Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Green Carbon Disulfide Surrogate via Combination of Potassium Sulfide and Chloroform for Benzothiazine-thione and Benzothiazole-thione Constructions

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I. General Information

All experiments were conducted under N_2 atmosphere. For column chromatography, 300-400 mesh silica gel was employed. ^1H NMR were recorded on 400 MHz spectrometer (Bruker AVANCE) in $CDCl_3$ or DMSO-d_6 solution and ^{13}C NMR were recorded on 100 MHz spectrometer in $CDCl_3$ or DMSO-d_6 solution. Chemical shifts are reported in parts per million (ppm). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. Unless otherwise noted, commercially available reagents were used as received.

Mass spectroscopy:

Mass spectra were in general recorded on a Shimadzu GCMS-QP2010 Ultra and a HP 5989A mass selective detector.

IR:

TENSOR (27) Series FT-IR Spectrometers.

II. Synthesis of Starting Materials.

1) General preparation of 1a-1k.[1]

To a solution of substituted *o*-iodobenzaldehyde (1.00 equiv) in MeOH at 0 ℃ was added various amines (2.00 equiv) slowly, and the reaction mixture was stirred at r.t for 3 h. The reaction mixture was again cooled to 0 ℃, and $NaBH_4$ (1.50 equiv) was added every 10 min in three portions. Then it was stirred at r.t for 1 h, and the solvent was evaporated to 1/3 of its original volume under reduced pressure. Saturated sodium bicarbonate was added, and the reaction mixture was stirred at r.t for 10 min. Aqueous phase was separated and extracted with CH_2Cl_2 three times. Combined organic layers were dried over K_2CO_3, filtered, and concentrated. The obtained residue was purified by silica gel column chromatography (PE/EA as eluting reagents) to afford corresponding product. PE = petroleum ether, EA = ethyl acetate.

2) General preparation of 1l-1n.[2]

To a solution of substituted *o*-iodobenzaldehyde (1.00 equiv) in MeOH at 0 ℃ was added various amines (2.00 equiv) slowly. The reaction mixture was stirred at r.t for 3 h, and the solvent was removed in vacuo. The crude imine was dissolved in toluene, cooled to -78 ^oC, and $BF_3 \cdot Et_2O$ (4.0 equiv) was added under N_2. After 10 min at -78 ^oC, the corresponding grignard reagent (2.5 equiv) was added dropwise. The resulting mixture was stirred at room temperature for 5 h, poured into 2 N aqueous NaOH, and extracted with Et_2O. The organic layer was dried and concentrated. The residue was purified by chromatography to give target product.

3) Preparation of 1p.[3]

To a solution of *o*-iodobenzaldehyde (771 mg, 3.0 mmol) in *t*-BuOH (30 mL) was added 1,3-diaminopropane (245 mg, 3.3 mmol). The mixture was stirred at 70 ℃ for 30 min, and then K_2CO_3, (1.24 g, 9.0 mmol) and I_2 (495 mg, 3.9 mmol) were added. After stirring at this temperature for 3 h, the mixture was quenched with sat. Na_2SO_3 until the iodine color almost disappeared. The organic layer was separated and concentrated in vacuo. The resulting solid was recrystallised from MeOH–Et_2O to give 2-(2-iodophenyl)-1,4,5,6-tetrahydropyrimidine hydroiodide. The resulting crystal was dissolved with H_2O, and then pH was adjusted to 12–14 with 2N NaOH. The whole was extracted with $CHCl_3$. The extract was dried over $MgSO_4$. The filtrate was concentrated in vacuo, and the resulting solid was recrystallised from $CHCl_3$–*n*-hexane to give 2-(2-iodophenyl)-1,4,5,6-tetrahydropyrimidine **1p** in 74% yield (632 mg) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.38 – 7.30 (m, 2H), 7.06 – 7.01 (m, 1H), 3.45 – 3.40 (m, 4H), 1.90 – 1.82 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.4, 142.6, 139.3, 130.3, 129.3, 128.2, 95.2, 42.1, 20.4. **HRMS** (EI) Calcd for $C_{10}H_{11}IN_2$ 285.9967, Found 285.9962.

4) General preparation of raw material for 3f-3r.[4]

To a solution of substituted *o*-iodoaniline (1.0 equiv) and the corresponding aldehyde (1.5 equiv) were dissolved in MeOH. Acetic acid (1.5 equiv) was added and the reaction was stirred at r.t for 30 min. Then, the reaction was cooled down to 0 ℃ and sodium cyanoborohydride (1.3 equiv) was added in two portions over 30 min. The reaction was allowed to stir from 0 ℃ to r.t overnight (or until complete by TLC). The reaction was quenched with a saturated *aq.* solution of sodium bicarbonate and then extracted with Et_2O. The combined organic layers were dried with Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was purified by chromatography to give target product.

5) Data of raw material for Ferrocene derivate 3q.

According to the above procedure, the title compound was isolated in 82% yield (performed on 4.0 mmol scale) as an orange solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.6 Hz, 1H), 7.26 – 7.23 (m, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.48 (t, *J* = 7.6 Hz, 1H), 4.31 – 4.29 (m, 7H), 4.21 (s, 2H), 3.95 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.2, 139.0, 129.5, 118.6, 110.6, 86.2, 85.1, 68.8, 68.0, 67.5, 43.1. **HRMS** (EI) Calcd for $C_{17}H_{16}FeIN$ 416.9677, Found 416.9681.

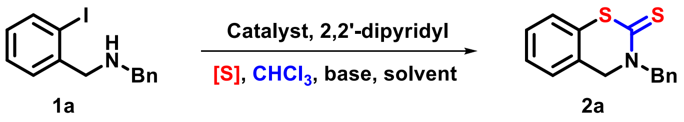
6) Data of raw material for Citronellal derivate 3r.

According to the above procedure, the title compound was isolated in 69% yield (performed on 4.0 mmol scale) as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.25 – 7.19 (m, 1H), 6.63 – 6.54 (m, 1H), 6.47 – 6.42 (m, 1H), 5.13 (t, *J* = 7.2 Hz, 1H), 4.20 (s, 1H), 3.24 – 3.12 (m, 2H), 2.09 – 1.97 (m, 2H), 1.76 – 1.69 (m, 4H), 1.66 – 1.59 (m, 4H), 1.56 – 1.49 (m, 1H), 1.44 – 1.37 (m, 1H), 1.29 – 1.21 (m, 1H), 0.98 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.3, 138.9, 131.4, 129.4, 124.6, 118.4, 110.6, 85.4, 42.2, 37.0, 36.2, 30.4, 25.7, 25.4, 19.6, 17.7. **HRMS** (EI) Calcd for $C_{16}H_{24}IN$ 357.0954, Found 357.0957.

7) Data of raw material for Lidocaine derivate 3s.

According to the modified procedure,[5] the title compound was isolated in 66% yield (performed on 6.0 mmol scale) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.73 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.09-7.07 (m, 1H), 7.06 – 7.03 (m, 2H), 6.70 (d, *J* = 8.4 Hz, 1H), 6.64 – 6.57 (m, 1H), 4.05 (s, 2H), 2.14 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.3, 138.9, 131.4, 129.4, 124.6, 118.4, 110.6, 85.4, 42.2, 37.0, 36.2, 30.4, 25.7, 25.4, 19.6, 17.7. **HRMS** (ESI^+) Calcd for $C_{16}H_{18}IN_2O^+$ [M + H^+] 381.0464, Found 381.0475.

III. Optimization for Carbon Disulfide Surrogate.^{a,b}

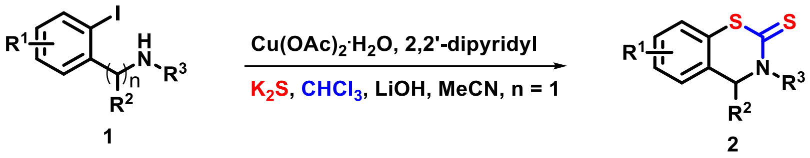


Entry	Catalyst	Sulfur source [S]	Base	Solvent	Yield (%)
1	$CuBr_2$	K_2S	NaOH	CH_3CN	33
2^c	$CuBr_2$	S_8	NaOH	CH_3CN	16
3	$CuBr_2$	$Na_2S\cdot 9H_2O$	NaOH	CH_3CN	trace
4	$CuBr_2$	Na_2S	NaOH	CH_3CN	15
5^c	$CuBr_2$	$NaHS\cdot H_2O$	NaOH	CH_3CN	11
6	$CuBr_2$	thiourea	NaOH	CH_3CN	n.r
7	$CuBr_2$	$Na_2S_2O_3$	NaOH	CH_3CN	n.r
8^d	$CuBr_2$	K_2S	NaOH	CH_3CN	n.r
9	--	K_2S	NaOH	CH_3CN	n.r
10	CuBr	K_2S	NaOH	CH_3CN	28
11	$Cu(OAc)_2\cdot H_2O$	K_2S	NaOH	CH_3CN	39
12	$Cu(OAc)_2\cdot H_2O$	K_2S	NaOH	DMSO	32
13	$Cu(OAc)_2\cdot H_2O$	K_2S	NaOH	DMF	30
14	$Cu(OAc)_2\cdot H_2O$	K_2S	NaOH	NMP	33
15	$Cu(OAc)_2\cdot H_2O$	K_2S	NaOH	dioxane	n.r

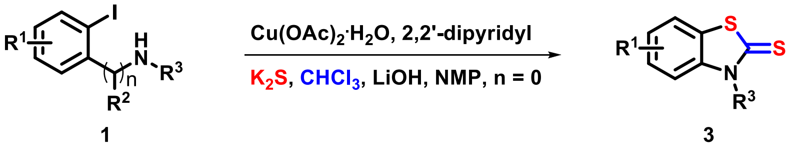
16	$Cu(OAc)_2 \cdot H_2O$	K_2S	NaOH	toluene	n.r
17	$Cu(OAc)_2 \cdot H_2O$	K_2S	NaOH	$ClCH_2CH_2Cl$	n.r
18	$Cu(OAc)_2 \cdot H_2O$	K_2S	NaOH	^tBuOH	n.r
19	$Cu(OAc)_2 \cdot H_2O$	K_2S	--	CH_3CN	trace
20	$Cu(OAc)_2 \cdot H_2O$	K_2S	KOH	CH_3CN	44
21	$Cu(OAc)_2 \cdot H_2O$	K_2S	^tBuOK	CH_3CN	54
22	$Cu(OAc)_2 \cdot H_2O$	K_2S	LiOH	CH_3CN	69
23[e]	$\boldsymbol{Cu(OAc)_2 \cdot H_2O}$	K_2S	***LiOH***	$\boldsymbol{CH_3CN}$	***82***

[a]The reaction conditions: **1a** (0.1 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.01 mmol), 2,2'-dipyridyl (0.01 mmol), K_2S (0.3 mmol), $CHCl_3$ (1.0 mmol), base (0.45 mmol), was stirred in solvent (1.0 mL) at 70 °C under N_2 atmosphere for 16 h. [b]Isolated yields. [c]^{1}H NMR yield. [d]Air instead of N_2 as atmosphere. [e]LiOH (0.6 mmol) and K_2S (0.4 mmol) at 80 °C.

IV. The Synthetic Procedure and Data for Compounds 2 and 3.

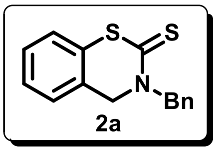


To a solution of substrate **1** (0.2 mmol, 1.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in MeCN (2.0 mL) was stirred at 80 °C for 16 h under N_2 atmosphere. After the reaction was finished, the solvent was removed under vacuum and purification by column chromatography on silica gel afforded product **2** (PE/EA as eluting reagents). PE = petroleum ether, EA = ethyl acetate.



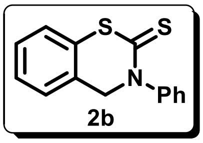
To a solution of substrate **1** (0.2 mmol, 1.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in NMP (2.0 mL) was stirred at 80

^{o}C for 16 h under N_2 atmosphere. After the reaction was finished, the solvent was removed under vacuum and purification by column chromatography on silica gel afforded product **3** (PE/EA as eluting reagents). NMP = N-methyl pyrrolidone, PE = petroleum ether, EA = ethyl acetate.



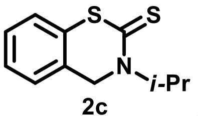
2a

The reaction mixture of N-benzyl-1-(2-iodophenyl)methanamine (0.2 mmol, 1.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in MeCN (2.0 mL) was stirred at 80 ^{o}C for 16 h under N_2 atmosphere, affording compound **2a** in 82% yield (44.4 mg) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.20 (m, 6H), 7.19 – 7.12 (m, 2H), 6.97 (d, *J* = 7.6 Hz, 1H), 5.29 (s, 2H), 4.36 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ191.5, 134.8, 133.0, 129.5, 128.9, 128.2, 128.0, 127.5, 126.0, 123.7, 57.2, 55.1. **IR** (neat) 3025, 2964, 2876, 1515, 1434, 1336, 1226, 1142, 1006, 750 cm^{-1}. **HRMS** (EI) Calcd for $C_{15}H_{13}NS_2$ 271.0489, Found 271.0486.



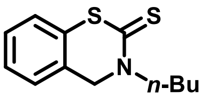
2b

The reaction mixture of N-(2-iodobenzyl)aniline (0.2 mmol, 1.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in MeCN (2.0 mL) was stirred at 80 ^{o}C for 16 h under N_2 atmosphere, affording compound **2b** in 67% yield (34.4 mg) as a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2H), 7.42 – 7.37 (m, 2H), 7.35 – 7.29 (m, 4H), 7.24 (d, *J* = 7.2 Hz, 1H), 4.92 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.0, 145.3, 133.6, 129.7, 129.1, 128.3, 127.6, 126.4, 126.3, 124.0, 59.7. **IR** (neat) 2922, 1636, 1591, 1410, 1316, 1263, 1198, 1129, 1056, 749 cm^{-1}. **HRMS** (EI) Calcd for $C_{14}H_{11}NS_2$ 257.0333, Found 257.0330.



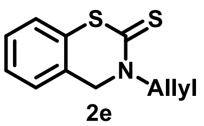
2c

The reaction mixture of N-(2-iodobenzyl)propan-2-amine (0.2 mmol, 1.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in MeCN (2.0 mL) was stirred at 80 ^{o}C for 16 h under N_2 atmosphere, affording compound **2c** in 76% yield (33.8 mg) as a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 1H), 7.22 – 7.18 (m, 3H), 5.67 – 5.60 (m, 1H), 4.31 (s, 2H), 1.23 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.4, 133.5, 130.2, 128.8, 127.6, 125.6, 123.9, 52.3, 49.0, 19.3. **IR** (neat) 2974, 2930, 1478, 1423, 1326, 1259, 1156, 1056, 955, 747 cm^{-1}. **HRMS** (EI) Calcd for $C_{11}H_{13}NS_2$ 223.0489, Found 223.0490.



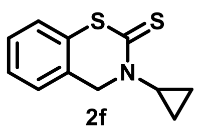
2d

The reaction mixture of N-(2-iodobenzyl)butan-1-amine (0.2 mmol, 1.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in MeCN (2.0 mL) was stirred at 80 ^{o}C for 16 h under N_2 atmosphere，affording compound **2d** in 80% yield (37.8 mg) as a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 1H), 7.24 – 7.15 (m, 3H), 4.47 (s, 2H), 4.08 – 3.95 (m, 2H), 1.70 – 1.63 (m, 2H), 1.34 – 1.24 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.1, 133.4, 129.6, 128.9, 127.5, 125.9, 123.9, 56.4, 54.9, 28.93, 20.0, 13.8. **IR** (neat) 2957, 2929, 2870, 1636, 1489, 1419, 1338, 1160, 1117, 1002, 747 cm^{-1}. **HRMS** (EI) Calcd for $C_{12}H_{15}NS_2$ 237.0646, Found 237.0645.



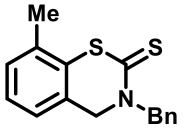
2e

The reaction mixture of N-(2-iodobenzyl)prop-2-en-1-amine (0.2 mmol, 1.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in MeCN (2.0 mL) was stirred at 80 ^{o}C for 16 h under N_2 atmosphere，affording compound **2e** in 71% yield (31.2 mg) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 1H), 7.30 – 7.26 (m, 1H), 7.26 – 7.22 (m, 2H), 5.92 – 5.82 (m, 1H), 5.33 – 5.86 (m, 2H), 4.75 (dt, *J* = 6.0, 1.2 Hz, 2H), 4.51 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.1, 133.1, 130.6, 129.5, 128.9, 127.6, 126.1, 123.8, 119.6, 56.8, 55.2. **IR** (neat) 3083, 2923, 1643, 1488, 1420, 1336, 1241, 1153, 1013, 922, 761 cm^{-1}. **HRMS** (EI) Calcd for $C_{11}H_{11}NS_2$ 221.0333, Found 221.0336.



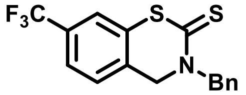
2f

The reaction mixture of N-(2-iodobenzyl)cyclopropanamine (0.2 mmol, 1.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in MeCN (2.0 mL) was stirred at 80 ^{o}C for 16 h under N_2 atmosphere，affording compound **2f** in 65% yield (28.6 mg) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 1H), 7.23 – 7.14 (m, 3H), 4.52 (s, 2H), 3.19 – 3.07 (m, 1H), 1.03 – 0.98 (m, 2H), 0.76 – 0.69 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.0, 133.1, 130.5, 128.8, 127.5, 125.7, 123.7, 57.5, 36.9, 10.1. **IR** (neat) 3072, 2987, 1443, 1420, 1346, 1320, 1260, 1172, 1013, 966, 756 cm^{-1}. **HRMS** (EI) Calcd for $C_{11}H_{11}NS_2$ 221.0333, Found 221.0332.



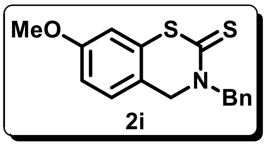
2g

The reaction mixture of N-benzyl-1-(2-iodo-3-methylphenyl)methanamine (0.2 mmol, 1.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in MeCN (2.0 mL) was stirred at 80 ^{o}C for 16 h under N_2 atmosphere，affording compound **2g** in 67% yield (38.1 mg) as a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 5H), 7.18 – 7.11 (m, 2H), 6.87 (d, *J* = 7.2 Hz, 1H), 5.36 (s, 2H), 4.42 (s, 2H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.1, 134.8, 132.8, 132.4, 130.0, 129.2, 128.9, 128.1, 128.1, 127.3, 123.7, 57.2, 55.4, 19.4, 19.4. **IR** (neat) 2958, 1496, 1449, 1418, 1340, 1227, 1141, 998, 771, 701 cm^{-1}. **HRMS** (EI) Calcd for $C_{16}H_{15}NS_2$ 285.0646, Found 285.0648.



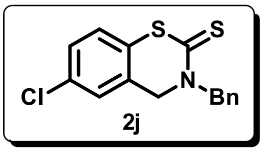
2h

The reaction mixture of N-benzyl-1-(2-iodo-4-(trifluoromethyl)phenyl)methanamine (0.2 mmol, 1.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in MeCN (2.0 mL) was stirred at 80 ^{o}C for 16 h under N_2 atmosphere，affording compound **2h** in 82% yield (55.5 mg) as a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.33 (m, 3H), 7.32 – 7.28 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 5.36 (s, 2H), 4.49 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.3, 134.5, 134.3, 133.1, 131.5 (q, J_{C-F} = 33 Hz), 129.0, 128.4, 128.1, 126.5, 124.3 (q, J_{C-F} = 3.0 Hz), 123.4 (q, J_{C-F} = 271 Hz), 120.8 (q, J_{C-F} = 4.0 Hz), 57.3, 54.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.74. **IR** (neat) 3028, 2963, 1648, 1496, 1399, 1323, 1263, 1174, 1142, 1083, 699 cm^{-1}. **HRMS** (EI) Calcd for $C_{16}H_{12}F_3NS_2$ 339.0363, Found 339.0367.



2i

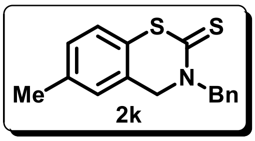
The reaction mixture of N-benzyl-1-(2-iodo-4-methoxyphenyl)methanamine (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in MeCN (2.0 mL) was stirred at 80 °C for 16 h under N_2 atmosphere，affording compound **2i** in 64% yield (38.5 mg) as a yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 5H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.78 – 6.73 (m, 2H), 5.36 (s, 2H), 4.39 (s, 2H), 3.79 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.3, 160.0, 134.8, 134.1, 128.9, 128.1, 128.0, 126.9, 121.5, 113.7, 108.6, 57.2, 55.5, 54.6. **IR** (neat) 2927, 1602, 1496, 1476, 1338, 1266, 1128, 1013, 697 cm^{-1}. **HRMS** (EI) Calcd for $C_{16}H_{15}NOS_2$ 301.0595, Found 301.0597.



2j

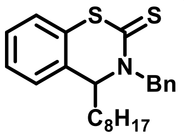
The reaction mixture of N-benzyl-1-(5-chloro-2-iodophenyl)methanamine (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in MeCN (2.0 mL) was stirred at 80 °C for 16 h under N_2 atmosphere，affording compound **2j** in 70% yield (42.7 mg) as a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 3H), 7.32 – 7.30 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 2.0 Hz, 1H), 5.34 (s, 2H), 4.40 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.1, 134.6, 133.3, 131.6, 131.1, 130.0, 129.1, 128.4, 128.1, 126.2, 125.0, 57.3, 54.6. **IR** (neat) 2924, 2853, 1652, 1493, 1401, 1335, 1227, 1125, 1031, 819, 704 cm^{-1}. **HRMS** (EI) Calcd for $C_{15}H_{12}ClNS_2$ 305.0100, Found

305.0105.



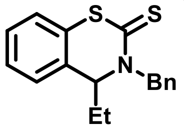
2k

The reaction mixture of N-benzyl-1-(2-iodo-5-methylphenyl)methanamine (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in MeCN (2.0 mL) was stirred at 80 ^{o}C for 16 h under N_2 atmosphere，affording compound **2k** in 72% yield (41.2 mg) as a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 5H), 7.13 (s, 2H), 6.87 (s, 1H), 5.36 (s, 2H), 4.40 (s, 2H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.1, 137.7, 134.9, 129.7, 129.6, 129.4, 128.9, 128.1, 128.0, 126.7, 123.6, 57.3, 55.2, 21.0. **IR** (neat) 2962, 2924, 2855, 1654, 1484, 1328, 1221, 1132, 1016, 817, 700 cm^{-1}. **HRMS** (EI) Calcd for $C_{16}H_{15}NS_2$ 285.0646, Found 285.0648.



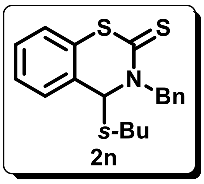
2l

The reaction mixture of N-benzyl-1-(2-iodophenyl)nonan-1-amine (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in MeCN (2.0 mL) was stirred at 80 ^{o}C for 16 h under N_2 atmosphere，affording compound **2l** in 54% yield (41.3 mg) as a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 4H), 7.19 – 7.16 (m, 2H), 7.13 – 7.08 (m, 2H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.12 (d, *J* = 15.2 Hz, 1H), 4.63 (d, *J* = 15.2 Hz, 1H), 4.47 (dd, *J* = 9.6, 5.6 Hz, 1H), 1.97 – 1.89 (m, 1H), 1.68 – 1.60 (m, 1H), 1.21 – 1.18 (m, 3H), 1.16 – 1.11 (m, 9H), 0.78 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.08, 135.1, 131.7, 131.1, 128.8, 128.5, 128.0, 128.0, 127.1, 126.8, 123.8, 65.84, 6.74, 31.7, 30.5, 29.2, 29.1, 29.0, 26.2, 22.6, 14.0. **IR** (neat) 2925, 2854, 1636, 1479, 1455, 1340, 1147, 1127, 752, 699 cm^{-1}. **HRMS** (EI) Calcd for $C_{23}H_{29}NS_2$ 383.1741, Found 383.1740.



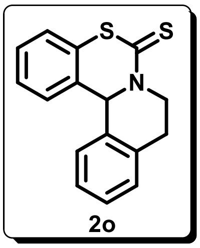
2m

The reaction mixture of N-benzyl-1-(2-iodophenyl)propan-1-amine (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in MeCN (2.0 mL) was stirred at 80 °C for 16 h under N_2 atmosphere, affording compound **2m** in 50% yield (30.0 mg) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 4H), 7.25 – 7.23 (m, 2H), 7.20 – 7.16 (m, 2H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.23 (d, *J* = 15.2 Hz, 1H), 4.69 (d, *J* = 15.2 Hz, 1H), 4.47 (dd, *J* = 9.6, 5.2 Hz, 1H), 2.09 – 2.00 (m, 1H), 1.84 – 1.74 (m, 1H), 0.79 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.1, 135.1, 131.3, 131.1, 128.8, 128.5, 128.0, 127.9, 127.0, 127.0, 123.8, 67.3, 56.8, 23.8, 10.9. **IR** (neat) 2965, 2927, 1654, 1479, 1437, 1340, 1150, 1126, 1002, 752, 698 cm^{-1}. **HRMS** (EI) Calcd for $C_{17}H_{17}NS_2$ 299.0802, Found 299.0800.



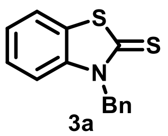
2n

The reaction mixture of N-benzyl-1-(2-iodophenyl)-2-methylbutan-1-amine (0.2 mmol, 1.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in MeCN (2.0 mL) was stirred at 80 °C for 16 h under N_2 atmosphere, affording compound **2n** in 53% yield (34.7 mg) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 6H), 7.22 – 7.14 (m, 2H), 6.88 (d, *J* = 7.2 Hz, 1H), 6.15 (d, *J* = 14.8 Hz, 1H), 4.69 (d, *J* = 15.2 Hz, 1H), 4.67 – 4.61 (m, 1H), 2.09 – 2.00 (m, 1H), 1.47 – 1.40 (m, 1H), 1.31 – 1.26 (m, 1H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.2, 135.1, 131.7, 131.1, 128.8, 128.5, 128.2, 128.1, 127.1, 126.5, 123.9, 63.7, 56.5, 39.0, 24.4, 23.2, 21.5. **IR** (neat) 3060, 2956, 2868, 1485, 1425, 1343, 1146, 1126, 1001, 700 cm^{-1}. **HRMS** (EI) Calcd for $C_{19}H_{21}NS_2$ 327.1115, Found 327.1113.

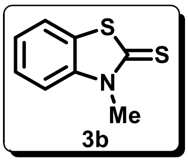


2o

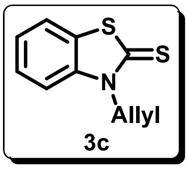
The reaction mixture of 1-(2-iodophenyl)-1,2,3,4-tetrahydroisoquinoline[6] (0.2 mmol, 1.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in MeCN (2.0 mL) was stirred at 80 ^{o}C for 16 h under N_2 atmosphere，affording compound **2o** in 51% yield (28.8 mg) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.37 (m, 4H), 7.35-7.31 (m, 1H), 7.24 – 7.13 (m, 2H), 6.41 (d, *J* = 7.6 Hz, 1H), 5.49 (s, 1H), 5.00 (d, *J* = 12.0 Hz, 1H), 3.45 (td, *J* = 12.8, 3.2 Hz, 1H), 2.98 – 2.75 (m, 2H). **^{3}C NMR** (100 MHz, $CDCl_3$) δ 191.5, 136.3, 135.2, 134.0, 130.6, 128.6, 128.5, 128.5, 128.4, 127.7, 127.1, 124.6, 124.6, 64.7, 64.7, 49.1, 28.8. **IR** (neat) 3061, 2920, 2868, 1467, 1408, 1192, 1148, 993, 889, 754 cm^{-1}. **HRMS** (EI) Calcd for $C_{16}H_{13}NS_2$ 283.0489, Found 283.0492.


3a

The reaction mixture of N-benzyl-2-iodoaniline (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in NMP (2.0 mL) was stirred at 80 ^{o}C for 16 h under N_2 atmosphere，affording compound **3a** in 84% yield (43.2 mg) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 1H), 7.36 – 7.28 (m, 5H), 7.28 – 7.24 (m, 2H), 7.12 – 7.10 (m, 1H), 5.71 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.2, 141.5, 134.3, 128.9, 127.9, 127.6, 127.1, 127.0, 124.8, 121.3, 113.0, 49.5. **IR** (neat) 2921, 1640, 1372, 1317, 1209, 1196, 1132, 990, 748, 701 cm^{-1}. **HRMS** (EI) Calcd for $C_{14}H_{11}NS_2$ 257.0333, Found 257.0334.

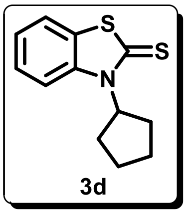

3b

The reaction mixture of 2-iodo-N-methylaniline[7] (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in NMP (2.0 mL) was stirred at 80 ^{o}C for 16 h under N_2 atmosphere，affording compound **3b** in 86% yield (31.1 mg) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 7.6, 0.4 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.32 – 7.28 (m, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 3.85 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.4, 142.0, 127.6, 127.0, 124.8, 121.3, 112.3, 33.1. **IR** (neat) 3053, 1460, 1427, 1342, 1314, 1267, 1138, 1102, 966, 744 cm^{-1}. **HRMS** (EI) Calcd for $C_8H_7NS_2$ 181.0020, Found 181.0019.



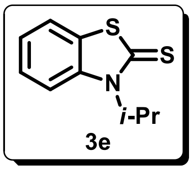
3c

The reaction mixture of N-allyl-2-iodoaniline[8] (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in NMP (2.0 mL) was stirred at 80 °C for 16 h under N_2 atmosphere, affording compound **3c** in 71% yield (29.2 mg) as a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.31 – 7.28 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 5.96 – 5.87 (m, 1H), 5.29 (d, *J* = 10.4 Hz, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 5.11 – 5.09 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.4, 141.3, 129.5, 127.6, 126.9, 124.7, 121.3, 118.7, 112.8, 48.3. **IR** (neat) 2957, 1461, 1378, 1375, 1314, 1221, 1134, 981, 930, 749 cm^{-1}. **HRMS** (EI) Calcd for $C_{10}H_9NS_2$ 207.0176, Found 207.0179.



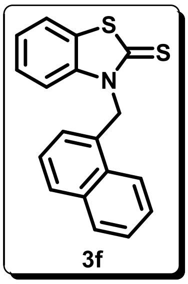
3d

The reaction mixture of N-cyclopentyl-2-iodoaniline[9] (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in NMP (2.0 mL) was stirred at 80 °C for 16 h under N_2 atmosphere, affording compound **3d** in 55% yield (25.8 mg) as a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.30 – 7.25 (m, 1H), 6.18 – 6.09 (m, 1H), 2.24 – 2.10 (m, 4H), 2.09 – 2.00 (m, 2H), 1.90 – 1.79 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.7, 139.8, 127.6, 126.1, 124.2, 121.5, 113.4, 58.3, 27.3, 25.5. **IR** (neat) 2951, 2869, 1459, 1400, 1376, 1263, 1131, 1171, 995, 747 cm^{-1}. **HRMS** (EI) Calcd for $C_{12}H_{13}NS_2$ 235.0489, Found 235.0493.

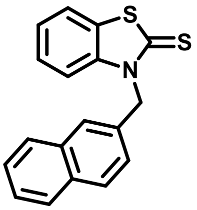


3e

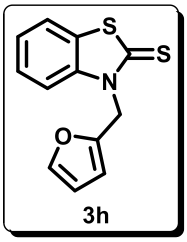
The reaction mixture of 2-iodo-N-isopropylaniline[10] (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in NMP (2.0 mL) was stirred at 80 °C for 16 h under N_2 atmosphere, affording compound **3e** in 53% yield (22.1 mg) as a pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 6.12 (s, 1H), 1.64 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.1, 140.3, 127.5, 126.2, 124.1, 121.4, 113.6, 50.2, 19.0. **IR** (neat) 2977, 2932, 1462, 1397, 1318, 1284, 1265, 1130, 1089, 747 cm^{-1}. **HRMS** (EI) Calcd for $C_{10}H_{11}NS_2$ 209.0333, Found 209.0336.


3f

The reaction mixture of 2-iodo-N-(naphthalen-1-ylmethyl)aniline (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in NMP (2.0 mL) was stirred at 80 ^{o}C for 16 h under N_2 atmosphere，affording compound **3f** in 74% yield (45.4 mg) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.25 – 7.23 (m, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 7.2 Hz, 1H), 6.14 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.2, 141.6, 133.8, 130.6, 129.1, 128.6, 128.3, 127.5, 127.1, 126.7, 126.1, 125.5, 124.9, 123.0, 122.3, 121.3, 113.2, 47.4. **IR** (neat) 2924, 1684, 1503, 1460, 1402, 1299, 1264, 1219, 1113, 986 cm^{-1}. **HRMS** (EI) Calcd for $C_{18}H_{13}NS_2$ 307.0489, Found 307.0494.

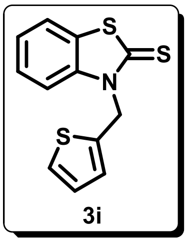

3g

The reaction mixture of 2-iodo-N-(naphthalen-2-ylmethyl)aniline (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in NMP (2.0 mL) was stirred at 80 ^{o}C for 16 h under N_2 atmosphere，affording compound **3g** in 78% yield (47.9 mg) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.64 (m, 3H), 7.62 (s, 1H), 7.43 – 7.30 (m, 4H), 7.18 – 7.12 (m, 2H), 7.08 – 7.01 (m, 1H), 5.76 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.2, 141.4, 133.2, 132.9, 131.8, 128.9, 127.8, 127. 7, 127.5, 126.9, 126.4, 126.2, 126.0, 124.8, 124.8, 121.3, 113.1, 49.7. **IR** (neat) 3049, 2968, 1458, 1372, 1345, 1315, 1197, 1137, 985, 750 cm^{-1}. **HRMS** (EI) Calcd for $C_{18}H_{13}NS_2$ 307.0489, Found 307.0477.



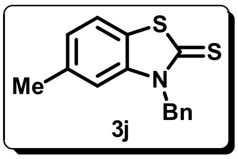
3h

The reaction mixture of N-(furan-2-ylmethyl)-2-iodoaniline (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in NMP (2.0 mL) was stirred at 80 °C for 16 h under N_2 atmosphere，affording compound **3h** in 79% yield (39.1 mg) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H), 7.44 – 7.39 (m, 1H), 7.34 (d, *J* = 1.2 Hz, 1H), 7.31 – 7.21 (m, 1H), 6.50 (d, *J* = 3.2 Hz, 1H), 6.33 – 6.32 (m, 1H), 5.64 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 189.4, 147.8, 142.6, 141.4, 127.4, 126.9, 124.8, 121.2, 113.0, 110.7, 110.1, 42.4. **IR** (neat) 3115, 3068, 2926, 1461, 1364, 1314, 1250, 1179, 1101, 975, 739 cm^{-1}. **HRMS** (EI) Calcd for $C_{12}H_9NOS_2$ 247.0126, Found 247.0127.



3i

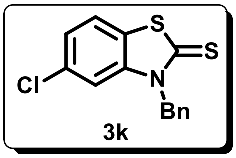
The reaction mixture of 2-iodo-N-(thiophen-2-ylmethyl)aniline (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in NMP (2.0 mL) was stirred at 80 °C for 16 h under N_2 atmosphere，affording compound **3i** in 83% yield (43.7 mg) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.28 – 7.24 (m, 1H), 7.21 – 7.18 (m, 2H), 6.93 (dd, *J* = 4.8, 3.6 Hz, 1H), 5.79 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.4, 141.0, 136.1, 127.6, 127.6, 126.9, 126.7, 126.0, 124.9, 121.4, 112.6, 44.3. **IR** (neat) 3070, 2965, 1460, 1379, 1342, 1248, 1201, 1155, 971, 752, 707 cm^{-1}. **HRMS** (EI) Calcd for $C_{12}H_9NS_3$ 262.9897, Found 262.9900.



3j

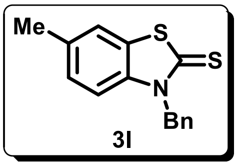
The reaction mixture of N-benzyl-2-iodo-5-methylaniline (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in NMP (2.0 mL) was stirred at 80 °C for 16 h under N_2 atmosphere，affording compound **3j** in 65% yield (35.2 mg) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 6H), 7.09

(d, J = 8.0 Hz, 1H), 6.92 (s, 1H), 5.68 (s, 2H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.3, 141.6, 137.4, 134.3, 128.9, 127.8, 127.0, 126.0, 124.3, 120.9, 113.4, 49.4, 21. 6, 21.5. **IR** (neat) 3068, 2876, 1493, 1400, 1319, 1226, 1125, 1009, 960, 728 cm^{-1}. **HRMS** (EI) Calcd for $C_{15}H_{13}NS_2$ 271.0489, Found 271.0490.



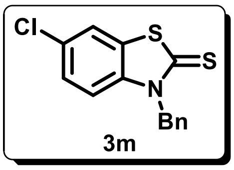
3k

The reaction mixture of N-benzyl-5-chloro-2-iodoaniline (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in NMP (2.0 mL) was stirred at 80 ^{o}C for 16 h under N_2 atmosphere，affording compound **3k** in 73% yield (42.3 mg) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 6H), 7.24 (dd, J = 8.4, 1.6 Hz, 1H), 7.09 (d, J = 1.6 Hz, 1H), 5.65 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.8, 142.3, 133.8, 133.3, 129.1, 128.2, 127.0, 125.7, 125.0, 121.9, 113.1, 49.5. **IR** (neat) 2966, 1415, 1356, 1300, 1198, 1132, 976, 803, 760, 697 cm^{-1}. **HRMS** (EI) Calcd for $C_{14}H_{10}ClNS_2$ 290.9943, Found 290.9945.



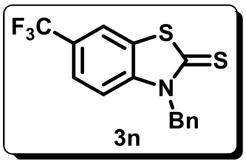
3l

The reaction mixture of N-benzyl-2-iodo-4-methylaniline (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in NMP (2.0 mL) was stirred at 80 ^{o}C for 16 h under N_2 atmosphere，affording compound **3l** in 71% yield (38.6 mg) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.16 (m, 6H), 7.01 (d, J = 8.4 Hz, 1H), 6.91 (d, J = 8.4 Hz, 1H), 5.60 (s, 2H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.6, 139.4, 135.0, 134.4, 128.9, 127.9, 127.9, 127.5, 127.1, 121.4, 112.7, 49.5, 21.0, 21.0. **IR** (neat) 2966, 1479, 1364, 1309, 1206, 1198, 984, 806, 699 cm^{-1}. **HRMS** (EI) Calcd for $C_{15}H_{13}NS_2$ 271.0489, Found 271.0486.



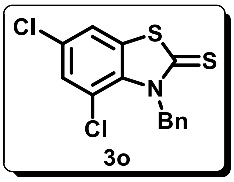
3m

The reaction mixture of N-benzyl-4-chloro-2-iodoaniline (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in NMP (2.0 mL) was stirred at 80 °C for 16 h under N_2 atmosphere，affording compound **3m** in 84% yield (48.8 mg) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 2.0 Hz, 1H), 7.36 – 7.26 (m, 5H), 7.26 – 7.23 (m, 1H), 7.00 (d, *J* = 8.8 Hz, 1H), 5.66 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.9, 140.0, 133.9, 130.8, 129.0, 128.8, 128.1, 127.3, 127.0, 121.0, 113.5, 49.5. **IR** (neat) 2966, 1458, 1415, 1356, 1300, 1198, 1132, 976, 804, 698 cm^{-1}. **HRMS** (EI) Calcd for $C_{14}H_{10}ClNS_2$ 290.9943, Found 290.9947.



3n

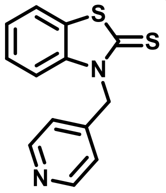
The reaction mixture of N-benzyl-2-iodo-4-(trifluoromethyl)aniline (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in NMP (2.0 mL) was stirred at 80 °C for 16 h under N_2 atmosphere，affording compound **3n** in 75% yield (49.0 mg) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.36 – 7.28 (m, 5H), 7.17 (d, *J* = 8.8 Hz, 1H), 5.71 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.1, 143.7, 133.8, 129.1, 128.2, 128.0, 127.2 (q, $J_{C\text{-}F}$ = 33 Hz), 127.0, 124.2 (q, $J_{C\text{-}F}$ = 4 Hz), 123.7 (q, $J_{C\text{-}F}$ = 270 Hz), 118.6 (q, $J_{C\text{-}F}$ = 4 Hz), 112.8, 49.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -61.79. **IR** (neat) 2964, 1517, 1362, 1326, 1300, 1198, 1126, 977, 816, 697 cm^{-1}. **HRMS** (EI) Calcd for $C_{15}H_{10}F_3NS_2$ 325.0207, Found 325.0208.



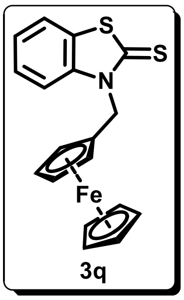
3o

The reaction mixture of N-benzyl-2,4-dichloro-6-iodoaniline (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in NMP (2.0 mL) was stirred at 80 °C for 16 h under N_2 atmosphere，affording compound **3o** in 68% yield (44.4 mg) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 2.0 Hz, 1H), 7.32 – 7.27 (m, 3H), 7.25 – 7.22 (m, 1H), 7.07 (d, *J* = 7.2 Hz, 2H), 6.16 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.7, 136.3, 135.4, 131.1, 130.7, 129.7, 128.7, 127.4, 125.9, 119.6, 118.3, 51.4. **IR** (neat) 2931, 1444, 1353, 1292, 1188, 1154, 1070, 985, 848, 694 cm^{-1}. **HRMS** (EI) Calcd for $C_{14}H_9Cl_2NS_2$ 324.9553, Found

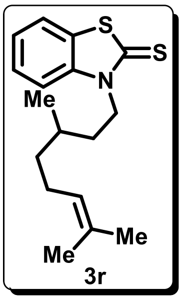
324.9547.


3p

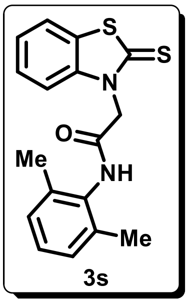
The reaction mixture of 2-iodo-N-(pyridin-4-ylmethyl)aniline (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in NMP (2.0 mL) was stirred at 80 ^oC for 16 h under N_2 atmosphere， affording compound **3p** in 70% yield (36.3 mg) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 5.2 Hz, 2H), 7.53 – 7.51 (m, 1H), 7.33 – 7.28 (m, 2H), 7.17 (d, *J* = 5.2 Hz, 2H), 7.00 – 6.98 (m, 1H), 5.70 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.4, 150.2, 143.4, 141.0, 127.4, 127.2, 125.2, 121.8, 121.6, 112.5, 48.3. **IR** (neat) 1637, 1600, 1460, 1415, 1368, 1212, 1194, 1142, 991, 750 cm^{-1}. **HRMS** (EI) Calcd for $C_{13}H_{10}N_2S_2$ 258.0285, Found 258.0288.


3q

The reaction mixture of N-(ferrocene-2-ylmethyl)-2-iodoaniline (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in NMP (2.0 mL) was stirred at 80 ^oC for 16 h under N_2 atmosphere， affording compound **3q** in 82% yield (59.5 mg) as a yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.19 – 7.13 (m, 1H), 5.35 (s, 2H), 4.43 (s, 2H), 4.16 (s, 5H), 4.04 (s, 2H). **^{3}C NMR** (1001 MHz, $CDCl_3$) δ 189.0, 141.2, 127.6, 126.6, 124.6, 121.2, 112.7, 81.2, 69.7, 68.9, 68.3, 45.4. **IR** (neat) 3080, 2947, 1462, 1374, 1361, 1300, 1271, 1177, 961, 814, 737 cm^{-1}. **HRMS** (EI) Calcd for $C_{18}H_{15}FeNS_2$ 364.9995, Found 365.0000.


3r

The reaction mixture of N-(3,7-dimethyloct-6-enyl)-2-iodoaniline (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in NMP (2.0 mL) was stirred at 80 °C for 16 h under N_2 atmosphere，affording compound **3r** in 50% yield (30.3 mg) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 5.10 (t, *J* = 7.2 Hz, 1H), 4.50 – 4.35 (m, 2H), 2.09 – 1.96 (m, 2H), 1.82 – 1.77 (m, 1H), 1.71 – 1.57 (m, 8H), 1.48 – 1.41 (m, 1H), 1.32 – 1.23 (m, 1H), 1.06 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.6, 141.3, 131.5, 127.9, 126.8, 124.6, 124.3, 121.4, 112.2, 44.8, 36.7, 33.2, 30.6, 25.7, 25.4, 19.5, 17.7. **IR** (neat) 2923, 1637, 1586, 1459, 1373, 1316, 1264, 1204, 1132, 747 cm^{-1}. **HRMS** (EI) Calcd for $C_{17}H_{23}NS_2$ 305.1272, Found 305.1275.

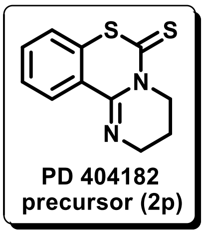


3s

The reaction mixture of N-(2,6-dimethylphenyl)-2-(2-iodophenylamino)acetamide (0.2 mmol, 1.0 equiv), $Cu(OAc)_2·H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02 mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in NMP (2.0 mL) was stirred at 80 °C for 16 h under N_2 atmosphere，affording compound **3s** in 51% yield (33.5 mg) as a pale yellow solid. **^{1}H NMR** (400 MHz, DMSO) δ 9.77 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.41 – 7.36 (m, 1H), 7.08 – 7.04 (m, 3H), 5.42 (s, 2H), 2.19 (s, 6H). **^{13}C NMR** (100 MHz, DMSO) δ 189.2, 163.5, 142.0, 135.2, 134.4, 127.6, 127.1, 126.6, 126.3, 124.9, 121.8, 113.6, 48.1, 18.2. **IR** (neat) 3282, 2921, 1655, 1592, 1532, 1466, 1370, 1315, 1212, 1146, 999, 751 cm^{-1}. **HRMS** (EI) Calcd for $C_{17}H_{16}N_2OS_2$ 328.0704, Found 328.0708.

V. The Application of The Reaction.

1) The Synthetic Procedure and Data for chloromethiuron.

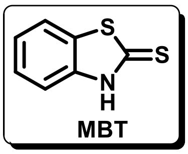


PD 404182
precursor (2p)

The reaction mixture of 2-(2-iodophenyl)-1,4,5,6-tetrahydropyrimidine (0.2 mmol, 1.0 equiv), $Cu(OAc)_2·H_2O$ (0.02 mmol, 0.1 equiv), 2,2'-dipyridyl (0.02

mmol, 0.1 equiv), K_2S (0.8 mmol, 4.0 equiv), LiOH (1.2 mmol, 6.0 equiv) and $CHCl_3$ (2 mmol, 10 equiv) in NMP (2.0 mL) was stirred at 80 °C for 16 h under N_2 atmosphere，affording compound **2p** in 55% yield (25.9 mg) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.39 (m, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 4.44 (t, *J* = 6.0 Hz, 2H), 3.76 (t, *J* = 5.6 Hz, 2H), 2.04 (dt, *J* = 12.0, 6.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.8, 144.4, 131.9, 131.2, 128.9, 127.5, 126.2, 121.6, 48.7, 45.4, 21.5. **IR** (neat) 2920, 2850, 1626, 1459, 1359, 1307, 1286, 1155, 1039, 954, 771, 726 cm^{-1}. **HRMS** (EI) Calcd for $C_{11}H_{10}N_2S_2$ 234.0285, Found 234.0283.

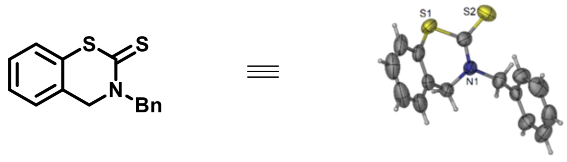
2) The Synthetic Procedure and Data for 2-Mercaptobenzothiazole (MBT).

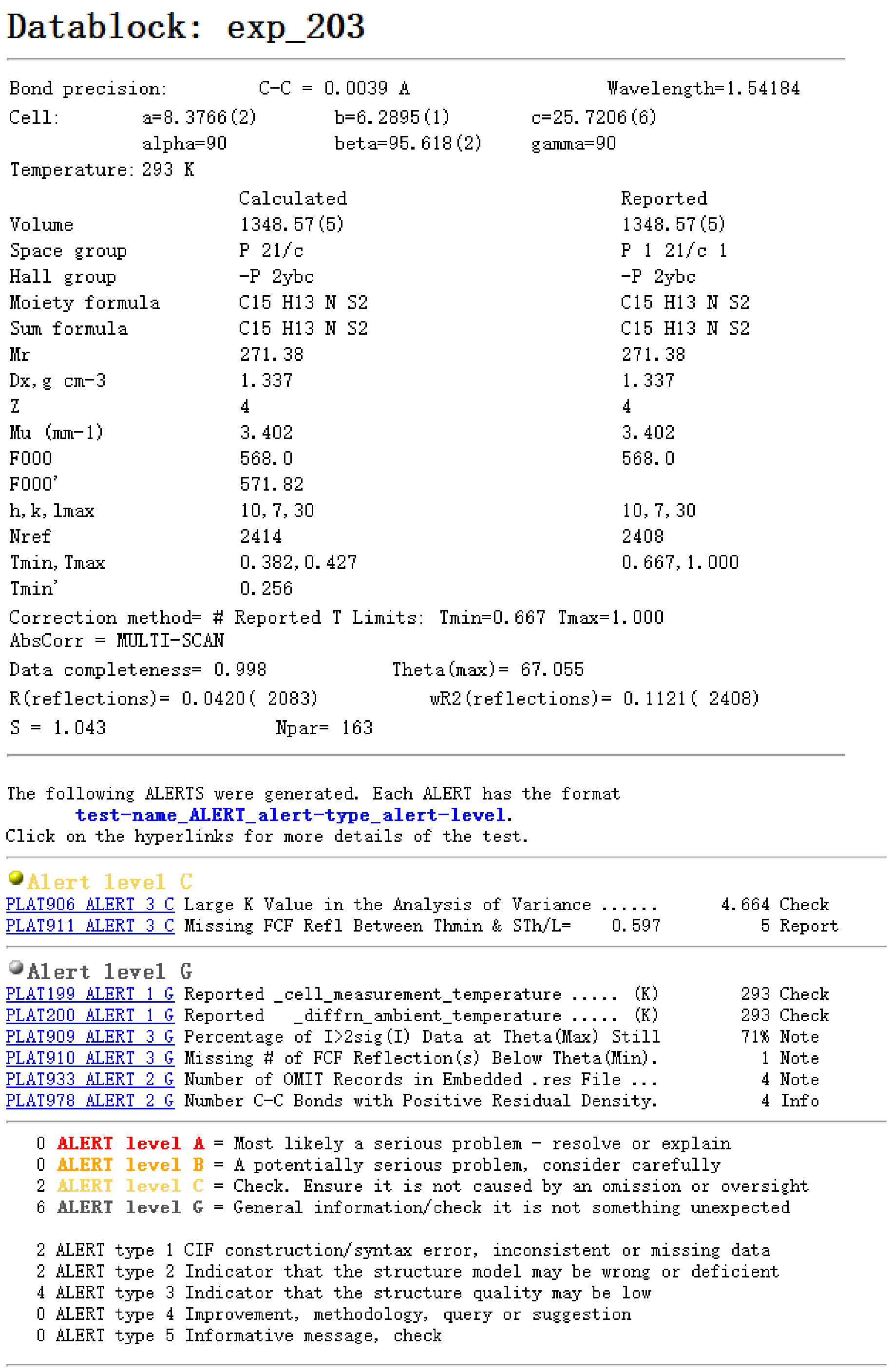


The reaction mixture of *o*-iodoaniline (10.0 mmol, 1.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (1.0 mmol, 0.1 equiv), 2,2'-dipyridyl (1.0 mmol, 0.1 equiv), K_2S (40.0 mmol, 4.0 equiv), LiOH (60.0 mmol, 6.0 equiv) and $CHCl_3$ (100 mmol, 10 equiv) in NMP (80 mL) was stirred at 80 °C for 22 h under N_2 atmosphere, affording **MBT** in 73% yield (1.22 g) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.95 (s, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.32 – 7.25 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.9, 140.2, 130.0, 127.2, 124.7, 121.4, 112.3. **IR** (neat) 3112, 3041, 2963, 2894, 1497, 1427, 1321, 1077, 1035, 751, 669 cm^{-1}. **HRMS** (EI) Calcd for $C_7H_5NS_2$ 166.9863, Found 166.9865.

VI. X-ray Crystallography Analysis of Compound 2a and 3a.

1) X-ray Crystallography Analysis of Compound 2a (CCDC-1816889)





Datablock: exp_203

```
Bond precision:        C-C = 0.0039 A                Wavelength=1.54184
Cell:          a=8.3766(2)        b=6.2895(1)        c=25.7206(6)
               alpha=90           beta=95.618(2)     gamma=90
Temperature: 293 K
                         Calculated                          Reported
Volume                   1348.57(5)                          1348.57(5)
Space group              P 21/c                              P 1 21/c 1
Hall group               -P 2ybc                             -P 2ybc
Moiety formula           C15 H13 N S2                        C15 H13 N S2
Sum formula              C15 H13 N S2                        C15 H13 N S2
Mr                       271.38                              271.38
Dx,g cm-3                1.337                               1.337
Z                        4                                   4
Mu (mm-1)                3.402                               3.402
F000                     568.0                               568.0
F000'                    571.82
h,k,lmax                 10,7,30                             10,7,30
Nref                     2414                                2408
Tmin,Tmax                0.382,0.427                         0.667,1.000
Tmin'                    0.256
Correction method= # Reported T Limits: Tmin=0.667 Tmax=1.000
AbsCorr = MULTI-SCAN
Data completeness= 0.998              Theta(max)= 67.055
R(reflections)= 0.0420( 2083)            wR2(reflections)= 0.1121( 2408)
S = 1.043                  Npar= 163
```

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The following ALERTS were generated. Each ALERT has the format
      test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

```
●Alert level C
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      4.664 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.597        5 Report
```

```
●Alert level G
PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)       293 Check
PLAT200_ALERT_1_G Reported   _diffrn_ambient_temperature ..... (K)       293 Check
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still       71% Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).         1 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...         4 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         4 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   2 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   6 ALERT level G = General information/check it is not something unexpected

   2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   4 ALERT type 3 Indicator that the structure quality may be low
   0 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
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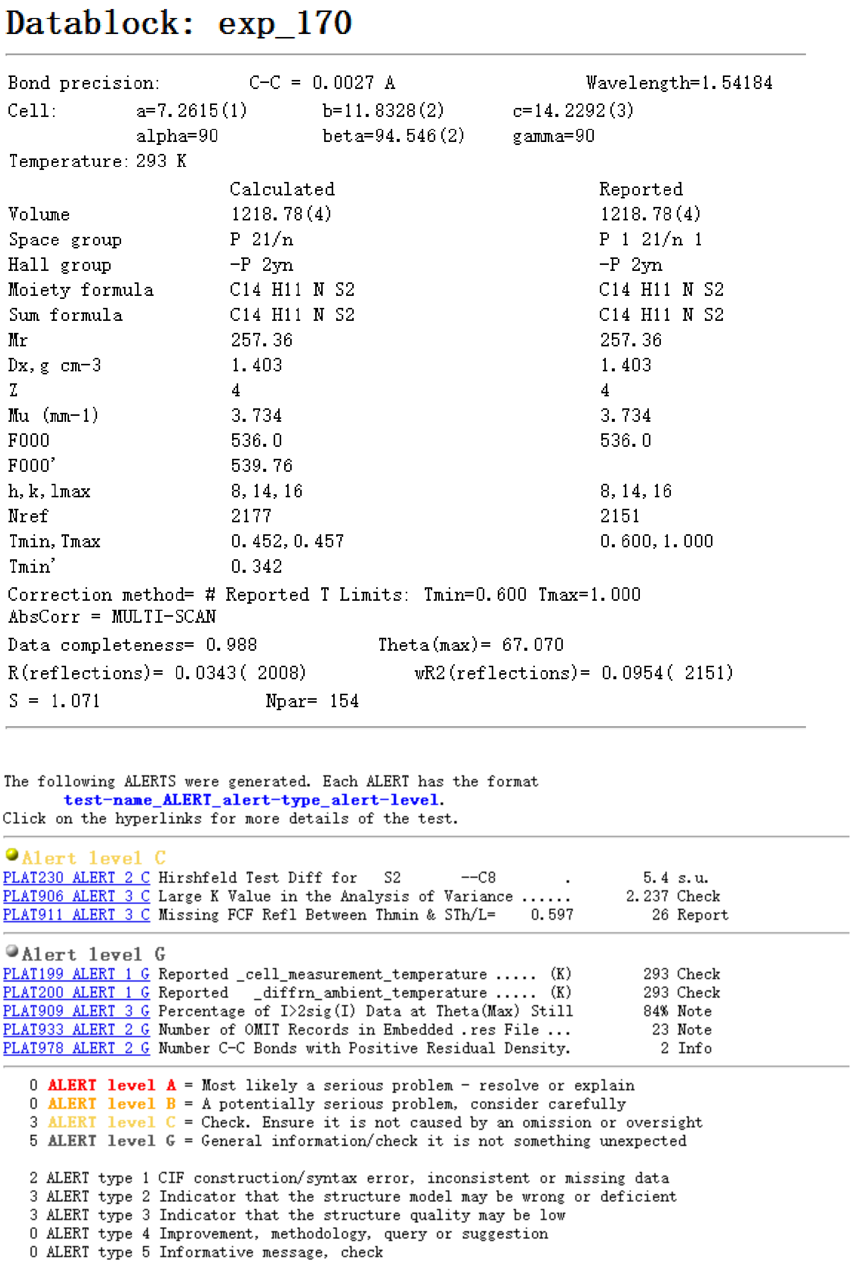
2) X-ray Crystallography Analysis of Compound 3a (CCDC-1816887)



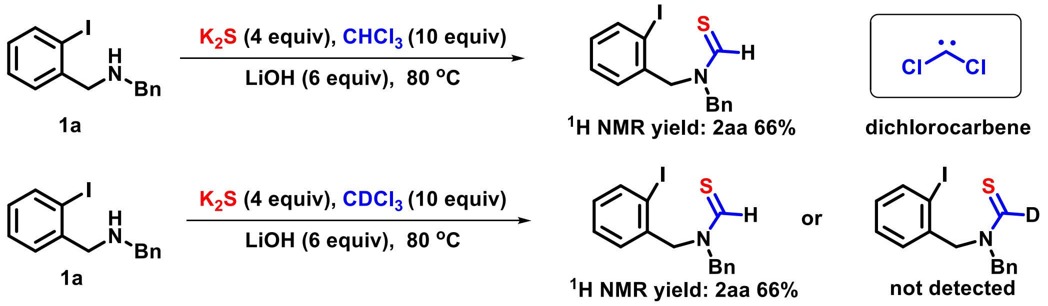
```
Datablock: exp_170

Bond precision:        C-C = 0.0027 A              Wavelength=1.54184
Cell:          a=7.2615(1)       b=11.8328(2)     c=14.2292(3)
               alpha=90          beta=94.546(2)   gamma=90
Temperature: 293 K
                     Calculated                      Reported
Volume               1218.78(4)                      1218.78(4)
Space group          P 21/n                          P 1 21/n 1
Hall group           -P 2yn                          -P 2yn
Moiety formula       C14 H11 N S2                    C14 H11 N S2
Sum formula          C14 H11 N S2                    C14 H11 N S2
Mr                   257.36                          257.36
Dx,g cm-3            1.403                           1.403
Z                    4                               4
Mu (mm-1)            3.734                           3.734
F000                 536.0                           536.0
F000'                539.76
h,k,lmax             8,14,16                         8,14,16
Nref                 2177                            2151
Tmin,Tmax            0.452,0.457                     0.600,1.000
Tmin'                0.342
Correction method= # Reported T Limits: Tmin=0.600 Tmax=1.000
AbsCorr = MULTI-SCAN
Data completeness= 0.988             Theta(max)= 67.070
R(reflections)= 0.0343( 2008)          wR2(reflections)= 0.0954( 2151)
S = 1.071                  Npar= 154

The following ALERTS were generated. Each ALERT has the format
       test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C
PLAT230_ALERT_2_C Hirshfeld Test Diff for    S2        --C8         .        5.4 s.u.
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......       2.237 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=     0.597         26 Report

Alert level G
PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)        293 Check
PLAT200_ALERT_1_G Reported   _diffrn_ambient_temperature ..... (K)        293 Check
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still        84% Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...         23 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          2 Info

   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   3 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   5 ALERT level G = General information/check it is not something unexpected

   2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   3 ALERT type 2 Indicator that the structure model may be wrong or deficient
   3 ALERT type 3 Indicator that the structure quality may be low
   0 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/ci.

VII. Mechanistic Studies.

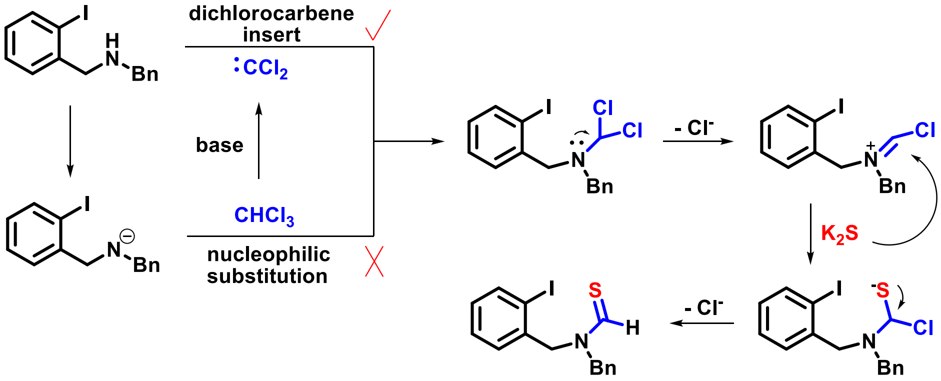
1) Studies for $CHCl_3$:

Scheme S1. Procedure for the reaction of **1a** with $CHCl_3$ in the presence of K_2S:

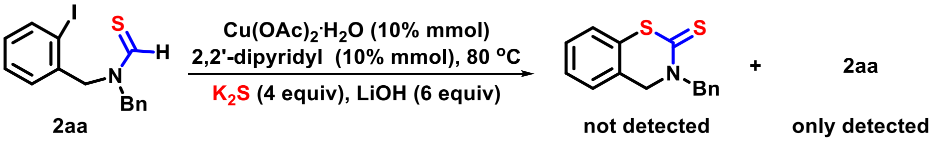


To a solution of substrate **1a** (0.1 mmol, 1.0 equiv), K_2S (0.4 mmol, 4.0 equiv), LiOH (0.6 mmol, 6.0 equiv) and $CHCl_3$ or $CDCl_3$ (1 mmol, 10 equiv) in MeCN/H_2O (0.5/0.5 mL) was stirred at 80 °C for 12 h under N_2 atmosphere, which was monitored by ^{1}H NMR using CH_2Br_2 as an internal standard, affording compound **2aa** in 66% ^{1}HNMR yield as a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.63 (d, *J* = 30.8 Hz, 1H), 7.86 (t, *J* = 8.4 Hz, 1H), 7.39 – 7.29 (m, 5H), 7.19 – 7.08 (m, 2H), 7.07 – 6.98 (m, 1H), 5.05 (d, *J* = 11.2 Hz, 2H), 4.59 (d, *J* = 17.2 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.8, 190.0, 140.2, 139.7, 136.4, 136.3, 134.4, 133.9, 130.2, 129.5, 129.4, 129.0, 128.8, 128.7, 128.6, 128.5, 128.5, 128.0, 128.0, 99.0, 98.9, 63.0, 59.2, 54.7, 49.9. **IR** (neat) 3060, 2923, 2855, 1672, 1495, 1436, 1211, 1015, 752, 699 cm^{-1}. **HRMS** (EI) Calcd for $C_{15}H_{14}INS$ 366.9892, Found 366.9898.

Scheme S2. Possible approaches to the formation of **2aa**.[11]



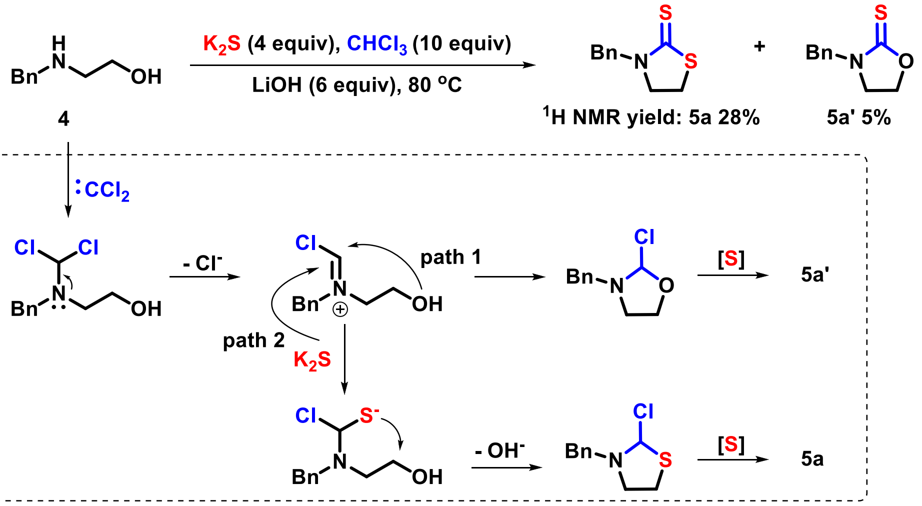
Scheme S3. Procedure for the reaction of **2aa** as possible intermediate excluded.



To a solution of substrate **2aa** (0.1 mmol, 1.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (0.01 mmol, 0.1 equiv), 2,2'-dipyridyl (0.01 mmol, 0.1 equiv), K_2S (0.4 mmol, 4.0 equiv), LiOH (0.6 mmol, 6.0 equiv) and $CHCl_3$ (1 mmol, 10 equiv) in MeCN (1.0 mL) was stirred at 80 ^{o}C for 16 h under N_2 atmosphere. The reaction was monitored by ^{1}H NMR using CH_2Br_2 as an internal standard.

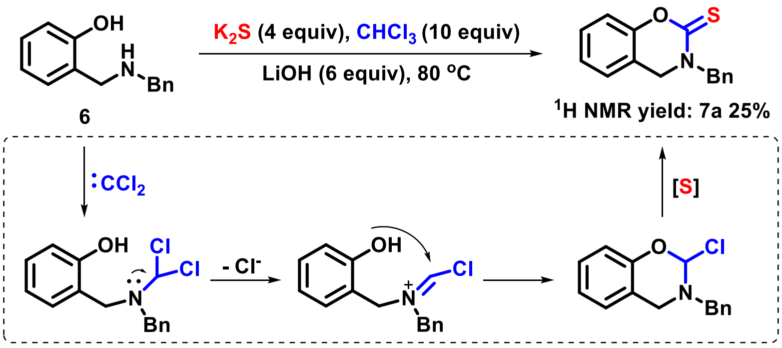
2) Studies for K_2S:

Scheme S4. Procedure for the reaction of **4** with $CHCl_3$ in the presence of K_2S and possible approaches to the formation of **5a and 5a′**.



To a solution of substrate **4** (0.1 mmol, 1.0 equiv), K_2S (0.4 mmol, 4.0 equiv), LiOH (0.6 mmol, 6.0 equiv) and $CHCl_3$ (1 mmol, 10 equiv) in MeCN (1.0 mL) was stirred at 80 ^{o}C for 16 h under N_2 atmosphere, which was monitored by ^{1}H NMR using CH_2Br_2 as an internal standard, affording corresponding compounds **5a** and **5a′**. Compound **5a** in 28% ^{1}HNMR yield as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 4.99 (s, 2H), 3.94 (t, *J* = 8.0 Hz, 2H), 3.24 (t, *J* = 8.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.2, 135.0, 128.9, 128.2, 128.1, 55.8, 52. 6, 27.0. **IR** (neat) 2944, 1661, 1489, 1449, 1411, 1316, 1245, 1045, 916, 731 cm^{-1}. **HRMS** (EI) Calcd for $C_{10}H_{11}NS_2$ 209.0333, Found 209.0336. Compound **5a′** in 5% ^{1}HNMR yield as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 4.84 (s, 2H), 4.47 (t, *J* = 8.8 Hz, 2H), 3.63 (t, *J* = 9.2 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.0, 134.5, 128.9, 128.3, 128.1, 65.9, 52.0, 47.2. **IR** (neat) 3027, 2914, 1521, 1427, 1325, 1255, 1155, 940, 735, 702 cm^{-1}. **HRMS** (EI) Calcd for $C_{10}H_{11}NOS$ 193.0561, Found 193.0564.

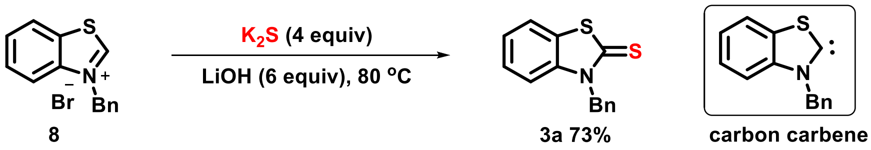
Scheme S5. Procedure for the reaction of **6** with $CHCl_3$ in the presence of K_2S and possible approaches to the formation of **7a and 7aa**.



To a solution of substrate **6** (0.1 mmol, 1.0 equiv), K_2S (0.4 mmol, 4.0 equiv), LiOH (0.6 mmol, 6.0 equiv) and $CHCl_3$ (1 mmol, 10 equiv) in MeCN (1.0 mL) was stirred at 80 ^oC for 16 h under N_2 atmosphere, which was monitored by ^1H NMR using CH_2Br_2 as an internal standard, affording corresponding compounds **7a**. Compound **7a** in 25% ^{1}HNMR yield as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.35 (m, 2H), 7.32 – 7.24 (m, 3H), 7.23 – 7.18 (m, 1H), 7.09 – 6.99 (m, 2H), 6.92 (d, *J* = 7.6 Hz, 1H), 5.24 (s, 2H), 4.32 (s, 2H). **^{13}C NMR** (100 MHz, DMSO) δ 183.3, 148.9, 135.7, 130.3, 129.8, 128.9, 128.6, 127.1, 126.3, 118.7, 116.1, 58.6, 47.8. **IR** (neat) 2251, 2125, 1655, 1055, 1028, 1008, 823, 761, 626 cm^{-1}. **HRMS** (EI) Calcd for $C_{15}H_{13}NOS$ 255.0718, Found 255.0723.

3) Coupling of carbon carbene and [S].

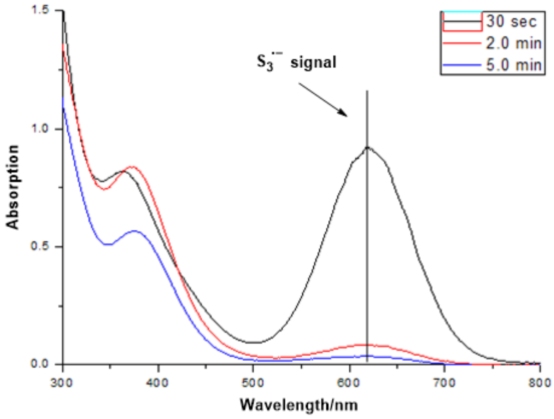
Scheme S6. Procedure for the coupling of carbon carbene and [S]:[12]



To a solution of substrate **8** (0.1 mmol, 1.0 equiv), K_2S (0.4 mmol, 4.0 equiv) and LiOH (0.6 mmol, 6.0 equiv) in MeCN (1.0 mL) was stirred at 80 ^oC for 7 h under N_2 atmosphere. After the reaction was finished, the solvent was removed under vacuum and purification by column chromatography on silica gel afforded product **3a** in 73% isolated yield. In the reaction, carbon carbene was considered as the intermediate according to literatures.

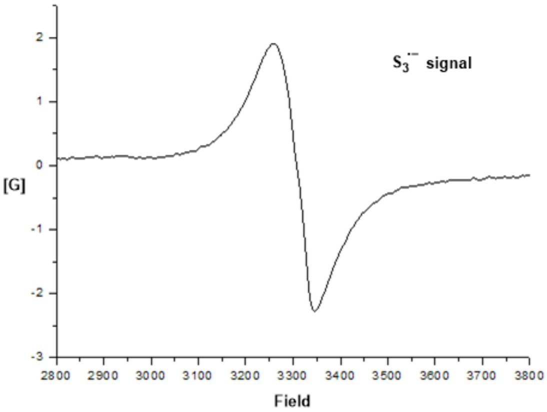
Scheme S7. The studies of trisulfur radical anion ($S_3^{\bullet-}$) by UV-visible spectra and EPR spectra:[13]

To a 25 mL of Schlenk tube with a stir bar were added K_2S (0.4 mmol) in NMP (2.0 mL) and was stirred at room temperature under N_2 atmosphere for an hour. Then, 0.05 mL of the reaction solution was taken out into a small sample cell containing 2.5 mL NMP solvent quickly and analyzed by UV spectrometer at room temperature, which were operated within 30 seconds (Picture S1, blue line). Notably, when this cell containing solution sample was placed under the air and detected again in 2 minutes (red line), the trisulfur radical anion ($S_3^{\bullet-}$) signal was markedly weakened. If in 5 minutes (green line), the signal reduced furtherly. Typical spectrometer parameters are shown as follows, scan range: 800 nm; wavelength from 300 nm-800 nm; Scan speed: 800 nm/min.



Picture S1. UV-visible spectra of K_2S in NMP.

To a 25 mL of Schlenk tube with a stir bar were added K_2S (0.4 mmol) in NMP (1.0 mL) and was stirred at room temperature under N_2 atmosphere for an hour. Then, the solution sample under N_2 atmosphere was taken out into a small tube and analyzed by EPR spectrometer at room temperature (Picture S2). EPR spectra was recorded on EPR spectrometer operated at 9.370 GHz. Typical spectrometer parameters are shown as follows, center field set: 3322.5 G; scan time: 60 s; modulation amplitude: 8.0 G; modulation frequency: 100 kHz.



Picture S2. EPR spectra of K_2S in NMP.

VIII. Reference.

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[12] a) N. E. Kamber, W. Jeong, R. M. Waymouth, *Chem. Rev.* **2007**, *107*, 5813. For selected examples: b) S. Alwarsh, Y. Xu, S. Y. Qian, M. C. McIntosh, *Angew. Chem. Int. Ed.* **2016**, *55*, 355.

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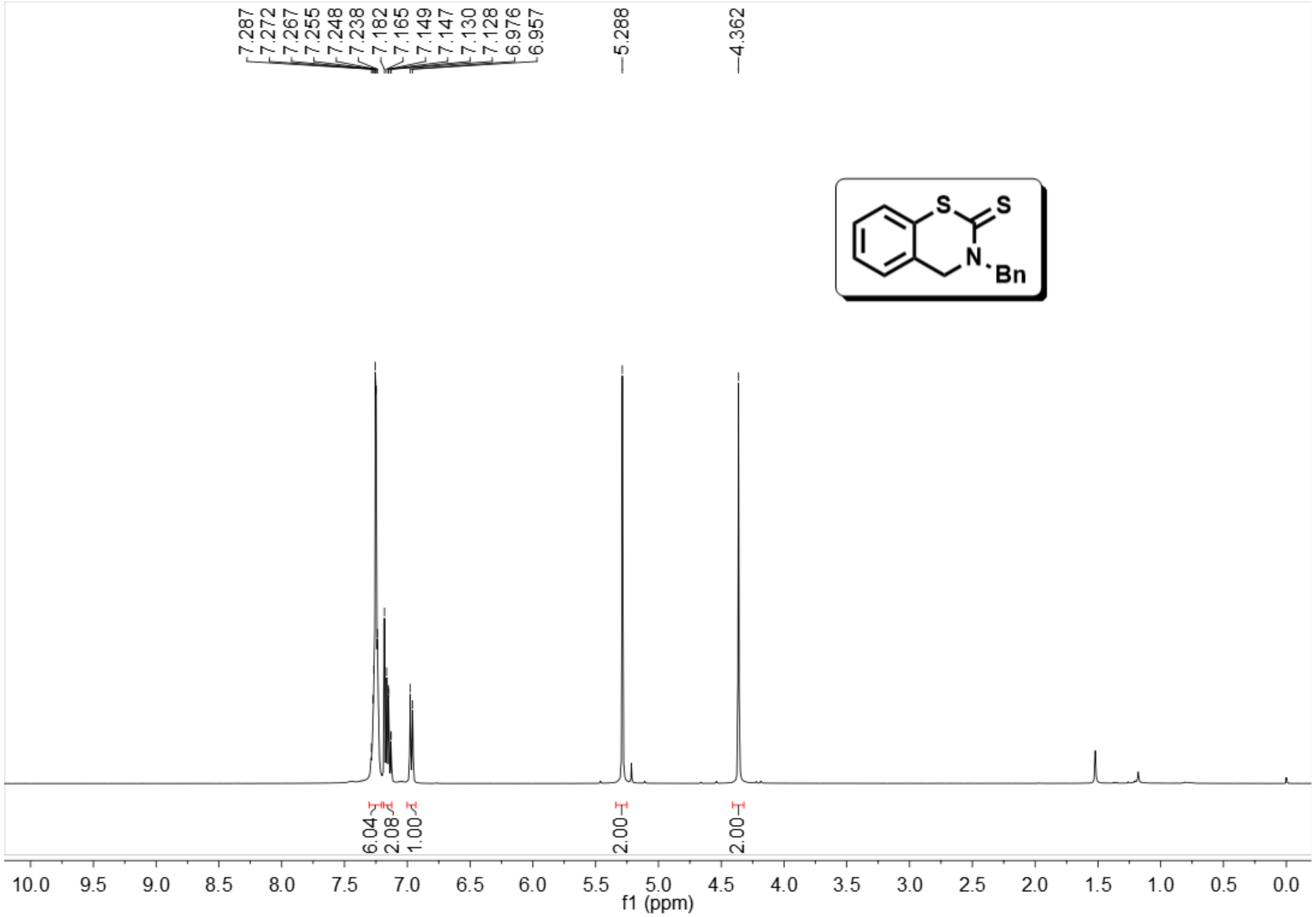
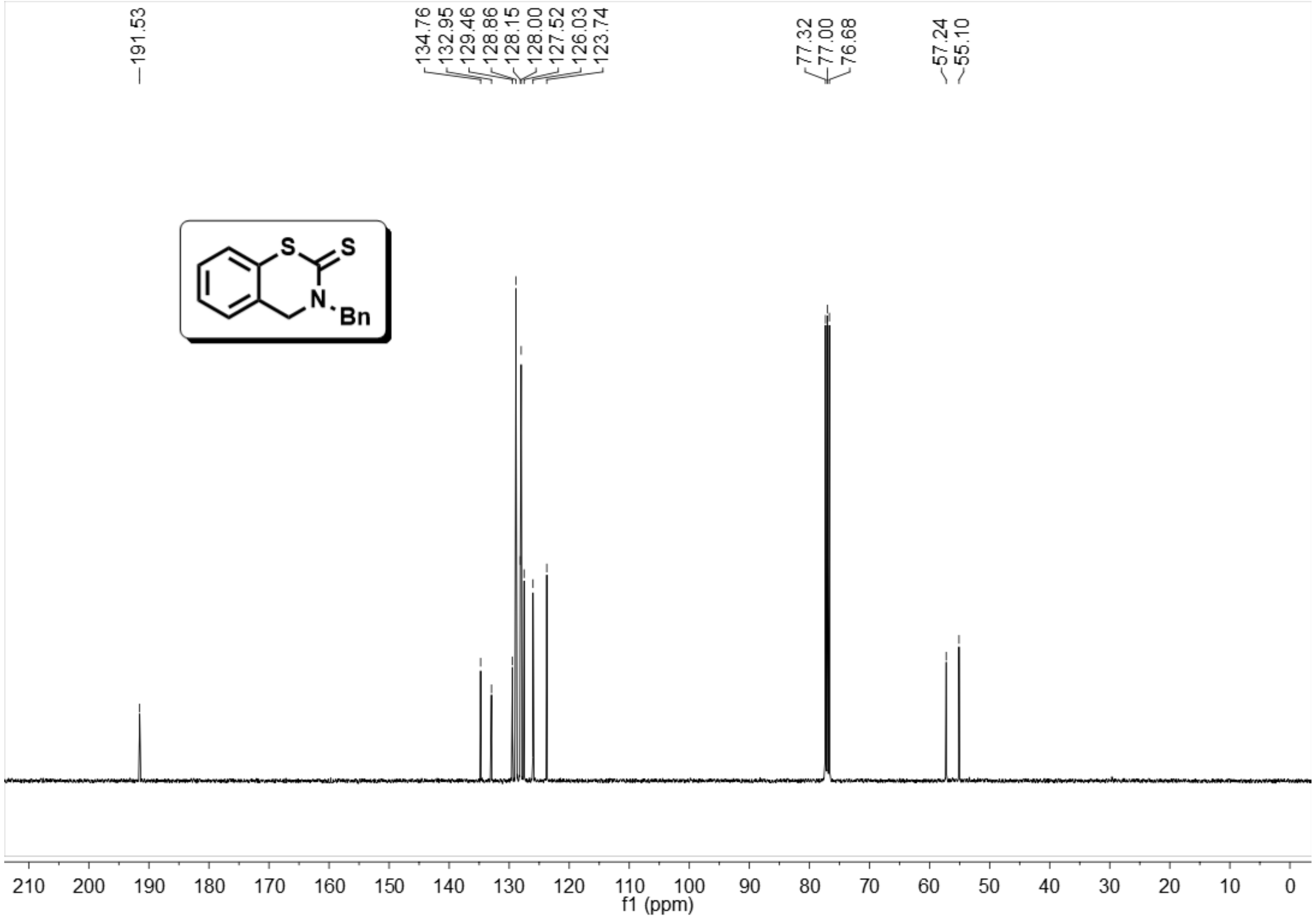
IX. NMR Spectra

2a



2a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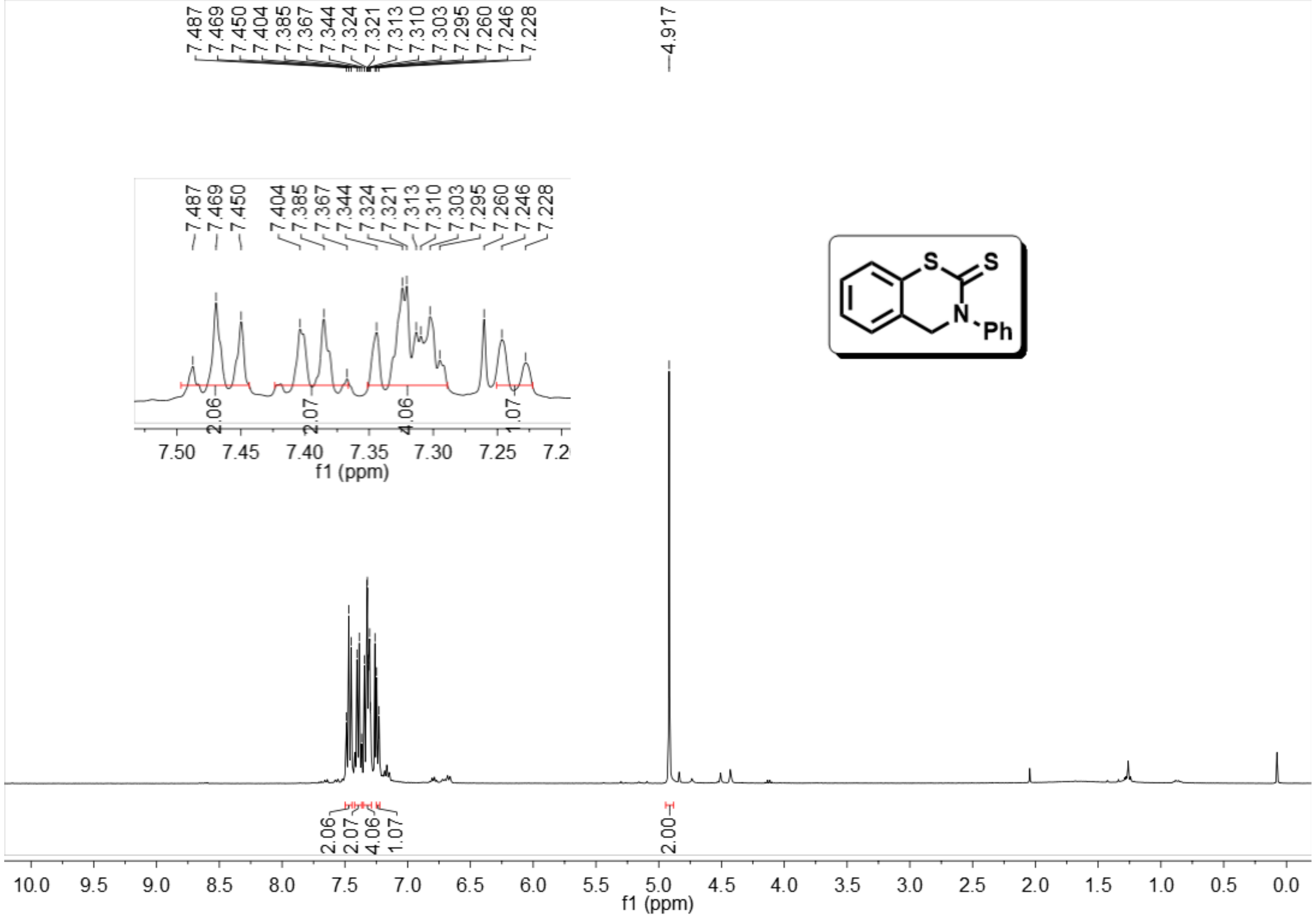
132.95
129.46
128.86
128.15
128.00
127.52
126.03
123.74
77.32
77.00
76.68
57.24
55.10
S
S
N
Bn
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2b



7.487
7.469
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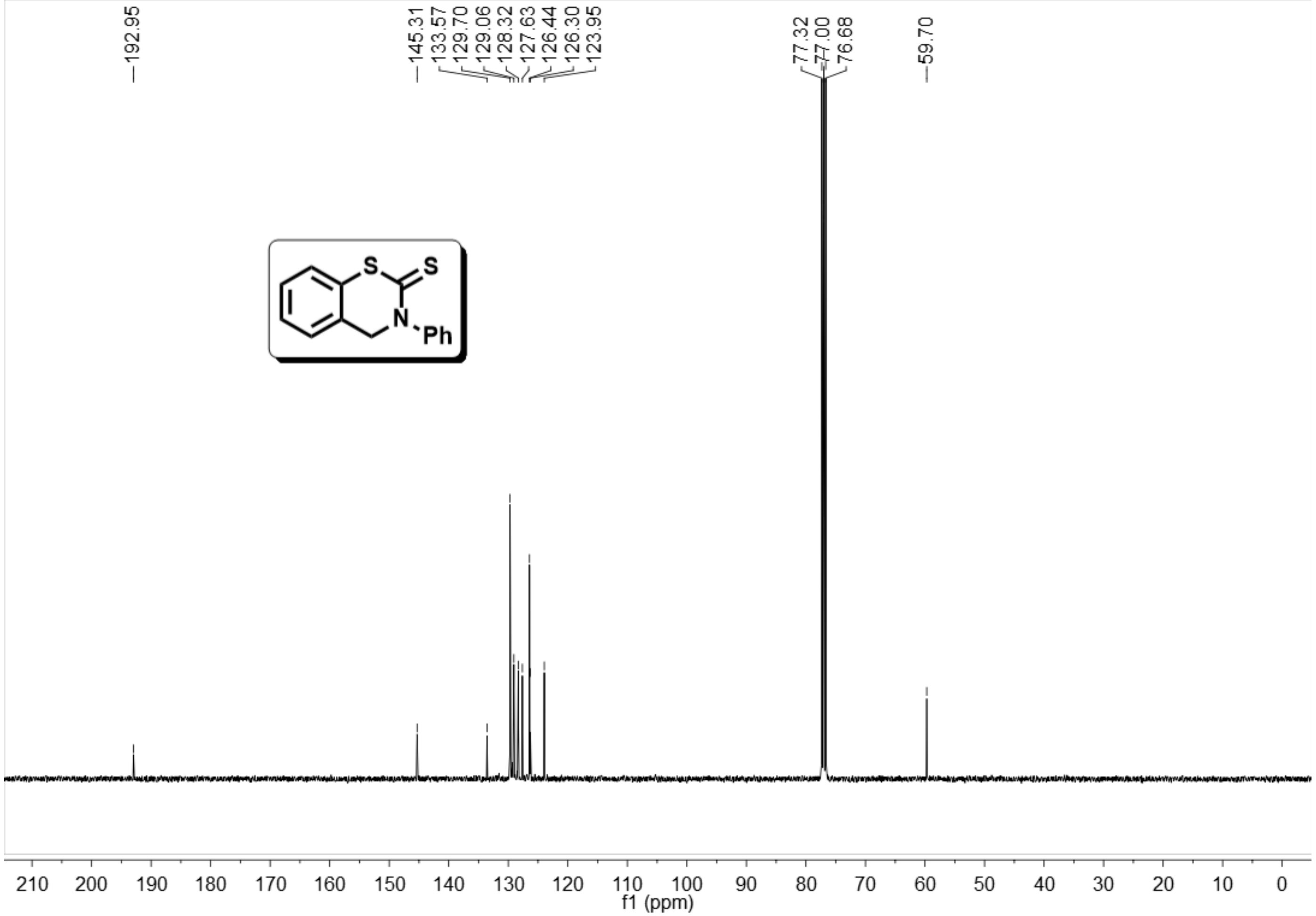
7.404
7.385
7.367
7.344
7.324
7.321
7.313
7.310
7.303
7.295
7.260
7.246
7.228
4.917
2.06
2.07
4.06
1.07
2.00
7.50 7.45 7.40 7.35 7.30 7.25 7.2
f1 (ppm)
S
S
N
Ph
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

2b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129.06
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127.63
126.44
126.30
123.95
77.32
77.00
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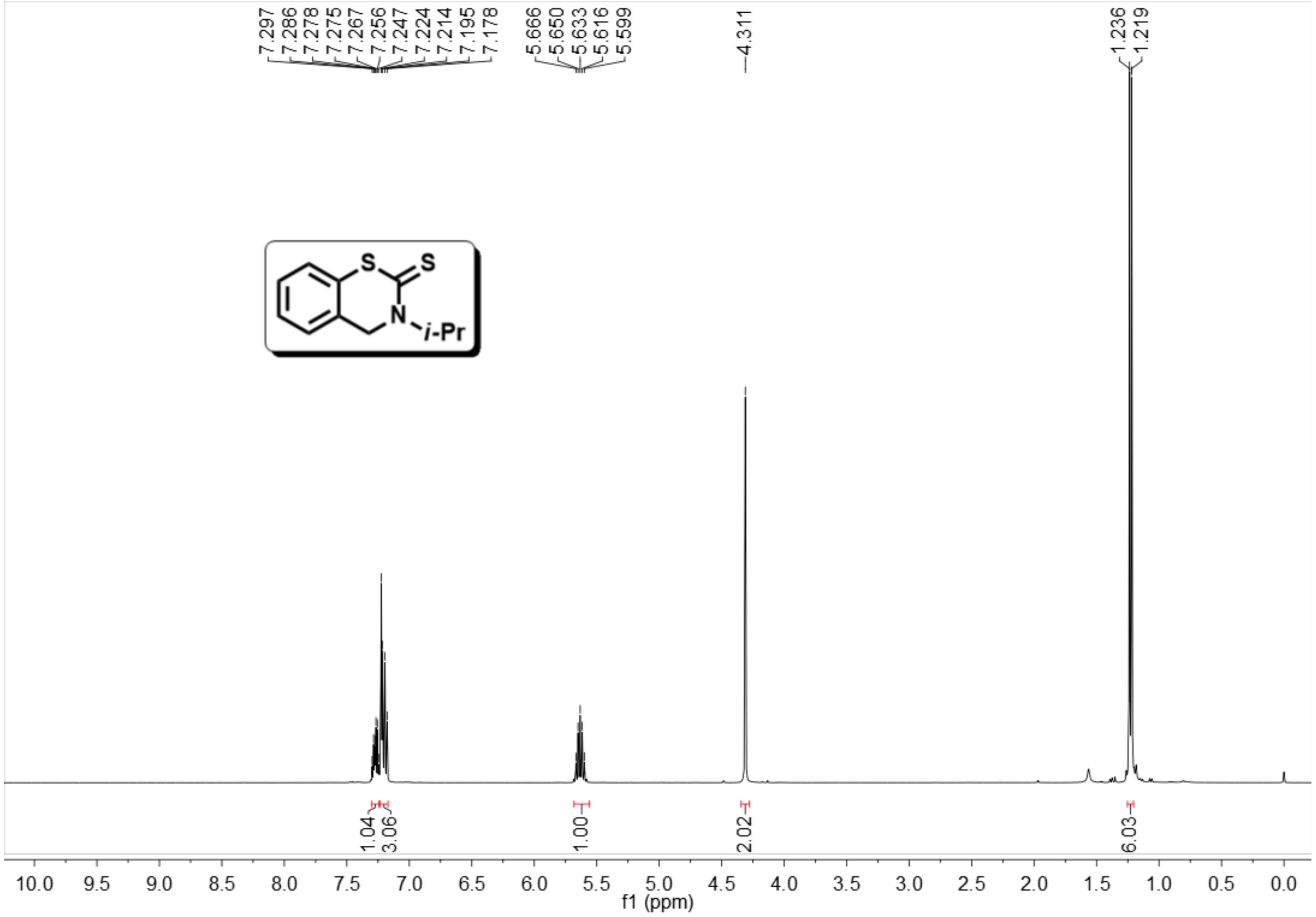
59.70
S
S
N
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2c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7.286
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7.178
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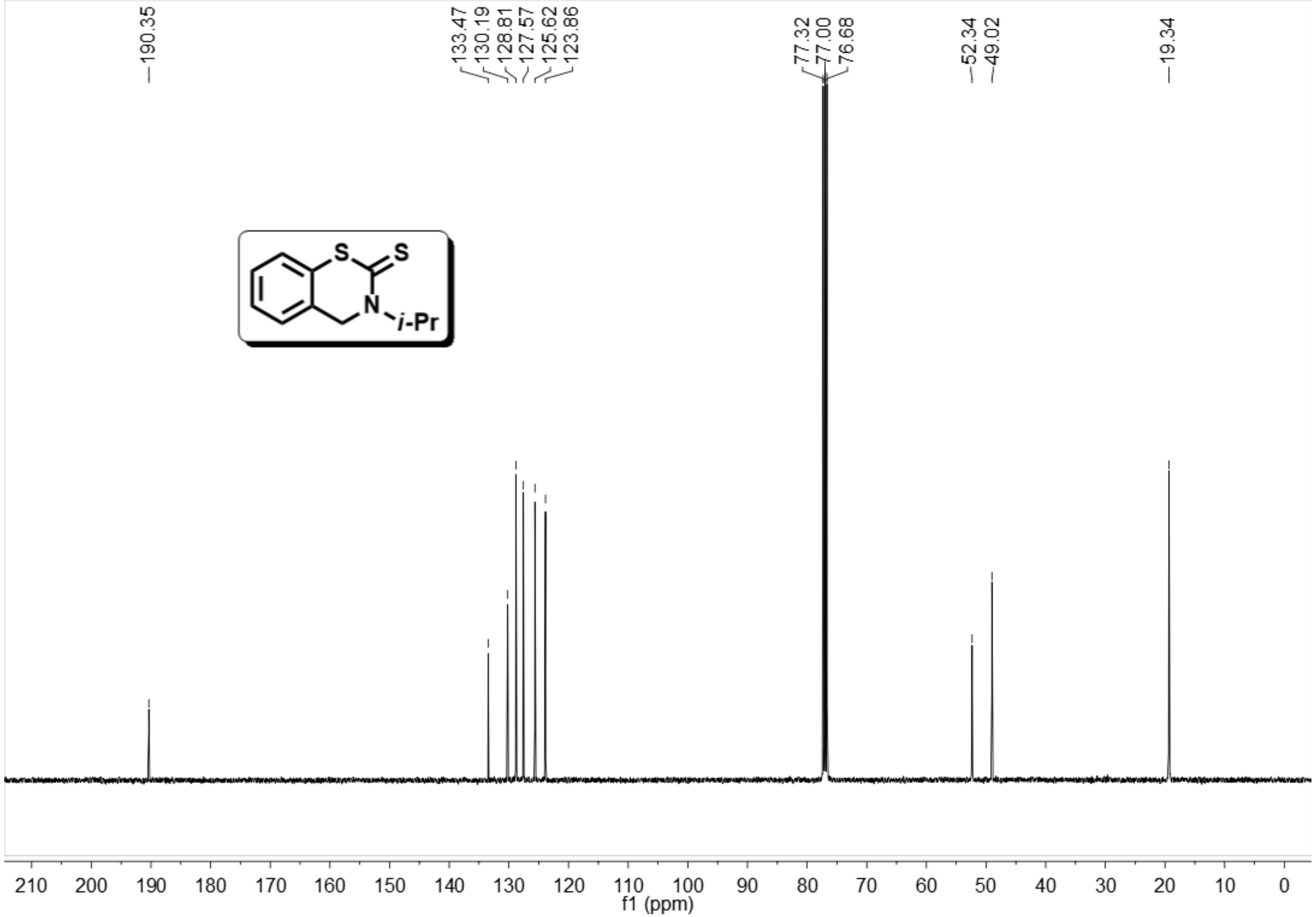
5.650
5.633
5.616
5.599
4.311
1.236
1.219
S
S
N
i-Pr
1.04
3.06
1.00
2.02
6.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2c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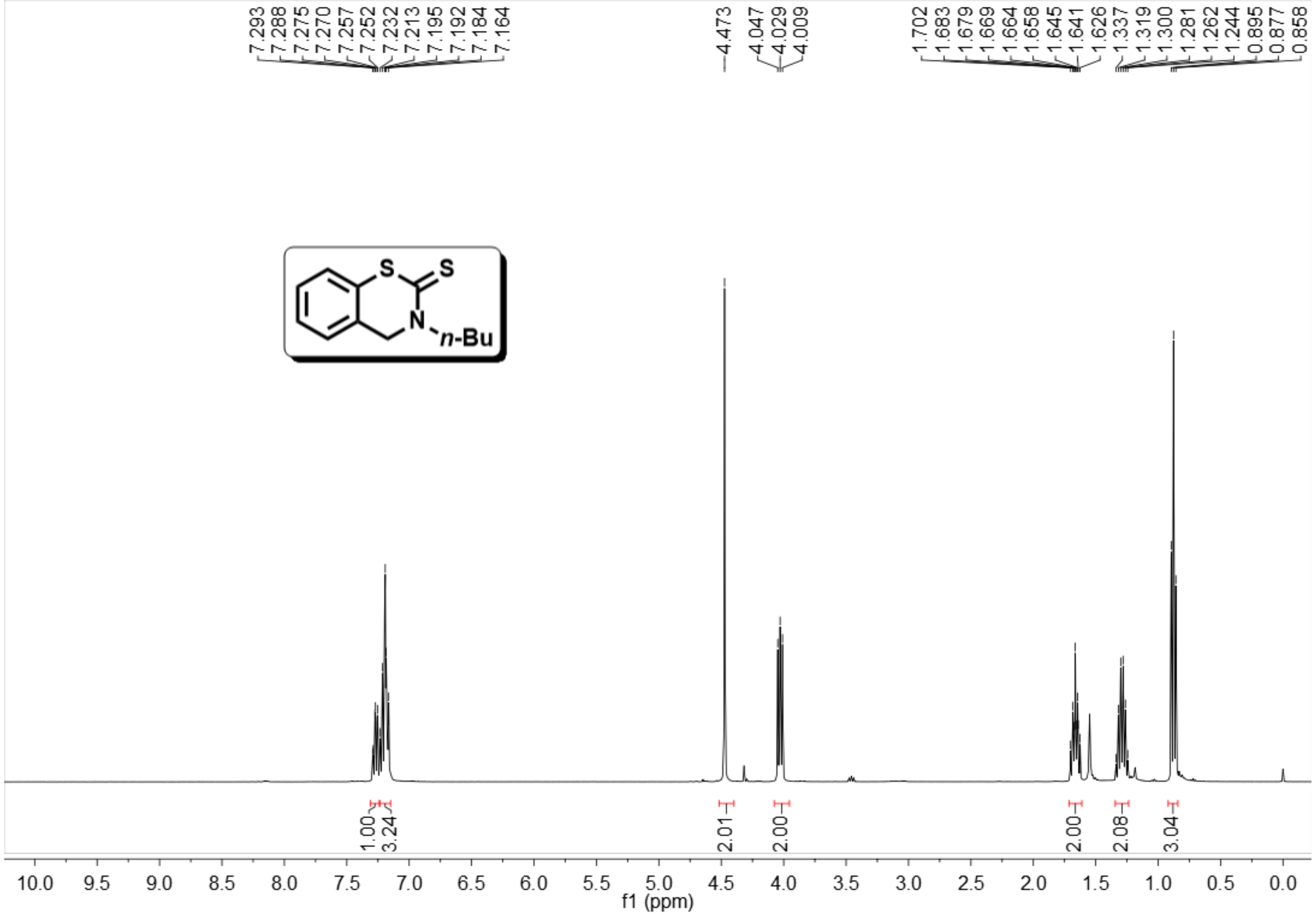
S
S
N
i-Pr
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2d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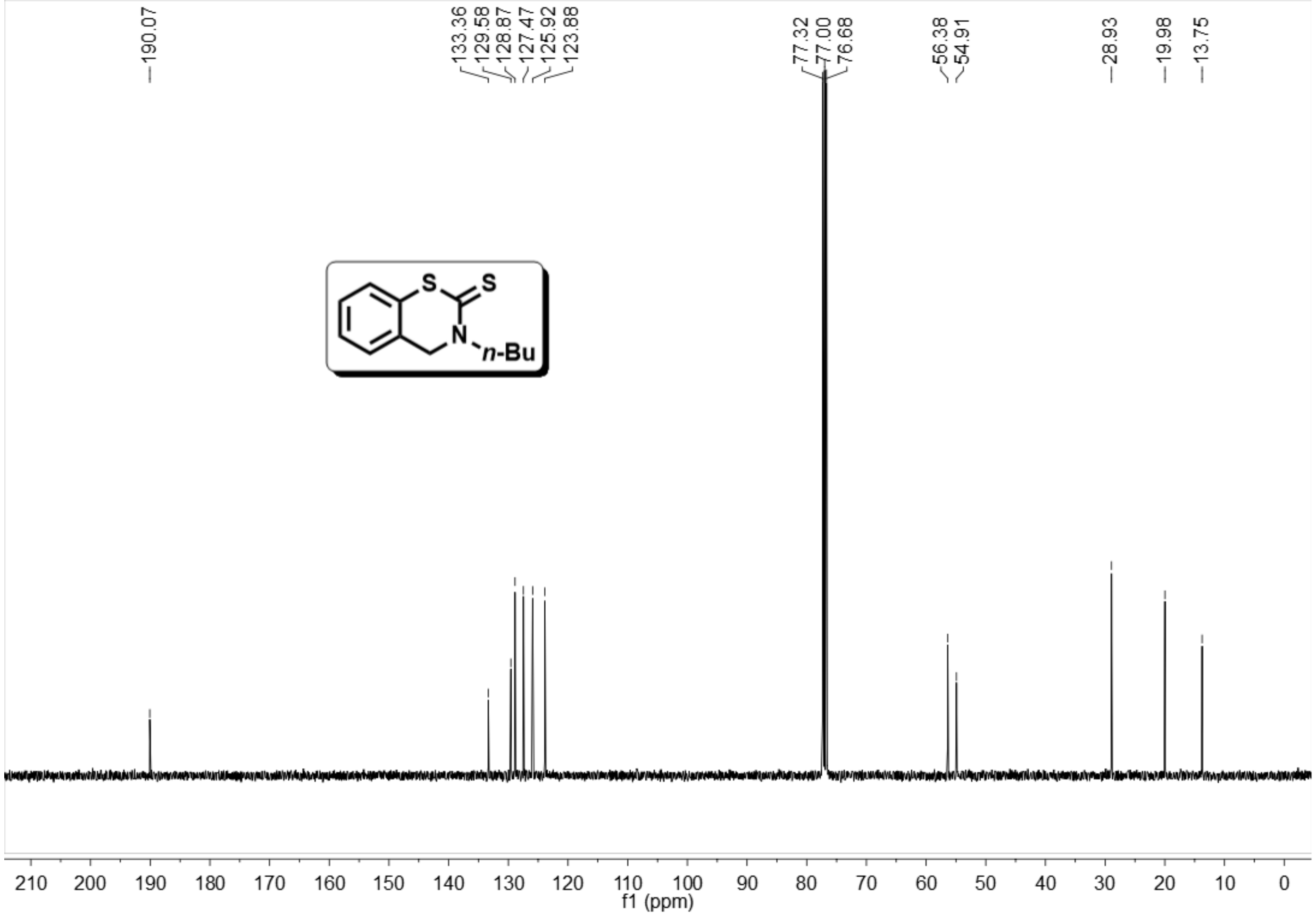
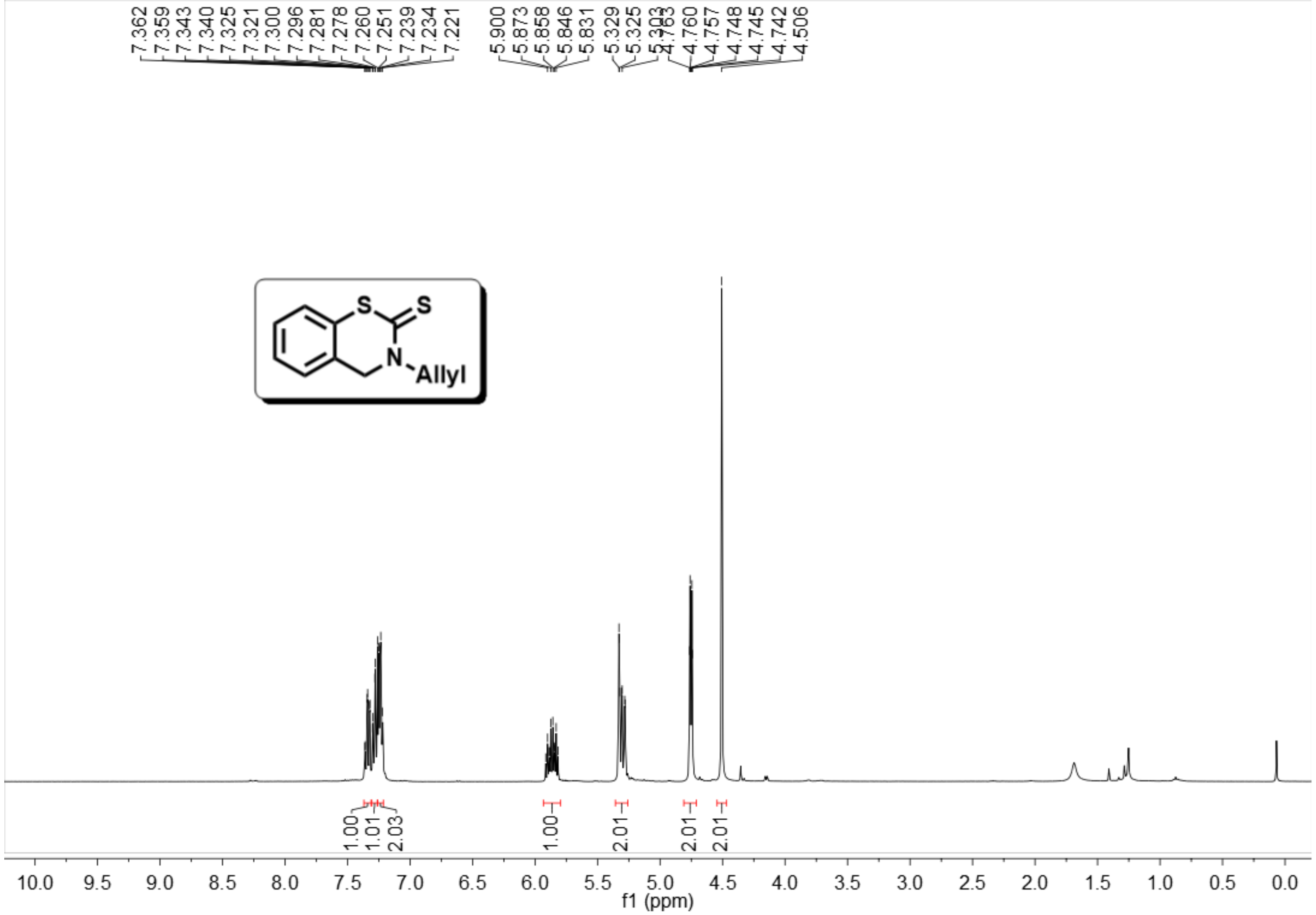
7.275
7.270
7.257
7.252
7.232
7.213
7.195
7.192
7.184
7.164
4.473
4.047
4.029
4.009
1.702
1.683
1.679
1.669
1.664
1.658
1.645
1.641
1.626
1.337
1.319
1.300
1.281
1.262
1.244
0.895
0.877
0.858
S
S
N
n-Bu
1.00
3.24
2.01
2.00
2.00
2.08
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

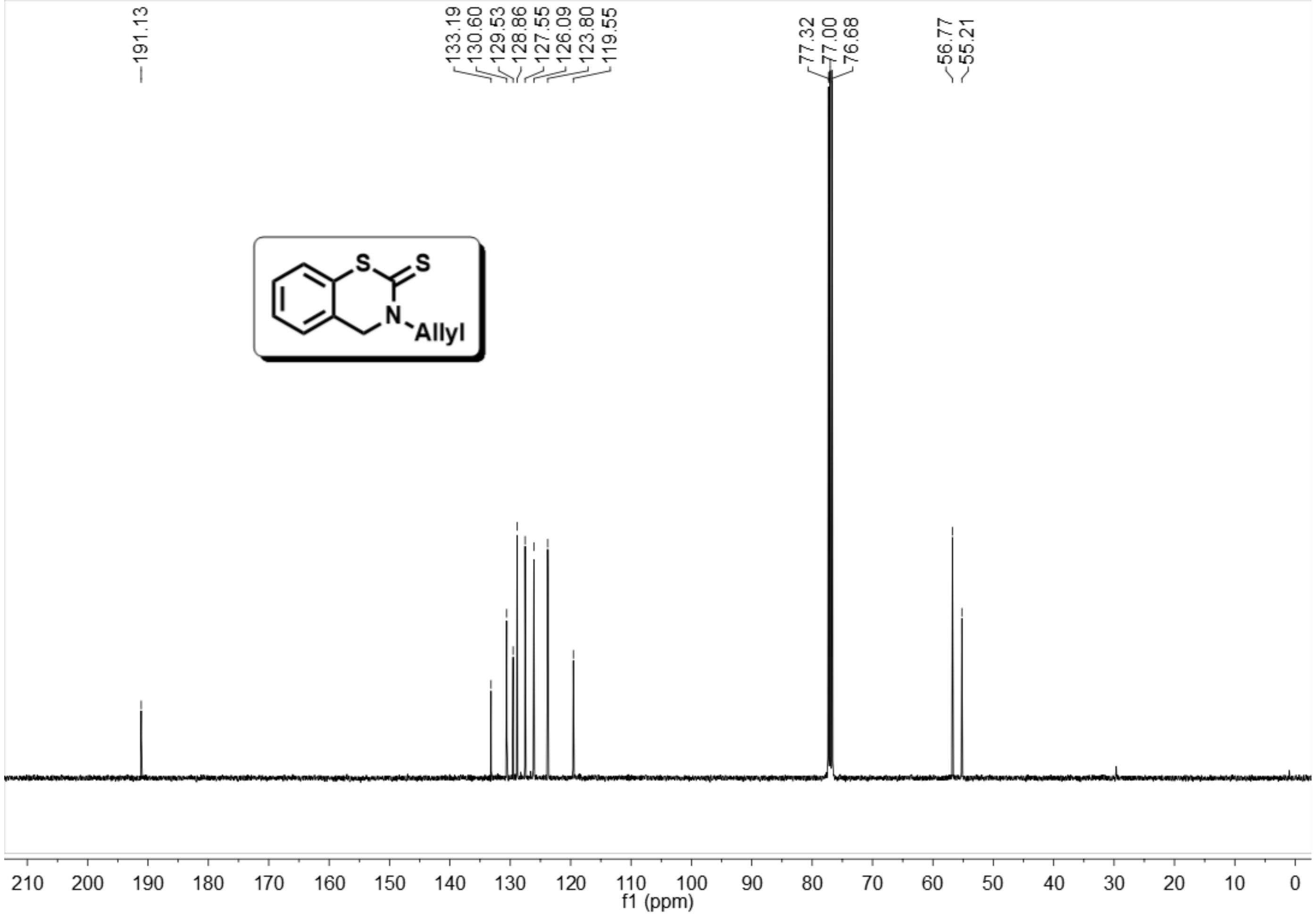
2d


190.07
133.36
129.58
128.87
127.47
125.92
123.88
77.32
77.00
76.68
56.38
54.91
28.93
19.98
13.75
S
S
N
n-Bu
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2e

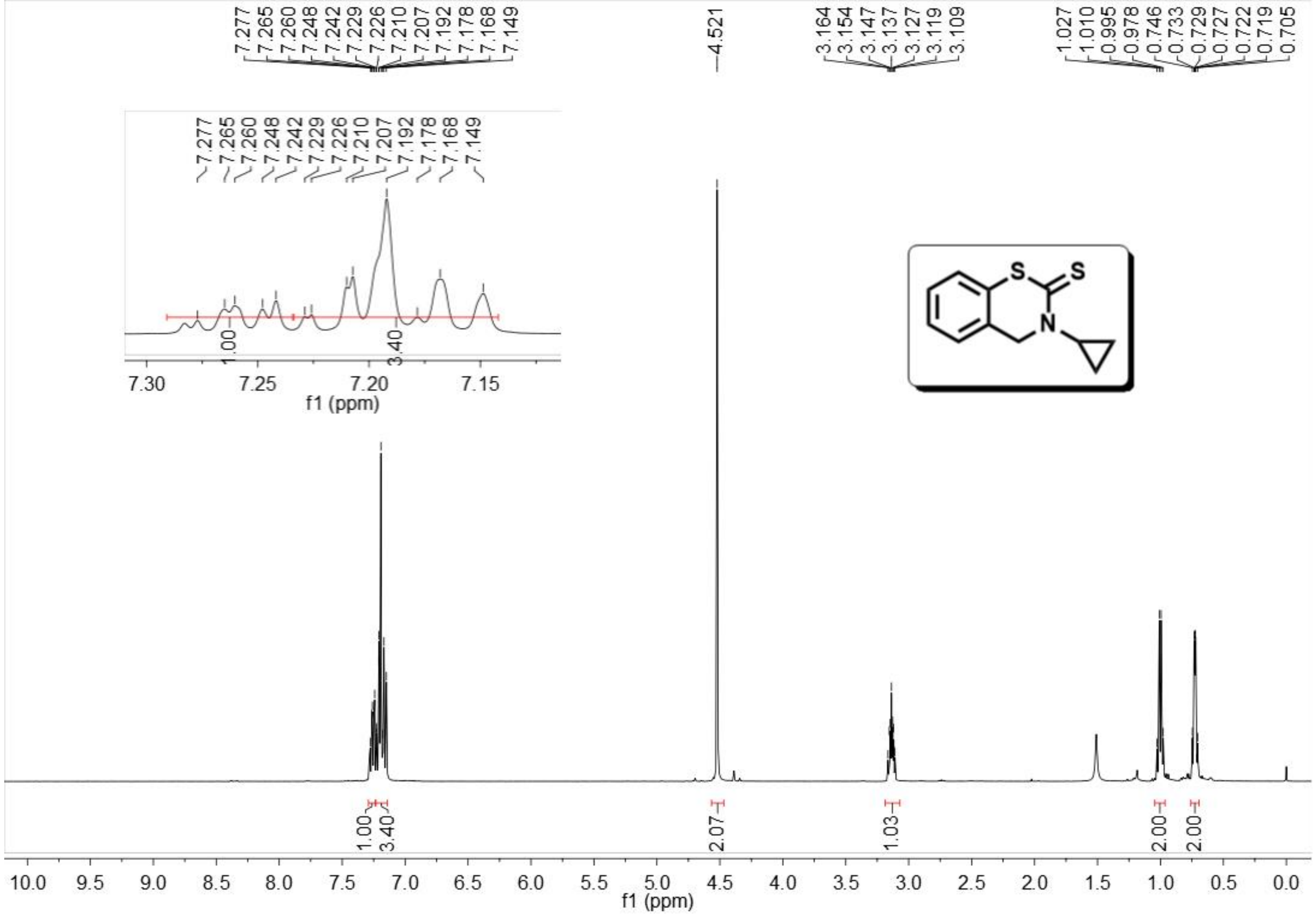

7.362
7.359
7.343
7.340
7.325
7.321
7.300
7.296
7.281
7.278
7.260
7.251
7.239
7.234
7.221
5.900
5.873
5.858
5.846
5.831
5.329
5.325
5.303
4.763
4.760
4.757
4.748
4.745
4.742
4.506
S
S
N
Allyl
1.00
1.01
2.03
1.00
2.01
2.01
2.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2e

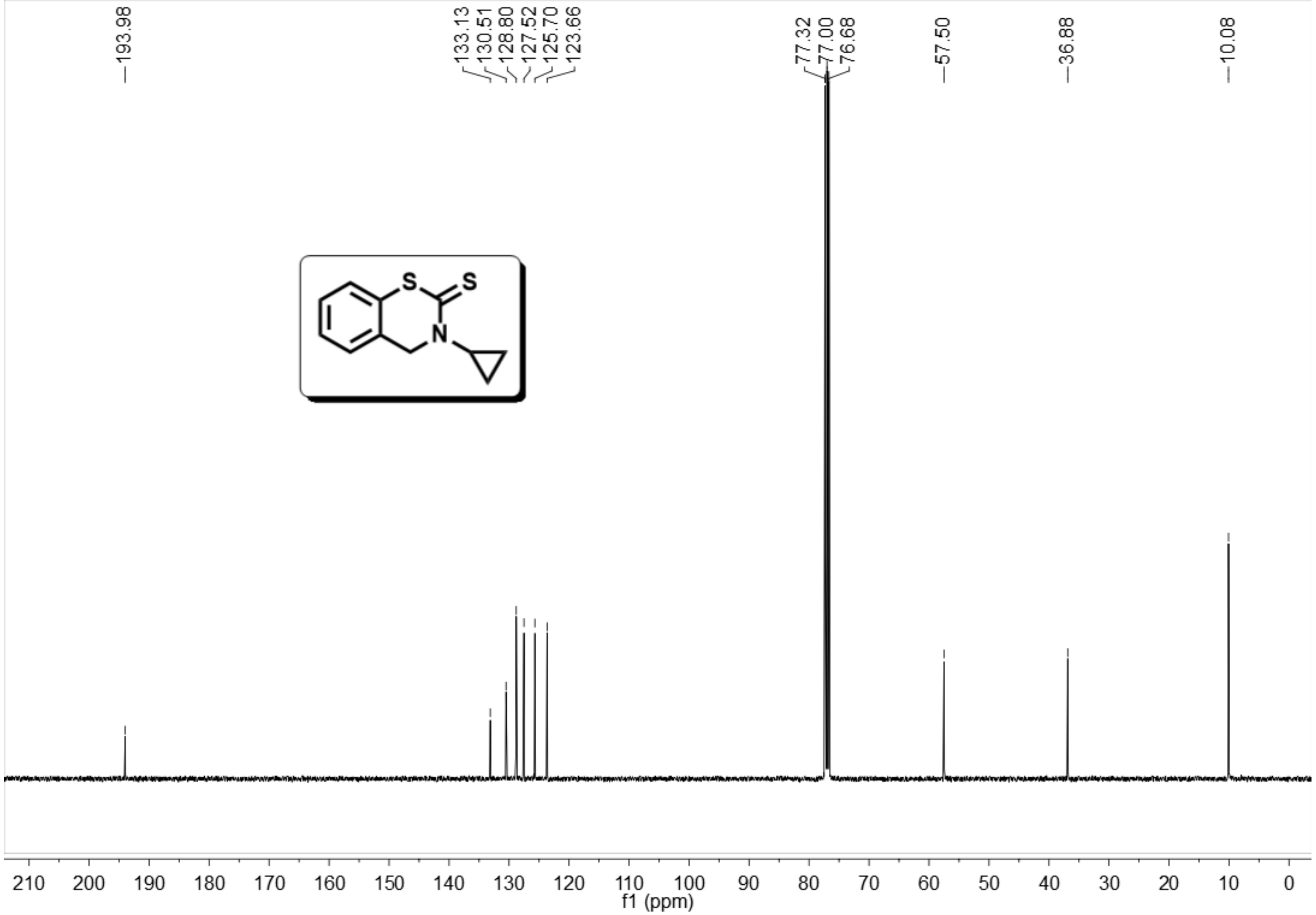


191.13
133.19
130.60
129.53
128.86
127.55
126.09
123.80
119.55
77.32
77.00
76.68
56.77
55.21
S
S
N
Allyl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2f

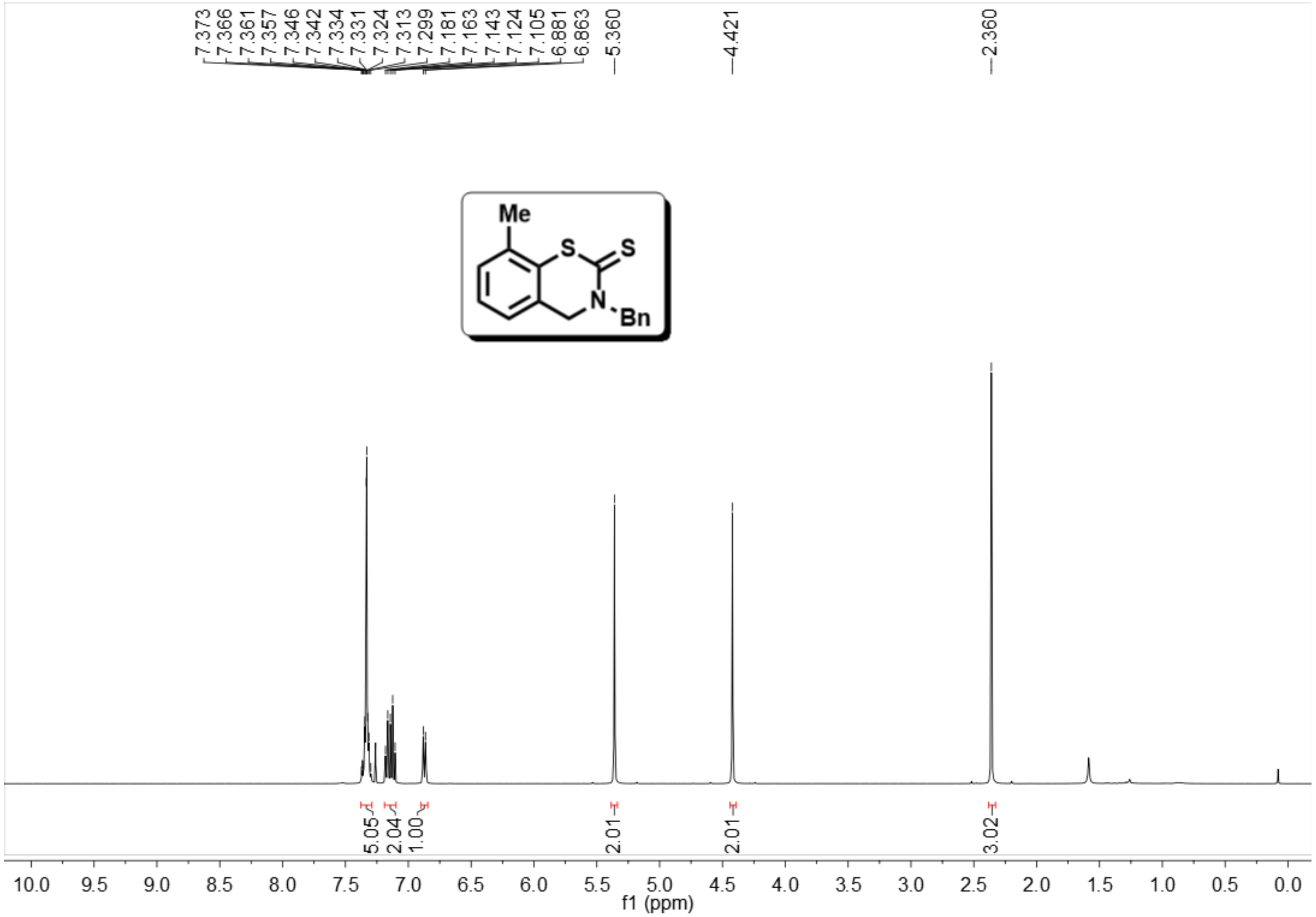

7.277
7.265
7.260
7.248
7.242
7.229
7.226
7.210
7.207
7.192
7.178
7.168
7.149
4.521
3.164
3.154
3.147
3.137
3.127
3.119
3.109
1.027
1.010
0.995
0.978
0.746
0.733
0.729
0.727
0.722
0.719
0.705
1.00
3.40
7.30
7.25
7.20
7.15
f1 (ppm)
S
S
N
1.00
3.40
2.07
1.03
2.00
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2f

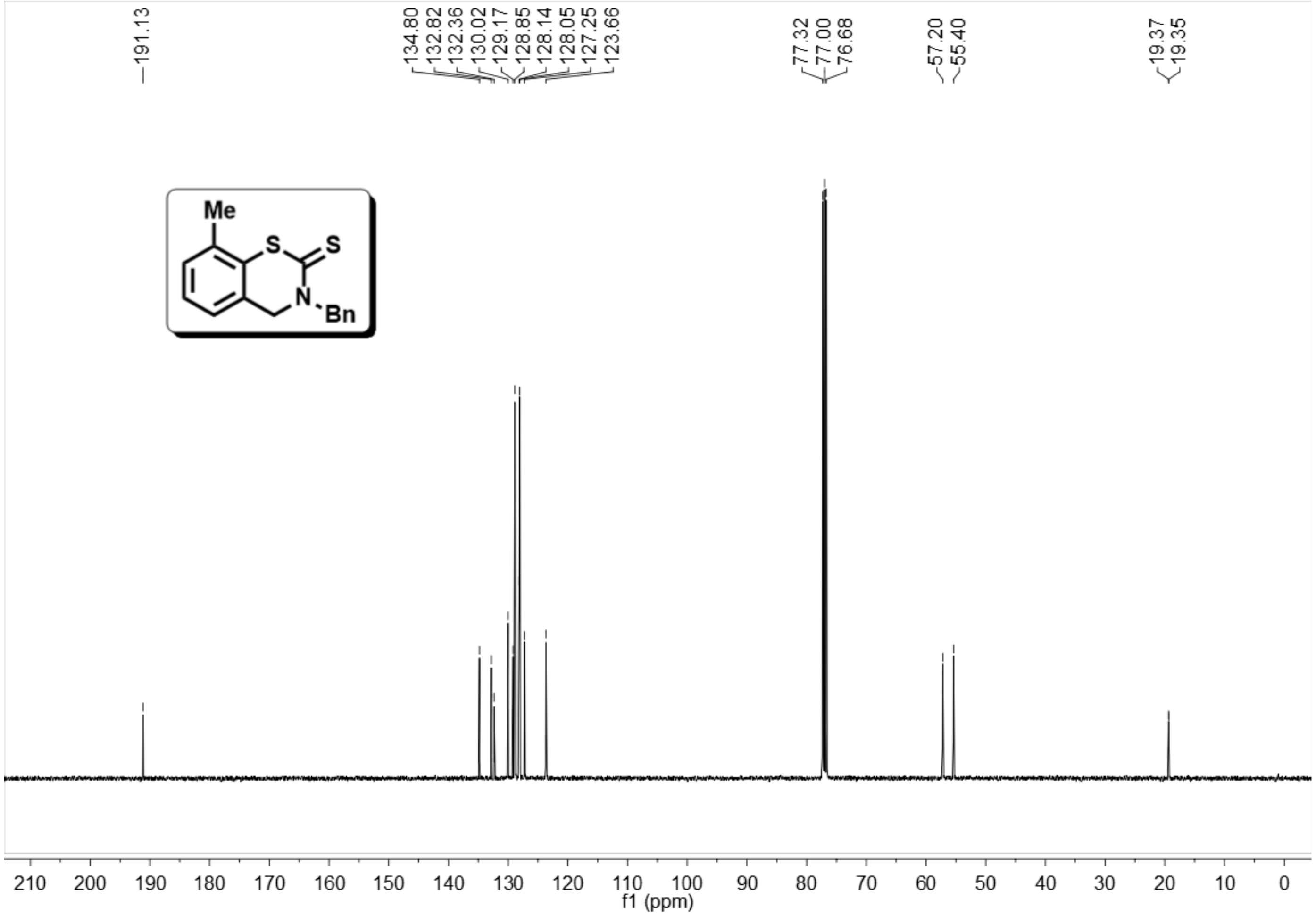


193.98
133.13
130.51
128.80
127.52
125.70
123.66
77.32
77.00
76.68
57.50
36.88
10.08
S
S
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

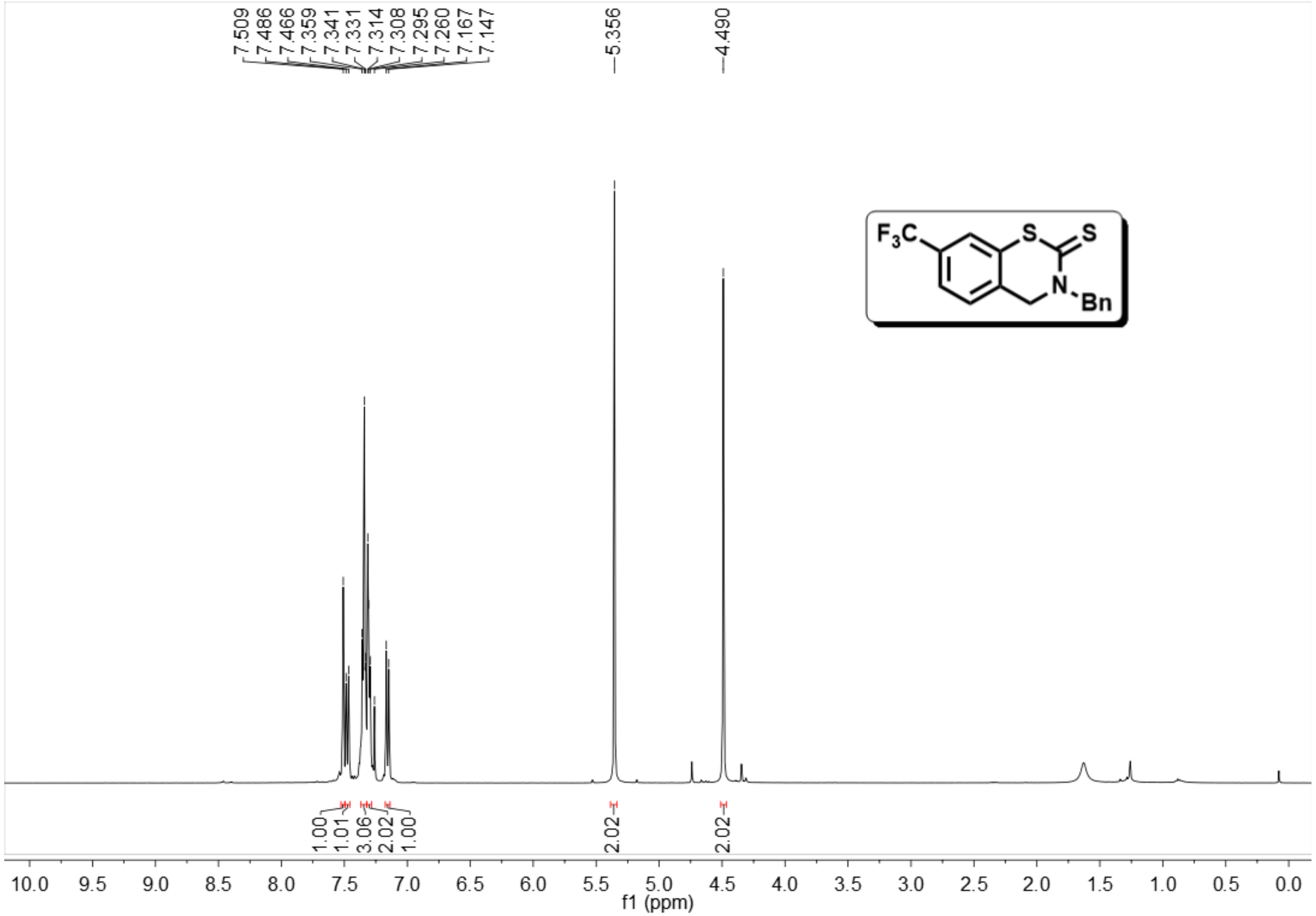
2g


7.373
7.366
7.361
7.357
7.346
7.342
7.334
7.331
7.324
7.313
7.299
7.181
7.163
7.143
7.124
7.105
6.881
6.863
5.360
4.421
2.360
Me
S
S
N
Bn
5.05
2.04
1.00
2.01
2.01
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

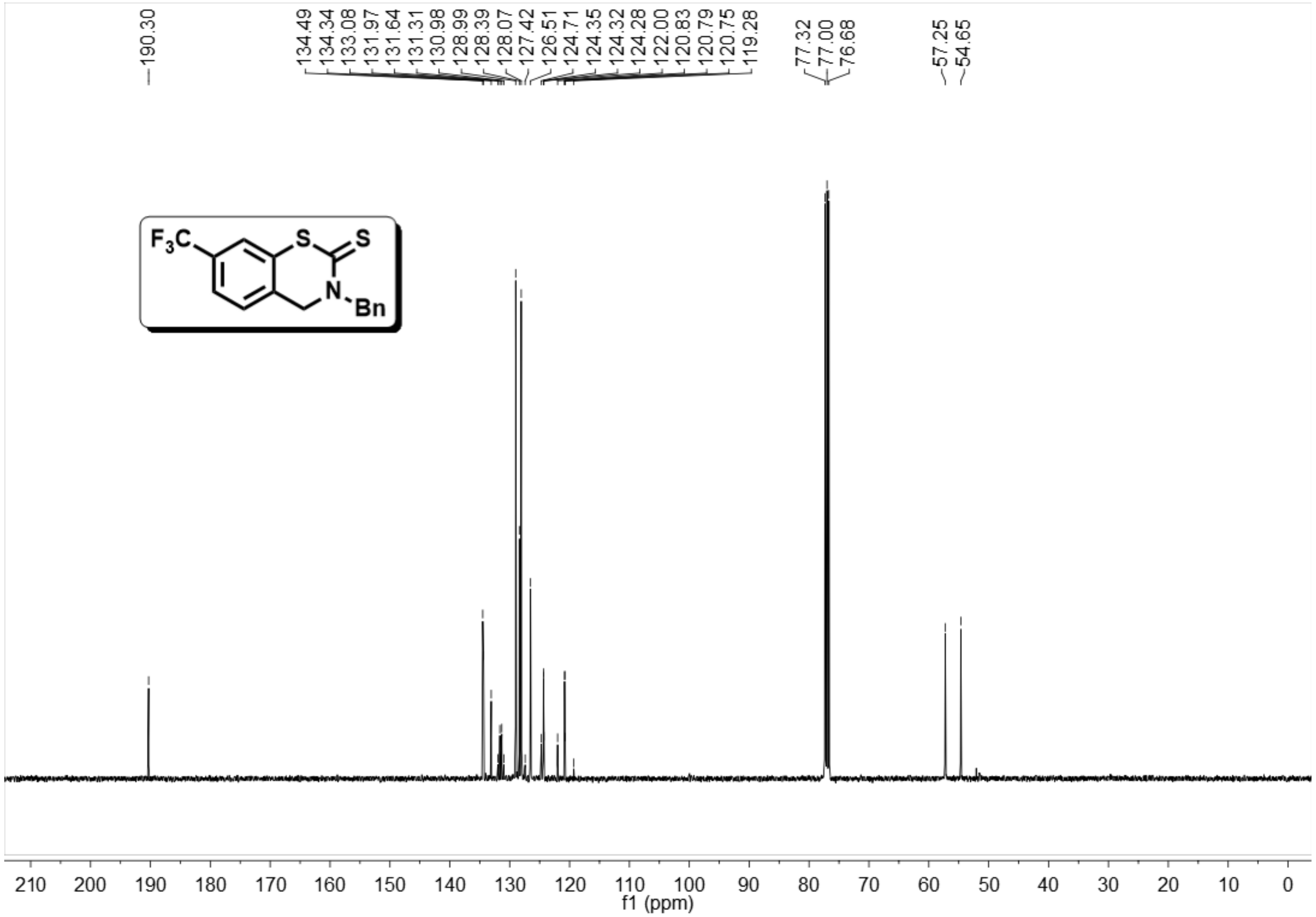
2g


191.13
134.80
132.82
132.36
130.02
129.17
128.85
128.14
128.05
127.25
123.66
77.32
77.00
76.68
57.20
55.40
19.37
19.35
Me
S
S
N
Bn
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2h

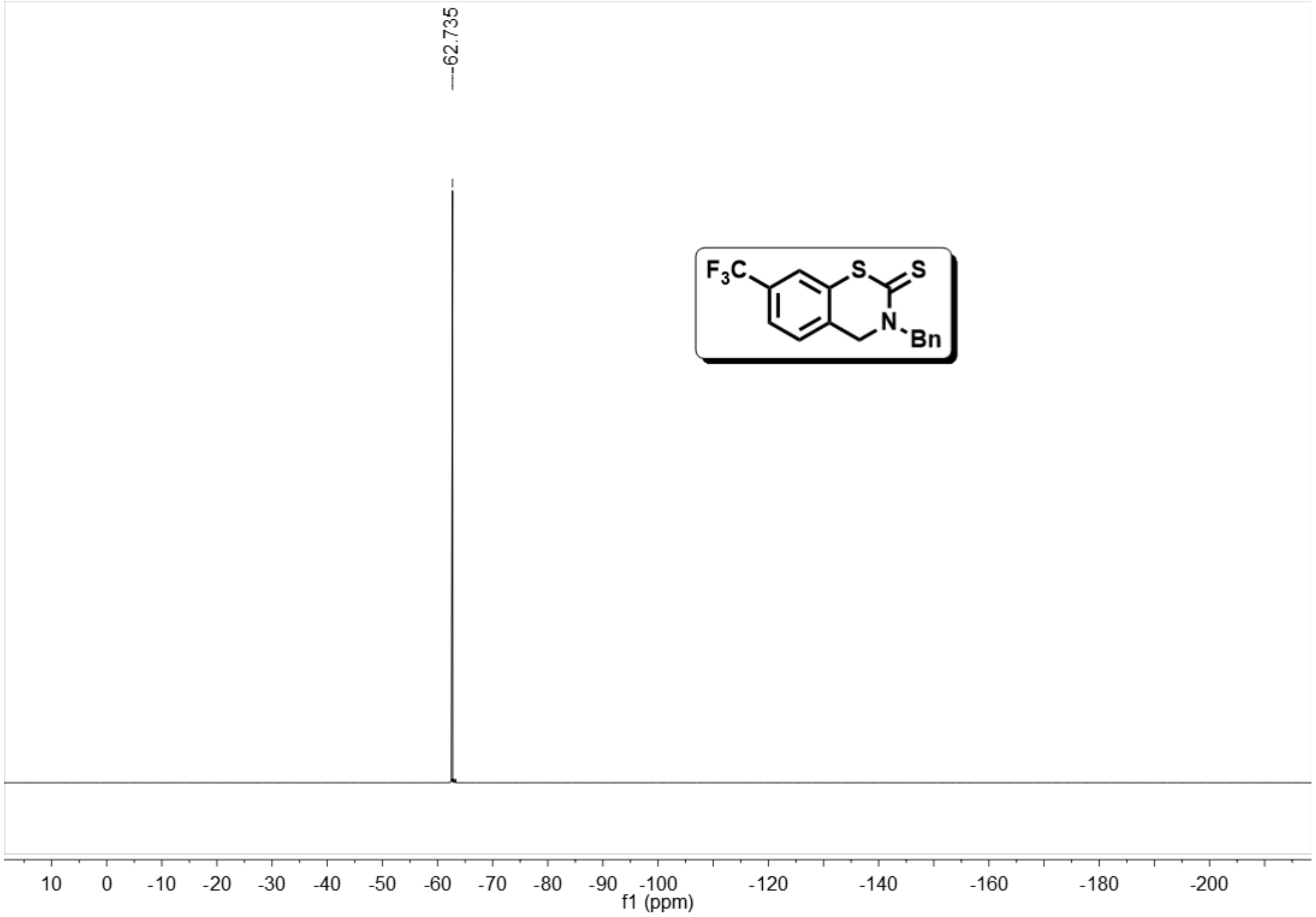

7.509
7.486
7.466
7.359
7.341
7.331
7.314
7.308
7.295
7.260
7.167
7.147
5.356
4.490
F_3C
S
S
N
Bn
1.00
1.01
3.06
2.02
1.00
2.02
2.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2h

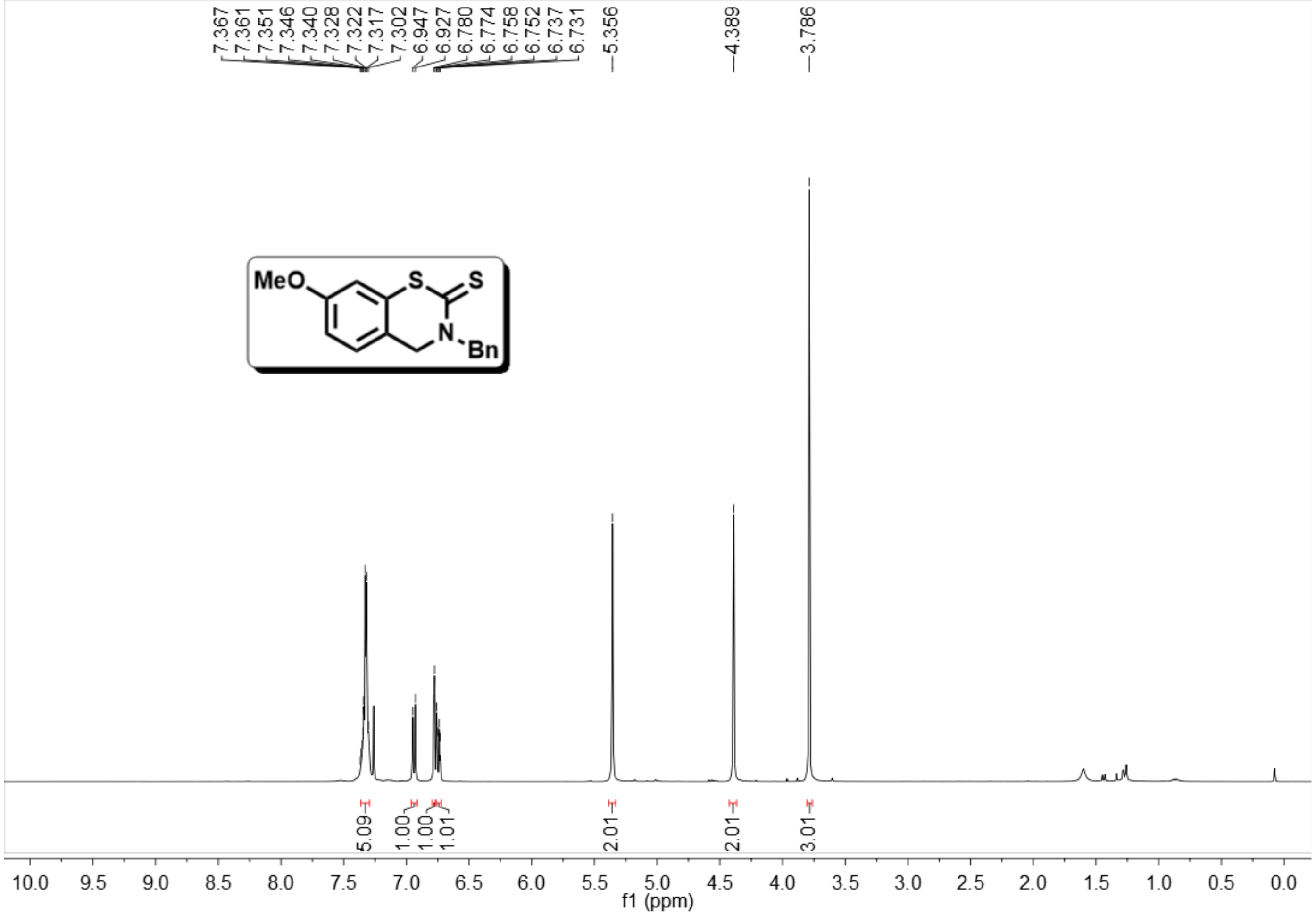


190.30
134.49
134.34
133.08
131.97
131.64
131.31
130.98
128.99
128.39
128.07
127.42
126.51
124.71
124.35
124.32
124.28
122.00
120.83
120.79
120.75
119.28
77.32
77.00
76.68
57.25
54.65
F3C
S
S
N
Bn
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

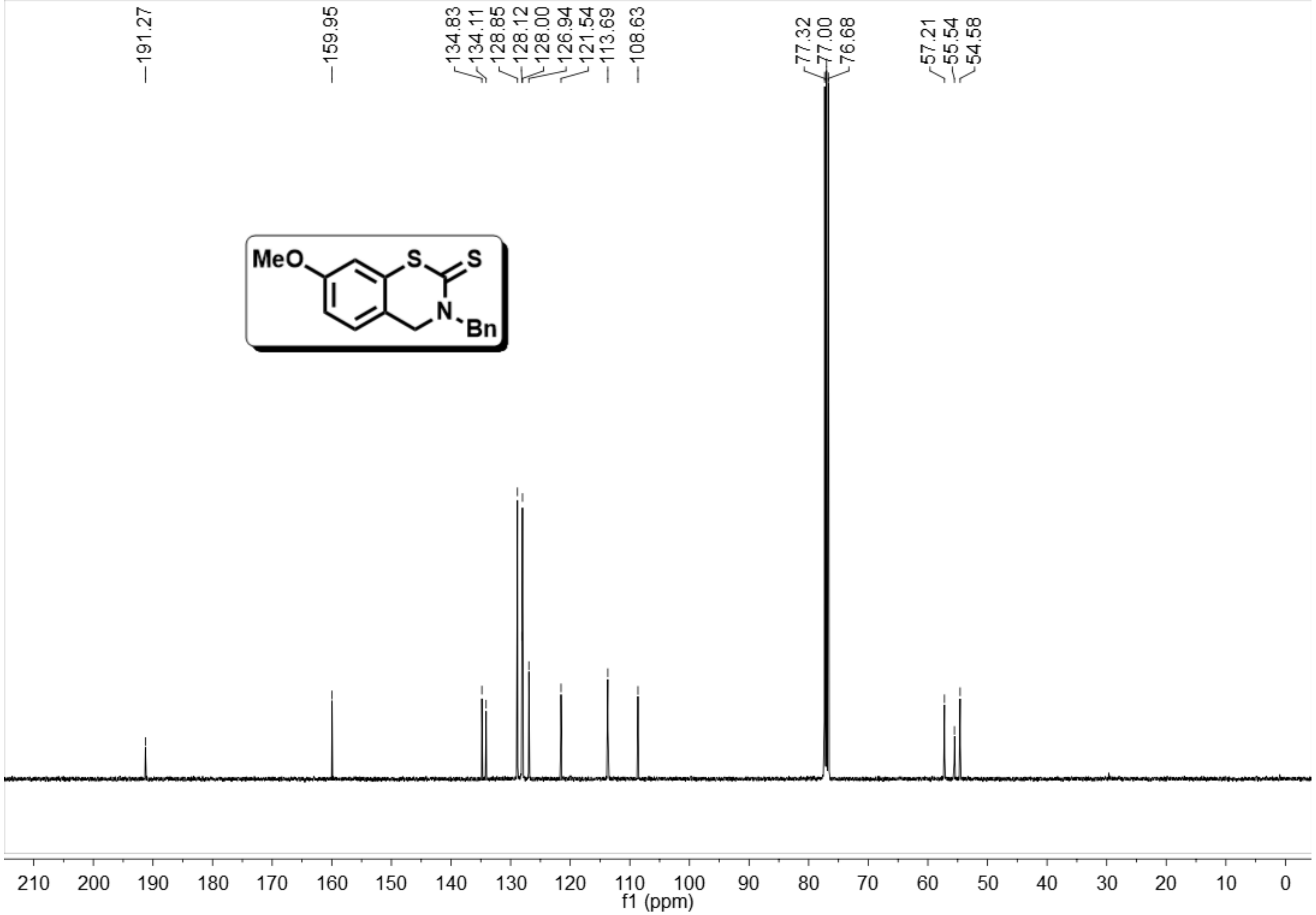
2h


-62.735
F3C
S
S
N
Bn
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

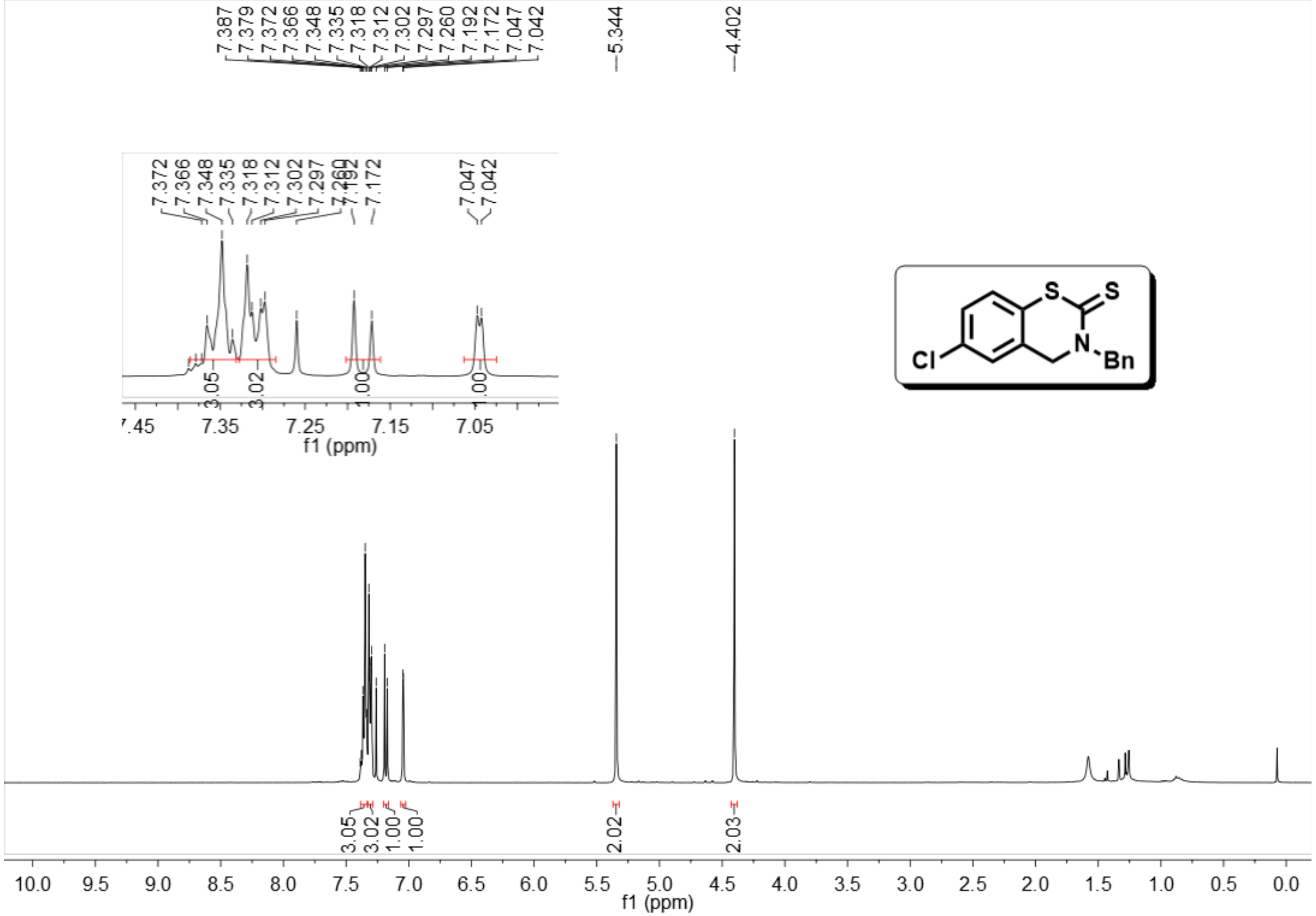
2i


7.367
7.361
7.351
7.346
7.340
7.328
7.322
7.317
7.302
6.947
6.927
6.780
6.774
6.758
6.752
6.737
6.731
5.356
4.389
3.786
MeO
S
S
N
Bn
5.09
1.00
1.00
1.01
2.01
2.01
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

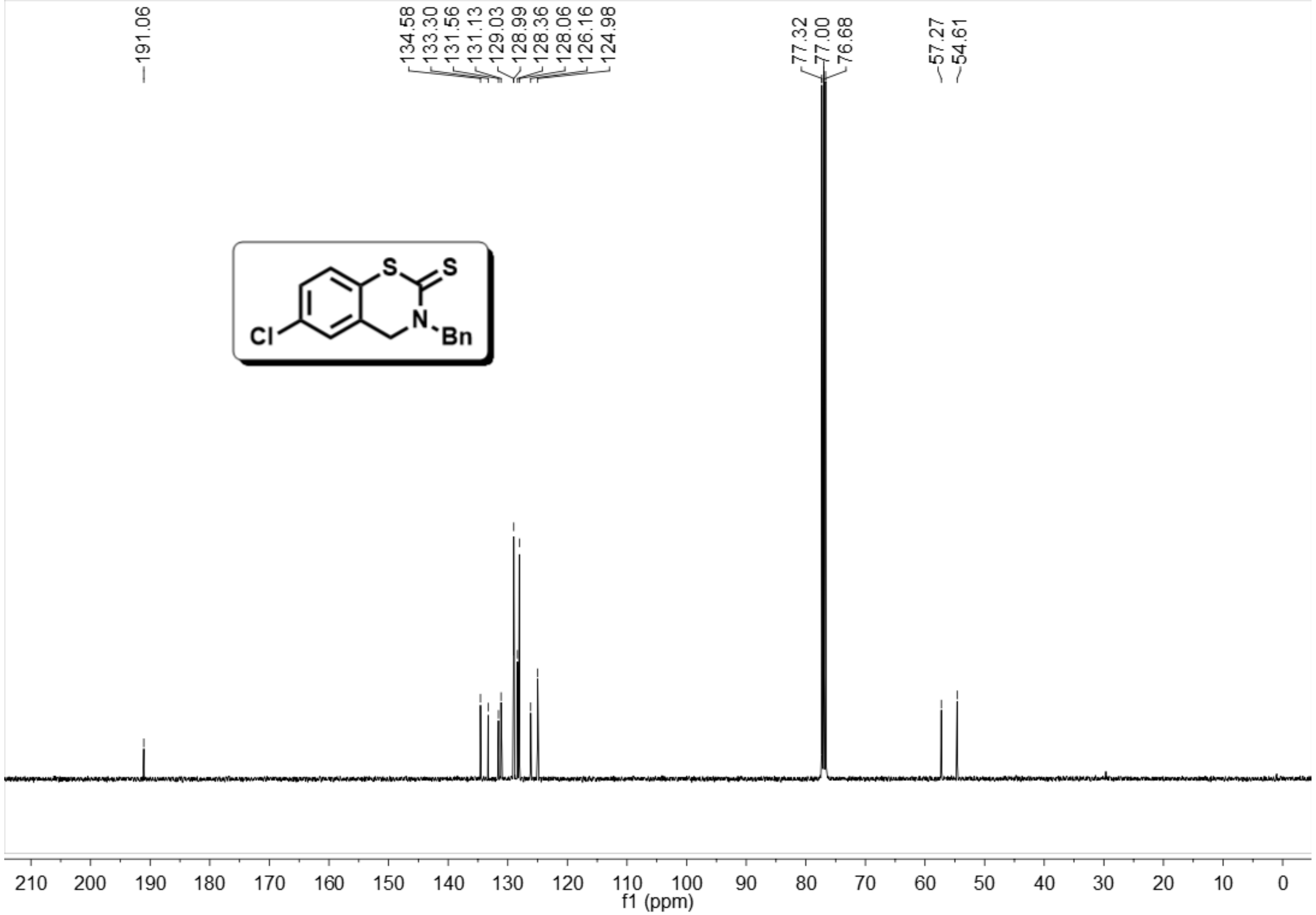
2i


191.27
159.95
134.83
134.11
128.85
128.12
128.00
126.94
121.54
113.69
108.63
77.32
77.00
76.68
57.21
55.54
54.58
MeO
S
S
N
Bn
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

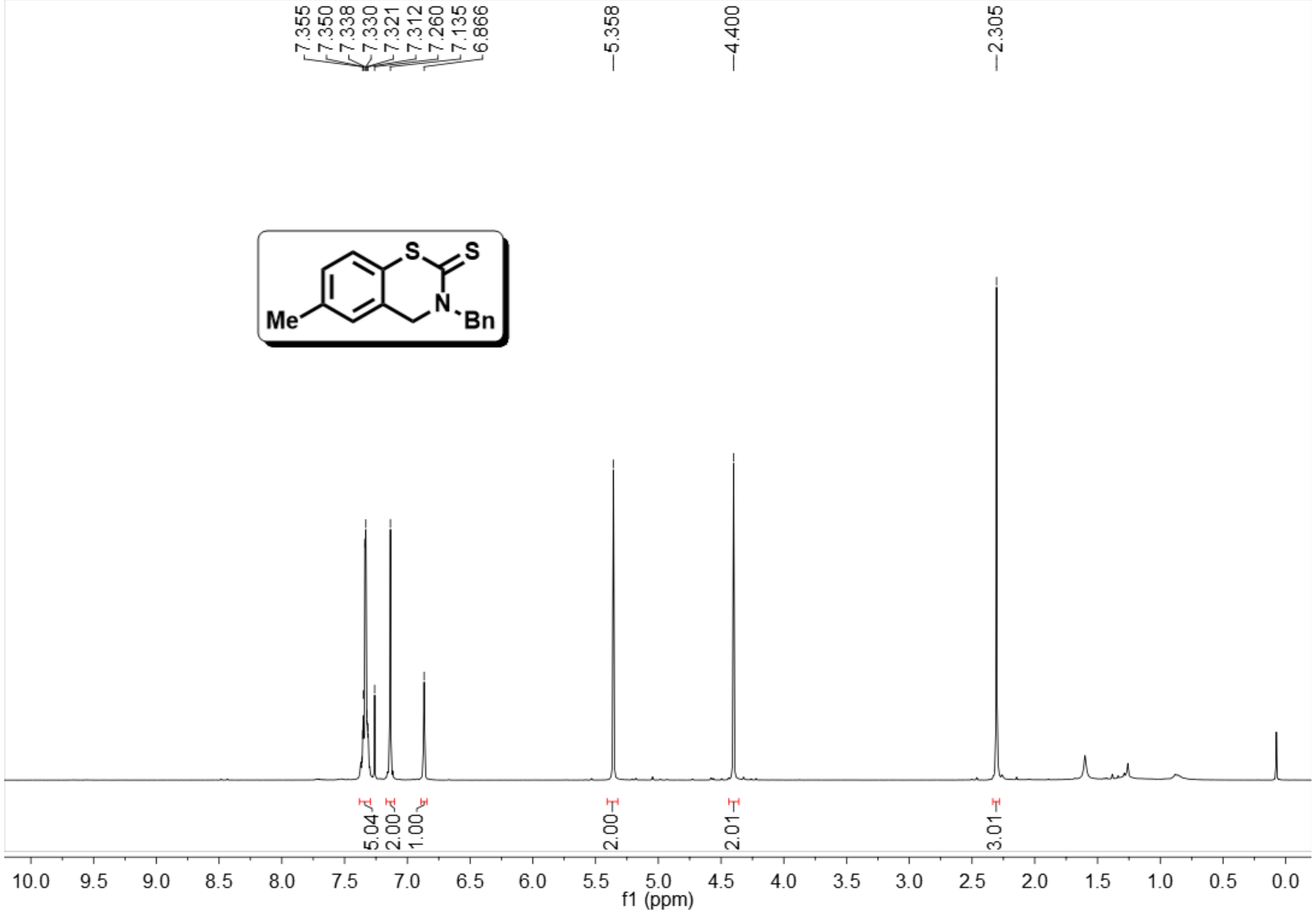
2j


7.387
7.379
7.372
7.366
7.348
7.335
7.318
7.312
7.302
7.297
7.260
7.192
7.172
7.047
7.042
5.344
4.402
3.05
3.02
1.00
1.00
2.02
2.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
7.45
7.35
7.25
7.15
7.05
S
S
N
Bn
Cl

2j

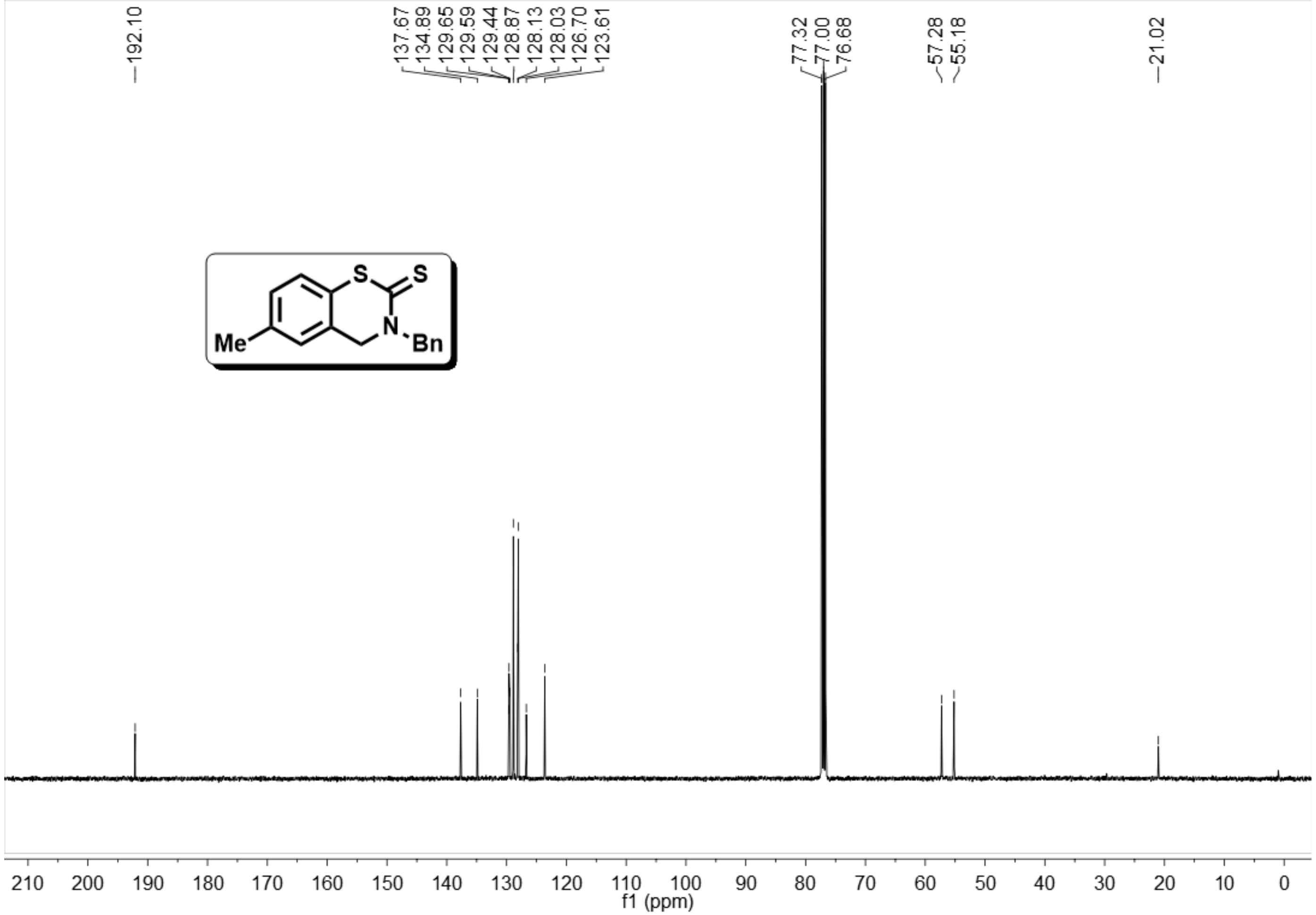

191.06
134.58
133.30
131.56
131.13
129.03
128.99
128.36
128.06
126.16
124.98
77.32
77.00
76.68
57.27
54.61
S
S
N
Bn
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2k

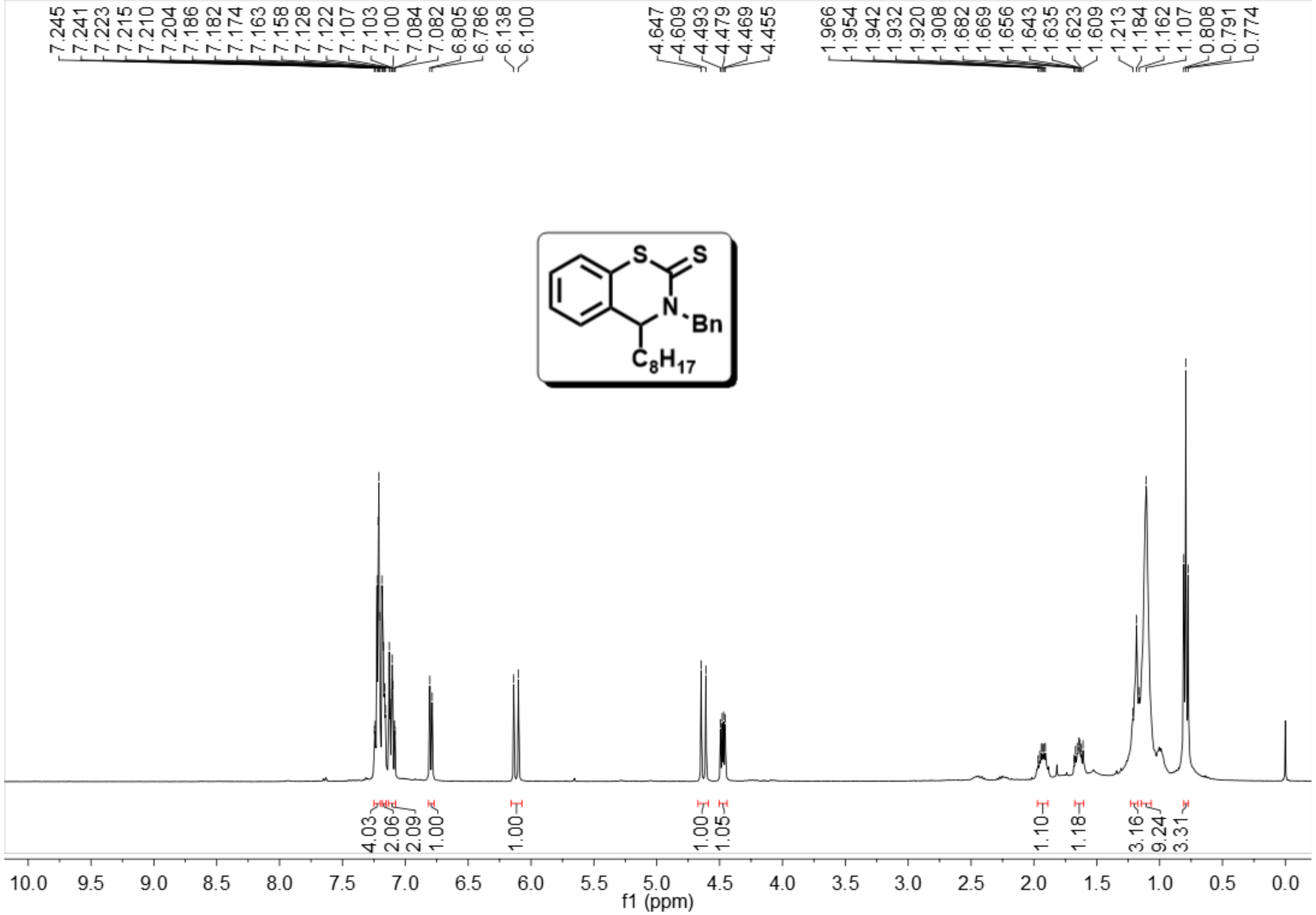


7.355
7.350
7.338
7.330
7.321
7.312
7.260
7.135
6.866
5.358
4.400
2.305
S
S
N
Bn
Me
5.04
2.00
1.00
2.00
2.01
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

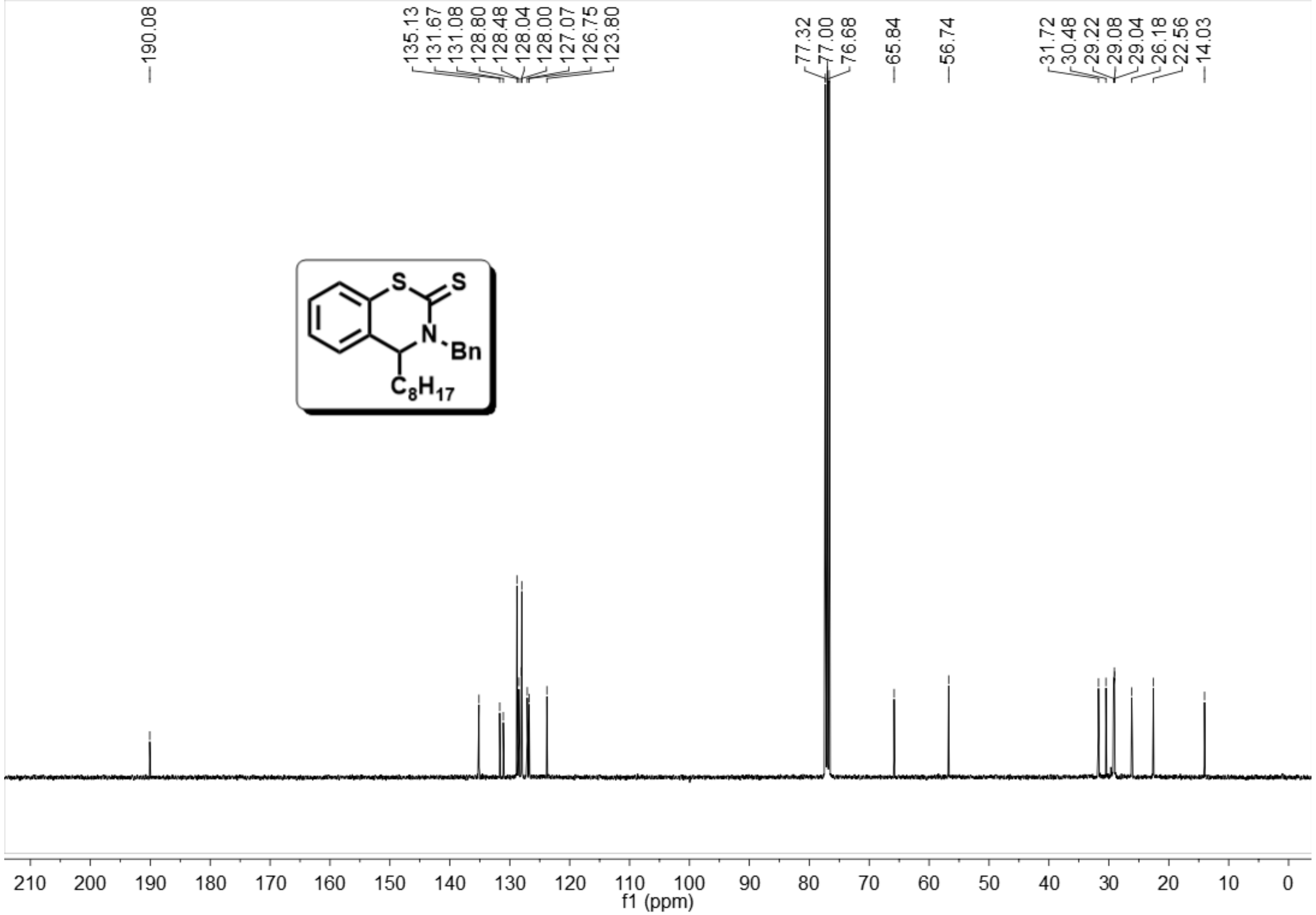
2k


192.10
137.67
134.89
129.65
129.59
129.44
128.87
128.13
128.03
126.70
123.61
77.32
77.00
76.68
57.28
55.18
21.02
S
S
N
Bn
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

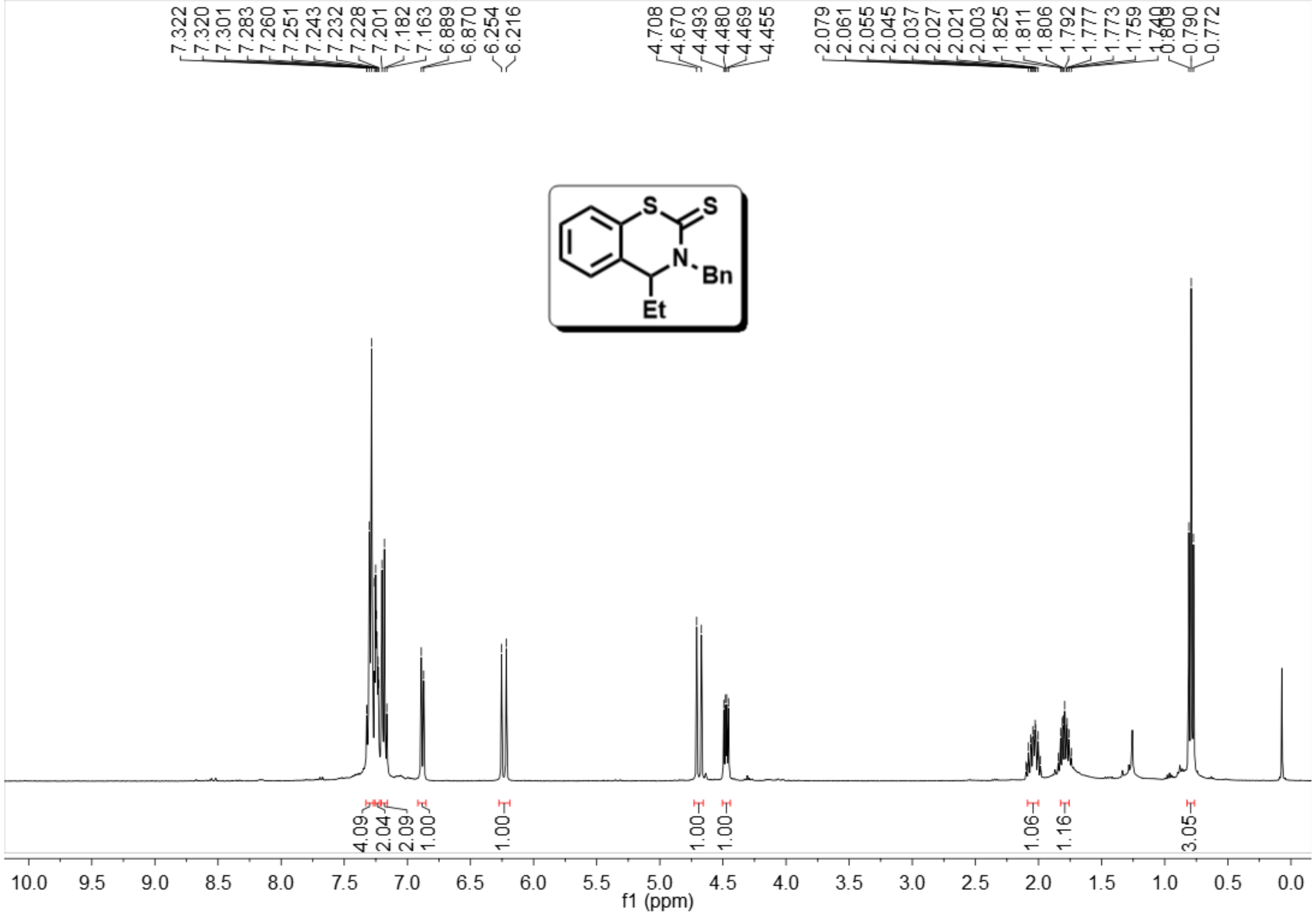
3l


7.245
7.241
7.223
7.215
7.210
7.204
7.186
7.182
7.174
7.163
7.158
7.128
7.122
7.107
7.103
7.100
7.084
7.082
6.805
6.786
6.138
6.100
4.647
4.609
4.493
4.479
4.469
4.455
1.966
1.954
1.942
1.932
1.920
1.908
1.682
1.669
1.656
1.643
1.635
1.623
1.609
1.213
1.184
1.162
1.107
0.808
0.791
0.774
S
S
N
Bn
C_8H_{17}
4.03
2.06
2.09
1.00
1.00
1.00
1.05
1.10
1.18
3.16
9.24
3.31
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

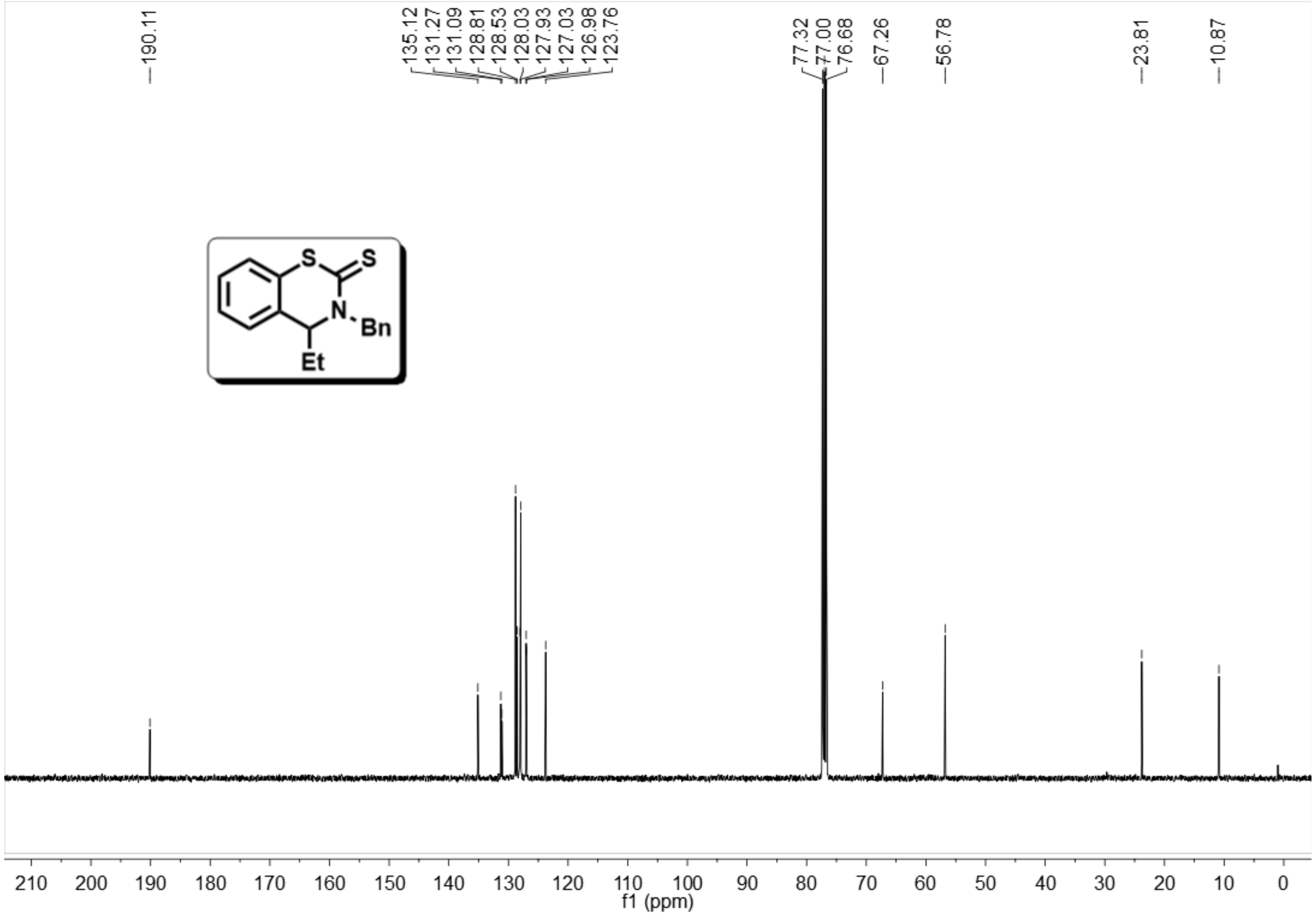
3l


190.08
135.13
131.67
131.08
128.80
128.48
128.04
128.00
127.07
126.75
123.80
77.32
77.00
76.68
65.84
56.74
31.72
30.48
29.22
29.08
29.04
26.18
22.56
14.03
S
S
N
Bn
C8H17
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

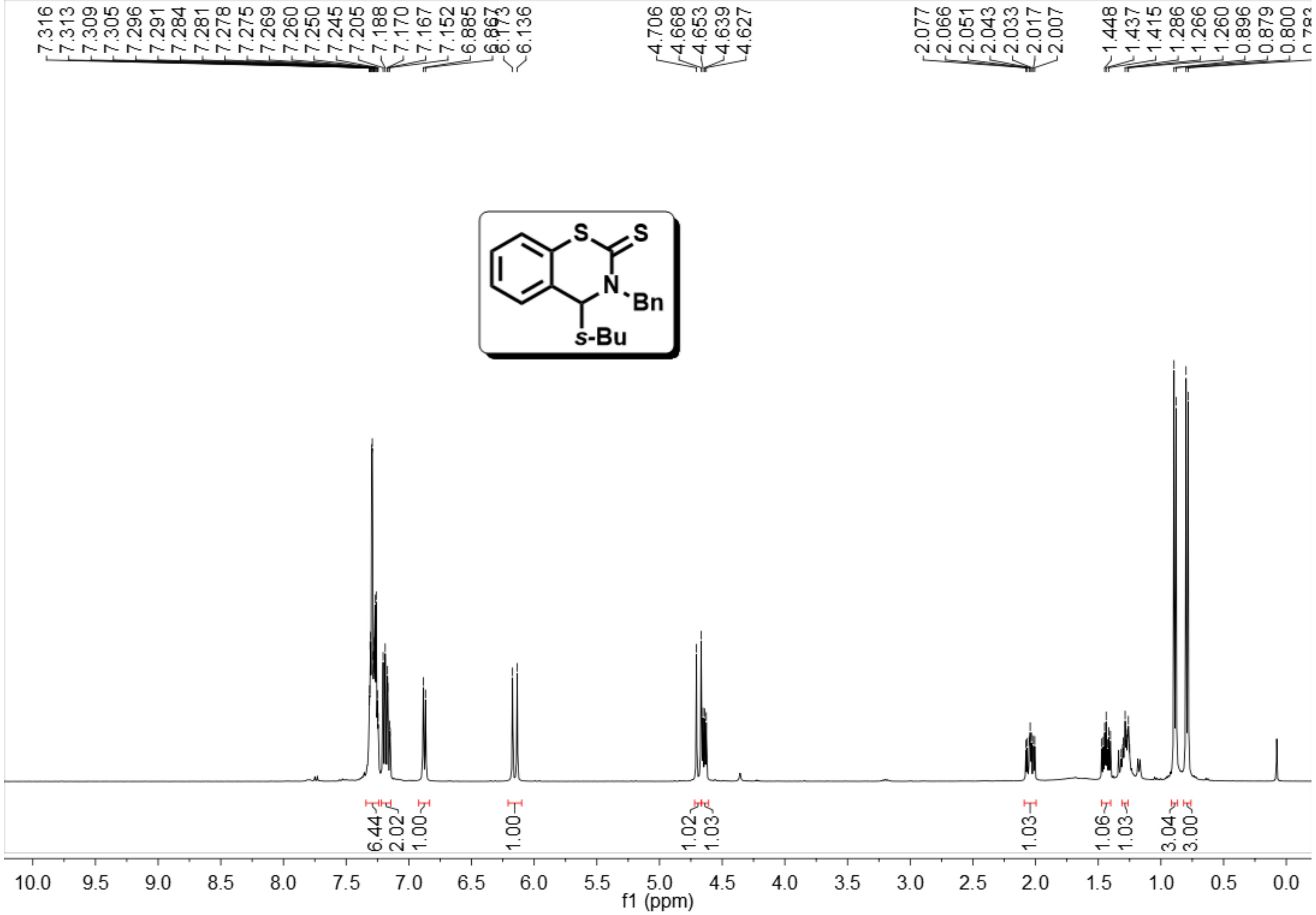
3m


7.322
7.320
7.301
7.283
7.260
7.251
7.243
7.232
7.228
7.201
7.182
7.163
6.889
6.870
6.254
6.216
4.708
4.670
4.493
4.480
4.469
4.455
2.079
2.061
2.055
2.045
2.037
2.027
2.021
2.003
1.825
1.811
1.806
1.792
1.777
1.773
1.759
1.740
0.809
0.790
0.772
S
S
N
Bn
Et
4.09
2.04
2.09
1.00
1.00
1.00
1.00
1.06
1.16
3.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

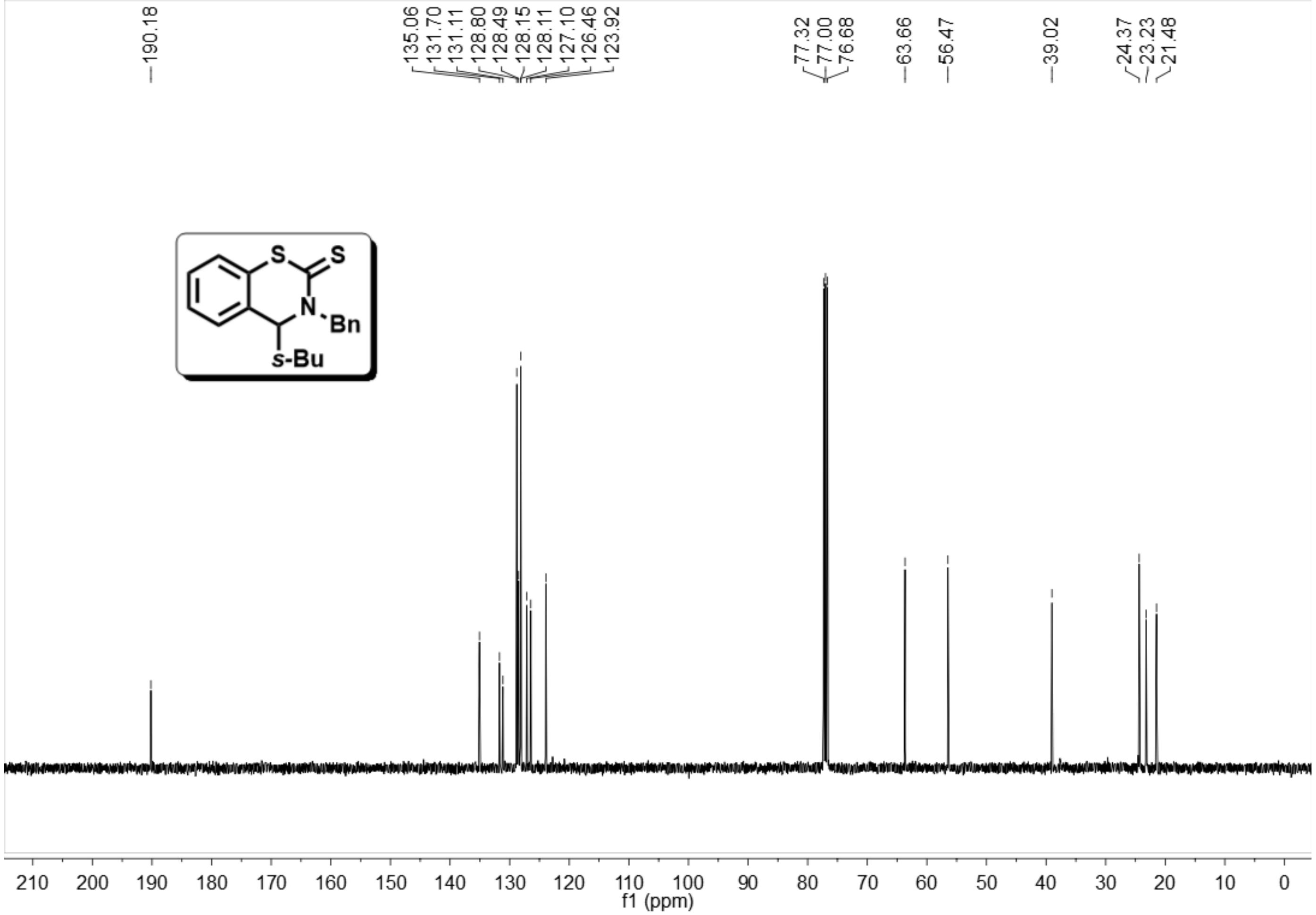
3m


190.11
135.12
131.27
131.09
128.81
128.53
128.03
127.93
127.03
126.98
123.76
77.32
77.00
76.68
67.26
56.78
23.81
10.87
S
S
N
Bn
Et
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

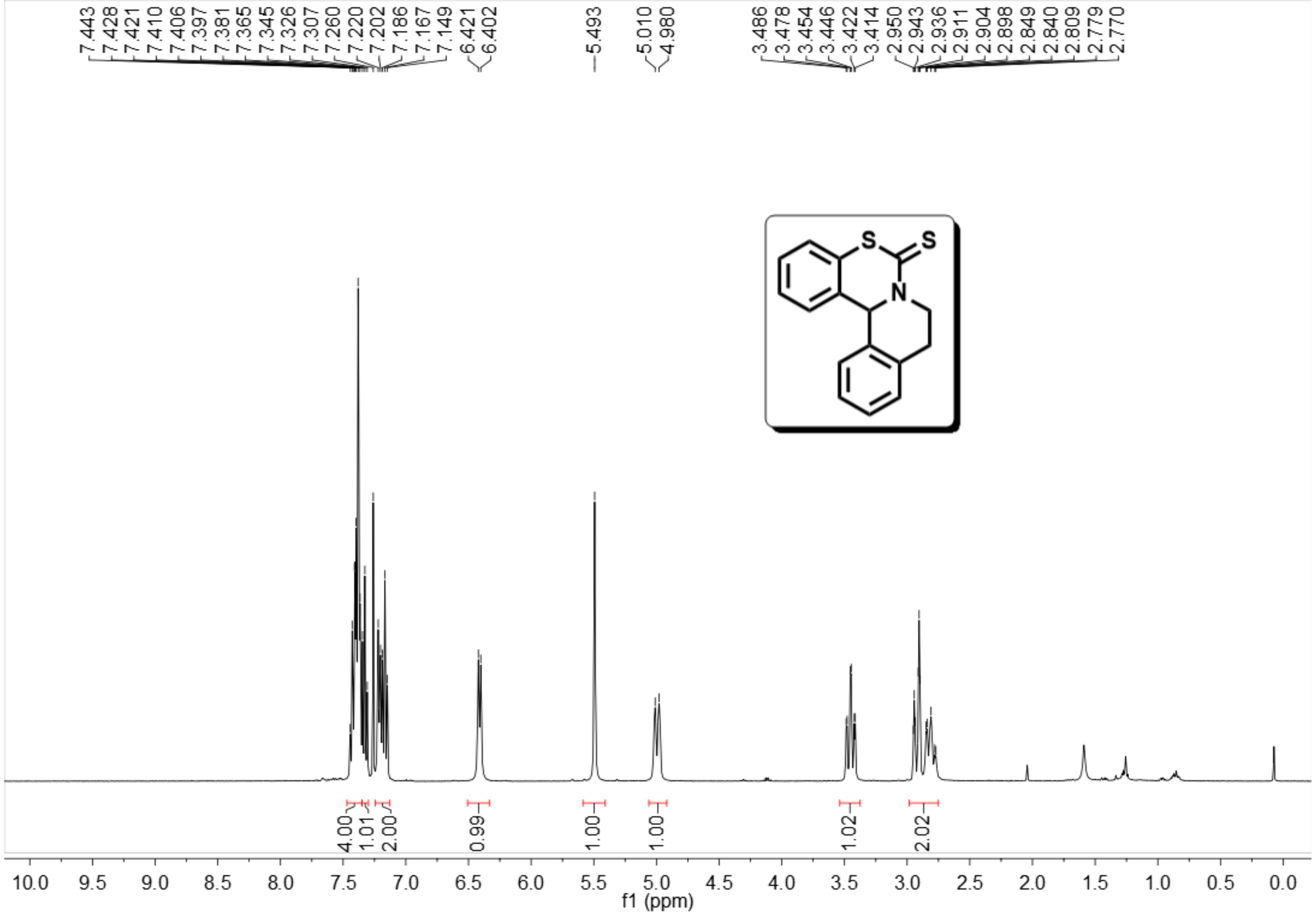
3n


7.316
7.313
7.309
7.305
7.296
7.291
7.284
7.281
7.278
7.275
7.269
7.260
7.250
7.245
7.205
7.188
7.170
7.167
7.152
6.885
6.867
6.173
6.136
4.706
4.668
4.653
4.639
4.627
2.077
2.066
2.051
2.043
2.033
2.017
2.007
1.448
1.437
1.415
1.286
1.266
1.260
0.896
0.879
0.800
S
S
N
Bn
s-Bu
6.44
2.02
1.00
1.00
1.02
1.03
1.03
1.06
1.03
3.04
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

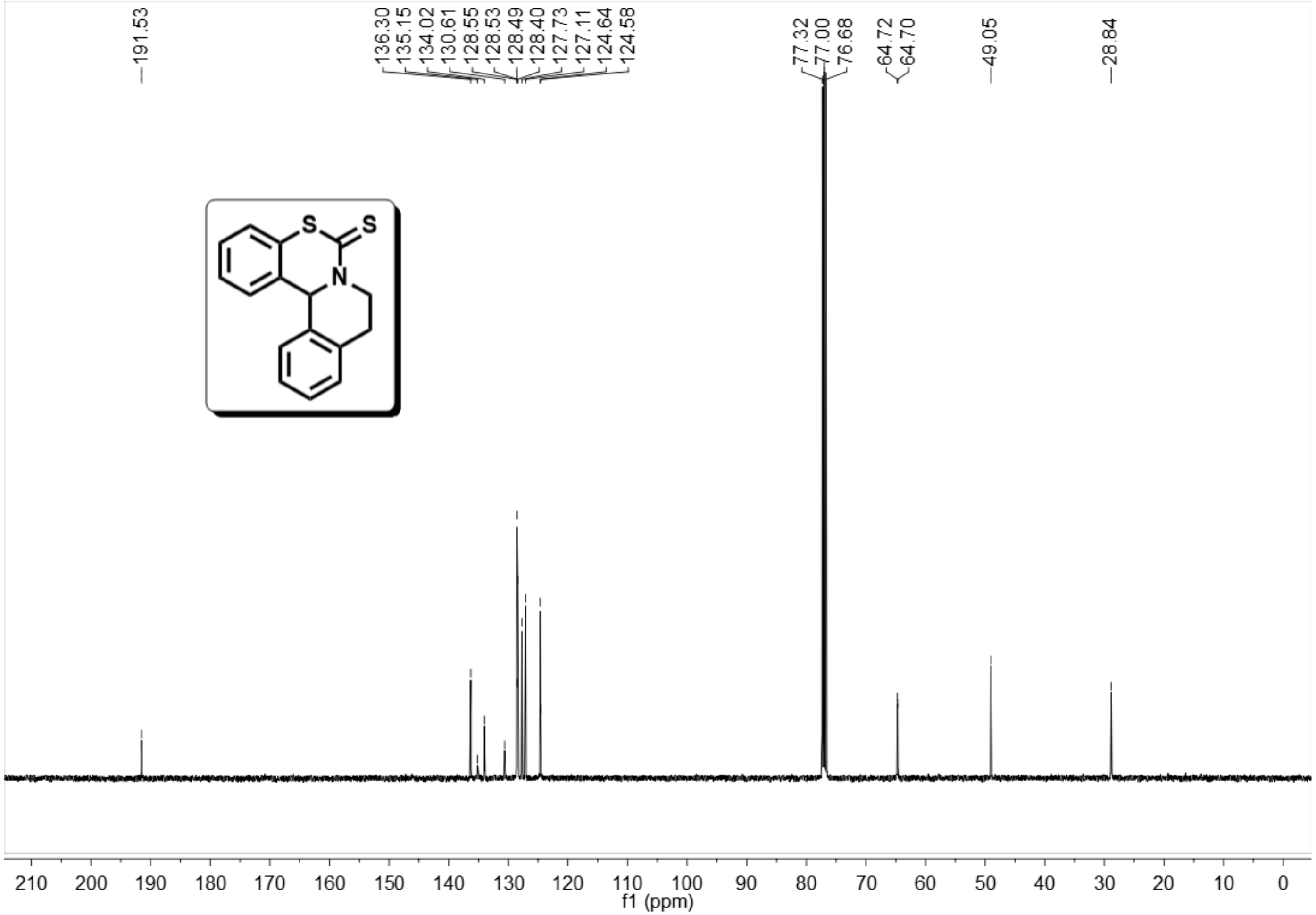
3n


190.18
135.06
131.70
131.11
128.80
128.49
128.15
128.11
127.10
126.46
123.92
77.32
77.00
76.68
63.66
56.47
39.02
24.37
23.23
21.48
S
S
N
Bn
s-Bu
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

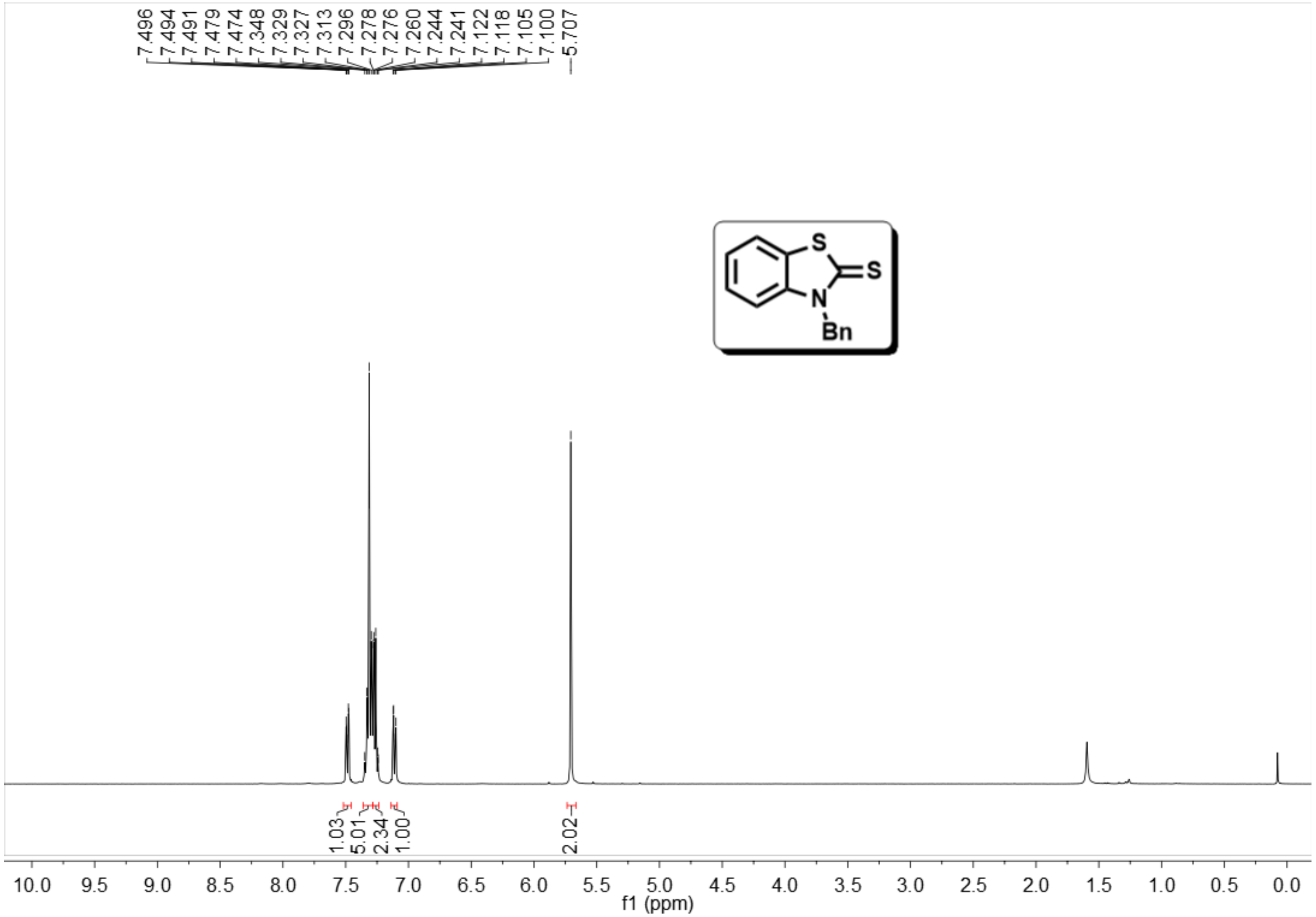
3o


7.443
7.428
7.421
7.410
7.406
7.397
7.381
7.365
7.345
7.326
7.307
7.260
7.220
7.202
7.186
7.167
7.149
6.421
6.402
5.493
5.010
4.980
3.486
3.478
3.454
3.446
3.422
3.414
2.950
2.943
2.936
2.911
2.904
2.898
2.849
2.840
2.809
2.779
2.770
S
S
N
4.00
1.01
2.00
0.99
1.00
1.00
1.02
2.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3o


191.53
136.30
135.15
134.02
130.61
128.55
128.53
128.49
128.40
127.73
127.11
124.64
124.58
77.32
77.00
76.68
64.72
64.70
49.05
28.84
S
S
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3a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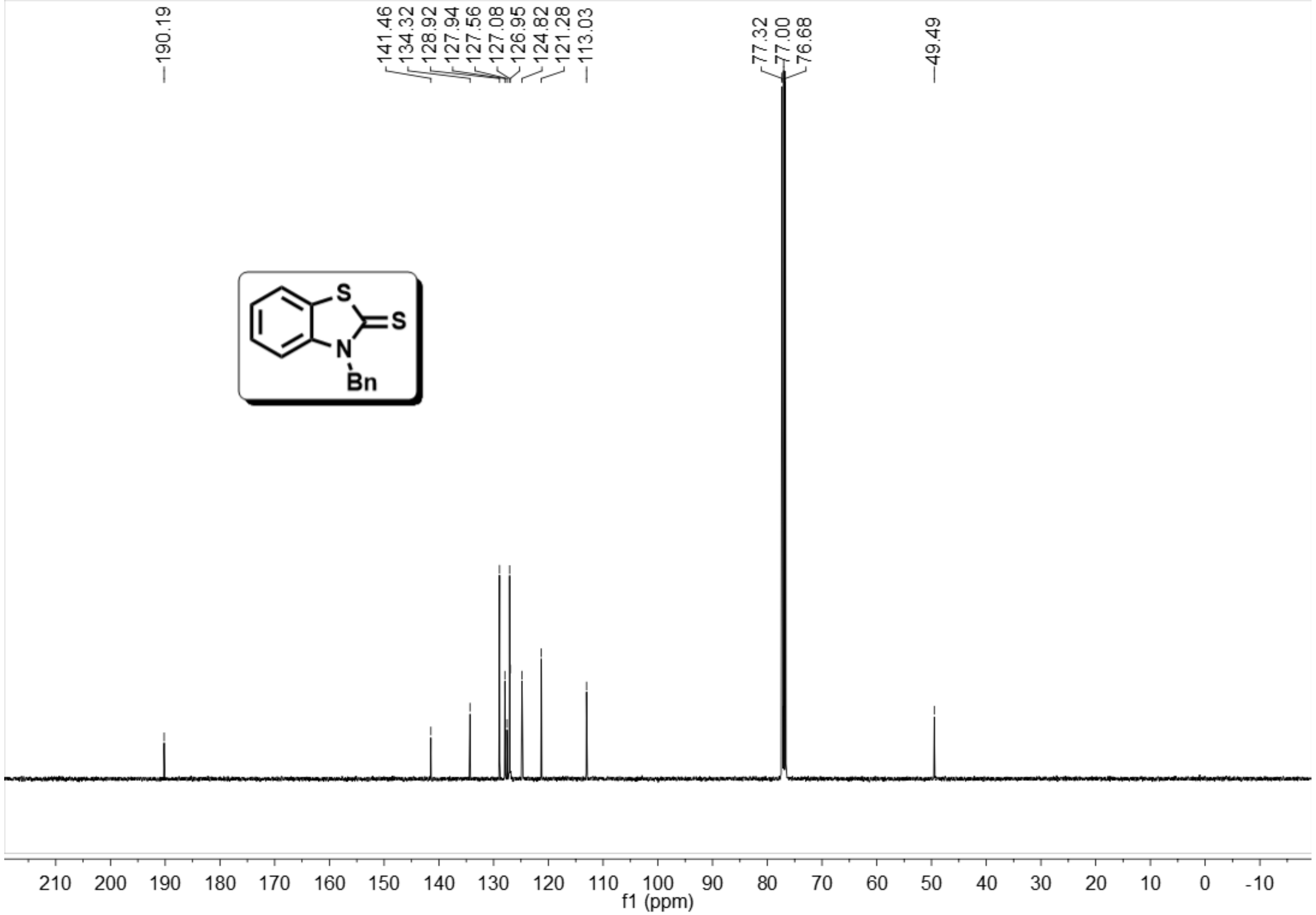
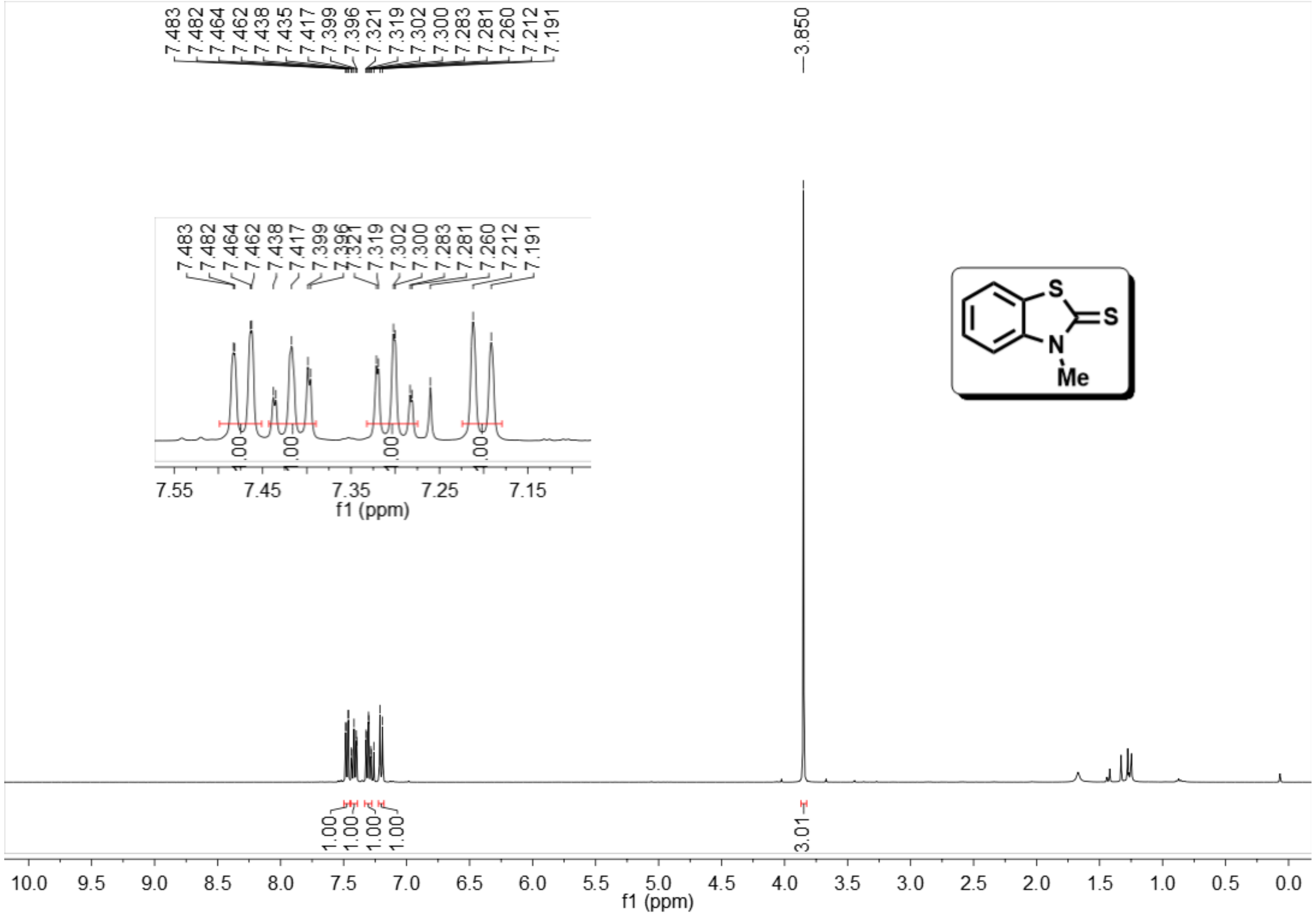
7.494
7.491
7.479
7.474
7.348
7.329
7.327
7.313
7.296
7.278
7.276
7.260
7.244
7.241
7.122
7.118
7.105
7.100
5.707
S
S
N
Bn
1.03
5.01
2.34
1.00
2.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

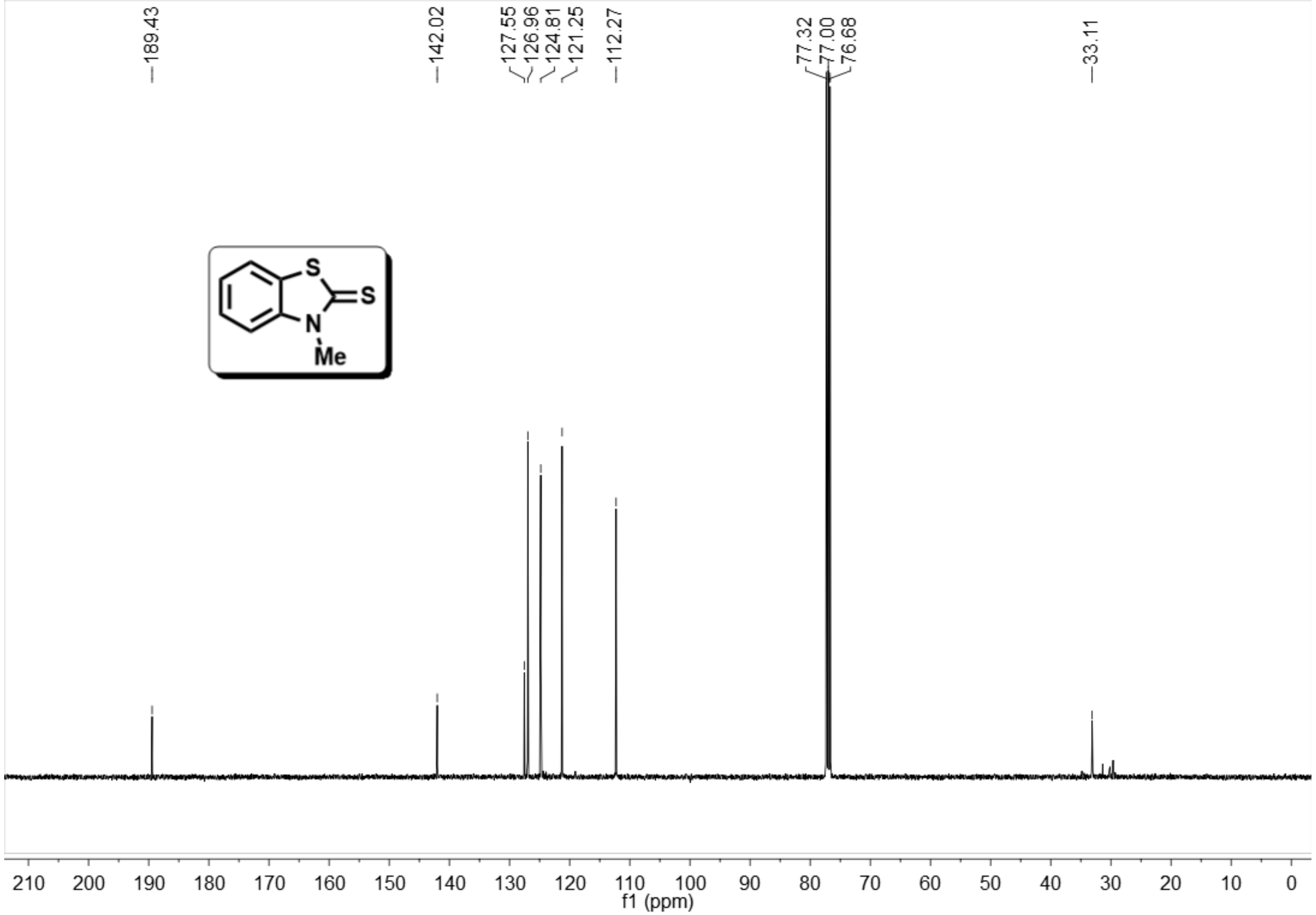
3a


190.19
141.46
134.32
128.92
127.94
127.56
127.08
126.95
124.82
121.28
113.03
77.32
77.00
76.68
49.49
S
S
N
Bn
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

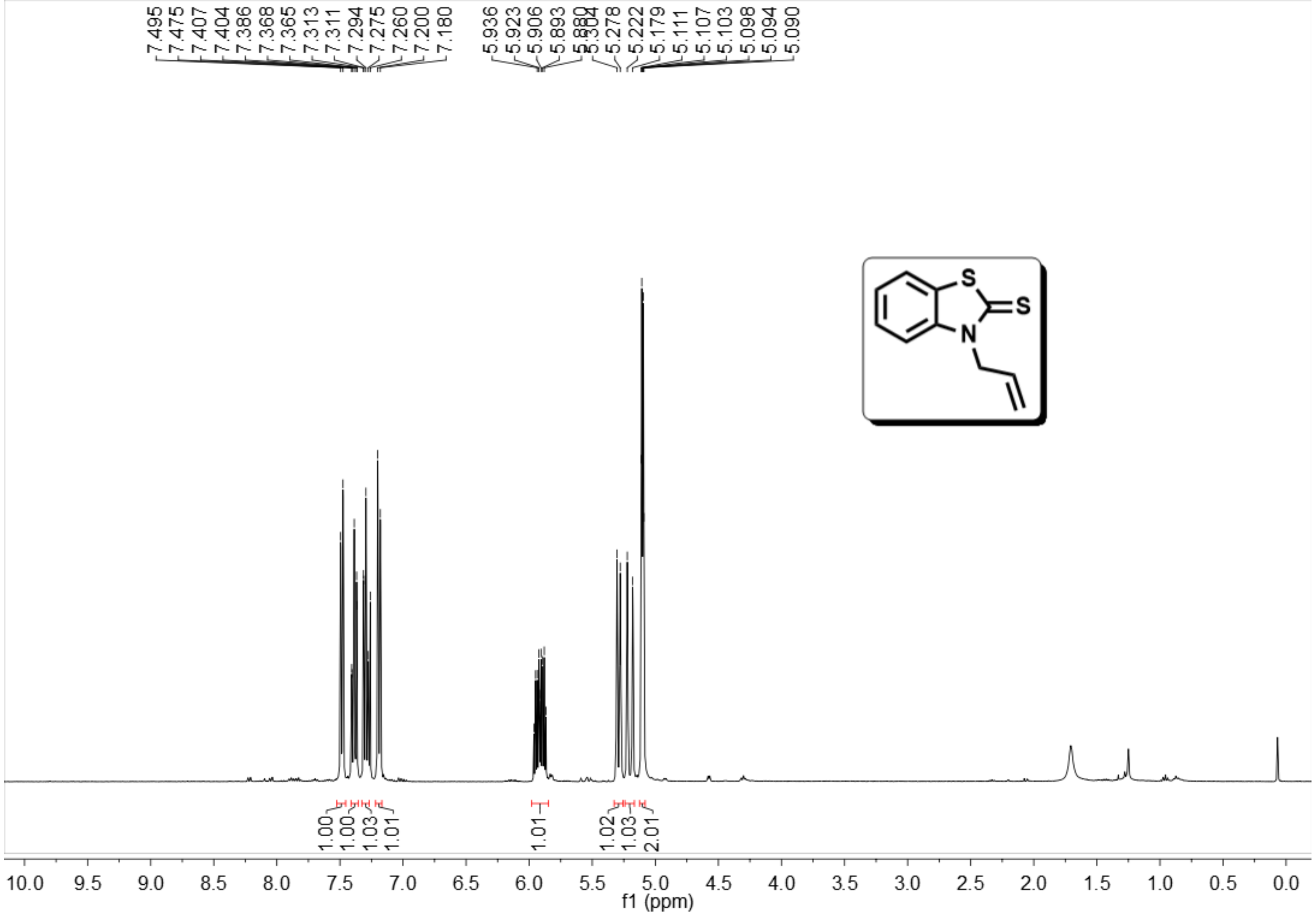
3b


7.483
7.482
7.464
7.462
7.438
7.435
7.417
7.399
7.396
7.321
7.319
7.302
7.300
7.283
7.281
7.260
7.212
7.191
3.850
1.00
1.00
1.00
1.00
3.01
7.55
7.45
7.35
7.25
7.15
f1 (ppm)
S
S
N
Me
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

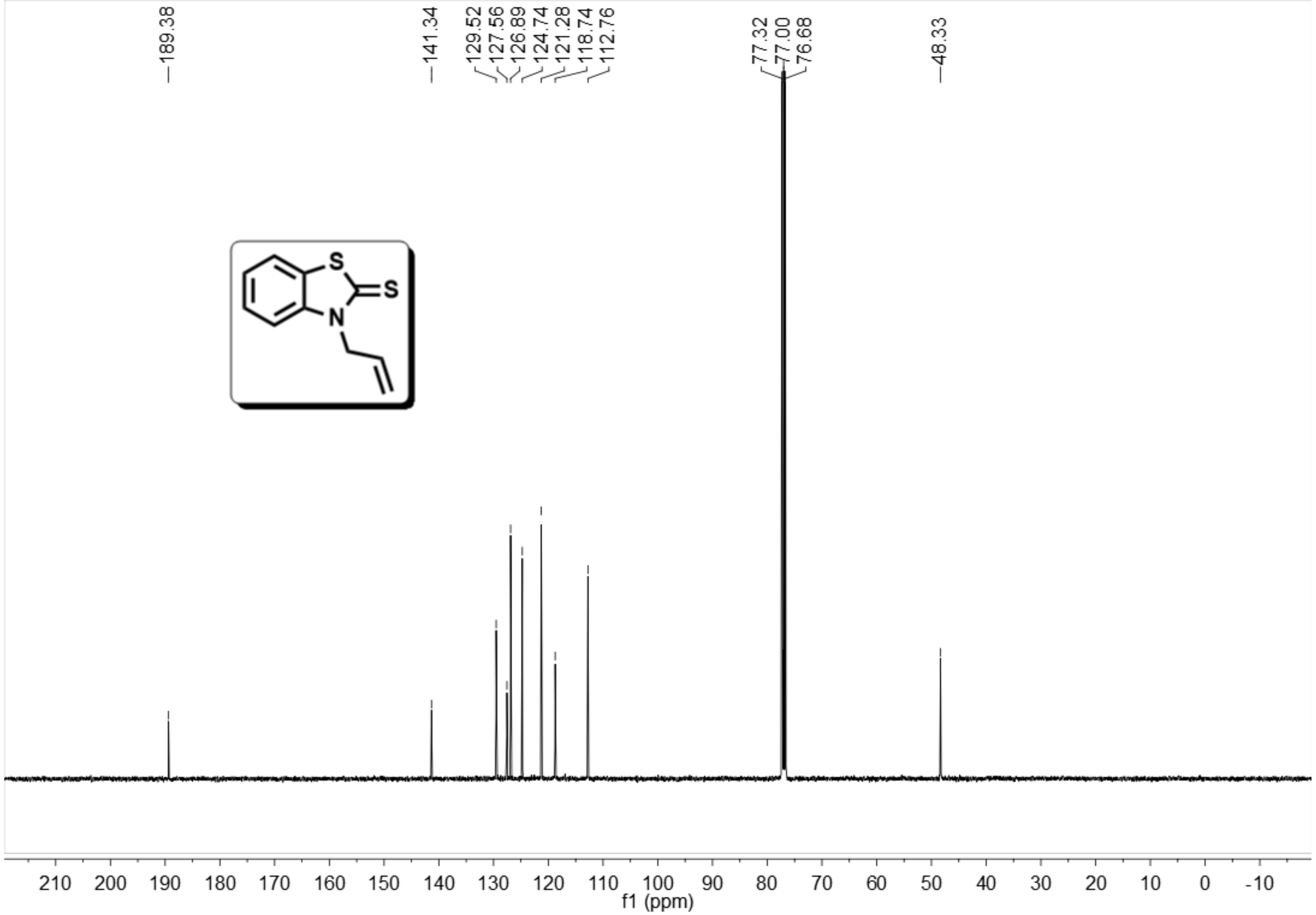
3b


189.43
142.02
127.55
126.96
124.81
121.25
112.27
77.32
77.00
76.68
33.11
S
S
N
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

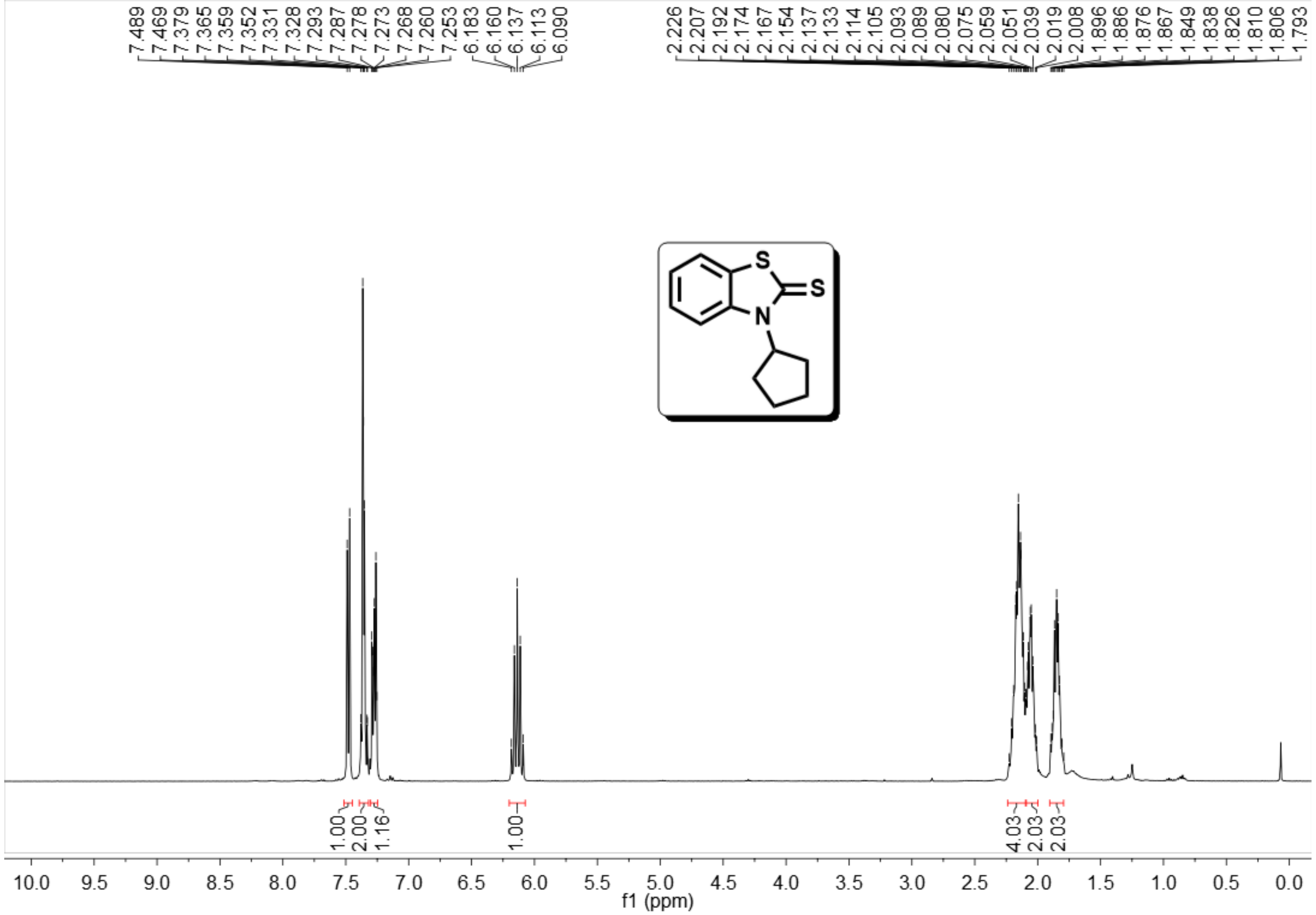
3c


7.495
7.475
7.407
7.404
7.386
7.368
7.365
7.313
7.311
7.294
7.275
7.260
7.200
7.180
5.936
5.923
5.906
5.893
5.880
5.304
5.278
5.222
5.179
5.111
5.107
5.103
5.098
5.094
5.090
1.00
1.00
1.03
1.01
1.01
1.02
1.03
2.01
S
S
N
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

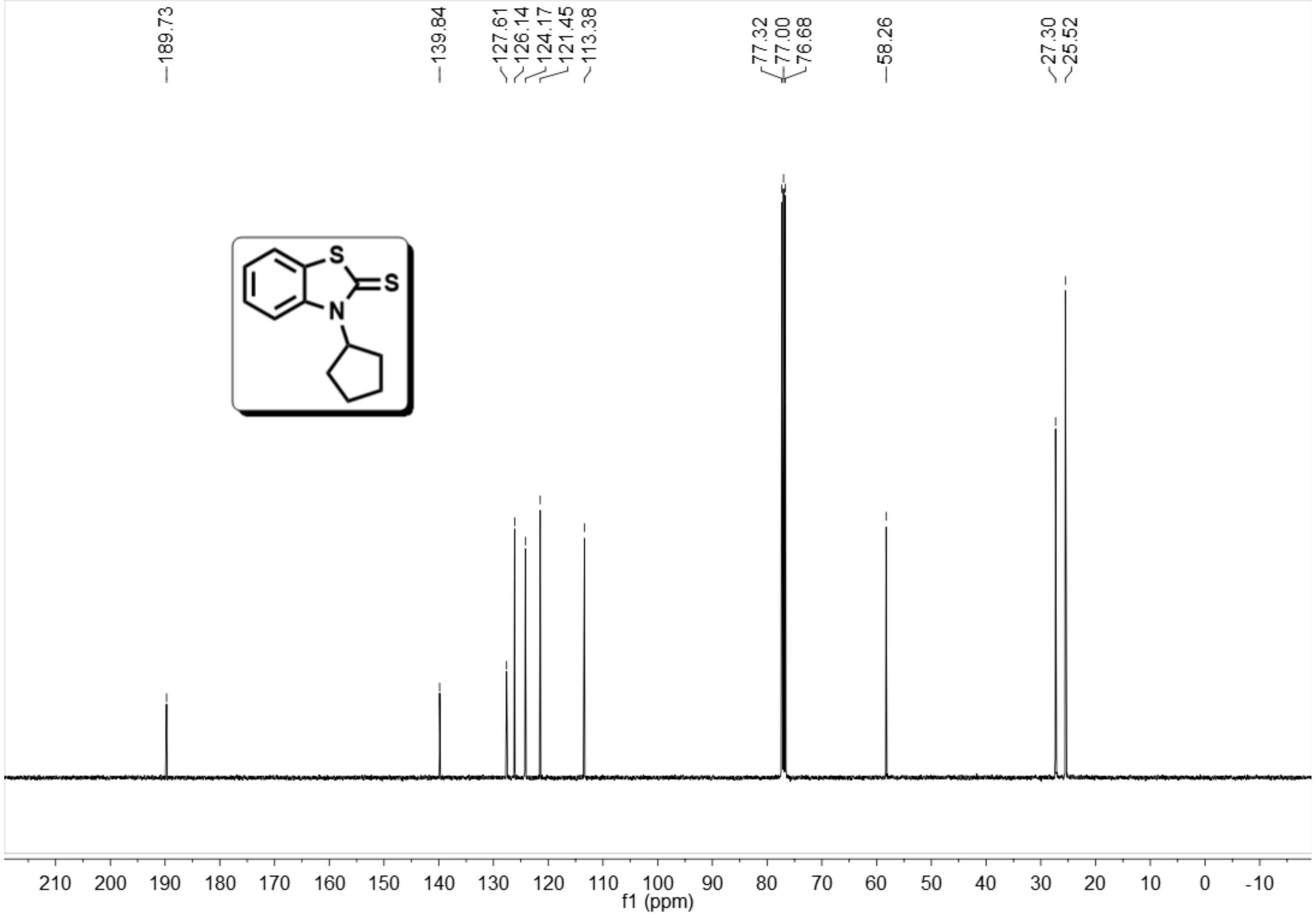
3c


189.38
141.34
129.52
127.56
126.89
124.74
121.28
118.74
112.76
77.32
77.00
76.68
48.33
S
S
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

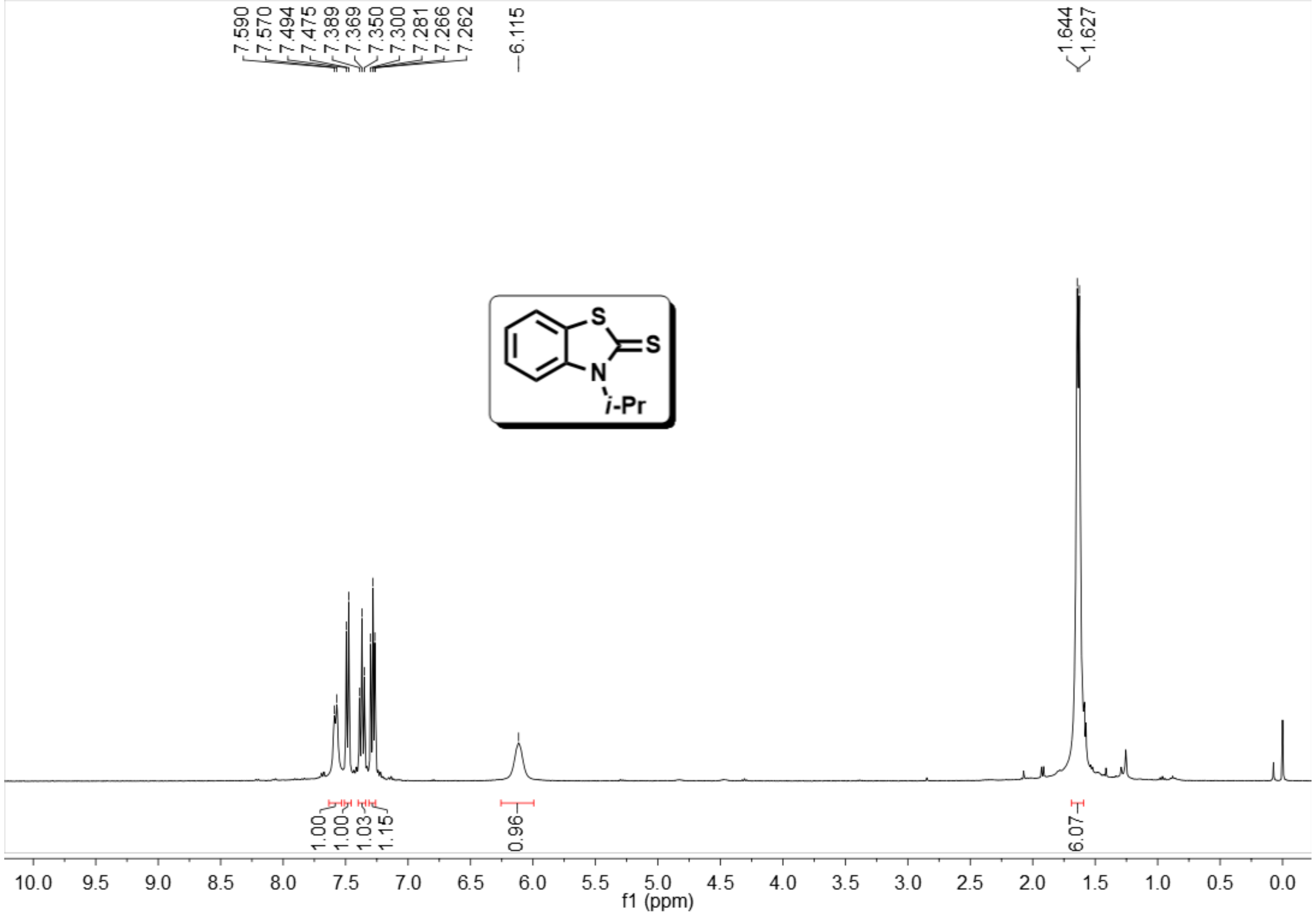
3d


7.489
7.469
7.379
7.365
7.359
7.352
7.331
7.328
7.293
7.287
7.278
7.273
7.268
7.260
7.253
6.183
6.160
6.137
6.113
6.090
2.226
2.207
2.192
2.174
2.167
2.154
2.137
2.133
2.114
2.105
2.093
2.089
2.080
2.075
2.059
2.051
2.039
2.019
2.008
1.896
1.886
1.876
1.867
1.849
1.838
1.826
1.810
1.806
1.793
S
S
N
1.00
2.00
1.16
1.00
4.03
2.03
2.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

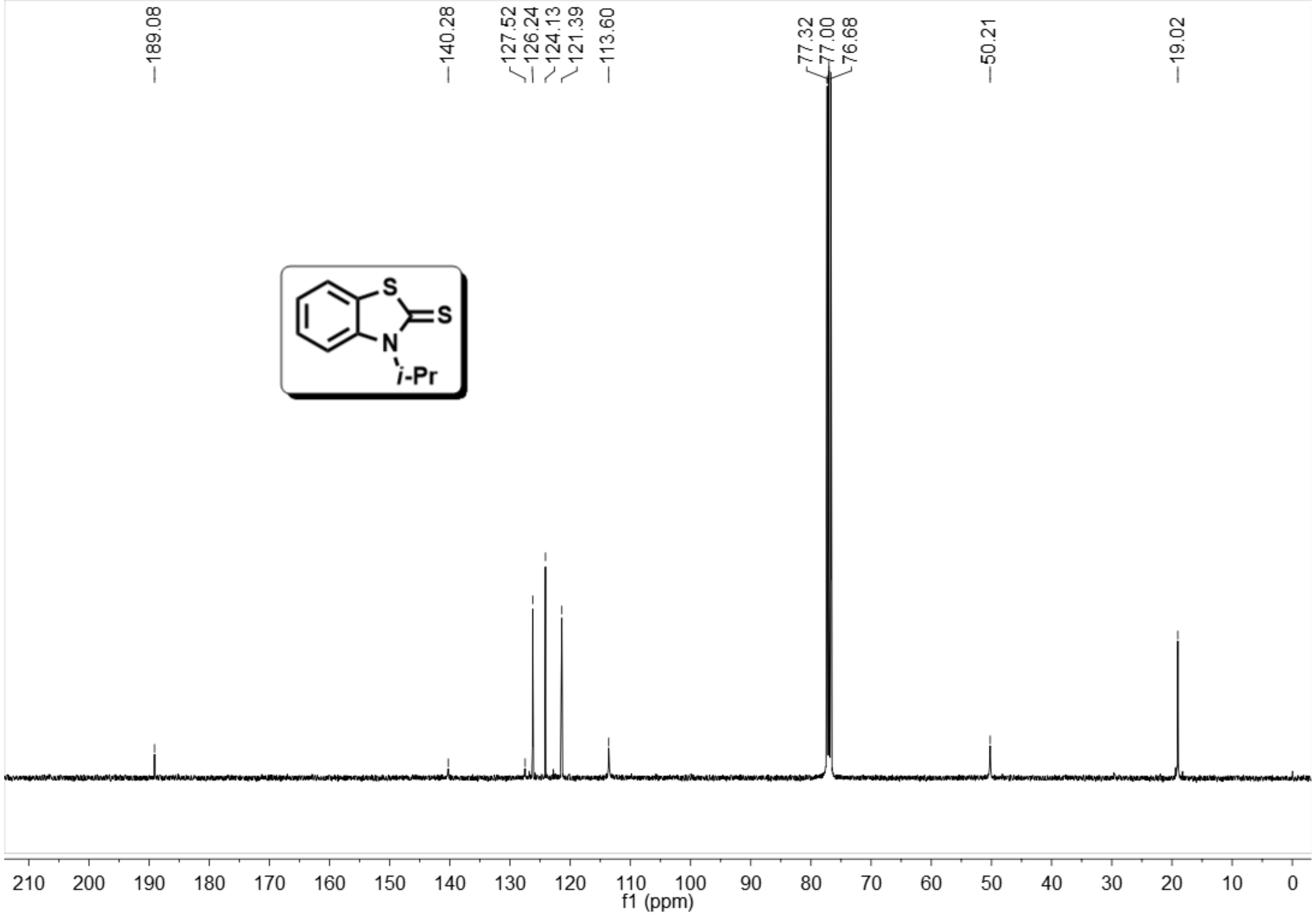
3d


189.73
139.84
127.61
126.14
124.17
121.45
113.38
77.32
77.00
76.68
58.26
27.30
25.52
S
S
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

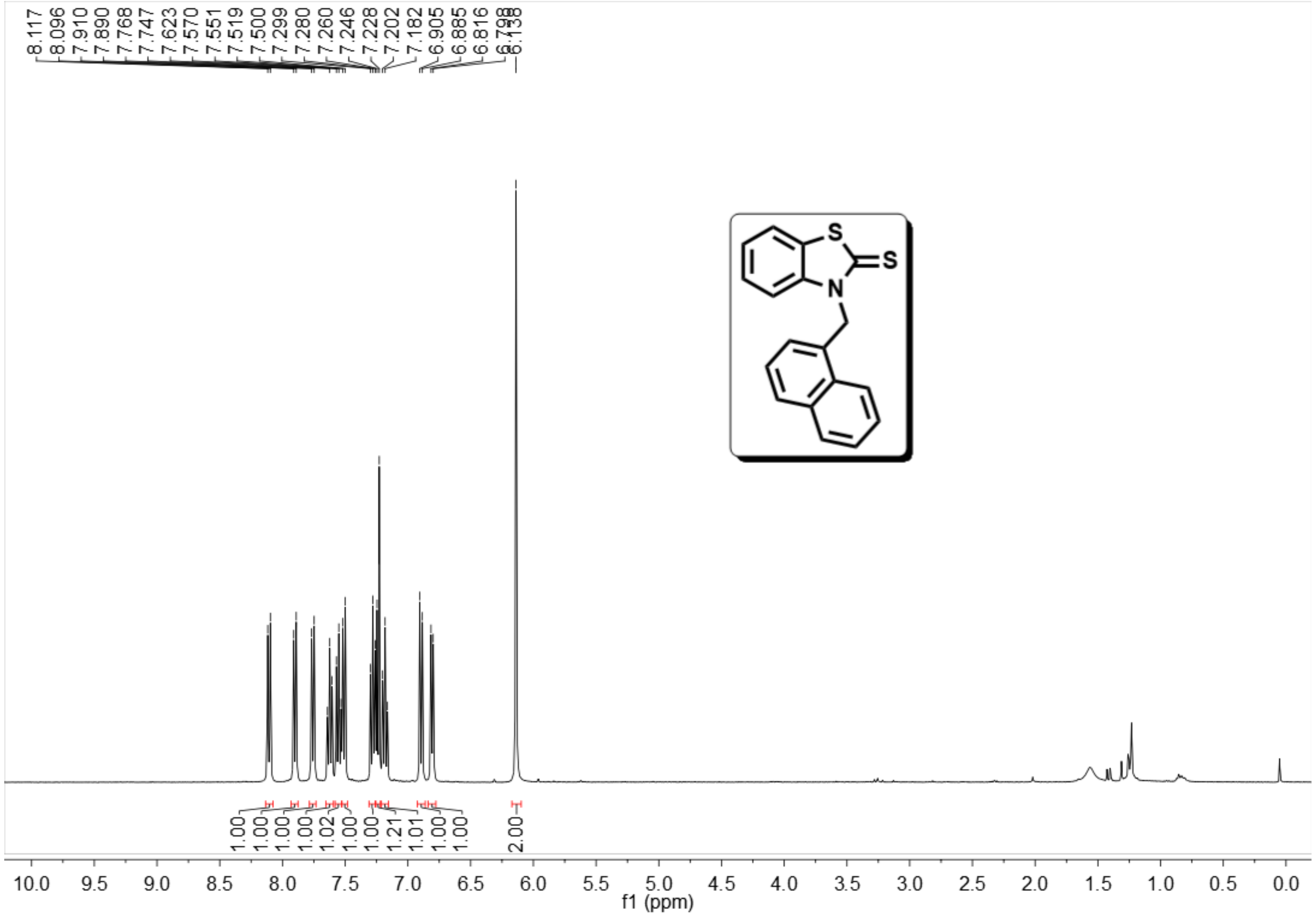
3e


7.590
7.570
7.494
7.475
7.389
7.369
7.350
7.300
7.281
7.266
7.262
6.115
1.644
1.627
S
S
N
i-Pr
1.00
1.00
1.03
1.15
0.96
6.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

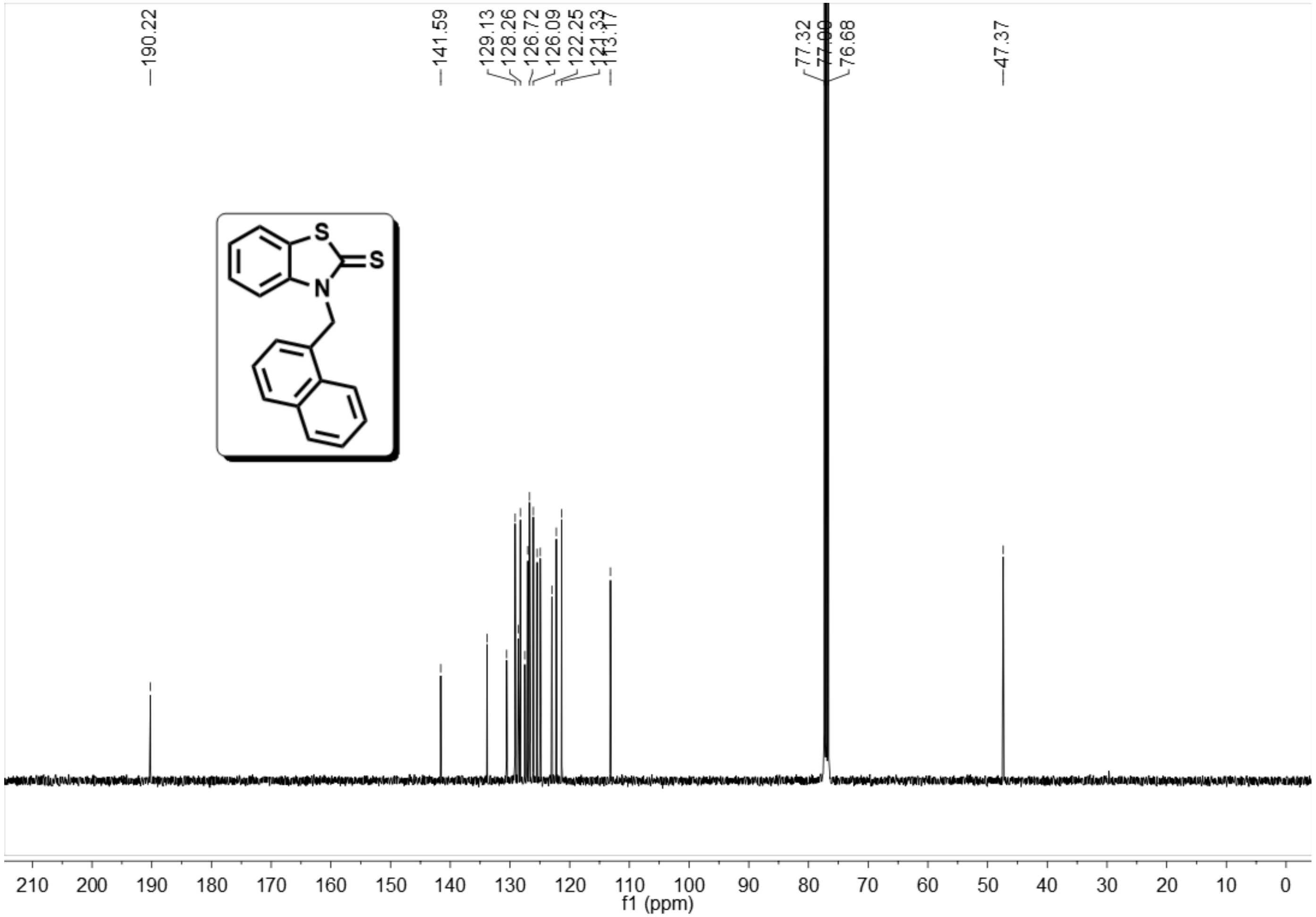
3e


189.08
140.28
127.52
126.24
124.13
121.39
113.60
77.32
77.00
76.68
50.21
19.02
S
S
N
i-Pr
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

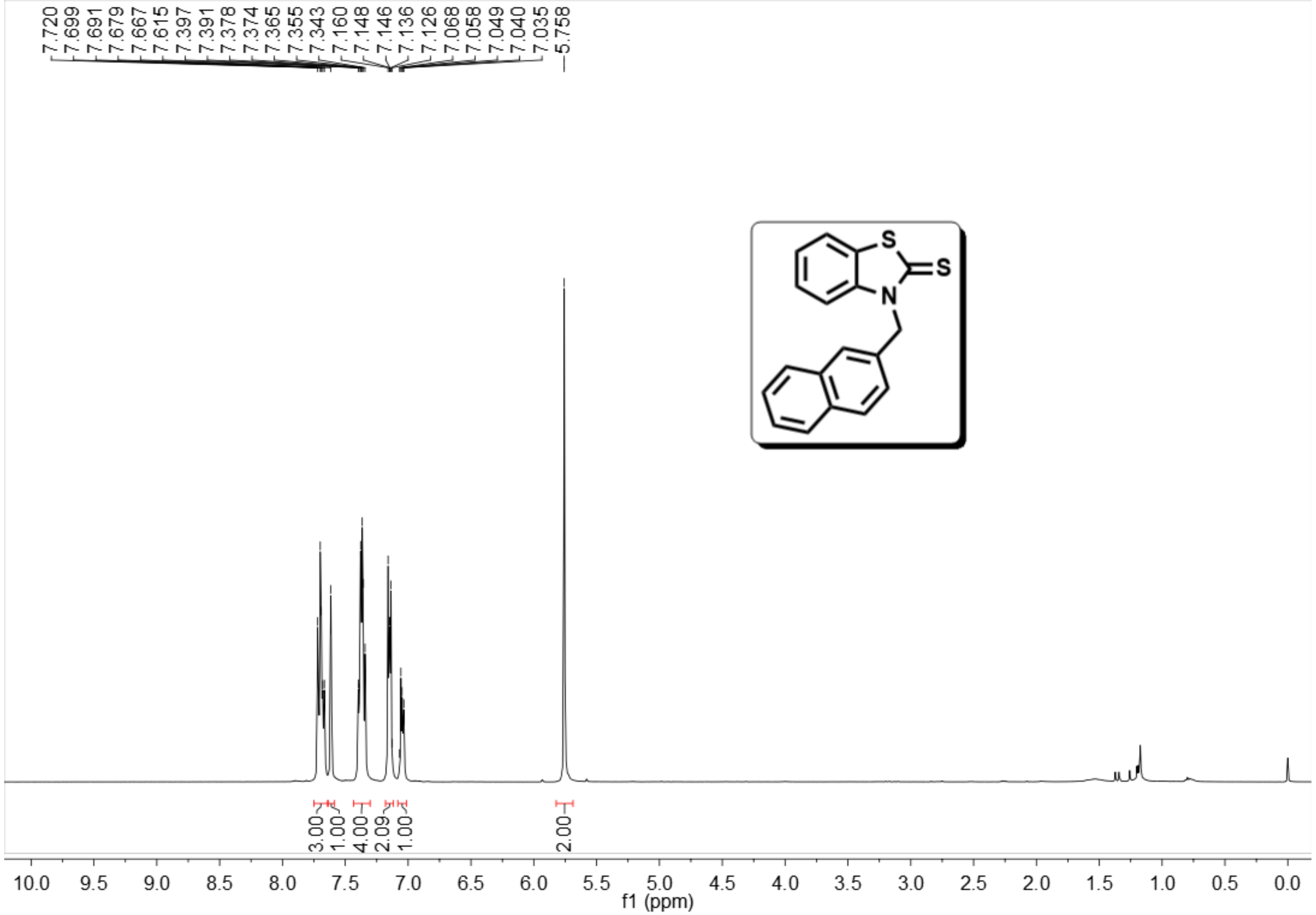
3f


8.117
8.096
7.910
7.890
7.768
7.747
7.623
7.570
7.551
7.519
7.500
7.299
7.280
7.260
7.246
7.228
7.202
7.182
6.905
6.885
6.816
6.798
6.138
S
S
N
1.00
1.00
1.00
1.00
1.02
1.00
1.21
1.01
1.00
1.00
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

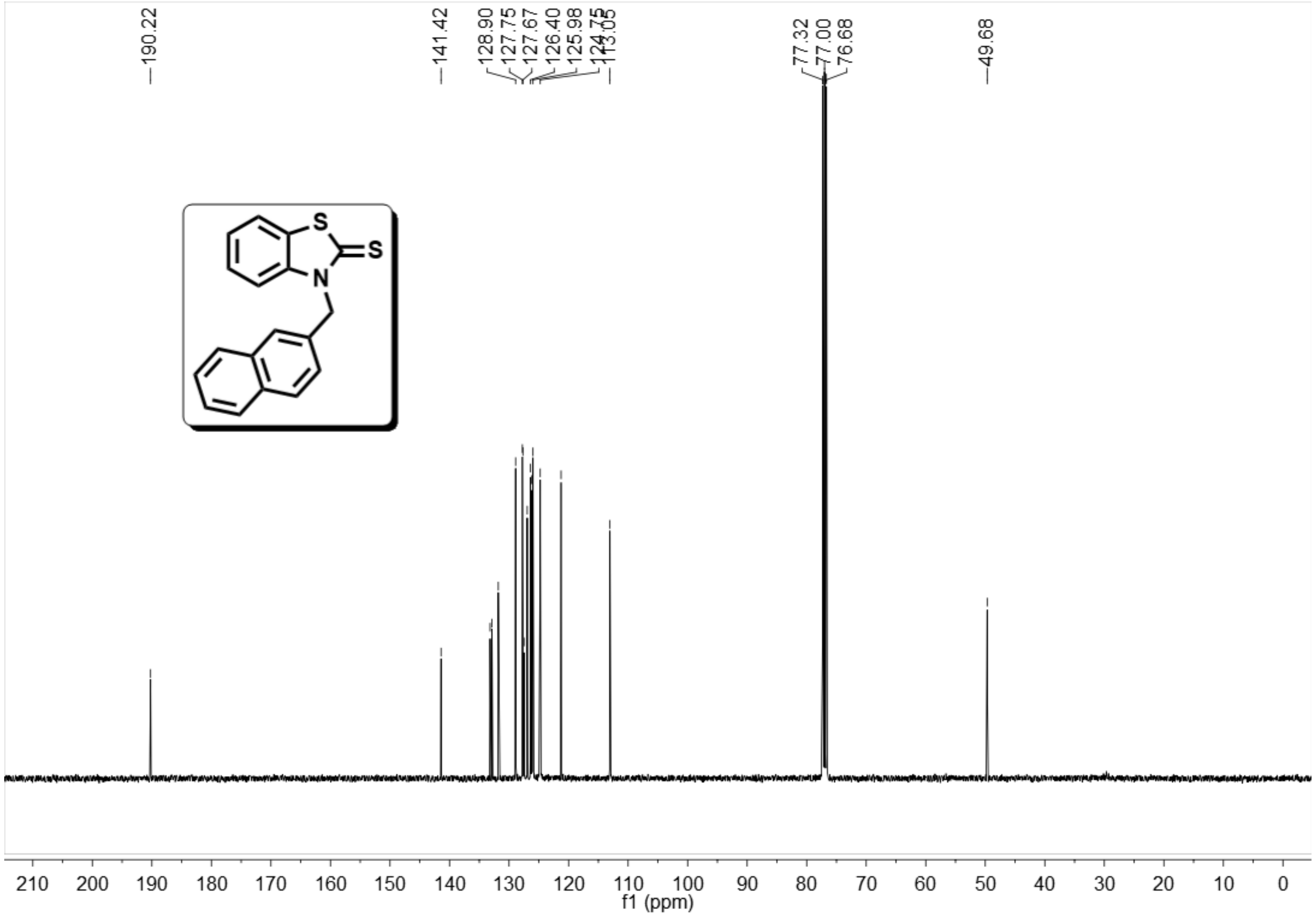
3f


190.22
141.59
129.13
128.26
126.72
126.09
122.25
121.33
113.17
77.32
77.00
76.68
47.37
S
S
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3g

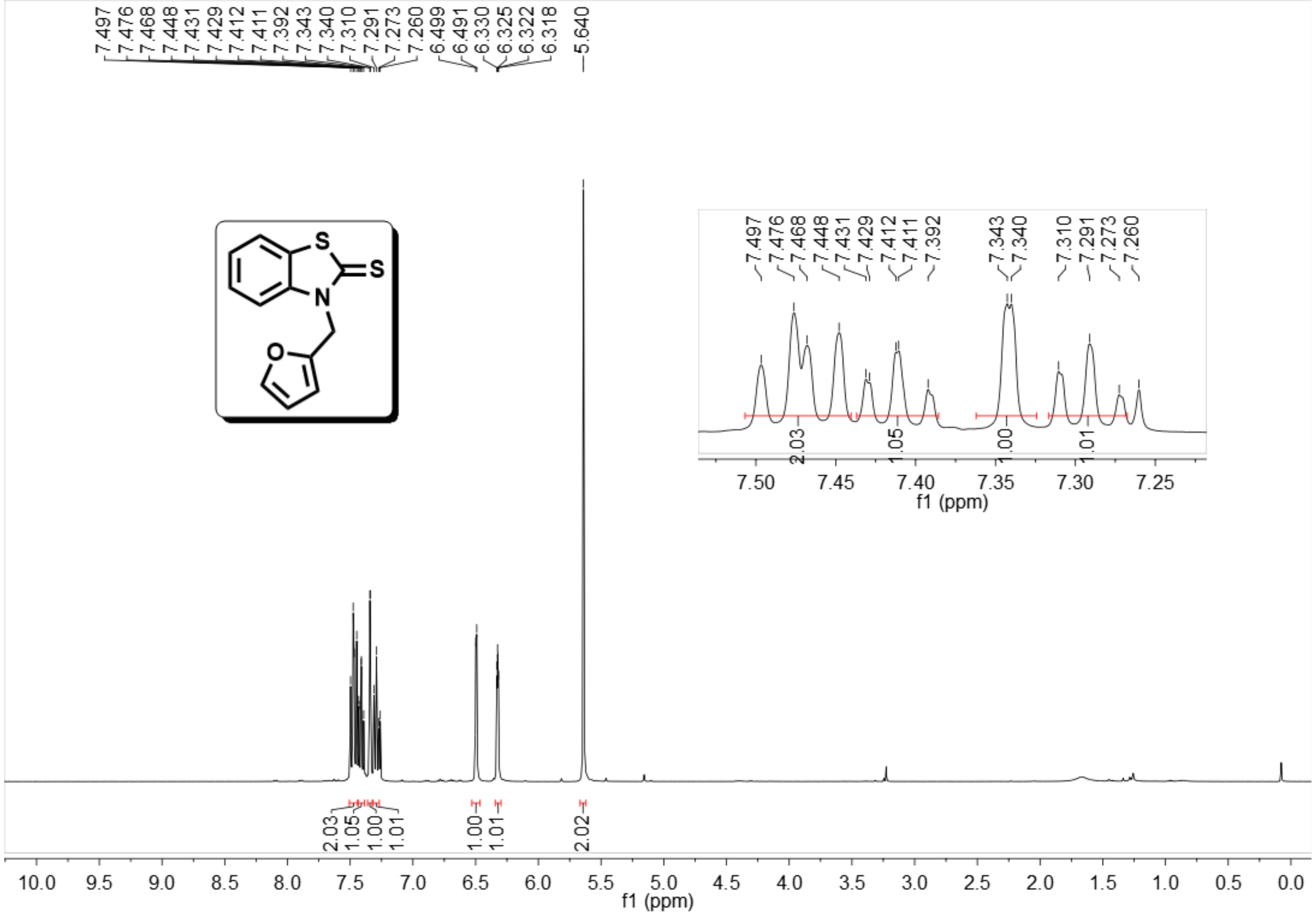

7.720
7.699
7.691
7.679
7.667
7.615
7.397
7.391
7.378
7.374
7.365
7.355
7.343
7.160
7.148
7.146
7.136
7.126
7.068
7.058
7.049
7.040
7.035
5.758
S
S
N
3.00
1.00
4.00
2.09
1.00
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3g



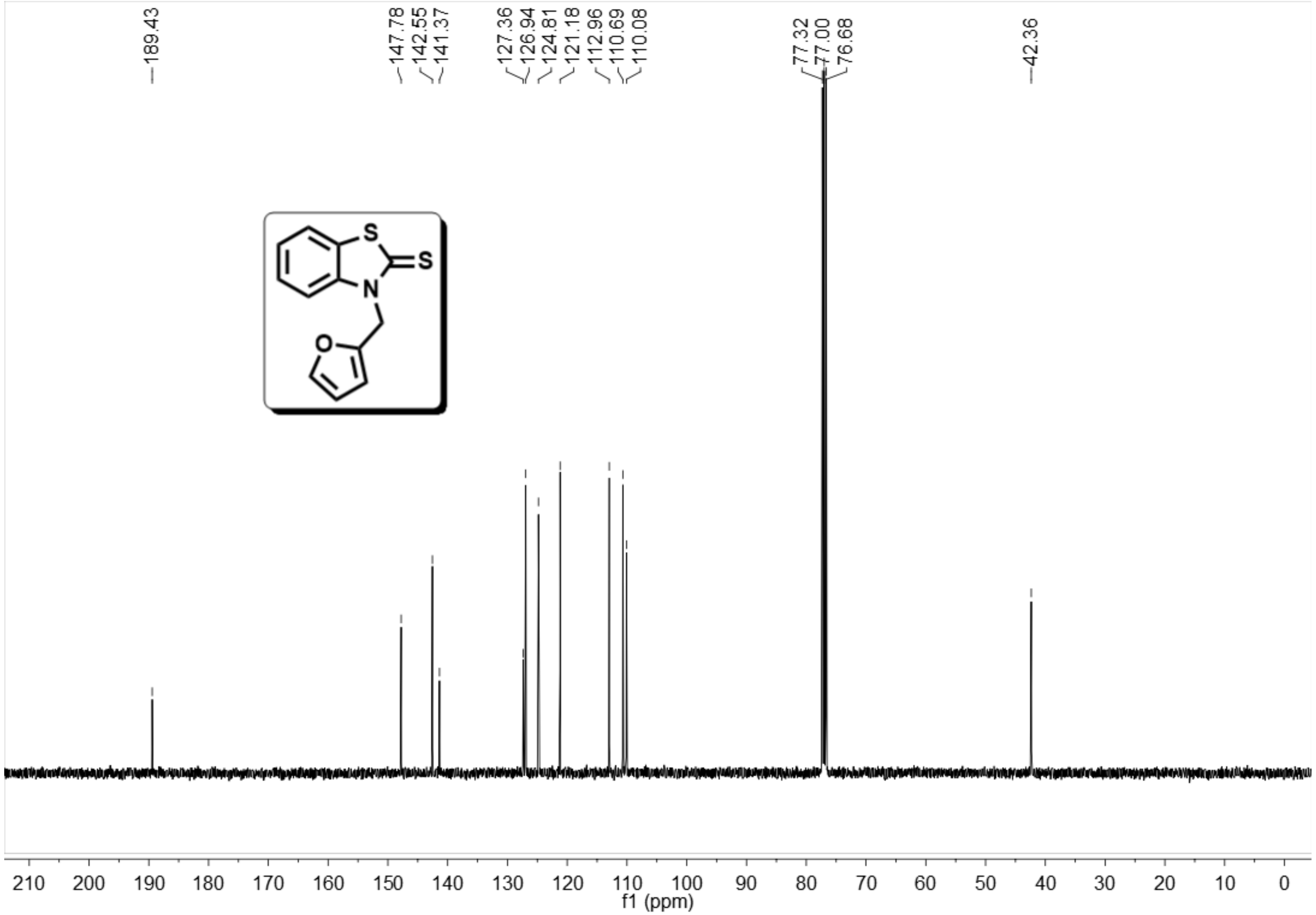
190.22
141.42
128.90
127.75
127.67
126.40
125.98
124.75
113.05
77.32
77.00
76.68
49.68
S
S
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3h

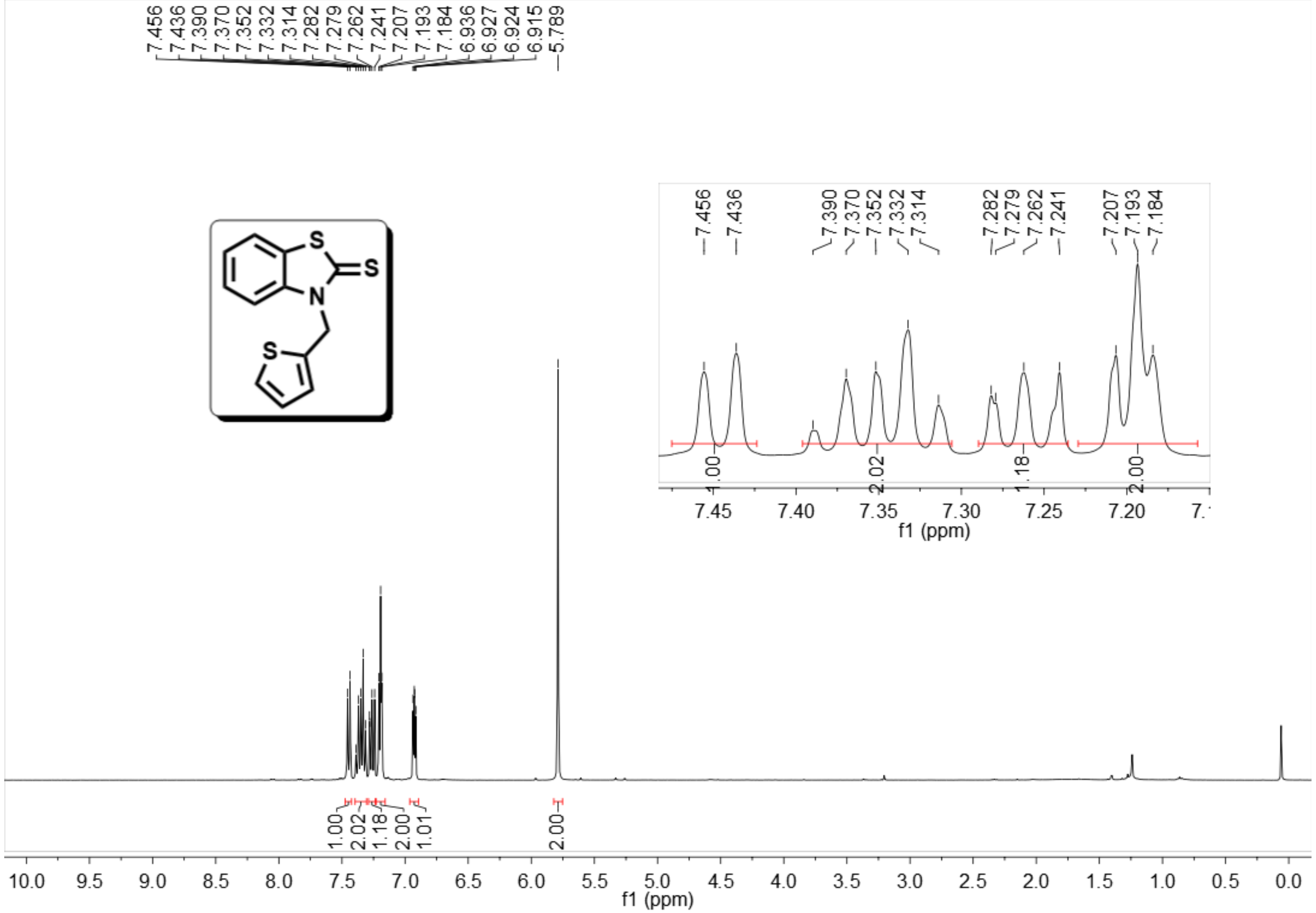


7.497
7.476
7.468
7.448
7.431
7.429
7.412
7.411
7.392
7.343
7.340
7.310
7.291
7.273
7.260
6.499
6.491
6.330
6.325
6.322
6.318
5.640
S
S
N
O
2.03
1.05
1.00
1.01
1.00
1.01
2.02
7.50
7.45
7.40
7.35
7.30
7.25
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3h

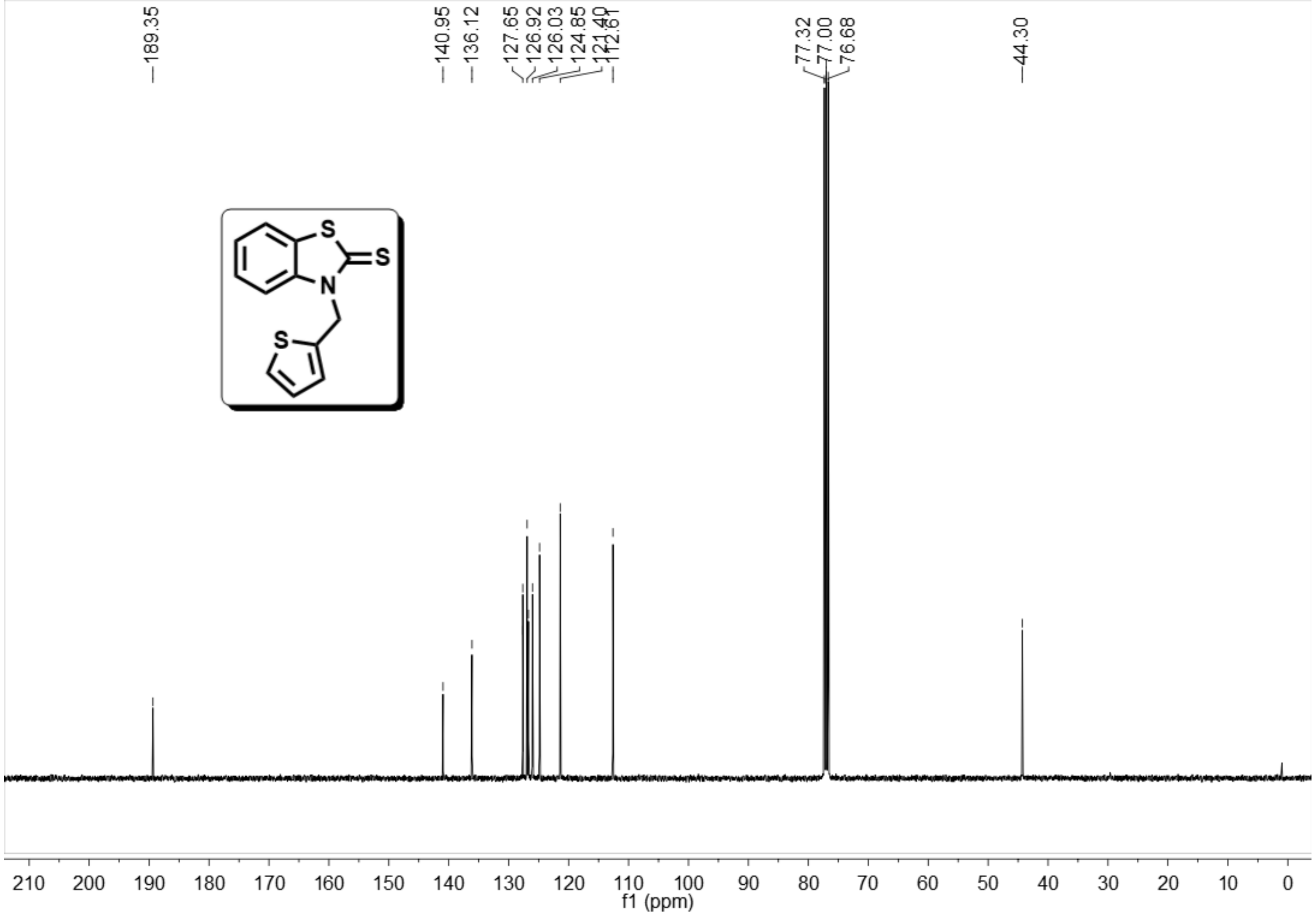

189.43
147.78
142.55
141.37
127.36
126.94
124.81
121.18
112.96
110.69
110.08
77.32
77.00
76.68
42.36
S
S
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3i



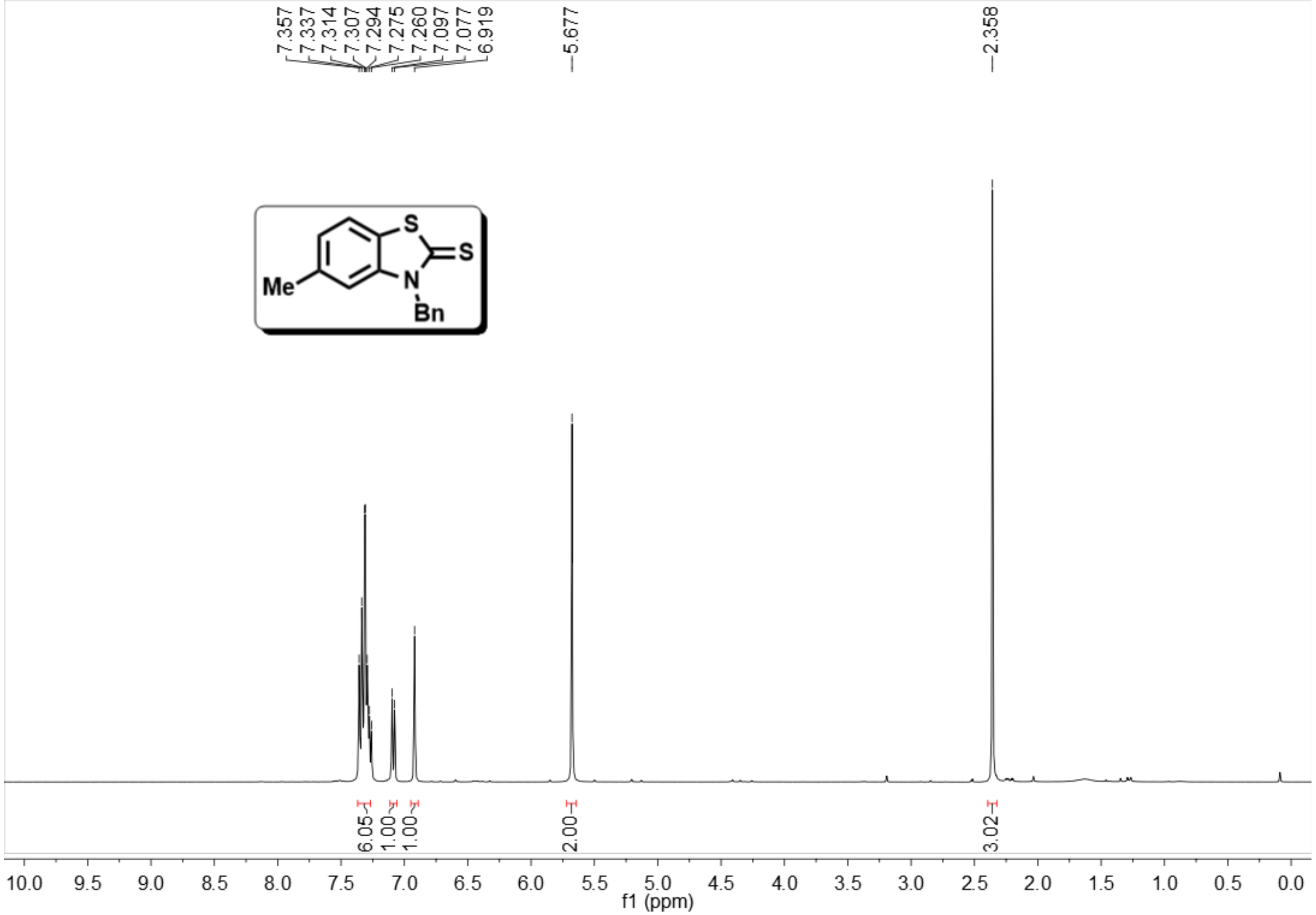
7.456
7.436
7.390
7.370
7.352
7.332
7.314
7.282
7.279
7.262
7.241
7.207
7.193
7.184
6.936
6.927
6.924
6.915
5.789
S
S
N
S
1.00
2.02
1.18
2.00
1.01
2.00
7.45
7.40
7.35
7.30
7.25
7.20
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3i

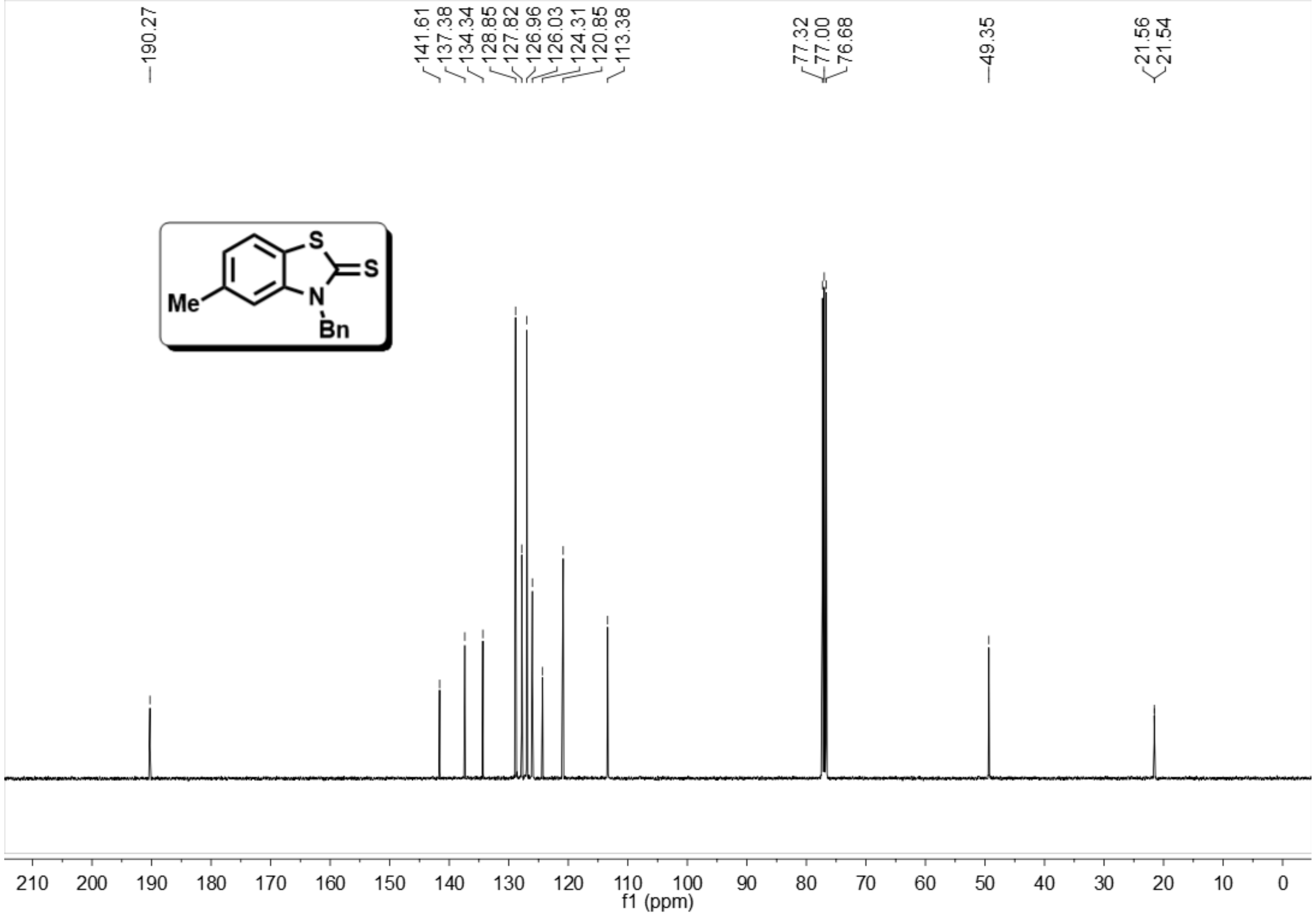


189.35
140.95
136.12
127.65
126.92
126.03
124.85
121.40
112.61
77.32
77.00
76.68
44.30
S
S
N
S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

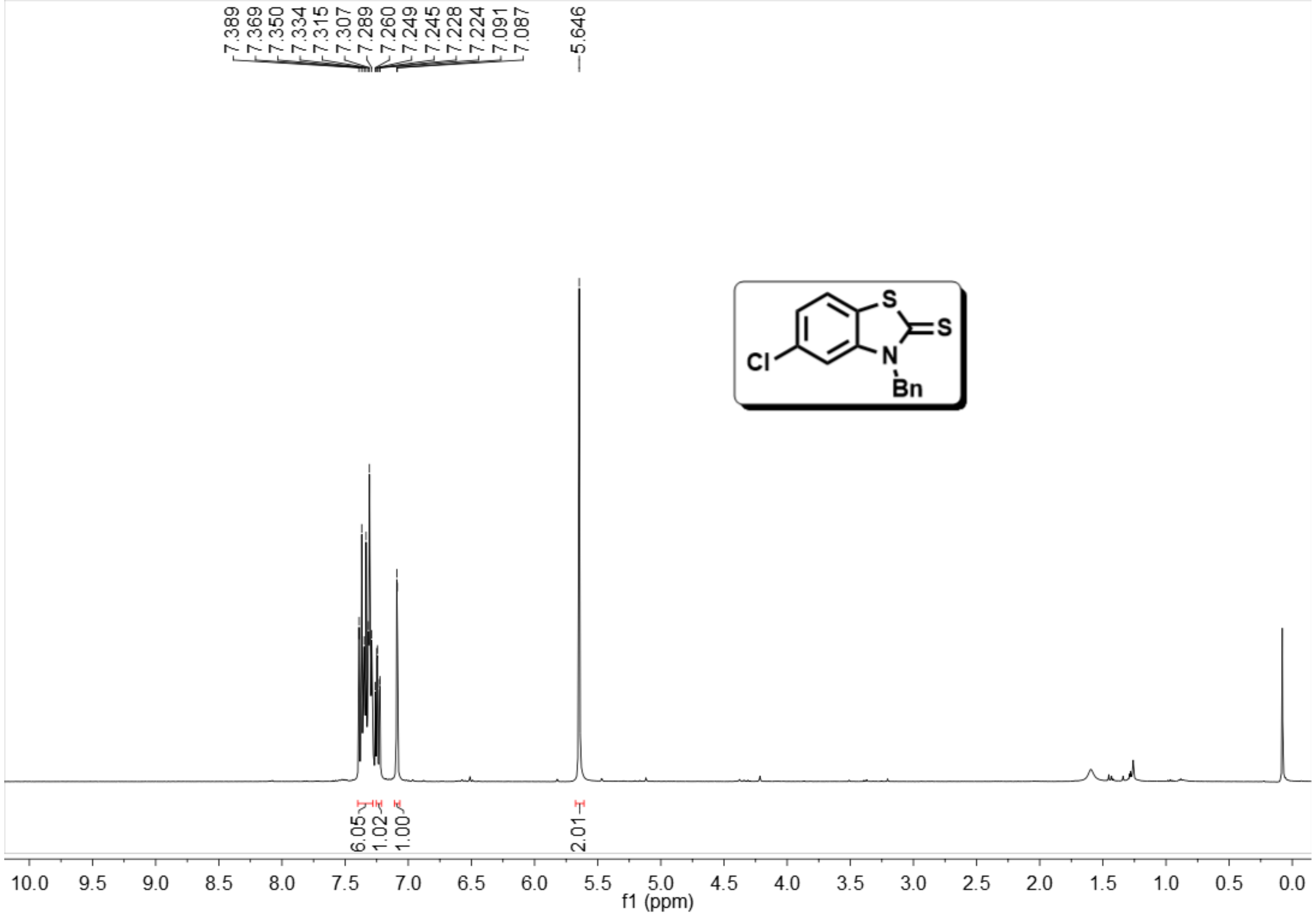
3j


7.357
7.337
7.314
7.307
7.294
7.275
7.260
7.097
7.077
6.919
5.677
2.358
S
S
N
Me
Bn
6.05
1.00
1.00
2.00
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

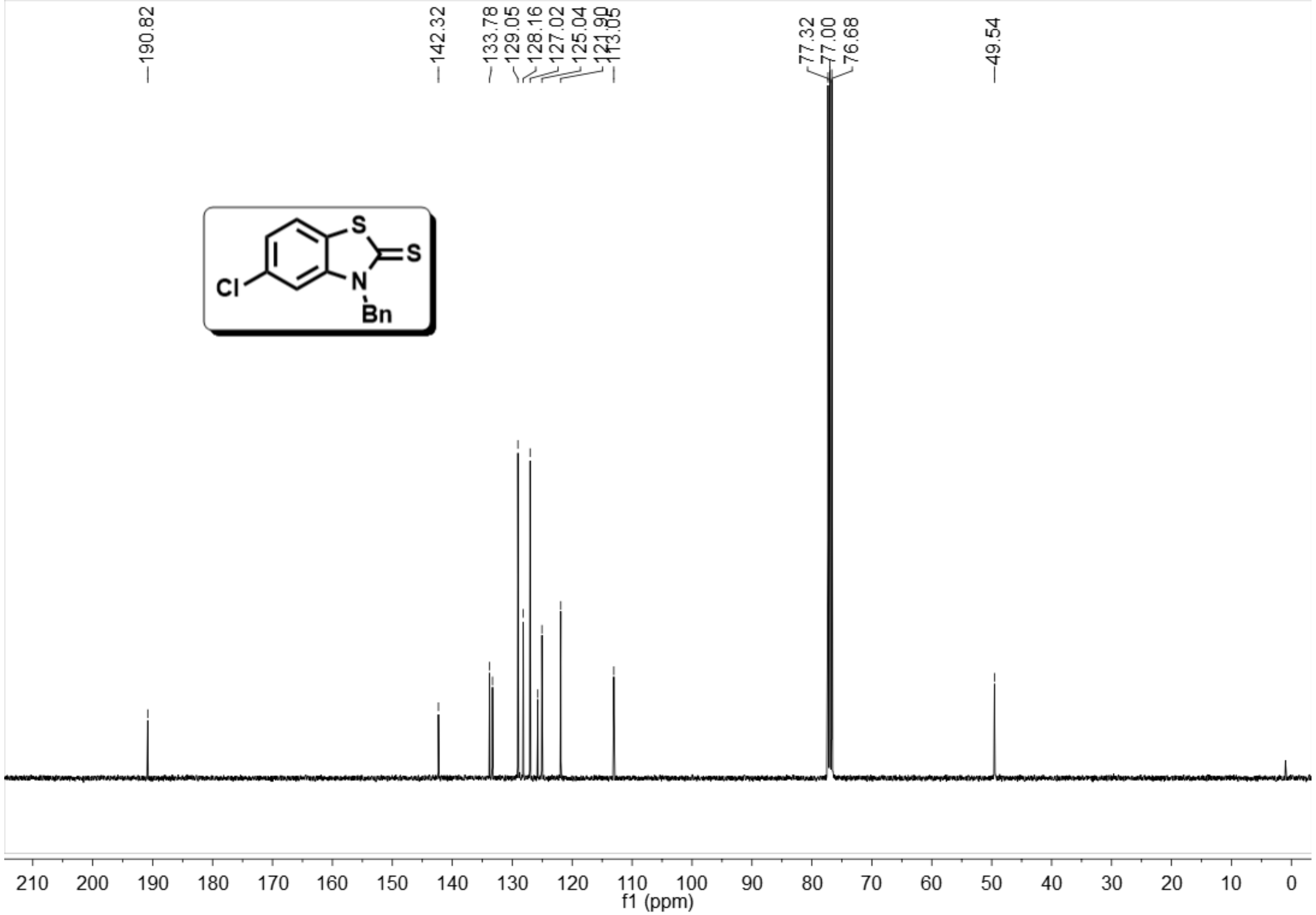
3j


190.27
141.61
137.38
134.34
128.85
127.82
126.96
126.03
124.31
120.85
113.38
77.32
77.00
76.68
49.35
21.56
21.54
S
S
N
Me
Bn
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

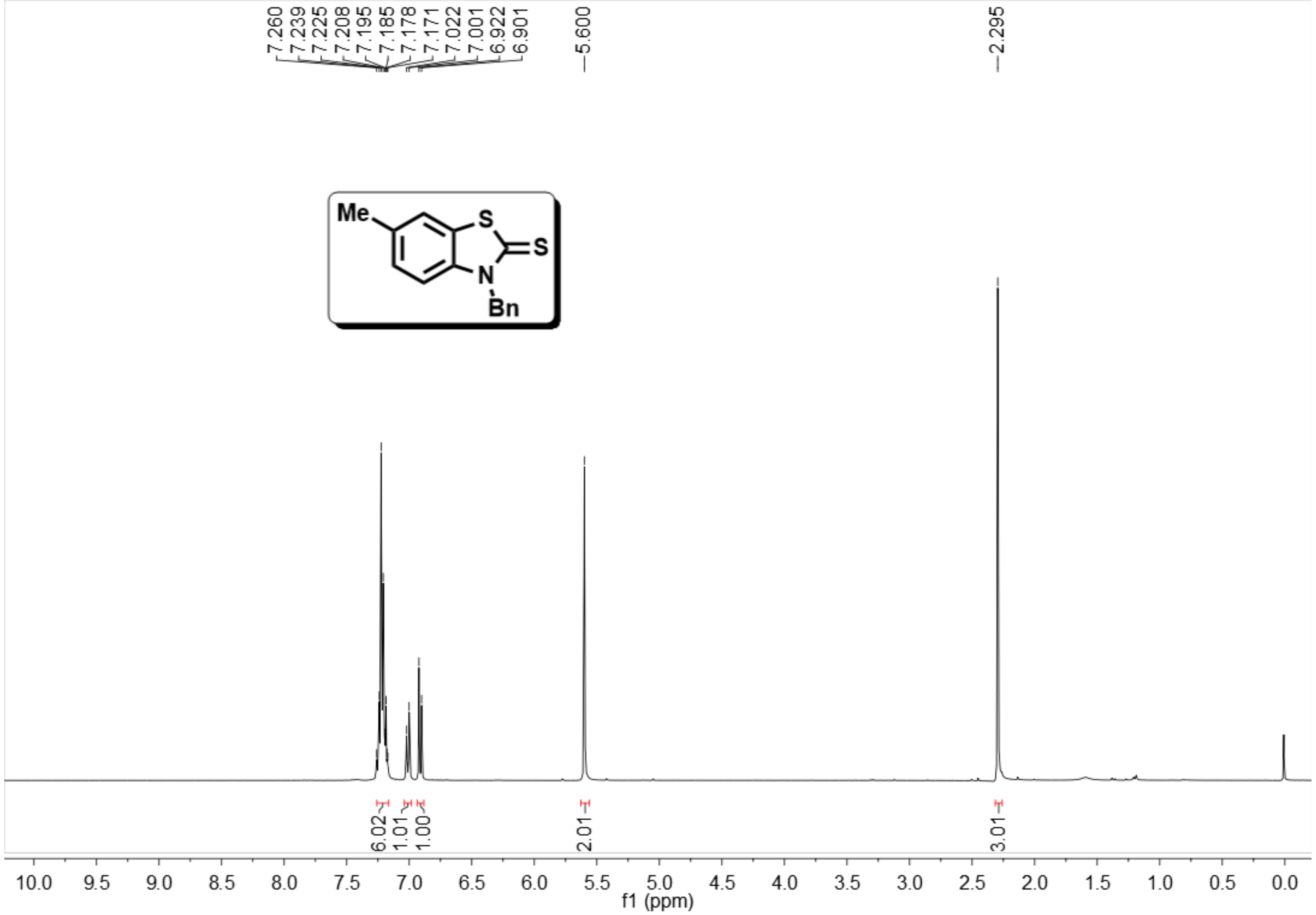
3k


7.389
7.369
7.350
7.334
7.315
7.307
7.289
7.260
7.249
7.245
7.228
7.224
7.091
7.087
5.646
S
S
N
Cl
Bn
6.05
1.02
1.00
2.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

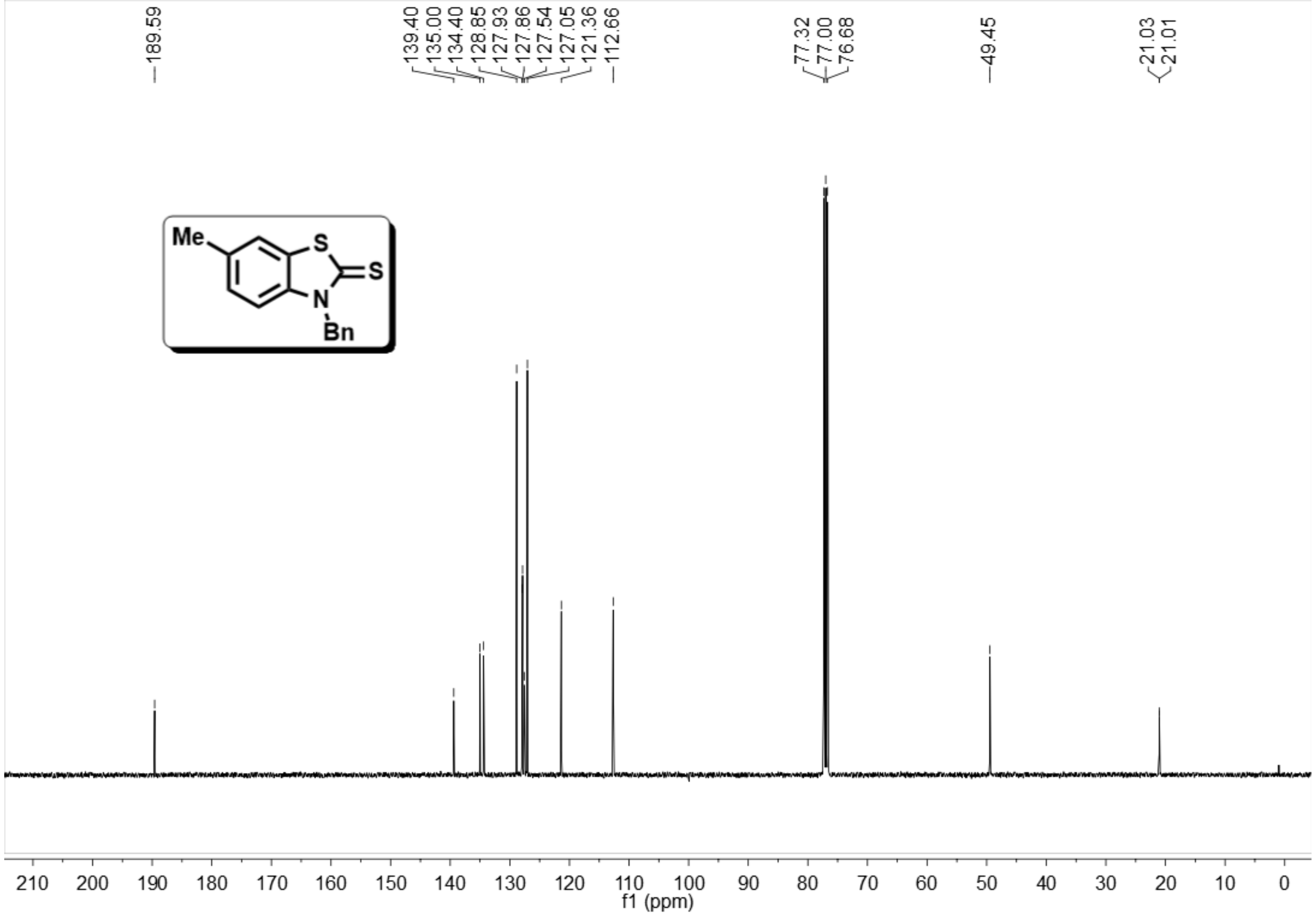
3k


190.82
142.32
133.78
129.05
128.16
127.02
125.04
121.90
113.05
77.32
77.00
76.68
49.54
S
S
N
Cl
Bn
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

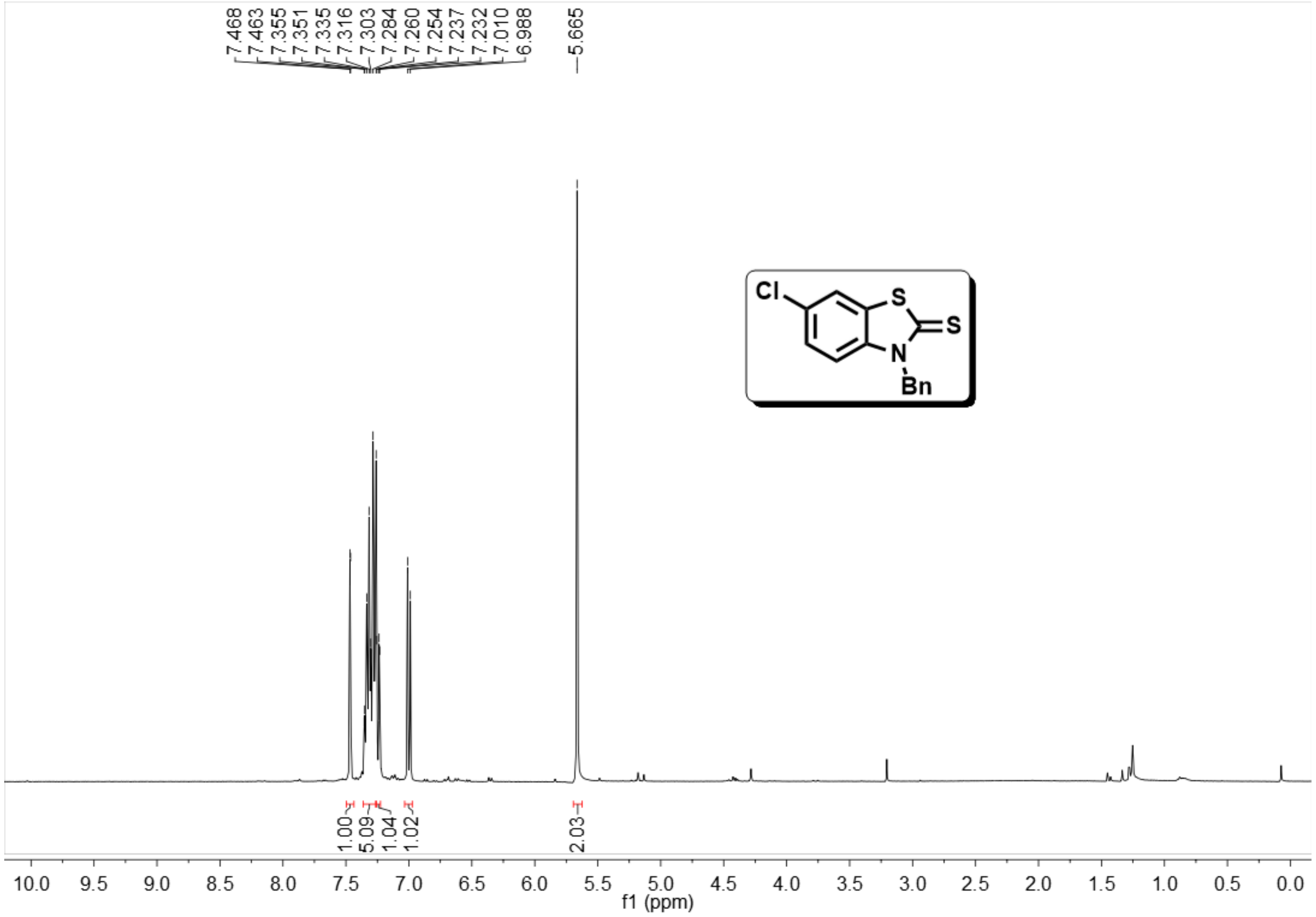
3l


7.260
7.239
7.225
7.208
7.195
7.185
7.178
7.171
7.022
7.001
6.922
6.901
5.600
2.295
Me
S
S
N
Bn
6.02
1.01
1.00
2.01
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

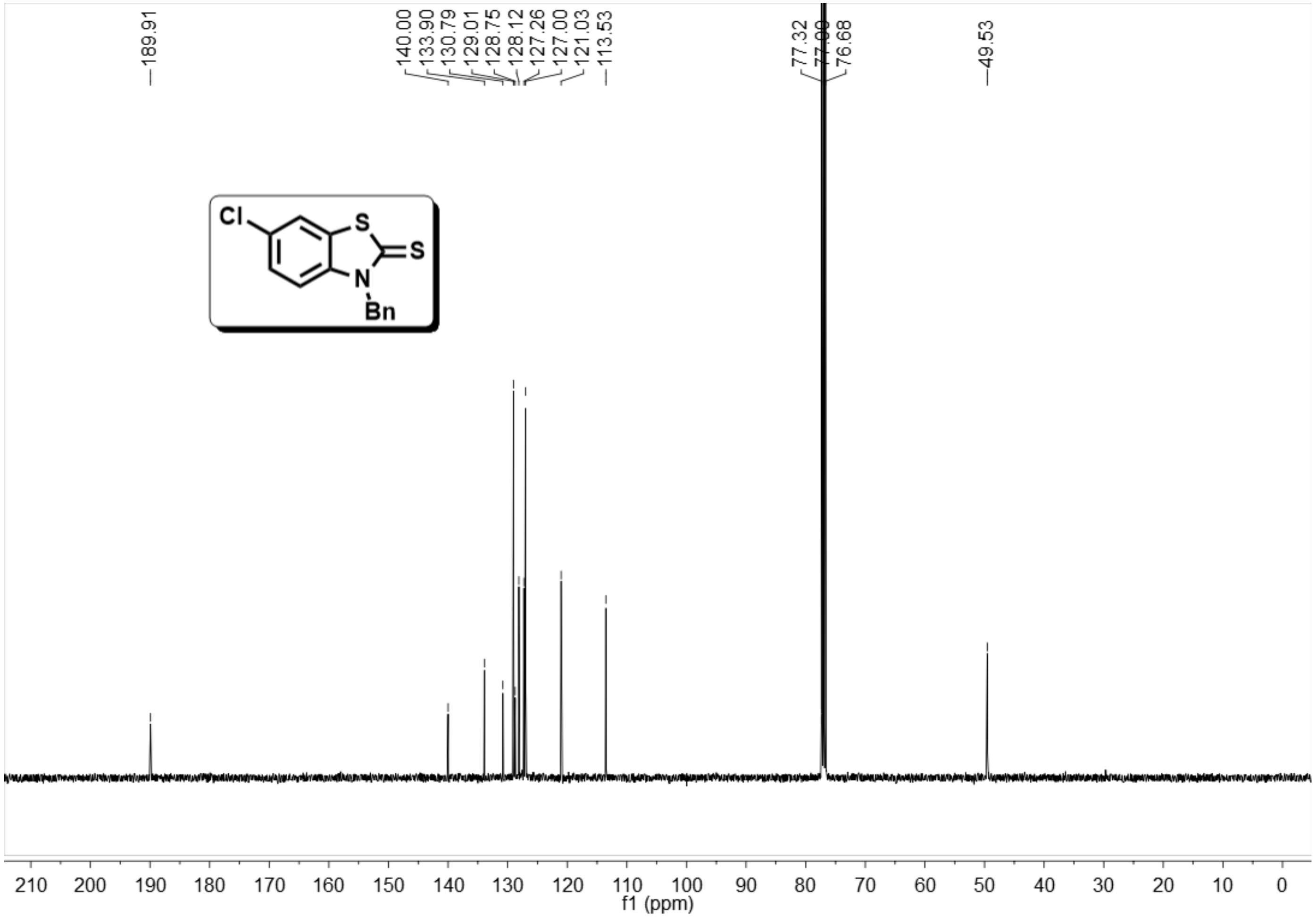
3l


189.59
139.40
135.00
134.40
128.85
127.93
127.86
127.54
127.05
121.36
112.66
77.32
77.00
76.68
49.45
21.03
21.01
Me
S
S
N
Bn
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

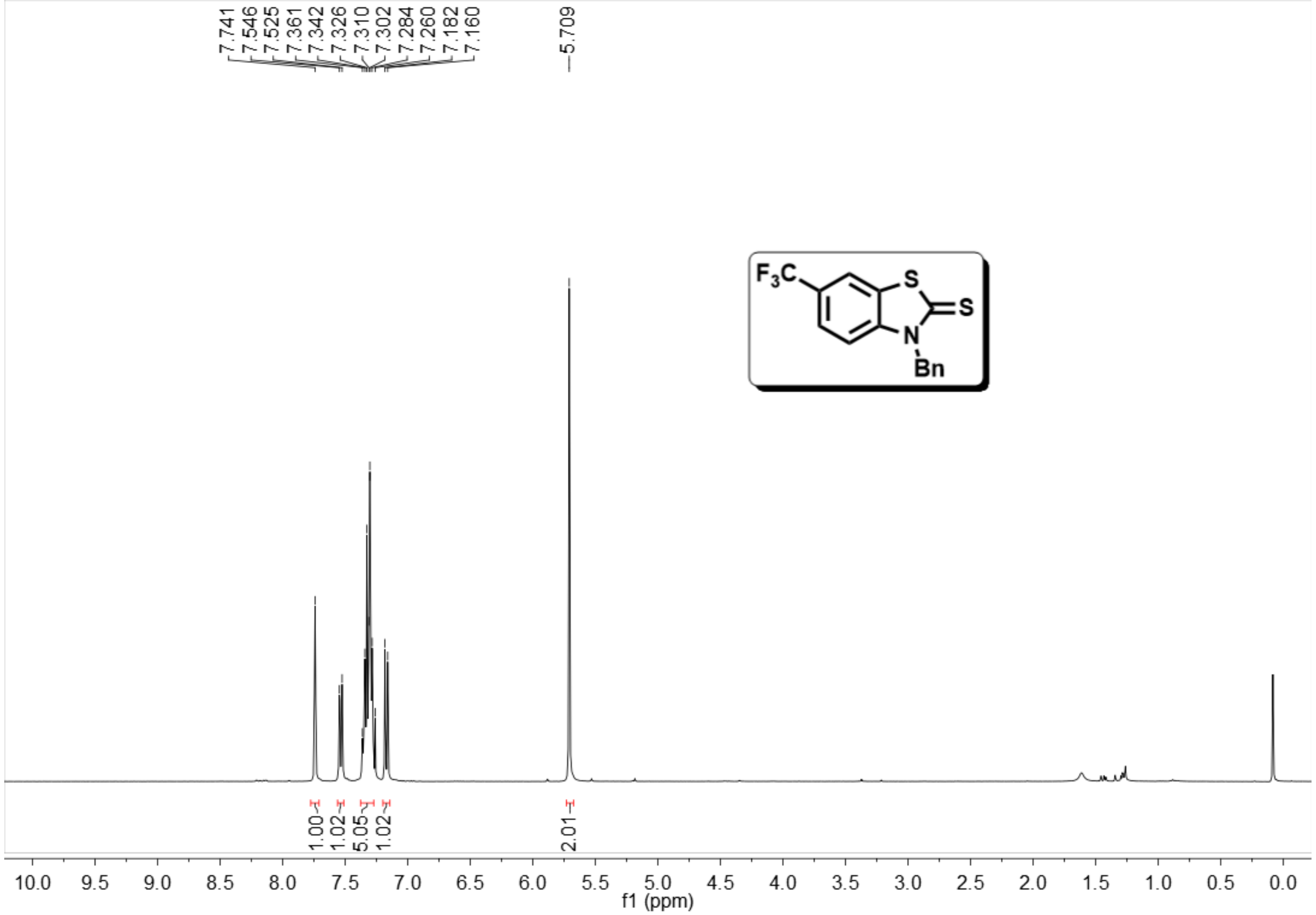
3m


7.468
7.463
7.355
7.351
7.335
7.316
7.303
7.284
7.260
7.254
7.237
7.232
7.010
6.988
5.665
Cl
S
S
N
Bn
1.00
5.09
1.04
1.02
2.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

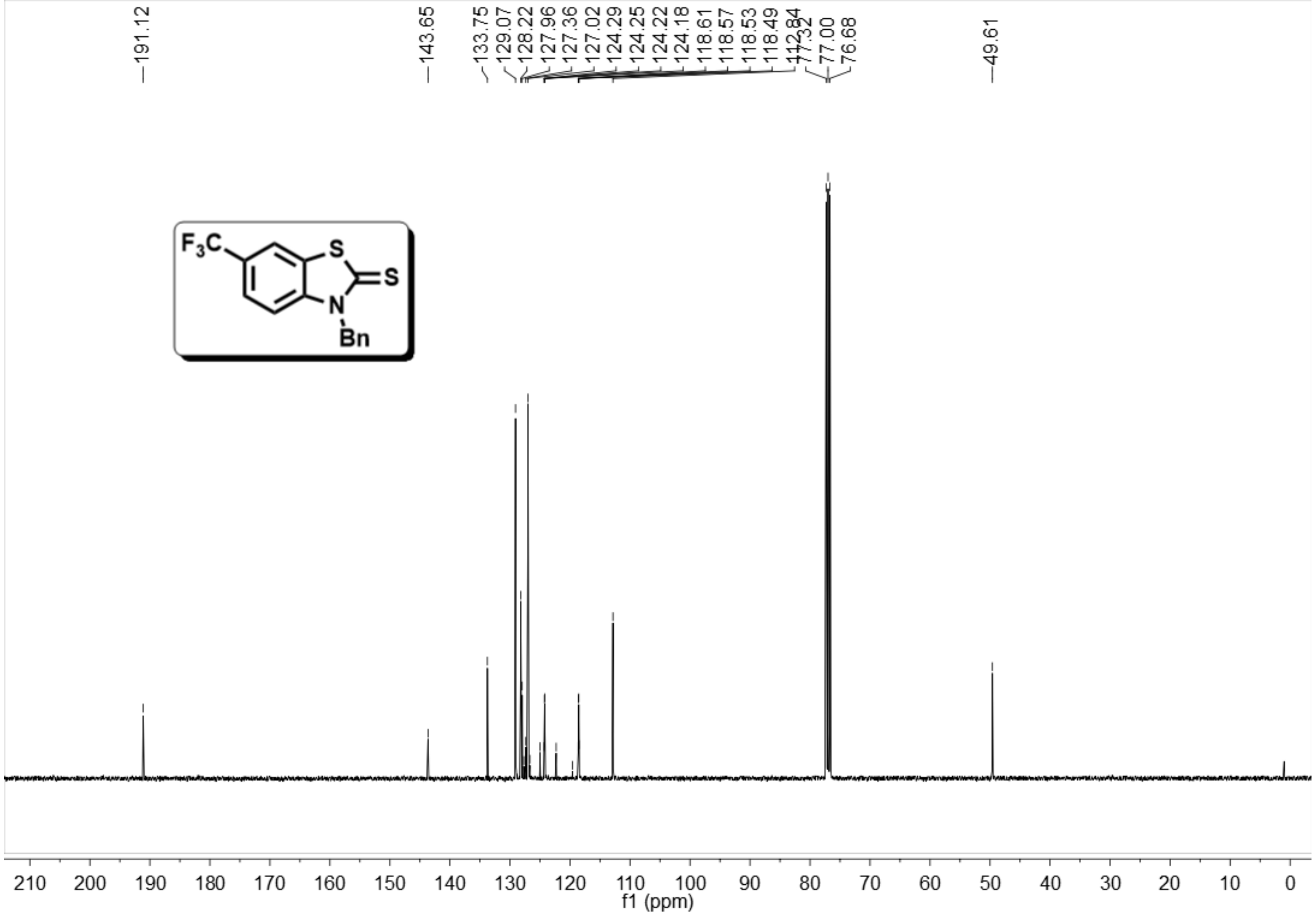
3m


189.91
140.00
133.90
130.79
129.01
128.75
128.12
127.26
127.00
121.03
113.53
77.32
77.00
76.68
49.53
Cl
S
S
N
Bn
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

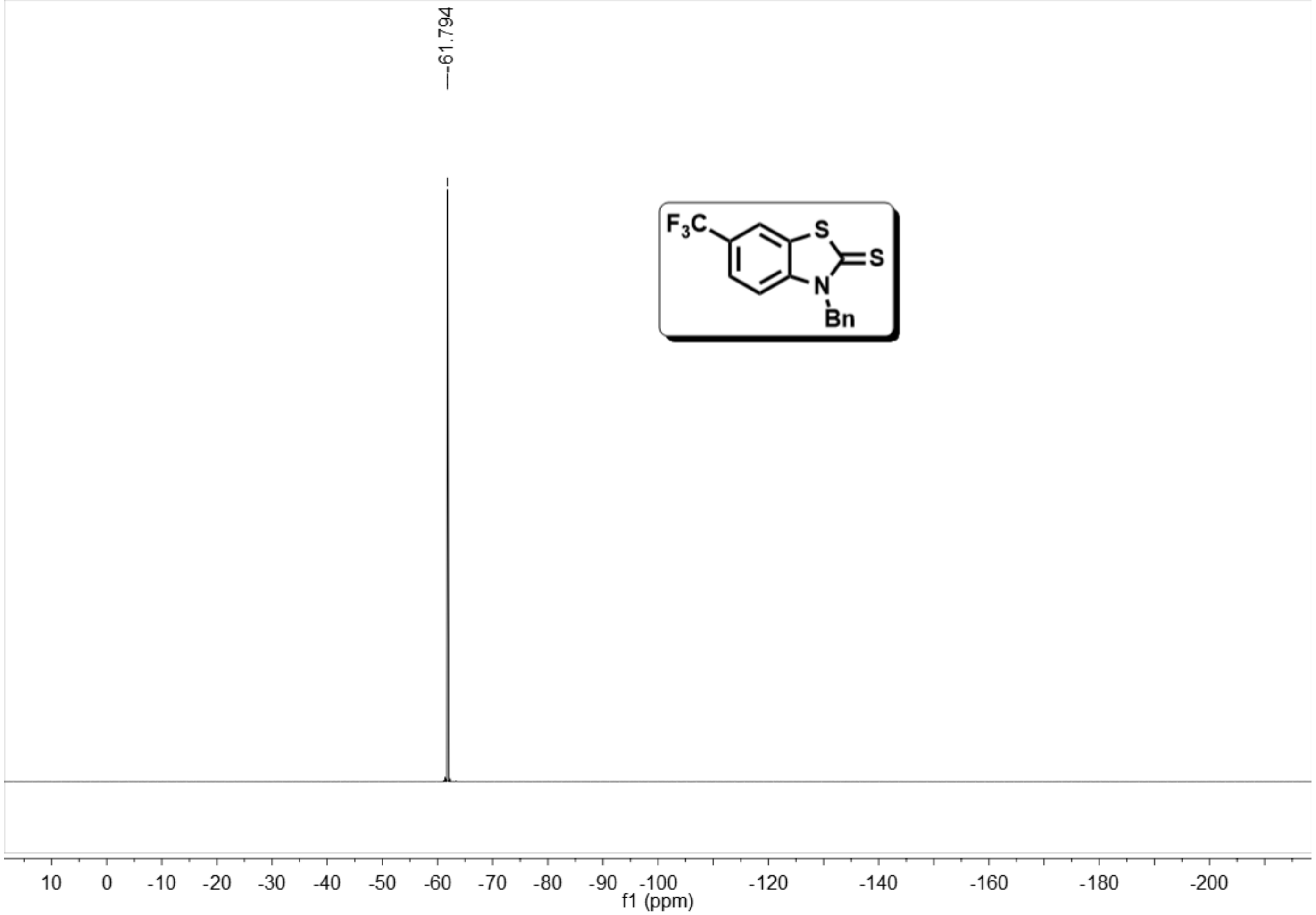
3n


7.741
7.546
7.525
7.361
7.342
7.326
7.310
7.302
7.284
7.260
7.182
7.160
5.709
F3C
S
S
N
Bn
1.00
1.02
5.05
1.02
2.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

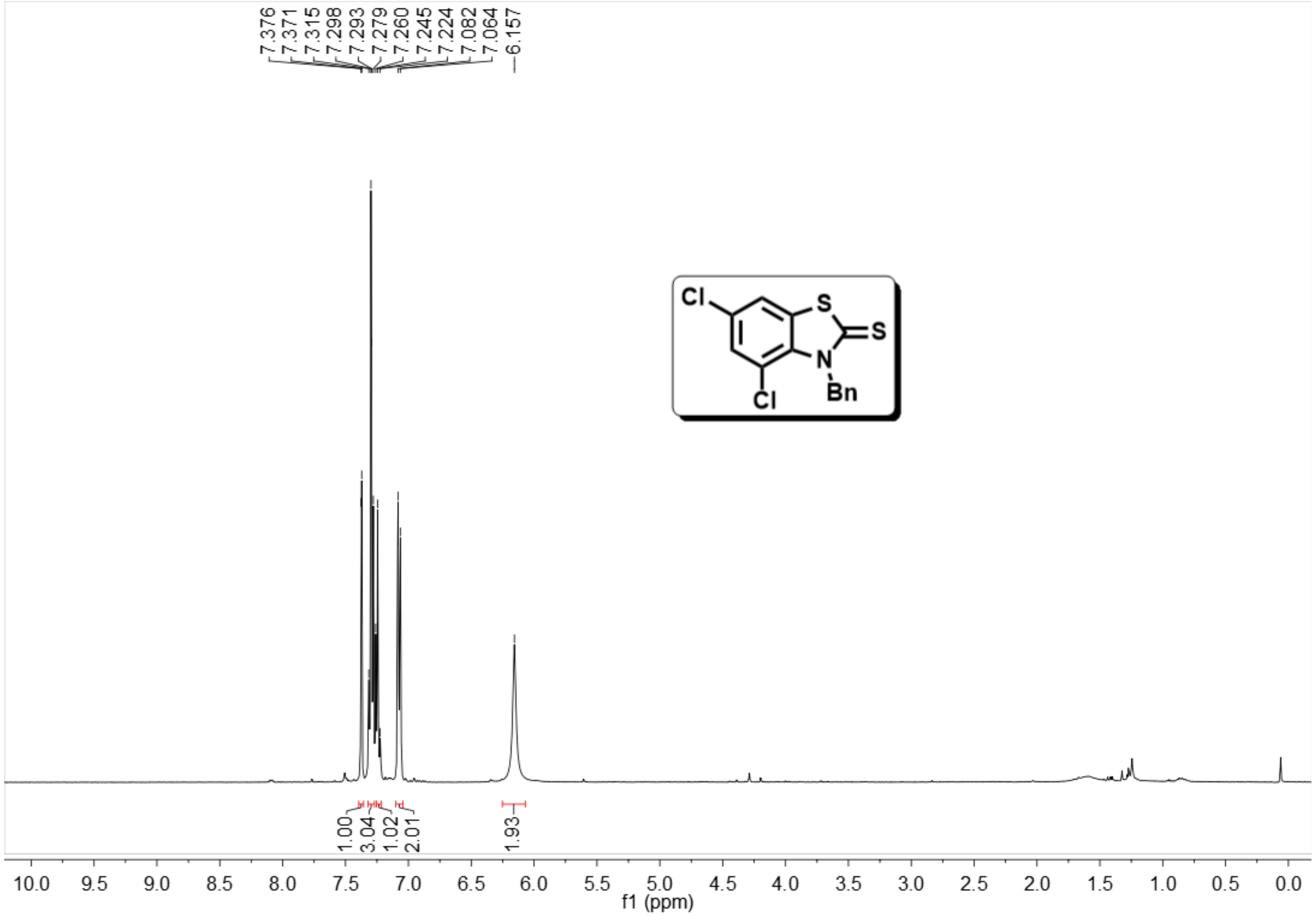
3n


191.12
143.65
133.75
129.07
128.22
127.96
127.36
127.02
124.29
124.25
124.22
124.18
118.61
118.57
118.53
118.49
112.84
77.32
77.00
76.68
49.61
F_3C
S
S
N
Bn
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

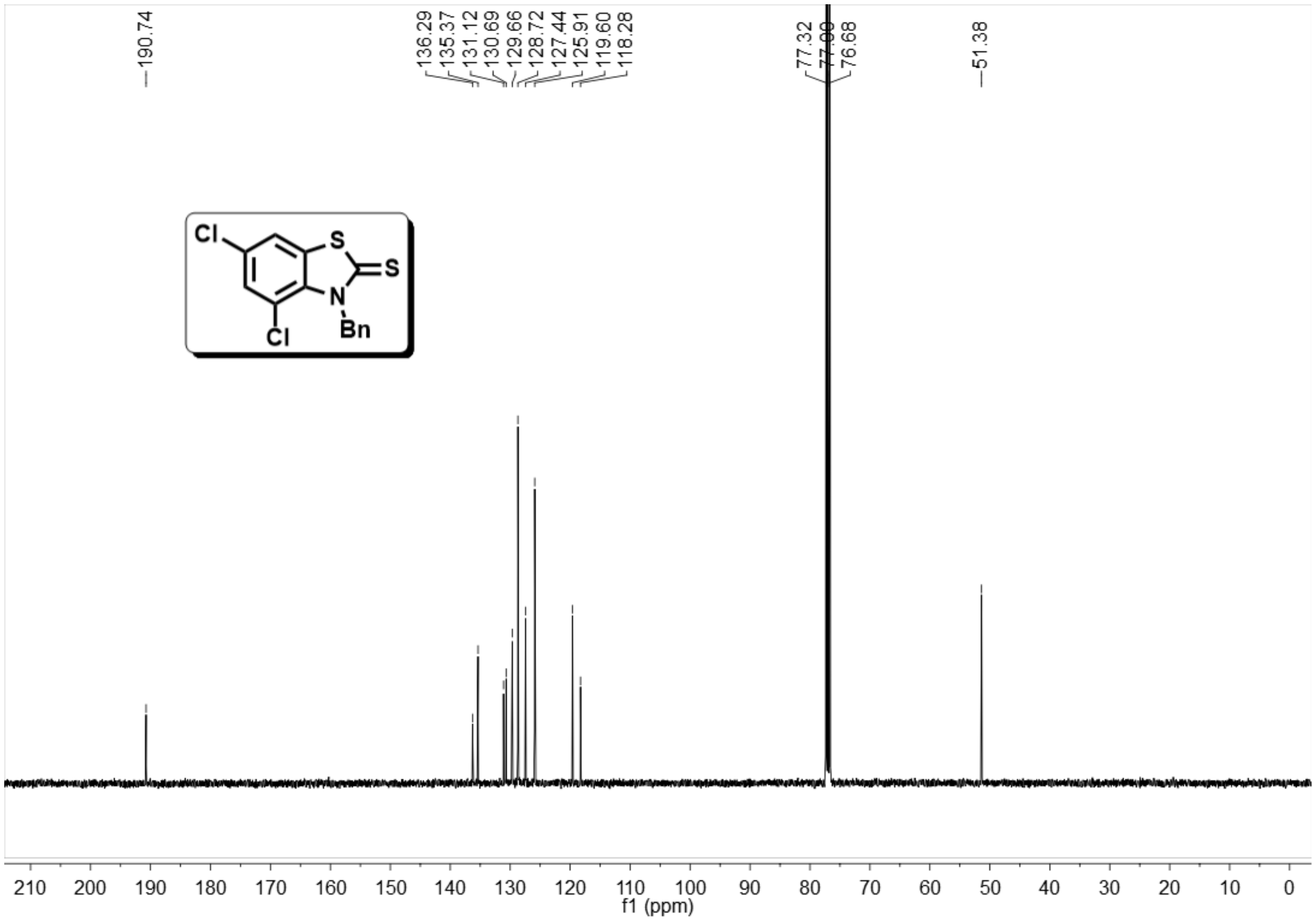
3n


-61.794
F3C
S
S
N
Bn
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

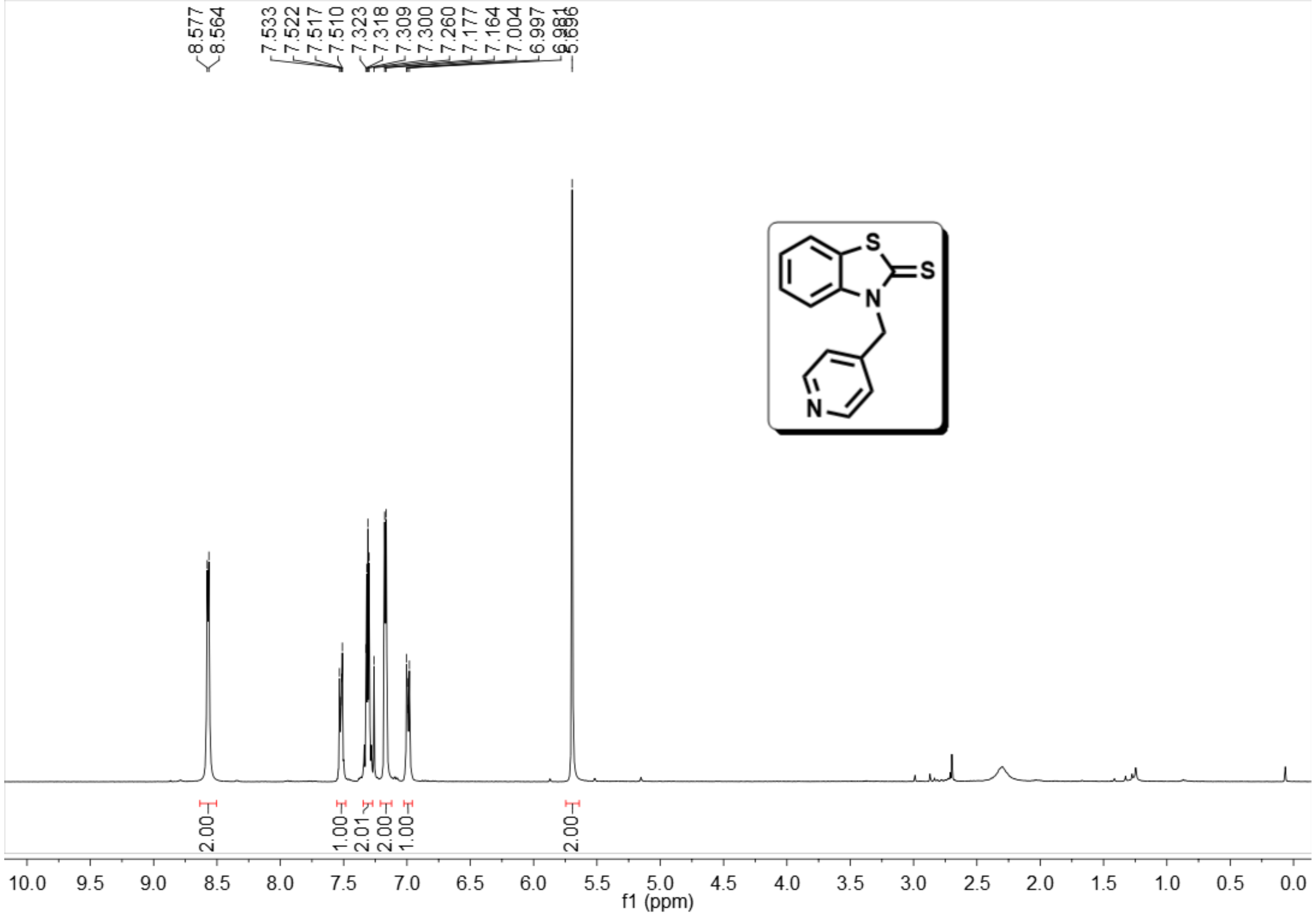
3o


7.376
7.371
7.315
7.298
7.293
7.279
7.260
7.245
7.224
7.082
7.064
6.157
Cl
S
S
N
Bn
Cl
1.00
3.04
1.02
2.01
1.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

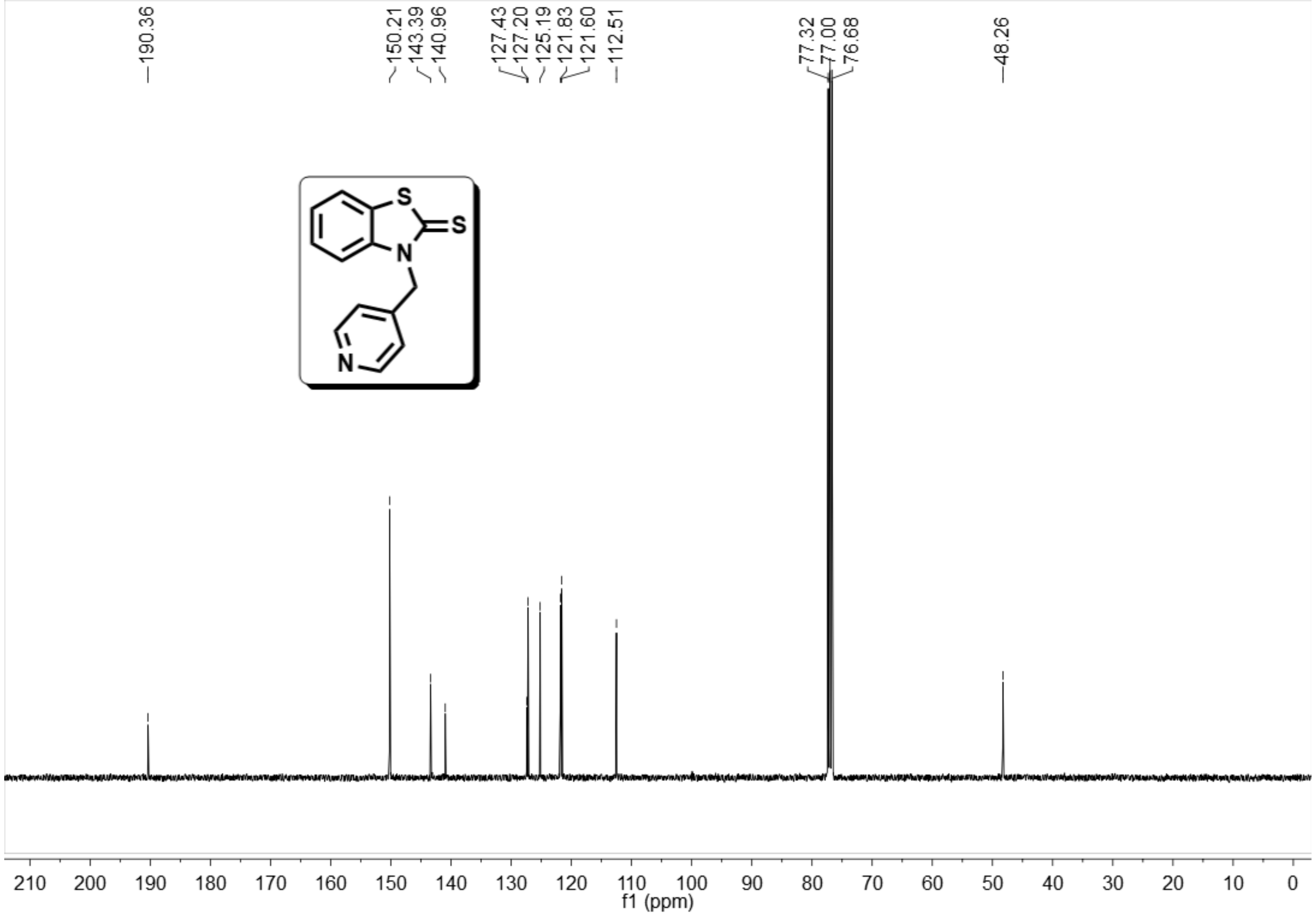
3o


190.74
136.29
135.37
131.12
130.69
129.66
128.72
127.44
125.91
119.60
118.28
77.32
77.00
76.68
51.38
Cl
S
S
N
Bn
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

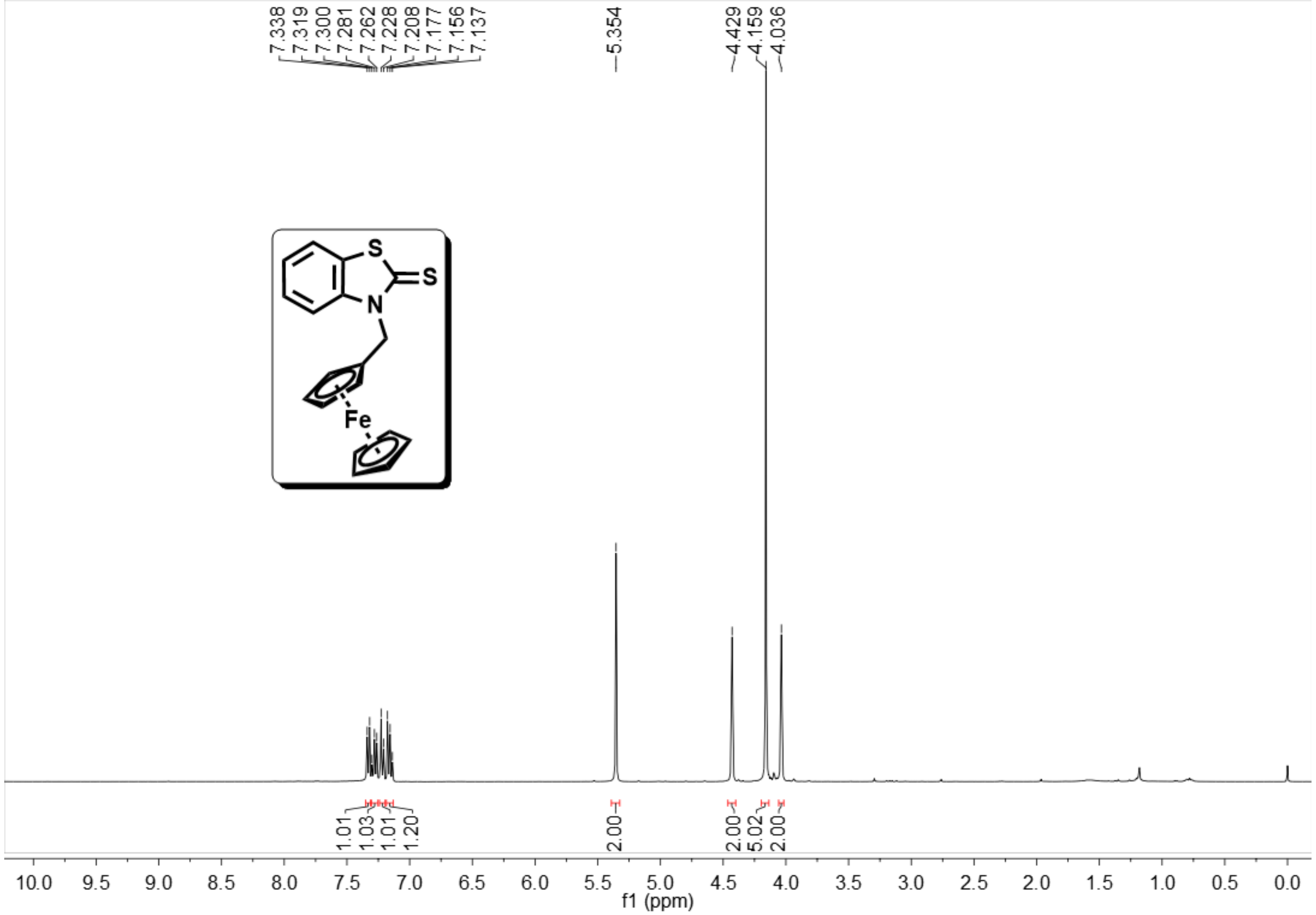
3p


8.577
8.564
7.533
7.522
7.517
7.510
7.323
7.318
7.309
7.300
7.260
7.177
7.164
7.004
6.997
6.981
5.696
S
S
N
N
2.00
1.00
2.01
2.00
1.00
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

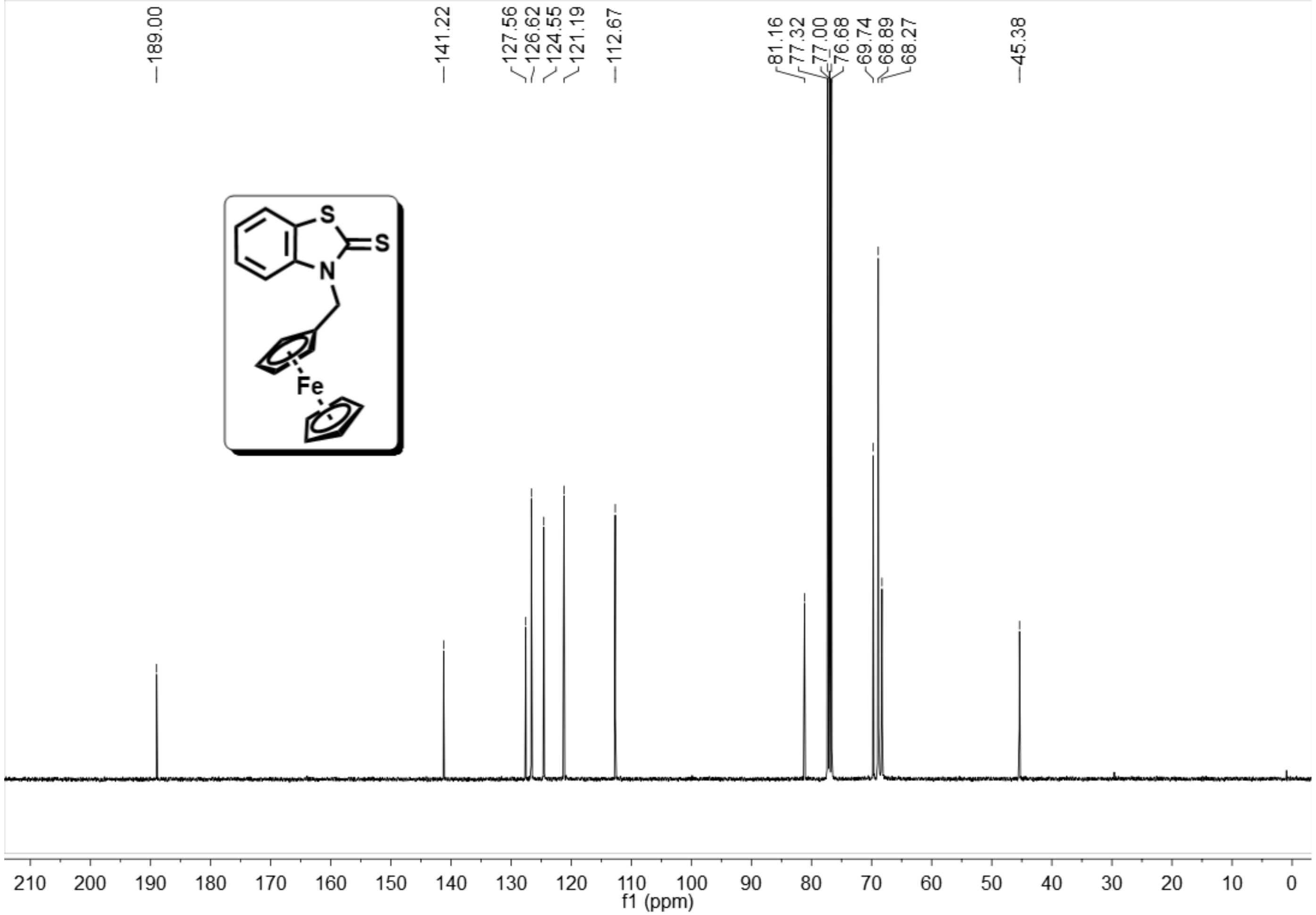
3p


190.36
150.21
143.39
140.96
127.43
127.20
125.19
121.83
121.60
112.51
77.32
77.00
76.68
48.26
S
S
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

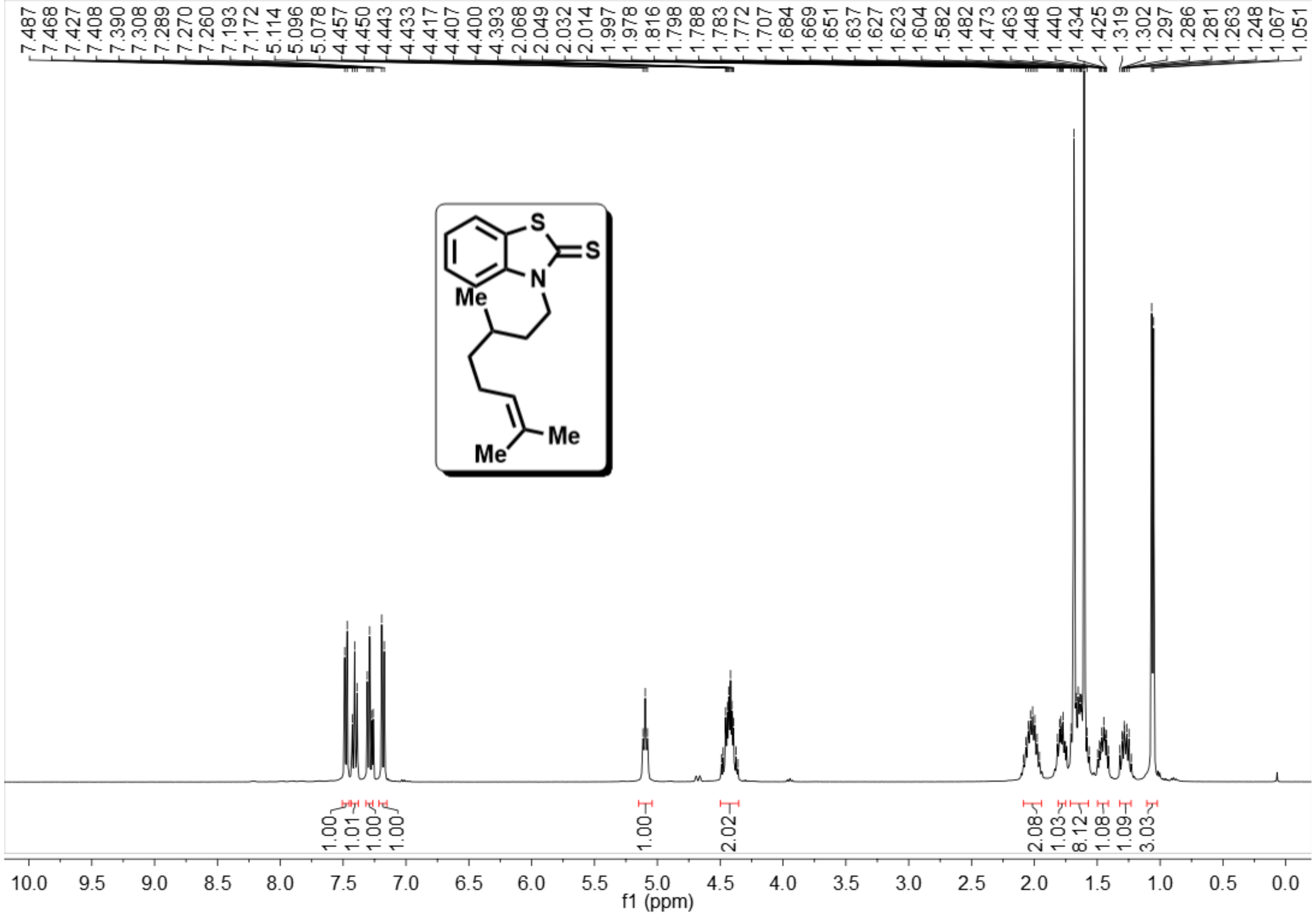
3q


7.338
7.319
7.300
7.281
7.262
7.228
7.208
7.177
7.156
7.137
5.354
4.429
4.159
4.036
S
S
N
Fe
1.01
1.03
1.01
1.20
2.00
2.00
5.02
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

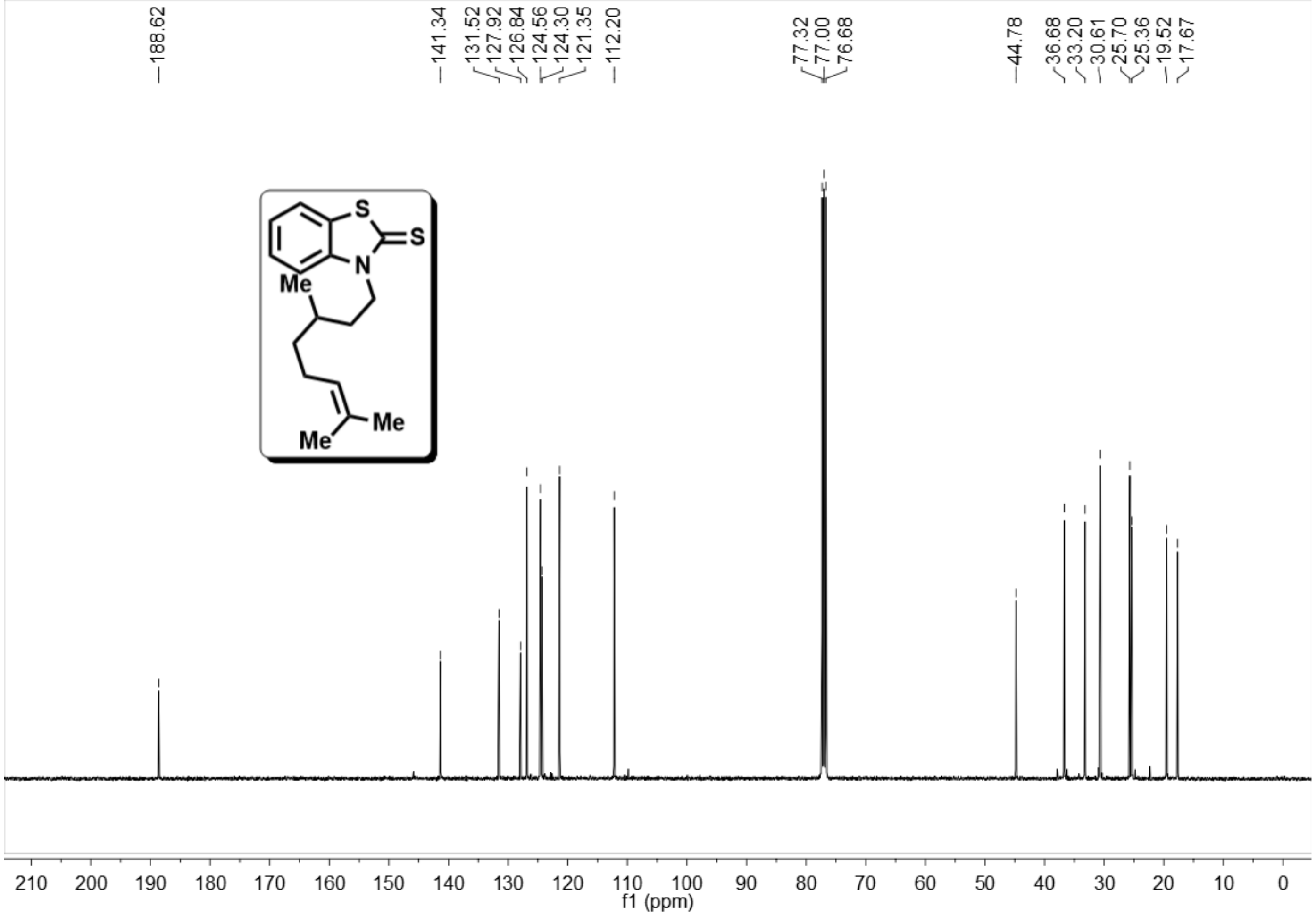
3q


189.00
141.22
127.56
126.62
124.55
121.19
112.67
81.16
77.32
77.00
76.68
69.74
68.89
68.27
45.38
S
S
N
Fe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

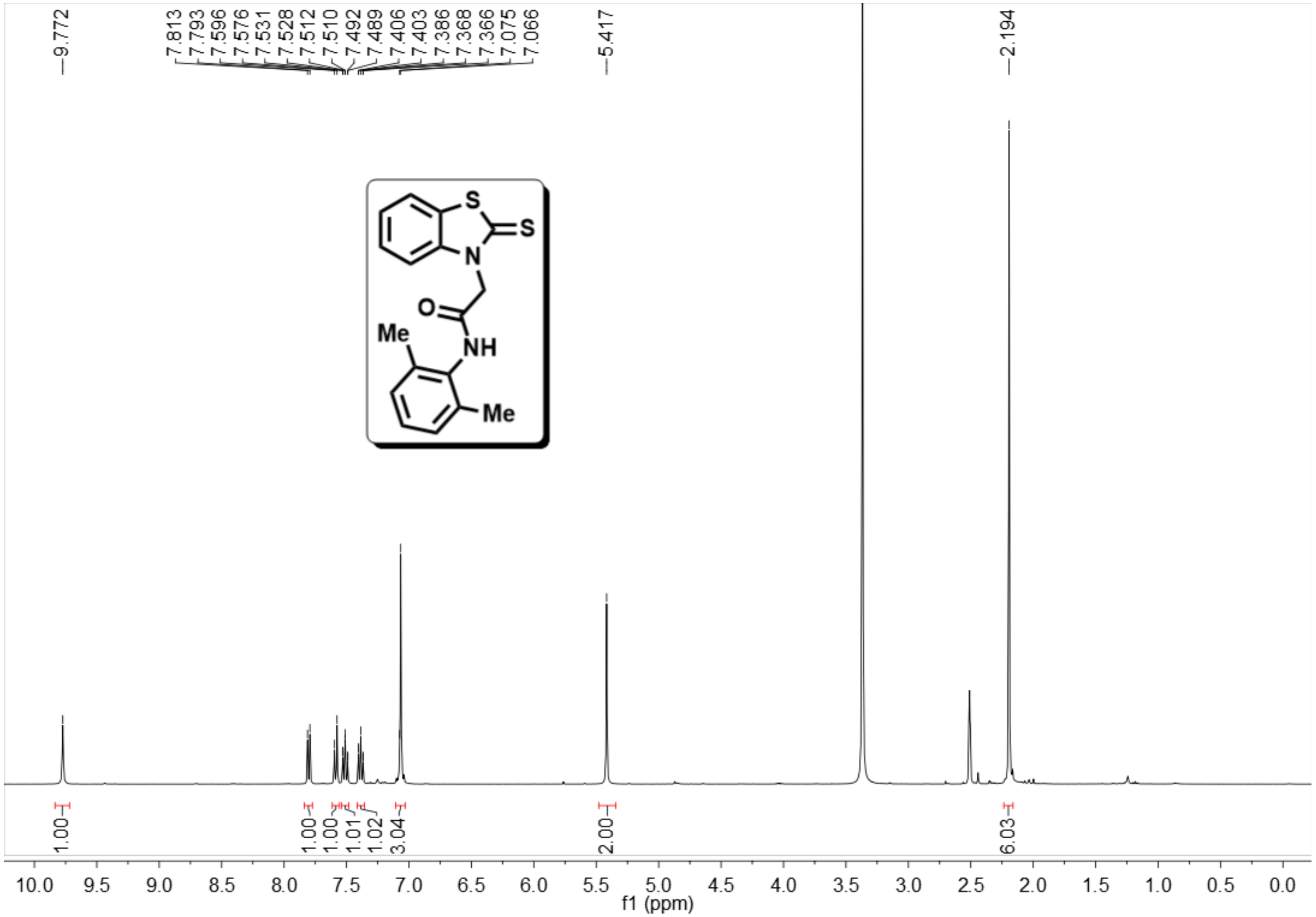
3r


7.487
7.468
7.427
7.408
7.390
7.308
7.289
7.270
7.260
7.193
7.172
5.114
5.096
5.078
4.457
4.450
4.443
4.433
4.417
4.407
4.400
4.393
2.068
2.049
2.032
2.014
1.997
1.978
1.816
1.798
1.788
1.783
1.772
1.707
1.684
1.669
1.651
1.637
1.627
1.623
1.604
1.582
1.482
1.473
1.463
1.448
1.440
1.434
1.425
1.319
1.302
1.297
1.286
1.281
1.263
1.248
1.067
1.051
S
S
N
Me
Me
Me
1.00
1.01
1.00
1.00
1.00
2.02
2.08
1.03
8.12
1.08
1.09
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

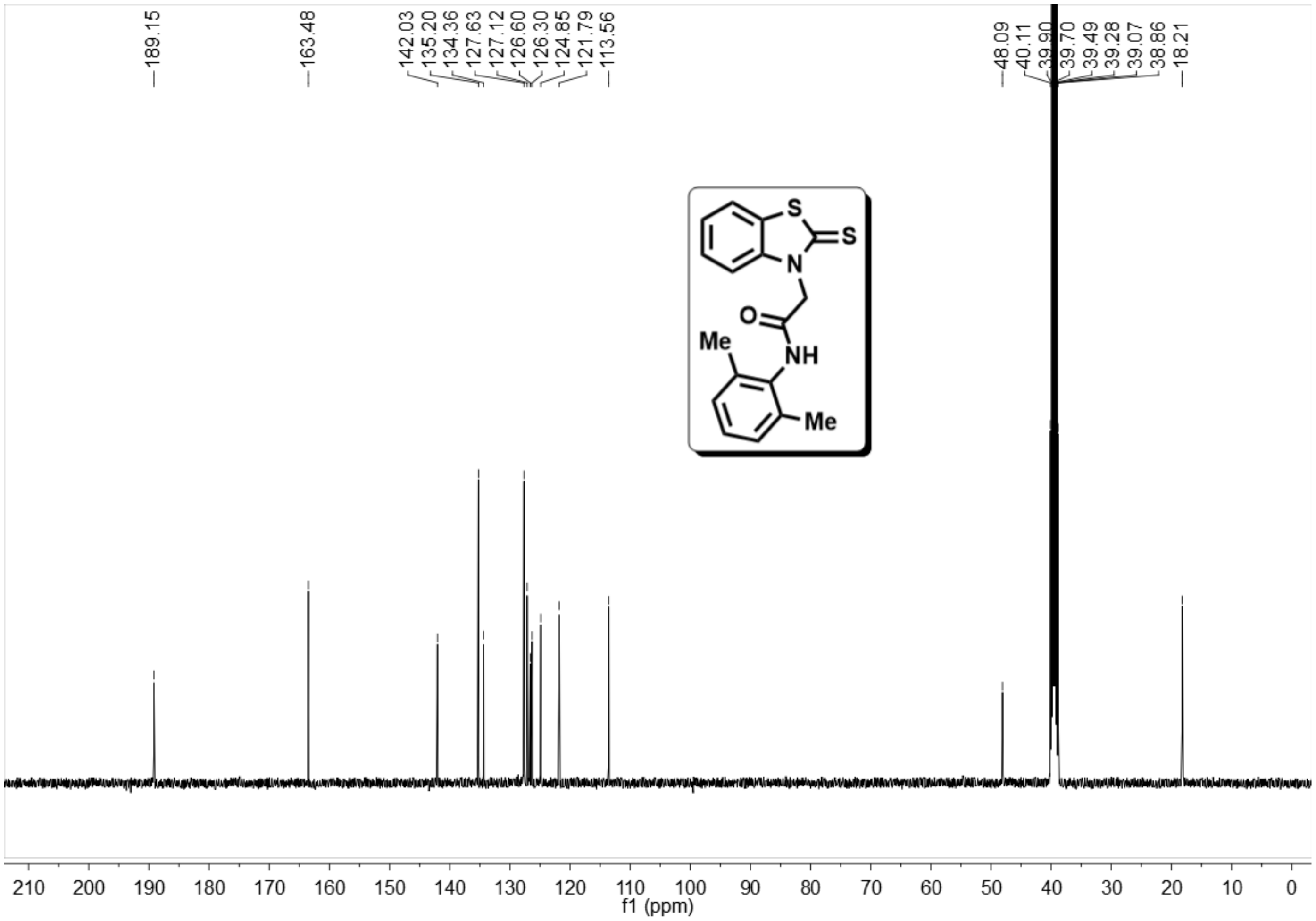
3r


188.62
141.34
131.52
127.92
126.84
124.56
124.30
121.35
112.20
77.32
77.00
76.68
44.78
36.68
33.20
30.61
25.70
25.36
19.52
17.67
S
S
N
Me
Me
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

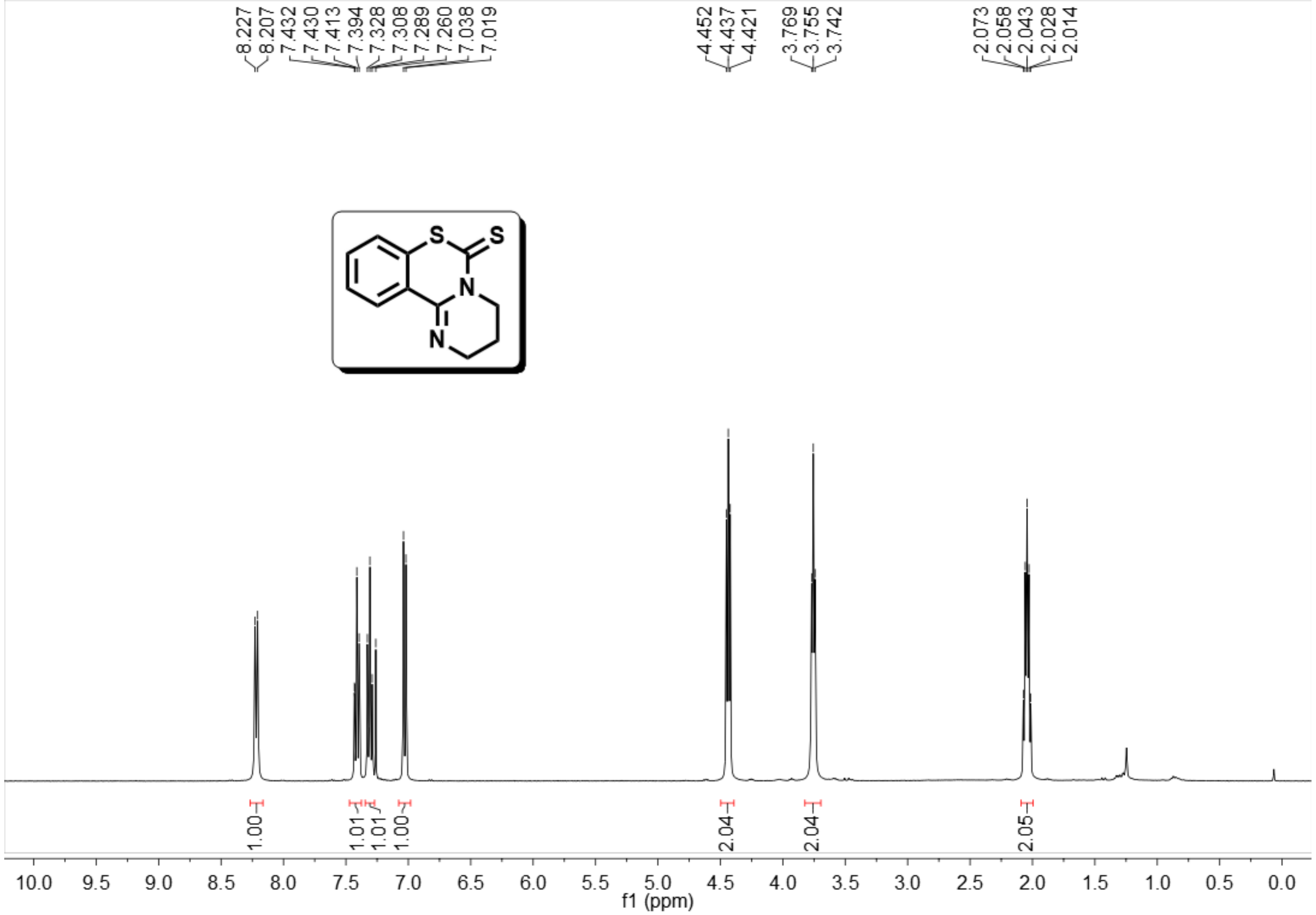
3s


9.772
7.813
7.793
7.596
7.576
7.531
7.528
7.512
7.510
7.492
7.489
7.406
7.403
7.386
7.368
7.366
7.075
7.066
5.417
2.194
S
S
N
O
NH
Me
Me
1.00
1.00
1.00
1.01
1.02
3.04
2.00
6.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

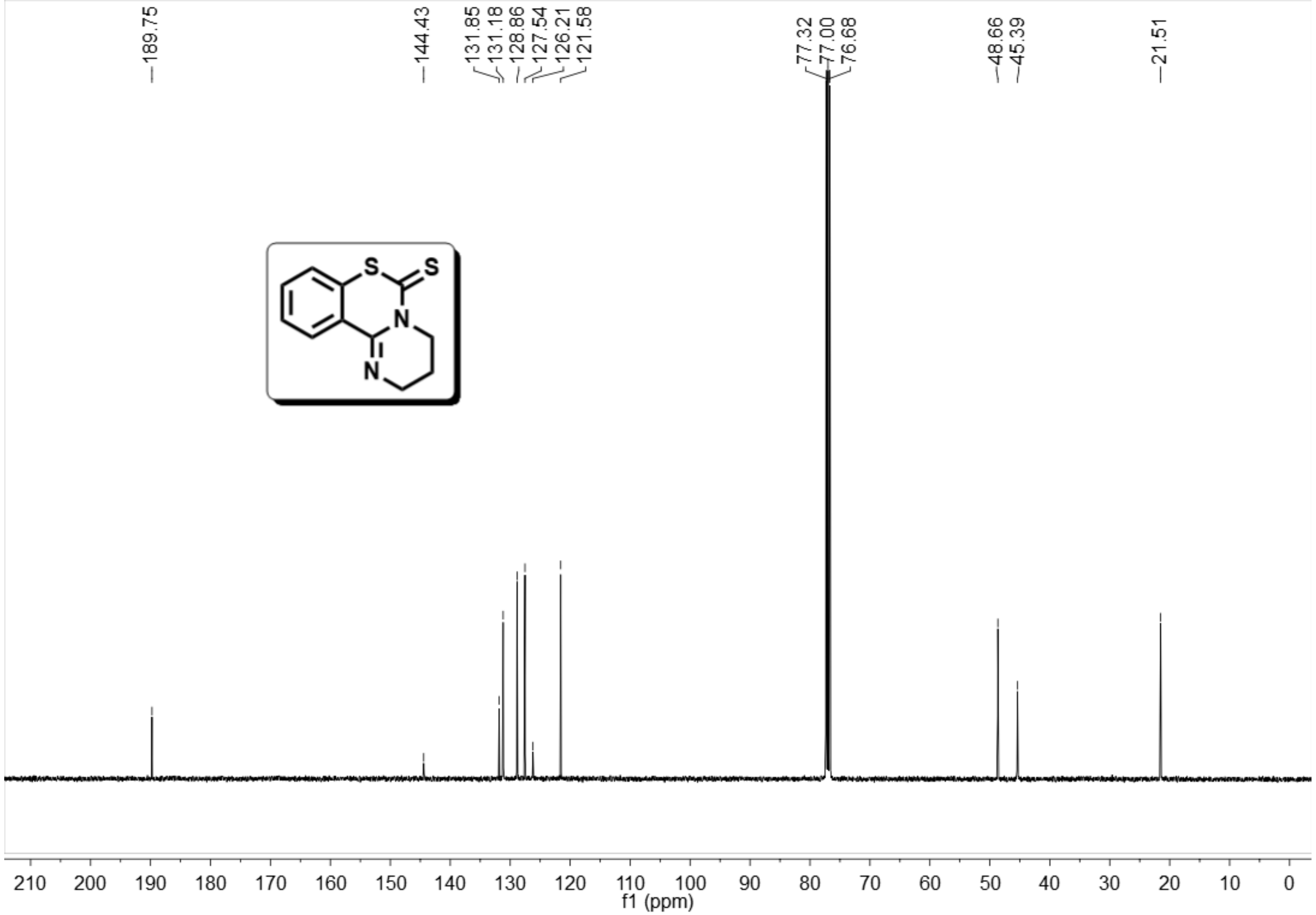
3s


189.15
163.48
142.03
135.20
134.36
127.63
127.12
126.60
126.30
124.85
121.79
113.56
48.09
40.11
39.90
39.70
39.49
39.28
39.07
38.86
18.21
S
S
N
O
NH
Me
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

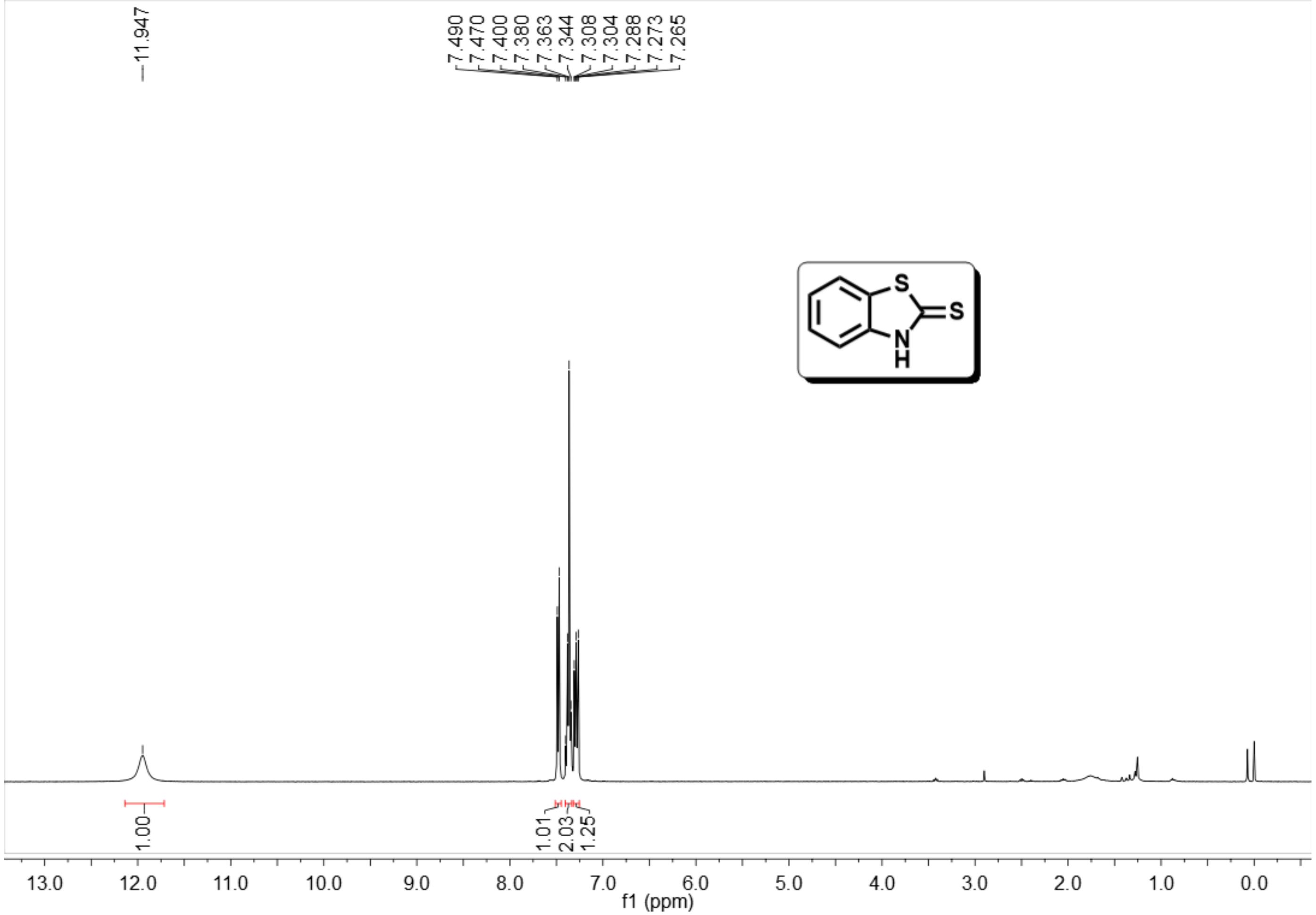
2p


8.227
8.207
7.432
7.430
7.413
7.394
7.328
7.308
7.289
7.260
7.038
7.019
4.452
4.437
4.421
3.769
3.755
3.742
2.073
2.058
2.043
2.028
2.014
S
S
N
N
1.00
1.01
1.01
1.00
2.04
2.04
2.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

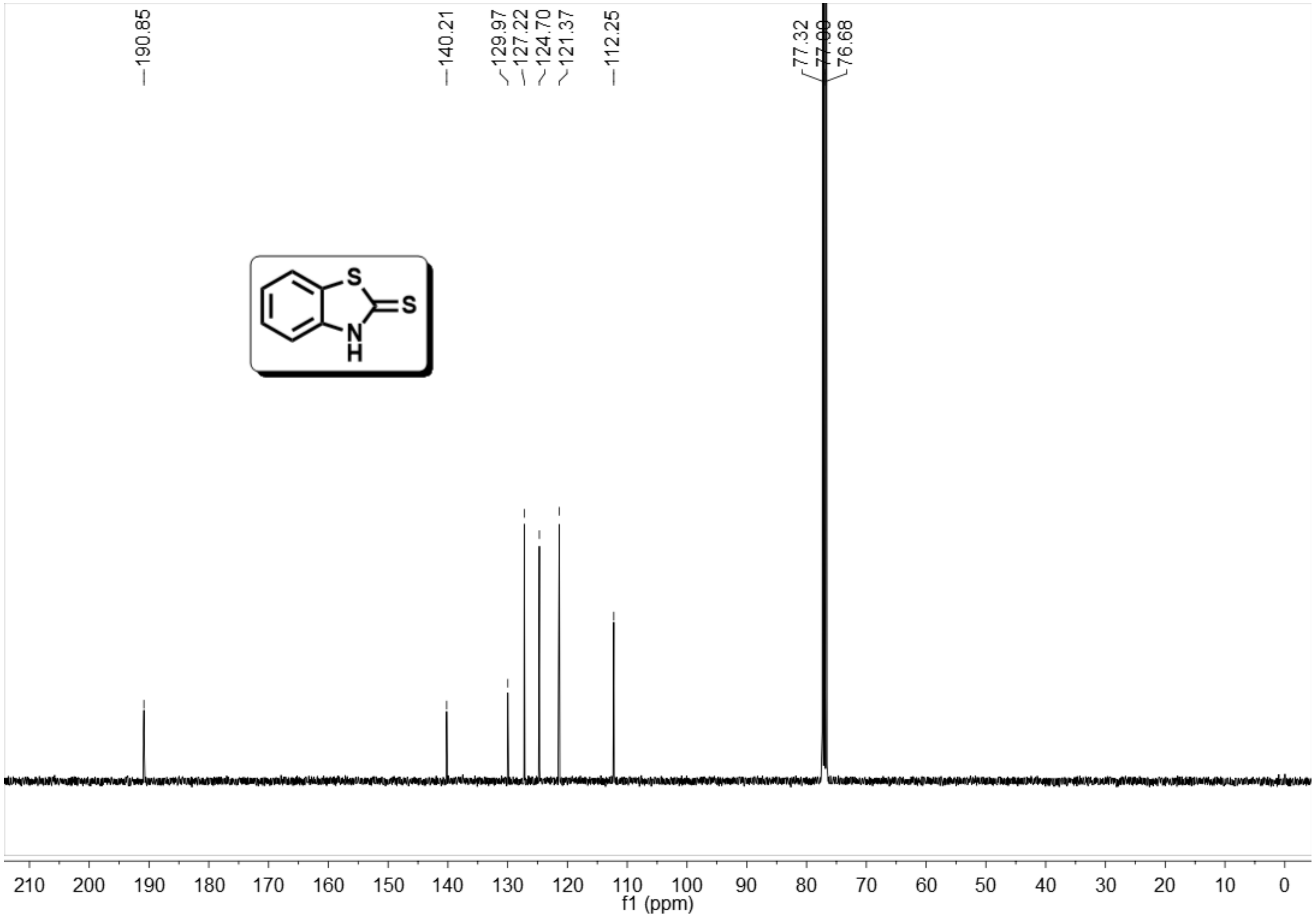
2p


189.75
144.43
131.85
131.18
128.86
127.54
126.21
121.58
77.32
77.00
76.68
48.66
45.39
21.51
S
S
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

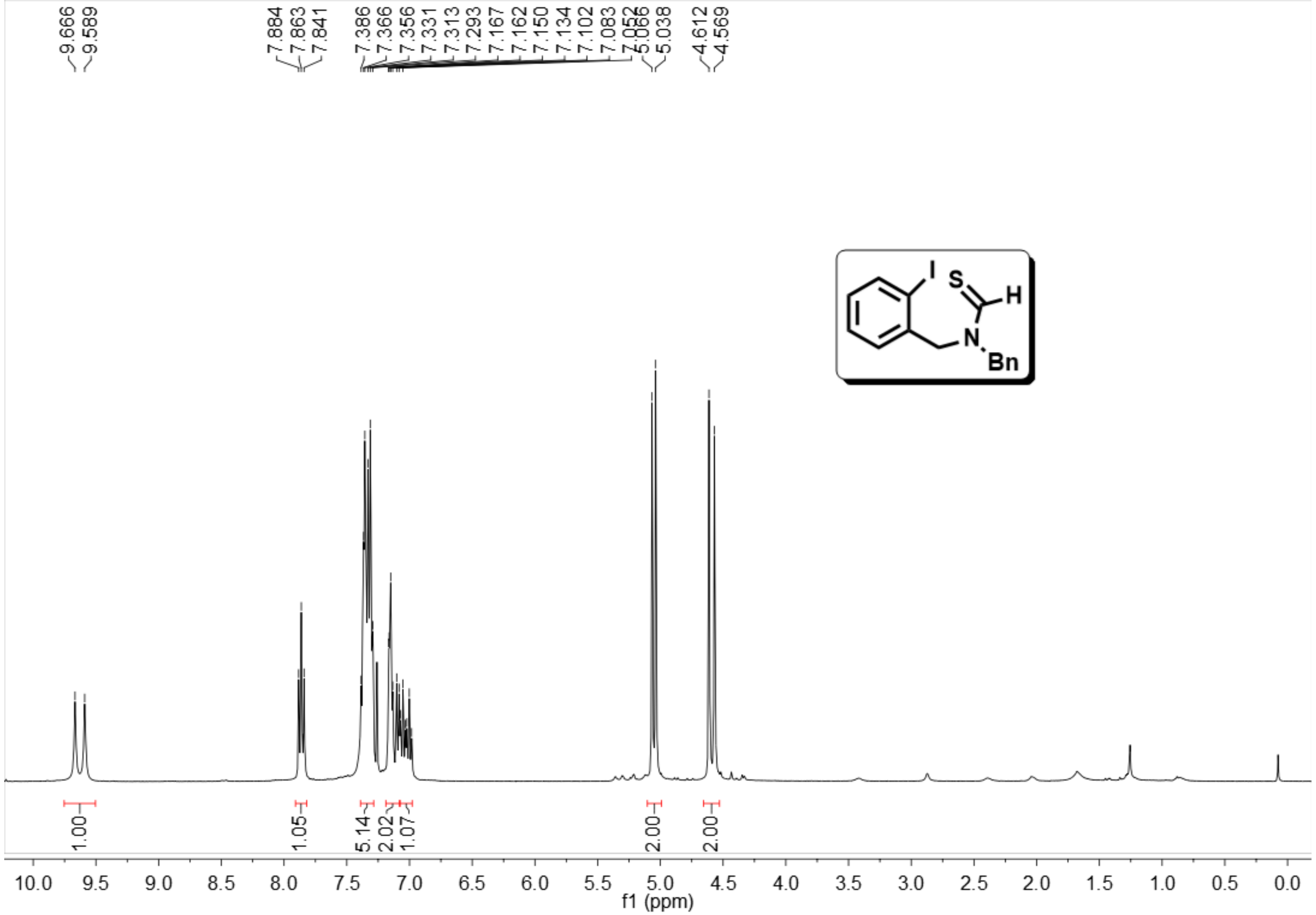
MBT


11.947
7.490
7.470
7.400
7.380
7.363
7.344
7.308
7.304
7.288
7.273
7.265
S
S
N
H
1.00
1.01
2.03
1.25
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

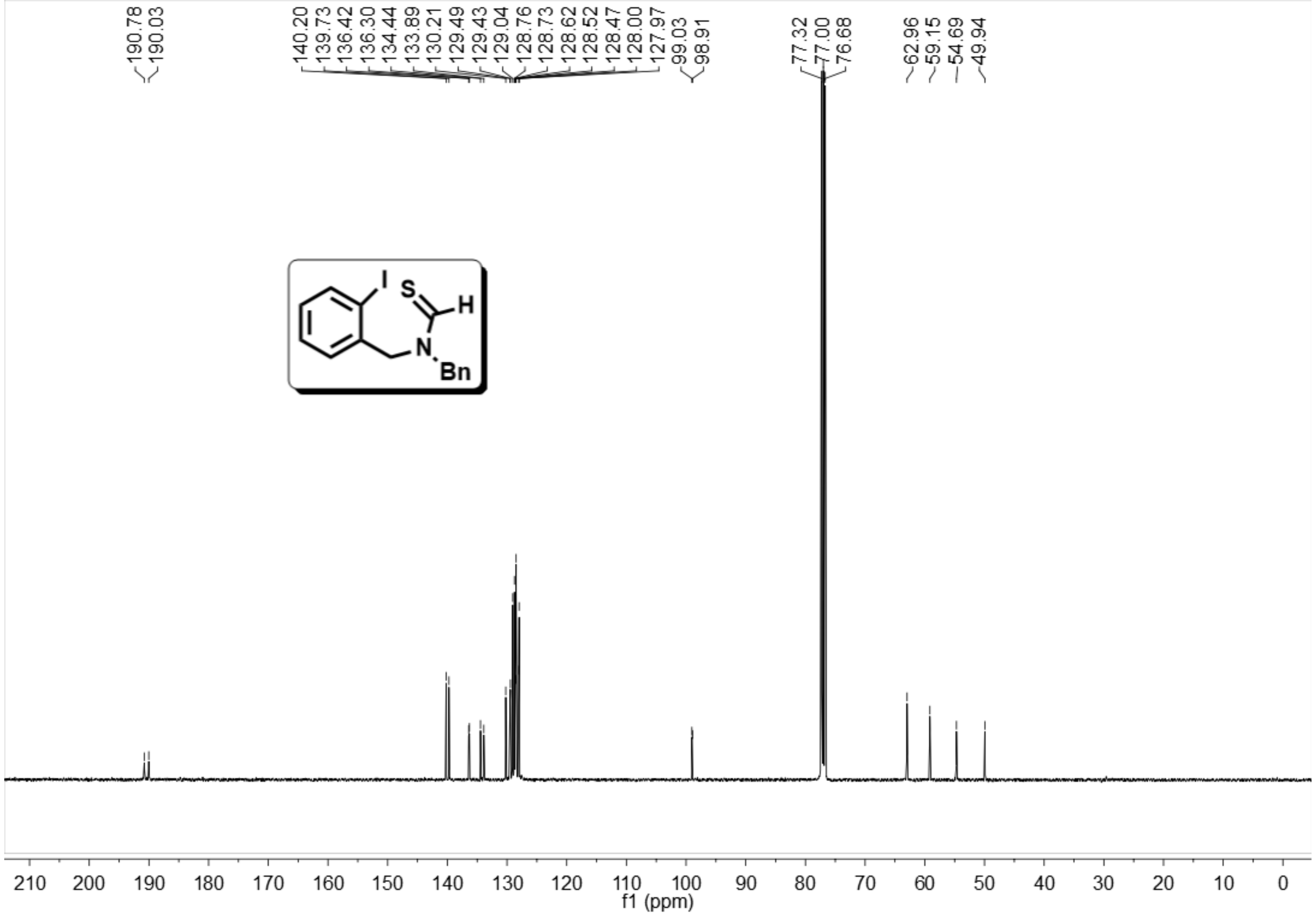
MBT


190.85
140.21
129.97
127.22
124.70
121.37
112.25
77.32
77.00
76.68
S
S
N
H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

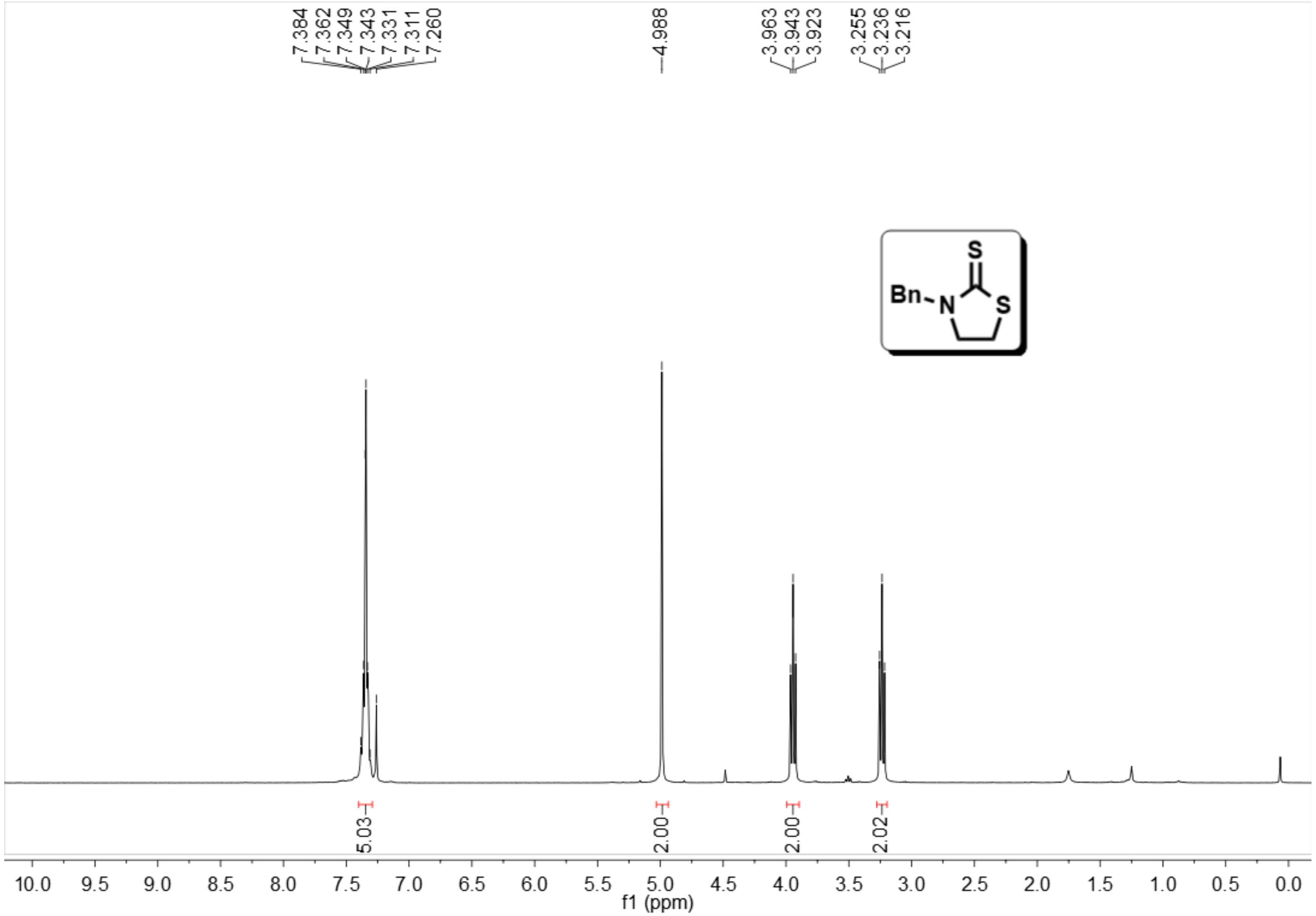
2aa


9.666
9.589
7.884
7.863
7.841
7.386
7.366
7.356
7.331
7.313
7.293
7.167
7.162
7.150
7.134
7.102
7.083
7.052
5.066
5.038
4.612
4.569
1.00
1.05
5.14
2.02
1.07
2.00
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
I
S
H
N
Bn

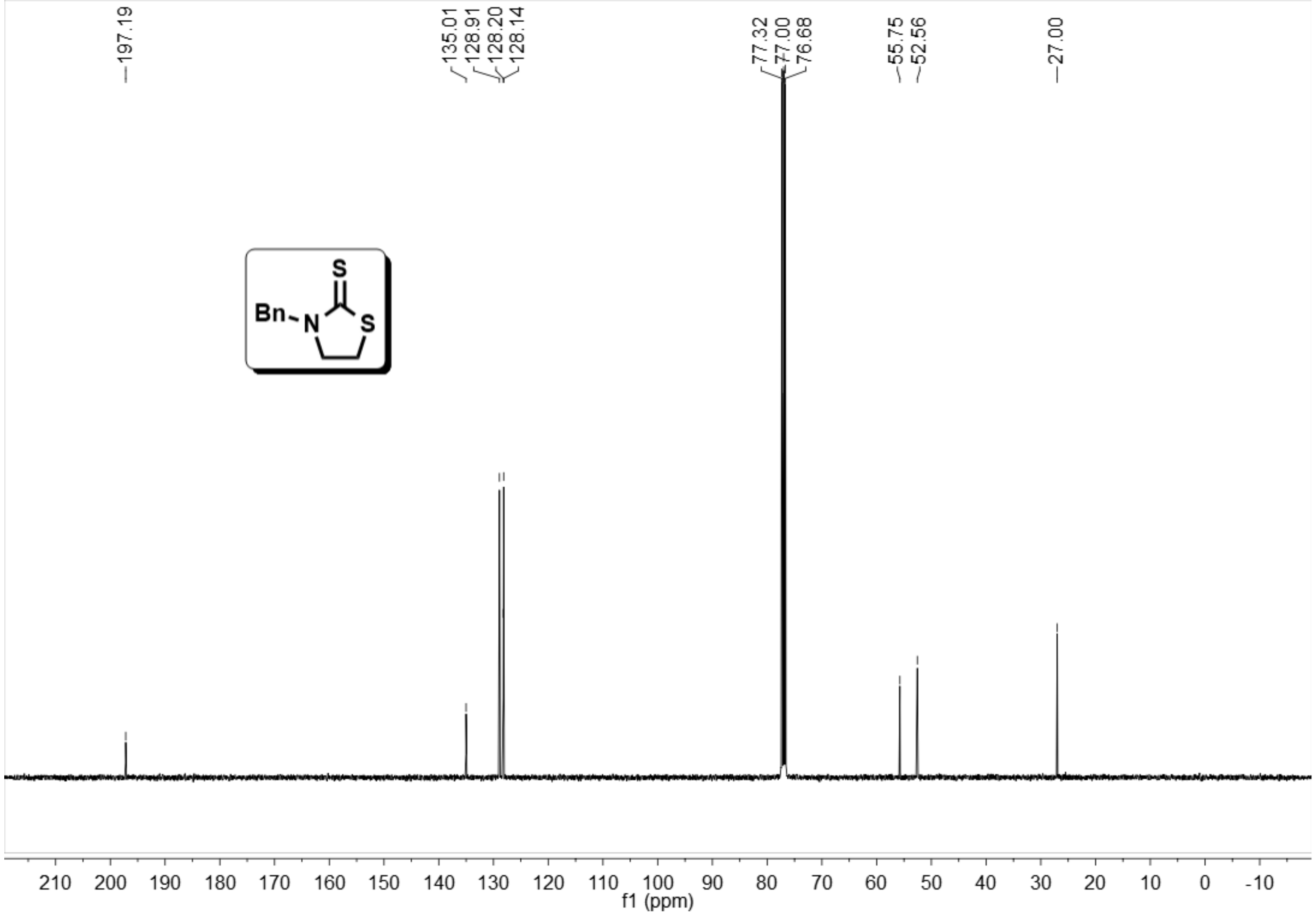
2aa


190.78
190.03
140.20
139.73
136.42
136.30
134.44
133.89
130.21
129.49
129.43
129.04
128.76
128.73
128.62
128.52
128.47
128.00
127.97
99.03
98.91
77.32
77.00
76.68
62.96
59.15
54.69
49.94
I
S
H
N
Bn
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

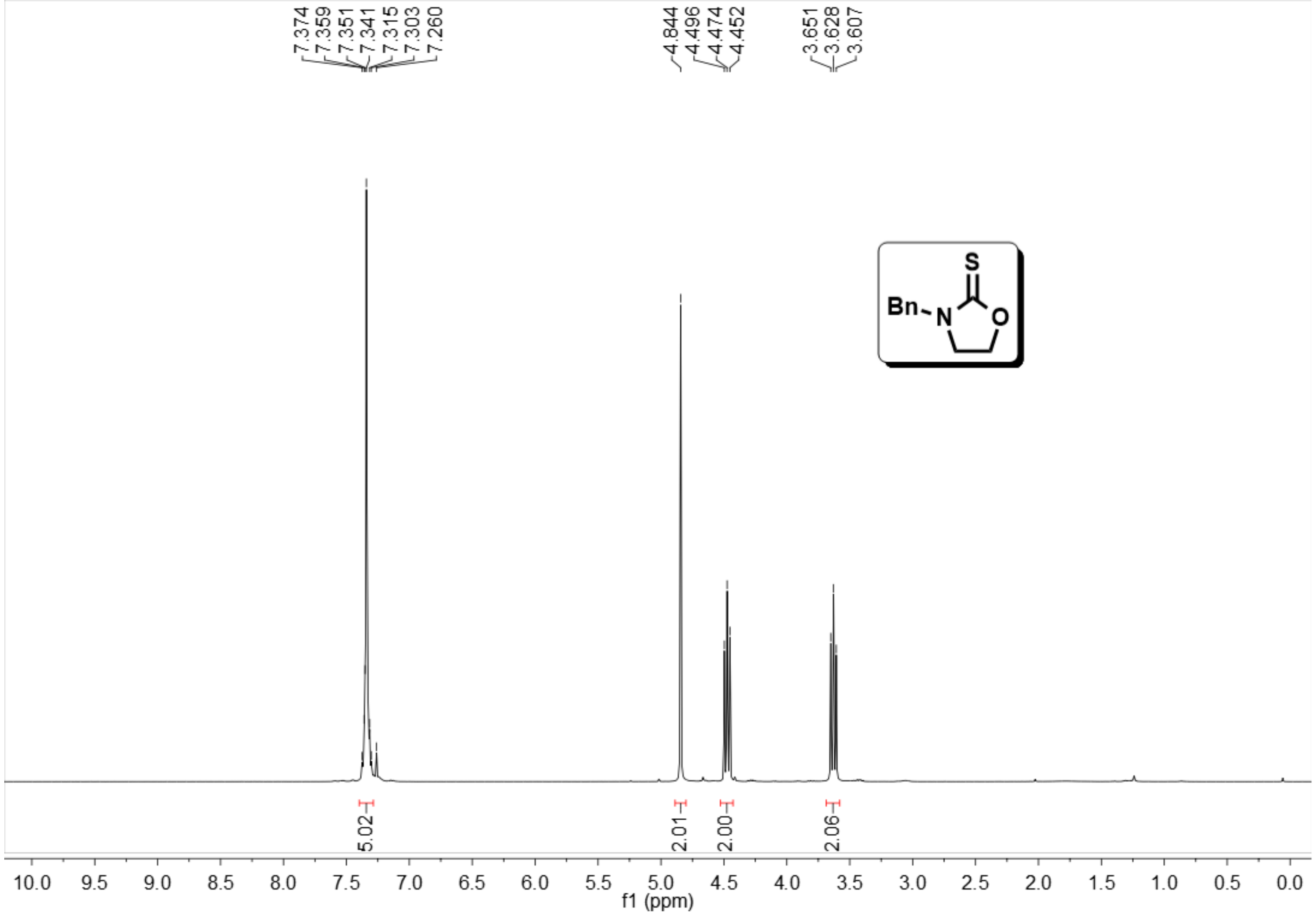
5a


7.384
7.362
7.349
7.343
7.331
7.311
7.260
4.988
3.963
3.943
3.923
3.255
3.236
3.216
S
Bn
N
S
5.03
2.00
2.00
2.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

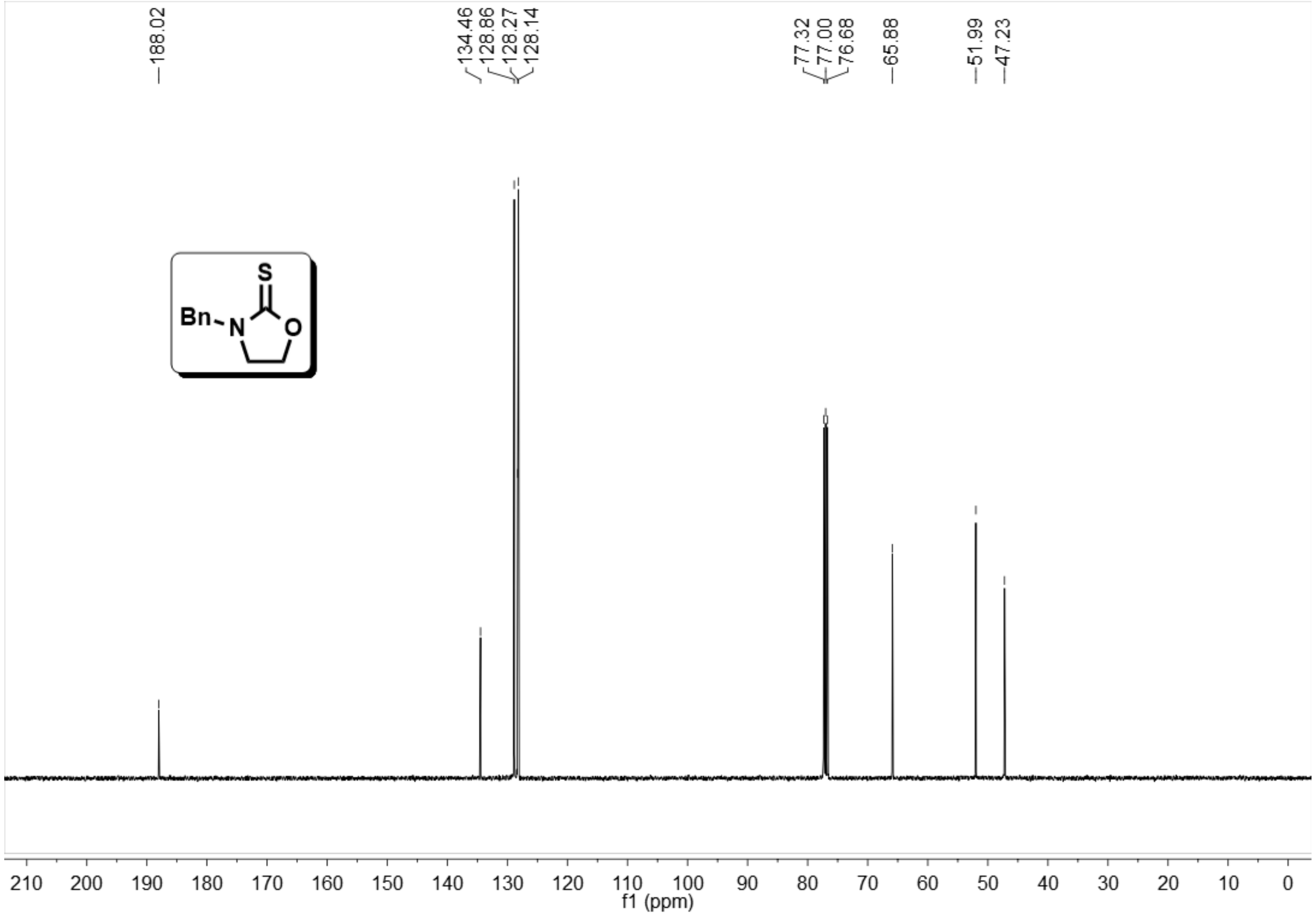
5a


197.19
135.01
128.91
128.20
128.14
77.32
77.00
76.68
55.75
52.56
27.00
S
Bn
N
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

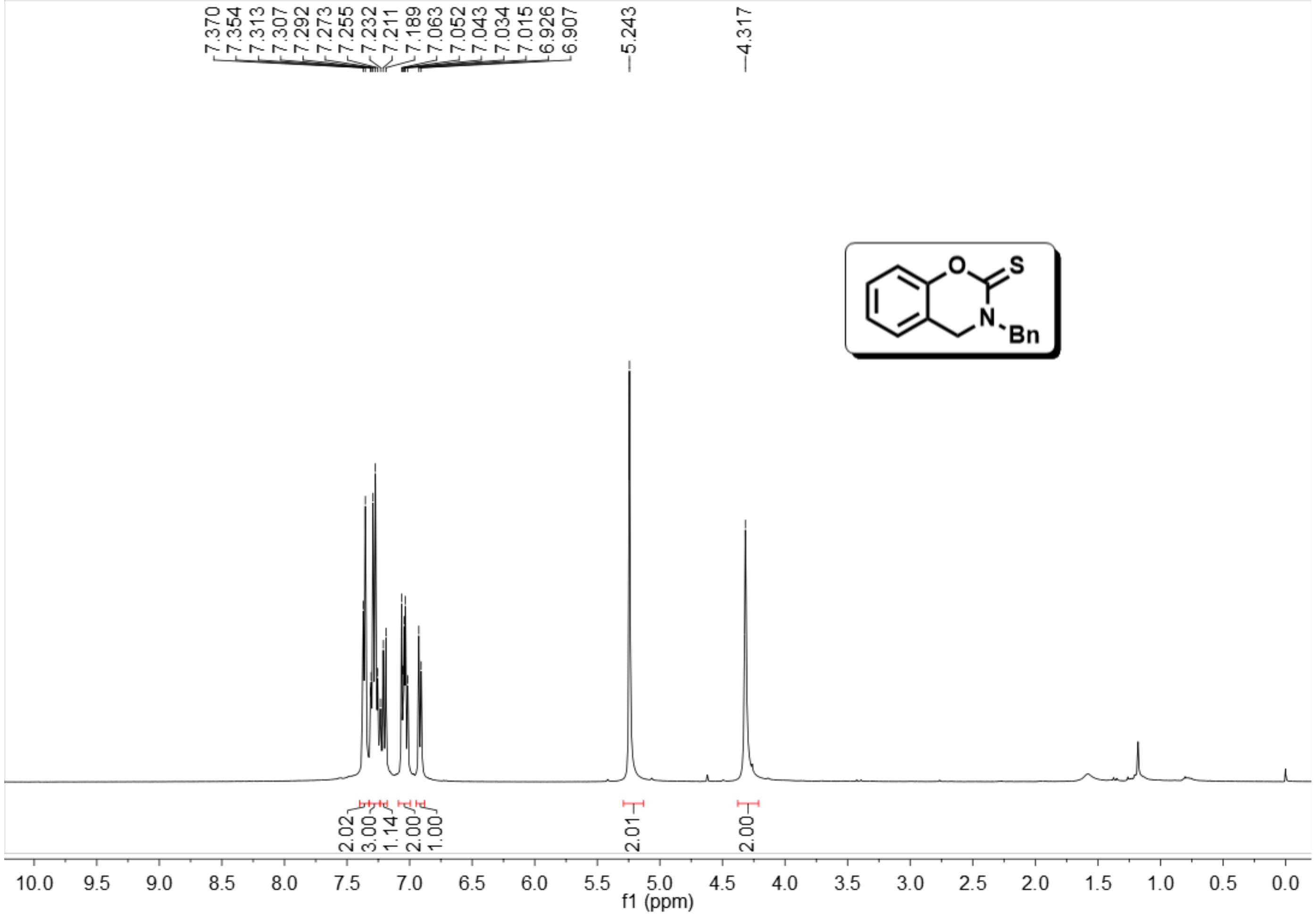
5a′


7.374
7.359
7.351
7.341
7.315
7.303
7.260
4.844
4.496
4.474
4.452
3.651
3.628
3.607
S
Bn
N
O
5.02
2.01
2.00
2.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

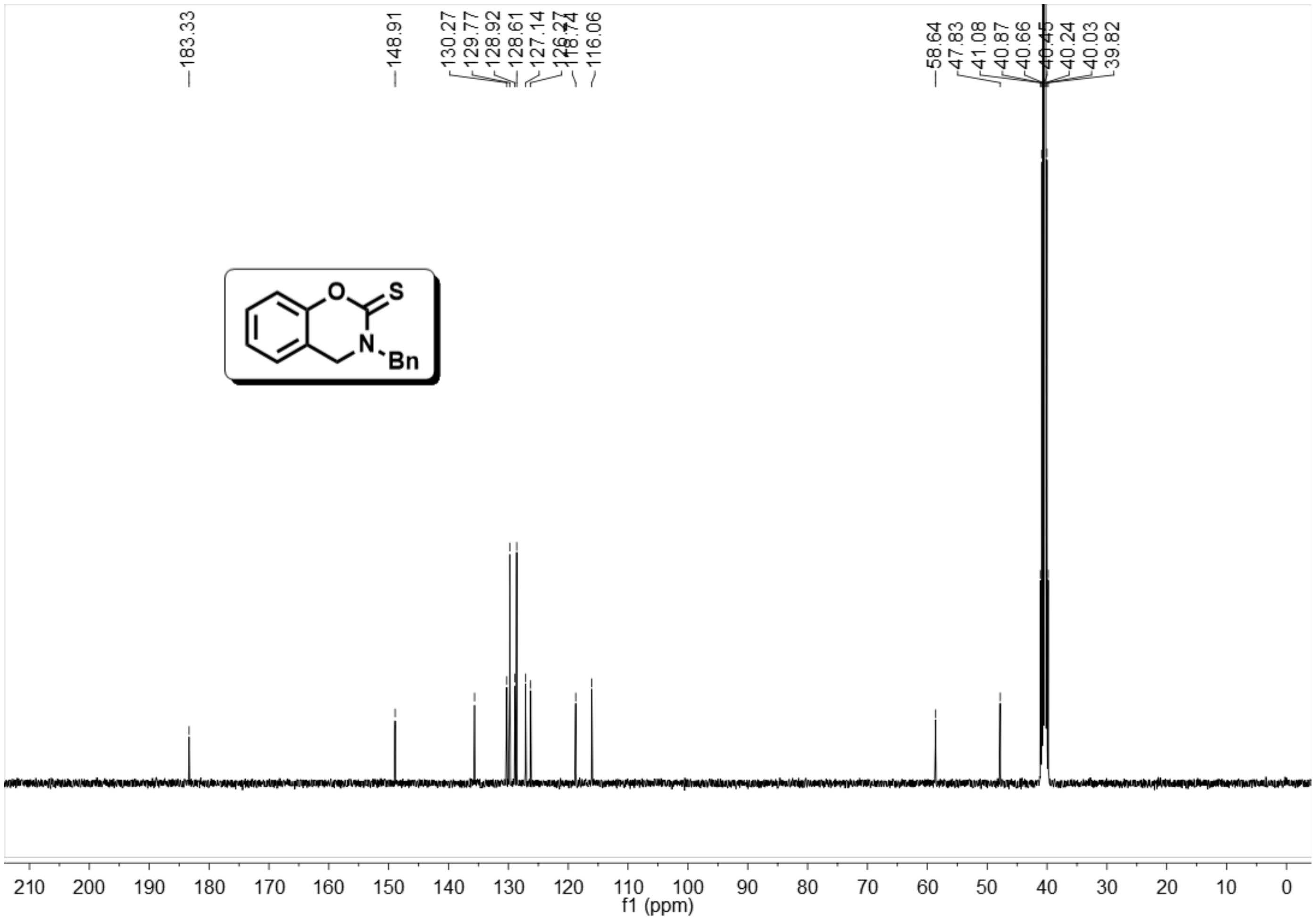
5a′


188.02
134.46
128.86
128.27
128.14
77.32
77.00
76.68
65.88
51.99
47.23
S
Bn
N
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

7a


7.370
7.354
7.313
7.307
7.292
7.273
7.255
7.232
7.211
7.189
7.063
7.052
7.043
7.034
7.015
6.926
6.907
5.243
4.317
O
S
N
Bn
2.02
3.00
1.14
2.00
1.00
2.01
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

7a



183.33
148.91
130.27
129.77
128.92
128.61
127.14
126.27
118.74
116.06
58.64
47.83
41.08
40.87
40.66
40.45
40.24
40.03
39.82
O
S
N
Bn
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)