

## Supporting Information

### Photocatalyst-free regioselective sulfonamidation of *N*-(2-hydroxyaryl)amides in visible light

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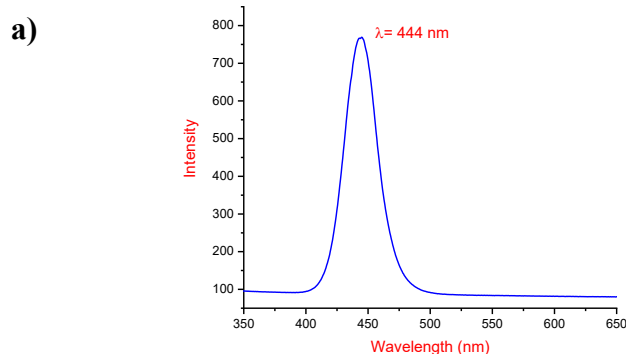
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## 1. General Information

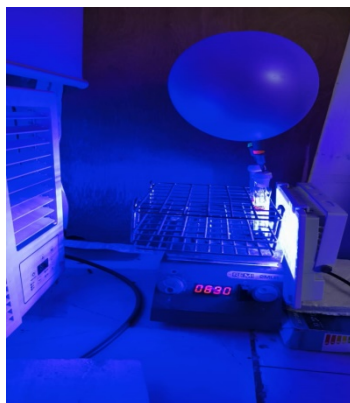
The  $^1\text{H}$  NMR and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded using 400 MHz and 500 MHz spectrometers.  $\text{CDCl}_3$  and  $\text{DMSO-d}_6$  were used as NMR solvent and tetramethylsilane (TMS) was used as an internal standard. Chemical shifts are given in  $\delta$  (ppm). The coupling constants,  $J$ , are reported in Hertz (Hz). Mass spectral data (HRMS) was recorded on electrospray ionization-time of-flight (ESI-TOF) reflectron. All photocatalytic experiments were performed in vessels from borosilicate glass using commercial blue LED(s) as a light source: DEEPSUN; Model No HC2436A1, 50 W, 444 nm. All reagents and solvents were of pure analytical grade. Thin-layer chromatography (TLC) was performed on 60 F254 silica gel, precoated on aluminium plates, and revealed with either a UV lamp ( $\lambda_{\text{max}} = 254$  nm) or iodine vapors. The products were purified by column chromatography on silica gel 100-200 mesh. Melting points were recorded on an Electrothermal digital melting point apparatus.

## 2. LED emission spectra and reaction setup:

The measurement was recorded using Open Spectrophotometer Ava Light-DH-S-BAL Avantes. The light source used for illuminating the reaction vessel is 50 W blue LEDs ( $\lambda_{\text{max}} = 444$  nm). Light source: DEEPSUN; Model No HC2436A1. Material of the irradiation vessel: borosilicate glass. Distance from the light source to the irradiation vessel: 2.5 cm. No filters were used.

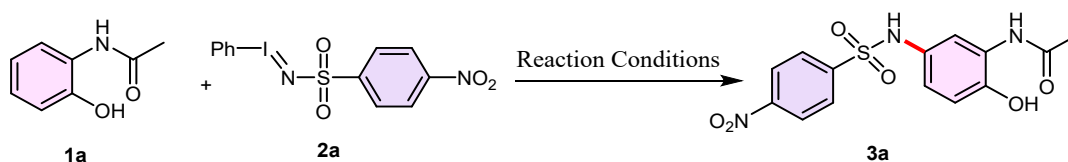


**b**



**Figure S1:** (a) The emission spectrum of 50 W blue LED (b) Reaction setup

### 3. Detailed optimization studies (Tables S1-S3)



**Table S1.** Solvent optimization<sup>a</sup>

Solvent	Yield <sup>b</sup>
MeCN	21
MeOH	NR
DMSO	NR
1,4-dioxane	NR
Toluene	NR
Xylene	NR
Chlorobenzene	NR
DCM	64
DCE	34
CHCl <sub>3</sub>	39

<sup>a</sup>Reaction conditions: **1a** (20 mg, 0.13 mmol, 1.0 equiv.), **2a** (68 mg, 0.17 mmol, 1.3 equiv.), and I<sub>2</sub> (42 mg, 0.17 mmol, 1.3 equiv.), Solvent = 2.0 mL, 50 W blue LEDs, rt, open-air, 17 h. <sup>b</sup>Isolated yield, NR = No reaction.

**Table S2.** Optimization of the stoichiometry of substrates<sup>a</sup>

<b>1a (equiv.)</b>	<b>2a (equiv.)</b>	<b>I<sub>2</sub> (equiv.)</b>	<b>Yield<sup>b</sup></b>
1.0	1.0	1.0	46
1.0	1.3	1.3	64
1.0	2.0	2.0	66
1.0	1.3	0.6	37
1.0	1.3	0.2	18

<sup>a</sup>Reaction conditions: DCM = 2.0 mL, 50 W blue LEDs, rt, open-air, 17 h. <sup>b</sup>Isolated yield.

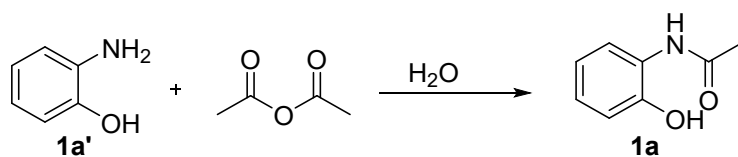
**Table S3.** Effect of light source, atmosphere and time<sup>a</sup>

<b>Light Source</b>	<b>Atmosphere</b>	<b>Time (h)</b>	<b>Yield(%)<sup>b</sup></b>
50 W blue LEDs	Open air	17	64
10 W blue LEDs	Open air	17	52
Green LEDs	Open air	17	22
50 W blue LEDs	O <sub>2</sub>	17	61
50 W blue LEDs	N <sub>2</sub>	17	58
50 W blue LEDs	Open air	24	64
50 W blue LEDs	Open air	10	46

<sup>a</sup>Reaction conditions: **1a** (20 mg, 0.13 mmol, 1.0 equiv.), **2a** (68 mg, 0.17 mmol, 1.3 equiv.), and I<sub>2</sub> (42 mg, 0.17 mmol, 1.3 equiv.), DCM = 2.0 mL, light source, rt, atmosphere, time. <sup>b</sup>Isolated yield, NR = No reaction

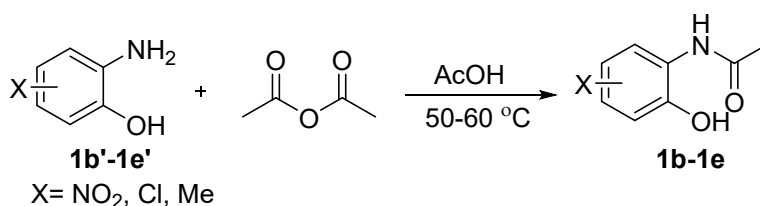
#### 4. Procedure A: Synthesis and characterization of 2-acetaminophenol derivatives

##### Procedure A.1



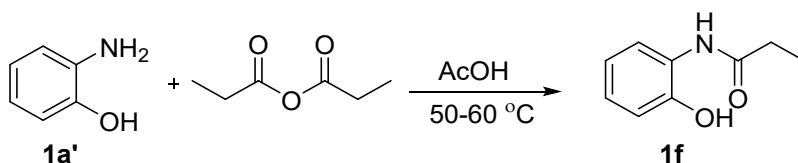
A round bottom flask containing the solution of aminophenol (1090 mg, 10.0 mmol, 1.0 equiv.) (**1a'**) in water was stirred at room temperature, and acetic anhydride (1122 mg, 11 mmol, 1.1 equiv.) was added dropwise. The reaction mixture was stirred for about 20 min till full consumption of substrates was observed on TLC. After reaction completion, the contents were poured into ice water and the aqueous layer was separated with EtOAc (3 x 30 mL). Na<sub>2</sub>SO<sub>4</sub> was used to dry the organic layer and resultant solution was concentrated in vacuo. The resulting residue was purified by column chromatography on silica gel (EtOAc/hexane) to give the desired product **1a**.<sup>[1]</sup>

##### Procedure A.2



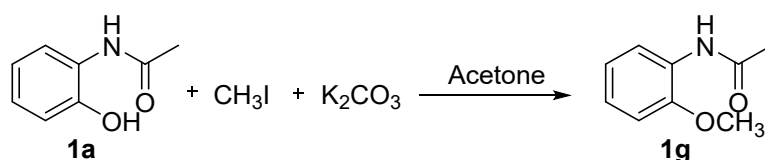
To stirred solution of 2-aminophenol derivatives (10.0 mmol, 1.0 equiv.) in acetic acid (3 ml), a solution of acetic anhydride (1122 mg, 11 mmol, 1.1 equiv.) was added. The mixture was stirred at 50-60 °C for 1-2 hour. After reaction completion, the contents were poured into ice water and the aqueous layer was separated with EtOAc. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The resulting residue was purified by column chromatography on silica gel (EtOAc/hexane) to give the desired product **1b-1e**<sup>[2]</sup> in good yields.

##### Procedure A.3

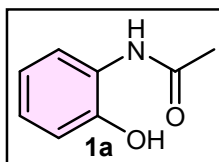


To a stirred solution of aminophenols (1090 mg, 10.0 mmol, 1.0 equiv.) (**1a'**) in acetic acid (3 ml) propionic anhydride (1419 mg, 11 mmol, 1.1 equiv.) was added dropwise and the temperature was maintained at 50-60 °C. The reaction mixture was stirred for about 2-3 hours till full consumption of the substrates was observed on TLC. After reaction completion, the contents were poured into ice water. Then the mixture was extracted by EtOAc and the organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum. The crude product was purified by column chromatography on silica gel (EtOAc/hexane) to give the desired product **1f**.

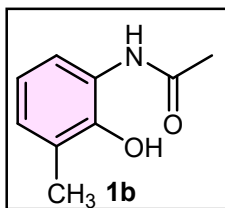
#### Procedure A.4



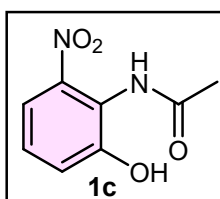
Iodomethane (596 mg, 4.2 mmol, 1.75 equiv.) was added to a mixture of N-(2-hydroxyphenyl)acetamide (362 mg, 2.4 mmol, 1.0 equiv.) and potassium carbonate (662 mg, 4.8 mmol, 2.0 equiv.) in acetone (7-8 mL) over 30 minutes. The reaction mixture was stirred for 24 hours at 20-25 °C. After completion of the reaction as monitored by TLC, the reaction mixture was washed with water, and the organic layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The resulting residue was purified by column chromatography on silica gel to give desired product **1g**.<sup>[3]</sup>



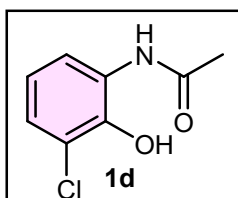
**N-(2-hydroxyphenyl)acetamide (1a):** The starting material **1a** was prepared by following the general procedure A.1 and obtained as a light brown solid (96%, 1.45 g); <sup>1</sup>H NMR (500 MHz, DMSO) δ 9.72 (s, 1H), 9.31 (s, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 2.10 (s, 3H). <sup>13</sup>C NMR (125 MHz, DMSO) δ 169.2, 148.0, 126.5, 124.8, 122.5, 119.0, 116.1, 23.6.



***N*-(2-hydroxy-3-methylphenyl)acetamide (1b):** The starting material **1b** was prepared by following the general procedure **A.2** and obtained as a brown solid (87%, 1.43 g);  $^1\text{H}$  NMR (500 MHz, DMSO)  $\delta$  9.87 (s, 1H), 9.26 (s, 1H), 7.10 (d,  $J = 8.0$  Hz, 1H), 6.92 (d,  $J = 7.0$  Hz, 1H), 6.71 (t,  $J = 8.0$  Hz, 1H), 2.16 (s, 3H), 2.12 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz, DMSO)  $\delta$  170.2, 146.9, 127.1, 126.7, 126.2, 120.8, 119.1, 23.1, 16.4. HRMS (G2XSQTOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_9\text{H}_{12}\text{NO}_2$  166.0863; found 166.0863.

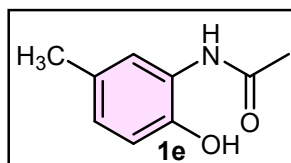


***N*-(2-hydroxy-4-nitrophenyl)acetamide (1c):** The starting material **1d** was prepared by following the general procedure **A.2** and obtained as a yellow solid (90%, 1.7 g);  $^1\text{H}$  NMR (400 MHz, )  $\delta$  9.48 (s), 8.27 (d,  $J = 9.2$  Hz, 1H), 7.63-7.60 (m, 2H), 2.16 (s).  $^{13}\text{C}$  NMR (125 MHz, DMSO)  $\delta$  169.4, 148.4, 142.4, 134.2, 119.1, 114.0, 109.1, 24.2. HRMS (G2XSQTOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_8\text{H}_9\text{N}_2\text{O}_4$  197.0557; found 197.0568.

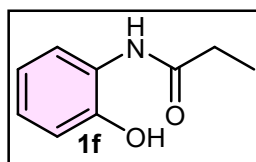


***N*-(3-chloro-2-hydroxyphenyl)acetamide (1d):** The starting material **1d** was prepared by following the general procedure **A.2** and obtained as a brown solid (89%, 1.6 g);  $^1\text{H}$  NMR (500 MHz, DMSO)  $\delta$  9.95 (s, 1H), 9.84 (s, 1H), 7.38 (d,  $J = 8.0$  Hz, 1H), 7.17 (d,  $J = 8.0$  Hz, 1H), 6.82 (t,  $J = 8.0$  Hz, 1H), 2.13 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz, DMSO)  $\delta$  170.3, 144.9,

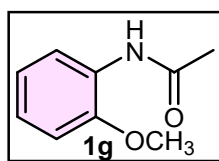
128.3, 125.8, 122.0, 121.9, 120.0, 23.3. HRMS (G2XSQTOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_8H_9ClNO_2$  186.0316; found 186.0320.



***N*-(2-hydroxy-5-methylphenyl)acetamide (1e)**: The starting material **1e** was prepared by following the general procedure **A.2** and obtained as a white solid (95%, 1.5 g);  $^1H$  NMR (500 MHz, DMSO)  $\delta$  9.45 (s, 1H), 9.26 (s, 1H), 7.47 (s, 1H), 6.74 (s, 2H), 2.17 (s, 3H), 2.08 (s, 3H).  $^{13}C$  NMR (125 MHz, DMSO)  $\delta$  169.0, 145.6, 127.5, 126.1, 125.1, 122.8, 115.9, 23.6, 20.4. HRMS (G2XSQTOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_9H_{12}NO_2$  166.0863; found 166.0866.



***N*-(2-hydroxyphenyl)propionamide (1f)**: The starting material **1f** was prepared by following the general procedure **A.3** and obtained as a pale yellow solid (94%, 1.5 g);  $^1H$  NMR (500 MHz, DMSO)  $\delta$  9.72 (s, 1H), 9.20 (s, 1H), 7.69 (d,  $J = 8.0$  Hz, 1H), 6.93 (t,  $J = 7.5$  Hz, 1H), 6.87-6.85 (m, 1H), 6.78-6.74 (m, 1H), 2.40 (q,  $J = 7.5$  Hz, 2H), 1.08 (t,  $J = 7.5$  Hz, 3H).  $^{13}C$  NMR (125 MHz, DMSO)  $\delta$  172.6, 147.8, 126.4, 124.5, 122.2, 119.0, 116.0, 29.1, 9.7. HRMS (G2XSQTOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_9H_{12}NO_2$  166.0863; found 166.0868.



***N*-(2-methoxyphenyl)acetamide (1g)**: The starting material **1g** was prepared by following the general procedure **A.4** and obtained as a off white solid (98%, 388 mg);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.34 (d,  $J = 8.0$  Hz, 1H), 7.80 (s, 1H), 7.02 (t,  $J = 7.6$  Hz, 1H), 6.95-6.91 (m, 1H), 6.85 (d,  $J = 8.0$  Hz, 1H), 3.85 (s, 3H), 2.18 (s, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  168.5, 148.0, 128.0, 123.9, 121.3, 120.1, 110.2, 55.9, 25.2. HRMS (G2XSQTOF)  $m/z$ :  $[M + Na]^+$  Calcd for  $C_9H_{11}NNaO_2$  188.0682; found 188.0689.



## **Procedure B:** Synthesis of iminoiodinane (2)<sup>[4]</sup>

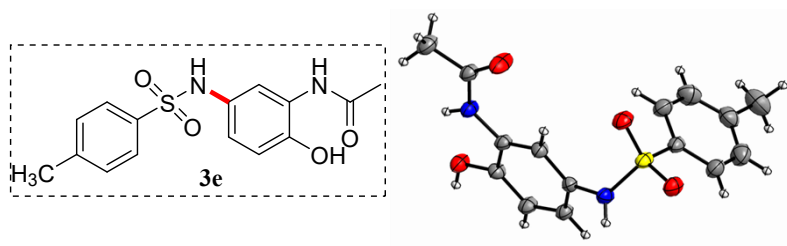
To a solution of ArSO<sub>2</sub>NH<sub>2</sub> (10 mmol, 1.0 equiv.), potassium hydroxide (25 mmol, 2.5 equiv.) and methanol (120 ml) were stirred in a conical flask in an ice bath, ensuring the reaction mixture was below 10 °C. (It's not essential to have a solution, a suspension is more likely at this temp). Iodobenzene diacetate (10 mmol, 1.0 equiv.) was added to the stirred mixture and the resulting yellow colored solution was stirred at room temperature for 3.5 h. The reaction mixture was poured into a large excess of iced water and stirred for 1 h. A yellow coloured solid precipitated on standing overnight. (It's important to allow the solid to stand as the particle size appears to increase giving higher yield on filtration). The light yellow solid was isolated by filtration and dried with a flow of air through the buchner funnel. Several portions of ether, in which the product is insoluble were used to wash away any iodobenzene present. The yellow solid was dissolved in a minimum of boiling methanol. The solution was placed in a freezer overnight whereupon an off-white solid (iminoiodinane, PhINNs) was recovered via filtration.

## **5. Gram scale synthesis**

To an oven dried 100 mL round bottom flask, *N*-(2-hydroxyphenyl)acetamide **1a** (500 mg, 3.3 mmol, 1.0 equiv.), PhINNs **2a** (1.7 g, 4.3 mmol, 1.3 equiv.), I<sub>2</sub> (1.0 g, 4.3 mmol, 1.3 equiv.) were dissolved in DCM (55 mL) in an oven-dried 100 mL round bottom flask equipped with a magnetic stirring bar, and irradiated using 50 W Blue LED at room temperature under air for 48 h. After completion of the reaction as monitored by TLC, the reaction mixture was washed with saturated solution of sodium thiosulphate, and the organic layer extracted with EtOAc (3 x 50 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The resulting residue was purified by column chromatography on silica gel (hexane/EtOAc = 67:33) to give desired product **3a** in 47% yield (0.54 g).

## **6. Crystallographic description of compounds 3e**

Single crystal X-ray diffraction data of compound **3e** was collected using a Bruker SMART APEX diffractometer equipped with a 3-axis goniometer. The crystal was grown by dissolving 10 mg of **3e** in 0.5 mL of chloroform. The clear solution was covered and kept at room temperature for 105 h.



**Figure S2:** ORTEP diagram of compound **3e** (with 40% probability ellipsoids).

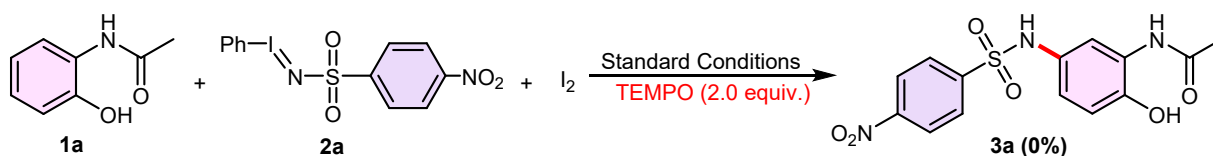
Identification code	rajat_nts_0m_a
Empirical formula	C <sub>15</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> S
Formula weight	320.36
Temperature	273.15 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 7.453(4) Å; α = 84.04(3)° b = 10.846(5) Å; β = 75.55(3)° c = 11.701(6) Å; γ = 76.36(3)°
Volume	889.1(7) Å <sup>3</sup>
Z	2
Density (calculated)	1.197 g/cm <sup>3</sup>
Absorption coefficient	0.199
F(000)	336.0
Crystal size	0.014 × 0.012 × 0.012 mm <sup>3</sup>
Theta range for data collection	3.598 to 49.988°

Index ranges	-8 ≤ h ≤ 8, -12 ≤ k ≤ 12, -13 ≤ l ≤ 13
Reflections collected	21802
Independent reflections	3112 [Rint = 0.0680]
Completeness to theta = 24.994°	99.9 %
Data / restraints / parameters	3112/0/206
Goodness-of-fit on F <sup>2</sup>	1.316
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0972, WR <sub>2</sub> = 0.2816
R indices (all data)	R <sub>1</sub> = 0.1182, WR <sub>2</sub> = 0.3037
CCDC	2370283

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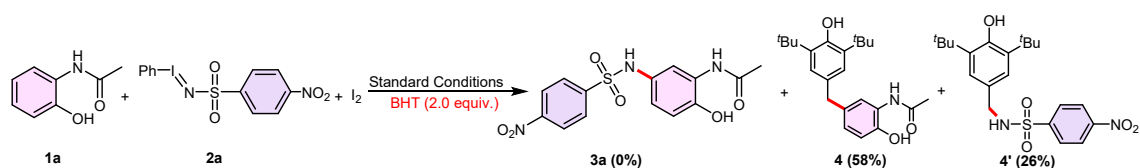
## 7. Mechanistic Studies

### a) Free radical-trapping experiment with TEMPO



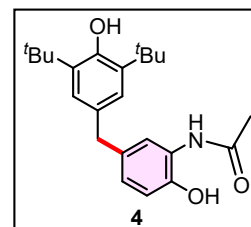
2-acetaminophenol **1a** (20 mg, 0.13 mmol, 1.0 equiv.), 4-nitro-*N*-(phenyl-λ<sup>3</sup>-iodaneylidene)benzenesulfonamide **2a** (68 mg, 0.17 mmol, 1.3 equiv.), I<sub>2</sub> (42 mg, 0.17 mmol, 1.3 equiv.), and 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO, 0.26 mmol, 2.0 equiv.) were dissolved in DCM (2 mL) in an oven-dried reaction vessel equipped with a magnetic stirring bar, and the reaction vessel was irradiated using 50 W Blue LED at room temperature under air for 17 h. The desired product **3a** was not detected.

## b) Free radical-trapping experiment with BHT

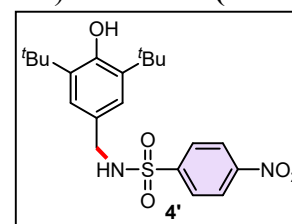


2-acetaminophenol **1a** (20 mg, 0.13 mmol, 1.0 equiv.), 4-nitro-*N*-(phenyl-λ<sup>3</sup>-iodaneylidene)benzenesulfonamide **2a** (68 mg, 0.17 mmol, 1.3 equiv.), I<sub>2</sub> (42 mg, 0.17 mmol, 1.3 equiv.), and 2,6-ditert-butyl-4-methylphenol (57 mg, 0.26 mmol, 2.0 equiv.) were dissolved in DCM (2 mL) in an oven-dried reaction vessel equipped with a magnetic stirring bar, and the reaction vessel was irradiated using 50 W Blue LED at room temperature under air for 17 h. After completion of the reaction as monitored by TLC, the desired product **3a** was not detected. The reaction mixture was washed with a saturated solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, the organic layer was extracted with EtOAc and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The resulting residue was purified by column chromatography on silica gel to give desired BHT adducts **4** and **4'** were obtained in 58% and 26% yields and characterized by <sup>1</sup>HNMR, <sup>13</sup>CNMR and HRMS.

*N*-(5-(3,5-di-tert-butyl-4-hydroxybenzyl)-2-hydroxyphenyl)acetamide (**4**). The BHT adduct **4** was obtained as off white solid in (28 mg, 58%); hexane/EtOAc (76/24), <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 9.51 (s, 1H), 9.28 (s, 1H), 7.52 (s, 1H), 6.91 (s, 2H), 6.79-6.74 (m, 2H), 6.70 (s, 1H), 3.67 (s, 2H), 2.07 (s, 3H), 1.34 (s, 18H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 170.60, 152.29, 147.06, 136.07, 134.33, 131.71, 128.00, 125.57, 125.47, 122.44, 120.04, 40.93, 34.48, 30.49, 23.88 ppm. HRMS (microTOF-Q) *m/z*: [M+Na]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>31</sub>NNaO<sub>3</sub> 392.2196; found 392.2187.



*N*-(3,5-di-tert-butyl-4-hydroxybenzyl)-4-nitrobenzenesulfonamide (**4'**). The BHT adduct **4'** was obtained as brown liquid in (14 mg, 26%); hexane/EtOAc (82/18) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.27 (d, *J* = 7.0 Hz, 2H), 7.96 (d, *J* = 7.5 Hz, 2H), 6.92 (s, 2H), 5.20 (s, 1H), 4.14 (s, 2H), 1.35 (s, 18H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 153.8, 150.0, 146.5, 136.5, 128.4, 126.2, 125.1, 124.3, 47.9, 34.4, 30.2 ppm. HRMS (microTOF-Q) *m/z*: [M-H]<sup>-</sup> Calcd for C<sub>21</sub>H<sub>28</sub>N<sub>2</sub>O<sub>5</sub>S 419.1641; found 419.1641.



Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

166 formula(e) evaluated with 1 results within limits (up to 10 closest results for each mass)

Elements Used:

C: 0-40 H: 0-45 N: 0-2 O: 0-6 Na: 0-1

XEVO-G2XSQTOF#TFC2176

Capillary V 3, Cone V 40, Desolvation Gas 800 ESI

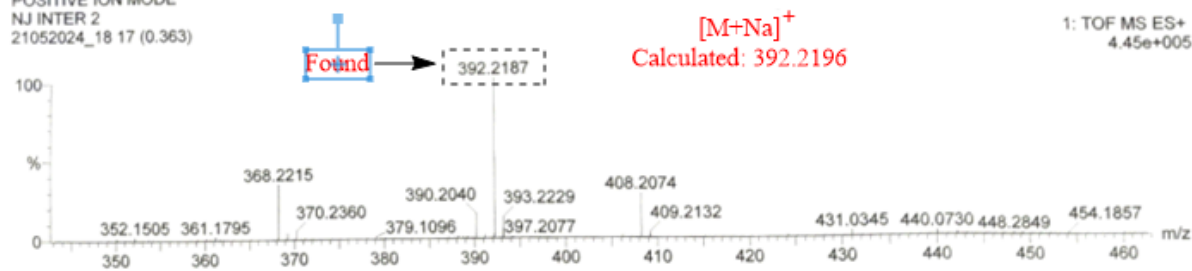
21-May-2024

POSITIVE ION MODE

NJ INTER 2

21052024\_18 17 (0.363)

1: TOF MS ES+  
4.45e+005



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
392.2187	392.2202	-1.5	-3.8	8.5	761.6	n/a	n/a	C23 H31 N O3 Na

Figure S3: HRMS of the BHT adduct 4

Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

64 formula(e) evaluated with 1 results within limits (up to 10 closest results for each mass)

Elements Used:

C: 0-21 H: 0-30 N: 0-2 O: 0-5 Na: 0-1 S: 0-1

XEVO-G2XSQTOF#TFC2176

Capillary V 3, Cone V 40, Desolvation Gas 800 ESI

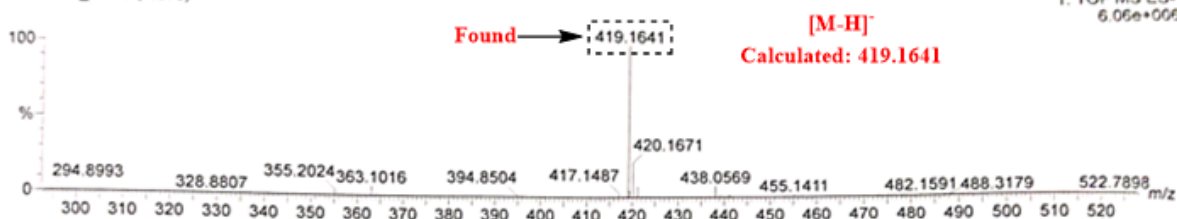
18-Sep-2024

NEGATIVE ION MODE

NJ SPOT 2

18092024\_27 96 (1.878)

1: TOF MS ES-  
6.06e+006



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
419.1641	419.1641	0.0	0.0	9.5	732.6	n/a	n/a	C21 H27 N2 O5 S

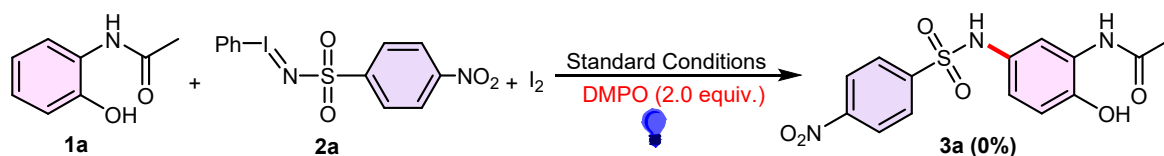
Figure S4: HRMS of the BHT adduct 4'

### c) Isolation and characterization of Intermediate (I)<sup>[5]</sup>

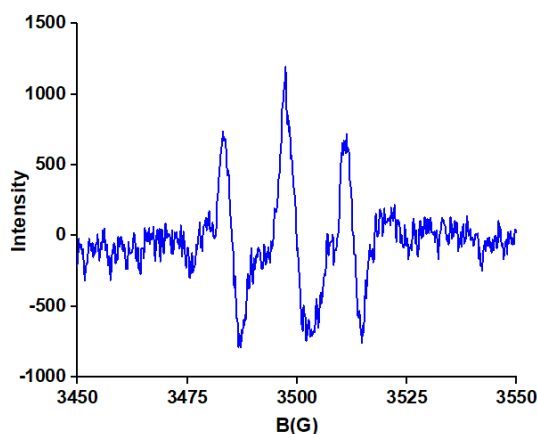
To a solution of PhINNs (100 mg, 0.25 mmol, 1.0 equiv.) and iodine (63 mg, 0.25 mmol, 1.0 equiv.) in 3-4mL of DCM. The reaction mixture was stirred at room temperature in air 15 min. The dark orange precipitate was then filtered in air and rinsed three times with DCM. The solid (~65 mg) was then dried in vacuo and flushed with argon before storage <0°C. Samples stored at rt evolve I<sub>2</sub>. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 8.44 (d, *J* = 7.0 Hz, 2H), 8.14 (d, *J* = 4.5 Hz, 2H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 149.4, 142.2, 129.8, 124.1 ppm.

### d) EPR Studies

EPR measurements were performed on Bruker A300-9.5/12/S/W instrument using microwave strength 9.8 GHz, sweep time 60 seconds, and one scan. The EPR spectrum of the reaction mixture was recorded after 15 min of irradiation using 5,5- dimethyl-1-pyrroline N-oxide (DMPO) as a spin trap. **The signal indicated the presence of paramagnetic species.**

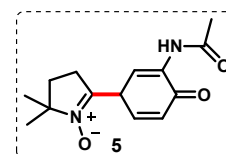


Reaction Conditions: **1a** (1.0 equiv.), **2a** (1.3 equiv.), and I<sub>2</sub> (1.3 equiv), DCM = 2.0 mL, rt, open air. After 15 min of stirring under 50 W blue LEDs, DMPO (2.0 equiv.) was added and EPR spectrum was recorded.



**Figure S5:** EPR spectrum of Carbon radical with spin trap (DMPO).

The adduct of carbon radical and spin trap DMPO **5** was also identified by HRMS.



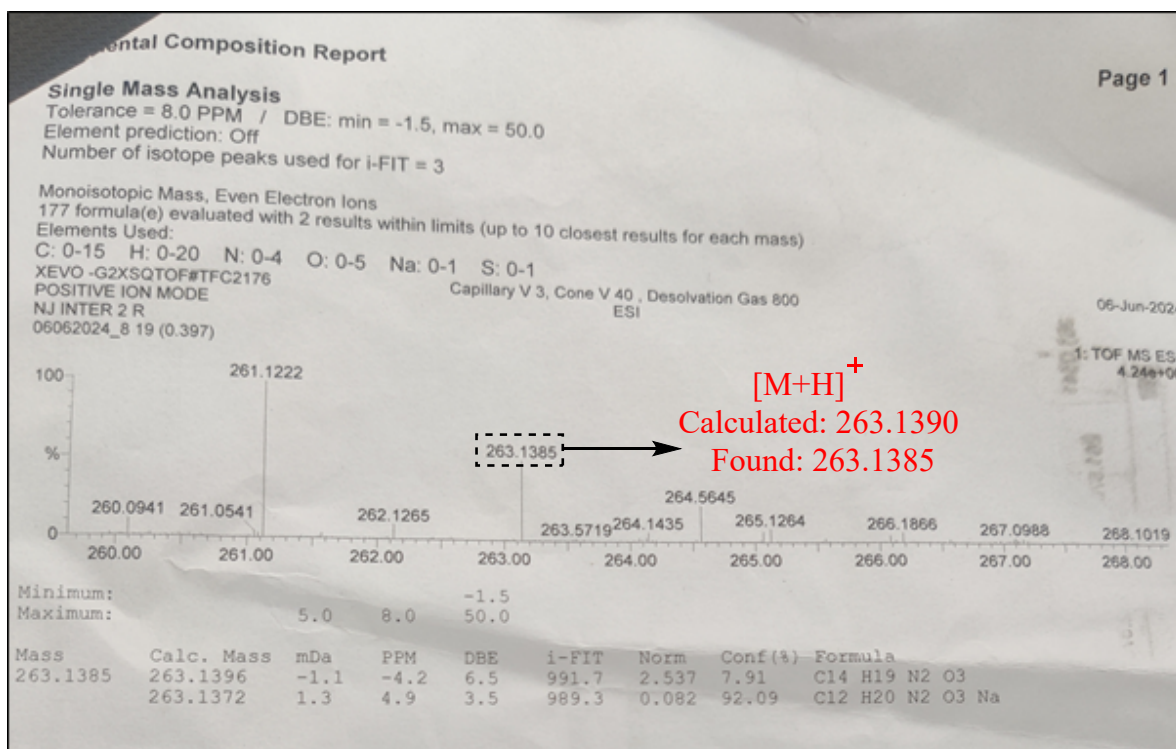
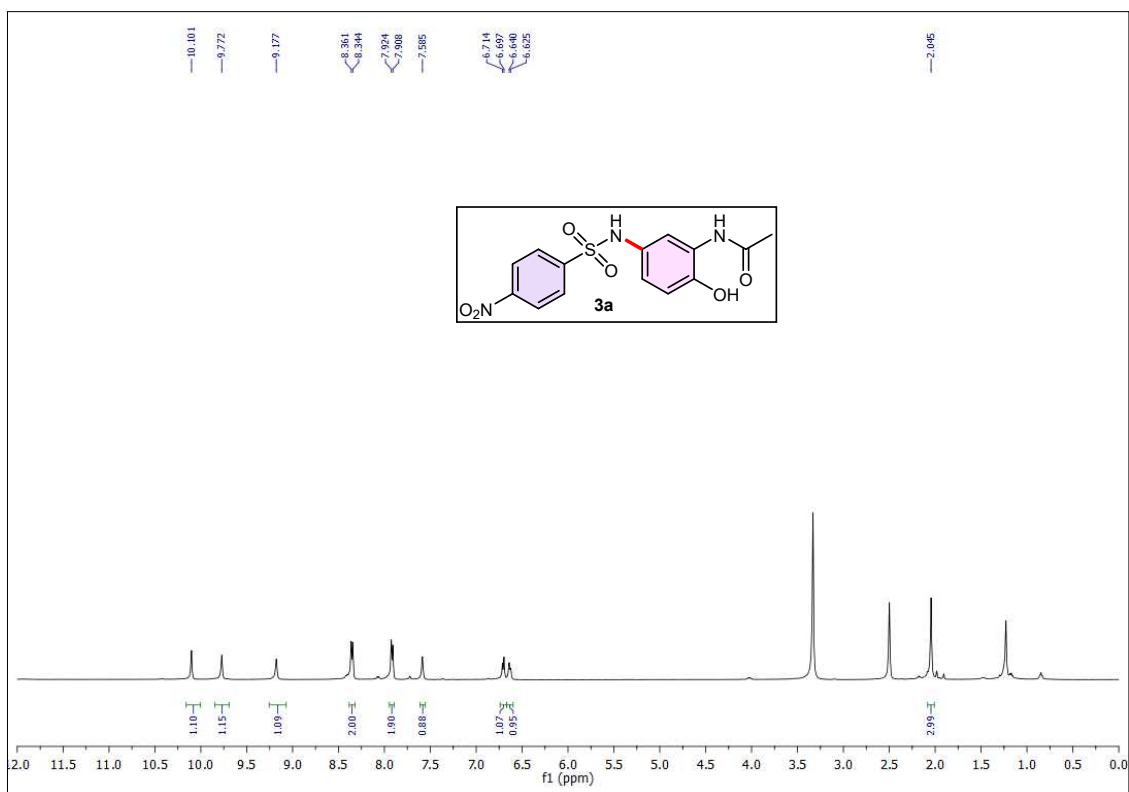


Figure S6: HRMS of the reaction mixture

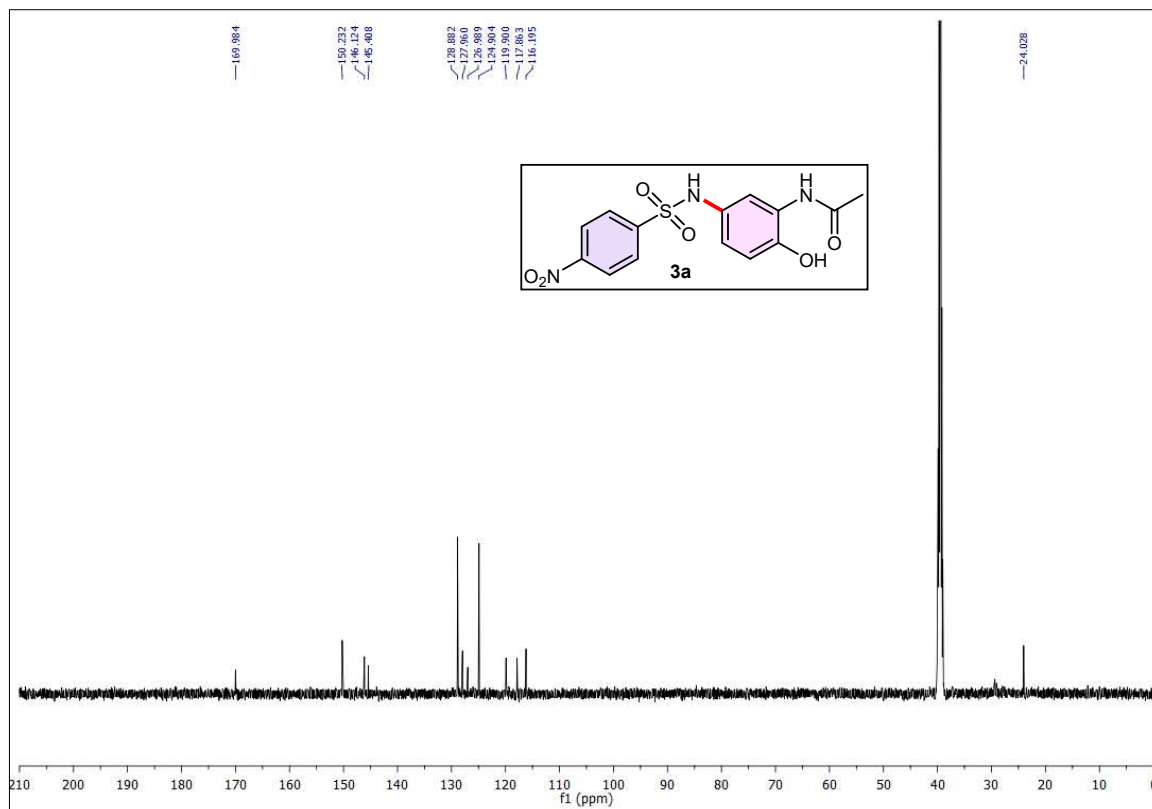
## 8. References

- 1) K.-L. Li, Z.-B. Du, C.-C. Guo, and Q.-Y. Chen, *J. Org. Chem.* **2009**, *74*, 3286–3292.
- 2) H.-R. Tsou, E. G. O.-Klumpers, W. A. Hallett, M. F. Reich, M. B. Floyd, B. D. Johnson, R. S. Michalak, R. Nilakantan, C. Discafani, J. Golas, S. K. Rabindran, R. Shen, X. Shi, Y.-F. Wang, J. Upešlacis, A. Wissner, *J. Med. Chem.* **2005**, *48*, 1107-1131.
- 3) D. E. Knutson, R. Kodali, B. Divović, M. Treven, M. R. Stephen, N. M. Zahn, V. Dobricic, A. T. Huber, M. A. Meirelles, R. S. Verma, L. Wimmer, C. Witzigmann, L. A. Arnold, L.-C. Chiou, M. Ernst, M. D. Mihovilovic, M. M. Savic, W. Sieghart, J. M. Cook, *J. Med. Chem.* **2018**, *61*, 2422–2446.
- 4) Y. Guo, C. Pei, S. Jana, and R. M. Koenigs, *ACS Catal.* **2021**, *11*, 337–342.
- 5) A. A. Lamar and K. M. Nicholas, *J. Org. Chem.* **2010**, *75*, 7644–7650.

## 9. Copies of $^1\text{H}$ NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of synthesized compounds

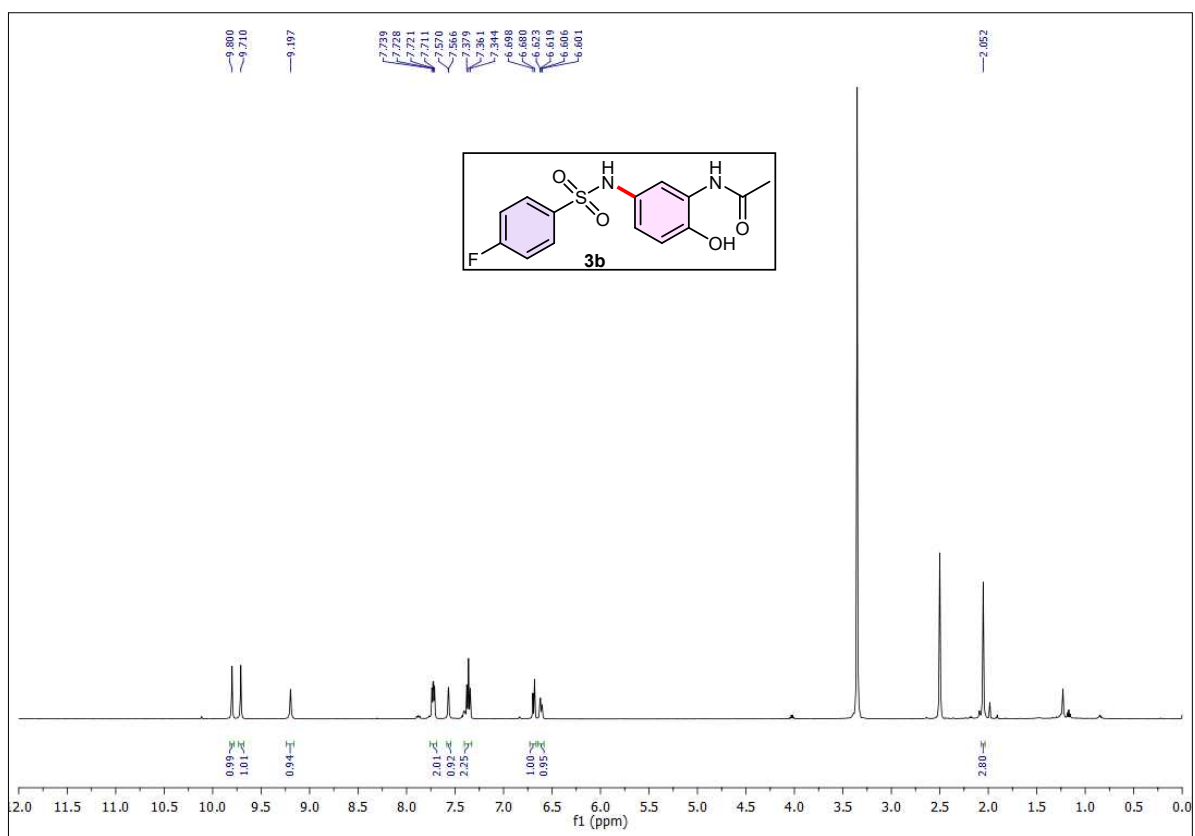


**Spectrum 1.** 500 MHz  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ ) of compound **3a**

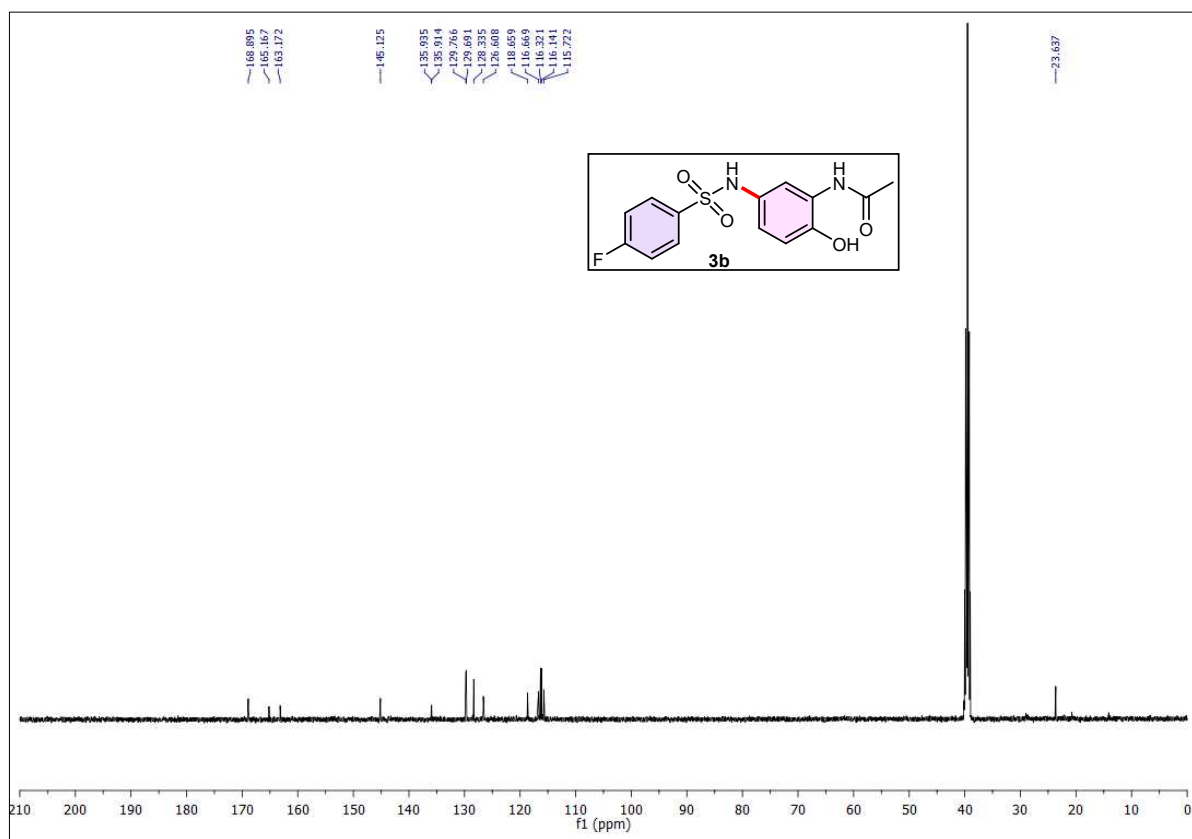


**Spectrum 2.** 125 MHz  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{DMSO-}d_6$ ) NMR of compound **3a**

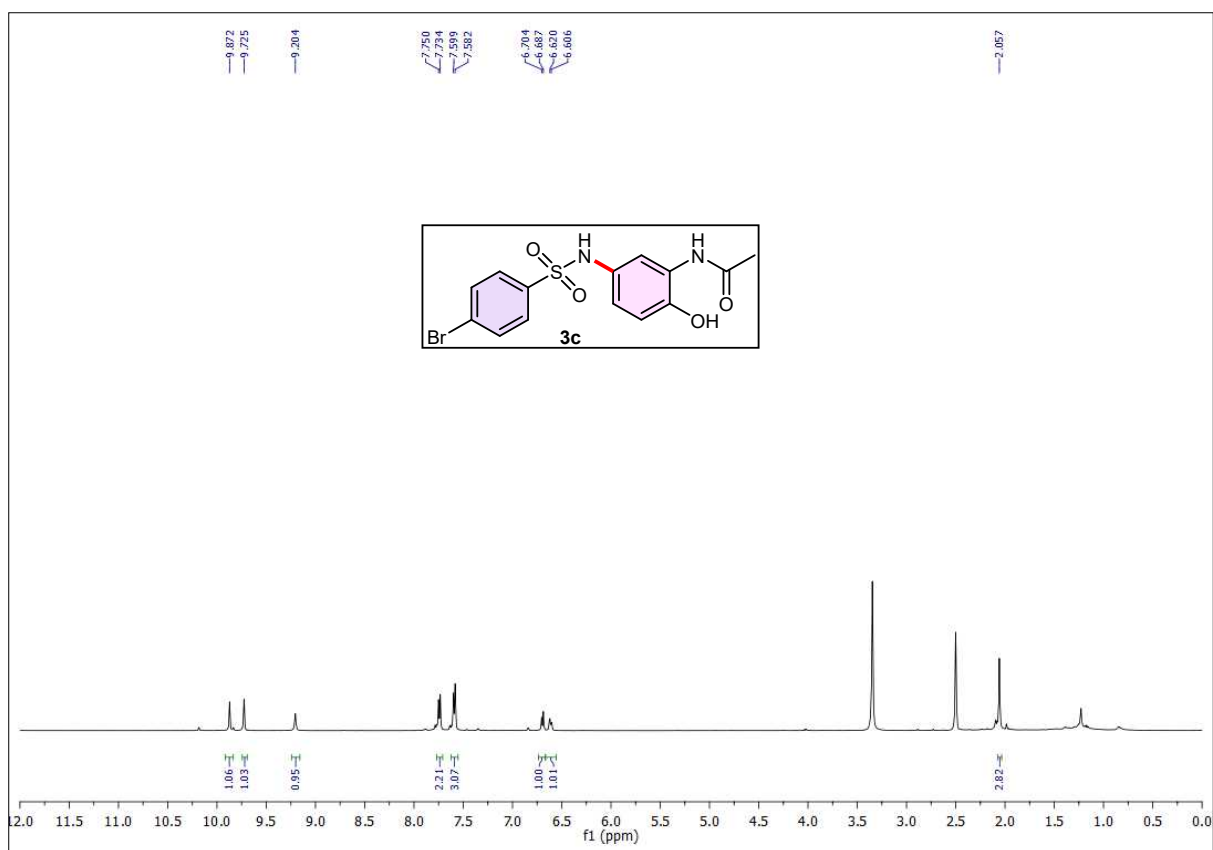




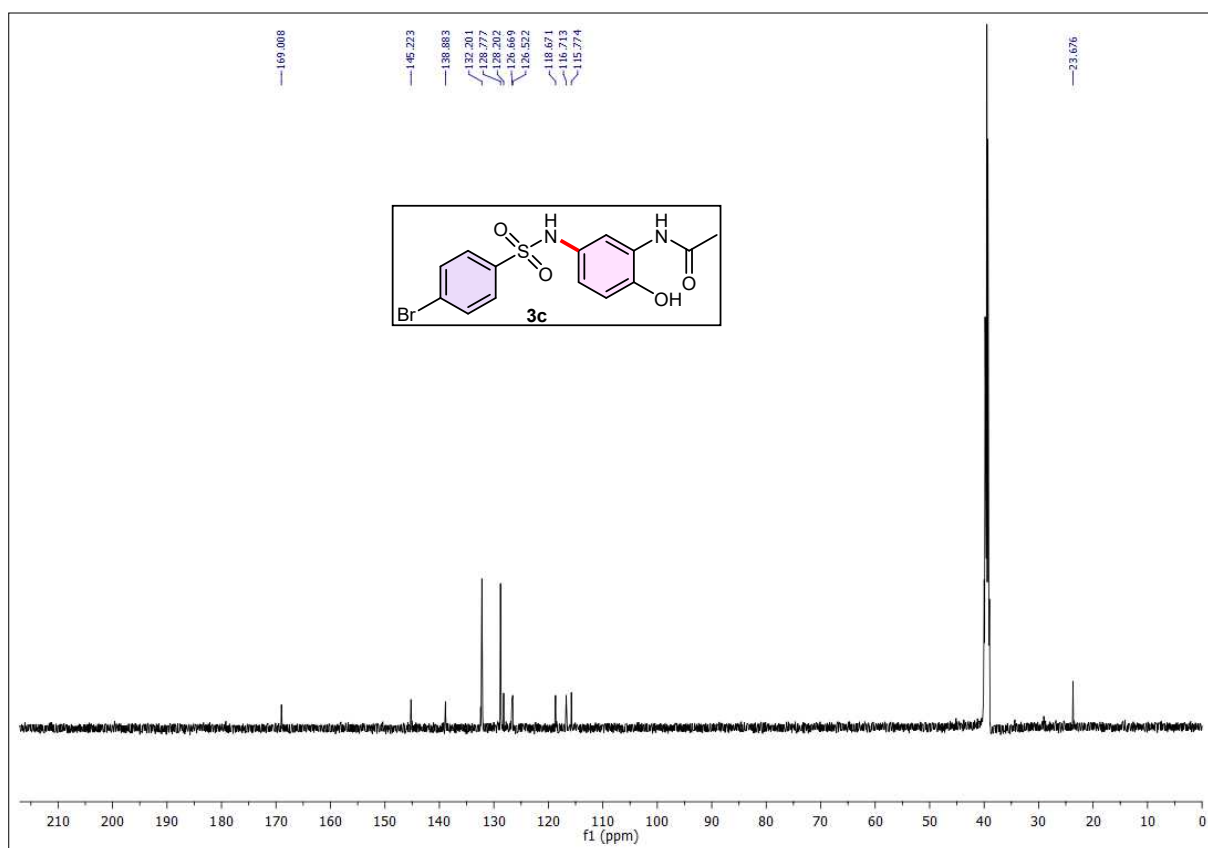
**Spectrum 3.** 500 MHz  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ ) of compound **3b**



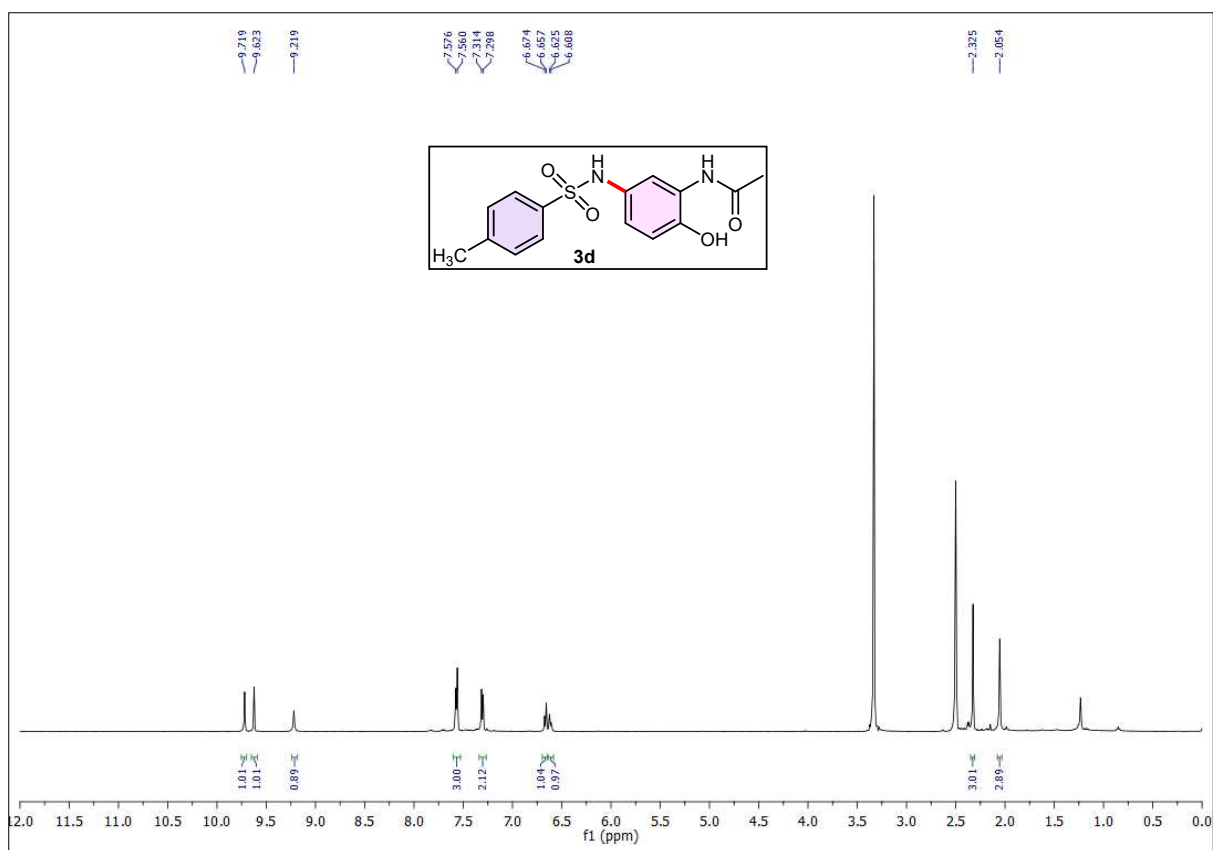
**Spectrum 4.** 125 MHz  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{DMSO-}d_6$ ) NMR of compound **3b**



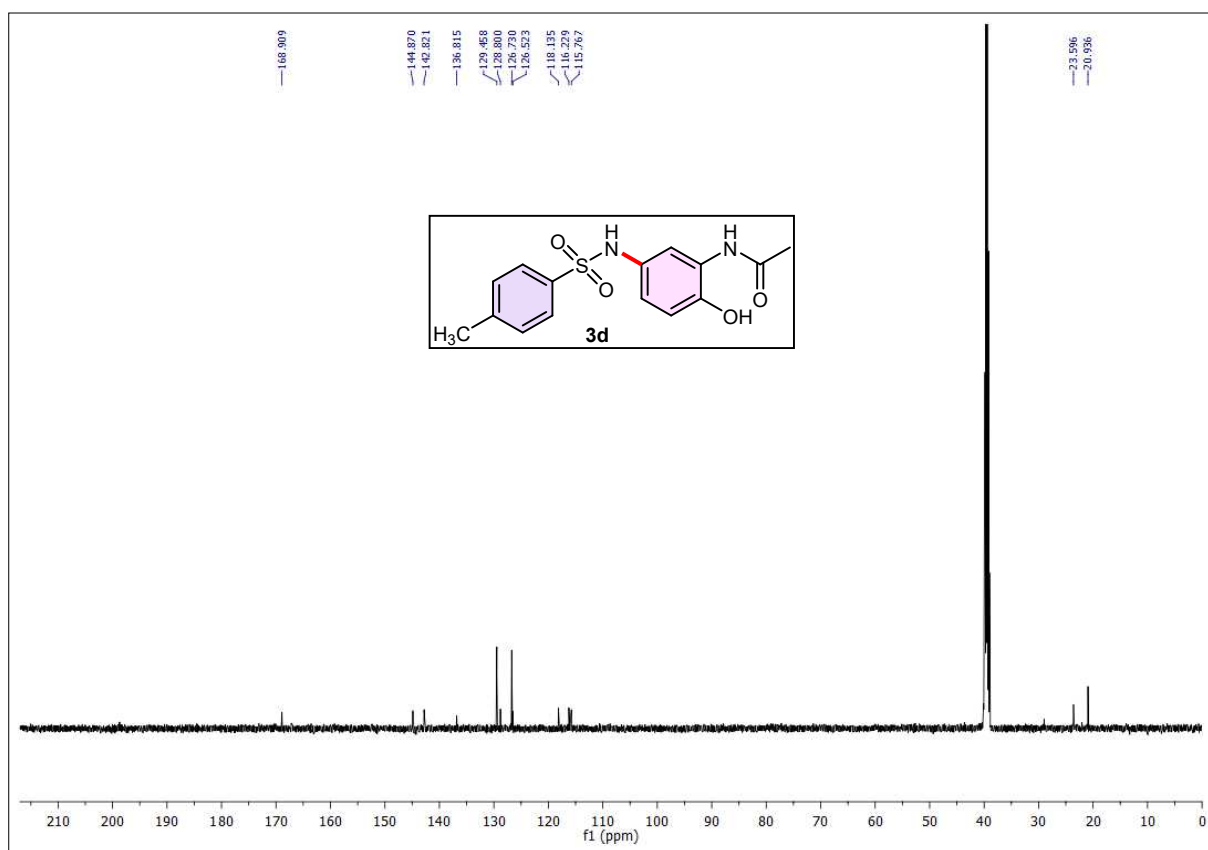
**Spectrum 5.** 500 MHz  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ ) of compound **3c**



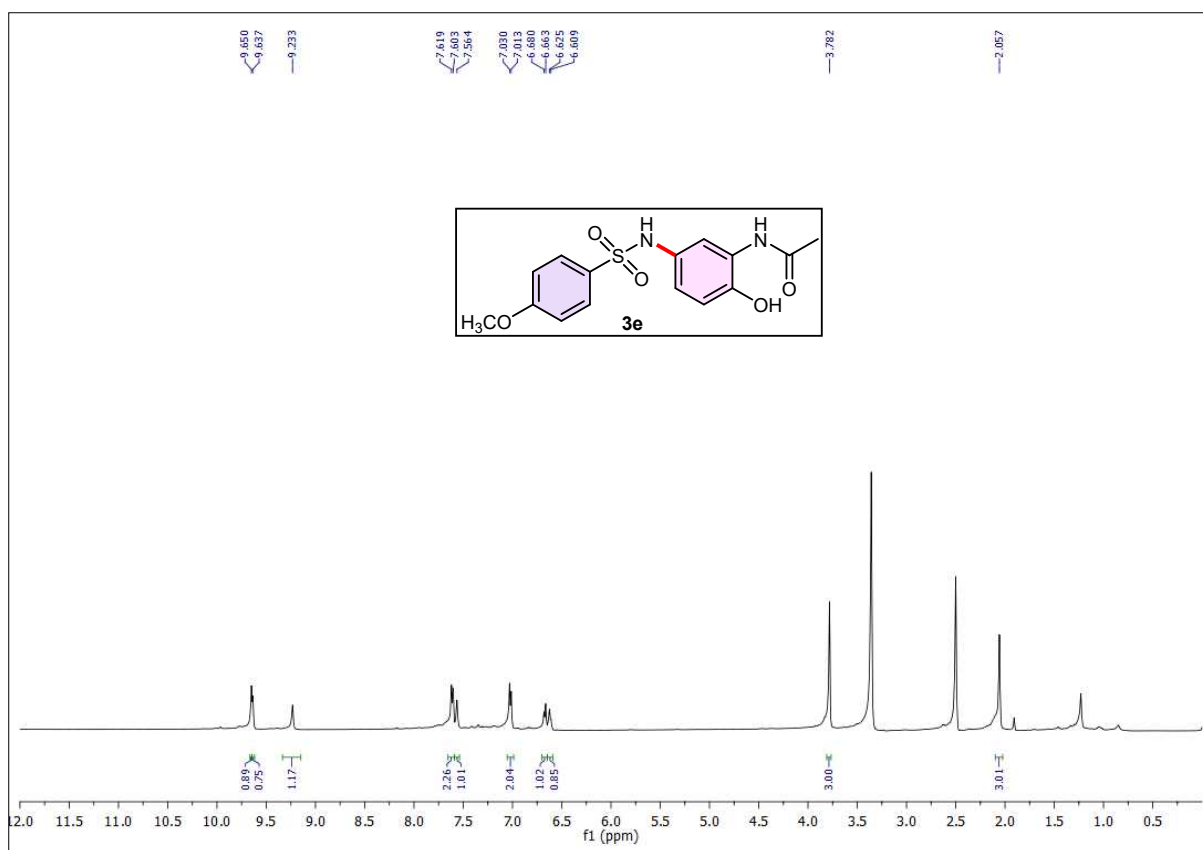
**Spectrum 6.** 125 MHz  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{DMSO-}d_6$ ) NMR of compound **3c**



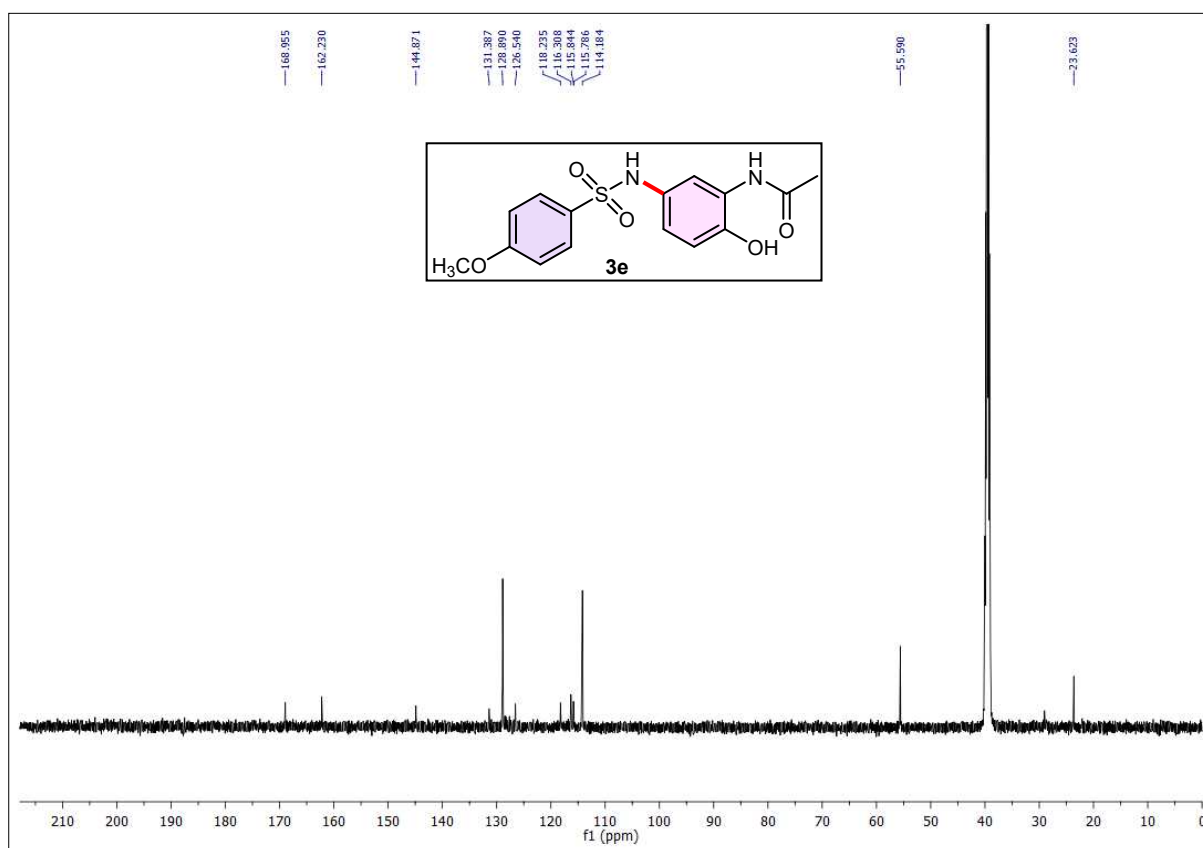
**Spectrum 7.** 500 MHz  $^1\text{H}$  NMR (DMSO- $d_6$ ) of compound **3d**



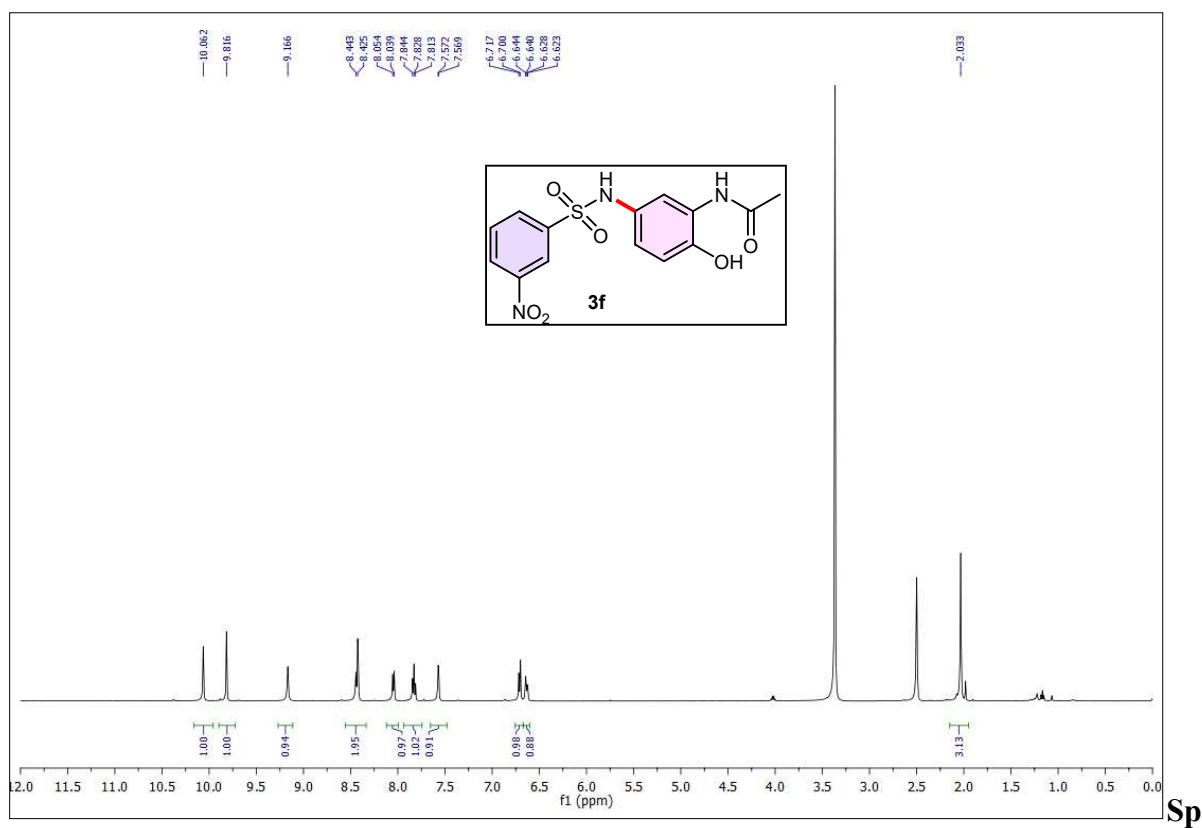
**Spectrum 8.** 125 MHz  $^{13}\text{C}\{^1\text{H}\}$  (DMSO- $d_6$ ) NMR of compound **3d**



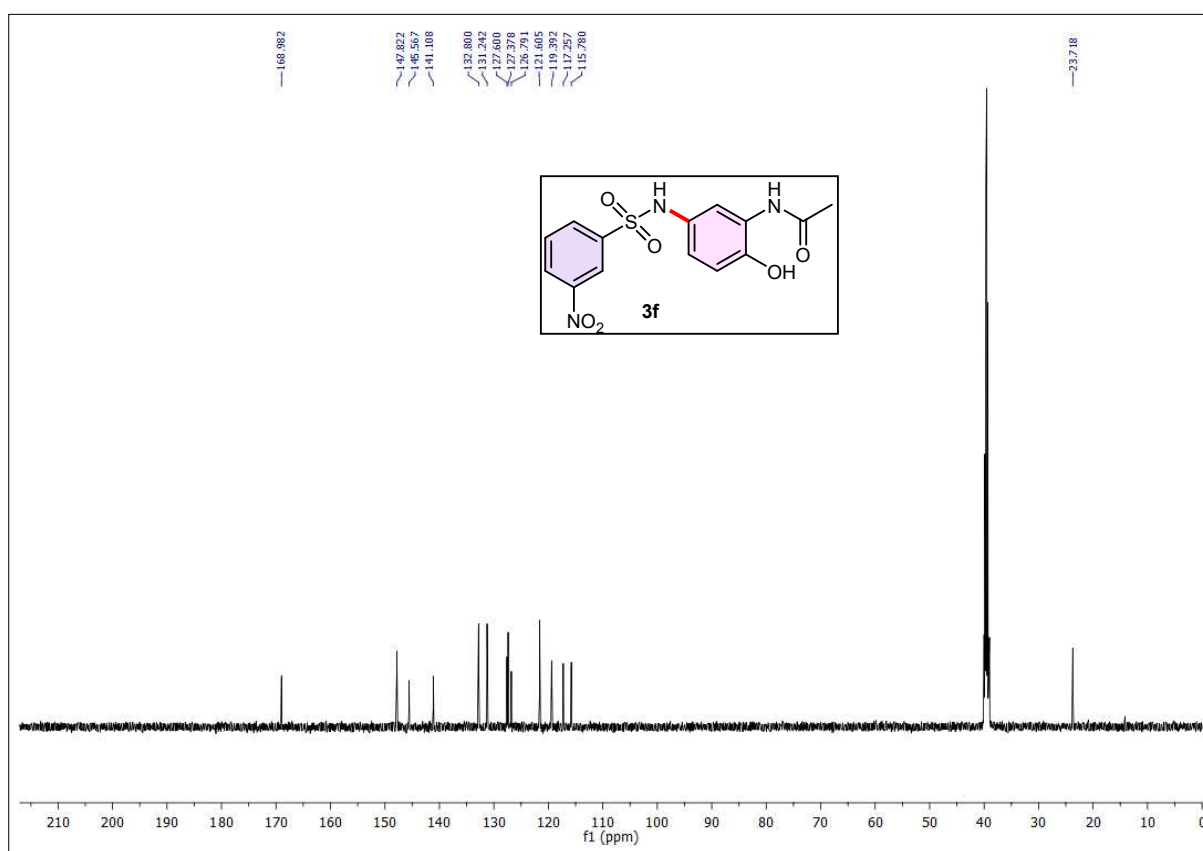
**Spectrum 9.** 500 MHz <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) of compound **3e**



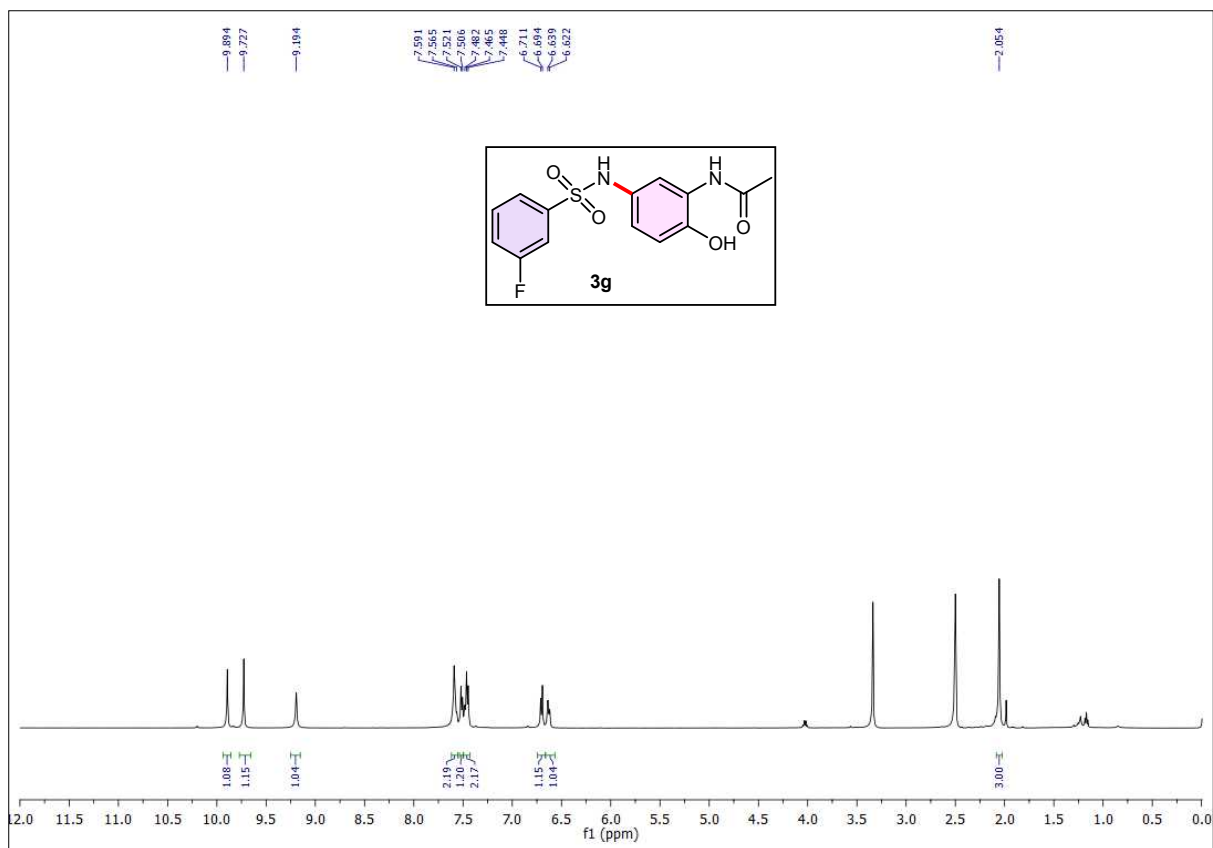
**Spectrum 10.** 125 MHz <sup>13</sup>C{<sup>1</sup>H} (DMSO-*d*<sub>6</sub>) NMR of compound **3e**



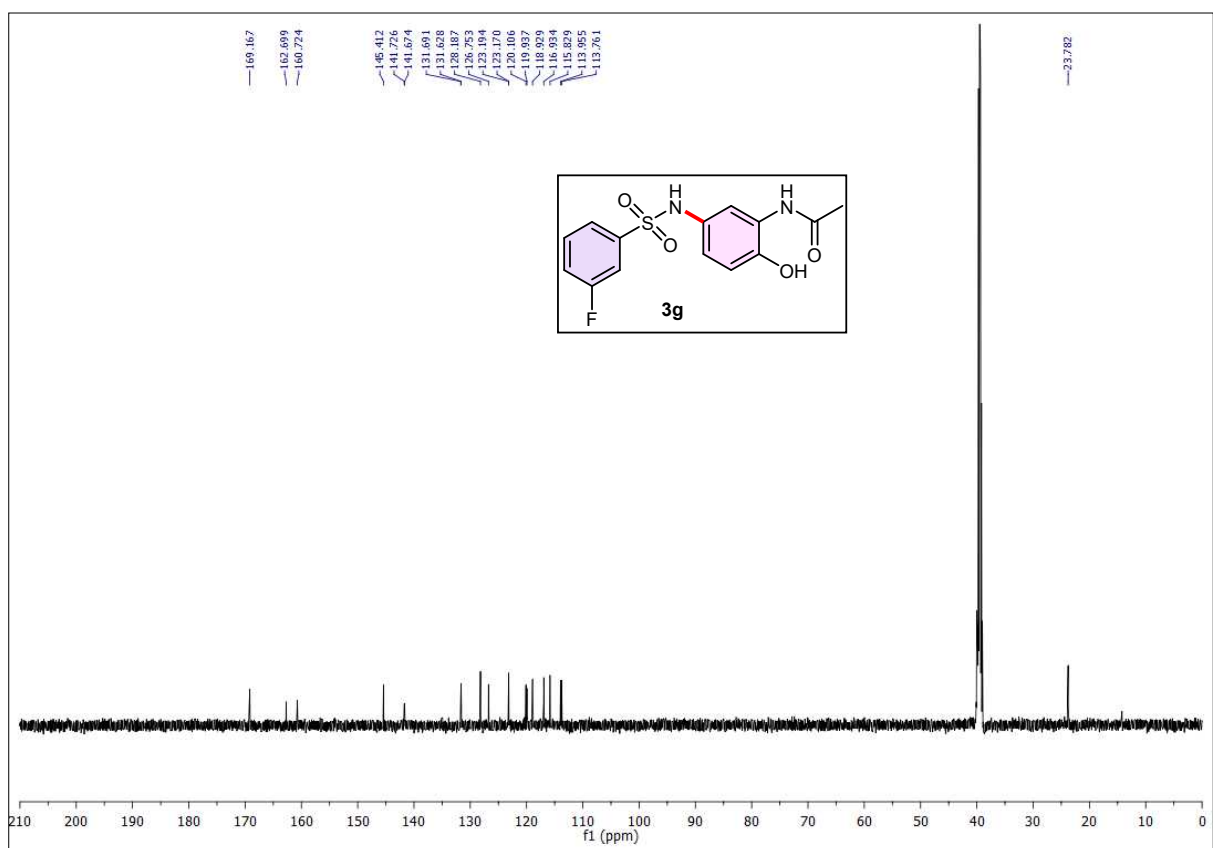
Spectrum 11. 500 MHz  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ ) of compound **3f**



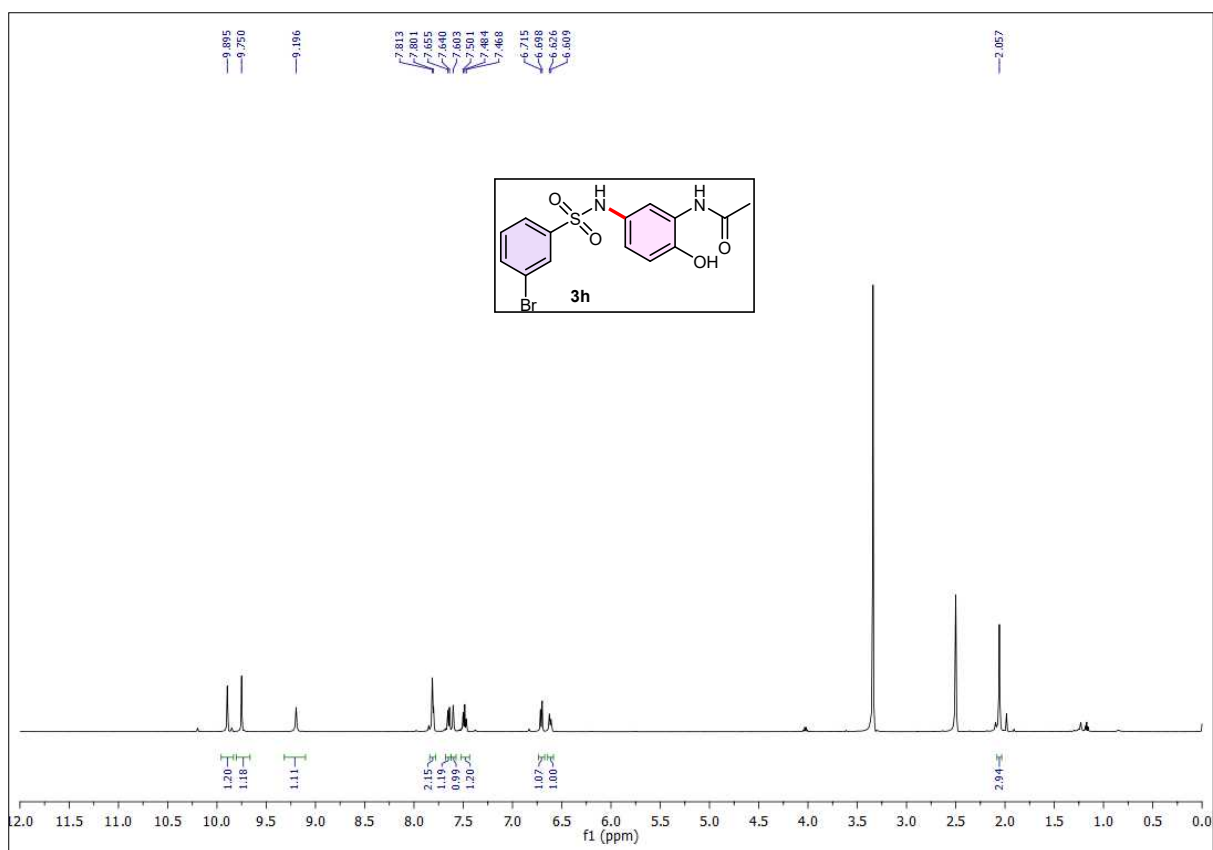
Spectrum 12. 125 MHz  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{DMSO-}d_6$ ) NMR of compound **3f**



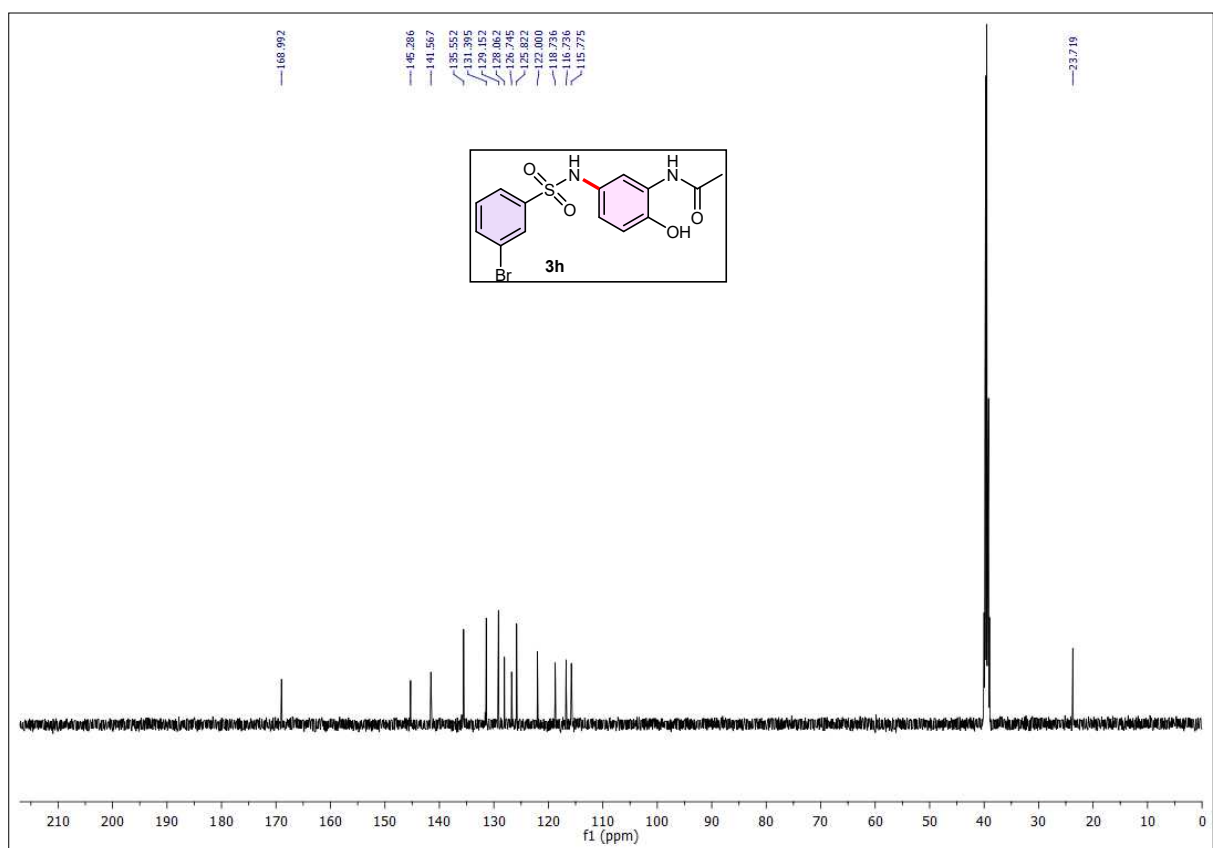
**Spectrum 13.** 500 MHz <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) of compound **3g**



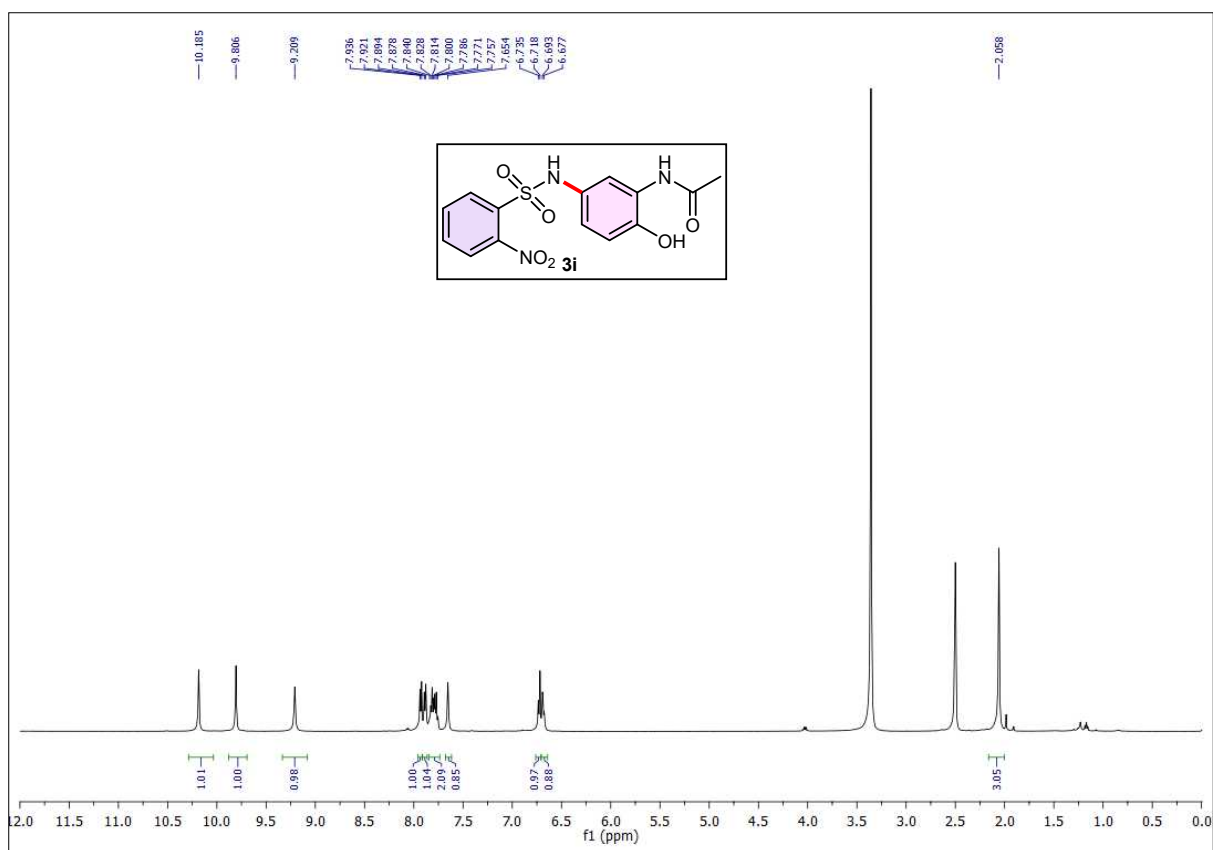
**Spectrum 14.** 125 MHz <sup>13</sup>C{<sup>1</sup>H} (DMSO-*d*<sub>6</sub>) NMR of compound **3g**



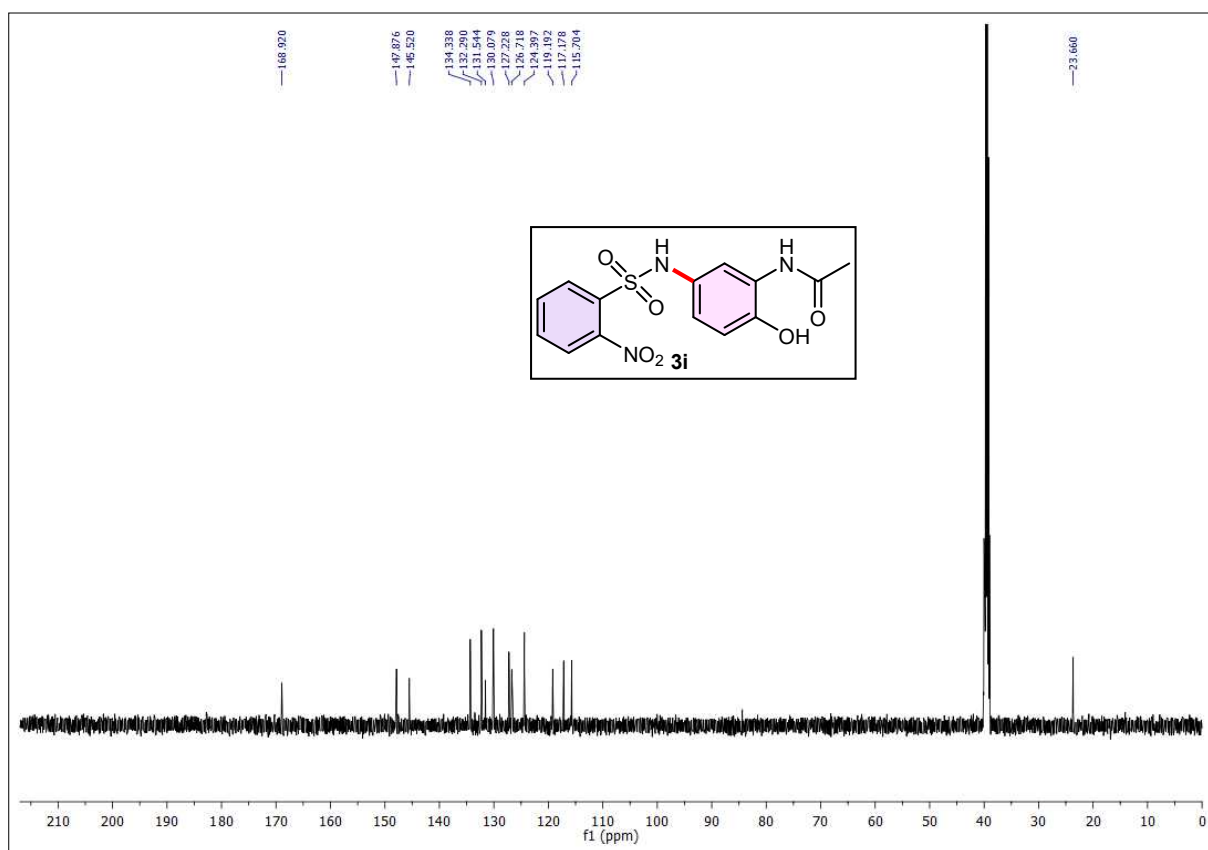
**Spectrum 15.** 500 MHz  $^1\text{H}$  NMR (DMSO- $d_6$ ) of compound **3h**



**Spectrum 16.** 125 MHz  $^{13}\text{C}\{^1\text{H}\}$  (DMSO- $d_6$ ) NMR of compound **3h**

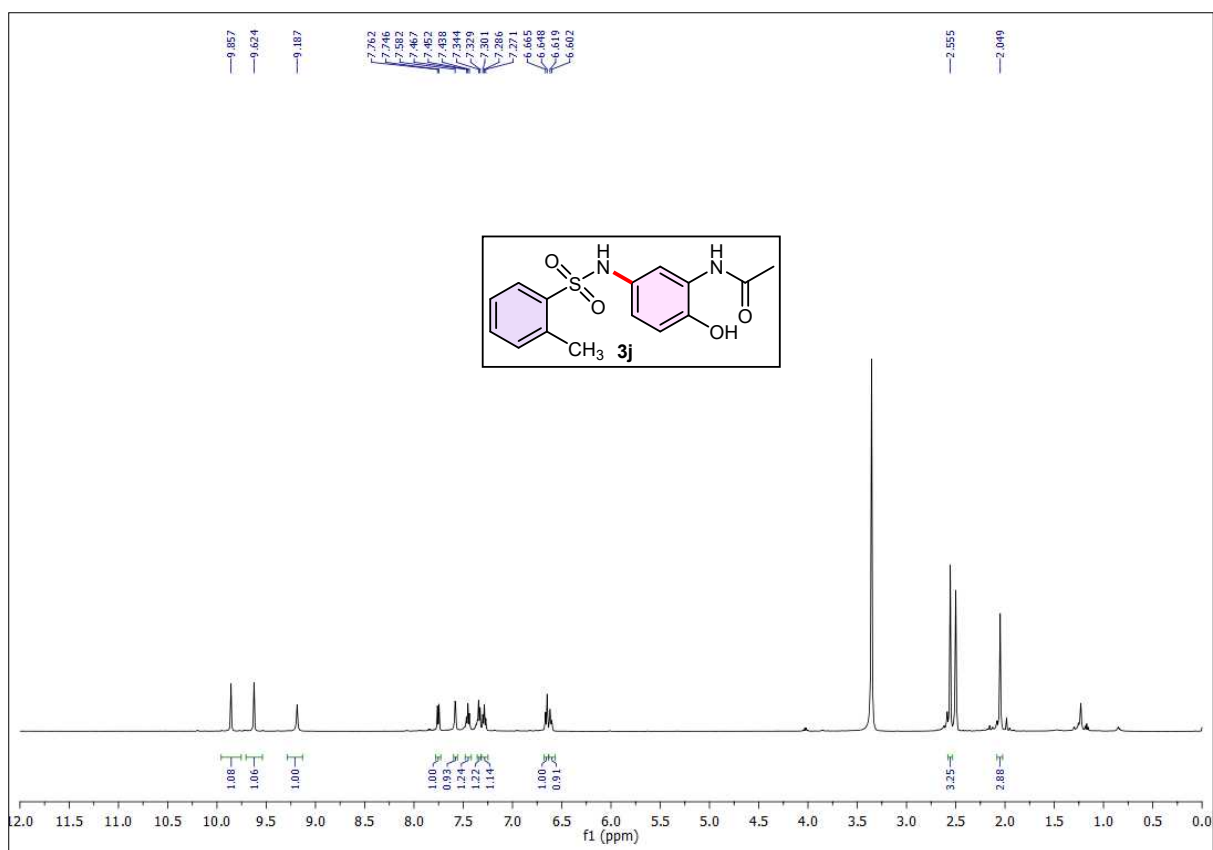


Spectrum 17. 500 MHz  $^1\text{H}$  NMR (DMSO- $d_6$ ) of compound **3i**

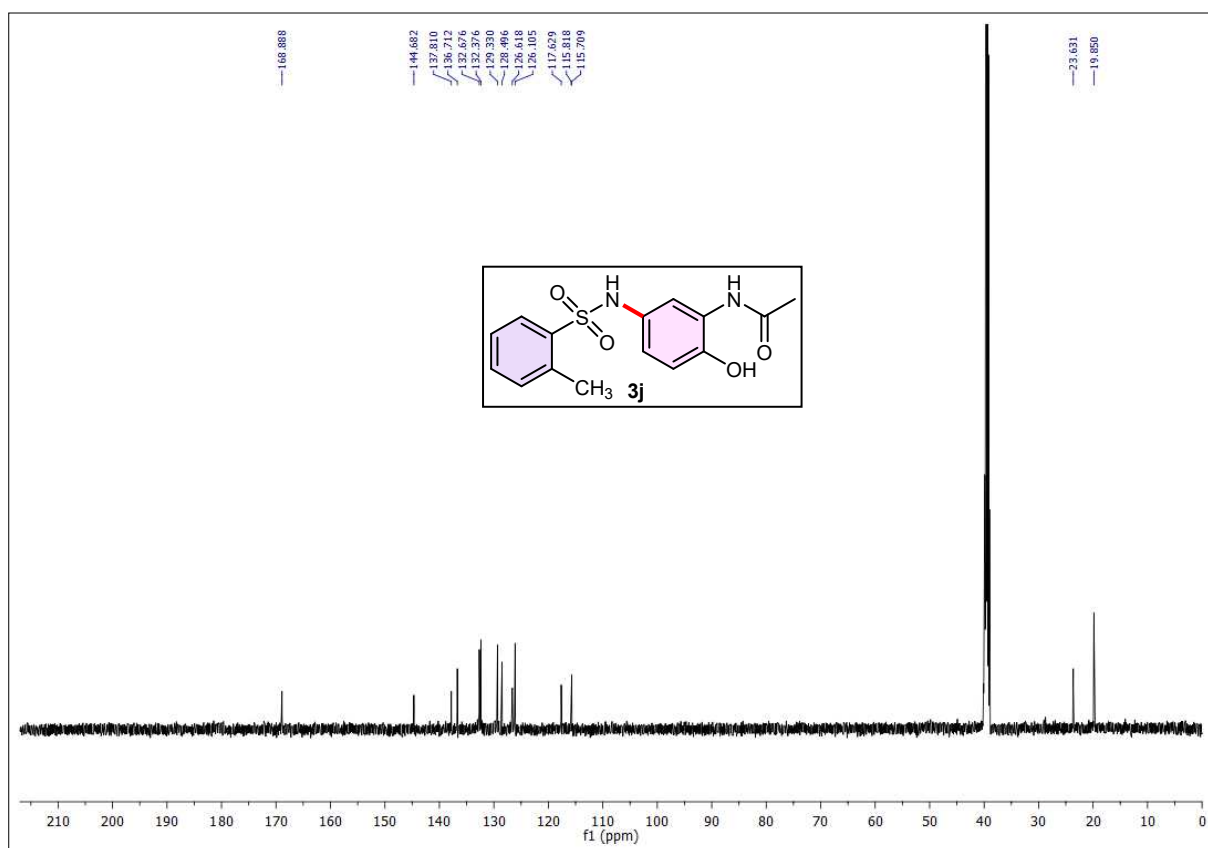


Spectrum 18. 125 MHz  $^{13}\text{C}\{^1\text{H}\}$  (DMSO- $d_6$ ) NMR of compound **3i**

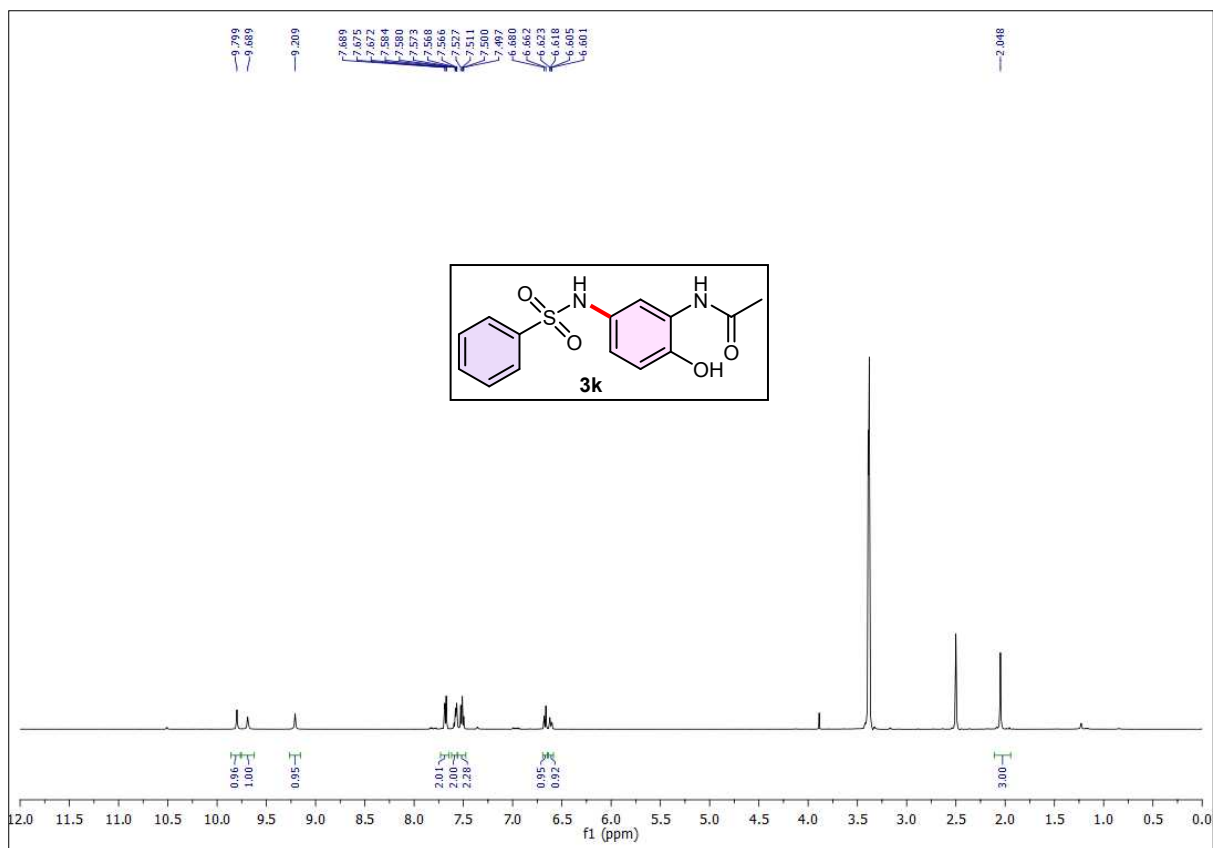




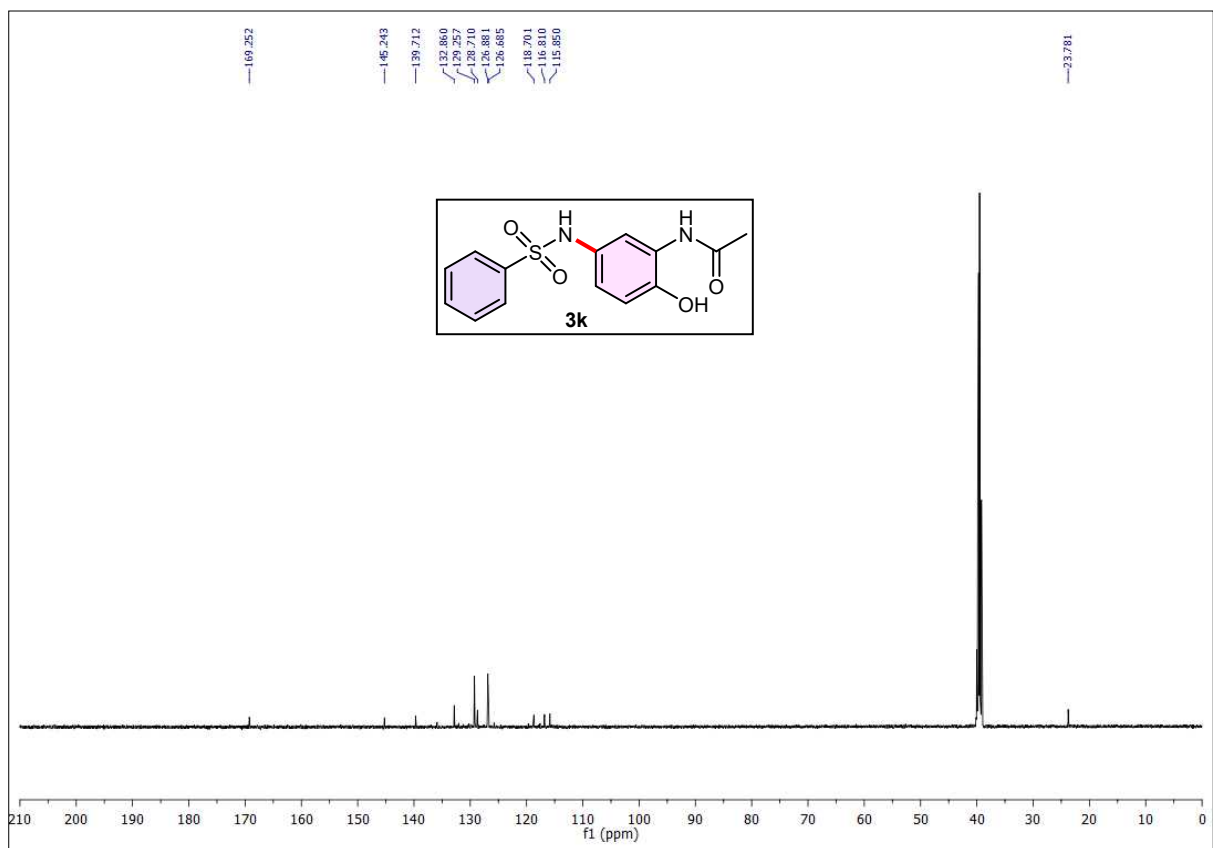
**Spectrum 19.** 500 MHz  $^1\text{H}$  NMR (DMSO- $d_6$ ) of compound **3j**



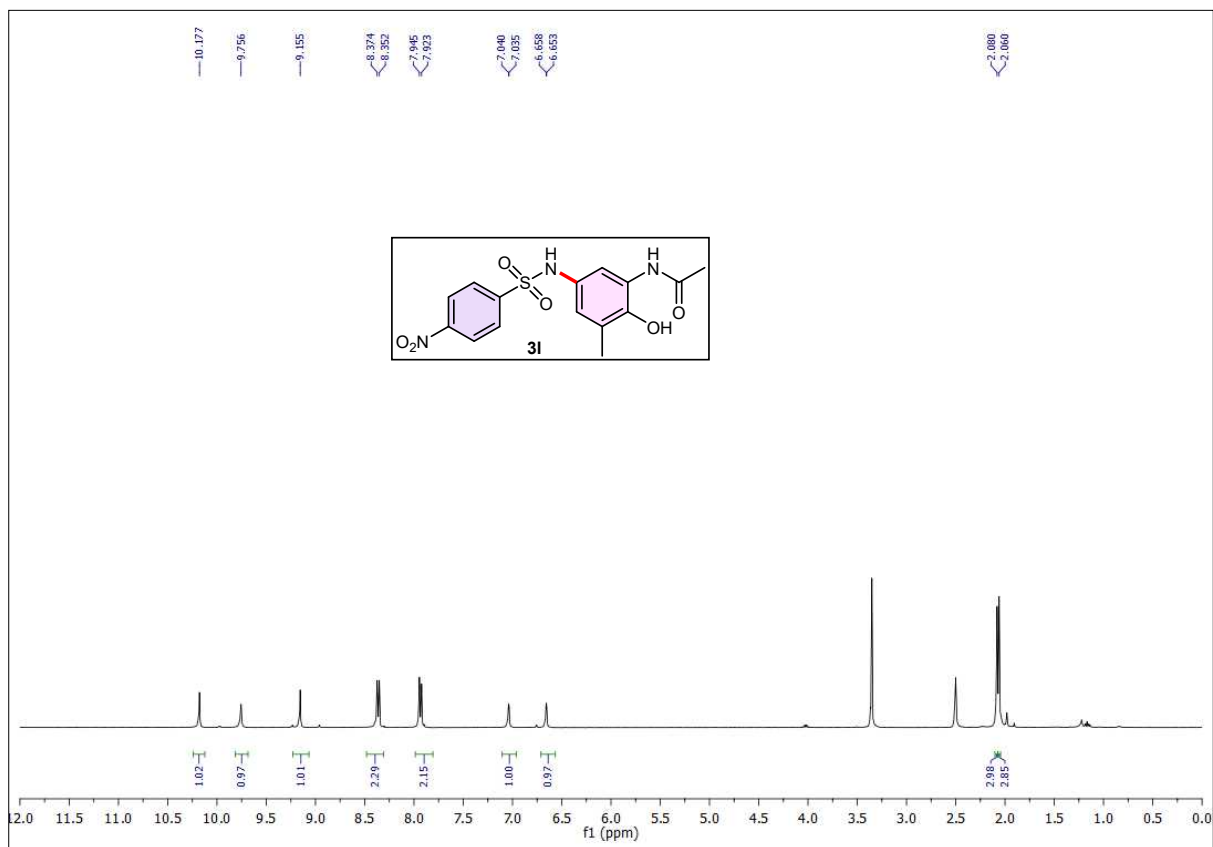
**Spectrum 20.** 125 MHz  $^{13}\text{C}\{^1\text{H}\}$  (DMSO- $d_6$ ) NMR of compound **3j**



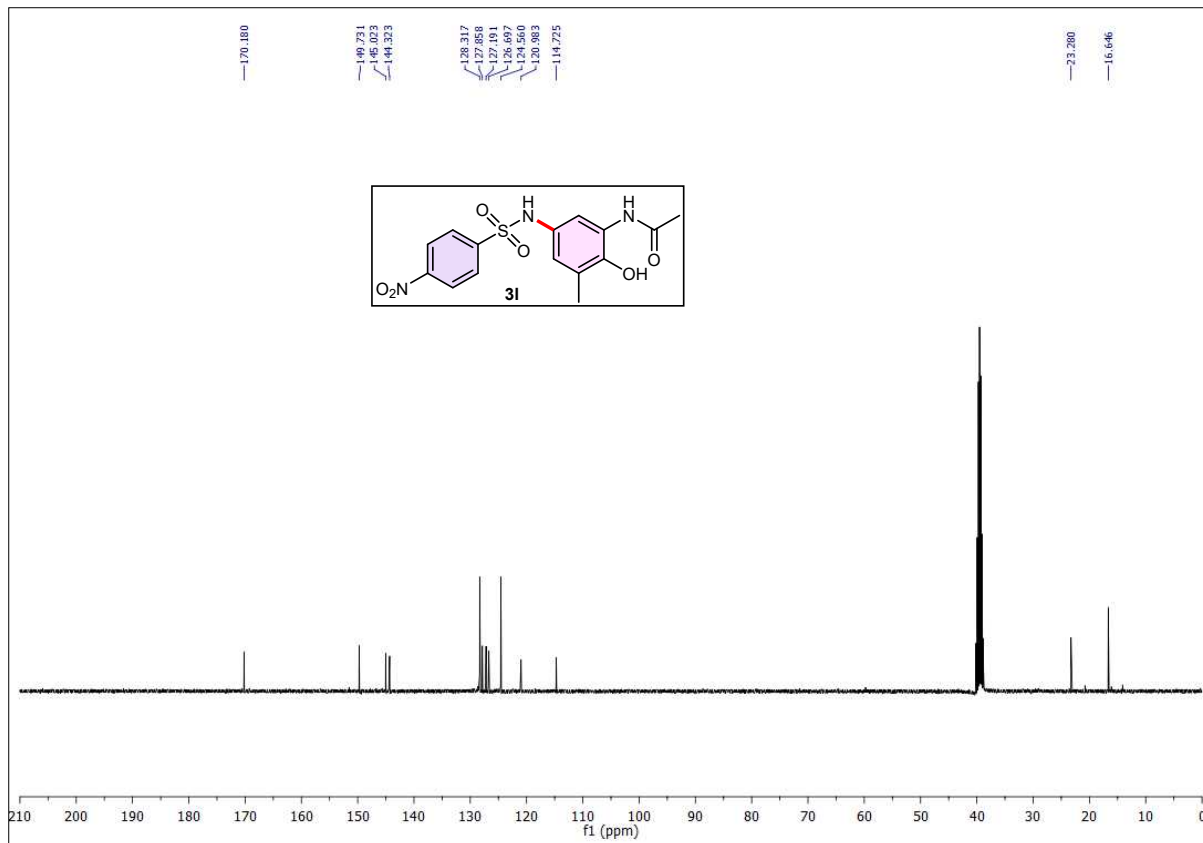
Spectrum 21. 500 MHz <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) of compound **3k**



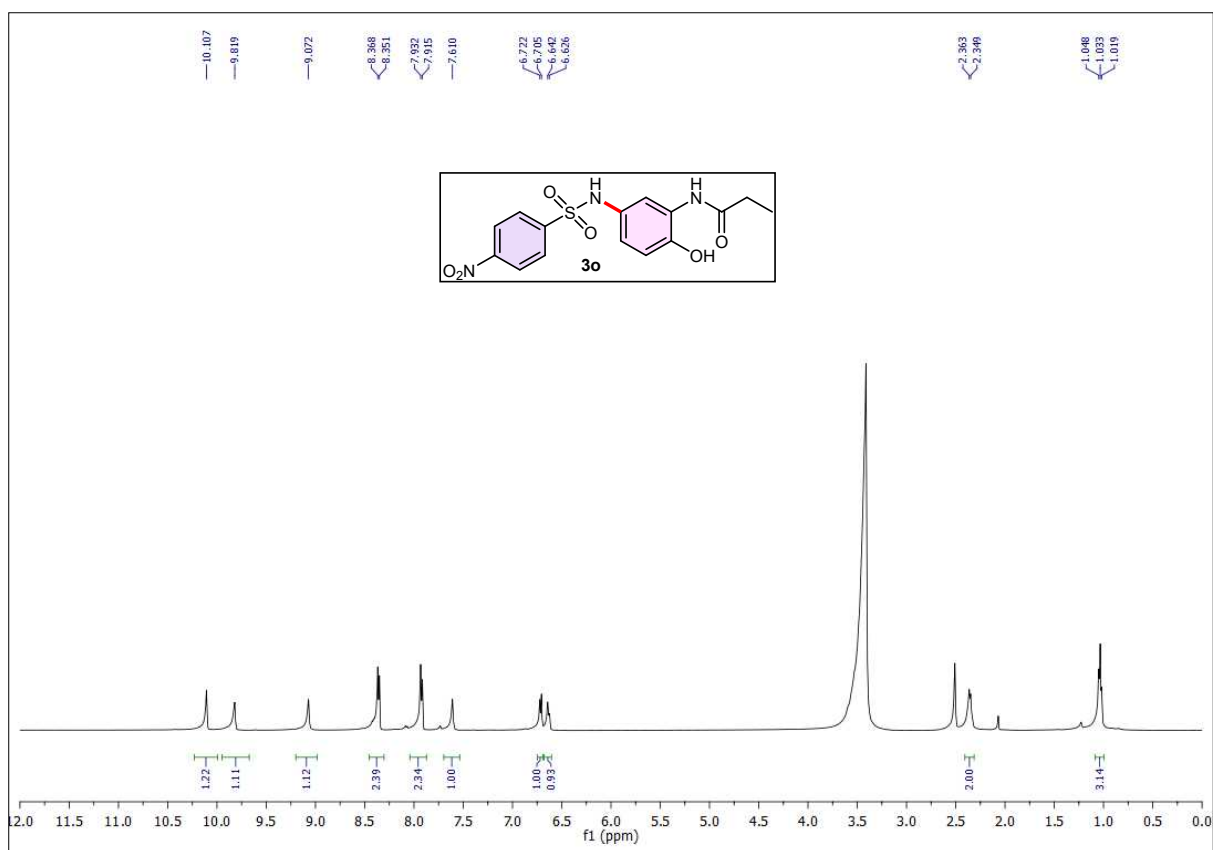
Spectrum 22. 125 MHz <sup>13</sup>C{<sup>1</sup>H} (DMSO-*d*<sub>6</sub>) NMR of compound **3k**



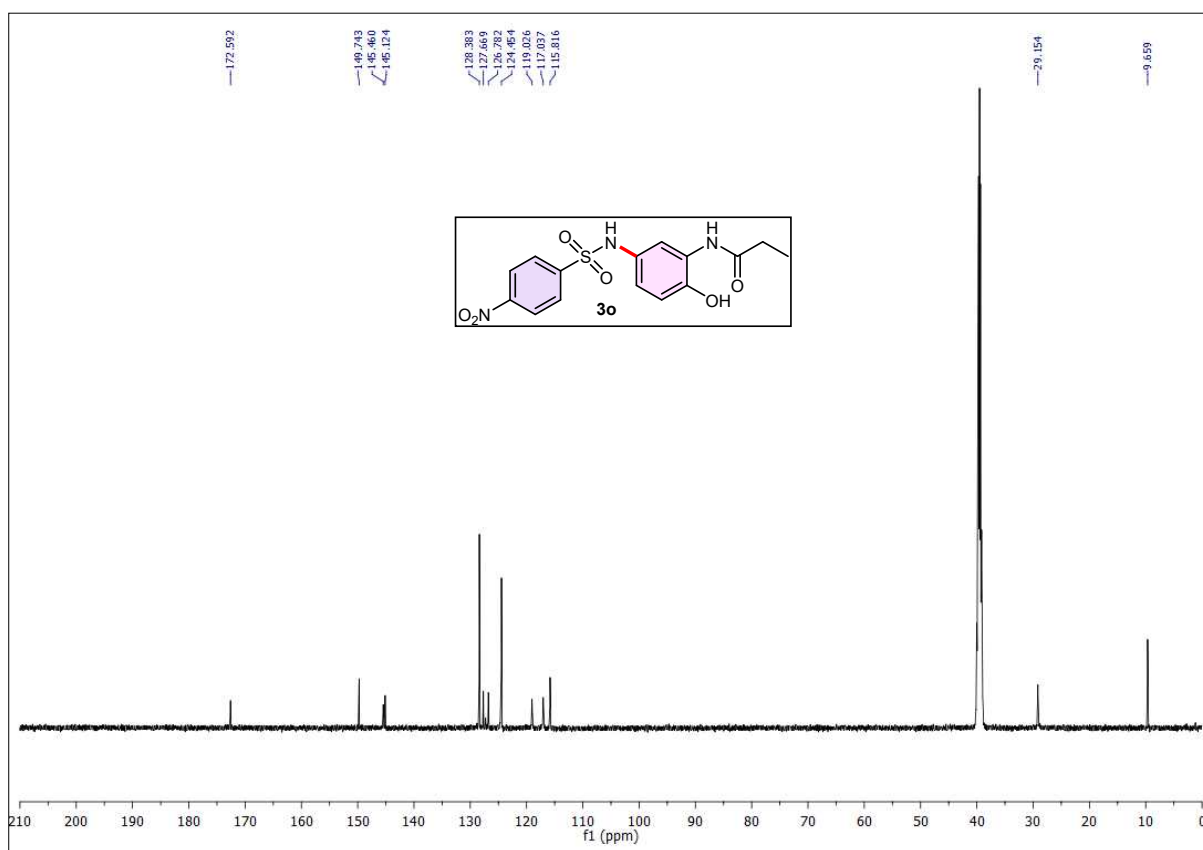
Spectrum 23. 400 MHz  $^1\text{H}$  NMR (DMSO- $d_6$ ) of compound **31**



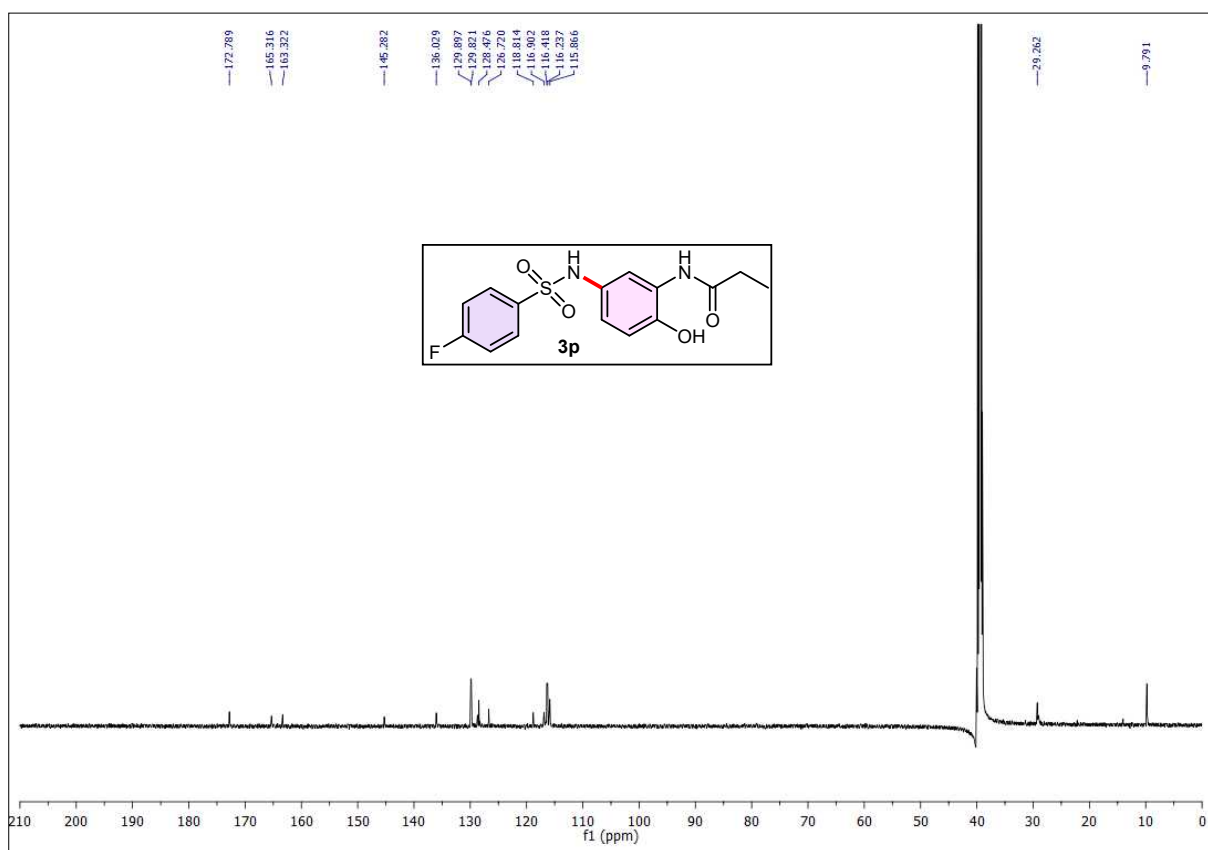
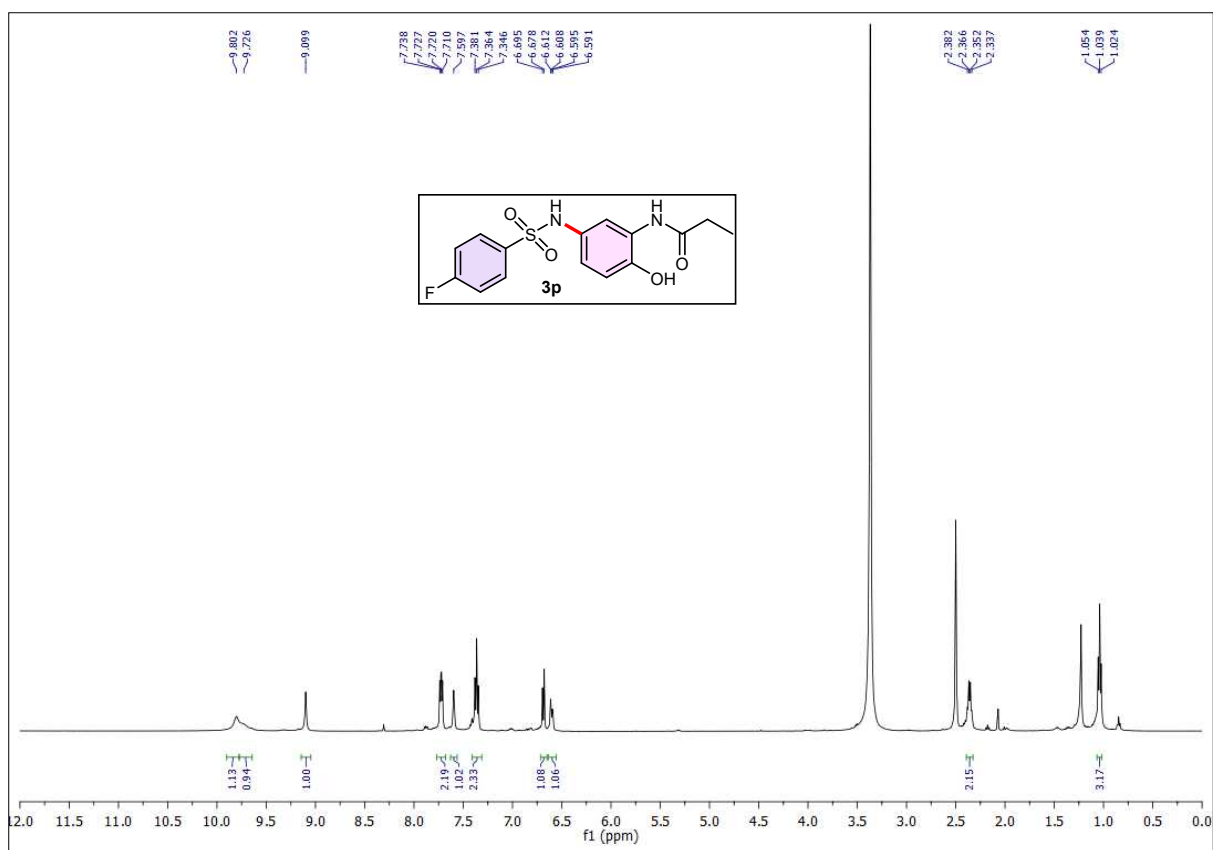
Spectrum 24. 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  (DMSO- $d_6$ ) NMR of compound **31**

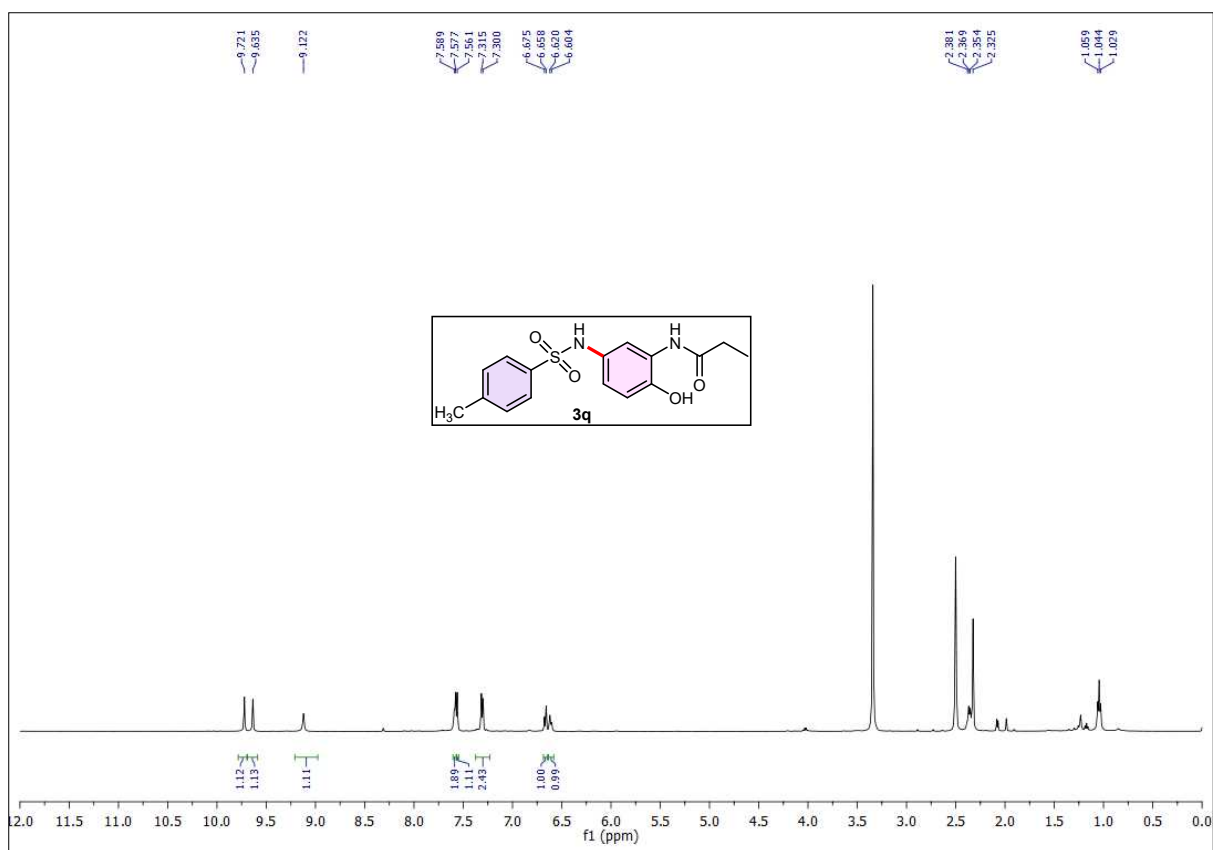


Spectrum 25. 500 MHz <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) NMR of compound **3o**

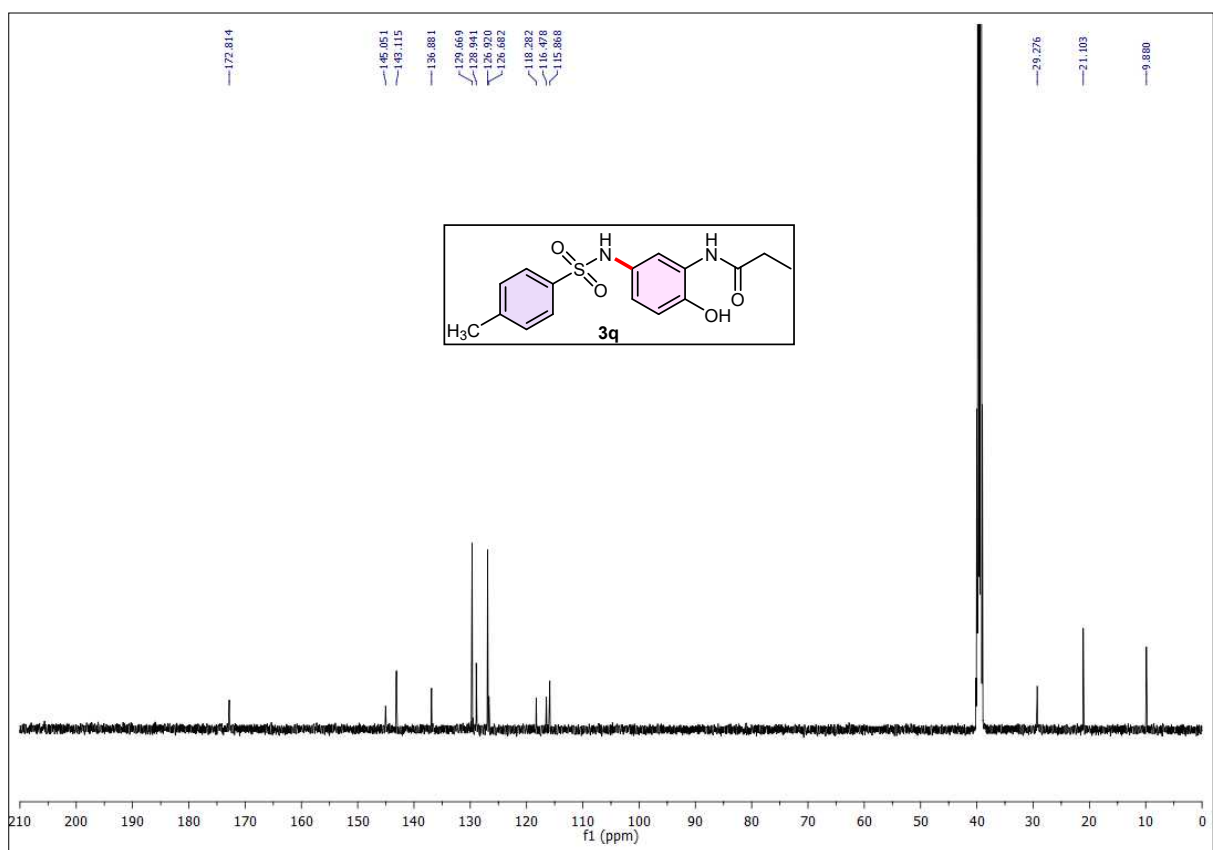


Spectrum 26. 125 MHz <sup>13</sup>C{<sup>1</sup>H} (DMSO-*d*<sub>6</sub>) NMR of compound **3o**

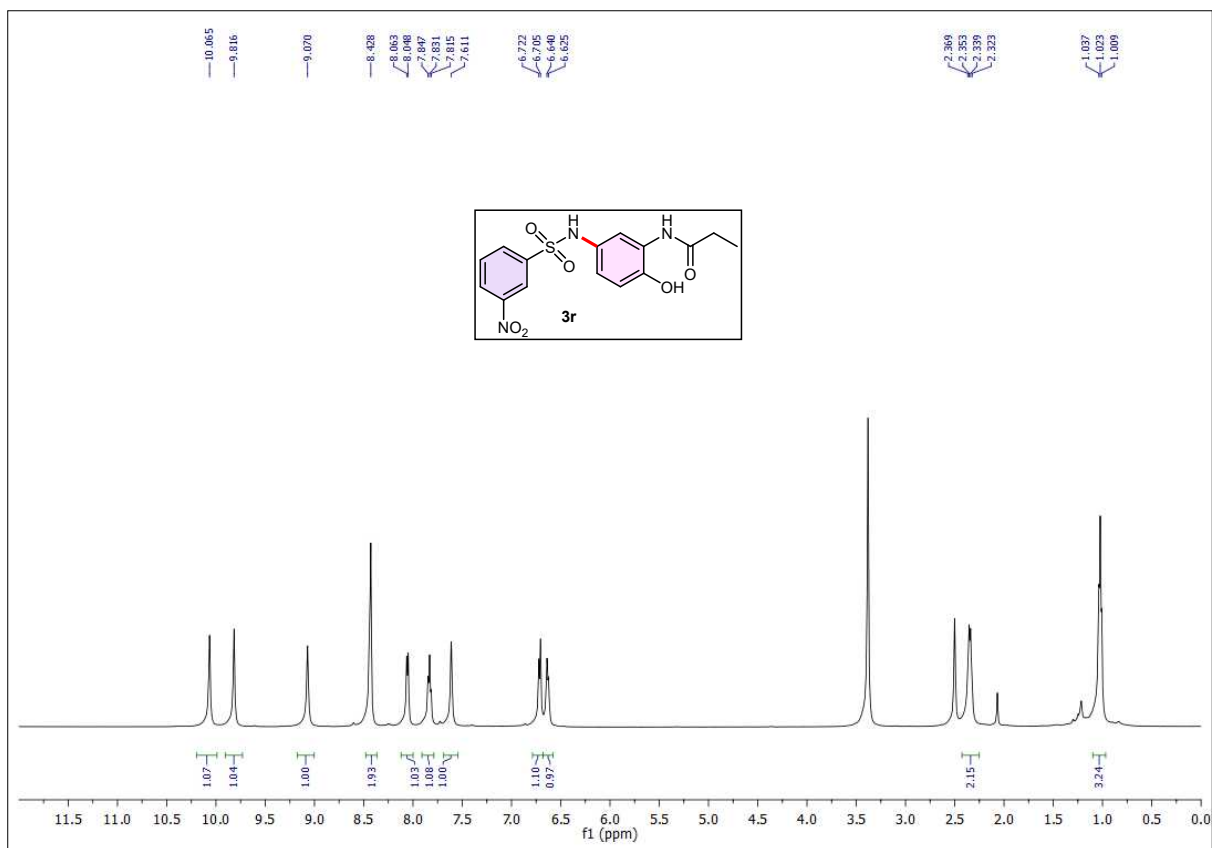




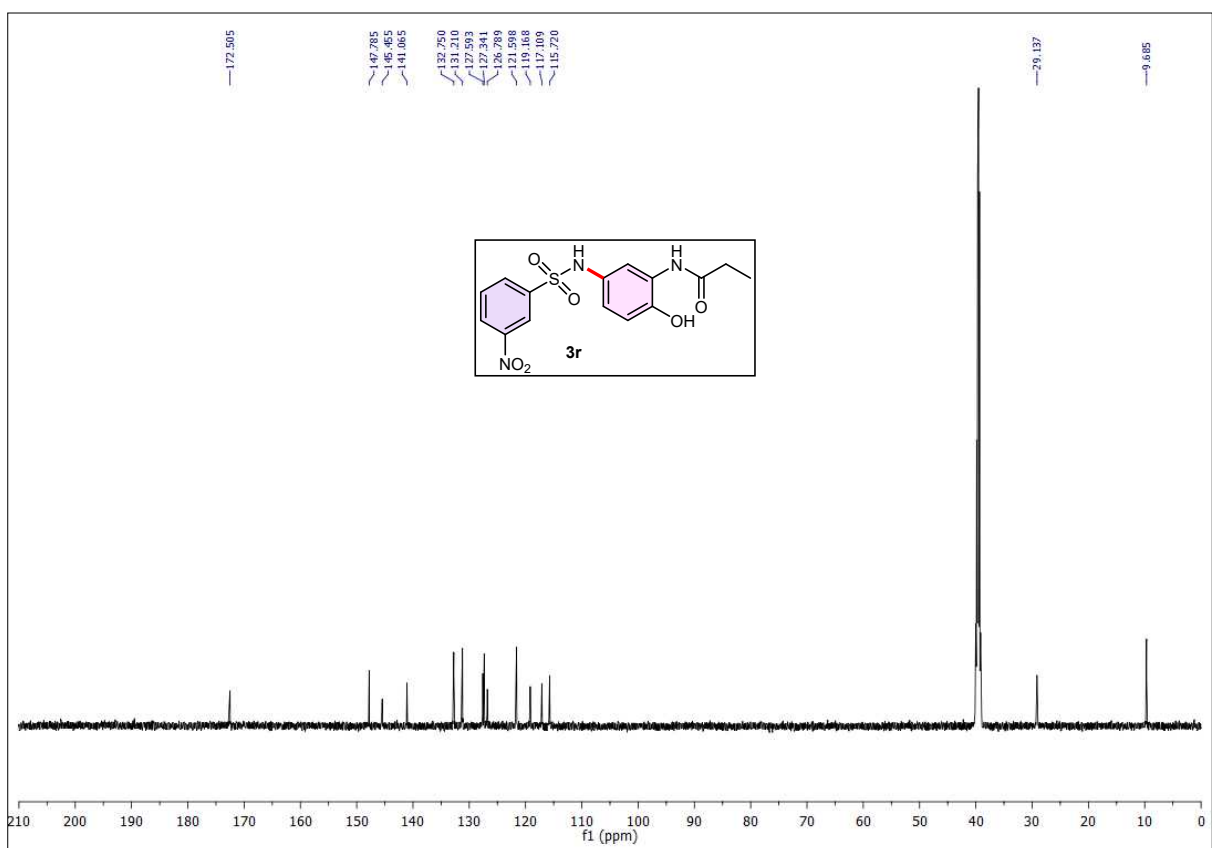
Spectrum 29. 500 MHz  $^1\text{H}$  NMR (DMSO- $d_6$ ) of compound **3q**



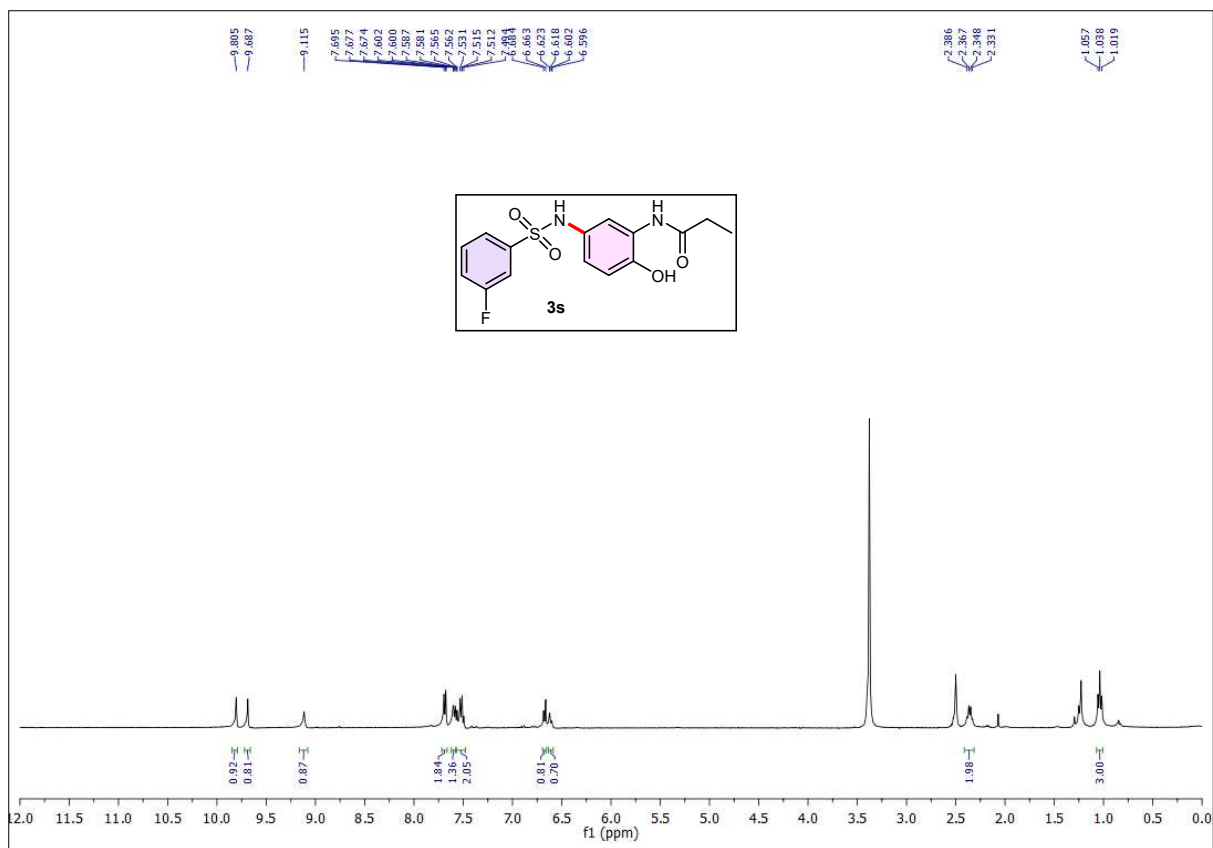
Spectrum 30. 125 MHz  $^{13}\text{C}\{^1\text{H}\}$  (DMSO- $d_6$ ) NMR of compound **3q**



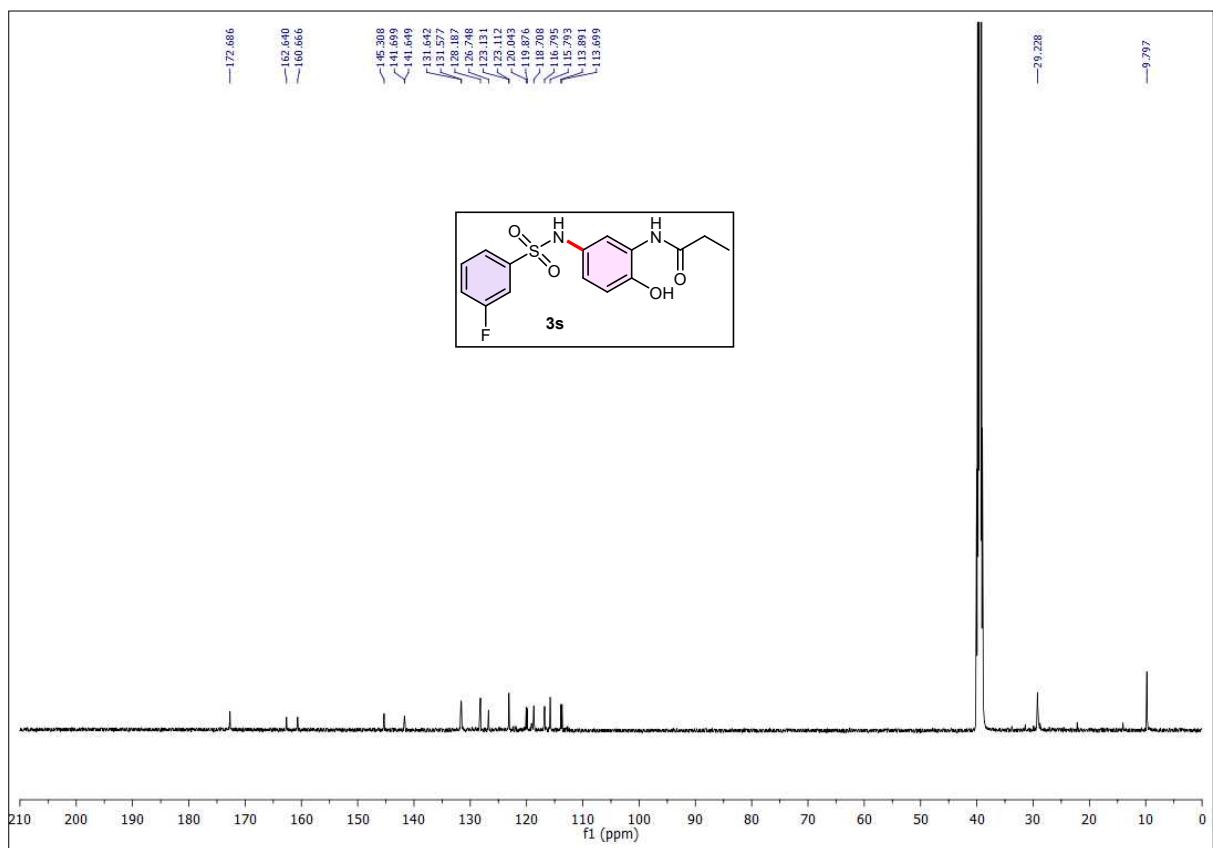
**Spectrum 31.** 500 MHz  $^1\text{H}$  NMR (DMSO- $d_6$ ) of compound **3r**



**Spectrum 32.** 125 MHz  $^{13}\text{C}\{^1\text{H}\}$  (DMSO- $d_6$ ) NMR of compound **3r**

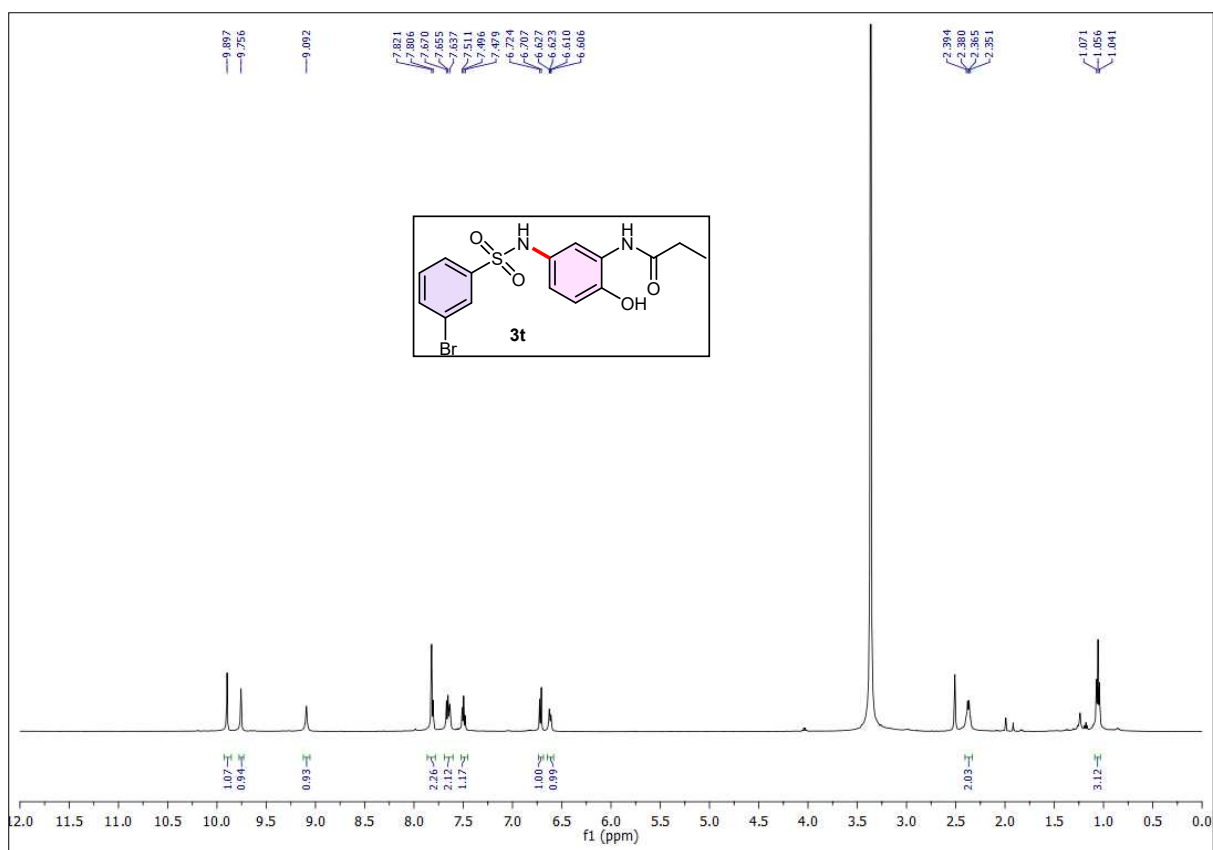


**Spectrum 33.** 400 MHz <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) NMR of compound **3s**

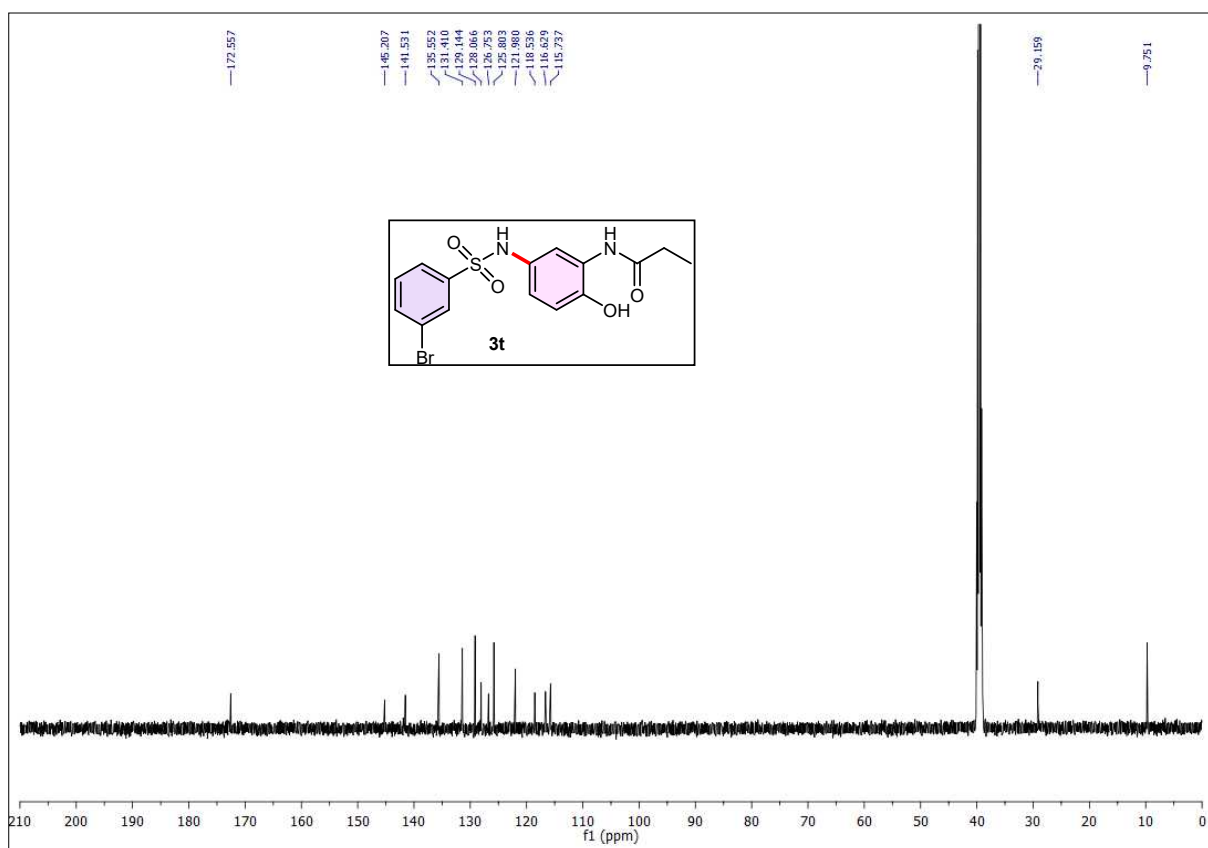


**Spectrum 34.** 100 MHz <sup>13</sup>C{<sup>1</sup>H} (DMSO-*d*<sub>6</sub>) NMR of compound **3s**

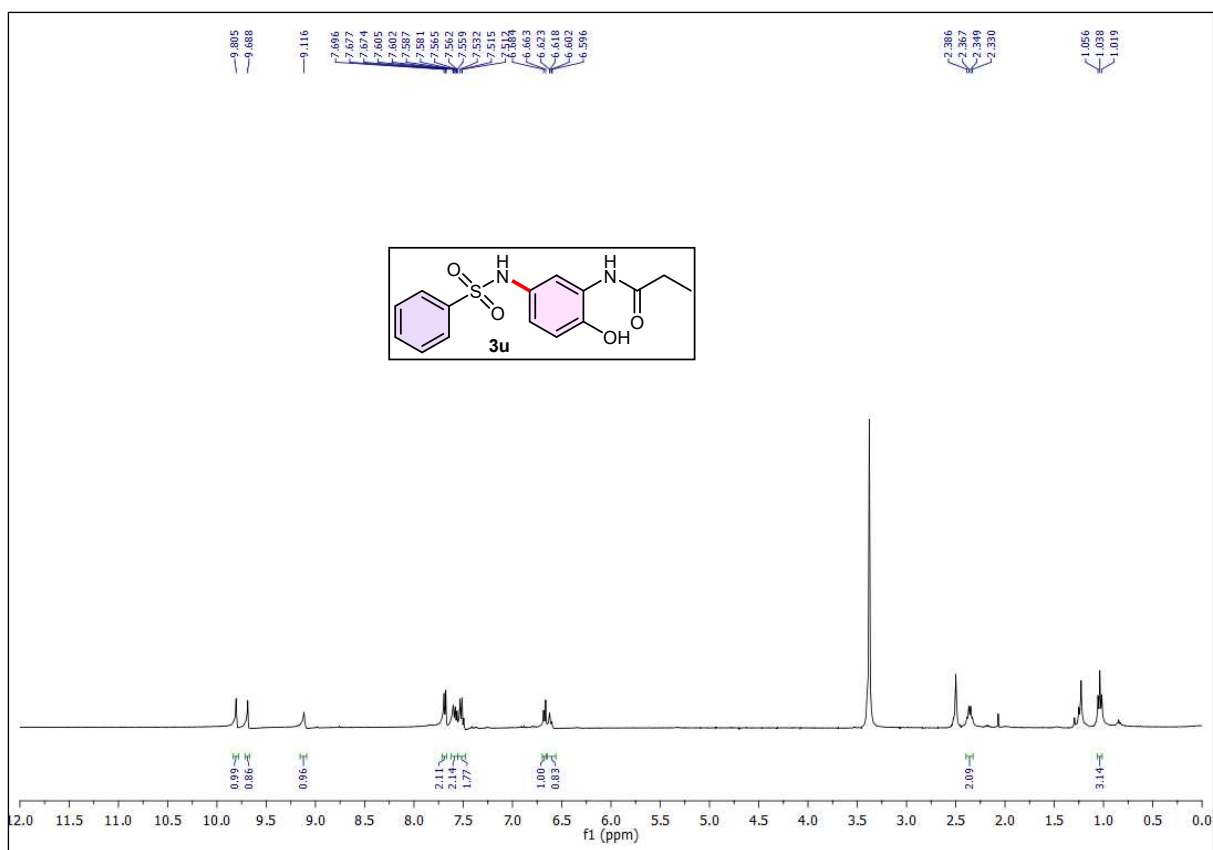




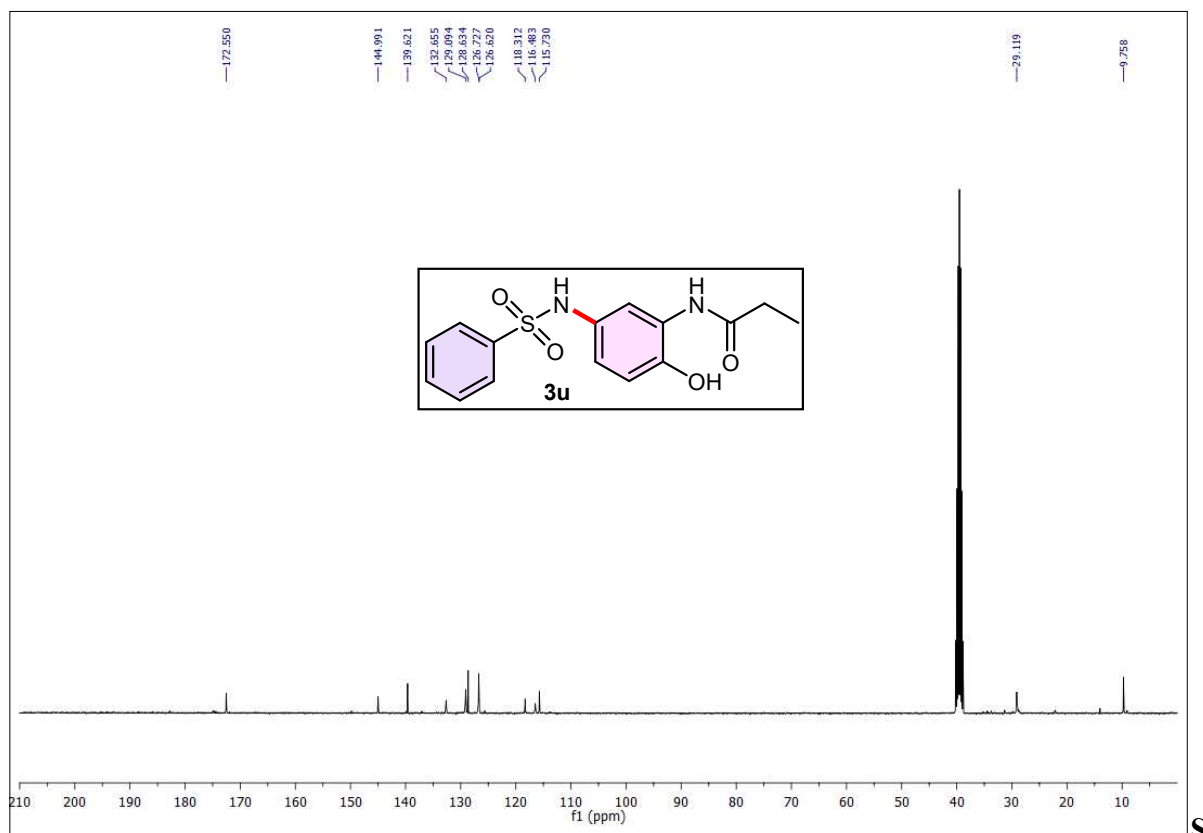
Spectrum 35. 500 MHz  $^1\text{H}$  NMR (DMSO- $d_6$ ) of compound **3t**



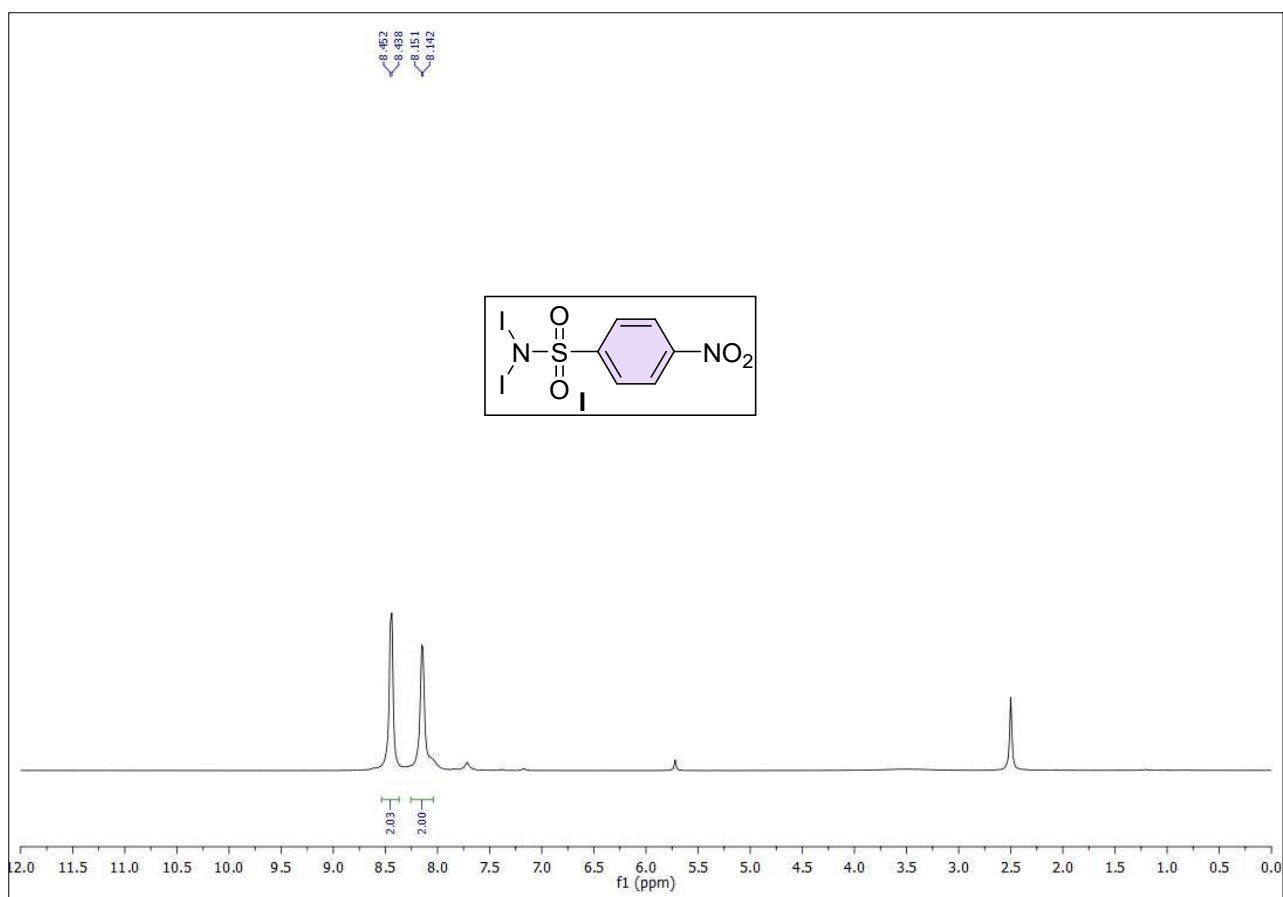
Spectrum 36. 125 MHz  $^{13}\text{C}\{^1\text{H}\}$  (DMSO- $d_6$ ) NMR of compound **3t**



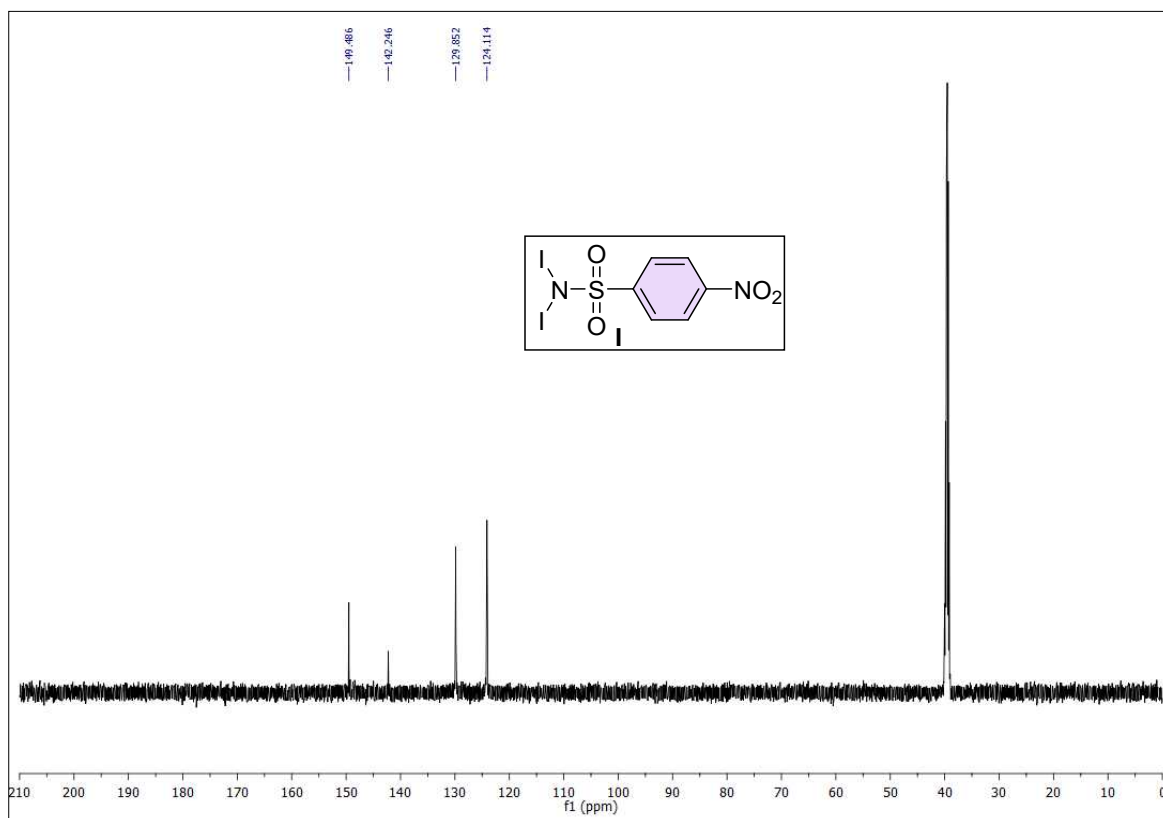
Spectrum 37. 400 MHz  $^1\text{H}$  NMR (DMSO- $d_6$ ) of compound **3u**



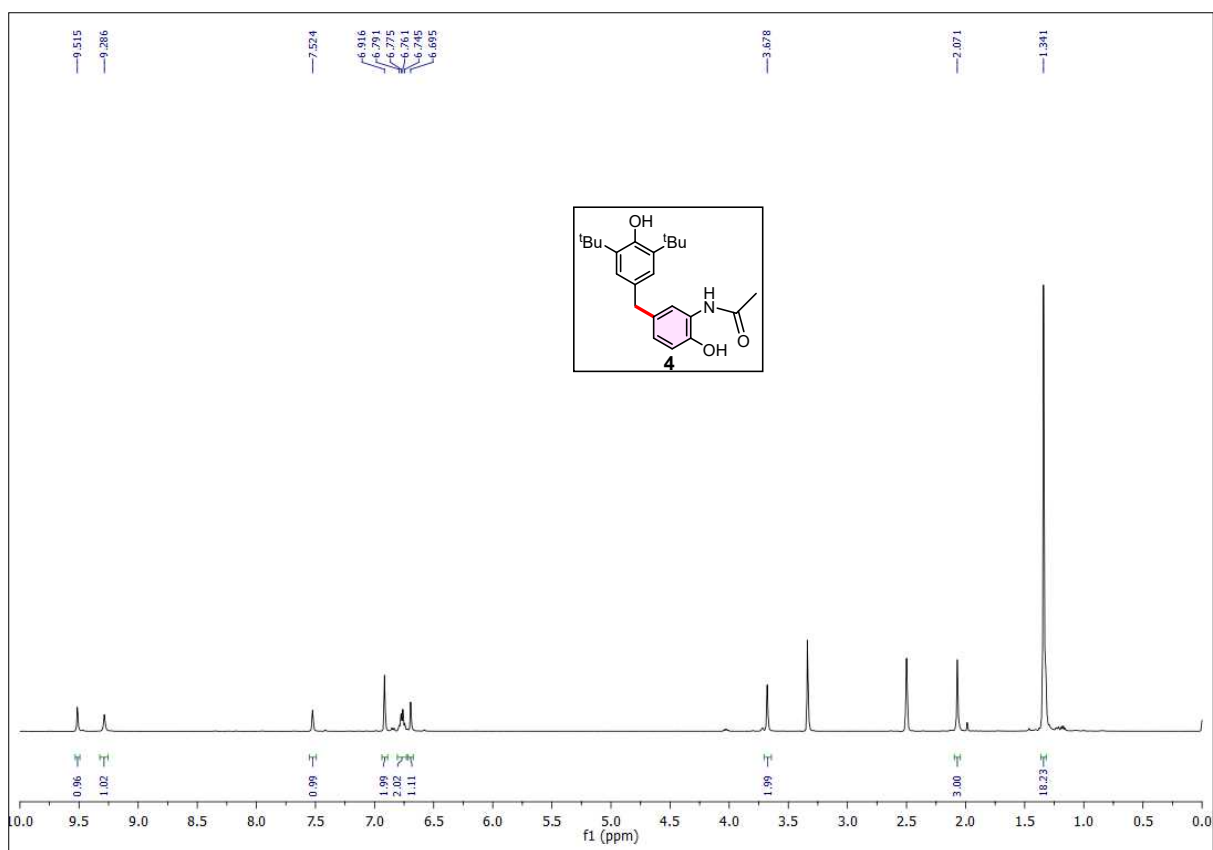
pectrum 38. 100 MHz  $^{13}\text{C}\{^1\text{H}\}$  (DMSO- $d_6$ ) NMR of compound **3u**



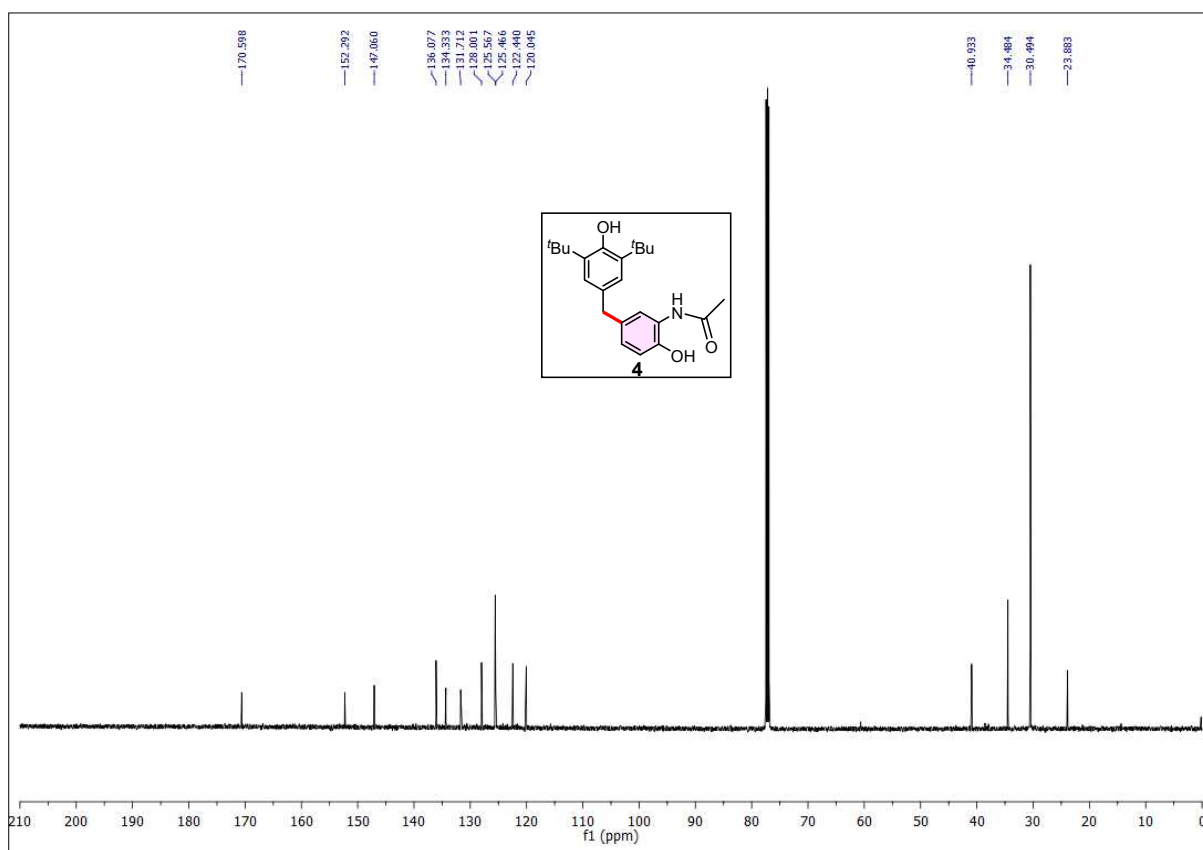
**Spectrum 39.** 500 MHz  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ ) of Intermediate I



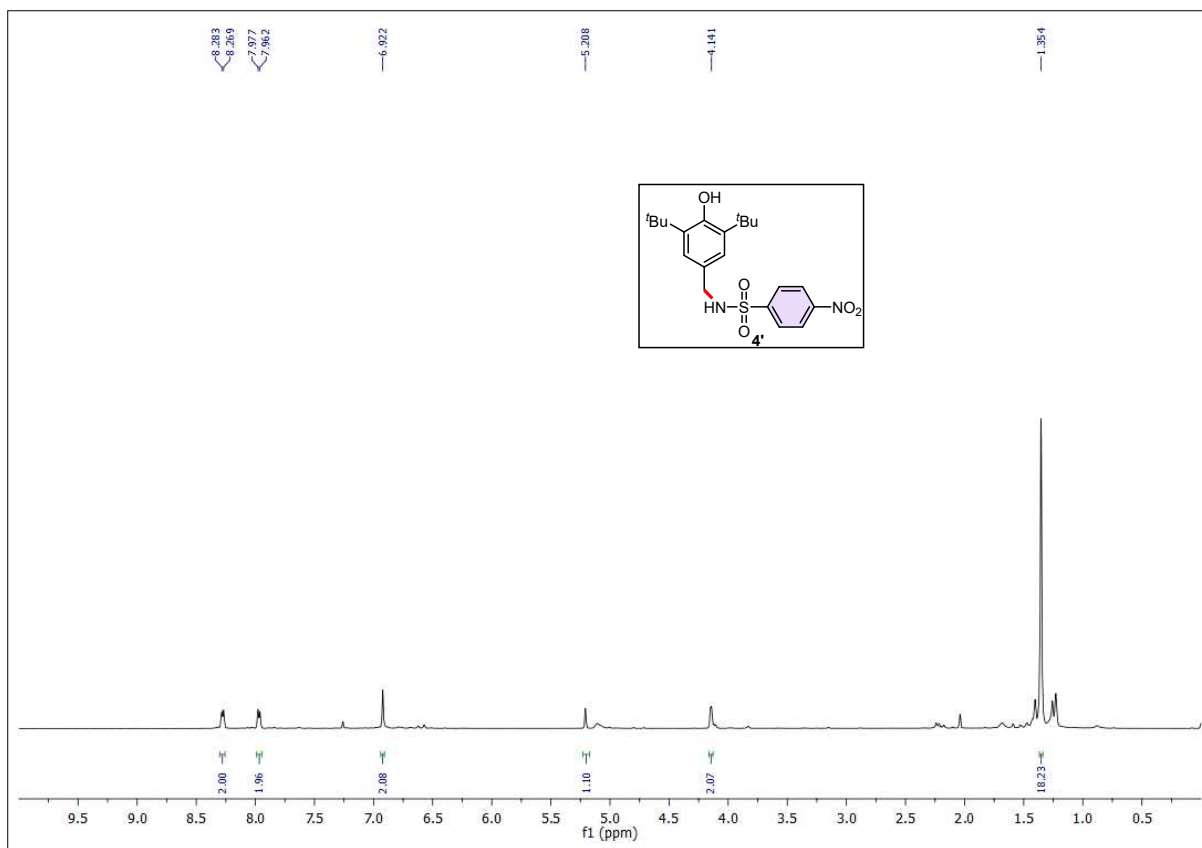
**Spectrum 40.** 125 MHz  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{DMSO-}d_6$ ) NMR of Intermediate I



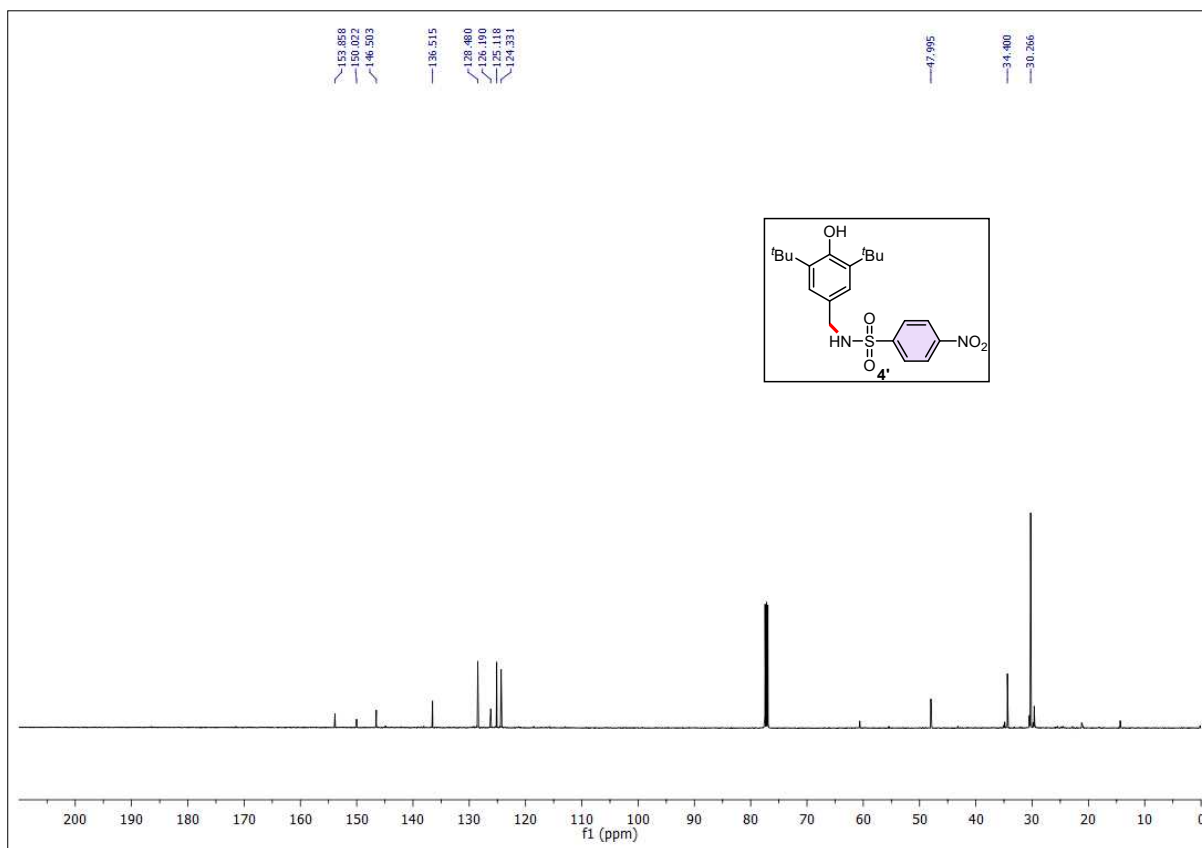
**Spectrum 41.** 500 MHz  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ ) of BHT adduct 4



**Spectrum 42.** 125 MHz  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{CDCl}_3$ ) NMR of BHT adduct 4



**Spectrum 43.** 500 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) of BHT adduct **4'**



**Spectrum 44.** 125 MHz  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{CDCl}_3$ ) NMR of BHT adduct **4'**