

Photoredox-Enabled Late-Stage Functionalization of Pyrrolidines in Batch and Flow: Rapid Access to Benzothiazole Hybrids as a new class of Cholinesterase Inhibitors

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1. General Remarks:

All reactions were monitored by thin-layer chromatography using Merck 60 F254 precoated silica gel plates (0.25 mm thickness). Preparative thin layer chromatography was performed using Merck 60 F254 silica gel purchased from Merck KGA. Column chromatography was carried out on silica gel (12-26, ICN Biomedicals) using petrol ether/ethyl acetate as eluents. ¹H-NMR and ¹³C-NMR spectra were measured on a Bruker Ultrashield Advance III spectrometer (¹H at 500 MHz, ¹³C at 125 MHz) and Varian 400 spectrometer (¹H at 400 MHz, ¹³C at 100 MHz) using CDCl₃ as solvent with TMS as internal standard. Chemical shifts (δ) are given in parts per million (ppm) and coupling constants are given in Hertz (Hz). The proton spectra are reported as follows δ /ppm (multiplicity, coupling constant J/Hz, number of protons). High-resolution mass spectral analyses (HRMS) were carried out using Bruker ESI-TOF MS. IR spectra were measured on a PerkinElmer FT-IR 1725X spectrophotometer using ATR technique. The peak intensities are defined as very strong (vs), strong (s), middle (m) or weak (w).

LEDs

For the irradiation of reaction mixtures 12 Avonec, Model: 3W455460m, 3W High Power LED on pcb 455nm-460nm blue, were used at 75% power (24W total)

<https://www.avonec.de/3w-high-power-led/3w-high-power-led-10000k-20000k-kaltweiss-46-51-52-53.html>

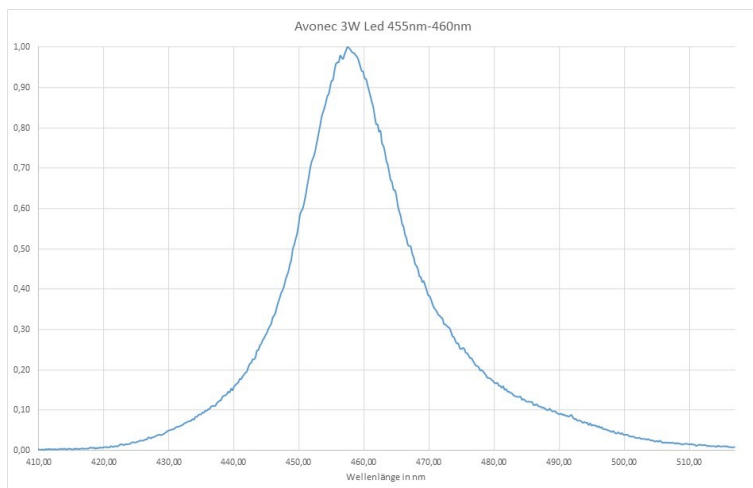


Figure 1. Emission spectra of Avonec 3W High Power LED

Microreactor fabrication

For PDMS microreactor fabrication we used SYLGARD silicone elastomer kit 184 obtained by Dow Corning Corporation. This is a two-part liquid component kit consisting of base and curing agents. Microchannels are designed with 3-D printer Wanhao Duplicator i3 Mini using transparent ABS (1,75mm) as a filament (Fig.S1.a). SYLGARD Components are well mixed 10 minutes in weight mix ratio 10:1 (base: curing agent). During mixing, air bubbles are formed, which were degassed under a vacuum. One part of PDMS was transferred into a Petri dish and heated in the oven at 60 °C for 20-30 min (Fig.S1.b). ABS printed filament was placed over baked PDMS. Then, the remaining amount of PDMS was poured out over ABS filament (1 mm layer thickness) and left for 48h at room temperature (Fig.S1.c). The PDMS with embedded ABS filament was then removed from a Petri dish and baked for about 10 minutes at 60 °C (Fig.S1.d). To enable free entrance and exit from microreactor, one side of PDMS was cut (Fig.S1.e). The removal of ABS filament from PDMS was achieved by placing the whole system in acetone overnight. The formed microchannels were cleaned from ABS with a syringe and acetone. Finally, the obtained microreactor was left in the oven at 60 °C for 24h to remove acetone completely. Reactors with internal volume of 500 μ L are obtained. Microreactor in operation (Figure S2).



Figure S1. PDMS microreactor fabrication

For fabrication of FEP reactor the FEP tubing is wrapped in figure eights around glass tube so that a total of 100 cm (corresponding to 500 μ L total volume) is used. The tubing is secured in place by 2 plastic joint clips. The coiled tubing is then placed approximately 2 cm from the LED stripes placed inside metal housing. An aluminum mirror is then placed above the coiled tubing to close the metal housing. At the bottom of the housing cooling fan is placed to maintain desired room temperature. The photoreactor tubing is connected to the syringe pump by means of a conical adapter (IDEX Health and Science, Part # P-797) which contains the appropriate female nut, ferrule, and washer. Figure S2 depicts the assembled reactor.



Figure S2. Setup of FEP tube microreactor, during reaction reactor is covered with plastic lid

For fabrication of silicone/glass microreactor photolithography was used along with wet-etching of pyrex glass and anodic bonding technique. A close up photograph of the assembled photoreactor is shown in Figure S4.

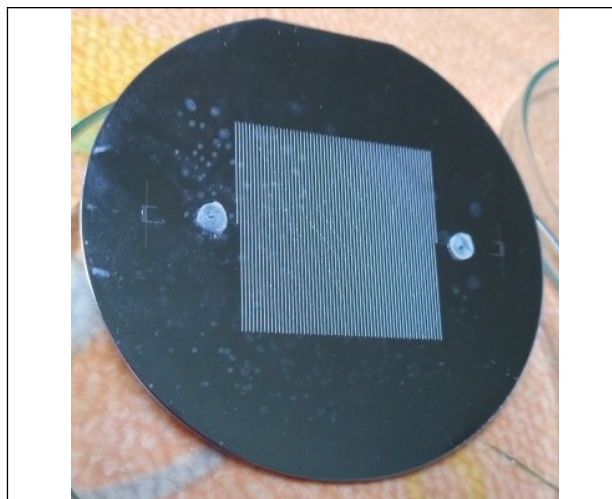


Figure S3. Glass/silicon microreactor $V_{\text{total}} = 25\mu\text{l}$

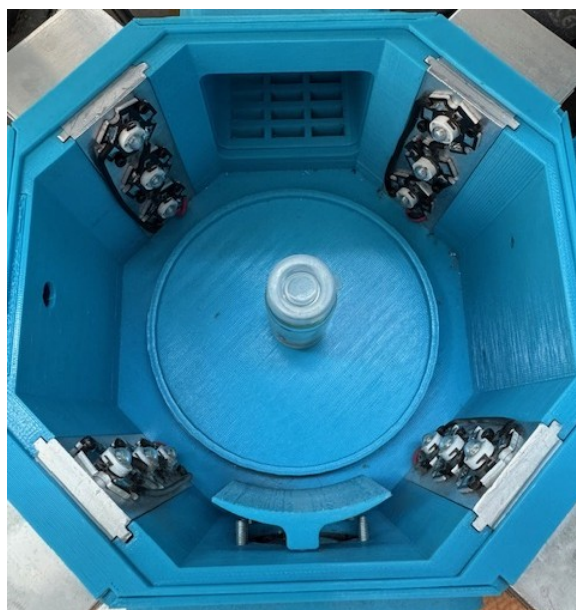


Figure S4. Setup for batch reaction, 12 LEDs at 90° , each 3W of power, used 8 LEDs, 2 at each side, 24W of power in total, during reaction reactor is placed on a magnetic stirrer and covered by plastic lid.

Essential metrics for evaluating reaction performance in batch and microflow conditions

Besides product yield, other essential metrics for evaluating reaction performance in batch and microflow conditions are space-time yield (STY) and productivity.

$$\text{Space time yield} = \frac{\text{amount of product}}{\text{reactor volume} \cdot \text{residence time}} \left[\frac{\text{mmol}}{\text{l.h}} \right]$$

$$STY = \frac{n_{\text{product}}}{V_r \cdot t_r}$$

STY can be defined as a measure of reaction effectiveness quantified through the product mass obtained for a certain time in a certain reactor volume.

Productivity describes how much product the reactor produces per unit time. Productivity does not include reactor volume normalization, while STY includes reactor volume normalization.

$$\text{Troughput} = \frac{\text{the mass of product}}{\text{residence time}} \left[\frac{\text{mg}}{\text{h}} \right]$$

$$\text{Troughput} = \frac{m_{\text{product}}}{t_r}$$

2. Chemistry

General procedure for the photoredox catalyzed functionalization of *N*-aryl amines in batch

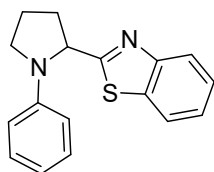
N-aryl amine (2 equiv., 0.5 mmol), benzothiazole (1 equiv., 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (0.0025 mmol, 1 mol%), sodium acetate (2 equiv., 0.5 mmol) were added in a mixture of dimethylacetamide (1 ml) and H₂O (65 equiv., 0.3 mL) in a flame dried glass vial. The solution was sparged with argon for 15 minutes to remove oxygen. The mixture was stirred for 24 hours under 24W blue LED irradiation in a custom-made photo reactor. Reaction progress was followed with thin layer chromatography (TLC). Upon completion of the reaction, reaction mixture was diluted with ethyl acetate (20mL) and water (30 mL). This solution was transferred to separatory funnel and extracted with 30 mL brine (4x). Organic layer was dried with anhydrous MgSO₄, filtered and solvent was evaporated under reduced pressure on the vacuum evaporator. Crude residue was submitted for 1H NMR analysis in order to establish conversion rate. Purification was performed using SiO₂ column chromatography or preparative thin layer

chromatography (PTLC) using petrol ether/ethyl acetate or toluene/ethyl acetate mixtures as an eluent.

General procedure for the photoredox catalyzed functionalization of N-aryl amines in flow

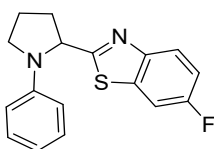
N-aryl amine (2 equiv., 0.5 mmol), benzothiazole (1 equiv., 0.25 mmol), [Ir(dtbbpy)(ppy)₂]⁺PF₆⁻ cat. (0.0025 mmol, 1 mol%), sodium acetate (2 equiv., 0.5 mmol) were added in a mixture of dimethylacetamide (1 ml) and H₂O (65 equiv., 0.3 mL) in a flame dried glass vial. The solution was sparged with argon for 15 minutes to remove oxygen and subsequently taken into 5ml gas-tight syringe. Solution was pumped through a microfluidic reactor (0.5mL internal volume) using a syringe pump at a flow rate of 0.083mL/h. The system is irradiated blue LEDs, 24W of power. The residence time that was applied was 6h and was calculated taking into account volume of the microreactor. Upon completion of the reaction, an excess of solvent was evaporated under reduced pressure on the vacuum evaporator. The crude residue was submitted for ¹H NMR analysis. Purification was performed using SiO₂ thin layer chromatography with petrol ether/ethyl acetate as eluents.

2-(1-phenylpyrrolidin-2-yl)benzo[d]thiazole (3a)



General procedure was followed with 1-phenylpyrrolidine (75.7 mg, 0.5 mmol), 2-chlorobenzo[d]thiazole (44.1 mg, 34 μ l, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]⁺PF₆⁻ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 7/1) to give the title compound (61 mg, 87 %). ¹H NMR (CDCl₃, 500 MHz): δ 8.0 (d, *J* = 8.2 Hz, 1H), 7.8 (d, *J* = 8.1 Hz, 1H), 7.5 (t, *J* = 8.1 Hz, 1H), 7.3 (t, *J* = 7.6 Hz, 1H), 7.2 (t, *J* = 8.0 Hz, 2H), 6.7 (t, *J* = 7.3 Hz, 1H), 6.7 (d, *J* = 8.2 Hz, 2H), 5.1 (dd, *J* = 8.9, 2.0 Hz, 1H), 3.9 – 3.7 (m, 1H), 3.4 (td, *J* = 9.4, 6.5 Hz, 1H), 2.6 – 2.4 (m, 1H), 2.4 – 2.2 (m, 1H), ~ 2.2 (m, 1H, partially hidden by 2.2 and 2.1), 2.3 – 2.0 (m, 1H). ¹³C NMR (CDCl₃, 125.8 MHz): δ 179.6, 154.2, 147.0, 135.0, 129.2, 125.9, 124.7, 122.7, 121.8, 117.5, 112.8, 62.3, 49.3, 34.6, 23.7. IR (ATR) : ν = 3061 (w), 2971 (m), 2945 (m), 2842 (m), 1599 (vs), 1504 (vs), 1358 (s), 1339 (s), 1314 (s), 750 (s), 731 (s), 692 (m) cm⁻¹ Spectroscopic data are in agreement with the published data [S1].

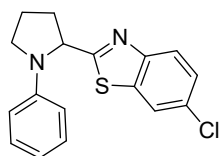
6-fluoro-2-(1-phenylpyrrolidin-2-yl)benzo[d]thiazole (3b)



General procedure was followed with 1-phenylpyrrolidine (75.7 mg, 0.5 mmol), 2-chloro-6-fluorobenzo[d]thiazole (46.5 mg, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]⁺PF₆⁻ cat. (1 mol%, 2.3 mg, 0.0025 mmol), sodium acetate (41 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 7/1) to give the title compound (45.5

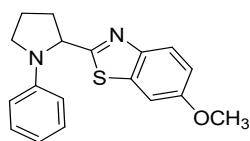
mg, 61 %) as a clear, pale yellow oil. **¹H NMR (CDCl₃, 500 MHz):** δ 7.9 (dd, *J* = 8.9, 4.8 Hz, 1H), 7.4 (dd, *J* = 8.1, 2.6 Hz, 1H), 7.2 – 7.1 (m, 3H), 6.7 (t, *J* = 7.3 Hz, 1H), 6.7 (d, *J* = 7.7 Hz, 2H), 5.1 (dd, *J* = 8.8, 2.0 Hz, 1H), 3.8 – 3.8 (m, 1H), 3.4 (td, *J* = 9.5, 6.4 Hz, 1H), 2.6 – 2.4 (m, 1H), 2.3 – 2.3 (m, 1H), 2.3 – 2.1 (m, 1H), 2.1 – 2.1 (m, 1H). **¹³C NMR (CDCl₃, 125.8 MHz):** δ 179.3, 179.3, 161.3, 158.9, 150.8, 150.8, 146.9, 136.1, 136.0, 129.2, 123.6, 123.5, 117.7, 114.6, 114.3, 112.8, 108.0, 107.8, 62.1, 49.3, 34.5, 23.7. **IR (ATR):** ν = 3064 (w), 2973 (m), 2843 (m), 1601 (vs), 1504 (vs), 1456 (vs), 1358 (s), 1339 (s), 1249 (m), 1191 (s), 813 (m), 750 (s), 694 (m), cm⁻¹. Spectroscopic data are in agreement with the published data [S1].

6-chloro-2-(1-phenylpyrrolidin-2-yl)benzo[d]thiazole (3c)



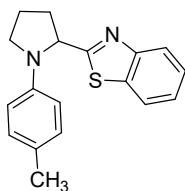
General procedure was followed with 1-phenylpyrrolidine (75.7 mg, 0.5 mmol), 2,6-dichlorobenzo[d]thiazole (53 mg, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 7/1) to give the title compound (54.3 mg, 69 %). **¹H NMR (CDCl₃, 500 MHz):** δ 7.9 (d, *J* = 8.7 Hz, 1H), 7.7 (d, *J* = 2.1 Hz, 1H), 7.4 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.2 (dd, *J* = 8.7, 7.3 Hz, 2H), 6.7 (t, *J* = 7.3 Hz, 1H), 6.6 (d, *J* = 7.6 Hz, 2H), 5.1 (dd, *J* = 8.9, 2.0 Hz, 1H), 3.9 – 3.7 (m, 1H), 3.4 – 3.3 (m, 1H), 2.6 – 2.4 (m, 1H), 2.4 – 2.2 (m, 1H), 2.2 – 2.0 (m, 2H). **¹³C NMR (CDCl₃, 125.8 MHz):** δ 180.3, 152.7, 146.8, 136.2, 130.5, 129.2, 126.6, 123.4, 121.3, 117.7, 112.8, 62.2, 49.3, 34.5, 23.6. **IR (ATR):** ν = 3061 (w), 2972 (m), 2841 (m), 1600 (vs), 1504 (vs), 1440 (m), 1358 (s), 1338 (s), 817 (m), 750 (s), 693 (m), cm⁻¹. **HRMS:** *m/z* (ESI/TOF) calc for C₁₇H₁₆ClN₂S (M+H⁺) 315.0717, found 315.0712;

6-methoxy-2-(1-phenylpyrrolidin-2-yl)benzo[d]thiazole (3d)



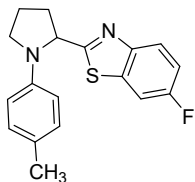
General procedure was followed with 1-phenylpyrrolidine (75.7 mg, 0.5 mmol), 2-chloro-6-methoxybenzo[d]thiazole (52 mg, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 7/1, then toluene/ethyl acetate = 9/1) to give the title compound (60 mg, 75 %). **¹H NMR (CDCl₃, 500 MHz):** δ 7.9 (d, *J* = 9.0 Hz, 1H), 7.3 – 7.2 (m, 3H), 7.1 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.7 (t, *J* = 7.3 Hz, 1H), 6.7 (d, *J* = 7.7 Hz, 2H), 5.1 (dd, *J* = 8.7, 2.0 Hz, 1H), 3.8 (s, 3H), 3.8 – 3.7 (m, 1H), 3.4 – 3.3 (m, 1H), 2.5 – 2.4 (m, 1H), 2.3 – 2.3 (m, 1H), 2.3 – 2.1 (m, 1H), 2.1 – 2.0 (m, 1H). **¹³C NMR (CDCl₃, 125.8 MHz):** δ 176.8, 157.3, 148.6, 147.0, 136.3, 129.1, 123.1, 117.5, 115.1, 112.8, 104.3, 62.1, 55.8, 49.2, 34.5, 23.7. **IR (ATR):** ν = 3062 (w), 2969 (m), 2833 (m), 1601 (vs), 1504 (vs), 1465 (s), 1358 (s), 1340 (s), 1259 (s), 1225 (s), 1056 (m), 750 (m), 693 (m), cm⁻¹. **HRMS:** *m/z* (ESI/TOF) calc for C₁₈H₁₉N₂OS (M+H⁺) 311.1213, found 311.1201;

2-(1-(*p*-tolyl)pyrrolidin-2-yl)benzo[*d*]thiazole (3e)



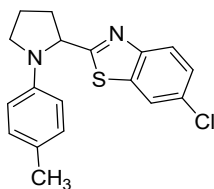
General procedure was followed with 1-(*p*-tolyl)pyrrolidin (80.7 mg, 0.5 mmol), 2-chlorobenzo[*d*]thiazole (42 mg, 33 μ l, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 7/1) to give the title compound (55 mg, 75 %). **¹H NMR (CDCl₃, 500 MHz):** δ 8.0 (d, *J* = 8.2 Hz, 1H), 7.7 (d, *J* = 7.9 Hz, 1H), 7.5 – 7.4 (m, 1H), 7.4 – 7.2 (m, 1H), 7.0 (d, *J* = 8.2 Hz, 2H), 6.6 (d, *J* = 8.5 Hz, 2H), 5.1 (dd, *J* = 8.9, 2.1 Hz, 1H), 3.9 – 3.7 (m, 1H), 3.3 (td, *J* = 9.4, 6.4 Hz, 1H), 2.6 – 2.4 (m, 1H), 2.3 – 2.2 (m, 1H), 2.2 (s, 3H), 2.2 – 2.1 (m, 1H), 2.1 – 2.0 (m, 1H). **¹³C NMR (CDCl₃, 125.8 MHz):** δ 180.0, 154.1, 144.8, 135.0, 129.6, 126.6, 125.8, 124.5, 122.6, 121.7, 112.8, 62.3, 49.4, 34.5, 23.7, 20.2. **IR (ATR):** ν = 3064 (w), 2972 (m), 2917 (m), 2860 (m), 1617 (s), 1520 (vs), 803 (s), 761 (s), cm⁻¹. **HRMS:** *m/z* (ESI/TOF) calc for C₁₈H₁₉N₂S (M+H⁺) 295.1263, found 295.1254. Spectroscopic data are in agreement with the published data [S2].

6-fluoro-2-(1-(*p*-tolyl)pyrrolidin-2-yl)benzo[*d*]thiazole (3f)



General procedure was followed with 1-(*p*-tolyl)pyrrolidin (80.7 mg, 0.5 mmol), 2-chloro-6-fluorobenzo[*d*]thiazole (47 mg, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (1 mol%, 2.3 mg, 0.0025 mmol), sodium acetate (41 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (toluene/ethyl acetate = 9/1) to give the title compound (51.5 mg, 66 %). **¹H NMR (CDCl₃, 500 MHz):** δ 7.9 (dd, *J* = 8.9, 4.8 Hz, 1H), 7.4 (dd, *J* = 8.2, 2.6 Hz, 1H), 7.2 (td, *J* = 8.9, 2.6 Hz, 1H), 7.0 (d, *J* = 8.4 Hz, 2H), 6.6 (d, *J* = 8.5 Hz, 2H), 5.0 (dd, *J* = 9.0, 2.1 Hz, 1H), 3.8 – 3.7 (m, 1H), 3.3 (td, *J* = 9.4, 6.4 Hz, 1H), 2.6 – 2.4 (m, 1H), 2.3 – 2.2 (m, 1H), 2.2 (s, 3H), 2.2 – 2.1 (m, 4H), 2.1 – 2.0 (m, 1H). **¹³C NMR (CDCl₃, 125.8 MHz):** δ 179.8, 179.8, 161.3, 158.9, 150.8, 150.8, 144.8, 136.1, 136.0, 129.7, 126.8, 123.5, 123.4, 114.5, 114.3, 112.8, 108.0, 107.8, 62.3, 49.5, 34.5, 23.7, 20.2, 20.2. **IR (ATR):** ν = 3066 (w), 2973 (m), 2860 (m), 1619 (m), 1567 (m), 1520 (vs), 1456 (s), 1358 (m), 1336 (m), 1249 (m), 1191 (m), 813 (m), cm⁻¹. **HRMS:** *m/z* (ESI/TOF) calc for C₁₈H₁₈FN₂S (M+H⁺) 313.1169, found 313.1175;

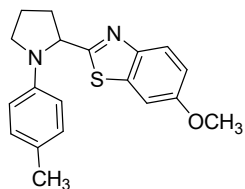
6-chloro-2-(1-(*p*-tolyl)pyrrolidin-2-yl)benzo[*d*]thiazole (3g)



General procedure was followed with 1-(*p*-tolyl)pyrrolidin (80.7 mg, 0.5 mmol), 2,6-dichlorobenzo[*d*]thiazole (51 mg, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 7/1, then toluene/ethyl acetate = 9/1) to give the title compound (75 mg, 70 %). **¹H NMR (CDCl₃, 500**

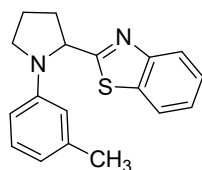
MHz): δ 7.9 (d, J = 8.7 Hz, 1H), 7.7 (d, J = 2.1 Hz, 1H), 7.4 (dd, J = 8.7, 2.1 Hz, 1H), 7.0 (d, J = 8.4 Hz, 2H), 6.6 (d, J = 8.6 Hz, 2H), 5.0 (dd, J = 9.0, 2.1 Hz, 1H), 3.8 – 3.7 (m, 1H), 3.3 (td, J = 9.4, 6.4 Hz, 1H), 2.6 – 2.4 (m, 1H), 2.3 – 2.2 (m, 1H), 2.2 (s, 3H), 2.2 – 2.1 (m, 2H), 2.1 – 2.0 (m, 1H). **^{13}C NMR (CDCl₃, 125.8 MHz):** ^{13}C NMR (101 MHz, cdCl₃) δ 180.8, 152.8, 144.8, 136.3, 130.6, 129.7, 126.9, 126.6, 123.4, 121.4, 112.9, 62.3, 49.5, 34.5, 23.8, 20.3, 20.2. **IR (ATR):** ν = 3064 (w), 2972 (m), 2857 (m), 1617 (m), 1519 (vs), 1357 (s), 1334 (s), 804 (s), cm⁻¹; **HRMS:** m/z (ESI/TOF) calc for C₁₈H₁₈ClN₂S (M+H⁺) 329.0874, found 329.0872;

6-methoxy-2-(1-(*p*-tolyl)pyrrolidin-2-yl)benzo[*d*]thiazole (3h)



General procedure was followed with 1-(*p*-tolyl)pyrrolidin (80.7 mg, 0.5 mmol), 2-chloro-6-methoxybenzo[*d*]thiazole (50 mg, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 7/1, then toluene/ethyl acetate = 9/1) to give the title compound (66.5 mg, 82 %). **^1H NMR (CDCl₃, 500 MHz):** δ 7.9 (d, J = 8.9 Hz, 1H), 7.2 (d, J = 2.5 Hz, 1H), 7.1 (dd, J = 8.9, 2.6 Hz, 1H), 7.0 (d, J = 8.0 Hz, 2H), 6.6 (d, J = 8.6 Hz, 2H), 5.0 (dd, J = 8.8, 2.1 Hz, 1H), 3.8 (s, 3H), 3.8 – 3.7 (m, 1H), 3.3 (td, J = 9.4, 6.4 Hz, 1H), 2.5 – 2.4 (m, 1H), 2.3 – 2.2 (m, 1H), 2.2 (s, 3H), 2.2 – 2.1 (m, 4H), 2.1 – 2.0 (m, 1H). **^{13}C NMR (CDCl₃, 125.8 MHz):** δ 177.2, 157.2, 148.6, 144.9, 136.3, 129.6, 126.5, 123.0, 115.0, 112.8, 104.3, 62.2, 55.7, 49.4, 34.5, 23.7, 20.2, 20.2. **IR (ATR):** ν = 3066 (w), 2969 (m), 2861 (m), 1604 (s), 1520 (vs), 1465 (s), 1435 (m), 1358 (s), 1338 (s), 1260 (s), 1225 (s), 1057 (m), 804 (s), cm⁻¹. **HRMS:** m/z (ESI/TOF) calc for C₁₉H₂₁N₂OS (M+H⁺) 325.1369, found 325.1366;

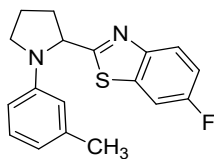
2-(1-(*m*-tolyl)pyrrolidin-2-yl)benzo[*d*]thiazole (3i)



General procedure was followed with 1-(*m*-tolyl)pyrrolidine (81 mg, 0.5 mmol), 2-chlorobenzo[*d*]thiazole (42 mg, 33 μl , 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 7/1, then toluene/ethyl acetate = 9/1) to give the title compound (56.7 mg, 77 %). **^1H NMR (CDCl₃, 500 MHz):** δ 8.0 (d, J = 8.2 Hz, 1H), 7.8 (d, J = 7.9 Hz, 1H), 7.5 – 7.4 (m, 1H), 7.4 – 7.3 (m, 1H), 7.1 (t, J = 7.8 Hz, 1H), 6.6 (d, J = 7.5 Hz, 1H), 6.5 (dd, J = 11.5, 3.2 Hz, 2H), 5.1 (dd, J = 8.8, 1.9 Hz, 1H), 3.9 – 3.7 (m, 1H), 3.4 (td, J = 9.5, 6.5 Hz, 1H), 2.6 – 2.4 (m, 1H), 2.3 (s, 3H), ~ 2.3 (m, 1H, partially hidden by 2.3 singlet), 2.2 – 2.1 (m, 1H), 2.1 – 2.0 (m, 1H). **^{13}C NMR (CDCl₃, 125.8 MHz):** δ 191.8, 179.9, 154.2, 147.1, 139.0, 135.1, 129.0, 125.8, 124.6, 122.7, 121.8, 118.6, 113.5, 110.1, 62.2, 49.3, 34.6, 23.7, 21.8. **IR (ATR):** ν = 3040 (w), 2971 (m), 2850 (m), 1602 (vs), 1582 (m), 1496

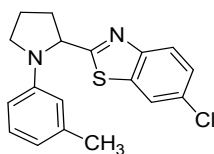
(s), 1450 (m), 1358 (s), 1191 (m), 761 (m), 731 (m), 692 (m), cm^{-1} . **HRMS:** m/z (ESI/TOF) calc for $\text{C}_{18}\text{H}_{19}\text{N}_2\text{S}$ ($\text{M}+\text{H}^+$) 295.1263, found 295.1258;

6-fluoro-2-(1-(*m*-tolyl)pyrrolidin-2-yl)benzo[*d*]thiazole (3j)



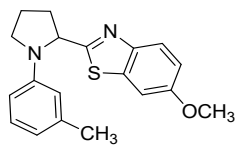
General procedure was followed with 1-(*m*-tolyl)pyrrolidine (81 mg, 0.5 mmol), 2-chloro-6-fluorobenzo[*d*]thiazole (47 mg, 0.25 mmol), $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ cat. (1 mol%, 2.3 mg, 0.0025 mmol), sodium acetate (41 mg, 0.5 mmol) in DMA (1 ml) and H_2O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 7/1, then toluene/ethyl acetate = 9/1) to give the title compound (61 mg, 78 %). **^1H NMR (CDCl_3 , 500 MHz):** δ 7.9 (dd, $J = 9.0, 4.8$ Hz, 1H), 7.4 (dd, $J = 8.2, 2.6$ Hz, 1H), 7.2 (td, $J = 8.9, 2.6$ Hz, 1H), 7.1 (t, $J = 7.8$ Hz, 1H), 6.6 (d, $J = 7.5$ Hz, 1H), 6.5 – 6.4 (m, 2H), 5.1 (dd, $J = 8.8, 1.9$ Hz, 1H), 3.8 – 3.7 (m, 1H), 3.3 (td, $J = 9.5, 6.4$ Hz, 1H), 2.6 – 2.4 (m, 1H), 2.4 – 2.3 (m, 3H), 2.3 (s, 3H), ~ 2.3 (m, 1H, partially hidden by 2.3 singlet), 2.2 – 2.1 (m, 1H), 2.1 – 2.0 (m, 1H). **^{13}C NMR (CDCl_3 , 125.8 MHz):** δ 179.6, 179.5, 161.3, 158.9, 150.8, 150.8, 147.0, 139.0, 136.1, 136.0, 129.0, 123.5, 123.5, 118.7, 114.5, 114.3, 113.5, 110.1, 108.0, 107.8, 62.1, 49.3, 34.5, 23.6. **IR (ATR):** $\nu = 3041$ (w), 2973 (m), 2846 (m), 1603 (vs), 1583 (m), 1567 (m), 1495 (s), 1455 (vs), 1358 (s), 1250 (m), 1195 (m), 816 (m), 769 (m), cm^{-1} . **HRMS:** m/z (ESI/TOF) calc for $\text{C}_{18}\text{H}_{18}\text{FN}_2\text{S}$ ($\text{M}+\text{H}^+$) 313.1169, found 313.1170;

6-chloro-2-(1-(*m*-tolyl)pyrrolidin-2-yl)benzo[*d*]thiazole (3k)



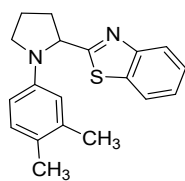
General procedure was followed with 1-(*m*-tolyl)pyrrolidine (81 mg, 0.5 mmol), 2,6-dichlorobenzo[*d*]thiazole (51 mg, 0.25 mmol), $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H_2O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 7/1, then toluene/ethyl acetate = 9/1) to give the title compound (66.5 mg, 81 %). **^1H NMR (CDCl_3 , 500 MHz):** δ 7.9 (dd, $J = 8.8, 1.7$ Hz, 1H), 7.7 (d, $J = 2.1$ Hz, 1H), 7.4 (dd, $J = 8.7, 2.1$ Hz, 1H), 7.1 (t, $J = 7.8$ Hz, 1H), 6.6 (d, $J = 7.5$ Hz, 1H), 6.5 – 6.4 (m, 2H), 5.1 (dd, $J = 9.0, 2.0$ Hz, 1H), 3.8 – 3.7 (m, 1H), 3.3 (td, $J = 9.6, 6.5$ Hz, 1H), 2.6 – 2.4 (m, 1H), 2.3 (t, $J = 6.4$ Hz, 2H), 2.3 (s, 3H), ~ 2.3 (m, 1H, partially hidden by 2.3 singlet), 2.2 – 2.1 (m, 1H), 2.1 – 2.0 (m, 1H). **^{13}C NMR (CDCl_3 , 125.8 MHz):** δ 180.5, 152.8, 147.0, 139.0, 136.3, 130.5, 129.0, 126.6, 123.4, 121.3, 118.7, 113.5, 110.1, 62.1, 49.3, 34.5, 23.6. **IR (ATR):** $\nu = 3042$ (w), 2973 (m), 2846 (m), 1603 (vs), 1495 (s), 1441 (s), 1357 (s), 1191 (m), 817 (m), 766 (s), cm^{-1} . **HRMS:** m/z (ESI/TOF) calc for $\text{C}_{18}\text{H}_{18}\text{ClN}_2\text{S}$ ($\text{M}+\text{H}^+$) 329.0874, found 329.0870;

6-methoxy-2-(1-(*m*-tolyl)pyrrolidin-2-yl)benzo[*d*]thiazole (3l)



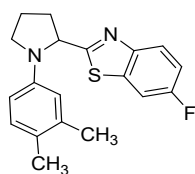
General procedure was followed with 1-(*m*-tolyl)pyrrolidine (81 mg, 0.5 mmol), 2-chloro-6-methoxybenzo[*d*]thiazole (50 mg, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 7/1, then toluene/ethyl acetate = 9/1) to give the title compound (66 mg, 82 %). ¹H NMR (CDCl₃, 500 MHz): δ 7.9 (dd, *J* = 9.0, 1.8 Hz, 1H), 7.2 (d, *J* = 2.5 Hz, 1H), 7.1 – 7.0 (m, 2H), 6.6 (d, *J* = 7.4 Hz, 1H), 6.5 – 6.4 (m, 2H), 5.1 (dd, *J* = 8.8, 1.9 Hz, 1H), 3.8 (s, 3H), 3.8 – 3.7 (m, 1H), 3.3 (td, *J* = 9.5, 6.4 Hz, 1H), 2.6 – 2.3 (m, 1H), 2.3 – 2.3 (m, 1H), 2.3 (s, 3H), ~ 2.3 (m, 1H, partially hidden by 2.3 singlet), 2.2 – 2.1 (m, 1H), 2.1 – 2.0 (m, 1H). ¹³C NMR (CDCl₃, 125.8 MHz): δ 177.0, 157.3, 148.7, 147.1, 138.9, 136.3, 129.0, 123.0, 118.5, 115.0, 113.4, 110.1, 104.3, 62.1, 55.8, 55.7, 55.7, 49.2, 34.5, 23.6, 21.8, 21.7. IR (ATR): ν = 3041 (w), 2969 (m), 2833 (m), 1603 (vs), 1495 (s), 1466 (s), 1358 (s), 1260 (s), 1226 (m), 1057 (m), 769 (m), cm⁻¹. HRMS: *m/z* (ESI/TOF) calc for C₁₉H₂₁ClN₂OS (M+H⁺) 325.1369, found 325.1363;

2-(1-(3,4-dimethylphenyl)pyrrolidin-2-yl)benzo[*d*]thiazole (3m)



General procedure was followed with 1-(3,4-dimethylphenyl)pyrrolidine (88 mg, 0.5 mmol), 2-chlorobenzo[*d*]thiazole (42 mg, 33 μl, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 7/1) to give the title compound (51 mg, 67 %). ¹H NMR (CDCl₃, 500 MHz): δ 7.4 (t, *J* = 7.7 Hz, 1H), 7.3 (t, *J* = 7.6 Hz, 1H), 6.9 (d, *J* = 8.2 Hz, 1H), 6.5 (d, *J* = 2.5 Hz, 1H), 6.4 (dd, *J* = 8.2, 2.7 Hz, 1H), 5.1 (dd, *J* = 8.9, 2.0 Hz, 1H), 3.9 – 3.6 (m, 1H), 3.3 (td, *J* = 9.4, 6.4 Hz, 1H), 2.6 – 2.4 (m, 1H), 2.3 – 2.2 (m, 1H), 2.2 (s, 3H), ~ 2.2 (m, 1H, partially hidden by 2.2 and 2.1 singlet), 2.1 (s, 2H), 2.1 – 2.0 (m, 1H). ¹³C NMR (CDCl₃, 125.8 MHz): δ 191.7, 180.3, 154.2, 145.3, 137.2, 135.1, 130.2, 125.8, 125.5, 124.5, 122.6, 121.7, 114.3, 110.3, 62.3, 49.5, 34.5, 23.7, 20.2, 18.5. IR (ATR): ν = 3059 (w), 2969 (m), 2858 (m), 1616 (s), 1570 (m), 1511 (vs), 1455 (m), 1356 (s), 1313 (s), 760 (s), 731 (s), cm⁻¹. HRMS: *m/z* (ESI/TOF) calc for C₁₉H₂₁N₂S (M+H⁺) 309.1420, found 309.1424;

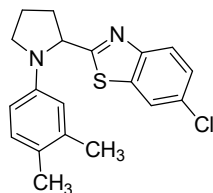
2-(1-(3,4-dimethylphenyl)pyrrolidin-2-yl)-6-fluorobenzo[*d*]thiazole (3n)



General procedure was followed with 1-(3,4-dimethylphenyl)pyrrolidine (88 mg, 0.5 mmol), 2-chloro-6-fluorobenzo[*d*]thiazole (47 mg, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (1 mol%, 2.3 mg, 0.0025 mmol), sodium acetate (41 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative

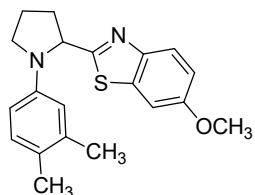
thin layer chromatography on silica gel (petrolether/ethyl acetate = 7/1, then toluene/ethyl acetate = 9/1) to give the title compound (60 mg, 73 %). **¹H NMR (CDCl₃, 500 MHz):** δ 7.9 (dd, *J* = 9.0, 4.8 Hz, 1H), 7.4 (dd, *J* = 8.1, 2.6 Hz, 1H), 7.2 (td, *J* = 8.9, 2.6 Hz, 1H), 6.9 (d, *J* = 8.2 Hz, 1H), 6.5 (d, *J* = 2.7 Hz, 1H), 6.4 (dd, *J* = 8.2, 2.7 Hz, 1H), 5.0 (dd, *J* = 9.0, 2.0 Hz, 1H), 3.9 – 3.7 (m, 1H), 3.3 (td, *J* = 9.4, 6.4 Hz, 1H), 2.5 – 2.4 (m, 1H), 2.3 – 2.2 (m, 1H), 2.2 (s, 3H), ~ 2.2 (m, 1H, partially hidden by 2.2 and 2.1 singlet), 2.1 (s, 4H), 2.1 – 2.0 (m, 1H). **¹³C NMR (CDCl₃, 125.8 MHz):** δ 180.1, 161.0, 159.1, 150.9, 145.3, 137.3, 136.1, 136.0, 130.2, 125.7, 123.5, 123.4, 114.4, 114.3, 114.2, 110.3, 108.0, 107.8, 62.2, 49.5, 34.5, 23.7, 20.2, 18.6. **IR (ATR):** ν = 3064 (w), 2970 (m), 2859 (m), 1614 (s), 1567 (m), 1510 (vs), 1455 (vs), 1356 (s), 1250 (m), 1193 (m), 846 (w), 816 (m), 733 (w), cm⁻¹. **HRMS:** *m/z* (ESI/TOF) calc for C₁₉H₂₀FN₂S (M+H⁺) 327.1326, found 327.1321;

6-chloro-2-(1-(3,4-dimethylphenyl)pyrrolidin-2-yl)benzo[d]thiazole (3o)



General procedure was followed with 1-(3,4-dimethylphenyl)pyrrolidine (88 mg, 0.5 mmol), 2,6-dichlorobenzo[d]thiazole (51 mg, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 7/1, then toluene/ethyl acetate = 9/1) to give the title compound (76 mg, 89 %). **¹H NMR (CDCl₃, 500 MHz):** δ 7.9 (d, *J* = 8.7 Hz, 1H), 7.7 (d, *J* = 2.1 Hz, 1H), 7.4 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.9 (d, *J* = 8.2 Hz, 1H), 6.5 (d, *J* = 2.7 Hz, 1H), 6.4 (dd, *J* = 8.3, 2.7 Hz, 1H), 5.0 (dd, *J* = 9.0, 2.0 Hz, 1H), 3.8 – 3.7 (m, 1H), 3.3 (td, *J* = 9.4, 6.4 Hz, 1H), 2.5 – 2.4 (m, 1H), 2.3 – 2.2 (m, 1H), 2.2 (s, 3H), ~ 2.2 (m, 1H, partially hidden by 2.2 and 2.1 singlet), 2.1 (s, 4H), 2.1 – 2.0 (m, 1H). **¹³C NMR (CDCl₃, 125.8 MHz):** δ 191.7, 181.0, 152.9, 145.3, 137.3, 136.3, 130.5, 130.2, 126.5, 125.8, 123.4, 121.3, 114.3, 110.3, 62.3, 49.5, 34.5, 23.7, 20.2, 20.2, 18.6, 18.5. **IR (ATR):** ν = 3058 (w), 2970 (m), 2857 (m), 1615 (s), 1511 (vs), 1441 (m), 1356 (s), 1338 (m), 817 (m), cm⁻¹. **HRMS:** *m/z* (ESI/TOF) calc for C₁₉H₂₀ClN₂S (M+H⁺) 343.1030, found 343.1021;

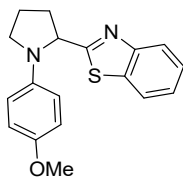
2-(1-(3,4-dimethylphenyl)pyrrolidin-2-yl)-6-methoxybenzo[d]thiazole (3p)



General procedure was followed with 1-(3,4-dimethylphenyl)pyrrolidine (88 mg, 0.5 mmol), 2-chloro-6-methoxybenzo[d]thiazole (50 mg, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 7/1, then toluene/ethyl acetate = 9/1) to give the title compound (67 mg, 79 %). **¹H NMR (CDCl₃, 500 MHz):** δ 7.9 (d, *J* = 8.9 Hz, 1H), 7.2 (d, *J* = 2.6 Hz, 1H), 7.1 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.9 (d, *J* = 8.2 Hz, 1H), 6.5 (d, *J* = 2.7 Hz, 1H), 6.4 (dd, *J* = 8.2, 2.7 Hz, 1H), 5.0 (dd, *J* = 8.9, 2.0 Hz, 1H), 3.8 (s, 3H), 3.8 – 3.7 (m, 1H), 3.3 (td, *J* = 9.4, 6.3 Hz, 1H), 2.5 – 2.4 (m, 1H), 2.3 – 2.2 (m,

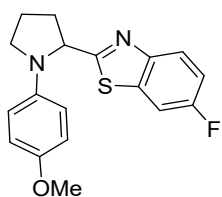
1H), 2.2 (s, 4H), ~ 2.2 (m, 1H, partially hidden by 2.2 and 2.1 singlet), 2.1 (s, 3H), 2.1 – 2.0 (m, 1H). **¹³C NMR (CDCl₃, 125.8 MHz):** ¹³C NMR (101 MHz, cdcl₃) δ 177.5, 157.2, 148.7, 145.4, 137.2, 136.3, 130.2, 125.5, 123.0, 115.0, 114.3, 110.3, 104.4, 62.2, 55.7, 55.7, 49.5, 34.5, 23.7, 20.2, 20.2, 18.6, 18.5. **IR (ATR):** ν = 3060 (w), 2967 (m), 2832 (m), 1605 (s), 1559 (m), 1511 (vs), 1465 (s), 1356 (m), 1260 (s), 1225 (m), 1057 (m), 832 (m), cm⁻¹. **HRMS:** m/z (ESI/TOF) calc for C₂₀H₂₃ClN₂OS (M+H⁺) 339.1526, found 339.1523;

2-(1-(4-methoxyphenyl)pyrrolidin-2-yl)benzo[d]thiazole (3q)



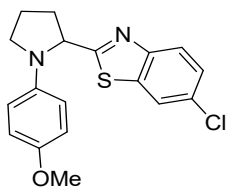
General procedure was followed with 1-(4-methoxyphenyl)pyrrolidine (88 mg, 0.5 mmol), 2-chlorobenzo[d]thiazole (42 mg, 33 μl, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 5/1, then toluene/ethyl acetate = 9/1) to give the title compound (68 mg, 88 %). **¹H NMR (CDCl₃, 500 MHz):** δ 8.0 (d, *J* = 8.2 Hz, 1H), 7.8 (d, *J* = 7.9 Hz, 1H), 7.5 – 7.4 (m, 1H), 7.4 – 7.3 (m, 1H), 6.8 (d, *J* = 9.0 Hz, 2H), 6.6 (d, *J* = 9.1 Hz, 2H), 5.0 (dd, *J* = 9.0, 2.1 Hz, 1H), 3.8 – 3.7 (m, 1H), 3.7 (s, 3H), 3.3 (td, *J* = 9.2, 6.3 Hz, 1H), 2.6 – 2.4 (m, 1H), 2.3 – 2.2 (m, 1H), 2.2 – 2.1 (m, 1H), 2.1 – 2.0 (m, 1H). **¹³C NMR (CDCl₃, 125.8 MHz):** δ 180.3, 154.2, 151.9, 141.7, 135.0, 125.8, 124.6, 122.6, 121.7, 114.8, 113.6, 62.7, 55.7, 49.8, 34.6, 23.8. **IR (ATR):** ν = 3060 (w), 2946 (m), 2830 (m), 1513 (vs), 1314 (m), 1242 (s), 1041 (m), 815 (m), 762 (m), cm⁻¹. **HRMS:** m/z (ESI/TOF) calc for C₁₈H₁₉N₂OS (M+H⁺) 311.1213, found 311.1217;

6-fluoro-2-(1-(4-methoxyphenyl)pyrrolidin-2-yl)benzo[d]thiazole (3r)



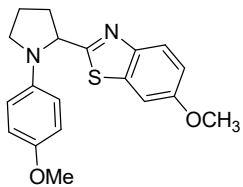
General procedure was followed with 1-(4-methoxyphenyl)pyrrolidine (88 mg, 0.5 mmol), 2-chloro-6-fluorobenzo[d]thiazole (47 mg, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (1 mol%, 2.3 mg, 0.0025 mmol), sodium acetate (41 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 7/1, then toluene/ethyl acetate = 9/1) to give the title compound (64 mg, 77 %). **¹H NMR (CDCl₃, 500 MHz):** δ 7.9 (dd, *J* = 9.0, 4.8 Hz, 1H), 7.4 (dd, *J* = 8.1, 2.6 Hz, 1H), 7.2 (td, *J* = 8.9, 2.6 Hz, 1H), 6.8 (d, *J* = 9.0 Hz, 2H), 6.6 (d, *J* = 9.0 Hz, 2H), 5.0 (dd, *J* = 9.0, 2.1 Hz, 1H), 3.8 – 3.7 (m, 1H), 3.7 (s, 3H), 3.3 (td, *J* = 9.2, 6.4 Hz, 1H), 2.6 – 2.4 (m, 1H), 2.3 – 2.2 (m, 1H), 2.2 – 2.1 (m, 1H), 2.1 – 2.0 (m, 1H). **¹³C NMR (CDCl₃, 125.8 MHz):** δ 180.1, 180.0, 161.3, 158.9, 152.1, 150.8, 150.8, 141.6, 136.1, 136.0, 123.5, 123.4, 114.8, 114.5, 114.3, 113.7, 108.0, 107.8, 62.6, 55.7, 55.6, 49.9, 34.6, 23.8. **IR (ATR):** ν = 3060 (w), 2946 (w), 2832 (w), 1513 (vs), 1456 (s), 1244 (s), 1190 (m), 1143 (m), 816 (m), cm⁻¹. **HRMS:** m/z (ESI/TOF) calc for C₁₈H₁₈FN₂OS (M+H⁺) 329.1118, found 329.1114;

6-chloro-2-(1-(4-methoxyphenyl)pyrrolidin-2-yl)benzo[*d*]thiazole (3s)



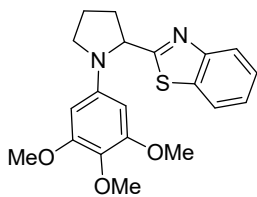
General procedure was followed with 1-(4-methoxyphenyl)pyrrolidine (88 mg, 0.5 mmol), 2,6-dichlorobenzo[*d*]thiazole (51 mg, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 3/1, then toluene/ethyl acetate = 9/1) to give the title compound (66 mg, 76 %). **¹H NMR (CDCl₃, 500 MHz):** δ 7.9 (d, *J* = 8.7 Hz, 1H), 7.7 (d, *J* = 2.1 Hz, 1H), 7.4 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.8 (d, *J* = 9.1 Hz, 2H), 6.6 (d, *J* = 9.1 Hz, 2H), 5.0 (dd, *J* = 9.0, 2.1 Hz, 1H), 3.8 – 3.7 (m, 1H), 3.7 (s, 3H), 3.3 (td, *J* = 9.3, 6.5 Hz, 1H), 2.6 – 2.4 (m, 1H), 2.3 – 2.2 (m, 1H), 2.2 – 2.1 (m, 1H), 2.1 – 2.0 (m, 1H). **¹³C NMR (CDCl₃, 125.8 MHz):** δ 181.0, 152.8, 152.1, 141.6, 136.3, 130.5, 126.6, 121.4, 121.3, 114.8, 113.7, 62.6, 55.7, 49.9, 34.6, 23.8. **IR (ATR):** ν = 3064 (w), 2945 (m), 2831 (m), 1512 (vs), 1440 (m), 1242 (s), 1042 (m), 815 (s), cm⁻¹. **HRMS:** *m/z* (ESI/TOF) calc for C₁₈H₁₈ClN₂OS (M+H⁺) 345.0823, found 345.0819;

6-methoxy-2-(1-(4-methoxyphenyl)pyrrolidin-2-yl)benzo[*d*]thiazole (3t)



General procedure was followed with 1-(4-methoxyphenyl)pyrrolidine (88 mg, 0.5 mmol), 2-chloro-6-methoxybenzo[*d*]thiazole (50 mg, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 3/1, then toluene/ethyl acetate = 9/1) to give the title compound (70 mg, 81 %). **¹H NMR (CDCl₃, 500 MHz):** δ 7.9 (d, *J* = 8.9 Hz, 1H), 7.2 (d, *J* = 2.5 Hz, 1H), 7.1 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.8 (d, *J* = 9.0 Hz, 2H), 6.6 (d, *J* = 9.0 Hz, 2H), 5.0 (dd, *J* = 8.9, 2.1 Hz, 1H), 3.8 (s, 3H), 3.8 – 3.7 (m, 1H), 3.7 (s, 3H), 3.3 (td, *J* = 9.1, 6.4 Hz, 1H), 2.6 – 2.4 (m, 1H), 2.3 – 2.2 (m, 1H), 2.2 – 2.1 (m, 1H), 2.1 – 2.0 (m, 1H). **¹³C NMR (CDCl₃, 125.8 MHz):** δ 177.5, 157.3, 151.9, 148.6, 141.7, 136.3, 123.0, 115.0, 114.8, 113.6, 104.4, 62.6, 55.7, 55.7, 49.8, 34.6, 23.8. **IR (ATR):** ν = 3044 (w), 2943 (m), 2831 (m), 1604 (m), 1512 (vs), 1465 (s), 1260 (s), 1056 (m), 816 (s), cm⁻¹. **HRMS:** *m/z* (ESI/TOF) calc for C₁₉H₂₁N₂O₂S (M+H⁺) 341.1318, found 341.1311;

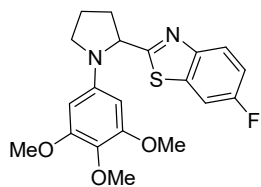
2-(1-(3,4,5-trimethoxyphenyl)pyrrolidin-2-yl)-benzo[*d*]thiazole (3u)



General procedure was followed with 1-(3,4,5-trimethoxyphenyl)pyrrolidine (118 mg, 0.5 mmol), 2-chlorobenzo[*d*]thiazole (42 mg, 33 μl, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 1/1, then toluene/ethyl acetate = 9/1) to give the title

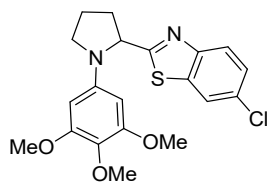
compound (78 mg, 84 %). **¹H NMR (CDCl₃, 500 MHz):** δ 8.0 (d, *J* = 8.0 Hz, 1H), 7.8 (d, *J* = 7.9 Hz, 1H), 7.6 – 7.4 (m, 1H), 7.4 – 7.3 (m, 1H), 5.9 (s, 2H), 5.1 (dd, *J* = 8.8, 2.1 Hz, 1H), 3.7 (d, *J* = 3.3 Hz, 9H), ~ 3.7 (m, 1H, partially hidden by 3.7 singlet), 3.4 (td, *J* = 9.1, 6.5 Hz, 1H), 2.6 – 2.4 (m, 1H), 2.4 – 2.2 (m, 2H), 2.2 – 2.1 (m, 1H). **¹³C NMR (CDCl₃, 125.8 MHz):** δ 179.2, 153.8, 153.7, 153.6, 143.8, 134.9, 130.1, 125.8, 124.7, 122.5, 121.7, 90.5, 62.4, 60.9, 55.8, 49.5, 34.5, 23.7. **IR (ATR):** ν = 3061 (w), 2940 (m), 2826 (m), 2248 (w), 1610 (s), 1512 (vs), 1454 (s), 1313 (m), 1250 (s), 1191 (m), 1126 (s), 1019 (m), 910 (m), 793 (m), 761 (m), 731 (s), cm⁻¹. **HRMS:** m/z (ESI/TOF) calc for C₂₀H₂₃N₂O₃S (M+H⁺) 371.1424, found 371.1420;

6-fluoro-2-(1-(3,4,5-trimethoxyphenyl)pyrrolidin-2-yl)-benzo[d]thiazole (3v)



General procedure was followed with 1-(3,4,5-trimethoxyphenyl)pyrrolidine (118 mg, 0.5 mmol), 2-chloro-6-fluorobenzo[d]thiazole (47 mg, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 1/1, then toluene/ethyl acetate = 9/1) to give the title compound (72 mg, 74 %). **¹H NMR (CDCl₃, 500 MHz):** δ 7.9 (dd, *J* = 8.9, 4.7 Hz, 1H), 7.5 (dd, *J* = 8.1, 2.6 Hz, 1H), 7.2 (tdd, *J* = 8.9, 2.6, 0.9 Hz, 1H), 5.1 (dd, *J* = 8.8, 2.1 Hz, 1H), 3.7 (s, 8H), 3.7 (s, 7H) (m, 1H, partially hidden by 3.7 singlet), 3.4 – 3.3 (m, 1H), 2.6 – 2.4 (m, 1H), 2.3 – 2.2 (m, 1H), 2.3 – 2.1 (m, 1H), 2.2 – 2.1 (m, 1H). **¹³C NMR (CDCl₃, 125.8 MHz):** δ 179.1, 179.1, 161.4, 159.0, 153.7, 150.5, 150.5, 143.9, 136.0, 135.9, 130.4, 123.6, 123.5, 114.6, 114.4, 108.1, 107.9, 62.4, 61.0, 55.9, 49.7, 34.5, 23.8. **IR (ATR):** ν = 3067 (w), 2941 (m), 2842 (m), 2249 (w), 1609 (s), 1512 (vs), 1450 (s), 1250 (vs), 1191 (m), 1127 (vs), 1020 (m), 816 (m), 732 (m) cm⁻¹. **HRMS:** m/z (ESI/TOF) calc for C₂₀H₂₂FN₂O₃S (M+H⁺) 389.1330, found 389.1330;

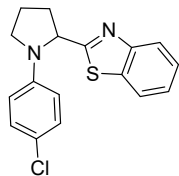
6-chloro-2-(1-(3,4,5-trimethoxyphenyl)pyrrolidin-2-yl)-benzo[d]thiazole (3w)



General procedure was followed with 1-(3,4,5-trimethoxyphenyl)pyrrolidine (118 mg, 0.5 mmol), 2,6-dichlorobenzo[d]thiazole (51 mg, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 1/1, then toluene/ethyl acetate = 9/1) to give the title compound (76 mg, 75 %). **¹H NMR (CDCl₃, 500 MHz):** δ 7.9 (d, *J* = 8.7 Hz, 1H), 7.8 (d, *J* = 2.1 Hz, 1H), 7.4 (dd, *J* = 8.7, 2.1 Hz, 1H), 5.9 (s, 2H), 5.1 (dd, *J* = 8.8, 2.1 Hz, 1H), 3.7 (d, *J* = 2.6 Hz, 10H), 3.4 (td, *J* = 9.0, 6.5 Hz, 1H), 2.7 – 2.4 (m, 1H), 2.3 – 2.2 (m, 1H), 2.2 – 2.2 (m, 0H), 2.2 – 2.1 (m, 1H). **¹³C NMR (CDCl₃, 125.8 MHz):** δ 180.0, 153.7, 152.4, 143.8, 136.2, 130.7, 130.3, 126.6, 123.3, 121.4, 90.6, 90.6, 62.4, 60.9, 55.9, 49.6, 34.4, 23.7. **IR (ATR):** ν = 3061 (w), 2939 (m), 2827 (m), 2249 (w), 1610 (s), 1512 (vs), 1450 (m), 1250 (vs), 1191 (m),

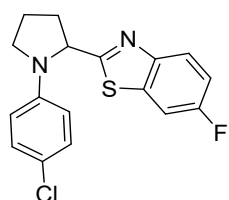
1127 (vs), 1020 (m), 732 (m), cm^{-1} . **HRMS:** m/z (ESI/TOF) calc for $\text{C}_{20}\text{H}_{22}\text{ClN}_2\text{O}_3\text{S}$ ($\text{M}+\text{H}^+$) 405.1034, found 405.1025;

2-(1-(4-chlorophenyl)pyrrolidin-2-yl)benzo[*d*]thiazole (3x)



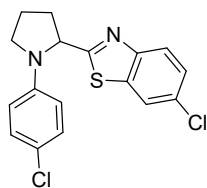
General procedure was followed with 1-(4-chlorophenyl)pyrrolidine (90 mg, 0.5 mmol), 2-chlorobenzo[*d*]thiazole (42 mg, 33 μl , 0.25 mmol), $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H_2O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 3/1, then toluene/ethyl acetate = 9/1) to give the title compound (62 mg, 79 %). **^1H NMR (CDCl_3 , 500 MHz):** δ 8.0 (d, $J = 8.2$ Hz, 1H), 7.8 (d, $J = 8.0$ Hz, 1H), 7.5 – 7.4 (m, 1H), 7.4 – 7.3 (m, 1H), 7.1 (d, $J = 9.0$ Hz, 2H), 6.6 (d, $J = 8.9$ Hz, 2H), 5.1 (dd, $J = 8.8, 2.1$ Hz, 1H), 3.9 – 3.7 (m, 1H), 3.3 (td, $J = 9.4, 6.5$ Hz, 1H), 2.6 – 2.4 (m, 1H), 2.3 – 2.3 (m, 1H), 2.3 – 2.1 (m, 1H), 2.1 – 2.0 (m, 1H). **^{13}C NMR (CDCl_3 , 125.8 MHz):** δ 178.6, 154.0, 145.4, 134.9, 128.9, 126.0, 124.8, 122.7, 122.4, 121.8, 113.8, 62.3, 49.3, 34.5, 23.6. **IR (ATR):** $\nu = 3064$ (w), 2974 (m), 2847 (m), 1598 (s), 1497 (vs), 1360 (s), 810 (s), 761 (s), 731 (m), cm^{-1} . **HRMS:** m/z (ESI/TOF) calc for $\text{C}_{17}\text{H}_{16}\text{ClN}_2\text{S}$ ($\text{M}+\text{H}^+$) 315.0717, found 315.0728;

2-(1-(4-chlorophenyl)pyrrolidin-2-yl)-6-fluorobenzo[*d*]thiazole (3y)



General procedure was followed with 1-(4-chlorophenyl)pyrrolidine (90 mg, 0.5 mmol), 2-chloro-6-fluorobenzo[*d*]thiazole (47 mg, 0.25 mmol), $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ cat. (1 mol%, 2.3 mg, 0.0025 mmol), sodium acetate (41 mg, 0.5 mmol) in DMA (1 ml) and H_2O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 3/1, then toluene/ethyl acetate = 9/1) to give the title compound (53 mg, 63 %). **^1H NMR (CDCl_3 , 500 MHz):** δ 7.9 (dd, $J = 9.0, 4.8$ Hz, 1H), 7.4 (dd, $J = 8.1, 2.5$ Hz, 1H), 7.2 (td, $J = 8.9, 2.5$ Hz, 1H), 7.1 (d, $J = 8.9$ Hz, 2H), 6.5 (d, $J = 9.0$ Hz, 2H), 5.0 (dd, $J = 8.9, 2.1$ Hz, 1H), 3.8 – 3.7 (m, 1H), 3.3 (td, $J = 9.4, 6.6$ Hz, 1H), 2.6 – 2.5 (m, 1H), 2.3 – 2.3 (m, 1H), 2.2 – 2.1 (m, 1H), 2.2 – 2.1 (m, 1H). **^{13}C NMR (CDCl_3 , 125.8 MHz):** δ 178.4, 178.3, 161.4, 158.9, 150.6, 150.6, 145.4, 136.0, 135.8, 129.0, 123.6, 123.5, 122.5, 114.7, 114.4, 113.8, 108.0, 107.8, 62.2, 49.4, 34.5, 23.7. **IR (ATR):** $\nu = 3069$ (w), 2974 (m), 2848 (m), 1600 (s), 1567 (m), 1497 (vs), 1456 (s), 1359 (s), 1249 (m), 1191 (s), 813 (s), cm^{-1} . **HRMS:** m/z (ESI/TOF) calc for $\text{C}_{17}\text{H}_{15}\text{ClFN}_2\text{S}$ ($\text{M}+\text{H}^+$) 333.0623, found 333.0617;

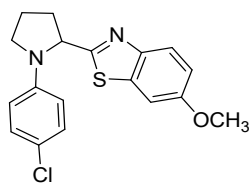
6-chloro-2-(1-(4-chlorophenyl)pyrrolidin-2-yl)benzo[*d*]thiazole (3z)



General procedure was followed with 1-(4-chlorophenyl)pyrrolidine (90 mg, 0.5 mmol), 2,6-dichlorobenzo[*d*]thiazole (51 mg, 0.25 mmol), $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ cat. (1 mol%, 2.3 mg, 0.0025 mmol), sodium acetate (41

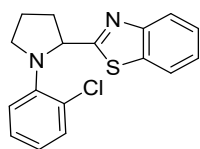
mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 3/1, then toluene/ethyl acetate = 9/1) to give the title compound (60 mg, 69 %). **¹H NMR (CDCl₃, 500 MHz):** δ 7.9 (d, *J* = 8.7 Hz, 1H), 7.7 (d, *J* = 2.1 Hz, 1H), 7.4 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.1 (d, *J* = 9.0 Hz, 2H), 6.5 (d, *J* = 9.0 Hz, 2H), 5.0 (dd, *J* = 8.9, 2.1 Hz, 1H), 3.8 – 3.7 (m, 1H), 3.3 (td, *J* = 9.4, 6.5 Hz, 1H), 2.6 – 2.5 (m, 1H), 2.3 – 2.3 (m, 1H), 2.2 – 2.1 (m, 1H), 2.1 – 2.1 (m, 1H). **¹³C NMR (CDCl₃, 125.8 MHz):** δ 179.3, 152.6, 145.4, 136.1, 130.7, 129.0, 126.7, 123.5, 122.6, 121.3, 113.9, 62.2, 49.4, 34.5, 23.7. **IR (ATR):** ν = 3044 (w), 2974 (m), 2846 (m), 1597 (s), 1497 (vs), 1440 (m), 1359 (s), 1097 (m), 810 (s), 733 (m), cm⁻¹. **HRMS:** *m/z* (ESI/TOF) calc for C₁₇H₁₅Cl₂N₂S (M+H⁺) 349.0328, found 349.0327;

2-(1-(4-chlorophenyl)pyrrolidin-2-yl)-6-methoxybenzo[*d*]thiazole (3aa)



General procedure was followed with 1-(4-chlorophenyl)pyrrolidine (90 mg, 0.5 mmol), 2-chloro-6-methoxybenzo[*d*]thiazole (50 mg, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (1 mol%, 2.3 mg, 0.0025 mmol), sodium acetate (41 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 3/1, then toluene/ethyl acetate = 9/1) to give the title compound (62 mg, 72 %). **¹H NMR (CDCl₃, 500 MHz):** δ 7.9 (d, *J* = 9.0 Hz, 1H), 7.2 (d, *J* = 2.5 Hz, 1H), 7.1 (d, *J* = 9.0 Hz, 2H), 7.1 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.6 (d, *J* = 9.0 Hz, 2H), 5.0 (dd, *J* = 8.7, 2.1 Hz, 1H), 3.8 (s, 3H), 3.8 – 3.7 (m, 1H), 3.3 (td, *J* = 9.4, 6.5 Hz, 1H), 2.6 – 2.4 (m, 1H), 2.3 – 2.3 (m, 1H), 2.2 – 2.2 (m, 1H), 2.1 – 2.1 (m, 1H). **¹³C NMR (CDCl₃, 125.8 MHz):** δ 175.8, 157.4, 148.5, 145.5, 136.2, 128.9, 123.1, 122.3, 115.2, 113.8, 104.3, 62.2, 55.8, 49.3, 34.6, 23.7. **IR (ATR):** ν = 3069 (w), 2970 (m), 2833 (m), 1602 (s), 1497 (vs), 1466 (s), 1359 (s), 1260 (s), 1225 (s), 1057 (m), 811 (s), cm⁻¹. **HRMS:** *m/z* (ESI/TOF) calc for C₁₈H₁₈ClN₂OS (M+H⁺) 345.0823, found 345.0820;

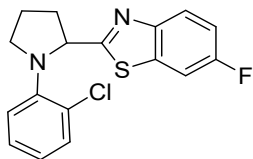
2-(1-(2-chlorophenyl)pyrrolidin-2-yl)benzo[*d*]thiazole (3ab)



General procedure was followed with 1-(2-chlorophenyl)pyrrolidine (90.8 mg, 0.5 mmol), 2-chlorobenzo[*d*]thiazole (42 mg, 33 μl, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 7/1) to give the title compound (57.5 mg, 75 %). **¹H NMR (CDCl₃, 500 MHz):** δ 7.9 (d, *J* = 8.1 Hz, 1H), 7.8 (d, *J* = 8.0 Hz, 1H), 7.4 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.3 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.3 – 7.2 (m, 1H), 7.1 – 7.0 (m, 2H), 6.8 (ddd, *J* = 7.9, 6.7, 2.1 Hz, 1H), 5.3 (t, *J* = 7.2 Hz, 1H), 4.3 – 4.2 (m, 1H), 3.1 (ddd, *J* = 9.7, 7.9, 4.4 Hz, 1H), 2.7 – 2.6 (m, 1H), 2.2 – 2.1 (m, 3H), 2.0 (ddd, *J* = 15.1, 7.4, 4.8 Hz, 1H). **¹³C NMR (CDCl₃, 125.8 MHz):** δ 178.0, 153.4, 145.6, 134.9, 131.0, 127.2, 127.1, 125.6, 124.6, 122.8, 122.4, 121.8, 119.6, 62.5, 53.8, 35.2, 24.9. **IR (ATR):** ν = 3061 (w), 2973 (m), 2873 (m),

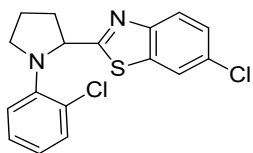
1588 (s), 1480 (vs), 1438 (s), 1314 (s), 1040 (m), 758 (s), 731 (m), cm^{-1} . **HRMS:** m/z (ESI/TOF) calc for $\text{C}_{17}\text{H}_{16}\text{ClN}_2\text{S}$ ($\text{M}+\text{H}^+$) 315.0717, found 315.0710;

2-(1-(2-chlorophenyl)pyrrolidin-2-yl)-6-fluorobenzo[*d*]thiazole (3ac)



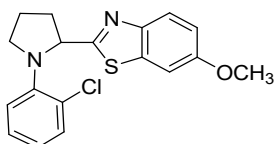
General procedure was followed with 1-(2-chlorophenyl)pyrrolidine (90.8 mg, 0.5 mmol), 2-chloro-6-fluorobenzo[*d*]thiazole (47 mg, 0.25 mmol), $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ cat. (1 mol%, 2.3 mg, 0.0025 mmol), sodium acetate (41 mg, 0.5 mmol) in DMA (1 ml) and H_2O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (toluene/ethyl acetate = 9/1) to give the title compound (65 mg, 80 %). **^1H NMR (CDCl_3 , 500 MHz):** δ 7.8 (dd, $J = 8.9, 4.8$ Hz, 1H), 7.4 (dd, $J = 8.2, 2.6$ Hz, 1H), 7.3 (d, $J = 7.6$ Hz, 1H), 7.1 (td, $J = 8.9, 2.6$ Hz, 1H), 7.1 (dd, $J = 4.0, 1.0$ Hz, 2H), 6.9 (ddd, $J = 7.9, 5.2, 3.5$ Hz, 1H), 5.3 (t, $J = 7.2$ Hz, 1H), 4.2 (dt, $J = 9.7, 7.1$ Hz, 1H), 3.2 – 3.0 (m, 1H), 2.7 – 2.5 (m, 1H), 2.2 – 2.1 (m, 2H), 2.1 – 2.0 (m, 1H). **^{13}C NMR (CDCl_3 , 125.8 MHz):** δ 177.7, 177.7, 161.3, 158.9, 150.1, 150.1, 145.6, 136.1, 135.9, 131.1, 127.4, 127.2, 123.4, 123.3, 123.0, 119.7, 114.3, 114.1, 108.1, 107.9, 62.4, 53.9, 35.1, 24.9. **IR (ATR):** $\nu = 3065$ (w), 2974 (m), 2874 (m), 1588 (s), 1567 (s), 1480 (vs), 1456 (vs), 1312 (s), 1295 (s), 1249 (s), 1187 (m), 851 (m), 814 (m), 783 (m), 752 (s), cm^{-1} . **HRMS:** m/z (ESI/TOF) calc for $\text{C}_{17}\text{H}_{15}\text{ClFN}_2\text{S}$ ($\text{M}+\text{H}^+$) 333.0623, found 333.0624;

6-chloro-2-(1-(2-chlorophenyl)pyrrolidin-2-yl)benzo[*d*]thiazole (3ad)



General procedure was followed with 1-(2-chlorophenyl)pyrrolidine (90.8 mg, 0.5 mmol), 2,6-dichlorobenzo[*d*]thiazole (51 mg, 0.25 mmol), $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H_2O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 7/1, then toluene/ethyl acetate = 9/1) to give the title compound (65 mg, 79 %). **^1H NMR (CDCl_3 , 500 MHz):** δ 7.8 (d, $J = 8.7$ Hz, 1H), 7.7 (d, $J = 2.2$ Hz, 1H), 7.3 (td, $J = 8.5, 1.5$ Hz, 2H), 7.1 – 7.0 (m, 2H), 6.9 (dt, $J = 7.9, 4.4$ Hz, 1H), 5.3 (t, $J = 7.2$ Hz, 1H), 4.2 (dt, $J = 9.6, 7.1$ Hz, 1H), 3.2 – 3.0 (m, 1H), 2.8 – 2.5 (m, 1H), 2.3 – 2.1 (m, 2H), 2.1 – 2.0 (m, 1H). **^{13}C NMR (CDCl_3 , 125.8 MHz):** δ 178.7, 152.1, 145.5, 136.2, 131.1, 130.5, 127.4, 127.3, 126.4, 123.2, 123.1, 121.5, 119.7, 62.4, 53.9, 35.1, 25.0. **IR (ATR):** $\nu = 3062$ (w), 2974 (m), 2873 (m), 1590 (vs), 1520 (m), 1480 (vs), 1441 (vs), 1296 (s), 1140 (m), 816 (m), 752 (s), cm^{-1} . **HRMS:** m/z (ESI/TOF) calc for $\text{C}_{17}\text{H}_{15}\text{Cl}_2\text{N}_2\text{S}$ ($\text{M}+\text{H}^+$) 349.0328, found 349.0325;

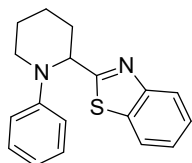
2-(1-(2-chlorophenyl)pyrrolidin-2-yl)-6-methoxybenzo[*d*]thiazole (3ae)



General procedure was followed with 1-(2-chlorophenyl)pyrrolidine (90.8 mg, 0.5 mmol), 2-chloro-6-methoxybenzo[*d*]thiazole (50 mg, 0.25 mmol), $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ cat. (1 mol%, 2.4 mg, 0.0025 mmol),

sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 7/1, then toluene/ethyl acetate = 9/1) to give the title compound (59.5 mg, 70 %). **¹H NMR (CDCl₃, 500 MHz):** δ 7.8 (d, *J* = 8.9 Hz, 1H), 7.4 – 7.3 (m, 1H), 7.2 (d, *J* = 2.6 Hz, 1H), 7.1 – 7.0 (m, 2H), 7.0 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.8 (ddd, *J* = 7.8, 6.2, 2.5 Hz, 1H), 5.3 (t, *J* = 7.2 Hz, 1H), 4.2 (dt, *J* = 9.5, 7.2 Hz, 1H), 3.8 (s, 3H), 3.2 – 3.0 (m, 1H), 2.7 – 2.5 (m, 1H), 2.2 – 2.1 (m, 2H), 2.1 – 2.0 (m, 1H). **¹³C NMR (CDCl₃, 125.8 MHz):** δ 175.1, 157.3, 147.9, 145.7, 136.3, 131.0, 127.2, 127.2, 122.9, 122.8, 119.7, 114.9, 104.4, 62.4, 55.7, 55.7, 53.8, 35.1, 24.9. **IR (ATR):** ν = 3424, 3063 (w), 2966 (m), 2876 (m), 2832 (m), 1604 (vs), 1559 (m), 1479 (vs), 1436 (s), 1259 (s), 1226 (s), 1058 (s), 832 (m), 752 (m), cm⁻¹. **HRMS:** *m/z* (ESI/TOF) calc for C₁₈H₁₈ClN₂OS (M+H⁺) 345.0823, found 345.0814;

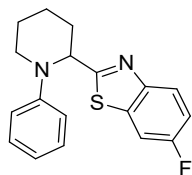
2-(1-phenylpiperidin-2-yl)benzo[*d*]thiazole (4a)



General procedure was followed with 1-phenylpiperidine (80 mg, 0.5 mmol), 2-chlorobenzo[*d*]thiazole (42 mg, 33 μl, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h.

Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 7/1, then toluene/ethyl acetate = 9/1) to give the title compound (46 mg, 62 %). **¹H NMR (CDCl₃, 500 MHz):** δ 8.0 (d, *J* = 8.2 Hz, 0H), 7.7 (d, *J* = 8.0 Hz, 0H), 7.4 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.3 – 7.2 (m, 1H), 7.2 – 7.1 (m, 2H), 7.1 – 7.0 (m, 2H), 6.8 (tt, *J* = 7.2, 1.1 Hz, 1H), 5.2 (t, *J* = 4.9 Hz, 1H), 3.5 – 3.3 (m, 2H), 2.5 – 2.3 (m, 1H), 2.2 – 2.1 (m, 1H), 1.8 – 1.6 (m, 4H). **¹³C NMR (CDCl₃, 125.8 MHz):** IR (ATR): δ 175.7, 153.1, 150.7, 135.4, 129.2, 129.1, 125.6, 124.6, 122.7, 121.6, 120.0, 117.5, 60.0, 48.0, 30.5, 24.8, 20.9. ν = 3060 (w), 2937 (s), 2857 (m), 1596 (vs), 1502 (vs), 1436 (s), 1384 (m), 1345 (m), 1253 (ms), 1142 (m), 1033 (m), 760 (s), 694 (s), cm⁻¹. **HRMS:** *m/z* (ESI/TOF) calc for C₁₈H₁₉N₂S (M+H⁺) 295.1263, found 295.1257;

6-fluoro-2-(1-phenylpiperidin-2-yl)benzo[*d*]thiazole (4b)

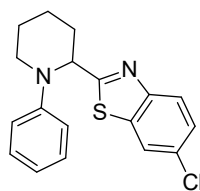


General procedure was followed with 1-phenylpiperidine (80 mg, 0.5 mmol), 2-chloro-6-fluorobenzo[*d*]thiazole (47 mg, 0.25 mmol), [Ir(dtbbpy)(ppy)₂]PF₆ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H₂O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h.

Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 7/1, then toluene/ethyl acetate = 9/1) to give the title compound (50 mg, 64 %). **¹H NMR (CDCl₃, 500 MHz):** δ 7.9 (dd, *J* = 8.9, 4.8 Hz, 1H), 7.4 (dd, *J* = 8.2, 2.6 Hz, 1H), 7.2 (dd, *J* = 8.5, 7.2 Hz, 2H), 7.1 (td, *J* = 8.9, 2.6 Hz, 1H), 7.0 (d, *J* = 8.0 Hz, 2H), 6.8 (t, *J* = 7.3 Hz, 1H), 5.1 (t, *J* = 4.9 Hz, 1H), 3.4 (q, *J* = 6.8, 5.7 Hz, 2H), 2.4 – 2.3 (m, 1H), 2.1 (ddt, *J* = 12.9, 8.4, 4.1 Hz, 1H), 1.8 – 1.6 (m, 4H). **¹³C NMR (CDCl₃, 125.8 MHz):** δ

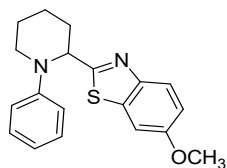
175.6, 175.5, 161.4, 158.9, 150.6, 149.7, 149.7, 136.5, 136.4, 129.2, 123.6, 123.5, 120.2, 117.7, 114.3, 114.0, 107.9, 107.7, 60.0, 48.2, 30.4, 24.7, 20.9. **IR (ATR):** $\nu = 3063$ (w), 2937 (s), 2857 (m), 1598 (s), 1567 (m), 1500 (s), 1455 (s), 1384 (m), 1250 (s), 1198 (s), 1167 (m), 817 (m), 753 (m), 694 (m), cm^{-1} ; **HRMS:** m/z (ESI/TOF) calc for $\text{C}_{18}\text{H}_{18}\text{FN}_2\text{S}$ ($\text{M}+\text{H}^+$) 313.1169, found 313.1161;

6-chloro-2-(1-phenylpiperidin-2-yl)benzo[d]thiazole (4c)



General procedure was followed with 1-phenylpiperidine (80 mg, 0.5 mmol), 2,6-dichlorobenzo[d]thiazole (51 mg, 0.25 mmol), $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H_2O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 7/1, then toluene/ethyl acetate = 9/1) to give the title compound (46 mg, 56 %). **^1H NMR (CDCl_3 , 500 MHz):** δ 7.9 (d, $J = 8.7$ Hz, 1H), 7.7 (d, $J = 2.1$ Hz, 1H), 7.4 (dd, $J = 8.7, 2.1$ Hz, 1H), 7.2 (dd, $J = 8.8, 7.3$ Hz, 2H), 7.0 (d, $J = 7.7$ Hz, 2H), 6.8 (t, $J = 7.3$ Hz, 1H), 5.1 (t, $J = 5.0$ Hz, 1H), 3.4 (q, $J = 5.7, 5.1$ Hz, 2H), 2.4 – 2.3 (m, 1H), 2.1 (ddt, $J = 12.7, 8.4, 4.2$ Hz, 1H), 1.8 – 1.6 (m, 4H). **^{13}C NMR (CDCl_3 , 125.8 MHz):** δ 176.5, 151.7, 150.6, 136.7, 130.6, 129.2, 126.4, 123.4, 121.3, 120.3, 117.7, 60.1, 48.3, 30.4, 24.7, 21.0. **IR (ATR):** $\nu = 3060$ (w), 2937 (s), 2856 (m), 1596 (vs), 1499 (vs), 1439 (s), 1384 (m), 1345 (m), 1303 (m), 1278 (s), 1102 (m), 1033 (m), 817 (s), 766 (s), 694 (s), cm^{-1} . **HRMS:** m/z (ESI/TOF) calc for $\text{C}_{18}\text{H}_{18}\text{ClN}_2\text{S}$ ($\text{M}+\text{H}^+$) 329.0874, found 329.0873;

6-methoxy-2-(1-phenylpiperidin-2-yl)benzo[d]thiazole (4d)

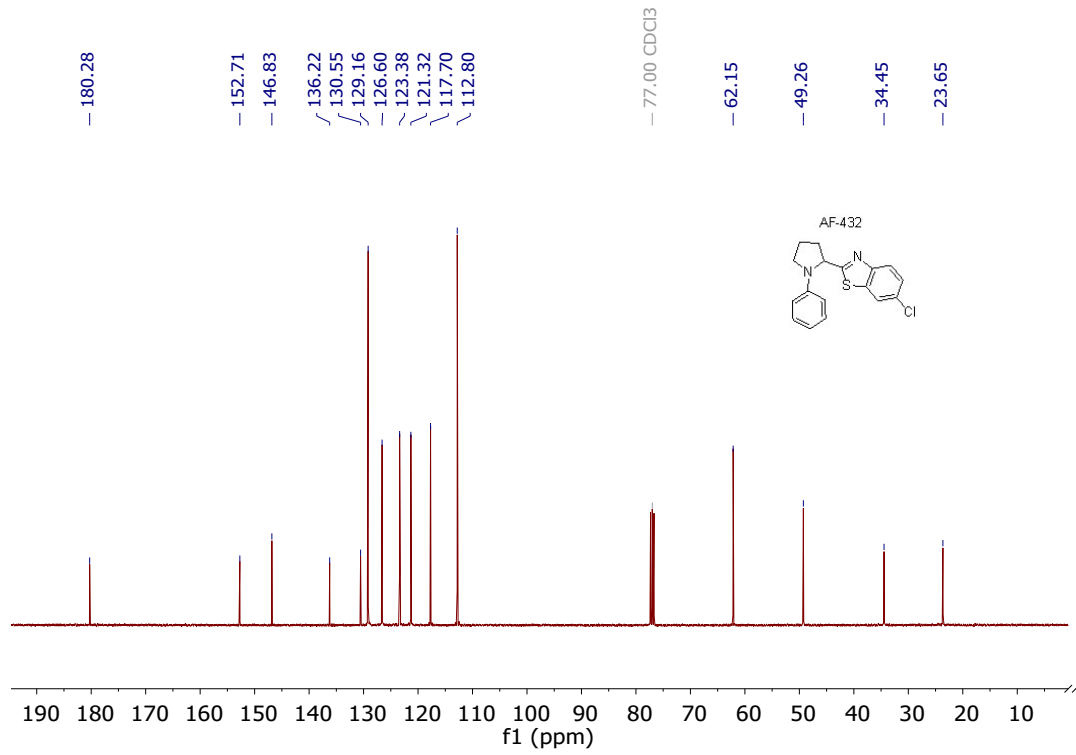
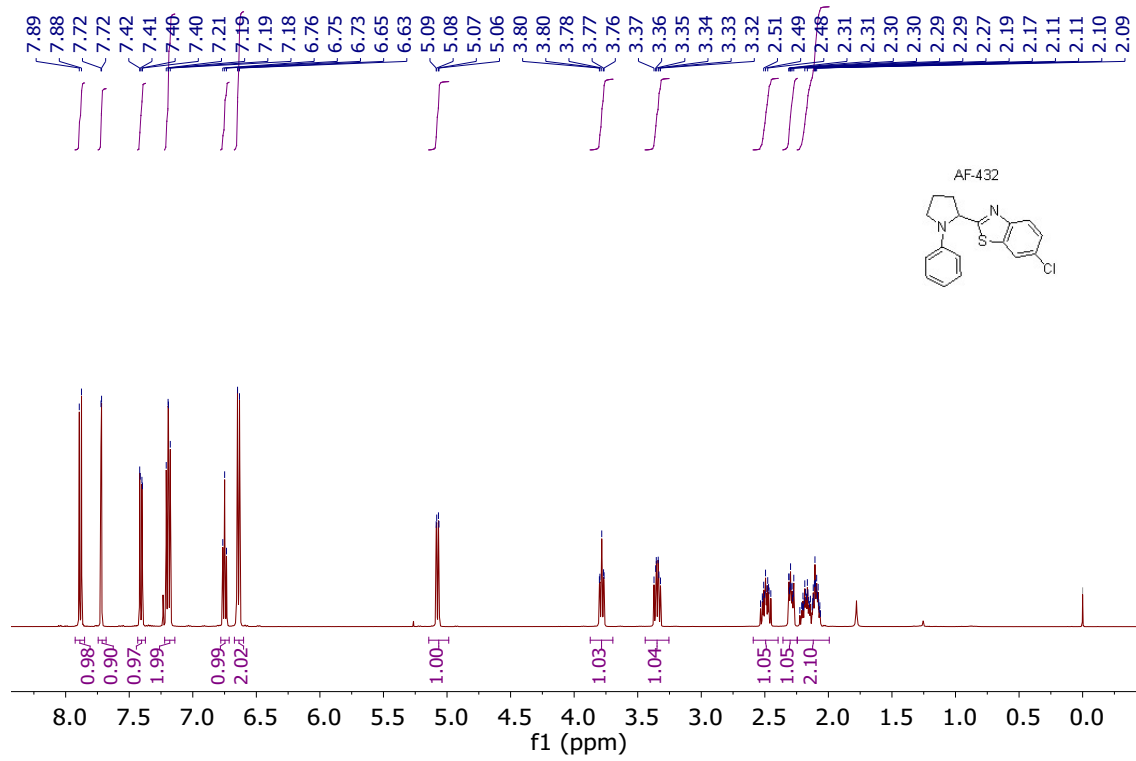


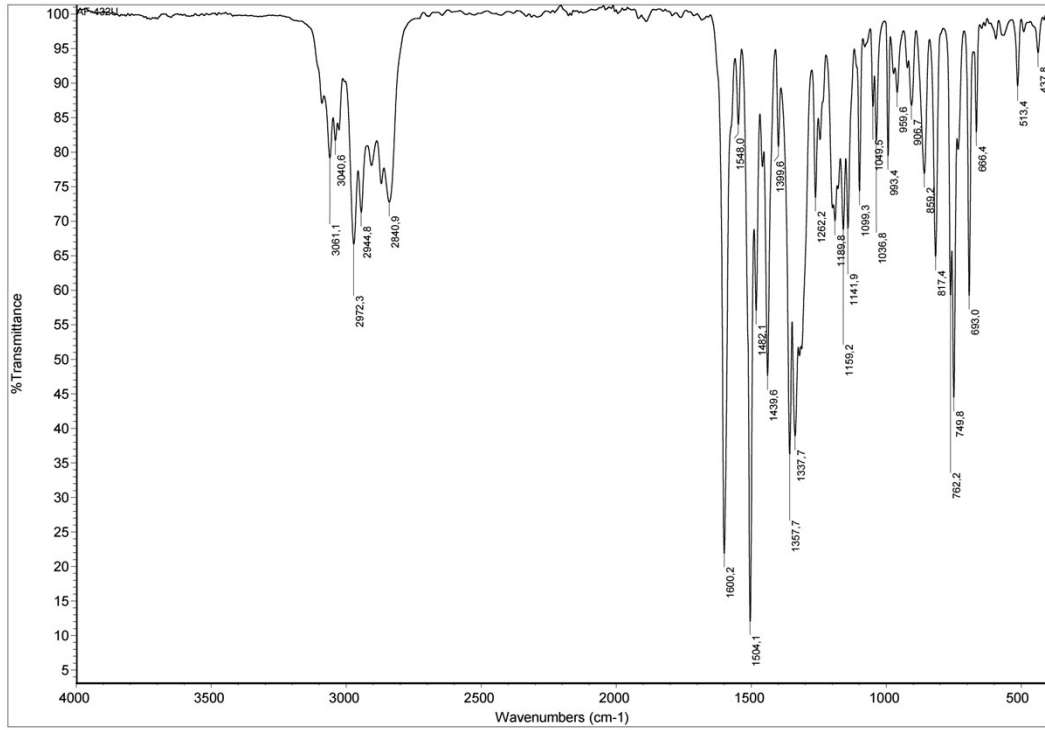
General procedure was followed with 1-phenylpiperidine (80 mg, 0.5 mmol), 2-chloro-6-methoxybenzo[d]thiazole (50mg, 0.25 mmol), $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ cat. (1 mol%, 2.4 mg, 0.0025 mmol), sodium acetate (42 mg, 0.5 mmol) in DMA (1 ml) and H_2O (0.3 ml). The reaction was irradiated with blue LEDs for 24 h. Crude reaction mixture was purified by preparative thin layer chromatography on silica gel (petrolether/ethyl acetate = 7/1, then toluene/ethyl acetate = 9/1) to give the title compound (61 mg, 76 %). **^1H NMR (CDCl_3 , 500 MHz):** δ 7.8 (d, $J = 8.9$ Hz, 1H), 7.3 – 7.1 (m, 3H), 7.0 – 6.9 (m, 3H), 6.8 (tt, $J = 7.3, 1.1$ Hz, 1H), 5.1 (t, $J = 4.9$ Hz, 1H), 3.8 (s, 3H), 3.5 – 3.3 (m, 2H), 2.4 – 2.3 (m, 1H), 2.2 – 2.0 (m, 1H), 1.8 – 1.6 (m, 5H). **^{13}C NMR (CDCl_3 , 125.8 MHz):** δ 173.0, 157.3, 150.7, 147.6, 136.7, 129.1, 123.1, 119.9, 117.5, 114.8, 104.2, 59.9, 55.7, 48.0, 30.4, 24.8, 20.9. **IR (ATR):** $\nu = 3060$ (w), 2937 (s), 2855 (m), 1600 (vs), 1501 (vs), 1501 (s), 1466 (s), 1384 (m), 1345 (m), 1257 (s), 1255 (s), 1056 (m), 1028 (m), 832 (m), 753 (m), 695 (m), cm^{-1} . **HRMS:** m/z (ESI/TOF) calc for $\text{C}_{19}\text{H}_{21}\text{ClN}_2\text{OS}$ ($\text{M}+\text{H}^+$) 325.1369, found 325.1371;

1. Prier, C. K., & MacMillan, D. W. C. (2014). Amine α -heteroarylation via photoredox catalysis: a homolytic aromatic substitution pathway. *Chem. Sci.*, 5(11), 4173–4178. <https://doi.org/10.1039/C4SC02155J>
2. Ma, J., Zhong, Y., Cai, H., & Xu, W. (2025). Photocatalytic α -C(sp³)-H Arylation/Heteroarylation of Amines Enabled by Pyrylium Salt. *The Journal of Organic Chemistry*, 90(11), 4080–4089. <https://doi.org/10.1021/acs.joc.5c00090>

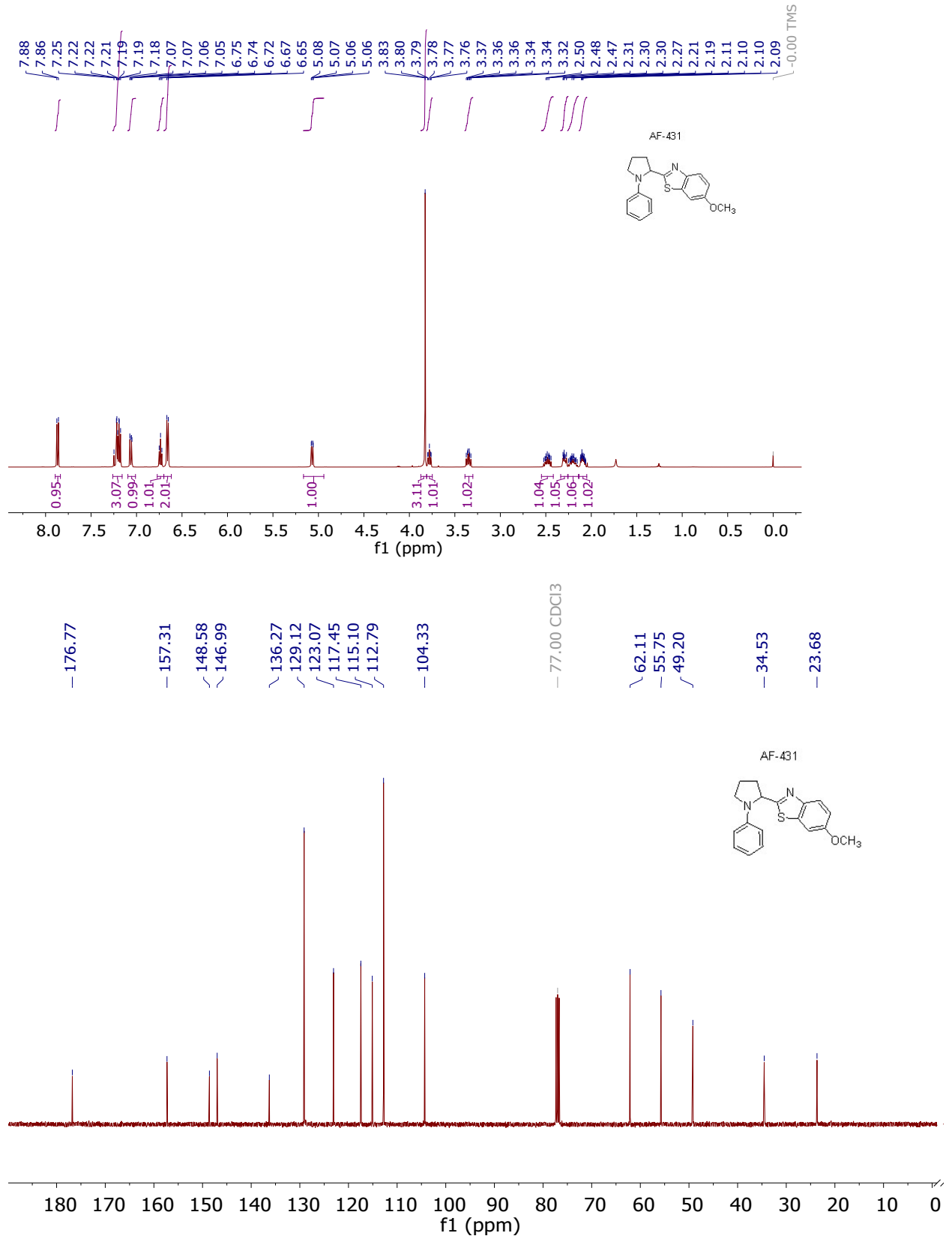
Copies of ¹H-NMR and ¹³C-NMR spectra for new starting material and products

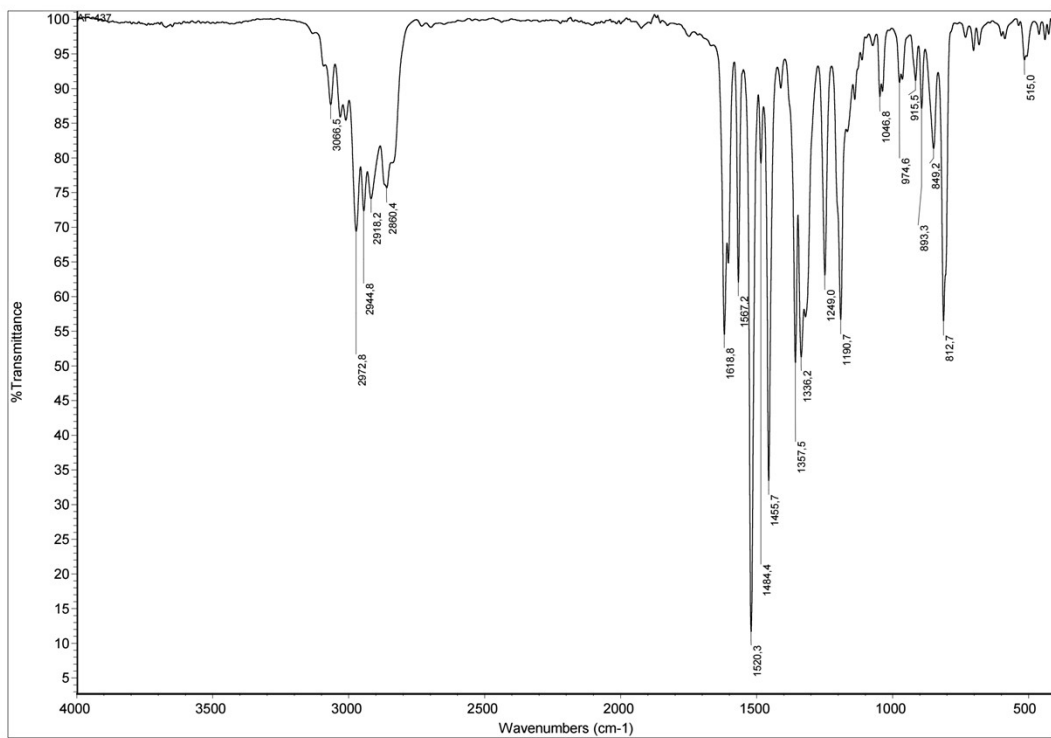
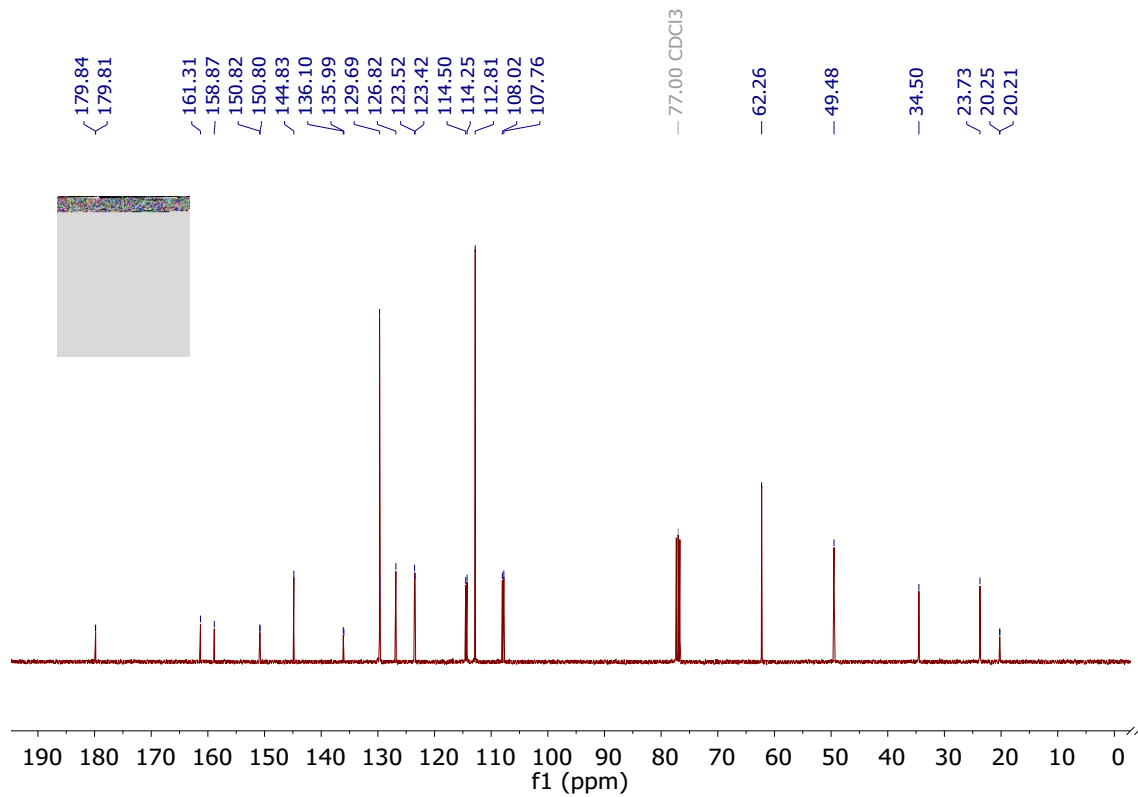
3c



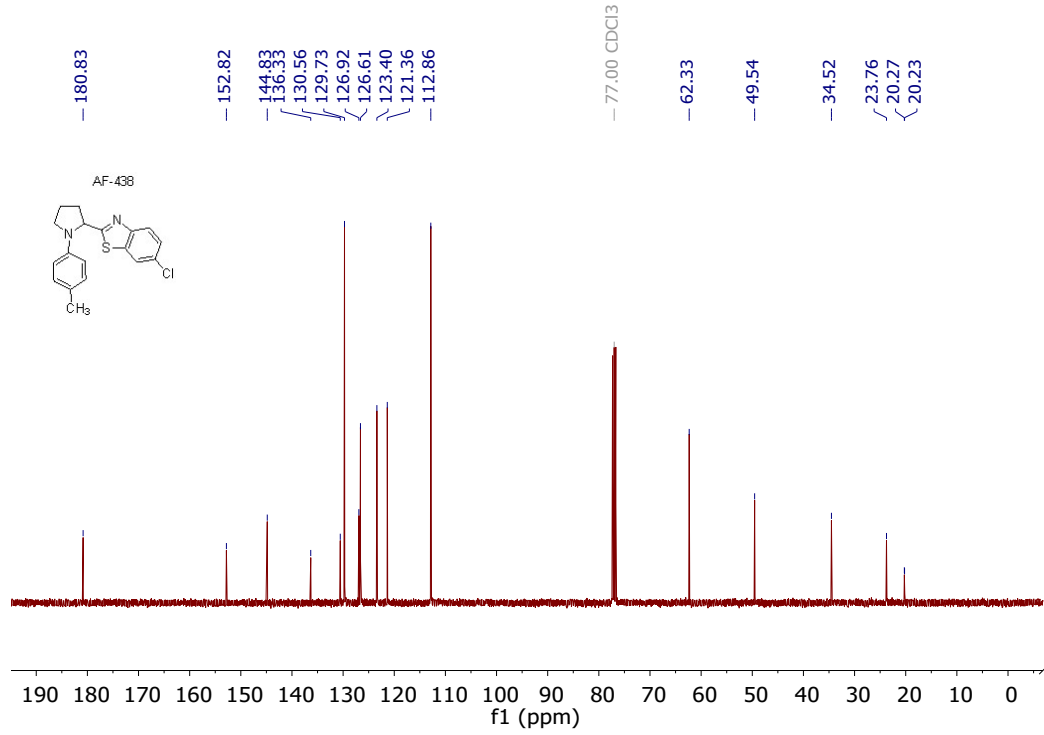
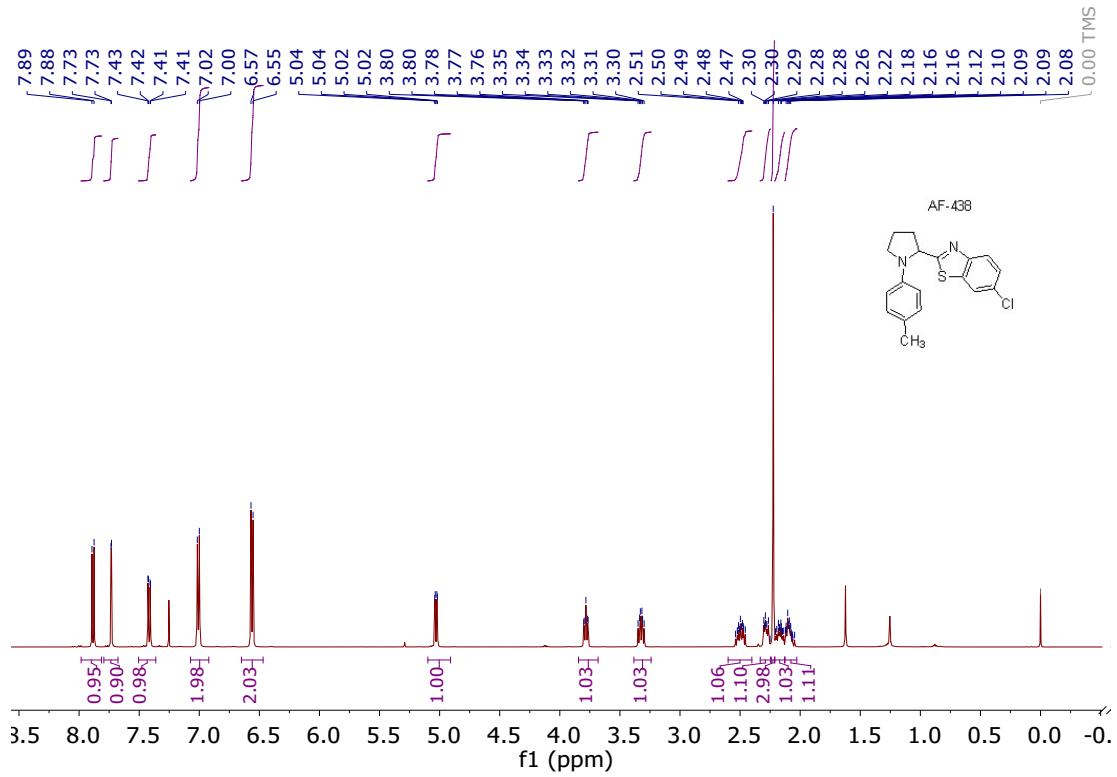


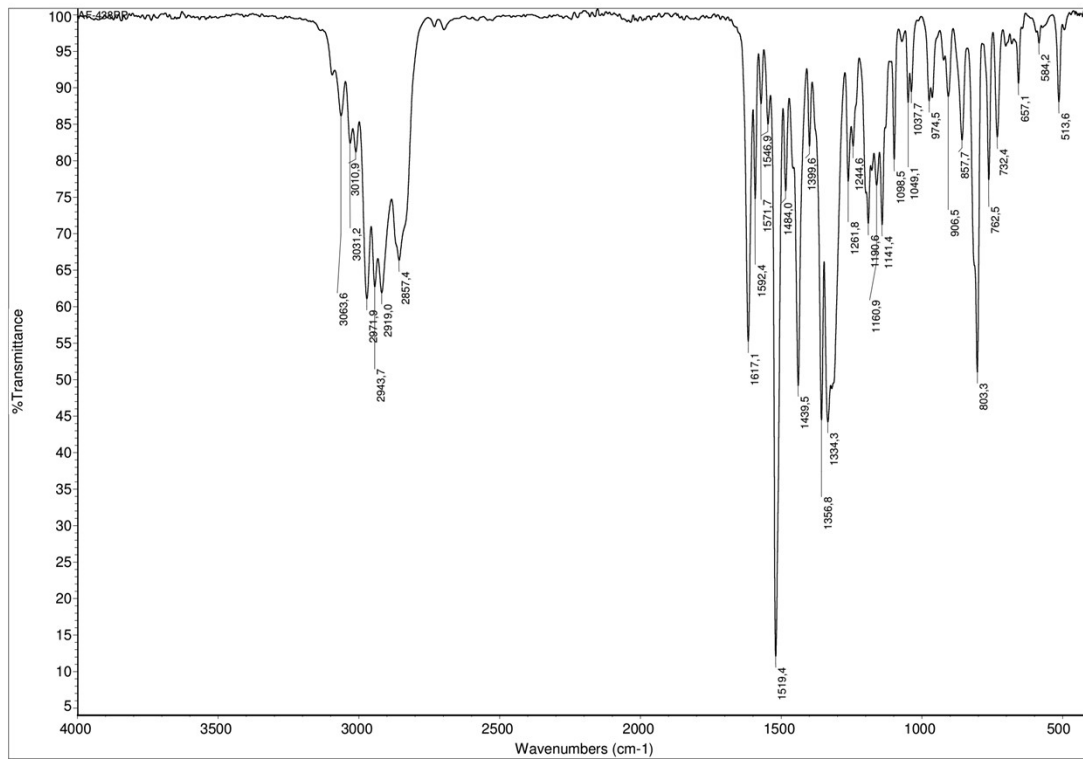
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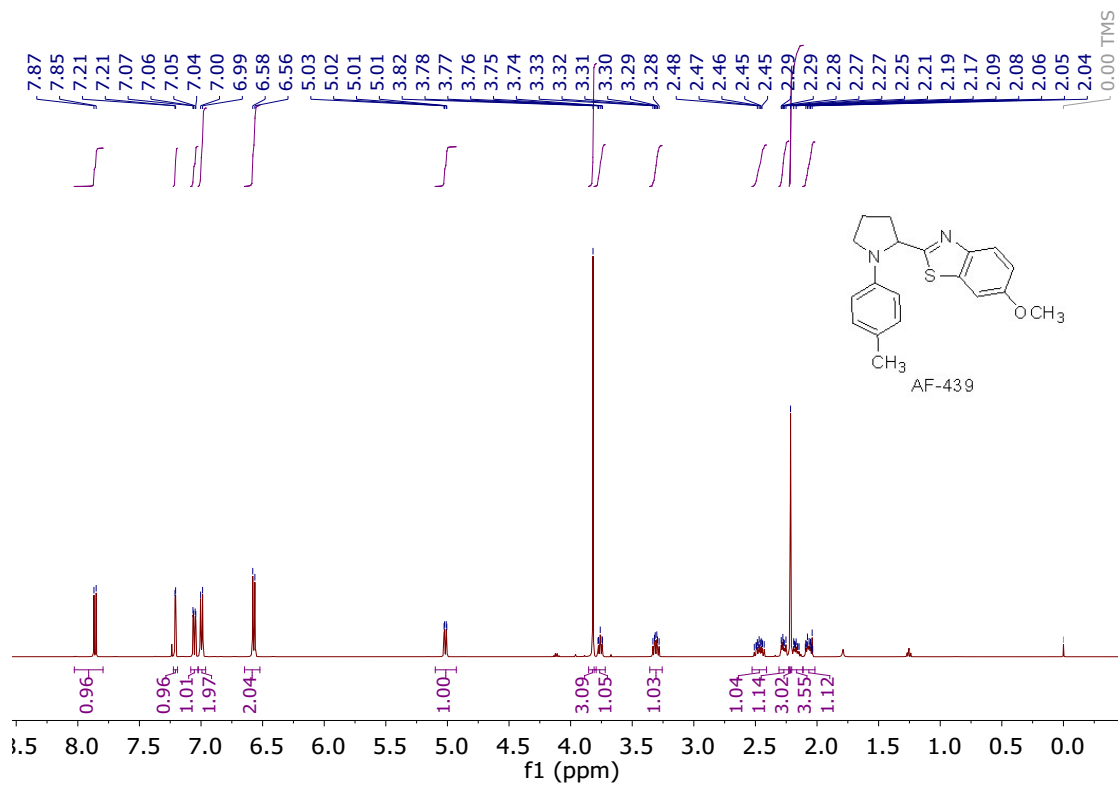


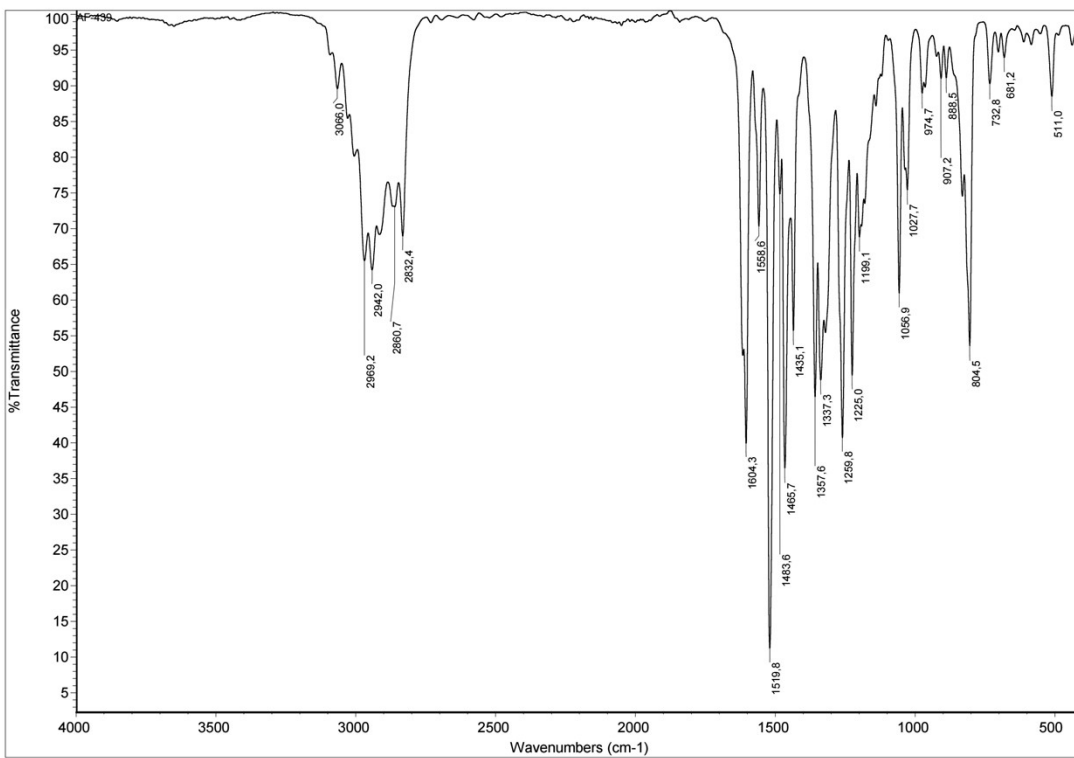
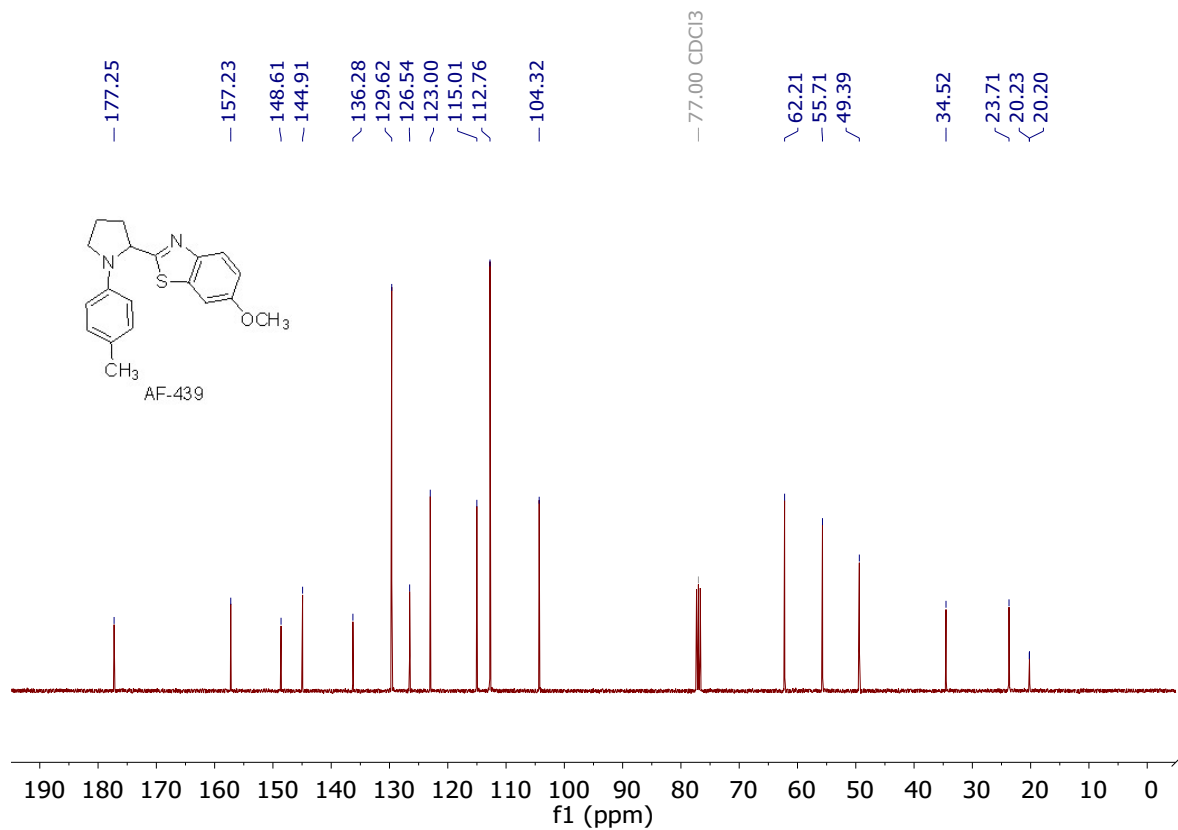
3g



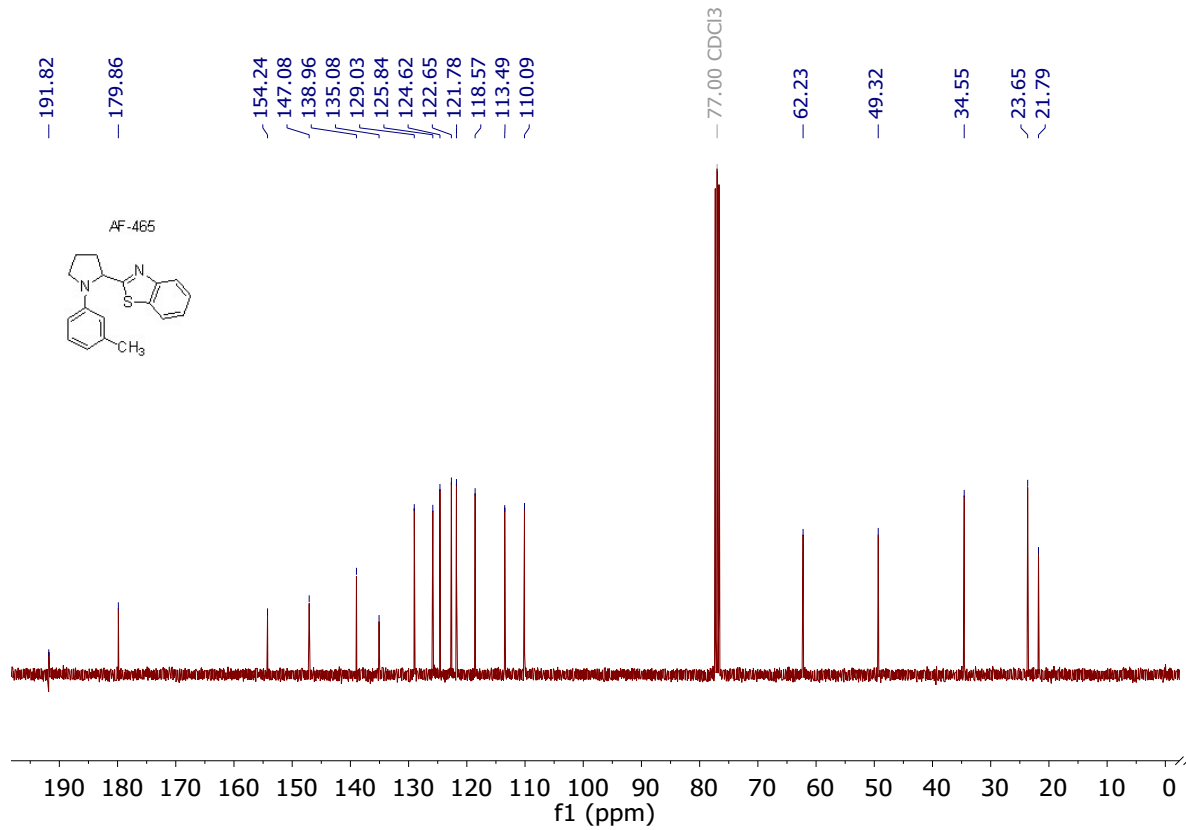
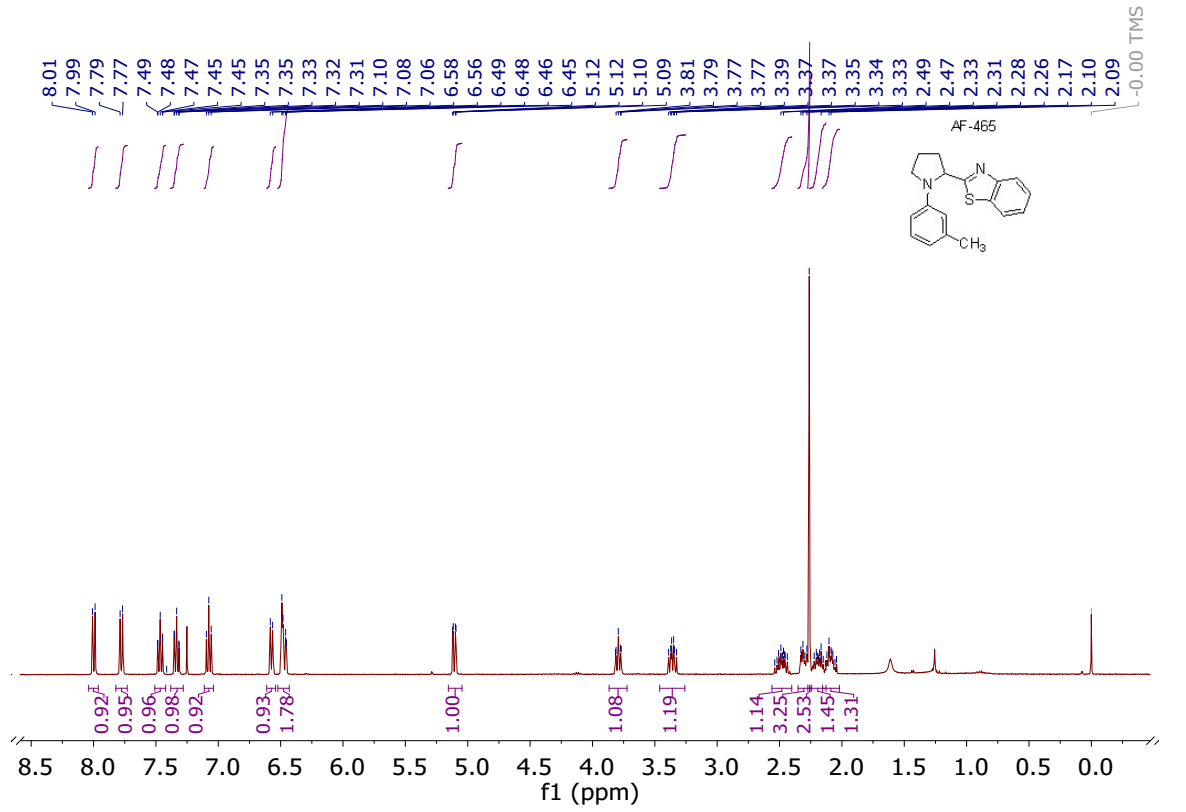


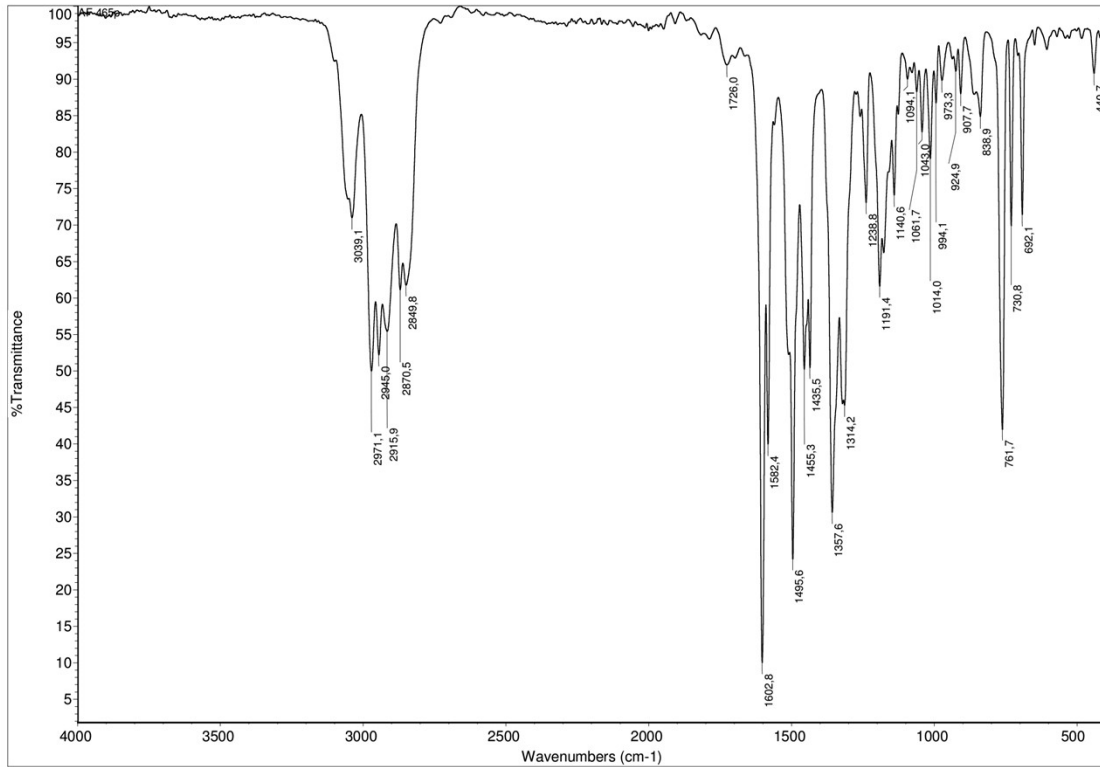
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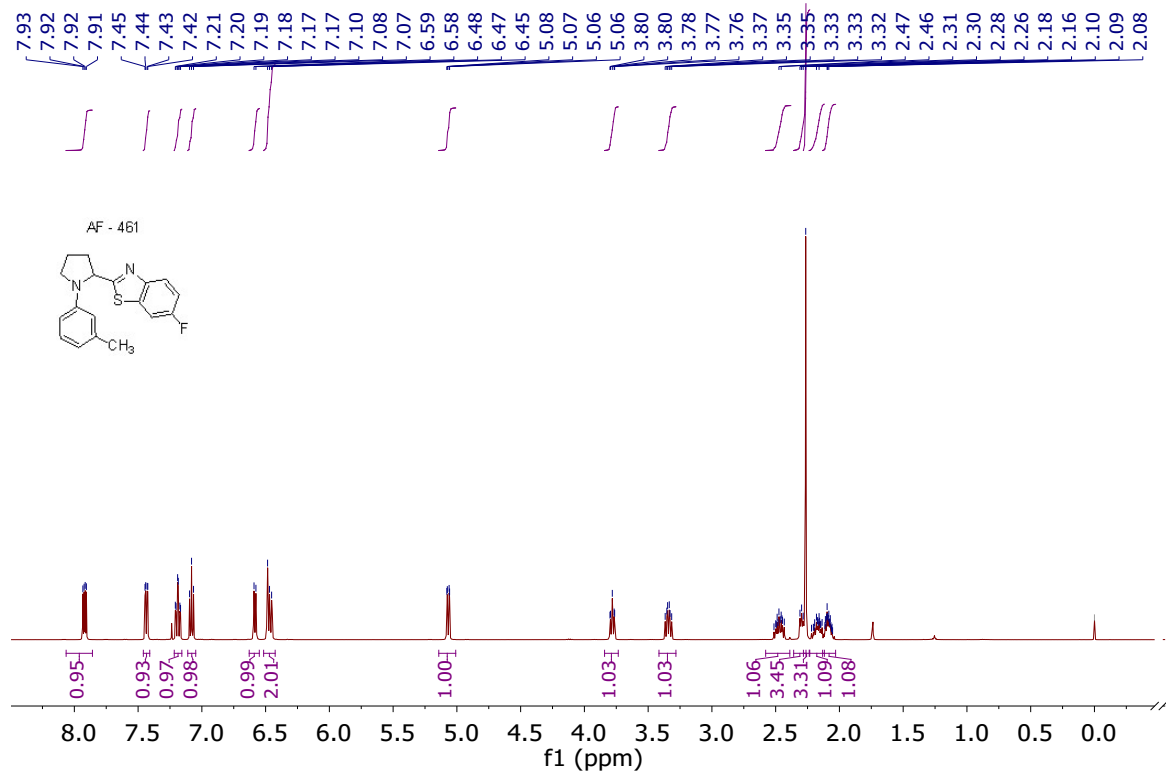


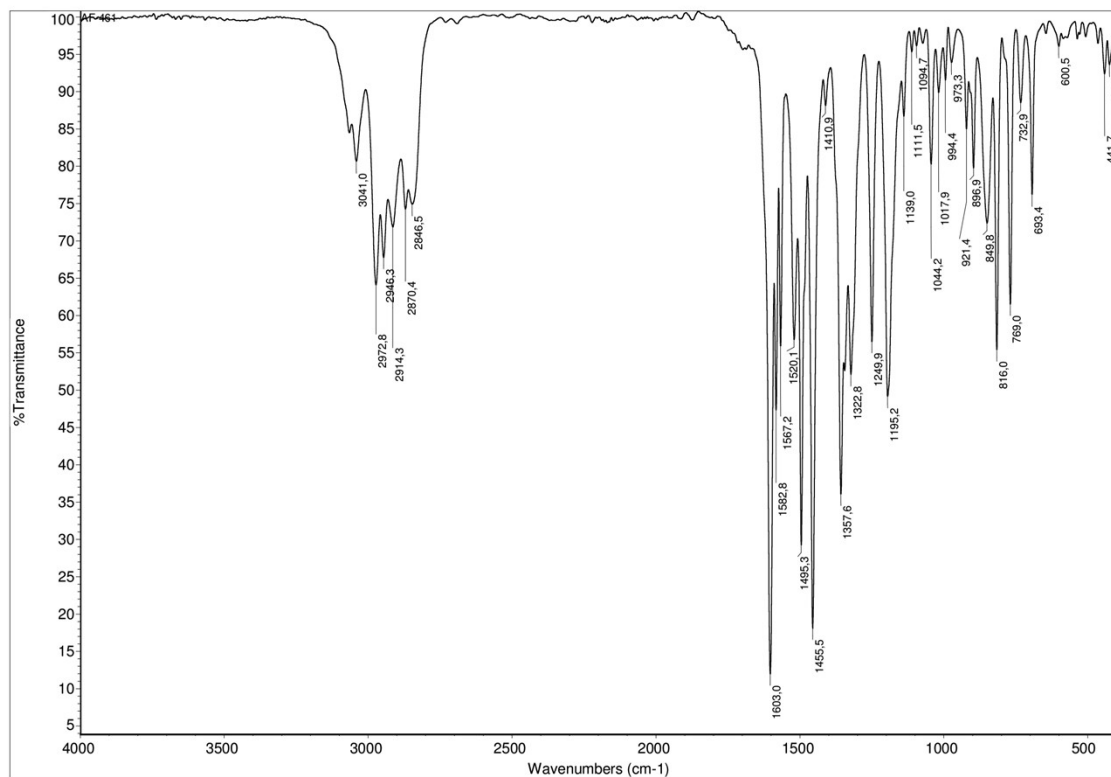
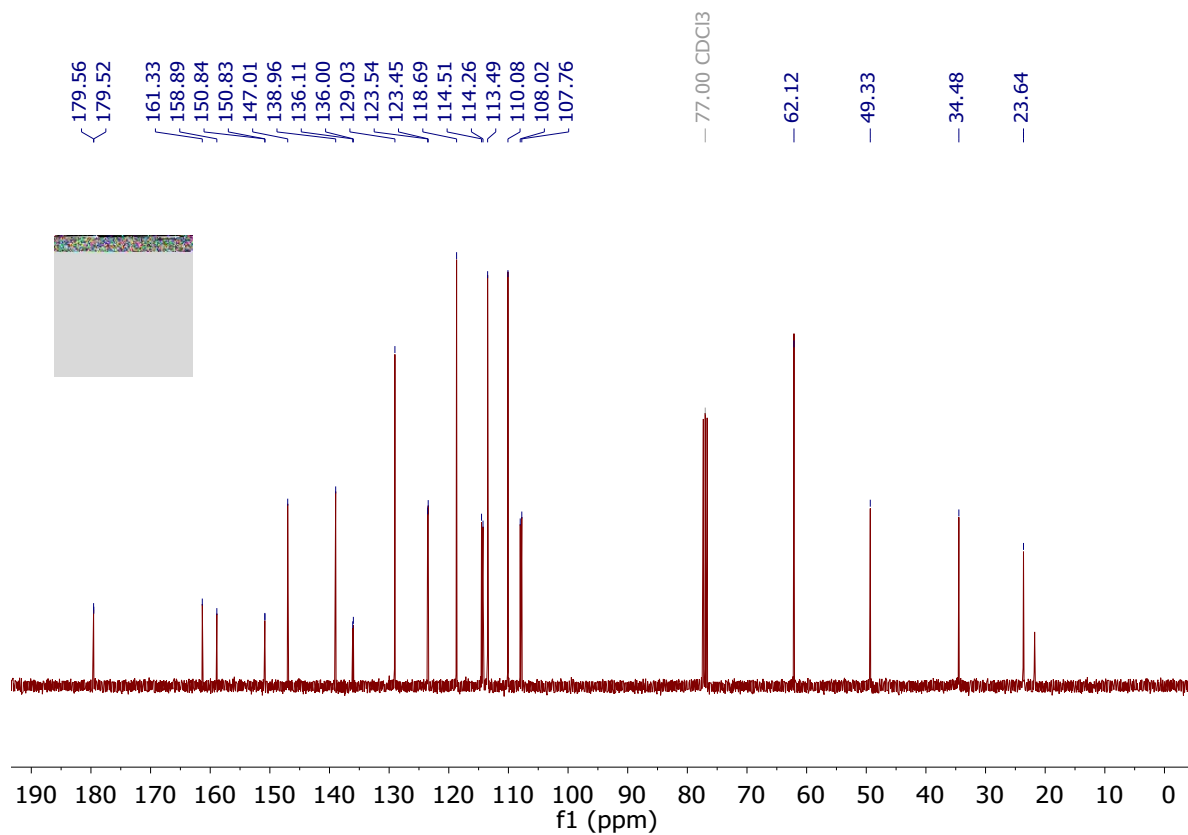
3i



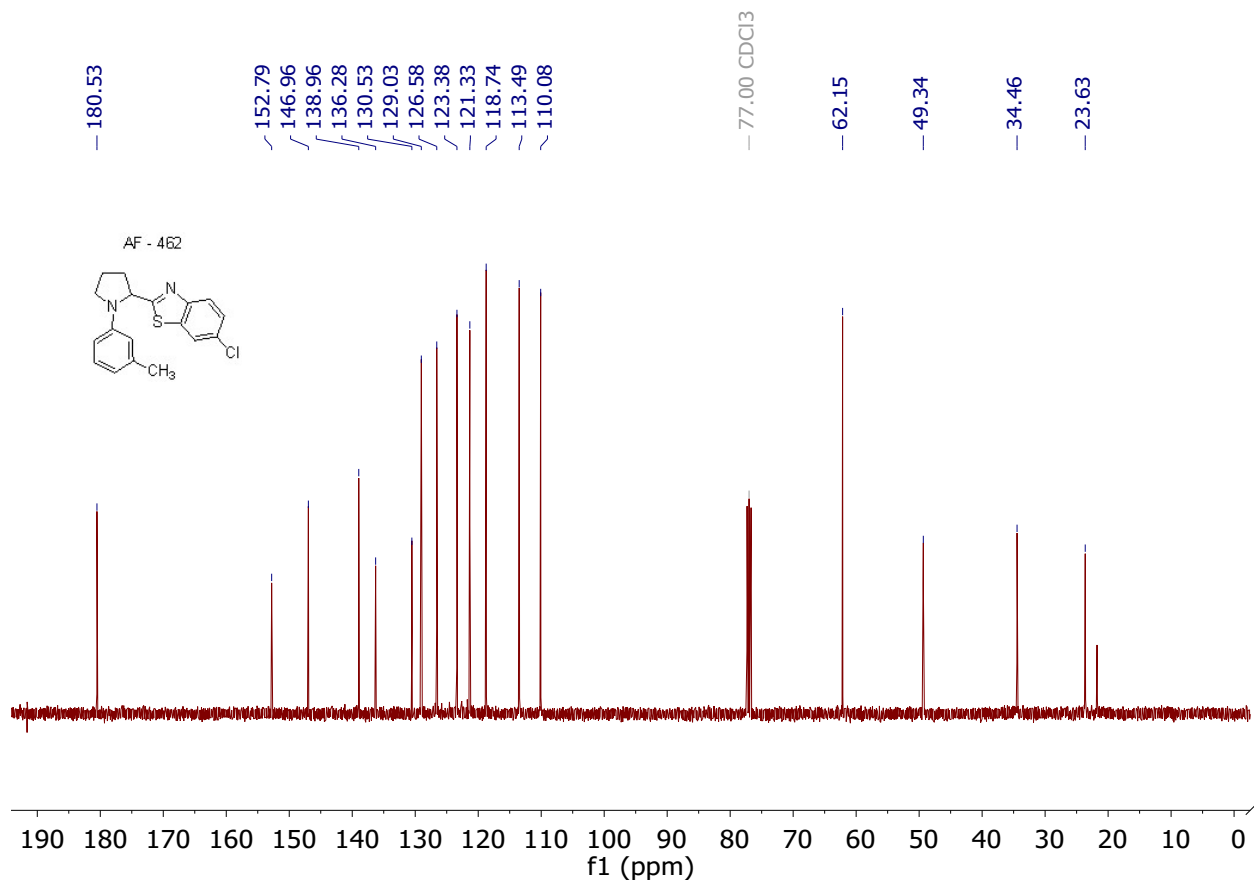
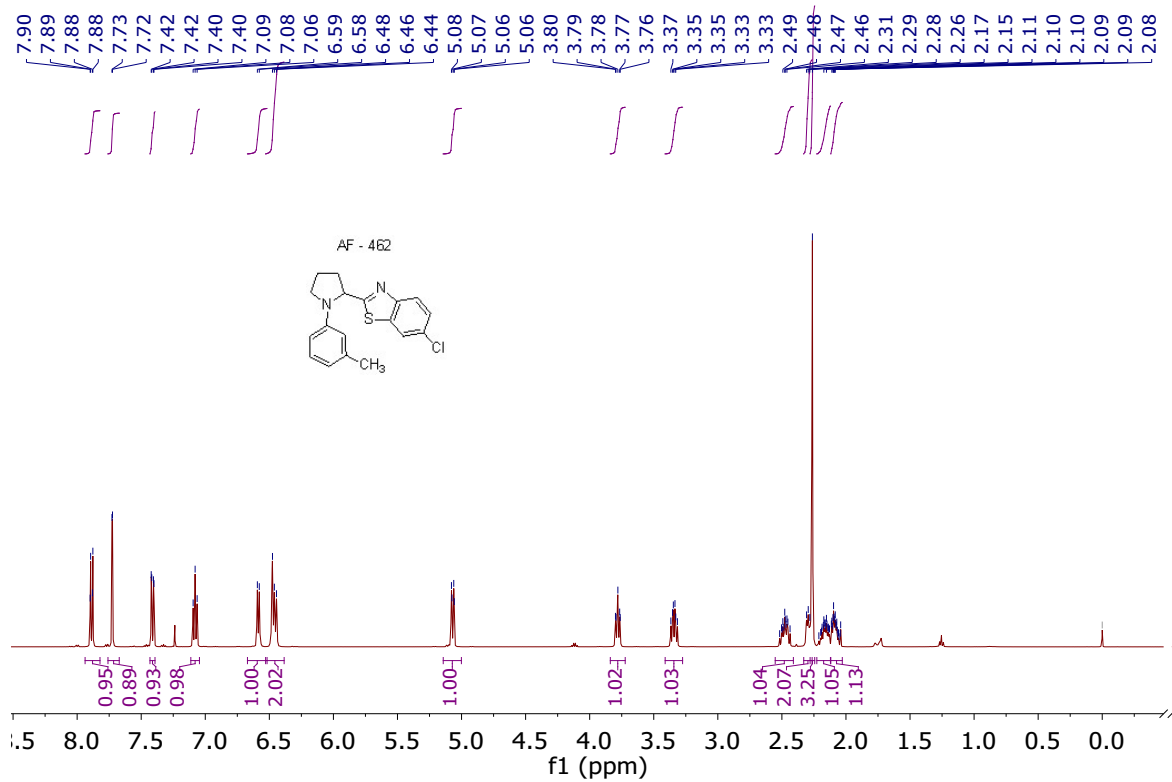


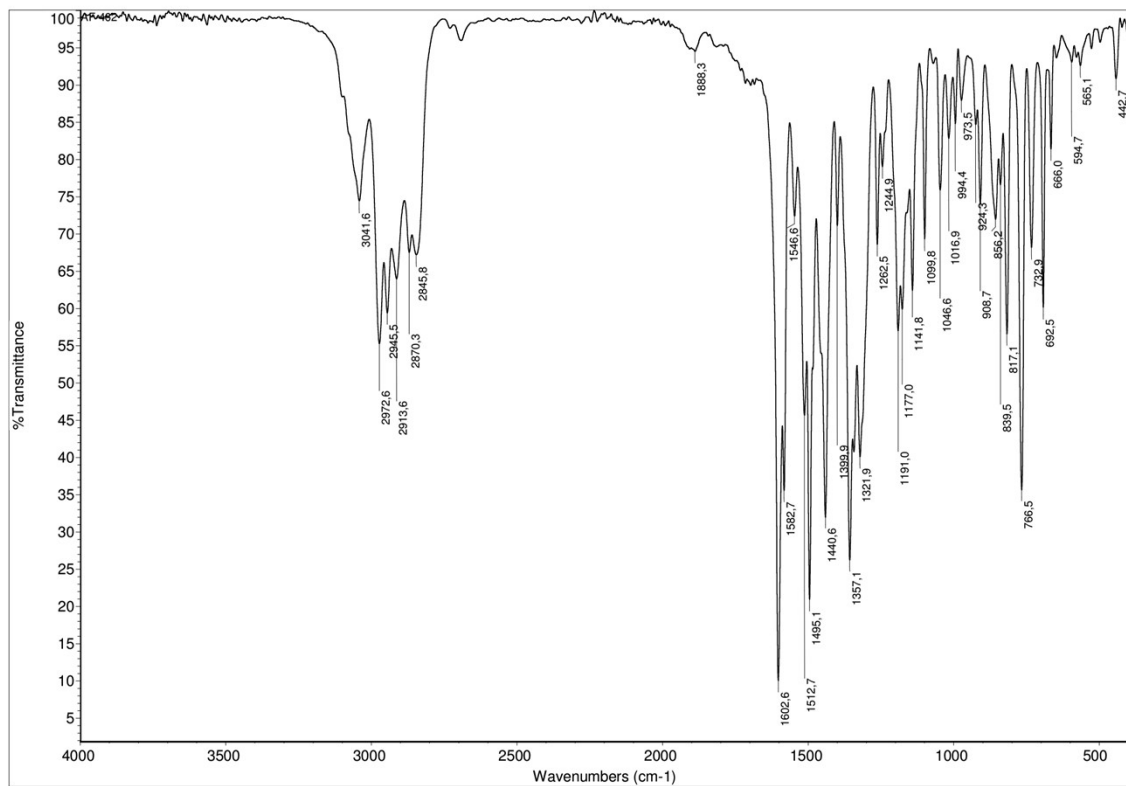
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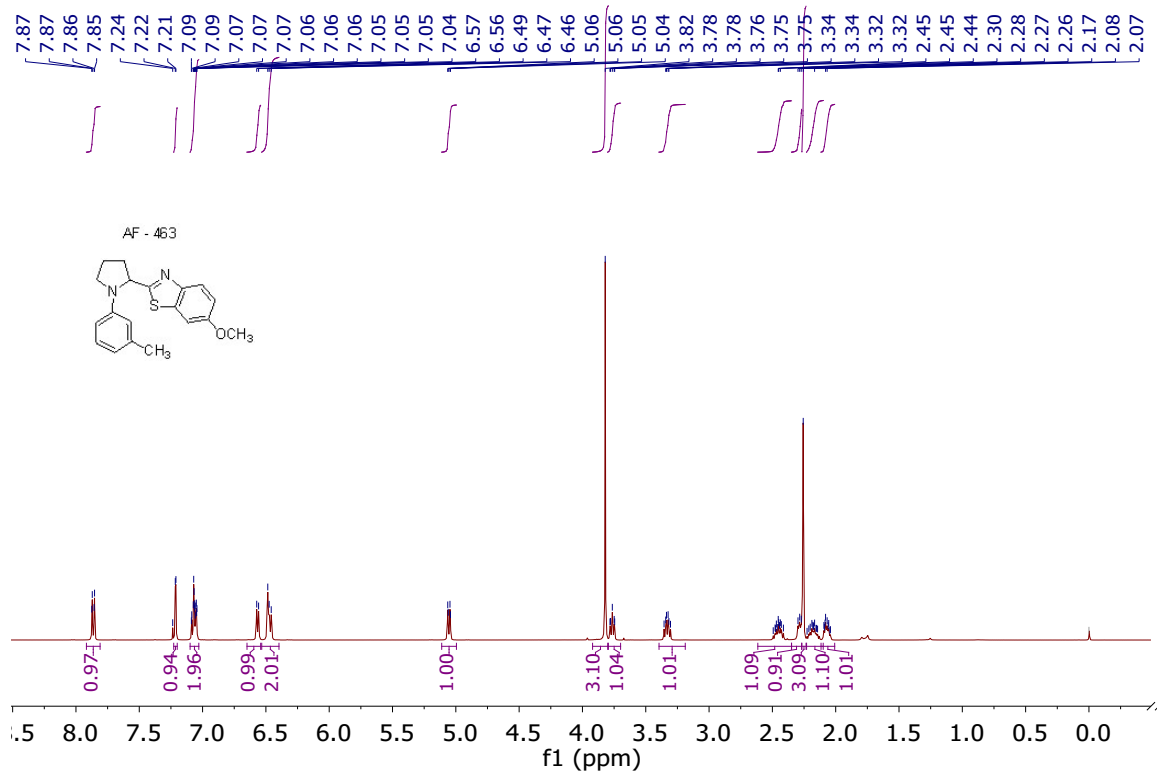


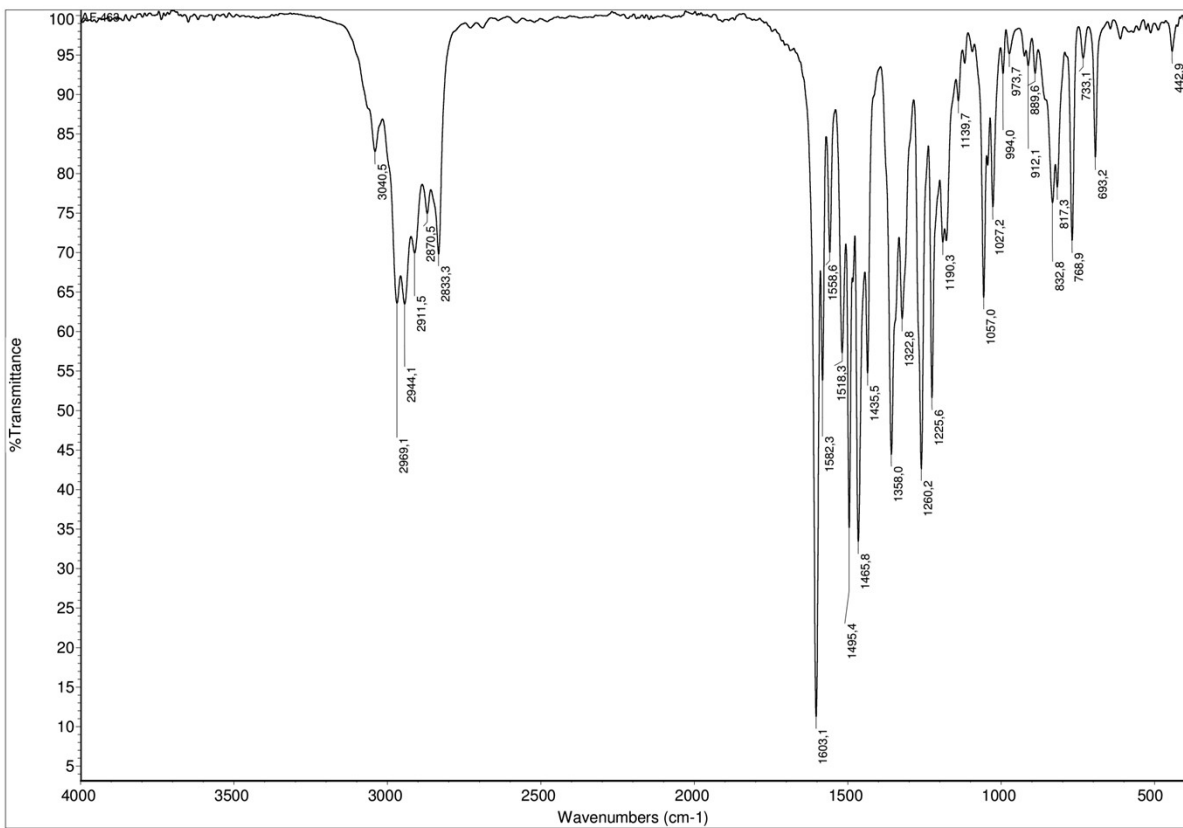
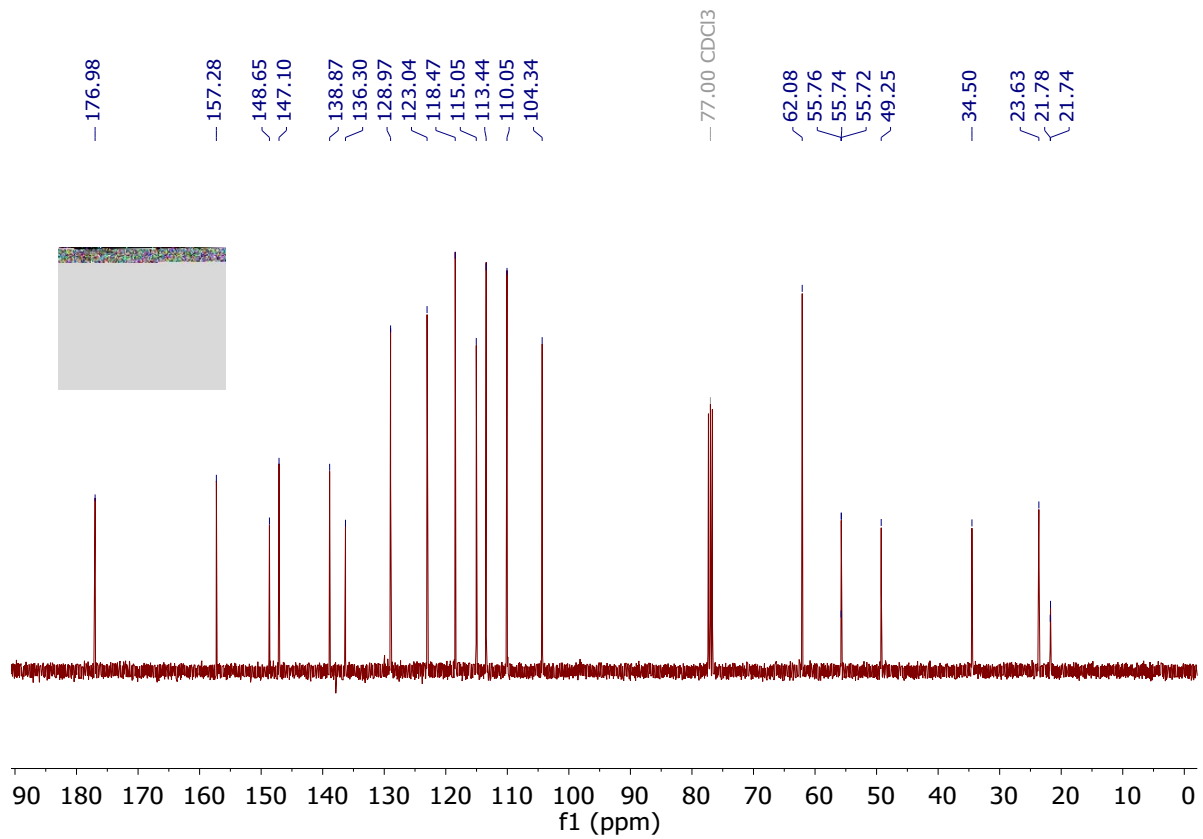
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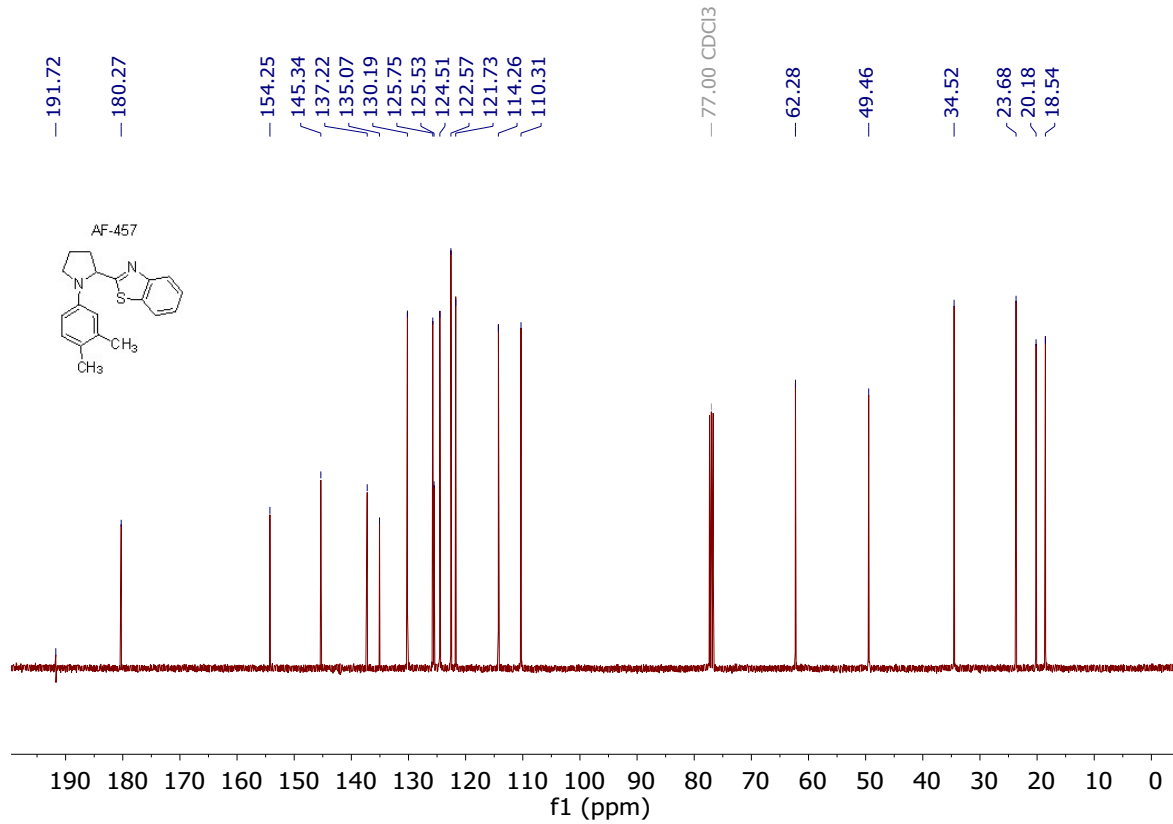
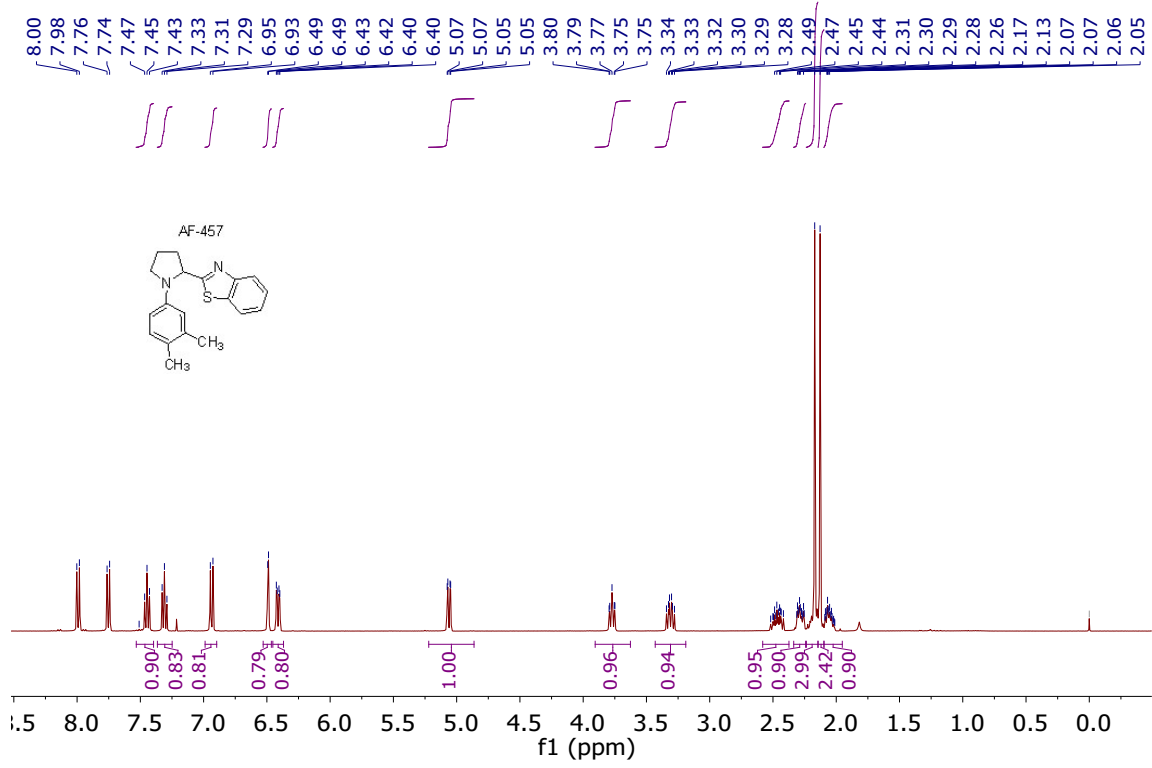


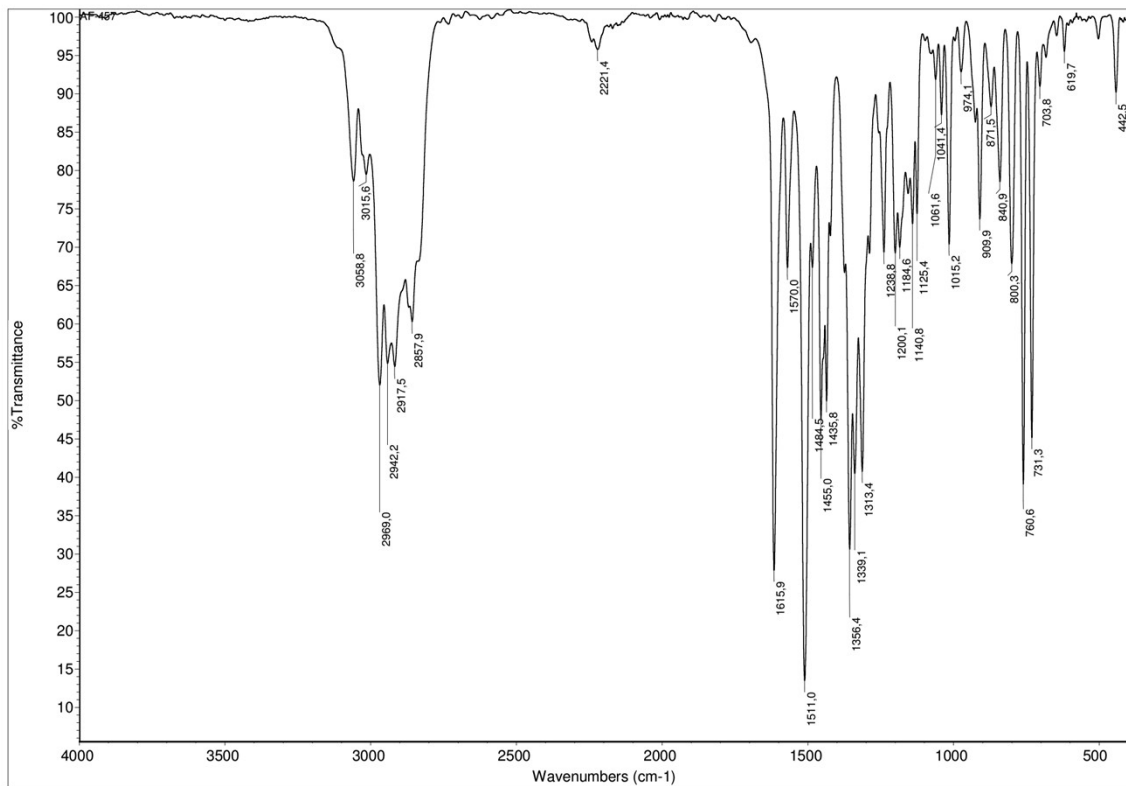
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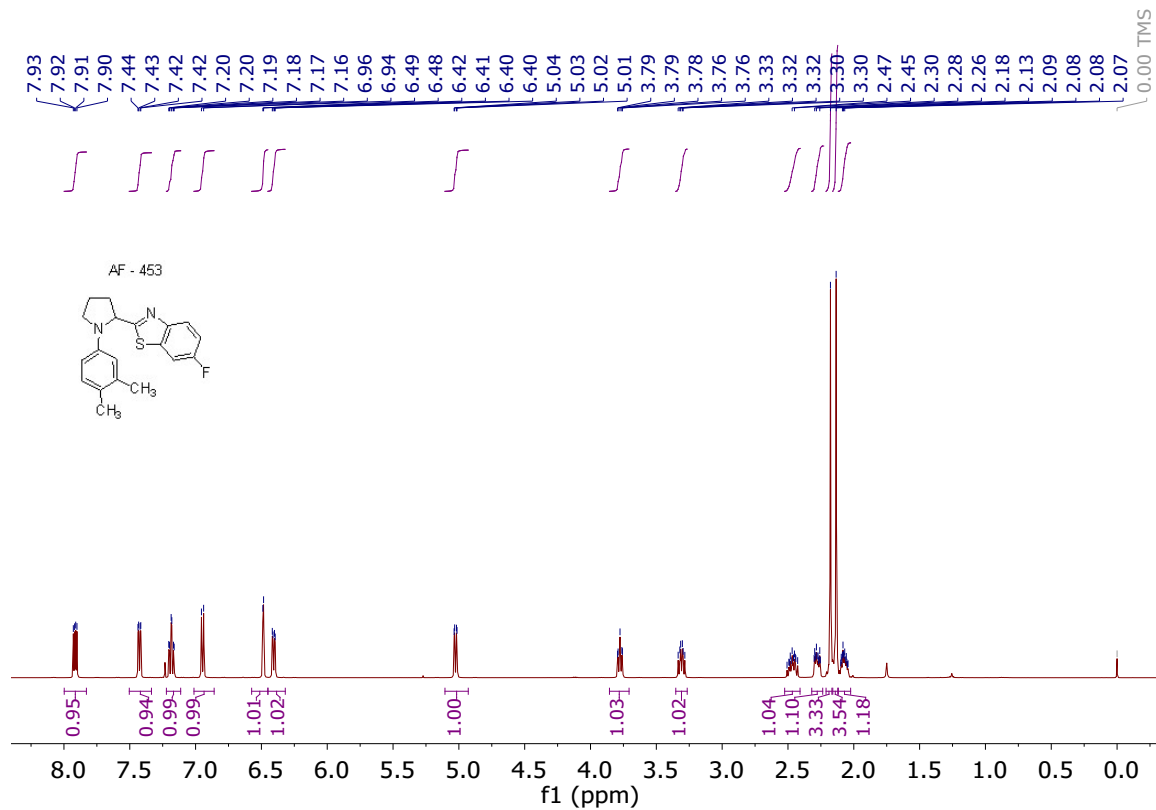


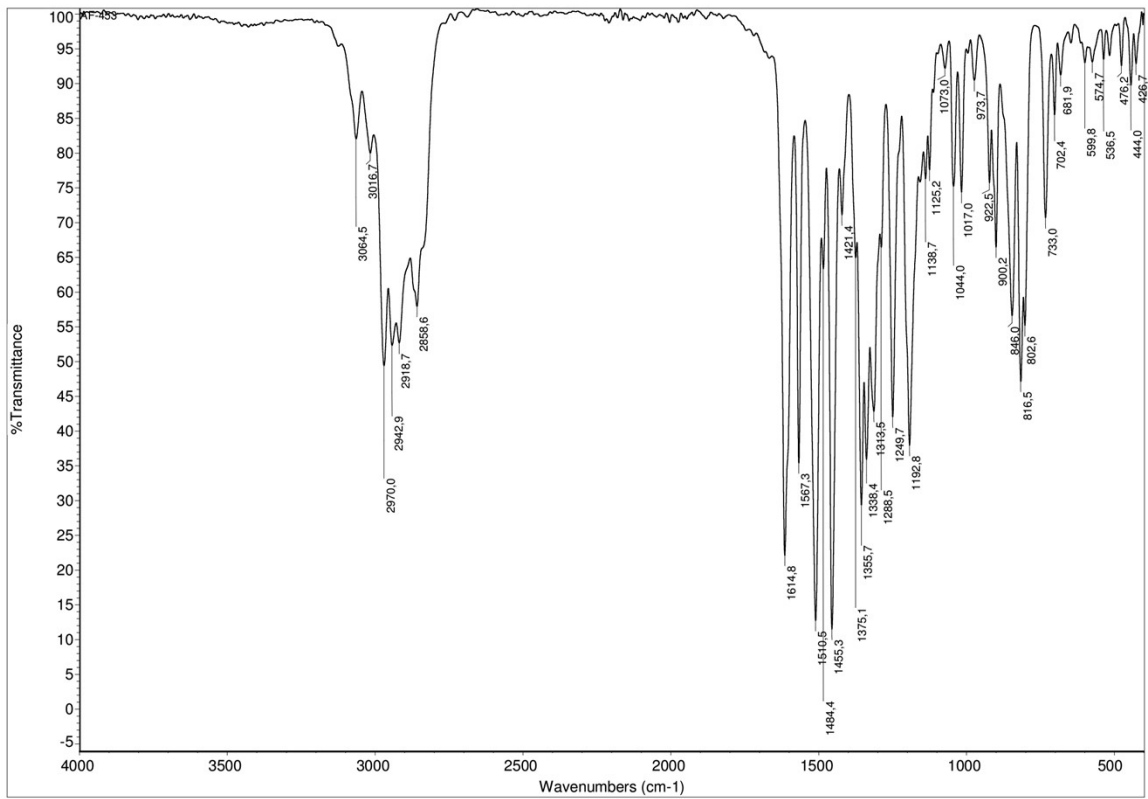
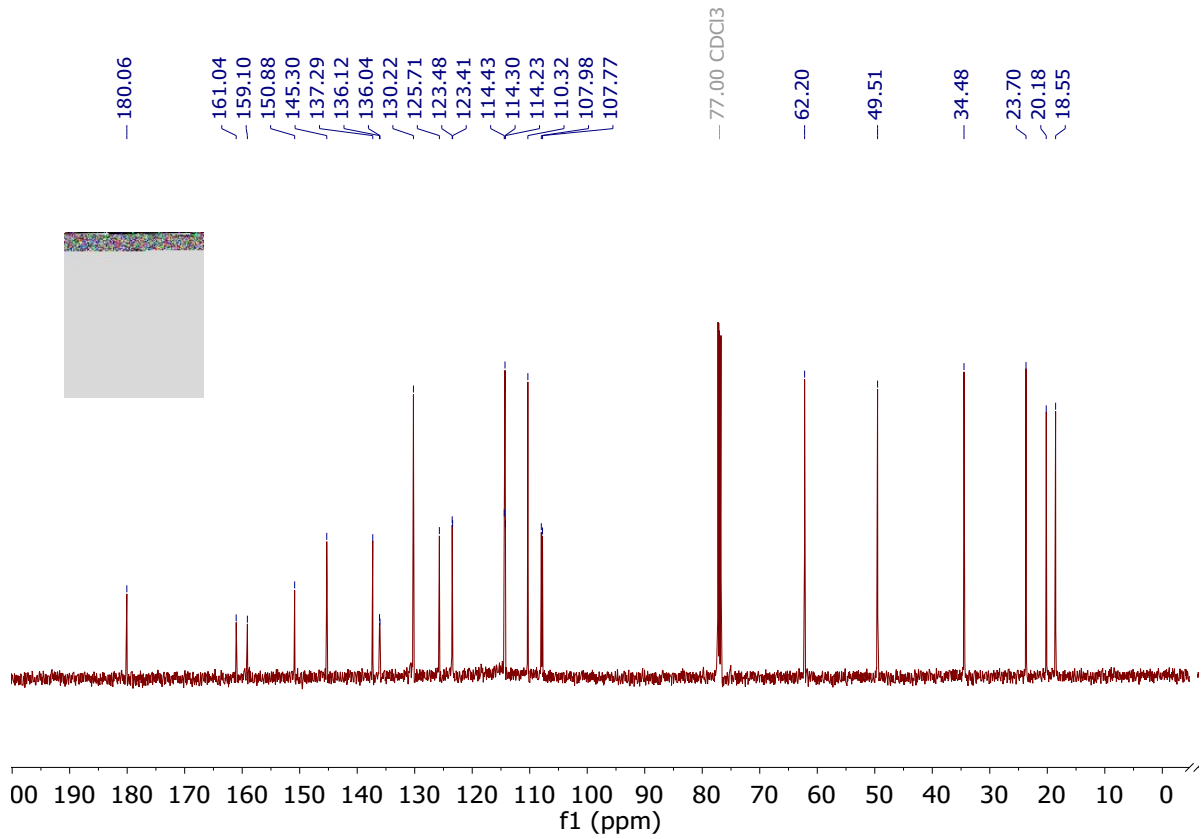
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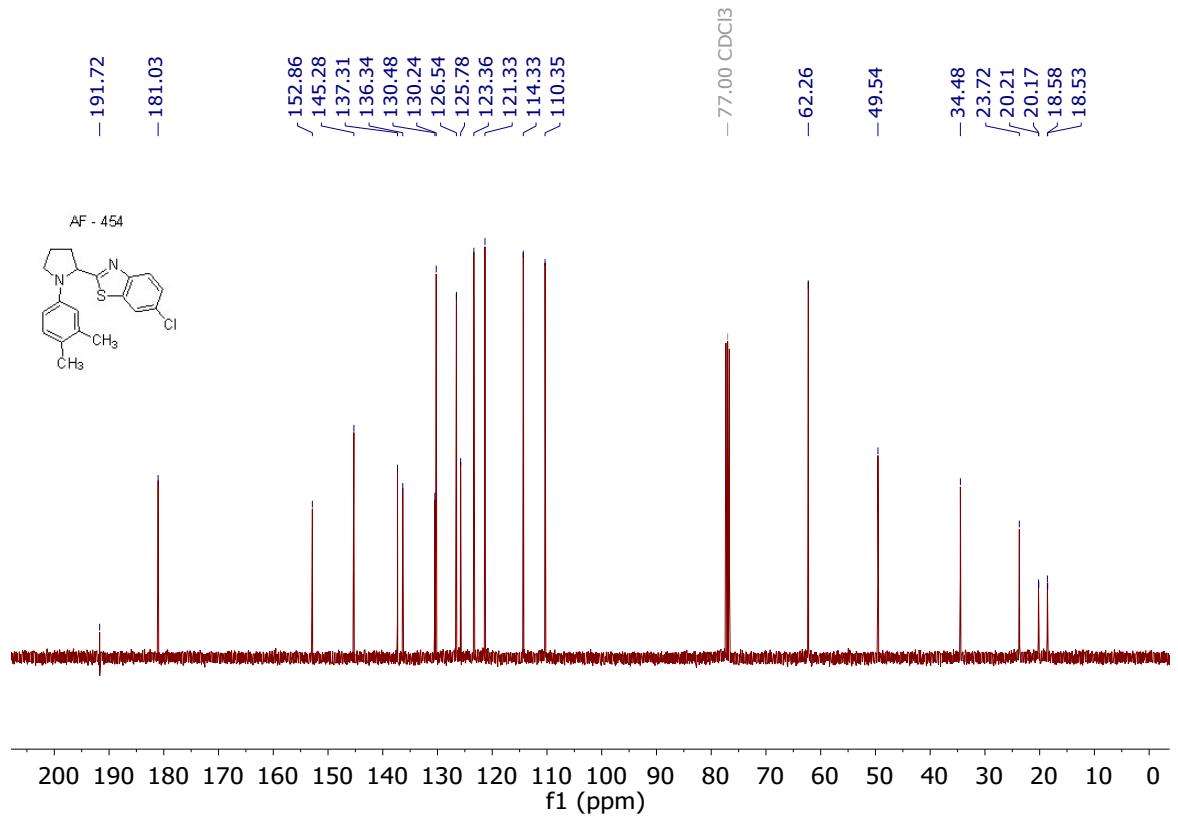
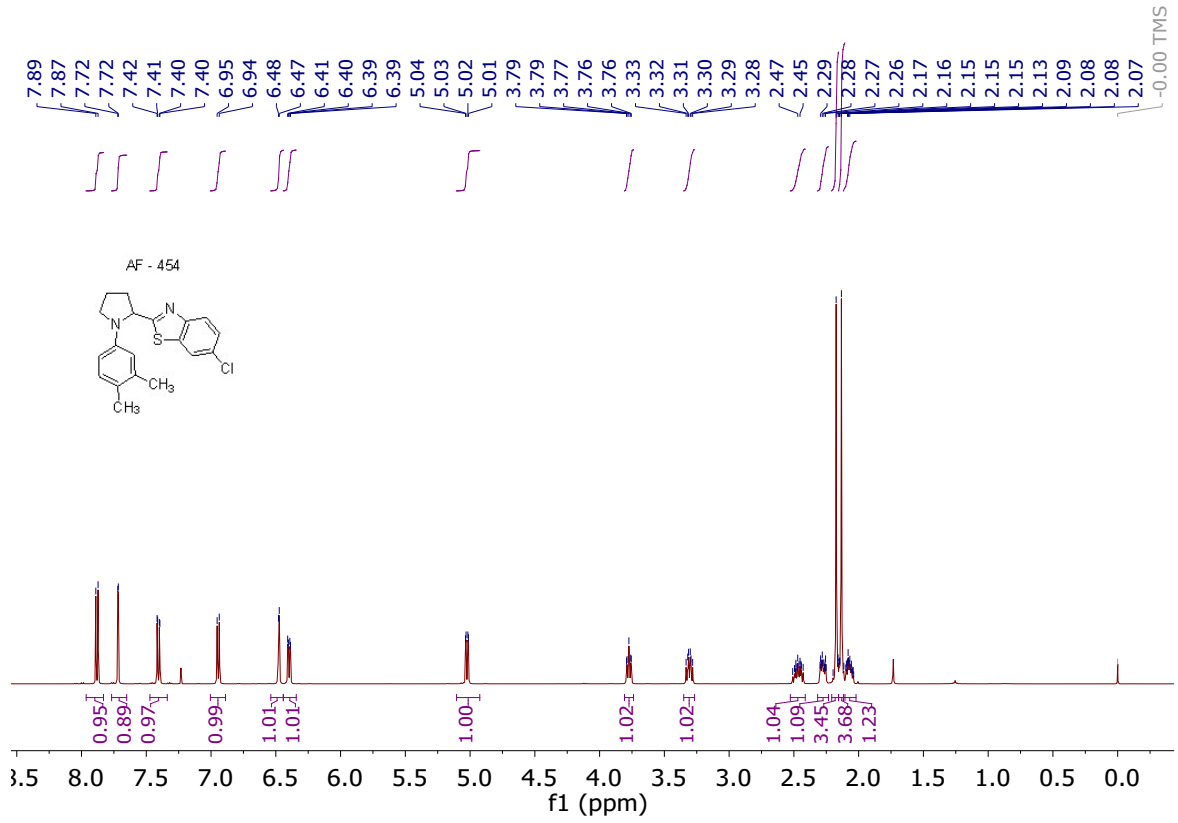


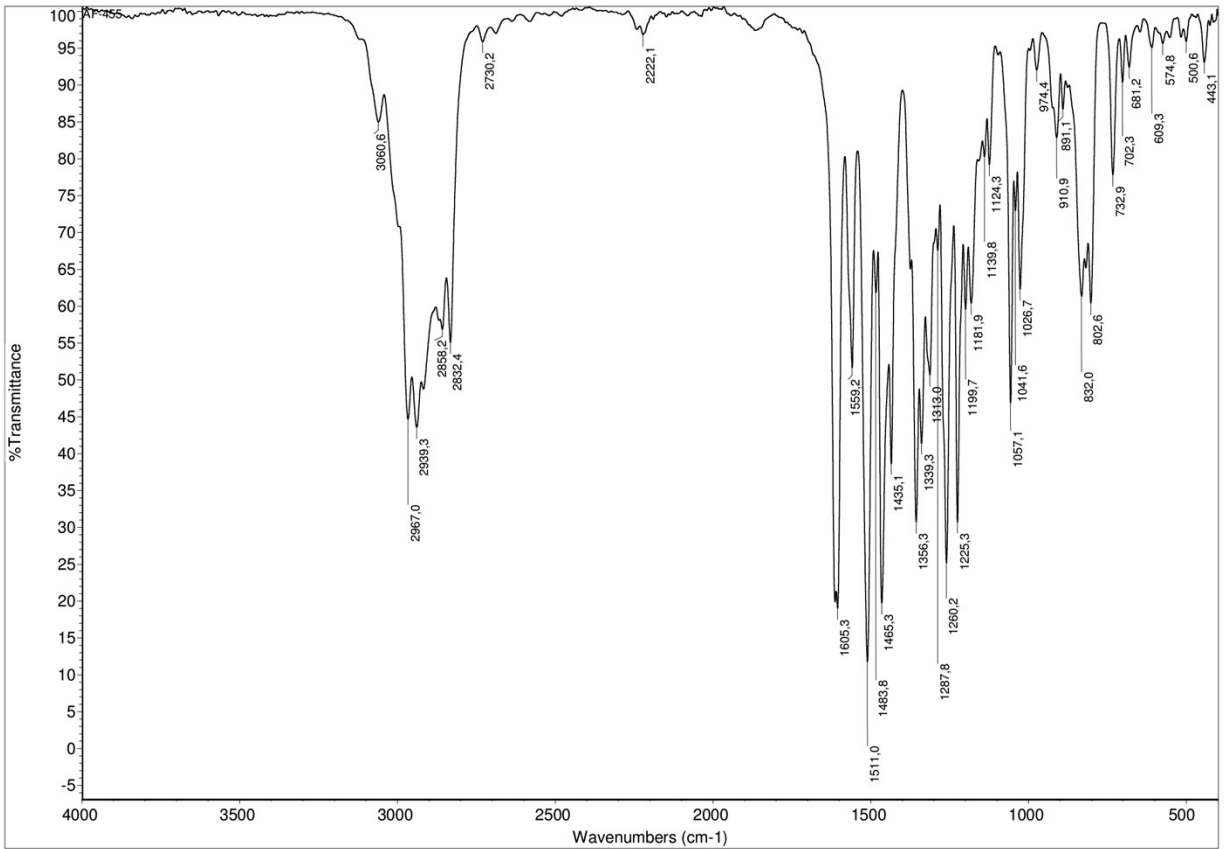
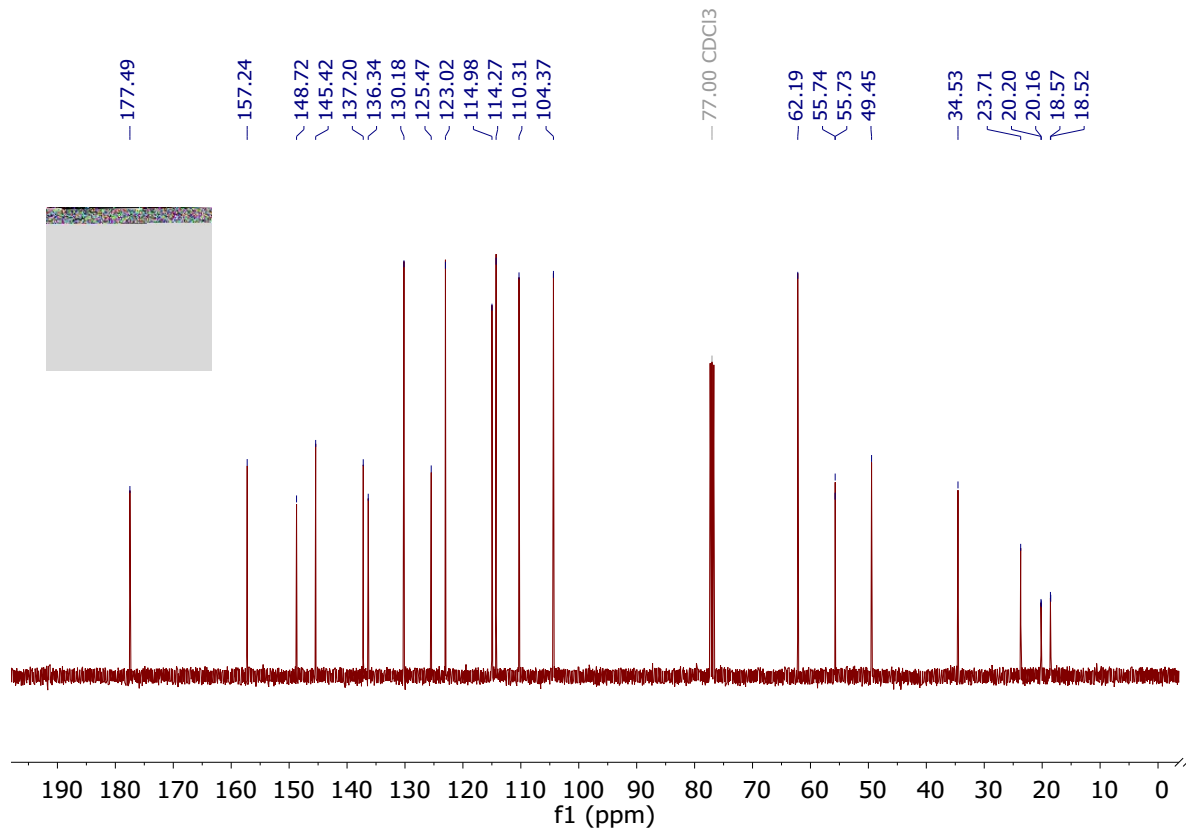
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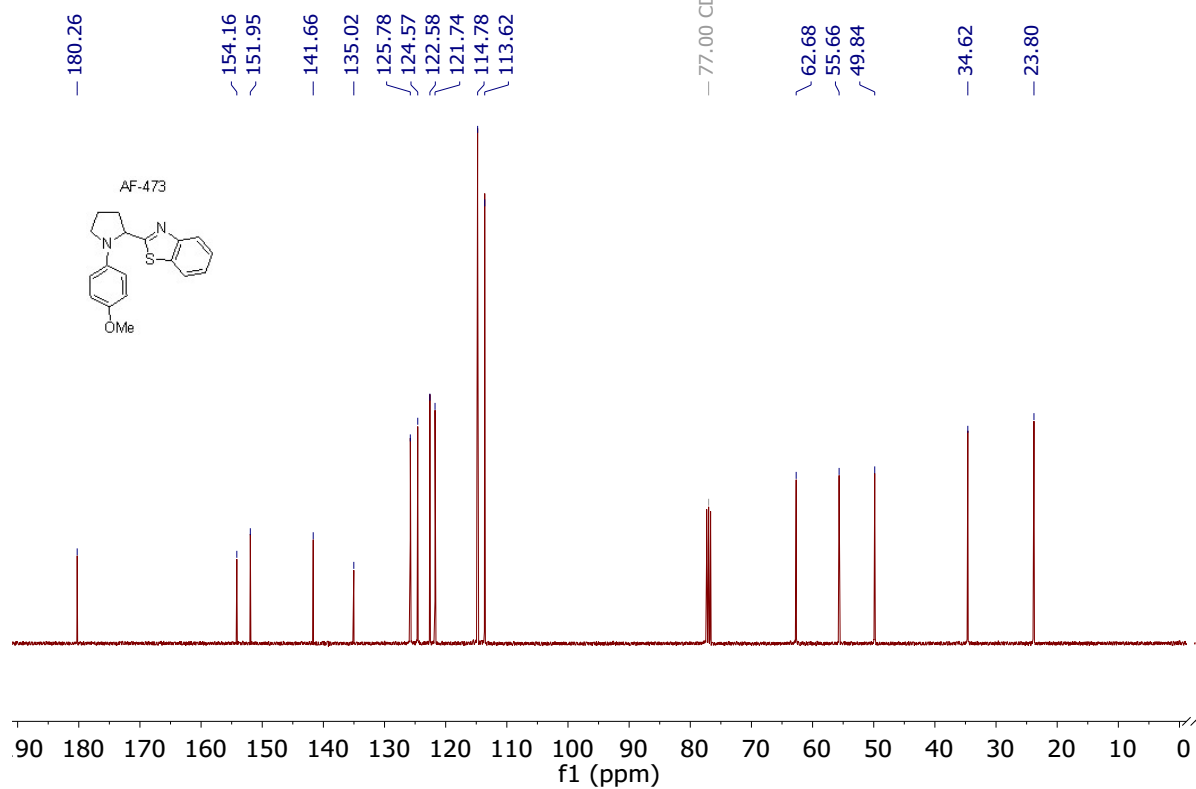
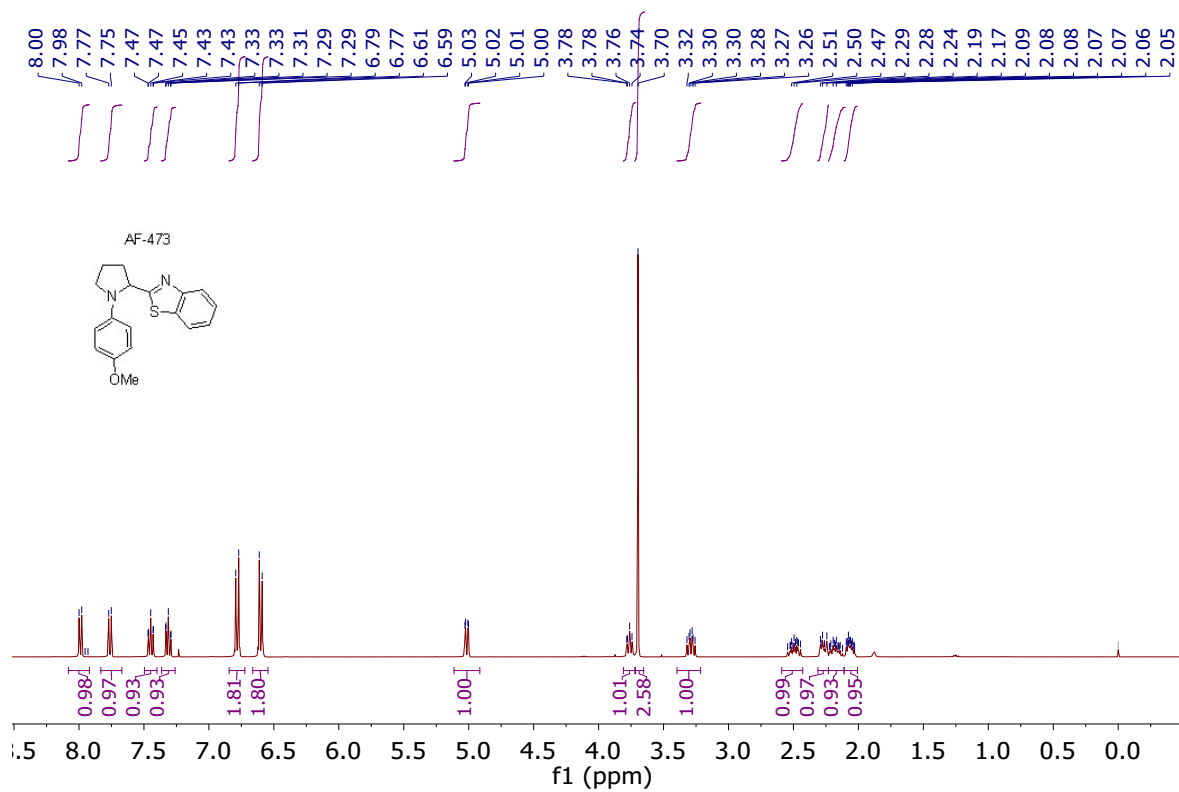


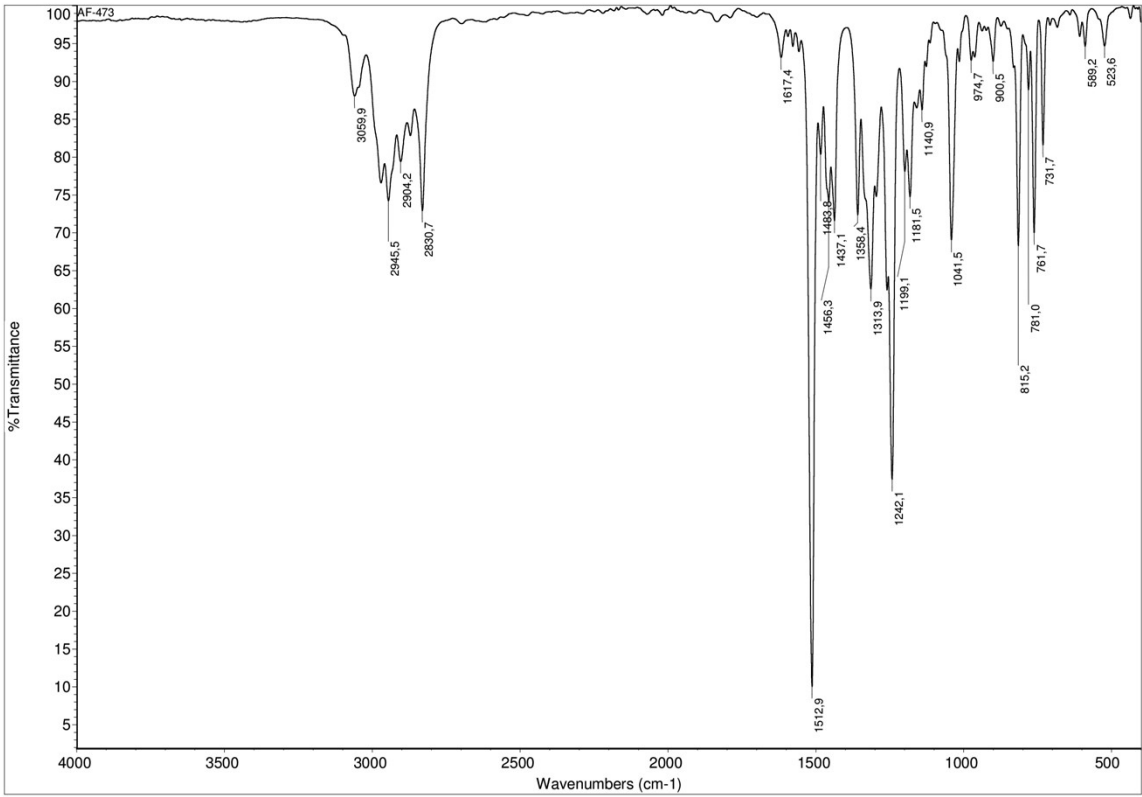
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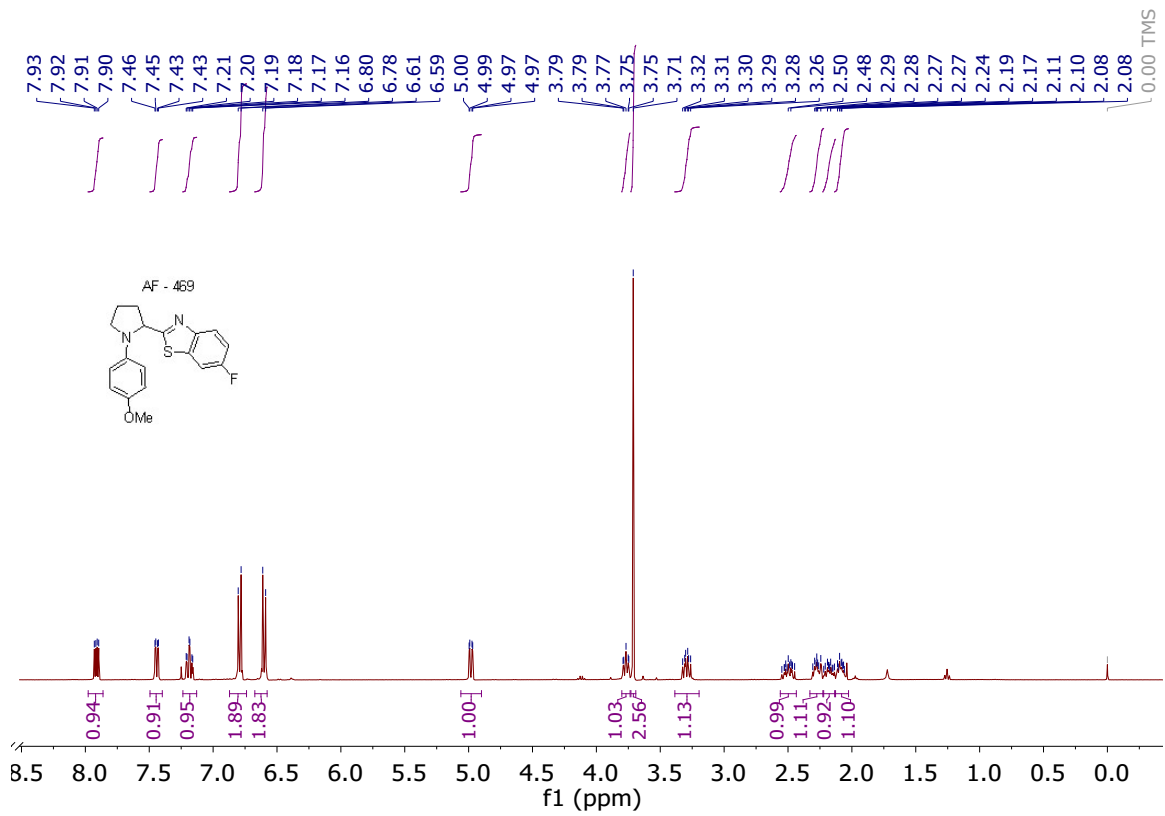


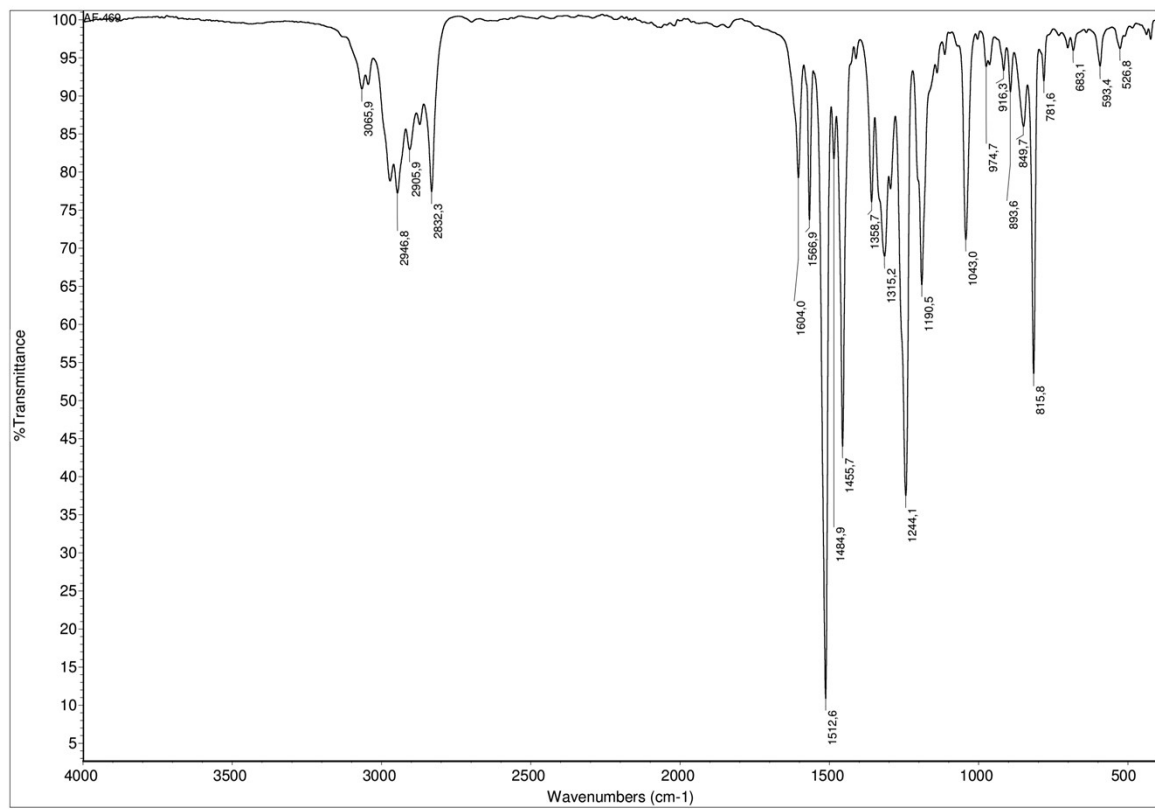
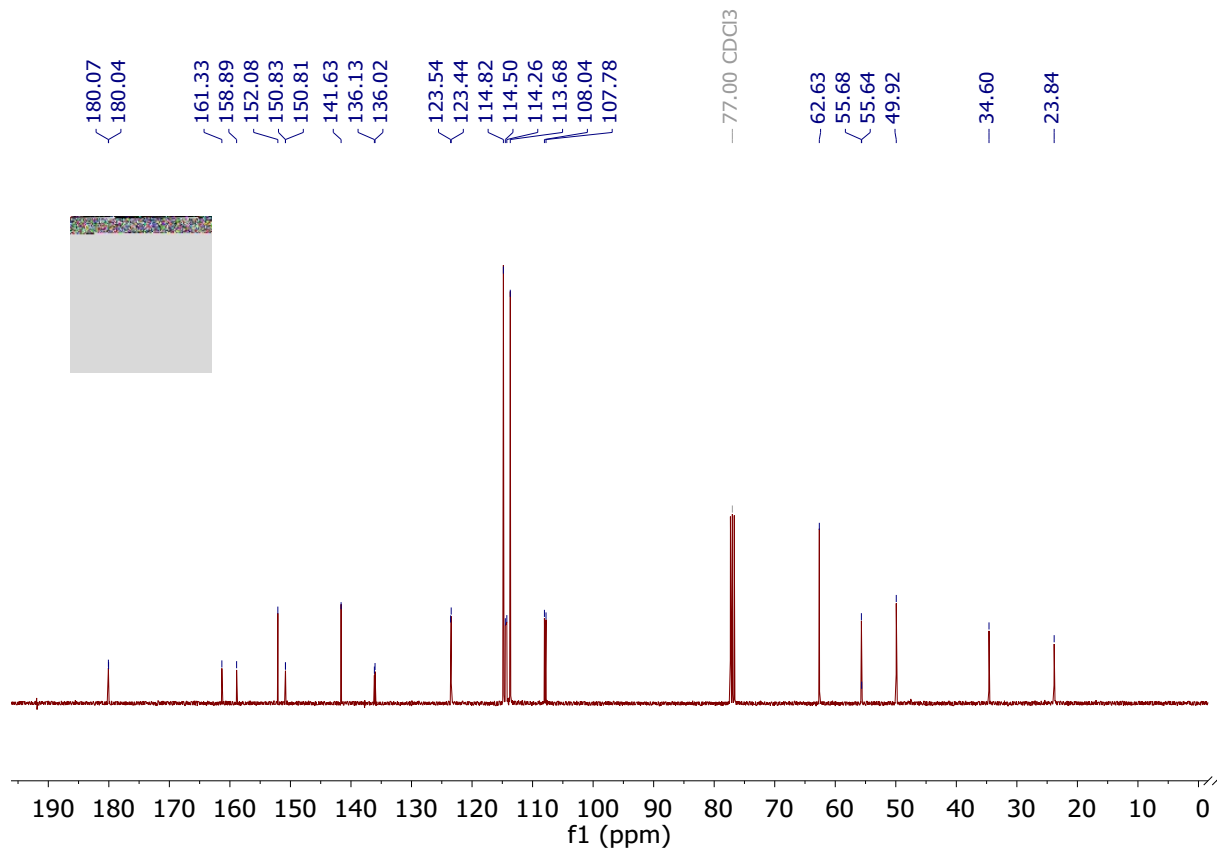
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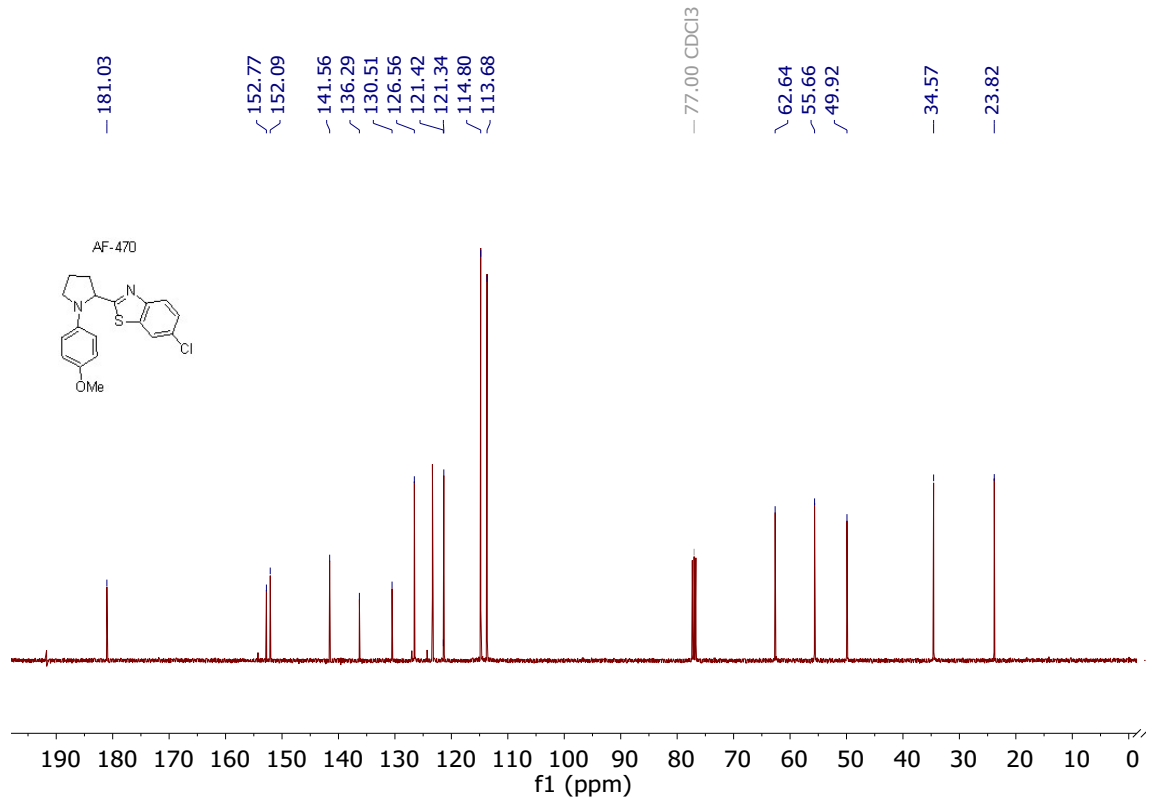
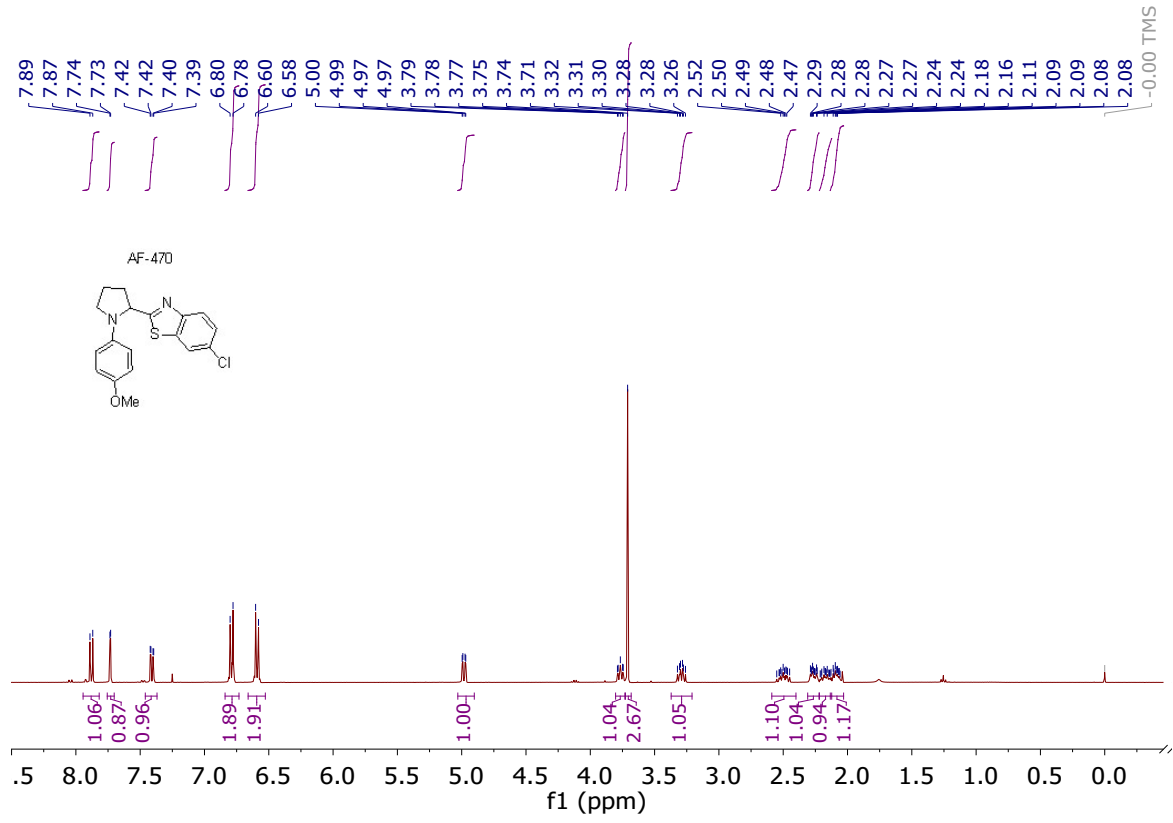


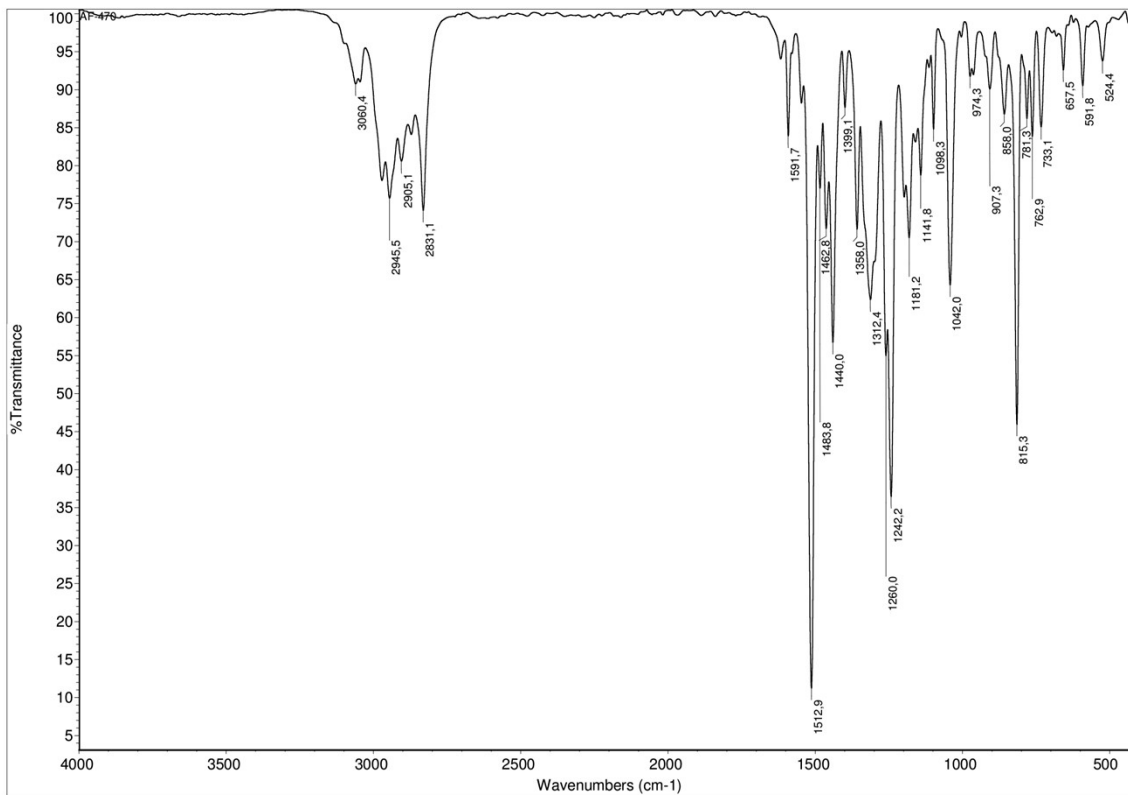
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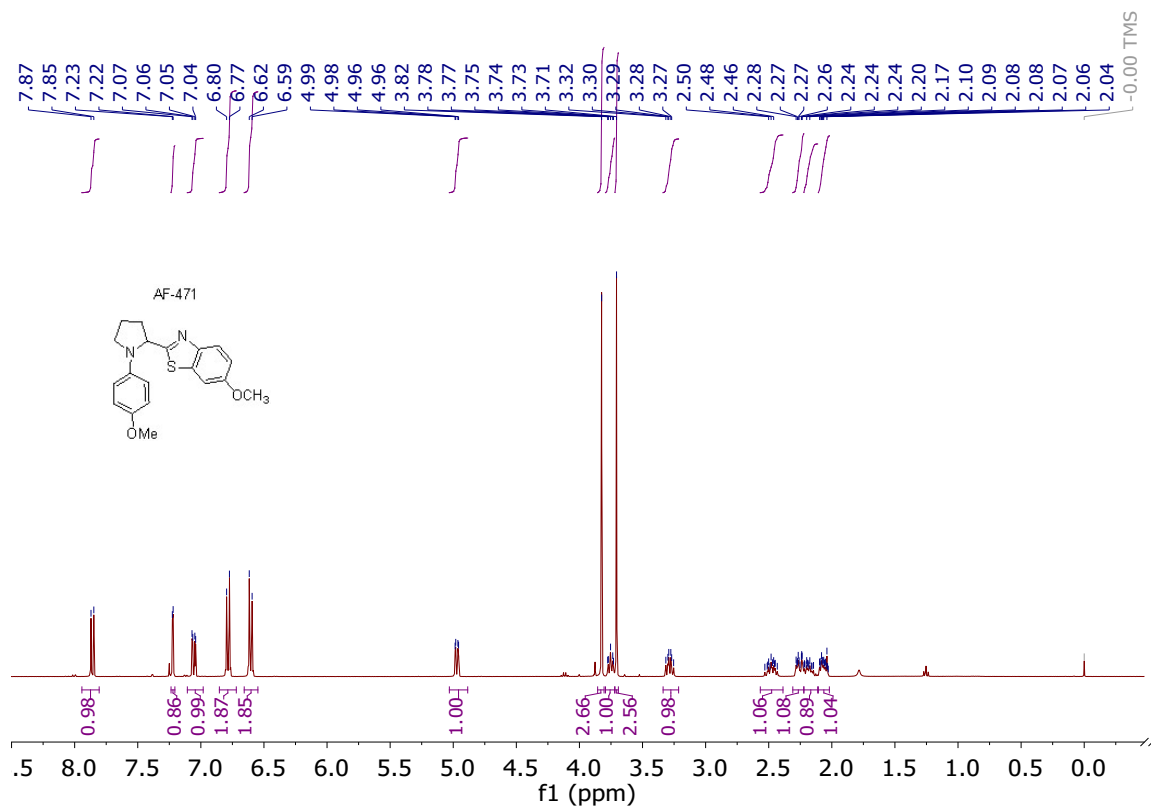


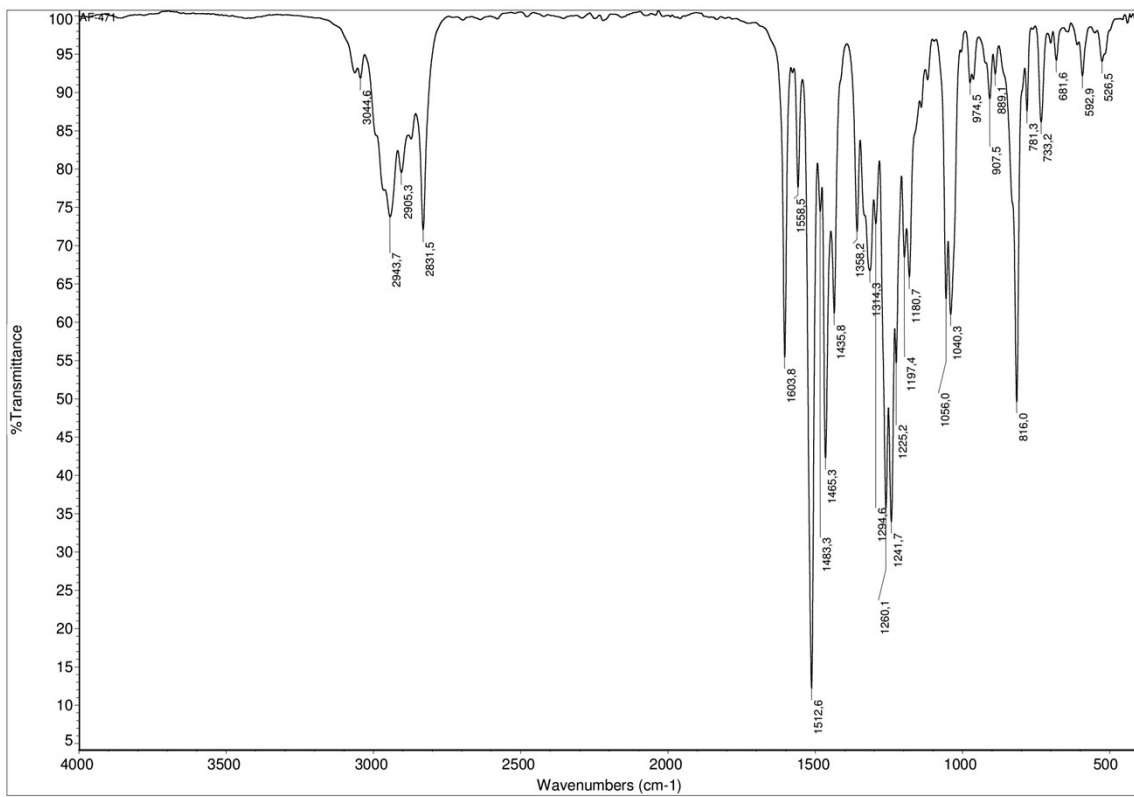
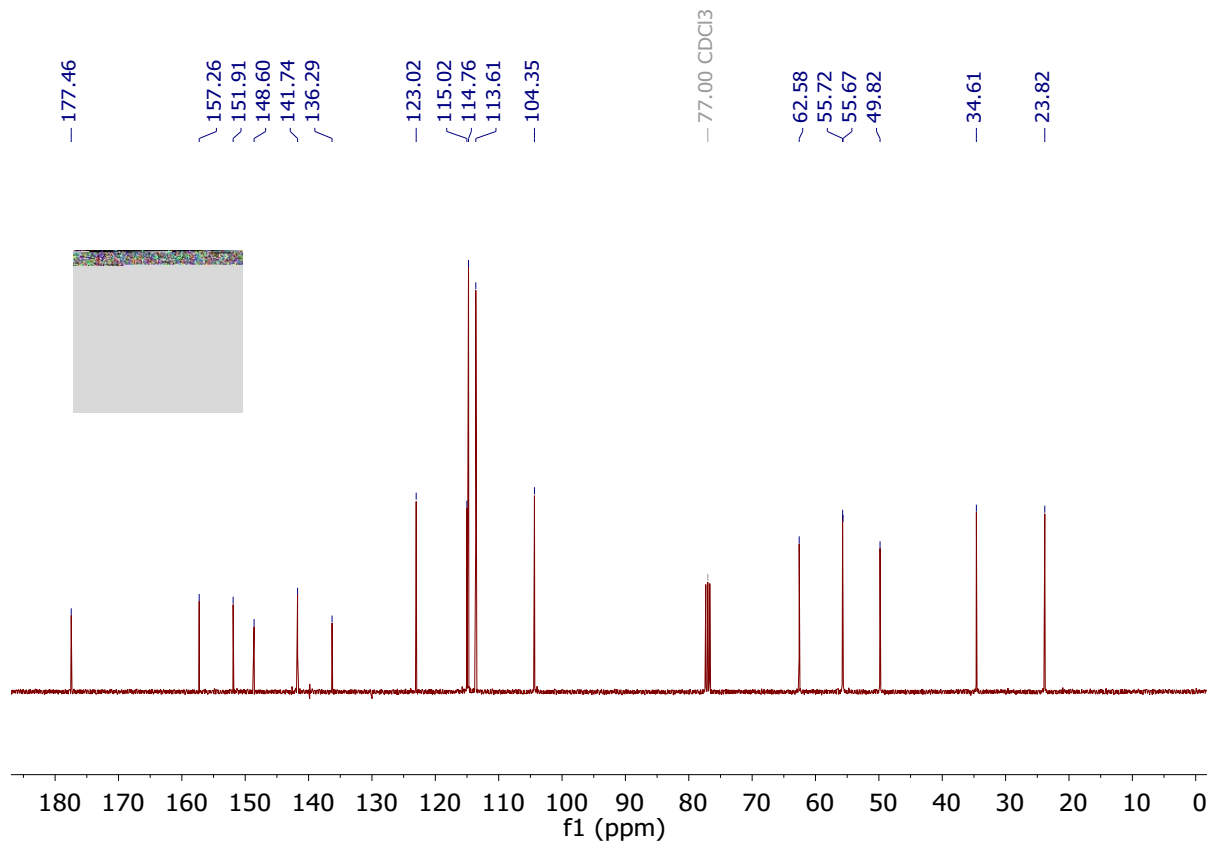
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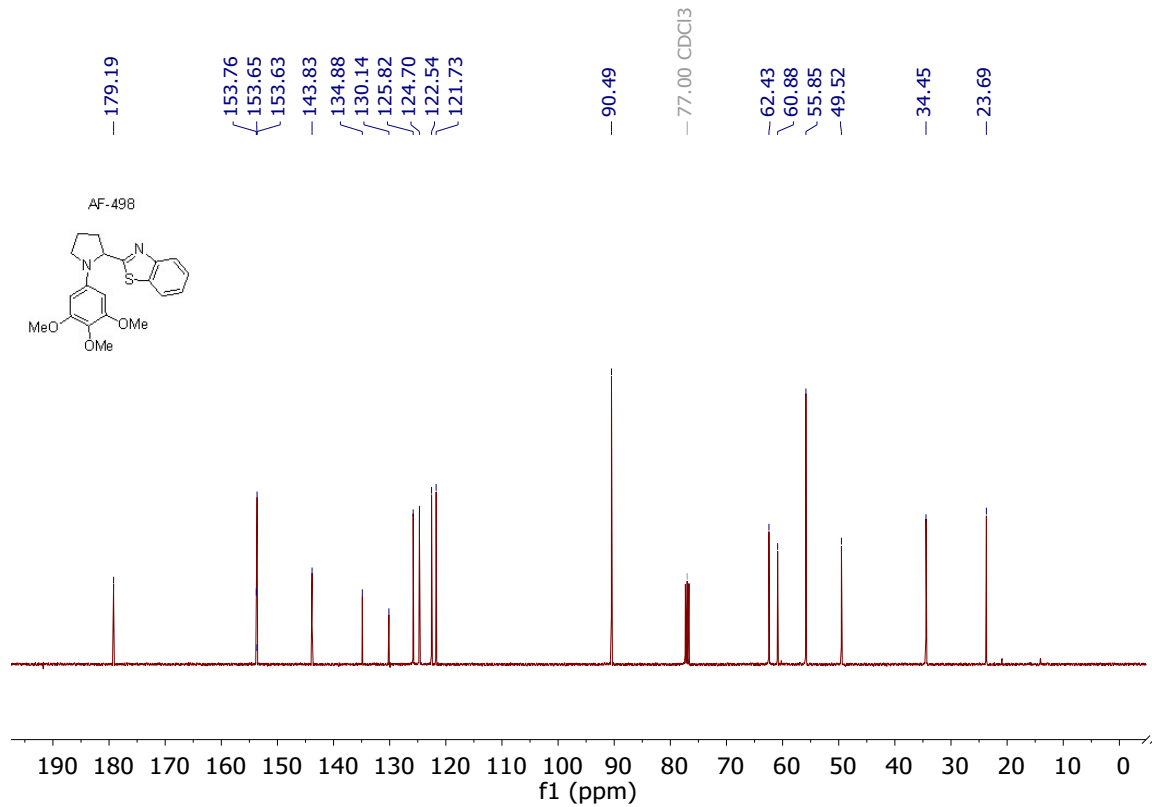
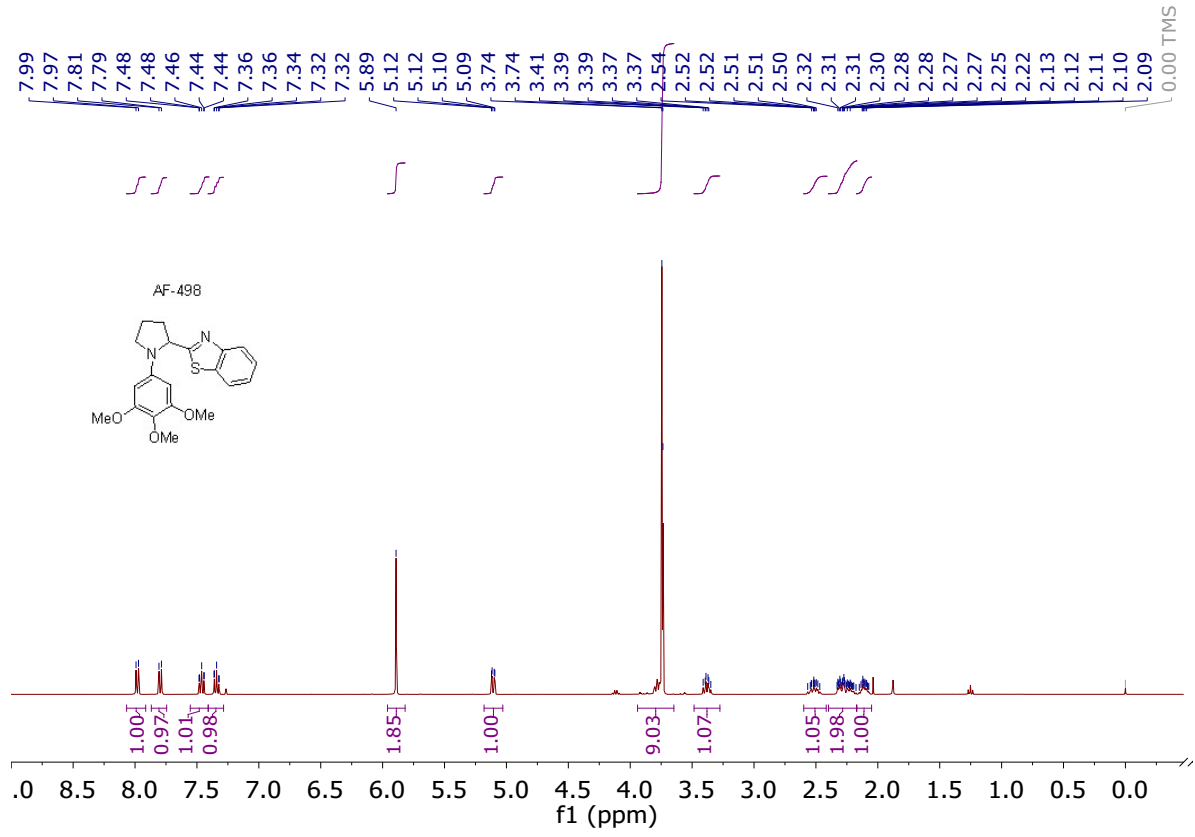


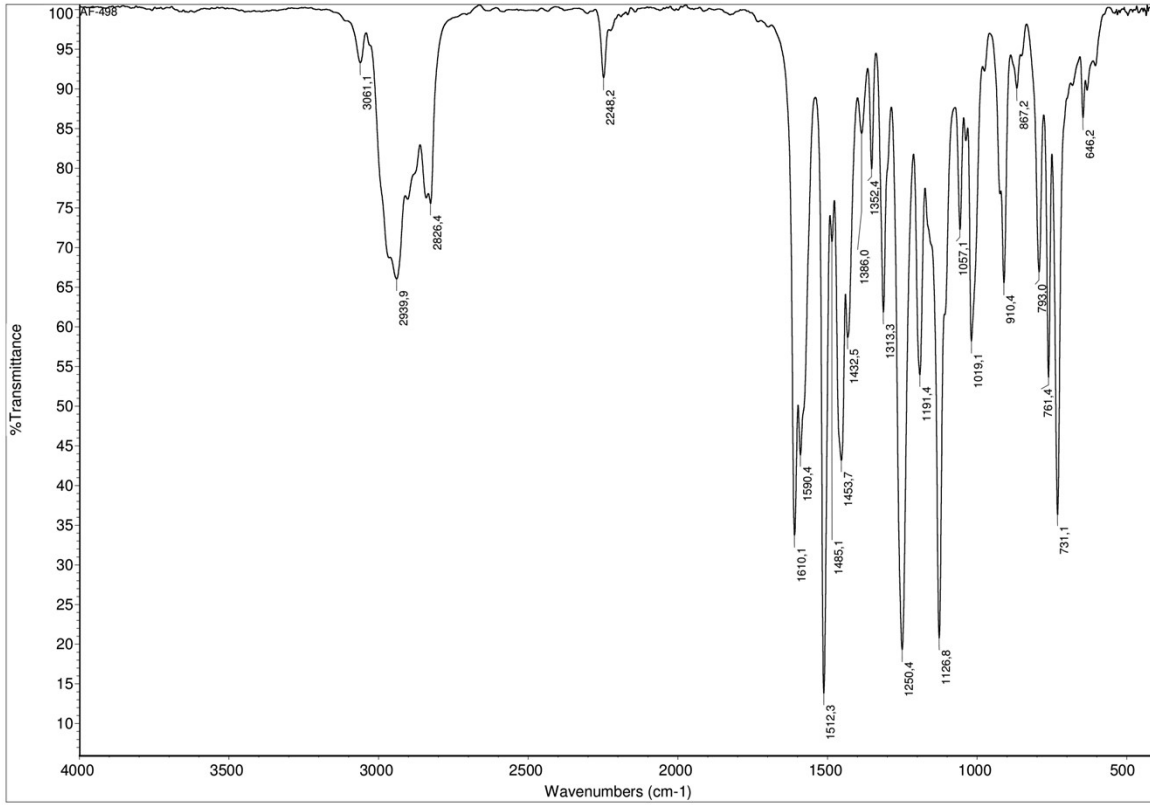
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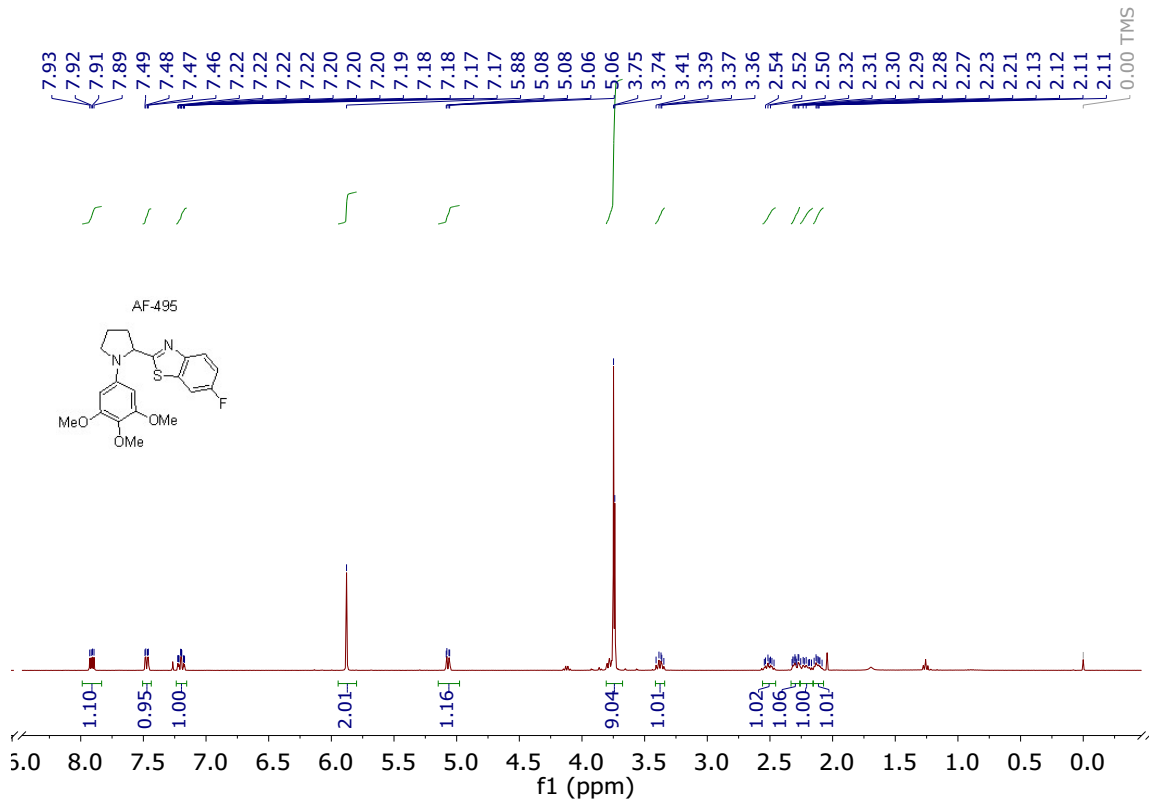


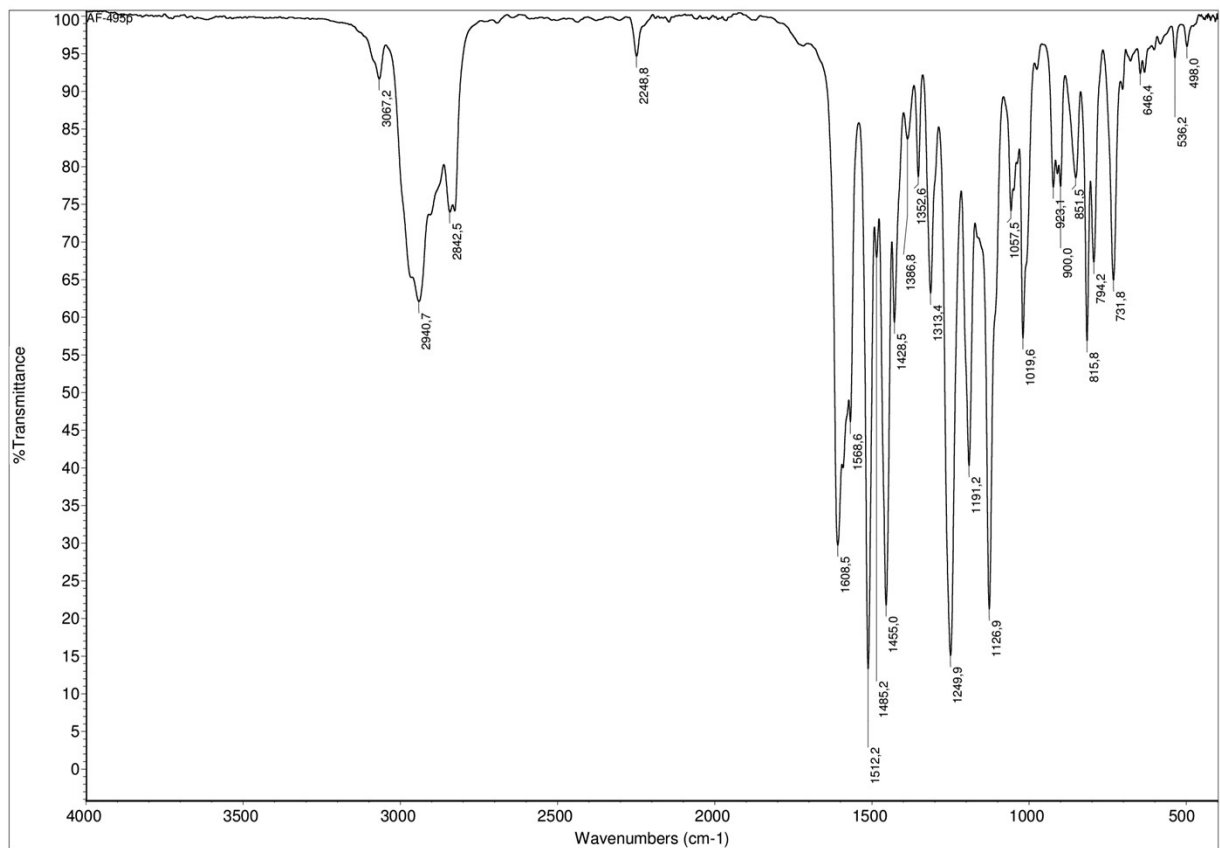
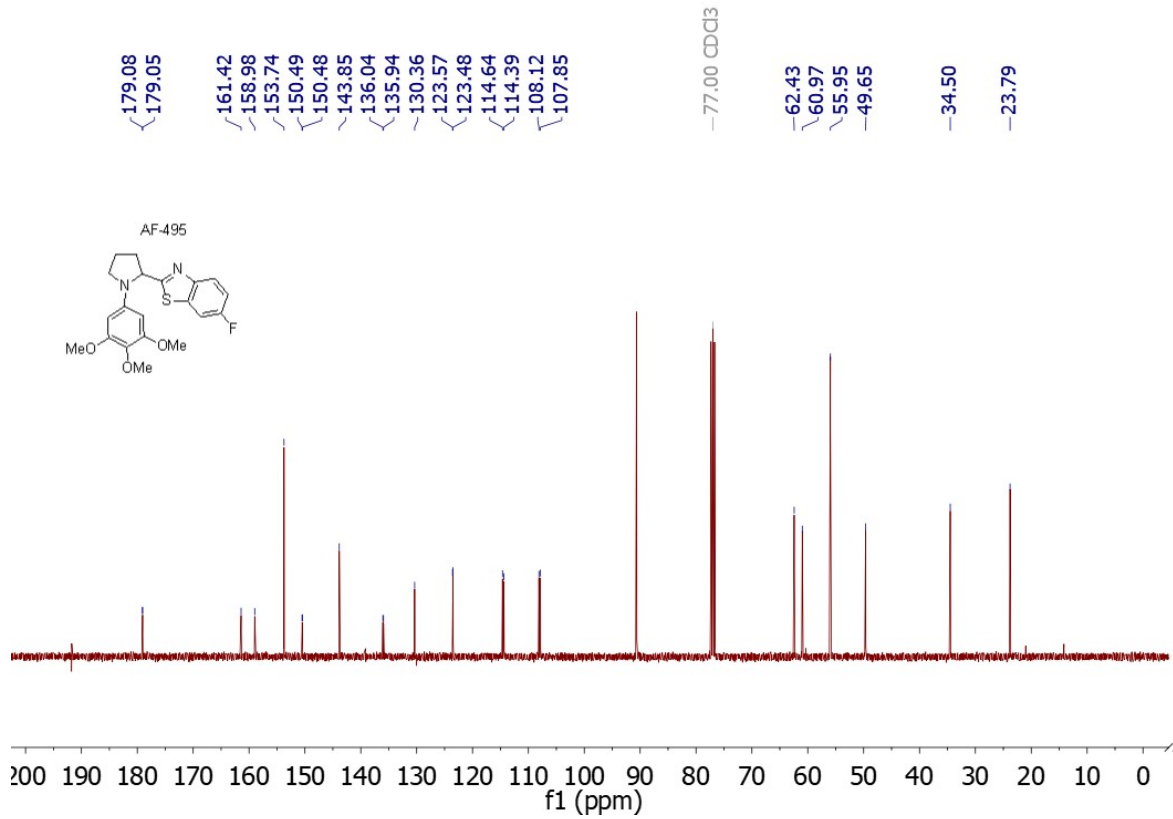
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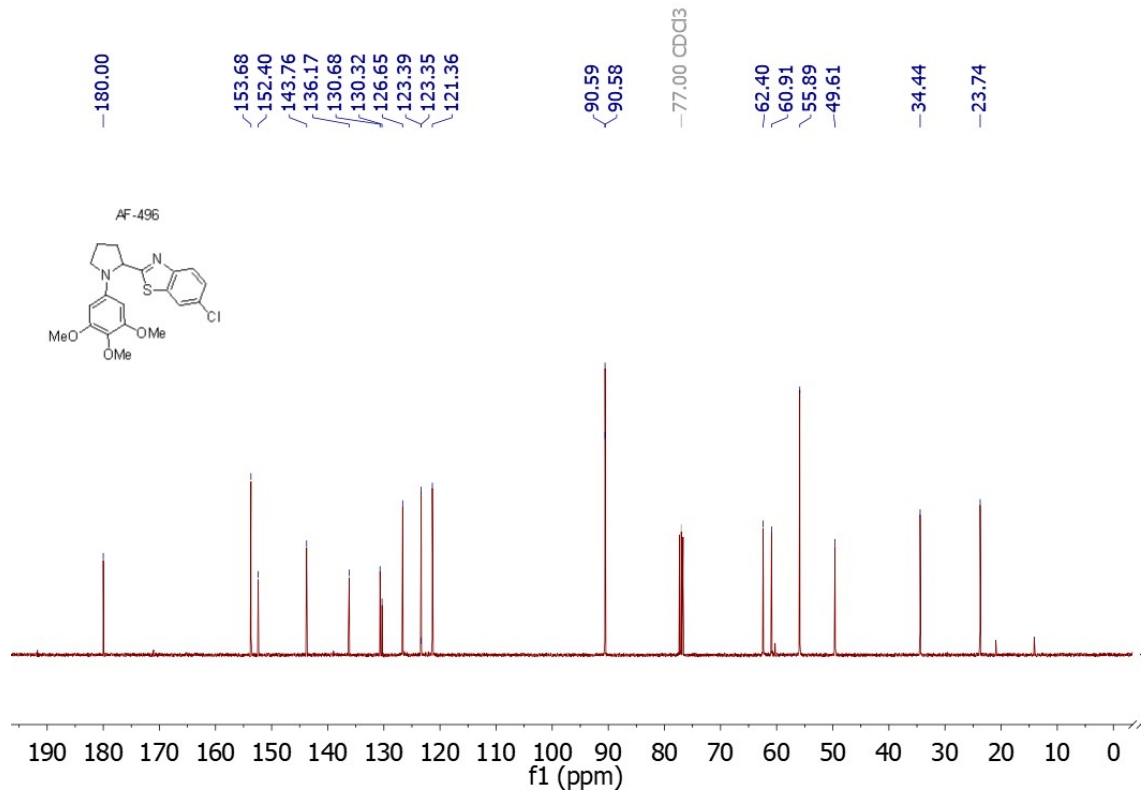
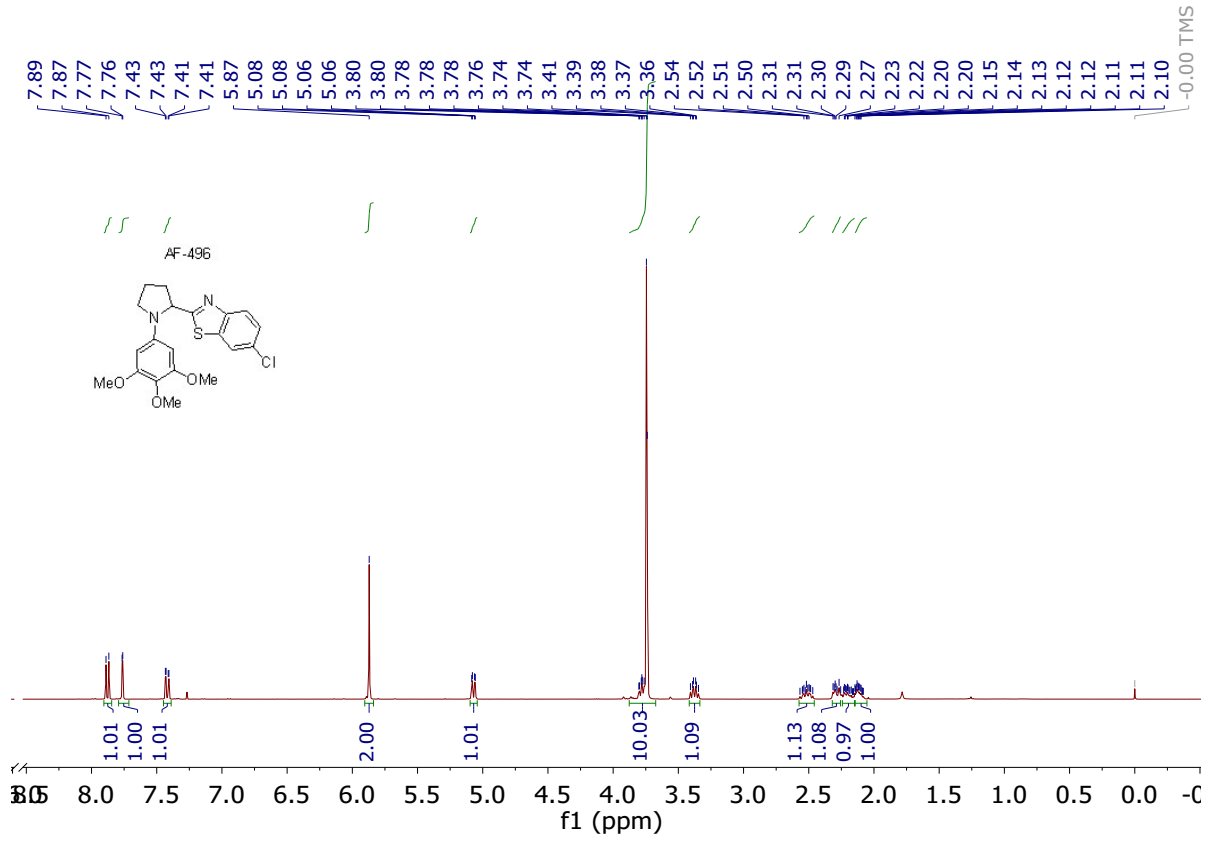


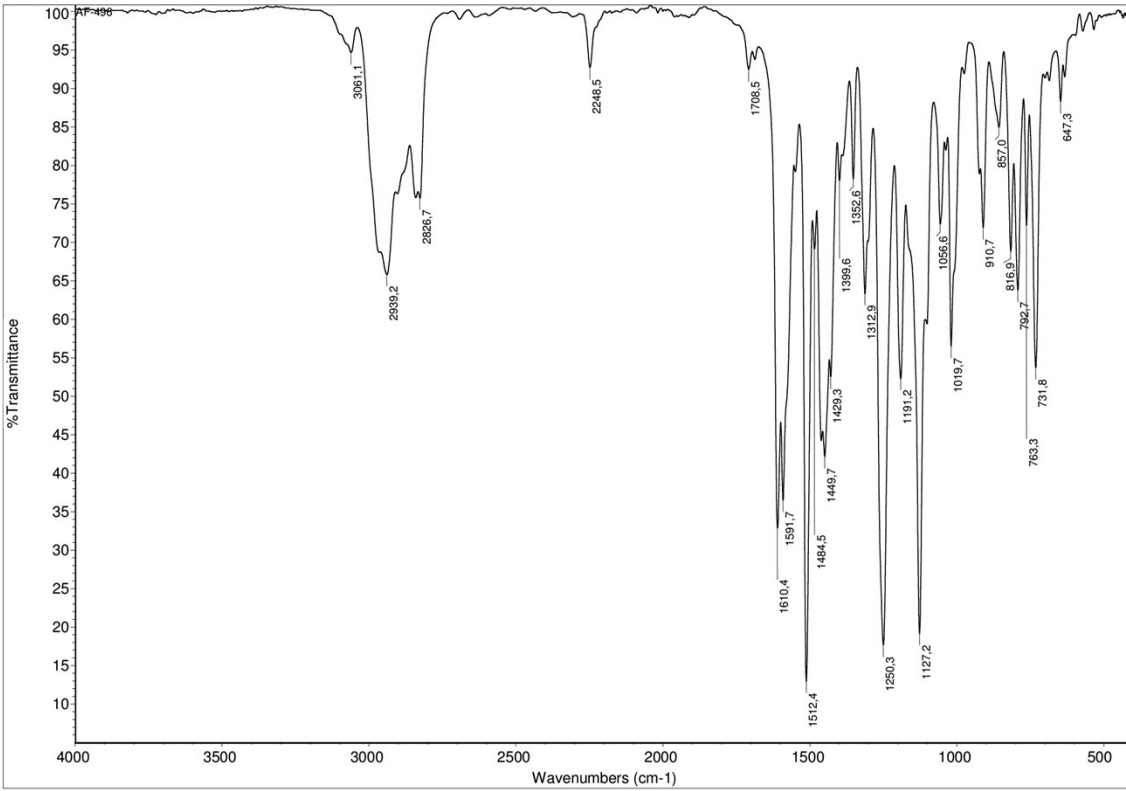
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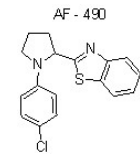
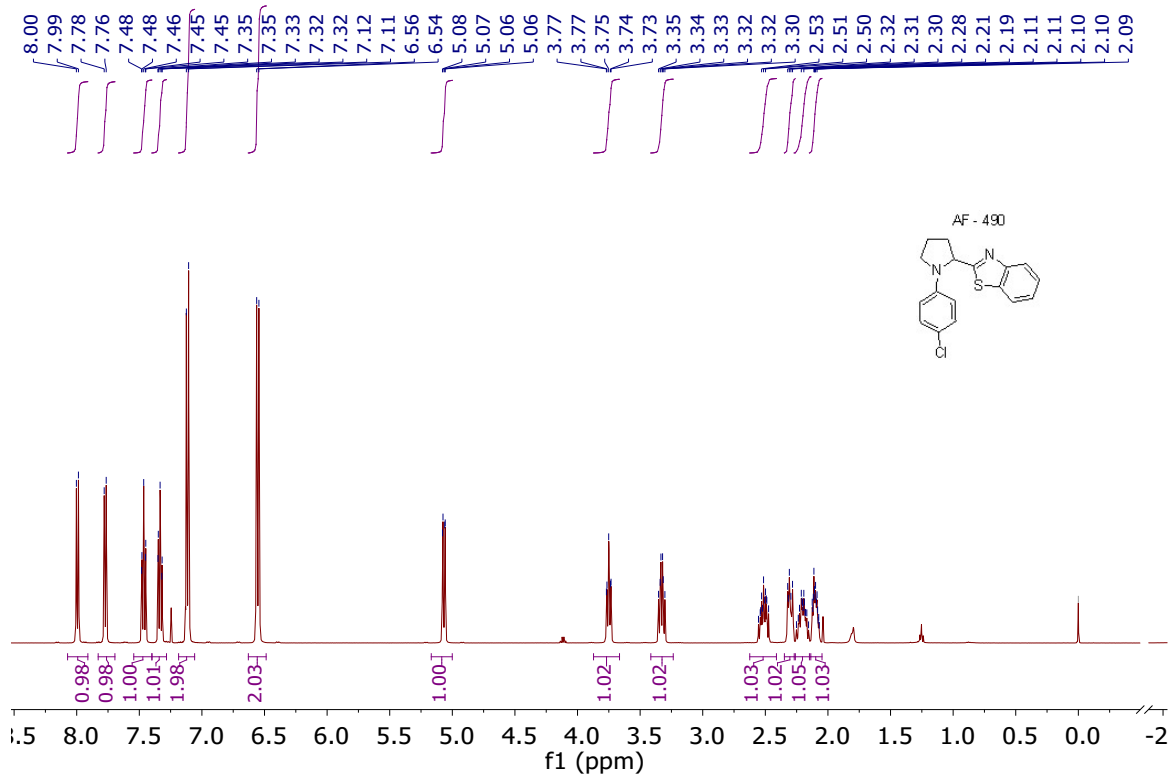


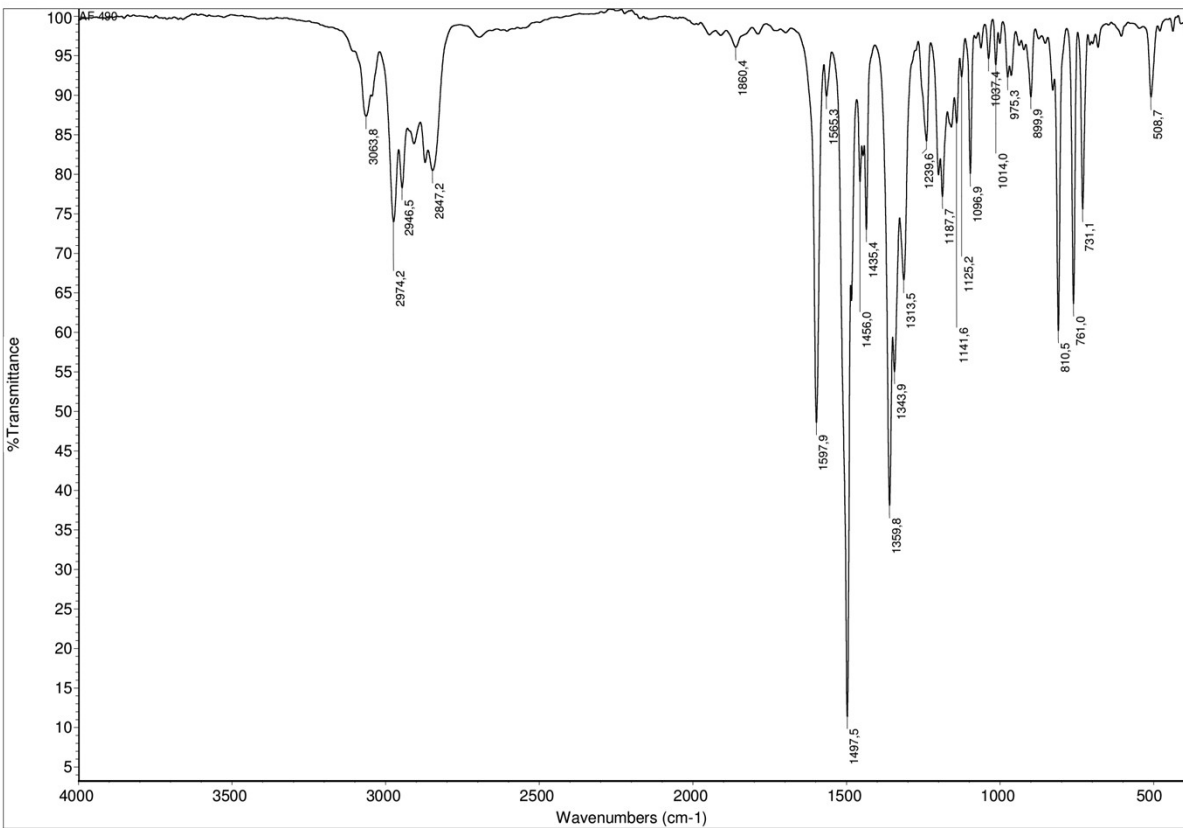
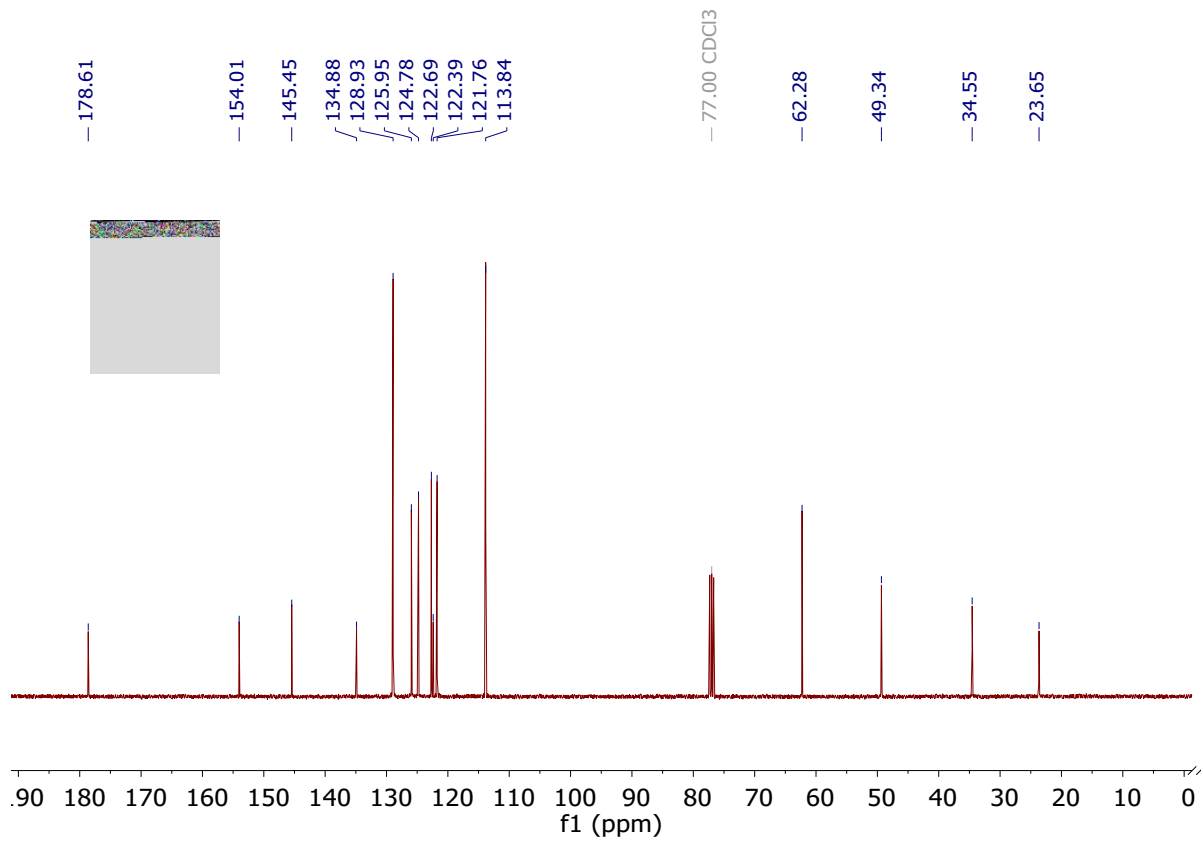
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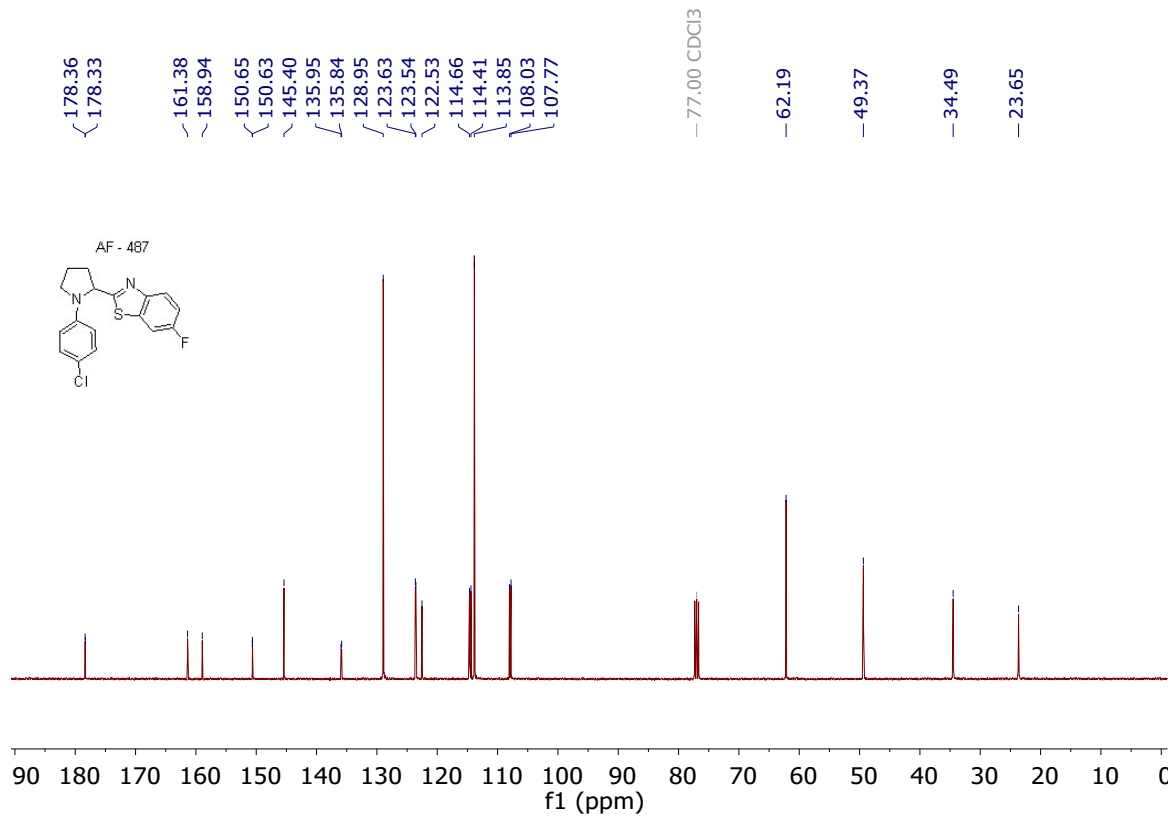
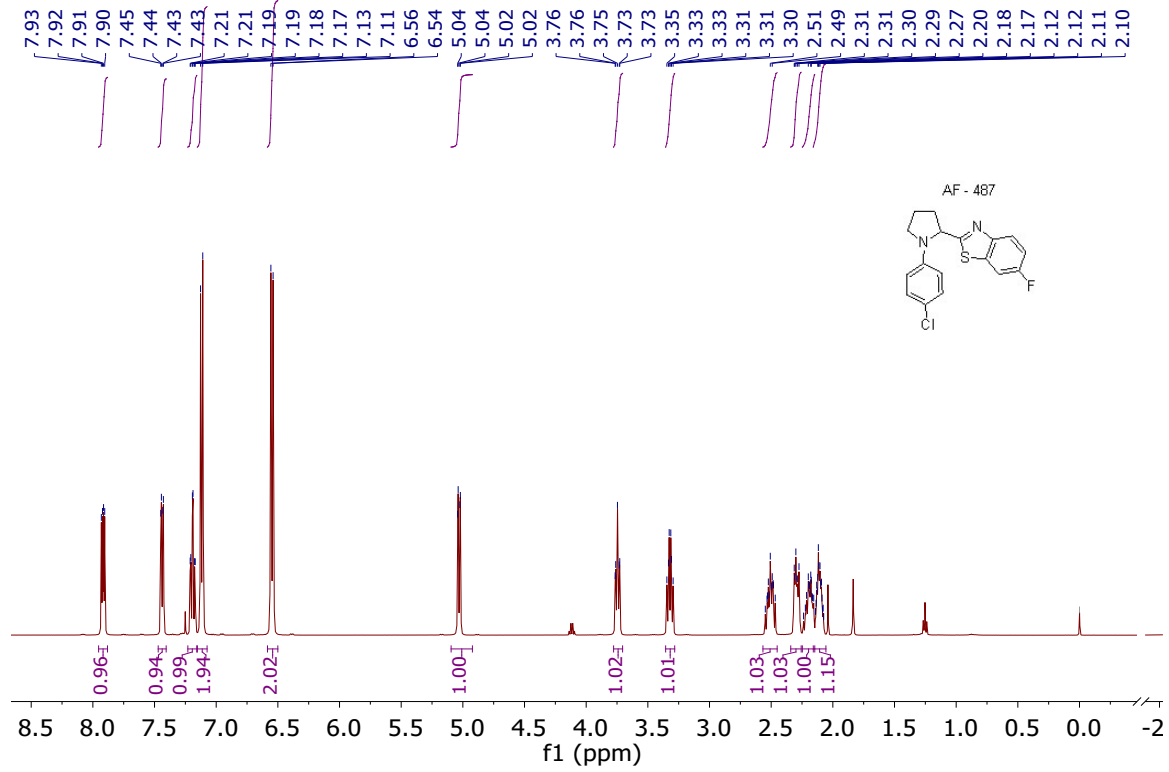


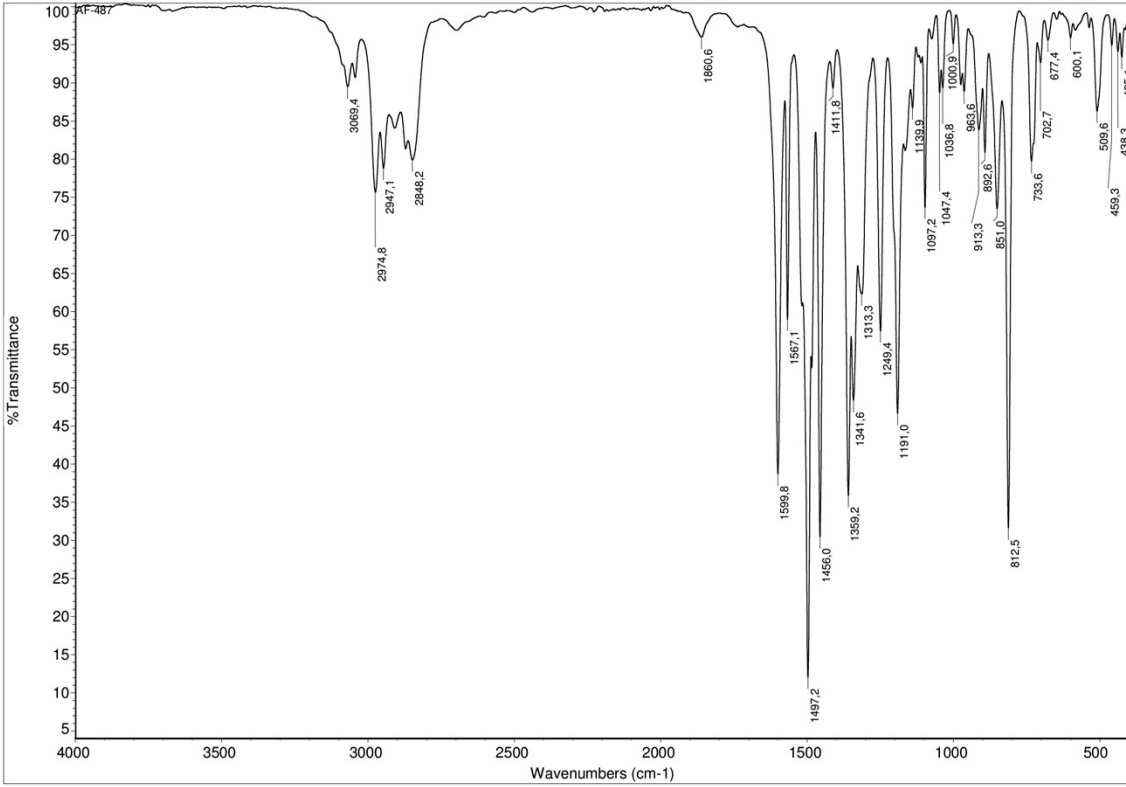
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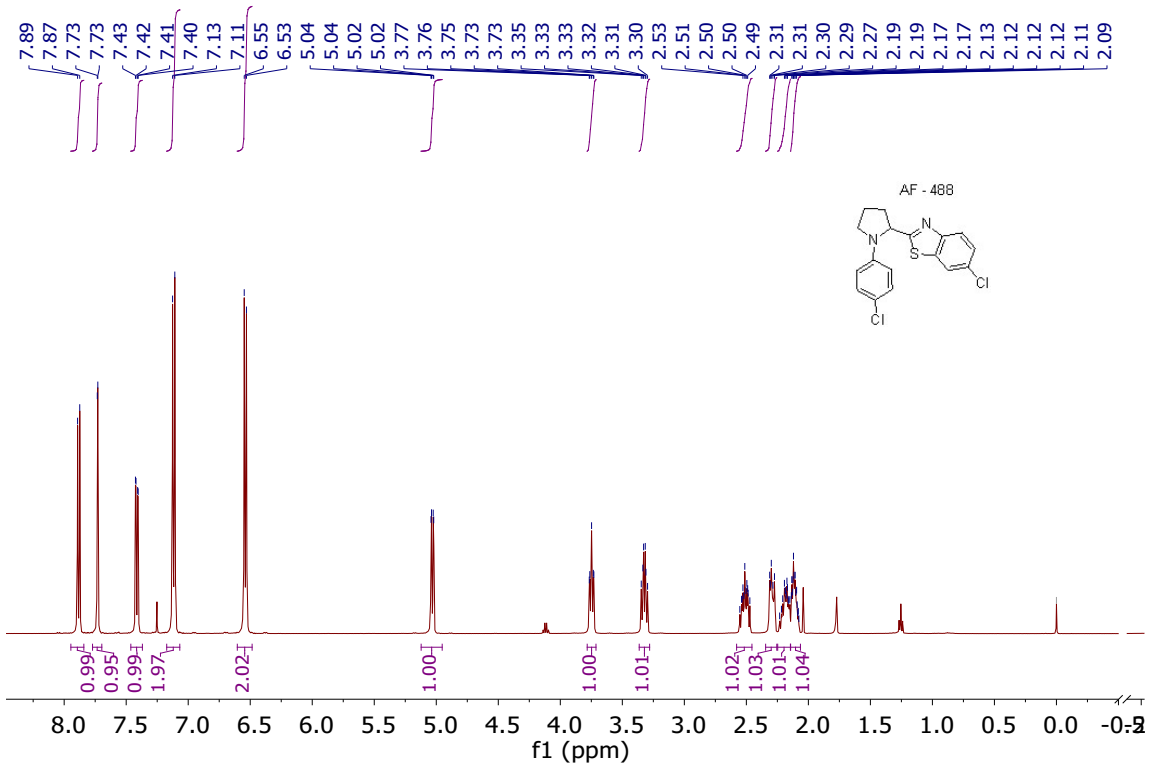


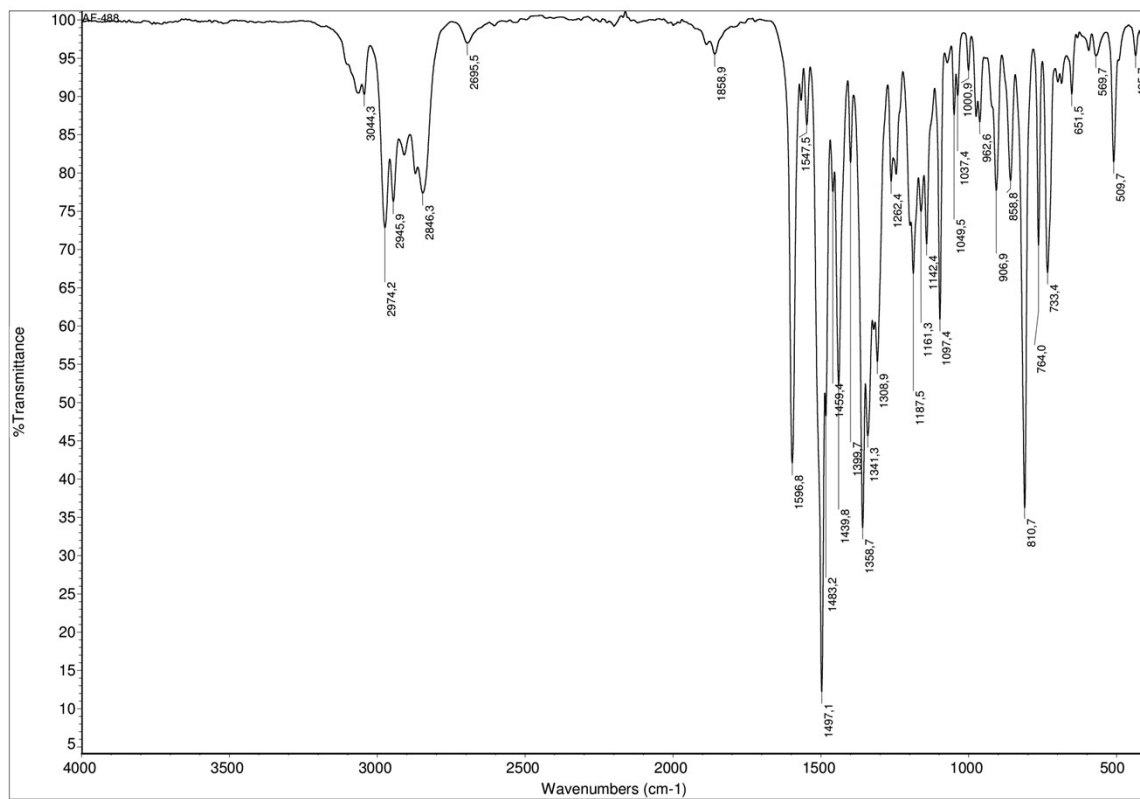
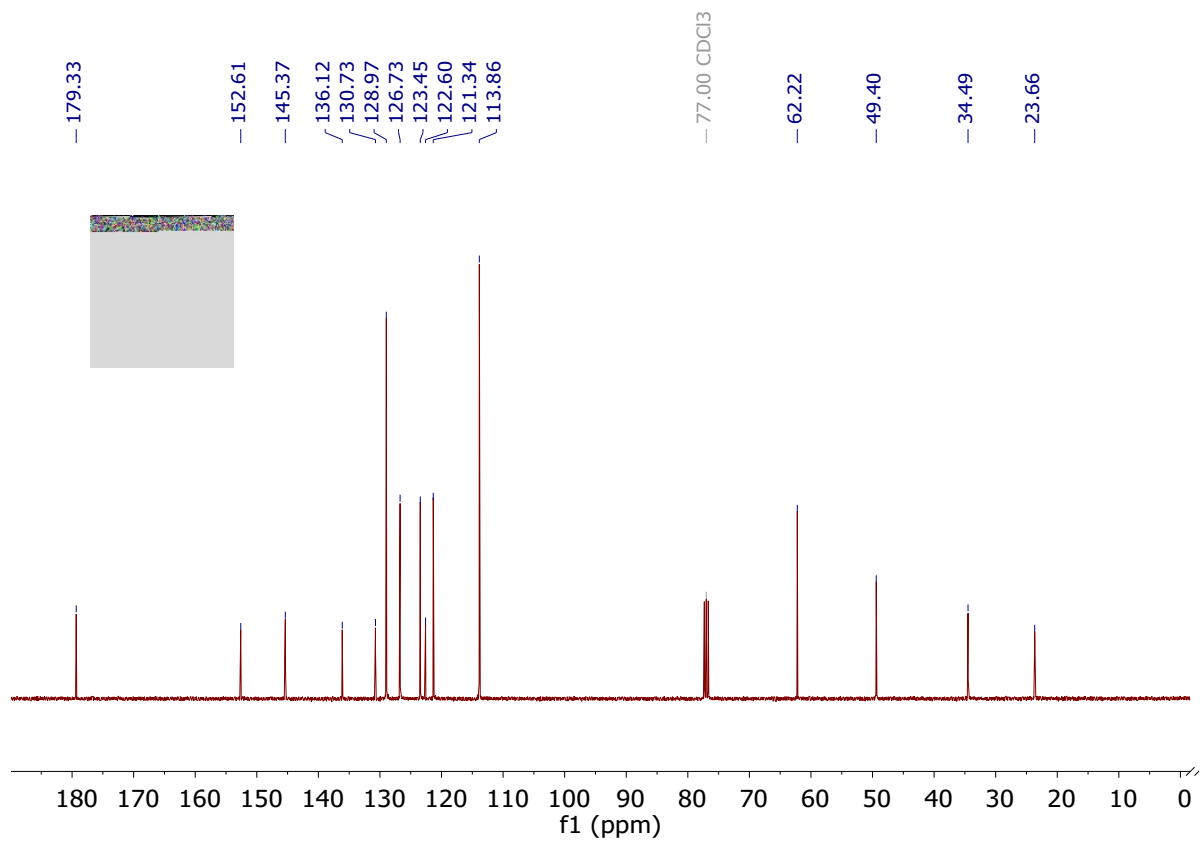
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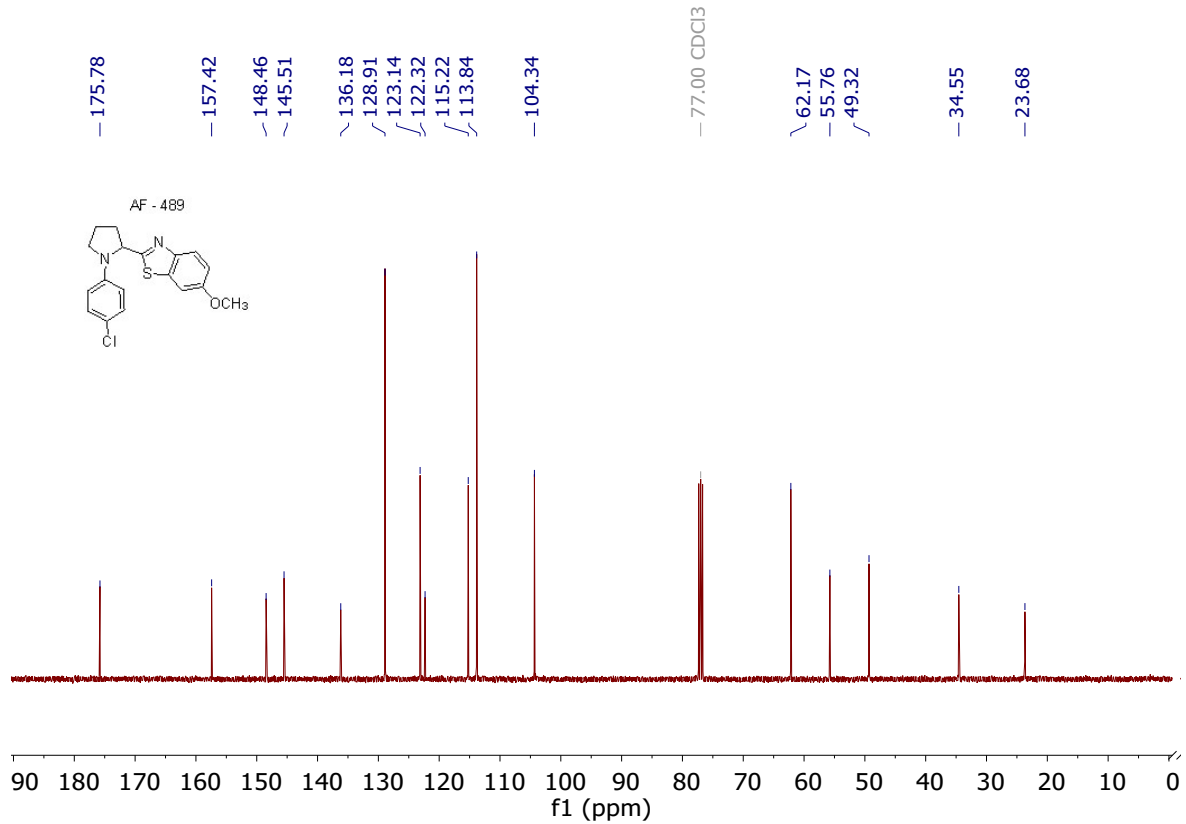
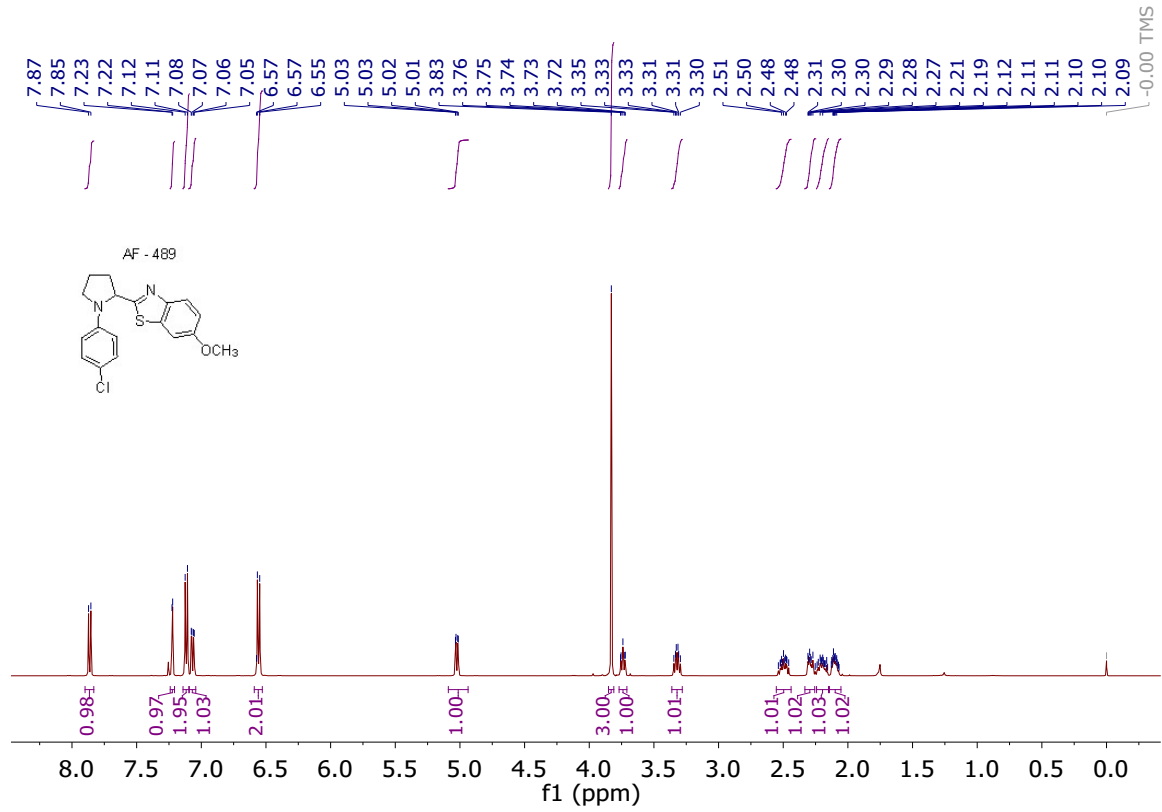


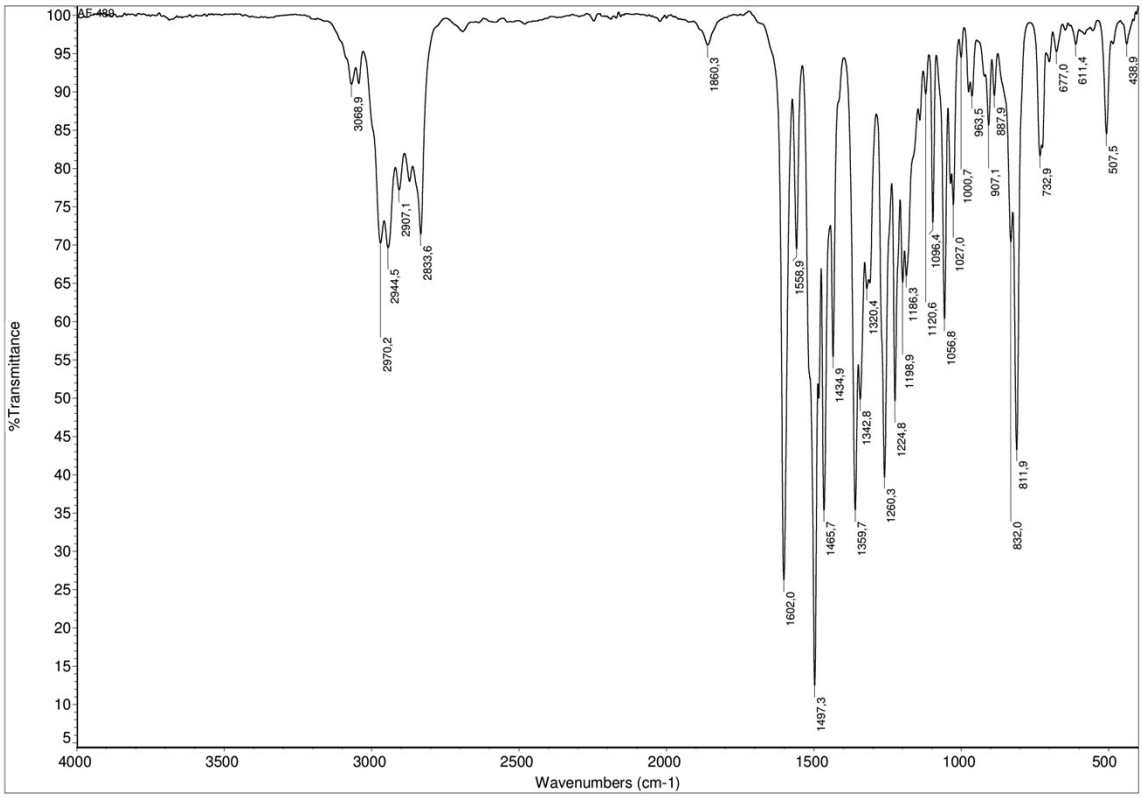
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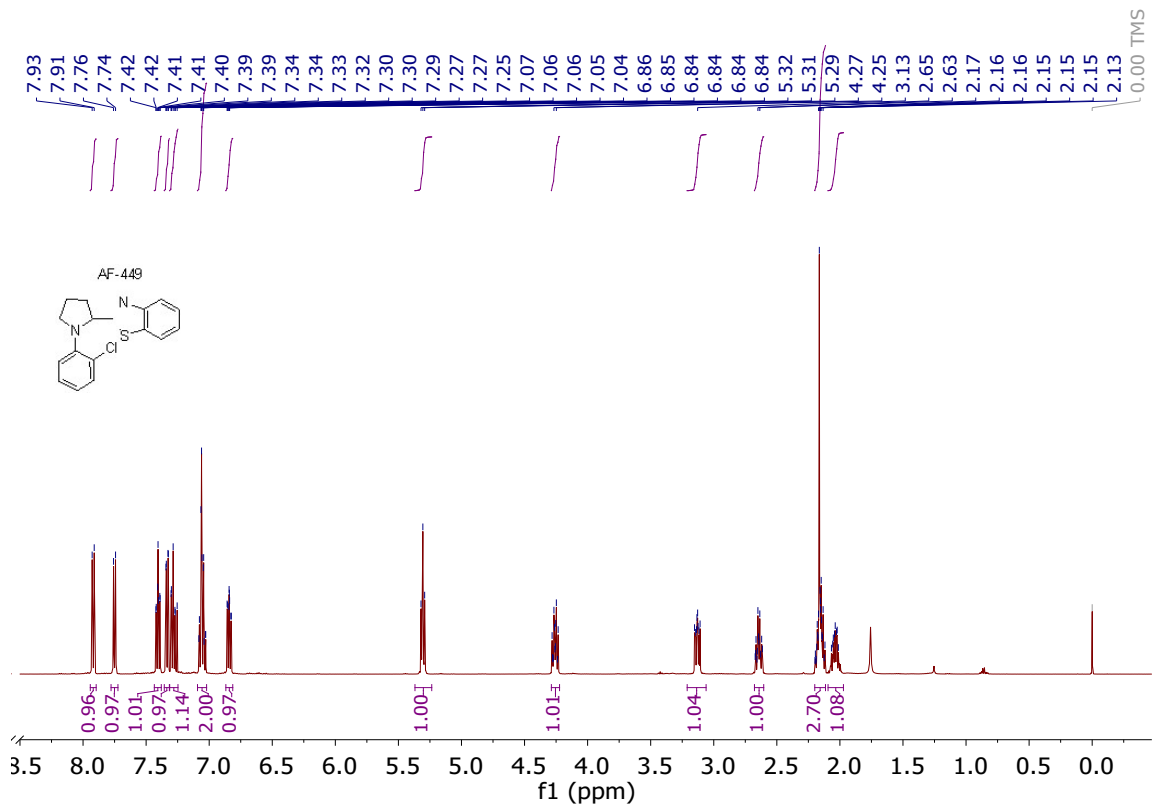


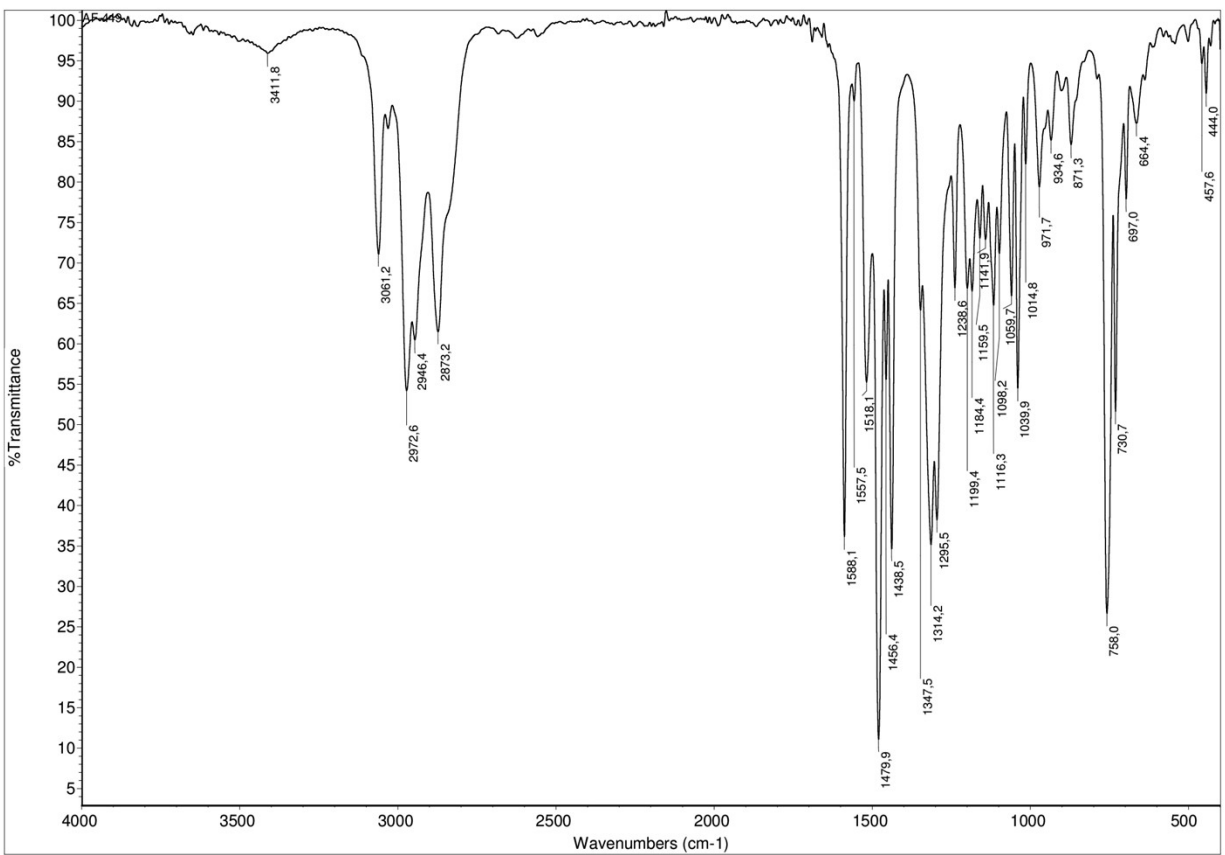
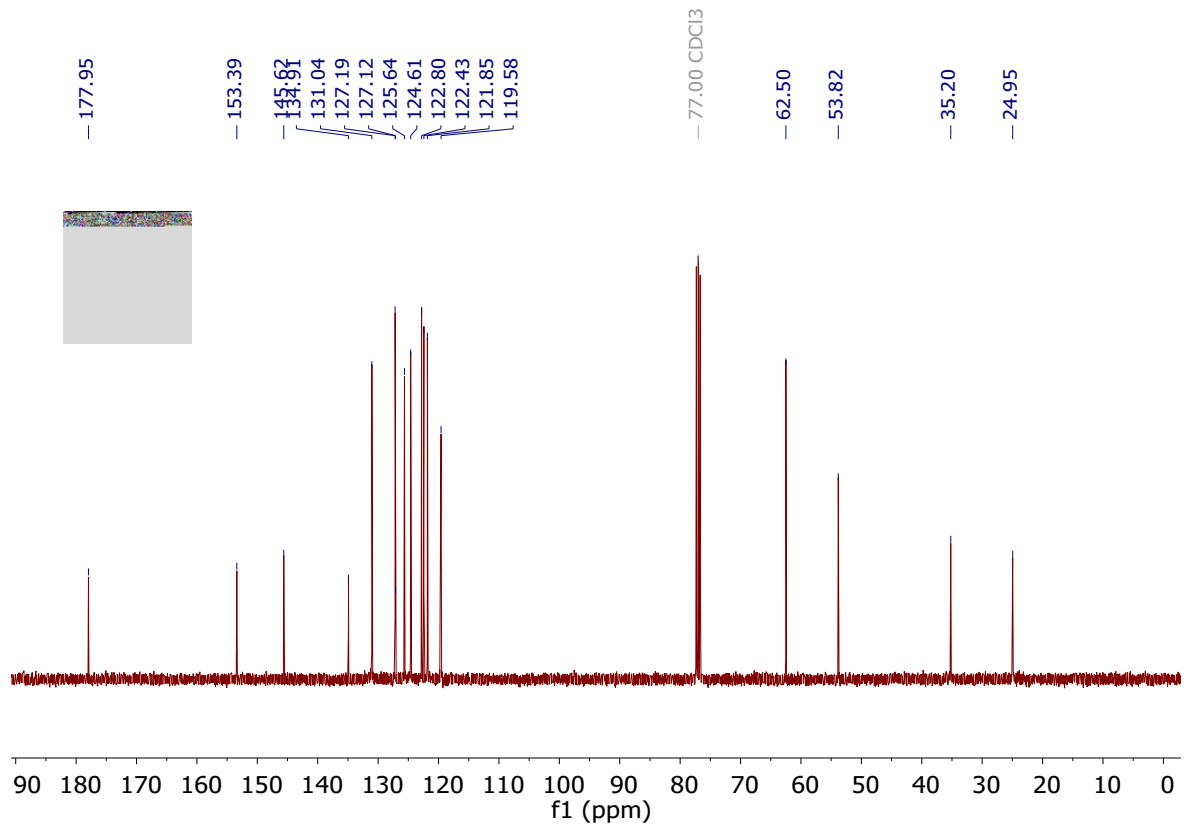
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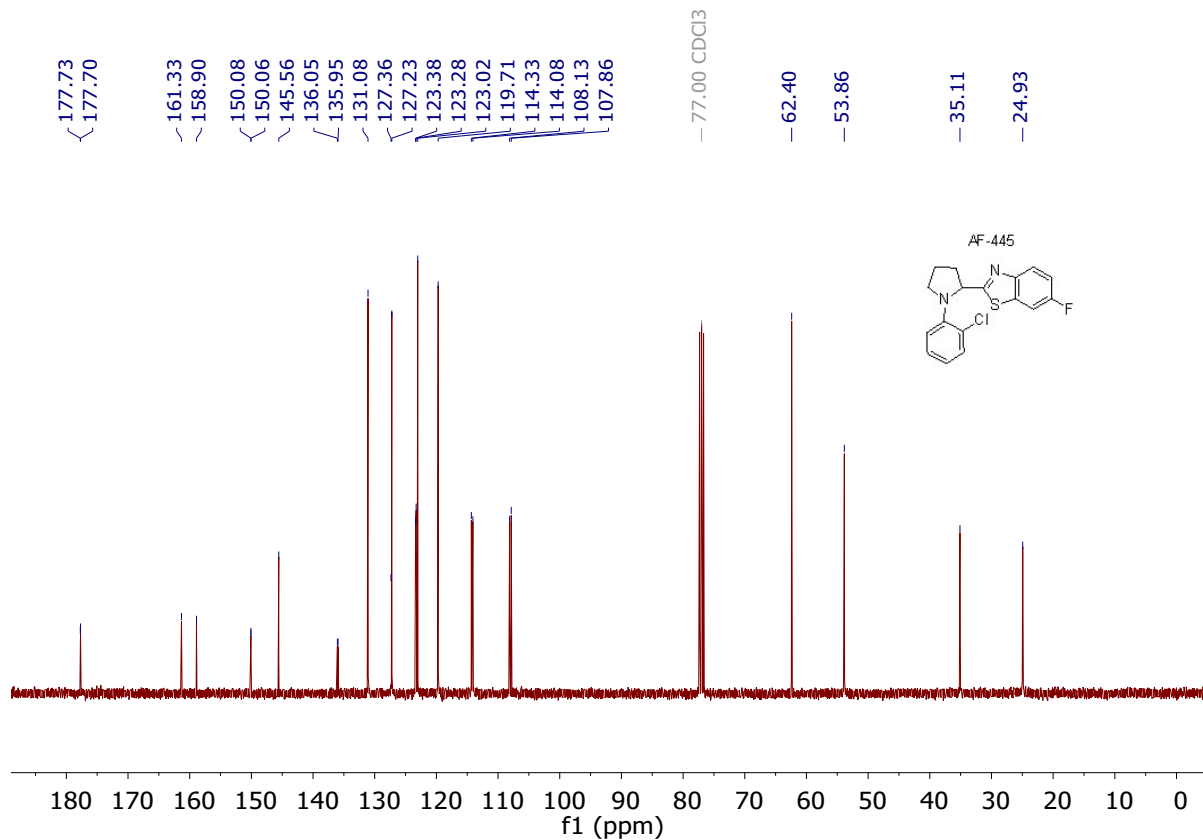
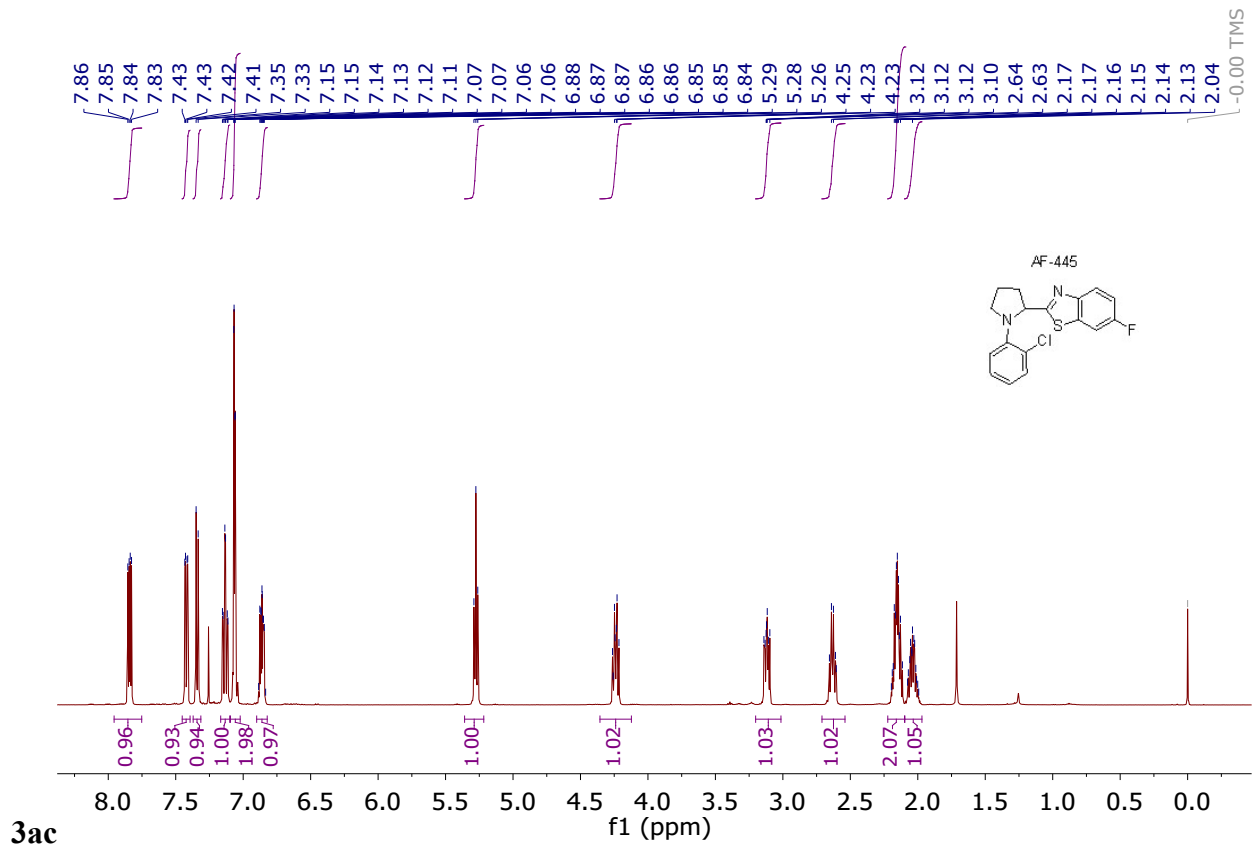


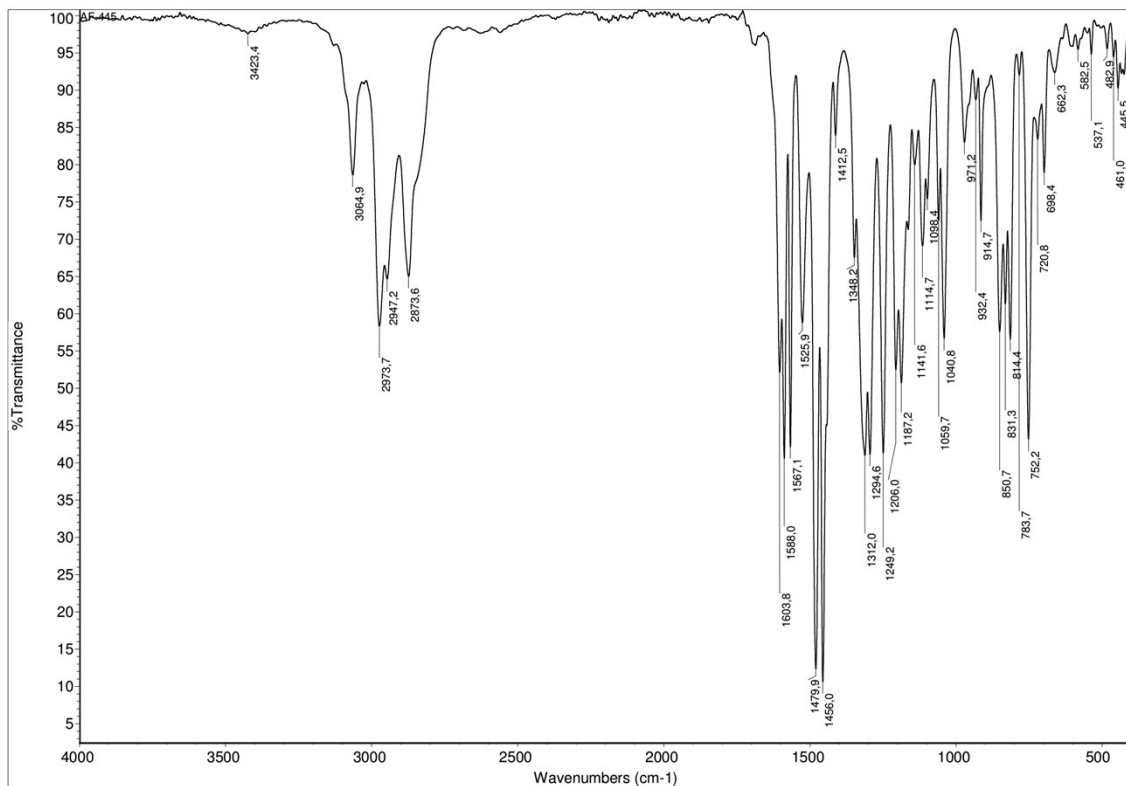


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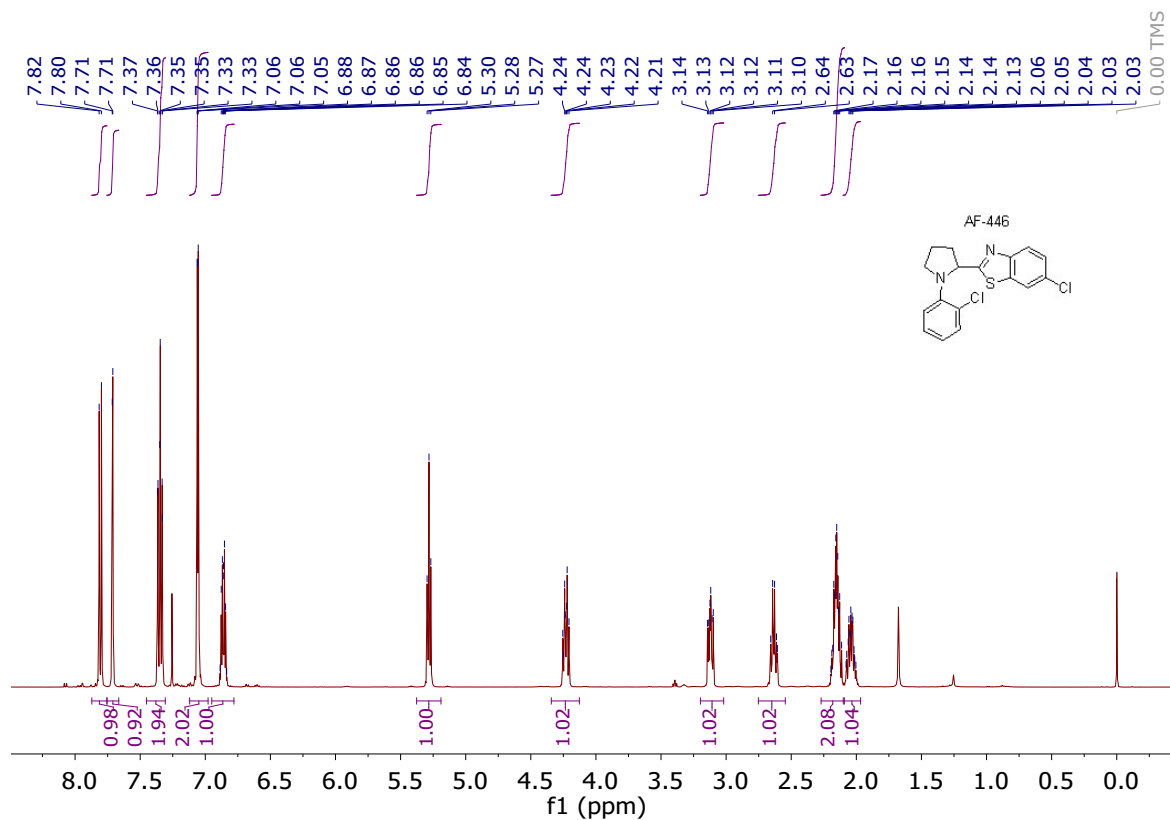


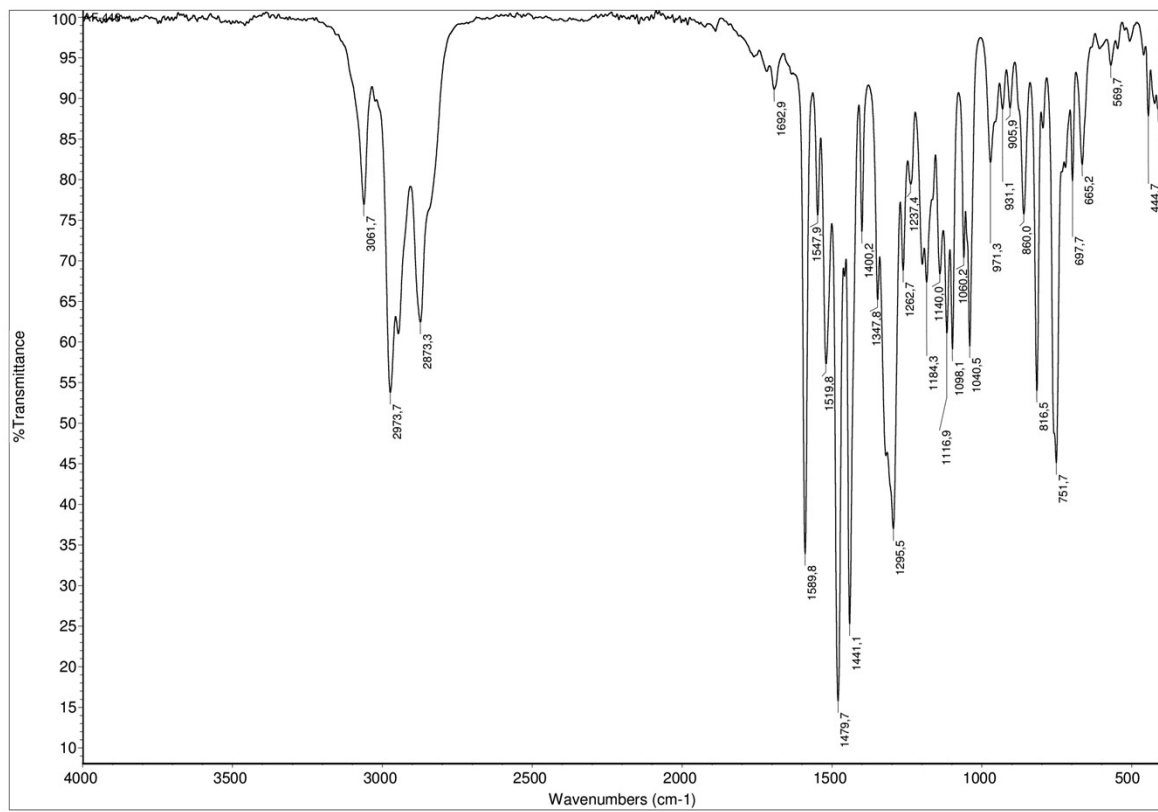
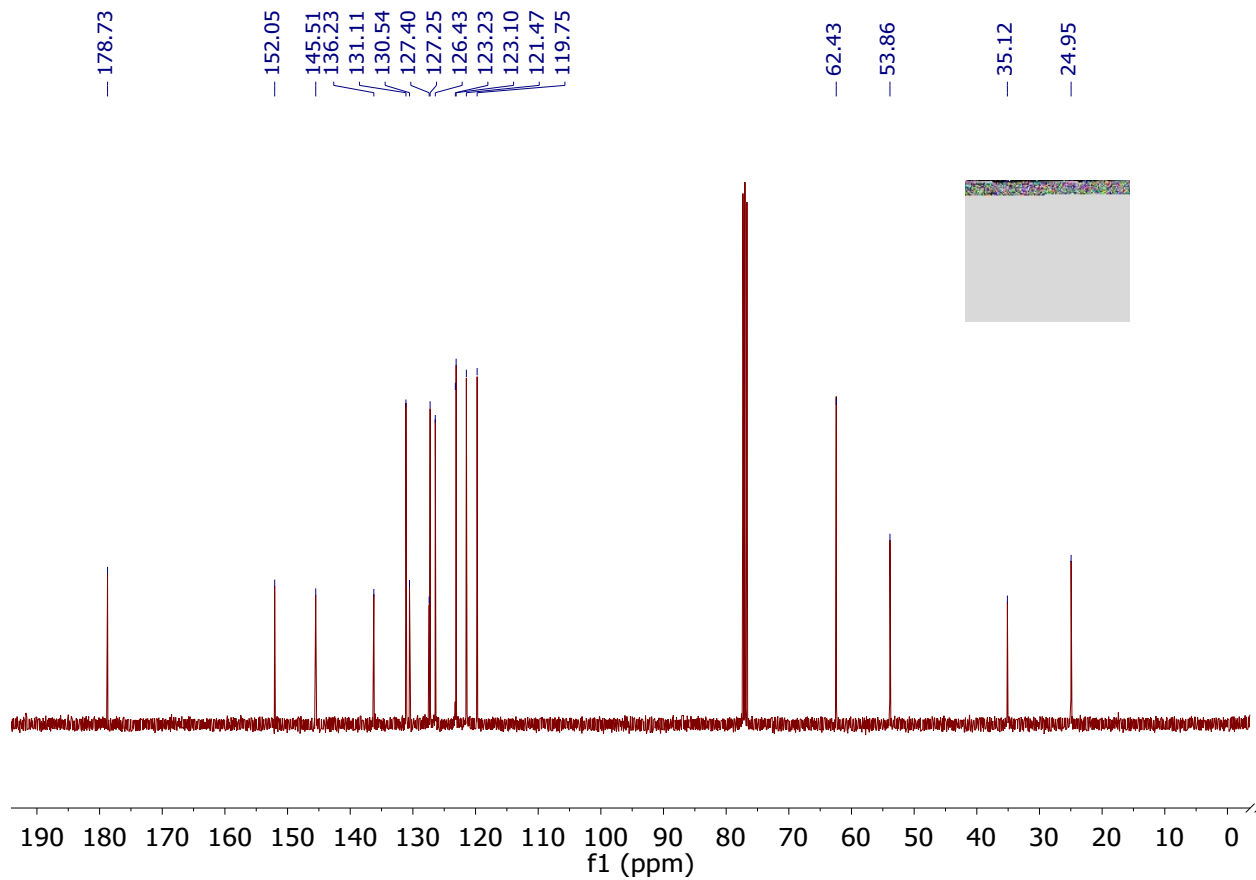




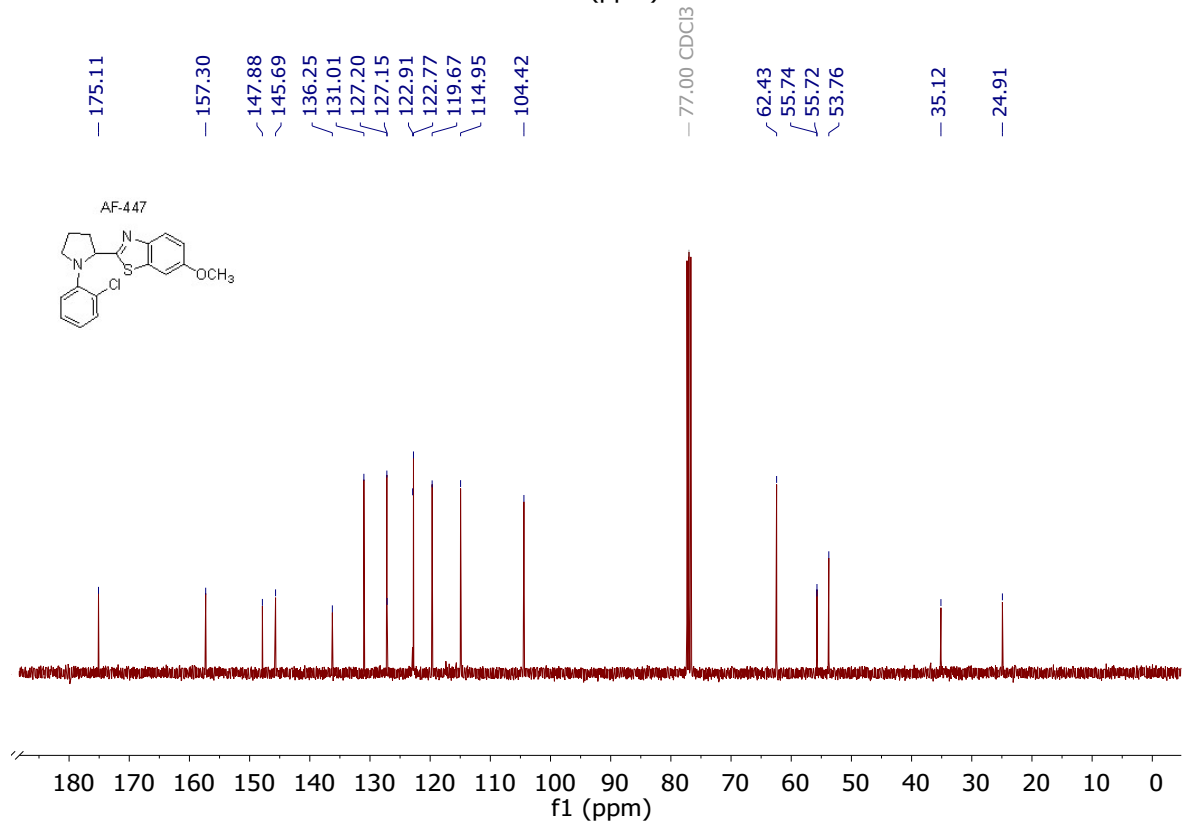
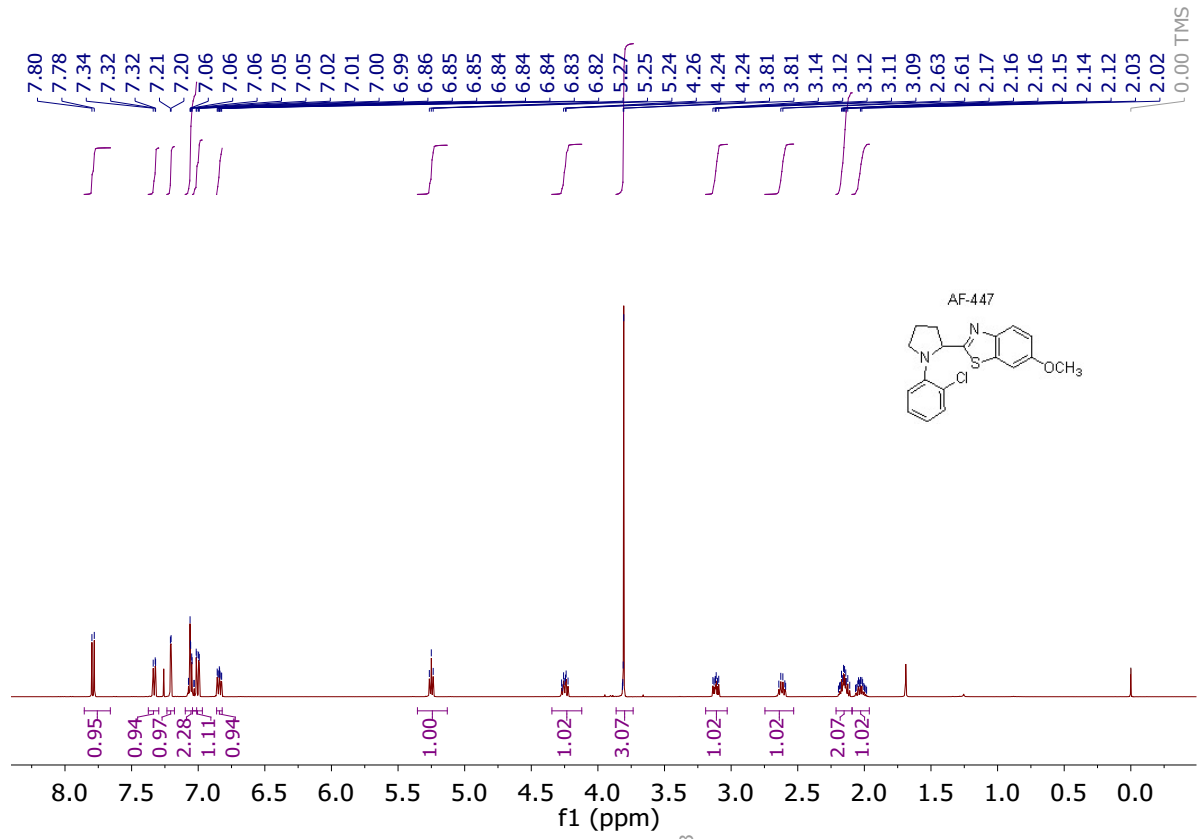


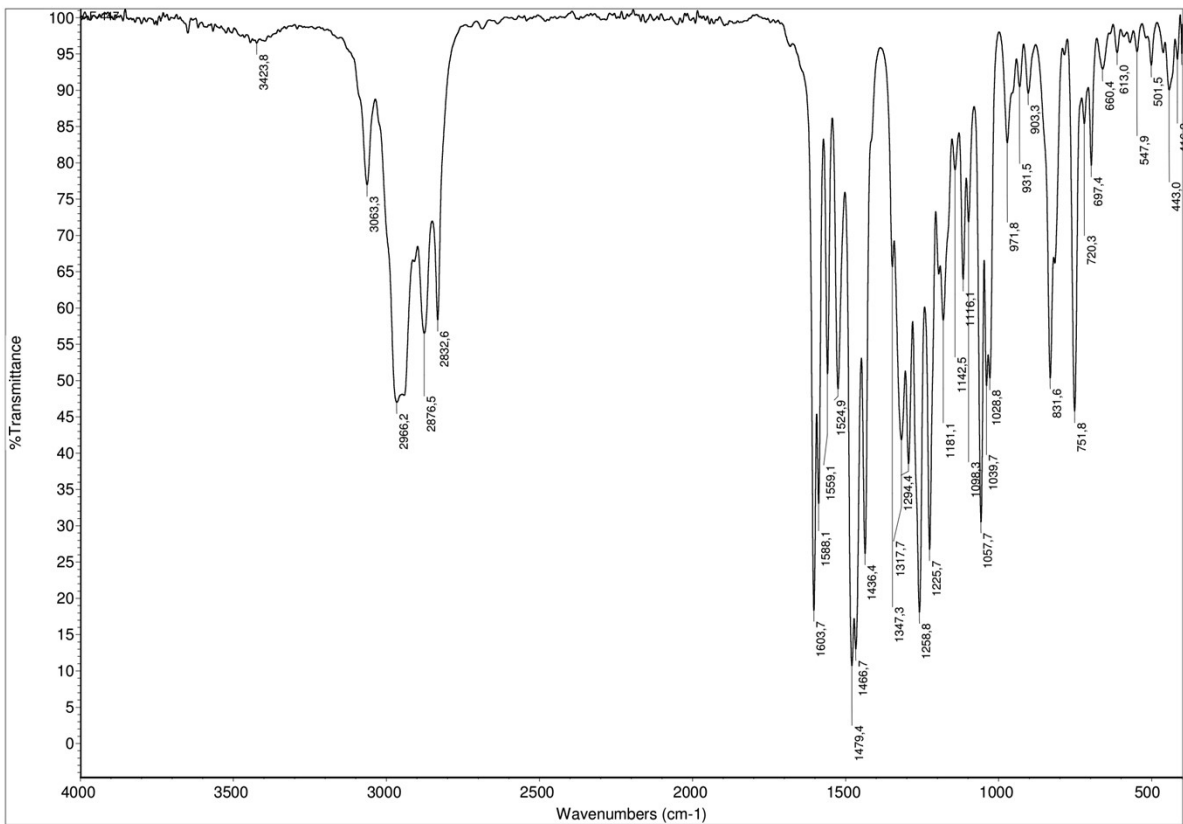
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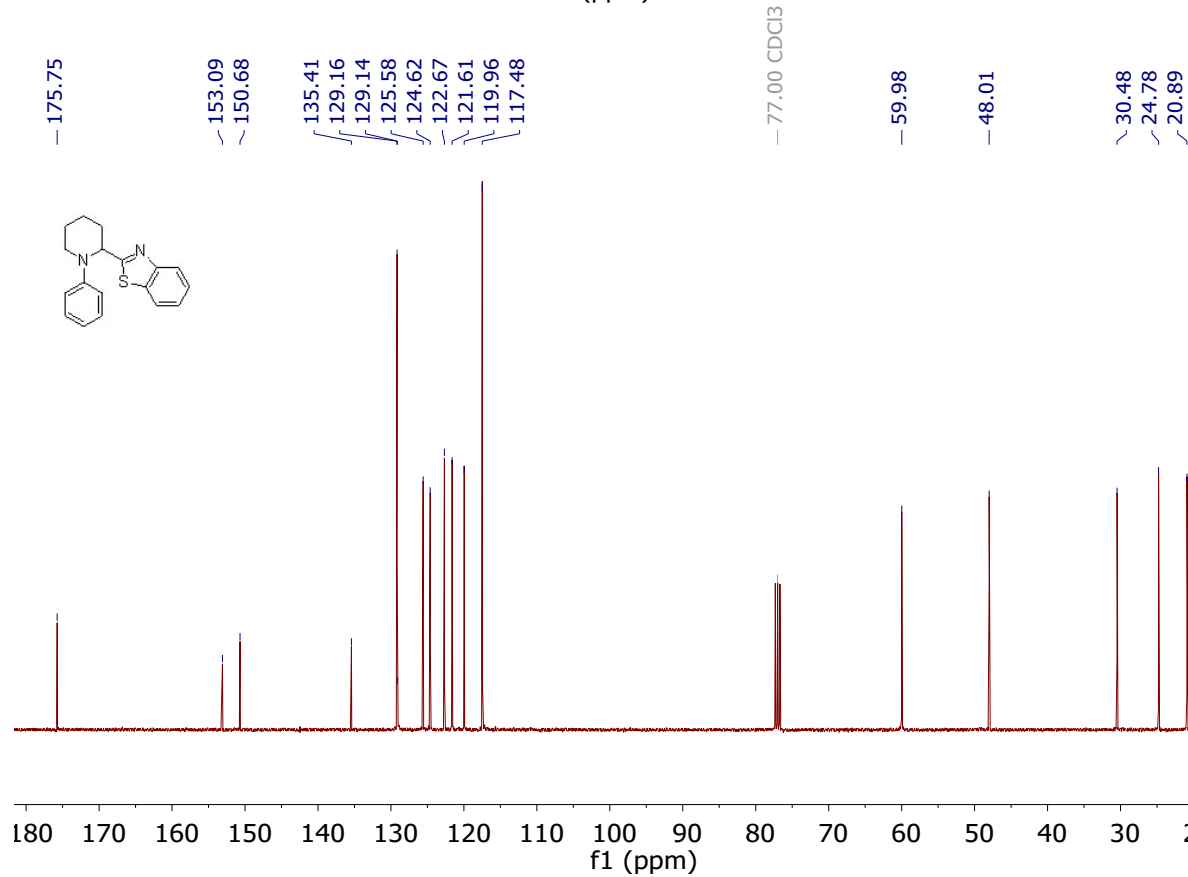
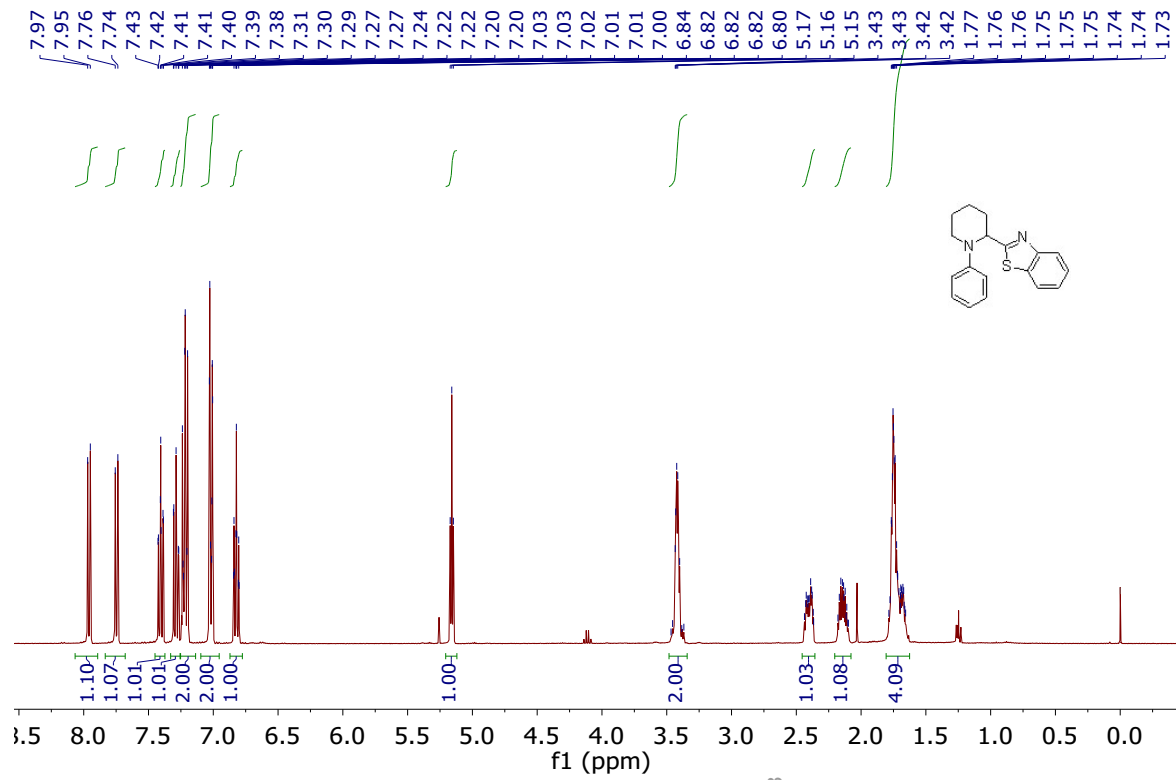


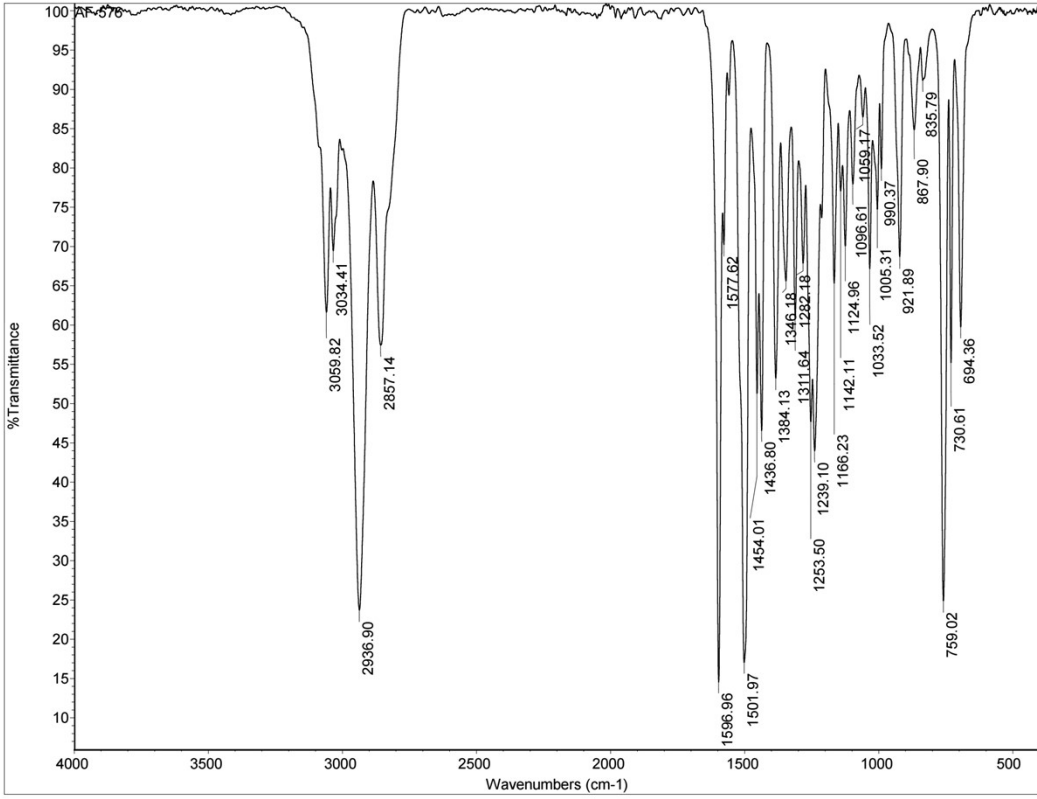
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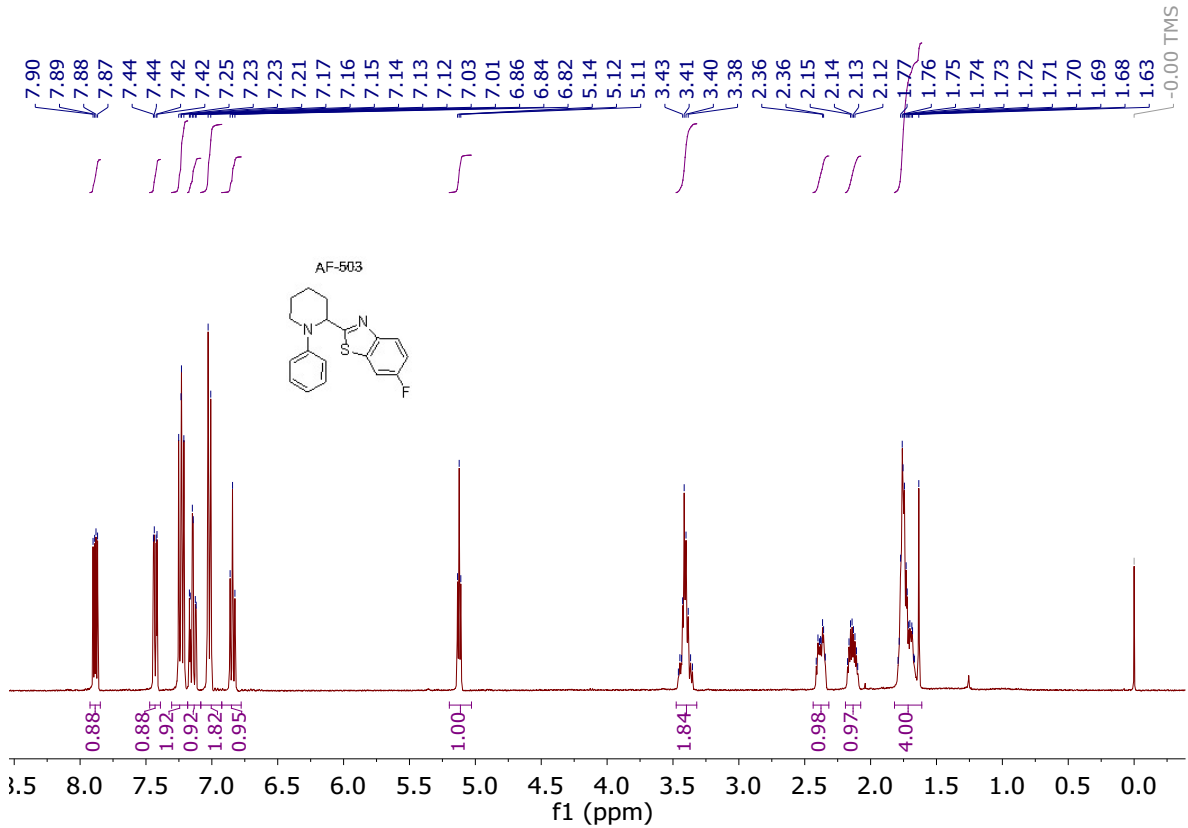


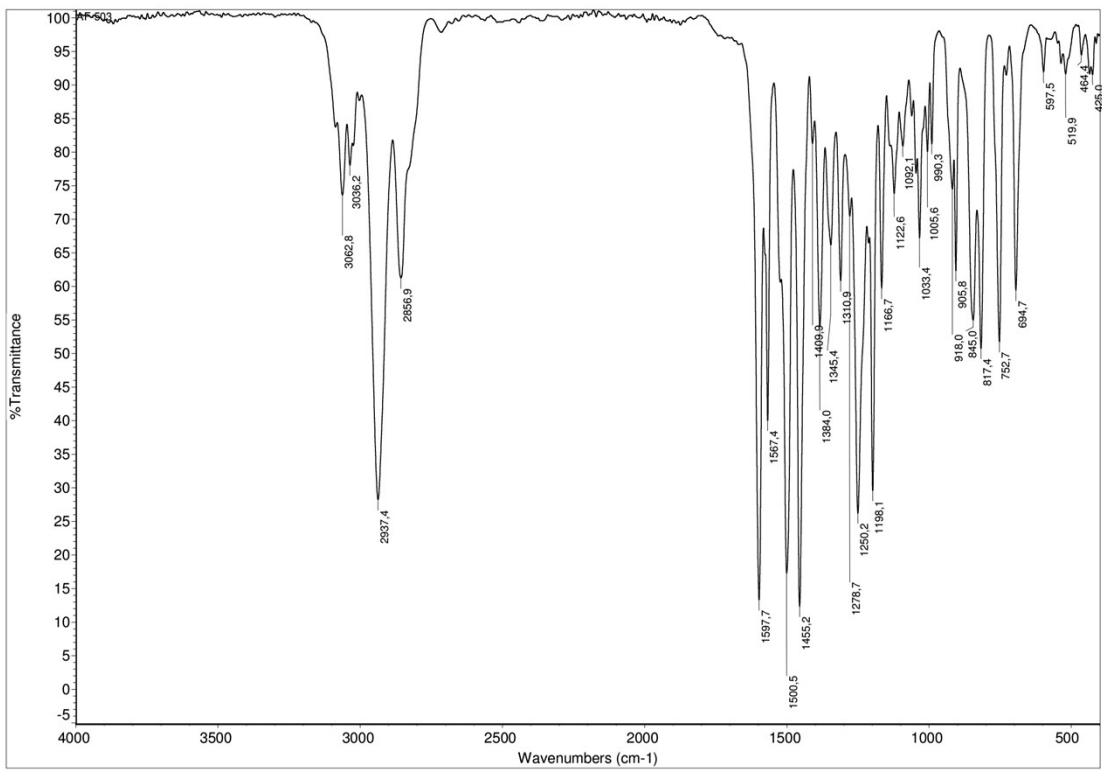
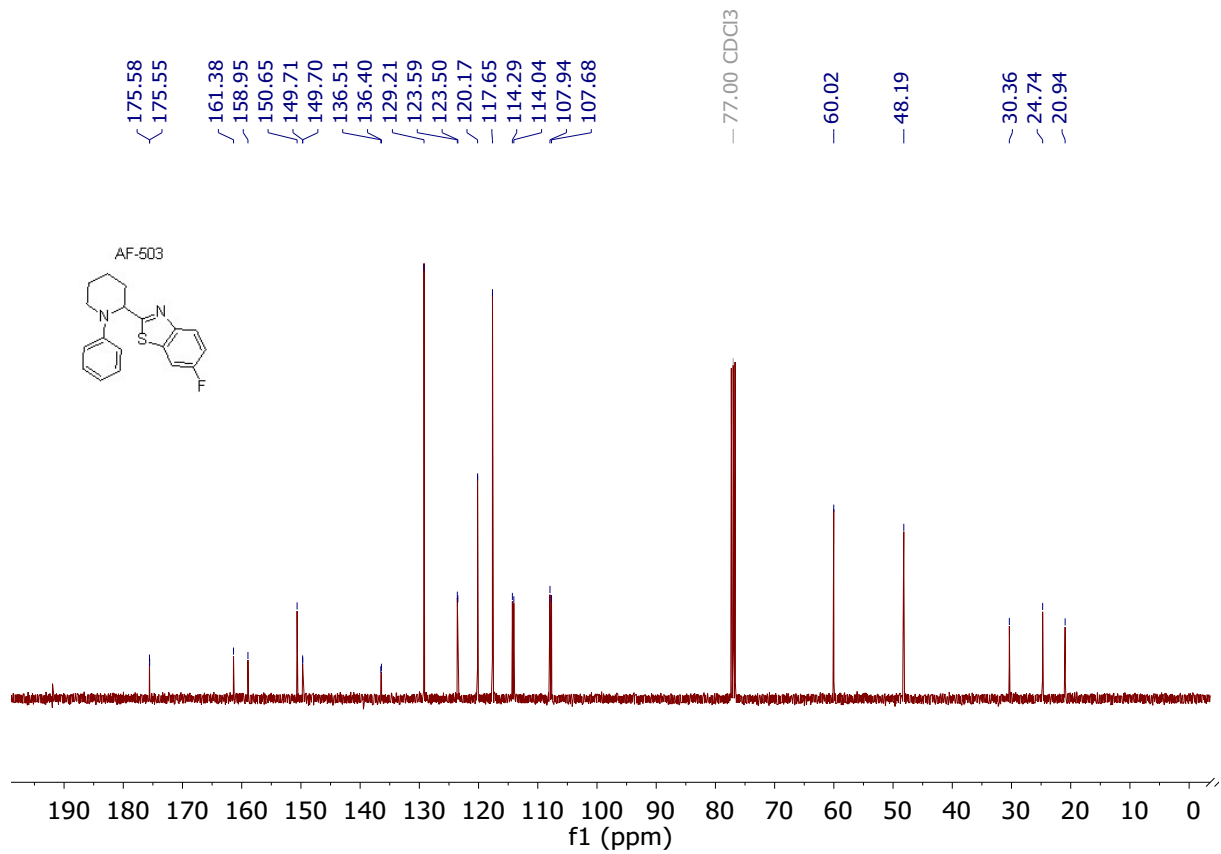
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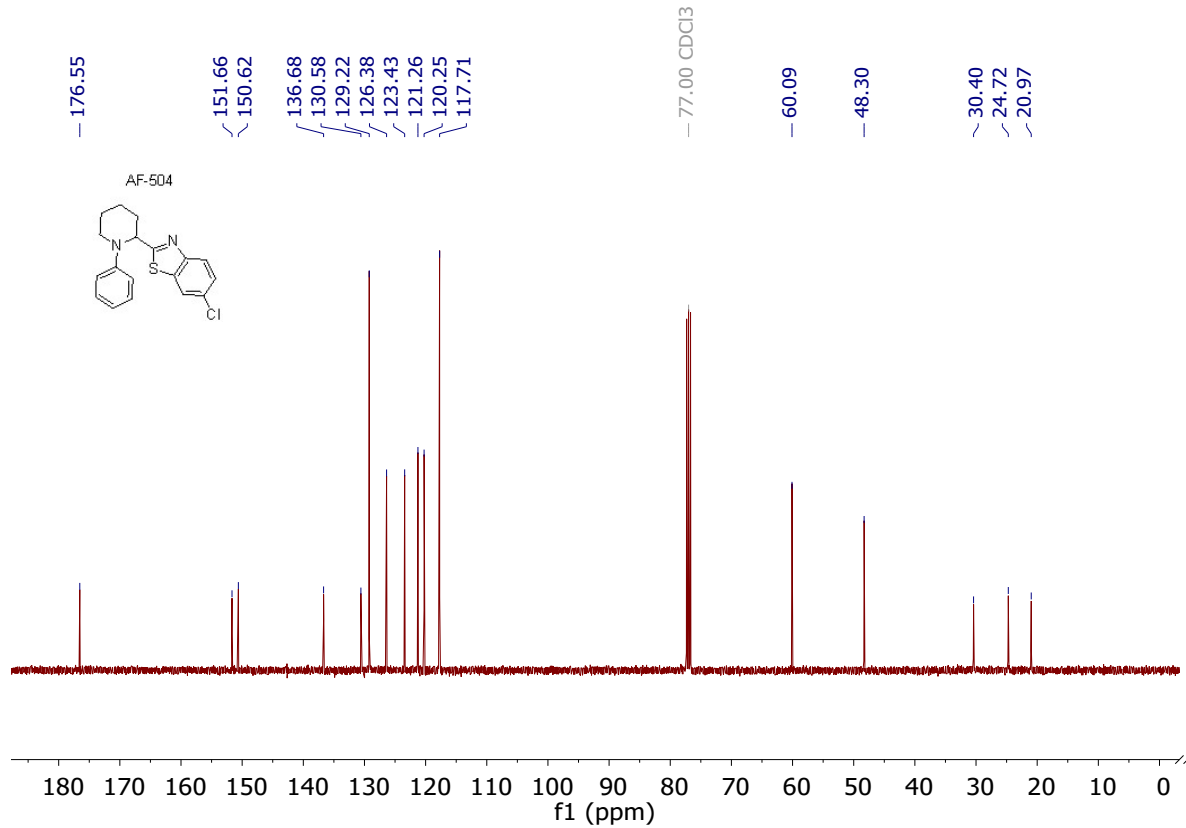
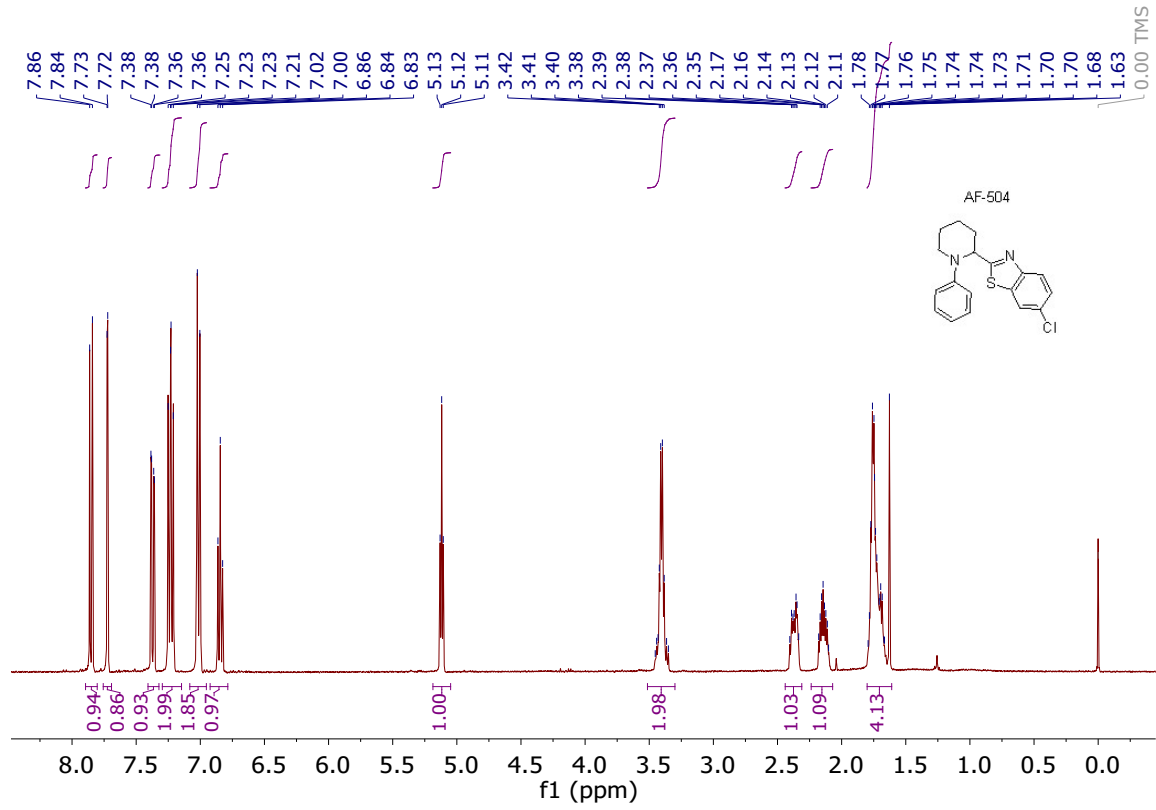


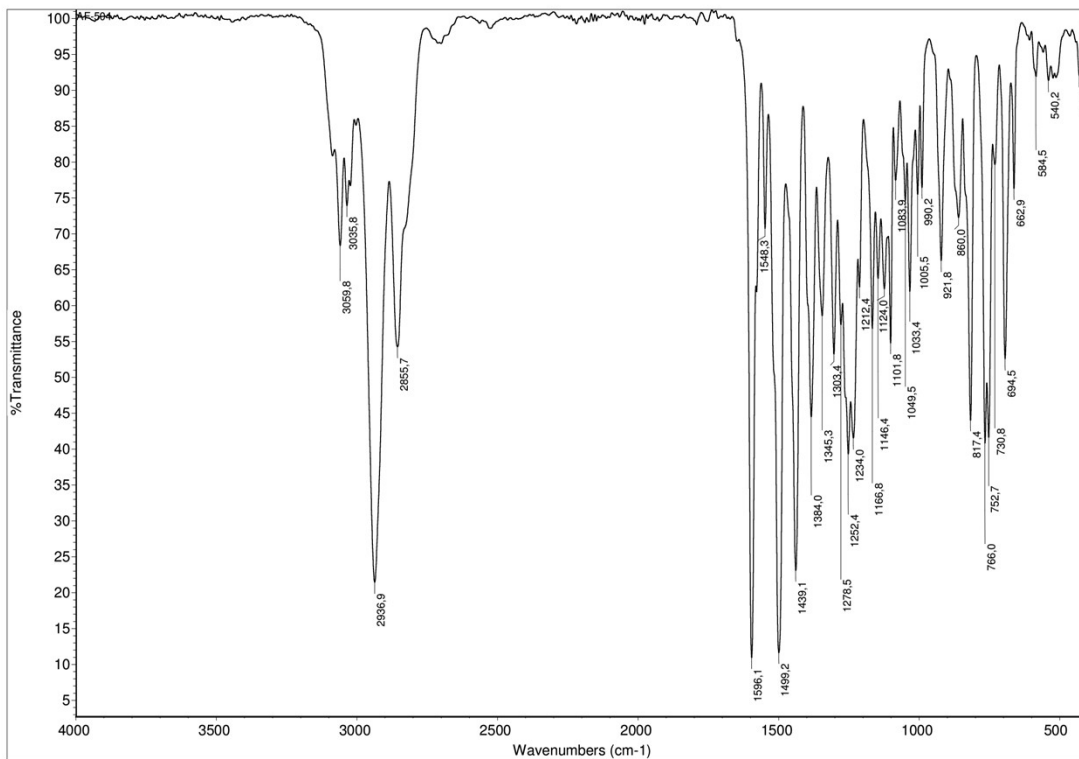
4b





4c





4d

