

Supporting Information

Photoredox Catalytic Aminomethylation of Sulfonylthiazoles

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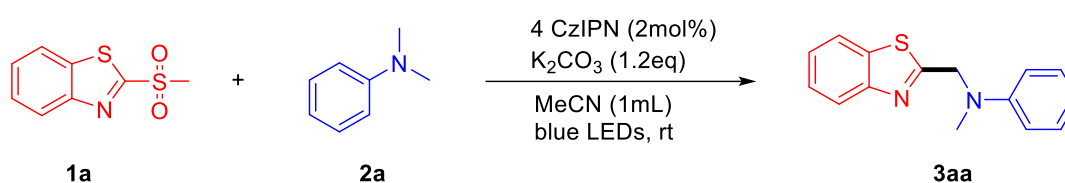
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1、 General information:

2-(methylsulfonyl) benzothiazole was synthesized according to the steps described in the literature. A series of 2-(methylsulfonyl) benzothiazole containing different substituents were synthesized by literature method. Purchase other commercially available reagents and solvents and use them without further purification. All catalytic experiments were performed in a glove-box in an argon atmosphere, with ^1H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra recorded on the Bruker NMR spectrometer of CDCl_3 , using TMS as an internal reference and chemical shift values reported in ppm. Abbreviations used in subsequent NMR experiments :s, singlet; d) Tight top; t, in groups of three; Ask, foursquare; Meter, multiplet. A high resolution mass spectrum was obtained by fast atomic bombardment (FAB) using a double focusing magnetic sector mass spectrometer and electrospray ionization electron shock (ESI) ionization technique.

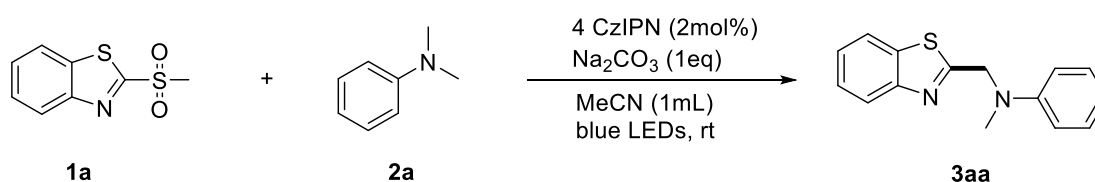
2、 General experimental methods:



In Ar or N_2 atmosphere, a magnetic stirring rod was installed on the oven-dried Schlenk tube. 4CzIPN (2 mol%, 0.02 equiv), K_2CO_3 (0.12 mmol,1.2 equiv), 2-(methylsulfonyl)benzo[d]thiazole (0.1 mmol, 1.0 equiv), N,N-dimethylaniline (0.15 mmol, 1.5 equiv) and MeCN (1 mL) were added. The mixture is then irradiated at room temperature with a 30 W blue LEDs (450 nm-470 nm) until the starting material disappears from the TLC. The reaction mixture was concentrated by vacuum, purified by silica gel chromatography, and eluted by ethyl acetate/petroleum ether mixture to obtain N-(benzo[d]thiazol-2-ylmethyl)-N-methylaniline products.

3、 Investigation of the Key Reaction Parameters:

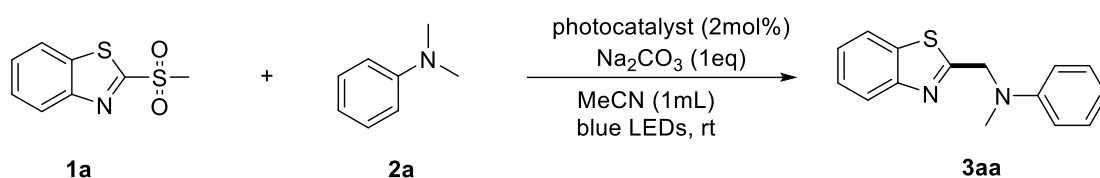
3-1、 controlled experiment:^[a]



Entry	light source	PC	Base	solvent	Time	Yield(%) ^[b]
1	Blue LEDs	4CzIPN	Na ₂ CO ₃	MeCN	18	71
2	-----	4CzIPN	Na ₂ CO ₃	MeCN	48	N.R. ^[c]
3	Blue LEDs	-----	Na ₂ CO ₃	MeCN	18	33
4	60°C	-----	Na ₂ CO ₃	MeCN	48	N.R. ^[c]
5	Blue LEDs	4CzIPN	-----	MeCN	18	46
6	Blue LEDs	-----	-----	MeCN	48	Trace ^[d]

^[a]General conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), base (0.1 mmol), photocatalyst (2 mol %) in MeCN (1 mL) was irradiated with 30 W blue LEDs at room temperature under argon. ^[b]Isolated yields are provided. ^[c]N.R.= no reaction. ^[d] trace=Raw material is declining but no product is being monitored.

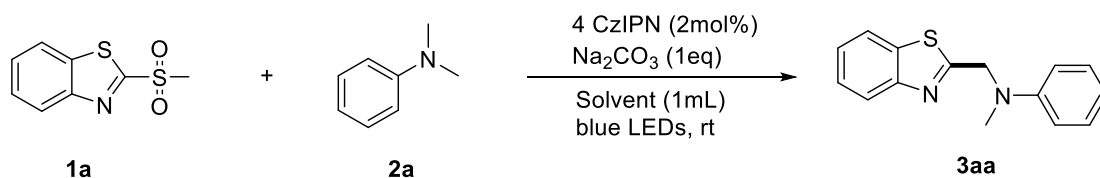
3-2、 Screening for photosensitizers: ^[a]



Entry	PC(%)	Base	solvent	Time	Yield(%) ^[b]
1	4CzIPN	Na ₂ CO ₃	MeCN	18	71
2	Fac-Ir	Na ₂ CO ₃	MeCN	18	60
3	Ir(dF,CF ₃ , ^t Bu)	Na ₂ CO ₃	MeCN	18	66
4	Ru(bpy) ₃ Cl ₂	Na ₂ CO ₃	MeCN	18	61
5	EoSInY	Na ₂ CO ₃	MeCN	18	58
6	4CzIPN(1mol%)	Na ₂ CO ₃	MeCN	16	54
7	4CzIPN(2mol%)	Na ₂ CO ₃	MeCN	18	71

^[a]General conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), base (0.1 mmol), photocatalyst (2 mol %) in MeCN (1 mL) was irradiated with 30 W blue LEDs at room temperature under argon. ^[b]Isolated yields are provided.

3-3、 Screening of solvent: ^[a]



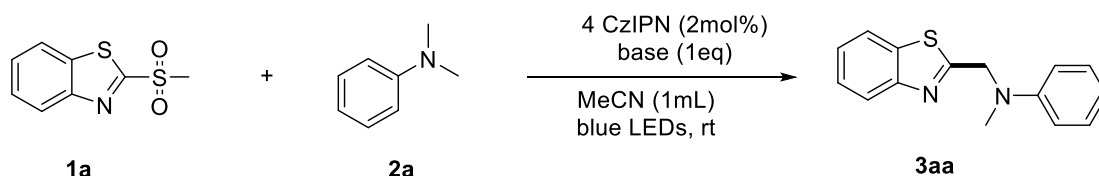
Entry	PC	Base	solvent	Time	Yield(%) ^[b]
1	4CzIPN	Na ₂ CO ₃	MeCN	16	71
2	4CzIPN	Na ₂ CO ₃	DCM	18	55
3	4CzIPN	Na ₂ CO ₃	DCE	18	52
4	4CzIPN	Na ₂ CO ₃	Tol.	18	Trace ^[d]
5	4CzIPN	Na ₂ CO ₃	THF	18	42

6	4CzIPN	Na ₂ CO ₃	1,4-dioxane	18	48
7	4CzIPN	Na ₂ CO ₃	DMF	18	36

^[a]General conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), base (0.1 mmol), photocatalyst (2 mol %) in solvent (1 mL) was irradiated with 30 W blue LEDs at room temperature under argon.

^[b]Isolated yields are provided. ^[d] trace=Raw material is declining but no product is being monitored.

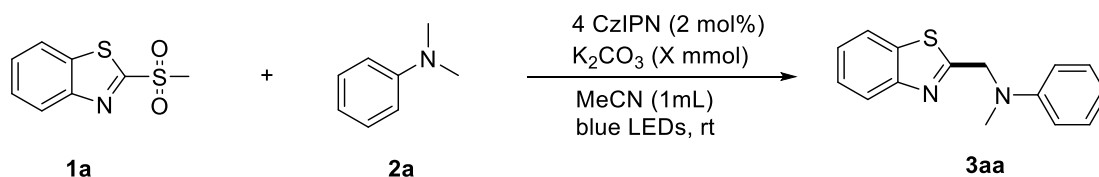
3-4、 Screening of base: ^[a]



Entry	PC	Base	solvent	Time	Yield(%) ^[b]
1	4CzIPN	Na ₂ CO ₃	MeCN	16	71
2	4CzIPN	NaHCO ₃	MeCN	19	77
3	4CzIPN	K ₂ CO ₃	MeCN	20	82
4	4CzIPN	KHCO ₃	MeCN	18	80
5	4CzIPN	Li ₂ CO ₃	MeCN	25	63
6	4CzIPN	Cs ₂ CO ₃	MeCN	21	40
7	4CzIPN	DBU	MeCN	25	53
8	4CzIPN	2,6-lutidine	MeCN	16	35

^[a]General conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), base (0.1 mmol), photocatalyst (2 mol %) in MeCN (1 mL) was irradiated with 30 W blue LEDs at room temperature under argon. ^[b]Isolated yields are provided.

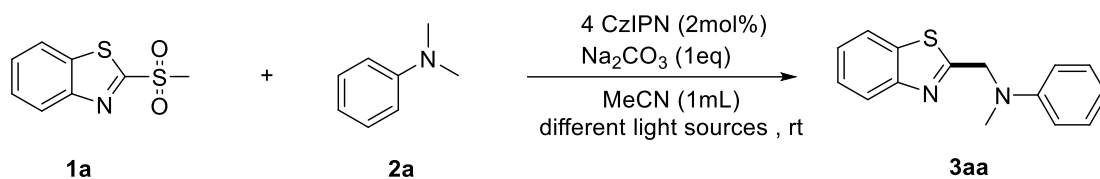
3-5、 screening of amount of base: ^[a]



Entry	PC	Base	eq	solvent	Time	Yield(%) ^[b]
1	4CzIPN	K ₂ CO ₃	0.5	MeCN	19	35
2	4CzIPN	K ₂ CO ₃	1	MeCN	19	82
3	4CzIPN	K ₂ CO ₃	1.2	MeCN	19	85
4	4CzIPN	K ₂ CO ₃	1.5	MeCN	19	82
5	4CzIPN	K ₂ CO ₃	2.0	MeCN	24	36

^[a]General conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), K₂CO₃ (X mmol), photocatalyst (2 mol %) in MeCN (1 mL) was irradiated with 30 W blue LEDs at room temperature under argon. ^[b]Isolated yields are provided.

3-6、 Light source screening:



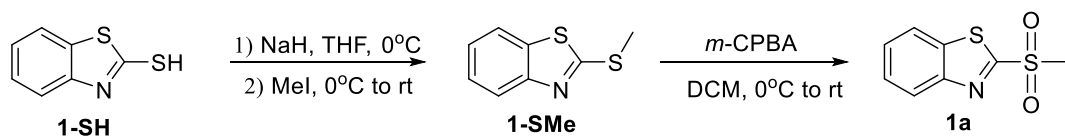
Entry	light source	PC	Base	solvent	Time(h)	Yield(%) ^[b]
1	Blue LED (450nm)	4CzIPN	K ₂ CO ₃	MeCN	18	85
2	Purple LED (365nm)	4CzIPN	K ₂ CO ₃	MeCN	23	52
3	Purple LED (383nm)	4CzIPN	K ₂ CO ₃	MeCN	12	53
4	Green LED (515nm)	4CzIPN	K ₂ CO ₃	MeCN	24	Trace ^[d]

^[a]General conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), K₂CO₃ (0.12 mmol), photocatalyst (2 mol %) in MeCN (1 mL) was irradiated with different light sources at room temperature under argon.

^[b]Isolated yields are provided. ^[d] trace=Raw material is declining but no product is being monitored.

4、 General procedure for synthesis of substrates:

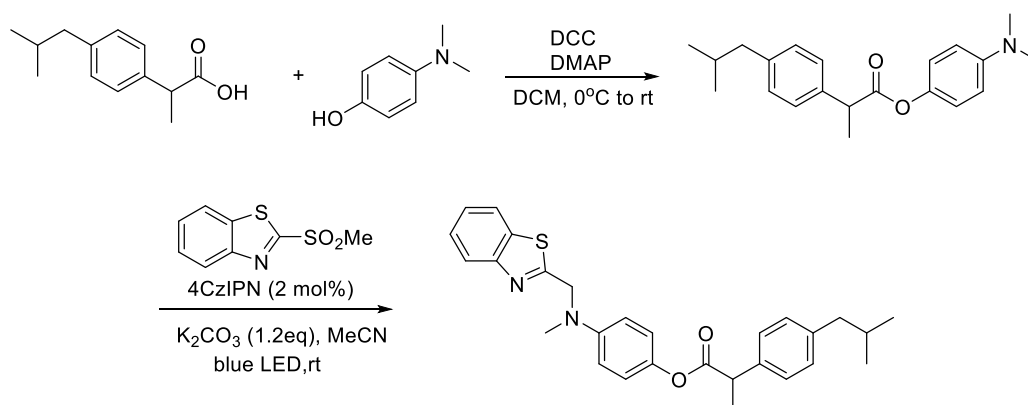
Preparation of 2-(Methylsulfonyl)benzothiazoles^[1-3]:



According to the reported literature,^[1,2] under N₂ atmosphere, a solution of **1-SH** (18.9 mmol) in THF (60 mL) was cooled to 0 °C and NaH (0.811 g, 20.2 mmol) was added within 10 min. The resulting solution was stirred at 0 °C for 30 min, then methyl iodide (1.6 mL, 26.5 mmol) was added dropwise. The formed mixture was stirred at room temperature for overnight. Saturated aqueous NH₄Cl (30 mL) was added and resulting layers were separated. The aqueous layer was extracted with EtOAc (3 x 50 mL) and the combined organic layers were washed with brine (50 mL), dried over Na₂SO₄, filtered and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography (PE) yielding the desired sulfide (**1-SMe**). Then, to a 100 mL glass tube, sulfide (**1-SMe**) (10 mmol), *m*-CPBA (9.221 g, 15 mmol), DCM (50 mL) were added and the mixture was stirred at 0 °C to room temperature for 12 h. The mixture was then cooled to room temperature and extracted by ethyl acetate (100 mL × 4). The combined organic phase was washed

successively with saturated NaHCO₃ solution and NaCl solution, and then dried over anhydrous Na₂SO₄. After the solution was filtered and the solvent was evaporated under vacuum, the residue was subjected to silica gel column chromatography using a mixture of ethyl acetate and petroleum ether (1:5, v/v) as eluent to give the desired product.

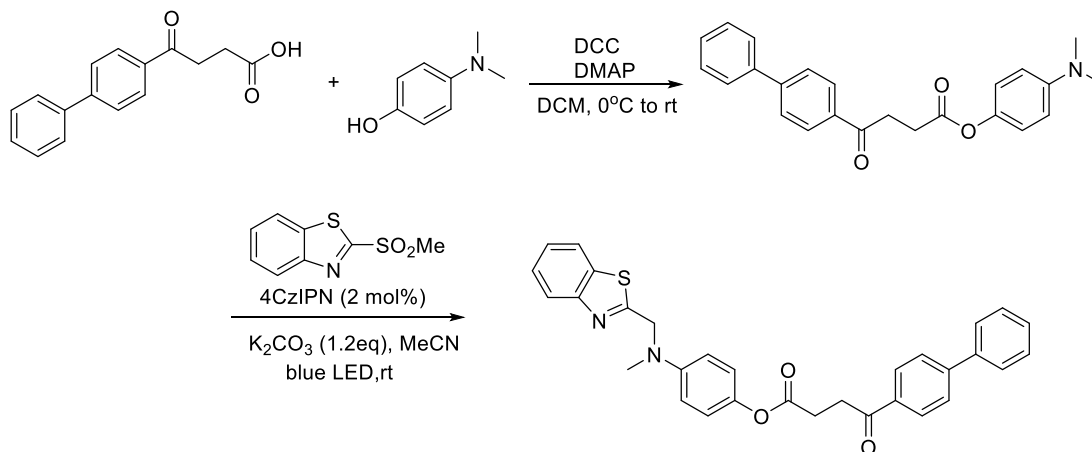
5、 Synthesis of drug Substrate:



Aldehyde **4a** was synthesized according to literature report.^[4] 4-(dimethylamino)phenol (5.0 mmol, 0.7 g) and ibuprofen (5.0 mmol, 1.03 g) and dry DCM (50 mL) were added sequentially to a dry round-bottom flask at room temperature. The reaction was cooled to 0 °C and a catalytic amount of 4-dimethylaminopyridine (DMAP, 0.75 mmol, 0.15 equiv.) and dicyclohexylcarbodiimide (DCC, 7.5 mmol, 1.5 equiv.) were added. The natural return to room temperature and further stirred for 8 hours. Upon completion, the product extracted with DCM (3 × 20 mL). The combined organic phases was washed with brine (20 mL), dried with Na₂SO₄, then filtered and concentrated in vacuo. The crude product was purified by flash column chromatography. The residue was purified by chromatography (PE: EA = 20: 1 v/v) to give **4a** with 72% yield.

Under argon, to an oven dried Schlenk-tube, **4a** (48.8 mg, 0.15 mmol, 1.5 equiv.), 2-(methylsulfonyl)benzo[d]thiazole (21.3 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (1.6 mg, 0.02 mmol), K₂CO₃ (16.6 mg, 0.12 mmol) and MeCN (1 mL) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W blue LED (450 nm) at room temperature. After completion of the reaction, the solvent was

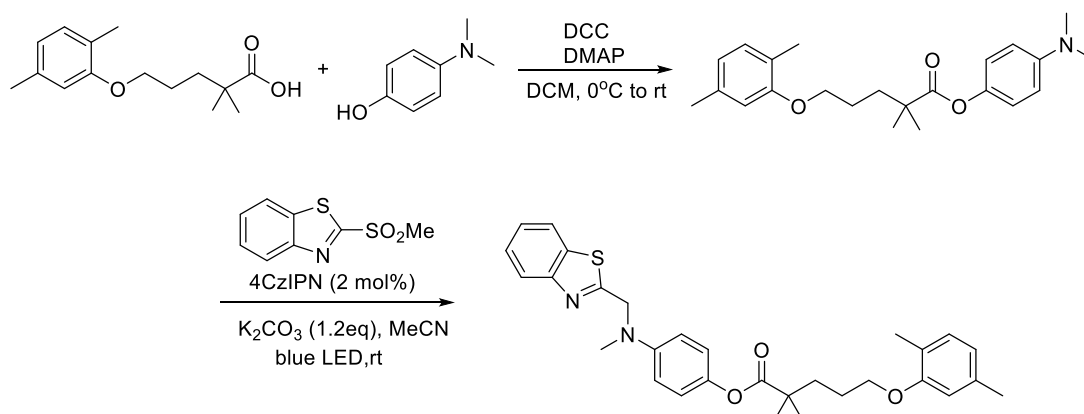
evaporated under vacuum and the residue was purified by flash chromatography eluting with PE: EA (15:1 v/v) on a silica gel to afford the **4aa** as a yellow oil in 90% yield.



Aldehyde **4b** was synthesized according to literature report.^[4] 4-(dimethylamino)phenol (5.0 mmol, 0.7 g) and Fenbufen (5.0 mmol, 1.27 g) and dry DCM (50 mL) were added sequentially to a dry round-bottom flask at room temperature. The reaction was cooled to 0 °C and a catalytic amount of 4-dimethylaminopyridine (DMAP, 0.75 mmol, 0.15 equiv.) and dicyclohexylcarbodiimide (DCC, 7.5 mmol, 1.5 equiv.) were added. The natural return to room temperature and further stirred for 8 hours. Upon completion, the product extracted with DCM (3 × 20 mL). The combined organic phases was washed with brine (20 mL), dried with Na₂SO₄, then filtered and concentrated in vacuo. The crude product was purified by flash column chromatography. The residue was purified by chromatography (PE: EA = 5: 1 v/v) to give **4a** with 77% yield.

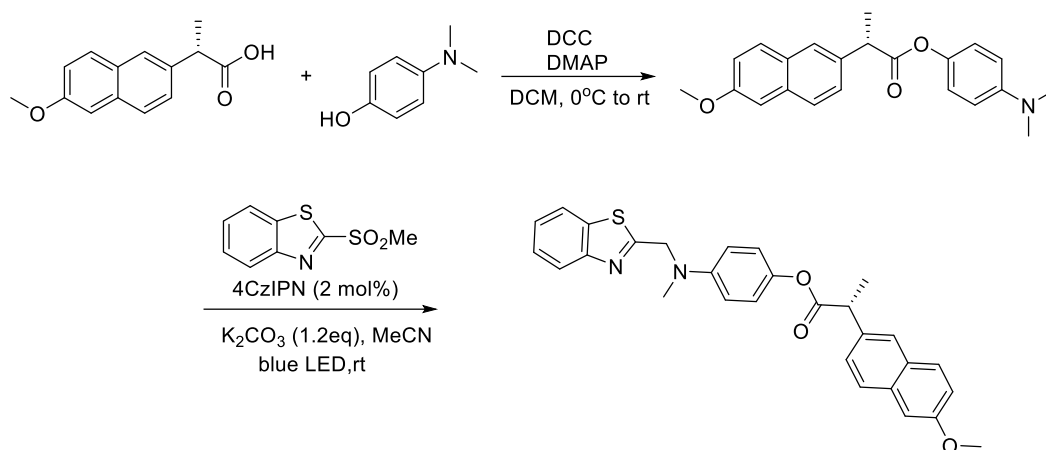
Under argon, to an oven dried Schlenk-tube, **4a** (56.0 mg, 0.15 mmol, 1.5 equiv.), 2-(methylsulfonyl)benzo[d]thiazole (21.3 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (1.6 mg, 0.02 mmol), K₂CO₃ (16.6 mg, 0.12 mmol) and MeCN (1 mL) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W blue LED (450 nm) at room temperature. After completion of the reaction, the solvent was evaporated under vacuum and the residue was purified by flash chromatography eluting with PE: EA (5:1 v/v) on a silica gel to afford the **4ab** as a white solid in 52%

yield.



Aldehyde **4c** was synthesized according to literature report.^[4] 4-(dimethylamino)phenol (5.0 mmol, 0.7 g) and gefilozil (5.0 mmol, 1.25 g) and dry DCM (50 mL) were added sequentially to a dry round-bottom flask at room temperature. The reaction was cooled to 0 °C and a catalytic amount of 4-dimethylaminopyridine (DMAP, 0.75 mmol, 0.15 equiv.) and dicyclohexylcarbodiimide (DCC, 7.5 mmol, 1.5 equiv.) were added. The natural return to room temperature and further stirred for 8 hours. Upon completion, the product extracted with DCM (3 × 20 mL). The combined organic phases was washed with brine (20 mL), dried with Na₂SO₄, then filtered and concentrated in vacuo. The crude product was purified by flash column chromatography. The residue was purified by chromatography (PE: EA = 10: 1 v/v) to give **4c** with 50% yield.

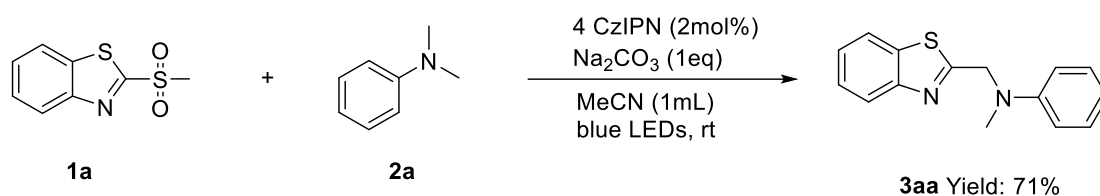
Under argon, to an oven dried Schlenk-tube, **4c** (55.4 mg, 0.15 mmol, 1.5 equiv.), 2-(methylsulfonyl)benzo[d]thiazole (21.3 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (1.6 mg, 0.02 mmol), K₂CO₃ (16.6 mg, 0.12 mmol) and MeCN (1 mL) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W blue LED (450 nm) at room temperature. After completion of the reaction, the solvent was evaporated under vacuum and the residue was purified by flash chromatography eluting with PE: EA (15:1 v/v) on a silica gel to afford the **4ac** as a yellow oil in 81% yield.



Aldehyde **4d** was synthesized according to literature report.^[4] 4-(dimethylamino)phenol (5.0 mmol, 0.7 g) and naproxen (5.0 mmol, 1.15 g) and dry DCM (50 mL) were added sequentially to a dry round-bottom flask at room temperature. The reaction was cooled to 0 °C and a catalytic amount of 4-dimethylaminopyridine (DMAP, 0.75 mmol, 0.15 equiv.) and dicyclohexylcarbodiimide (DCC, 7.5 mmol, 1.5 equiv.) were added. The natural return to room temperature and further stirred for 8 hours. Upon completion, the product extracted with DCM (3 × 20 mL). The combined organic phases was washed with brine (20 mL), dried with Na₂SO₄, then filtered and concentrated in vacuo. The crude product was purified by flash column chromatography. The residue was purified by chromatography (PE: EA = 5: 1 v/v) to give **4d** with 78% yield.

Under argon, to an oven dried Schlenk-tube, **4d** (52.4 mg, 0.15 mmol, 1.5 equiv.), 2-(methylsulfonyl)benzo[d]thiazole (21.3 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (1.6 mg, 0.02 mmol), K₂CO₃ (16.6 mg, 0.12 mmol) and MeCN (1 mL) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W blue LED (450 nm) at room temperature. After completion of the reaction, the solvent was evaporated under vacuum and the residue was purified by flash chromatography eluting with PE: EA (3:1 v/v) on a silica gel to afford the **4ad** as a white solid in 72% yield.

6、Gram-scale reaction:



Based on the reaction system established above, in order to further prove the feasibility and practicability of this reaction system, we conducted a gram experiment on this reaction. 2-(methylsulfonyl)benzo[*d*]thiazole **1a** (1.1 g, 5 mmol, 1 equiv), *N,N*-dimethylaniline **2a** (0.9 g, 7.5 mmol, 1.5 equiv), 4CZIPN (0.08 g, 2 mol%), K₂CO₃ (0.8 g, 6 mmol, 1.2 equiv), MeCN (30 mL) were added to a 100 mL round-bottomed flask. After that, the reaction bottle was stirred under a 30 W blue light and cooled by a fan to ensure a constant reaction temperature. TLC was used to monitor the reaction process, and then the reaction liquid was concentrated by vacuum and the reaction products were purified by silica gel column. *N*-(benzo[*d*]thiazol-2-ylmethyl)-*N*-methylaniline (0.92 g, 72% yield) was obtained.

7、Mechanistic studies:

7-1、Free radical trapping experiment:

In Ar or N₂ atmosphere, a magnetic stirring rod was installed on the oven-dried Schlenk tube. 4CZIPN photosensitizer (0.002 mmol, 0.02 equiv), K₂CO₃ (0.12 mmol, 1.2 equiv), 2-(methylsulfonyl)benzo[*d*]thiazole (0.1 mmol, 1.0 equiv), *N,N*-dimethylaniline (0.15 mmol, 1.5 equiv), TEMPO (0.2 mmol, 2 equiv) or 1,1-diphenylethylene (0.2 mmol, 2 equiv) and MeCN (1 mL) were added. The mixture was then irradiated at room temperature with a 30 W blue LED (450 nm) until the starting material disappears from the TLC. In this process, TEMPO acts as a free radical trapping agent and completely inhibits the production of the target product **3aa**. The molecular weight of benzoyl radical products captured by 1, 1-stilbene was detected by GC-MS temperament instrument.

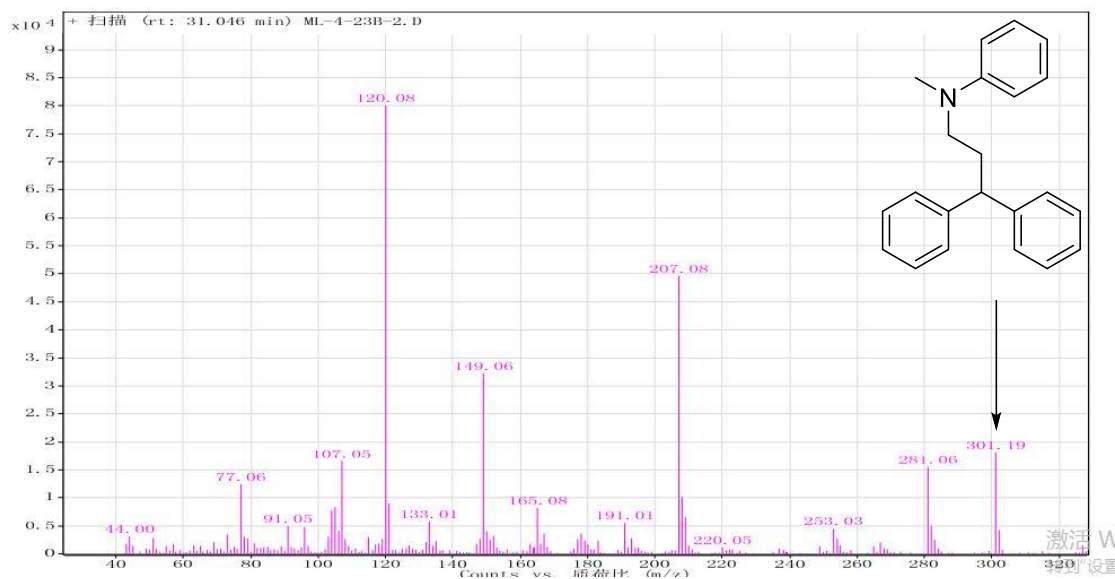
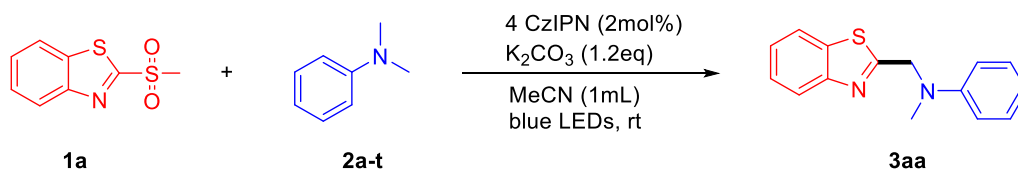


Figure 1. Free radical trapping experiment

7-2、Light/Dark experiment:



An acetonitrile (1mL) sample containing K_2CO_3 and 4CzIPN was added to an oven drying reaction tube fitted with a magnetic stirring rod, followed by 2-methylsulfonylbenzothiazole **1a** (0.1 mmol), N, N-dimethylaniline (0.15 mmol). Stir the reaction mixture under room temperature irradiation of a 30 W LED. The reaction tube was wrapped with tin foil and 20 μ L reaction mixture sample was taken by syringe for gas chromatographic determination. After stirring in the dark for 3 hours, a sample of 20 μ L reaction mixture was taken with a syringe and determined by gas chromatography. The reaction mixture is then illuminated with a 30 W blue LED lamp and stirred for 3 hours. This process was repeated five times.

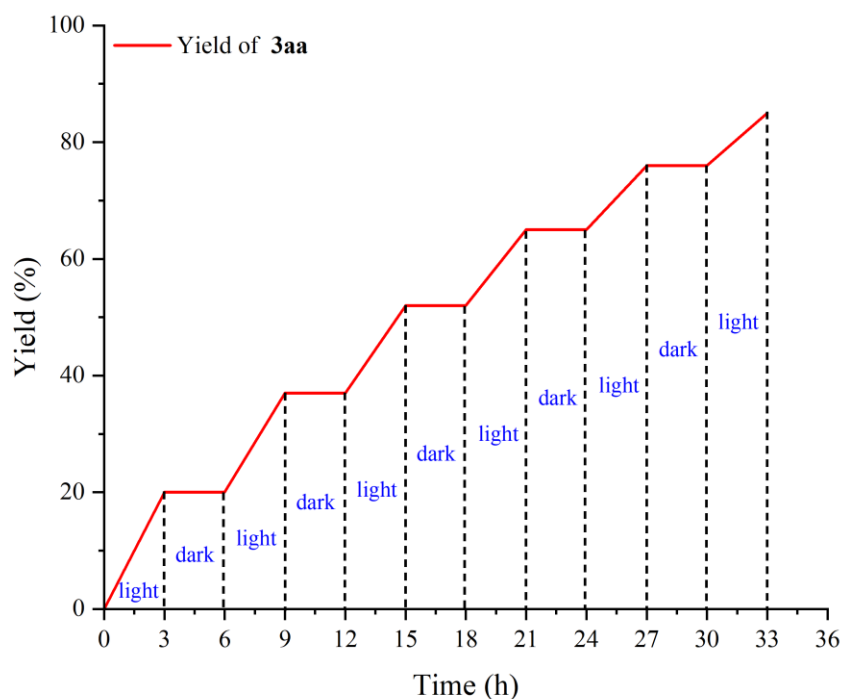


Figure 2. Light on-off experiments.

7-3、Stern-Volmer quenching experiments

Formulation solution: 2-methylsulfonyl benzothiazole (**1a**, 10.7 mg) was dissolved in MeCN in a 5 mL volumetric flask to set the concentration to be 0.1 M. N, N-dimethylaniline (**2a**, 13.6 mg) was dissolved in MeCN in a 5 mL volumetric flask to set the concentration to be 0.15 M. K_2CO_3 (10.0 mg) was dissolved in MeCN in a 5 mL volumetric flask to set the concentration to be 0.12 M. Photocatalyst 4CzIPN (3.9 mg) was dissolved in MeCN (25.0 mL) to set the concentration to be 0.2 mM.

Experimental procedure: The resulting 0.2 mM solution of 4CzIPN in MeCN (100 μ L) was added to cuvette to obtain different concentrations of catalyst solution. This solution was then diluted to a volume of 2.0 mL by adding MeCN to prepare a 10 μ M solution. The resulting mixture was sparged with argon for 3 minutes and then irradiated at 420 nm. Fluorescence emission spectra were recorded (3 trials per sample). Into this solution, 50.0 μ L of a 2-methylsulfonyl benzothiazole solution was

successively added and uniformly stirred, and the resulting mixture was bubbled with argon for 3 minutes and irradiated at 420 nm. Fluorescence emission spectra of 0 μL , 50.0 μL , 100.0 μL , 150.0 μL , 200.0 μL fluorescence intensity. Follow this method and make changes to the amount to obtain the Stern–Volmer relationship in turn. The results were shown in the following figures.

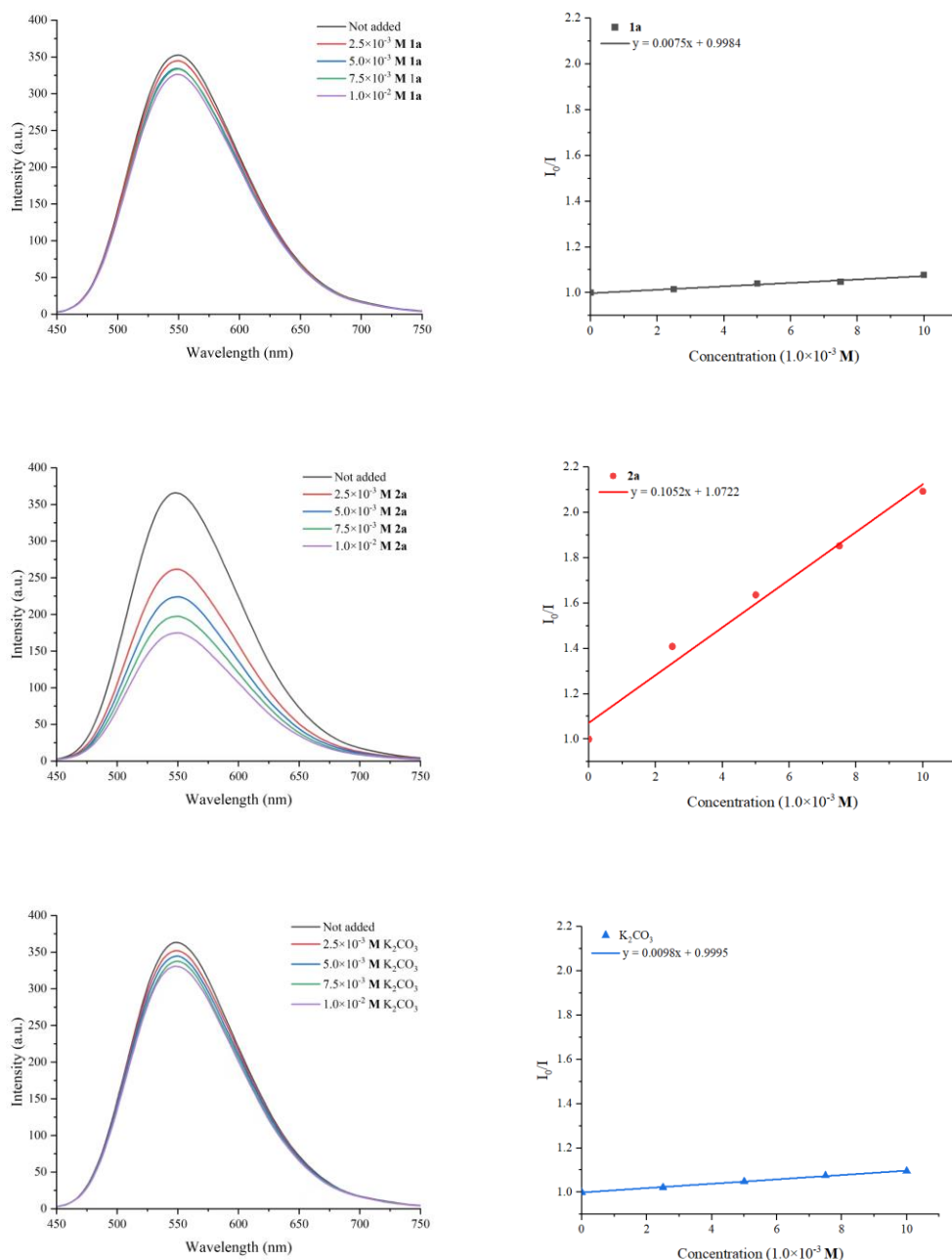


Figure 3. Fluorescence quenching experiment

7-4、 Measurement of Quantum Yields:

The photon flux of blue LED was determined by standard ferrioxalate actinometry.

0.15 mol/L solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (328 mg, 0.750 mmol) in 5.0 mL of 0.20 mol/L aqueous sulfuric acid. 0.15 mol/L buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (54.1 mg, 0.3 mmol) and sodium acetate (1.23 g, 15.0 mmol) in 20 mL of 0.20 mol/L aqueous sulfuric acid. The actinometry measurements were done as follows: To a reaction tube equipped with a stir bar was added 0.50 mL of the ferrioxalate solution. The reaction tube was sealed and placed 2 cm away from a 20 W blue LEDs. After irradiation for 5 seconds, 1.5 mL of the aqueous sulfuric acid and 2.0 mL of the buffered solution was added to the reaction tube. The solution was then allowed to rest for 1 hour to allow the resultant ferrous ions to react completely with 1,10-phenanthroline. 50 μ L of the resulting solution was taken as an aliquot and diluted with 3.0 mL of 0.20 mol/L aqueous sulfuric acid. The absorbance of the resulting solution in a cuvette ($l = 1.0$ cm) at 510 nm was measured by UV-V is spectrometer. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured.

$$\text{mol Fe}^{2+} = \frac{V \times \Delta A}{l \times \varepsilon}$$

The amount of ferrous ion formed was calculated as follows:

where V is the total volume (0.024 L) of the solution that was analyzed, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated samples, l is the path length (1.00 cm), and ε is the molar absorptivity at 510 nm (11,100 L/(mol•cm)).

The photon flux was calculated as follows:

$$\text{photo flux} = \frac{\text{mol Fe}^{2+}}{\Phi \times t \times f}$$

where Φ is the quantum yield for the ferrioxalate actinometer (approximated as

0.845, which was reported for a 0.15 mol/L solution at $\lambda = 457.9$ nm), t is the irradiation time, and f is the fraction of light absorbed at 450 nm (0.2649).

The fraction of light absorbed was determined by the following equation:

$$f = 1.0000 - 10^{-A}$$

where A is the measured absorbance (0.1337) of the 0.15 mol/L solution of potassium ferrioxalate at 450 nm.

The photo flux is 3.35×10^{-7} Einstein/s.

Determination of quantum yield:

In an oven-dried reaction tube containing a magnetic stirring bar was charged with a sample of 2-(methylsulfonyl)benzo[*d*]thiazole **1a** (0.10 mmol), *N,N*-dimethylaniline **2a** (0.15 mmol), 4CzIPN (2 mol%), K_2CO_3 (0.15 mmol), MeCN (1mL). The reaction mixture was stirred under the irradiation of 30 W LED at room temperature and placed 2 cm away from 30 W blue LEDs. After irradiation for 4 hours, the moles of product **3aa** formed for the model reaction were determined by determined by 1H NMR spectroscopy with (1,3-Benzodioxole) as the internal standard revealed 35% yield of **3aa** (3.5×10^{-5} mol).

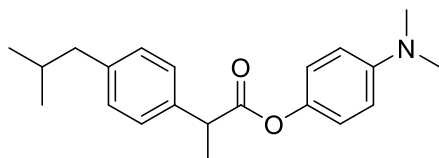
The quantum yield was calculated as follows:

$$\Phi = \frac{\text{mol product}}{\text{flux} \times t \times f}$$

where flux is the photon flux determined by ferrioxalate actinometry (3.35×10^{-7} Einstein/s), t is the time, and f is the fraction of light absorbed by the irradiated reaction system at 450 nm, and the absorbance of the irradiated reaction system at 450 nm was 0.1629. The fraction of light absorbed at 450 nm was calculated: $f = 1.0000 - 10^{-A} = 1.0000 - 10^{-0.041} = 0.3128$.

The quantum yield was calculated: $\Phi = 0.03$

8、¹H NMR and ¹³C NMR spectra data of products.

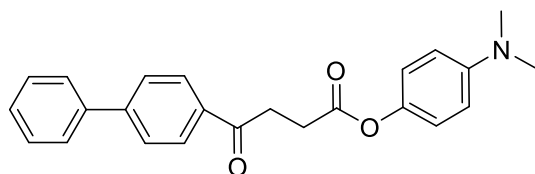


4-((benzo[d]thiazol-2-ylmethyl)(methyl)amino)phenyl-2-(4-isobutylphenyl)propanoate (4a)

77% yield, yellow oil, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.28 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.13 – 7.05 (m, 2H), 6.89 – 6.80 (m, 2H), 6.63 – 6.55 (m, 2H), 3.87 (q, *J* = 7.1 Hz, 1H), 2.80 (s, 6H), 2.44 (d, *J* = 7.3 Hz, 2H), 1.84 (dd, *J* = 7.3, 5.6 Hz, 1H), 1.58 – 1.52 (m, 3H), 0.92 – 0.83 (m, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 173.5, 148.4, 141.7, 140.4, 137.5, 129.3, 127.1, 121.5, 112.8, 45.1, 44.9, 40.6, 30.1, 22.3, 18.6.

HRMS-ESI⁺ (*m/z*) calcd for C₂₁H₂₈NO₂⁺ [M+H]⁺ 326.2115, found 326.2112.



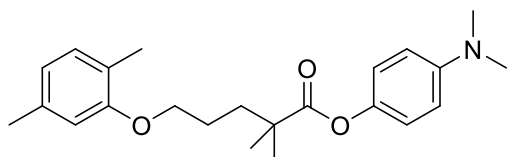
4-((benzo[d]thiazol-2-ylmethyl)(methyl)amino)phenyl-4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate (4b)

72% yield, white solid, ¹H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 8.01 (m, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.65 – 7.58 (m, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.02 – 6.94 (m, 2H), 6.72 – 6.64 (m, 2H), 3.42 (t, *J* = 6.6 Hz, 2H), 2.99 (t, *J* = 6.6 Hz, 2H), 2.90 (s, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 197.7, 172.3, 148.8, 145.9, 141.7, 139.9, 135.3, 129.1, 128.8, 128.4, 127.3, 127.3, 121.9, 113.2, 41.0, 33.6, 28.6.

MP: 120°C

HRMS-ESI⁺ (*m/z*) calcd for C₂₄H₂₄NO₃⁺ [M+H]⁺ 374.1751, found 374.1744.



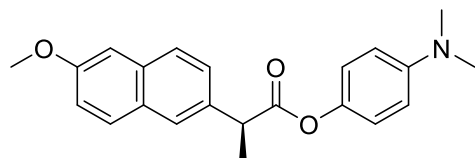
4-((benzo[d]thiazol-2-ylmethyl)(methyl)amino)phenyl-5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (4c)

50% yield, yellow oil, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.11 (d, *J* = 4.5 Hz, 1H), 7.06 – 6.98 (m, 2H), 6.83 – 6.71 (m, 4H), 4.08 (s, 2H), 3.01 (dd, *J* = 3.4, 1.6 Hz, 6H), 2.43 (dd,

$J = 5.6, 2.8$ Hz, 3H), 2.32 (dd, $J = 6.5, 3.3$ Hz, 3H), 1.98 (dd, $J = 5.3, 2.7$ Hz, 4H), 1.48 (dd, $J = 5.7, 2.9$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.9, 157.0, 148.6, 141.9, 136.4, 130.7, 123.6, 121.8, 120.7, 113.4, 111.9, 67.8, 42.3, 41.0, 37.2, 25.3, 25.2, 21.5, 15.9.

HRMS-ESI⁺ (m/z) calcd for $\text{C}_{23}\text{H}_{32}\text{NO}_3^+$ $[\text{M}+\text{H}]^+$ 370.2377, found 370.2373.



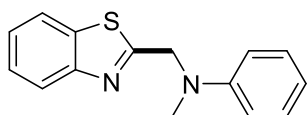
4-((benzo[*d*]thiazol-2-ylmethyl)(methyl)amino)phenyl-(*S*)-2-(6-methoxynaphthalen-2-yl)propanoate(4d)

78% yield, white solid, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.75 (m, 3H), 7.56 (dt, $J = 8.5, 1.7$ Hz, 1H), 7.25 – 7.15 (m, 2H), 6.92 (dq, $J = 7.9, 3.7, 2.8$ Hz, 2H), 6.73 – 6.64 (m, 2H), 4.17 – 4.07 (m, 1H), 3.94 (s, 3H), 2.91 (s, 6H), 1.73 (dd, $J = 7.2, 1.3$ Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.9, 157.8, 148.7, 141.8, 135.6, 133.9, 129.4, 129.1, 127.4, 126.3, 126.2, 121.7, 119.1, 113.1, 105.7, 55.4, 45.6, 41.0, 18.8.

MP: 123°C

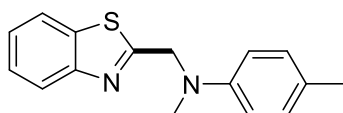
HRMS-ESI⁺ (m/z) calcd for $\text{C}_{22}\text{H}_{24}\text{NO}_3^+$ $[\text{M}+\text{H}]^+$ 350.1751, found 350.1741.



N-(benzo[*d*]thiazol-2-ylmethyl)-*N*-methylaniline (3aa)^[5]

21.6 mg, 85% yield, light yellow oil, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, $J = 8.1$ Hz, 1H), 7.77 (dt, $J = 8.0, 1.0$ Hz, 1H), 7.45 (ddd, $J = 8.3, 7.2, 1.3$ Hz, 1H), 7.32 (ddd, $J = 8.2, 7.2, 1.2$ Hz, 1H), 7.24 (ddt, $J = 9.1, 7.4, 0.9$ Hz, 2H), 6.86 – 6.75 (m, 3H), 4.85 (s, 2H), 3.12 (s, 3H).

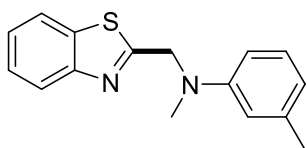
^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.0, 153.8, 149.0, 135.2, 129.5, 126.1, 125.0, 122.9, 121.9, 118.3, 113.3, 56.4, 39.5.



N-(benzo[*d*]thiazol-2-ylmethyl)-*N*,4-dimethylaniline (3ab)^[5]

23.3 mg, 87% yield, light yellow oil, ^1H NMR (400 MHz, Chloroform-*d*) δ 8.00 (dt, $J = 8.2, 0.9$ Hz, 1H), 7.81 (dt, $J = 7.9, 1.0$ Hz, 1H), 7.47 (ddd, $J = 8.3, 7.2, 1.3$ Hz, 1H), 7.35 (ddd, $J = 8.3, 7.2, 1.2$ Hz, 1H), 7.14 – 7.04 (m, 2H), 6.82 – 6.74 (m, 2H), 4.85 (s, 2H), 3.12 (s, 3H), 2.27 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.6, 153.8, 146.9, 135.2, 130.0, 127.6, 126.1, 125.0, 122.8, 122.0, 113.6, 56.8, 39.8, 20.5.

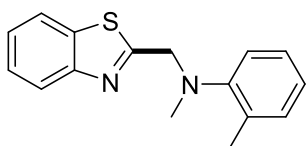


***N*-(benzo[*d*]thiazol-2-ylmethyl)-*N*,3-dimethylaniline (3ac)**

19.6 mg, 73% yield, light yellow oil, ^1H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.99 (m, 1H), 7.82 (dd, $J = 7.9, 1.3$ Hz, 1H), 7.49 (ddd, $J = 8.3, 7.2, 1.3$ Hz, 1H), 7.37 (td, $J = 7.6, 1.2$ Hz, 1H), 7.17 (td, $J = 7.4, 1.5$ Hz, 1H), 6.72 – 6.63 (m, 3H), 4.88 (s, 2H), 3.15 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.4, 153.8, 149.0, 139.2, 135.2, 129.3, 126.1, 125.0, 122.8, 121.9, 119.2, 114.0, 110.4, 56.5, 39.5, 22.1.

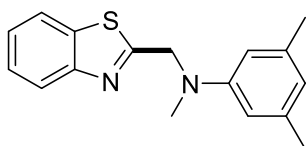
HRMS-ESI⁺ (m/z) calcd for $\text{C}_{16}\text{H}_{17}\text{N}_2\text{S}^+$ [$\text{M}+\text{H}$]⁺ 269.1107, found 269.1116.



***N*-(benzo[*d*]thiazol-2-ylmethyl)-*N*,2-dimethylaniline (3ad) ^[5]**

23.9 mg, 89% yield, light yellow oil, ^1H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.94 (m, 1H), 7.86 (dt, $J = 7.9, 0.9$ Hz, 1H), 7.45 (ddd, $J = 8.3, 7.3, 1.3$ Hz, 1H), 7.36 (ddd, $J = 8.3, 7.2, 1.2$ Hz, 1H), 7.27 – 7.20 (m, 1H), 7.21 – 7.12 (m, 2H), 7.03 (td, $J = 7.1, 1.8$ Hz, 1H), 4.50 (s, 2H), 2.78 (s, 3H), 2.48 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.4, 153.3, 151.3, 135.5, 133.4, 131.5, 126.9, 126.0, 125.1, 124.3, 122.9, 122.0, 120.4, 59.1, 42.8, 18.6.

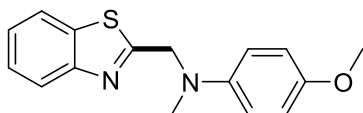


***N*-(benzo[*d*]thiazol-2-ylmethyl)-*N*,3,5-trimethylaniline (3ae)**

21.5 mg, 76% yield, light yellow oil, ^1H NMR (400 MHz, Chloroform-*d*) δ 8.02 (dt, $J = 8.2, 0.8$ Hz, 1H), 7.86 – 7.79 (m, 1H), 7.49 (ddd, $J = 8.3, 7.2, 1.3$ Hz, 1H), 7.37 (ddd, $J = 8.3, 7.2, 1.2$ Hz, 1H), 6.51 (s, 3H), 4.87 (s, 2H), 3.13 (s, 3H), 2.30 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.71, 153.9, 149.2, 139.1, 135.2, 126.1, 125.0, 122.8, 122.0, 120.4, 111.2, 56.5, 39.5, 21.9.

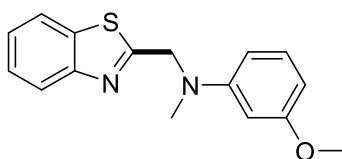
HRMS-ESI⁺ (m/z) calcd for $\text{C}_{17}\text{H}_{19}\text{N}_2\text{S}^+$ [$\text{M}+\text{H}$]⁺ 283.1264, found 283.1262.



***N*-(benzo[*d*]thiazol-2-ylmethyl)-4-methoxy-*N*-methylaniline (3af) ^[5]**

21.0 mg, 74% yield, yellow oil, ¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 (dt, *J* = 8.4, 0.9 Hz, 1H), 7.81 (ddd, *J* = 8.0, 1.3, 0.6 Hz, 1H), 7.47 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.35 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 6.89 – 6.77 (m, 4H), 4.79 (s, 2H), 3.76 (s, 3H), 3.07 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 173.5, 153.7, 152.9, 143.7, 135.2, 126.1, 125.0, 122.8, 122.0, 115.4, 114.9, 57.6, 55.8, 40.3.

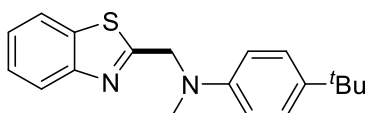


***N*-(benzo[*d*]thiazol-2-ylmethyl)-3-methoxy-*N*-methylaniline (3ag)**

23.0 mg, 81% yield, yellow oil, ¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.81 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.47 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.35 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 7.17 (t, *J* = 8.2 Hz, 1H), 6.46 (ddd, *J* = 8.3, 2.5, 0.8 Hz, 1H), 6.43 – 6.35 (m, 2H), 4.88 (s, 2H), 3.78 (s, 3H), 3.14 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 172.9, 160.9, 153.7, 150.3, 135.2, 130.2, 126.1, 125.1, 122.8, 122.0, 106.2, 102.9, 99.8, 56.3, 55.3, 39.5.

HRMS-ESI⁺ (*m/z*) calcd for C₁₆H₁₇N₂OS⁺ [M+H]⁺ 285.1056, found 285.1054.

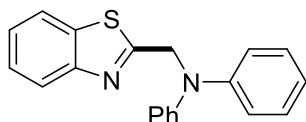


***N*-(benzo[*d*]thiazol-2-ylmethyl)-4-(tert-butyl)-*N*-methylaniline (3ah)**

23.6 mg, 76% yield, light yellow oil, ¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.82 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.48 (d, *J* = 1.1 Hz, 1H), 7.36 (t, *J* = 1.0 Hz, 1H), 7.28 (dd, *J* = 9.6, 7.3 Hz, 2H), 6.85 – 6.77 (m, 2H), 4.84 (s, 2H), 3.13 (s, 3H), 1.29 (s, 9H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 173.9, 153.9, 146.9, 141.1, 135.3, 126.3, 126.1, 125.0, 122.8, 122.0, 113.1, 56.9, 39.77, 34.0, 31.7.

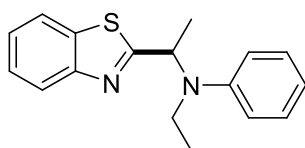
HRMS-ESI⁺ (*m/z*) calcd for C₁₉H₂₃N₂S⁺ [M+H]⁺ 311.1576, found 311.1570.



***N*-(benzo[*d*]thiazol-2-ylmethyl)-*N*-phenylaniline (3ai)**^[5]

13.6 mg, 43% yield, colorless oil, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.99 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.79 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.50 – 7.41 (m, 1H), 7.38 – 7.26 (m, 4H), 7.27 (d, *J* = 2.0 Hz, 1H), 7.18 – 7.10 (m, 4H), 7.01 (tt, *J* = 7.3, 1.1 Hz, 2H), 5.33 (s, 2H).

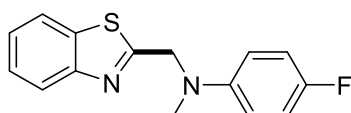
¹³C NMR (101 MHz, Chloroform-*d*) δ 173.3, 153.5, 147.6, 135.2, 129.7, 126.2, 125.2, 122.9, 122.6, 122.0, 121.2, 56.0.



***N*-(1-(benzo[*d*]thiazol-2-yl)ethyl)-*N*-ethylaniline (3aj)**^[6]

17.8 mg, 63% yield, colorless oil, ¹H NMR (400 MHz, Chloroform-*d*) δ 8.01 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.81 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.46 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.35 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.30 – 7.21 (m, 2H), 6.96 – 6.88 (m, 2H), 6.82 (tt, *J* = 7.2, 1.1 Hz, 1H), 5.21 (q, *J* = 6.9 Hz, 1H), 3.36 (ddt, *J* = 31.8, 14.6, 7.2 Hz, 2H), 1.78 (d, *J* = 6.9 Hz, 3H), 1.20 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 177.6, 153.8, 147.8, 135.8, 129.4, 126.0, 125.1, 123.0, 121.9, 119.0, 116.2, 59.6, 41.4, 17.1, 14.1.



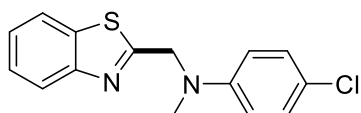
***N*-(benzo[*d*]thiazol-2-ylmethyl)-4-fluoro-*N*-methylaniline (3ak)**

26.1 mg, 96% yield, yellow oil, ¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 (dt, *J* = 8.2, 0.8 Hz, 1H), 7.82 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.47 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.36 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 7.01 – 6.90 (m, 2H), 6.83 – 6.73 (m, 2H), 4.82 (s, 2H), 3.11 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 172.8, 157.6, 155.3, 153.7, 145.7 (d, *J* = 2.0 Hz), 135.2, 126.2, 125.2, 122.9, 122.0, 116.0, 115.8, 114.7 (d, *J* = 7.5 Hz), 57.2, 40.2.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -127.04.

HRMS-ESI⁺ (*m/z*) calcd for C₁₅H₁₄FN₂S⁺ [*M*+*H*]⁺ 273.0856, found 273.0854.

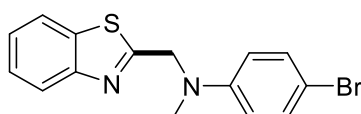


***N*-(benzo[*d*]thiazol-2-ylmethyl)-4-chloro-*N*-methylaniline (3al)**

26.9 mg, 93% yield, yellow oil, ¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.81 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.48 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.36 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.23 – 7.14 (m, 2H), 6.80 – 6.70 (m, 2H), 4.85 (s, 2H), 3.14 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 172.3, 153.7, 147.5, 135.1, 129.3, 126.3, 125.2, 123.2, 122.9, 122.0, 114.3, 56.4, 39.8.

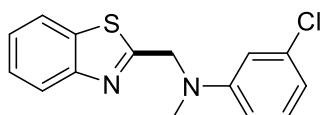
HRMS-ESI⁺ (*m/z*) calcd for C₁₅H₁₄ClN₂S⁺ [M+H]⁺ 289.0561, found 289.0558.



***N*-(benzo[*d*]thiazol-2-ylmethyl)-4-bromo-*N*-methylaniline (3am)**^[5]

27.0 mg, 81% yield, light yellow oil, ¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.81 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.48 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.39 – 7.29 (m, 3H), 6.73 – 6.65 (m, 2H), 4.85 (s, 2H), 3.14 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 172.0, 153.6, 147.7, 134.9, 132.0, 126.1, 125.1, 122.8, 121.9, 114.6, 110.2, 56.1, 39.6.

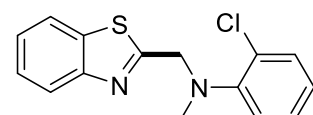


***N*-(benzo[*d*]thiazol-2-ylmethyl)-3-chloro-*N*-methylaniline (3an)**

26.6 mg, 92% yield, yellow oil, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.99 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.80 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.47 (ddd, *J* = 8.3, 7.3, 1.3 Hz, 1H), 7.35 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.19 – 7.00 (m, 1H), 6.83 – 6.62 (m, 3H), 4.86 (s, 2H), 3.13 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 172.0, 153.7, 149.9, 135.4, 135.1, 130.4, 126.3, 125.2, 123.0, 122.0, 118.1, 113.0, 111.2, 56.0, 39.5.

HRMS-ESI⁺ (*m/z*) calcd for C₁₅H₁₄ClN₂S⁺ [M+H]⁺ 289.0561, found 289.0560.

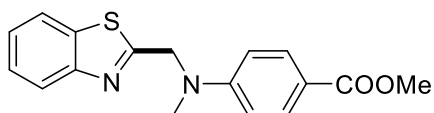


***N*-(benzo[*d*]thiazol-2-ylmethyl)-2-chloro-*N*-methylaniline (3ao)**

19.1 mg, 66% yield, yellow oil, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.99 (dt, $J = 8.1$, 1.0 Hz, 1H), 7.88 (dt, $J = 8.0$, 0.9 Hz, 1H), 7.58 – 7.28 (m, 3H), 7.27 – 7.15 (m, 2H), 7.02 (ddd, $J = 7.9$, 7.2, 1.7 Hz, 1H), 4.63 (s, 2H), 2.89 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.2, 153.1, 148.7, 135.7, 131.0, 129.2, 127.8, 126.0, 125.1, 124.6, 122.9, 122.0, 121.7, 58.7, 41.2.

HRMS-ESI⁺ (m/z) calcd for $\text{C}_{15}\text{H}_{14}\text{ClN}_2\text{S}^+$ [$\text{M}+\text{H}$]⁺ 289.0561, found 289.0558.



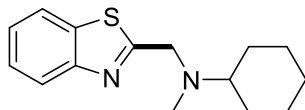
methyl 4-((benzo[*d*]thiazol-2-ylmethyl)(methyl)amino)benzoate (3ap)

18.7 mg, 60% yield, white solid, ^1H NMR (400 MHz, Chloroform-*d*) δ 8.00 (dt, $J = 8.3$, 0.9 Hz, 1H), 7.96 – 7.88 (m, 2H), 7.80 (ddd, $J = 8.0$, 1.2, 0.7 Hz, 1H), 7.48 (ddd, $J = 8.3$, 7.3, 1.3 Hz, 1H), 7.36 (ddd, $J = 8.2$, 7.2, 1.2 Hz, 1H), 6.84 – 6.75 (m, 2H), 4.96 (s, 2H), 3.85 (s, 3H), 3.24 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.1, 167.4, 153.7, 152.0, 135.0, 131.6, 126.4, 125.3, 123.0, 122.0, 119.1, 111.7, 55.6, 39.5.

MP: 108°C

HRMS-ESI⁺ (m/z) calcd for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_2\text{S}^+$ [$\text{M}+\text{H}$]⁺ 313.1005, found 311.1002.

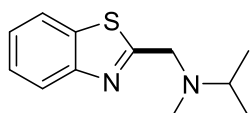


N-(benzo[*d*]thiazol-2-ylmethyl)-N-methylcyclohexanamine (3aq)

22.1 mg, 85% yield, Colorless oil, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, $J = 8.1$ Hz, 1H), 7.86 (dd, $J = 7.9$, 1.5 Hz, 1H), 7.44 (tt, $J = 8.2$, 1.6 Hz, 1H), 7.34 (td, $J = 7.5$, 1.5 Hz, 1H), 4.00 (s, 2H), 2.53 (td, $J = 11.1$, 7.7 Hz, 1H), 2.40 (s, 3H), 1.91 (d, $J = 10.3$ Hz, 2H), 1.85 – 1.77 (m, 2H), 1.63 (dd, $J = 12.3$, 1.7 Hz, 1H), 1.27 (q, $J = 12.2$ Hz, 4H), 1.11 (q, $J = 10.4$, 8.5 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.9, 153.7, 135.6, 125.8, 124.8, 122.8, 121.9, 63.0, 56.0, 38.8, 29.0, 26.4, 26.0.

HRMS-ESI⁺ (m/z) calcd for $\text{C}_{15}\text{H}_{21}\text{N}_2\text{S}^+$ [$\text{M}+\text{H}$]⁺ 261.1420, found 261.1410.

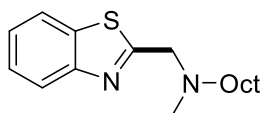


N-(benzo[*d*]thiazol-2-ylmethyl)-N-methylpropan-2-amine (3ar) ^[6]

17.6 mg, 80% yield, yellow oil, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.94 (dd, $J = 8.1$, 1.1 Hz, 1H), 7.86 (dd, $J = 8.1$, 1.2 Hz, 1H), 7.44 (ddd, $J = 8.1$, 7.2, 1.3 Hz, 1H), 7.34 (td, J

= 7.6, 1.2 Hz, 1H), 3.96 (s, 2H), 3.01 (p, $J = 6.6$ Hz, 1H), 2.36 (s, 3H), 1.11 (d, $J = 6.6$ Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.6, 153.7, 135.6, 125.9, 124.8, 122.8, 121.9, 55.7, 54.1, 38.0, 18.2.

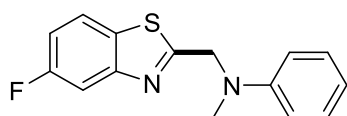


***N*-(benzo[*d*]thiazol-2-ylmethyl)-*N*-methyloctan-1-amine (3as)**

19.2 mg, 66% yield, yellow oil, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.96 (dt, $J = 8.3$, 0.9 Hz, 1H), 7.90 – 7.83 (m, 1H), 7.44 (ddd, $J = 8.3$, 7.2, 1.3 Hz, 1H), 7.35 (ddd, $J = 8.3$, 7.2, 1.2 Hz, 1H), 3.93 (s, 2H), 2.55 – 2.47 (m, 2H), 2.38 (s, 3H), 1.54 (qd, $J = 7.4$, 6.5, 3.7 Hz, 2H), 1.37 – 1.23 (m, 10H), 0.91 – 0.83 (m, 3H).

^{13}C NMR (101 MHz,) δ 173.8, 153.3, 135.5, 125.8, 124.8, 122.7, 121.8, 59.9, 57.9, 42.9, 31.9, 29.6, 29.3, 27.5, 27.3, 22.7, 14.2.

HRMS-ESI⁺ (m/z) calcd for $\text{C}_{17}\text{H}_{27}\text{N}_2\text{S}^+$ [$\text{M}+\text{H}$]⁺ 291.1890, found 291.1881.



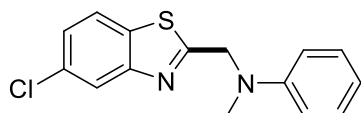
***N*-((5-fluorobenzo[*d*]thiazol-2-yl)methyl)-*N*-methylaniline (3ba)**

20.7 mg, 76% yield, light yellow oil, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.63 (m, 2H), 7.30 – 7.21 (m, 2H), 7.12 (td, $J = 8.8$, 2.5 Hz, 1H), 6.86 – 6.76 (m, 3H), 4.86 (s, 2H), 3.14 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.1, 161.9 (d, $J = 243.2$ Hz), 154.8 (d, $J = 11.8$ Hz), 148.9, 130.6 (d, $J = 2.0$ Hz), 129.5, 122.7 (d, $J = 9.8$ Hz), 118.4, 113.8 (d, $J = 24.9$ Hz), 113.3, 109.1 (d, $J = 23.5$ Hz), 56.6, 39.6.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -116.14.

HRMS-ESI⁺ (m/z) calcd for $\text{C}_{15}\text{H}_{14}\text{FN}_2\text{S}^+$ [$\text{M}+\text{H}$]⁺ 273.0856, found 273.0854.

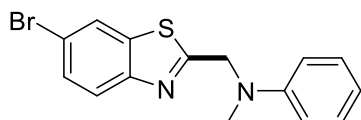


***N*-((5-chlorobenzo[*d*]thiazol-2-yl)methyl)-*N*-methylaniline (3ca)**

20.8 mg, 72% yield, light yellow oil, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, J = 2.0 Hz, 1H), 7.69 (d, J = 8.5 Hz, 1H), 7.32 (dd, J = 8.5, 2.0 Hz, 1H), 7.29 – 7.22 (m, 2H), 6.85 – 6.77 (m, 3H), 4.85 (s, 2H), 3.14 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.53, 154.73, 148.86, 133.48, 132.19, 129.53, 125.58, 122.76, 122.69, 118.48, 113.28, 56.52, 39.64.

HRMS-ESI $^+$ (m/z) calcd for $\text{C}_{15}\text{H}_{14}\text{ClN}_2\text{S}^+$ [M+H] $^+$ 289.0561, found 289.0560.

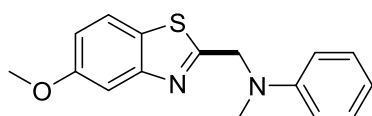


***N*-((6-bromobenzo[*d*]thiazol-2-yl)methyl)-*N*-methylaniline (3da)**

23.7 mg, 71% yield, yellow oil, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, J = 1.9 Hz, 1H), 7.83 (d, J = 8.7 Hz, 1H), 7.56 (dd, J = 8.7, 2.0 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.25 – 7.23 (m, 1H), 6.82 (ddt, J = 9.7, 7.3, 1.1 Hz, 3H), 4.84 (s, 2H), 3.14 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.1, 152.8, 148.9, 136.9, 129.7, 129.5, 124.5, 124.0, 118.7, 118.5, 113.3, 56.5, 39.6.

HRMS-ESI $^+$ (m/z) calcd for $\text{C}_{15}\text{H}_{14}\text{BrN}_2\text{S}^+$ [M+H] $^+$ 333.0056, found 333.0053.

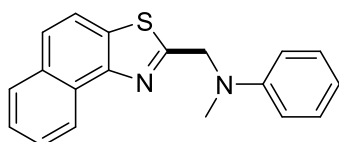


***N*-((5-methoxybenzo[*d*]thiazol-2-yl)methyl)-*N*-methylaniline (3ea)**

22.8 mg, 80% yield, yellow oil, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, J = 8.8 Hz, 1H), 7.48 (d, J = 2.5 Hz, 1H), 7.28 – 7.22 (m, 2H), 6.99 (dd, J = 8.8, 2.5 Hz, 1H), 6.86 – 6.77 (m, 3H), 4.85 (s, 2H), 3.88 (s, 3H), 3.13 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.3, 159.0, 155.0, 149.0, 129.5, 127.0, 122.2, 118.2, 115.1, 113.2, 105.4, 56.5, 55.8, 39.5.

HRMS-ESI $^+$ (m/z) calcd for $\text{C}_{16}\text{H}_{17}\text{N}_2\text{OS}^+$ [M+H] $^+$ 285.1056, found 285.1049.



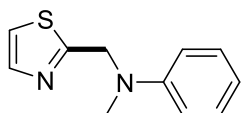
***N*-methyl-*N*-(naphtho[1,2-*d*]thiazol-2-ylmethyl)aniline (3fa)**

25.0 mg, 82% yield, yellow oil, ^1H NMR (400 MHz, Chloroform-*d*) δ 8.78 (dd, J = 8.2, 1.2 Hz, 1H), 8.03 – 7.90 (m, 1H), 7.77 (q, J = 8.8 Hz, 2H), 7.67 (ddd, J = 8.2, 6.9, 1.3 Hz,

1H), 7.57 (ddd, $J = 8.2, 6.9, 1.3$ Hz, 1H), 7.26 (ddt, $J = 9.3, 6.8, 2.3$ Hz, 2H), 6.91 – 6.83 (m, 2H), 6.84 – 6.76 (m, 1H), 4.98 (s, 2H), 3.17 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.0, 150.1, 149.0, 132.0, 131.8, 129.5, 128.6, 128.3, 127.1, 126.2, 125.7, 123.8, 119.3, 118.2, 113.3, 56.5, 39.5.

HRMS-ESI⁺ (m/z) calcd for $\text{C}_{19}\text{H}_{17}\text{N}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 305.1107, found 305.1106.

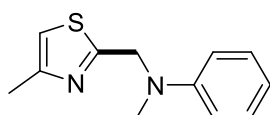


***N*-methyl-*N*-(thiazol-2-ylmethyl)aniline (3ga)**

17.8 mg, 87% yield, yellow oil, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, $J = 3.3$ Hz, 1H), 7.29 – 7.19 (m, 3H), 6.84 – 6.74 (m, 3H), 4.79 (s, 2H), 3.09 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.2, 149.0, 143.0, 129.4, 119.2, 118.0, 113.2, 55.7, 39.2.

HRMS-ESI⁺ (m/z) calcd for $\text{C}_{11}\text{H}_{13}\text{N}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 205.0794, found 205.0793.

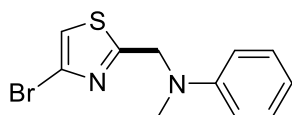


***N*-methyl-*N*-((4-methylthiazol-2-yl)methyl)aniline (3ha)**

14.4 mg, 66% yield, Colorless oil, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, $J = 3.2$ Hz, 1H), 7.24 (d, $J = 8.2$ Hz, 1H), 6.83 – 6.74 (m, 4H), 4.74 (s, 2H), 3.09 (s, 3H), 2.45 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.7, 153.0, 149.1, 129.4, 118.0, 113.5, 113.2, 55.9, 39.2, 17.3.

HRMS-ESI⁺ (m/z) calcd for $\text{C}_{12}\text{H}_{15}\text{N}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 219.0951, found 219.0949.

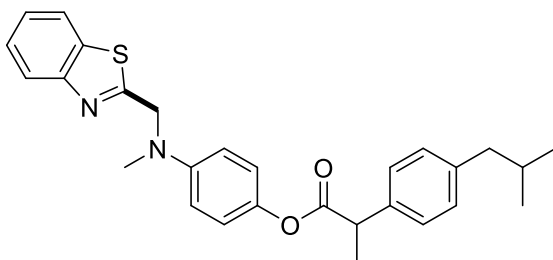


***N*-((4-bromothiazol-2-yl)methyl)-*N*-methylaniline (3ia)**

23.2 mg, 82% yield, Colorless oil, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.26 (dd, $J = 8.8, 7.2$ Hz, 2H), 7.12 (s, 1H), 6.80 (dd, $J = 17.7, 7.8$ Hz, 3H), 4.75 (s, 2H), 3.09 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.0, 148.8, 129.5, 124.7, 118.5, 117.1, 113.3, 56.1, 39.5.

HRMS-ESI⁺ (m/z) calcd for $\text{C}_{11}\text{H}_{12}\text{BrN}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 282.9899, found 282.9896.

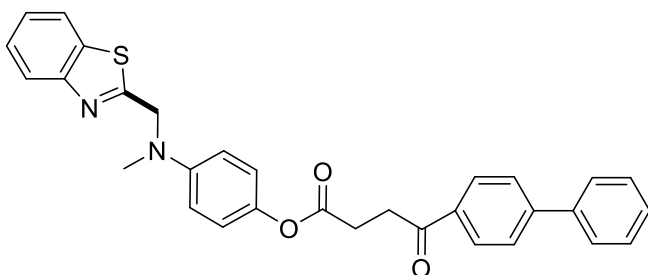


4-((benzo[d]thiazol-2-ylmethyl)(methyl)amino)phenyl-2-(4-isobutylphenyl)propanoate (4aa)

41.3 mg, 90% yield, yellow oil, $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.97 (d, $J = 8.2$ Hz, 1H), 7.79 (d, $J = 8.0$ Hz, 1H), 7.50 – 7.41 (m, 1H), 7.38 – 7.29 (m, 1H), 7.28 (dd, $J = 7.7$, 5.5 Hz, 2H), 7.11 (d, $J = 7.8$ Hz, 2H), 6.91 – 6.83 (m, 2H), 6.80 – 6.72 (m, 2H), 4.82 (s, 2H), 3.89 (q, $J = 7.1$ Hz, 1H), 3.10 (s, 2H), 2.45 (dd, $J = 7.1$, 3.8 Hz, 2H), 1.90 – 1.77 (m, 1H), 1.57 (dd, $J = 7.2$, 2.6 Hz, 3H), 0.89 (d, $J = 6.6$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 173.9, 172.8, 153.7, 146.9, 142.9, 140.9, 137.6, 135.1, 129.6, 127.4 (d, $J = 1.8$ Hz), 126.2, 125.1, 122.8, 122.1, 113.8, 56.8, 45.3, 45.2 (d, $J = 1.5$ Hz), 39.9, 30.4, 22.6, 18.8.

HRMS-ESI⁺ (m/z) calcd for $\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_2\text{S}^+$ [$\text{M}+\text{H}$]⁺ 459.2101, found 459.2101.

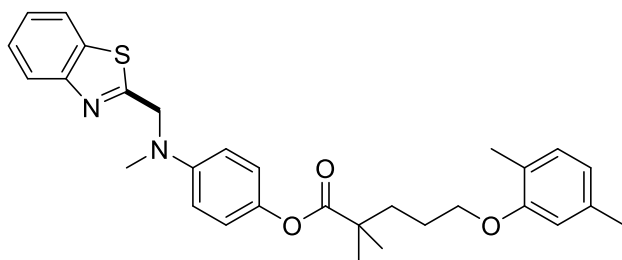


4-((benzo[d]thiazol-2-ylmethyl)(methyl)amino)phenyl-4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate (4ab)

31.4 mg, 52% yield, white solid, $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.11 – 8.04 (m, 2H), 7.99 (d, $J = 8.1$ Hz, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.73 – 7.66 (m, 2H), 7.66 – 7.59 (m, 2H), 7.51 – 7.45 (m, 2H), 7.48 – 7.38 (m, 2H), 7.40 – 7.32 (m, 1H), 7.04 – 6.97 (m, 2H), 6.84 – 6.74 (m, 2H), 4.85 (s, 2H), 3.44 (t, $J = 6.6$ Hz, 2H), 3.13 (s, 3H), 3.01 (t, $J = 6.6$ Hz, 2H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 197.8, 173.0, 172.3, 153.8, 147.0, 146.2, 142.9, 140.0, 135.4, 135.2, 129.2, 128.9, 128.5, 127.5, 126.2, 125.2, 122.9, 122.3, 122.0, 113.9, 56.9, 39.9, 33.7, 28.7.

HRMS-ESI⁺ (m/z) calcd for $\text{C}_{31}\text{H}_{27}\text{N}_2\text{O}_3\text{S}^+$ [$\text{M}+\text{H}$]⁺ 507.1737, found 507.1732.

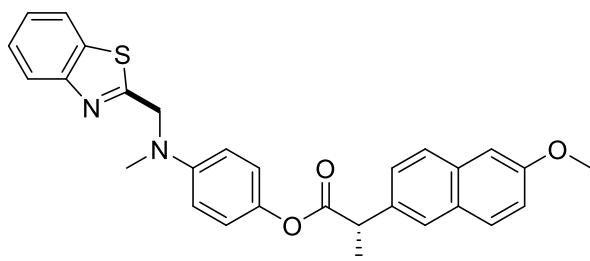


4-((benzo[d]thiazol-2-ylmethyl)(methyl)amino)phenyl-5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (4ac)

40.7 mg, 81% yield, yellow oil, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.99 (t, $J = 8.2$ Hz, 1H), 7.81 (d, $J = 8.0$ Hz, 1H), 7.51 – 7.42 (m, 1H), 7.39 – 7.31 (m, 1H), 6.99 (d, $J = 7.4$ Hz, 1H), 6.95 – 6.87 (m, 2H), 6.84 – 6.76 (m, 2H), 6.68 – 6.59 (m, 2H), 4.84 (s, 2H), 3.95 (s, 2H), 3.12 (s, 3H), 2.29 (s, 2H), 2.16 (s, 3H), 1.84 (s, 4H), 1.34 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.0, 172.8, 157.0, 153.7, 146.8, 143.1, 136.6, 135.2, 130.5, 126.2, 125.1, 123.8, 122.9, 122.2, 122.0, 120.9 (d, $J = 1.5$ Hz), 113.9, 112.1, 68.0, 56.8, 42.6, 42.5, 39.9, 37.3, 25.4, 25.4, 21.6 (d, $J = 1.5$ Hz), 16.0 (d, $J = 1.7$ Hz).

HRMS-ESI⁺ (m/z) calcd for $\text{C}_{30}\text{H}_{35}\text{N}_2\text{O}_3\text{S}^+$ [$\text{M}+\text{H}$]⁺ 503.2363, found 503.2359.



4-((benzo[d]thiazol-2-ylmethyl)(methyl)amino)phenyl(S)-2-(6-methoxynaphthalen-2-yl)propanoate (4ad)

34.7 mg, 72% yield, white solid, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.97 (dd, $J = 8.1, 1.1$ Hz, 1H), 7.78 (dt, $J = 7.8, 1.0$ Hz, 1H), 7.77 – 7.67 (m, 3H), 7.51 – 7.42 (m, 2H), 7.33 (ddd, $J = 8.2, 7.2, 1.2$ Hz, 1H), 7.17 – 7.09 (m, 2H), 6.90 – 6.83 (m, 2H), 6.78 – 6.69 (m, 2H), 4.80 (s, 2H), 4.05 (q, $J = 7.0$ Hz, 1H), 3.90 (s, 3H), 3.08 (s, 3H), 1.66 (d, $J = 7.1$ Hz, 3H).

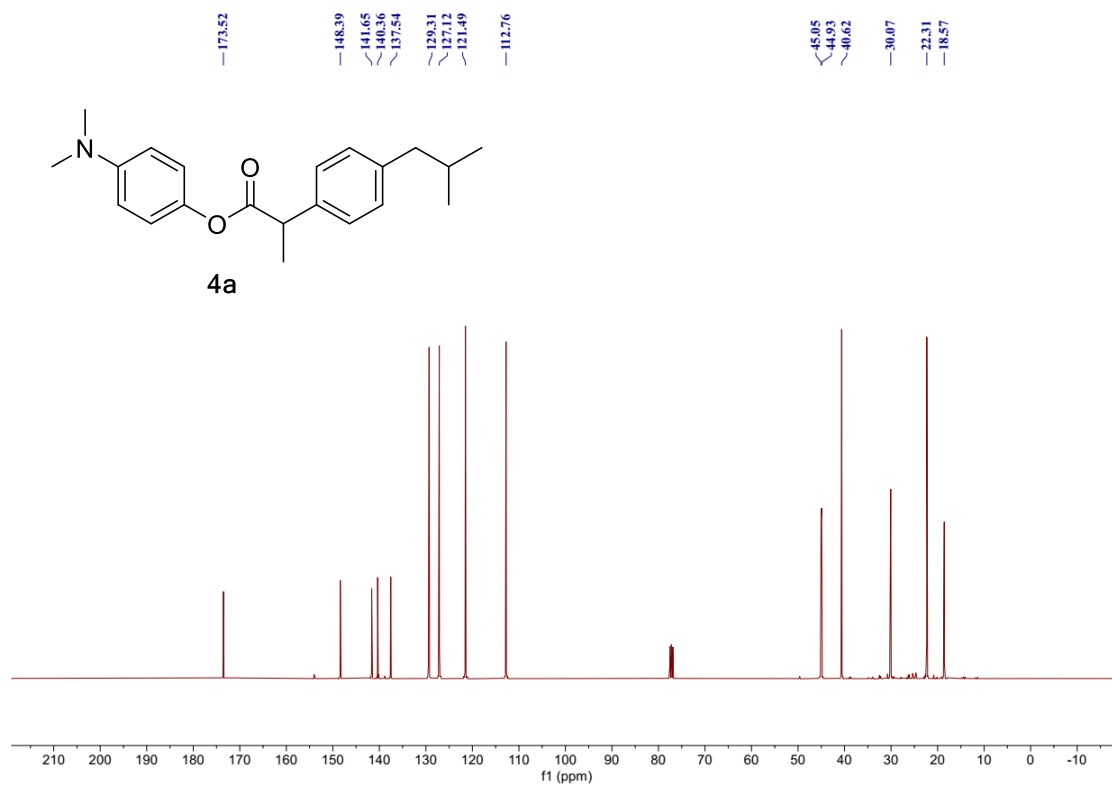
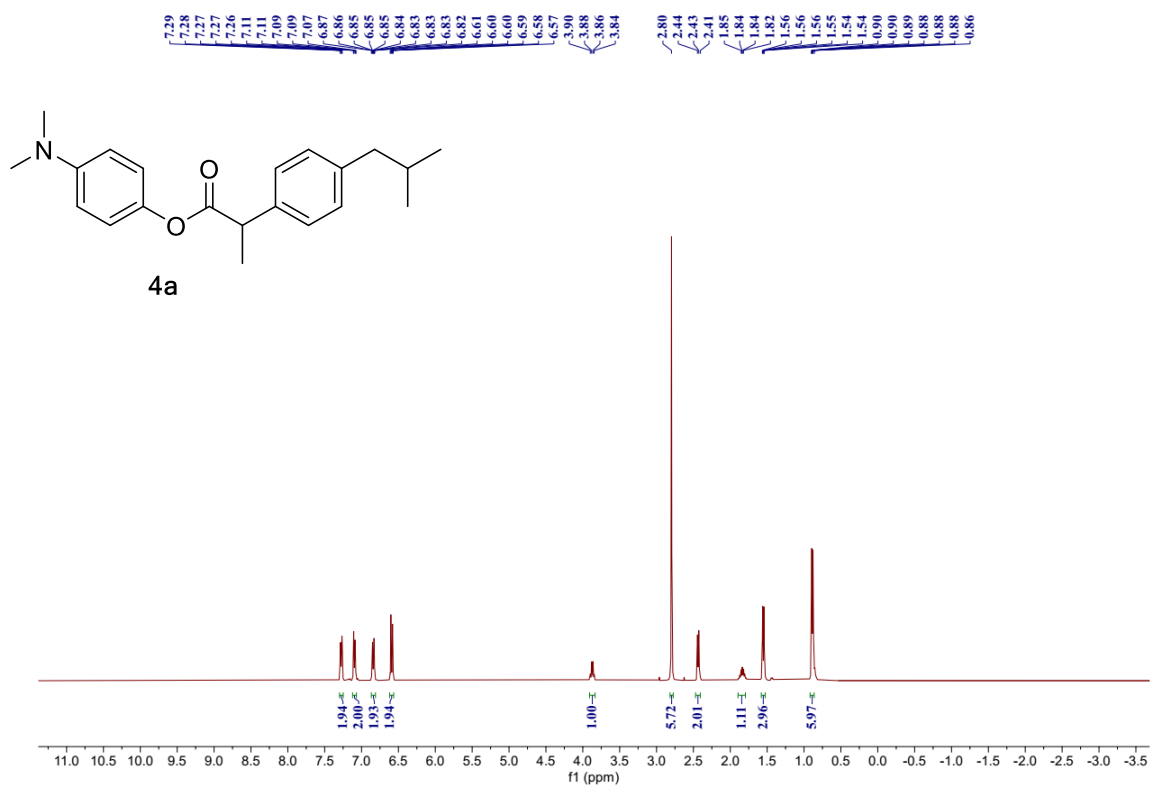
^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.7, 172.7, 157.7, 153.6, 146.8, 142.8, 135.4, 135.0, 133.8, 129.4, 129.0, 127.4, 126.2, 126.1, 126.0, 125.0, 122.7, 122.0, 121.9, 119.1, 113.7, 105.6, 56.6, 55.4, 45.6, 39.7, 18.6.

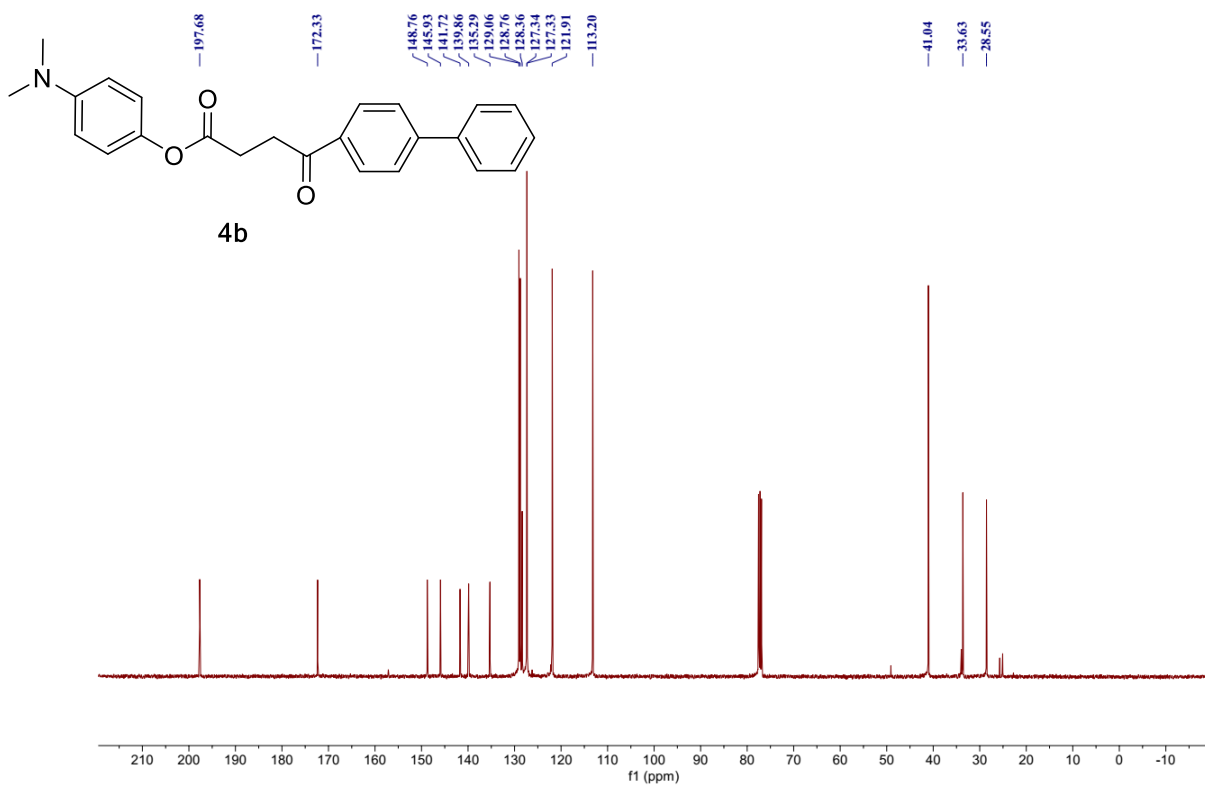
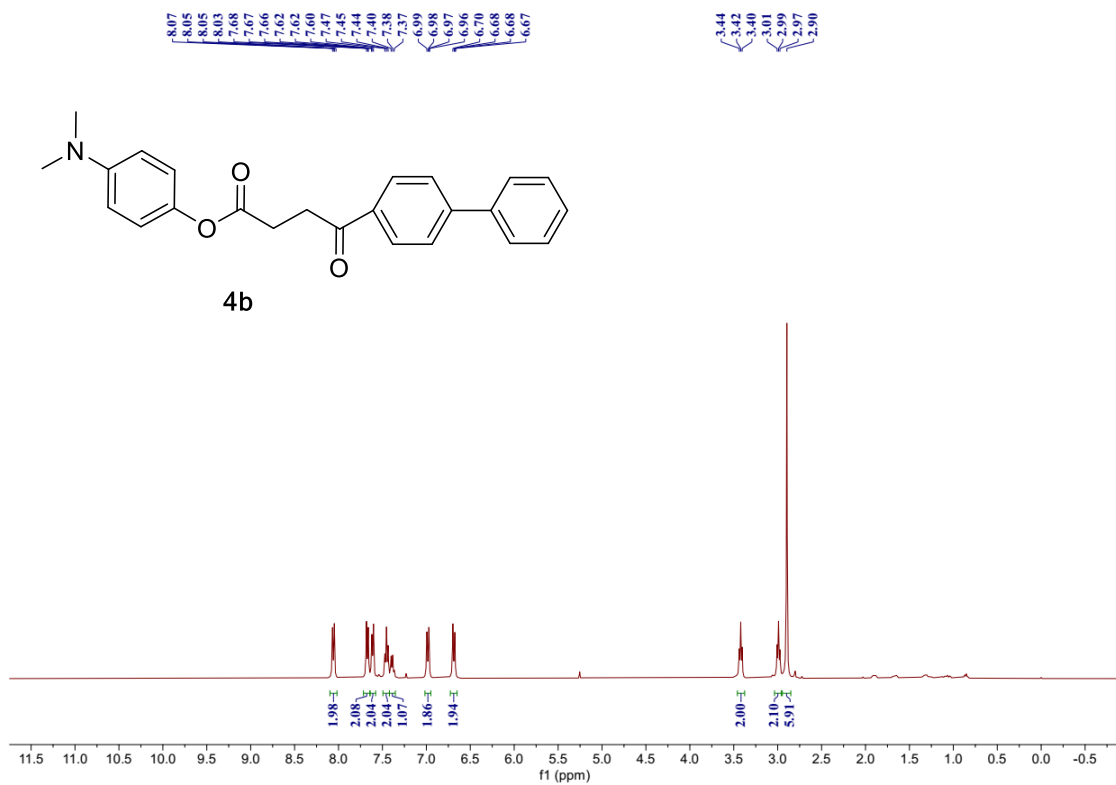
HRMS-ESI⁺ (m/z) calcd for $\text{C}_{29}\text{H}_{27}\text{N}_2\text{O}_3\text{S}^+$ [$\text{M}+\text{H}$]⁺ 483.1737, found 483.1750.

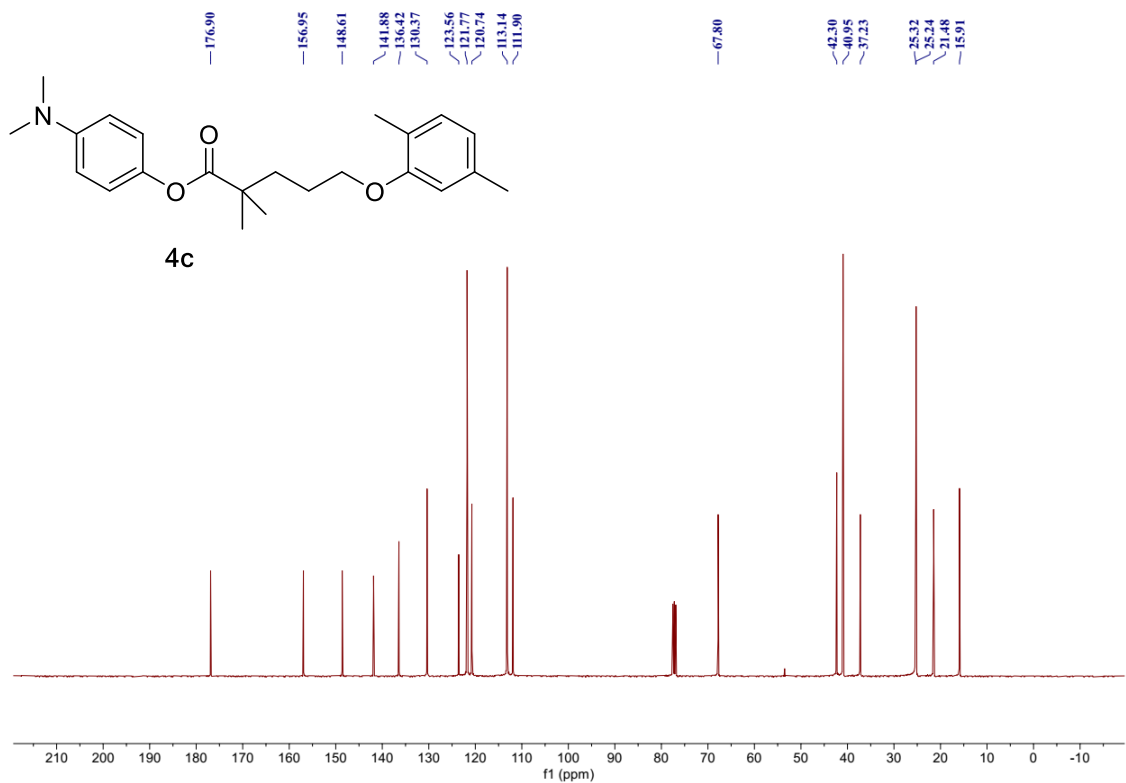
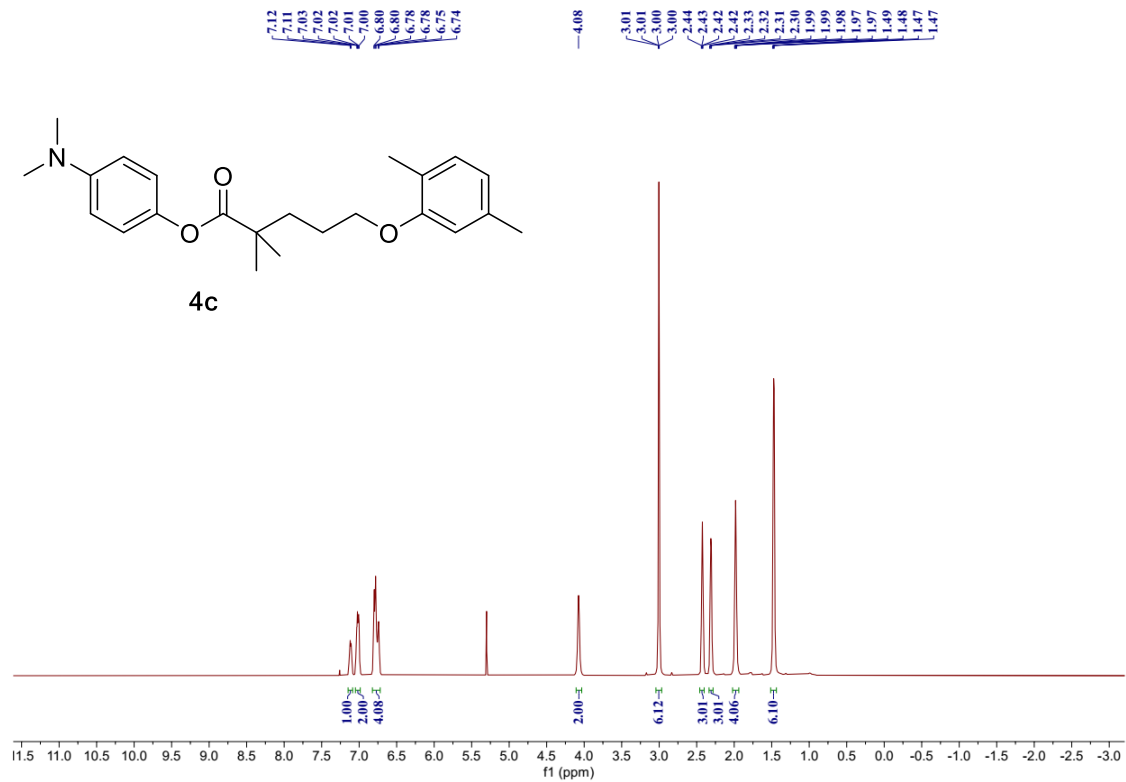
9、Reference

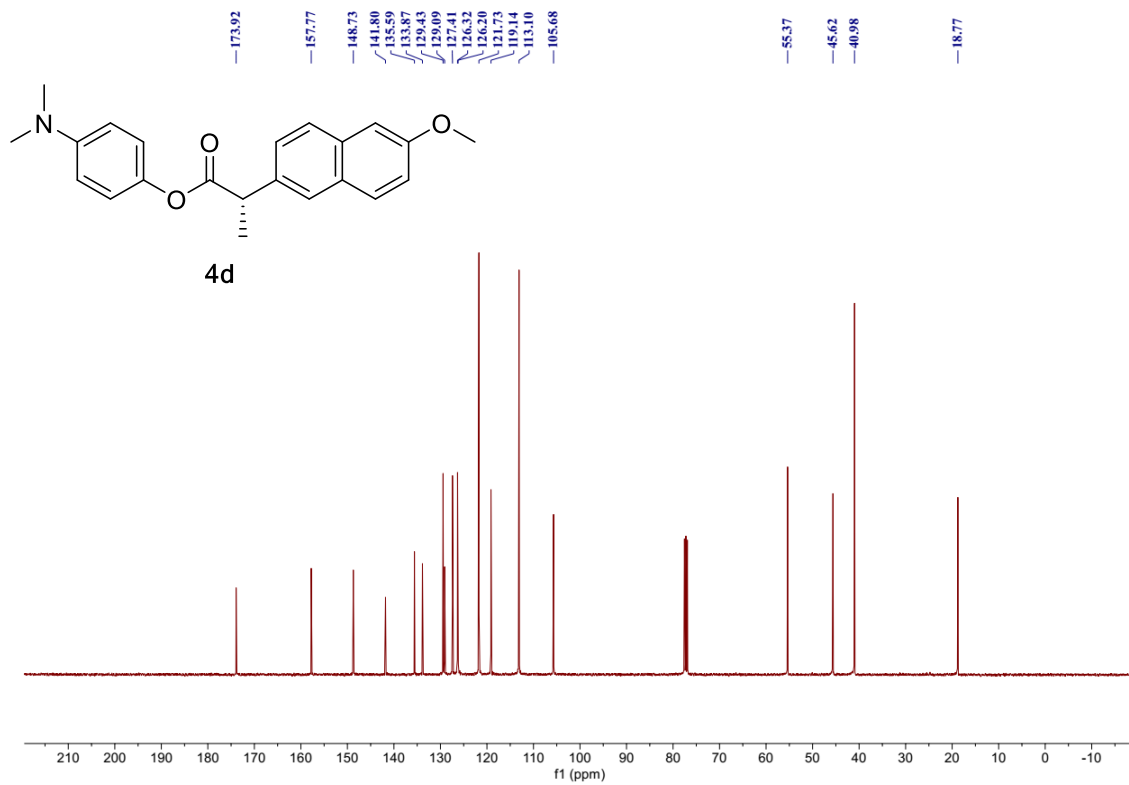
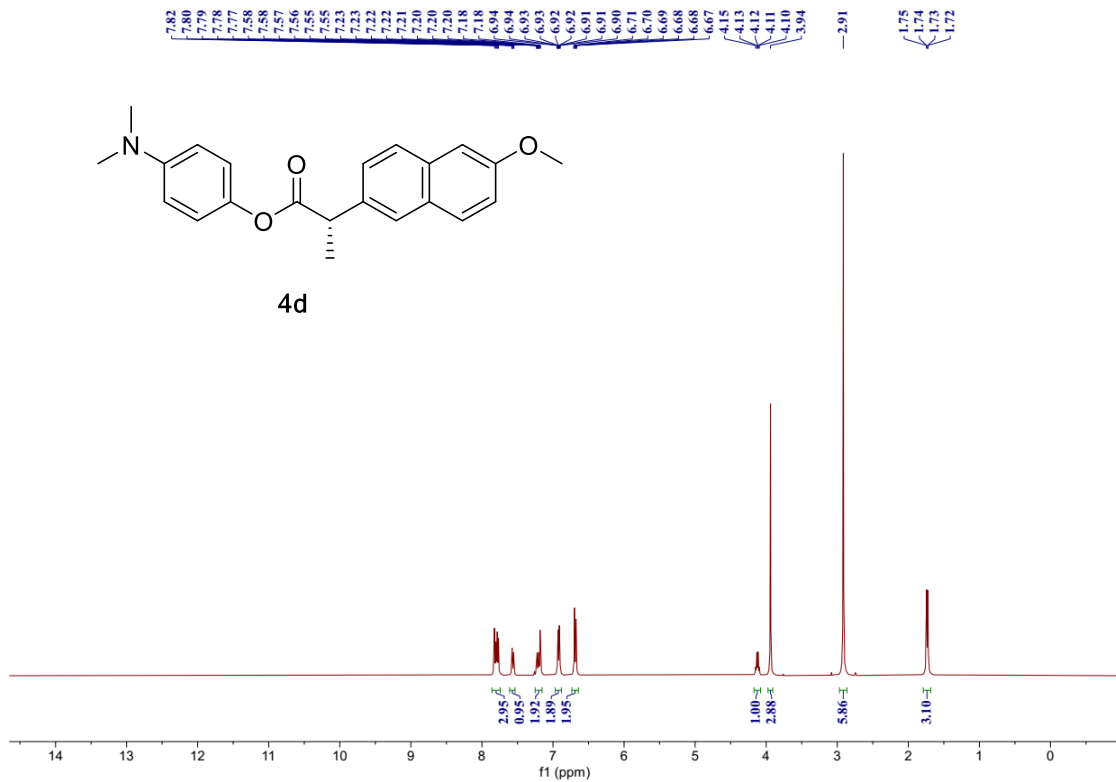
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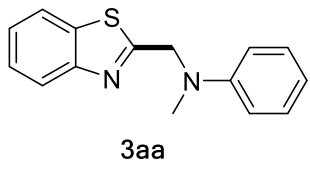
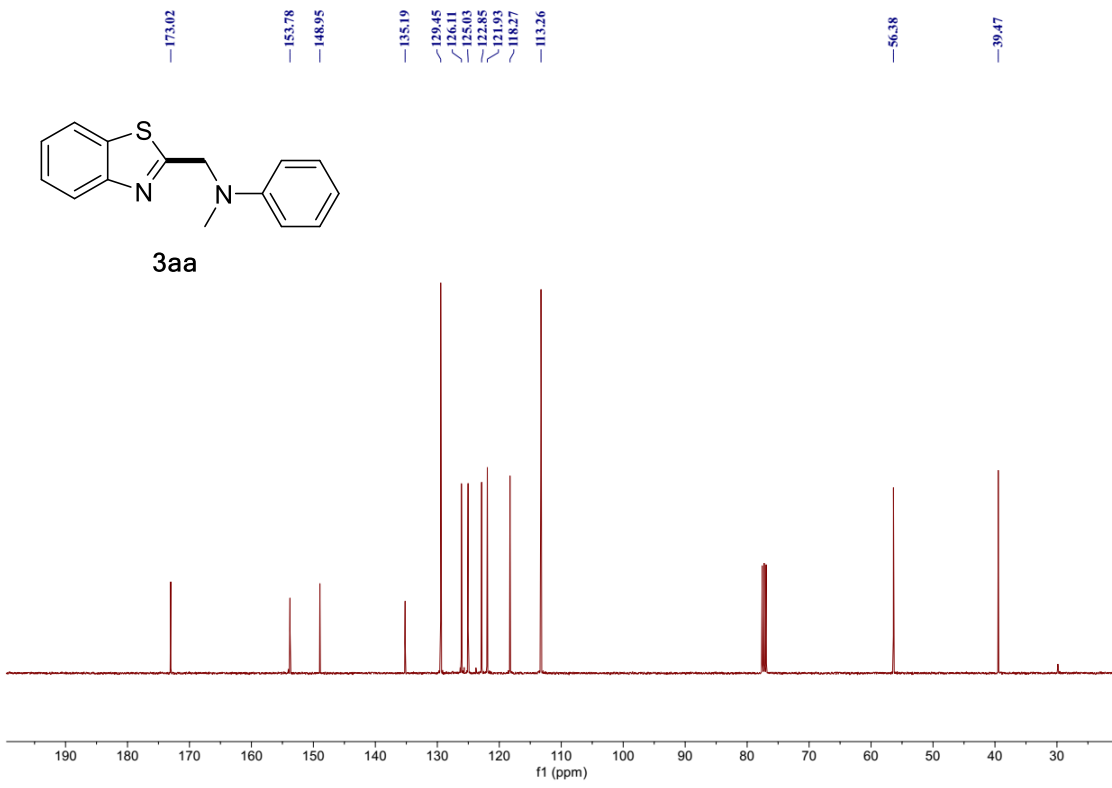
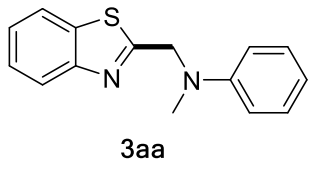
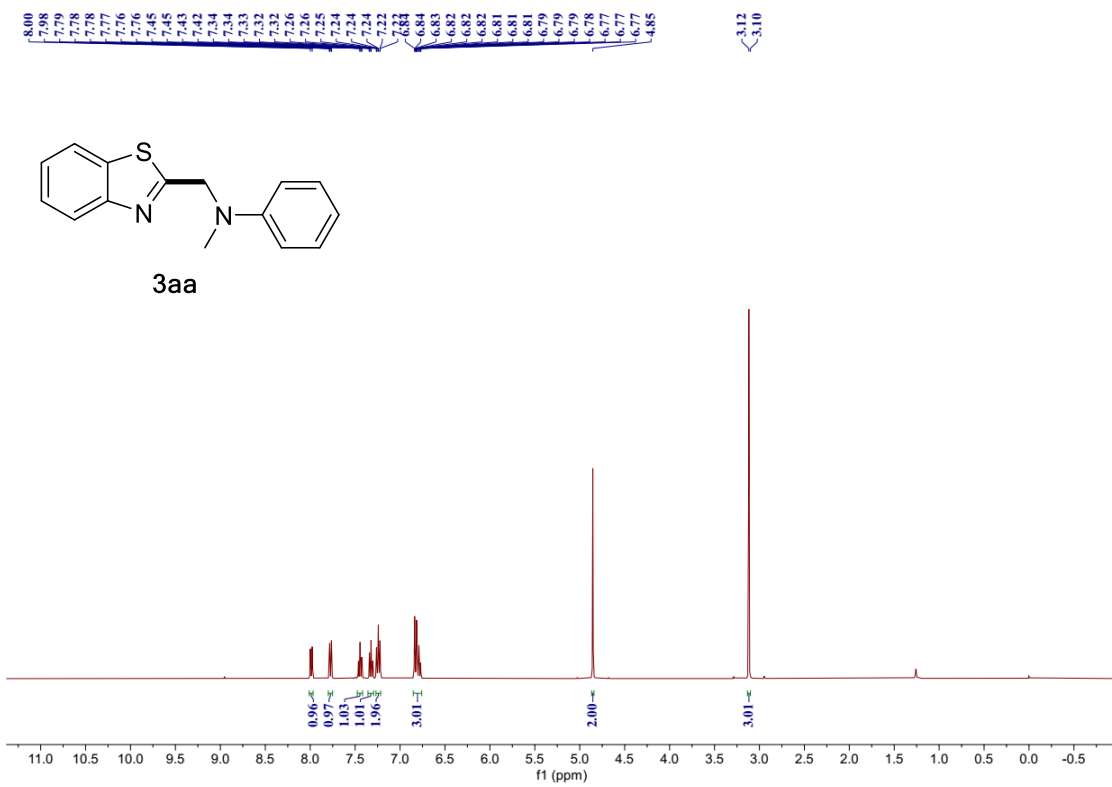
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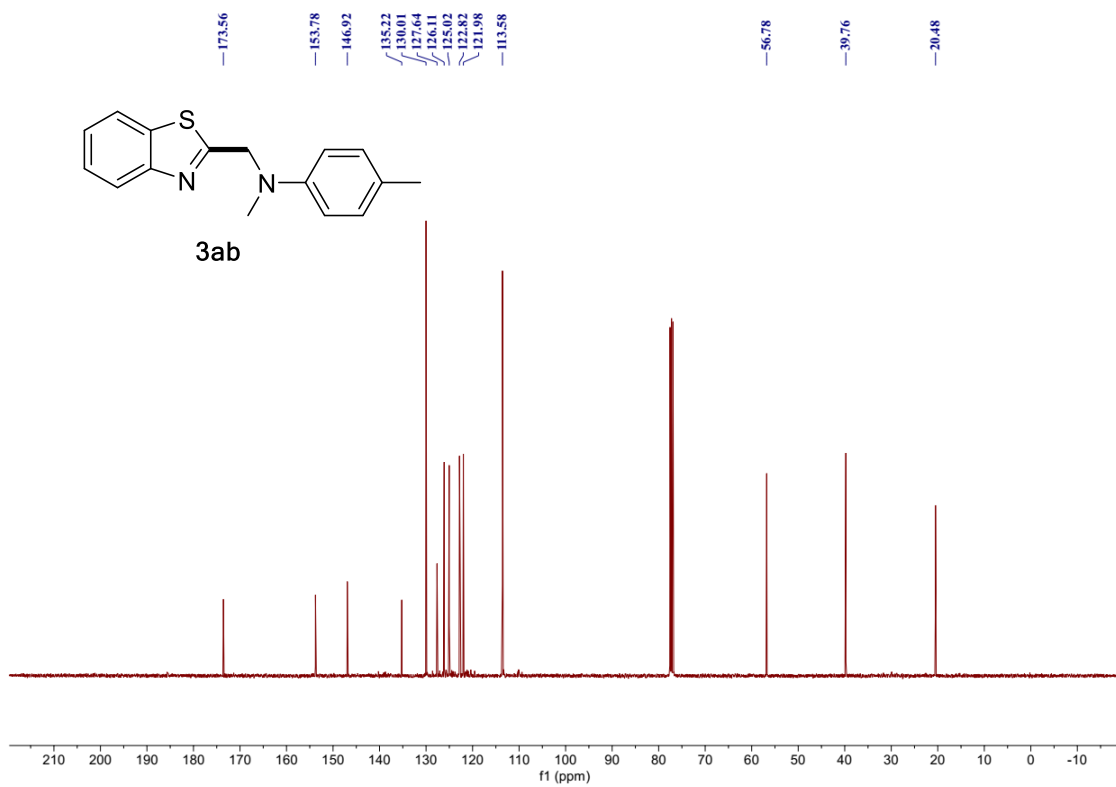
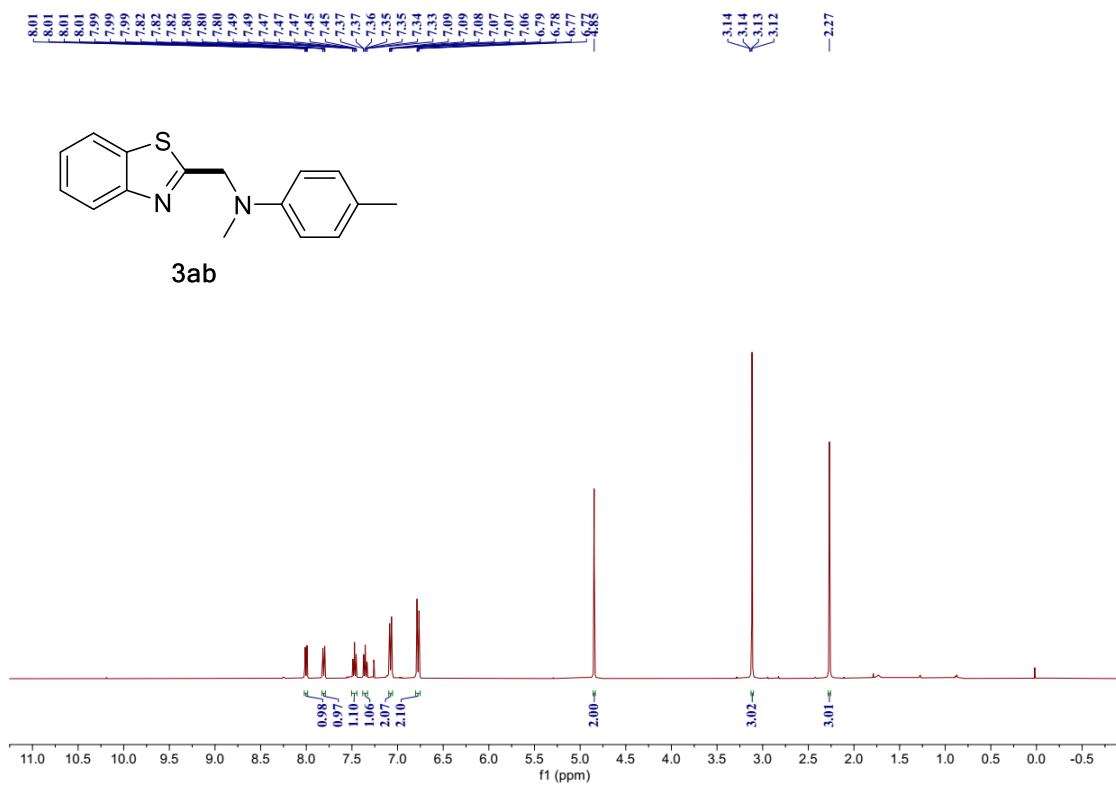


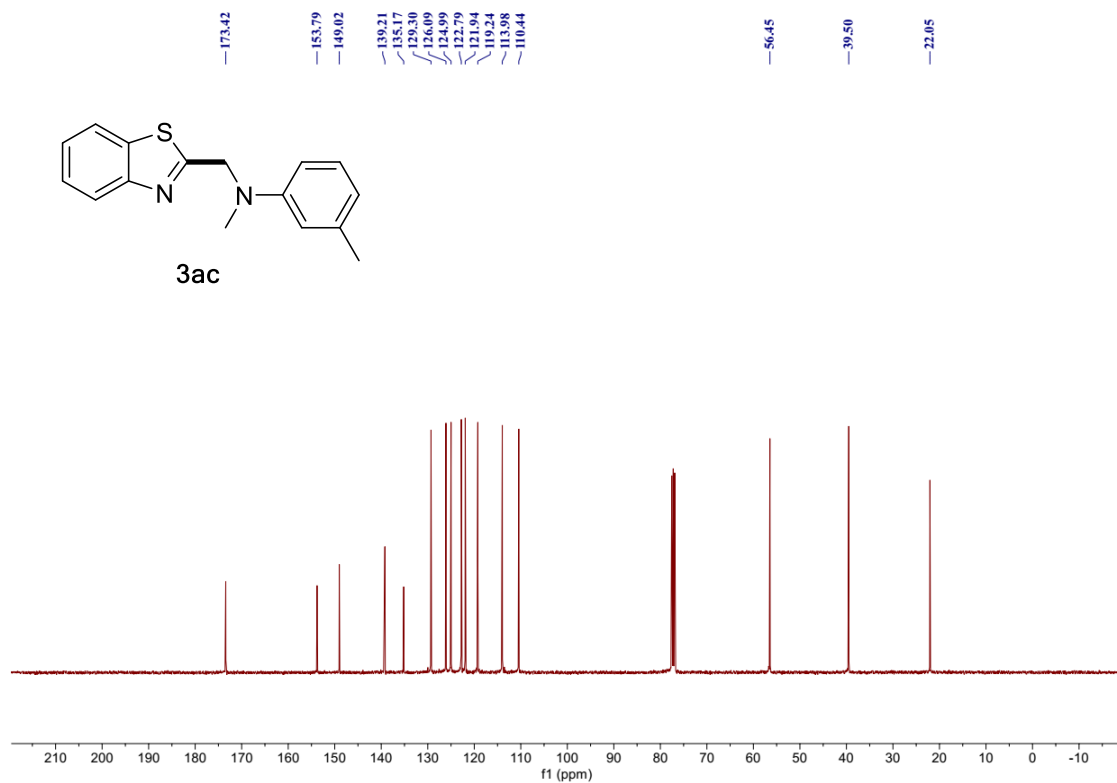
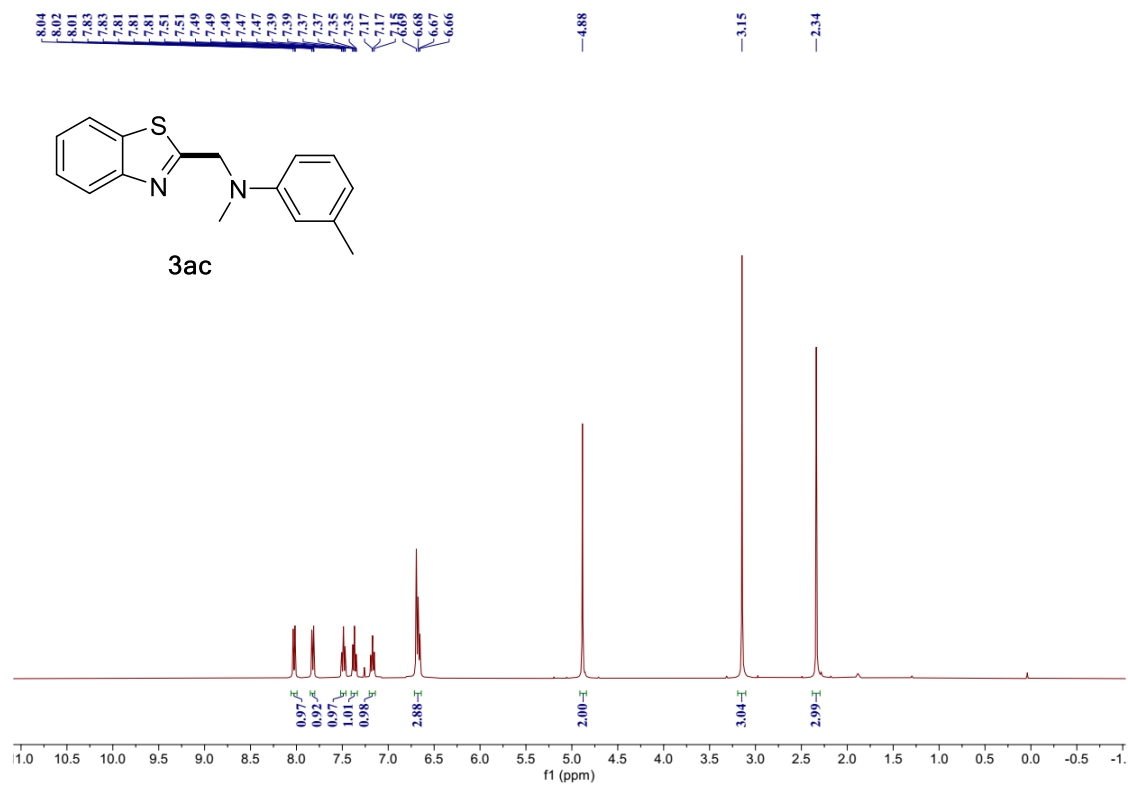


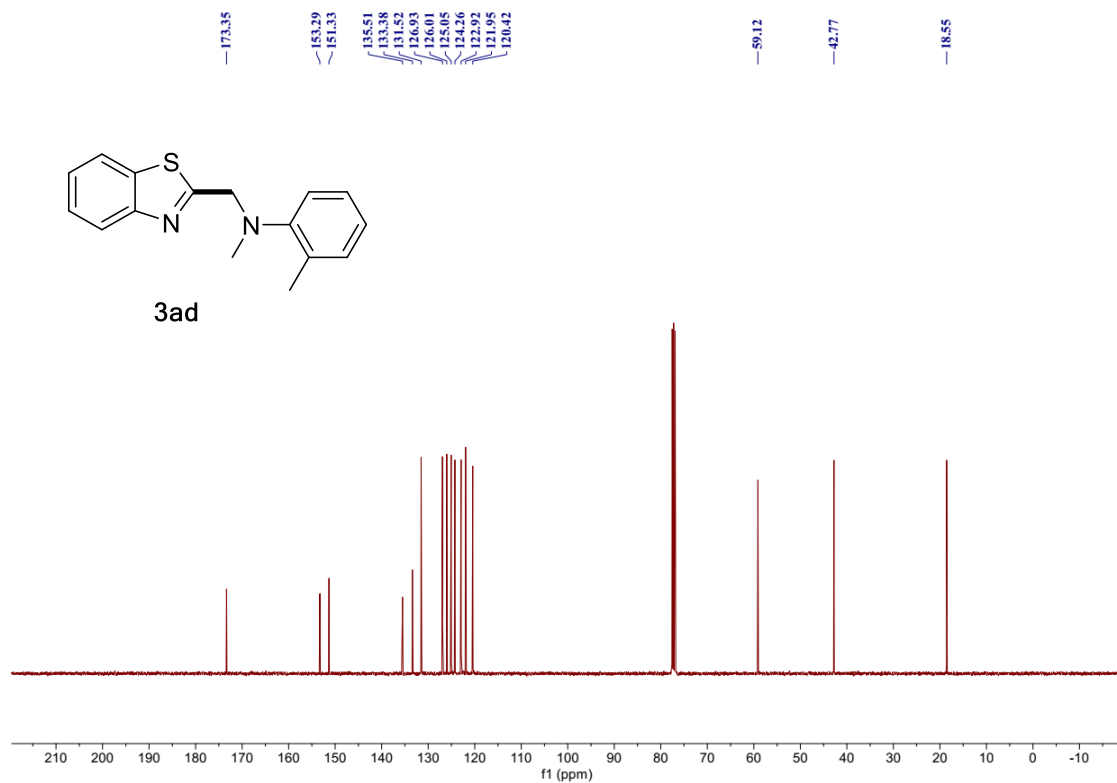
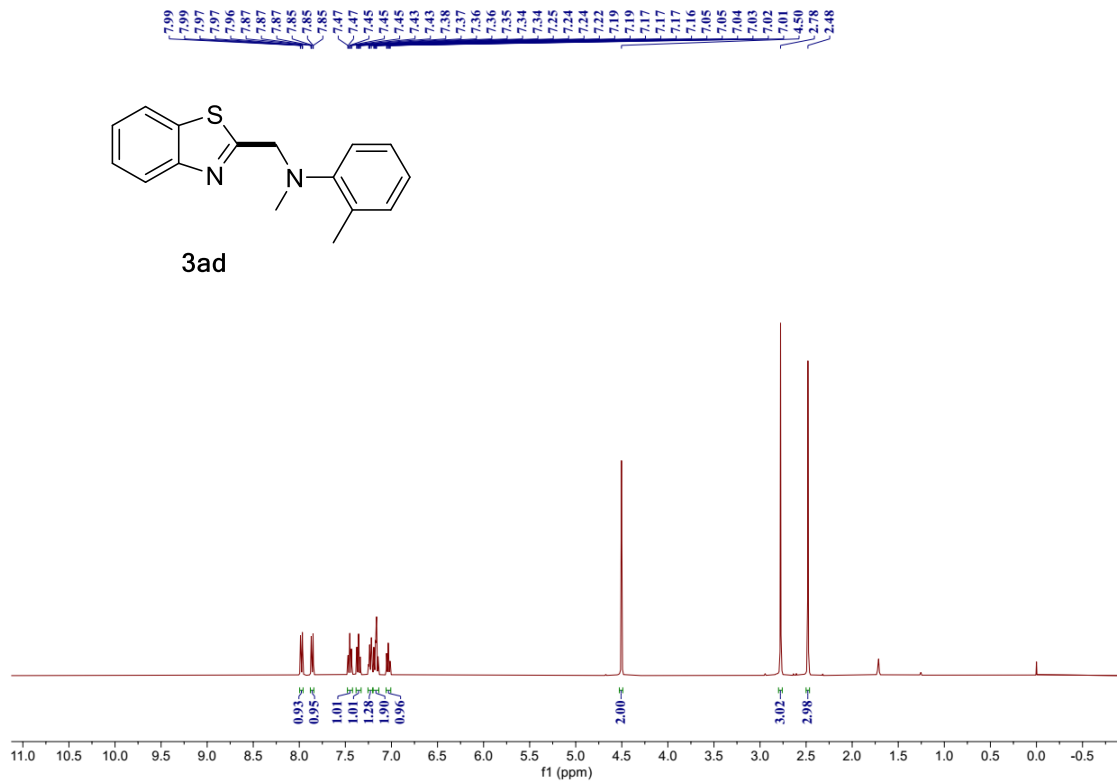


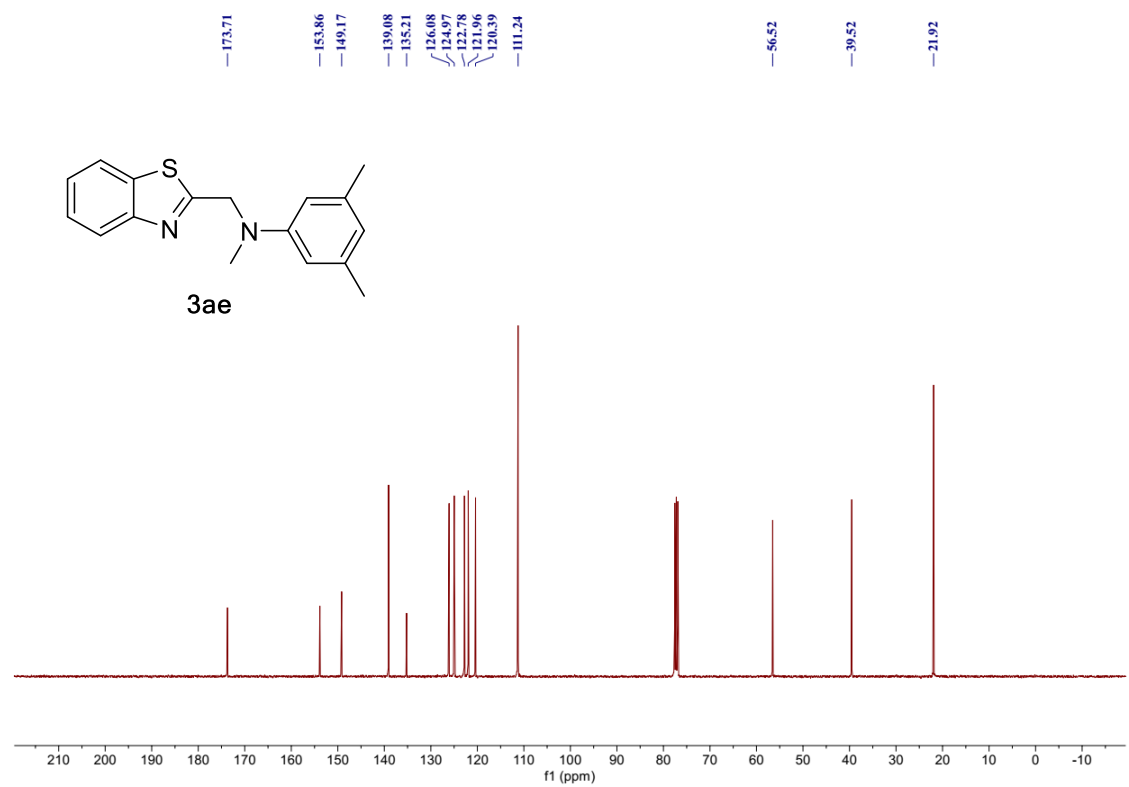
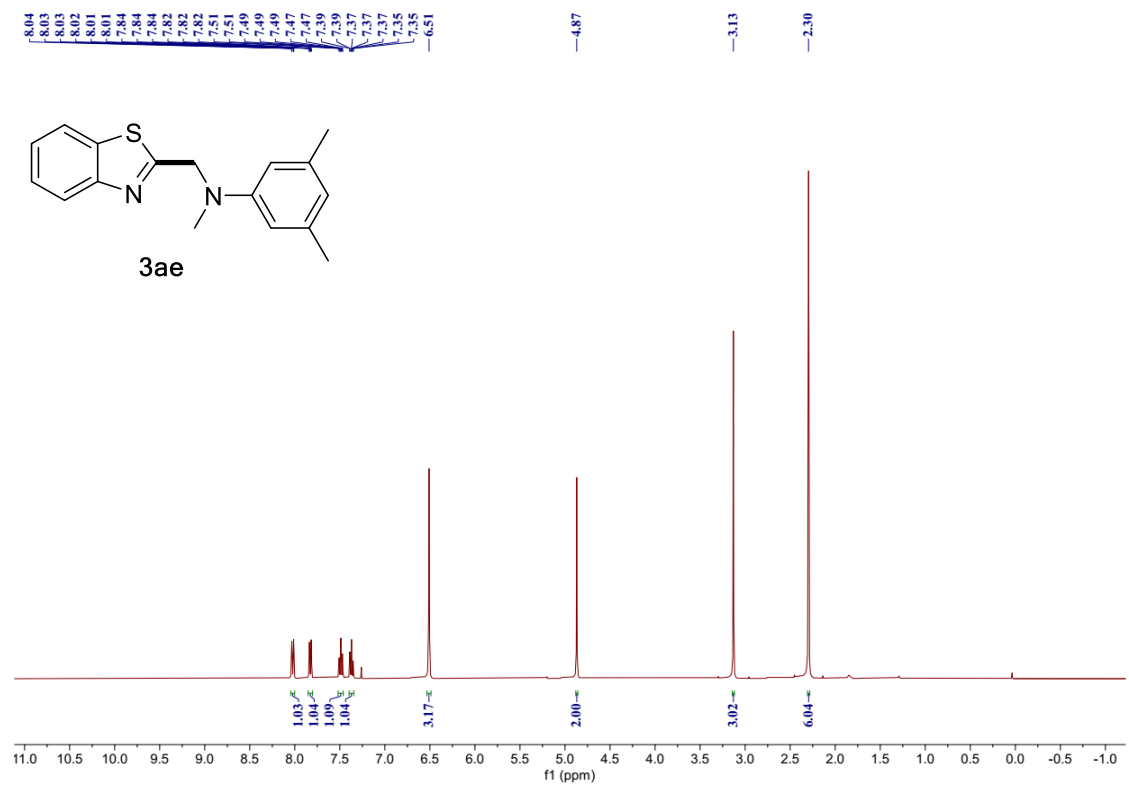


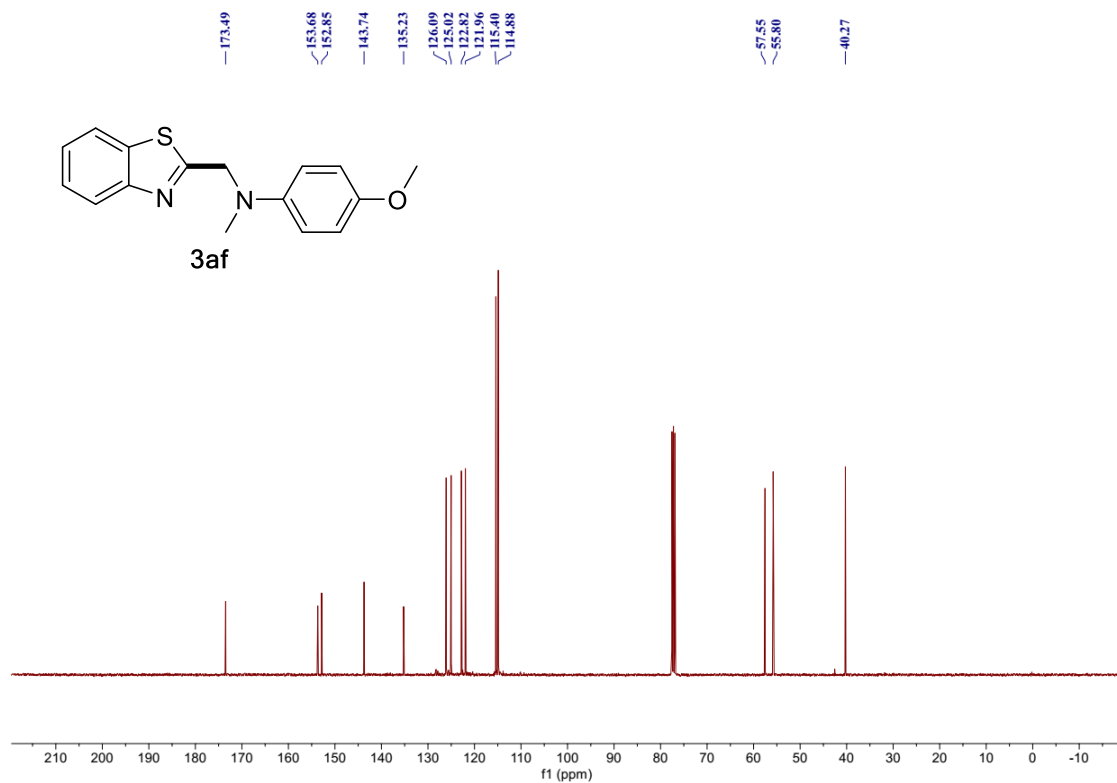
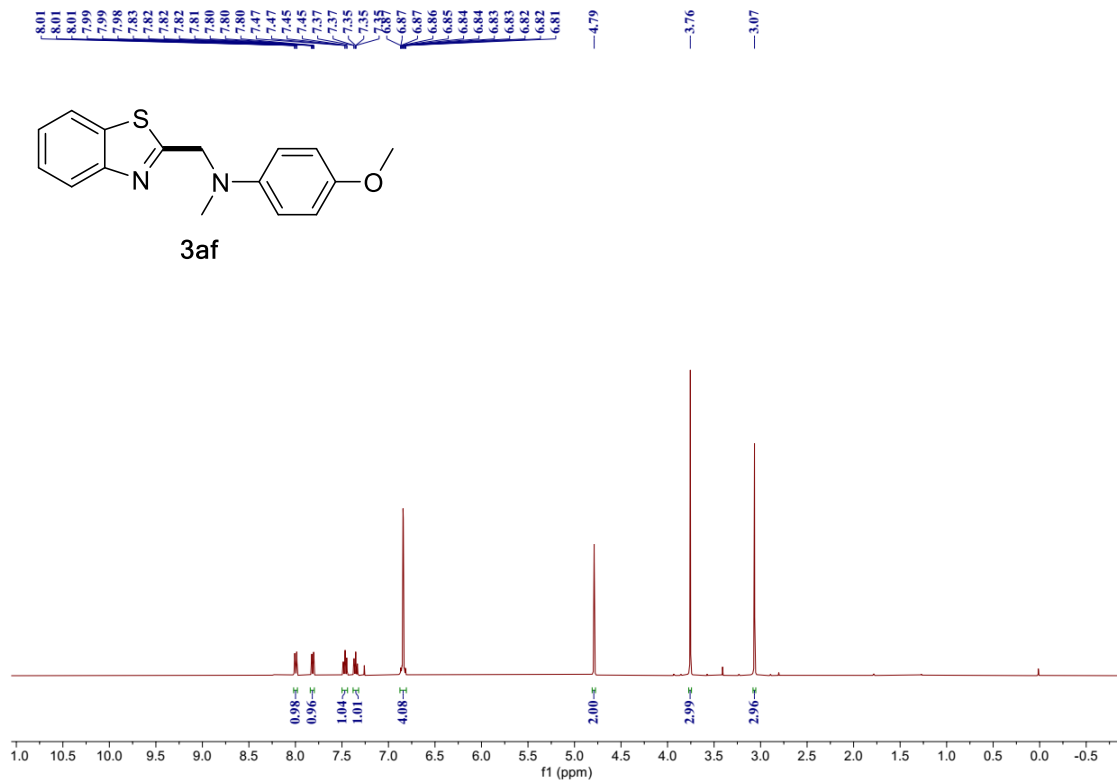


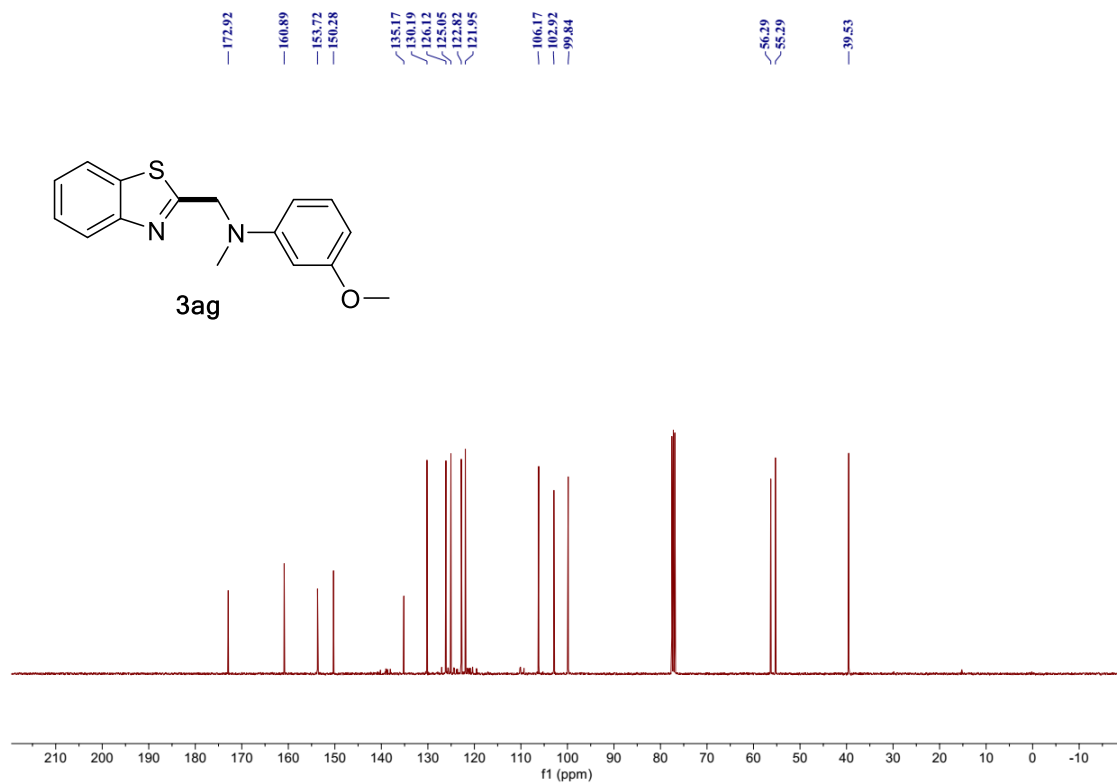
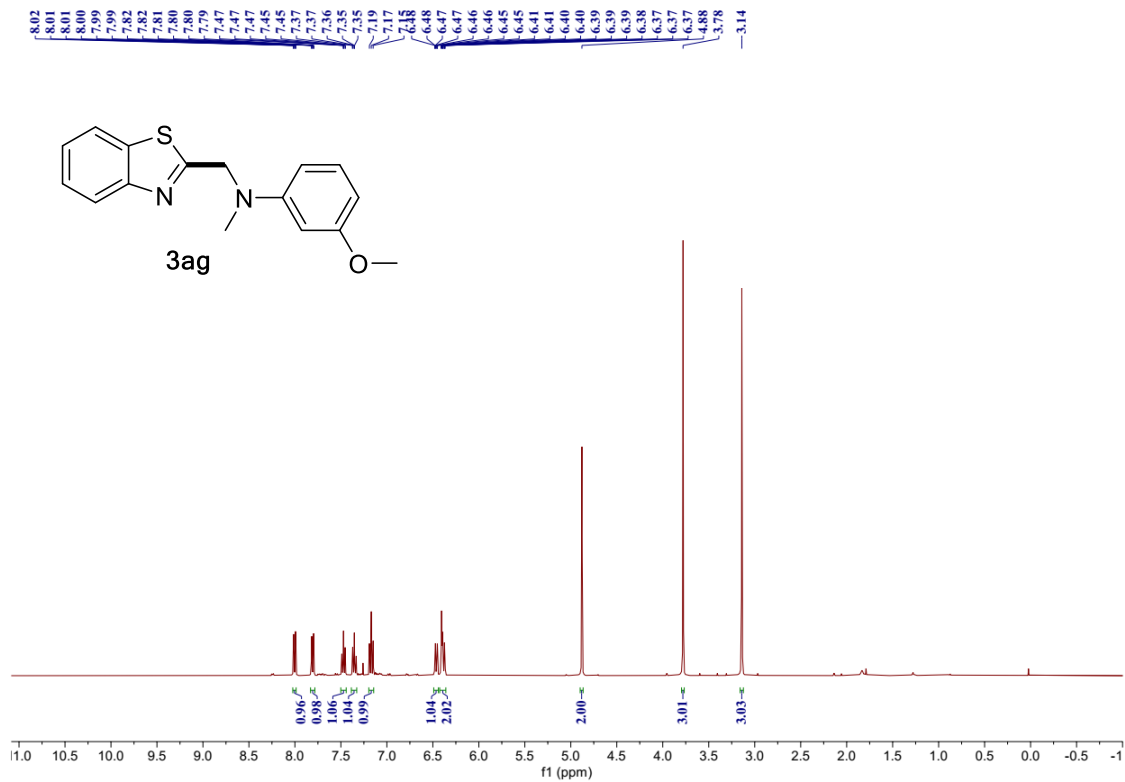


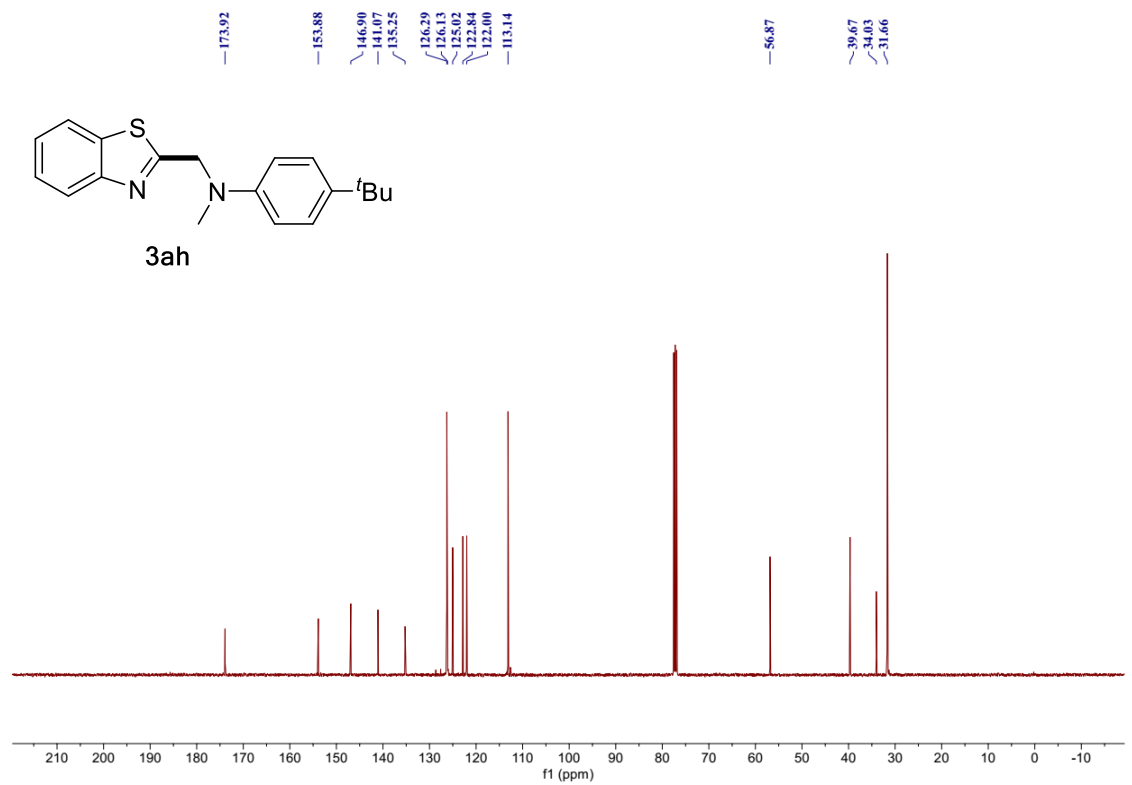
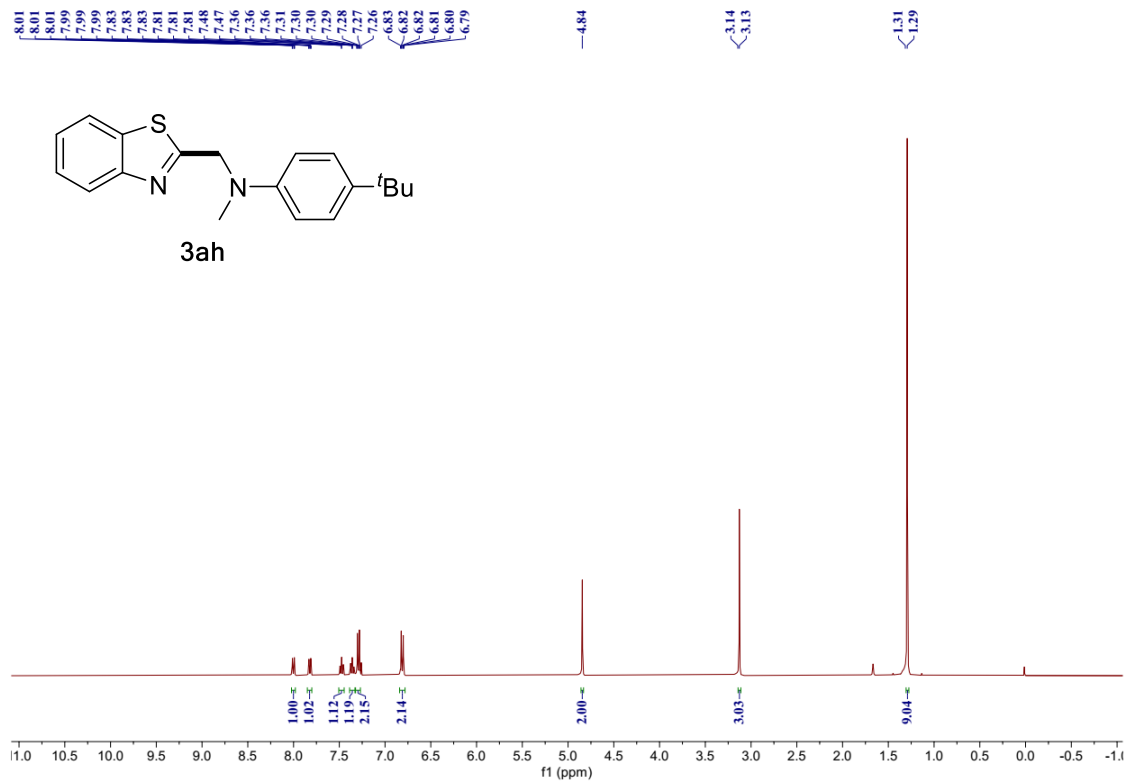




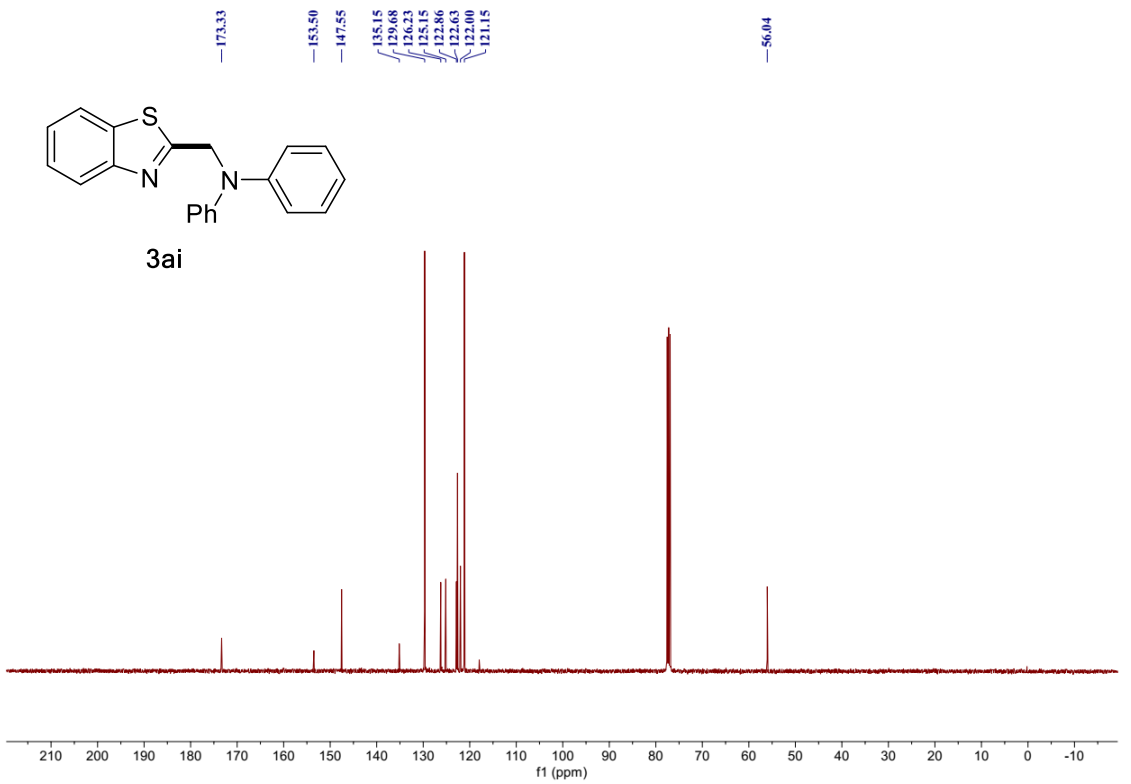
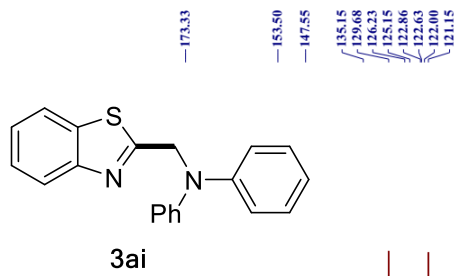
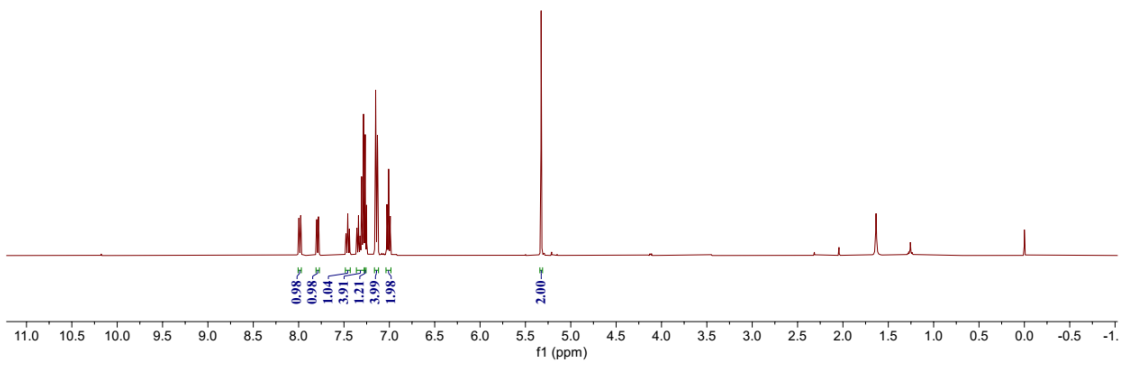
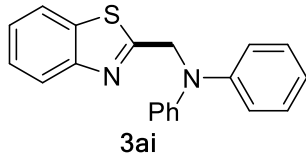


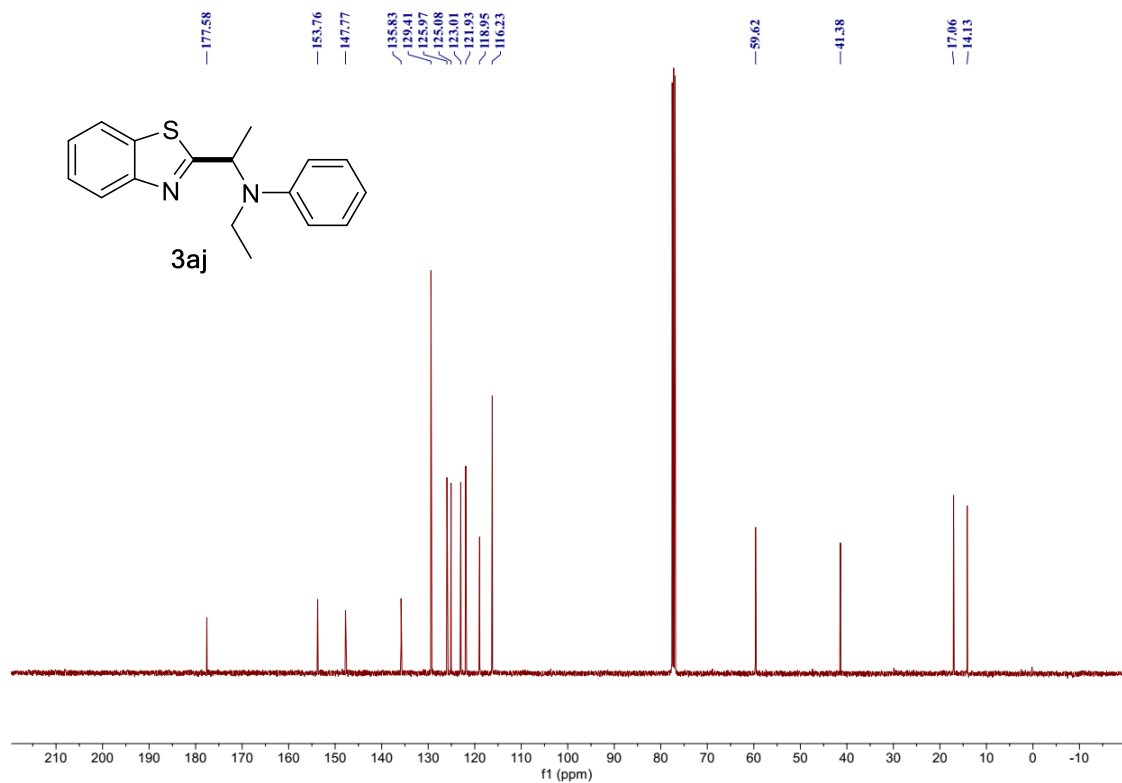
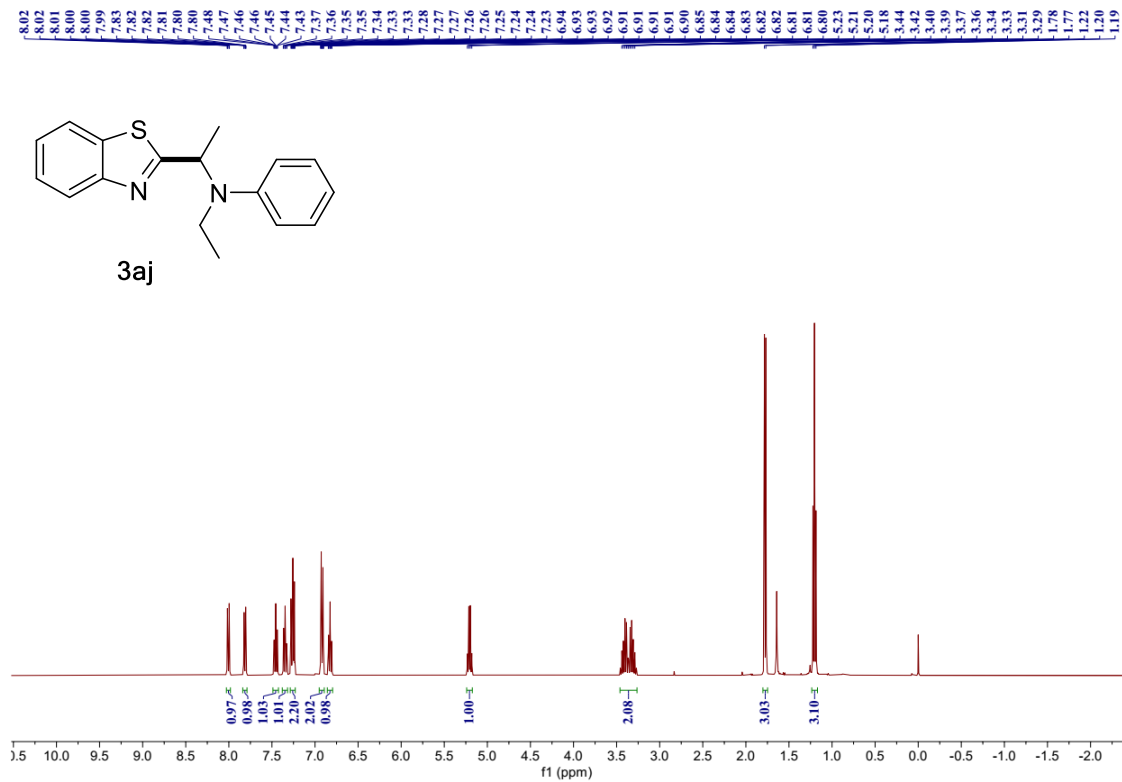


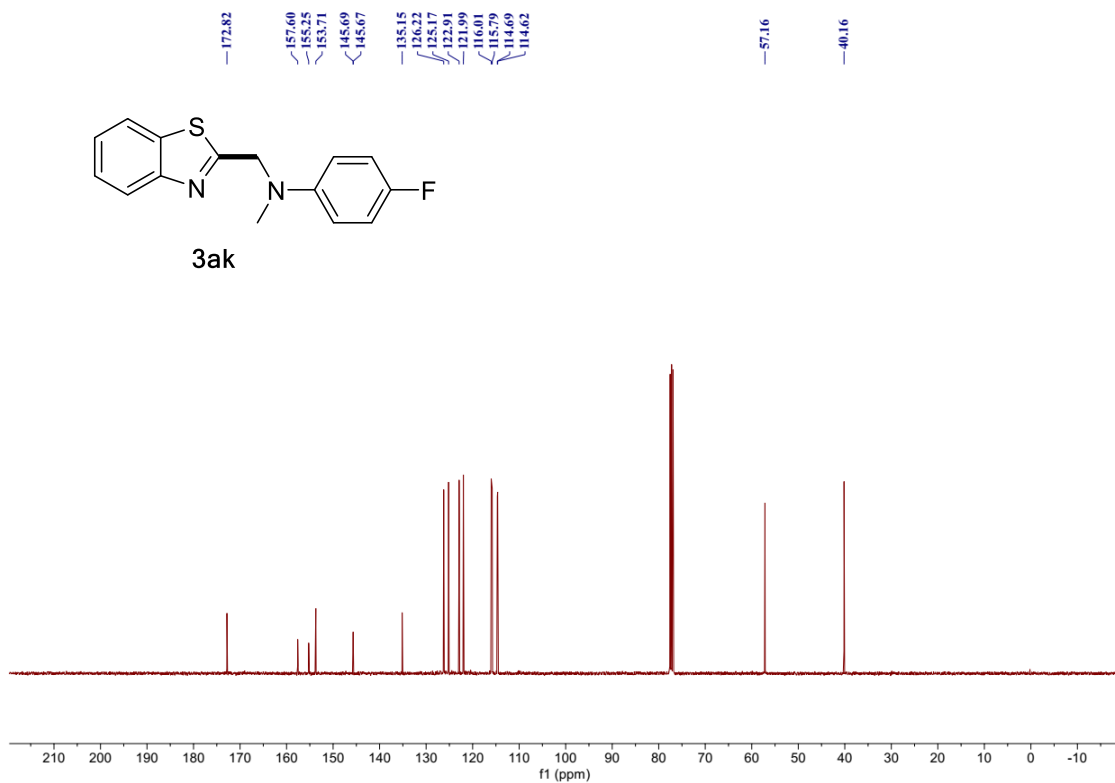
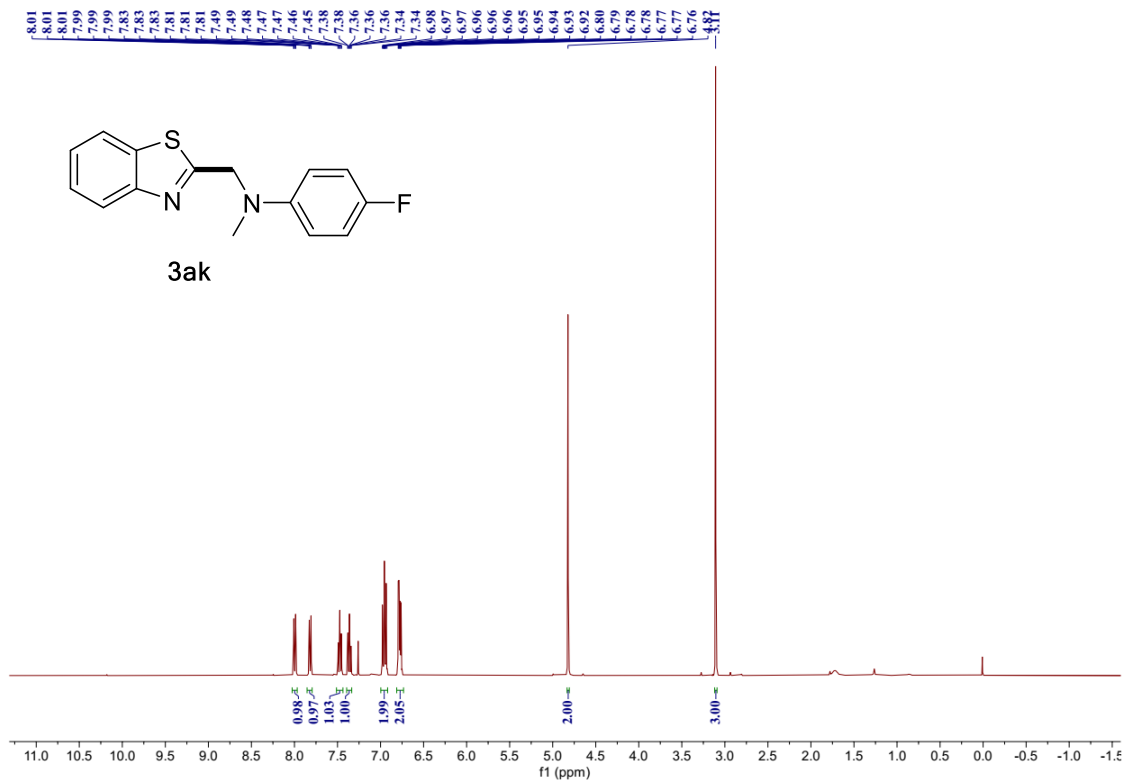


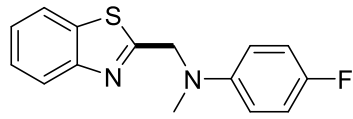


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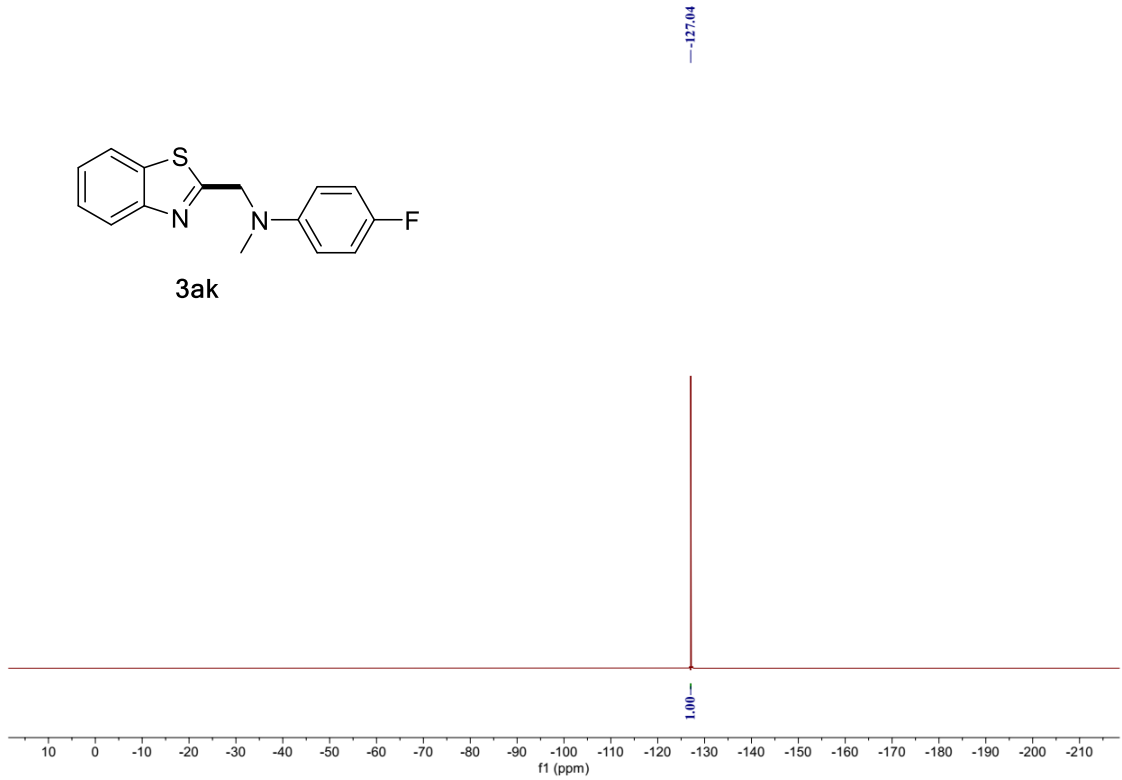








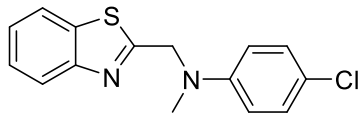
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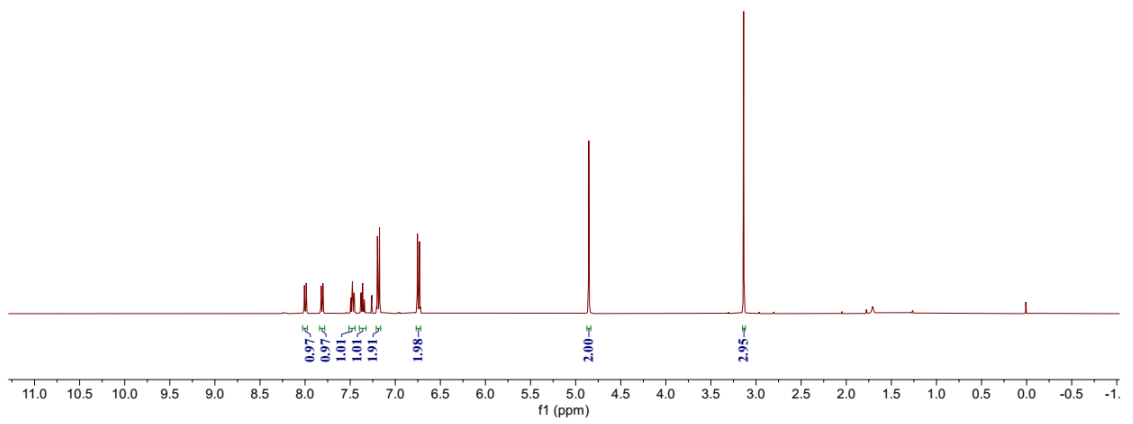
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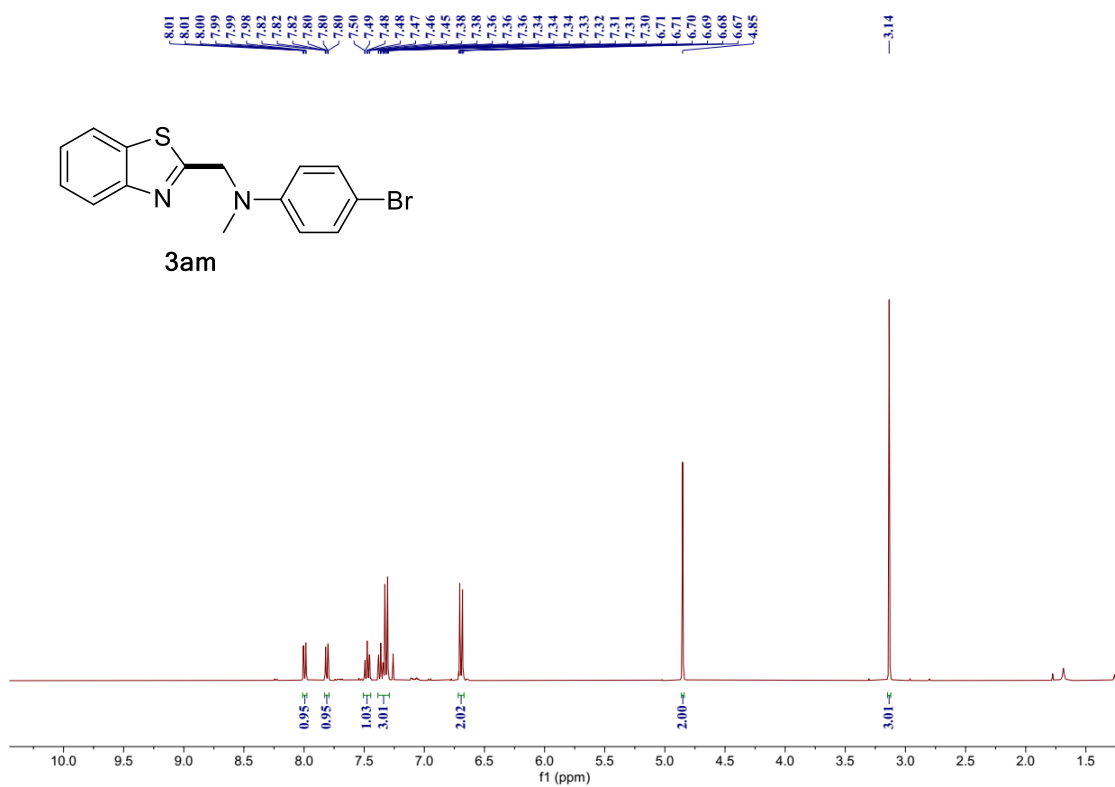
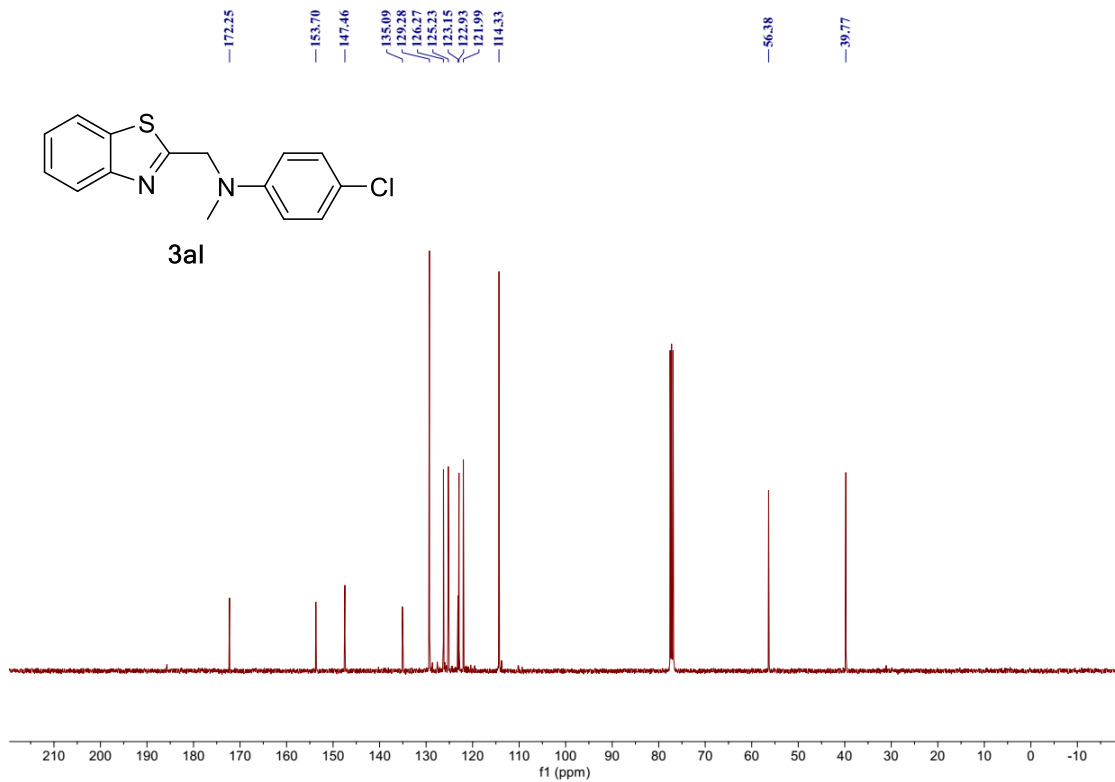


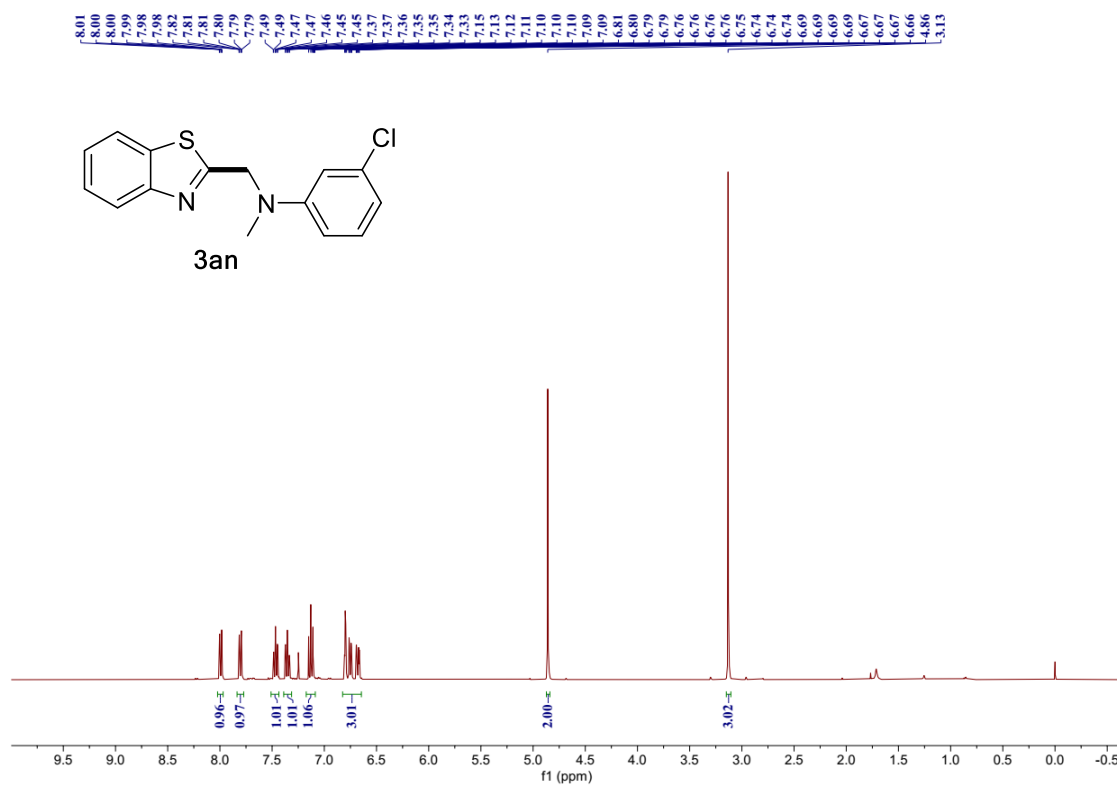
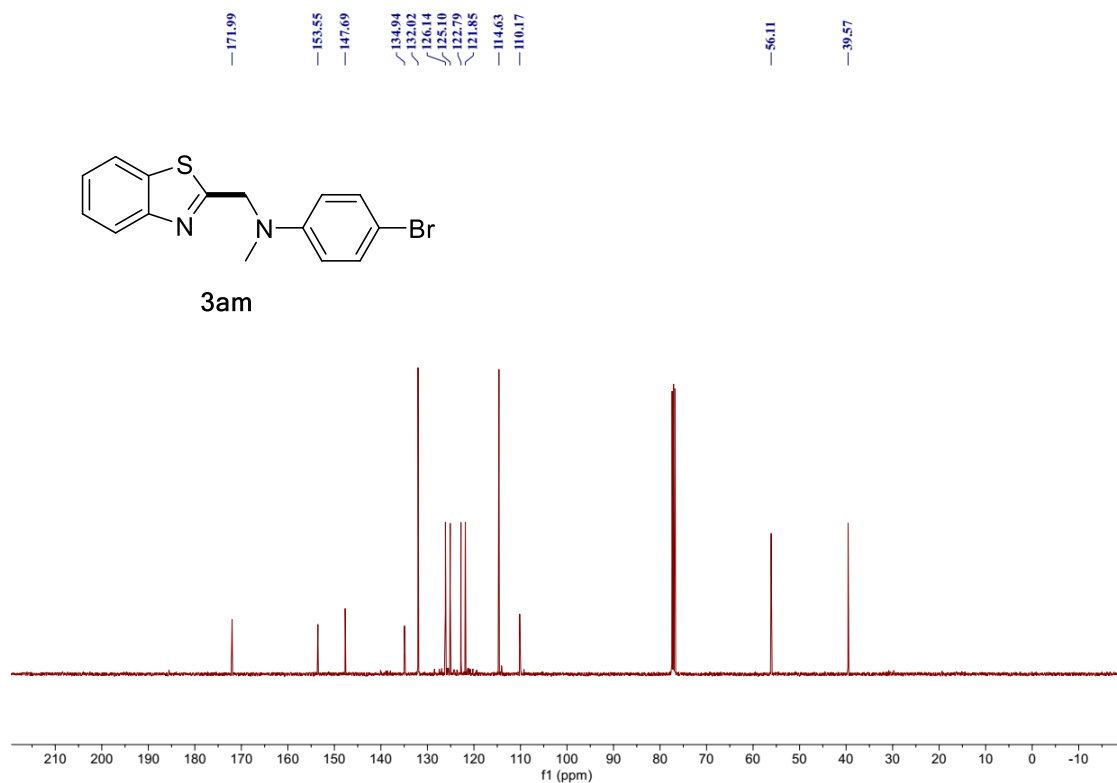
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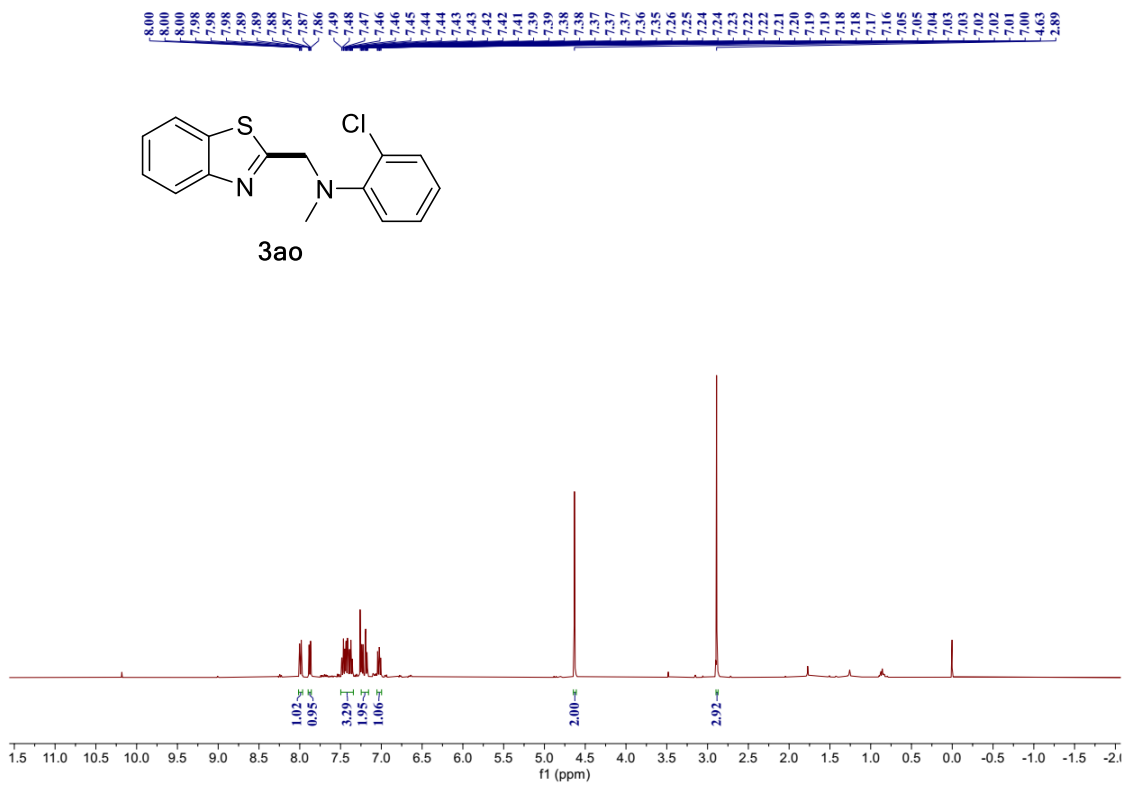
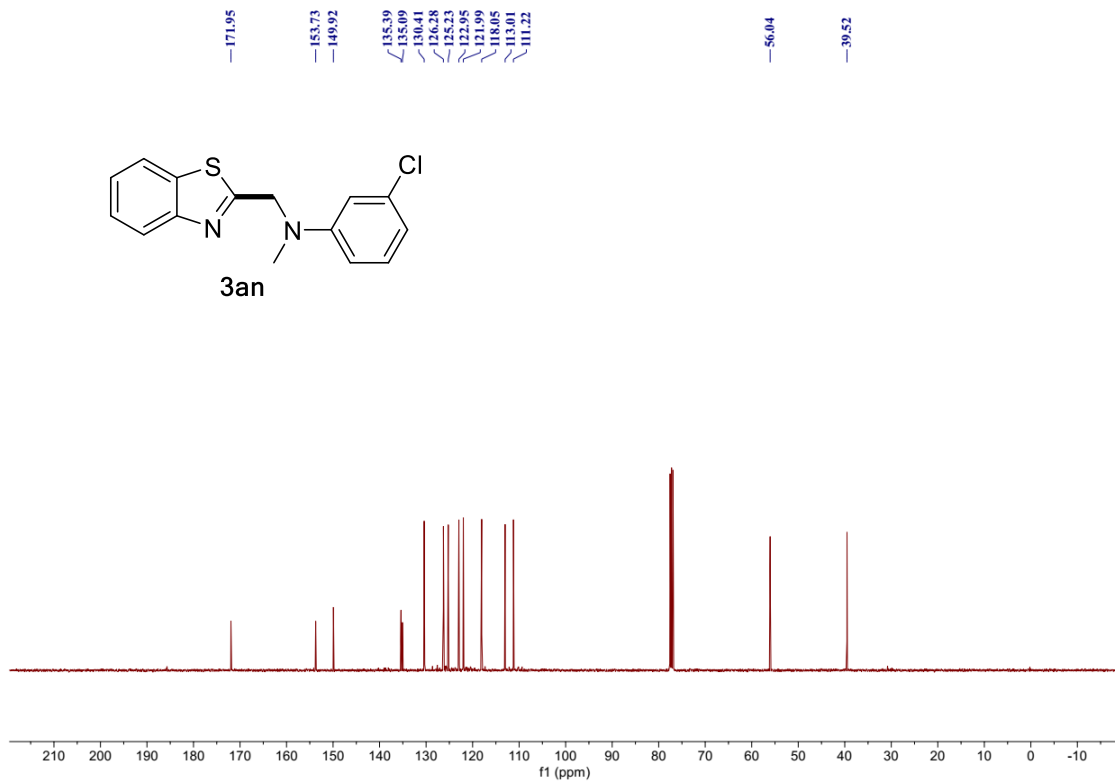
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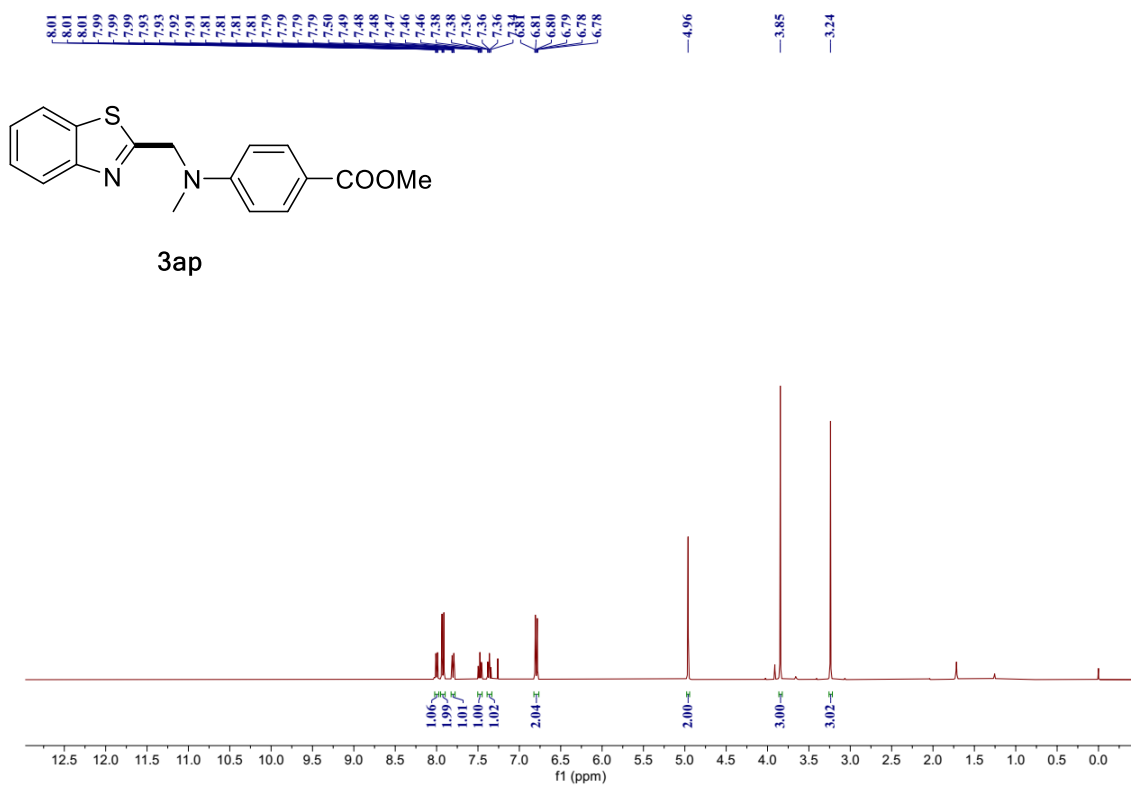
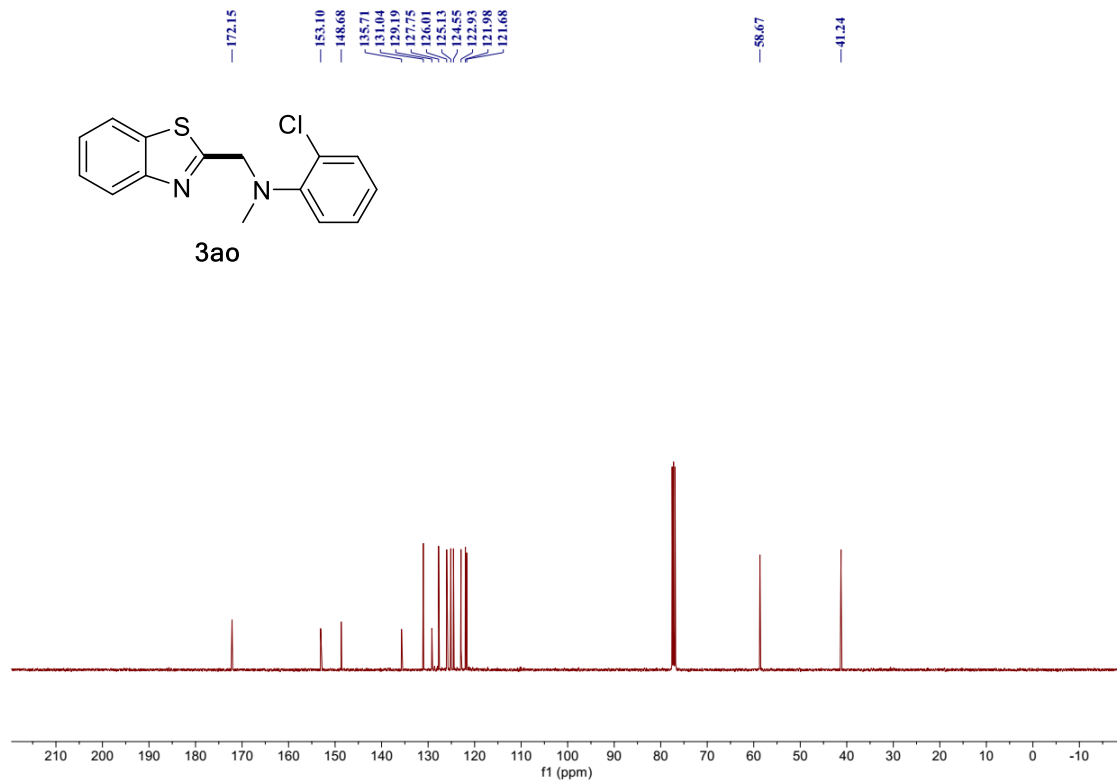
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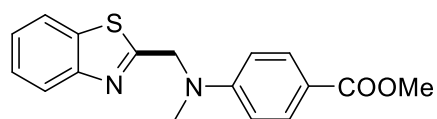




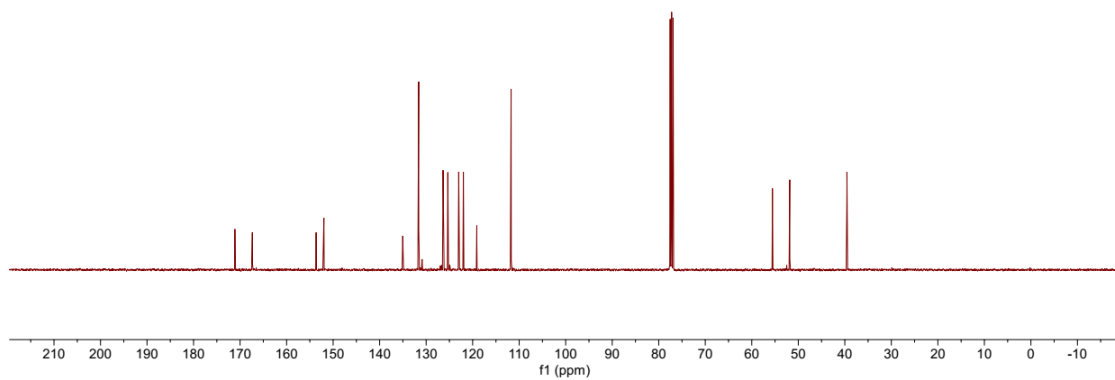


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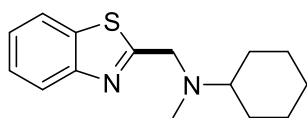
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