

Supporting Information

For

Transition-metal-free radical tri-/difluoromethylation of *N,N*-dialkylhydrazones with sodium sulfinates

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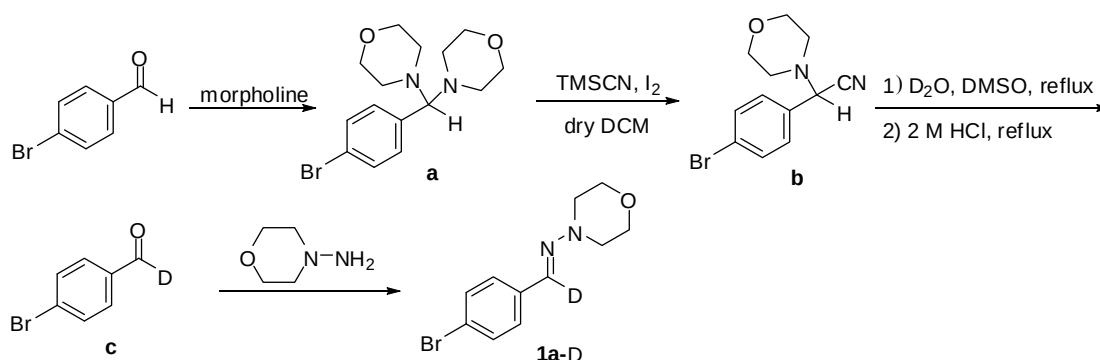
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1. General remarks

^1H NMR spectra were recorded on 400 or 600 MHz (100 or 150 MHz for ^{13}C NMR, 376 or 564 MHz for ^{19}F NMR) agilent NMR spectrometer with CDCl_3 as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to the CDCl_3 at 7.26 ppm (for ^1H NMR) or 77.16 ppm (for ^{13}C NMR). HRMS was recorded on a GCT PremierTM (CI) Mass Spectrometer. Infrared (FT-IR) spectra were recorded on a Varian 1000FT-IR, ν_{max} in cm^{-1} . Melting points were measured using SGW, X-4B and values are uncorrected. All commercially available reagents and solvents were used as received unless otherwise specified. The substrates we are readily prepared according to known methods (*Org. Lett.*, **2011**, 13, 15; *J. Am. Chem. Soc.* **2012**, 134, 4573; *J. Org. Chem.* **2012**, 77, 11232).

2. Procedure for preparation of 1a-D



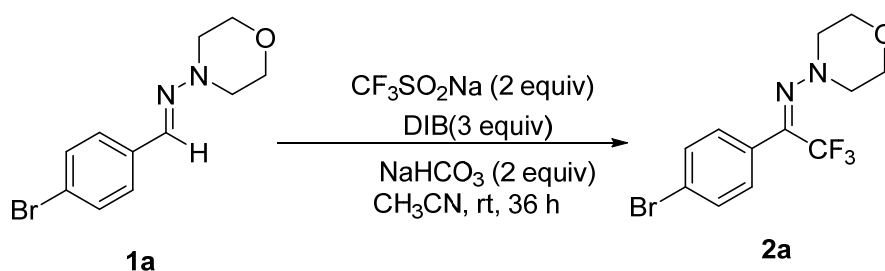
To a solution of 4-bromobenzaldehyde (1.85 g, 10 mmol) in benzene (15 mL) was added morpholine (1.74 g, 2.0 eq). The reaction mixture was heated at reflux for 24 h. The resulting mixture was cooled down to room temperature, concentrated *in vacuo*, washed with cold diethyl ether to remove trace of remaining aldehyde starting material, and dried under vacuum at 40 °C for 12 h to give 2.72 g (80% yield) of 4,4'-((4-bromophenyl)methylene)dimorpholine (**a**). (*Tetrahedron Lett.* **2010**, 51, 6031) Iodine (0.13 g, 1 mmol) was added to a mixture of aminor **a** (1.7 g, 5 mmol) and trimethylsilyl cyanide (0.8 mL, 1.2 mmol) in dry CH_2Cl_2 (5 mL) at room temperature. After TLC analysis showed the reaction was complete, the resulting mixture was quenched with aqueous sodium thiosulphate and extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were washed with a solution of sodium hydroxide (2 M), brined, dried over anhydrous sodium sulfate, and concentrated *in vacuo*, giving 1.33 g (95% yield) of 2-(4-bromophenyl)-2-morpholinoacetonitrile (**b**). The crude product was used directly without further purification. (*J. Iran. Chem. Soc.* **2004**, 1, 136)

A solution of **b** (1 g, 3.5 mmol) in DMSO (2 mL) and D_2O (2 mL) was heated at 100 °C for 5 h. The reaction mixture was poured into cold water and the crystals were collected and dried. The deuterated morpholino-nitrile was hydrolyzed with a solution

of 2M HCl at reflux for 5 h, yielding 4-bromobenzaldehyde- α -D (0.62 g, 98% yield). (*J. Org. Chem.* **2005**, 70, 179)

N-Aminomorpholine (0.33g, 3.2 mmol) was added to a solution of **c** (0.50 g, 2.7mmol) in DCM (5 mL). Anhydrous MgSO₄ (2.0 g) was added to the mixture and the resulting suspension was stirred overnight at room temperature. After filtration, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to give **1a**-D (ca. 90% deuterium).

3. Typical experimental procedure

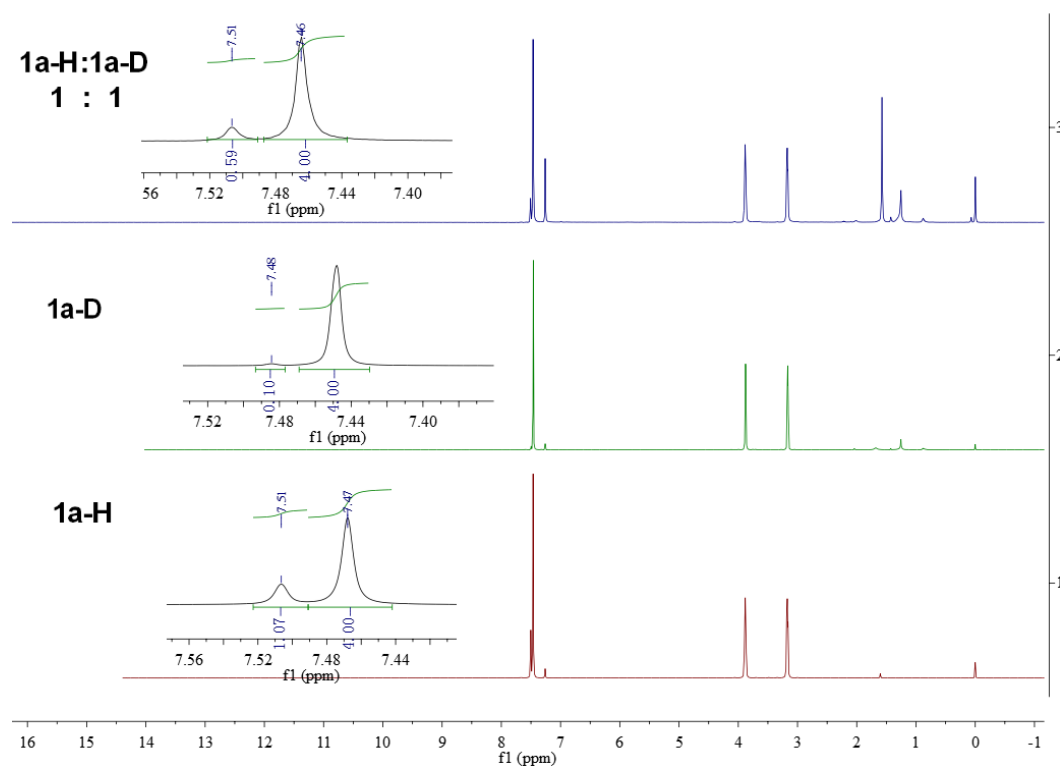
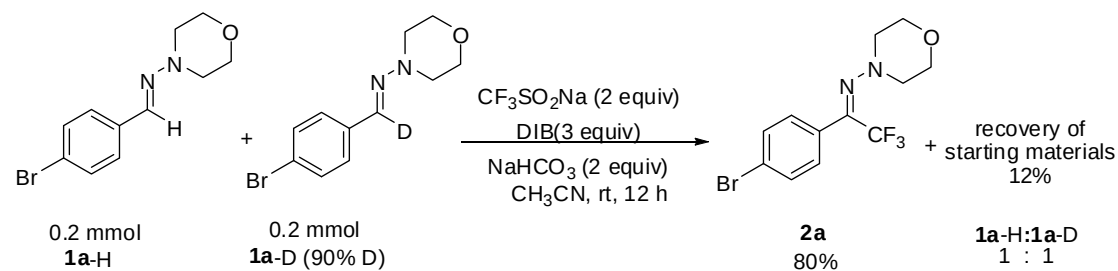


To a suspension of aldehyde hydrazone **1a** (53.6 mg, 0.2 mmol), CF₃SO₂Na (62.4 mg, 0.4 mmol) and NaHCO₃ (33.6 mg, 0.4 mmol) in CH₃CN (2 mL) was added DIB (193.2 mg, 0.6 mmol) at rt under argon atmosphere. The resulting mixture was stirred for 36 h. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to give **2a** as a yellow oil (85% yield, 57 mg).

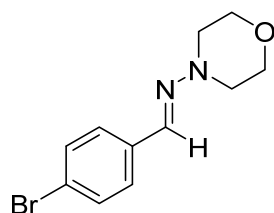
4. References for known products

Entry	Reference	Compounds
1	<i>Angew. Chem. Int. Ed.</i> 2013 , 52, 5346 –5349.	2g, 2x, 2y

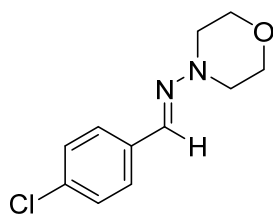
5. Isotope effect experiment



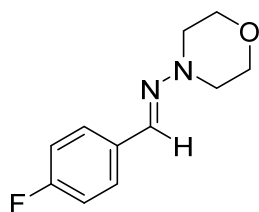
6. Characterization of the substrates and products



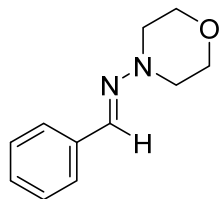
(E)-1-(4-bromophenyl)-N-morpholinomethanimine (1a): ^1H NMR (400 MHz, CDCl_3) δ 7.50 (s, 1H), 7.46 (s, 4H), 4.26 – 3.67 (m, 4H), 3.51 – 2.83 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 135.1, 134.6, 131.8, 127.7, 122.2, 66.5, 51.8.



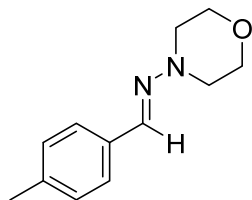
(E)-1-(4-chlorophenyl)-N-morpholinomethanimine (1b): ^1H NMR (400 MHz, CDCl_3) δ 7.59 – 7.47 (m, 3H), 7.31 (d, J = 8.3 Hz, 2H), 3.95 – 3.80 (m, 4H), 3.24 – 3.06 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 134.7, 134.6, 134.0, 128.9, 127.4, 66.5, 51.9.



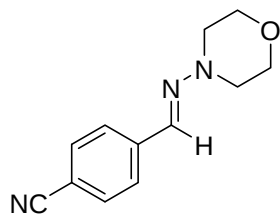
(E)-1-(4-fluorophenyl)-N-morpholinomethanimine (1c): ^1H NMR (400 MHz, CDCl_3) δ 7.66 – 7.49 (m, 3H), 7.04 (t, J = 8.5 Hz, 2H), 4.04 – 3.78 (m, 4H), 3.30 – 3.02 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.0 (d, $J_{\text{C-F}}$ = 247.8 Hz), 135.2, 132.3 (d, $J_{\text{C-F}}$ = 3.2 Hz), 127.9 (d, $J_{\text{C-F}}$ = 8.1 Hz), 115.7 (d, $J_{\text{C-F}}$ = 21.8 Hz), 66.6, 52.0.



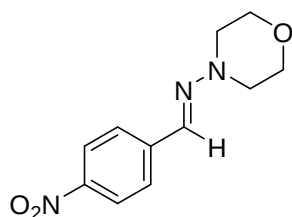
(E)-N-morpholino-1-phenylmethanimine (1d): ^1H NMR (400 MHz, CDCl_3) δ 7.65 – 7.53 (m, 3H), 7.35 (t, J = 7.4 Hz, 2H), 7.31 – 7.24 (m, 1H), 3.95 – 3.79 (m, 4H), 3.27 – 3.08 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.4, 136.1, 128.7, 128.5, 126.3, 66.6, 52.0.



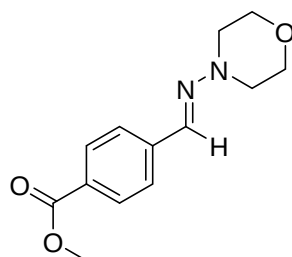
(E)-N-morpholino-1-(p-tolyl)methanimine (1e): ^1H NMR (400 MHz, CDCl_3) δ 7.59 (s, 1H), 7.50 (d, J = 7.8 Hz, 1H), 7.16 (d, J = 7.7 Hz, 1H), 4.08 – 3.74 (m, 4H), 3.35 – 3.02 (m, 4H), 2.35 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 138.5, 136.9, 133.3, 129.4, 126.3, 66.6, 52.1, 21.5.



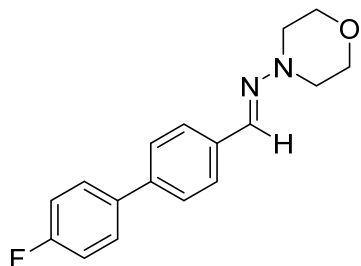
(E)-4-((morpholinoimino)methyl)benzonitrile (1f): ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, $J = 8.2$ Hz, 2H), 7.60 (d, $J = 8.2$ Hz, 2H), 7.49 (s, 1H), 4.01 – 3.73 (m, 4H), 3.33 – 3.09 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 140.6, 132.5, 132.4, 126.4, 119.2, 111.0, 66.4, 51.5.



(E)-N-morpholino-1-(4-nitrophenyl)methanimine (1g): ^1H NMR (400 MHz, CDCl_3) δ 8.19 (d, $J = 8.5$ Hz, 2H), 7.70 (d, $J = 8.5$ Hz, 2H), 7.53 (s, 1H), 4.06 – 3.68 (m, 4H), 3.48 – 3.07 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 147.1, 142.5, 131.8, 126.3, 124.1, 66.4, 51.4.

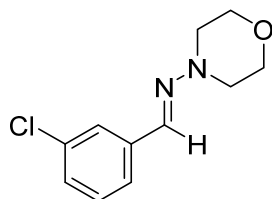


Methyl (E)-4-((morpholinoimino)methyl)benzoate (1h): ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 8.1$ Hz, 2H), 7.64 (d, $J = 8.1$ Hz, 2H), 7.55 (s, 1H), 3.94 – 3.84 (m, 7H), 3.35 – 3.07 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 167.0, 140.5, 134.1, 130.0, 129.5, 125.9, 66.5, 52.2, 51.6.

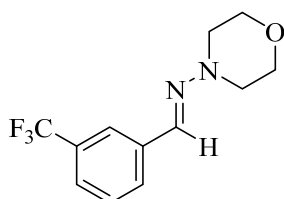


(E)-1-(4'-fluoro-[1,1'-biphenyl]-4-yl)-N-morpholinomethanimine (1i): ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, $J = 7.2$ Hz, 2H), 7.62 (s, 1H), 7.60 – 7.50 (m, 4H), 7.22 – 7.02 (m, 2H), 4.01 – 3.76 (m, 4H), 3.30 – 3.07 (m, 4H); ^{13}C NMR (150 MHz,

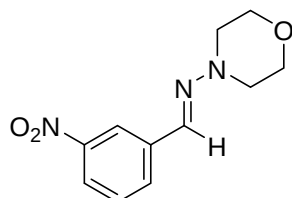
CDCl₃) δ 162.6 (d, J_{C-F} = 246.6 Hz), 140.0, 136.9 (d, J_{C-F} = 3.0 Hz), 135.6, 135.1, 128.6 (d, J_{C-F} = 8.0 Hz), 127.2, 126.7, 115.7 (d, J_{C-F} = 21.4 Hz), 66.5, 51.9.



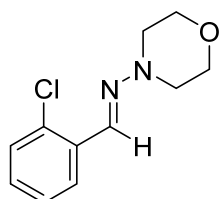
(E)-1-(3-chlorophenyl)-N-morpholinomethanimine (1j): ¹H NMR (400 MHz, CDCl₃) δ 7.62 (s, 1H), 7.49 (s, 1H), 7.43 (d, J = 7.1 Hz, 1H), 7.32 – 7.18 (m, 2H), 3.99 – 3.79 (m, 4H), 3.34 – 2.99 (m, 4H); ¹³C NMR (150 MHz, CDCl₃) δ 138.0, 134.7, 134.1, 129.9, 128.2, 125.9, 124.5, 66.5, 51.8.



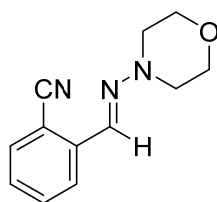
(E)-N-morpholino-1-(3-(trifluoromethyl)phenyl)methanimine (1k): ¹H NMR (400 MHz, CDCl₃) δ 7.87 (s, 1H), 7.75 (d, J = 7.5 Hz, 1H), 7.56 (s, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.44 (t, J = 7.7 Hz, 1H), 4.01 – 3.76 (m, 4 H), 3.28 – 3.11 (m, 4 H); ¹³C NMR (150 MHz, CDCl₃) δ 137.0, 133.7, 131.1 (q, J_{C-F} = 32.2 Hz), 129.3, 129.1, 124.6 (q, J_{C-F} = 3.6 Hz), 124.2 (q, J_{C-F} = 272.4 Hz), 122.8 (q, J_{C-F} = 3.8 Hz), 66.5, 51.7.



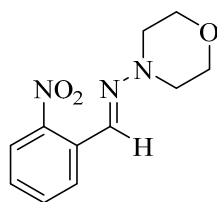
(E)-N-morpholino-1-(3-nitrophenyl)methanimine (1l): ¹H NMR (400 MHz, CDCl₃) δ 8.39 (s, 1H), 8.05 (d, J = 7.7 Hz, 1H), 7.87 (d, J = 7.7 Hz, 1H), 7.52 (d, J = 12.5 Hz, 1H), 7.47 (t, J = 7.9 Hz, 1H), 3.97 – 3.72 (m, 4H), 3.32 – 3.06 (m, 4H); ¹³C NMR (150 MHz, CDCl₃) δ 148.7, 138.1, 132.1, 131.6, 129.4, 122.4, 120.7, 66.4, 51.5.



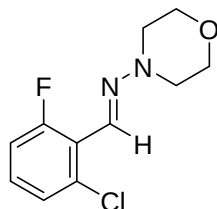
(E)-1-(2-chlorophenyl)-N-morpholinomethanimine (1m): ¹H NMR (400 MHz, CDCl₃) δ 8.07 – 7.95 (m, 2H), 7.41 (d, J = 7.6 Hz, 1H), 7.36 – 7.26 (m, 2H), 4.05 – 3.89 (m, 4H), 3.46 – 3.15 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 133.4, 133.1, 132.3, 129.7, 129.2, 127.0, 126.5, 66.5, 51.8.



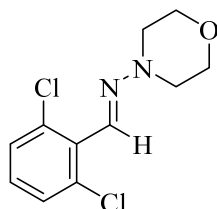
(E)-2-((morpholinoimino)methyl)benzonitrile (1n): ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 8.1$ Hz, 1H), 7.81 (s, 1H), 7.61 (d, $J = 7.7$ Hz, 1H), 7.54 (t, $J = 7.7$ Hz, 1H), 7.31 (t, $J = 7.5$ Hz, 1H), 4.00 – 3.79 (m, 4H), 3.38 – 3.18 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 139.2, 132.9, 132.8, 130.2, 127.9, 125.3, 117.9, 110.2, 66.4, 51.4.



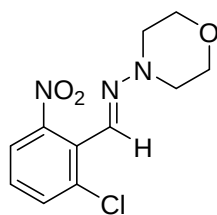
(E)-N-morpholino-1-(2-nitrophenyl)methanimine (1o): ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, $J = 8.0$ Hz, 1H), 8.08 (s, 1H), 7.96 (d, $J = 8.2$ Hz, 1H), 7.57 (t, $J = 7.6$ Hz, 1H), 7.38 (t, $J = 7.7$ Hz, 1H), 4.12 – 3.65 (m, 4H), 3.48 – 3.08 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.5, 133.2, 131.1, 130.2, 128.2, 127.7, 124.8, 66.4, 51.6.



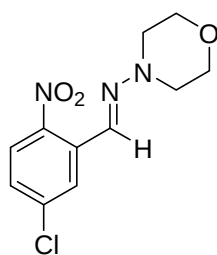
(E)-1-(2-chloro-6-fluorophenyl)-N-morpholinomethanimine (1p): ^1H NMR (400 MHz, CDCl_3) δ 7.67 (s, 1H), 7.22 – 7.11 (m, 2H), 7.01 (t, $J = 9.2$ Hz, 1H), 3.99 – 3.75 (m, 4H), 3.32 – 3.13 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 160.7 (d, $J_{\text{C-F}} = 255.6$ Hz), 134.2 (d, $J_{\text{C-F}} = 4.7$ Hz), 128.9 (d, $J_{\text{C-F}} = 9.7$ Hz), 128.8 (d, $J_{\text{C-F}} = 2.9$ Hz), 125.7 (d, $J_{\text{C-F}} = 3.5$ Hz), 122.7 (d, $J_{\text{C-F}} = 13.2$ Hz), 115.1 (d, $J_{\text{C-F}} = 22.7$ Hz), 66.4, 51.4.



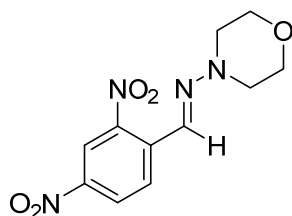
(E)-1-(2,6-dichlorophenyl)-N-morpholinomethanimine (1q): ^1H NMR (400 MHz, CDCl_3) δ 7.62 (s, 1H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.11 (t, $J = 8.0$ Hz, 1H), 4.04 – 3.68 (m, 4H), 3.39 – 3.03 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 134.5, 132.2, 131.1, 128.8, 128.7, 66.2, 51.5.



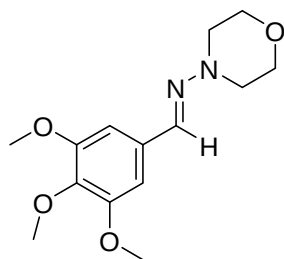
(E)-1-(2-chloro-6-nitrophenyl)-N-morpholinomethanimine (1r): ^1H NMR (400 MHz, CDCl_3) δ 7.63 (s, 1H), 7.53 (d, $J = 8.0$ Hz, 1H), 7.47 (d, $J = 7.9$ Hz, 1H), 7.29 (t, $J = 8.3$ Hz, 1H), 3.96 – 3.73 (m, 4H), 3.38 – 3.07 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 149.8, 134.5, 132.6, 128.3, 127.5, 126.4, 122.4, 66.2, 51.0.



(E)-1-(5-chloro-2-nitrophenyl)-N-morpholinomethanimine (1s): ^1H NMR (400 MHz, CDCl_3) δ 8.10 (s, 1H), 8.02 (s, 1H), 7.92 (d, $J = 8.8$ Hz, 1H), 7.30 (d, $J = 8.4$ Hz, 1H), 4.00 – 3.76 (m, 4H), 3.43 – 3.16 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 145.3, 139.7, 133.0, 128.1, 127.8, 127.2, 126.4, 66.3, 51.4.

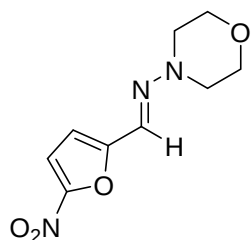


(E)-1-(2,4-dinitrophenyl)-N-morpholinomethanimine (1t): ^1H NMR (400 MHz, CDCl_3) δ 8.80 (s, 1H), 8.43 – 8.23 (m, 1H), 8.00 (s, 1H), 3.99 – 3.78 (m, 4H), 3.52 – 3.19 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 145.9, 145.7, 137.0, 128.2, 126.8, 125.5, 121.0, 66.2, 51.1.

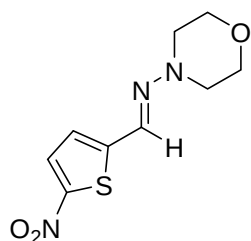


(E)-N-morpholino-1-(3,4,5-trimethoxyphenyl)methanimine (1u): ^1H NMR (400 MHz, CDCl_3) δ 7.52 (s, 1H), 6.85 (s, 2H), 3.96 – 3.87 (m, 10H), 3.86 (s, 3H), 3.24 –

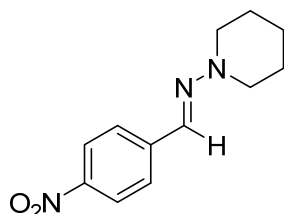
3.08 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.6, 138.6, 136.2, 131.7, 103.3, 66.6, 61.1, 56.2, 52.1.



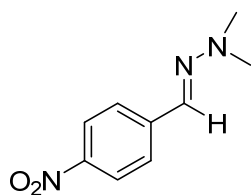
(E)-N-morpholino-1-(5-nitrofuran-2-yl)methanimine (1v): ^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, $J = 3.6$ Hz, 1H), 7.33 (s, 1H), 6.68 (d, $J = 3.5$ Hz, 1H), 3.94 – 3.76 (m, 4H), 3.38 – 3.13 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.3, 151.3, 121.7, 114.4, 108.4, 66.2, 51.0.



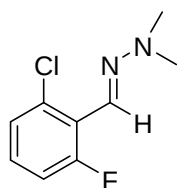
(E)-N-morpholino-1-(5-nitrothiophen-2-yl)methanimine (1w): ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J = 3.9$ Hz, 1H), 7.51 (s, 1H), 6.90 (d, $J = 3.8$ Hz, 1H), 3.96 – 3.71 (m, 4H), 3.35 – 3.10 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 150.1, 149.8, 129.4, 126.7, 123.6, 66.2, 51.2.



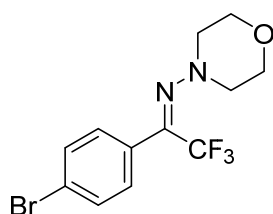
(E)-1-(4-nitrophenyl)-N-(piperidin-1-yl)methanimine (1x): ^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, $J = 8.5$ Hz, 2H), 7.65 (d, $J = 8.5$ Hz, 2H), 7.43 (s, 1H), 3.34 – 3.16 (m, 4H), 1.87 – 1.66 (m, 4H), 1.65 – 1.48 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 146.4, 143.5, 129.5, 125.7, 124.0, 51.6, 25.1, 24.0.



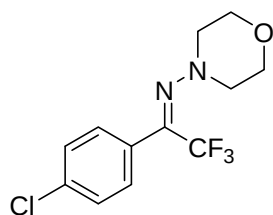
(E)-1,1-dimethyl-2-(4-nitrobenzylidene)hydrazine (1y): ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, $J = 8.5$ Hz, 2H), 7.63 (d, $J = 8.5$ Hz, 2H), 7.10 (s, 1H), 3.10 (s, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 146.0, 143.8, 127.2, 125.2, 124.2, 42.6.



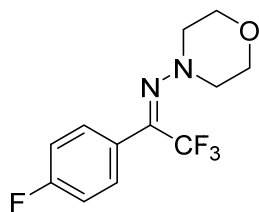
(E)-2-(2-chloro-6-fluorobenzylidene)-1,1-dimethylhydrazine (1z): ^1H NMR (400 MHz, CDCl_3) δ 7.25 (s, 1H), 7.16 (d, $J = 7.9$ Hz, 1H), 7.08 (dd, $J = 13.7, 7.9$ Hz, 1H), 6.99 (t, $J = 9.3$ Hz, 1H), 3.05 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.4 (d, $J_{\text{C-F}} = 254.5$ Hz), 133.6 (d, $J_{\text{C-F}} = 5.2$ Hz), 127.7 (d, $J_{\text{C-F}} = 9.7$ Hz), 125.6 (d, $J_{\text{C-F}} = 3.6$ Hz), 124.3 (d, $J_{\text{C-F}} = 3.4$ Hz), 123.5 (d, $J_{\text{C-F}} = 13.1$ Hz), 115.0 (d, $J_{\text{C-F}} = 22.8$ Hz), 42.5.



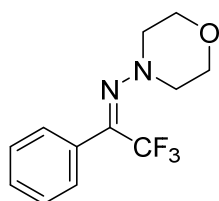
(Z)-1-(4-bromophenyl)-2,2,2-trifluoro-N-morpholinoethan-1-imine (2a): Yellow oil; 85% yield (57 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.56 (d, $J = 8.2$ Hz, 2H), 7.31 (d, $J = 8.1$ Hz, 2H), 3.70 – 3.56 (m, 4H), 3.06 – 2.92 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 134.9 (q, $J_{\text{C-F}} = 33.5$ Hz), 132.3, 130.5, 130.2, 124.4, 121.1 (q, $J_{\text{C-F}} = 274.6$ Hz), 66.1, 54.4; ^{19}F NMR (564 MHz, CDCl_3) δ -66.67 (s, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2854, 1610, 1584, 1318, 826; HRMS (CI) calcd $\text{C}_{12}\text{H}_{13}^{79}\text{BrF}_3\text{N}_2\text{O}$ $[\text{M} + \text{H}]^+$: 337.0163, found: 337.0150.



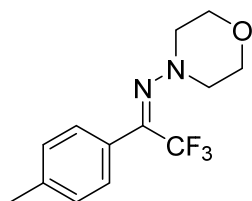
(Z)-1-(4-chlorophenyl)-2,2,2-trifluoro-N-morpholinoethan-1-imine (2b): Yellow oil; 71% yield (41 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.45 – 7.34 (m, 4H), 3.69 – 3.56 (m, 4H), 3.06 – 2.92 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3 , overlapping peaks) δ 136.2, 135.0 (q, $J_{\text{C-F}} = 33.5$ Hz), 130.0, 129.4, 121.2 (q, $J_{\text{C-F}} = 274.6$ Hz), 66.2, 54.4; ^{19}F NMR (376 MHz, CDCl_3) δ -66.68 (s, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2855, 1592, 1489, 1319, 831; HRMS (CI) calcd $\text{C}_{12}\text{H}_{13}^{35}\text{ClF}_3\text{N}_2\text{O}$ $[\text{M} + \text{H}]^+$: 293.0669, found: 293.0666.



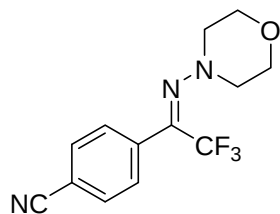
(Z)-2,2,2-trifluoro-1-(4-fluorophenyl)-N-morpholinoethan-1-imine (2c): Colorless oil; 52% yield (28 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.35 (m, 2H), 7.12 (t, J = 8.4 Hz, 2H), 3.70 – 3.53 (m, 4H), 3.05 – 2.86 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 163.4 (d, $J_{\text{C-F}}$ = 251.2 Hz), 135.5 (q, $J_{\text{C-F}}$ = 33.4 Hz), 130.7 (d, $J_{\text{C-F}}$ = 8.3 Hz), 127.5 (d, $J_{\text{C-F}}$ = 3.7 Hz), 121.2 (q, $J_{\text{C-F}}$ = 274.6 Hz), 116.3 (d, $J_{\text{C-F}}$ = 21.8 Hz), 66.2, 54.3; ^{19}F NMR (564 MHz, CDCl_3) δ -66.90 (s, 3F), -109.48 – -109.58 (m, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2855, 1602, 1507, 1226, 841; HRMS (CI) calcd $\text{C}_{12}\text{H}_{13}\text{F}_4\text{N}_2\text{O}$ $[\text{M} + \text{H}]^+$: 277.0964, found: 277.0954.



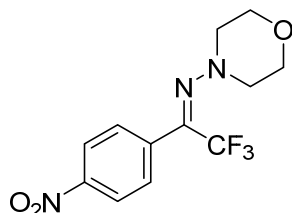
(Z)-2,2,2-trifluoro-N-morpholino-1-phenylethan-1-imine (2d): Colorless oil; 67% yield (35 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.42 (s, 5H), 3.73 – 3.47 (m, 4H), 3.12 – 2.82 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 136.4 (q, $J_{\text{C-F}}$ = 33.2 Hz), 131.7, 130.0, 129.0, 128.6, 121.4 (q, $J_{\text{C-F}}$ = 274.9 Hz), 66.2, 54.4; ^{19}F NMR (564 MHz, CDCl_3) δ -66.80 (s, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2856, 1607, 1448, 1314, 709; HRMS(CI) calcd $\text{C}_{12}\text{H}_{14}\text{F}_3\text{N}_2\text{O}$ $[\text{M} + \text{H}]^+$: 259.1058, found: 259.1061.



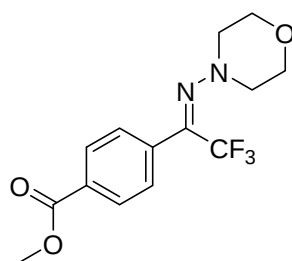
(Z)-2,2,2-trifluoro-N-morpholino-1-(p-tolyl)ethan-1-imine (2e): Colorless oil; 49% yield (27 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.32 (d, J = 7.7 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 3.78 – 3.41 (m, 4H), 3.11 – 2.80 (m, 4H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 140.2, 136.9 (q, $J_{\text{C-F}}$ = 33.0 Hz), 129.6, 128.6, 128.4, 121.4 (q, $J_{\text{C-F}}$ = 274.8 Hz), 66.3, 54.3, 21.6; ^{19}F NMR (564 MHz, CDCl_3) δ -66.85 (s, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2919, 2857, 1612, 1311, 864; HRMS (CI) calcd $\text{C}_{13}\text{H}_{16}\text{F}_3\text{N}_2\text{O}$ $[\text{M} + \text{H}]^+$: 273.1215, found: 273.1213.



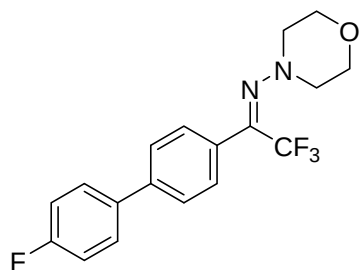
(Z)-4-(2,2,2-trifluoro-1-(morpholinoimino)ethyl)benzonitrile (2f): White solid; m.p. 112-114 °C; 77% yield (44 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, $J = 8.0$ Hz, 2H), 7.55 (d, $J = 7.9$ Hz, 2H), 3.74 – 3.44 (m, 4H), 3.13 – 2.82 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 136.3, 132.8 (q, $J_{\text{C-F}} = 33.9$ Hz), 132.6, 129.5, 121.0 (q, $J_{\text{C-F}} = 274.5$ Hz), 117.9, 113.9, 66.0, 54.4; ^{19}F NMR (564 MHz, CDCl_3) δ -66.22 (s, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2843, 2233, 1615, 1334, 847; HRMS (CI) calcd $\text{C}_{13}\text{H}_{13}\text{F}_3\text{N}_3\text{O}$ $[\text{M} + \text{H}]^+$: 284.1011, found: 284.1021.



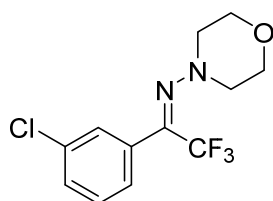
(Z)-2,2,2-trifluoro-N-morpholino-1-(4-nitrophenyl)ethan-1-imine (2g): Yellowish solid; m.p. 151-153 °C; 92% yield (56 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.29 (d, $J = 8.3$ Hz, 2H), 7.63 (d, $J = 8.2$ Hz, 2H), 3.72 – 3.54 (m, 4H), 3.08 – 2.92 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 147.5, 137.3, 131.5 (q, $J_{\text{C-F}} = 34.0$ Hz), 129.0, 123.1, 120.1 (q, $J_{\text{C-F}} = 274.5$ Hz), 65.0, 53.6; ^{19}F NMR (564 MHz, CDCl_3) δ -66.17 (s, 3F).



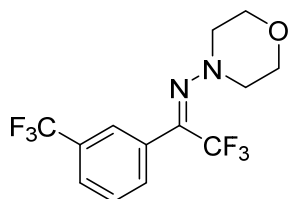
Methyl (Z)-4-(2,2,2-trifluoro-1-(morpholinoimino)ethyl)benzoate (2h): White solid; m.p. 73-75 °C; 73% yield (46 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, $J = 8.1$ Hz, 2H), 7.51 (d, $J = 8.0$ Hz, 2H), 3.93 (s, 3H), 3.65 – 3.51 (m, 4H), 3.05 – 2.91 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 166.3, 136.3, 134.5 (q, $J_{\text{C-F}} = 33.6$ Hz), 131.5, 130.1, 128.8, 121.2 (q, $J_{\text{C-F}} = 274.6$ Hz), 66.1, 54.4, 52.5; ^{19}F NMR (564 MHz, CDCl_3) δ -66.46 (s, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2919, 2851, 1717, 1274, 1091, 865; HRMS (CI) calcd $\text{C}_{14}\text{H}_{16}\text{F}_3\text{N}_2\text{O}_3$ $[\text{M} + \text{H}]^+$: 317.1113, found: 317.1115.



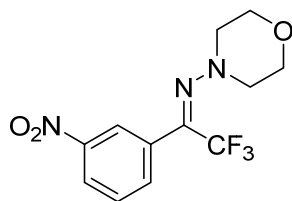
(Z)-2,2,2-trifluoro-1-(4'-fluoro-[1,1'-biphenyl]-4-yl)-N-morpholinoethan-1-imine (2i): Yellowish solid; m.p. 129-131 °C; 43% yield (30 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.65 – 7.55 (m, 4H), 7.51 (d, $J = 7.9$ Hz, 2H), 7.21 – 7.09 (m, 2H), 3.75 – 3.56 (m, 4H), 3.14 – 2.83 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 162.9 (d, $J_{\text{C-F}} = 247.7$ Hz), 141.7, 136.1 (q, $J_{\text{C-F}} = 33.2$ Hz), 136.1 (d, $J_{\text{C-F}} = 3.1$ Hz), 130.4, 129.0, 128.9 (d, $J_{\text{C-F}} = 8.1$ Hz), 127.3, 121.3 (q, $J_{\text{C-F}} = 274.8$ Hz), 116.0 (d, $J_{\text{C-F}} = 21.5$ Hz), 66.2, 54.4; ^{19}F NMR (564 MHz, CDCl_3) δ -66.59 (s, 3F), -106.41 – -128.96 (m, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2852, 1607, 1493, 1318, 826; HRMS (CI) calcd $\text{C}_{18}\text{H}_{17}\text{F}_4\text{N}_2\text{O}$ $[\text{M} + \text{H}]^+$: 353.1277, found: 353.1284.



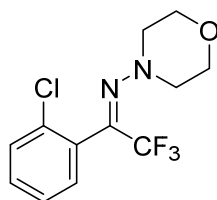
(Z)-1-(3-chlorophenyl)-2,2,2-trifluoro-N-morpholinoethan-1-imine (2j): Colorless oil; 74% yield (43 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.43 (s, 1H), 7.42 – 7.28 (m, 3H), 3.73 – 3.53 (m, 4H), 3.07 – 2.95 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 134.1, 133.0 (q, $J_{\text{C-F}} = 33.6$ Hz), 132.4, 129.3, 129.2, 127.7, 125.9, 120.2 (q, $J_{\text{C-F}} = 274.6$ Hz), 65.1, 53.4; ^{19}F NMR (376 MHz, CDCl_3) δ -66.57 (s, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2855, 1608, 1566, 1316, 725; HRMS (CI) calcd $\text{C}_{12}\text{H}_{13}^{35}\text{ClF}_3\text{N}_2\text{O}$ $[\text{M} + \text{H}]^+$: 293.0669, found: 293.0676.



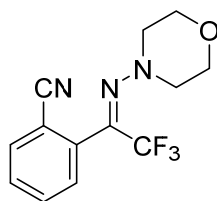
(Z)-2,2,2-trifluoro-N-morpholino-1-(3-(trifluoromethyl)phenyl)ethan-1-imine (2k): Colorless oil; 86% yield (56 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.74 (s, 1H), 7.69 (d, $J = 7.5$ Hz, 1H), 7.63 (d, $J = 7.4$ Hz, 1H), 7.57 (t, $J = 7.6$ Hz, 1H), 3.71 – 3.54 (m, 4H), 3.07 – 2.84 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 134.1 (q, $J_{\text{C-F}} = 33.7$ Hz), 132.5, 131.9, 131.6 (q, $J_{\text{C-F}} = 32.9$ Hz), 129.6, 126.7 (q, $J_{\text{C-F}} = 3.6$ Hz), 125.6 (q, $J_{\text{C-F}} = 3.6$ Hz), 123.6 (q, $J_{\text{C-F}} = 272.6$ Hz), 121.1 (q, $J_{\text{C-F}} = 274.5$ Hz), 66.1, 54.4; ^{19}F NMR (564 MHz, CDCl_3) δ -62.98 (s, 3F), -66.54 (s, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2857, 1614, 1454, 1331, 724; HRMS (CI) calcd $\text{C}_{13}\text{H}_{13}\text{F}_6\text{N}_2\text{O}$ $[\text{M} + \text{H}]^+$: 327.0932, found: 327.0939.



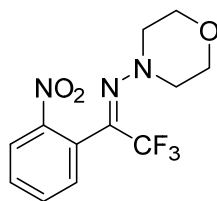
(Z)-2,2,2-trifluoro-N-morpholino-1-(3-nitrophenyl)ethan-1-imine (2l): Yellow solid; m.p. 121-123 °C; 64% yield (39 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.32 (s, 1H), 8.29 (d, J = 8.3 Hz, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.65 (t, J = 7.9 Hz, 1H), 3.71 – 3.57 (m, 4H), 3.10 – 2.95 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 148.4, 134.7, 133.3, 132.4 (q, $J_{\text{C-F}}$ = 34.0 Hz), 130.2, 124.8, 123.8, 121.1 (q, $J_{\text{C-F}}$ = 274.5 Hz), 66.0, 54.5; ^{19}F NMR (564 MHz, CDCl_3) δ -66.35 (s, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2856, 1606, 1530, 1350, 716; HRMS (CI) calcd $\text{C}_{12}\text{H}_{13}\text{F}_3\text{N}_3\text{O}_3$ $[\text{M} + \text{H}]^+$: 304.0909, found: 304.0905.



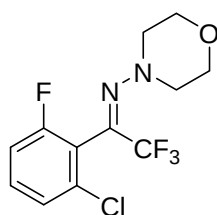
(Z)-1-(3-chlorophenyl)-2,2,2-trifluoro-N-morpholinoethan-1-imine (2m): White solid; m.p. 85-87 °C; 87% yield (50 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, J = 7.9 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.37 – 7.28 (m, 2H), 3.74 – 3.52 (m, 4H), 3.22 – 2.93 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 134.6, 131.8, 131.2, 131.1, 129.8, 128.3 (q, $J_{\text{C-F}}$ = 34.7 Hz), 127.1, 121.5 (q, $J_{\text{C-F}}$ = 274.4 Hz), 66.5, 53.6; ^{19}F NMR (564 MHz, CDCl_3) δ -66.4 (s, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2853, 1601, 1447, 1311, 769; HRMS (CI) calcd $\text{C}_{12}\text{H}_{13}^{35}\text{ClF}_3\text{N}_2\text{O}$ $[\text{M} + \text{H}]^+$: 293.0669, found: 293.0670.



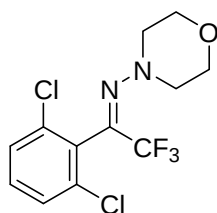
(Z)-2-(2,2,2-trifluoro-1-(morpholinoimino)ethyl)benzonitrile (2n): Colorless oil; 65% yield (37 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, J = 7.7 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.48 (d, J = 7.7 Hz, 1H), 3.64 (m, J = 4.8 Hz, 4H), 3.05 (m, J = 3.1 Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.1, 133.4, 133.1, 130.5, 130.4, 128.0 (q, $J_{\text{C-F}}$ = 35.0 Hz), 121.3 (q, $J_{\text{C-F}}$ = 274.3 Hz), 116.8, 113.9, 66.2, 53.8, ^{19}F NMR (376 MHz, CDCl_3) δ -66.14 (s, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2857, 2230, 1602, 1450, 731; HRMS (CI) calcd $\text{C}_{13}\text{H}_{13}\text{F}_3\text{N}_3\text{O}$ $[\text{M} + \text{H}]^+$: 284.1011, found: 284.1006.



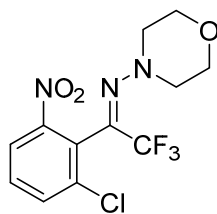
(Z)-2,2,2-trifluoro-N-morpholino-1-(2-nitrophenyl)ethan-1-imine (2o): Yellow oil; 77% yield (47 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.17 (d, J = 8.1 Hz, 1H), 7.73 (t, J = 7.4 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.49 (d, J = 7.4 Hz, 1H), 3.67 – 3.49 (m, 4H), 3.08 – 2.86 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.8, 134.1, 131.5 (q, $J_{\text{C-F}}$ = 35.0 Hz), 131.4, 131.3, 127.3, 125.2, 120.8 (q, $J_{\text{C-F}}$ = 274.6 Hz), 66.2, 53.9; ^{19}F NMR (376 MHz, CDCl_3) δ -66.48 (s, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2858, 1612, 1529, 1347, 714; HRMS (CI) calcd $\text{C}_{12}\text{H}_{13}\text{F}_3\text{N}_3\text{O}_3$ $[\text{M} + \text{H}]^+$: 304.0909, found: 304.0911.



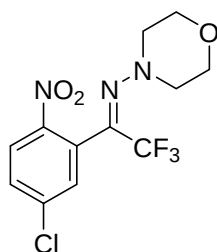
(Z)-1-(2-chloro-6-fluorophenyl)-2,2,2-trifluoro-N-morpholinoethan-1-imine (2p): Yellow solid; m.p. 65-67 °C; 87% yield (54 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.38 (dd, J = 14.3, 7.9 Hz, 1H), 7.27 (d, J = 7.9 Hz, 1H), 7.07 (t, J = 8.2 Hz, 1H), 3.73 – 3.62 (m, 4H), 3.22 – 3.09 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 160.5 (d, $J_{\text{C-F}}$ = 251.5 Hz), 135.8 (d, $J_{\text{C-F}}$ = 3.8 Hz), 132.3 (d, $J_{\text{C-F}}$ = 9.1 Hz), 125.5 (d, $J_{\text{C-F}}$ = 3.4 Hz), 121.5 (q, $J_{\text{C-F}}$ = 36.5 Hz), 121.2 (q, $J_{\text{C-F}}$ = 274.3 Hz), 120.5 (d, $J_{\text{C-F}}$ = 21.9 Hz), 114.5 (d, $J_{\text{C-F}}$ = 22.2 Hz), 66.4, 53.1; ^{19}F NMR (564 MHz, CDCl_3) δ -66.30 (d, J = 5.5 Hz, 3F), -106.34 – -106.46 (m, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2850, 1599, 1446, 1310, 786; HRMS (CI) calcd $\text{C}_{12}\text{H}_{12}^{35}\text{ClF}_4\text{N}_2\text{O}$ $[\text{M} + \text{H}]^+$: 311.0574, found: 311.0583.



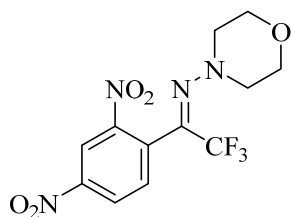
(Z)-1-(2,6-dichlorophenyl)-2,2,2-trifluoro-N-morpholinoethan-1-imine (2q): White solid; m.p. 101-103 °C; 85% yield (55 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.35 (m, 2H), 7.35 – 7.28 (m, 1H), 3.75 – 3.56 (m, 4H), 3.21 – 3.07 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 136.1, 131.7, 131.6, 128.2, 124.5 (q, $J_{\text{C-F}}$ = 36.1 Hz), 121.2 (q, $J_{\text{C-F}}$ = 275.0 Hz), 66.6, 53.0; ^{19}F NMR (564 MHz, CDCl_3) δ -64.6 (s, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2853, 1597, 1426, 1299, 788; HRMS(CI) calcd $\text{C}_{12}\text{H}_{12}^{35}\text{Cl}_2\text{F}_3\text{N}_2\text{O}$ $[\text{M} + \text{H}]^+$: 327.0279, found: 327.0271.



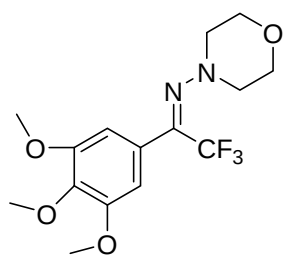
(Z)-1-(2-chloro-6-nitrophenyl)-2,2,2-trifluoro-N-morpholinoethan-1-imine (2r): Yellow solid; m.p. 112-115 °C; 59% yield (39 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, $J = 6.8$ Hz, 1H), 7.76 (d, $J = 6.6$ Hz, 1H), 7.66 – 7.51 (m, 1H), 3.79 – 3.52 (m, 4H), 3.34 – 3.05 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 149.9, 137.1, 134.6, 131.6, 127.1, 123.3, 121.4 (q, $J_{\text{C-F}} = 36.1$ Hz), 121.2 (q, $J_{\text{C-F}} = 274.3$ Hz), 66.6, 53.0; ^{19}F NMR (564 MHz, CDCl_3) δ -65.78 (s, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2849, 1604, 1542, 1356, 758; HRMS (CI) calcd $\text{C}_{12}\text{H}_{12}^{35}\text{ClF}_3\text{N}_3\text{O}_3$ $[\text{M} + \text{H}]^+$: 338.0519, found: 338.0522.



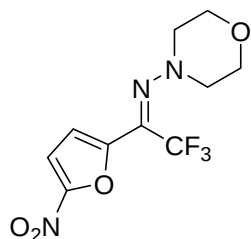
(Z)-1-(5-chloro-2-nitrophenyl)-2,2,2-trifluoro-N-morpholinoethan-1-imine (2s): Yellowish solid; m.p. 132-134 °C; 72% yield (49 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, $J = 8.7$ Hz, 1H), 7.61 (d, $J = 8.6$ Hz, 1H), 7.46 (s, 1H), 3.70 – 3.56 (m, 4H), 3.14 – 2.96 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 146.2, 140.7, 131.4, 131.3, 129.1, 128.8 (q, $J_{\text{C-F}} = 35.4$ Hz), 126.6, 120.8 (q, $J_{\text{C-F}} = 274.5$ Hz), 66.2, 53.9; ^{19}F NMR (564 MHz, CDCl_3) δ -66.25 (s, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2855, 1606, 1526, 1369, 858; HRMS (CI) calcd $\text{C}_{12}\text{H}_{12}^{35}\text{ClF}_3\text{N}_3\text{O}_3$ $[\text{M} + \text{H}]^+$: 338.0519, found: 338.0515.



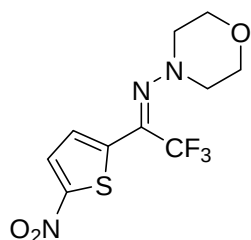
(Z)-1-(2,4-dinitrophenyl)-2,2,2-trifluoro-N-morpholinoethan-1-imine (2t): Yellow solid; m.p. 124-126 °C; 75% yield (52 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.97 (s, 1H), 8.55 (d, $J = 7.5$ Hz, 1H), 7.75 (d, $J = 7.9$ Hz, 1H), 3.51 (m, 4H), 3.05 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 148.9, 148.4, 145.9, 133.2, 128.0, 127.3 (q, $J = 36.0$ Hz), 120.7 (q, $J = 274.6$ Hz), 120.6, 66.2, 54.0; ^{19}F NMR (564 MHz, CDCl_3) δ -65.86 (s, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2851, 1603, 1541, 1347, 836; HRMS (CI) calcd $\text{C}_{12}\text{H}_{12}\text{F}_3\text{N}_4\text{O}_5$ $[\text{M} + \text{H}]^+$: 349.0760, found: 349.0761.



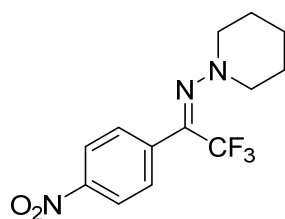
(Z)-2,2,2-trifluoro-N-morpholino-1-(3,4,5-trimethoxyphenyl)ethan-1-imine (2u): White solid; m.p. 73-75 °C; 20% yield (14 mg); ^1H NMR (400 MHz, CDCl_3) δ 6.64 (s, 2H), 3.88 (s, 3H), 3.85 (s, 6H), 3.77 – 3.51 (m, 4H), 3.11 – 2.91 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 153.6, 139.2, 135.5 (q, $J_{\text{C-F}} = 33.2$ Hz), 126.5, 121.3 (q, $J_{\text{C-F}} = 274.8$ Hz), 105.7, 66.4, 61.1, 56.4, 54.3; ^{19}F NMR (564 MHz, CDCl_3) δ -66.56 (s, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2938, 2848, 1580, 1294, 875; HRMS (CI) calcd $\text{C}_{15}\text{H}_{20}\text{F}_3\text{N}_2\text{O}_4$ $[\text{M} + \text{H}]^+$: 349.1375, found: 349.1388.



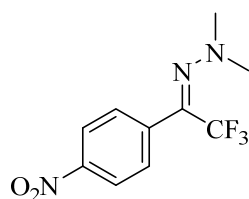
(Z)-2,2,2-trifluoro-N-morpholino-1-(5-nitrofuran-2-yl)ethan-1-imine (2v): Yellowish solid; m.p. 88-90 °C; 89% yield (52 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, $J = 3.3$ Hz, 1H), 6.80 (d, $J = 2.6$ Hz, 1H), 3.86 – 3.73 (m, 4H), 3.35 – 3.25 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 152.1, 144.6, 121.4 (q, $J_{\text{C-F}} = 273.0$ Hz), 117.3 (q, $J_{\text{C-F}} = 36.0$ Hz), 115.9, 112.3, 66.2, 54.4; ^{19}F NMR (564 MHz, CDCl_3) δ -65.42 (s, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2921, 2873, 1547, 1351, 1317; HRMS (CI) calcd $\text{C}_{10}\text{H}_{11}\text{F}_3\text{N}_3\text{O}_4$ $[\text{M} + \text{H}]^+$: 294.0702, found: 294.0695.



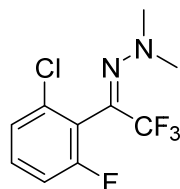
(E)-2,2,2-trifluoro-N-morpholino-1-(5-nitrothiophen-2-yl)ethan-1-imine (2w): Brown solid; m.p. 65-67 °C; 92% yield (57 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 4.3$ Hz, 1H), 7.50 – 7.37 (m, 1H), 4.04 – 3.67 (m, 4H), 3.22 – 2.64 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 154.5, 143.7 (q, $J_{\text{C-F}} = 33.0$ Hz), 131.8, 131.0 (d, $J_{\text{C-F}} = 2.3$ Hz), 127.1, 120.3 (q, $J_{\text{C-F}} = 276.9$ Hz), 65.9, 55.0; ^{19}F NMR (564 MHz, CDCl_3) δ -65.92 (s, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2923, 2848, 1498, 1344, 716; HRMS (CI) calcd $\text{C}_{10}\text{H}_{11}\text{F}_3\text{N}_3\text{O}_3\text{S}$ $[\text{M} + \text{H}]^+$: 310.0473, found: 310.0478.



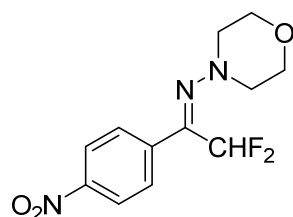
(Z)-2,2,2-trifluoro-1-(4-nitrophenyl)-N-(piperidin-1-yl)ethan-1-imine (2x): Yellow oil; 57% yield (34 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.27 (d, $J = 8.3$ Hz, 2H), 7.61 (d, $J = 8.3$ Hz, 2H), 3.10 – 2.90 (m, 4H), 1.67 – 1.39 (m, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 148.2, 139.3, 130.0, 128.4 (q, $J_{\text{C-F}} = 33.7$ Hz), 123.9, 121.6 (q, $J_{\text{C-F}} = 273.8$ Hz), 55.3, 25.0, 23.7; ^{19}F NMR (564 MHz, CDCl_3) δ -65.33 (s, 3F).



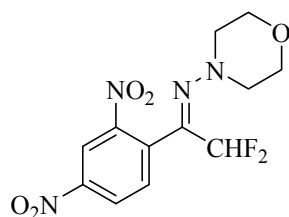
(Z)-1,1-dimethyl-2-(2,2,2-trifluoro-1-(4-nitrophenyl)ethylidene)hydrazine (2y): Yellow solid; m.p. 108-110 °C; 61% yield (32 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.23 (d, $J = 8.4$ Hz, 2H), 7.54 (d, $J = 8.3$ Hz, 2H), 2.82 (s, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 148.0, 139.2, 131.0, 124.6 (q, $J_{\text{C-F}} = 33.9$ Hz), 123.2, 121.9 (q, $J_{\text{C-F}} = 273.1$ Hz), 47.2; ^{19}F NMR (564 MHz, CDCl_3) δ -64.73 (s, 3F).



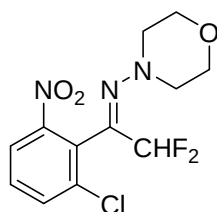
(Z)-2-(1-(2-chloro-6-fluorophenyl)-2,2,2-trifluoroethylidene)-1,1-dimethylhydrazine (2z): Yellowish oil; 43% yield (23 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.29 (m, 1H), 7.27 – 7.19 (m, 1H), 7.03 (t, $J = 8.2$ Hz, 1H), 2.89 (s, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 161.4 (d, $J_{\text{C-F}} = 249.9$ Hz), 136.9 (d, $J_{\text{C-F}} = 3.5$ Hz), 131.9 (d, $J_{\text{C-F}} = 9.2$ Hz), 125.0 (d, $J_{\text{C-F}} = 3.4$ Hz), 121.8 (q, $J_{\text{C-F}} = 273.0$ Hz), 121.1 (d, $J_{\text{C-F}} = 22.3$ Hz), 115.5 (q, $J_{\text{C-F}} = 36.7$ Hz), 114.0 (d, $J_{\text{C-F}} = 22.6$ Hz), 45.2; ^{19}F NMR (564 MHz, CDCl_3) δ -65.00 (d, $J = 4.5$ Hz), -102.91 – -110.72 (m); FT-IR (thin film, KBr): ν (cm^{-1}) 2929, 1591, 1447, 1311, 787; HRMS (CI) calcd $\text{C}_{10}\text{H}_{10}^{35}\text{ClF}_4\text{N}_2$ $[\text{M} + \text{H}]^+$: 269.0469, found: 269.0467.



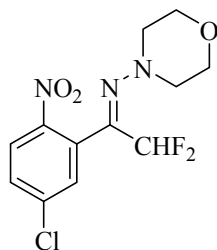
(Z)-2,2-difluoro-N-morpholino-1-(4-nitrophenyl)ethan-1-imine (3a): White solid; m.p. 100-102 °C; 35% yield (20 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.28 (d, $J = 8.4$ Hz, 2H), 7.72 (d, $J = 8.3$ Hz, 2H), 6.20 (t, $J = 55.4$ Hz, 1H), 3.73 – 3.57 (m, 4H), 3.02 – 2.88 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 148.3, 141.1 (t, $J_{\text{C-F}} = 29.2$ Hz), 138.2, 129.6, 124.0, 116.4 (t, $J_{\text{C-F}} = 240.1$ Hz), 66.1, 54.7; ^{19}F NMR (564 MHz, CDCl_3) δ -112.77 (d, $J = 55.4$ Hz, 2F); FT-IR (thin film, KBr): ν (cm^{-1}) 2916, 2843, 1517, 1351, 856; HRMS (CI) calcd $\text{C}_{12}\text{H}_{14}\text{F}_2\text{N}_3\text{O}_3$ $[\text{M} + \text{H}]^+$: 286.1003, found: 286.1016.



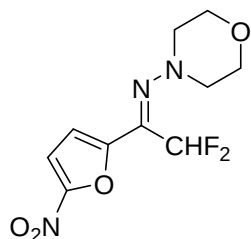
(Z)-1-(2,4-dinitrophenyl)-2,2-difluoro-N-morpholinoethan-1-imine (3b): Yellow solid; m.p. 175-177 °C; 45% yield (29 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.93 (s, 1H), 8.54 (d, $J = 8.3$ Hz, 1H), 7.74 (d, $J = 8.3$ Hz, 1H), 6.30 (t, $J = 55.3$ Hz, 1H), 3.70 – 3.54 (m, 4H), 3.06 – 2.86 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 148.7, 148.6, 136.5 (dd, $J_{\text{C-F}} = 33.8, 25.3$ Hz), 133.3, 132.8, 127.7, 120.3, 115.4 (t, $J_{\text{C-F}} = 240.7$ Hz), 66.2, 54.1; ^{19}F NMR (564 MHz, CDCl_3) δ -110.03 (dd, $J = 309.4, 56.1$ Hz, 1F), -117.47 (dd, $J = 309.4, 54.5$ Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2852, 1601, 1522, 1346, 795; HRMS (CI) calcd $\text{C}_{12}\text{H}_{13}\text{F}_2\text{N}_4\text{O}_5$ $[\text{M} + \text{H}]^+$: 331.0854, found: 331.0843.



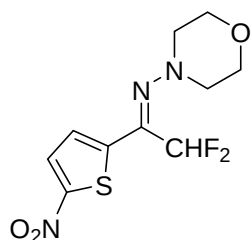
(Z)-1-(2-chloro-6-nitrophenyl)-2,2-difluoro-N-morpholinoethan-1-imine (3c): Yellow solid; m.p. 108-110 °C; 37% yield (23 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 8.1$ Hz, 1H), 7.73 (d, $J = 8.0$ Hz, 1H), 7.54 (t, $J = 8.1$ Hz, 1H), 6.24 (t, $J = 55.7$ Hz, 1H), 3.73 – 3.59 (m, 4H), 3.26 – 3.11 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 150.1, 136.9, 134.3, 131.0, 128.4 (t, $J_{\text{C-F}} = 30.1$ Hz), 127.4, 123.1, 116.3 (dd, $J_{\text{C-F}} = 241.8, 238.1$ Hz), 66.7, 53.0; ^{19}F NMR (564 MHz, CDCl_3) δ -112.61 (dd, $J = 303.1, 55.9$ Hz, 1F), -115.36 (dd, $J = 303.1, 55.3$ Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2924, 2853, 1530, 1351, 727; HRMS (CI) calcd $\text{C}_{12}\text{H}_{13}^{35}\text{ClF}_2\text{N}_3\text{O}_3$ $[\text{M} + \text{H}]^+$: 320.0614, found: 320.0608.



(Z)-1-(5-chloro-2-nitrophenyl)-2,2-difluoro-N-morpholinoethan-1-imine (3d): Yellowish solid; m.p. 100-102 °C; 43% yield (27 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 8.7$ Hz, 1H), 7.57 (d, $J = 8.5$ Hz, 1H), 7.46 (s, 1H), 6.26 (t, $J = 55.5$ Hz, 1H), 3.67 – 3.52 (m, 4H), 3.07 – 2.88 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 146.5, 140.2, 137.6 (dd, $J_{\text{C-F}} = 33.6, 24.9$ Hz), 131.0, 130.8, 128.9, 126.3, 115.4 (t, $J_{\text{C-F}} = 240.7$ Hz), 66.2, 54.0; ^{19}F NMR (564 MHz, CDCl_3) δ -110.45 (dd, $J = 308.2, 56.3$ Hz, 1F), -118.02 (dd, $J = 308.2, 54.8$ Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2975, 2853, 1528, 1345, 835; HRMS (CI) calcd $\text{C}_{12}\text{H}_{13}^{35}\text{ClF}_2\text{N}_3\text{O}_3$ $[\text{M} + \text{H}]^+$: 320.0614, found: 320.0615.



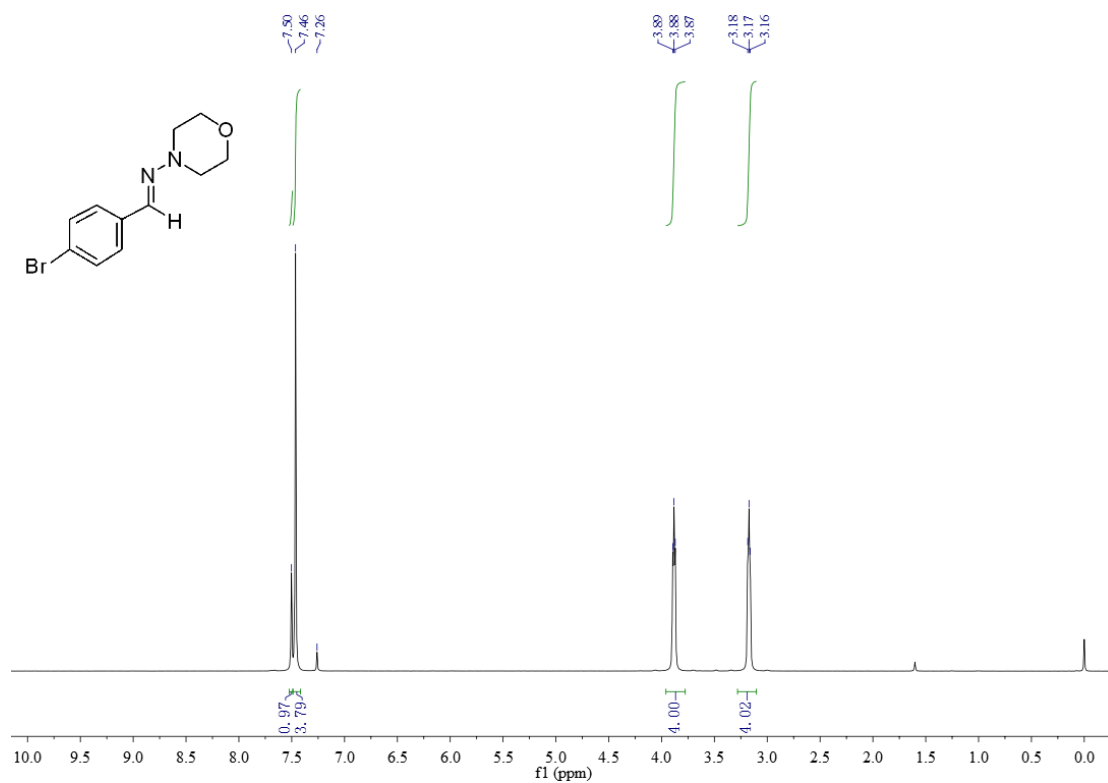
(Z)-2,2-difluoro-N-morpholino-1-(5-nitrofuran-2-yl)ethan-1-imine (3e): Yellow solid; m.p. 89-91 °C; 47% yield (25 mg); ^1H NMR (600 MHz, CDCl_3) δ 7.36 (s, 1H), 6.95 (s, 1H), 6.25 (t, $J = 54.5$ Hz, 1H), 3.89 – 3.67 (m, 4H), 3.31 – 3.13 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 152.1, 144.7, 128.1 (t, $J_{\text{C-F}} = 29.7$ Hz), 116.4 (t, $J_{\text{C-F}} = 240.6$ Hz), 116.0, 112.4, 66.2, 54.8; ^{19}F NMR (564 MHz, CDCl_3) δ -113.39 (d, $J = 54.8$ Hz, 2F). FT-IR (thin film, KBr): ν (cm^{-1}) 2924, 2857, 1523, 1348, 1262; HRMS (CI) calcd $\text{C}_{10}\text{H}_{12}\text{F}_2\text{N}_3\text{O}_4$ $[\text{M} + \text{H}]^+$: 276.0796, found: 276.0793.



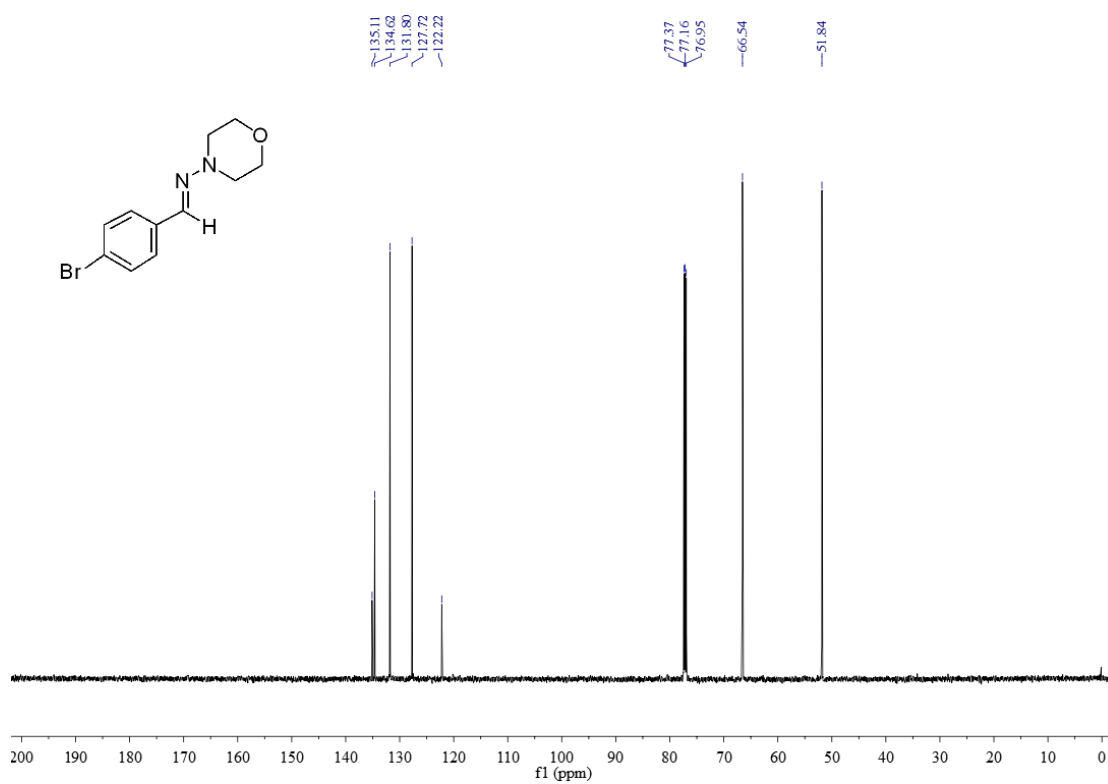
(E)-2,2-difluoro-N-morpholino-1-(5-nitrothiophen-2-yl)ethan-1-imine (3f): Red solid; m.p. 92-94 °C; 42% yield (24 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 4.3$ Hz, 1H), 7.73 – 7.60 (m, 1H), 6.35 (t, $J = 54.1$ Hz, 1H), 4.06 – 3.79 (m, 4H), 3.06 – 2.75 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 154.5, 152.5 (t, $J_{\text{C-F}} = 27.7$ Hz), 131.5 (t, $J_{\text{C-F}} = 4.1$ Hz), 131.3, 127.2, 116.1 (t, $J_{\text{C-F}} = 244.9$ Hz), 66.0, 55.0; ^{19}F NMR (564 MHz, CDCl_3) δ -115.08 (dd, $J = 54.1, 1.7$ Hz, 2F); FT-IR (thin film, KBr): ν (cm^{-1}) 2930, 2852, 1509, 1368, 734; HRMS (CI) calcd $\text{C}_{10}\text{H}_{12}\text{F}_2\text{N}_3\text{O}_3\text{S}$ $[\text{M} + \text{H}]^+$: 292.0567, found: 292.0572.

7. NMR Spectra for the substrates and products

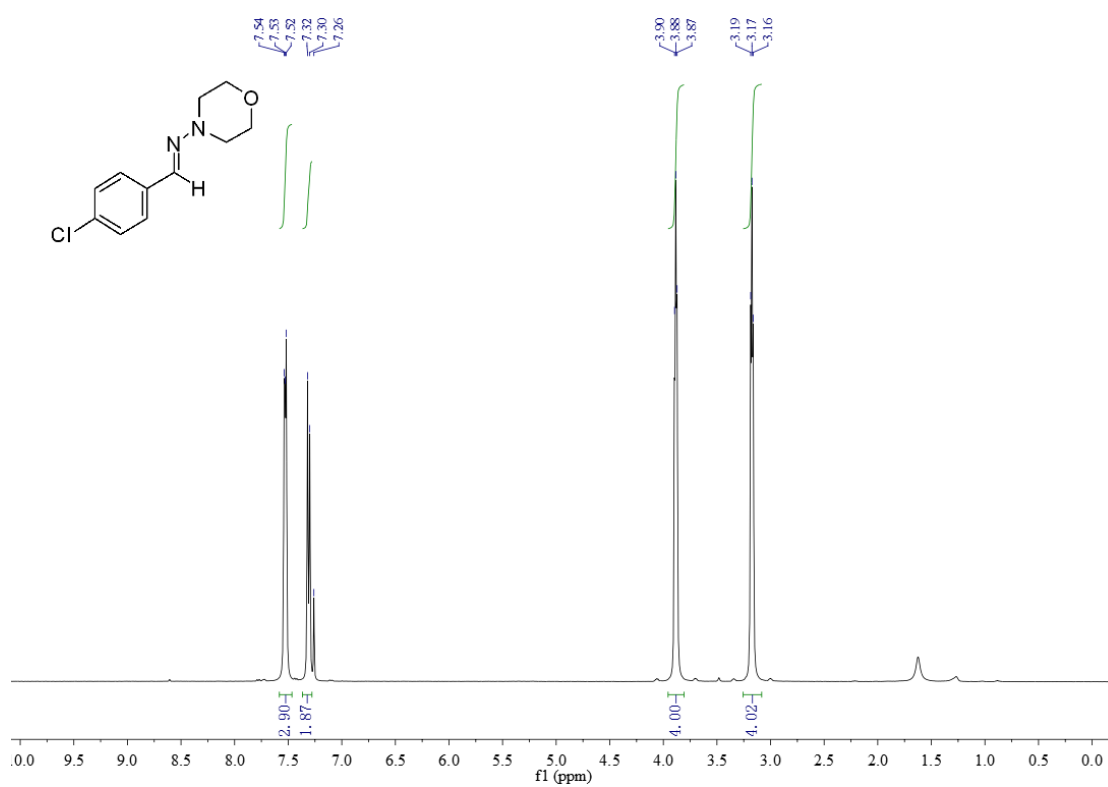
^1H NMR of **1a**



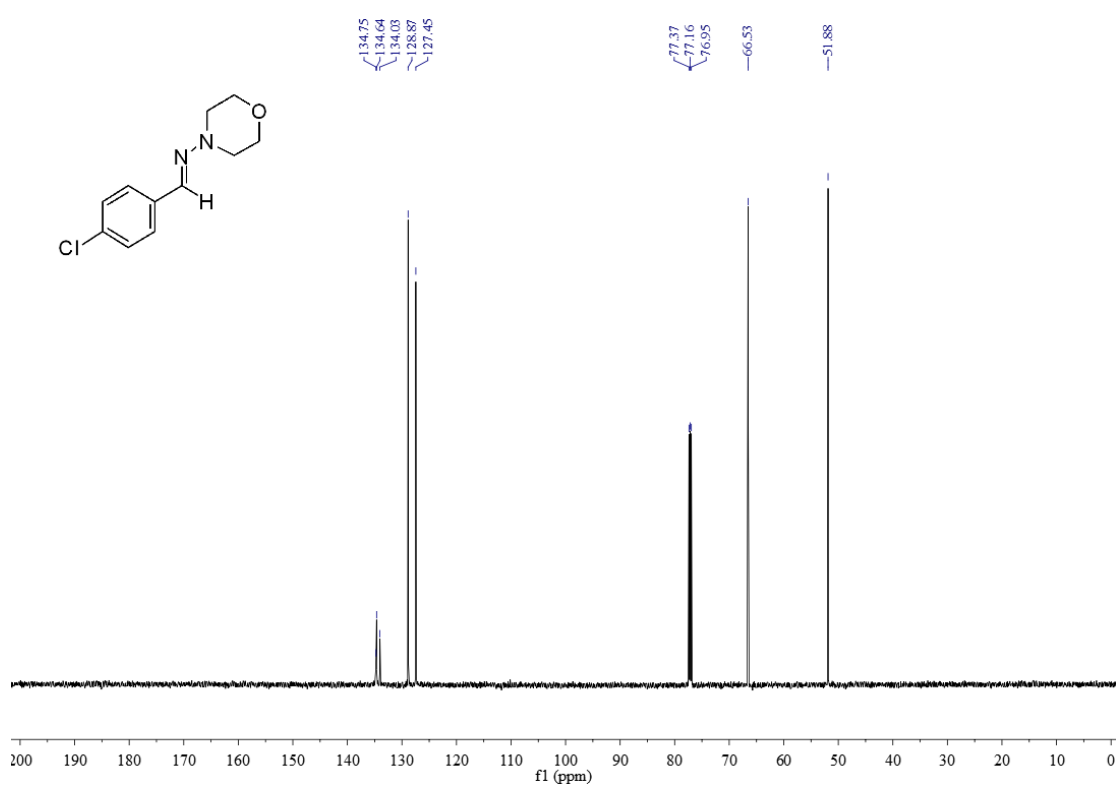
^{13}C NMR of **1a**



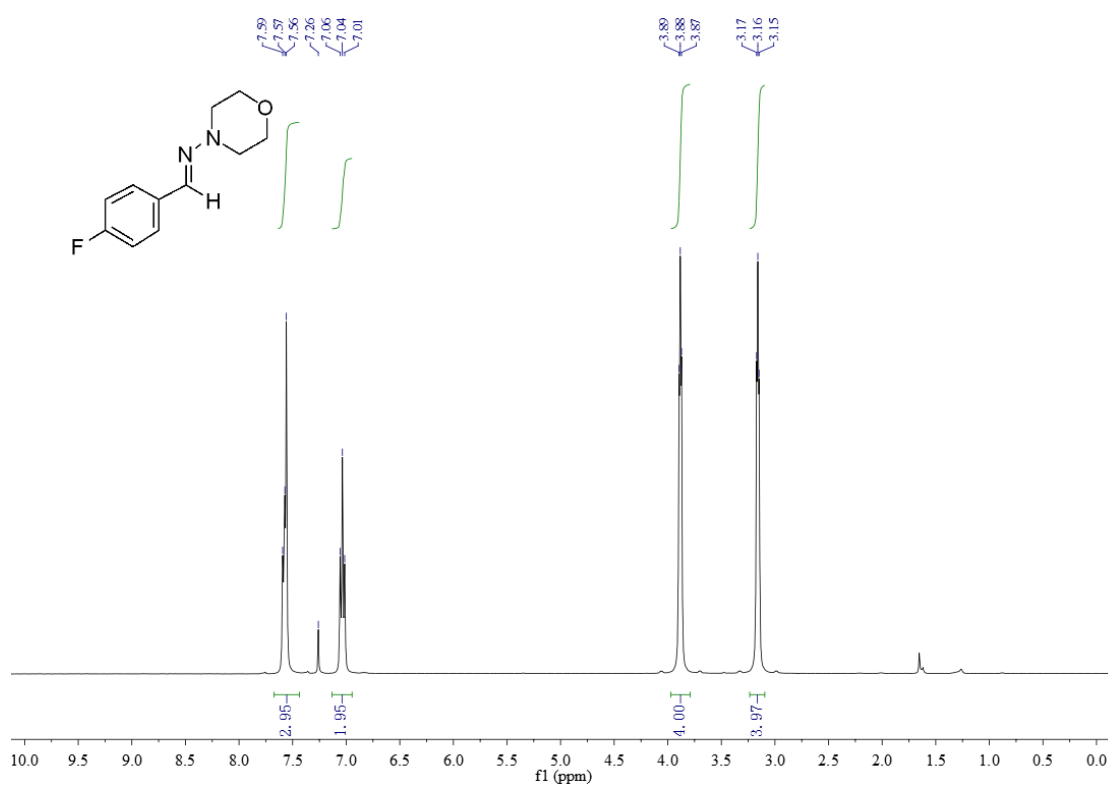
¹H NMR of **1b**



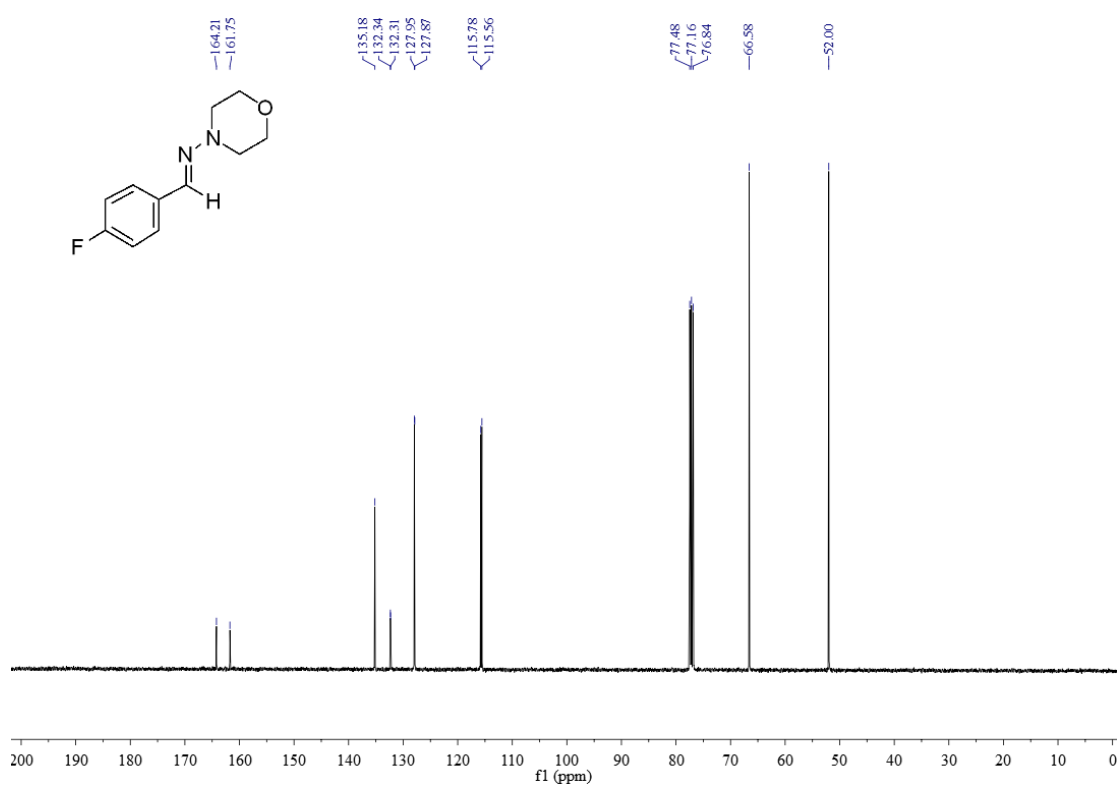
¹³C NMR of **1b**



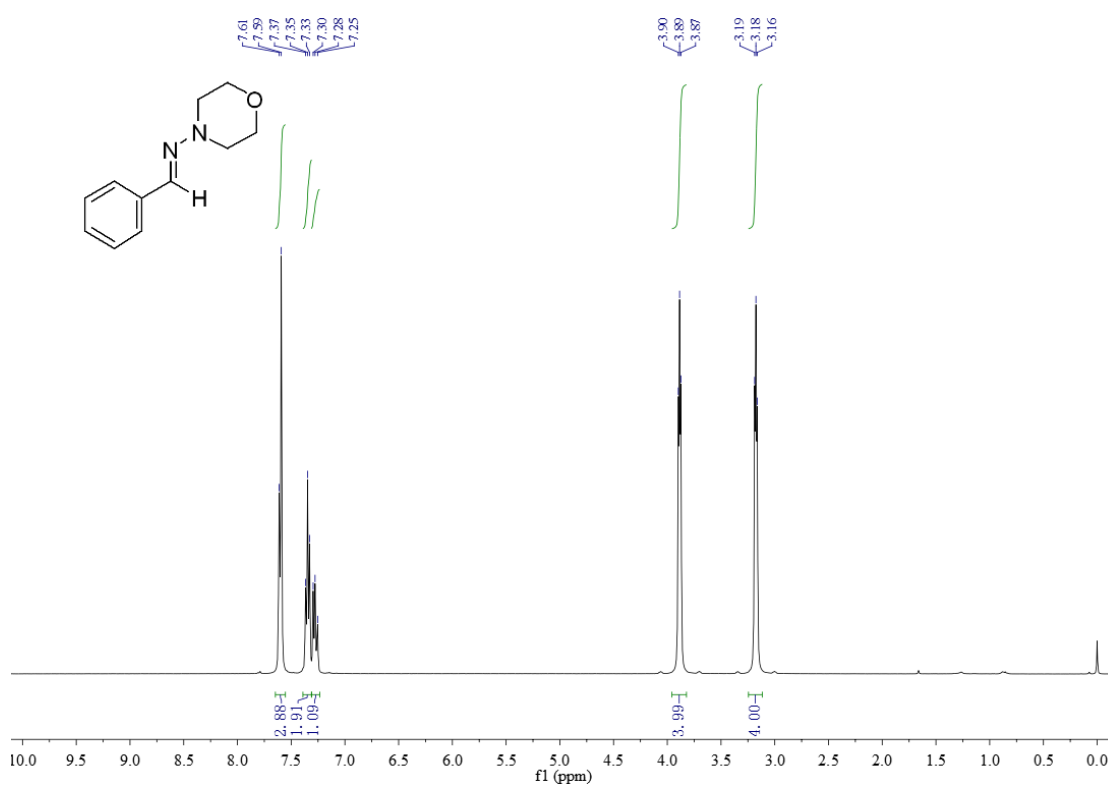
¹H NMR of **1c**



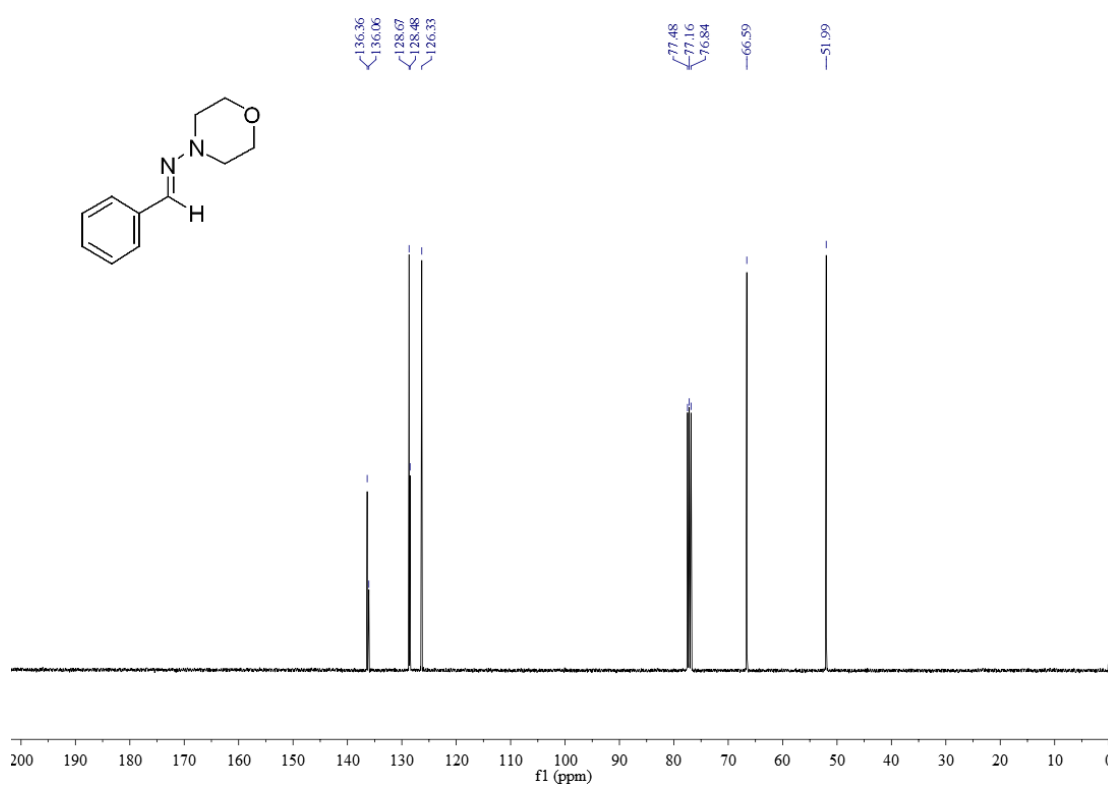
¹³C NMR of **1c**



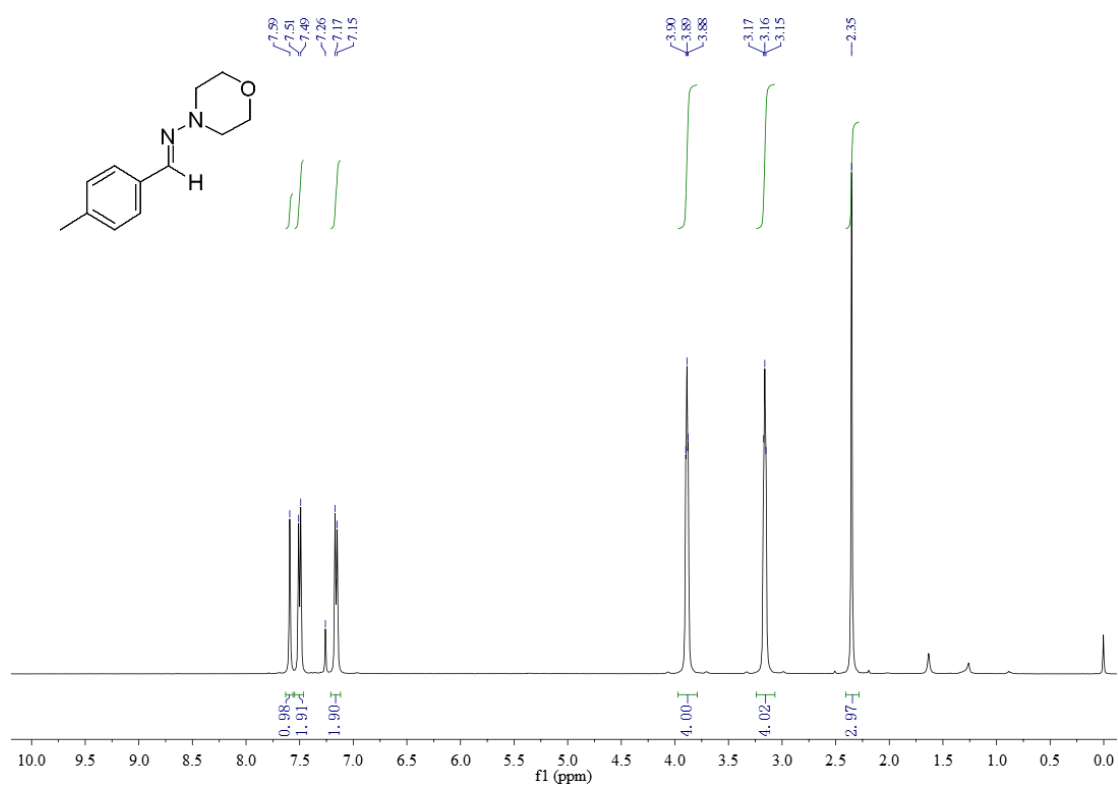
¹H NMR of **1d**



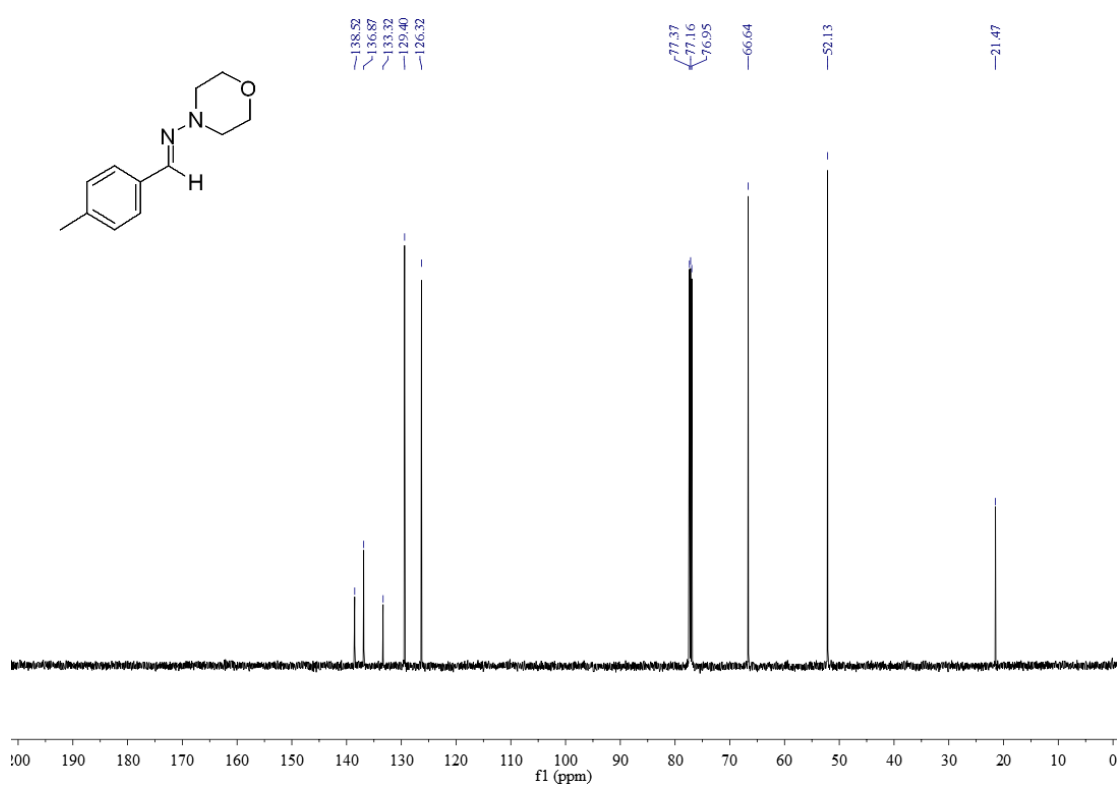
¹³C NMR of **1d**



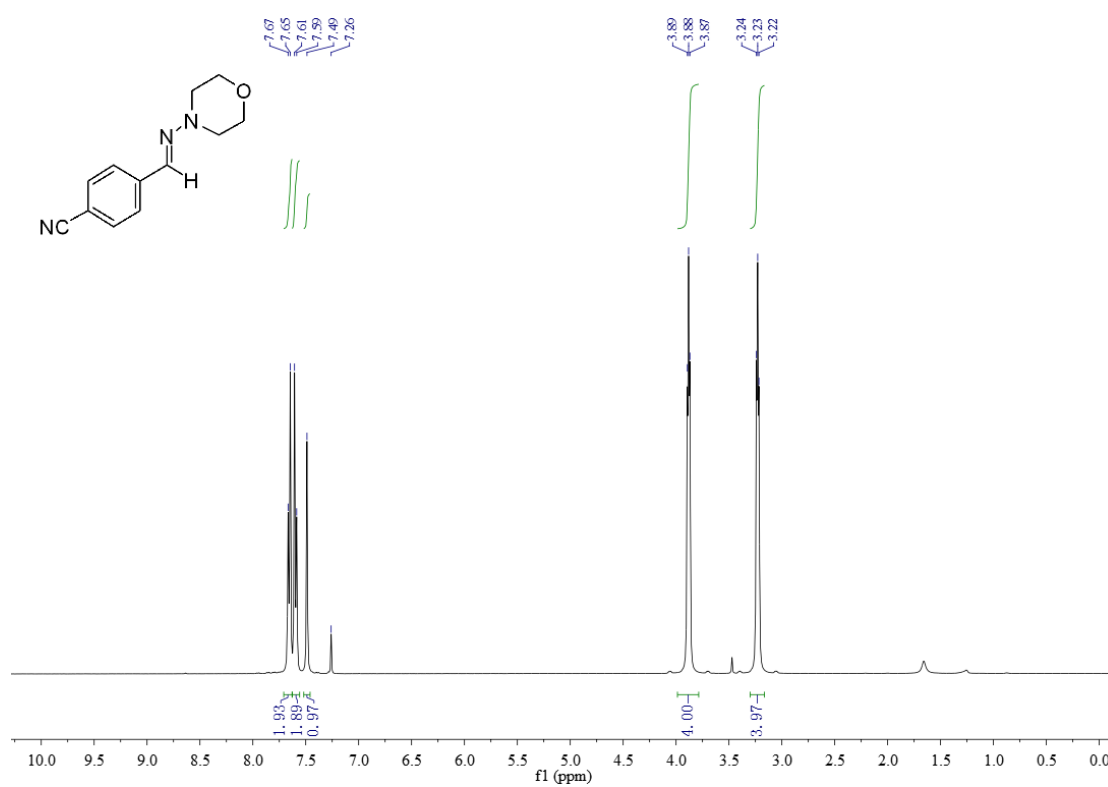
¹H NMR of **1e**



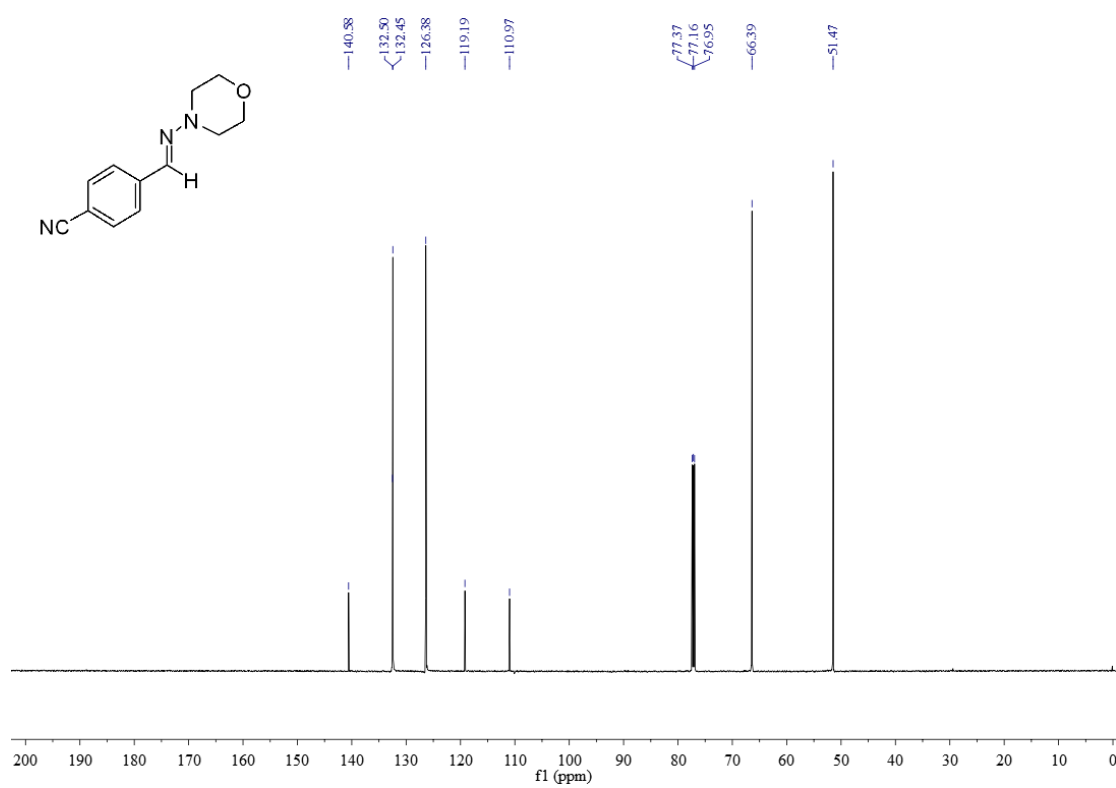
¹³C NMR of **1e**



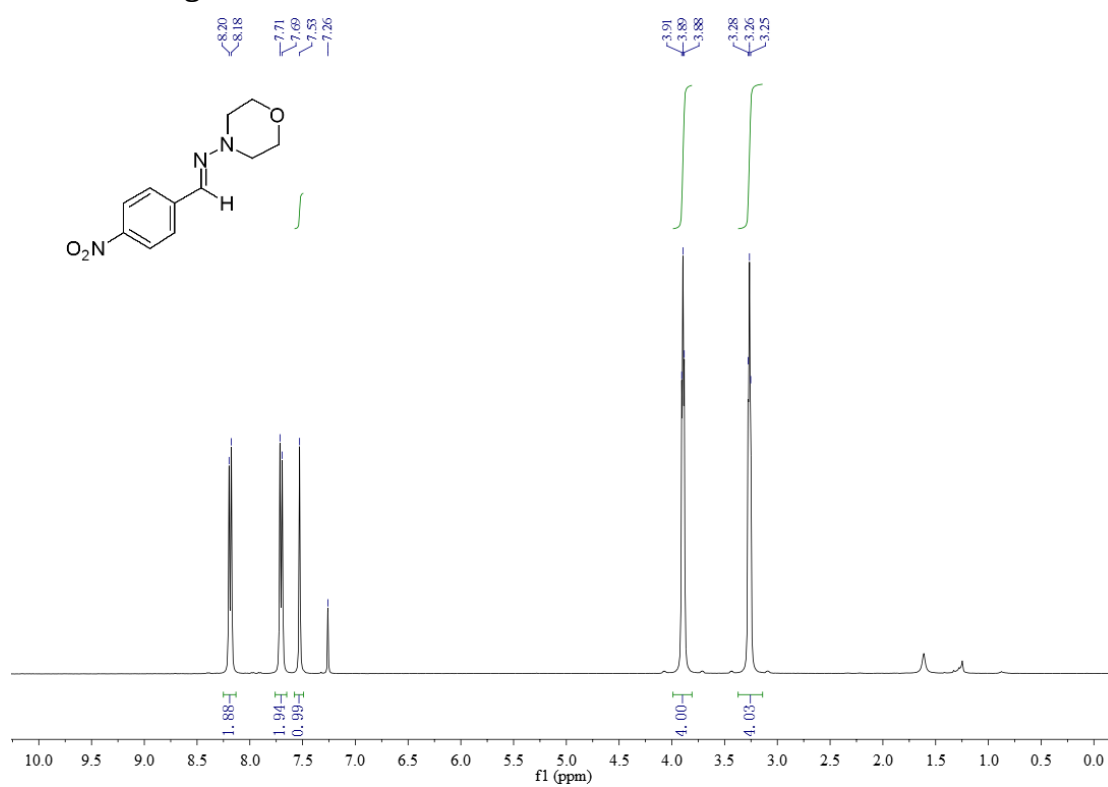
¹H NMR of **1f**



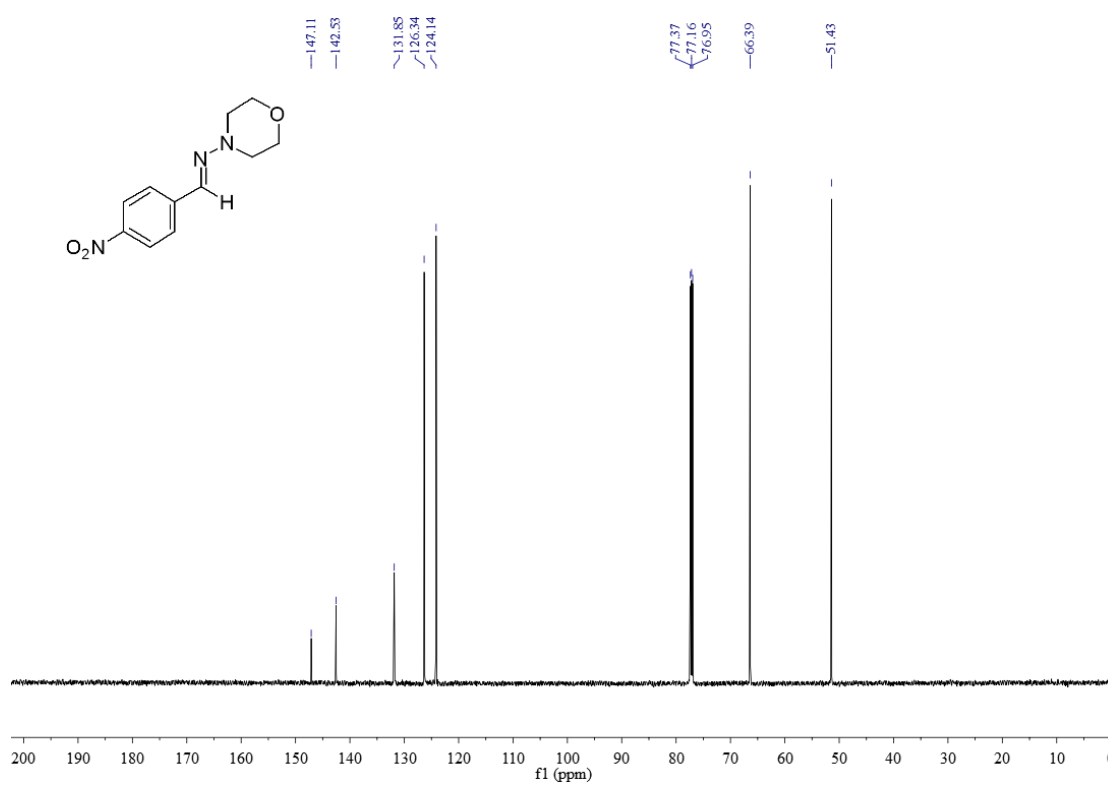
¹³C NMR of **1f**



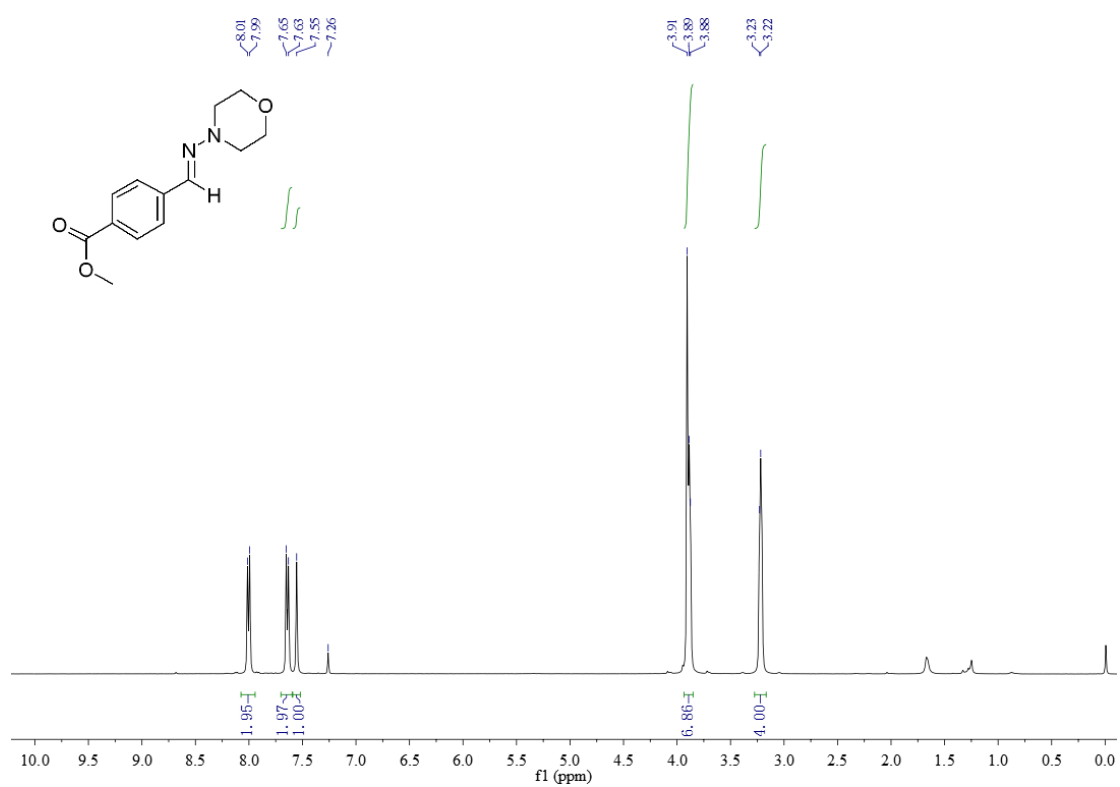
¹H NMR of **1g**



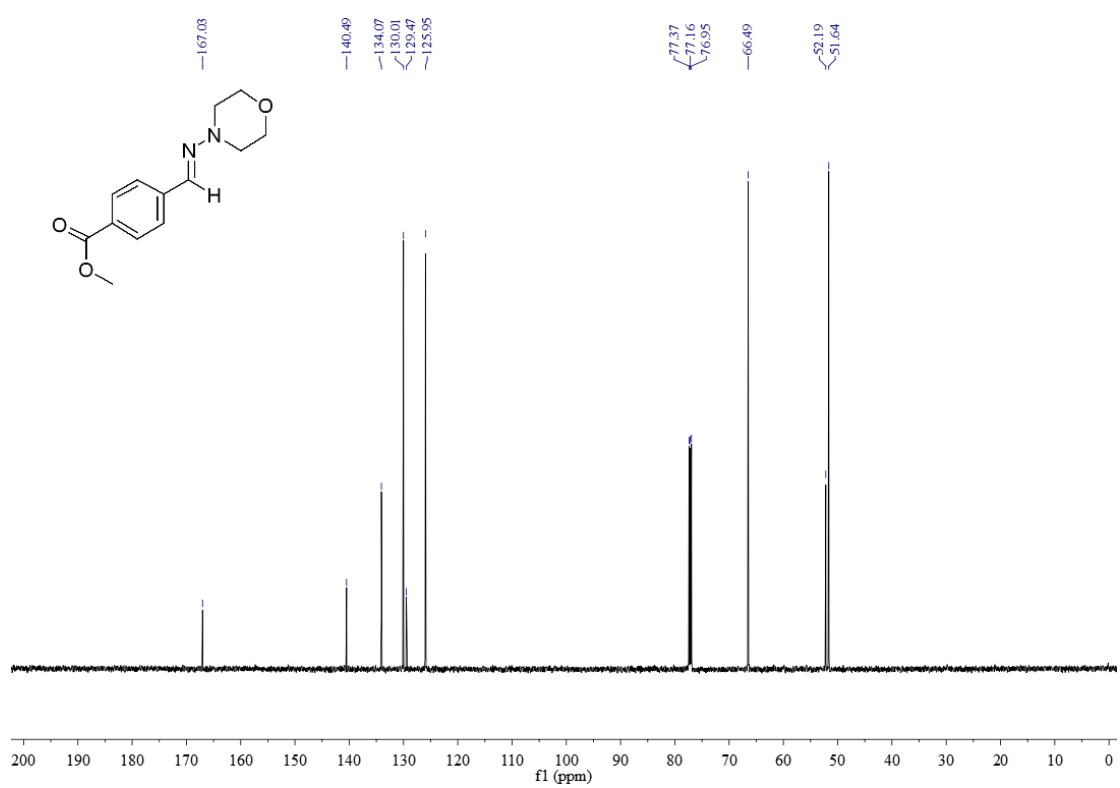
¹³C NMR of **1g**



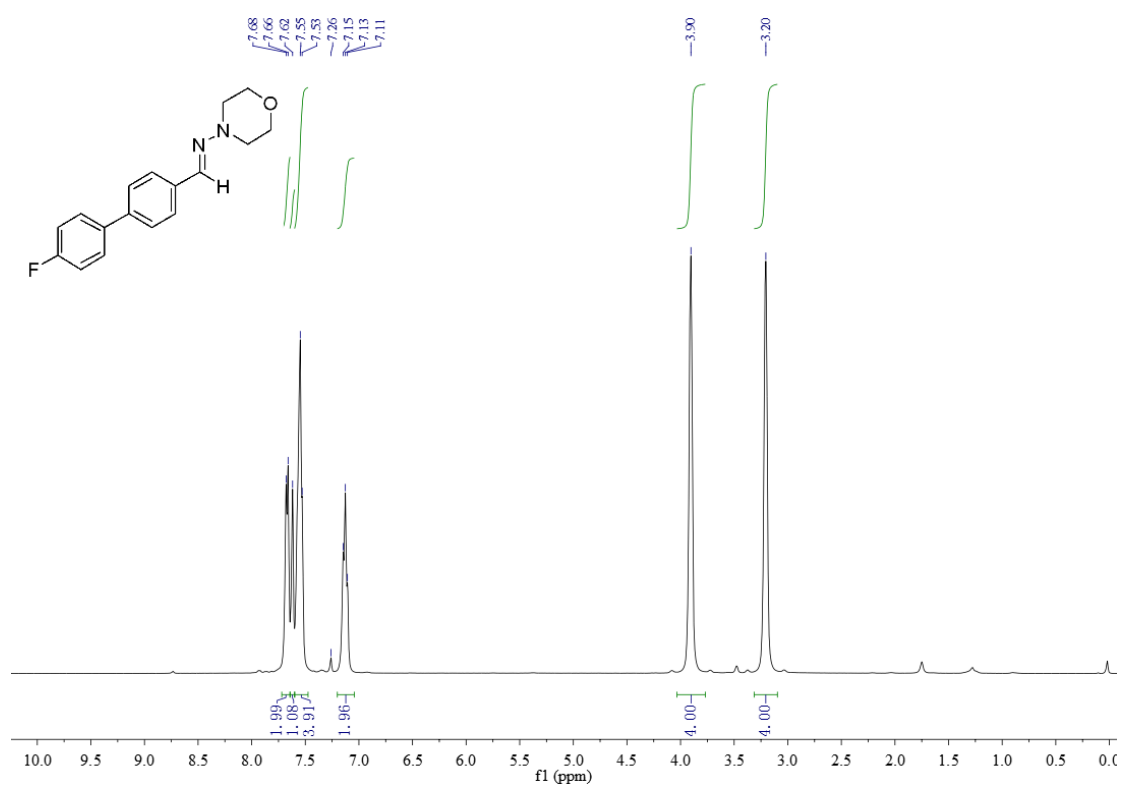
¹H NMR of **1h**



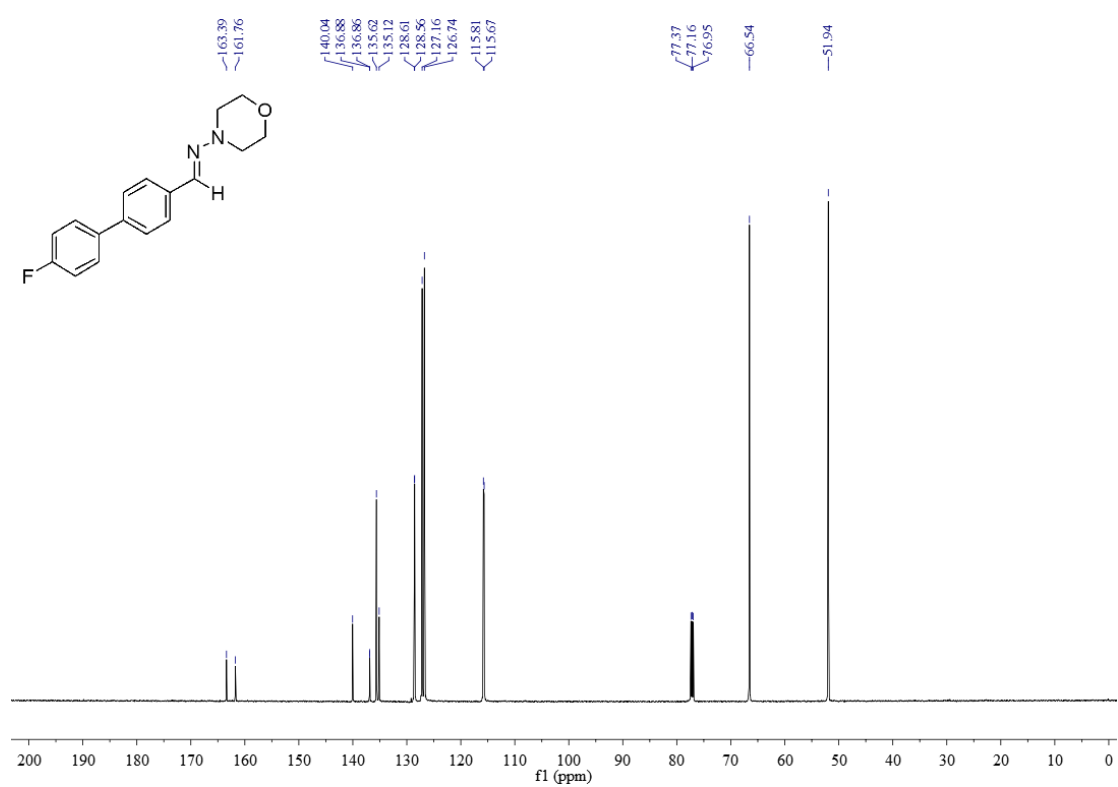
¹³C NMR of **1h**



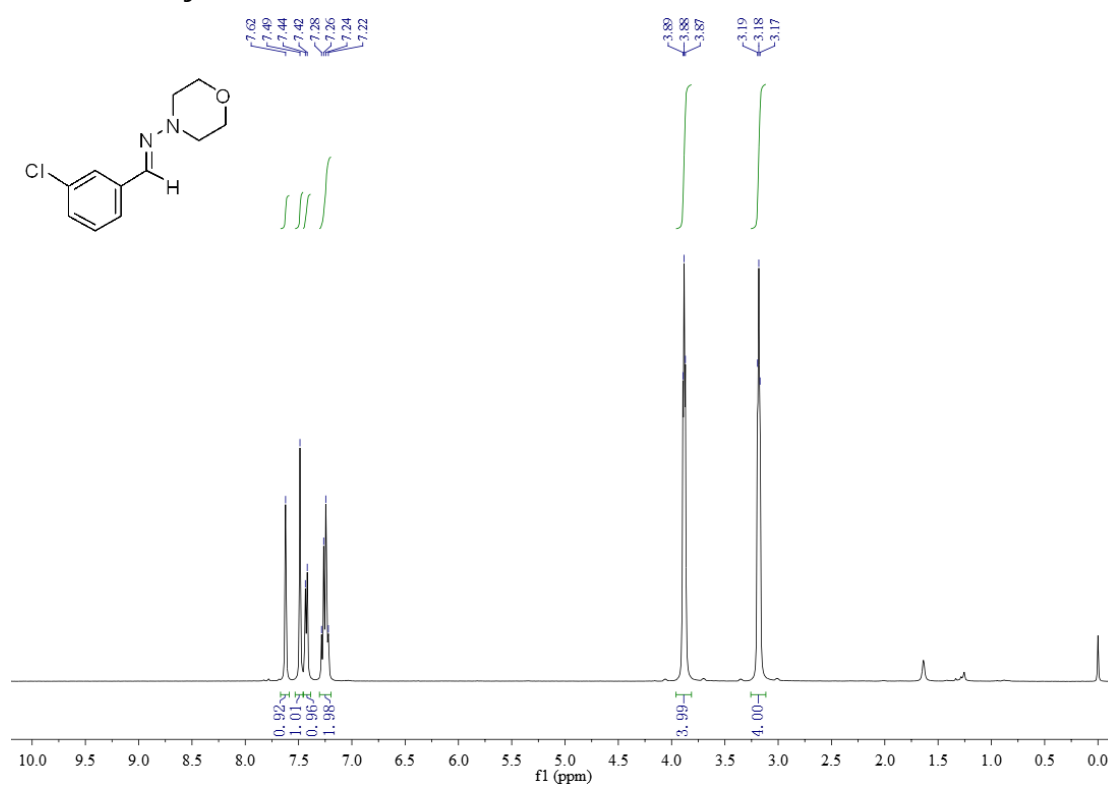
¹H NMR of **1i**



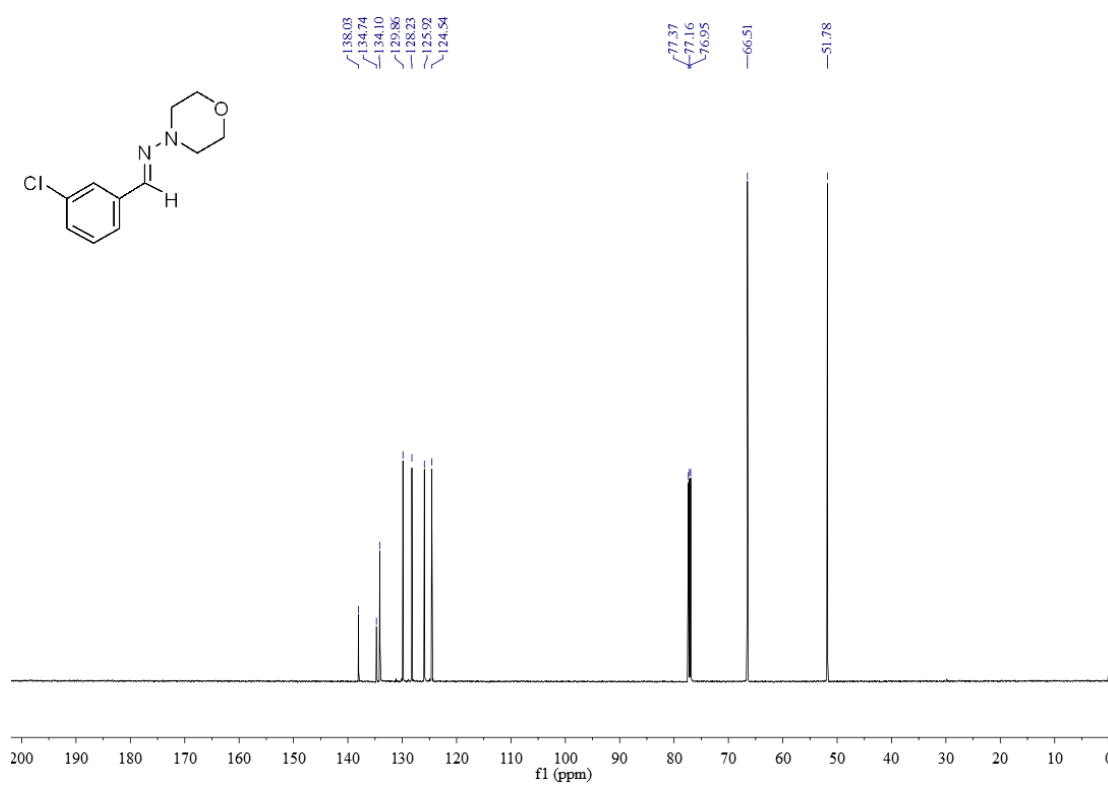
¹³C NMR of **1i**



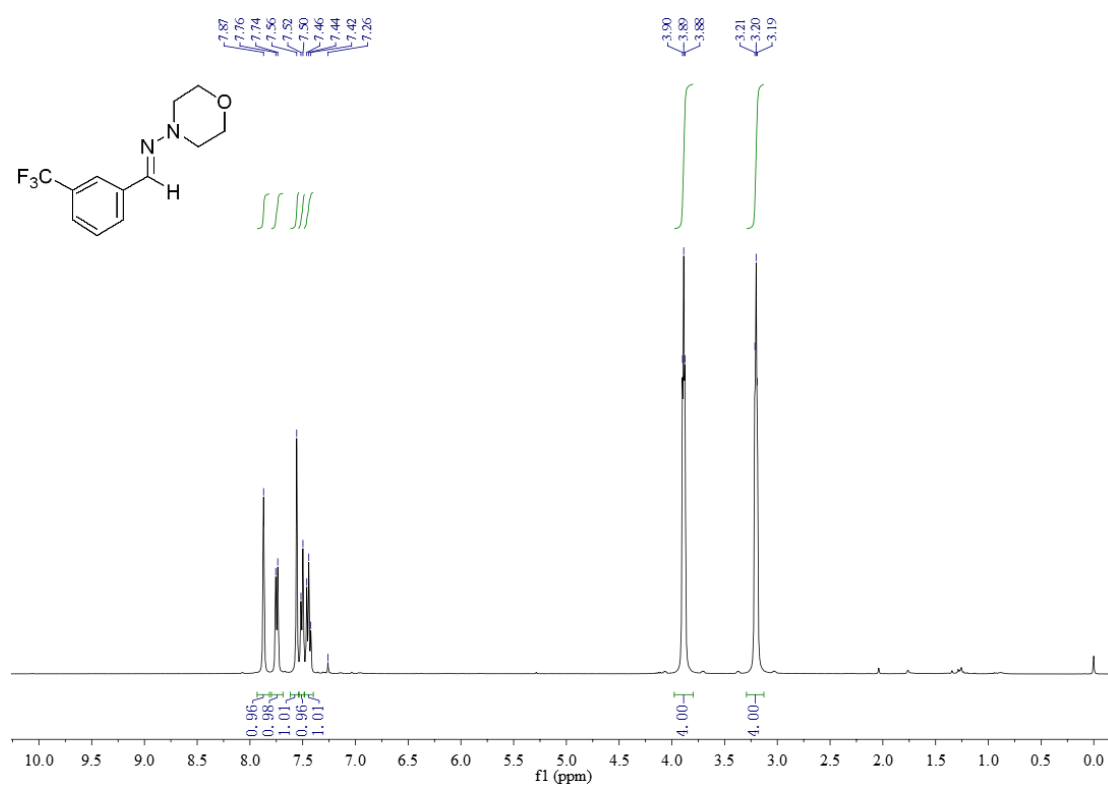
¹H NMR of **1j**



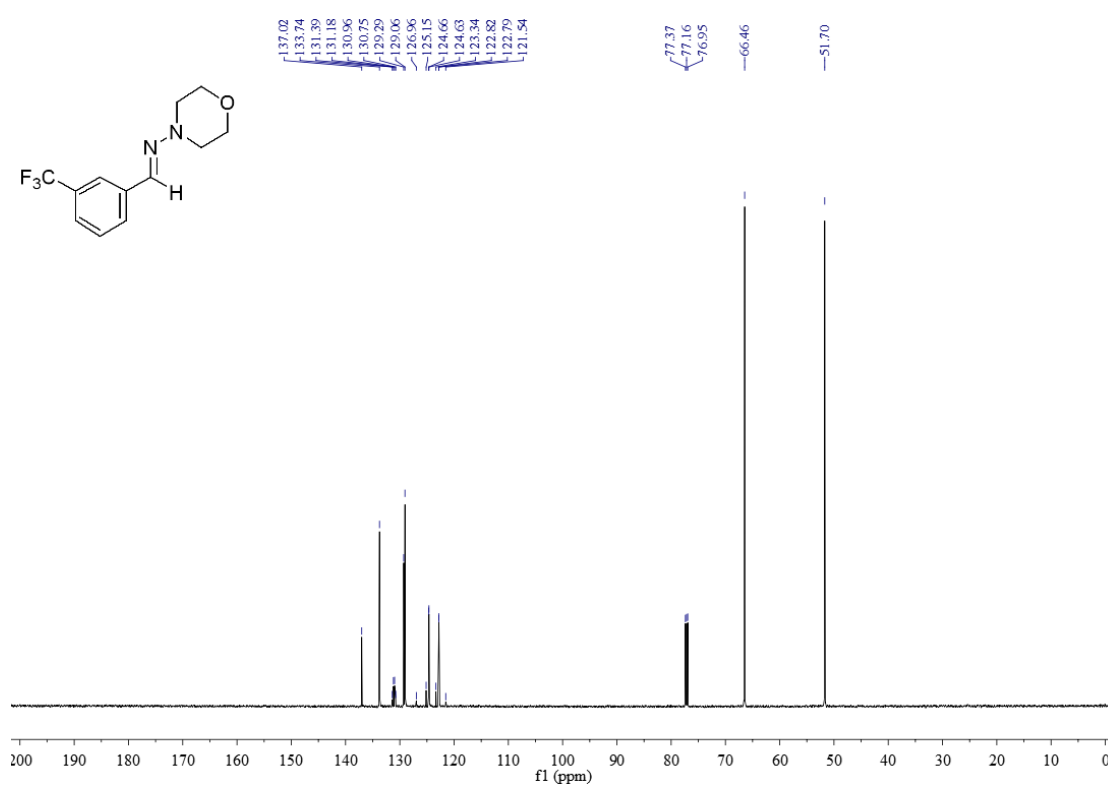
¹³C NMR of **1j**



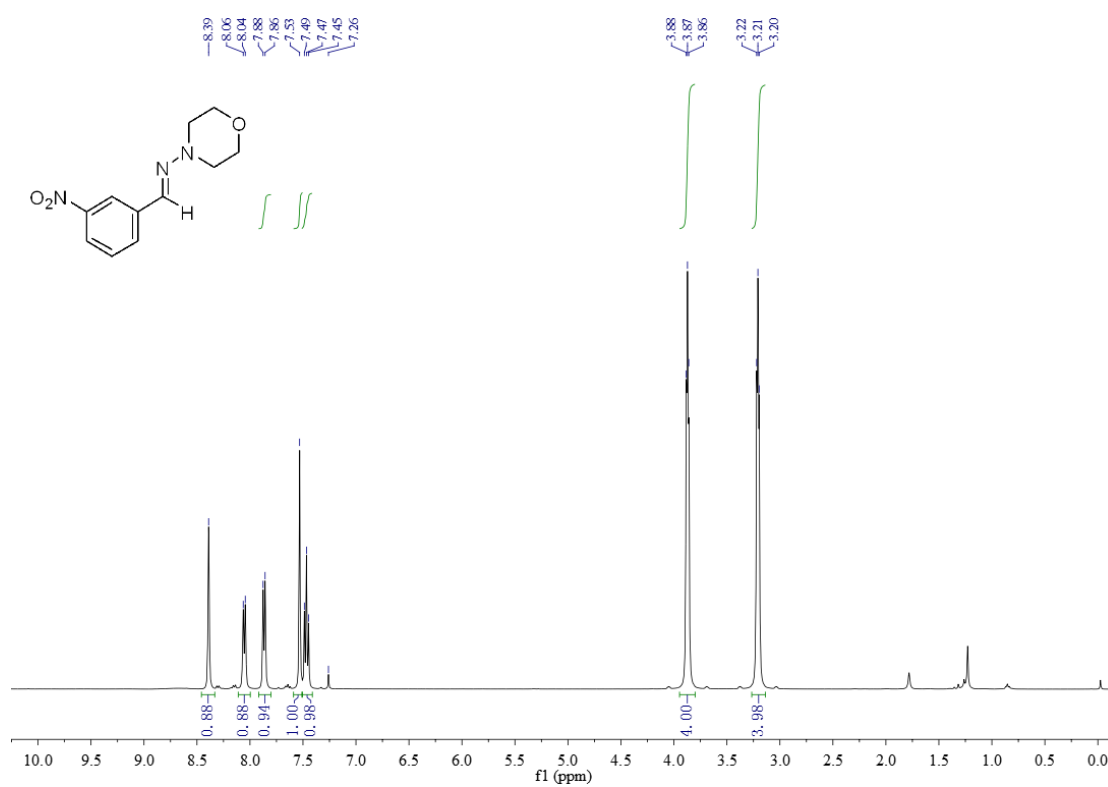
¹H NMR of **1k**



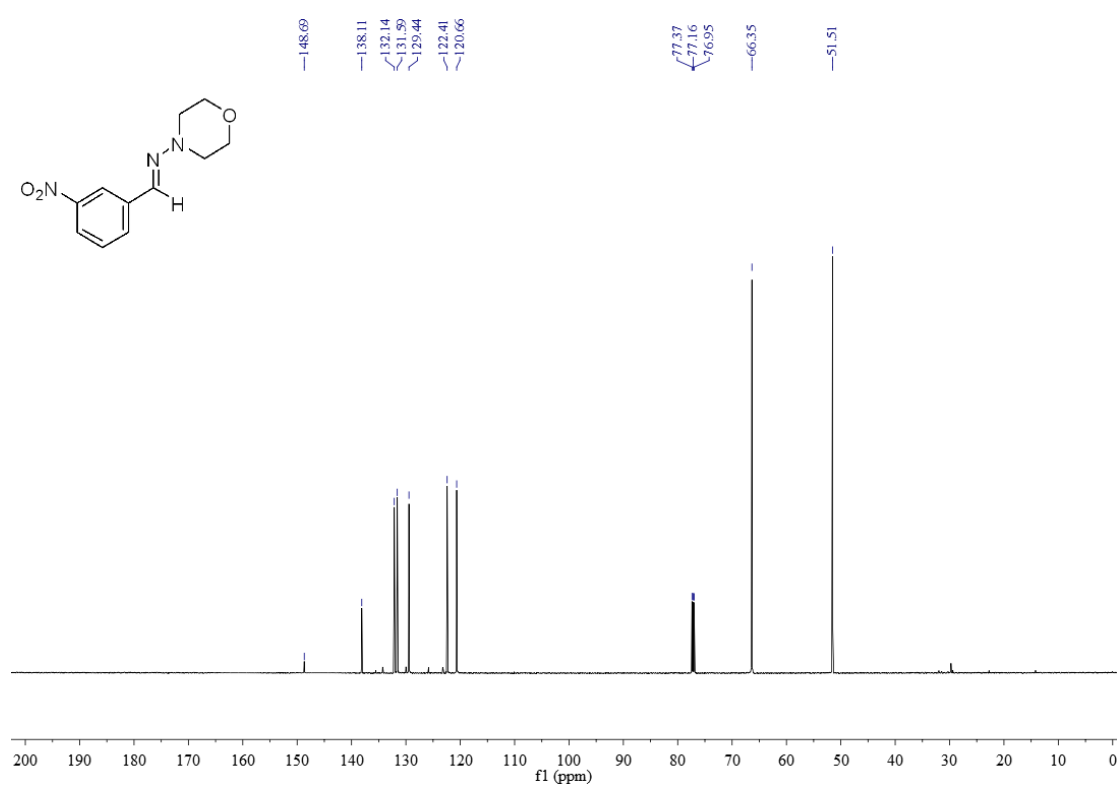
¹³C NMR of **1k**



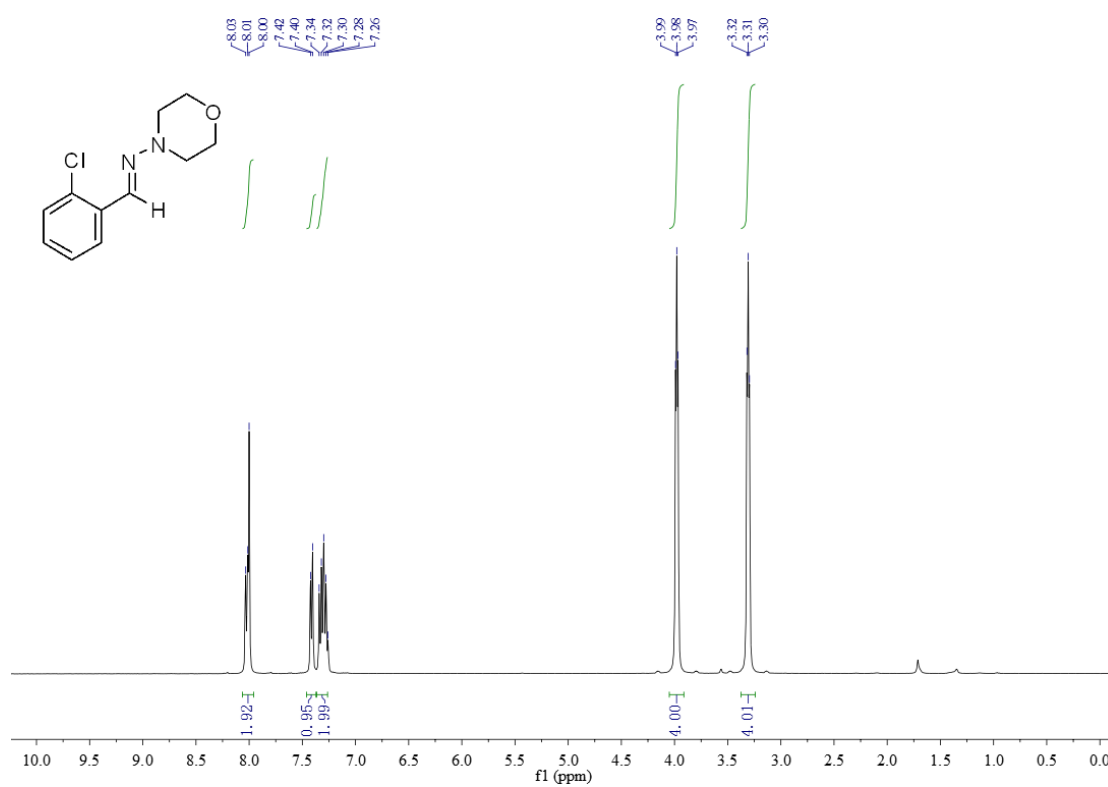
¹H NMR of **11**



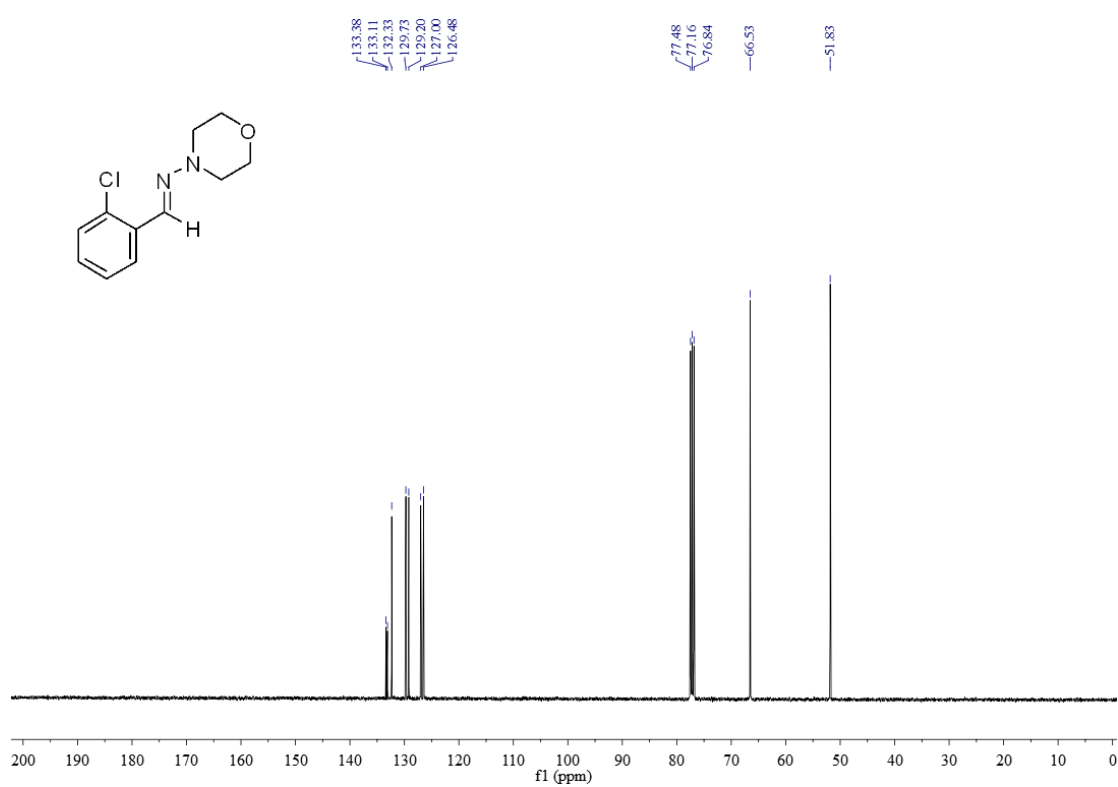
¹³C NMR of **11**



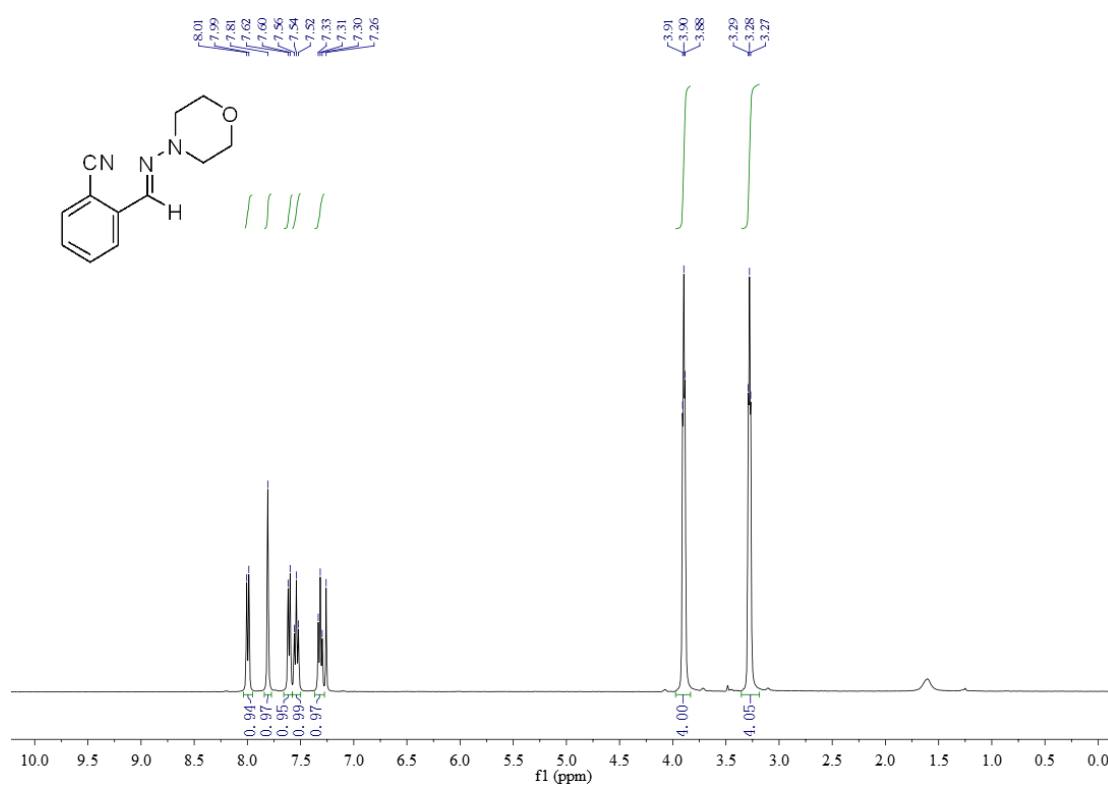
¹H NMR of **1m**



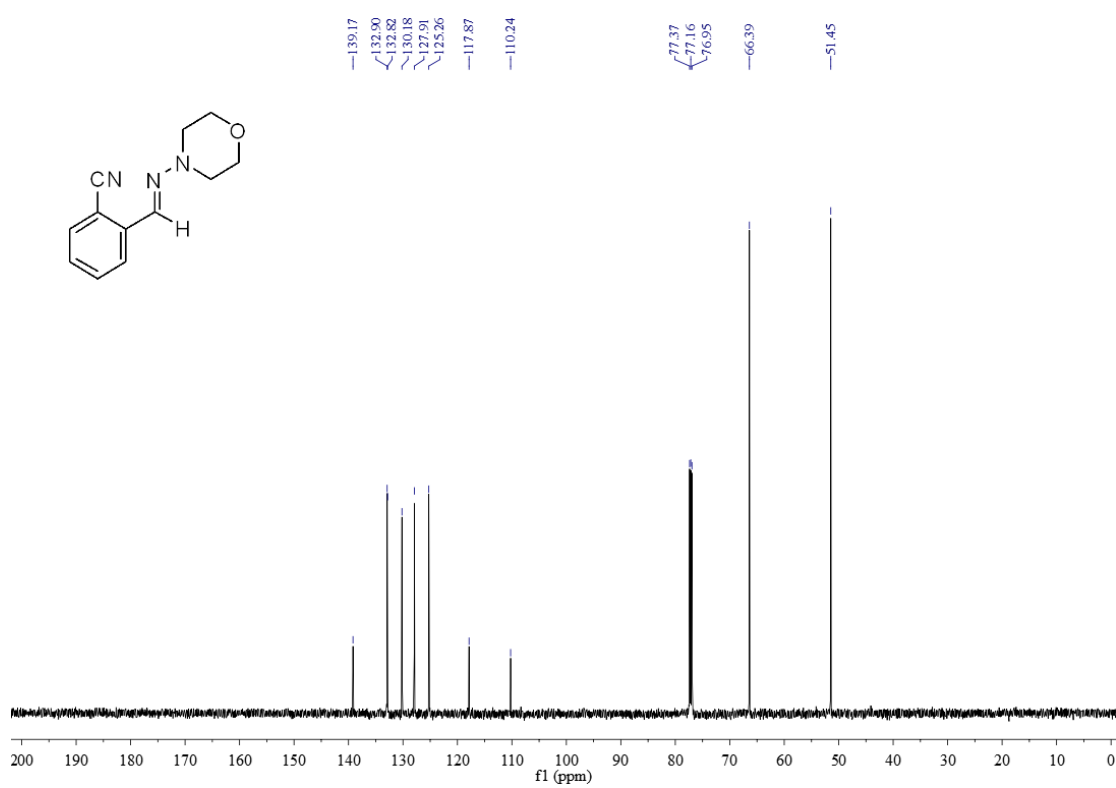
¹³C NMR of **1m**



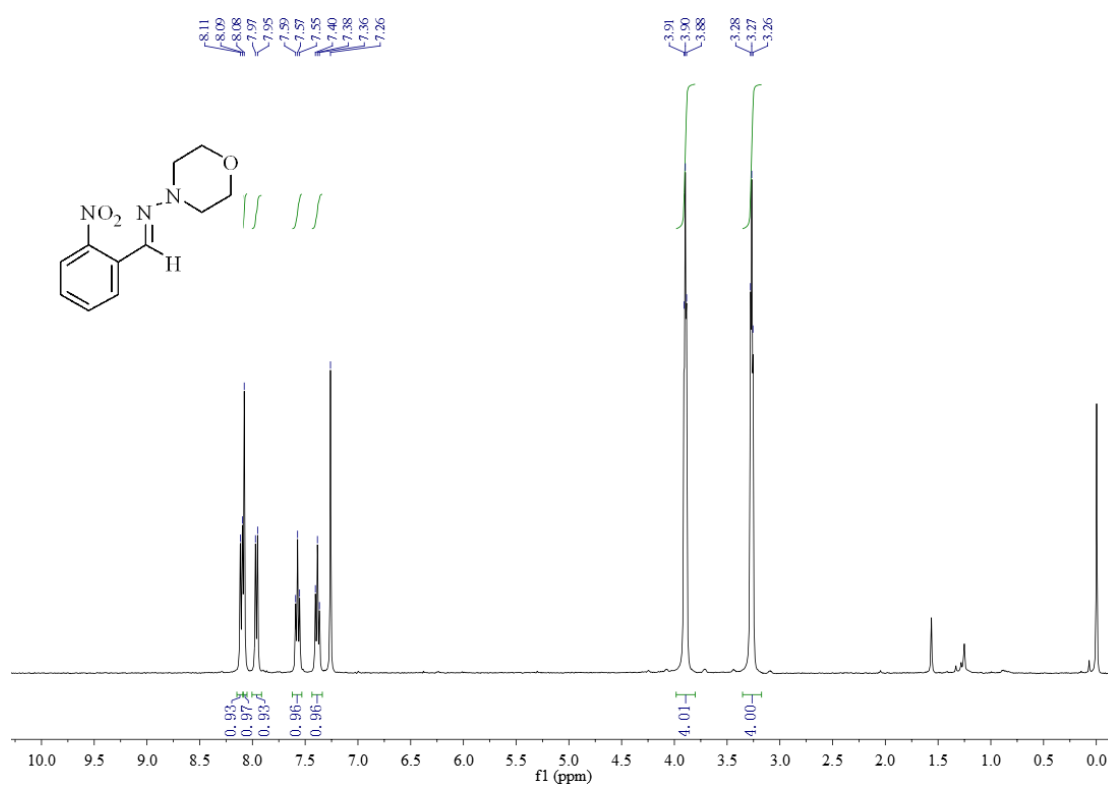
¹H NMR of **1n**



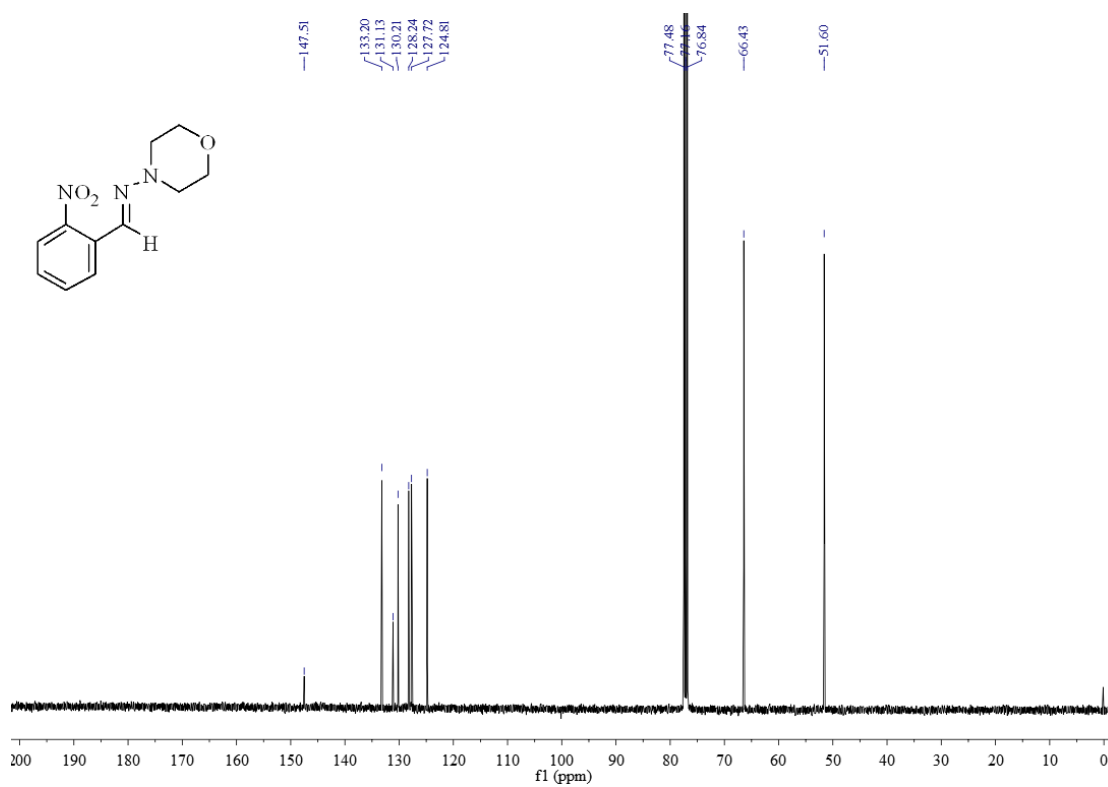
¹³C NMR of **1n**



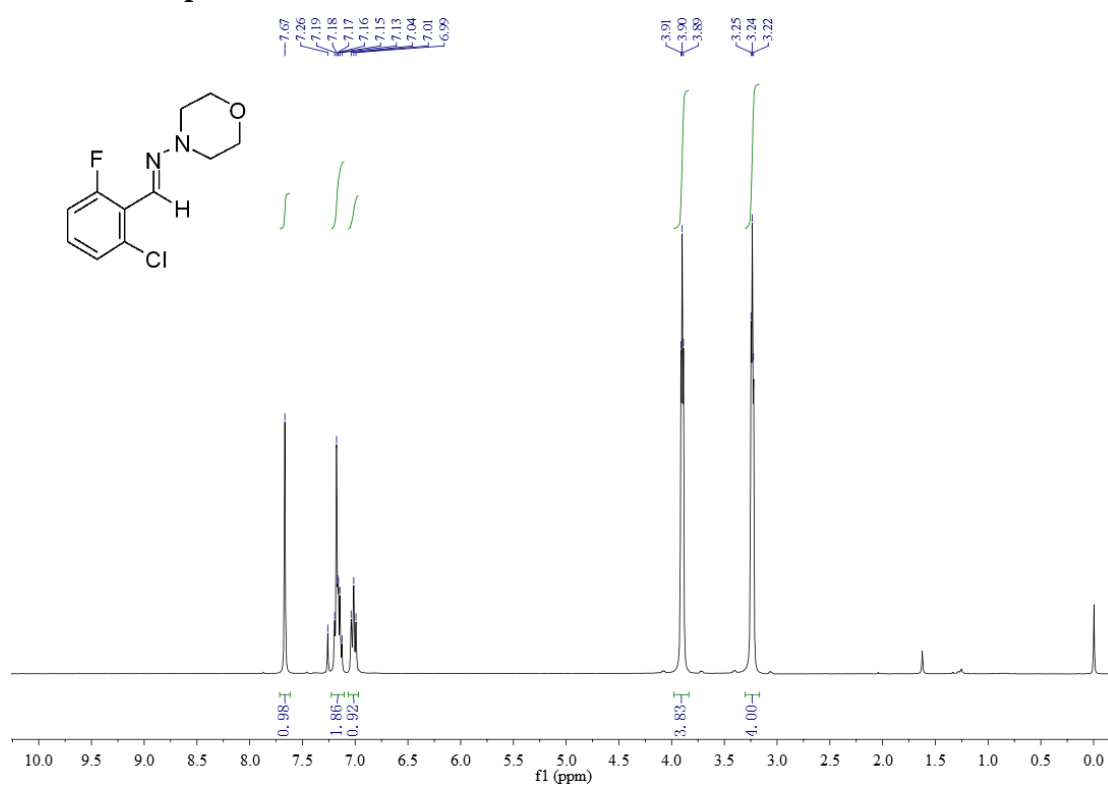
¹H NMR of **1o**



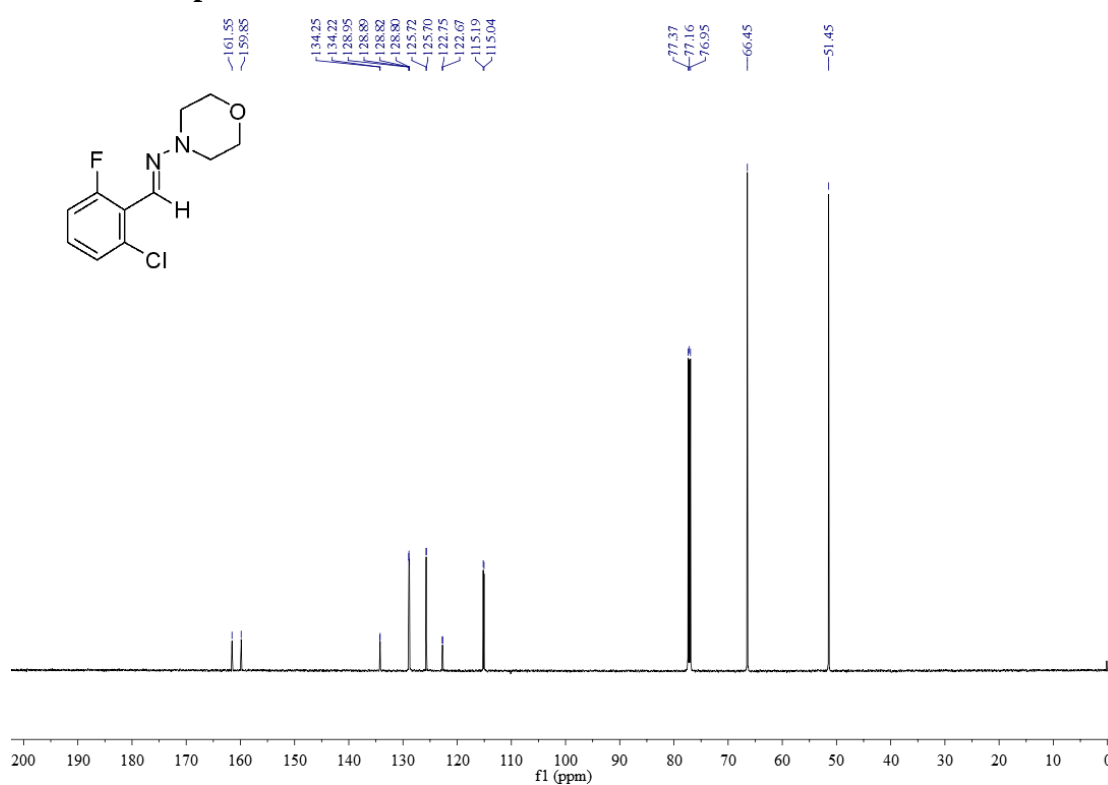
¹³C NMR of **1o**



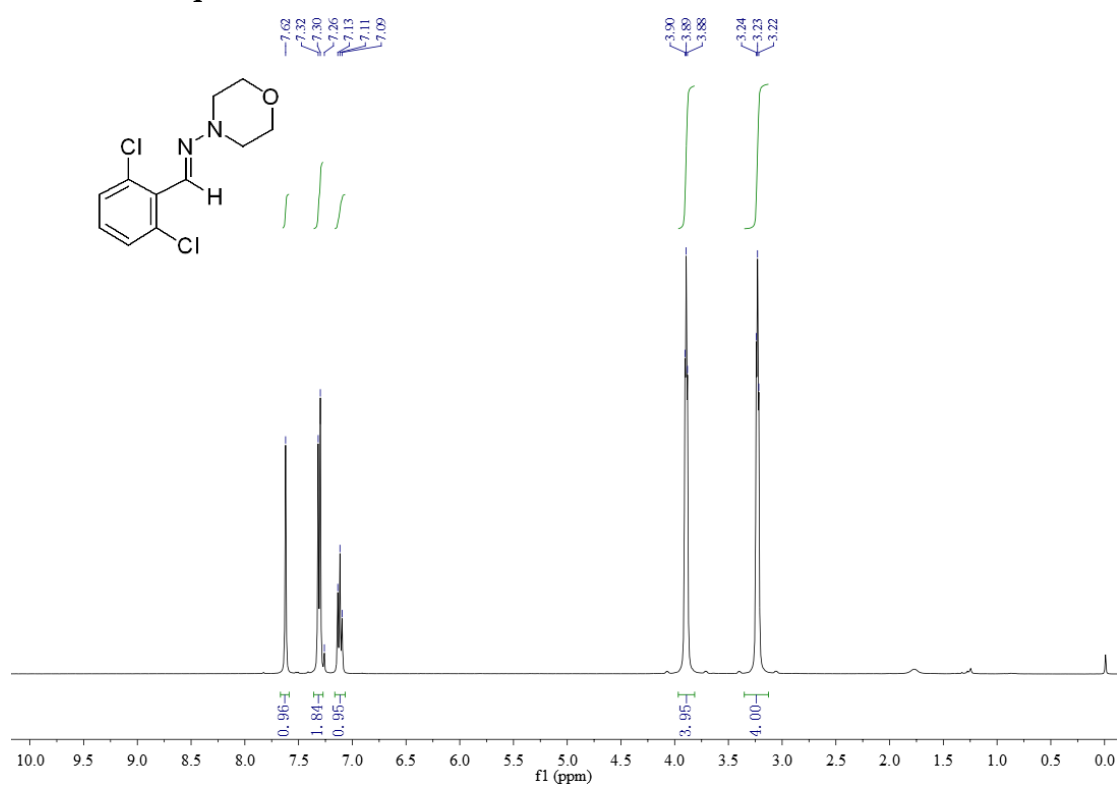
¹H NMR of **1p**



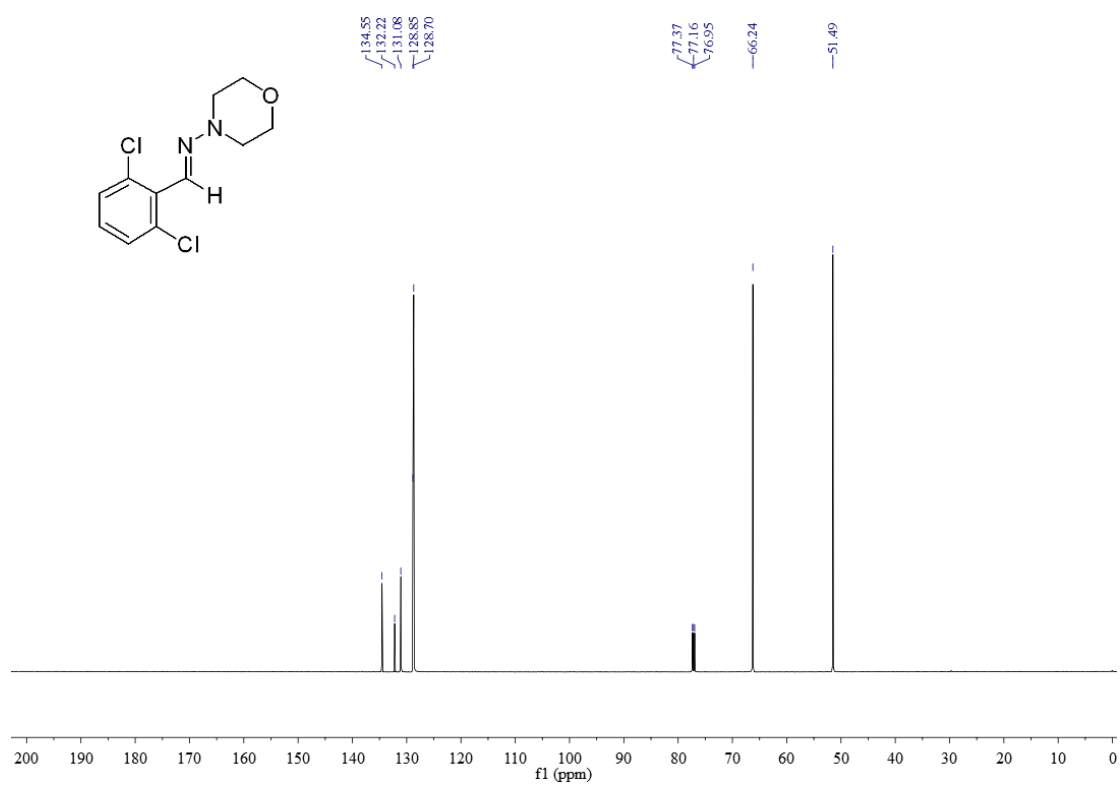
¹³C NMR of **1p**



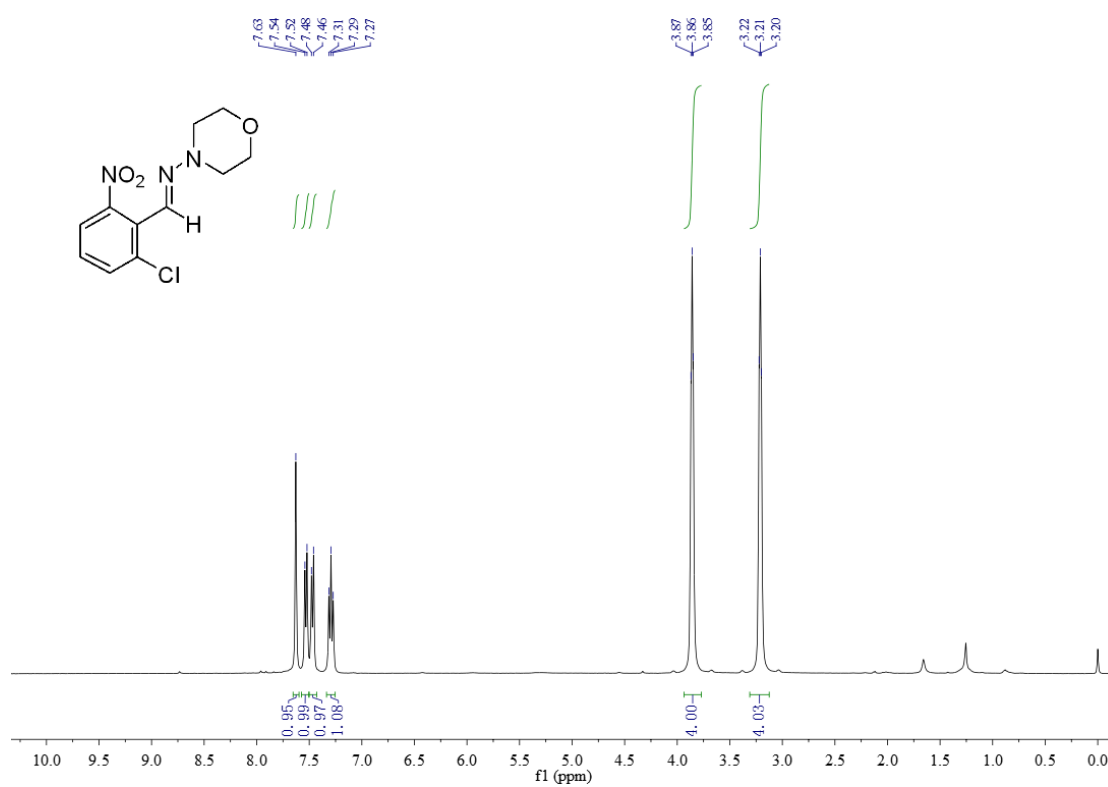
¹H NMR of **1q**



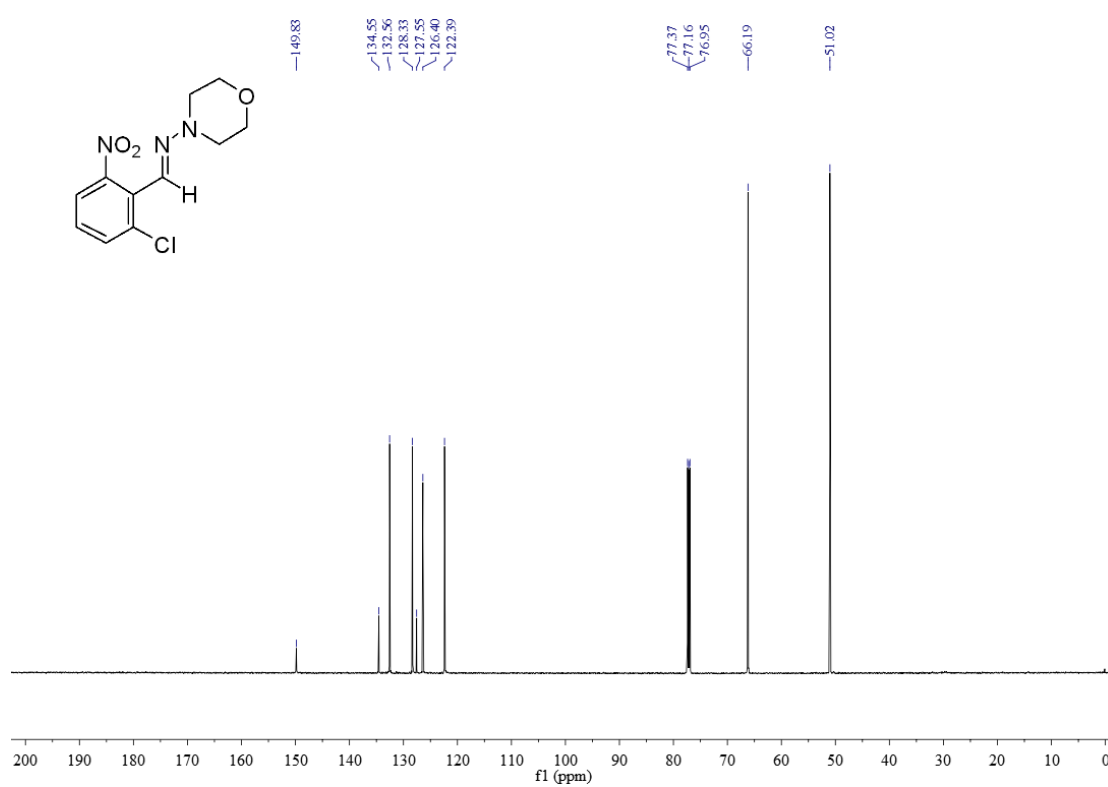
¹³C NMR of **1q**



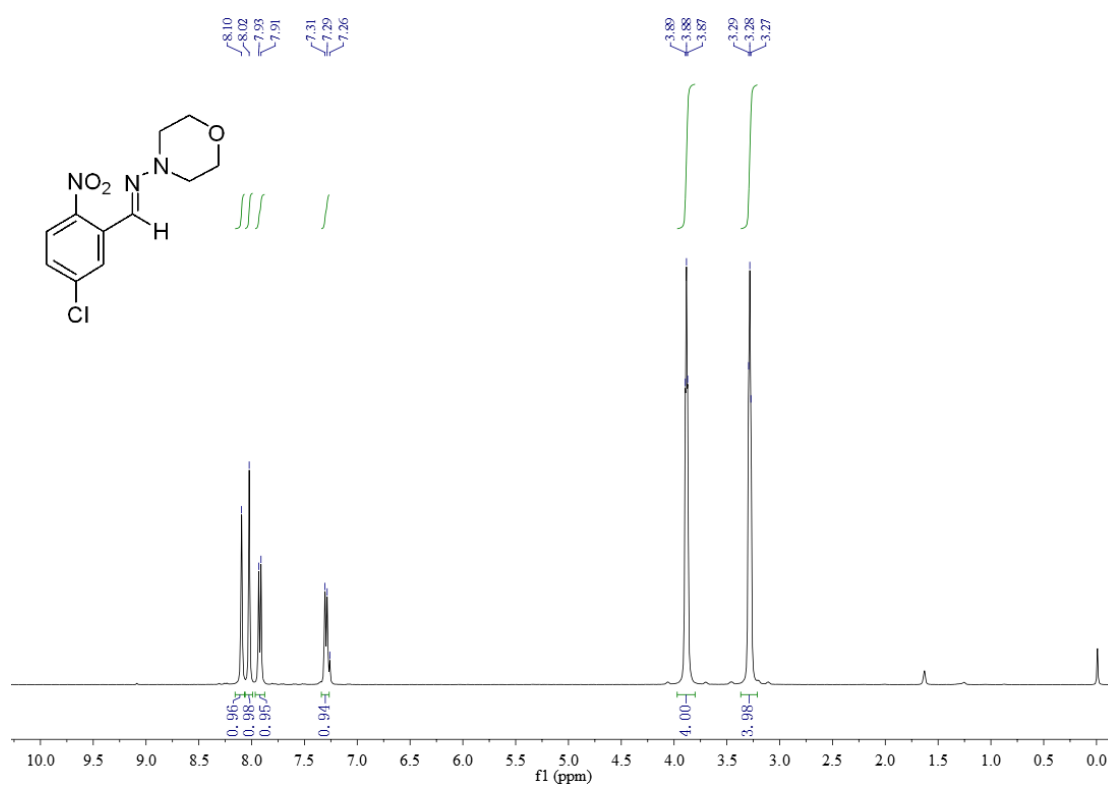
¹H NMR of **1r**



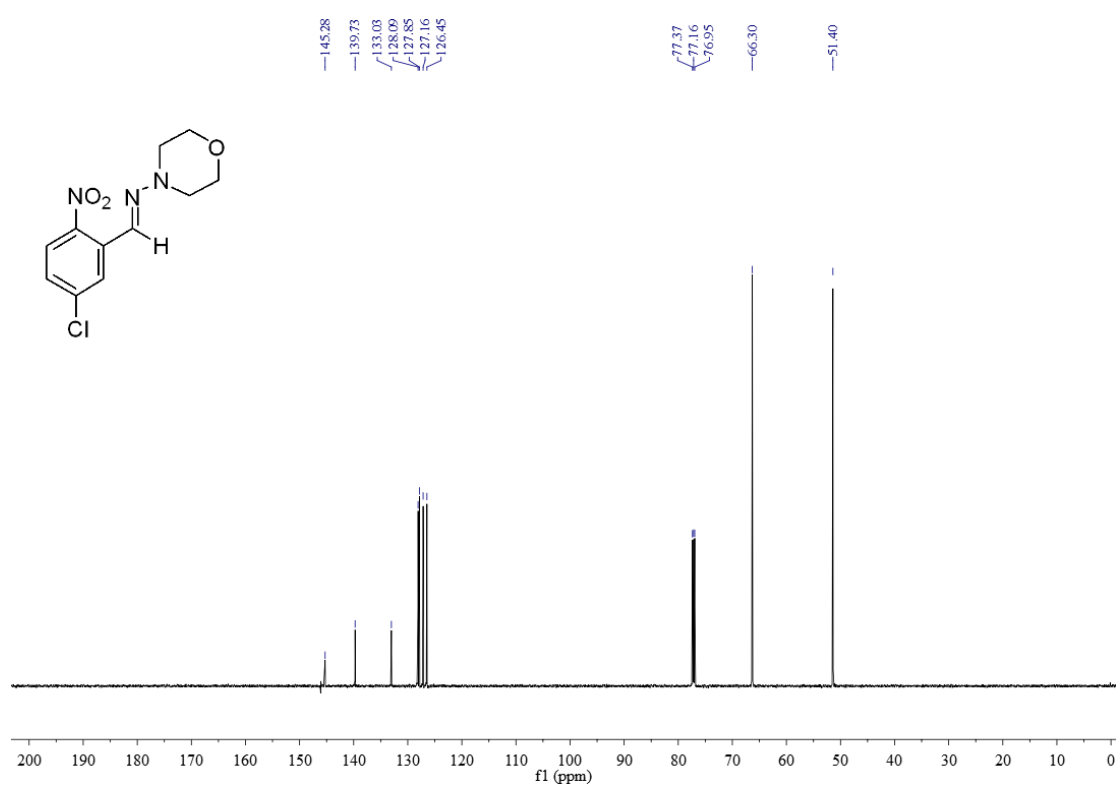
¹³C NMR of **1r**



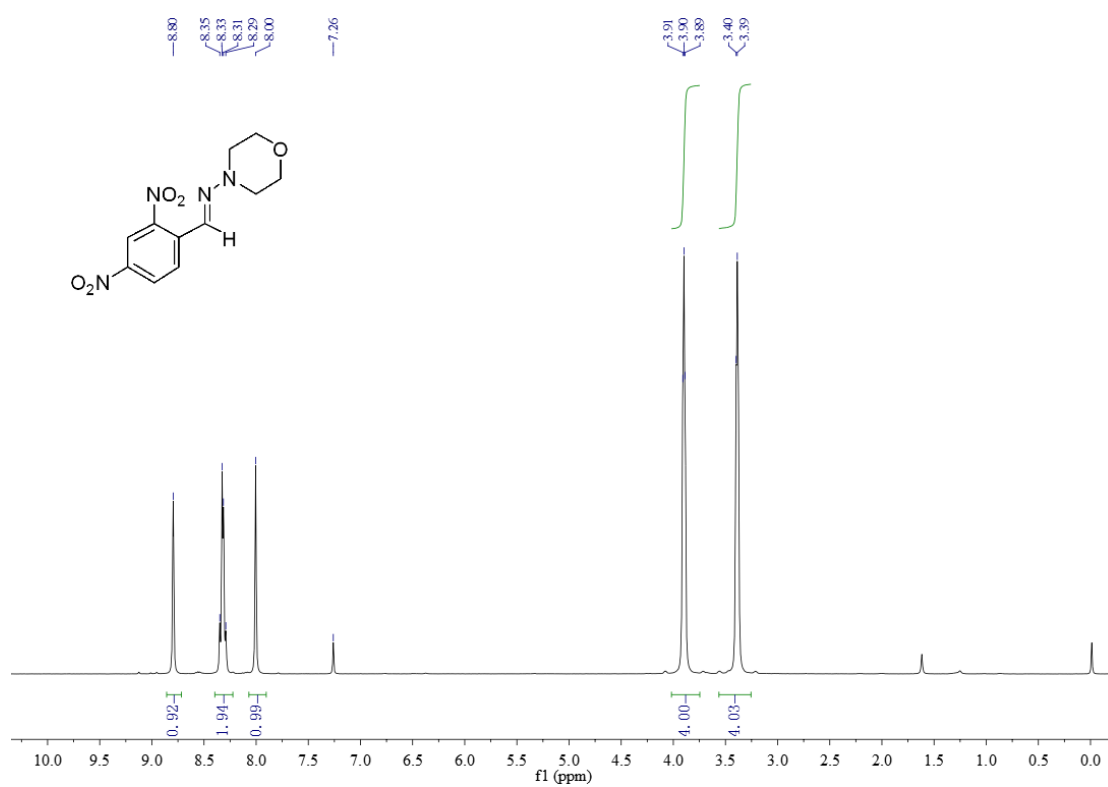
¹H NMR of **1s**



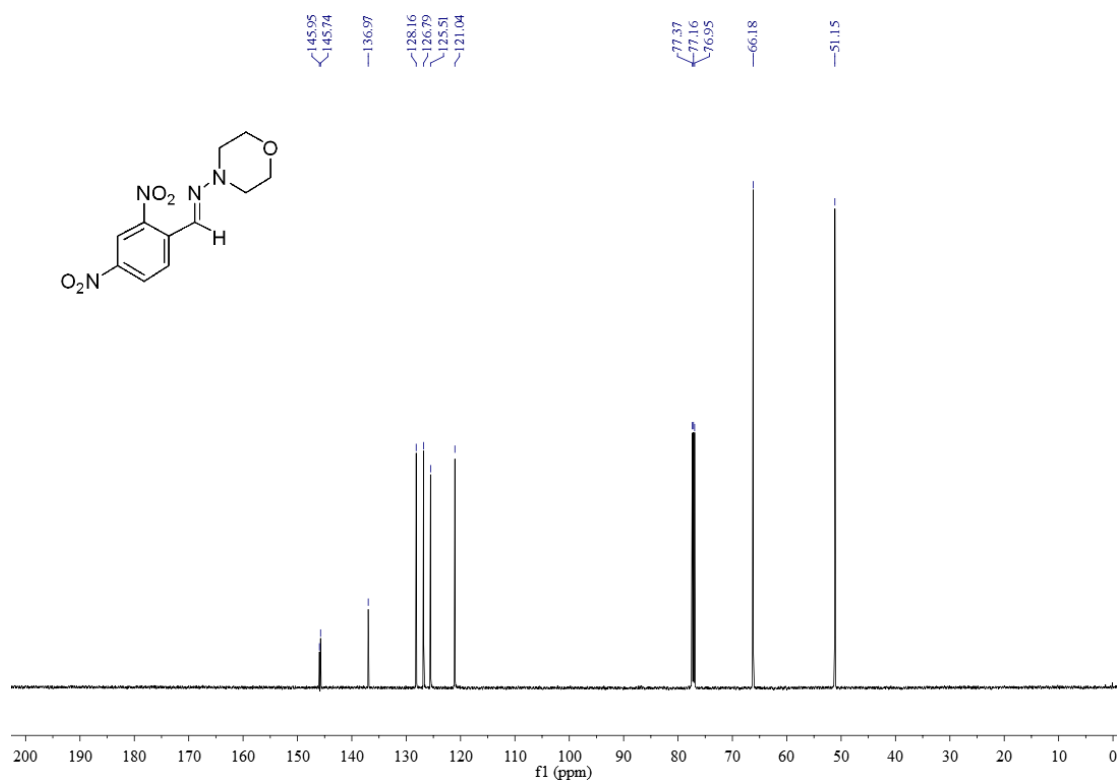
¹³C NMR of **1s**



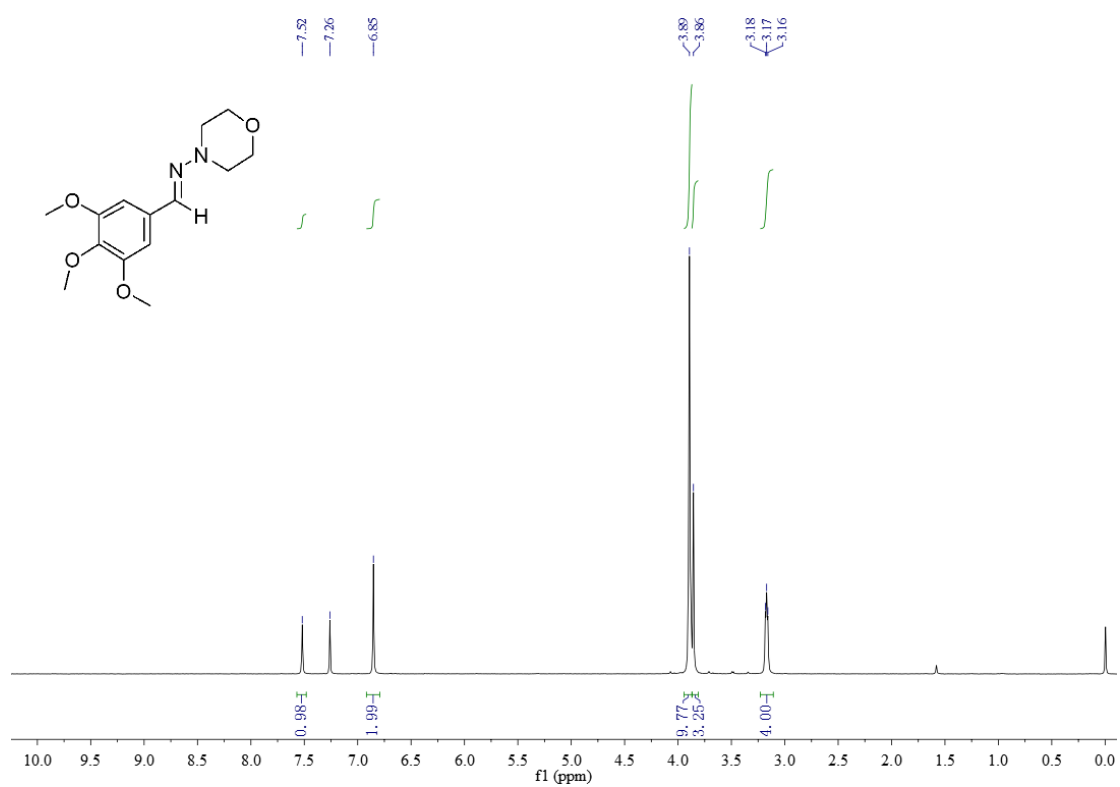
¹H NMR of **1t**



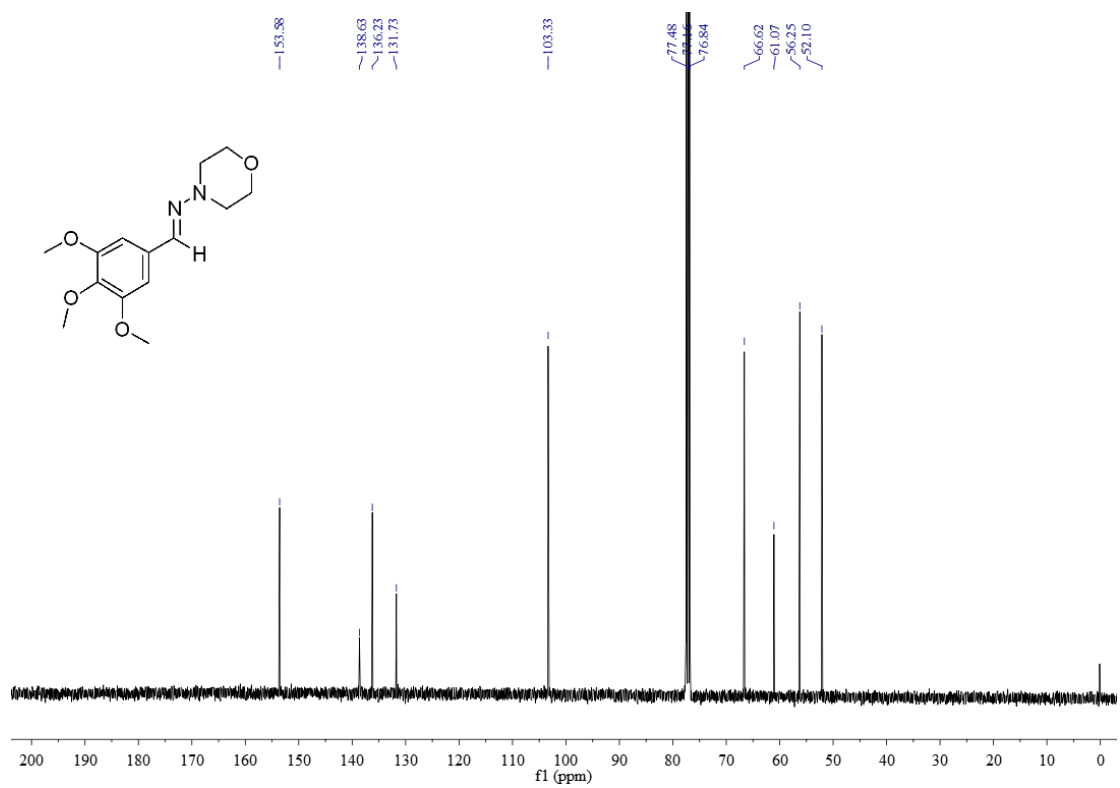
¹³C NMR of **1t**



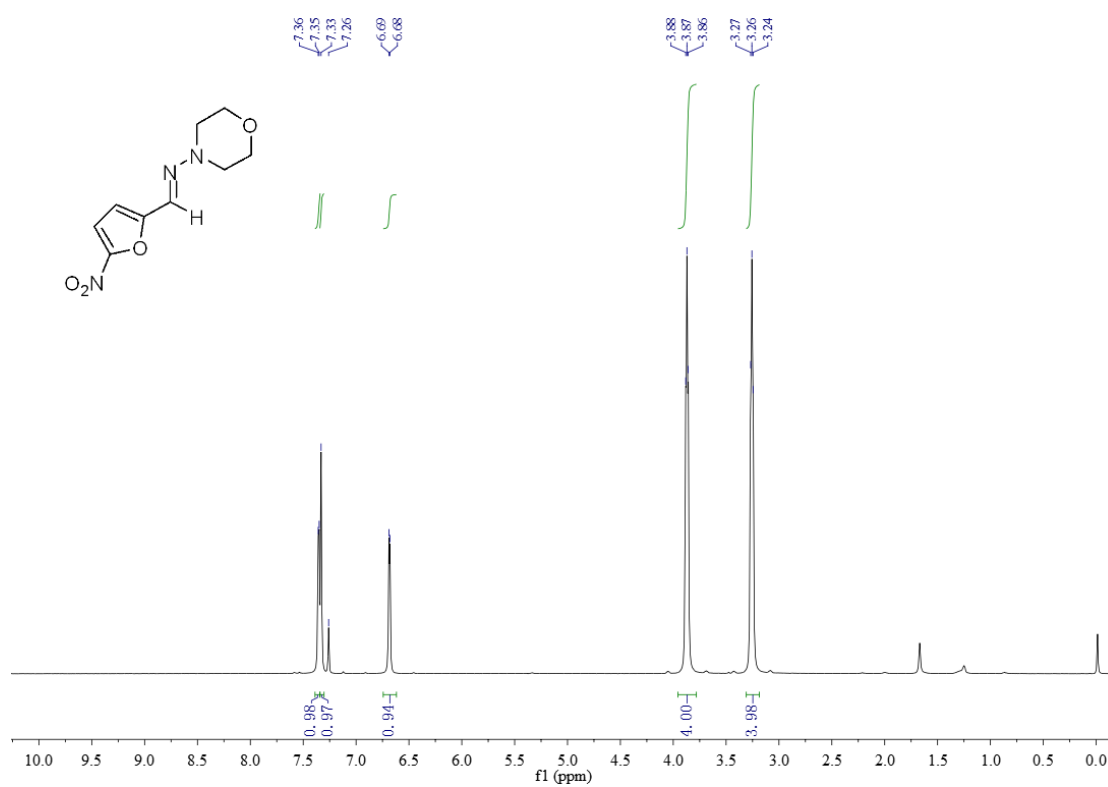
¹H NMR of **1u**



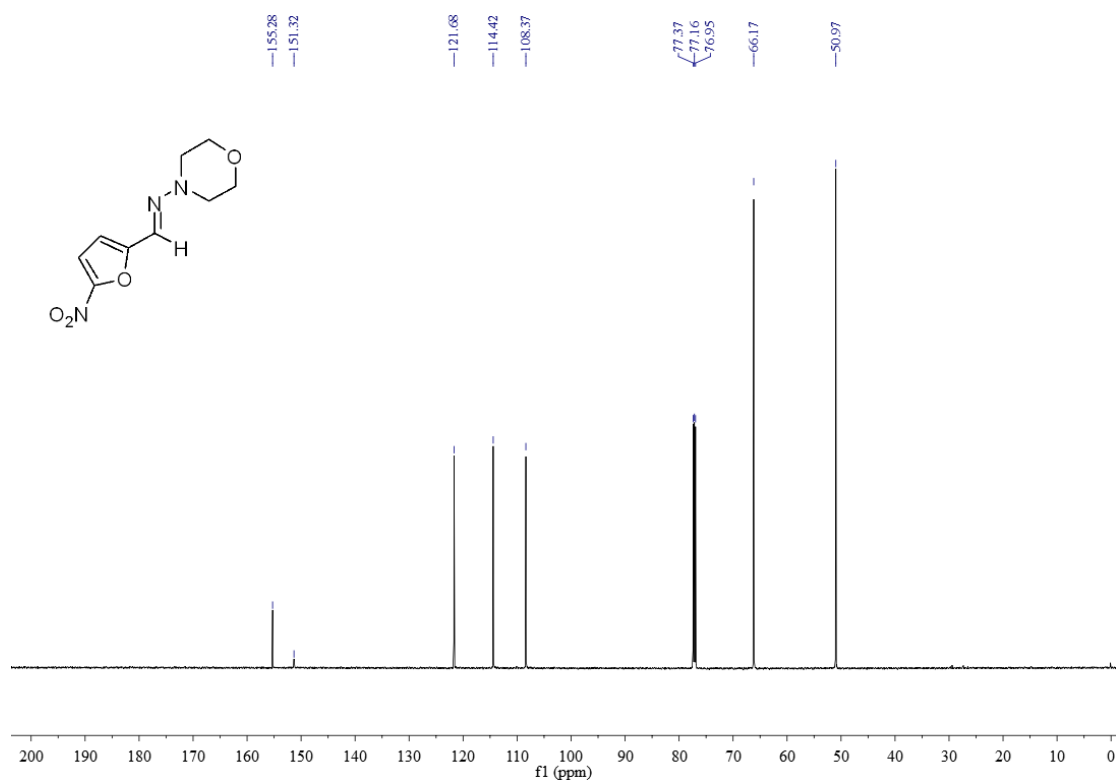
¹³C NMR of **1u**



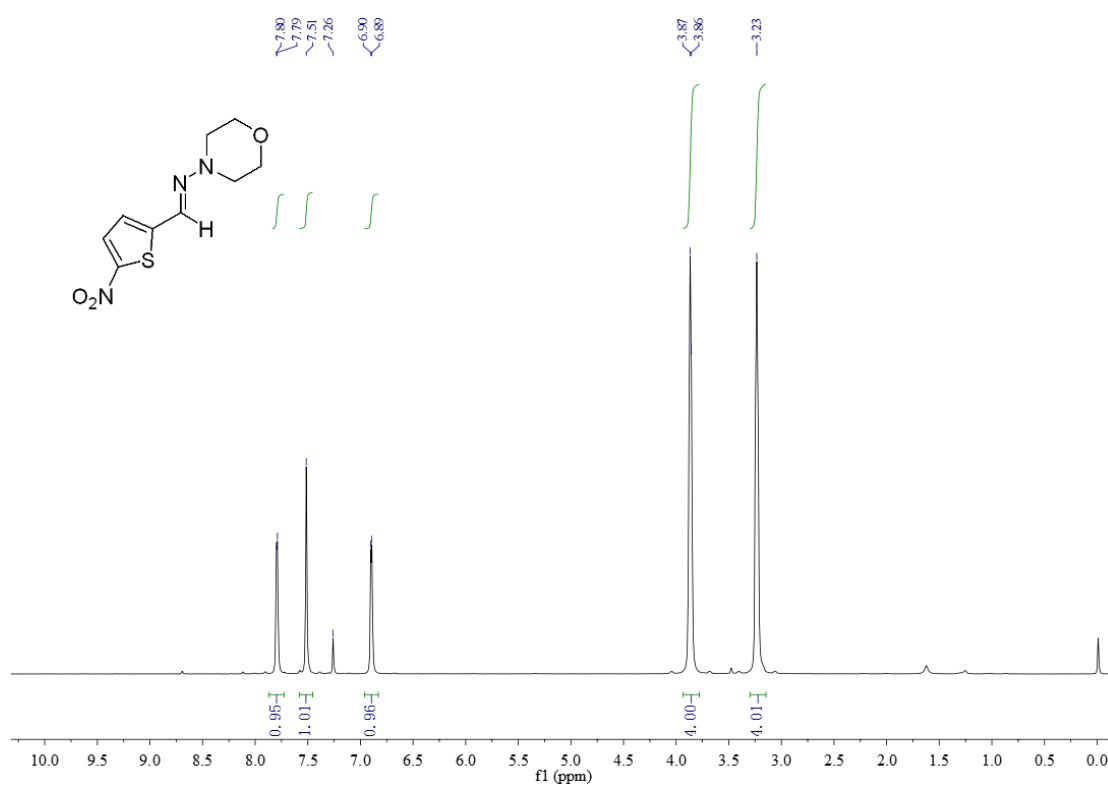
¹H NMR of **1v**



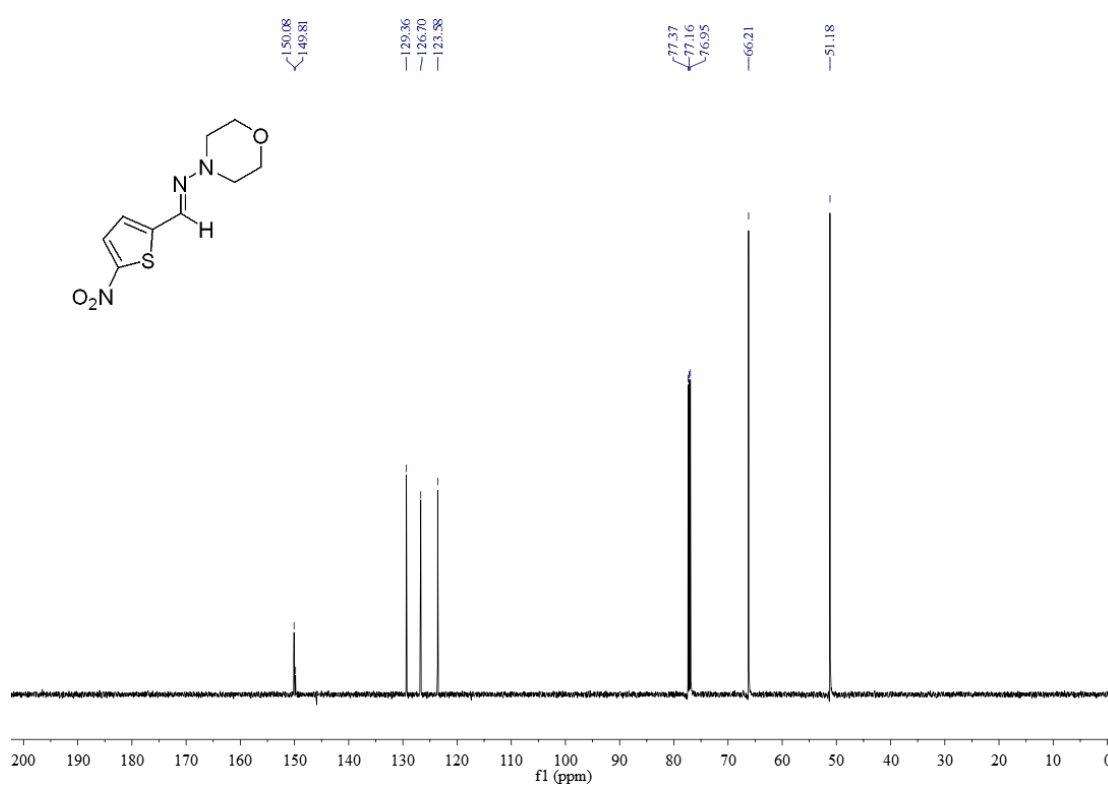
¹³C NMR of **1v**



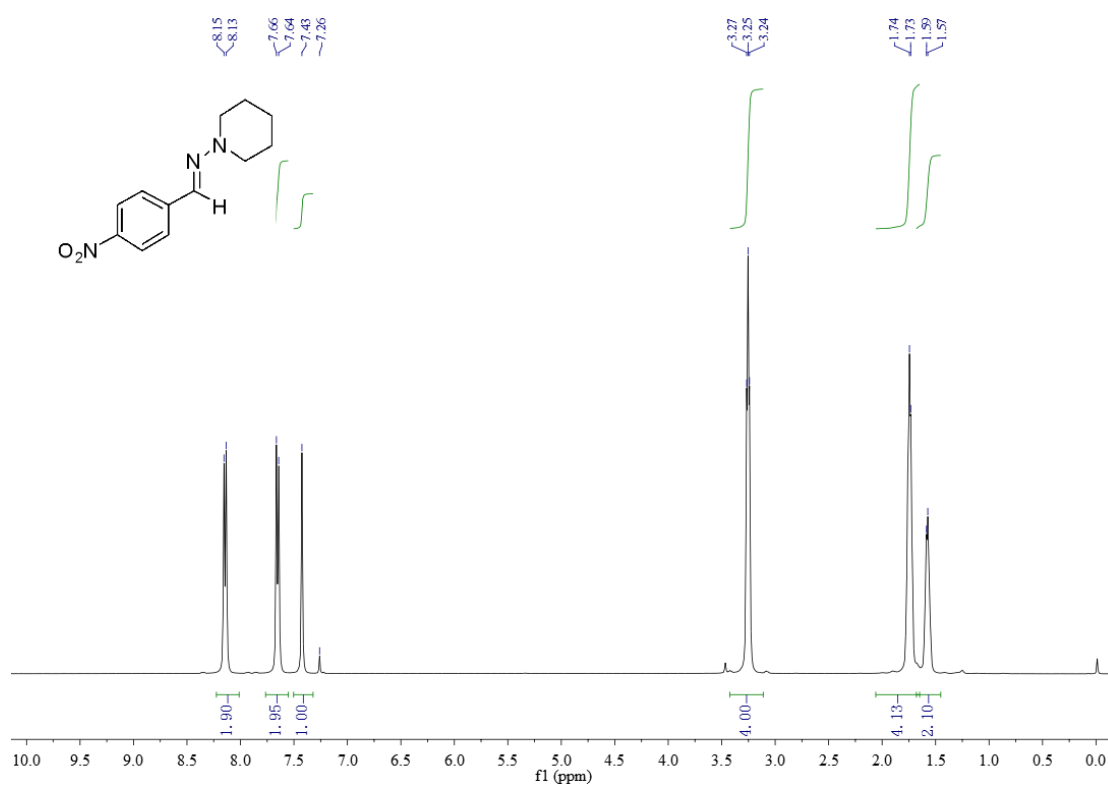
¹H NMR of **1w**



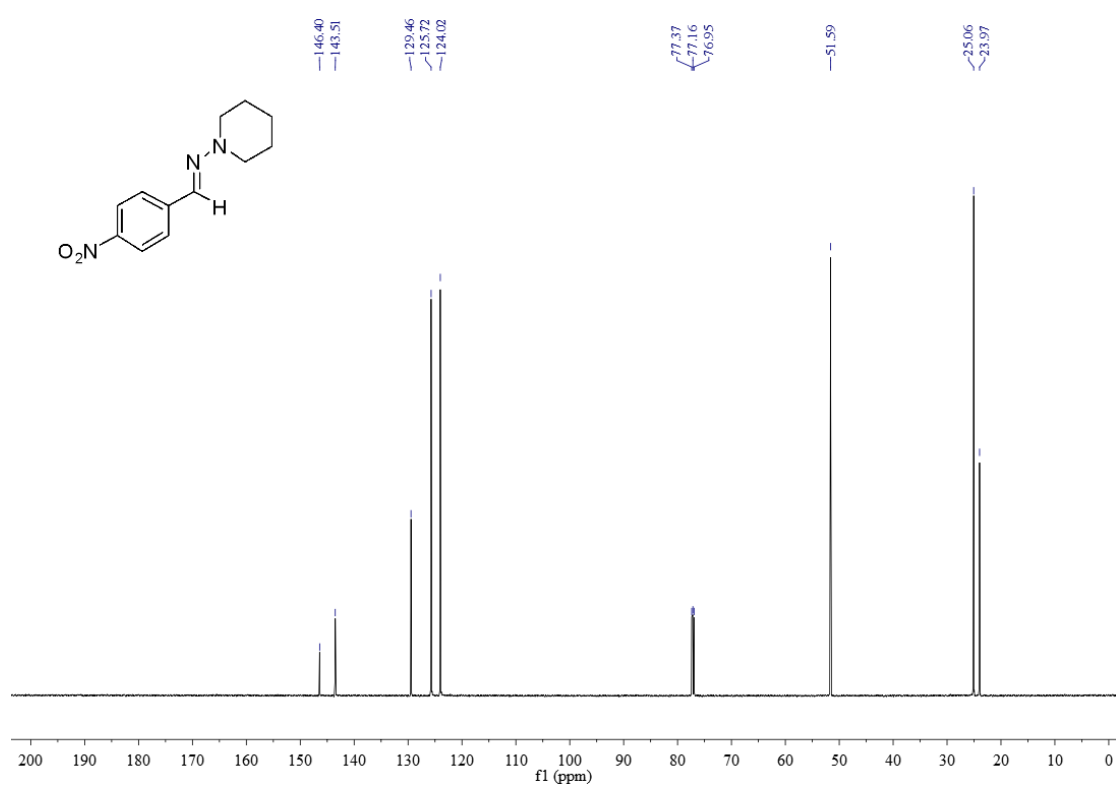
¹³C NMR of **1w**



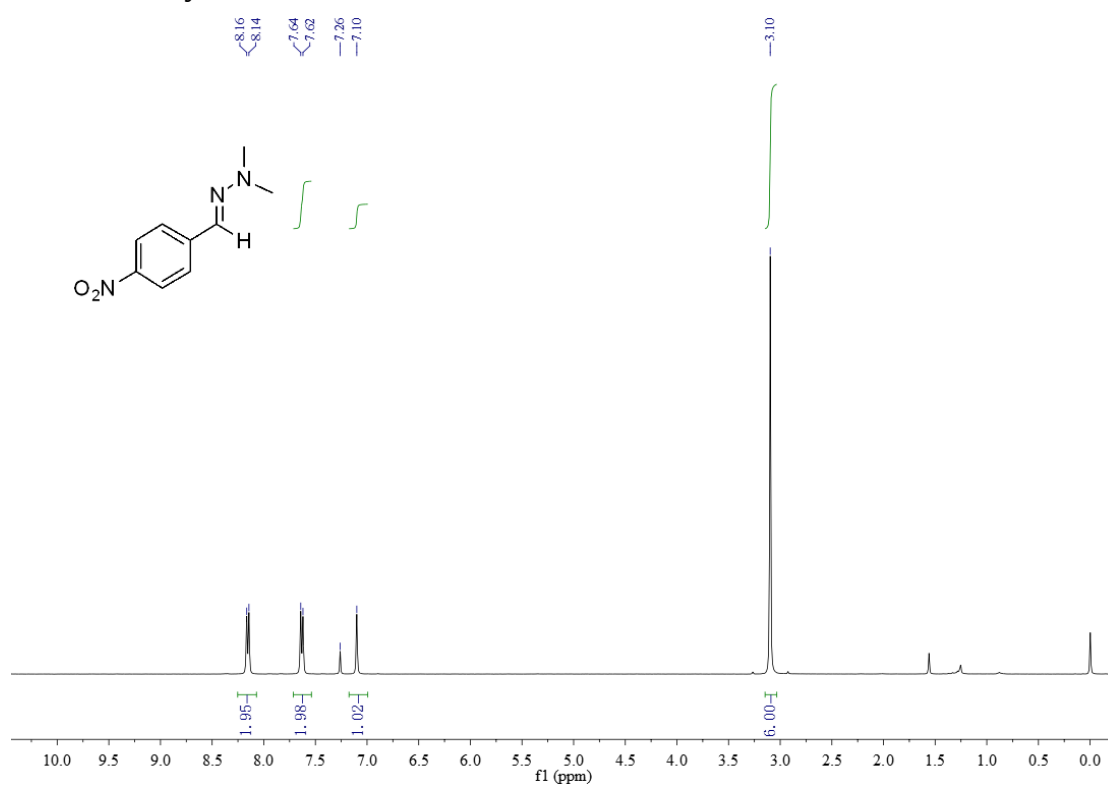
¹H NMR of **1x**



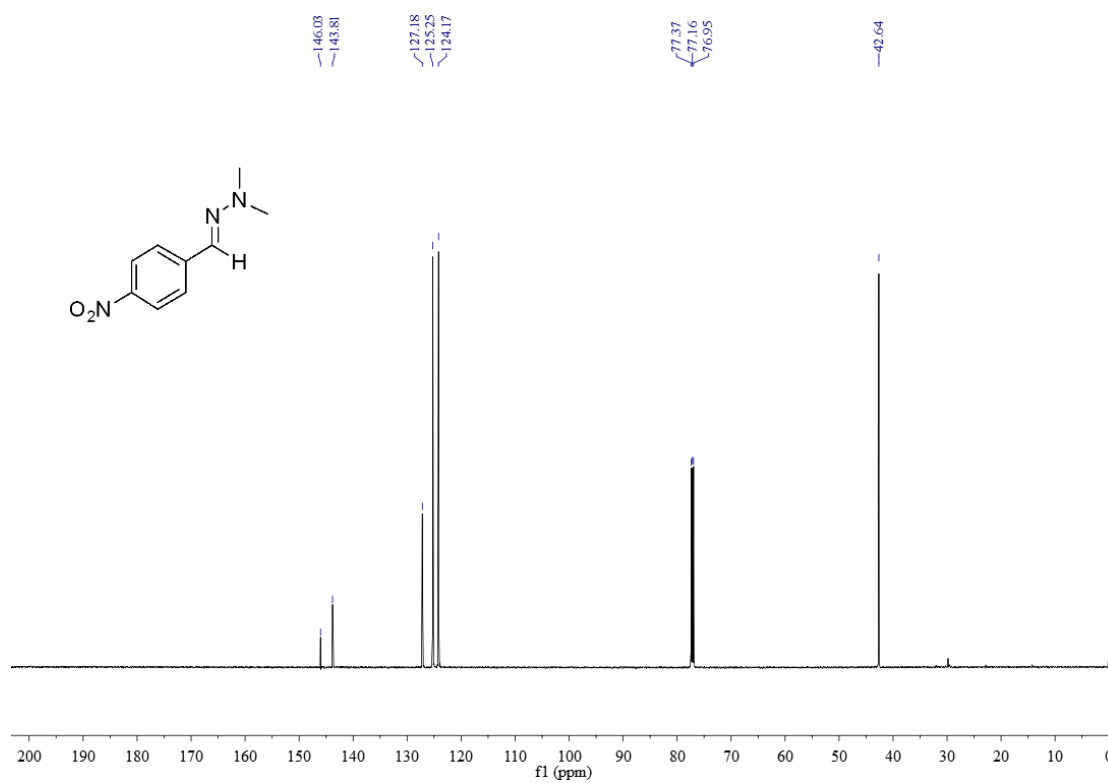
¹³C NMR of **1x**



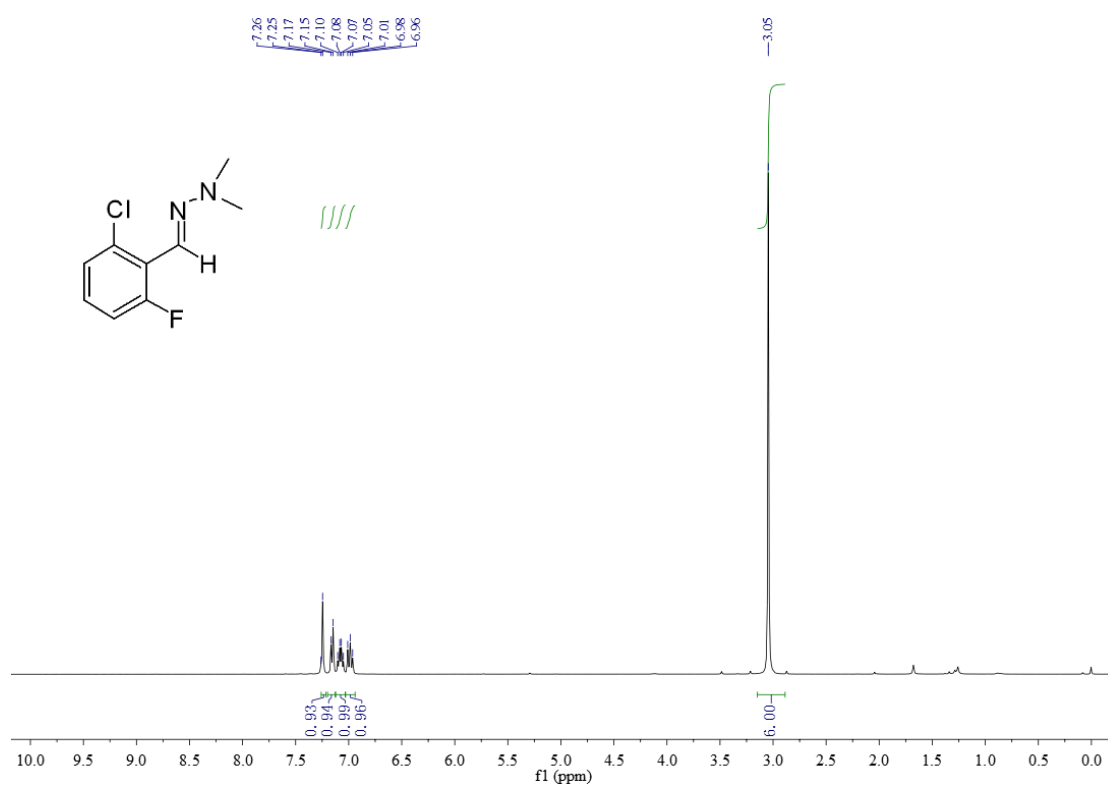
¹H NMR of **1y**



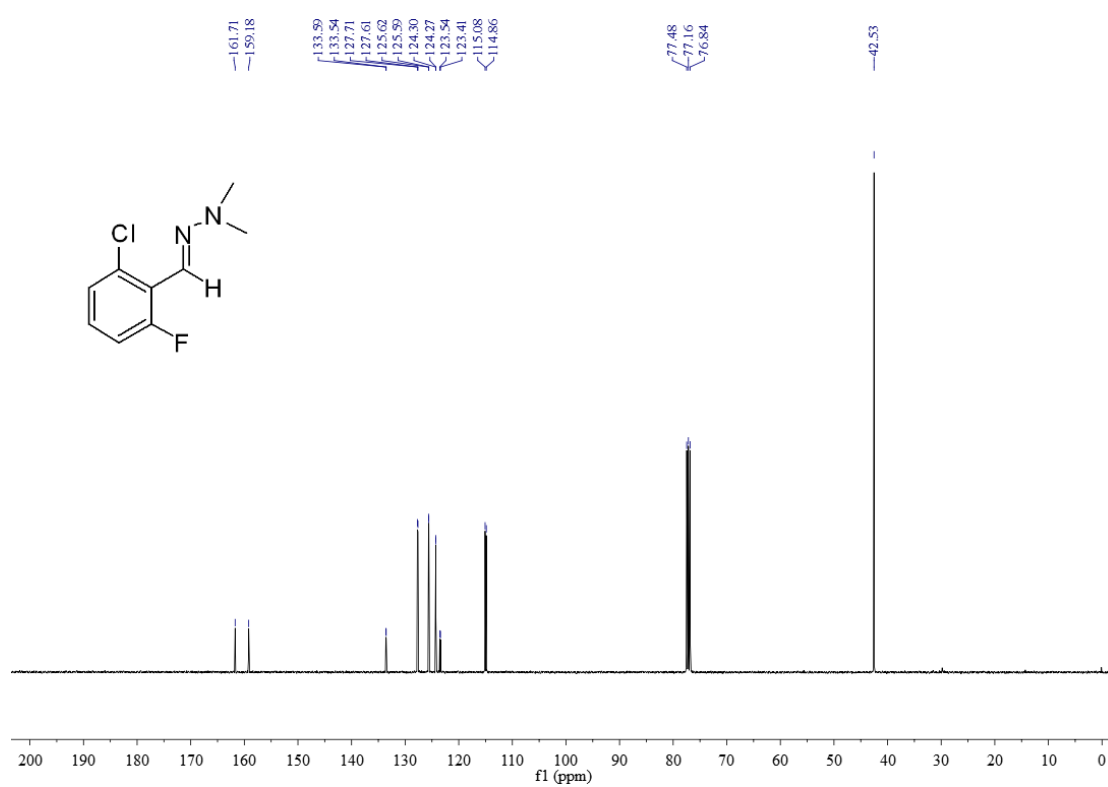
¹³C NMR of **1y**



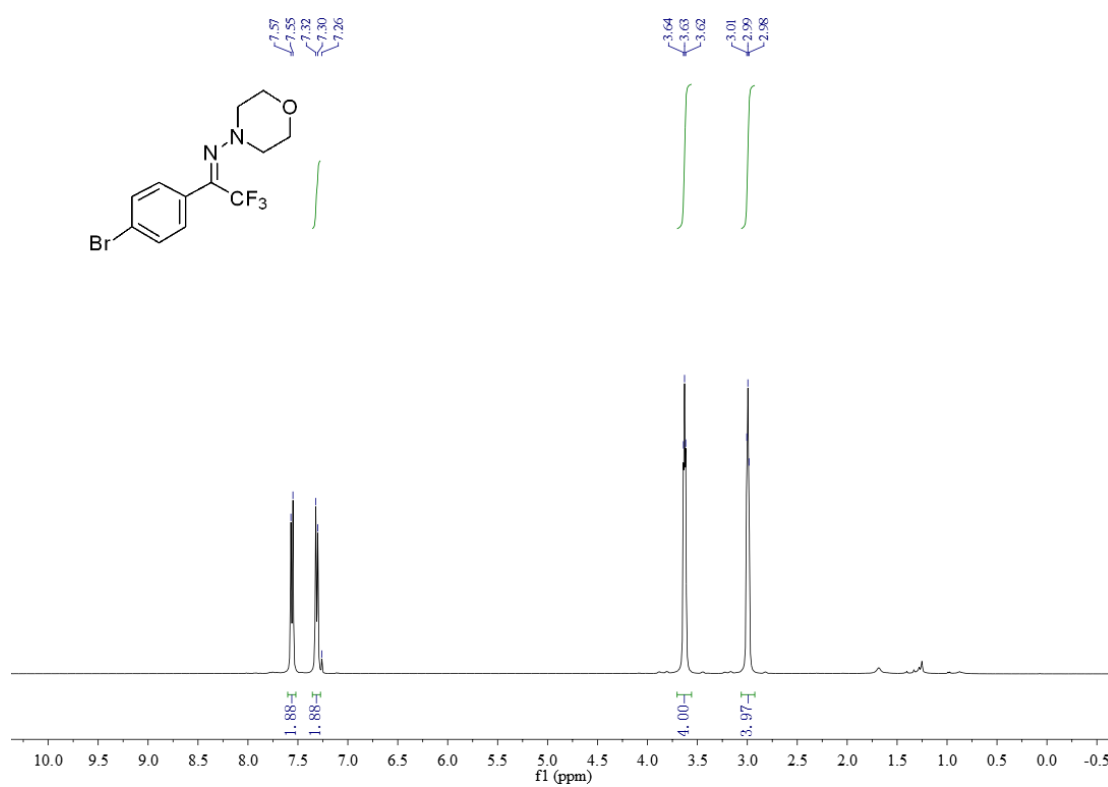
¹H NMR of **1z**



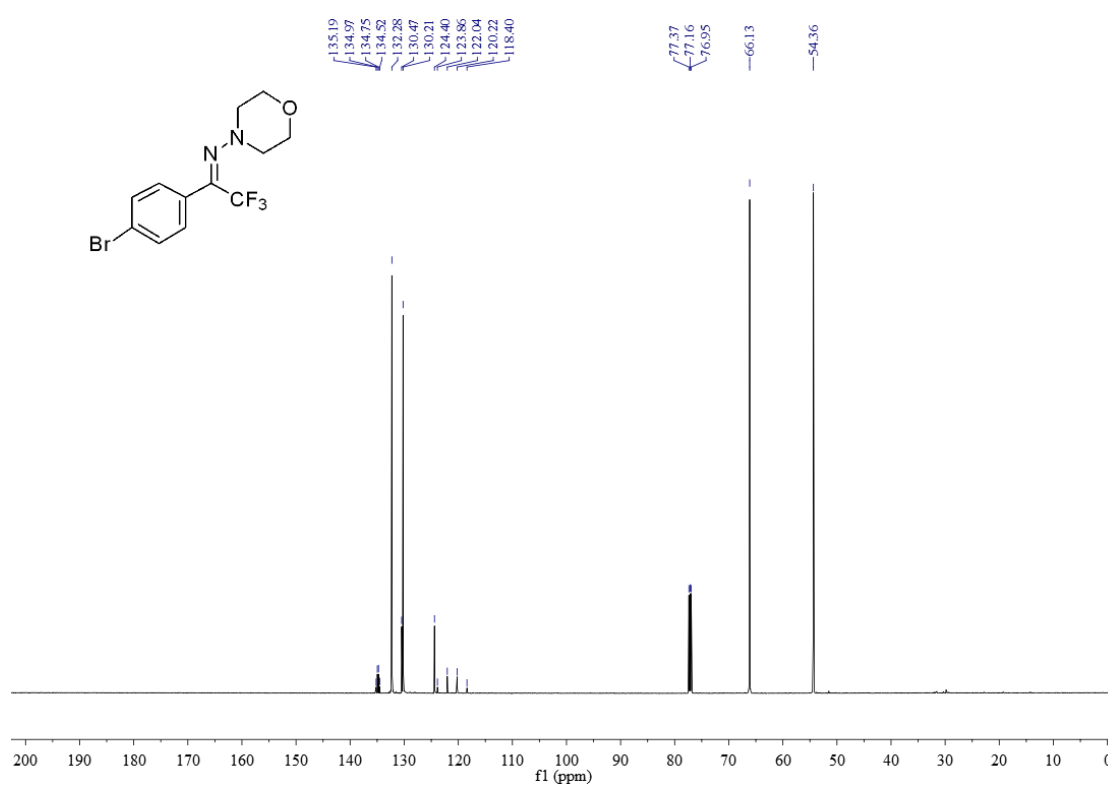
¹³C NMR of **1z**



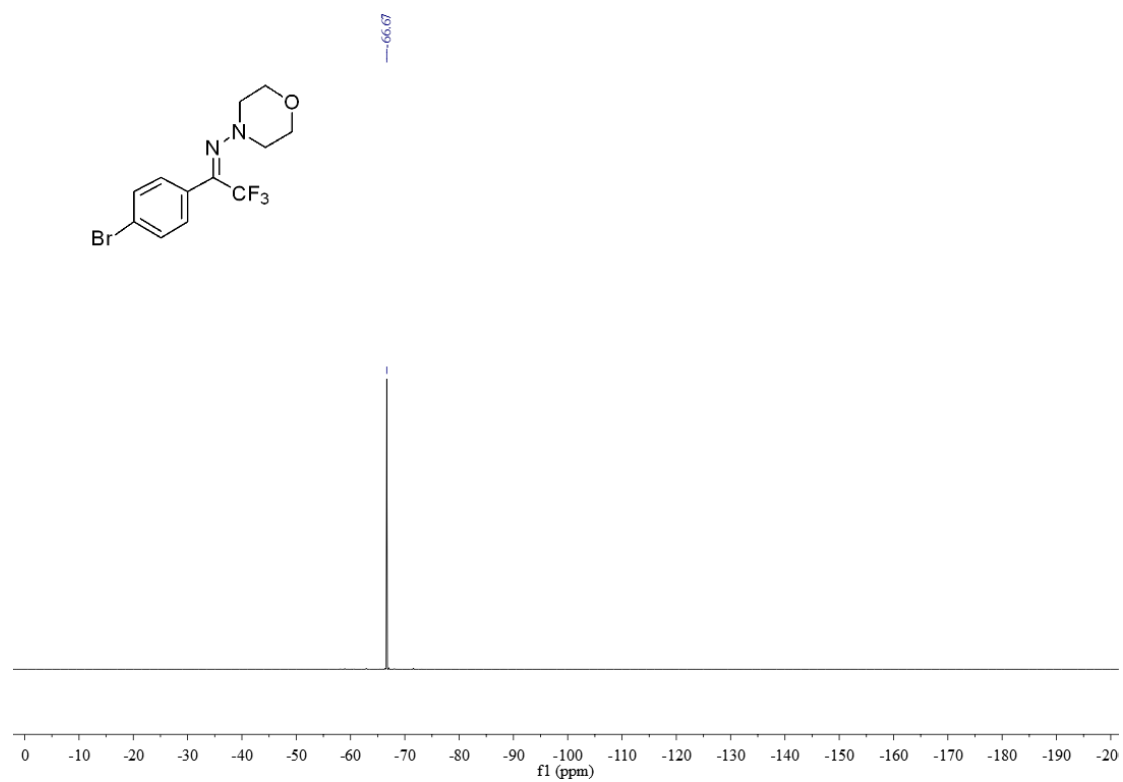
¹H NMR of 2a



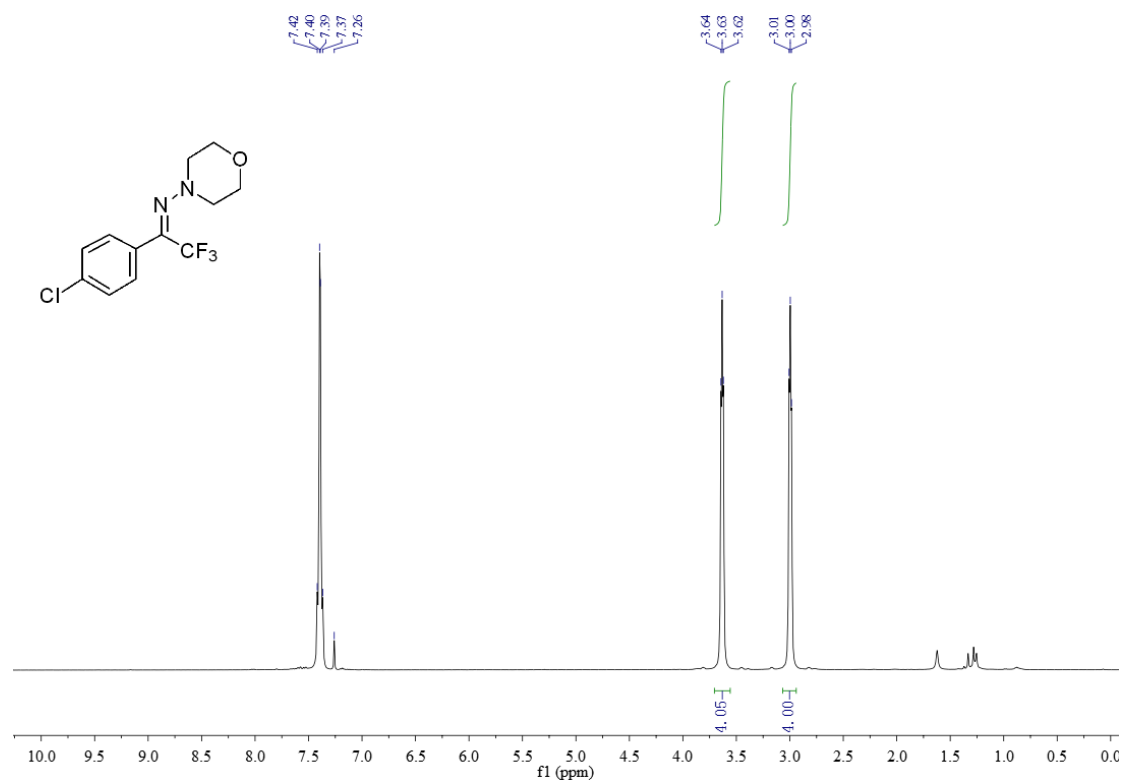
¹³C NMR of 2a



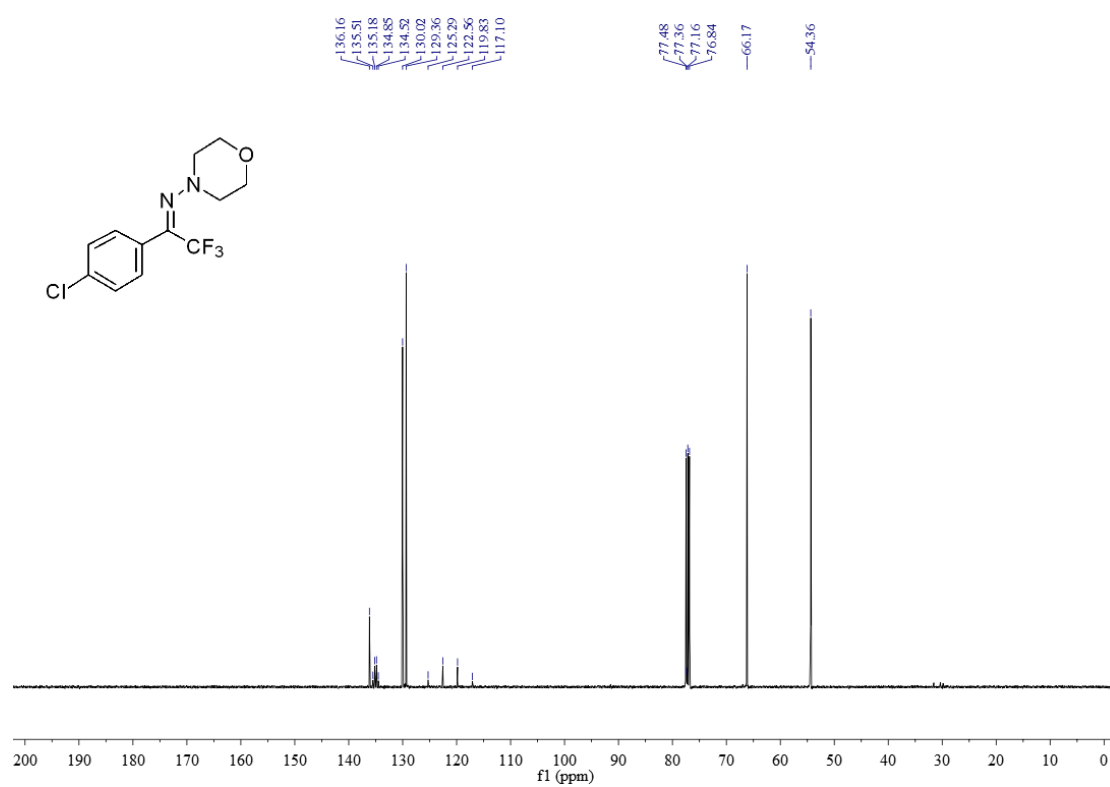
¹⁹F NMR of **2a**



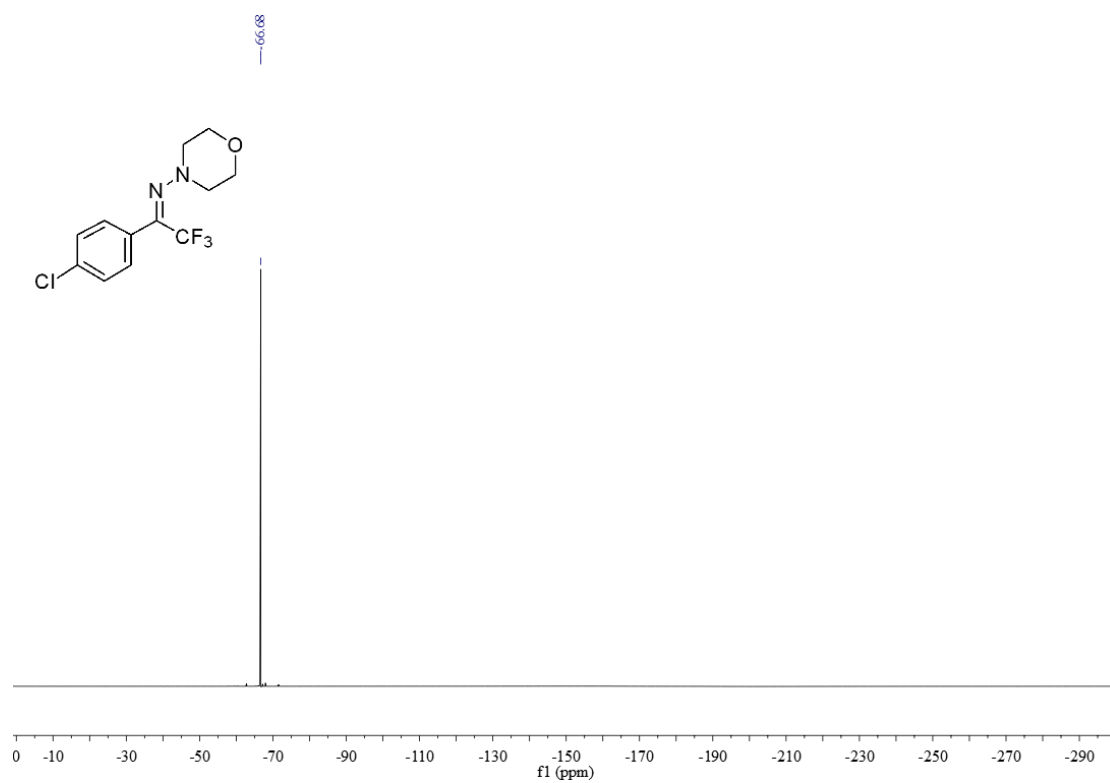
¹H NMR of **2b**



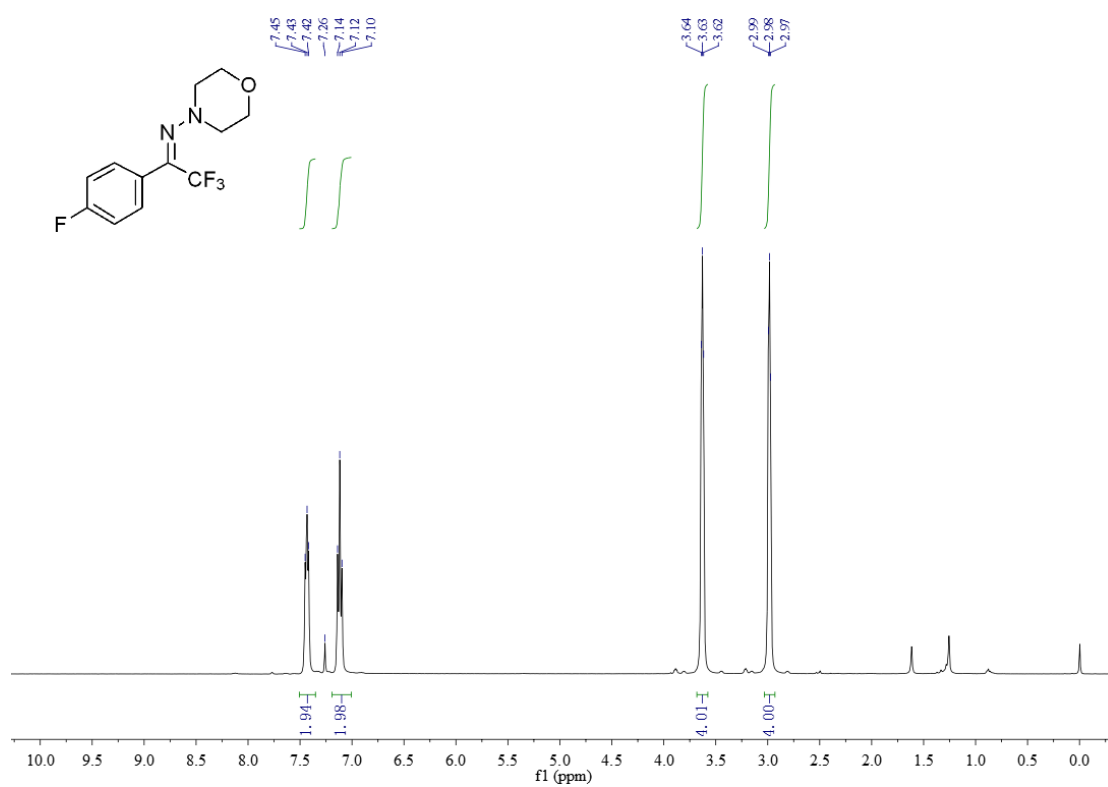
¹³C NMR of **2b**



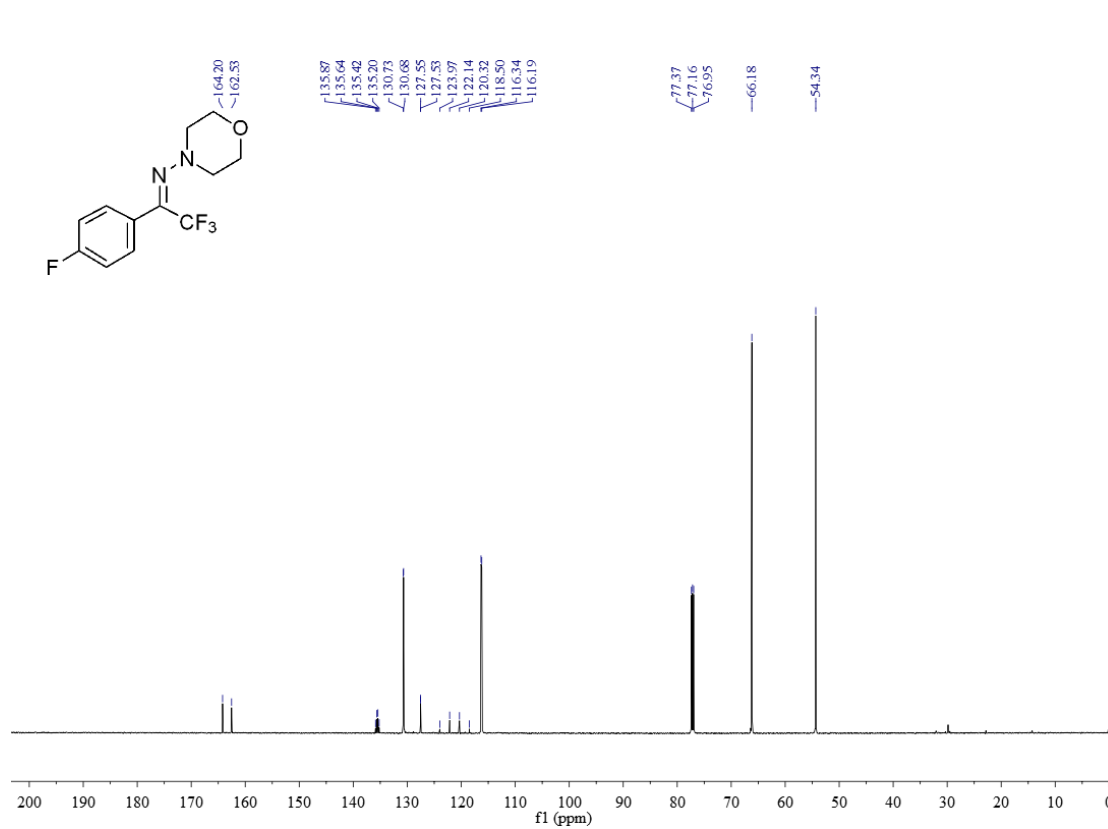
¹⁹F NMR of **2b**



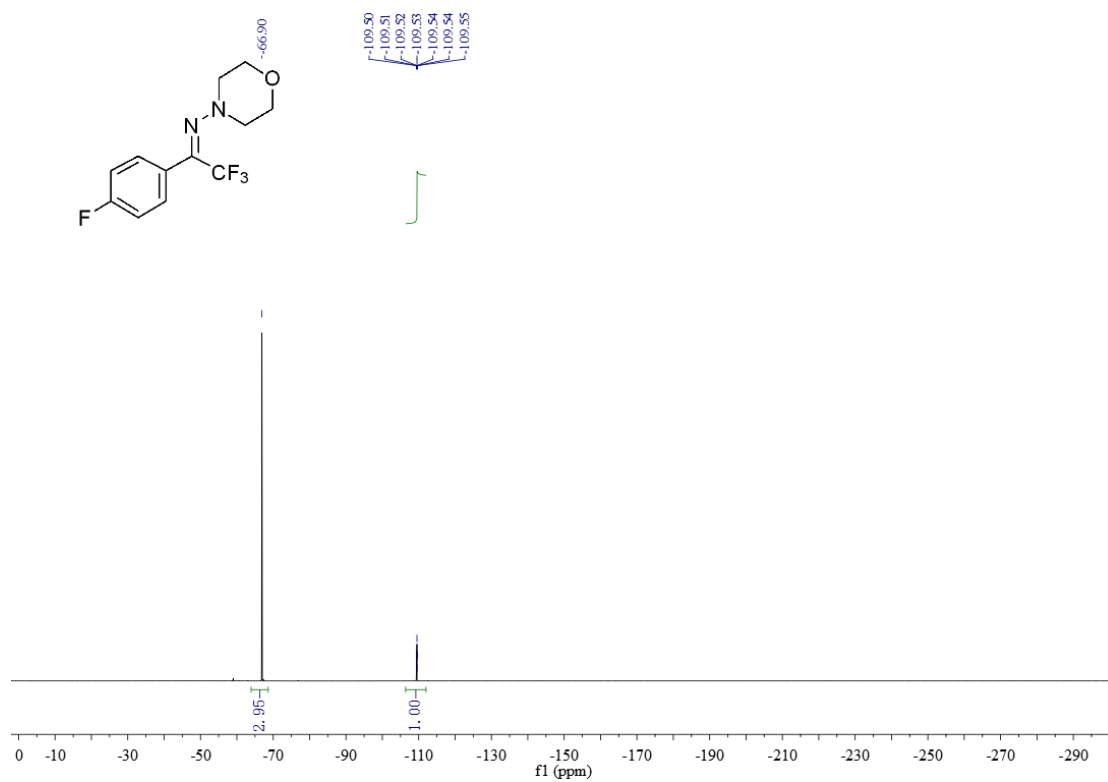
¹H NMR of **2c**



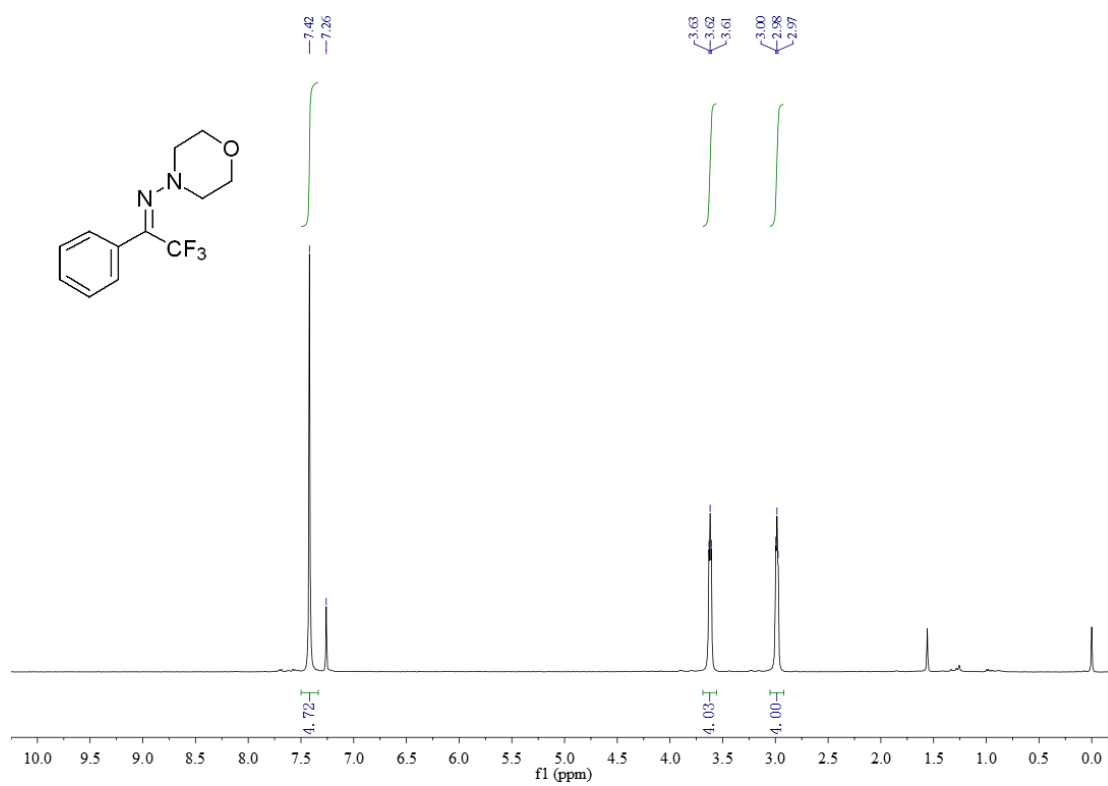
¹³C NMR of **2c**



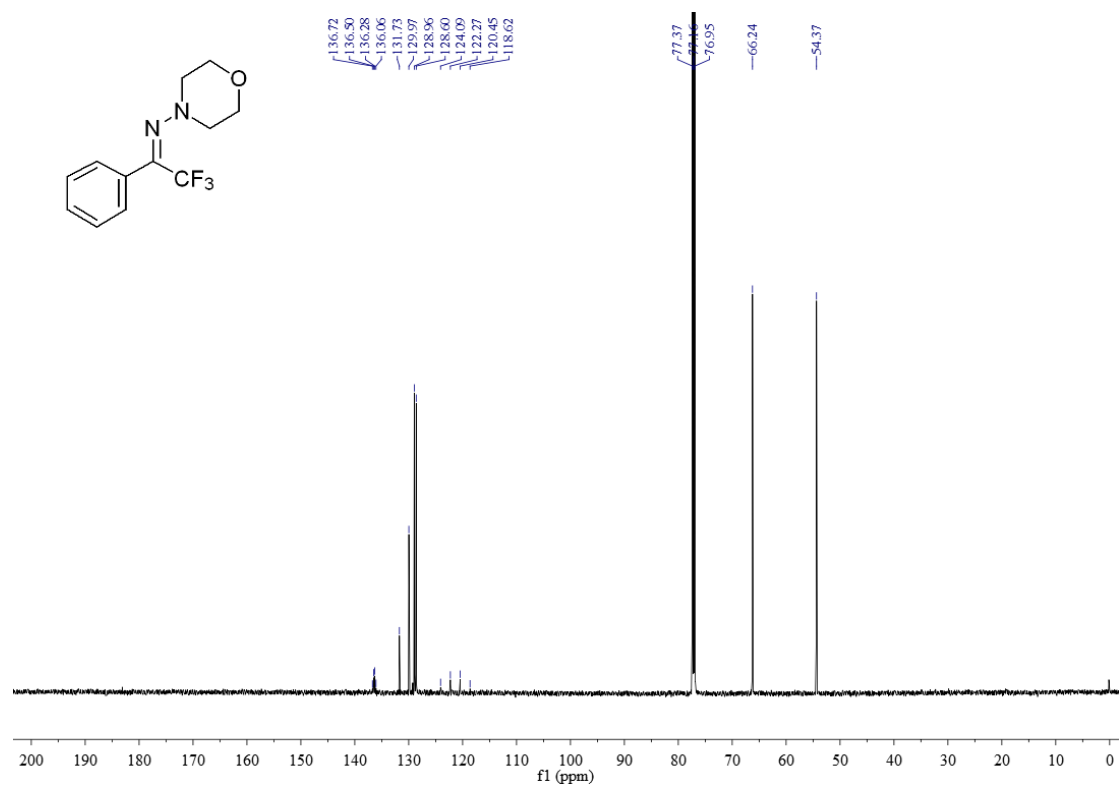
¹⁹F NMR of **2c**



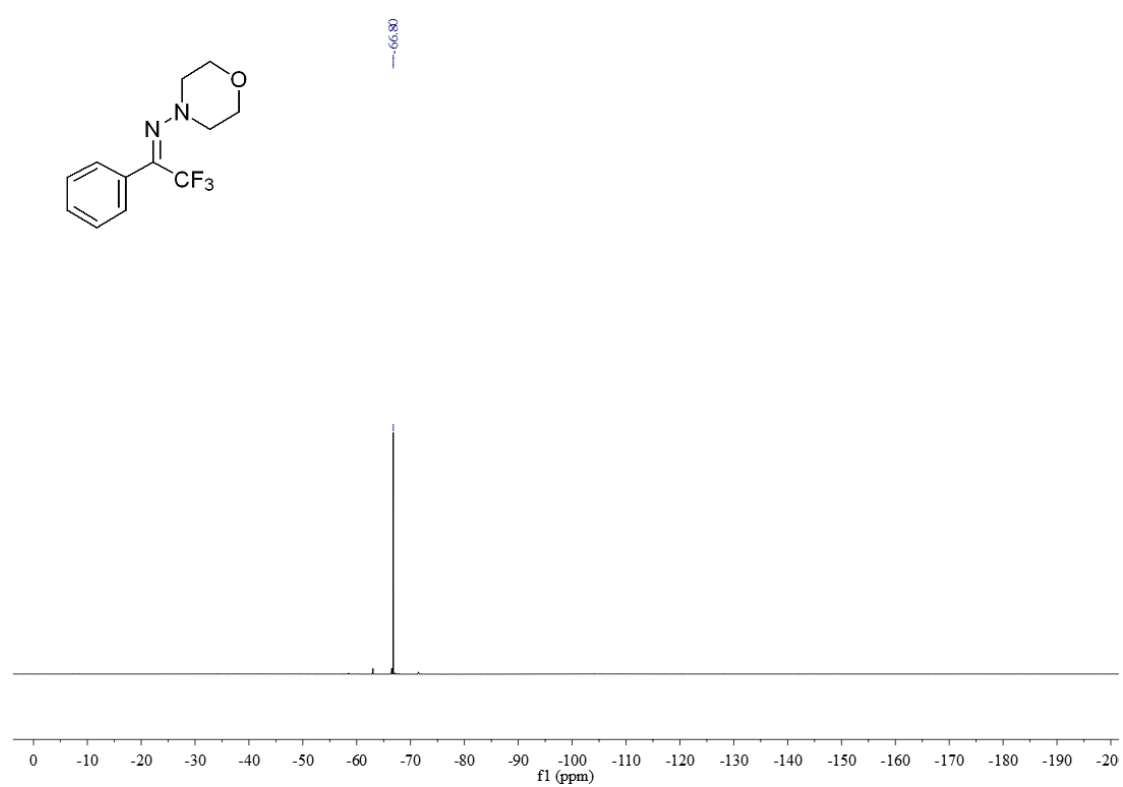
¹H NMR of **2d**



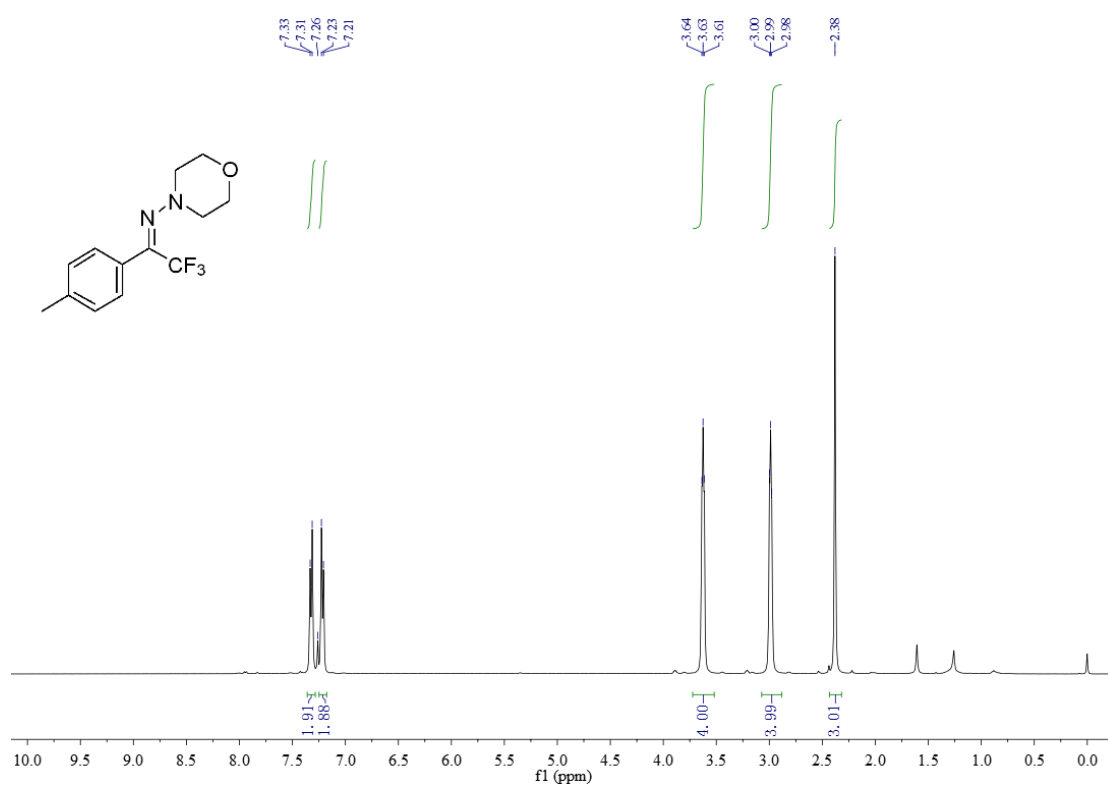
¹³C NMR of **2d**



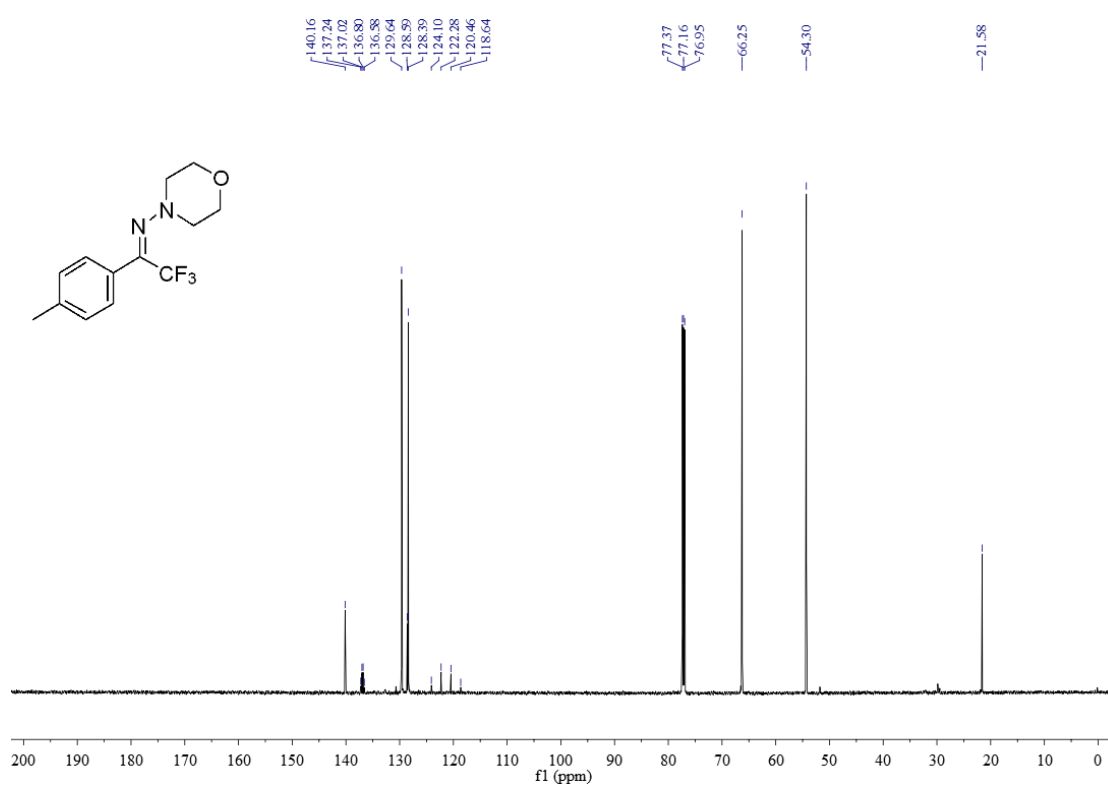
¹⁹F NMR of **2d**



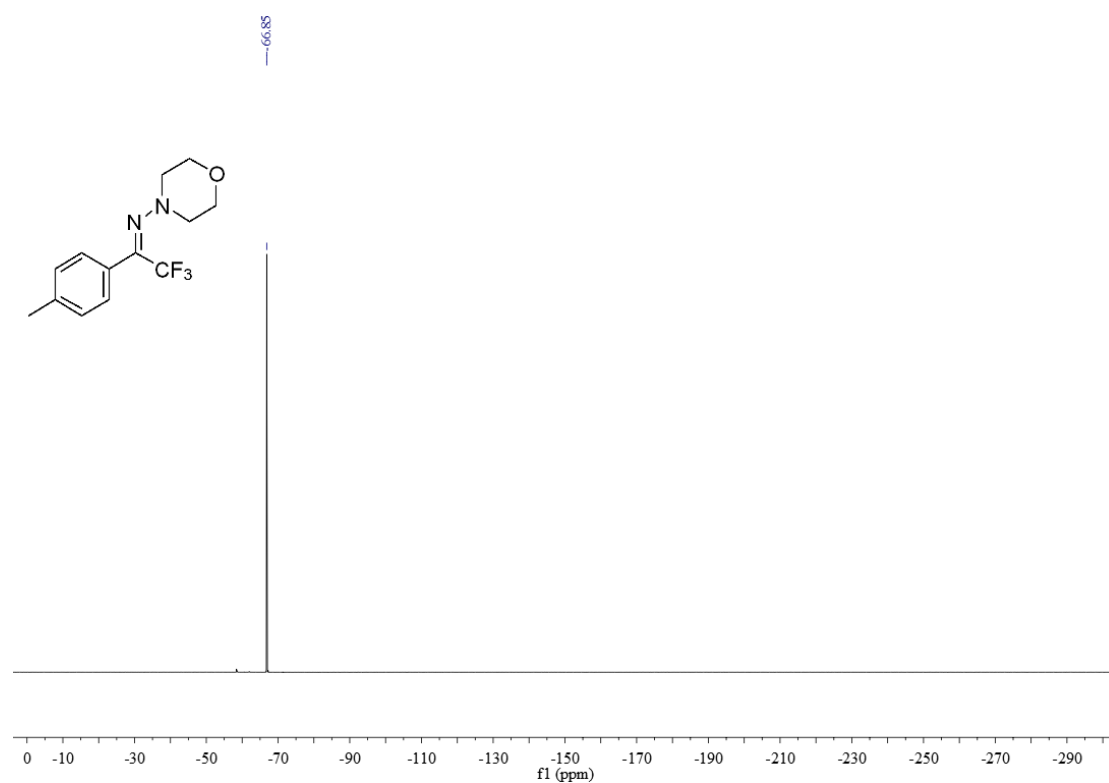
¹H NMR of **2e**



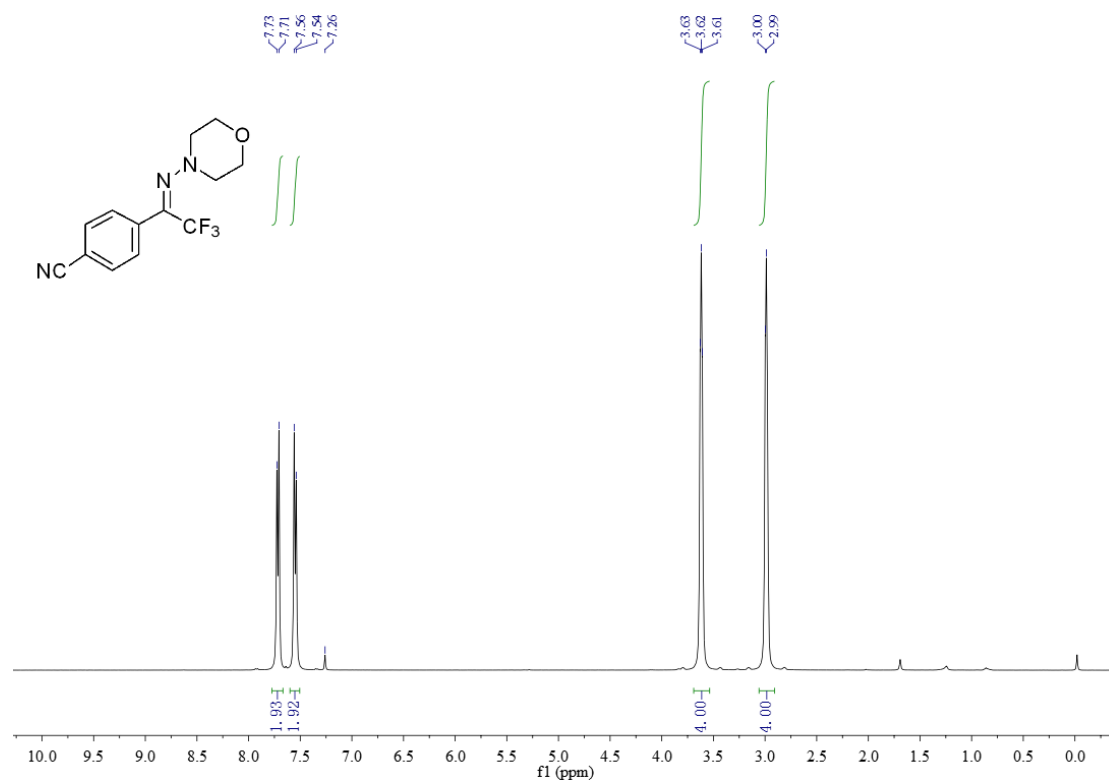
¹³C NMR of **2e**



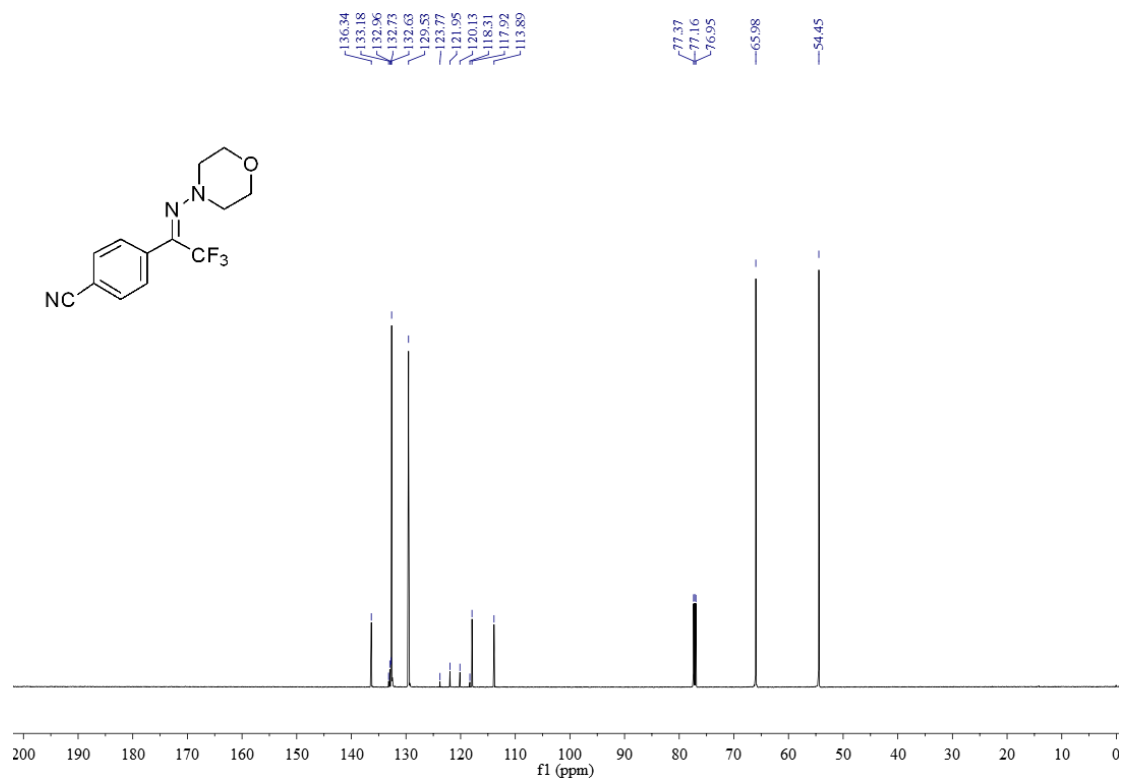
^{19}F NMR of **2e**



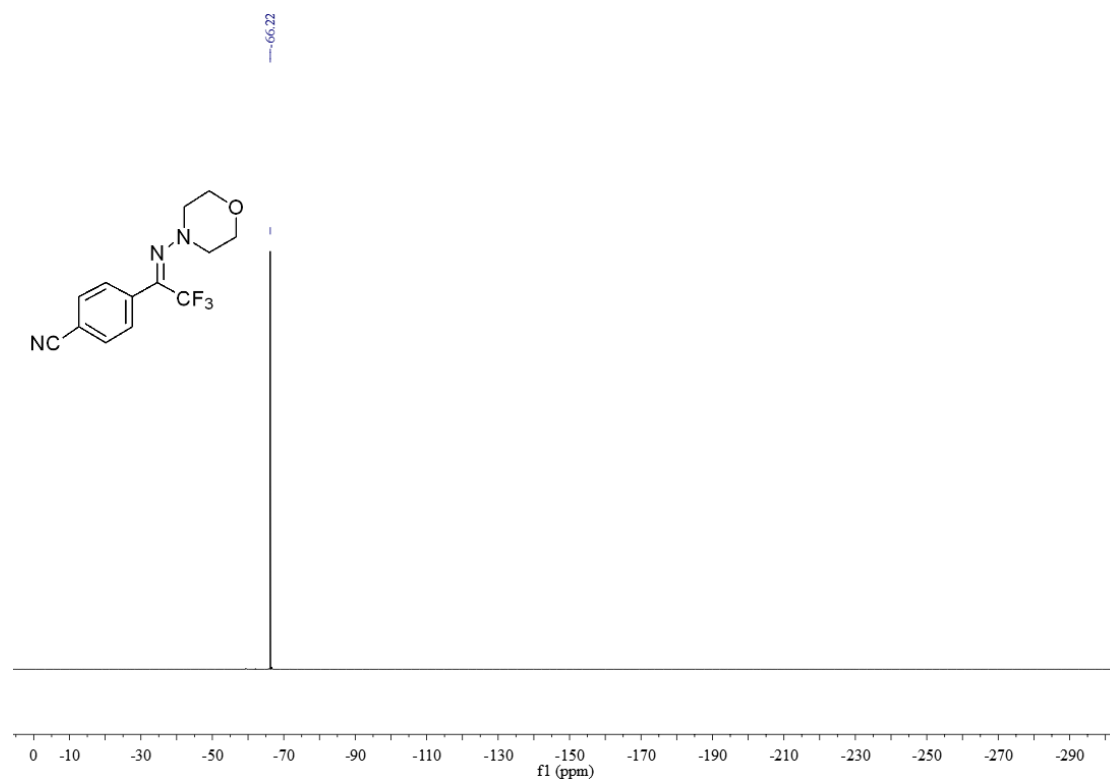
^1H NMR of **2f**



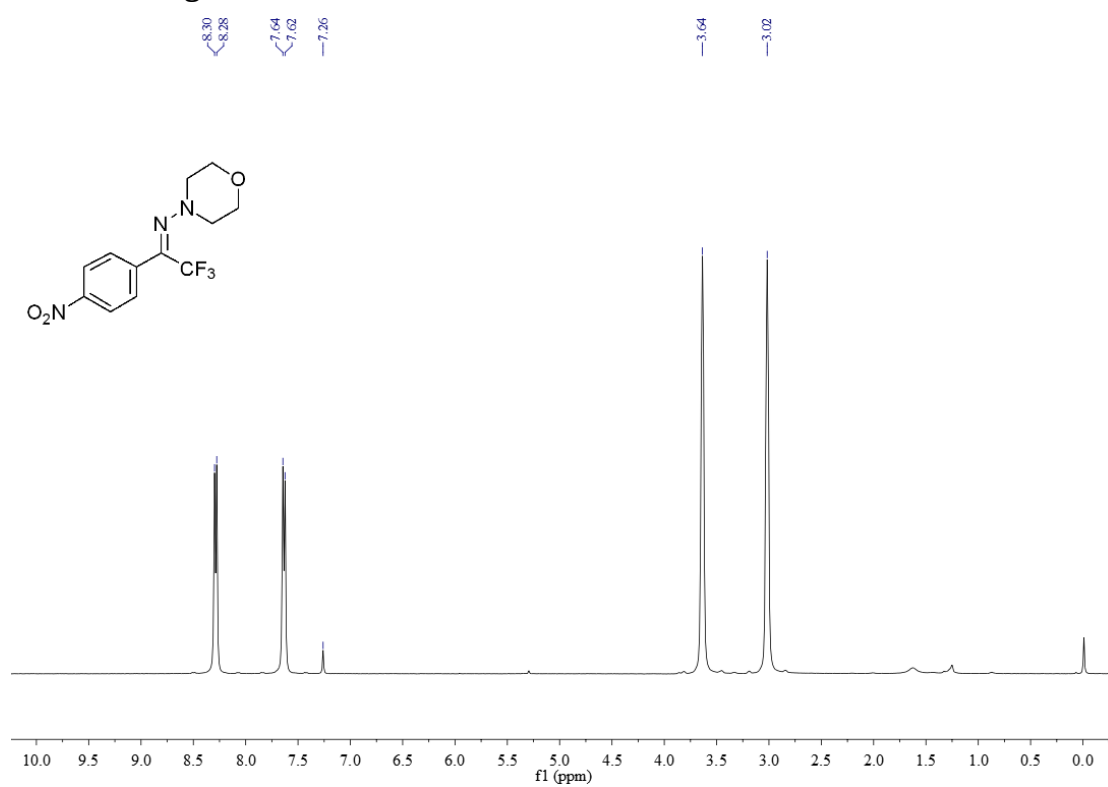
¹³C NMR of **2f**



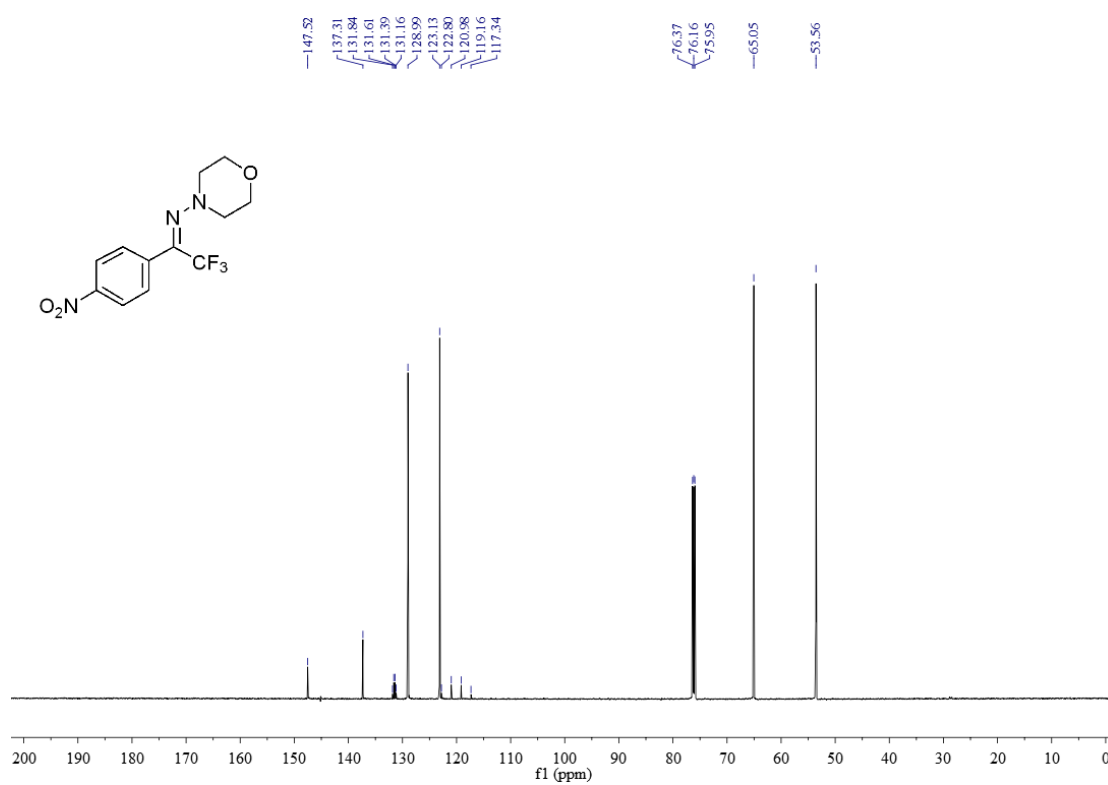
¹⁹F NMR of **2f**



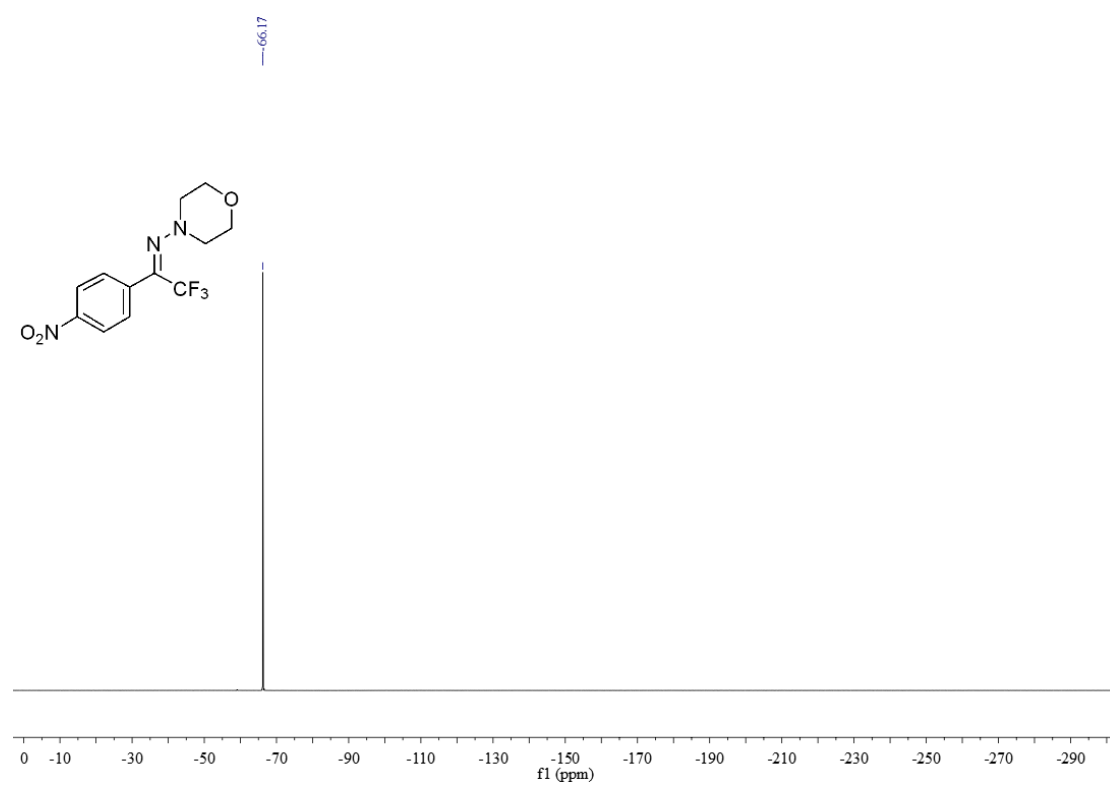
¹H NMR of **2g**



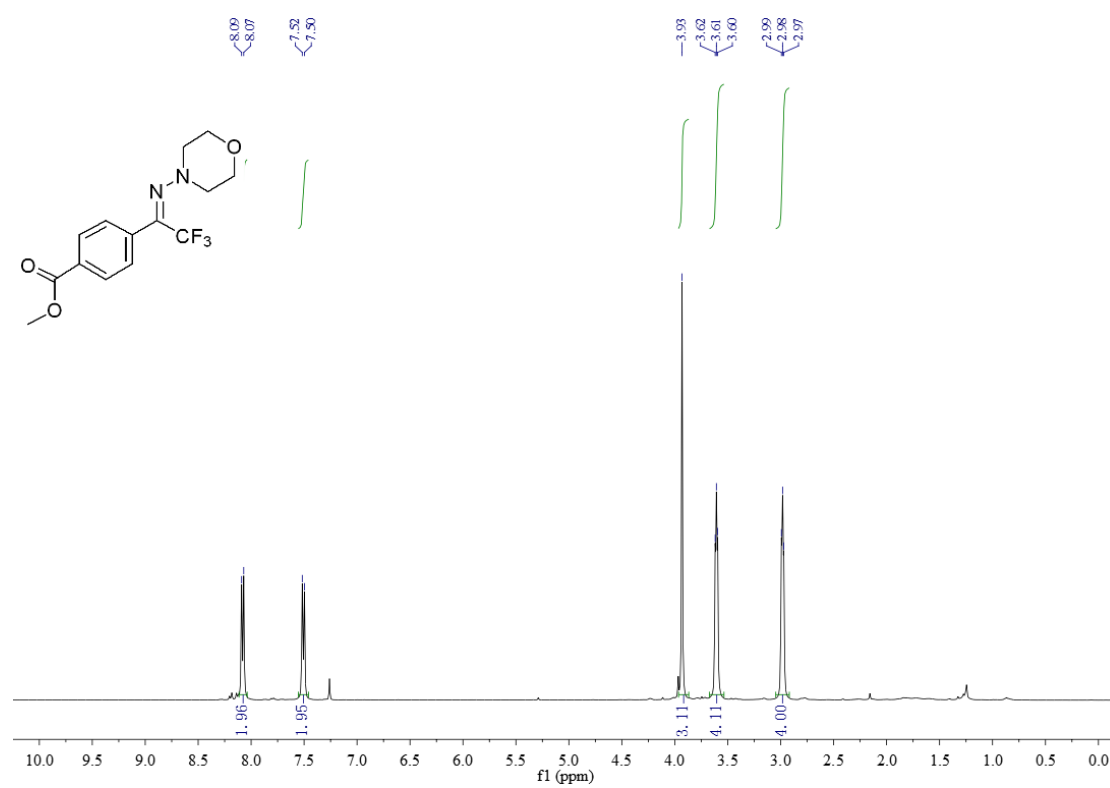
¹³C NMR of **2g**



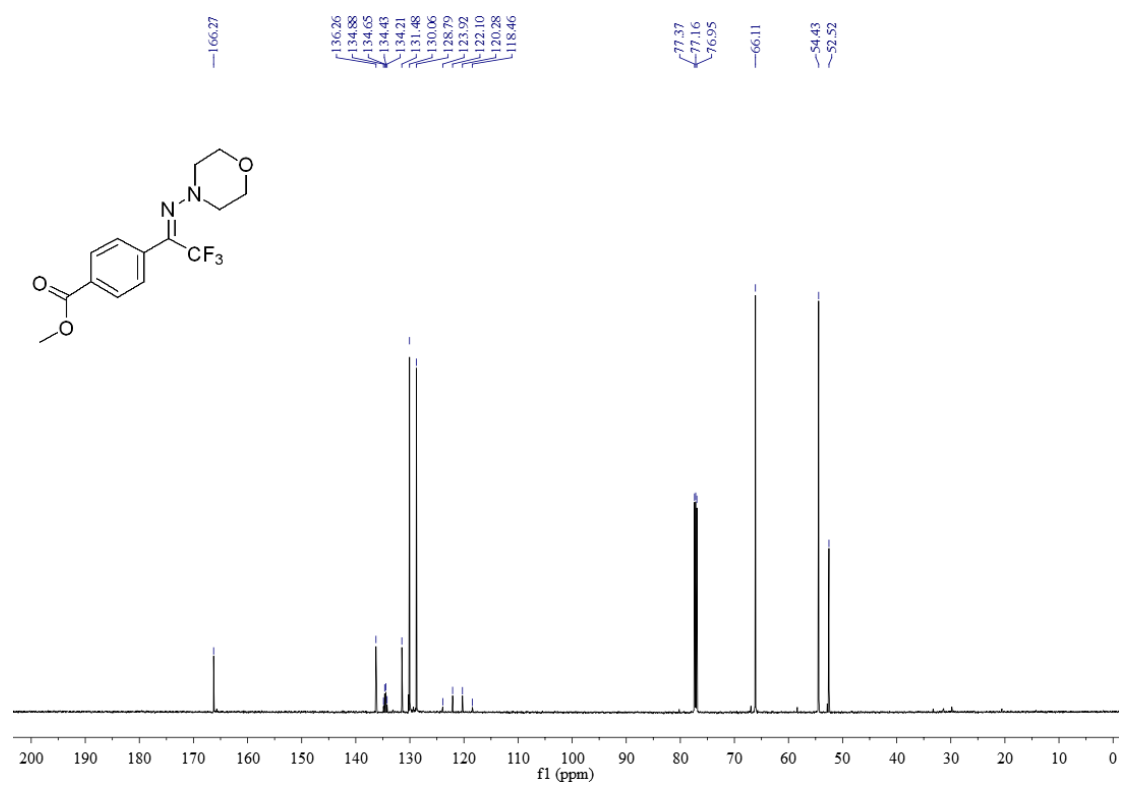
¹⁹F NMR of **2g**



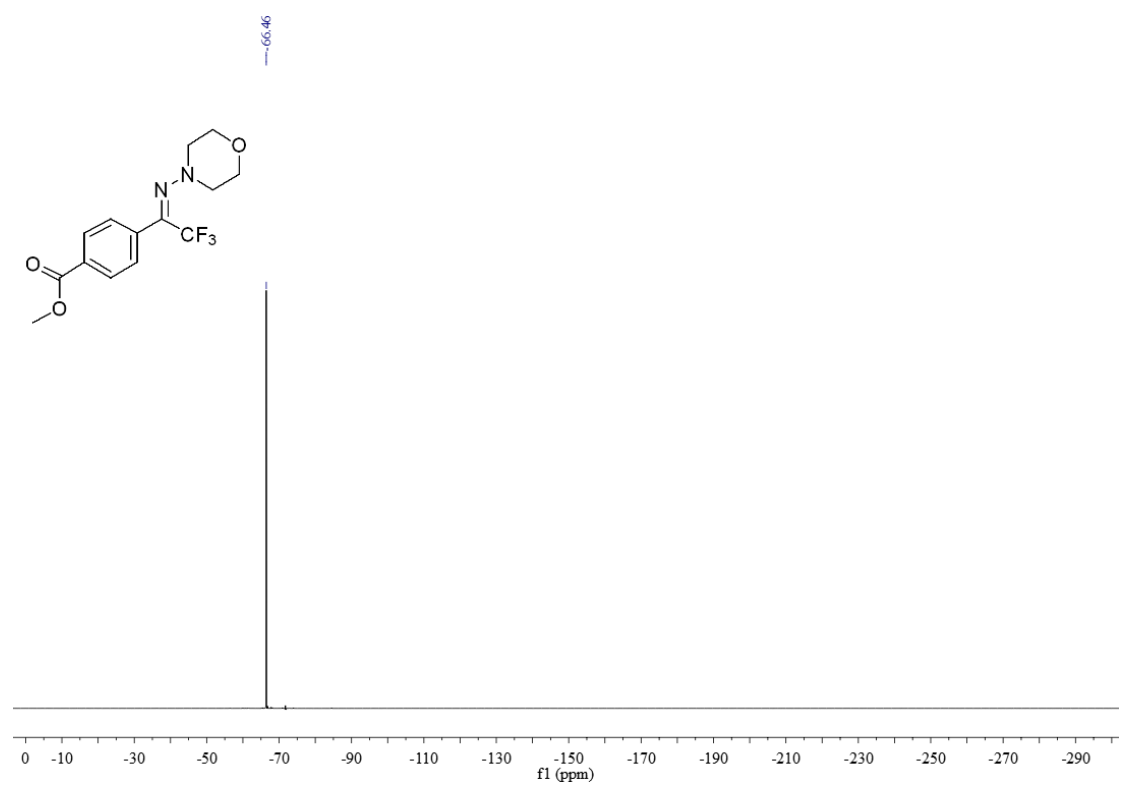
¹H NMR of **2h**



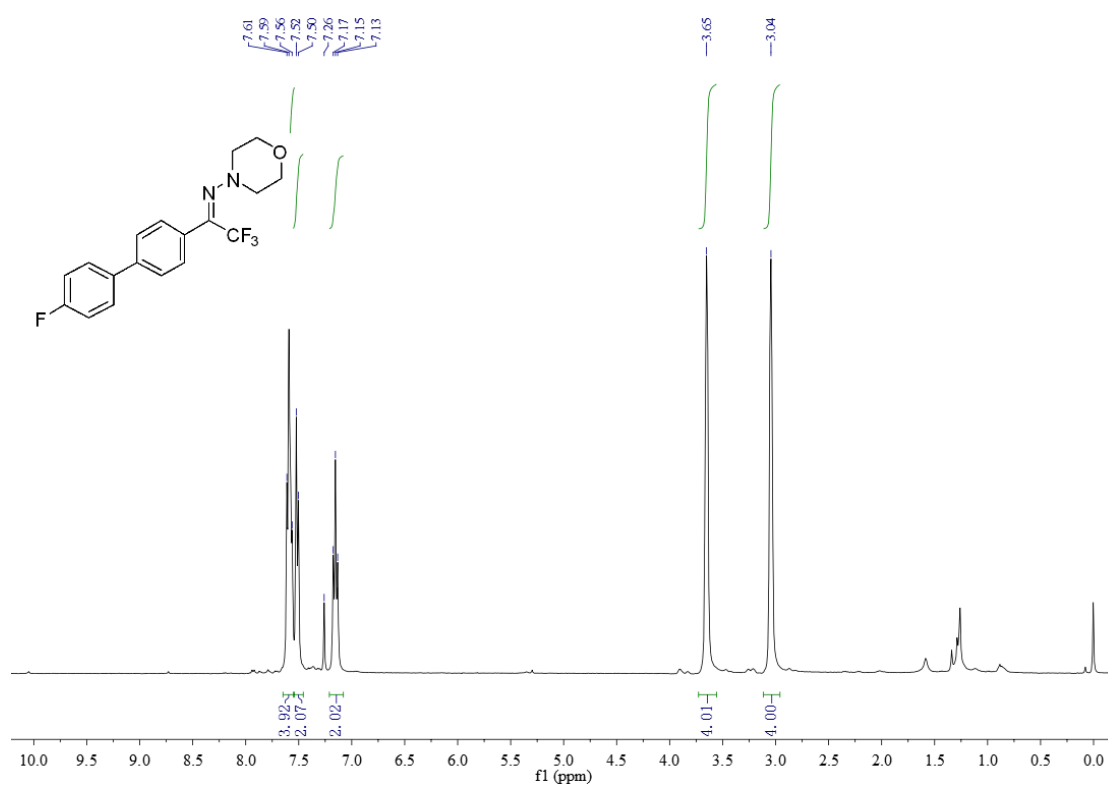
^{13}C NMR of **2h**



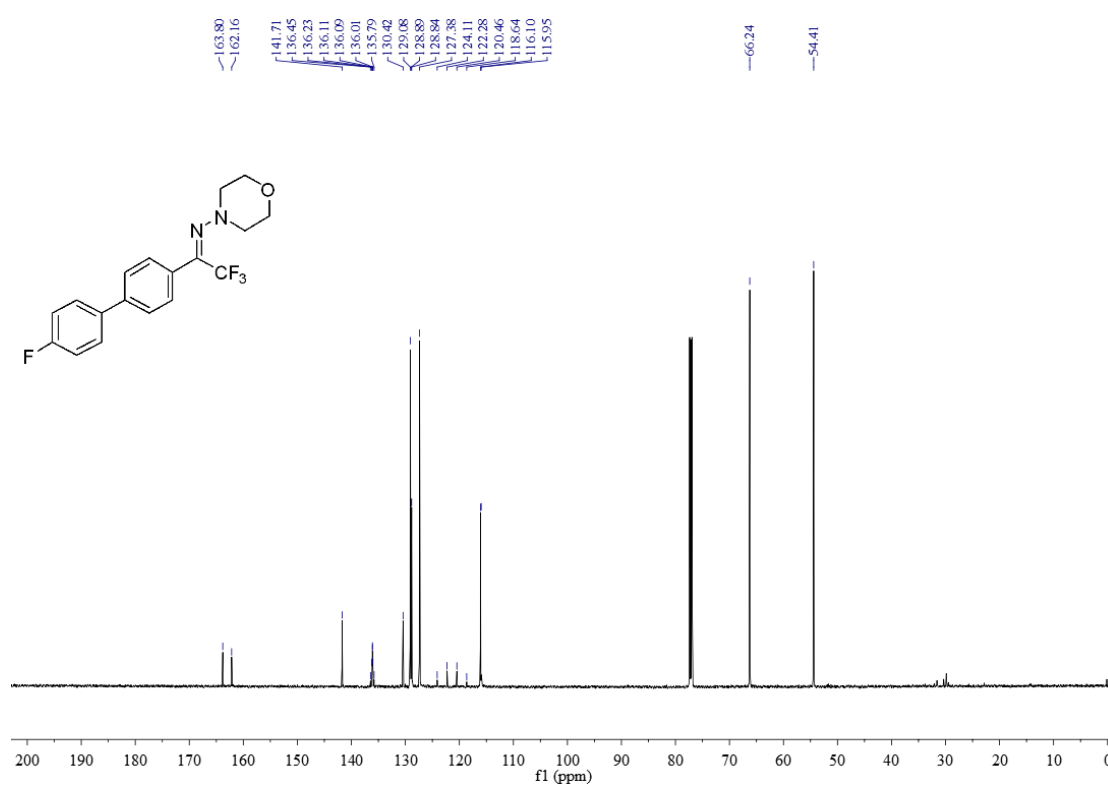
^{19}F NMR of **2h**



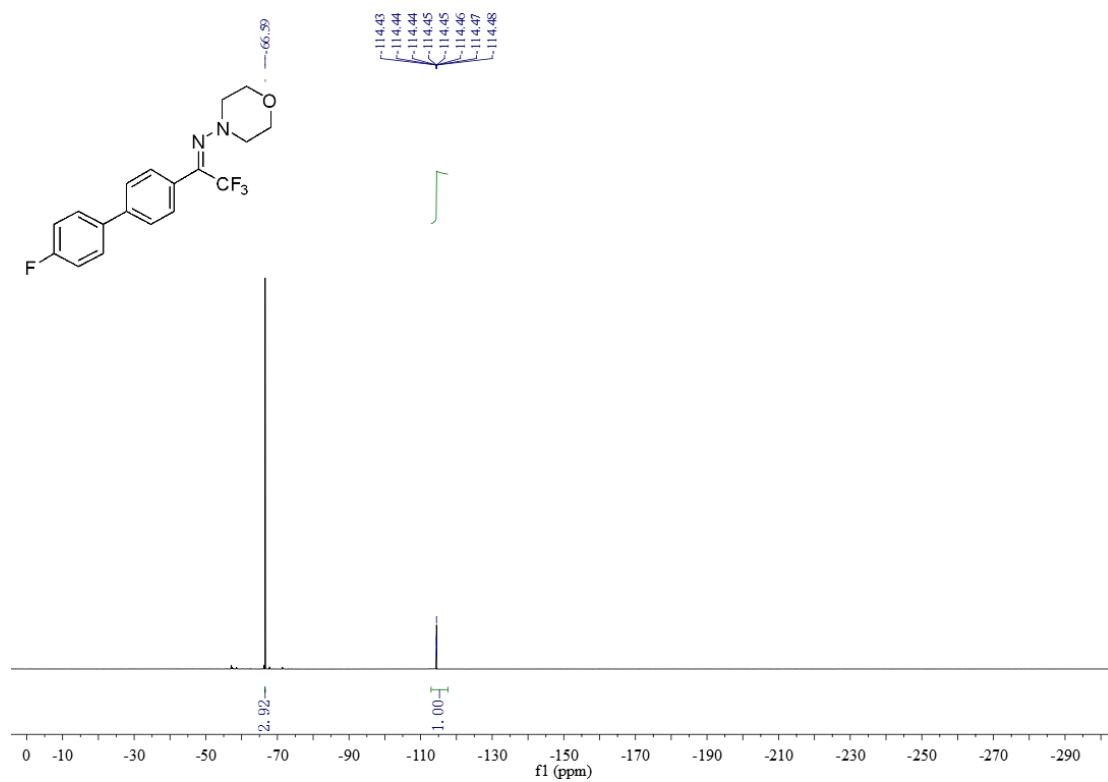
¹H NMR of **2i**



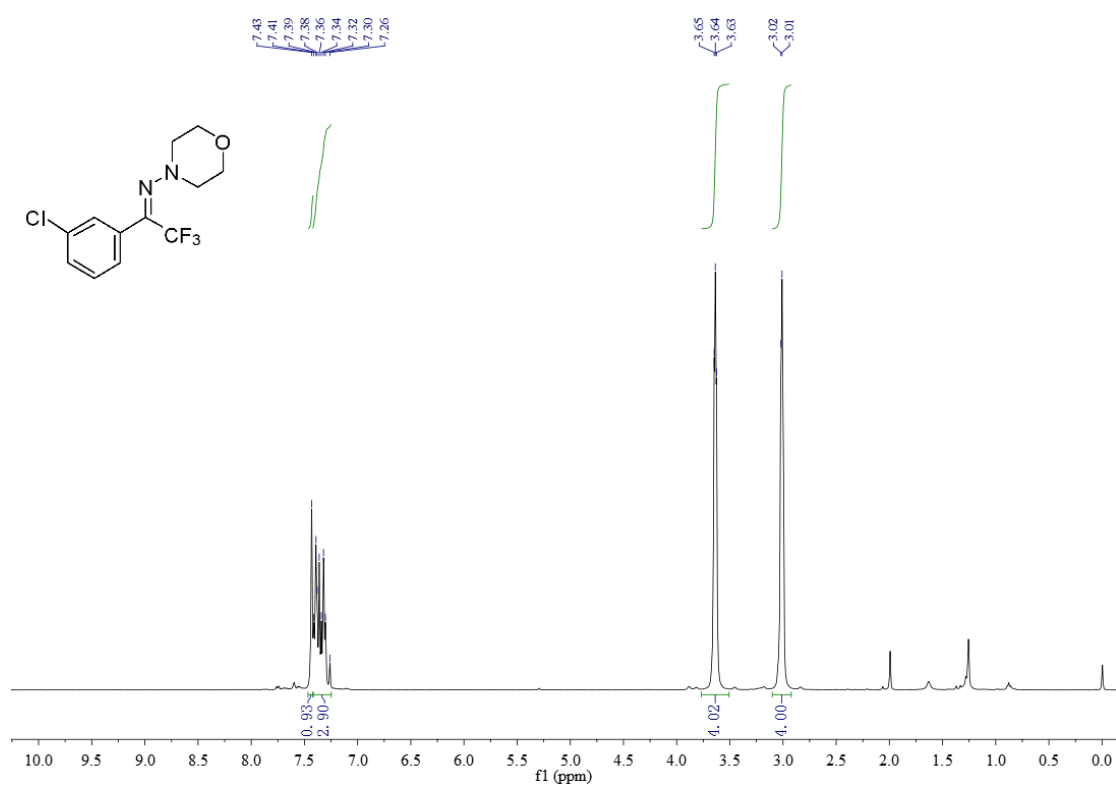
¹³C NMR of **2i**



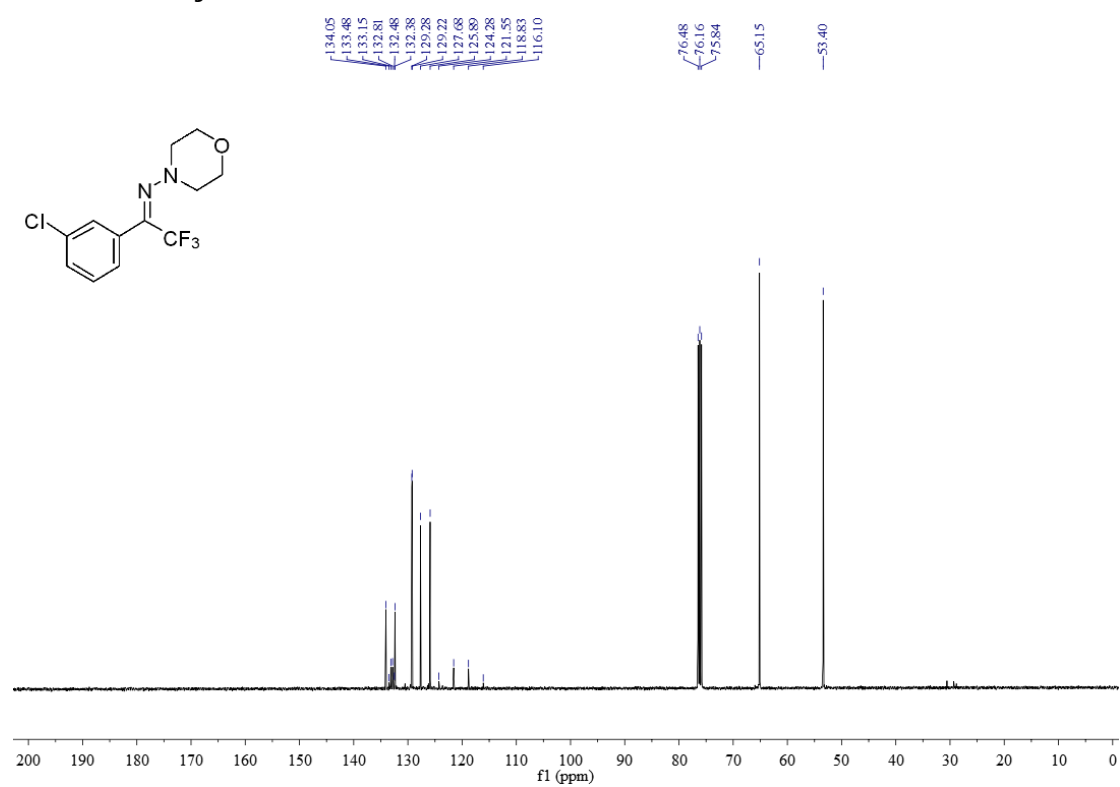
¹⁹F NMR of **2i**



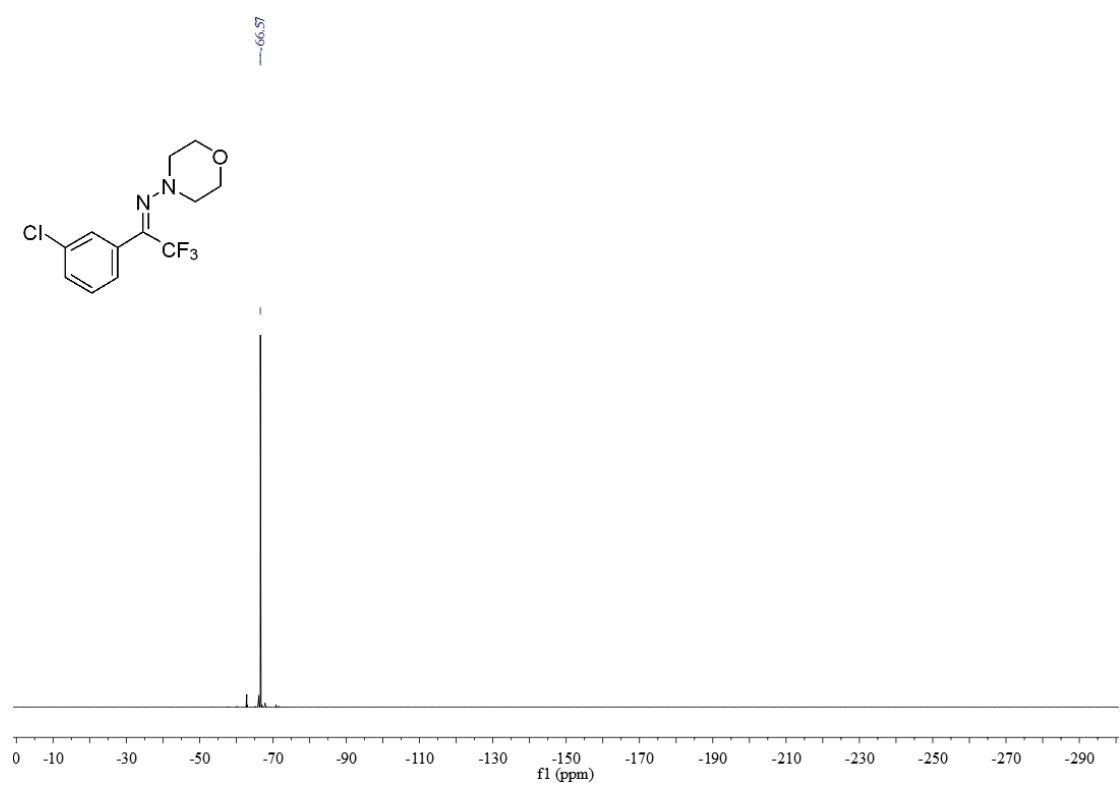
¹H NMR of **2j**



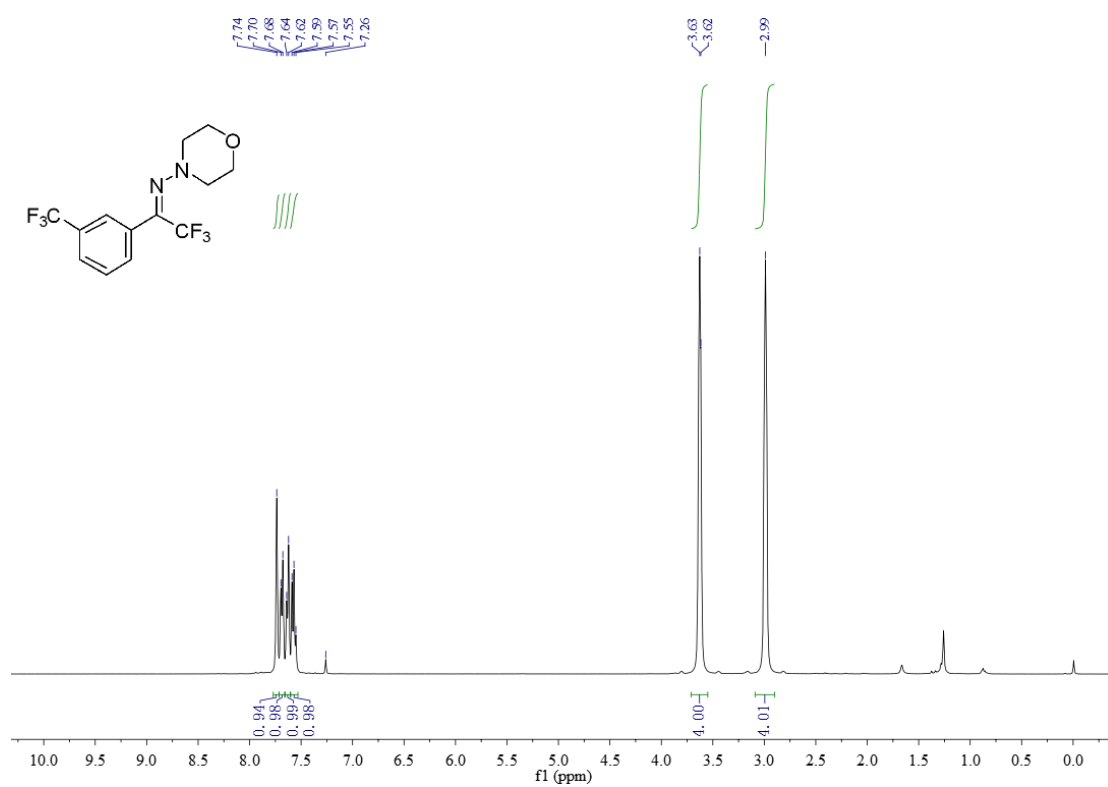
¹³C NMR of **2j**



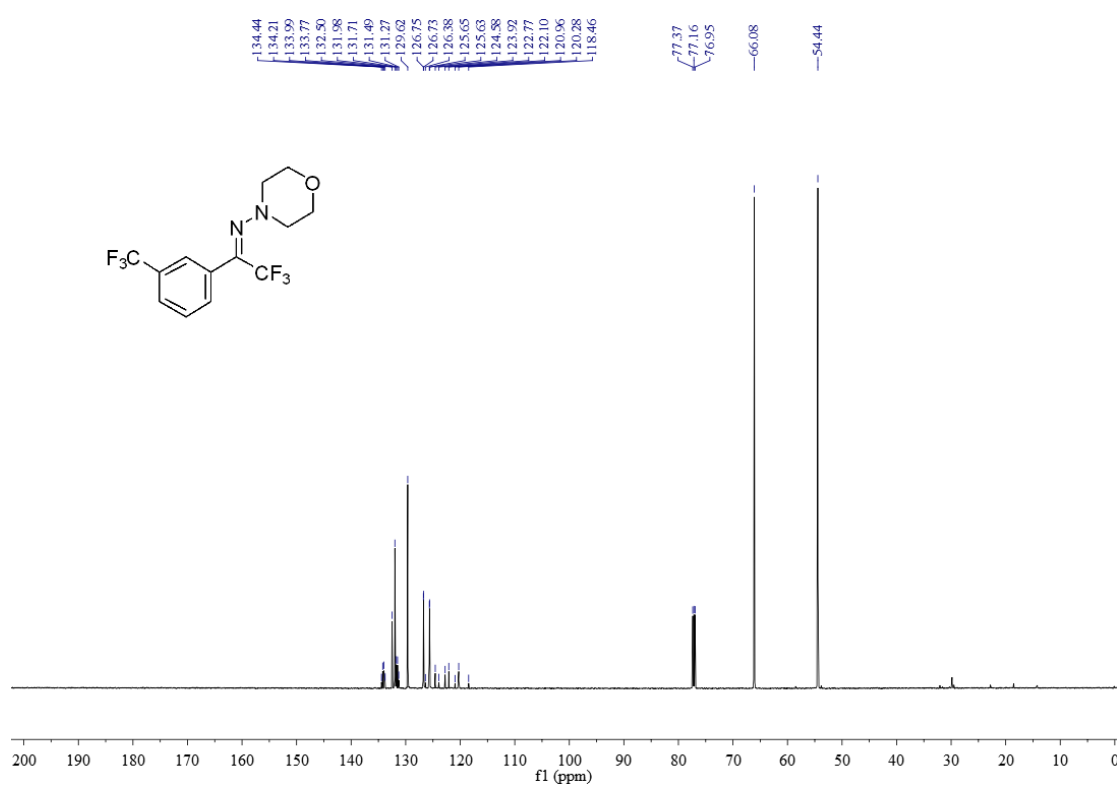
¹⁹F NMR of **2j**



¹H NMR of **2k**



¹³C NMR of **2k**



FC(F)(F)c1ccc(cc1)/C(F)(F)=N/N2CCOCC2

Chemical structure: FC(F)(F)c1ccc(cc1)/C(F)(F)=N/N2CCOCC2

¹³C NMR spectrum (ppm):

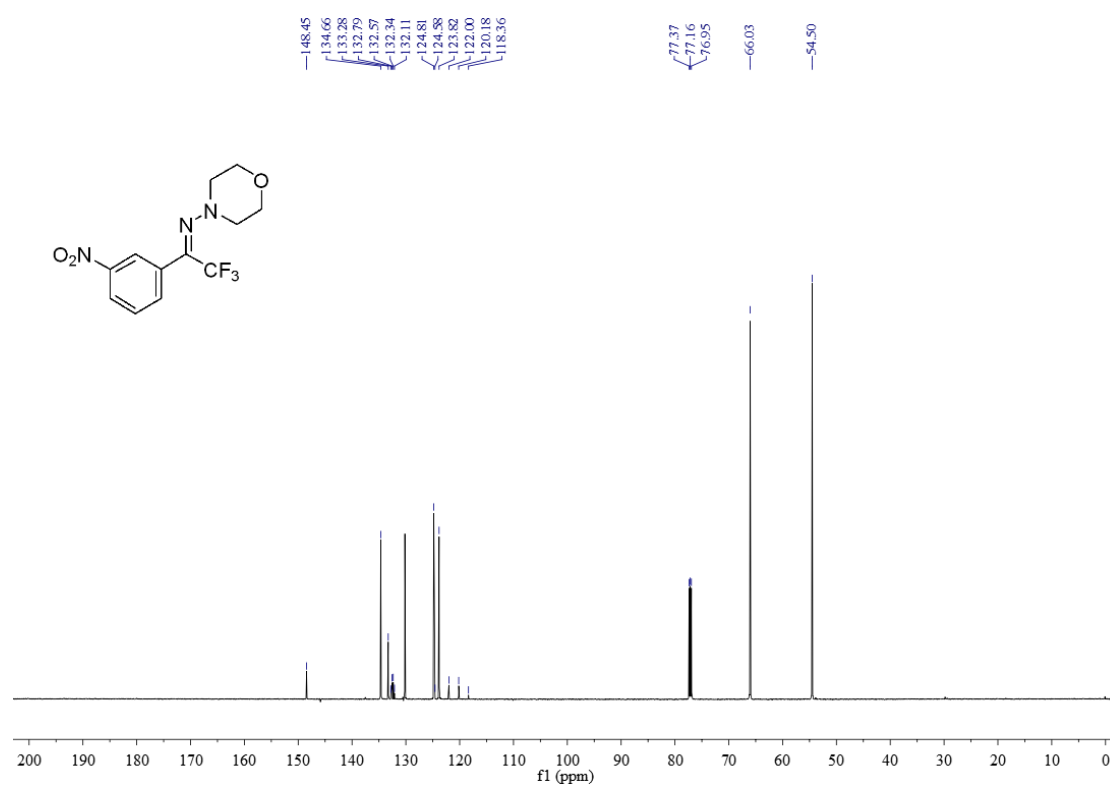
- Peak 1: -62.98 ppm (Integration: 3.00)
- Peak 2: -66.54 ppm (Integration: 2.98)

O=[N+]([O-])c1ccc(cc1)C(=N2CCOCC2)C(F)(F)F

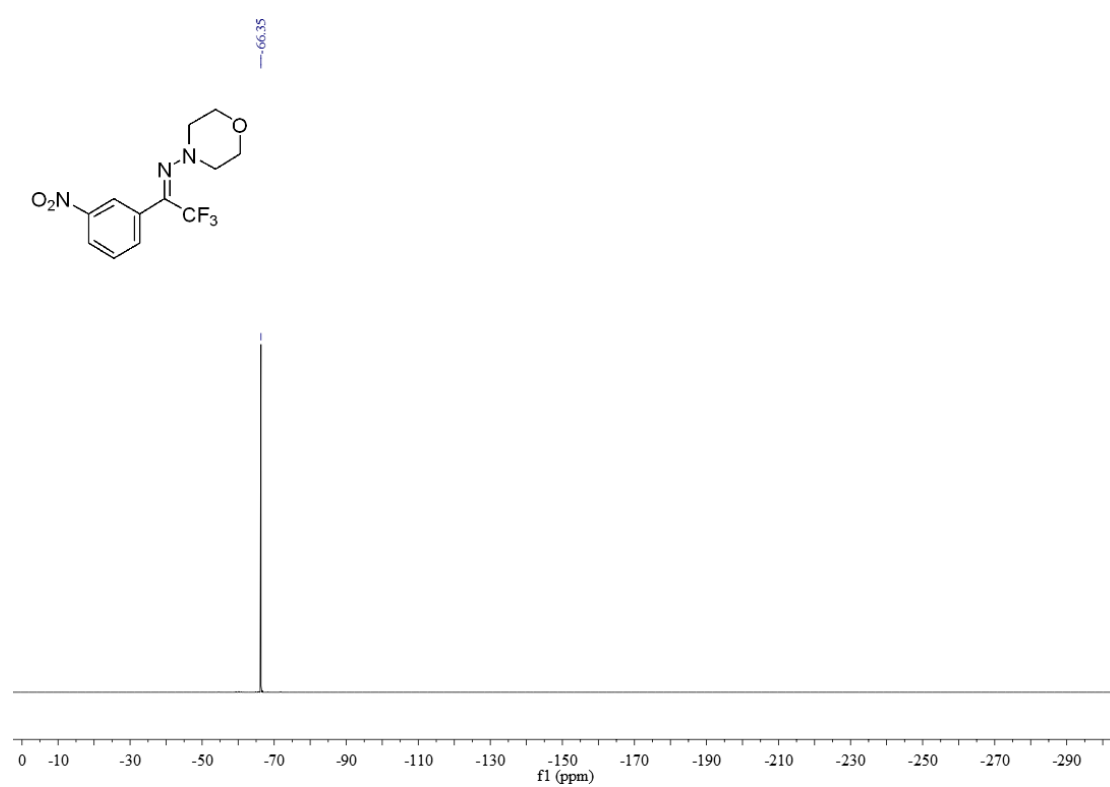
Chemical structure: 4-nitro-2-(2,2,2-trifluoro-1-(4-oxa-1,2,3,4-tetrahydropyrimidin-5-ylidene)ethyl)benzene.

¹H NMR spectrum (CDCl₃) showing peaks at 8.32, 8.30, 8.28, 7.78, 7.76, 7.67, 7.65, 7.26, 3.65, 3.64, 3.63, 3.03, 3.02, and 3.01 ppm. Integration values are provided for each group of peaks.

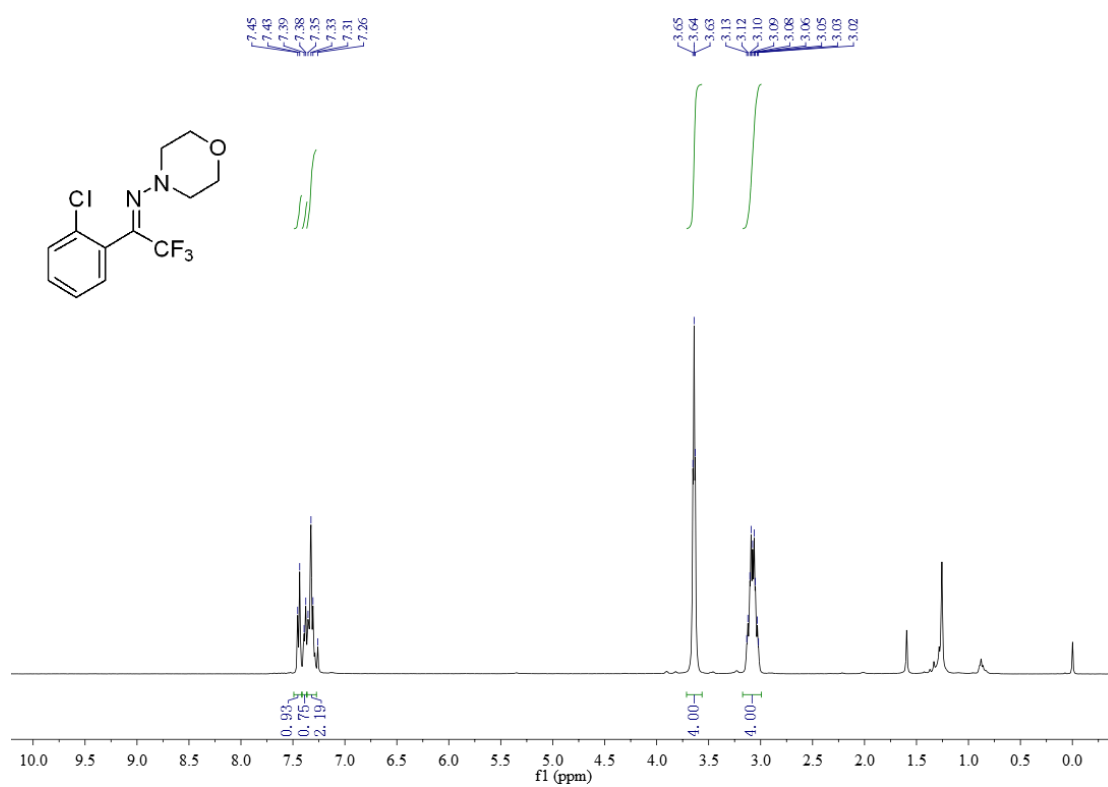
¹³C NMR of **2l**



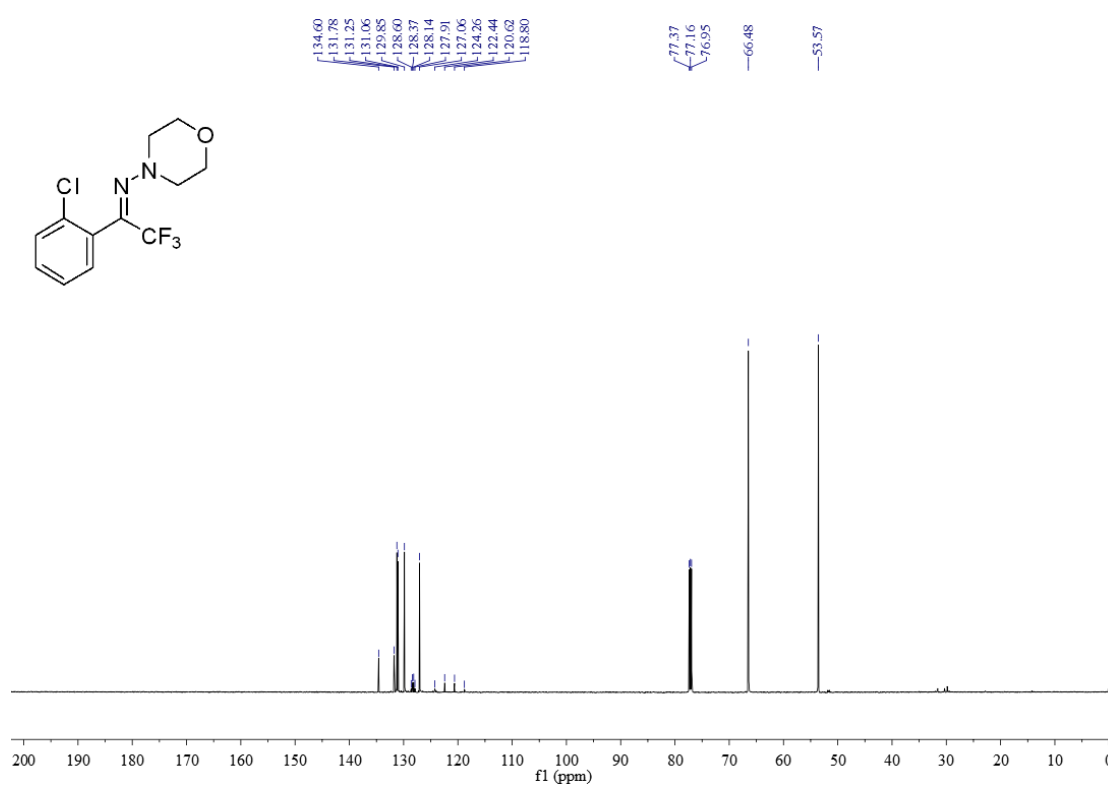
¹⁹F NMR of **2l**



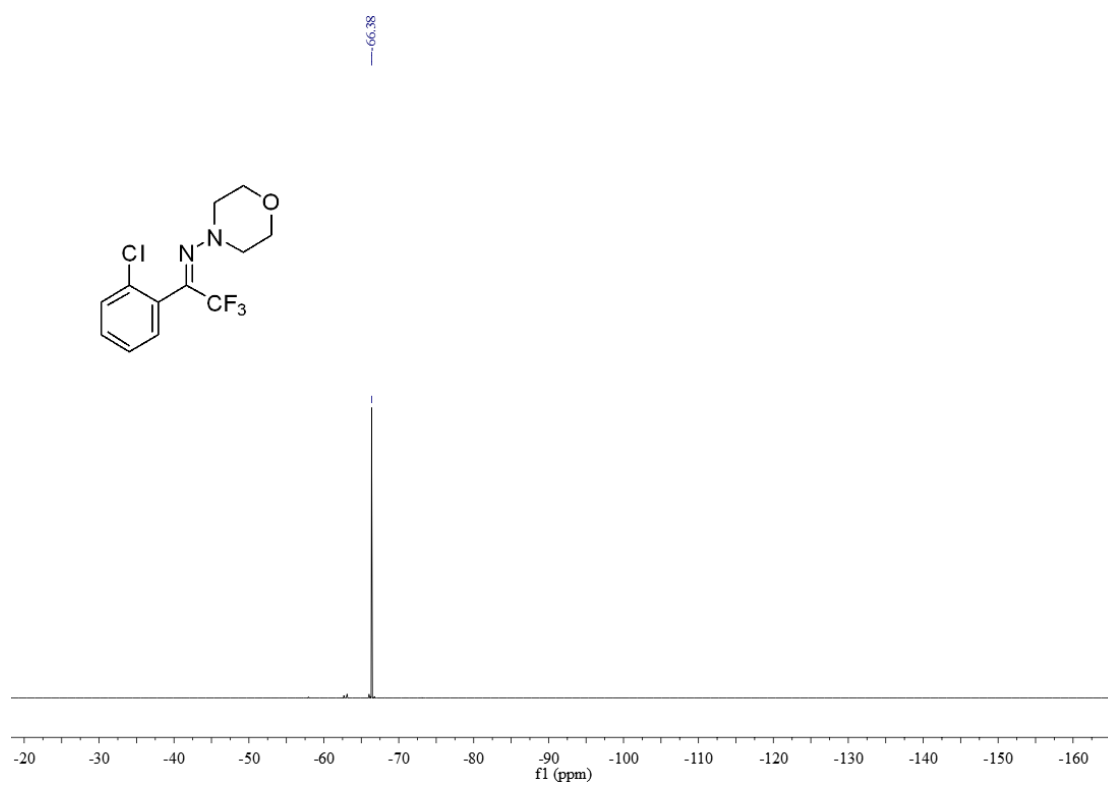
¹H NMR of **2m**



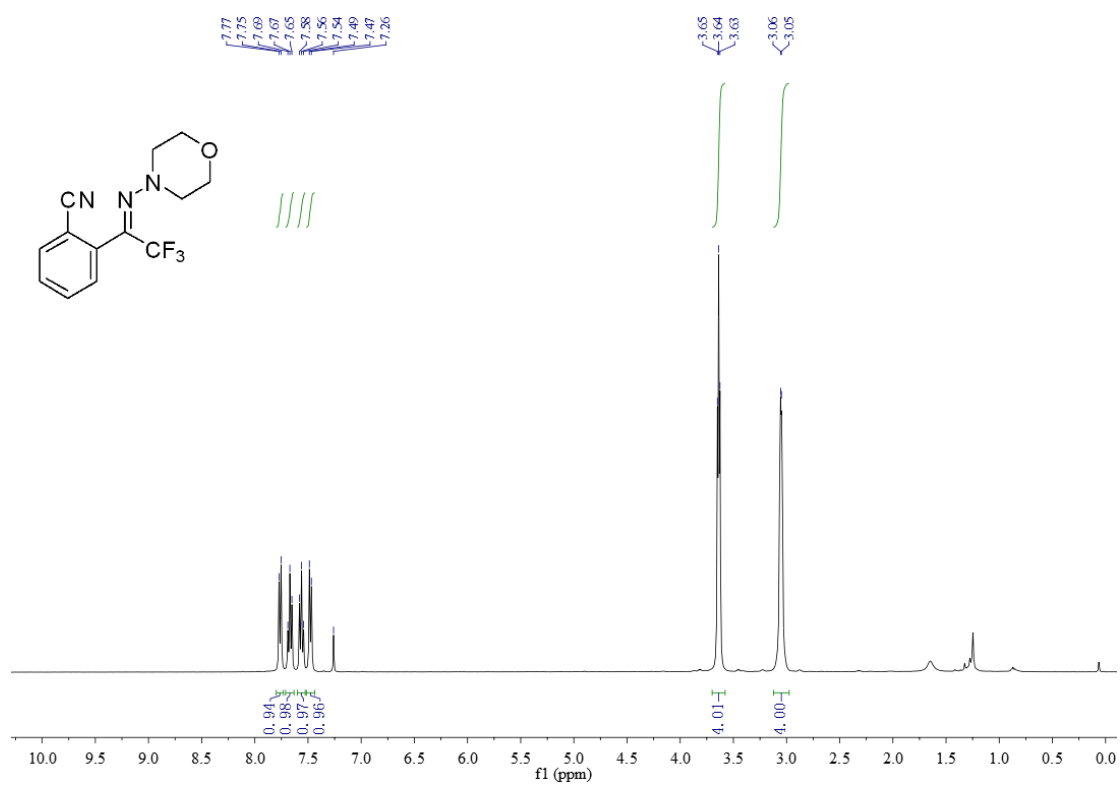
¹³C NMR of **2m**



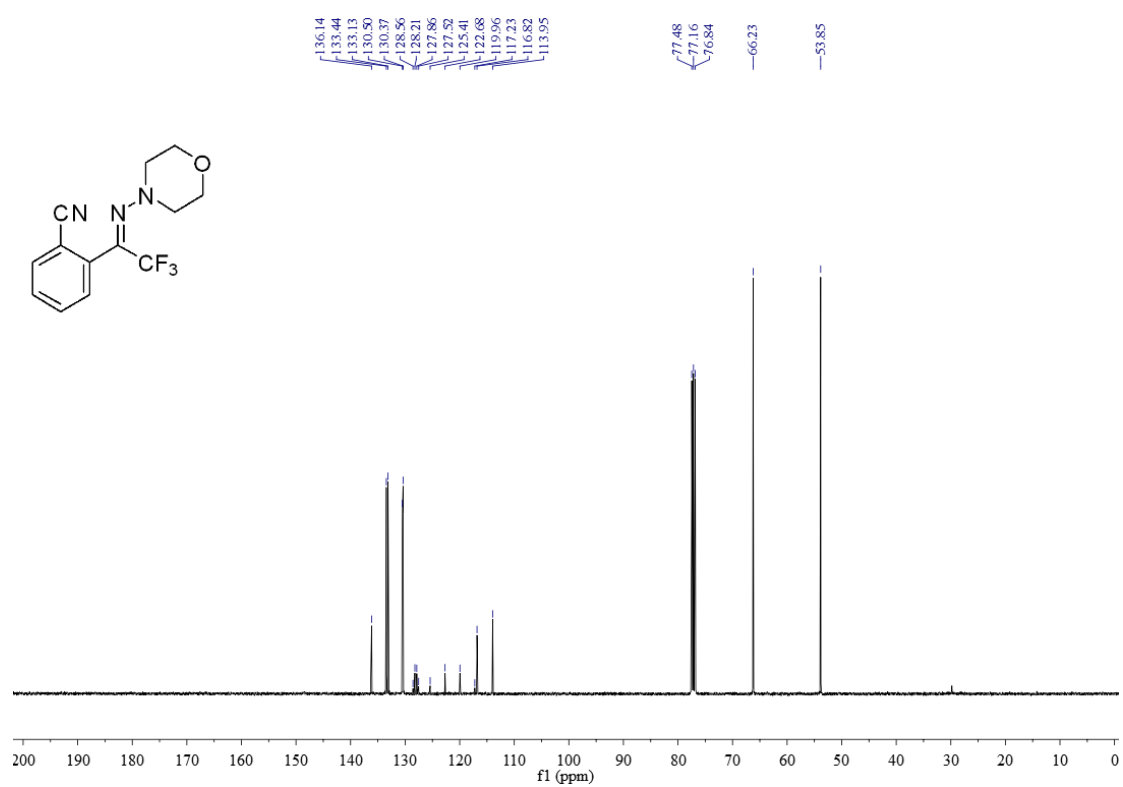
^{19}F NMR of **2m**



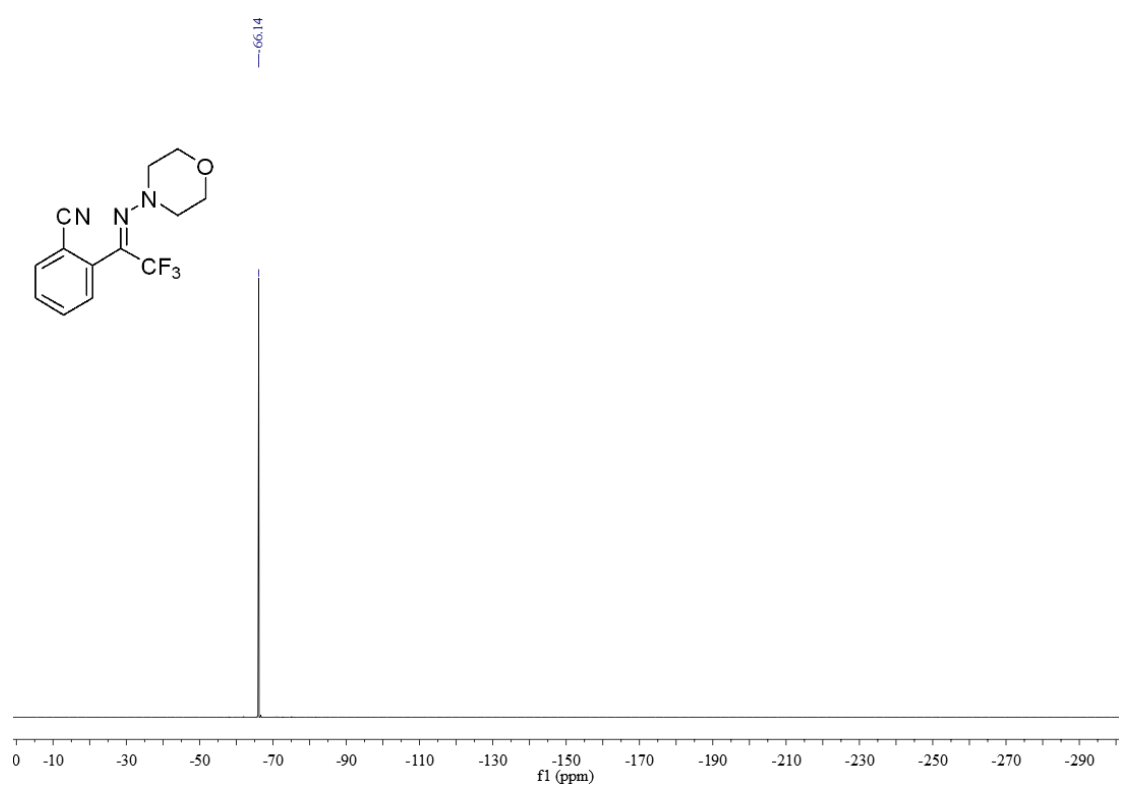
^1H NMR of **2n**



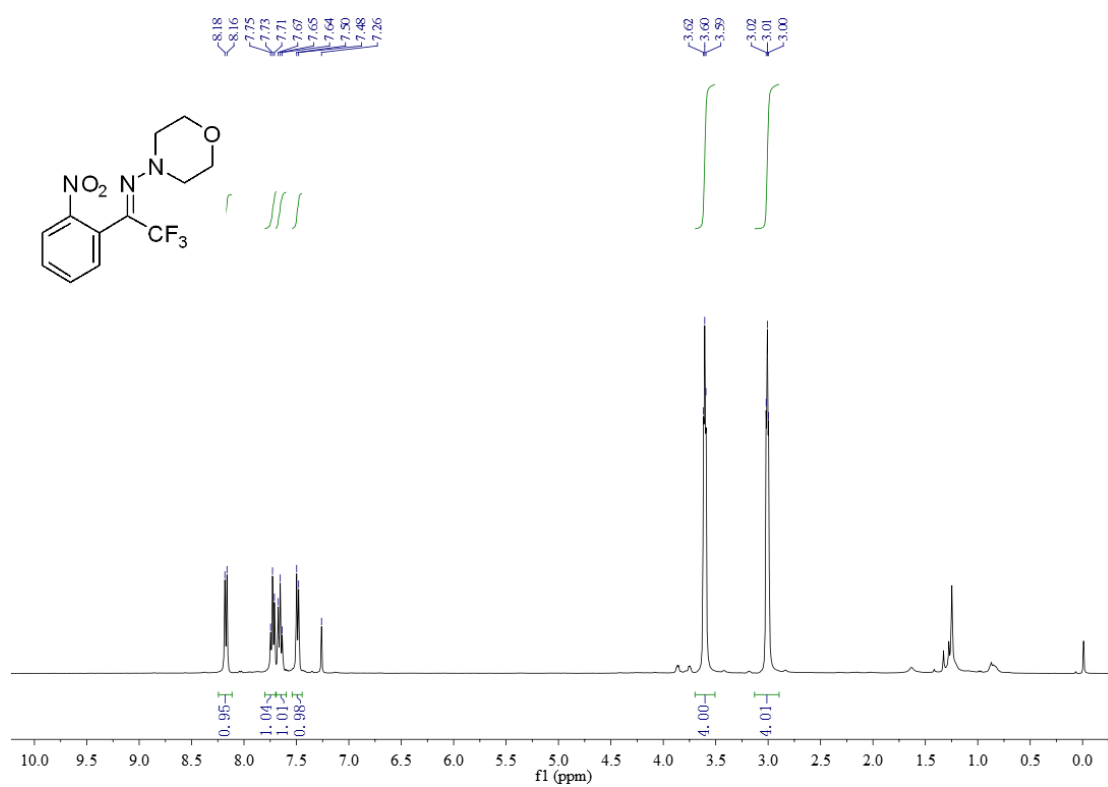
¹³C NMR of **2n**



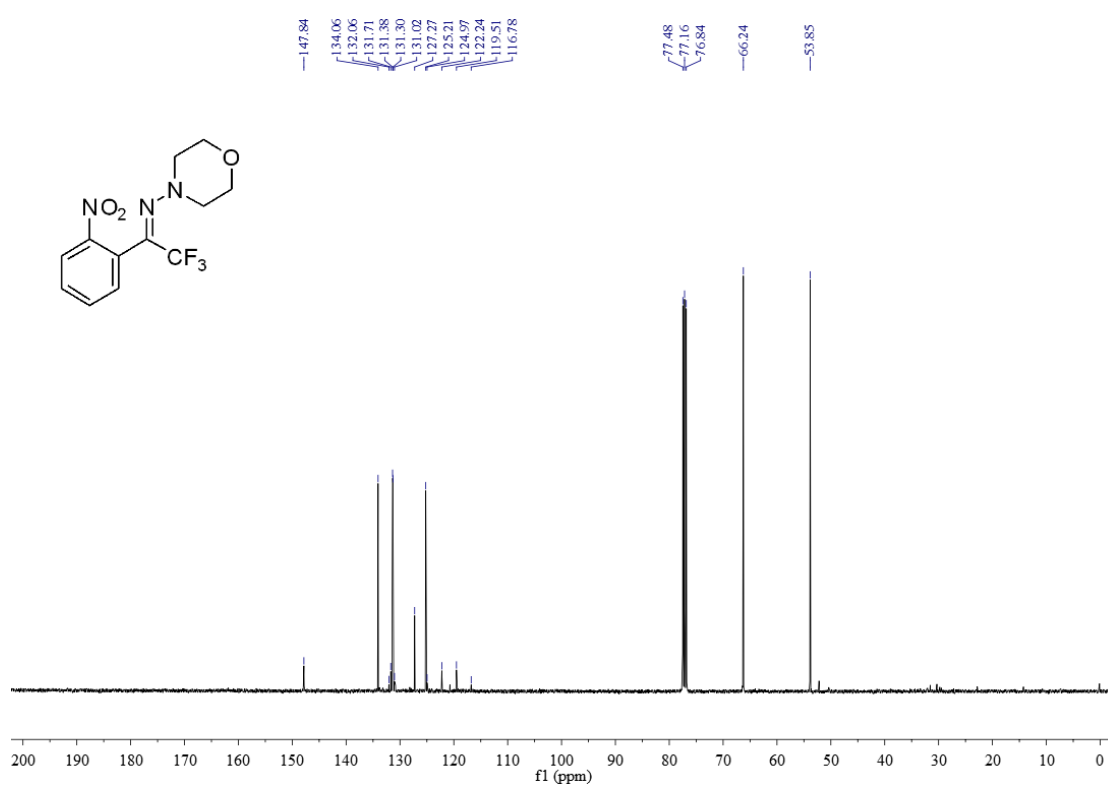
¹⁹F NMR of **2n**



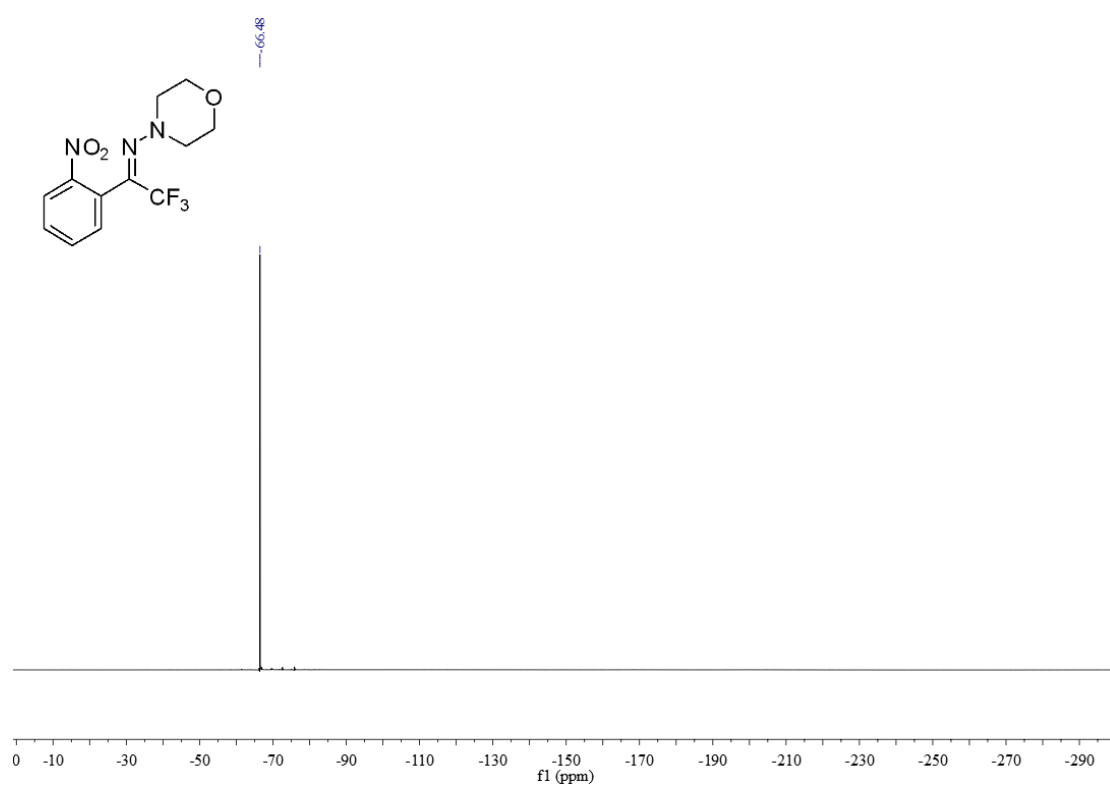
¹H NMR of **2o**



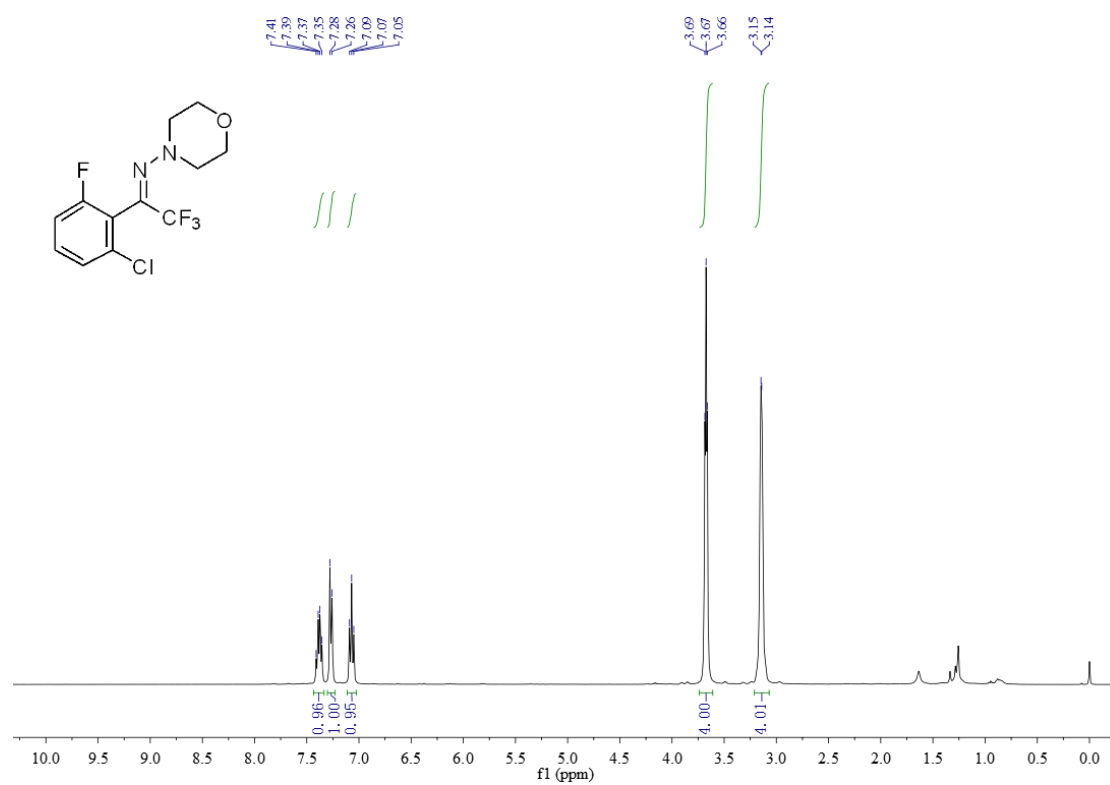
¹³C NMR of **2o**



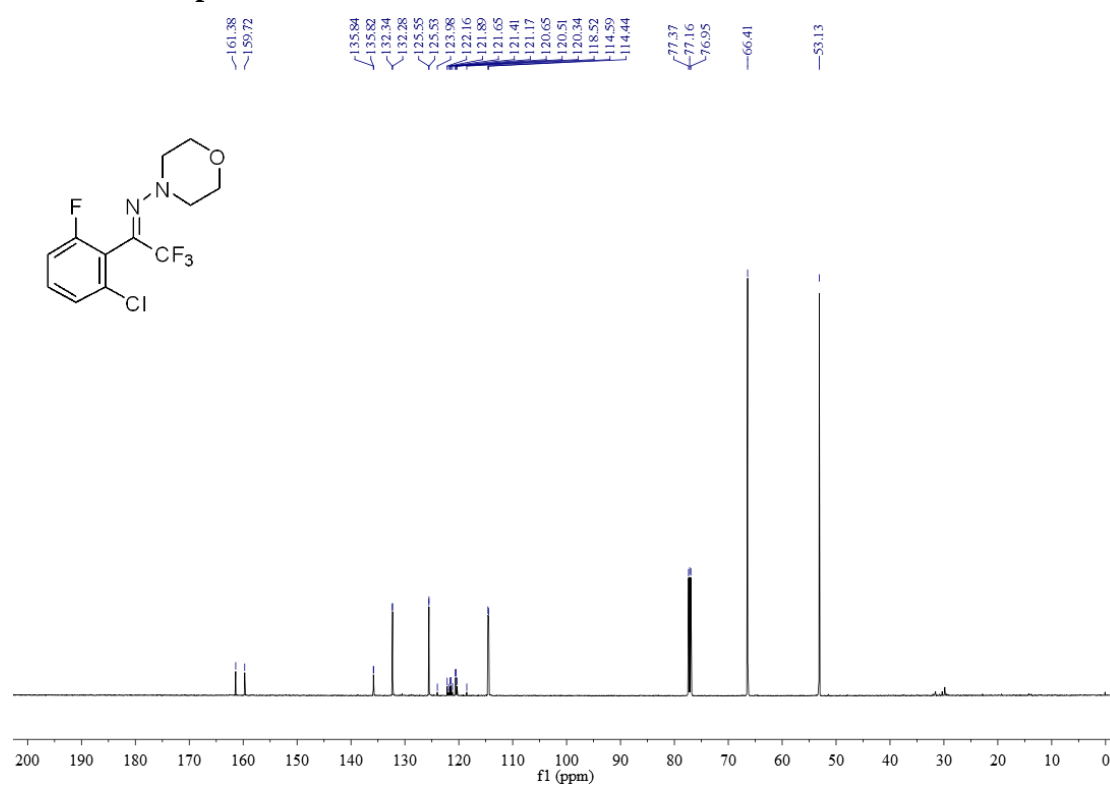
^{19}F NMR of **2o**



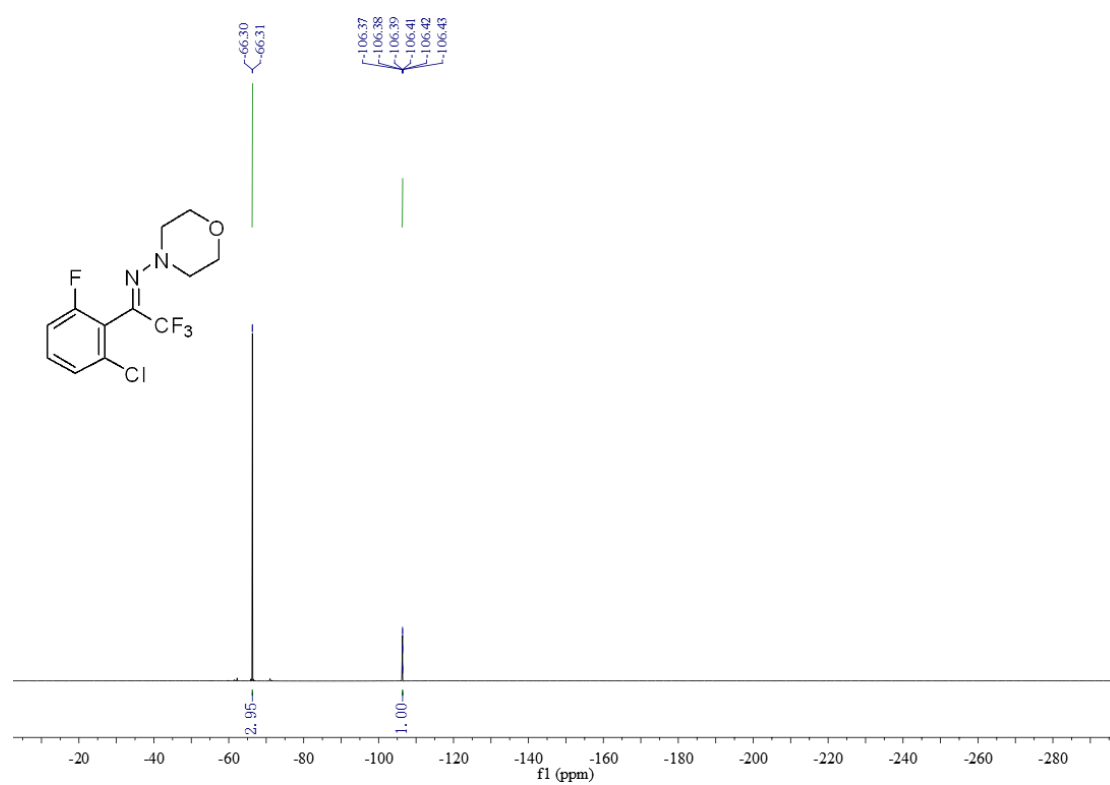
^1H NMR of **2p**



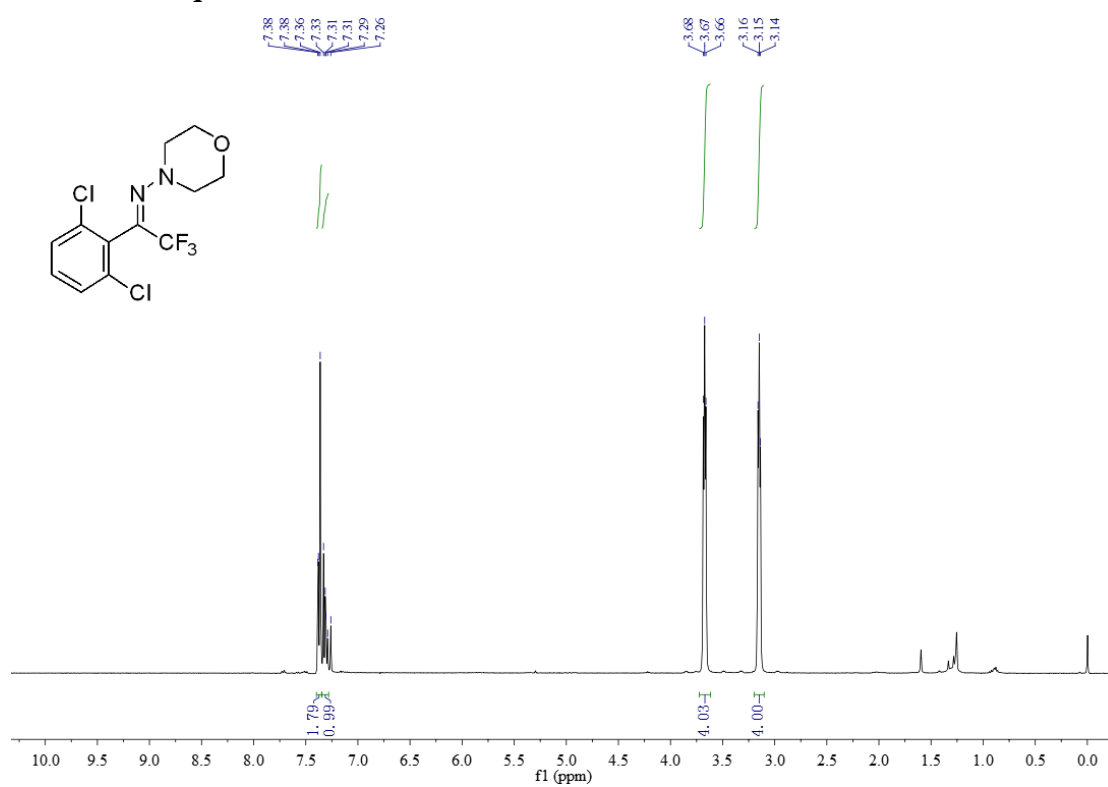
¹³C NMR of **2p**



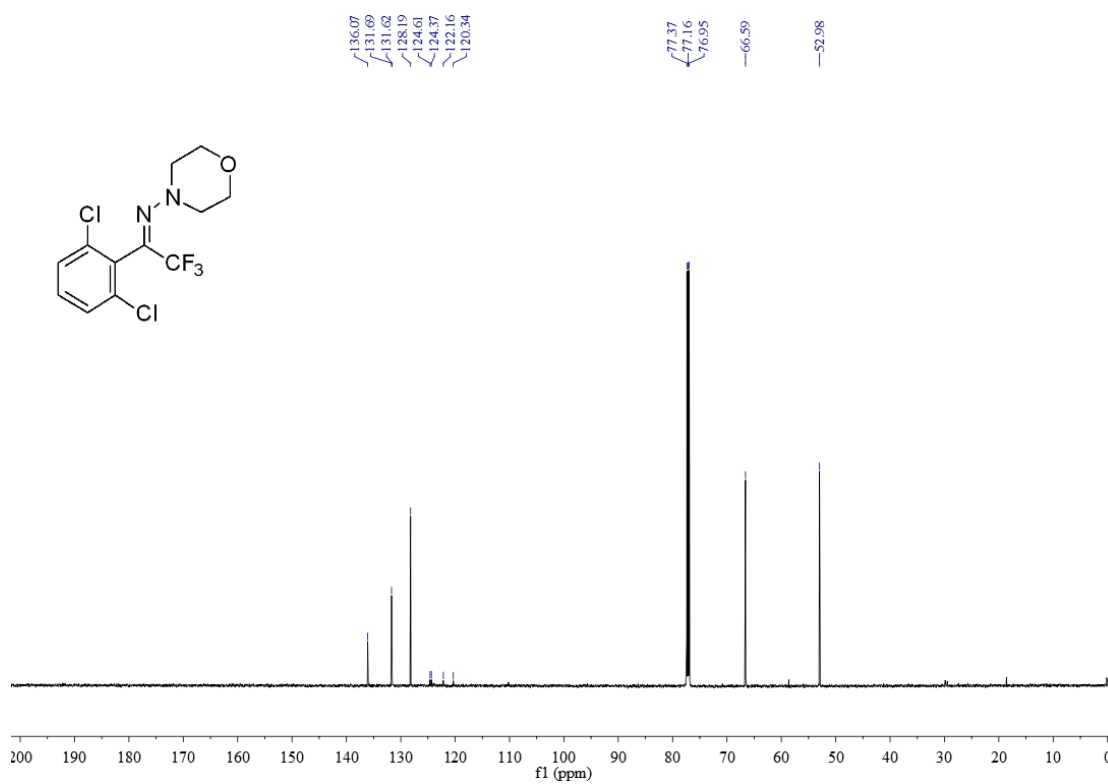
¹⁹F NMR of **2p**



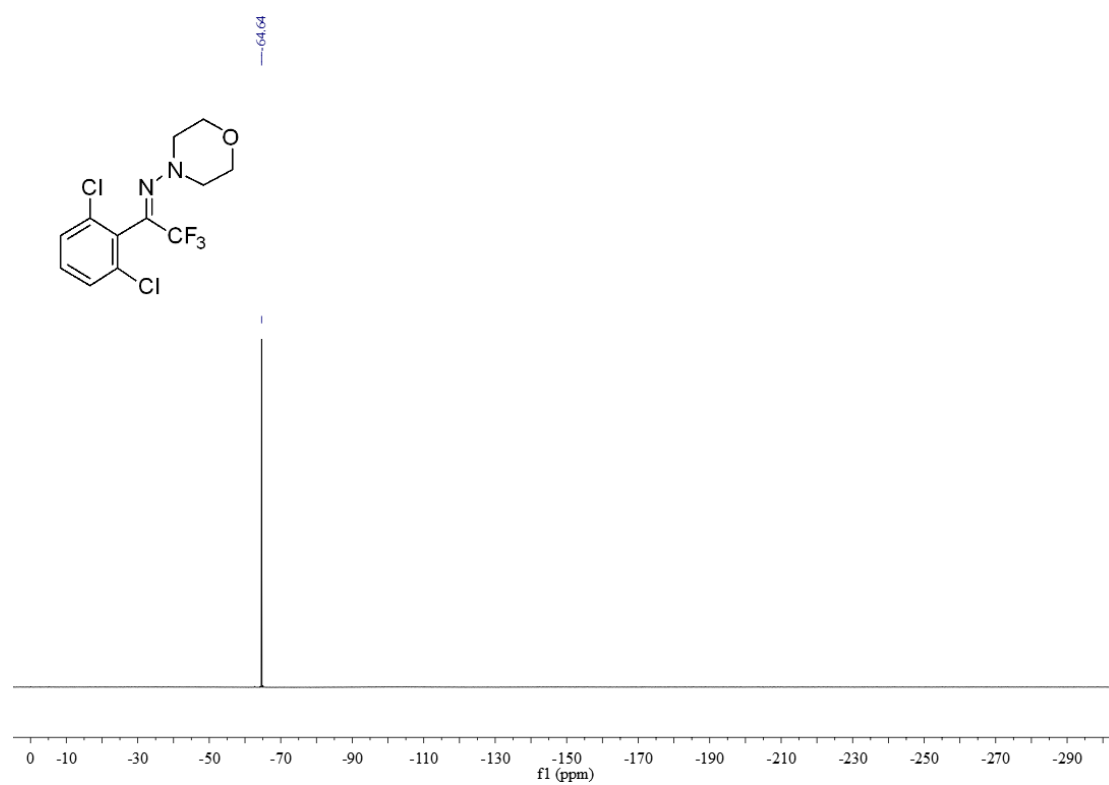
¹H NMR of **2q**



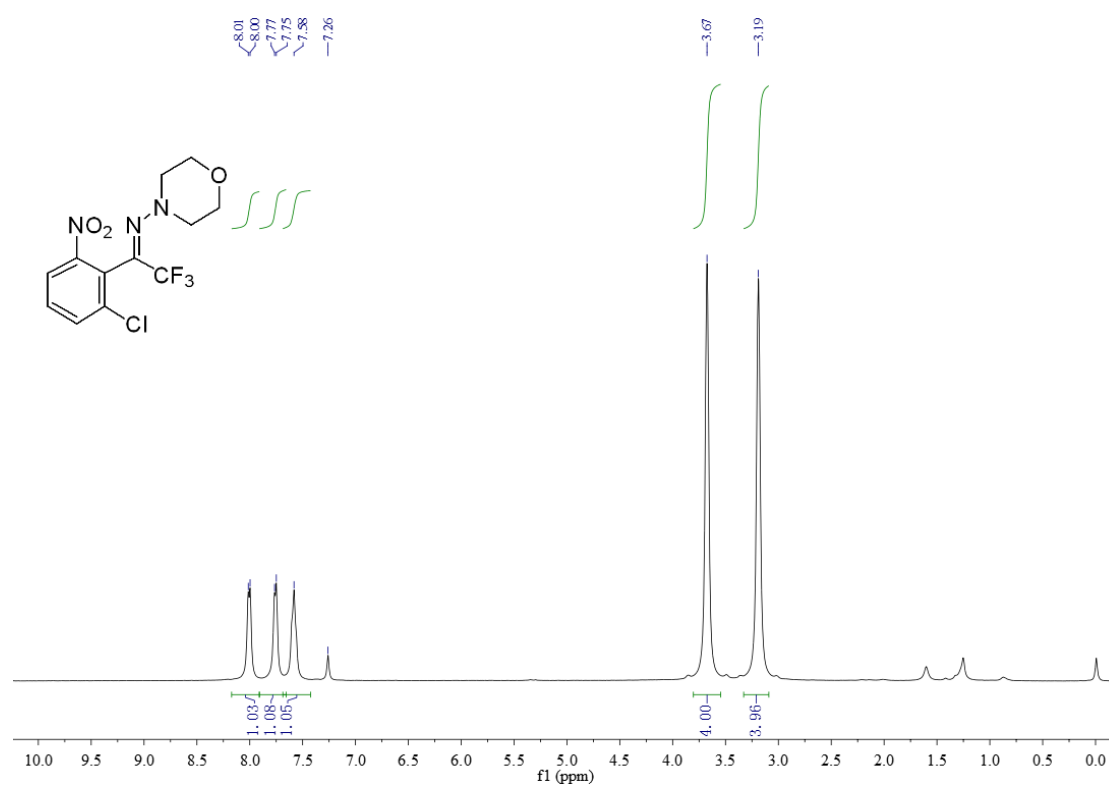
¹³C NMR of **2q**



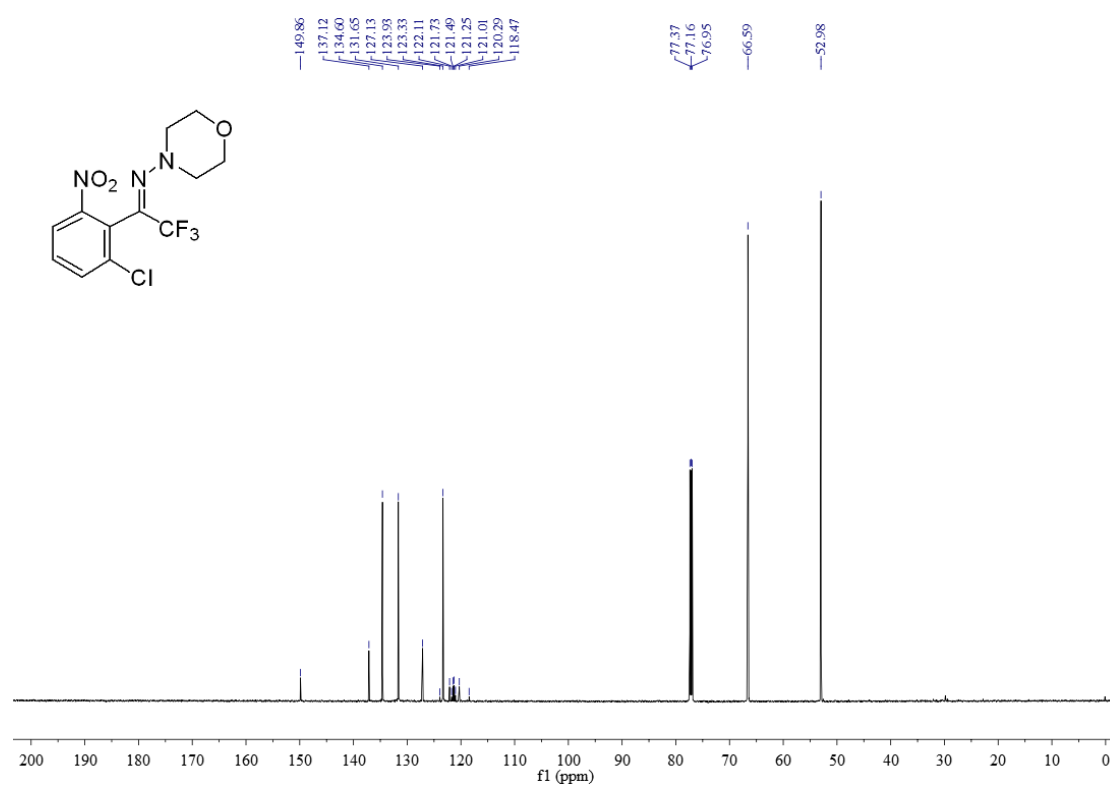
¹⁹F NMR of **2q**



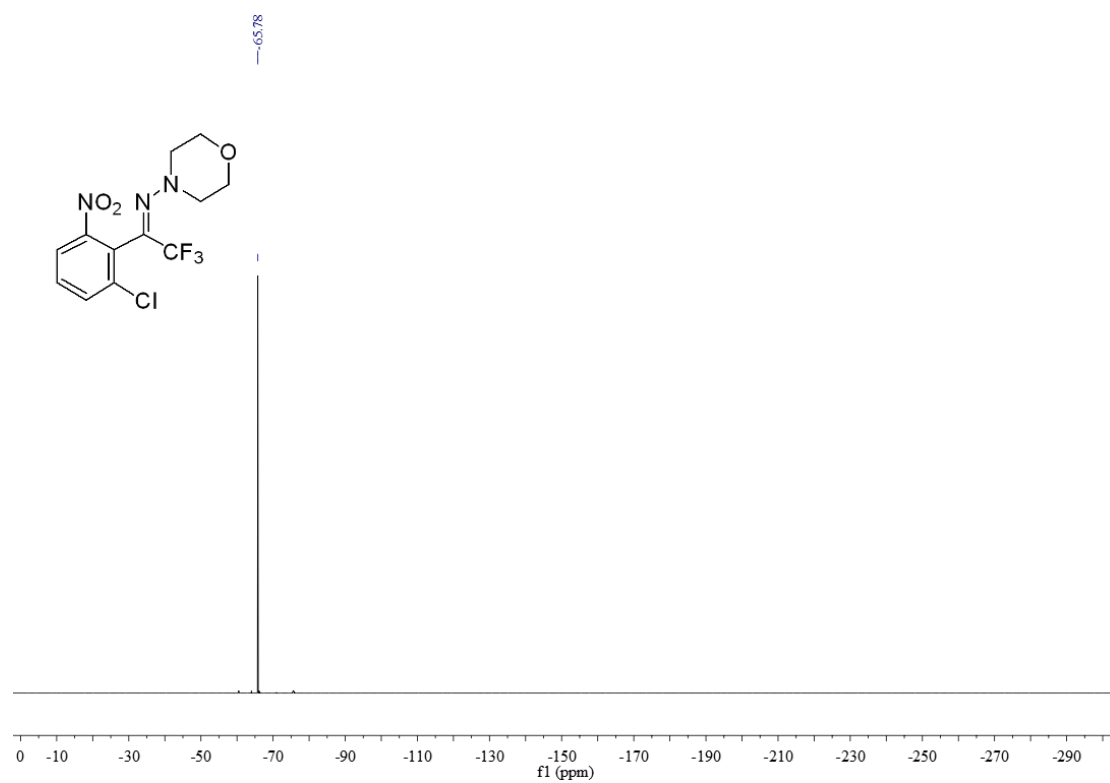
¹H NMR of **2r**



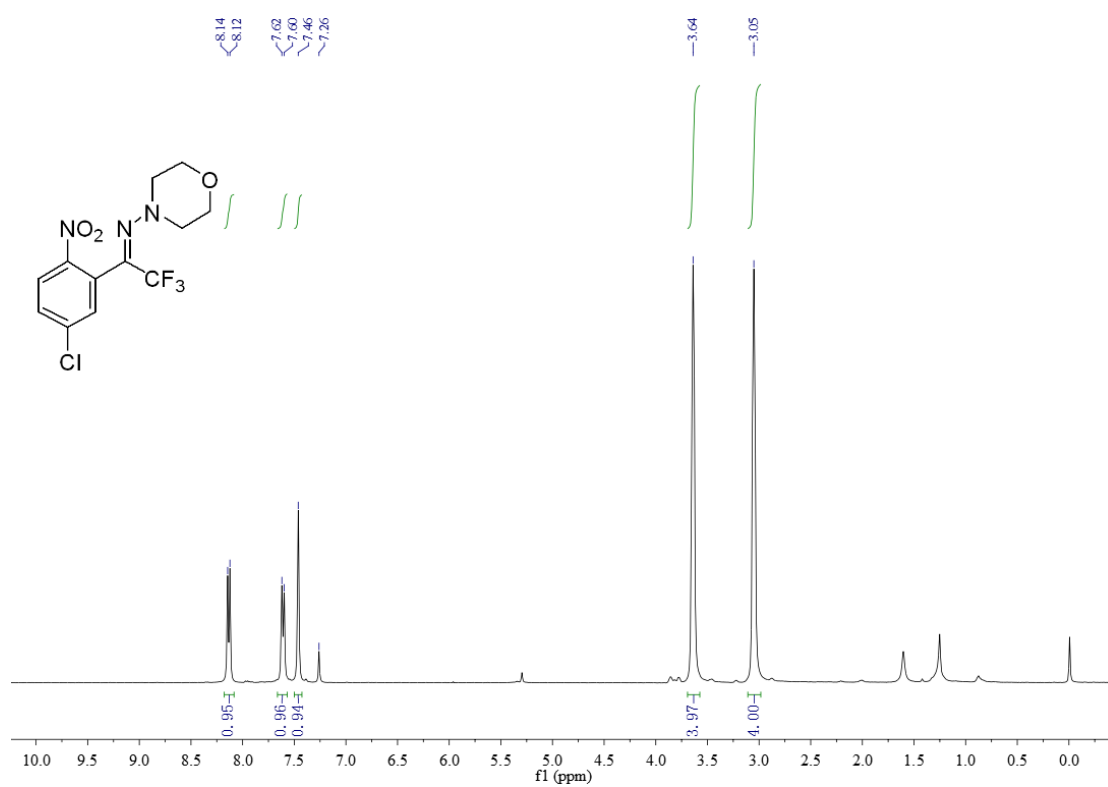
¹³C NMR of **2r**



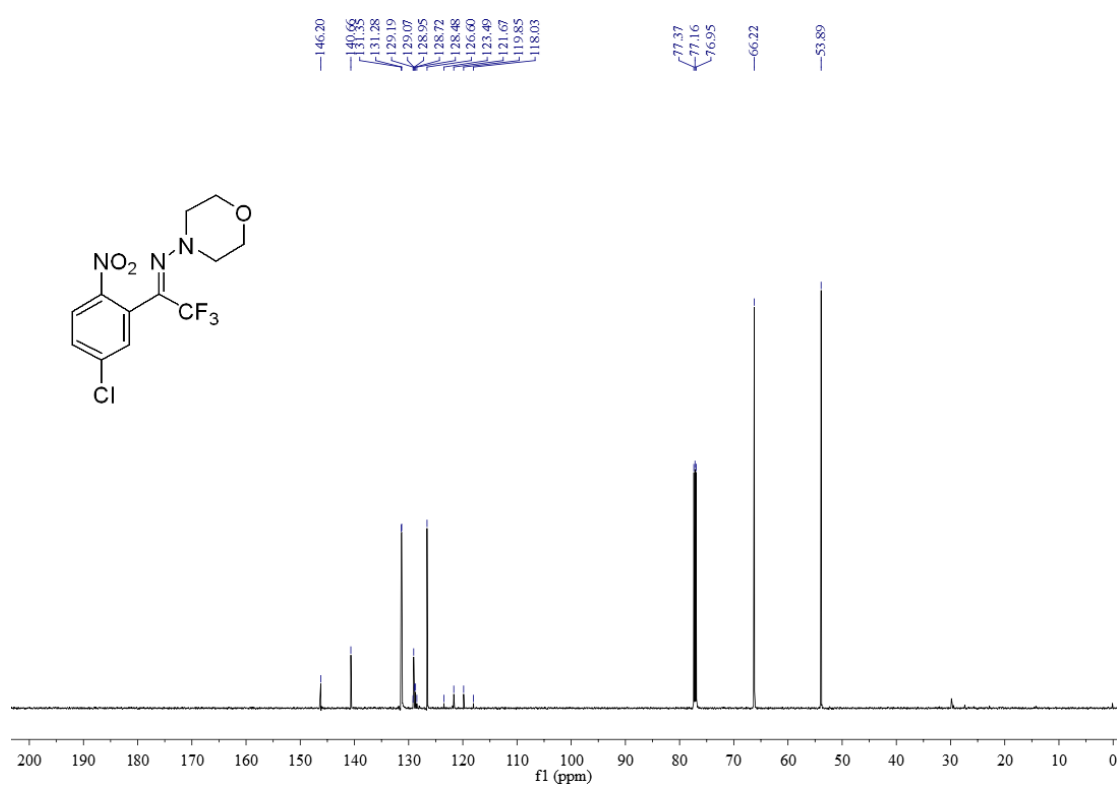
¹⁹F NMR of **2r**



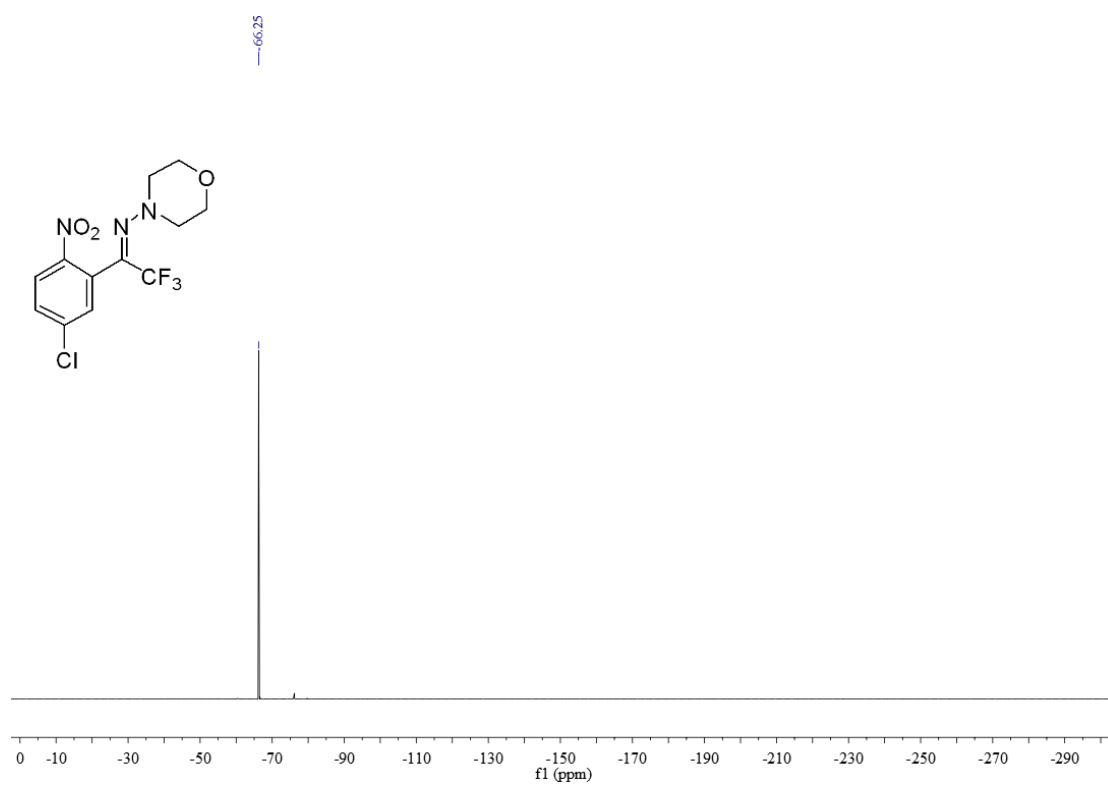
¹H NMR of 2s



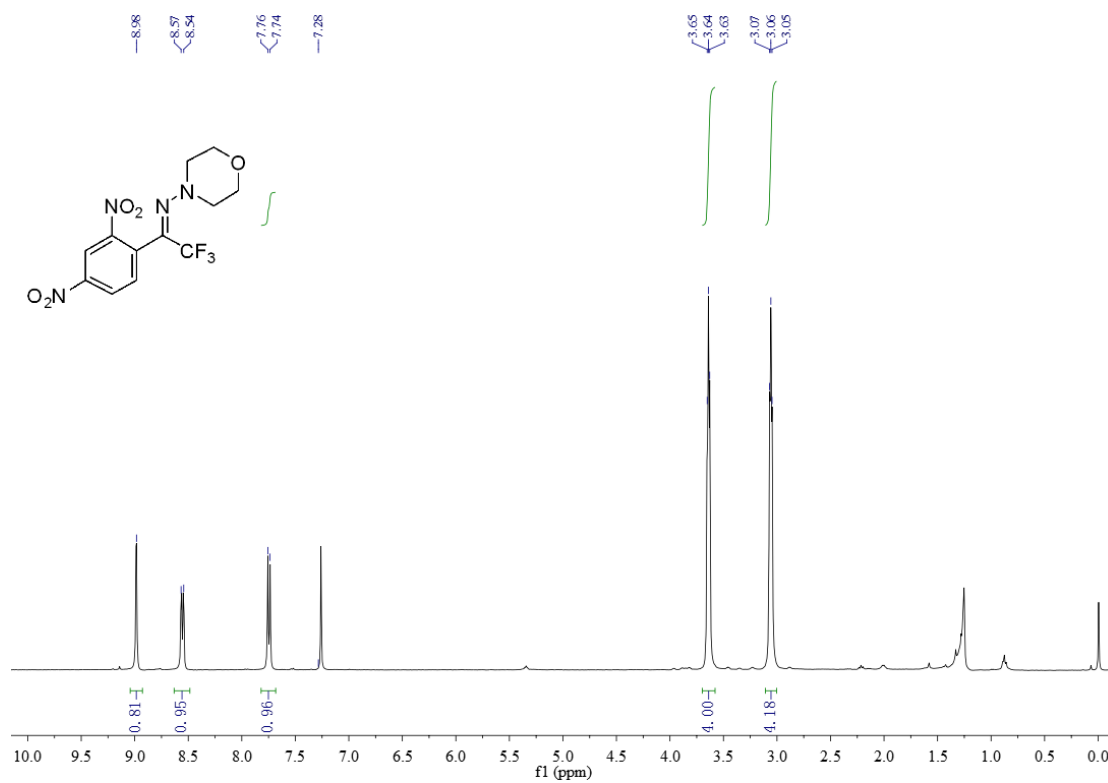
¹³C NMR of 2s



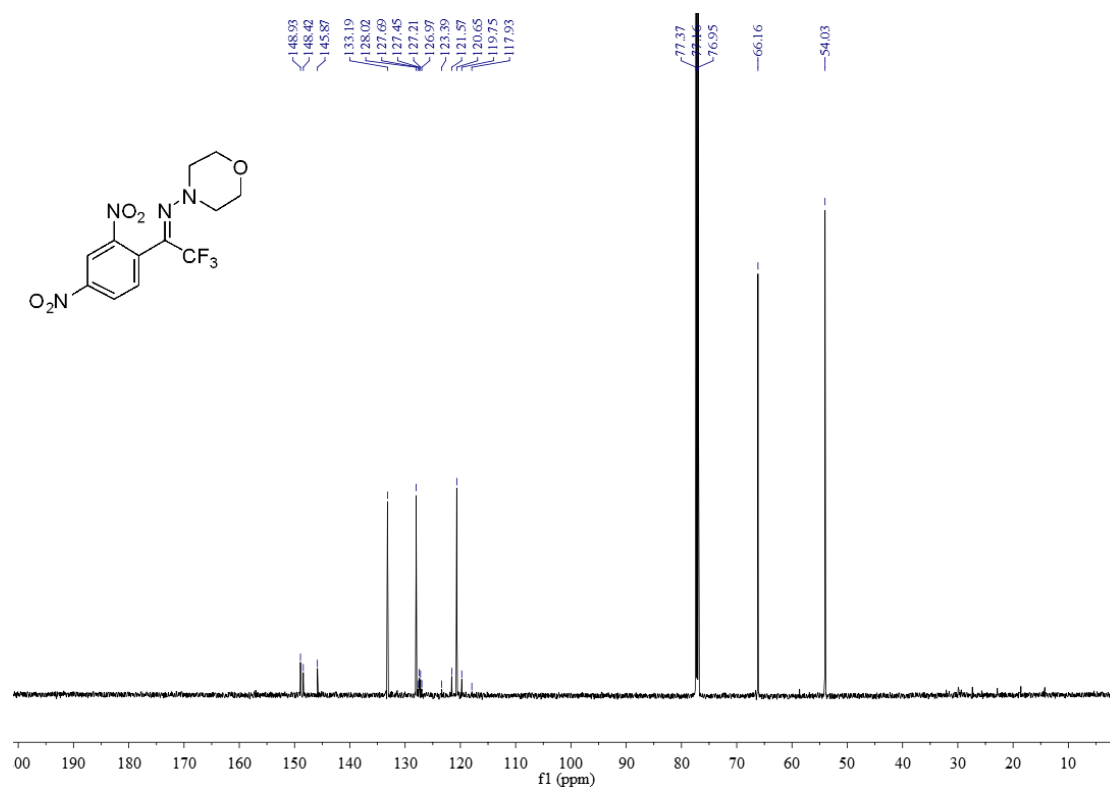
¹⁹F NMR of **2s**



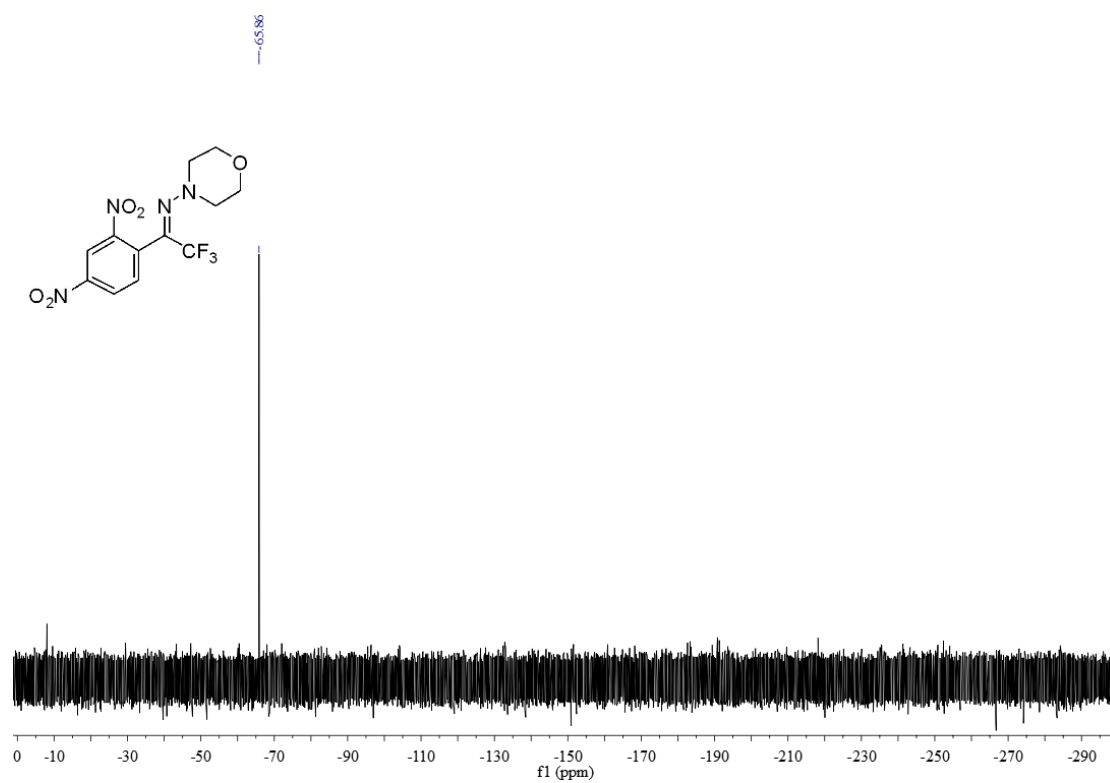
¹H NMR of **2t**



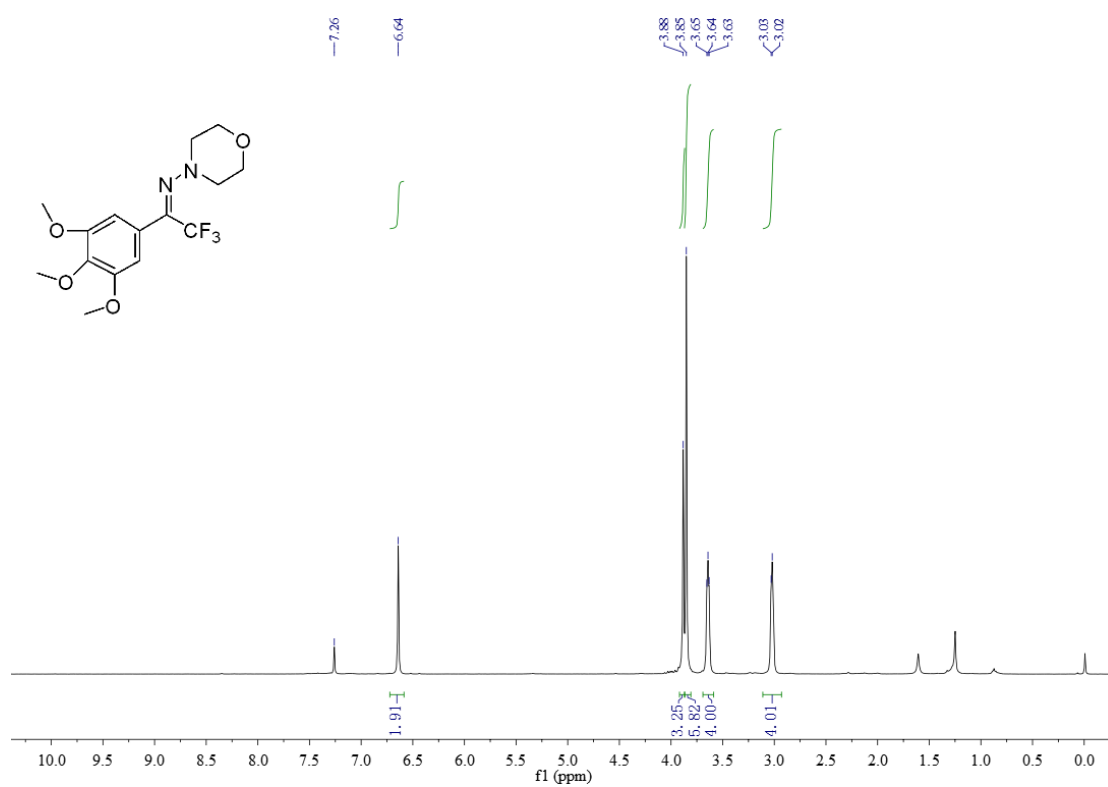
¹³C NMR of **2t**



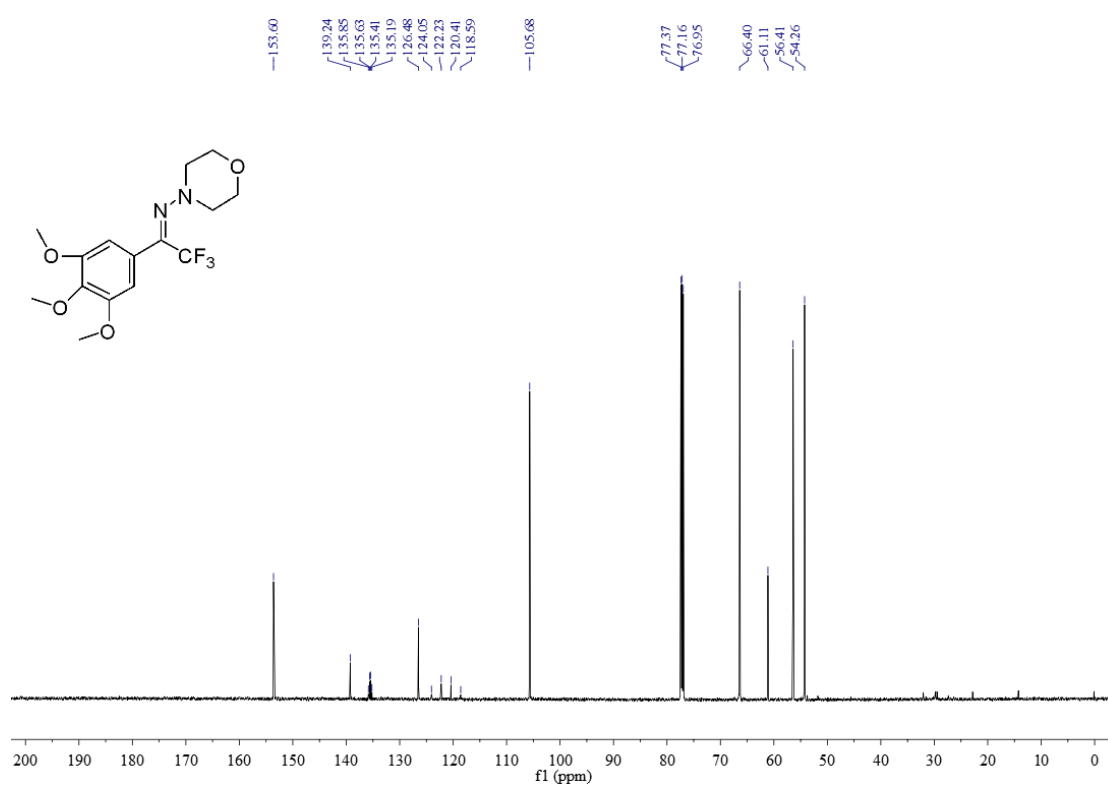
¹⁹F NMR of **2t**



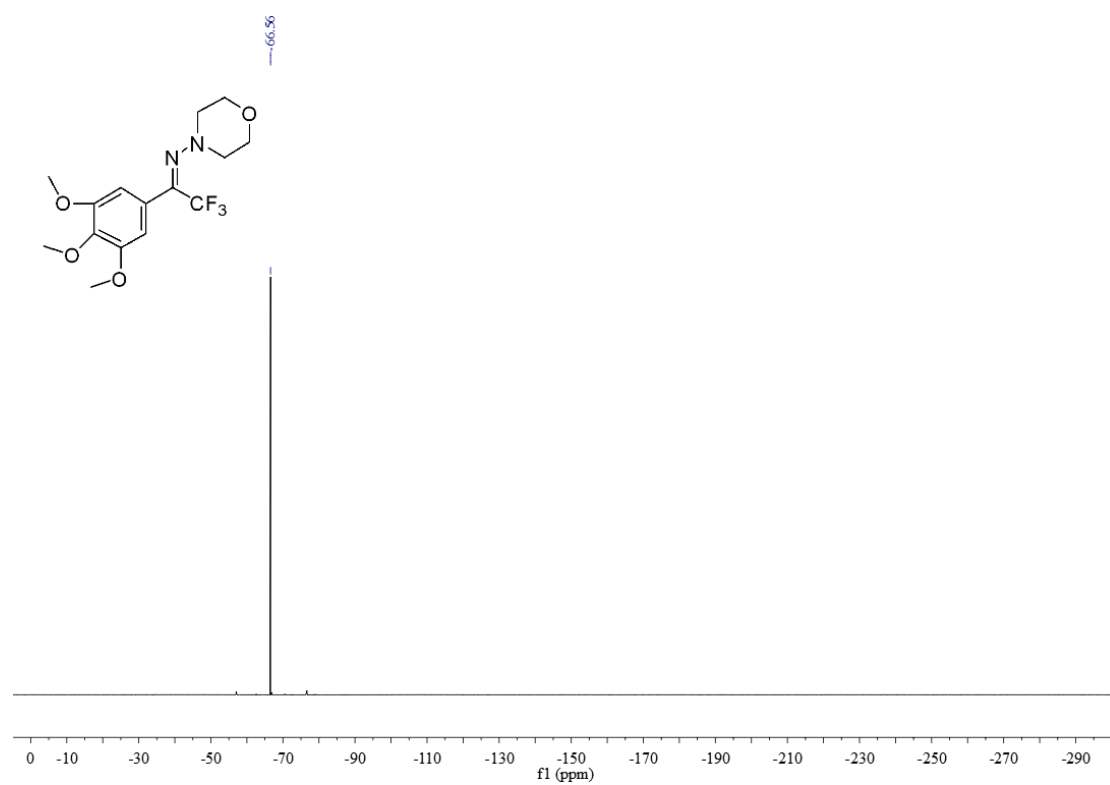
¹H NMR of **2u**



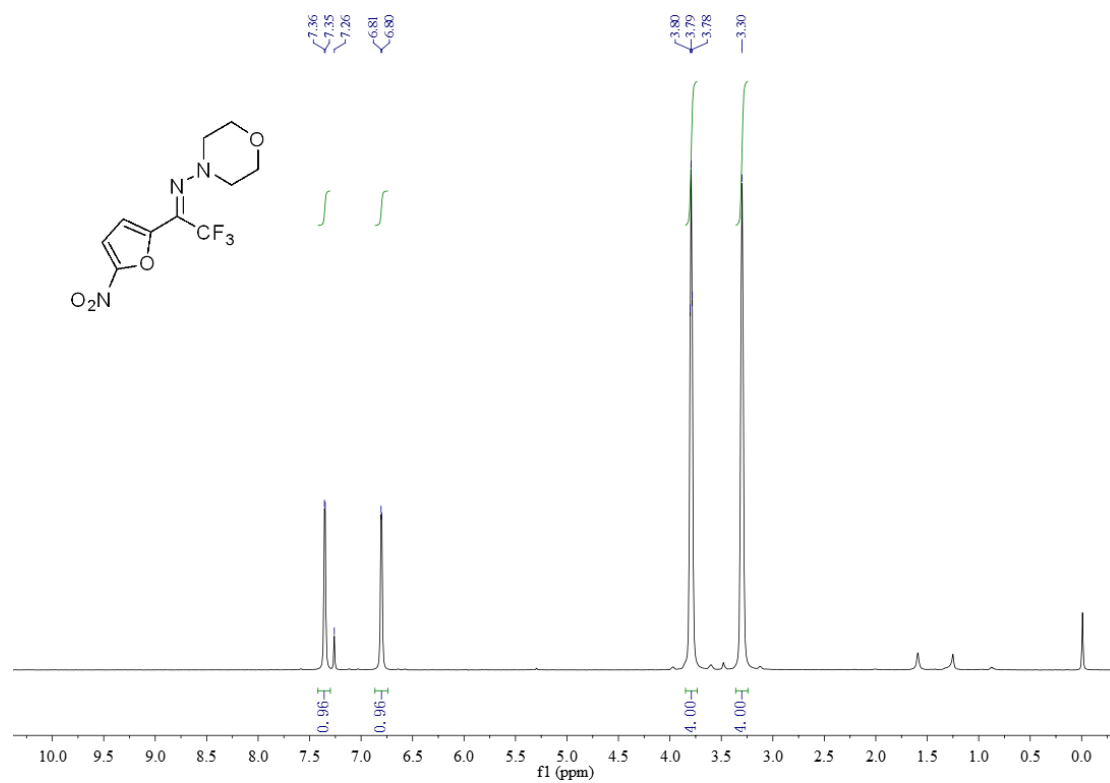
¹³C NMR of **2u**



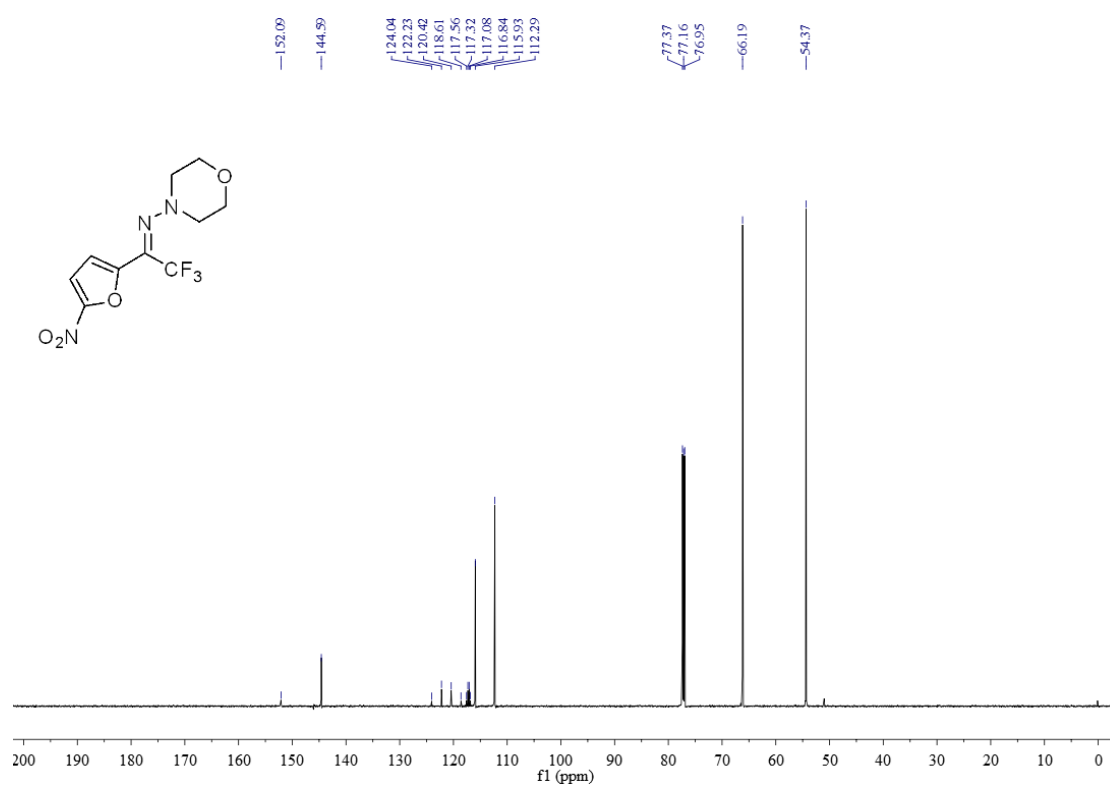
¹⁹F NMR of **2u**



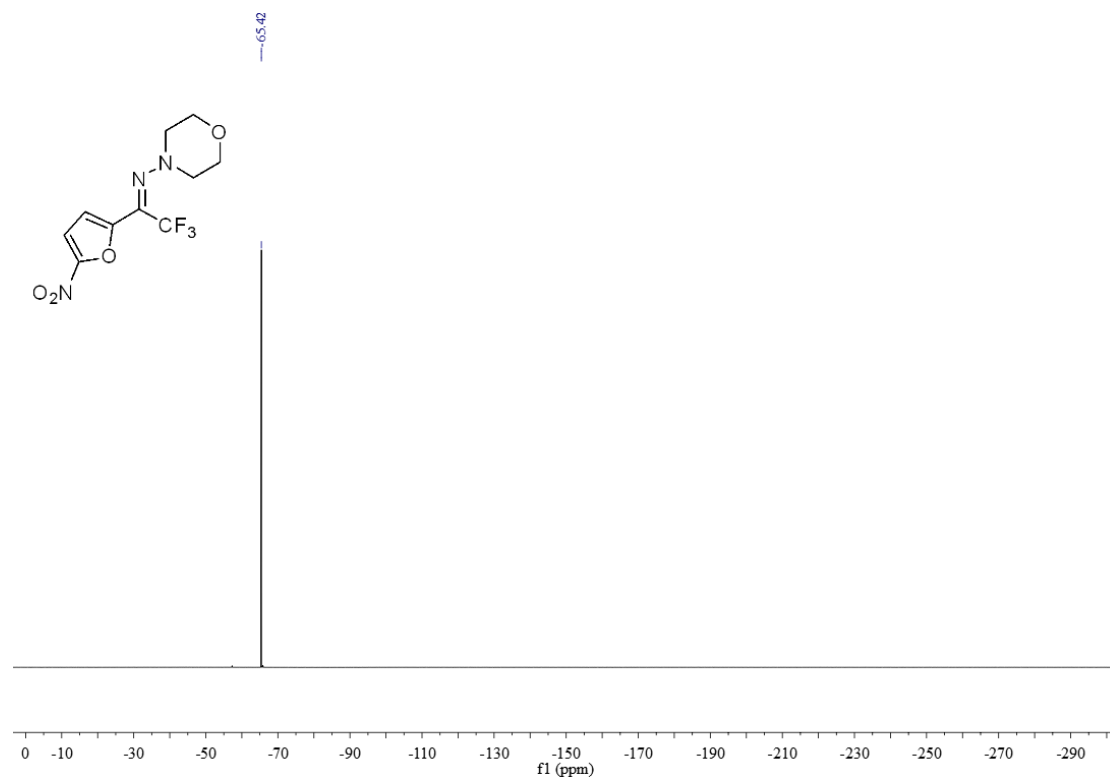
¹H NMR of **2v**



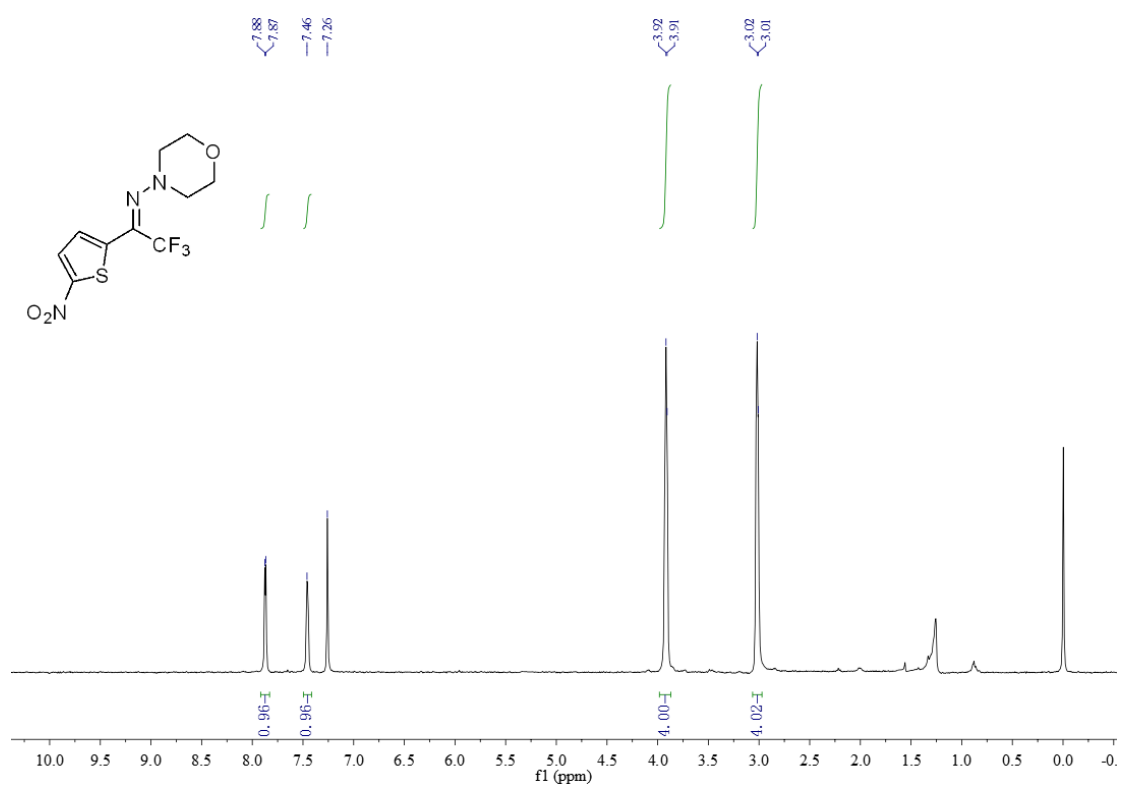
¹³C NMR of **2v**



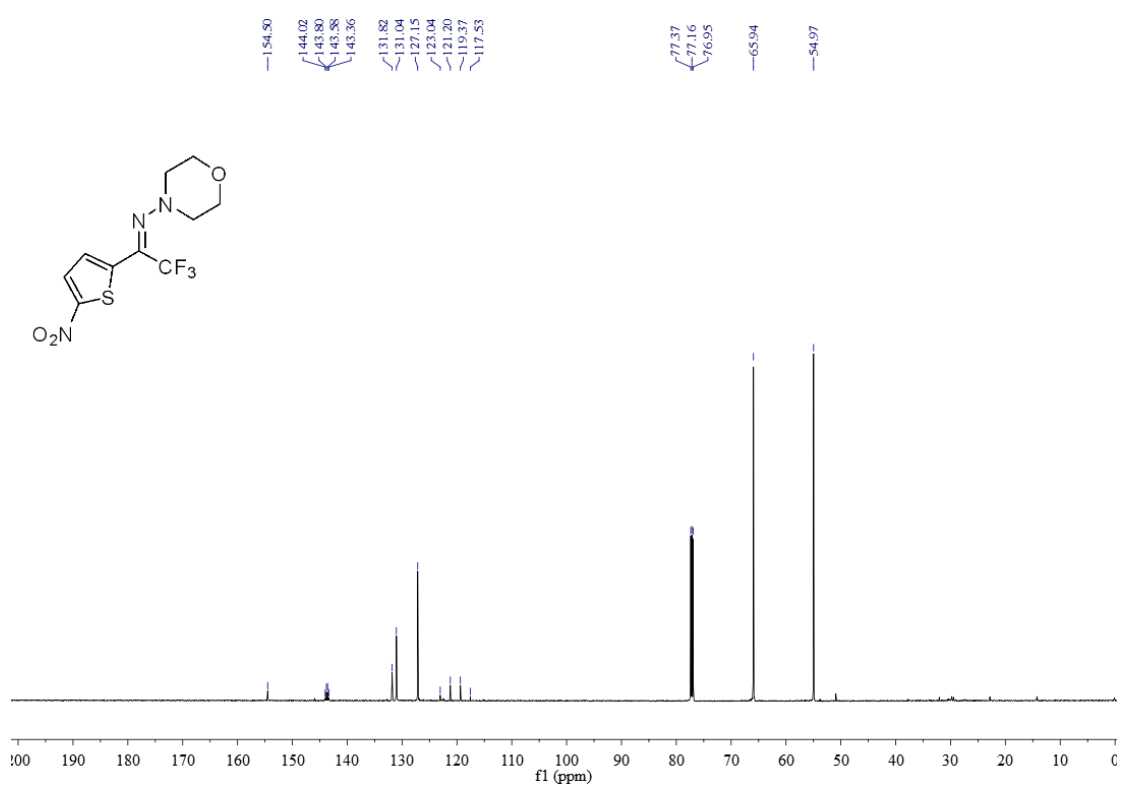
¹⁹F NMR of **2v**



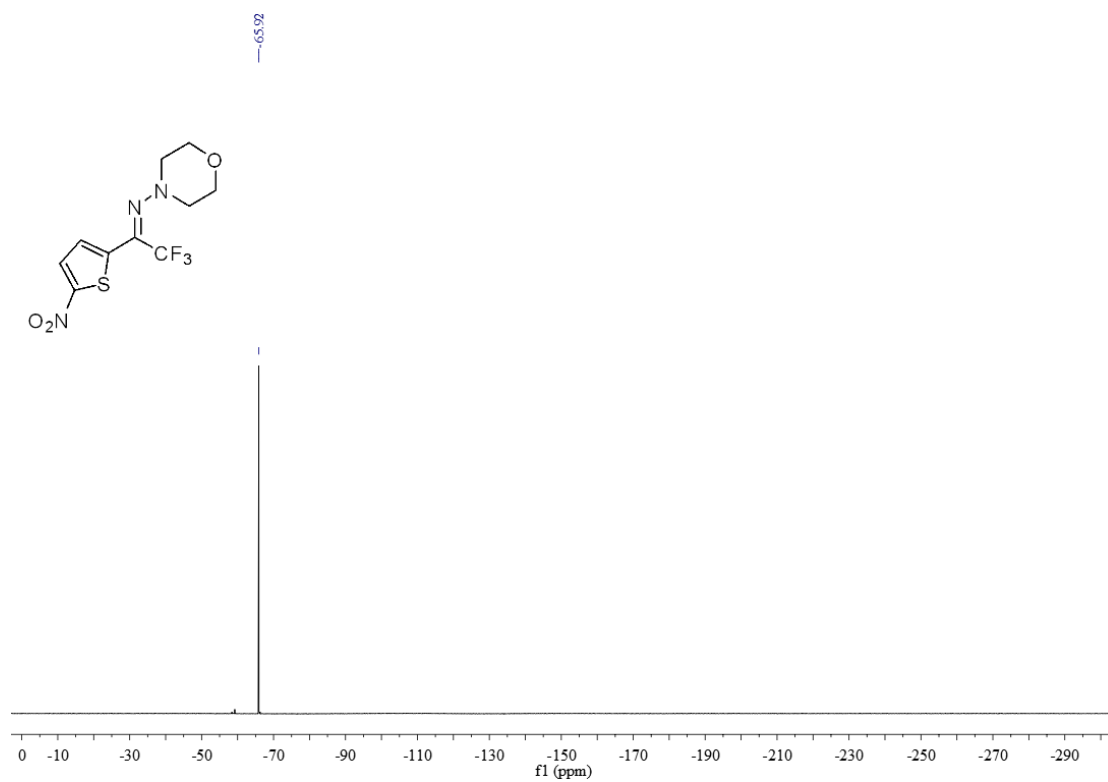
¹H NMR of **2w**



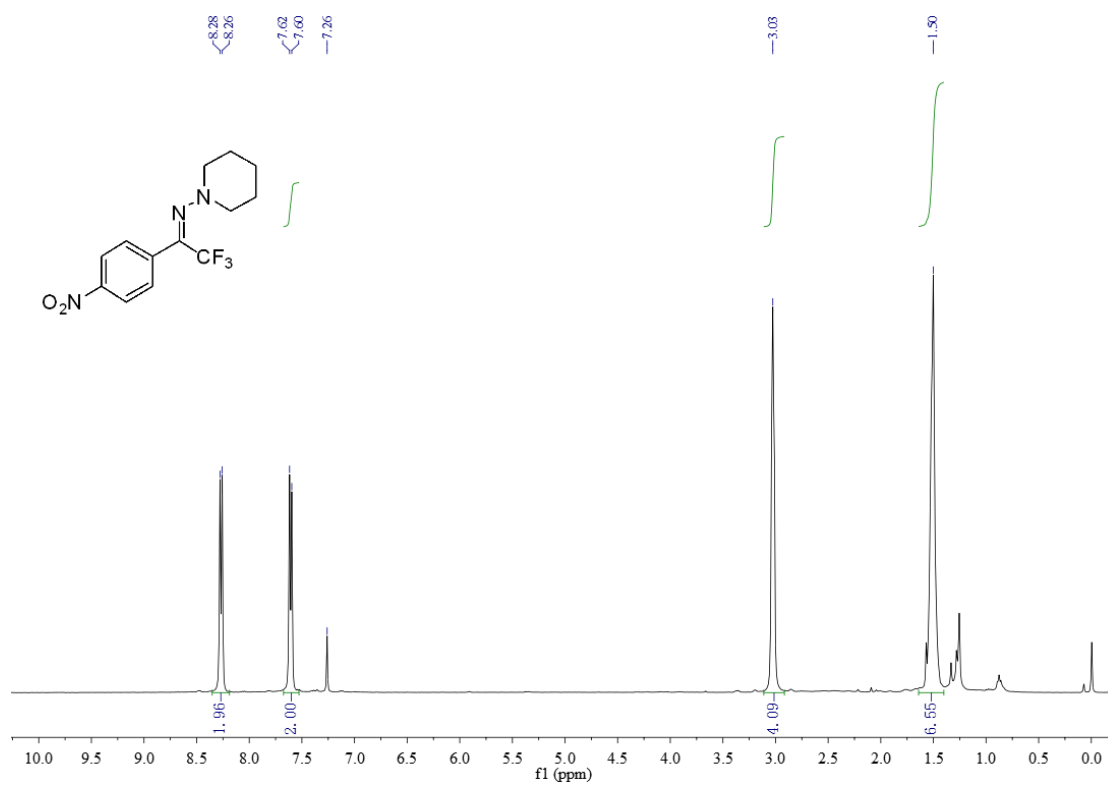
¹³C NMR of **2w**



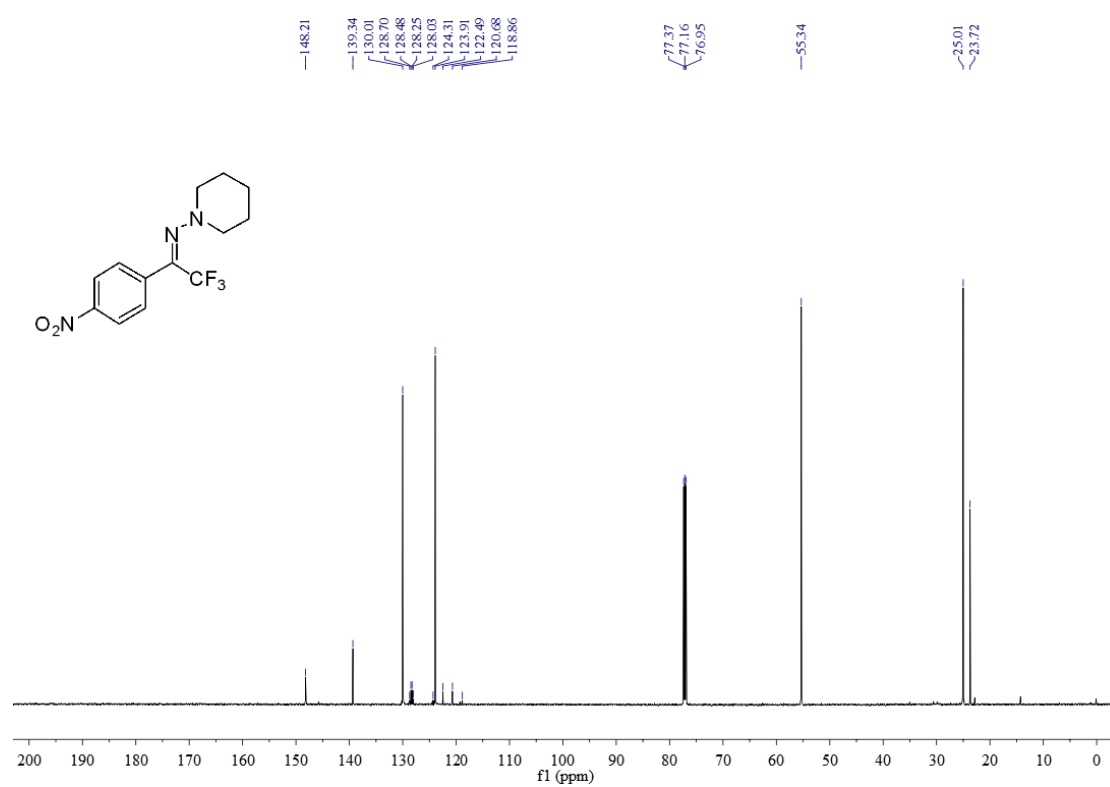
¹⁹F NMR of **2w**



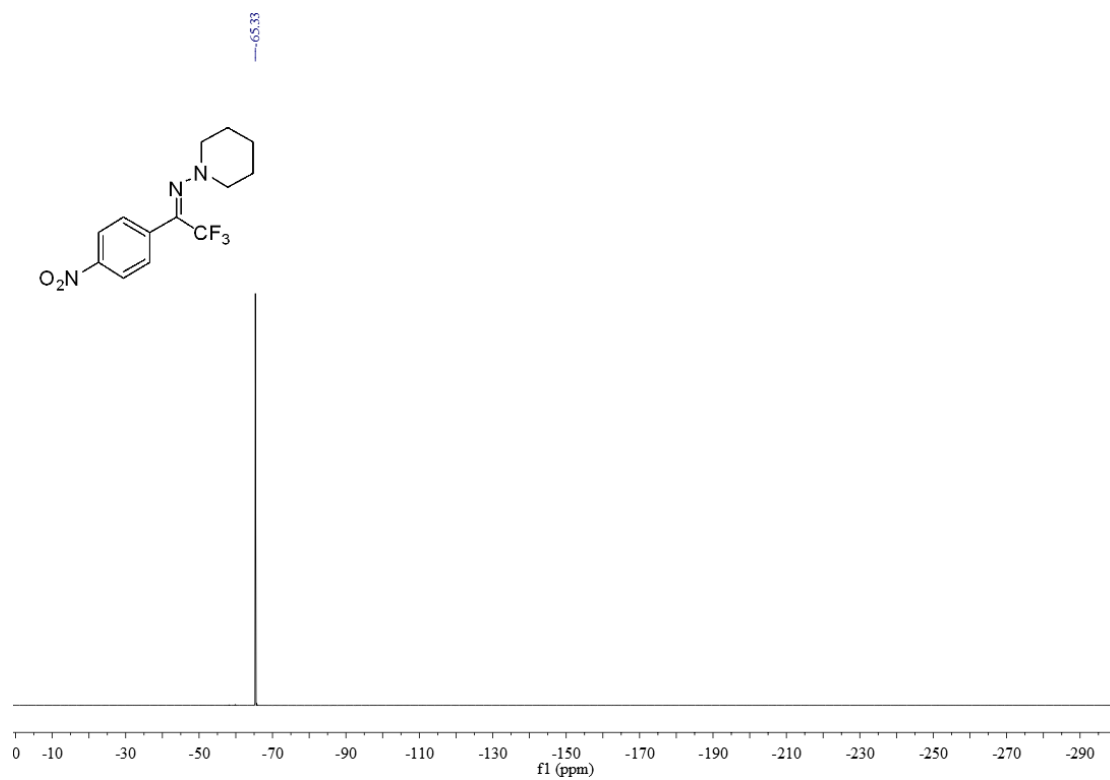
¹H NMR of **2x**



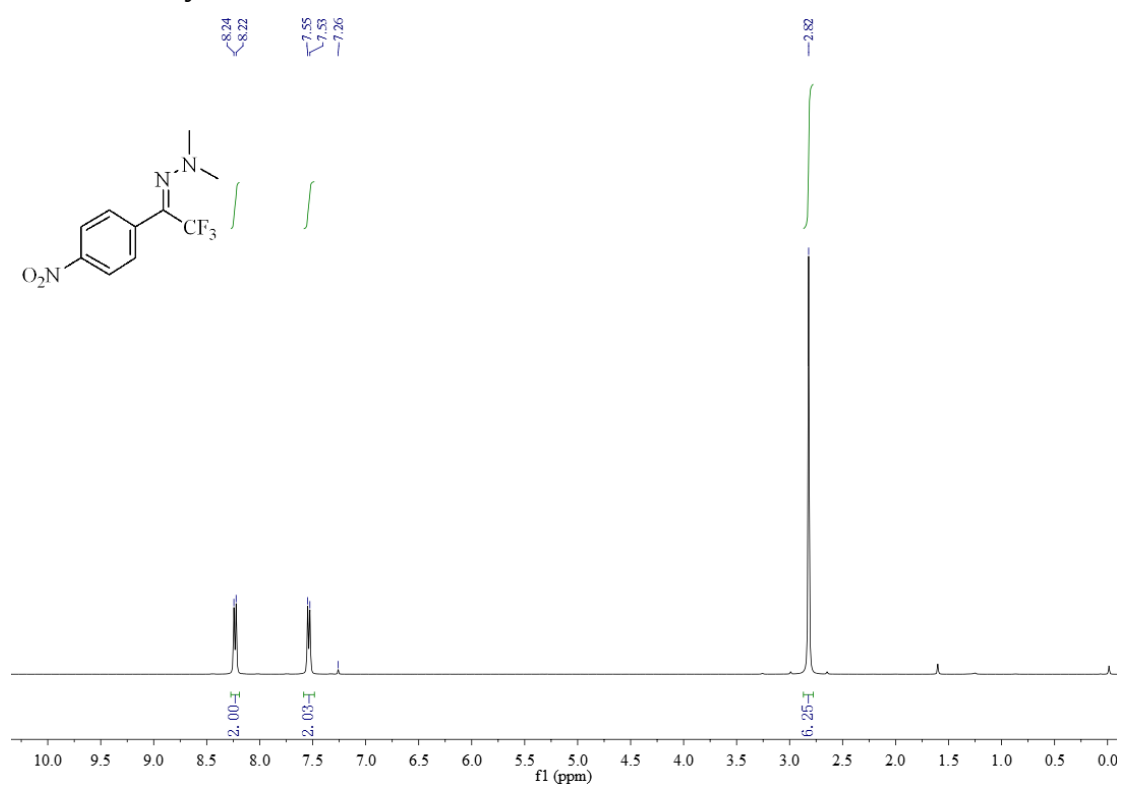
¹³C NMR of **2x**



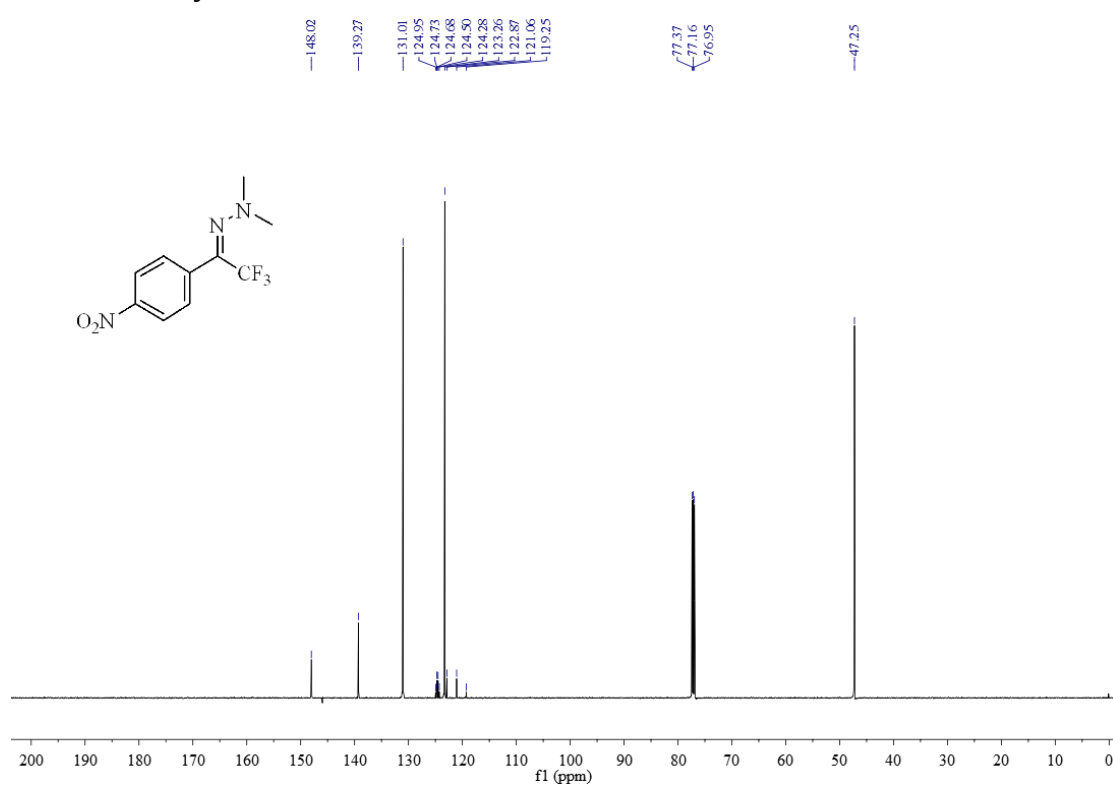
¹⁹F NMR of **2x**



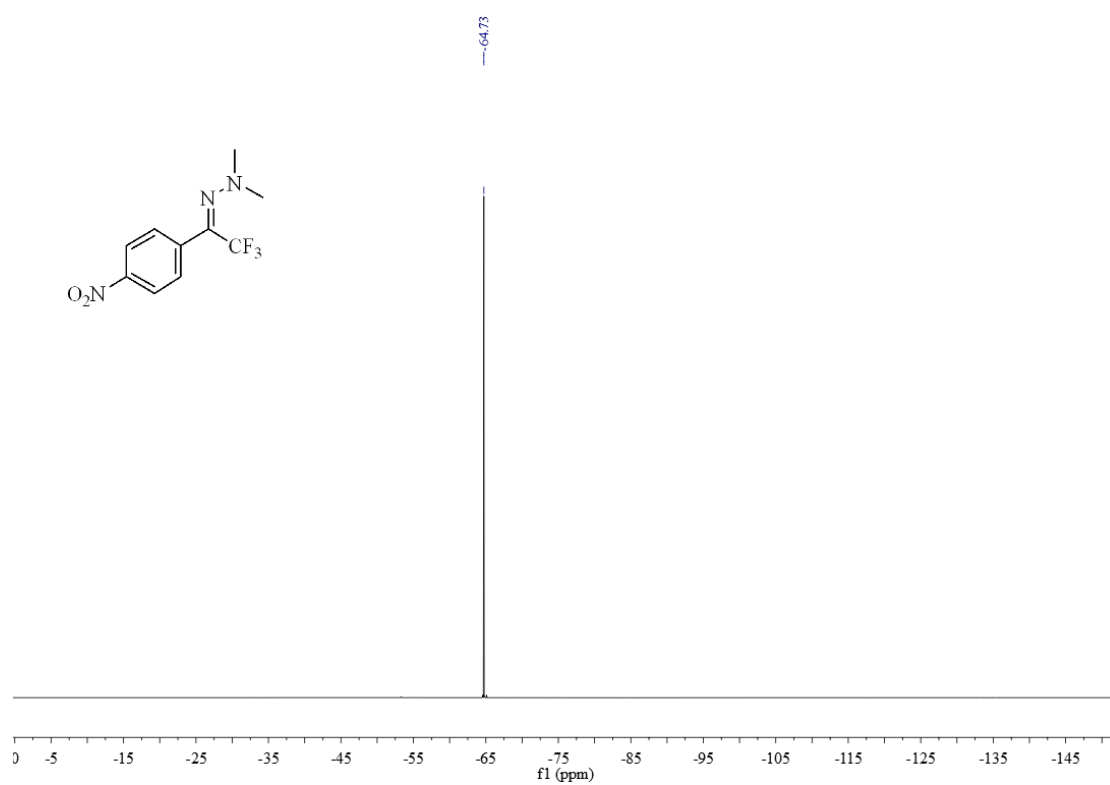
¹H NMR of **2y**



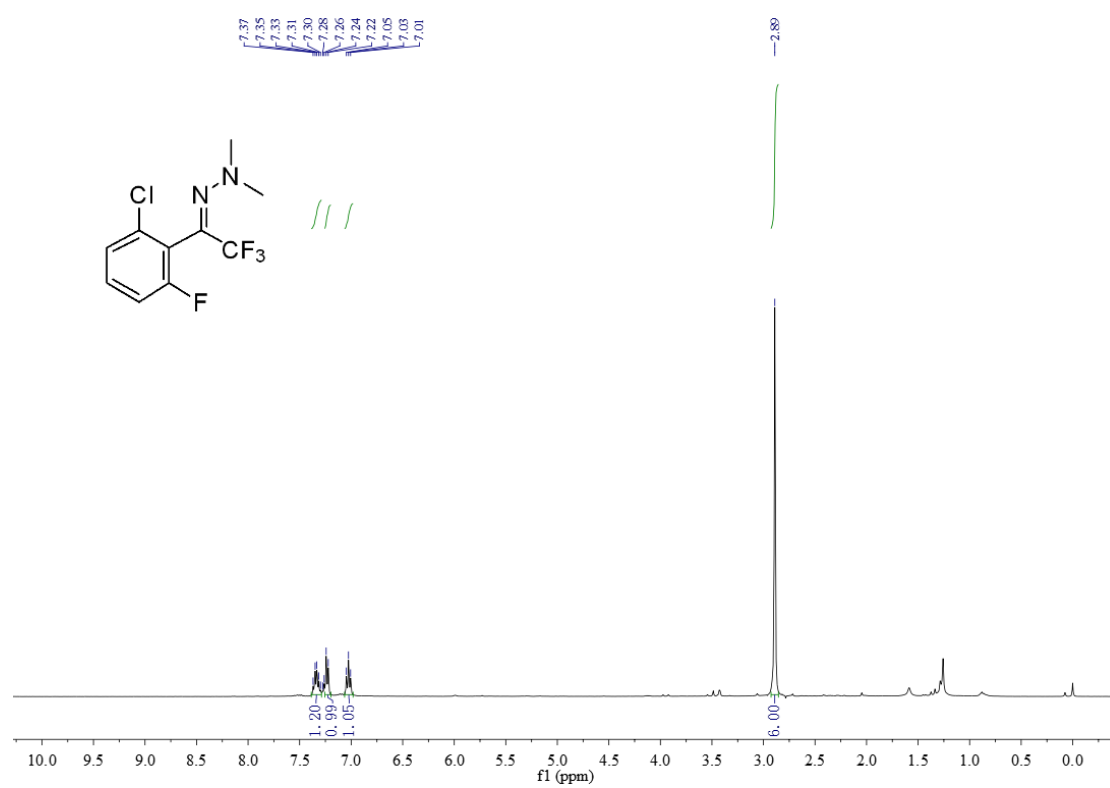
¹³C NMR of **2y**



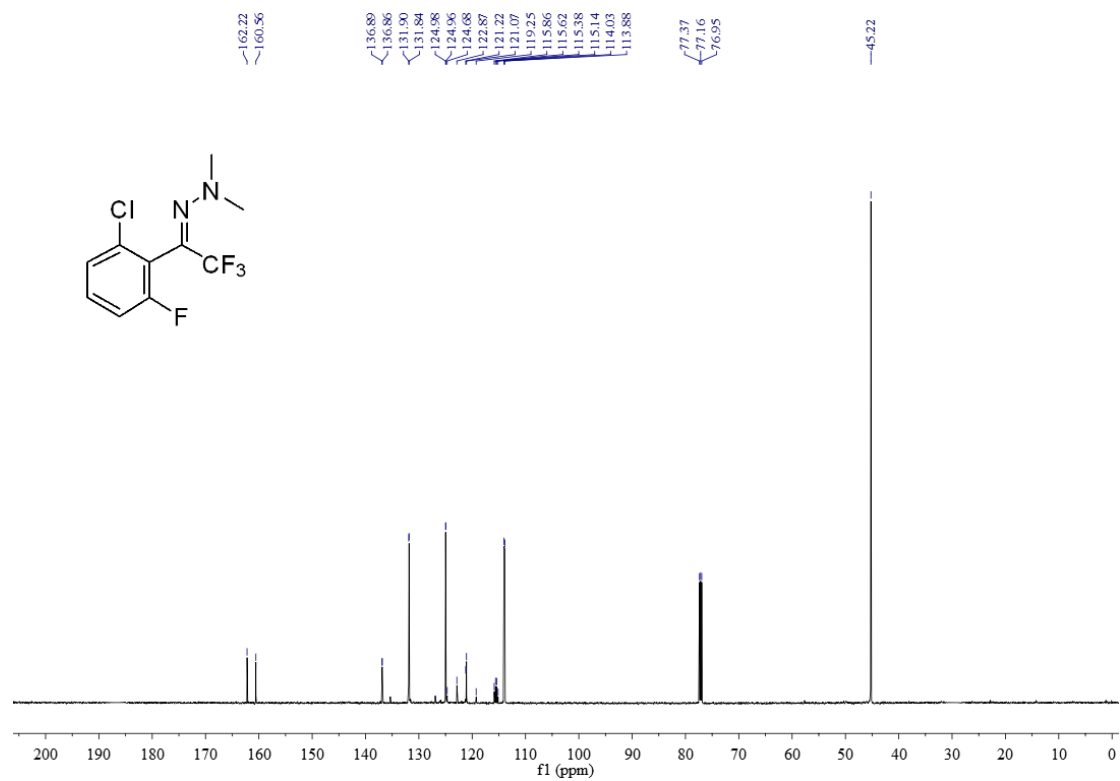
¹⁹F NMR of **2y**



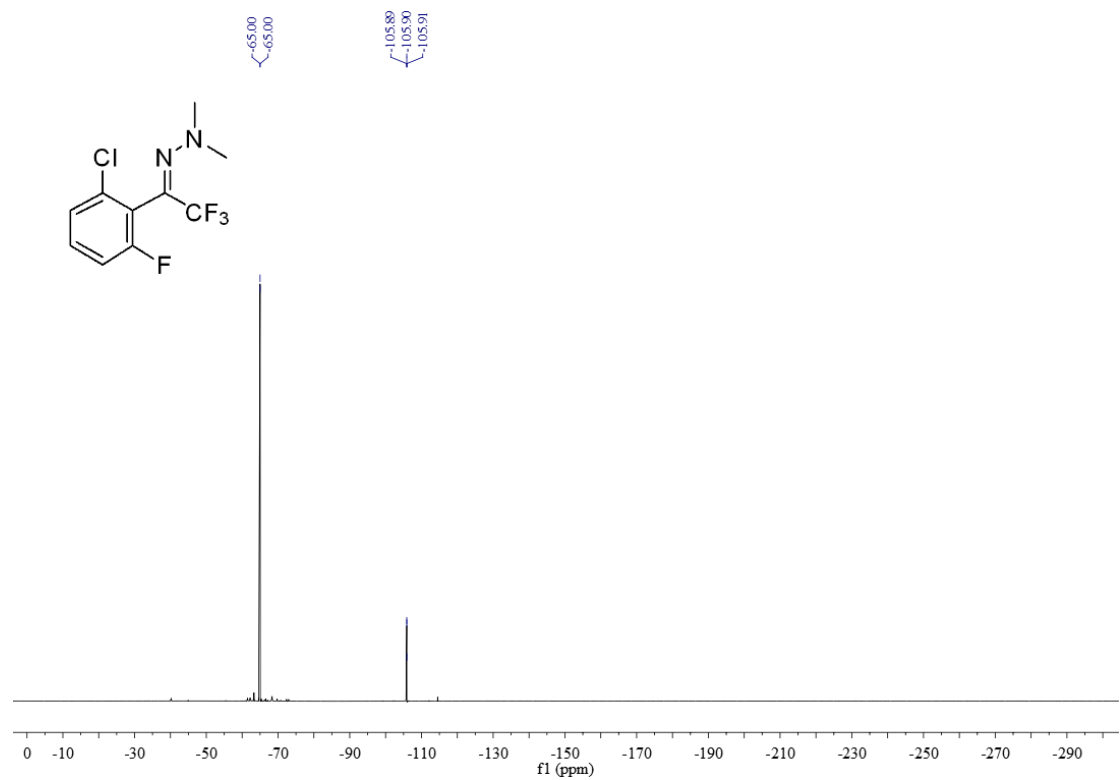
¹H NMR of **2z**



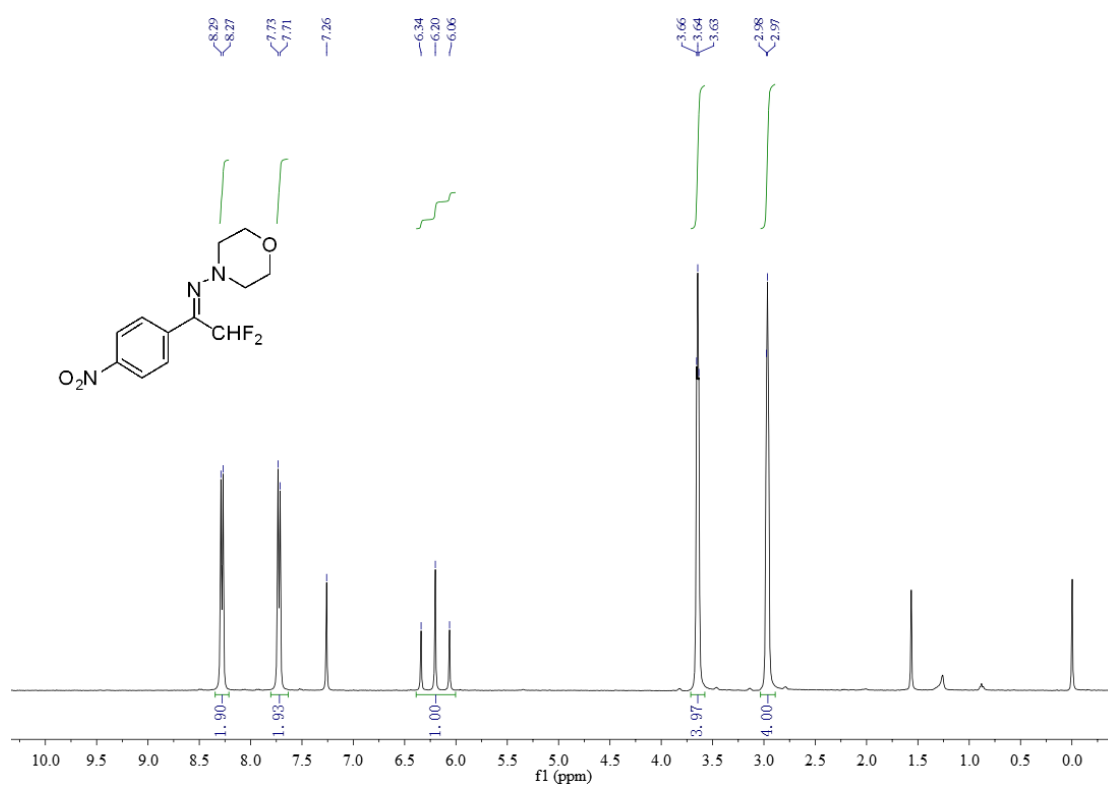
¹³C NMR of **2z**



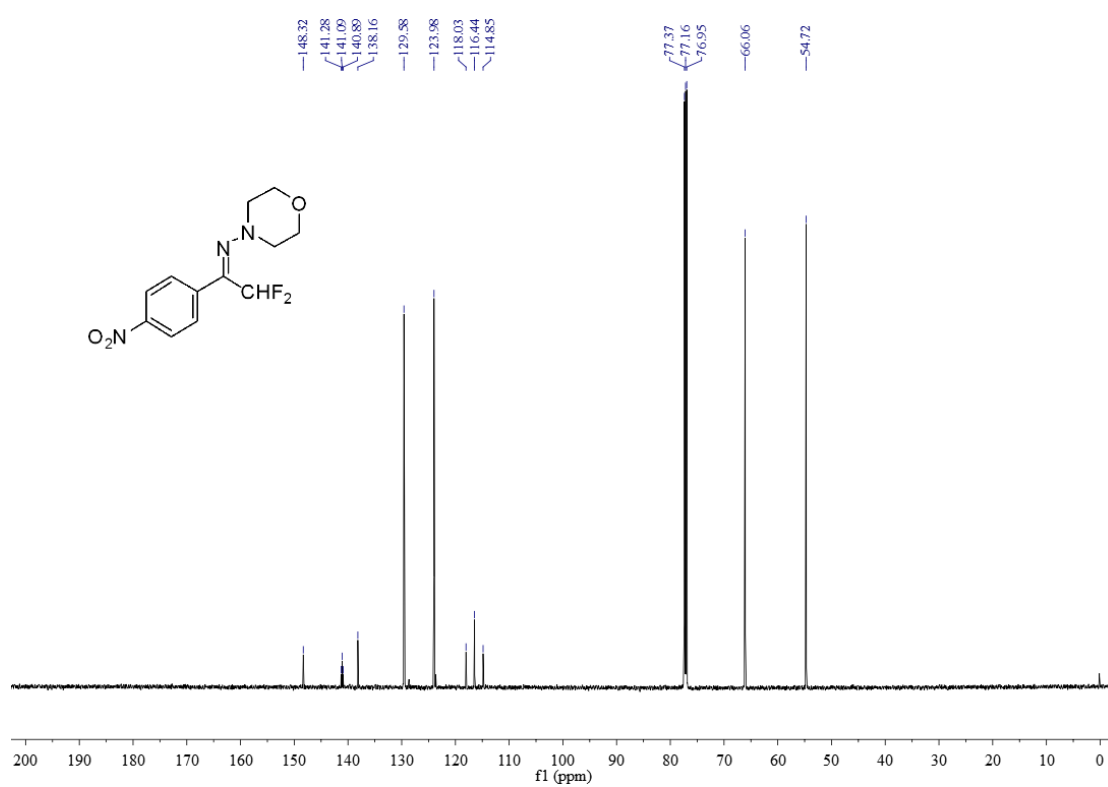
¹⁹F NMR of **2z**



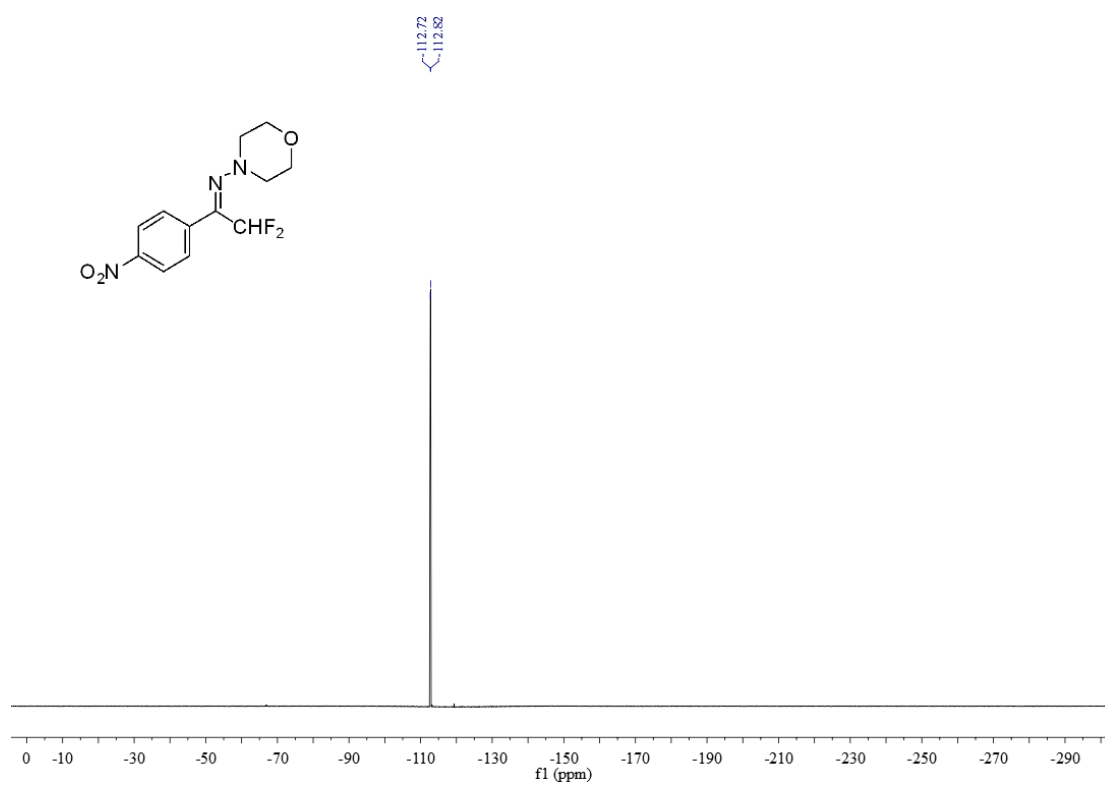
¹H NMR of **3a**



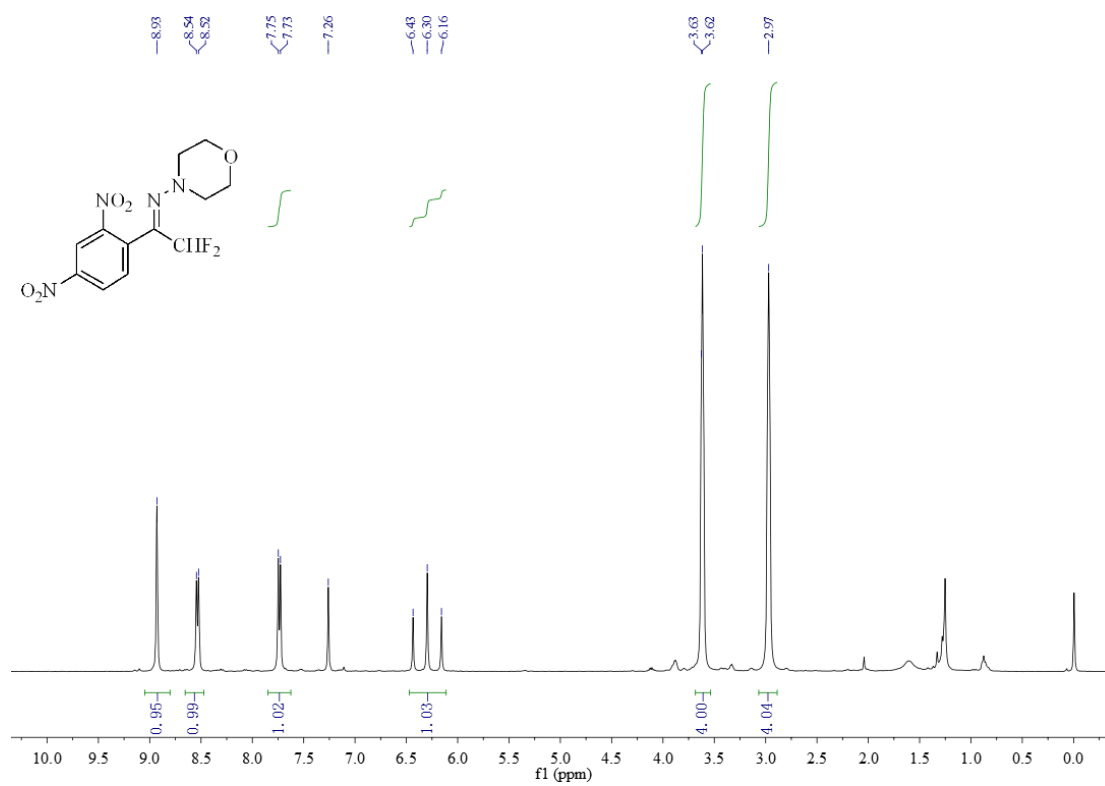
¹³C NMR of **3a**



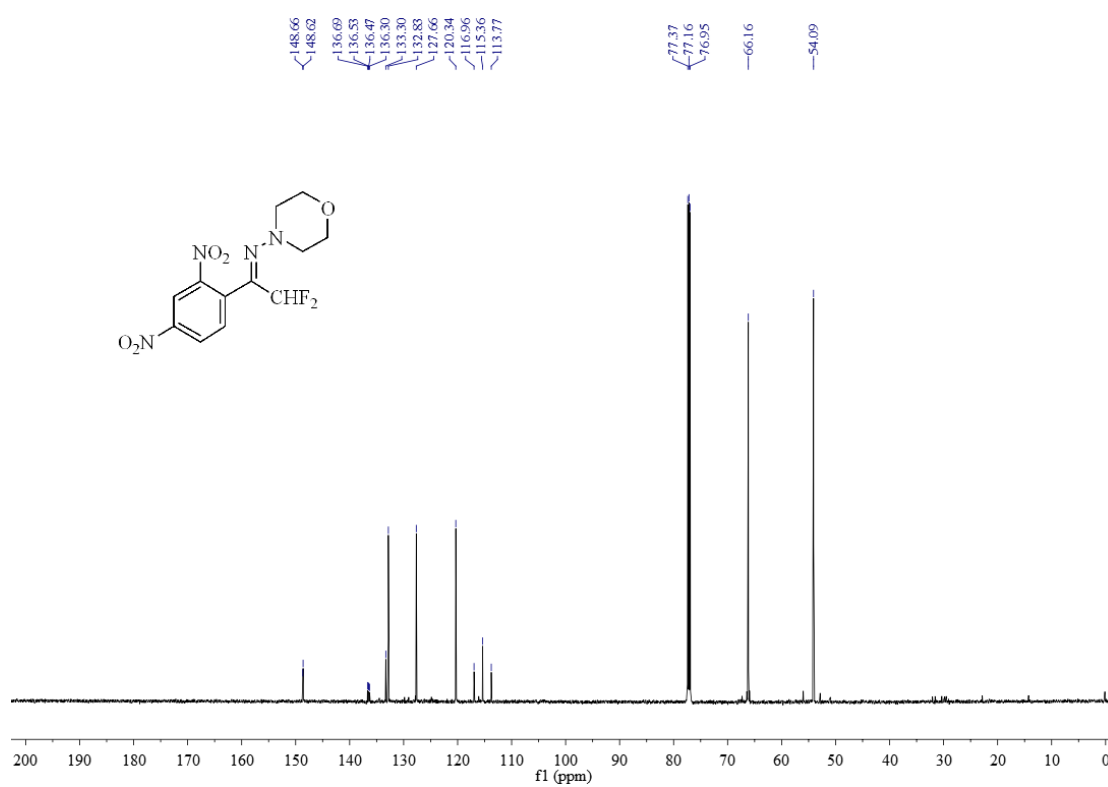
¹⁹F NMR of **3a**



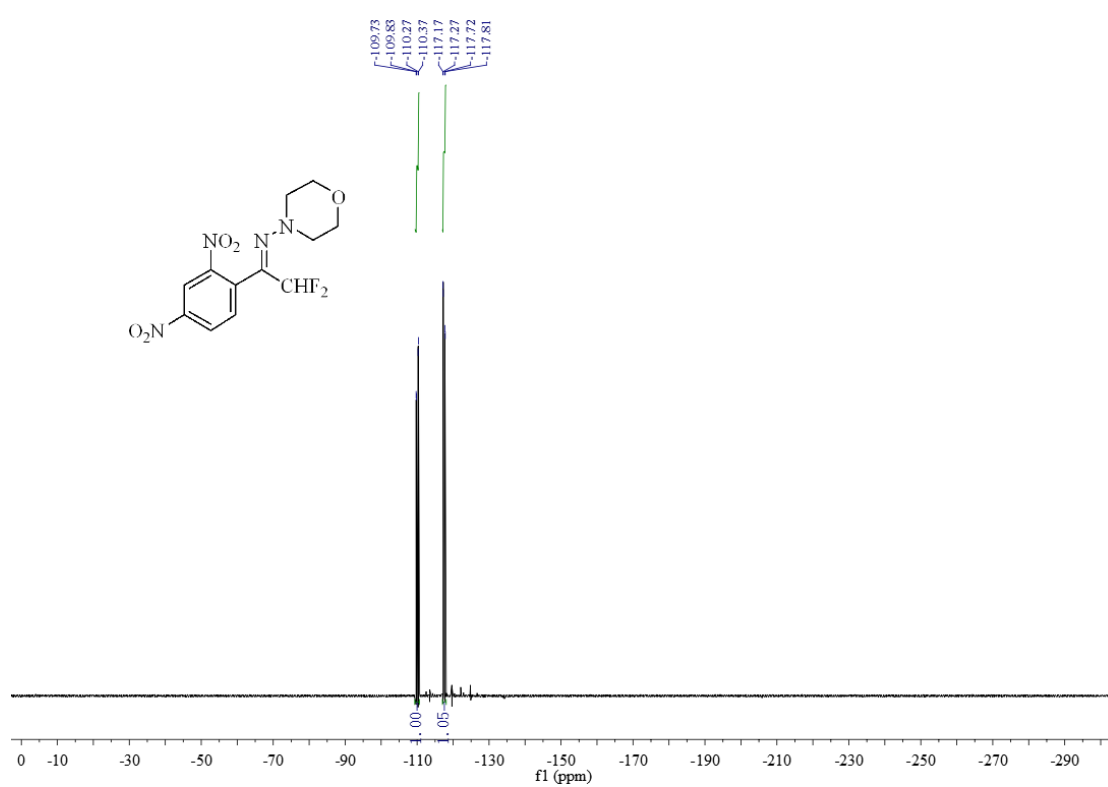
¹H NMR of **3b**



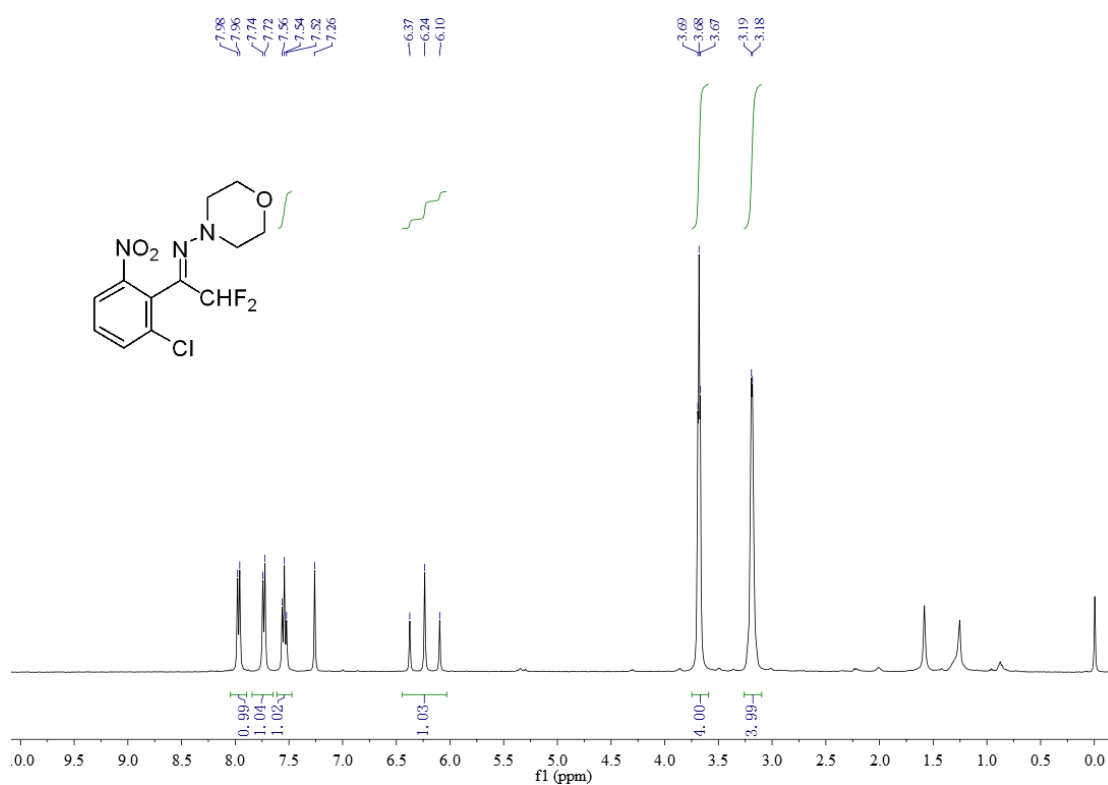
¹³C NMR of **3b**



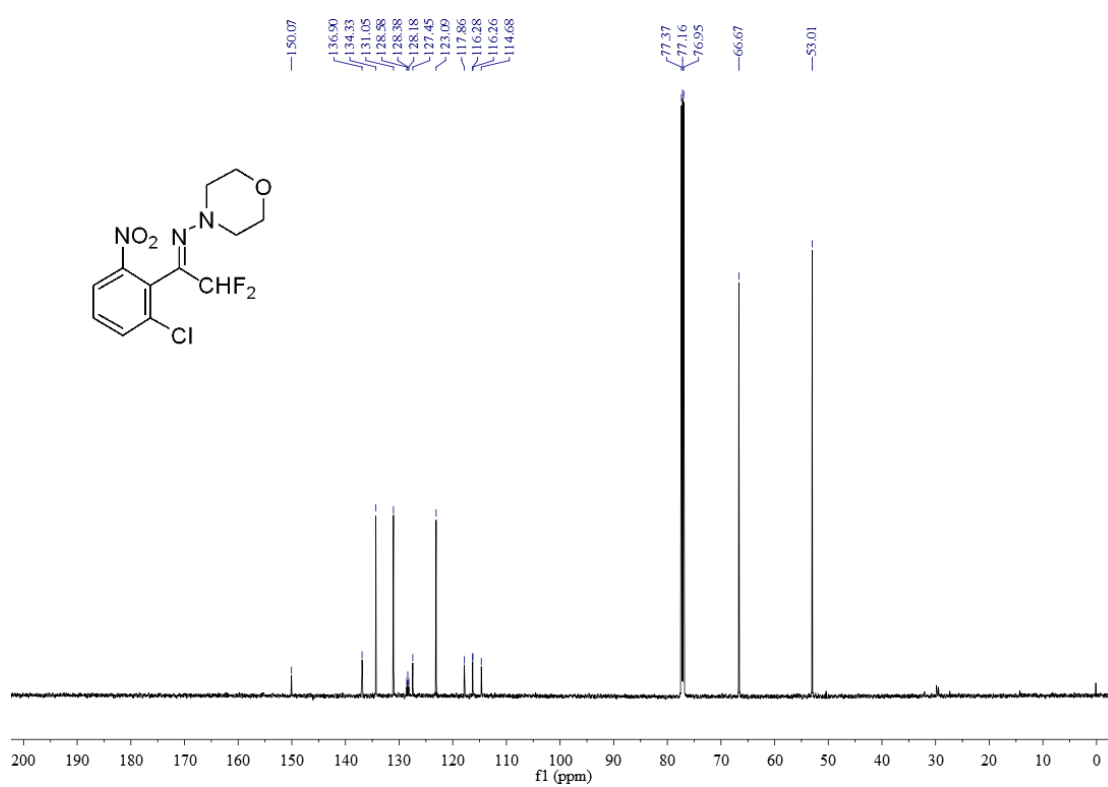
¹⁹F NMR of **3b**



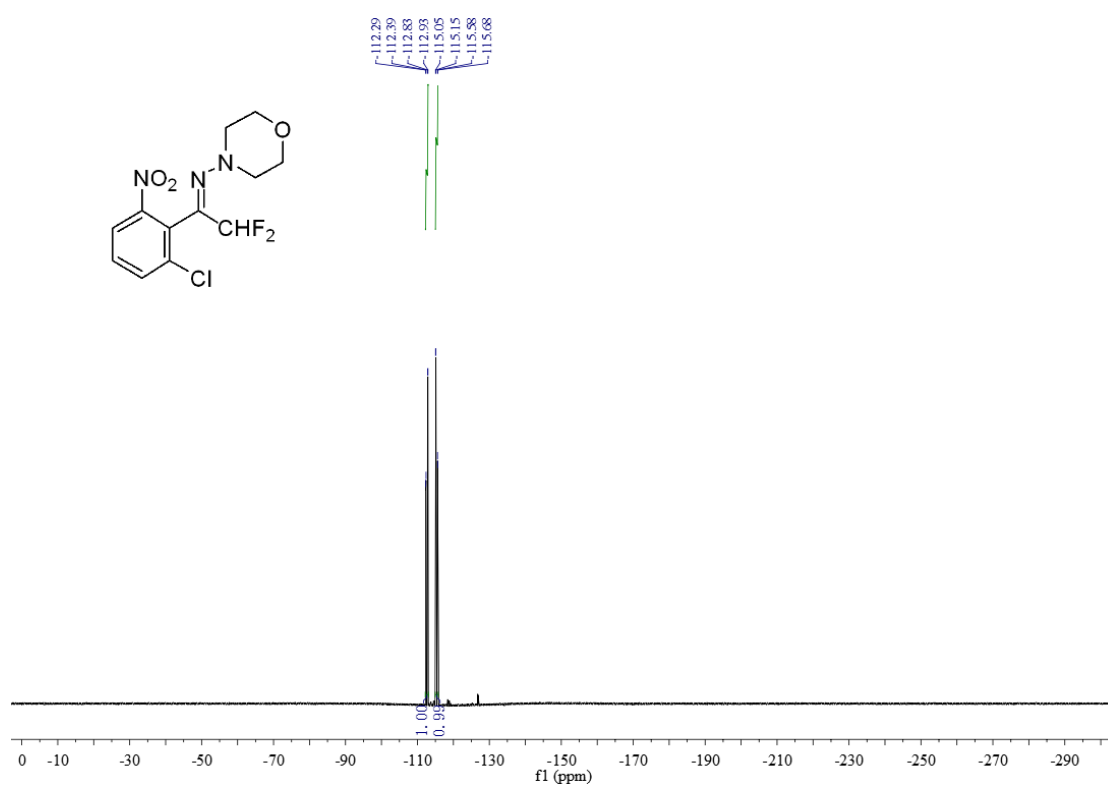
¹H NMR of **3c**



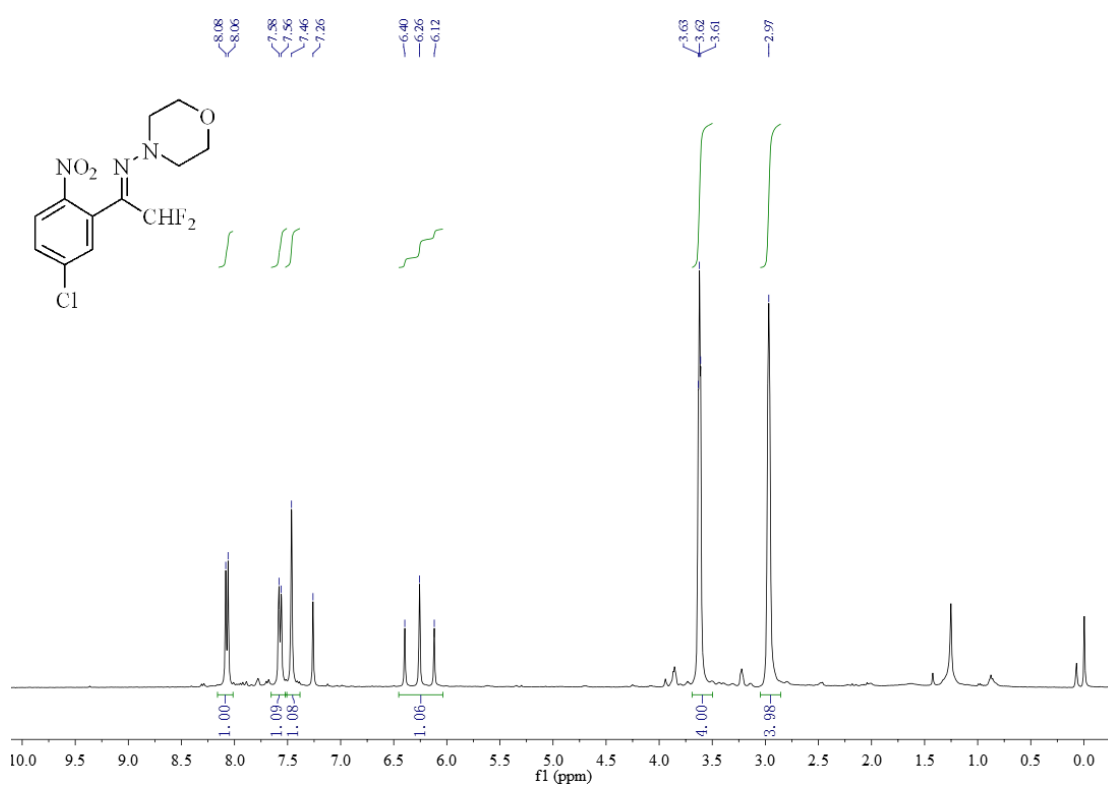
¹³C NMR of **3c**



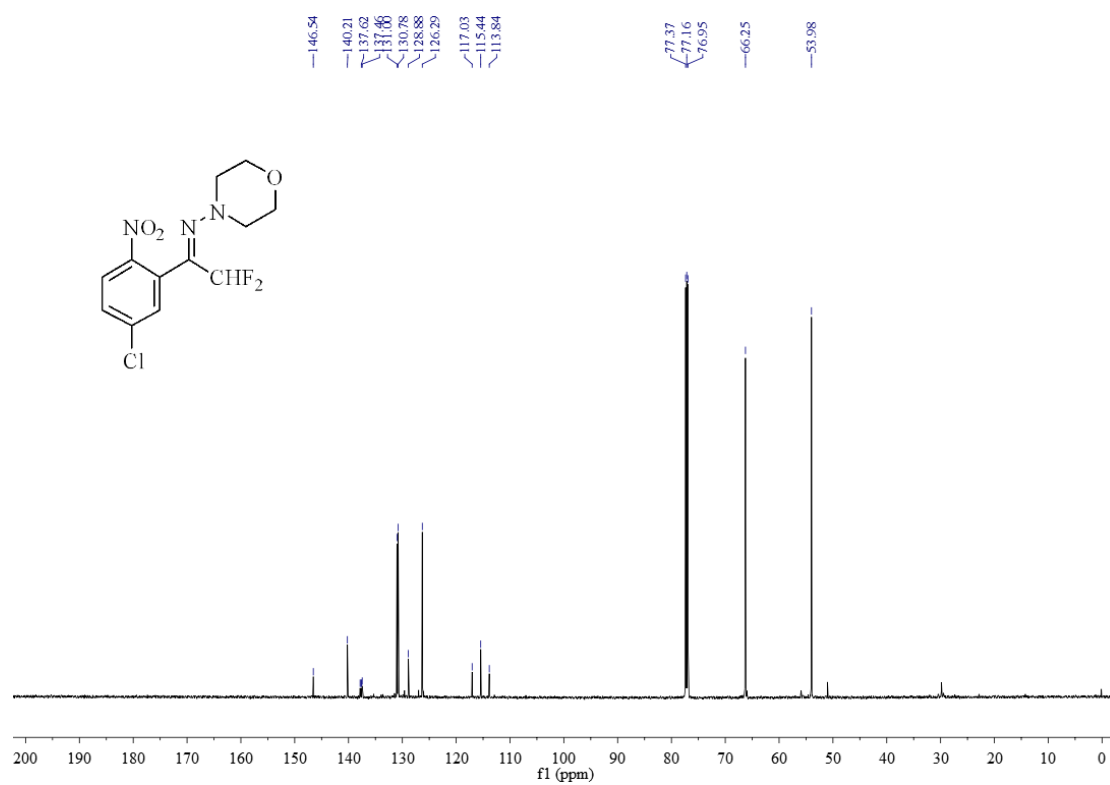
¹⁹F NMR of **3c**



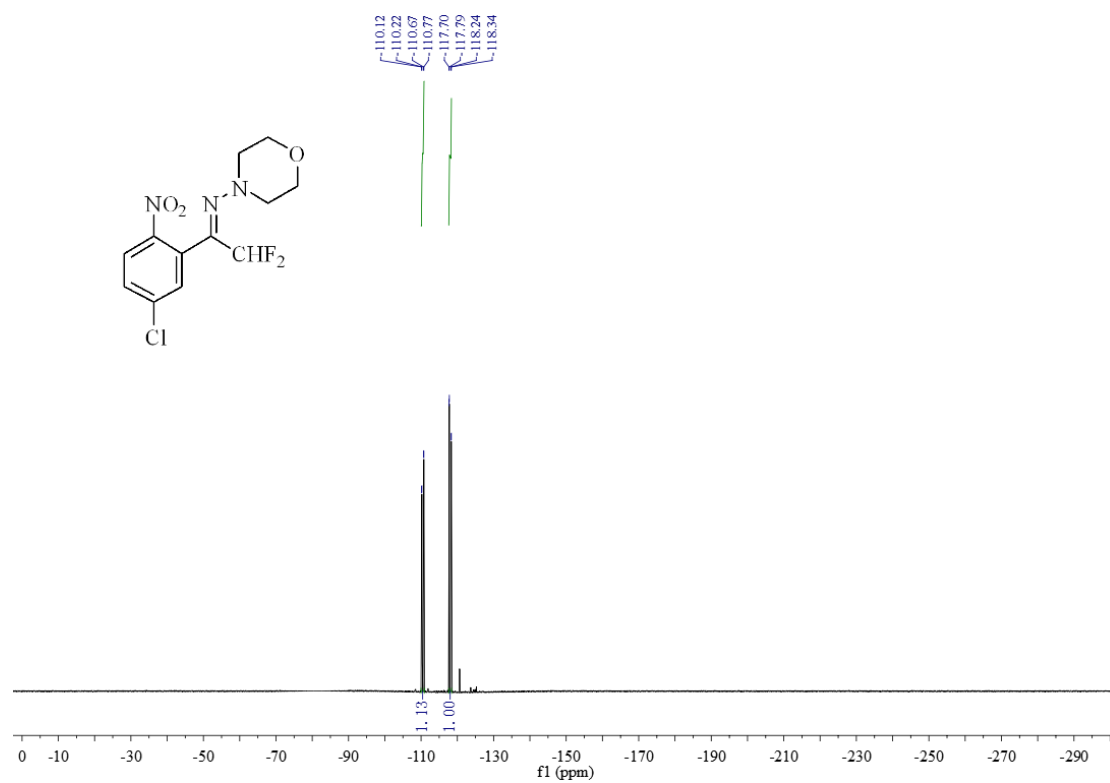
¹H NMR of **3d**



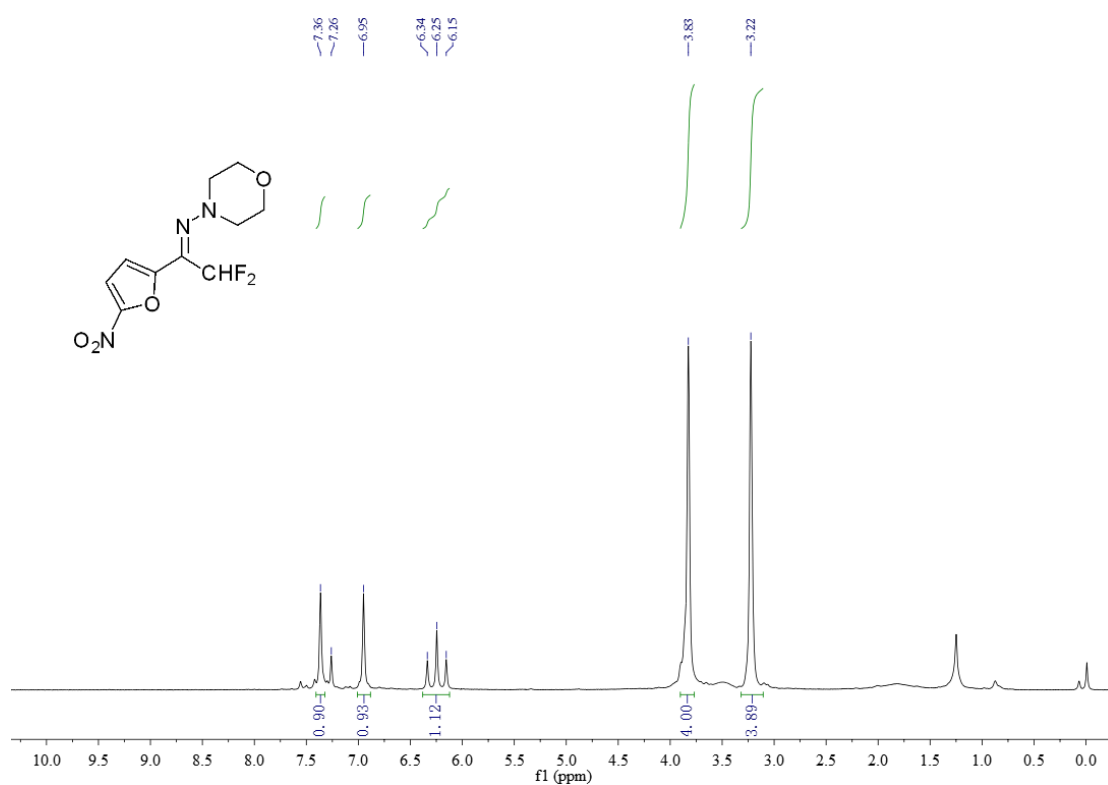
¹³C NMR of **3d**



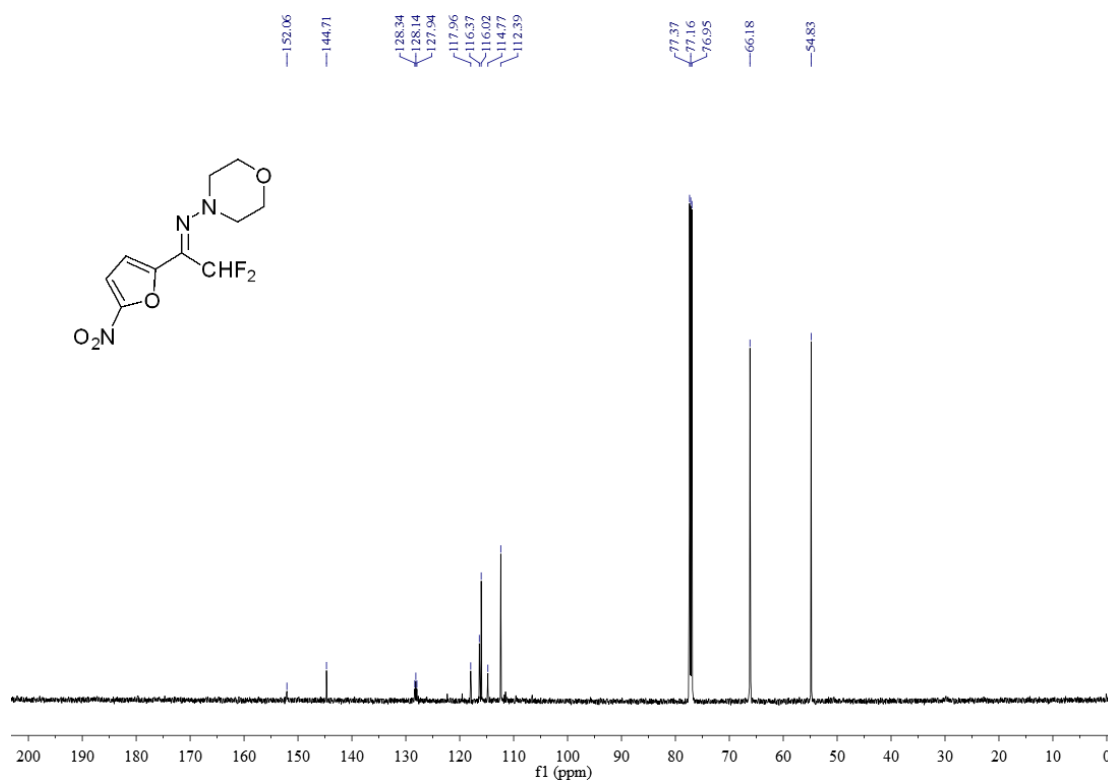
¹⁹F NMR of **3d**



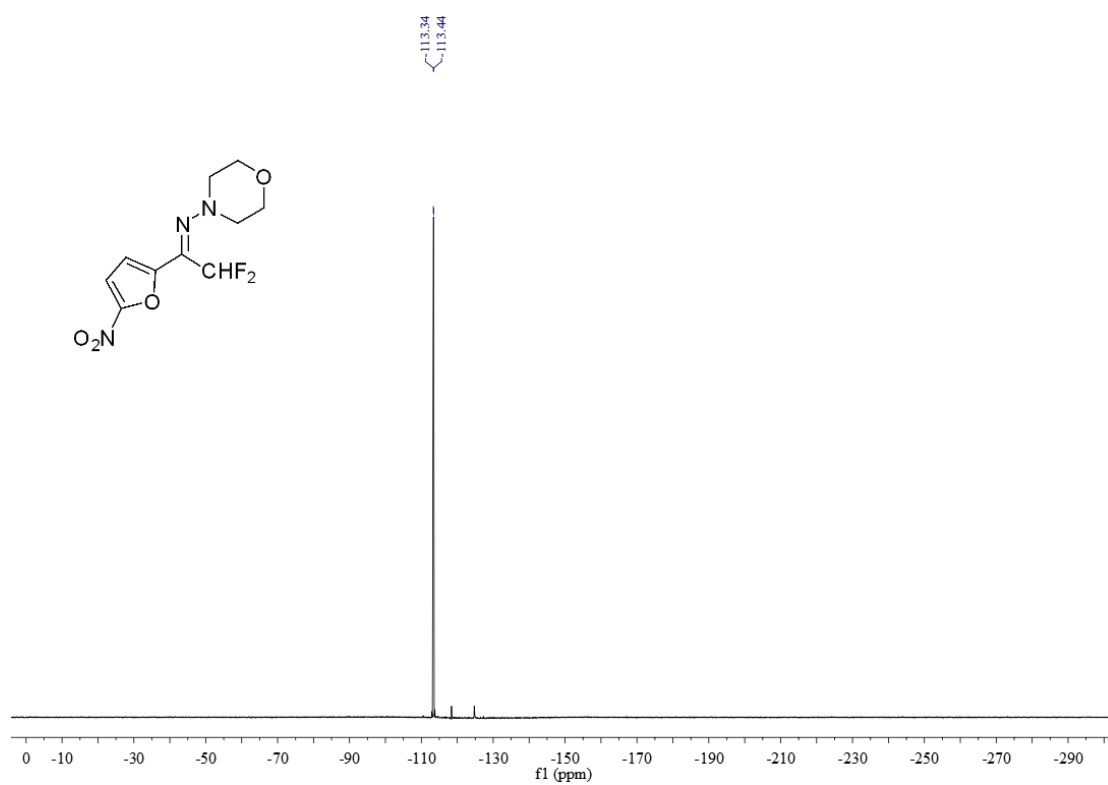
¹H NMR of **3e**



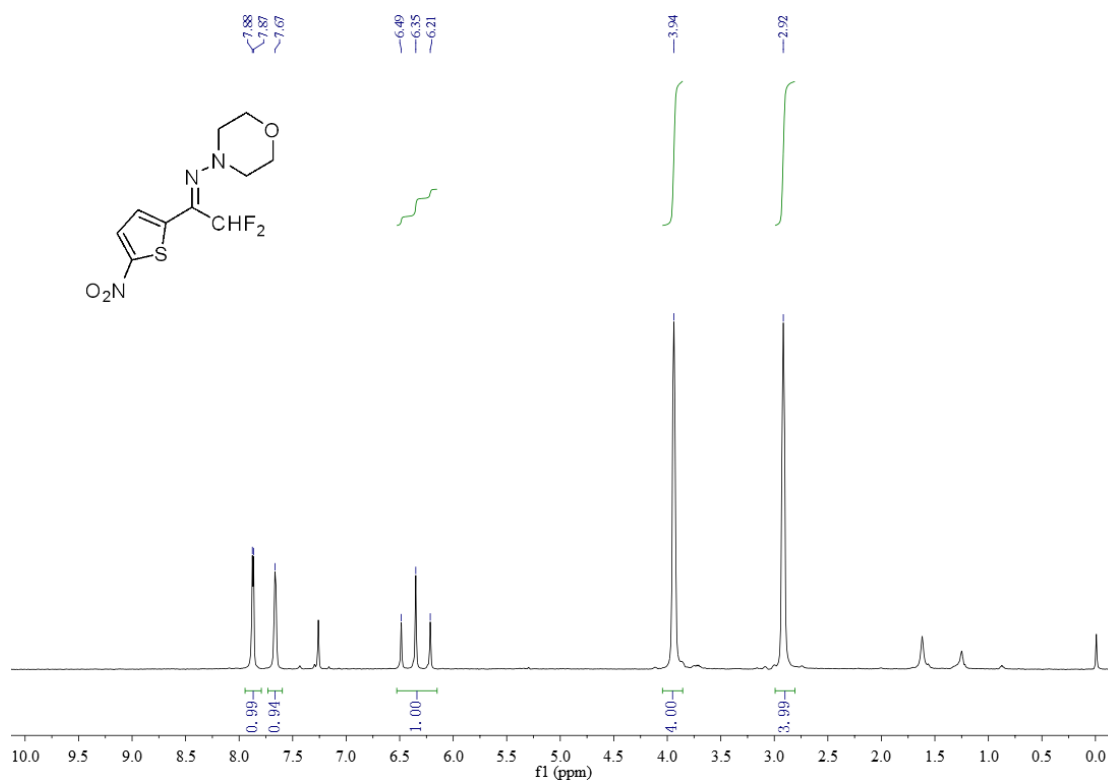
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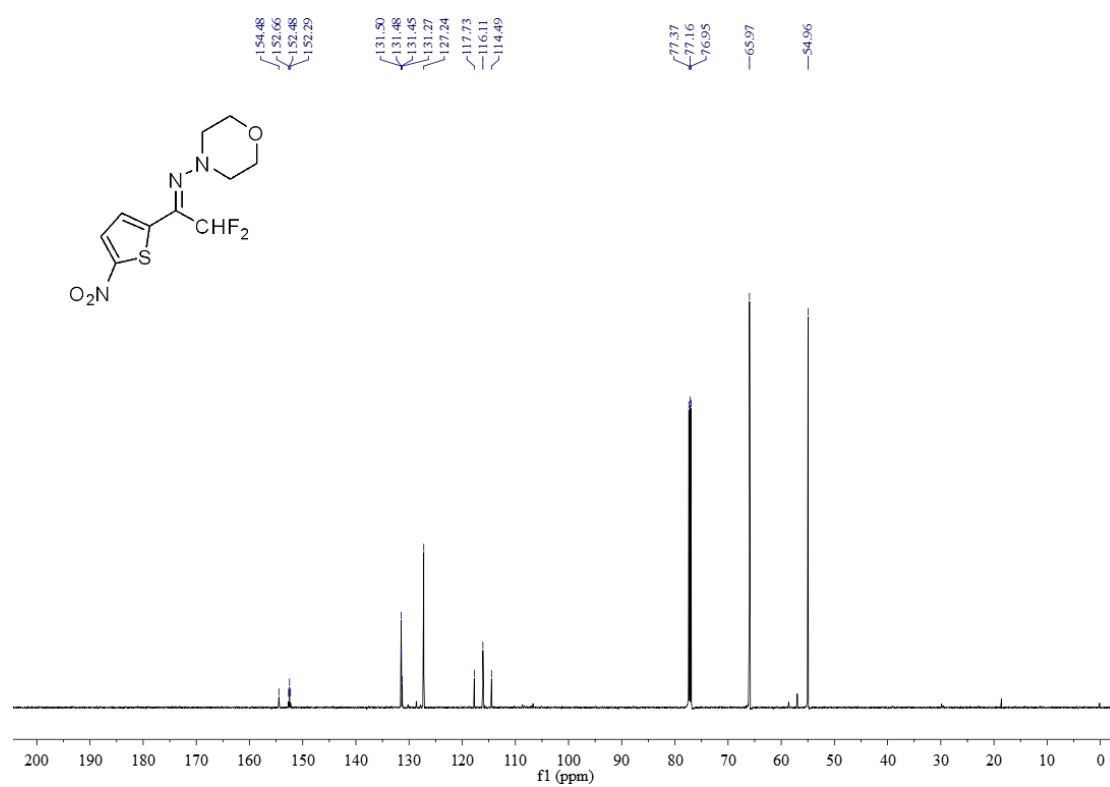
¹⁹F NMR of **3e**



¹H NMR of **3f**



¹³C NMR of **3f**



¹⁹F NMR of **3f**

