

**Ru-g-C<sub>3</sub>N<sub>4</sub> as highly active heterogeneous catalyst for transfer hydrogenation  
of  $\alpha$ -keto amide into  $\beta$ -aminol or  $\alpha$ -hydroxyl amide**

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Sr. No.	Content	Page No.
1.	General material and methods for the synthesis of catalyst	S2
2.	FEG-SEM of g-C <sub>3</sub> N <sub>4</sub> and Ru-g-C <sub>3</sub> N <sub>4</sub>	S3
3.	XPS of Ru-g-C <sub>3</sub> N <sub>4</sub>	S4
4.	EDX Spectra of Ru-g-C <sub>3</sub> N <sub>4</sub>	S4
5.	Powder X-Ray Diffraction of (Ru, Pd, Ni) metal loaded on g-C <sub>3</sub> N <sub>4</sub> and plain g-C <sub>3</sub> N <sub>4</sub>	S5
6.	XRD, FEG-SEM and EDX Spectra of Recycled Ru-g-C <sub>3</sub> N <sub>4</sub> ; Catalyst Recyclability	S6
7.	AT-IR spectra and TGA graph of (Ru, Pd, Ni) metal loaded on g-C <sub>3</sub> N <sub>4</sub> and plain g-C <sub>3</sub> N <sub>4</sub>	S7
8.	Control Experiment	S8
9.	General method and data for the synthesis of $\beta$ -aminol & $\alpha$ -hydroxyl amide	S9-S18
10.	Copy of <sup>1</sup> H and <sup>13</sup> C-NMR of $\beta$ -aminol & $\alpha$ -hydroxyl amide compounds	S19-S47

### **General material and methods for the synthesis of catalyst:**

For the preparation of  $g\text{-C}_3\text{N}_4$ ,  $\text{Ni-g-C}_3\text{N}_4$ ,  $\text{Pd-g-C}_3\text{N}_4$ ,  $\text{Ru-g-C}_3\text{N}_4$  various chemicals used as: Urea,  $\text{RuCl}_3$ ,  $\text{NiCl}_2$ ,  $\text{PdCl}_2$  were procured from Oxford Product Pvt. Ltd., Spectrochem, Sigma Aldrich, Distilled water purchased from High Purity Laboratory Chemicals, Conc. HCl from Advent. For the preparation of  $\alpha$ -keto amide  $\text{SeO}_2$  and  $\text{NaBH}_4$  were purchased from Oxford Product Pvt. Ltd. and s.d. fine chemical limited, and acetophenone derivatives were purchased from Alfa Aesar & Sigma Aldrich. Thin Layer Chromatography Silica Gel 60 F254 was purchased from Merck Specialities Pvt. Ltd., Silica gel for column chromatography (100-200 mesh) was purchased from SRL, India. NMR spectra were recorded with 500 MHz for  $^1\text{H}$  NMR and 126 MHz for  $^{13}\text{C}$  NMR spectrometer. The chemical shifts are reported in parts per million related to tetramethyl silane as an internal standard and the coupling constant  $J$  in hertz.  $^1\text{H}$  NMR spectra are reported relative to residual  $\text{CDCl}_3$  ( $\delta = 7.26$  ppm),  $\text{DMSO-d}_6$  ( $\delta = 2.50$  ppm).  $^{13}\text{C}$  NMR are reported relative to  $\text{CDCl}_3$  ( $\delta = 77.02$  ppm),  $\text{DMSO-d}_6$  ( $\delta = 39.52$  ppm). The reaction was monitored by GC and TLC. The products were analysed by GC-MS and NMR-Spectroscopy.

### **Preparation of catalyst:**

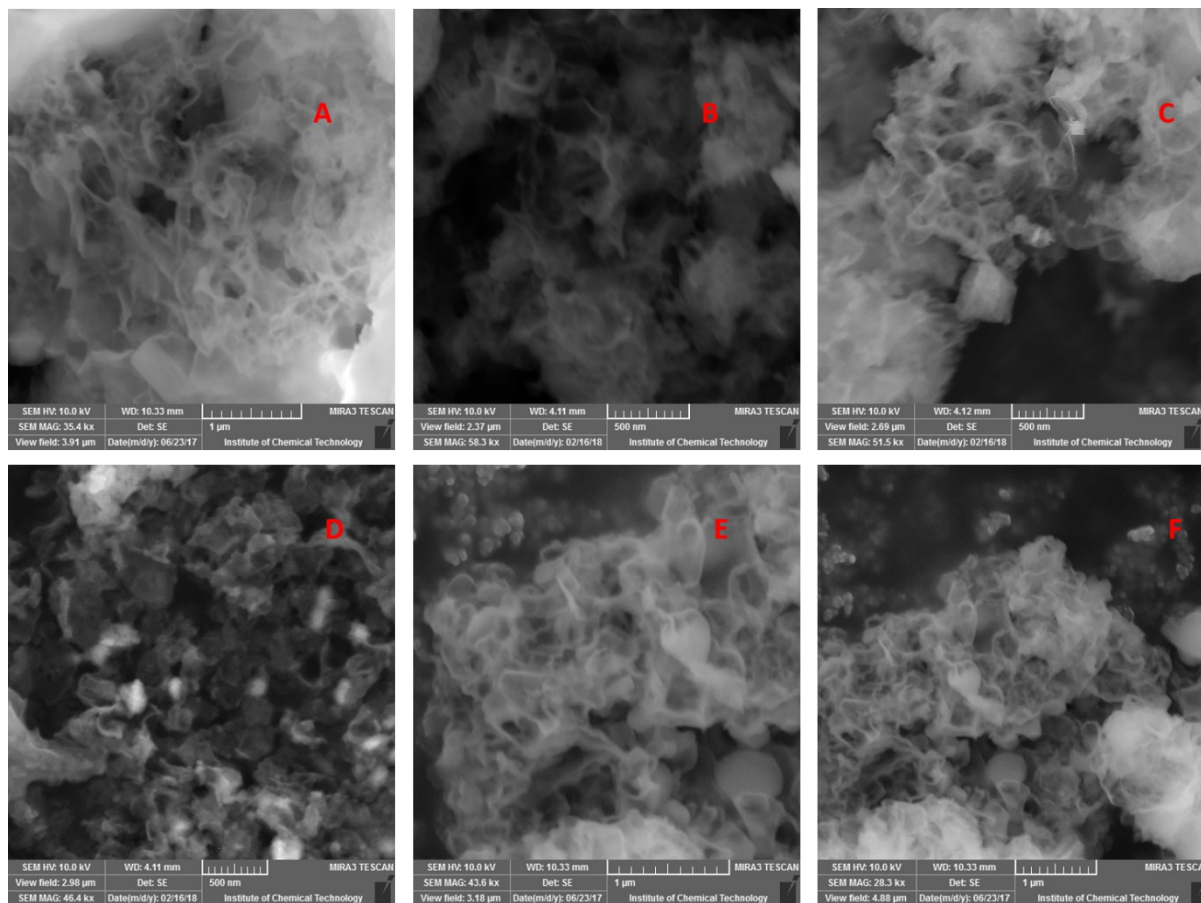
*Preparation of  $g\text{-C}_3\text{N}_4$  catalyst* <sup>[1]</sup>:  $\text{C}_3\text{N}_4$  was synthesized by using pyrolytic method disclosed by Wei Chen. Typically, 20 gm of urea was first heated at  $80^\circ\text{C}$  for 8 h to remove the presence of moisture in the urea. It is then kept in covered crucible and then heated under static air at heating rate of  $3^\circ\text{C}/\text{min}$  until it reaches the temperature at  $520^\circ\text{C}$  and then kept at this temperature for 4 hr so that complete polymerization of urea takes place. After 4 hr pale yellow colour powder was obtained.

*Preparation of  $\text{Ru-g-C}_3\text{N}_4$  catalyst*: For the preparation of  $\text{Ru-g-C}_3\text{N}_4$  catalyst Ultrasonic deposition method was used to increase the effectiveness of loading of Ru on  $g\text{-C}_3\text{N}_4$  support <sup>[2]</sup>. Typically, 500 mg of yellow colour powder ( $g\text{-C}_3\text{N}_4$ ) obtained in previous step was dispersed in 60ml of  $\text{H}_2\text{O}$  and ultrasonicated for 2h. Further 12 mg of  $\text{RuCl}_3$  was added into mixture and again kept for ultrasonication for another 30 min. To the resultant mixture, 10 ml  $\text{NaBH}_4$  solution was added with continuous stirring. The grey-blue product was filtered, washed with water and ethanol. Process of washing is repeated twice to thrice, further it is dried at  $60^\circ\text{C}$  and used for the application. Similarly,  $\text{Ni-g-C}_3\text{N}_4$  and  $\text{Pd-g-C}_3\text{N}_4$  also has been prepared just like above mentioned method.

## Characterization of $g\text{-C}_3\text{N}_4$ :

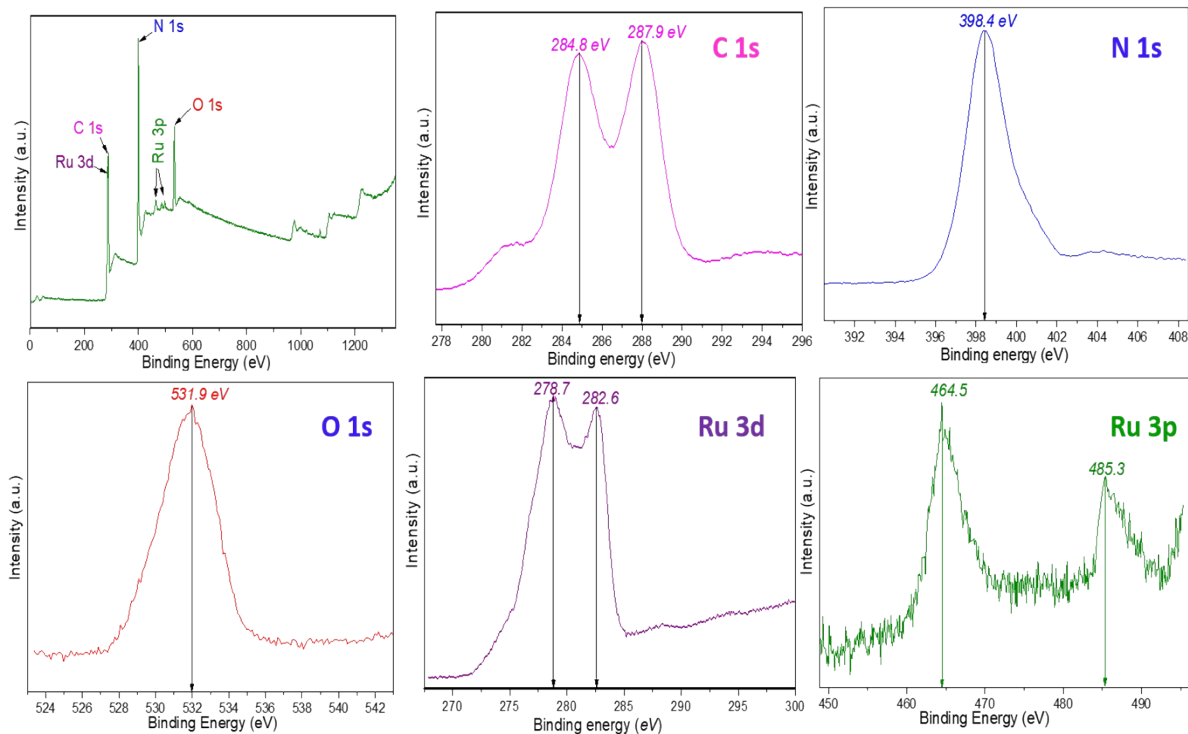
### 1. SEM IMAGES and Electron Microscopy/Energy Dispersive X-ray Spectroscopy

Morphology of Ru- $g\text{-C}_3\text{N}_4$  was investigated using field emission gun-scanning electron microscopy (FEG-SEM, Tescan MIRA 3 model) at 10 eV. The compositions of Ru- $\text{C}_3\text{N}_4$  were characterized by energy dispersive X-ray spectroscopy (EDS) scans in oxford X-act model.



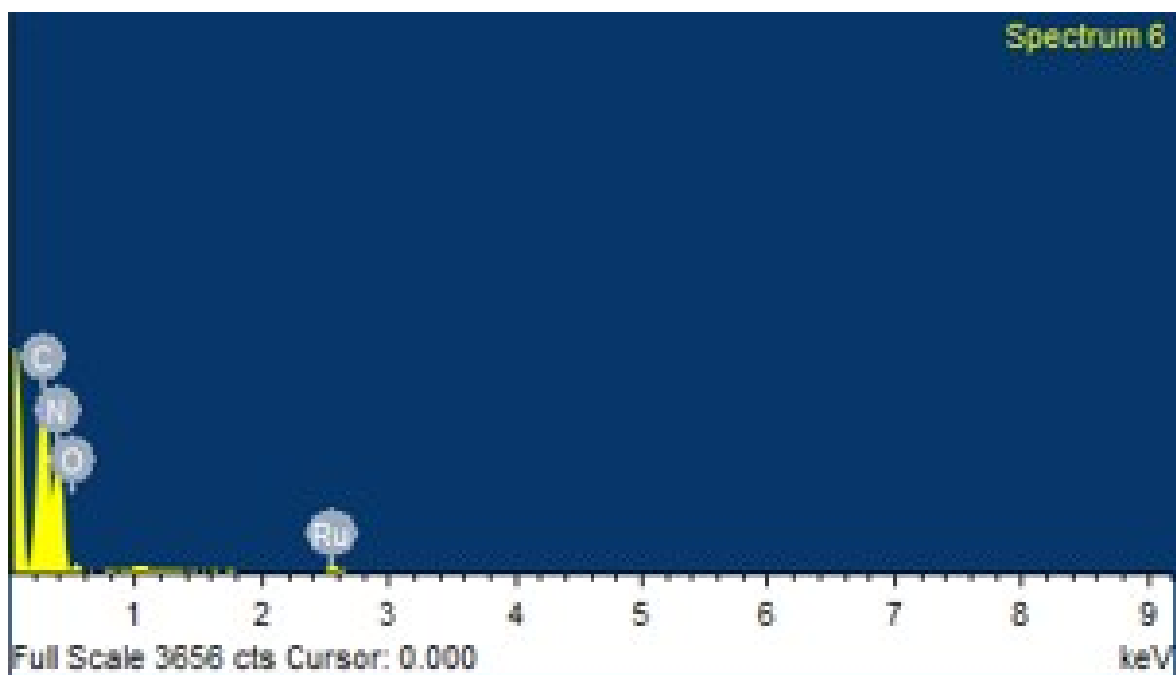
**Figure S1:** SEM images: A), B), C)  $g\text{-C}_3\text{N}_4$ ; D), E), F) Ru- $g\text{-C}_3\text{N}_4$

## 2. X-Ray Photoelectron Spectroscopy (XPS) SPECTRA OF Ru-g-C<sub>3</sub>N<sub>4</sub> material: [3]



**Figure S2:** XPS spectra: a) full scan of Ru-g-C<sub>3</sub>N<sub>4</sub>; b) C 1s region of Ru-g-C<sub>3</sub>N<sub>4</sub>; c) N 1s region of Ru-g-C<sub>3</sub>N<sub>4</sub>; d) O 1s region of Ru-g-C<sub>3</sub>N<sub>4</sub>; 5) Ru 3d region of Ru-g-C<sub>3</sub>N<sub>4</sub>; 6) Ru 3p region of Ru-g-C<sub>3</sub>N<sub>4</sub>

## 3. EDX Spectra of catalyst Ru-g-C<sub>3</sub>N<sub>4</sub>

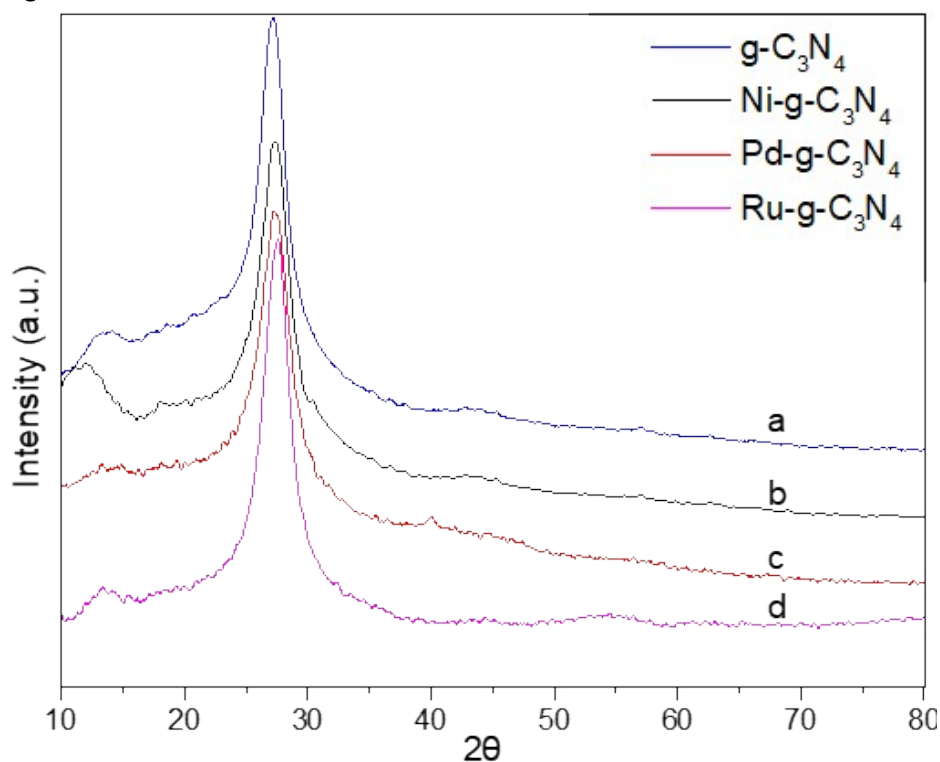


**Figure S3:** EDX spectra of catalyst Ru-g-C<sub>3</sub>N<sub>4</sub>

**4. Powder X-Ray Diffraction pattern of g-C<sub>3</sub>N<sub>4</sub> [3], Ni-g-C<sub>3</sub>N<sub>4</sub> [4], Pd-g-C<sub>3</sub>N<sub>4</sub> [4], Ru-g-C<sub>3</sub>N<sub>4</sub> [3] material:**

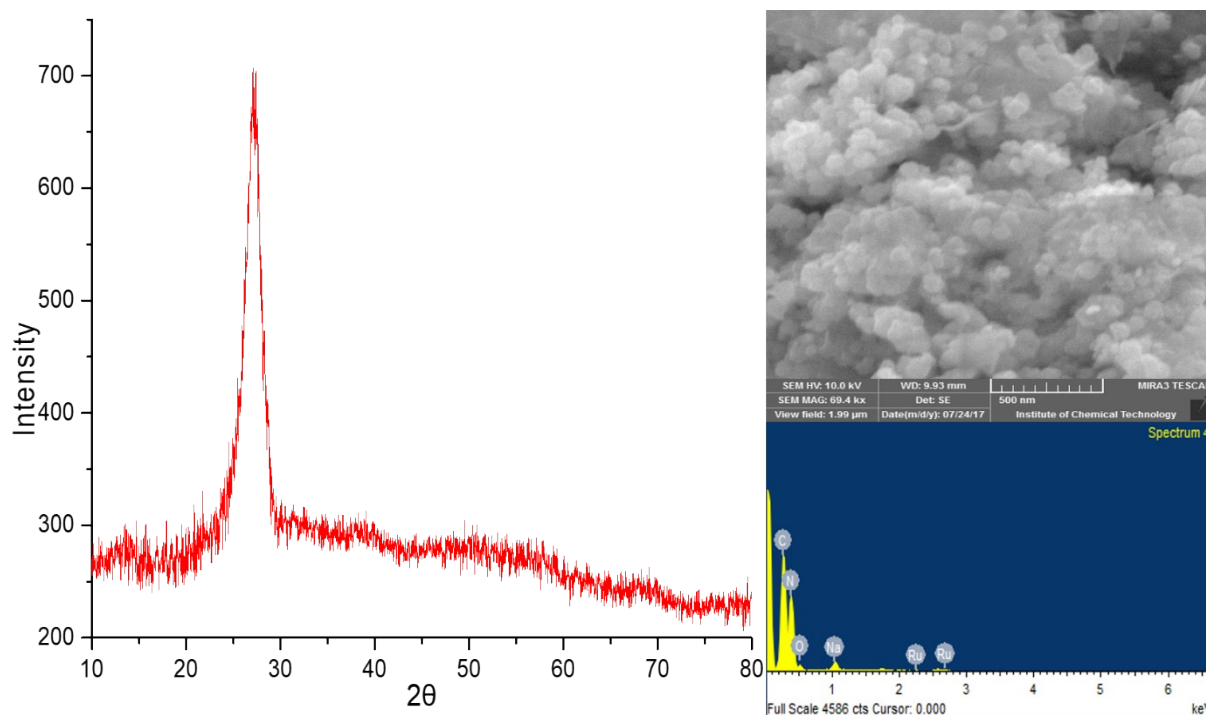
XRD patterns were collected using Shimadzu XRD-6100 (Cu K<sub>α1</sub> radiations, λ<sub>avg</sub> = 1.5405 Å) with scanning rate 2° per min and 2 theta (2θ) angle ranging from 10° to 80°. Powder XRD samples were prepared by placing sample onto a glass sample holder. Crystallite sizes were calculated using the Scherrer equation  $D_{hkl} = K\lambda / \beta \cos\theta$ ; where K is the shape factor (0.9) of the average crystallite, λ is the X- ray wavelength (1.5405 Å), β is the full width at half-maximum (radians), and θ is the Bragg angle (radians).

Typical X-Ray Diffraction (XRD) patterns of g-C<sub>3</sub>N<sub>4</sub>, Ni-g-C<sub>3</sub>N<sub>4</sub>, Pd-g-C<sub>3</sub>N<sub>4</sub>, Ru-g-C<sub>3</sub>N<sub>4</sub> can be shown in Figure S4. From the XRD spectra two peaks observed in all the materials one at nearly 27.18° and other at 13.38°. For g-C<sub>3</sub>N<sub>4</sub> peak observed at 13.67 ° and at 27.08 ° and for Ni- g-C<sub>3</sub>N<sub>4</sub> peaks observed at 11.89° and 27.14° similarly Pd-g-C<sub>3</sub>N<sub>4</sub> shows peak at 13.30° and 27.04° and Ru-g-C<sub>3</sub>N<sub>4</sub> at 13.39° and 27.18°. The intense peak observed at 27.18° is corresponds to characteristic interlayer stacking structure of conjugated aromatic systems with interlayer distance of 0.326 nm. The other weak peak at 13.38° is due to an in-plane structural packing, such as the hole-to-hole distance of the nitride pores. The average size of the Ru-g-C<sub>3</sub>N<sub>4</sub> crystallites was calculated to be 4.29 nm with lattice strain 0.036 having peak width 1.989 degree at 2θ value 27.18 °.



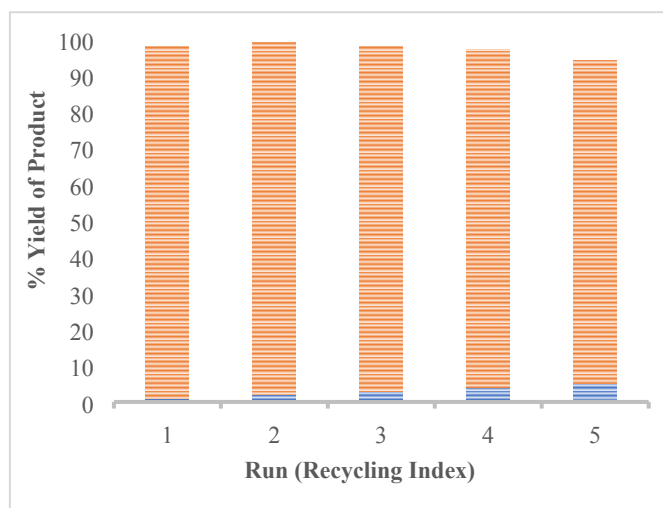
**Figure S4:** XRD Pattern: a) g-C<sub>3</sub>N<sub>4</sub>; b) Ni-g-C<sub>3</sub>N<sub>4</sub>; c) Pd-g-C<sub>3</sub>N<sub>4</sub>; d) Ru-g-C<sub>3</sub>N<sub>4</sub>

## 5. XRD-PATTERN; SEM IMAGES AND EDX SPECTRA OF RECYCLED Ru-g-C<sub>3</sub>N<sub>4</sub> material:



**Figure S5:** XRD pattern of 4<sup>th</sup> recycled Ru-g-C<sub>3</sub>N<sub>4</sub>, SEM-Images and EDX spectra of 4<sup>th</sup> recycled Ru-g-C<sub>3</sub>N<sub>4</sub>

## 6. Recycle study of Ru-g-C<sub>3</sub>N<sub>4</sub> catalyst



**Figure S6:** Recycling study of Ru-g-C<sub>3</sub>N<sub>4</sub> catalyst under the optimised condition for complete transfer hydrogenation of  $\alpha$ -ketoamide into  $\beta$ -aminol

## 7) COMPARATIVE DATA [3]:

a) AT-IR SPECTRA OF SYNTHESIZED  $g-C_3N_4$ ; Ru- $g-C_3N_4$ ; Pd- $g-C_3N_4$ ; Ni- $g-C_3N_4$

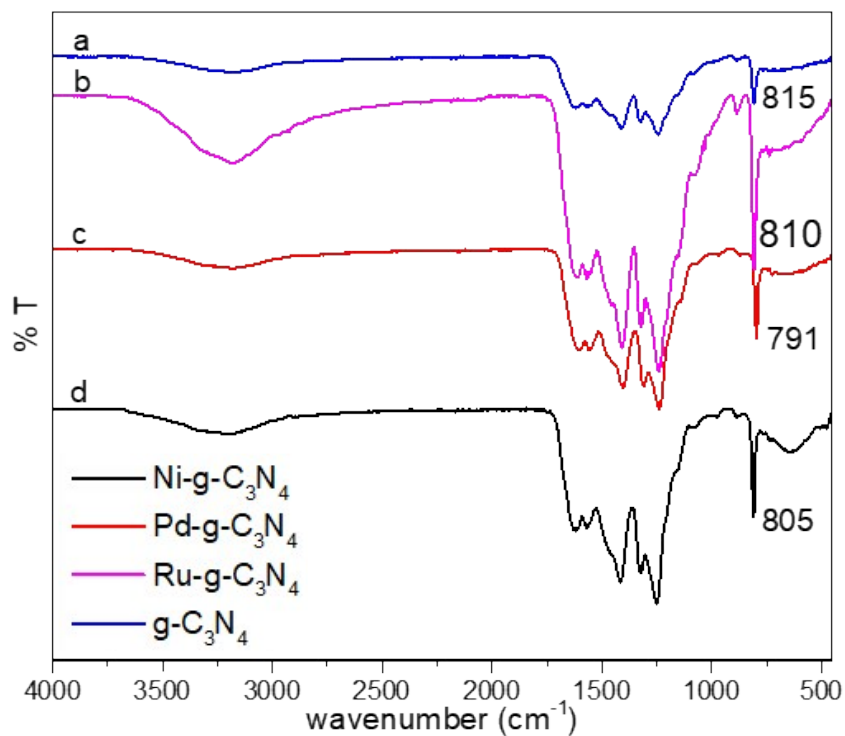


Figure S7: AT-IR spectra: From top a)  $g-C_3N_4$ , b) Ru- $g-C_3N_4$ , c) Pd- $g-C_3N_4$ , d) Ni- $g-C_3N_4$

b) TGA GRAPH OF SYNTHESIZED Ru- $g-C_3N_4$ ; Pd- $g-C_3N_4$ ; Ni- $g-C_3N_4$

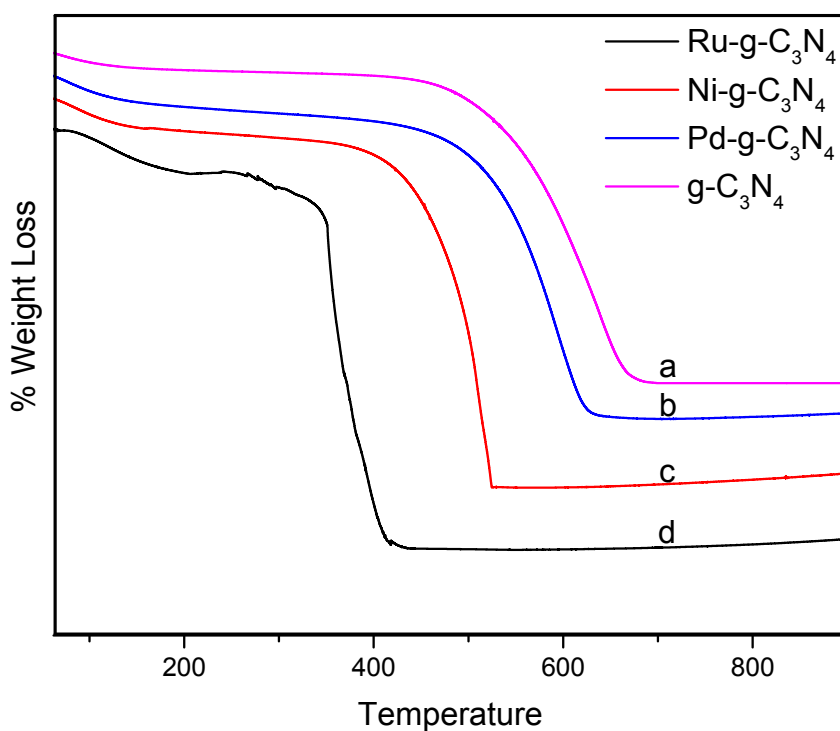


Figure S8: TGA graph: From top a) g-C<sub>3</sub>N<sub>4</sub>, b) Pd-g-C<sub>3</sub>N<sub>4</sub>, c) Ni-g-C<sub>3</sub>N<sub>4</sub>, d) Ru-g-C<sub>3</sub>N<sub>4</sub>

8. Control Experiment drawn based on optimization pattern:

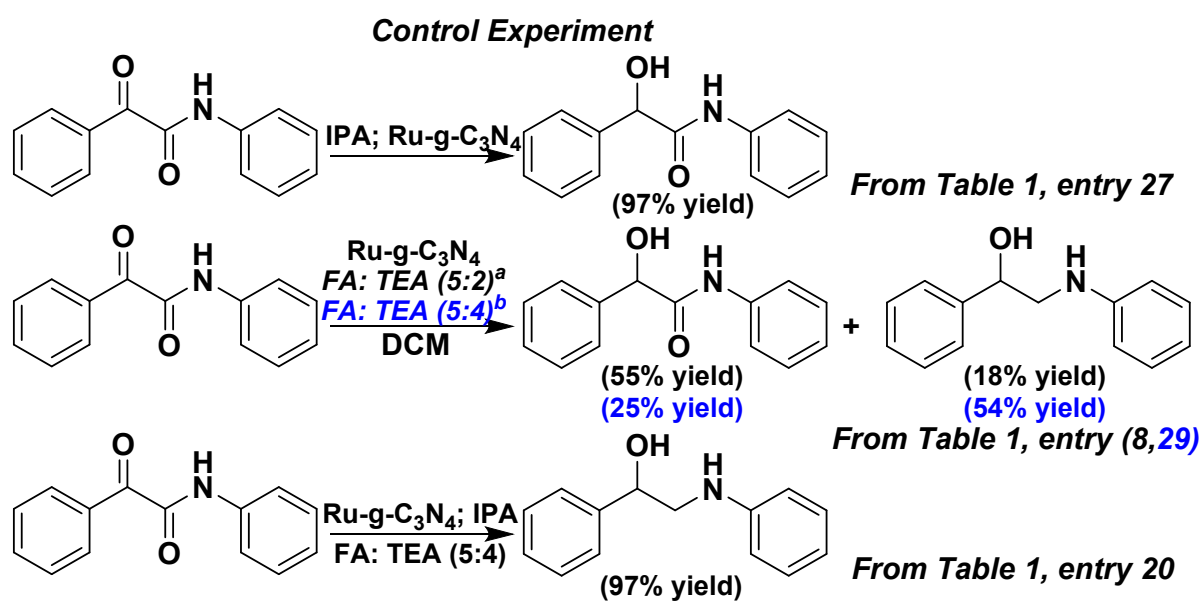


Figure S9: Control experiment for partial and complete transfer hydrogenation of  $\alpha$ -ketoamide.

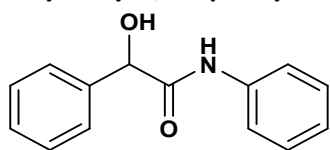


### Preparation of $\alpha$ -keto amide: <sup>[5]</sup>

100 ml round bottom flask employed with 5 mmol of ketone and its derivatives which is dissolved in 20 ml of acetonitrile in which 10 mmol (1.1 g) anhydrous  $\text{SeO}_2$  is added and stirred thoroughly. Slowly into which 5 mmol of primary amine and 10 mmol of pyridine is added at 80 °C for 10-15 h. Synthesis of product determined by the help of Thin Layer Chromatography (TLC) after which solution is extracted with DCM, water. For removal of extra base, conc. HCl is added in portion (3 x 5 ml) after which organic layer is washed with brine solution and dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and solvent removed under vacuum on rotary evaporator. Resulting mixture then purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure  $\alpha$ -keto amide.

### Analytical data of $\alpha$ -hydroxyl amide:

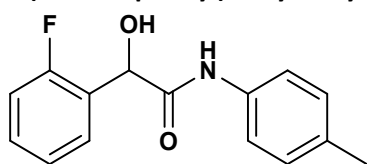
#### 2-hydroxy-*N*,2-diphenylacetamide [2a]



In 100 ml of round bottom flask 1 mmol of  $\alpha$ -keto amide is added along with 30 mg of Ru-g- $\text{C}_3\text{N}_4$  dissolved in 5 ml of IPA and reaction mixture is heated at 50 °C for 3 h. Synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with ethyl acetate and water, after this organic layer is dried over anhydrous  $\text{Na}_2\text{SO}_4$  filtered and solvent removed under vacuum on rotary evaporator. Final mixture then purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure 2-hydroxy-*N*,2-diphenylacetamide.

White solid; Yield = 222 mg (97%); mp = 150–152 °C;  $R_f$  = 0.50 (toluene: ethyl acetate, 90:10 v/v).  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  9.93 (s, 1H), 7.67 (d,  $J$  = 8.1 Hz, 2H), 7.50 (d,  $J$  = 7.5 Hz, 2H), 7.33 (t,  $J$  = 7.5 Hz, 2H), 7.26 (t,  $J$  = 7.8 Hz, 3H), 7.02 (t,  $J$  = 7.3 Hz, 1H), 6.51 (s, 1H), 5.09 (s, 1H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  171.64, 141.31, 138.97, 129.04, 128.51, 128.02, 127.01, 123.96, 120.11, 74.41.

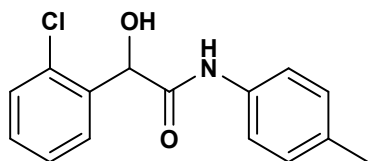
#### 2-(2-fluorophenyl)-2-hydroxy-*N*-(*p*-tolyl)acetamide [2b]



Synthesis of this product is parallel to synthesis of 2a and then it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure 2-(2-fluorophenyl)-2-hydroxy-*N*-(*p*-tolyl)acetamide.

White solid; Yield = 254 mg (98%); mp = 127–128 °C;  $R_f$  = 0.49 (toluene: ethyl acetate, 90:10 v/v).  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  9.86 (s, 1H), 7.56 (d,  $J$  = 8.3 Hz, 2H), 7.50 (t,  $J$  = 6.9 Hz, 1H), 7.33 (dd,  $J$  = 14.1, 6.9 Hz, 1H), 7.17 (dt,  $J$  = 14.1, 8.3 Hz, 2H), 7.08 (d,  $J$  = 8.2 Hz, 2H), 6.59 (s, 1H), 5.31 (s, 1H), 2.22 (s, 3H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  170.43, 161.30, 159.35, 136.33, 133.01, 130.18, 130.12, 129.56, 129.53, 129.42, 128.77, 128.65, 124.74, 124.72, 120.21, 115.76, 115.59, 70.20, 68.58, 20.88.

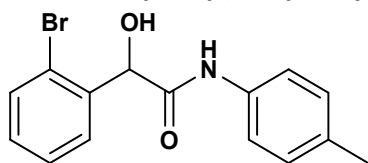
### 2-(2-chlorophenyl)-2-hydroxy-*N*-(*p*-tolyl)acetamide [2c]



Synthesis of this product is parallel to synthesis of 2a and then it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure 2-(2-chlorophenyl)-2-hydroxy-*N*-(*p*-tolyl)acetamide.

White solid; Yield = 260 mg (95%); mp = 136–138 °C;  $R_f$  = 0.51 (toluene: ethyl acetate, 90:10 v/v).  $^1\text{H NMR}$  (500 MHz, DMSO- $d_6$ ):  $\delta$  9.96 (s, 1H), 7.55 (dd,  $J$  = 14.1, 8.6 Hz, 3H), 7.41 (dd,  $J$  = 7.5, 1.0 Hz, 1H), 7.37 – 7.26 (m, 2H), 7.08 (d,  $J$  = 8.1 Hz, 2H), 6.69 (s, 1H), 5.44 (s, 1H), 2.22 (s, 3H);  $^{13}\text{C NMR}$  (126 MHz, DMSO- $d_6$ ):  $\delta$  170.22, 139.20, 136.43, 133.00, 132.97, 129.77, 129.59, 129.54, 129.41, 127.59, 120.19, 71.50, 20.89.

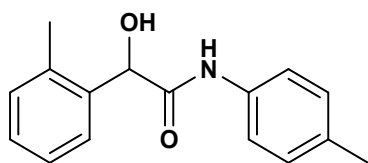
### 2-(2-bromophenyl)-2-hydroxy-*N*-(*p*-tolyl)acetamide [2d]



Synthesis of this product is parallel to synthesis of 2a and then it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure 2-(2-bromophenyl)-2-hydroxy-*N*-(*p*-tolyl)acetamide.

White solid; Yield = 301 mg (94%); mp = 149–150 °C;  $R_f$  = 0.52 (toluene: ethyl acetate, 80:20 v/v).  $^1\text{H NMR}$  (500 MHz, DMSO- $d_6$ )  $\delta$  10.01 (s, 1H), 7.57 (t,  $J$  = 8.1 Hz, 2H), 7.56 (s, 1H) 7.52 (d,  $J$  = 7.6 Hz, 1H), 7.37 (t,  $J$  = 7.4 Hz, 1H), 7.22 (t,  $J$  = 7.6 Hz, 1H), 7.08 (d,  $J$  = 8.1 Hz, 2H), 6.82 (s, 1H), 5.40 (s, 1H), 2.22 (s, 3H);  $^{13}\text{C NMR}$  (126 MHz, DMSO- $d_6$ )  $\delta$  170.22, 140.86, 136.48, 132.93, 132.80, 130.04, 129.61, 129.40, 128.13, 123.55, 120.17, 73.63, 20.89.

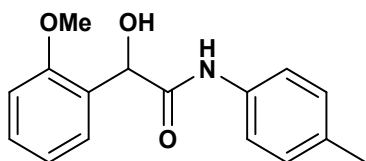
### 2-hydroxy-2-(*o*-tolyl)-*N*-(*p*-tolyl)acetamide [2e]



Synthesis of this product is parallel to synthesis of 2a and then it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure 2-hydroxy-2-(*o*-tolyl)-*N*-(*p*-tolyl)acetamide.

White solid; Yield = 227 mg (89%); mp = 150–151 °C;  $R_f$  = 0.55 (toluene: ethyl acetate, 90:10 v/v).  $^1\text{H NMR}$  (500 MHz, DMSO- $d_6$ )  $\delta$  9.79 (s, 1H), 7.56 (d,  $J$  = 8.3 Hz, 2H), 7.42 – 7.35 (m, 1H), 7.14 (d,  $J$  = 3.2 Hz, 3H), 7.06 (d,  $J$  = 8.3 Hz, 2H), 6.44 (s, 1H), 5.25 (s, 1H), 2.38 (s, 3H), 2.21 (s, 3H);  $^{13}\text{C NMR}$  (126 MHz, DMSO- $d_6$ )  $\delta$  171.50, 139.98, 136.52, 136.42, 132.85, 130.53, 129.38, 127.86, 127.51, 126.07, 120.18, 71.77, 20.86, 19.62.

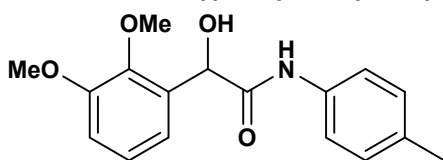
### 2-hydroxy-2-(2-methoxyphenyl)-*N*-(*p*-tolyl)acetamide [2f]



Synthesis of this product is parallel to synthesis of 2a and then it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure 2-hydroxy-2-(2-methoxyphenyl)-*N*-(*p*-tolyl)acetamide.

White solid; Yield = 248 mg (90%); mp = 100–102 °C;  $R_f$  = 0.50 (toluene: ethyl acetate, 90:10 v/v).  $^1\text{H NMR}$  (500 MHz, DMSO- $d_6$ )  $\delta$  9.68 (s, 1H), 7.54 (d,  $J$  = 8.3 Hz, 2H), 7.34 (d,  $J$  = 7.6 Hz, 1H), 7.25 (t,  $J$  = 7.8 Hz, 1H), 7.06 (d,  $J$  = 8.2 Hz, 2H), 6.97 (d,  $J$  = 8.2 Hz, 1H), 6.90 (t,  $J$  = 7.4 Hz, 1H), 6.12 (s, 1H), 5.33 (s, 1H), 3.75 (s, 3H), 2.22 (s, 3H);  $^{13}\text{C NMR}$  (126 MHz, DMSO- $d_6$ )  $\delta$  171.32, 157.17, 136.58, 132.72, 129.80, 129.39, 129.35, 128.53, 120.67, 120.05, 111.60, 69.01, 56.02, 20.86.

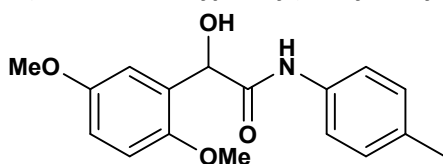
### 2-(2,3-dimethoxyphenyl)-2-hydroxy-*N*-(*p*-tolyl)acetamide [2g]



Synthesis of this product is parallel to synthesis of 2a and then it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure 2-(2,3-dimethoxyphenyl)-2-hydroxy-*N*-(*p*-tolyl)acetamide.

White solid; Yield = 280 mg (93%); mp = 104–105 °C;  $R_f$  = 0.56 (toluene: ethyl acetate, 90:10 v/v).  $^1\text{H NMR}$  (500 MHz, DMSO- $d_6$ )  $\delta$  9.72 (s, 1H), 7.55 (d,  $J$  = 8.3 Hz, 2H), 7.07 (d,  $J$  = 8.3 Hz, 2H), 6.98 (d,  $J$  = 3.0 Hz, 1H), 6.89 (d,  $J$  = 8.9 Hz, 1H), 6.80 (dd,  $J$  = 8.9, 3.0 Hz, 1H), 6.20 (s, 1H), 5.33 (s, 1H), 3.70 (s, 3H), 3.66 (s, 3H), 2.22 (s, 3H);  $^{13}\text{C NMR}$  (126 MHz, DMSO- $d_6$ )  $\delta$  171.13, 153.61, 151.26, 136.59, 132.75, 130.97, 129.40, 120.07, 114.55, 113.56, 112.90, 69.06, 56.70, 55.81, 20.85.

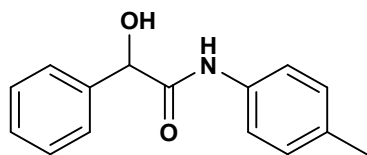
### 2-(2,5-dimethoxyphenyl)-2-hydroxy-*N*-(*p*-tolyl)acetamide [2h]



Synthesis of this product is parallel to synthesis of 2a and then it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure 2-(2,5-dimethoxyphenyl)-2-hydroxy-*N*-(*p*-tolyl)acetamide.

White solid; Yield = 274 mg (91%); mp = 91–92 °C;  $R_f$  = 0.56 (toluene: ethyl acetate, 90:10 v/v).  $^1\text{H NMR}$  (500 MHz, DMSO- $d_6$ )  $\delta$  9.73 (s, 1H), 7.56 (d,  $J$  = 8.3 Hz, 2H), 7.08 (d,  $J$  = 8.2 Hz, 2H), 6.99 (d,  $J$  = 2.9 Hz, 1H), 6.90 (d,  $J$  = 8.9 Hz, 1H), 6.81 (dd,  $J$  = 8.9, 3.0 Hz, 1H), 6.21 (s, 1H), 5.34 (s, 1H), 3.71 (s, 3H), 3.67 (s, 3H), 2.22 (s, 3H);  $^{13}\text{C NMR}$  (126 MHz, DMSO- $d_6$ )  $\delta$  171.15, 153.58, 151.24, 136.61, 132.75, 130.94, 129.41, 120.06, 114.53, 113.52, 112.84, 69.04, 56.67, 55.80, 20.87.

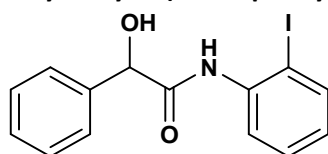
### 2-hydroxy-2-phenyl-*N*-(*p*-tolyl)acetamide [2i]



Synthesis of this product is parallel to synthesis of 2a and then it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure 2-hydroxy-2-phenyl-*N*-(*p*-tolyl)acetamide.

White solid; Yield = 224 mg (93%); mp = 168-169 °C;  $R_f$  = 0.47 (toluene: ethyl acetate, 80:20 v/v).  $^1\text{H NMR}$  (500 MHz, DMSO- $d_6$ )  $\delta$  9.77 (s, 1H), 7.51 (d,  $J$  = 8.3 Hz, 2H), 7.47 (d,  $J$  = 7.5 Hz, 2H), 7.30 (t,  $J$  = 7.5 Hz, 2H), 7.23 (t,  $J$  = 7.3 Hz, 1H), 7.04 (d,  $J$  = 8.3 Hz, 2H), 6.40 (s, 1H), 5.06 (s, 1H), 2.17 (s, 3H);  $^{13}\text{C NMR}$  (126 MHz, DMSO- $d_6$ )  $\delta$  171.37, 141.36, 136.45, 132.87, 129.42, 128.50, 128.04, 126.99, 120.09, 74.38, 20.89.

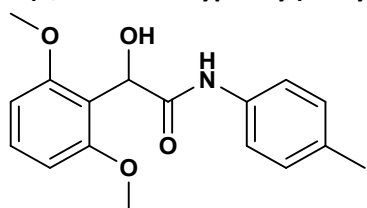
### 2-hydroxy-*N*-(2-iodophenyl)-2-phenylacetamide [2j]



In 100 ml of round bottom flask 1 mmol of  $\alpha$ -keto amide is added along with 35 mg of Ru-g-C<sub>3</sub>N<sub>4</sub> dissolved in 5 ml of IPA and reaction mixture is heated at 60 °C for 5 h. Synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with ethyl acetate and water, after this organic layer is dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> filtered and solvent removed under vacuum on rotary evaporator. Then it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 80-20) to obtain pure 2-hydroxy-*N*-(2-iodophenyl)-2-phenylacetamide.

Yellow solid; Yield = 307 mg (87%); mp = 47–48 °C;  $R_f$  = 0.45 (toluene: ethyl acetate, 70:30 v/v).  $^1\text{H NMR}$  (500 MHz, DMSO- $d_6$ )  $\delta$  9.52 (s, 1H), 8.01 (d,  $J$  = 8.2 Hz, 1H), 7.87 (dd,  $J$  = 7.9, 1.5 Hz, 1H), 7.51 (d,  $J$  = 7.7 Hz, 2H), 7.39 – 7.34 (m, 3H), 7.33 – 7.29 (m, 1H), 6.99 (d,  $J$  = 4.3 Hz, 1H), 6.90 (td,  $J$  = 7.7, 1.5 Hz, 1H), 5.15 (d,  $J$  = 4.3 Hz, 1H);  $^{13}\text{C NMR}$  (126 MHz, DMSO- $d_6$ )  $\delta$  171.30, 140.87, 139.39, 138.58, 129.42, 128.64, 128.26, 127.19, 126.75, 122.16, 92.07, 74.13.

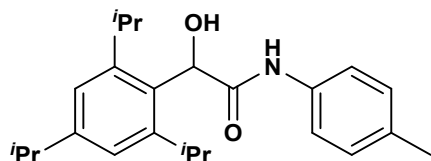
### 2-(2,6-dimethoxyphenyl)-2-hydroxy-*N*-(*p*-tolyl)acetamide [2k]



Synthesis of this product is parallel to synthesis of 2a and then it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure 2-(2,6-dimethoxyphenyl)-2-hydroxy-*N*-(*p*-tolyl)acetamide.

White solid; Yield = 288 mg (96%); mp = 104–105 °C;  $R_f$  = 0.50 (toluene: ethyl acetate, 90:10 v/v).  $^1\text{H NMR}$  (500 MHz, DMSO- $d_6$ )  $\delta$  9.38 (s, 1H), 7.55 (d,  $J$  = 8.2 Hz, 2H), 7.21 (t,  $J$  = 8.3 Hz, 1H), 7.07 (d,  $J$  = 8.1 Hz, 2H), 6.60 (d,  $J$  = 8.4 Hz, 2H), 6.00 (s, 1H), 5.42 (s, 1H), 3.66 (s, 6H), 2.22 (s, 3H);  $^{13}\text{C NMR}$  (126 MHz, DMSO- $d_6$ )  $\delta$  172.50, 158.86, 136.68, 132.45, 129.87, 129.39, 120.02, 117.98, 104.95, 64.93, 56.33, 20.87.

### 2-hydroxy-*N*-(*p*-tolyl)-2-(2,4,6-triisopropylphenyl)acetamide [2I]



In 100 ml of round bottom flask 1 mmol of  $\alpha$ -keto amide is added along with 30 mg of Ru-g-C<sub>3</sub>N<sub>4</sub> dissolved in 5 ml of IPA and reaction mixture is heated at 70 °C for 4 h. Synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with ethyl acetate and water, after this organic layer is dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> filtered and solvent removed under vacuum on rotary evaporator. Then it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 85-15) to obtain pure 2-hydroxy-*N*-(*p*-tolyl)-2-(2,4,6-triisopropylphenyl)acetamide.

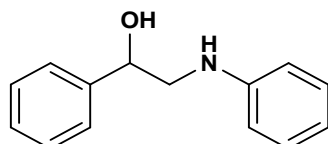
White solid; Yield = 355 mg (98%); Colourless solid; mp = 285–286 °C; R<sub>f</sub> = 0.45 (toluene: ethyl acetate, 90:10 v/v)

<sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>)  $\delta$  9.73 (s, 1H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.95 (s, 2H), 6.53 (s, 1H), 5.55 (s, 1H), 3.29 (dd, *J* = 13.4, 6.8 Hz, 2H), 2.82 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.22 (s, 3H), 1.17 (dd, *J* = 6.6, 3.8 Hz, 12H), 1.08 (s, 6H); <sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>)  $\delta$  172.54, 147.76, 136.56, 133.96, 132.75, 129.33, 120.45, 68.27, 34.01, 29.36, 25.06, 24.46, 24.40, 24.17, 20.89.

# All the  $\alpha$ -hydroxyl amide synthesised are less soluble in CDCl<sub>3</sub> so best solvent for NMR analysis is DMSO-d<sub>6</sub> solvent.

### Analytical data of $\beta$ -aminol:

#### 1-phenyl-2-(phenylamino)ethan-1-ol [2aa]

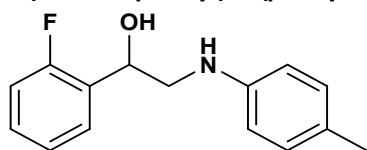


In 100 ml of round bottom flask 1 mmol of  $\alpha$ -keto amide is added along with 30 mg of Ru-g-C<sub>3</sub>N<sub>4</sub> dissolved in 5 ml of IPA and reaction mixture is stirred for 3 h then 0.2 ml (200  $\mu$ l) of FA:TEA (5:4) is added into it hence after heated at 80 °C for 5 h. Synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with DCM and water, after this organic layer is dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> filtered and solvent removed under vacuum on rotary evaporator. Final mixture then purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure 1-phenyl-2-(phenylamino)ethan-1-ol.

Yellow liquid; Yield = 207 mg (97%); R<sub>f</sub> = 0.65 (*n*-hexane: ethyl acetate, 90:10 v/v).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.43 – 7.31 (m, 5H), 7.18 (t, *J* = 7.0 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 2H), 4.91 (dd, *J* = 8.6, 3.8 Hz, 1H), 3.42 (dd, *J* = 12.7, 3.8 Hz, 1H), 3.28 (dd, *J* = 12.7, 8.6 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  147.87, 142.04, 129.34, 128.63, 127.99, 125.89, 118.13, 113.48, 72.46, 51.79.

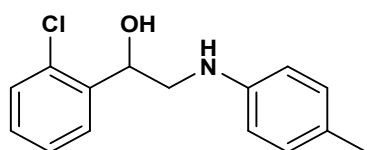
### 1-(2-fluorophenyl)-2-(*p*-tolylamino)ethan-1-ol [2ab]



In 100 ml of round bottom flask 1 mmol of  $\alpha$ -keto amide is added along with 30 mg of Ru-g-C<sub>3</sub>N<sub>4</sub> dissolved in 5 ml of IPA and reaction mixture is stirred for 3 h then 0.2 ml (200  $\mu$ l) of FA:TEA (5:4) is added into it hence after heated at 80 °C for 6 h. Synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with DCM and water, after this organic layer is dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> filtered and solvent removed under vacuum on rotary evaporator. Final mixture then purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure 1-(2-fluorophenyl)-2-(*p*-tolylamino)ethan-1-ol.

Colourless liquid; Yield = 227 mg (93%);  $R_f$  = 0.59 (*n*-hexane: ethyl acetate, 90:10 v/v). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.60 – 7.52 (m, 1H), 7.33 – 7.27 (m, 1H), 7.18 (dd,  $J$  = 10.8, 4.0 Hz, 1H), 7.10 – 7.04 (m, 1H), 7.02 (d,  $J$  = 8.0 Hz, 2H), 6.65 (d,  $J$  = 8.3 Hz, 2H), 5.24 (dd,  $J$  = 8.9, 2.9 Hz, 1H), 3.52 (dd,  $J$  = 13.3, 2.9 Hz, 1H), 3.22 (dd,  $J$  = 13.3, 8.9 Hz, 1H), 2.26 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  160.76, 158.81, 145.37, 129.83, 129.19, 129.13, 127.53, 127.31, 127.28, 124.41, 124.39, 115.37, 115.19, 113.65, 66.67, 51.02, 20.37.

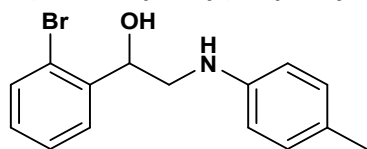
### 1-(2-chlorophenyl)-2-(*p*-tolylamino)ethan-1-ol [2ac]



Synthesis of this product is parallel to synthesis of 2aa and then it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure 1-(2-chlorophenyl)-2-(*p*-tolylamino)ethan-1-ol.

Colourless liquid; Yield = 240 mg (92%);  $R_f$  = 0.59 (*n*-hexane: ethyl acetate, 90:10 v/v). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 (dd,  $J$  = 7.6, 1.3 Hz, 1H), 7.36 (dd,  $J$  = 7.9, 1.1 Hz, 1H), 7.33 (td,  $J$  = 7.5, 0.9 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.02 (d,  $J$  = 8.0 Hz, 2H), 6.68 (d,  $J$  = 8.3 Hz, 2H), 5.32 (dd,  $J$  = 9.0, 2.9 Hz, 1H), 3.58 (dd,  $J$  = 13.4, 3.0 Hz, 1H), 3.11 (dd,  $J$  = 13.4, 9.0 Hz, 1H), 2.25 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  145.39, 139.39, 131.80, 129.81, 129.42, 128.79, 127.57, 127.26, 127.19, 113.74, 69.07, 50.52, 20.37.

### 1-(2-bromophenyl)-2-(*p*-tolylamino)ethan-1-ol [2ad]

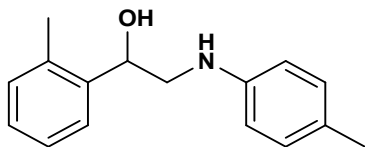


Synthesis of this product is parallel to synthesis of 2aa and then it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 85-15) to obtain pure 1-(2-bromophenyl)-2-(*p*-tolylamino)ethan-1-ol.

Colourless liquid; Yield = 184 mg (90%);  $R_f$  = 0.58 (*n*-hexane: ethyl acetate, 90:10 v/v). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 (dd,  $J$  = 7.7, 1.4 Hz, 1H), 7.55 (dd,  $J$  = 8.0, 1.0 Hz, 1H), 7.37 (td,  $J$  = 7.7, 0.7 Hz, 1H), 7.17 (td,  $J$  = 7.9, 1.7 Hz, 1H), 7.02 (d,  $J$  = 8.0 Hz, 2H), 6.70 (d,  $J$  = 8.4 Hz, 2H), 5.26 (dd,  $J$  =

9.1, 3.0 Hz, 1H), 3.58 (dd,  $J = 13.4, 3.0$  Hz, 1H), 3.09 (dd,  $J = 13.4, 9.1$  Hz, 1H), 2.25 (s, 3H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  145.39, 140.99, 132.69, 129.80, 129.17, 127.80, 127.61, 127.58, 121.81, 113.82, 71.23, 50.58, 20.38.

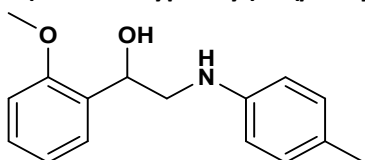
#### 1-(*o*-tolyl)-2-(*p*-tolylamino)ethan-1-ol [2ae]



Synthesis of this product is parallel to synthesis of 2aa and then it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90:10) to obtain pure 1-(*o*-tolyl)-2-(*p*-tolylamino)ethan-1-ol.

Colourless liquid; Yield = 205 mg (85%);  $R_f = 0.65$  (*n*-hexane: ethyl acetate, 90:10 v/v).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J = 7.2$  Hz, 1H), 7.27 (t,  $J = 6.6$  Hz, 1H), 7.22 (td,  $J = 7.3, 1.3$  Hz, 1H), 7.17 (d,  $J = 6.9$  Hz, 1H), 7.01 (d,  $J = 8.0$  Hz, 2H), 6.62 (d,  $J = 8.3$  Hz, 2H), 5.15 (dd,  $J = 9.0, 3.3$  Hz, 1H), 3.40 (dd,  $J = 13.2, 3.3$  Hz, 1H), 3.20 (dd,  $J = 13.2, 9.1$  Hz, 1H), 2.38 (s, 3H), 2.25 (s, 3H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  145.62, 140.07, 134.68, 130.48, 129.81, 127.64, 127.44, 126.41, 125.44, 113.65, 69.11, 51.03, 20.38, 19.12.

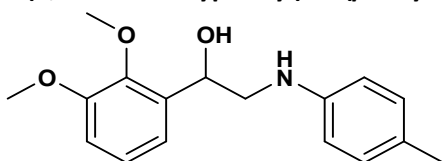
#### 1-(2-methoxyphenyl)-2-(*p*-tolylamino)ethan-1-ol [2af]



Synthesis of this product is parallel to synthesis of 2aa and then it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90:10) to obtain pure 1-(2-methoxyphenyl)-2-(*p*-tolylamino)ethan-1-ol.

Colourless liquid; Yield = 224 mg (87%);  $R_f = 0.60$  (*n*-hexane: ethyl acetate, 90:10 v/v).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (d,  $J = 8.4$  Hz, 2H), 7.01 (d,  $J = 8.0$  Hz, 2H), 6.92 (d,  $J = 8.7$  Hz, 2H), 6.61 (d,  $J = 8.3$  Hz, 2H), 4.86 (dd,  $J = 8.6, 3.9$  Hz, 1H), 3.82 (s, 3H), 3.37 (dd,  $J = 13.0, 4.0$  Hz, 1H), 3.27 (dd,  $J = 13.0, 8.6$  Hz, 1H), 2.25 (s, 3H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.35, 145.60, 134.18, 129.79, 127.76, 127.37, 127.16, 114.20, 114.00, 113.67, 72.06, 55.31, 52.18, 20.38.

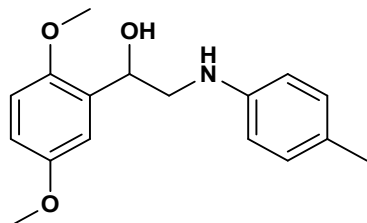
#### 1-(2,3-dimethoxyphenyl)-2-(*p*-tolylamino)ethan-1-ol [2ag]



Synthesis of this product is parallel to synthesis of 2aa and then it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90:10) to obtain pure 1-(2,3-dimethoxyphenyl)-2-(*p*-tolylamino)ethan-1-ol.

Colourless liquid; Yield = 256 mg (89%);  $R_f = 0.62$  (*n*-hexane: ethyl acetate, 90:10 v/v).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.01 (dd,  $J = 7.2, 5.7$  Hz, 3H), 6.81 (dt,  $J = 8.9, 5.9$  Hz, 2H), 6.65 (d,  $J = 8.4$  Hz, 2H), 5.11 (dd,  $J = 8.8, 3.5$  Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 3.49 (dd,  $J = 13.0, 3.5$  Hz, 1H), 3.20 (dd,  $J = 13.0, 8.8$  Hz, 1H), 2.25 (s, 3H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.89, 150.57, 145.78, 131.07, 129.72, 127.02, 113.55, 112.99, 112.94, 111.45, 68.94, 55.79, 55.76, 50.49, 20.36.

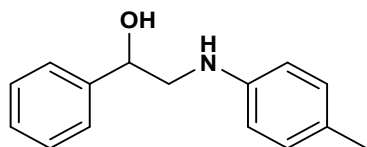
### 1-(2,5-dimethoxyphenyl)-2-(*p*-tolylamino)ethan-1-ol [2ah]



Synthesis of this product is parallel to synthesis of 2aa and then it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure 1-(2,5-dimethoxyphenyl)-2-(*p*-tolylamino)ethan-1-ol.

Colourless liquid; Yield = 259 mg (88%);  $R_f$  = 0.59 (n-hexane: ethyl acetate, 90:10 v/v)  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.04 – 6.96 (m, 3H), 6.81 (dt,  $J$  = 8.9, 5.9 Hz, 2H), 6.65 (d,  $J$  = 8.4 Hz, 2H), 5.11 (dd,  $J$  = 8.4, 2.9 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 3.49 (dd,  $J$  = 13.0, 3.4 Hz, 1H), 3.20 (dd,  $J$  = 13.0, 8.8 Hz, 1H), 2.25 (s, 3H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.89, 150.57, 145.78, 131.07, 129.72, 127.02, 113.55, 112.99, 112.94, 111.44, 68.95, 55.79, 55.76, 50.49, 20.36.

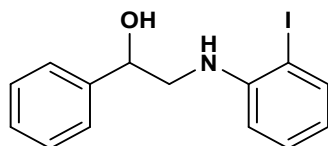
### 1-phenyl-2-(*p*-tolylamino)ethan-1-ol [2ai]



Synthesis of this product is parallel to synthesis of 2aa and then it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure 1-phenyl-2-(*p*-tolylamino)ethan-1-ol.

Colourless liquid; Yield = 198 mg (87%);  $R_f$  = 0.59 (n-hexane: ethyl acetate, 90:10 v/v)  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (dd,  $J$  = 25.2, 5.7 Hz, 5H), 7.00 (d,  $J$  = 6.2 Hz, 2H), 6.60 (d,  $J$  = 6.8 Hz, 2H), 4.90 (dd,  $J$  = 7.4, 3.9 Hz, 1H), 3.40 (dd,  $J$  = 12.7, 3.8 Hz, 1H), 3.25 (dt,  $J$  = 12.7, 7.4 Hz, 1H), 2.24 (d,  $J$  = 5.5 Hz, 3H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  145.55, 142.12, 129.82, 128.59, 127.92, 127.46, 125.89, 113.74, 72.41, 52.26, 20.40.

### 2-((2-iodophenyl)amino)-1-phenylethan-1-ol (2aj)



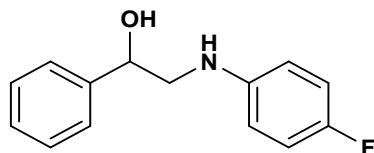
In 100 ml of round bottom flask 1 mmol of  $\alpha$ -keto amide is added along with 30 mg of  $\text{Ru-g-C}_3\text{N}_4$  dissolved in 5 ml of IPA and reaction mixture is stirred for 5 h then 0.2 ml (200  $\mu\text{l}$ ) of FA:TEA (5:4) is added into it hence after heated at 100  $^\circ\text{C}$  for 6 h. Synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with DCM and water, after this organic layer is dried over anhydrous  $\text{Na}_2\text{SO}_4$  filtered and solvent removed under vacuum on rotary evaporator. Final mixture then purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 75-25) to obtain pure 2-((2-iodophenyl)amino)-1-phenylethan-1-ol.

Dark Yellow liquid; Yield = 295 mg (87%);  $R_f$  = 0.59 (n-hexane: ethyl acetate, 90:10 v/v)  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 – 7.38 (m, 4H), 7.34 (ddd,  $J$  = 7.2, 5.9, 3.2 Hz, 1H), 7.13 (dd,  $J$  = 6.8, 2.1 Hz, 2H), 6.58 (d,  $J$  = 8.7 Hz, 2H), 4.91 (dd,  $J$  = 8.0, 3.7 Hz, 1H), 3.38 (dd,  $J$  = 13.0, 3.7 Hz, 1H), 3.28



(dd,  $J = 12.9, 8.0$  Hz, 1H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  145.85, 141.55, 138.00, 129.19, 128.74, 128.26, 125.86, 122.44, 111.23, 85.30, 72.36, 51.80.

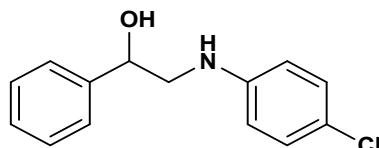
### 2-((4-fluorophenyl)amino)-1-phenylethan-1-ol (2ak)



Synthesis of this product is parallel to synthesis of 2aa and then it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure 2-((4-fluorophenyl)amino)-1-phenylethan-1-ol.

Yellow liquid; Yield = 215 mg (93%);  $R_f = 0.68$  (*n*-hexane: ethyl acetate, 90:10 v/v)  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 (d,  $J = 6.0$  Hz, 1H), 7.35 (d,  $J = 4.1$  Hz, 3H), 7.28 (dd,  $J = 8.4, 4.3$  Hz, 1H), 6.93 – 6.78 (m, 2H), 6.63 – 6.47 (m, 2H), 4.43 (dd,  $J = 7.2, 4.1$  Hz, 1H), 3.93 (dd,  $J = 11.1, 4.1$  Hz, 1H), 3.74 (dd,  $J = 11.1, 7.2$  Hz, 1H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  143.54, 139.92, 128.84, 128.65, 128.07, 127.68, 126.70, 125.86, 115.82, 115.81, 115.64, 115.46, 114.77, 114.72, 114.44, 114.38, 72.48, 67.31, 60.53, 52.45.

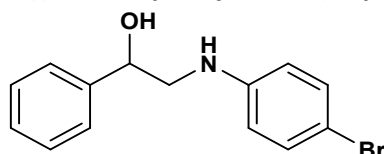
### 2-((4-chlorophenyl)amino)-1-phenylethan-1-ol (2al)



Synthesis of this product is parallel to synthesis of 2aa and then it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure 2-((4-chlorophenyl)amino)-1-phenylethan-1-ol.

Yellow liquid; Yield = 228 mg (92%);  $R_f = 0.69$  (*n*-hexane: ethyl acetate, 90:10 v/v)  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (d,  $J = 4.1$  Hz, 4H), 7.34 – 7.26 (m, 1H), 7.11 (d,  $J = 8.6$  Hz, 2H), 6.56 (d,  $J = 8.4$  Hz, 2H), 4.88 (dd,  $J = 8.5, 3.8$  Hz, 1H), 3.36 (dd,  $J = 13.0, 3.8$  Hz, 1H), 3.25 (dd,  $J = 13.0, 8.5$  Hz, 1H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  146.47, 141.85, 129.13, 128.69, 128.13, 125.86, 122.60, 114.49, 72.46, 51.72.

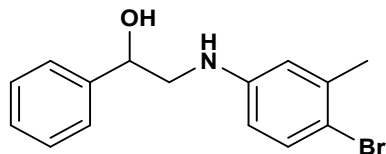
### 2-((4-bromophenyl)amino)-1-phenylethan-1-ol (2am)



Synthesis of this product is parallel to synthesis of 2aa and then it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure 2-((4-bromophenyl)amino)-1-phenylethan-1-ol.

Yellow liquid; Yield = 266 mg (91%);  $R_f = 0.67$  (*n*-hexane: ethyl acetate, 90:10 v/v)  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (d,  $J = 4.3$  Hz, 4H), 7.34 – 7.30 (m, 1H), 7.24 (d,  $J = 8.8$  Hz, 2H), 6.51 (d,  $J = 8.8$  Hz, 2H), 4.87 (dd,  $J = 8.5, 3.9$  Hz, 1H), 3.35 (dd,  $J = 13.1, 3.9$  Hz, 1H), 3.25 (dd,  $J = 13.1, 8.5$  Hz, 1H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  146.91, 141.85, 132.00, 128.69, 128.13, 125.87, 114.98, 109.60, 72.41, 51.58.

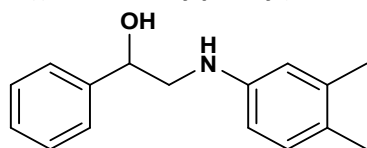
### 2-((4-bromo-3-methylphenyl)amino)-1-phenylethan-1-ol (2an)



In 100 ml of round bottom flask 1 mmol of  $\alpha$ -keto amide is added along with 30 mg of Ru-g-C3N4 dissolved in 5 ml of IPA and reaction mixture is stirred for 3 h then 0.2 ml (200  $\mu$ l) of FA:TEA (5:4) is added into it hence after heated at 100  $^{\circ}$ C for 4 h. Synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with DCM and water, after this organic layer is dried over anhydrous  $\text{Na}_2\text{SO}_4$  filtered and solvent removed under vacuum on rotary evaporator. Finally it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain 2-((4-bromo-3-methylphenyl)amino)-1-phenylethan-1-ol.

Yellow liquid; Yield = 263 mg (86%);  $R_f$  = 0.62 (*n*-hexane: ethyl acetate, 90:10 v/v)  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (s, 1H), 7.43 (d,  $J$  = 7.6 Hz, 1H), 7.29 (d,  $J$  = 7.5 Hz, 1H), 7.23 (d,  $J$  = 7.6 Hz, 1H), 7.00 (d,  $J$  = 7.9 Hz, 2H), 6.59 (d,  $J$  = 8.1 Hz, 2H), 4.83 (dd,  $J$  = 8.8, 3.3 Hz, 1H), 3.36 (dd,  $J$  = 13.2, 3.5 Hz, 1H), 3.18 (dd,  $J$  = 13.2, 8.8 Hz, 1H), 2.25 (s, 3H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  145.23, 144.40, 130.92, 130.14, 129.87, 128.95, 127.74, 124.48, 122.73, 113.78, 71.61, 52.24, 20.42.

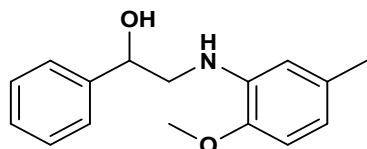
### 2-((3,4-dimethylphenyl)amino)-1-phenylethan-1-ol (2ao)



Synthesis of this product is parallel to synthesis of 2aa and then it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 80-20) to obtain pure 2-((3,4-dimethylphenyl)amino)-1-phenylethan-1-ol.

Yellow liquid; Yield = 193 mg (80%);  $R_f$  = 0.58 (*n*-hexane: ethyl acetate, 90:10 v/v)  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 (dd,  $J$  = 8.2, 4.1 Hz, 4H), 7.34 (dd,  $J$  = 7.8, 4.5 Hz, 1H), 6.98 (d,  $J$  = 8.0 Hz, 1H), 6.52 (s, 1H), 6.47 (dd,  $J$  = 7.9, 2.2 Hz, 1H), 4.90 (dd,  $J$  = 8.6, 3.7 Hz, 1H), 3.41 (dd,  $J$  = 12.9, 3.7 Hz, 1H), 3.26 (dd,  $J$  = 12.9, 8.8 Hz, 1H), 2.22 (s, 3H), 2.19 (s, 3H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  145.92, 142.15, 137.43, 130.34, 128.58, 127.90, 126.30, 125.90, 115.53, 111.03, 72.35, 52.27, 20.07, 18.75.

### 2-((2-methoxy-5-methylphenyl)amino)-1-phenylethan-1-ol (2ap)

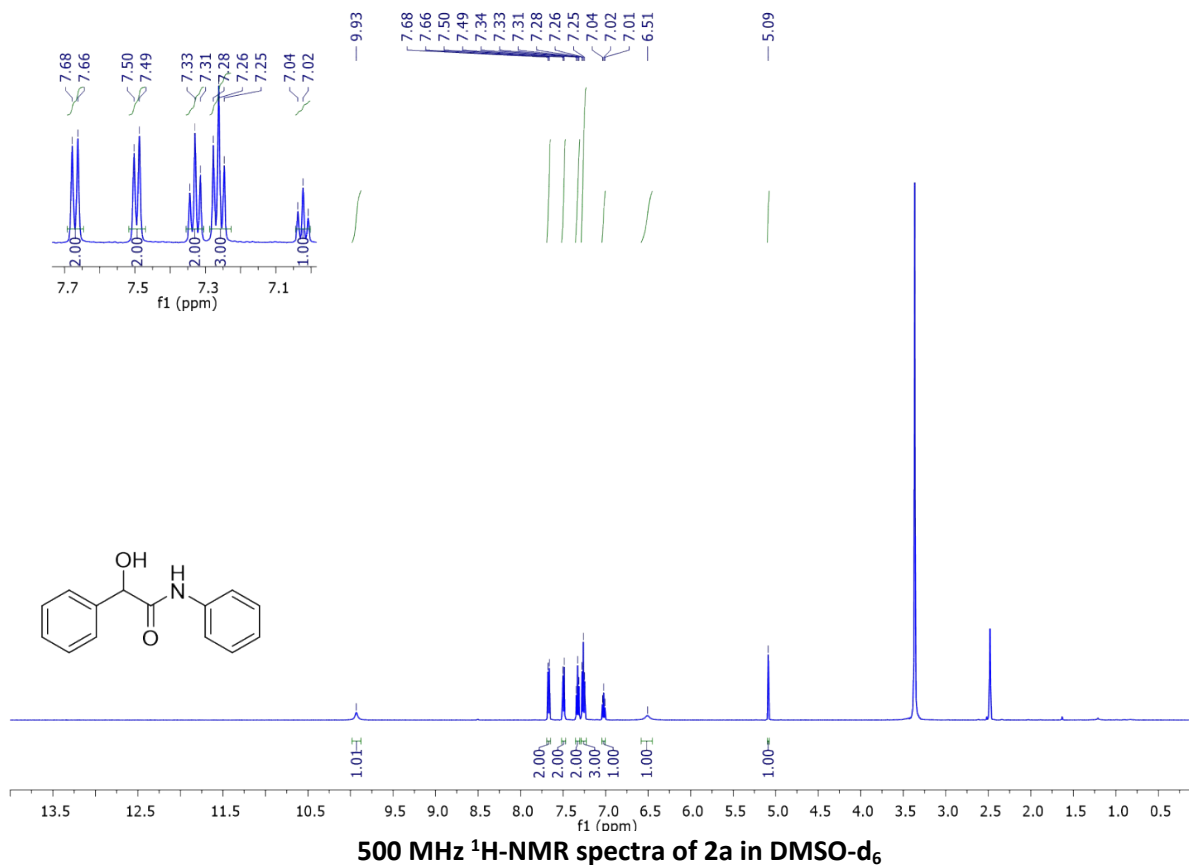


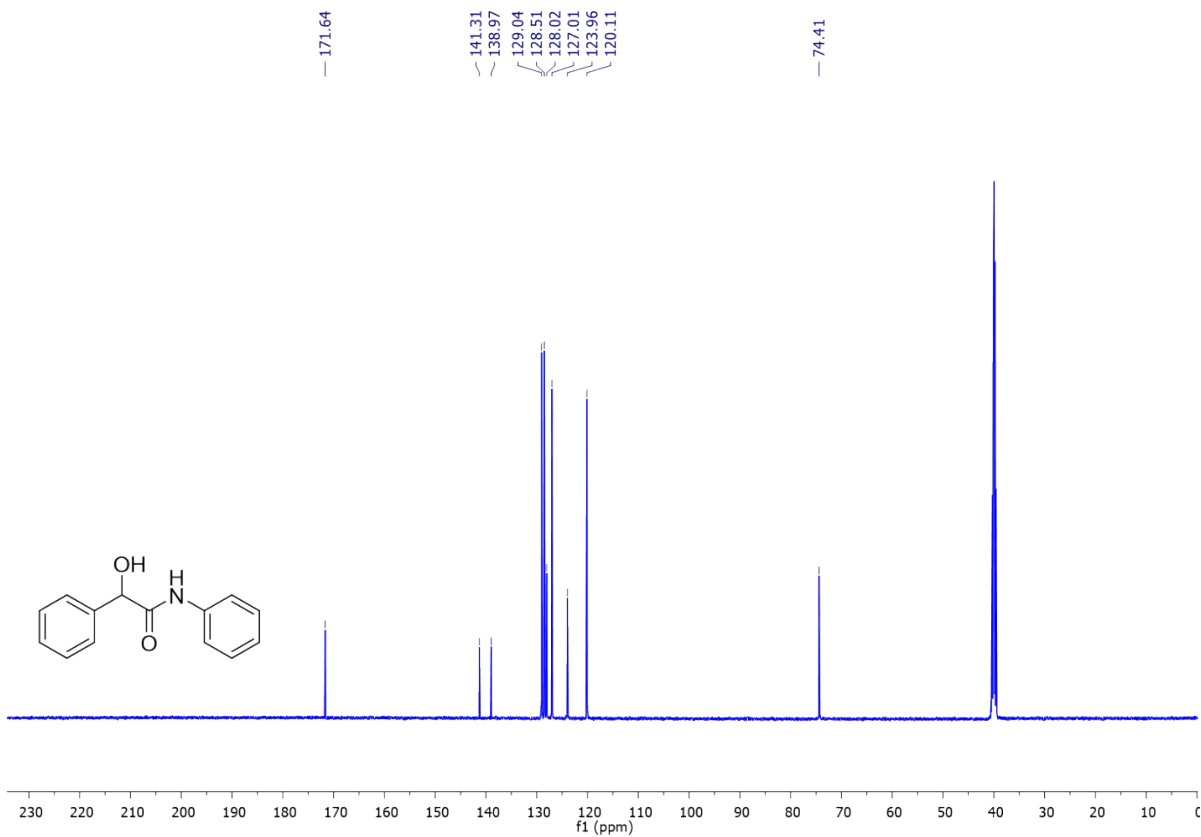
Synthesis of this product is parallel to synthesis of 2aa and then it is purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 80-20) to obtain pure 2-((2-methoxy-5-methylphenyl)amino)-1-phenylethan-1-ol.

Yellow liquid; Yield = 211 mg (82%);  $R_f$  = 0.65 (*n*-hexane: ethyl acetate, 90:10 v/v)  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.36 (m, 4H), 7.33 (dd,  $J$  = 11.4, 4.3 Hz, 1H), 6.68 (d,  $J$  = 8.5 Hz, 1H), 6.51 (d,  $J$  = 5.4 Hz, 2H), 4.95 (dd,  $J$  = 8.8, 3.6 Hz, 1H), 3.82 (s, 3H), 3.43 (dd,  $J$  = 13.1, 3.6 Hz, 1H), 3.31

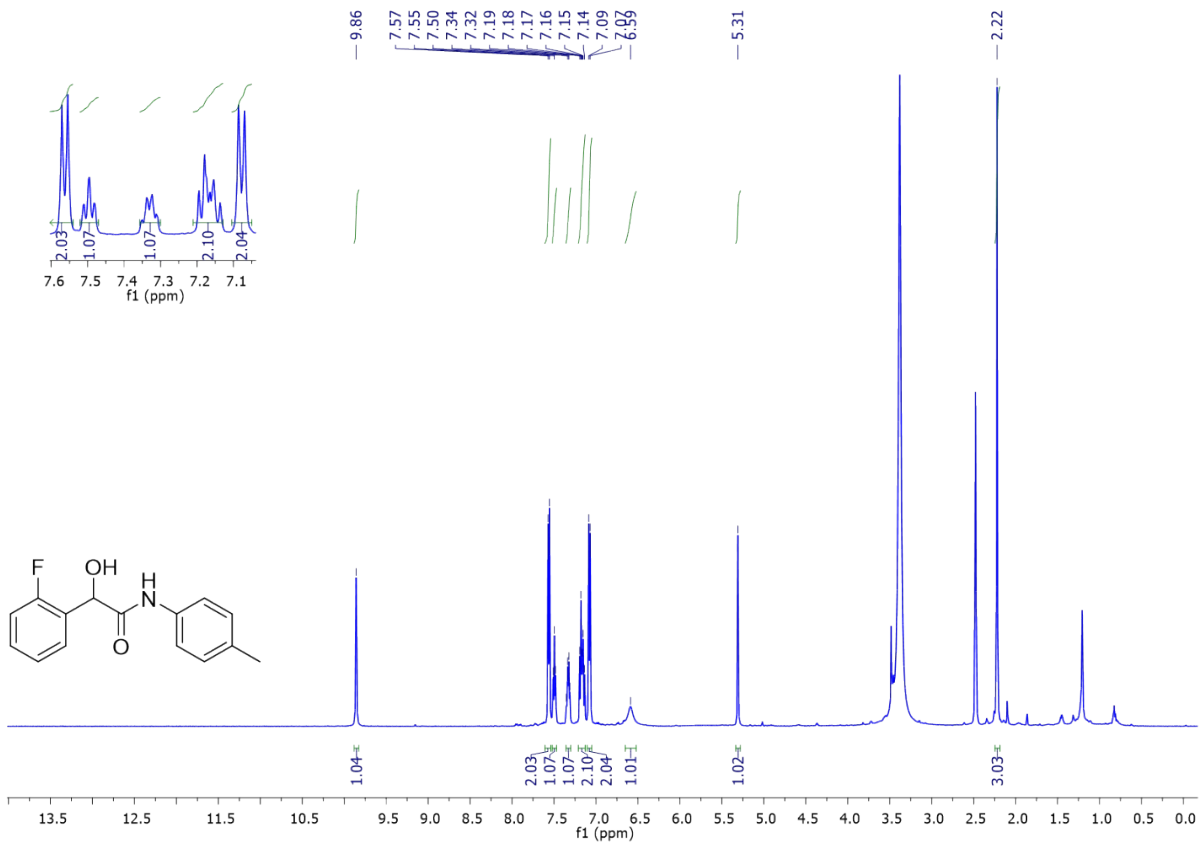
(dd,  $J = 13.1, 8.9$  Hz, 1H), 2.27 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  145.28, 140.49, 133.56, 129.85, 128.71, 127.71, 127.24, 113.74, 71.66, 52.27, 20.40.

$^1\text{H}$  and  $^{13}\text{C}$  NMR of  $\alpha$ -hydroxyl amide:

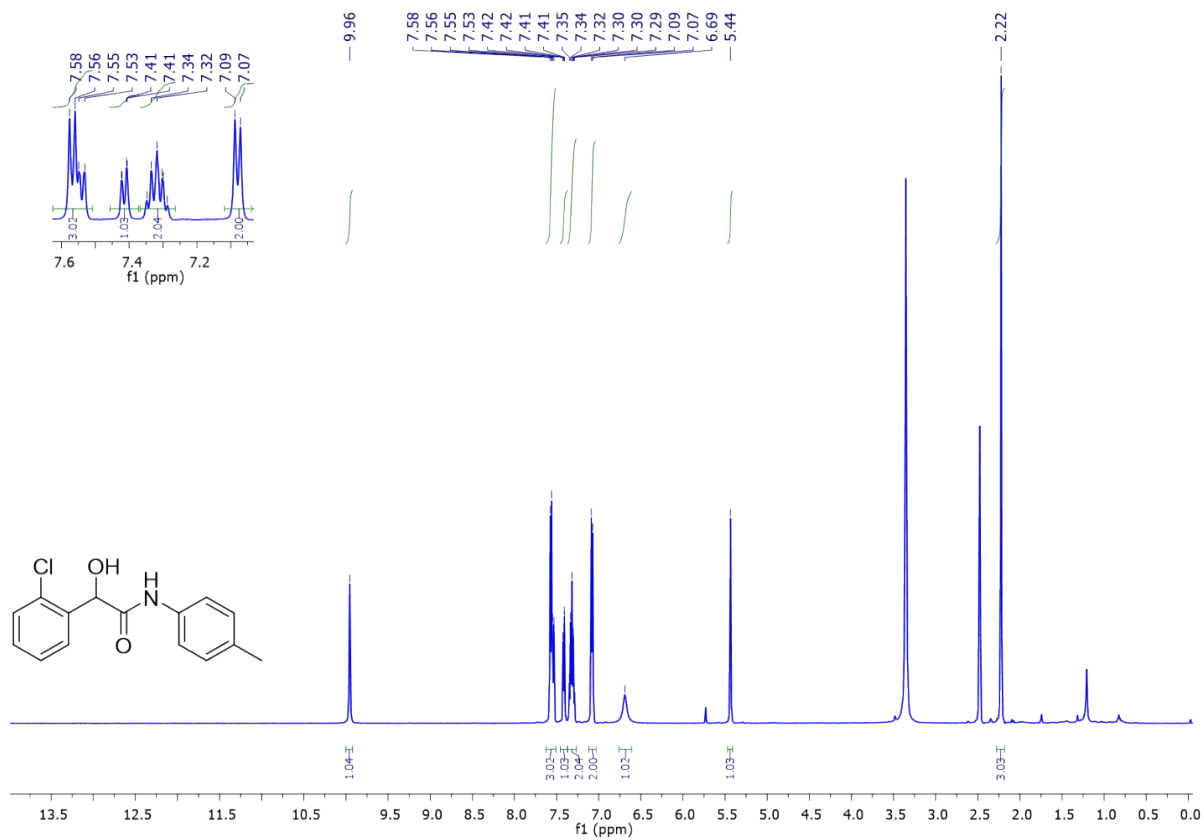
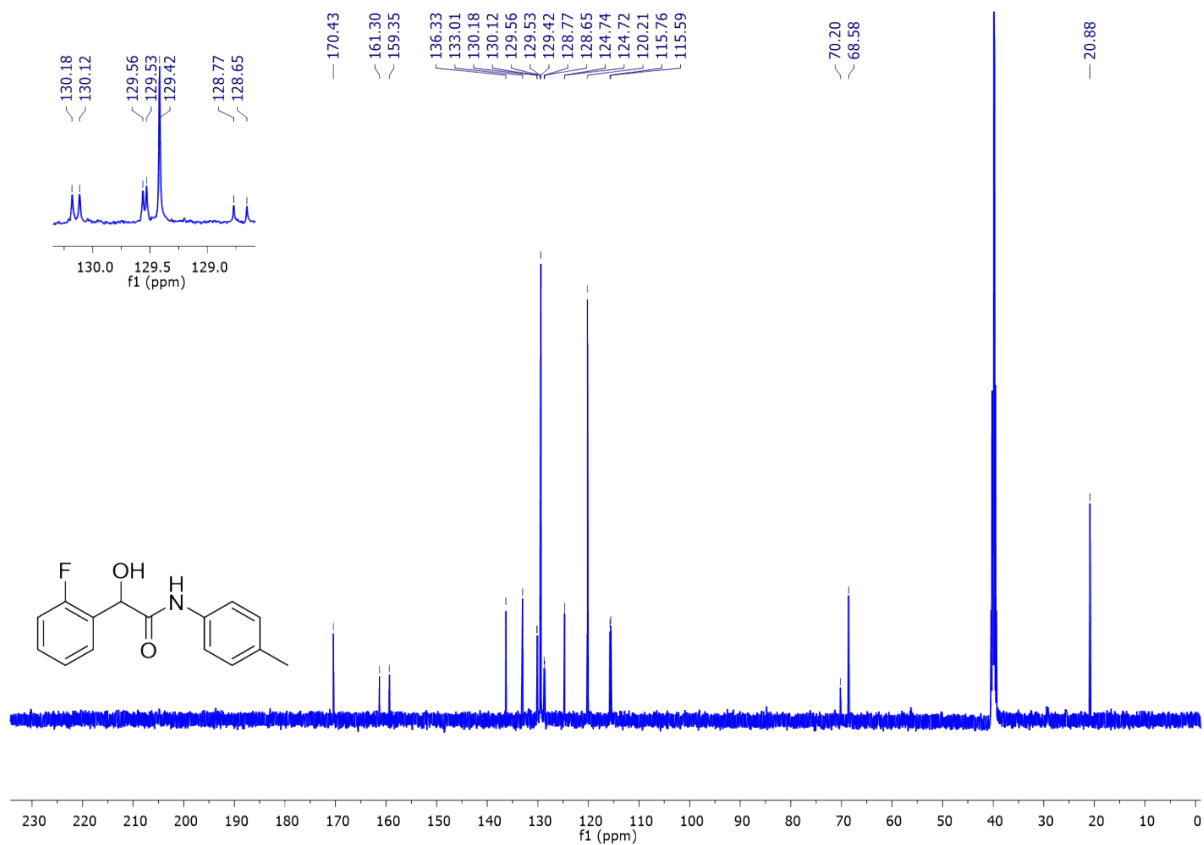


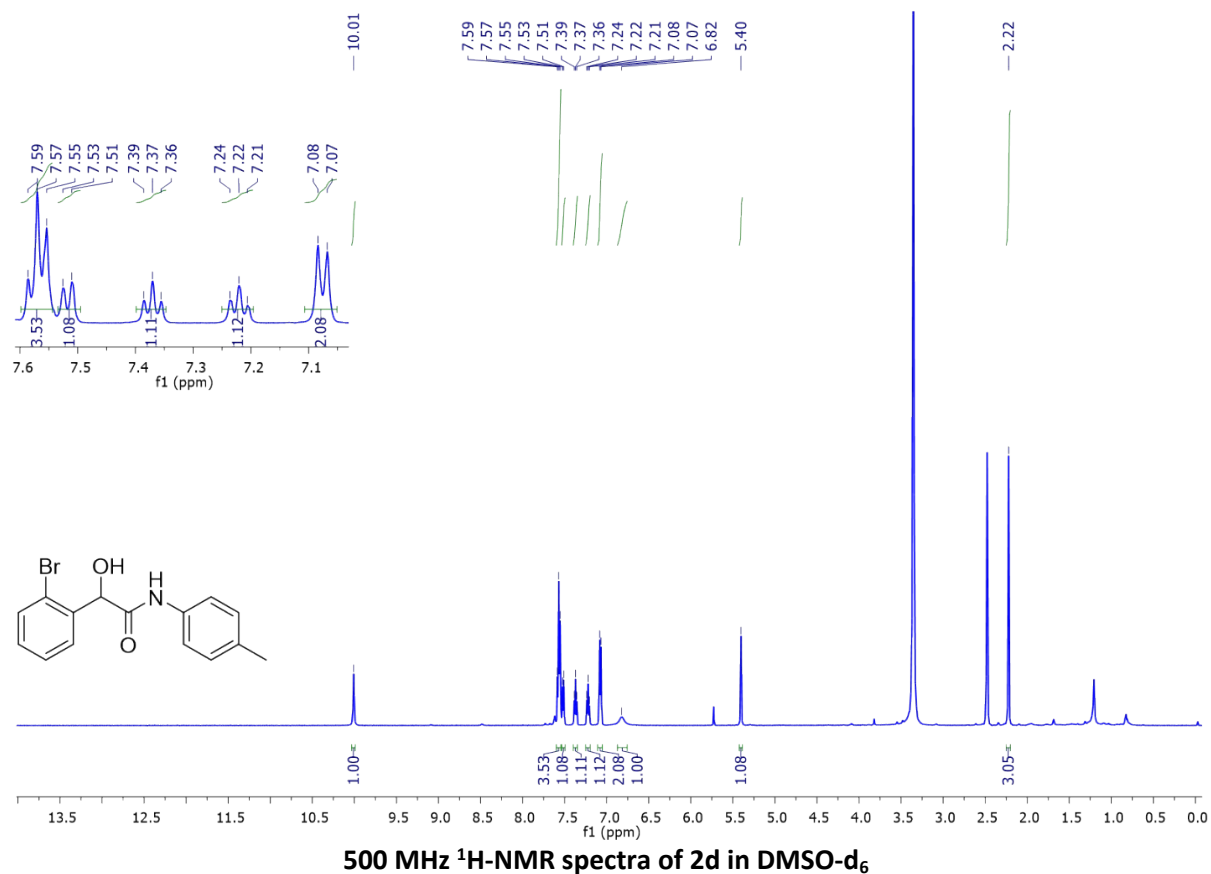
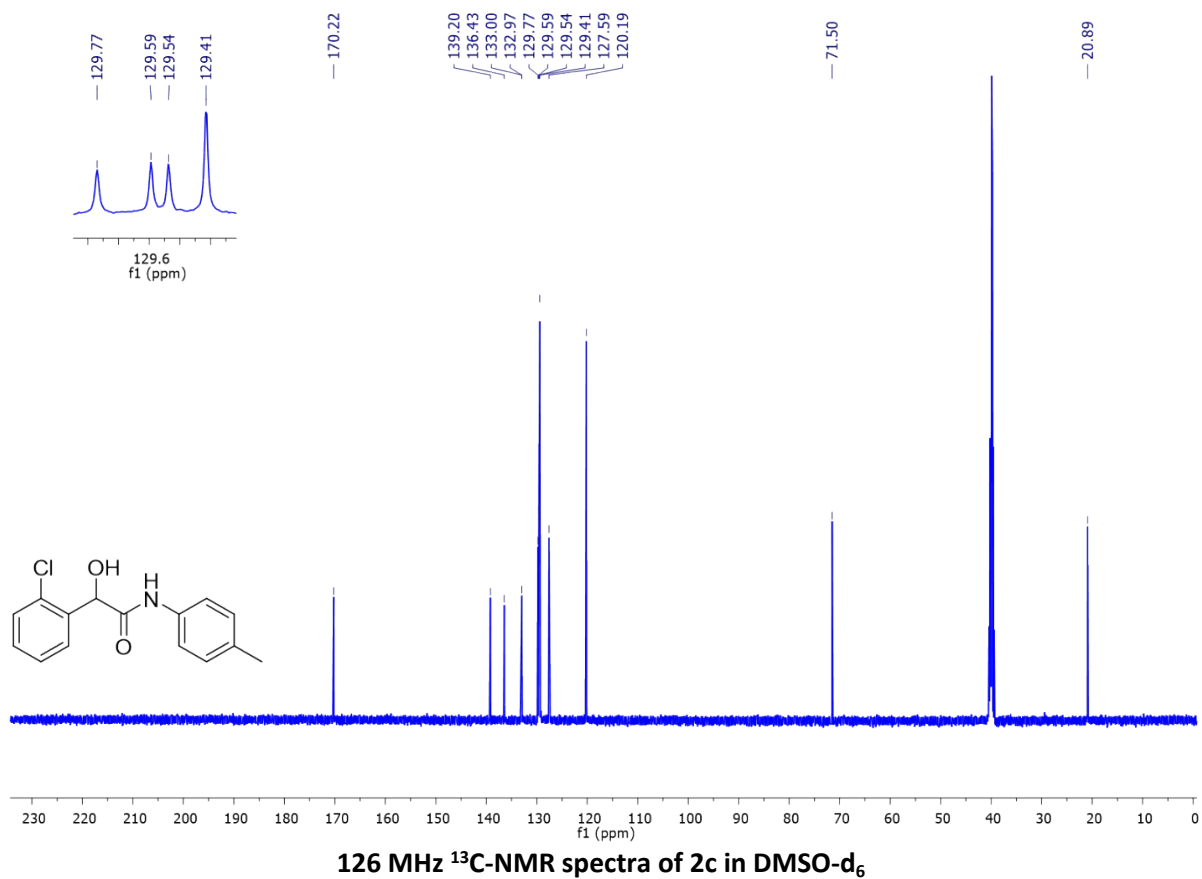


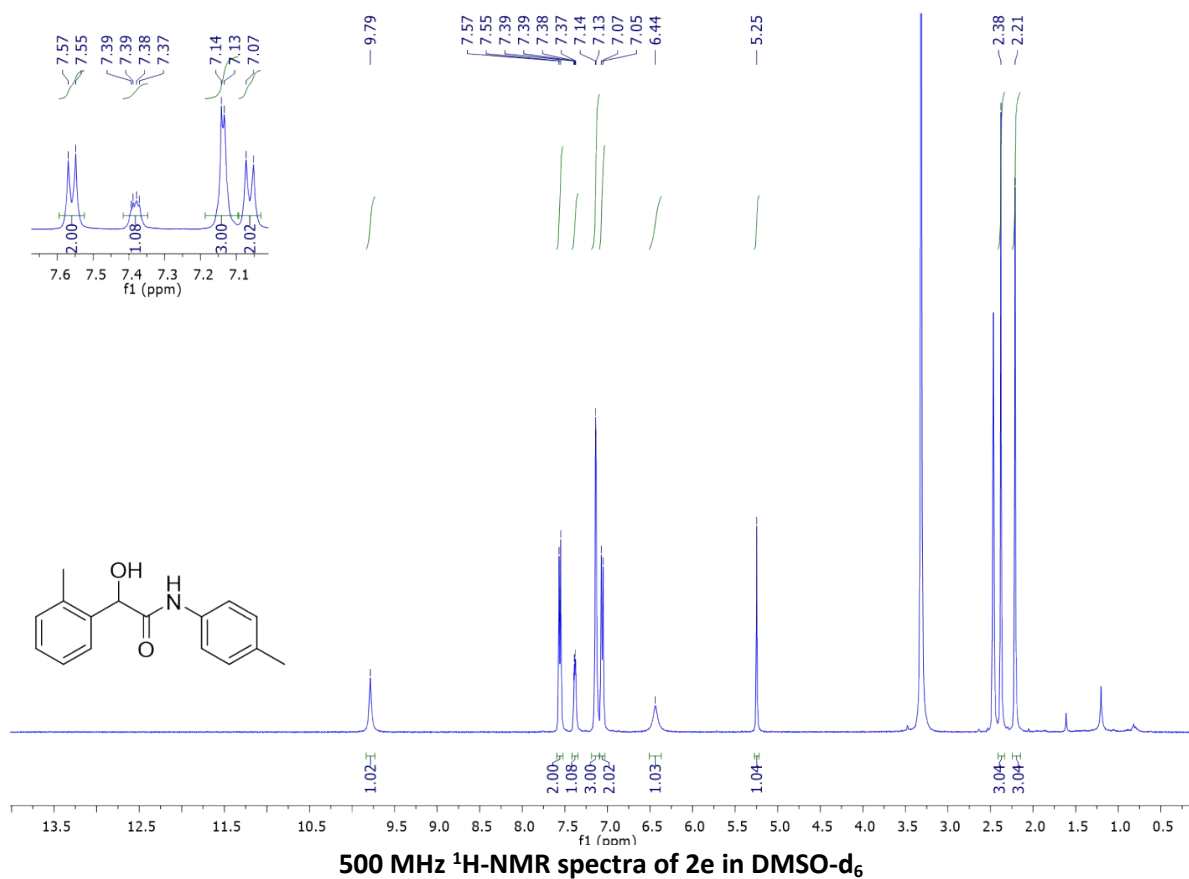
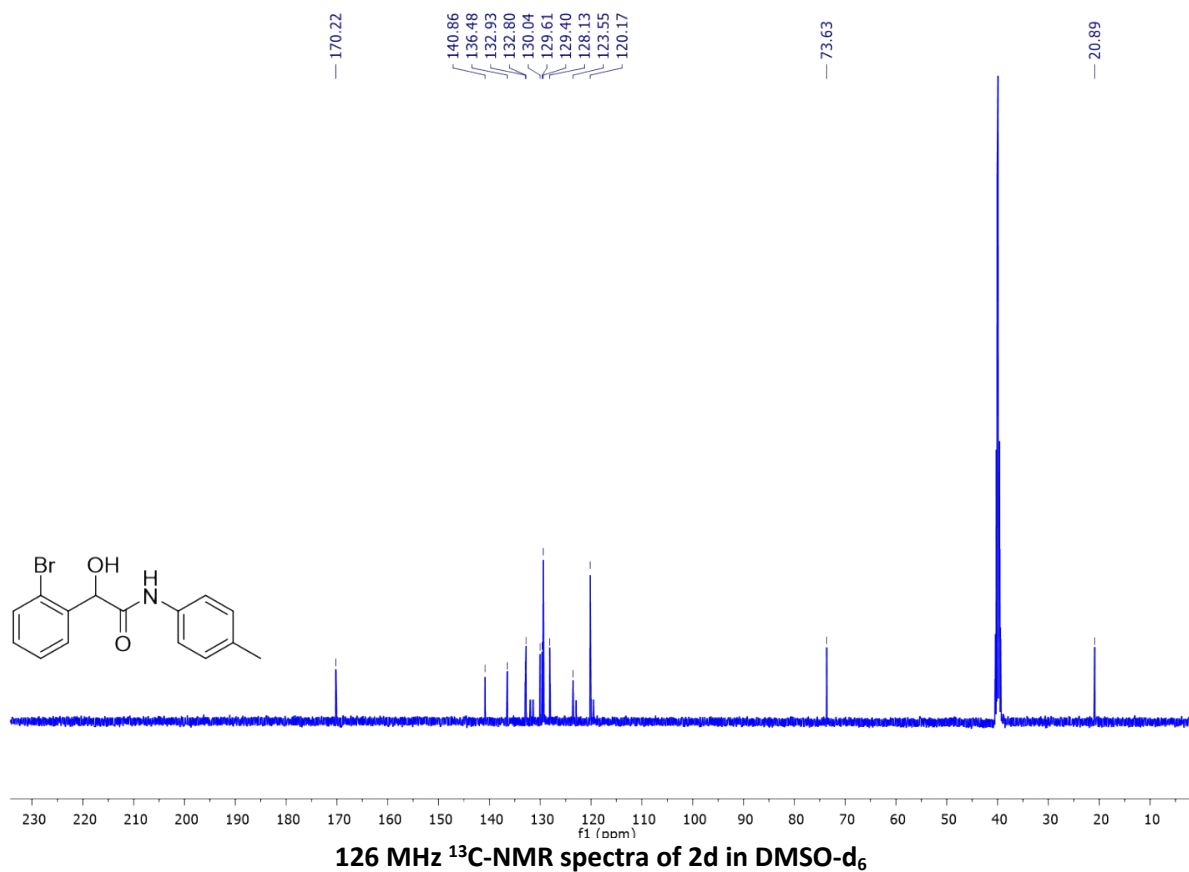
126 MHz  $^{13}\text{C}$ -NMR spectra of 2a in DMSO- $d_6$

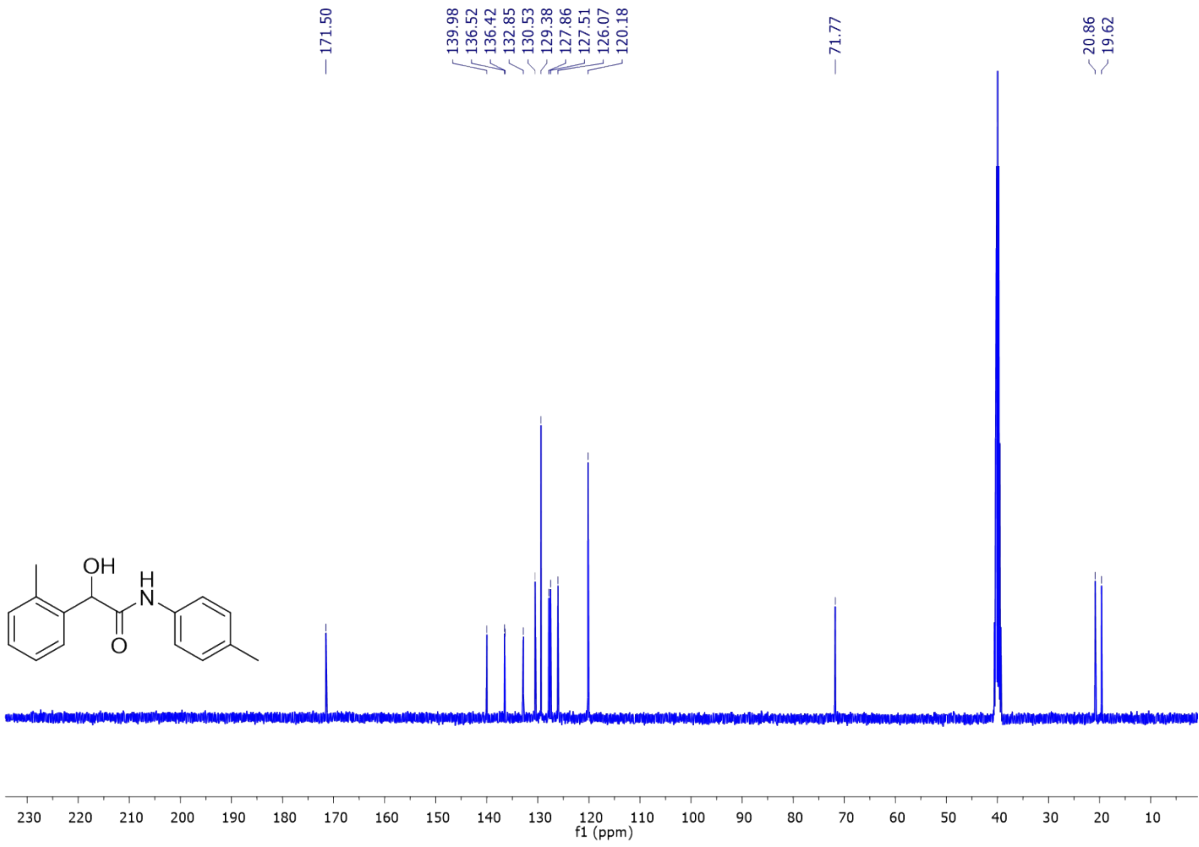


500 MHz  $^1\text{H}$ -NMR spectra of 2b in DMSO- $d_6$

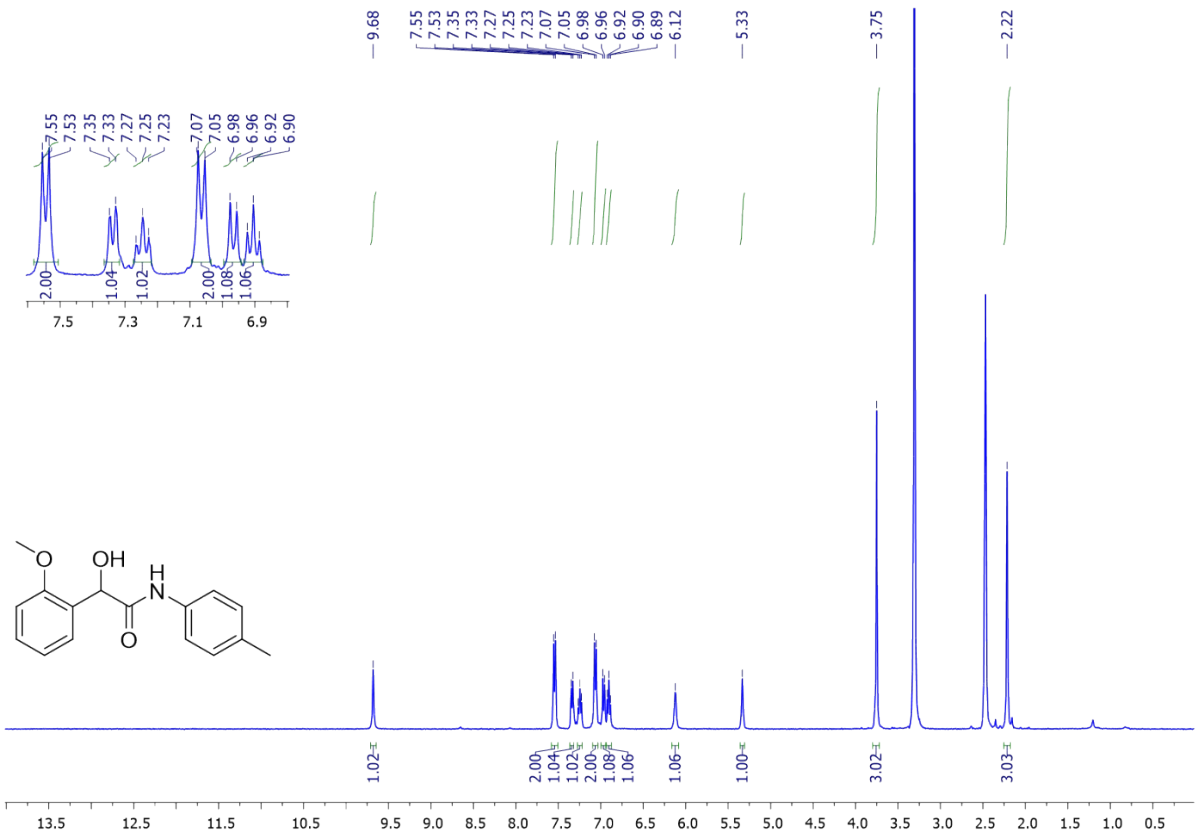






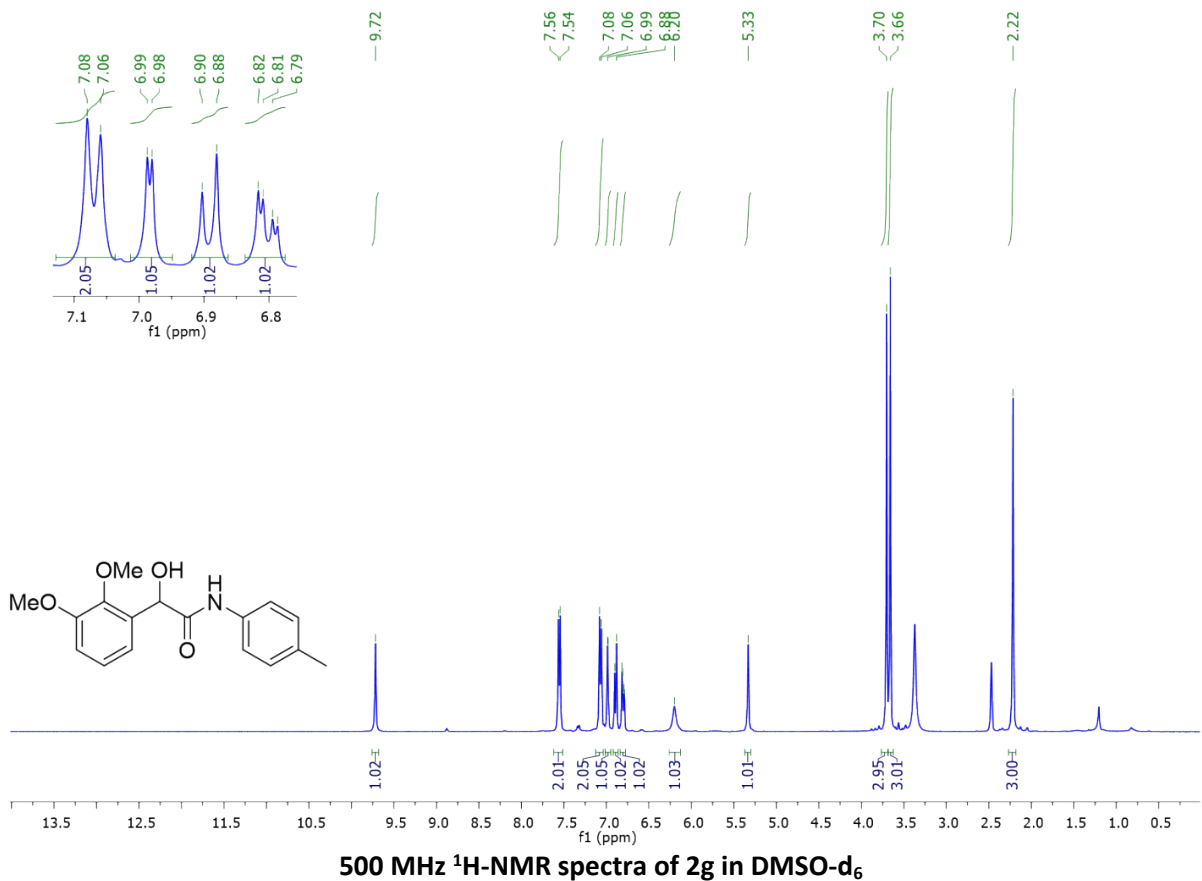
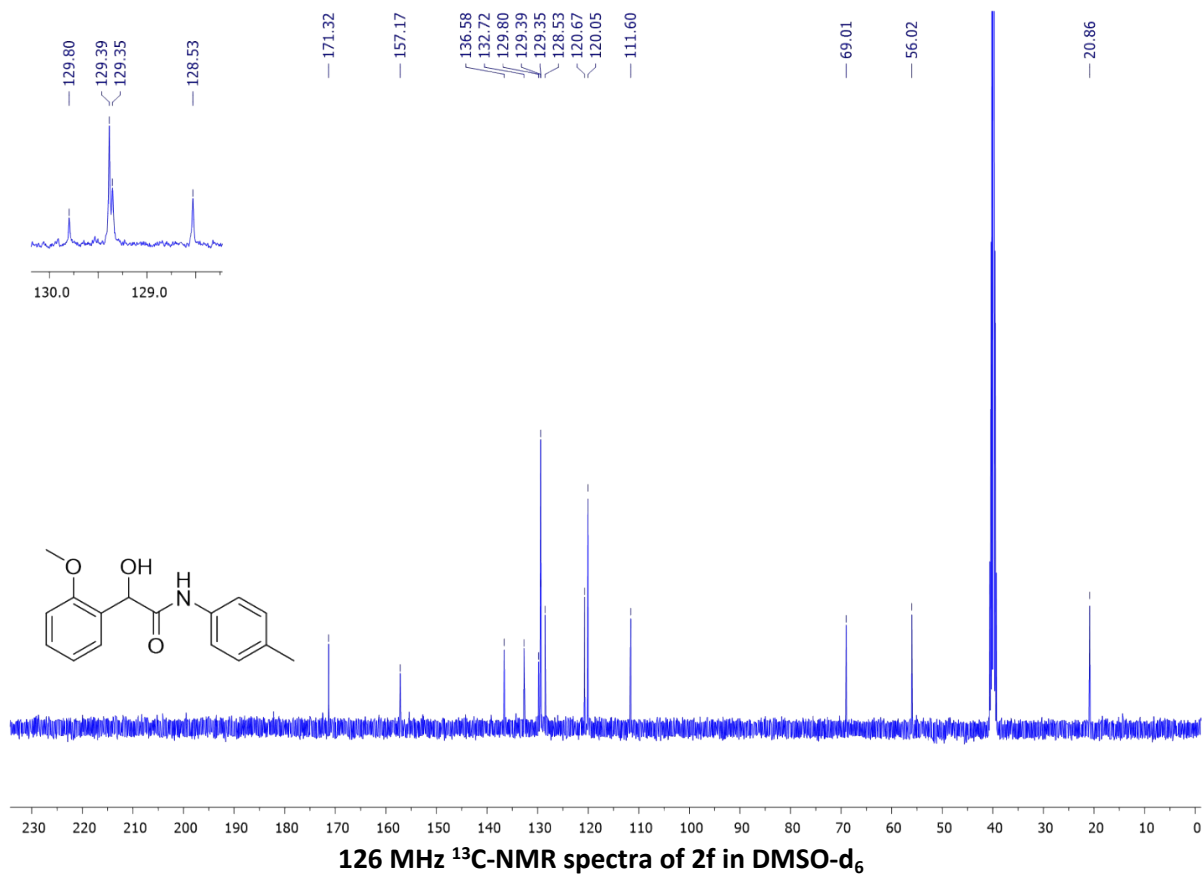


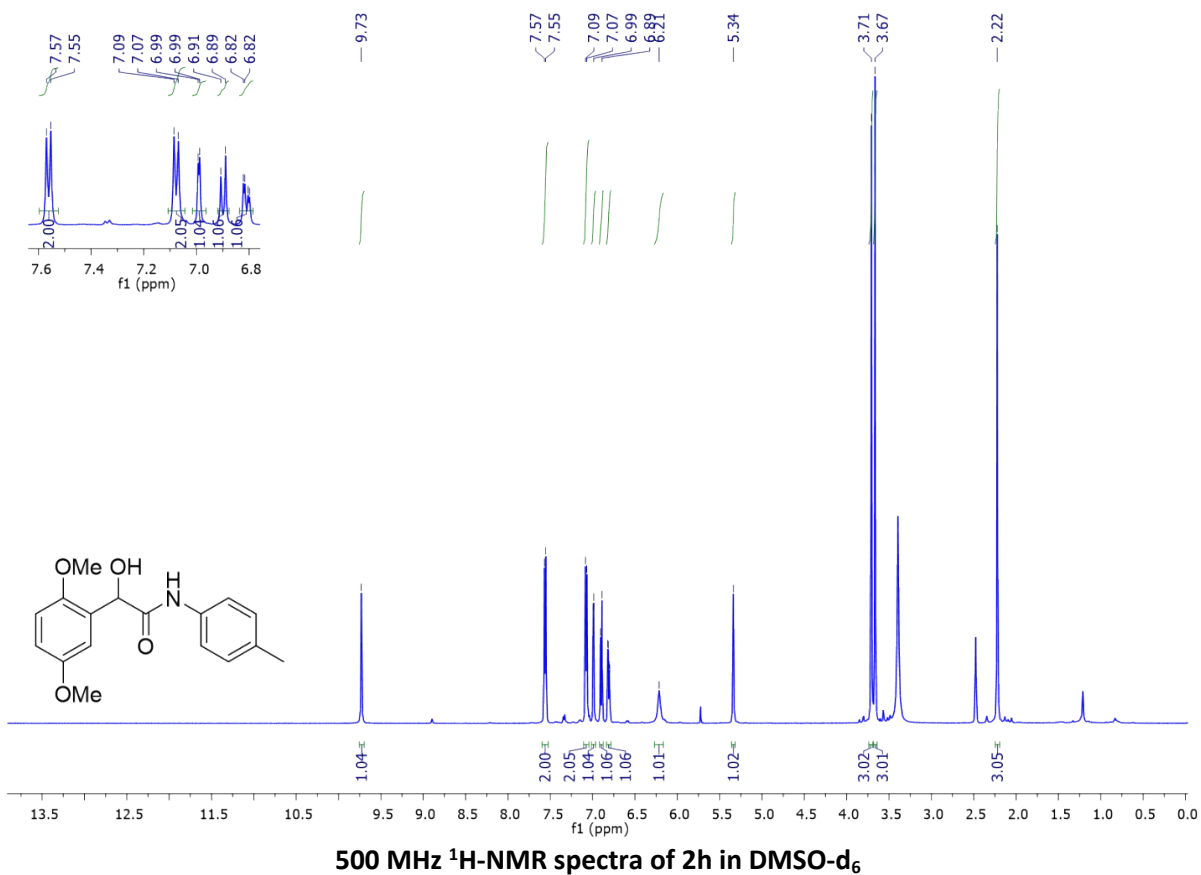
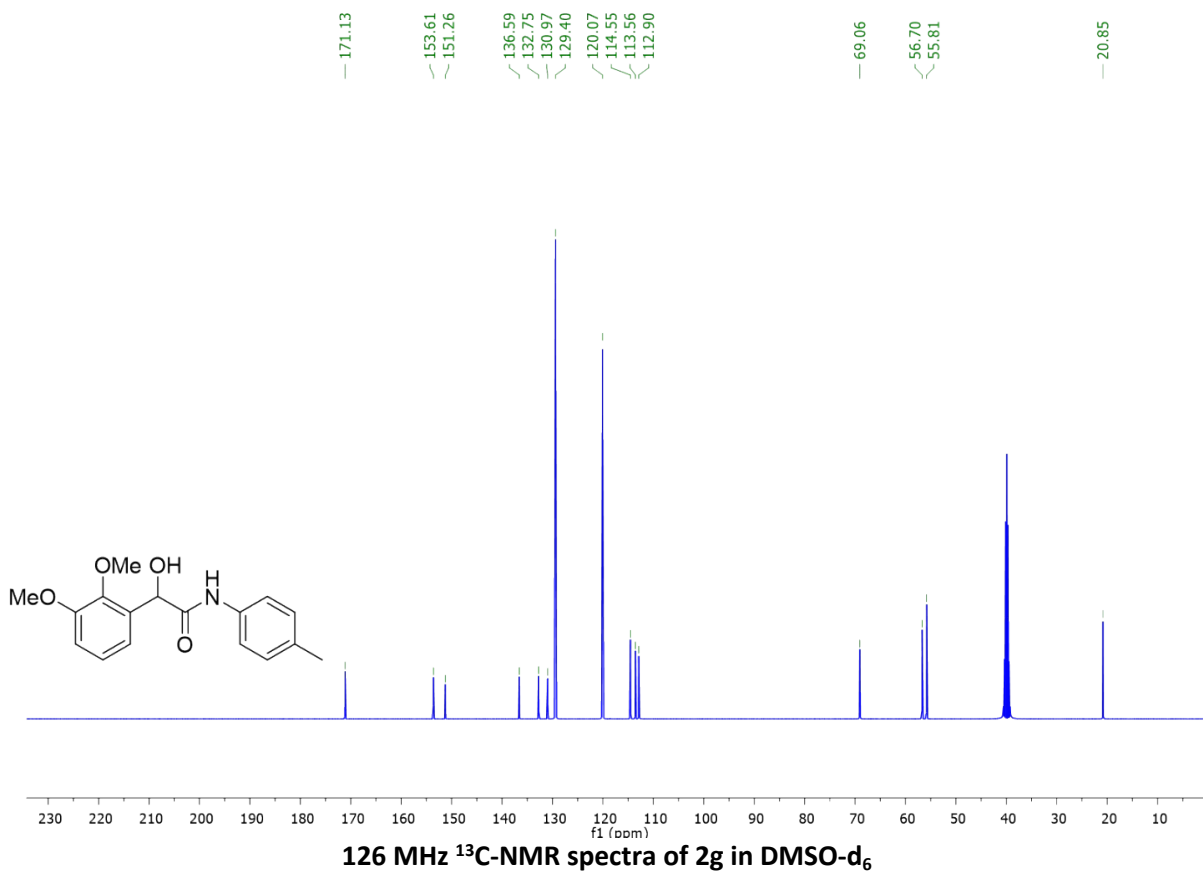
126 MHz  $^{13}\text{C}$ -NMR spectra of 2e in  $\text{DMSO-d}_6$

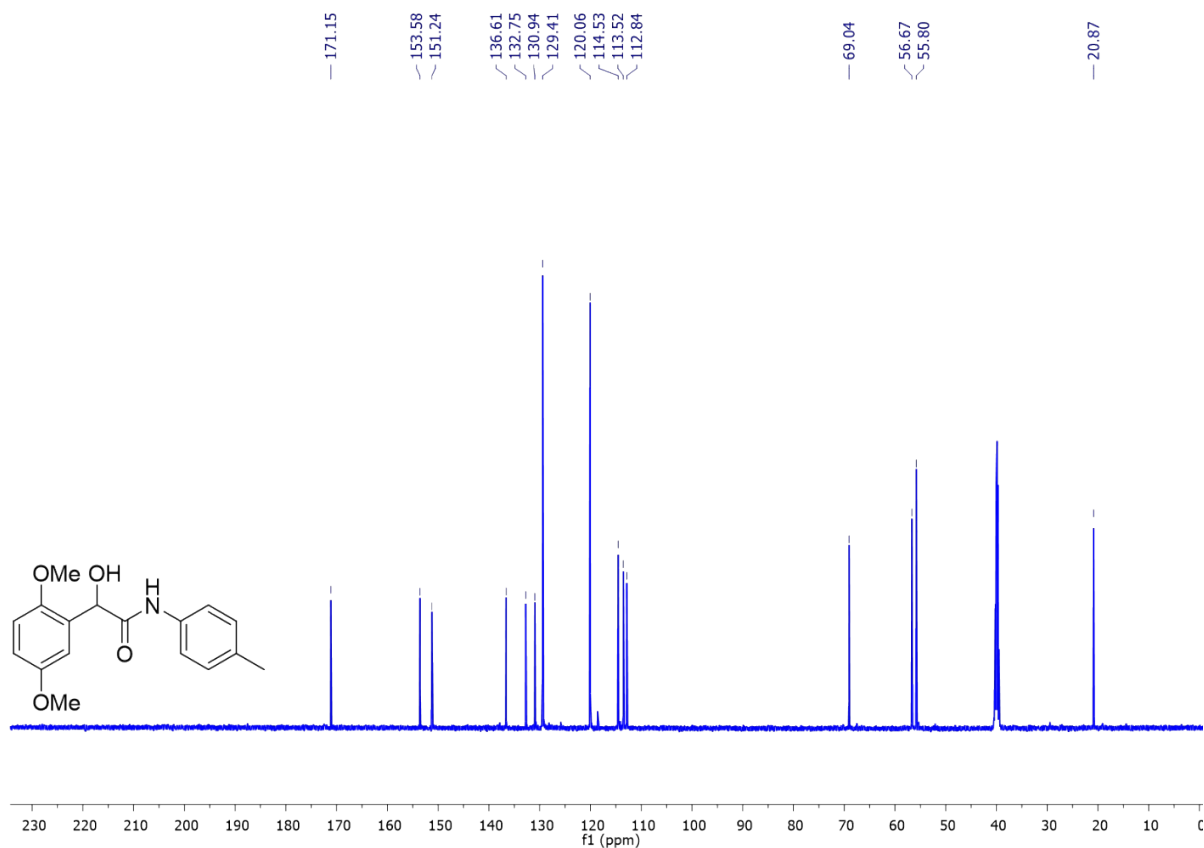


500 MHz  $^1\text{H}$ -NMR spectra of 2f in  $\text{DMSO-d}_6$

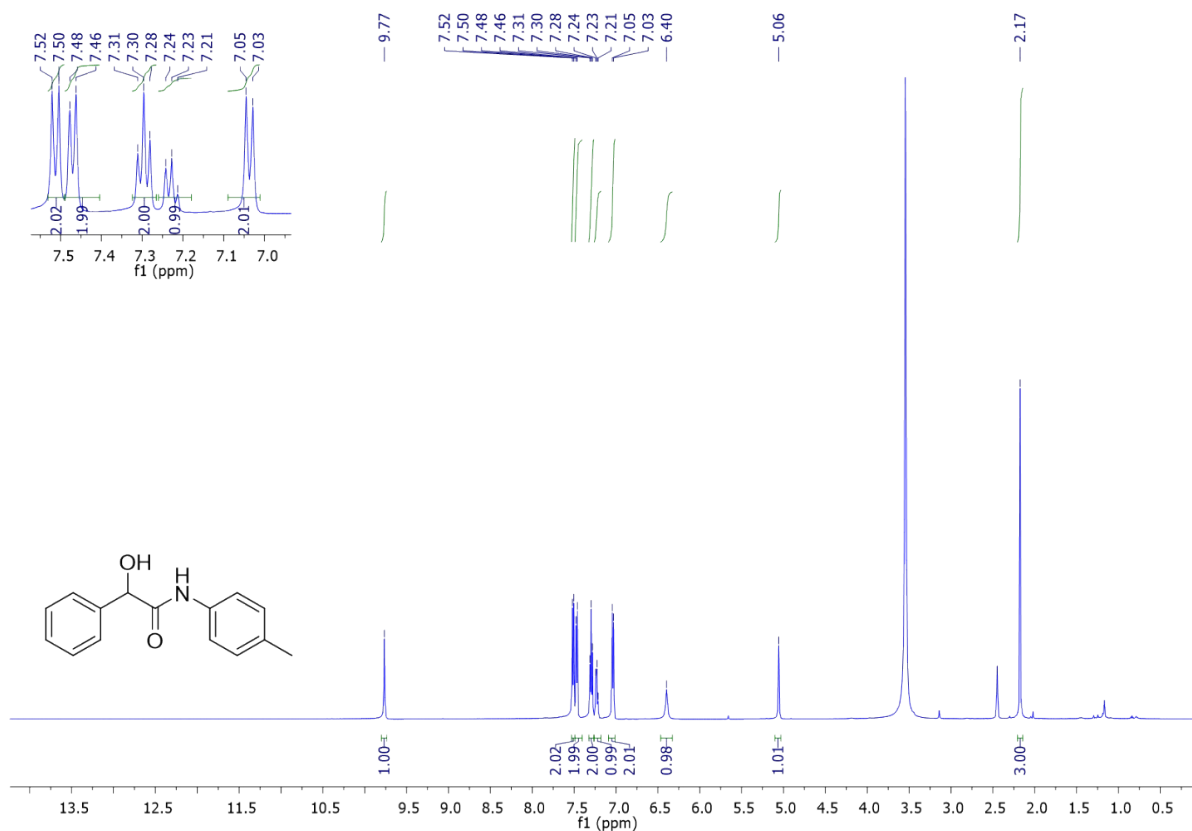




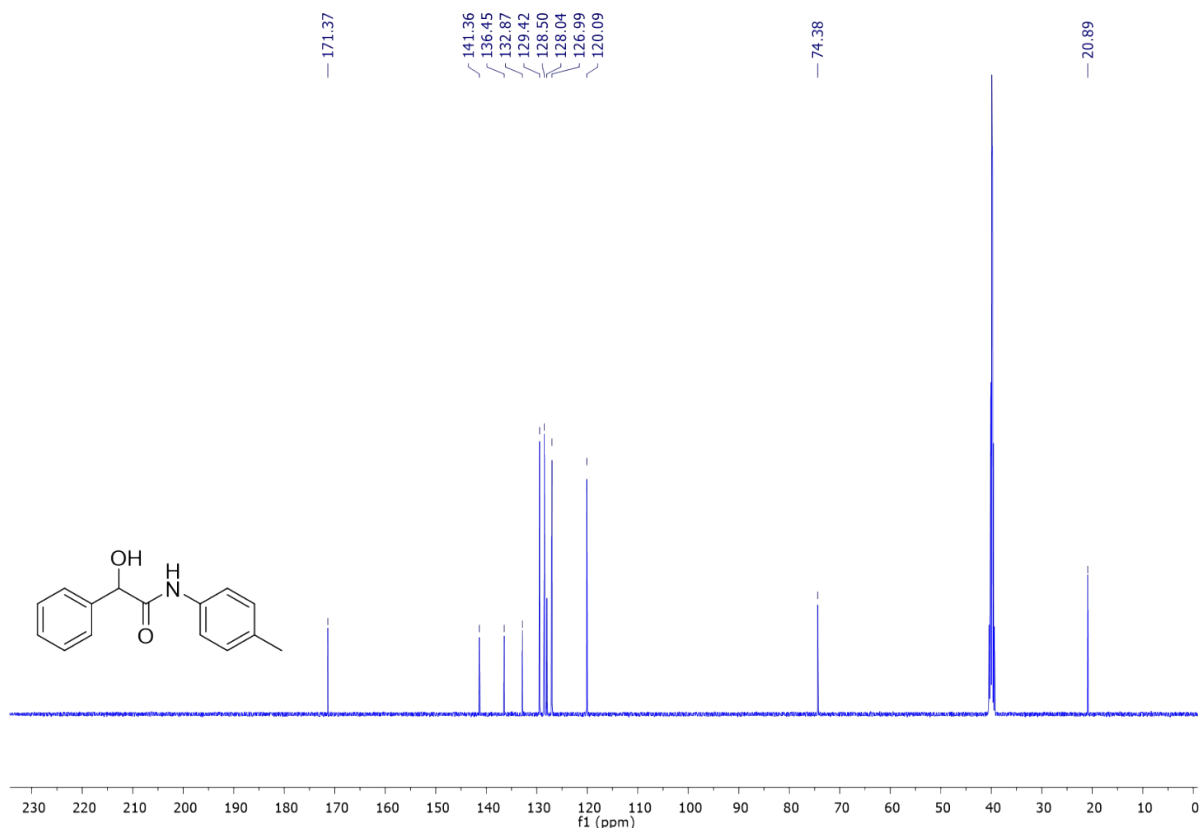




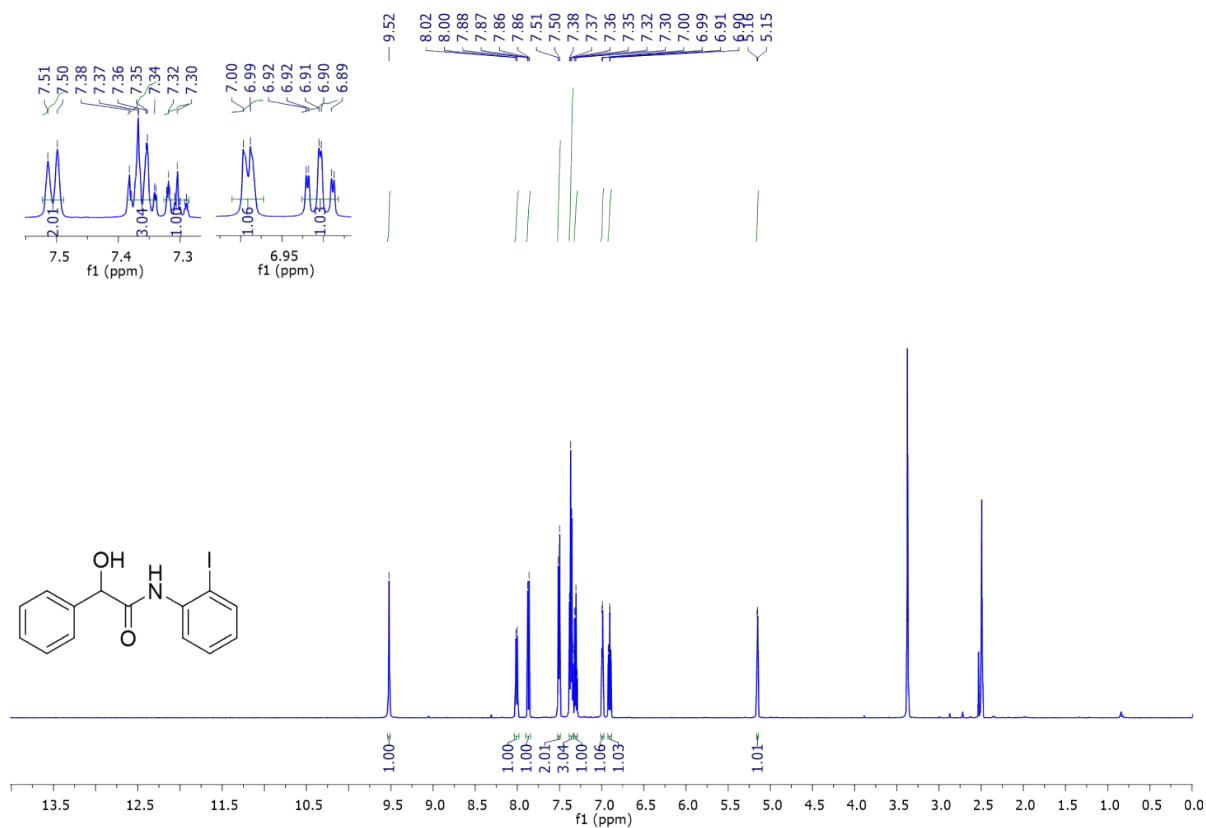
126 MHz  $^{13}\text{C}$ -NMR spectra of 2h in  $\text{DMSO-d}_6$



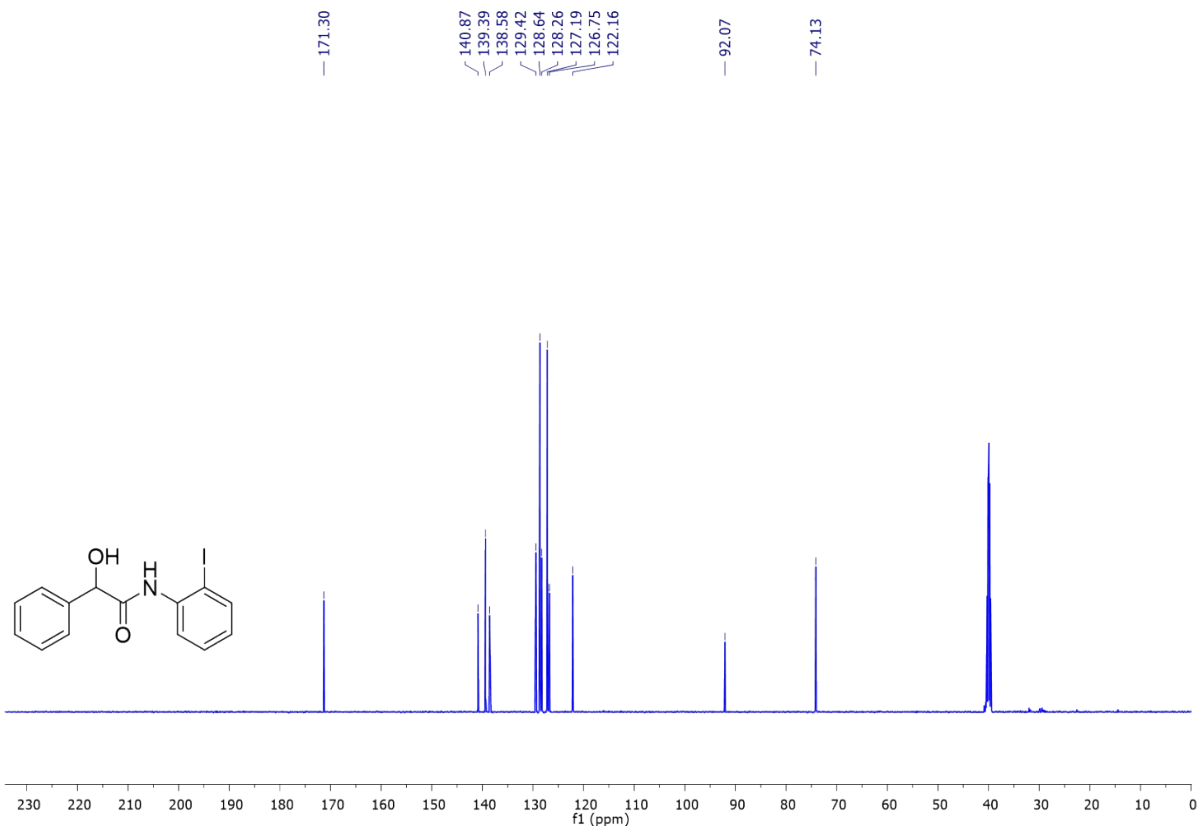
500 MHz  $^1\text{H}$ -NMR spectra of 2i in  $\text{DMSO-d}_6$



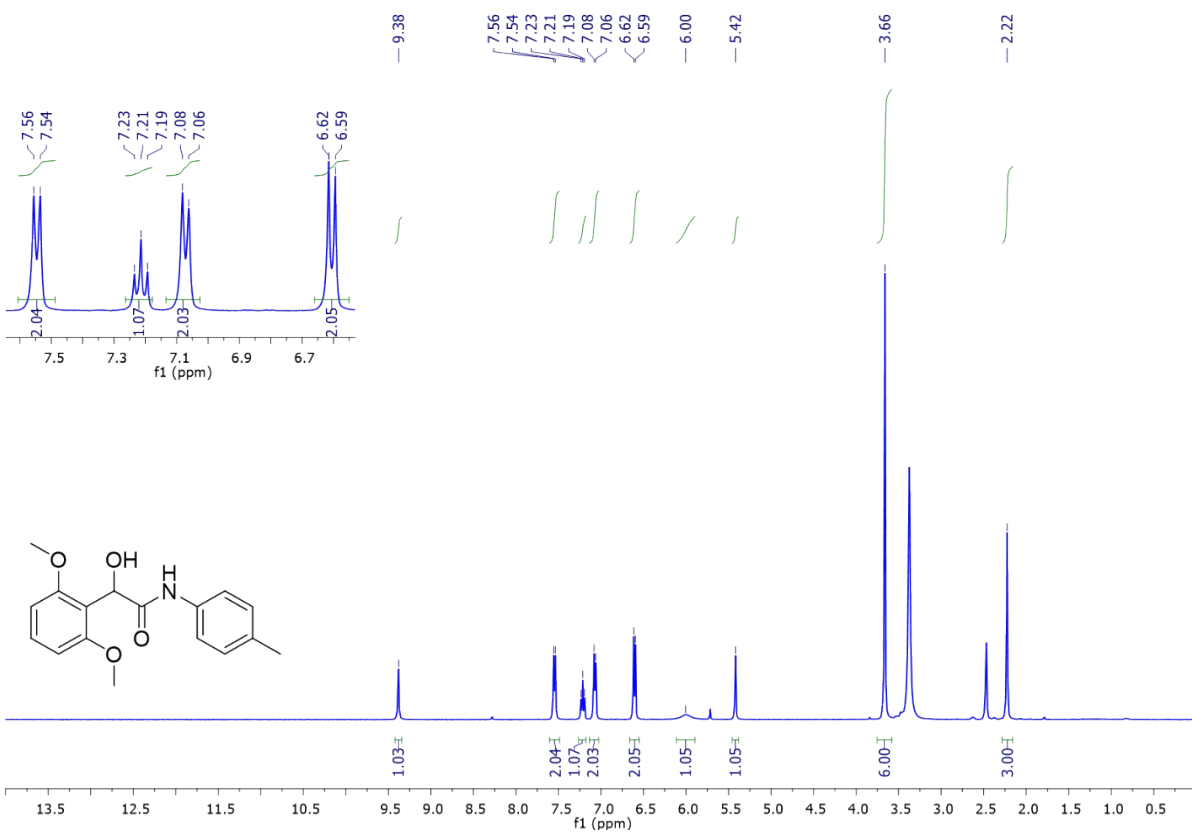
126 MHz  $^{13}\text{C}$ -NMR spectra of 2i in  $\text{DMSO-d}_6$



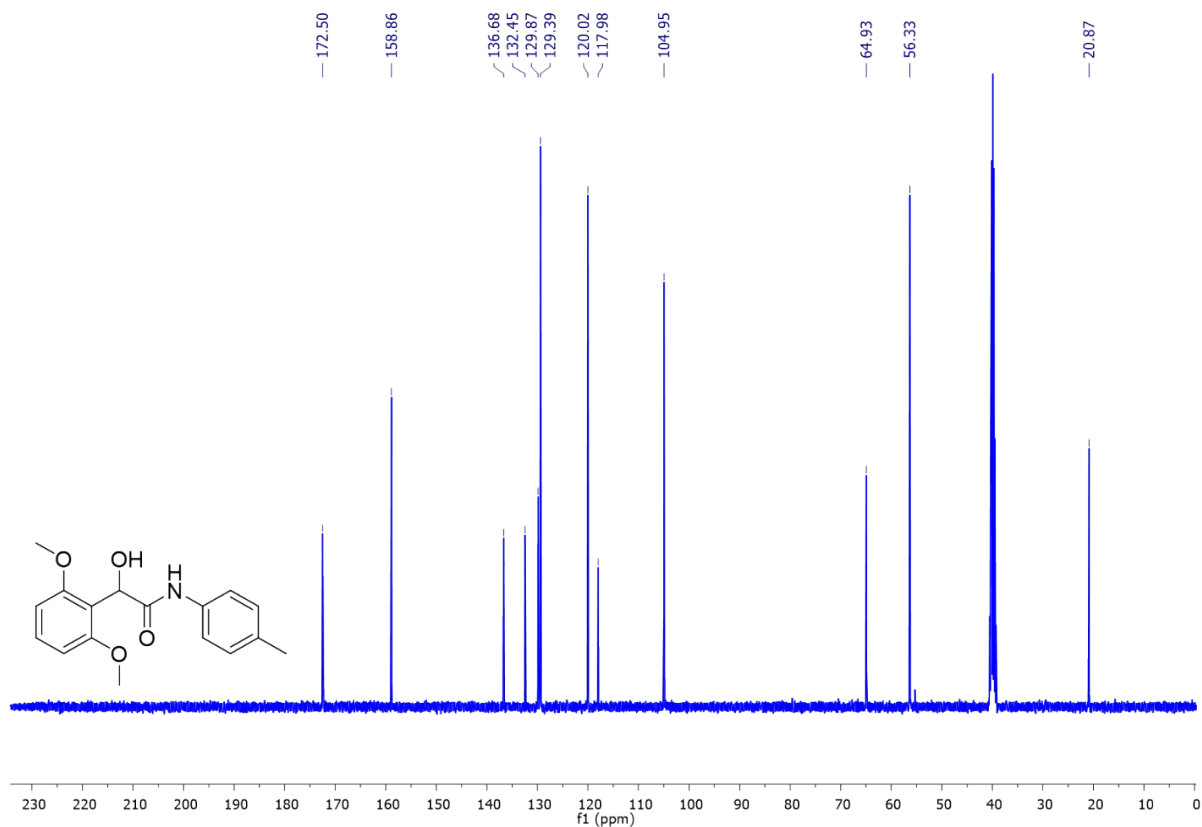
500 MHz  $^1\text{H}$ -NMR spectra of 2j in  $\text{DMSO-d}_6$



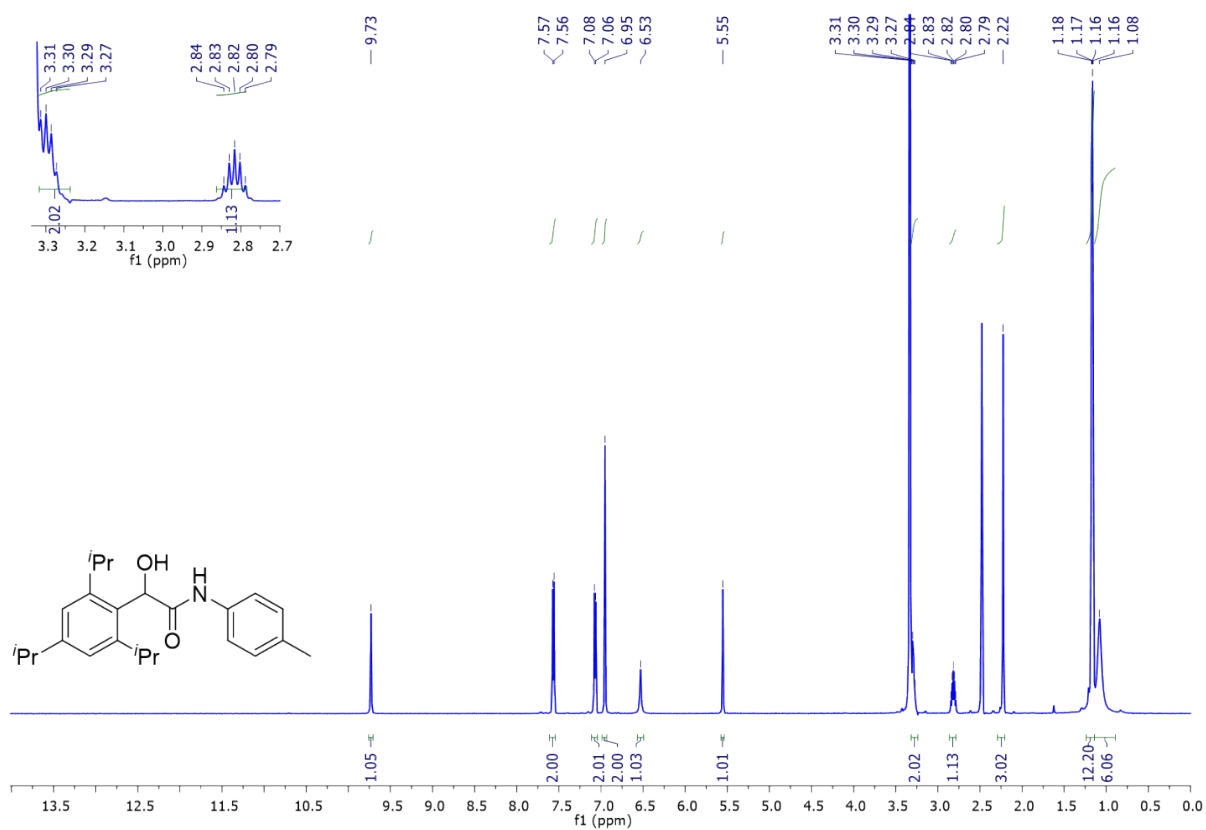
126 MHz  $^{13}\text{C}$ -NMR spectra of 2j in  $\text{DMSO-d}_6$



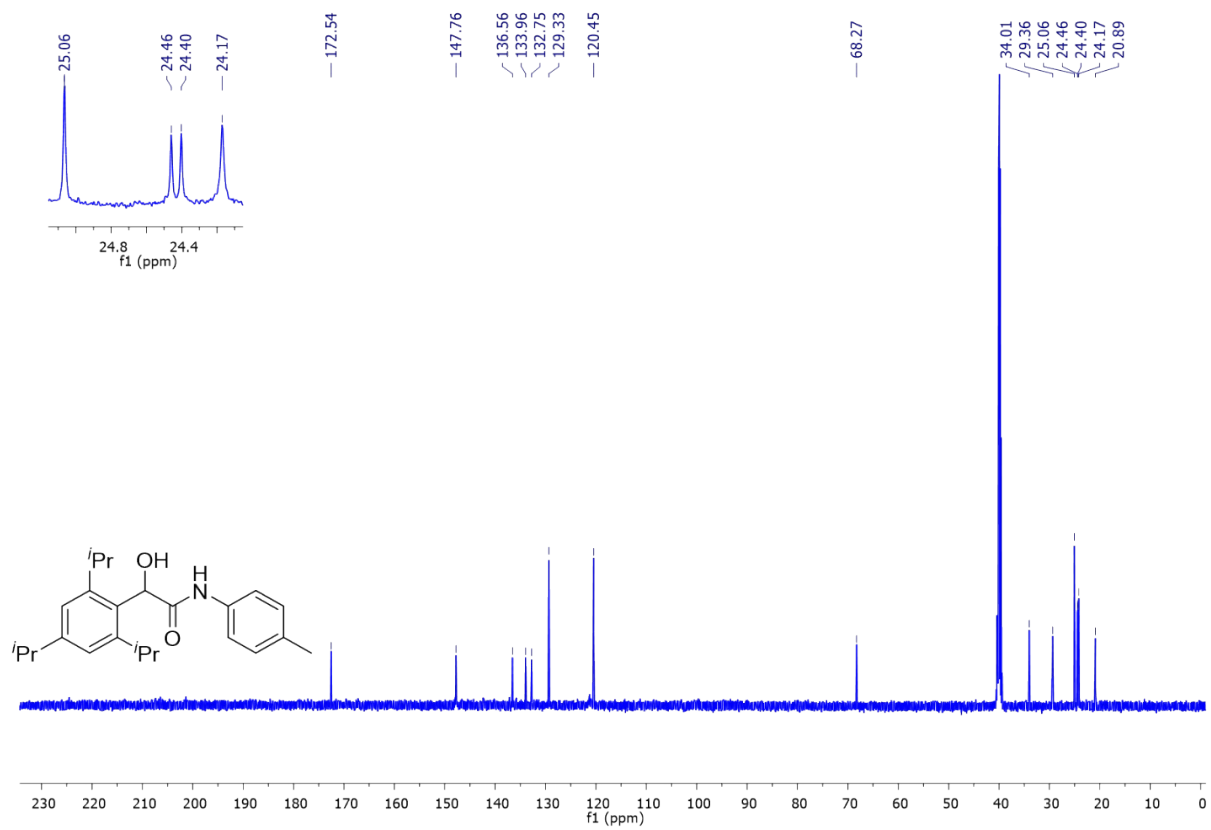
500 MHz  $^1\text{H}$ -NMR spectra of 2k in  $\text{DMSO-d}_6$



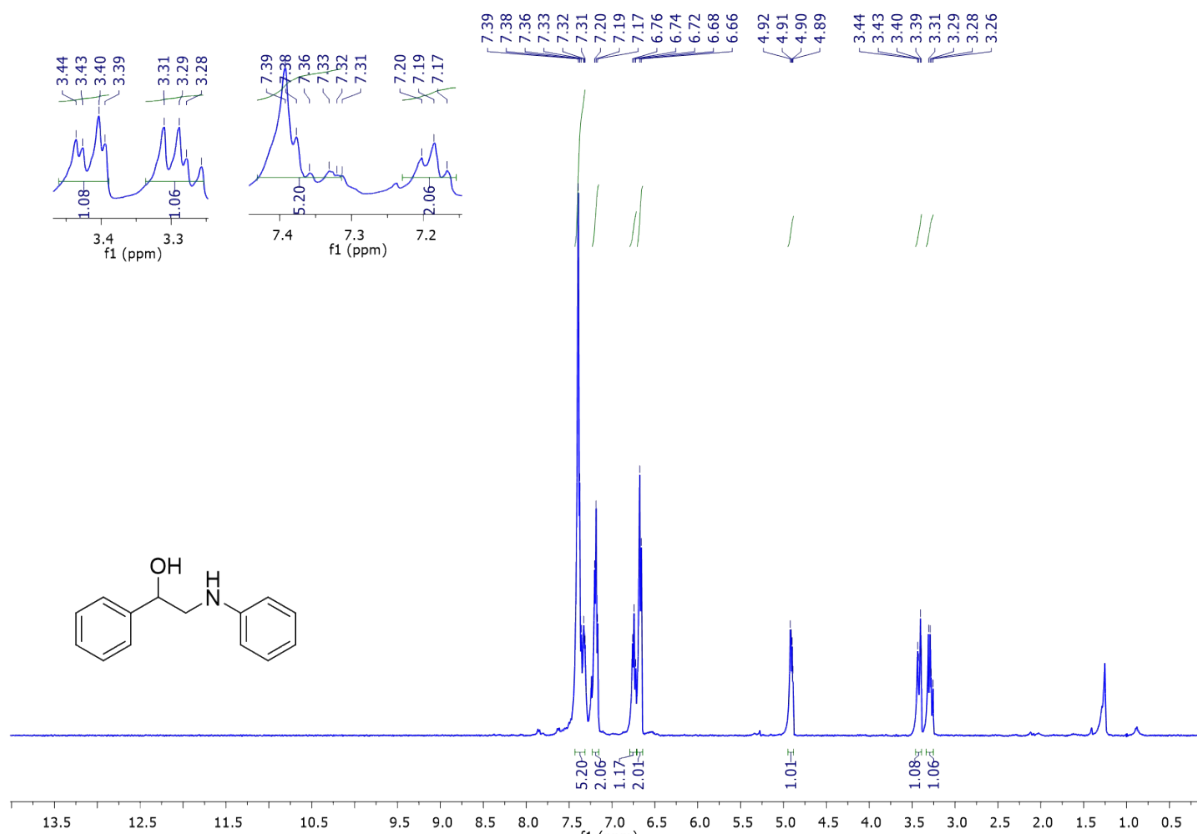
126 MHz  $^{13}\text{C}$ -NMR spectra of 2k in DMSO- $d_6$



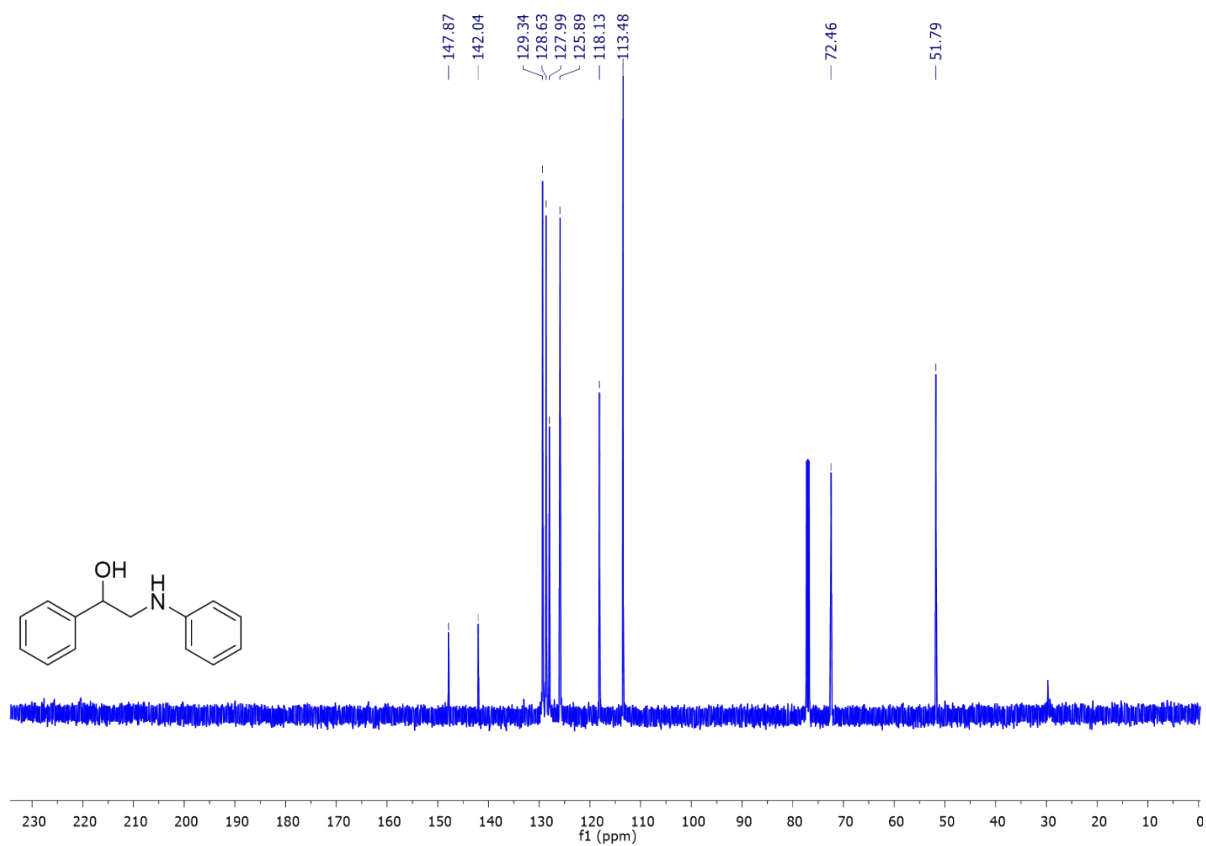
500 MHz  $^1\text{H}$ -NMR spectra of 2l in DMSO- $d_6$



**$^1\text{H}$  and  $^{13}\text{C}$  NMR of  $\beta$ -aminol:**

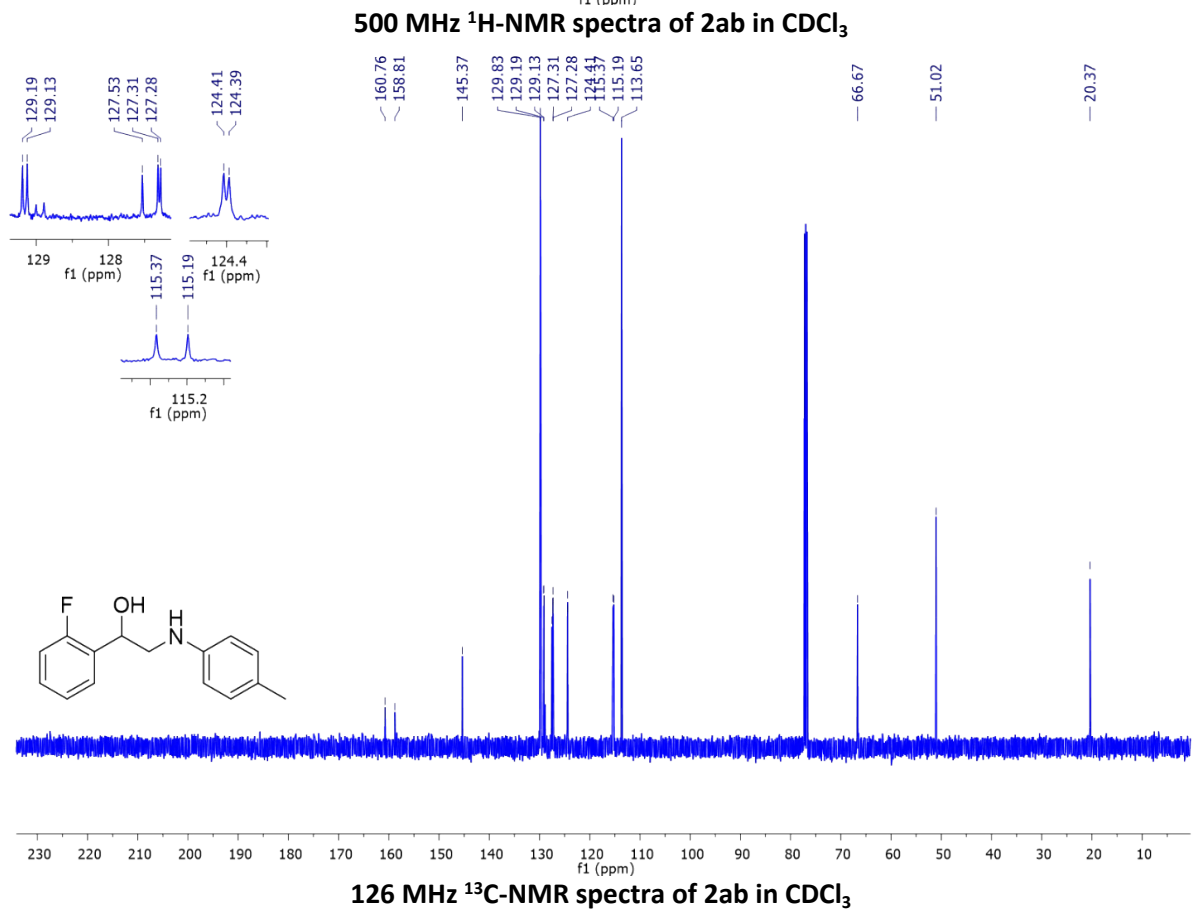
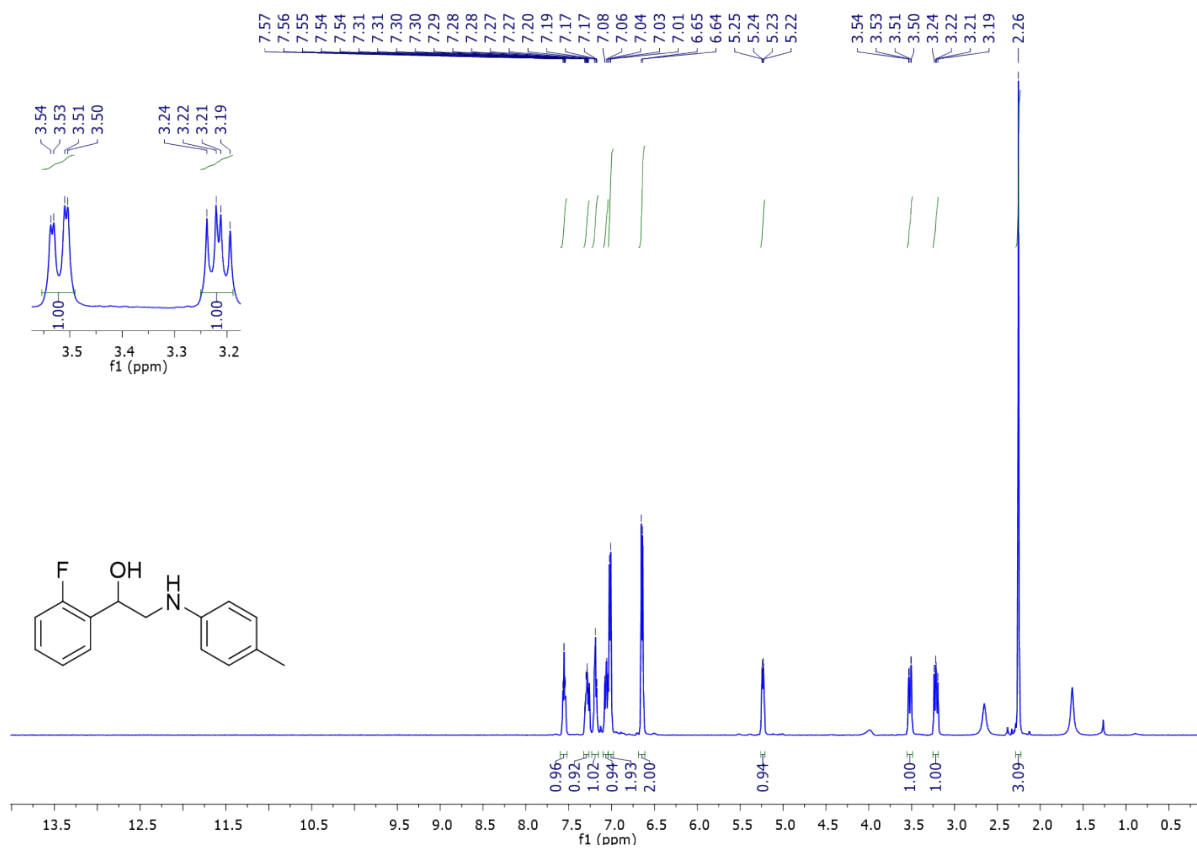


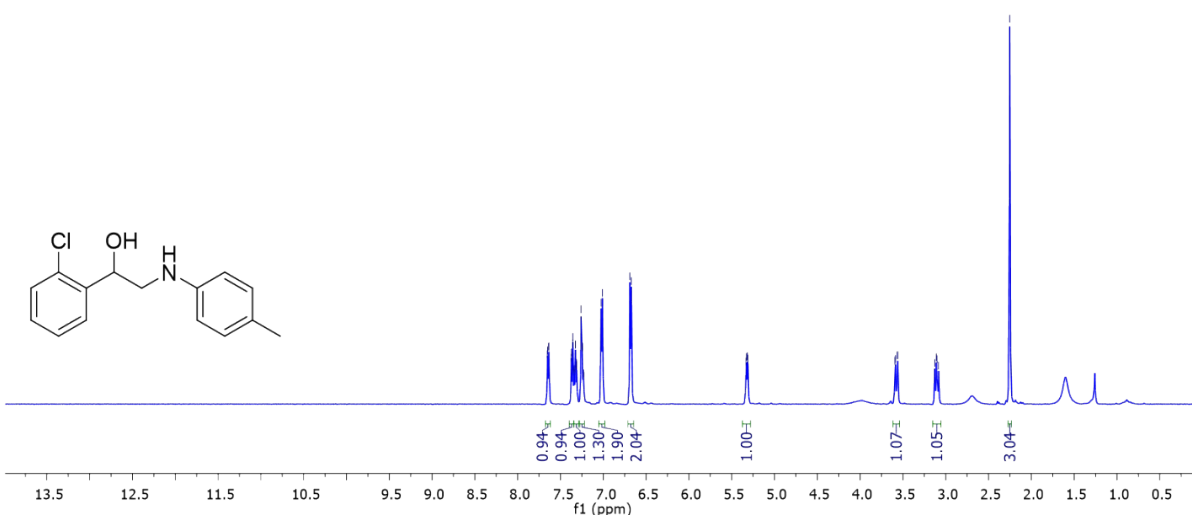
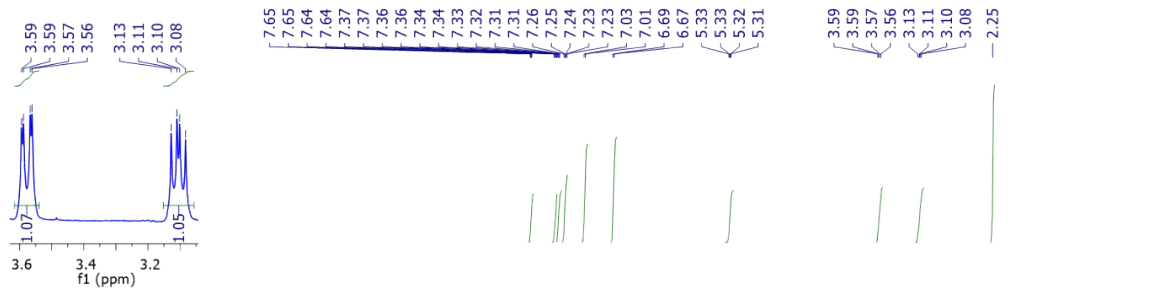
500 MHz <sup>1</sup>H-NMR spectra of 2aa in CDCl<sub>3</sub>



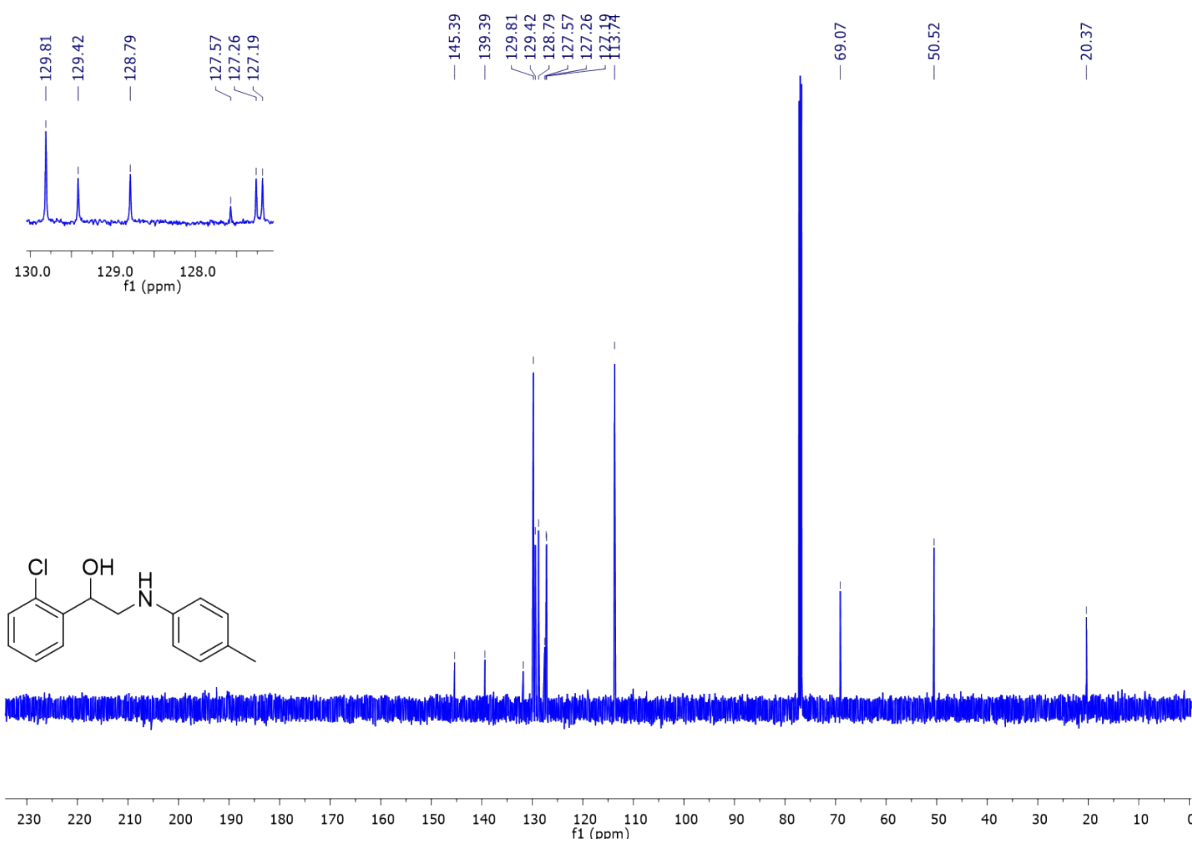
126 MHz <sup>13</sup>C-NMR spectra of 2aa in CDCl<sub>3</sub>



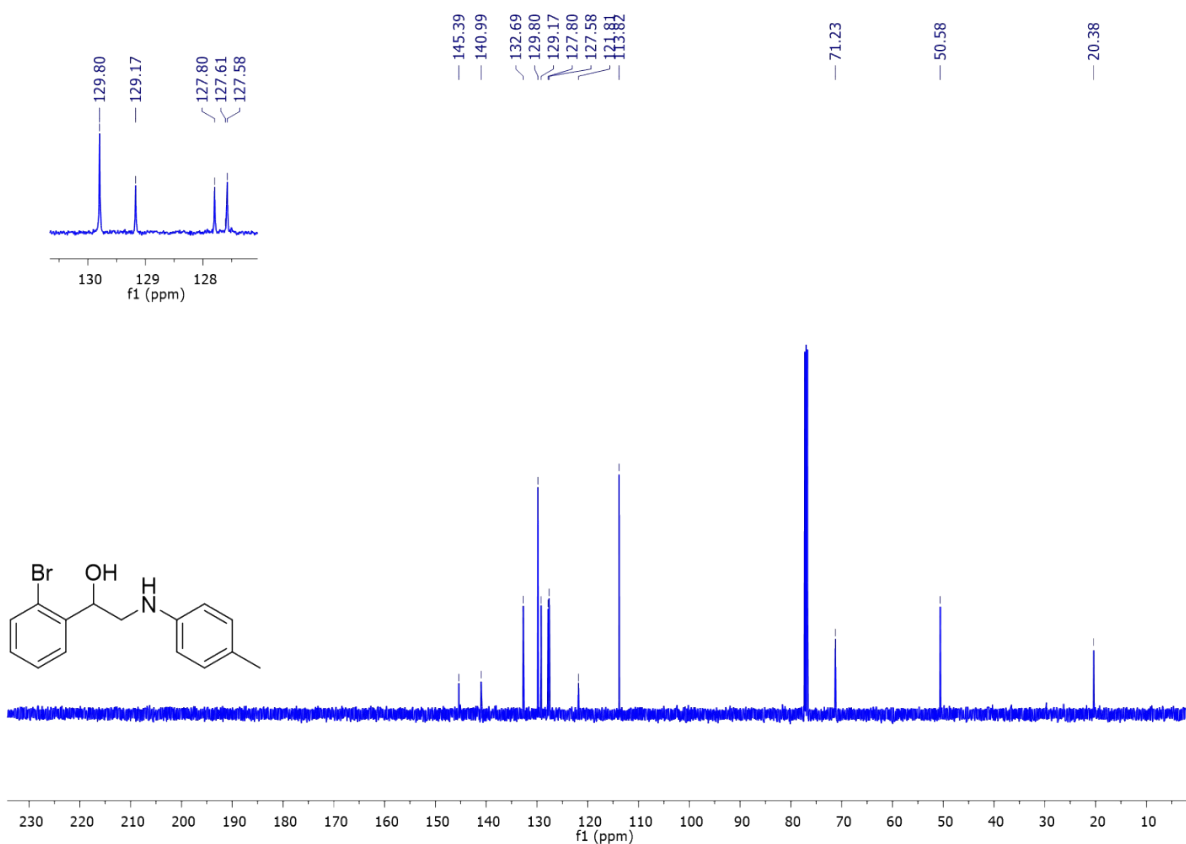
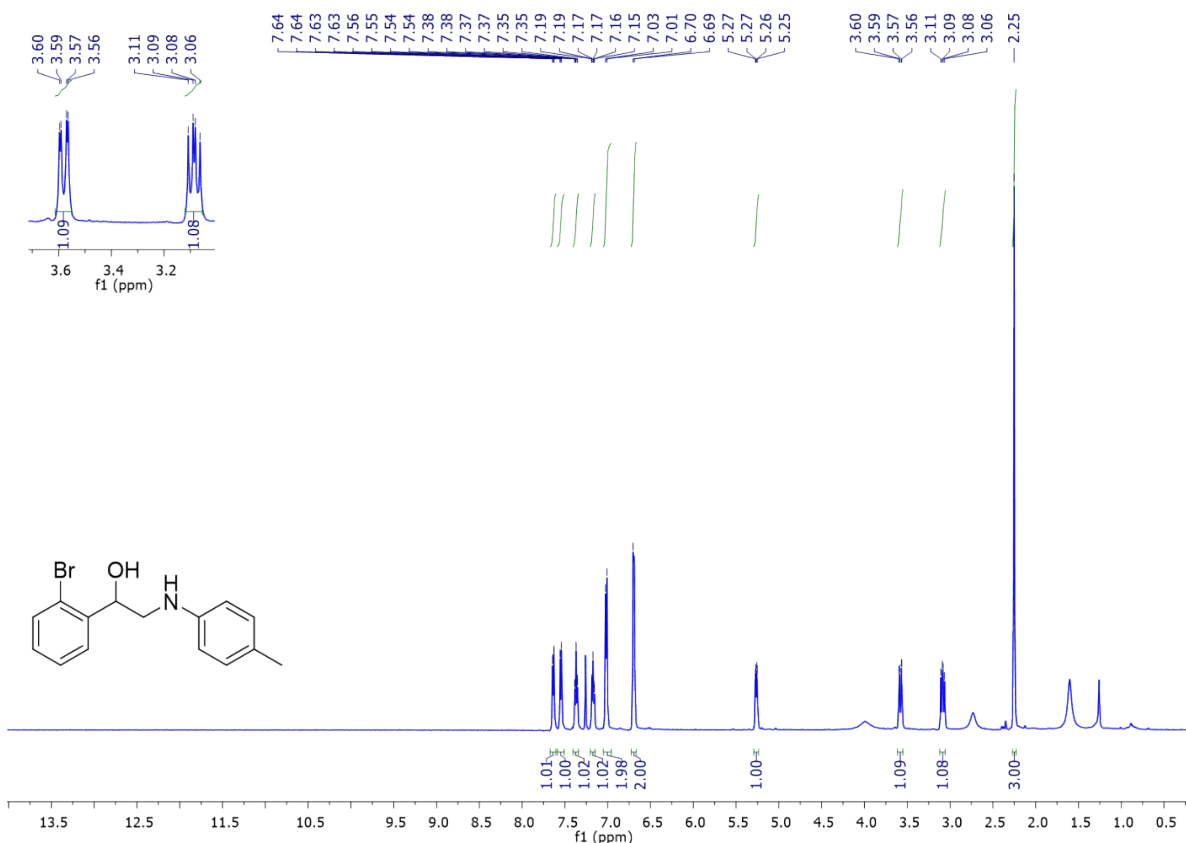


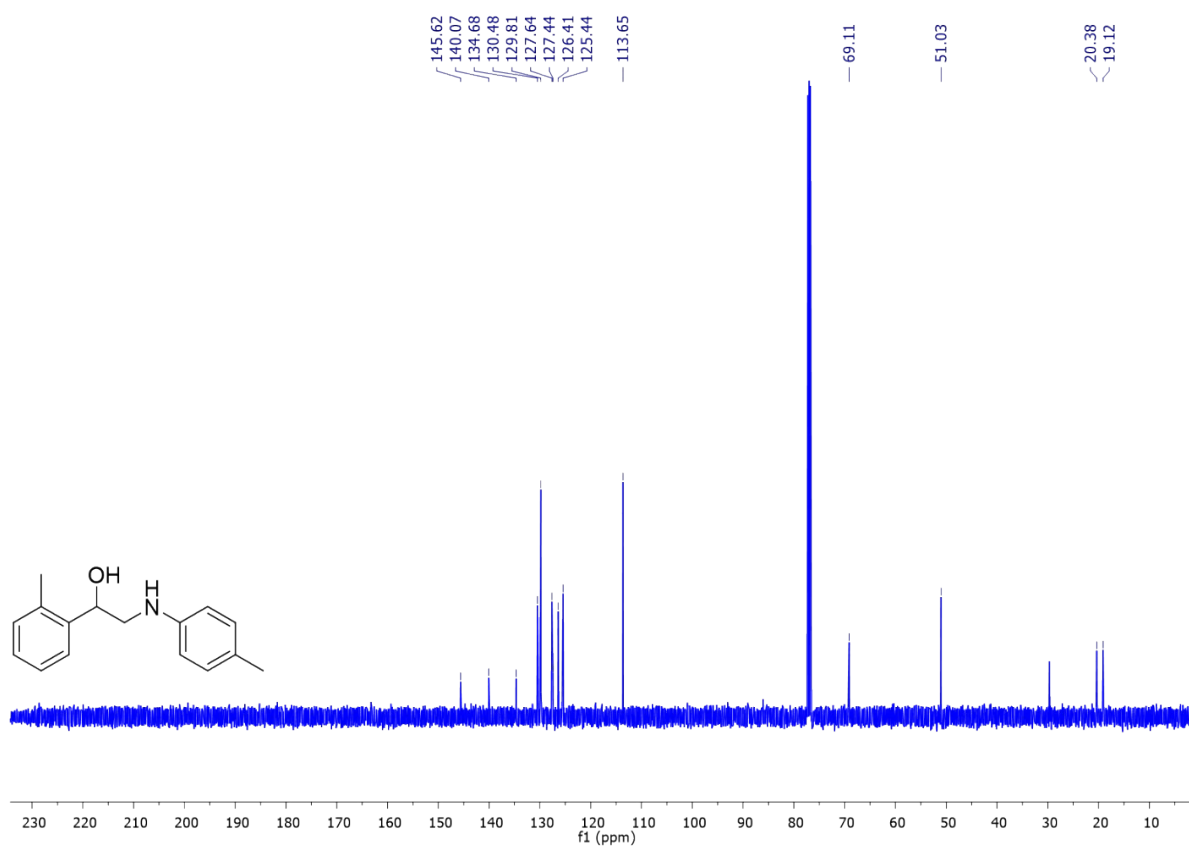
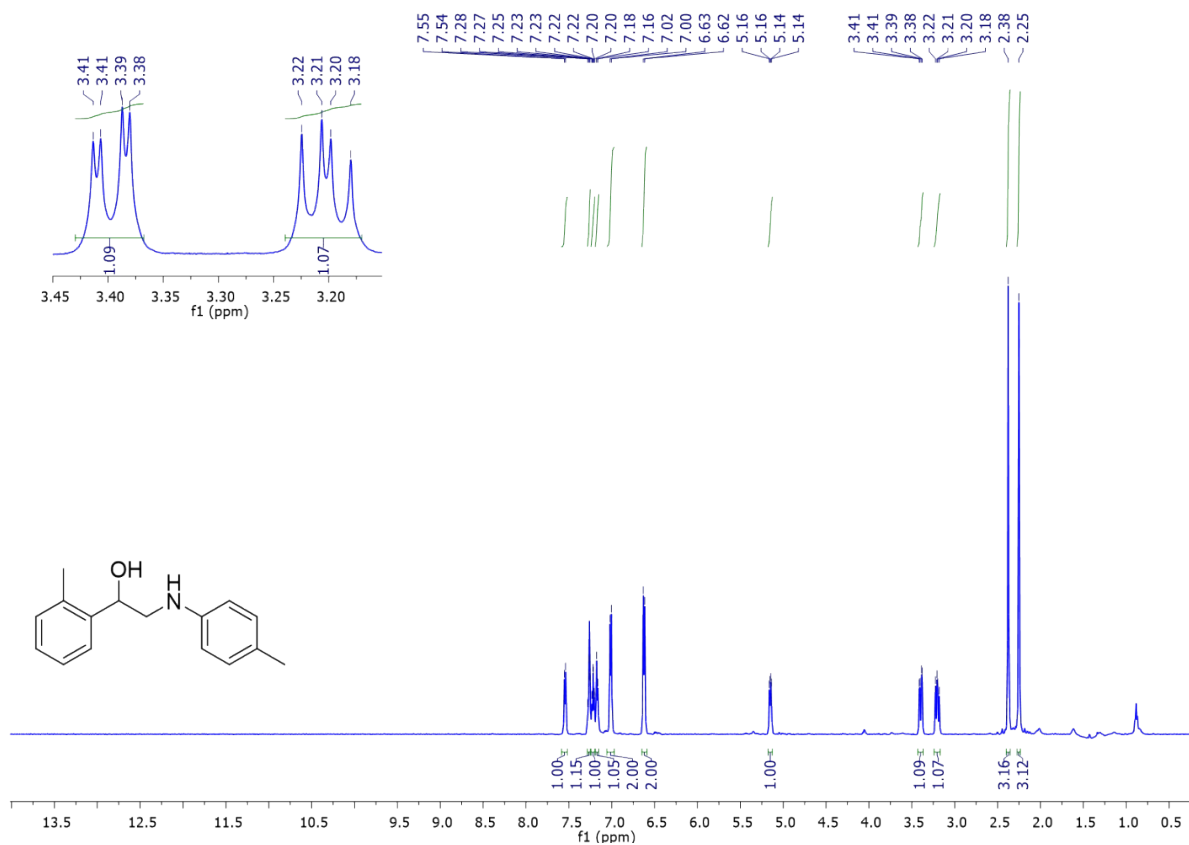


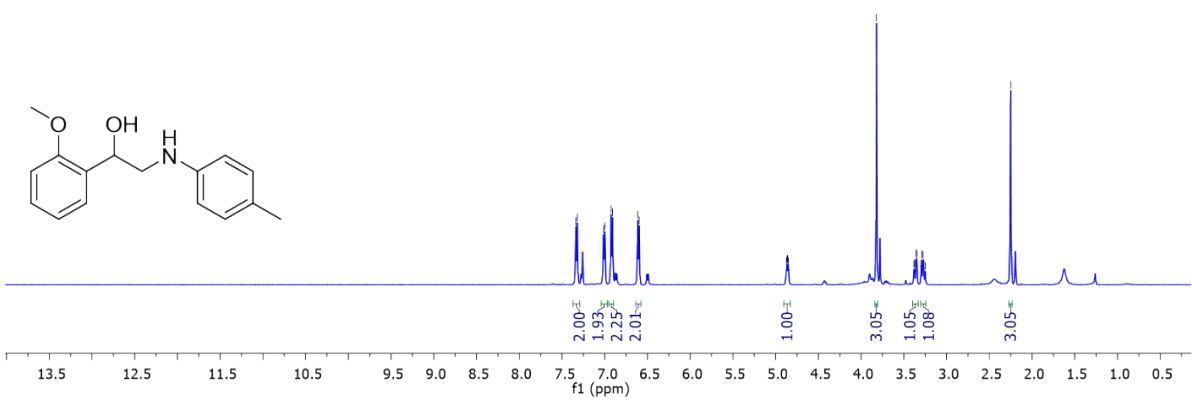
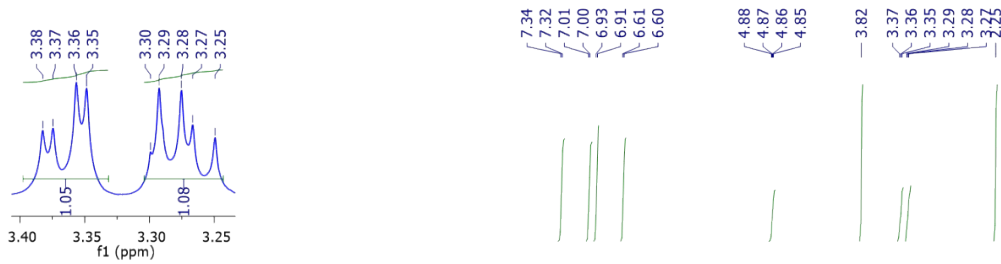
500 MHz  $^1\text{H}$ -NMR spectra of 2ac in  $\text{CDCl}_3$



126 MHz  $^{13}\text{C}$ -NMR spectra of 2ac in  $\text{CDCl}_3$

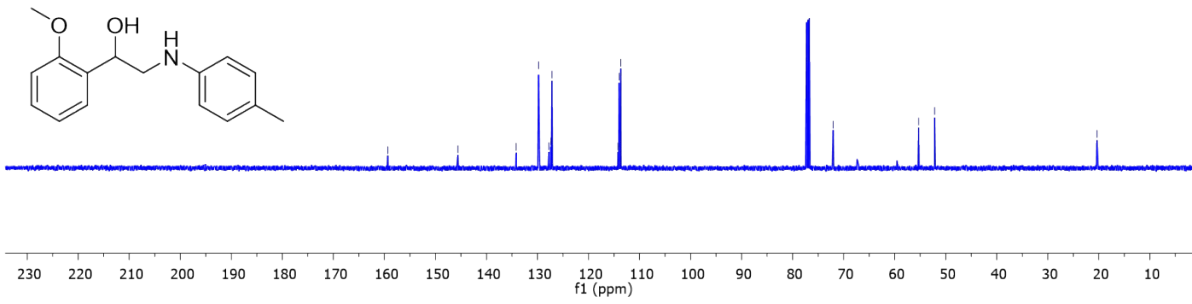




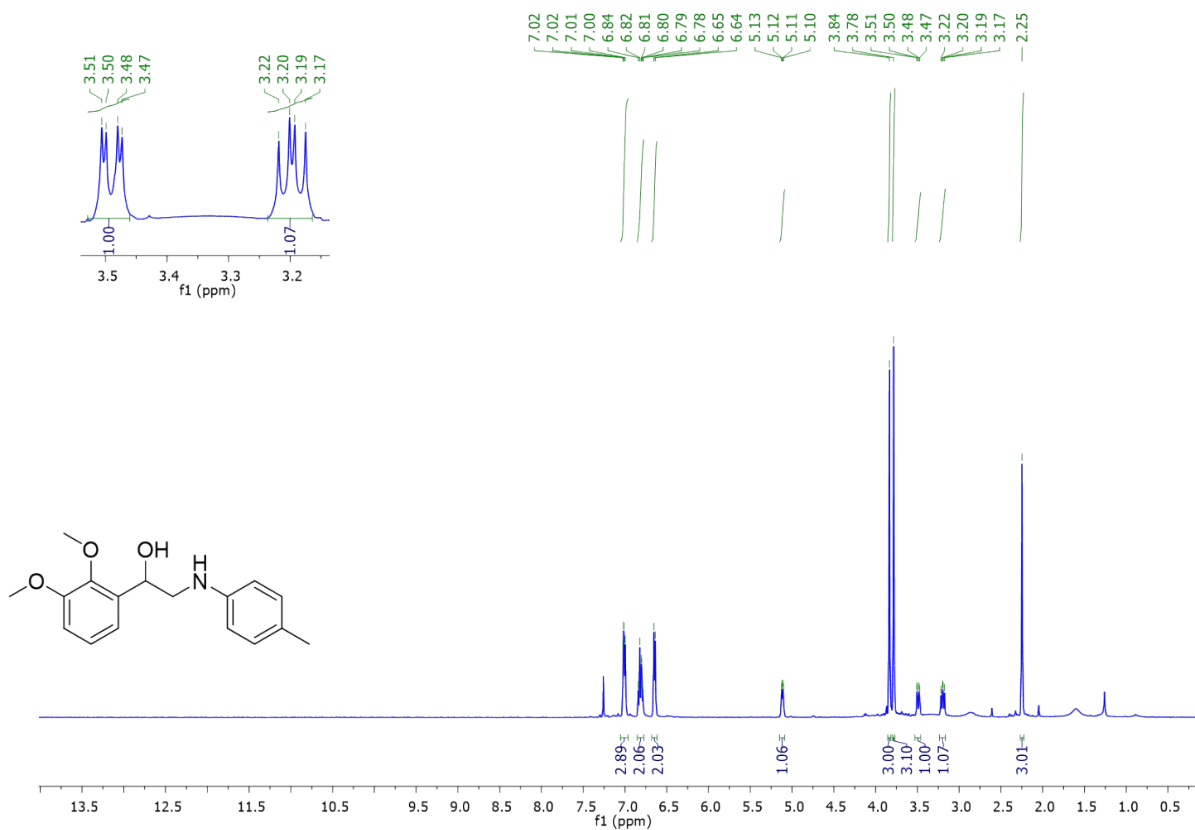


500 MHz <sup>1</sup>H-NMR spectra of 2af in CDCl<sub>3</sub>

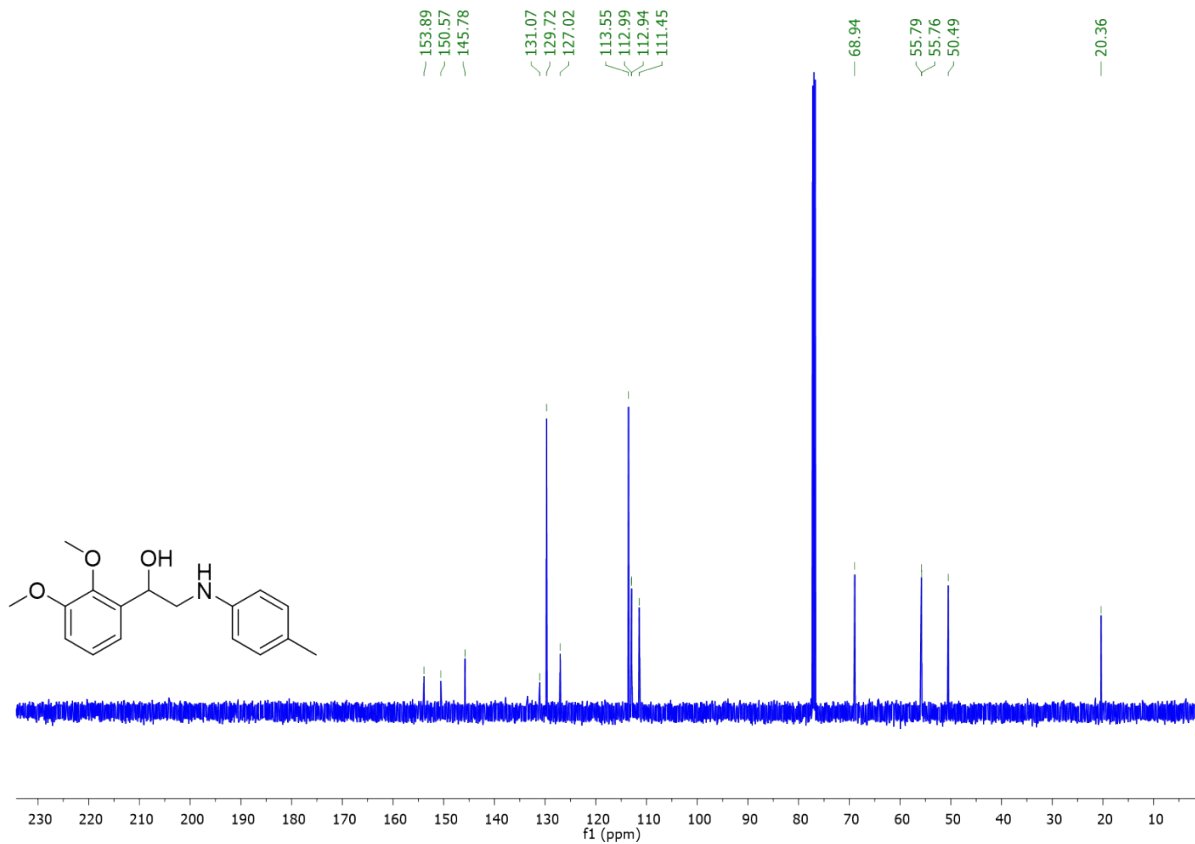
- 159.35
- 145.60
- 134.18
- 129.79
- 127.76
- 127.37
- 127.16
- 114.20
- 114.00
- 113.67
- 72.06
- 55.31
- 52.18
- 20.38



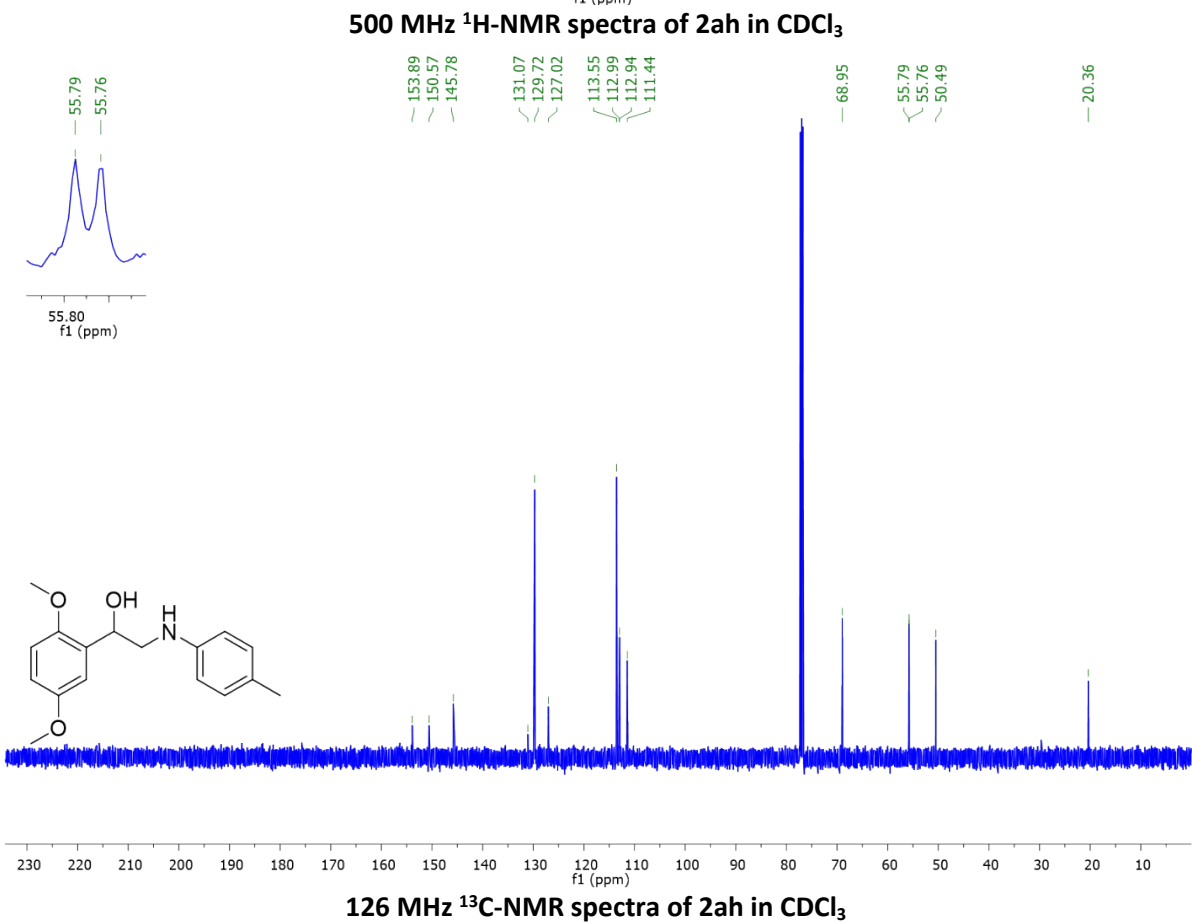
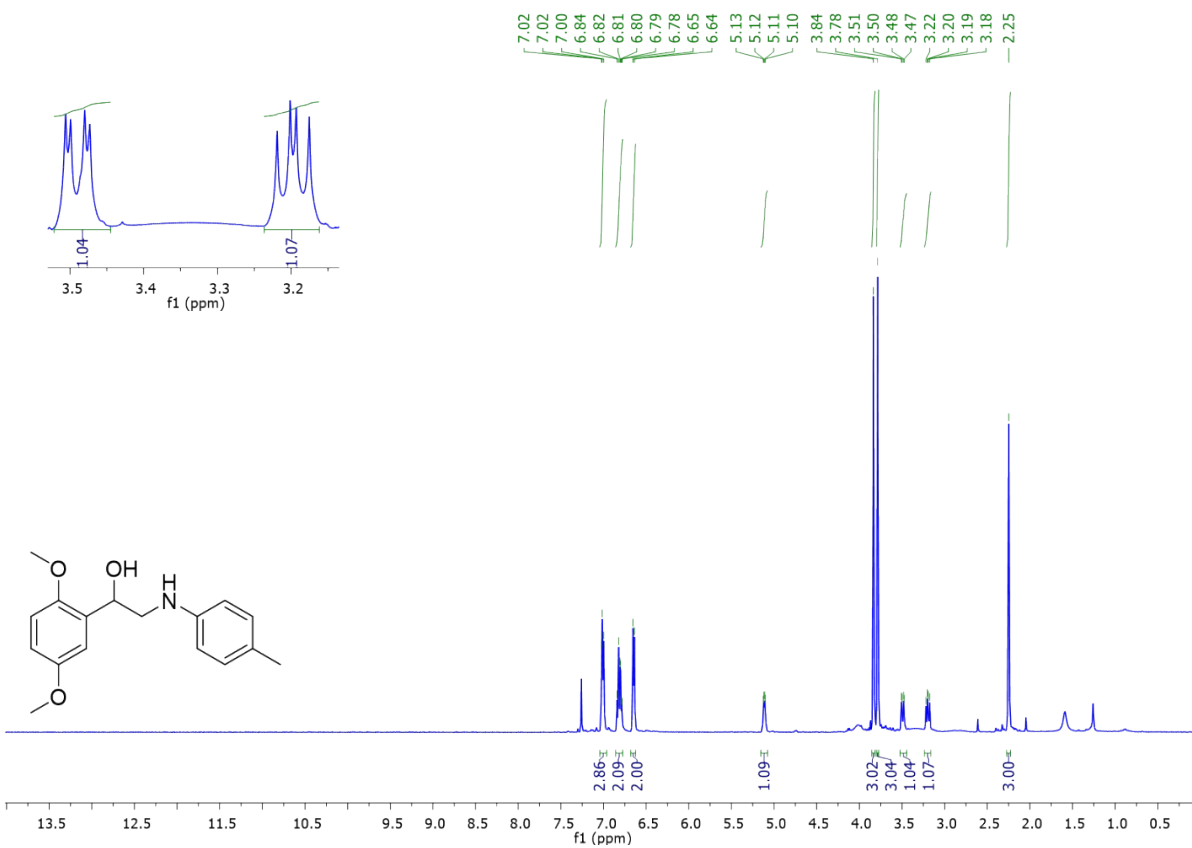
126 MHz <sup>13</sup>C-NMR spectra of 2af in CDCl<sub>3</sub>

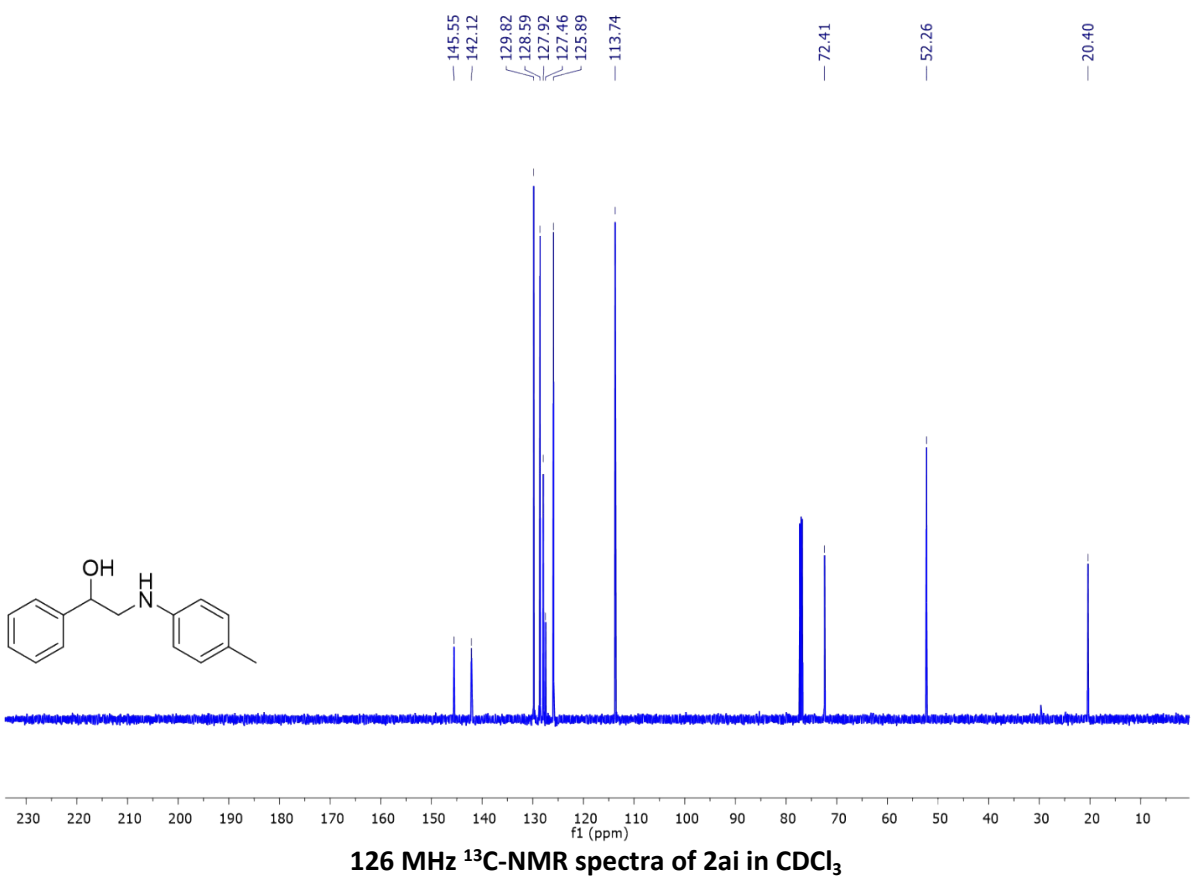
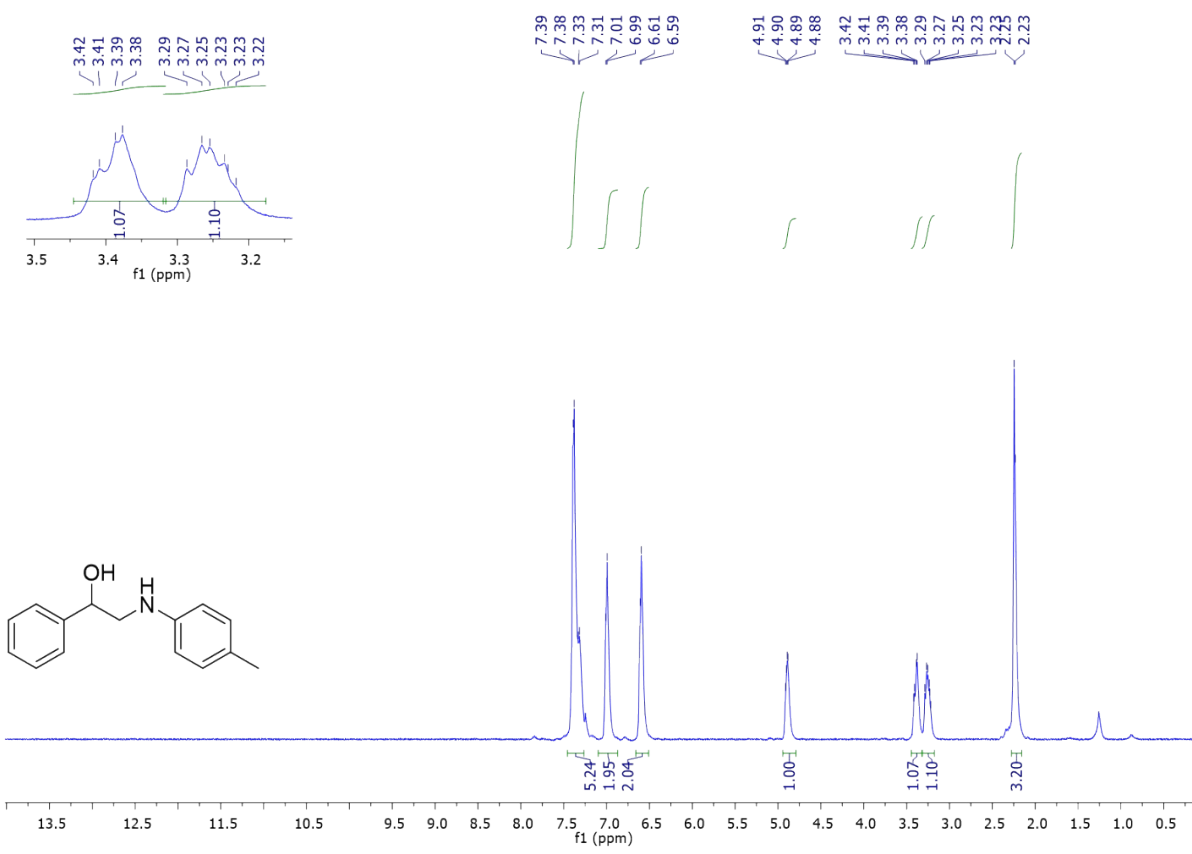


500 MHz  $^1\text{H-NMR}$  spectra of 2ag in  $\text{CDCl}_3$

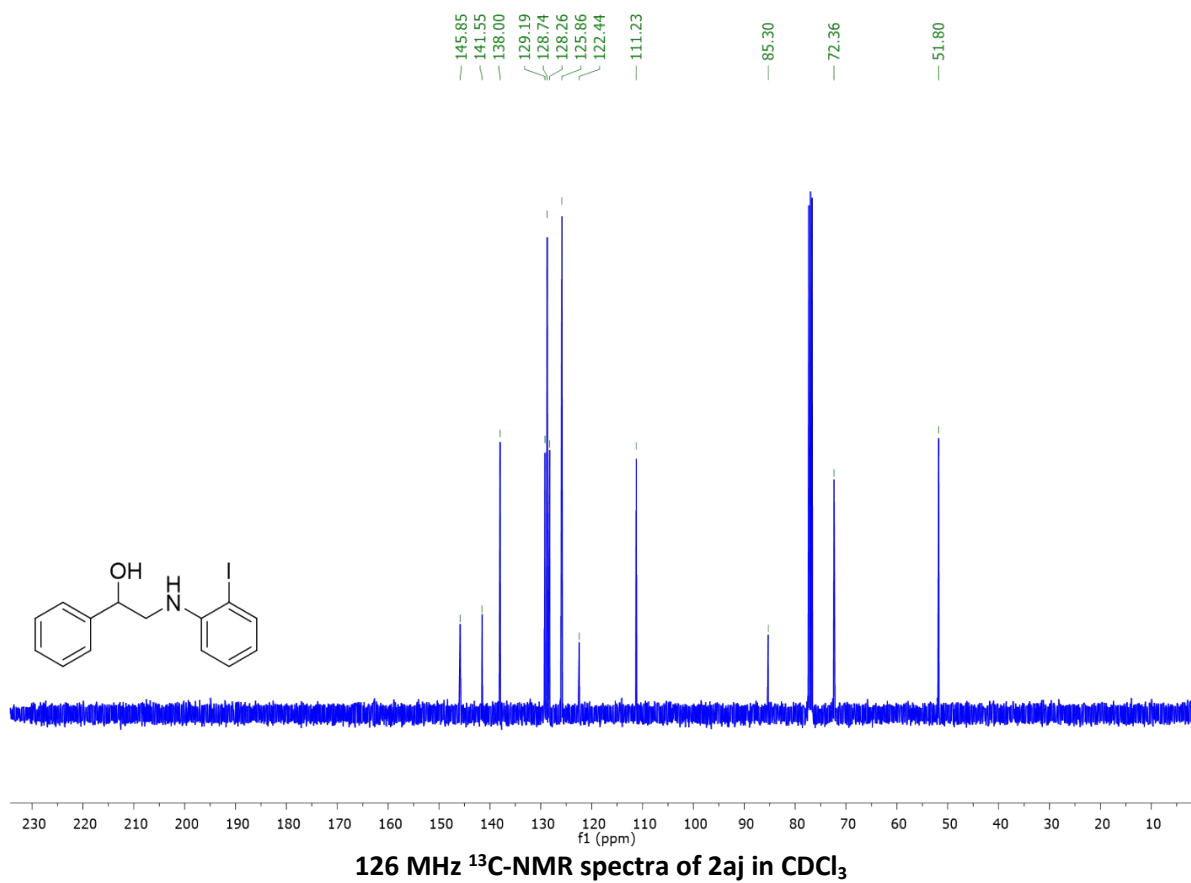
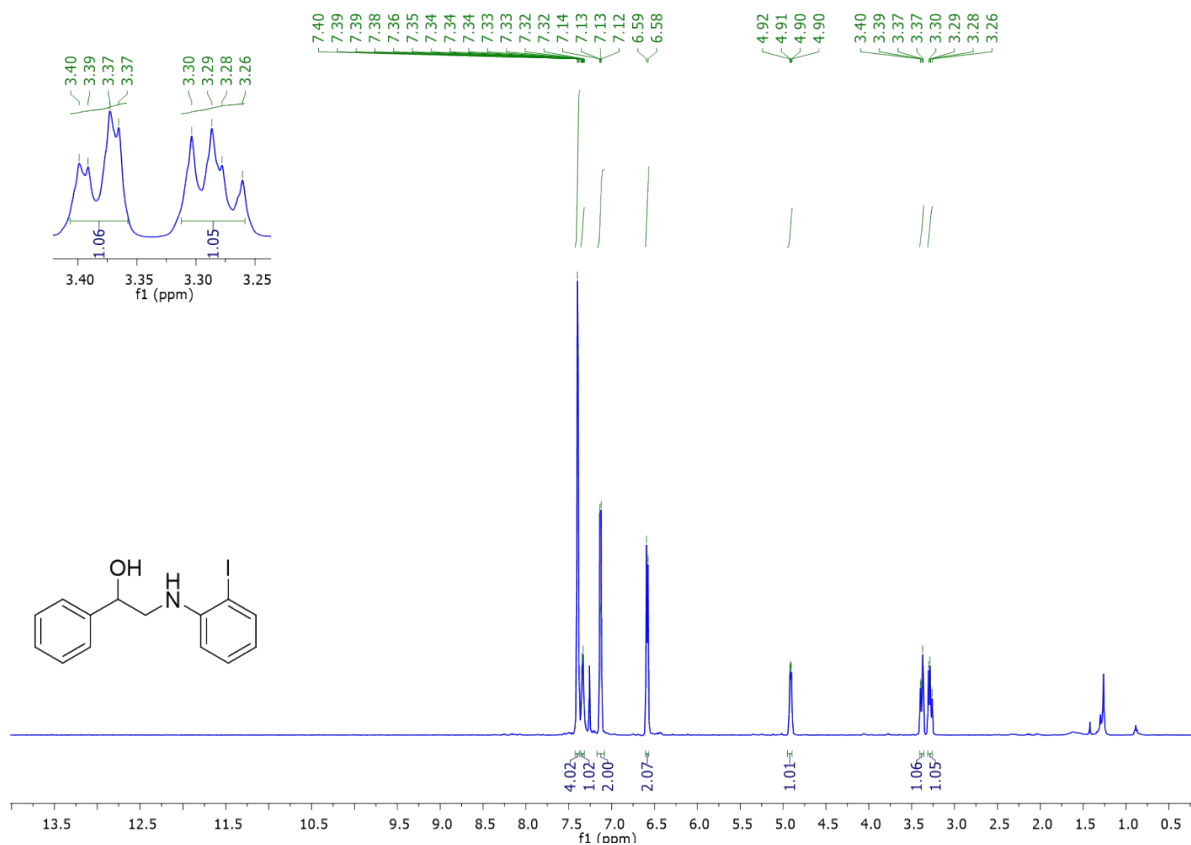


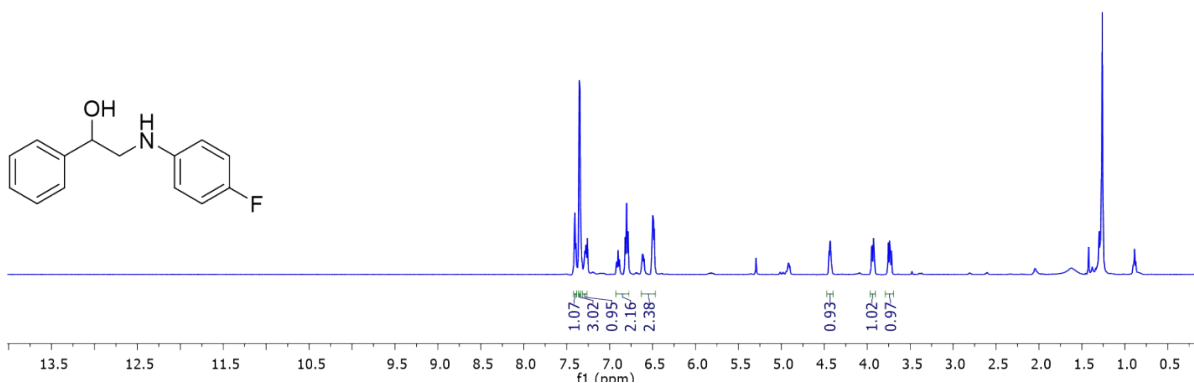
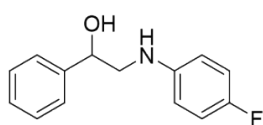
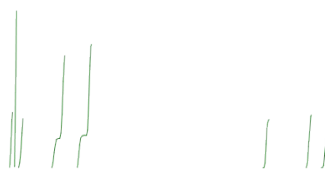
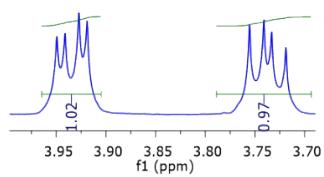
126 MHz  $^{13}\text{C-NMR}$  spectra of 2ag in  $\text{CDCl}_3$



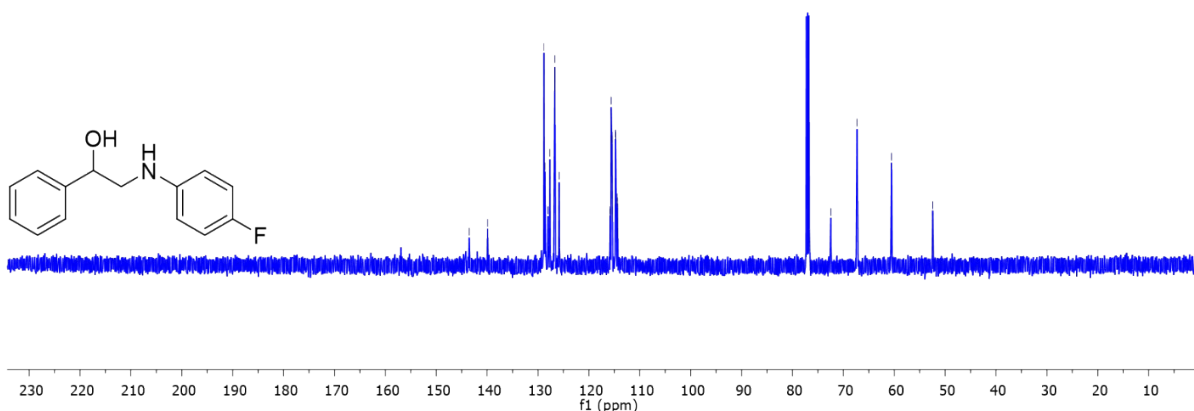
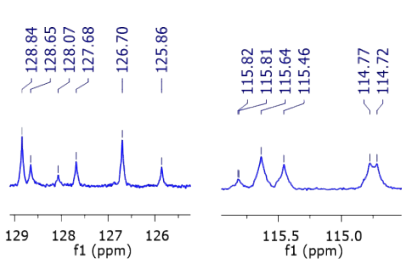




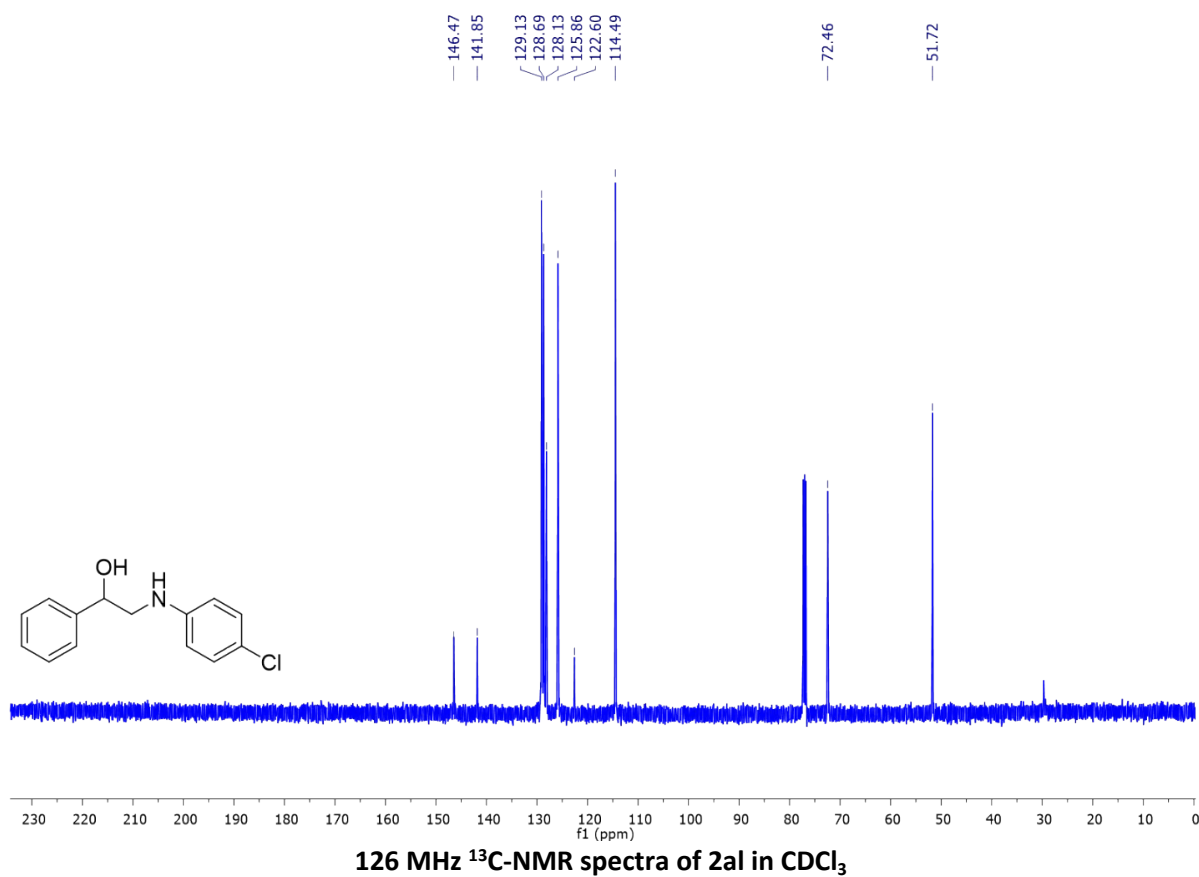
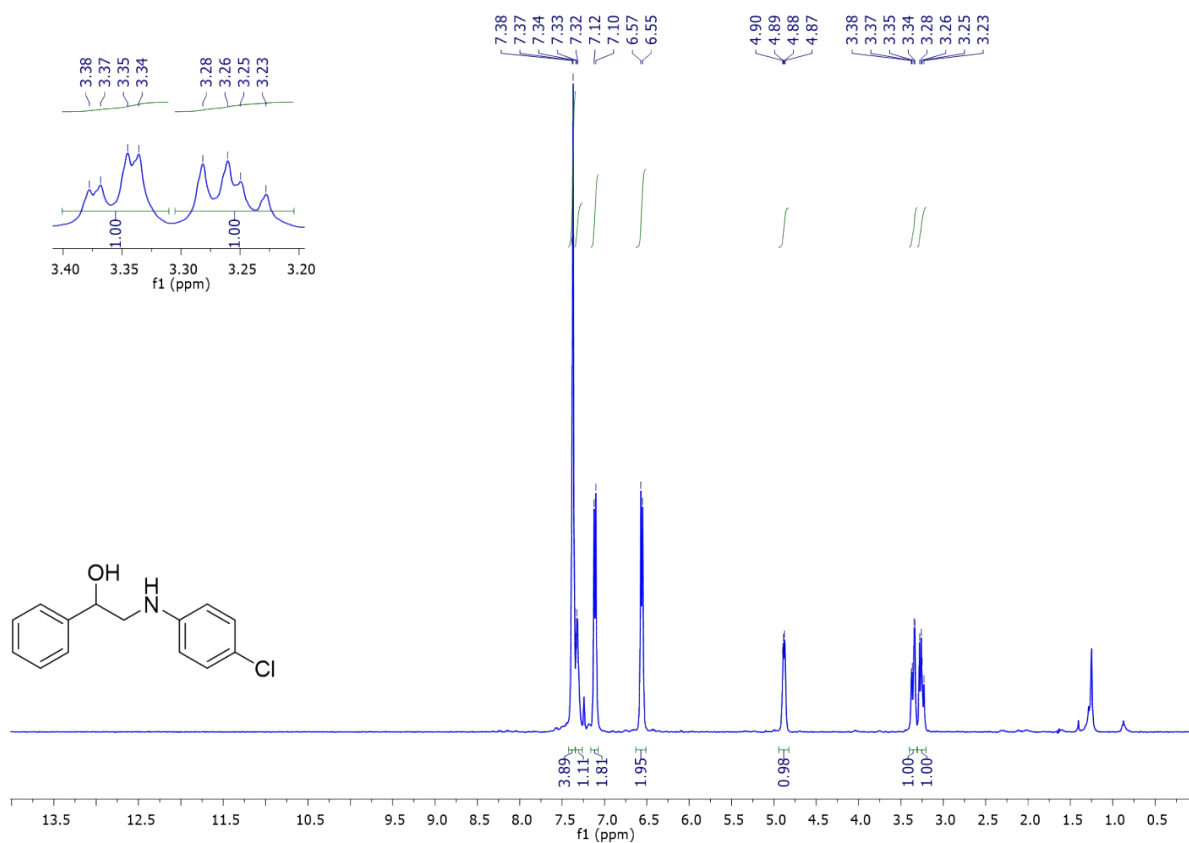


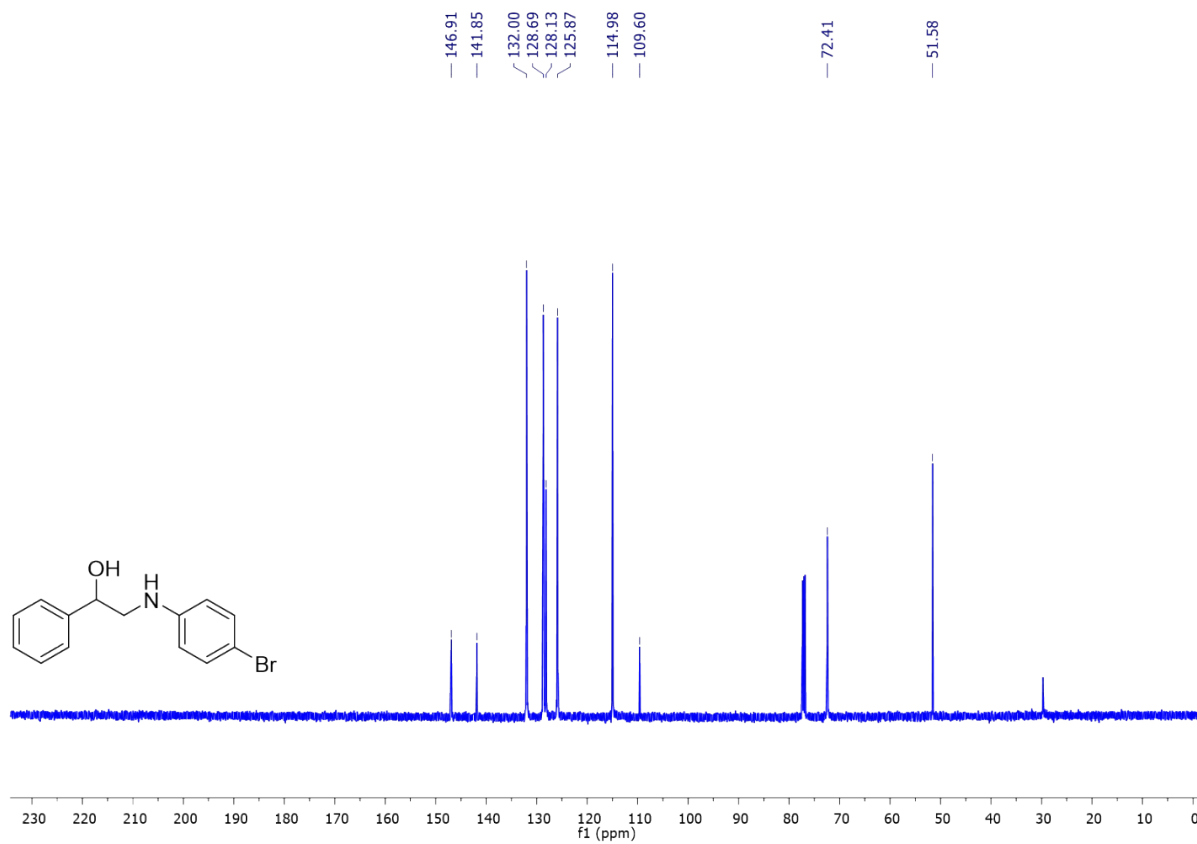
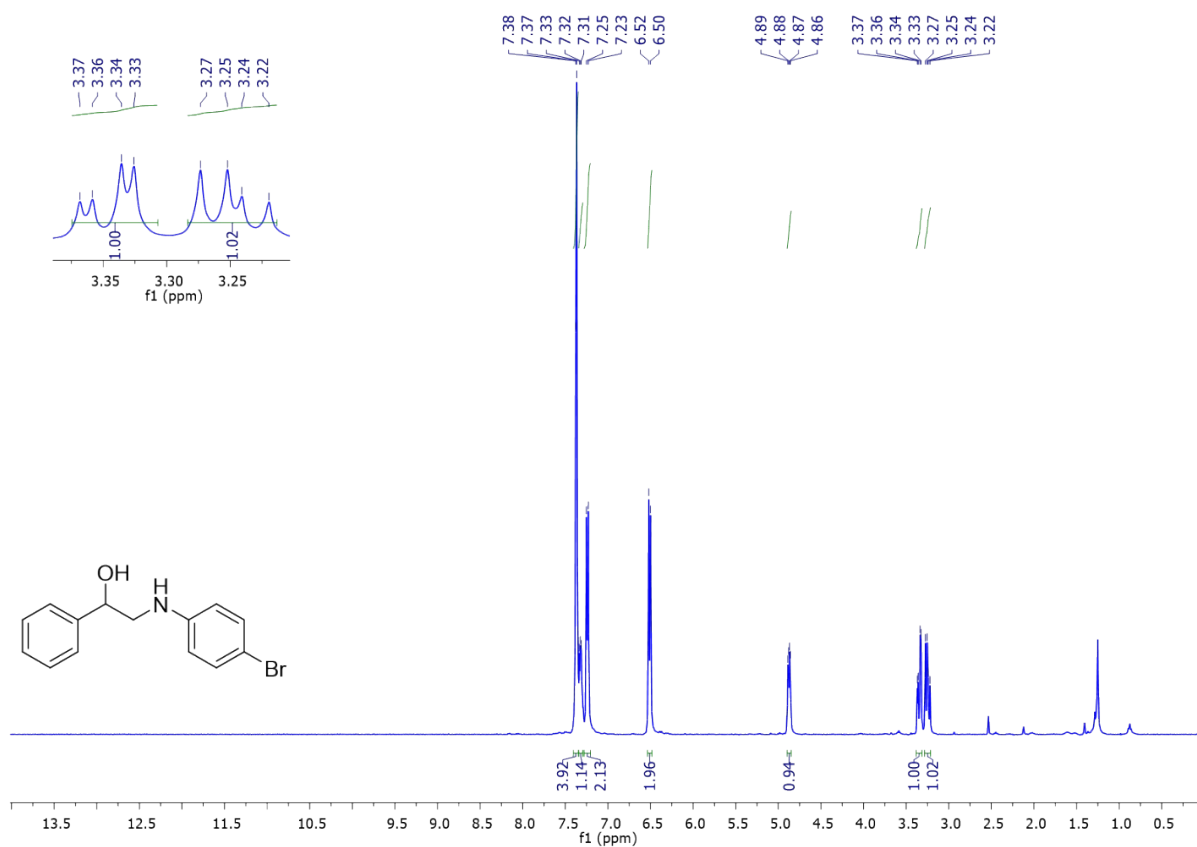


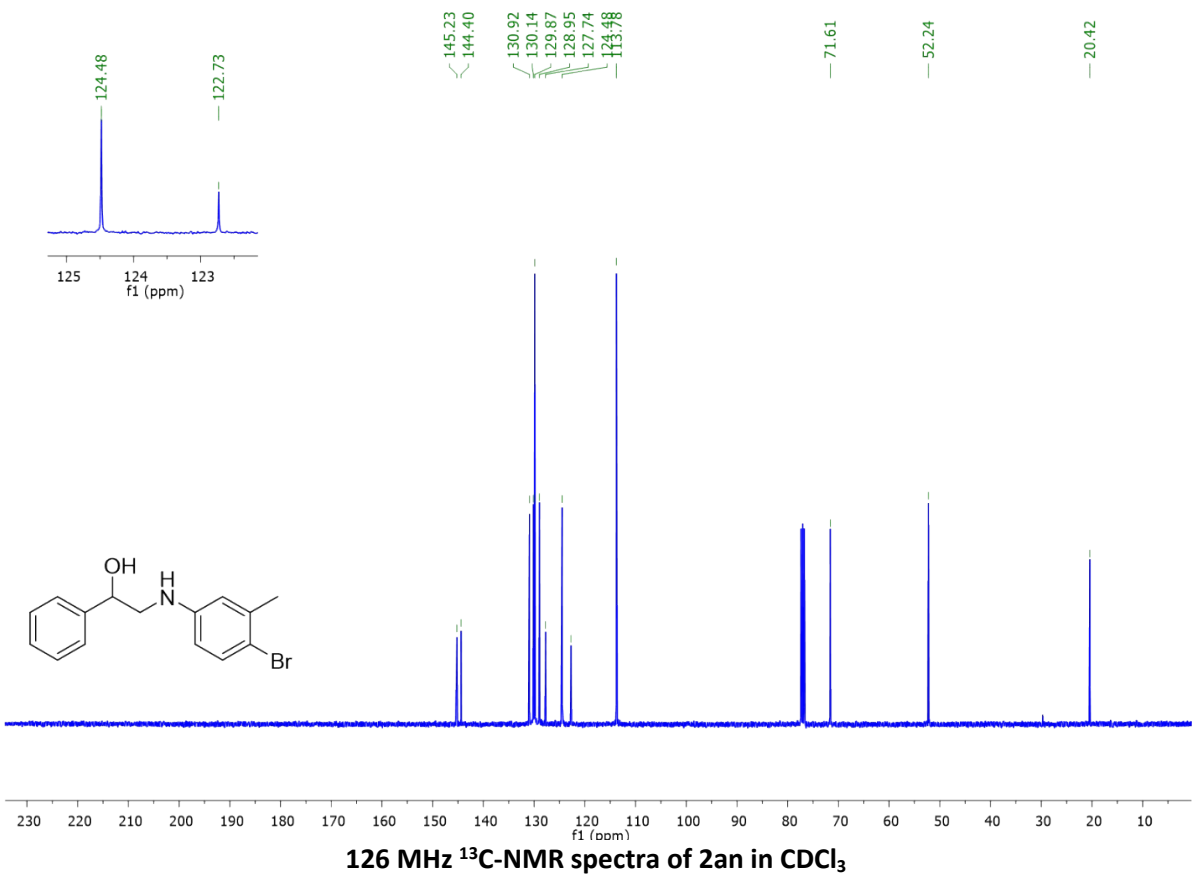
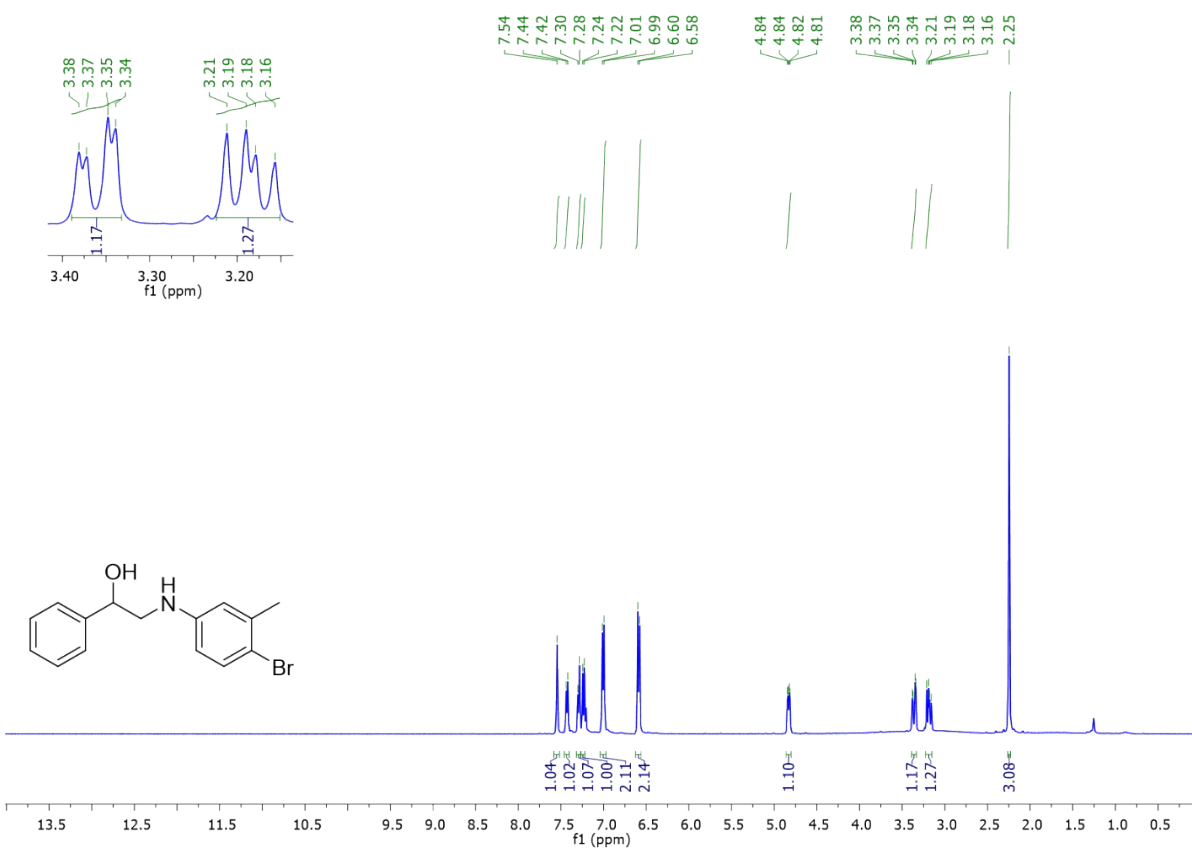
500 MHz  $^1\text{H}$ -NMR spectra of 2ak in  $\text{CDCl}_3$

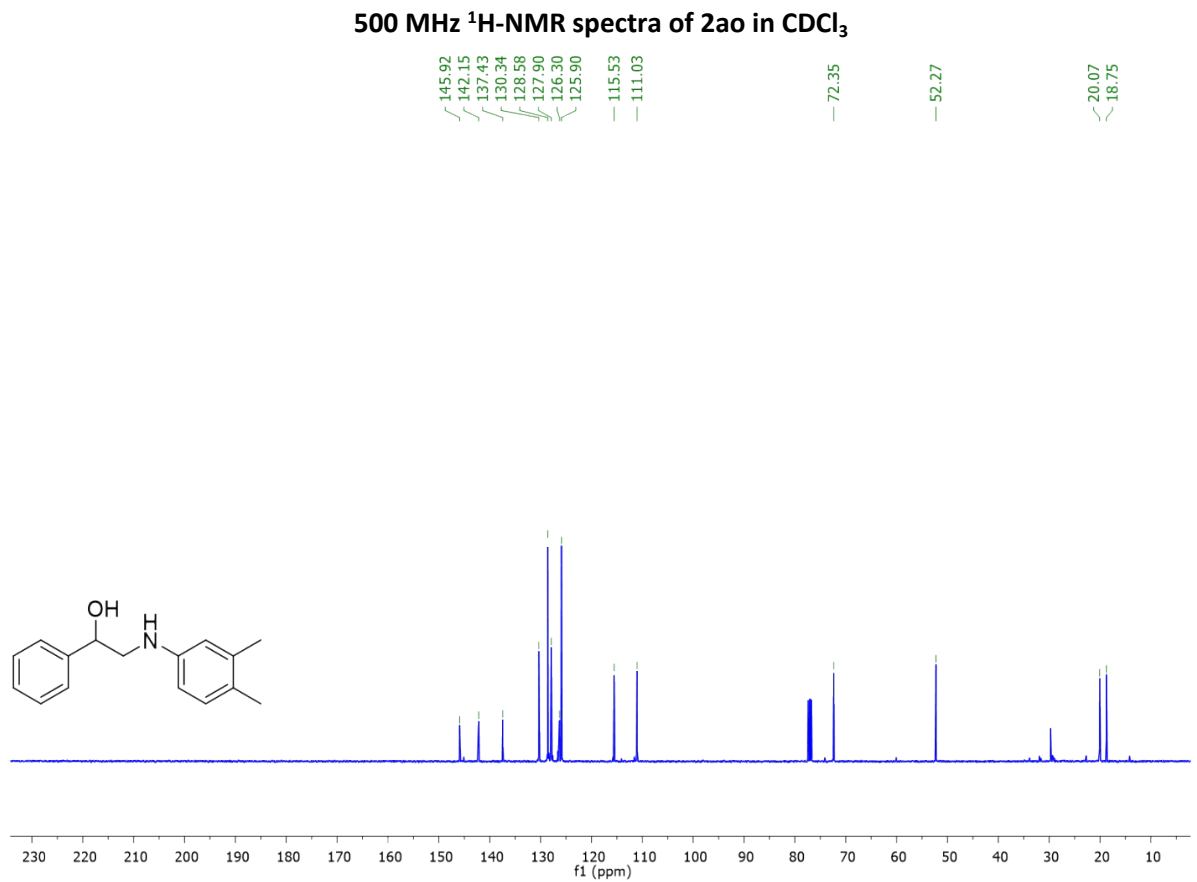
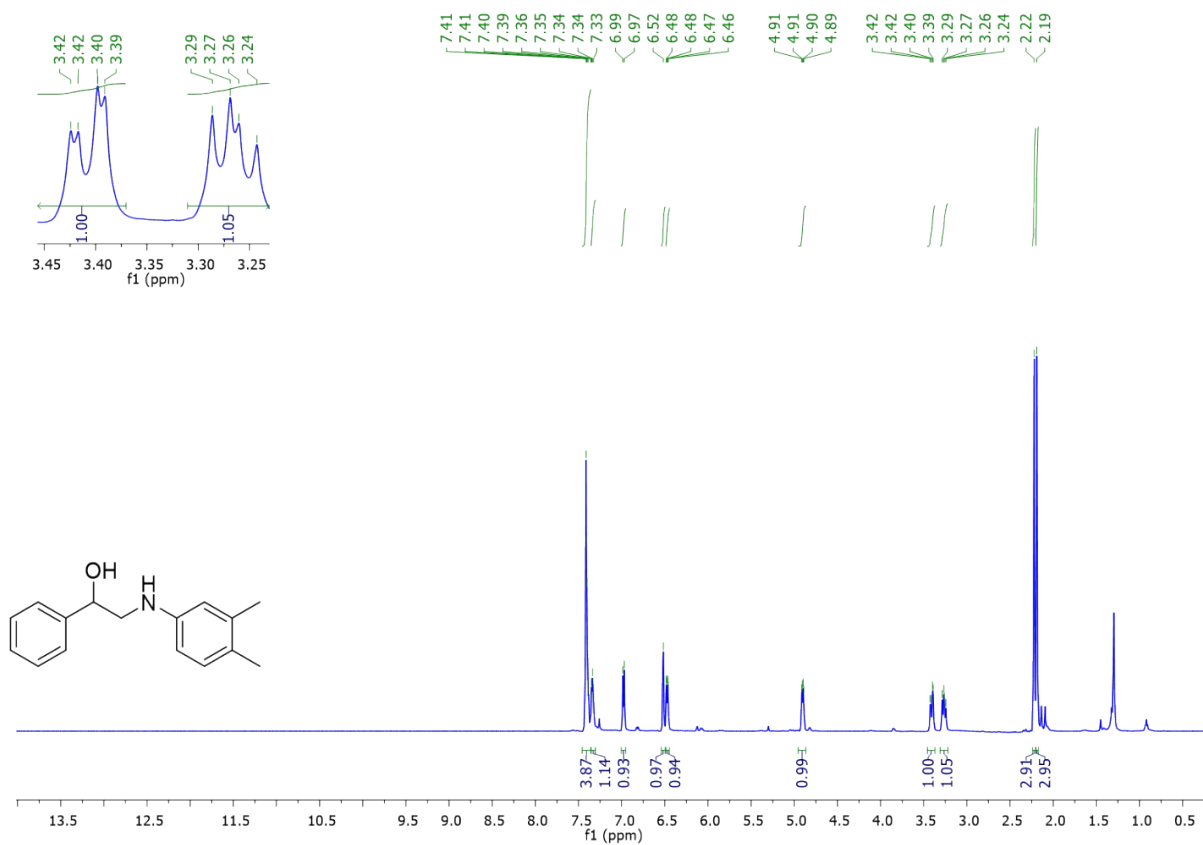


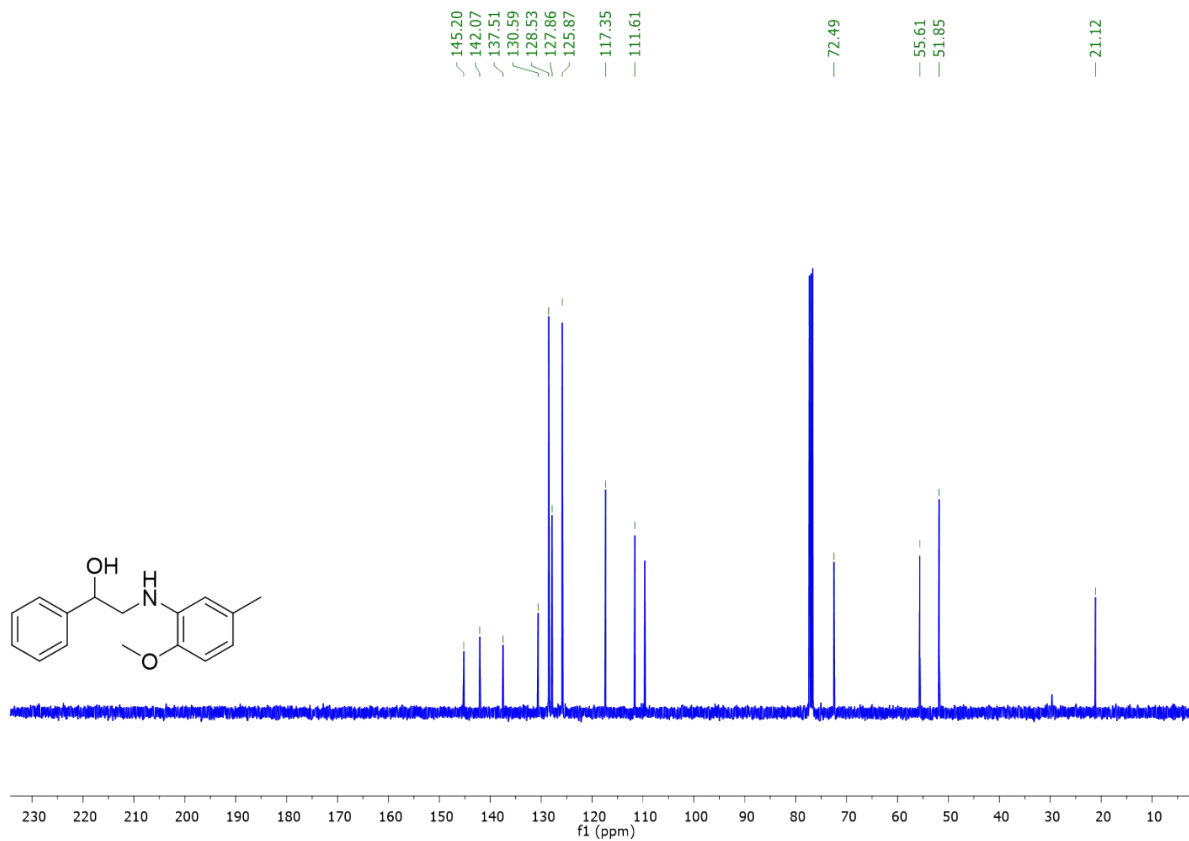
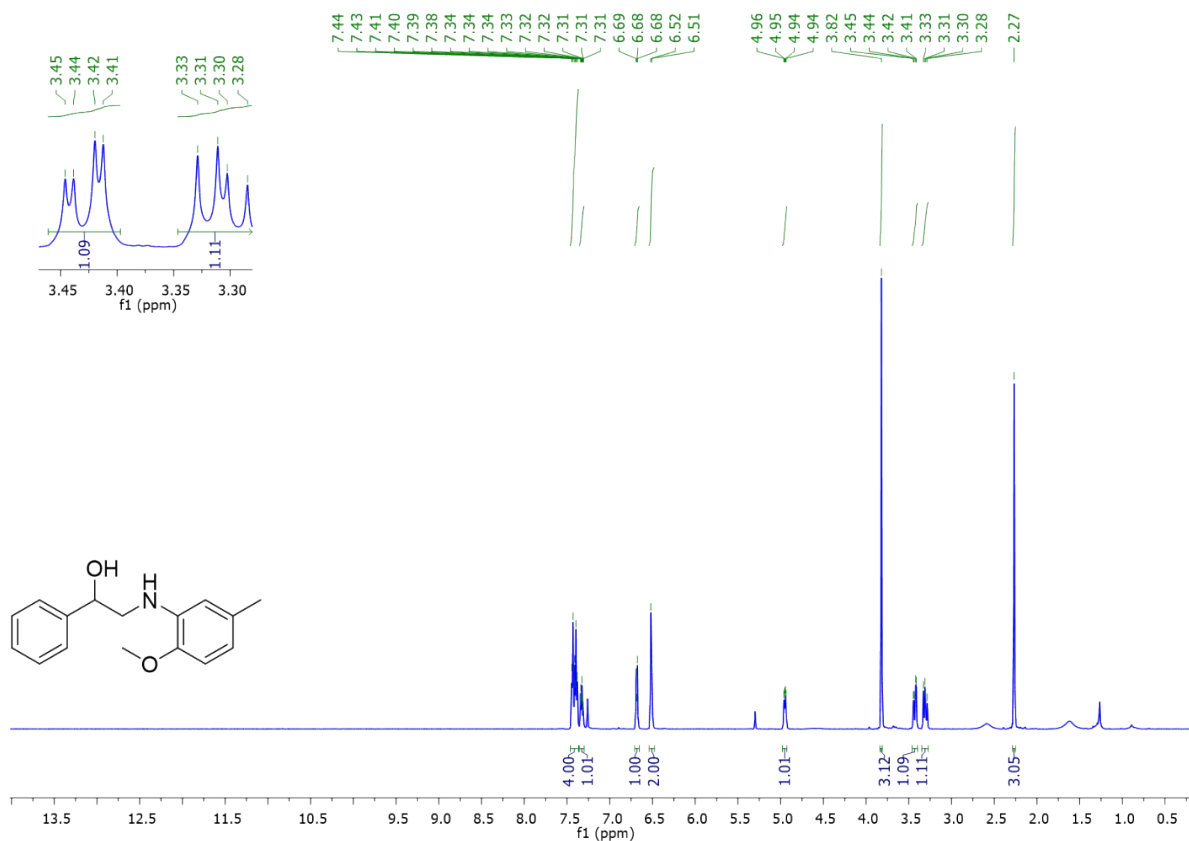
126 MHz  $^{13}\text{C}$ -NMR spectra of 2ak in  $\text{CDCl}_3$











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