Supporting Information

Organic Photoredox Catalytic Amino-heteroarylation of Unactivated Olefins to Access Distal Amino Ketones

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General information

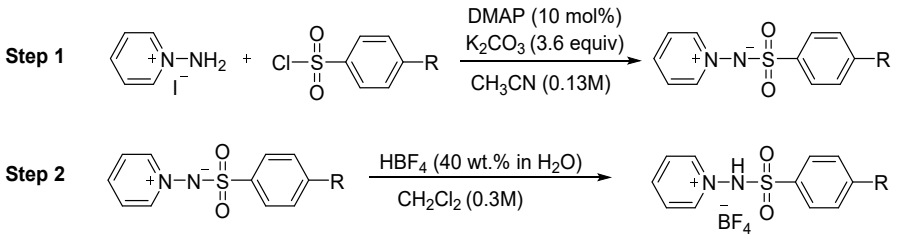
All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography (TLC) plates were visualized by exposure to ultraviolet light and/or staining with phosphomolybdic acid followed by heating on a hot plate. Flash chromatography was carried out using silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 (400 MHz) or Agilent Inova 600 MHz. The spectra were recorded in $CDCl_3$ as solvent at room temperature, ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.00 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q=quartet, m = multiplet, dd = doublet), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported as chemical shift. HRMS were performed on a Bruker Apex II mass instrument (ESI).

Experimental Procedures

1. Synthesis of substrates

1.1 Synthesis of N-protected 1-aminopyridinium salts

N-protected 1-aminopyridinium salts were synthesized according to reported procedures with some modifications.[1]



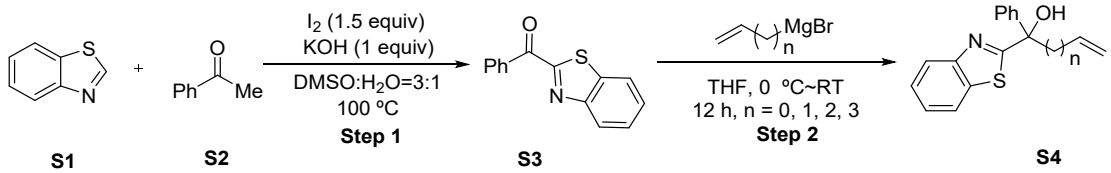
General Procedure:

Step 1: To a mixture of 1-aminopyridinium iodide (1 equiv) and distilled-CH_3CN (0.13 M) were added DMAP (10 mol%), K_2CO_3 (3.6 equiv) and sulfonyl chloride (1 equiv) at 0 °C (ice water bath) under N_2. Then, the cooling bath was removed and the reaction mixture was stirred at rt for 6 h. The suspension was filtered and concentrated in vacuo. The residue was suspended in CH_2Cl_2 and filtered to remove inorganic impurities. After the solvent was removed under reduced pressure, the crude product was purified by silica gel flash column chromatography (CH_2Cl_2/MeOH = 10/1) and washed with a small amount of CH_2Cl_2 to afford aminopyridinium ylide.

Step 2: The ylide product (1 equiv) was diluted with CH_2Cl_2 (0.3M) and tetrafluoroboric acid solution (40 wt.% in H_2O) (1.3 equiv) was added to the solution at rt. The mixture was stirred for 30 min, then the product was precipitated. The mixture was filtered, washed with diethyl ether and pentane, and dried in vacuo. The pure product was obtained as a white solid.

1.2 Synthesis of heteroaryl-substituted tertiary bishomoallylic alcohols

Heteroaryl-substituted tertiary bishomoallylic alcohols were synthesized according to reported procedures with modifications. [2]

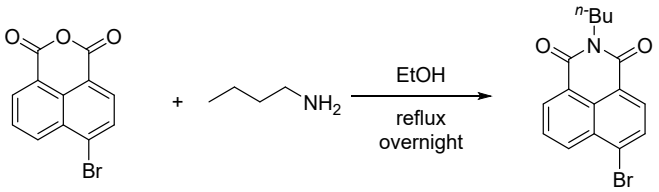


General procedure:

Step 1: A mixture of acetophenone **S2** (1.0 mmol), benzothiazole **S1** (1.5 mmol), I_2 (1.5 mmol), and KOH (1.0 mmol) in solvent 4.0 mL (DMSO/H_2O = 3:1) was stirred at 100 °C (oil bath). After the disappearance of the reactant (monitored by TLC), 50 mL of water was added to the mixture, which was then extracted with ethyl acetate 3 times (3 × 20.0 mL). The extract was washed with $Na_2S_2O_3$ solution, dried over anhydrous Na_2SO_4, and evaporated. The residue was purified by column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1/50) to afford yellow solid **S3** in 78% yield (0.19 g).

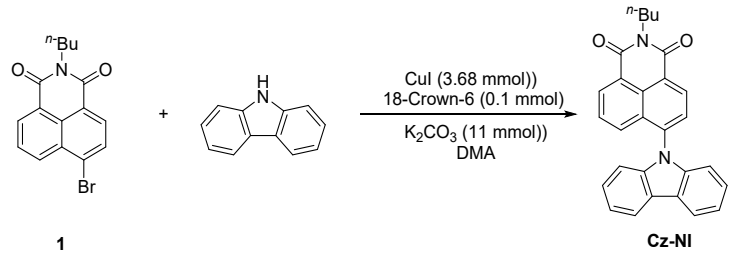
Step 2: To an oven-dried 100 mL double-neck round bottom flask, vinyl magnesium bromide (3.0 equiv) was added dropwise to a solution of ketone **S3** (1.0 equiv) in dry THF (0.2 M) under N_2 atmosphere at 0 °C (ice water bath). The resulting mixture was warmed gradually to room temperature and stirred for 6 – 8 h. After completion of the reaction, the reaction mixture was quenched with a saturated NH_4Cl solution, extracted with ethyl acetate, and dried before being purified on a silica column using an eluent of ethyl acetate/petroleum ether (1/20) to afford the desired product **S4**.

2. Synthesis of Photocatalyst [3]



1

General procedure: 4-Bromo-1,8-naphthalic anhydride (3.0 g, 10.83 mmol) was dissolved in distilled ethanol (150 mL). n-Butylamine (1.28 mL, 12.99 mmol) was added to the solution, and then the solution was refluxed overnight under nitrogen. The solution was cooled and the precipitate was filtered with no further purification. The product was an ivory powder (2.94 g, 82% yield)

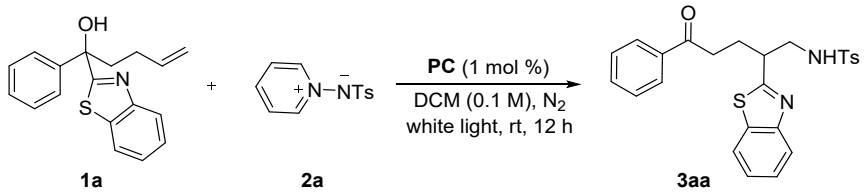


1 Cz-NI

CuI (0.7 g, 3.68 mmol), 18-crown-6 (0.026 g, 0.1 mmol), K_2CO_3 (1.53 g, 11 mmol), carbazole (0.47 g, 2.8 mmol) dissolved in DMA (10 mL) and the mixture was stirred at 165 °C (oil bath) under argon. After 2 h a solution of **1** (0.5 g, 1.4 mmol) in hot DMA (5 mL) was added into the mixture slowly. The final mixture was heated to reflux for 16 h. The reaction solution was poured into 500 ml of ice water and the precipitated crude product was collected, dried and purified by column chromatography (silica gel, 1/20; PE/EA). Cz-NI was obtained as a yellow solid in 43% yield; mp = 136 – 137 ˚C.

3. Screening of Reaction Conditions

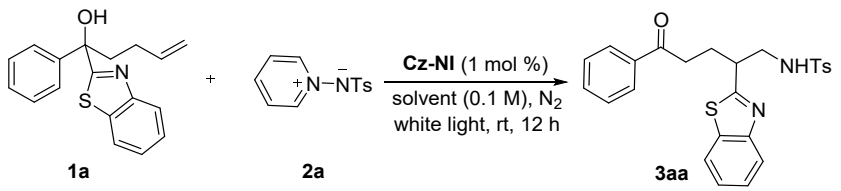
Table S1. Optimization of the photocatalyst. [a]



Entry	PC (mol %)	Yield (%) [b]
1	**Cz-NI**	44
2	4CzIPN	19
3	$Ir(ppy)_3$	27
4	$Ru(bpy)_3(PF_6)_2$	4
5	$[Ir(dtbbpy)(ppy)_2]PF_6$	34

[a] Reaction condition: **1a** (0.1 mmol), **2a** (0.1 mmol), and PC (1 mol %) in DCM (1 mL) at 25 °C for 12 h under irradiation with white light. [b] Isolated yield.

Table S2. Optimization of solvent. [a]

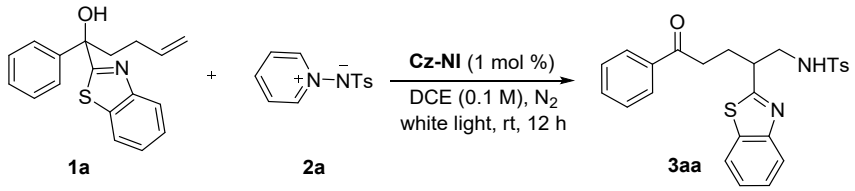


Entry	Solvent	Yield (%) [b]
1	THF	26

2	$CHCl_3$	52
3	DCE	55
4	n-hexane	14
5	CH_3CN	11
6	CCl_4	Trace
7	EA	Trace

[a] Reaction condition: **1a** (0.1 mmol), **2a** (0.1 mmol), and **Cz-NI** (1 mol %) in Solvent (1 mL) at 25 ºC for 12 h under irradiation with white light. [b] Isolated yield.

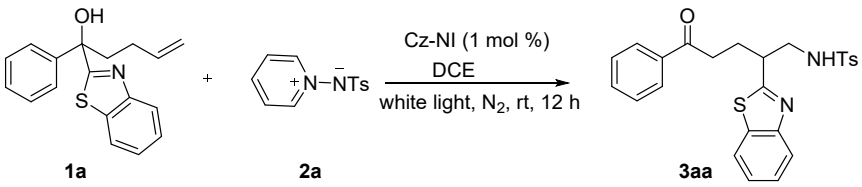
Table S3. Optimization of the loading of **1a**. [a]



Entry	1a	Yield (%) [b]
1	1.2 equiv	67
2	1.4 equiv	81
3	1.5 equiv	83
4	1.6 equiv	84
5	1.8 equiv	77

[a] Reaction condition: **1a**, **2a** (0.1 mmol), and **Cz-NI** (1 mol %) in DCE (1 mL) at 25 ºC for 12 h under irradiation with white light. [b] Isolated yield.

Table S4. Optimization of concentration. [a]

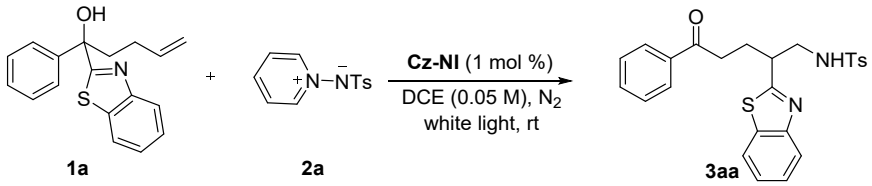


Entry	DCE	Yield (%) [b]

1	0.5 ml	84
2	2 ml	91
3	4 ml	92
4	6 ml	84

[a] Reaction condition: **1a** (0.16 mmol), **2a** (0.1 mmol), and **Cz-NI** (1 mol %) in DCE at 25 ºC for 12 h under irradiation with white light. [b] Isolated yield.

Table S5. Optimization of reaction time. [a]



Entry	Time	Yield (%) [b]
1	6 h	60
2	8 h	81
3	9 h	96
4	10 h	92
5	12 h	91
6	18 h	90
7	24 h	91

[a] Reaction condition: **1a** (0.16 mmol), **2a** (0.1 mmol), and **Cz-NI** (1 mol %) in DCE (2 ml) at 25 ºC under irradiation with white light. [b] Isolated yield.

4. General procedure for the synthesis of products and analytical data

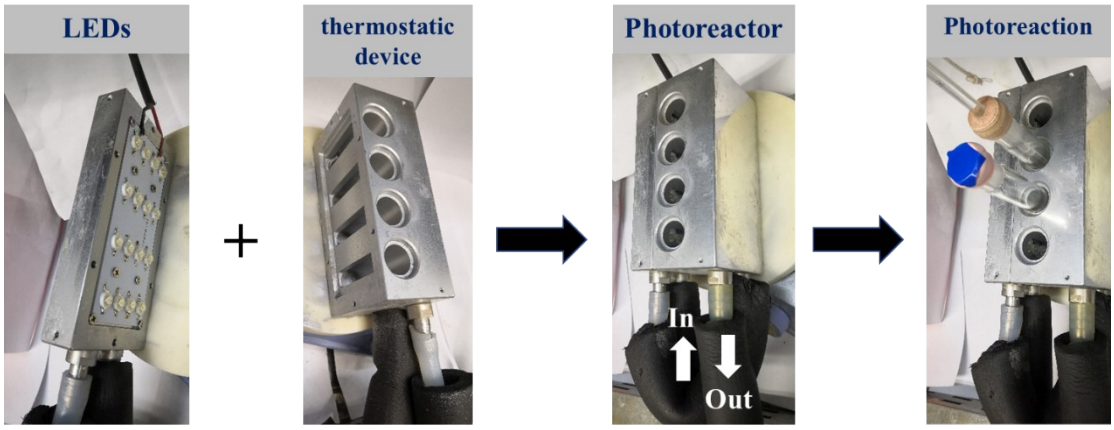
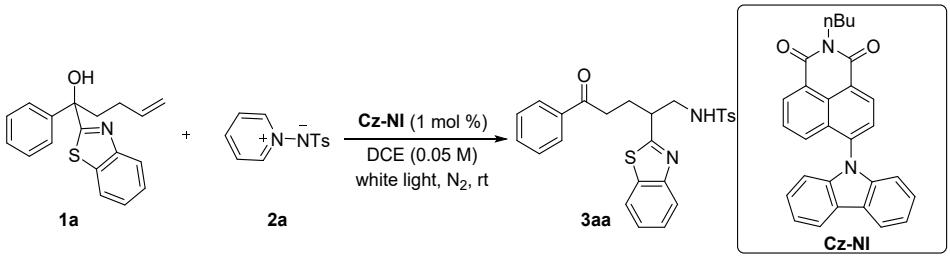
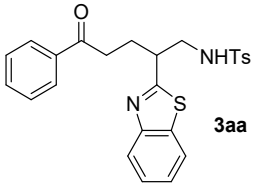


Figure S1. Thermostatic photoreaction device



General catalysis procedure: A dried 10 mL reaction tube was charged with the photocatalyst (0.001 mmol, 0.42 mg), the heteroaryl-substituted tertiary bishomoallylic alcohol **1a** (0.16 mmol, 1.6 equiv), N-protected 1-aminopyridinium **2a** (0.1 mmol, 1 equiv) and 2.0 mL DCE. The reaction mixture was degassed by three cycles of freeze-pump-thaw. After the mixture was thoroughly degassed, the vial was placed beside a white LED light. The reaction was stirred at 25 °C for 9 h. After completion of the reaction as checked by TLC. The reaction mixture was purified by silica gel flash column chromatography (petroleum ether/EtOAc) to give the corresponding product **3aa.**

N-(2-(benzo[*d*]thiazol-2-yl)-5-oxo-5-phenylpentyl)-4-methylbenzenesulfonamide (3aa)



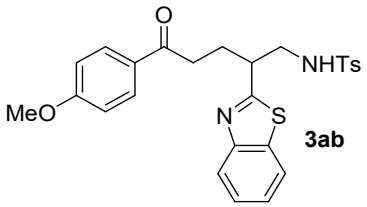
Following the general procedure, compound **3aa** was obtained as a yellow oil in 96% yield (44.6 mg); R_f = 0.48 (PE/EA = 1/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (dd, *J* = 13.7, 5.2 Hz, 3H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 2H), 7.57 – 7.49 (m, 1H), 7.48 – 7.30 (m, 4H), 7.18 (d, *J* = 6.6 Hz, 2H), 5.91 – 5.69 (m, 1H), 3.69 – 3.15 (m, 3H), 3.08 – 2.86 (m, 2H), 2.34 (s, 3H), 2.27 (dd, *J* = 12.8, 6.7 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 198.9, 172.3, 152.7, 143.3, 136.7, 136.5, 134.5, 133.2, 129.6, 128.6, 128.0, 126.9, 126.2, 125.2, 122.8, 121.6, 45.8, 42.9, 35.2, 26.9, 21.4.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{25}N_2O_3S_2$ 465.1301, found: 465.1304.

N-(2-(benzo[*d*]thiazol-2-yl)-5-oxo-5-(4-methoxylphenylpentyl))-4-methylbenzenesulfonamide (3ab)



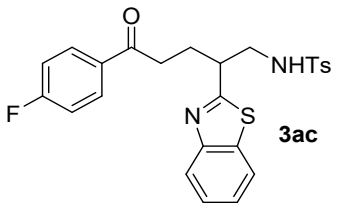
Following the general procedure, compound **3ab** was obtained as a white solid in 85% yield (42.0 mg); mp= 111 – 112 °C; R_f = 0.36 (PE/EA = 1/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.91 – 7.86 (m, 2H), 7.85 – 7.80 (m, 1H), 7.73 – 7.67 (m, 2H), 7.48 (m, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.38 (m, *J* = 8.2, 7.2, 1.2 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.94 – 6.87 (m, 2H), 5.67 (d, *J* = 6.0 Hz, 1H), 3.86 (s, 3H), 3.49 – 3.36 (m, 3H), 2.99 (t, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 2.27 (m, *J* = 6.8, 4.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 197.5, 172.5, 163.6, 152.7, 143.3, 136.8, 134.6, 130.3, 129.7, 128.6 127.9, 126.2, 125.2, 122.8, 121.6, 114.1, 77.3, 77.0, 76.7, 55.4, 45.8, 42.9, 34.81, 27.1, 21.4.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{27}N_2O_4S_2$ 495.1407, found:495.1409.

N-(2-(benzo[*d*]thiazol-2-yl)-5-oxo-5-(4-flurophenylpentyl))-4-methylbenzenesulfonamide (3ac)



Following the general procedure, compound **3ac** was obtained as a yellow solid in 80% yield (38.6 mg); mp = 104 – 105 °C; R_f = 0.55 (PE/EA = 1/1).

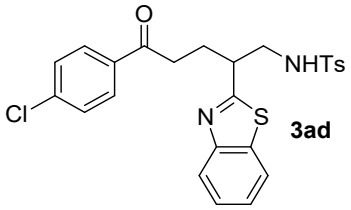
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 2.4 Hz, 1H), 7.94 – 7.90 (m, 2H), 7.83 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.48 (m, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.39 (m, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.14 – 7.07 (m, 2H), 5.60 (t, *J* = 5.9 Hz, 1H), 3.51 – 3.37 (m, 3H), 3.03 (t, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 2.29 (m, *J* = 7.0, 2.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 197.4, 172.2, 166.3 (C-F, $J_{C\text{-}F}$ = 253.4), 152.7, 143.4, 136.7, 134.5, 132.8 (C-F, $J_{C\text{-}F}$ = 4.1), 130.6 (C-F, $J_{C\text{-}F}$ = 8.3), 129.6, 126.9, 126.3 (C-F, $J_{C\text{-}F}$ = 19.8), 125.2, 122.8, 121.6, 115.6 (C-F, $J_{C\text{-}F}$ = 20.6), 45.9, 42.9, 35.1, 26.9, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -104.85.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{24}FN_2O_3S_2$ 483.1207, found: 483.1209.

N-(2-(benzo[*d*]thiazol-2-yl)-5-oxo-5-(4-chlorophenylpentyl))-4-methylbenzenesulfonamide (3ad)



Following the general procedure, compound **3ad** was obtained as a yellow solid in 85% yield (42.4 mg); mp = 131 – 132 °C; R_f = 0.61(PE/EA = 2/1).

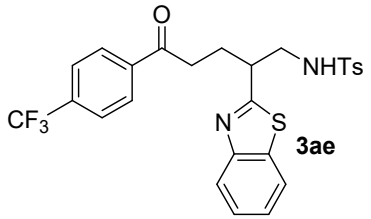
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.8 Hz, 1H), 7.89 – 7.80 (m, 3H), 7.74 – 7.67 (m, 2H), 7.49 (m, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.45 – 7.35 (m, 3H), 7.22 (d, *J* = 8.1 Hz, 2H), 5.57 (t, *J* = 6.0 Hz, 1H), 3.51 – 3.36 (m, 3H), 3.03 (t, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 2.29 (m, *J* = 7.0, 2.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 197.8, 172.2, 152.7, 143.4, 139.7, 136.7, 134.8, 134.5, 129.6, 129.4, 128.9, 126.9, 126.2, 125.2, 122.8, 121.6, 45.9, 42.9, 35.2, 26.9, 21.4.

$C_{25}H_{24}ClN_2O_3S_2$ 499.0911, found: 499.0915.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{24}ClN_2O_3S_2$ 499.0911, found: 499.0915.

N-(2-(benzo[*d*]thiazol-2-yl)-5-oxo-5-(4-trifluoromethylphenylpentyl))-4-methylbenzenesulfonamide (3ae)



Following the general procedure, compound **3ae** was obtained as a gray solid in 90% yield (47.9 mg); mp = 156 – 157 °C; R_f = 0.54 (PE/EA = 2/1).

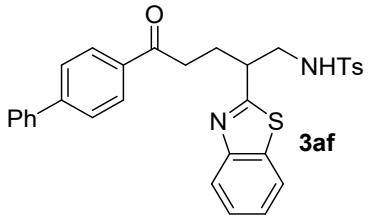
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.1 Hz, 2H), 7.95 – 7.89 (m, 1H), 7.83 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.74 – 7.66 (m, 4H), 7.47 (m, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.38 (td, *J* = 7.6, 1.2 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.67 (t, *J* = 6.1 Hz, 1H), 3.46 (m, *J* = 12.6, 6.3, 4.2 Hz, 3H), 3.08 (t, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 2.31 (q, *J* = 7.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 198.1, 172.1, 152.7, 143.4, 139.1, 136.8, 134.9 (C-F, $J_{C\text{-}F}$ =32.9), 134.5, 129.7, 128.4, 126.9, 126.2, 125.7 (C-F, $J_{C\text{-}F}$ =3.3), 122.9, 121.6, 45.9, 42.9, 35.6, 26.9, 21.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ -63.14.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{24}F_3N_2O_3S_2$ 533.1175, found: 533.1179.

N-(2-(benzo[*d*]thiazol-2-yl)-5-oxo-5-Biphenyl)-4-methylbenzenesulfonamide (3af)



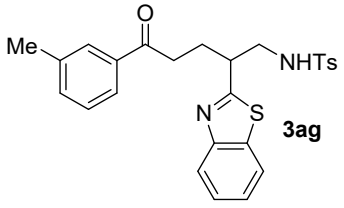
Following the general procedure, compound **3af** was obtained as a white solid in 84% yield (45.4 mg); mp = 131 – 132 °C; R_f = 0.51 (PE/EA = 1/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.99 – 7.94 (m, 2H), 7.95 – 7.91 (m, 1H), 7.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.73 – 7.69 (m, 2H), 7.66 – 7.63 (m, 2H), 7.60 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.49 – 7.44 (m, 3H), 7.41 – 7.36 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.71 (q, *J* = 6.0, 5.5 Hz, 1H), 3.51 – 3.39 (m, 3H), 3.07 (t, *J* = 6.9 Hz, 2H), 2.35 (s, 3H), 2.30 (m, *J* = 12.1, 7.0 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 198.6, 172.3, 152.7, 145.8, 143.3, 139.7, 136.7, 135.1, 134.5, 129.6, 128.9, 128.6, 128.2, 127.2, 126.9, 126.1, 125.1, 122.8, 121.6, 77.2, 77.0, 76.7, 45.9, 43.0, 35.2, 27.0, 21.4.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{31}H_{29}N_2O_3S_2$ 541.1614, found: 541.1614.

N-(2-(benzo[*d*]thiazol-2-yl)-5-oxo-5-(3-methylphenylpentyl))-4-methylbenzenesulfonamide (3ag)



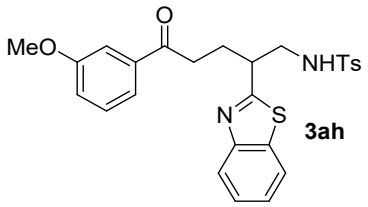
Following the general procedure, compound **3ag** was obtained as a yellow oil in 93% yield (44.5 mg); R_f = 0.53 (PE/EA = 2/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96 – 7.90 (m, 1H), 7.84 – 7.80 (m, 1H), 7.72 – 7.66 (m, 4H), 7.47 (m, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 5.69 (t, *J* = 6.0 Hz, 1H), 3.48 – 3.37 (m, 3H), 3.02 (t, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 2.35 (s, 3H), 2.26 (m, *J* = 16.1, 9.3, 8.1 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 199.2, 172.3, 152.7, 143.3, 138.3, 136.7, 136.5, 134.0, 133.9, 129.7, 129.5, 128.5, 127.0, 126.9, 126.8, 125.2, 122.8, 121.6, 77.2, 77.0, 76.8, 45.9, 43.0, 35.2, 27.0, 21.4, 21.2.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{27}N_2O_3S_2$ 479.1458, found: 479.1459.

N-(2-(benzo[*d*]thiazol-2-yl)-5-oxo-5-(3-methoxylhenylpentyl))-4-methylbenzenesulfonamide (3ah)



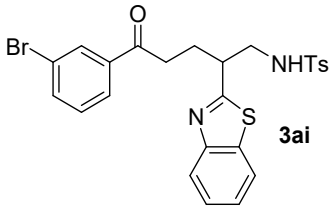
Following the general procedure, compound **3ah** was obtained as a yellow oil in 94% yield (46.4 mg); R_f = 0.45 (PE/EA = 2/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.93 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.83 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.72 – 7.67 (m, 2H), 7.50 – 7.44 (m, 2H), 7.43 (dd, *J* = 2.7, 1.6 Hz, 1H), 7.38 (m, *J* = 8.2, 7.2, 1.2 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.09 (m, *J* = 8.2, 2.7, 1.0 Hz, 1H), 5.64 (t, *J* = 5.9 Hz, 1H), 3.83 (s, 3H), 3.48 – 3.38 (m, 3H), 3.06 – 2.99 (m, 2H), 2.36 (s, 3H), 2.28 (m, *J* = 6.9 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 198.8, 172.3, 159.8, 152.7, 143.3, 137.8, 136.7, 134.5, 129.7, 129.6, 126.9, 126.2, 125.2, 122.8, 121.6, 120.6, 119.7, 112.2, 55.4, 45.9, 42.9, 35.3, 27.0, 21.4.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{27}N_2O_4S_2$ 495.1407, found: 495.1411.

N-(2-(benzo[*d*]thiazol-2-yl)-5-oxo-5-(3-bromophenylpentyl))-4-methylbenzenesulfonamide (3ai)



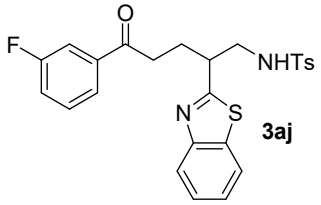
Following the general procedure, compound **3ai** was obtained as a yellow oil in 78% yield (42.3 mg); R_f = 0.42 (PE/EA = 1/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (t, *J* = 1.9 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.82 (td, *J* = 7.2, 6.5, 1.2 Hz, 2H), 7.72 – 7.68 (m, 2H), 7.66 (dt, *J* = 8.1, 1.2 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.40 – 7.35 (m, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.66 (t, *J* = 6.0 Hz, 1H), 3.51 – 3.36 (m, 3H), 3.00 (t, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 2.28 (q, *J* = 6.9 Hz, 2H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 197.6, 172.1, 152.7, 143.4, 138.2, 136.7, 136.1, 134.5, 131.0, 130.2, 129.7, 126.9, 126.6, 126.2, 125.3, 122.9, 122.8, 121.6, 45.9, 42.9, 35.3, 26.8, 21.5.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{24}BrN_2O_3S_2$ 543.0406, found: 543.0409.

N-(2-(benzo[*d*]thiazol-2-yl)-5-oxo-5-(3-flurophenylpentyl))-4-methylbenzenesulfonamide (3aj)



Following the general procedure, compound **3aj** was obtained as a yellow solid in 87% yield (42.0 mg); mp = 92 – 93 °C; R_f = 0.49 (PE/EA = 1/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.69 (dd, *J* = 10.9, 8.1 Hz, 3H), 7.57 (dt, *J* = 9.5, 2.1 Hz, 1H), 7.55 – 7.44 (m, 1H), 7.39 (m, *J* = 7.9, 1.9 Hz, 2H), 7.25 (d, *J* = 2.6 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 5.63 (t, *J* = 6.0 Hz, 1H), 4.20 – 3.34 (m, 3H), 3.42 – 2.76 (m, 2H), 2.36 (s, 3H), 2.28 (m, *J* = 7.0, 2.0 Hz, 2H).

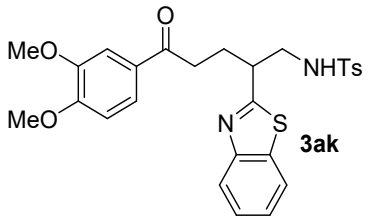
^{13}C NMR (101 MHz, $CDCl_3$): δ 197.7, 172.1, 162.8 (C-F, 1 J_{C-F} = 248.0 Hz), 152.7, 143.4, 138.5 (C-F, 3 J_{C-F} = 6.1 Hz), 136.7, 134.5, 130.3 (C-F, 3J_{C-F} = 7.6 Hz), 129.6,

126.9, 126.2, 125.2, 123.8 (C-F, 4 J_{C-F} = 3.1 Hz), 122.8, 121.6, 120.2 (C-F, 2 J_{C-F} = 21.6 Hz), 114.7 (C-F, 2 J_{C-F} = 22.3 Hz), 45.9, 42.9, 35.4, 26.8, 21.4.

^{19}F NMR (565 MHz, $CDCl_3$): δ -111.67, -111.68, -111.69, -111.70.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{24}FN_2O_3S_2$ 483.1207, found: 483.1209.

N-(2-(benzo[*d*]thiazol-2-yl)-5-oxo-5-(3,4-bimethoxylphenylpentyl))-4-methylbenzenesulfonamide (3ak)



3ak

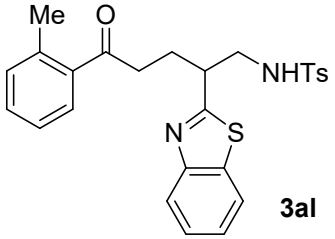
Following the general procedure, compound **3ak** was obtained as a yellow oil in 81% yield (42.5 mg); R_f = 0.41 (PE/EA = 1/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92 (dd, *J* = 19.0, 8.3 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.54 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.41 – 7.37 (m, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 1H), 5.67 (q, *J* = 6.1 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.54 – 3.37 (m, 3H), 3.03 (t, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 2.35 – 2.22 (m, *J* = 7.0 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 197.7, 172.4, 153.4, 152.7, 149.0, 143.3, 136.8, 134.7, 134.6, 133.2, 129.8, 129.6, 126.9, 126.2, 125.2, 122.8, 121.6, 110.0, 56.1, 55.9, 45.8, 43.0, 34.7, 27.3, 21.4.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{27}H_{29}N_2O_5S_2$ 525.1512, found: 525.1515.

N-(2-(benzo[*d*]thiazol-2-yl)-5-oxo-5-(o-tolyl)pentyl)-4-methylbenzenesulfonamide



3al

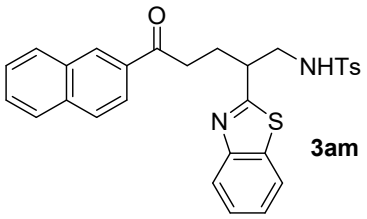
Following the general procedure, compound **3al** was obtained as a yellow oil in 31% yield (14.8 mg); R_f = 0.41 (PE/EA = 2/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.87 – 7.75 (m, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.57 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.47 (ddd, J = 8.3, 7.2, 1.3 Hz, 1H), 7.43 – 7.31 (m, 2H), 7.21 (dd, *J* = 9.5, 7.5 Hz, 4H), 5.68 (t, *J* = 6.2 Hz, 1H), 3.53 – 3.27 (m, 3H), 2.96 (t, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 202.7, 172.2, 152.7, 143.3, 138.2, 137.2, 134.5, 131.9, 131.4, 129.6, 128.5, 126.9, 126.3, 126.1, 125.7, 125.1, 122.7, 121.5, 77.2, 77.0, 76.6, 46.0, 43.0, 37.9, 27.1, 21.4, 21.3.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{27}N_2O_3S_2$ 479.1458, found: 479.1456.

N-(2-(benzo[*d*]thiazol-2-yl)-5-oxo-5-Naphthyl)-4-methylbenzenesulfonamide (3am)



3am

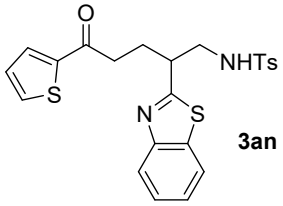
Following the general procedure, compound **3am** was obtained as a yellow oil in 67% yield (34.5 mg); R_f = 0.51 (PE/EA = 1/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, *J* = 1.7 Hz, 1H), 8.01 – 7.89 (m, 3H), 7.90 – 7.75 (m, 3H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.60 (m, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.54 (m, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.48 (m, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.38 (td, *J* = 7.7, 1.2 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 5.66 (t, *J* = 5.9 Hz, 1H), 3.47 (pd, *J* = 7.1, 4.5 Hz, 3H), 3.19 (t, *J* = 7.1 Hz, 2H), 2.43 – 2.28 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 199.0, 172.3, 152.7, 143.3, 136.8, 135.6, 134.6, 133.8, 132.4, 129.8, 129.6, 129.6, 128.5, 128.4, 127.7, 127.0, 126.8, 126.2, 125.2, 123.6, 122.8, 121.6, 45.8, 43.0, 35.3, 27.2, 21.4.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{29}H_{27}N_2O_3S_2$ 515.1458, found: 515.1460.

N-(2-(benzo[*d*]thiazol-2-yl)-5-oxo-5-thienyl)-4-methylbenzenesulfonamide (3an)



3an

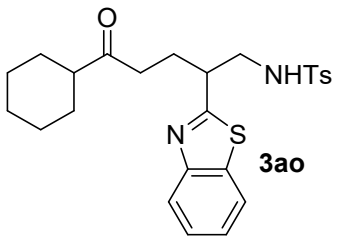
Following the general procedure, compound **3an** was obtained as a yellow oil in 61% yield (28.7 mg); R_f = 0.33 (PE/EA = 2/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 3.8 Hz, 1H), 7.63 (d, *J* = 5.1 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.11 (t, *J* = 4.3 Hz, 1H), 5.65 – 5.58 (m, 1H), 3.51 – 3.38 (m, 3H), 3.00 (t, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 2.28 (dh, *J* = 21.1, 7.0 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 191.9, 172.2, 152.7, 143.8, 143.4, 136.8, 134.5, 133.8, 132.2, 129.6, 128.1, 126.9, 126.2, 125.2, 122.8, 121.6, 45.7, 42.8, 35.8, 27.2, 21.4.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{23}N_2O_3S_3$ 471.0865, found: 471.0868.

N-(2-(benzo[*d*]thiazol-2-yl)-5-oxo-5-Cyclohexyl)-4-methylbenzenesulfonamide (3ao)



3ao

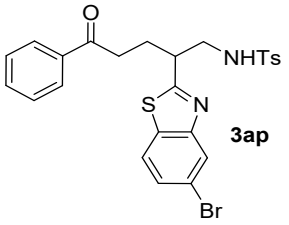
Following the general procedure, compound **3ao** was obtained as a yellow oil in 62% yield (29.2 mg); R_f = 0.48 (PE/EA = 2/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 – 7.89 (m, 1H), 7.84 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.48 (m, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.39 (td, *J* = 7.6, 7.2, 1.2 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 5.56 (t, *J* = 5.9 Hz, 1H), 3.53 – 3.18 (m, 3H), 2.51 (t, *J* = 7.0 Hz, 2H), 2.39 (s, 3H), 2.32 – 2.21 (m, 1H), 2.14 – 2.04 (m, 2H), 1.75 (tq, *J* = 6.2, 3.1 Hz, 4H), 1.70 – 1.61 (m, 2H), 1.39 – 1.12 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 213.0, 172.3, 152.7, 143.3, 136.8, 134.5, 129.6, 126.9, 126.1, 125.1, 122.8, 121.6, 50.7, 45.8, 42.9, 37.1, 28.4, 26.4, 25.7, 25.5, 21.48.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{31}N_2O_3S_2$ 471.1771, found: 471.1772.

N-(2-(5-bromobenzo[*d*]thiazol-2-yl)-5-oxo-5-phenylpentyl)-4-methylbenzenesulfonamide (3ap)



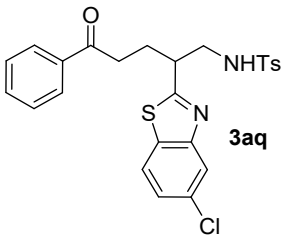
Following the general procedure, compound **3ap** was obtained as a white solid as in 70% yield (38.1 mg); mp = 154 – 155 °C; R_f = 0.42 (PE/EA = 2/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 1.8 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.69 (t, *J* = 8.2 Hz, 3H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.51 – 7.40 (m, 3H), 7.28 – 7.18 (m, 2H), 5.60 (t, *J* = 6.2 Hz, 1H), 3.43 (m, *J* = 10.2, 6.8 Hz, 3H), 3.04 (td, *J* = 6.9, 1.5 Hz, 2H), 2.37 (s, 3H), 2.27 (q, *J* = 8.3, 7.1 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 197.9, 173.2, 152.9, 142.4, 135.8, 135.4, 132.4, 132.3, 128.6, 127.6, 127.3, 127.0, 125.9, 125.4, 121.6, 118.8, 44.7, 42.1, 34.1, 25.9, 20.4.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{24}BrN_2O_3S_2$ 543.0406, found: 543.0410.

N-(2-(5-chlorobenzo[*d*]thiazol-2-yl)-5-oxo-5-phenylpentyl)-4-methylbenzenesulfonamide (3aq)



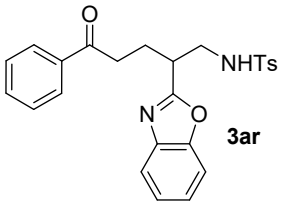
Following the general procedure, compound **3aq** was obtained as a yellow solid in 89% yield (44.4 mg); mp = 124 – 125 °C; R_f = 0.50 (PE/EA = 2/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.87 (d, *J* = 2.0 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.58 – 7.52 (m, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.34 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.65 (t, *J* = 6.2 Hz, 1H), 3.50 – 3.37 (m, 3H), 3.04 (td, *J* = 7.0, 2.5 Hz, 2H), 2.36 (s, 3H), 2.27 (m, *J* = 7.1, 2.4 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 198.9, 174.5, 153.6, 143.4, 136.8, 136.5, 133.3, 132.9, 132.2, 129.7, 128.6, 128.0, 127.0, 125.7, 122.7, 122.3, 45.9, 43.3, 35.1, 26.9, 21.5.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{24}ClN_2O_3S_2$ 499.0911, found: 499.0913.

N-(2-(benzoxazole-2-yl)-5-oxo-5-phenylpentyl)-4-methylbenzenesulfonamide (3ar)



3ar

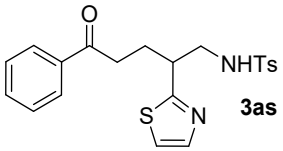
Following the general procedure, compound **3ar** was obtained as a yellow oil in 58% yield (26.1 mg); R_f = 0.31 (PE/EA = 2/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91 – 7.86 (m, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.42 (m, *J* = 8.6, 6.0, 2.0 Hz, 2H), 7.30 (m, *J* = 5.4, 2.9, 2.5 Hz, 5H), 7.23 – 7.19 (m, 2H), 5.76 (dd, *J* = 28.9, 14.5 Hz, 1H), 3.48 (dt, *J* = 13.9, 7.1 Hz, 3H), 3.36 (m, *J* = 7.2, 5.0 Hz, 2H), 3.05 (m, *J* = 8.8, 5.6, 1.9 Hz, 3H), 2.36 (s, 1H), 2.23 (m, *J* = 14.0, 6.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 198.8, 166.6, 150.4, 143.3, 140.5, 136.8, 136.4, 134.0, 133.2, 129.6, 128.5, 127.9, 126.9, 125.0, 124.4, 119.7, 110.5, 77.2, 77.0, 76.7, 44.3, 38.8, 35.1, 24.5, 21.4.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{25}N_2O_4S$ 449.1530, found: 449.1531.

N-(2-(thiazol-2-yl)-5-oxo-5-phenylpentyl)-4-methylbenzenesulfonamide (3as)



3as

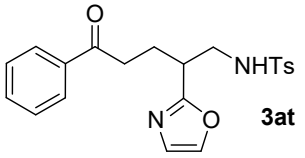
Following the general procedure, compound **3as** was obtained as a yellow oil in 70% yield (29.0 mg); R_f = 0.35 (PE/EA = 1/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 – 7.87 (m, 2H), 7.75 – 7.70 (m, 2H), 7.68 (d, *J* = 3.3 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.48 – 7.42 (m, 2H), 7.29 – 7.25 (m, 2H), 7.24 (d, *J* = 3.3 Hz, 1H), 5.71 – 5.64 (m, 1H), 3.43 – 3.28 (m, 3H), 3.00 (t, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 2.21 (q, *J* = 6.9 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 199.1, 171.4, 143.3, 142.3, 136.9, 136.5, 133.2, 129.7, 128.6, 128.0, 127.0, 118.7, 46.0, 41.8, 35.1, 27.2, 21.4.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{23}N_2O_3S_2$ 415.1145, found: 415.1147.

N-(2-(oxazole-2-yl)-5-oxo-5-phenylpentyl)-4-methylbenzenesulfonamide (3at)



3at

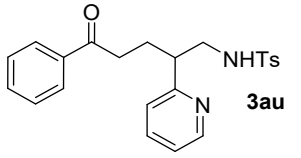
Following the general procedure, compound **3at** was obtained as a yellow solid in 79% yield (31.5 mg); mp = 114 – 115 °C; R_f = 0.54 (PE/EA = 1/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.60 – 7.53 (m, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.24 (m, 1H), 6.99 (d, *J* = 9.7 Hz, 1H), 5.62 (t, *J* = 6.5 Hz, 1H), 3.38 – 3.25 (m, 2H), 3.24 – 3.14 (m, 1H), 3.00 (t, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 2.16 (m, *J* = 34.9, 14.1, 7.1 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 198.9, 164.7, 143.4, 138.8, 136.9, 136.5, 133.2, 129.74, 128.6, 128. 0, 127.0, 126.7, 44.4, 38.2, 35.1, 24.7, 21.4.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{23}N_2O_4S$ 399.1373, found: 399.1375.

N-(2-(pyridine-2-yl)-5-oxo-5-phenylpentyl)-4-methylbenzenesulfonamide (3au)



3au

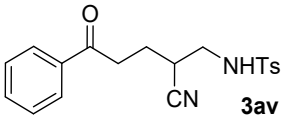
Following the general procedure, compound **3au** was obtained as a yellow oil in 74% yield (30.3 mg); R_f = 0.32 (PE/EA = 1/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (dt, *J* = 4.7, 1.5 Hz, 1H), 7.91 – 7.84 (m, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.63 – 7.51 (m, 2H), 7.44 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.15 (m, *J* = 7.6, 4.9, 1.2 Hz, 1H), 7.10 (dd, *J* = 7.9, 1.1 Hz, 1H), 5.88 (t, *J* = 6.4 Hz, 1H), 3.37 (dt, *J* = 12.4, 7.1 Hz, 1H), 3.25 (m, *J* = 12.4, 5.2, 3.9 Hz, 1H), 3.05 (m, *J* = 7.2, 3.8 Hz, 1H), 2.89 (td, *J* = 7.1, 1.3 Hz, 2H), 2.38 (s, 3H), 2.12 (q, *J* = 7.3 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 199.6, 161.9, 149.2, 143.1, 136.9, 136.8, 136.6, 133.1, 129.6, 128.5, 128.0, 127.0, 123.5, 122.0, 45.7, 44.6, 35.4, 27.0, 21.4.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{25}N_2O_3S$ 409.1580, found: 409.1582.

N-(2-cyano-5-oxo-5-phenylpentyl)-4-methylbenzenesulfonamide (3av)



3av

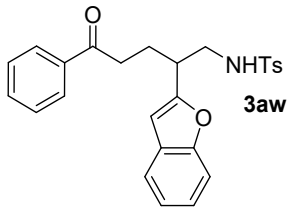
Following the general procedure, compound **3av** was obtained as a yellow oil in 38% yield (13.6 mg); R_f = 0.36 (PE/EA = 2/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.58 – 7.48 (m, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 1H), 7.13 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.07 (d, *J* = 1.7 Hz, 1H), 5.13 (dd, *J* = 10.4, 5.1 Hz, 2H), 3.87 (m, *J* = 14.8, 10.5, 4.1 Hz, 1H), 3.36 (m, *J* = 15.1, 5.2, 3.8 Hz, 1H), 3.28 – 2.96 (m, 2H), 2.78 (dd, *J* = 9.9, 4.5 Hz, 1H), 2.30 (s, 3H), 2.26 – 2.12 (m, 1H), 2.05 (m, *J* = 14.7, 7.4, 5.2 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 199.3, 142.7, 139.0, 136.3, 134.5, 133.6, 129.6, 128.7, 128.0, 126.4, 124.4, 44.5, 36.6, 35.3, 27.2, 21.5.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{21}N_2O_3S$ 357.1267, found: 357.1268.

N-(2-(benzofuran-2-yl)-5-oxo-5-phenylpentyl)-4-methylbenzenesulfonamide (3aw)



3aw

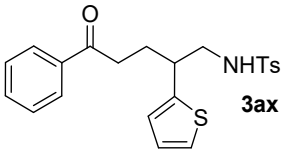
Following the general procedure, compound **3aw** was obtained as a yellow oil in 73% yield (32.7 mg); R_f = 0.32 (PE/EA = 2/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 – 7.78 (m, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.60 – 7.48 (m, 1H), 7.46 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.34 (dd, *J* = 8.8, 4.2 Hz, 1H), 7.27 – 7.12 (m, 5H), 4.87 (q, *J* = 6.5, 4.9 Hz, 1H), 3.39 – 3.18 (m, 2H), 3.11 (ddt, *J* = 13.0, 6.4, 3.8 Hz,1H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.36 (s, 3H), 2.25 – 1.97 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): 199.2, 157.1, 154.6, 143.3, 136.6, 136.5, 133.1, 129.6, 128.5, 127.9, 126.9, 126.2, 123.8, 122.7, 120.6, 110.9, 104.5, 45.8, 39.0, 35.4, 24.7, 21.4.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{26}NO_4S$ 448.1577, found: 448.1579.

4-methyl-N-(5-oxo-5-phenyl-2-(thiophen-2-yl)pentyl)benzenesulfonamide (3ax)



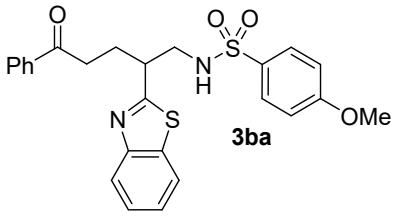
3ax

Following the general procedure, compound **3ax** was obtained as a yellow oil in 53% yield (21.9 mg); R_f = 0.32 (PE/EA = 2/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.9 – 7.8 (m, 3H), 7.8 – 7.6 (m, 2H), 7.6 – 7.5 (m, 1H), 7.4 (t, *J*=7.7 Hz, 2H), 7.3 (d, *J*=8.3 Hz, 3H), 7.2 (dd, *J*=5.1, 1.1 Hz, 1H), 6.9 (dd, *J*=5.1, 3.4 Hz, 1H), 6.8 (dd, *J*=3.5, 1.2 Hz, 1H), 4.6 (dd, *J*=8.1, 4.7 Hz, 1H), 3.3 (ddd, *J*=12.3, 8.2, 5.5 Hz, 1H), 3.2 (tt, *J*=9.9, 4.2 Hz, 1H), 3.0 (ddd, *J*=12.7, 8.3, 4.7 Hz, 1H), 2.9 (dd, *J*=8.0, 6.5 Hz, 2H), 2.4 (s, 3H), 2.2 (dtd, *J*=14.9, 7.6, 4.6 Hz, 1H), 1.9 (ddt, *J*=13.8, 9.9, 6.9 Hz, 1H)**^{13}C NMR (101 MHz, $CDCl_3$):** δ 199.3, 144.3, 143.5, 136.7, 133.1, 129.7, 129.7, 128.5, 127.93, 127.1, 127.0, 126.4, 125.6, 124.5, 49.1, 40.6, 35.6, 28.5, 21.5.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{24}NO_3S_2$ 414.1192, found: 414.1195.

N-(2-(benzo[*d*]thiazol-2-yl)-5-oxo-5-phenylpentyl)-4-methoxylbenzenesulfonamide (3ba)



3ba

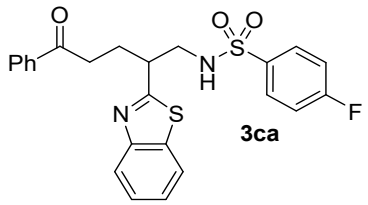
Following the general procedure, compound **3ba** was obtained as a white solid in 88% yield (42.3 mg); mp = 127 – 128 °C; R_f = 0.47 (PE/EA = 1/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.2 Hz, 1H), 7.89 – 7.86 (m, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.54 (td, *J* = 7.5, 1.2 Hz, 1H), 7.48 – 7.45 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.35 (m, 1H), 6.88 – 6.85 (m, 2H), 5.66 (t, *J* = 4.4 Hz, 1H), 3.80 (d, *J* = 1.0 Hz, 3H), 3.43 (m, *J* = 22.1, 15.7, 12.1, 5.9 Hz, 3H), 3.05 – 3.01 (m, 2H), 2.28 (m, *J* = 7.1, 2.8 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 198.9, 172.3, 162.7, 152.7, 136.4, 134.5, 133.2, 131.3, 129.0, 128.5, 127.9, 126.1, 125.1, 122.8, 121.6, 114.1, 55.4, 45.9, 43.0, 35.2, 26.9.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{25}N_2O_4S_2$ 481.1250, found: 481.1255.

N-(2-(benzo[*d*]thiazol-2-yl)-5-oxo-5-phenylpentyl)-4-fluorobenzenesulfonamide (3ca)



3ca

Following the general procedure, compound **3ca** was obtained as a white solid in 85% yield (39.8 mg); mp = 113 – 114 °C; R_f = 0.52 (PE/EA = 2/1).

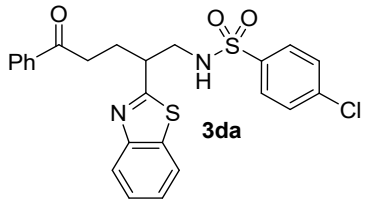
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 – 7.86 (m, 3H), 7.85 – 7.77 (m, 3H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.50 – 7.34 (m, 4H), 7.05 (t, *J* = 8.5 Hz, 2H), 5.86 (s, 1H), 3.46 (m, *J* = 8.0, 3.0 Hz, 1H), 3.05 (t, *J* = 7.1 Hz, 2H), 2.28 (q, *J* = 6.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 198.9, 172.1, 164.8 (C-F, $1J_{C-F}$ = 254.5 Hz), 152.6, 136.4, 135.8 (C-F, $4J_{C-F}$ = 3.3 Hz), 134.4, 133.2, 129.6 (C-F, $3J_{C-F}$ = 9.4 Hz), 128.5, 127.9, 126.2, 125.2, 122.7, 121.6, 116.1 (C-F, $2J_{C-F}$ = 22.6 Hz), 46.0, 43.0, 35.1, 26.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ -105.33

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{24}H_{22}FN_2O_3S_2$ 469.1050, found: 469.1052.

N-(2-(benzo[*d*]thiazol-2-yl)-5-oxo-5-phenylpentyl)-4-chlorobenzenesulfonamide (3da)



3da

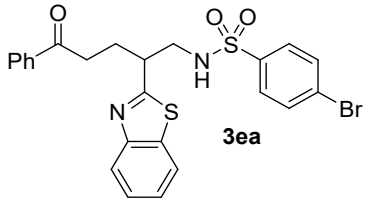
Following the general procedure, compound **3da** was obtained as a yellow solid in 85% yield (41.3 mg); mp = 114 – 115 °C; R_f = 0.57 (PE/EA = 2/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.2 Hz, 1H), 7.89 – 7.87 (m, 2H), 7.83 – 7.80 (m, 1H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.58 – 7.52 (m, 1H), 7.47 (m, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.38 (td, *J* = 7.6, 7.1, 1.2 Hz, 1H), 7.34 (d, *J* = 8.6 Hz, 2H), 5.86 (t, *J* = 5.9 Hz, 1H), 3.51 – 3.40 (m, 3H), 3.10 – 2.96 (m, 2H), 2.28 (m, *J* = 7.0, 3.9 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 198.9, 172.1, 152.6, 138.9, 138.3, 136.4, 134.5, 133.3, 129.2, 128.6, 128.3, 127.9, 126.2, 125.2, 122.7, 121.6, 46.1, 43. 0, 35.1, 26.9.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{24}H_{22}ClN_2O_3S_2$ 485.0755, found: 485.0757.

N-(2-(benzo[*d*]thiazol-2-yl)-5-oxo-5-phenylpentyl)-4-bromobenzenesulfonamide (3ea)



3ea

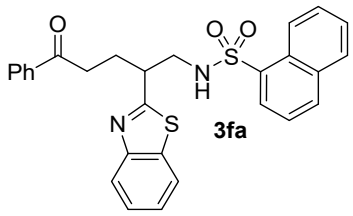
Following the general procedure, compound **3ea** was obtained as a white solid in 96% yield (51.0 mg); mp = 131 – 132 °C; R_f = 0.40 (PE/EA = 2/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 7.1 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.46 (td, *J* = 8.3, 1.1 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.40 – 7.35 (m, 1H), 5.90 (t, *J* = 5.9 Hz, 1H), 3.45 (m, *J* = 12.8, 11.2, 6.6 Hz, 3H), 3.04 (t, *J* = 7.0 Hz, 2H), 2.35 – 2.20 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 198.9, 172.1, 152.6, 138.8, 136.4, 134.4, 133.2, 132.2, 128.5, 128.4, 127.9, 127.4, 126.2, 125.2, 122.7, 121.6, 46.1, 43.0, 35.1, 26.9.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{24}H_{22}BrN_2O_3S_2$ 529.0250, found: 529.0254.

N-(2-(benzo[*d*]thiazol-2-yl)-5-oxo-5-phenylpentyl)-1-naphthylsulfonamide (3fa)



3fa

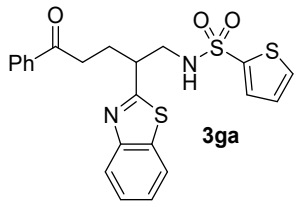
Following the general procedure, compound **3fa** was obtained as a white solid in 78% yield (39.1 mg); mp = 141 – 142 °C; R_f = 0.48 (PE/EA = 2/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (d, *J* = 1.7 Hz, 1H), 7.95 – 7.70 (m, 8H), 7.67 – 7.49 (m, 4H), 7.48 – 7.29 (m, 4H), 5.92 (t, *J* = 6.0 Hz, 1H), 3.57 – 3.41 (m, 3H), 2.99 (t, *J* = 7.1 Hz, 2H), 2.26 (q, *J* = 6.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 198.9, 172.2, 152.6, 136.5, 136.4, 134.6, 134.4, 133.1, 132.0, 129.4, 129.1, 128.6, 128.5, 128.2, 127.9, 127.8, 127.4, 126.1, 125.1, 122.7, 122.1, 121.5, 46.0, 43.0, 35.1, 26.9.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{25}N_2O_3S_2$ 501.1301, found: 501.1304.

N-(2-(benzo[*d*]thiazol-2-yl)-5-oxo-5-phenylpentyl)-2-thienylsulfonamide (3ga)



3ga

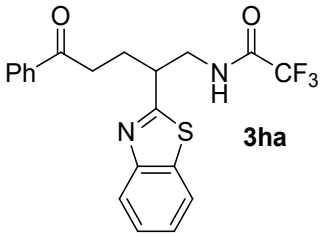
Following the general procedure, compound **3ga** was obtained as a yellow oil in 92% yield (42.0 mg); R_f = 0.32 (PE/EA = 2/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.94 – 7.91 (m, 1H), 7.91 – 7.88 (m, 2H), 7.84 – 7.80 (m, 1H), 7.57 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.50 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.45 (m, *J* = 8.5, 7.3, 1.3 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.36 (m, *J* = 8.2, 7.2, 1.2 Hz, 1H), 7.00 (dd, *J* = 5.0, 3.7 Hz, 1H), 5.98 (t, *J* = 6.2 Hz, 1H), 3.59 – 3.46 (m, 3H), 3.06 (t, *J* = 7.1 Hz, 2H), 2.37 – 2.24 (m, *J* = 7.1 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 198.9, 172.2, 152.6, 140.7, 136.4, 134.5, 133.2, 131.9, 131.7, 128.5, 127.9, 127.3, 126.1, 125.1, 122.8, 121.6, 46.1, 42.8, 35.1, 27.0.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{21}N_2O_3S_3$ 457.0709, found: 457.0711.

N-(2-(benzo[*d*]thiazol-2-yl)-5-oxo-5-phenylpentyl)-trifluoroacetylbenzenesulfonamide (3ha)



3ha

Following the general procedure, compound **3ha** was obtained as a yellow oil in 61% yield (24.8 mg); R_f = 0.46 (PE/EA = 1/1).

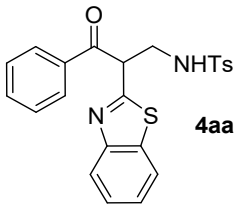
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 – 7.97 (m, 1H), 7.95 – 7.92 (m, 2H), 7.91 (s, 1H), 7.89 – 7.86 (m, 1H), 7.56 (m, *J* = 8.8, 7.0, 1.3 Hz, 1H), 7.50 (m, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.41 (m, *J* = 8.3, 7.2, 1.2 Hz, 1H), 3.95 (dt, *J* = 13.4, 6.6 Hz, 1H), 3.82 (dt, *J* = 13.7, 4.8 Hz, 1H), 3.58 (m, *J* = 6.9, 4.4 Hz, 1H), 3.15 (td, *J* = 6.9, 2.0 Hz, 2H), 2.40 (m, *J* = 14.0, 7.0 Hz, 1H), 2.24 (m, *J* = 14.0, 7.0 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 198.9, 172.2, 157.4 (C-F, 2 J_{C-F} = 37.1 Hz), 152.7, 136.4, 134.4, 133.3, 128.6, 128.0, 126.3, 125.4, 122.9, 121.7, 115.8 (C-F, 1 J_{C-F} = 287.7 Hz), 42.1, 42.0, 35.2, 26.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ -75.98.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{18}F_3N_2O_2S$ 407.1036, found: 407.1040.

N-(2-(benzo[*d*]thiazol-2-yl)-3-oxo-3-phenylpropyl)-4-methylbenzenesulfonamide (4aa)



4aa

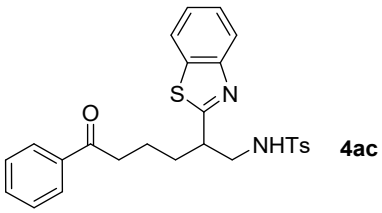
Following the general procedure, compound **4aa** was obtained as a yellow oil in 59% yield (25.8 mg); R_f = 0.42 (PE/EA = 2/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 – 7.92 (m, 3H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.68 (t, *J* = 9.8 Hz, 2H), 7.57 – 7.52 (m, 4H), 7.44 (dt, *J* = 15.2, 5.9 Hz, 2H), 7.35 (dd, *J* = 13.1, 5.5 Hz, 3H), 7.18 (t, *J* = 12.0 Hz, 1H), 5.38 (t, *J* = 6.7 Hz, 1H), 3.81 (dt, *J* = 13.8, 7.0 Hz, 1H), 3.69 (dd, *J* = 13.5, 6.7 Hz, 1H), 2.36 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 195.3, 164.6, 155.3, 152.7, 144.7, 143.5, 136.8, 135.3, 135.1, 134.0, 129.7, 129.0, 128.8, 126.9, 126.2, 125.5, 123.3, 121.5, 77.2, 77.00, 76.79, 52.3, 44.8, 21.4.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{21}N_2O_3S_2$ 437.0988, found:437.0992.

N-(2-(benzo[*d*]thiazol-2-yl)-6-oxo-6-phenylhexyl)-4-methylbenzenesulfonamide (4ac)



4ac

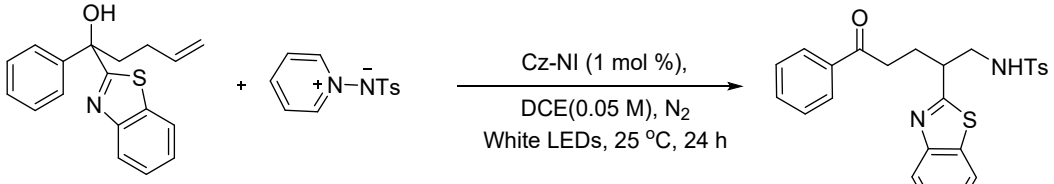
Following the general procedure, compound **4ac** was obtained as a colorless oil in 79% yield (37.8 mg); R_f = 0.53 (PE/EA = 1/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96 (t, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 3H), 7.82 – 7.71 (m, 3H), 7.67 (d, *J* = 7.8 Hz, 4H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.42 (dd, *J* = 16.7, 8.6 Hz, 4H), 7.34 (dd, *J* = 16.5, 8.5 Hz, 3H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 2H), 5.76 (s, 1H), 3.39 (t, *J* = 6.1 Hz, 3H), 3.36 – 3.22 (m, 1H), 2.93 (dd, *J* = 17.1, 7.5 Hz, 2H), 2.33 (s, 3H), 1.94 – 1.83 (m, 2H), 1.81 – 1.66 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 199.6, 172.6, 152.6, 143.2, 136.7, 136.6, 134.4, 133.0, 129.5, 128.5, 127.9, 126.8, 126.2, 126.0, 125.0, 122.6, 121.5, 60.3, 46.2, 43.9, 37.8, 32.3, 21.3.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{27}N_2O_3S_2$ 479.1458, found: 479.1460.

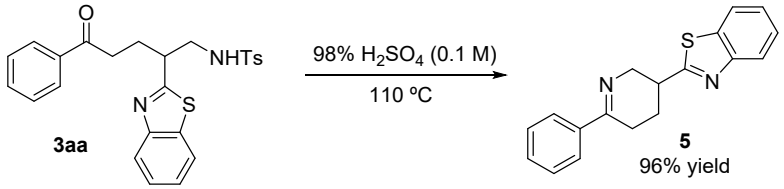
5. The Gram Scale Reaction



1a 4.8 mmol | **2a** 3.0 mmol | **3aa** 83% yield, 1.16g

General Procedure: A dried 100 mL round bottom flask was charged with the photocatalyst (0.03 mmol, 12.6 mg), the heteroaryl-substituted tertiary bishomoallylic alcohol **1a** (4.8 mmol, 1.6 equiv), N-protected 1-aminopyridinium **2a** (3 mmol, 1 equiv) and 60 mL DCE. The reaction mixture was degassed by three cycles of freeze-pump-thaw. After the mixture was thoroughly degassed, the vial was placed beside a white LED light. The reaction was stirred at 25 ºC for 24 h. After completion of the reaction as checked by TLC. The reaction mixture was purified by silica gel flash column chromatography (petroleum ether/EtOAc) to give the corresponding product**.**

6. Transformations of Product

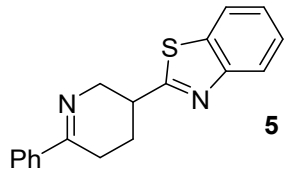


3aa | **5** 96% yield

A solution of compound **3aa** (46.4 mg, 0.1 mmol) in H_2SO_4 (1 mL) (98 wt%) was stirred at 110 °C (oil bath) for 1 hour to give a black-brown solution.[4] TLC showed the reaction was completed. The reaction solution was cooled to 0 – l0 °C with ice-water

(3 mL), neutralized to pH = 7 – 8 with Na_2CO_3 (solid) and extracted with EtOAc (5 mL x 2). The combined extracts were collected, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give compound **5** as a gray solid (96% yield, 28.2 mg).

3-(2-(benzo[*d*]thiazol-2-yl)-6-phenyl-2,3,4,5-tetrahydropyridine (5)



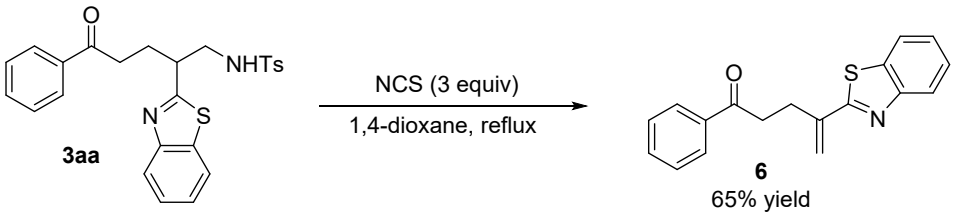
5

Compound **5** was obtained in 96% yield (28.1 mg) as a gray solid; mp= 115-116 °C; R_f = 0.54 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.05 (s, 1H), 8.07 – 7.99 (m, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 1H), 6.55 (s, 1H), 6.44 (d, *J* = 8.2 Hz, 2H), 3.96-3.87 (m, 2H) 3.62-3.56 (m, 2H), 3.08-3.01 (m, 1H) 2.05-2.04 (m, 2H), 1.94-1.83 (m, 2H), 1.30 (s, 9H).

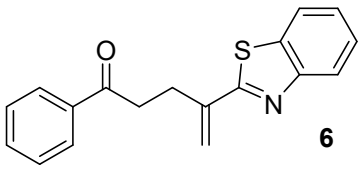
^{13}C NMR (101 MHz, $CDCl_3$): δ 174.7, 161.5, 145.7, 140.3, 129.6, 129.4, 129.2, 126.3, 124.0, 115.4, 113.1, 64.6, 51.3, 49.8, 35.3, 31.2, 28.4, 24.0.

HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{16}N_2SNa$ 293.1107, found: 293.1111.



To a solution of **3aa** (46.4 mg, 0.1 mmol) in 1,4-dioxane (1 ml), NCS (0.3 mmol) was added, and the resulted mixture was sequentially stirred under reflux temperature until the complete conversion was detected by TLC analysis. Finally, the reaction was quenched with saturated sodium bicarbonate solution, extracted with EtOAc (3×5 mL), washed with saturated brine (3×5 mL), dried over anhydrous $Na_2SO_4$and concentrated in vacuo to give a residue. The residue was purified by silica gel with petroleum ether/EtOAc as the elute to afford product **3** (65% yield, 19.1 mg).

4-(benzo[*d*]thiazol-2-yl)-1-phenylpent-4-en-1-one (6)



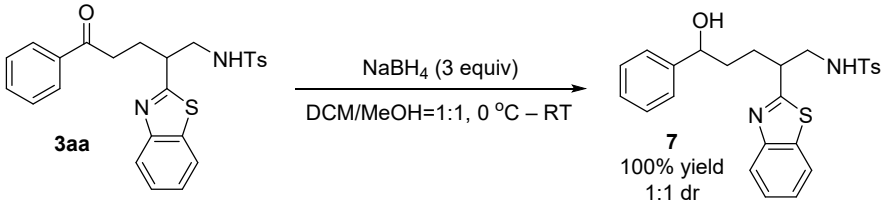
6

Compound **6** was obtained in 65% yield (19.1 mg) as a yellow oil; R_f = 0.59 (PE/EA = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 – 7.96 (m, 3H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.61 – 7.52 (m, 1H), 7.50 – 7.42 (m, 3H), 7.42 – 7.33 (m, 1H), 5.99 (s, 1H), 5.62 (s, 1H), 3.40 (t, *J* = 7.5 Hz, 2H), 3.17 (t, *J* = 7.5 Hz, 2H).

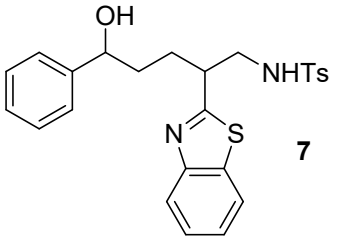
^{13}C NMR (101 MHz, $CDCl_3$): δ 199.3, 168.5, 153.7, 142.5, 136.8, 134.7, 133.0, 128.5, 128.1, 126.0, 125.5, 123.3, 121.4, 120.4, 77.3, 77.0, 76.6, 37.8, 28.9.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{24}ClN_2O_3S_2$ 294.0947, found: 294.0950.



To a solution of **3aa** (46.4 mg, 0.1 mmol) in dichloromethane (0.5 ml) and methanol (0.5 ml) was added sodium borohydride (11.4 mg, 0.3 mmol) at 0 °C (ice water bath). The reaction mixture was then allowed to warm to room temperature. After stirring for 1.5 h, the reaction mixture was quenched with water. The resulting solution was extracted three times with dichloromethane. The combined organic phases were dried over sodium sulfate and filtered. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography (PE/EA = 1/1) to give **2**(46.6 mg, 100%) as a colorless liquid.

N-(2-(benzo[*d*]thiazol-2-yl)-5-hydroxyl-5-phenylpentyl)-4-methylbenzenesulfonamide (7)



7

Compound **7** was obtained in 100% yield (46.6 mg) as a colorless oil (dr = 1:1); R_f = 0.61 (PE/EA = 1/1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.5 Hz, 1H), δ 7.80 (d, *J* = 8.5 Hz, 1H), δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 7.6 Hz,2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.28 (dd, *J* = 6.1, 3.5 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 5.65 – 5.46 (m, 1H), 4.64 (dt, *J* = 12.5, 5.6 Hz, 1H), 3.45 (t, *J* = 6.6 Hz, 3H), 3.33 (m, *J* = 16.5, 12.5, 6.2 Hz, 3H), 2.37 (s, 3H), 1.95 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.8, 172.7, 152.6, 144.1, 143.2, 136.8, 134.5, 129.61, 128.5, 127.6, 126.9, 126.1, 125.7, 125.1, 122.7, 121.5, 77.3, 77.0, 76.6, 73.9, 73.8, 46.2, 46.1, 43.9, 43.7, 36.0, 35.8, 29.3, 29.2, 21.4.

HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{27}N_2O_3S_2$ 467.1458, found: 467.1461.

7. Mechanistic Investigations

7.1 Luminescence Quenching Experiments

Stern-Volmer experiments were conducted on an Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer using the Cary Eclipse Scan Application. Rigorously purged (with nitrogen) solutions of each component were prepared before each set of experiments. Luminescence quenching experiments were run with CH_3CN as the solvent. The solutions were irradiated at 420 nm and the luminescence was measured from 400 nm to 800 nm (emission maximum is at 550 nm). The concentration of Cz-NI stock solution was 0.3 mM in CH_3CN. After being stirred with a thin glass rod, the emission spectrum was collected. Linear regression of I_0/I against concentration is done in Origin.

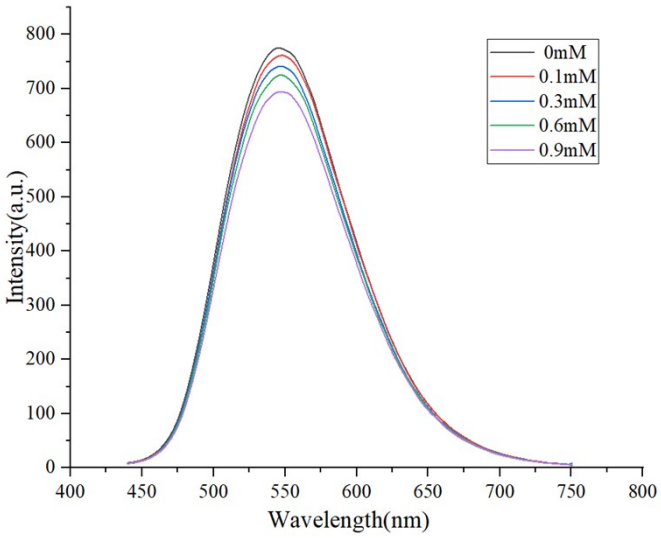


Figure S2: Fluorescence quenching data with Cz-NI and variable N-Ts pyridinium

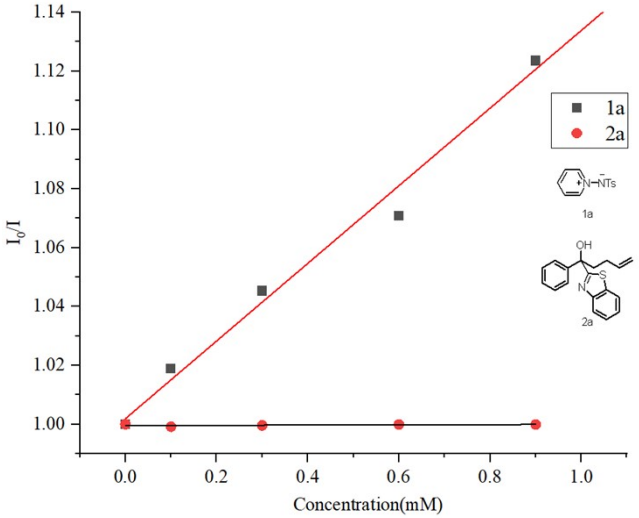
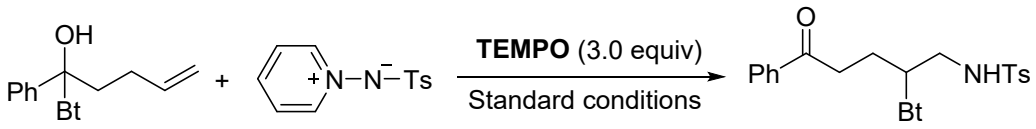


Figure S3: Stern-Volmer plot of Cz-NI with variables 1a and 2a

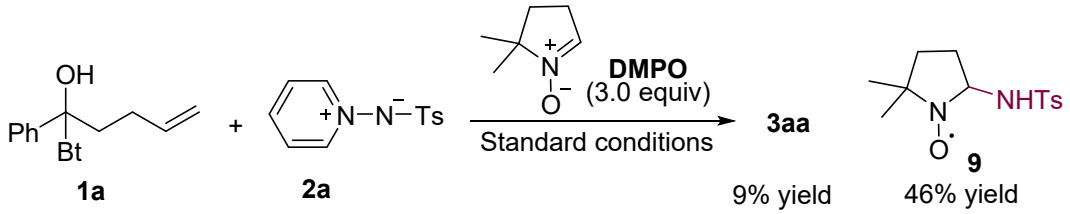
7.2 Capture of Radical Species



1a **2a** **3aa,** Trace

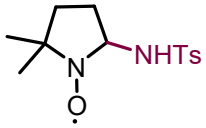
A dried 10 mL reaction tube was charged with the **Cz-NI** (0.001 mmol, 0.42 mg), the heteroaryl-substituted tertiary bishomoallylic alcohol **1a** (0.16 mmol, 1.6 equiv), N-protected 1-aminopyridinium **2a** (0.1 mmol, 1.0 equiv), TEMPO (3.0 equiv) and 2.0 mL DCE. The reaction mixture was degassed by three cycles of freeze-pump-thaw. After the mixture was thoroughly degassed, the vial was placed beside a white LED

light. The reaction was stirred at 25 °C for 9 h. We found that the product sites are close to disappearing, proving that the reaction is a free radical course.



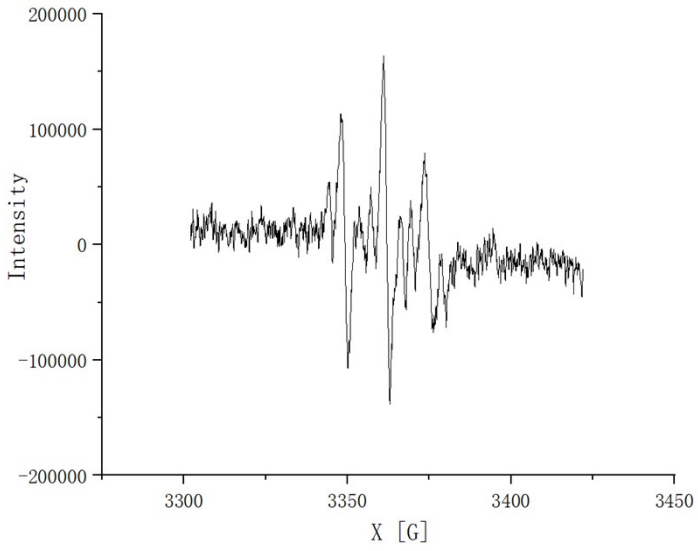
A dried 10 mL reaction tube was charged with the **Cz-NI** (0.001 mmol, 0.42 mg), the heteroaryl-substituted tertiary bishomoallylic alcohol **1a** (0.16 mmol, 1.6 equiv), N-protected 1-aminopyridinium **2a** (0.1 mmol, 1.0 equiv), DMPO (3.0 equiv) and 2.0 mL DCE. The reaction mixture was degassed by three cycles of freeze-pump-thaw. After the mixture was thoroughly degassed, the vial was placed beside a white LED light. The reaction was stirred at 25 °C for 9 h, the reaction mixture was measured by EPR, indicating there existed nitrogen radical species in the reaction mixture. Finally, the reaction mixture was concentrated and purified by flash chromatography (silica gel, mixtures of petroleum ether/ethyl acetate) to afford compound **9** (13.1 mg, 46% yield) as a purple-black oil, the yield of **3aa** is only 9% (4.1 mg).

Radical species **8**:



HRMS (ESI-TOF) m/z: $[M]^+$ Calcd for 283.1111, found 283.1111

g = 2.00541, a(N) = 12.79, a(H^{β}) = 4.19.



8. X-Ray Crystallographic Data of product 3ab

Single crystals of **3ab** were grown from slow evaporation of dichloromethane solution at room temperature. The data was collected on an XtaLAB Synergy R, HyPix diffractometer. The crystal was kept at 292 K during data collection. The data of the crystal structure **3ab** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 2121369.

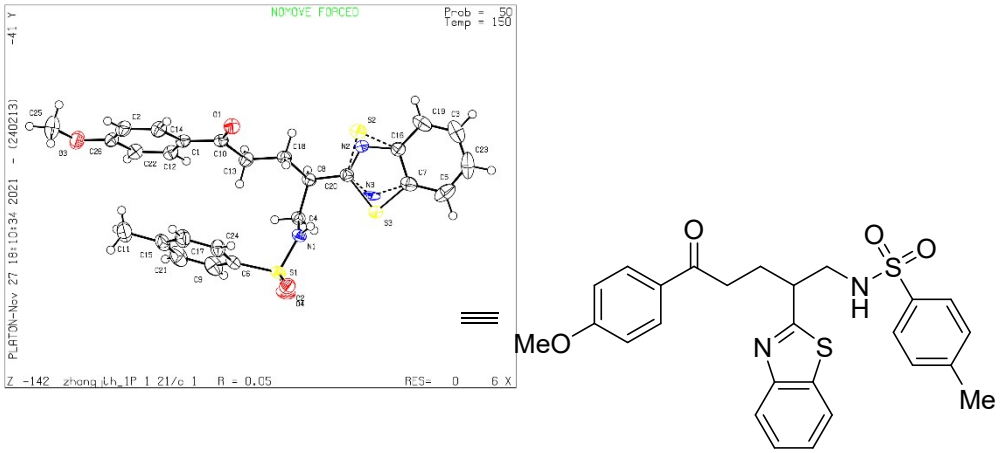


Figure S4: ORTEP diagram of **3ab**. The thermal ellipsoids are drawn at the 50% probability level

Table S6: X-Ray Crystallographic Data of 3ab

Bond precision:	C-C = 0.0024 A	Wavelength=1.54184	
Cell:	a=9.8319(3)	b=11.5048(3)	c=21.1845(6)
	alpha=90	beta=96.606(3)	gamma=90
Temperature:	150 K		
	Calculated	Reported	
Volume	2380.36(12)	2380.36(12)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C26 H26 N1.95 O4 S2.05	C26 H26 N1.95 O4 S2.05	
Sum formula	C26 H26 N1.95 O4 S2.05	C26 H26 N1.95 O4 S2.05	
Mr	495.51	495.51	
Dx,g cm-3	1.383	1.383	
Z	4	4	
Mu (mm-1)	0.265	0.265	
F000	1041.8	1042.0	
F000’	1043.24		
h, k, lmax	14,16,30	13,16,29	
Nref	7349	6031	
Tmin, Tmax	0.984,0.992	0.625,1.000	
Tmin’	0.982		
Tmax= 1.000			
AbsCorr = MULTI-SCAN			
Data completeness= 0.821	Theta(max)= 30.648		

R(reflections)= 0.0486(4789)	wR2(reflections)= 0.1309(6031)
S = 1.074	Npar= 327

9. Mechanistic Computational Analysis

All the DFT calculations at the M062X(D3)/6-31G(d)[8-9] level for neutral molecules or UM062X(D3)/6-31G(d) level for radical ions with the SMD[10] solvation model and DCM as the solvent were carried out to study the mechanism by Gaussian 09[11]. Frequency calculations were carried out at the same level of theory to confirm their character as minima (no imaginary frequencies) or transition states (a single imaginary frequency). And the intrinsic reaction coordinate (IRC) calculations have confirmed that all stationary points were smoothly connected. We have used GaussView[12] programs to generate ball and stick geometries of optimized structures. The electron spin density with the value of 0.02 is visualized by wave function analysis software Multiwfn-3.8[13] program and visualization software VMD[14] to generate the scheme of the electron spin density.

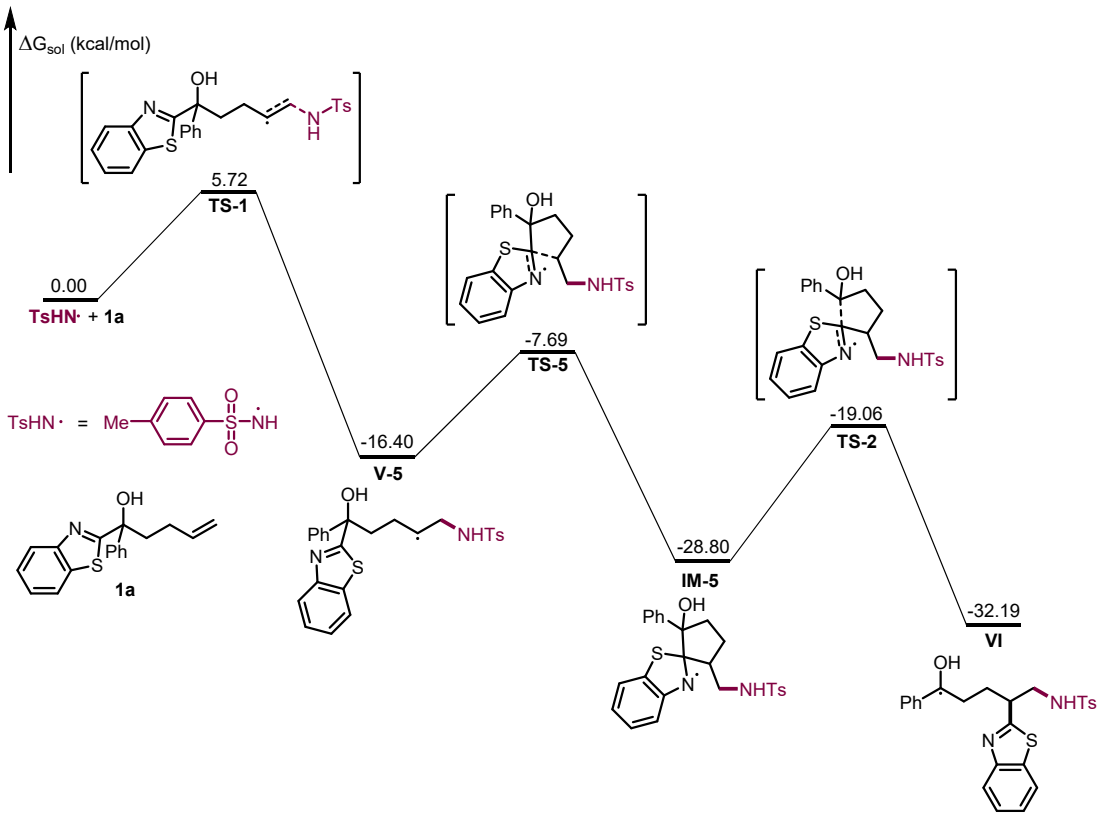


Figure S5. a) Free energy profiles from TsNH radical ion and reactant **1a** to **VI**. Free energies are given in kcal/mol at the UM062X(D3)/6-31G(d)/SMD(CH_2Cl);

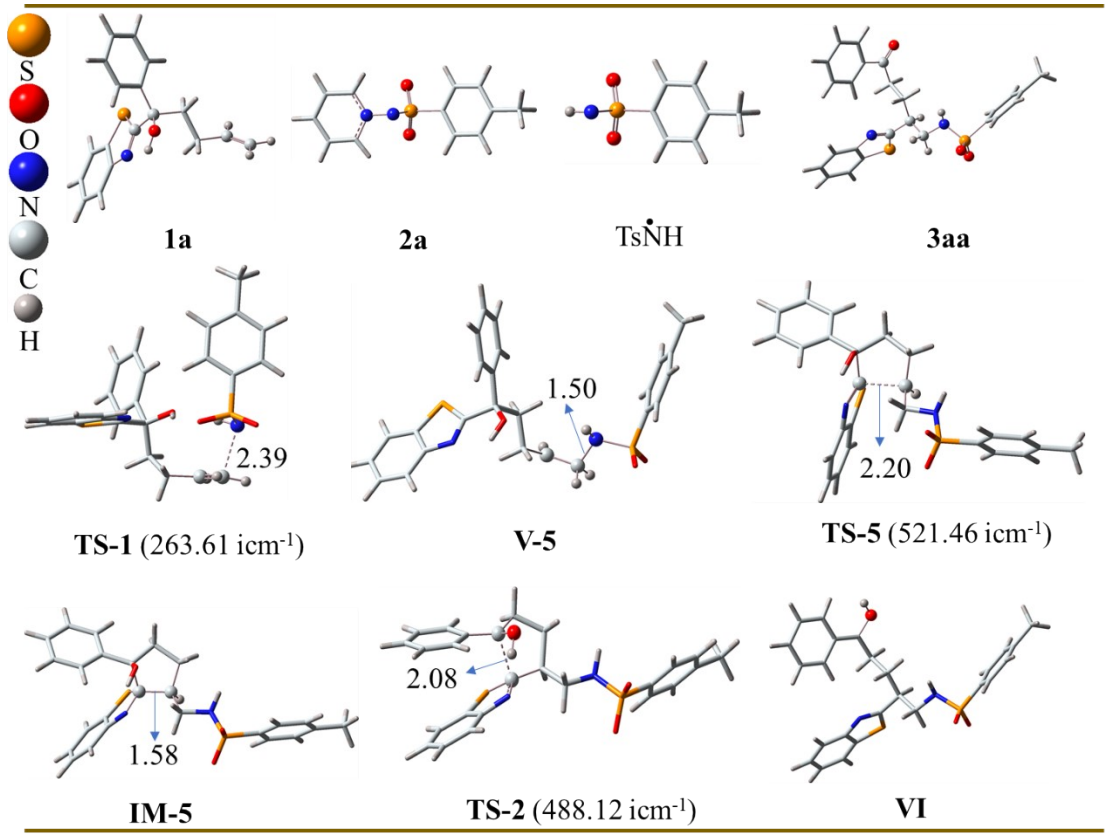
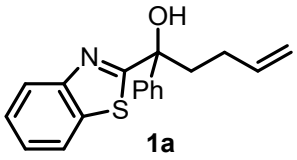


Figure S6. Optimized structures of reaction, production, and the transition state at M062X(D3)/6-31g(d) level with the SMD solvation model and dichloroethane as the solvent. UM062X(D3) functional was used for radical structure optimization. The data in brackets is the unique virtual frequency of the transition state. The bond length in Å.

Table S7. Standard orientation of All Stationary Points and the only imaginary frequencies of each transition state



1a

1. Charge = 0 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.722203	-0.944445	-0.970673
2	6	0	-2.065993	-0.780472	0.251090
3	6	0	-2.203143	-1.766268	1.233525
4	6	0	-2.987207	-2.891397	1.001692
5	6	0	-3.642899	-3.049349	-0.219271
6	6	0	-3.506964	-2.074587	-1.202931
7	1	0	-2.636377	-0.196153	-1.752230
8	1	0	-1.696104	-1.634957	2.183885

9	1	0	-3.087571	-3.646564	1.775734
10	1	0	-4.256053	-3.926876	-0.400988
11	1	0	-4.014984	-2.186225	-2.156116
12	6	0	-1.148590	0.410821	0.539992
13	8	0	-1.253005	0.728507	1.912444
14	1	0	-0.348604	0.875062	2.246461
15	6	0	-1.499064	1.658187	-0.298346
16	1	0	-1.385019	1.442402	-1.366598
17	1	0	-2.557254	1.882653	-0.120979
18	6	0	-0.643550	2.876451	0.064165
19	1	0	-0.762744	3.104722	1.128302
20	1	0	0.416528	2.639910	-0.105106
21	6	0	-1.021871	4.072362	-0.761699
22	1	0	-0.889017	3.970071	-1.839805
23	6	0	-1.511061	5.207222	-0.268537
24	1	0	-1.659948	5.341898	0.801098
25	1	0	-1.777850	6.041801	-0.911033
26	6	0	2.433020	-0.709264	-0.687614
27	6	0	2.462516	-0.207682	0.627153
28	6	0	3.675352	-0.136523	1.320991
29	6	0	4.829475	-0.567331	0.685831
30	6	0	4.788420	-1.066685	-0.626259
31	6	0	3.593254	-1.145166	-1.328474
32	6	0	0.291959	0.001377	0.257944
33	1	0	3.691224	0.251846	2.334292
34	1	0	5.779316	-0.518670	1.208528
35	1	0	5.706105	-1.397844	-1.101926
36	1	0	3.563613	-1.531943	-2.341875
37	7	0	1.226622	0.187831	1.124813
38	16	0	0.788982	-0.686095	-1.279148

---

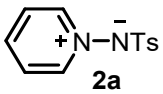
0 imaginary frequencies

Zero-point Energies= -1223.635168

Thermal Energies= -1223.616689

Thermal Enthalpies= -1223.615745

Thermal Free Energies= -1223.683855



2a

2. Charge = 0 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.897355	1.107402	-0.666926
2	6	0	4.276779	1.130486	-0.581325
3	6	0	4.968061	-0.064078	-0.398449
4	6	0	4.256019	-1.256885	-0.306671
5	6	0	2.877033	-1.230319	-0.398031

6	1	0	6.050725	-0.065942	-0.333007
7	1	0	2.275851	1.981085	-0.813723
8	1	0	4.792701	2.079819	-0.659585
9	1	0	4.755612	-2.207789	-0.165797
10	1	0	2.240163	-2.103401	-0.343231
11	7	0	2.228023	-0.061107	-0.578916
12	7	0	0.831706	-0.066906	-0.730586
13	16	0	0.170605	0.106845	0.753361
14	8	0	0.464333	-1.038001	1.637246
15	8	0	0.444404	1.429020	1.348375
16	6	0	-1.540834	0.040618	0.291953
17	6	0	-2.244870	1.225721	0.107587
18	6	0	-2.151286	-1.198855	0.121835
19	6	0	-3.585248	1.162475	-0.260106
20	1	0	-1.747237	2.179062	0.254681
21	6	0	-3.490760	-1.244357	-0.247318
22	1	0	-1.584017	-2.110866	0.280905
23	6	0	-4.224951	-0.068223	-0.441166
24	1	0	-4.145066	2.082081	-0.408438
25	1	0	-3.977802	-2.206021	-0.385544
26	6	0	-5.684073	-0.127476	-0.807408
27	1	0	-6.305922	-0.149261	0.095057
28	1	0	-5.981069	0.747743	-1.391546
29	1	0	-5.910958	-1.027150	-1.385864

---

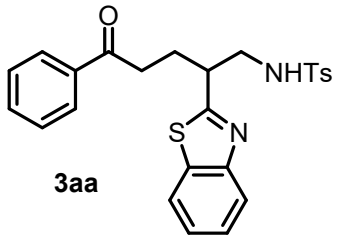
0 imaginary frequencies

Zero-point Energies= -1121.985069

Thermal Energies= -1121.970123

Thermal Enthalpies= -1121.969179

Thermal Free Energies= -1122.031198



3aa

3. Charge = 0 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.708539	2.046906	1.186658
2	6	0	0.632279	1.755805	-0.190018
3	6	0	0.976595	2.736595	-1.128188
4	6	0	1.394999	3.976998	-0.673512
5	6	0	1.481699	4.250929	0.702261
6	6	0	1.138746	3.292956	1.646984
7	6	0	-0.046091	-0.204812	0.571256
8	1	0	0.916113	2.506246	-2.187634

9	1	0	1.666265	4.747797	-1.388309
10	1	0	1.816784	5.228886	1.033635
11	1	0	1.201144	3.507625	2.709037
12	7	0	0.207893	0.471297	-0.498404
13	16	0	0.210999	0.643153	2.090446
14	6	0	-0.531738	-1.631105	0.546093
15	1	0	-0.795848	-1.934394	1.567144
16	6	0	0.603593	-2.530647	0.046219
17	1	0	0.244075	-3.555578	-0.093100
18	1	0	0.942649	-2.157163	-0.925928
19	6	0	-1.762610	-1.777935	-0.356384
20	1	0	-2.064756	-2.830217	-0.367219
21	1	0	-1.489618	-1.511884	-1.383249
22	7	0	1.729092	-2.484523	0.984298
23	1	0	1.636069	-3.100488	1.792470
24	16	0	3.259533	-2.618747	0.358855
25	8	0	3.295811	-3.529631	-0.783300
26	8	0	4.118142	-2.884073	1.509985
27	6	0	3.565592	-0.982671	-0.251299
28	6	0	3.642418	-0.763158	-1.623100
29	6	0	3.750698	0.052120	0.664289
30	6	0	3.925791	0.519728	-2.080765
31	1	0	3.492245	-1.586020	-2.314405
32	6	0	4.038732	1.325425	0.187517
33	1	0	3.681207	-0.139918	1.731209
34	6	0	4.141257	1.573658	-1.186840
35	1	0	3.990300	0.704194	-3.149864
36	1	0	4.186235	2.141088	0.890396
37	6	0	4.494634	2.943041	-1.701385
38	1	0	5.527873	2.957385	-2.066971
39	1	0	3.848135	3.227940	-2.537221
40	1	0	4.402062	3.698078	-0.916795
41	6	0	-2.929518	-0.915891	0.105011
42	1	0	-2.673518	0.151048	0.051270
43	1	0	-3.172632	-1.116307	1.157510
44	6	0	-4.176969	-1.141282	-0.725108
45	8	0	-4.180295	-1.930525	-1.652080
46	6	0	-5.416509	-0.371216	-0.378853
47	6	0	-5.448787	0.563609	0.661013
48	6	0	-6.573847	-0.608536	-1.128666
49	6	0	-6.625905	1.251223	0.945601
50	1	0	-4.559949	0.763178	1.251504
51	6	0	-7.748179	0.077073	-0.843379
52	1	0	-6.533342	-1.336458	-1.932833
53	6	0	-7.775000	1.008242	0.195749
54	1	0	-6.645391	1.976270	1.753328
55	1	0	-8.643159	-0.112463	-1.428030
56	1	0	-8.692137	1.544745	0.420214

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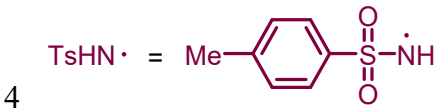
0 imaginary frequencies

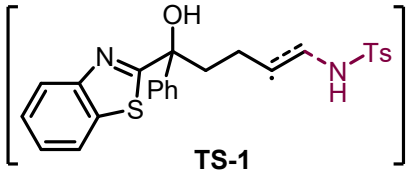
Zero-point Energies= -2097.623894
Thermal Energies= -2097.595398
Thermal Enthalpies= -2097.594454
Thermal Free Energies= -2097.686423

TsHN· = 

4 Charge = 0 Multiplicity = 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-2.309295	-0.002082	1.532549
2	16	0	-1.901626	0.000110	-0.097575
3	8	0	-2.371241	-1.264092	-0.655551
4	8	0	-2.371452	1.265552	-0.652500
5	6	0	-0.138754	0.000208	-0.060390
6	6	0	0.536661	1.217645	-0.039176
7	6	0	0.536760	-1.217324	-0.039322
8	6	0	1.925442	1.205789	0.007192
9	1	0	-0.014029	2.152556	-0.063817
10	6	0	1.925399	-1.205403	0.007058
11	1	0	-0.013908	-2.152248	-0.064091
12	6	0	2.636296	0.000262	0.029317
13	1	0	2.468211	2.146624	0.024082
14	1	0	2.468256	-2.146210	0.023850
15	6	0	4.140661	-0.000317	0.045327
16	1	0	4.531614	-0.013522	-0.978618
17	1	0	4.531413	0.894114	0.537383
18	1	0	4.530125	-0.883049	0.559209
19	1	0	-3.343842	-0.002288	1.559737

0 imaginary frequencies
Zero-point Energies= -874.449590
Thermal Energies= -874.438703
Thermal Enthalpies= -874.437759
Thermal Free Energies= -874.488320

5. 
TS-1 Charge = 0 Multiplicity = 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.353089	3.176094	1.053416

2	6	0	1.373342	2.338404	0.513998
3	6	0	0.571187	2.811291	-0.528365
4	6	0	0.741429	4.102837	-1.017758
5	6	0	1.721040	4.935104	-0.477665
6	6	0	2.526307	4.467729	0.557136
7	1	0	2.986597	2.835006	1.867135
8	1	0	-0.193806	2.163039	-0.943228
9	1	0	0.106911	4.460235	-1.823390
10	1	0	1.853678	5.942542	-0.860270
11	1	0	3.289948	5.108665	0.987237
12	6	0	1.197788	0.898388	0.991705
13	8	0	-0.150739	0.528730	0.802679
14	1	0	-0.183602	-0.434763	0.616073
15	6	0	1.594888	0.711194	2.475745
16	1	0	2.684556	0.743594	2.566493
17	1	0	1.201751	1.565706	3.038613
18	6	0	1.058220	-0.595733	3.085552
19	1	0	1.015056	-1.404884	2.345312
20	1	0	1.771111	-0.922908	3.854973
21	6	0	-0.267340	-0.438108	3.767162
22	1	0	-0.398964	0.481983	4.338027
23	6	0	-1.270191	-1.344877	3.773546
24	1	0	-1.161724	-2.300581	3.265653
25	1	0	-2.130062	-1.220575	4.422170
26	6	0	3.810303	-1.206843	-1.098032
27	6	0	2.545809	-1.823622	-1.060901
28	6	0	2.345897	-3.051911	-1.700081
29	6	0	3.414320	-3.636575	-2.361398
30	6	0	4.672339	-3.012368	-2.393309
31	6	0	4.886846	-1.792678	-1.765471
32	6	0	2.049560	-0.024075	0.123731
33	1	0	1.367140	-3.519656	-1.663519
34	1	0	3.279178	-4.590050	-2.861867
35	1	0	5.493573	-3.490819	-2.917508
36	1	0	5.859964	-1.313319	-1.792288
37	7	0	1.576475	-1.120378	-0.357183
38	16	0	3.741182	0.307749	-0.230162
39	7	0	-2.664877	-0.264468	2.166694
40	1	0	-1.901693	0.363984	1.862558
41	16	0	-2.720533	-1.498887	1.048159
42	8	0	-3.673464	-2.491179	1.533789
43	8	0	-1.376919	-1.966102	0.665735
44	6	0	-3.408734	-0.641391	-0.341618
45	6	0	-4.781786	-0.396256	-0.370904
46	6	0	-2.563578	-0.192673	-1.354137
47	6	0	-5.310609	0.310264	-1.442198
48	1	0	-5.419633	-0.758627	0.429706
49	6	0	-3.114881	0.512795	-2.418589
50	1	0	-1.497873	-0.395919	-1.311253
51	6	0	-4.487903	0.773527	-2.477869

52	1	0	-6.378489	0.507631	-1.480210
53	1	0	-2.468801	0.864799	-3.218083
54	6	0	-5.082447	1.517269	-3.642661
55	1	0	-4.315399	2.061683	-4.198836
56	1	0	-5.567853	0.819161	-4.334202
57	1	0	-5.843546	2.227902	-3.307684

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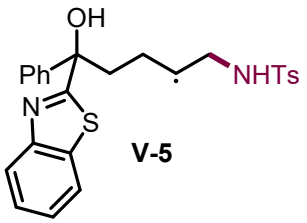
1 imaginary frequencies (-263.61)

Zero-point Energies= -2098.097746

Thermal Energies= -2098.06841

Thermal Enthalpies= -2098.067466

Thermal Free Energies= -2098.163058



V-5

6. Charge = 0 Multiplicity = 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.182977	2.688153	-0.871851
2	6	0	-1.592074	2.095544	0.324746
3	6	0	-2.009490	2.912795	1.379911
4	6	0	-2.011638	4.296951	1.243991
5	6	0	-1.599747	4.884392	0.047832
6	6	0	-1.187084	4.076880	-1.007484
7	1	0	-0.851649	2.080778	-1.708173
8	1	0	-2.322814	2.450535	2.310313
9	1	0	-2.335208	4.918844	2.073420
10	1	0	-1.600217	5.964924	-0.059128
11	1	0	-0.861836	4.523677	-1.942185
12	6	0	-1.660511	0.577351	0.510596
13	8	0	-1.354875	0.280090	1.857247
14	1	0	-2.005935	-0.377935	2.164486
15	6	0	-0.684278	-0.183950	-0.411653
16	1	0	-0.932764	-0.004004	-1.463158
17	1	0	0.314842	0.232920	-0.238019
18	6	0	-0.680384	-1.700708	-0.153379
19	1	0	-0.459505	-1.884576	0.904470
20	1	0	-1.690380	-2.092933	-0.345145
21	6	0	0.310061	-2.412010	-1.014210
22	1	0	0.197773	-2.353821	-2.092940
23	6	0	1.597346	-2.918994	-0.465253
24	1	0	1.435928	-3.427305	0.495020
25	1	0	2.073827	-3.617353	-1.156501
26	6	0	-5.272231	-0.458347	-0.697502

27	6	0	-4.970885	-0.991626	0.569803
28	6	0	-5.903530	-1.800965	1.227462
29	6	0	-7.114546	-2.058604	0.604556
30	6	0	-7.405548	-1.520023	-0.659534
31	6	0	-6.491817	-0.714142	-1.325297
32	6	0	-3.083380	0.109962	0.232973
33	1	0	-5.664208	-2.209842	2.203913
34	1	0	-7.849726	-2.685159	1.099252
35	1	0	-8.361220	-1.736338	-1.126432
36	1	0	-6.719043	-0.298466	-2.301585
37	7	0	-3.716938	-0.647403	1.060542
38	16	0	-3.928576	0.511426	-1.252192
39	7	0	2.547139	-1.777018	-0.292649
40	1	0	2.174941	-1.091323	0.370474
41	16	0	4.077780	-2.222340	0.210950
42	8	0	4.566429	-3.177099	-0.781416
43	8	0	4.104671	-2.617551	1.620529
44	6	0	4.937032	-0.681881	0.052048
45	6	0	5.130265	-0.145278	-1.221887
46	6	0	5.413551	-0.045589	1.191102
47	6	0	5.810389	1.056972	-1.342699
48	1	0	4.751665	-0.662757	-2.098365
49	6	0	6.095646	1.161131	1.048476
50	1	0	5.254428	-0.488597	2.168795
51	6	0	6.300689	1.726830	-0.211427
52	1	0	5.968373	1.487947	-2.327832
53	1	0	6.474177	1.668686	1.931144
54	6	0	7.028147	3.034854	-0.367861
55	1	0	7.412587	3.393025	0.590017
56	1	0	7.868693	2.932021	-1.061672
57	1	0	6.360759	3.800912	-0.777188

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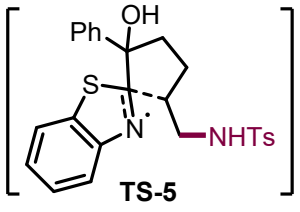
0 imaginary frequencies

Zero-point Energies= -2098.129726

Thermal Energies= -2098.099892

Thermal Enthalpies= -2098.098948

Thermal Free Energies= -2098.198310

7. 

TS-5 Charge =0 Multiplicity = 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.816828	-2.326771	0.869917

2	6	0	-4.104880	-1.644195	-0.117122
3	6	0	-4.812615	-1.016516	-1.148533
4	6	0	-6.200849	-1.072980	-1.194062
5	6	0	-6.906036	-1.759914	-0.205142
6	6	0	-6.210567	-2.385326	0.824473
7	1	0	-4.295083	-2.824145	1.681362
8	1	0	-4.271951	-0.476448	-1.921787
9	1	0	-6.733836	-0.580106	-2.001656
10	1	0	-7.990352	-1.805704	-0.239587
11	1	0	-6.749090	-2.924624	1.598092
12	6	0	-2.576488	-1.542212	-0.115950
13	8	0	-2.063460	-1.858896	-1.396230
14	1	0	-2.054693	-1.032305	-1.913835
15	6	0	-1.877809	-2.456471	0.887281
16	1	0	-2.212339	-2.215116	1.902909
17	1	0	-2.131038	-3.502658	0.691240
18	6	0	-0.370920	-2.199571	0.756485
19	1	0	0.156374	-2.644869	1.608415
20	1	0	-0.007404	-2.677023	-0.158375
21	6	0	-0.116527	-0.718279	0.691090
22	1	0	-0.006197	-0.195613	1.638845
23	6	0	0.716708	-0.169654	-0.426429
24	1	0	0.404810	-0.604633	-1.383697
25	1	0	0.621502	0.917542	-0.483821
26	6	0	-2.449644	2.242834	0.955979
27	6	0	-2.093757	2.059552	-0.400625
28	6	0	-1.849651	3.180266	-1.210043
29	6	0	-1.964721	4.444301	-0.655733
30	6	0	-2.317051	4.611767	0.693708
31	6	0	-2.559765	3.515648	1.513265
32	6	0	-2.169220	-0.090669	0.188148
33	1	0	-1.572799	3.035324	-2.249522
34	1	0	-1.775898	5.318796	-1.270257
35	1	0	-2.400497	5.612427	1.105719
36	1	0	-2.830276	3.648608	2.555826
37	7	0	-2.018806	0.752094	-0.817600
38	16	0	-2.703291	0.689336	1.711524
39	7	0	2.140463	-0.468393	-0.129038
40	1	0	2.315404	-1.477397	-0.125369
41	16	0	3.227628	0.256961	-1.174978
42	8	0	2.955744	1.690339	-1.108697
43	8	0	3.237103	-0.385794	-2.489801
44	6	0	4.757739	-0.113348	-0.365394
45	6	0	5.026168	0.473931	0.872109
46	6	0	5.667073	-0.963011	-0.982541
47	6	0	6.230987	0.189981	1.496746
48	1	0	4.301613	1.138985	1.332680
49	6	0	6.872651	-1.234710	-0.338852
50	1	0	5.434930	-1.399870	-1.948343
51	6	0	7.169120	-0.667445	0.902027

52	1	0	6.455162	0.639243	2.460620
53	1	0	7.593297	-1.896901	-0.810127
54	6	0	8.467792	-0.963301	1.602224
55	1	0	9.106515	-1.610975	0.997117
56	1	0	9.014525	-0.038503	1.813368
57	1	0	8.285766	-1.459328	2.561580

---

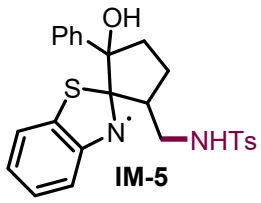
1 imaginary frequencies (-521.46)

Zero-point Energies= -2098.120979

Thermal Energies= -2098.092470

Thermal Enthalpies= -2098.091526

Thermal Free Energies= -2098.184437



IM-5

8. Charge = 0 Multiplicity = 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.330338	-2.408821	0.723884
2	6	0	-3.627814	-1.688816	-0.246734
3	6	0	-4.355917	-1.034436	-1.247651
4	6	0	-5.746913	-1.086608	-1.270153
5	6	0	-6.436176	-1.805578	-0.295793
6	6	0	-5.722358	-2.469746	0.698330
7	1	0	-3.796369	-2.932500	1.510434
8	1	0	-3.837203	-0.479506	-2.024237
9	1	0	-6.290998	-0.568106	-2.053977
10	1	0	-7.520938	-1.851120	-0.314271
11	1	0	-6.247661	-3.039329	1.459259
12	6	0	-2.110287	-1.590082	-0.247062
13	8	0	-1.596664	-1.740995	-1.561430
14	1	0	-1.724182	-0.890814	-2.019350
15	6	0	-1.343579	-2.583731	0.619577
16	1	0	-1.732148	-2.571408	1.642894
17	1	0	-1.438616	-3.601515	0.230990
18	6	0	0.092790	-2.048826	0.585188
19	1	0	0.673231	-2.369564	1.453297
20	1	0	0.595110	-2.421988	-0.313178
21	6	0	-0.028624	-0.503606	0.511533
22	1	0	0.282108	-0.048741	1.455350
23	6	0	0.845198	0.104730	-0.583353
24	1	0	0.580434	-0.311584	-1.562323
25	1	0	0.717265	1.188561	-0.615190
26	6	0	-3.097287	1.641234	1.131792
27	6	0	-2.659235	1.745954	-0.233410

28	6	0	-3.143498	2.823284	-1.029237
29	6	0	-4.012316	3.733444	-0.474111
30	6	0	-4.428406	3.610787	0.870107
31	6	0	-3.976634	2.569856	1.676387
32	6	0	-1.550390	-0.204466	0.281883
33	1	0	-2.812700	2.897909	-2.060102
34	1	0	-4.388164	4.556910	-1.072683
35	1	0	-5.116375	4.341305	1.283327
36	1	0	-4.306853	2.486029	2.706529
37	7	0	-1.826286	0.812082	-0.677757
38	16	0	-2.366804	0.269087	1.899828
39	7	0	2.255811	-0.165324	-0.240606
40	1	0	2.469015	-1.165805	-0.274664
41	16	0	3.365453	0.640736	-1.194970
42	8	0	3.068904	2.063717	-1.052026
43	8	0	3.437103	0.083677	-2.546599
44	6	0	4.868205	0.239522	-0.349298
45	6	0	5.061529	0.715667	0.948580
46	6	0	5.833207	-0.519449	-0.998992
47	6	0	6.246970	0.411418	1.600213
48	1	0	4.293664	1.309670	1.435372
49	6	0	7.018559	-0.812587	-0.327618
50	1	0	5.658463	-0.871890	-2.010293
51	6	0	7.240426	-0.355612	0.972818
52	1	0	6.411598	0.772800	2.611867
53	1	0	7.781811	-1.404857	-0.824159
54	6	0	8.519717	-0.670087	1.700031
55	1	0	9.178790	-1.294303	1.092053
56	1	0	9.056109	0.250037	1.955008
57	1	0	8.313823	-1.196513	2.637826

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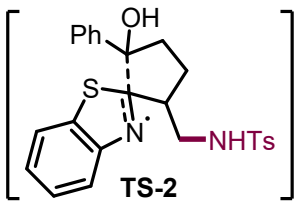
0 imaginary frequencies

Zero-point Energies= -2098.153990

Thermal Energies= -2098.125707

Thermal Enthalpies= -2098.124762

Thermal Free Energies= -2098.218073

9. 

TS-2 Charge = 0 Multiplicity = 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.160398	-2.276322	-0.513446
2	6	0	3.538065	-1.642623	0.577678

3	6	0	4.344893	-0.930550	1.483359
4	6	0	5.717543	-0.829621	1.289129
5	6	0	6.317589	-1.447956	0.193242
6	6	0	5.534130	-2.180971	-0.698767
7	1	0	3.570231	-2.845967	-1.223322
8	1	0	3.895899	-0.454434	2.349435
9	1	0	6.319318	-0.266555	1.996162
10	1	0	7.389335	-1.367321	0.039258
11	1	0	5.995952	-2.678639	-1.546215
12	6	0	2.079380	-1.634645	0.739053
13	8	0	1.596357	-1.271887	1.970474
14	1	0	1.790247	-0.320378	2.099087
15	6	0	1.164875	-2.616860	0.065311
16	1	0	1.508358	-2.812591	-0.954814
17	1	0	1.157755	-3.573283	0.603485
18	6	0	-0.221588	-1.974323	0.056798
19	1	0	-0.911005	-2.521412	-0.591203
20	1	0	-0.623943	-2.004173	1.074870
21	6	0	-0.086497	-0.498234	-0.400633
22	1	0	-0.416275	-0.422696	-1.442315
23	6	0	-0.973359	0.437990	0.420034
24	1	0	-0.685375	0.396478	1.477595
25	1	0	-0.866083	1.466405	0.068836
26	6	0	3.381535	1.136740	-1.252855
27	6	0	2.923366	1.556700	0.022763
28	6	0	3.675679	2.501033	0.746616
29	6	0	4.854896	2.980330	0.204259
30	6	0	5.305210	2.539620	-1.052539
31	6	0	4.573921	1.615542	-1.790956
32	6	0	1.368951	-0.010168	-0.355592
33	1	0	3.323853	2.823287	1.721913
34	1	0	5.446127	3.702506	0.758705
35	1	0	6.237195	2.924771	-1.453870
36	1	0	4.924391	1.275482	-2.760297
37	7	0	1.766766	0.977458	0.462869
38	16	0	2.247876	-0.000593	-1.926461
39	7	0	-2.380655	0.040787	0.220083
40	1	0	-2.577327	-0.877546	0.627295
41	16	0	-3.497677	1.129793	0.821423
42	8	0	-3.226591	2.401466	0.156796
43	8	0	-3.549279	1.111320	2.283872
44	6	0	-4.998914	0.423894	0.203589
45	6	0	-5.222647	0.411678	-1.174169
46	6	0	-5.931665	-0.084400	1.098626
47	6	0	-6.406159	-0.129996	-1.652014
48	1	0	-4.480362	0.818434	-1.854582
49	6	0	-7.115282	-0.623400	0.598323
50	1	0	-5.734178	-0.056174	2.165258
51	6	0	-7.367385	-0.654458	-0.774535
52	1	0	-6.595317	-0.147516	-2.722062

53	1	0	-7.853329	-1.024144	1.287253
54	6	0	-8.644426	-1.235917	-1.318118
55	1	0	-9.197414	-0.485713	-1.892994
56	1	0	-8.433139	-2.071748	-1.993361
57	1	0	-9.289818	-1.597674	-0.514231

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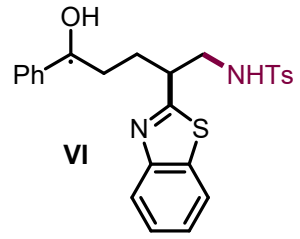
1 imaginary frequencies (-488.12)

Zero-point Energies= -2098.139381

Thermal Energies= -2098.111198

Thermal Enthalpies= -2098.110254

Thermal Free Energies= -2098.202551



VI

10. Charge = 0 Multiplicity = 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-0.008074	1.216122	-0.288557
2	1	0	0.088132	1.906497	-1.492684
3	6	0	1.478405	0.264036	-0.098256
4	6	0	1.580902	-0.701472	0.913962
5	6	0	2.562519	0.545306	-0.939007
6	6	0	2.780379	-1.381565	1.080188
7	1	0	0.732122	-0.923506	1.556394
8	6	0	3.755407	-0.147483	-0.765173
9	1	0	2.470637	1.290909	-1.724213
10	6	0	3.861958	-1.103871	0.242781
11	1	0	2.872300	-2.130661	1.859542
12	1	0	4.598885	0.059687	-1.415013
13	1	0	4.795788	-1.640685	0.376902
14	6	0	-1.477507	0.213355	-0.180373
15	6	0	-1.441293	-1.142821	-0.527769
16	6	0	-2.674273	0.825081	0.216451
17	6	0	-2.614207	-1.887693	-0.470477
18	1	0	-0.511575	-1.612096	-0.835888
19	6	0	-3.837618	0.067034	0.271502
20	1	0	-2.693594	1.878396	0.481063
21	6	0	-3.805654	-1.284528	-0.070887
22	1	0	-2.596069	-2.939736	-0.734408
23	1	0	-4.768182	0.530765	0.581118
24	1	0	-4.717188	-1.872143	-0.026262
25	8	0	-0.125964	2.431800	0.747039
26	1	0	-0.156543	2.164078	1.687834

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0 imaginary frequencies

Zero-point Energies= -2098.156363

Thermal Energies= -2098.126968

Thermal Enthalpies= -2098.126023

Thermal Free Energies= -2098.223466

Table S8. The Gibbs free energies and thermal Enthalpies of all optimized stationary points in the solvent.

Gibbs free energies and thermal Enthalpies for all reactants intermediates, transition states, and products at the M062X(D3)/6-31G(d) level with the SMD solvation model and dichloroethane as the solvent. The UM062X functional was used for the radical optimization calculations. 1 hartree=627.51 kcal/mol		
Structure	Gsol (Hartree)	Hsol (Hartree)
1	-1223.683855	-1223.615745
2	-1122.031198	-1121.969179
3	-2097.686423	-2097.594454
TsNH.	-874.48832	-874.437759
TS1	-2098.163058	-2098.067466
IM1	-2098.19831	-2098.098948
TS2	-2098.184437	-2098.091526
IM2	-2098.218073	-2098.124762
TS3	-2098.202551	-2098.110254
IM3	-2098.223466	-2098.126023

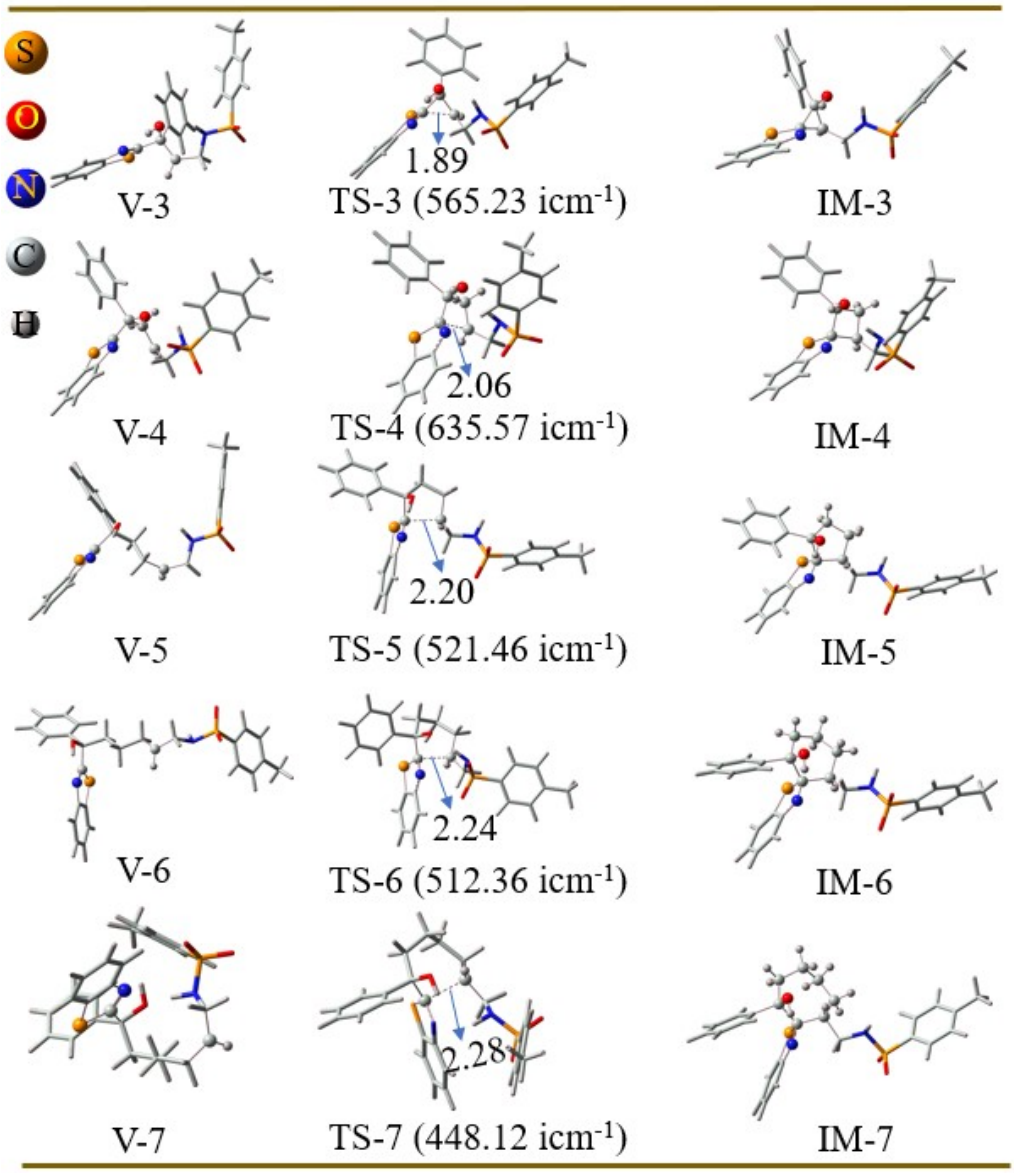
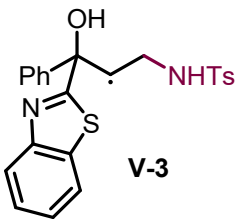


Figure S7. Optimized structures of reaction, production, and the transition state at M062X(D3)/6-31g(d) level with the SMD solvation model and dichloroethane as the solvent. UM062X(D3) functional was used for radical structure optimization. The data in brackets is the unique virtual frequency of the transition state. The bond length in Å.

Table S9. Standard orientation of All Stationary Points and the only imaginary frequencies of each transition state



V-3

1. Charge = 0 Multiplicity = 2

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	-0.204292	0.894298	-1.779208
2	6	0	-0.384000	0.705038	-0.406634
3	6	0	0.065241	1.678594	0.486995
4	6	0	0.690065	2.828772	0.010988
5	6	0	0.868802	3.017639	-1.359157
6	6	0	0.420024	2.047498	-2.253423
7	1	0	-0.549690	0.139133	-2.481636
8	1	0	-0.072397	1.526613	1.552119
9	1	0	1.040404	3.579164	0.713847
10	1	0	1.356176	3.915372	-1.727882
11	1	0	0.557581	2.183344	-3.321890
12	6	0	-1.137671	-0.518110	0.112334
13	8	0	-0.695153	-0.780498	1.444688
14	1	0	-1.428138	-1.247775	1.888740
15	6	0	-0.943182	-1.746272	-0.737608
16	1	0	-1.802457	-2.354503	-0.995457
17	6	0	0.413706	-2.273616	-1.073693
18	1	0	0.396177	-3.371284	-1.027776
19	1	0	0.701495	-2.001728	-2.098070
20	6	0	-4.961208	0.412298	-0.197056
21	6	0	-4.696418	-0.362900	0.947840
22	6	0	-5.742484	-0.729104	1.802452
23	6	0	-7.027614	-0.313651	1.493352
24	6	0	-7.280930	0.460651	0.348743
25	6	0	-6.254968	0.834261	-0.508106
26	6	0	-2.631865	-0.216780	0.178086
27	1	0	-5.530552	-1.326845	2.683199
28	1	0	-7.851724	-0.588835	2.143672
29	1	0	-8.296649	0.773883	0.129050
30	1	0	-6.453740	1.433696	-1.390563
31	7	0	-3.360789	-0.703207	1.121401
32	16	0	-3.466888	0.721043	-1.047171
33	7	0	1.423478	-1.693202	-0.177776
34	1	0	1.171289	-1.733587	0.811213
35	16	0	3.007564	-2.076666	-0.447219
36	8	0	3.159251	-2.154087	-1.899257
37	8	0	3.450258	-3.217568	0.354651
38	6	0	3.823330	-0.632074	0.176140
39	6	0	3.424922	0.623038	-0.286343
40	6	0	4.877509	-0.777520	1.069089
41	6	0	4.104183	1.745628	0.162839
42	1	0	2.589202	0.715604	-0.976188
43	6	0	5.546667	0.362776	1.509182
44	1	0	5.163628	-1.764858	1.416569
45	6	0	5.173158	1.632393	1.064025
46	1	0	3.799693	2.729630	-0.185337
47	1	0	6.370012	0.262562	2.210780
48	6	0	5.892334	2.866627	1.537743

49	1	0	6.695319	2.615767	2.234832
50	1	0	6.327811	3.409850	0.692469
51	1	0	5.200220	3.549945	2.041033

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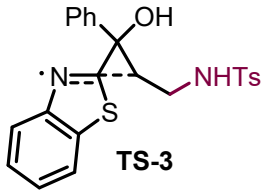
0 imaginary frequencies

Zero-point Energies= -2019.602970

Thermal Energies= -2019.575820

Thermal Enthalpies= -2019.574876

Thermal Free Energies= -2019.664703



TS-3

2. Charge = 0 Multiplicity = 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.281537	3.035177	-0.689318
2	6	0	-1.126172	2.380491	0.204956
3	6	0	-1.959126	3.121830	1.047686
4	6	0	-1.955166	4.510679	0.984138
5	6	0	-1.114288	5.165047	0.082182
6	6	0	-0.276448	4.428220	-0.750735
7	1	0	0.377394	2.455616	-1.330804
8	1	0	-2.607324	2.604532	1.751281
9	1	0	-2.606814	5.084284	1.636043
10	1	0	-1.113092	6.249718	0.031639
11	1	0	0.383475	4.935035	-1.448074
12	6	0	-1.108818	0.880235	0.328765
13	8	0	-0.475940	0.471069	1.515597
14	1	0	-0.987824	-0.283948	1.869186
15	6	0	-0.774699	0.067876	-0.871232
16	1	0	-0.931370	0.503872	-1.851758
17	6	0	0.033323	-1.180485	-0.727740
18	1	0	-0.410084	-1.855313	0.015016
19	1	0	0.098436	-1.705075	-1.681760
20	6	0	-4.680127	-0.638437	-0.384385
21	6	0	-3.921212	-1.427539	0.513917
22	6	0	-4.485921	-2.598829	1.046297
23	6	0	-5.770874	-2.954001	0.672555
24	6	0	-6.508659	-2.163525	-0.224307
25	6	0	-5.971620	-0.999167	-0.761544
26	6	0	-2.399159	0.139485	0.099449
27	1	0	-3.904119	-3.202735	1.735292
28	1	0	-6.215479	-3.858172	1.076143
29	1	0	-7.513764	-2.463405	-0.503013
30	1	0	-6.543877	-0.389026	-1.452954

31	7	0	-2.664745	-0.960187	0.799009
32	16	0	-3.758823	0.770954	-0.859626
33	7	0	1.406068	-0.768515	-0.337908
34	1	0	1.379987	-0.317131	0.582347
35	16	0	2.520622	-2.013254	-0.318263
36	8	0	2.483991	-2.607724	-1.652429
37	8	0	2.341095	-2.895197	0.835937
38	6	0	4.022670	-1.103905	-0.094355
39	6	0	4.448303	-0.243797	-1.108013
40	6	0	4.759204	-1.280090	1.070031
41	6	0	5.634595	0.452856	-0.936232
42	1	0	3.857165	-0.124475	-2.011215
43	6	0	5.949624	-0.571909	1.222636
44	1	0	4.407068	-1.959242	1.839576
45	6	0	6.400844	0.299035	0.229197
46	1	0	5.979378	1.126944	-1.715855
47	1	0	6.535775	-0.700727	2.128034
48	6	0	7.684482	1.067288	0.391891
49	1	0	7.494143	2.145737	0.379736
50	1	0	8.180836	0.817058	1.332508
51	1	0	8.373550	0.849746	-0.430721

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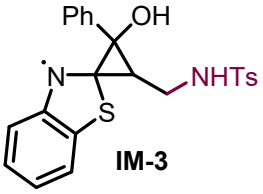
1 imaginary frequencies (-565.23)

Zero-point Energies= -2019.583534

Thermal Energies= -2019.557148

Thermal Enthalpies= -2019.556204

Thermal Free Energies= -2019.644902



IM-3

3. Charge = 0 Multiplicity = 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.092624	2.881264	-0.979318
2	6	0	-1.119244	2.190314	0.236813
3	6	0	-1.259192	2.914558	1.426173
4	6	0	-1.372134	4.300973	1.398289
5	6	0	-1.351822	4.983565	0.183311
6	6	0	-1.211969	4.268438	-1.003897
7	1	0	-0.967153	2.350514	-1.918447
8	1	0	-1.270719	2.382041	2.370727
9	1	0	-1.476979	4.849026	2.329851
10	1	0	-1.440911	6.065369	0.161885
11	1	0	-1.186889	4.789971	-1.955781
12	6	0	-1.037794	0.703471	0.312553

13	8	0	-0.568095	0.238110	1.538092
14	1	0	-1.140095	-0.507581	1.809062
15	6	0	-0.779113	-0.170709	-0.870036
16	1	0	-0.684703	0.320896	-1.834110
17	6	0	0.110060	-1.378908	-0.679092
18	1	0	-0.292788	-2.045769	0.088884
19	1	0	0.191254	-1.934288	-1.615265
20	6	0	-4.653583	-0.556742	-0.440521
21	6	0	-3.934052	-1.406903	0.454702
22	6	0	-4.647196	-2.376641	1.202085
23	6	0	-6.012845	-2.478367	1.041085
24	6	0	-6.703214	-1.630892	0.151578
25	6	0	-6.031781	-0.664728	-0.591482
26	6	0	-2.193871	-0.183227	-0.298502
27	1	0	-4.099872	-3.020807	1.882617
28	1	0	-6.567549	-3.220275	1.606512
29	1	0	-7.778413	-1.731137	0.043939
30	1	0	-6.571316	-0.012967	-1.271022
31	7	0	-2.606393	-1.221268	0.525365
32	16	0	-3.567174	0.557636	-1.225035
33	7	0	1.451054	-0.875391	-0.321792
34	1	0	1.418326	-0.431401	0.601652
35	16	0	2.656293	-2.030642	-0.338799
36	8	0	2.656100	-2.595201	-1.686301
37	8	0	2.553535	-2.950856	0.794611
38	6	0	4.084169	-1.012455	-0.100405
39	6	0	4.444721	-0.109373	-1.101778
40	6	0	4.827446	-1.144038	1.065617
41	6	0	5.571508	0.676768	-0.915597
42	1	0	3.849501	-0.026528	-2.006291
43	6	0	5.957257	-0.345800	1.232912
44	1	0	4.526698	-1.857811	1.825534
45	6	0	6.342099	0.570425	0.252230
46	1	0	5.864820	1.385652	-1.685335
47	1	0	6.547460	-0.438064	2.140132
48	6	0	7.560331	1.435642	0.430411
49	1	0	8.055423	1.233716	1.383174
50	1	0	8.280397	1.261579	-0.375979
51	1	0	7.289714	2.496337	0.400610

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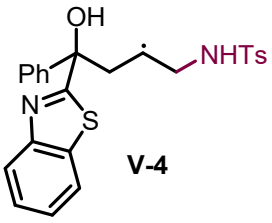
0 imaginary frequencies

Zero-point Energies= -2019.596395

Thermal Energies= -2019.569793

Thermal Enthalpies= -2019.568849

Thermal Free Energies= -2019.658512



V-4

4. Charge = 0 Multiplicity = 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.595026	3.196762	0.814580
2	6	0	1.603637	2.525665	0.090960
3	6	0	1.097824	3.116245	-1.068177
4	6	0	1.566147	4.358482	-1.491570
5	6	0	2.549052	5.024387	-0.764125
6	6	0	3.063278	4.437725	0.390273
7	1	0	3.016410	2.762761	1.717331
8	1	0	0.328735	2.600298	-1.631084
9	1	0	1.158773	4.805394	-2.393624
10	1	0	2.913059	5.992891	-1.093382
11	1	0	3.831364	4.945264	0.965955
12	6	0	1.085589	1.143424	0.520910
13	8	0	-0.096383	0.843688	-0.193070
14	1	0	0.050194	0.064783	-0.767612
15	6	0	0.744024	1.114819	2.027653
16	1	0	1.568519	1.536739	2.611518
17	1	0	-0.092601	1.823573	2.147491
18	6	0	0.403664	-0.230116	2.595850
19	1	0	0.553591	-0.363231	3.660964
20	6	0	-0.341554	-1.291971	1.858128
21	1	0	0.214964	-1.597852	0.959828
22	1	0	-0.470648	-2.172620	2.489222
23	6	0	4.054499	-1.411605	0.001498
24	6	0	3.022982	-1.600600	-0.936796
25	6	0	3.127447	-2.612087	-1.897625
26	6	0	4.260583	-3.409859	-1.899154
27	6	0	5.284692	-3.211988	-0.958342
28	6	0	5.196483	-2.213334	0.002167
29	6	0	2.133375	0.094348	0.170087
30	1	0	2.325848	-2.752837	-2.615522
31	1	0	4.359484	-4.200071	-2.636438
32	1	0	6.161804	-3.851002	-0.979719
33	1	0	5.988290	-2.063620	0.728745
34	7	0	1.951685	-0.726747	-0.805363
35	16	0	3.632325	-0.091381	1.064956
36	7	0	-1.704805	-0.809742	1.470769
37	1	0	-1.612271	0.153126	1.128792
38	16	0	-2.320183	-1.684456	0.181501
39	8	0	-2.596728	-3.033163	0.667033
40	8	0	-1.463437	-1.544156	-1.003938

41	6	0	-3.831956	-0.819768	-0.125466
42	6	0	-4.988260	-1.213819	0.545210
43	6	0	-3.827912	0.250582	-1.014186
44	6	0	-6.163381	-0.512535	0.312336
45	1	0	-4.963509	-2.057429	1.228060
46	6	0	-5.015777	0.943140	-1.229664
47	1	0	-2.913929	0.532675	-1.528493
48	6	0	-6.193475	0.573010	-0.573877
49	1	0	-7.075595	-0.809250	0.823237
50	1	0	-5.029225	1.780789	-1.921131
51	6	0	-7.480553	1.315655	-0.811869
52	1	0	-7.333874	2.155111	-1.495462
53	1	0	-8.236823	0.650457	-1.241889
54	1	0	-7.885213	1.702550	0.129020

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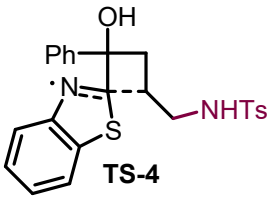
0 imaginary frequencies

Zero-point Energies= -2058.868911

Thermal Energies= -2058.841770

Thermal Enthalpies= -2058.840826

Thermal Free Energies= -2058.93025

5. 

TS-4 Charge = 0 Multiplicity = 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.613086	3.386761	1.091214
2	6	0	2.253789	2.319252	0.269038
3	6	0	2.737636	2.273183	-1.043258
4	6	0	3.577206	3.273738	-1.521159
5	6	0	3.939980	4.334569	-0.691042
6	6	0	3.455005	4.390384	0.612709
7	1	0	2.233173	3.446326	2.107103
8	1	0	2.458348	1.445357	-1.693083
9	1	0	3.950718	3.224509	-2.539399
10	1	0	4.598436	5.114475	-1.061325
11	1	0	3.729769	5.216198	1.261870
12	6	0	1.267381	1.260840	0.728868
13	8	0	-0.010088	1.530712	0.166011
14	1	0	0.034573	1.306101	-0.782386
15	6	0	1.066647	1.059297	2.241329
16	1	0	1.938419	1.394302	2.807282
17	1	0	0.177318	1.583555	2.604449
18	6	0	0.976261	-0.454299	2.274886
19	1	0	1.770825	-0.983264	2.794921

20	6	0	-0.308710	-1.221517	2.273440
21	1	0	-0.136833	-2.176400	1.754102
22	1	0	-0.593408	-1.457139	3.307955
23	6	0	2.906977	-2.143269	-0.518767
24	6	0	1.553333	-2.026813	-0.914392
25	6	0	0.971538	-3.039931	-1.693499
26	6	0	1.743250	-4.129590	-2.061368
27	6	0	3.087237	-4.229655	-1.665082
28	6	0	3.681545	-3.241346	-0.888757
29	6	0	1.654659	-0.196585	0.351984
30	1	0	-0.072130	-2.955084	-1.979570
31	1	0	1.303161	-4.921300	-2.659396
32	1	0	3.672038	-5.093445	-1.965042
33	1	0	4.718995	-3.323698	-0.580750
34	7	0	0.906659	-0.889913	-0.493113
35	16	0	3.367362	-0.746405	0.423466
36	7	0	-1.401206	-0.458887	1.652557
37	1	0	-1.053878	0.111073	0.870090
38	16	0	-2.673273	-1.392022	1.114610
39	8	0	-3.515761	-1.719150	2.263076
40	8	0	-2.206664	-2.504478	0.283033
41	6	0	-3.490871	-0.211935	0.078083
42	6	0	-4.634944	0.430677	0.538954
43	6	0	-2.951334	0.060720	-1.177481
44	6	0	-5.249868	1.367946	-0.283786
45	1	0	-5.031176	0.197618	1.522204
46	6	0	-3.576357	1.007093	-1.981129
47	1	0	-2.057139	-0.456710	-1.516779
48	6	0	-4.731837	1.668394	-1.548707
49	1	0	-6.145077	1.878335	0.061068
50	1	0	-3.165637	1.234288	-2.960913
51	6	0	-5.422677	2.669315	-2.435037
52	1	0	-4.750886	3.038638	-3.213849
53	1	0	-6.287910	2.211194	-2.927630
54	1	0	-5.788817	3.521472	-1.855429

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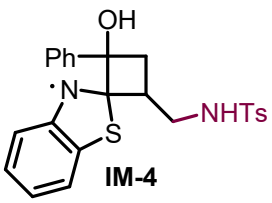
1 imaginary frequencies (-635.57)

Zero-point Energies= -2058.843415 3

Thermal Energies= -2058.817016

Thermal Enthalpies= -2058.816072

Thermal Free Energies= -2058.902349



IM-4

6. Charge = 0 Multiplicity = 2

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	-2.460012	3.523181	-0.693985
2	6	0	-2.221730	2.327391	-0.020102
3	6	0	-2.924607	2.056429	1.160204
4	6	0	-3.854013	2.963846	1.653627
5	6	0	-4.089575	4.159794	0.972573
6	6	0	-3.391320	4.437409	-0.198233
7	1	0	-1.915663	3.753509	-1.605302
8	1	0	-2.749814	1.120605	1.689985
9	1	0	-4.397619	2.739312	2.566358
10	1	0	-4.816325	4.869770	1.355648
11	1	0	-3.567473	5.367299	-0.730613
12	6	0	-1.180411	1.338375	-0.485155
13	8	0	-0.084796	1.327102	0.416097
14	1	0	-0.386077	0.892984	1.235582
15	6	0	-0.614437	1.396345	-1.915143
16	1	0	-1.265830	1.927886	-2.611274
17	1	0	0.397803	1.802923	-1.971311
18	6	0	-0.760220	-0.137511	-2.057439
19	1	0	-1.340068	-0.442726	-2.930807
20	6	0	0.490022	-1.006536	-2.039841
21	1	0	0.188728	-2.029411	-1.777346
22	1	0	0.926172	-1.025050	-3.041598
23	6	0	-3.532751	-1.678000	0.027565
24	6	0	-2.254826	-1.875264	0.654430
25	6	0	-2.125682	-2.886395	1.648017
26	6	0	-3.222847	-3.646054	1.981817
27	6	0	-4.470098	-3.431741	1.354617
28	6	0	-4.632888	-2.451536	0.379581
29	6	0	-1.637041	-0.171875	-0.748753
30	1	0	-1.156500	-3.035441	2.113065
31	1	0	-3.134473	-4.421720	2.735621
32	1	0	-5.320581	-4.043479	1.637858
33	1	0	-5.596806	-2.297355	-0.094218
34	7	0	-1.260072	-1.081242	0.268273
35	16	0	-3.441482	-0.401079	-1.143513
36	7	0	1.512831	-0.480021	-1.118953
37	1	0	1.104548	-0.070965	-0.270322
38	16	0	2.710793	-1.558366	-0.733949
39	8	0	3.209565	-2.082093	-2.004796
40	8	0	2.293237	-2.523234	0.285446
41	6	0	3.908563	-0.476993	-0.001634
42	6	0	4.482969	0.524974	-0.785560
43	6	0	4.274757	-0.660985	1.325284
44	6	0	5.435705	1.355514	-0.215747
45	1	0	4.181872	0.651078	-1.821345
46	6	0	5.234562	0.183649	1.880255
47	1	0	3.814706	-1.450212	1.910717
48	6	0	5.824108	1.197495	1.123320

49	1	0	5.890054	2.141362	-0.813416
50	1	0	5.528276	0.050902	2.917679
51	6	0	6.857552	2.114212	1.720273
52	1	0	7.071436	1.849257	2.758422
53	1	0	7.792623	2.067129	1.152487
54	1	0	6.514002	3.153767	1.694470

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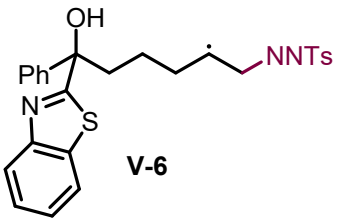
0 imaginary frequencies

Zero-point Energies= -2058.863147

Thermal Energies= -2058.835639

Thermal Enthalpies= -2058.834694

Thermal Free Energies= -2058.927275



V-6

7. Charge = 0 Multiplicity = 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.918352	2.644989	-1.623323
2	6	0	-4.357302	2.034807	-0.448108
3	6	0	-5.709490	2.124270	-0.099154
4	6	0	-6.605294	2.812538	-0.908561
5	6	0	-6.160956	3.422373	-2.082766
6	6	0	-4.818510	3.336917	-2.436074
7	1	0	-2.874768	2.597074	-1.916578
8	1	0	-6.047069	1.653999	0.819665
9	1	0	-7.651494	2.875128	-0.624159
10	1	0	-6.859161	3.961585	-2.715855
11	1	0	-4.462093	3.811400	-3.345439
12	6	0	-3.435851	1.224732	0.467358
13	8	0	-3.764504	1.543211	1.804883
14	1	0	-3.785896	0.706570	2.305244
15	6	0	-1.937339	1.497013	0.226551
16	1	0	-1.669663	1.242551	-0.806050
17	1	0	-1.782887	2.576351	0.347942
18	6	0	1.350364	0.328454	1.893343
19	1	0	1.135476	-0.721870	2.072076
20	6	0	2.717455	0.823368	2.212340
21	1	0	2.703404	1.905723	2.398618
22	1	0	3.126464	0.320905	3.091670
23	6	0	-3.963062	-2.545783	-0.575626
24	6	0	-4.116123	-2.359482	0.811145
25	6	0	-4.396698	-3.453394	1.636900
26	6	0	-4.517620	-4.707443	1.059204

27	6	0	-4.363920	-4.882040	-0.325797
28	6	0	-4.086503	-3.806993	-1.159674
29	6	0	-3.711049	-0.258365	0.253989
30	1	0	-4.512767	-3.302104	2.705359
31	1	0	-4.734566	-5.567653	1.684356
32	1	0	-4.463801	-5.874206	-0.754379
33	1	0	-3.969173	-3.945221	-2.229560
34	7	0	-3.962298	-1.046724	1.241226
35	16	0	-3.631618	-1.005803	-1.332848
36	7	0	3.632613	0.499692	1.075444
37	1	0	3.298868	0.924560	0.206113
38	16	0	5.221852	0.955364	1.314910
39	8	0	5.631788	0.336085	2.573108
40	8	0	5.412860	2.398750	1.159827
41	6	0	6.012927	0.145886	-0.047414
42	6	0	6.043741	-1.249311	-0.077820
43	6	0	6.605660	0.909636	-1.044703
44	6	0	6.679189	-1.879398	-1.136875
45	1	0	5.575794	-1.825754	0.714675
46	6	0	7.240348	0.257551	-2.100149
47	1	0	6.572014	1.992956	-0.992589
48	6	0	7.285830	-1.136452	-2.161044
49	1	0	6.711270	-2.965061	-1.175011
50	1	0	7.708888	0.842726	-2.886305
51	6	0	7.972457	-1.843412	-3.298176
52	1	0	8.391940	-1.131321	-4.012741
53	1	0	8.784514	-2.476982	-2.926254
54	1	0	7.270889	-2.494090	-3.830713
55	6	0	-1.030479	0.729294	1.183940
56	1	0	-1.147085	-0.351939	1.029645
57	1	0	-1.327348	0.937942	2.217755
58	6	0	0.442857	1.099474	0.995086
59	1	0	0.714127	0.926938	-0.062753
60	1	0	0.583363	2.176309	1.165488

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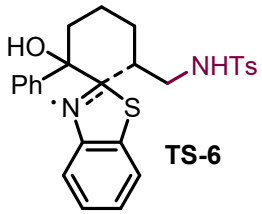
0 imaginary frequencies

Zero-point Energies= -2137.395095

Thermal Energies= -2137.363657

Thermal Enthalpies= -2137.362713

Thermal Free Energies= -2137.466705



TS-6

8. Charge = 0 Multiplicity = 2

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	-4.980693	-0.107933	-0.293964
2	6	0	-4.232517	-1.280354	-0.173659
3	6	0	-4.829196	-2.495889	-0.533503
4	6	0	-6.144926	-2.541102	-0.981005
5	6	0	-6.889148	-1.366054	-1.084839
6	6	0	-6.300685	-0.152425	-0.745199
7	1	0	-4.546428	0.856121	-0.050702
8	1	0	-4.245608	-3.410239	-0.478450
9	1	0	-6.587887	-3.494055	-1.255195
10	1	0	-7.916017	-1.397556	-1.436353
11	1	0	-6.864072	0.771620	-0.834621
12	6	0	-2.776754	-1.342898	0.322682
13	8	0	-2.022589	-2.094646	-0.616527
14	1	0	-2.001879	-1.568359	-1.436946
15	6	0	-2.725614	-2.101943	1.661427
16	1	0	-3.563988	-1.767567	2.282513
17	1	0	-2.924092	-3.149088	1.409526
18	6	0	-0.071822	-0.569195	0.888354
19	1	0	0.109652	0.289368	1.535205
20	6	0	0.679298	-0.508231	-0.409144
21	1	0	0.348773	-1.300904	-1.089197
22	1	0	0.538663	0.460329	-0.893805
23	6	0	-2.095792	2.487595	0.845770
24	6	0	-1.817127	2.068051	-0.477084
25	6	0	-1.447942	3.020882	-1.441212
26	6	0	-1.366249	4.352490	-1.070976
27	6	0	-1.644588	4.754782	0.246319
28	6	0	-2.008282	3.829181	1.216791
29	6	0	-2.156952	0.053013	0.410946
30	1	0	-1.231108	2.694860	-2.453680
31	1	0	-1.078696	5.097133	-1.806431
32	1	0	-1.573095	5.804534	0.512779
33	1	0	-2.219012	4.142451	2.234279
34	7	0	-1.943982	0.720242	-0.709457
35	16	0	-2.523038	1.106177	1.822460
36	7	0	2.127143	-0.631995	-0.098347
37	1	0	2.360036	-1.570962	0.235787
38	16	0	3.143596	-0.251472	-1.370453
39	8	0	2.811085	1.116103	-1.761318
40	8	0	3.140287	-1.285347	-2.406880
41	6	0	4.713833	-0.289811	-0.553187
42	6	0	4.985480	0.658864	0.433937
43	6	0	5.649364	-1.249052	-0.920096
44	6	0	6.220852	0.630703	1.063157
45	1	0	4.238888	1.400100	0.703247
46	6	0	6.885497	-1.259324	-0.277181
47	1	0	5.412819	-1.971986	-1.693934
48	6	0	7.186897	-0.326317	0.716936

49	1	0	6.446518	1.360594	1.836051
50	1	0	7.625825	-2.004455	-0.554012
51	6	0	8.524794	-0.328335	1.405806
52	1	0	9.119048	-1.198834	1.117974
53	1	0	9.091768	0.572753	1.147635
54	1	0	8.403121	-0.335090	2.493577
55	6	0	-1.419228	-2.000267	2.464057
56	1	0	-1.344812	-2.880795	3.109599
57	1	0	-1.449069	-1.132770	3.133587
58	6	0	-0.166297	-1.893023	1.590845
59	1	0	0.719311	-2.002381	2.236744
60	1	0	-0.143192	-2.707144	0.859273

---

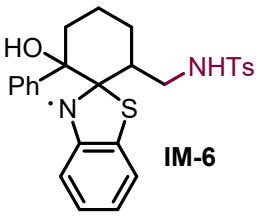
1 imaginary frequencies (-512.36)

Zero-point Energies= -2137.380202

Thermal Energies= -2137.350632

Thermal Enthalpies= -2137.349688

Thermal Free Energies= -2137.444899



IM-6

9. Charge = 0 Multiplicity = 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.688188	-1.351462	0.629403
2	6	0	-3.708487	-1.412692	-0.369384
3	6	0	-4.111661	-1.202794	-1.693108
4	6	0	-5.438911	-0.922367	-2.008244
5	6	0	-6.398645	-0.848049	-1.002373
6	6	0	-6.016728	-1.068664	0.317808
7	1	0	-4.424107	-1.515380	1.668265
8	1	0	-3.391003	-1.271216	-2.500531
9	1	0	-5.720077	-0.764340	-3.045237
10	1	0	-7.433828	-0.627858	-1.245235
11	1	0	-6.753334	-1.024587	1.114605
12	6	0	-2.227000	-1.667522	-0.052532
13	8	0	-1.536437	-2.061844	-1.229641
14	1	0	-1.489124	-1.277673	-1.806006
15	6	0	-2.027365	-2.806412	0.961786
16	1	0	-2.883564	-2.873121	1.635698
17	1	0	-2.018667	-3.725434	0.365608
18	6	0	0.048336	-0.588571	0.599319
19	1	0	0.365715	0.050034	1.429860
20	6	0	0.856208	-0.123286	-0.616733

21	1	0	0.592789	-0.698728	-1.511502
22	1	0	0.673257	0.933974	-0.813265
23	6	0	-2.937357	1.616825	1.218501
24	6	0	-2.546181	1.629279	-0.164577
25	6	0	-3.029109	2.672860	-1.004770
26	6	0	-3.853458	3.638383	-0.474793
27	6	0	-4.223969	3.605720	0.886989
28	6	0	-3.771068	2.599747	1.737181
29	6	0	-1.493639	-0.340969	0.417923
30	1	0	-2.736451	2.676164	-2.049687
31	1	0	-4.229444	4.435413	-1.108089
32	1	0	-4.877170	4.378131	1.280032
33	1	0	-4.065432	2.585311	2.781515
34	7	0	-1.756722	0.647870	-0.582895
35	16	0	-2.216989	0.270217	2.042835
36	7	0	2.289996	-0.270499	-0.293560
37	1	0	2.570005	-1.253147	-0.243193
38	16	0	3.323600	0.518066	-1.342804
39	8	0	2.927960	1.923947	-1.328493
40	8	0	3.417292	-0.160198	-2.636431
41	6	0	4.863214	0.310515	-0.493501
42	6	0	5.049050	0.955778	0.730170
43	6	0	5.859643	-0.470324	-1.065061
44	6	0	6.260083	0.802173	1.387554
45	1	0	4.256028	1.563853	1.155369
46	6	0	7.069987	-0.611647	-0.388775
47	1	0	5.690436	-0.955881	-2.020647
48	6	0	7.285808	0.017462	0.838769
49	1	0	6.419968	1.297435	2.341662
50	1	0	7.857839	-1.219700	-0.824155
51	6	0	8.592451	-0.131259	1.570312
52	1	0	9.276501	-0.791115	1.031502
53	1	0	9.079337	0.841852	1.694052
54	1	0	8.431892	-0.543594	2.571882
55	6	0	-0.732845	-2.691325	1.778084
56	1	0	-0.430876	-3.685429	2.120795
57	1	0	-0.905451	-2.095630	2.684551
58	6	0	0.382769	-2.047714	0.961839
59	1	0	1.319818	-2.063012	1.528349
60	1	0	0.538114	-2.627804	0.044299

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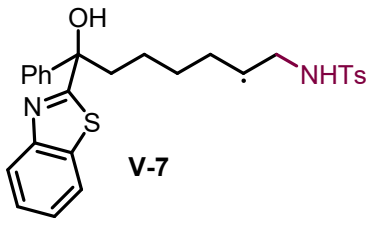
0 imaginary frequencies

Zero-point Energies= -2137.415627

Thermal Energies= -2137.386591

Thermal Enthalpies= -2137.385647

Thermal Free Energies= -2137.479117



V-7

10. Charge = 0 Multiplicity = 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.655949	3.092559	-0.922063
2	6	0	-2.936100	2.461167	0.291428
3	6	0	-3.645745	3.160689	1.272924
4	6	0	-4.062093	4.468397	1.048004
5	6	0	-3.778013	5.095426	-0.165276
6	6	0	-3.075652	4.404207	-1.147528
7	1	0	-2.105033	2.576213	-1.701678
8	1	0	-3.858516	2.670098	2.217221
9	1	0	-4.609118	4.999941	1.821097
10	1	0	-4.101870	6.116729	-0.341589
11	1	0	-2.846605	4.883788	-2.094471
12	6	0	-2.549645	1.006879	0.571743
13	8	0	-2.232787	0.891945	1.943993
14	1	0	-2.646045	0.070738	2.268787
15	6	0	-1.350783	0.525512	-0.272366
16	1	0	-1.589218	0.594176	-1.339880
17	1	0	-0.524796	1.220748	-0.077149
18	6	0	2.022852	-3.149053	-1.114717
19	1	0	1.998283	-3.155892	-2.200791
20	6	0	3.348333	-3.230277	-0.442479
21	1	0	3.256028	-3.717473	0.537741
22	1	0	4.066554	-3.789464	-1.045823
23	6	0	-5.612426	-1.151180	-0.669371
24	6	0	-5.216311	-1.505219	0.634089
25	6	0	-5.880135	-2.533874	1.311280
26	6	0	-6.923481	-3.184553	0.671636
27	6	0	-7.311894	-2.821844	-0.628341
28	6	0	-6.664598	-1.802611	-1.313930
29	6	0	-3.749886	0.113101	0.287214
30	1	0	-5.569034	-2.802470	2.315787
31	1	0	-7.449031	-3.985636	1.181394
32	1	0	-8.132638	-3.345919	-1.107670
33	1	0	-6.967371	-1.523439	-2.317867
34	7	0	-4.153518	-0.765215	1.138772
35	16	0	-4.611833	0.162503	-1.241551
36	7	0	3.909377	-1.852607	-0.284482
37	1	0	3.285317	-1.267609	0.278459
38	16	0	5.435908	-1.801827	0.393694
39	8	0	6.278323	-2.649765	-0.446742
40	8	0	5.411500	-2.063814	1.834195

41	6	0	5.850385	-0.097357	0.149030
42	6	0	6.013507	0.376189	-1.153911
43	6	0	6.022954	0.729386	1.251732
44	6	0	6.350087	1.707919	-1.342297
45	1	0	5.875927	-0.289817	-2.000591
46	6	0	6.362469	2.064551	1.041437
47	1	0	5.895706	0.333856	2.254124
48	6	0	6.528592	2.569775	-0.249428
49	1	0	6.479573	2.091625	-2.350837
50	1	0	6.501113	2.721848	1.895114
51	6	0	6.891233	4.011966	-0.480138
52	1	0	7.025556	4.543793	0.464696
53	1	0	7.819160	4.091333	-1.055915
54	1	0	6.108837	4.521006	-1.052988
55	6	0	-0.919685	-0.902102	0.053702
56	1	0	-1.725920	-1.605822	-0.195275
57	1	0	-0.742464	-0.990450	1.132395
58	6	0	0.343868	-1.301852	-0.704544
59	1	0	0.169784	-1.219281	-1.785425
60	1	0	1.153567	-0.599373	-0.465695
61	6	0	0.793747	-2.737471	-0.375580
62	1	0	-0.038184	-3.415130	-0.618662
63	1	0	0.964161	-2.823082	0.706116

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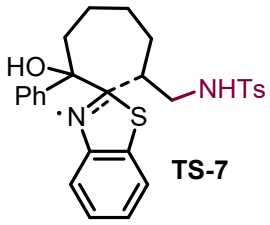
0 imaginary frequencies

Zero-point Energies= -2176.659914

Thermal Energies= -2176.627394

Thermal Enthalpies= -2176.626450

Thermal Free Energies= -2176.73259



TS-7

11. Charge = 0 Multiplicity = 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.136299	1.719174	0.559866
2	6	0	-2.915608	1.999445	-0.064983
3	6	0	-2.270088	3.198834	0.242783
4	6	0	-2.823948	4.092425	1.158379
5	6	0	-4.035308	3.802775	1.779293
6	6	0	-4.690745	2.612002	1.473236
7	1	0	-4.668099	0.797772	0.343569
8	1	0	-1.335598	3.450059	-0.246190
9	1	0	-2.304156	5.019664	1.381272

10	1	0	-4.467290	4.498660	2.492081
11	1	0	-5.639067	2.373425	1.945549
12	6	0	-2.280912	1.020012	-1.079151
13	8	0	-1.154258	1.615847	-1.684912
14	1	0	-0.443093	1.629110	-1.017337
15	6	0	-3.297618	0.744543	-2.195300
16	1	0	-4.211305	0.333926	-1.748667
17	1	0	-3.565720	1.738204	-2.572346
18	6	0	-0.650110	-1.300614	-1.885268
19	1	0	-0.405092	-0.364743	-2.378004
20	6	0	0.497675	-1.939282	-1.166410
21	1	0	0.151508	-2.499277	-0.283109
22	1	0	0.977384	-2.666430	-1.836611
23	6	0	-1.873522	-1.795957	1.639654
24	6	0	-0.795201	-0.882239	1.626056
25	6	0	0.193264	-0.965774	2.619803
26	6	0	0.081755	-1.944474	3.593820
27	6	0	-0.995421	-2.845731	3.594367
28	6	0	-1.980883	-2.784814	2.615944
29	6	0	-1.795590	-0.198811	-0.256500
30	1	0	1.025543	-0.268409	2.605931
31	1	0	0.841062	-2.020582	4.365676
32	1	0	-1.059964	-3.604019	4.368194
33	1	0	-2.810150	-3.485059	2.614478
34	7	0	-0.813644	0.032822	0.601144
35	16	0	-2.925691	-1.472508	0.286108
36	7	0	1.511038	-0.927896	-0.821330
37	1	0	1.145710	-0.267711	-0.126883
38	16	0	2.979935	-1.533940	-0.322303
39	8	0	3.488373	-2.339922	-1.430786
40	8	0	2.914511	-2.158475	0.999938
41	6	0	3.899885	-0.027410	-0.179617
42	6	0	4.163493	0.715519	-1.331462
43	6	0	4.353030	0.378607	1.069281
44	6	0	4.890595	1.890475	-1.215151
45	1	0	3.801576	0.376827	-2.297715
46	6	0	5.082792	1.561959	1.165018
47	1	0	4.139743	-0.222781	1.947157
48	6	0	5.359023	2.330072	0.032287
49	1	0	5.103894	2.480238	-2.102745
50	1	0	5.443382	1.891093	2.135390
51	6	0	6.141031	3.611711	0.133345
52	1	0	5.524860	4.465325	-0.168945
53	1	0	6.488775	3.784943	1.154469
54	1	0	7.011982	3.588940	-0.529607
55	6	0	-2.894485	-0.134694	-3.385166
56	1	0	-1.932780	0.195612	-3.793985
57	1	0	-3.636533	0.063601	-4.165902
58	6	0	-2.893587	-1.644233	-3.104603
59	1	0	-3.678028	-1.859876	-2.368918

60	1	0	-3.187064	-2.180610	-4.012630
61	6	0	-1.555729	-2.233046	-2.626045
62	1	0	-0.981459	-2.564177	-3.507641
63	1	0	-1.733609	-3.137467	-2.030873

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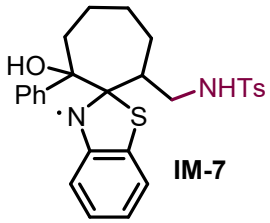
1 imaginary frequencies (-448.12)

Zero-point Energies= -2176.645642

Thermal Energies= -2176.615128

Thermal Enthalpies= -2176.614184

Thermal Free Energies= -2176.710285



IM-7

12. Charge = 0 Multiplicity = 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.655508	3.092468	-0.922122
2	6	0	-2.935741	2.461107	0.291367
3	6	0	-3.645371	3.160680	1.272834
4	6	0	-4.061627	4.468415	1.047891
5	6	0	-3.777466	5.095414	-0.165383
6	6	0	-3.075118	4.404140	-1.147609
7	1	0	-2.104607	2.576073	-1.701716
8	1	0	-3.858207	2.670111	2.217129
9	1	0	-4.608641	4.999999	1.820966
10	1	0	-4.101252	6.116736	-0.341719
11	1	0	-2.846015	4.883702	-2.094549
12	6	0	-2.549398	1.006798	0.571716
13	8	0	-2.232519	0.891899	1.943961
14	1	0	-2.645707	0.070661	2.268763
15	6	0	-1.350611	0.525306	-0.272425
16	1	0	-1.589112	0.593909	-1.339929
17	1	0	-0.524570	1.220509	-0.077315
18	6	0	2.022860	-3.149419	-1.114690
19	1	0	1.998245	-3.156334	-2.200763
20	6	0	3.348371	-3.230499	-0.442485
21	1	0	3.256147	-3.717694	0.537742
22	1	0	4.066639	-3.789611	-1.045843
23	6	0	-5.612385	-1.151040	-0.669281
24	6	0	-5.216231	-1.505123	0.634155
25	6	0	-5.880074	-2.533758	1.311358
26	6	0	-6.923483	-3.184373	0.671751
27	6	0	-7.311937	-2.821618	-0.628201
28	6	0	-6.664619	-1.802407	-1.313802

29	6	0	-3.749728	0.113117	0.287244
30	1	0	-5.568936	-2.802388	2.315845
31	1	0	-7.449048	-3.985440	1.181518
32	1	0	-8.132731	-3.345638	-1.107503
33	1	0	-6.967431	-1.523201	-2.317717
34	7	0	-4.153370	-0.765191	1.138803
35	16	0	-4.611755	0.162606	-1.241479
36	7	0	3.909270	-1.852766	-0.284506
37	1	0	3.285210	-1.267873	0.278547
38	16	0	5.435865	-1.801843	0.393529
39	8	0	6.278325	-2.649572	-0.447073
40	8	0	5.411631	-2.063985	1.834005
41	6	0	5.850060	-0.097287	0.148997
42	6	0	6.012887	0.376443	-1.153914
43	6	0	6.022741	0.729336	1.251773
44	6	0	6.349281	1.708234	-1.342194
45	1	0	5.875231	-0.289473	-2.000653
46	6	0	6.362059	2.064567	1.041583
47	1	0	5.895724	0.333666	2.254138
48	6	0	6.527883	2.569973	-0.249249
49	1	0	6.478549	2.092081	-2.350709
50	1	0	6.500793	2.721770	1.895318
51	6	0	6.890258	4.012251	-0.479844
52	1	0	7.025311	4.543820	0.465031
53	1	0	7.817699	4.091841	-1.056367
54	1	0	6.107351	4.521404	-1.051898
55	6	0	-0.919556	-0.902306	0.053718
56	1	0	-1.725850	-1.606009	-0.195117
57	1	0	-0.742223	-0.990573	1.132398
58	6	0	0.343901	-1.302179	-0.704626
59	1	0	0.169689	-1.219750	-1.785497
60	1	0	1.153641	-0.599682	-0.465974
61	6	0	0.793789	-2.737767	-0.375531
62	1	0	-0.038156	-3.415447	-0.618508
63	1	0	0.964258	-2.823268	0.706165

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0 imaginary frequencies

Zero-point Energies= -2176.684650

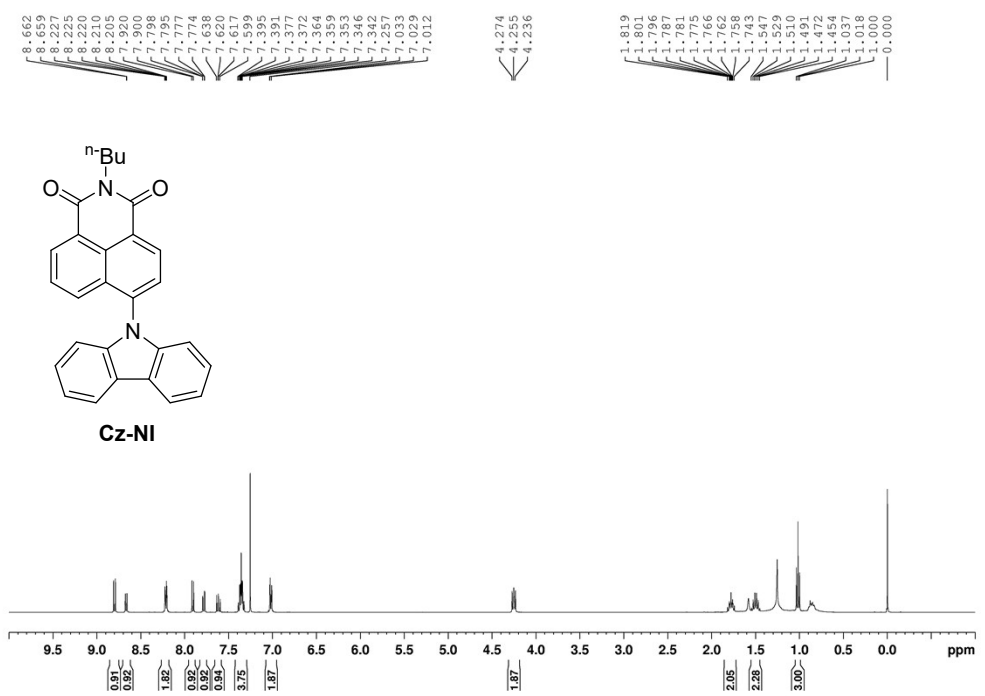
Thermal Energies= -2176.654499

Thermal Enthalpies= -2176.653555

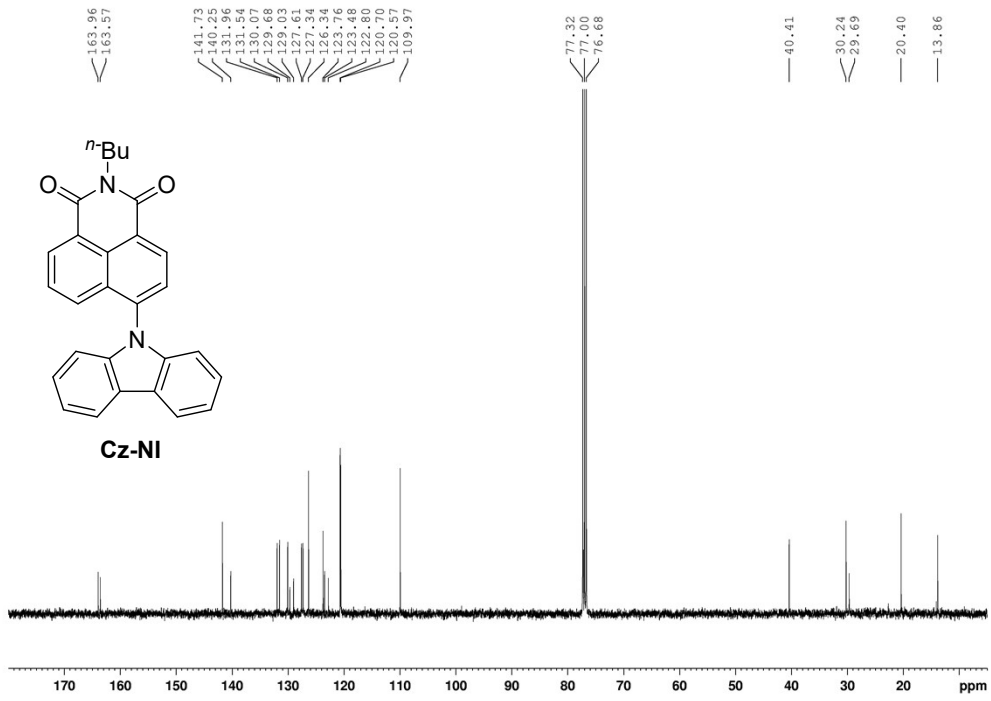
Thermal Free Energies= -2176.749534

10. NMR spectra of compound

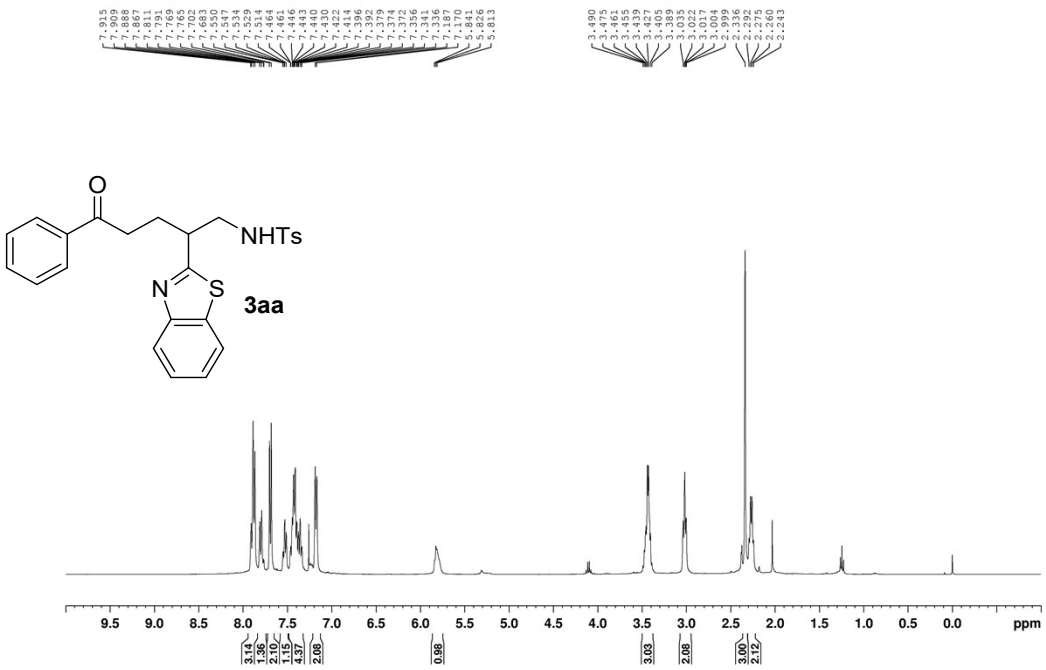
^{1}H NMR of **Cz-NI** in $CDCl_3$ (400 MHz, $CDCl_3$)



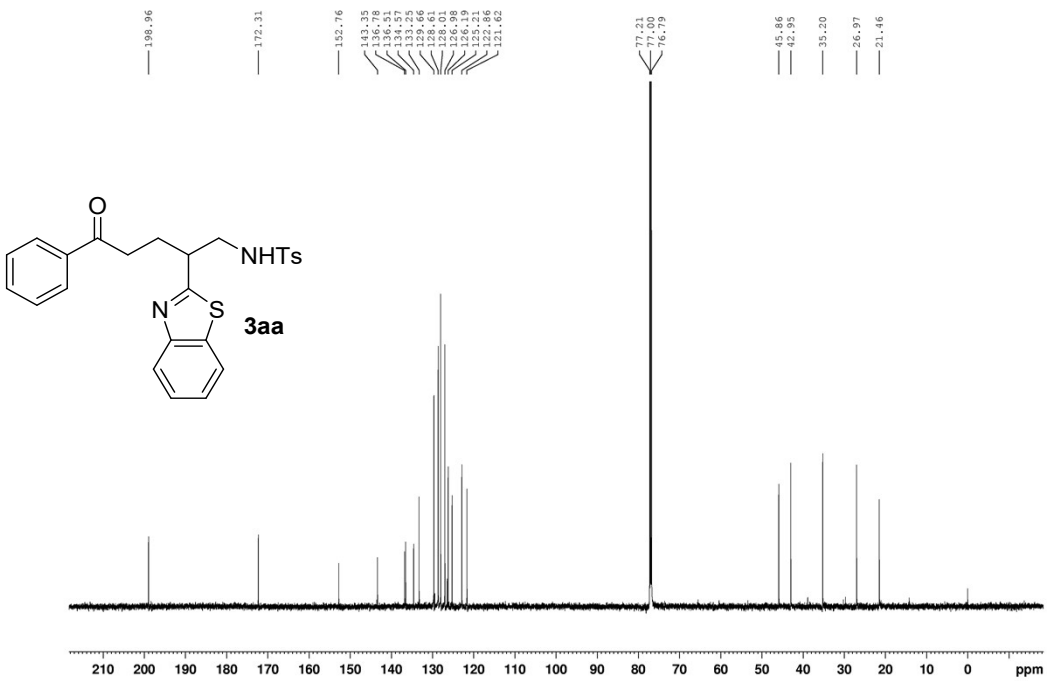
^{13}C NMR of **Cz-NI** in $CDCl_3$(400 MHz, $CDCl_3$)



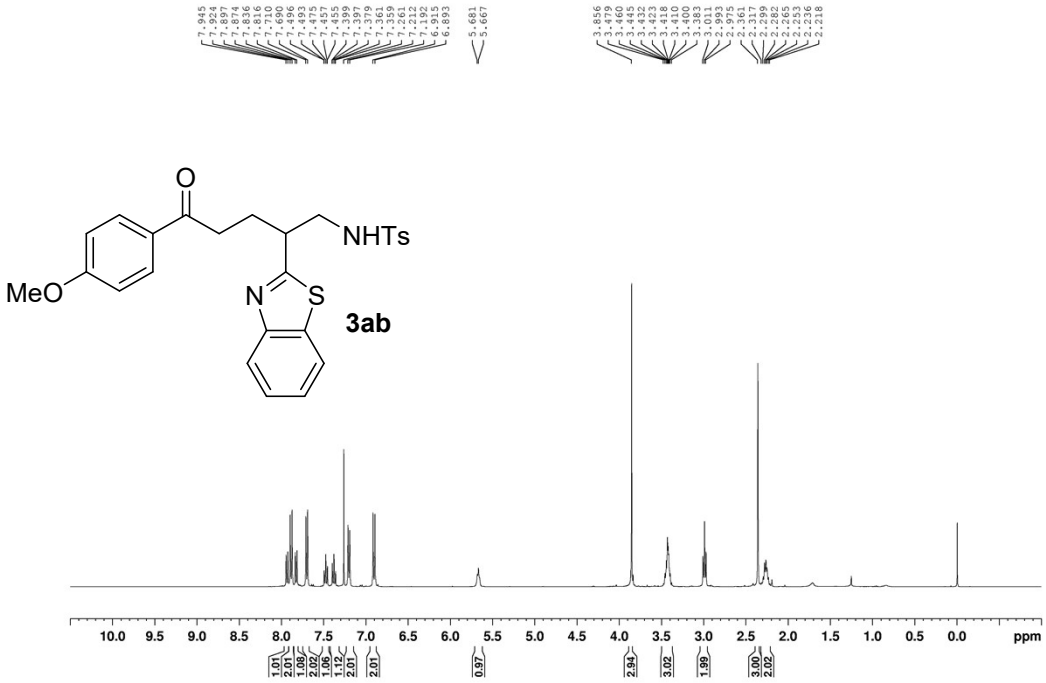
^{1}H NMR of **3aa** in $CDCl_3$(400 MHz, $CDCl_3$)



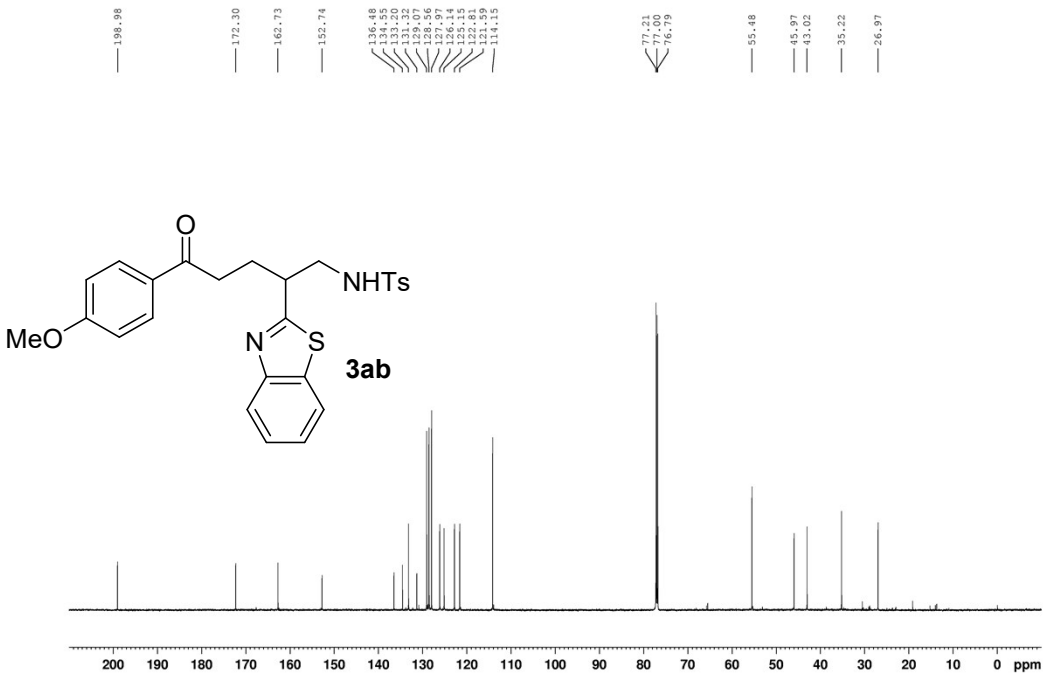
^{13}C NMR of **3aa** in $CDCl_3$(151 MHz, $CDCl_3$)



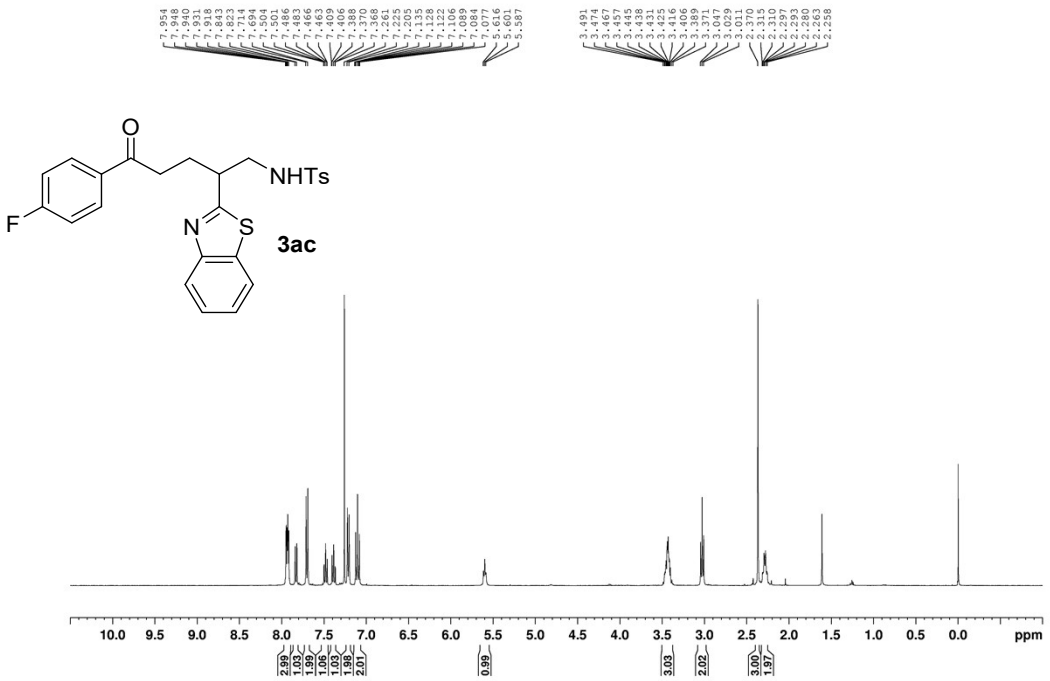
^{1}H NMR of **3ab** in $CDCl_3$(400 MHz, $CDCl_3$)



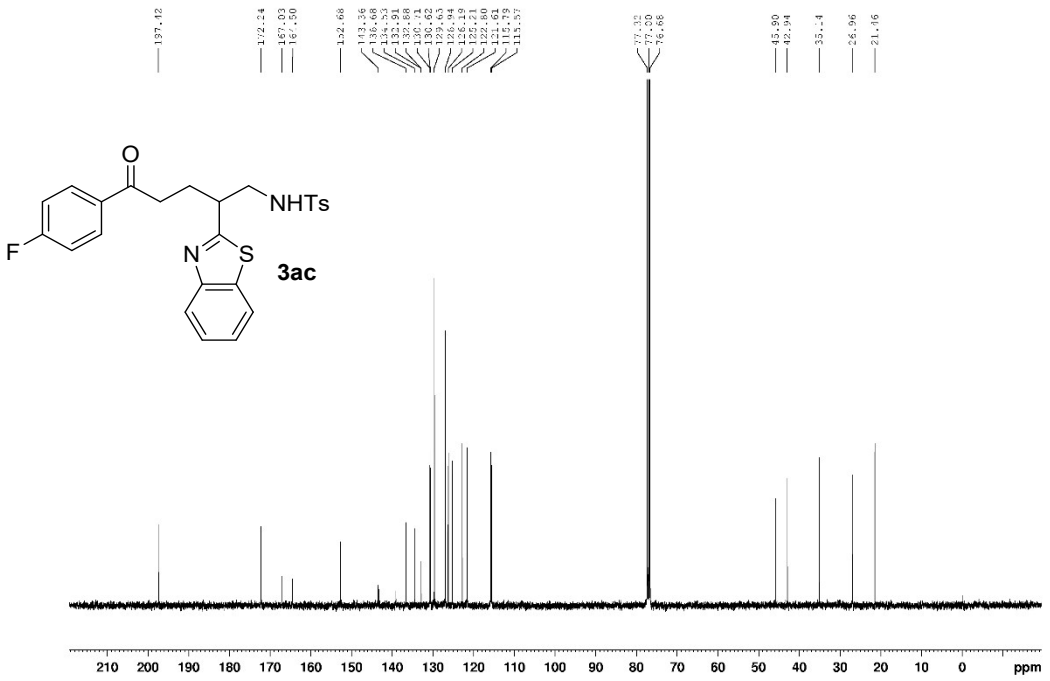
^{13}C NMR of **3ab** in $CDCl_3$(101 MHz, $CDCl_3$)



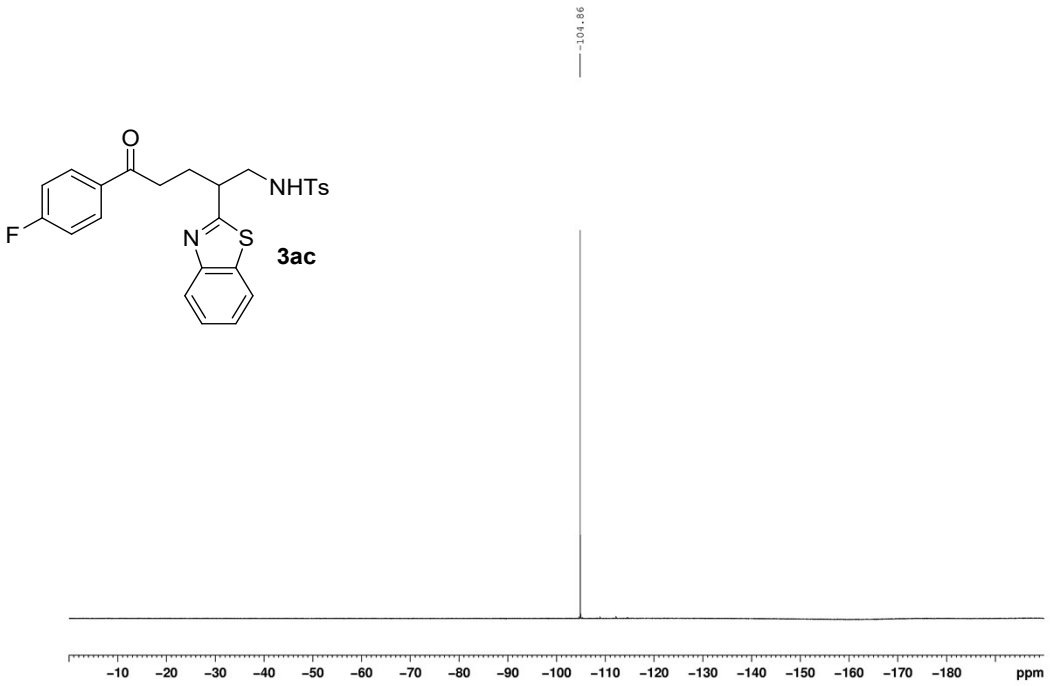
^{1}H NMR of **3ac** in $CDCl_3$(400 MHz, $CDCl_3$)



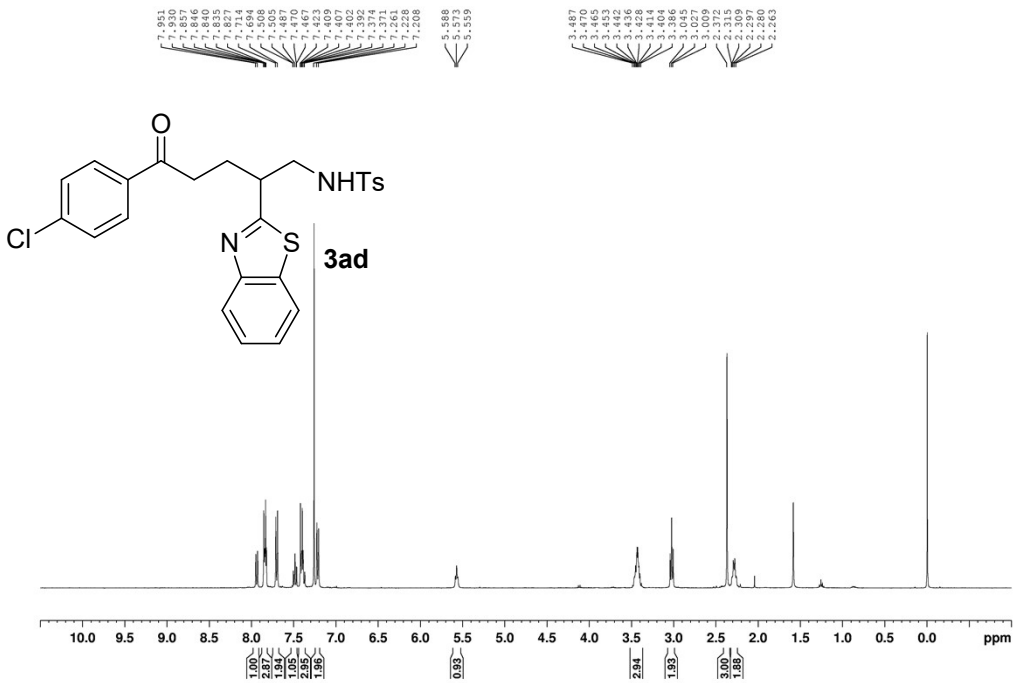
^{13}C NMR of **3ac** in $CDCl_3$(101 MHz, $CDCl_3$)



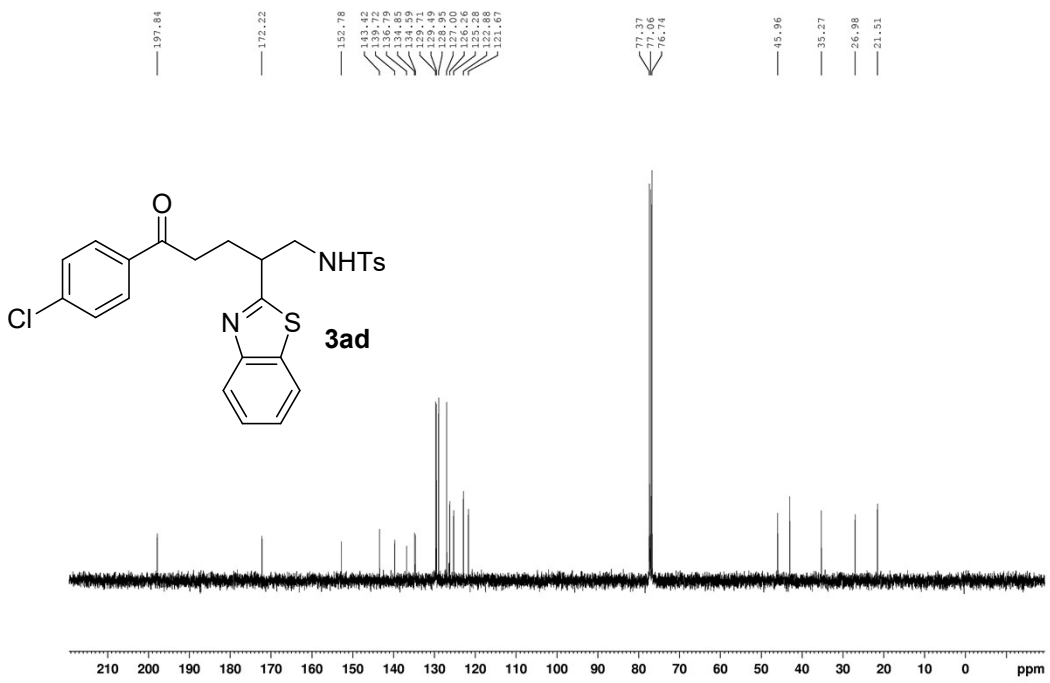
^{19}F NMR of **3ac** in $CDCl_3$(376 MHz, $CDCl_3$)



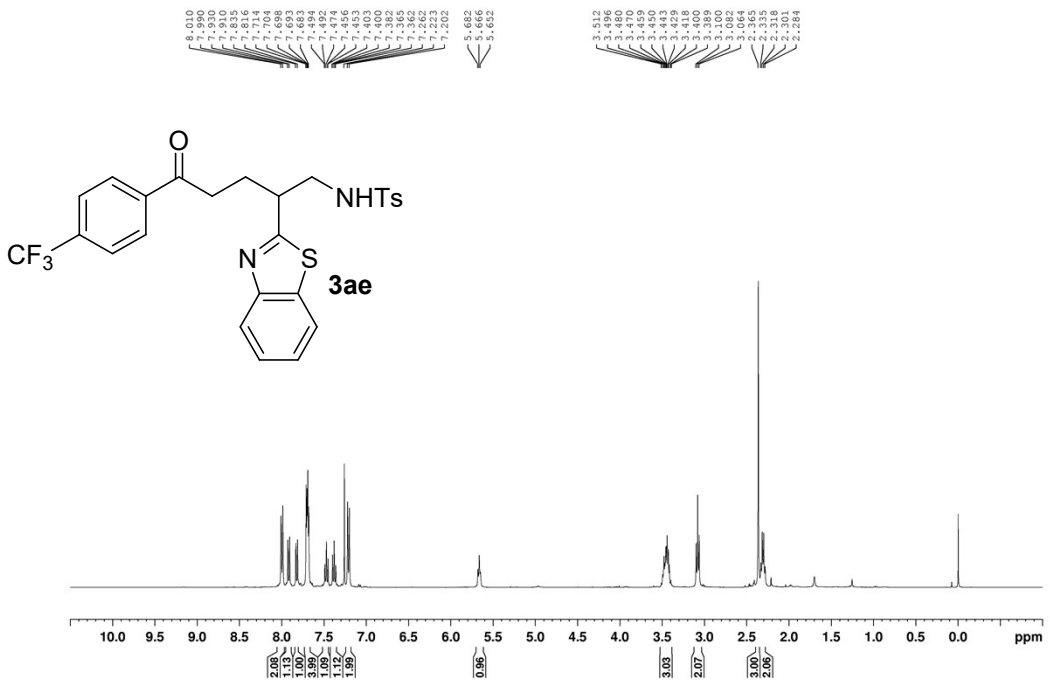
^{1}H NMR of **3ad** in $CDCl_3$(400 MHz, $CDCl_3$)



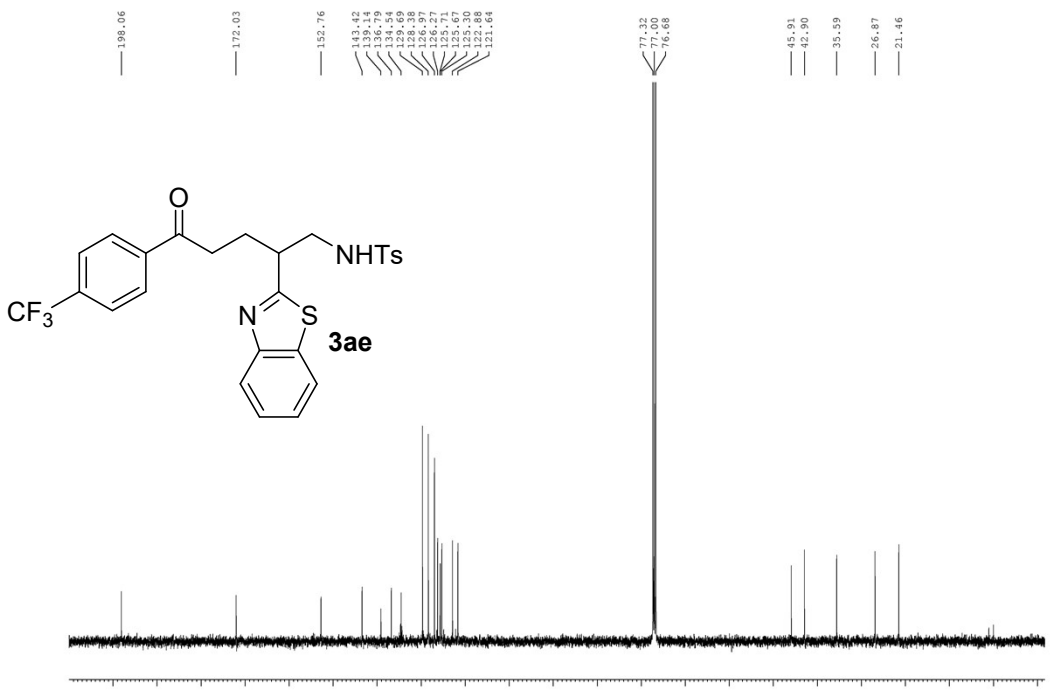
^{13}C NMR of **3ad** in $CDCl_3$(101 MHz, $CDCl_3$)



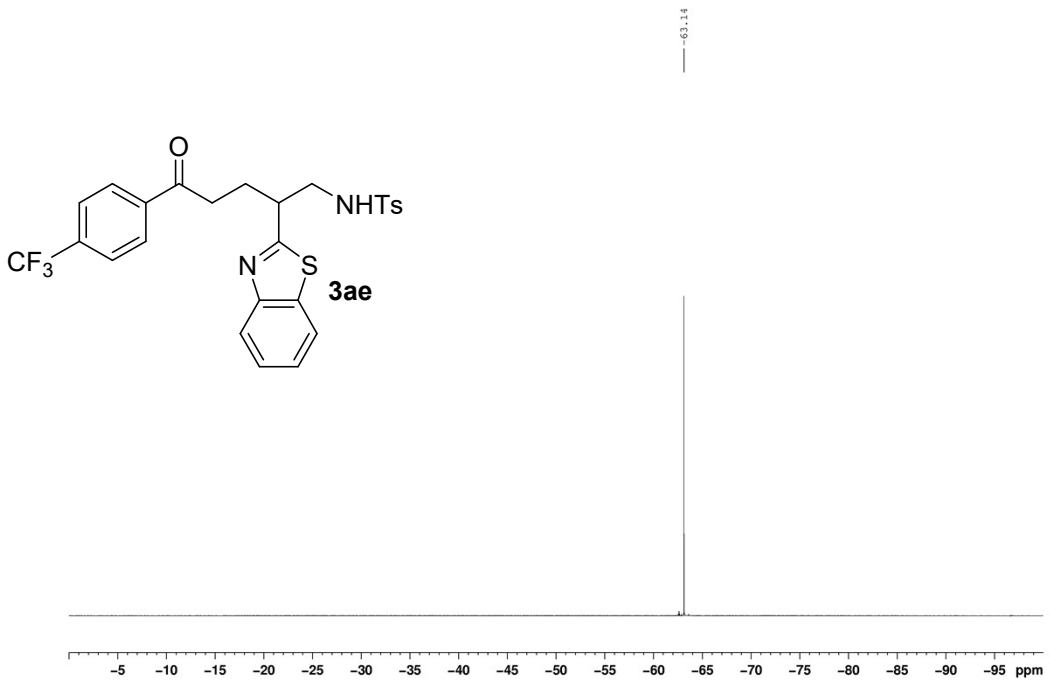
^{1}H NMR of **3ae** in $CDCl_3$(400 MHz, $CDCl_3$)



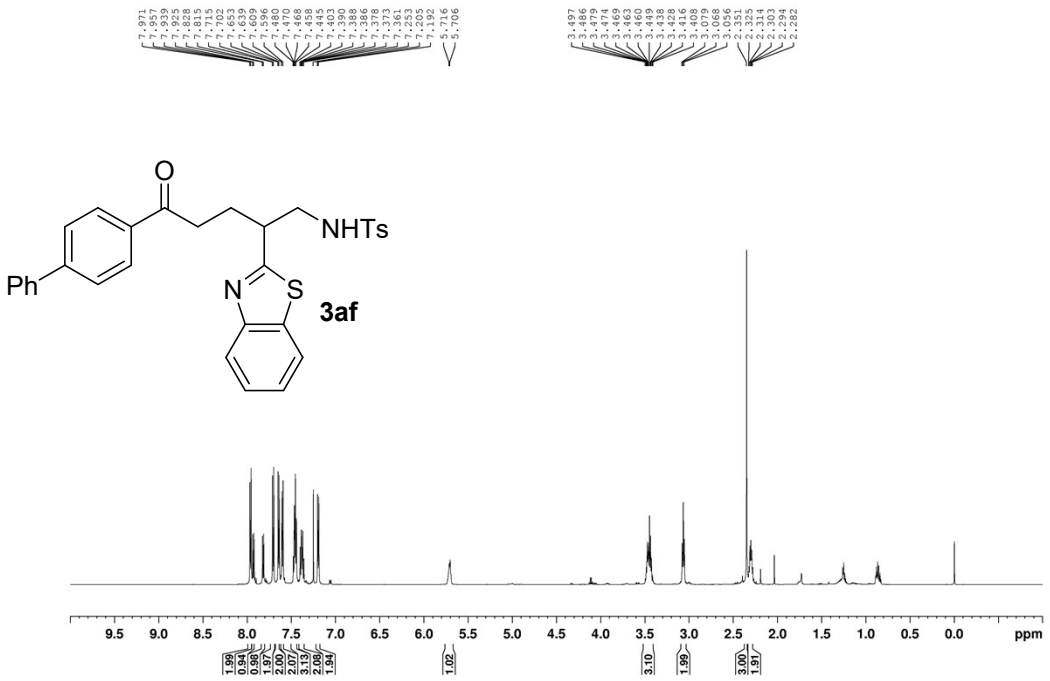
^{13}C NMR of **3ae** in $CDCl_3$(101 MHz, $CDCl_3$)



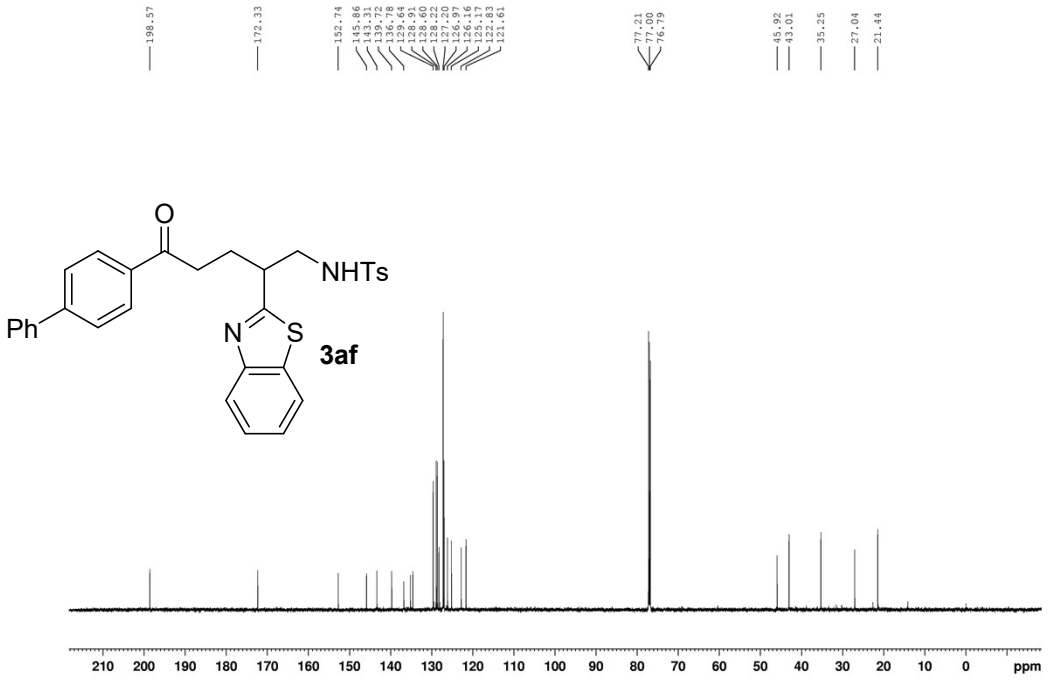
^{19}F NMR of **3ae** in $CDCl_3$(376 MHz, $CDCl_3$)



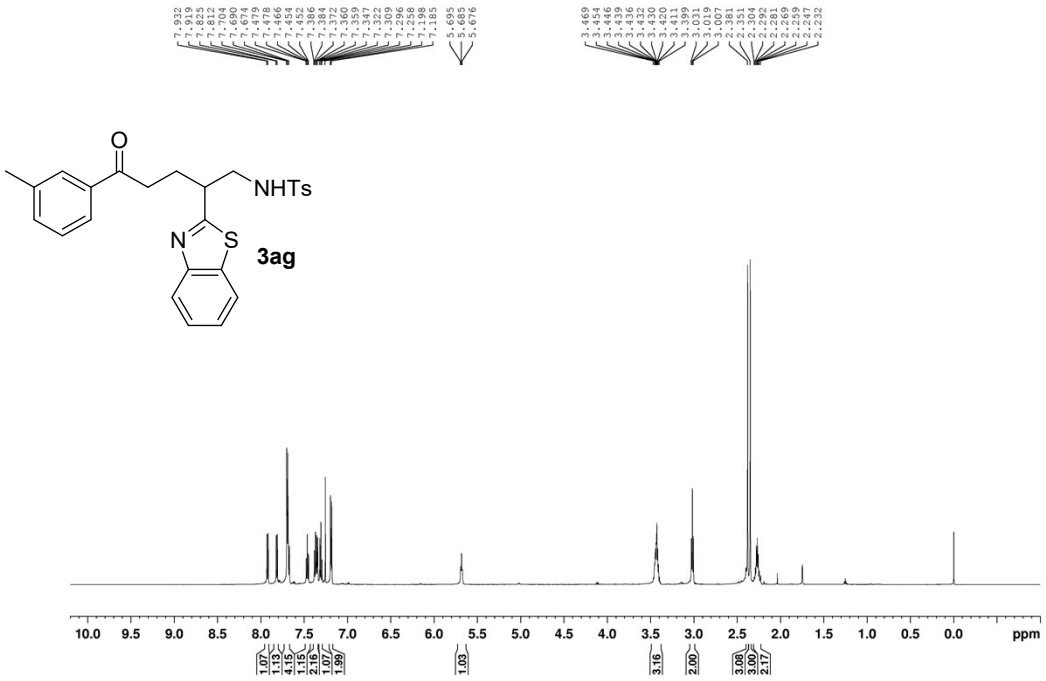
^{1}H NMR of **3af** in $CDCl_3$(600 MHz, $CDCl_3$)



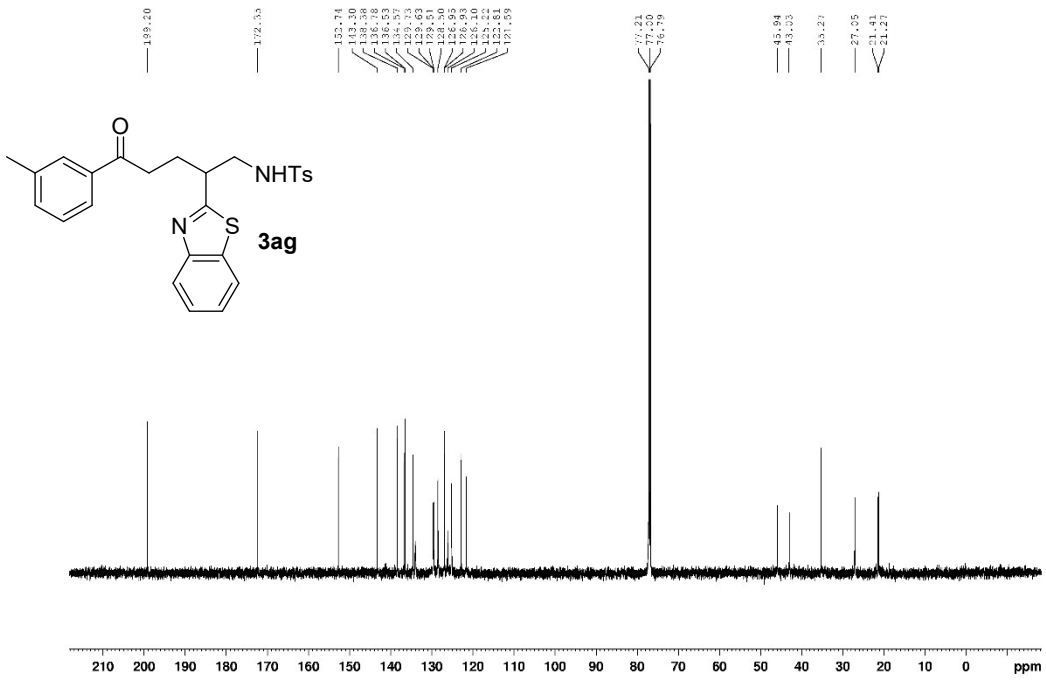
^{13}C NMR of **3af** in $CDCl_3$(151 MHz, $CDCl_3$)



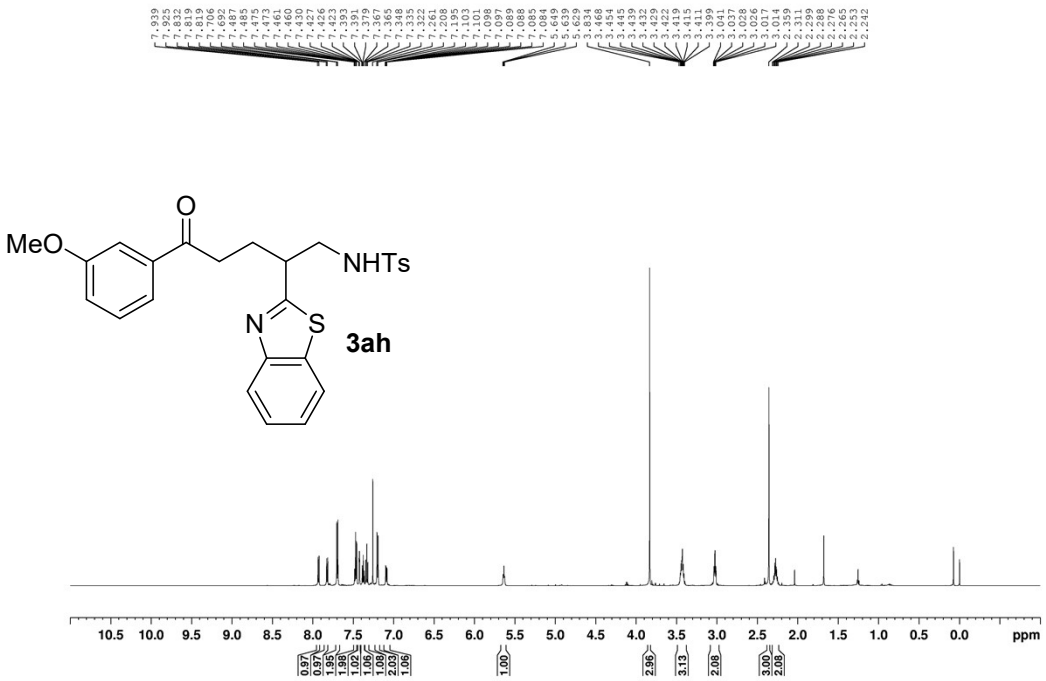
^{1}H NMR of **3ag** in $CDCl_3$(600 MHz, $CDCl_3$)



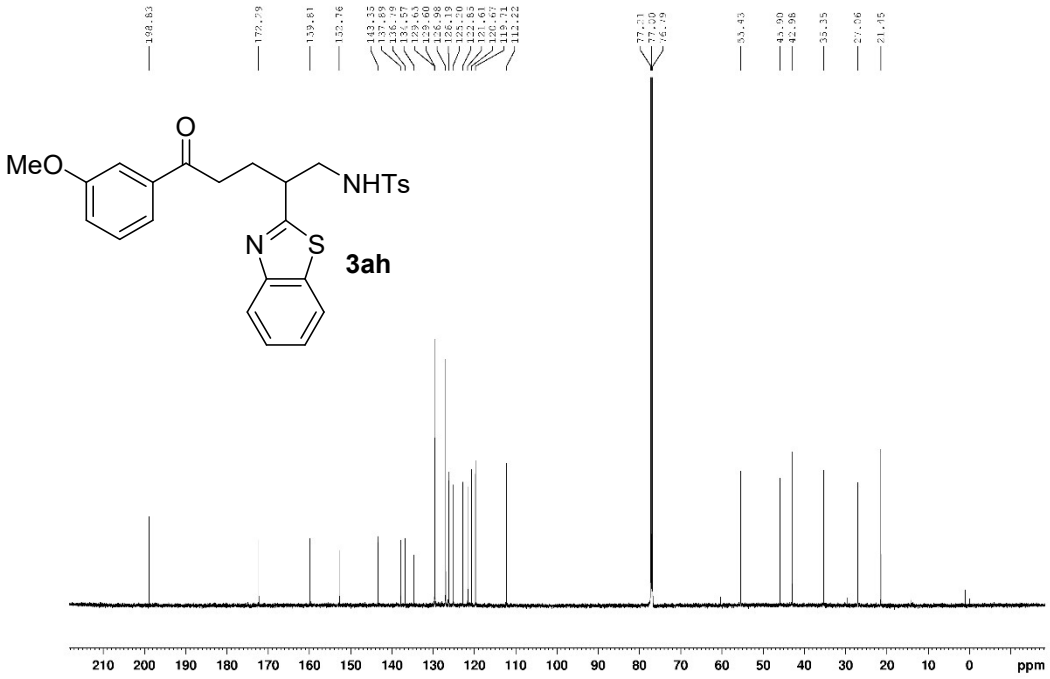
^{13}C NMR of **3ag** in $CDCl_3$(151 MHz, $CDCl_3$)



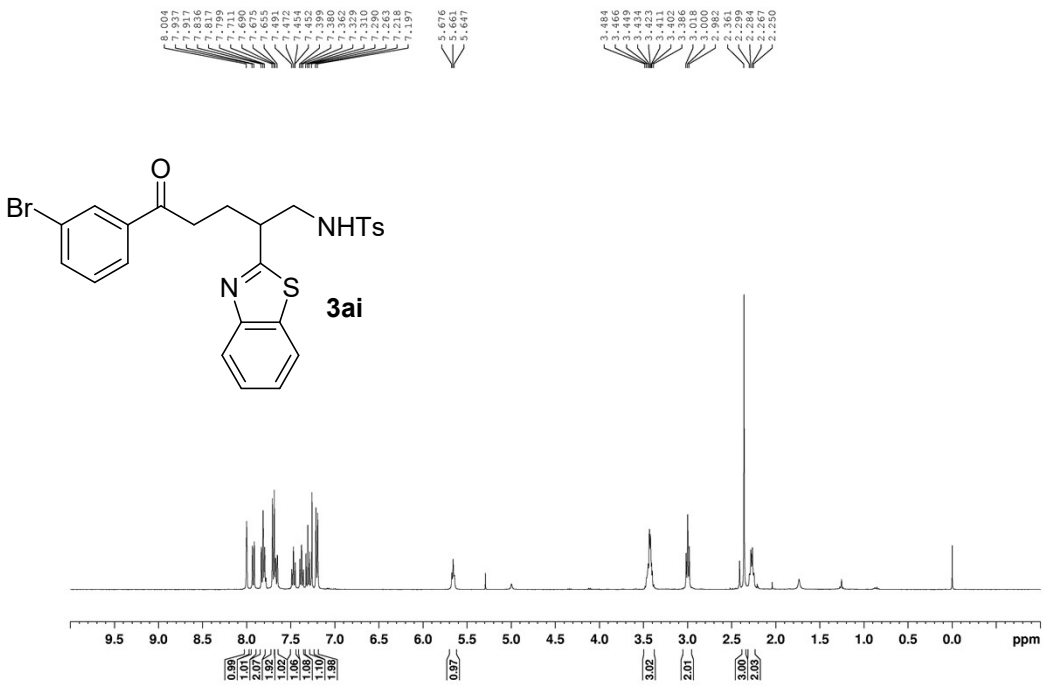
^{1}H NMR of **3ah** in $CDCl_3$(600 MHz, $CDCl_3$)



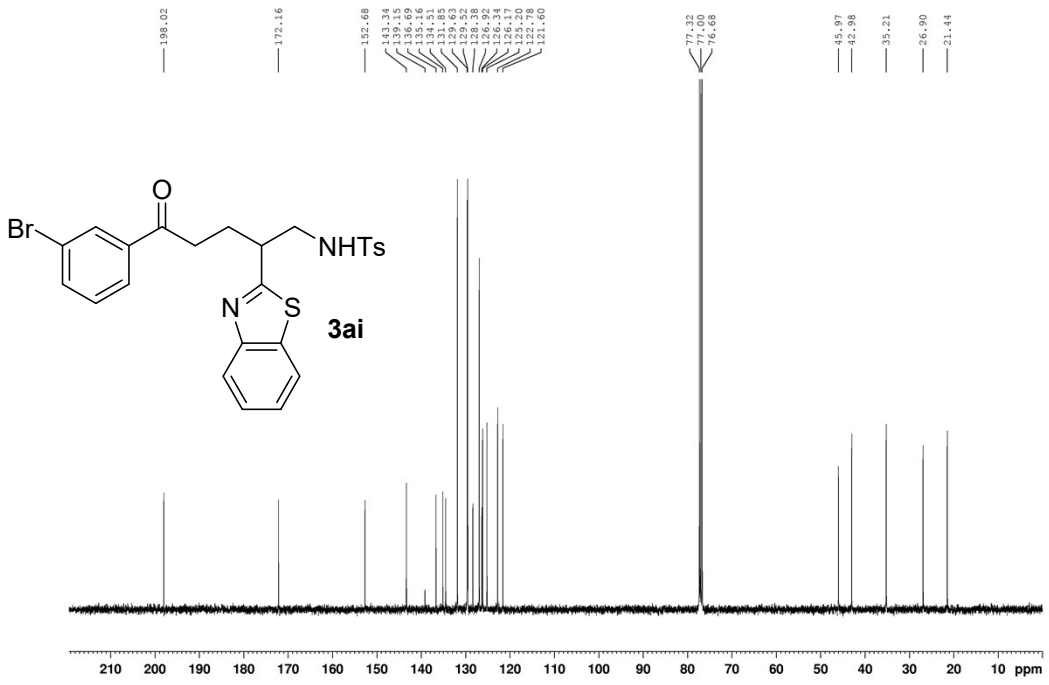
^{13}C NMR of **3ah** in $CDCl_3$(151 MHz, $CDCl_3$)



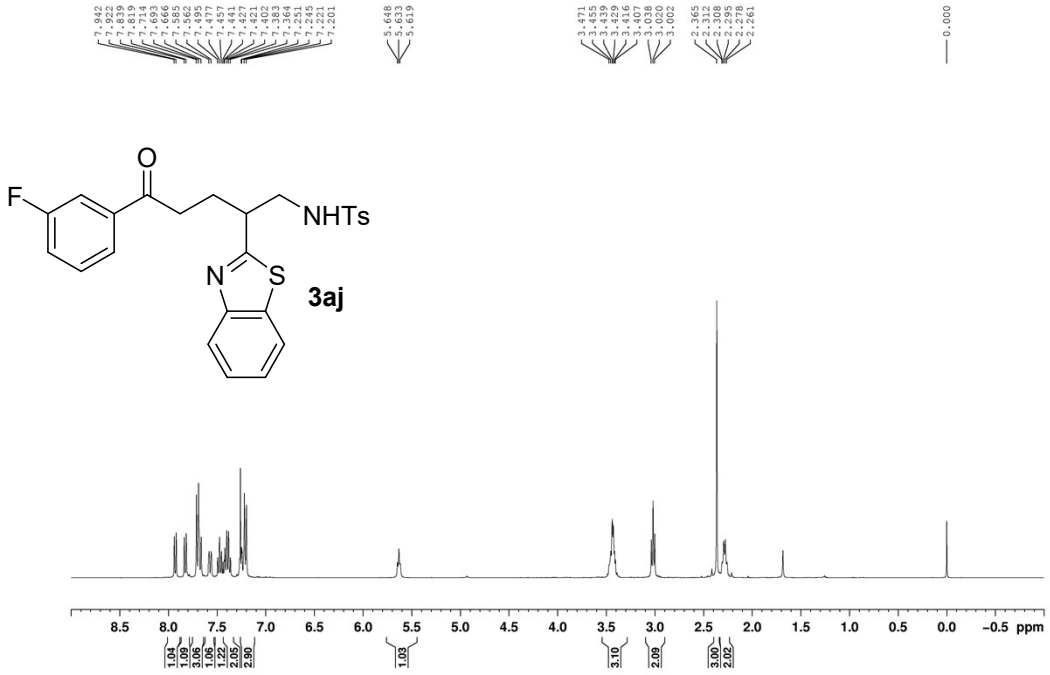
^{1}H NMR of **3ai** in $CDCl_3$(400 MHz, $CDCl_3$)



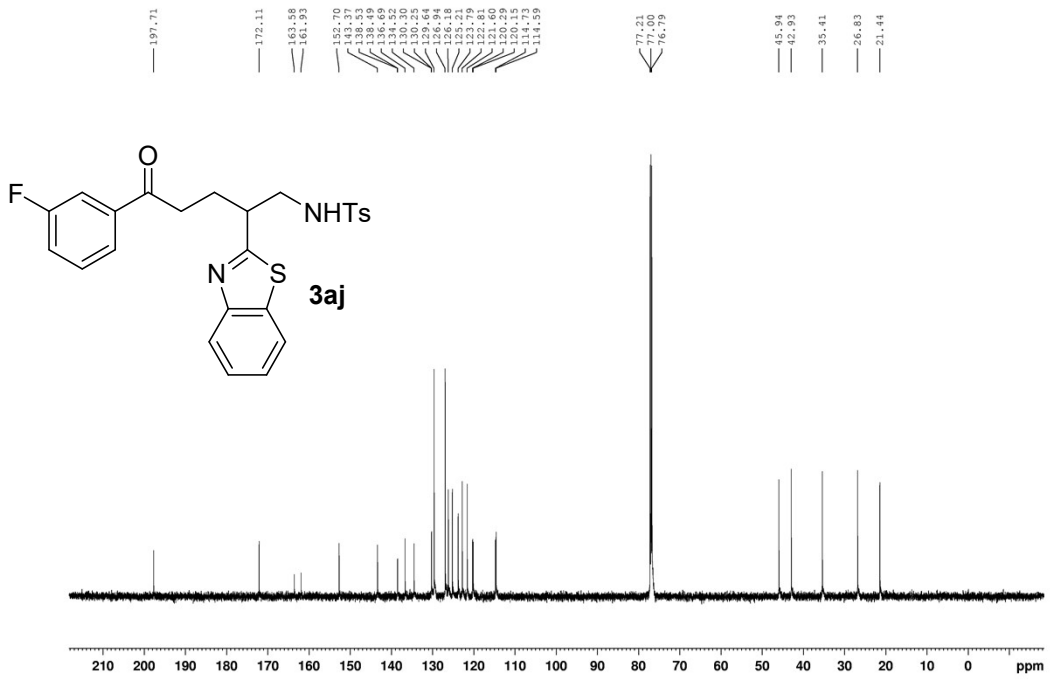
^{13}C NMR of **3ai** in $CDCl_3$(101 MHz, $CDCl_3$)



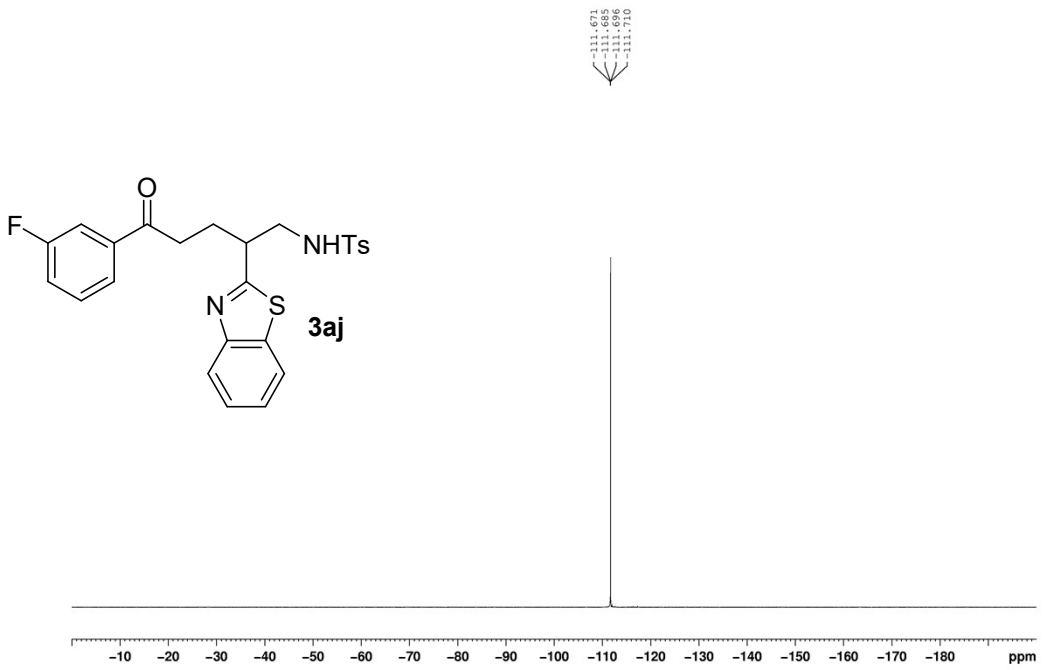
^{1}H NMR of **3aj** in $CDCl_3$(400 MHz, $CDCl_3$)



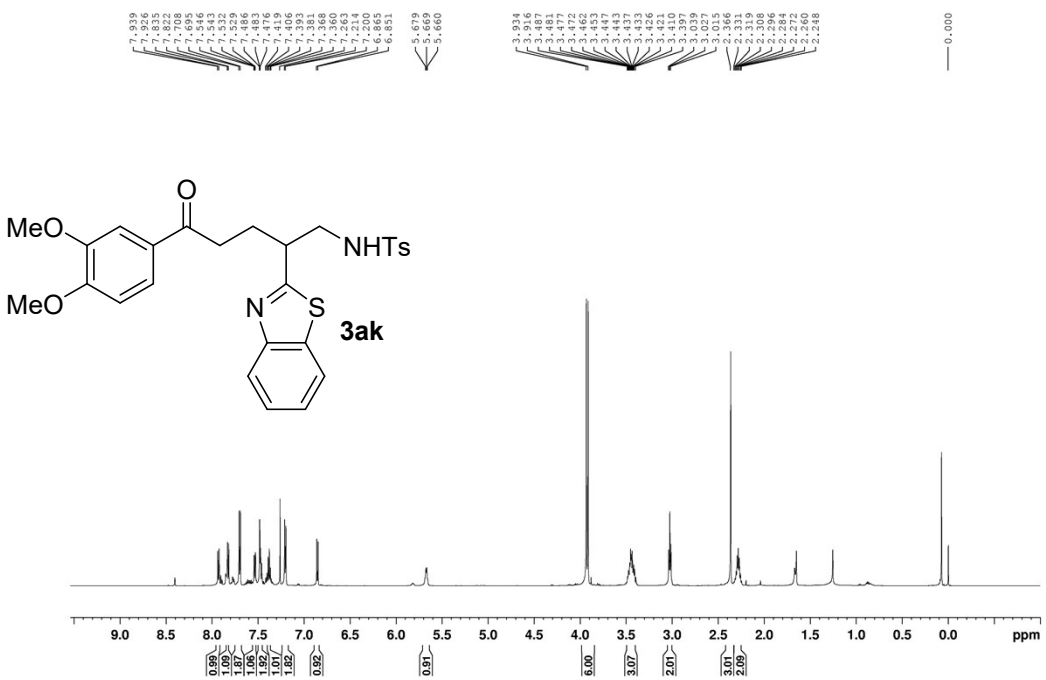
^{13}C NMR of **3aj** in $CDCl_3$(101 MHz, $CDCl_3$)



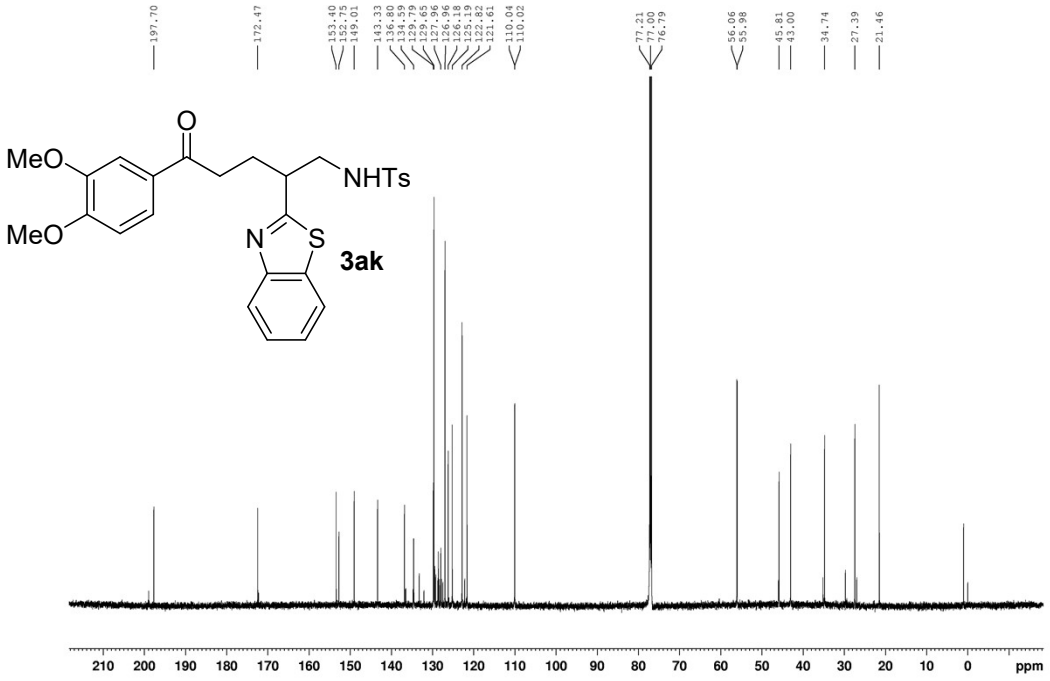
^{19}F NMR of **3aj** in $CDCl_3$(565 MHz, $CDCl_3$)



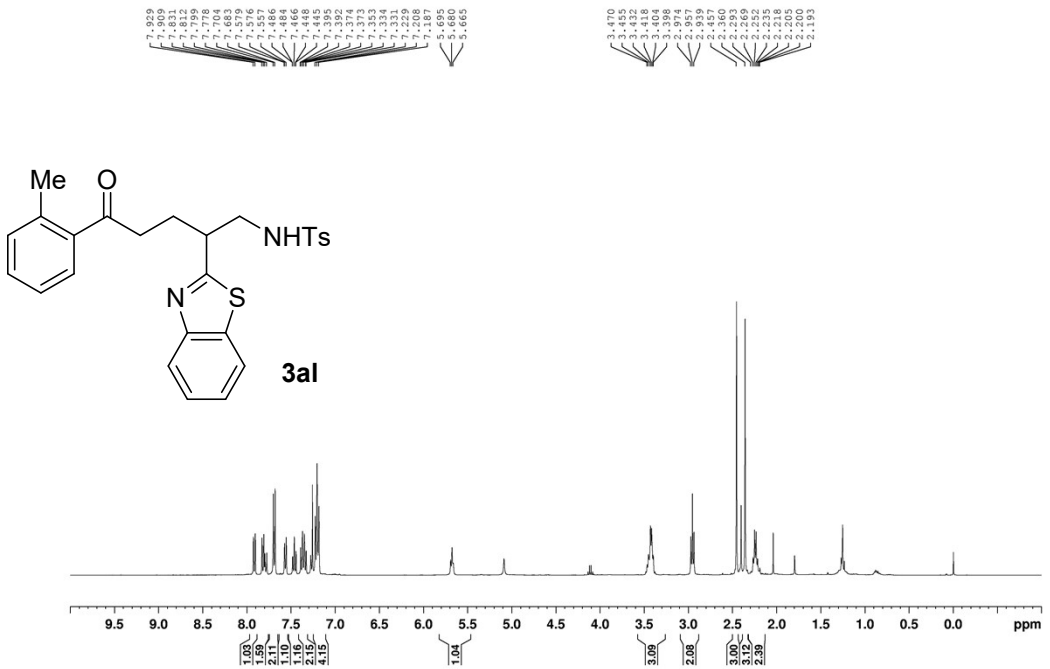
^{1}H NMR of **3ak** in $CDCl_3$(600 MHz, $CDCl_3$)



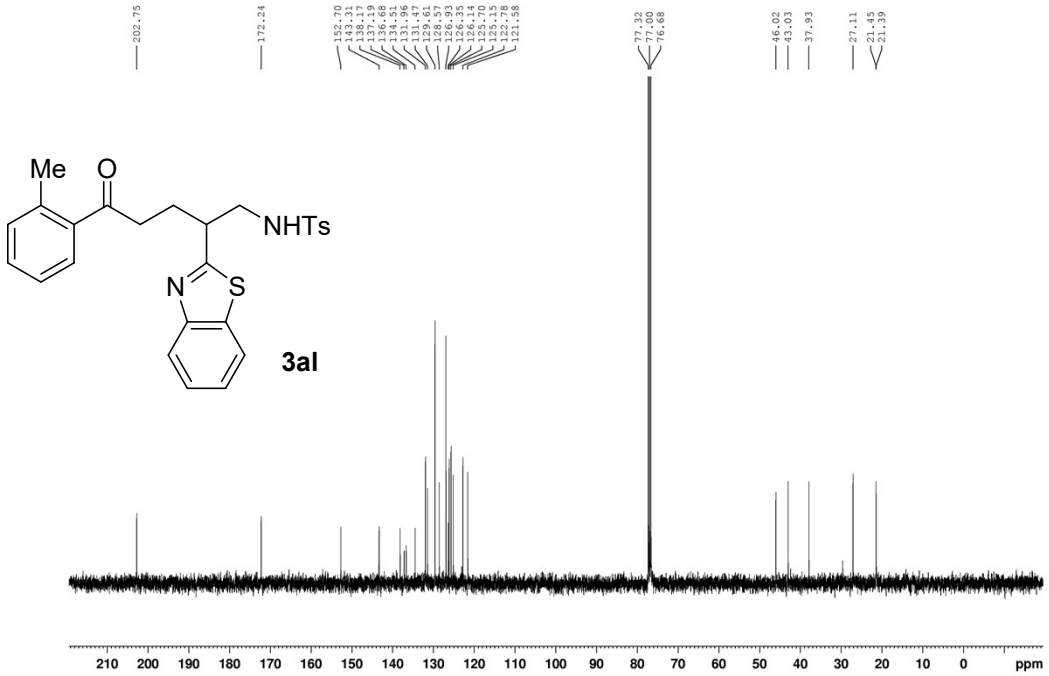
^{13}C NMR of **3ak** in $CDCl_3$(151 MHz, $CDCl_3$)



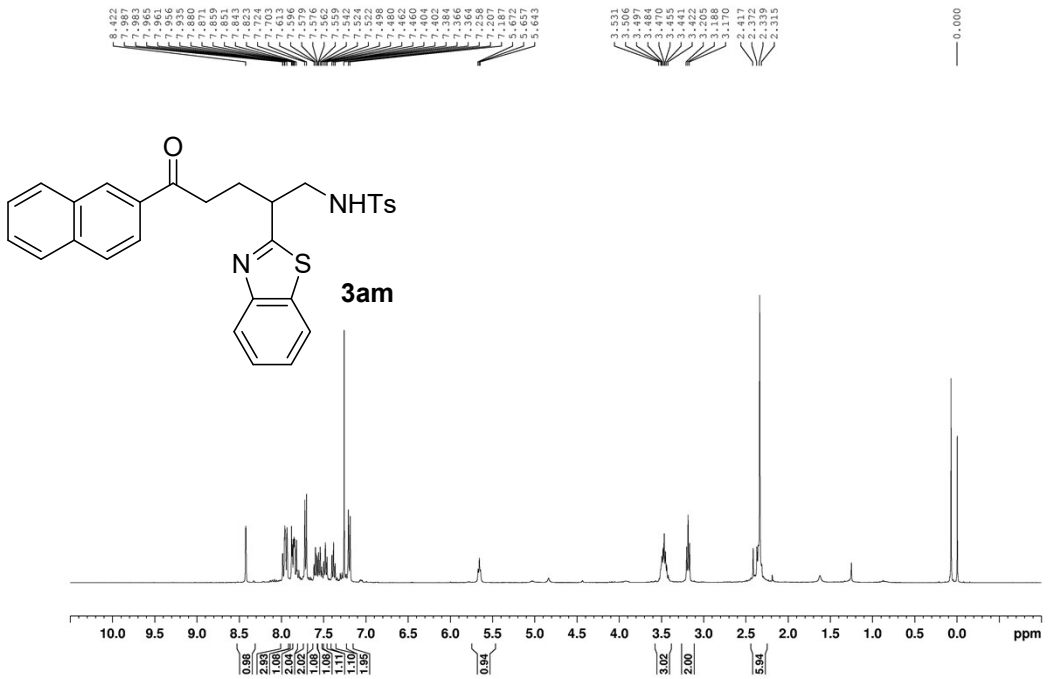
^{1}H NMR of **3al** in $CDCl_3$(400 MHz, $CDCl_3$)



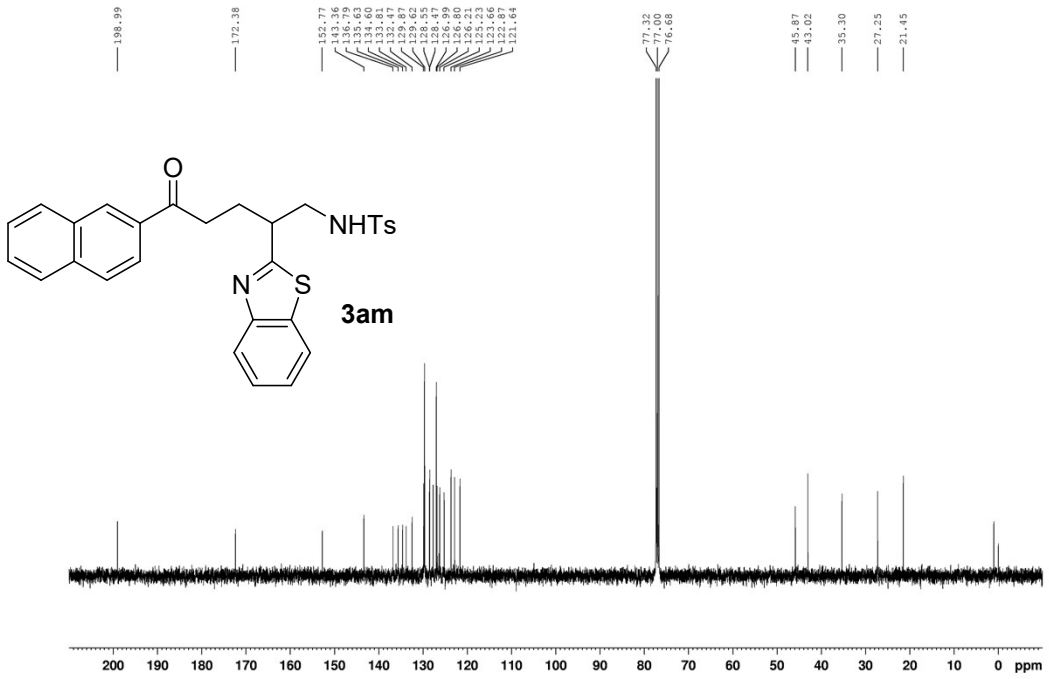
^{13}C NMR of **3al** in $CDCl_3$(101 MHz, $CDCl_3$)



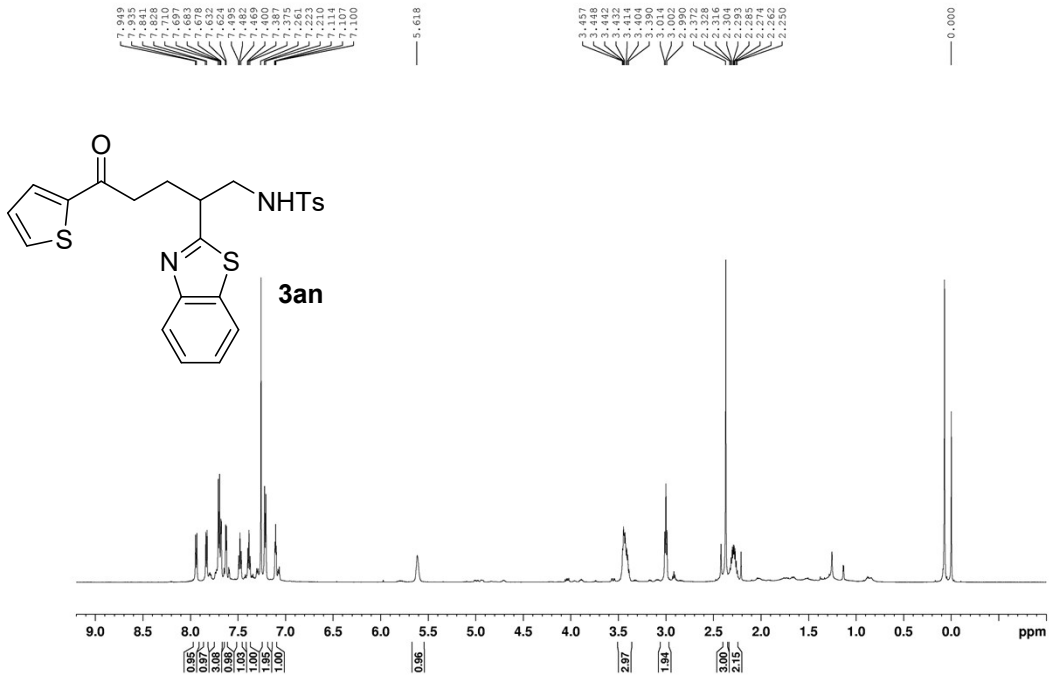
^{1}H NMR of **3am** in $CDCl_3$(400 MHz, $CDCl_3$)



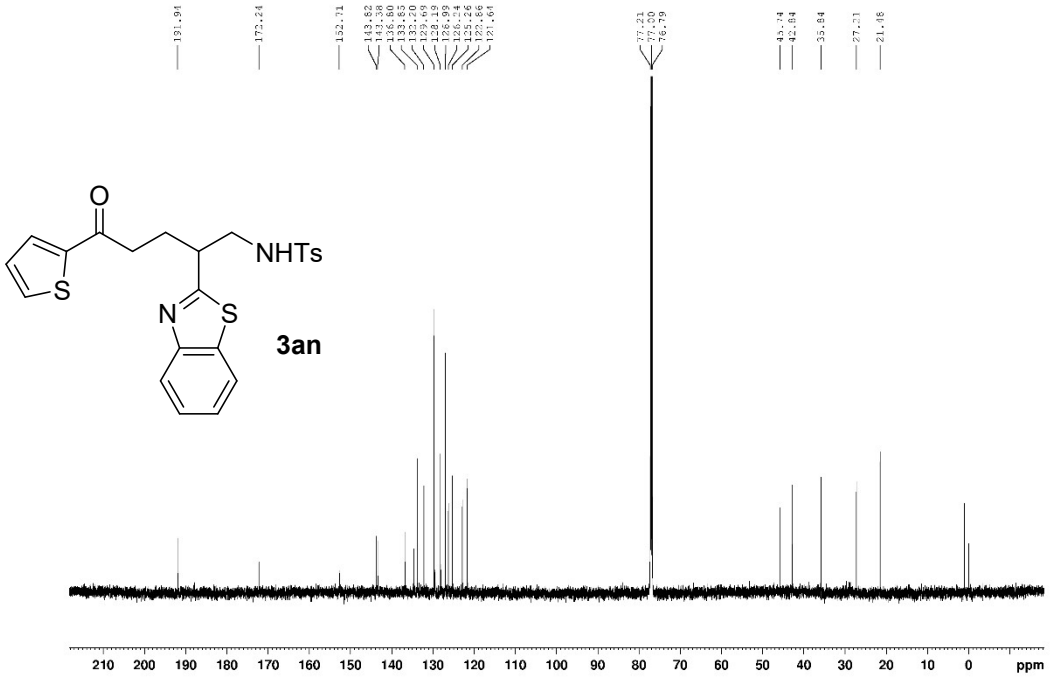
^{13}C NMR of **3am** in $CDCl_3$(101 MHz, $CDCl_3$)



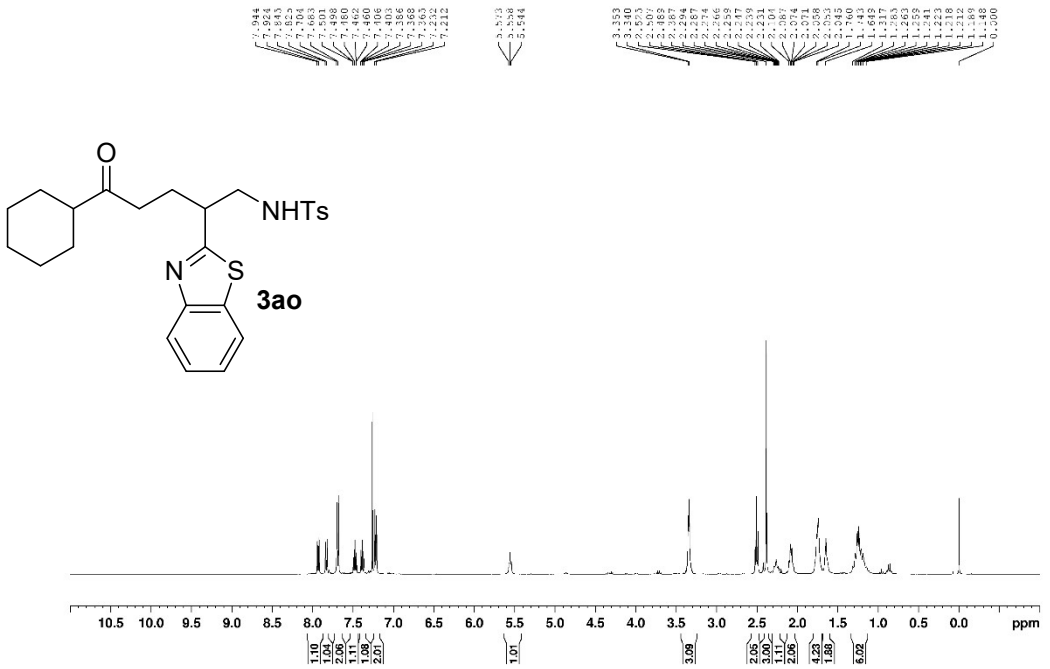
^{1}H NMR of **3an** in $CDCl_3$(600 MHz, $CDCl_3$)



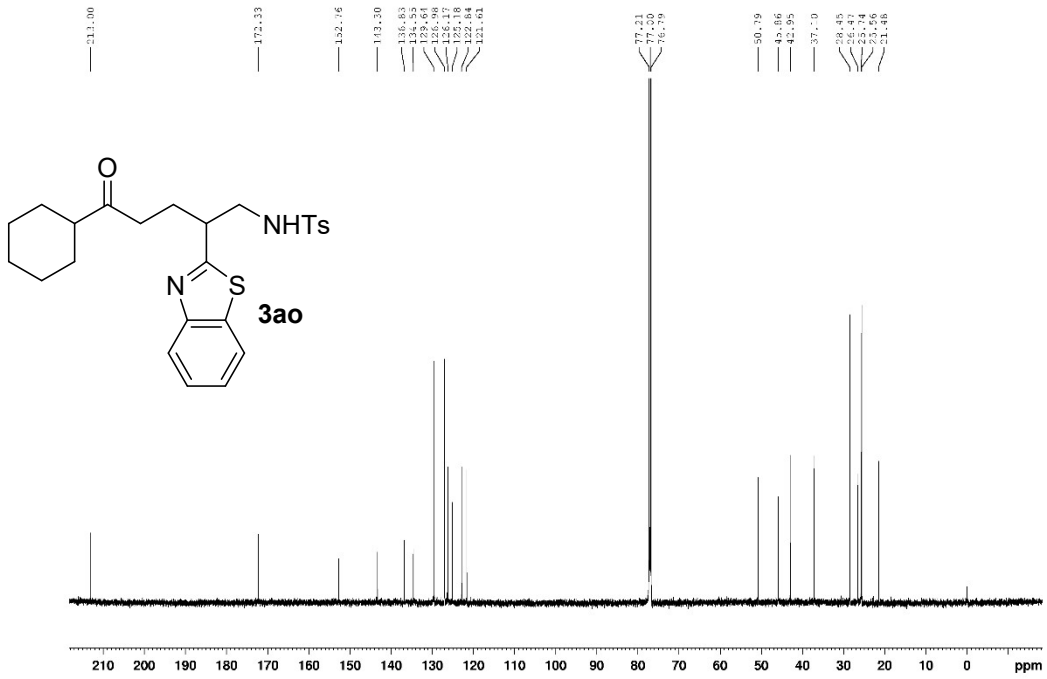
^{13}C NMR of **3an** in $CDCl_3$(151 MHz, $CDCl_3$)



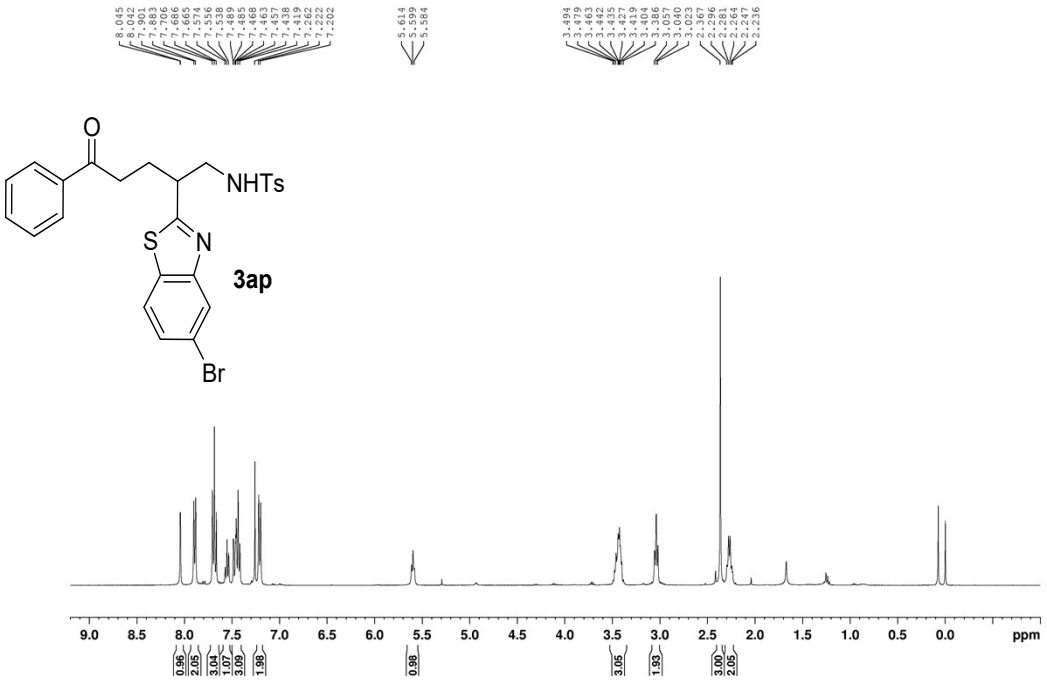
^{1}H NMR of **3ao** in $CDCl_3$(400 MHz, $CDCl_3$)



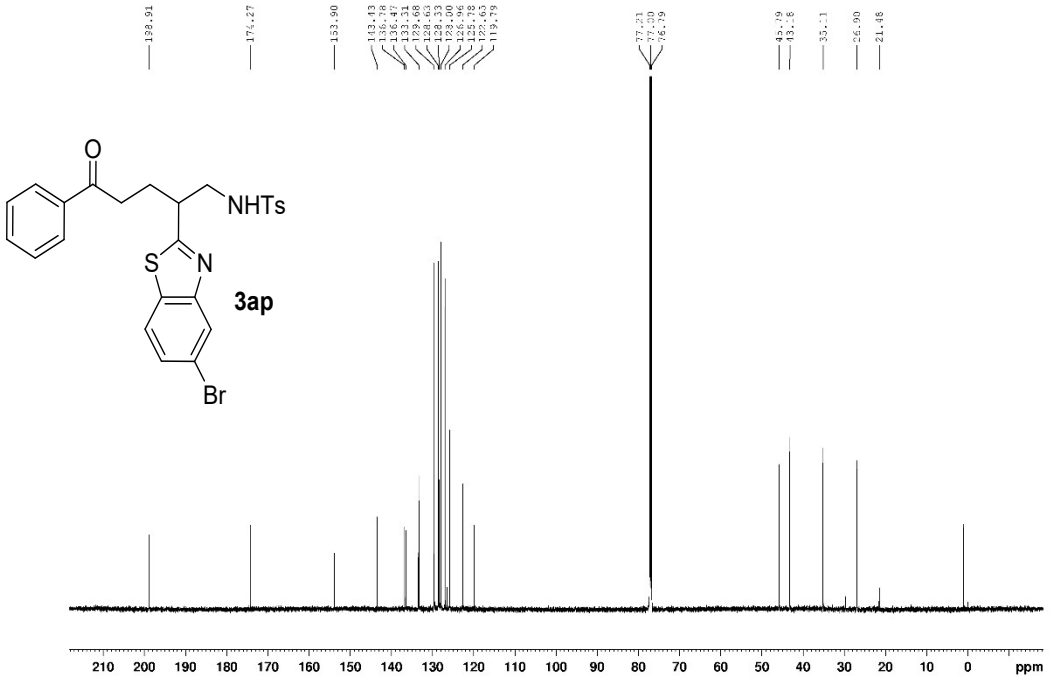
^{13}C NMR of **3ao** in $CDCl_3$(101 MHz, $CDCl_3$)



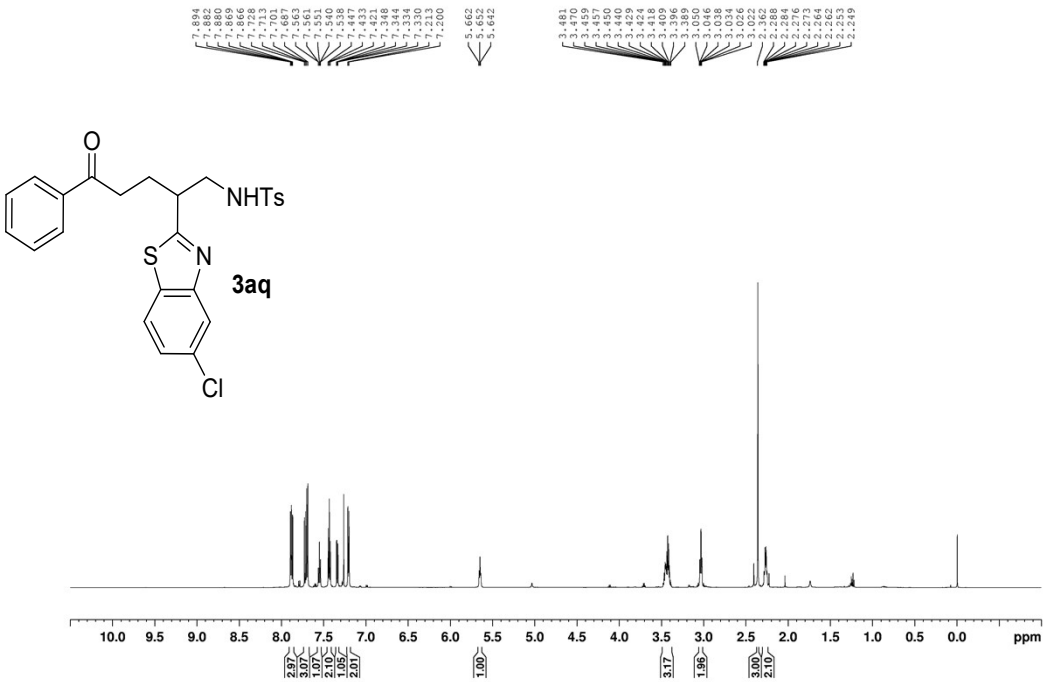
^{1}H NMR of **3ap** in $CDCl_3$(400 MHz, $CDCl_3$)



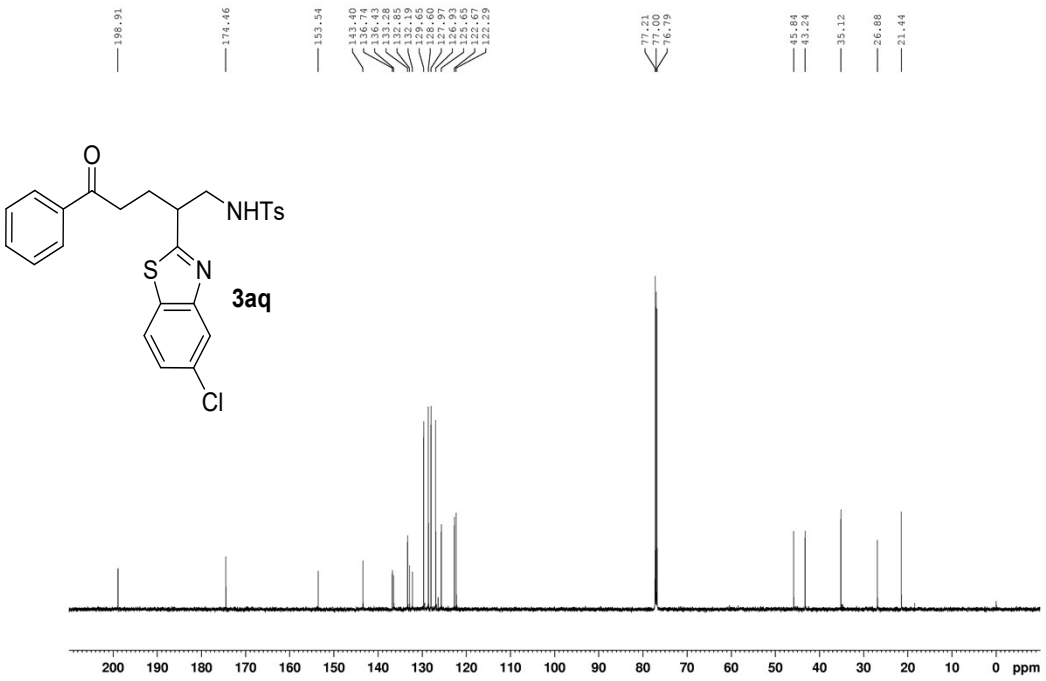
^{13}C NMR of **3ap** in $CDCl_3$(151 MHz, $CDCl_3$)



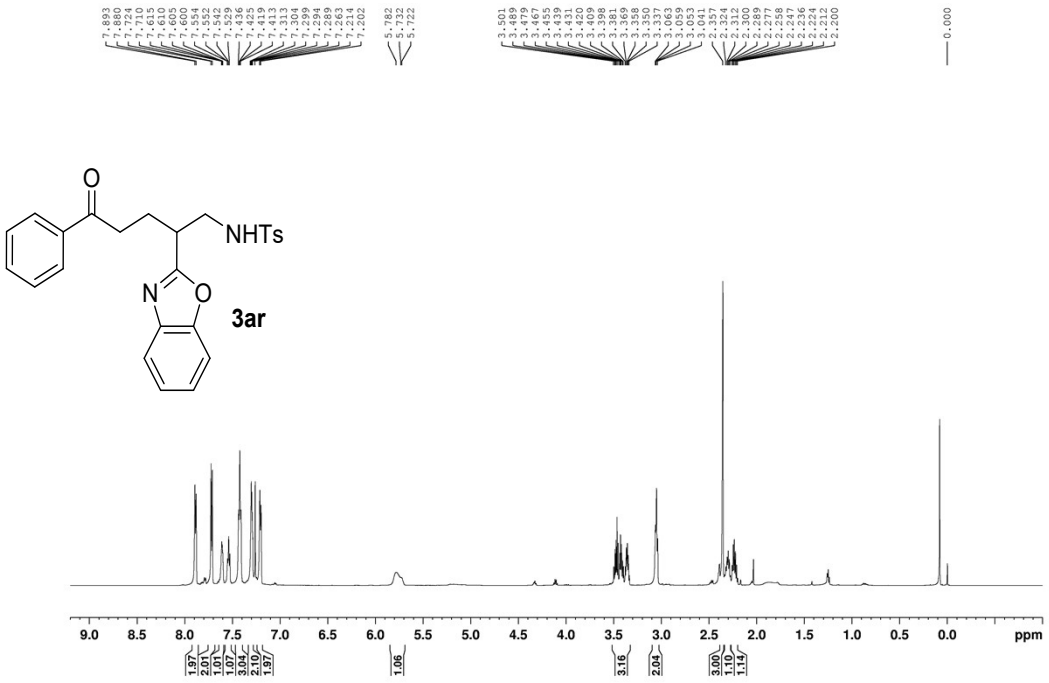
^{1}H NMR of **3aq** in $CDCl_3$(600 MHz, $CDCl_3$)



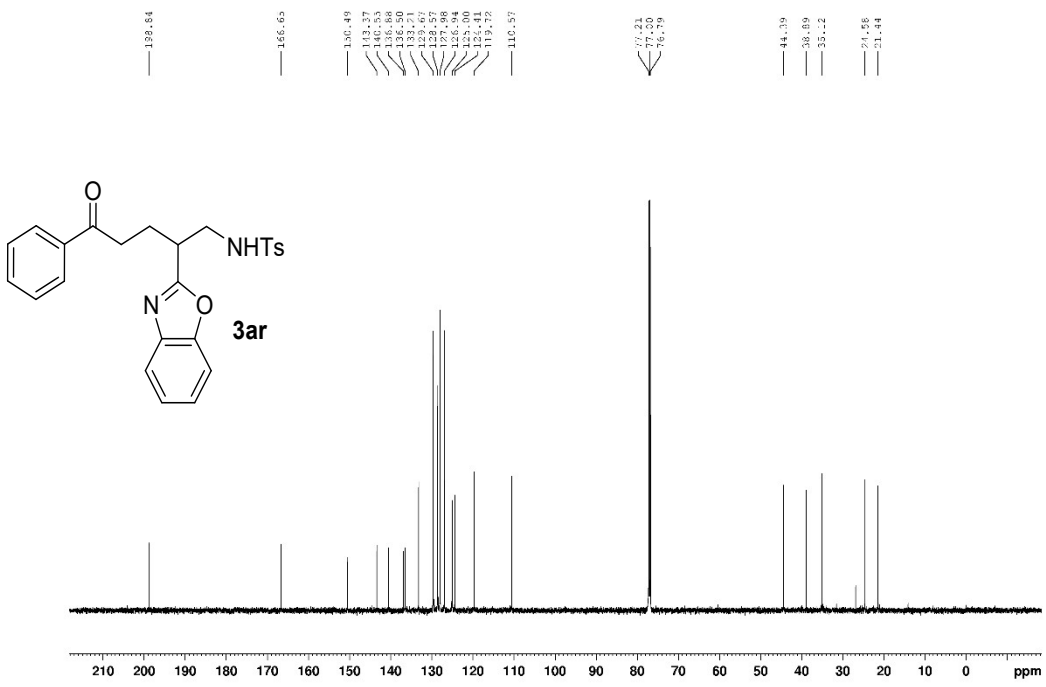
^{13}C NMR of **3aq** in $CDCl_3$(151 MHz, $CDCl_3$)



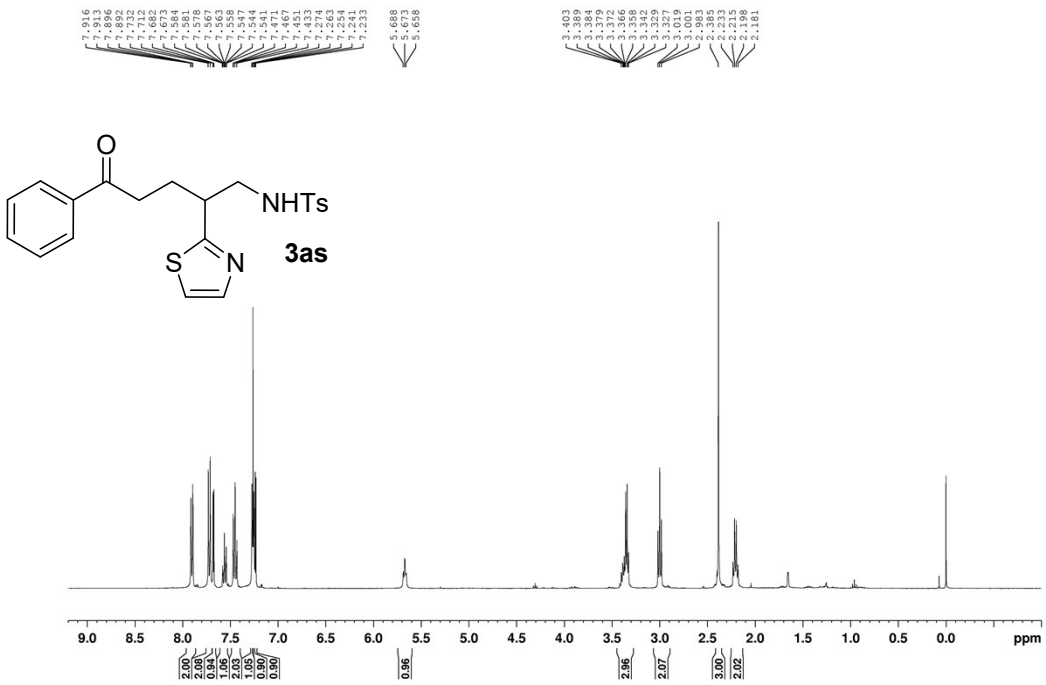
^{1}H NMR of **3ar** in $CDCl_3$(600 MHz, $CDCl_3$)



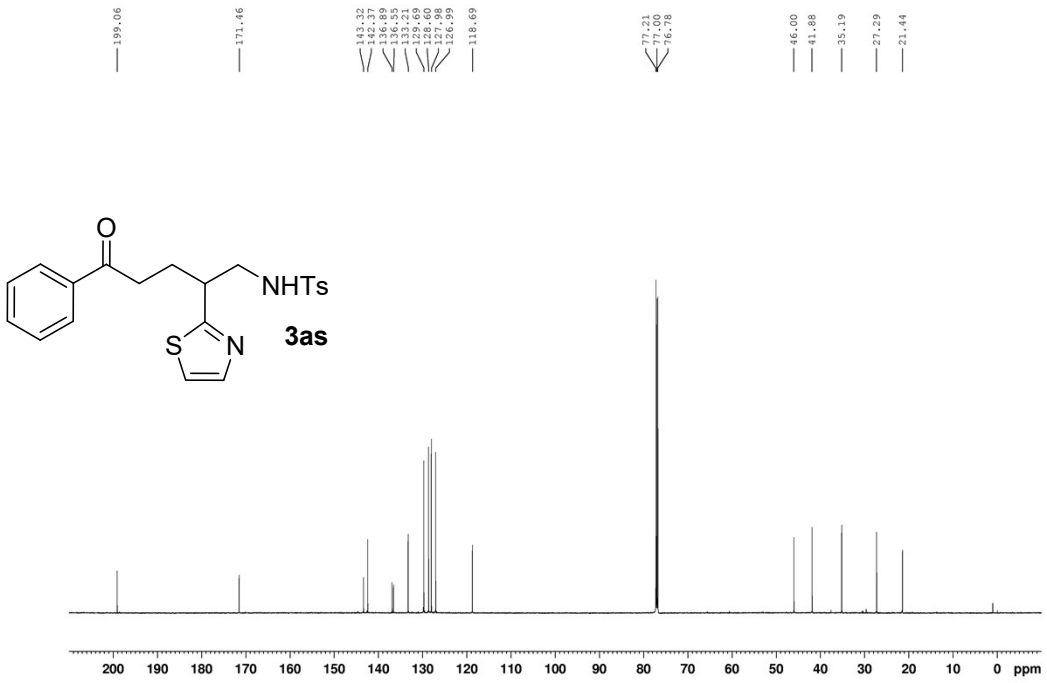
^{13}C NMR of **3ar** in $CDCl_3$(151 MHz, $CDCl_3$)



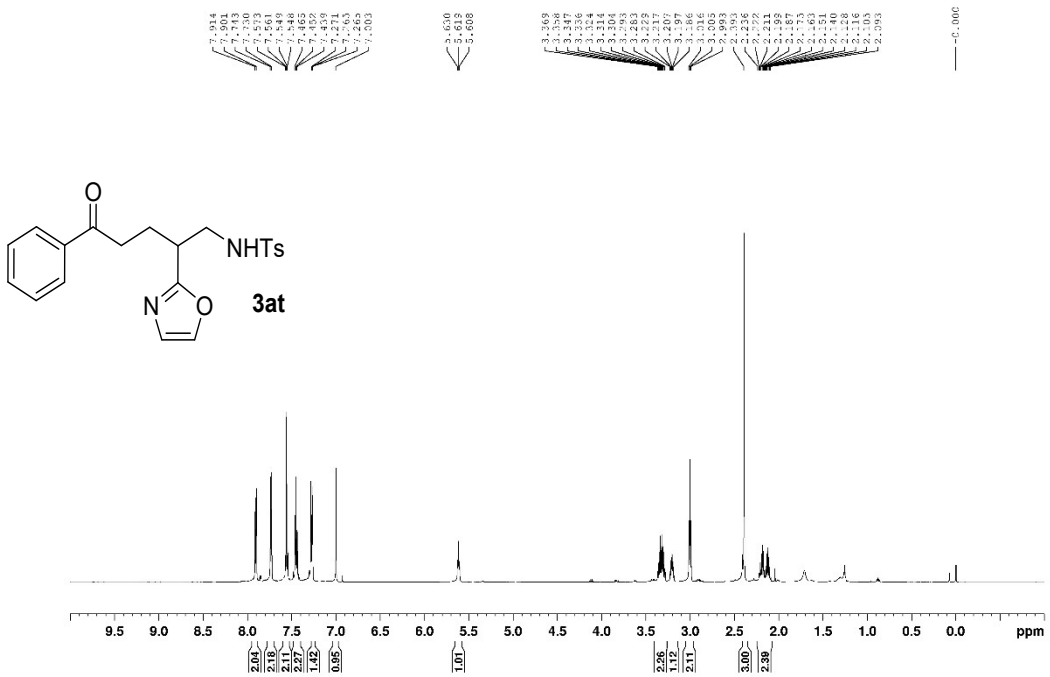
^{1}H NMR of **3as** in $CDCl_3$(400 MHz, $CDCl_3$)



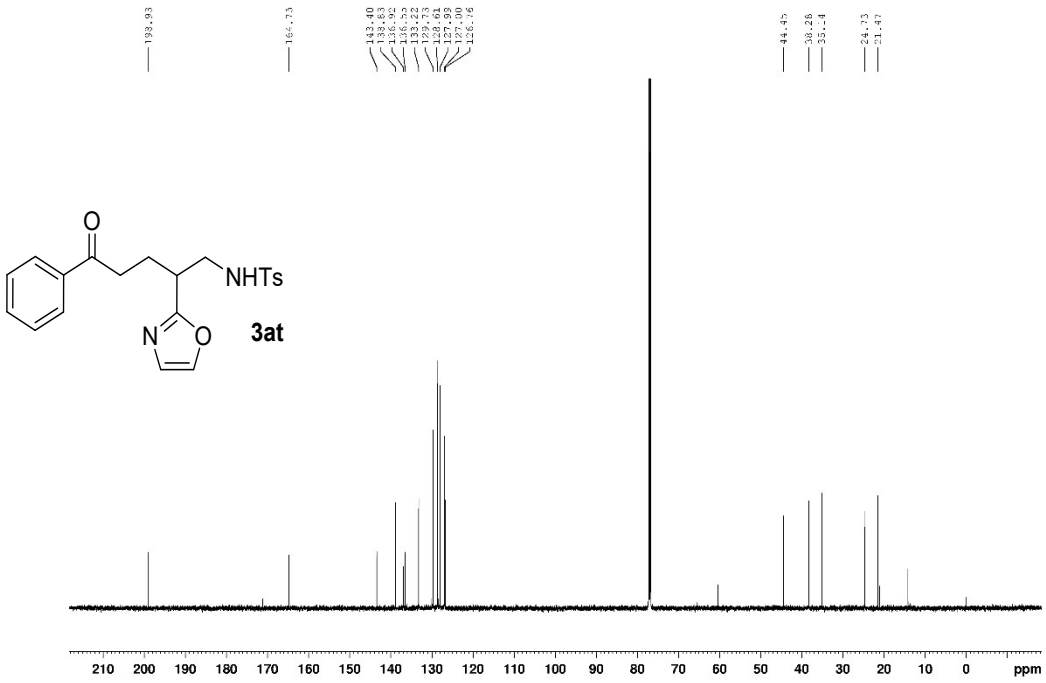
^{13}C NMR of **3as** in $CDCl_3$(151 MHz, $CDCl_3$)



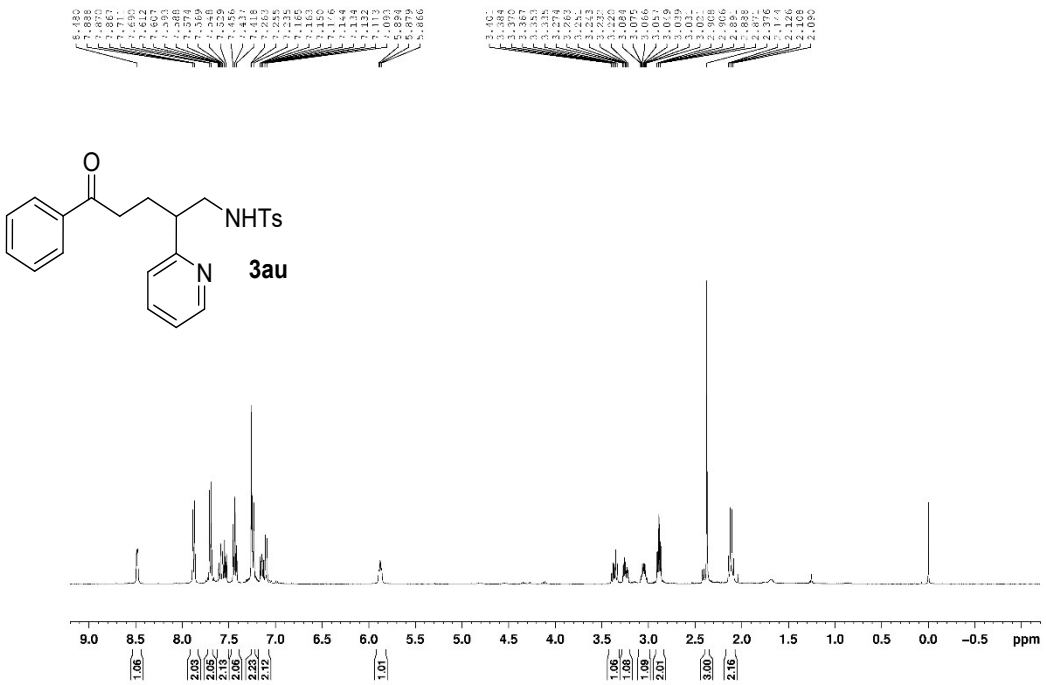
^{1}H NMR of **3at** in $CDCl_3$(600 MHz, $CDCl_3$)



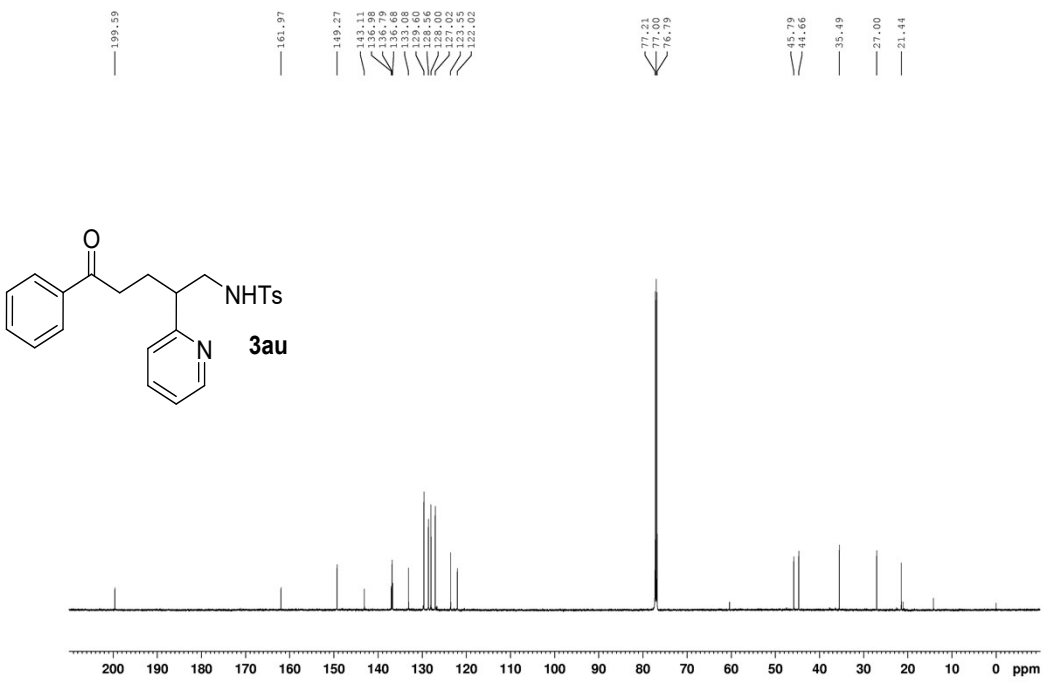
^{13}C NMR of **3at** in $CDCl_3$(151 MHz, $CDCl_3$)



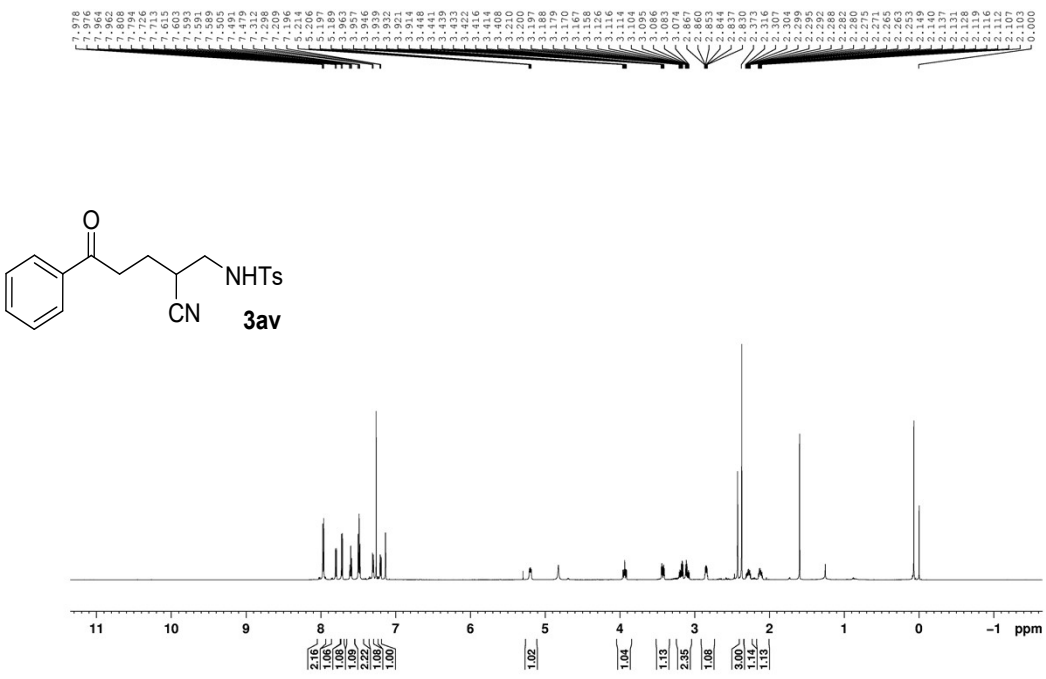
^{1}H NMR of **3au** in $CDCl_3$(400 MHz, $CDCl_3$)



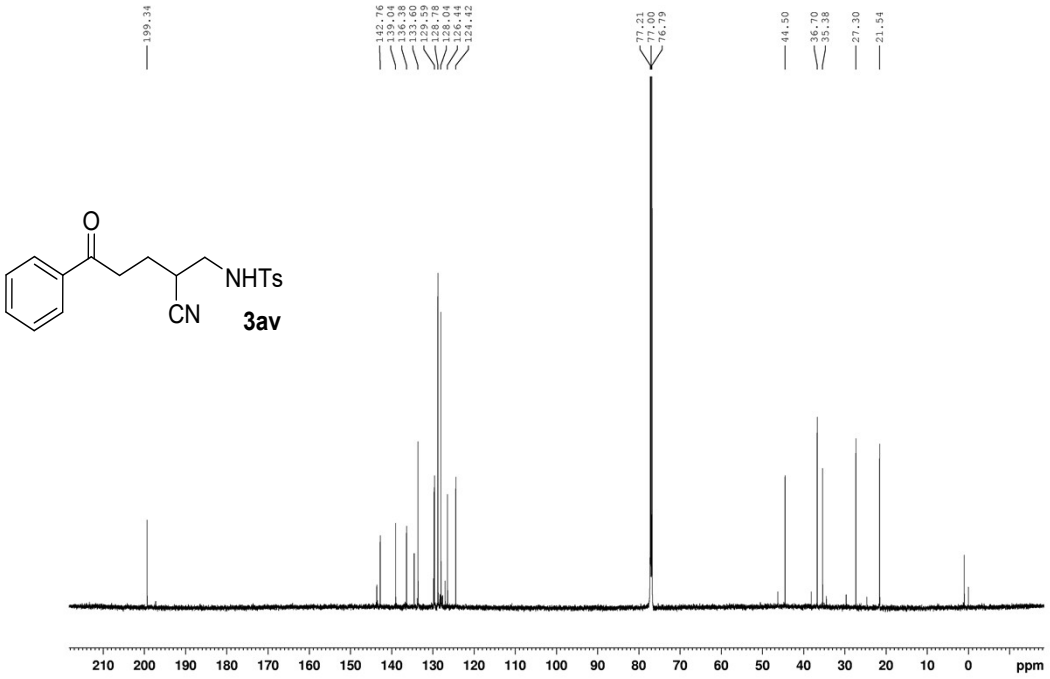
^{13}C NMR of **3au** in $CDCl_3$(151 MHz, $CDCl_3$)



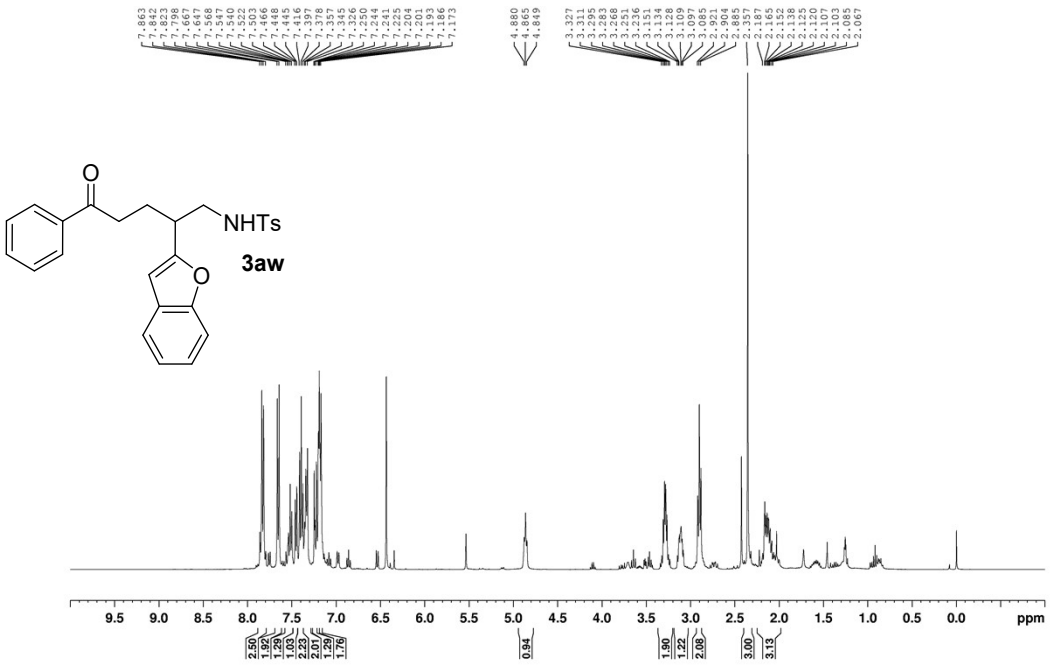
^{1}H NMR of **3av** in $CDCl_3$(600 MHz, $CDCl_3$)



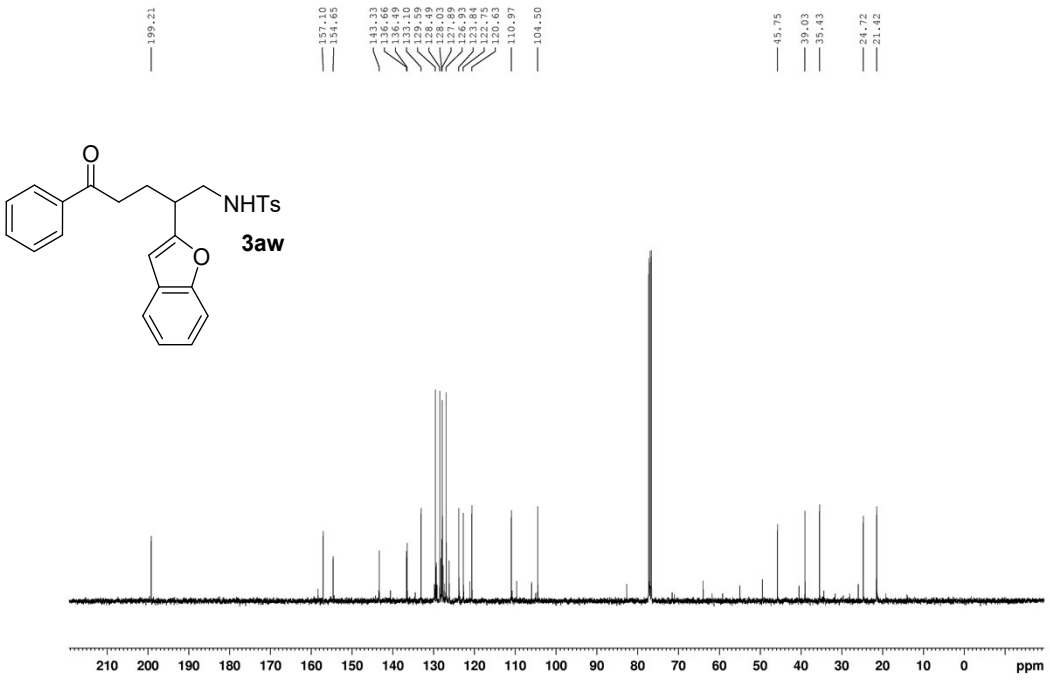
^{13}C NMR of **3av** in $CDCl_3$(151 MHz, $CDCl_3$)



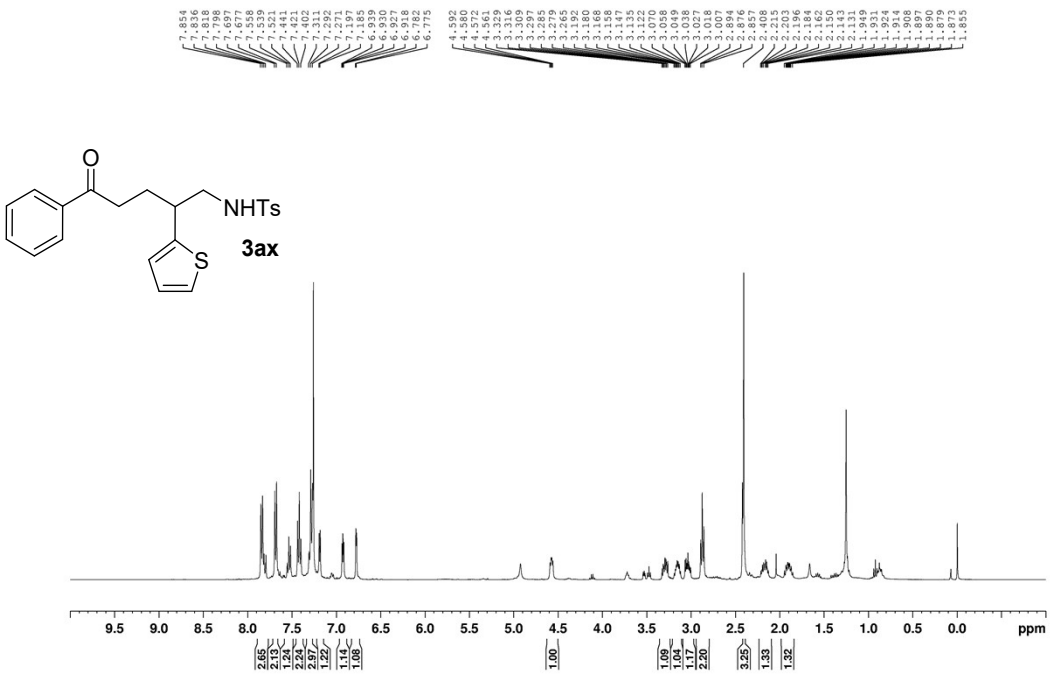
^{1}H NMR of **3aw** in $CDCl_3$(400 MHz, $CDCl_3$)



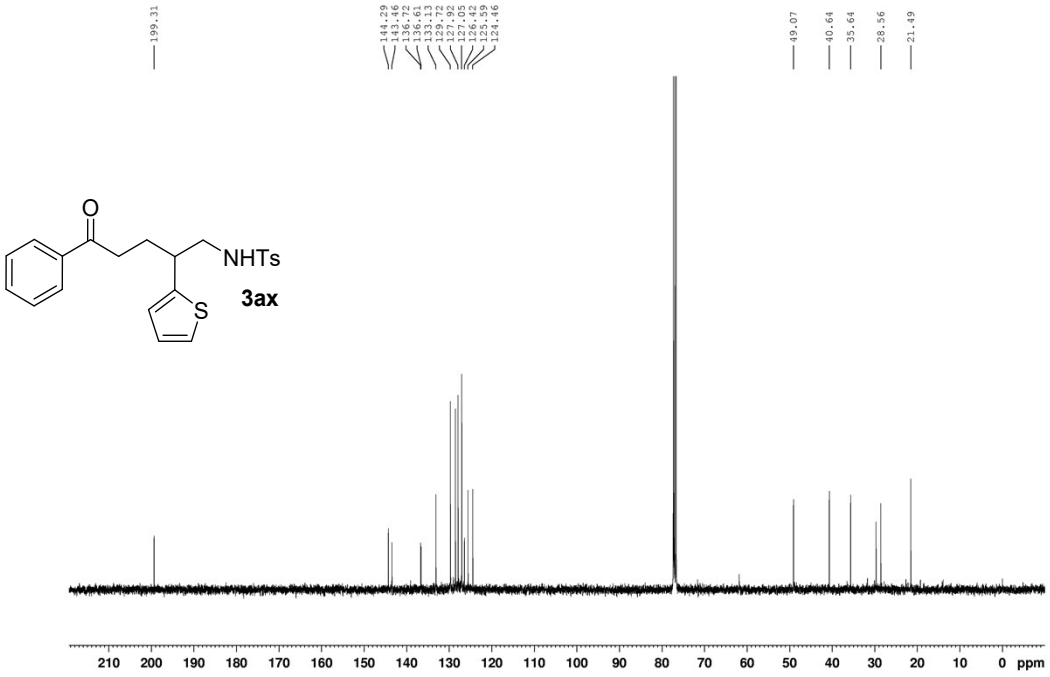
^{13}C NMR of **3aw** in $CDCl_3$(101 MHz, $CDCl_3$)



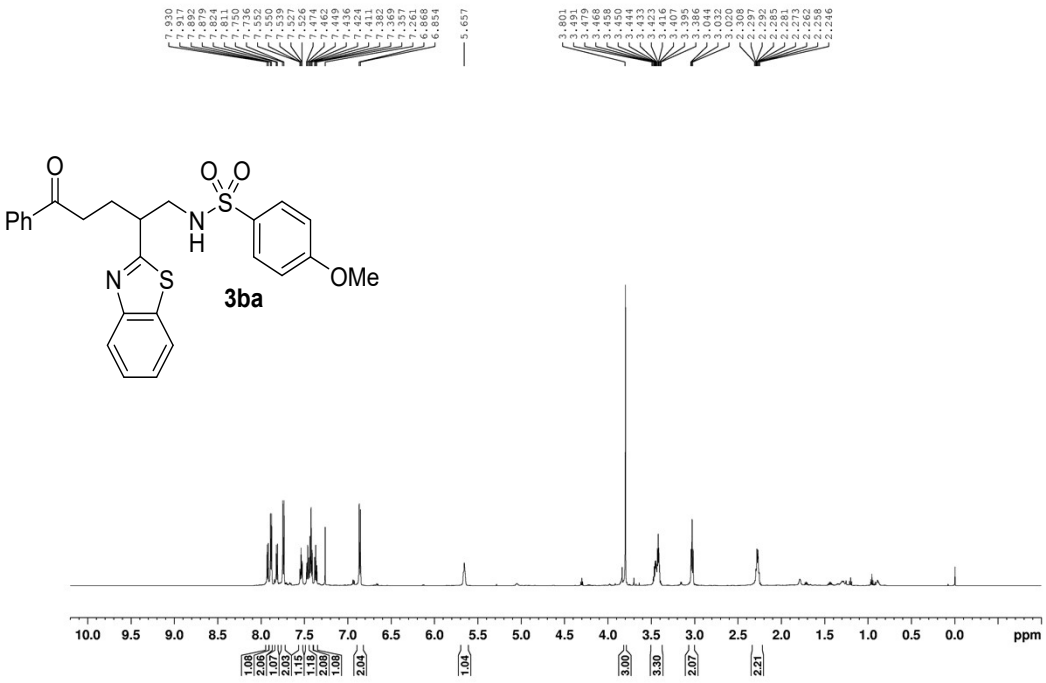
^{1}H NMR of **3ax** in $CDCl_3$(400 MHz, $CDCl_3$)



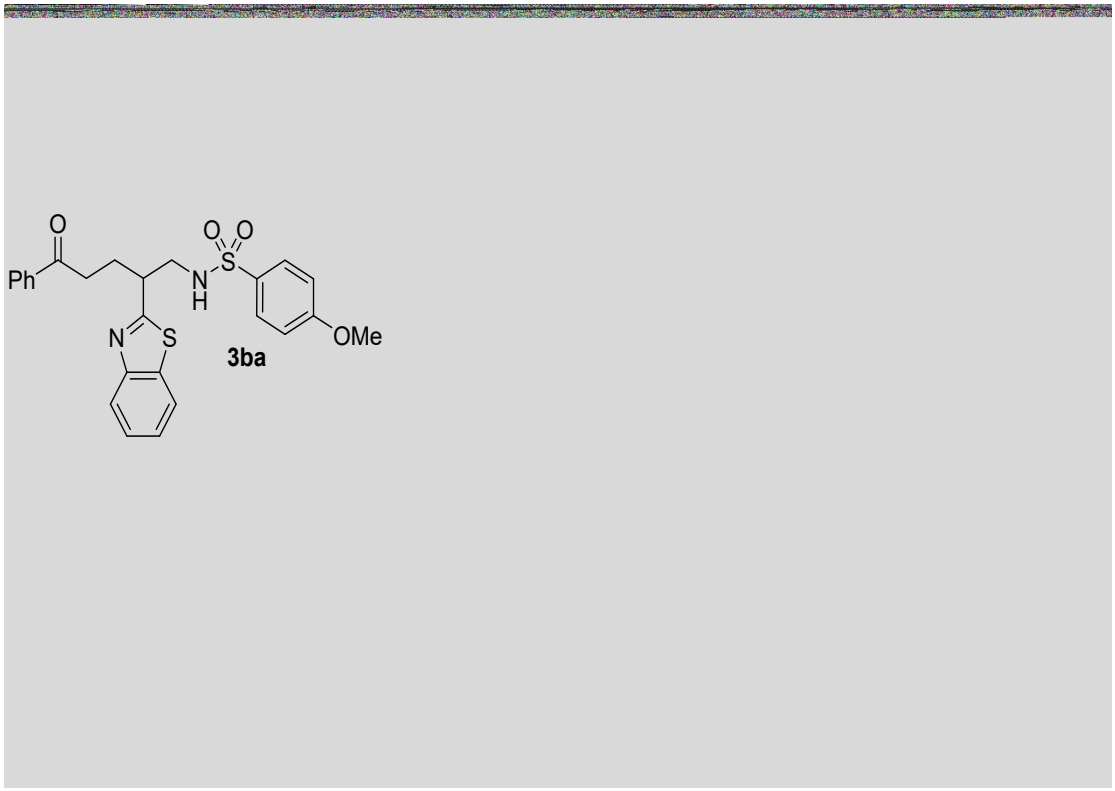
^{13}C NMR of **3ax** in $CDCl_3$(101 MHz, $CDCl_3$)



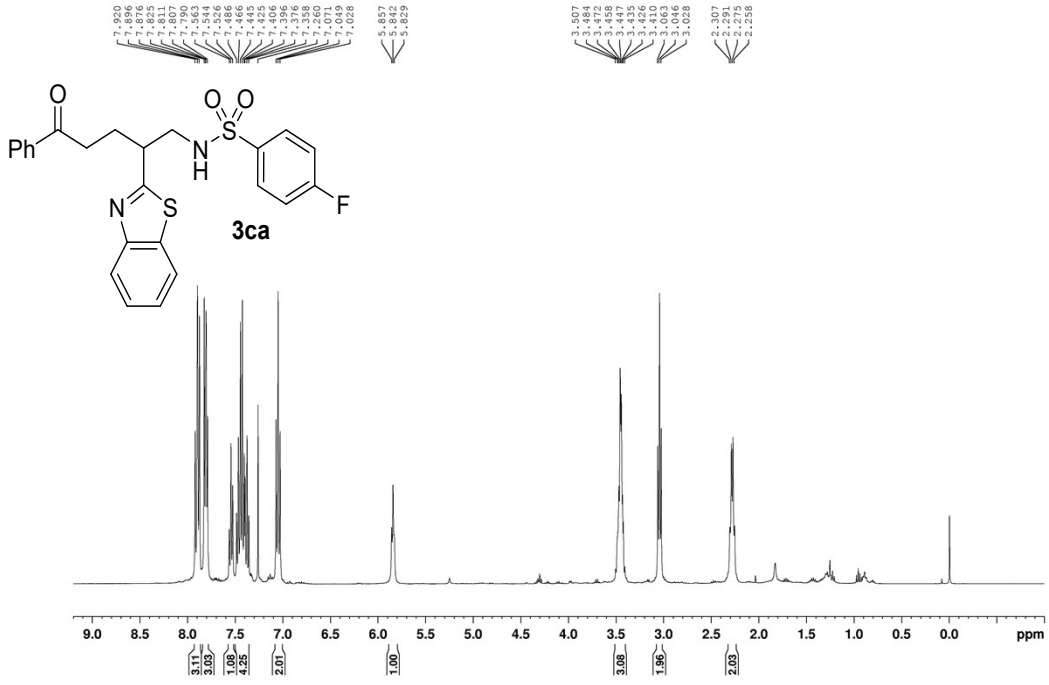
^{1}H NMR of **3ba** in $CDCl_3$(400 MHz, $CDCl_3$)



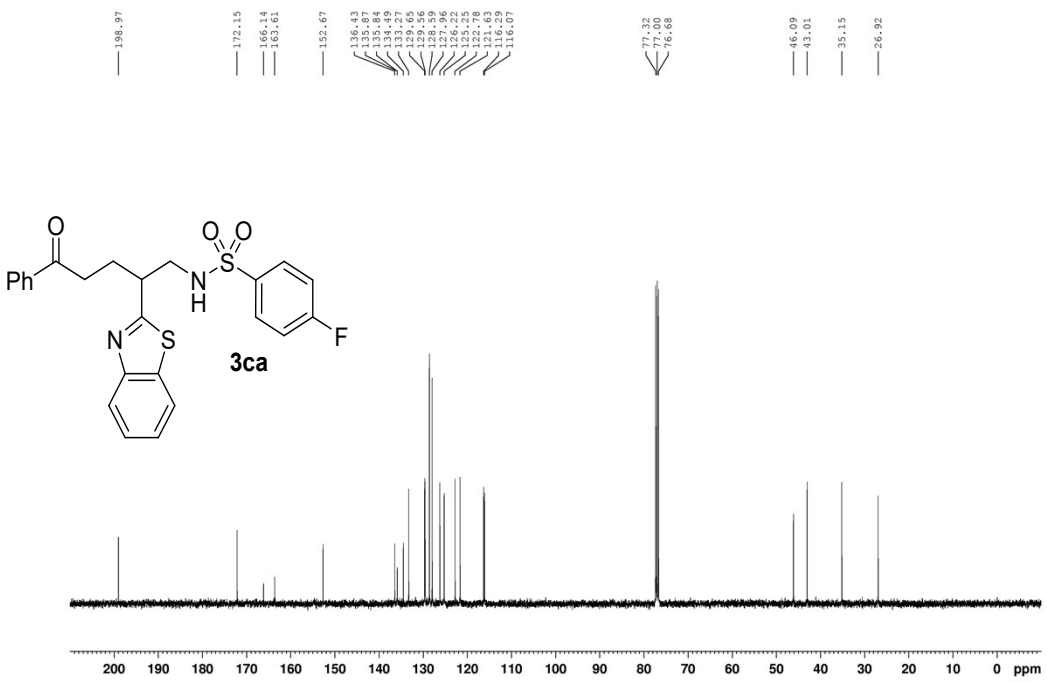
^{13}C NMR of **3ba** in $CDCl_3$(151 MHz, $CDCl_3$)



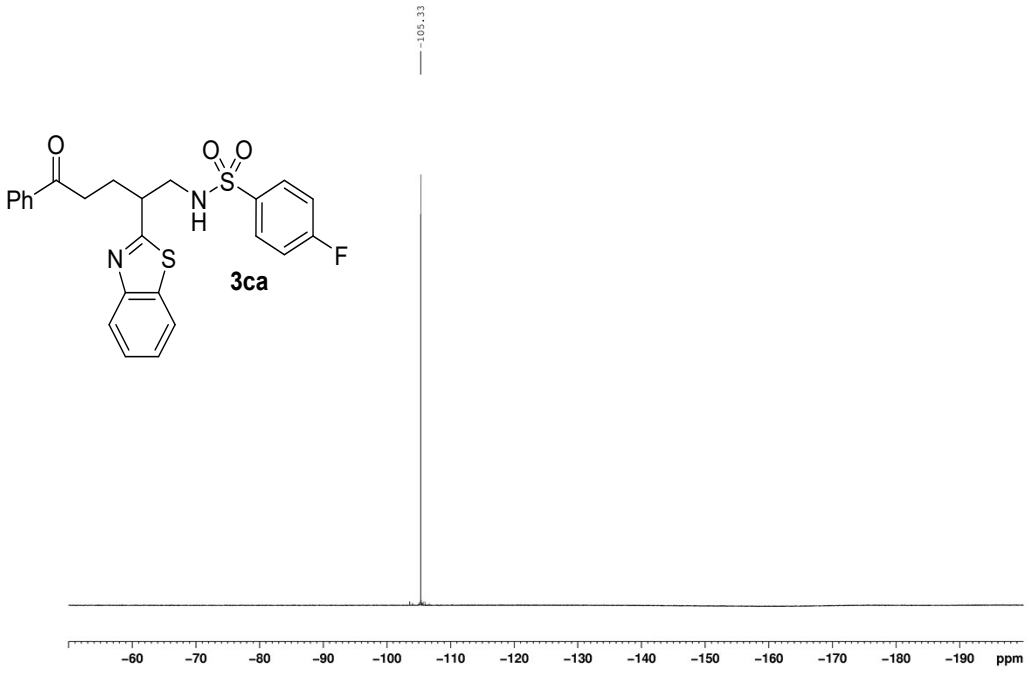
^{1}H NMR of **3ca** in $CDCl_3$(400 MHz, $CDCl_3$)



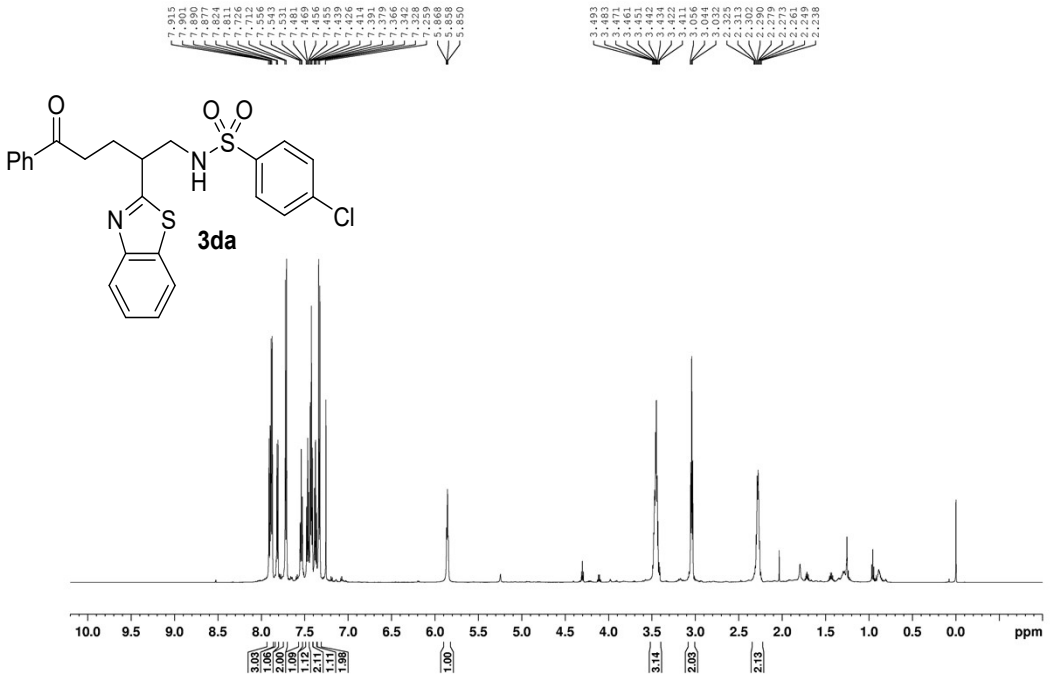
^{13}C NMR of **3ca** in $CDCl_3$(101 MHz, $CDCl_3$)



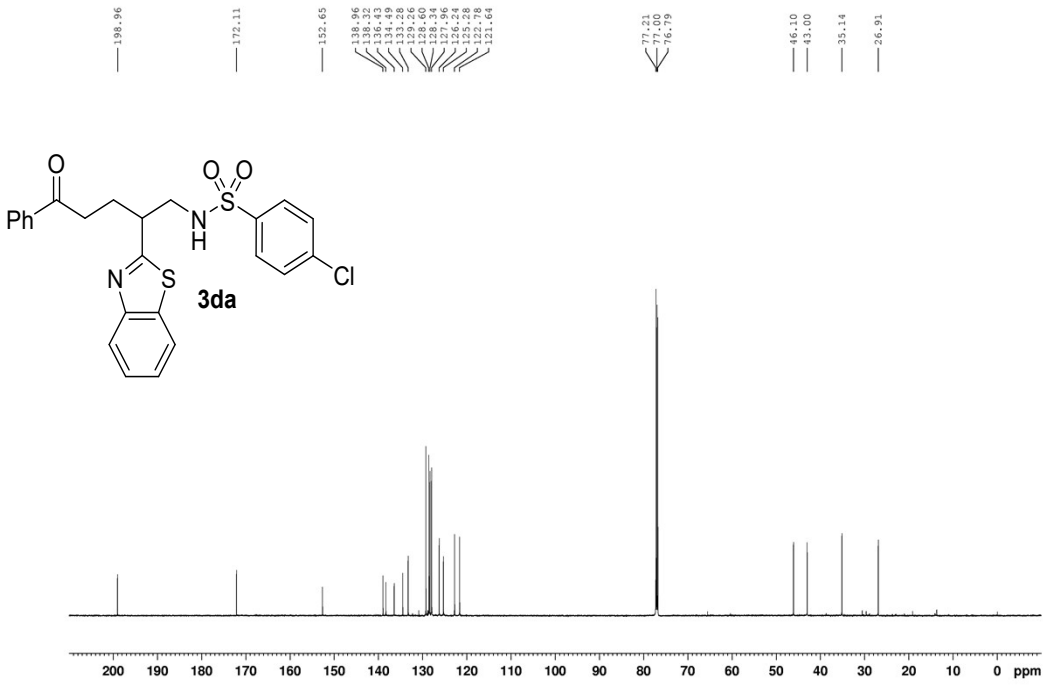
^{19}F NMR of **3ca** in $CDCl_3$(376 MHz, $CDCl_3$)



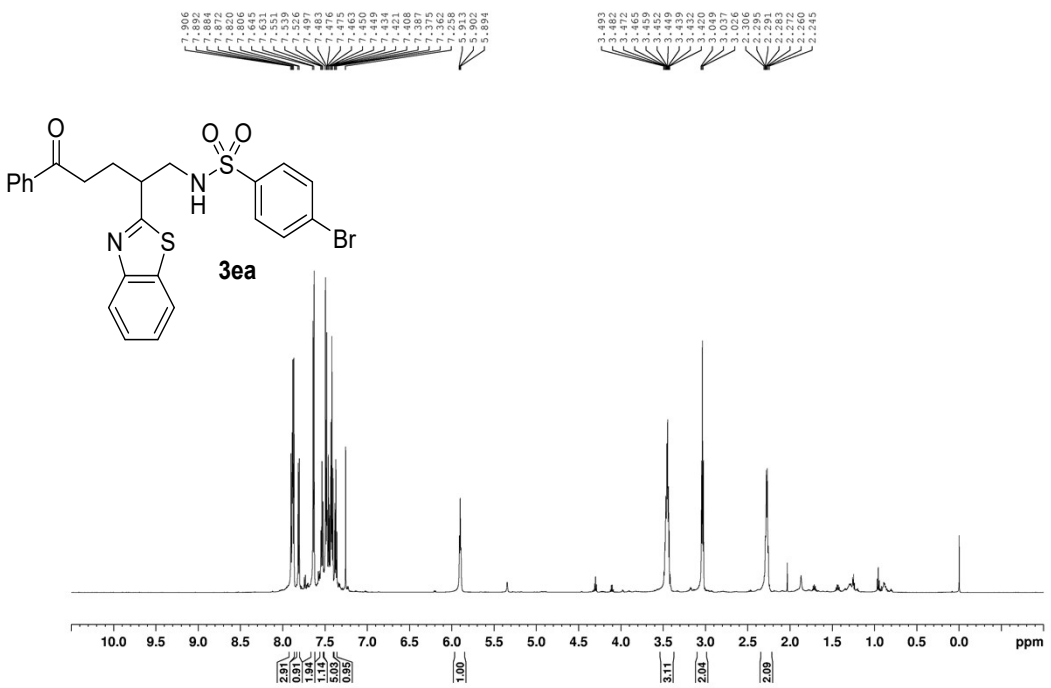
^{1}H NMR of **3da** in $CDCl_3$(400 MHz, $CDCl_3$)



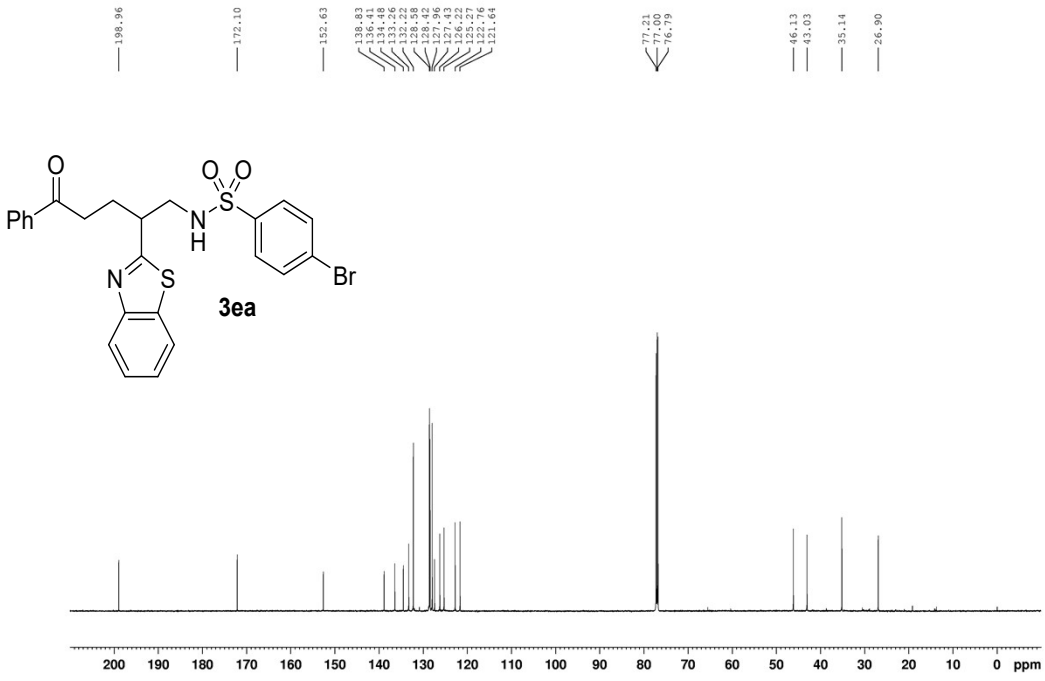
^{13}C NMR of **3da** in $CDCl_3$(151 MHz, $CDCl_3$)



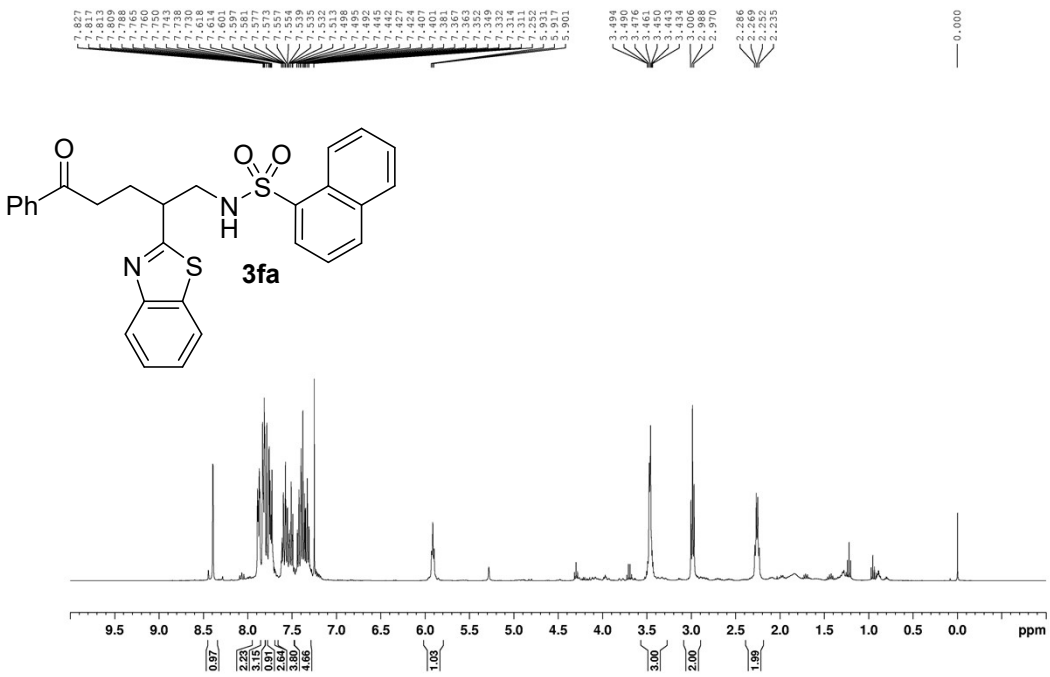
^{1}H NMR of **3ea** in $CDCl_3$(600 MHz, $CDCl_3$)



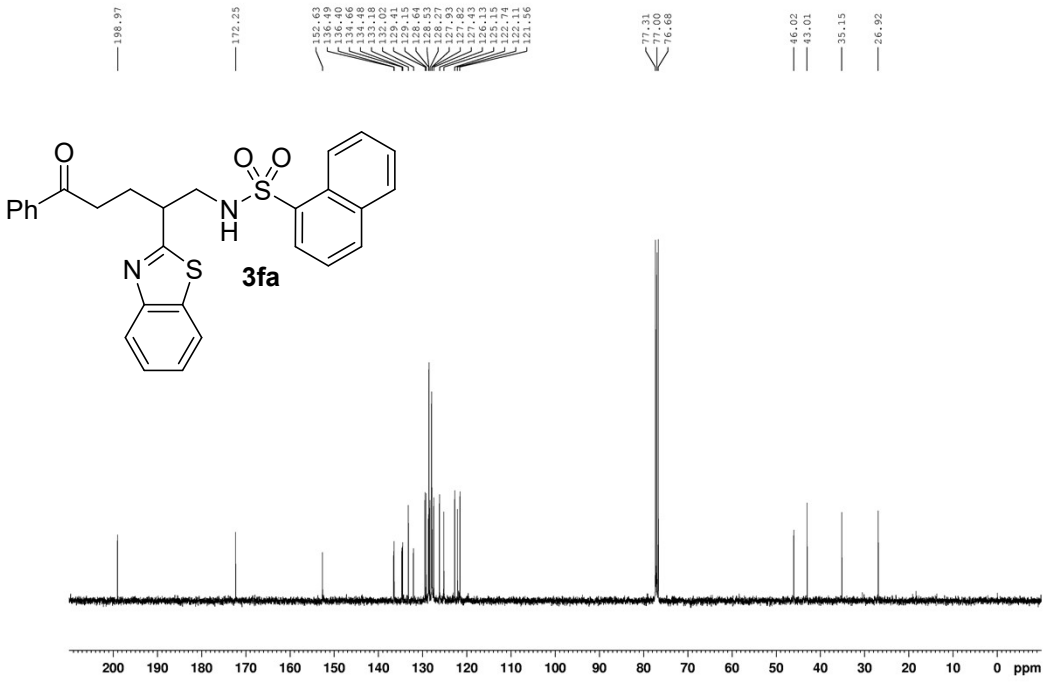
^{13}C NMR of **3ea** in $CDCl_3$(151 MHz, $CDCl_3$)



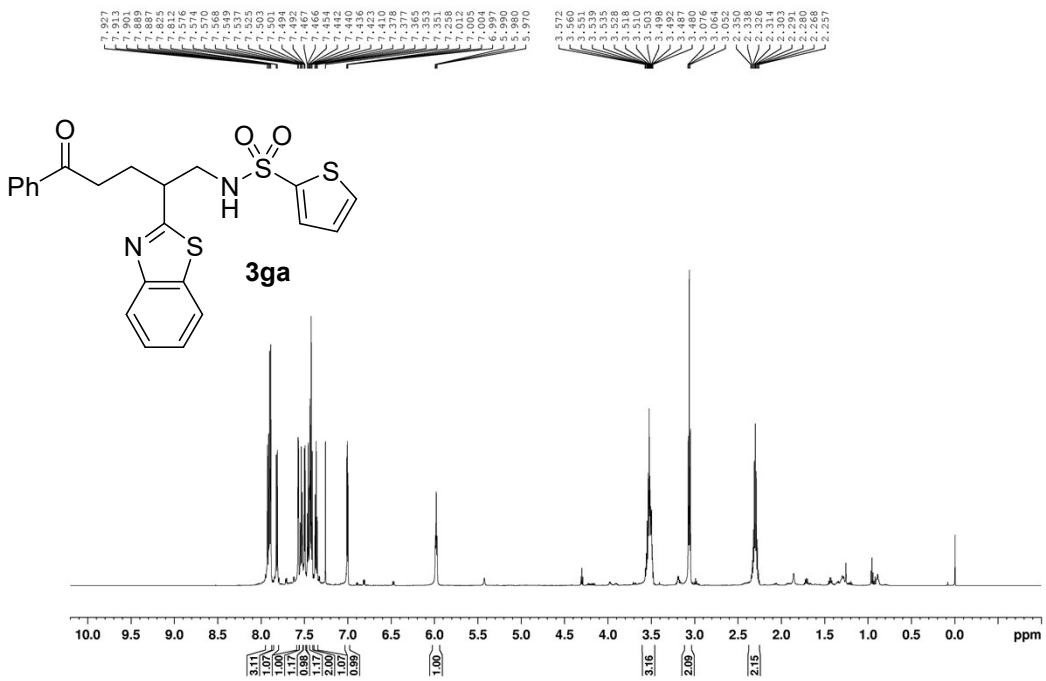
^{1}H NMR of **3fa** in $CDCl_3$(400 MHz, $CDCl_3$)



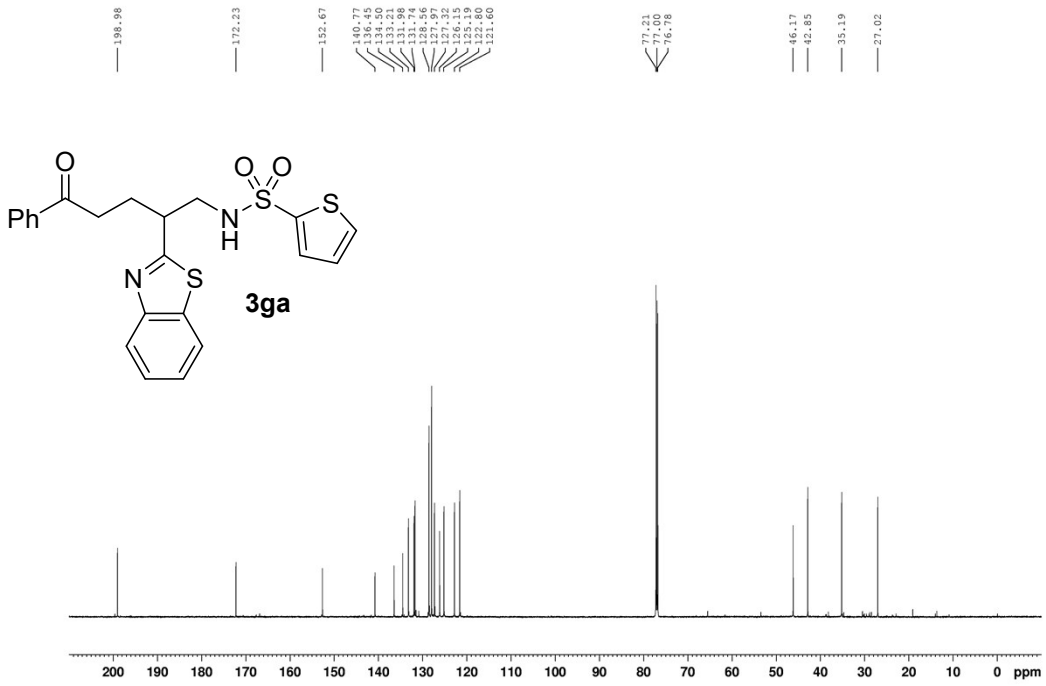
^{13}C NMR of **3fa** in $CDCl_3$(101 MHz, $CDCl_3$)



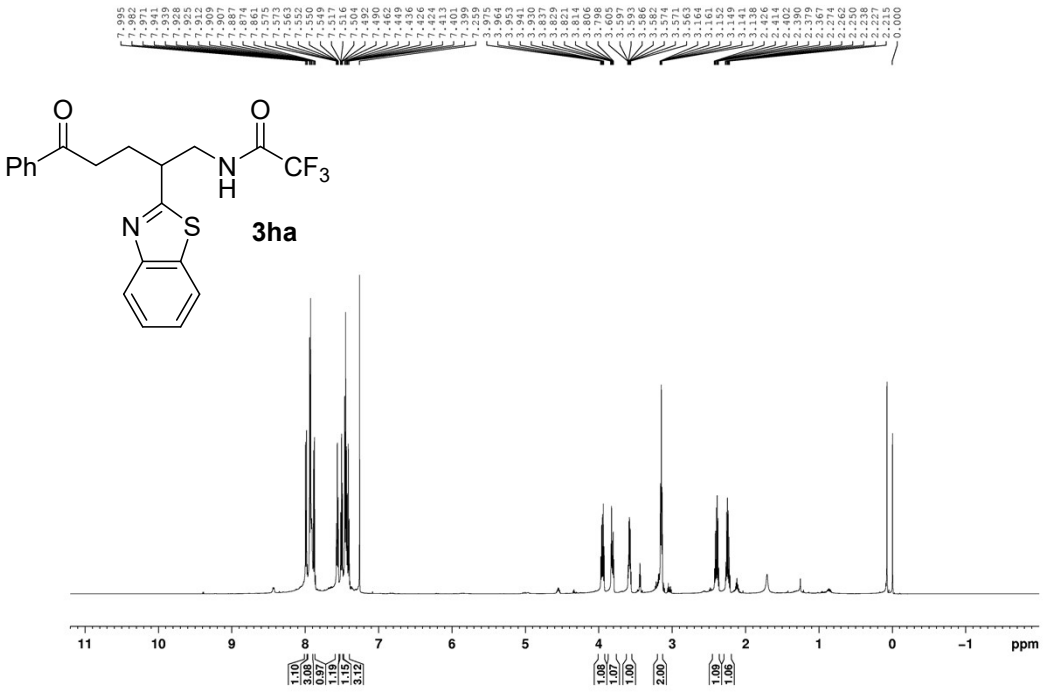
^{1}H NMR of **3ga** in $CDCl_3$(600 MHz, $CDCl_3$)



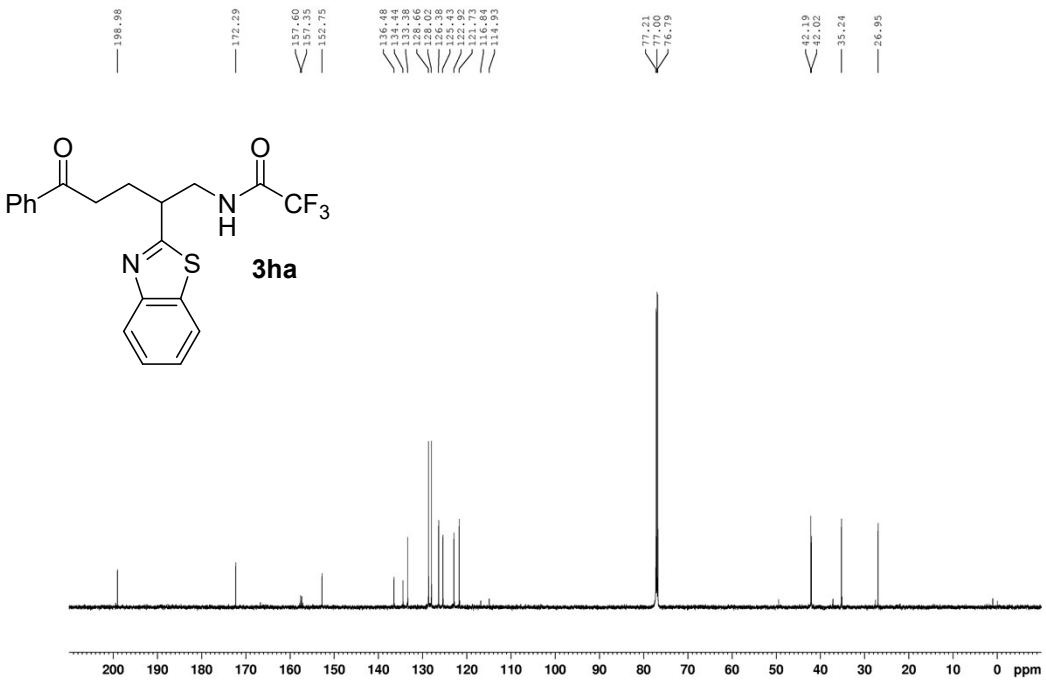
^{13}C NMR of **3ga** in $CDCl_3$(151 MHz, $CDCl_3$)



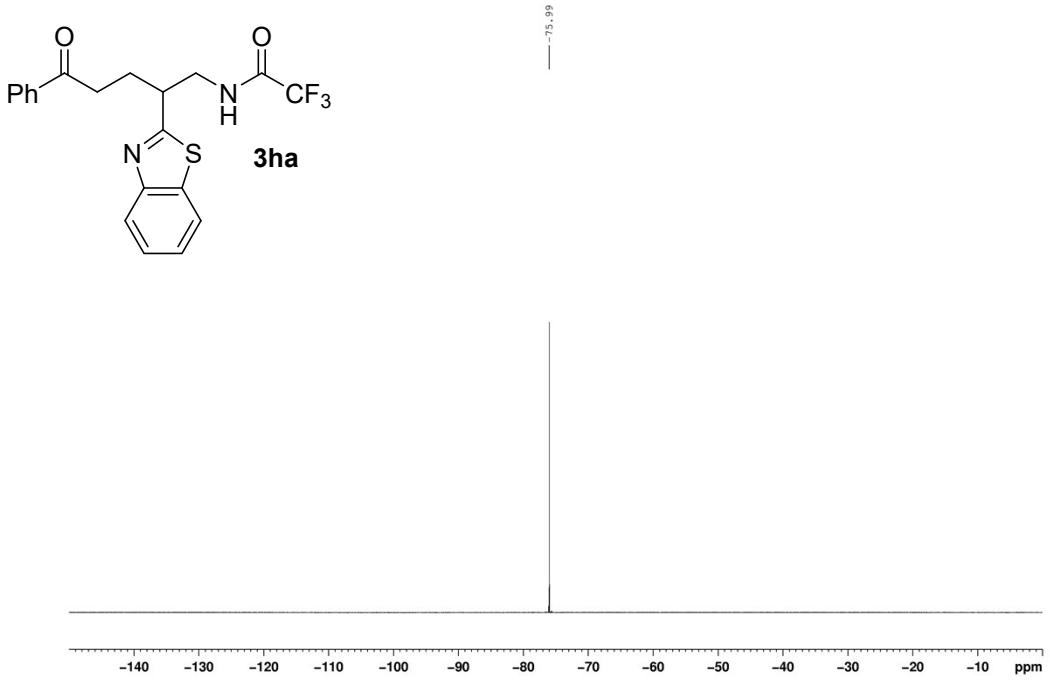
^{1}H NMR of **3ha** in $CDCl_3$(600 MHz, $CDCl_3$)



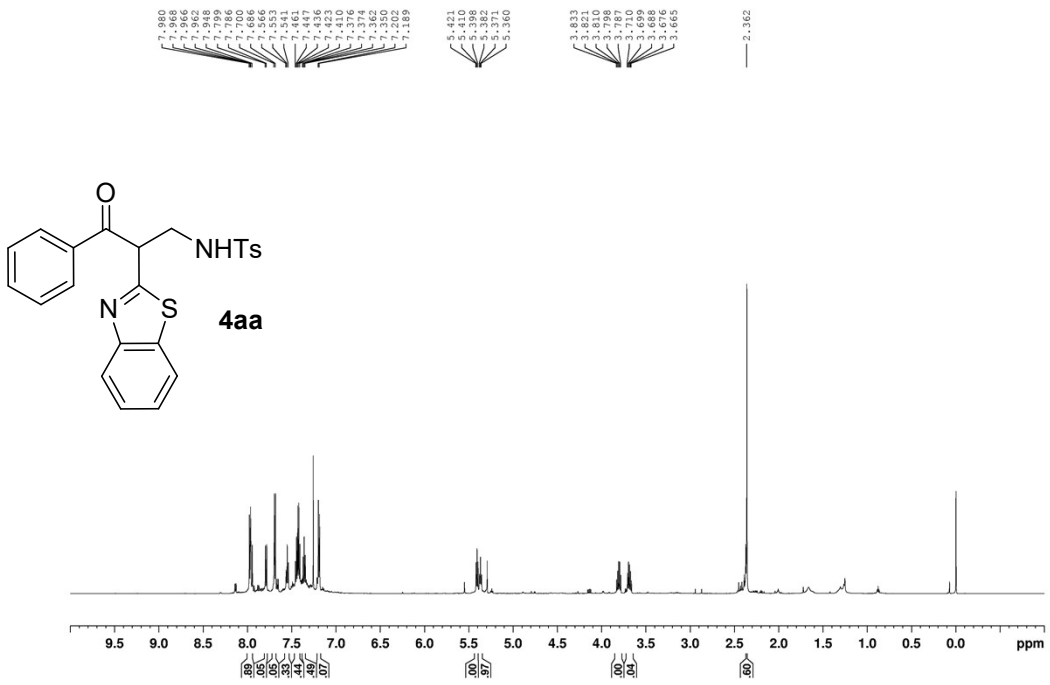
^{13}C NMR of **3ha** in $CDCl_3$(151 MHz, $CDCl_3$)



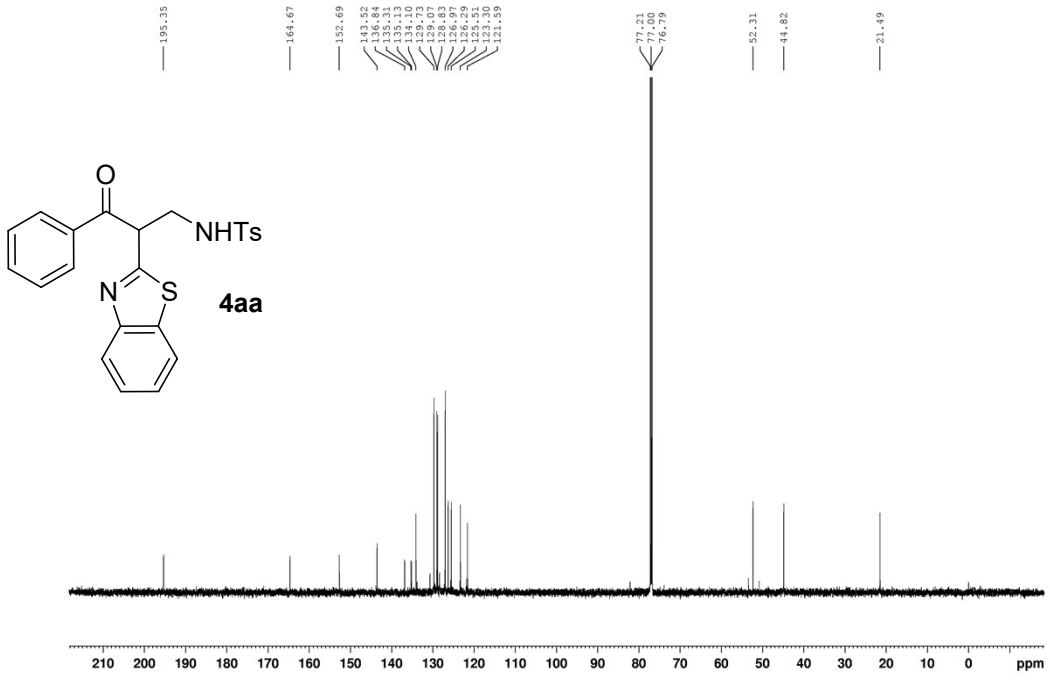
^{19}F NMR of **3ha** in $CDCl_3$(376 MHz, $CDCl_3$)



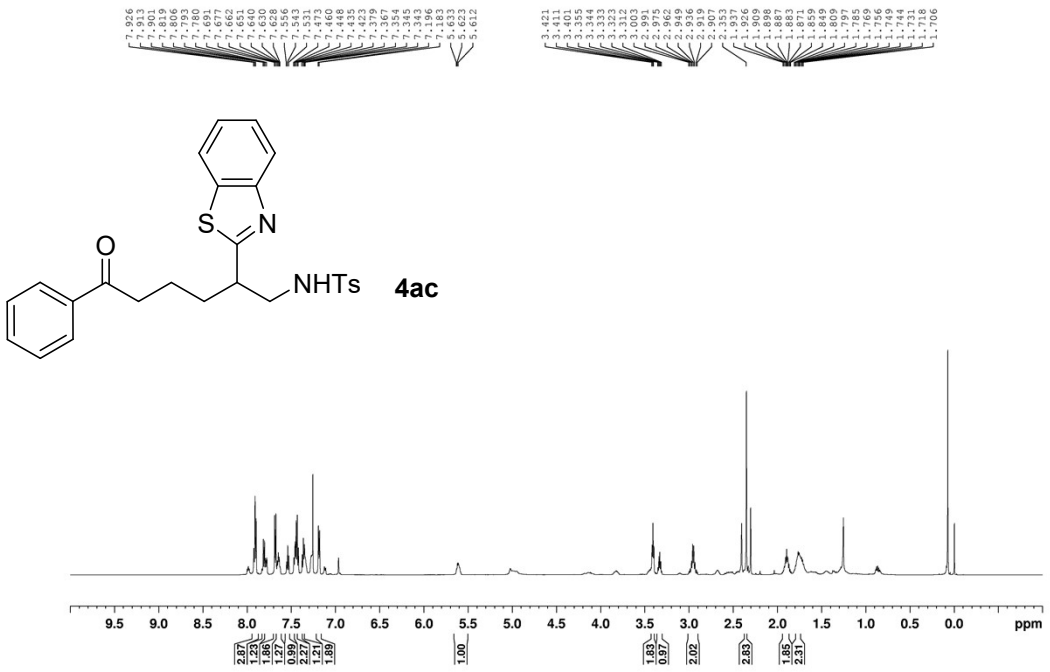
^{1}H NMR of **4aa** in $CDCl_3$(600 MHz, $CDCl_3$)



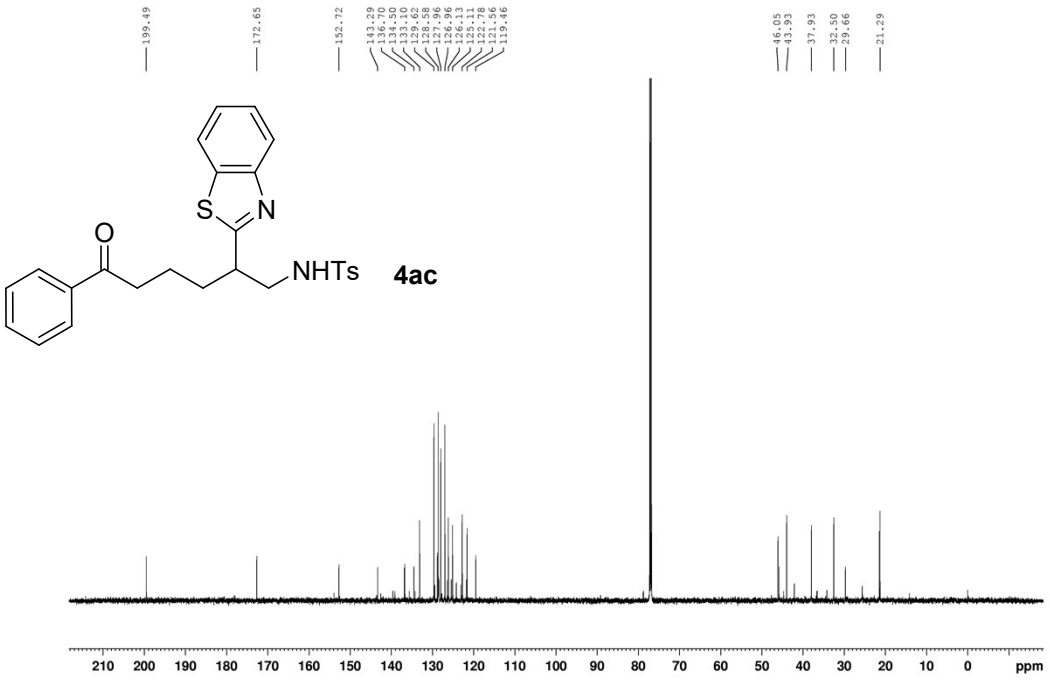
^{13}C NMR of **4aa** in $CDCl_3$(151 MHz, $CDCl_3$)



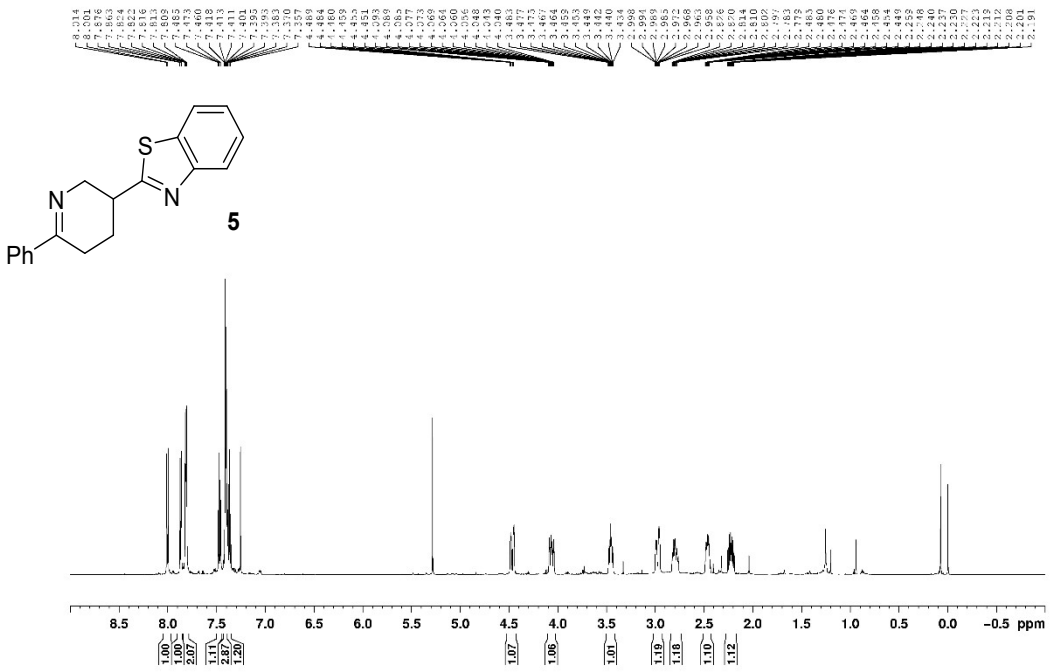
^{1}H NMR of **4ac** in $CDCl_3$(600 MHz, $CDCl_3$)



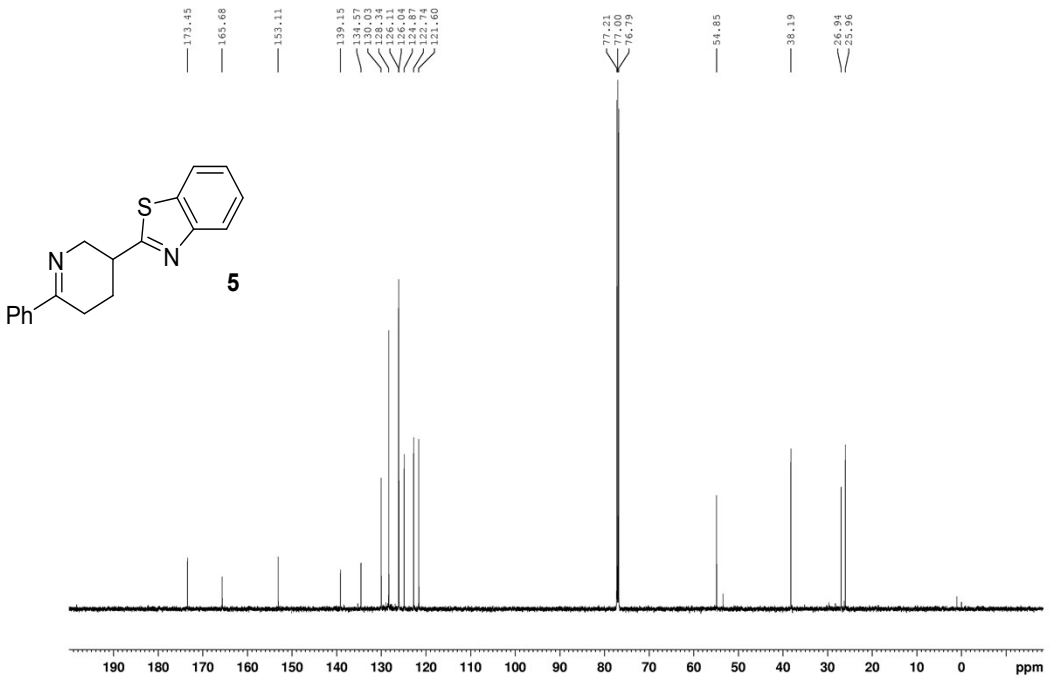
^{13}C NMR of **4ac** in $CDCl_3$(151 MHz, $CDCl_3$)



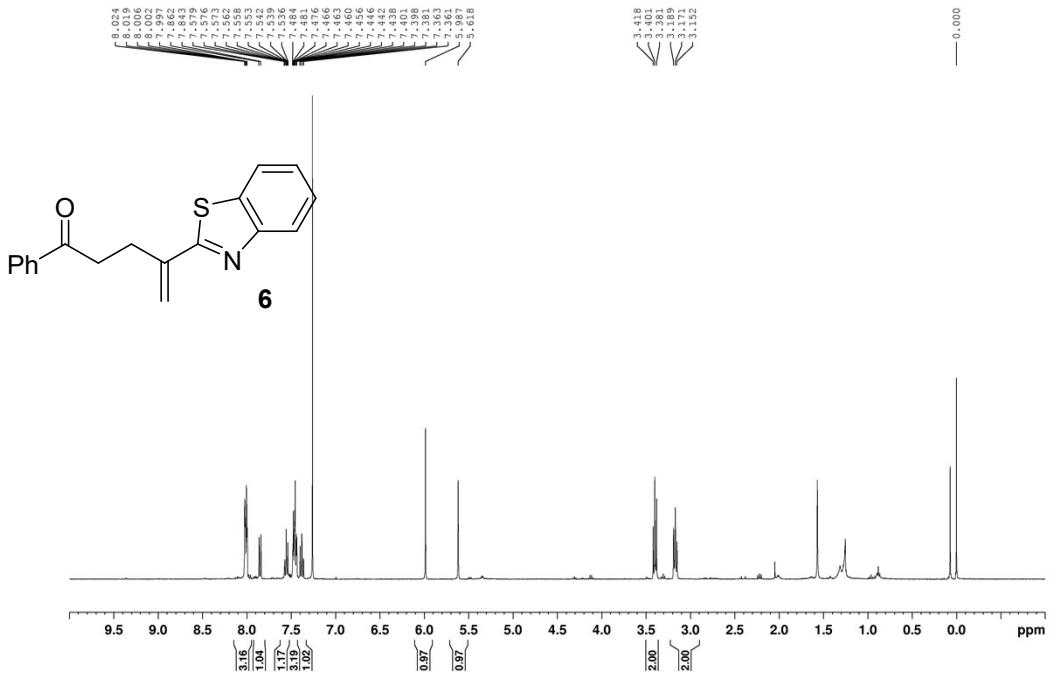
^{1}H NMR of **5** in $CDCl_3$(400 MHz, $CDCl_3$)



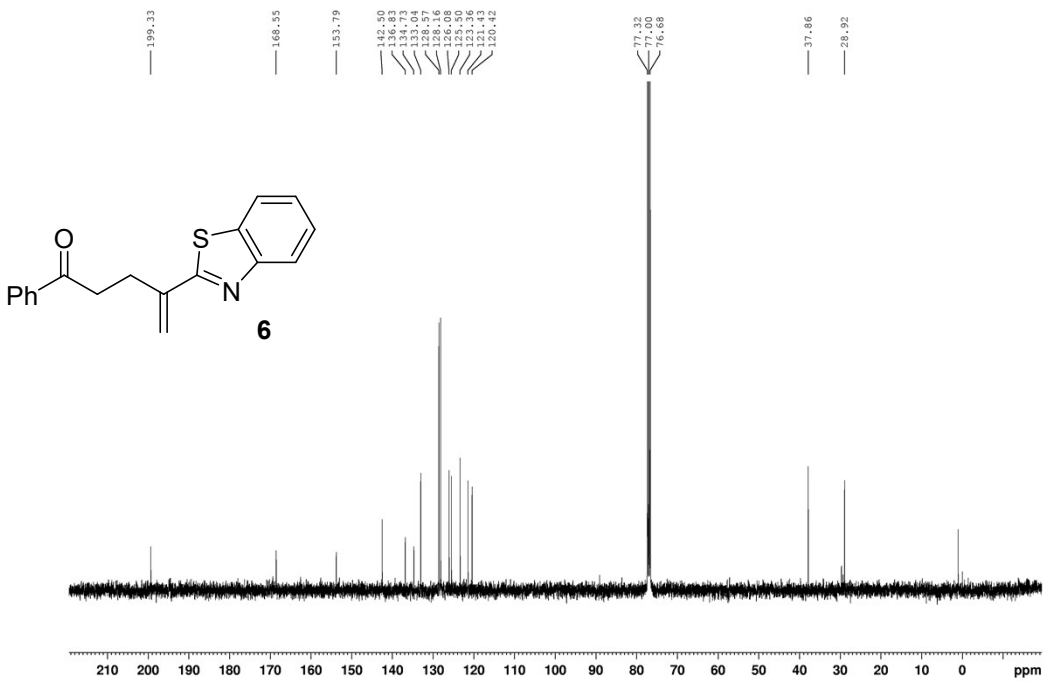
^{13}C NMR of **5** in $CDCl_3$(101 MHz, $CDCl_3$)



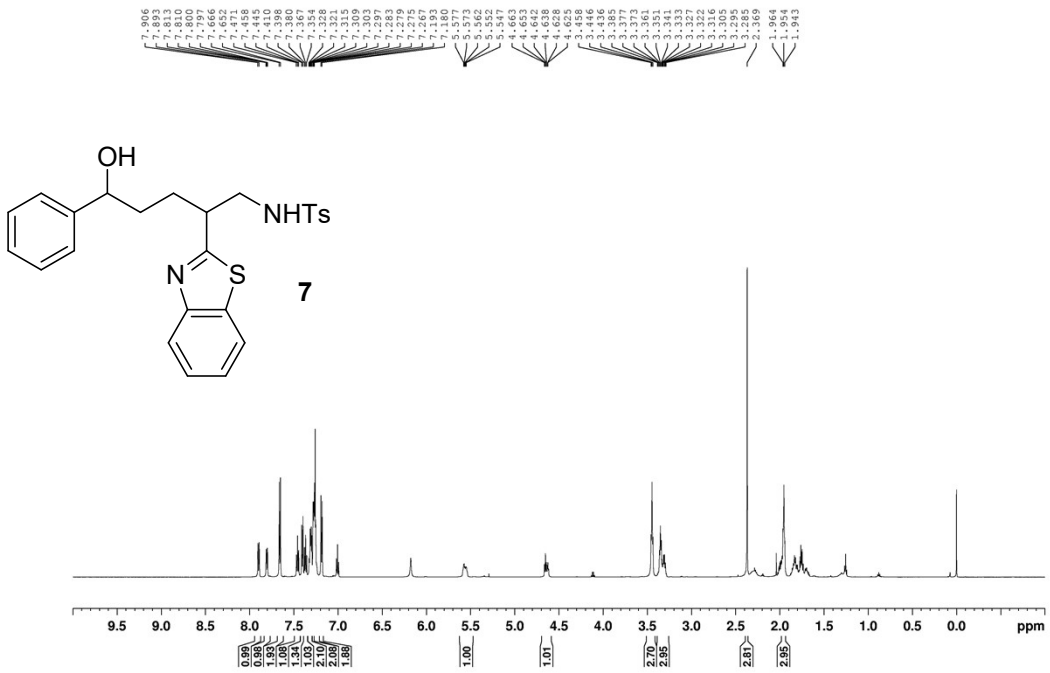
^{1}H NMR of **6** in $CDCl_3$(400 MHz, $CDCl_3$)



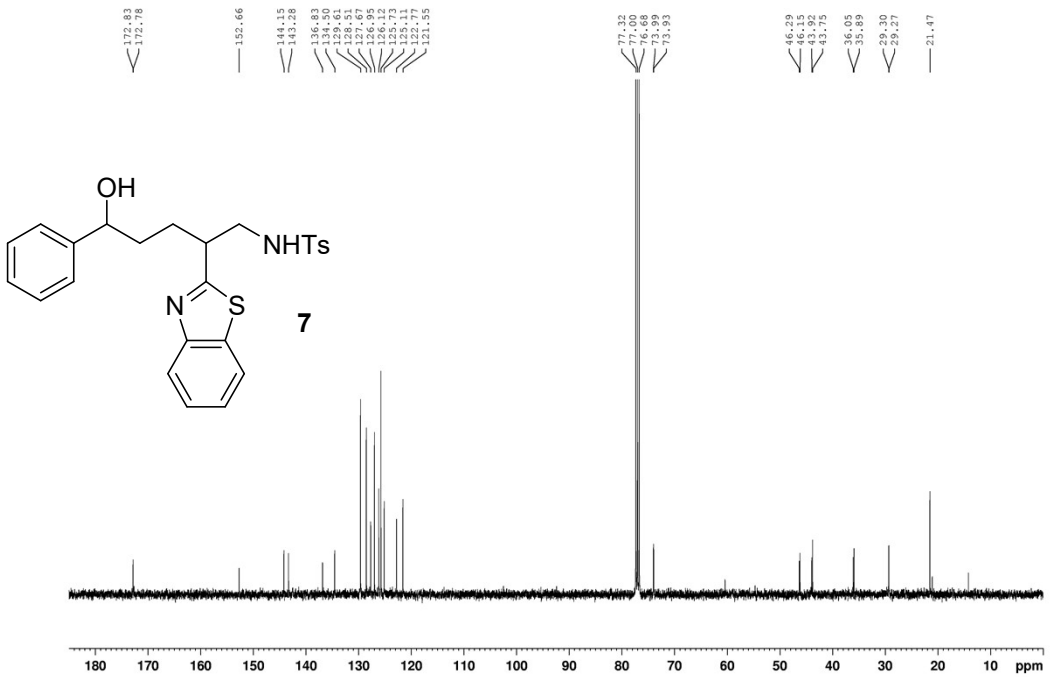
^{13}C NMR of **6** in $CDCl_3$(101 MHz, $CDCl_3$)



^{1}H NMR of **7** in $CDCl_3$(400 MHz, $CDCl_3$)



^{13}C NMR of **7** in $CDCl_3$(101 MHz, $CDCl_3$)



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