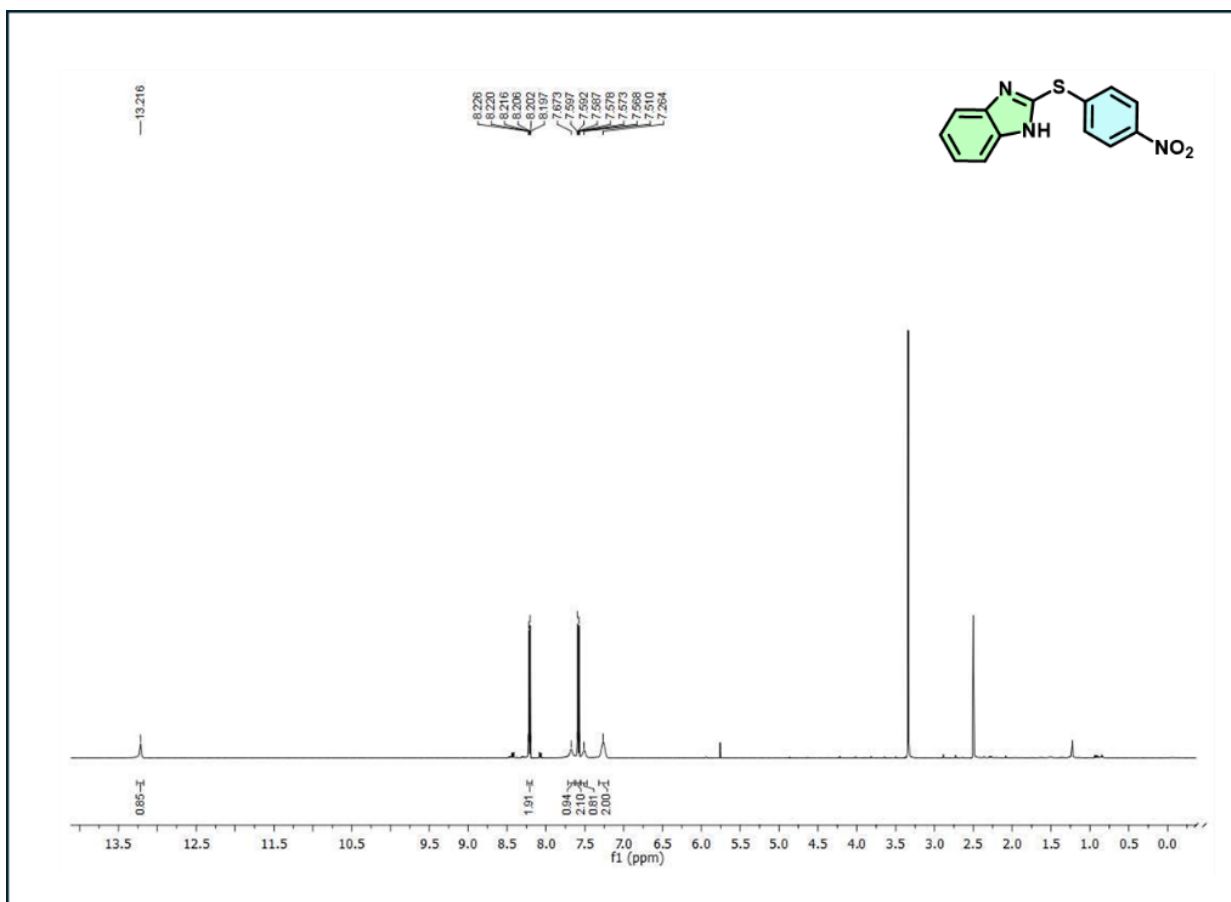


Fig. S64: ¹H NMR spectra of **3ii** (DMSO-d₆)

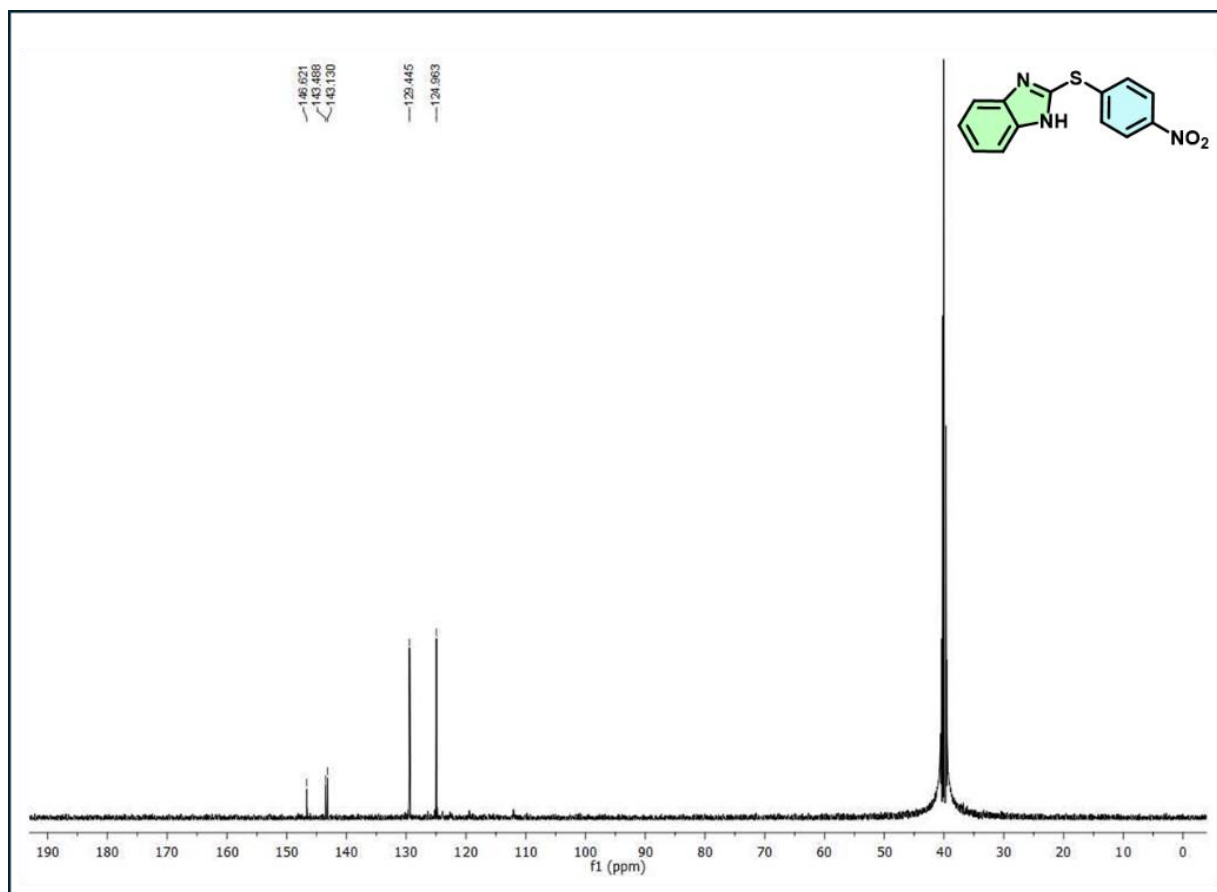


Fig. S65: ^{13}C NMR spectra of **3ii** (DMSO-d_6)

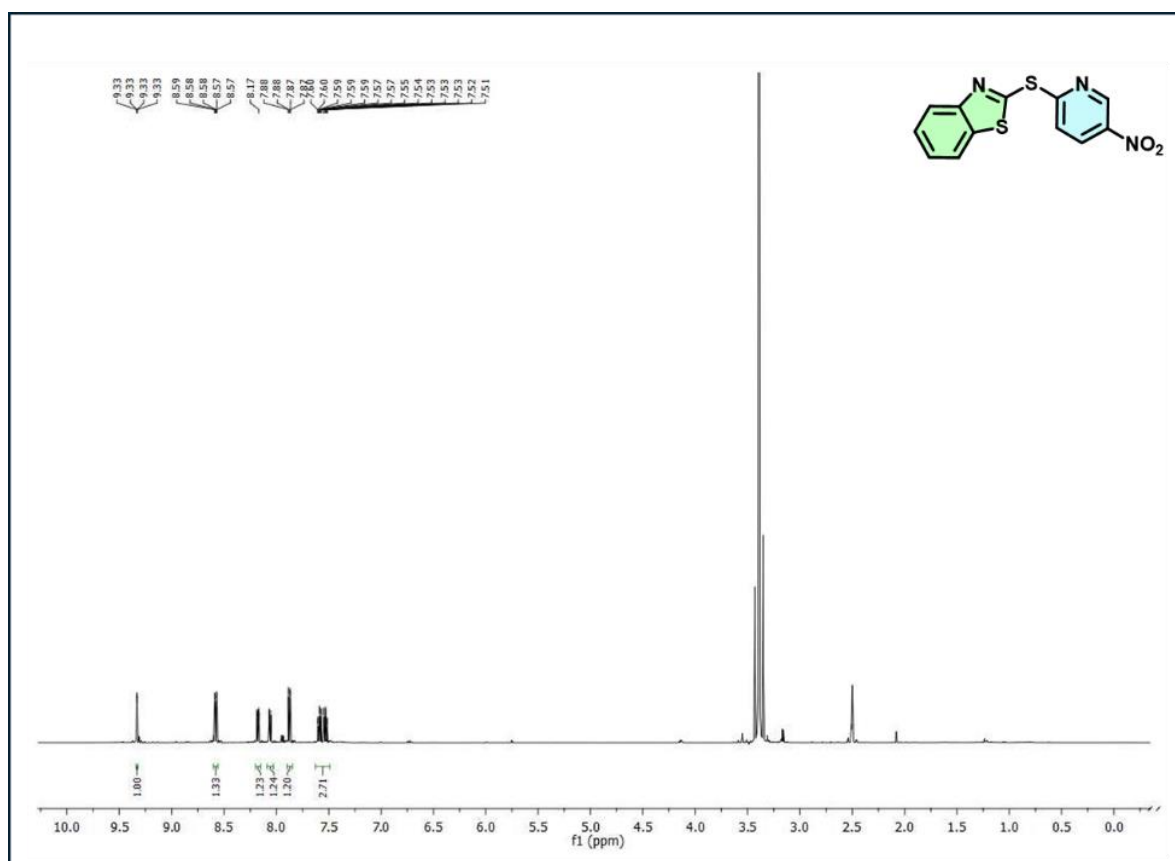


Fig. S66: ¹H NMR spectra of **3iii** (DMSO-d₆)

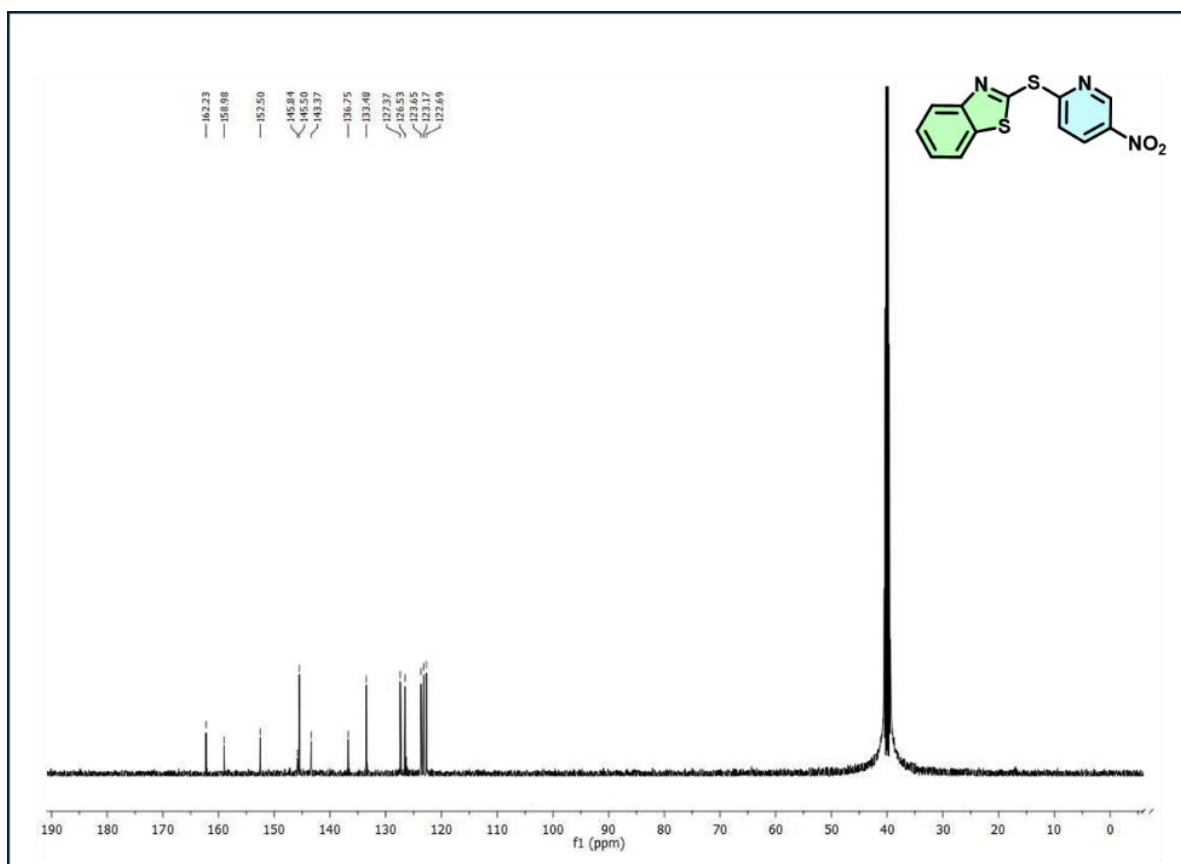


Fig. S67: ^{13}C NMR spectra of **3iii** (DMSO-d_6)

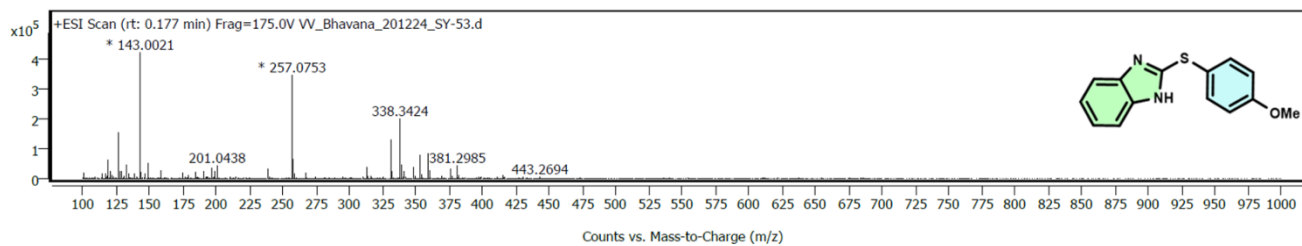


Fig.S68: HRMS spectra of **3a**

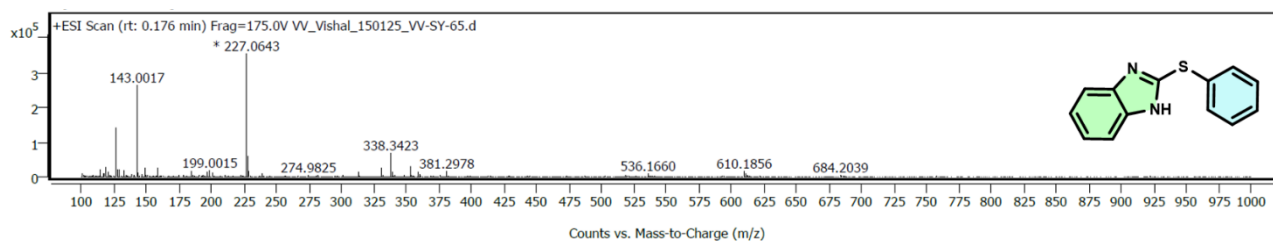


Fig.S69: HRMS spectra of **3b**

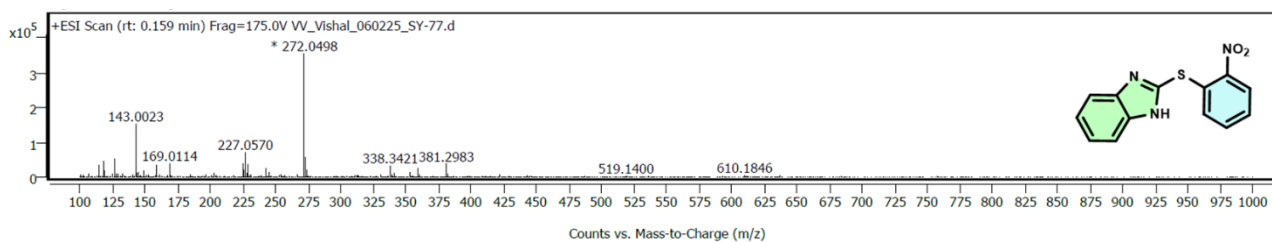


Fig.S70: HRMS spectra of **3c**

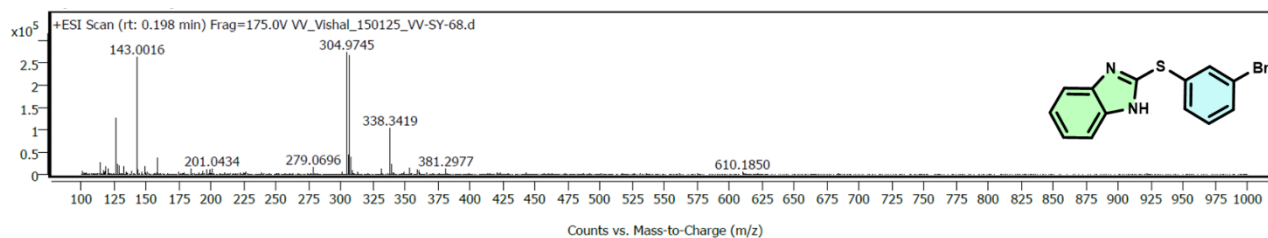


Fig.S71: HRMS spectra of **3d**

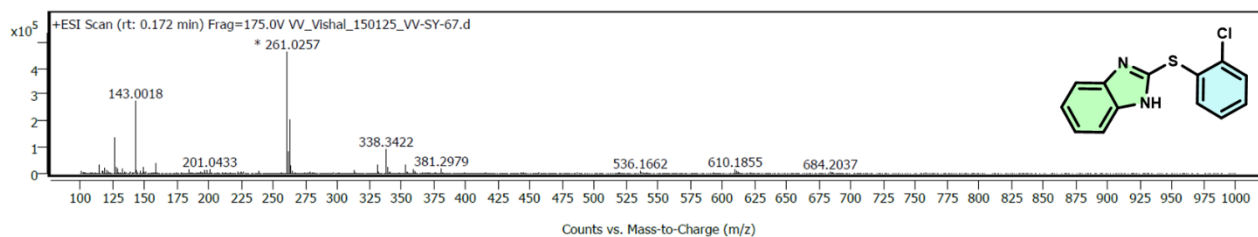


Fig.S72: HRMS spectra of **3e**

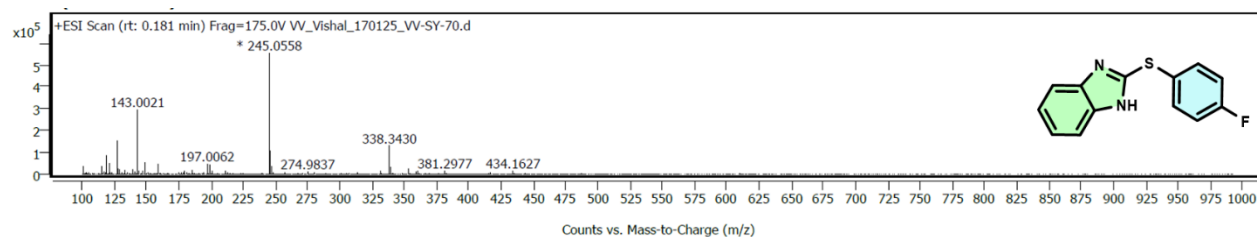


Fig.S73: HRMS spectra of **3f**

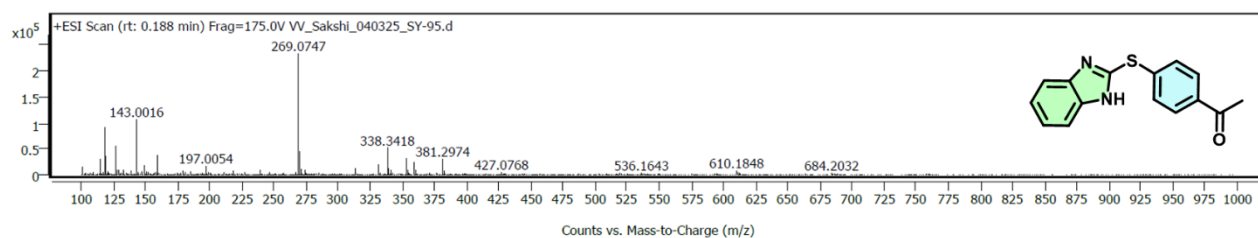


Fig.S74: HRMS spectra of **3g**

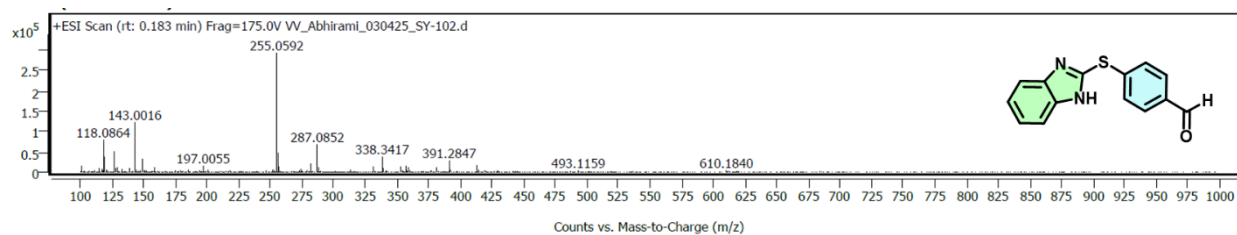


Fig.S75: HRMS spectra of **3h**

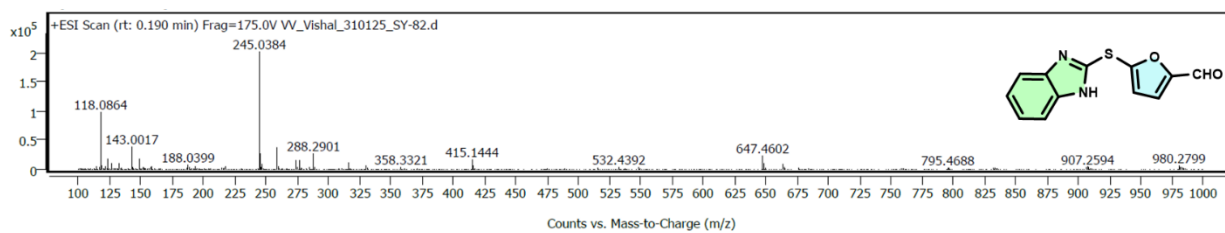


Fig.S76: HRMS spectra of **3i**

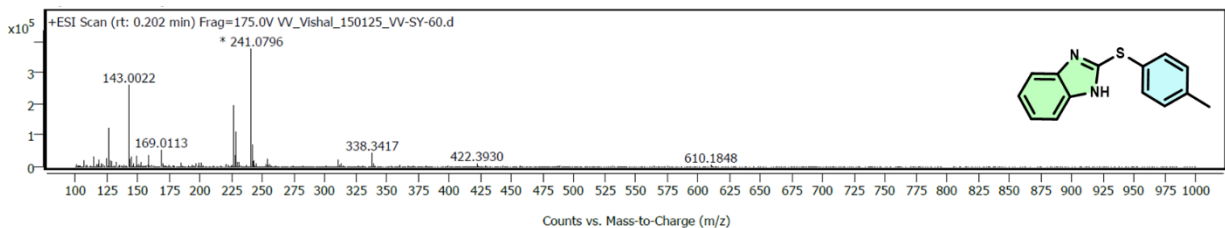


Fig.S77: HRMS spectra of **3j**

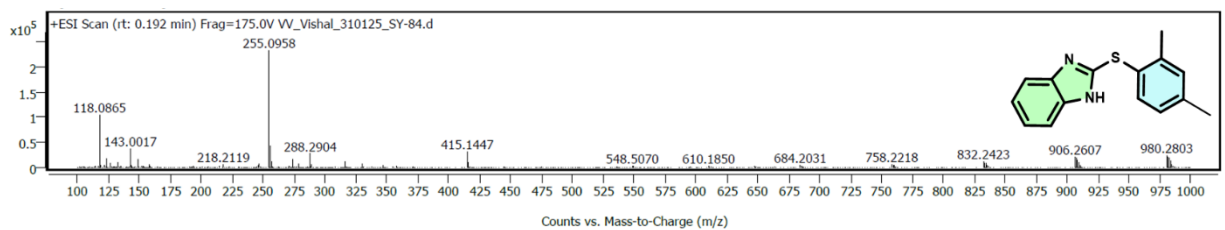


Fig.S78: HRMS spectra of **3k**

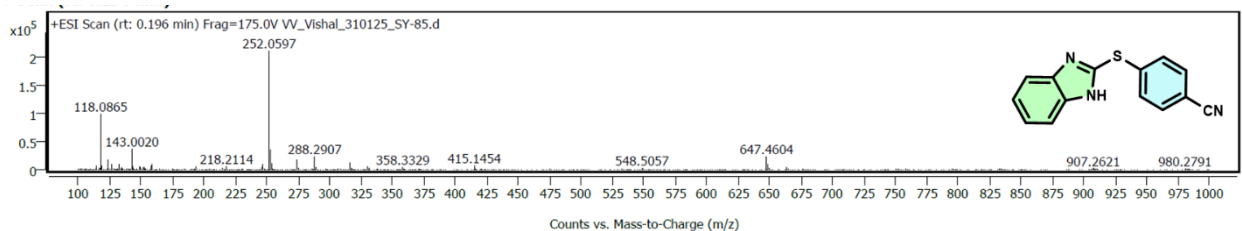


Fig.S79: HRMS spectra of **3l**

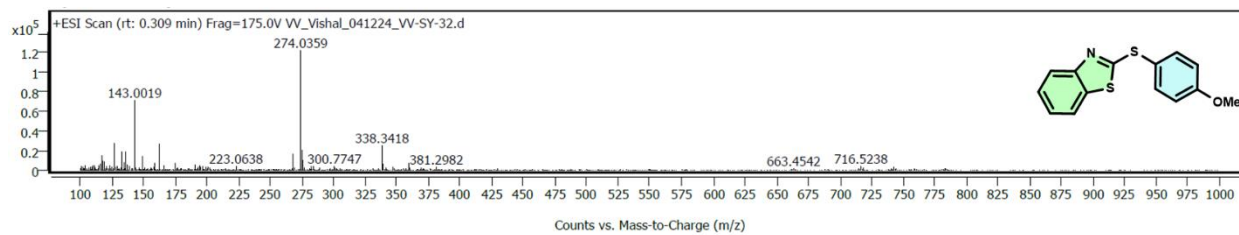


Fig.S80: HRMS spectra of **3m**

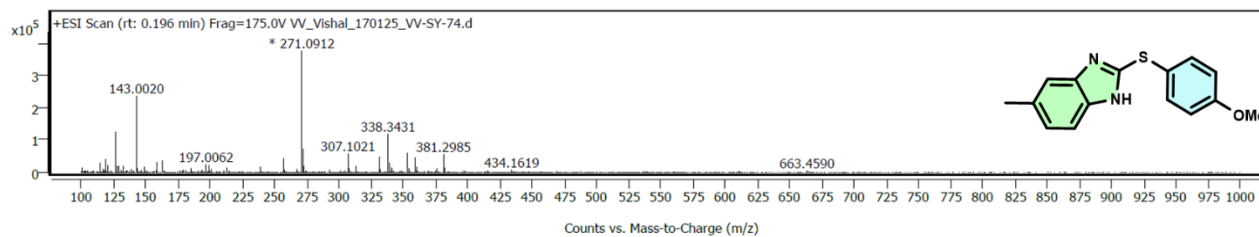


Fig.S81: HRMS spectra of **3n**

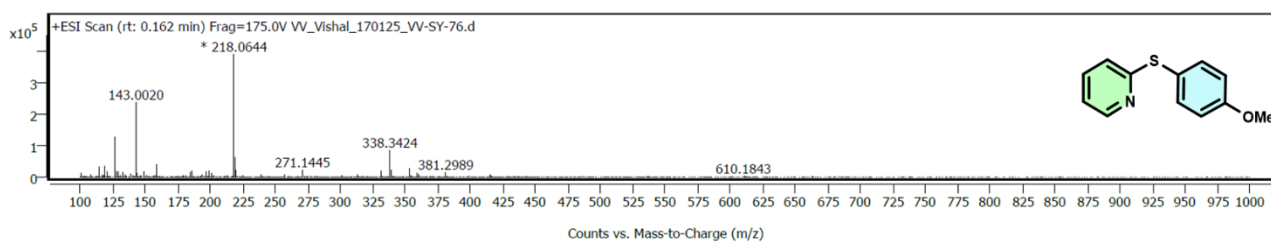


Fig.S82: HRMS spectra of **3o**

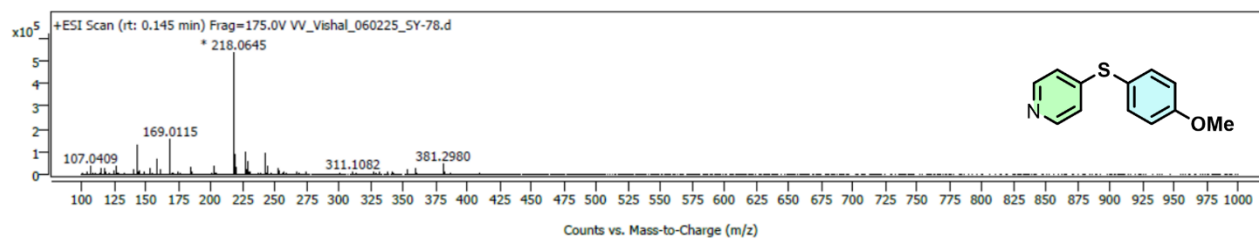


Fig.S83: HRMS spectra of **3p**

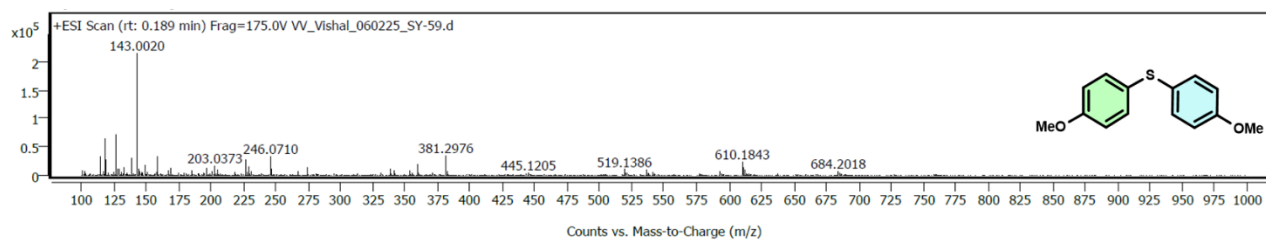


Fig.S84: HRMS spectra of **3q**

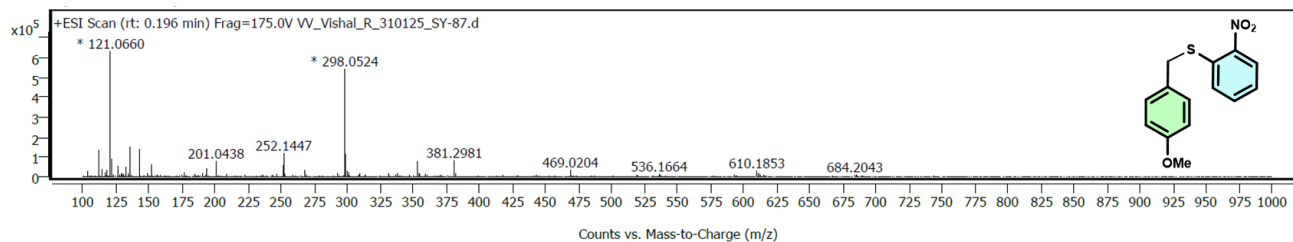


Fig.S85: HRMS spectra of **3r**

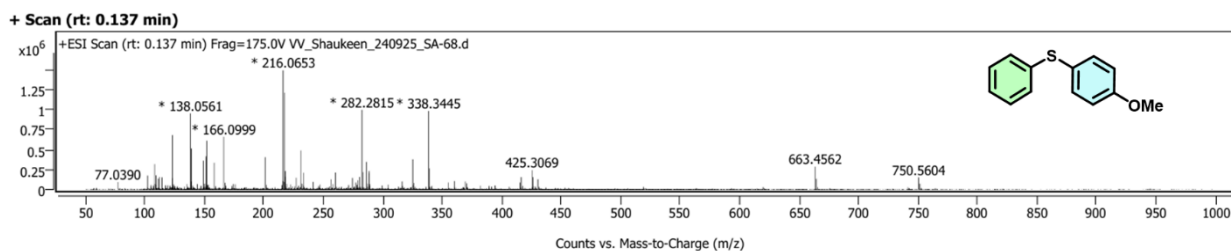


Fig.S86: HRMS spectra of **3s**

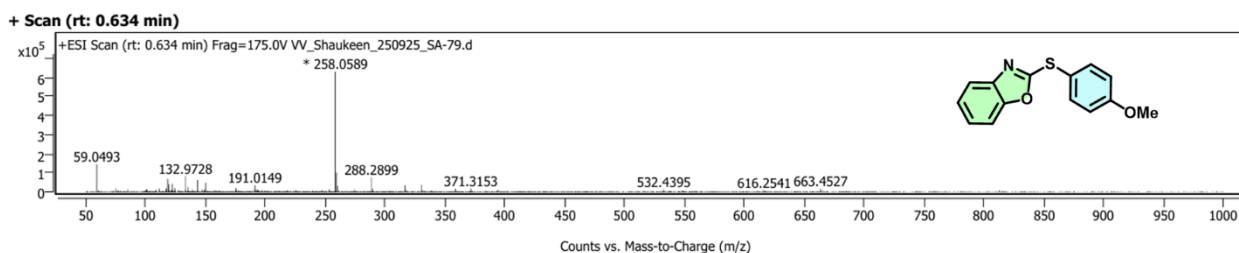


Fig.S87: HRMS spectra of **3t**

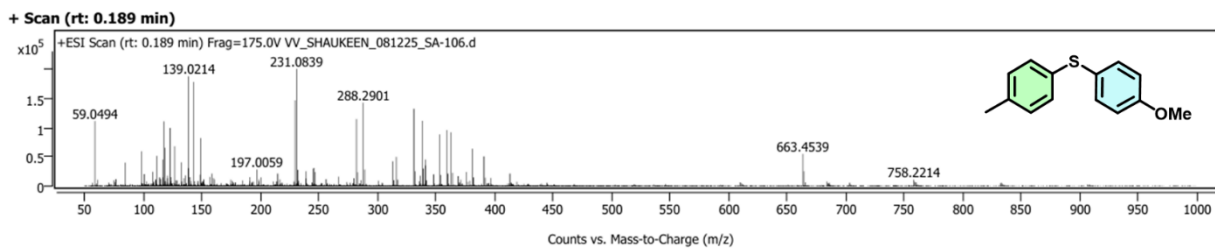


Fig.S88: HRMS spectra of **3u**

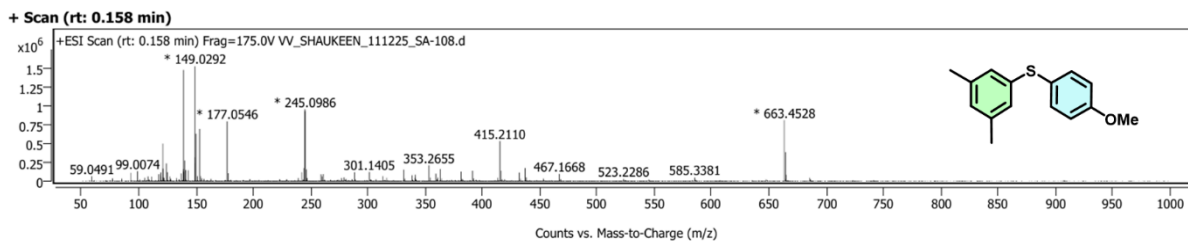


Fig. S89: HRMS spectra of **3v**

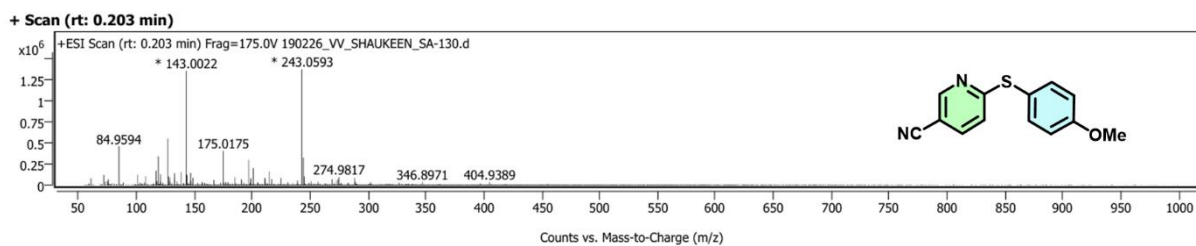


Fig. S90: HRMS spectra of **3w**

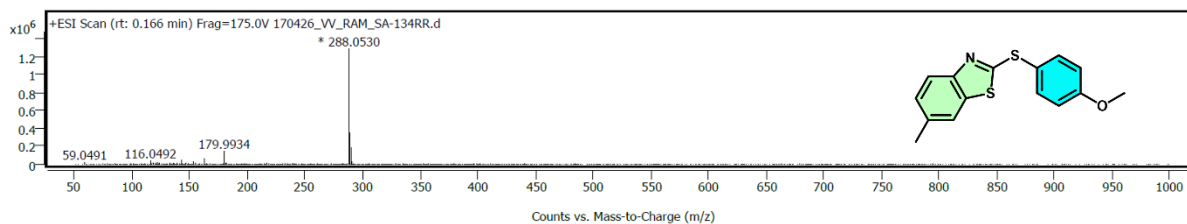


Fig. S91: HRMS spectra of **3x**

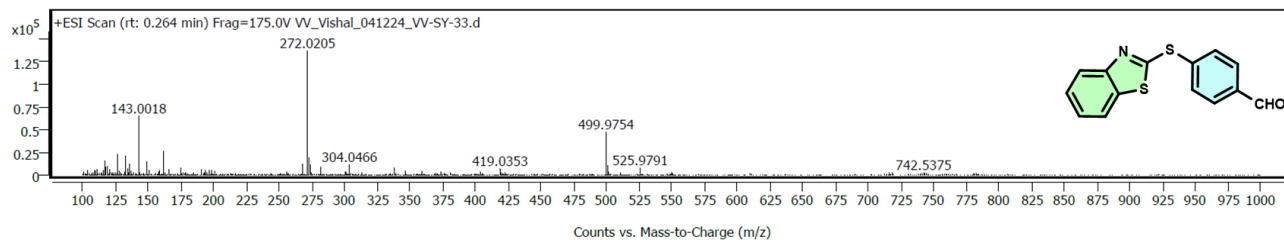


Fig.S92: HRMS spectra of **3i**

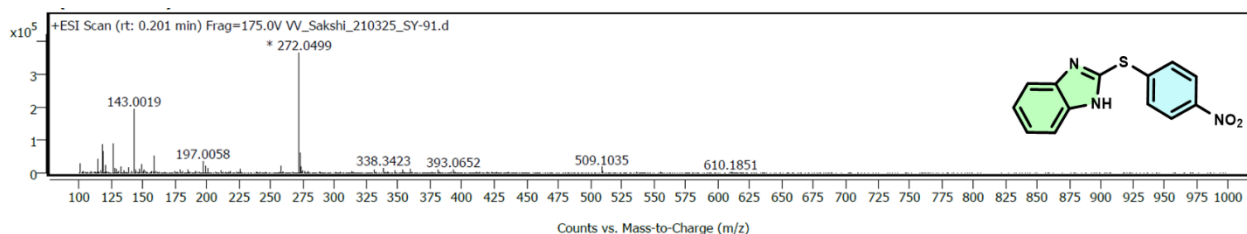


Fig.S93: HRMS spectra of **3ii**

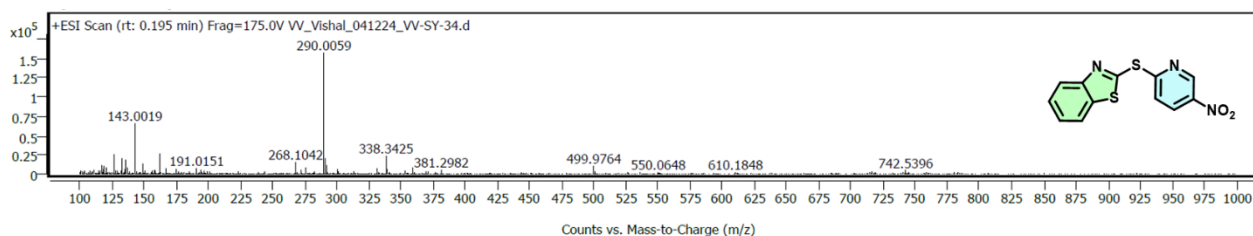


Fig.S94: HRMS spectra of **3iii**

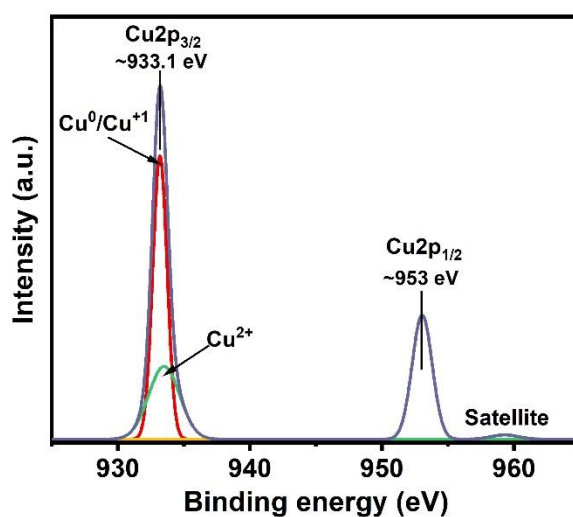


Fig. S95: XPS of CuNCs after completing the catalysis. The red-coloured peak corresponds to Cu⁰/Cu⁺ and the green-coloured peak corresponds to Cu²⁺ as indicated by the arrows.

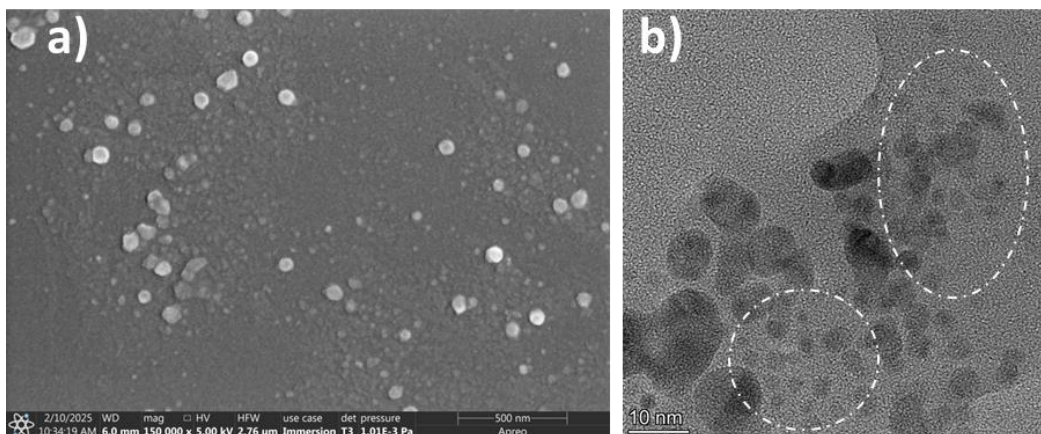


Fig. S96: a) FE-SEM and b) HR-TEM images of post-catalysis morphology of CuNCs@2MB.

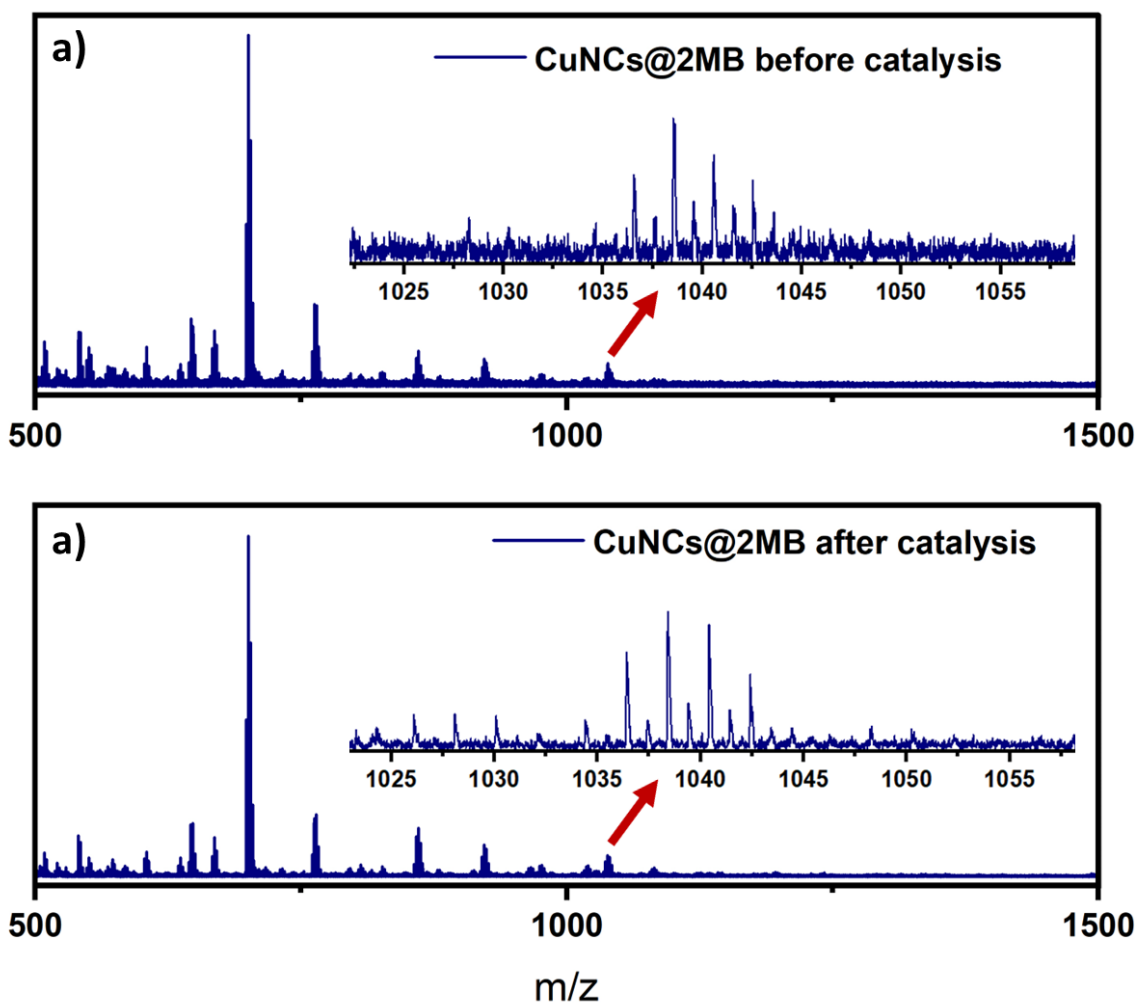


Fig. S97: a) & b) MALDI mass spectra of CuNCs@2MB before and after catalysis