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Supporting Information

Photocatalyzed Hydroxyalkylation of *N*-Heteroaromatics with Aldehydes in Aqueous Phase

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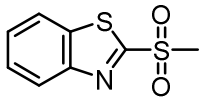
Table of Contents

1 General considerations

Unless otherwise noted, all reagents were used as received from the commercial suppliers. The tungstate-based complex tetrabutylammonium decatungstate,[1] substituted 2-(methylsulfonyl)benzo[*d*]thiazoles (6-F, 6-Br, 5-Cl, 6-OMe),[2,3] 2-(methylsulfonyl)naphtho[1,2-*d*]thiazole, 2-(methylsulfonyl)thiazole[2,3] and 1-methyl-2-(methylsulfonyl)-1H-benzo[d]imidazole[4] are synthesized according to the reported literature. Reactions were monitored using thin-layer chromatography (TLC). TLC plates were visualized with UV light (254 nm) or $KMnO_4$ stain. GC-MS measurements were conducted on Thermo Fisher. HPLC measurements were conducted on Agilent 1260. Light irradiation was performed with a 10 W LED lamp at λir = 380 ± 10 nm for photocatalytic reactions. Flash chromatography was carried out silica gel (200-300 mesh). ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker 400 MHz or Keysight 600 MHz spectrometer, and are internally referenced to the residual proto-solvent signals (note: $CDCl_3$: δ H = 7.26 ppm, δ C = 77.16 ppm; CD_3CN : δ H = 1.94 ppm, δ C = 1.32 ppm and 118.26 ppm). Data for ^{1}H are reported as: chemical shift (δ ppm), integration, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, dd: doublet of doublets, br: broad peak), coupling constant (Hz) and assignment. HRMS ESI-mass data were acquired on Thermo LTQ Orbitrap XL instrument. All measurements were carried out at room temperature unless otherwise stated.

2 Experimental section

2.1 Procedures for synthesis of starting materials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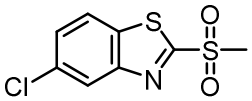
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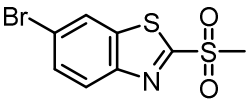
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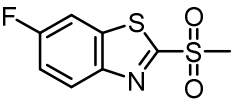
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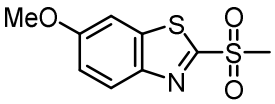
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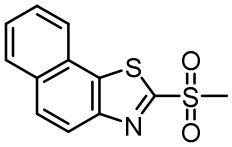
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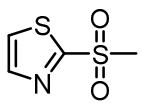
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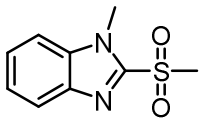
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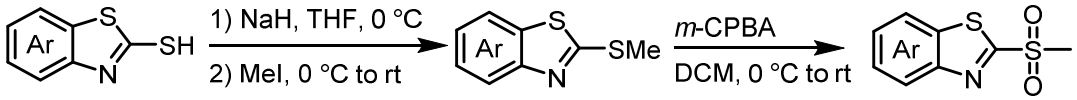
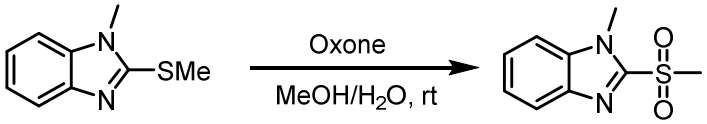
Preparation of 2-(Methylsulfonyl)benzothiazoles 1a-1g



1-SH **1-SMe** **1**

According to the reported literature,[2,3] under N_2 atmosphere, a solution of **1-SH** (18.9 mmol) in THF (60 mL) was cooled to 0 °C and NaH (0.811 g, 20.2 mmol) was added within 10 min. The resulting solution was stirred at 0 °C for 30 min, then methyl iodide (1.6 mL, 26.5 mmol) was added dropwise. The formed mixture was stirred at room temperature for overnight. Saturated aqueous NH_4Cl (30 mL) was added and resulting layers were separated. The aqueous layer was extracted with EtOAc (3 x 50 mL) and the combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, filtered and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography (PE) yielding the desired sulfide **(1-SMe)**. Then, to a 100 mL glass tube, sulfide **(1-SMe)** (10 mmol), oxone (9.221 g, 15 mmol), water (50 mL) were added and the mixture was stirred at 60 °C for 12 h. The mixture was then cooled to room temperature and extracted by ethyl acetate (100 mL × 4). The combined organic phase was washed successively with saturated $NaHCO_3$ solution and NaCl solution, and then dried over anhydrous Na_2SO_4. After the solution was filtered and the solvent was evaporated under vacuum, the residue was subjected to silica gel column chromatography using a mixture of ethyl acetate and petroleum ether (1:5, v/v) as eluent to give the desired product.

Preparation of 1-methyl-2-(methylsulfonyl)-1H-benzo[d]imidazole 1h



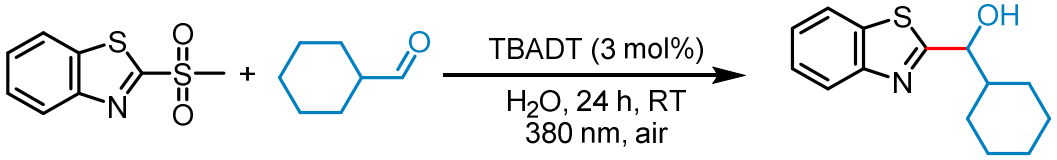
1h-SMe **1h**

According to the reported literature,[4] to a solution of 1-*i*-propyl-2-methylthiobenzimidazole **(1h-SMe)** (0.430 g, 2.0 mmol) in MeOH (10 mL) was added an aqueous solution (10 mL) of oxone (4.099 g, 6.0 mmol). After the mixture was stirred at room temperature for 5 h, the mixture was filtered by using H_2O (10 mL) and AcOEt (20 mL). The aqueous layer of the filtrate was extracted

with AcOEt (10 mL x 7) and the combined extracts were washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude residue was subjected to flash column chromatography on silica gel eluting with ethyl acetate/petroleum ether (1:5, v/v) to give the product **1h**.

2.2 Optimization of reaction conditions

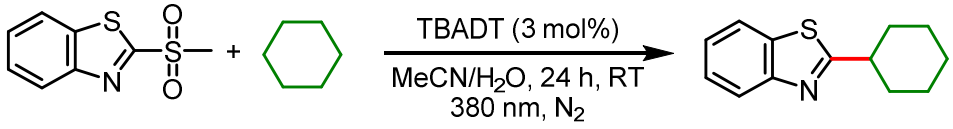
Table S1. Photocatalyzed hydroxyalkylation of *N*-heteroaromatics with aldehydes



Entry	Deviation from standard conditions	Yield (%)[b]
1	**None**	**62**
2	365 nm	58
3	395 nm	50
4	405 nm	37
5	415 nm	42
6	MeCN	53
7	MeCN/H_2O = 4 : 1	59
8	MeCN/H_2O = 2 : 3	60
9	DCM	41
10	Acetone	20
11	2.0 mL H_2O	55
12	2 eq Cyclohexanecarbaldehyde	17
13	5 eq Cyclohexanecarbaldehyde	51
14	8 eq Cyclohexanecarbaldehyde	57
15	20 eq Cyclohexanecarbaldehyde	64
16	1 mol% TBADT	56
17	2 mol% TBADT	60
18	5 mol% TBADT	63
19	10 mol% TBADT	65
20	6 h	20
21	12 h	37
22	20 h	58
23	36 h	65
24	60 °C	31
25	N_2	65
26	no TBADT	N.D.
27	no light	N.D.

[a] Reaction conditions: benzothiazole (0.2 mmol), cyclohexanecarbaldehyde (10 equiv), TBADT (3 mol %), in H_2O (1.0 mL) under open air, irradiated with 10 W LEDs at 25 °C for 24 h. [b] Yields were determined by HPLC using 2-(methylthio)-benzo[d]thiazole as an internal standard. N.D.= Not Detected.

Table S2. Photocatalyzed alkylation of *N*-heteroaromatics with alkanes



Entry	Deviation from standard conditions	Yield (%)[b]
1	**None**	**67**
2	365 nm	40
3	395 nm	49
4	405 nm	51
5	415 nm	47
6	MeCN	65
7	MeCN/H_2O = 2 : 1	50
8	MeCN/H_2O = 2 : 3	37
9	DCM	23
10	Acetone	32
11	H_2O	trace
12	2 eq Cyclohexane	15
13	5 eq Cyclohexane	44
14	8 eq Cyclohexane	63
15	20 eq Cyclohexane	71
16	1 mol% TBADT	50
17	2 mol% TBADT	56
18	5 mol% TBADT	69
19	10 mol% TBADT	72
20	6 h	23
21	12 h	41
22	20 h	61
23	36 h	69
24	air	15
25	60 °C	42
26	no TBADT	N.D.
27	no light	N.D.

[a] Reaction conditions: benzothiazole (0.2 mmol), cyclohexane (10 equiv), TBADT (3 mol%), in CH_3CN (0.4 mL) and H_2O (0.1 mL) under a nitrogen atmosphere, irradiated with 10 W 380 nm LEDs at 25 °C for 24 h. [b] Yields were determined by HPLC using 2-(methylthio)benzo[d]thiazole as an internal standard. N.D.=Not Detecte.

2.3 Procedure for the photochemical reactions

General procedure A:

To a flame-dried 8-mL vial equipped with a magnetic stir bar was charged with the heteroarene (0.2 mmol, 1.0 equiv), TBADT (0.006 mmol, 3 mol%), deionized water (1 mL) and aldehydes (2 mmol, 10.0 equiv). Then, the reaction mixture was irradiated under 380 LED strips (10W) for 24 h

at room temperature with stirring. After the reaction was complete, the reaction was quenched with saturated sodium bicarbonate solution and extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was subjected to flash column chromatography on silica gel eluting with ethyl acetate/petroleum ether to give the target product.

General procedure B:

To a flame-dried 8-mL vial equipped with a magnetic stir bar was charged with the heteroarene (0.2 mmol, 1.0 equiv), TBADT (0.006 mmol, 3 mol%), acetonitrile (0.4 mL), deionized water (0.1 mL) and aldehydes (2 mmol, 10.0 equiv). Then, the reaction mixture was irradiated under 380 LED strips (10W) for 24 h at room temperature with stirring. After the reaction was complete, the reaction was quenched with saturated sodium bicarbonate solution and extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was subjected to flash column chromatography on silica gel eluting with ethyl acetate/petroleum ether to give the target product.

General procedure C:

To an flame-dried 8-mL vial equipped with a magnetic stir bar was charged with the heteroarene (0.2 mmol, 1.0 equiv), TBADT (0.006 mmol, 3 mol%), sodium dodecyl sulfate (0.06 mmol, 30 mol%), deionized water (1 mL) and aldehydes (2 mmol, 10.0 equiv). Then, the reaction mixture was irradiated under 380 LED strips (10W) for 24 h at room temperature with stirring. After the reaction was complete, the reaction was quenched with saturated sodium bicarbonate solution and extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na2SO4, filtered and concentrated under reduced pressure. The crude residue was subjected to flash column chromatography on silica gel eluting with ethyl acetate/petroleum ether to give the target product.

General procedure D:

To a flame-dried 8-mL vial equipped with a magnetic stir bar was charged with the heteroarene (0.2 mmol, 1.0 equiv), TBADT (0.006 mmol, 3 mol%). Acetonitrile (0.4 mL), deionized water (0.1 mL) and alkanes (2 mmol, 10.0 equiv) are added via a syringe under N_2 atmosphere. Then, the reaction mixture was irradiated under 380 LED strips (10W) for 24 h at room temperature with stirring. After the reaction was complete, the reaction was quenched with saturated sodium bicarbonate solution and extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was subjected to flash column chromatography on silica gel eluting with ethyl acetate/petroleum ether to give the target product.

General procedure E:

To a flame-dried 8-mL vial equipped with a magnetic stir bar was charged with the heteroarene (0.2 mmol, 1.0 equiv), TBADT (0.006 mmol, 3 mol%). Acetonitrile (0.8 mL), deionized water (0.2 mL) and alkanes (2 mmol, 10.0 equiv) are added via a syringe under N_2 atmosphere. Then, the reaction mixture was irradiated under 380 LED strips (10W) for 24 h at room temperature with stirring. After the reaction was complete, the reaction was quenched with saturated sodium bicarbonate solution and extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was subjected to flash column chromatography on silica gel eluting with ethyl

acetate/petroleum ether to give the target product.

General procedure F:

To a flame-dried 8-mL vial equipped with a magnetic stir bar was charged with the heteroarene (0.2 mmol, 1.0 equiv), TBADT (0.006 mmol, 3 mol%). Acetonitrile (0.8 mL), deionized water (0.2 mL) and alkanes (2 mmol, 5.0 equiv) are added via a syringe under N_2 atmosphere. Then, the reaction mixture was irradiated under 380 LED strips (10W) for 24 h at room temperature with stirring. After the reaction was complete, the reaction was quenched with saturated sodium bicarbonate solution and extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was subjected to flash column chromatography on silica gel eluting with ethyl acetate/petroleum ether to give the target product.

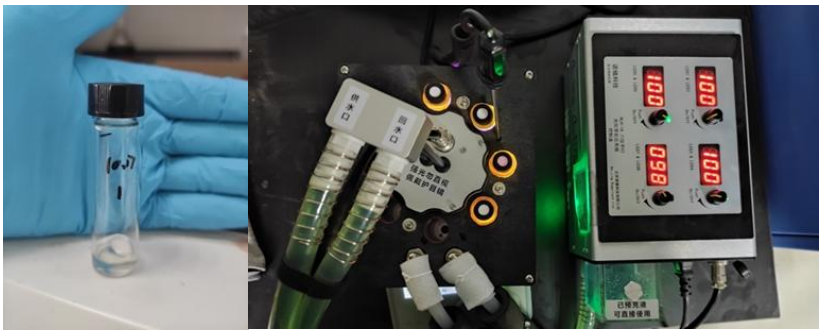
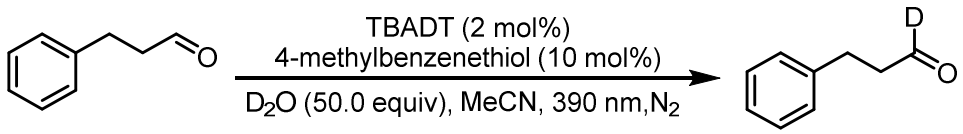


Figure S1. Photoreactor of standard reaction

2.4 Preparation of deuterated formyl C-H bonds



According to the reported literature,[5] 3-phenylpropanal (3 mmol), TBADT (199.2 mg, 2 mol%), 4-methylbenzenethiol (37.2 mg, 10 mol%), D_2O (2.7 mL, 50.0 equiv) and CH_3CN (3 mL, 1.0 M) were added to a 25 mL high borosilicate glass tube equipped with a stir bar. The reaction mixture was degassed via vacuum evacuation and backfilled with nitrogen for three times, irradiated with 390 nm lamp for 20 h. The deuterium incorporation was determined by the analysis of the ^1H NMR spectra. The reaction was quenched with water and extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was subjected to flash column chromatography on silica gel eluting with ethyl acetate/petroleum ether to give the target product (70% D, 55% yield).

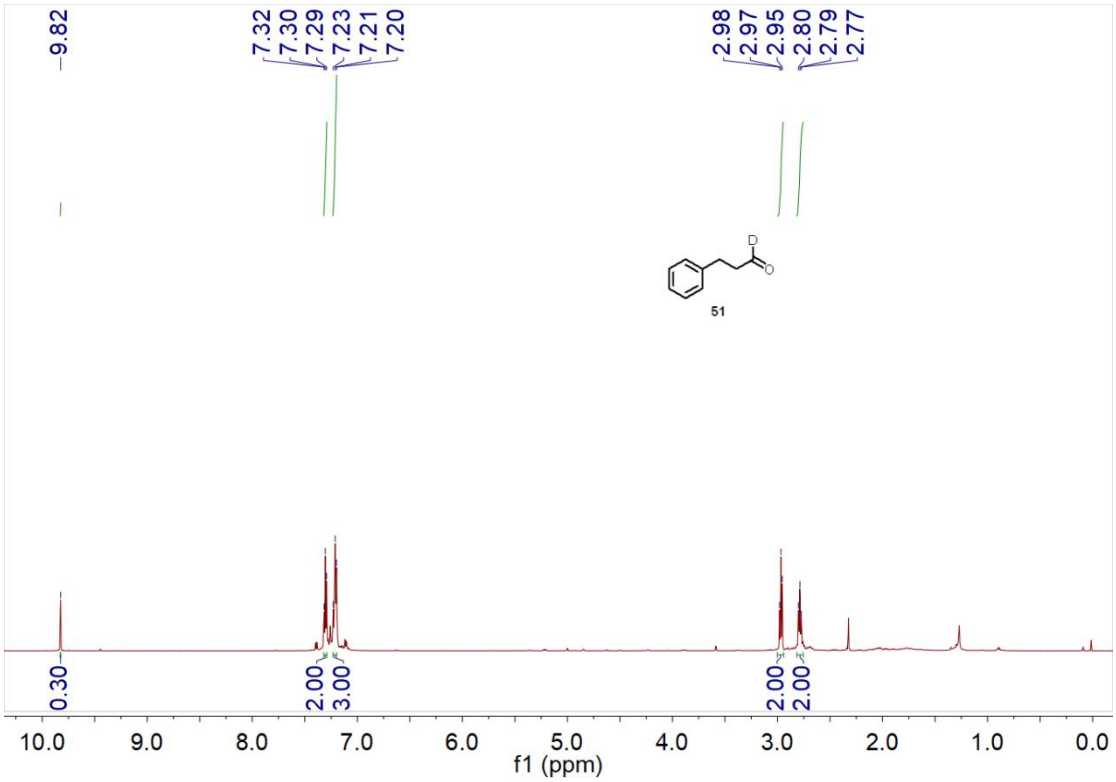
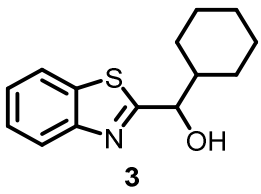


Figure S2. ^{1}H NMR spectrum of 51

3 Characterization of products and Unsuccessful substrates

3.1 Characterization of products

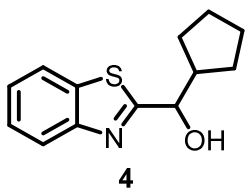
Benzo[d]thiazol-2-yl(cyclohexyl)methanol (3)[6]



3

Following the Synthesis of products from hydroxyl alkylation reaction (General procedure A), the product was purified by column chromatography (PE/EA = 5:1) as a yellow solid (30.6 mg, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 4.85 (d, *J* = 5.3 Hz, 1H), 3.48 (br, 1H), 1.89 (s, 1H), 1.77 – 1.59 (m, 5H), 1.28 – 1.09 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 176.2, 152.6, 134.9, 126.1, 125.1, 122.9, 121.9, 76.6, 45.1, 29.5, 27.2, 26.3, 26.2, 26.0.

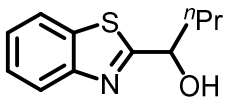
Benzo[d]thiazol-2-yl(cyclopentyl)methanol (4)



4

Following the Synthesis of products from hydroxyl alkylation reaction (General procedure A), the product was purified by column chromatography (PE/EA = 5:1) as a light yellow oil (35.9 mg, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 4.92 (d, *J* = 6.7 Hz, 1H), 3.86 (br, 1H), 2.51 – 2.37 (m, 1H), 1.77 – 1.43 (m, 8H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.4, 152.5, 134.9, 126.1, 125.1, 122.9, 121.9, 75.4, 46.8, 29.0, 28.0, 25.9, 25.8. **HRMS (ESI)** Calcd for $[C_{13}H_{16}NOS]^{+}$: 234.0947; found 234.0951.

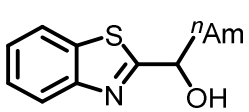
1-(Benzo[d]thiazol-2-yl)butan-1-ol (5)[6]



5

Following the Synthesis of products from hydroxyl alkylation reaction (General procedure A), the product was purified by column chromatography (PE/EA = 5:1) as a yellow solid (24.4 mg, 59% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 5.10 (dd, *J* = 8.0, 4.7 Hz, 1H), 3.48 (br, 1H), 2.07 – 1.81 (m, 2H), 1.64 – 1.36 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.5, 152.7, 134.8, 126.1, 125.0, 122.8, 121.8, 72.1, 40.2, 18.5, 13.8.

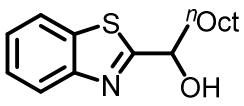
1-(Benzo[d]thiazol-2-yl)hexan-1-ol (6)[6]



6

Following the Synthesis of products from hydroxyl alkylation reaction (General procedure A), the product was purified by column chromatography (PE/EA = 5:1) as a yellow solid (21.1 mg, 51% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 5.08 (dd, J = 8.0, 4.7 Hz, 1H), 3.57 (br, 1H), 2.04 – 1.89 (m, 2H), 1.55 – 1.45 (m, 2H), 1.34 – 1.28 (m, 4H), 0.89 – 0.85 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.8, 152.8, 134.9, 126.2, 125.1, 122.9, 121.9, 72.4, 38.2, 31.7, 25.0, 22.6, 14.1.

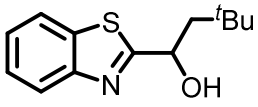
1-(Benzo[d]thiazol-2-yl)nonan-1-ol (7)



7

Following the Synthesis of products from hydroxyl alkylation reaction (General procedure A), the product was purified by column chromatography (PE/EA = 5:1) as a light yellow solid (25.5 mg, 46% yield), mp: 34-36 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 5.08 (dd, *J* = 8.0, 4.7 Hz, 1H), 3.52 (br, 1H), 2.05 – 1.88 (m, 2H), 1.54 – 1.44 (m, 2H), 1.31 – 1.23 (m, 10H), 0.89 – 0.85 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.8, 152.9, 134.9, 126.2, 125.1, 122.9, 121.9, 72.5, 38.3, 32.0, 29.6, 29.5, 29.4, 25.3, 22.8, 14.2. **HRMS (ESI)** Calcd for $[C_{16}H_{24}NOS]^+$: 278.1573; found 278.1578.

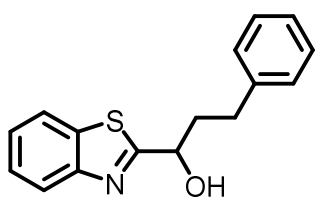
1-(Benzo[d]thiazol-2-yl)-3,3-dimethylbutan-1-ol (8)



8

Following the Synthesis of products from hydroxyl alkylation reaction (General procedure A), the product was purified by column chromatography (PE/EA = 5:1) as a yellow solid (21.2 mg, 48% yield), mp: 40-42 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.0 Hz, 1H), 7.35 (t, *J* = 7.0 Hz, 1H), 5.22 (dd, *J* = 9.3, 2.9 Hz, 1H), 3.06 (br, 1H), 2.00 – 2.00 – 1.97 (dd, *J* = 14.6, 2.9 Hz, 1H), 1.84 (dd, *J* = 14.6, 9.3 Hz, 1H), 1.07 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.9, 152.9, 135.0, 126.2, 125.1, 123.0, 121.94, 70.8, 51.8, 30.9, 30.3. **HRMS (ESI)** Calcd for $[C_{13}H_{18}NO_2S]^+$: 236.1104; found 236.1101.

1-(Benzo[d]thiazol-2-yl)-3-phenylpropan-1-ol (9)[7]

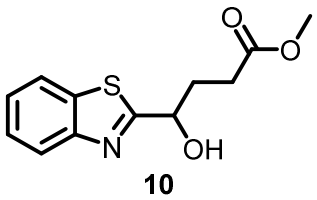


9

Following the Synthesis of products from hydroxyl alkylation reaction (General procedure A), the product was purified by column chromatography (PE/EA = 5:1) as a light yellow oil (44.1 mg,

82% yield). **^{1}H NMR** (400 MHz, CD_3Cl_3) δ 7.97 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.47 (t, *J* = 8.3 Hz, 1H), 7.37 (t, *J* = 7.0 Hz, 1H), 7.31 – 7.22 (m, 4H), 7.19 (t, *J* = 6.9 Hz, 1H), 5.10 (dd, *J* = 8.3, 4.3 Hz, 1H), 3.46 (br, 1H), 2.93 – 2.78 (m, 2H), 2.41 – 2.29 (m, 1H), 2.28 – 2.15 (m, 1H). **^{13}C NMR** (101 MHz, CD_3CN) δ 178.9, 154.5, 142.8, 135.8, 129.5, 129.4, 126.9, 126.8, 125.8, 123.5, 123.0, 71.9, 40.4, 32.0.

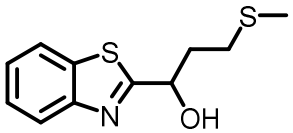
Methyl 4-(benzo[d]thiazol-2-yl)-4-hydroxybutanoate (10)



10

Following the Synthesis of products from hydroxyl alkylation reaction (General procedure A), the product was purified by column chromatography (PE/EA = 2:1) as a light yellow oil (22.6 mg, 45% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.3 Hz, 1H), 5.20 (dd, *J* = 7.8, 4.0 Hz, 1H), 3.85 (br, 1H), 3.69 (s, 3H), 2.66 – 2.53 (m, 2H), 2.49 – 2.38 (m, 1H), 2.32 – 2.22 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.2, 174.8, 152.8, 134.9, 126.3, 125.2, 122.9, 122.0, 71.7, 52.1, 32.6, 30.1. **HRMS (ESI)** Calcd for $[C_{12}H_{14}NO_3S]^+$: 252.0689; found 252.0691.

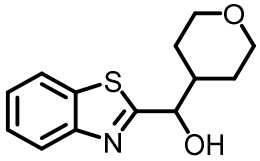
1-(Benzo[d]thiazol-2-yl)-3-(methylthio)propan-1-ol (11)



11

Following the Synthesis of products from hydroxyl alkylation reaction (General procedure A), the product was purified by column chromatography (PE/EA = 5:1) as a brown oil (24.4 mg, 51% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 5.29 (dd, *J* = 8.4, 3.9 Hz, 1H), 3.63 (br, 1H), 2.79 – 2.70 (m, 2H), 2.44 – 2.31 (m, 1H), 2.28 – 2.18 (m, 1H), 2.14 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.0, 152.8, 134.9, 126.3, 125.2, 122.9, 122.0, 71.7, 36.5, 30.2, 15.5. **HRMS (ESI)** Calcd for $[C_{11}H_{14}NOS_2]^+$: 240.0511; found 240.0517.

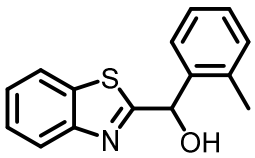
Benzo[d]thiazol-2-yl(tetrahydro-2H-pyran-4-yl)methanol (12)



12

Following the Synthesis of products from hydroxyl alkylation reaction (General procedure A), the product was purified by column chromatography (PE/EA = 5:1) as a colorless oil (32.4 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 4.87 (d, *J* = 5.7 Hz, 1H), 3.99 – 3.93 (m, 2H), 3.82 (br, 1H), 3.37 – 3.31 (m, 2H), 2.21 – 2.10 (m, 1H), 1.68 – 1.57 (m, 3H), 1.51 – 1.45 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.4, 152.6, 134.7, 126.3, 125.3, 122.9, 121.9, 75.7, 67.8, 67.7, 42.2, 29.1, 27.5. **HRMS (ESI)** Calcd for $[C_{13}H_{16}NO_2S]^+$: 250.0896; found 250.0992.

Benzo[d]thiazol-2-yl(o-tolyl)methanol (13)[8]

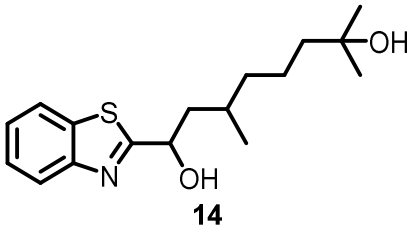


13

Following the Synthesis of products from hydroxyl alkylation reaction (General procedure A), the product was purified by column chromatography (PE/EA = 4:1) as a white solid (20.4 mg, 40% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H),

7.53 (dd, *J* = 6.9, 2.1 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.30 – 7.23 (m, 2H), 7.23 – 7.18 (m, 1H), 6.34 (s, 1H), 3.92 (br, 1H), 2.43 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.0, 152.7, 139.1, 136.2, 135.5, 131.0, 128.8, 127.1, 126.6, 126.3, 125.3, 123.2, 121.9, 71.8, 19.6.

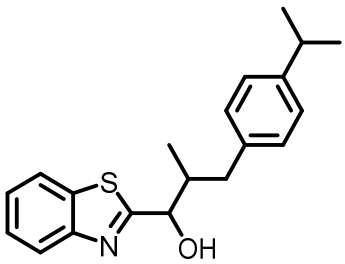
1-(Benzo[d]thiazol-2-yl)-3,7-dimethyloctane-1,7-diol (14)



14

Following the Synthesis of products from hydroxyl alkylation reaction (General procedure C), the product was purified by column chromatography (PE/EA = 5:1) as a light yellow oil (34.4 mg, 56% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ δ 7.96 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 5.21 – 5.14 (m, 1H), 1.98 – 1.91 (m, 1H), 1.86 – 1.71 (m, 2H), 1.48 – 1.34 (m, 5H), 1.26 (s, 3H), 1.20 (d, *J* = 3.4 Hz, 6H), 1.00 (dd, *J* = 12.4, 6.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.6, 152.7, 134.8, 126.2, 125.2, 122.9, 122.0, 71.29, 70.7, 45.7, 44.0, 38.1, 36.6, 29.3, 21.6, 20.5, 19.2. **HRMS (ESI)** Calcd for $[C_{17}H_{26}NO_2S]^+$: 308.1679; found 308.1684.

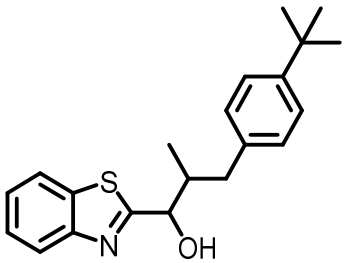
1-(Benzo[d]thiazol-2-yl)-3-(4-isopropylphenyl)-2-methylpropan-1-ol (15)



15

Following the Synthesis of products from hydroxyl alkylation reaction (General procedure B), the product was purified by column chromatography (PE/EA = 5:1) as a light yellow oil (40.3 mg, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.09 (s, 4H), 4.99 (d, *J* = 4.9 Hz, 1H), 3.51 (br, 1H), 2.92 – 2.83 (m, 2H), 2.52 – 2.44 (m, 1H), 2.43 – 2.36 (m, 1H), 1.21 (d, *J* = 7.0 Hz, 6H), 0.95 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.3, 152.6, 146.6, 137.6, 135.0, 129.3, 126.4, 126.2, 125.2, 123.0, 121.9, 76.2, 42.4, 37.1, 33.8, 24.2, 15.9. **HRMS (ESI)** Calcd for $[C_{20}H_{24}NOS]^+$: 326.1573; found 326.1579.

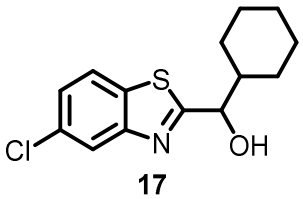
1-(Benzo[d]thiazol-2-yl)-3-(4-(tert-butyl)phenyl)-2-methylpropan-1-ol (16)



16

Following the Synthesis of products from hydroxyl alkylation reaction (General procedure B), the product was purified by column chromatography (PE/EA = 5:1) as a light yellow oil (37.3 mg, 55% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 2H), 7.10 (d, *J* = 6.7 Hz, 2H), 5.04 (d, *J* = 3.2 Hz, 1H), 3.32 (br, 1H), 2.88 (dd, *J* = 12.5, 3.5 Hz, 1H), 2.55 – 2.48 (m, 1H), 2.48 – 2.40 (m, 1H), 1.27 (s, 9H), 0.99 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.3, 152.6, 146.6, 137.6, 135.0, 129.3, 126.4, 126.2, 125.2, 123.0, 121.9, 76.2, 42.4, 37.1, 33.8, 24.2, 15.9. **HRMS (ESI)** Calcd for $[C_{21}H_{26}NOS]^+$: 340.1730; found 340.1733.

(5-Chlorobenzo[d]thiazol-2-yl)(cyclohexyl)methanol (17)

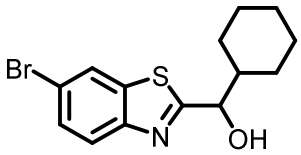


17

Following the Synthesis of products from hydroxyl alkylation

reaction (General procedure A), the product was purified by column chromatography (PE/EA = 5:1) as a white solid (24.2 mg, 43% yield), mp: 126-128 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 1.9 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.35 (dd, *J* = 8.5, 2.0 Hz, 1H), 4.88 (d, *J* = 5.0 Hz, 1H), 2.87 (br, 1H), 1.96 – 1.88 (m, 1H), 1.78 – 1.64 (m, 5H), 1.29 – 1.19 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.0, 153.6, 133.2, 132.2, 125.6, 122.8, 122.6, 76.7, 45.0, 29.5, 26.9, 26.3, 26.2, 26.0. **HRMS (ESI)** Calcd for $[C_{14}H_{17}ClNOS]^+$: 282.0714; found 282.0713.

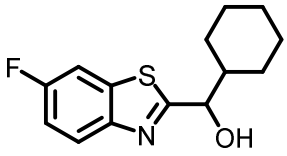
(6-Bromobenzo[d]thiazol-2-yl)(cyclohexyl)methanol (18)



18

Following the Synthesis of products from hydroxyl alkylation reaction (General procedure A), the product was purified by column chromatography (PE/EA = 5:1) as a yellow solid (29.3 mg, 45% yield), mp: 140-142 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 1.8 Hz, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.54 (dd, *J* = 8.6, 1.8 Hz, 1H), 4.84 (d, *J* = 5.1 Hz, 1H), 3.60 (br, 1H), 1.93 – 1.88 (m, 1H), 1.75 – 1.63 (m, 5H), 1.26 – 1.15 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.8, 151.7, 136.6, 129.6, 124.4, 124.0, 118.7, 76.6, 45.0, 29.5, 27.1, 26.3, 26.2, 26.0. **HRMS (ESI)** Calcd for $[C_{14}H_{17}BrNOS]^+$: 326.0209; found 326.0206.

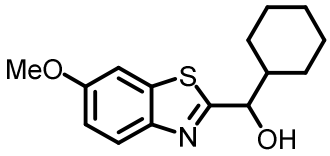
Cyclohexyl(6-fluorobenzo[d]thiazol-2-yl)methanol (19)



19

Following the Synthesis of products from hydroxyl alkylation reaction (General procedure A), the product was purified by column chromatography (PE/EA = 5:1) as a yellow oil (25.4 mg, 48% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.9, 4.8 Hz, 1H), 7.54 (d, *J* = 5.6 Hz, 1H), 7.22 – 7.16 (m, 1H), 4.85 (d, *J* = 5.1 Hz, 1H), 3.00 (br, 1H), 1.90 (s, 1H), 1.78 – 1.63 (m, 5H), 1.30 – 1.19 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.6 (d, *J* = 3.0 Hz), 160.4 (d, *J* = 245.3 Hz), 149.4 (d, *J* = 1.1 Hz), 135.9 (d, *J* = 11.0 Hz), 123.9 (d, *J* = 9.5 Hz), 114.8 (d, *J* = 24.6 Hz), 108.1 (d, *J* = 26.5 Hz), 76.6, 45.0, 29.5, 27.1, 26.3, 26.2, 26.0. **^{19}F NMR** (564 MHz, $CDCl_3$) δ -116.64. **HRMS (ESI)** Calcd for $[C_{14}H_{17}FNOS]^+$: 266.1009; found 266.1005.

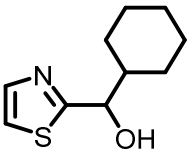
Cyclohexyl(6-methoxybenzo[d]thiazol-2-yl)methanol (20)



20

Following the Synthesis of products from hydroxyl alkylation reaction (General procedure B), the product was purified by column chromatography (PE/EA = 5:1) as a white solid (29.9 mg, 54% yield), mp: 112-114 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.9 Hz, 1H), 7.29 (d, *J* = 2.3 Hz, 1H), 7.04 (dd, *J* = 8.9, 2.4 Hz, 1H), 4.80 (d, *J* = 5.4 Hz, 1H), 3.86 (s, 3H), 3.46 (br, 1H), 1.79 – 1.70 (m, 3H), 1.64 (d, *J* = 12.5 Hz, 2H), 1.27 – 1.18 (m, 5H), 0.96 – 0.85 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.5, 157.6, 147.1, 136.2, 123.31, 115.5, 104.4, 76.5, 55.9, 45.0, 29.4, 27.3, 26.3, 26.2, 26.0. **HRMS (ESI)** Calcd for $[C_{15}H_{20}NO_2S]^+$: 278.1209; found 278.1204.

Cyclohexyl(thiazol-2-yl)methanol (21)[9]

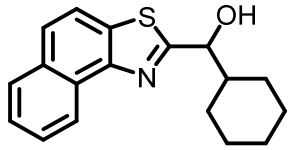


21

Following the Synthesis of products from hydroxyl alkylation reaction (General procedure A), the product was purified by column chromatography (PE/EA = 5:1) as a colorless oil (17.0 mg, 43% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d,

J = 3.2 Hz, 1H), 7.30 (d, *J* = 3.2 Hz, 1H), 4.80 (d, *J* = 5.3 Hz, 1H), 3.53 (br, 1H), 1.88 – 1.77 (m, 1H), 1.80 – 1.69 (m, 5H), 1.33 – 1.02 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.8, 142.0, 118.9, 76.2, 45.2, 29.4, 29.1, 27.3, 26.2, 25.5.

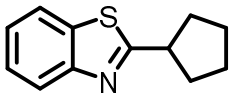
Cyclohexyl(naphtho[1,2-d]thiazol-2-yl)methanol (22)



22

Following the Synthesis of products from hydroxyl alkylation reaction (General procedure B), the product was purified by column chromatography (PE/EA = 5:1) as a colorless oil (30.9 mg, 52% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 8.2 Hz, 1H), 7.99 – 7.96 (m, 1H), 7.95 – 7.93 (m, 1H), 7.92 – 7.89 (m, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 3.95 – 3.87 (m, 1H), 2.14 (d, *J* = 11.6 Hz, 2H), 1.94 – 1.88 (m, 2H), 1.83 – 1.79 (m, 1H), 1.69 – 1.48 (m, 5H), 1.37 – 1.26 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.4, 165.2, 150.4, 135.6, 132.2, 129.7, 128.8, 128.4, 127.7, 126.9, 123.9, 119.4, 46.1, 29.2, 26.1, 25.9. **HRMS (ESI)** Calcd for $[C_{18}H_{20}NOS]^+$: 298.1260; found 298.1254.

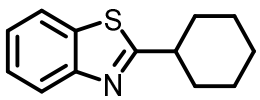
2-Cyclopentylbenzo[d]thiazole (23)[10]



23

Following the Synthesis of alkylation reaction products (General procedure D), the product was purified by column chromatography (PE/EA = 20:1) as a yellow oil (28.8 mg, 71% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.1 Hz, 1H), 7.32 (t, *J* = 7.0 Hz, 1H), 3.58 – 3.51 (m, 1H), 2.29 – 2.21 (m, 2H), 1.98 – 1.92 (m, 2H), 1.90 – 1.83 (m, 2H), 1.77 – 1.70 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.3, 153.3, 134.9, 125.9, 124.6, 122.6, 121.6, 44.9, 34.2, 25.7.

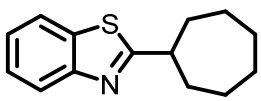
2-Cyclohexylbenzo[d]thiazole (24)[10]



24

Following the Synthesis of alkylation reaction products (General procedure D), the product was purified by column chromatography (PE/EA = 20:1) as a colorless oil (29.1 mg, 67% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 3.24 – 3.08 (m, 1H), 2.32 – 2.17 (m, 2H), 2.05 – 1.85 (m, 2H), 1.82 – 1.73 (m, 1H), 1.71 – 1.60 (m, 2H), 1.48 – 1.43 (m, 2H), 1.34 – 1.30 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.9, 153.1, 134.6, 126.0, 124.7, 122.6, 121.7, 43.5, 33.6, 26.2, 25.9.

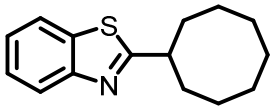
2-Cycloheptylbenzo[d]thiazole (25)[10]



25

Following the Synthesis of alkylation reaction products (General procedure D), the product was purified by column chromatography (PE/EA = 20:1) as a yellow oil (24.0 mg, 52% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 3.32 – 3.27 (m, 1H), 2.24 – 2.18 (m, 2H), 1.90 – 1.80 (m, 4H), 1.72 – 1.64 (m, 2H), 1.64 – 1.56 (m, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 178.9, 153.1, 134.8, 125.9, 124.6, 122.6, 121.6, 45.6, 35.5, 28.2, 26.6.

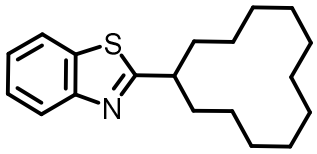
2-Cyclooctylbenzo[d]thiazole (26)[10]



26

Following the Synthesis of alkylation reaction products (General procedure E), the product was purified by column chromatography (PE/EA = 20:1) as a colorless oil (9.8 mg, 20% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 3.43 – 3.35 (m, 1H), 2.22 – 2.09 (m, 2H), 2.03 – 1.92 (m, 2H), 1.87 – 1.77 (m, 2H), 1.71 – 1.59 (m, 8H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.4, 152.9, 134.7, 126.0, 124.7, 122.6, 121.6, 43.8, 33.0, 27.0, 26.2, 25.5.

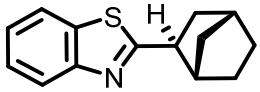
2-Cyclododecylbenzo[d]thiazole (27)[10]



27

Following the Synthesis of alkylation reaction products (General procedure E), the product was purified by column chromatography (PE/EA = 20:1) as a colorless oil (10.2 mg, 17% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.0 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 8.2 Hz, 1H), 3.40 – 3.35 (m, 1H), 1.98 – 1.92 (m, 2H), 1.83 – 1.77 (m, 2H), 1.52 – 1.35 (m, 18H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 178.3, 153.1, 134.8, 125.9, 124.6, 122.7, 121.6, 40.2, 31.1, 23.9, 23.7, 23.5,22.9, 22.8.

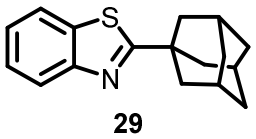
2-((1S,2S,4R)-Bicyclo[2.2.1]heptan-2-yl)benzo[d]thiazole (28)[11]



28

Following the Synthesis of alkylation reaction products (General procedure F), the product was purified by column chromatography (PE/EA = 20:1) as a colorless oil (24.3 mg, 53% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 3.24 – 3.15 (m, 1H), 2.64 (s, 1H), 2.43 (s, 1H), 2.17 – 2.08 (m, 1H), 1.94 – 1.83 (m, 1H), 1.71 – 1.57 (m, 3H), 1.50 – 1.40 (m, 1H), 1.34 – 1.24 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.8, 153.3, 135.0, 125.9, 124.6, 122.7, 121.6, 47.3, 44.5, 38.5, 36.7, 36.6, 29.9, 28.9.

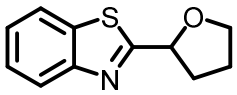
2-((3r,5r,7r)-Adamantan-1-yl)benzo[d]thiazole (29)[10]



29

Following the Synthesis of alkylation reaction products (General procedure F), the product was purified by column chromatography (PE/EA = 20:1) as a yellow soild (9.7 mg, 18% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 2.17 – 2.13 (m, 9H), 1.82 (t, *J* = 3.0 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 182.4, 153.3, 134.5, 125.8, 124.6, 122.8, 121.7, 43.1, 40.3, 36.7, 28.7.

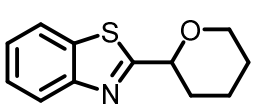
2-(Tetrahydrofuran-2-yl)benzo[d]thiazole (30)[12]



30

Following the Synthesis of alkylation reaction products (General procedure D), the product was purified by column chromatography (PE/EA = 10:1) as a colorless oil (31.4 mg, 82% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.0 Hz, 1H), 7.87 (d, *J* = 7.0 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 1H), 5.37 – 5.33 (m, 1H), 4.17 – 4.13 (m, 1H), 4.02 – 3.98 (m, 1H), 2.60 – 2.43 (m, 1H), 2.32 – 2.21 (m, 1H), 2.09 – 1.89 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.4, 153.8, 134.8, 126.0, 124.9, 122.9, 121.9, 78.8, 69.5, 33.4, 25.8.

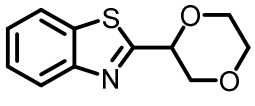
2-(Tetrahydro-2H-pyran-2-yl)benzo[d]thiazole (31)[13]



31

Following the Synthesis of alkylation reaction products (General procedure D), the product was purified by column chromatography (PE/EA = 10:1) as a light yellow oil (39.5 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 4.84 – 4.74 (m, 1H), 4.23 – 4.15 (m, 1H), 3.74 – 3.64 (m, 1H), 2.31 – 2.23 (m, 1H), 2.02 – 1.93 (m, 1H), 1.80 – 1.60 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.0, 153.1, 134.8, 126.0, 124.9, 123.0, 121.9, 78.0, 69.1, 32.6, 25.7, 23.1.

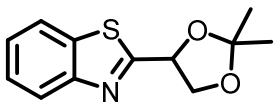
2-(1,4-Dioxan-2-yl)benzo[d]thiazole (32)[12]



32

Following the Synthesis of alkylation reaction products (General procedure D), the product was purified by column chromatography (PE/EA = 10:1) as a colorless oil (32.3 mg, 73% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.41 – 7.35 (m, 1H), 5.05 (dd, *J* = 9.7, 3.1 Hz, 1H), 4.30 (dd, *J* = 11.6, 3.1 Hz, 1H), 4.03 – 3.95 (m, 2H), 3.85 – 3.81 (m, 1H), 3.79 – 3.73 (m, 1H), 3.70 (dd, *J* = 11.6, 9.7 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.1, 153.1, 134.7, 126.2, 125.3, 123.2, 121.9, 75.5, 70.6, 67.1, 66.5.

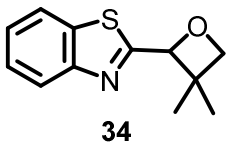
2-(2,2-Dimethyl-1,3-dioxolan-4-yl)benzo[d]thiazole (33)[14]



33

Following the Synthesis of alkylation reaction products (General procedure D), the product was purified by column chromatography (PE/EA = 10:1) as a colorless oil (27.8 mg, 59% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 5.53 – 5.40 (m, 1H), 4.52 (dd, *J* = 8.7, 6.8 Hz, 1H), 4.20 (dd, *J* = 8.7, 5.5 Hz, 1H), 1.61 (s, 3H), 1.50 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.4, 153.6, 134.9, 126.2, 125.2, 123.1, 121.9, 111.4, 76.0, 70.3, 26.5, 25.5.

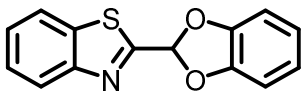
2-(3,3-Dimethyloxetan-2-yl)benzo[d]thiazole (34)



34

Following the Synthesis of alkylation reaction products (General procedure D), the product was purified by column chromatography (PE/EA = 10:1) as a colorless oil (20.2 mg, 46% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 5.77 (s, 1H), 4.58 (d, *J* = 5.6 Hz, 1H), 4.52 (d, *J* = 5.6 Hz, 1H), 1.55 (s, 3H), 1.02 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.4, 154.0, 134.7, 126.2, 124.9, 123.1, 122.0, 89.7, 82.8, 41.2, 27.2, 22.2. **HRMS (ESI)** Calcd for $[C_{12}H_{14}NS]^+$: 220.0791; found 220.0787.

2-(Benzo[d][1,3]dioxol-2-yl)benzo[d]thiazole (35)

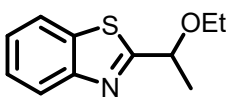


35

Following the Synthesis of alkylation reaction products (General procedure D), the product was purified by column chromatography (PE/EA = 10:1) as a colorless oil (24.5 mg, 48% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.30 (s, 1H), 6.99 – 6.87 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.1, 153.1, 146.7, 135.1, 126.7, 126.4, 124.3, 122.6, 122.2, 109.4, 105.8. **HRMS (ESI)** Calcd for

$[C_{14}H_{10}NO_2S]^+$: 256.0427; found 256.0422.

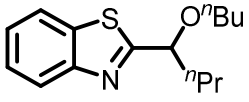
2-(1-Ethoxyethyl)benzo[d]thiazole (36)[15]



36

Following the Synthesis of alkylation reaction products (General procedure D), the product was purified by column chromatography (PE/EA = 10:1) as a colorless oil (17.8 mg, 43% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 4.91 – 4.82 (m, 1H), 3.66 – 3.58 (m, 2H), 1.64 (d, *J* = 6.6 Hz, 3H), 1.27 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.9, 153.2, 135.0, 126.1, 125.2, 123.0, 122.0, 76.2, 65.6, 22.9, 15.5.

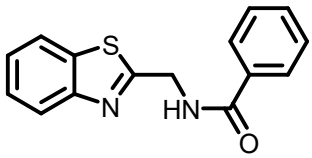
2-(1-Butoxybutyl)benzo[d]thiazole (37)[12]



37

Following the Synthesis of alkylation reaction products (General procedure D), the product was purified by column chromatography (PE/EA = 10:1) as a colorless oil (18.4 mg, 35% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 4.68 (dd, *J* = 8.0, 5.2 Hz, 1H), 3.61 – 3.46 (m, 2H), 1.98 – 1.82 (m, 2H), 1.63 – 1.37 (m, 6H), 0.98 – 0.88 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.7, 153.2, 135.1, 126.0, 125.0, 123.0, 122.0, 80.3, 70.5, 39.5, 32.1, 19.4, 18.8, 14.0, 13.9.

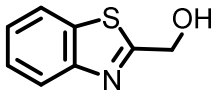
N-(benzo[d]thiazol-2-ylmethyl)benzamide (38)[16]



38

Following the Synthesis of alkylation reaction products (General procedure D), the product was purified by column chromatography (PE/EA = 10:1) as a colorless oil (20.4 mg, 38% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.20 – 7.08 (m, 5H), 3.22 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.8, 155.9, 151.9, 143.9, 140.4, 129.5, 127.3, 125.7, 124.1, 122.6, 121.4, 111.6, 110.1, 110.0, 39.9.

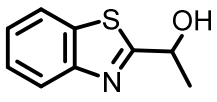
Benzo[d]thiazol-2-ylmethanol (39)[12]



39

Following the Synthesis of alkylation reaction products (General procedure D), the product was purified by column chromatography (PE/EA = 10:1) as a colorless oil (27.4mg, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 5.05 (s, 2H), 4.80 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.6, 152.7, 134.6, 126.3, 125.2, 122.7,121.9, 62.4.

1-(Benzo[d]thiazol-2-yl)ethan-1-ol (40)[12]

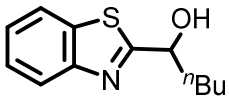


40

Following the Synthesis of alkylation reaction products (General procedure D), the product was purified by column chromatography (PE/EA = 10:1) as a colorless oil (17.9mg, 50% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 5.26 (q, *J* = 6.5 Hz, 1H), 3.51 (s, 1H), 1.71 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.1,

152.9, 135.0, 126.3, 125.2, 123.0, 122.0, 68.7, 24.2.

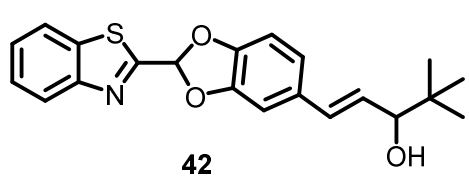
1-(Benzo[d]thiazol-2-yl)pentan-1-ol (41)[12]



41

Following the Synthesis of alkylation reaction products (General procedure D), the product was purified by column chromatography (PE/EA = 10:1) as a colorless oil (9.3mg, 21% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 5.15 – 5.03 (m, 1H), 3.38 (s, 1H), 2.06 – 1.88 (m, 2H), 1.55 – 1.42 (m, 2H), 1.41 – 1.33 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.7, 152.8, 134.9, 126.2, 125.1, 122.9, 122.0, 72.5, 38.0, 27.4, 22.6, 14.1.

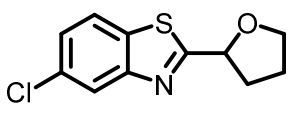
(E)-1-(2-(benzo[d]thiazol-2-yl)benzo[d][1,3]dioxol-5-yl)-4,4-dimethylpent-1-en-3-ol (42)



42

Following the Synthesis of alkylation reaction products (General procedure D), the product was purified by column chromatography (PE/EA = 2:1) as a white solid (52.2 mg, 71% yield), mp: 52-54 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.31 (s, 1H), 7.06 – 7.02 (m, 1H), 6.89 (q, *J* = 8.1 Hz, 2H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.16 (dd, *J* = 15.8, 7.2 Hz, 1H), 3.90 (d, *J* = 7.2 Hz, 1H), 1.66 (s, 1H), 0.96 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 153.1, 147.2, 146.3, 135.0, 132.4, 131.3, 128.7, 126.7, 126.4, 124.3, 122.2, 121.8, 109.0, 106.5, 106.2, 81.0, 35.5, 25.9. **HRMS (ESI)** Calcd for $[C_{21}H_{22}NO_3S]^+$: 368.1315; found 368.1318.

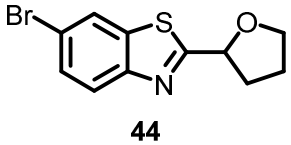
5-Chloro-2-(tetrahydrofuran-2-yl)benzo[d]thiazole (43)[17]



43

Following the Synthesis of alkylation reaction products (General procedure D), the product was purified by column chromatography (PE/EA = 10:1) as a light yellow oil (40.8 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 1.5 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.33 (dd, *J* = 8.5, 1.8 Hz, 1H), 5.33 (dd, *J* = 7.6, 5.5 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 1H), 4.00 (q, *J* = 7.2 Hz, 1H), 2.57 – 2.47 (m, 1H), 2.30 – 2.21 (m, 1H), 2.08 – 1.99 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.7, 154.7, 133.2, 132.0, 125.3, 122.8, 122.6, 78.8, 69.6, 33.5, 25.8.

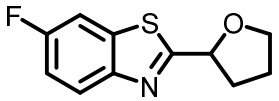
6-Bromo-2-(tetrahydrofuran-2-yl)benzo[d]thiazole (44)[17]



44

Following the Synthesis of alkylation reaction products (General procedure D), the product was purified by column chromatography (PE/EA = 10:1) as a light yellow oil (38.1 mg, 67% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 1.5 Hz, 1H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.60 – 7.50 (m, 1H), 5.31 (dd, *J* = 7.5, 5.6 Hz, 1H), 4.15 (q, *J* = 7.0 Hz, 1H), 4.00 (q, *J* = 7.3 Hz, 1H), 2.57 – 2.47 (m, 1H), 2.30 – 2.21 (m, 1H), 2.08 – 1.99 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.2, 152.7, 136.6, 129.5, 124.5, 124.0, 118.5, 78.7, 69.6, 33.4, 25.8.

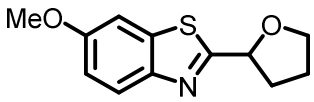
6-Fluoro-2-(tetrahydrofuran-2-yl)benzo[d]thiazole (45)[18]



45

Following the Synthesis of alkylation reaction products (General procedure D), the product was purified by column chromatography (PE/EA = 10:1) as a yellow oil (37.9 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 1H), 7.56 – 7.51 (m, 1H), 7.21 – 7.14 (m, 1H), 5.33 – 5.27 (m, 1H), 4.13 (q, *J* = 6.8 Hz, 1H), 3.98 (q, *J* = 7.2 Hz, 1H), 2.54 – 2.45 (m, 1H), 2.28 – 2.20 (m, 1H), 2.05 – 1.98 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.1 (d, *J* = 3.2 Hz), 160.2 (d, *J* = 245.0 Hz), 150.3, 135.8 (d, *J* = 11.1 Hz), 123.7 (d, *J* = 9.4 Hz), 114.5 (d, *J* = 24.8 Hz), 107.9 (d, *J* = 26.6 Hz), 78.6, 69.5, 33.3, 25.7. **^{19}F NMR (564 MHz, $CDCl_3$)** δ -116.27.

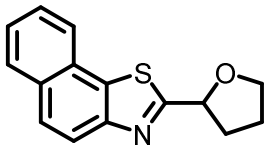
6-Methoxy-2-(tetrahydrofuran-2-yl)benzo[d]thiazole (46)[17]



46

Following the Synthesis of alkylation reaction products (General procedure D), the product was purified by column chromatography (PE/EA = 10:1) as a yellow oil (34.8 mg, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.9 Hz, 1H), 7.32 (d, *J* = 2.4 Hz, 1H), 7.04 (dd, *J* = 8.9, 2.5 Hz, 1H), 5.29 (dd, *J* = 7.6, 5.5 Hz, 1H), 4.12 (q, *J* = 6.7 Hz, 1H), 3.97 (q, *J* = 7.2 Hz, 1H), 3.85 (s, 3H), 2.52 – 2.43 (m, 1H), 2.29 – 2.21 (m, 1H), 2.06 – 1.98 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.6, 157.5, 148.1, 136.1, 123.3, 115.3, 104.4, 78.7, 69.4, 55.9, 33.4, 25.8.

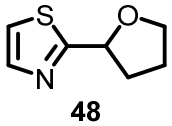
2-(Tetrahydrofuran-2-yl)naphtho[2,1-d]thiazole (47)



47

Following the Synthesis of alkylation reaction products (General procedure D), the product was purified by column chromatography (PE/EA = 10:1) as a yellow oil (27.0 mg, 53% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.67 – 7.62 (m, 1H), 7.58 – 7.53 (m, 1H), 5.47 (dd, *J* = 7.7, 5.2 Hz, 1H), 4.22 – 4.16 (m, 1H), 4.05 – 3.99 (m, 1H), 2.61 – 2.52 (m, 1H), 2.41 – 2.33 (m, 1H), 2.10 – 2.00 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.1, 149.9, 131.9, 131.4, 128.6, 128.1, 126.8, 125.9, 125.4, 123.7, 119.2, 79.0, 69.4, 33.6, 25.7. **HRMS (ESI)** Calcd for $[C_{15}H_{14}NS]^+$: 256.0791; found 256.0787.

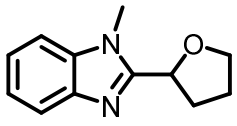
2-(Tetrahydrofuran-2-yl)thiazole (48)[18]



48

Following the Synthesis of alkylation reaction products (General procedure D), the product was purified by column chromatography (PE/EA = 10:1) as a colorless oil (12.4 mg, 40% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 3.1 Hz, 1H), 7.26 (d, *J* = 3.3 Hz, 1H), 5.26 (dd, *J* = 7.6, 5.5 Hz, 1H), 4.14 – 4.07 (m, 1H), 3.99 – 3.92 (m, 1H), 2.49 – 2.40 (m, 1H), 2.22 – 2.14 (m, 1H), 2.04 – 1.97 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.9, 142.8, 118.7, 78.6, 69.2, 33.4, 25.7.

1-Methyl-2-(tetrahydrofuran-2-yl)-1H-benzo[d]imidazole (49)[19]

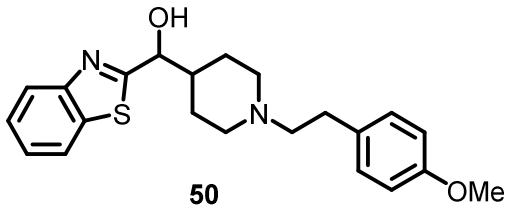


49

Following the Synthesis of alkylation reaction products (General procedure D), the product was purified by column chromatography (PE/EA = 10:1) as a white solid (12.1 mg, 30% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ δ 7.72 (d, *J* = 6.6 Hz, 1H), 7.32 – 7.20 (m, 3H), 5.17 (t, *J* = 6.9 Hz, 1H), 3.89 (t, *J* = 6.8 Hz, 2H), 3.82 (s, 3H), 2.78 – 2.70 (m, 1H), 2.36 – 2.28

(m, 1H), 2.18 – 2.11 (m, 1H), 2.05 – 1.97 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.6, 136.4, 123.1, 122.5, 119.8, 109.4, 77.3, 73.7, 69.0, 30.5, 29.6, 26.2.

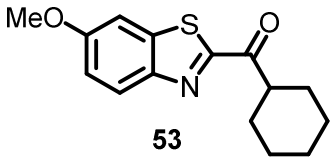
Benzo[d]thiazol-2-yl(1-(4-methoxyphenethyl)piperidin-4-yl)methanol (50)



50

The product was purified by column chromatography (DCM/MeOH = 5:1) as a white solid (36.7 mg, 48%), mp: 146-148 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.47 (*J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.73 (d, *J* = 8.7 Hz, 2H), 3.87 (dd, *J* = 11.3, 3.2 Hz, 1H), 3.84 – 3.74 (m, 1H), 3.73 (s, 3H), 3.50 – 3.40 (m, 1H), 3.11 (br, 1H), 2.84 – 2.81 (m, 2H), 2.79 – 2.65 (m, 2H), 2.50 – 2.36 (m, 2H), 2.36 – 2.25 (m, 2H), 2.13 – 2.03 (m, 1H), 1.82 – 1.67 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.7, 157.8, 152.4, 135.0, 131.7, 129.6, 125.9, 125.1, 122.9, 121.9, 113.7, 65.1, 57.9, 55.2, 51.5, 48.1, 34.5, 32.2, 29.7, 25.2. **HRMS (ESI)** Calcd for $[C_{22}H_{27}N_2O_2S]^+$: 383.1788; found 383.1784.

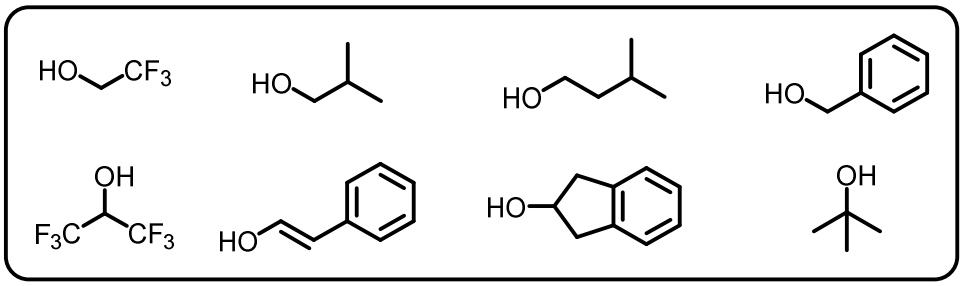
Cyclohexyl(6-methoxybenzo[d]thiazol-2-yl)methanone (53)



53

Following the Synthesis of products from hydroxyl alkylation reaction (General procedure B, the reaction time is 6 hours), the product was purified by column chromatography (PE/EA = 10:1) as a white solid (37.4 mg, 68%), mp: 49.5-51 °C. **^{1}H NMR** (600MHz, $CDCl_3$) δ 8.02 (d, *J* = 9.1 Hz, 1H), 7.33 (d, *J* = 2.6 Hz, 1H), 7.13 (dd, *J* = 9.0, 2.6 Hz, 1H), 3.87 (br, 3H), 3.87 – 3.68 (m, 1H), 2.06 – 1.97 (m, 2H), 1.87 – 1.80 (m, 2H), 1.73 (d, *J* = 13.1 Hz, 1H), 1.56 – 1.39 (m, 4H), 1.33 – 1.24 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.2, 163.8, 159.6, 148.2, 139.3, 126.0, 117.4, 103.6, 55.8, 45.7, 28.9, 25.9, 25.6. **HRMS (ESI)** Calcd for $[C_{15}H_{18}NO_2S]^+$: 276.1053; found 276.1055.

3.2 Unsuccessful substrates



4. Synthetic applications

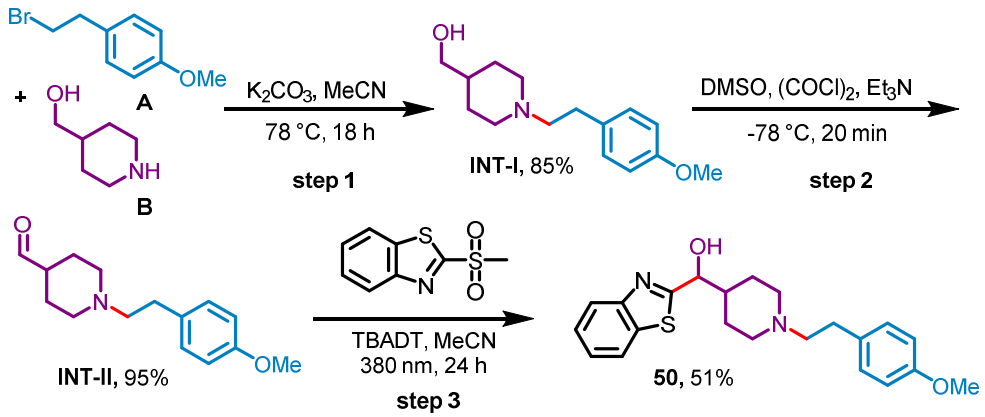
4.1 Synthesis of 3 in gram scale

To a 100 mL reaction flask equipped with a magnetic stir bar was charged with cyclohexane carboxaldehyde (7 mmol, 1.0 equiv), TBADT (0.21 mmol, 3 mol%), deionized water (15 mL) and

cyclohexane carboxaldehyde (70 mmol, 10.0 equiv). Then, the reaction mixture was irradiated under 380 LED strips (10W) for 24 h at room temperature with stirring. After the reaction was complete, the reaction was quenched with saturated sodium bicarbonate solution and extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was subjected to flash column chromatography on silica gel eluting with ethyl acetate/petroleum ether to give product **3** as a a yellow solid with 1.33 g (77%).

Figure S3. Reaction setup (7 mmol scale)

4.2 Synthesis of antihistaminic 50



Step 1. According to the reported literature,[22] a 250 mL Schlenk flask equipped with a magnetic stirrer was charged with 1-(2-bromoethyl)-4-methoxybenzene **A** (2.35 g, 11 mmol, 1.1 equiv), piperidin-4-ylmethanol **B** (1.15 g, 10 mmol) and potassium carbonate (5.52 g, 40 mmol, 4.0 equiv) in acetonitrile (70 mL). The reaction stirred at 78 °C for 18 h, then cooled to room temperature and filtered. The filtrate was washed with water (70 mL), brine (70 mL), and CH_2Cl_2 (70 mL). The organic layers were combined, dried with Na_2SO_4, and concentrated under reduced pressure. The crude residue was subjected to flash column chromatography on silica gel eluting with dichloromethane/methanol to give product **INT-I** (2.12 g, 85% yield) as a yellow solid.

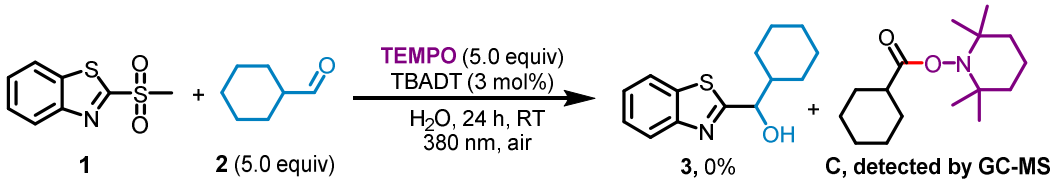
Step 2. According to the reported literature,[23] a solution oxalyl chloride (0.86 mL, 10 mmol, 2.0 equiv) in CH_2Cl_2 (40 mL) was cooled to -78 °C, treated dropwise with DMSO (1.42 mL, 20 mmol, 4.0 equiv), stirred for 20 min, treated with a solution of **INT-I** (1.24 g, 5 mmol) in CH_2Cl_2 (20 mL), and stirred for a further 20 min at -78 °C. The resulting mixture was treated with Et_3N (2.78 mL, 20 mol, 4.0 equiv), stirred at -78 °C for 30 min, warmed to 22 °C, stirred for 1h, and diluted with

water (50 mL). The separated aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phases were dried with Na_2SO_4, and concentrated under reduced pressure. The crude residue was subjected to flash column chromatography on silica gel eluting with dichloromethane/methanol to afford **INT-II** (1.17 g, 95%) as a yellow solid.

Step 3. To a flame-dried 8-mL vial equipped with a magnetic stir bar was charged with the heteroarene (0.2 mmol, 1.0 equiv), TBADT (0.006 mmol, 3 mol%), acetonitrile (0.4 mL), deionized water (0.1 mL) and **INT-II** (2 mmol, 10.0 equiv). Then, the reaction mixture was irradiated under 380 LED strips (10W) for 24 h at room temperature with stirring. After the reaction was complete, the reaction was quenched with saturated sodium bicarbonate solution and extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was subjected to flash column chromatography on silica gel eluting with dichloromethane/methanol to give the target product **50**.

5. Mechanism investigation

5.1 Radical trap experiment



To an 8 mL high glass tube equipped with a magnetic stir bar was charged with the 2-(methylsulfonyl)benzo[d]thiazole (0.2 mmol, 1.0 equiv), TBADT (0.006 mmol, 3 mol%), TEMPO ((1 mmol, 5.0 equiv), deionized water (1 mL) and aldehyde (1 mmol, 5.0 equiv). Then, the reaction mixture was irradiated under 380 LED strips (10W) for 24 h at room temperature with stirring. After the reaction was completed, the reaction was quenched with saturated sodium bicarbonate solution and extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Meanwhile, TEMPO-trapped product was detected by GC-MS, and the formation of **3** was completely suppressed. The crude residue was subjected to flash column chromatography on silica gel eluting with ethyl acetate/petroleum ether to give TEMPO-trapped product **C**.

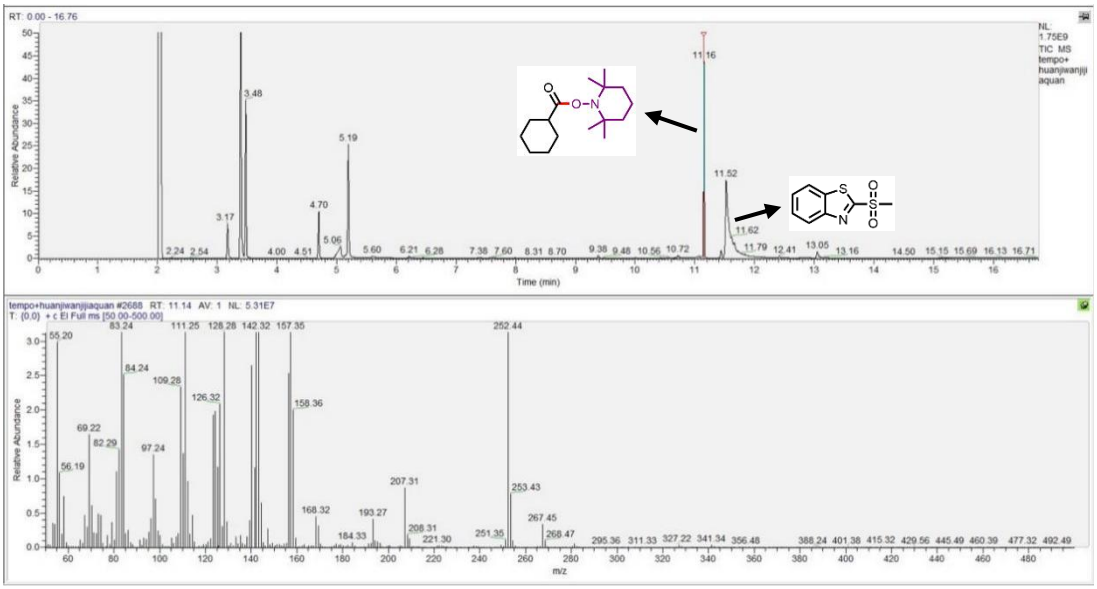
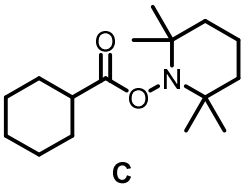


Figure S4. TEMPO-adduct of acyl radical

2,2,6,6-tetramethylpiperidin-1-yl cyclohexanecarboxylate (C)[20]



C

The product was purified by column chromatography (PE/EA = 20:1) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.44 – 2.32 (m, 1H), 1.97 (d, *J* = 12.5 Hz, 2H), 1.86 – 1.60 (m, 6H), 1.59 – 1.46 (m, 4H), 1.44 – 1.22 (m, 4H), 1.16 (s, 6H), 1.04 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.9, 59.6, 42.7, 38.6, 31.6, 29.1, 25.5, 25.3, 20.3, 16.7.

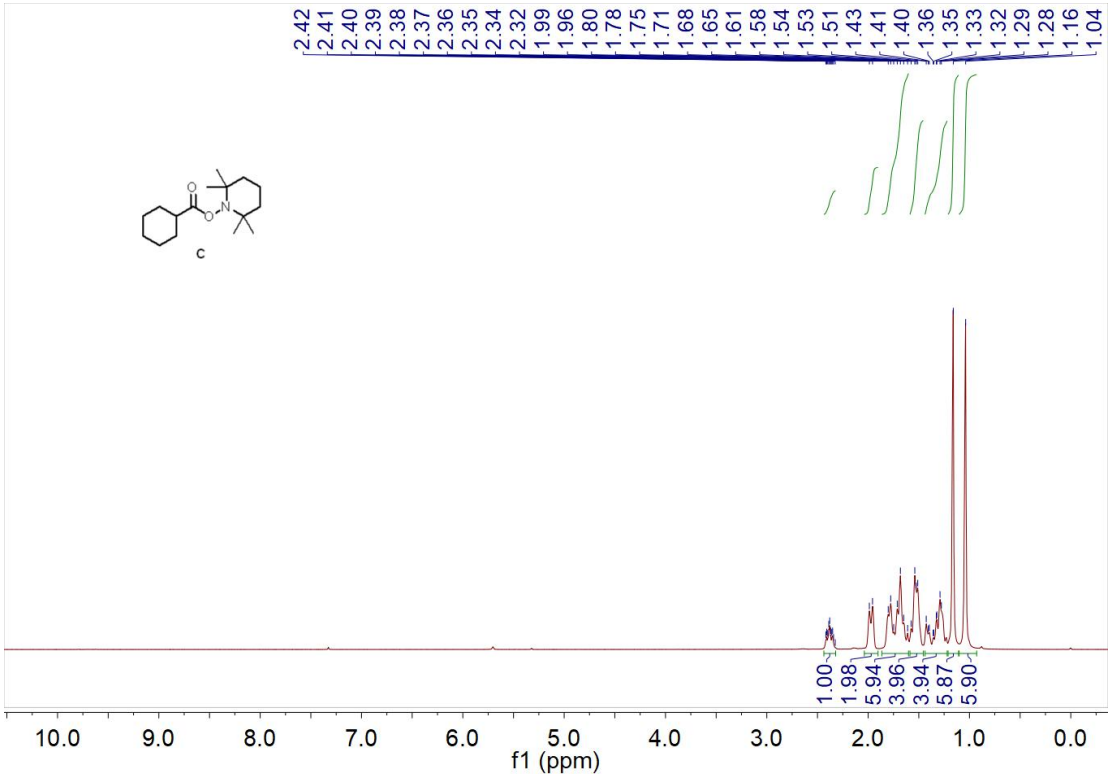


Figure S5. ^{1}H NMR spectrum of C

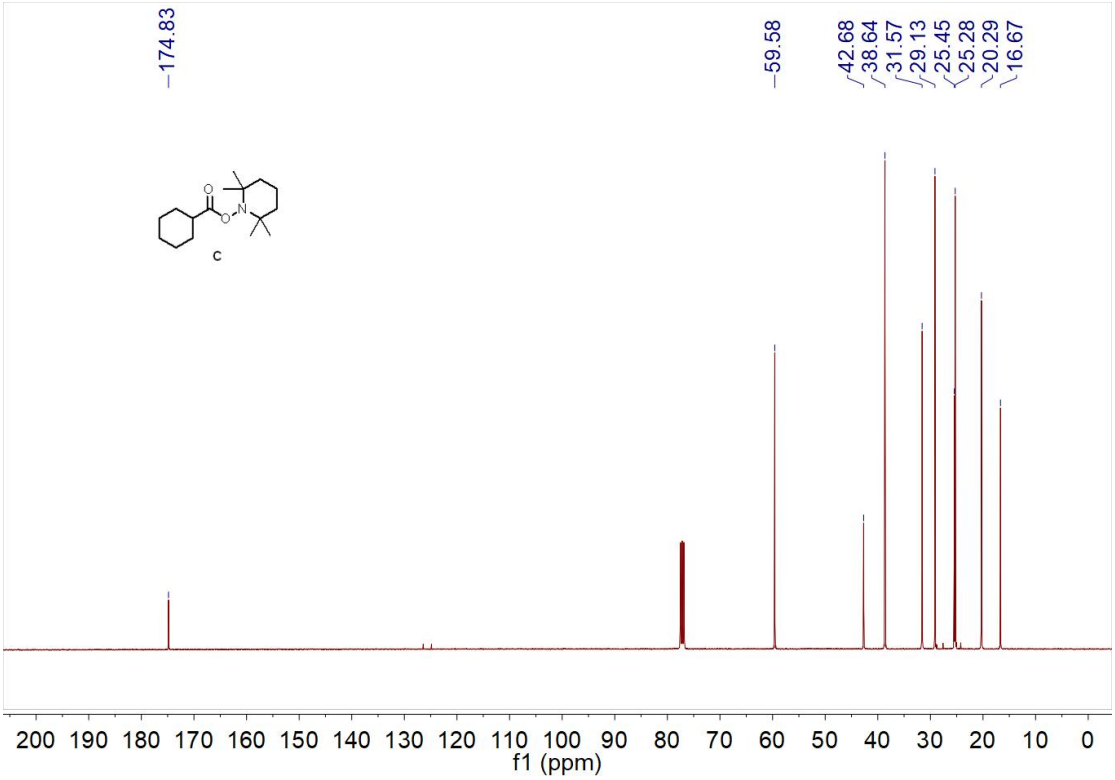
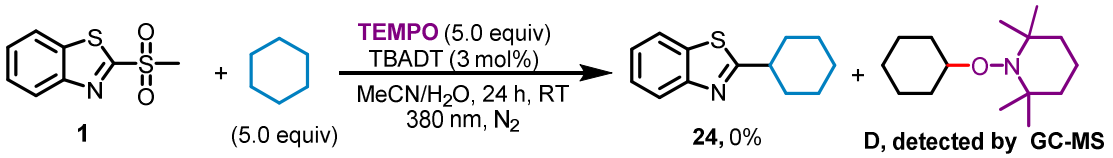


Figure S6. ^{13}C NMR spectrum of C



To a flame-dried 8-mL vial equipped with a magnetic stir bar was charged with the 2-(methylsulfonyl)benzo[d]thiazole (0.2 mmol, 1.0 equiv), TBADT (0.006 mmol, 3 mol%), TEMPO ((1 mmol, 5.0 equiv). Acetonitrile (0.8 mL), deionized water (0.2 mL) and alkanes (1 mmol, 5.0 equiv) are added via a syringe under N_2 atmosphere. Then, the reaction mixture was irradiated under 380 LED strips (10W) for 24 h at room temperature with stirring. After the reaction was completed, the reaction was quenched with saturated sodium bicarbonate solution and extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Meanwhile, TEMPO-trapped product was detected by GC-MS, and the formation of **24** was completely suppressed. The crude residue was subjected to flash column chromatography on silica gel eluting with ethyl acetate/petroleum ether to give TEMPO-trapped product **D**.

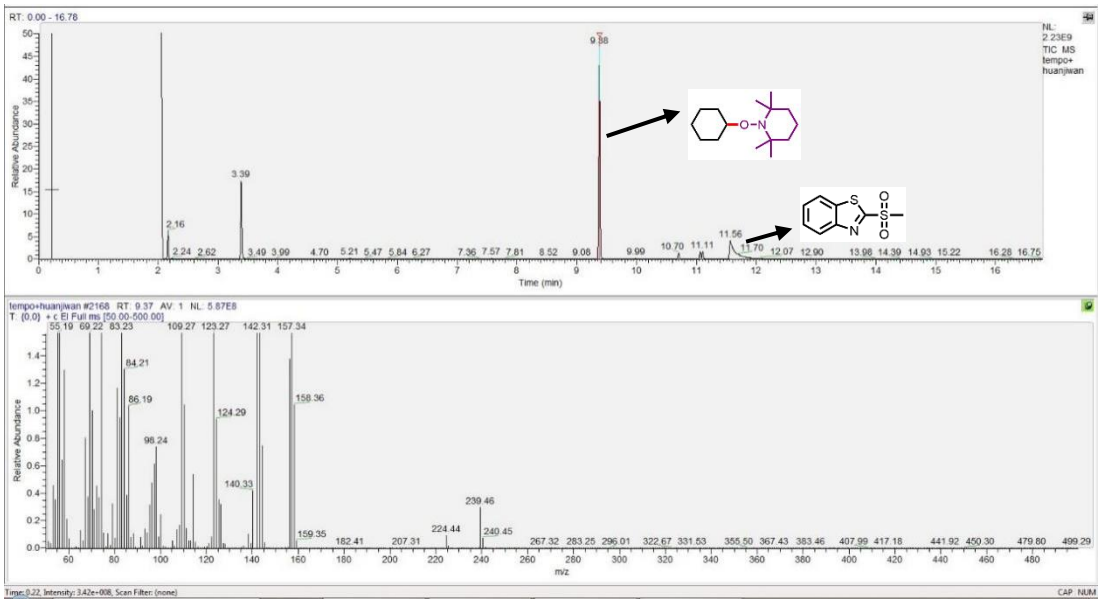
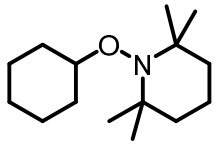


Figure S7. TEMPO-adduct of alkyl radical

1-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine (D)[21]



D

The product was purified by column chromatography (PE) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.44 – 2.32 (m, 1H), 1.97 (d, *J* = 12.5 Hz, 2H), 1.86 – 1.60 (m, 6H), 1.59 – 1.46 (m, 4H), 1.44 – 1.22 (m, 4H), 1.16 (s, 6H), 1.04 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.9, 59.6, 42.7, 38.6, 31.6, 29.1, 25.5, 25.3, 20.3, 16.7.

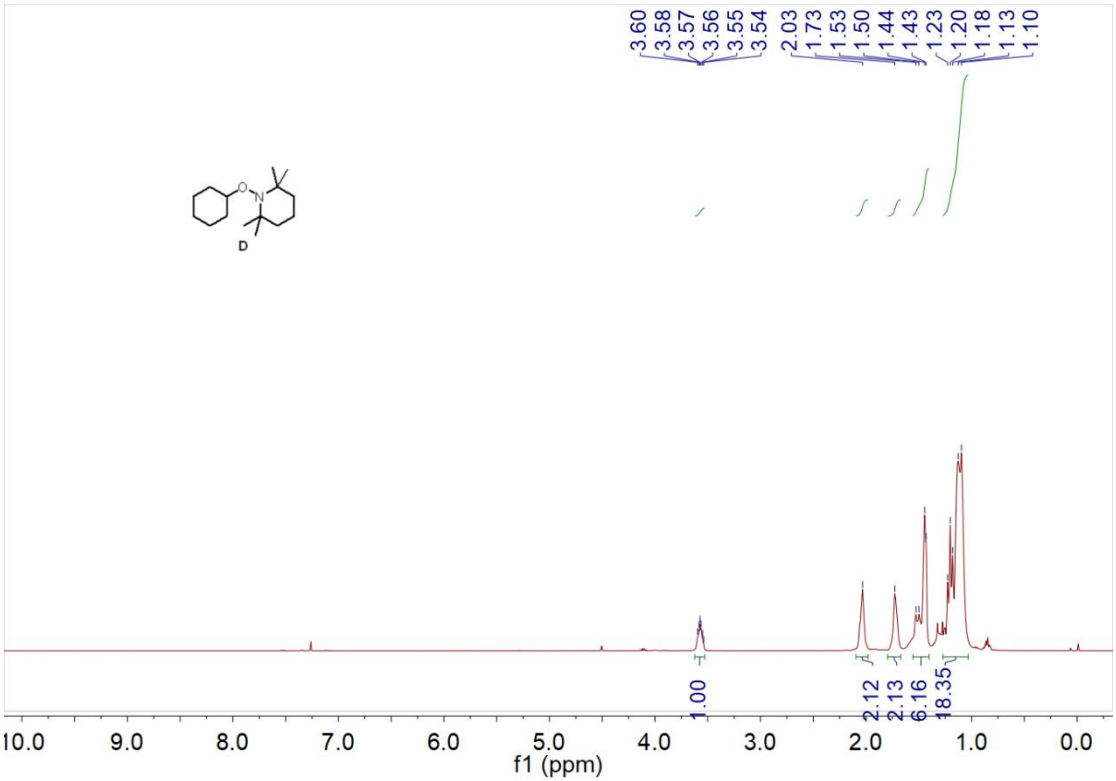


Figure S8. ^{1}H NMR spectrum of D

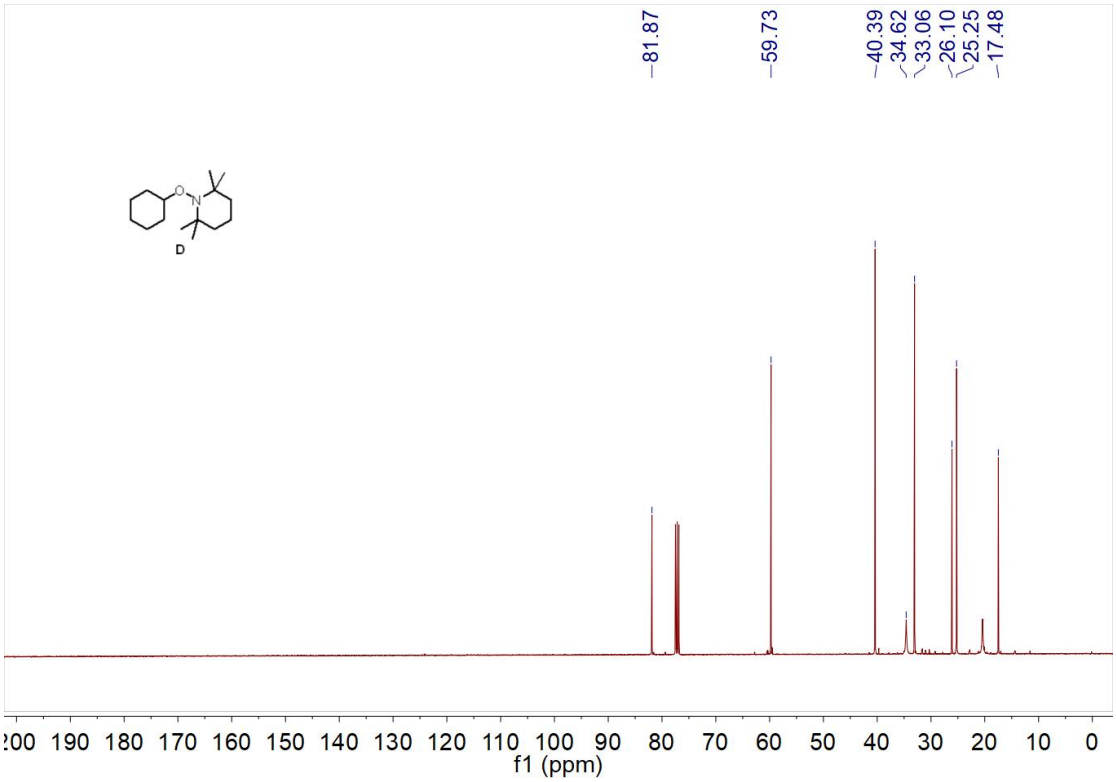
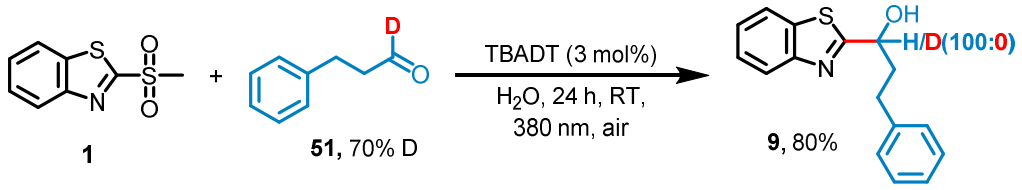


Figure S9. ^{13}C NMR spectrum of D

5.2 Experiments of H/D exchange



To a flame-dried 8-mL vial equipped with a magnetic stir bar was charged with the 2-(methylsulfonyl)benzo[d]thiazole **1** (0.2 mmol, 1.0 equiv), TBADT (0.006 mmol, 3 mol%), deionized water (1 mL) and phenylpropyl aldehyde **51** (2 mmol, 10.0 equiv). Then, the reaction mixture was irradiated under 380 LED strips (10W) for 24 h at room temperature with stirring. After the reaction was complete, the reaction was quenched with saturated sodium bicarbonate solution and extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was subjected to flash column chromatography on silica gel eluting with ethyl acetate/petroleum ether to give the target product. The deuterium incorporation was determined by the analysis of the ^{1}H NMR spectra.

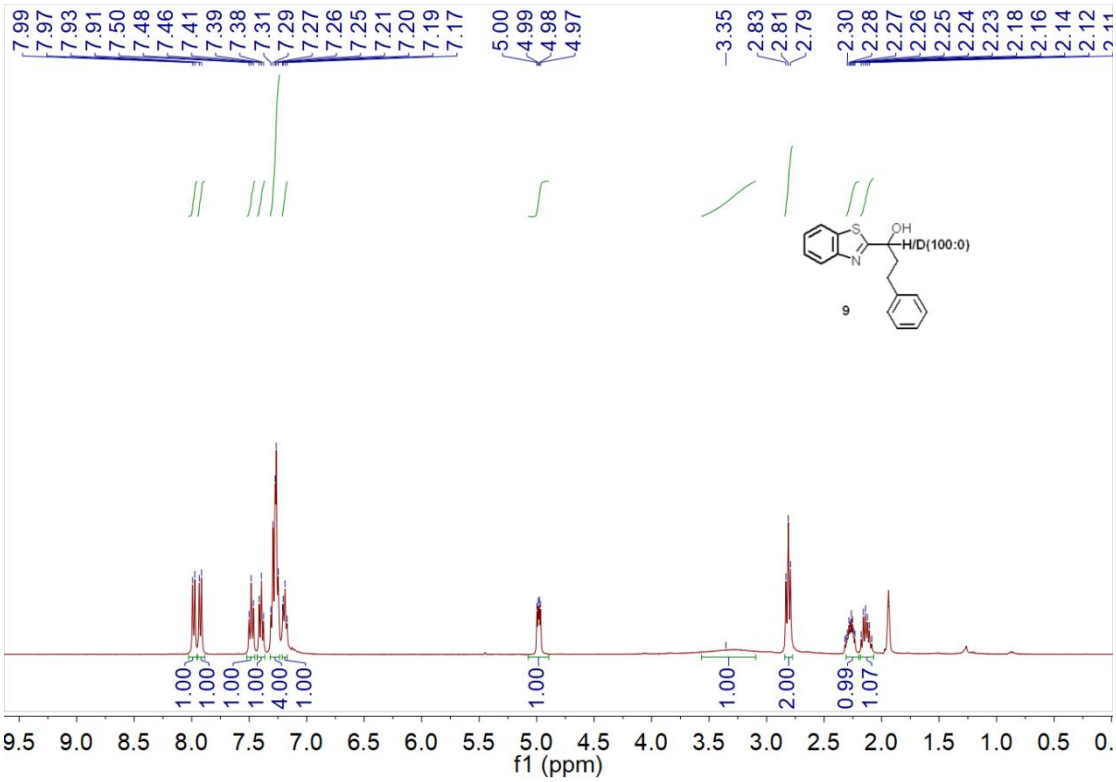
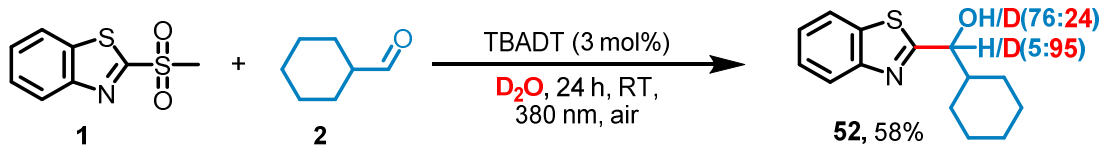


Figure S10. ^{1}H NMR spectrum of 9



To a flame-dried 8-mL vial equipped with a magnetic stir bar was charged with the 2-(methylsulfonyl)benzo[*d*]thiazole **1** (0.2 mmol, 1.0 equiv), TBADT (0.006 mmol, 3 mol%), D_2O (1 mL) and cyclohexanecarboxaldehyde **2** (2 mmol, 10.0 equiv). Then, the reaction mixture was irradiated under 380 LED strips (10W) for 24 h at room temperature with stirring. After the reaction was complete, the reaction was quenched with saturated sodium bicarbonate solution and extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was subjected to flash column chromatography on silica gel eluting with ethyl acetate/petroleum ether to give the target product. The deuterium incorporation was determined by the analysis of the ^{1}H NMR spectra.

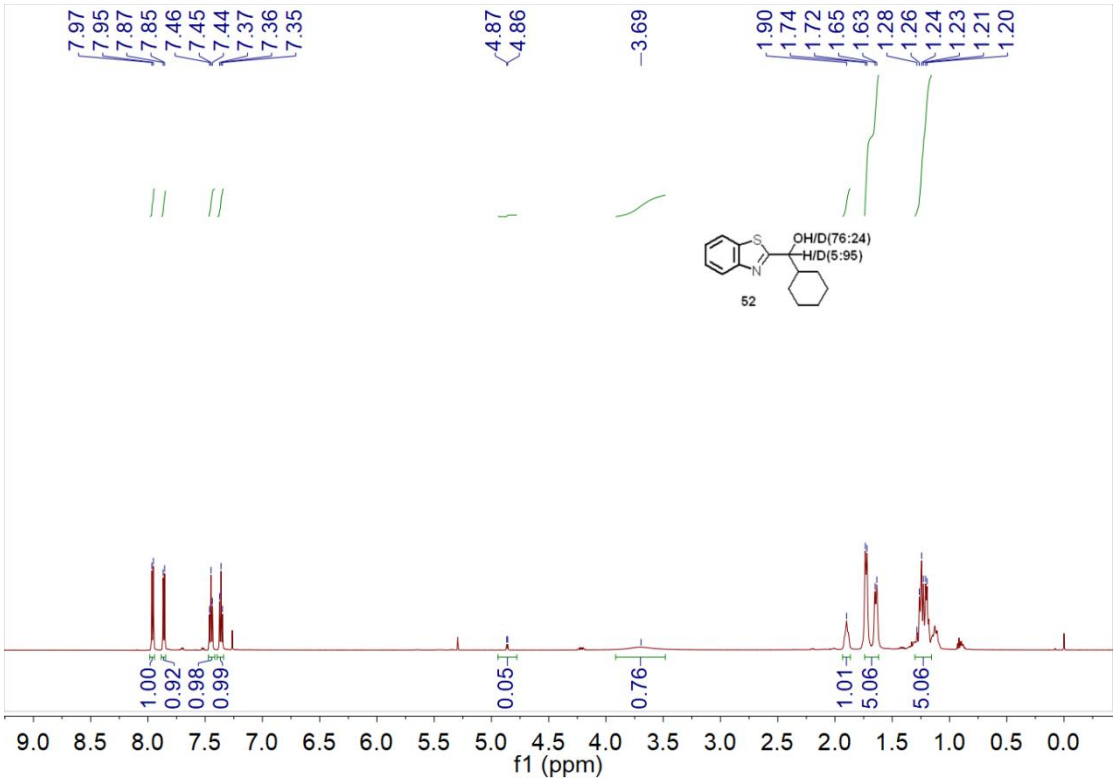
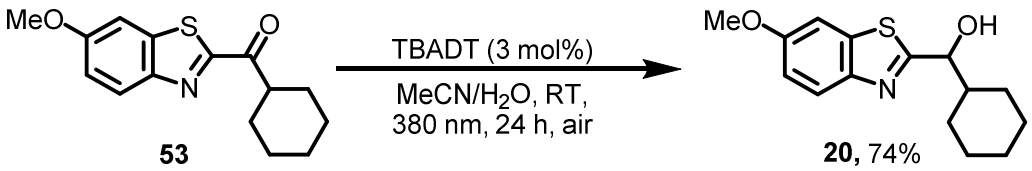
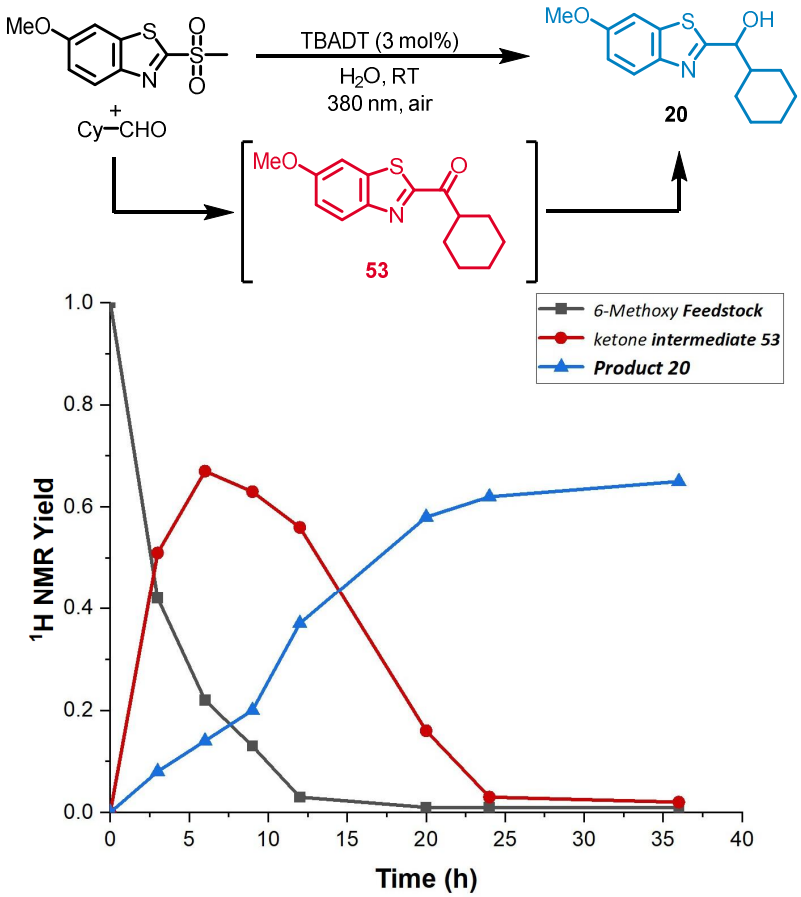


Figure S11. ^{1}H NMR spectrum of 52

5.3 Intermediate experiment



To a flame-dried 8-mL vial equipped with a magnetic stir bar was charged with the intermediate **53** (0.2 mmol, 1.0 equiv) and TBADT (0.006 mmol, 3 mol%), acetonitrile (0.4 mL), deionized water (0.1 mL). Then, the reaction mixture was irradiated under 380 LED strips (10W) for 24 h at room temperature with stirring. After the reaction was complete, the reaction was quenched with saturated sodium bicarbonate solution and extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was subjected to flash column chromatography on silica gel eluting with ethyl acetate/petroleum ether to give the target product in 74% isolated yield.



To a flame-dried 8-mL vial equipped with a magnetic stir bar was charged with the 6-methoxy-2-(methylsulfonyl)benzo[*d*]thiazole (0.2 mmol, 1.0 equiv), TBADT (0.006 mmol, 3 mol%), deionized water (1.0 mL) and cyclohexanecarbaldehyde (2 mmol, 10.0 equiv). Then, the reaction mixture was irradiated under 380 LED strips (10W) for different time (1 h, 3 h, 6 h, 12 h, 16 h, 20 h, 24 h and 36 h) at room temperature with stirring. After the reaction was complete, the reaction was quenched with saturated sodium bicarbonate solution and extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Thioanisole (10 uL, 0.2 mmol) was added to the crude residue as an internal standard, and yield was obtained by ^{1}H NMR. The conversion of 6-methoxy-2-(methylsulfonyl)benzo[d]thiazole and yield of Product **20** and ketone intermediate **53** was determined by ^{1}H NMR.

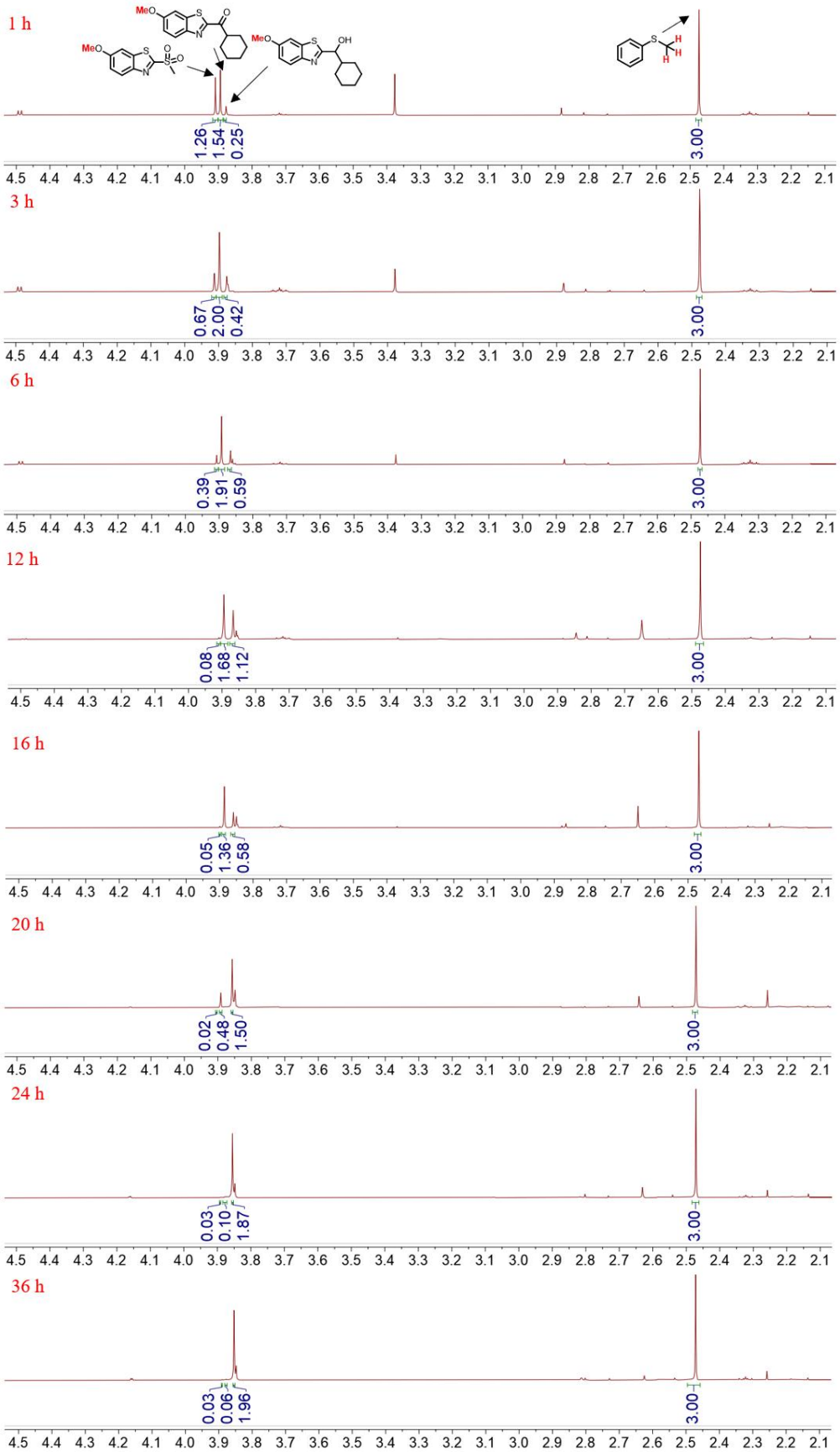


Figure S12. The reaction progress

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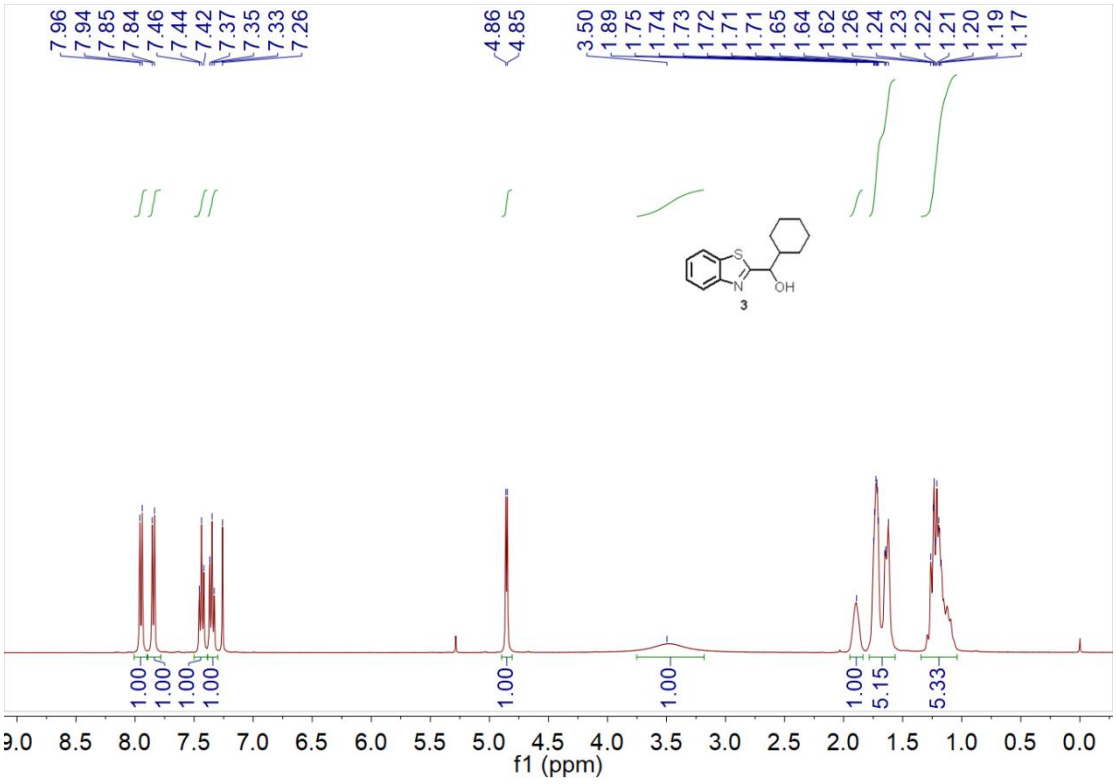
7. NMR Spectra of products



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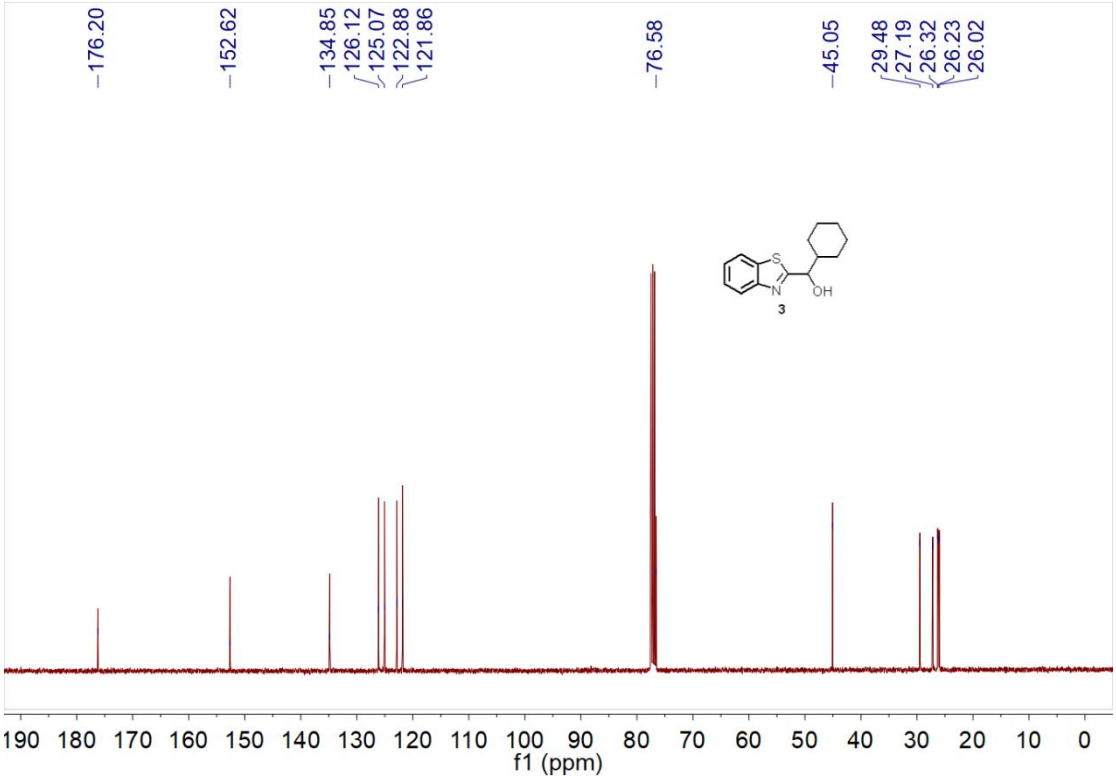

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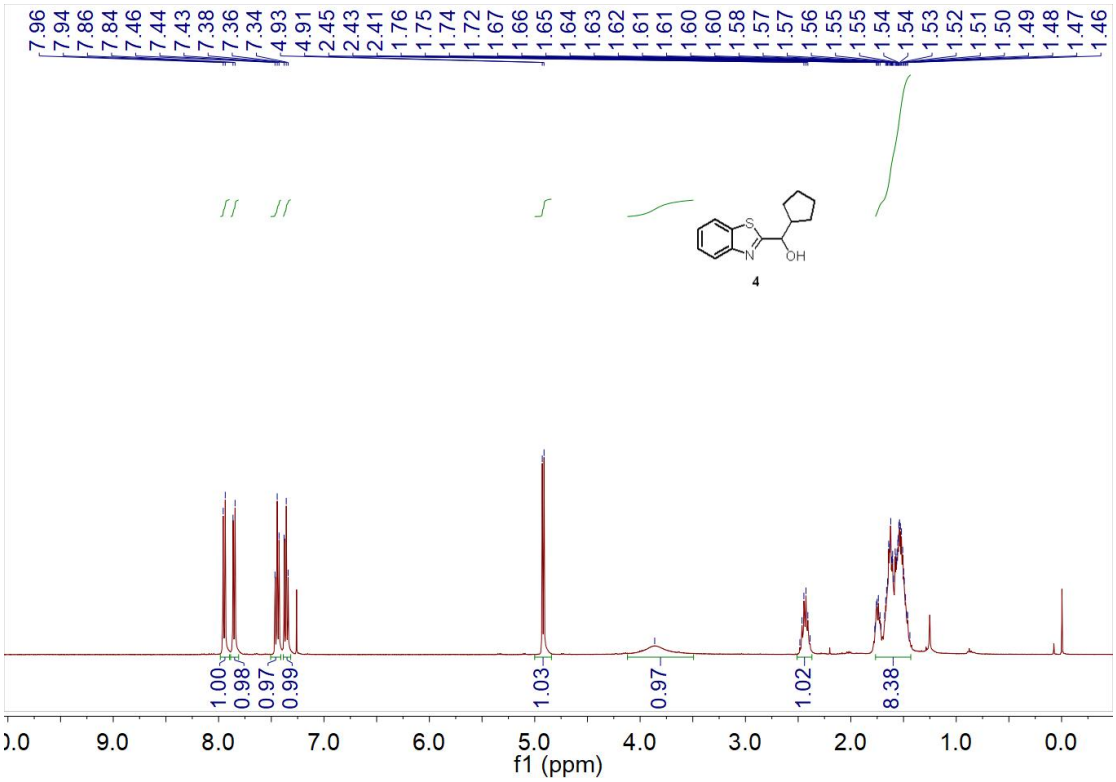

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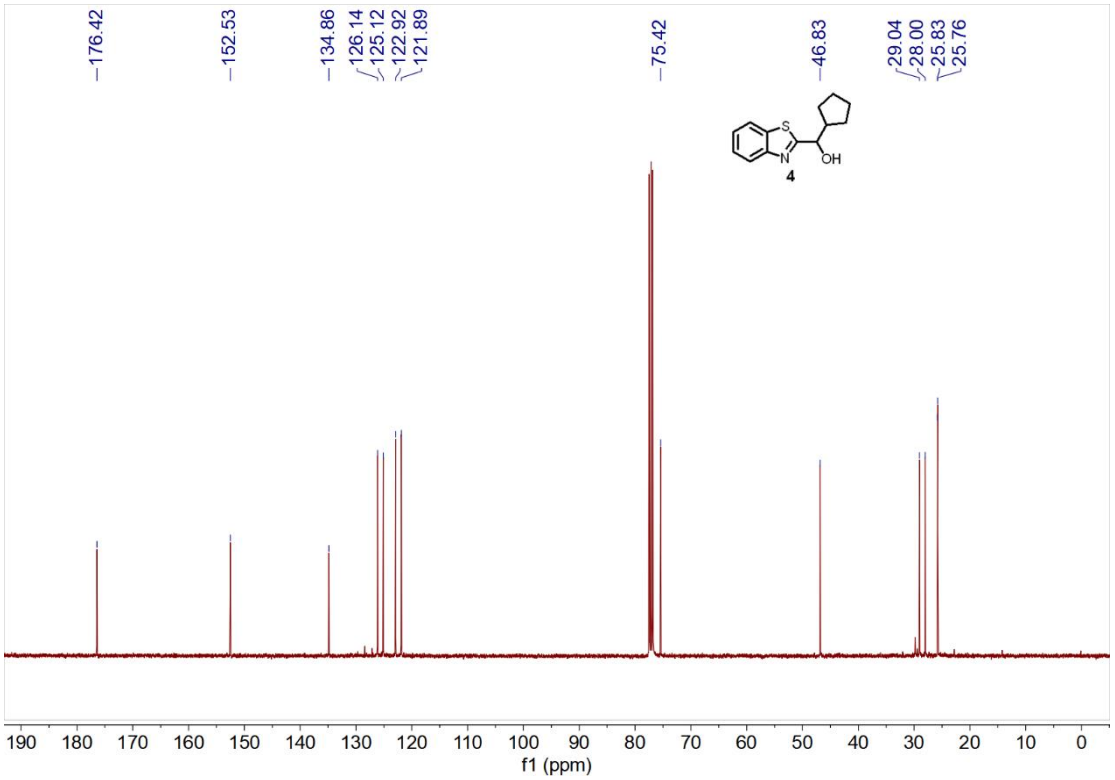

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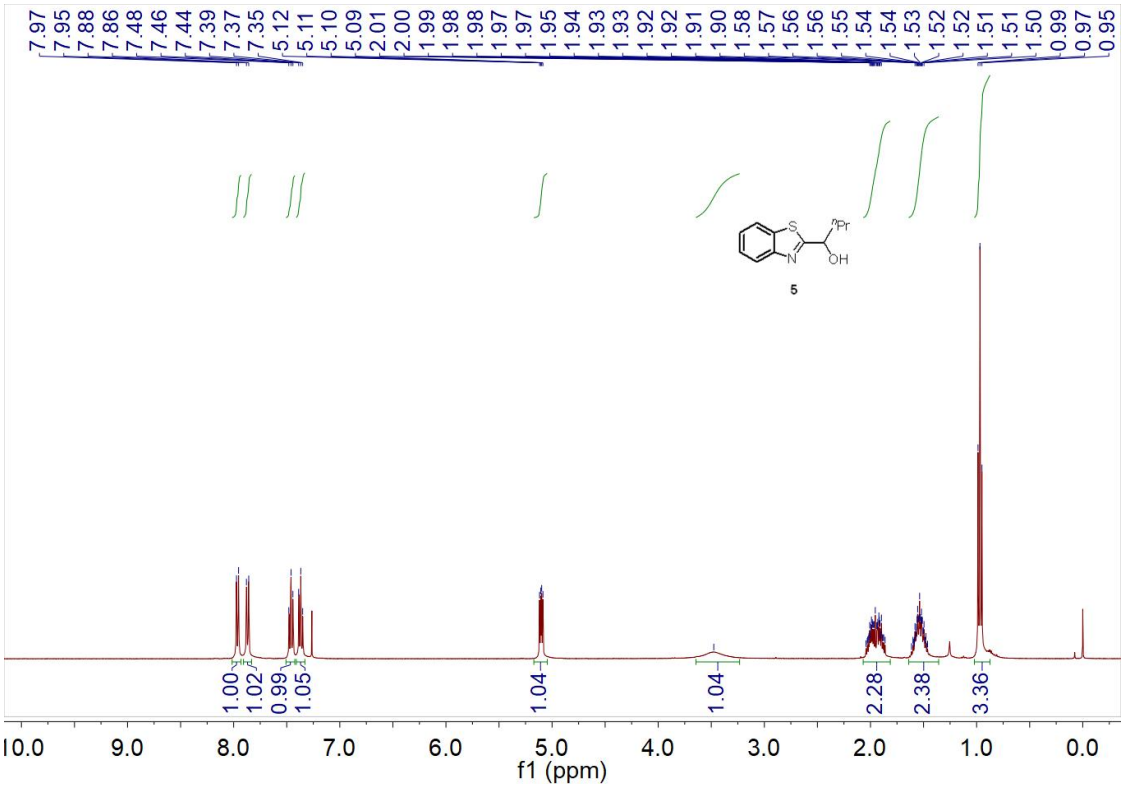

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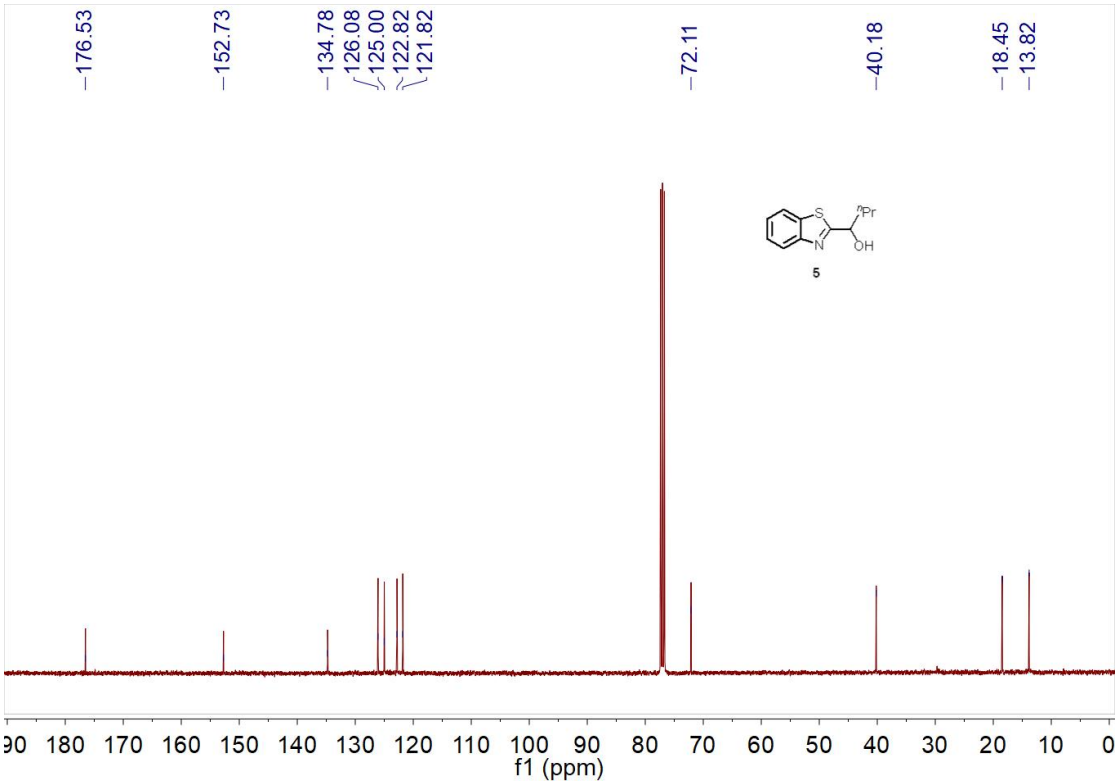

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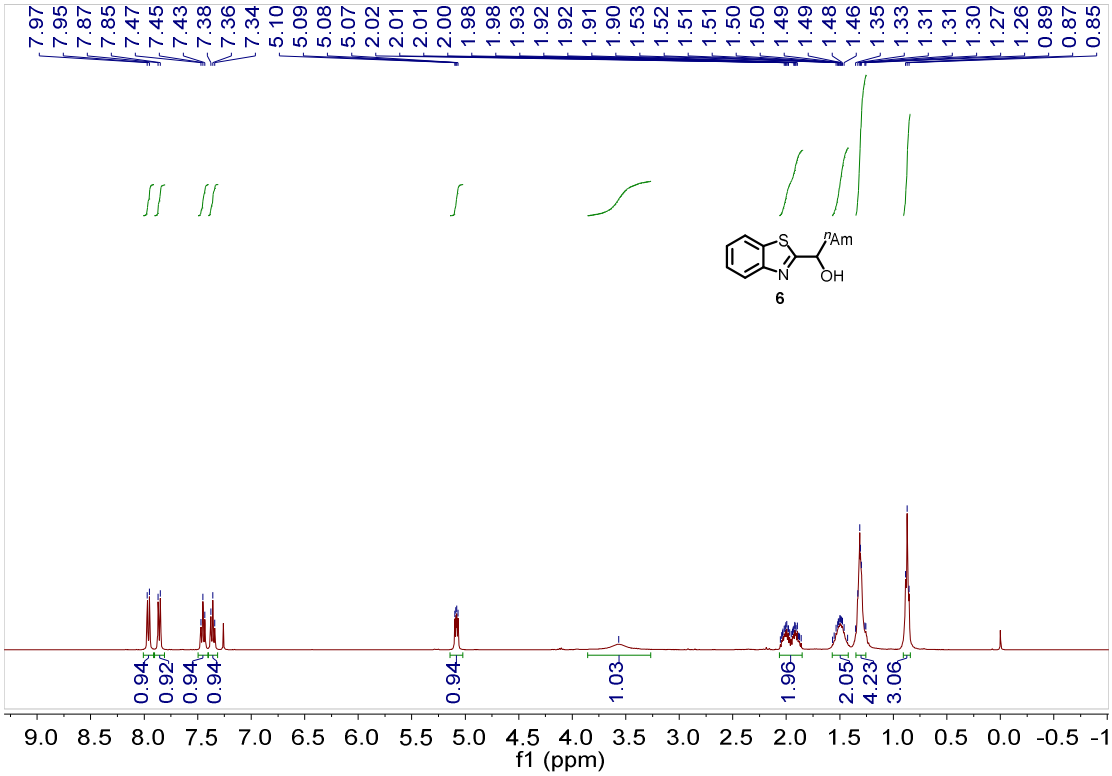

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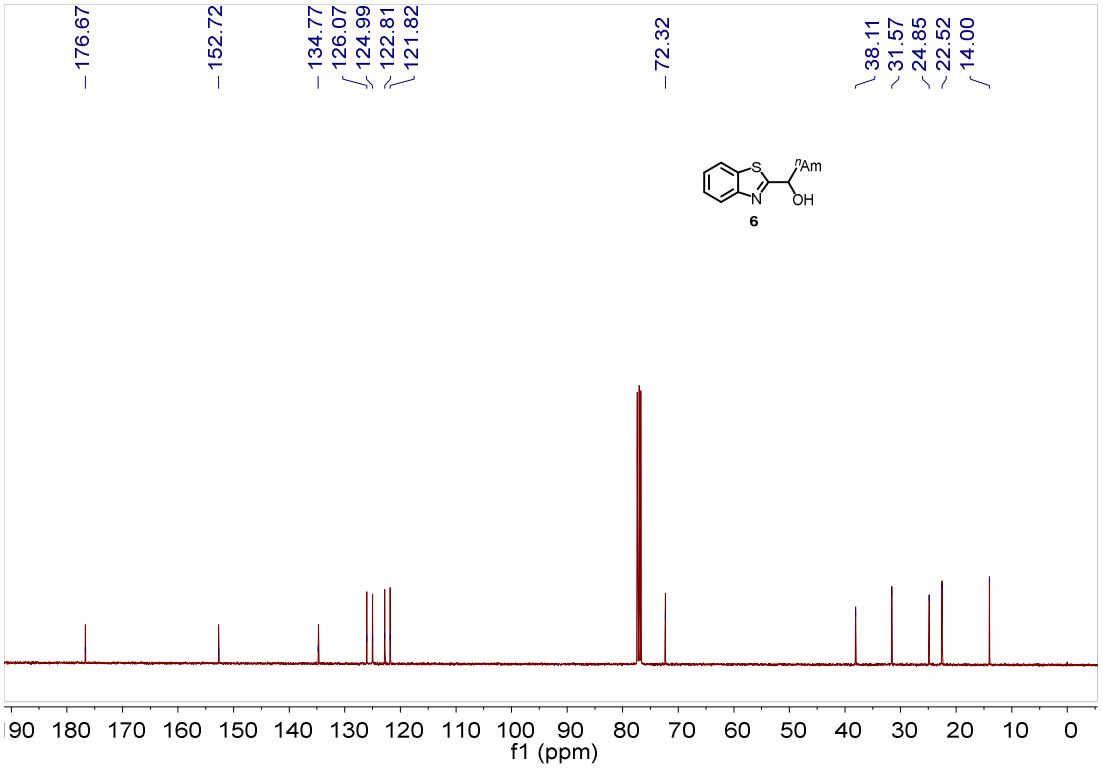

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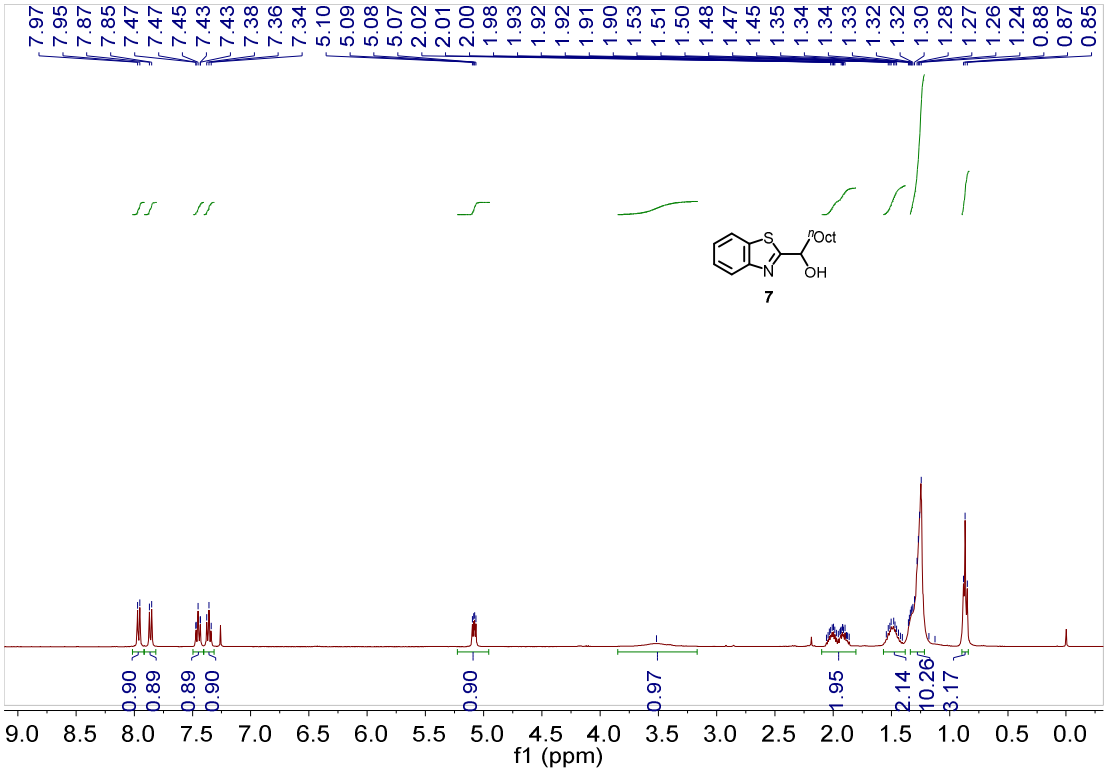

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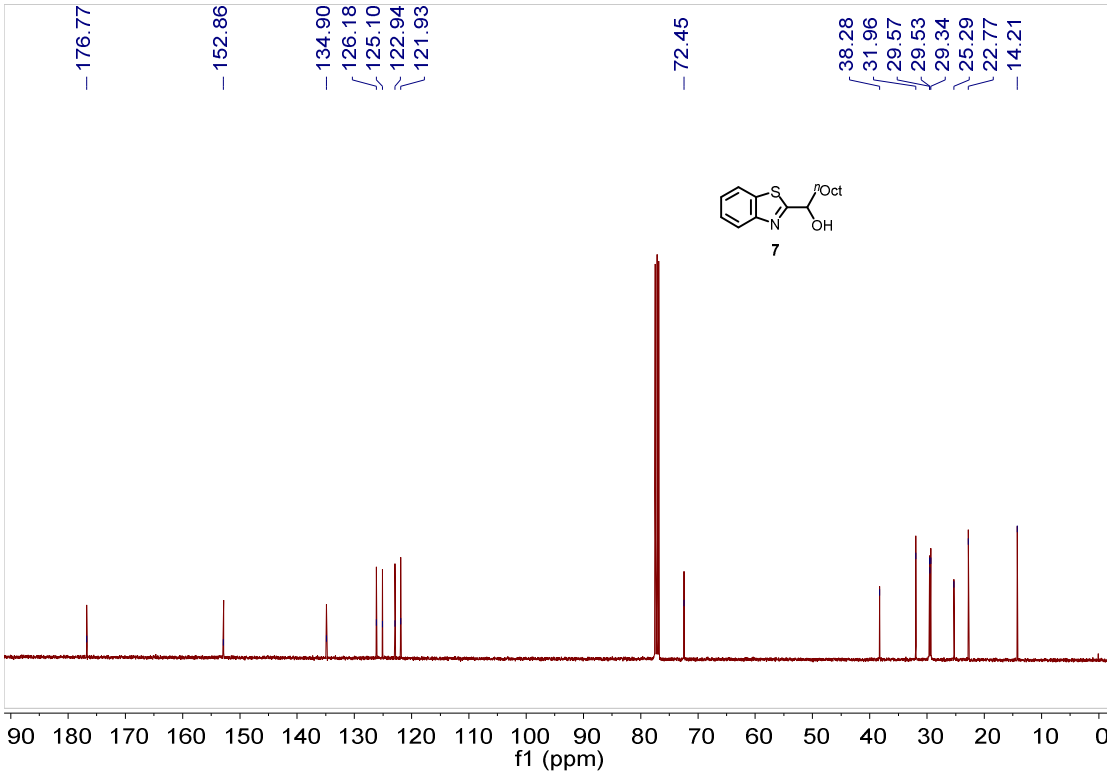

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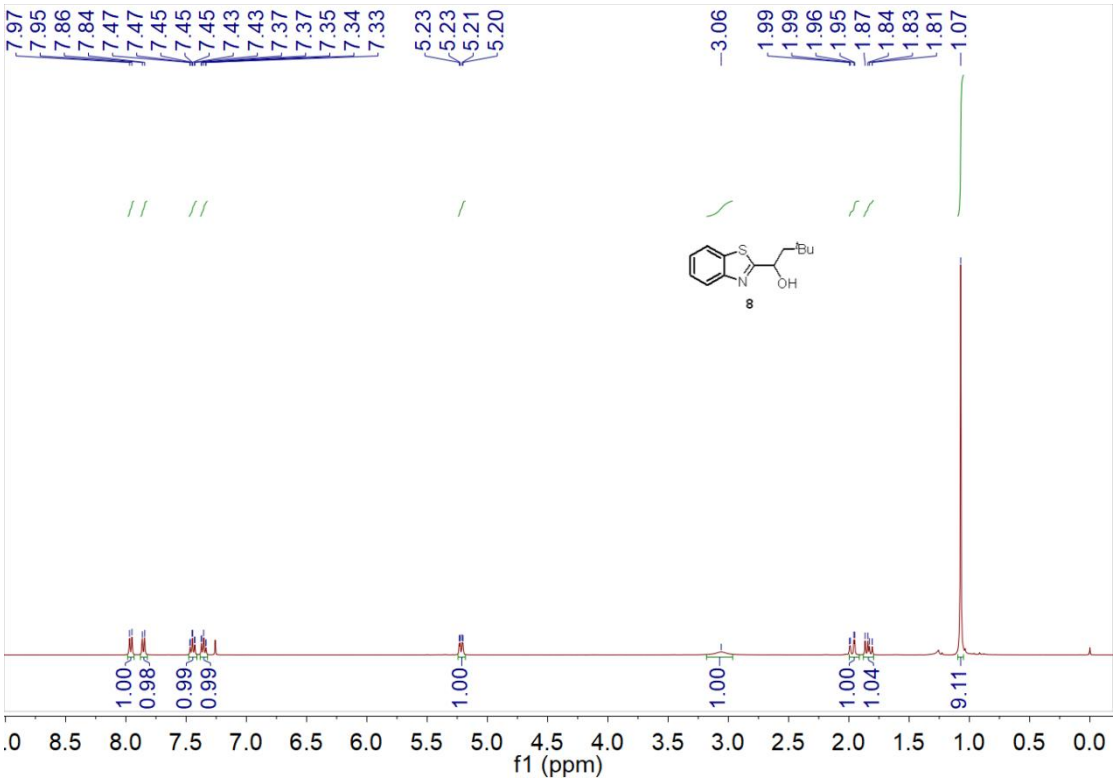

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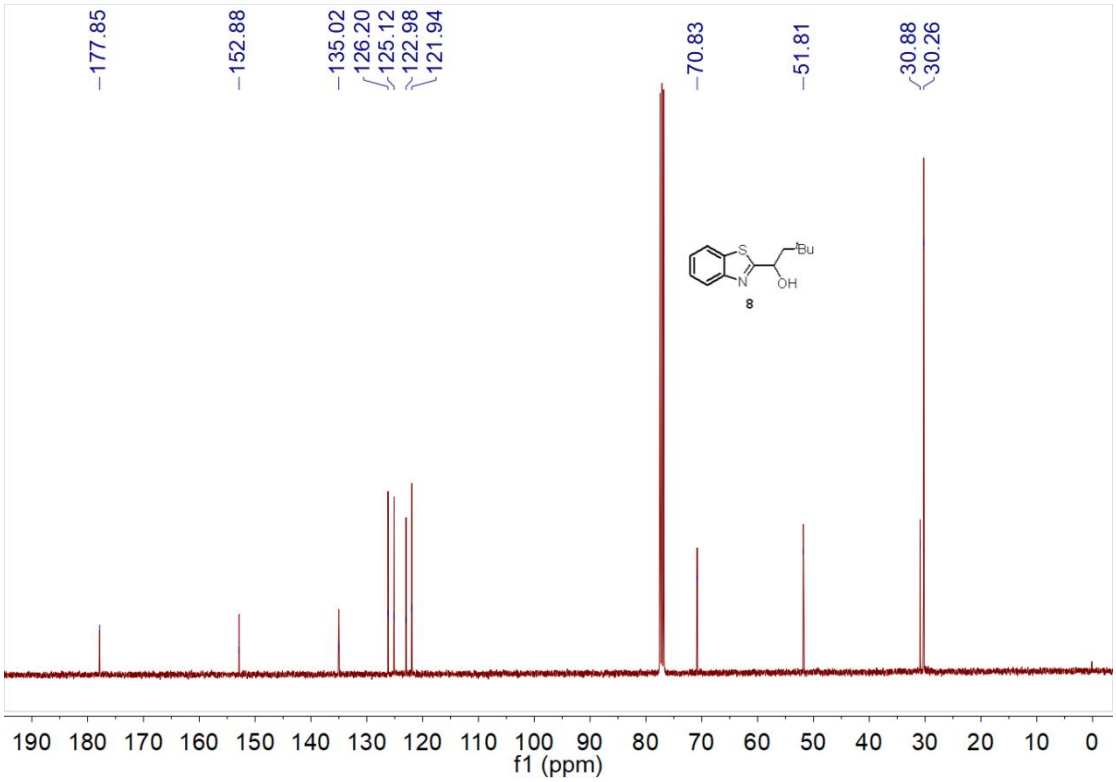

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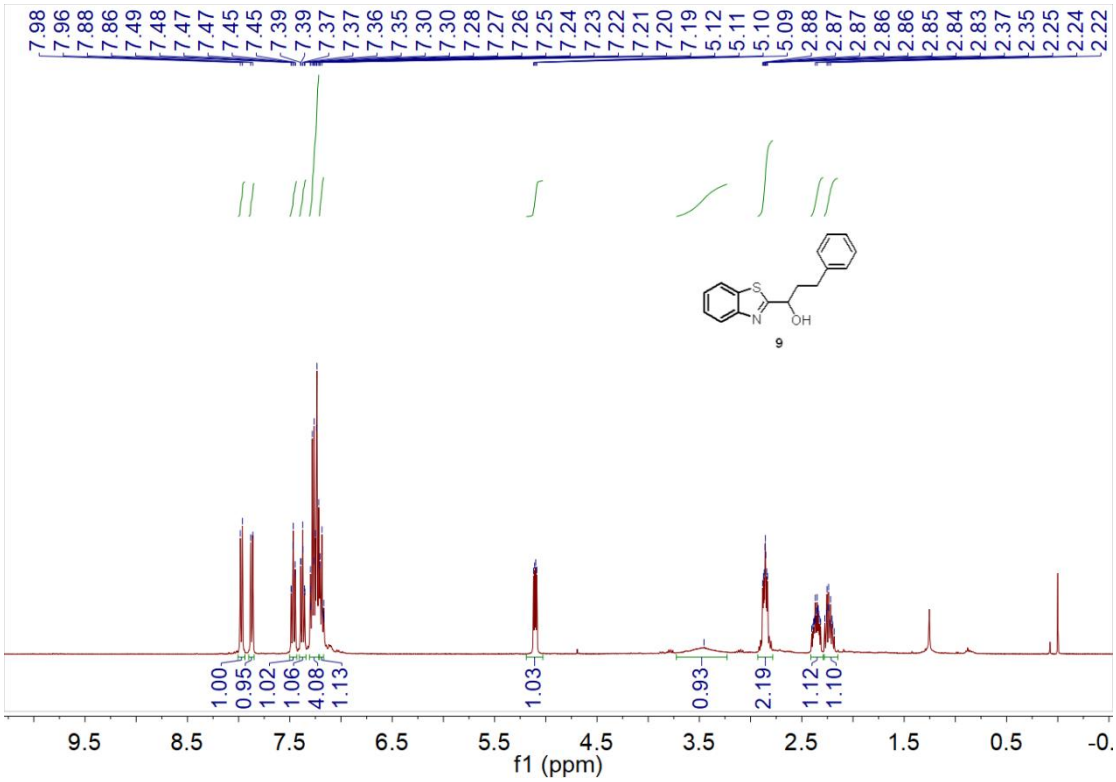
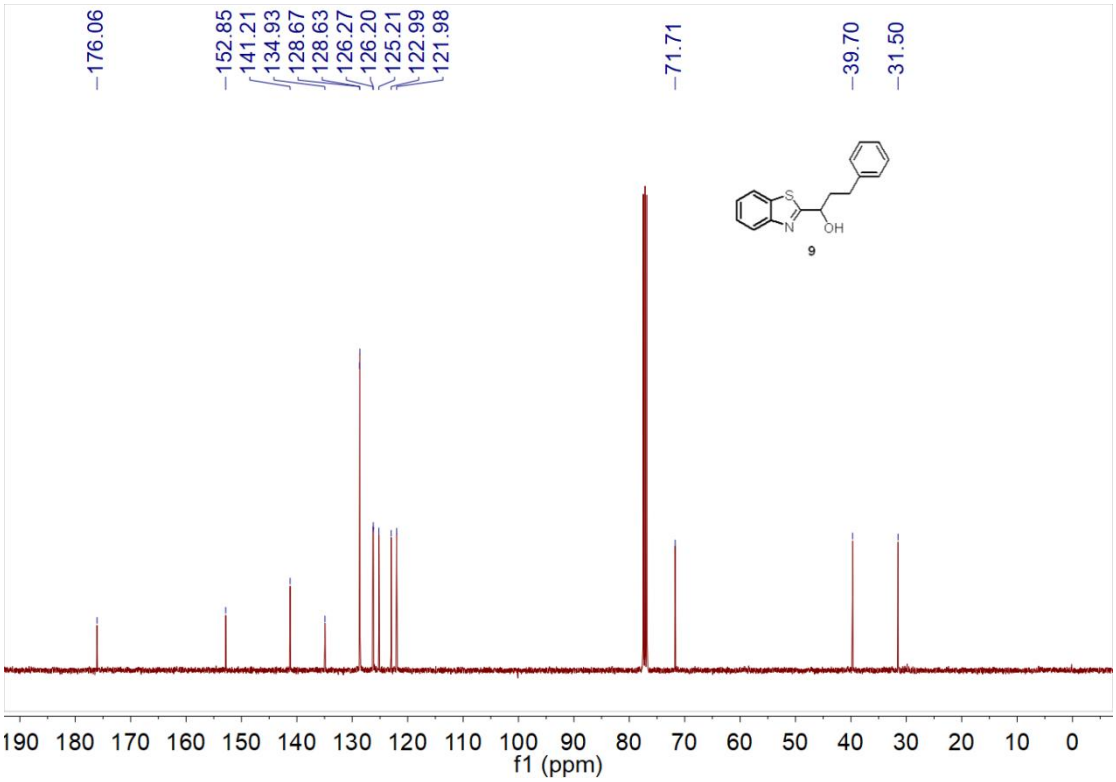


^{1}H NMR spectrum of 9



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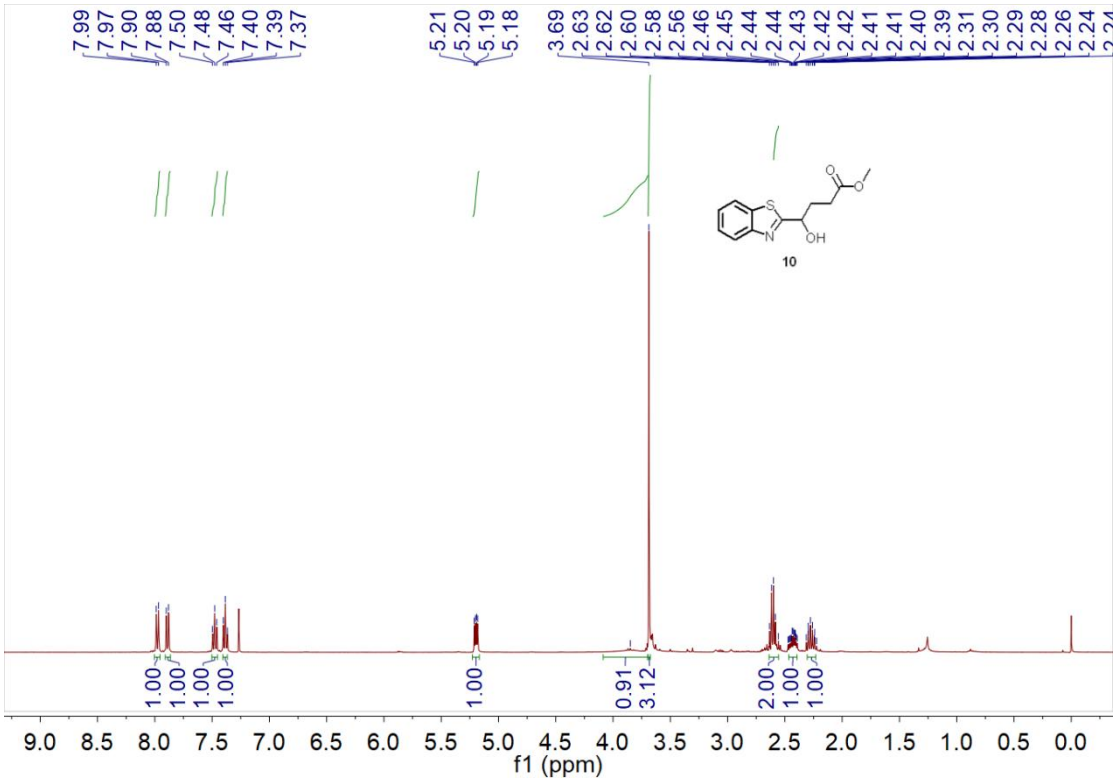

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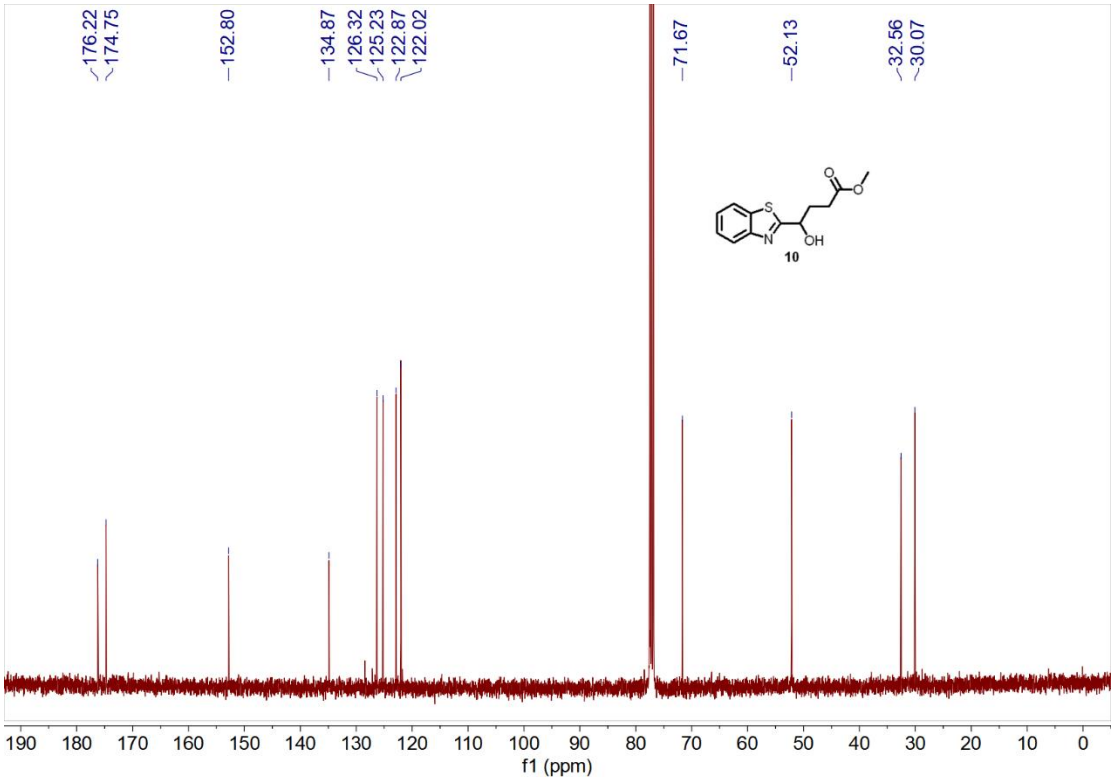

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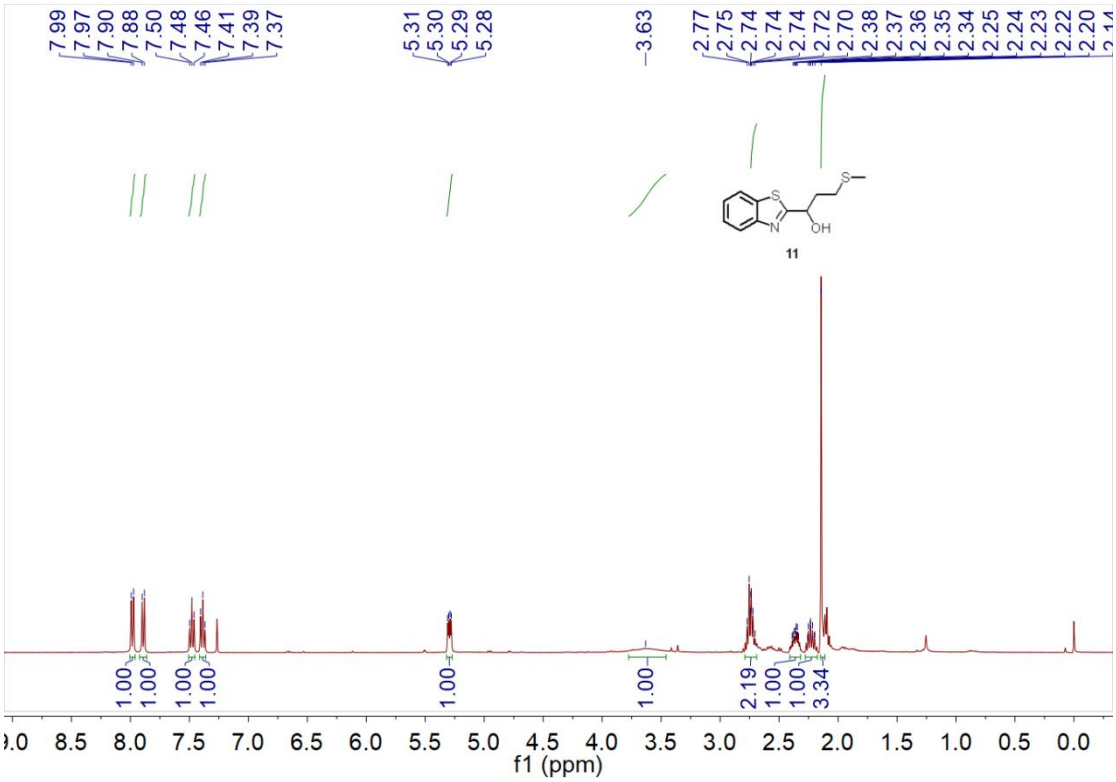

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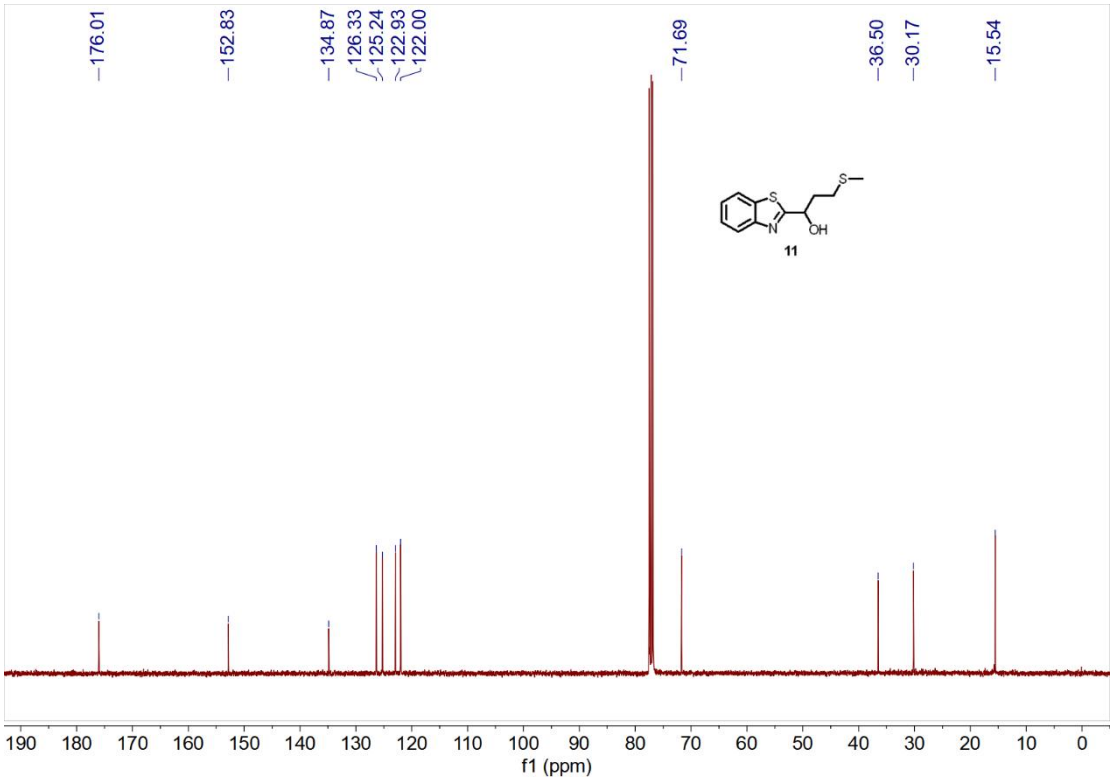

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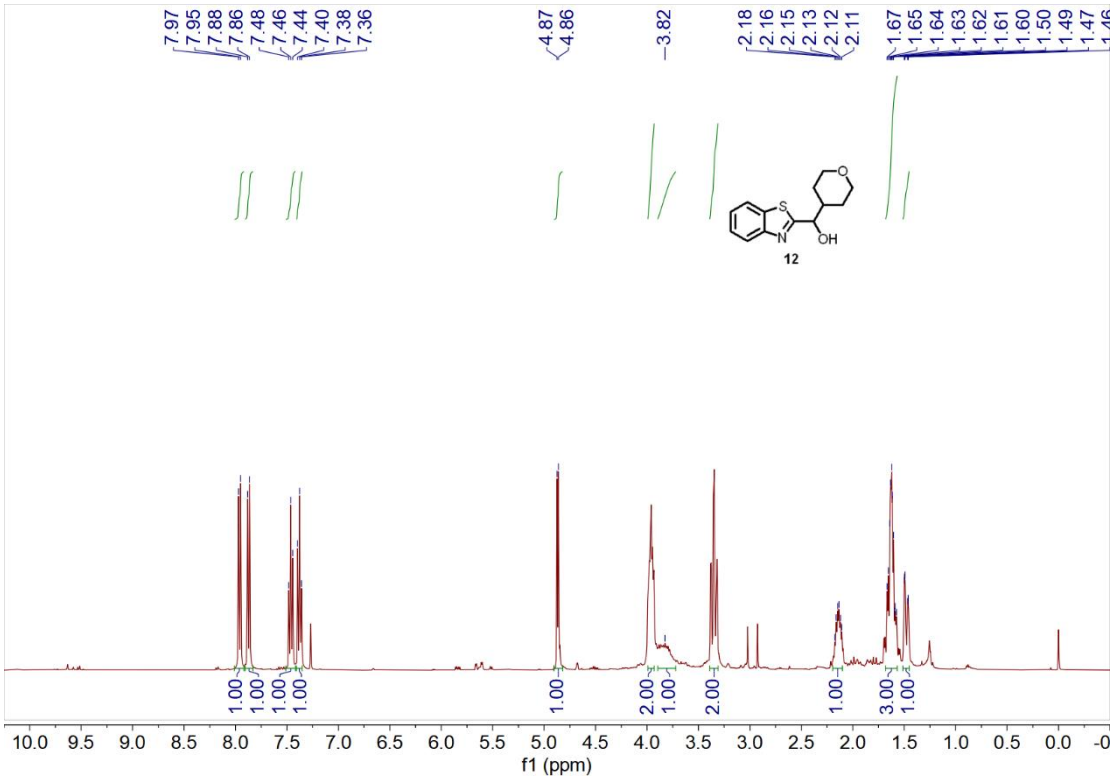

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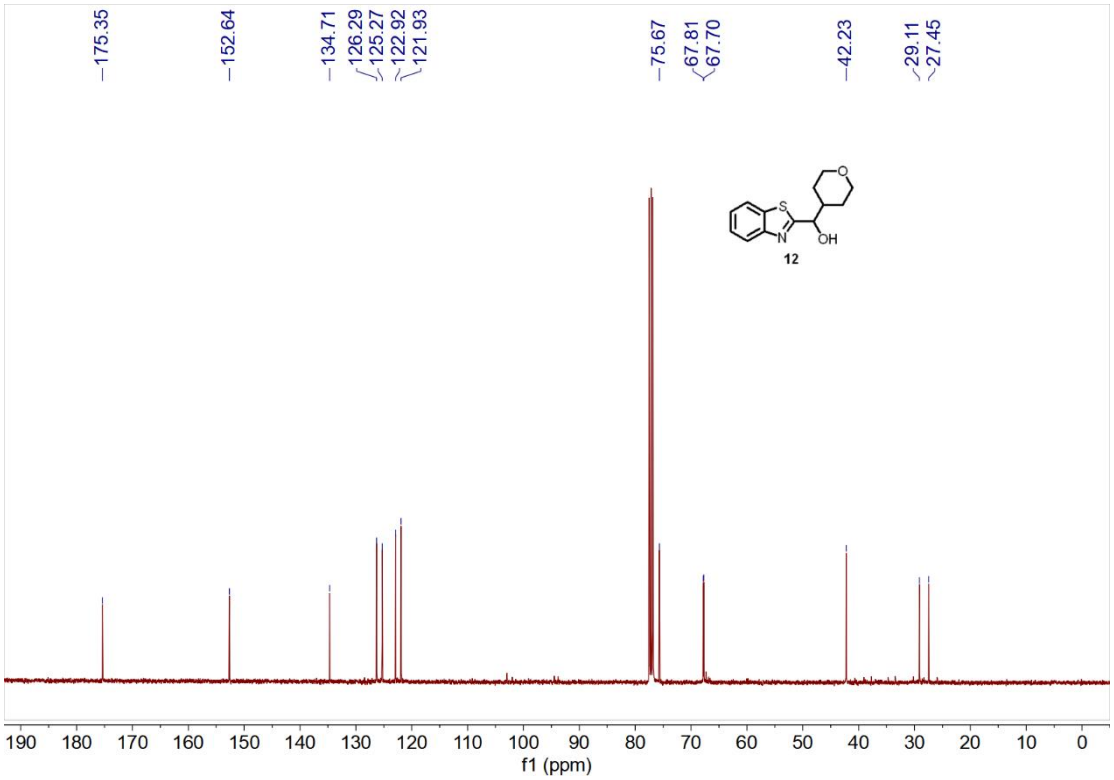

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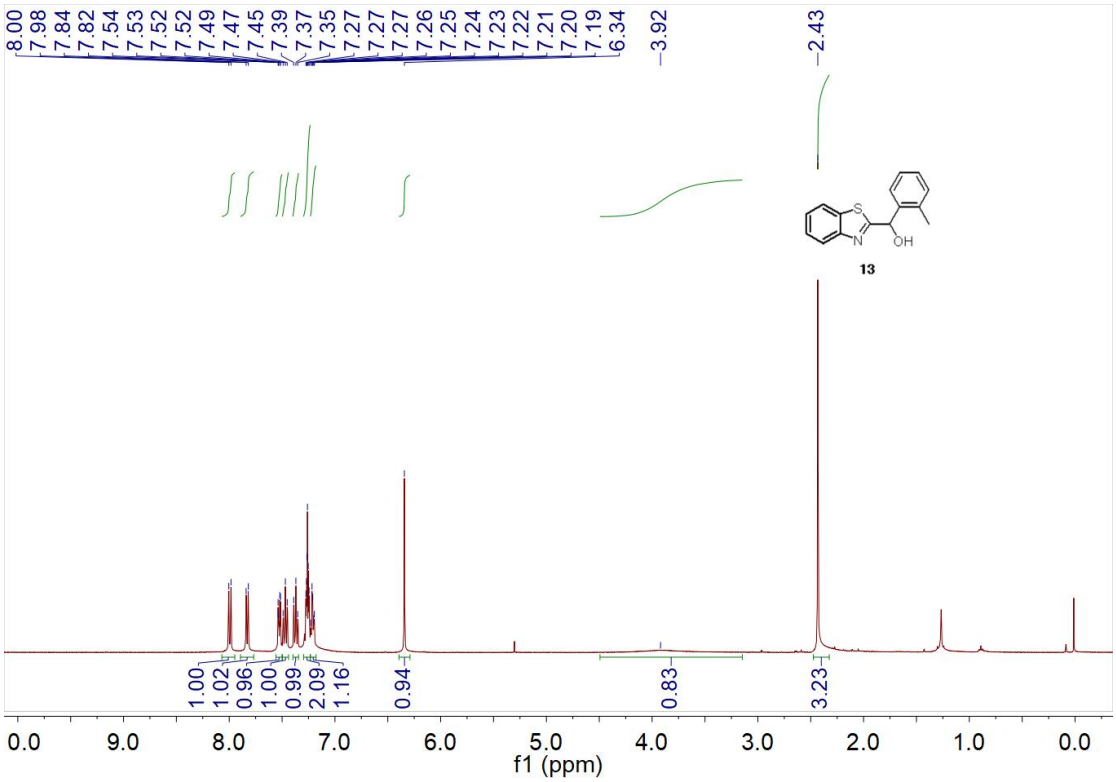

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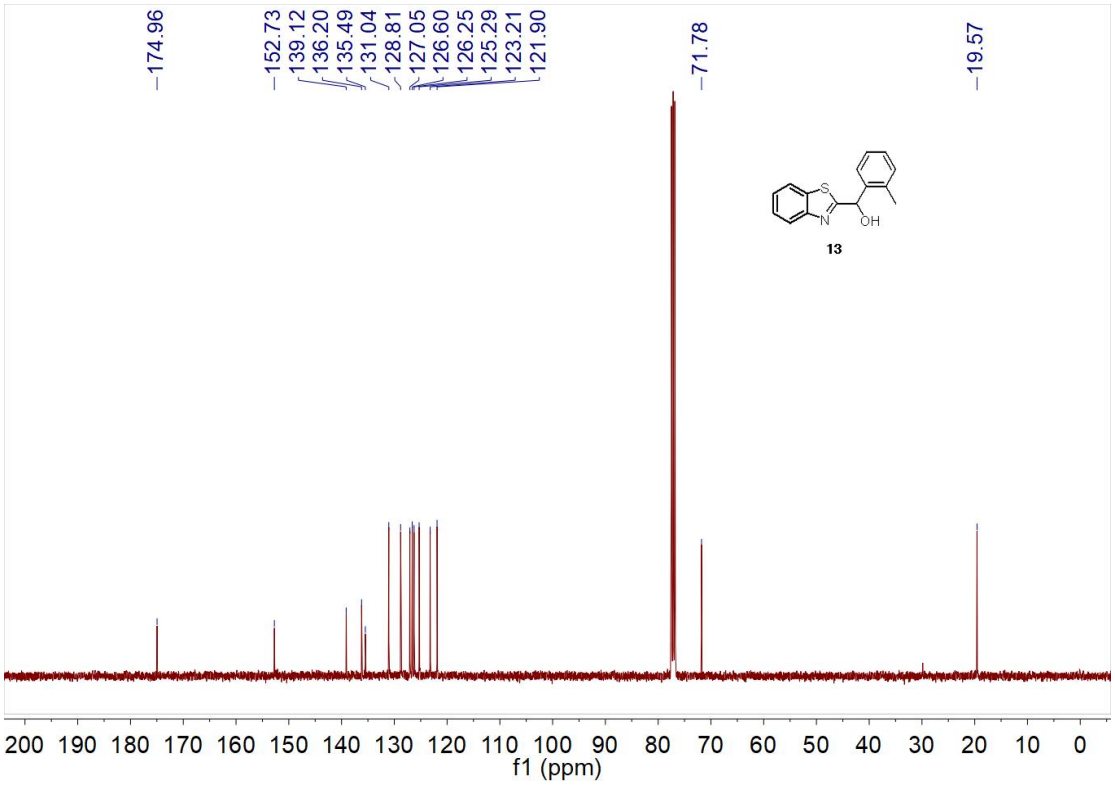

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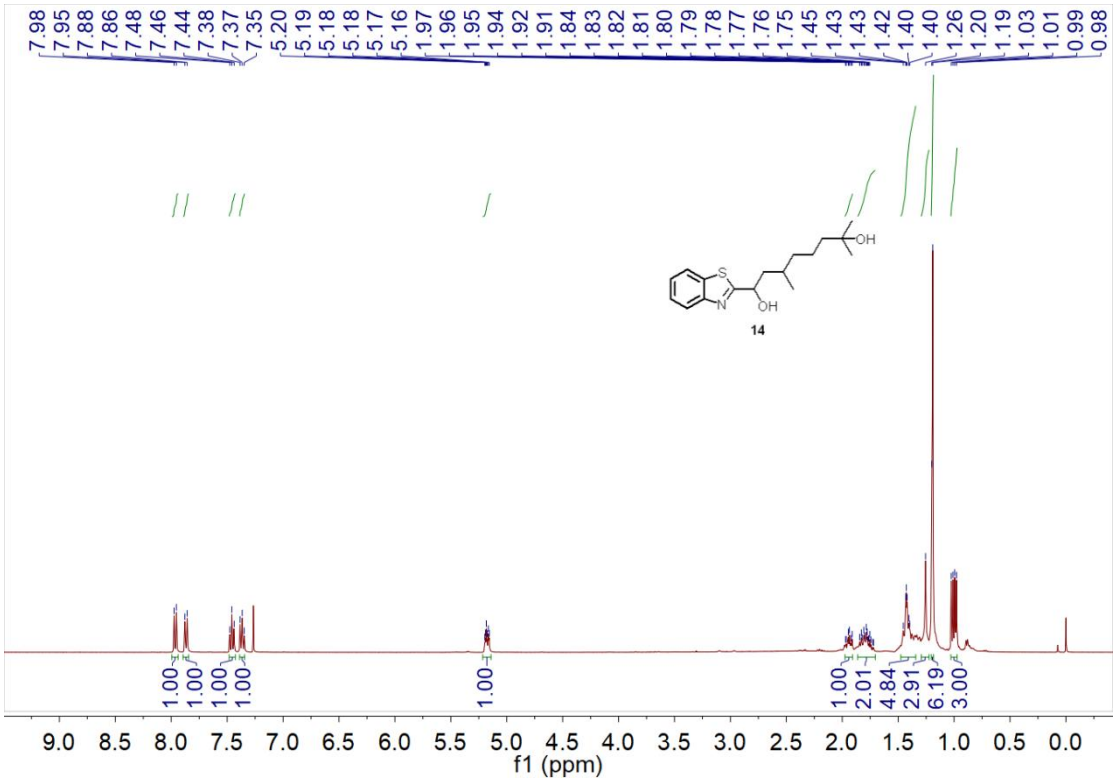

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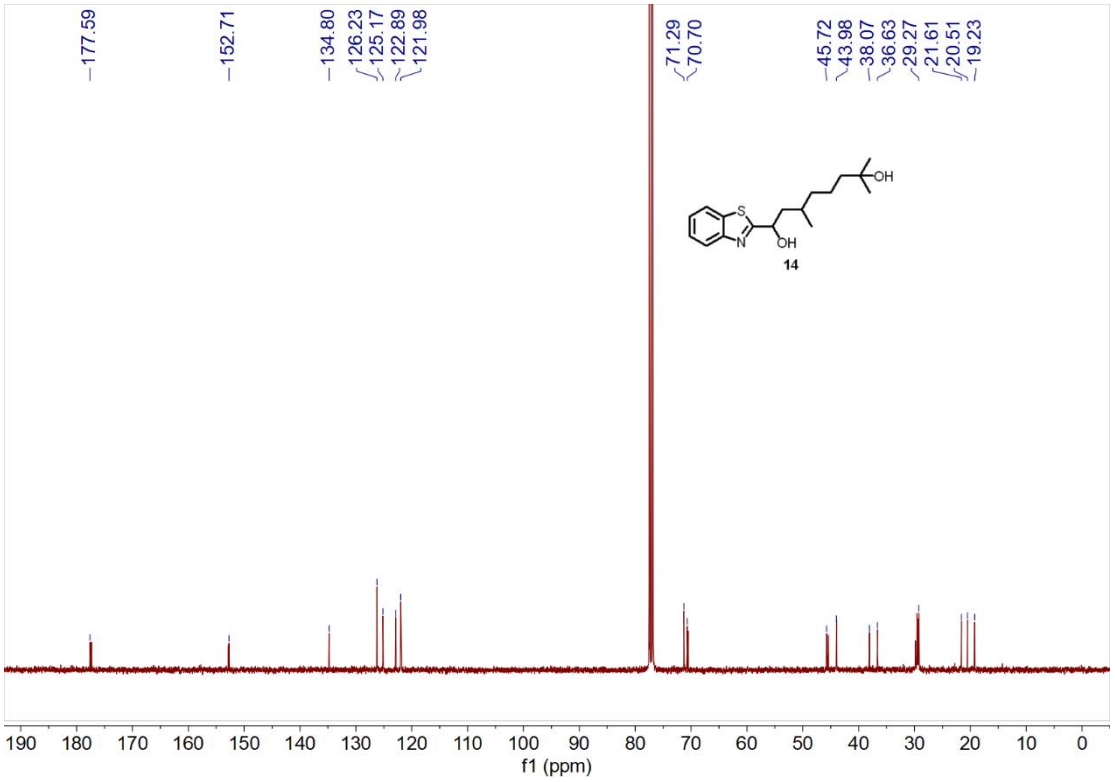

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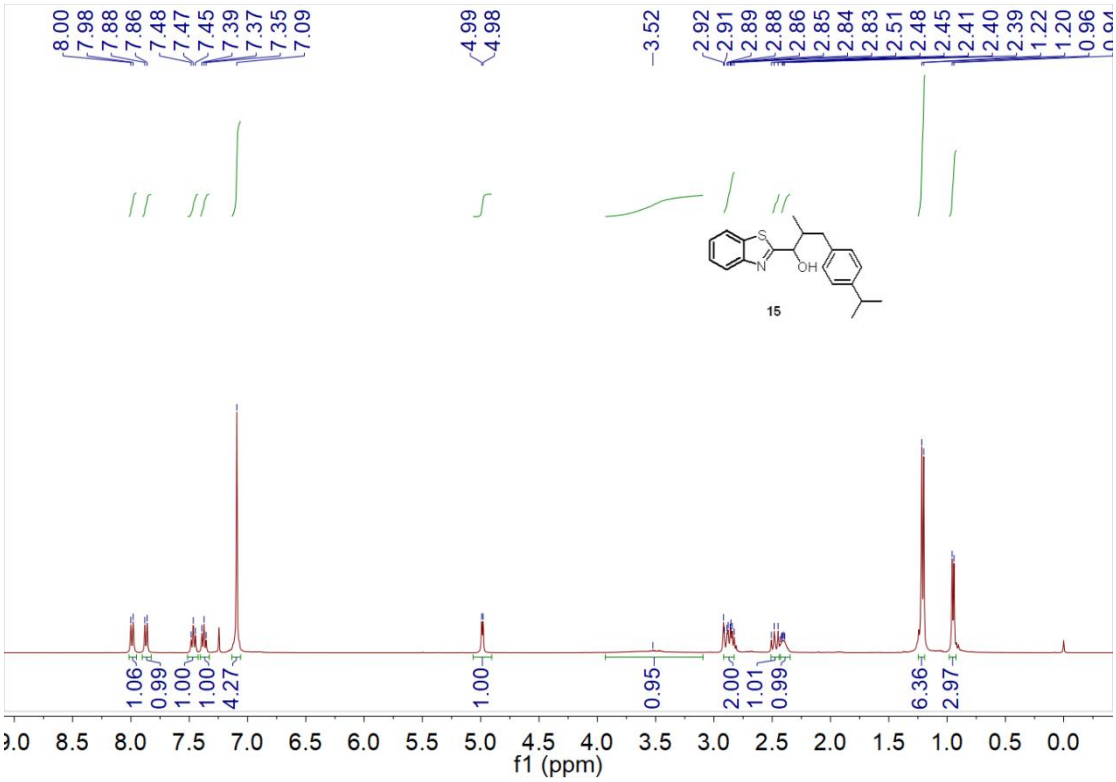

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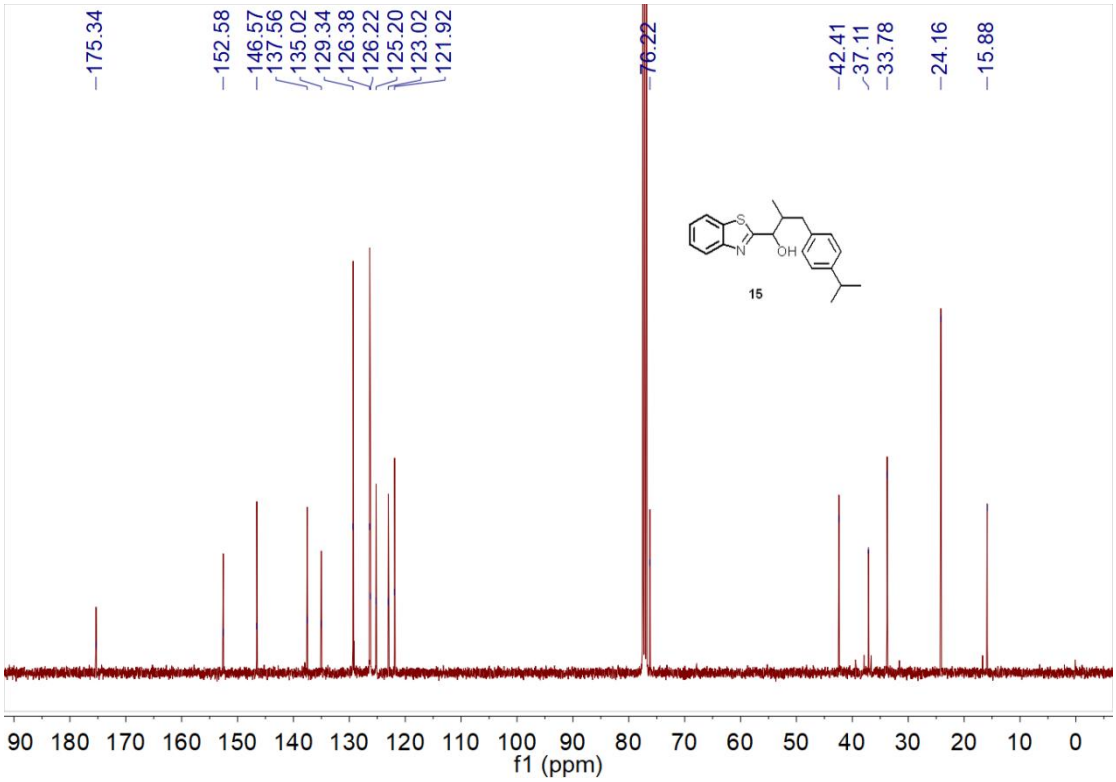

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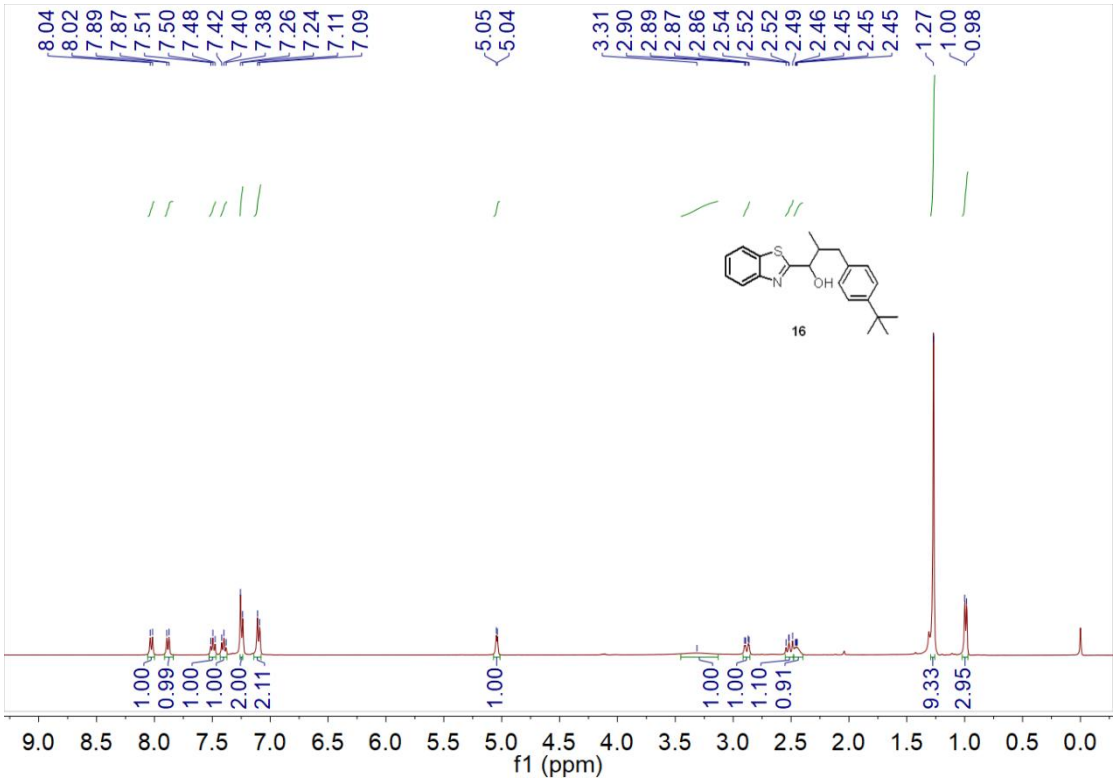

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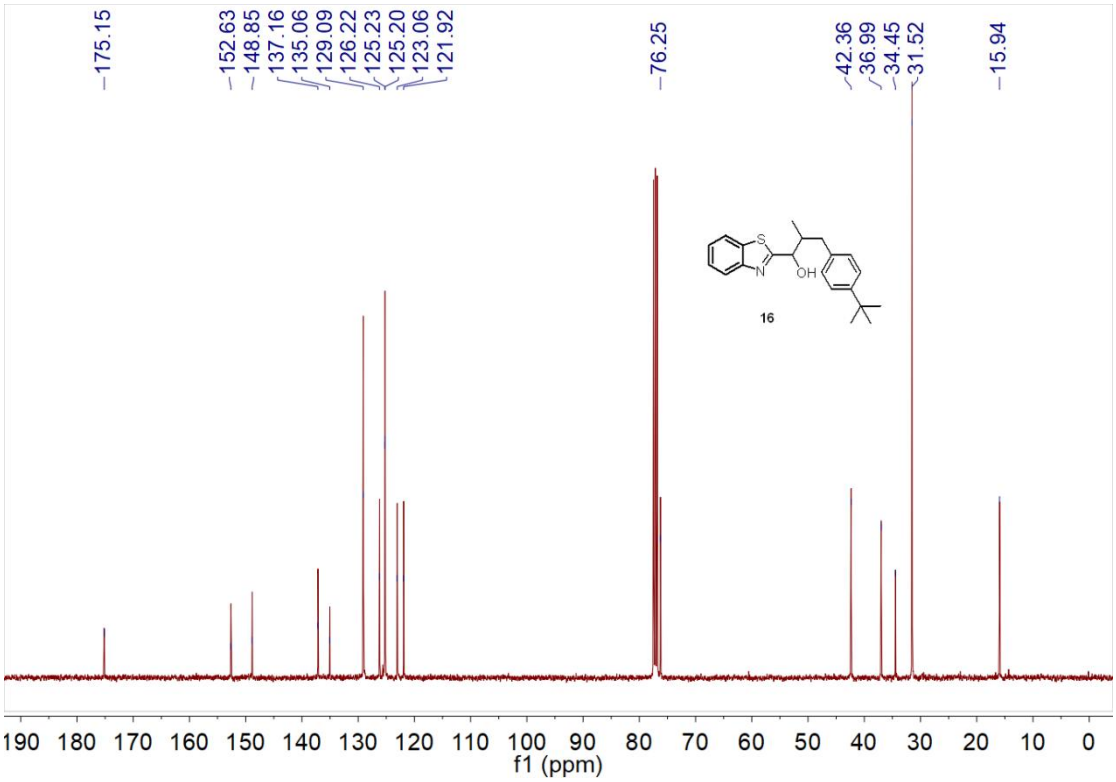

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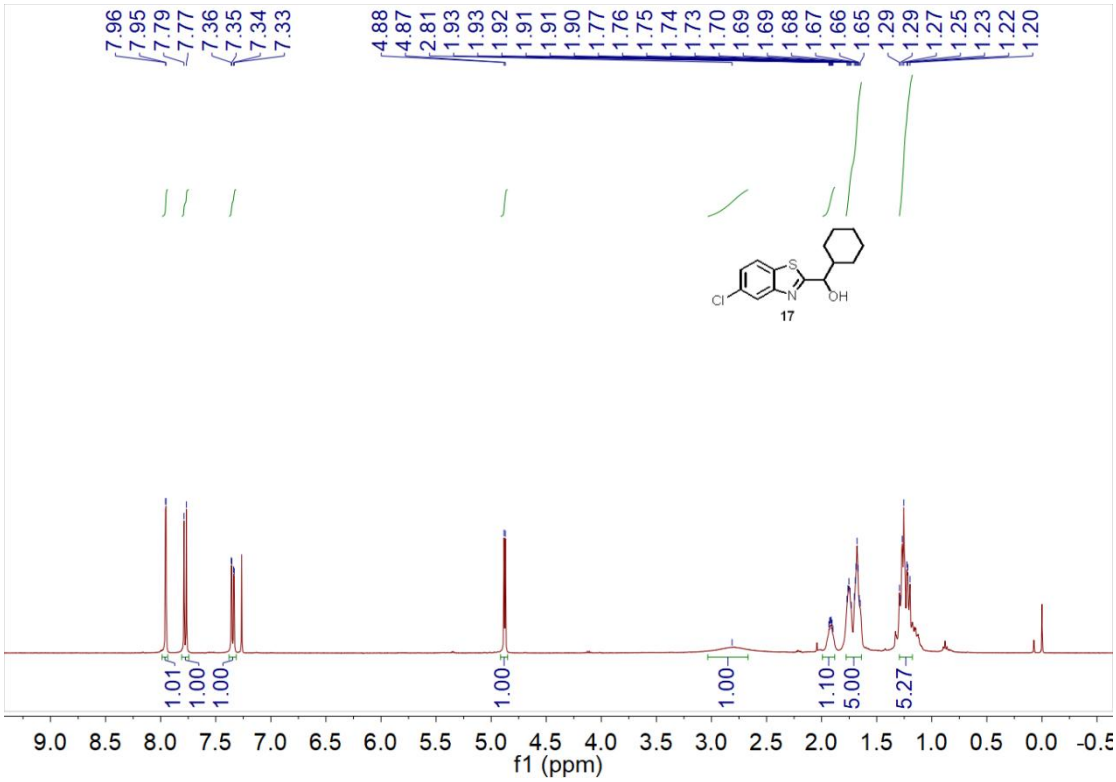

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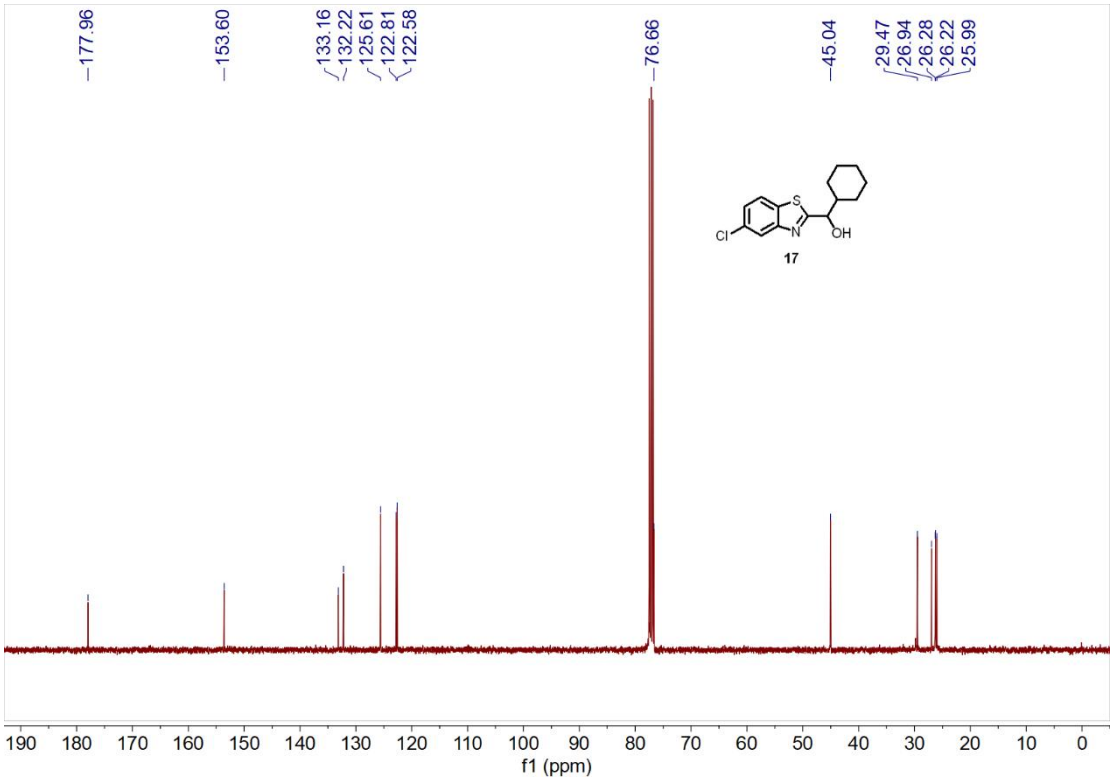

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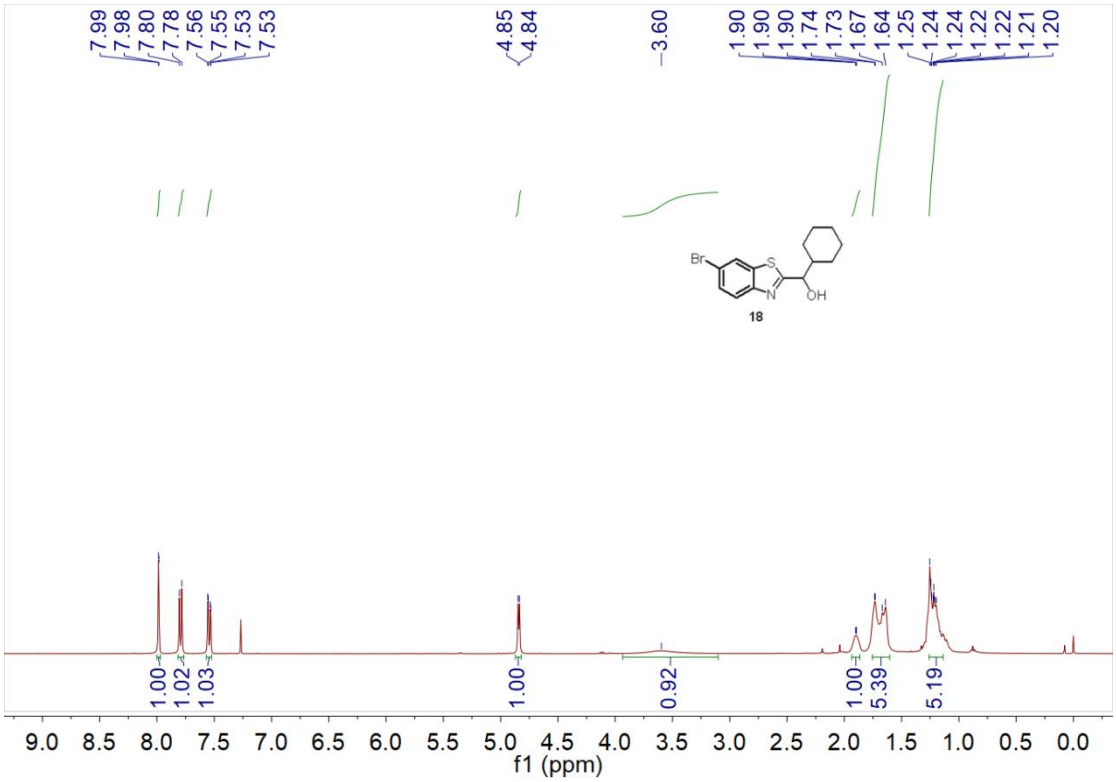

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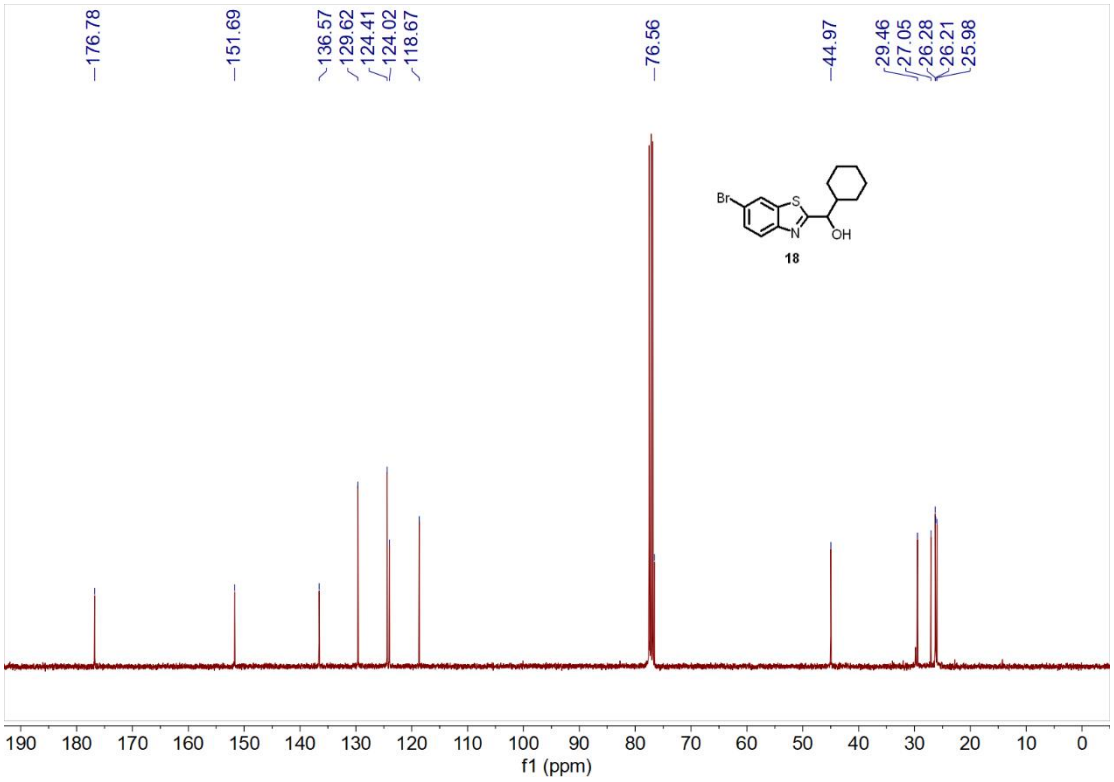

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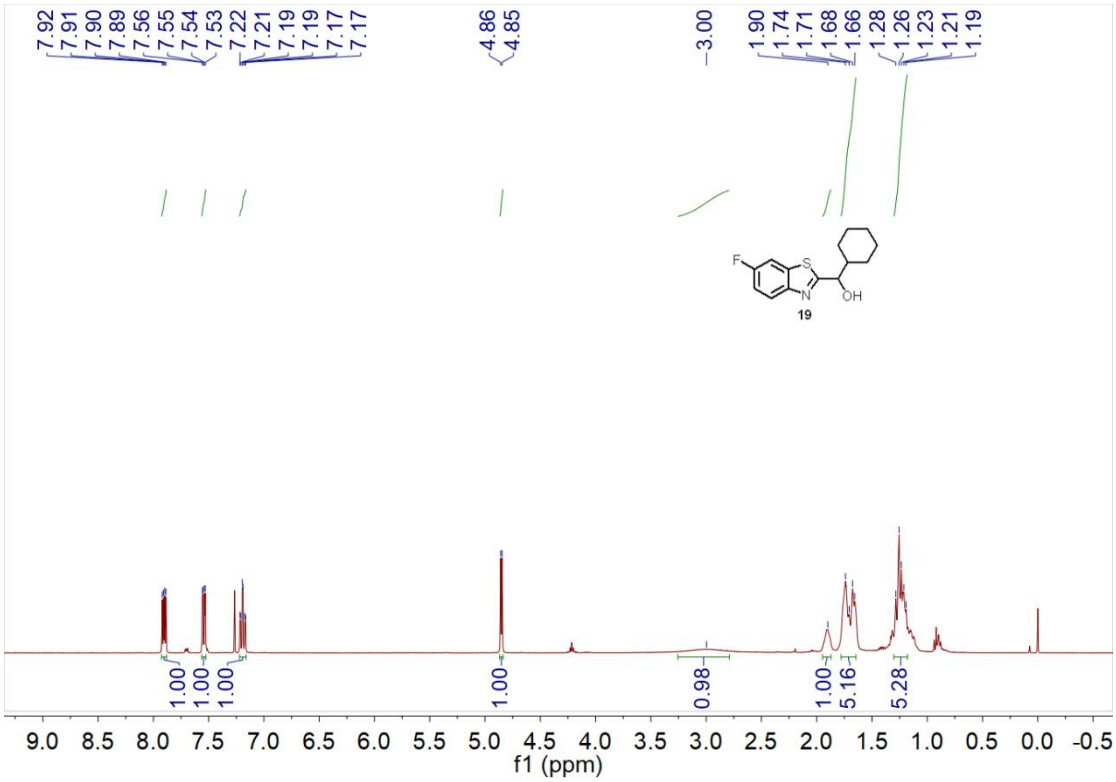

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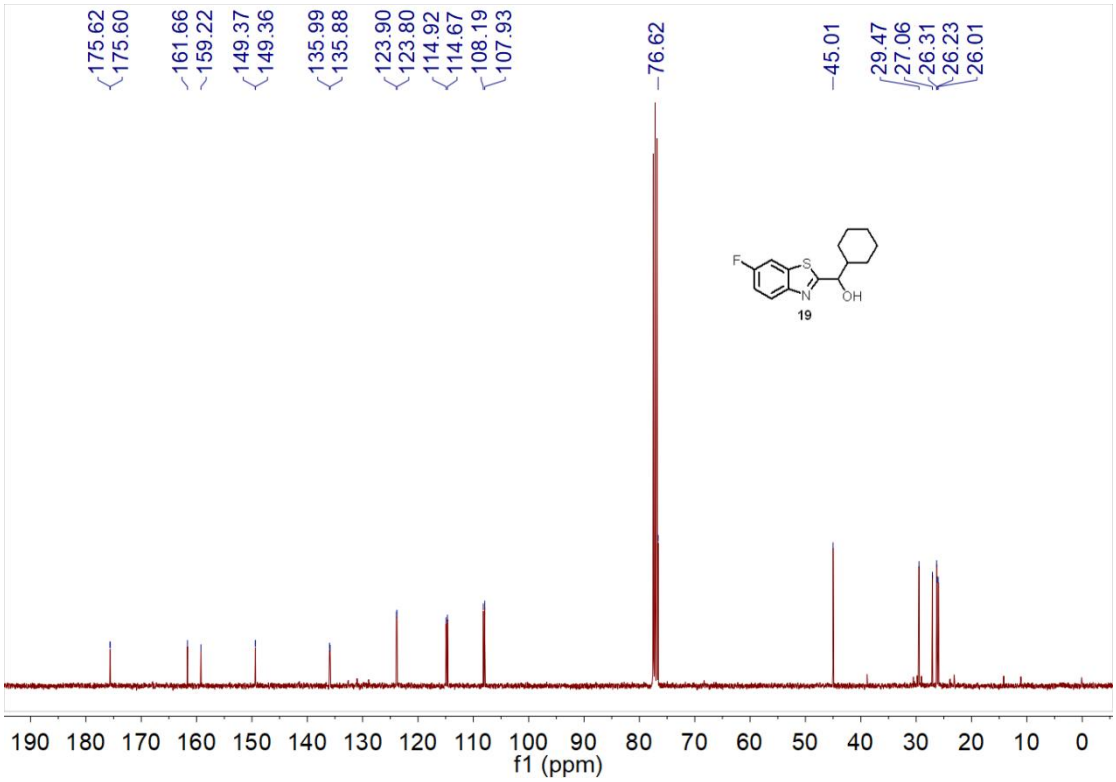
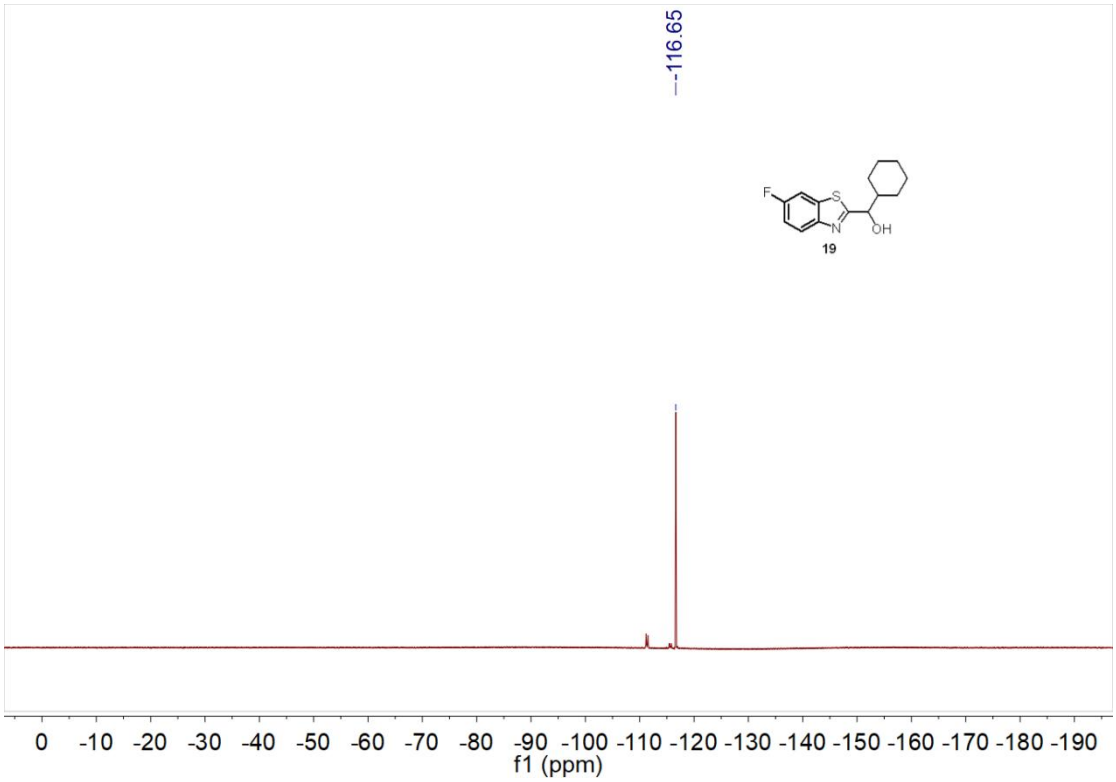
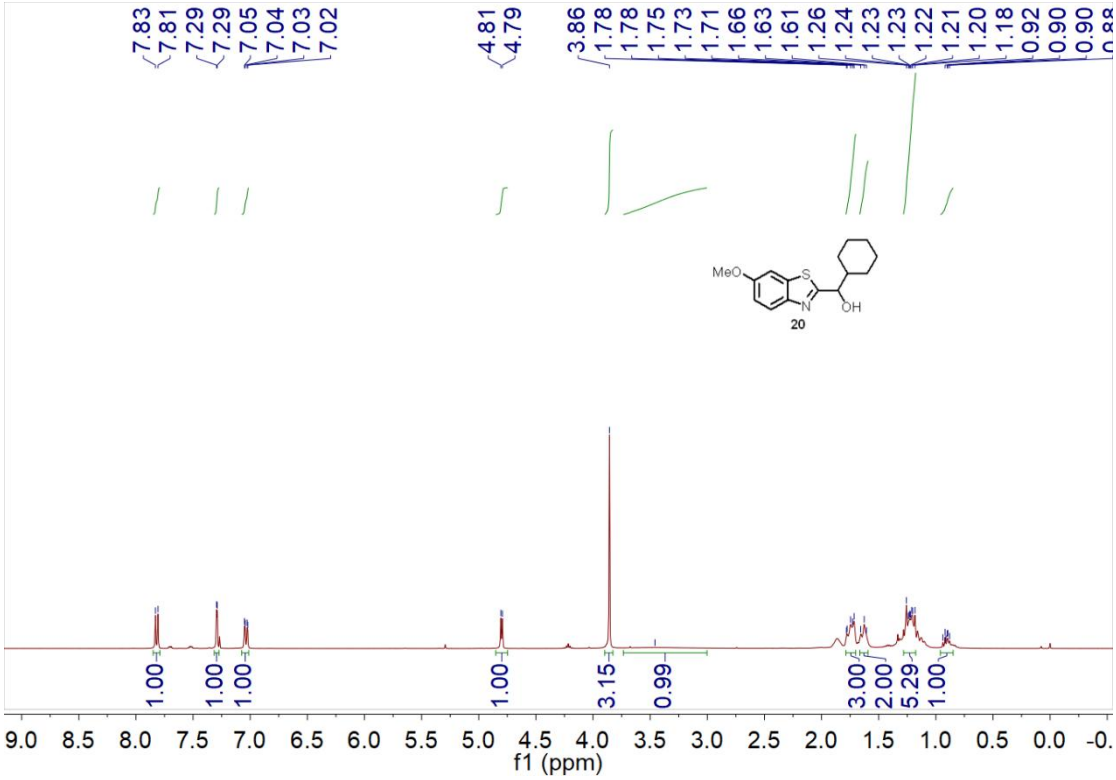


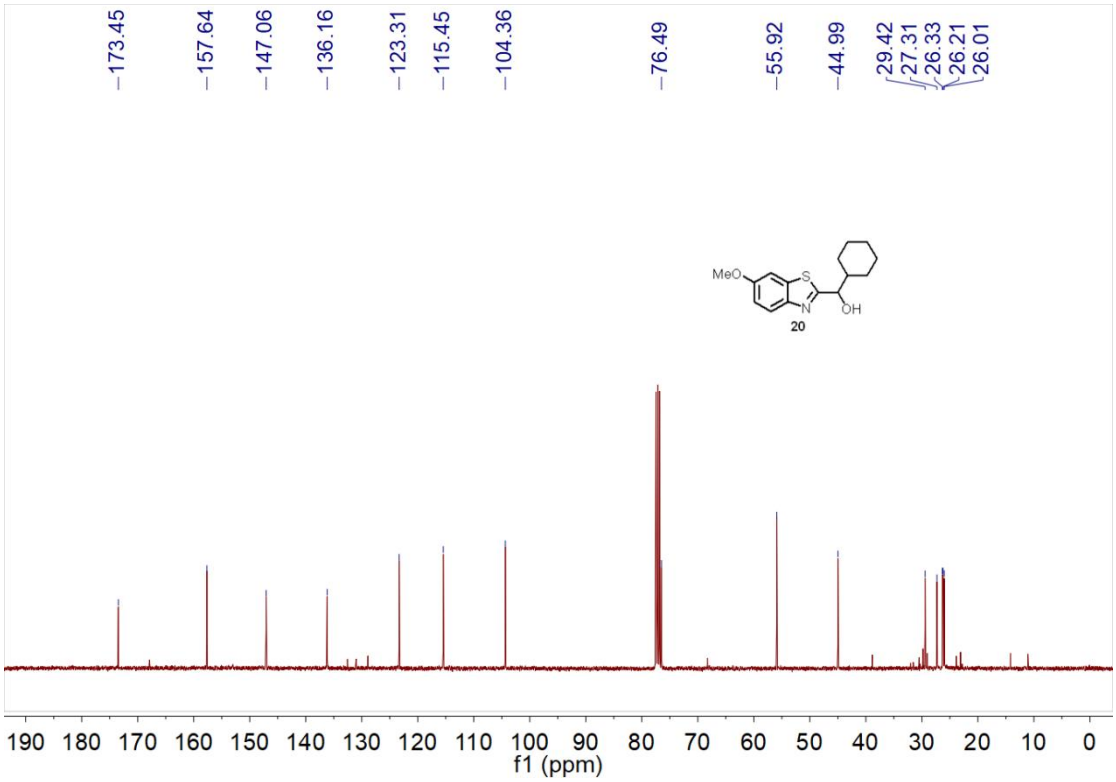
^{13}C NMR spectrum of 19



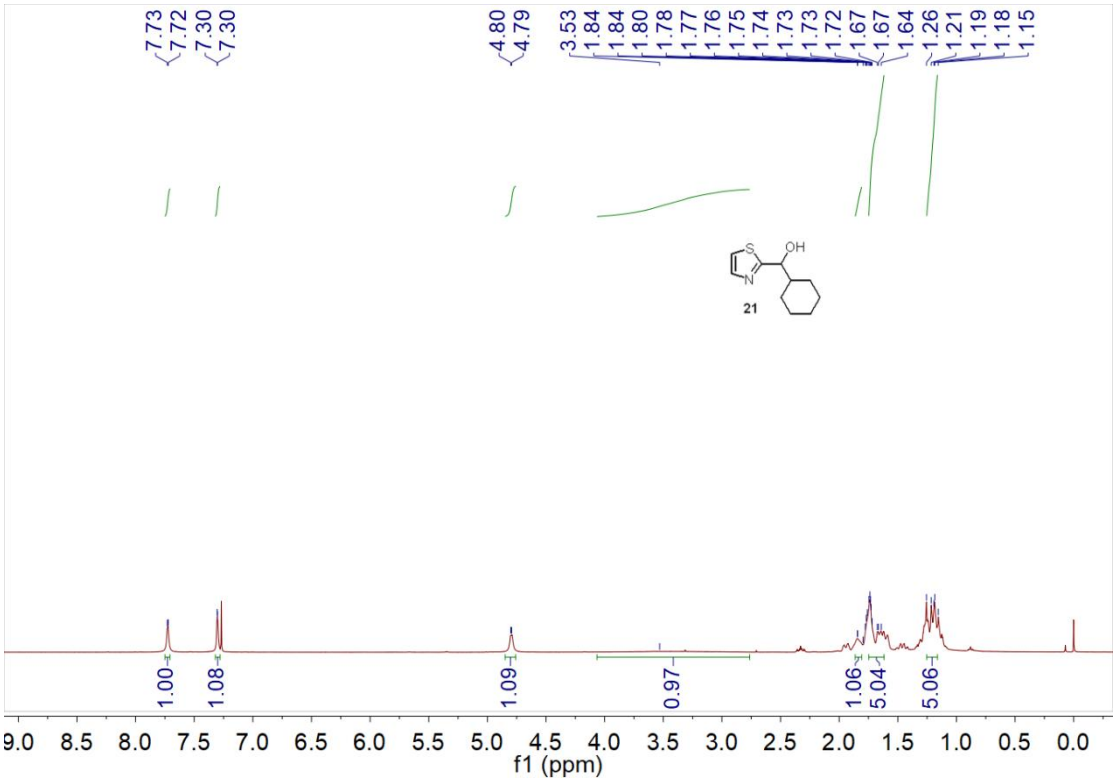
^{19}F NMR spectrum of 19



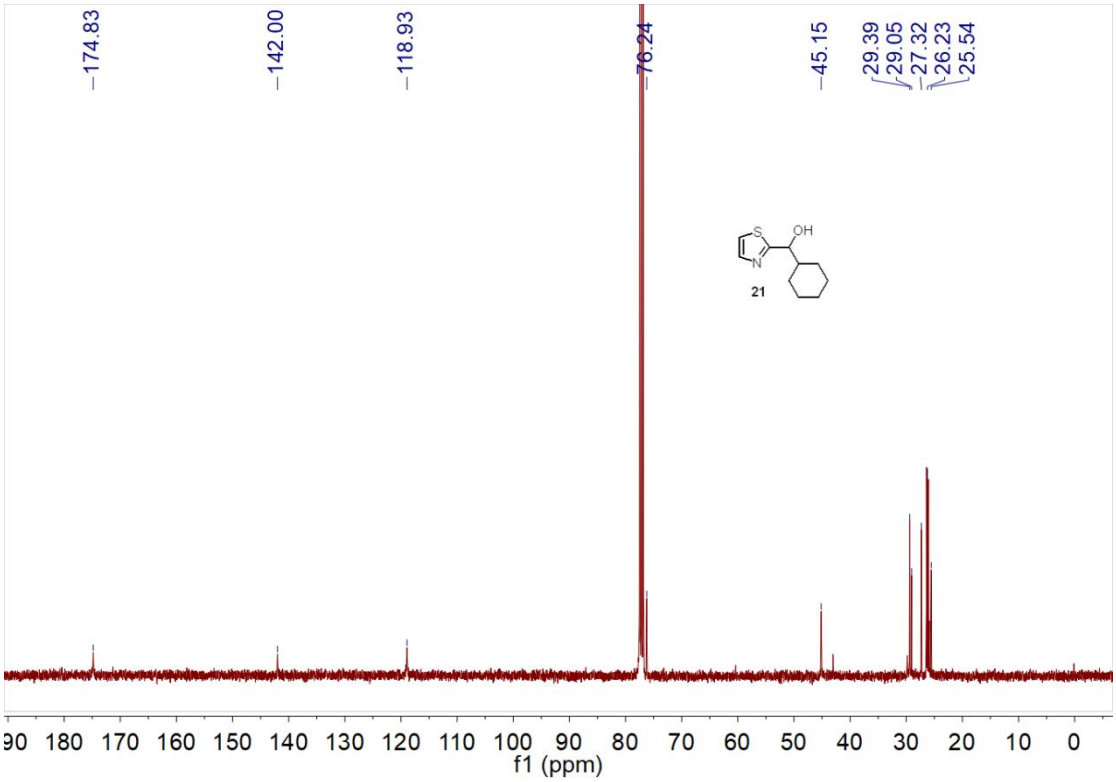
^{1}H NMR spectrum of 20



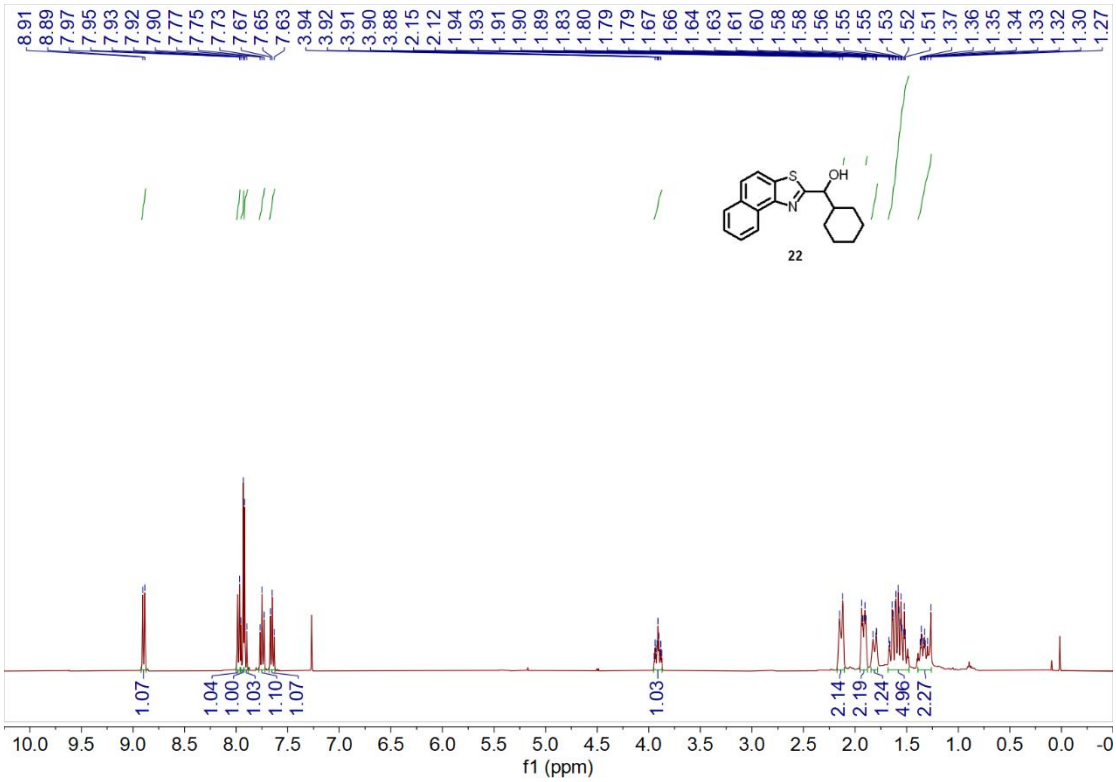
^{13}C NMR spectrum of 20



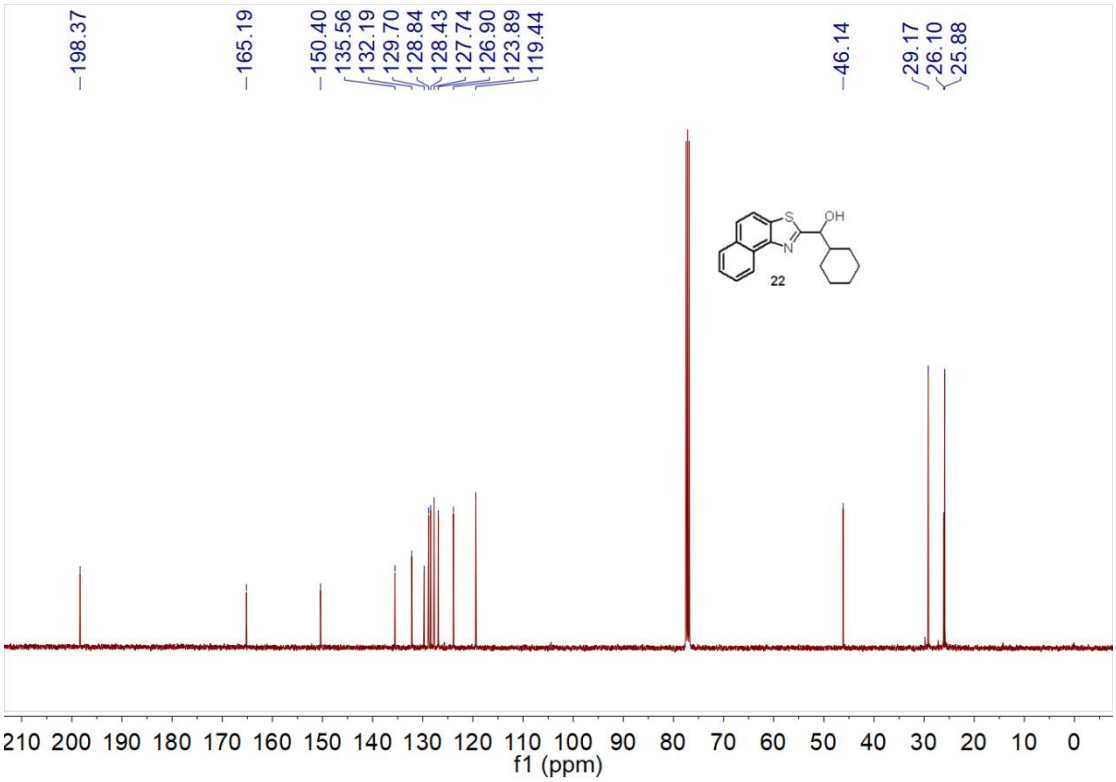
^{1}H NMR spectrum of 21



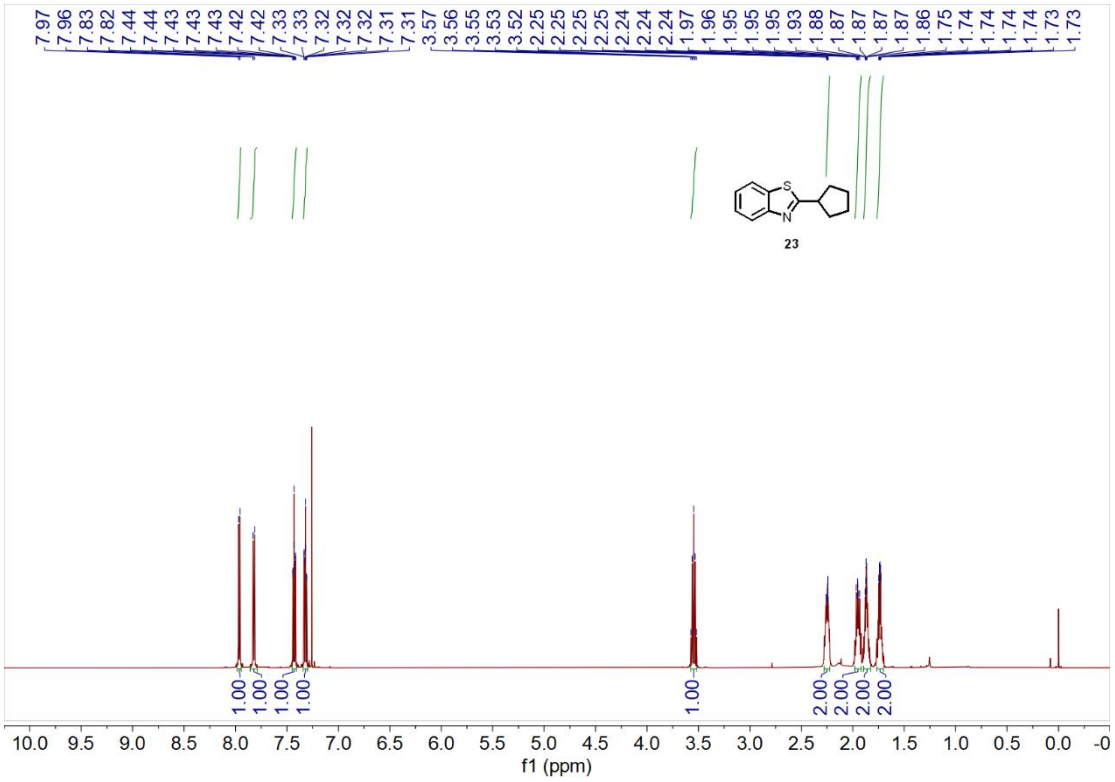
^{13}C NMR spectrum of 21



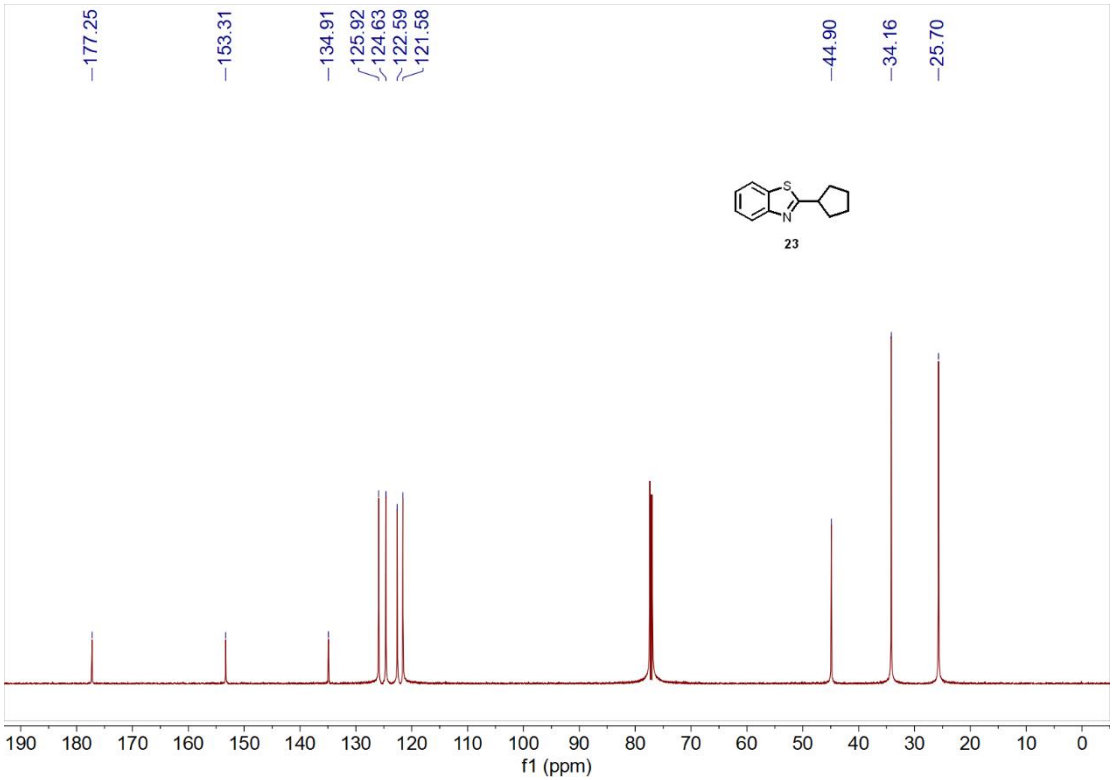
^{1}H NMR spectrum of 22



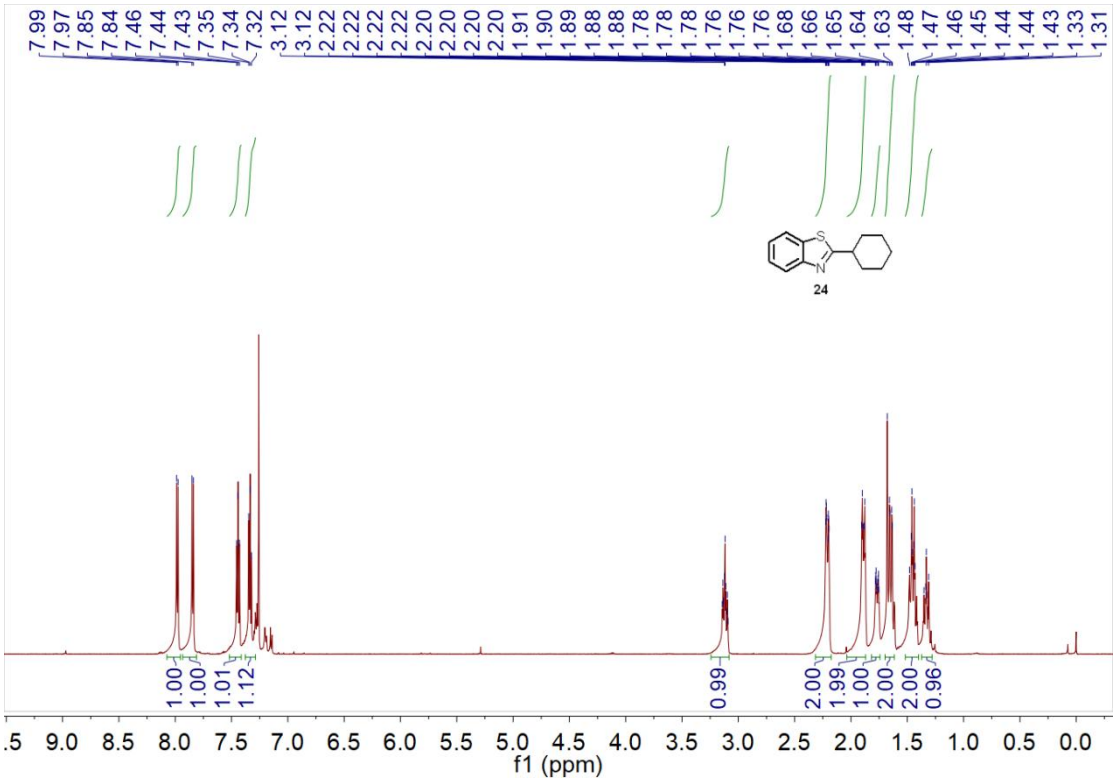
^{13}C NMR spectrum of 22



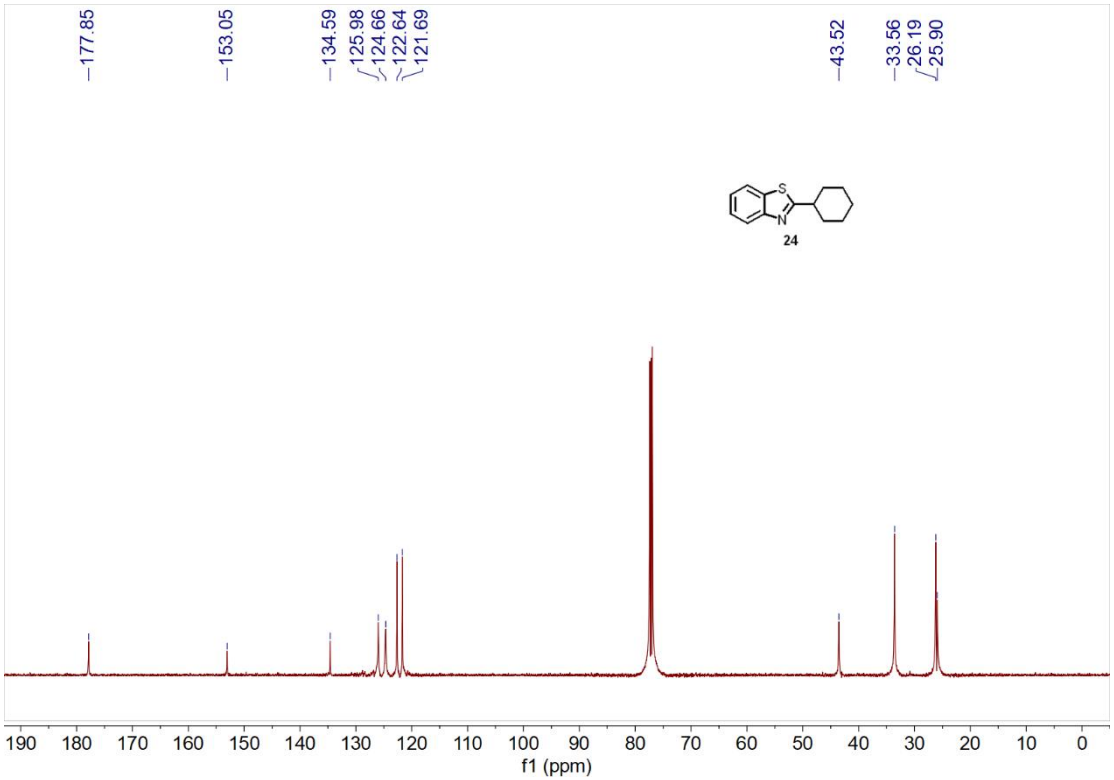
^{1}H NMR spectrum of 23



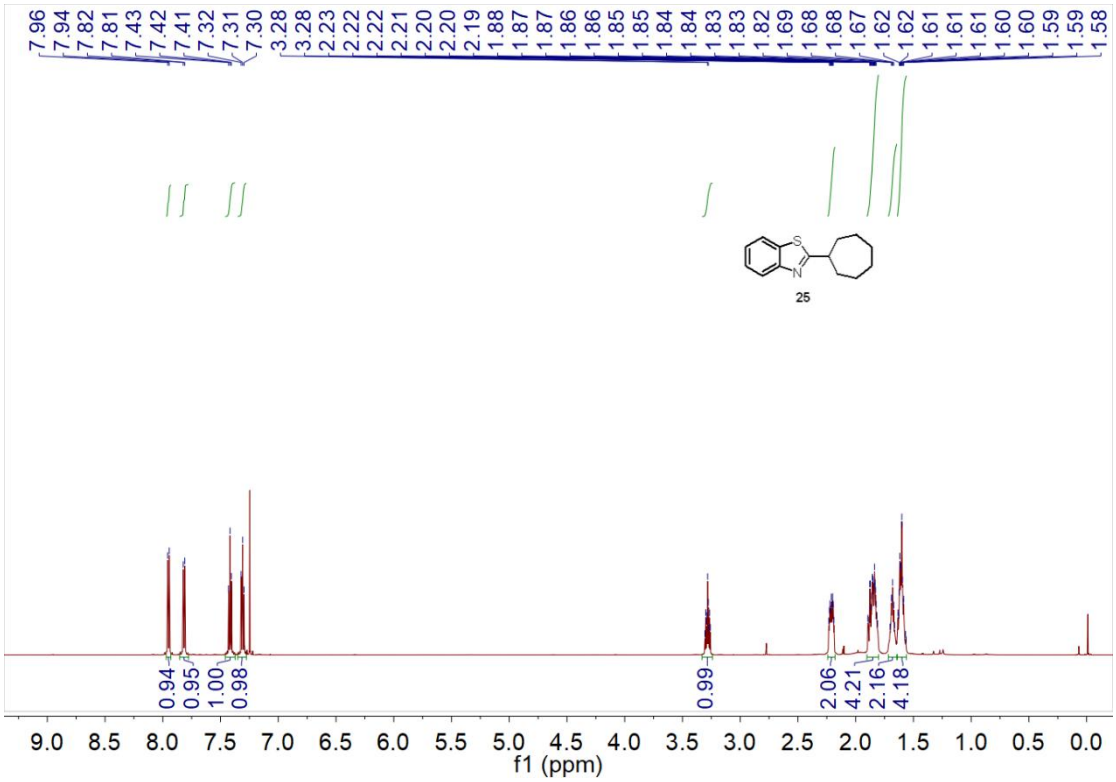
^{13}C NMR spectrum of 23



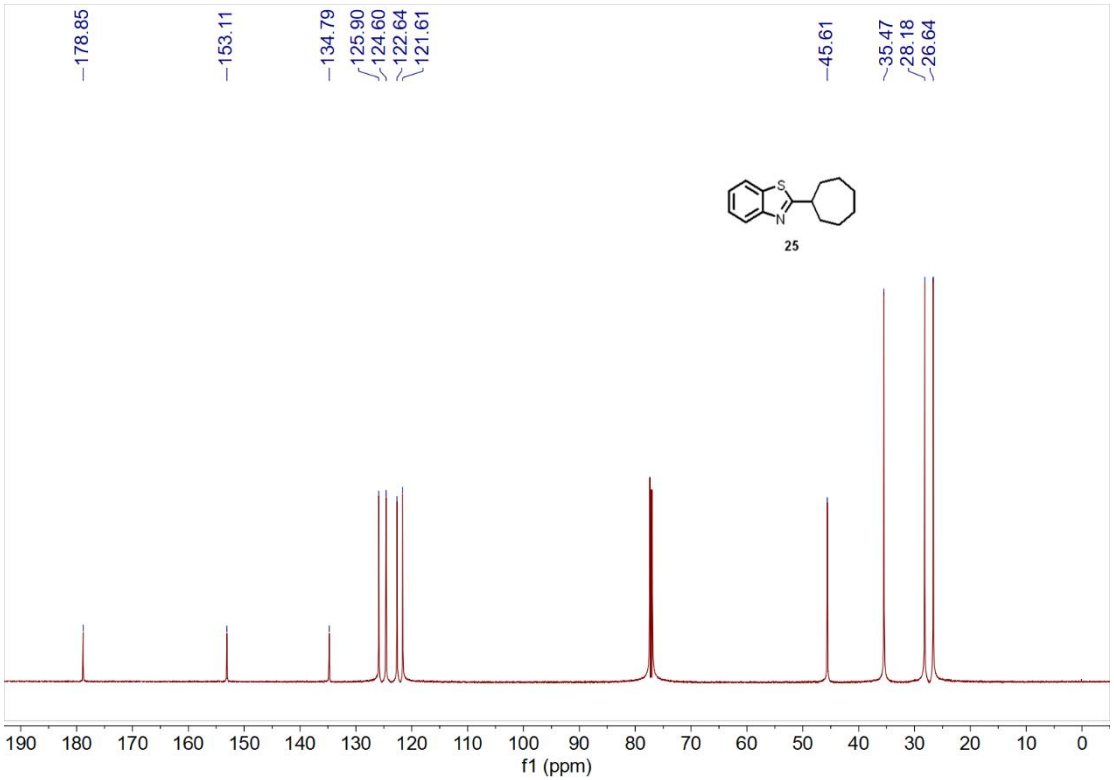
^{1}H NMR spectrum of 24



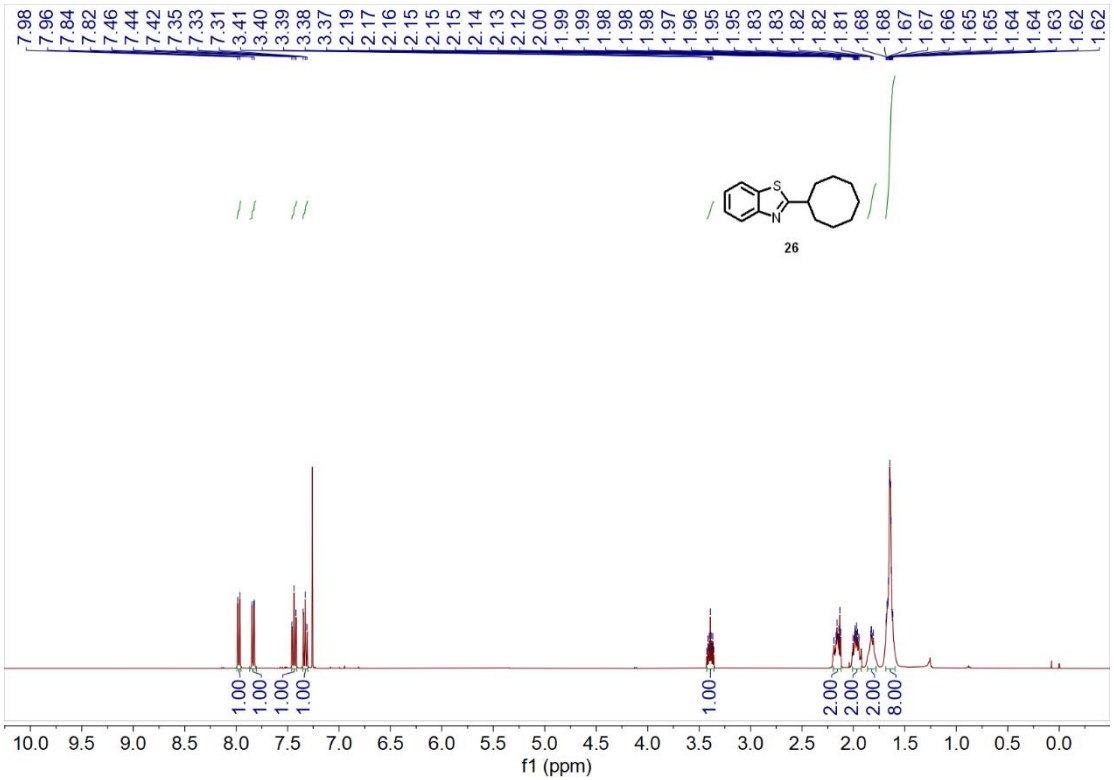
^{13}C NMR spectrum of 24



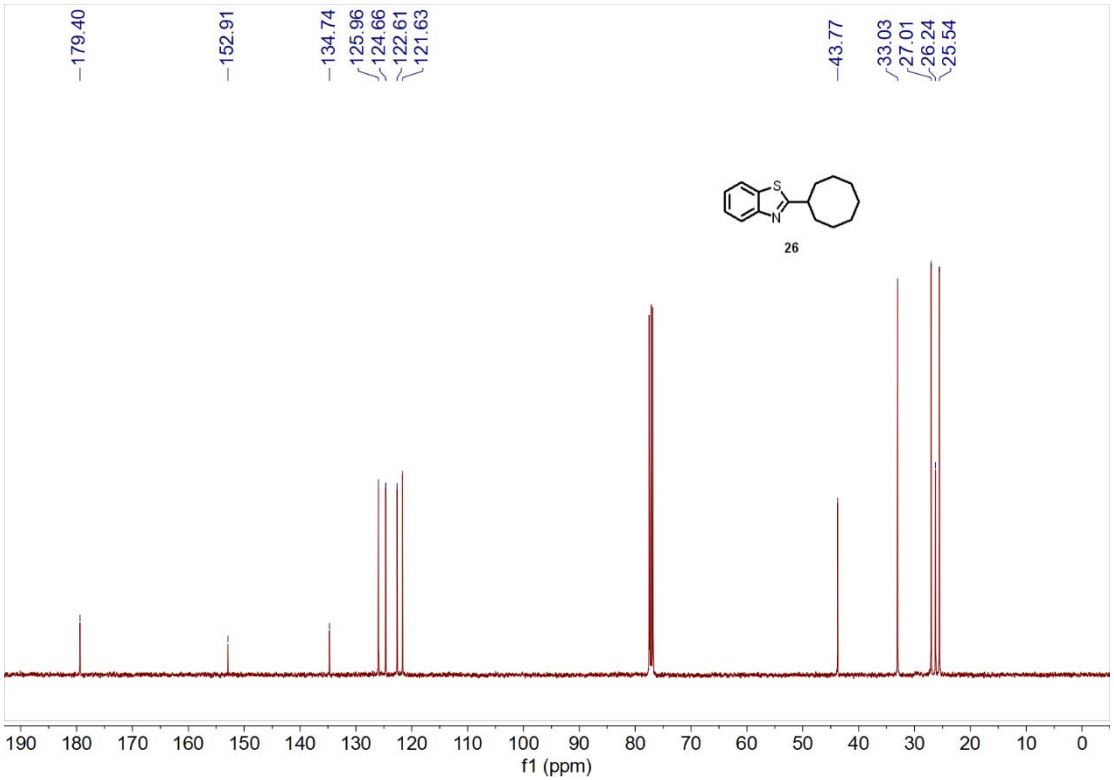
^{1}H NMR spectrum of 25



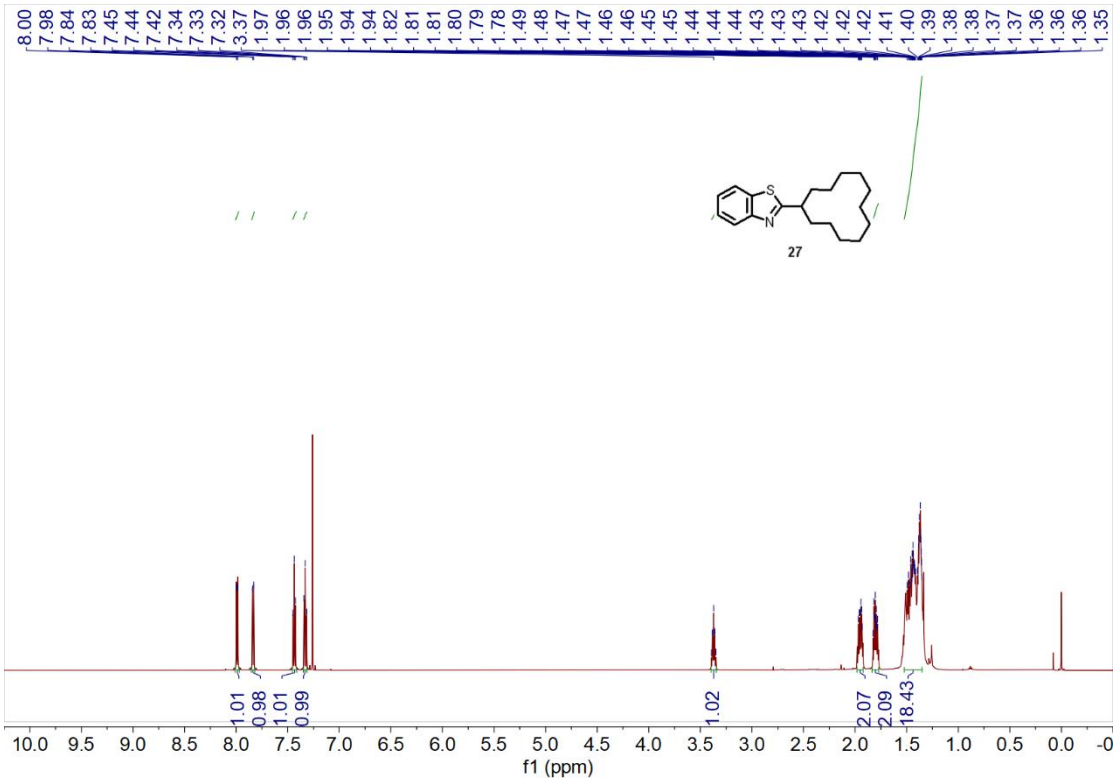
^{13}C NMR spectrum of 25



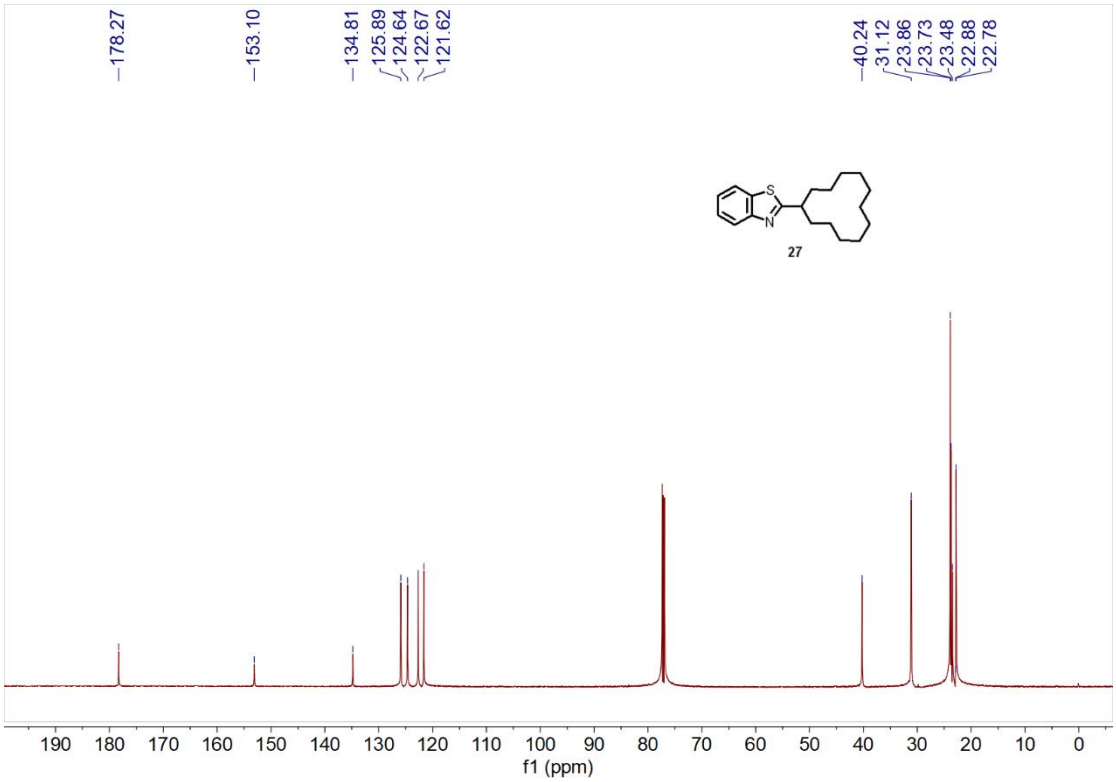
^{1}H NMR spectrum of 26



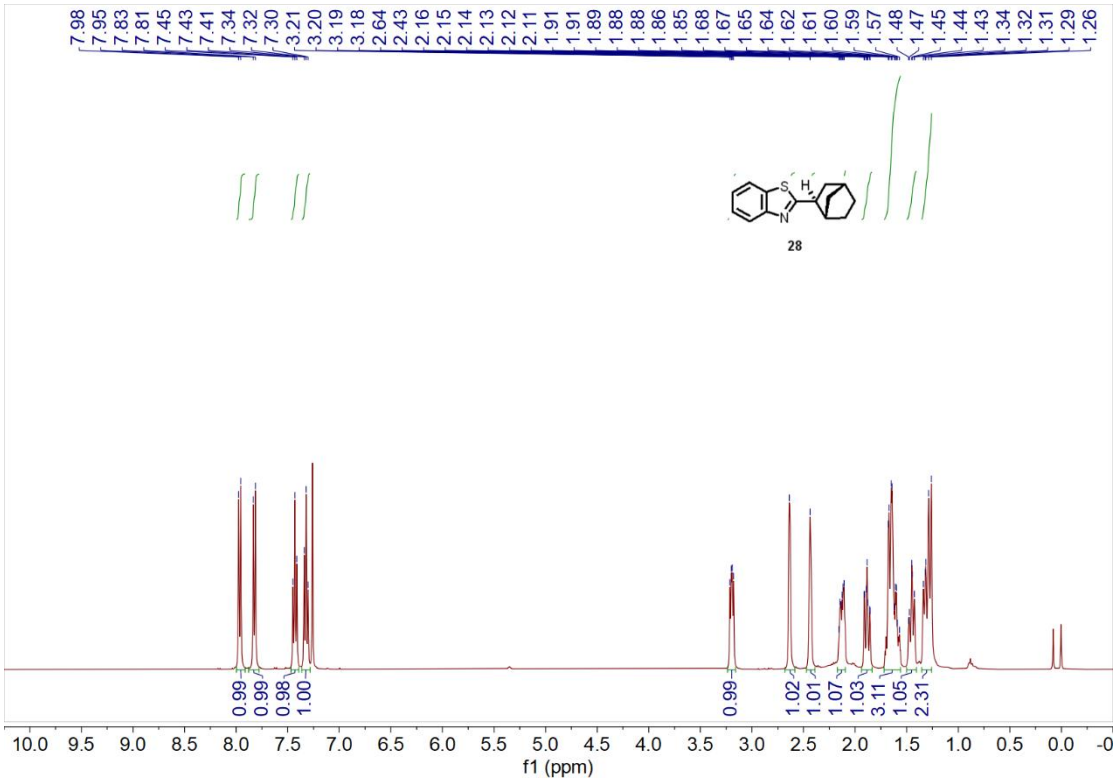
^{13}C NMR spectrum of 26



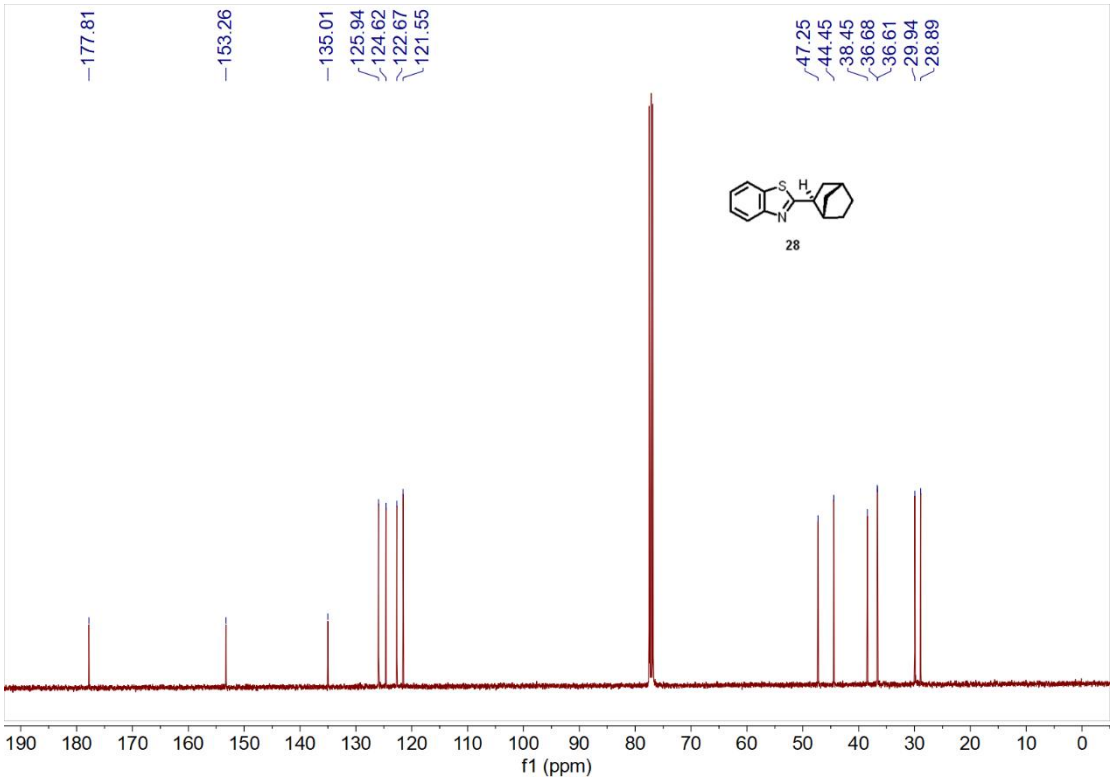
^{1}H NMR spectrum of 27



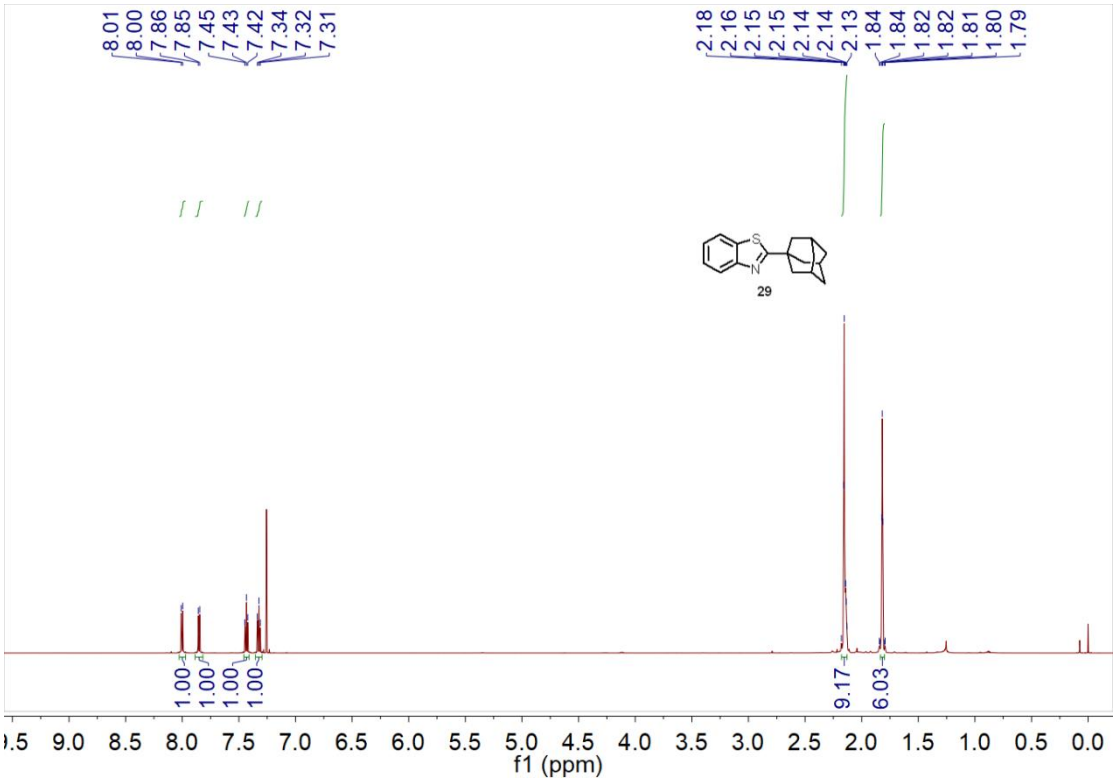
^{13}C NMR spectrum of 27



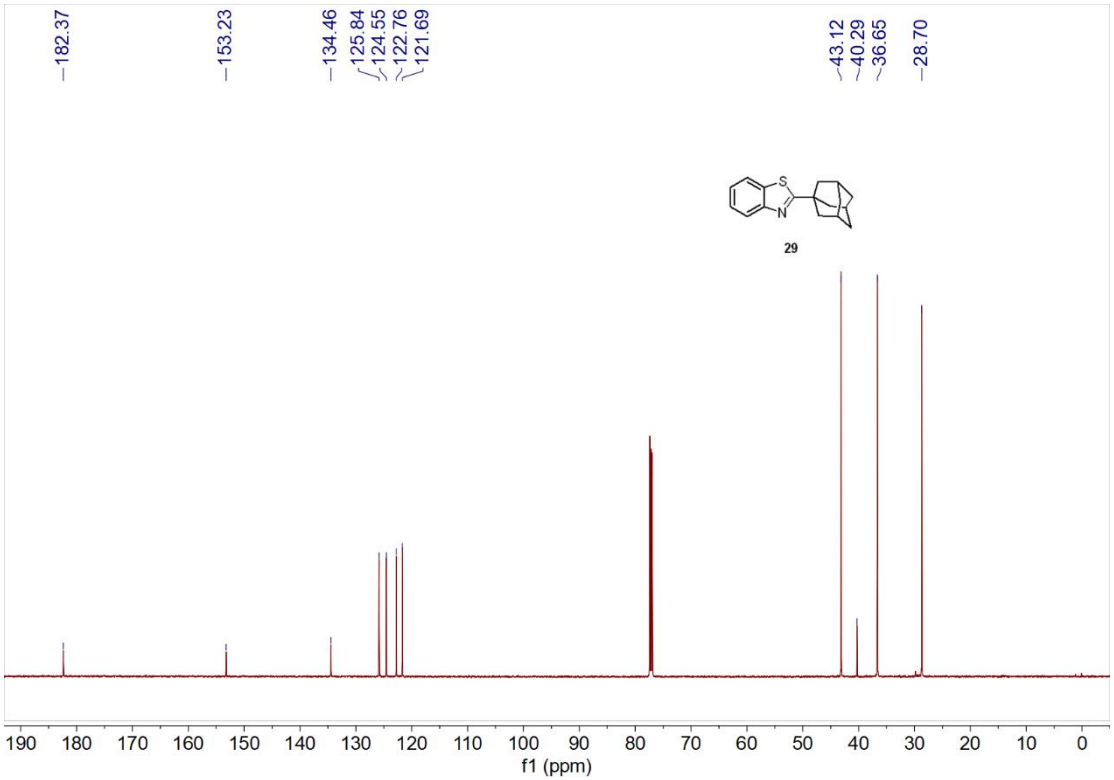
^{1}H NMR spectrum of 28



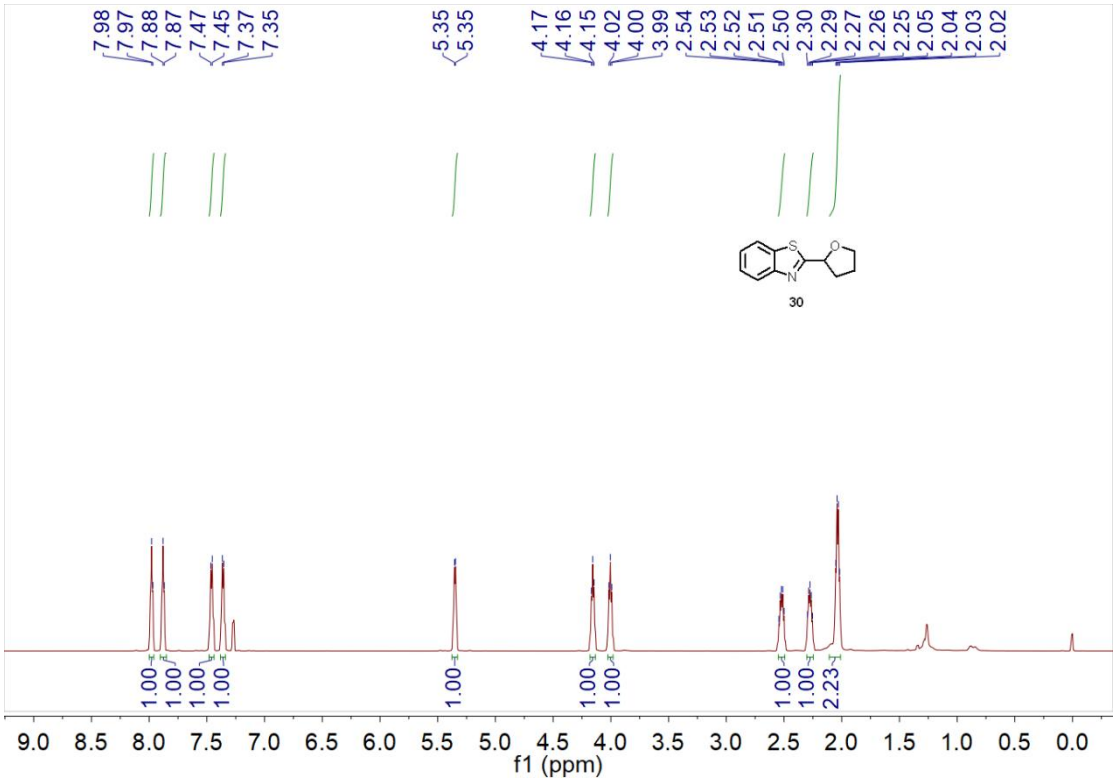
^{13}C NMR spectrum of 28



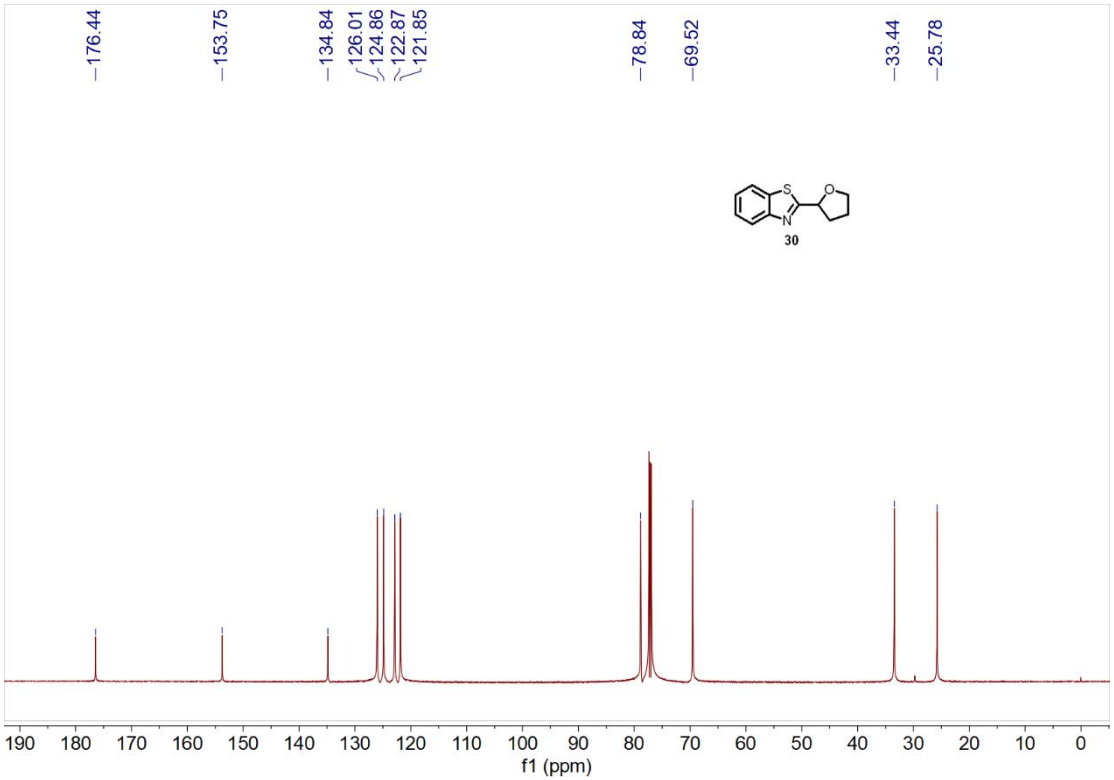
^{1}H NMR spectrum of 29



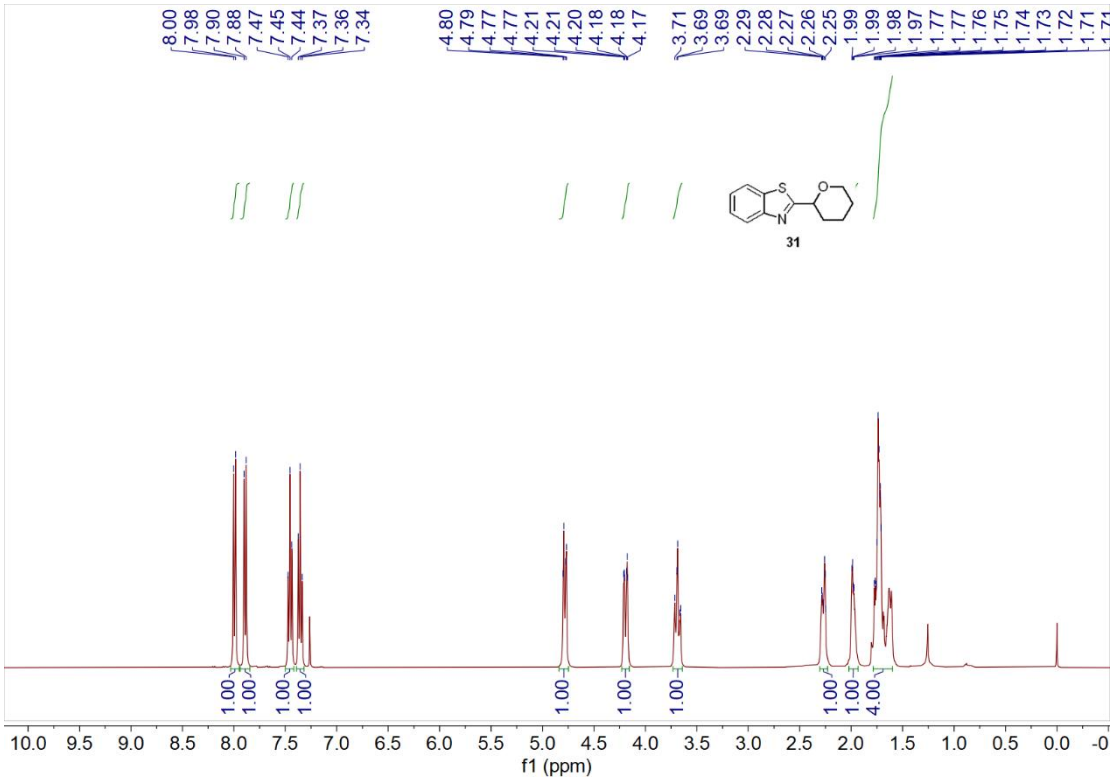
^{13}C NMR spectrum of 29



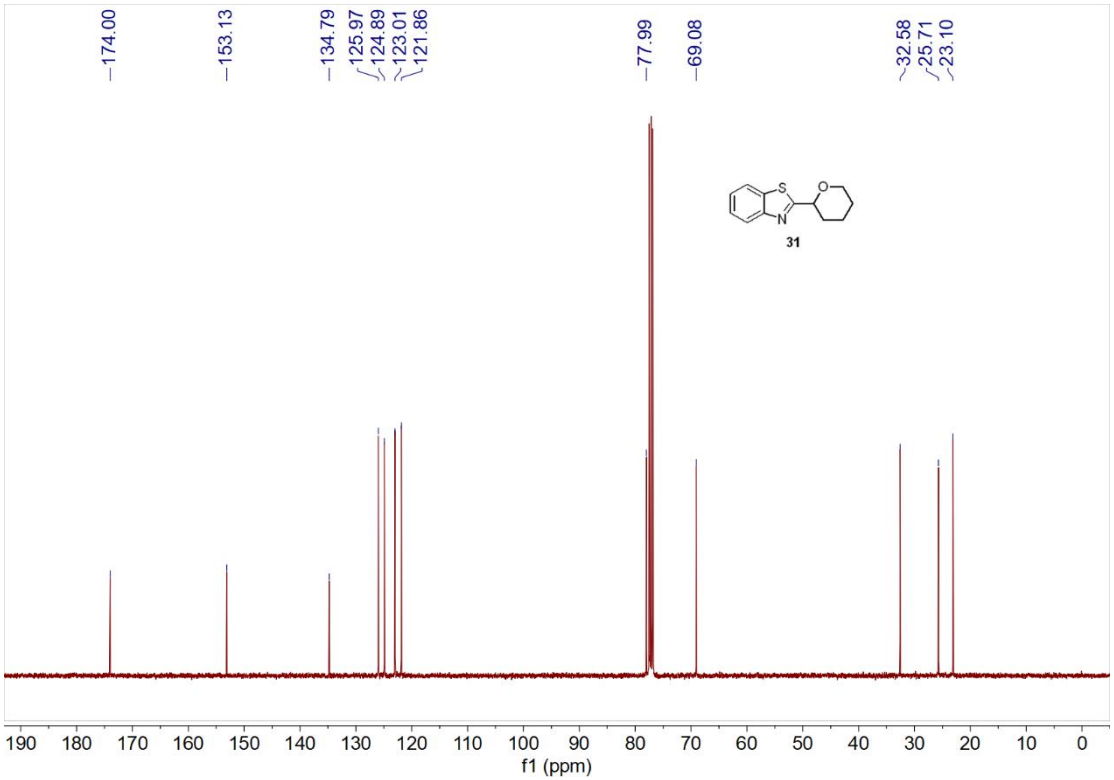
^{1}H NMR spectrum of 30



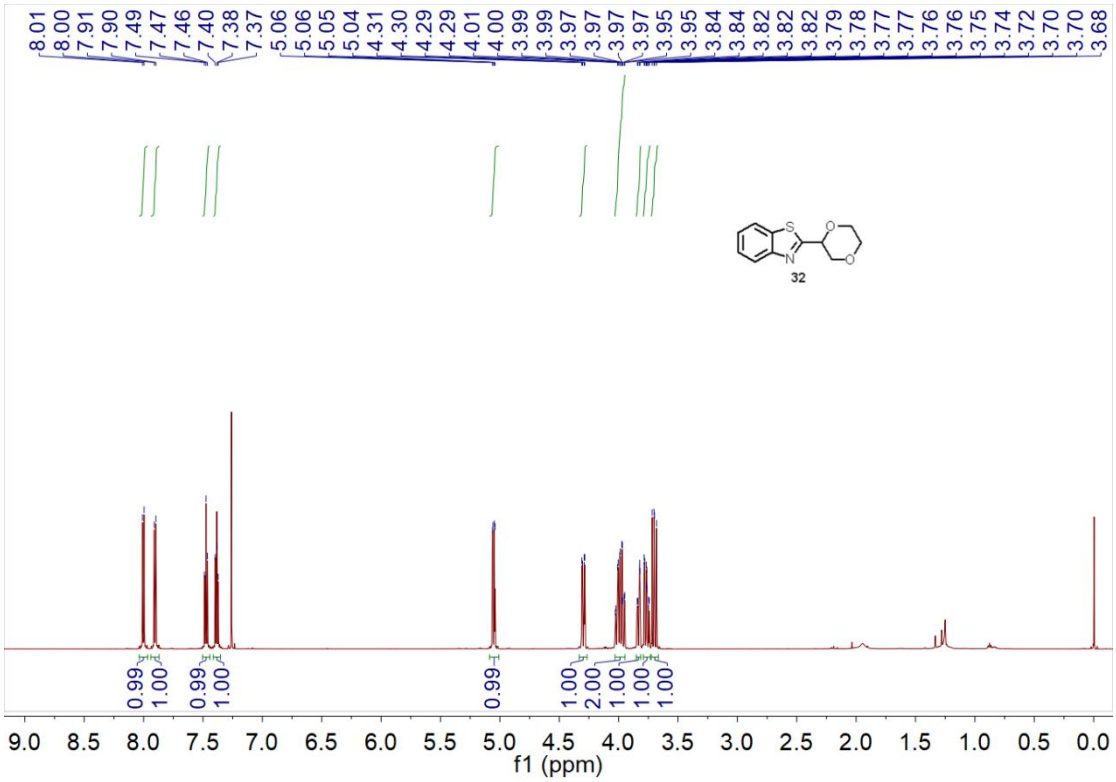
^{13}C NMR spectrum of 30



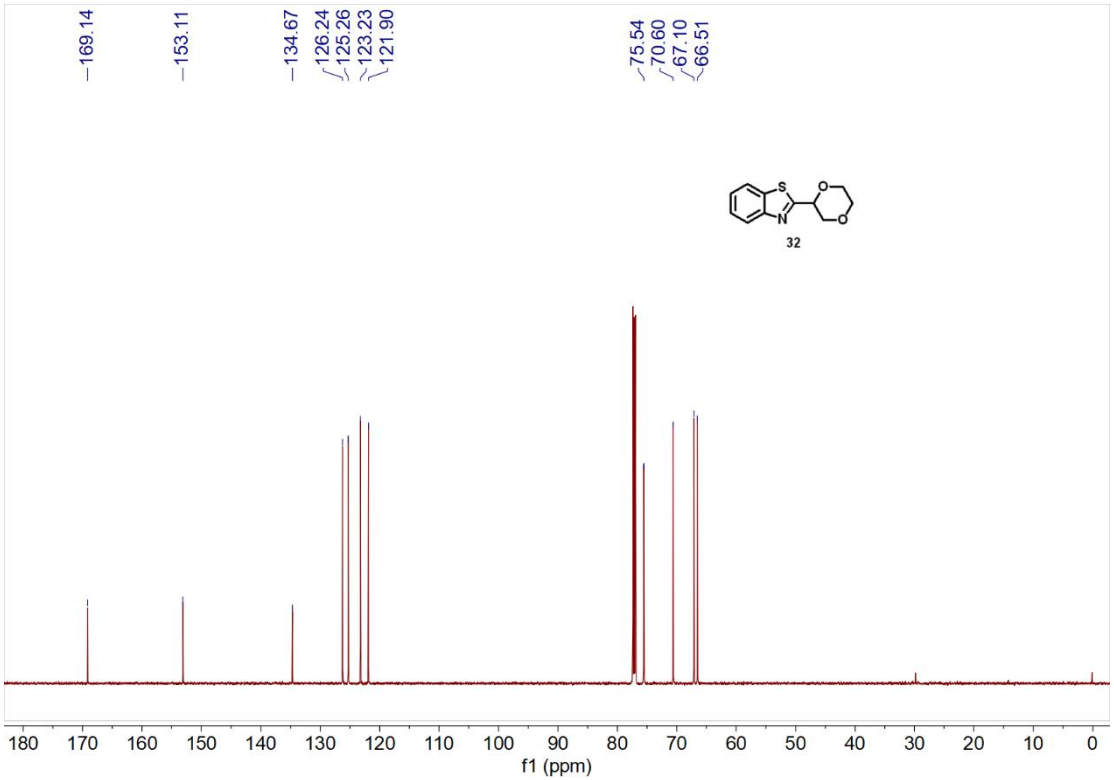
^{1}H NMR spectrum of 31



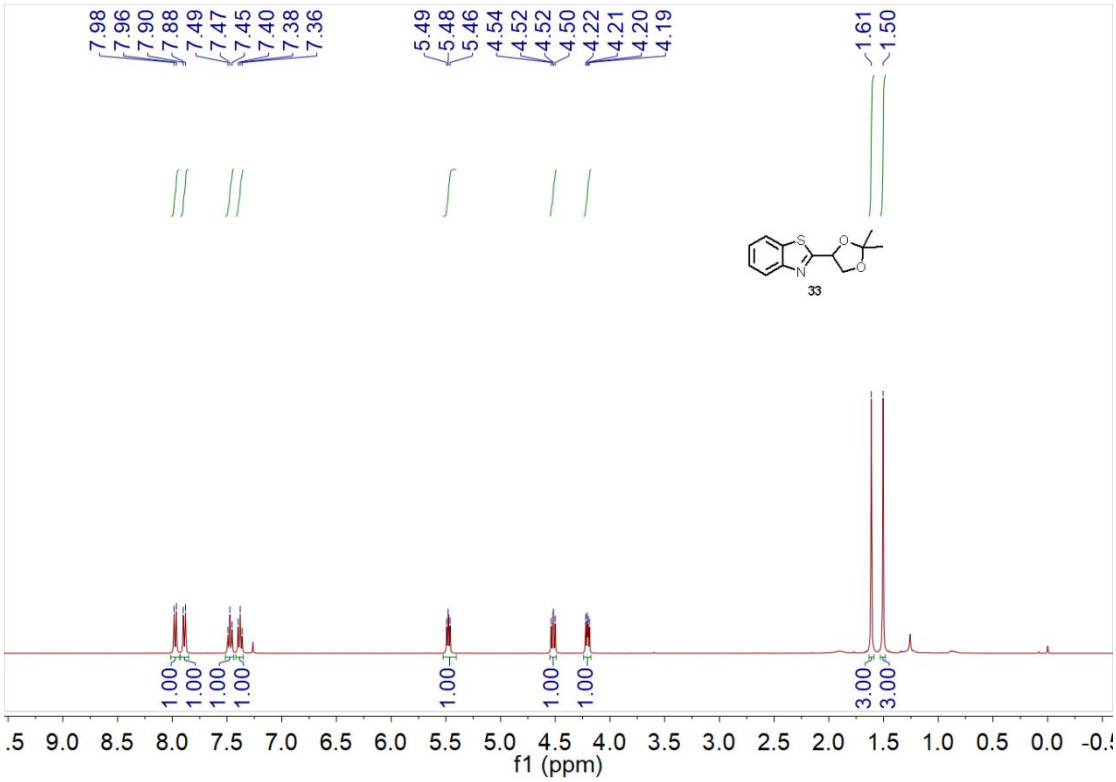
^{13}C NMR spectrum of 31



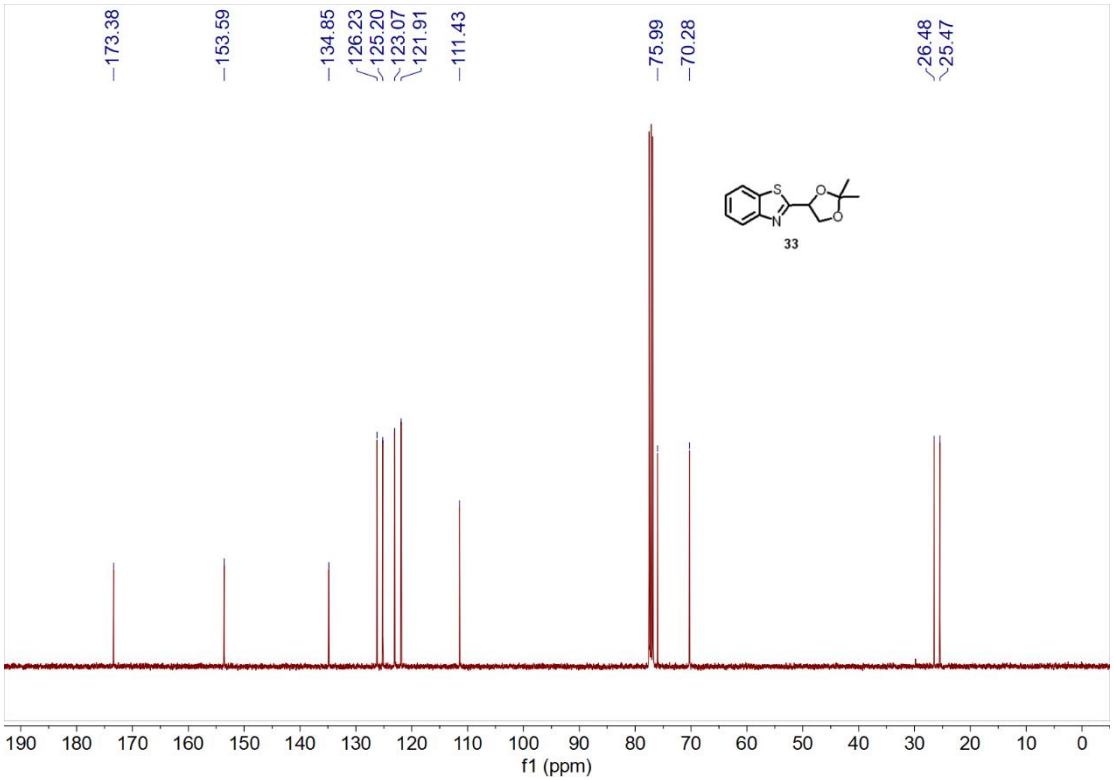
^{1}H NMR spectrum of 32



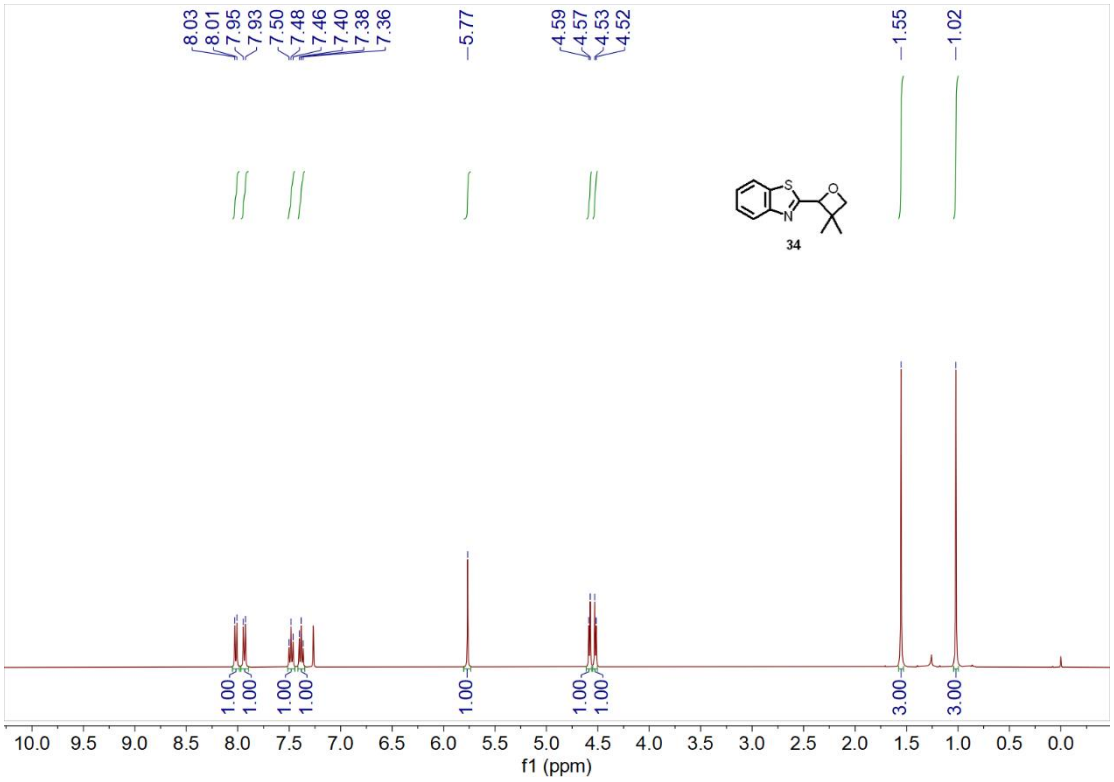
^{13}C NMR spectrum of 32



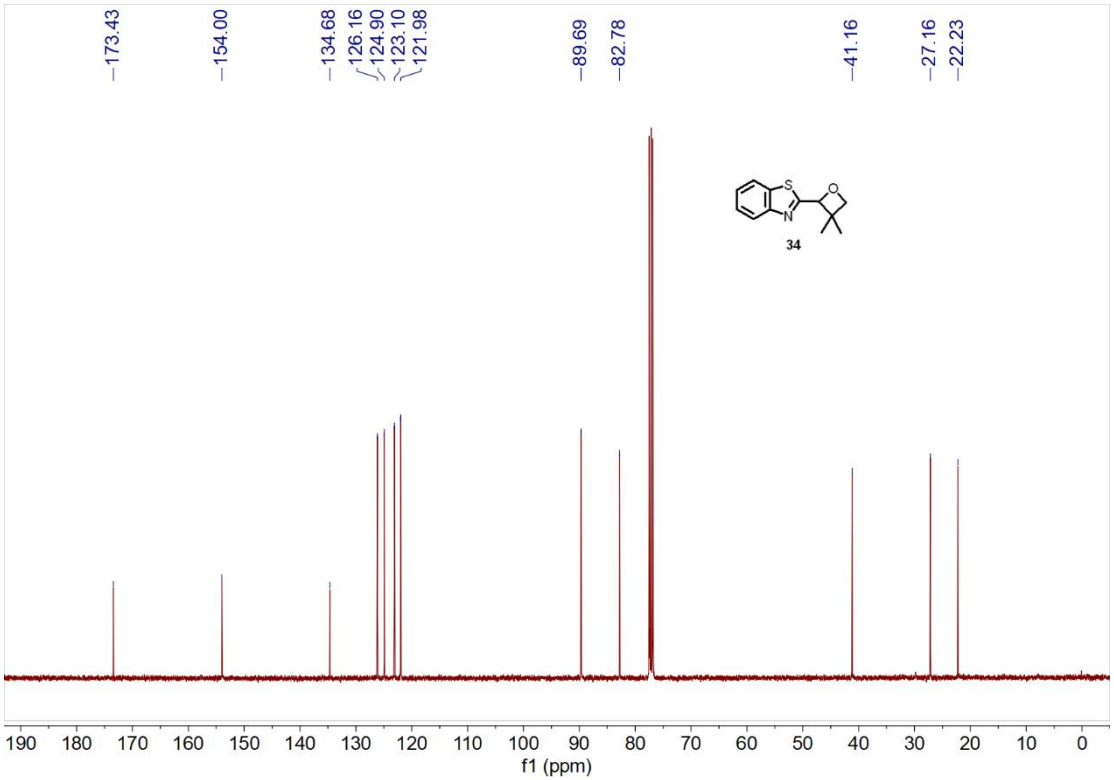
^{1}H NMR spectrum of 33



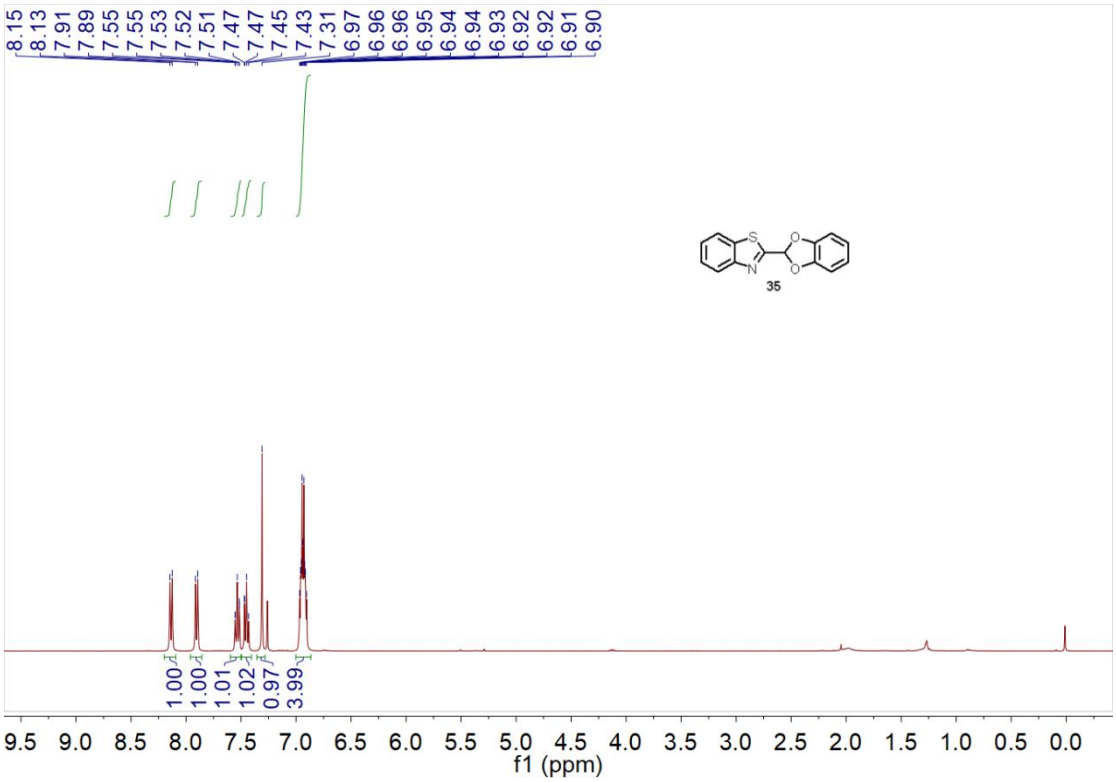
^{13}C NMR spectrum of 33



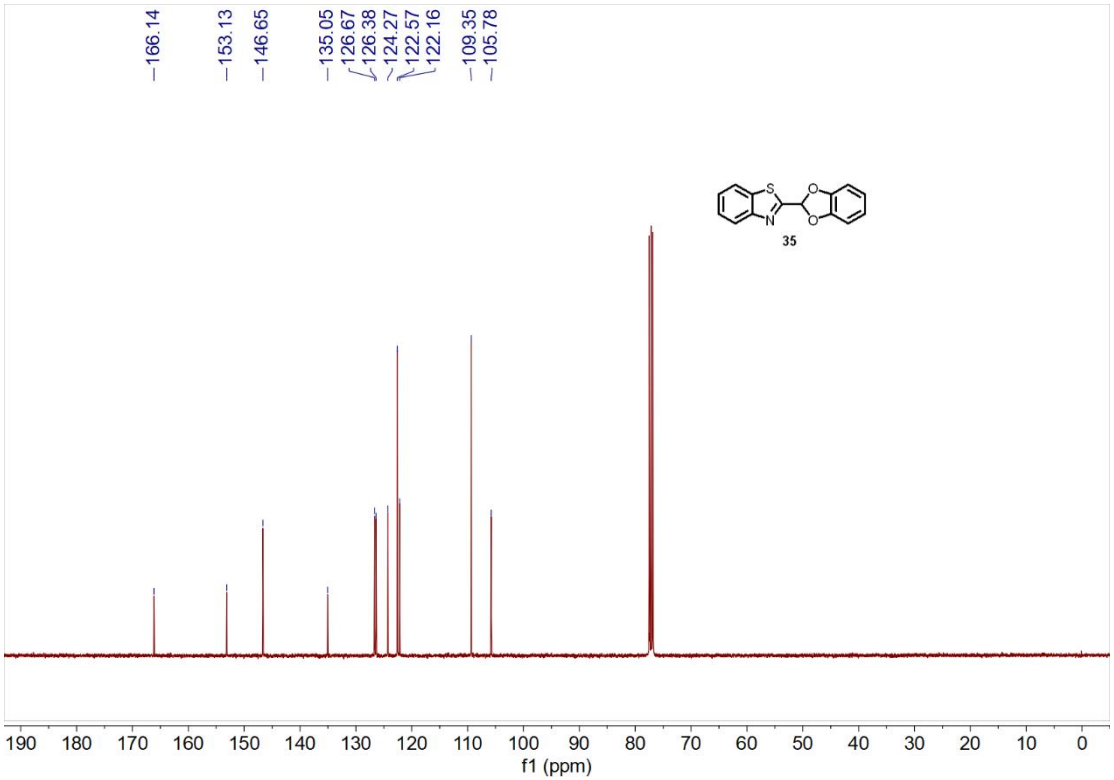
^{1}H NMR spectrum of 34



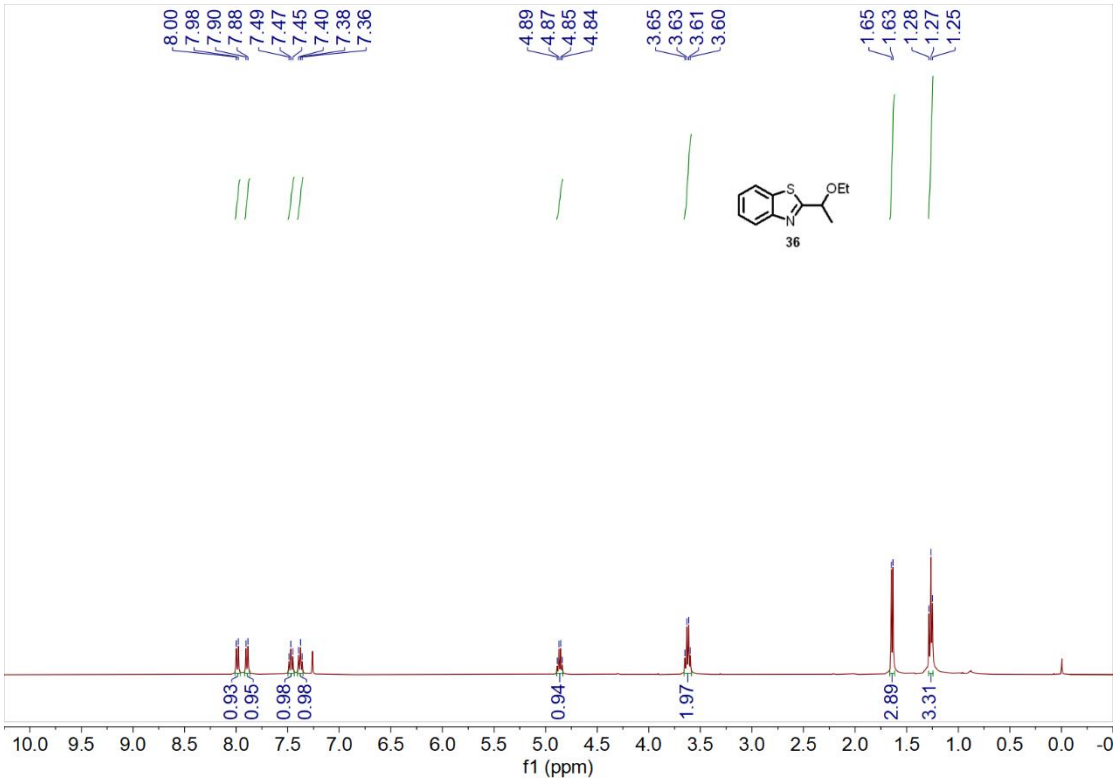
^{13}C NMR spectrum of 34



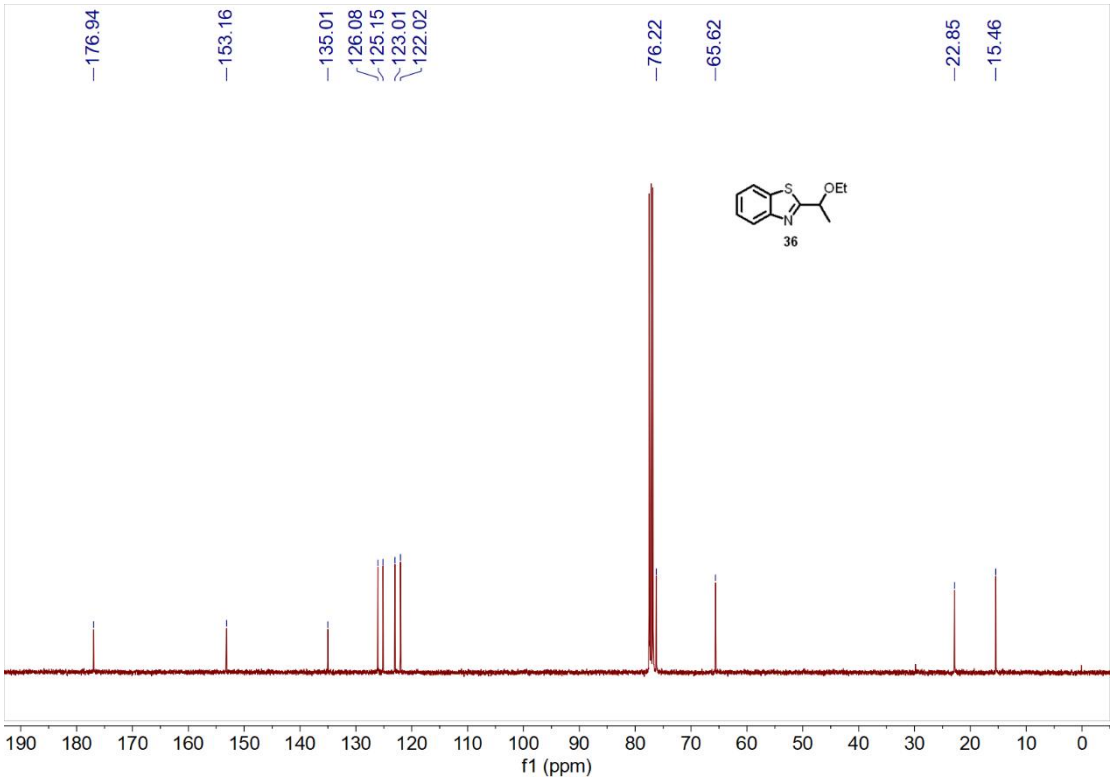
^{1}H NMR spectrum of 35



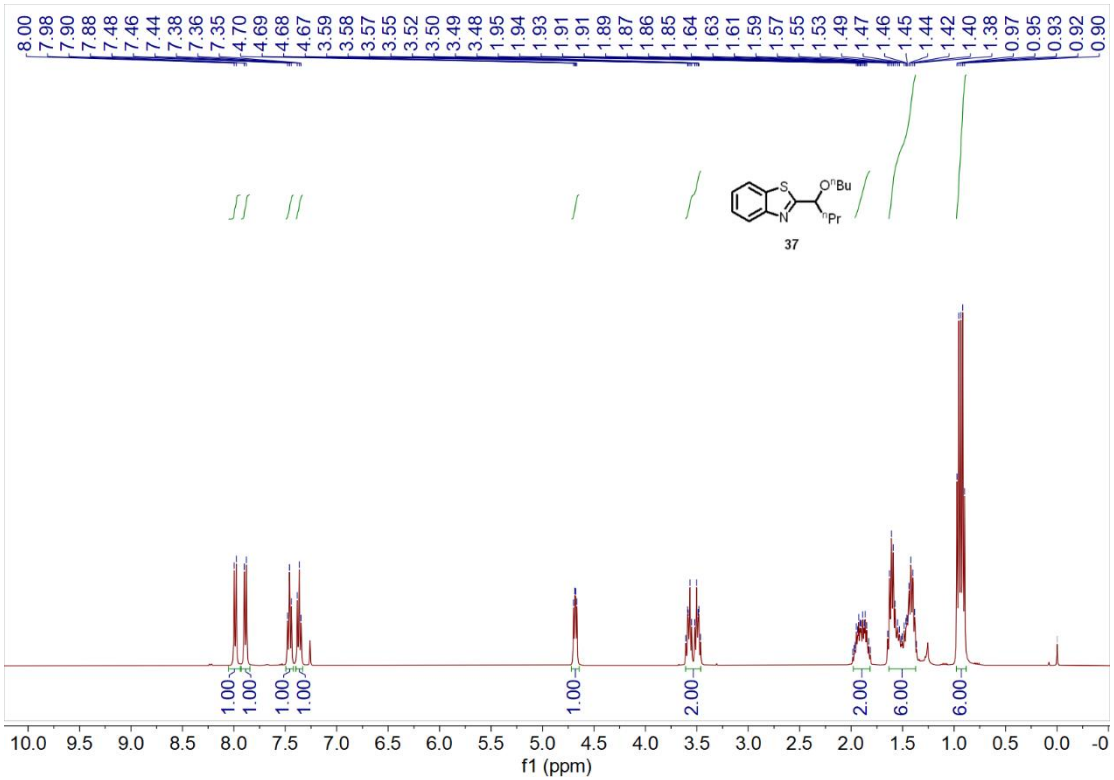
^{13}C NMR spectrum of 35



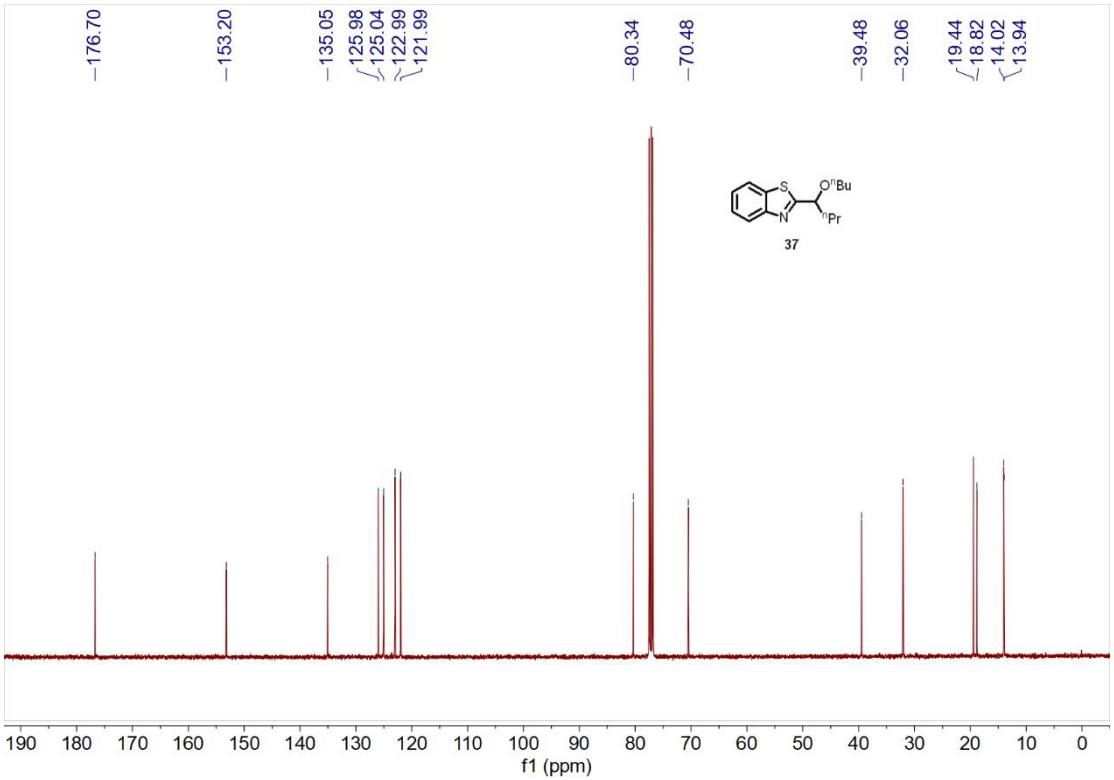
^{1}H NMR spectrum of 36



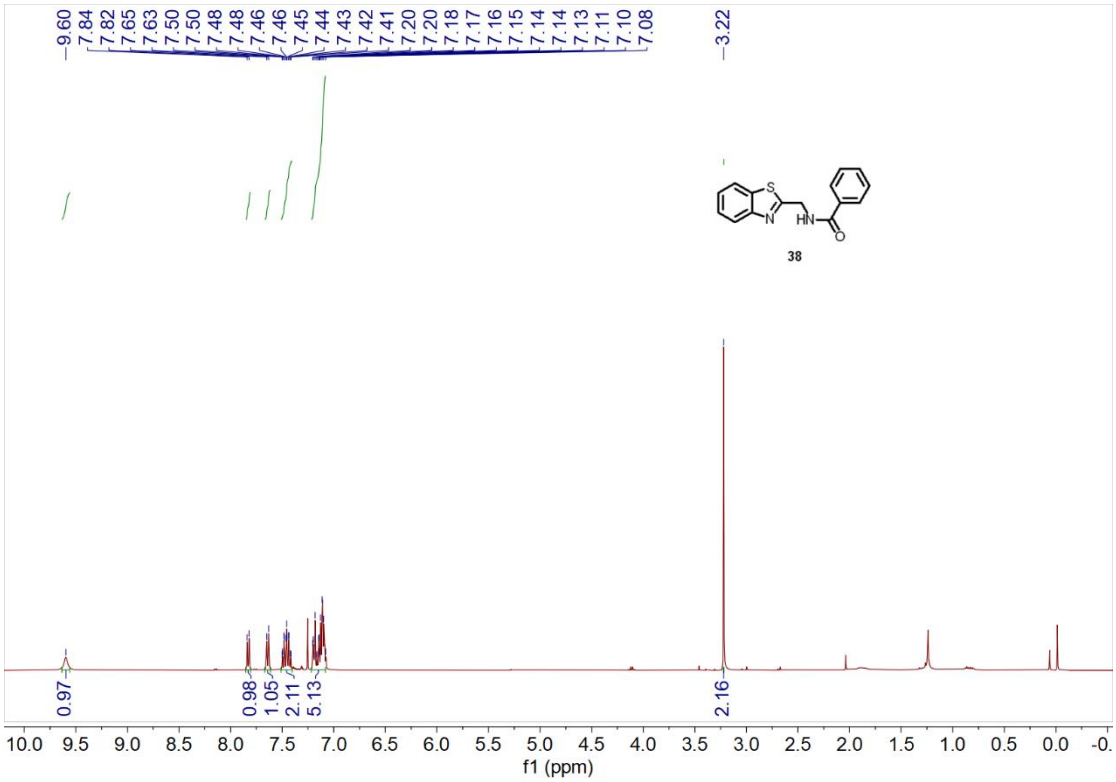
^{13}C NMR spectrum of 36



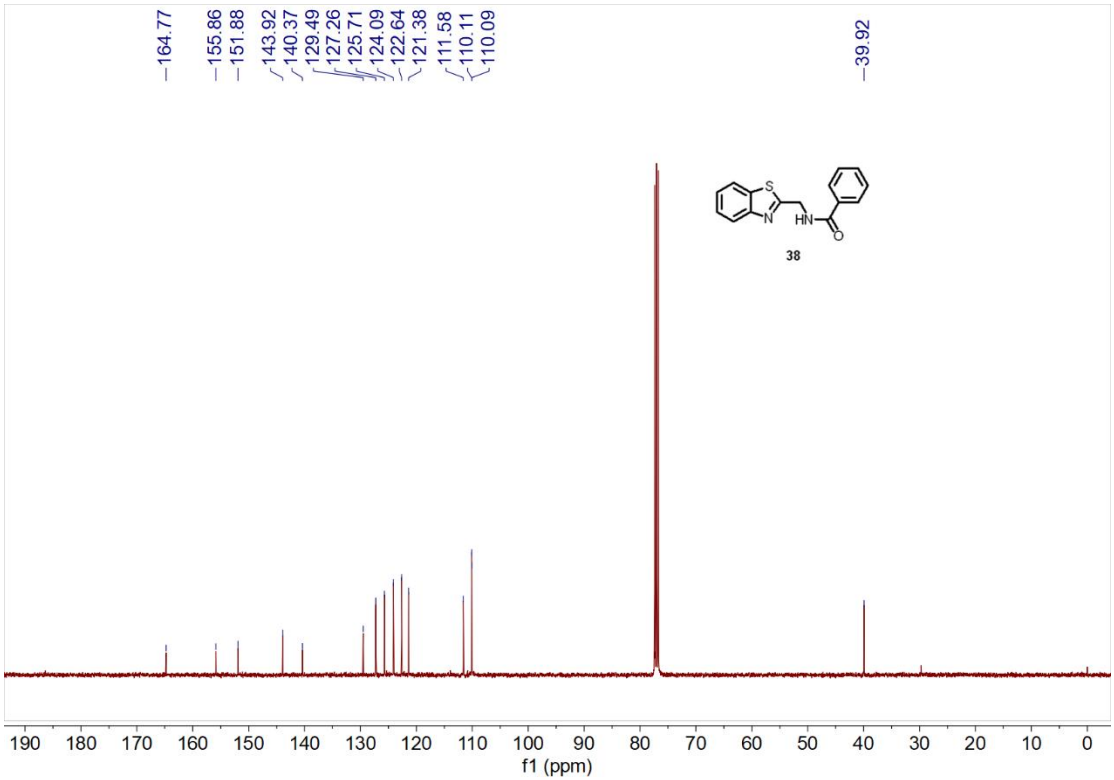
^{1}H NMR spectrum of 37



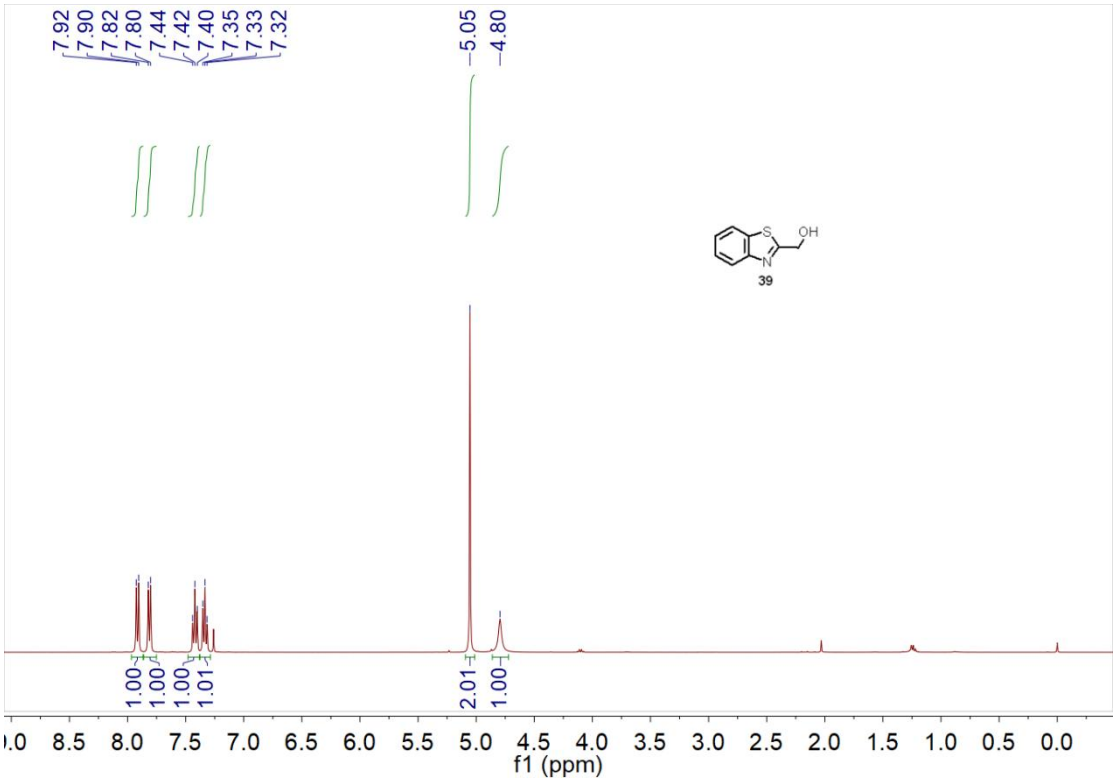
^{13}C NMR spectrum of 37



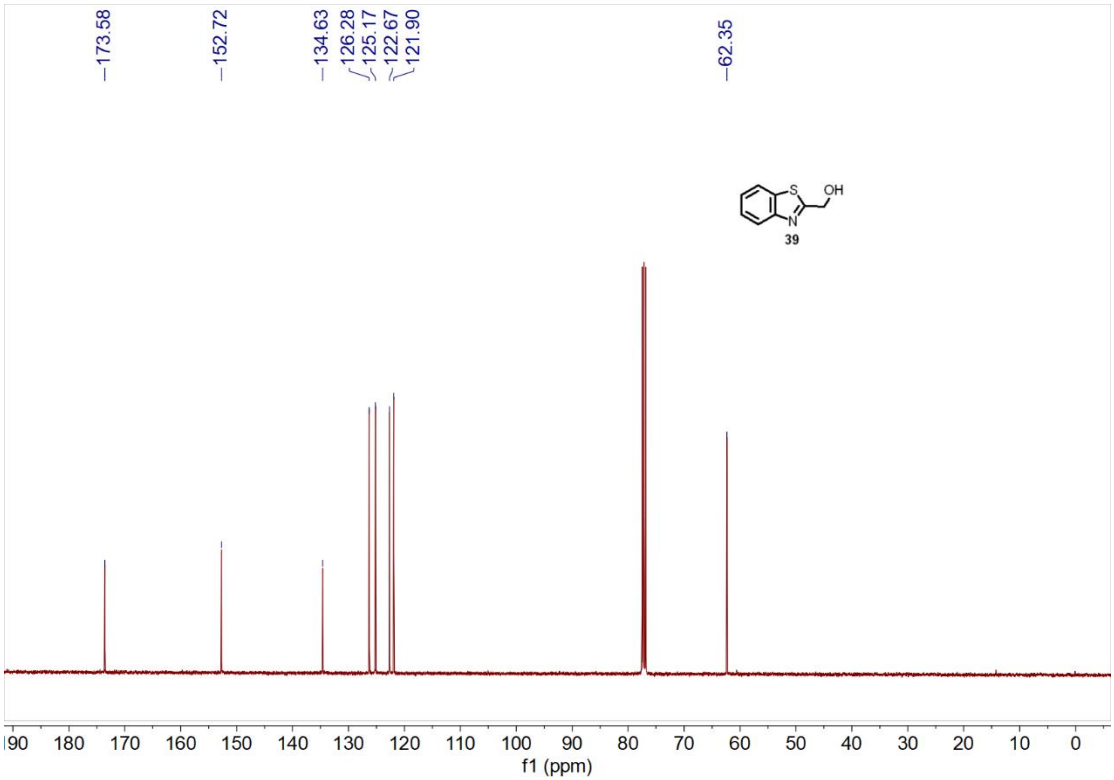
^{1}H NMR spectrum of 38



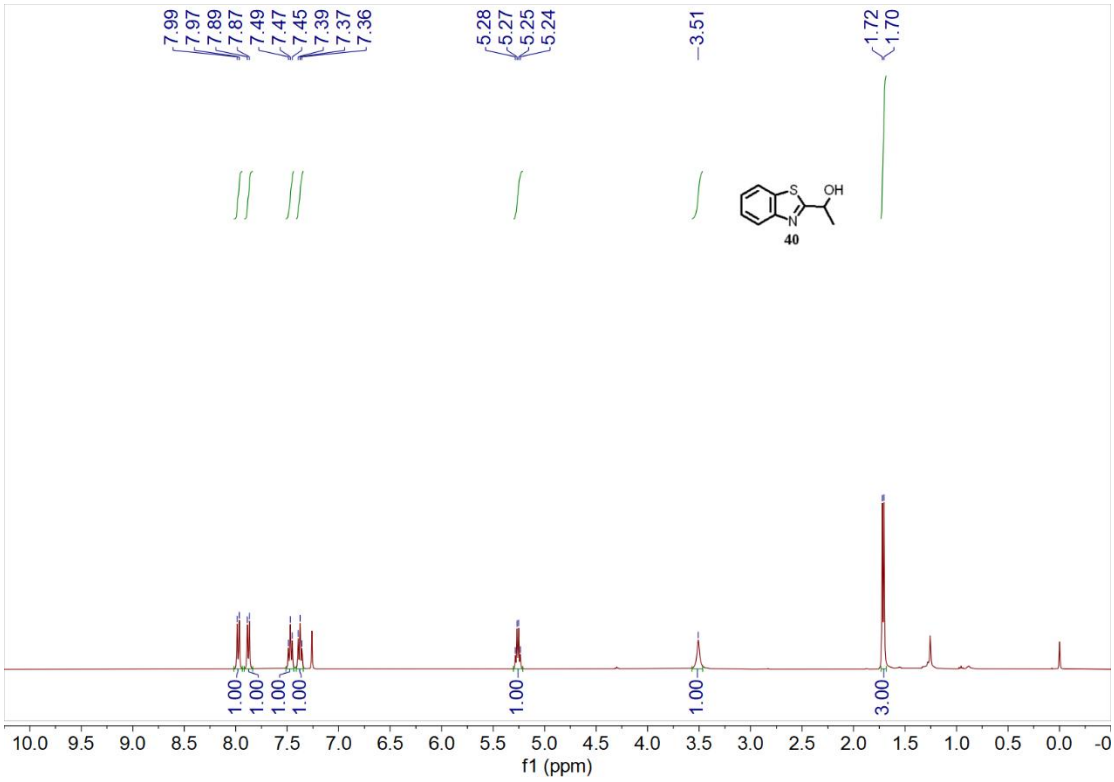
^{13}C NMR spectrum of 38



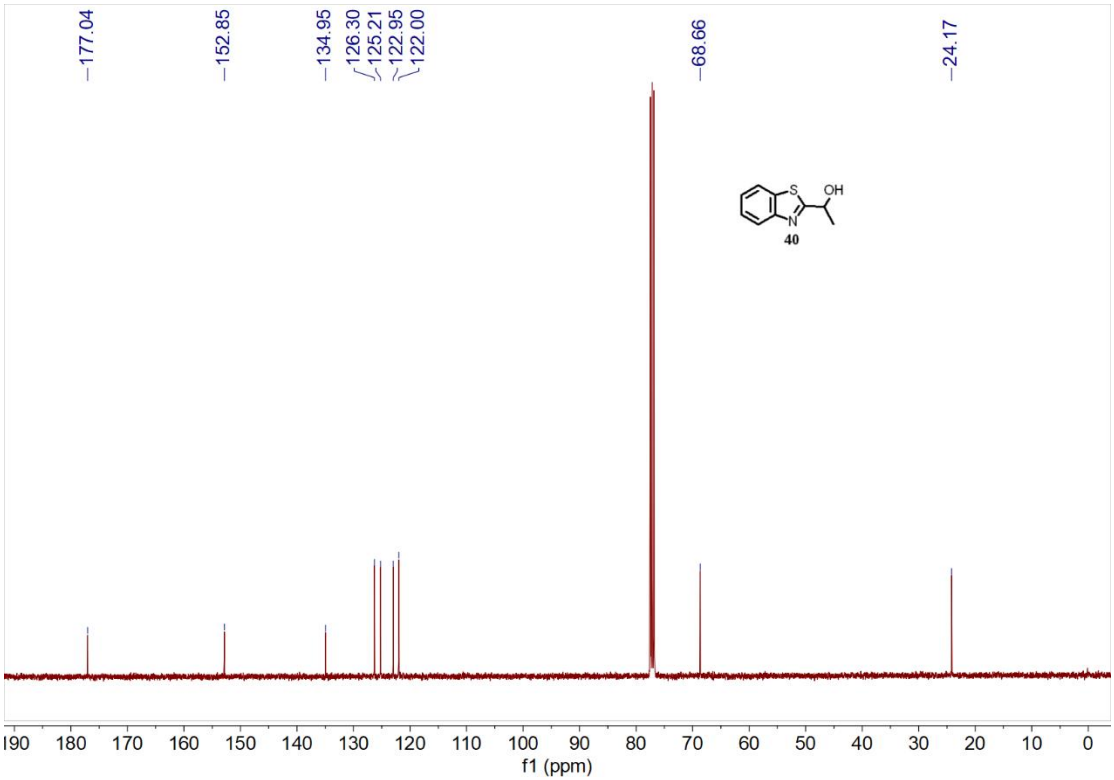
^{1}H NMR spectrum of 39



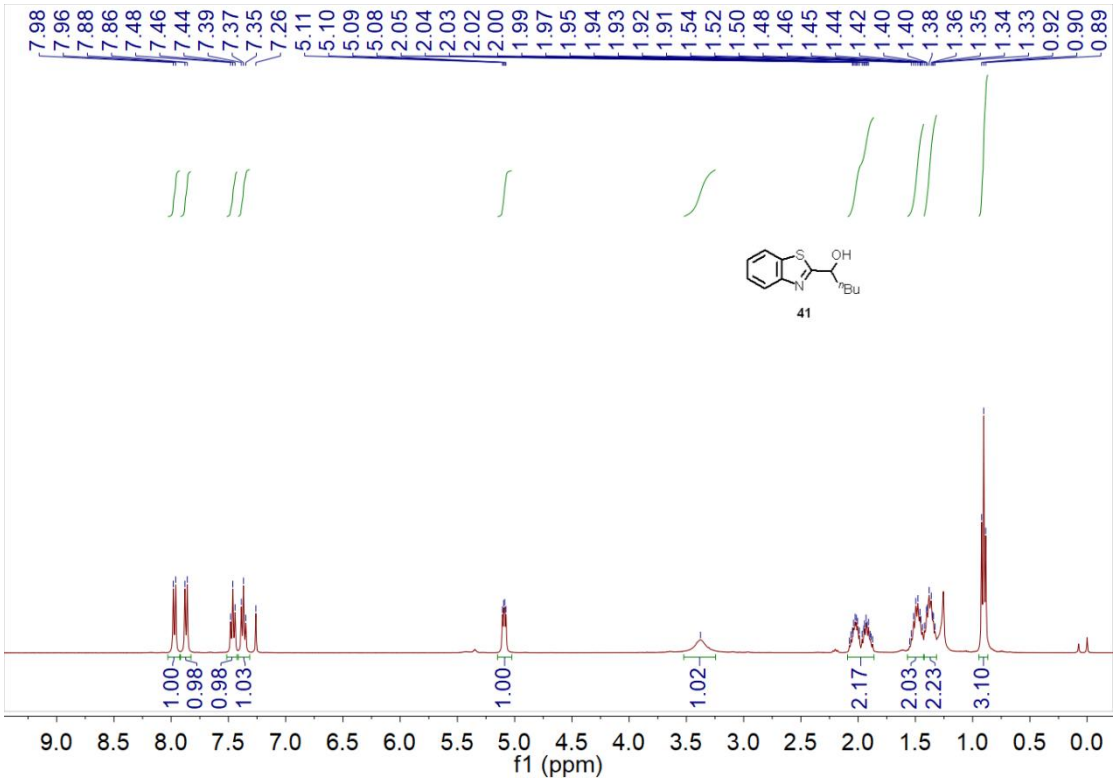
^{13}C NMR spectrum of 39



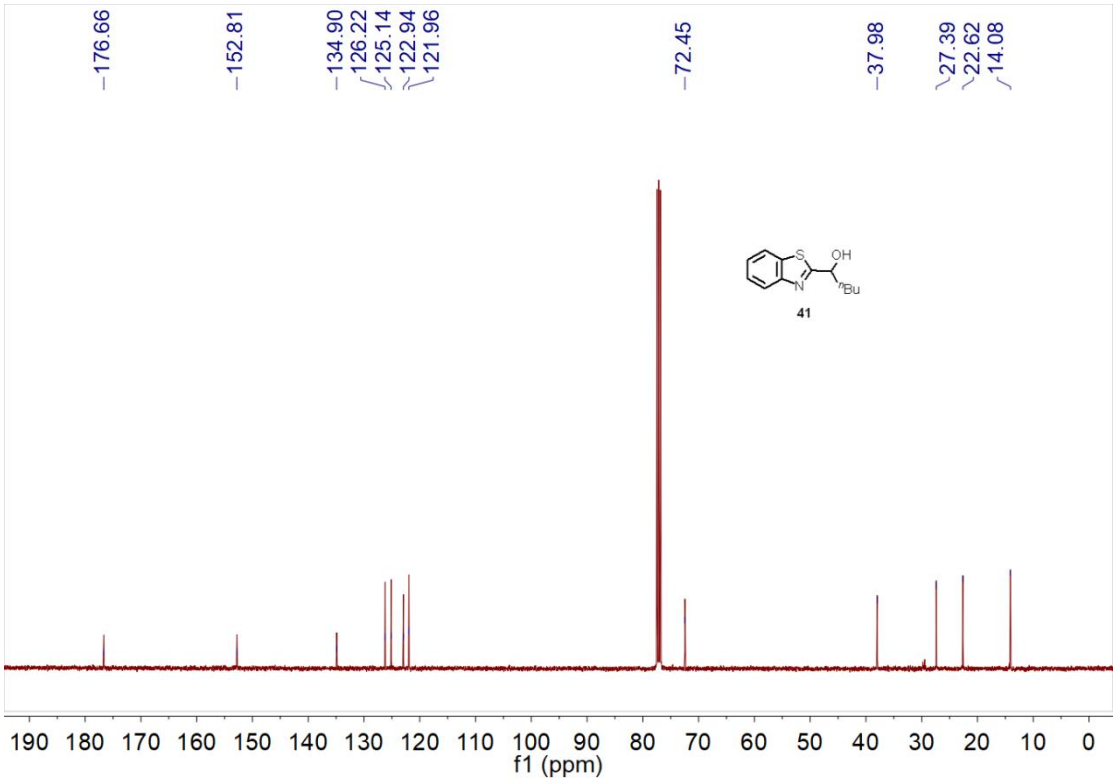
^{1}H NMR spectrum of 40



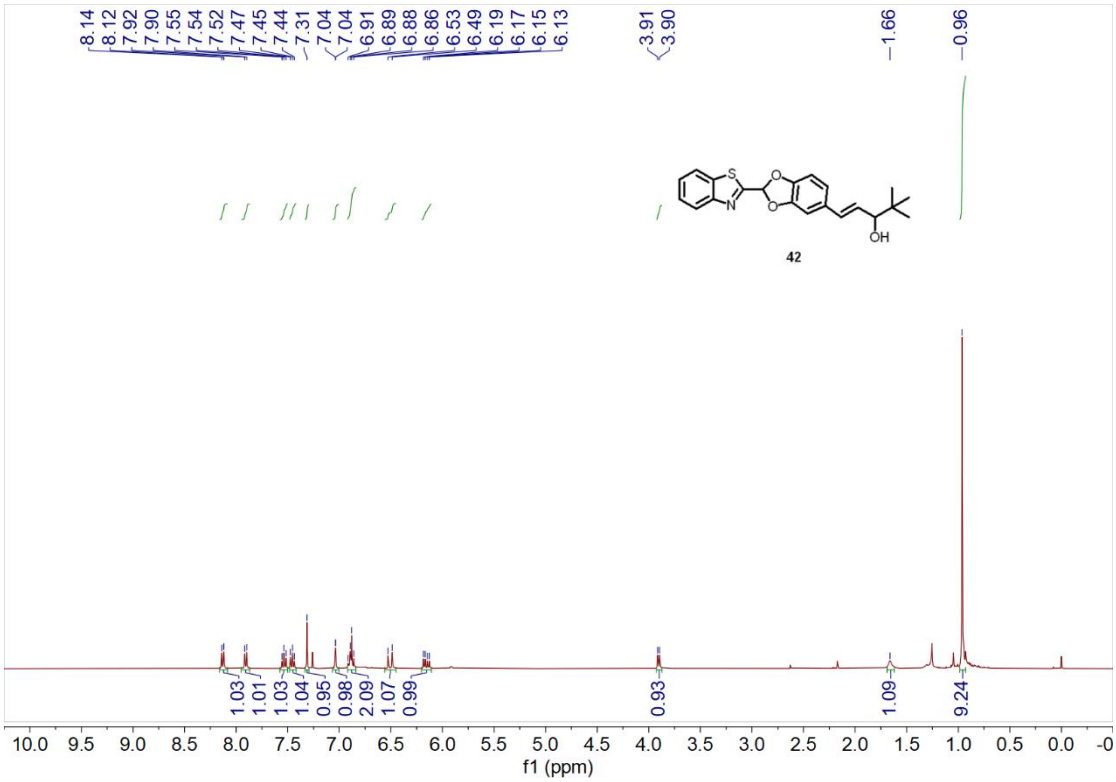
^{13}C NMR spectrum of 40



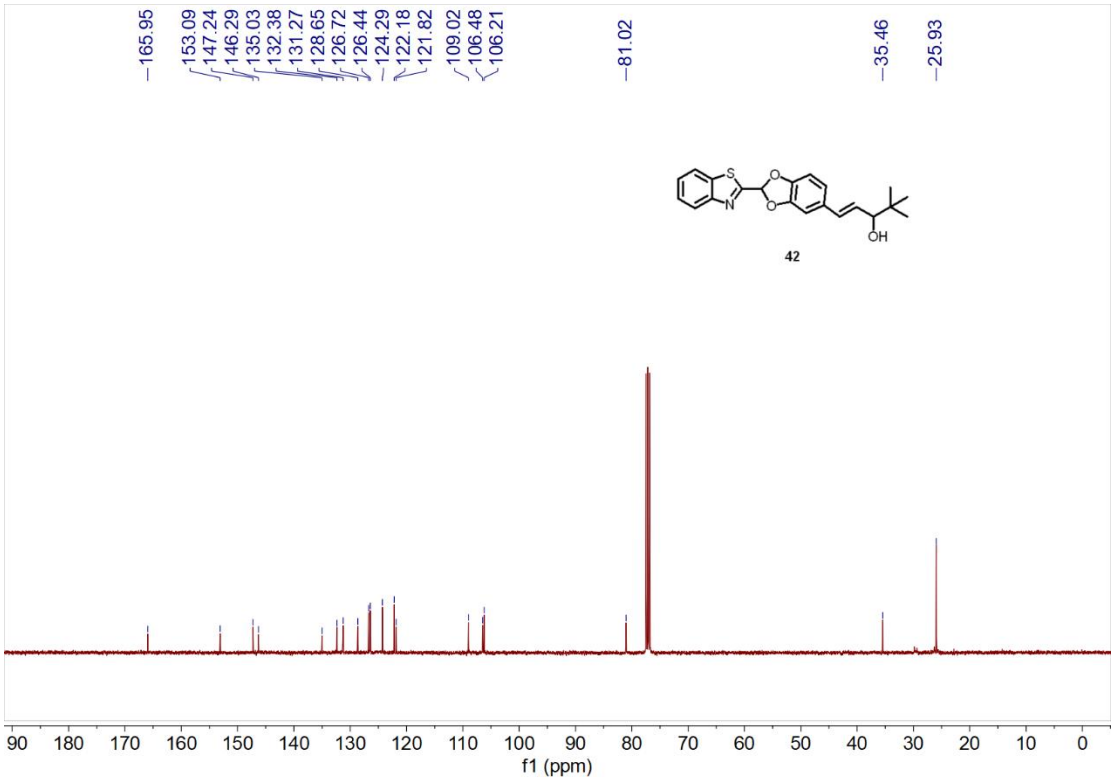
^{1}H NMR spectrum of 41



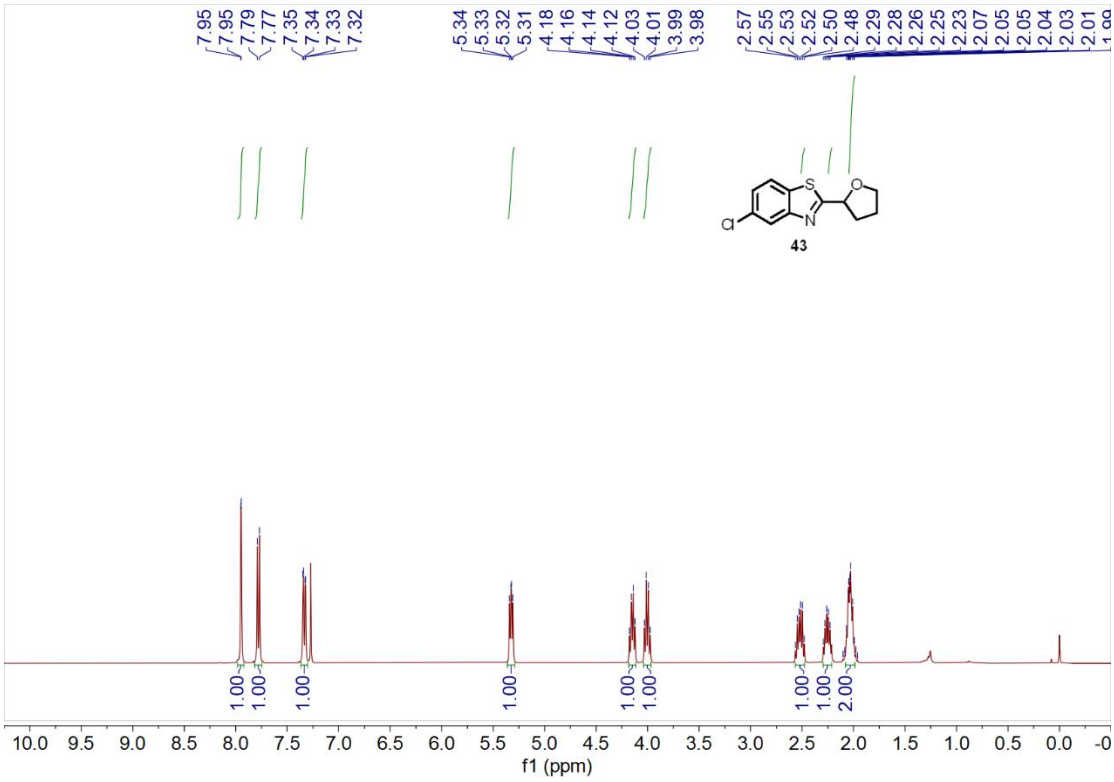
^{13}C NMR spectrum of 41



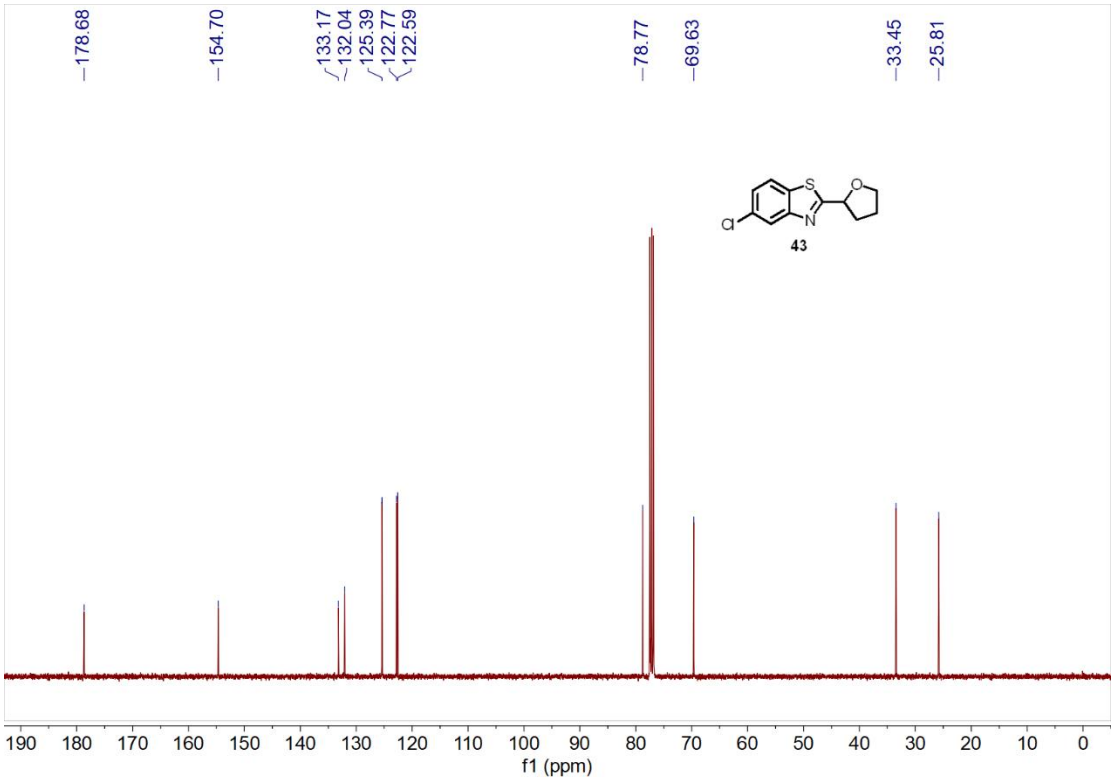
^{1}H NMR spectrum of 42



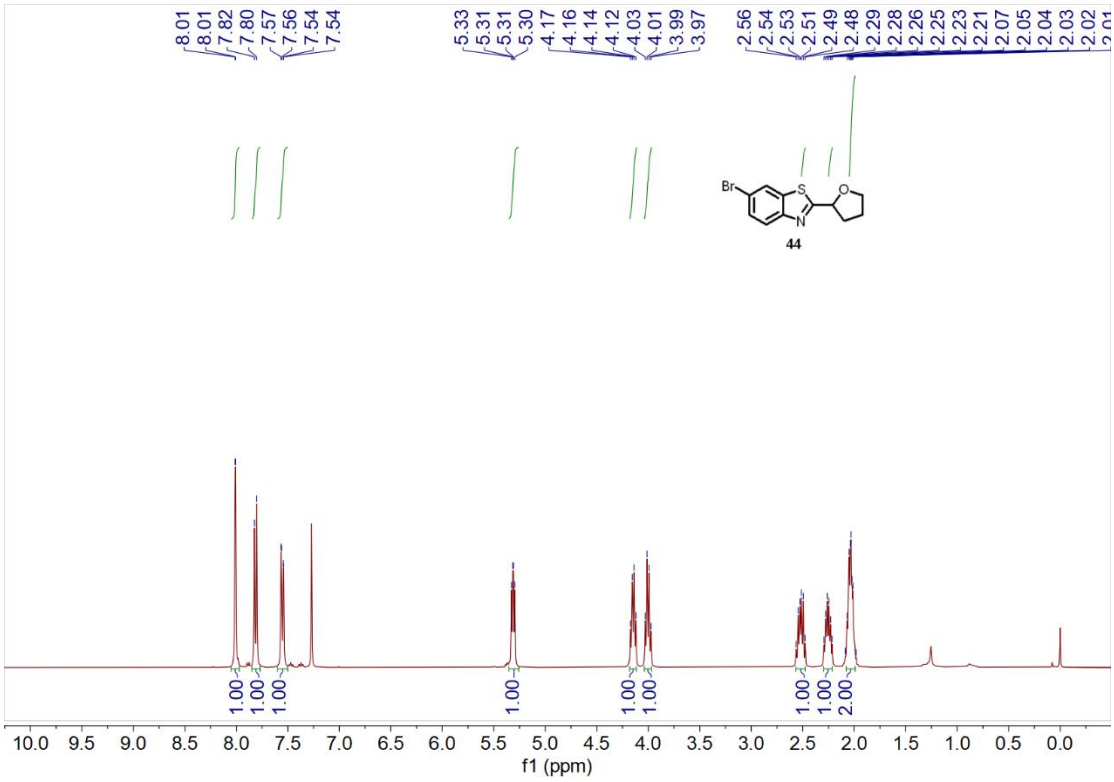
^{13}C NMR spectrum of 42



^{1}H NMR spectrum of 43

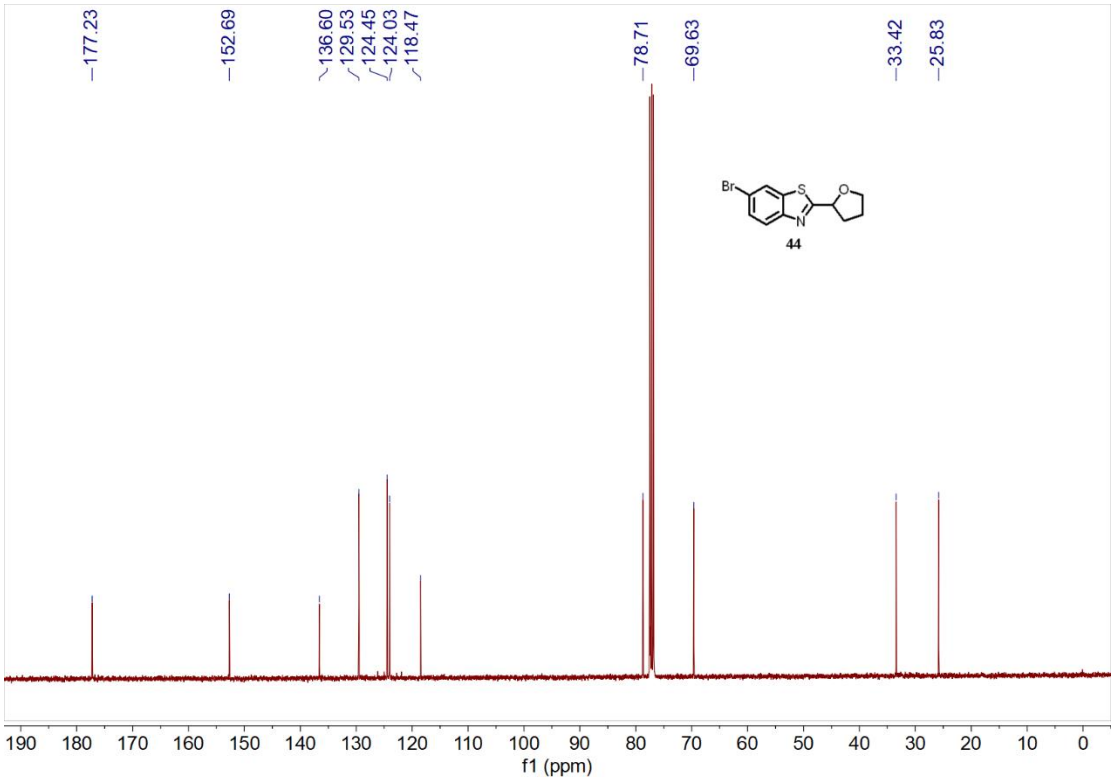


^{13}C NMR spectrum of 43

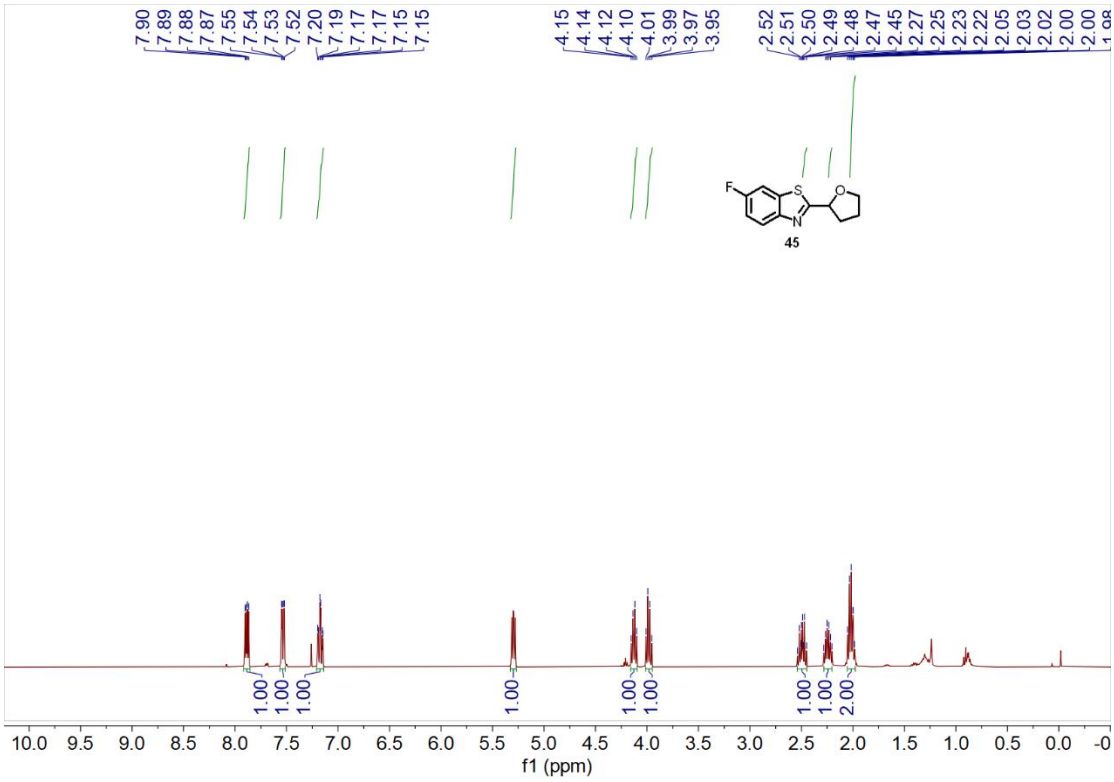


^{1}H NMR spectrum of

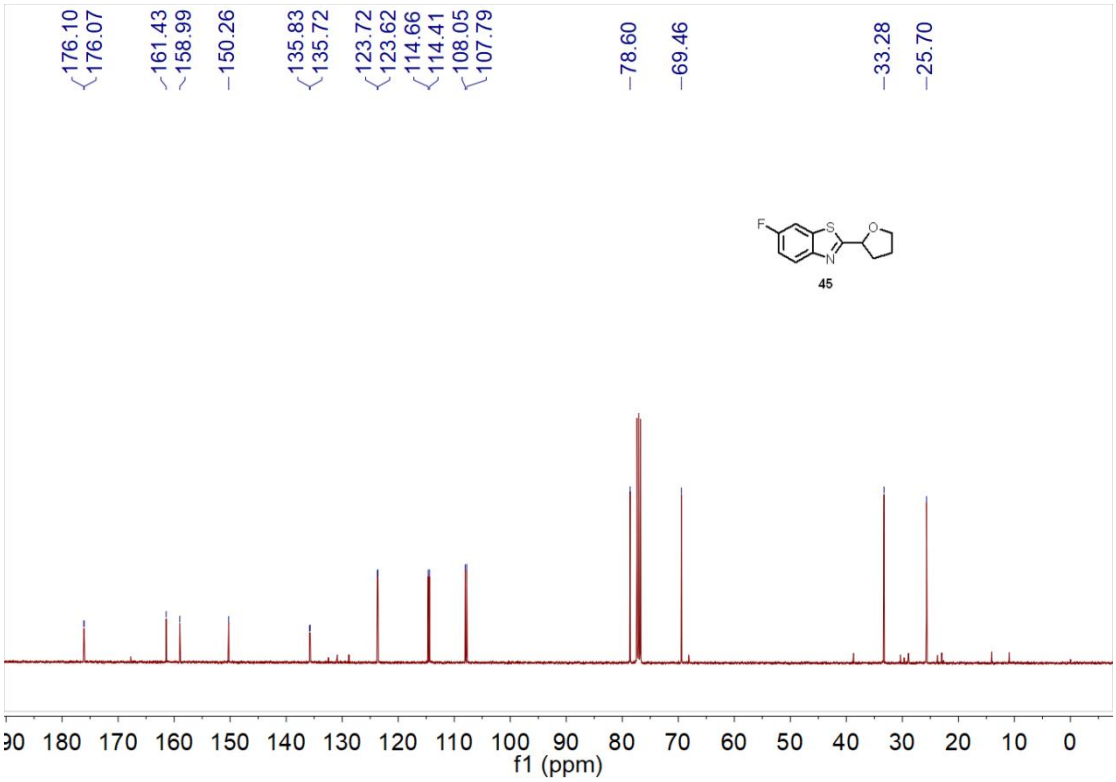
44



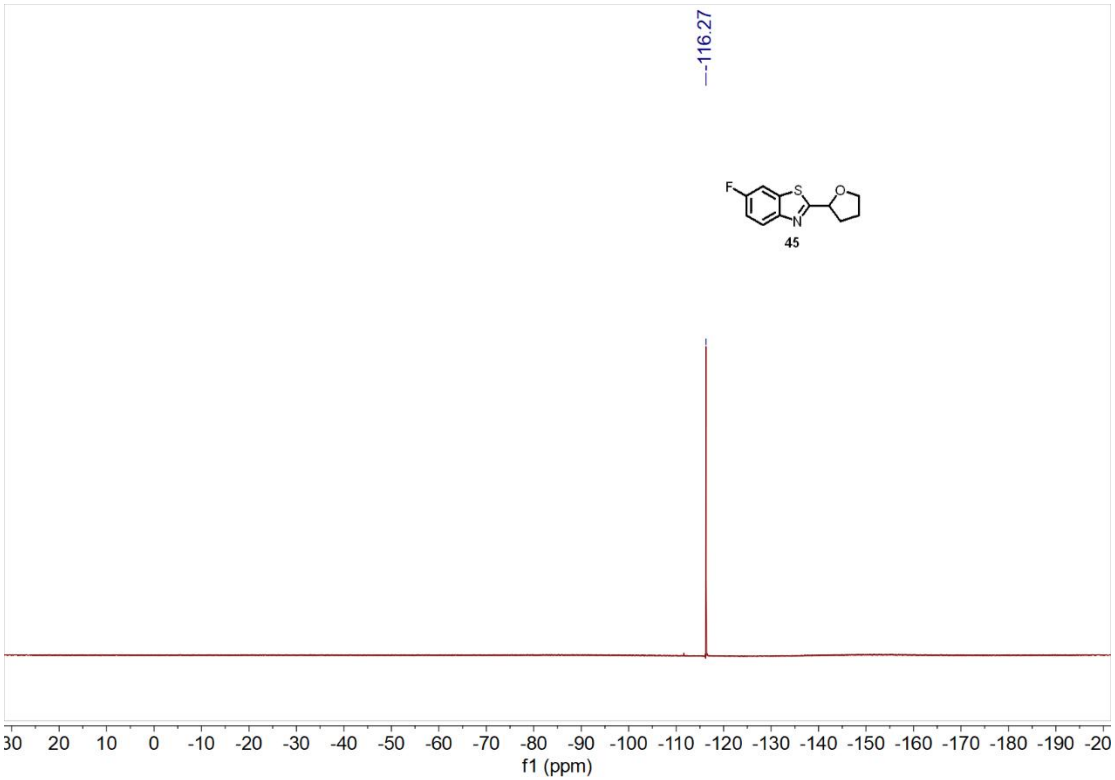
^{13}C NMR spectrum of 44



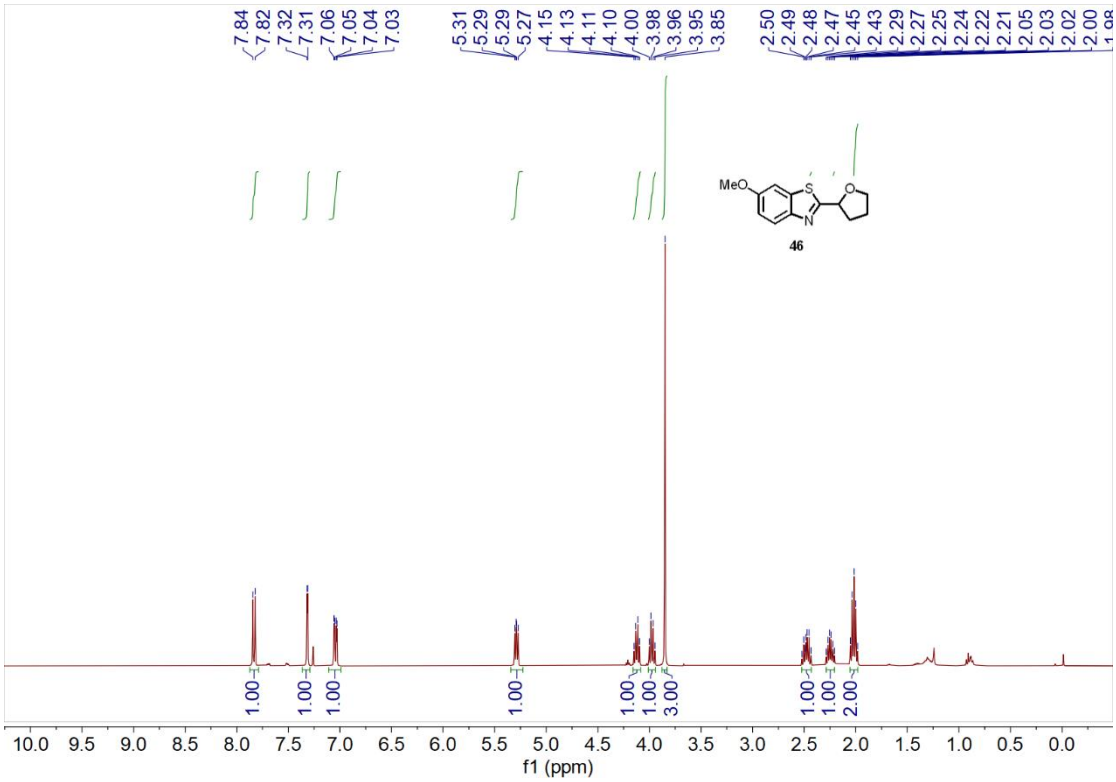
^{1}H NMR spectrum of 45



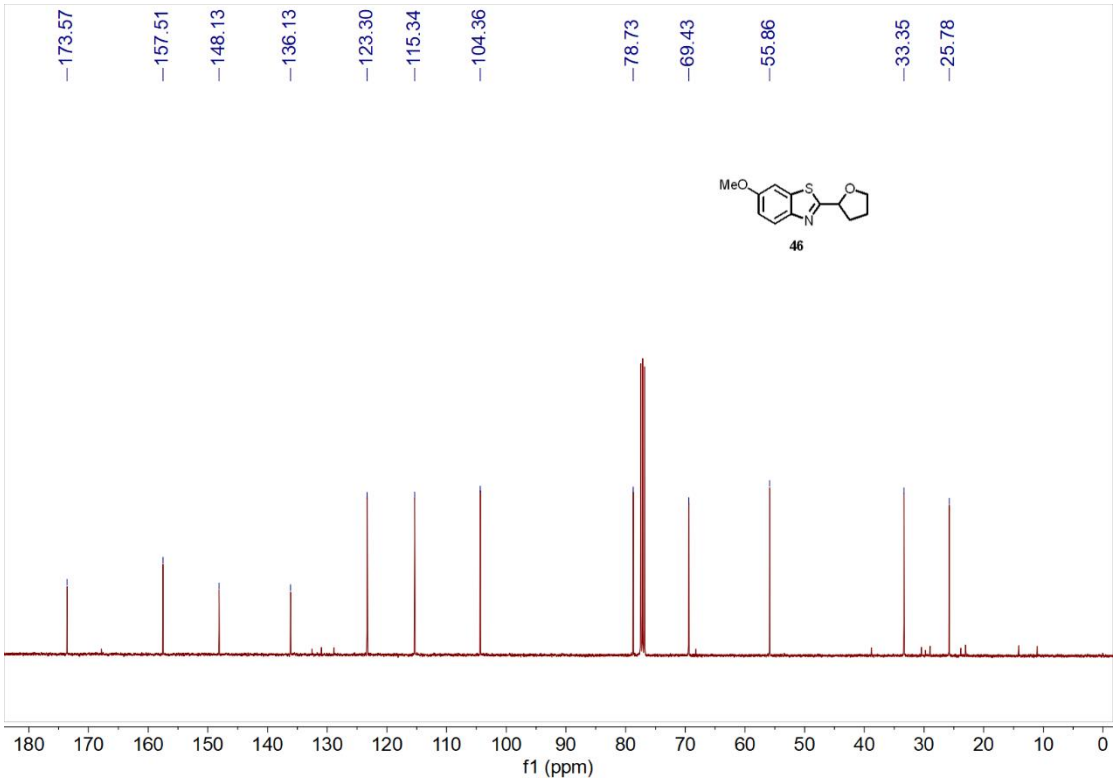
^{13}C NMR spectrum of 45



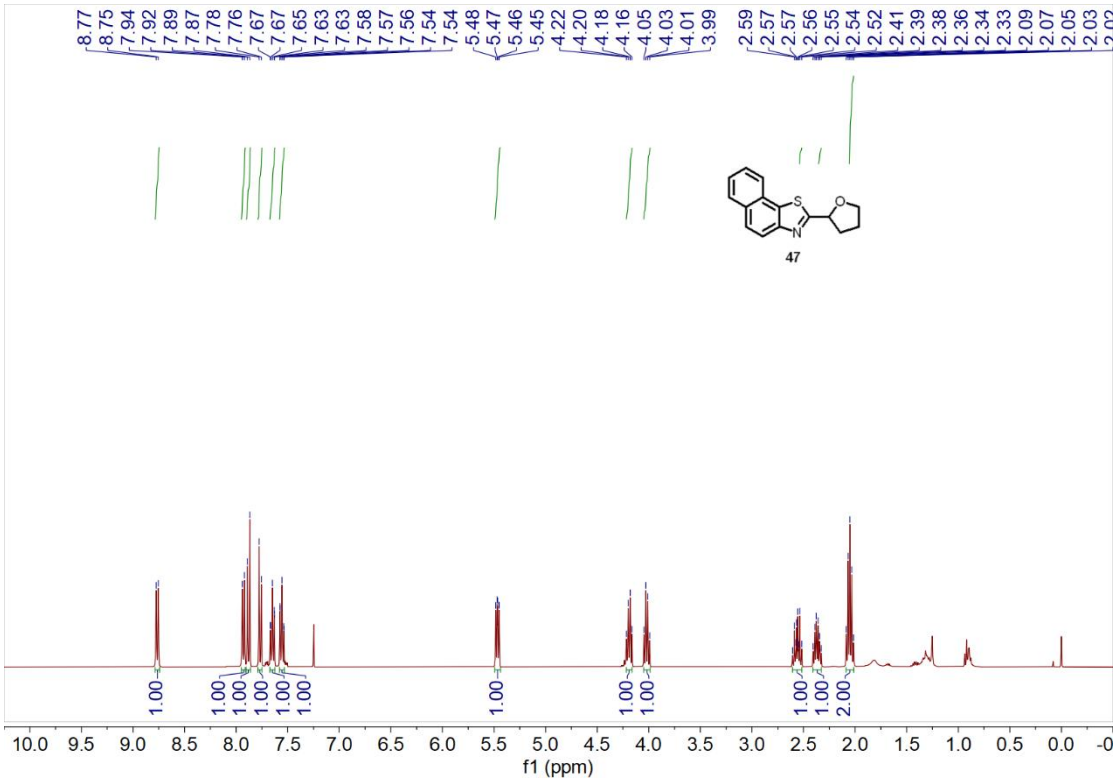
^{19}F NMR spectrum of 45



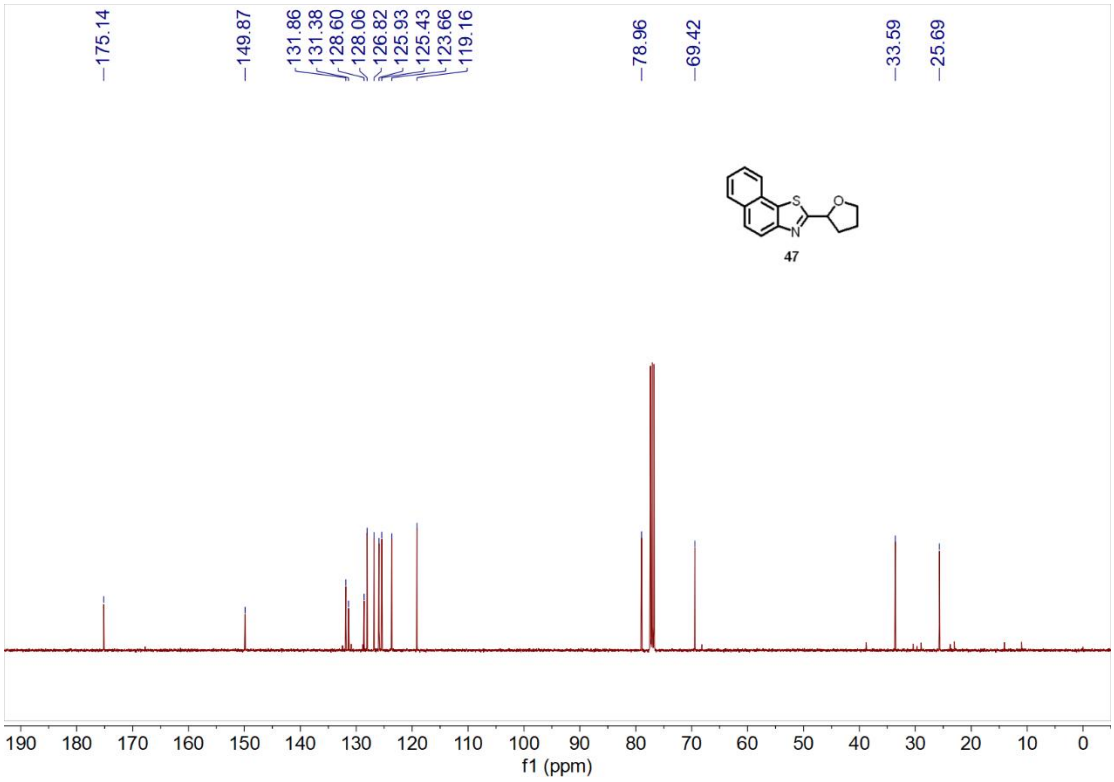
^{1}H NMR spectrum of 46



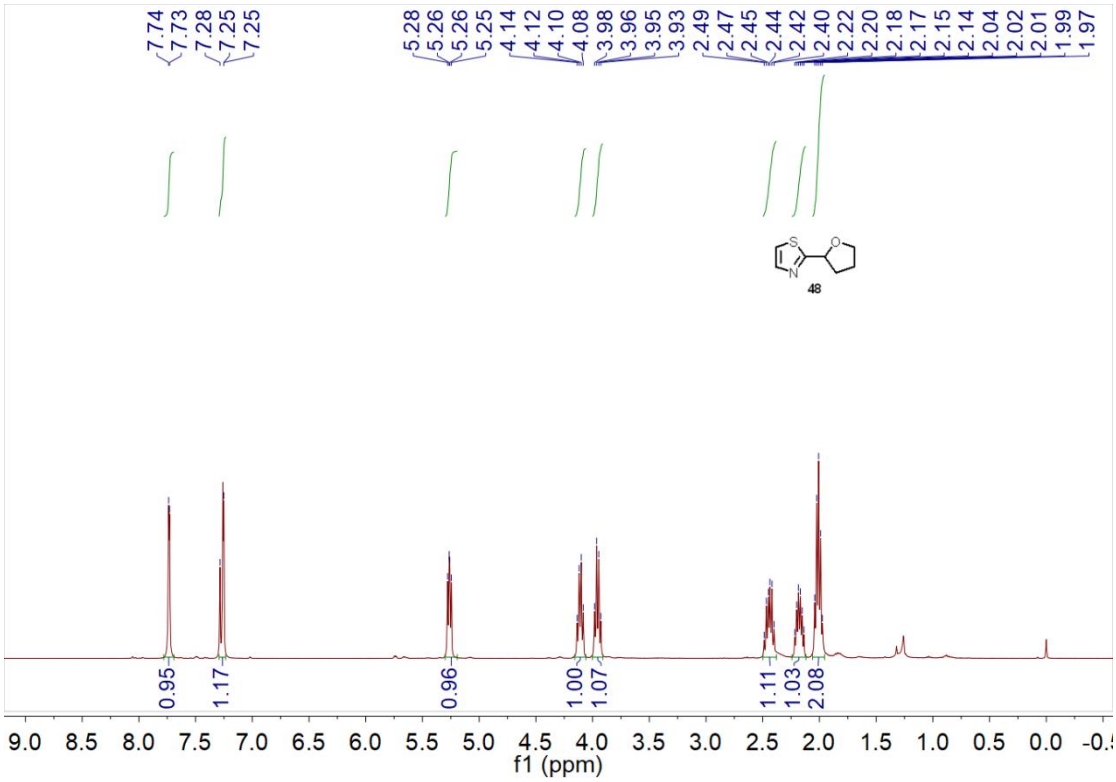
^{13}C NMR spectrum of 46



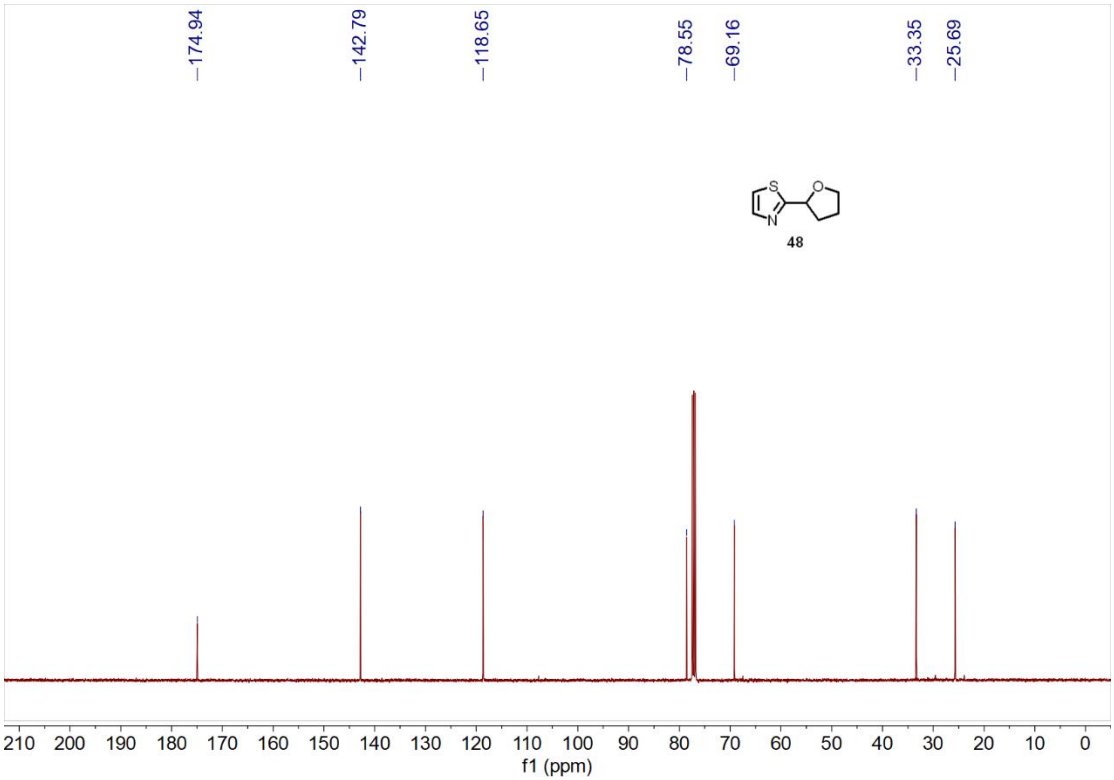
^{1}H NMR spectrum of 47



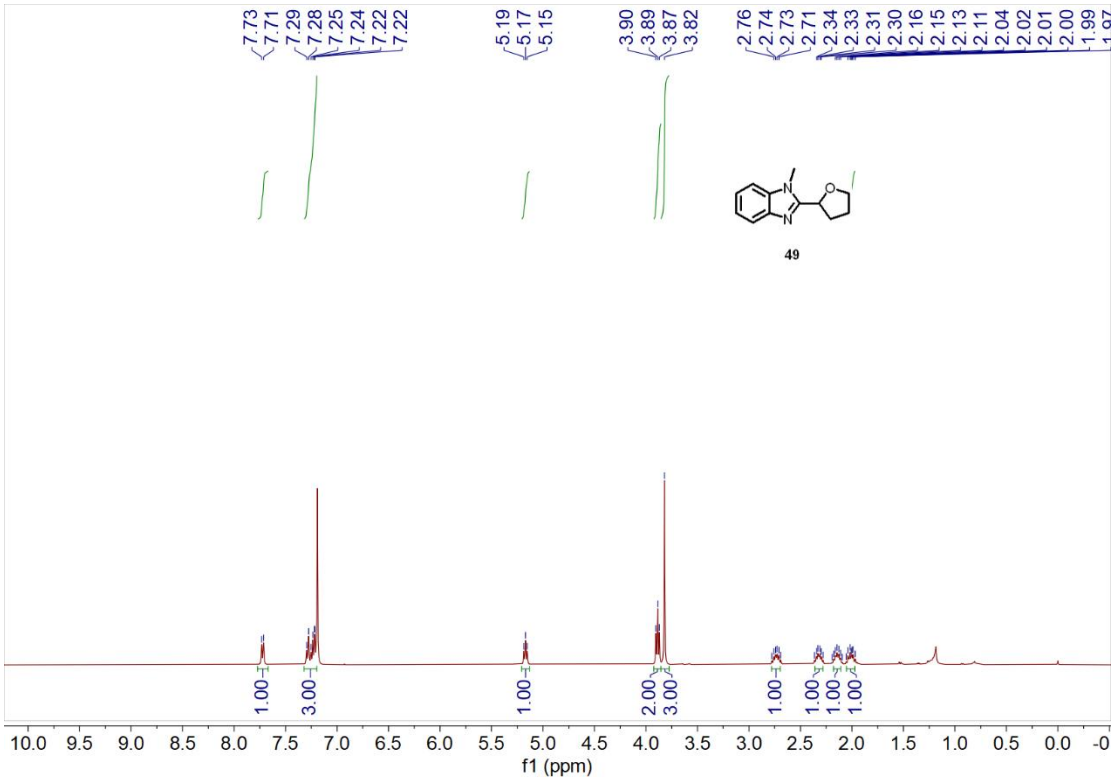
^{13}C NMR spectrum of 47



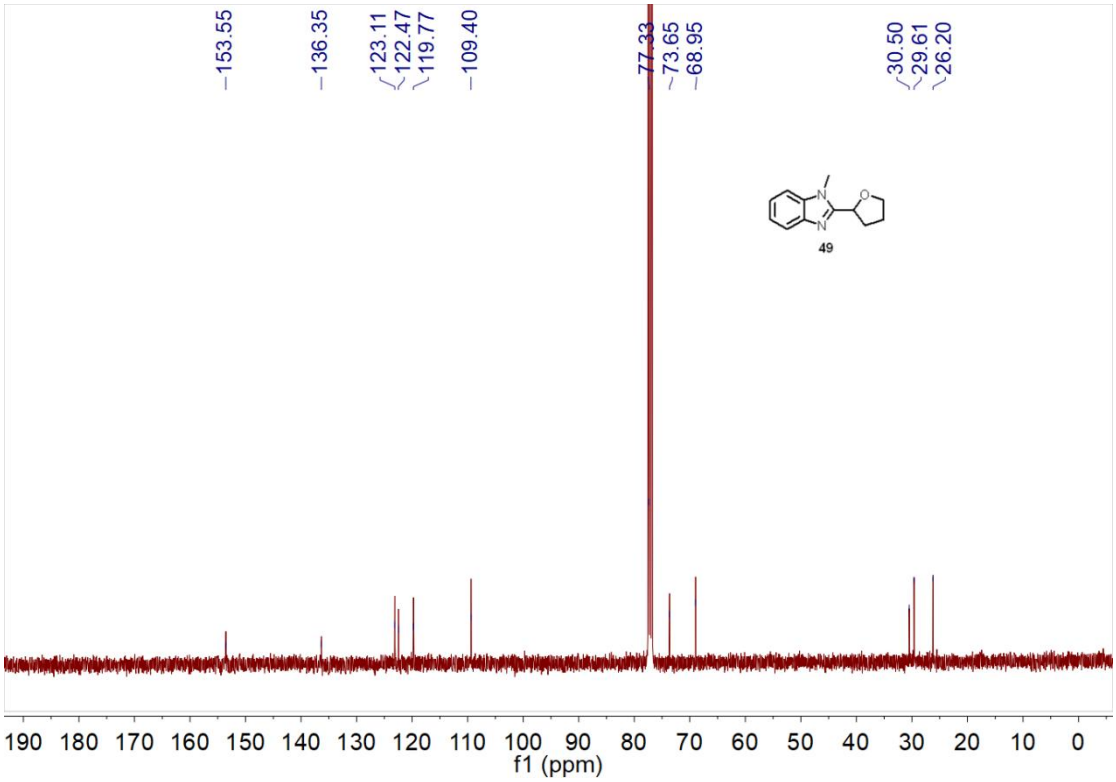
^{1}H NMR spectrum of 48



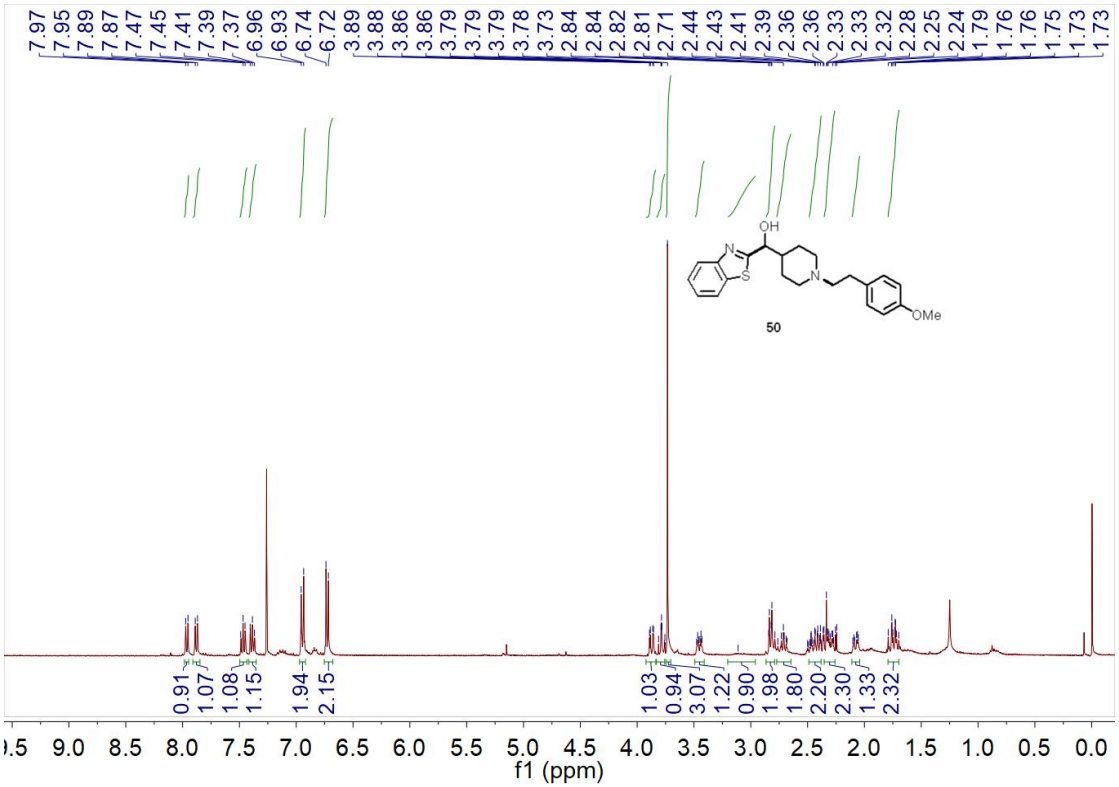
^{13}C NMR spectrum of 48



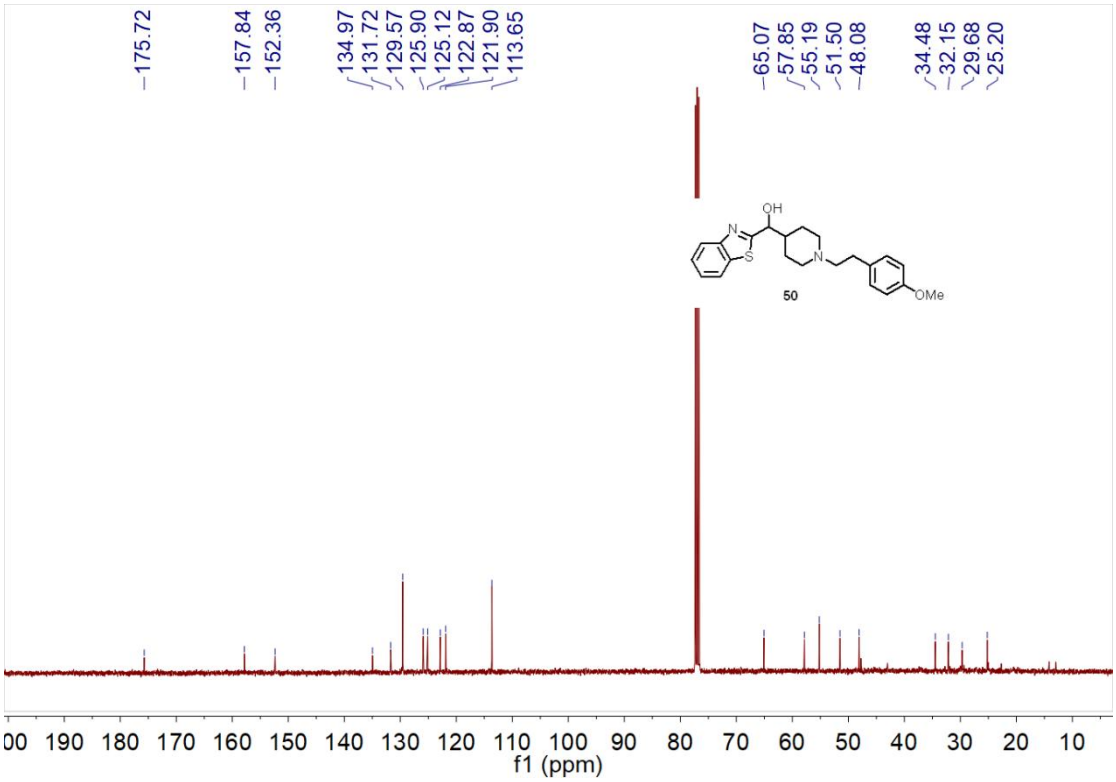
^{1}H NMR spectrum of 49



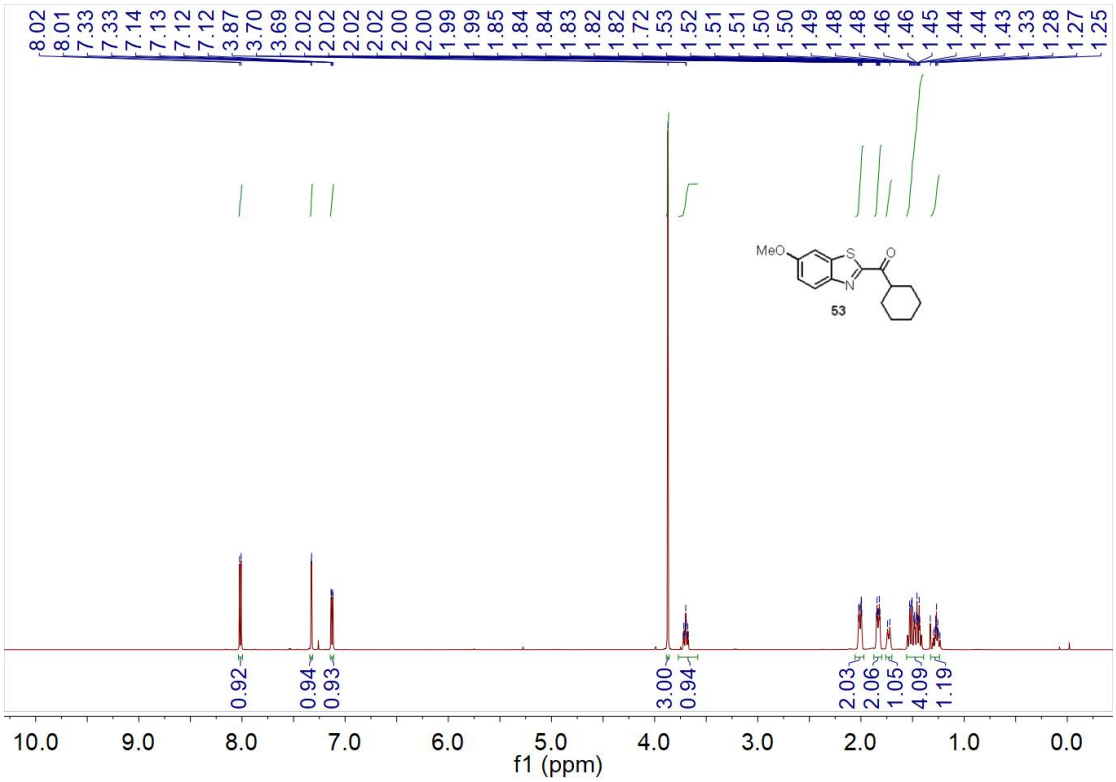
^{13}C NMR spectrum of 49



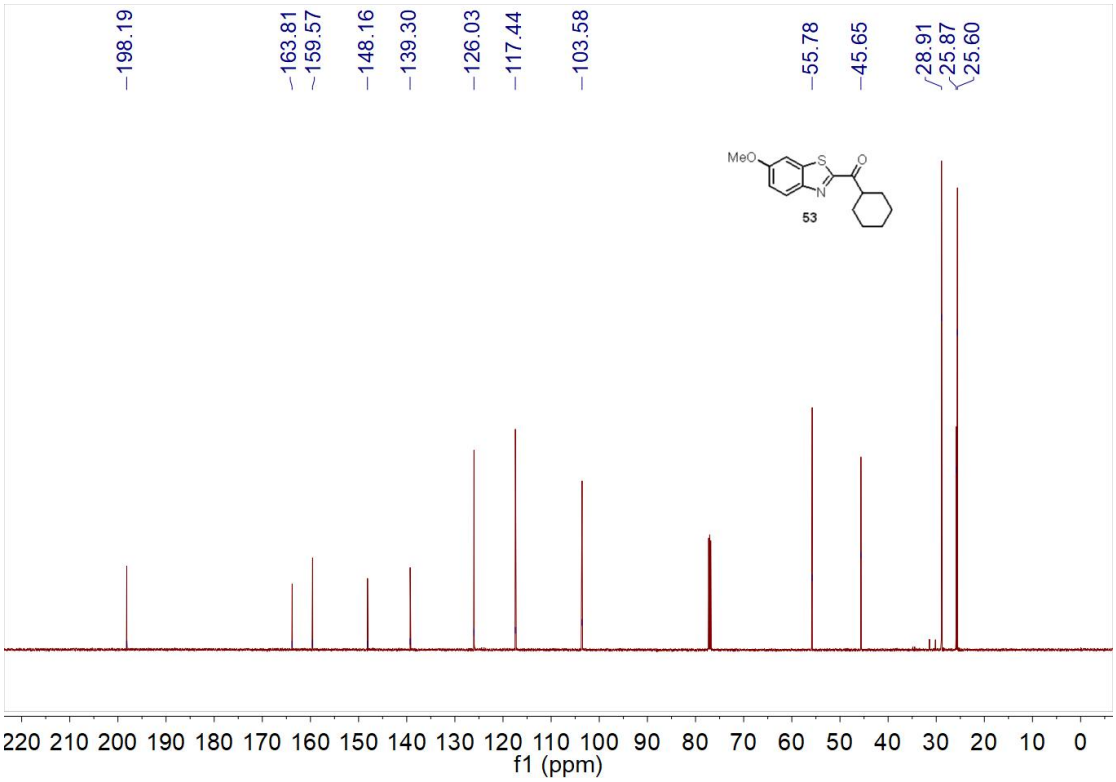
^{1}H NMR spectrum of 50



^{13}C NMR spectrum of 50



^{1}H NMR spectrum of 53



^{13}C NMR spectrum of 53