Supplementary Information

Scalable Catalyst Free Electrochemical Chlorination of Aminophenol Derivatives Enabled by a Quasi-Divided Cell Approach

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1. Materials and Methods

^{1}H NMR spectra were recorded on a Bruker 300 MHz instruments. ^{13}C NMR spectra were recorded on the same instrument at 75 MHz. Chemical shifts (δ) are expressed in ppm downfield from TMS as internal standard. The letters s, d, t, q, and m are used to indicate singlet, doublet, triplet, quadruplet, and multiplet, respectively. Analytical HPLC analysis was carried out on a C18 reversed-phase (RP) analytical column (150 × 4.6 mm, particle size 5 mm) at 37 °C by using mobile phases A [water/acetonitrile 90:10 (v/v) + 0.1% TFA] and B (acetonitrile + 0.1% TFA) at a flow rate of 1.5 mL/min. The following gradient was applied: linear increase from solution 3% B to 100% B within 10 min.

High resolution mass spectra were taken on an Agilent 6230 TOF LC/MS (G6230B) by flow injections (0.5 µL) on an Agilent 1260 Infinity Series HPLC (HiP Degasser G4225A, Binary Pump G1312B, ALS Autosampler G1329B, TCC Column thermostat G1316A, DAD Detector G4212B). The solvent was 40% H_2O (+0.1% 5 M NH_4HCO_2 solution) and 60% CH_3CN/H_2O 5:1 (NH_4HCO_2 solution) at a flow rate of 0.3 $mL \cdot min^{-1}$. For positive mode: A Dual AJS ESI source was used with the following settings: Gas temperature (N_2) 325 °C, drying gas (N_2): 5 $L \cdot min^{-1}$; nebulizer: 20 psig; fragmentor voltage: 175 V; skimmer voltage: 65 V, OCT 1 RF Vpp: 750 V; Vcap: 4000 V; nozzle voltage: 2000 V; reference mass: 966.0007. The scan range was 100–1100 m/z and 1 spectrum per s was recorded. For negative mode: A Dual AJS ESI source was used with the following settings: Gas temperature (N_2) 325 °C, drying gas (N_2): 5 $L \cdot min^{-1}$; nebulizer: 20 psig; fragmentor voltage: 175 V; skimmer voltage: 65 V, OCT 1 RF Vpp: 750 V; Vcap: 3500 V; nozzle voltage: 2000 V; reference mass: 966.0007. The scan range was 100–1100 m/z and 1 spectrum per s was recorded. All chemicals were purchased from Aldrich, TCI, Thermo and BLD pharma. All solvents were obtained from standard commercial vendors. HPLC grade DCM was obtained from Aldrich.

Batch electrolysis: All electrochemical reactions were carried out in undivided cells (5 mL IKA vials). Graphite felt (AvCarb G280A) was purchased from The Fuel Cell Store. Stainless steel was purchased from IKA. Stainless steel electrodes were polished with 3000 grit sandpaper before each reaction.

Flow electrolysis: Flow electrochemical reactions were carried out in a parallel plate reactor. A detailed description is provided below. Graphite felt (AvCarb G280A) was purchased from The Fuel Cell Store. Stainless steel (316) was purchased from Goodfellow. PTFE mesh was purchased from The Fuel Cell Store (SKU: 72500444, 18 x 28). After each reaction, the stainless steel electrodes were polished with 3000 grit sandpaper.

2. Experimental Setup for Batch Electrolysis

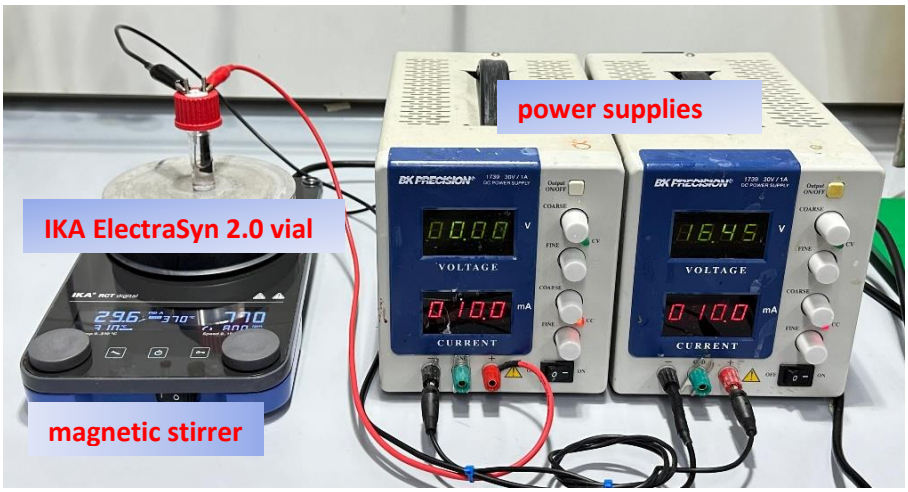


Fig. S1. Experimental setup for batch electrolysis quasi-divided cell reaction in batch mode (0.3 mmol scale) setup.

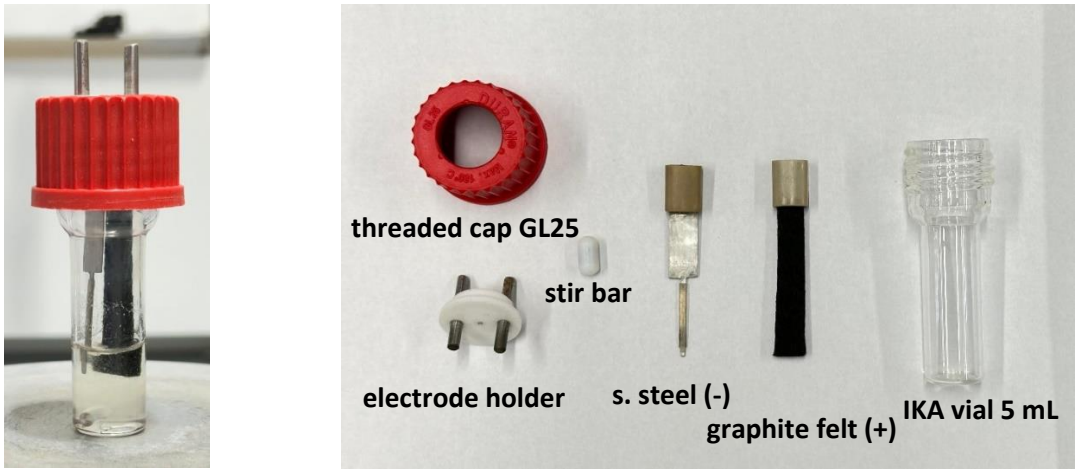


Fig. S2. Detailed photographs of the batch quasi-divided cell

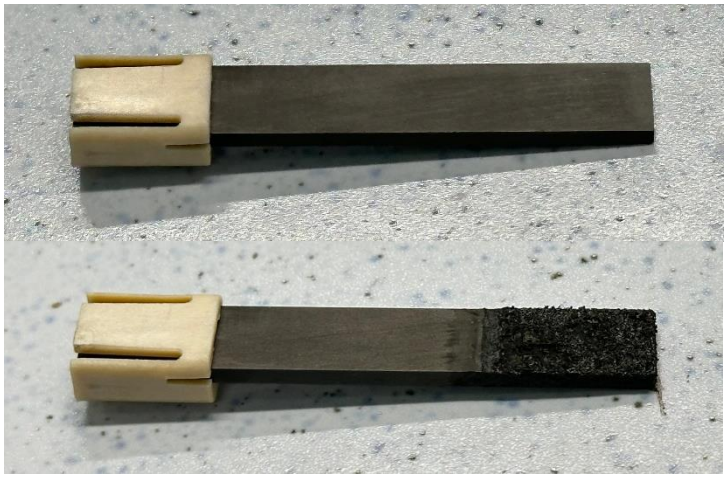


Fig. S3. Photograph of a graphite plate anode before (top) and after (bottom) electrolysis.

3. Experimental Setup for Quasi-Divided Flow Cell Electrolysis

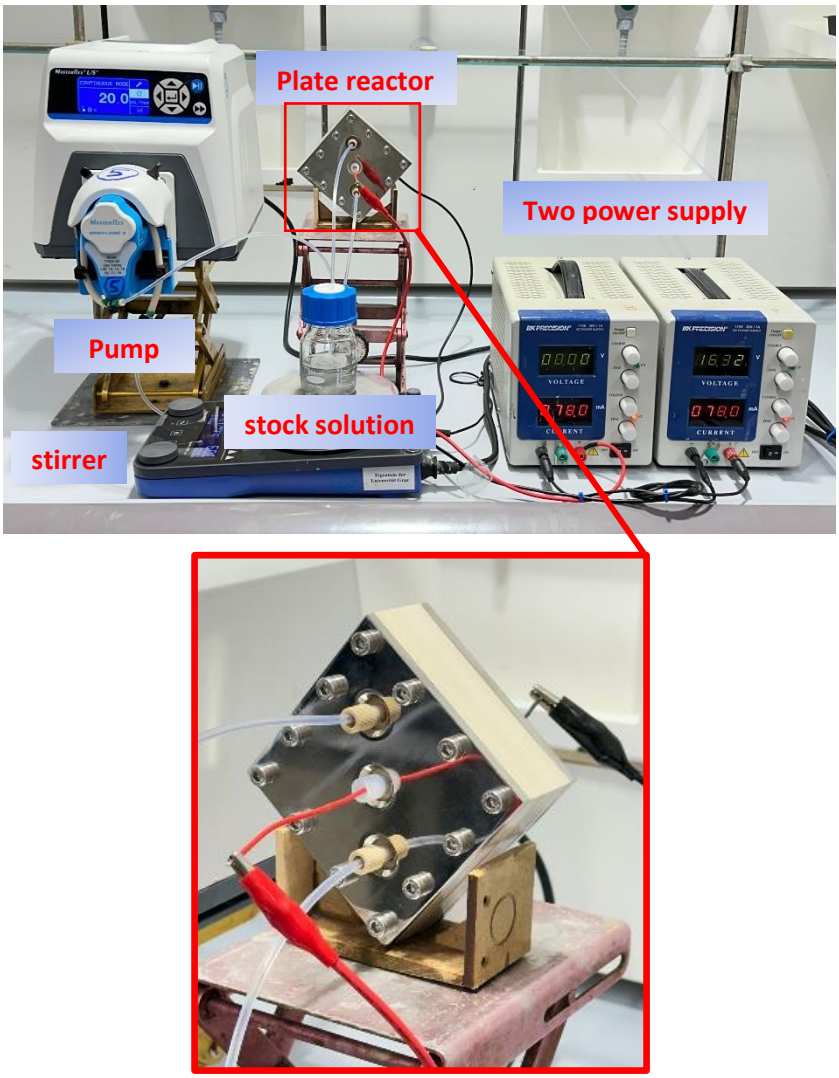


Fig. S4. Photographs of the flow experimental setup and close view of the assembled flow cell

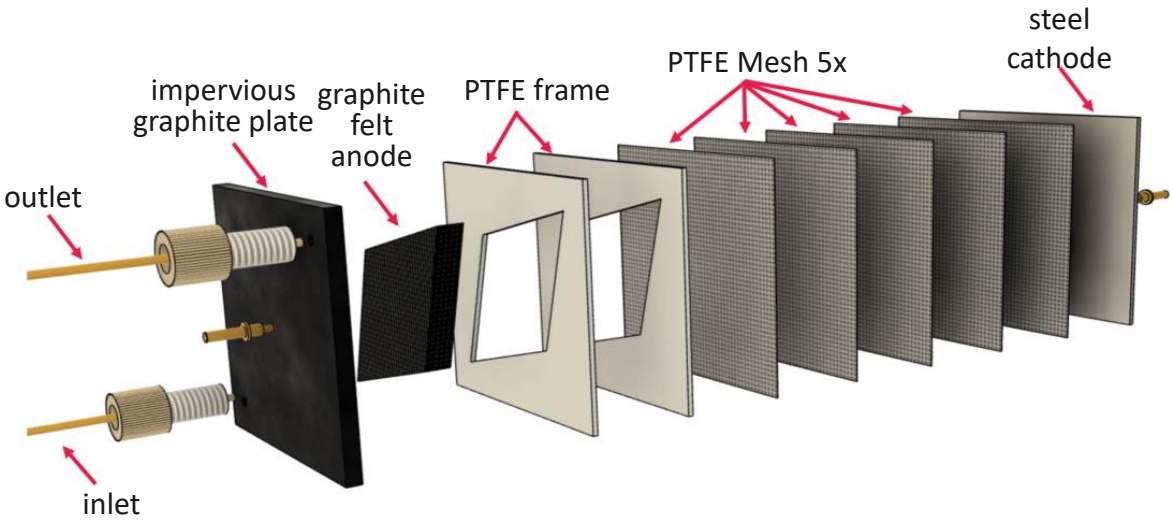


Fig. S5. Exploded view of the flow quasi-divided cell (end plates not shown)

4. Photographs and Technical Drawings of the Flow Electrolysis Cell

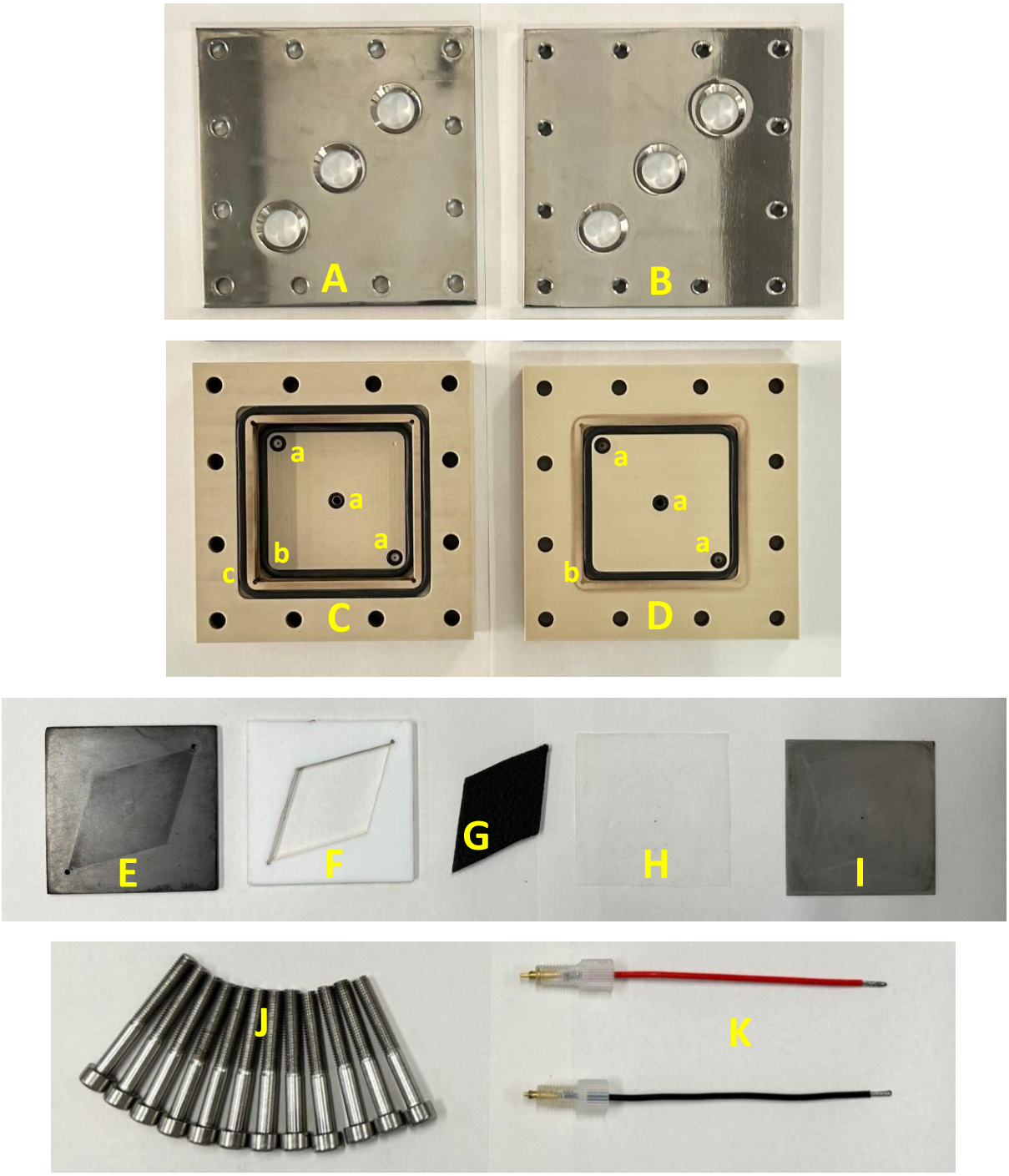


Fig. S6. Reactor parts: **A** = steel end plate 12 hole Ø 5.1 mm, **B** = steel end plate 12 threads M5 x 0.8, **C** = PEEK bottom frame (outer dimension 88 x 88 mm, internal dimension 50 x 50 mm)-O-rings **a** = 3 id x 1 mm, **b** = 53 id x 2 mm , **c** = 67 id x 2 mm, **D** = PEEK top frame (outer dimension 88 x 88 mm), **E** = Impervious graphite current collector (50 x 50 mm, 2 hole Ø 0.8 mm, thickness 3.2 mm), **F** = PTFE anode frame (50 x 50 mm, 2 x 1.25 mm thickness), **G** = rhombus shape carbon felt AvCarb G280A (30 mm x 52 mm), **H** = PTFE mesh size 18 x 28 (outer dimension 50x 50 mm), **I** = stainless steel plate cathode (50 x 50 mm, thickness 0.3 mm), **J** = screws (M5 x 0.8 , 40mm length), **K** = pogo pins for electrical connection

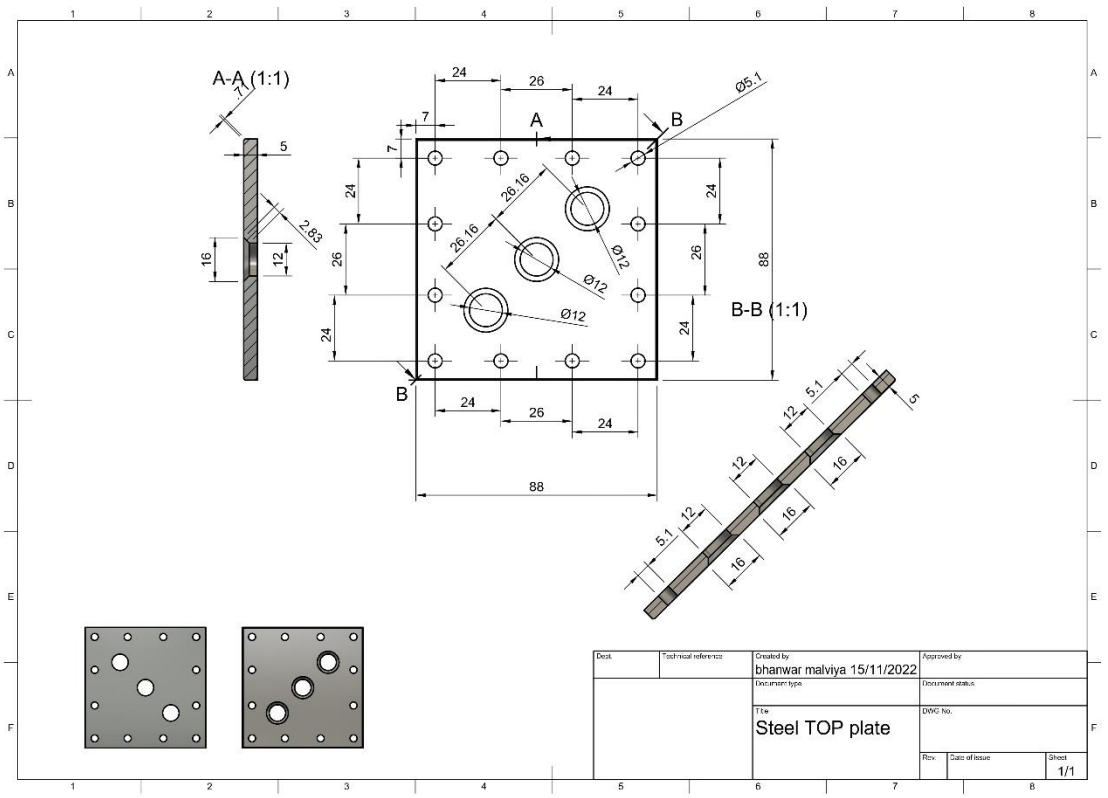


Fig. S7. Technical drawing of end plate **A**

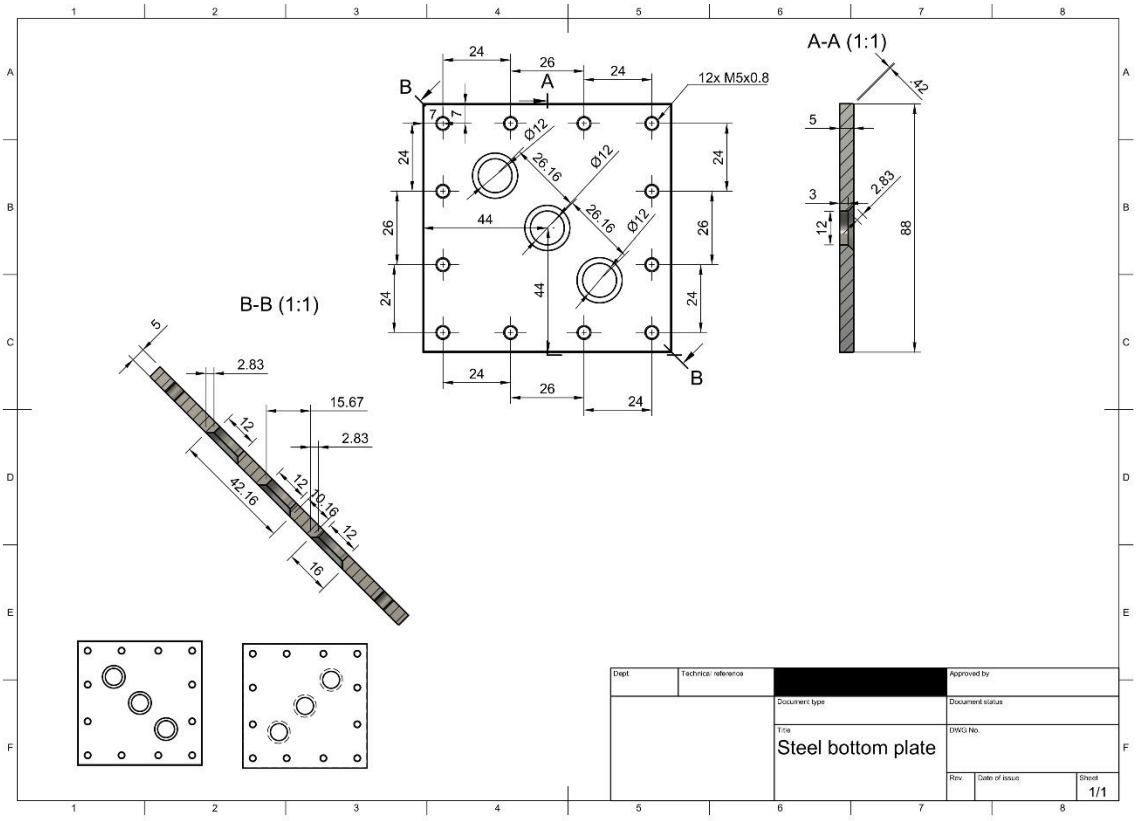


Fig. S8. Technical drawing of end plate **B**

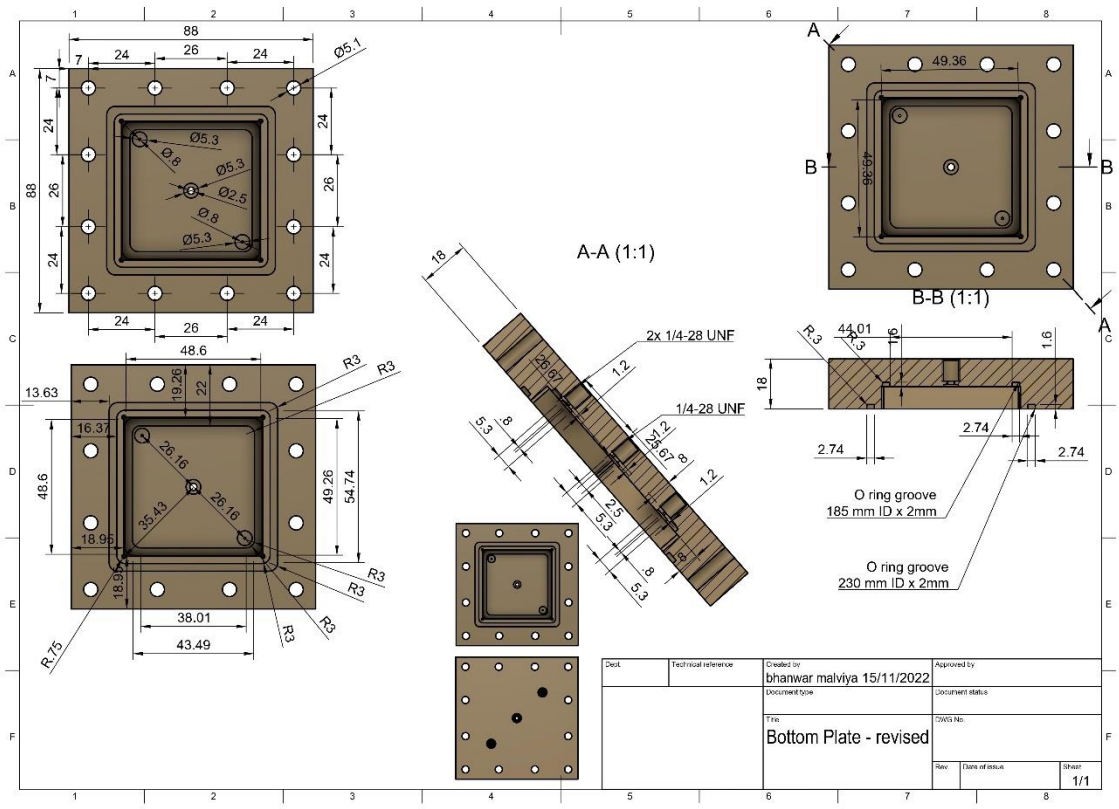


Fig. S9. Technical drawing of PEEK bottom frame **C**

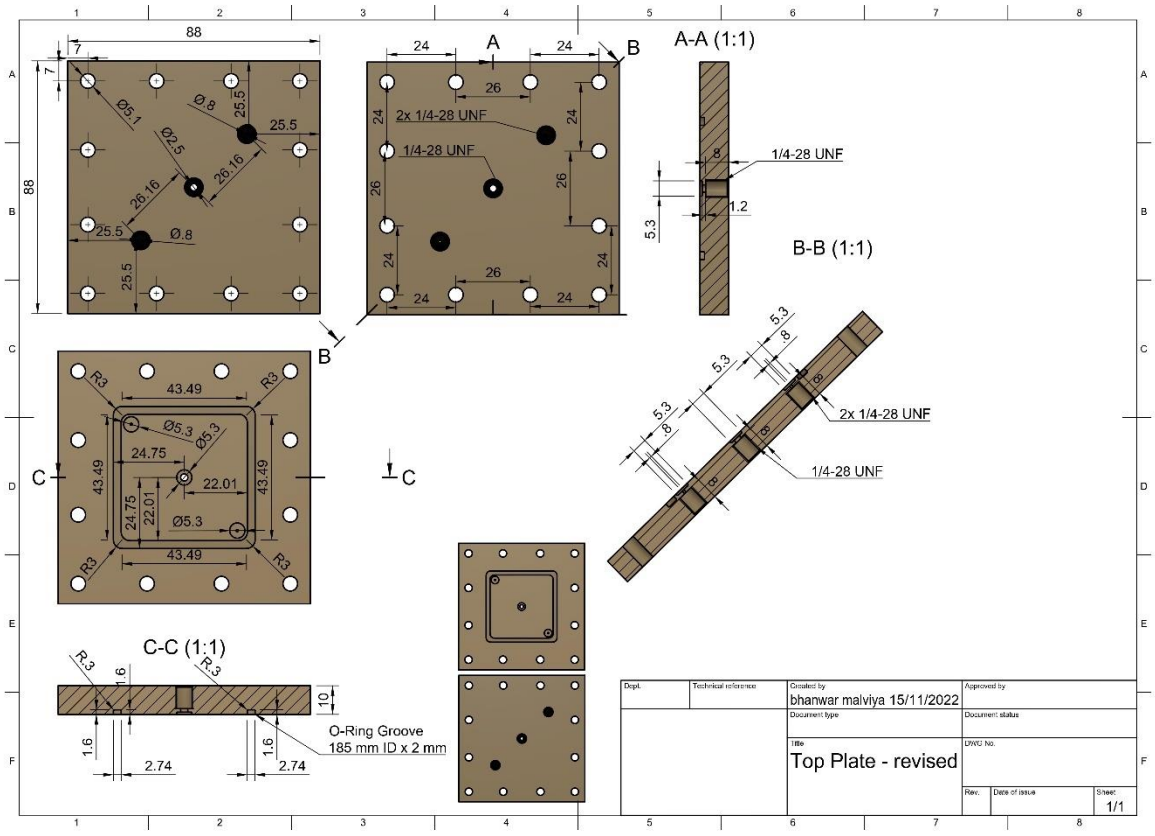


Fig. S10. Technical drawing of PEEK top frame **D**

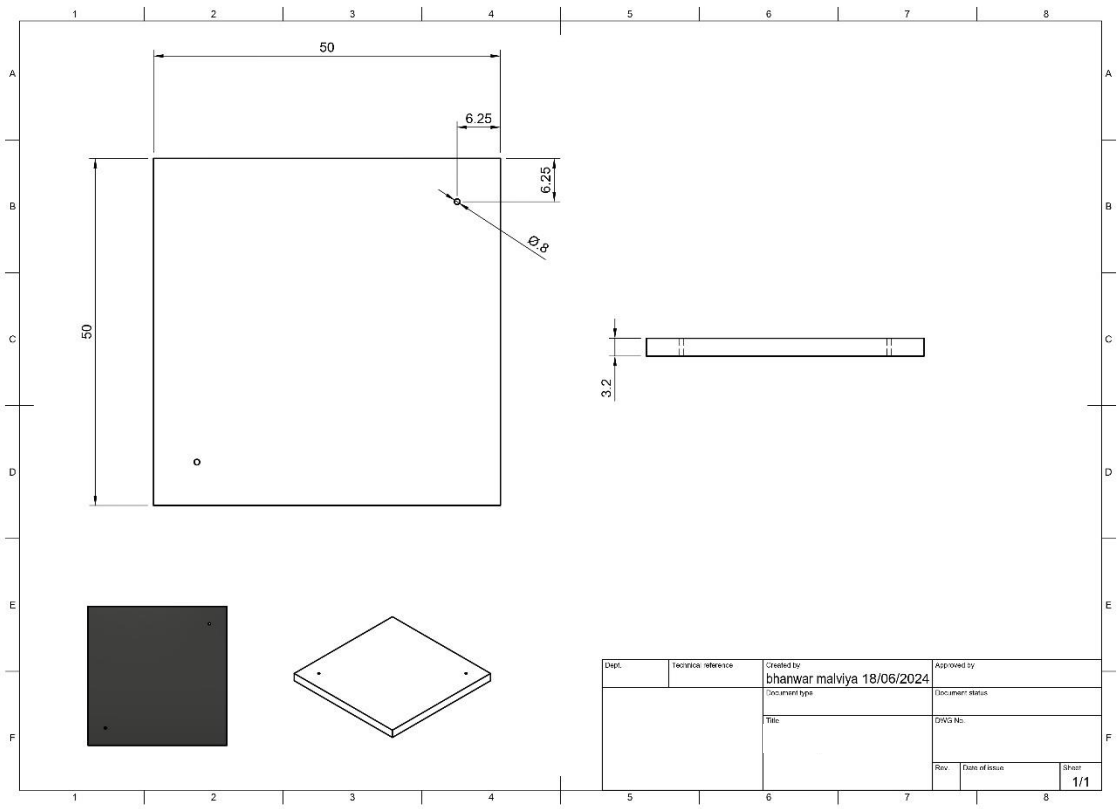


Fig. S11. Technical drawing of impervious graphite current collector **E**

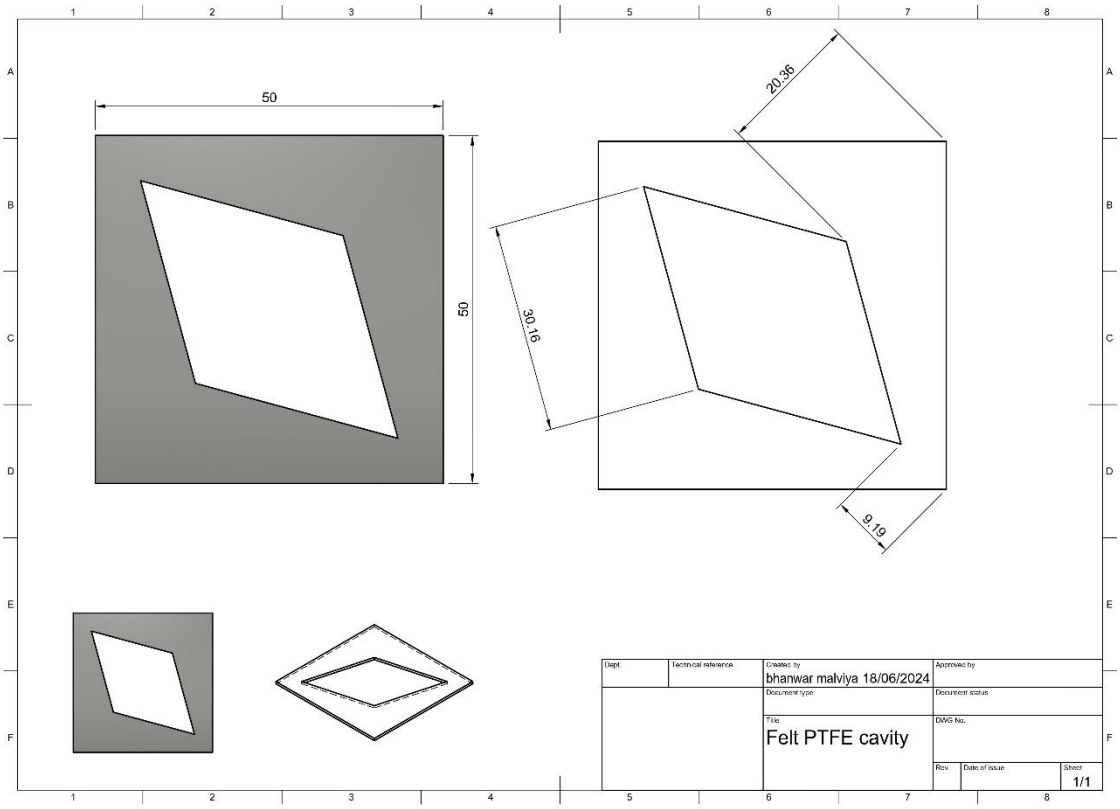


Fig. S12. Technical drawing of PTFE anode frame **F**

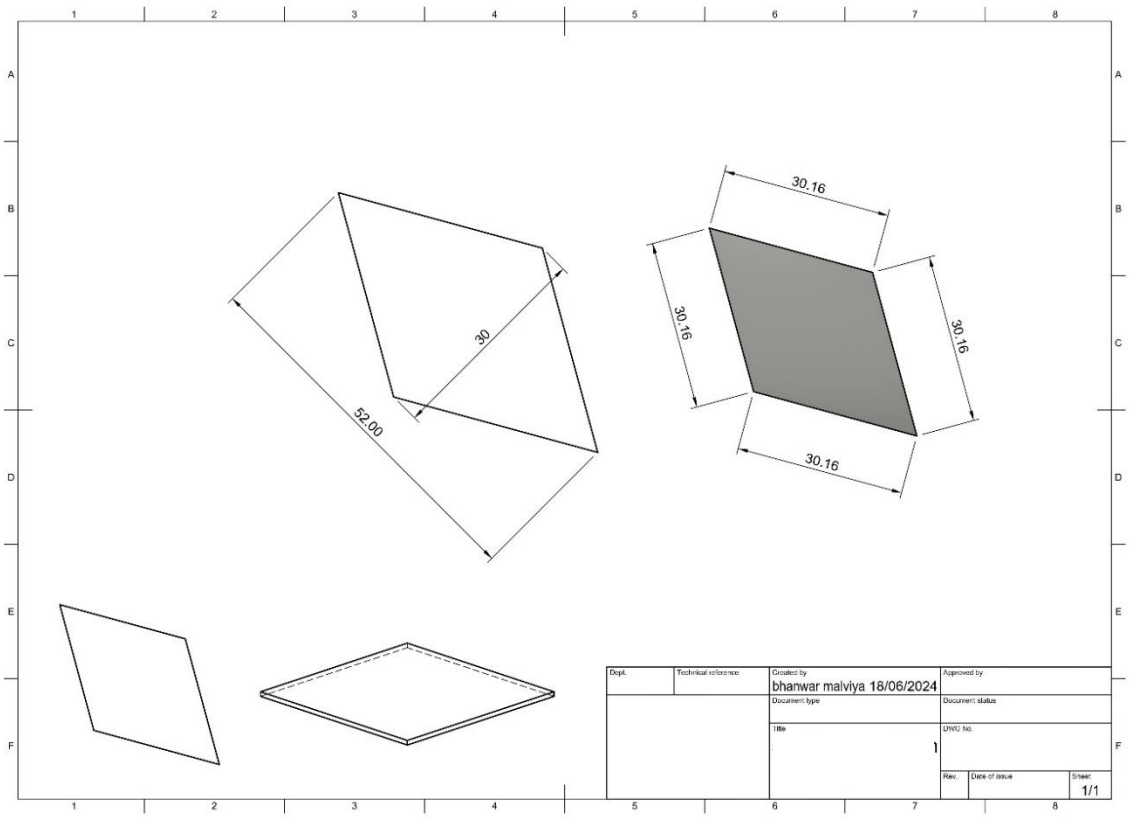


Fig. S13. Technical drawing of graphite felt **G**

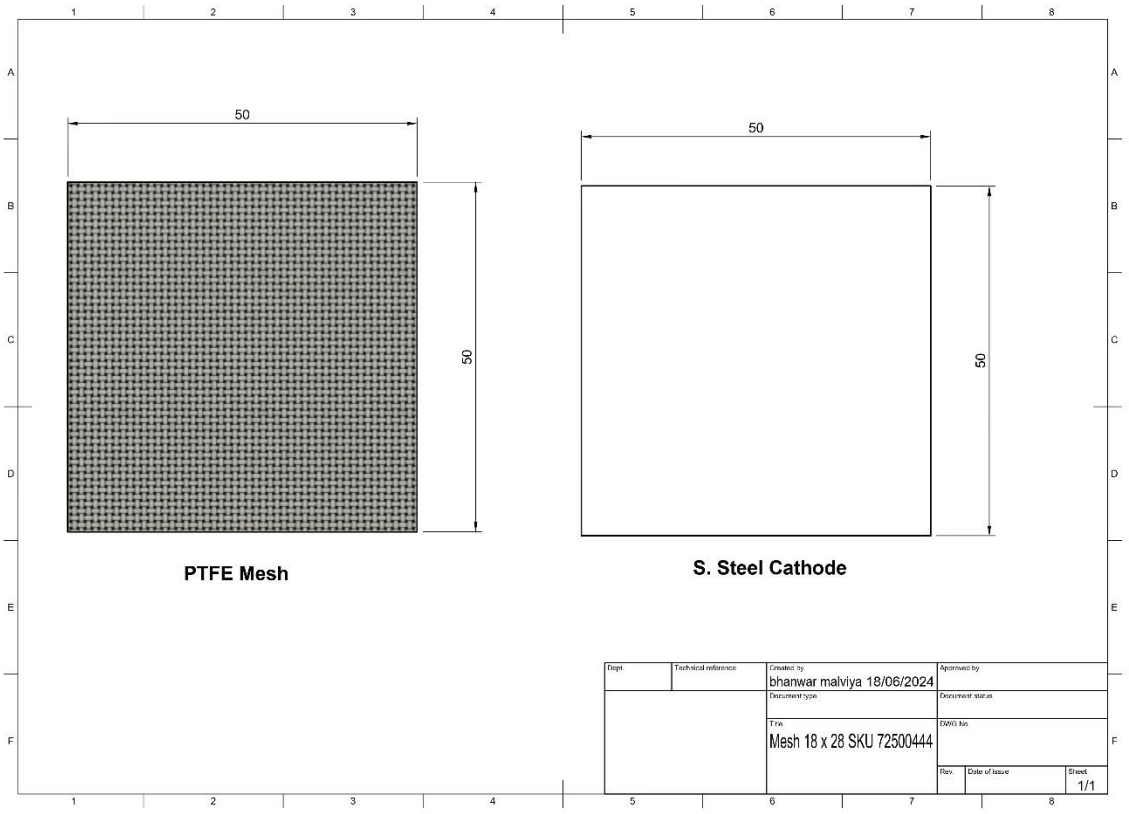
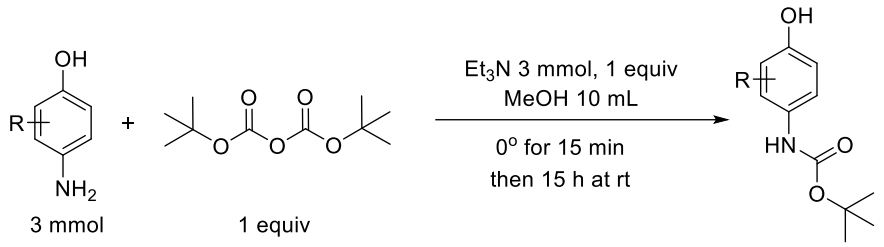


Fig. S14. Technical drawings of PTFE mesh **H** and stainless steel cathode **I**

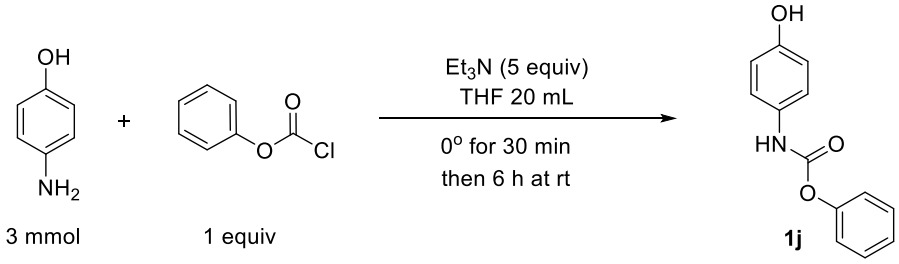
5. Experimental Procedures for the Synthesis of Starting Materials

(i) Synthesis of N-boc-protected 4-aminophenol derivatives (1a-1i, 1l-1n)



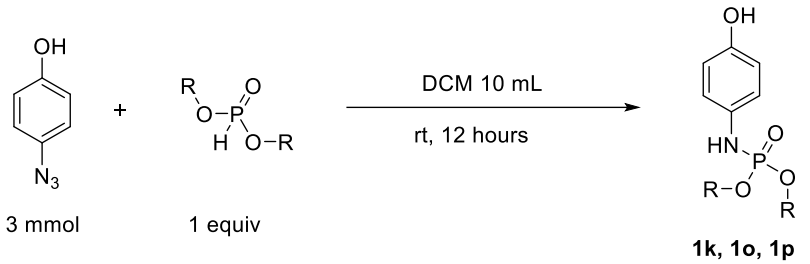
4-Aminophenol derivative (3 mmol) and triethylamine (1 equiv) were dissolved in 10 mL of MeOH and cooled to 0 °C. Then, di-tert-butyl dicarbonate (3 mmol, 1 equiv) was added portion wise. The mixture was stirred for 10 min, warmed to room temperature, and stirred for an additional 15 hours. The reaction was quenched with 5 mL of 0.25 M HCl and extracted with of EtOAc (3 x 12.5 mL). The combined organic layers were washed with 25 mL NH_4Cl (aq. sat), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (elution with petroleum ether/EtOAc 90:10).

(ii) Synthesis of phenyl (4-hydroxyphenyl)carbamate (1j):



To a solution of 4-aminolphenol (3 mmol) and triethylamine (5 mmol, 2 equiv) in THF (20 mL) at 0 ° C was added phenyl chloroformate (3 mmol, 1 equiv). The solution was stirred at 0 ° C for 30 min and then at room temperature for 6 h. After completion of the reaction, the reaction was quenched with water (30 mL) and extracted with DCM (20 mL x 3). The combined organic layers were washed with 25 mL NH_4Cl (aq. sat), dried over MgSO4, and concentrated under reduced pressure. The crude product was purified by column chromatography (elution with petroleum ether/EtOAc 80:20).

(iii) **Synthesis of phosphoramidates (1k, 1o, 1p):**

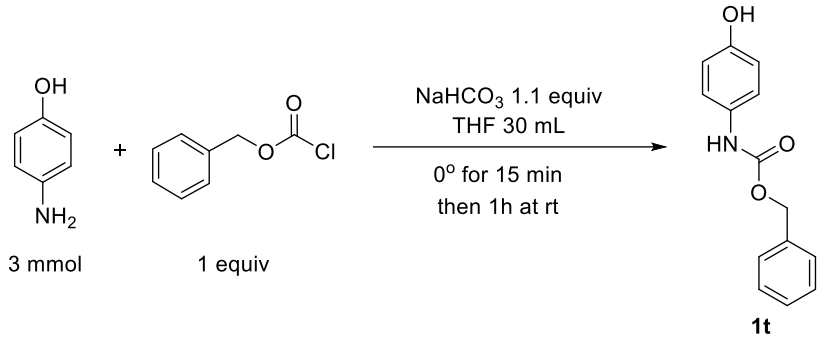


In a flame-dried flask 4-azidophenol (3 mmol) was dissolved in 10 mL of anhydrous DCM and 1 equiv of the corresponding phosphite was slowly added. The reaction mixture was stirred overnight at room temperature. Then, 10 mL of 0.5 M HCl were added to the reaction mixture and the solution was stirred for additional 2 h. The layers were separated and the aqueous phase was extracted twice with dichloromethane. The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the crude was purified by column chromatography (60% EtOAc, 40 % Hexanes).

(iv) **Synthesis of substrates 1r and 1s:**

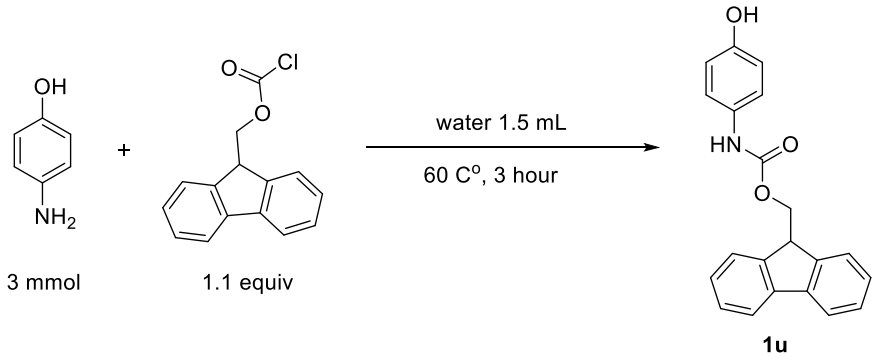
To a solution of 4-aminophenol (3 mmol) in DMF (5 ml) at 0 ^{0}C under argon atmosphere was added triethylamine (4.5 mmol, 1.5 equiv). The reaction was stirred for 10 minutes and then the corresponding chloride (1 equiv) was added over a period of 5 minutes. The reaction mixture was allowed to warm to room temperature and stirred for 18 h. The solvent was removed under reduced pressure and the mixture was treated with ethyl acetate/water. The mixture was filtered off to remove the solids precipitated and the solvent reduced under reduced pressure.

(v) Synthesis of benzyl (4-hydroxyphenyl)carbamate (1t):



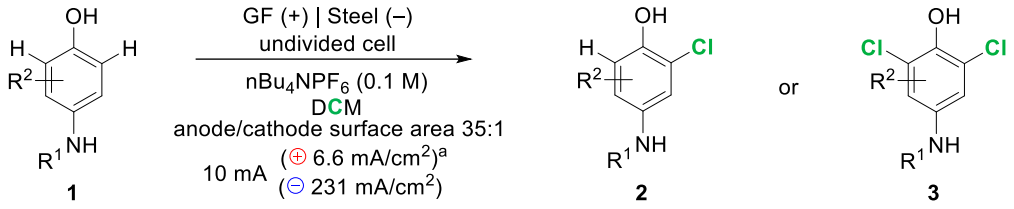
To a stirred solution of 4-aminophenol (3 mmol) in THF (30 mL) at 0 °C was added a saturated aqueous solution of $NaHCO_3$ (3.3 mmol, 1.1 equiv) followed by benzyl chloroformate (1.1 equiv). The reaction mixture was stirred for 15 min at 0 °C, and then for 1 h at rt. The reaction mixture was quenched with water (30 mL) and extracted with EtOAc (3 x 20 mL). The combined organic phases were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether/EtOAc 80:20).

(vi) <u>Synthesis of starting material (1u):</u>



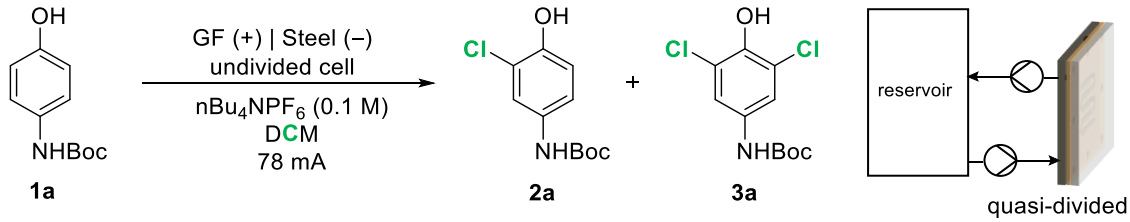
To Fmoc chloride (3.3 mmol, 1.1 equiv) were added 4-aminophenol (3 mmol) and water 1.5 mL and the reaction mixture was stirred at 60 °C. The reaction was monitored by thin layer chromatography using ethyl acetate and hexane as eluent (3:7). After consumption of the amine, the mixture was extracted with EtOAc (3 x 20 mL). The combined organic phases were dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (elution with petroleum ether EtOAc 70:30).

6. General Procedure for the Electrochemical Chlorination in Batch (see Fig. 4)



An undivided cell (5ml IKA ElectraSyn 2.0 vial) was equipped with a magnetic stirrer, a graphite felt electrode as the anode and a stainless steel cathode (1.5 x 1.5 mm contact surface area). The substrate **1** (0.3 mmol) was dissolved in DCM (3mL) containing 0.1 M nBu_4NPF_6. Electrolysis was initiated under a constant current of 10 mA. The amount of charge applied varied depending on the substrate and on if mono- or dichlorination was desired (amounts in F/mol used for each product are included in the characterization data). When the reaction was completed, the reaction mixture was poured into water (5 mL) and extracted with DCM (3 × 10 mL). The combined organic layers were washed with brine (10 mL) and dried over anhydrous Na_2SO_4. Subsequently, the solvent was removed under reduced pressure and the remaining crude product was purified by column chromatography over silica gel (Hexane/EtOAc)**.**

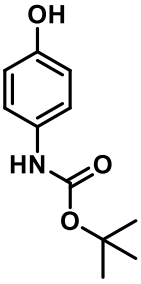
7. Electrochemical Chlorination of 1a in a Flow Electrolysis Cell



The setup and flow electrolysis cell described in Fig. S3 to S13 were used. Compound **1a** (522 mg, 2.5 mmol) was placed in a 25 mL volumetric flask. Then, 20 mL of DCM containing 0.1 M nBu_4NPF_6 were added. The mixture was sonicated until homogeneous and then diluted with additional DCM containing 0.1 M nBu_4NPF_6 "up to the mark". The reaction solution was pumped through the flow cell using a peristaltic pump (Masterflex) with a flow rate of 20 mL/min. Then cell outlet was returned to the reaction mixture vessel. When the system was stable (with no air bubbles exiting the cell) electrolysis was initiated under a constant current of 78 mA. Once the desired amount of charge had been passed (1.5 F/mol for the synthesis of

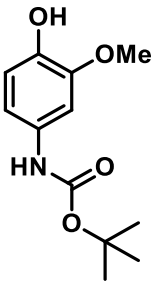
2a and 4.0 F/mol for the synthesis of **3a**) the power supply was turned off. The pump inlet was removed from the reservoir while the pump was still working to return all the reaction mixture to the reservoir. The reaction mixture was then transferred to a separatory funnel, diluted with 25 mL DCM and washed with water (100 mL). The aqueous layer was extracted with DCM (3 × 100 mL). The combined organic phases were dried over anhydrous Na_2SO_4. Subsequently, the solvent was removed under reduced pressure and the crude product was purified by column chromatography over silica gel (hexane/EtOAc 80:20) to afford the corresponding chlorinated products: **2a** with 1.5 F/mol (401 mg, 66%) or **3a** with 4.0 F/mol(623 mg, 90%).

8. Characterization Data



(1a)

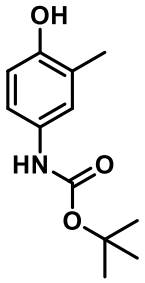
***tert*-Butyl (4-hydroxyphenyl)carbamate (1a).** White solid, **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.02 (s, 1H), 8.97 (s, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.66 (dt, *J* = 9.0, 2.1 Hz, 2H), 1.44 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 153.0, 152.5, 131.0, 120.0, 115.0, 78.4, 28.2. **HRMS (ESI)** calculated for $C_{11}H_{15}NO_3Na^+$ $[M+Na]^+$ m/z 232.0944 found m/z 232.0952.



(1b)

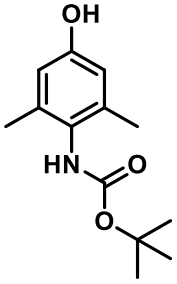
***tert*-Butyl (4-hydroxy-3-methoxyphenyl)carbamate (1b).** Brown solid, **^{1}H NMR** (300 MHz, DMSO-d_6) δ 8.99 (s, 1H), 8.54 (s, 1H), 7.13 (d, *J* = 0.9 Hz, 1H), 6.79 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 3.70 (s, 3H), 1.45 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ

152.9, 147.3, 141.6, 131.6, 115.2, 110.8, 104.0, 78.5, 55.5, 28.2. **HRMS (ESI)** calculated for $C_{12}H_{16}NO_4^-$ [M-H] $^-$ m/z 238.1074 found m/z 238.1089.



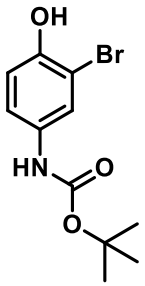
(1c)

***tert*-Butyl (4-hydroxy-3-methylphenyl)carbamate (1c).** Light brown solid, **^{1}H NMR** (300 MHz, DMSO-d_6) δ 8.88 (s, 2H), 7.13 (s, 1H), 7.03 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.64 (d, *J* = 8.7 Hz, 1H), 2.06 (s, 3H), 1.44 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 153.0, 150.6, 130.8, 123.6, 121.3, 117.3, 114.4, 78.3, 28.2, 16.2. **HRMS (ESI)** calculated for $C_{12}H_{16}NO_3^-$ [M-H] $^-$ m/z 222.1124 found m/z 222.1145.



(1d)

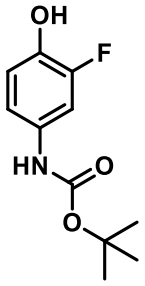
***tert*-Butyl (4-hydroxy-2,6-dimethylphenyl)carbamate (1d).** Off -White solid, **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.09 (s, 1H), 8.02 (s, 1H), 6.42 (s, 2H), 2.04 (s, 6H), 1.43 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 155.2, 154.1, 136.8, 126.6, 114.1, 77.8, 28.2, 18.1. **HRMS (ESI)** calculated for $C_{13}H_{18}NO_3^-$ [M-H] $^-$ m/z 236.1281found m/z 236.1302.



(1e)

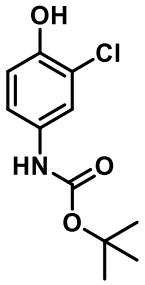
***tert*-Butyl (3-bromo-4-hydroxyphenyl)carbamate (1e).** Off-White solid, **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.80 (s, 1H), 9.18 (s, 1H), 7.63 (s, 1H), 7.20 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 1H), 1.45 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 152.8, 149.1, 132.2,

122.5, 119.0, 116.1, 108.7, 79.0, 28.1. **HRMS (ESI)** calculated for $C_{11}H_{13}BrNO_3^-$ [M-H] $^-$ m/z 286.0073 found m/z 286.0103.



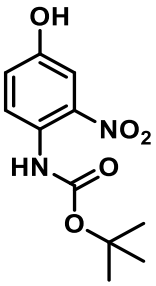
(1f)

***tert*-Butyl (3-fluoro-4-hydroxyphenyl)carbamate (1f).** White solid, **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.38 (s, 1H), 9.20 (s, 1H), 7.32 (dd, *J* = 13.5, 2.4 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.84 (t, *J* = 9.9 Hz, 1H), 1.45 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 152.4, 148.9, 139.5, 131.7, 117.6, 114.3, 106.7, 78.9, 28.1; **^{19}F NMR** (282 MHz, DMSO-d_6) δ -135.1 ppm. **HRMS (ESI)** calculated for $C_{11}H_{13}FNO_3^-$ [M-H] $^-$ m/z 226.0874 found m/z 226.0900.



(1g)

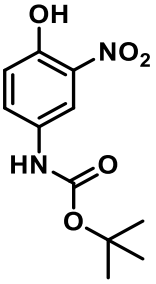
***tert*-Butyl (3-chloro-4-hydroxyphenyl)carbamate (1g).** Off-White solid, **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.73 (s, 1H), 9.20 (s, 1H), 7.48 (d, *J* = 2.1 Hz, 1H), 7.16 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 1H), 1.45 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 152.8, 148.1, 132.0, 119.6, 119.2, 118.3, 116.5, 79.0, 28.1. **HRMS (ESI)** calculated for $C_{11}H_{13}ClNO_3^-$ [M-H] $^-$ m/z 242.0578 found m/z 242.0591.



(1h)

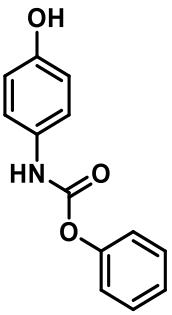
***tert*-Butyl (4-hydroxy-2-nitrophenyl)carbamate (1h).** Yellow solid, **^{1}H NMR** (300 MHz, DMSO-d_6) δ 7.63 (d, *J* = 3.0 Hz, 1H), 7.47 (s, 2H), 7.33 (dd, *J* = 9.3, 2.7 Hz, 1H), 7.05 (d, *J* =

9.3 Hz, 1H), 1.48 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 151.4, 144.4, 139.2, 130.5, 128.8, 120.0, 116.9, 83.4, 27.2. **HRMS (ESI)** calculated for $C_{11}H_{13}N_2O_5^-$ [M-H] $^-$ m/z 253.0819 found m/z 253.0834.



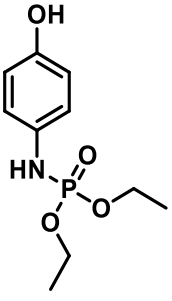
(1i)

***tert*-Butyl (4-hydroxy-3-nitrophenyl)carbamate (1i).** Yellow solid, **^{1}H NMR** (300 MHz, DMSO-d_6) δ 10.5 (s, 1H), 9.50 (s, 1H), 8.13 (d, *J* = 2.7 Hz, 1H), 7.53 (dd, *J* = 9.0, 2.7 Hz, 1H), 7.07 (d, *J* = 9.0 Hz, 1H), 1.47 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 152.8, 147.5, 135.7, 131.5, 126.2, 119.5, 113.4, 79.4, 28.1. **HRMS (ESI)** calculated for $C_{11}H_{13}N_2O_5^-$ [M-H] $^-$ m/z 253.0819 found m/z 253.0848.



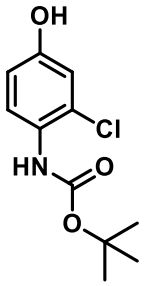
(1j)

Phenyl (4-hydroxyphenyl)carbamate (1j). Off-White solid, **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.90 (s, 1H), 9.19 (s, 1H), 7.44 – 7.38 (m, 2H), 7.30 – 7.16 (m, 5H), 6.74 (dt, *J* = 9.0, 2.1 Hz, 2H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 153.3, 151.8, 150.7, 130.0, 129.4, 125.2, 122.0, 120.4, 115.3. **HRMS (ESI)** calculated for $C_{13}H_{12}NO_3^-$ [M+H] $^+$ m/z 230.0812 found m/z 230.0814.



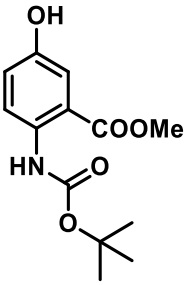
(1k)

Diethyl (4-hydroxyphenyl)phosphoramidate (1k). Brown solid, **^{1}H NMR** (300 MHz, DMSO-d_6) δ 8.89 (s, 1H), 7.56 (d, *J* = 9.3 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 2H), 6.62 (d, *J* = 8.7 Hz, 2H), 3.98 - 3.91 (m, 4H), 1.22 (td, *J* = 6.9, 0.6 Hz, 6H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 151.6, 132.3, 119.0, 118.9, 115.4, 61.7, 61.6, 16.1, 16.0; **^{31}P NMR** (121 MHz, DMSO-d_6) δ 3.33 ppm. **HRMS (ESI)** calculated for $C_{10}H_{17}NO_4P^+$ [M+H] $^+$ m/z 246.0890 found m/z 246.0893.



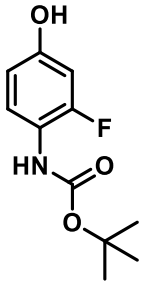
(1l)

***tert*-Butyl (2-chloro-4-hydroxyphenyl)carbamate (1l).** Off-White solid, **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.74 (s, 1H), 8.40 (s, 1H), 7.19 (d, *J* = 8.7 Hz, 1H), 6.82 (d, *J* = 2.7 Hz, 1H), 6.70 (dd, *J* = 8.7, 2.7 Hz, 1H), 1.42 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 155.9, 153.8, 129.7, 128.8, 126.5, 115.5, 114.3, 78.7, 28.1. **HRMS (ESI)** calculated for $C_{11}H_{13}ClNO_3^-$ [M-H] $^-$ m/z 242.0578 found m/z 242.0606.



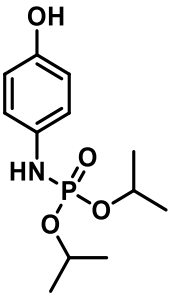
(1m)

Methyl 2-((tert-butoxycarbonyl)amino)-5-hydroxybenzoate (1m). Off-White solid, **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.65 (s, 1H), 9.53 (s, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.28 (d, *J* = 3.0 Hz, 1H), 7.02 (dd, *J* = 9.0, 3.0 Hz, 1H), 3.82 (s, 3H), 1.45 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 167.6, 152.4, 152.0, 132.4, 121.4, 117.6, 115.9, 79.5, 52.4, 28.0. **HRMS (ESI)** calculated for $C_{13}H_{16}NO_5^-$ [M-H] $^-$ m/z 266.1023 found m/z 266.1050.



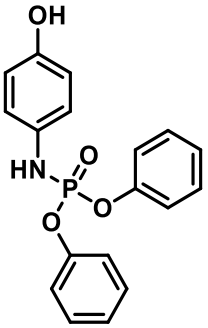
(1n)

***tert*-Butyl (2-fluoro-4-hydroxyphenyl)carbamate (1n).** White solid, **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.68 (s, 1H), 8.51 (s, 1H), 7.19 (t, *J* = 9.0 Hz, 1H), 6.58 – 6.50 (m, 2H), 1.42 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 157.7, 155.6, 153.7, 127.3, 117.1, 110.8, 102.7, 78.7, 28.1; **^{19}F NMR** (282 MHz, DMSO-d_6) δ -121.4 ppm. **HRMS (ESI)** calculated for $C_{11}H_{13}FNO_3^-$ [M-H] $^-$ m/z 226.0874 found m/z 226.0901.



(1o)

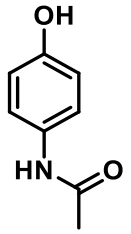
Diisopropyl (4-hydroxyphenyl)phosphoramidate (1o). Brown solid, **^{1}H NMR** (300 MHz, DMSO-d_6) δ 8.84 (s, 1H), 7.48 (d, *J* = 9.0 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 2H), 6.61 (d, *J* = 8.7 Hz, 2H), 4.51 – 4.40 (m, 2H), 1.25 (d, *J* = 6.3 Hz, 6H), 1.15 (d, *J* = 6.3 Hz, 1H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 151.4, 132.7, 118.8, 118.7, 115.3, 70.0, 69.9, 23.7, 23.6, 23.5, 23.4; **^{31}P NMR** (121 MHz, DMSO-d_6) δ 1.21 ppm. **HRMS (ESI)** calculated for $C_{12}H_{21}NO_4P^+$ [M+H] $^+$ m/z 274.1203 found m/z 274.1216.



(1p)

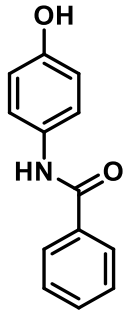
Diphenyl (4-hydroxyphenyl)phosphoramidate (1p). Off-White solid, **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.07 (s, 1H), 8.43 (d, *J* = 10.8 Hz, 1H), 7.42 – 7.37 (m, 4H), 7.23 – 7.18 (m, 6H),

7.00 (dt, *J* = 9.0, 2.4 Hz, 2H), 6.71 (dt, *J* = 8.7, 2.4 Hz, 2H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 152.5, 150.3, 150.2, 131.0, 129.9, 125.2, 120.2, 120.1, 119.9, 119.8, 115.8; **^{31}P NMR** (121 MHz, DMSO-d_6) δ -5.82 ppm. **HRMS (ESI)** calculated for $C_{18}H_{17}NO_4P^+$ $[M+H]^+$ m/z 342.0890 found m/z 342.0896.



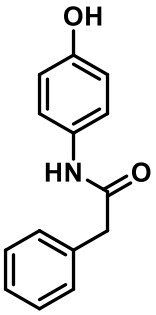
(1q)

***N*-(4-hydroxyphenyl)acetamide (1q).** White solid, **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.64 (s, 1H), 9.12 (s, 1H), 7.35 (dt, *J* = 8.9, 3.3 Hz, 2H), 6.69 (dt, *J* = 8.9, 3.3 Hz, 2H), 1.97 (s, 3H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 167.6, 153.2, 131.1, 120.9, 115.0, 23.8. **HRMS (ESI)** calculated for $C_8H_{10}NO_2^+$ $[M+H]^+$ m/z 152.0706 found m/z 152.0711.



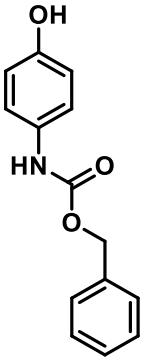
(1r)

***N*-(4-hydroxyphenyl)benzamide (1r).** Off-White solid, **^{1}H NMR** (300 MHz, DMSO-d_6) δ 10.01 (s, 1H), 9.27 (s, 1H), 7.95 (d, *J* = 7.5 Hz, 2H), 7.56 – 7.48 (m, 5H), 6.76 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 165.0, 153.7, 135.2, 131.3, 130.7, 128.3, 127.5, 122.3, 115.0. **HRMS (ESI)** calculated for $C_{13}H_{12}NO_2^+$ $[M+H]^+$ m/z 214.0863 found m/z 214.0871.



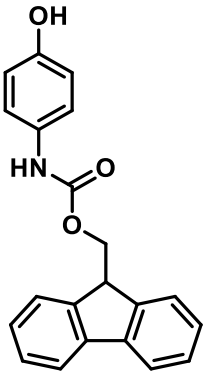
(1s)

***N*-(4-hydroxyphenyl)-2-phenylacetamide (1s).** Off-White solid, **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.90 (s, 1H), 9.18 (s, 1H), 7.39 – 7.20 (m, 7H), 6.71 (dt, *J* = 9.0, 2.1 Hz, 2H), 3.57 (s, 2H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 168.4, 153.3, 136.3, 130.9, 129.1, 128.3, 126.5, 120.9, 115.1, 43.2. **HRMS (ESI)** calculated for $C_{14}H_{12}NO_2^-$ [M-H] $^-$ m/z 226.0862 found m/z 226.0887.



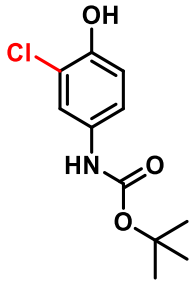
(1t)

Benzyl (4-hydroxyphenyl)carbamate (1t). White solid, **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.42 (s, 1H), 9.10 (s, 1H), 7.44 – 7.30 (m, 5H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.69 (dt, *J* = 8.9, 2.2 Hz, 2H), 5.11 (s, 2H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 153.6, 152.9, 136.9, 130.5, 128.4, 128.0, 127.9, 120.1, 115.2, 65.4. **HRMS (ESI)** calculated for $C_{14}H_{12}NO_3^-$ [M-H] $^-$ m/z 242.0811 found m/z 242.0834.



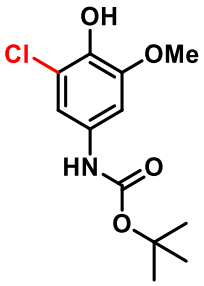
(1u)

(9H-Fluoren-9-yl)methyl (4-hydroxyphenyl)carbamate (1u). Off-White solid, **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.39 (s, 1H), 9.10 (s, 1H), 7.92 (d, *J* = 7.5 Hz, 2H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.45 (td, *J* = 7.5, 1.2 Hz, 2H), 7.37 (td, *J* = 7.2, 1.2 Hz, 2H), 7.23 (s, 2H), 6.67 (d, *J* = 8.1 Hz, 2H), 4.44 (d, *J* = 6.9 Hz, 2H), 4.30 (t, *J* = 6.3 Hz, 1H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 153.6, 152.9, 143.9, 140.8, 130.5, 127.7, 127.1, 125.1, 120.2, 115.1, 65.4, 46.7. **HRMS (ESI)** calculated for $C_{21}H_{16}NO_3^-$ [M-H] $^-$ m/z 330.1124 found m/z 330.1136.



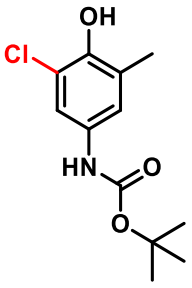
(2a)

***tert*-Butyl (3-chloro-4-hydroxyphenyl)carbamate (2a).** Off-White solid, isolated yield (44 mg, 60 %, 1.6 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.73 (s, 1H), 9.20 (s, 1H), 7.48 (d, *J* = 2.1 Hz, 1H), 7.16 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 1H), 1.45 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 152.8, 148.1, 132.0, 119.6, 119.2, 118.3, 116.5, 79.0, 28.1. **HRMS (ESI)** calculated for $C_{11}H_{13}ClNO_3^-$ [M-H] $^-$ m/z 242.0578 found m/z 242.0591.



(2b)

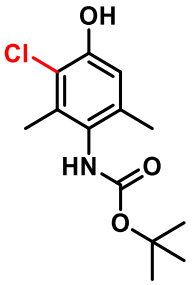
***tert*-Butyl (3-chloro-4-hydroxy-5-methoxyphenyl)carbamate (2b).** Brown solid, isolated yield (74 mg, 90 %, 2.0 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.20 (s, 1H), 8.97 (s, 1H), 7.09 (dd, *J* = 14.2, 2.1 Hz, 1H), 3.75 (s, 3H), 1.46 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 152.8, 148.6, 137.7, 131.8, 119.7, 79.1, 55.9, 28.1. **HRMS (ESI)** calculated for $C_{12}H_{15}ClNO_4^-$ [M-H] $^-$ m/z 272.0684 found m/z 272.0702.



(2c)

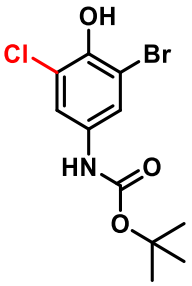
***tert*-Butyl (3-chloro-4-hydroxy-5-methylphenyl)carbamate (2c).** Light brown solid, isolated yield (72 mg, 94 %, 2.2 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.16 (s, 1H), 8.71 (s, 1H), 7.33 (d, *J* = 2.7 Hz, 1H), 7.10 (d, *J* = 2.7 Hz, 1H), 2.14 (s, 3H), 1.45 (s, 9H); **^{13}C**

NMR {1H} (75 MHz, DMSO-d_6) δ 152.8, 145.7, 132.0, 127.1, 120.4, 119.5, 116.7, 79.0, 28.1, 17.0. **HRMS (ESI)** calculated for $C_{12}H_{15}ClNO_3^-$ [M-H] $^-$ m/z 256.0735 found m/z 256.0753.



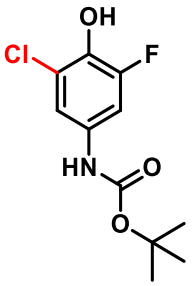
(2d)

***tert*-Butyl (3-chloro-4-hydroxy-2,6-dimethylphenyl)carbamate (2d).** Off-White solid, isolated yield (46 mg, 57 %, 1.8 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.85 (s, 1H), 8.29 (s, 1H), 6.67 (s, 1H), 2.14 (s, 3H), 2.05 (s, 3H), 1.43 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 154.5, 151.7, 135.6, 135.3, 127.8, 117.8, 114.9, 78.6, 28.6, 18.4, 16.2. **HRMS (ESI)** calculated for $C_{13}H_{17}ClNO_3^-$ [M-H] $^-$ m/z 270.0891 found m/z 270.0909.



(2e)

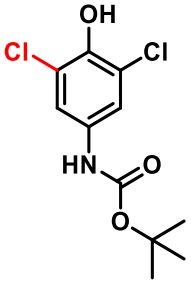
***tert*-Butyl (3-bromo-5-chloro-4-hydroxyphenyl)carbamate (2e).** Off-White solid, isolated yield (60 mg, 62 %, 2.0 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.68 (s, 1H), 9.42 (s, 1H), 7.45 (s, 2H), 1.45 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 152.7, 143.9, 132.8, 122.4, 117.9, 79.6, 28.1. **HRMS (ESI)** calculated for $C_{11}H_{12}BrClNO_3^-$ [M-H] $^-$ m/z 319.9683 found m/z 319.9702.



(2f)

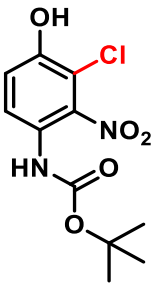
***tert*-Butyl (3-chloro-5-fluoro-4-hydroxyphenyl)carbamate (2f).** Off-White solid, isolated yield (51 mg, 65 %, 2.2 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.85 (s, 1H),

9.41 (s, 1H), 7.83 (m, 2H), 1.45 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 153.0, 150.1, 136.1, 131.9, 122.1, 114.3, 105.1, 79.5, 28.1; **^{19}F NMR** (282 MHz, DMSO-d_6) δ -130.5 ppm. **HRMS (ESI)** calculated for $C_{11}H_{12}ClFNO_3^-$ [M-H] $^-$ m/z 260.0484 found m/z 260.0506.



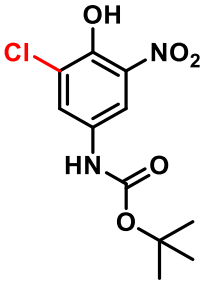
(2g)

***tert*-Butyl (3,5-dichloro-4-hydroxyphenyl)carbamate (2g).** Off-White solid, isolated yield (70 mg, 84 %, 2.0 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.69 (s, 1H), 9.42 (s, 1H), 7.45 (s, 2H), 1.46 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 152.7, 143.9, 132.8, 122.4, 117.9, 79.6, 28.1. **HRMS (ESI)** calculated for $C_{11}H_{12}Cl_2NO_3^-$ [M-H] $^-$ m/z 276.0188 found m/z 276.0204.



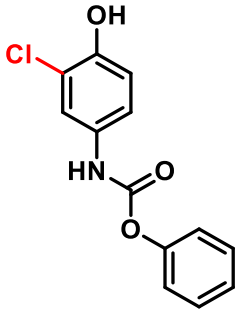
(2h)

***tert*-Butyl (3-chloro-4-hydroxy-2-nitrophenyl)carbamate (2h).** Yellow solid, isolated yield (56 mg, 65 %, 2.0 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 7.90 (d, *J* = 2.7 Hz, 1H), 7.79 (d, *J* = 3.0 Hz, 1H), 7.31 (s, 2H), 1.48 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 151.2, 140.4, 138.2, 130.7, 130.4, 121.2, 117.3, 83.5, 27.2. **HRMS (ESI)** calculated for $C_{11}H_{12}ClN_2O_5^-$ [M-H] $^-$ m/z 287.0429 found m/z 287.0444.



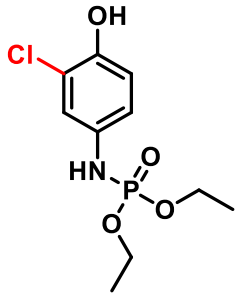
(2i)

***tert*-Butyl (3-chloro-4-hydroxy-5-nitrophenyl)carbamate (2i).** Yellow solid, isolated yield (60 mg, 70 %, 2.4 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 10.6 (s, 1H), 9.68 (s, 1H), 8.10 (d, *J* = 2.7 Hz, 1H), 7.80 (d, *J* = 2.7 Hz, 1H), 1.47 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 152.7, 143.3, 137.3, 131.8, 125.3, 123.9, 112.2, 80.0, 28.0. **HRMS (ESI)** calculated for $C_{11}H_{12}ClN_2O_5^-$ [M-H] $^-$ m/z 287.0429 found m/z 287.0454.



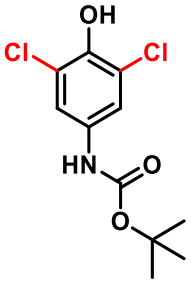
(2j)

Phenyl (3-chloro-4-hydroxyphenyl)carbamate (2j). White solid, isolated yield (54 mg, 69 %, 2.2 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 10.10 (s, 1H), 9.92 (s, 1H), 7.51 (s, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.27 – 7.19 (m, 4H), 6.94 (d, *J* = 8.7 Hz, 1H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 151.8, 150.5, 148.9, 131.0, 129.4, 125.4, 122.0, 120.1, 119.4, 118.7, 116.7. **HRMS (ESI)** calculated for $C_{13}H_9ClNO_3^-$ [M-H] $^-$ m/z 262.0265 found m/z 262.0290.



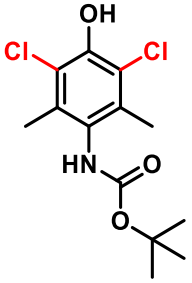
(2k)

Diethyl (3-chloro-4-hydroxyphenyl)phosphoramidate (2k). Brown solid, isolated yield (56 mg, 67 %, 2.0 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.64 (s, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 6.99 (d, *J* = 2.1 Hz, 1H), 6.85 – 6.78 (m, 2H), 4.00 – 3.93 (m, 4H), 1.22 (td, *J* = 6.9, 0.9 Hz, 6H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 147.3, 133.5, 119.6, 118.8, 118.7, 117.5, 117.4, 117.1, 62.0, 61.9, 16.1, 16.0; **^{31}P NMR** (121 MHz, DMSO-d_6) δ 2.69 ppm. **HRMS (ESI)** calculated for $C_{10}H_{16}ClNO_4P^+$ [M+H] $^+$ m/z 280.0500 found m/z 280.0513.



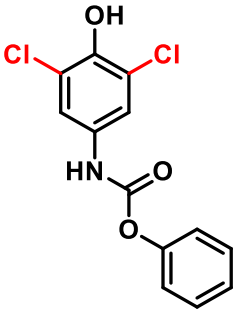
(3a)

***tert*-Butyl (3,5-dichloro-4-hydroxyphenyl)carbamate (3a).** Off-White solid, isolated yield (73 mg, 88 %, 4.0 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.69 (s, 1H), 9.42 (s, 1H), 7.45 (s, 2H), 1.46 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 152.7, 143.9, 132.8, 122.4, 117.9, 79.6, 28.1. **HRMS (ESI)** calculated for $C_{11}H_{12}Cl_2NO_3^-$ [M-H] $^-$ m/z 276.0188 found m/z 276.0204.



(3d)

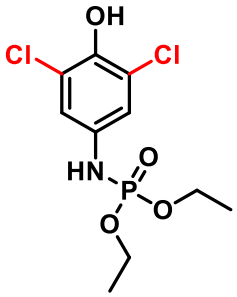
***tert*-Butyl (3,5-dichloro-4-hydroxy-2,6-dimethylphenyl)carbamate (3d).** Off-White solid, isolated yield (55 mg, 60 %, 4.3 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.79 (s, 1H), 8.58 (s, 1H), 2.17 (s, 6H), 1.44 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 154.5, 148.0, 134.1, 128.8, 120.1, 79.1, 28.6, 16.3. **HRMS (ESI)** calculated for $C_{13}H_{16}Cl_2NO_3^-$ [M-H] $^-$ m/z 304.0510 found m/z 304.0520.



(3j)

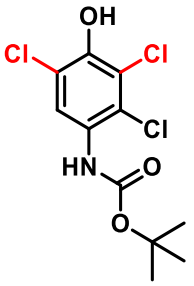
Phenyl (3,5-dichloro-4-hydroxyphenyl)carbamate (3j). Off-White solid, isolated yield (66 mg, 74 %, 4.0 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 10.30 (s, 1H), 9.87 (s, 1H), 7.50 (s, 2H), 7.46 – 7.39 (m, 2H), 7.29 – 7.20 (m, 3H); **^{13}C NMR {1H}** (75 MHz, DMSO-

d_6) δ 151.7, 150.4, 144.7, 131.8, 129.5, 125.6, 122.6, 121.9, 118.5. **HRMS (ESI)** calculated for $C_{13}H_8Cl_2NO_3^-$ [M-H] $^-$ m/z 295.9875 found m/z 295.9905.



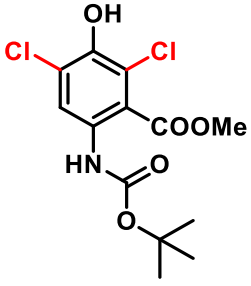
(3k)

Diethyl (3,5-dichloro-4-hydroxyphenyl)phosphoramidate (3k). Brown solid, isolated yield (86 mg, 92 %, 4.0 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.55 (s, 1H), 8.01 (d, *J* = 8.7 Hz, 1H), 7.00 (s, 2H), 4.03 -3.93 (m, 4H), 1.24 (td, *J* = 6.9, 0.9 Hz, 6H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 144.0, 134.4, 122.9, 117.3, 117.2, 62.2, 62.2, 16.0, 15.9; **^{31}P NMR** (121 MHz, DMSO-d_6) δ 1.98 ppm. **HRMS (ESI)** calculated for $C_{10}H_{15}Cl_2NO_4P^+$ [M+H] $^+$ m/z 314.0110 found m/z 314.0134.



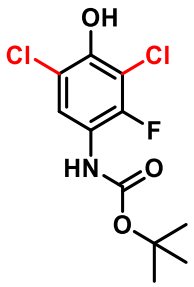
(3l)

***tert*-Butyl (2,3,5-trichloro-4-hydroxyphenyl)carbamate (3l).** Light brown solid, isolated yield (54 mg, 58 %, 4.2 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 10.50 (s, 1H), 8.82 (s, 1H), 7.51 (s, 1H), 1.44 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 153.3, 147.6, 128.9, 125.7, 121.6, 120.2, 79.5, 28.0. **HRMS (ESI)** calculated for $C_{11}H_{11}Cl_3NO_3^-$ [M-H] $^-$ m/z 309.9799 found m/z 309.9823.



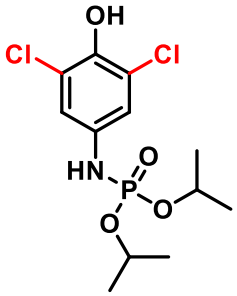
(3m)

Methyl 6-((tert-butoxycarbonyl)amino)-2,4-dichloro-3-hydroxybenzoate (3m). Off-White solid, isolated yield (82 mg, 82 %, 4.0 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 10.3 (s, 1H), 9.00 (s, 1H), 7.35 (s, 1H), 3.78 (s, 3H), 1.42 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 164.5, 153.5, 146.4, 128.8, 124.9, 123.4, 120.0, 79.5, 52.5, 28.0. **HRMS (ESI)** calculated for $C_{13}H_{14}Cl_2NO_5^-$ [M-H] $^-$ m/z 334.0243 found m/z 334.0267.



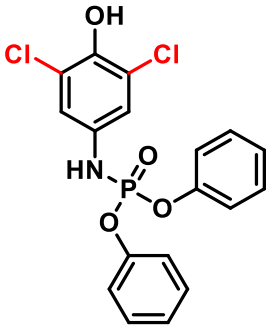
(3n)

***tert*-Butyl (3,5-dichloro-2-fluoro-4-hydroxyphenyl)carbamate (3n).** White solid, isolated yield (53 mg, 60 %, 4.1 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 10.5 (s, 1H), 9.04 (s, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 1.44 (s, 9H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 153.2, 151.8, 146.8, 123.5, 119.6, 116.5, 110.6, 79.7, 28.0; **^{19}F NMR** (282 MHz, DMSO-d_6) δ -122.4 ppm. **HRMS (ESI)** calculated for $C_{11}H_{11}Cl_2FNO_3^-$ [M-H] $^-$ m/z 294.0094 found m/z 294.0116.



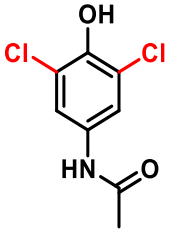
(3o)

Diisopropyl (3,5-dichloro-4-hydroxyphenyl)phosphoramidate (3o). Brown solid, isolated yield (83 mg, 81 %, 4.1 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.51 (s, 1H), 7.98 (d, *J* = 9.0 Hz, 1H), 6.99 (s, 2H), 4.57 – 4.42 (m, 2H), 1.27 (d, *J* = 6.3 Hz, 6H), 1.18 (d, *J* = 6.0 Hz, 6H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 142.8, 134.7, 122.8, 117.2, 117.1, 70.8, 70.7, 23.6, 23.5, 23.4, 23.3; **^{31}P NMR** (121 MHz, DMSO-d_6) δ -0.28 ppm. **HRMS (ESI)** calculated for $C_{12}H_{19}Cl_2NO_4P^+$ [M+H] $^+$ m/z 342.0423 found m/z 342.0429.



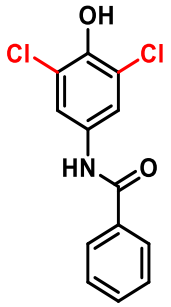
(3p)

Diphenyl (3,5-dichloro-4-hydroxyphenyl)phosphoramidate (3p). Off-White solid, isolated yield (105 mg, 86 %, 4.1 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.80 (s, 1H), 8.94 (d, *J* = 9.9 Hz, 1H), 7.45 – 7.40 (m, 4H), 7.27 – 7.20 (m, 6H), 7.11 (s, 2H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 149.9, 149.8, 144.0, 133.0, 130.1, 125.5, 123.0, 120.1, 120.0, 118.0, 117.9; **^{31}P NMR** (121 MHz, DMSO-d_6) δ -7.03 ppm. **HRMS (ESI)** calculated for $C_{18}H_{15}Cl_2NO_4P^+$ [M+H] $^+$ m/z 410.0110 found m/z 410.0116.



(3q)

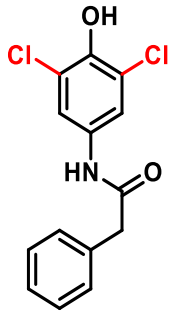
***N*-(3,5-dichloro-4-hydroxyphenyl)acetamide (3q).** Off-White solid, isolated yield (28 mg, 42 %, 5.0 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.97 (s, 1H), 9.82 (1, 1H), 7.58 (s, 2H), 2.01 (s, 3H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 168.3, 144.6, 132.5, 122.2, 118.9, 23.9. **HRMS (ESI)** calculated for $C_8H_8Cl_2NO_2^+$ [M+H] $^+$ m/z 219.9927 found m/z 219.9930.



(3r)

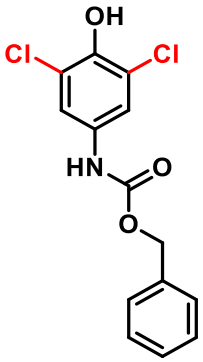
***N*-(3,5-dichloro-4-hydroxyphenyl)benzamide (3r).** Off-White solid, isolated yield (49 mg, 58 %, 4.5 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 10.27 (s, 1H), 9.94 (s, 1H), 7.94 – 7.91 (m, 2H), 7.84 (s, 2H), 7.63 – 7.51 (m, 3H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6)

δ 165.4, 145.2, 134.4, 132.2, 131.8, 128.5, 127.6, 122.1, 120.3. **HRMS (ESI)** calculated for $C_{13}H_{10}Cl_2NO_2^-$ [M-H] $^-$ m/z 279.9926 found m/z 279.9948.



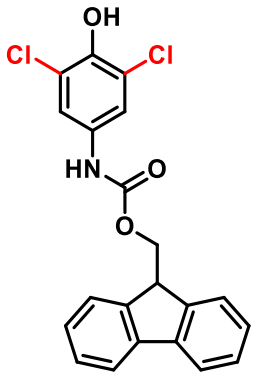
(3s)

***N*-(3,5-dichloro-4-hydroxyphenyl)-2-phenylacetamide (3s).** Off-White solid, isolated yield (46 mg, 52 %, 4.6 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 10.22 (s, 1H), 9.87 (s, 1H), 7.61 (s, 2H), 7.33 – 7.23 (m, 5H), 3.60 (s, 2H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 169.1, 144.8, 135.6, 132.3, 129.1, 128.3, 126.6, 122.2, 119.1. **HRMS (ESI)** calculated for $C_{14}H_{10}Cl_2NO_2^-$ [M-H] $^-$ m/z 294.0083 found m/z 294.0105.



(3t)

Benzyl (3,5-dichloro-4-hydroxyphenyl)carbamate (3t). White solid, isolated yield (65 mg, 70 %, 4.2 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.83 (s, 1H), 9.77 (s, 1H), 7.46 (s, 2H), 7.43 – 7.32 (m, 5H), 5.14 (s, 2H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 153.3, 144.3, 136.4, 132.3, 128.5, 128.2, 128.1, 122.5, 118.1, 66.0. **HRMS (ESI)** calculated for $C_{14}H_{10}Cl_2NO_3^-$ [M-H] $^-$ m/z 310.0032 found m/z 310.0057.

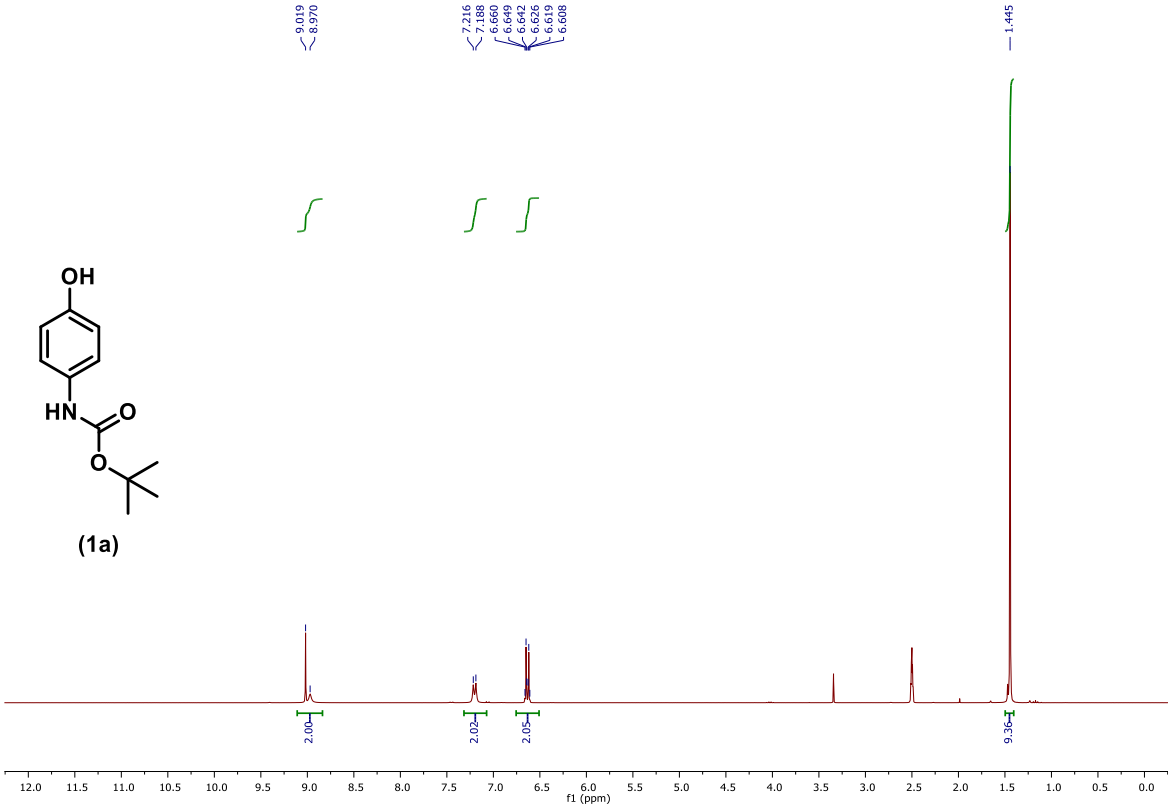


(3u)

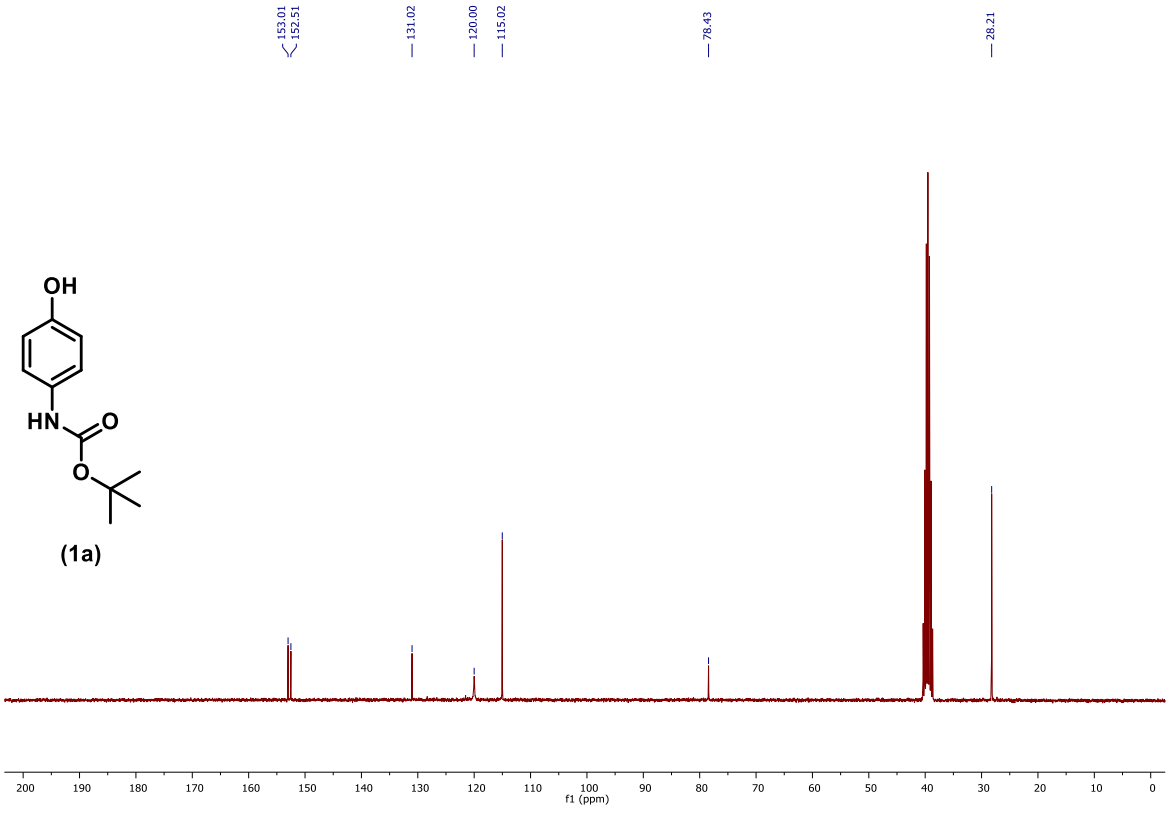
(9H-Fluoren-9-yl)methyl (3,5-dichloro-4-hydroxyphenyl)carbamate (3u). Off-White solid, isolated yield (78 mg, 65 %, 4.5 F/mol) (for 0.3 mmol), **^{1}H NMR** (300 MHz, DMSO-d_6) δ 9.76 (s, 1H), 9.73 (s, 1H), 7.92 (d, *J* = 6.9 Hz, 2H), 7.73 (d, *J* = 7.2 Hz, 2H), 7.45 – 7.32 (m 6H), 4.52 (d, *J* = 6.3 Hz, 2H), 4.32 (t, *J* = 6.3 Hz, 2H); **^{13}C NMR {1H}** (75 MHz, DMSO-d_6) δ 153.3, 144.3, 143.7, 140.8, 132.2, 127.7, 127.1, 125.0, 122.4, 120.2, 118.3, 65.6, 46.6. **HRMS (ESI)** calculated for $C_{21}H_{14}Cl_2NO_3^-$ [M-H] $^-$ m/z 398.0345 found m/z 398.372.

9. Copies of NMR Spectra of Isolated Compounds

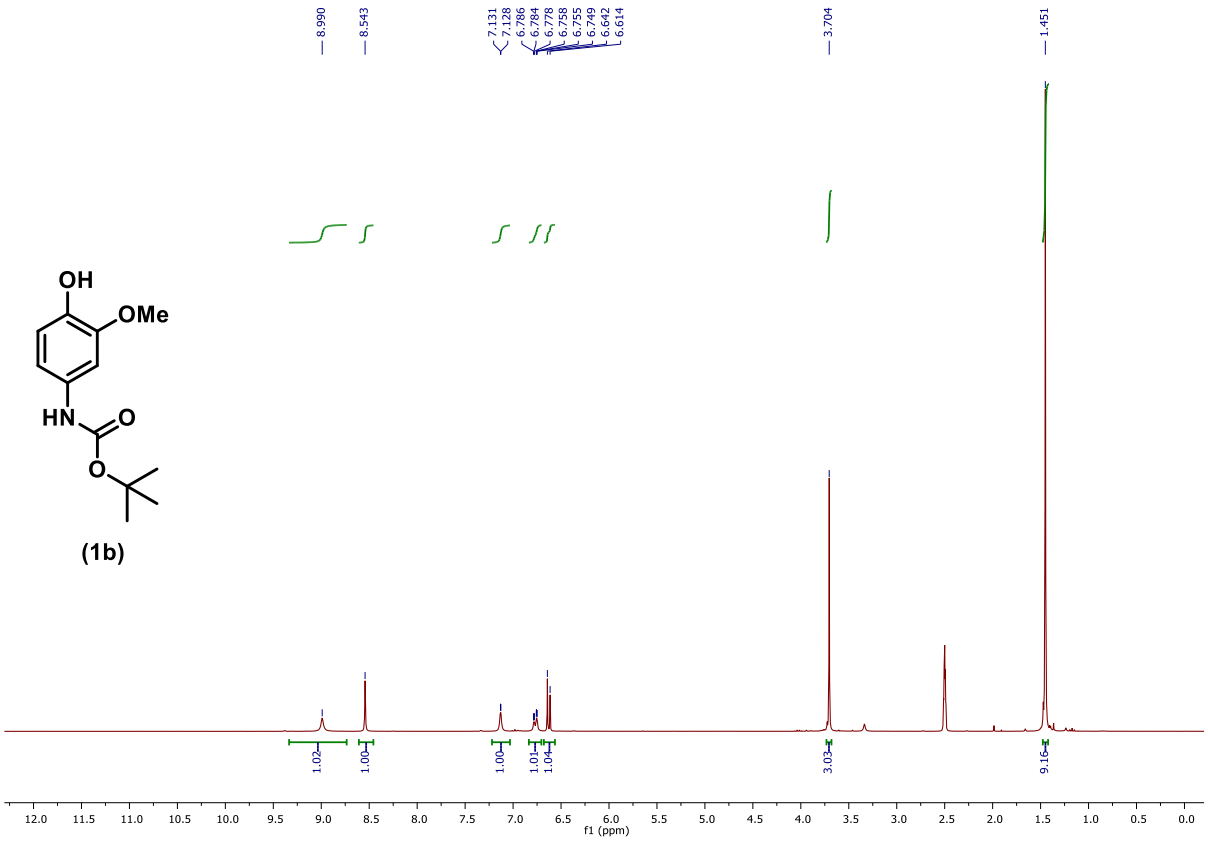
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **1a**



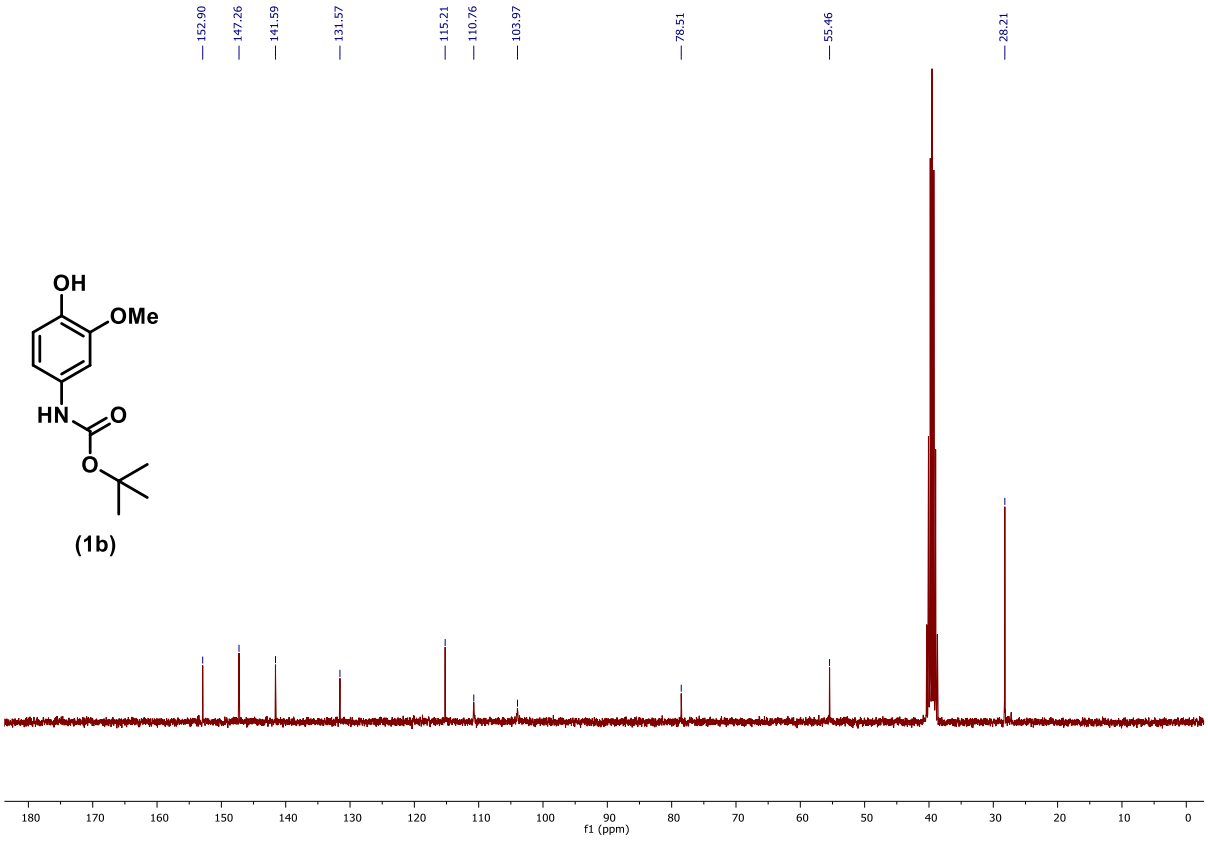
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **1a**



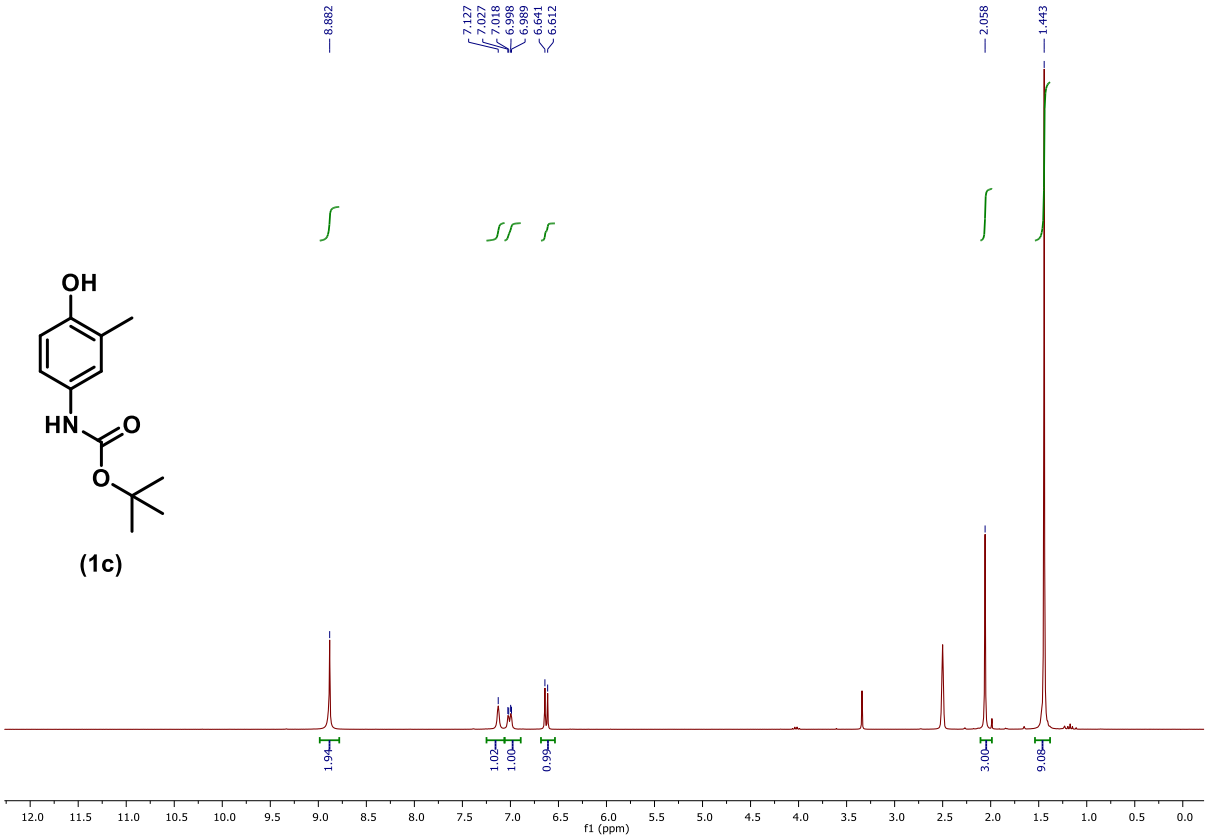
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **1b**



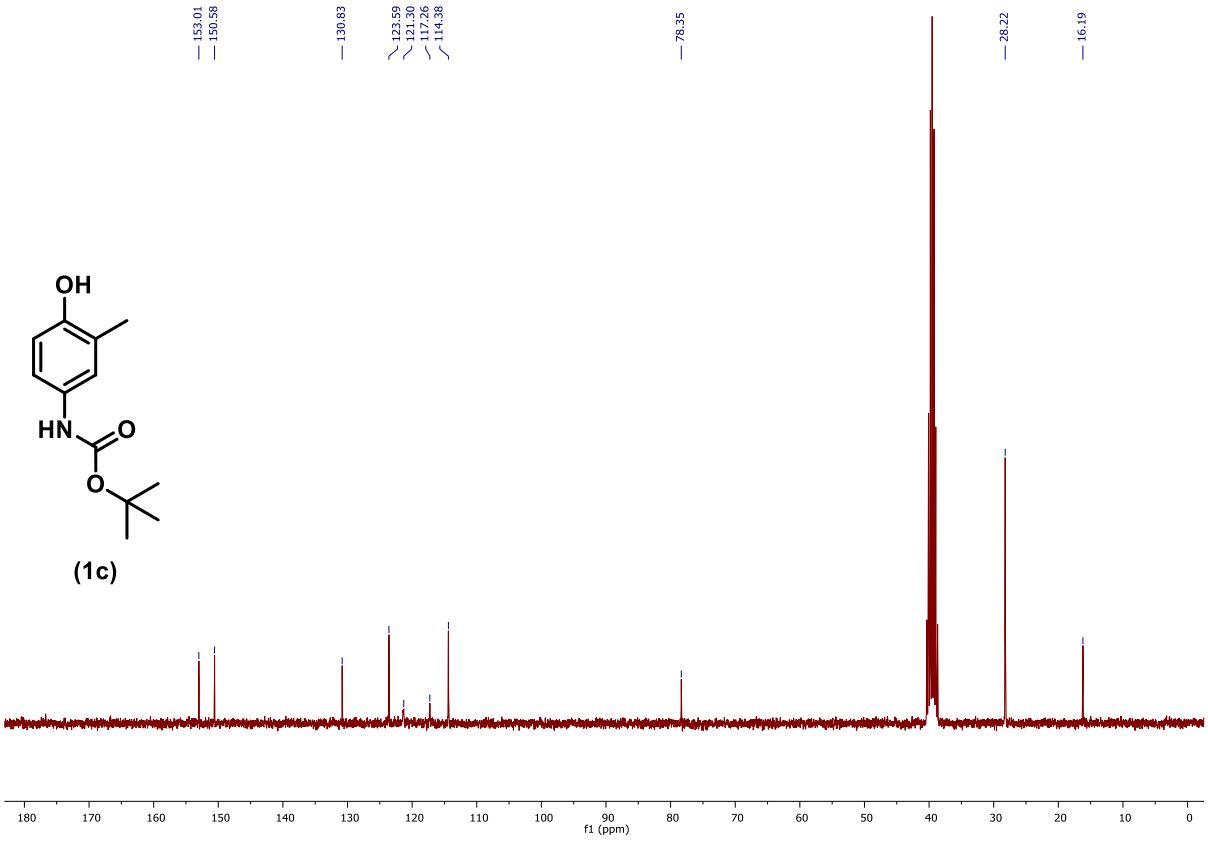
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **1b**



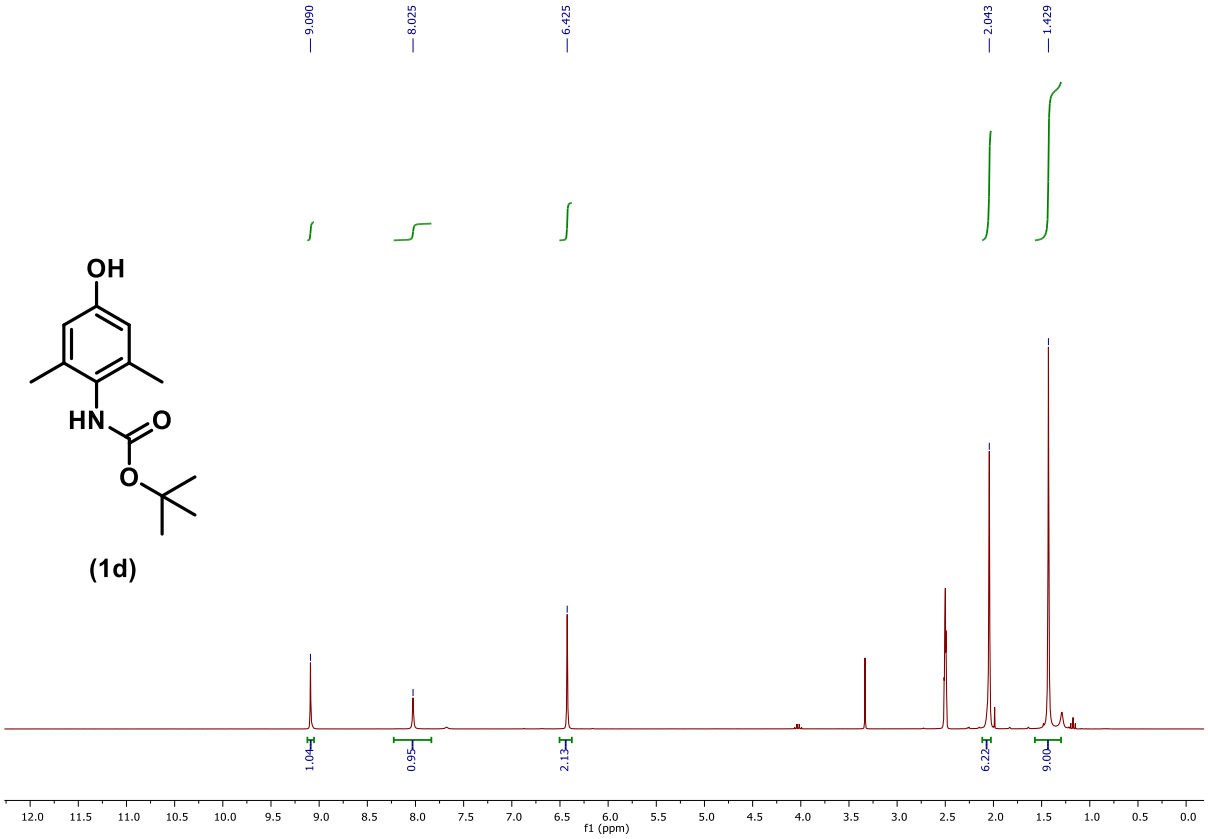
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **1c**



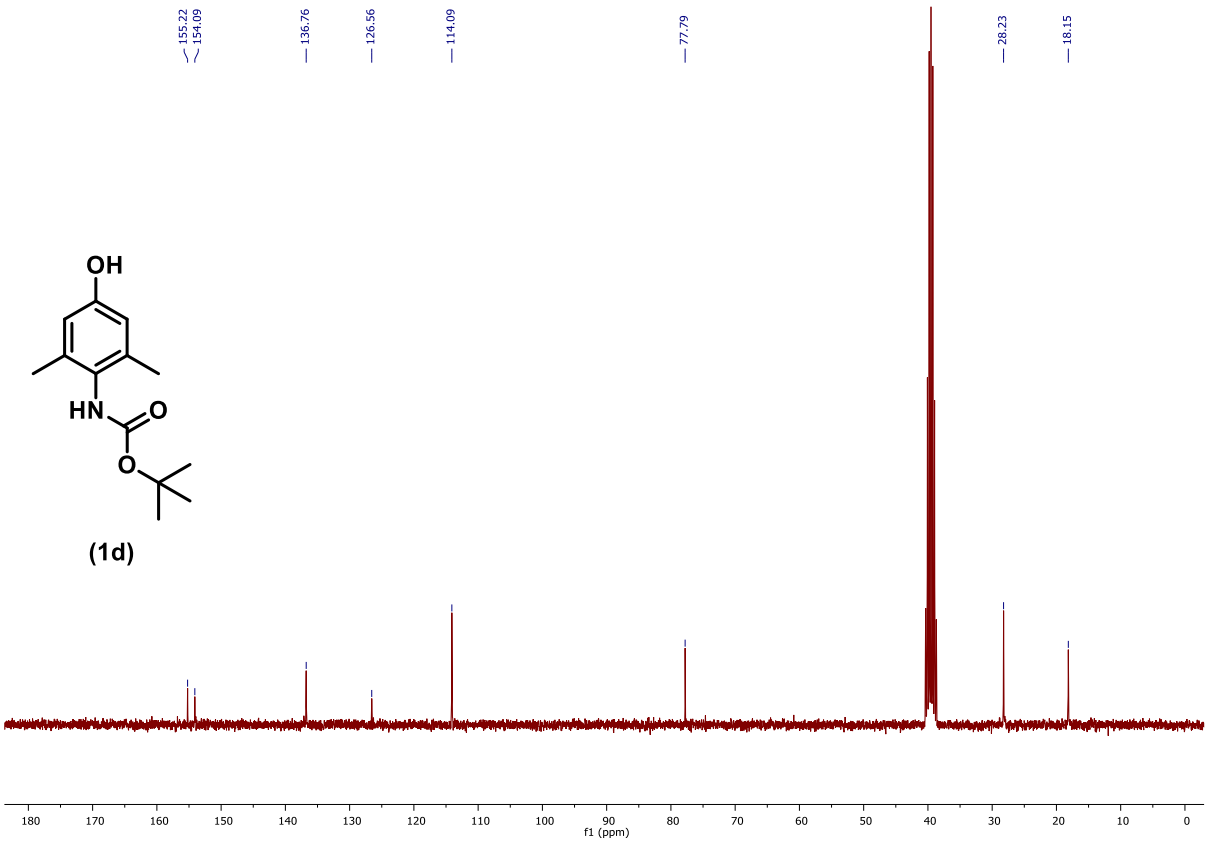
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **1c**



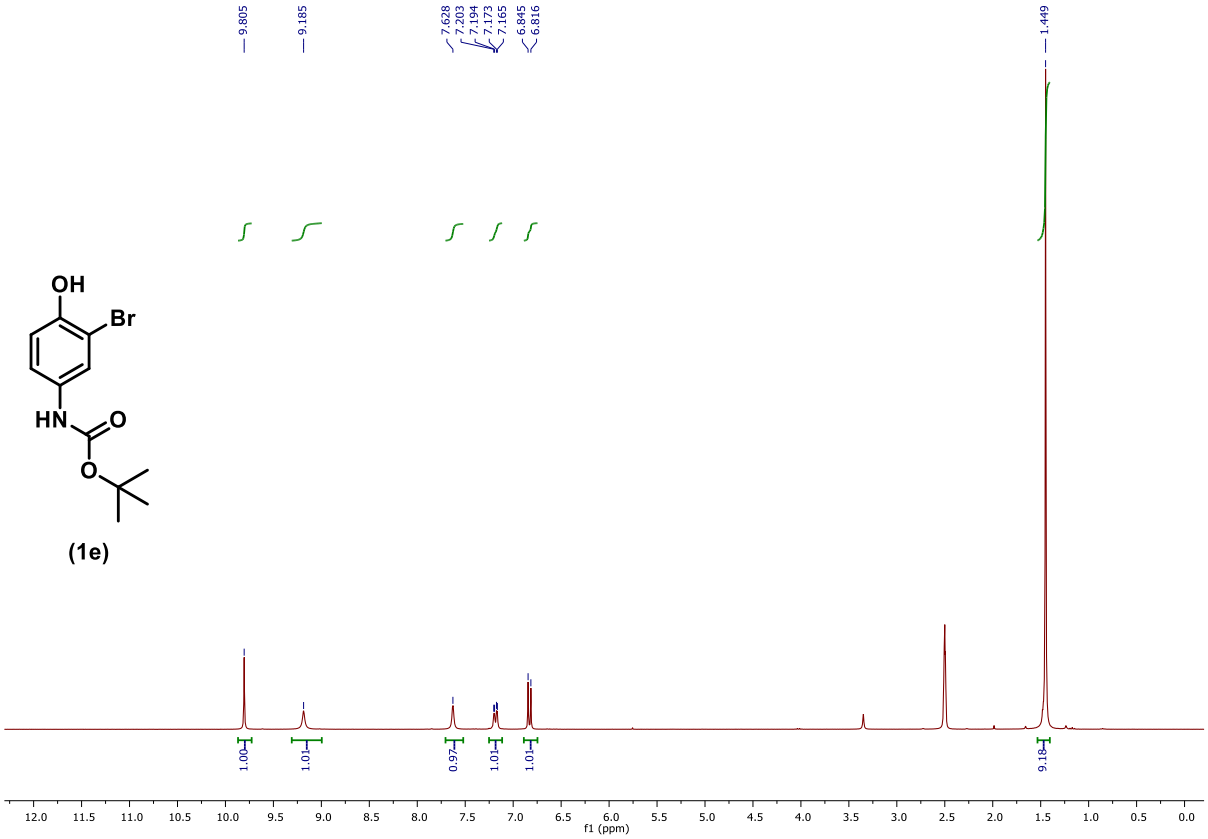
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **1d**



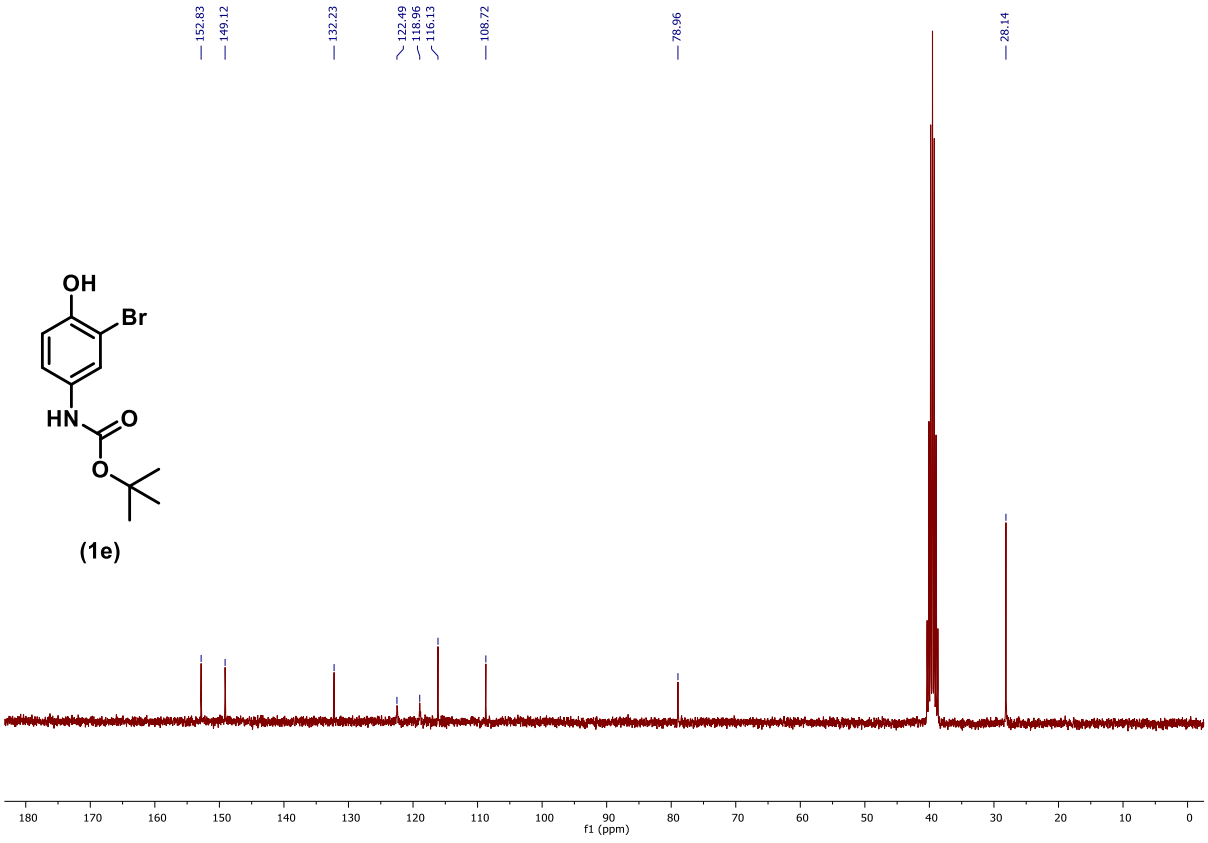
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **1d**



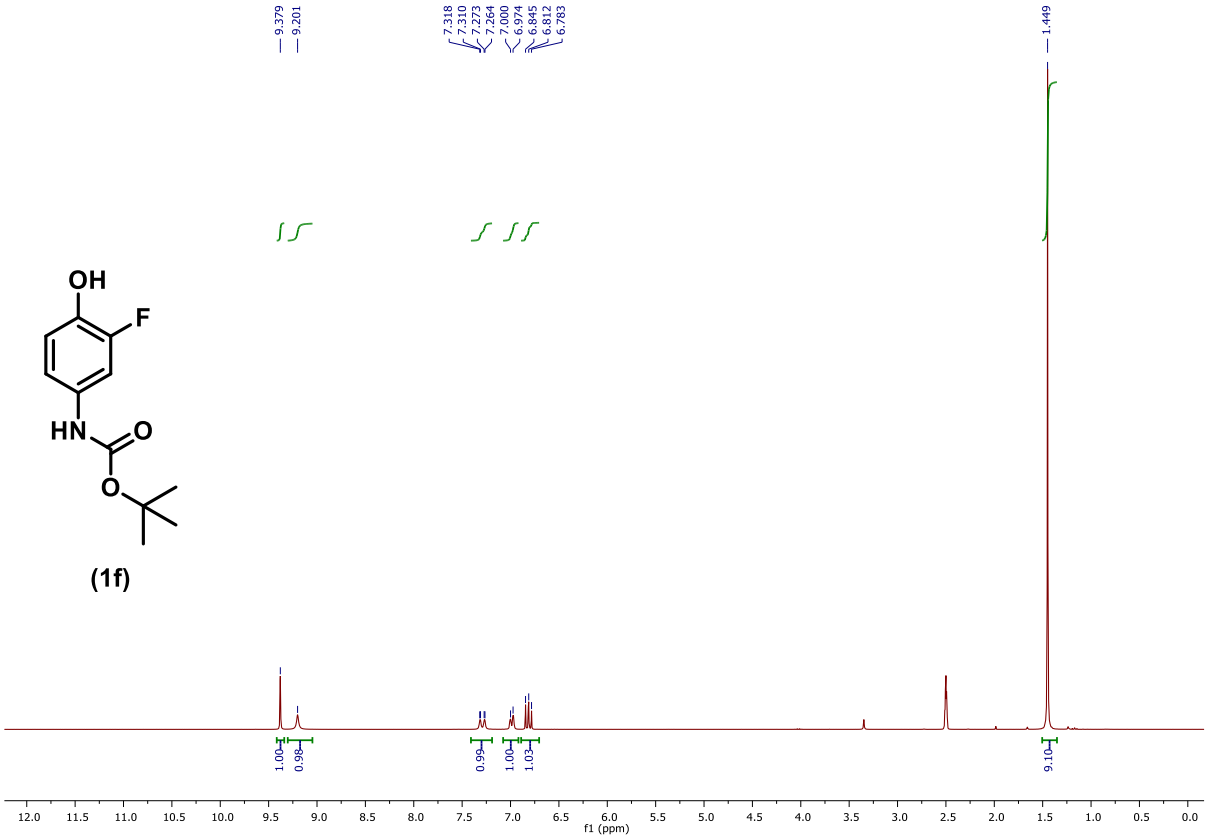
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **1e**



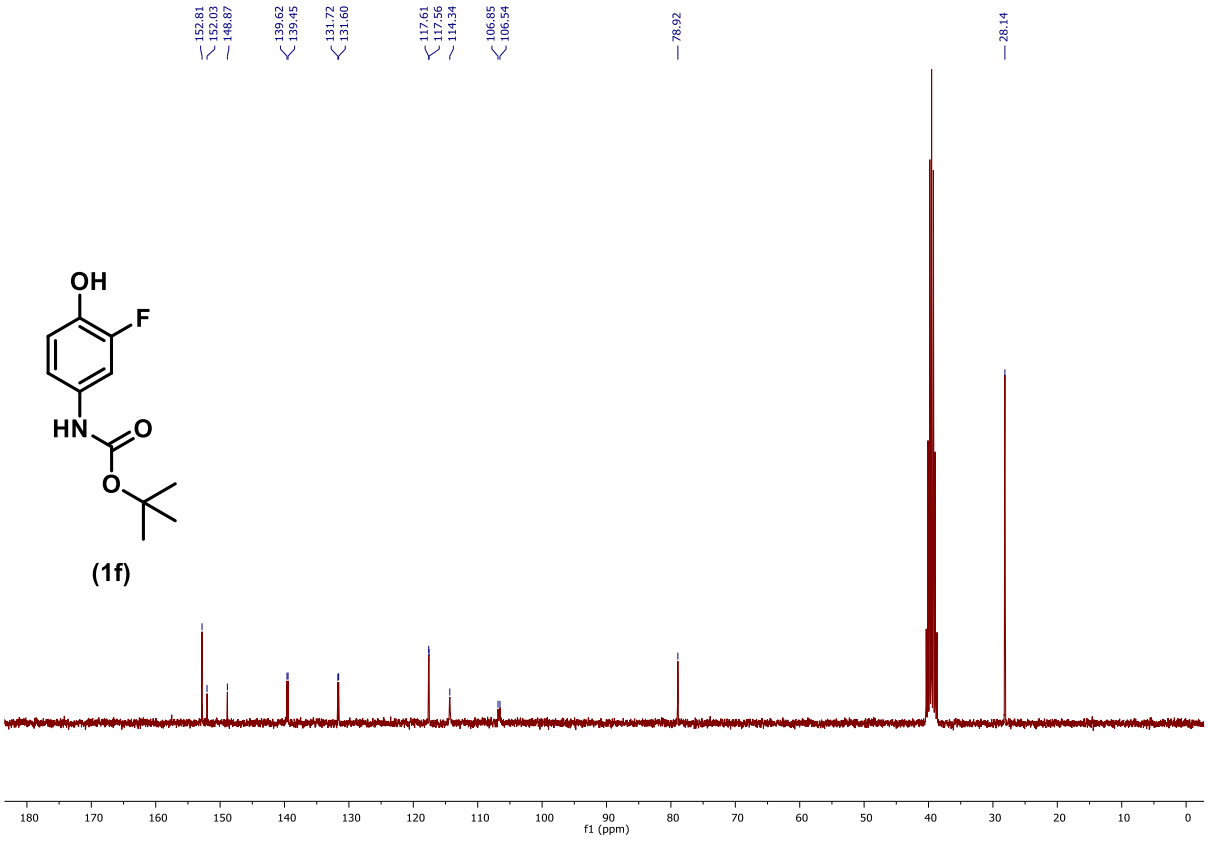
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **1e**



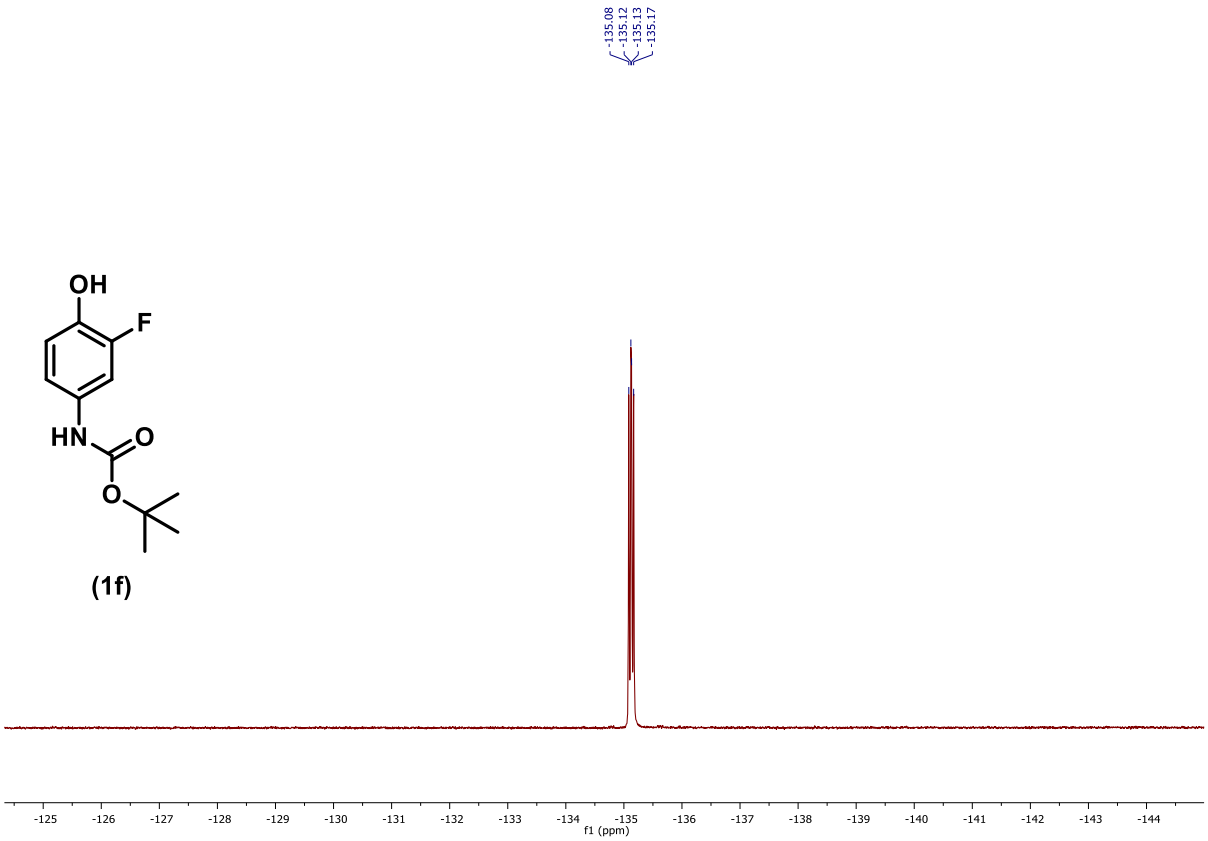
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **1f**



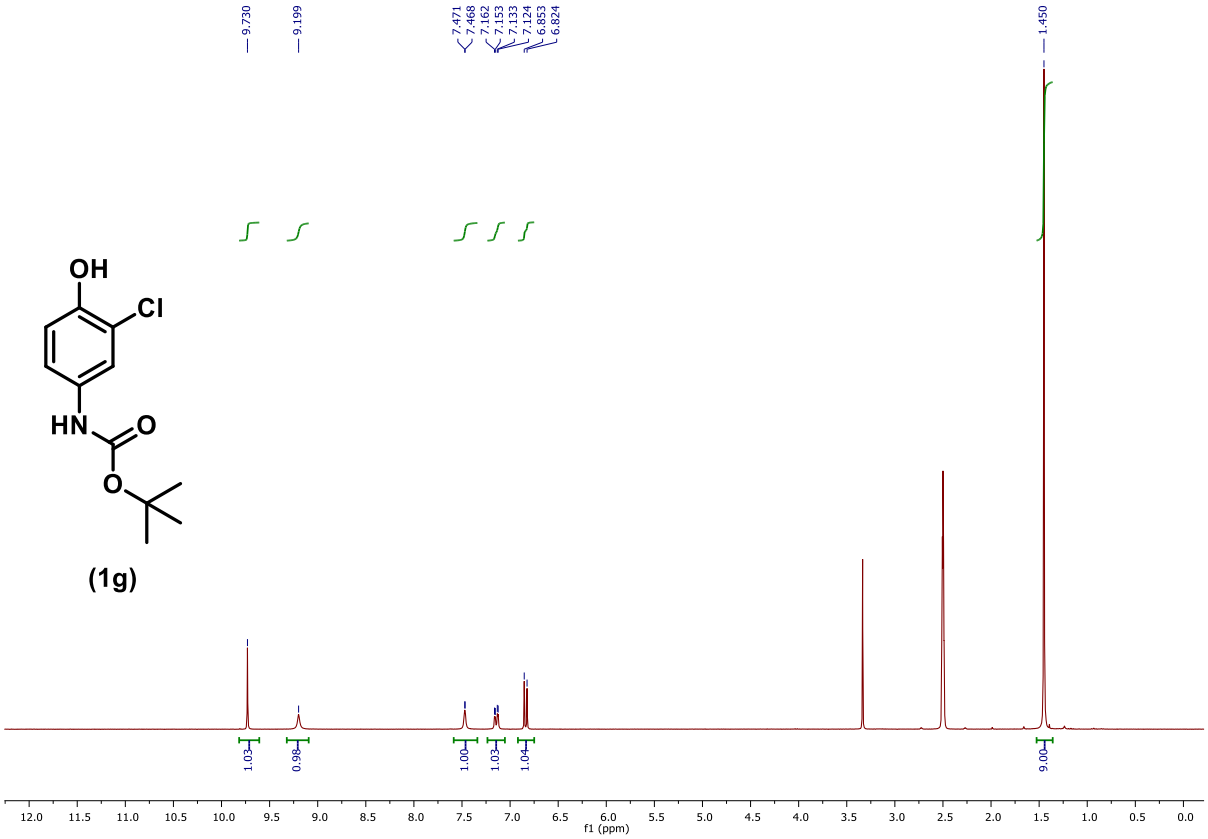
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **1f**



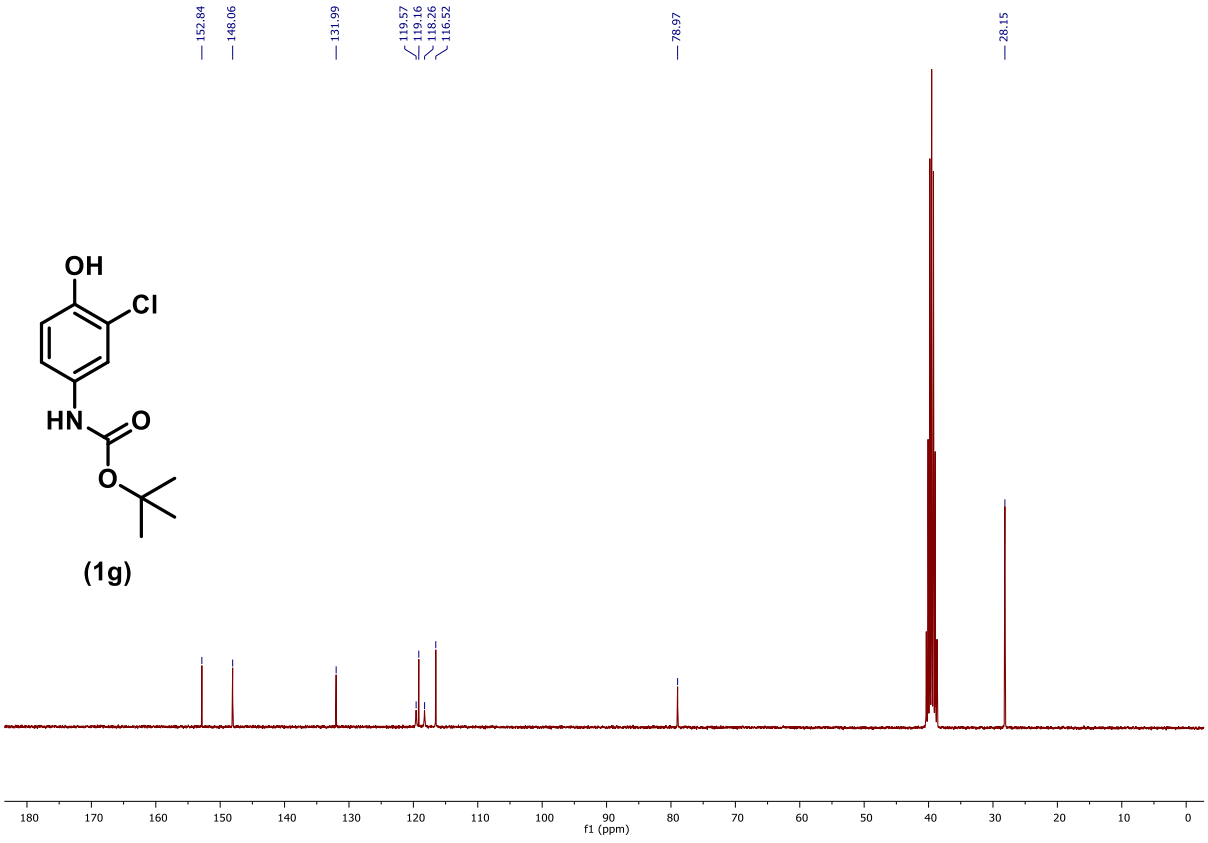
^{19}F NMR spectrum (282 MHz, DMSO-d_6) of **1f**



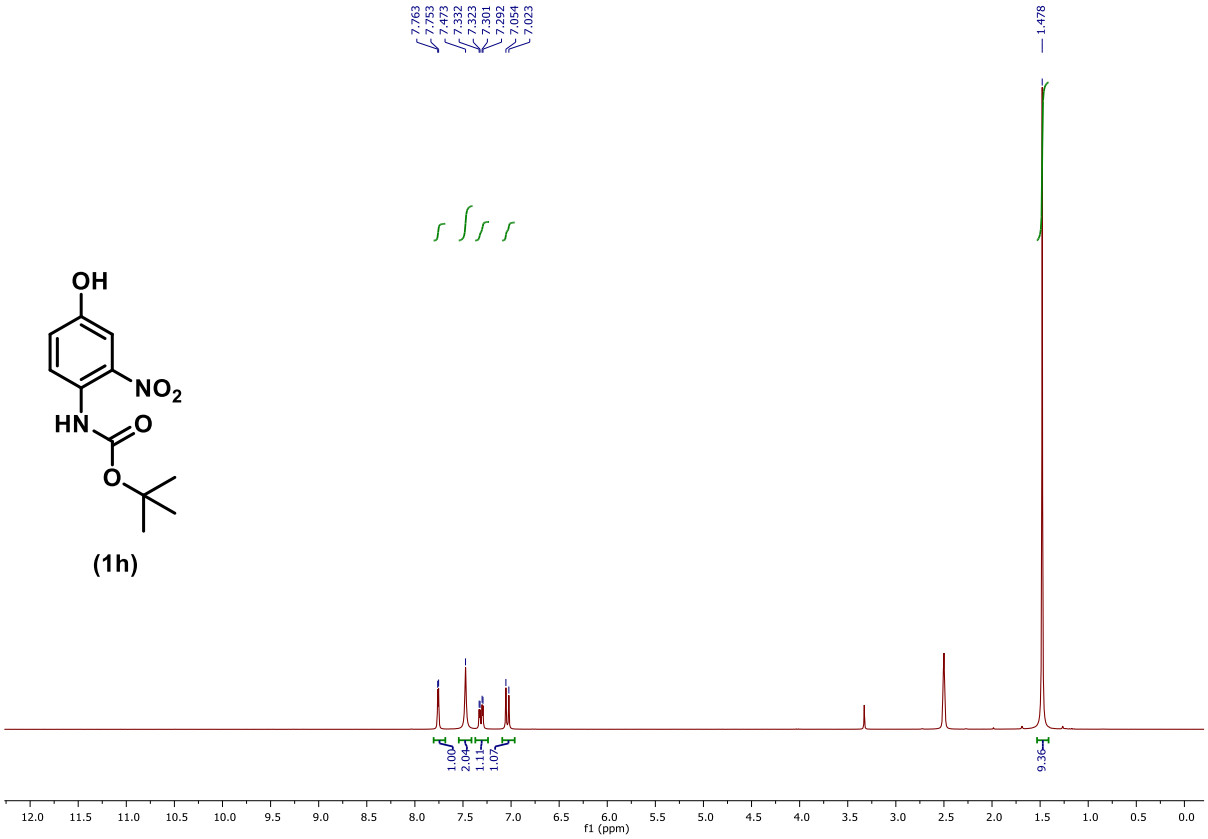
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **1g**



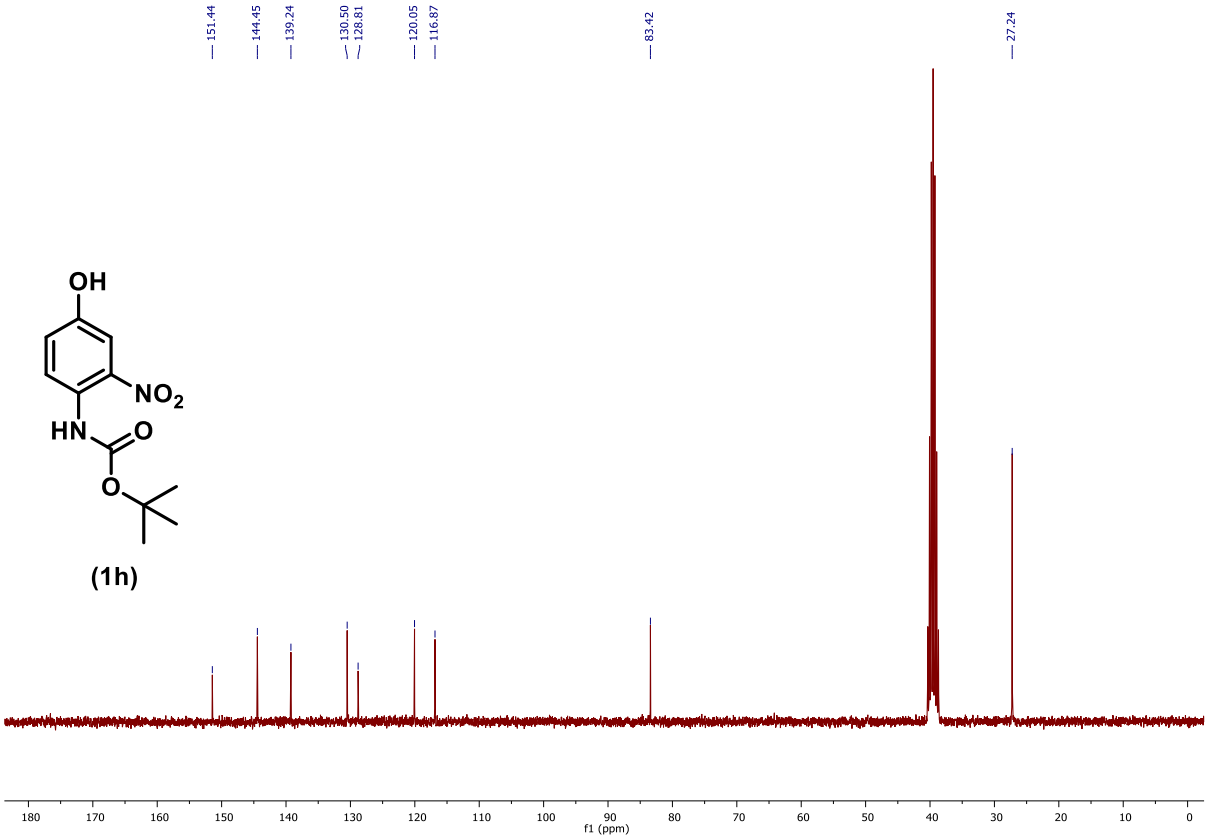
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **1g**



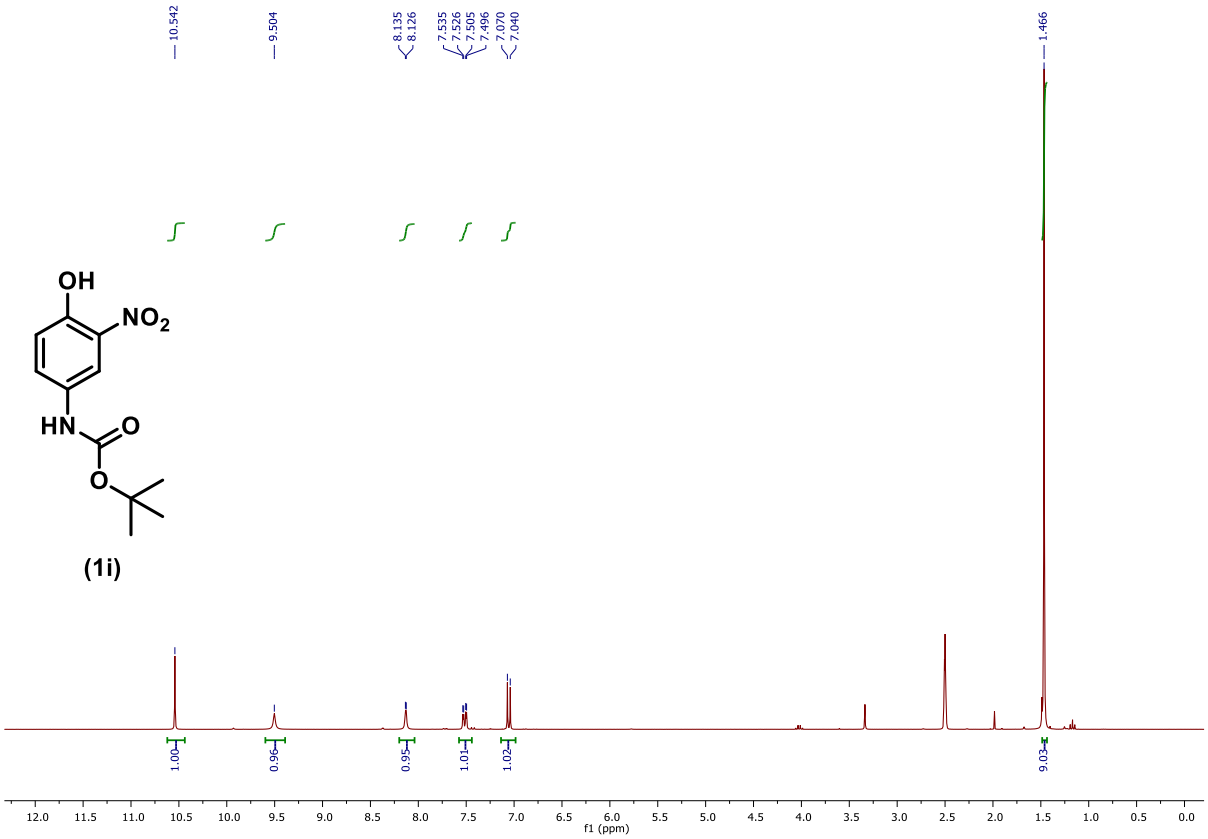
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **1h**



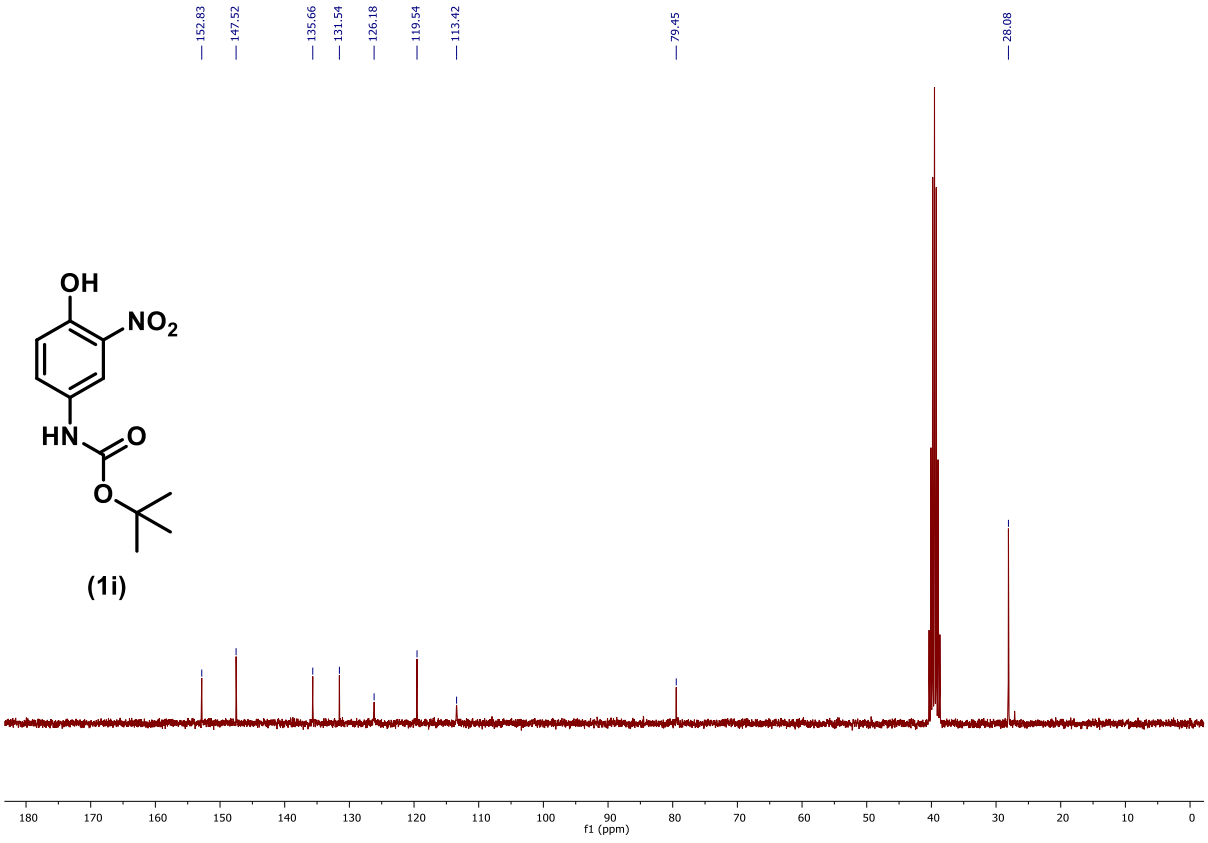
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **1h**



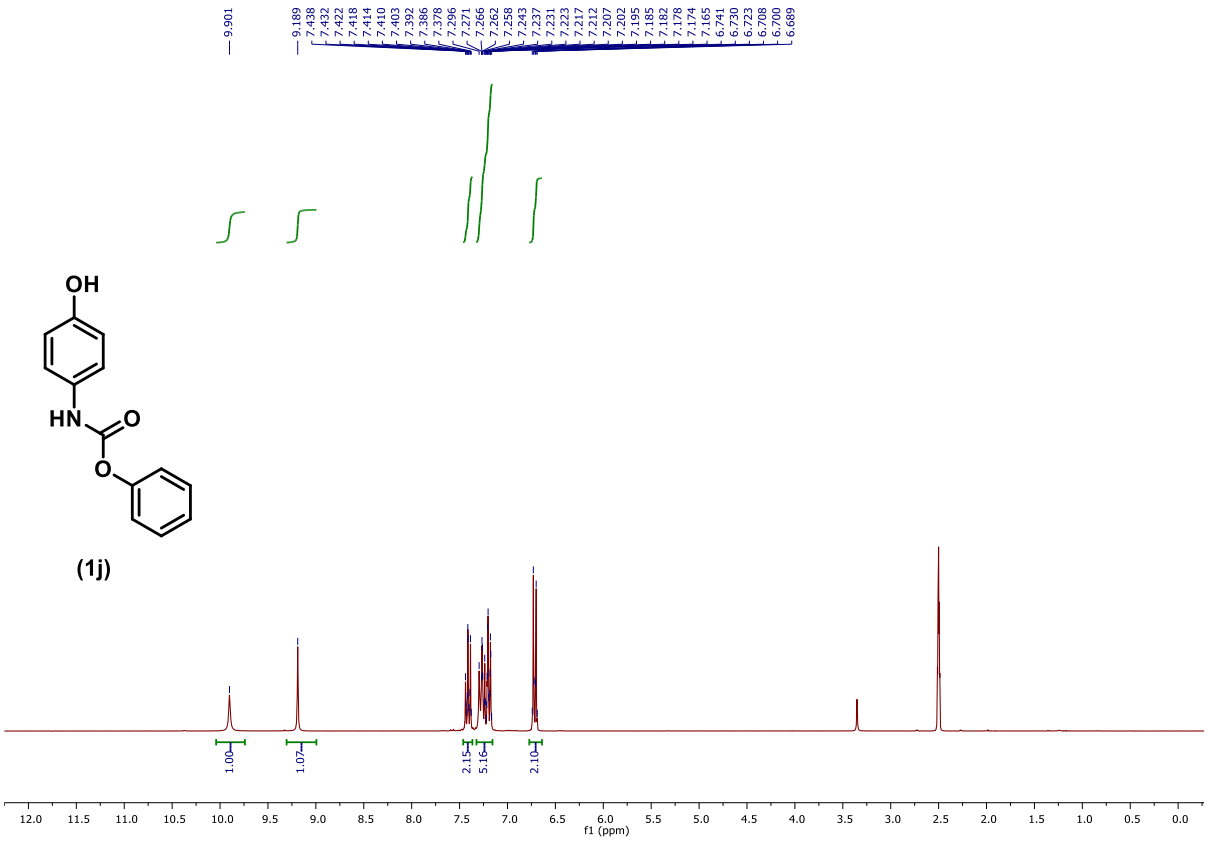
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **1i**



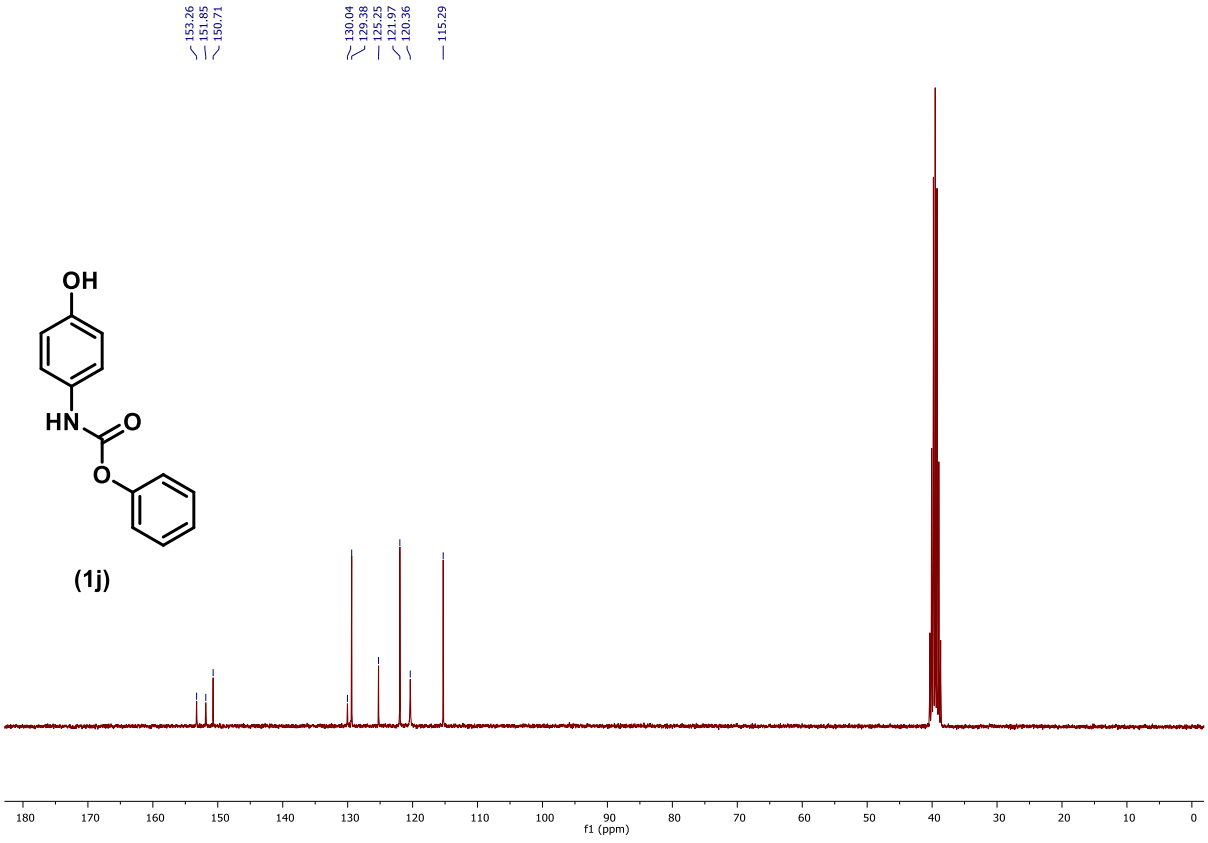
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **1i**



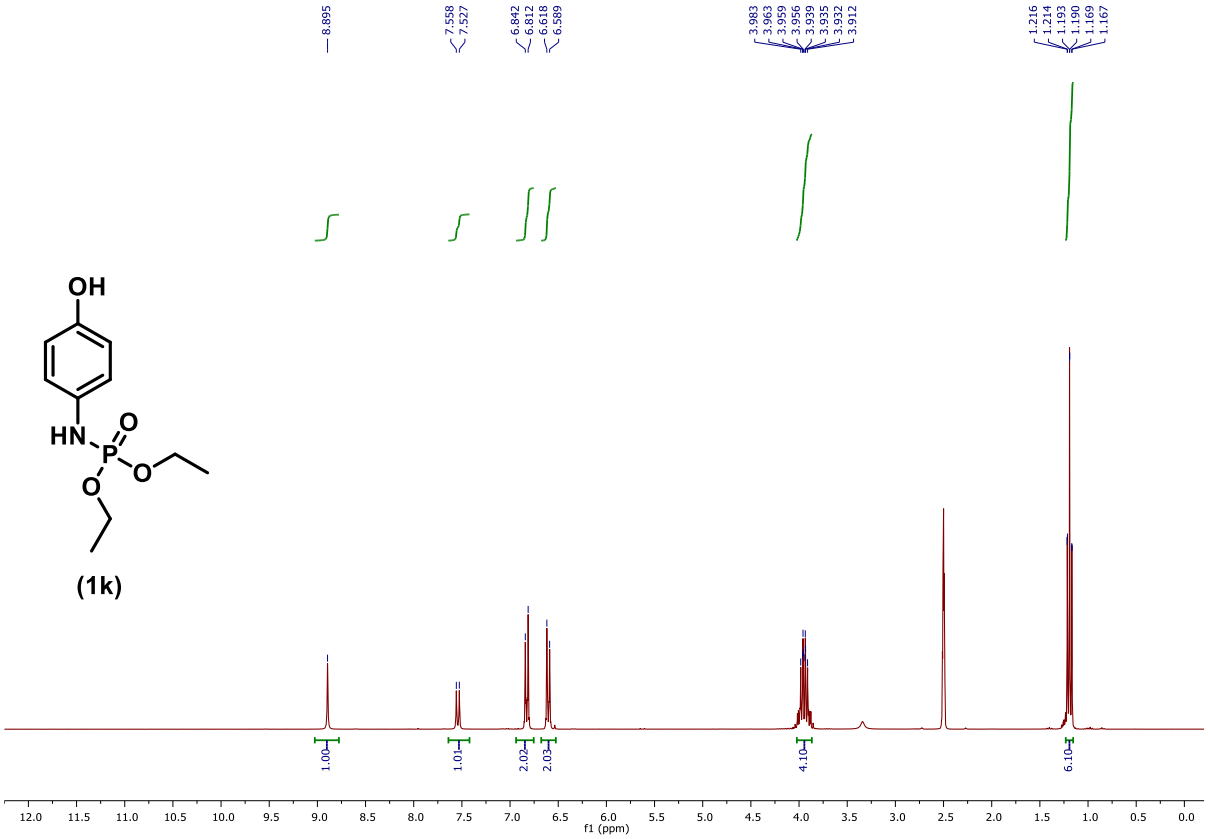
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **1j**



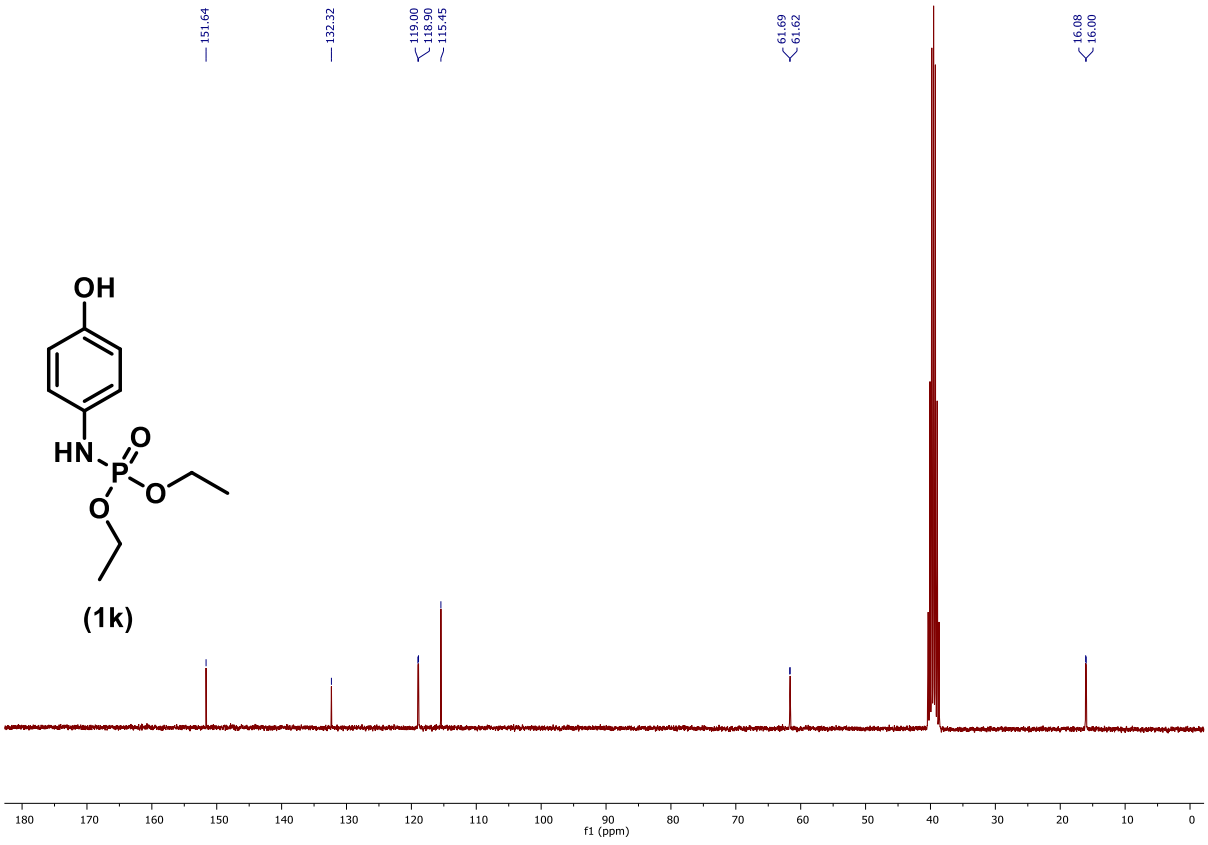
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **1j**



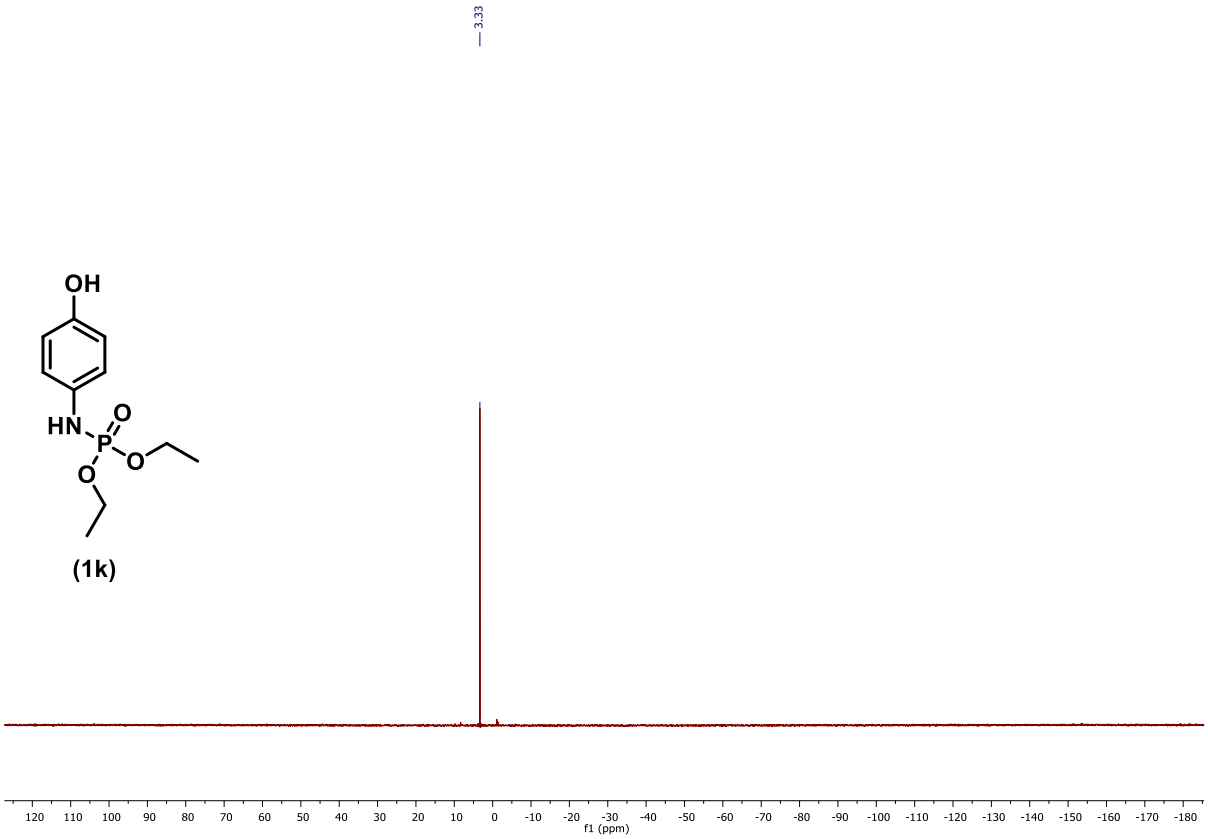
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **1k**



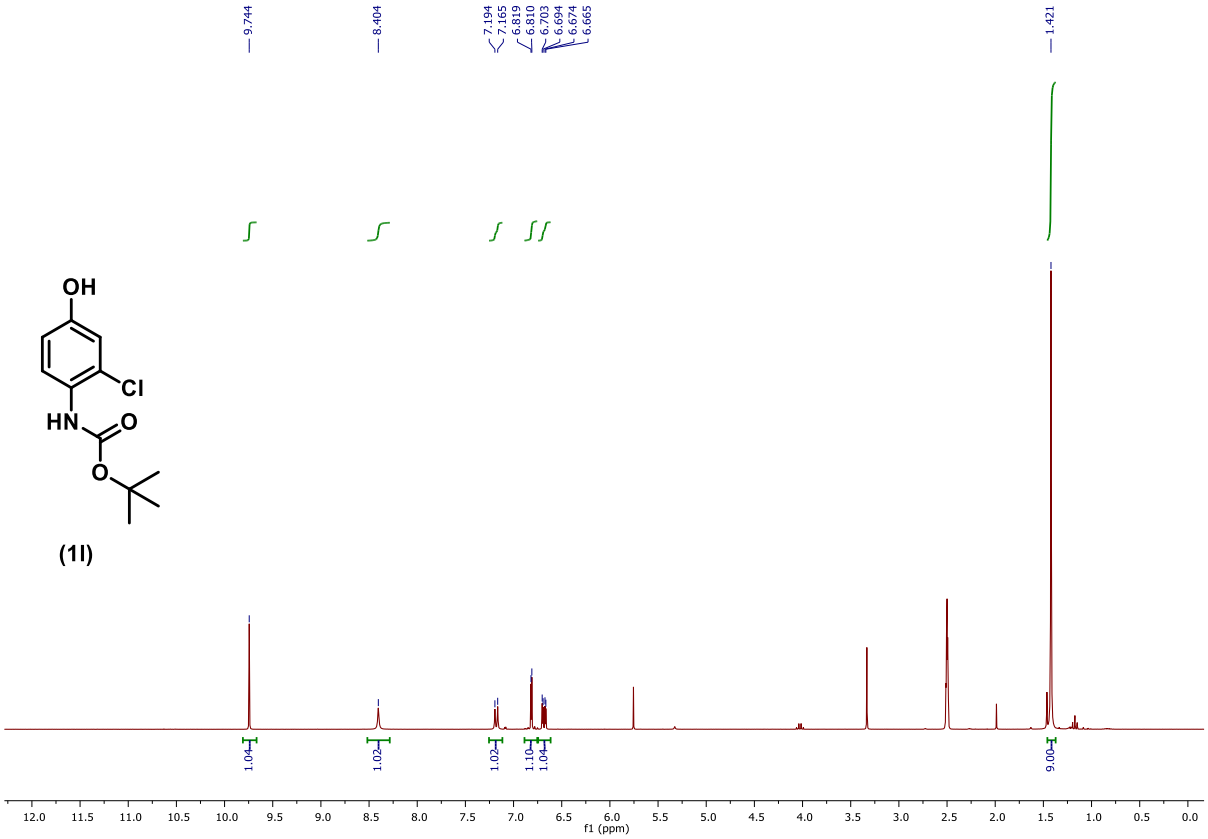
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **1k**



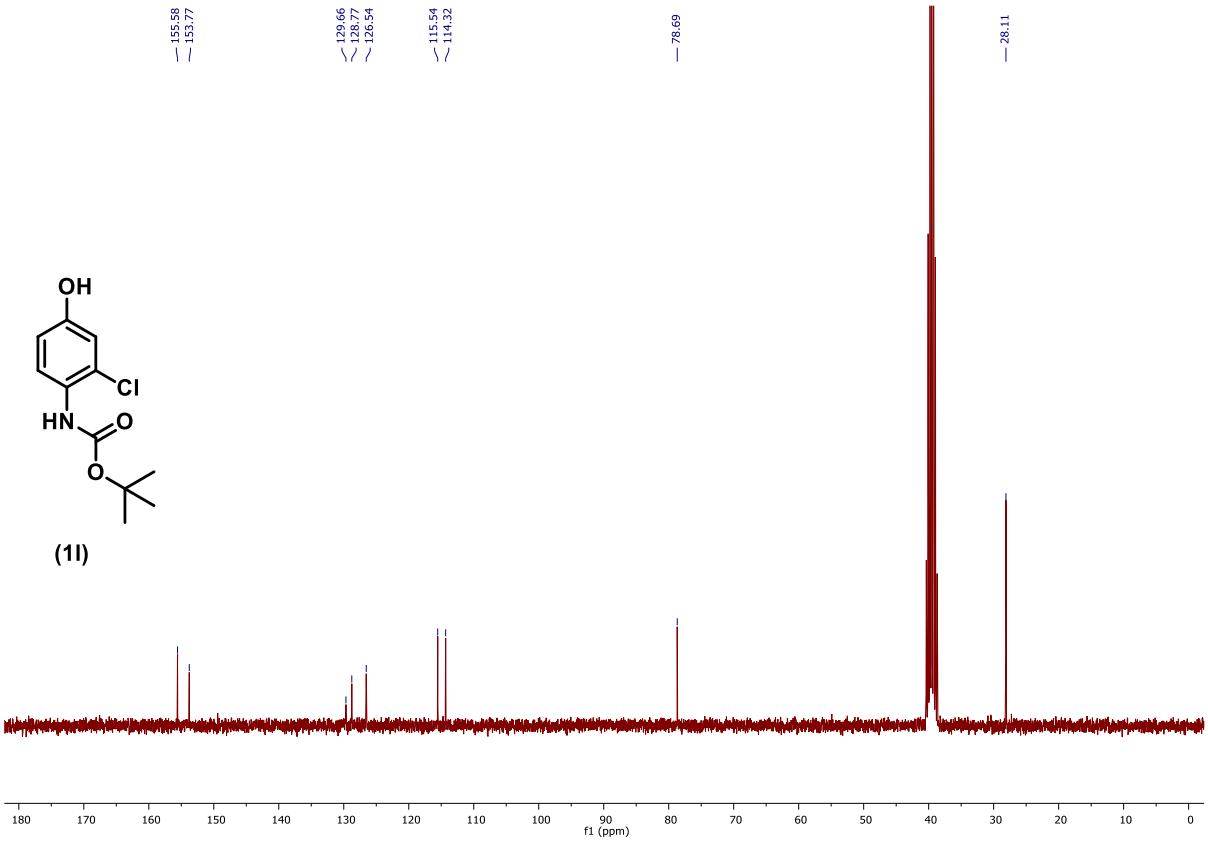
^{31}P NMR spectrum (121 MHz, DMSO-d_6) of **1k**



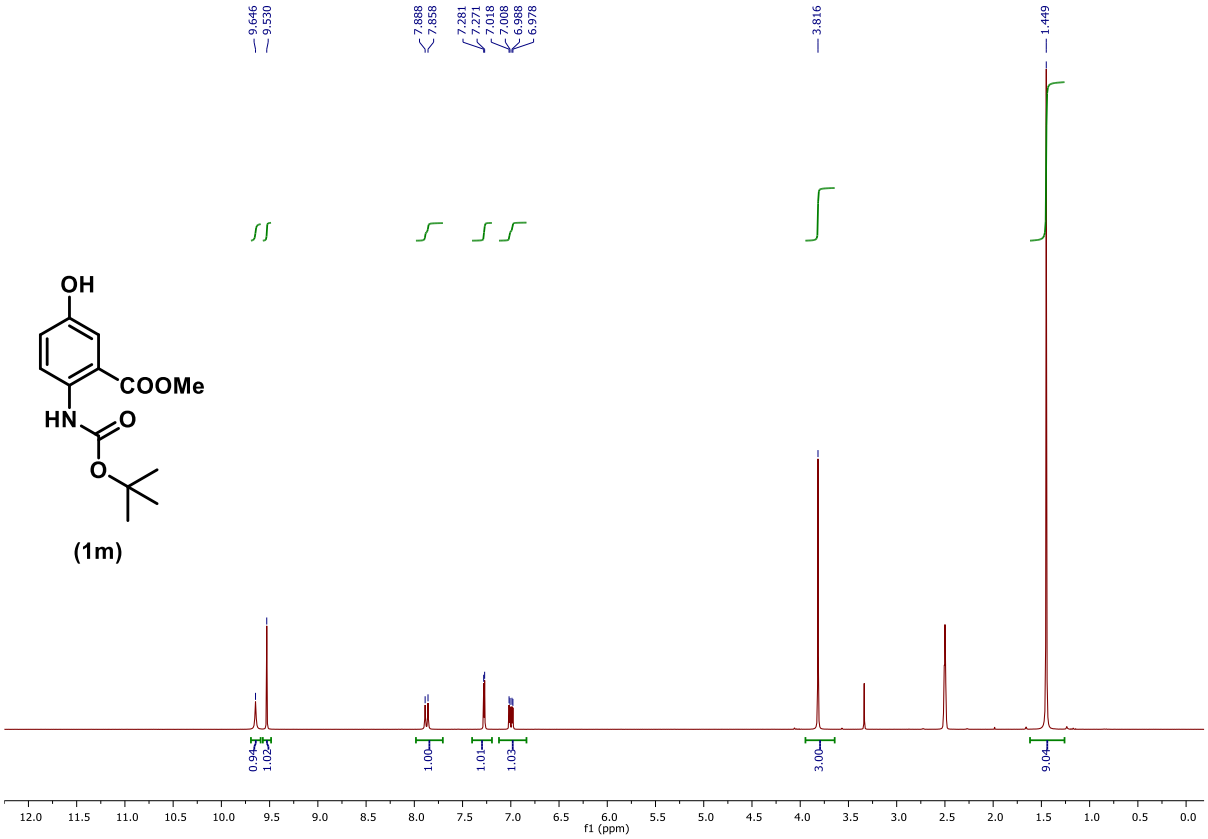
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **1l**



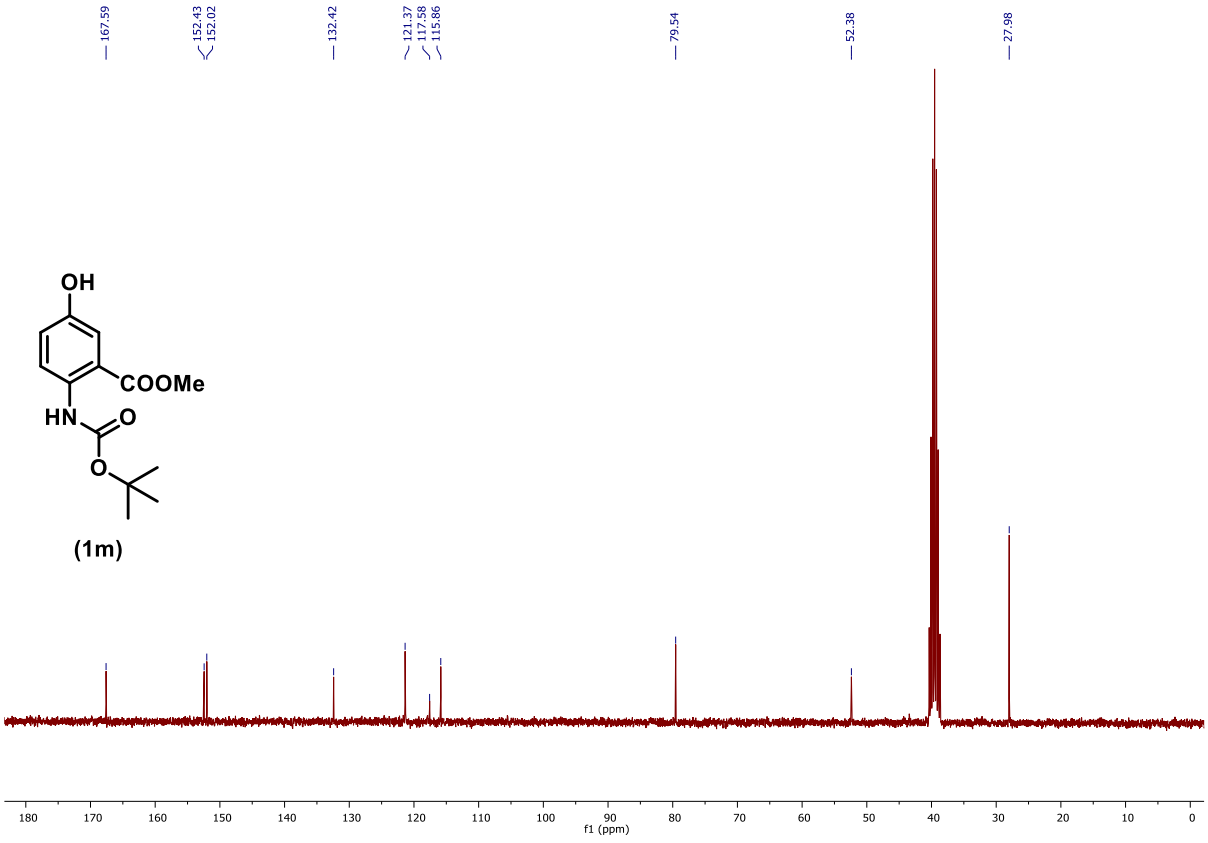
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **1l**



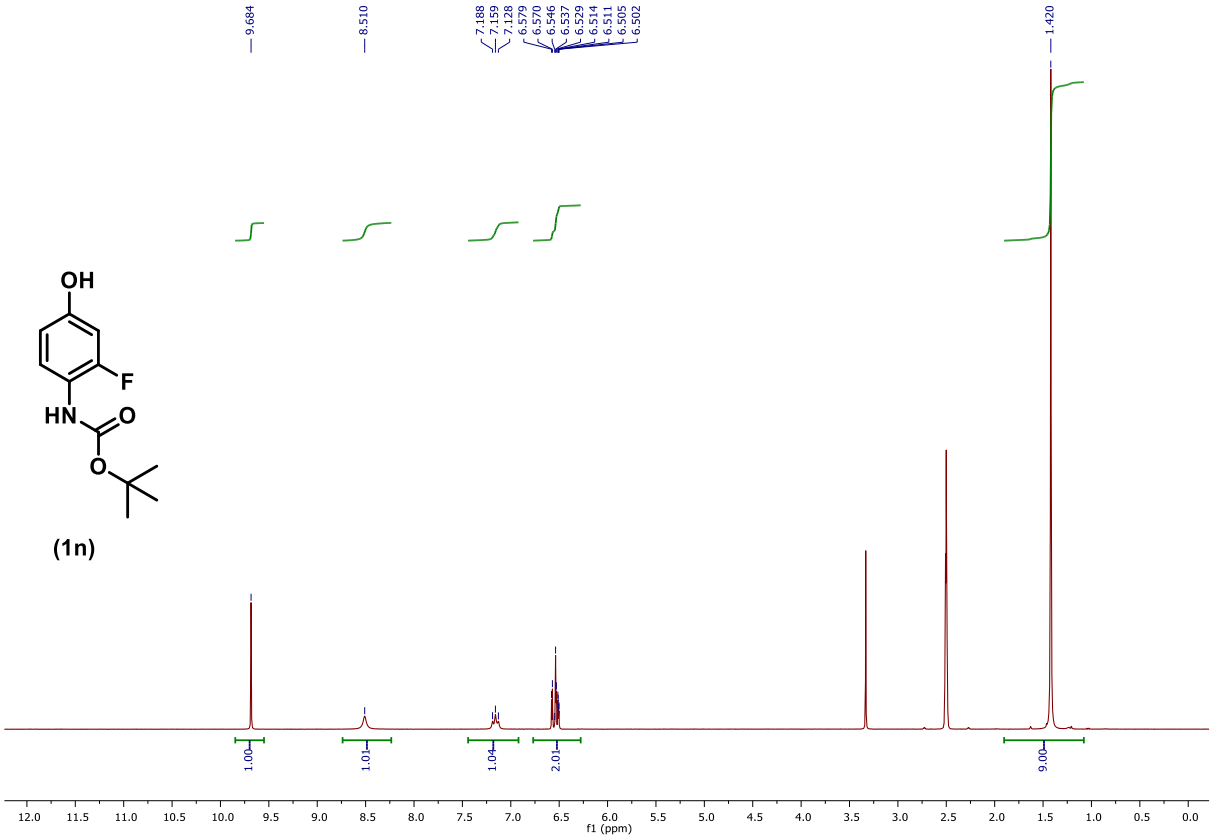
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **1m**



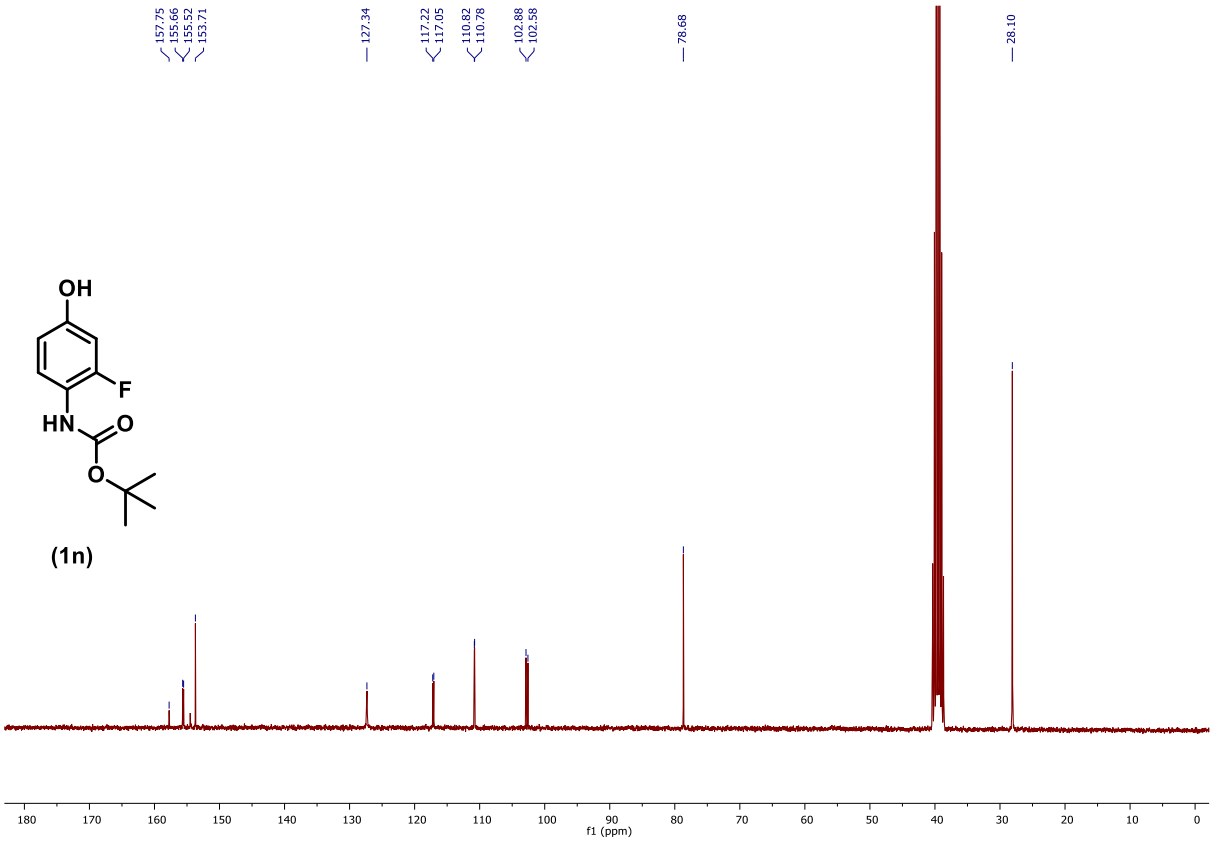
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **1m**



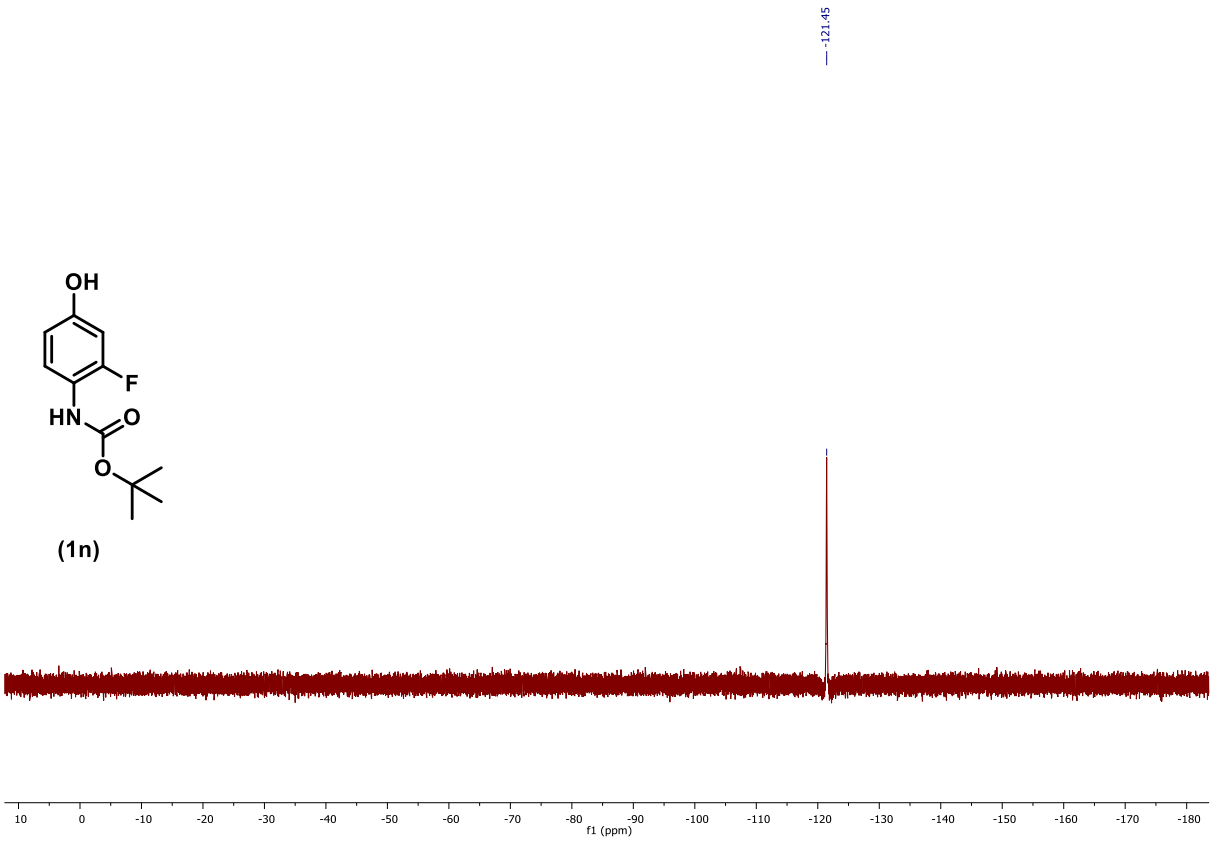
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **1n**



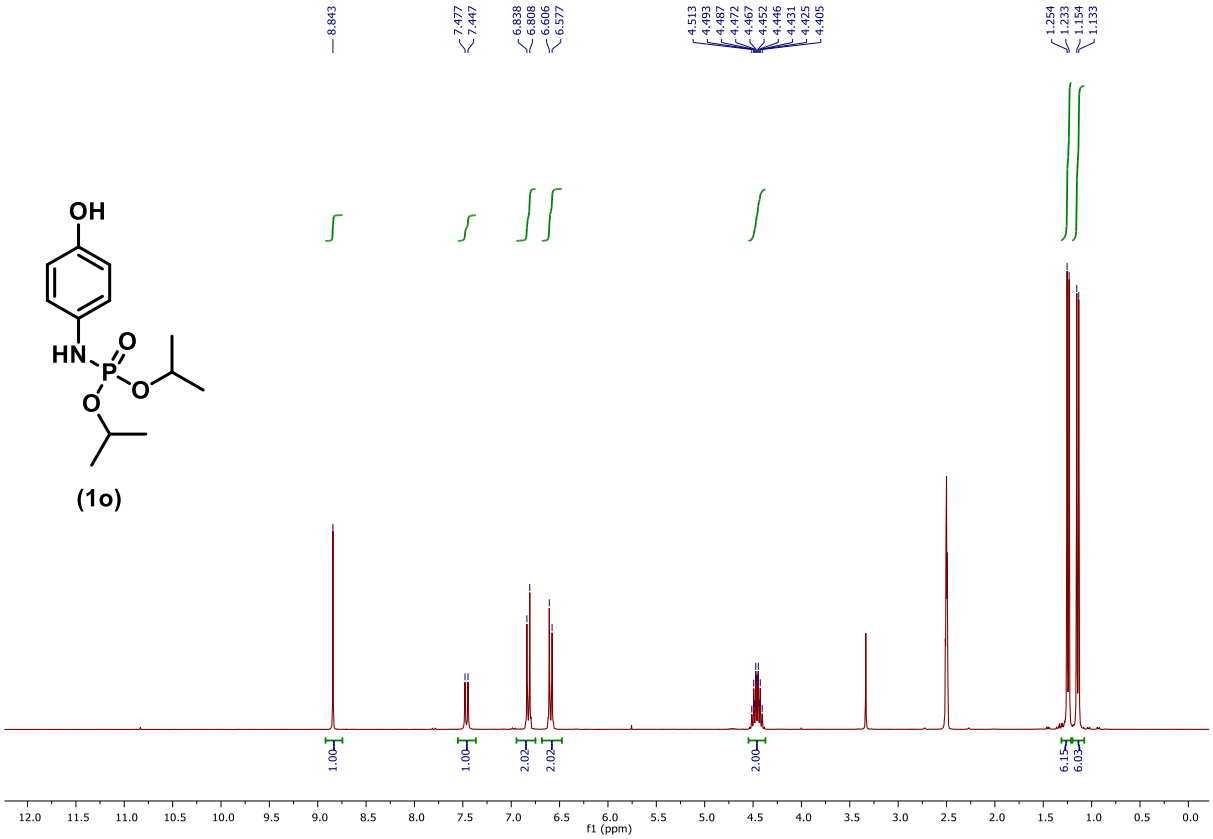
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **1n**



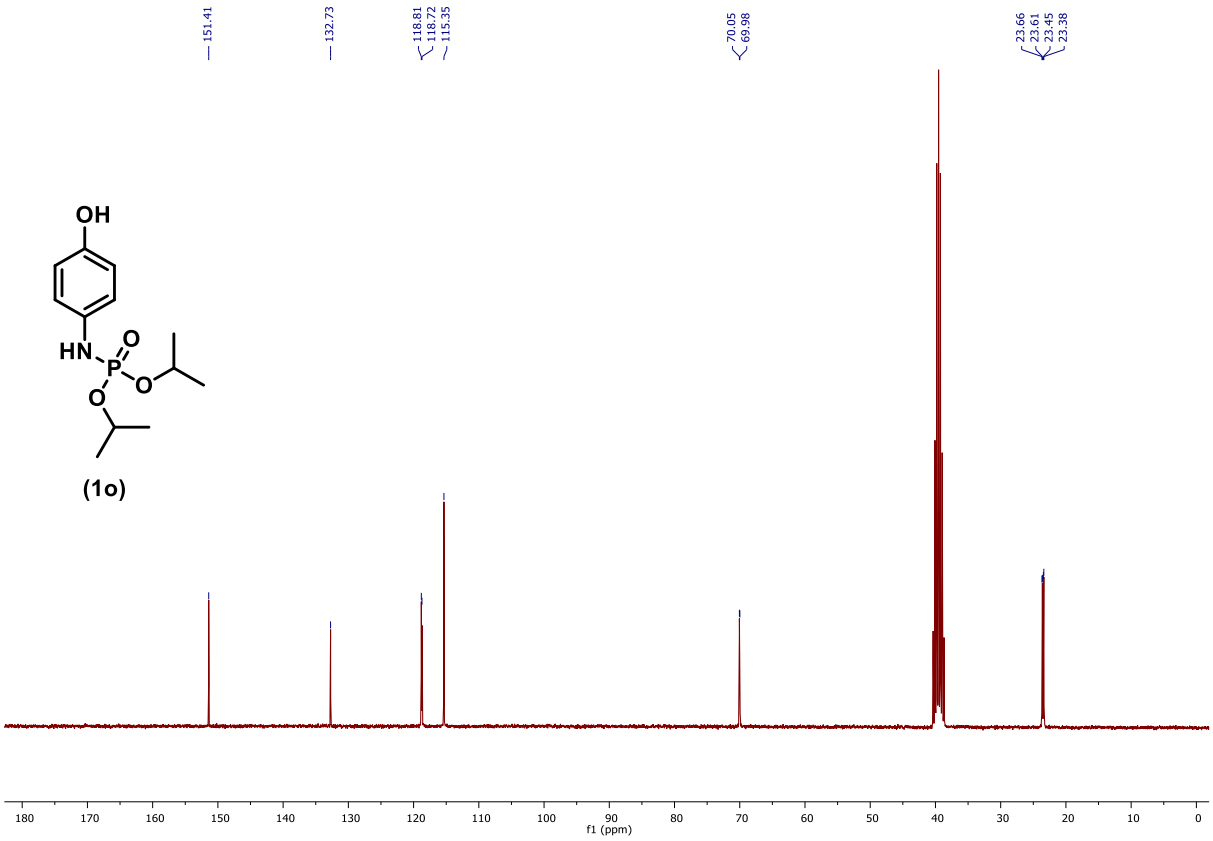
^{19}F NMR spectrum (282 MHz, DMSO-d_6) of **1n**



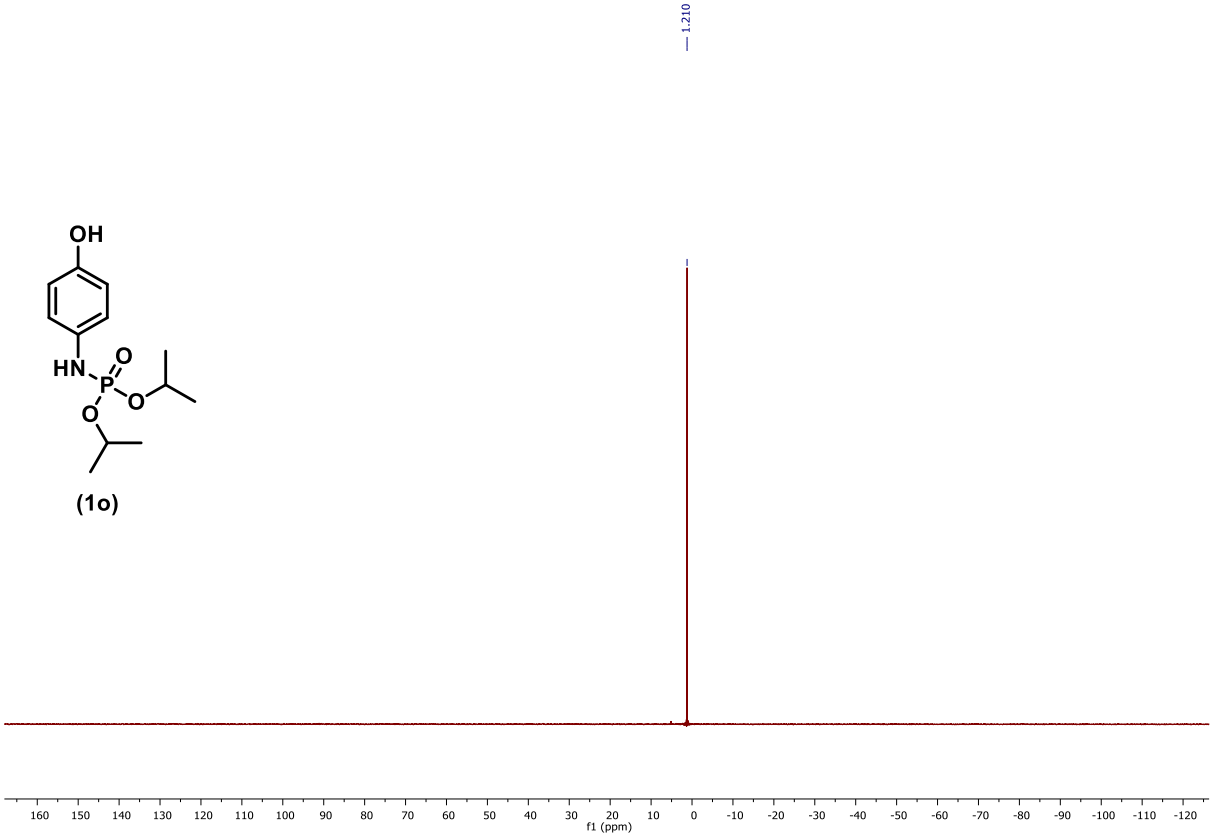
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **1o**



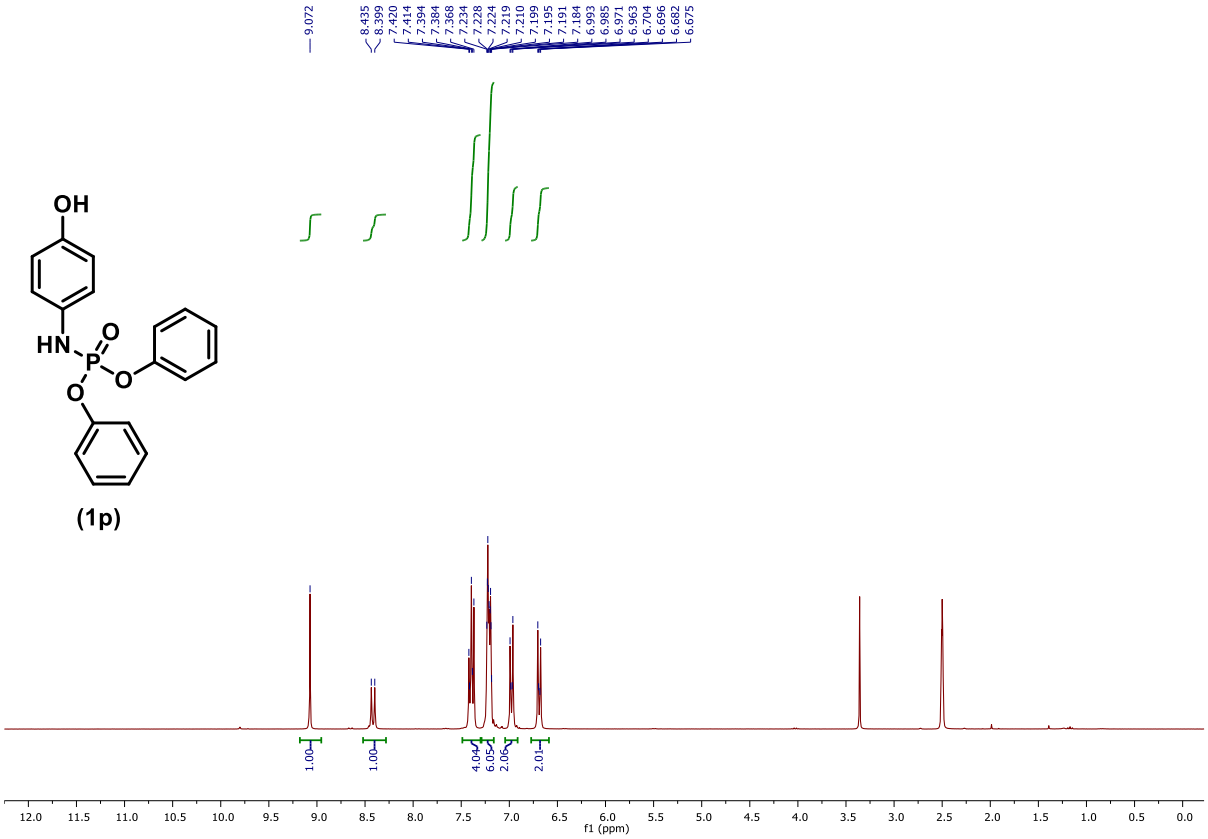
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **1o**



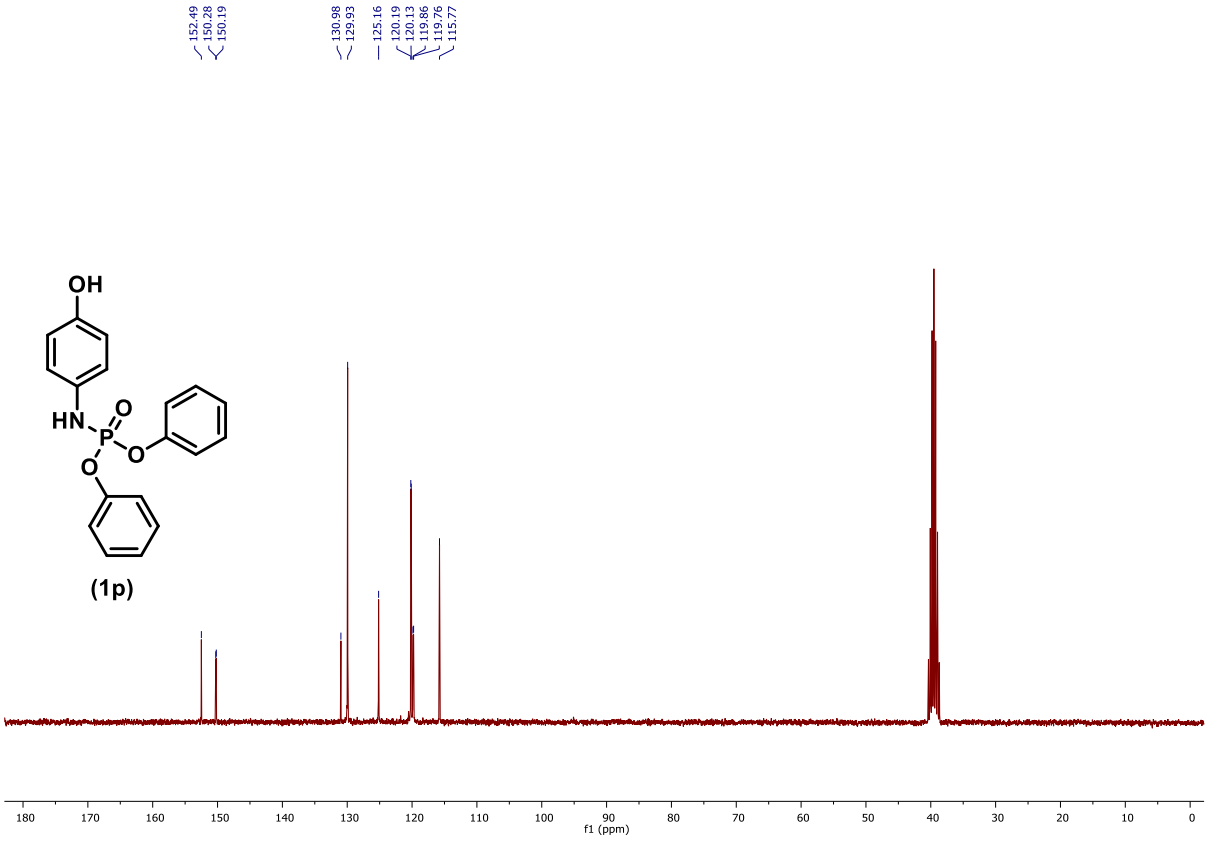
^{31}P NMR spectrum (121 MHz, DMSO-d_6) of **1o**



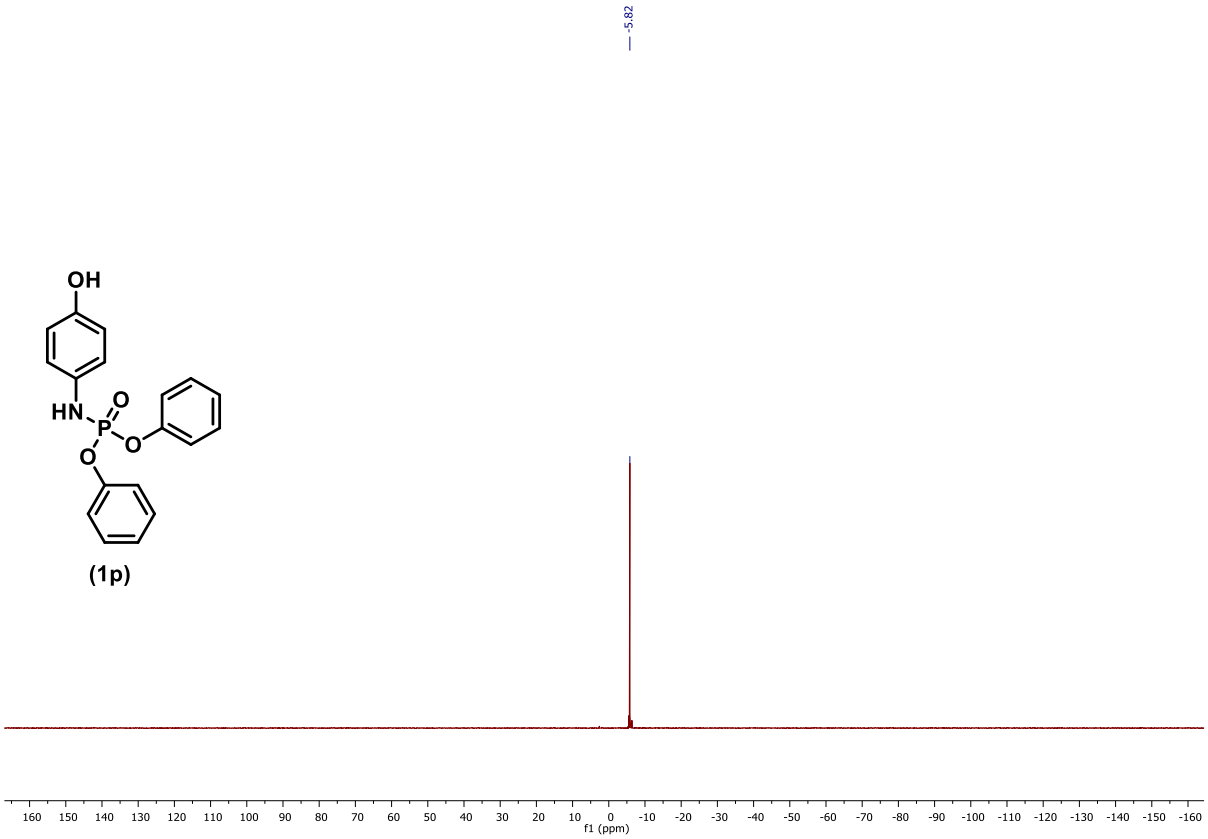
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **1p**



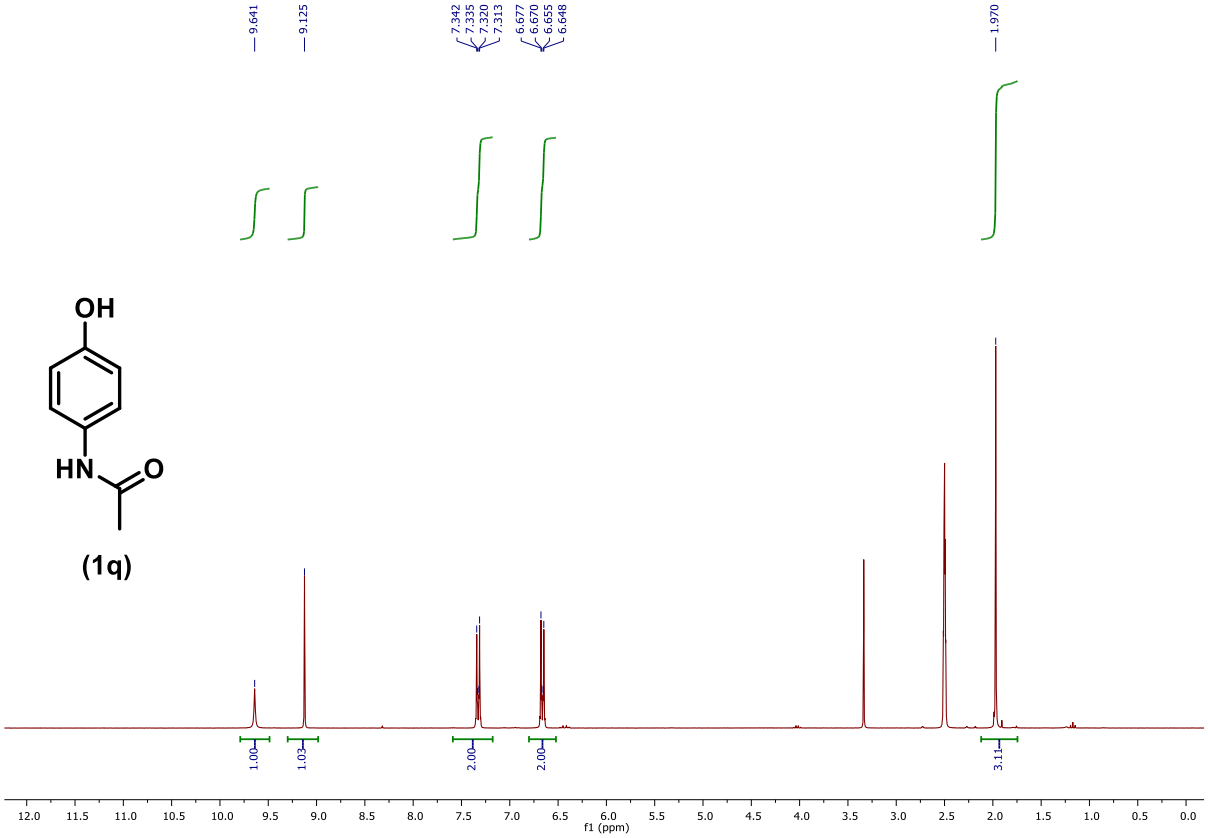
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **1p**



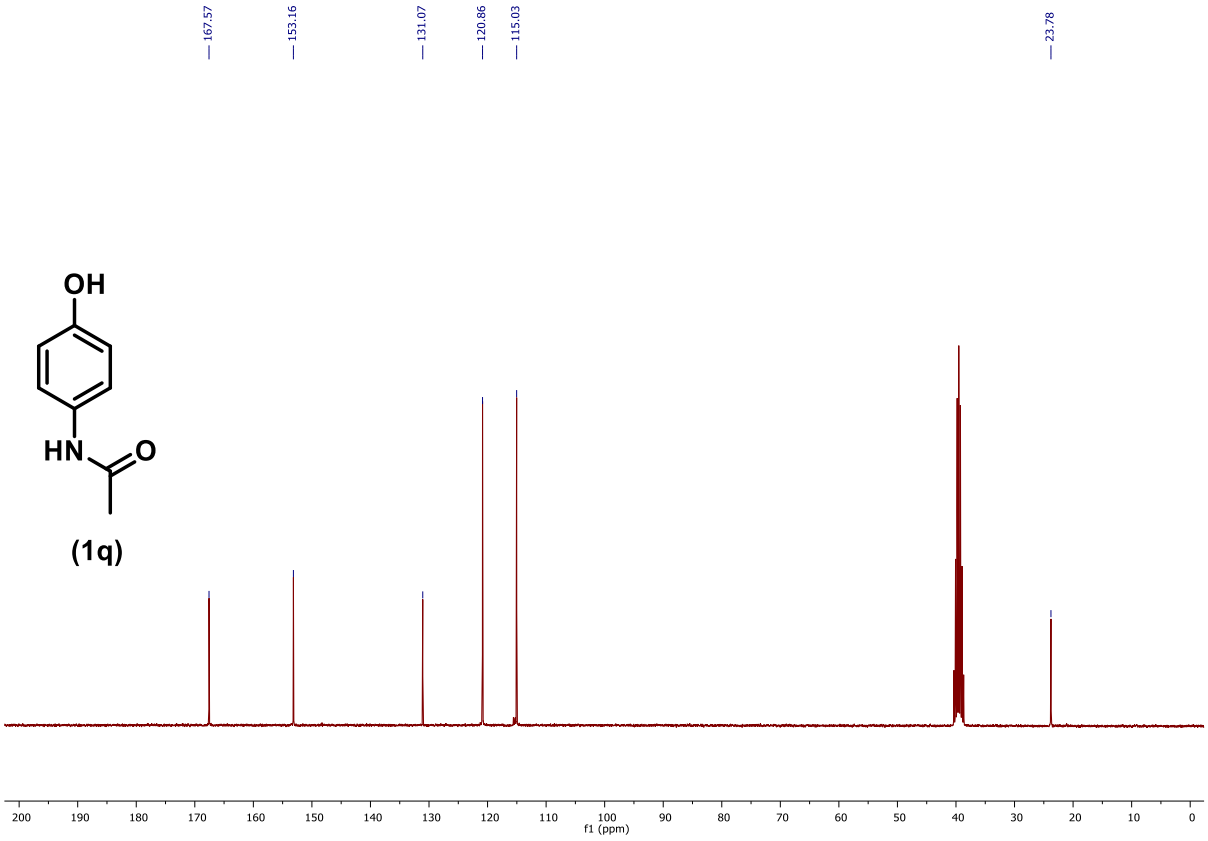
^{31}P NMR spectrum (121 MHz, DMSO-d_6) of **1p**



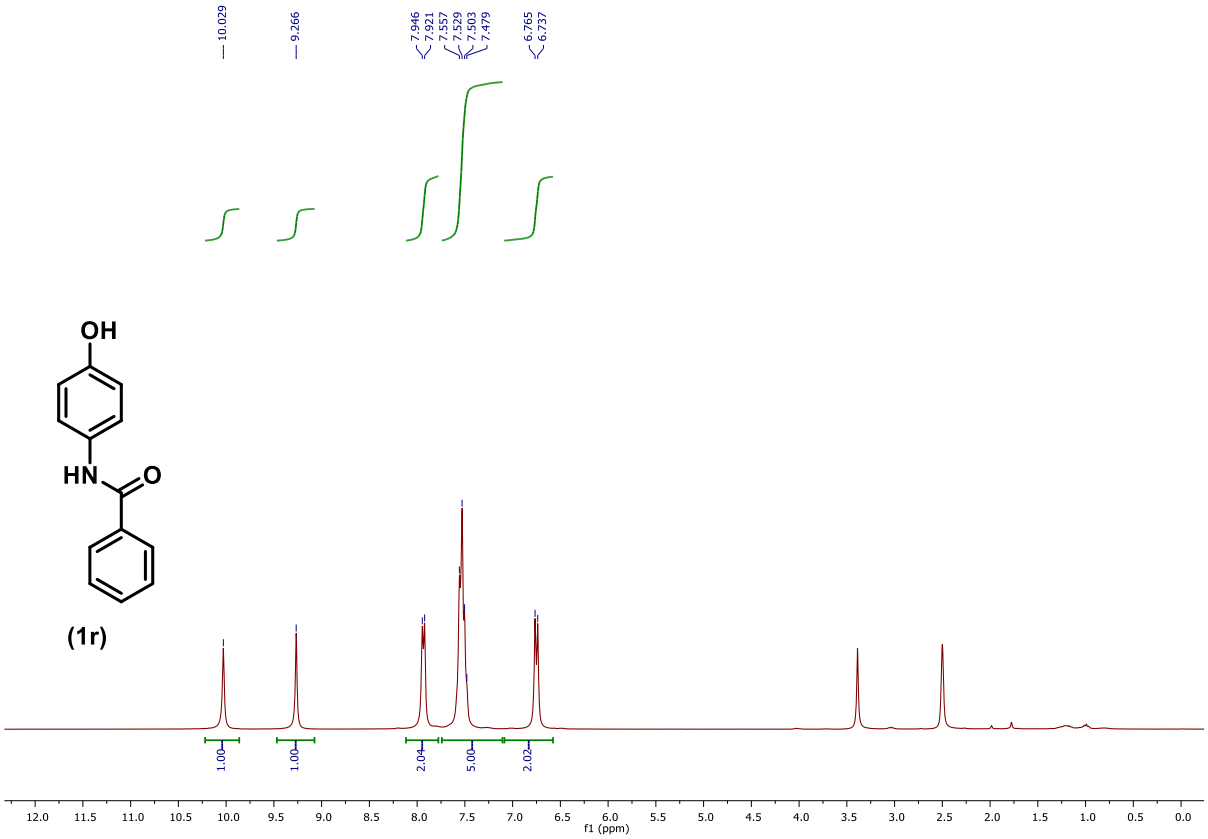
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **1q**



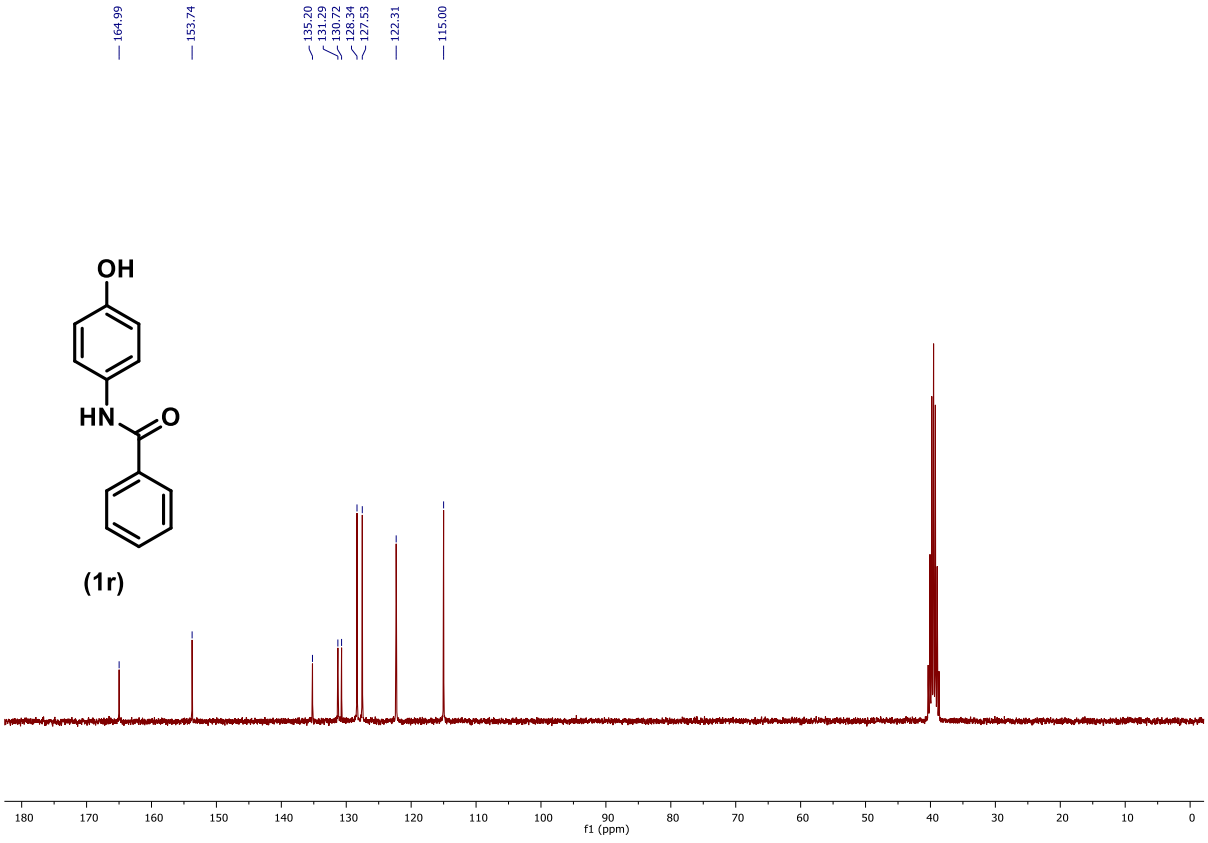
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **1q**



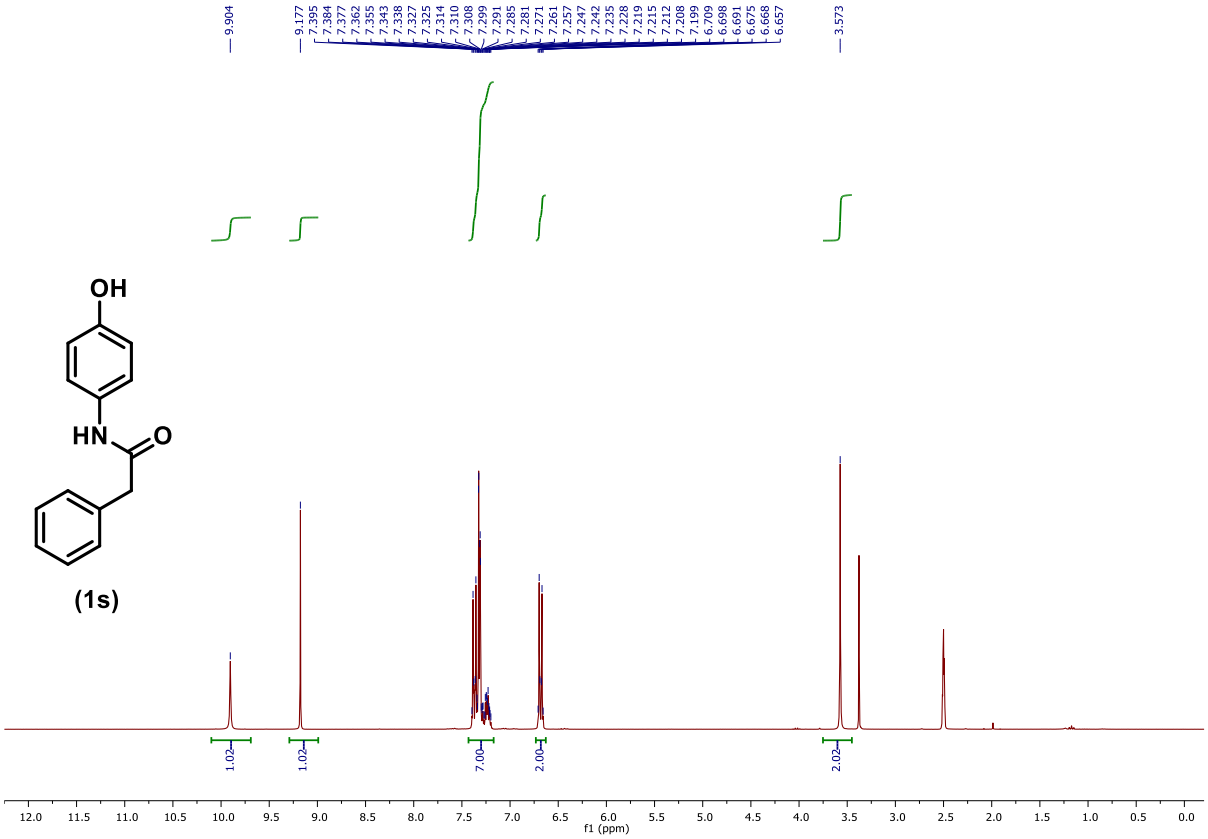
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **1r**



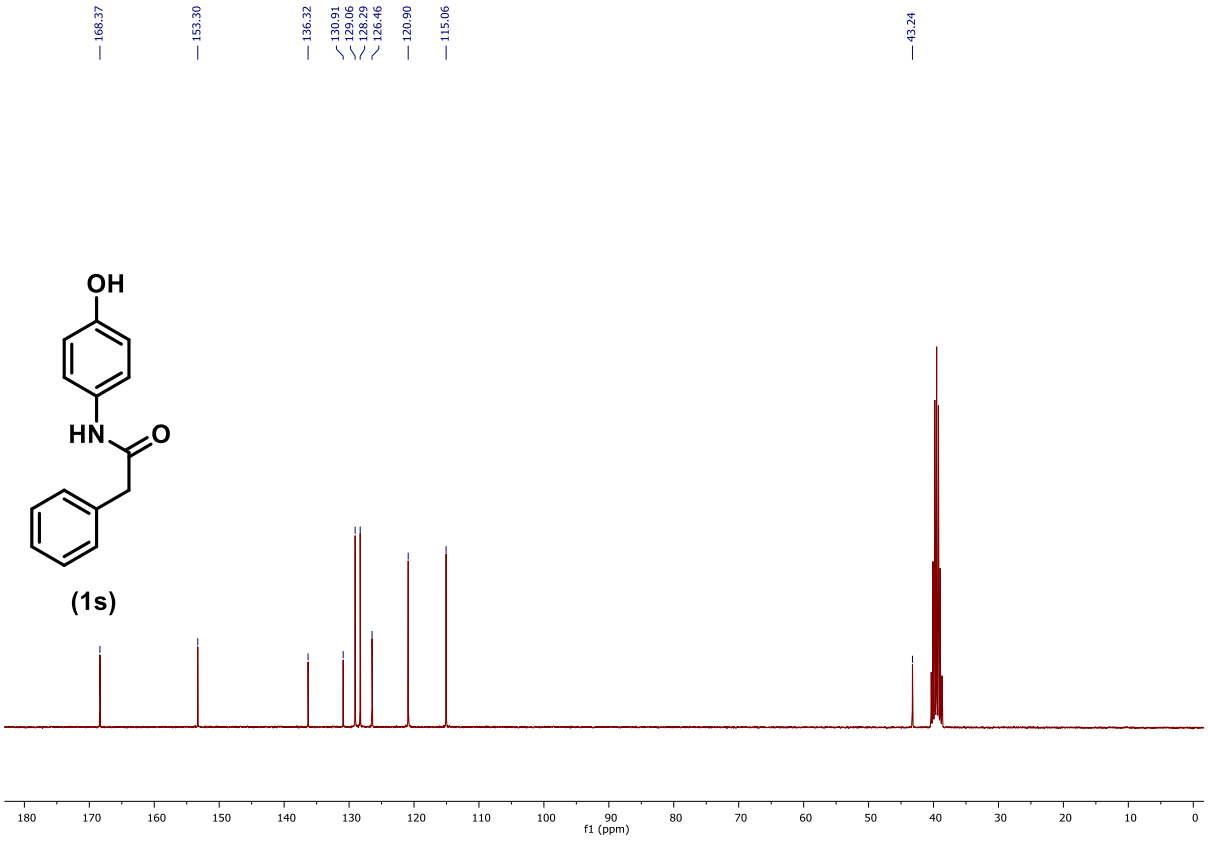
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **1r**



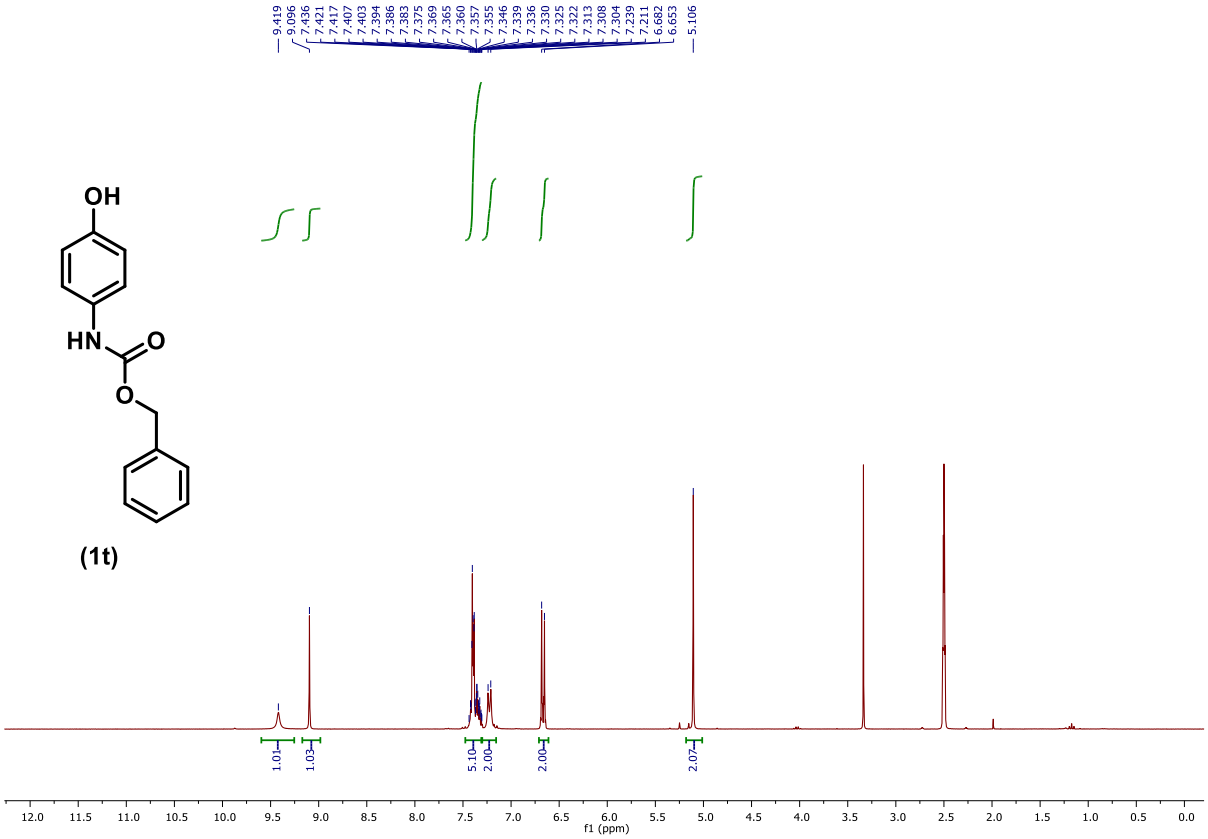
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **1s**



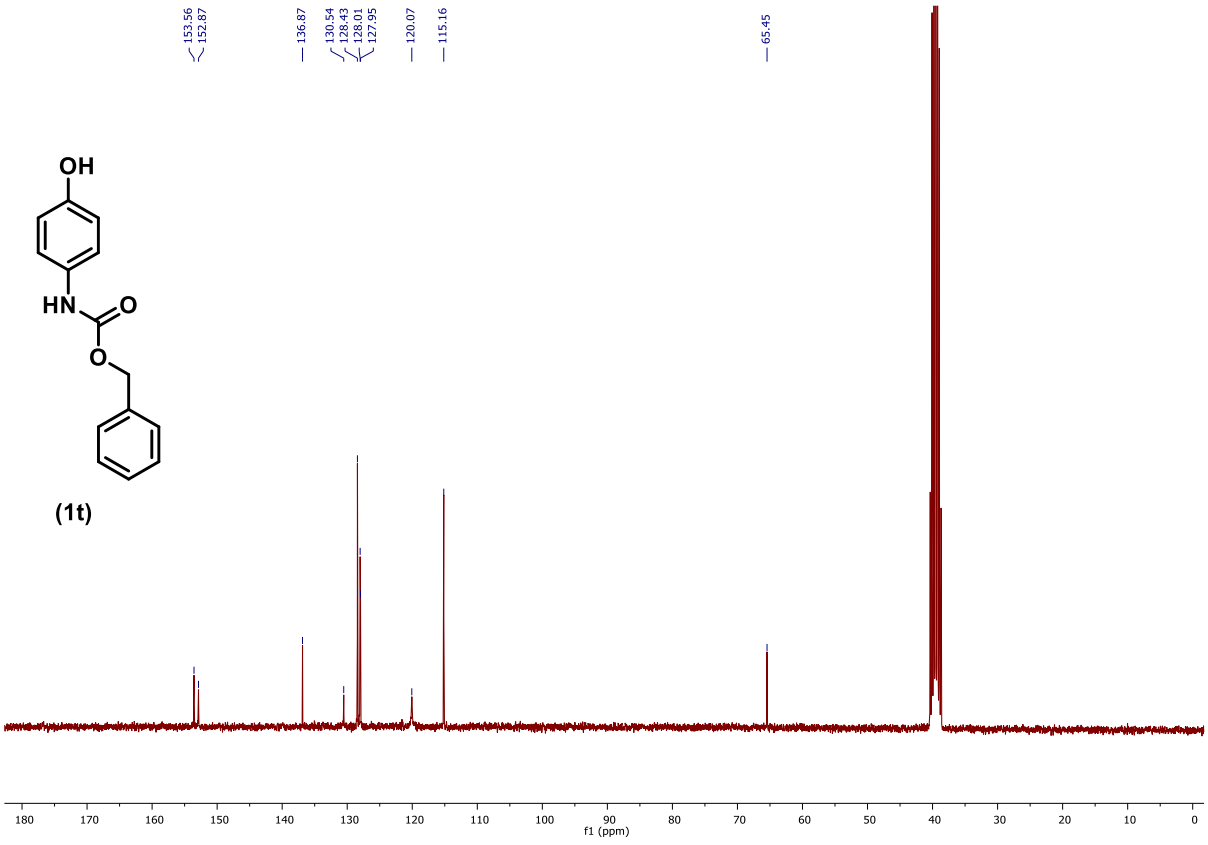
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **1s**



^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **1t**



^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **1t**



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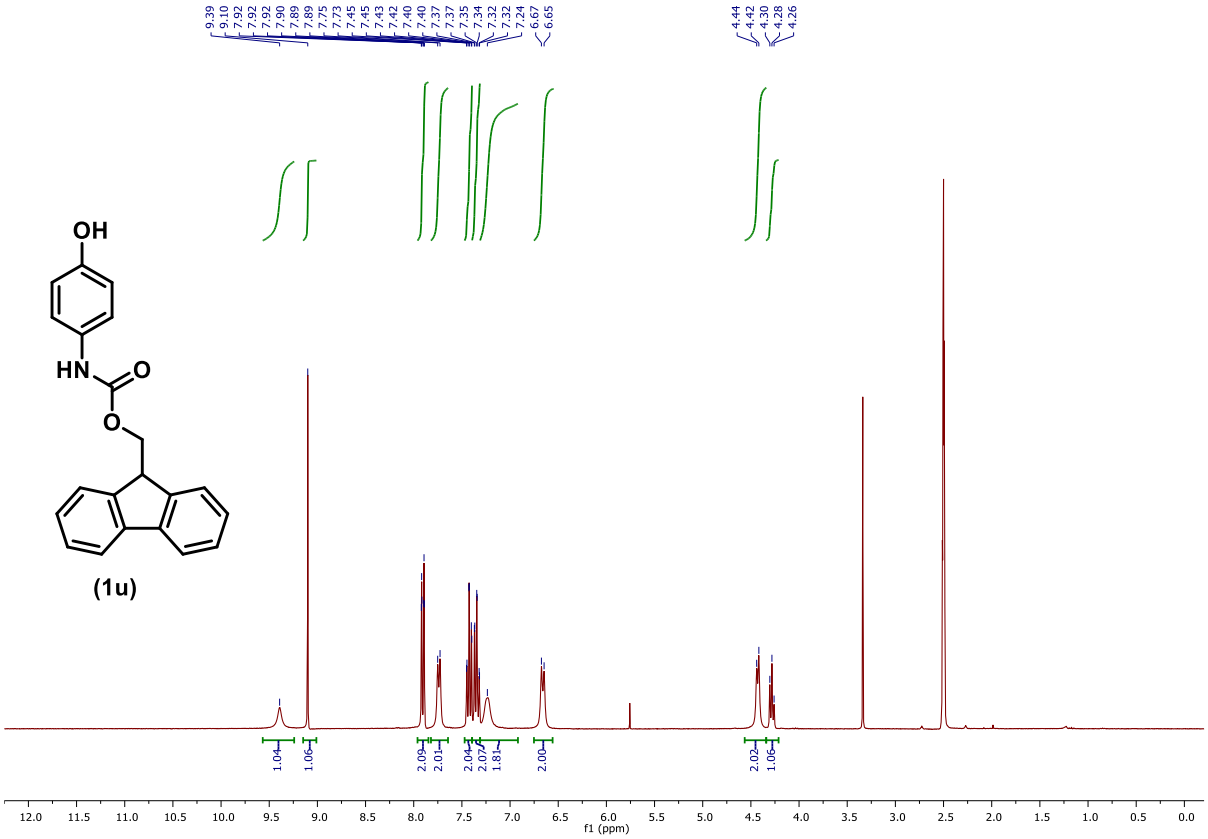
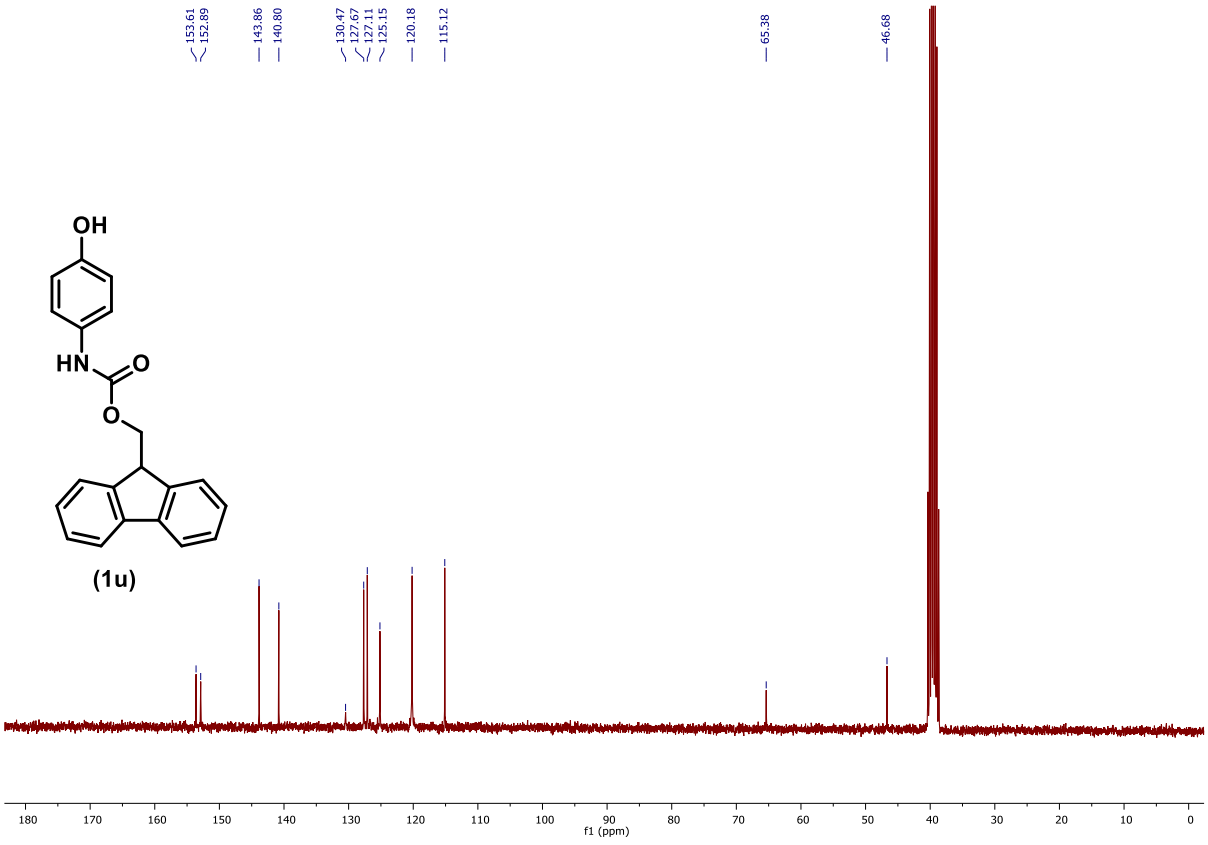
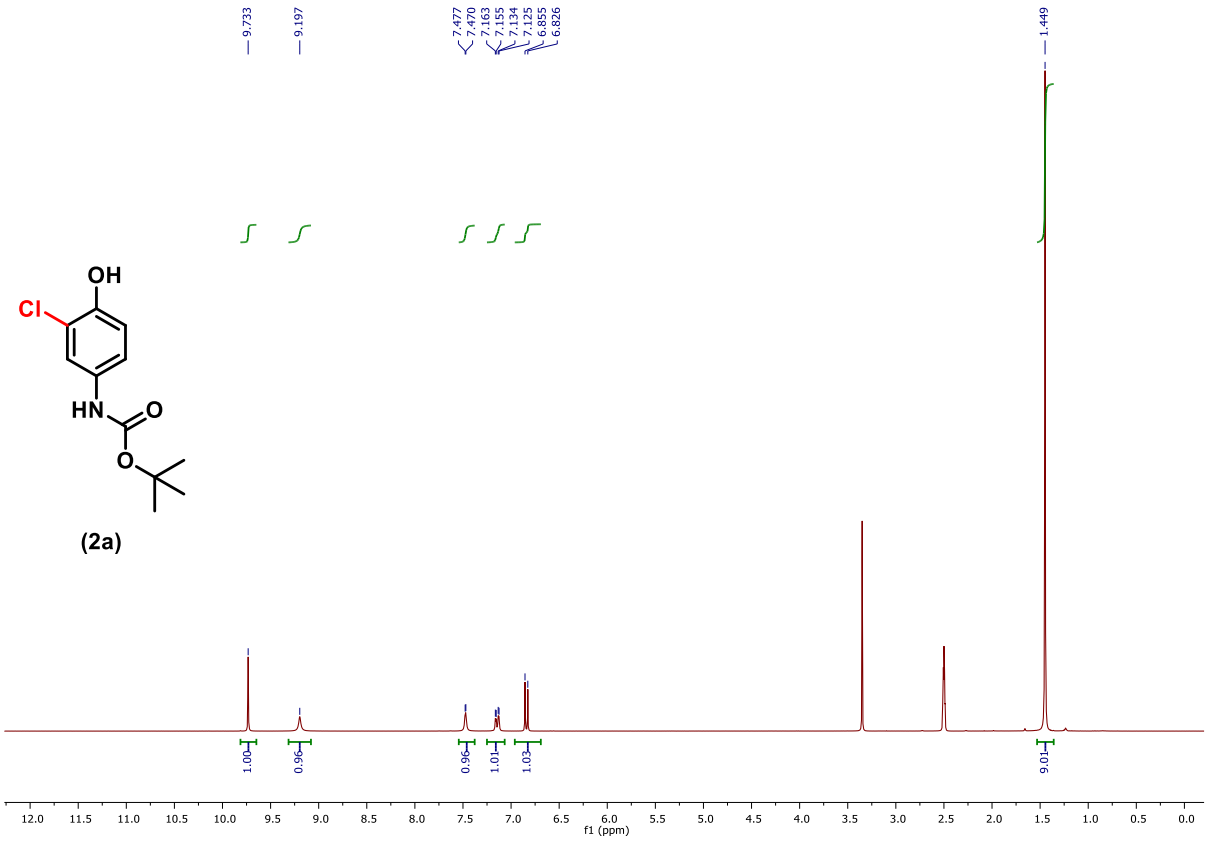


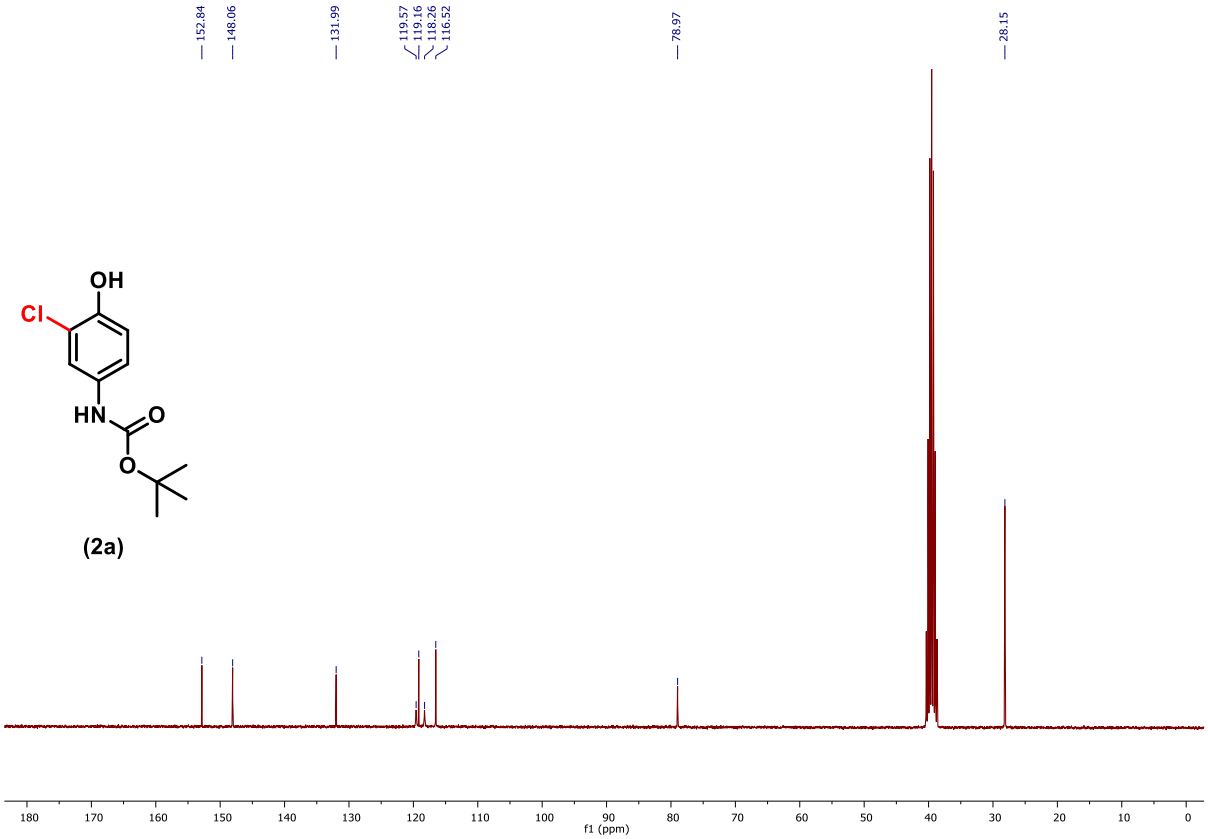
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **1u**



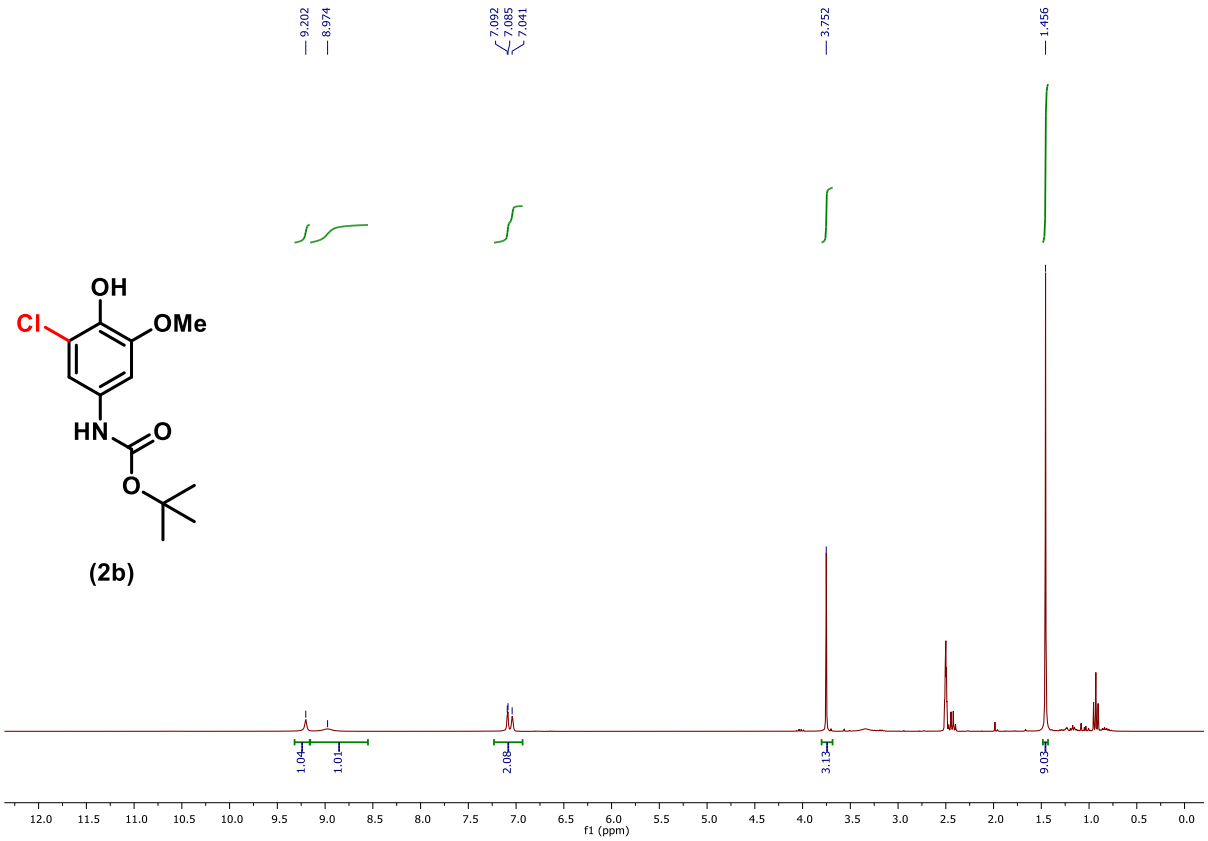
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **2a**



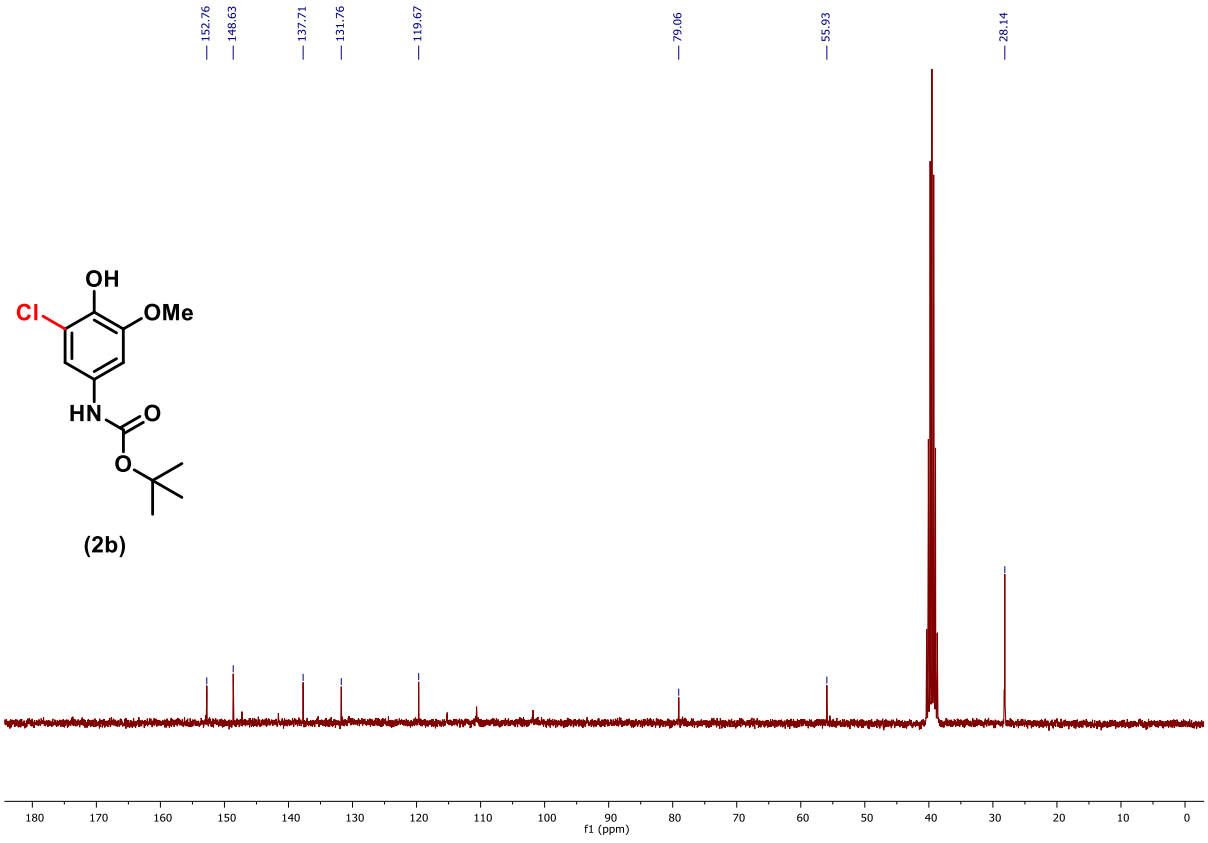
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **2a**



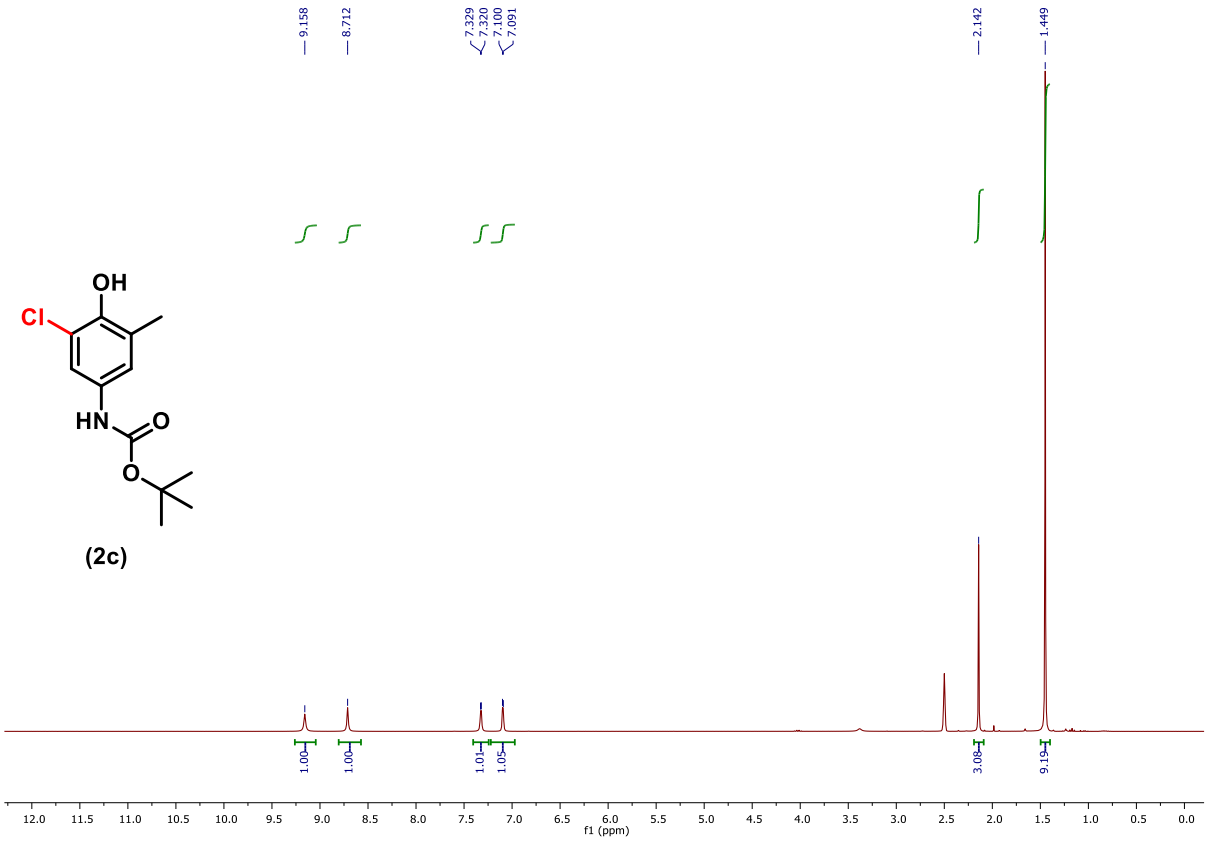
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **2b**



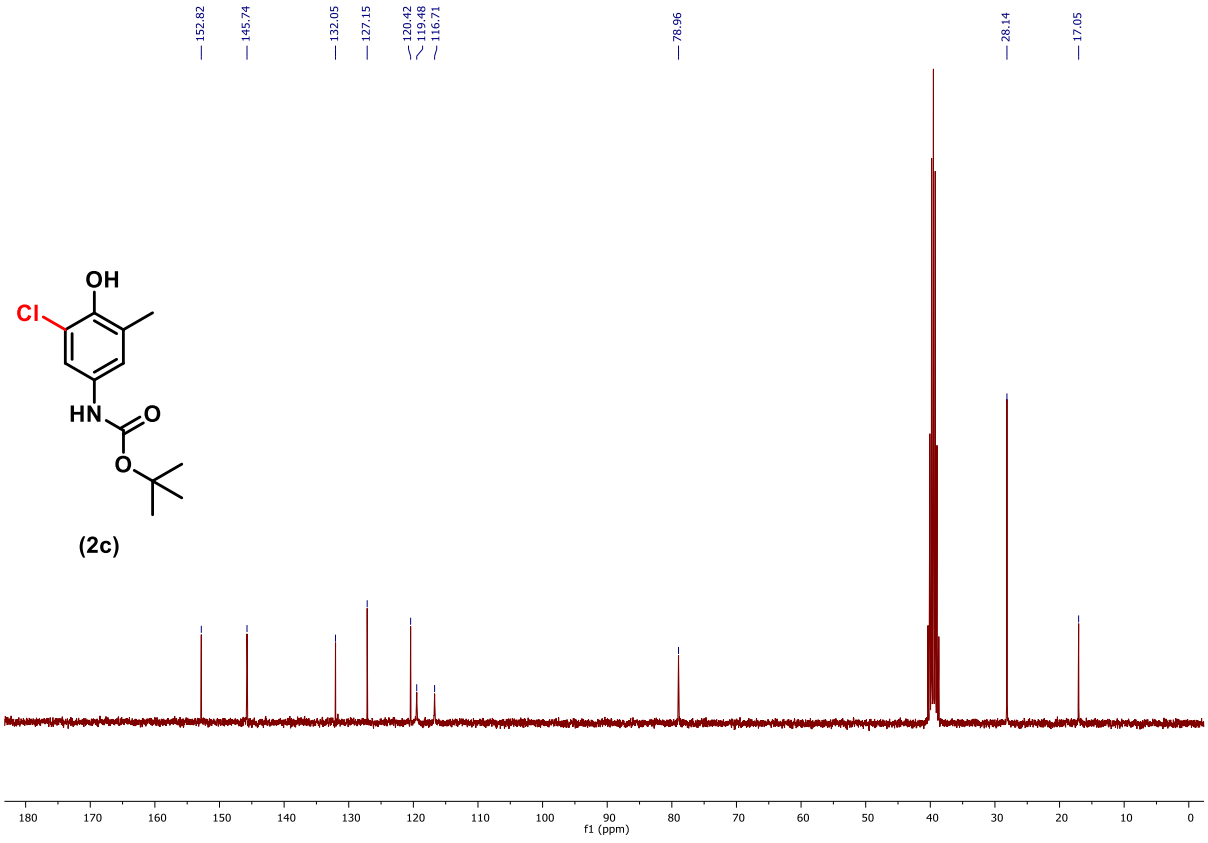
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **2b**



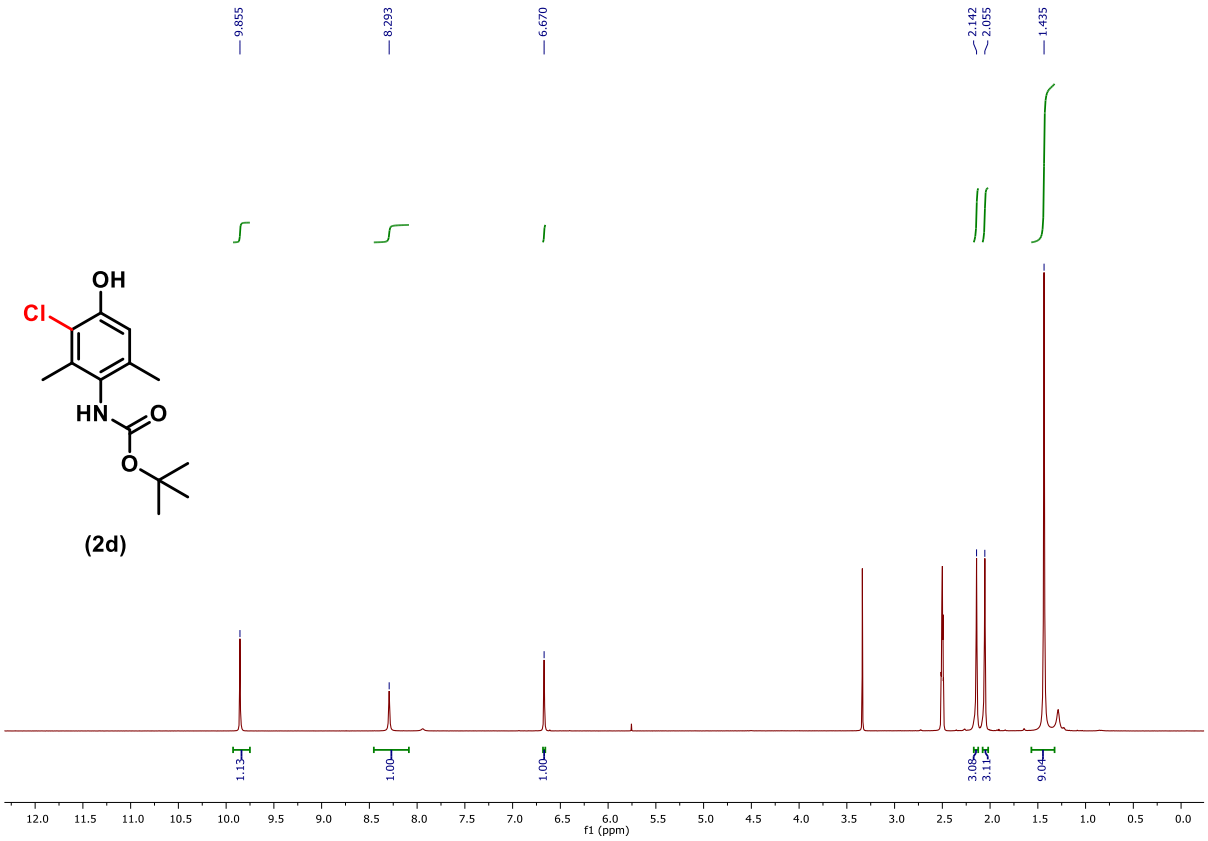
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **2c**



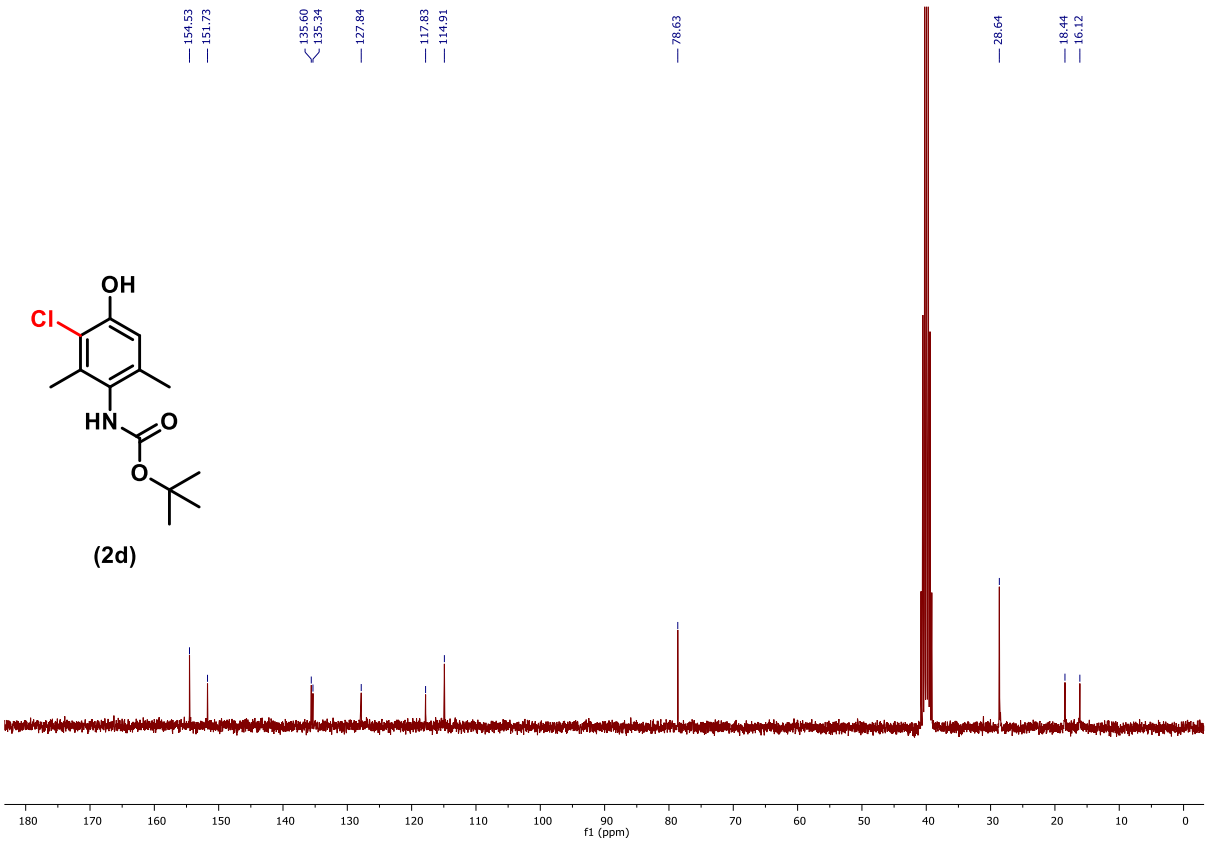
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **2c**



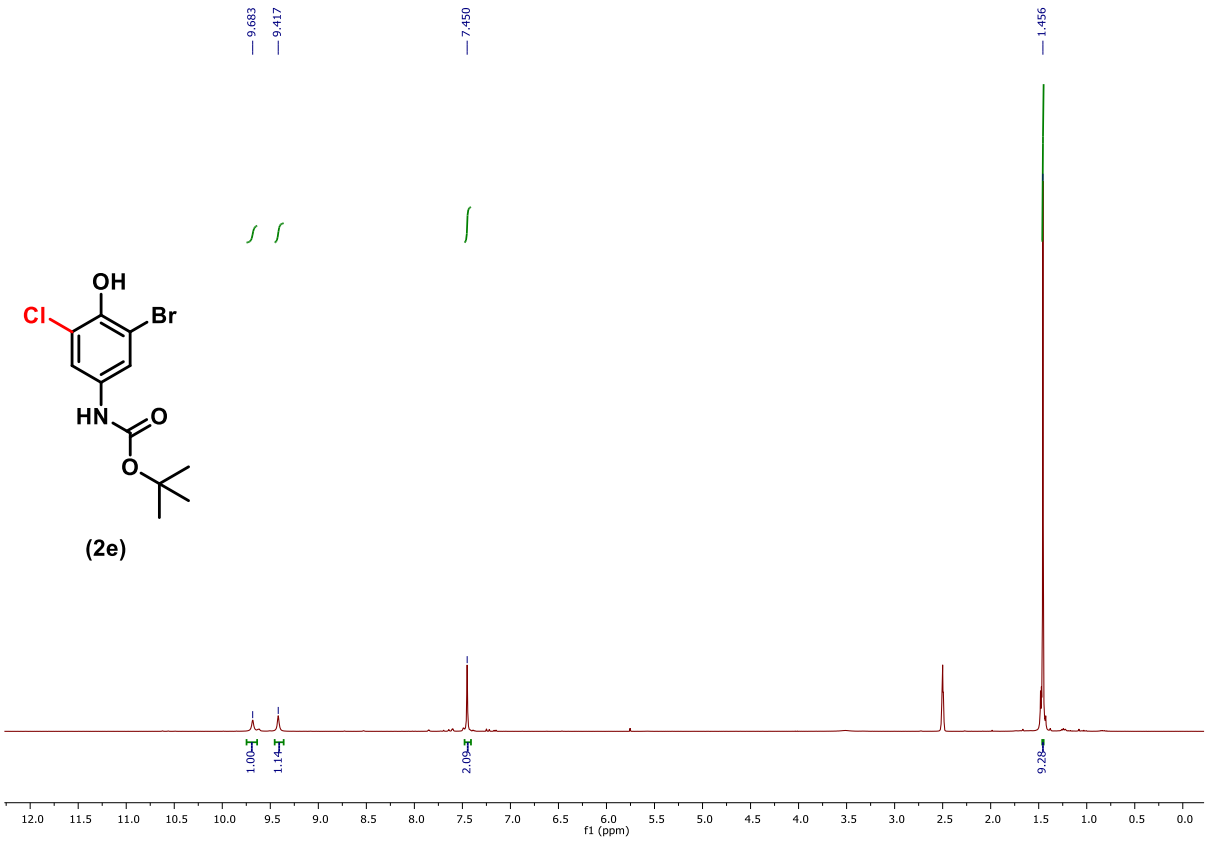
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **2d**



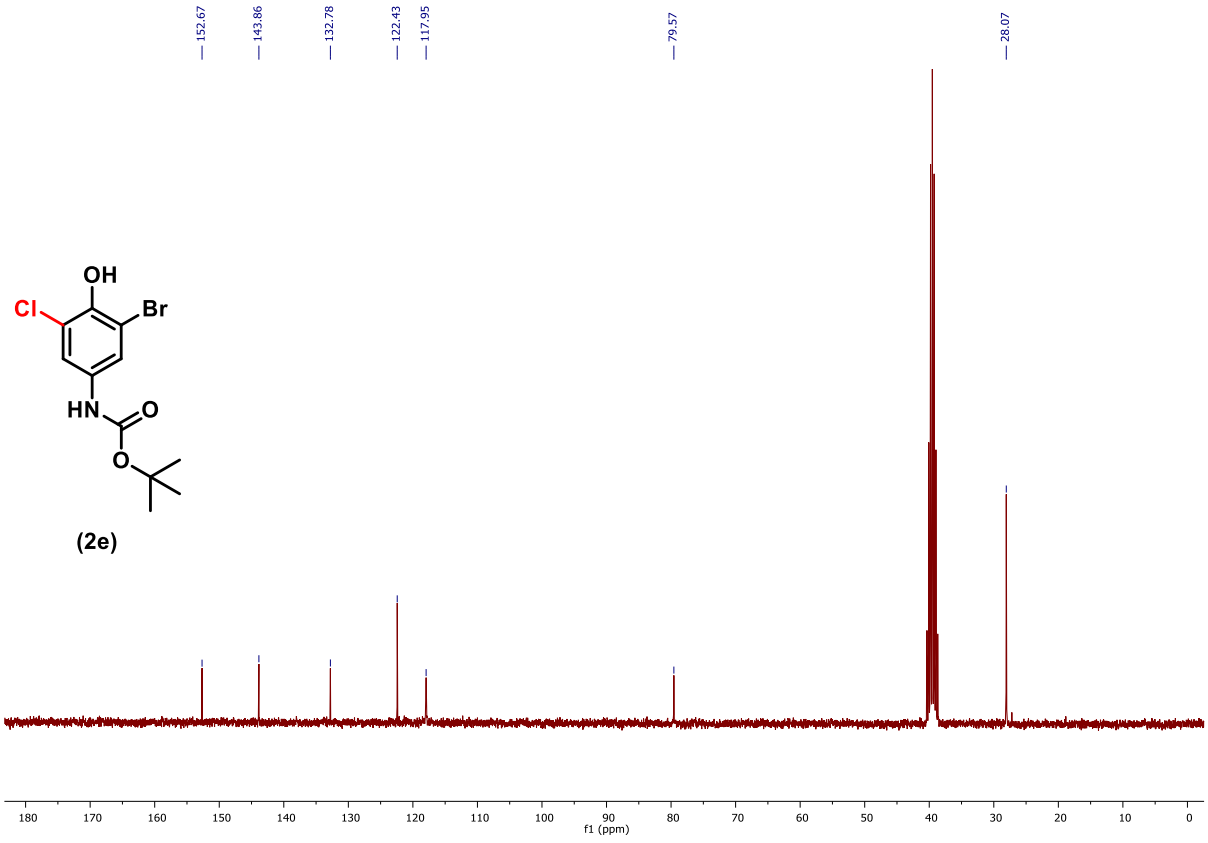
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **2d**



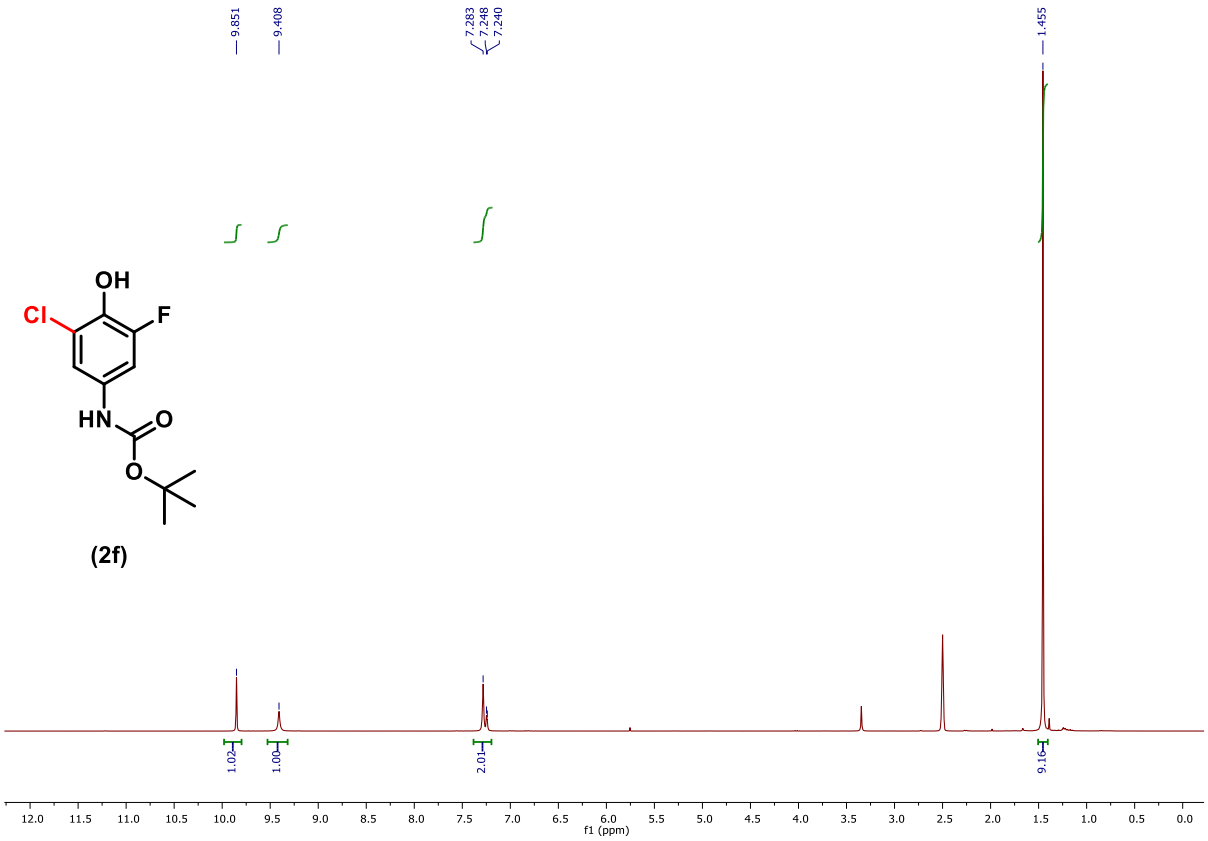
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **2e**



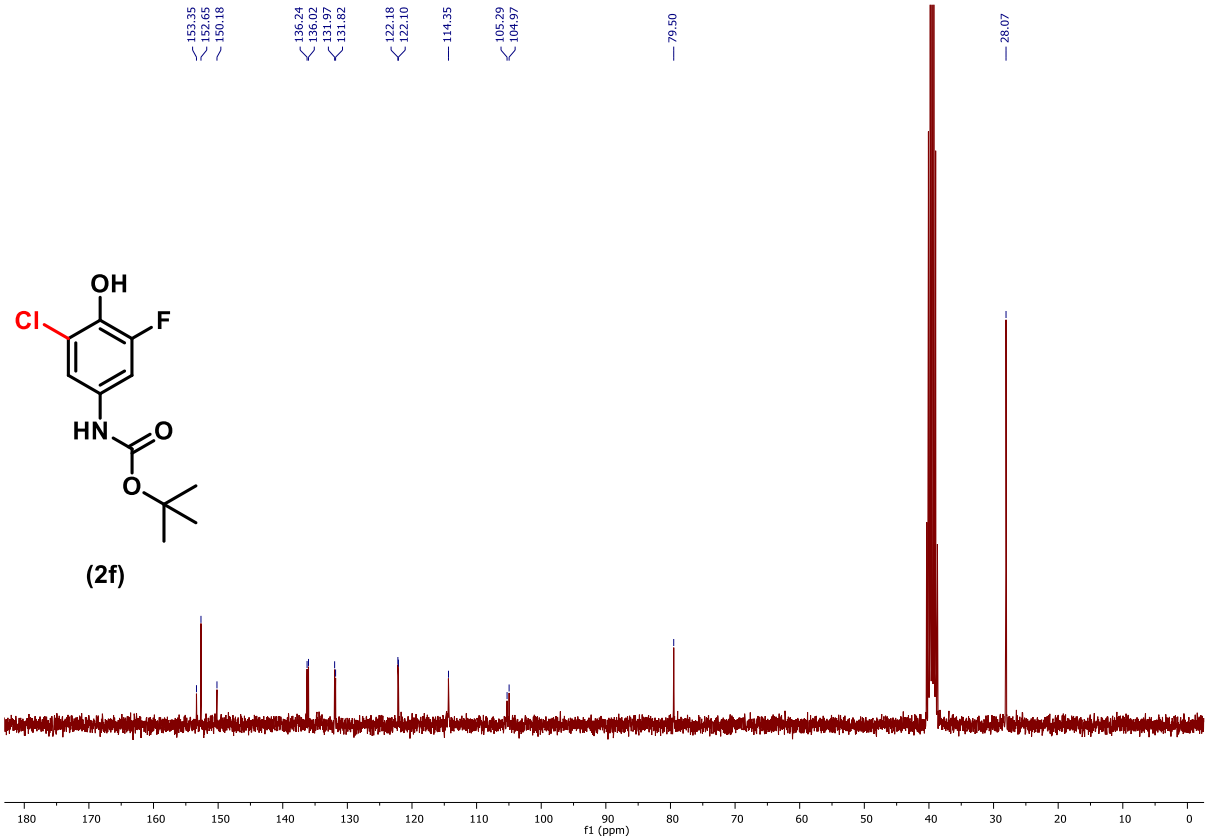
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **2e**



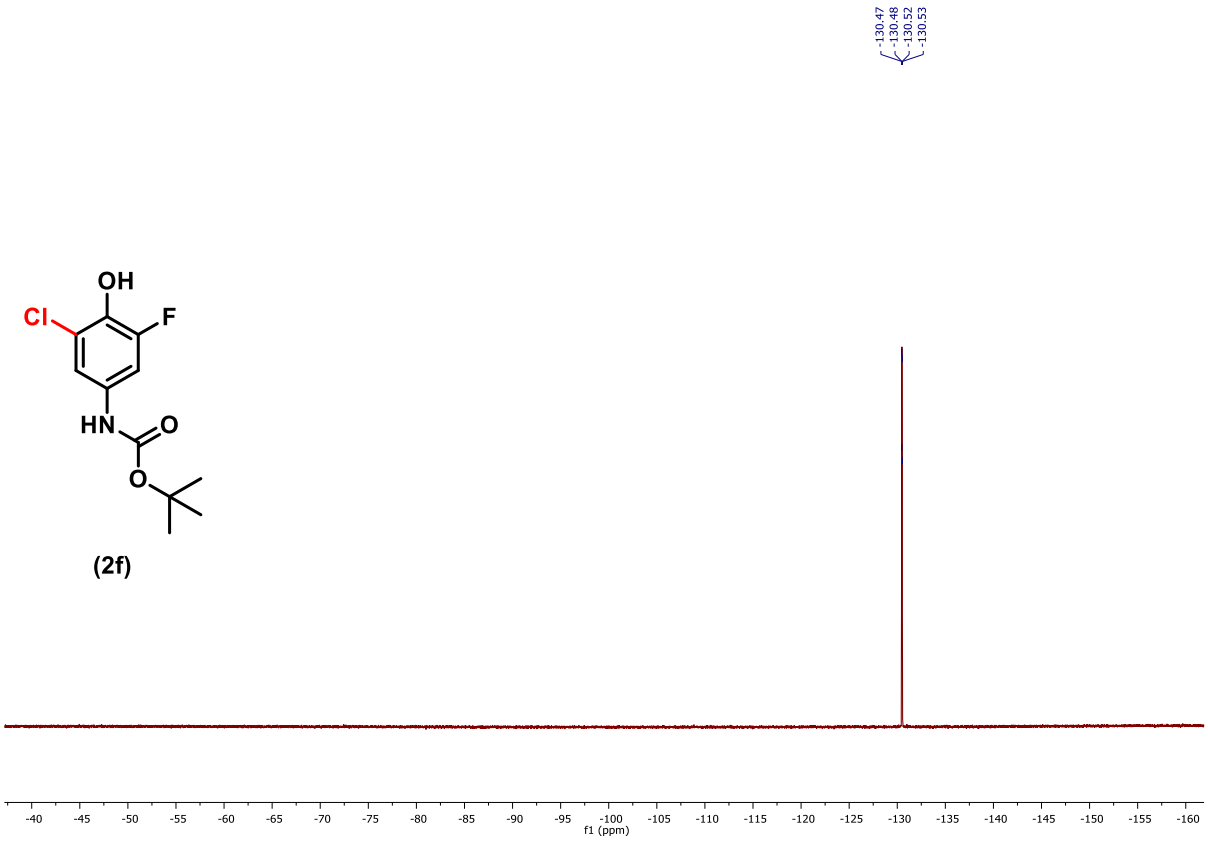
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **2f**



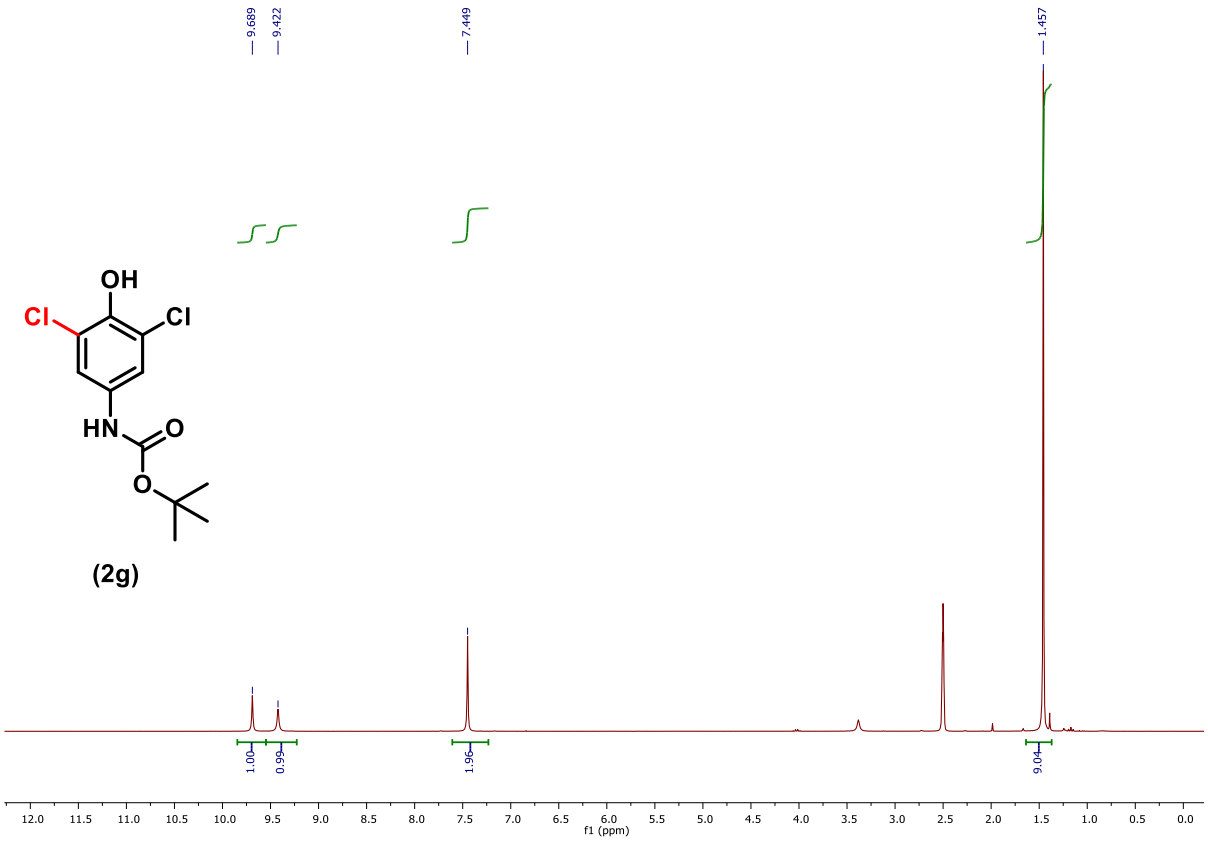
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **2f**



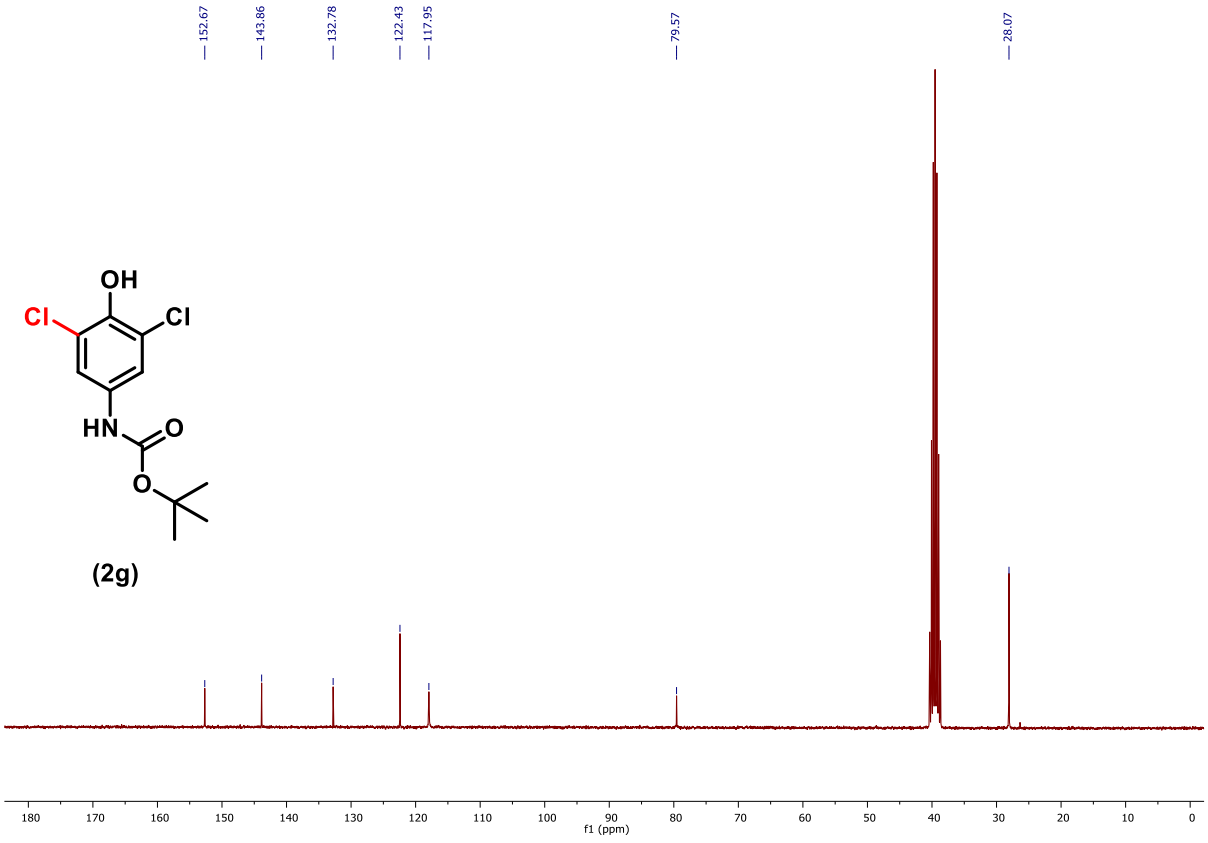
^{19}F NMR spectrum (282 MHz, DMSO-d_6) of **2f**



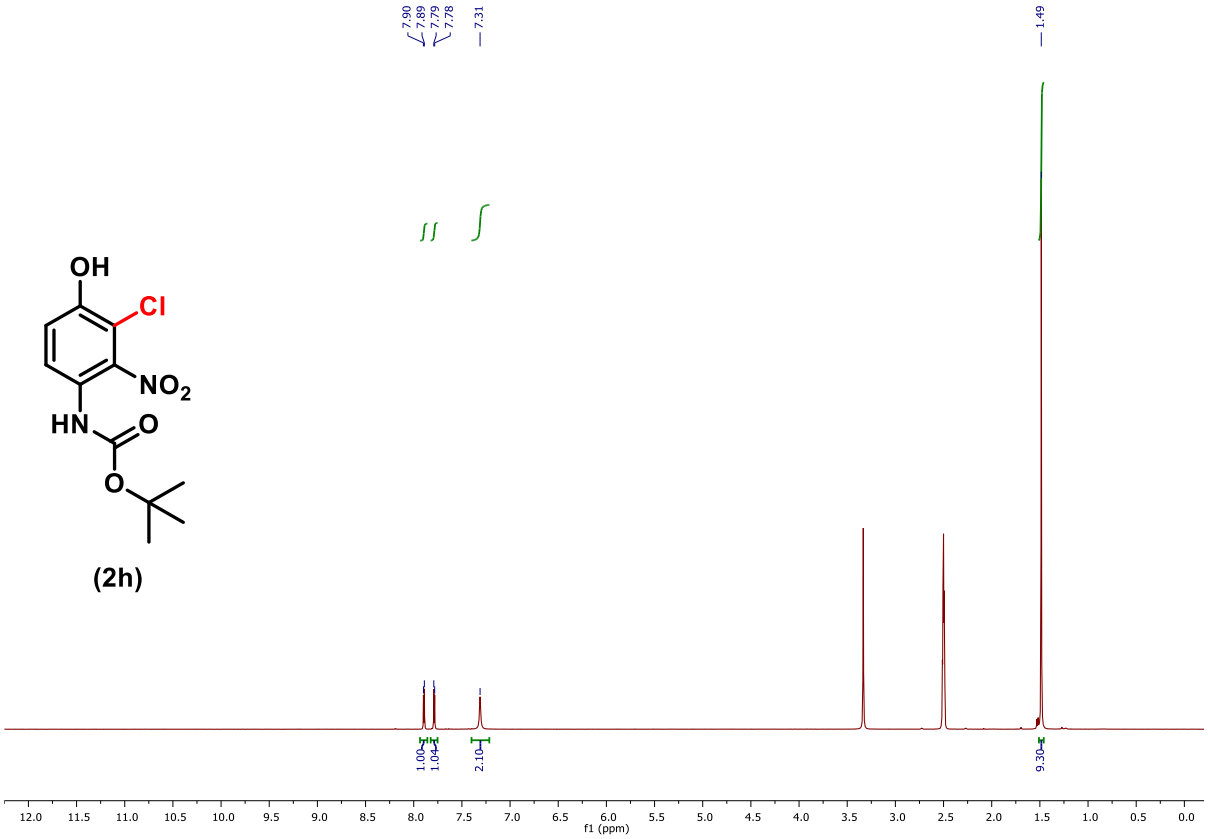
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **2g** (equivalent to **3a**, made from **1g**)



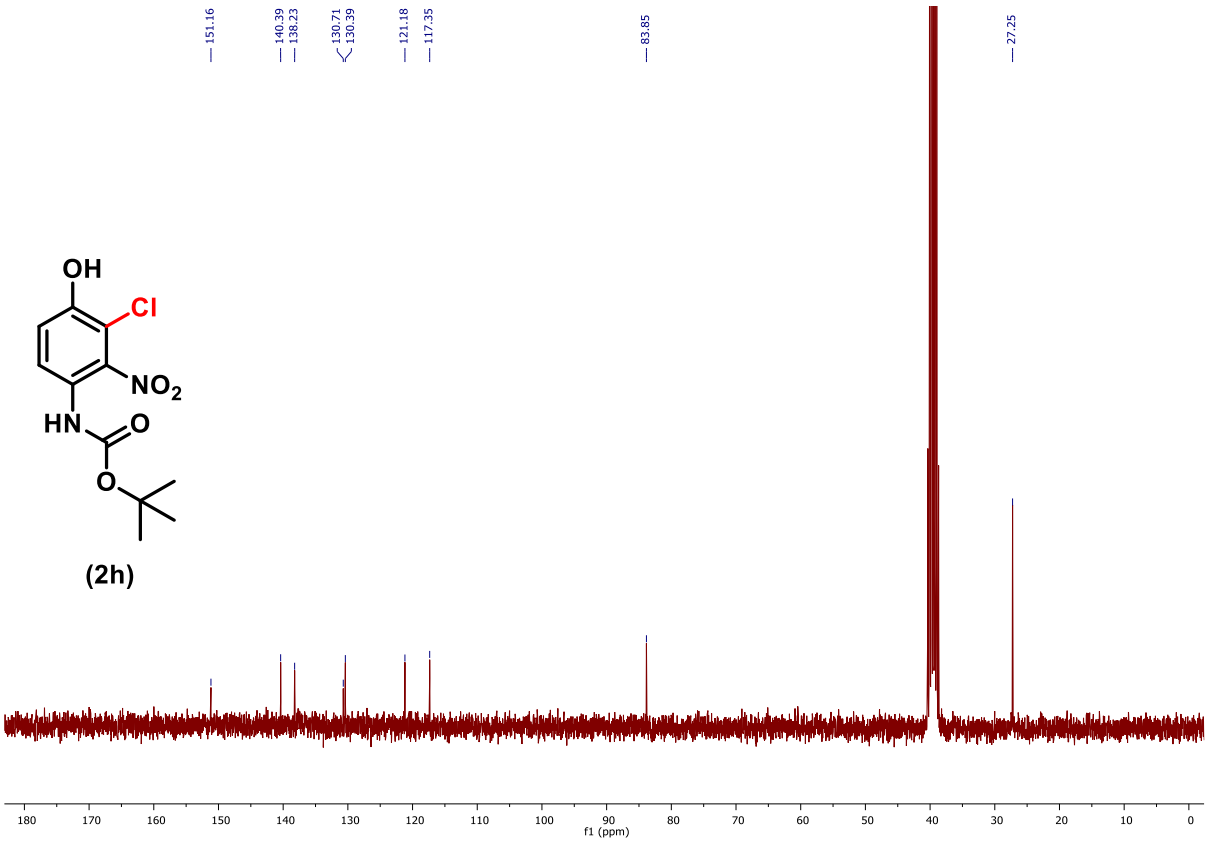
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **2g** (equiv to **3a**, made from **1g**)



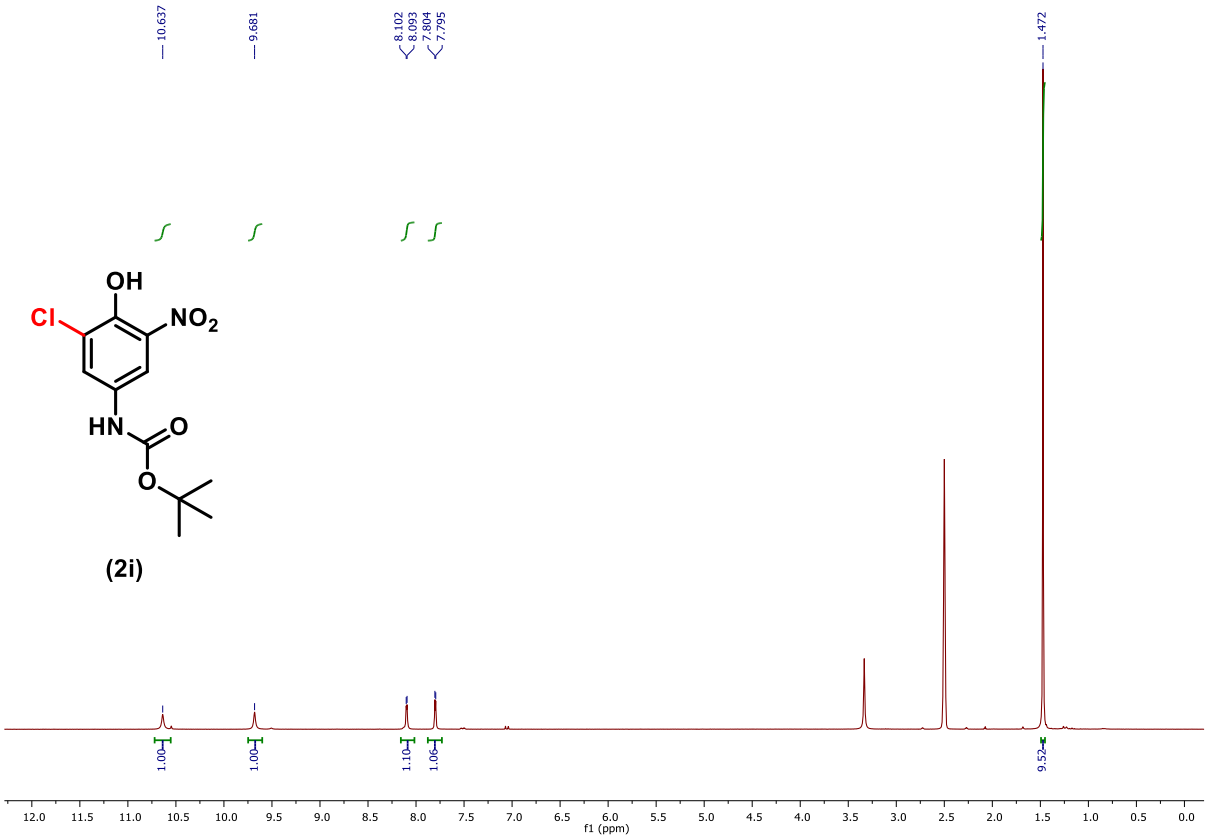
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **2h**



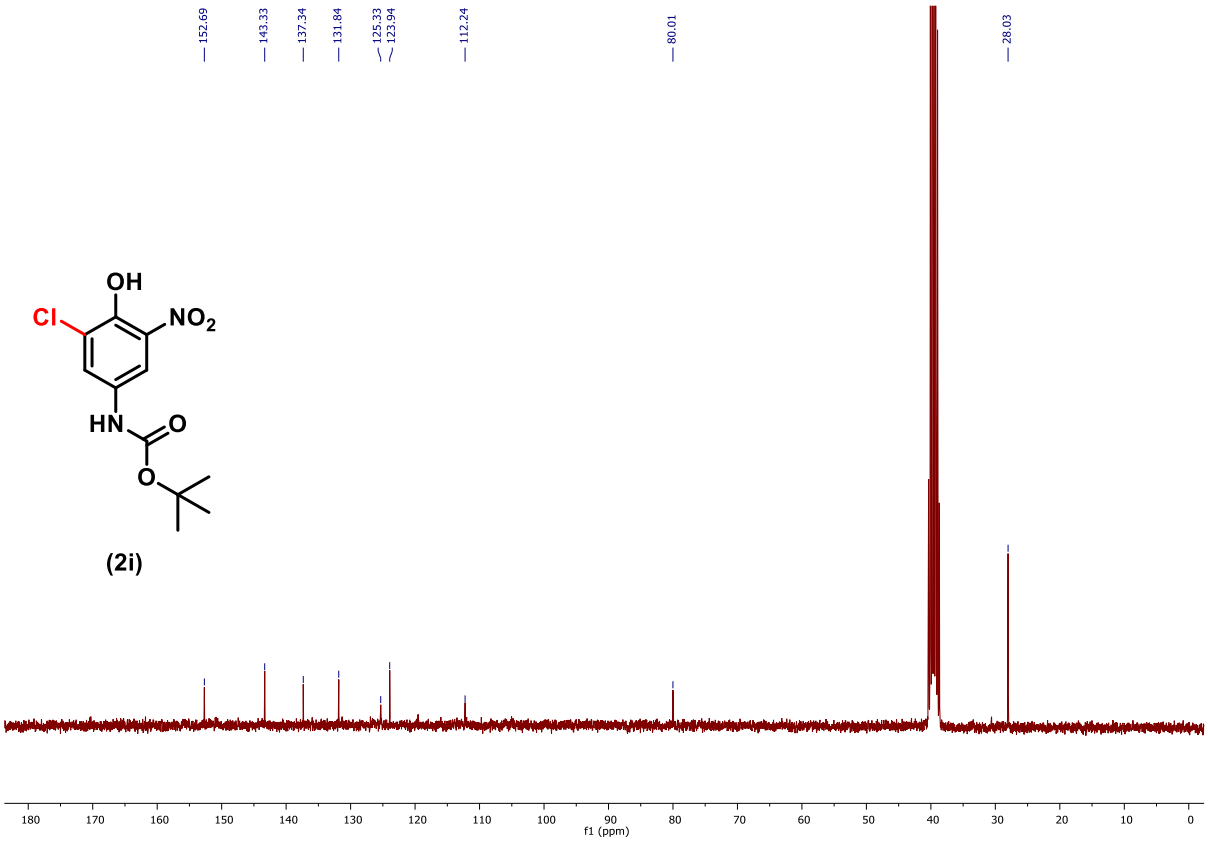
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **2h**



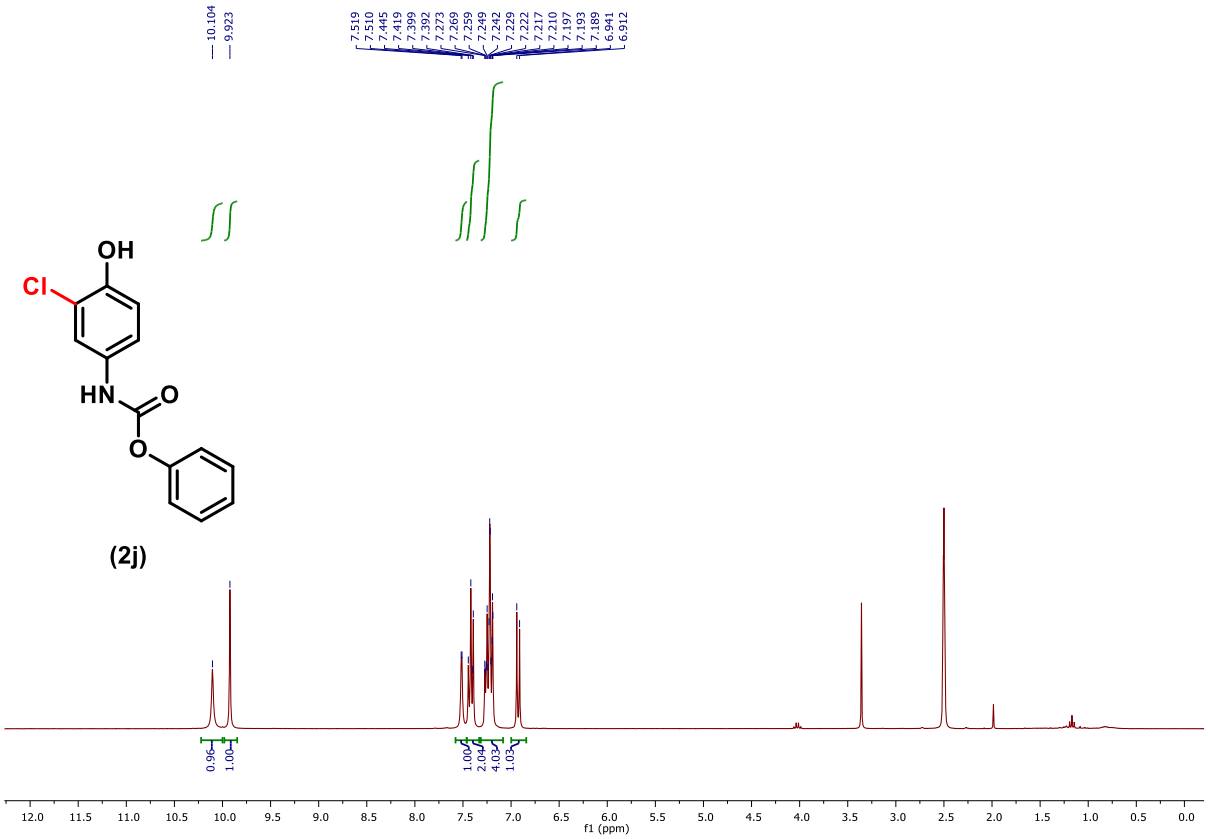
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **2i**



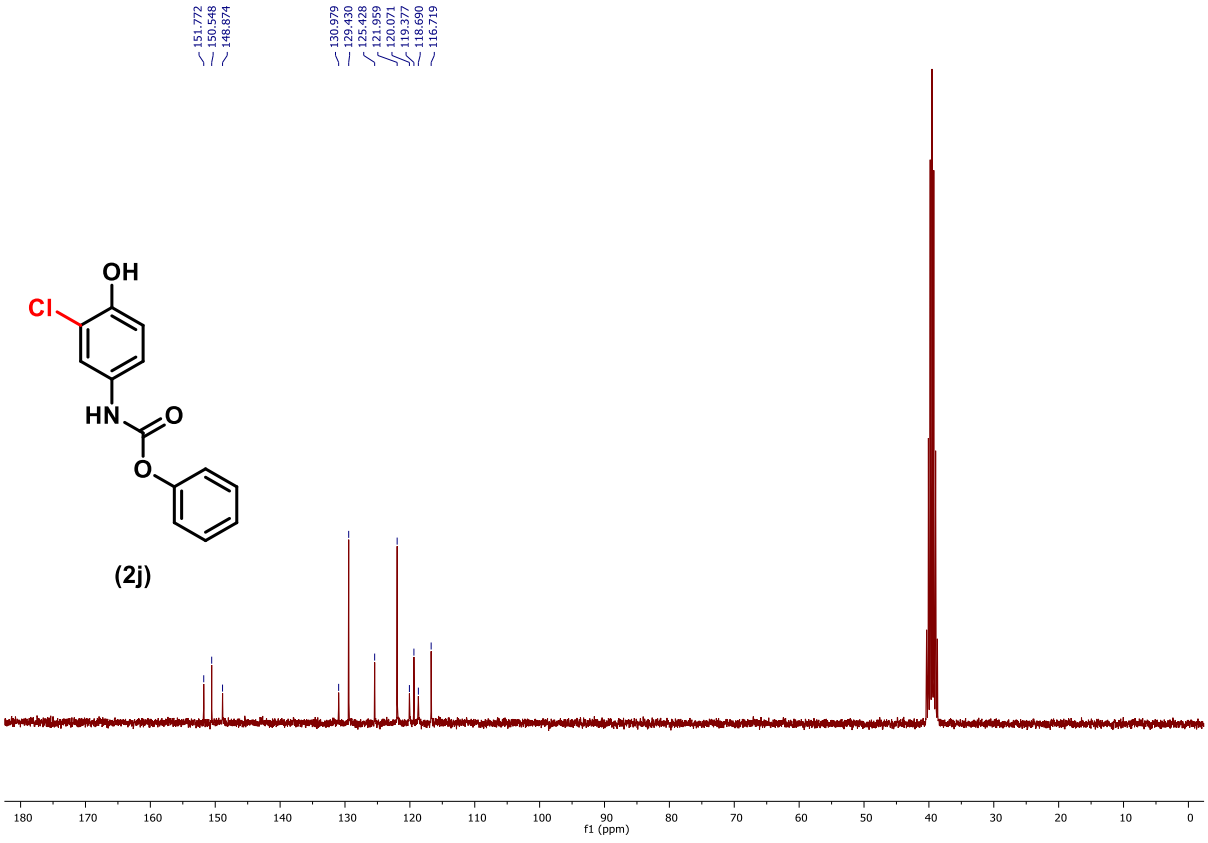
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **2i**



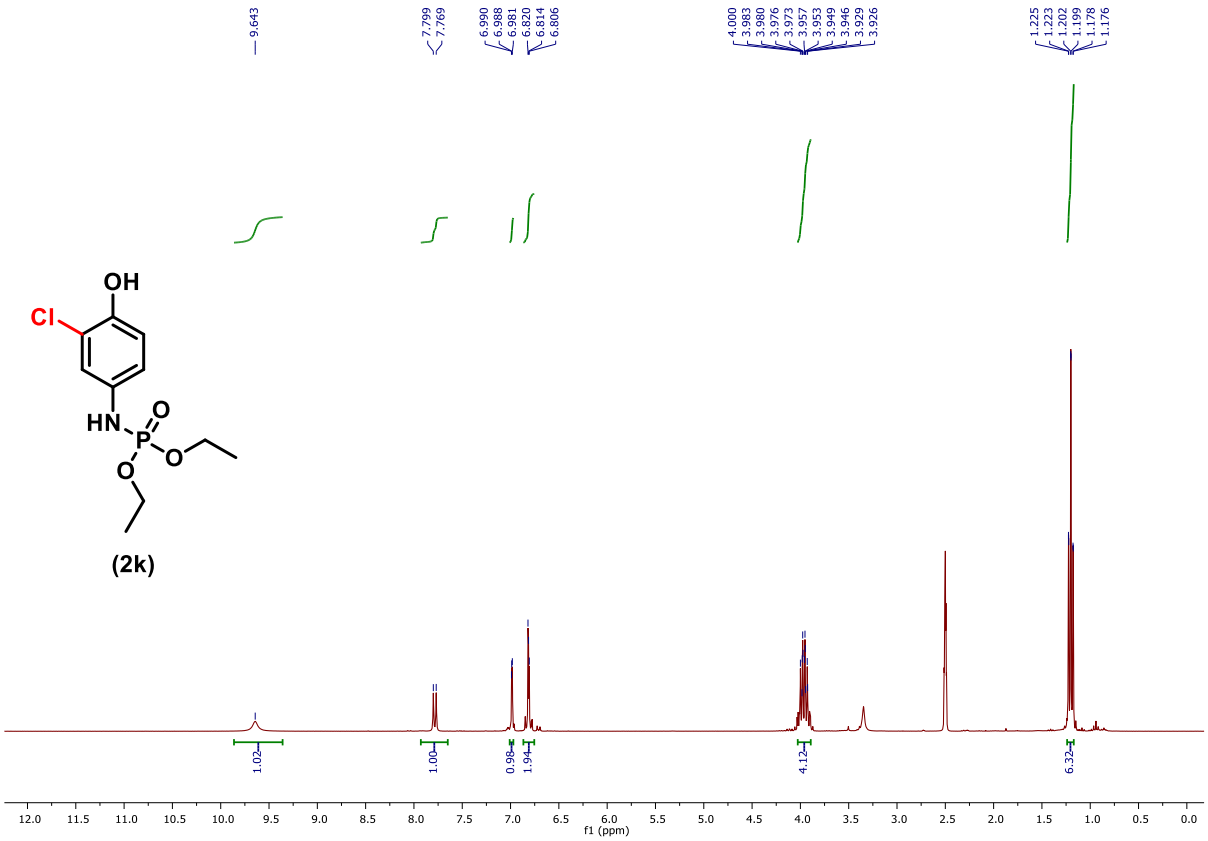
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **2j**



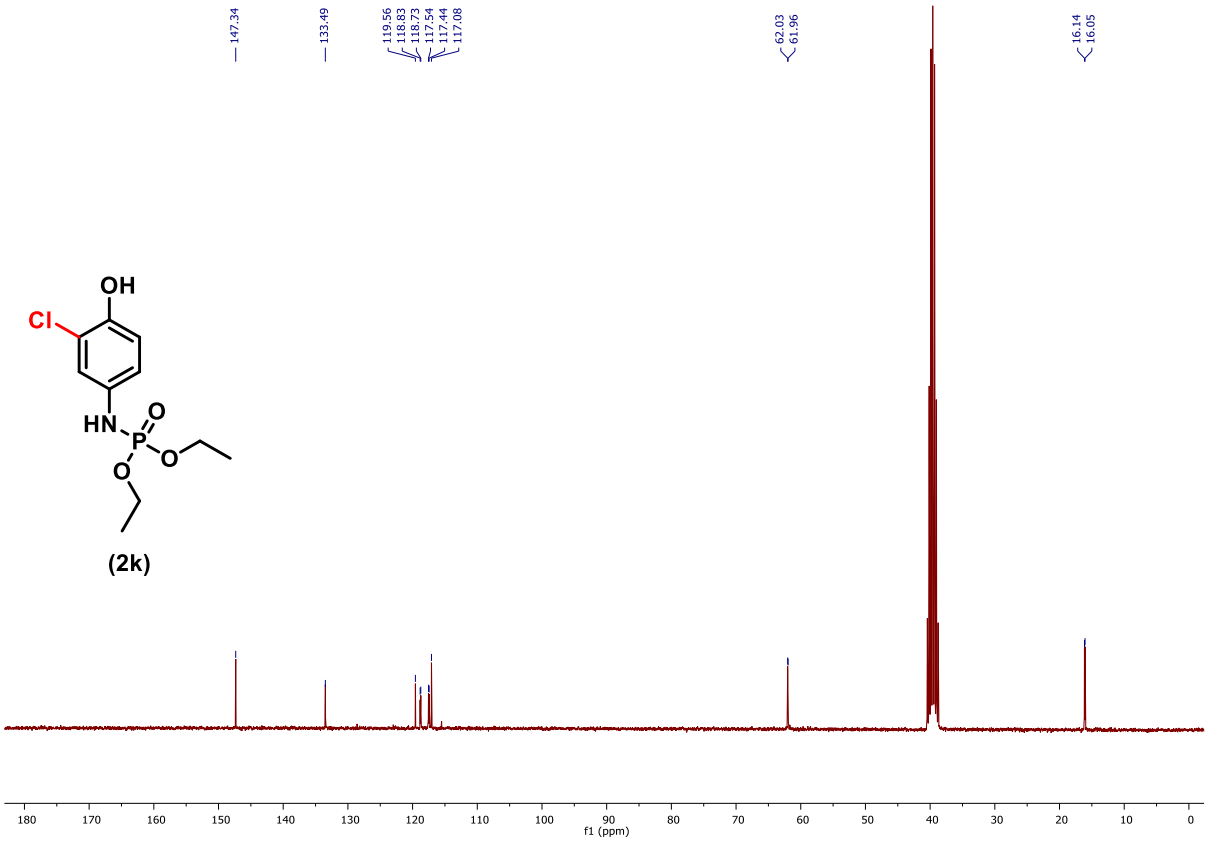
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **2j**



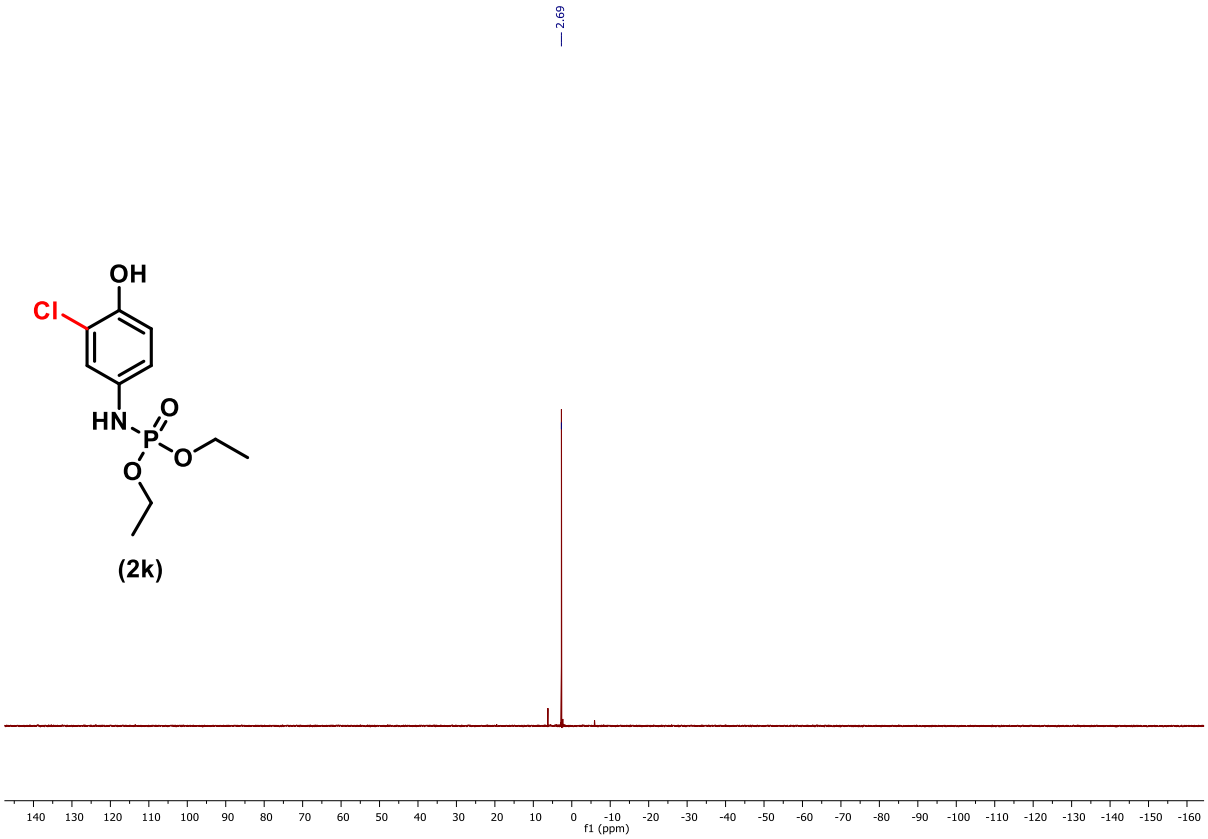
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **2k**



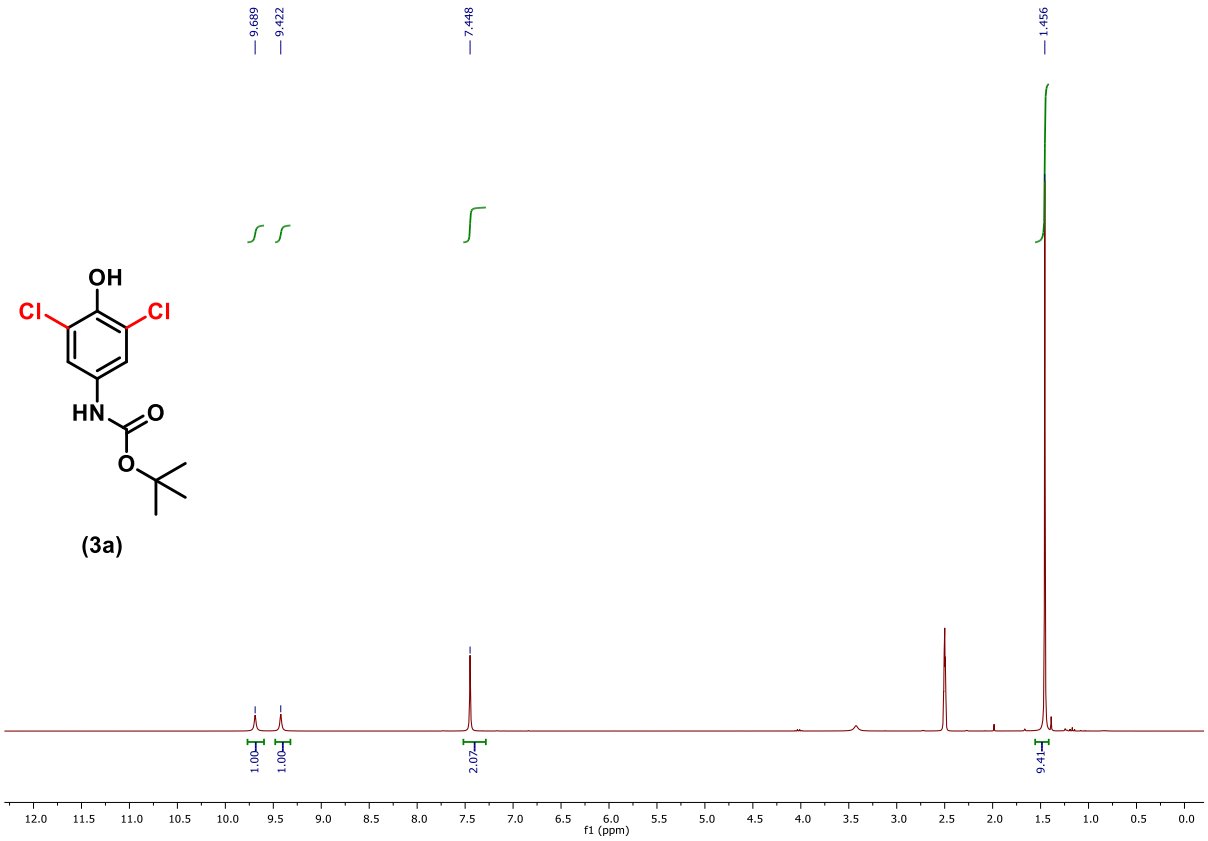
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **2k**



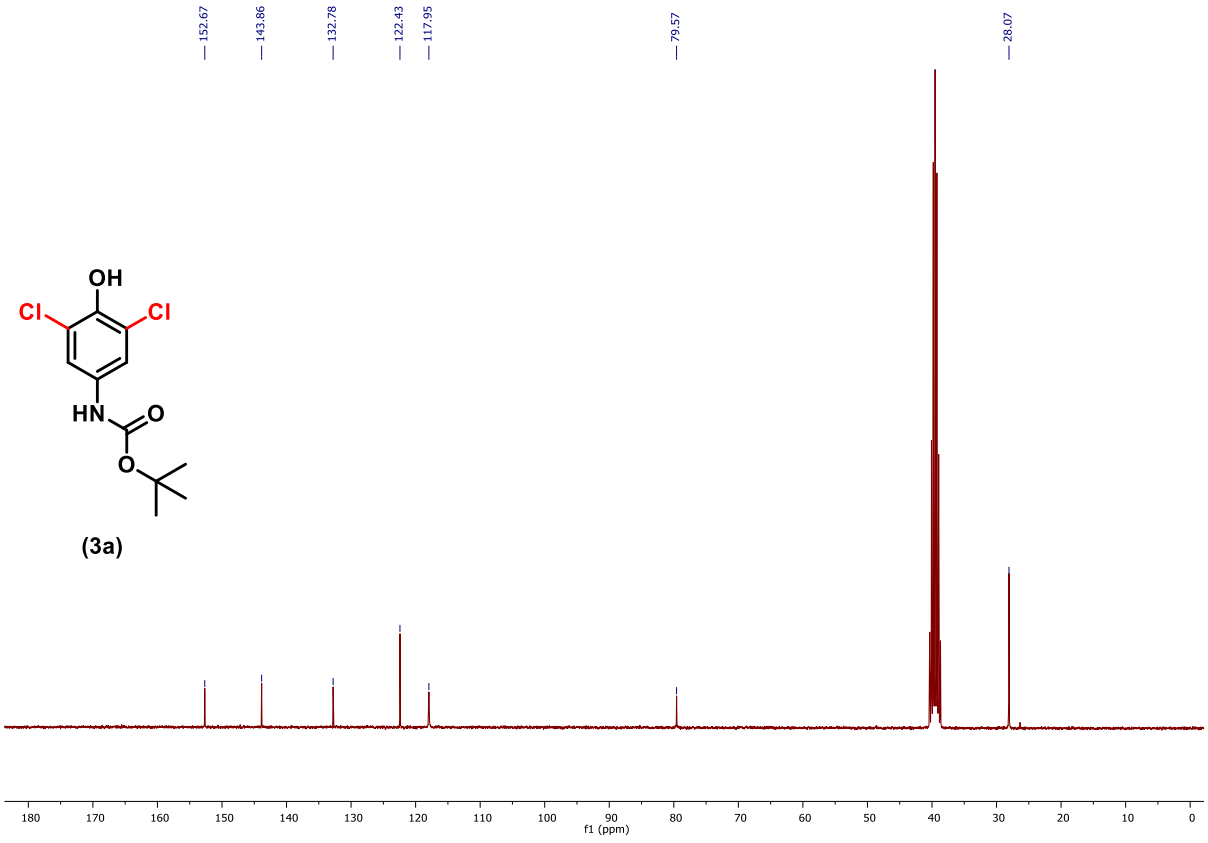
^{31}P NMR spectrum (121 MHz, DMSO-d_6) of **2k**



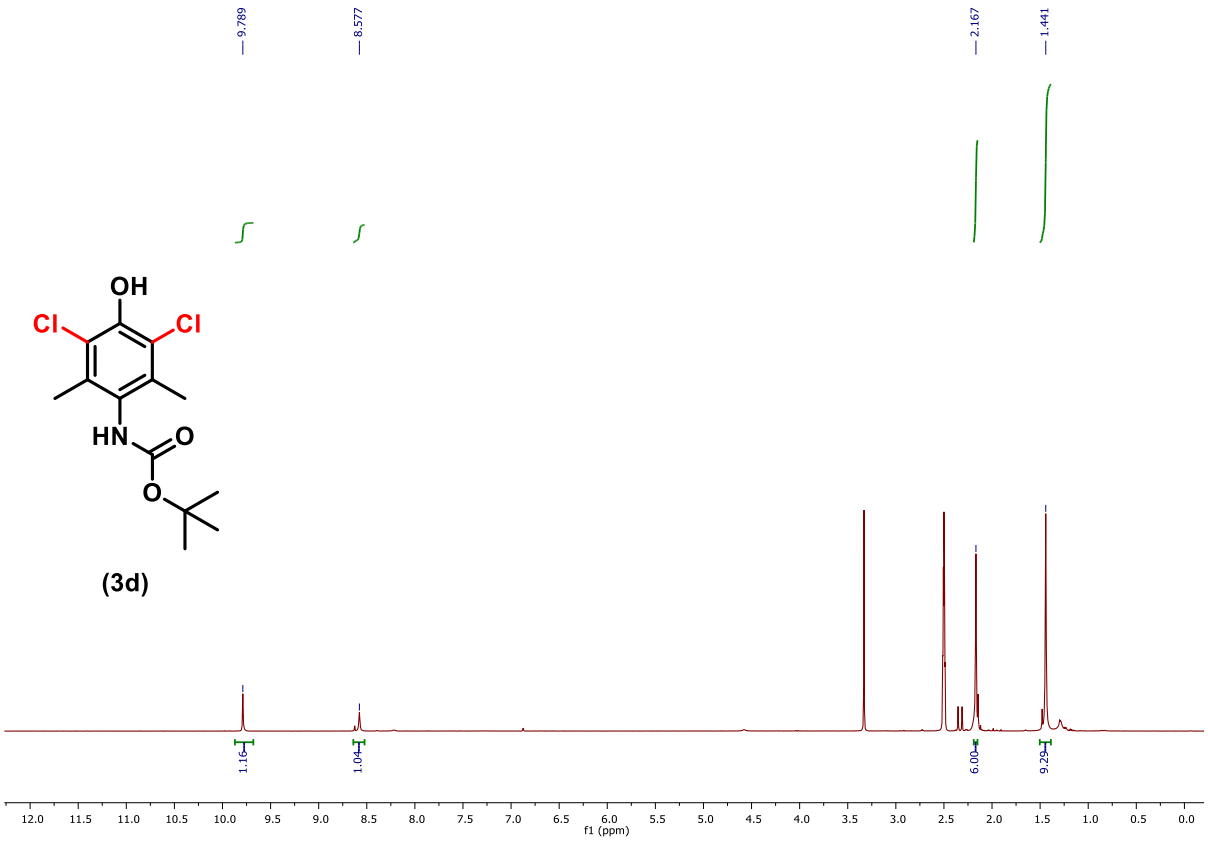
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **3a**



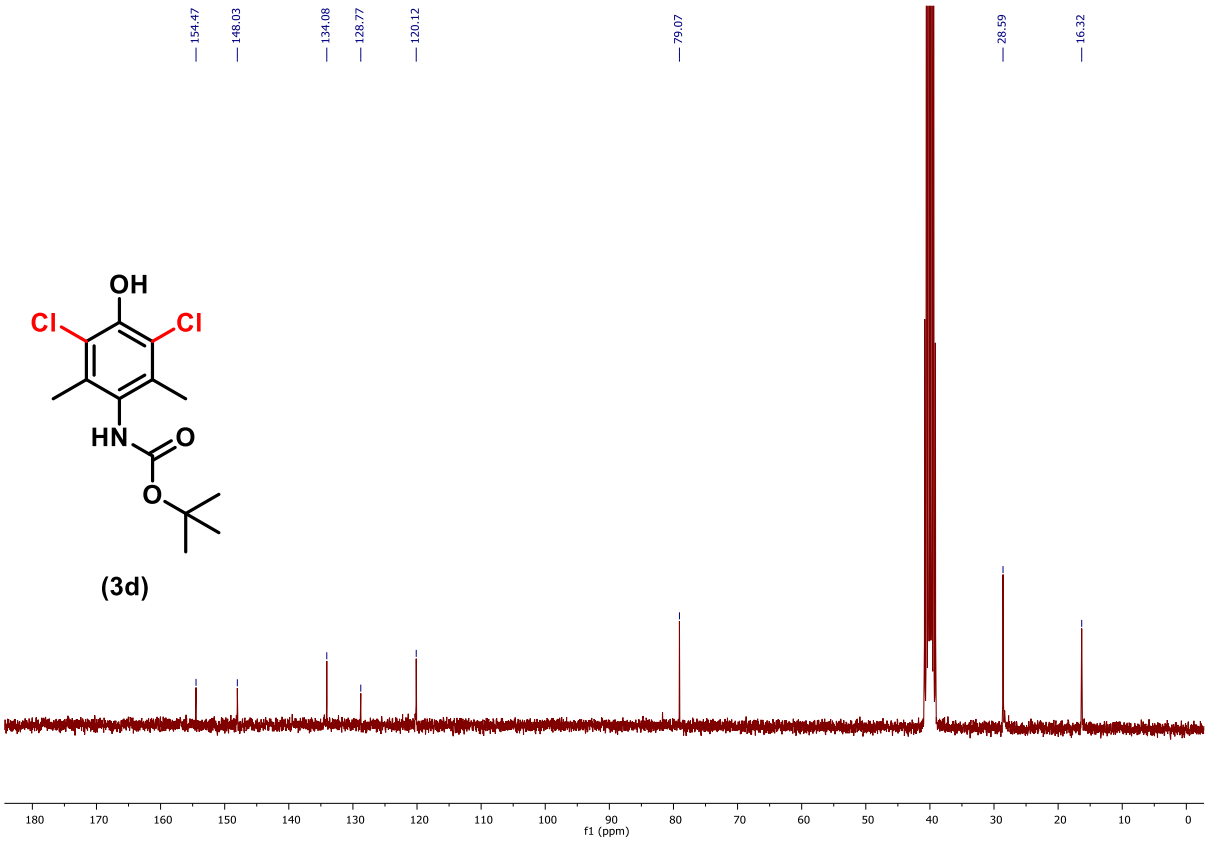
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **3a**



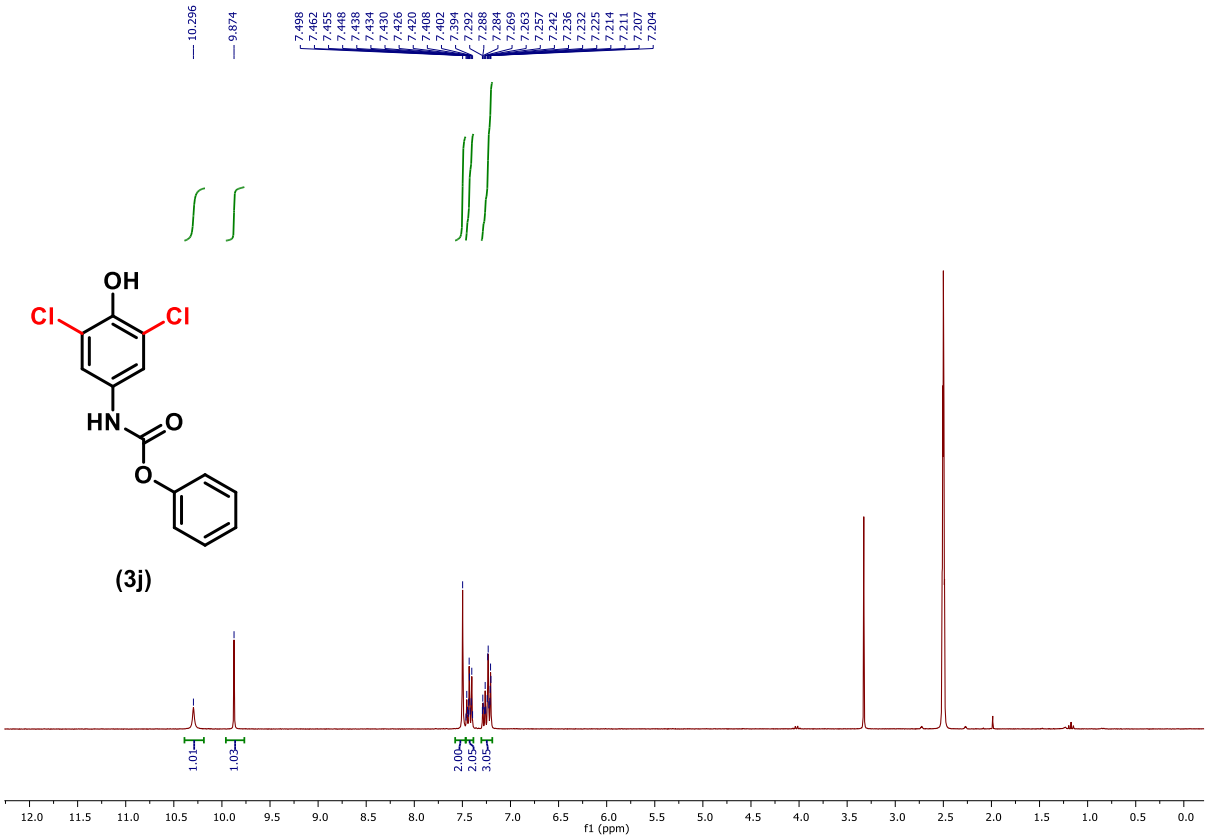
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **3d**



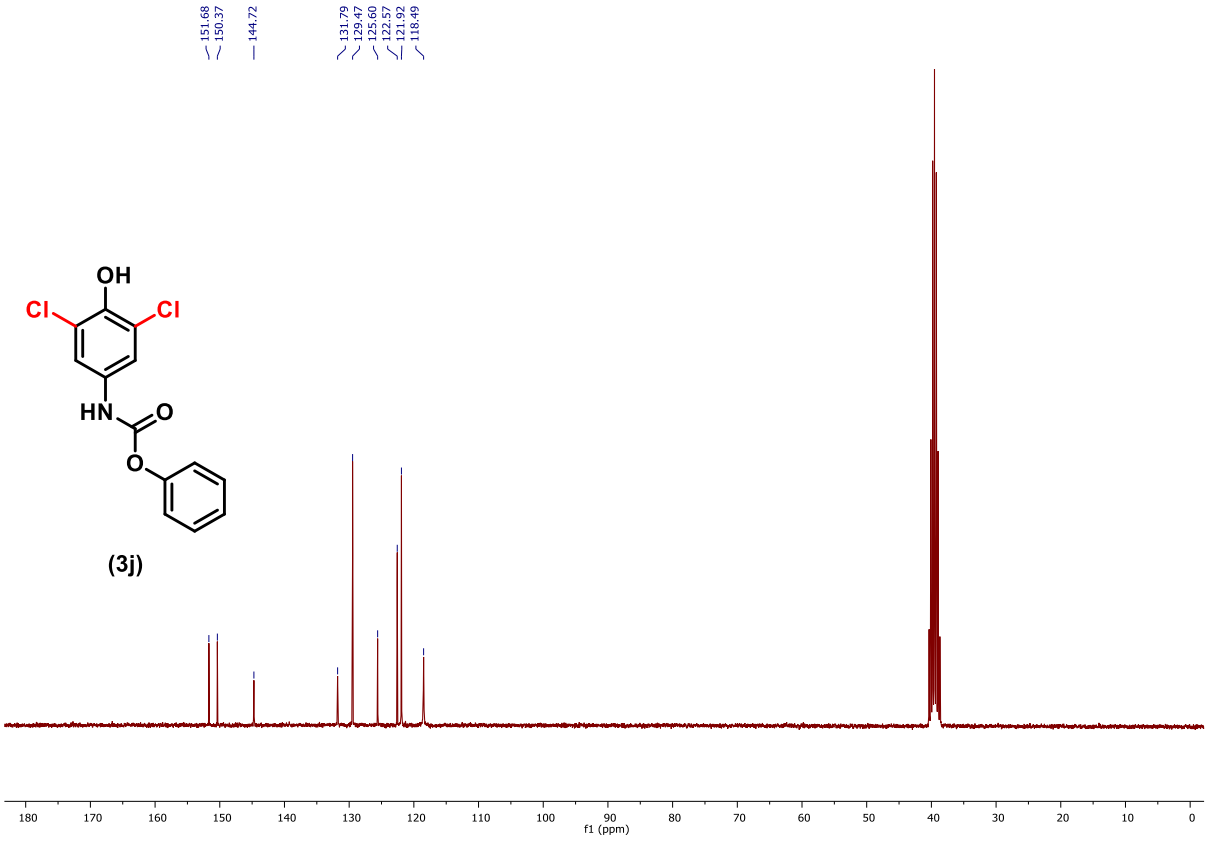
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **3d**



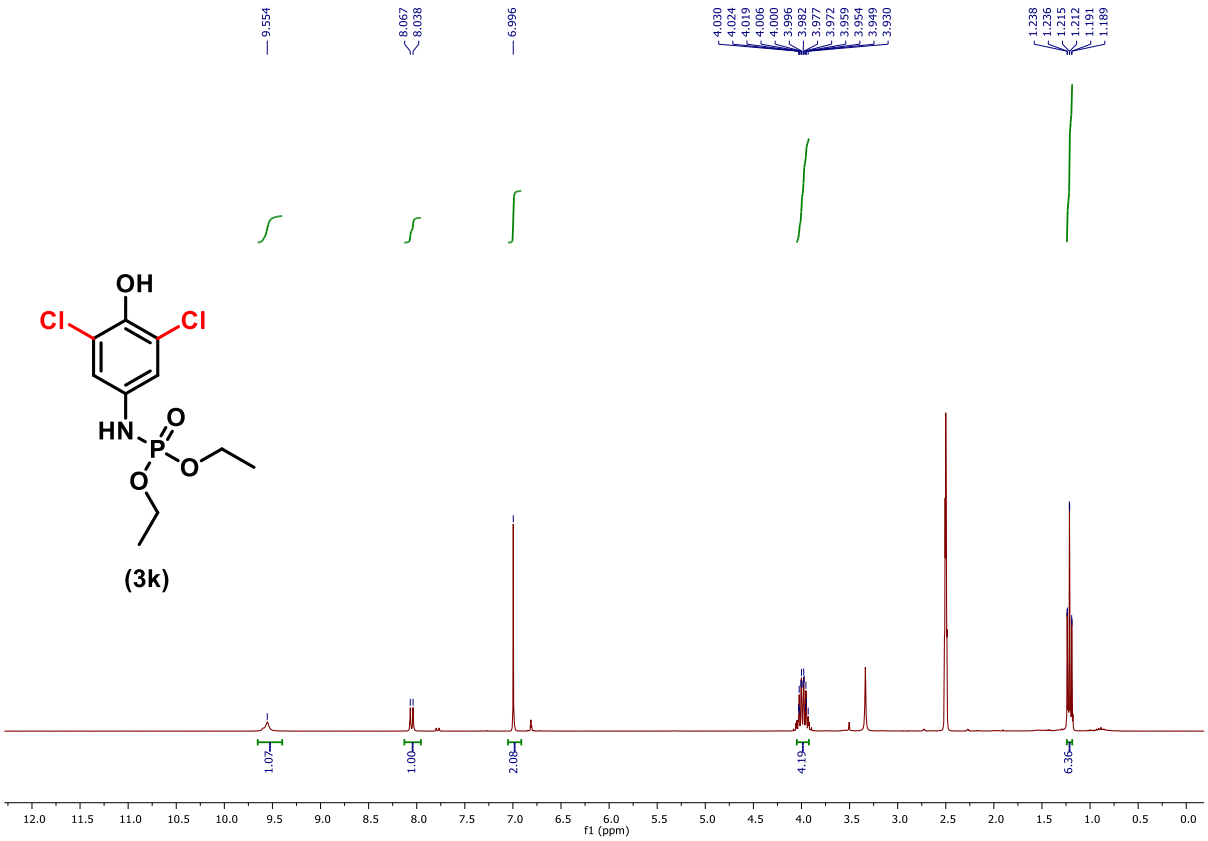
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **3j**



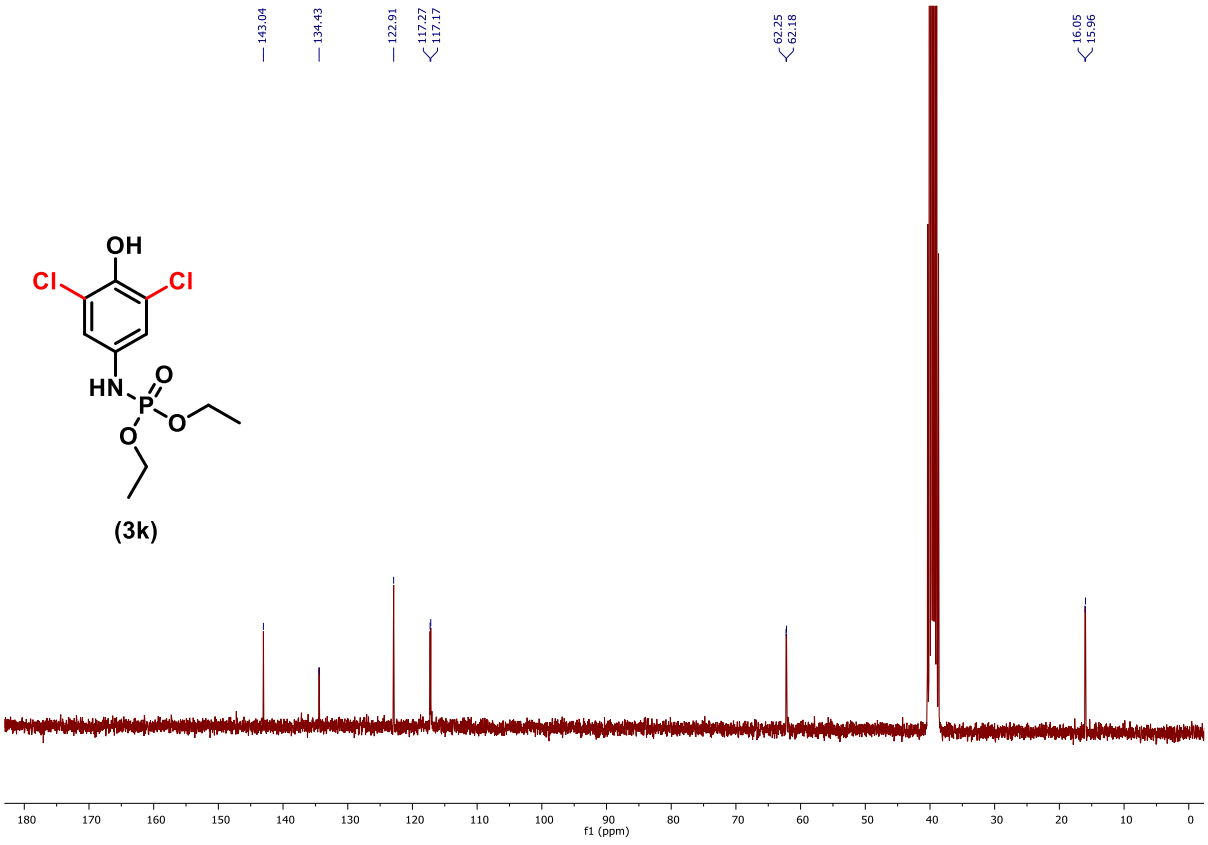
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **3j**



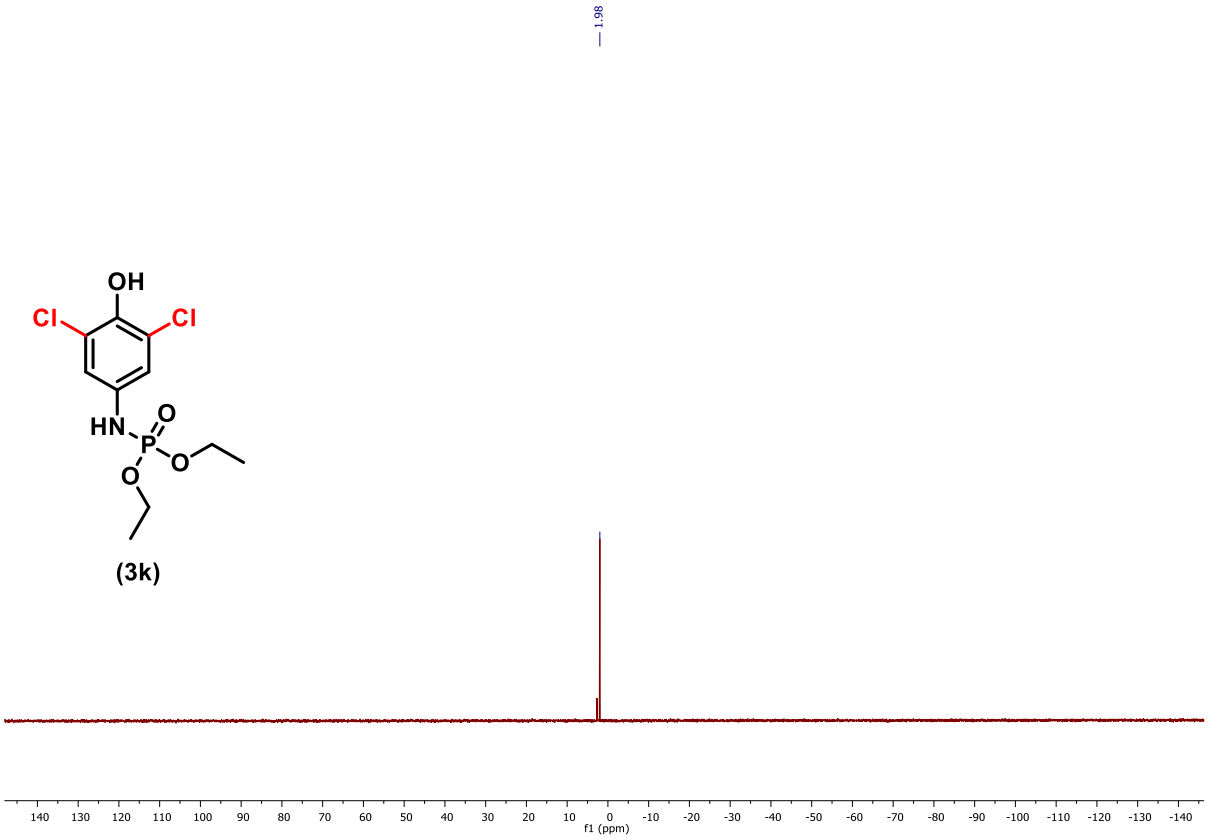
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **3k**



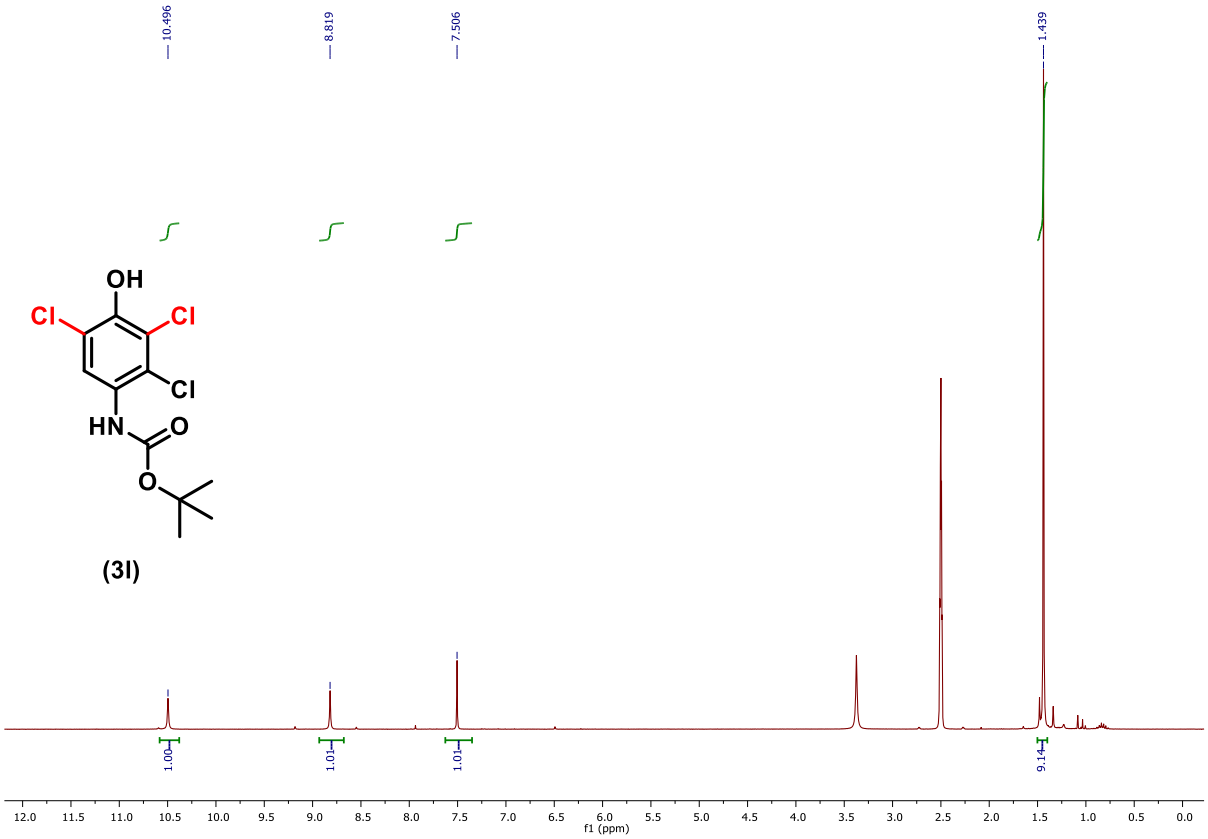
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **3k**



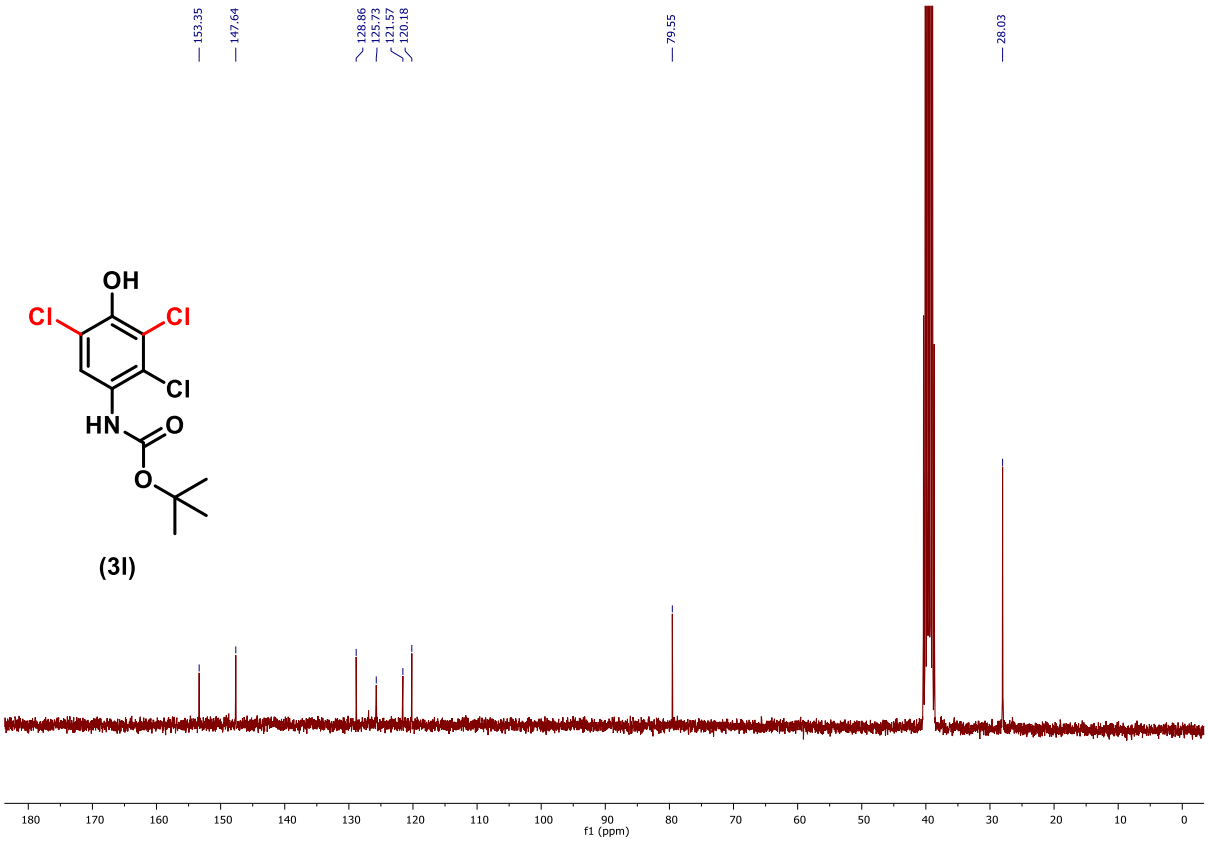
^{31}P NMR spectrum (121 MHz, DMSO-d_6) of **3k**



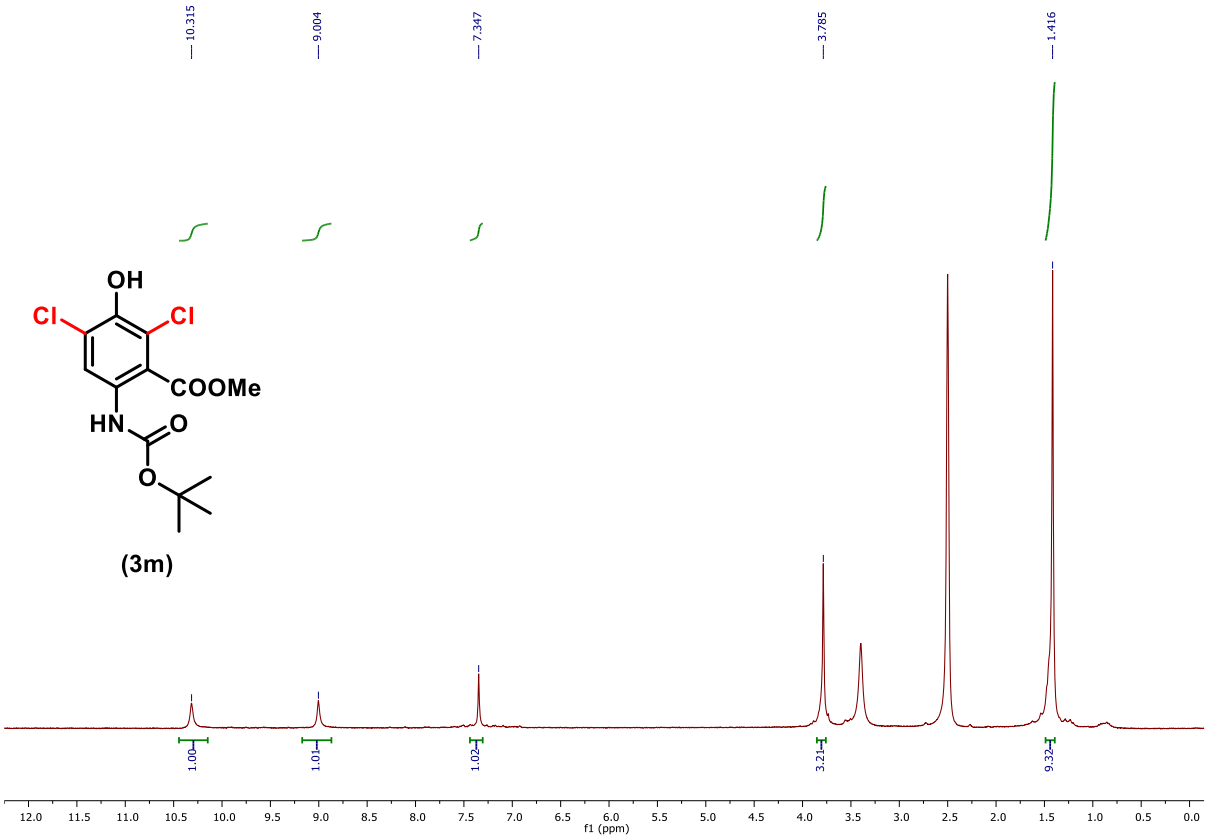
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **3l**



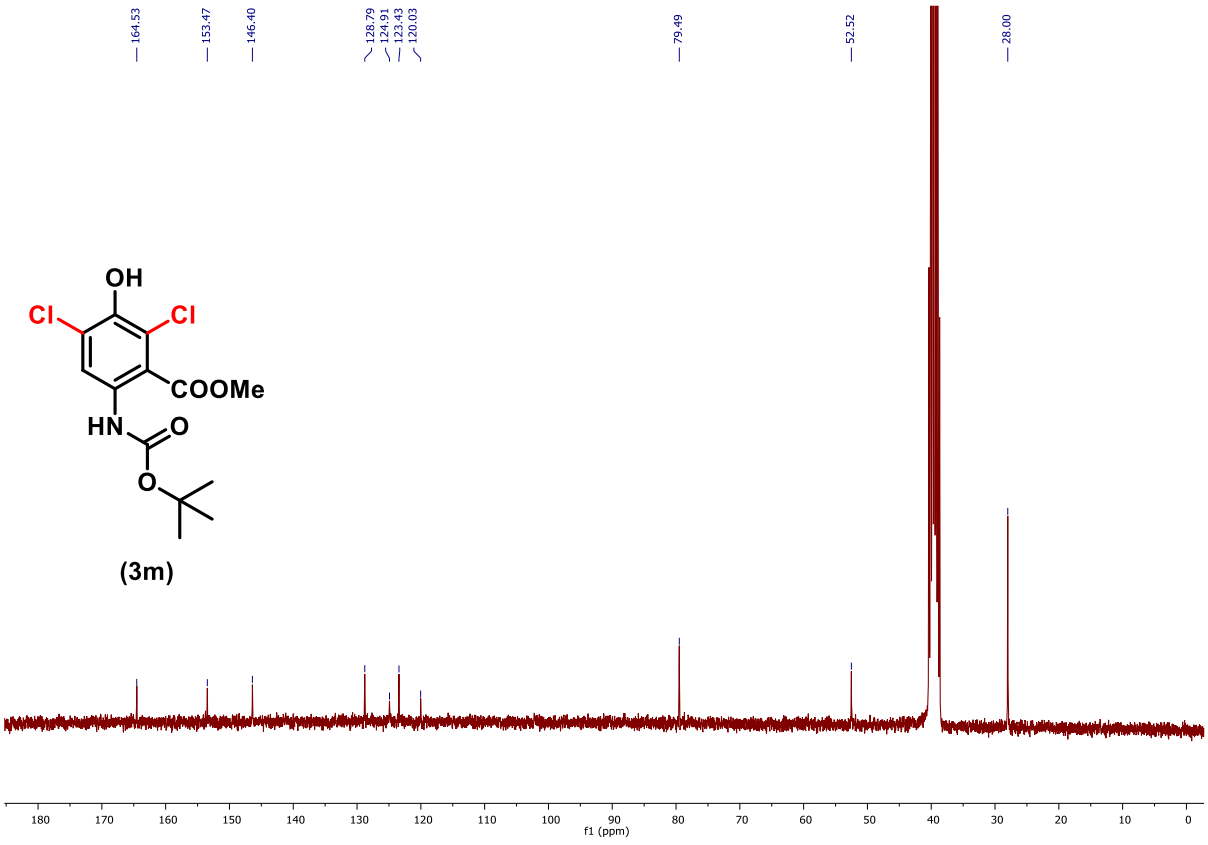
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **3l**



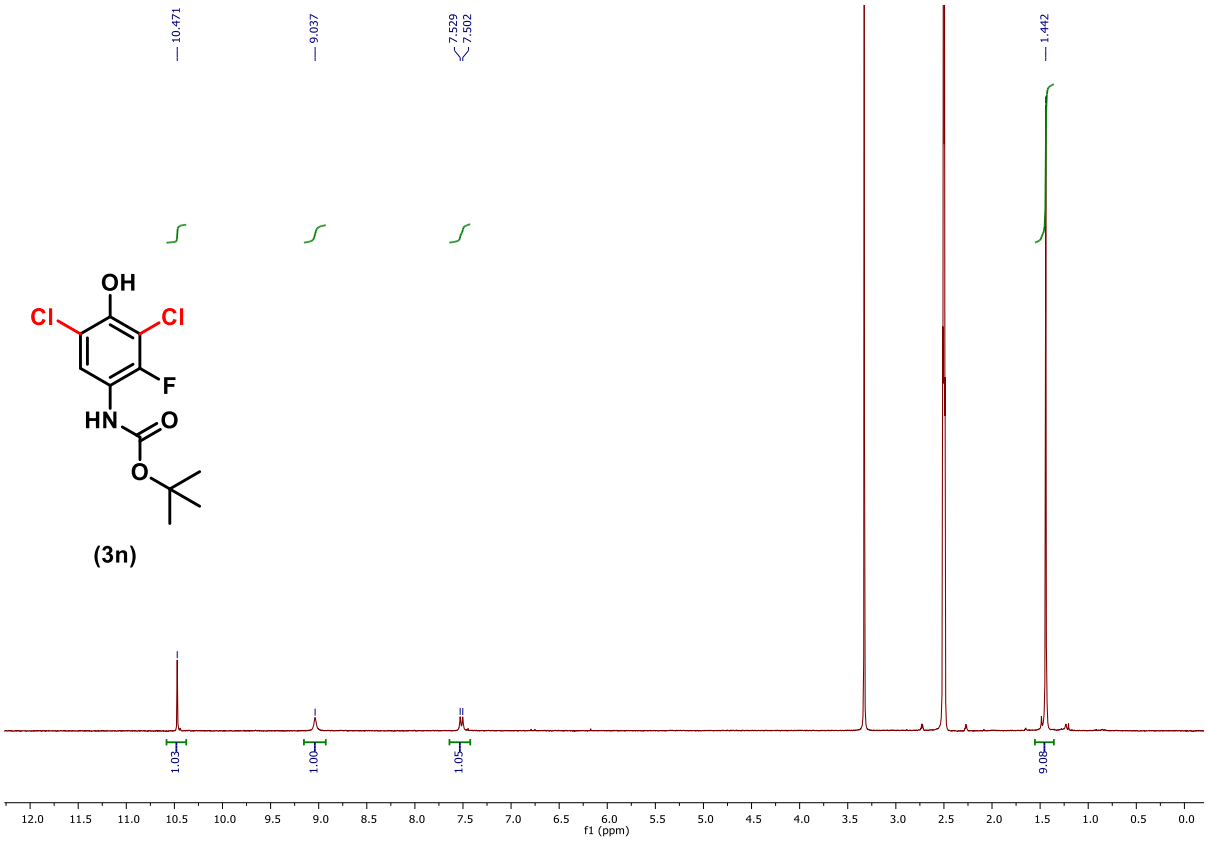
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **3m**



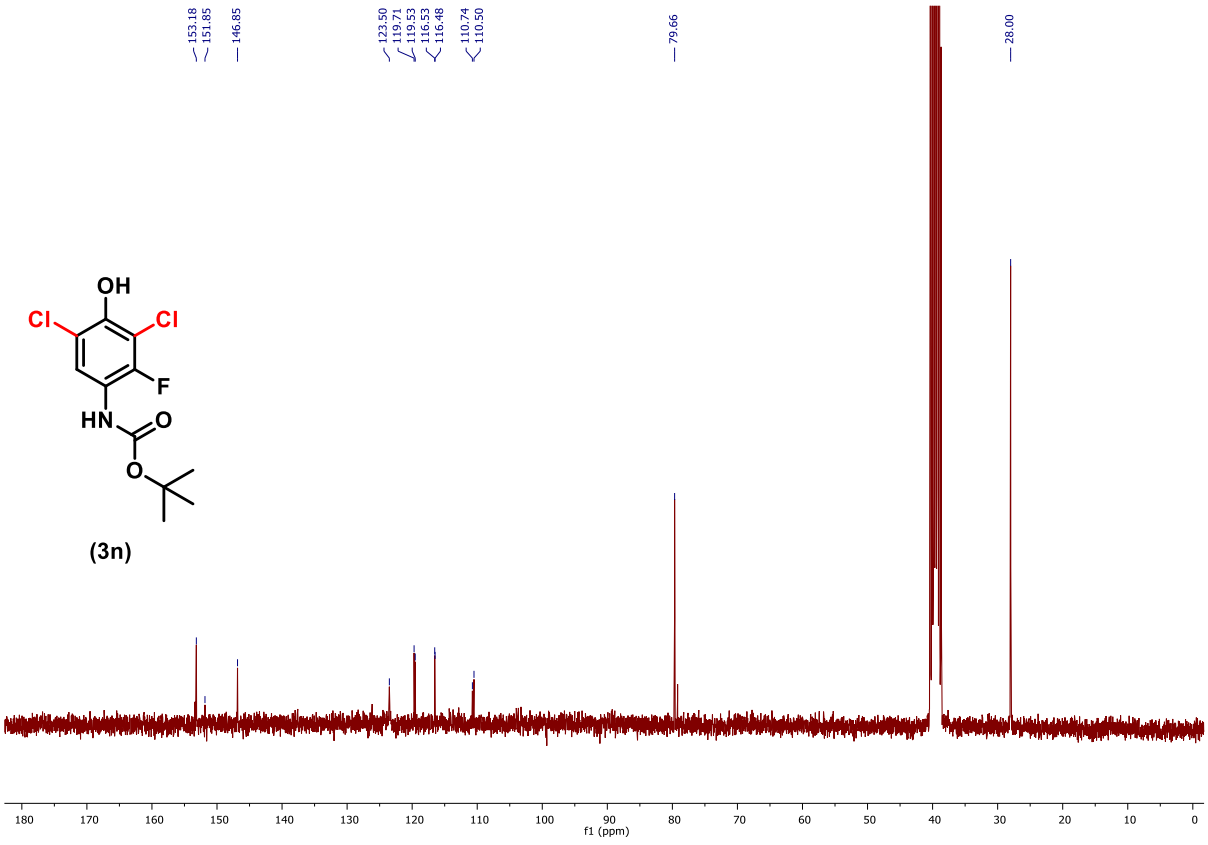
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **3m**



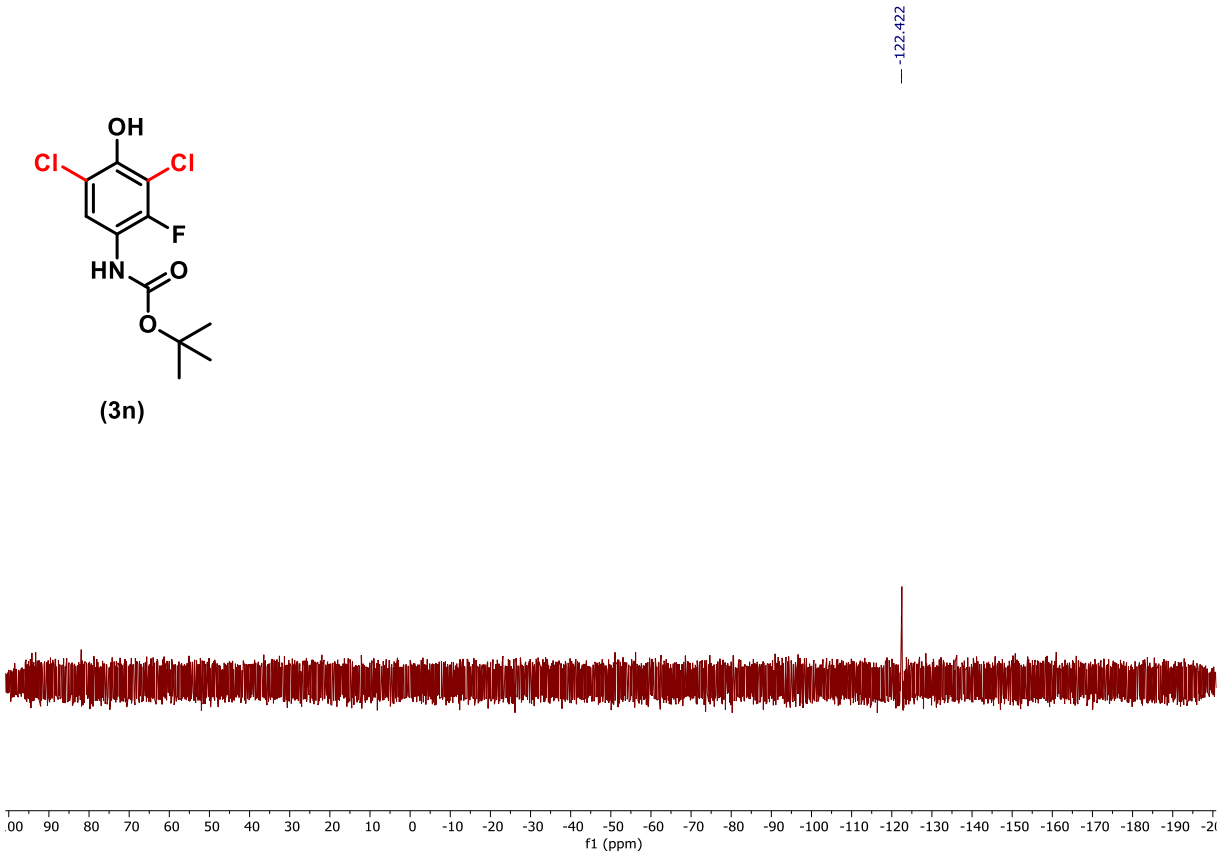
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of 3**n**



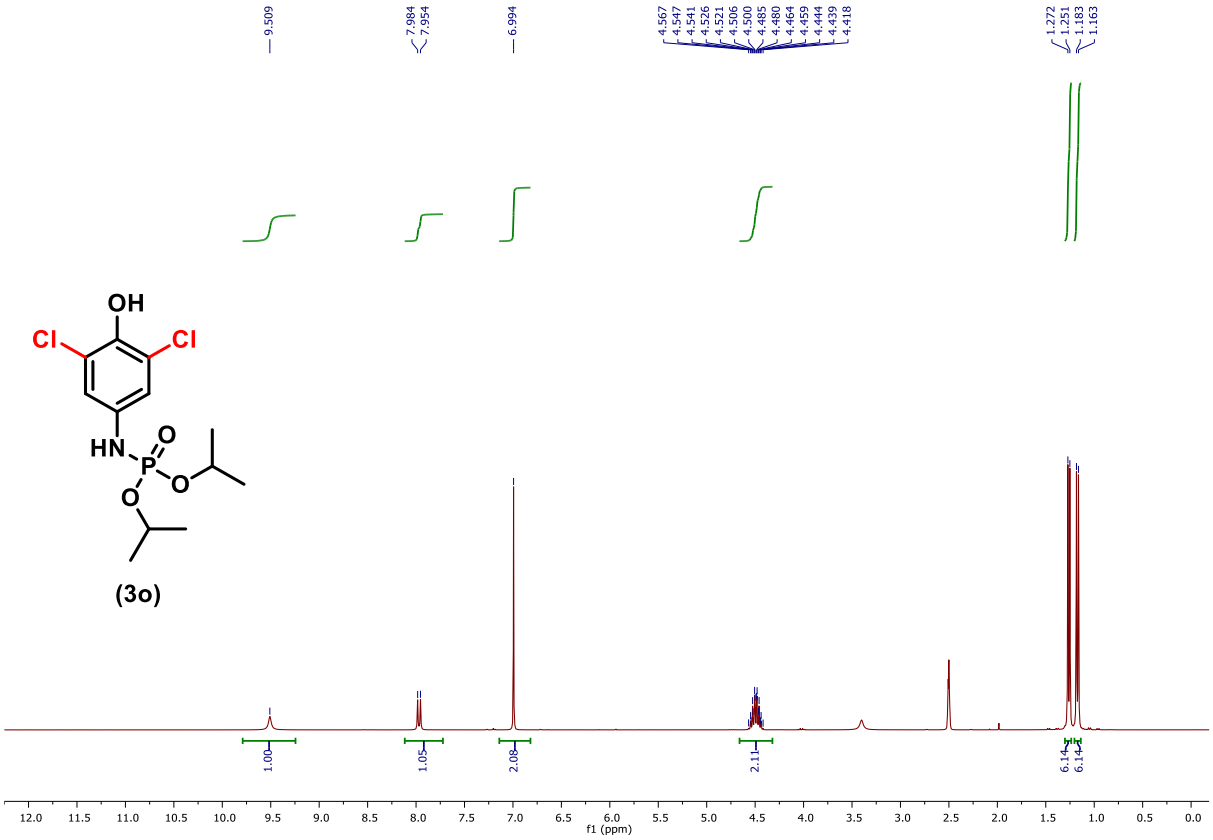
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of 3**n**



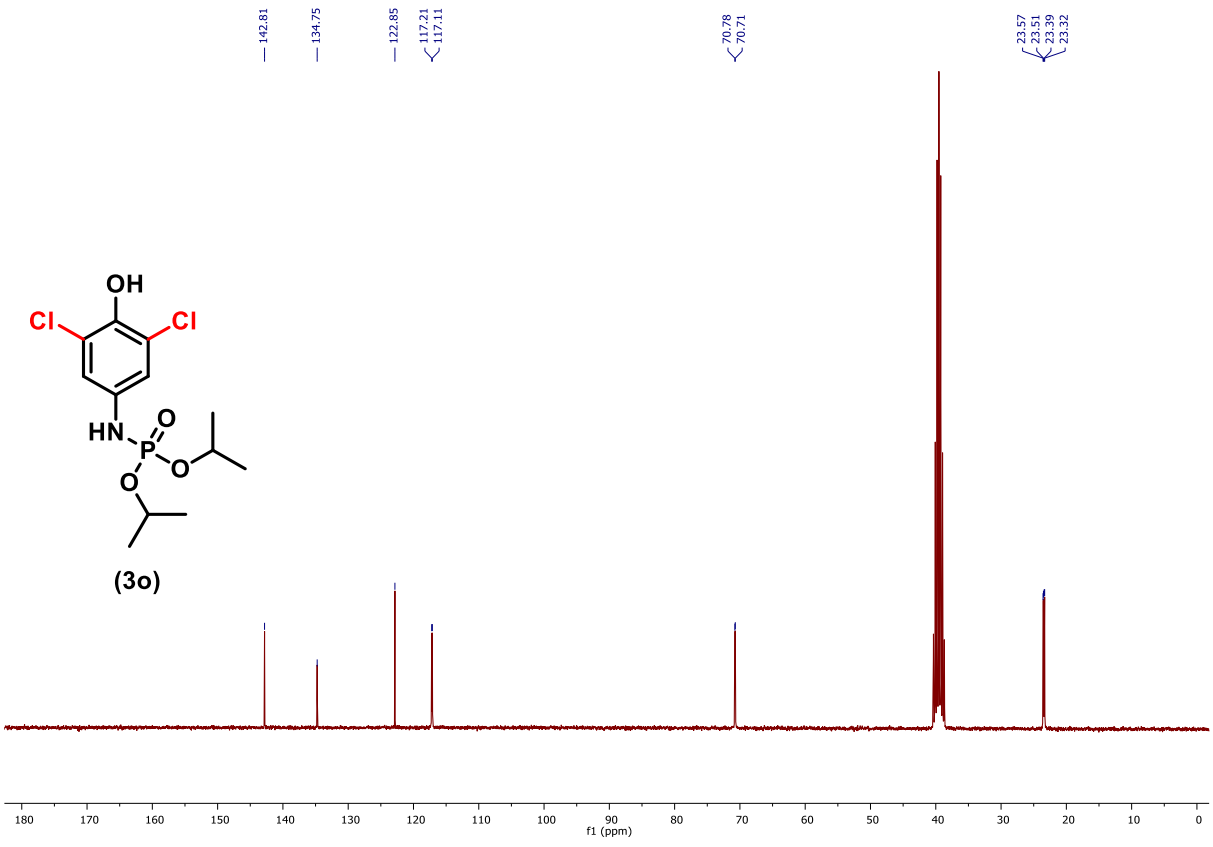
^{19}F NMR spectrum (282 MHz, DMSO-d_6) of **3n**



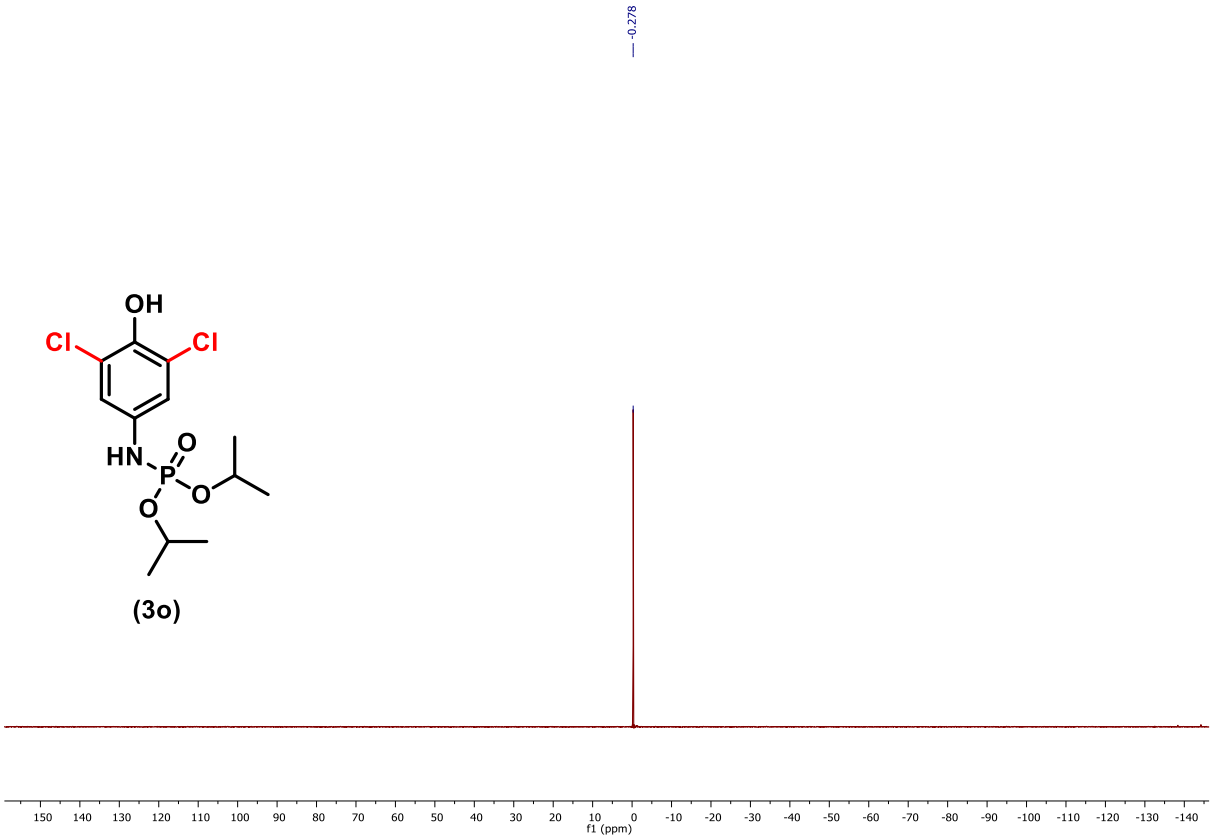
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **3o**



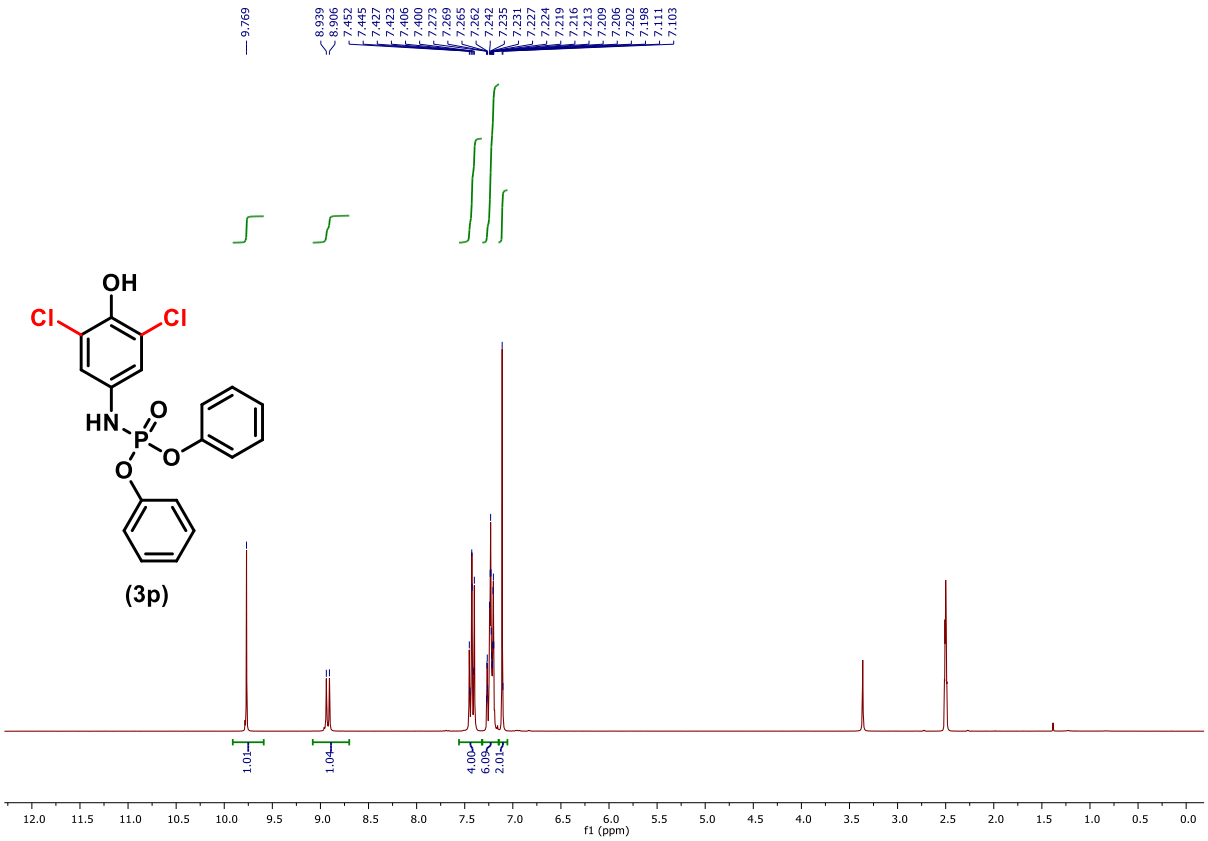
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **3o**



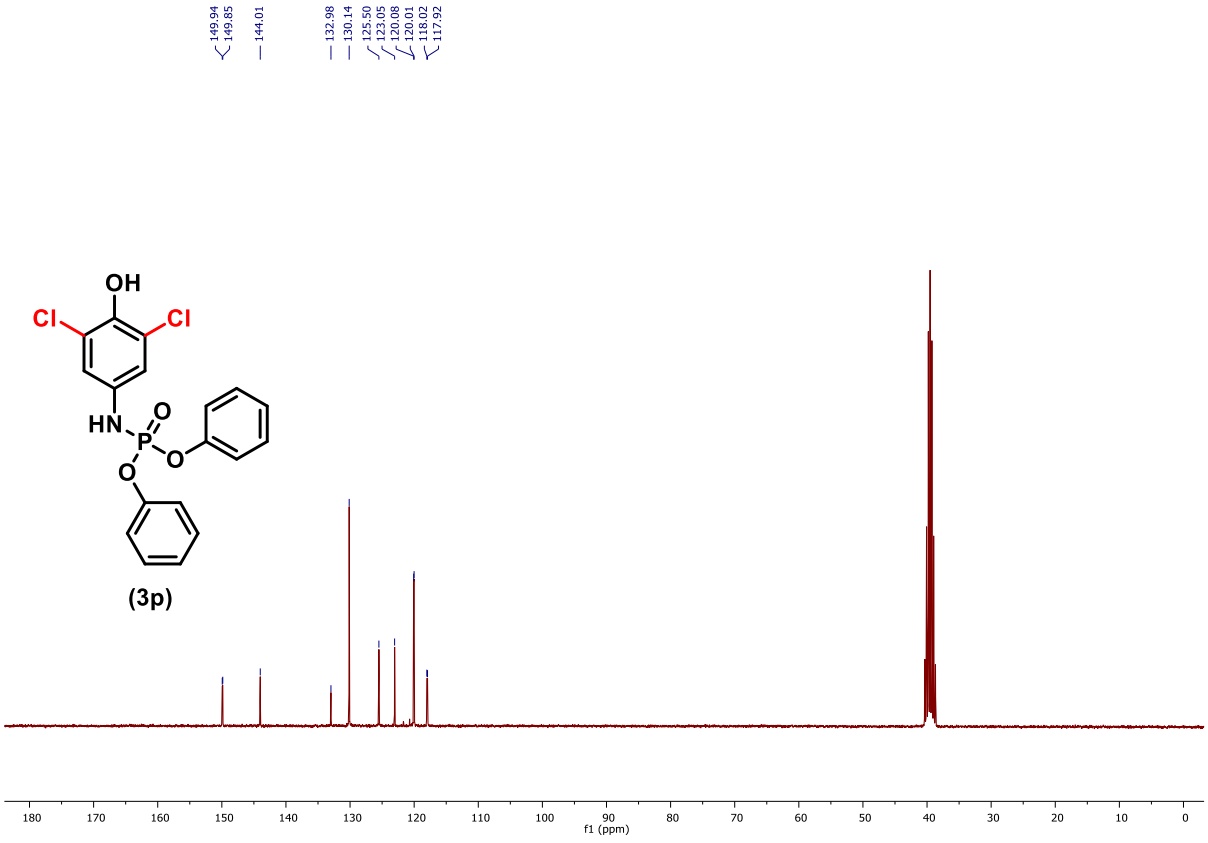
^{31}P NMR spectrum (121 MHz, DMSO-d_6) of **3o**



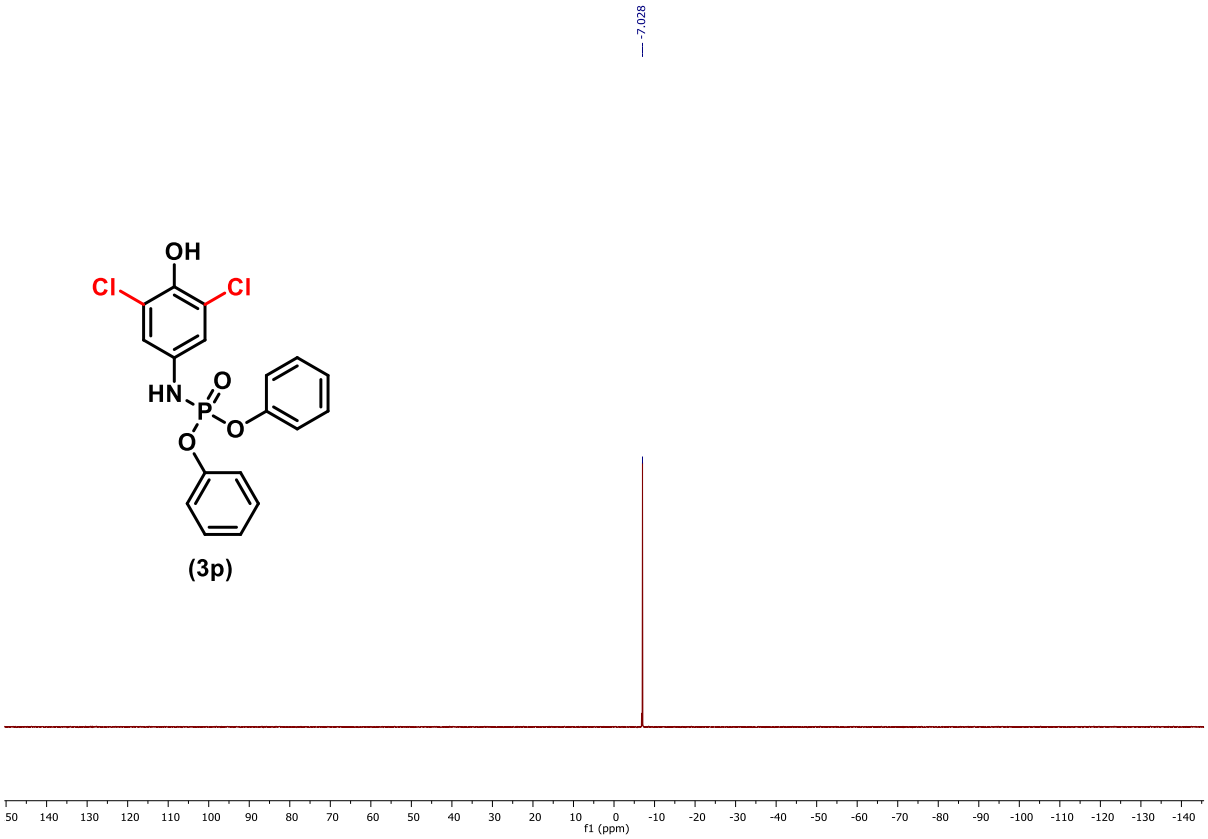
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **3p**



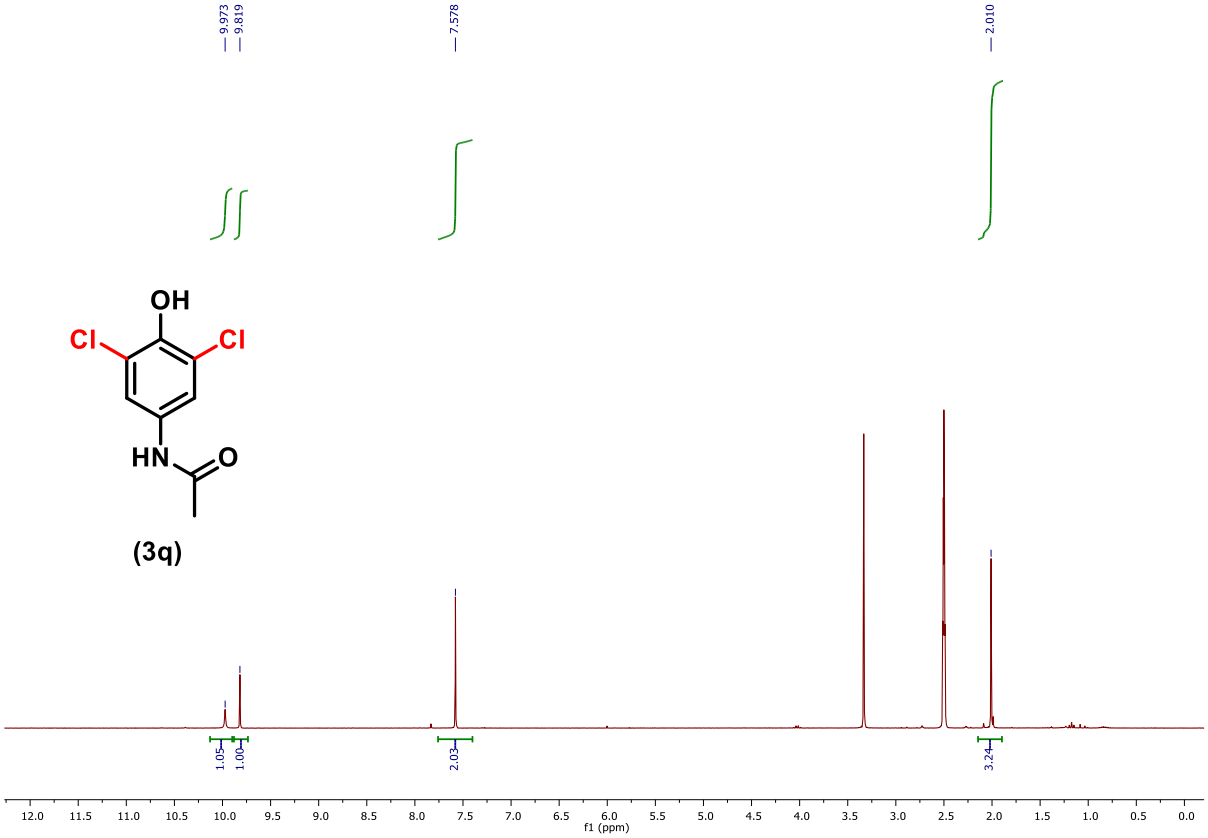
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **3p**



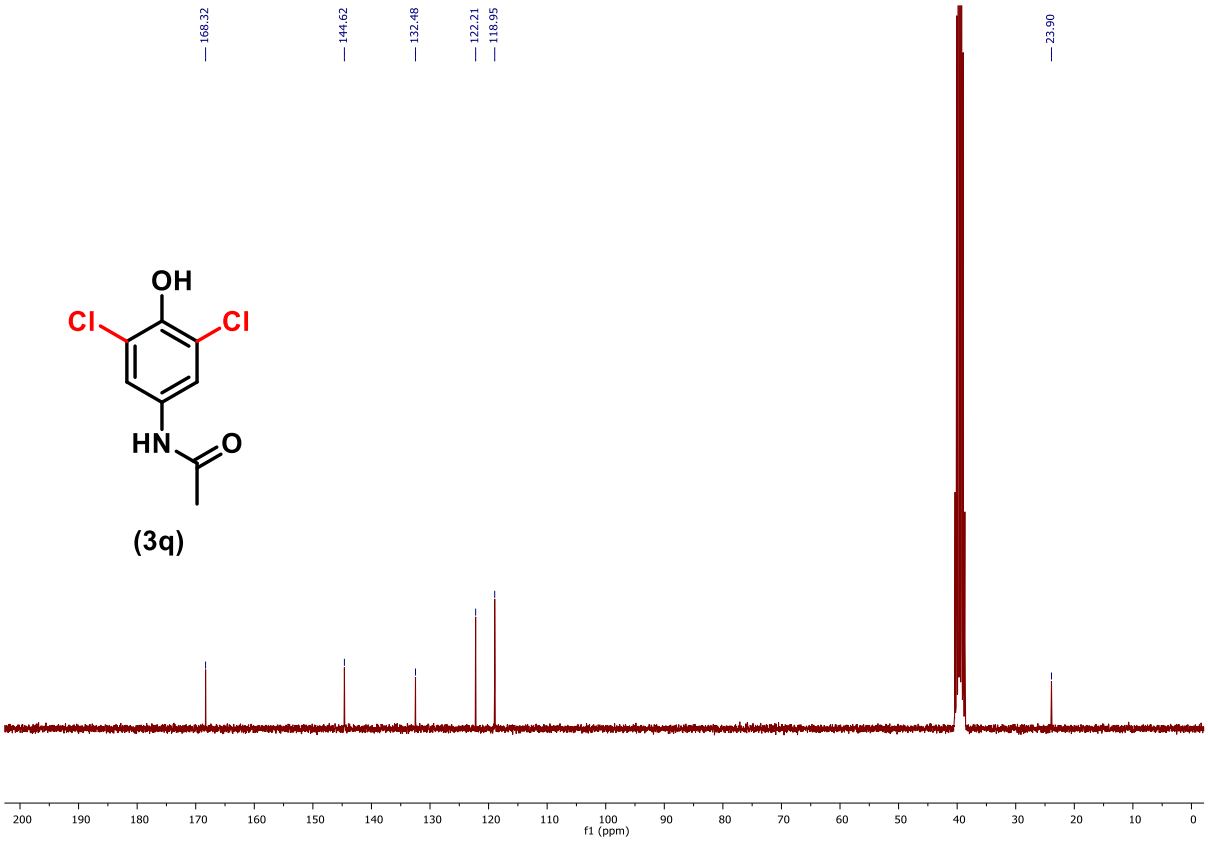
^{31}P NMR spectrum (121 MHz, DMSO-d_6) of **3p**



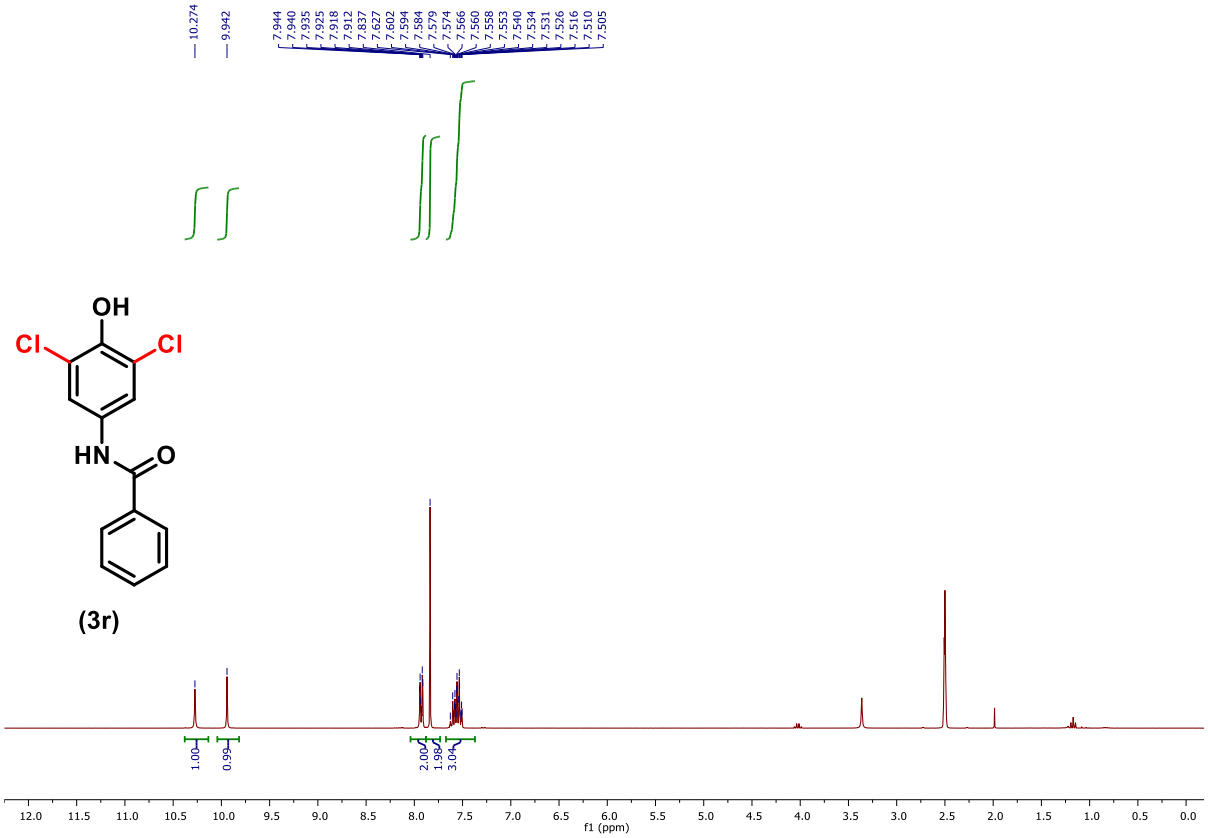
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **3q**



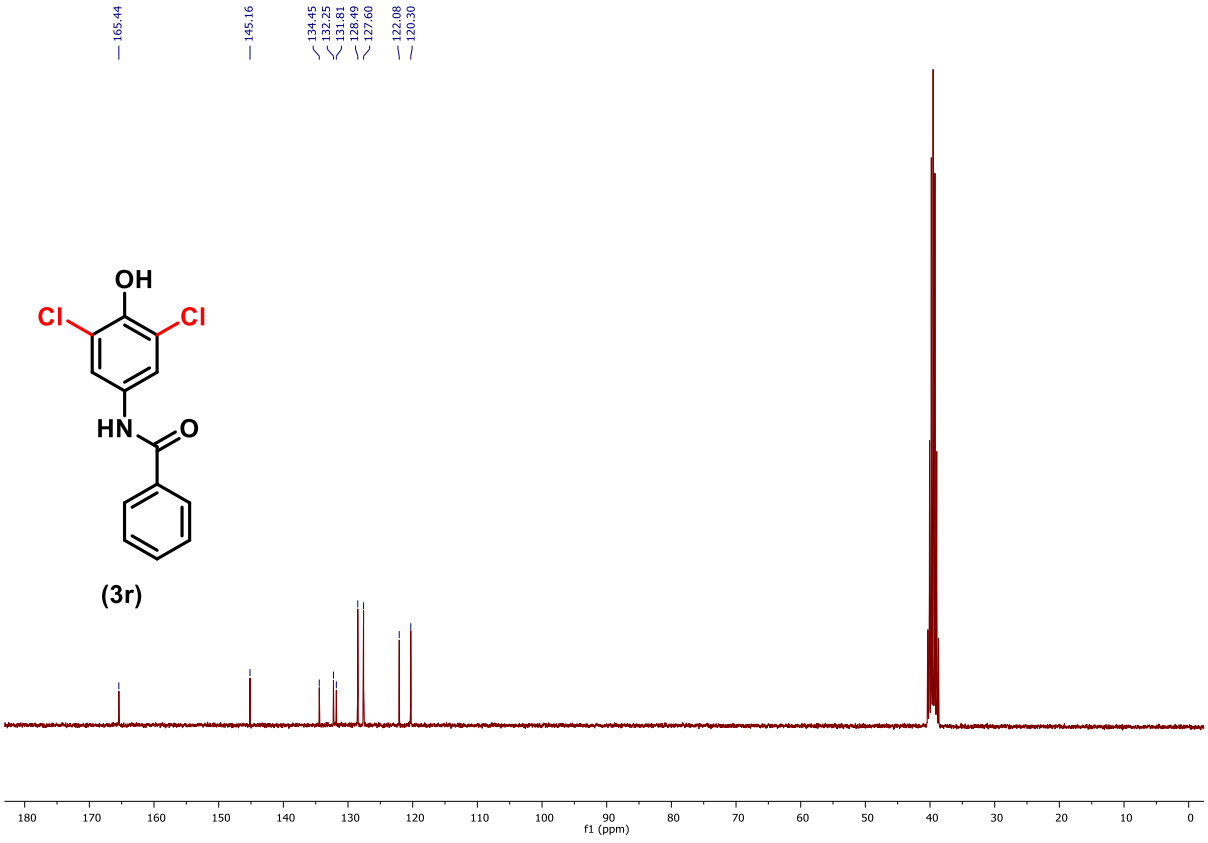
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **3q**



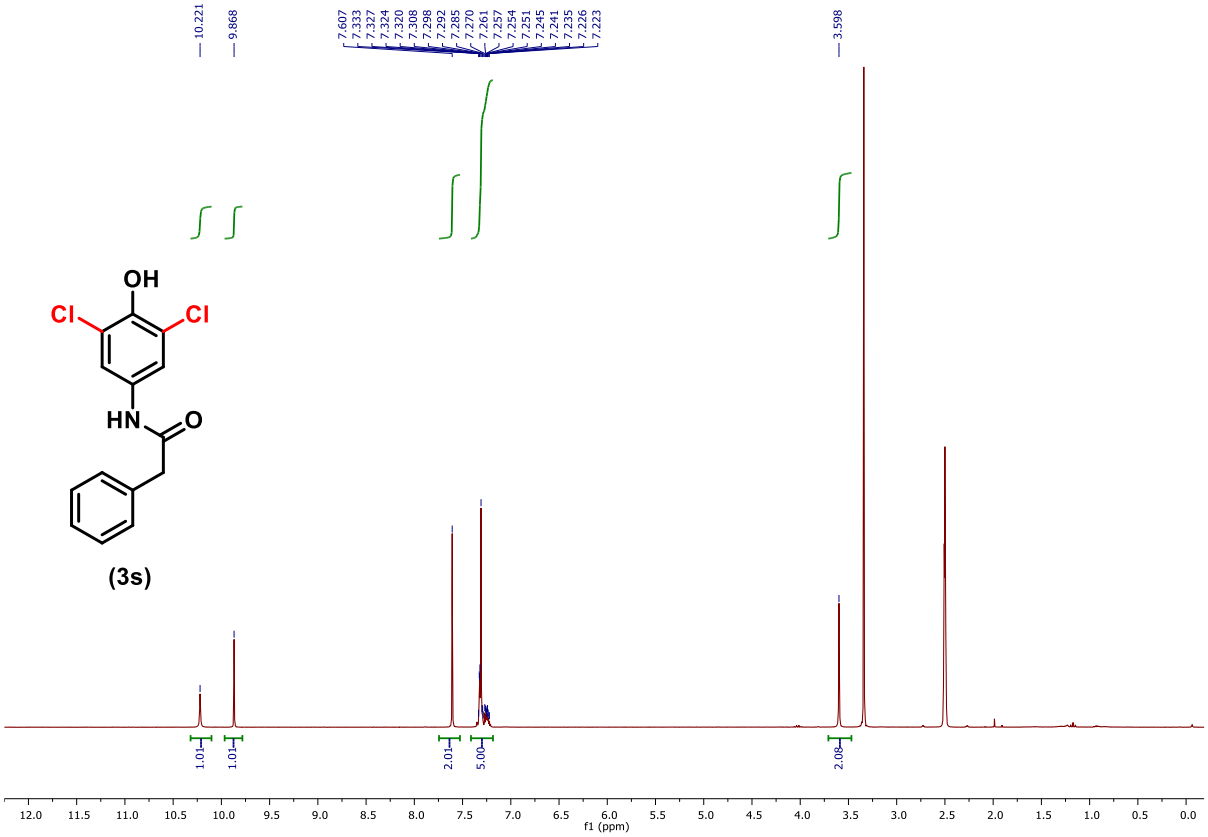
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **3r**



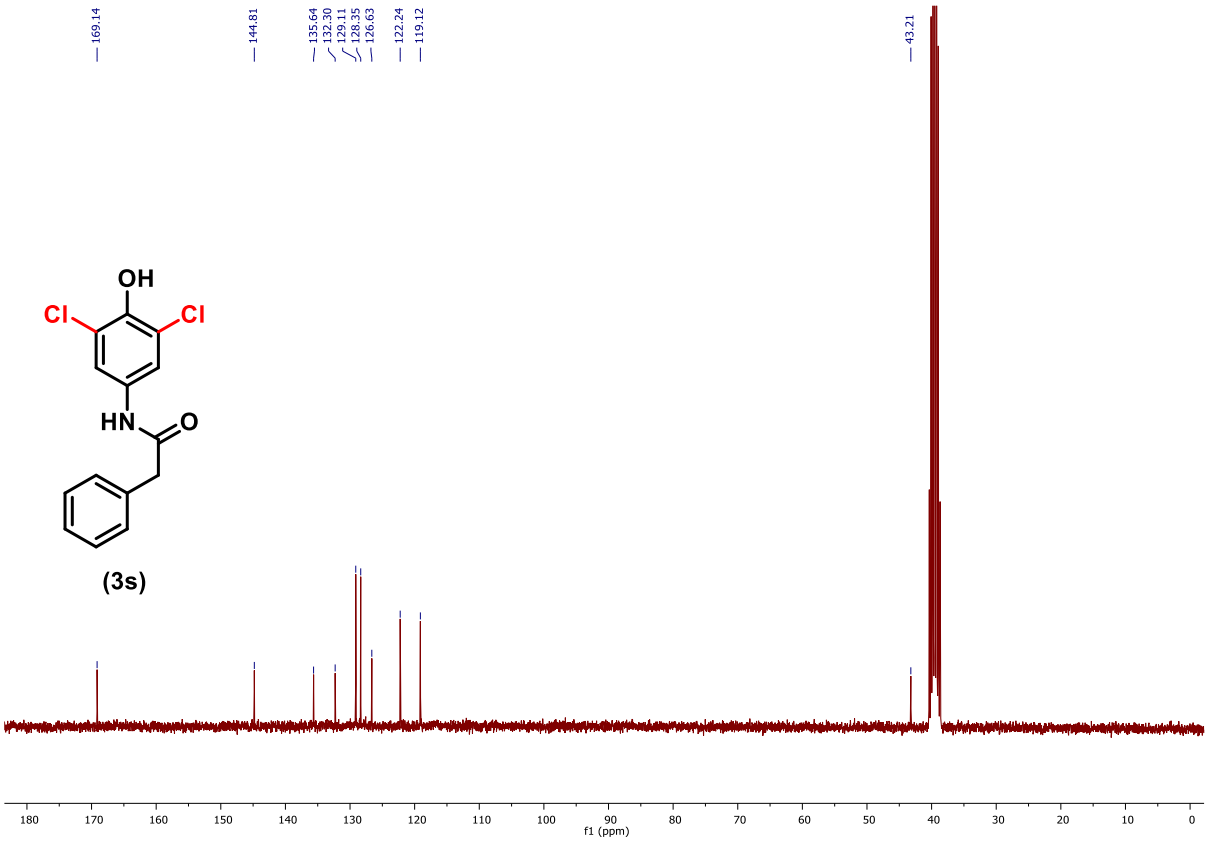
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **3r**



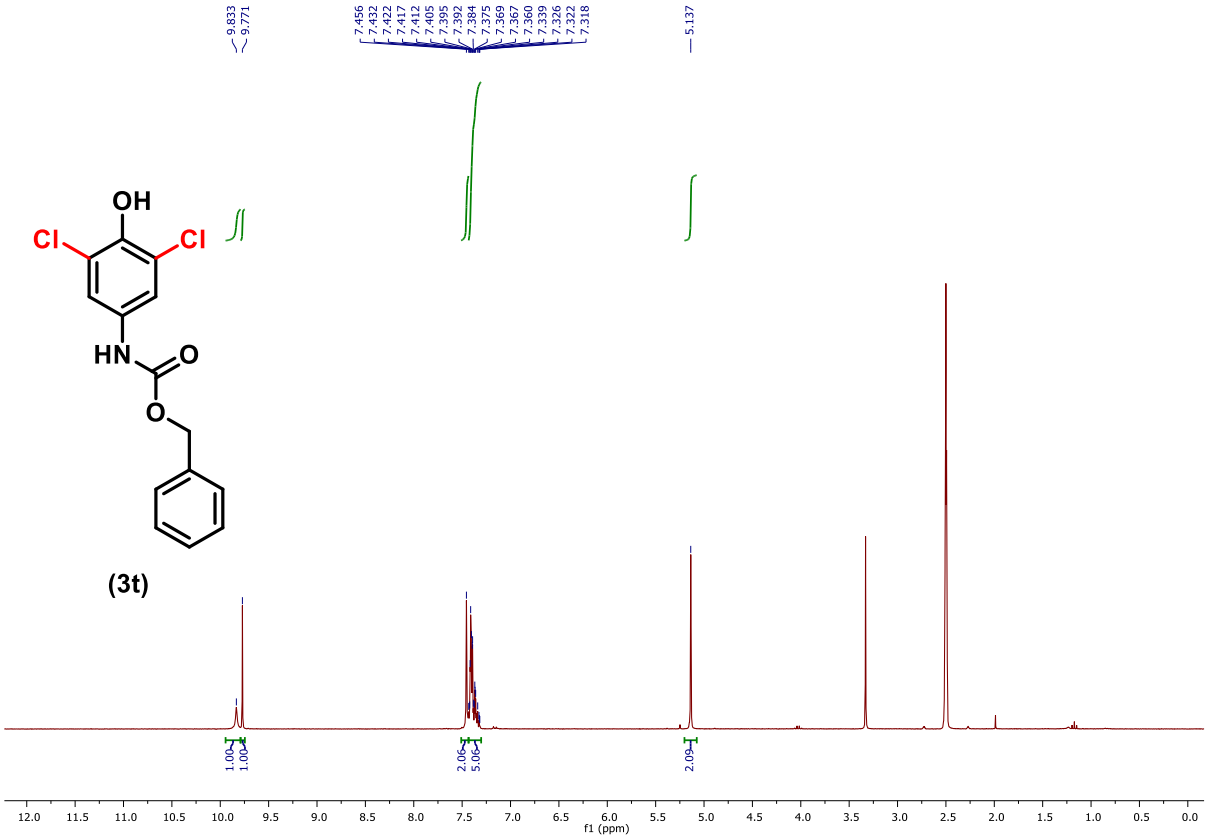
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **3s**



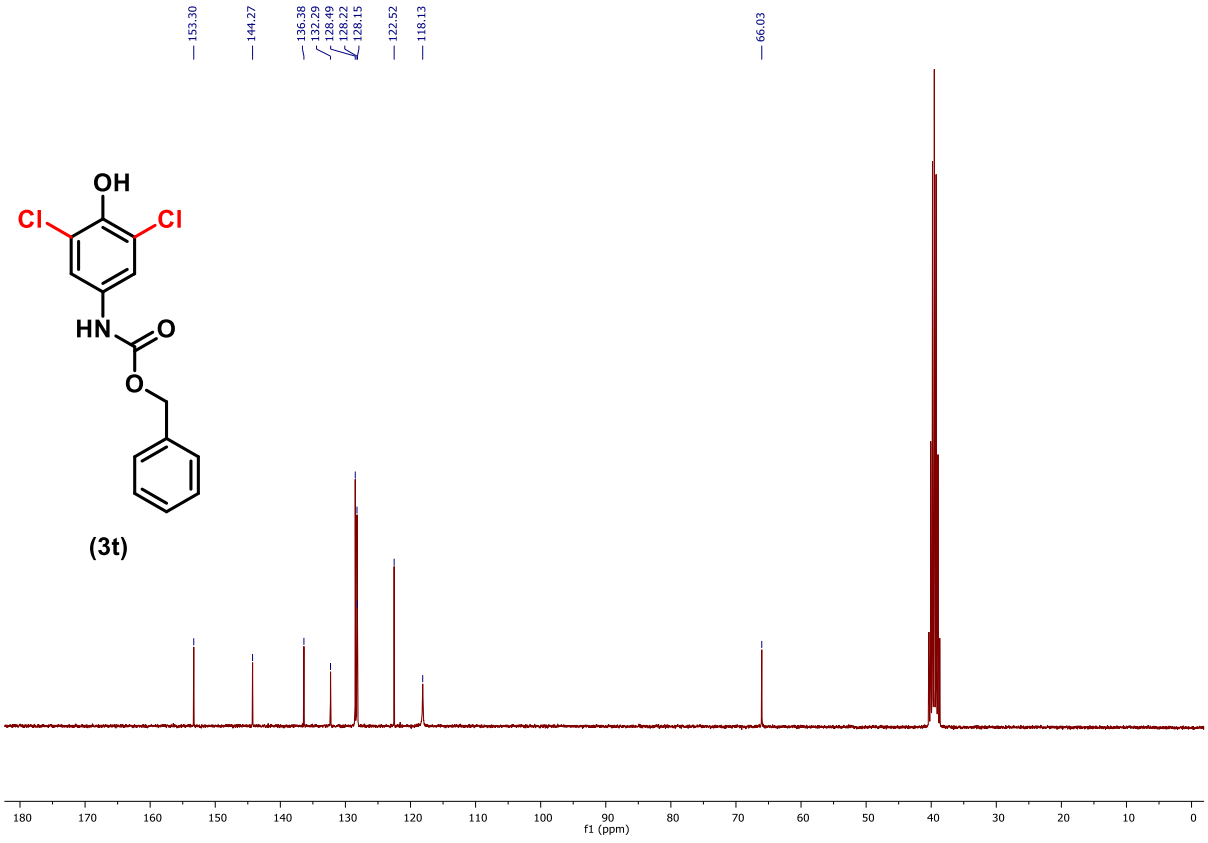
^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **3s**



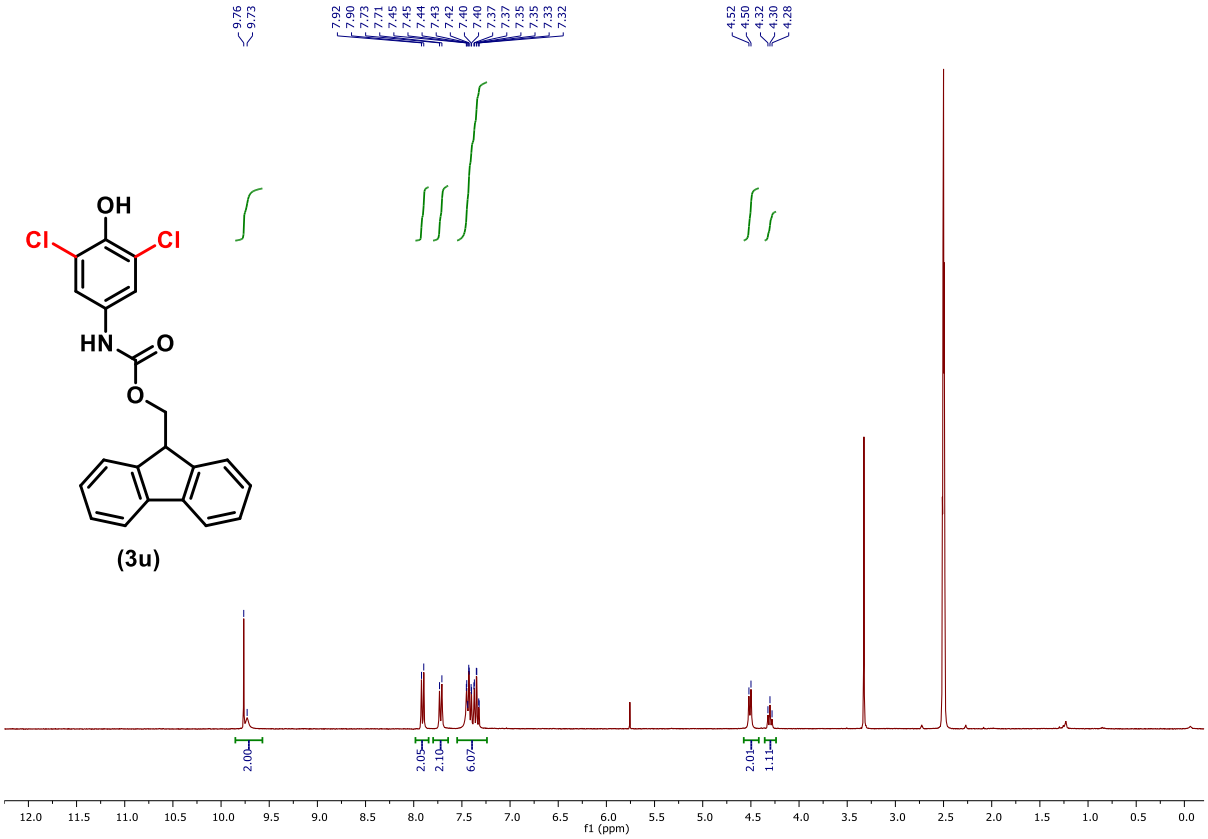
^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **3t**



^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **3t**



^{1}H NMR spectrum (300 MHz, DMSO-d_6) of **3u**



^{13}C NMR {1H} spectrum (75 MHz, DMSO-d_6) of **3u**