Urushiol Derivatives as Biomass-Based Photocatalysts for Transition-Metal-Free Synthesis of 1,2-Amino Alcohols

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1. General methods

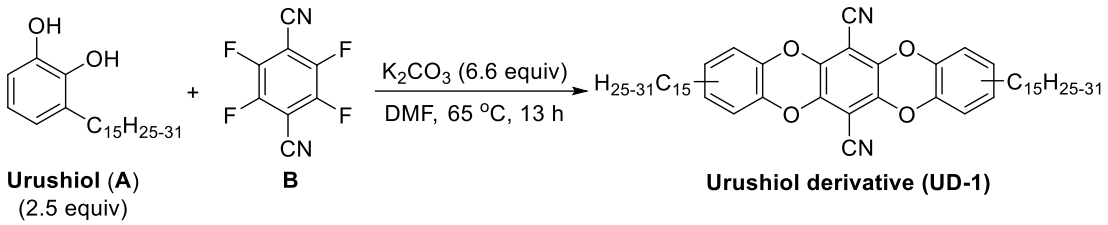
Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry nitrogen atmosphere. All solvents were purified and dried according to standard methods prior to use.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker instrument (400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). HRMS were obtained on FTICRMS bruker 15T LC-MS (ESI) mass spectrometer with the use of quadrupole analyzer. Fourier Transform Infrared spectra were recorded on a Nicolet IS50 FT-IR spectrophotometer.

Substrates **1** were synthesized according to the literature procedures.[1] Substrates **2** were purchased from Energy-chemical, solvents were purchased from Aladdin, and used without further purification.

2. Synthesis and characterization of UD-1

Synthesis of UD-1[2]



A 100-mL one-neck round bottom flask was charged with tetrafluorophthalonitrile (1.50 g, 7.50 mmol), urushiol (5.89 g, 18.75 mmol), and potassium carbonate (6.80 g, 49.50 mmol) in anhydrous DMF (60 mL) under N_2 atmosphere. The reaction mixture was stirred at 65 °C for 13 h (monitored by TLC) and cooled to room temperature. Afterwards, water was added to dissolve the salts. Then, the reaction mixture was repeatedly extracted with DCM, and the organic phase was concentrated and dried under vacuum to give **UD-1** as a brown solid (5.90 g).

NMR spectra of UD-1

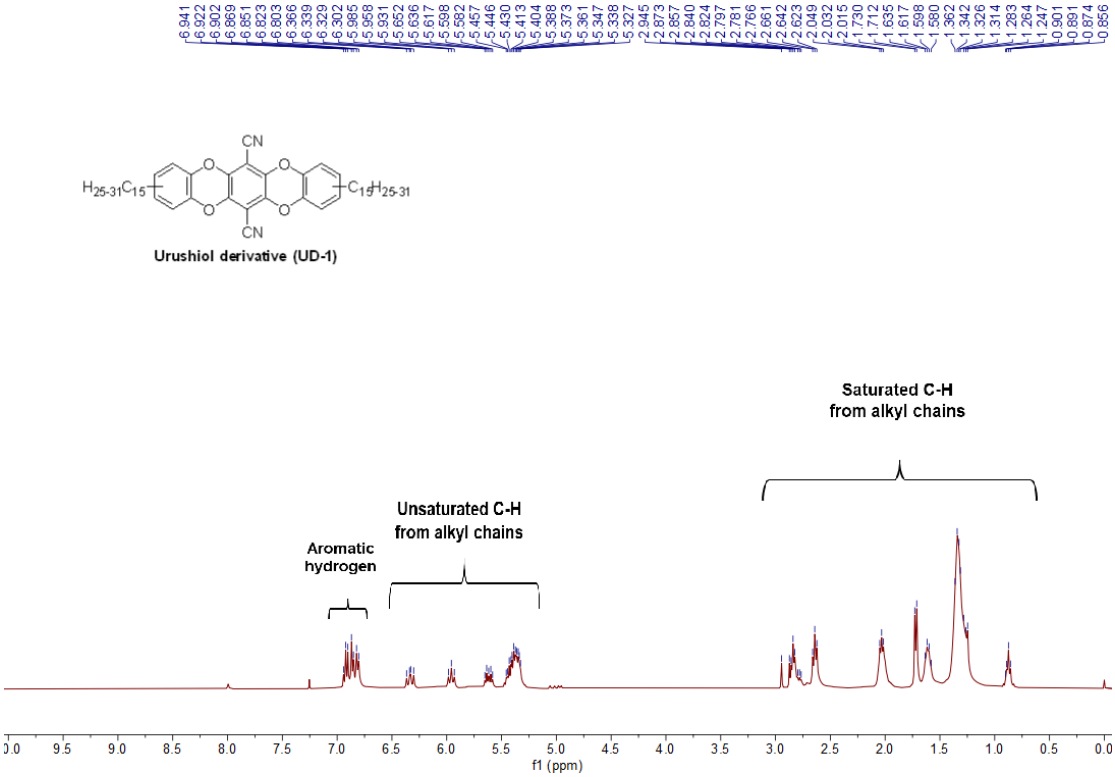


Figure S1. ^{1}H NMR spectrum of **UD-1**.

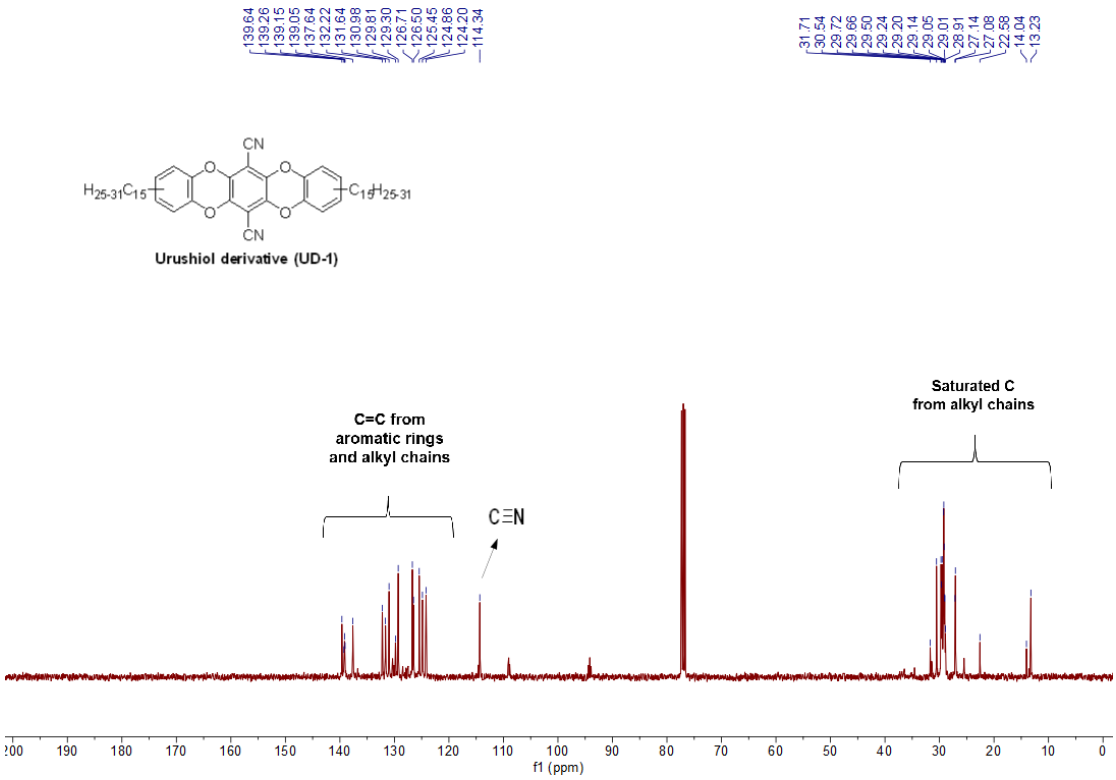
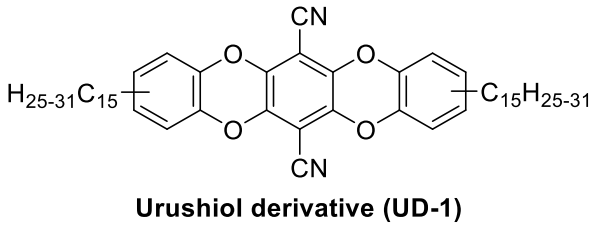


Figure S2. ^{13}C NMR spectrum of **UD-1**.



UD-1[3], brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94-6.80 (m), 6.37-6.30 (m), 5.96 (t), 5.65-5.58 (m), 5.46-5.33 (m), 2.95 (s), 2.87-2.77 (m), 2.64 (t), 2.03 (t), 1.72 (d), 1.64-1.58 (m), 1.36-1.25 (m), 0.90-0.86 (m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 139.3, 139.2, 139.1, 137.6, 132.2, 131.6, 131.0, 129.8, 129.3, 126.7, 126.5, 125.5, 124.9, 124.2, 114.3, 31.7, 30.5, 29.7, 29.7, 29.5, 29.2, 29.2, 29.1, 29.1, 29.0, 28.9, 27.1, 27.1, 22.6, 14.0, 13.0.

UV/Vis absorption spectrum of UD-1

UV/vis absorption spectrum of **UD-1** (0.01 mM in THF) was recorded in 1 cm path quartz cuvettes using Pgeneral TU-1901 UV/Vis spectrometer.

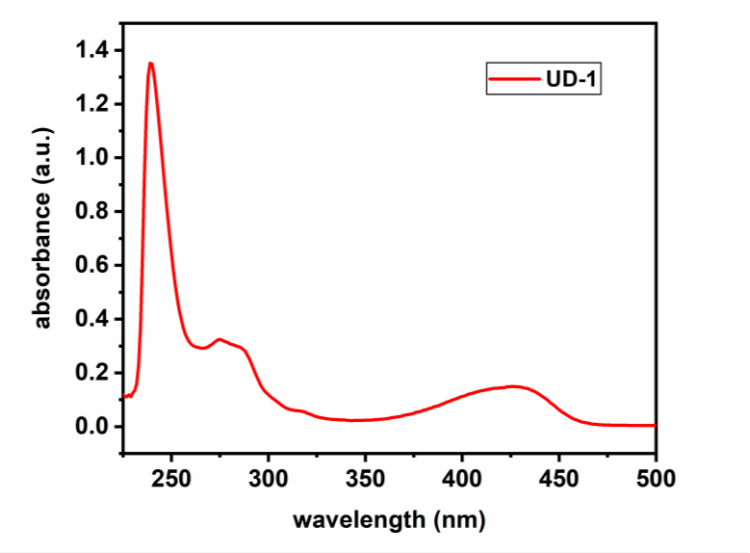


Figure S3. UV/vis absorption spectrum of **UD-1** in THF.

Emission spectrum of UD-1

Fluorescence spectrum was recorded on a Edinburgh Instruments FS5 Spectrofluorometer in a 1 cm quartz cuvette. The sample **UD-1** was prepared as a 0.01 mM solution in THF and used freshly for the measurement.

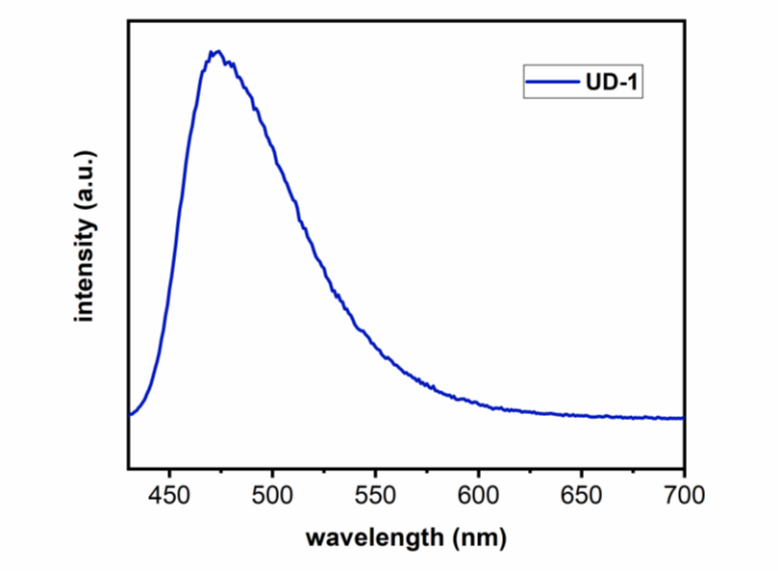


Figure S4. Emission spectrum of **UD-1** in THF.

Fluorescence decay curve of UD-1

Estimating lifetime of excited state of **UD-1** was based on the ultrafast transient absorption spectroscopic techniques. The luminescence decays were measured on an Edinburgh Instruments FLSP920 (EI) spectrometer. The sample compartment was home-built and designed as 10x10 mm cuvettes in 90° geometry between excitation and detection. The solution of **UD-1** in THF (0.01 mM) was excited at 426 nm. All decay traces were fitted by iterative reconvolution with an experimental instrument response function recorded directly after decay acquisition.

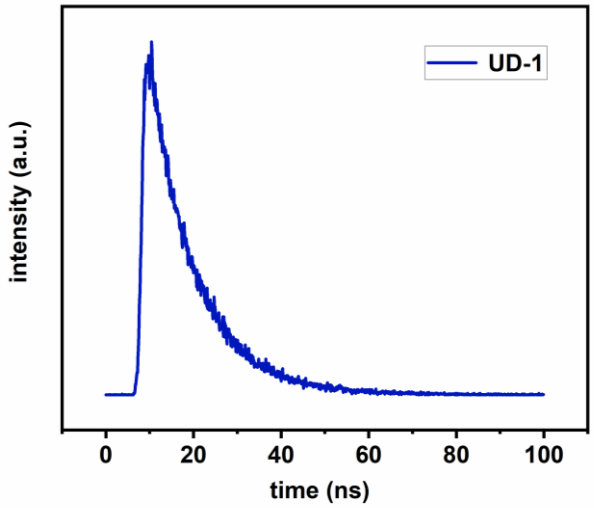


Figure S5. Fluorescence decay curve of **UD-1** in THF.

UV/Vis absorption and emission spectra of UD-1

The zero-zero vibrational state excitation energy $E_{0,0}$ was estimated by the corresponding energy of the wavelength at which emission and absorption overlap. This wavelength was determined setting the intensity of emission λ_{max} to the absorbance of **UD-1** at excitation wavelength (426 nm).

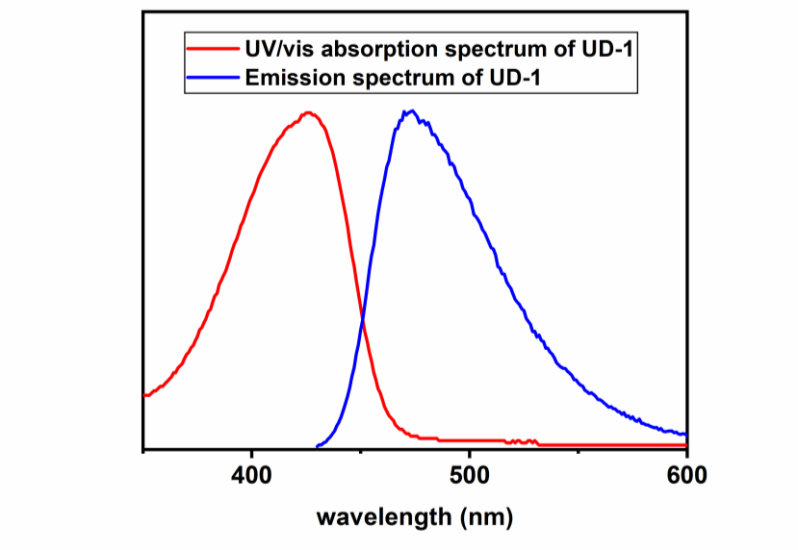


Figure S6. UV/Vis absorption and emission spectra of **UD-1** in THF (0.01 mM). Cross point λ: 451 nm. $E_{0\text{-}0}$: 2.75 V.

Cyclic voltammograms of UD-1

Voltammetric experiments were conducted with a computer-controlled Shanghai Chen Hua CHI660E containing glassy carbon electrode serving as the working electrode, saturated calomel reference electrode, Pt wire auxiliary electrode.

All solutions used for the voltammetric experiments were deoxygenated by purging with high purity nitrogen gas and measurements were performed in a electrolytic cell at room temperature. The supporting electrolyte, tetrabutylammonium hexafluorophosphate ($^{n}Bu_4NPF_6$), was purchased from commercial suppliers Energy-chemical.

Excited state oxidation and reduction potentials were calculated by the following approximating formulas: $E_{1/2}(PC^{*}/PC^{\bullet-}) = E_{1/2}(PC/PC^{\bullet-}) + E_{0,0}$ and $E_{1/2}(PC^{\bullet+}/PC^{*}) = E_{1/2}(PC^{\bullet+}/PC) - E_{0,0}$.

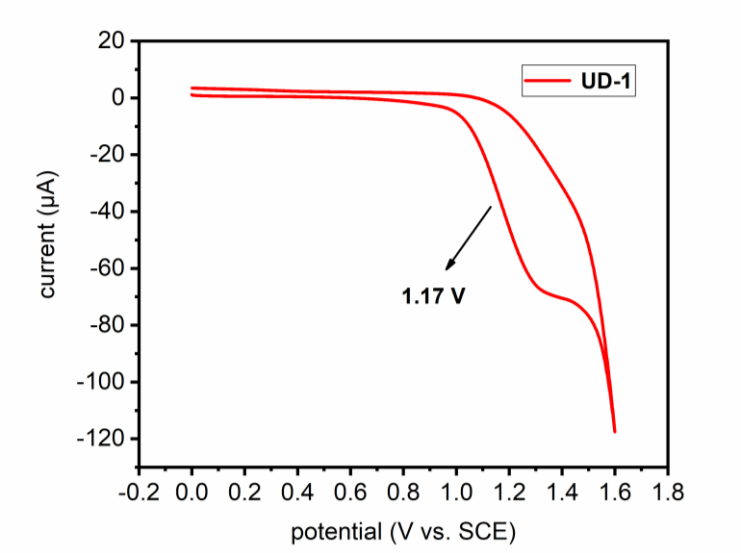


Figure S7. Cyclic voltammogram of **UD-1** in DMSO (1.0 mM) containing 0.1 M $^{n}Bu_4NPF_6$.

Scan rate: 0.1 V/s. $E_{1/2}(PC^{\bullet+}/PC)$ = +1.17 V, $E_{1/2}(PC^{\bullet+}/PC^{*})$ = -1.58 V

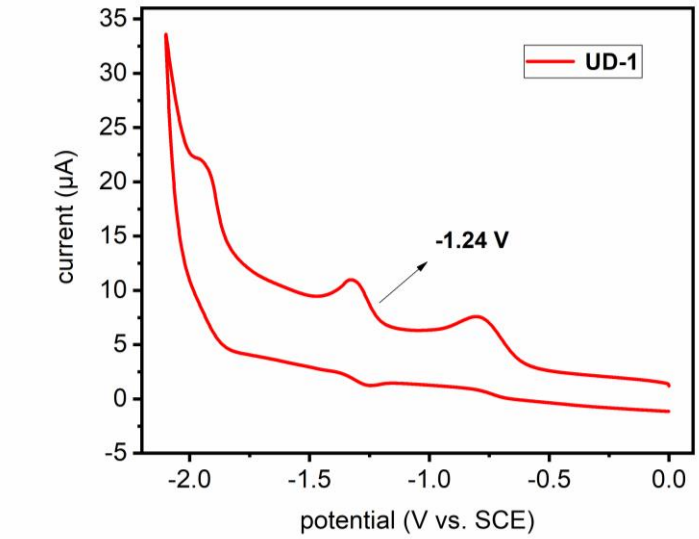


Figure S8. Cyclic voltammogram of **UD-1** in DMSO (1.0 mM) containing 0.1 M $^{n}Bu_4NPF_6$.

Scan rate: 0.1 V/s. $E_{1/2}(PC/PC^{\bullet-})$ = -1.24 V, $E_{1/2}(PC^{*}/PC^{\bullet-})$ = +1.51 V.

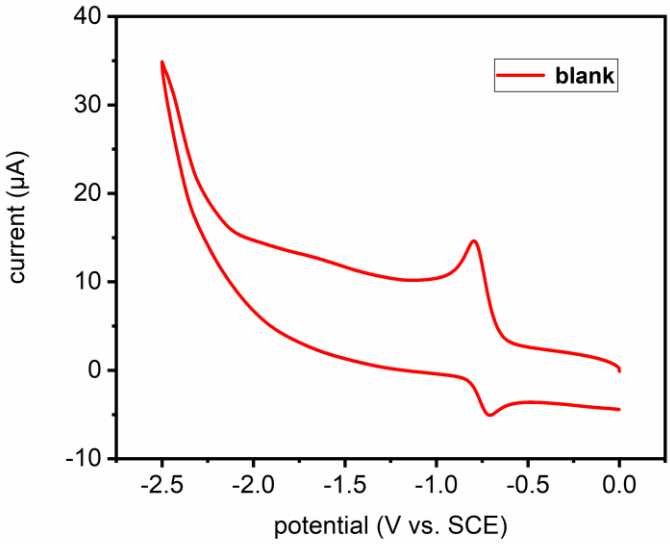
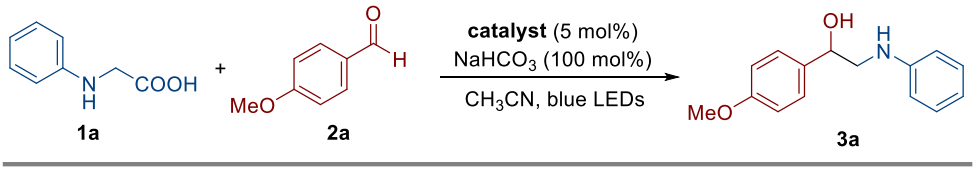
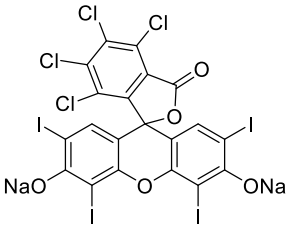


Figure S9. Cyclic voltammogram of DMSO containing 0.1 M $^{n}Bu_4NPF_6$. Scan rate: 0.1 V/s.

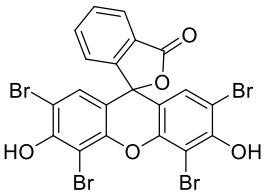
3. Optimization of the reaction conditions

Investigation of commercially available organic photocatalysts[a]

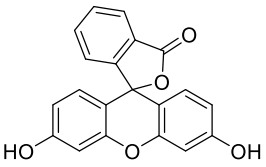




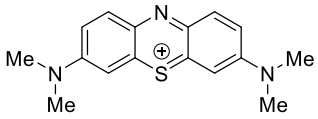
Rose Bengal
0% NMR yield



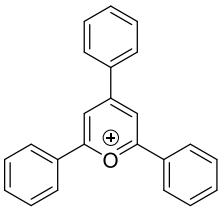
Eosin Y
0% NMR yield



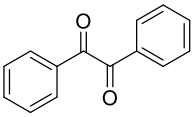
Fluorescein
0% NMR yield



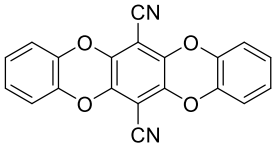
MB^{+}
Methylene Blue
0% NMR yield



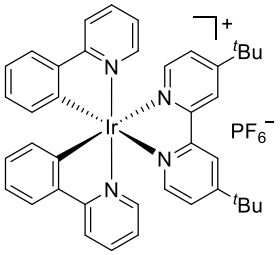
TPT^{+}
0% NMR yield



benzil
0% NMR yield



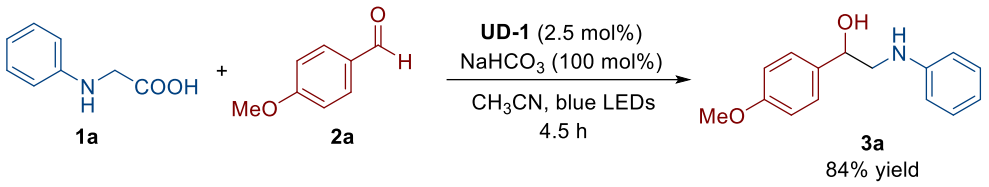
catechol-dervied catalyst (**CD-1**)
84% NMR yield

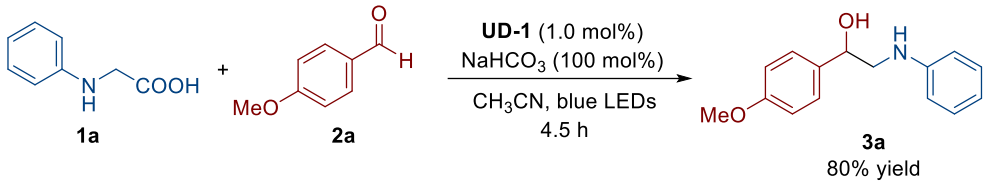


[Ir(ppy)$_2$(dtbbpy)]PF$_6$
92% yield
(Ref. *Green Chem.*, **2020**, *22*, 336)

[a]Reaction conditions: A solution of **catalyst** (5 mol%), **1a** (0.2 mmol), **2a** (0.8 mmol, 4.0 equiv), and $NaHCO_3$ (0.2 mmol) in CH_3CN (c = 0.1 M) was irradiated by 30 W blue LEDs at room temperature under nitrogen gas for 4.5 h.

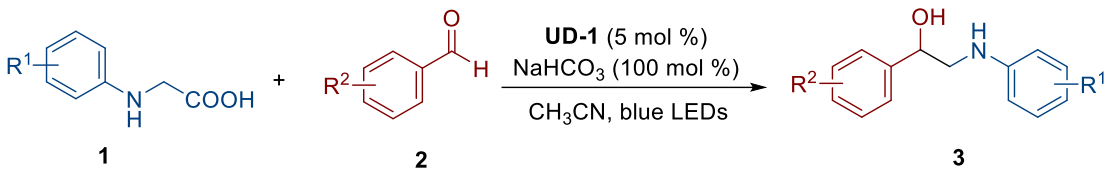
Investigation of decreased catalyst loadings[a]



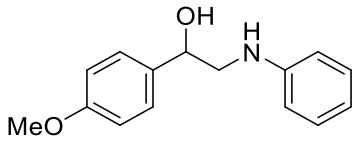


[a]Reaction conditions: A solution of **UD-1** (2.5 or 1.0 mol%), **1a** (0.2 mmol), **2a** (0.8 mmol, 4.0 equiv), and $NaHCO_3$ (0.2 mmol) in CH_3CN (*c* = 0.1 M) was irradiated by 30 W blue LEDs at room temperature under nitrogen gas for 4.5 h.

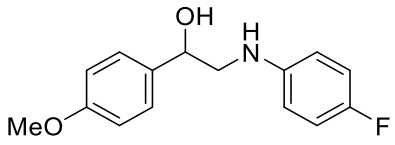
4. General procedure for the synthesis of 1,2-amino alcohols



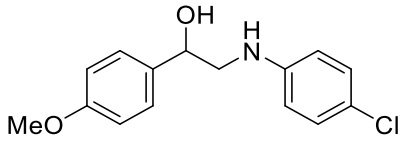
To a flame-dried sealed tube were added **UD-1** (5 mol %), **1** (0.2 mmol), **2** (0.8 mmol, 4.0 equiv), $NaHCO_3$ (0.2 mmol) and CH_3CN (2 mL). The reaction mixture was degassed via freeze-pump-thaw for 3 cycles. After the reaction mixture was thoroughly degassed, the vial was sealed and positioned approximately 2~3 cm from 30 W blue LEDs. Then the reaction mixture was stirred at room temperature for the indicated time (monitored by TLC) under nitrogen atmosphere. Afterwards, the reaction mixture was concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 6/1) to afford the desired products **3**. The analytical data of the products **3a**-**3ae** are summarized below.



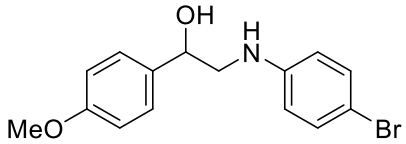
3a[4], yellow oil, 40.1 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 7.2 Hz, 2H), 4.85-4.81 (m, 1H), 3.80 (s, 3H), 3.37-3.23 (m, 2H).



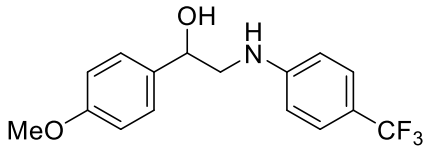
3b, yellow oil, 44.6 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.27 (m, 2H), 6.90-6.85 (m, 4H), 6.58-6.55 (m, 2H), 4.82-4.79 (m, 1H), 3.80 (s, 3H), 3.31-3.19 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 156.1 (d, *J* = 234.0 Hz), 144.2, 134.0, 127.1, 115.7 (d, *J* = 22.0 Hz), 114.3 (d, *J* = 7.0 Hz), 114.0, 72.0, 55.3, 52.3. ^{19}F NMR (375 MHz, $CDCl_3$) δ -127.2. IR (thin film): νmax (cm^{-1}) = 3385, 2837, 1611, 1507, 1463, 1303, 1244, 1214, 1174, 1112, 1030, 907, 819, 731, 541, 509. HRMS (ESI) calcd for $C_{15}H_{17}FNO_2$ $[M+H]^+$: 262.1243. Found: 262.1237.



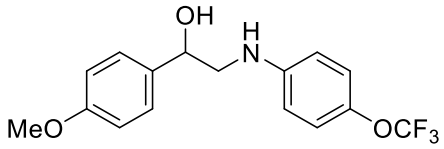
3c[4], orange solid, 48.0 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 9.2 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 8.8 Hz, 2H), 4.82-4.79 (m, 1H), 3.80 (s, 3H), 3.32-3.20 (m, 2H).



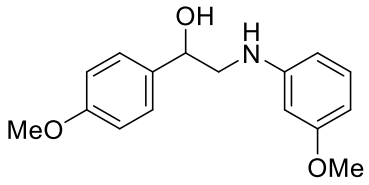
3d, brown solid, 56.0 mg, 87% yield. m.p. = 73.9-75.2 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.23 (m, 4H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.50 (d, *J* = 8.8 Hz, 2H), 4.83-4.80 (m, 1H), 3.80 (s, 3H), 3.32-3.21 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 146.9, 133.8, 131.9, 127.1, 114.9, 114.8, 114.0, 109.4, 71.9, 55.3, 51.4. IR (thin film): νmax (cm^{-1}) = 3327, 3240, 2836, 1612, 1593, 1582, 1513, 1489, 1420, 1295, 1237, 1179, 1124, 1067, 1028, 1004, 900, 884, 819, 766, 717, 613, 582, 528, 502, 472, 417. HRMS (ESI) calcd for $C_{15}H_{17}BrNO_2$ $[M+H]^+$: 322.0443. Found: 322.0436.



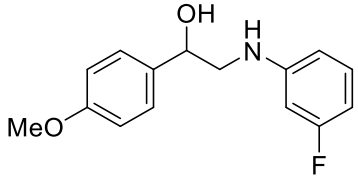
3e, brown oil, 31.5 mg, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.63 (d, *J* = 9.2 Hz, 2H), 4.87-4.84 (m, 1H), 3.81 (s, 3H), 3.41-3.30 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 150.4, 133.7, 127.2, 126.6 (q, *J* = 4.0 Hz), 124.9 (q, *J* = 269.0 Hz), 119.2 (q, *J* = 33.0 Hz), 114.1, 112.3, 72.1, 55.3, 50.8. ^{19}F NMR (375 MHz, $CDCl_3$) δ -61.0. IR (thin film): νmax (cm^{-1}) = 3404, 2839, 1614, 1533, 1512, 1464, 1320, 1247, 1159, 1104, 1064, 1032, 907, 826, 591, 433, 415, 406. HRMS (ESI) calcd for $C_{16}H_{17}F_3NO_2$ $[M+H]^+$: 312.1211. Found: 312.1207.



3f, yellow oil, 36.1 mg, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.59 (d, *J* = 9.2 Hz, 2H), 4.85-4.82 (m, 1H), 3.81 (s, 3H), 3.35-3.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 146.7, 140.8, 133.9, 127.1, 122.4, 120.7 (q, *J* = 253.0 Hz), 114.1, 113.6, 72.1, 55.3, 51.6. ^{19}F NMR (375 MHz, $CDCl_3$) δ -58.4. IR (thin film): νmax (cm^{-1}) = 3386, 2901, 1611, 1510, 1458, 1244, 1201, 1156, 1033, 915, 831, 733, 669, 553. HRMS (ESI) calcd for $C_{16}H_{17}F_3NO_3$ $[M+H]^+$: 328.1161. Found: 328.1155.

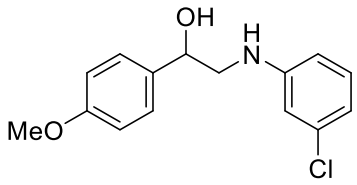


3g, yellow oil, 49.1 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.31-6.24 (m, 2H), 6.19 (t, *J* = 2.4 Hz, 1H), 4.83-4.80 (m, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 3.35-3.21 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 159.3, 149.3, 134.1, 130.0, 127.1, 113.9, 106.4, 103.1, 99.3, 71.9, 55.2, 55.0, 51.6. IR (thin film): νmax (cm^{-1}) = 3392, 2834, 1610, 1510, 1460, 1302, 1245, 1211, 1162, 1034, 831, 761, 689, 552. HRMS (ESI) calcd for $C_{16}H_{20}NO_3$ $[M+H]^+$: 274.1443. Found: 274.1437.

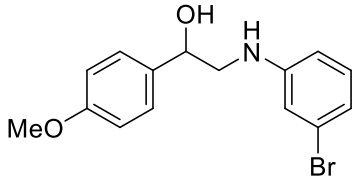


3h, yellow oil, 39.2 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.8 Hz, 2H), 7.12-7.06 (m, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.43-6.39 (m, 2H), 6.35-6.31 (m, 1H), 4.86-4.83 (m, 1H), 3.81 (s, 3H), 3.35-3.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0 (d, *J* = 242.0 Hz), 159.4, 149.7 (d, *J* = 10.0 Hz), 133.9, 130.3 (d, *J* = 11.0 Hz), 127.1, 114.0, 109.1 (d, *J* = 2.0 Hz), 104.2 (d, *J* = 22.0 Hz), 99.9 (d, *J* = 25.0 Hz), 72.0, 55.3, 51.3. ^{19}F NMR (375 MHz, $CDCl_3$) δ -112.7. IR (thin film): νmax (cm^{-1}) = 3399,

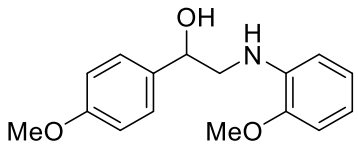
2901, 1612, 1586, 1510, 1456, 1245, 1174, 1150, 1030, 830, 761, 683, 550. HRMS (ESI) calcd for $C_{15}H_{17}FNO_2$ $[M+H]^+$: 262.1243. Found: 262.1237.



3i, brown oil, 40.5 mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.4, Hz, 2H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.69-6.66 (m, 1H), 6.59 (t, *J* = 2 Hz, 1H), 6.50-6.47 (m, 1H), 4.83-4.80 (m, 1H), 3.80 (s, 3H), 3.33-3.22 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 149.1, 135.0, 133.8, 130.2, 127.1, 117.7, 114.0, 112.9, 111.6, 72.0, 55.3, 51.2. IR (thin film): νmax (cm^{-1}) = 3675, 3396, 2901, 1597, 1510, 1408, 1303, 1246, 1174, 1066, 988, 902, 832, 766, 731, 683, 551, 442, 417. HRMS (ESI) calcd for $C_{15}H_{17}ClNO_2$ $[M+H]^+$: 278.0948. Found: 278.0942.

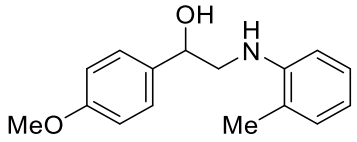


3j, yellow oil, 41.9 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.84-6.81 (m, 1H), 6.75 (t, *J* = 2.4 Hz, 1H), 6.55-6.52 (m, 1H), 4.83-4.80 (m, 1H), 3.80 (s, 3H), 3.33-3.22 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 149.2, 133.8, 130.5, 127.1, 123.2, 120.6, 115.8, 114.0, 112.0, 72.0, 55.3, 51.2. IR (thin film): νmax (cm^{-1}) = 3397, 2901, 1594, 1510, 1481, 1245, 1174, 1066, 985, 831, 765, 732, 682, 550, 421. HRMS (ESI) calcd for $C_{15}H_{17}BrNO_2$ $[M+H]^+$: 322.0443. Found: 322.0436.

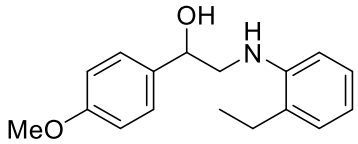


3k, yellow oil, 30.2 mg, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.0 Hz, 2H), 6.91-6.85 (m, 3H), 6.79-6.77 (m, 1H), 6.72-6.66 (m, 2H), 4.89-4.86 (m, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 3.39-3.26 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 147.1, 137.7, 134.2, 127.1, 121.2, 117.1, 113.9, 110.4, 109.6, 72.0, 55.4, 55.2, 51.7. IR (thin film): νmax (cm^{-1}) = 3675, 3404, 2901, 1601, 1509, 1455, 1302, 1243, 1221, 1175,

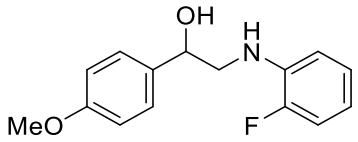
1130, 1028, 906, 832, 781, 737, 549. HRMS (ESI) calcd for $C_{16}H_{20}NO_3$ $[M+H]^+$: 274.1443. Found: 274.1437.



3l, yellow oil, 27.2 mg, 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.8 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.71-6.66 (m, 2H), 4.92-4.89 (m, 1H), 3.81 (s, 3H), 3.43-3.30 (m, 2H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 145.8, 134.2, 130.2, 127.1, 122.7, 117.6, 114.0, 110.3, 72.0, 55.3, 51.5, 17.4. IR (thin film): νmax (cm^{-1}) = 3675, 3407, 2971, 2901, 1606, 1585, 1509, 1449, 1302, 1245, 1174, 1135, 1049, 907, 832, 749, 557, 438, 417, 407. HRMS (ESI) calcd for $C_{16}H_{20}NO_2$ $[M+H]^+$: 258.1494. Found: 258.1488.

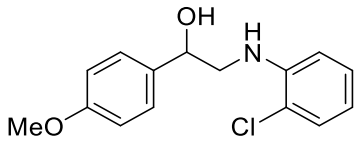


3m, yellow solid, 28.0 mg, 52% yield. m.p. = 48.3-50.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.8 Hz, 2H), 7.15-7.07 (m, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.76-6.68 (m, 2H), 4.92-4.89 (m, 1H), 3.81 (s, 3H), 3.43-3.30 (m, 2H), 2.50-2.44 (m, 2H), 1.21 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 145.2, 134.2, 128.4, 128.0, 127.1, 127.0, 117.8, 114.0, 110.6, 72.0, 55.3, 51.6, 23.8, 12.9. IR (thin film): νmax (cm^{-1}) = 3675, 2959, 1605, 1584, 1507, 1454, 1301, 1241, 1171, 1067, 1033, 925, 872, 825, 748, 538, 495, 444. HRMS (ESI) calcd for $C_{17}H_{22}NO_2$ $[M+H]^+$: 272.1651. Found: 272.1645.

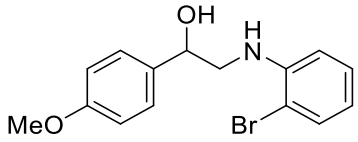


3n, yellow solid, 34.5 mg, 66% yield. m.p. = 62.5-66.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.8 Hz, 2H), 7.00-6.94 (m, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.76-6.71 (m, 1H), 6.67-6.62 (m, 1H), 4.87-4.84 (m, 1H), 3.80 (s, 3H), 3.39-3.28 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4 151.8 (d, *J* = 236.0 Hz), 136.3 (d, *J* = 12.0 Hz), 133.9, 127.1, 124.5 (d, *J* = 4.0 Hz), 117.2 (d, *J* = 7.0 Hz), 114.6 (d, *J* = 19.0 Hz), 114.0, 112.5 (d, *J* = 3.0 Hz), 72.1, 55.3, 51.2. ^{19}F NMR (375 MHz, $CDCl_3$) δ -135.8. IR (thin film): νmax

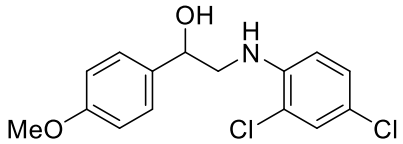
(cm^{-1}) = 3335, 2900, 1611, 1506, 1438, 1236, 1178, 1071, 1025, 821, 747, 583, 546, 454. HRMS (ESI) calcd for $C_{15}H_{17}FNO_2$ $[M+H]^+$: 262.1243. Found: 262.1237.



3o, green oil, 46.1 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.26-7.24 (m, 1H), 7.15-7.10 (m, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.71-6.63 (m, 2H), 4.89-4.86 (m, 1H), 3.80 (s, 3H), 3.41-3.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 143.7, 133.9, 129.2, 127.7, 127.1, 119.6, 117.7, 114.0, 111.6, 72.0, 55.3, 51.2. IR (thin film): νmax (cm^{-1}) = 3675, 3404, 2988, 2901, 1597, 1509, 1455, 1303, 1246, 1174, 1136, 1033, 906, 831, 743, 555, 438, 418, 406. HRMS (ESI) calcd for $C_{15}H_{17}ClNO_2$ $[M+H]^+$: 278.0948. Found: 278.0944.

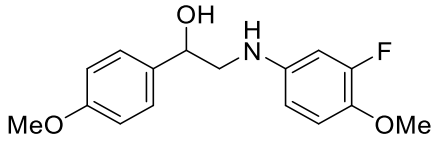


3p, green oil, 57.1 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.40 (m, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.18-7.14 (m, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.68-6.66 (m, 1H), 6.60-6.56 (m, 1H), 4.89-4.85 (m, 1H), 3.80 (s, 3H), 3.40-3.30 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 144.7, 133.8, 132.5, 128.4, 127.1, 118.3, 114.0, 111.7, 110.2, 72.0, 55.3, 51.3. IR (thin film): νmax (cm^{-1}) = 3675, 3393, 2988, 2901, 1594, 1508, 1454, 1303, 1246, 1174, 1019, 907, 831, 742, 662, 553, 434. HRMS (ESI) calcd for $C_{15}H_{17}BrNO_2$ $[M+H]^+$: 322.0443. Found: 322.0436.

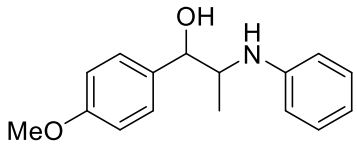


3q, yellow solid, 41.3 mg, 66% yield. m.p. = 86.2-88.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 2.4 Hz, 1H), 7.09-7.06 (m, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 1H), 4.87-4.84 (m, 1H), 3.80 (s, 3H), 3.37-3.28 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 142.6, 133.7, 128.8, 127.7, 127.1, 121.5, 119.9, 114.1, 112.1, 72.1, 55.3, 51.1. IR (thin film): νmax (cm^{-1}) = 3393, 2901, 1593, 1506,

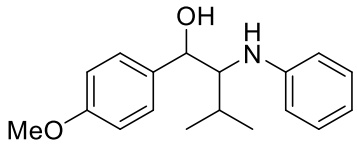
1395, 1321, 1247, 1176, 1069, 883, 830, 796, 523, 418. HRMS (ESI) calcd for $C_{15}H_{16}Cl_2NO_2$ $[M+H]^+$: 312.0558. Found: 312.0552.



3r, brown oil, 23.8 mg, 41% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.82 (t, *J* = 9.2 Hz, 1H), 6.46-6.42 (m, 1H), 6.36-6.33 (m, 1H), 4.84-4.81 (m, 1H), 3.810 (s, 3H), 3.807 (s, 3H), 3.30-3.19 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 153.4 (d, *J* = 243.0 Hz), 142.9 (d, *J* = 9.0 Hz), 139.8 (d, *J* = 11.0 Hz), 134.0, 127.1, 115.8, 114.0, 108.6 (d, *J* = 3.0 Hz), 102.5 (d, *J* = 22.0 Hz), 72.0, 57.4, 55.3, 52.2. ^{19}F NMR (375 MHz, $CDCl_3$) δ -133.4. IR (thin film): νmax (cm^{-1}) = 3387, 2970, 1611, 1586, 1512, 1462, 1245, 1225, 1172, 1028, 904, 831, 759, 548. HRMS (ESI) calcd for $C_{16}H_{19}FNO_3$ $[M+H]^+$: 292.1349. Found: 292.1343.

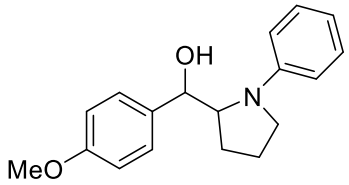


3s, yellow oil, 28.5 mg, 55% yield. Two diastereoisomers were observed in NMR spectra. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 8.0 Hz, 2H), 7.21-7.17 (m, 2H), 6.91-6.87 (m, 2H), 6.78-6.67 (m, 3H), 4.91-4.43 (m, 1H), 3.81 and 3.80 (s, 3H), 3.76-3.59 (m, 1H), 1.02-0.99 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 158.8, 147.4, 147.1, 133.4, 133.0, 129.4, 129.3, 128.2, 127.1, 118.4, 117.9, 114.4, 113.9, 113.68, 113.65, 74.1, 56.1, 55.2, 54.3, 16.9, 14.1. IR (thin film): νmax (cm^{-1}) = 3398, 2932, 2835, 1601, 1505, 1455, 1302, 1245, 1174, 1073, 1030, 991, 832, 808, 749, 693. HRMS (ESI) calcd for $C_{16}H_{20}NO_2$ $[M+H]^+$: 258.1494. Found: 258.1499.

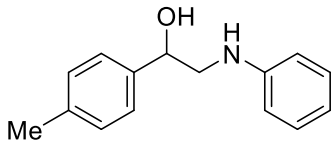


3t, yellow oil, 9 mg, 16% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.8 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.72-6.69 (m, 3H), 4.57 (d, *J* = 7.2 Hz, 1H), 3.80 (s, 3H), 3.43-3.40 (m, 1H), 2.96 (s, 1H), 1.79-1.75 (m, 1H), 0.93 (d, *J* = 7.6 Hz, 3H), 0.86 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 149.4,

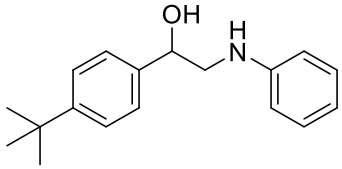
134.1, 129.3, 128.0, 117.9, 114.0, 113.9, 74.5, 66.1, 55.3, 29.6, 21.0, 16.6. IR (thin film): νmax (cm^{-1}) = 3400, 2956, 2835, 1600, 1509, 1464, 1388, 1301, 1246, 1174, 1102, 1033. 863, 831, 748, 692. HRMS (ESI) calcd for $C_{18}H_{24}NO_2$ $[M+H]^+$: 286.1807. Found: 286.1810.



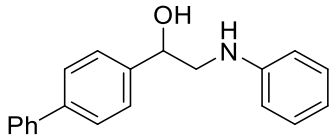
3u, yellow oil, 18 mg, 32% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.24 (m, 4H), 6.89 (d, *J* = 8.8 Hz, 4H), 6.77 (t, *J* = 7.6 Hz, 1H), 4.70 (d, *J* = 6.8 Hz, 1H), 4.01 (t, *J* = 7.6 Hz, 1H), 3.81 (s, 3H), 3.38 (t, *J* = 8.8 Hz, 1H), 3.12-3.06 (m, 1H), 2.48 (s, 1H), 1.88-1.71 (m, 3H), 1.51-1.42 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 148.9, 133.6, 129.2, 127.9, 116.8, 113.6, 112.8, 74.8, 65.2, 55.2, 49.9, 26.9, 23.3. IR (thin film): νmax (cm^{-1}) = 3424, 2835, 1596, 1504, 1459, 1363, 1332, 1301, 1246, 1172, 1033, 991, 829, 747, 693, 641. HRMS (ESI) calcd for $C_{18}H_{22}NO_2$ $[M+H]^+$: 284.1651. Found: 284.1655.



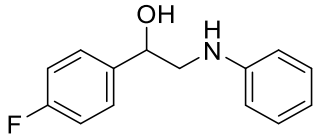
3v[4], yellow oil, 37.8 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.20-7.16 (m, 4H), 6.74 (t, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 2H), 4.87-4.84 (m, 1H), 3.40-3.23 (m, 2H), 2.35 (s, 3H).



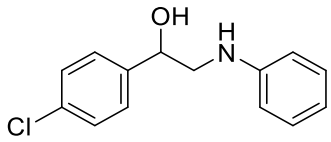
3w[4], yellow oil, 33.2 mg, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.20-7.16 (m, 2H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.67-6.65 (m, 2H), 4.89-4.86 (m, 1H), 3.42-3.26 (m, 2H), 1.33 (s, 9H).



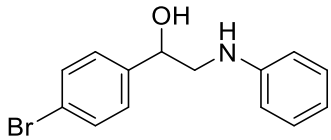
3x[4], yellow solid, 44.4 mg, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 4H), 7.45-7.41 (m, 4H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.21-7.17 (m, 2H), 6.75 (t, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 2H), 4.93-4.90 (m, 1H), 3.45-3.27 (m, 2H).



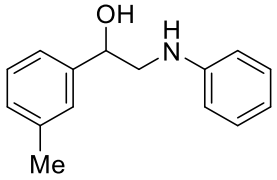
3y[4], yellow solid, 30.4 mg, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.34 (m, 2H), 7.19 (t, *J* = 8.8 Hz, 2H), 7.05 (t, *J* = 8.8 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.66 (d, *J* = 8.8 Hz, 2H), 4.89-4.86 (m, 1H), 3.39-3.21 (m, 2H).



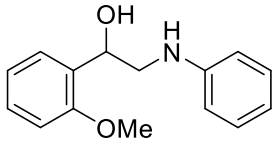
3z[4], yellow oil, 34.4 mg, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.28 (m, 4H), 7.20-7.16 (m, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 7.6 Hz, 2H), 4.86-4.83 (m, 1H), 3.36-3.33 (m, 1H), 3.23-3.18 (m, 1H).



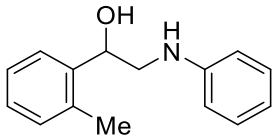
3aa[4], yellow oil, 40.2 mg, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.21-7.17 (m, 2H), 6.76 (t, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 2H), 4.86-4.83 (m, 1H), 3.39-3.34 (m, 1H), 3.24-3.19 (m, 1H).



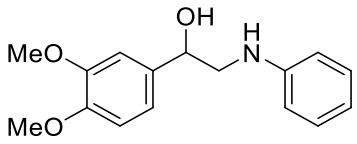
3ab[4], yellow oil, 41.3 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.11 (m, 6H), 6.74 (t, *J* = 7.6 Hz, 1H), 6.66-6.64 (m, 2H), 4.86-4.83 (m, 1H), 3.40-3.36 (m, 1H), 3.28-3.22 (m, 1H), 2.36 (s, 3H).



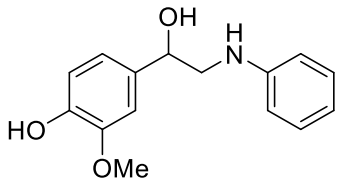
3ac[4], yellow oil, 21.0 mg, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.40 (m, 1H), 7.31-7.26 (m, 1H), 7.20-7.16 (m, 2H), 7.01-6.97 (m, 1H), 6.90 (d, *J* = 8. Hz, 1H), 6.74-6.69 (m, 3H), 5.16-5.13 (m, 1H), 3.87 (s, 3H), 3.52-3.48 (m, 1H), 3.27-3.21 (m, 1H).



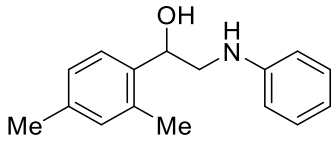
3ad[4], yellow solid, 23.3 mg, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.28-7.15 (m, 5H), 6.75 (t, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 2H), 5.15-5.12 (m, 1H), 3.41-3.37 (m, 1H), 3.23-3.18 (m, 1H), 2.36 (s, 3H).



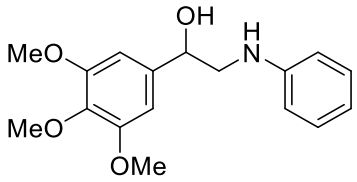
3ae, yellow oil, 50.7 mg, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.16 (m, 2H), 6.92-6.83 (m, 3H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.66-6.63 (m, 2H), 4.84-4.80 (m, 1H), 3.861 (s, 3H), 3.859 (s, 3H), 3.38-3.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 148.5, 147.7, 134.6, 129.2, 118.1, 117.9, 113.3, 111.0, 108.9, 72.1, 55.8, 55.7, 51.6. IR (thin film): νmax (cm^{-1}) = 3675, 3392, 2970, 1602, 1505, 1462, 1417, 1317, 1257, 1232, 1138, 1066, 1026, 908, 811, 751, 694, 646, 510, 415. HRMS (ESI) calcd for $C_{16}H_{20}NO_3$ $[M+H]^+$: 274.1443. Found: 274.1437.



3af, yellow oil, 34.6 mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.16 (m, 2H), 6.92-6.83 (m, 3H), 6.74 (t, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 7.2 Hz, 2H), 4.84-4.80 (m, 1H), 3.87 (s, 3H), 3.38-3.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 146.7, 145.3, 134.0, 129.3, 118.9, 118.1, 114.3, 113.5, 108.3, 72.3, 55.9, 51.7. IR (thin film): νmax (cm^{-1}) = 3385, 1601, 1505, 1463, 1431, 1267, 1152, 1122, 1032, 908, 820, 732, 694, 648, 420, 409. HRMS (ESI) calcd for $C_{15}H_{16}NO_3$ $[M-H]^-$: 258.1136. Found: 258.1132.



3ag, white solid, 37.0 mg, 77% yield. m.p. = 97.9-99.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 2H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.98 (s, 1H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 7.2 Hz, 2H), 5.10-5.07 (m, 1H), 3.38-3.33 (m, 1H), 3.21-3.16 (m, 1H), 2.31 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 137.3, 137.0, 134.6, 131.3, 129.3, 127.0, 125.4, 118.0, 113.4, 68.9, 50.6, 21.0, 19.0. IR (thin film): νmax (cm^{-1}) = 3267, 2922, 1604, 1498, 1299, 1243, 1067, 907, 872, 790, 747, 688, 594, 505, 480, 436. HRMS (ESI) calcd for $C_{16}H_{20}NO$ $[M+H]^+$: 242.1545. Found: 242.1539.



3ah, yellow solid, 56.0 mg, 92% yield. m.p. = 114.3-116.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.19 (m, 2H), 6.77 (t, *J* = 7.2 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 2H), 6.62 (s, 2H), 4.86-4.83 (m, 1H), 3.870 (s, 6H), 3.861 (s, 3H), 3.43-3.28 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 147.7, 137.9, 137.1, 129.2, 118.0, 113.3, 102.6, 72.4, 60.7, 56.0, 51.6. IR (thin film): νmax (cm^{-1}) = 3467, 3359, 2943, 1593, 1505, 1462, 1328, 1231, 1184, 1127, 1001, 831, 760, 687, 465. HRMS (ESI) calcd for $C_{17}H_{22}NO_4$ $[M+H]^+$: 304.1549. Found: 304.1543.

5. Mechanistic studies

Stern-Volmer quenching experiments

The concentration of **UD-1** was 0.01 mM in THF. The concentration of the quencher (**1a**, N-phenyl glycine) was 0.1 M in THF. For each quenching experiment, the quencher was titrated to a solution (10 mL) of N-phenyl glycine (**1a**) in a quartz glass bottle. The addition of the quencher refers to an increase of the quencher concentration of 1×10^{-3} M, 3×10^{-3} M, 5×10^{-3} M, 8×10^{-3} M, 1×10^{-2} M, 1.5×10^{-2} M, 2×10^{-2} M, 2.5×10^{-2} M, 3×10^{-2} M. Then the emission intensity of **UD-1** was collected respectively.

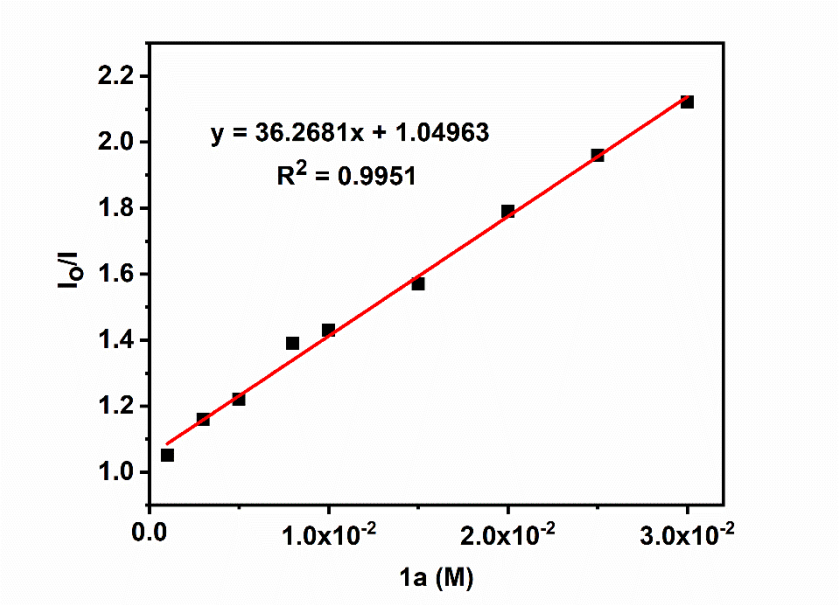


Figure S10. Stern-Volmer quenching experiments.

Cyclic voltammograms of 1a and 2a

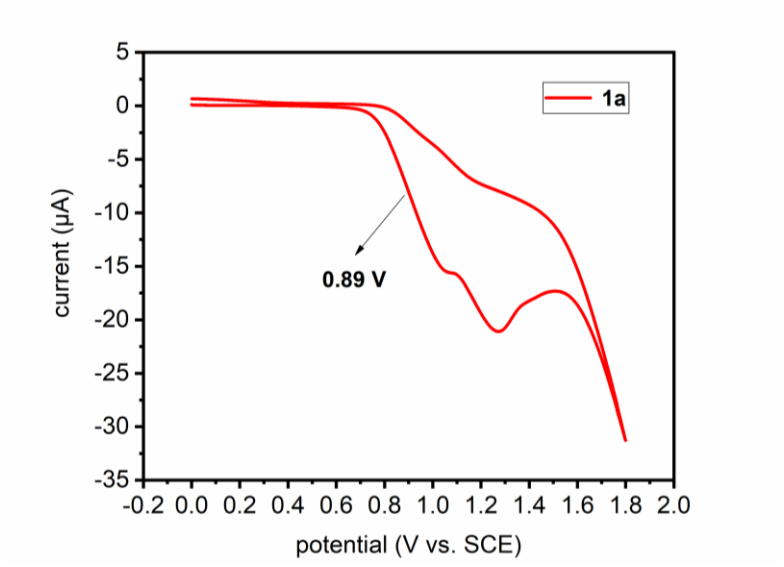


Figure S11. Cyclic voltammogram of **1a** in DMSO (10.0 mM) containing 0.1 M $^{n}Bu_4NPF_6$. Scan rate: 0.1 V/s. $E_{1/2}^{ox}$ = 0.89 V.

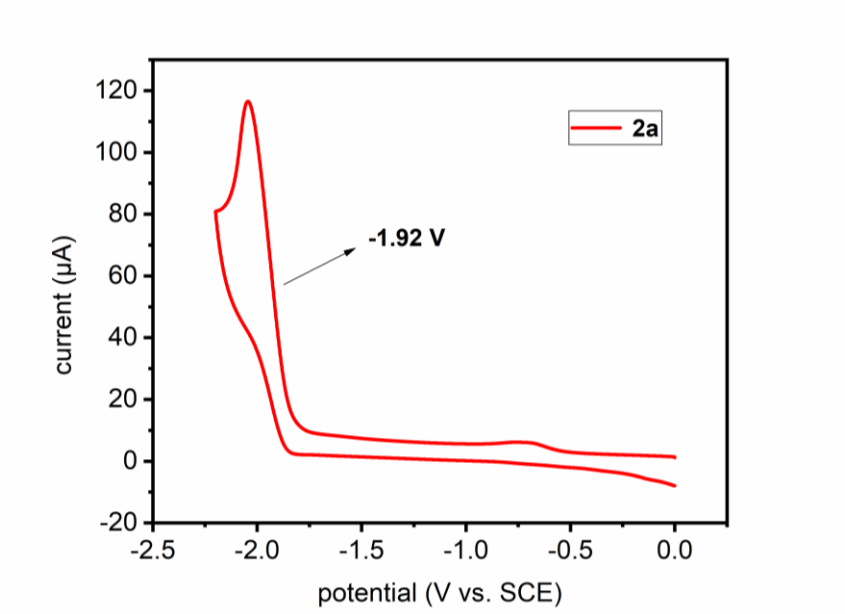


Figure S12. Cyclic voltammogram of **2a** in DMSO (10.0 mM) containing 0.1 M $^{n}Bu_4NPF_6$. Scan rate: 0.1 V/s. $E_{1/2}^{red}$ = -1.92 V.

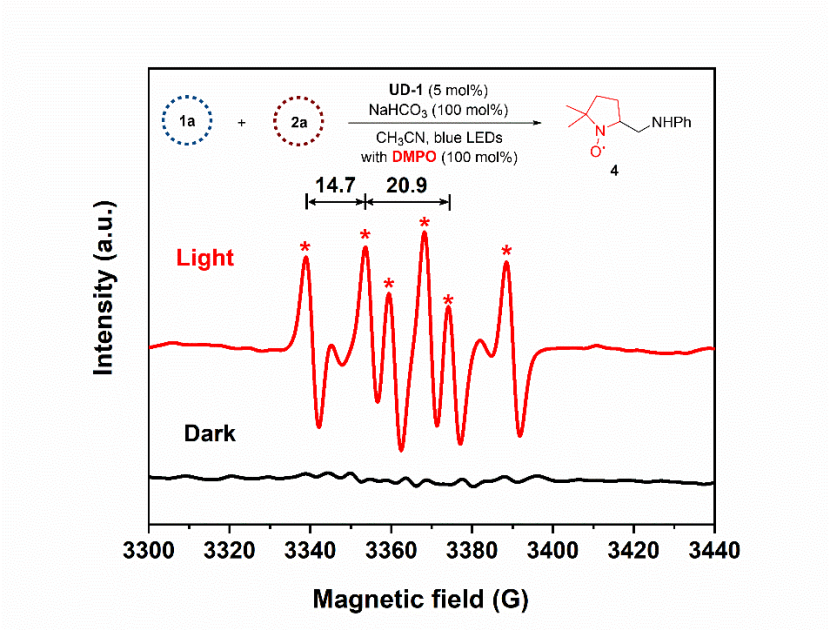
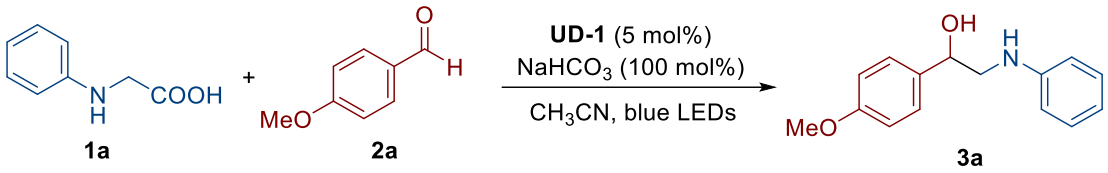


Figure S13. EPR spectra of standard reaction tested in N_2-saturated CH_3CN solution in the presence of DMPO.

6. Recyclability tests of UD-1

General procedure for recycling experiments:



To a flame-dried sealed tube were added **UD-1** (5 mol%), **1a** (0.2 mmol), **2a** (0.8 mmol, 4.0 equiv), $NaHCO_3$ (0.2 mmol) and CH_3CN (2 mL). The reaction mixture was degassed via freeze-pump-thaw for 3 cycles. After the reaction mixture was thoroughly degassed, the vial was sealed and positioned approximately 2~3 cm from 30 W blue LEDs. Then the reaction mixture was stirred at room temperature for the indicated time (monitored by TLC) under nitrogen atmosphere. Afterwards, the reaction mixture was washed with petroleum ether to remove the reactants. **UD-1** was left at the bottom of the sealed tube and directly used for the next cycle without any further purification.

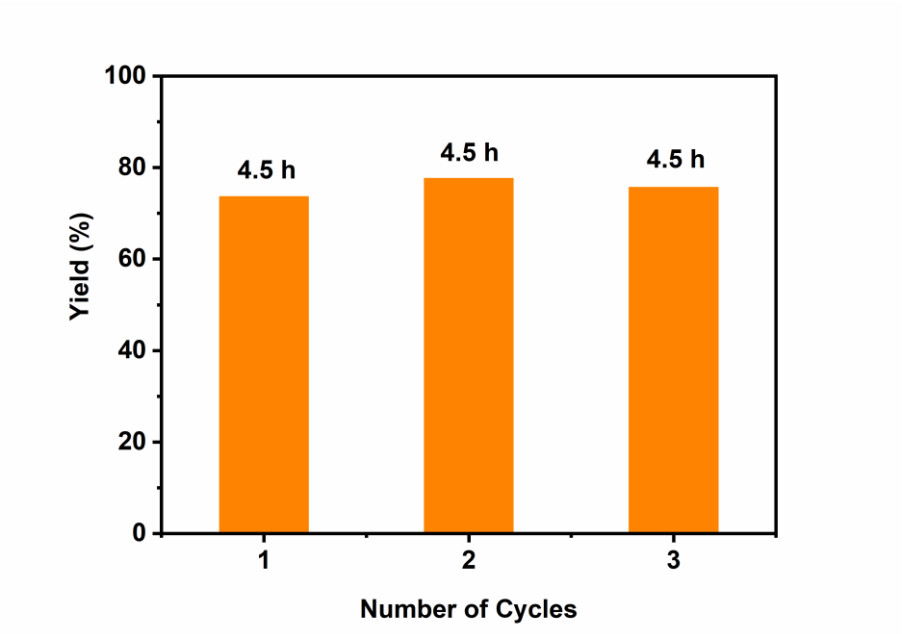


Figure S14. Recyclability tests of **UD-1** in the synthesis of 1,2-amino alcohol **3a**.

Table S1. Recyclability tests of **UD-1** in the synthesis of 1,2-amino alcohol **3a**

cycle	t (h)	yield (%)
1	4.5	74
2	4.5	78
3	4.5	76

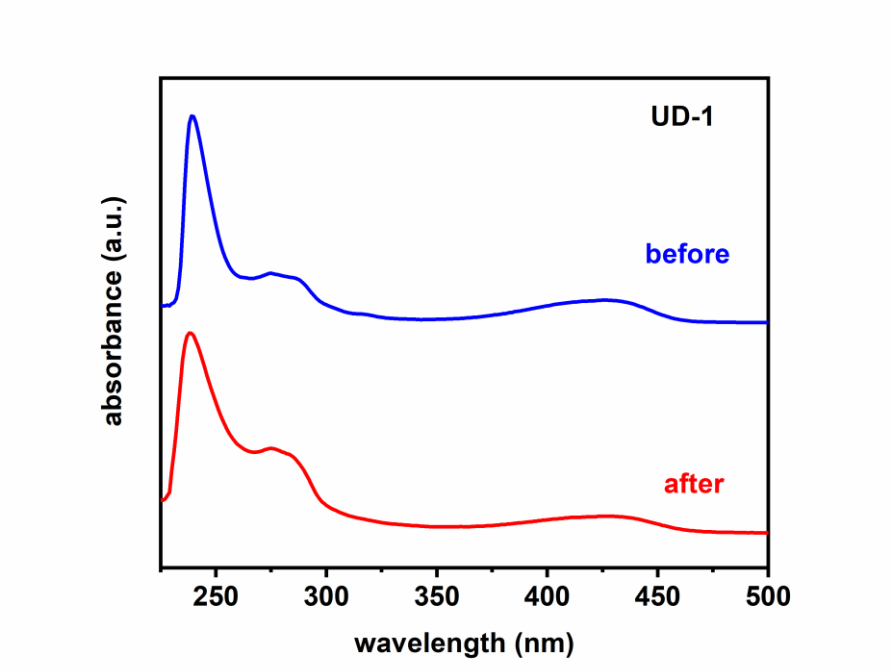
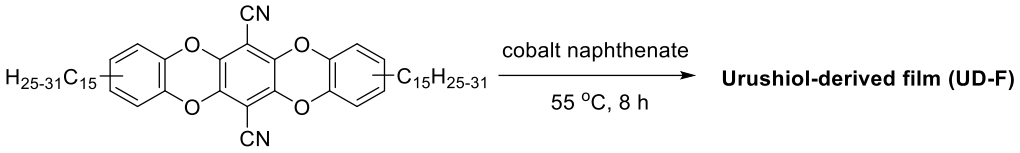


Figure S15. UV/vis absorption spectra of **UD-1** before and after recycling experiments.

7. Preparation and characterization of UD-F

Preparation of an urushiol-derived film (UD-F)



Urushiol derivative (UD-1)

UD-1 (0.1 g) was dissolved in DCM (0.5 mL), then the cobalt naphthenate (0.1 mL) was added and mixed uniformly. A piece of transparent glass was ultrasonically cleaned with ethanol and dried, the mixture was laid flat on the surface of the glass (~0.5 mm thick). The glass covered with the mixture was placed flat in an oven and heated at 55 °C for 8 h to form a film. The separated film was soaked in DCM, and ultrasonically washed with various solvents such as EtOAc and EtOH to remove the impurities. Upon filtration, the film **UD-F** was obtained after drying overnight in a vacuum drying oven.

Characterization of UD-F

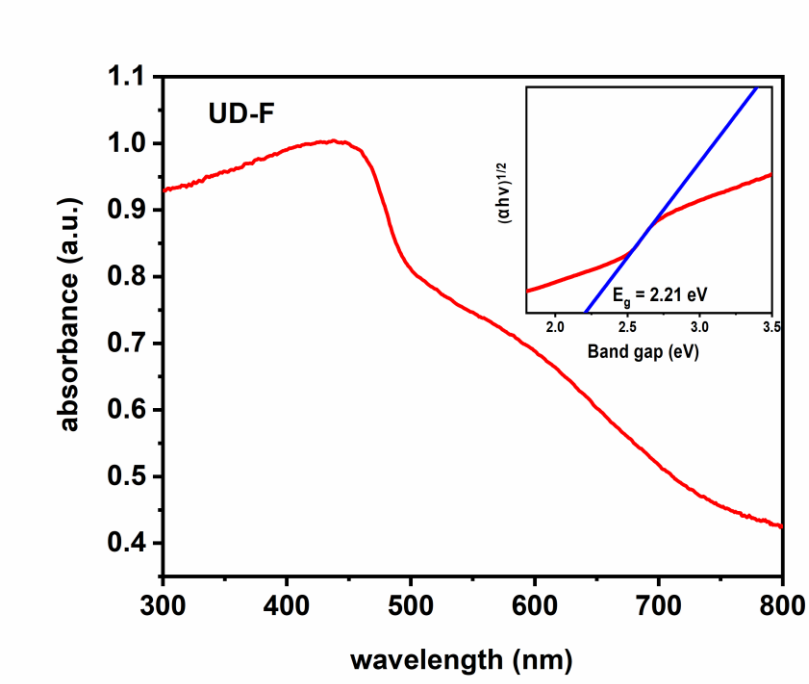


Figure S16. UV-vis diffuse reflectance spectrum (DRS) and Tauc plot calculating the optical band gap (inset) of **UD-F**.

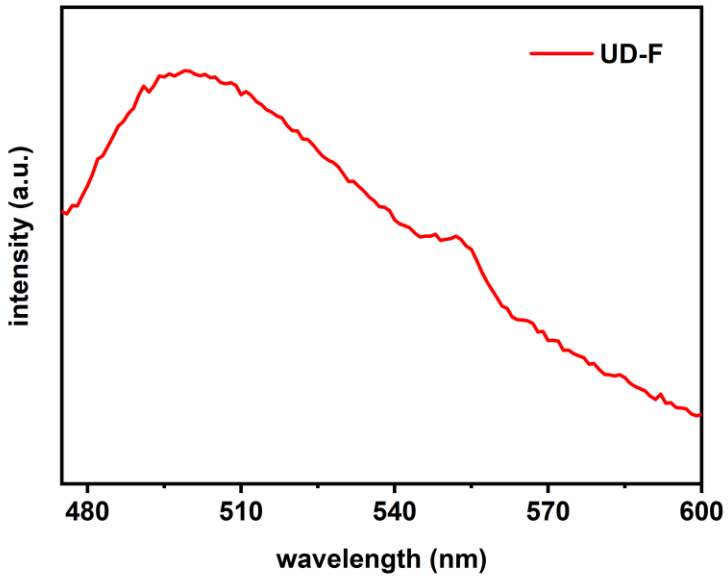


Figure S17. Fluorescence spectrum of **UD-F**.

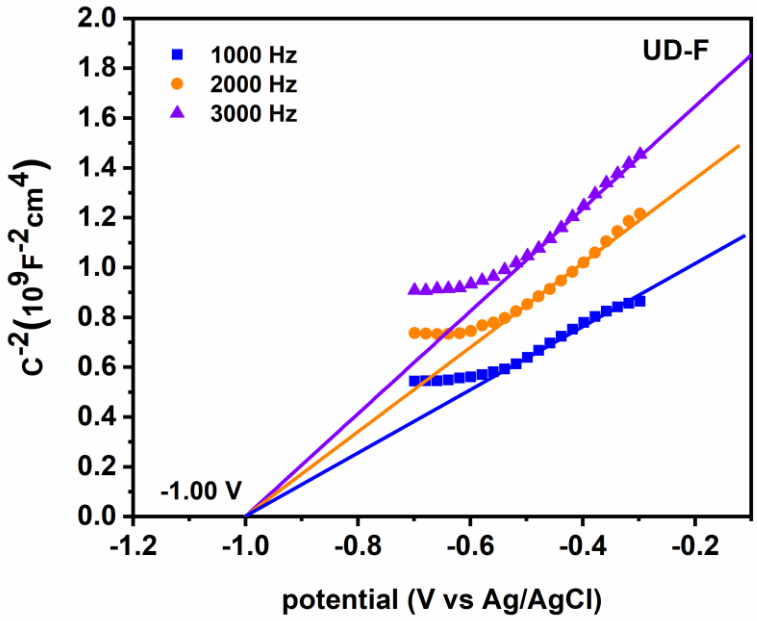


Figure S18. Mott-Schottky plots of **UD-F** at frequencies 1.0, 2.0 and 3.0 kHz.

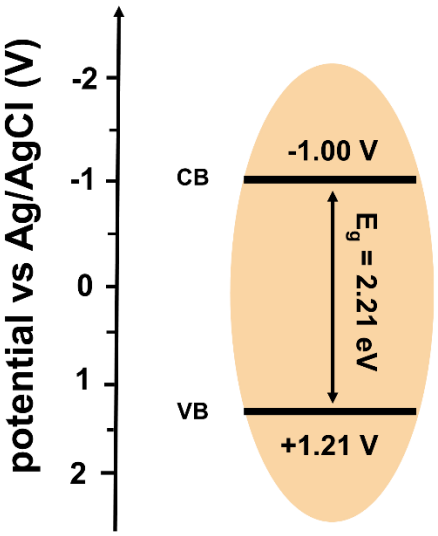


Figure S19. Band structure diagram of **UD-F**.

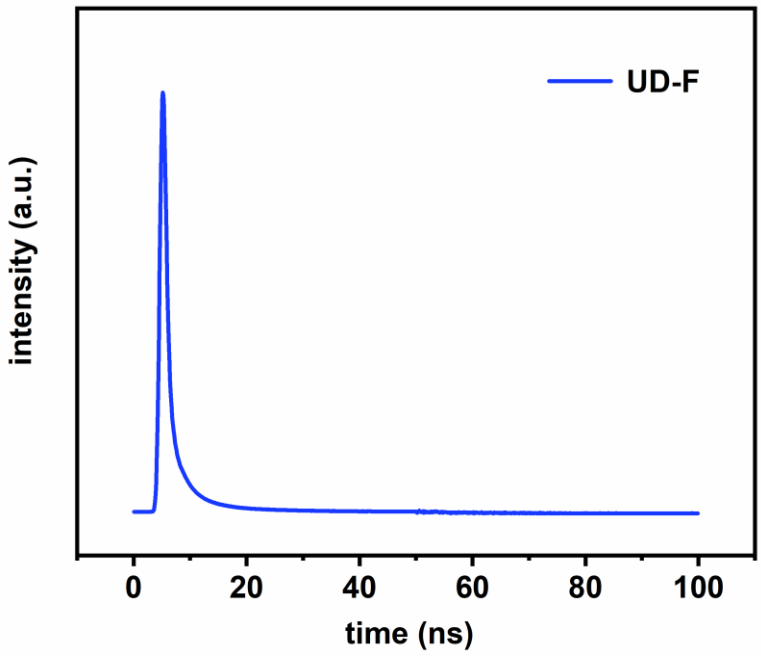


Figure S20. Time-resolved PL spectrum of **UD-F**.

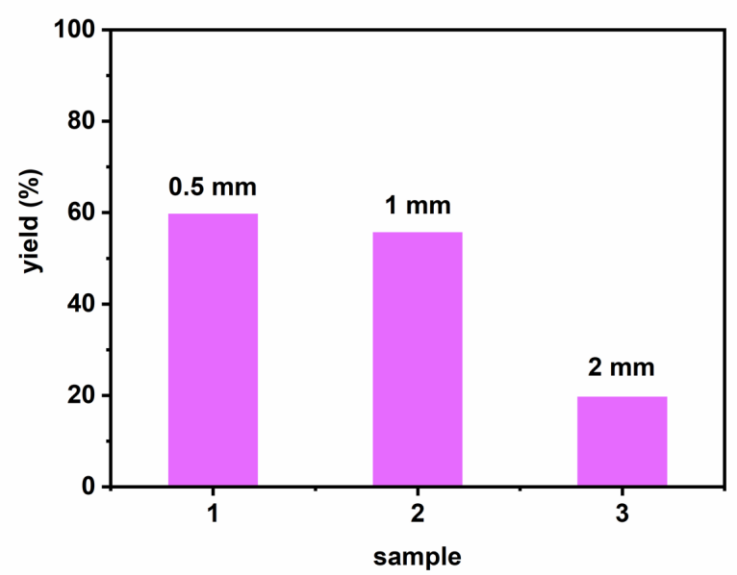


Figure S21. Effect of film thickness

8. Emission spectrum of the blue LED lamp

The following spectrum was recorded on EVERFINE Corporation HAAS-2000_VIS_V2 High-precision fast spectroradiometer. The forward current of the LEDs is 25 mA. Electroluminescence (EL) measurement of the LED lamp was carried out at room temperature using Everfine HAAS-2000. For the light collection, the LED was placed inside a 30 cm-diameter integrating sphere coupled to a high accuracy array spectroradiometer (wavelength accuracy <0.3 nm) and a programmable test power LED300E.

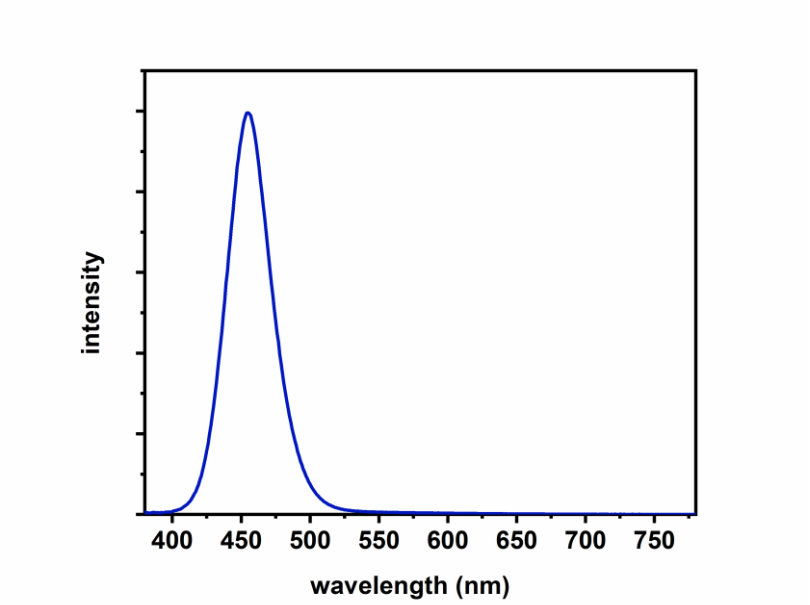


Figure S22. Emission spectrum of the blue LEDs lamp. Maximum wavelength: 455 nm; Emission width: 400-525 nm.

9. References

[1] (a) Yao, Z.; Wu, X.; Zhang, X.; Xiong, Q.; Jiang, S.; Yu, Z. Synthesis and evaluation of photo-activatable β-diarylsydnone-l-alanines for fluorogenic photo-click cyclization of peptides. *Org. Biomol. Chem.* **2019**, *17*, 6777-6781. (b) Pétry, N.; Vanderbeeken, T.; Malher, A.; Bringer, Y.; Retailleau, P.; Bantreil, X.; Lamaty, F. Mechanosynthesis of sydnone-containing coordination complexes. *Chem. Commun.* **2019**, *55*, 9495-9498.

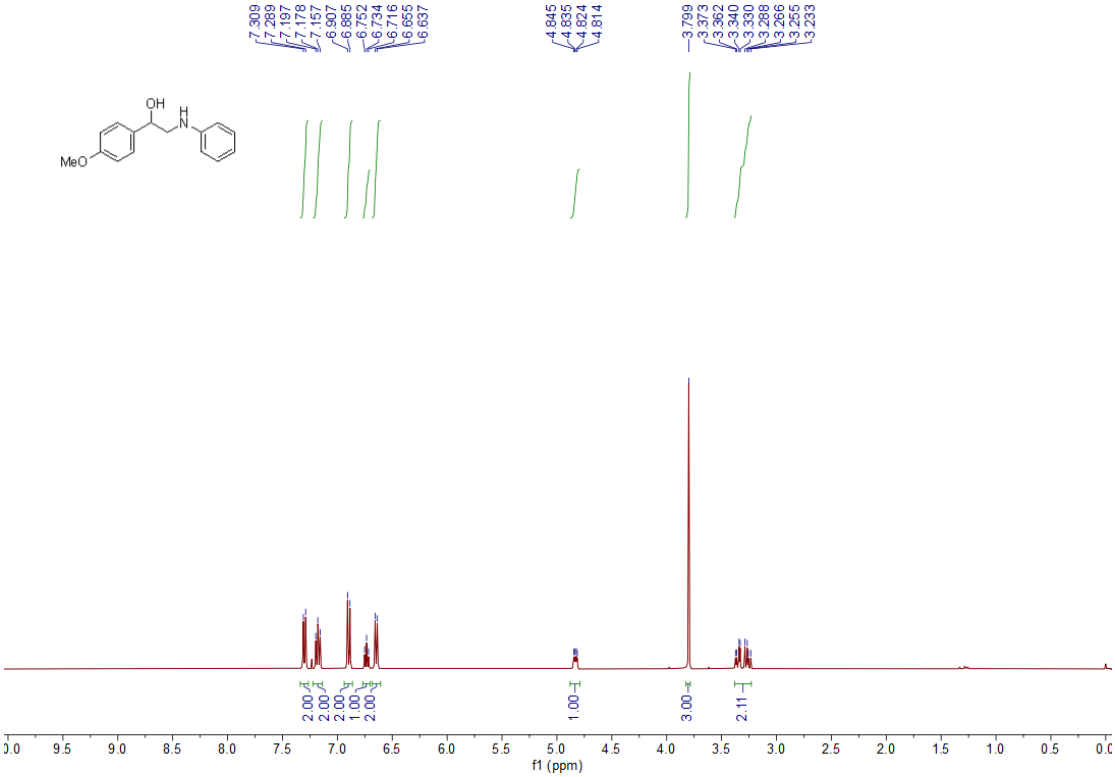
[2] Zhang, B.; Wei, M.; Mao, H.; Pei, X.; Alshmimri, S. A.; Reimer, Jeffrey A.; Yaghi O. M. Crystalline Dioxin-Linked Covalent Organic Frameworks from Irreversible Reactions. *J. Am. Chem. Soc.* **2018**, *140*, 12715-12719.

[3] Lu, L.; Miyakoshi, T. "Lacquer Chemistry and Applications", 2015, Elsevier, Amsterdam, Netherlands.

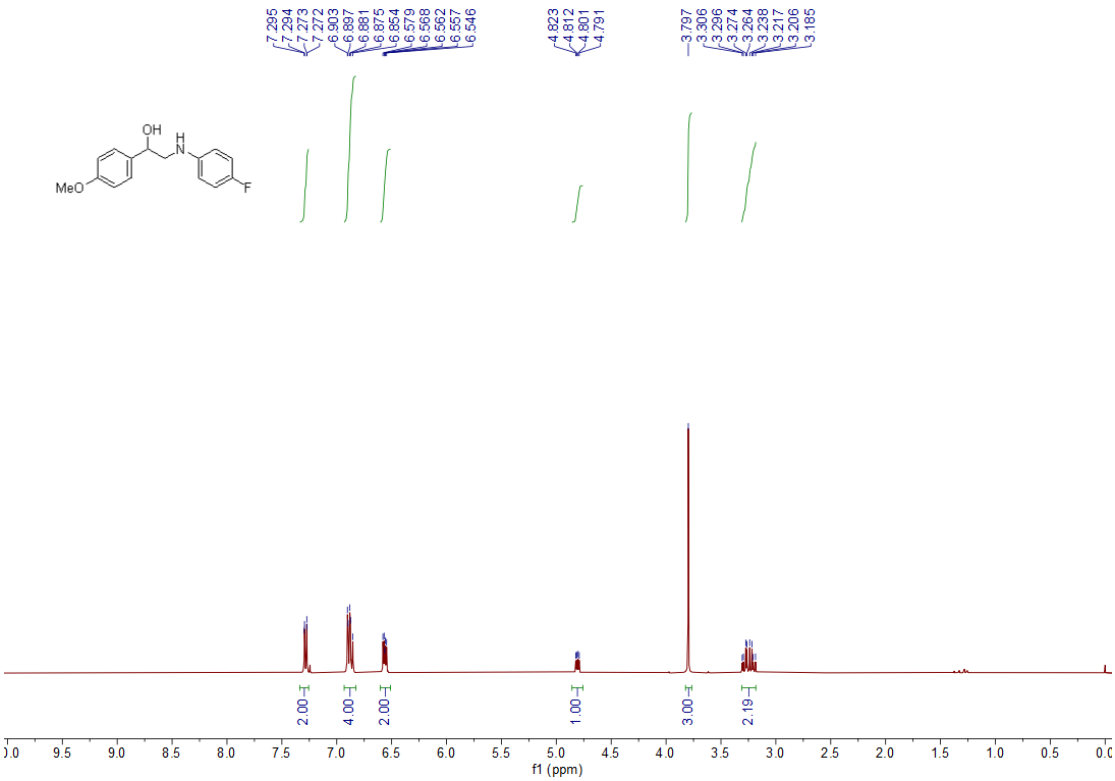
[4] (a) Pan, S.; Jiang, M.; Hu, J.; Xu, R.; Zeng, X.; Zhong, G. Synthesis of 1,2-amino alcohols by decarboxylative coupling of amino acid derived α-amino radicals to carbonyl compounds via visible-light photocatalyst in water. *Green Chem.* **2020**, *22*, 336-341. (b) Xu, Z.; Zhu, S.; Liu, Y.; He, L.; Geng, Z.; Zhang, Y. Synthesis of Optically Active b-Amino Alcohols by Asymmetric Transfer Hydrogenation of a-Amino Ketones. *Synthesis* **2010**, *5*, 811-817.

10. Copies of NMR spectra

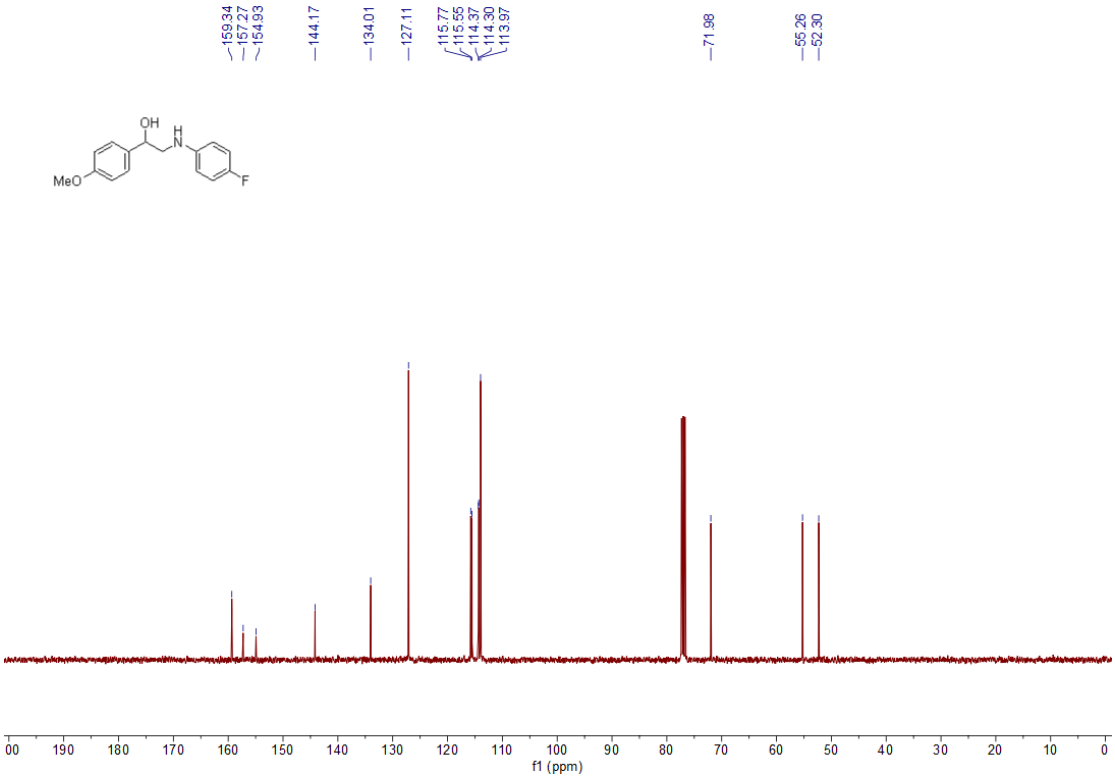
^{1}H NMR Spectrum of **3a**



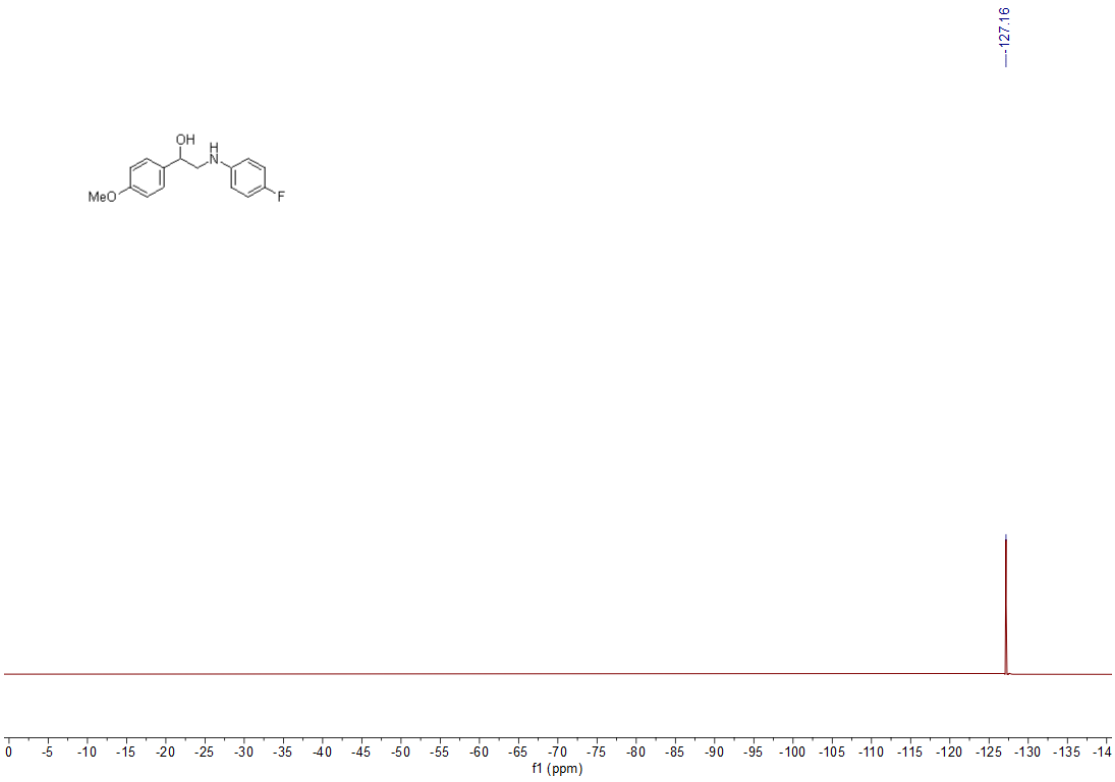
^{1}H NMR Spectrum of **3b**



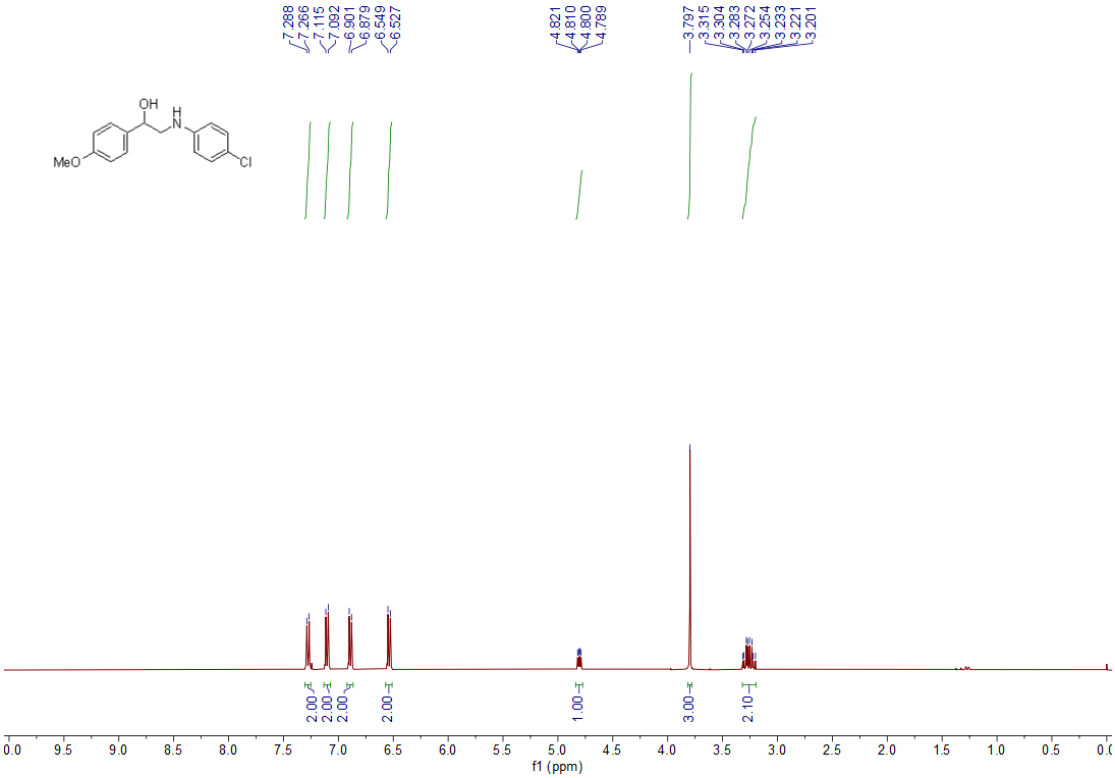
^{13}C NMR Spectrum of **3b**



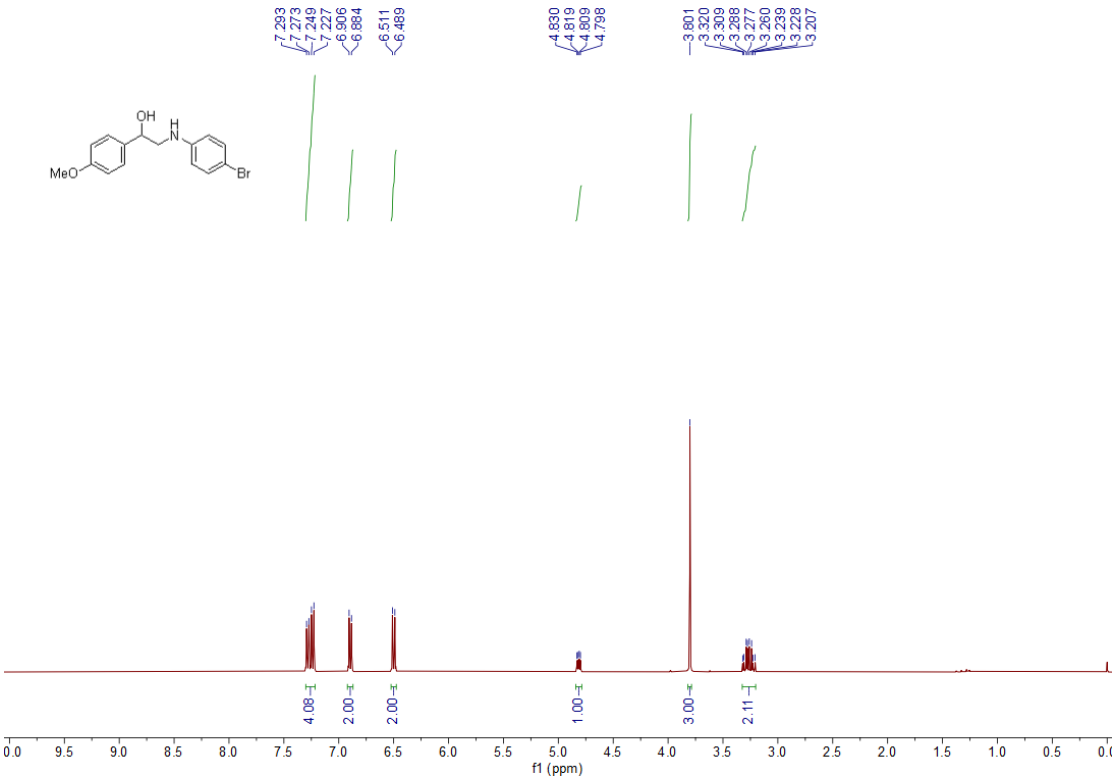
^{19}F NMR Spectrum of **3b**



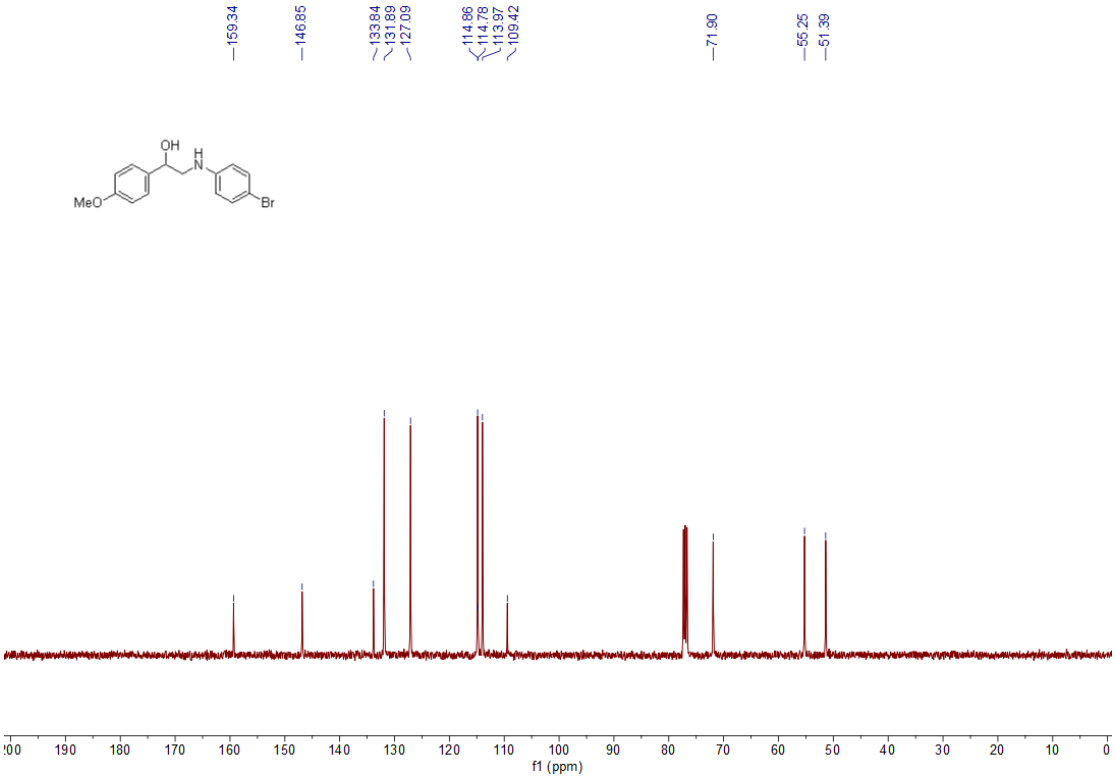
^{1}H NMR Spectrum of **3c**



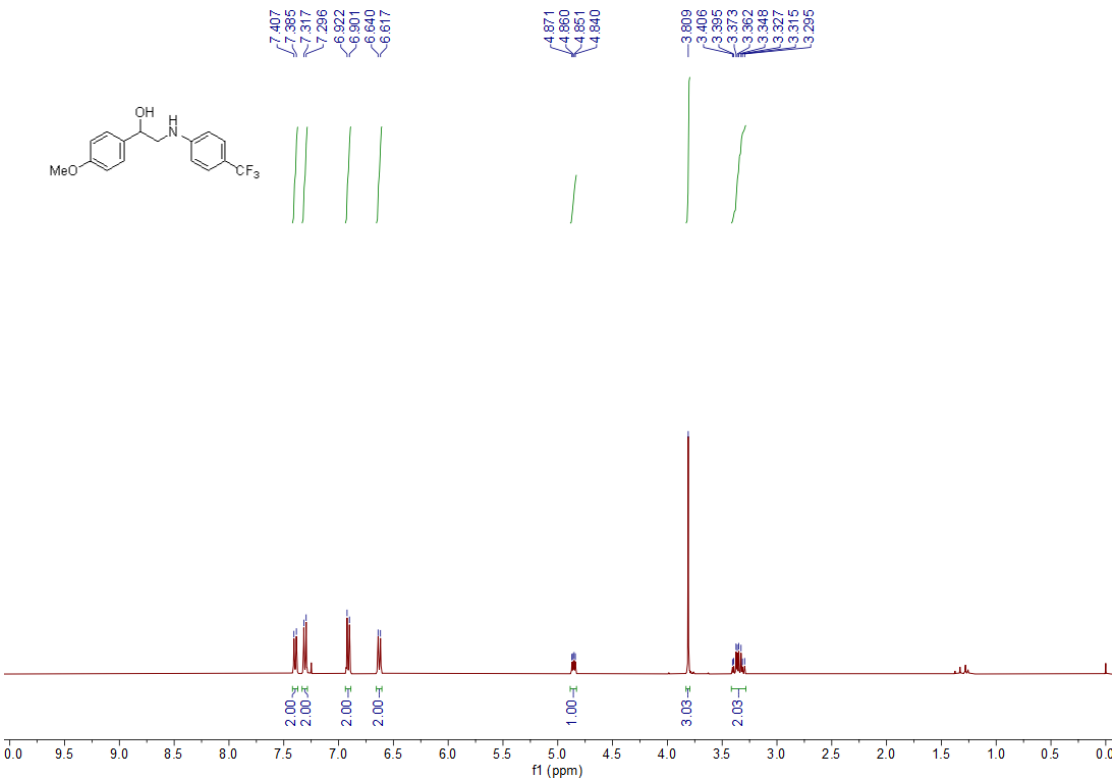
^{1}H NMR Spectrum of **3d**



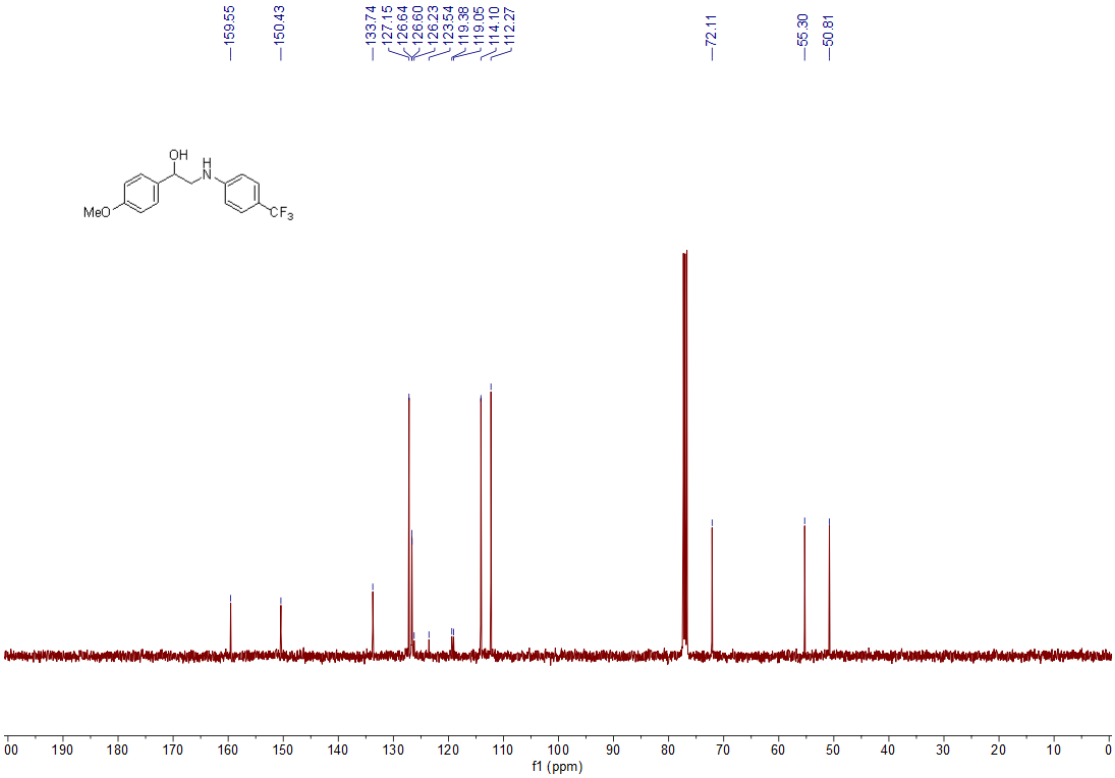
^{13}C NMR Spectrum of **3d**



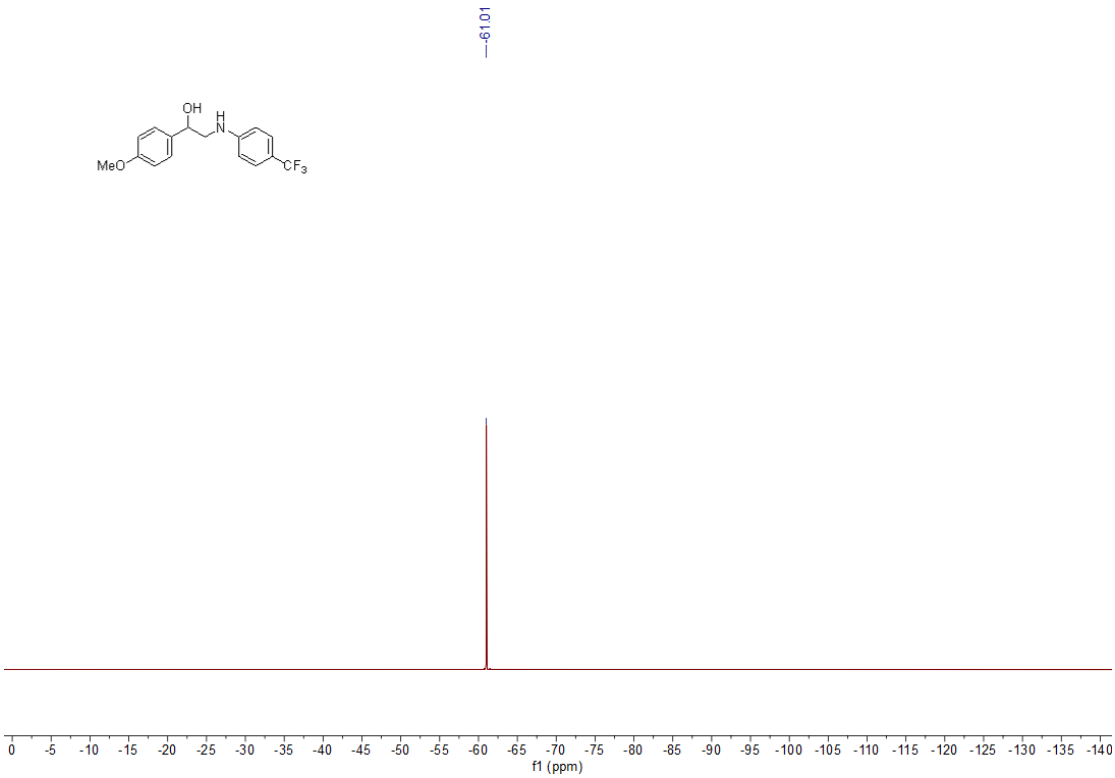
^{1}H NMR Spectrum of **3e**



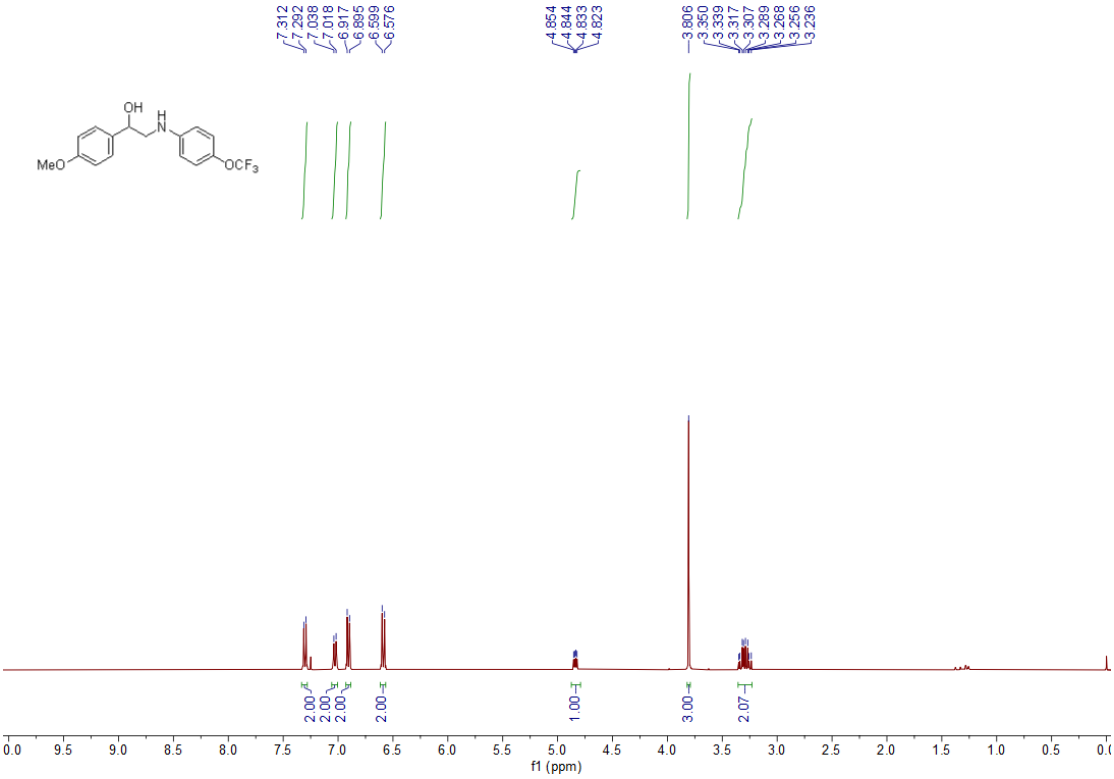
^{13}C NMR Spectrum of **3e**



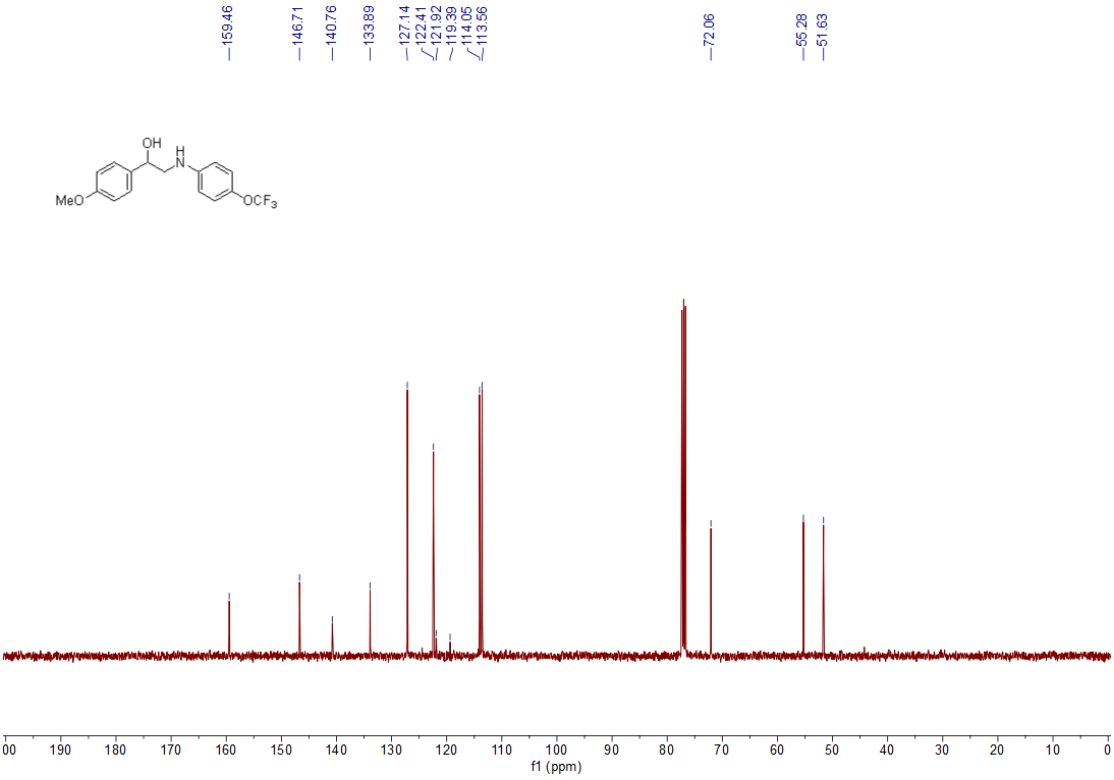
^{19}F NMR Spectrum of **3e**



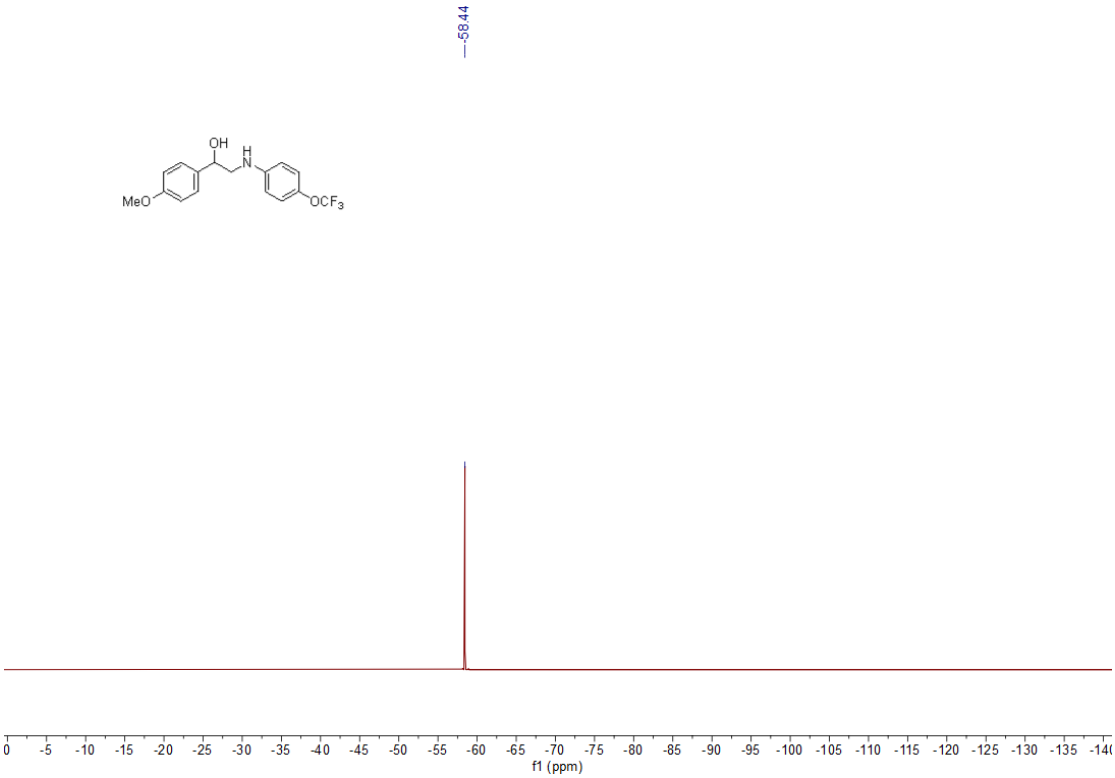
^{1}H NMR Spectrum of **3f**



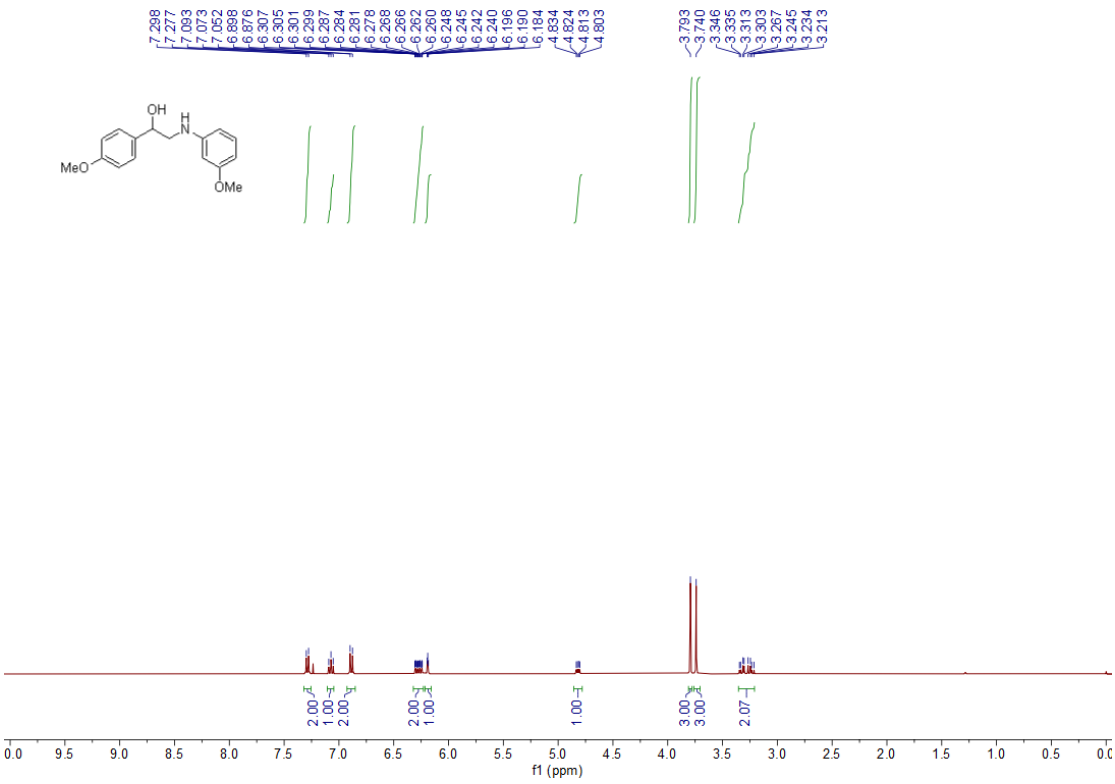
^{13}C NMR Spectrum of **3f**



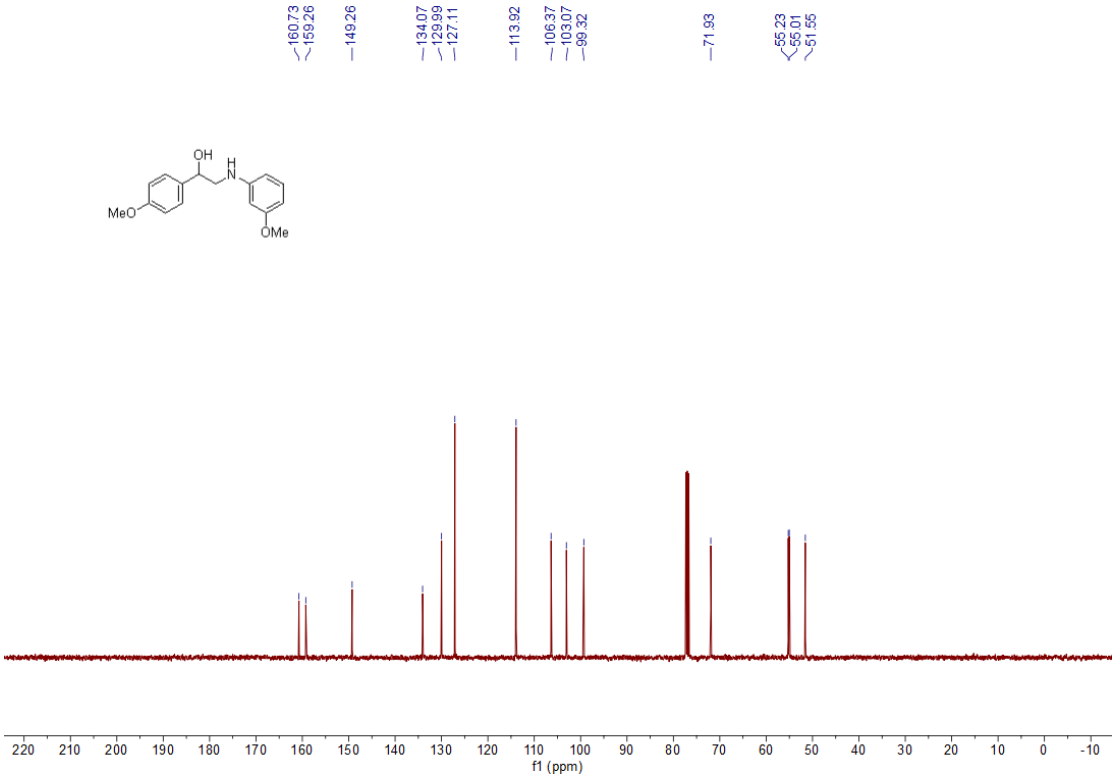
^{19}F NMR Spectrum of **3f**



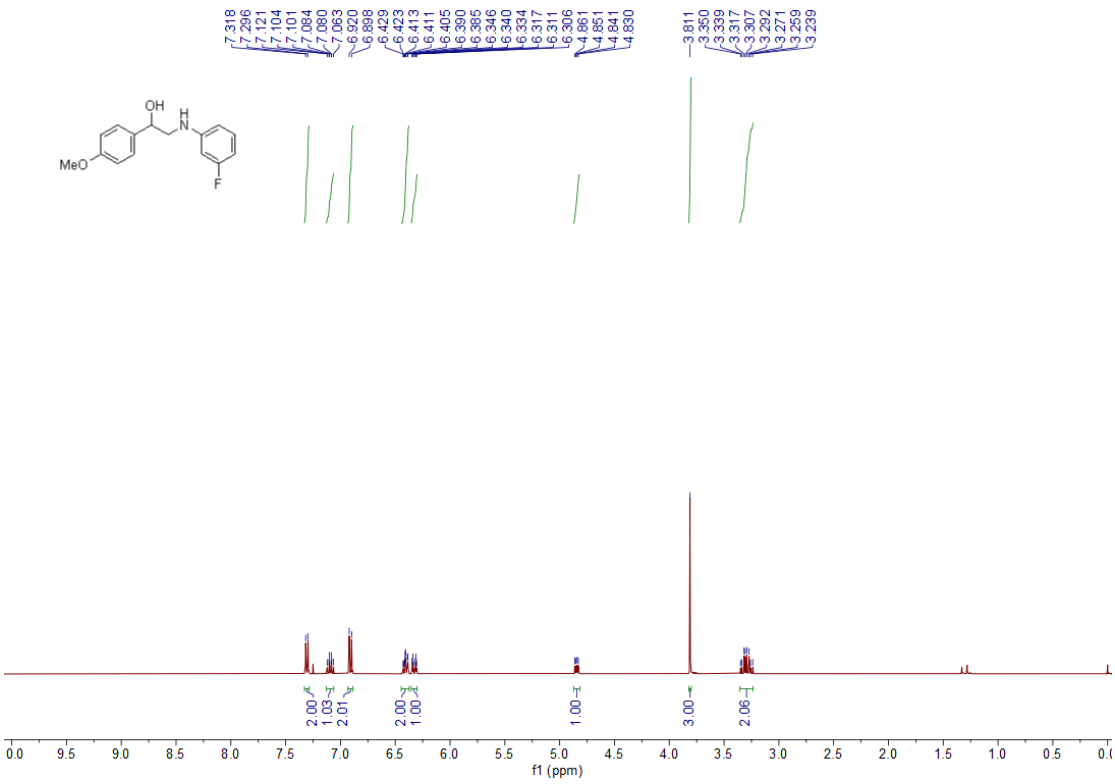
^{1}H NMR Spectrum of **3g**



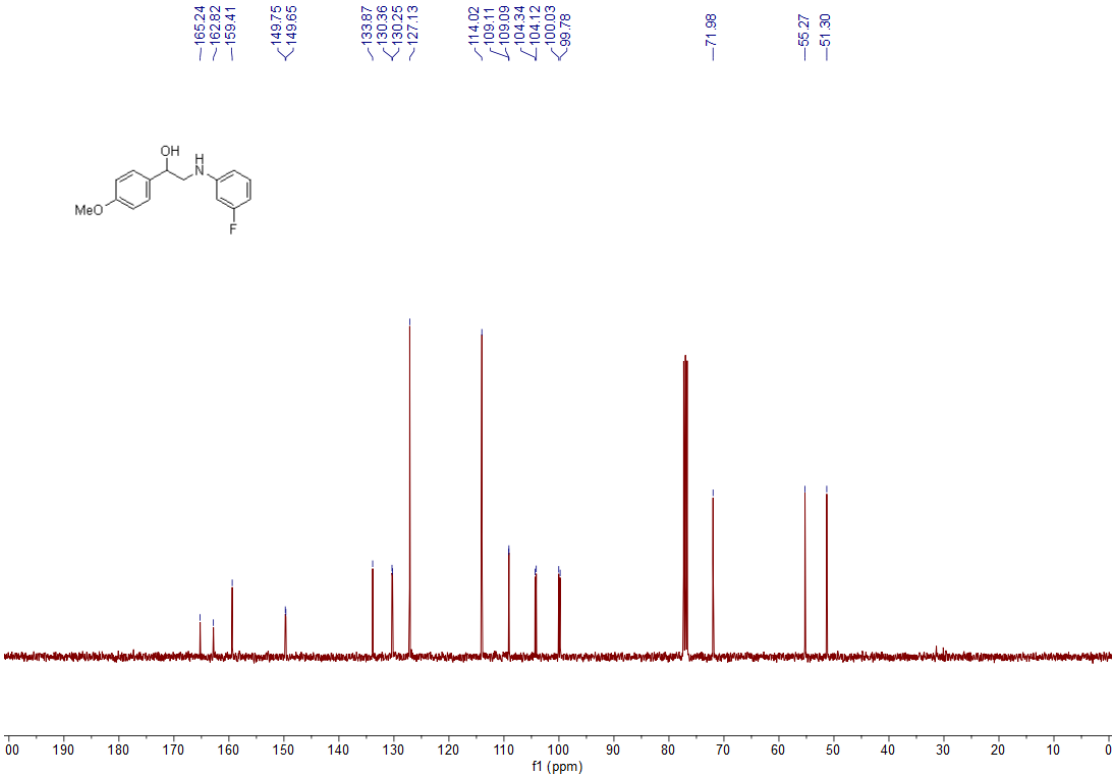
^{13}C NMR Spectrum of **3g**



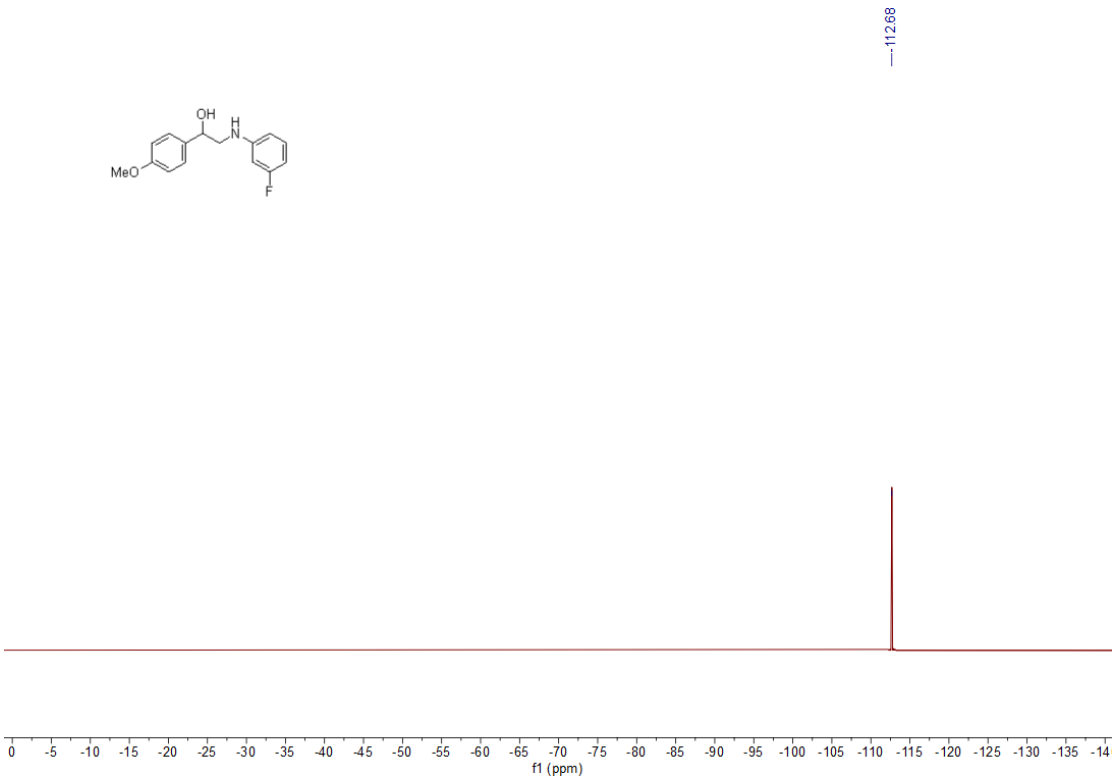
^{1}H NMR Spectrum of **3h**



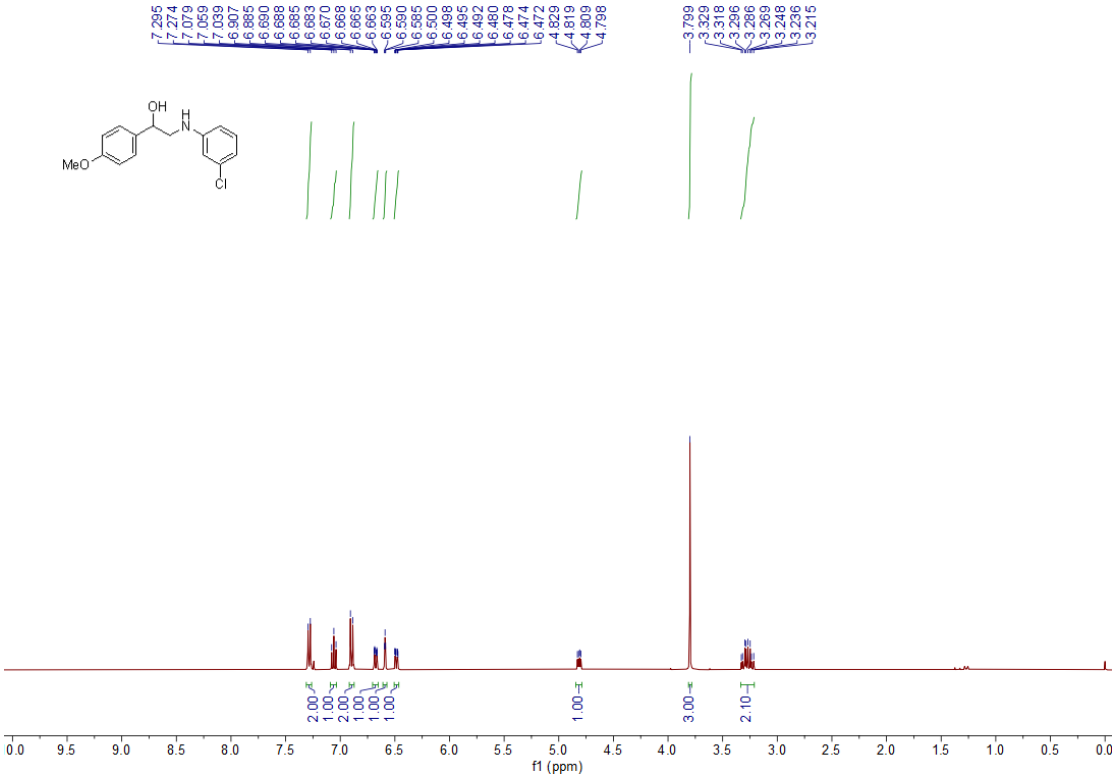
^{13}C NMR Spectrum of **3h**



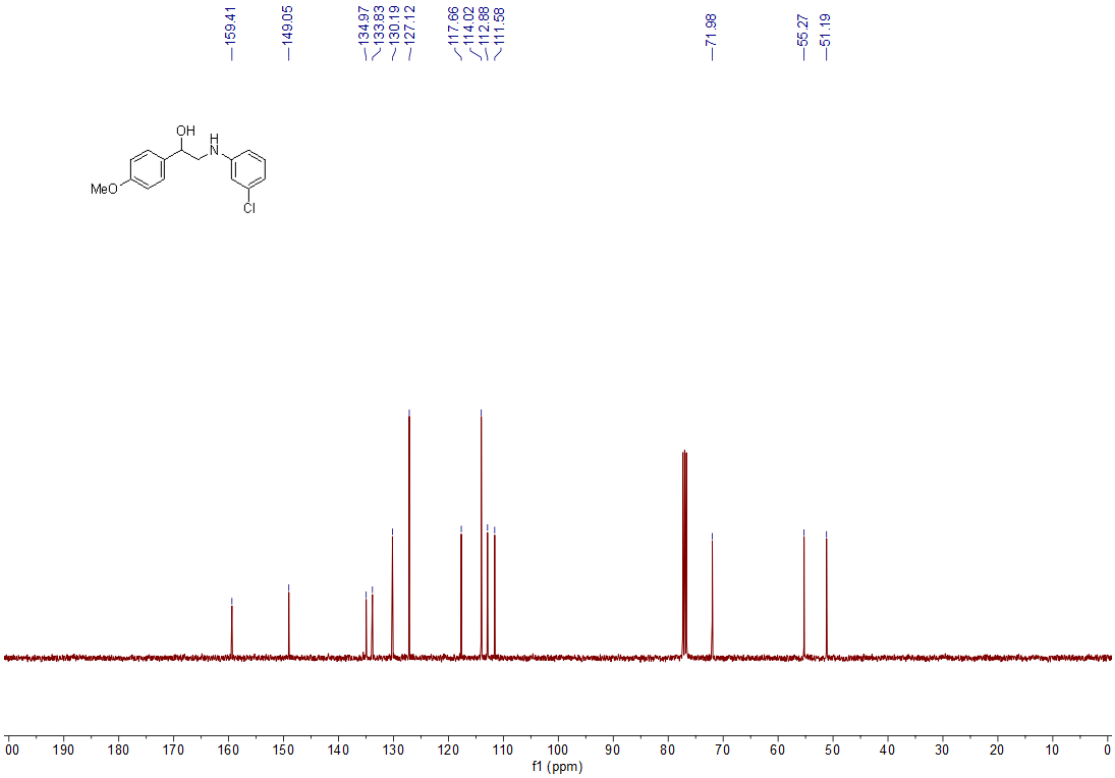
^{19}F NMR Spectrum of **3h**



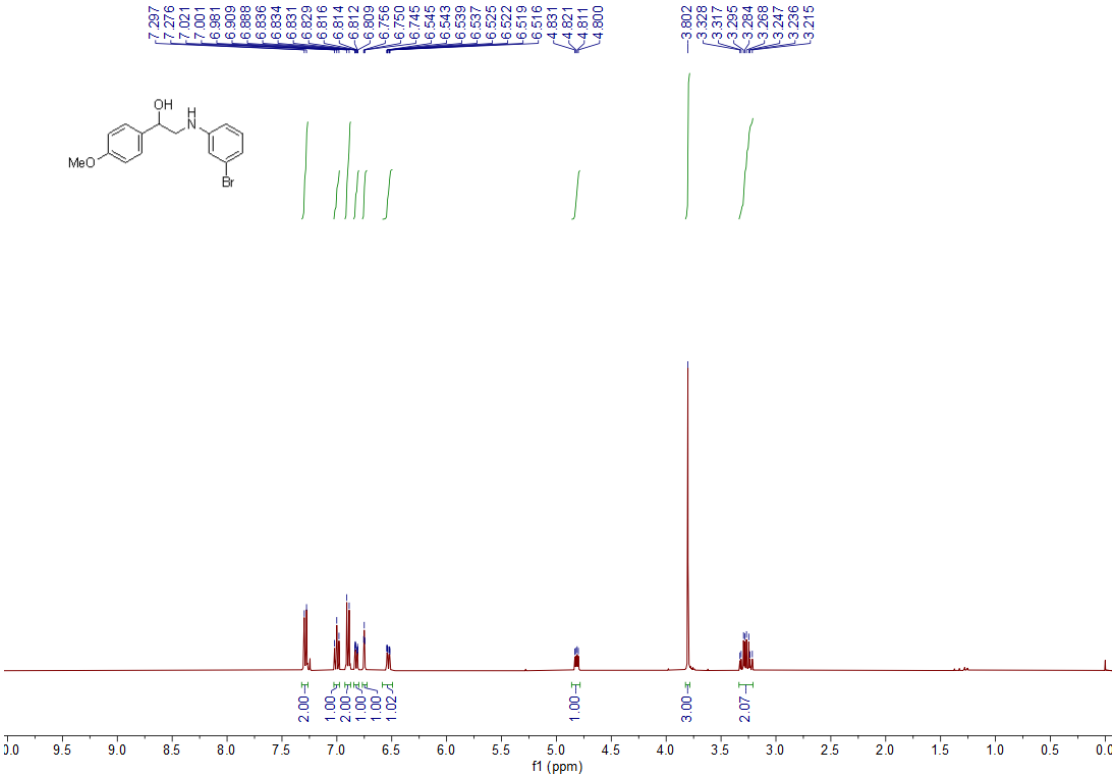
^{1}H NMR Spectrum of **3i**



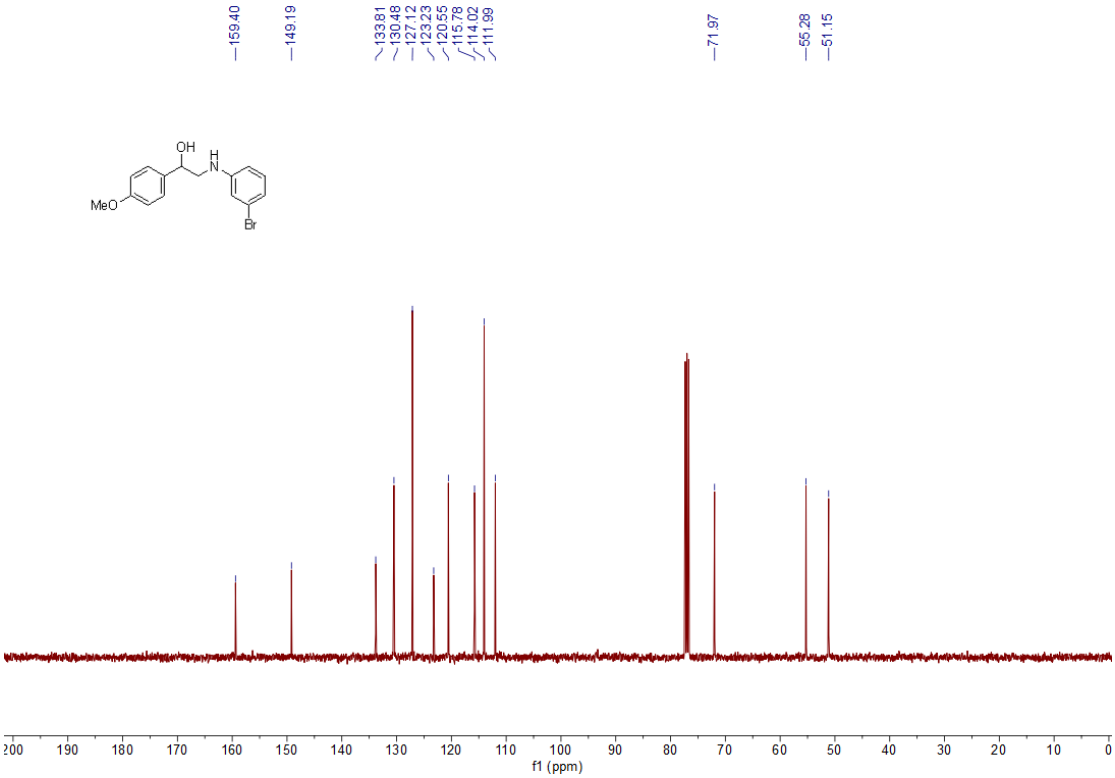
^{13}C NMR Spectrum of **3i**



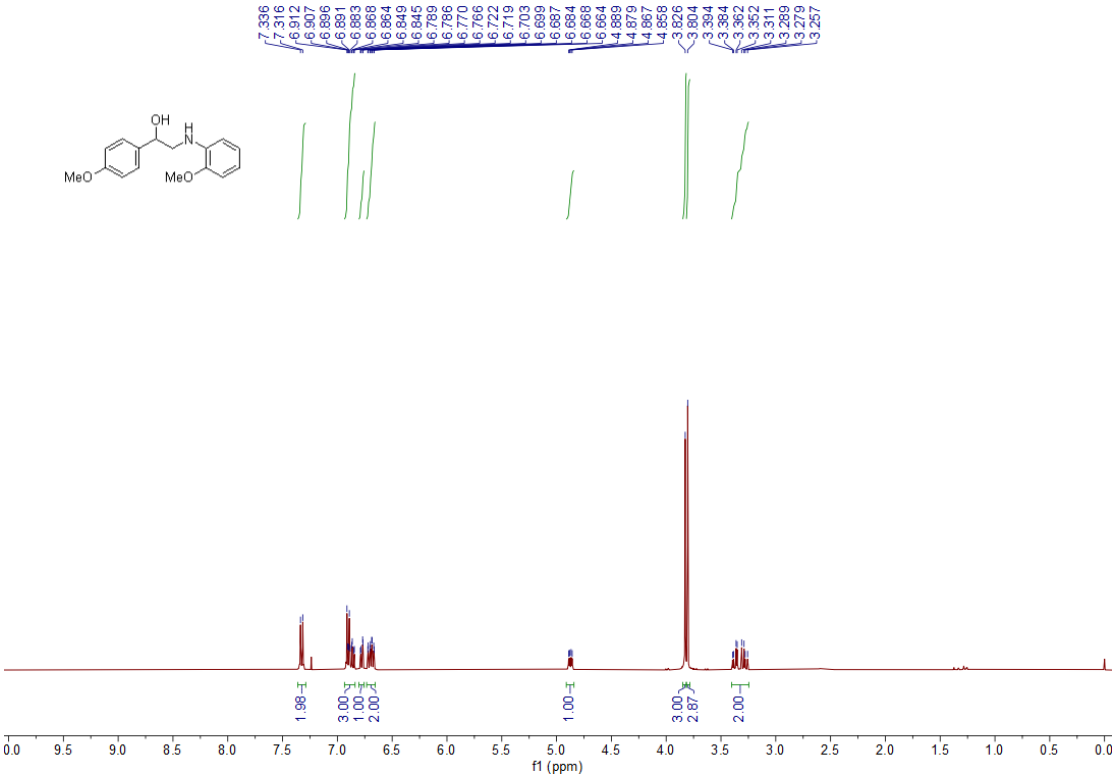
^{1}H NMR Spectrum of **3j**



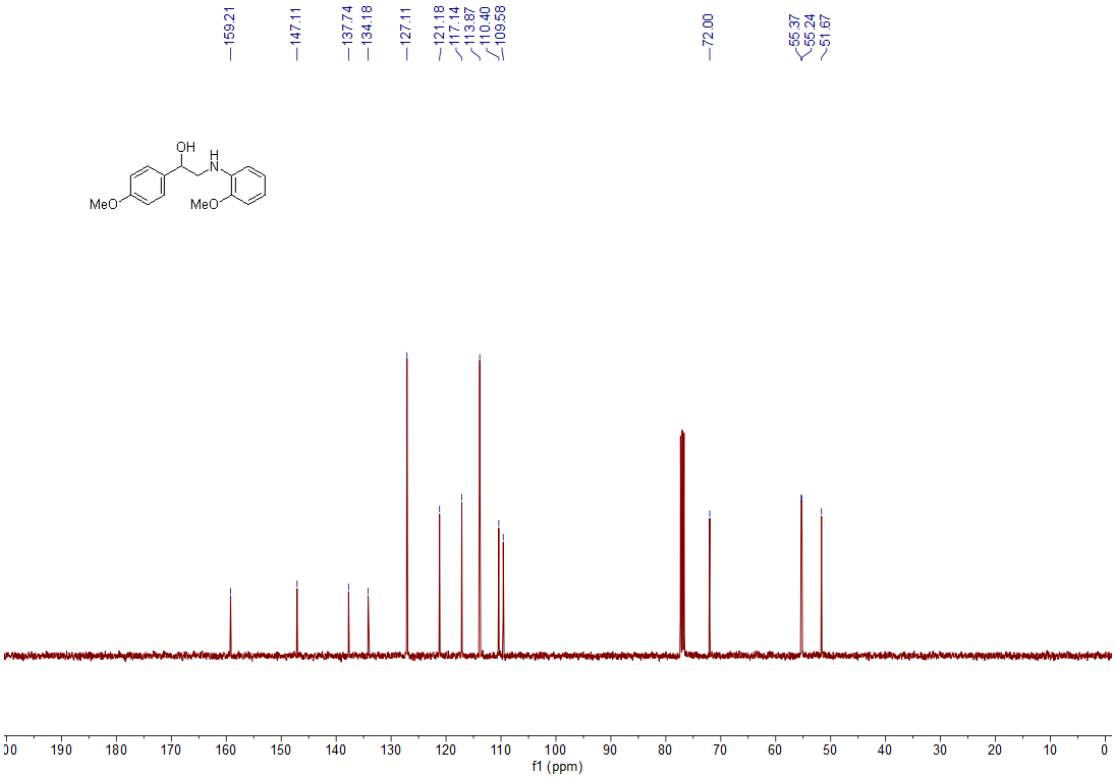
^{13}C NMR Spectrum of **3j**



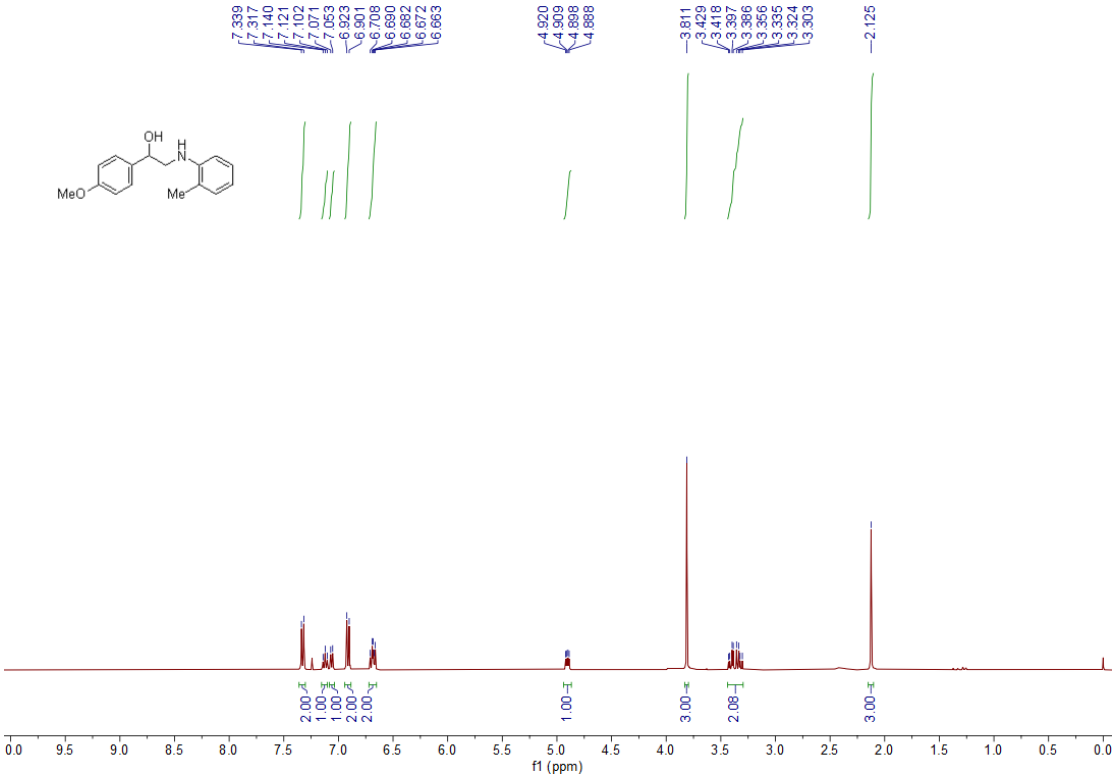
^{1}H NMR Spectrum of **3k**



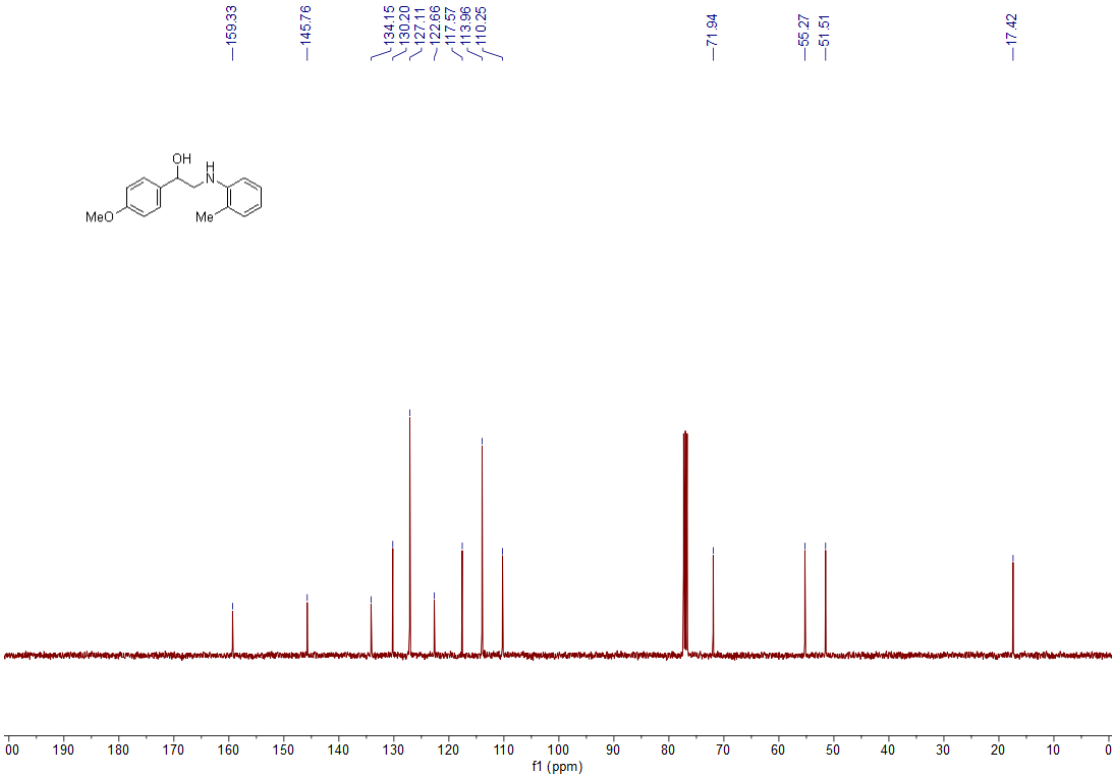
^{13}C NMR Spectrum of **3k**



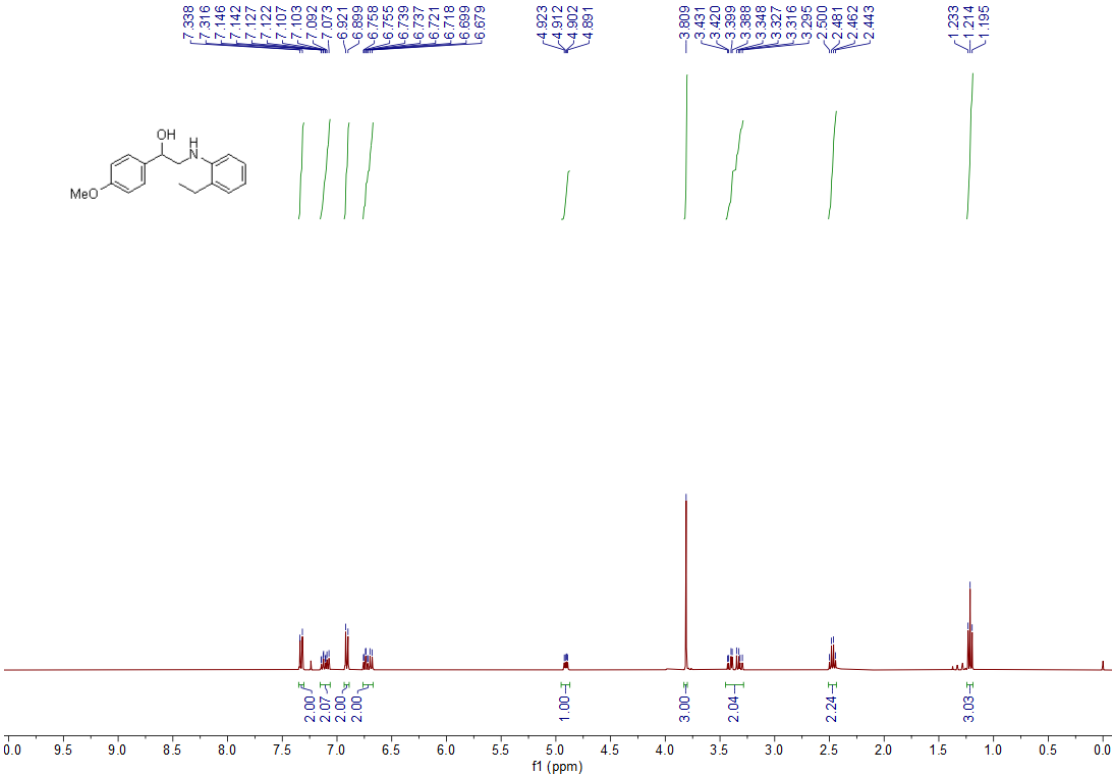
^{1}H NMR Spectrum of **3l**



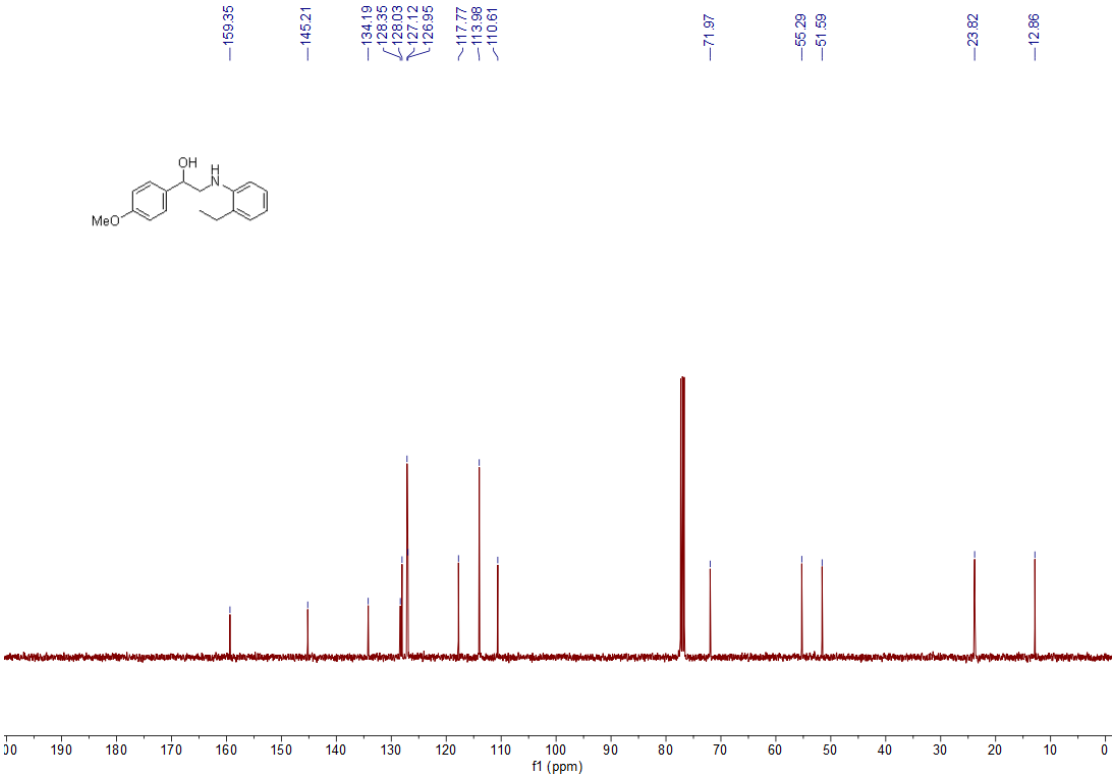
^{13}C NMR Spectrum of **3l**



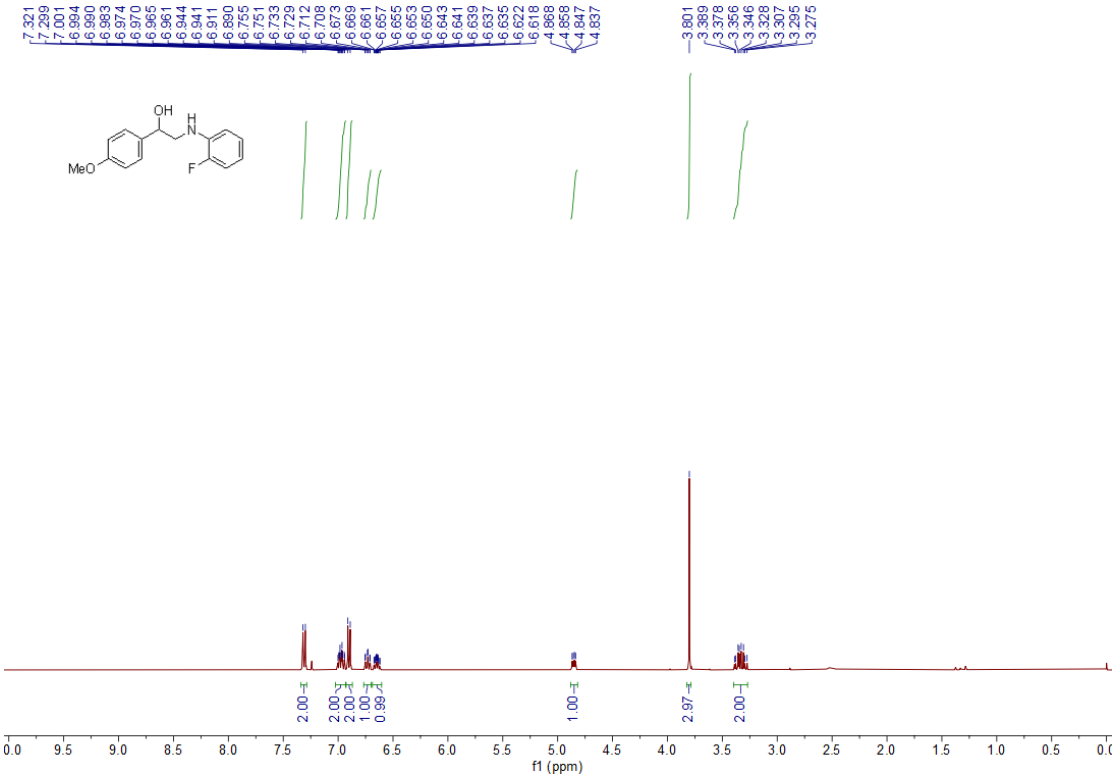
^{1}H NMR Spectrum of **3m**



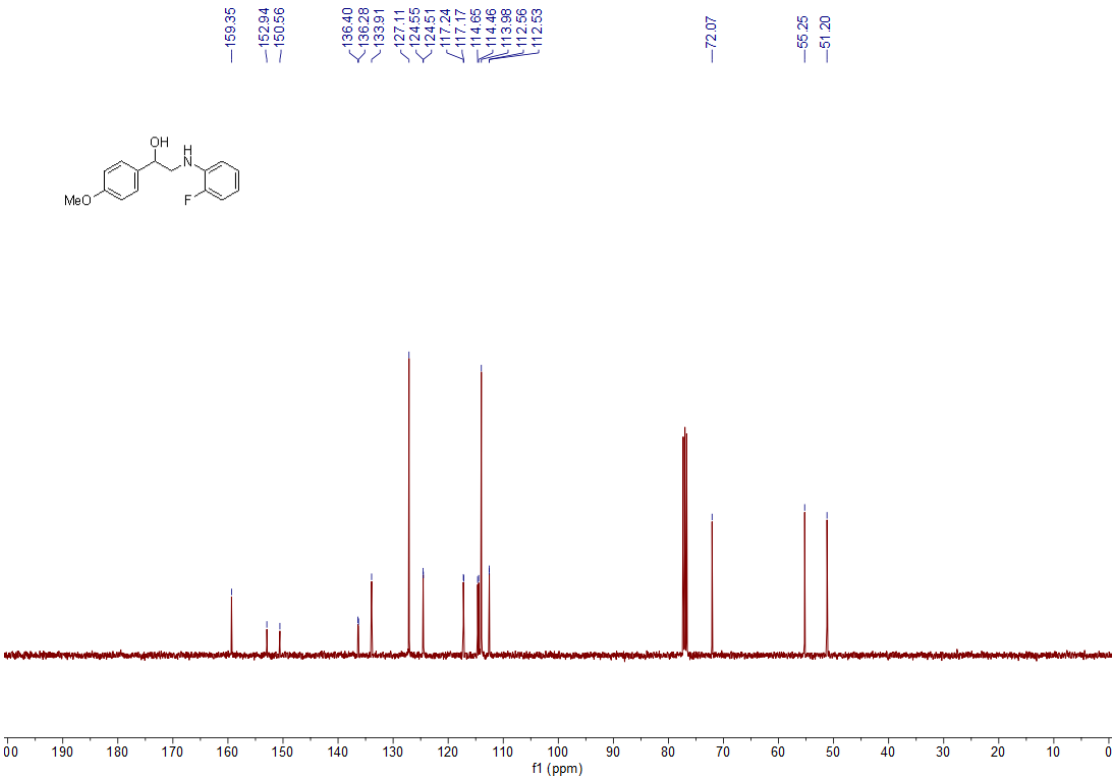
^{13}C NMR Spectrum of **3m**



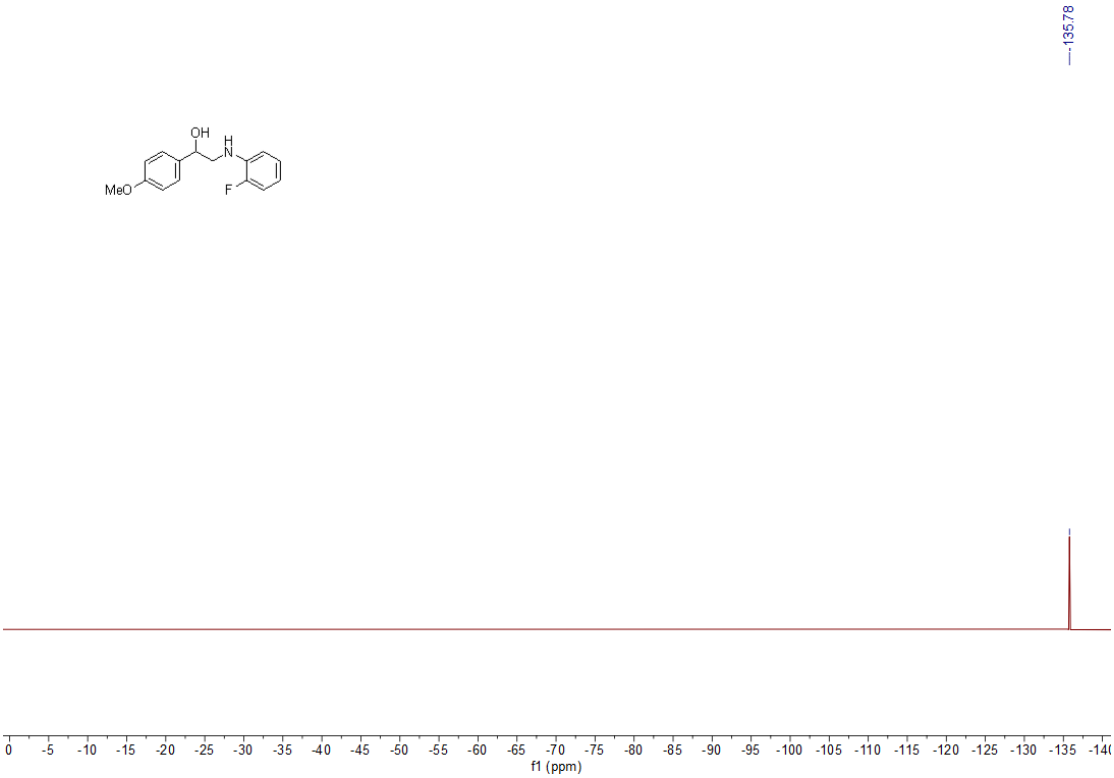
^{1}H NMR Spectrum of **3n**



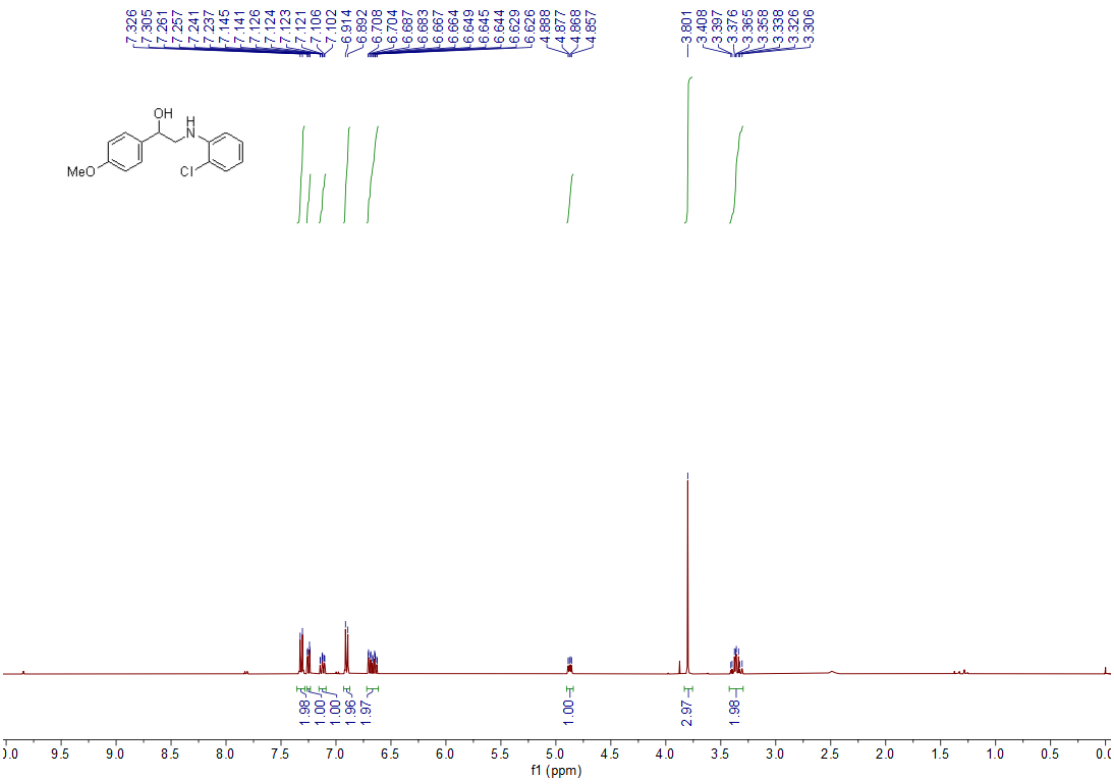
^{13}C NMR Spectrum of **3n**



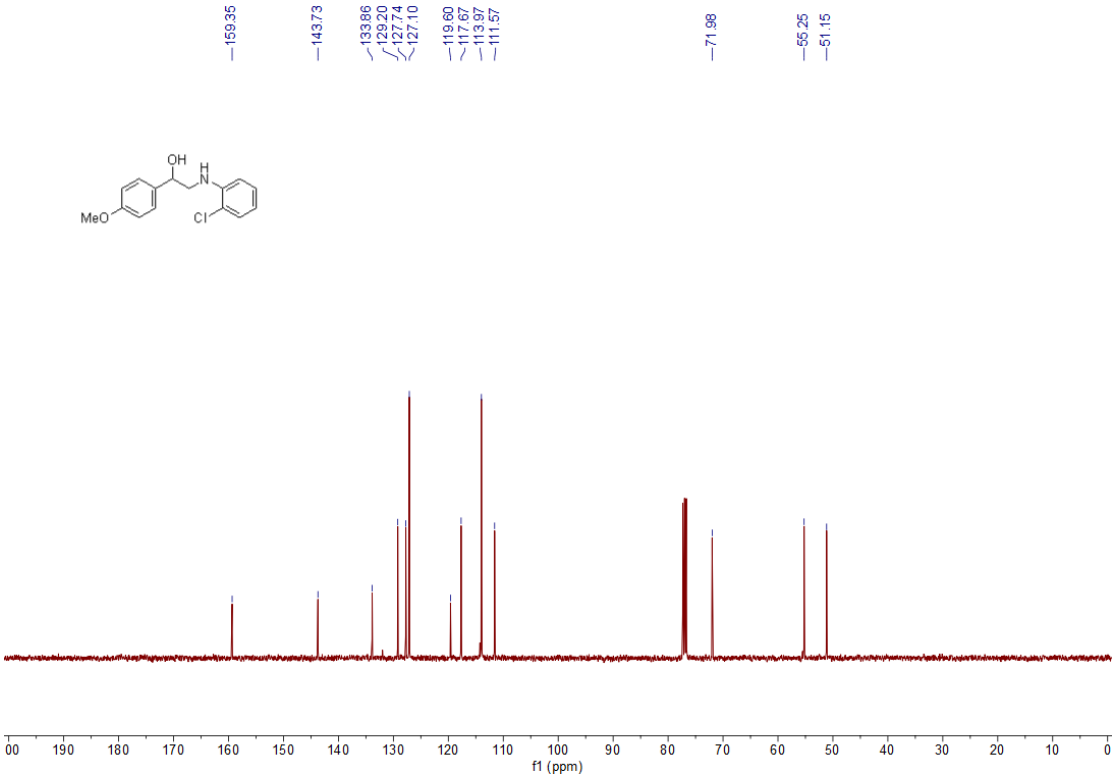
^{19}F NMR Spectrum of **3n**



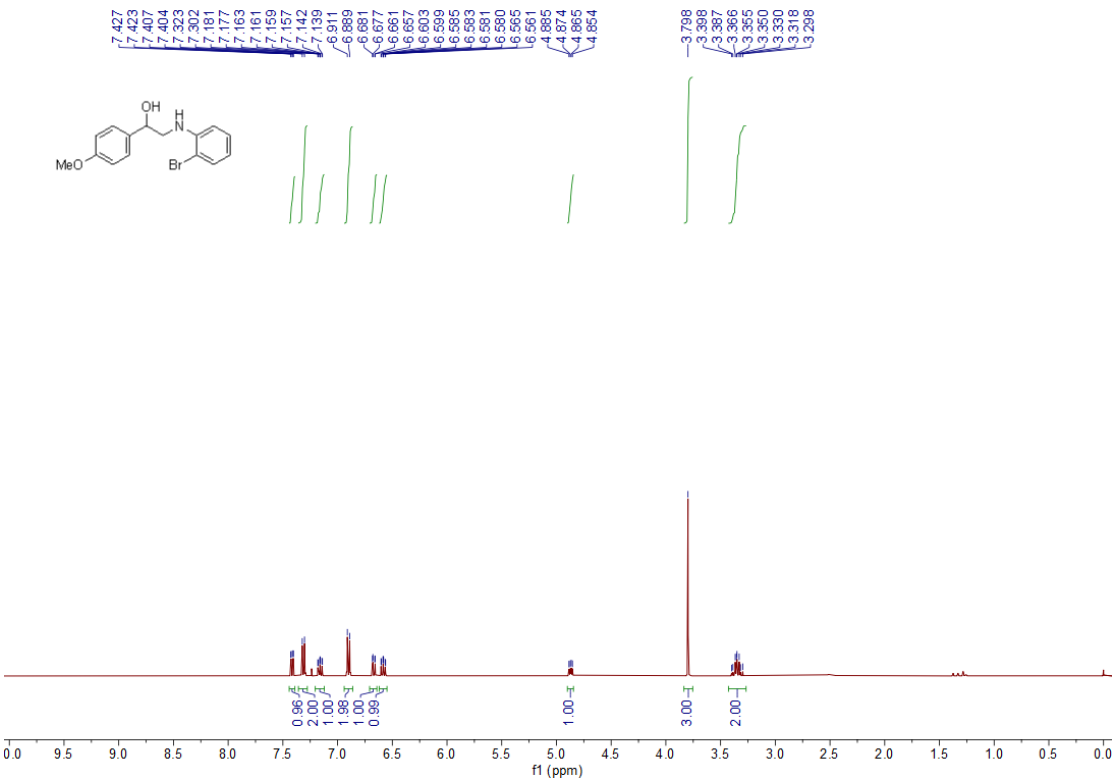
^{1}H NMR Spectrum of **3o**



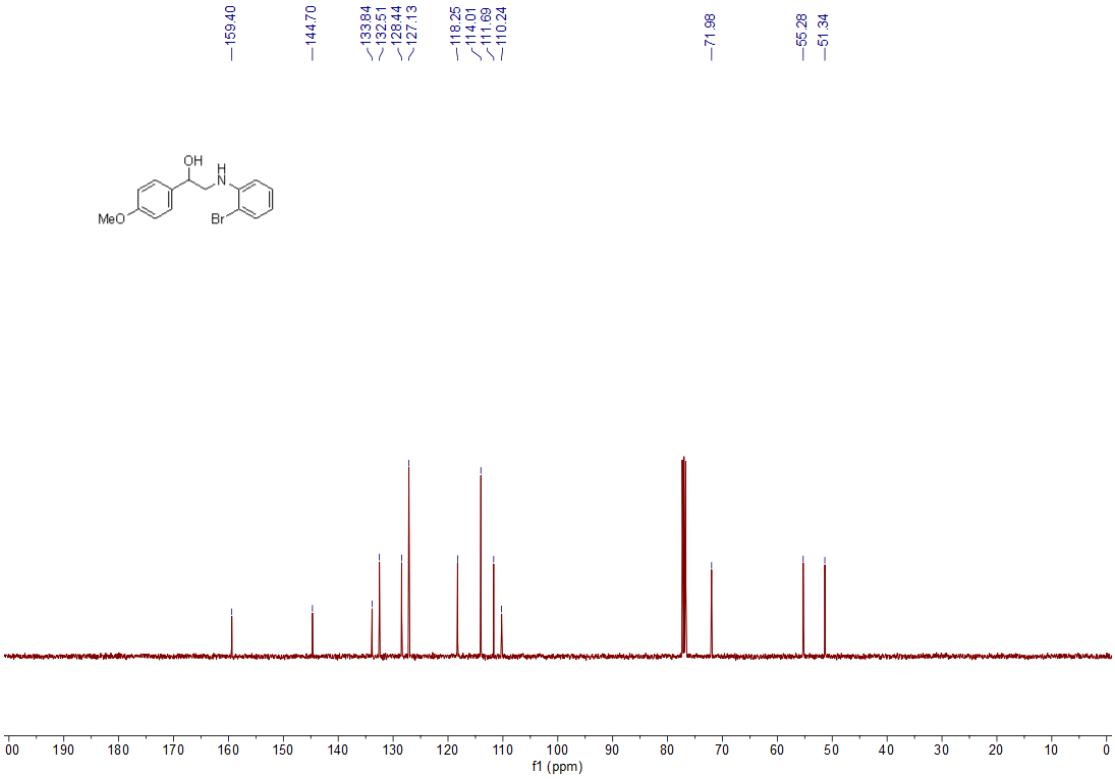
^{13}C NMR Spectrum of **3o**



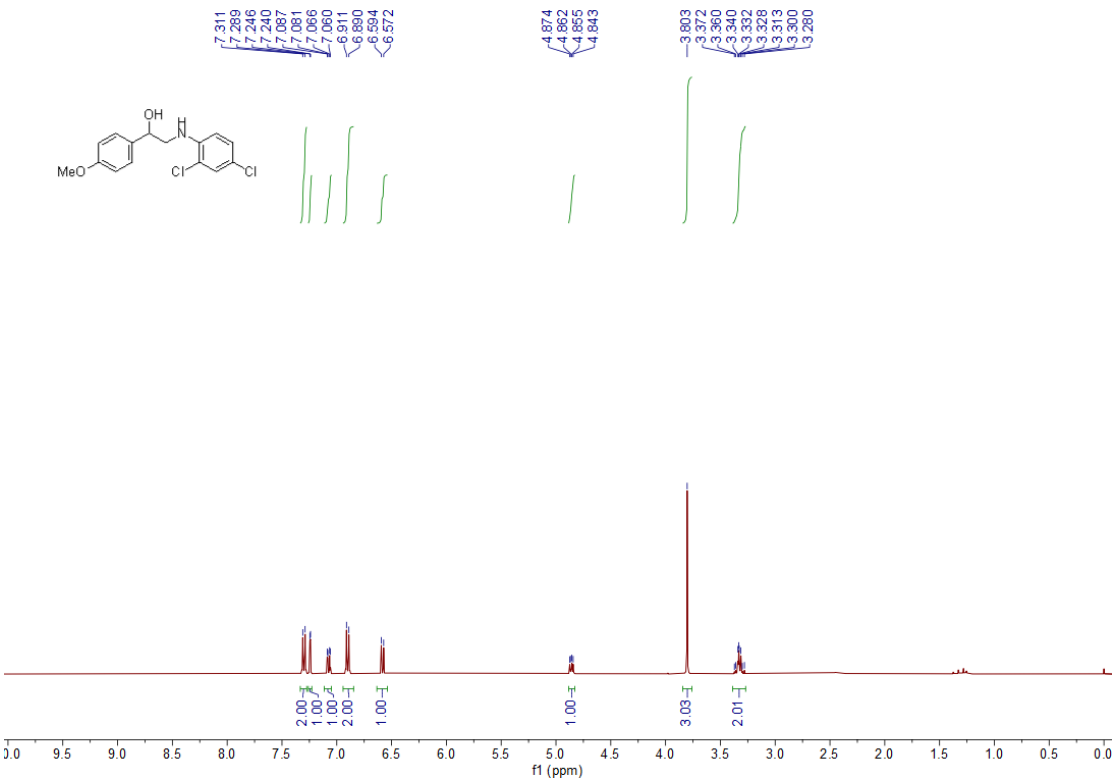
^{1}H NMR Spectrum of **3p**



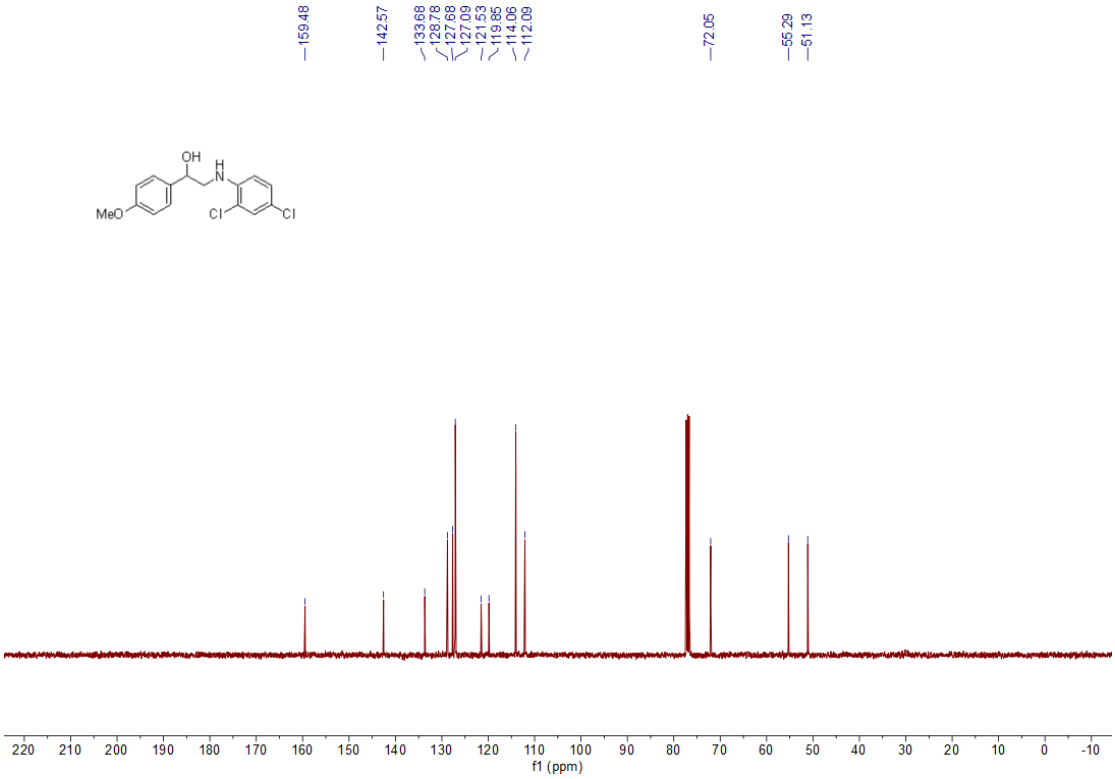
^{13}C NMR Spectrum of **3p**



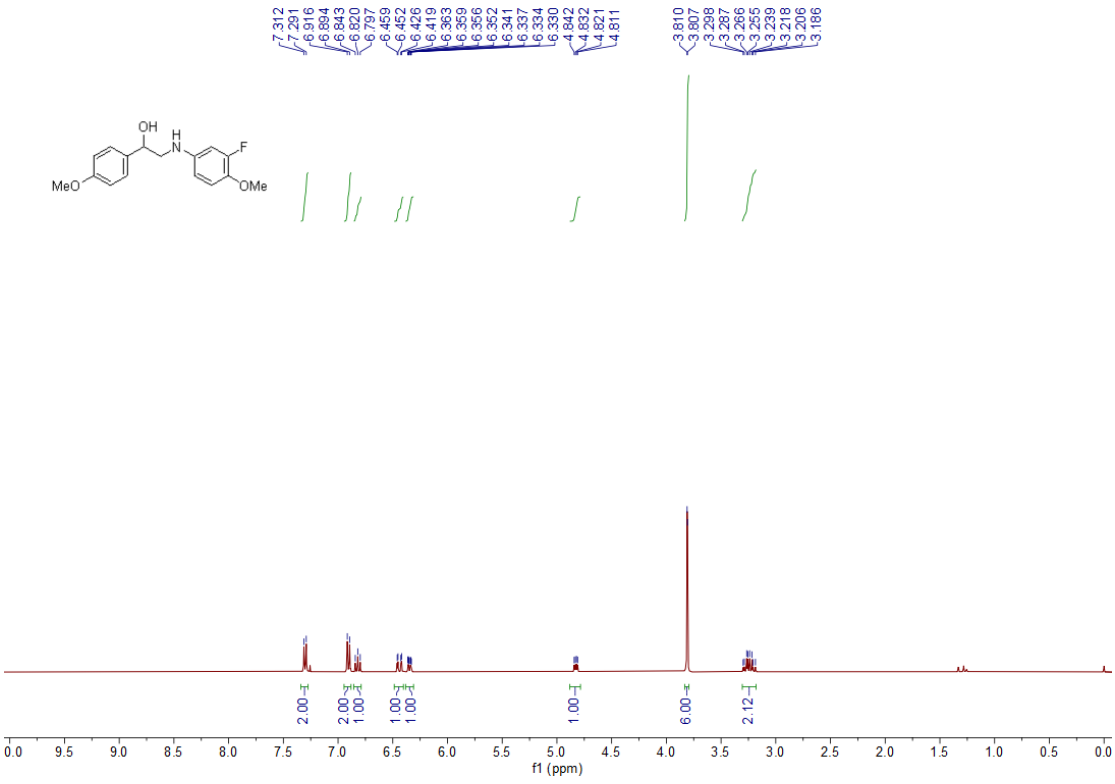
^{1}H NMR Spectrum of **3q**



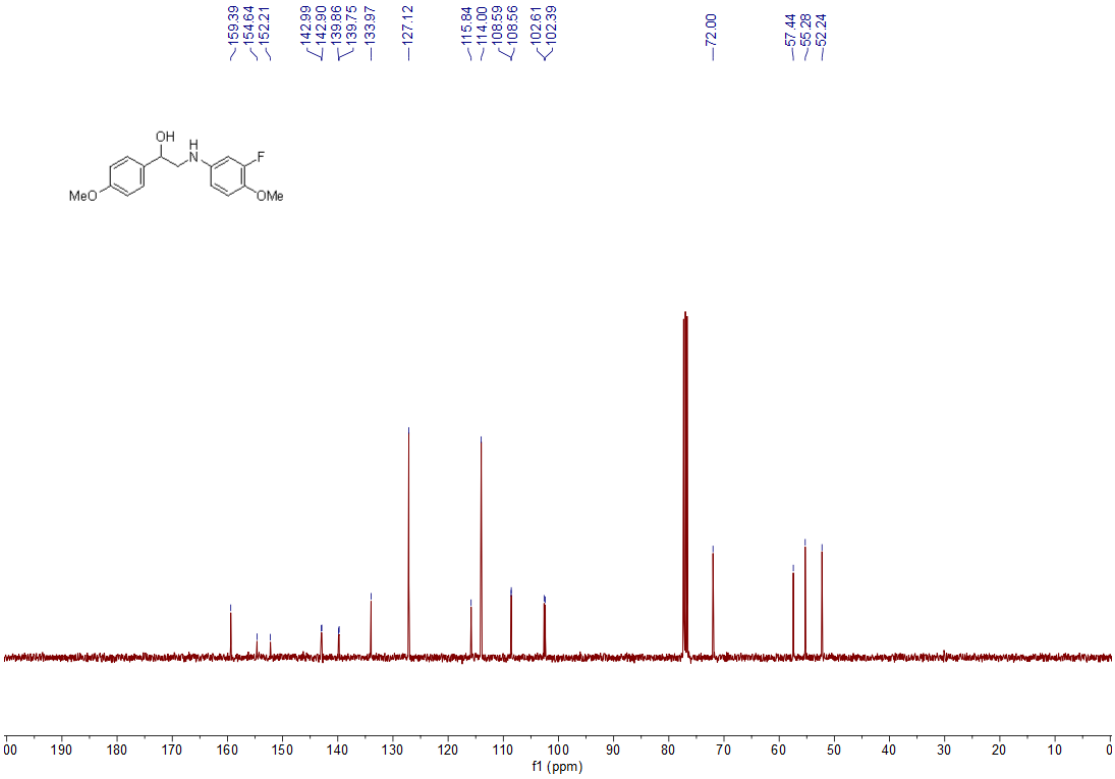
^{13}C NMR Spectrum of **3q**



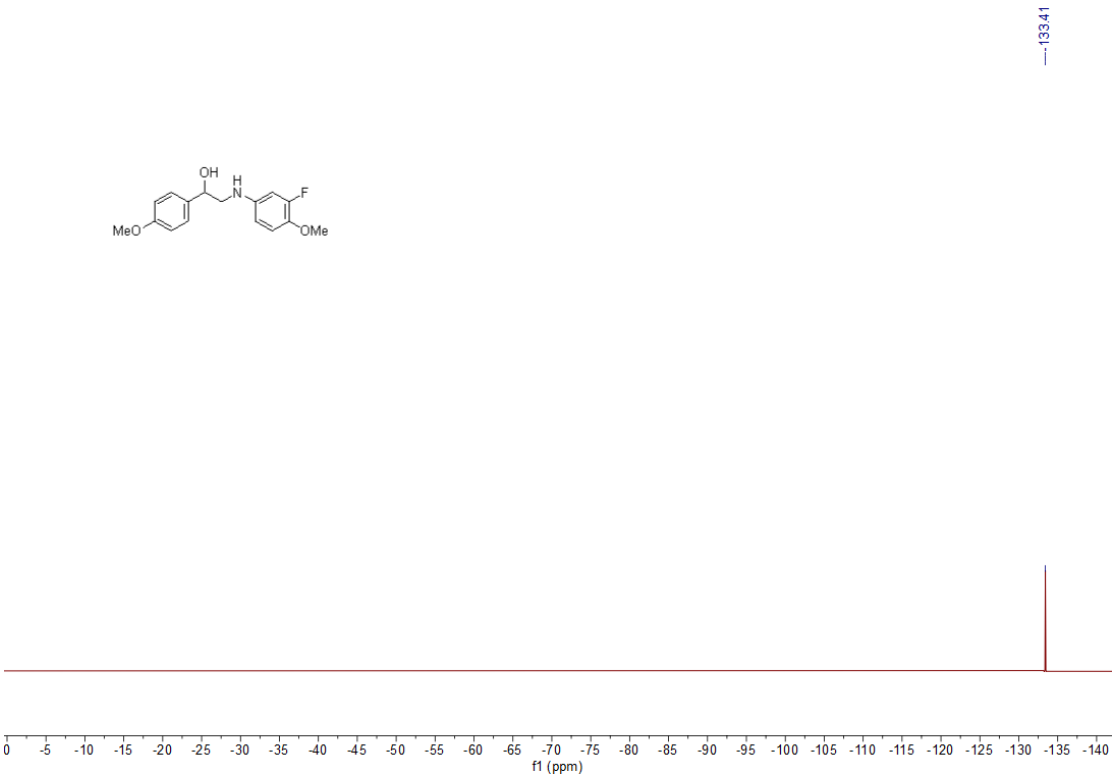
^{1}H NMR Spectrum of **3r**



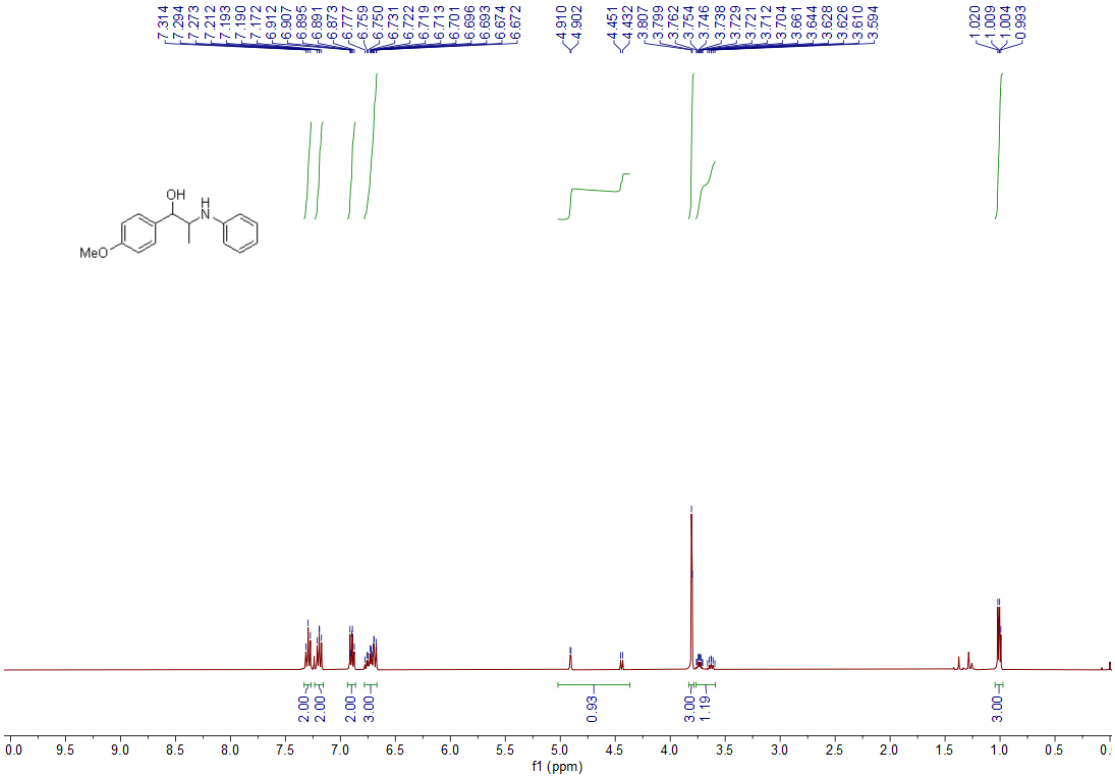
^{13}C NMR Spectrum of **3r**



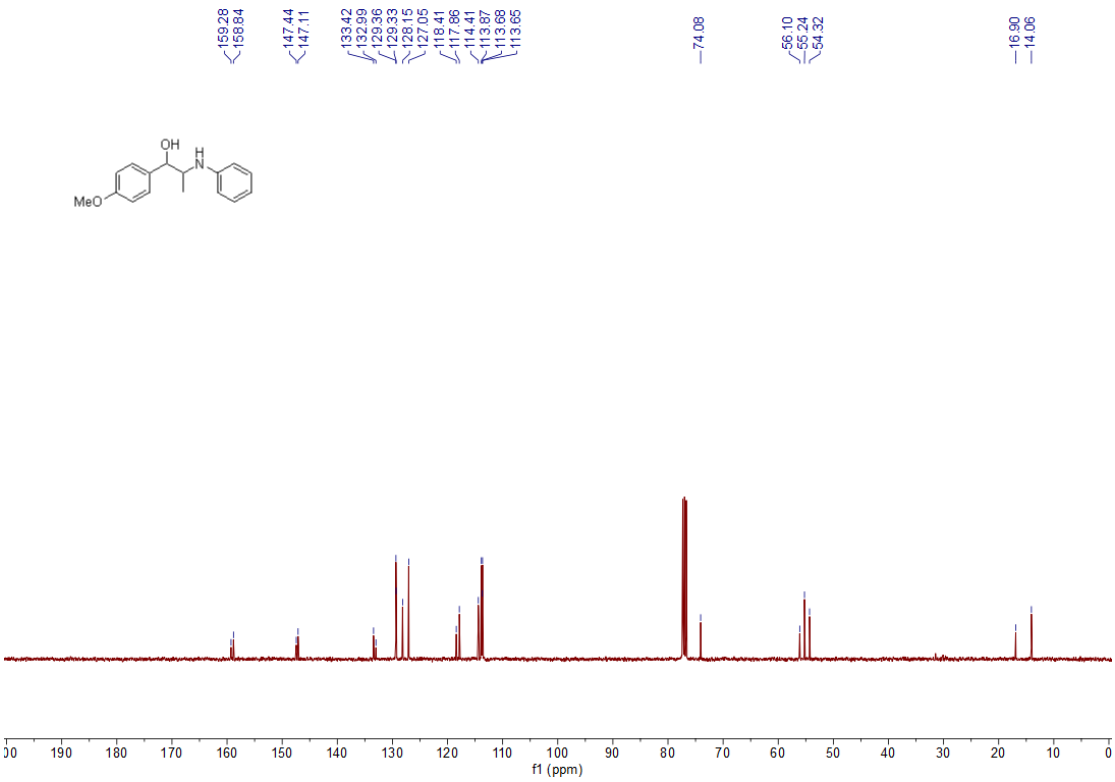
^{19}F NMR Spectrum of **3r**



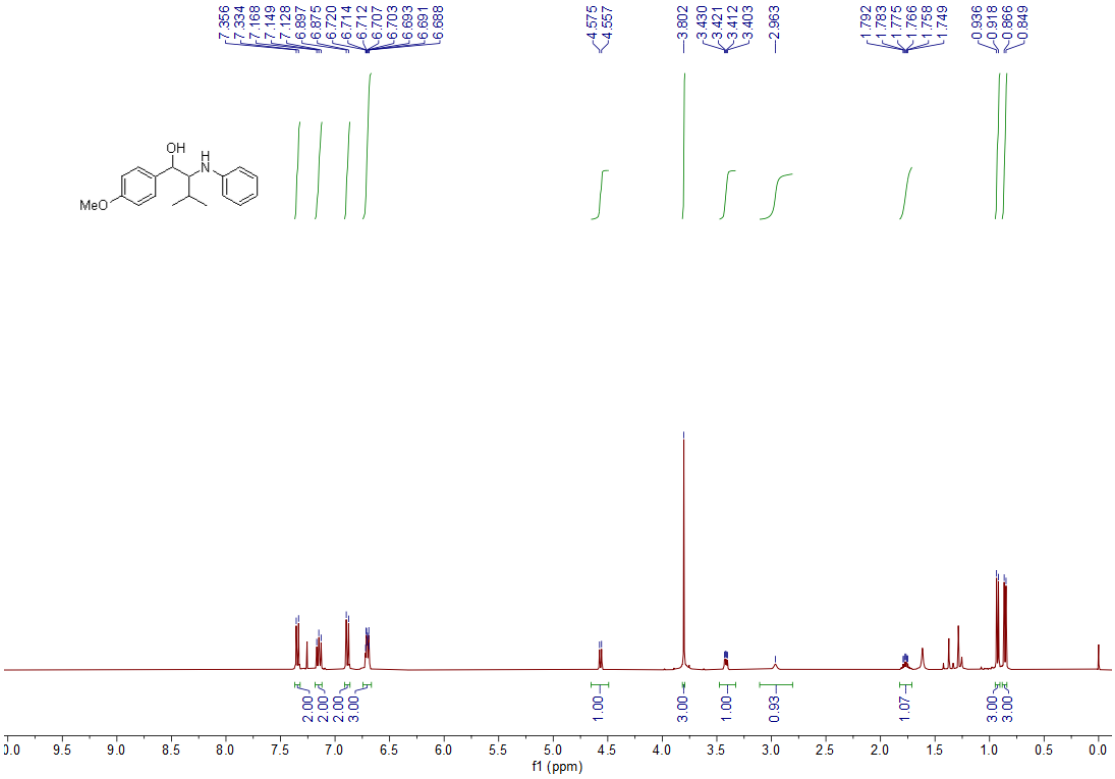
^{1}H NMR Spectrum of **3s**



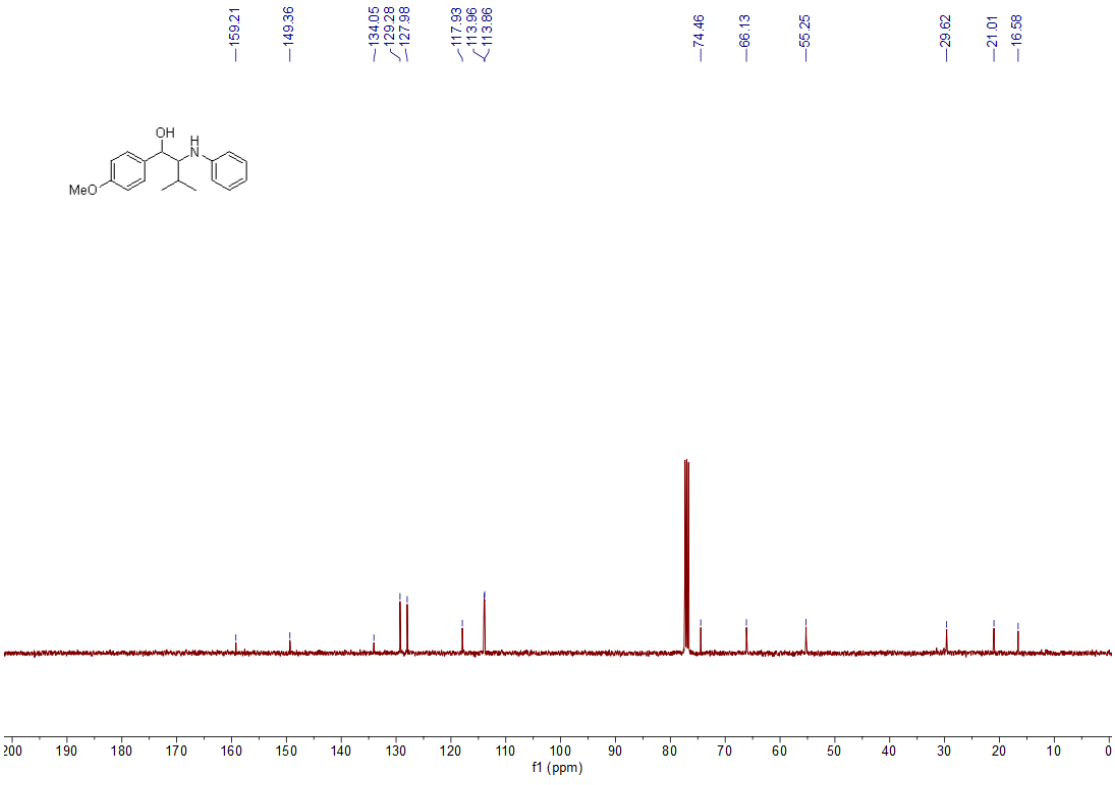
^{13}C NMR Spectrum of **3s**



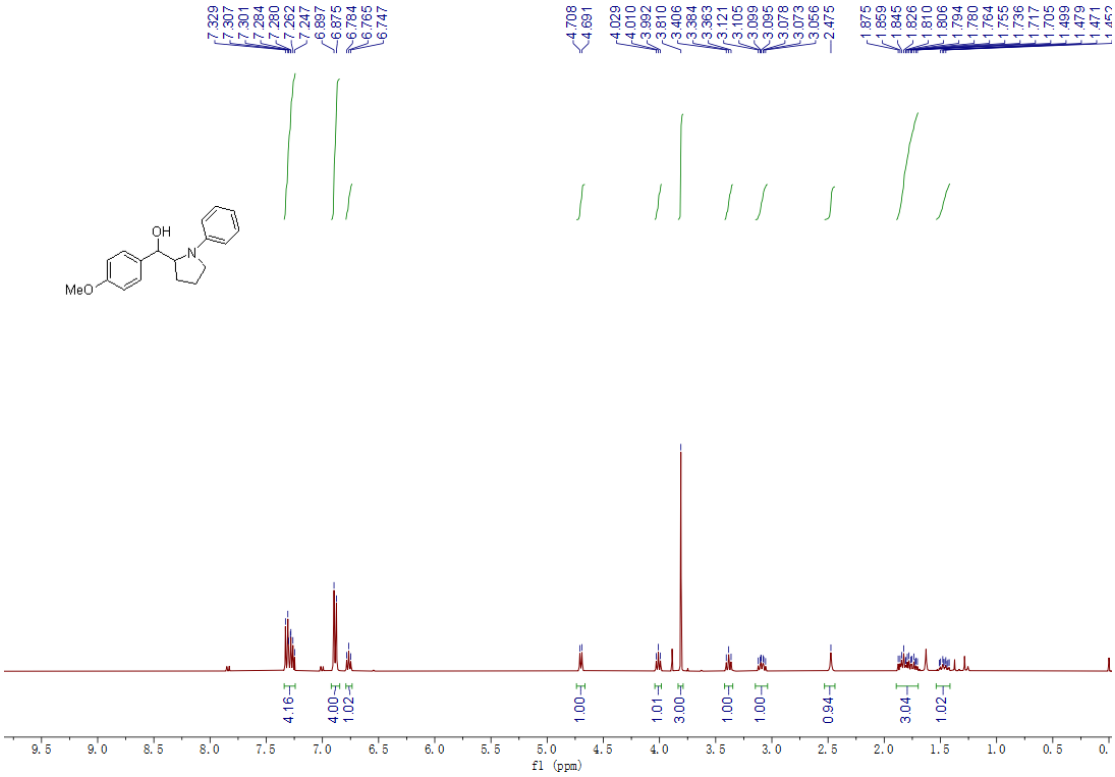
^{1}H NMR Spectrum of **3t**



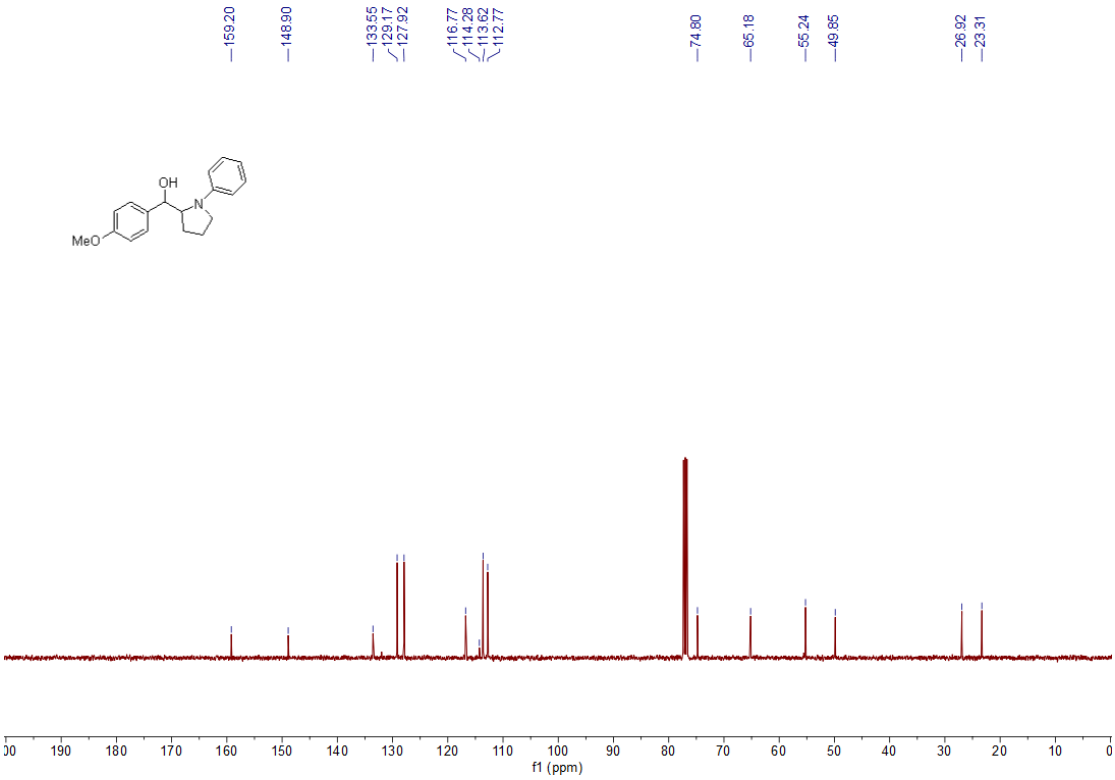
^{13}C NMR Spectrum of **3t**



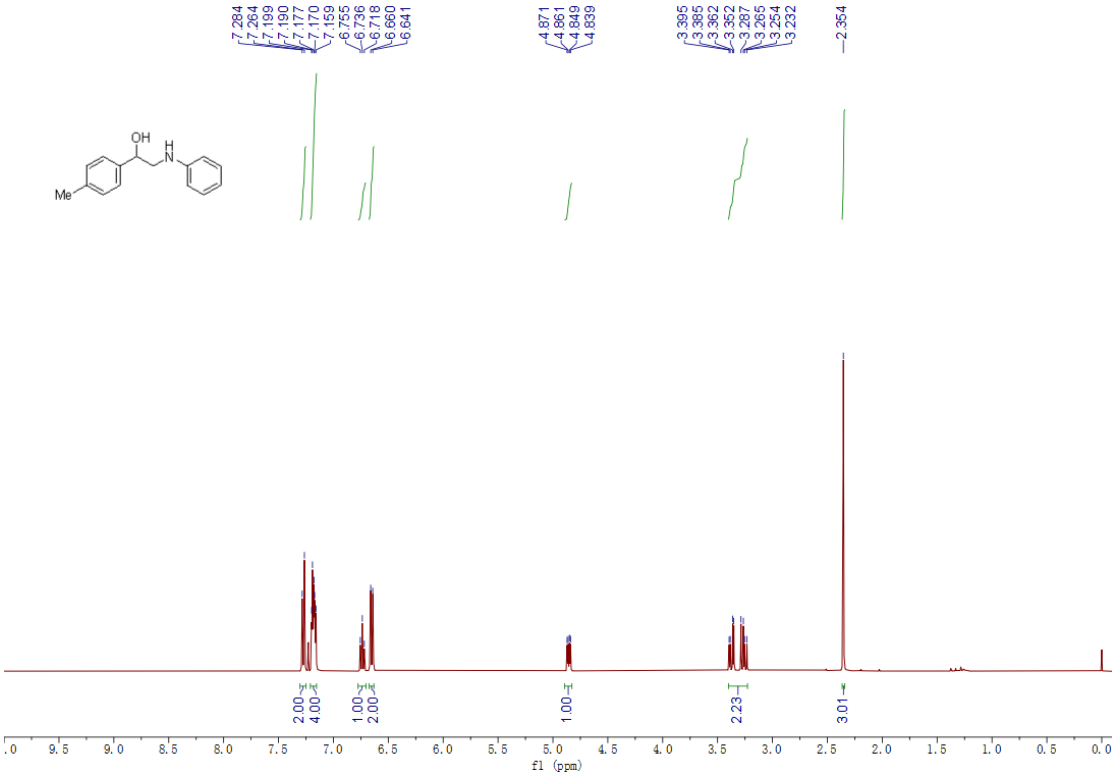
^{1}H NMR Spectrum of **3u**



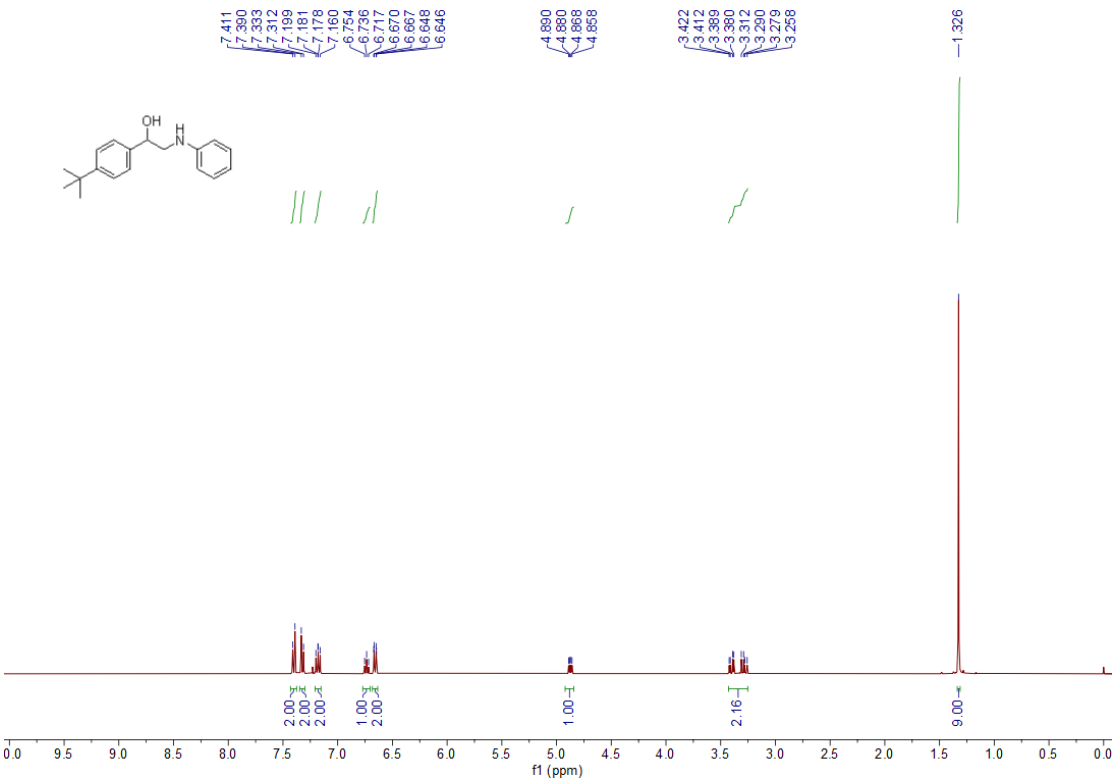
^{13}C NMR Spectrum of **3u**



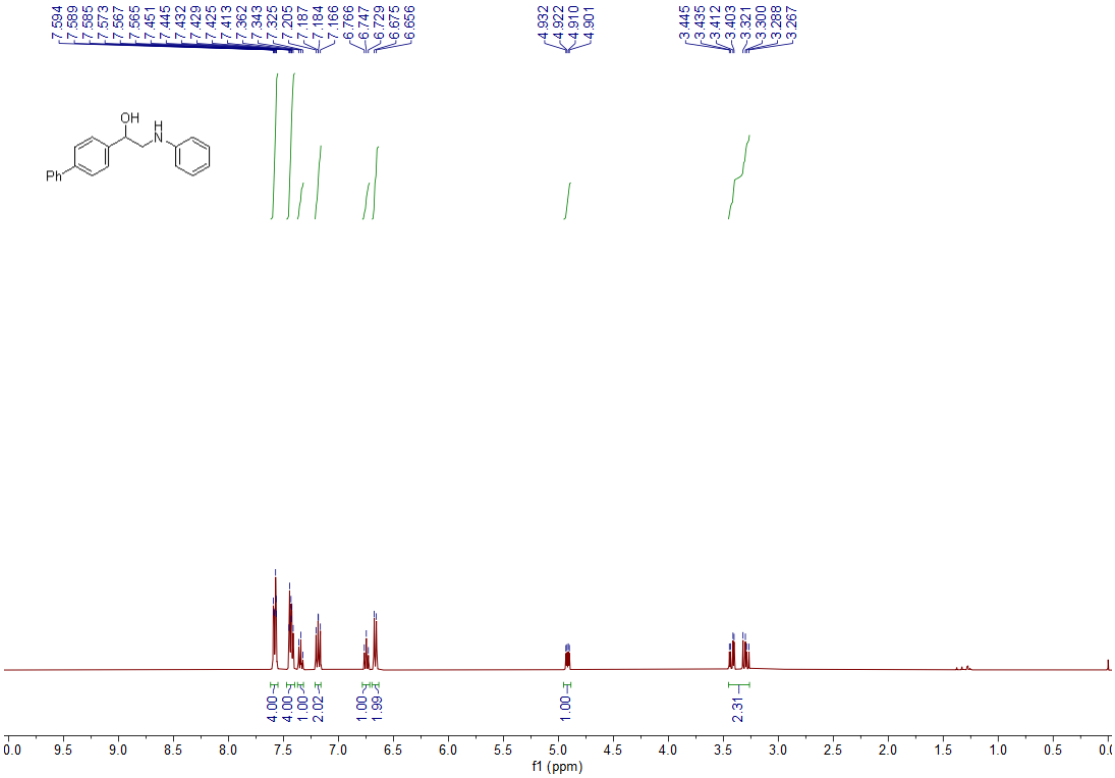
^{1}H NMR Spectrum of **3v**



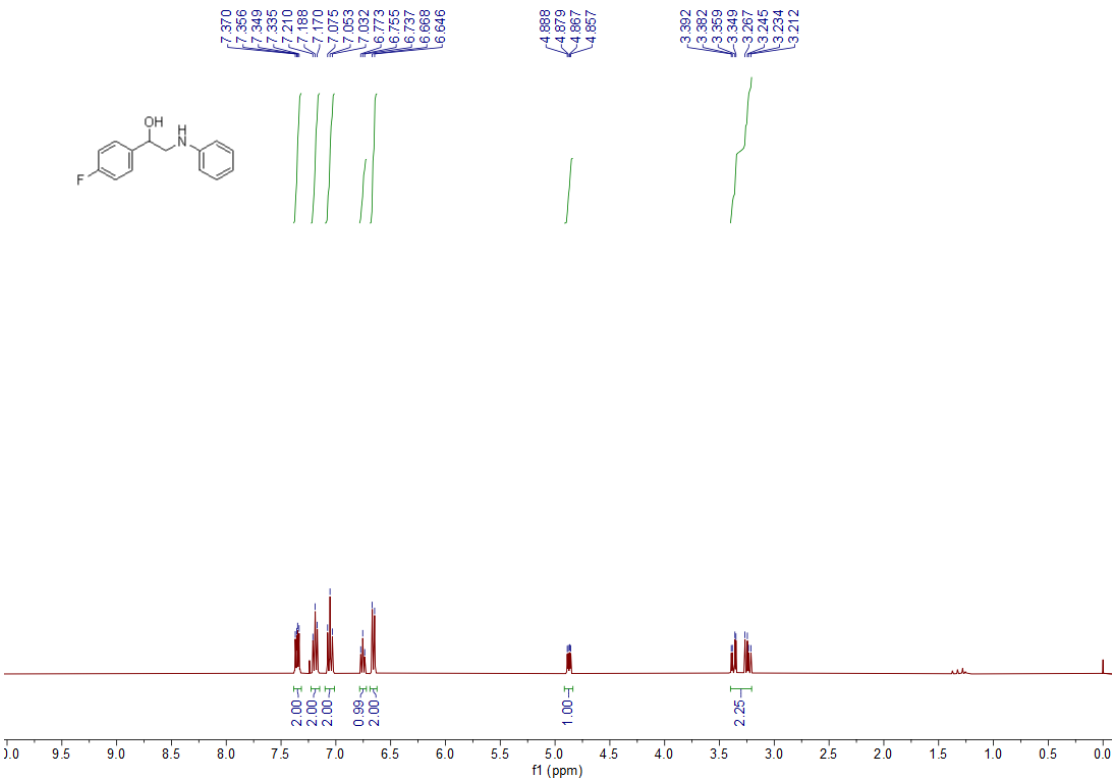
^{1}H NMR Spectrum of **3w**



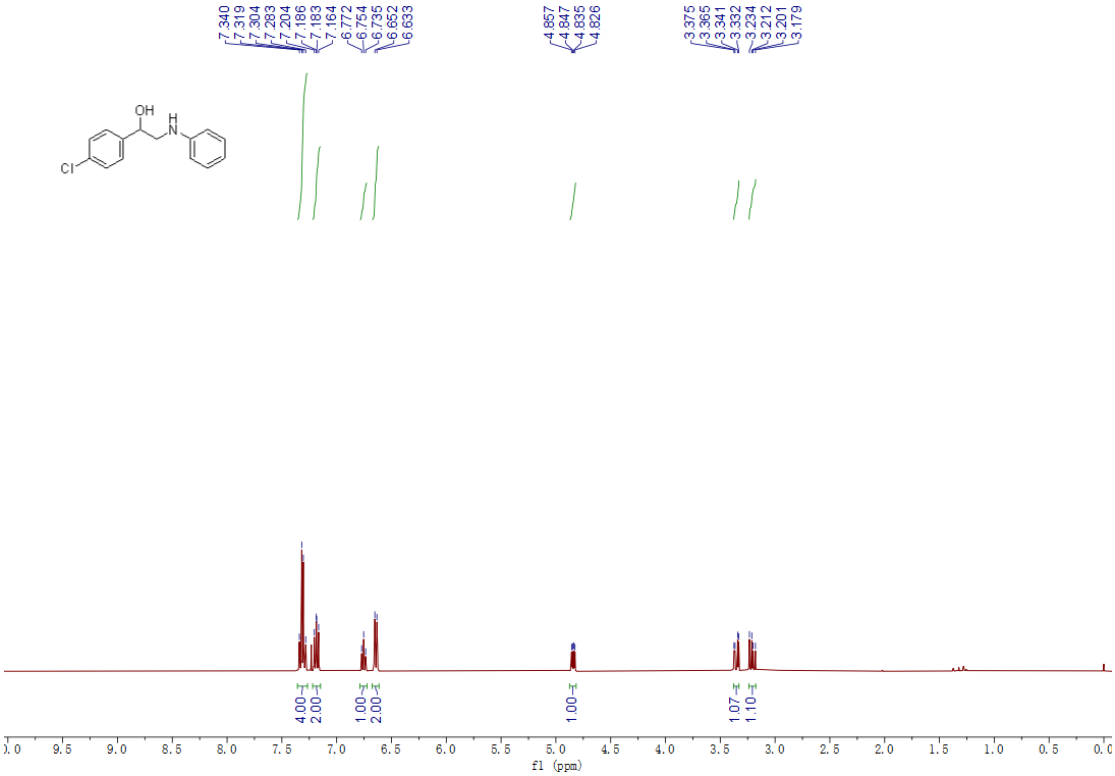
^{1}H NMR Spectrum of **3x**



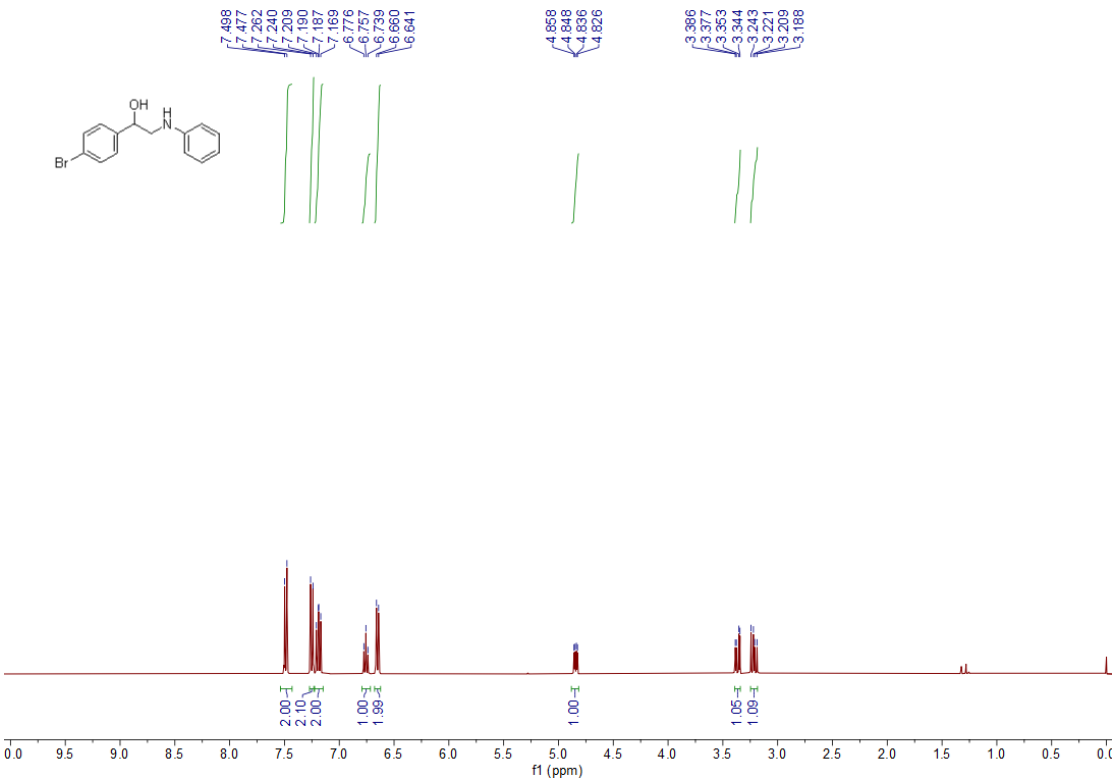
^{1}H NMR Spectrum of **3y**



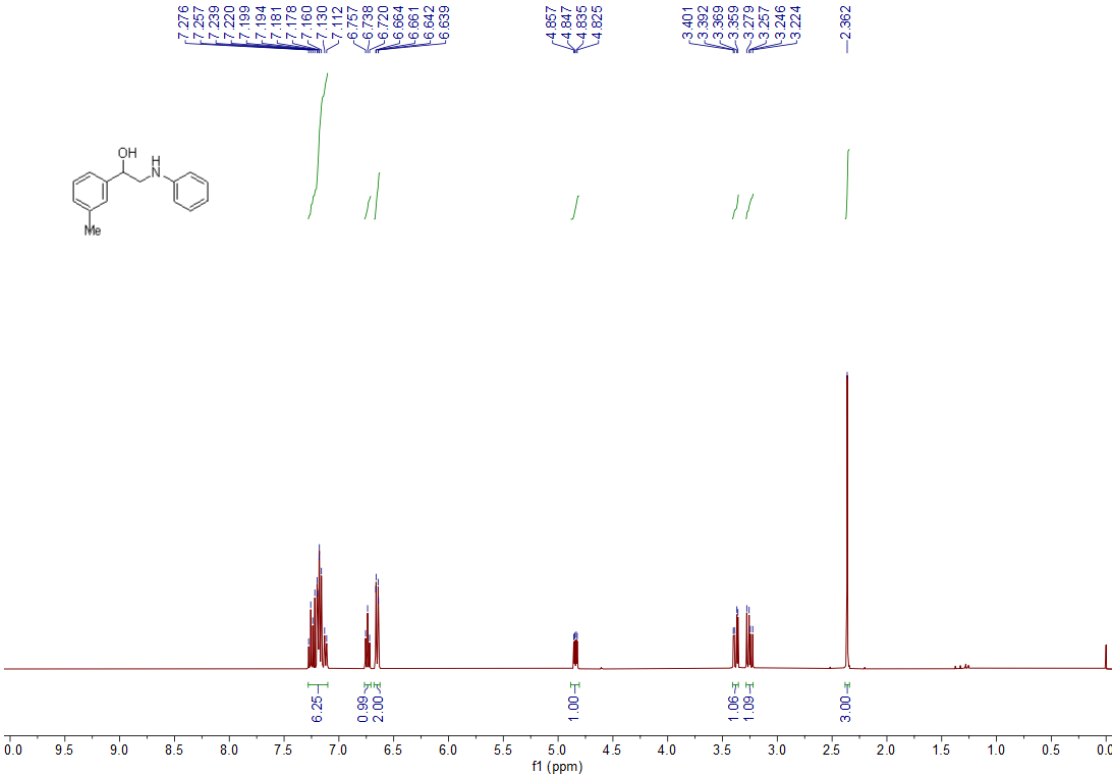
^{1}H NMR Spectrum of **3z**



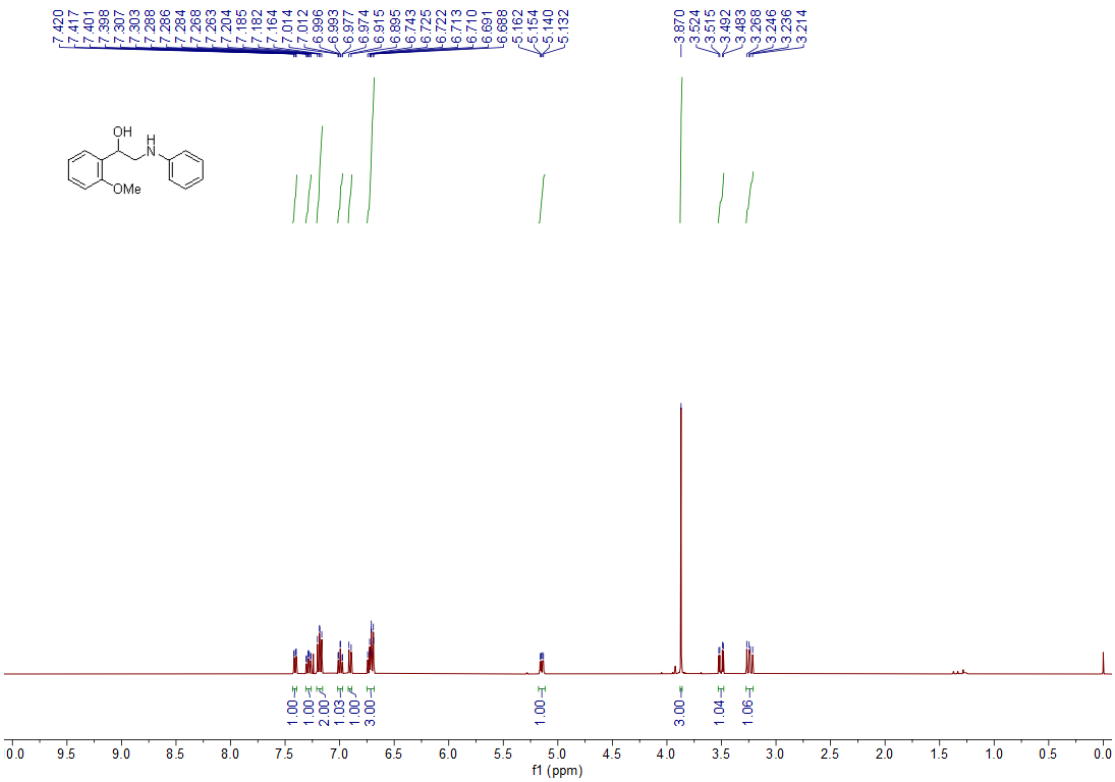
^{1}H NMR Spectrum of **3aa**



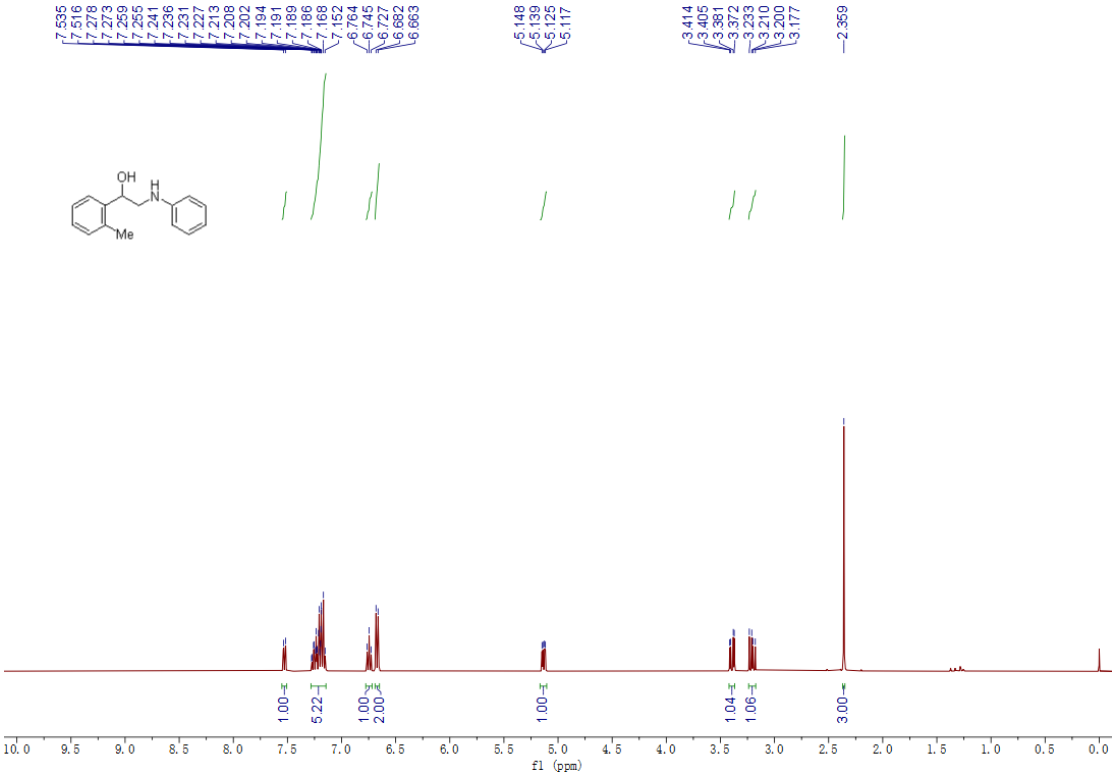
^{1}H NMR Spectrum of **3ab**



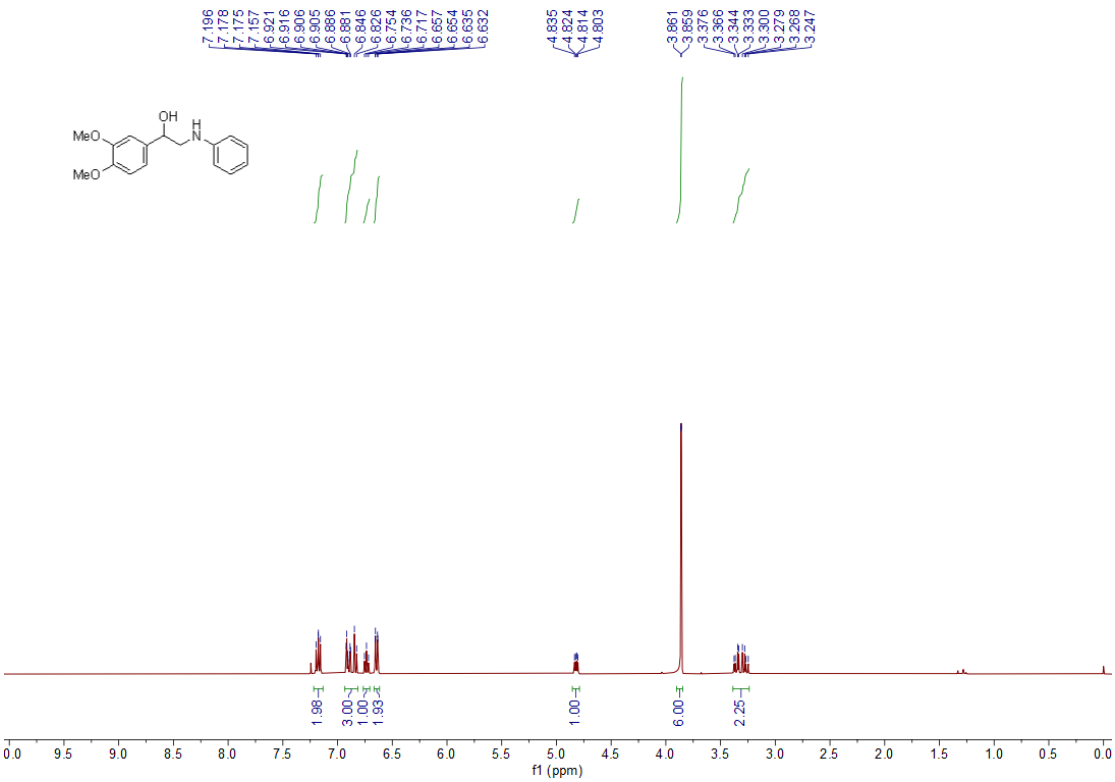
^{1}H NMR Spectrum of **3ac**



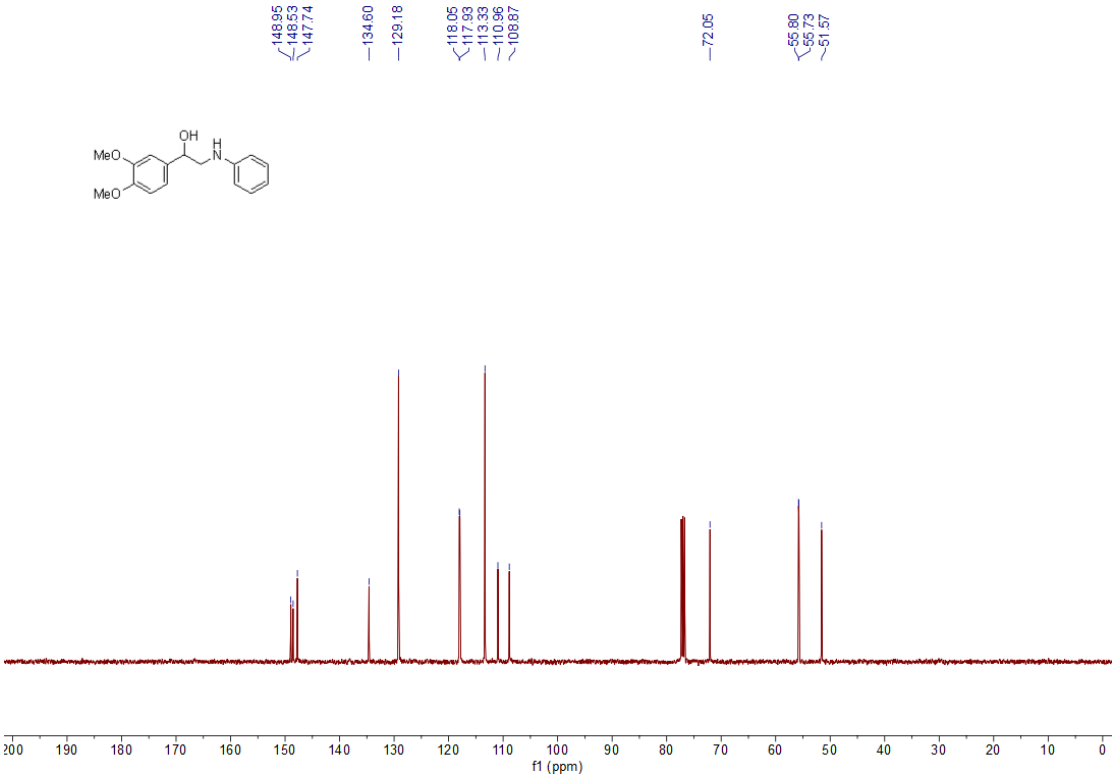
^{1}H NMR Spectrum of **3ad**



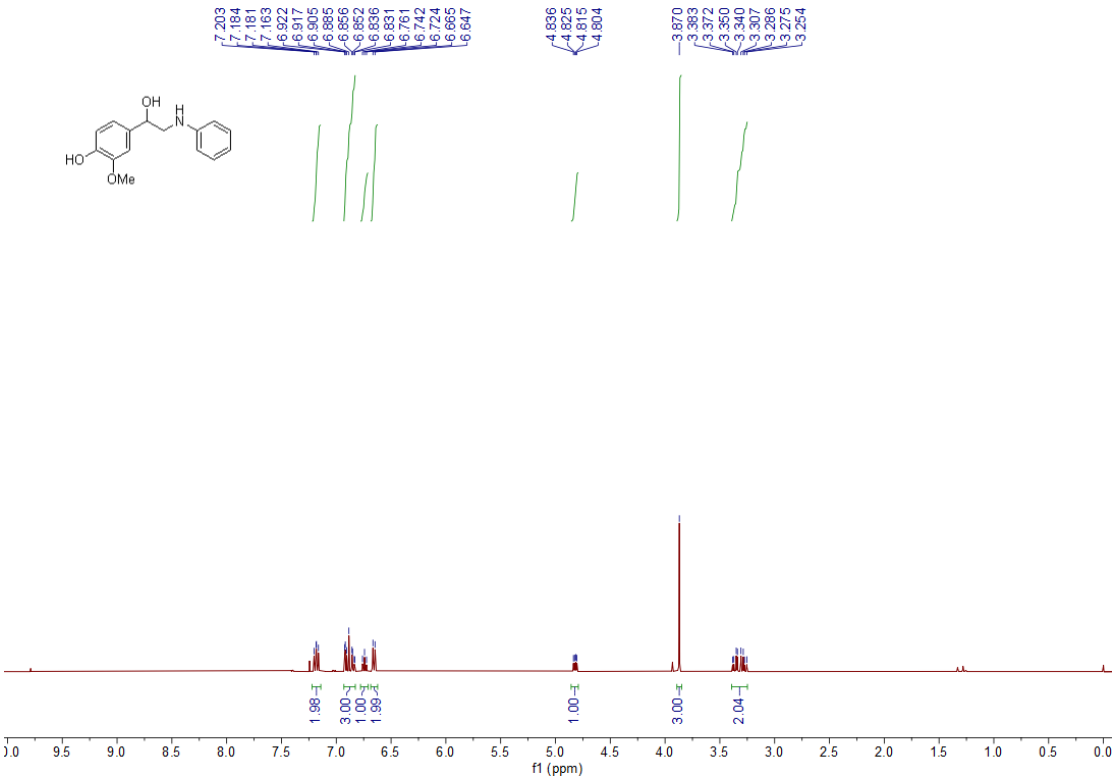
^{1}H NMR Spectrum of **3ae**



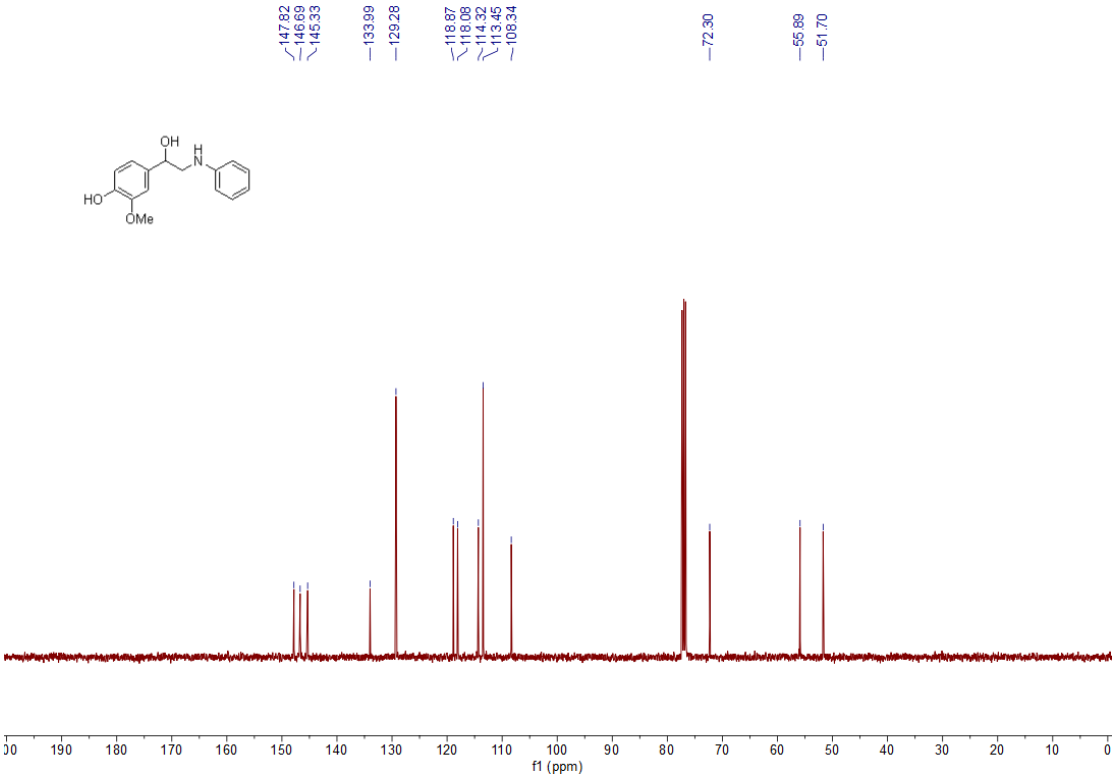
^{13}C NMR Spectrum of **3ae**



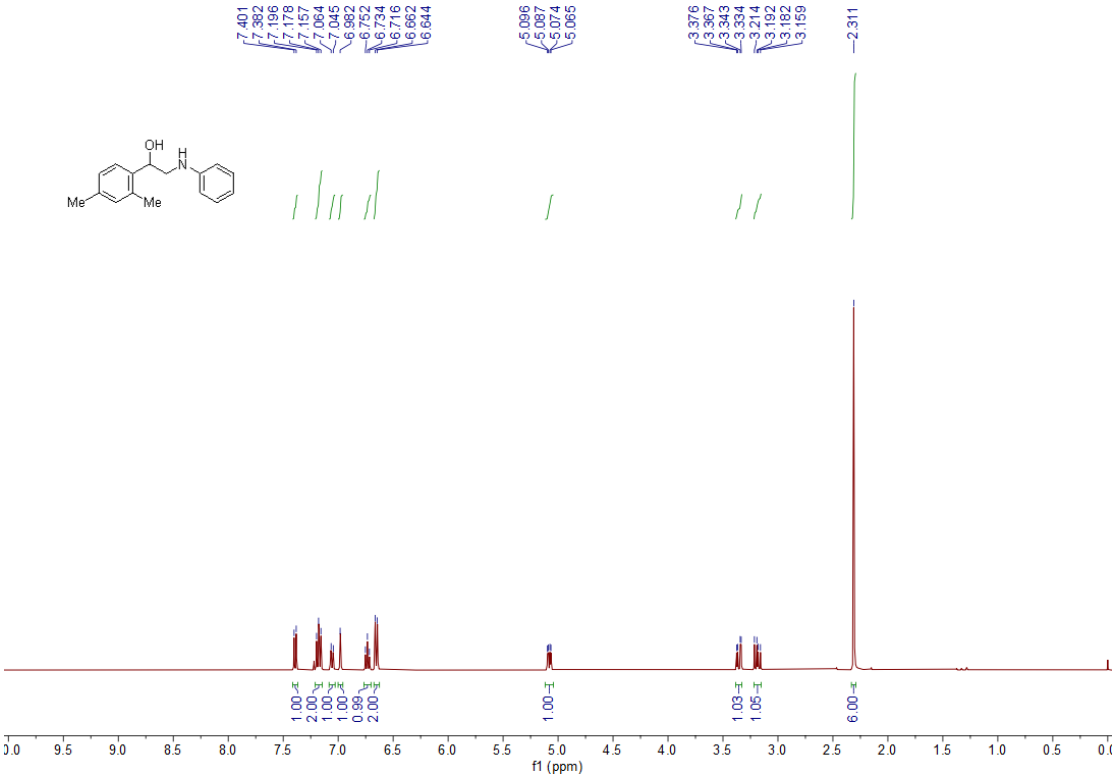
^{1}H NMR Spectrum of **3af**



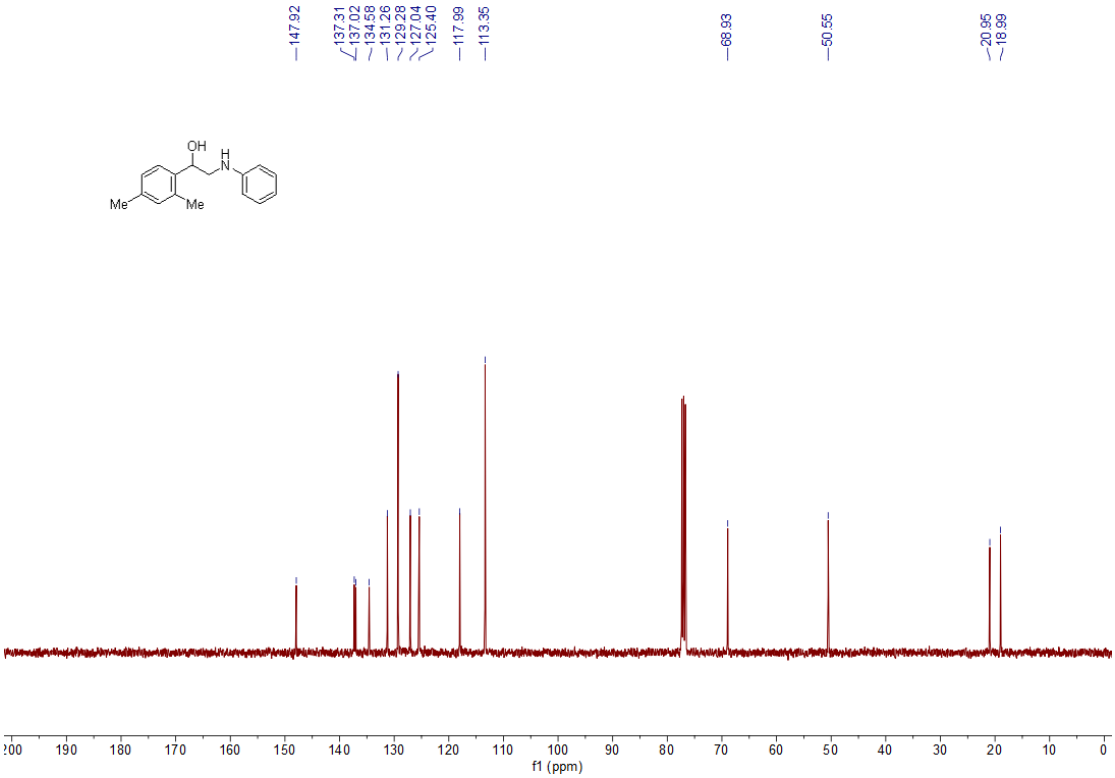
^{13}C NMR Spectrum of **3af**



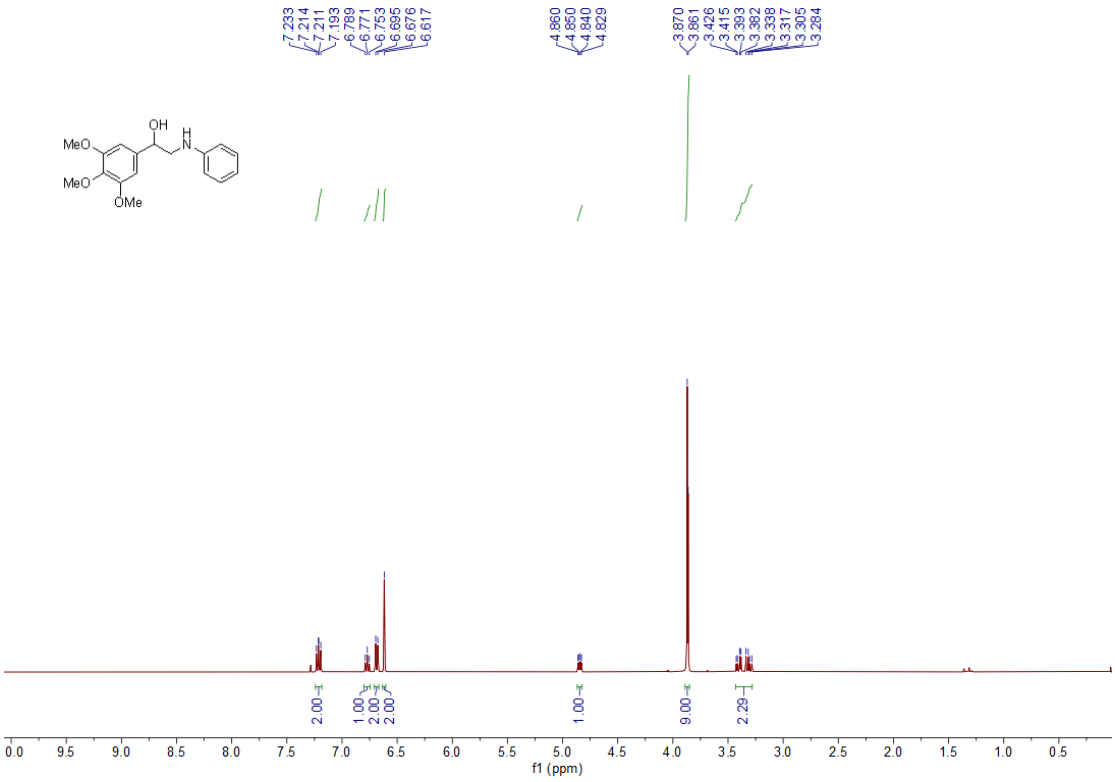
^{1}H NMR Spectrum of **3ag**



^{13}C NMR Spectrum of **3ag**



^{1}H NMR Spectrum of **3ah**



^{13}C NMR Spectrum of **3ah**