Supporting information for:

Miyaura Borylation Suzuki-Miyaura Coupling (BSC) Sequence of 4-bromo-2,4'-bithiazoles with Halides: Straightforward Access to Heterocyclic Cluster of D-series of Thiopeptide GE2270

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General information:

tert-Butyl 2-(2-chloro-6-(4-(ethoxycarbonyl)thiazol-2-yl)pyridine-3-yl)thiazole-4-carboxylate **2**,[1] Benzyl (2*S*,3*S*)-1-amino-3-(*tert*-butyldimethylsilyloxy)-3-phenyl-1-thioxopropan-2-ylcarbamate **8d**[1] were prepared according to procedures reported in the literature.

1. Solvents and reagents

All commercially available reagents were used as received, except otherwise specified. Palladium catalyst and phosphine ligands were stored in desiccators. Extra dry solvents were obtained from Accros Organic® in sealed bottles over 3Å or 4Å molecular sieves and stored under N_2.

2. Purification

Chromatography columns were performed using silica gel (mesh size 60-80 mesh). TLC were performed using Merck® TLC silica gel 60 F_{254} and product revealed by UV irradiation (λ = 254 nm).

3. Analysis

^1H and ^{13}C NMR spectra were recorded at room temperature on a Brucker Advance spectrometer operating at 300 MHz and 75 MHz respectively. Chemical shifts (δ) are given as ppm relative to the residual solvent peak (7.26 for ^1H and 77.16 for ^{13}C in $CDCl_3$). Splitting patterns are indicating as fellow: br: broad; s: singulet; d: doublet; t: triplet; q: quartet; qt: quintuplet; sp: septuplet; dd: doublet of doublet; dt: doublet of triplet; tt: triplet of triplet; qt: quintuplet; m: multiplet.

IR spectra were obtained with Bomen MB-100 (KBr pellet) or Perkin Elmer Spectrum 100 FT IR spectrometers.

Microanalyses were carried out on the flash 2000 series from Thermo Fisher.

Melting Point were measured on a Fisher Scientific hot stage melting point apparatus and are uncorrected.

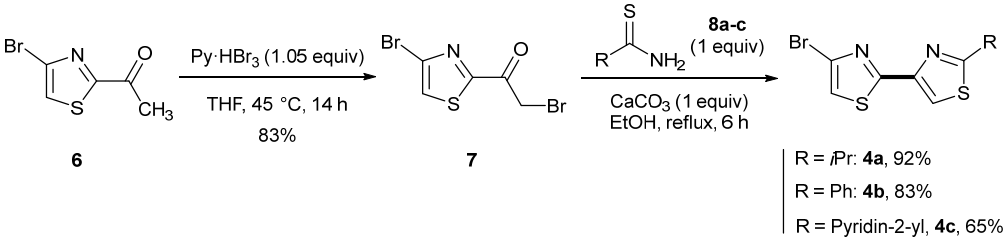
GC/MS analysis (EI, 70 Ev) were performed on the Agilent GC: 6850, MS: 5975 using HP-5MS column (30 m x 0.25 mm x 0.25 µm) with the following method: 50 °C (2 min) to 250 °C (15 min) with an increase of 25 °C.min^{-1}.

Mass analysis (ESI) were performed on a LCQ Advantage.

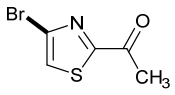
[1] C. Berini, T. Martin, P. Lassalas, F. Marsais, C.Baudequin, C. Hoarau, *Beilstein J. Org. Chem.*, 2017, **13**, 1407.

Experimental section

1. Synthesis of the 2'-alkyl and 2'-aryl 4-bromo-2,4'-bithiazole 4a-c



Scheme 1



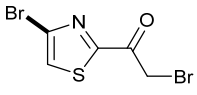
6

Prepared according to Cossy's procedure.[2]

To a solution of 2,4-dibromothiazole (6.0 g, 24.7 mmol) in Et_2O (60 mL) was added *n*BuLi 2.5 M in hexanes (27,2 mmol, 1.1 equiv.) at –78 °C. The reaction mixture was stirred for 30 min at –78 °C and *N*-acetylmorpholine (4.3 mL, 37.05 mmol, 1.5 equiv) was then added dropwise at –78 °C. The reaction mixture was warmed up to room temperature, stirred for 12 h and then quenched with H_2O and extracted with Et_2O (3 x 100 mL). The combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (PE/CH_2Cl_2 from 8:2 to 6:4) to afford **6** (4.39 g, 21.3 mmol) in 86% yield as a colorless solid. Exhibited spectra data identical to previous reports.[3]

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.57 (s, 1 H), 2.71 (s, 3 H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 190.4 (C), 166.9 (C), 126.8 (CH), 124.9 (C), 25.8 (CH_3).



7

Prepared according to Natile's procedure[4]

To a solution of 4-bromo-2-(bromoacetyl)thiazole **6** (1.263 g, 6.13 mmol) in 20 mL of anhydrous THF was added pyridinium bromide perbromide (2.056 g, 1.1 equiv). Then the

[2] J. Gebauer, S. Arseniyadis, J. Cossy, *Org. Lett.*, 2007, **9**, 3425.
[3] T. Martin, C. Laguerre, C. Hoarau, F. Marsais, *Org. Lett.*, 2009, **11**, 3690.
[4] N. Margiotta, R. Ostuni, R. Ranaldo, N. Denora, V. Laquintana, G. Trapani, G. Liso, G. Natile, *J. Med. Chem.*, 2007, **50**, 1019.

solution was heated at 45 °C for 14h. After cooling, the crude mixture was diluted with H_2O and extracted three times with Et_2O. The combined organic layers were washed with 10 % $Na_2S_2O_3$ aq. soln., brine and dried over $MgSO_4$. The crude product was purified by flash column chromatography (PE/CH_2Cl_2 from to 8:2 to 6:4) afforded **7** (1.45 g, 5.09 mmol) in 83% yield as colorless solid.

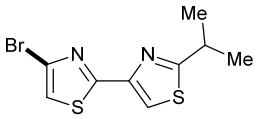
Exhibited spectra data identical to previous reports.[5]

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.68 (s, 1 H), 4.69 (s, 2 H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 183.8 (C), 163.6 (C), 127.7 (C), 126.4 (CH), 30.6 (CH_2).

General procedure A :

To a solution of α-bromoketone **7** (1 equiv) and $CaCO_3$ (1 equiv) in EtOH (0.25 M) was added thiobenzamide **8** (1.2 equiv), and the resulting solution was stirred for 6 h at reflux. After cooling, the solution was filtered and extracted three times with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated in vacuo.



4a

According to general procedure A, using **7** (1.34 g, 4.70 mmol) and 2-methylpropanethioamide **8a** (583 mg, 5.65 mmol, 1.2 equiv) and $CaCO_3$ (471 mg, 4.71 mmol, 1 equiv). Standard treatment (see general procedure A), and the crude product was purified by flash column chromatography (PE/EtOAc 8:2) afforded **4a** (1.25 g, 4.32 mmol) in 92% yield as a pale brown needles.

Mp = 78–80°C (Et_2O).

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.87 (s, 1H), 7.21 (s, 1H), 3.34 (sept, *J* = 6.9 Hz, 1H) 1.43 (d, *J* = 6.9 Hz, 6H).

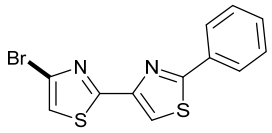
^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 179.0 (C), 163.9 (C), 147.5 (C), 125.9 (C), 117.2 (CH), 115.7 (CH), 33.4 (CH), 23.2 (2xCH_3).

IR (neat): 3116, 2957, 2923, 2865, 1483, 1442, 1305, 1283, 1181, 1072, 1020, 793 cm^{-1}.

MS (ES-TOF) *m/z* 288.9 [$M+H^+$; ^{79}Br] and 290.9 [$M+H^+$; ^{81}Br].

HRMS (ES-TOF): calcd for $C_9H_{10}N_2S_2Br$: 288.9469; found 288.9474.

[5] X. Just-Baringo, P. Bruno, F. Albericio, M. Álvarez, *Tetrahedron Lett.*, 2011, **52**, 5435.



4b

According to general procedure A, using **7** (415 mg, 1.46 mmol) and thiobenzamide **8b** (220 mg, 1.75 mmol, 1.2 equiv) and $CaCO_3$ (146 mg, 1.46 mmol, 1 equiv). Standard treatment (see general procedure A), and the crude product was purified by flash column chromatography (PE/CH_2Cl_2 9:1 to 6:4) afforded **4b** (390 mg, 1.21 mmol) in 83% yield as a colorless solid.

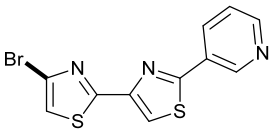
Mp = 196–197°C (PE/Et_2O).

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.02–7.99 (m, 3 H), 7.48–7.45 (m, 3 H), 7.27 (s, 1 H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 168.9 (C), 163.7 (C), 149.0 (C), 132.8 (C), 130.8 (CH), 129.1 (2xCH), 126.8 (2xCH), 126.0 (C), 117.7 (CH), 116.6 (CH).

IR (neat): 3126, 3111, 1474, 1451, 1298, 1253, 1184, 1179, 1087 cm^{-1}.

HRMS (ESI+): calcd for $C_{12}H_8BrN_2S$: 322.9307; found 322.9305.



4c

According to general procedure A, using **7** (415 mg, 1.46 mmol) and thionicotinamide **8c** (222 mg, 1.75 mmol, 1.2 equiv) and $CaCO_3$ (146 mg, 1.46 mmol, 1 equiv). Standard treatment (see general procedure A), and the crude product was purified by flash column chromatography (PE/EtOAc 9:1 to 7:3) afforded **4c** (306 mg, 0.94 mmol) in 65% yield as colorless solid.

Mp = 224–225°C (PE/Et_2O).

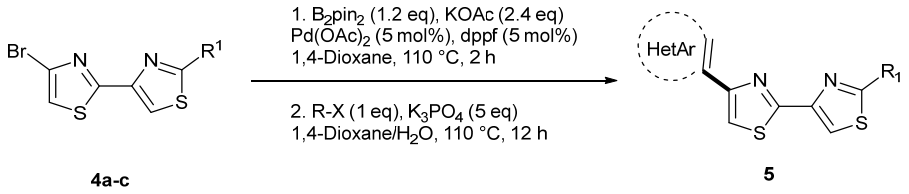
^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.22 (d, *J* = 1.7 Hz, 1 H), 8.70 (dd, *J* = 4.8 and 1.6 Hz, 1 H), 8.30 (dt, *J* = 8.0 and 1.9 Hz, 1H), 8.07 (s, 1 H), 7.43 (ddd, *J* = 7.9, 4.8 and 0.5 Hz, 1 H), 7.29 (s, 1 H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 165.5 (C), 163.2 (C), 151.5 (CH), 149.4 (C), 147.9 (CH), 133.9 (CH), 128.9 (C), 126.2 (C), 123.9 (CH), 117.9 (CH), 117.2 (CH).

IR (neat): 3127, 3117, 1573, 1465, 1442, 1422, 1308, 1256, 1187, 1083 cm^{-1}.

HRMS (ESI+): calcd for $C_{11}H_7BrN_3S_2$: 323.9259, found 323.9254.

2. Borylation Suzuki-Miyaura Coupling (BSC) of 4-bromo-2,4'-bithiazoles with various halides

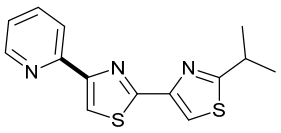


4a-c **5**

Scheme 2

General procedure B :

The 4-bromo-2,4'-bisthiazole (0.25 mmol, 1.2 equiv) was weighed in a sealed tube, followed by bis(pinacolato)diboron (64 mg, 1.2 equiv), potassium acetate (50 mg, 2.4 equiv), $Pd(OAc)_2$ (5 mol%) and dppf (5 mol%). The tube was evacuated and backfilled three times with N_2 and degassed anhydrous 1,4-dioxane (0.85 mL) was added. Then, the reaction mixture was heated at 110 °C until completion of the starting material (checked by TLC). Once, the reaction is completed, the sealing cap was removed and, the appropriate halide (1 equiv) and K_3PO_4 (5 equiv) were added. The tube was re-sealed and flushed with dry N_2, then degassed 1,4-dioxane (0.21 mL) and degassed water (0.21 mL) were added. The resulting mixture was stirred for 12 h at 110 °C. The crude mixture was cooled to room temperature, filtered through a short pad of Celite®, washed with EtOAc (50 mL) and the solvents were removed under reduced pressure. The crude product was then purified by flash column chromatography.



5aA

2'-isopropyl-4-(pyridin-2-yl)-2,4'-bithiazole 5aA : Compound **5aA w**as prepared according to the *procedure B* using **4a** (72 mg, 0.25 mmol, 1.2 eq) and 2-chloropyridine (20 µL, 0.21 mmol, 1 eq). The crude product was purified by flash chromatography (PE/EtOAc 8:2) to afford **5aA** in 98% (59 mg, 0.20 mmol) as a colorless solid.

Mp = 113–114°C (PE/EtOAc)

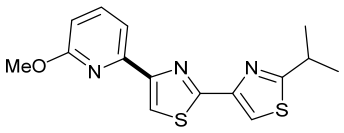
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.63 (ddd, *J* = 4.8, 1.7 and 0.9 Hz, 1H), 8.20 (dt, *J* = 8.0 and 0.9 Hz, 1H), 8.08 (s, 1H), 7.92 (s, 1H), 7.77 (td, *J* = 7.7 and 1.8 Hz, 1H), 7.23 (ddd, *J* = 7.5, 4.8 and 1.2 Hz, 1H), 3.38 (hept, *J* = 6.9 Hz, 1H), 1.45 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (75 MHz, CDCl3): δ (ppm) = 178.8 (C), 163.1 (C), 156.1 (C), 152.7 (C), 149.5 (CH), 148.8 (C), 137.1 (CH), 122.9 (CH), 121.3 (CH), 117.6 (CH), 115.0 (CH), 33.5 (CH), 23.3

(CH_3).

IR (neat): 3118, 3087, 2925, 2868, 1588, 1570, 1489, 1464, 1422, 1178, 1030 cm-^{1}.

HRMS (ESI+): calcd for $C_{14}H_{14}N_3S_2$: 288.0624; found 288.0622.



5aB

2'-isopropyl-4-(6-methoxypyridin-2-yl)-2,4'-bithiazole 5aB: Compound **5aB** was prepared according to the *procedure B* using **4a** (72 mg, 0.25 mmol, 1.2 eq) and 2-bromo-6-methoxypyridine (26 µL, 0.21 mmol, 1 eq). The crude product was purified by flash chromatography (PE/EtOAc 95:5) to afford **5aB** in 88% (59 mg, 0.19 mmol) as a colorless solid.

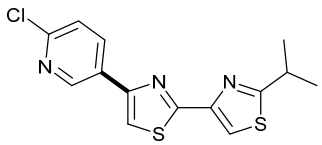
Mp = 90–91°C (PE/EtOAc)

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.07 (s, 1H), 7.91 (s, 1H), 7.81 (dd, *J* = 7.4 and 0.8 Hz, 1H), 7.66 (dd, *J* = 8.2 and 7.4 Hz, 1H), 6.70 (dd, *J* = 8.2 and 0.8 Hz, 1H), 4.02 (s, 3H), 3.39 (hept, *J* = 6.9 Hz, 1H), 1.45 (d, *J* = 6.9 Hz, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 178.8 (C), 163.7 (C), 162.9 (C), 156.2 (C), 150.0 (C), 148.8 (C), 139.5 (CH), 117.3 (CH), 114.8 (CH), 113.8 (CH), 110.2 (CH), 53.3 (CH_3), 33.4 (CH), 23.2 (2xCH_3).

IR (neat): 3118, 2943, 2869,2852, 1605, 1593, 1577, 1492, 1461, 1409, 1316, 1299, 1258, 1180, 1027 cm-^{1}.

HRMS (ESI+): calcd for $C_{15}H_{16}N_3OS_2$: 318.0729; found 318.0734.



5aC

4-(6-chloropyridin-3-yl)-2'-isopropyl-2,4'-bithiazole 5aC: Compound **5aC w**as prepared according to the *procedure B* using **4a** (72 mg, 0.25 mmol, 1.2 eq) and 2-chloro-5-iodopyridine (50 mg, 0.21 mmol, 1 eq). The crude product was purified by flash chromatography (PE/EtOAc 9:1) to afford **4aC** in 76% (51 mg, 0.16 mmol) as a colorless solid.

Mp = 157–158°C (PE/EtOAc)

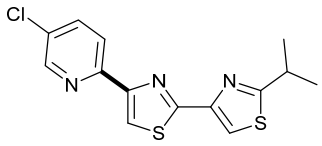
^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.94 (dd, *J* = 2.5 and 0.7 Hz, 1H), 8.22 (dd, *J* = 8.3

and 2.5 Hz, 1H), 7.92 (s, 1H), 7.57 (s, 1H), 7.39 (dd, *J* = 8.3 and 0.7 Hz, 1H), 3.38 (hept, *J* = 6.8 Hz, 1H), 1.45 (d, *J* = 6.9 Hz, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 179.0 (C), 163.8 (C), 151.9 (C), 150.6 (C), 148.4 (C), 147.6 (CH), 136.5 (CH), 129.4 (C), 124.3 (CH), 115.4 (CH), 114.9 (CH), 33.4 (CH), 23.2 (2xCH_3).

IR (neat): 3113, 3081, 3040, 2958, 1566, 1534, 1487, 1450, 1377, 1308, 1277, 1176, 1101 cm-[1].

HRMS (ESI+): calcd for $C_{14}H_{13}ClN_3S_2$: 322.0234; found 322.0237.



5aD

4-(5-chloropyridin-2-yl)-2'-isopropyl-2,4'-bithiazole 5aD: Compound **5aD w**as prepared according to the *procedure B* using **4a** (72 mg, 0.25 mmol, 1.2 eq) and 2,5-dichloropyridine (31 mg, 0.21 mmol, 1 eq). The crude product was purified by flash chromatography (PE/EtOAc 9:1) to afford **5aD** in 68% (46 mg, 0.14 mmol) as a colorless solid.

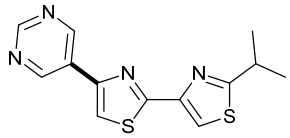
Mp = 155–156°C (PE/EtOAc)

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.57 (dd, *J* = 2.5 and 0.7 Hz, 1H), 8.17 (dd, *J* = 8.4 and 0.7 Hz, 1H), 8.07 (s, 1H), 7.91 (s, 1H), 7.75 (dd, *J* = 8.5 and 2.5 Hz, 1H), 3.39 (hept, *J* = 6.9 Hz, 1H), 1.46 (d, *J* = 6.9 Hz, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 178.9 (C), 163.3 (C), 155.0 (C), 150.8 (C), 148.6 (C), 148.4 (CH), 136.6 (CH), 130.9 (C), 122.0 (CH), 118.0 (CH), 115.0 (CH), 33.4 (CH), 23.2 (2xCH_3).

IR (neat): 3123, 2969, 2865, 1581, 1539, 1491, 1455, 1369, 1306, 1172, 1105, 1011 cm-[1].

HRMS (ESI+): calcd for $C_{14}H_{13}ClN_3S_2$: 322.0234; found 322.0238.



5aE

2'-isopropyl-4-(pyrimidin-5-yl)-2,4'-bithiazole 5aE: Compound **5aE w**as prepared according to the *procedure B* using **4a** (72 mg, 0.25 mmol, 1.2 eq) and 5-bromopyrimidine (33.4 mg, 0.21 mmol, 1 eq). The crude product was purified by flash chromatography (PE/EtOAc 6:4) to afford

5aE in 98% (59 mg, 0.205 mmol) as a pale yellow solid.

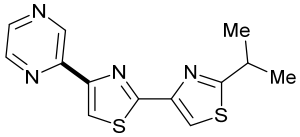
Mp = 166-167 °C (CH_2Cl_2/Pentane)

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.28 (s, 2H), 9.18 (s, 1H), 7.94 (s, 1H), 7.66 (s, 1H), 3.38 (hept, *J* = 6.9 Hz, 1H), 1.45 (d, *J* = 6.9 Hz, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 179.1 (C), 164.3 (C), 157.9 (CH), 154.5 (CH), 149.9 (C),148.3 (C), 128.4 (C), 115.8 (CH), 115.7 (CH), 33.5 (CH), 23.3 (2xCH_3).

IR (neat): 3118, 2961, 2927,, 2866, 1588, 1488, 1308, 1031, 797, 761

HRMS (ESI+): calcd for $C_{13}H_{13}N_4S_2$: 289.0582; found 289.0568.



5aF

2'-isopropyl-4-(pyrazine-2-yl)-2,4'-bithiazole 5aF : Compound **5aF w**as prepared according to the *procedure B* using **4a** (72 mg, 0.25 mmol, 1.2 eq) and 2-chloropyrazine (19 µL, 0.21 mmol, 1 eq). The crude product was purified by flash chromatography (PE/EtOAc 7:3) to afford **5aF** in 82% (50 mg, 0.17 mmol) as a colorless solid.

Mp = 83–84°C (PE/EtOAc)

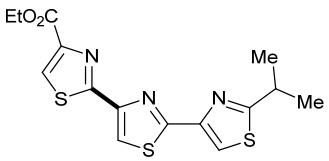
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.42 (s, 1H), 8.54 (s, 1H), 8.50 (s, 1H), 8.11 (s, 1H), 7.94 (s, 1H), 3.36 (hept, *J* = 6.9 Hz, 1H), 1.43 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (75 MHz, CDCl3): δ (ppm) = 179,0 (C), 163.8 (C), 153.5 (C), 148.4 (C), 148.1 (C), 144.0 (CH), 143.63 (CH), 143.1 (CH), 119.4 (CH), 115.4 (CH), 33.4 (CH), 23.2 (2xCH_3).

IR (neat): 3129, 3115, 2971, 2920, 2852, 1679, 1602, 1533, 1495, 1383, 1311, 1144, 1066 cm^{-1}.

MS (ES-TOF) *m/z* 289.0 [$M+H^+$].

HRMS (ES-TOF): calcd for $C_{15}H_{16}N_5S_2$: 289.0568; found 289.0582.



5aG

Ethyl 2''-isopropyl-[2,4':2',4''-terthiazole]-4-carboxylate 5aG: Compound **5aG w**as prepared according to the *procedure B* using **4a** (72 mg, 0.25 mmol, 1.2 eq) and ethyl 2-bromothiazole-4-carboxylate (49 mg, 0.208 mmol, 1 eq). The crude product was purified by

flash chromatography (PE/Et_2O 7:3) to afford **5aG** in 60% (45 mg, 0.125 mmol) as a colorless solid.

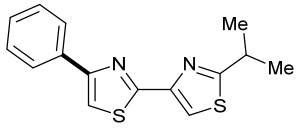
Mp = 187–188°C (PE/Et_2O).

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.19 (s, 1H), 8.14 (s, 1H), 7.93 (s, 1H), 4.45 (q, *J* = 7.0 Hz, 2H), 3.37 (hept, *J* = 7.0 Hz, 1H), 1.44 (d, *J* = 7.0 Hz, 6H), 1.43 (t, *J* = 7.0 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 179.0 (C), 163.6 (C), 163.5 (C), 161.6 (C), 149.1 (C), 148.1 (C), 148.0 (C), 127.9 (CH), 117.9 (CH), 115.8 (CH), 61.7 (CH_2), 33.4 (CH), 23.2 (2xCH_3), 14.5 (CH_3).

IR (neat): 3125, 2957, 2865, 1729, 1540, 1484, 1420, 1298, 1167, 1197, 1199 cm-^{1}.

HRMS (ESI+): calcd for $C_{15}H_{16}N_3O_2S_3$: 366.0405; found 366.0393.



5aH

2'-isopropyl-4-phenyl-2,4'-bithiazole 5aH: Compound **5aH w**as prepared according to the *procedure B* using **4a** (72 mg, 0.25 mmol, 1.2 eq) and iodobenzene (24 µL, 0.208 mmol, 1 eq). The crude product was purified by flash chromatography (PE/Et_2O 95:5) to afford **5aH** in 95% (56 mg, 0.20 mmol) as a colorless solid.

Mp = 81–82°C (CH_2Cl_2/pentane)

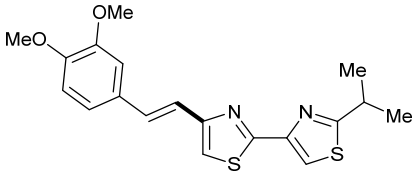
^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.99-7.96 (m, 2H), 7.93 (s, 1H), 7.49 (s, 1H), 7.47-7.42 (m, 2H), 7.37–7.32 (m, 1H), 3.37 (hept, *J* = 7.0 Hz, 1H), 1.44 (d, *J* = 7.0 Hz, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 178.7 (C), 162.9 (C), 156.3 (C), 148.9 (C), 134.6 (C), 128.8 (2xCH), 128.2 (CH), 126.5 (2xCH), 114.8 (CH), 113.4 (CH), 33.4 (CH), 23.2 (2xCH_3).

IR (neat): 3110, 2959, 2926, 2868, 1443, 1179, 759, 686 cm-^{1}.

MS (ES-TOF) *m/z* 287.0 [M+H$^+$].

HRMS (ESI-TOF): calcd for $C_{15}H_{15}N_2S_2$: 287.0677; found 287.0684.



5aI

(*E*)-4-(3,4-dimethoxystyryl)-2'-isopropyl-2,4'-bithiazole 5aI: Compound **5aI w**as prepared according to the *procedure B* using **4a** (72 mg, 0.25 mmol, 1.2 eq) and (*E*)-4-(2-bromovinyl)-

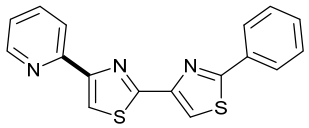
1,2-dimethoxybenzene (51 mg, 0.208 mmol, 1 eq). The crude product was purified by flash chromatography (PE/Et_2O 95:5) to afford **5aI** in 96% (74 mg, 0.20 mmol) as a yellow foam.

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.91 (s, 1H), 7.48 (d, *J* = 15.9 Hz, 1H), 7.15 (s, 1H), 7.10-7.08 (m, 2H), 7.01 (d, *J* = 15.9 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 1H), 3.94 (s, 3H), 3.91 (s, 3H), 3.39 (hept, *J* = 7.0 Hz, 1H), 1.45 (d, *J* = 7.0 Hz, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 178.8 (C), 162.9 (C), 155.2 (C), 149.1 (2xC), 148.7 (C), 131.3 (CH), 130.1 (C), 120.2 (CH), 119.6 (CH), 115.0 (CH), 114.9 (CH), 11.2 (CH), 108.8 (CH), 56.0 (CH_3), 55.9 (CH_3), 33.4 (CH), 23.2 (2xCH_3).

IR (neat): 3103, 2961, 2928, 2833, 1599, 1512, 1261, 1245, 1136, 1023 cm-^{1}.

HRMS (ES-TOF): calcd for $C_{19}H_{21}N_2O_2S_2$: 373.1044; found 373.1055.



5bA

2'-Phenyl-4-(pyridin-2-yl)-2,4'-bithiazole 5bA: Compound **5bA w**as prepared according to the *procedure B* using **4b** (81 mg, 0.25 mmol, 1.2 eq) and 2-chloropyridine (20 µL, 0.208 mmol, 1 eq). The crude product was purified by flash chromatography (PE/EtOAc 8:2) to afford **5bA** in 64% (43 mg, 0.13 mmol) as a colorless solid.

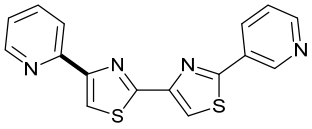
Mp = 194–195°C (Et_2O).

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.65 (ddd, *J* = 4.5, 1.5 and 0.6 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 8.13 (s, 1H), 8.07 (s, 1H), 8.06–8.03 (m, 2H), 7.81 (td, *J* = 7.8 and 1.5 Hz, 1H), 7.51–7.47 (m, 3H), 7.28–7.24 (m, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 168.7 (C), 163.0 (C), 156.2 (C), 152.7 (C), 150.3 (C), 149.6 (CH), 137.2 (CH), 133.1 (C), 130.7 (CH), 129.2 (2xCH), 126.8 (2xCH), 123.0 (CH), 121.4 (CH), 118.1 (CH), 115.9 (CH).

IR (neat): 3113, 3066, 3007, 1588, 1571, 1478, 1465, 1448, 1420, 1186 cm^{-1}.

HRMS (ESI+): calcd for $C_{17}H_{12}N_3S_2$: 322.0467 found 322.0461.



5cA

4-(pyridin-2-yl)-2'-(pyridin-3-yl)-2,4'-bithiazole 5cA: Compound **5cA w**as prepared according to the *procedure B* using **4c** (81 mg, 0.25 mmol, 1.2 eq) and 2-chloropyridine (20

μL, 0.208 mmol, 1 eq). The crude product was purified by flash chromatography (CH_2Cl_2/EtOAc from 95:5 to 9:1) to afford **5cA** in 49% (33 mg, 0.10 mmol) as a yellow solid. Mp = 232–233 °C (CH_2Cl_2/pentane).

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.24 (d, *J* = 2.0 Hz, 1H), 8.70 (dd, *J* = 1.5 and 4.8 Hz, 1H), 8.66 (d, *J* = 4.1 Hz, 1H), 8.35 (dt, *J* = 2.0 and 7.9 Hz, 1H), 8.23 (d, *J* = 7.9 Hz, 1H), 8.15 (s, 1H), 8.13 (s, 1H), 7.81 (td, *J* = 1.8 and 7.8 Hz, 1H), 7.44 (dd, *J* = 4.8 and 7.9 Hz, 1H), 7.28-7.25 (m, 1H).

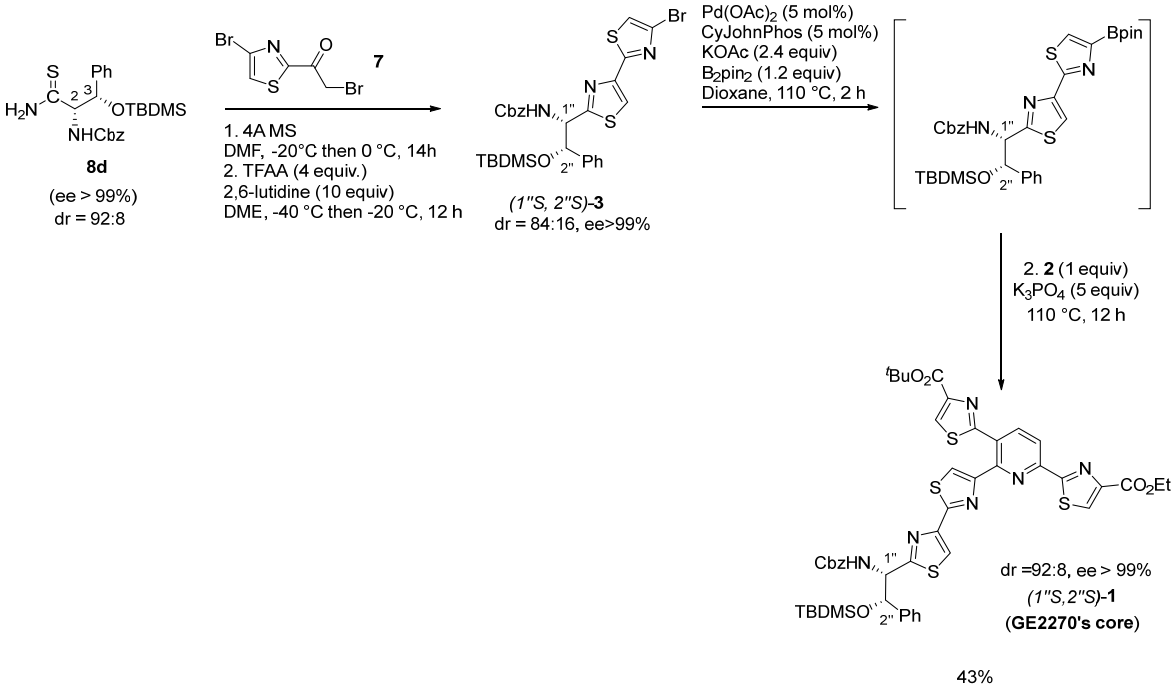
^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 165.2 (C), 162.0 (C), 156.4 (C), 152.5 (C), 151.3 (CH), 150.7 (C), 149.6 (CH), 147.9 (CH), 137.1 (CH), 133.9 (CH), 129.1 (C), 123.9 (CH), 123.0 (CH), 121.3 (CH), 118.1 (CH), 116.4 (CH).

IR (neat): 3664, 2988, 2901, 1406, 1066, 1056, 700 cm^{-1}.

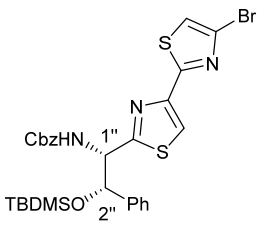
MS (ES-TOF) *m/z* 323.0 [$M+H^+$].

HRMS (ES-TOF): calcd for $C_{16}H_{11}N_4S_2$: 323.0425; found 323.0413.

3. Novel synthetic route to heterocyclic cluster of thiopeptide GE2270



Scheme 3



3

To a stirred solution of thioamide **8d**[1] (1.12 g, 2.50 mmol, 1 equiv) in anhydrous DMF (10 mL) at –20 °C were added MS 4° (2.5 g) and bromoketone **7** (0.86 g, 3.02 mmol, 1.2 equiv). The mixture was allowed to warm to 0 °C and was stirred at this temperature for 14 hours. Then the mixture was filtered through a Celite® pad and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (eluent: PE/EtOAc 9:1 to 8:2) affording the title compound (1.27 g, 1.96 mmol, 78%) which was dissolved in anhydrous DME (20 mL) and cooled at –40 °C before 2,6-lutidine (2.3 mL, 19.60 mmol) and trifluoroacetic anhydride (1.0 mL, 7.84 mmol) were added. The mixture was allowed to warm to –20 °C and stirred at this temperature for 12 hours. Then NEt_3 was added until pH 8-9, water was added and the aqueous layer was extracted three times with CH_2Cl_2. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (eluent: PE/EtOAc, 95:5 to 8:2) affording **3** (1.20 g, 1.90 mmol, 76% over two steps) as a yellow solid.

Mp = 66–67 °C

$[\alpha]_{D}^{20}$ –4.9 (*c* 1.03, $CHCl_3$).

^{1}H-NMR (300 MHz, CD_3CN): δ (ppm) = 7.96 (s, 1H), 7.44 (s, 1H), 7.37–7.29 (m, 8H), 7.21–7.17 (m, 2H), 6.30 (br s, 1H), 5.21–5.13 (m, 2H), 5.03–4.90 (m, 2H), 0.75 (s, 9H), –0.14 (s, 3H), –0.26 (s, 3H).

^{13}C-NMR (75 MHz, CD_3CN): δ (ppm) = 170.9 (C), 164.3 (C), 156.3 (C), 148.3 (C), 141.8 (C), 137.8 (C), 129.4 (CH), 129.1 (CH), 129.0 (CH), 128.8 (CH), 128.4 (CH), 128.0 (CH), 126.3 (C), 119.3 (CH), 118.6 (CH), 77.2 (CH), 67.2 (CH_2), 60.5 (CH), 25.9 (3×CH_3), 18.6 (C), –4.6 (CH_3), –5.1 (CH_3).

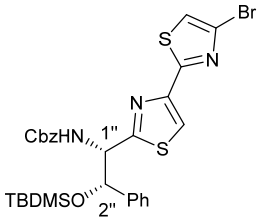
IR (neat): 3430, 3330, 3120, 3050, 3020, 2960, 2930, 2900, 2860, 1720, 1710, 1500 cm^{-1}.

Anal. Calcd for $C_{28}H_{32}BrN_3O_3S_2Si$: C, 53.32; H, 5.11; N, 6.66. Found: C, 53.38; H, 5.17; N, 6.54.

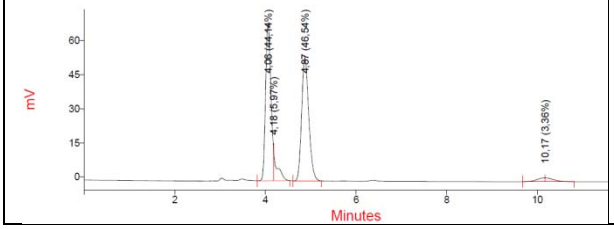
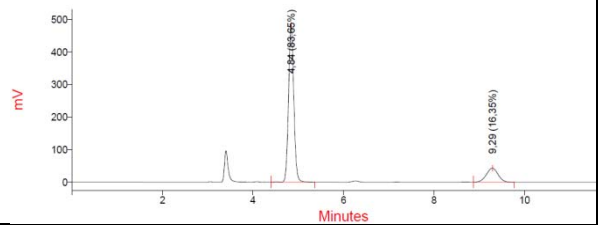
HPLC Chromatograms

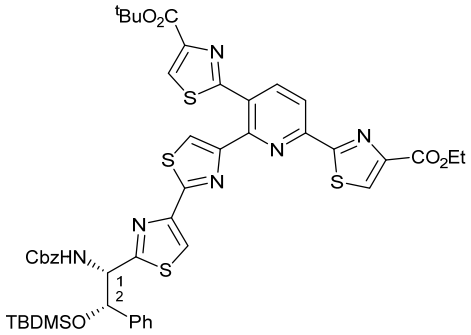
HPLC: Chiralpak IA (heptane/isopronol, 7/3), λ = 254 nm, 1 mL.min^{-1}.

t_R (major) = 4.84 min, t_R (minor) = 9.29 min. *ee* > 99%, dr = 84:16.



3

Racemic	99% *ee*, dr : 84:16
	



1

Bromothiazole **3** (378 mg, 0.60 mmol, 1.2 equiv), bis(pinacolato)diboron (152 mg, 0.60 mmol, 1.2 equiv), $Pd(OAc)_2$ (6 mg, 0.025 mmol), CyJohnPhos (35 mg, 0.10 mmol) and freshly dried KOAc (118 mg, 1.20 mmol) were charged in a Schlenk flask. It was then evacuated and backfilled three times with N_2 and then anhydrous degassed 1,4-dioxane (2.0 mL) was added and the reaction mixture was stirred at 110 °C in a preheated oil bath for 1 hour. Then the mixture was cooled to room temperature and chloropyridine **2**[1] (229 mg, 0.50 mmol, 1 equiv), freshly dried K_3PO_4 (531 mg, 2.50 mmol), degassed dioxane (0.5 mL) and degassed water (0.5 mL) were added and the mixture was stirred at 110 °C for further 14 hours. Then the mixture was filtered through a Celite® pad and washed with EtOAc. Water was added and the aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (eluent: PE/EtOAc 95:5 to 7:3) affording **GE2270A core** (210 mg, 0.22 mmol, 43%) as a pale beige solid.

Mp 119–120 °C.

$[\alpha]_D^{20}$ -10.2 (*c* 1.05, $CHCl_3$).

HPLC: Chiralpak IA (heptane/isopronol, 8/2), λ = 254 nm, 1 mL.min^{-1}. t_R (major) = 27.859 min, t_R (minor) = 32.804 min. *ee* > 99%, dr = 91:9.

IR (ATR diamond): 3430, 3330, 3120, 3050, 3020, 2960, 2930, 2900, 2860, 1710, 1500, 1370, 1330, 1250, 1200, 1160, 1100, 1020 cm^{-1}.

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.42 (s, 2H), 8.32 (s, 1H), 8.09 (s, 1H), 7.95 (s, 1H), 7.49(s, 1H), 7.33 (br s, 5H), 7.26 (br s, 5H), 5.74 (d, *J* = 7.7 Hz, 1H), 5.31-5.25 (m, 2H), 5.08 (s, 2H), 4.48 (q, *J* = 7.0 Hz, 2H), 1.59 (s, 9H), 1.45 (t, *J* = 7.1 Hz, 5H), 0.85 (s, 9H), –0.02 (s, 3H), –0.17 (s, 3H).

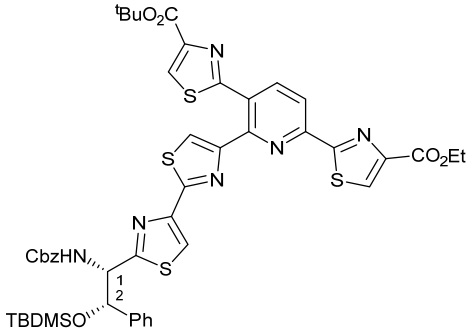
^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 169.0 (C), 167.7 (C), 165.2 (C), 162.2 (C), 161.5 (C), 160.5 (C), 155.5 (C), 153.5 (C), 150.9 (C), 150.7 (C), 148.6 (C), 148.5 (C), 148.5 (C), 140.2

(CH), 139.8 (C), 136.2 (C), 130.2 (CH), 129.5 (C), 128.6 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 126.7 (CH), 122.0 (CH), 119.2 (CH), 116.4 (CH), 82.3 (C), 76.4 (CH), 67.2 (CH_2), 61.8 (CH_2), 59.7 (CH), 28.3 (3xCH_3), 25.8 (3xCH_3), 18.2 (C), 14.5 (CH_3), –4.6 (CH_3), –5.2 (CH_3).

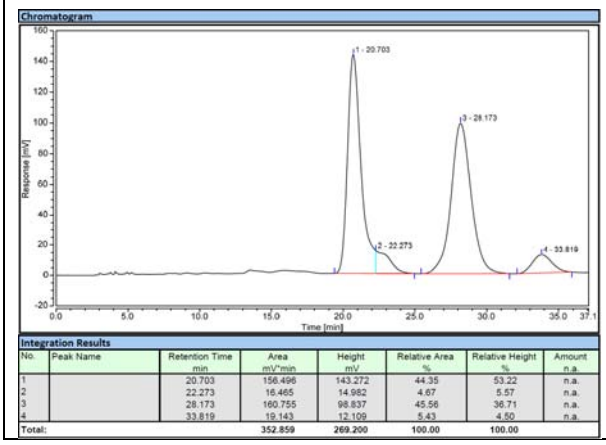
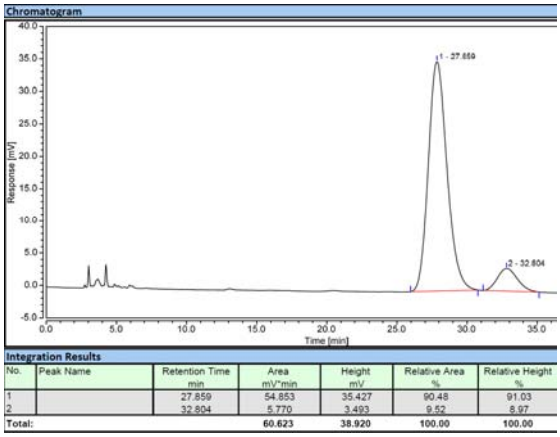
MS (ESI$^+$): *m/z* 966.8 [(M+H)$^+$], 988.9 [(M+Na)$^+$], 1949.9 [(M+NH_4)$^+$].

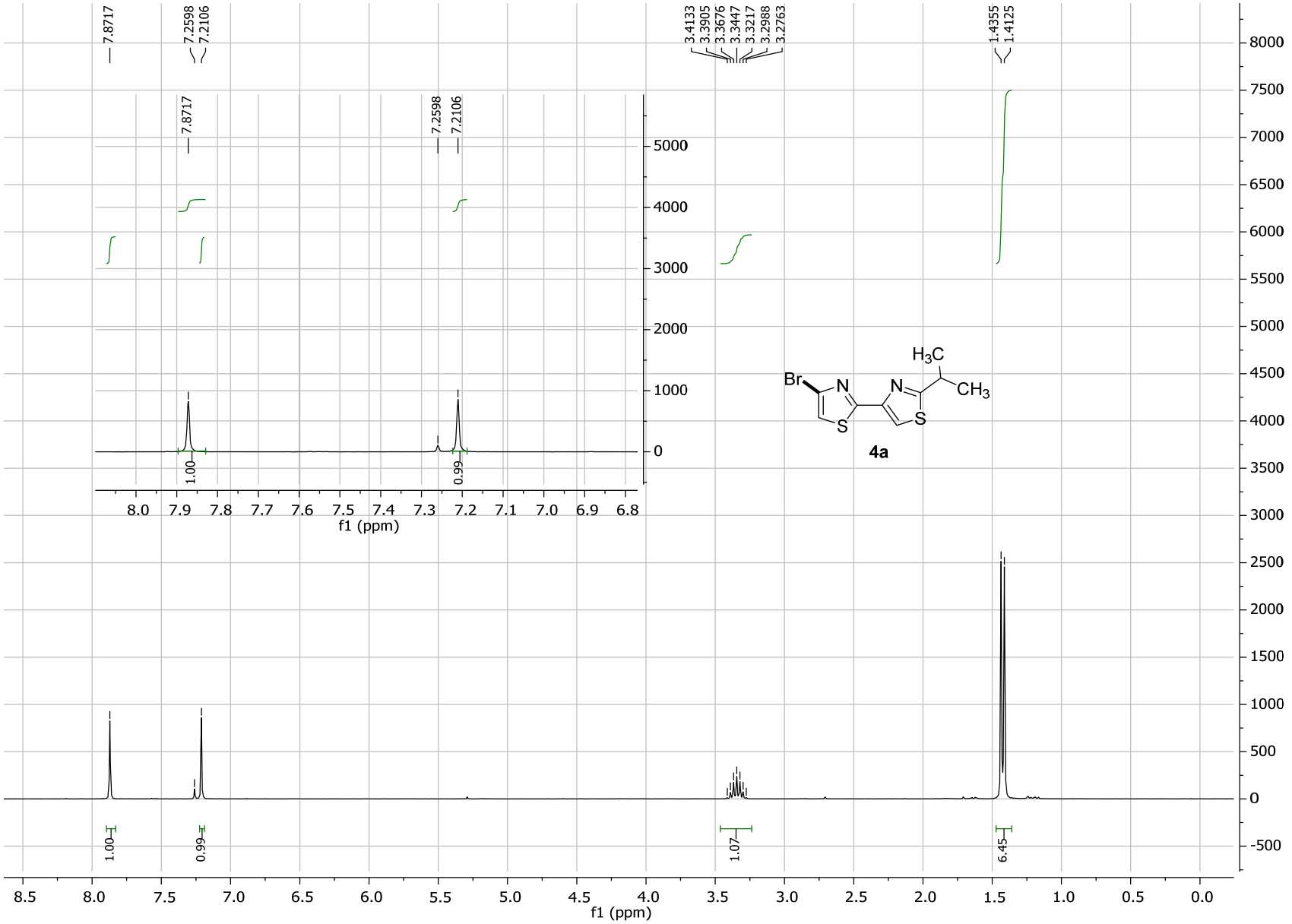
HRMS (ESI$^+$) Calcd for $C_{47}H_{51}N_6O_7S_4Si$: 967.2471. Found: 967.2461 [(M+H)$^+$].

HPLC Chromatograms
GE2270A core



1

Racemic	99% *ee*, dr: 91:9
	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3.3905
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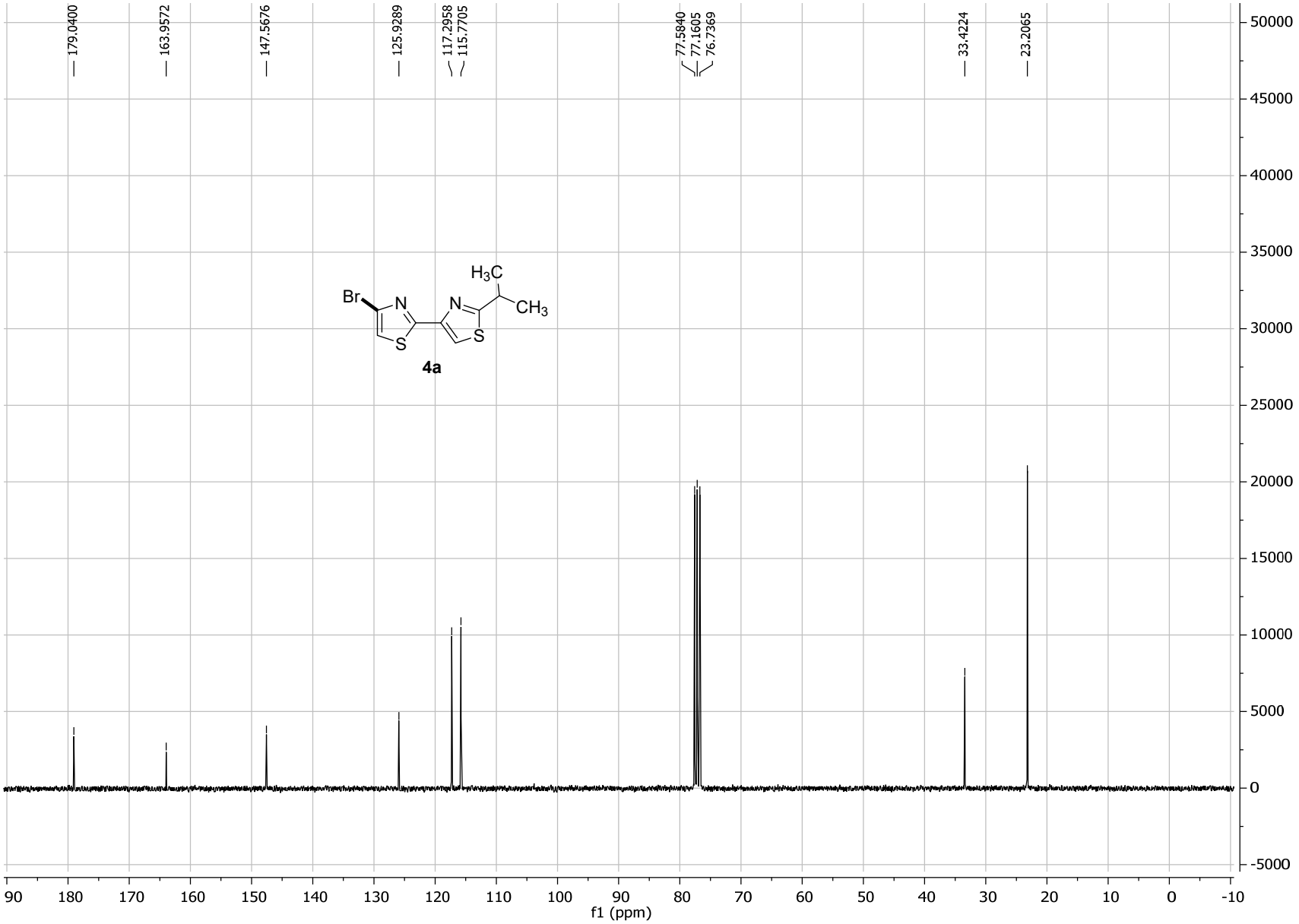
3.3447
3.3217
3.2988
3.2763
1.4355
1.4125
1.00
0.99
1.07
6.45
f1 (ppm)
Br
N
S
N
S
H3C
CH3
4a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S
N
S
H3C
CH3
4a
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
90
180
170
160
150
140
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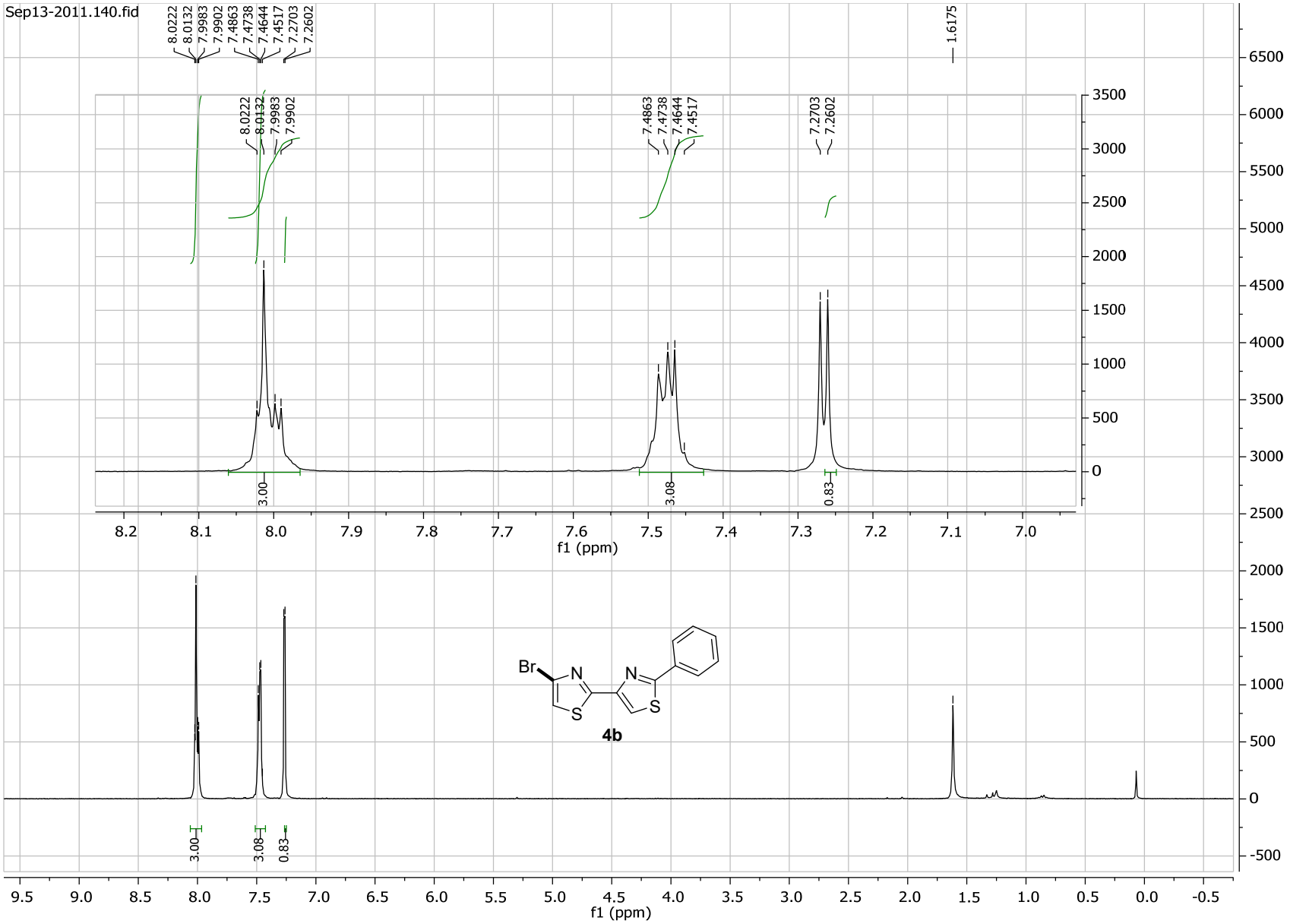
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.9902
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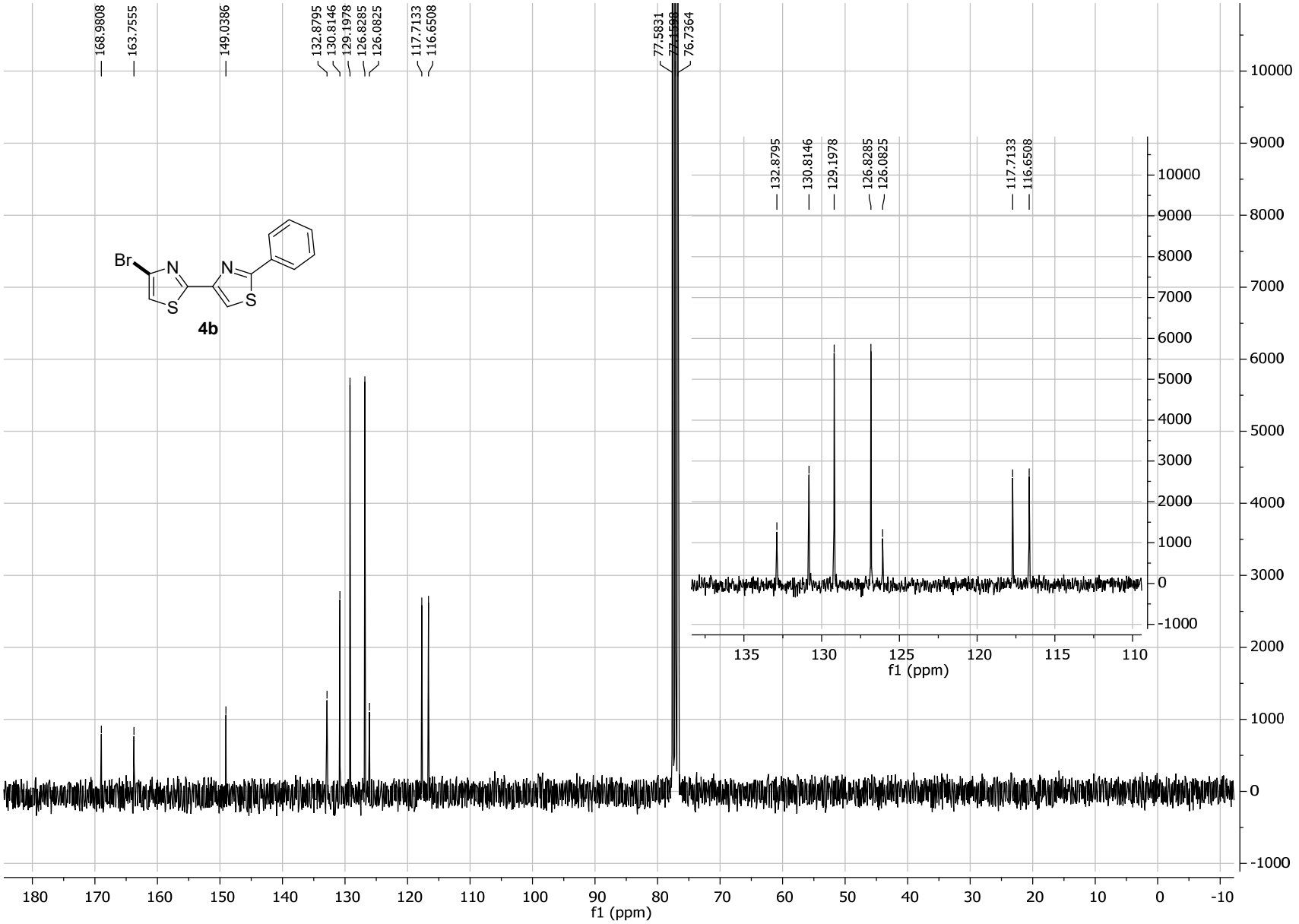
1.6175
3.00
3.08
0.83
f1 (ppm)
Br
N
N
S
S
4b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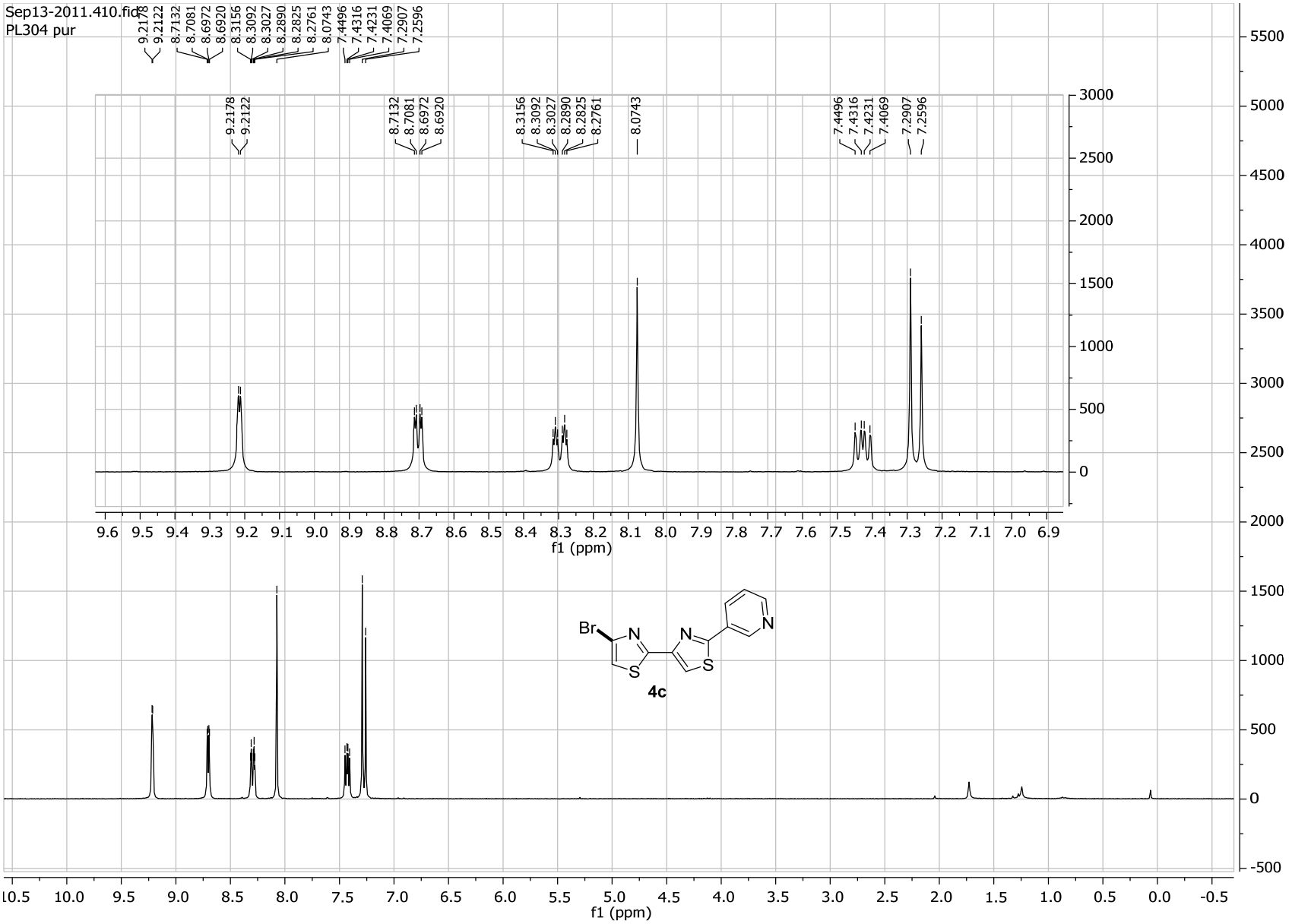
Br
N
S
N
S
4b
f1 (ppm)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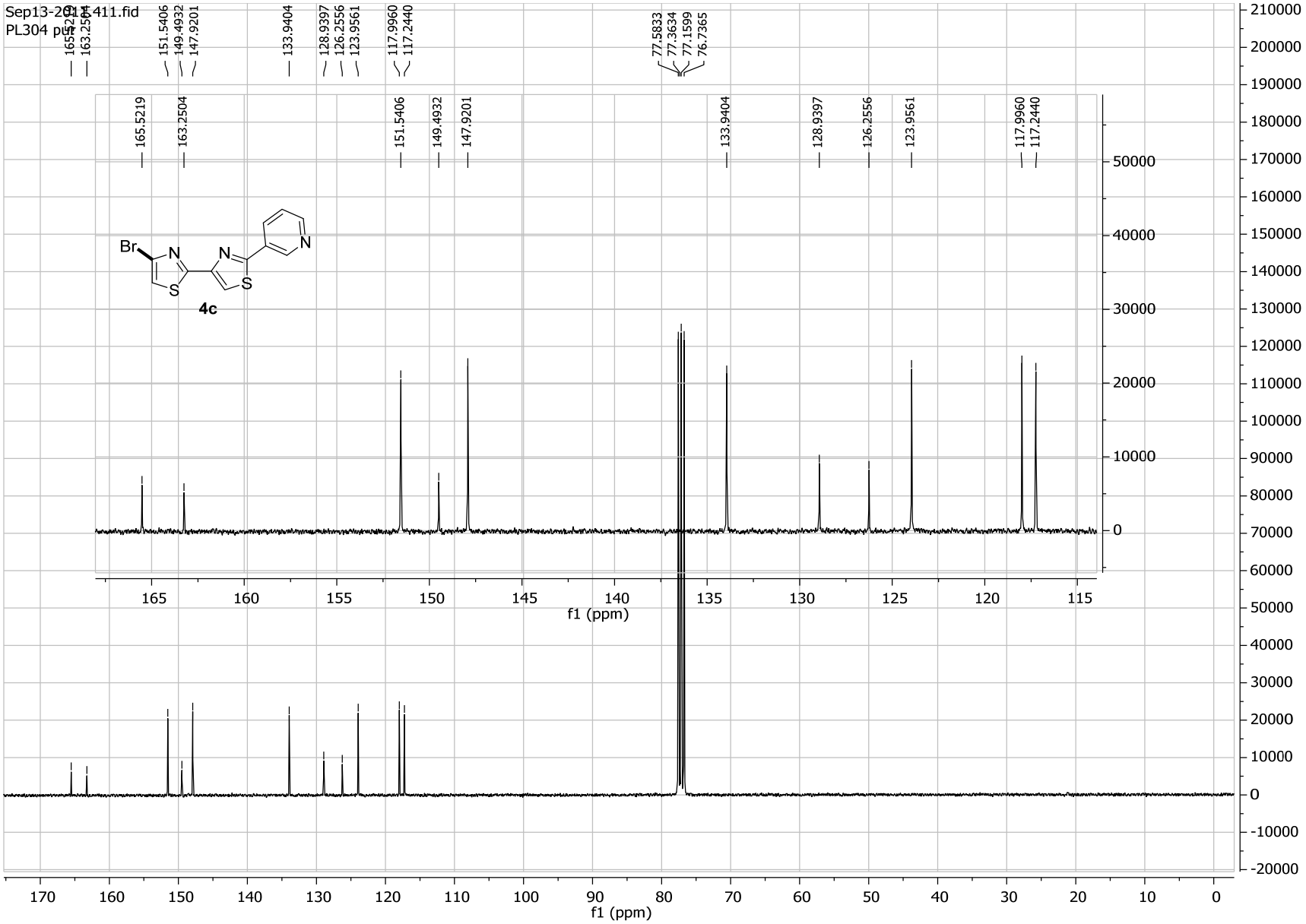
f1 (ppm)
Br
N
S
4c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77.1599
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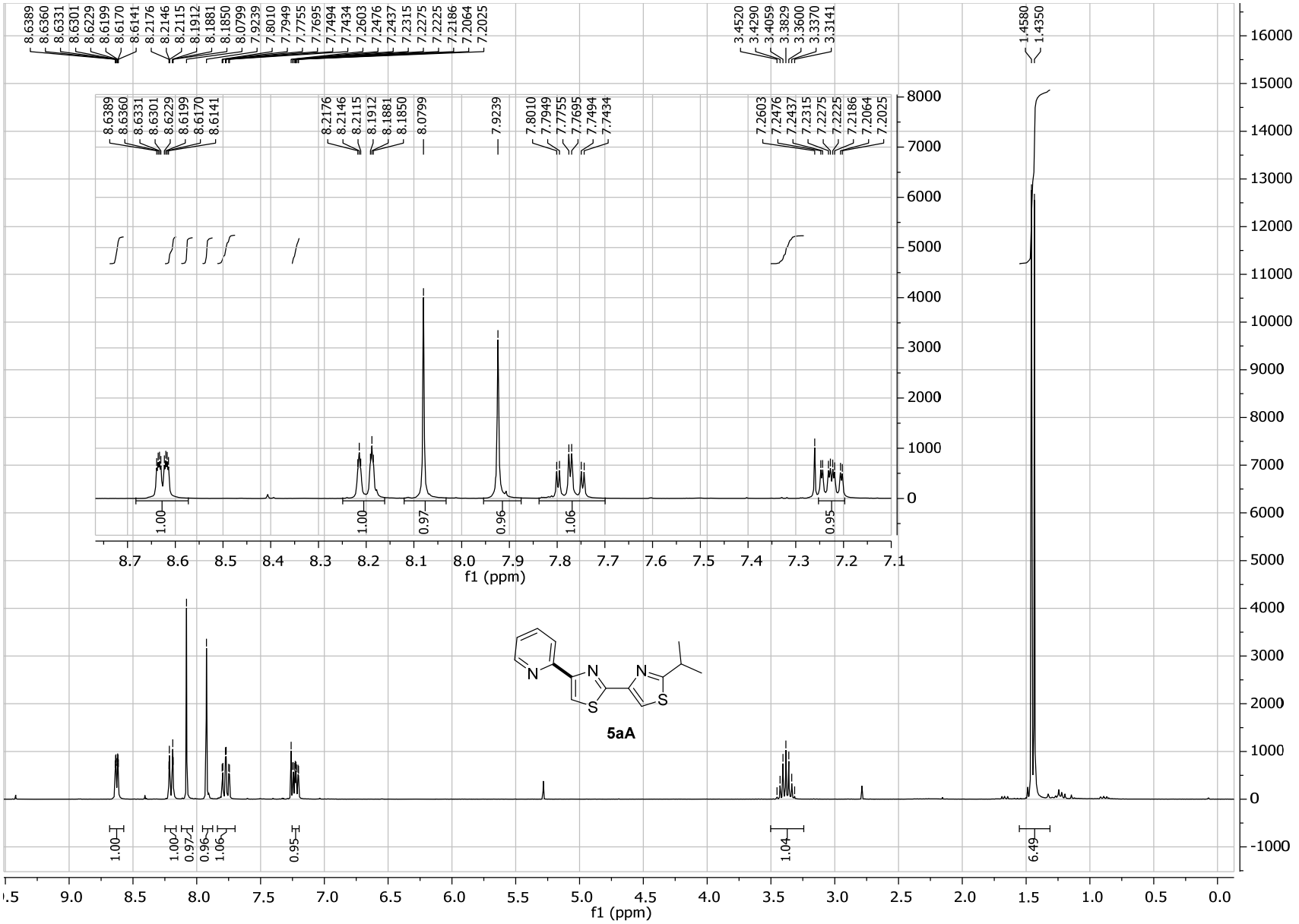
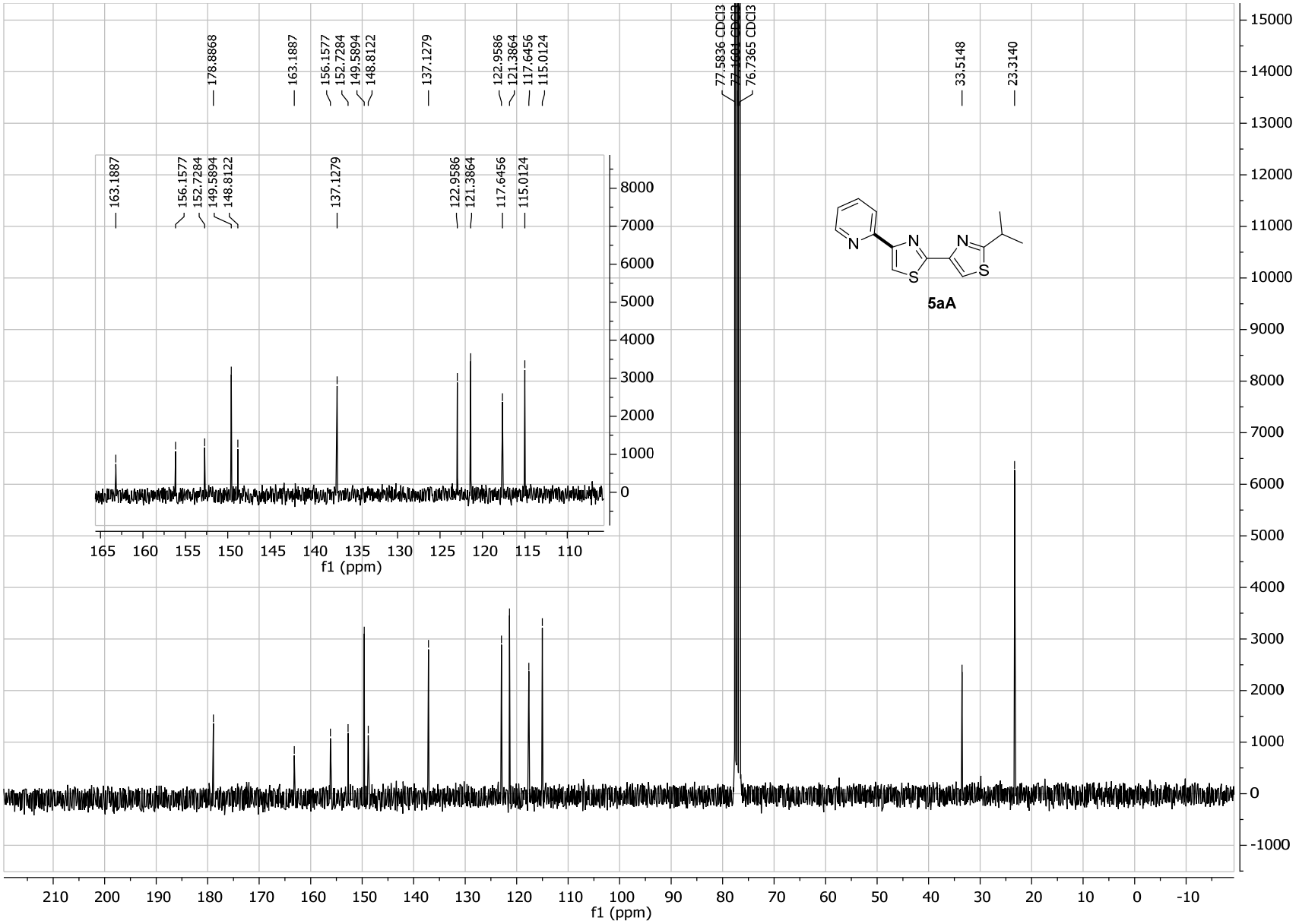
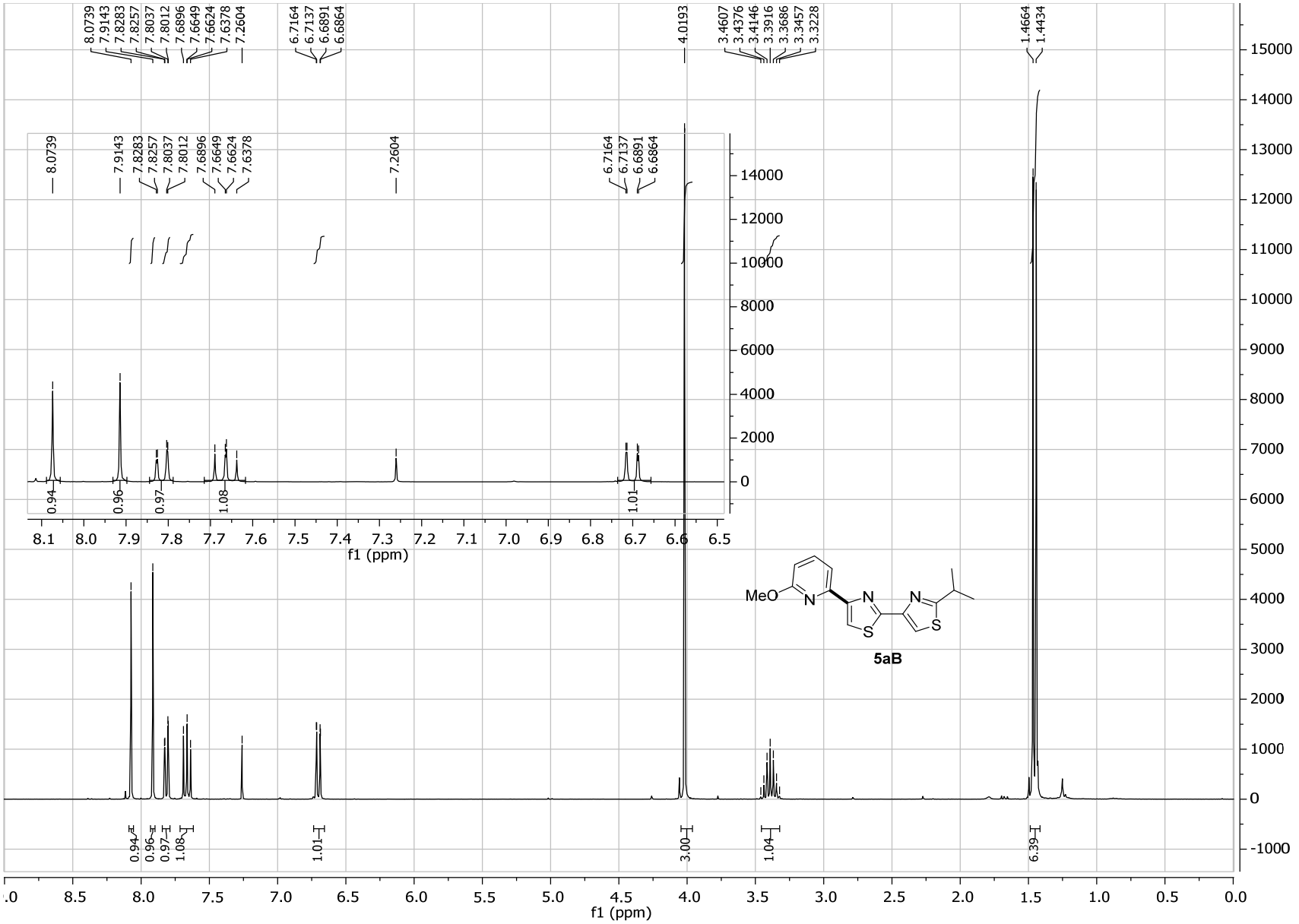
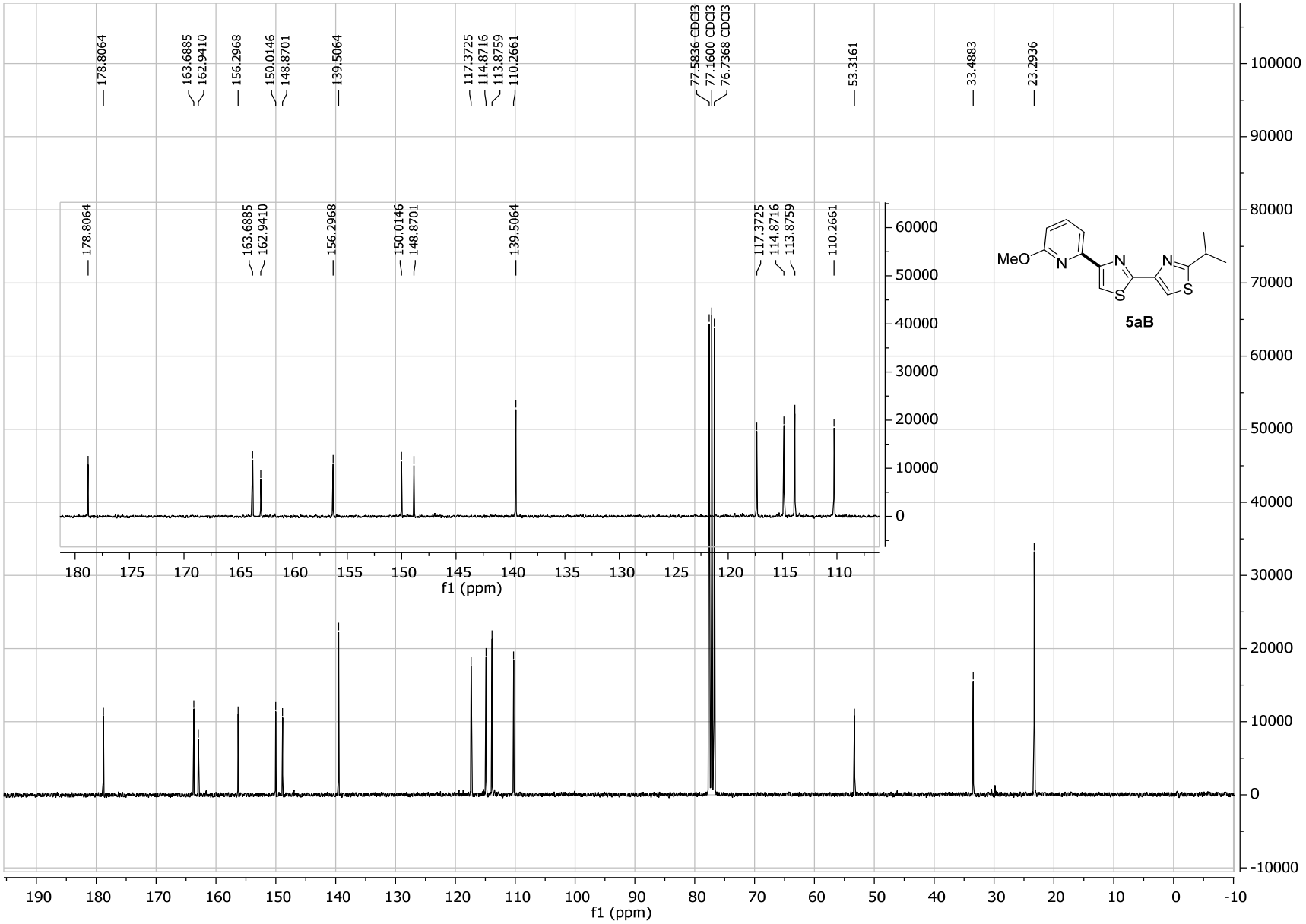
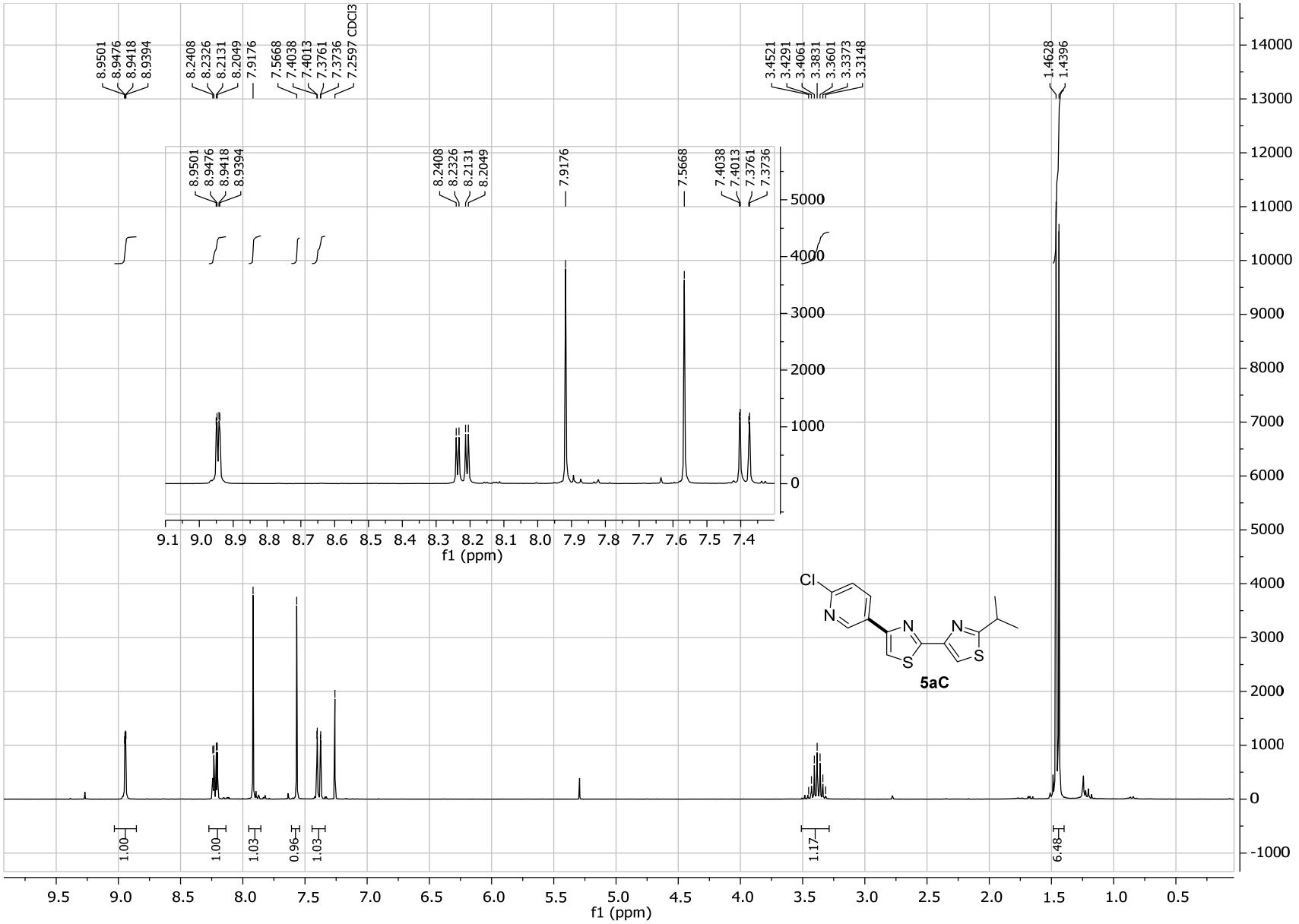
Br
N
N
N
S
S
4c
f1 (ppm)
f1 (ppm)

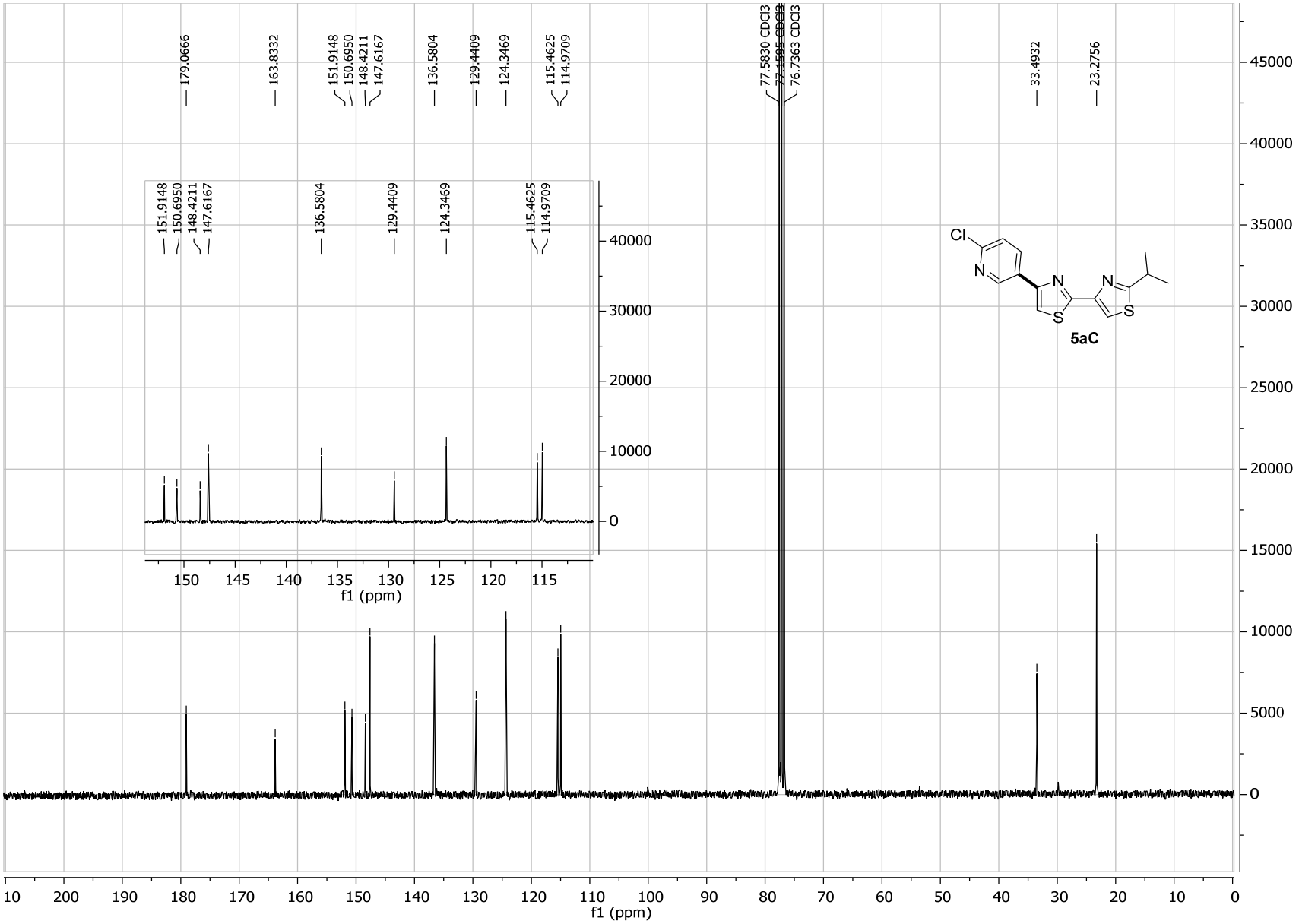

8.6389
8.6360
8.6331
8.6301
8.6229
8.6199
8.6170
8.6141
8.2176
8.2146
8.2115
8.1912
8.1881
8.1850
8.0799
7.9239
7.8010
7.7949
7.7755
7.7695
7.7494
7.7434
7.2603
7.2476
7.2437
7.2315
7.2275
7.2225
7.2186
7.2064
7.2025
3.4520
3.4290
3.4059
3.3829
3.3600
3.3370
3.3141
1.4580
1.4350
f1 (ppm)
1.00
1.00
0.97
0.96
1.06
0.95
1.04
6.49
N
N
N
S
S
5aA


178.8868
163.1887
156.1577
152.7284
149.5894
148.8122
137.1279
122.9586
121.3864
117.6456
115.0124
77.5836 CDCl3
77.1681 CDCl3
76.7365 CDCl3
33.5148
23.3140
5aA
f1 (ppm)


8.0739
7.9143
7.8283
7.8257
7.8037
7.8012
7.6896
7.6649
7.6624
7.6378
7.2604
6.7164
6.7137
6.6891
6.6864
4.0193
3.4607
3.4376
3.4146
3.3916
3.3686
3.3457
3.3228
1.4664
1.4434
f1 (ppm)
MeO
N
N
N
S
S
5aB


178.8064
163.6885
162.9410
156.2968
150.0146
148.8701
139.5064
117.3725
114.8716
113.8759
110.2661
77.5836 CDCl3
77.1600 CDCl3
76.7368 CDCl3
53.3161
33.4883
23.2936
MeO
N
N
N
S
S
5aB
f1 (ppm)
f1 (ppm)


8.9501
8.9476
8.9418
8.9394
8.2408
8.2326
8.2131
8.2049
7.9176
7.5668
7.4038
7.4013
7.3761
7.3736
7.2597 CDCl3
3.4521
3.4291
3.4061
3.3831
3.3601
3.3373
3.3148
1.4628
1.4396
f1 (ppm)
Cl
N
N
N
S
S
5aC
1.00
1.00
1.03
0.96
1.03
1.17
6.48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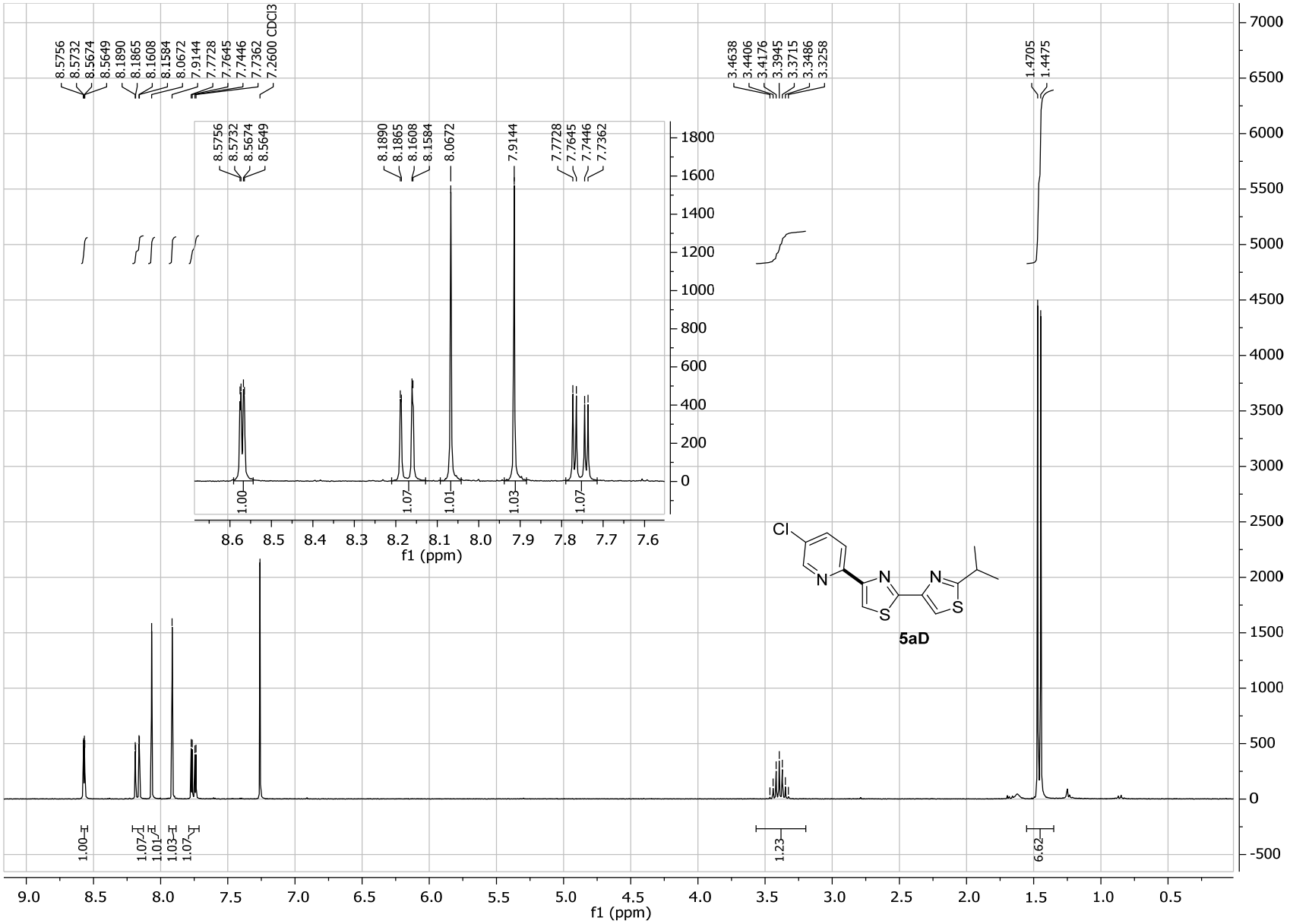
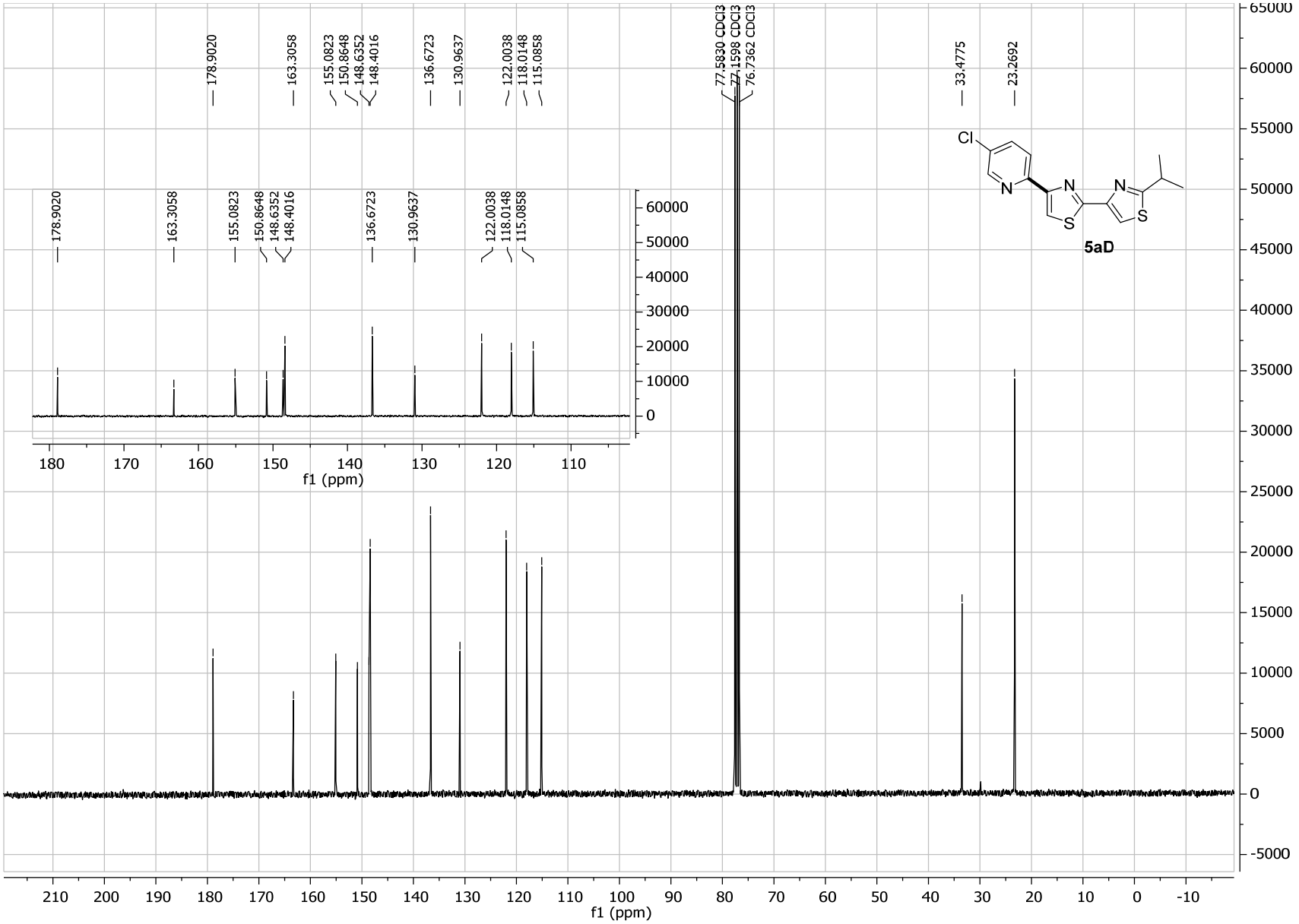
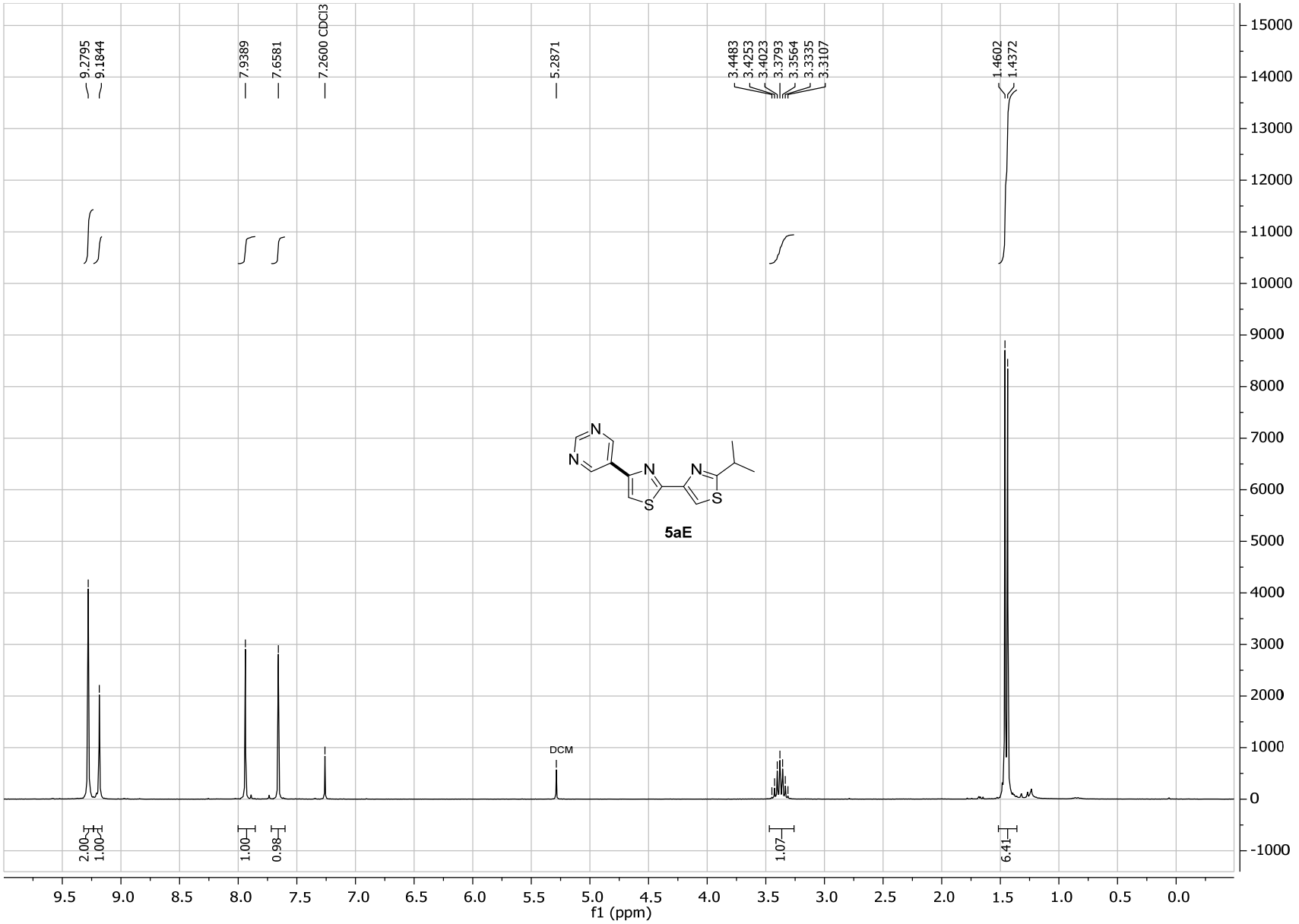
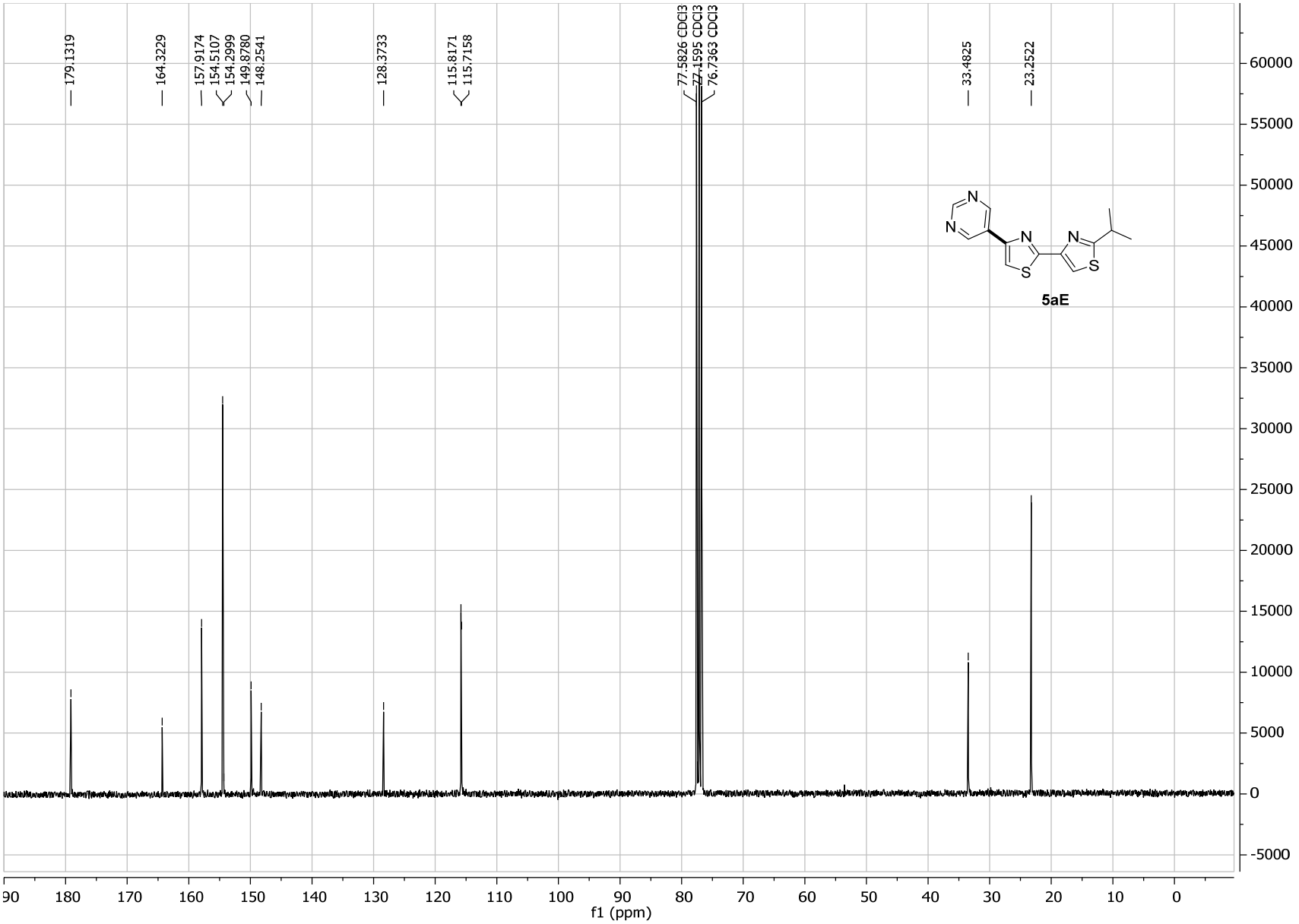
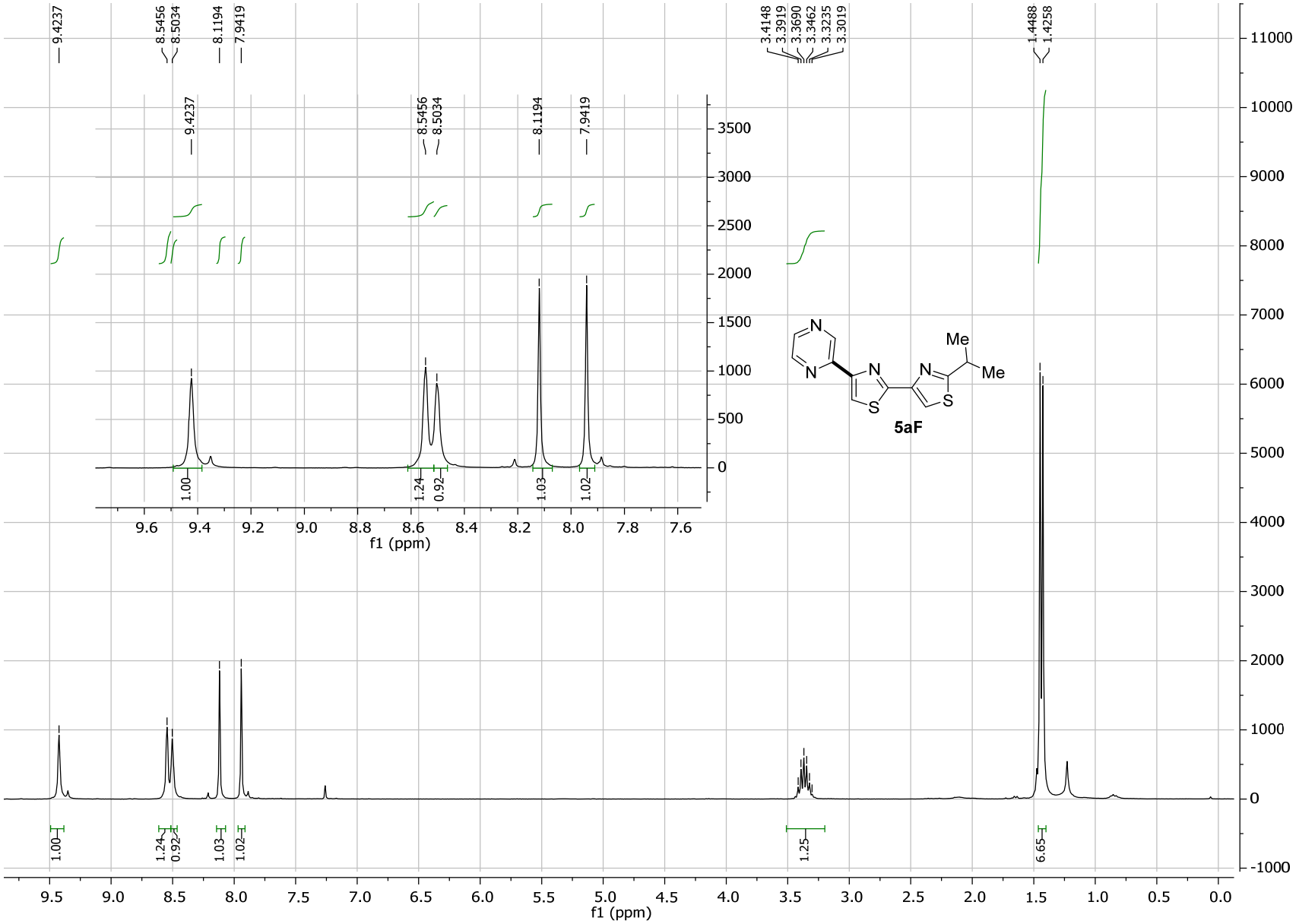
163.8332
151.9148
150.6950
148.4211
147.6167
136.5804
129.4409
124.3469
115.4625
114.9709
77.5830 CDCl3
77.1595 CDCl3
76.7363 CDCl3
33.4932
23.2756
f1 (ppm)
Cl
N
N
N
S
S
5aC

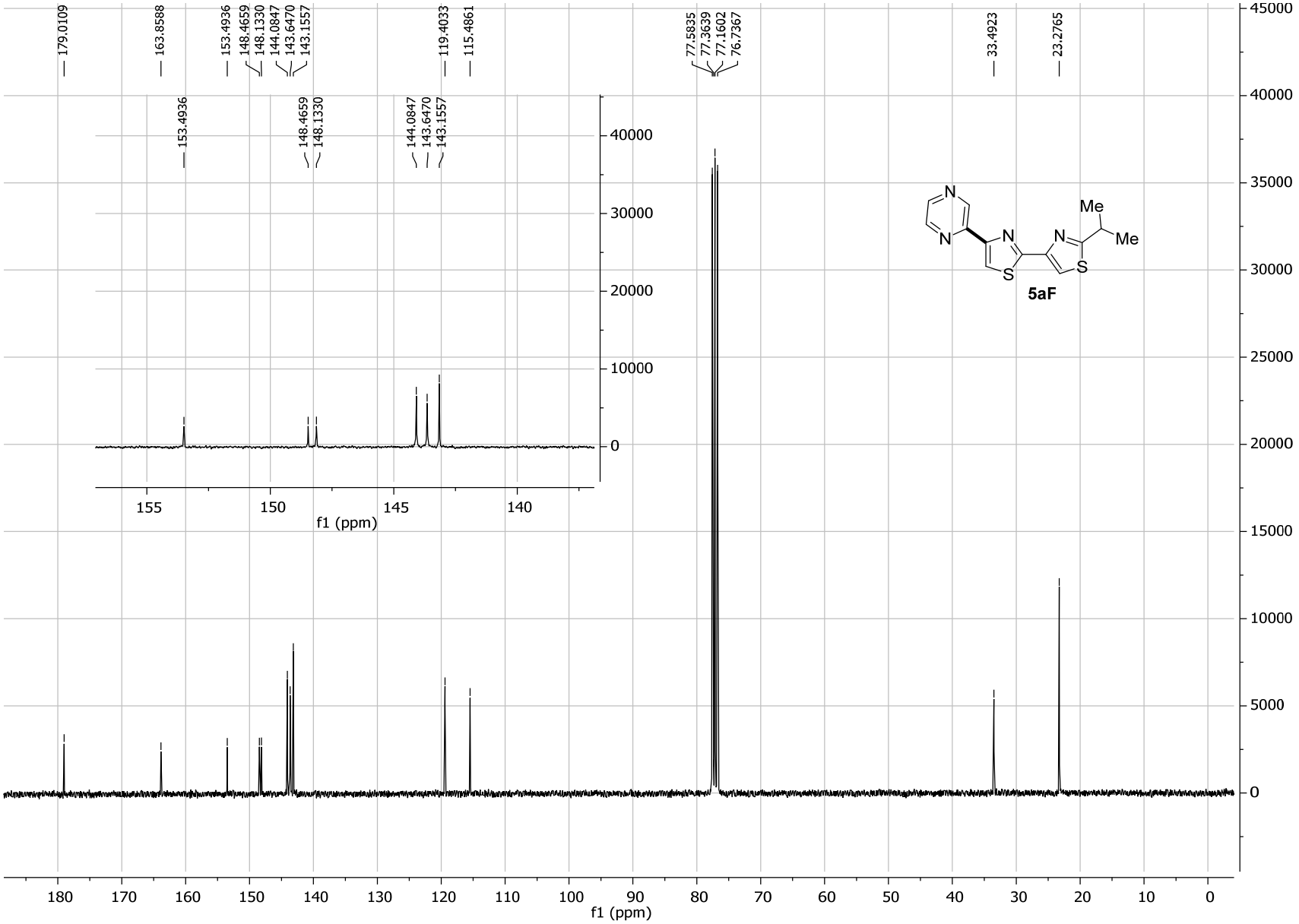

8.5756
8.5732
8.5674
8.5649
8.1890
8.1865
8.1608
8.1584
8.0672
7.9144
7.7728
7.7645
7.7446
7.7362
7.2600 CDCl3
3.4638
3.4406
3.4176
3.3945
3.3715
3.3486
3.3258
1.4705
1.4475
1.00
1.07
1.01
1.03
1.07
1.23
6.62
f1 (ppm)
Cl
N
N
N
S
S
5aD

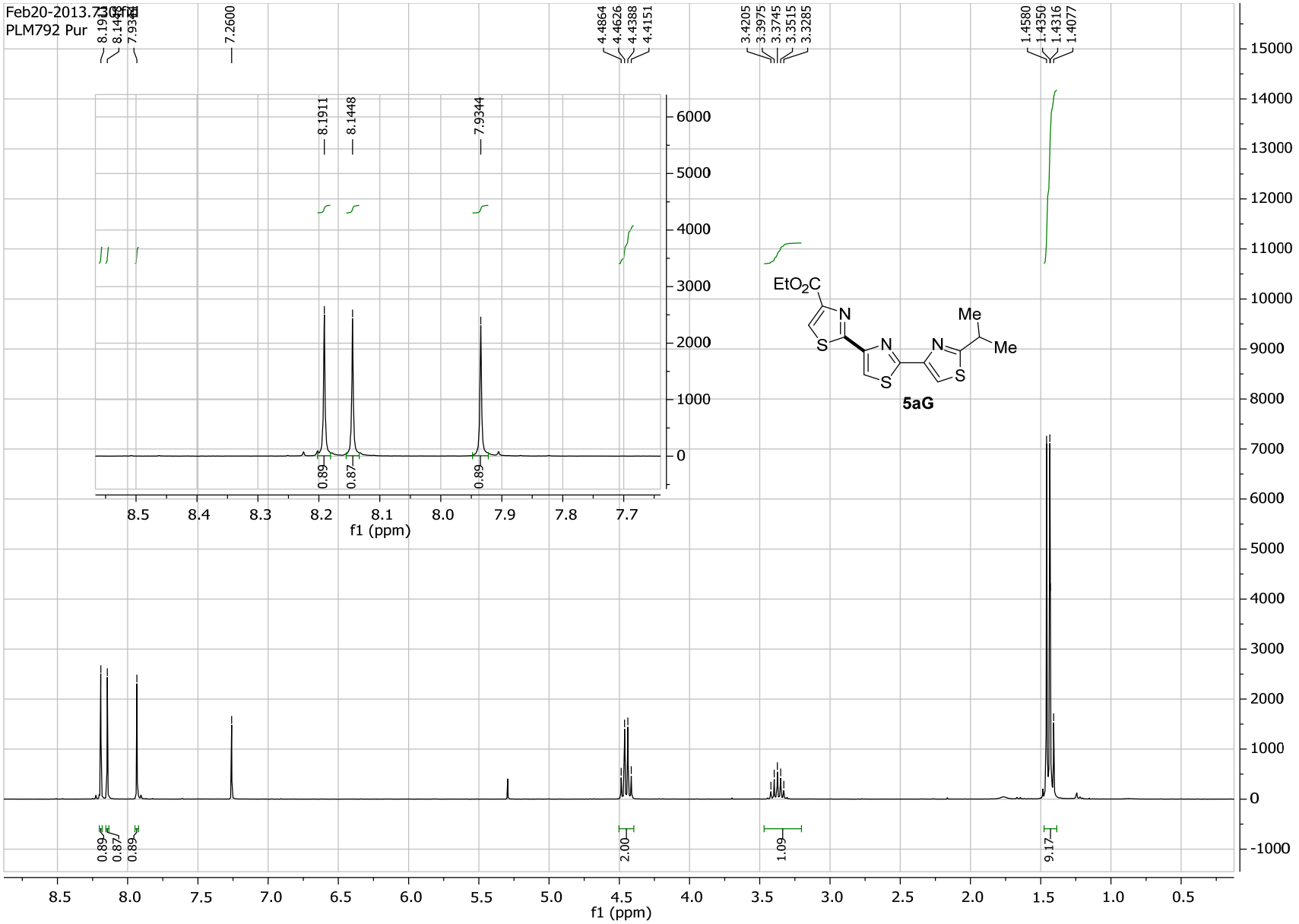

178.9020
163.3058
155.0823
150.8648
148.6352
148.4016
136.6723
130.9637
122.0038
118.0148
115.0858
77.5830 CDCl3
77.1598 CDCl3
76.7362 CDCl3
33.4775
23.2692
Cl
N
N
S
N
S
5aD
f1 (ppm)
f1 (ppm)

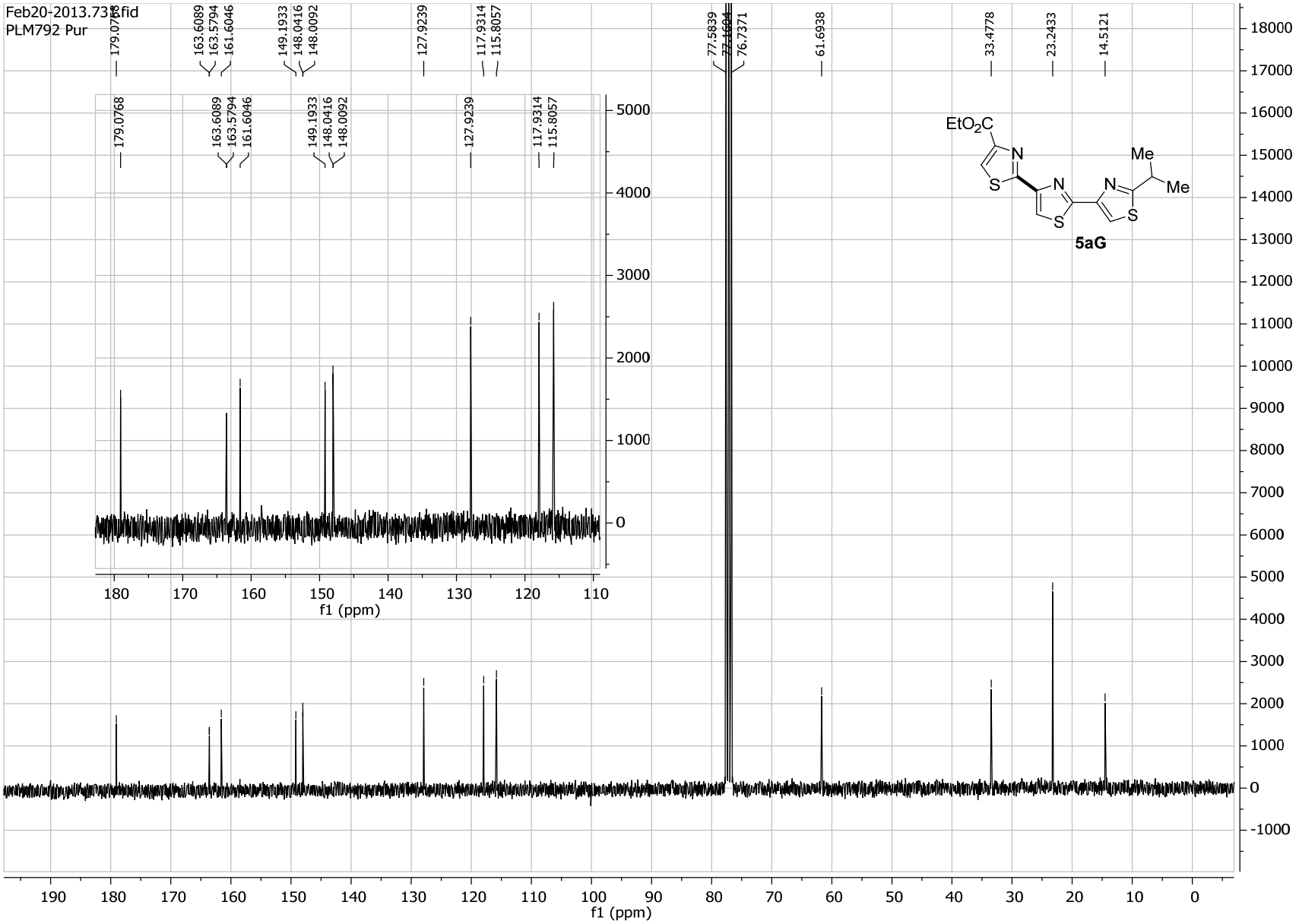

9.2795
9.1844
7.9389
7.6581
7.2600 CDCl3
5.2871
3.4483
3.4253
3.4023
3.3793
3.3564
3.3335
3.3107
1.4602
1.4372
DCM
5aE
2.00
1.00
1.00
0.98
1.07
6.41
f1 (ppm)

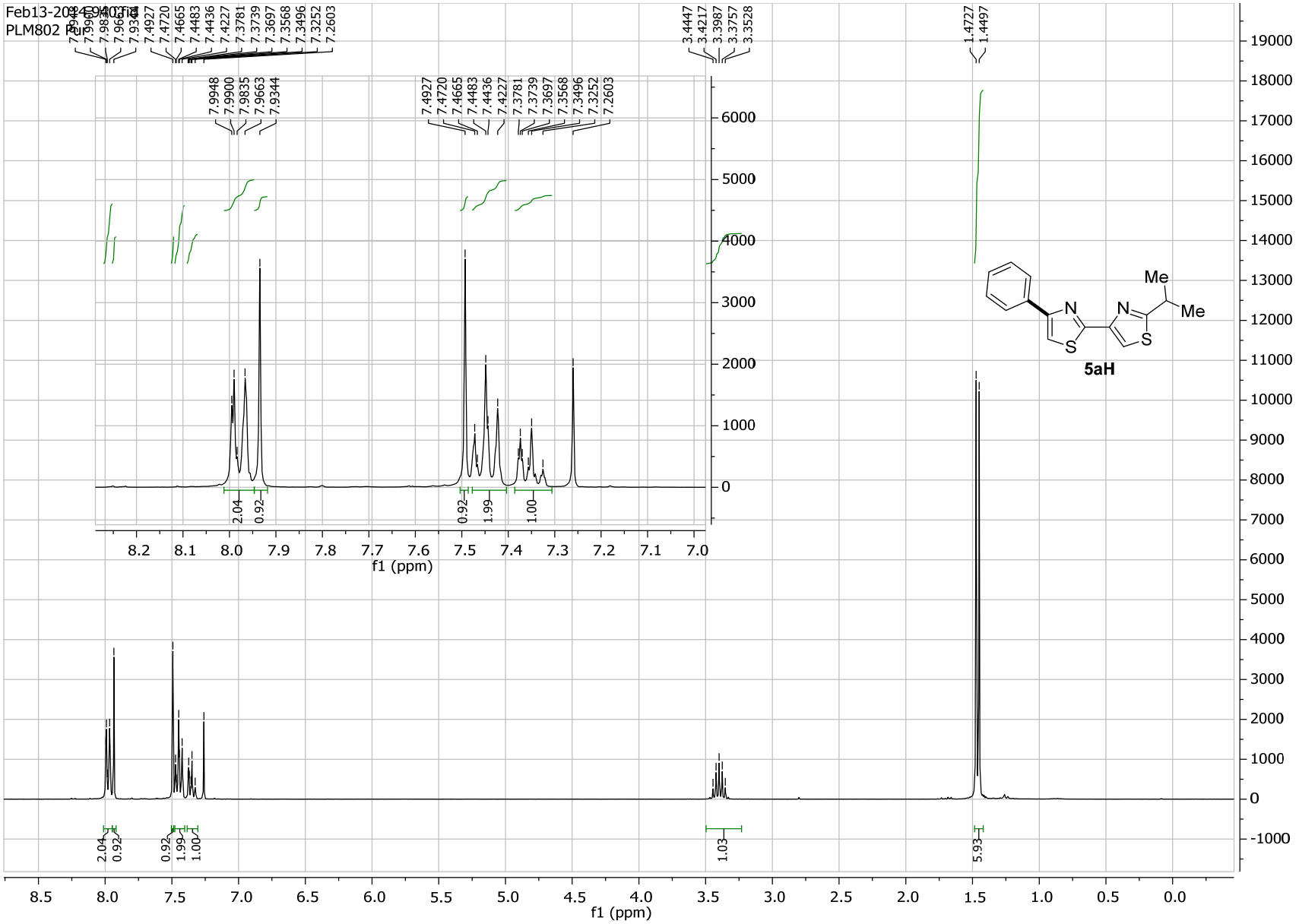

179.1319
164.3229
157.9174
154.5107
154.2999
149.8780
148.2541
128.3733
115.8171
115.7158
77.5826 CDCl3
77.1595 CDCl3
76.7363 CDCl3
33.4825
23.2522
5aE
f1 (ppm)

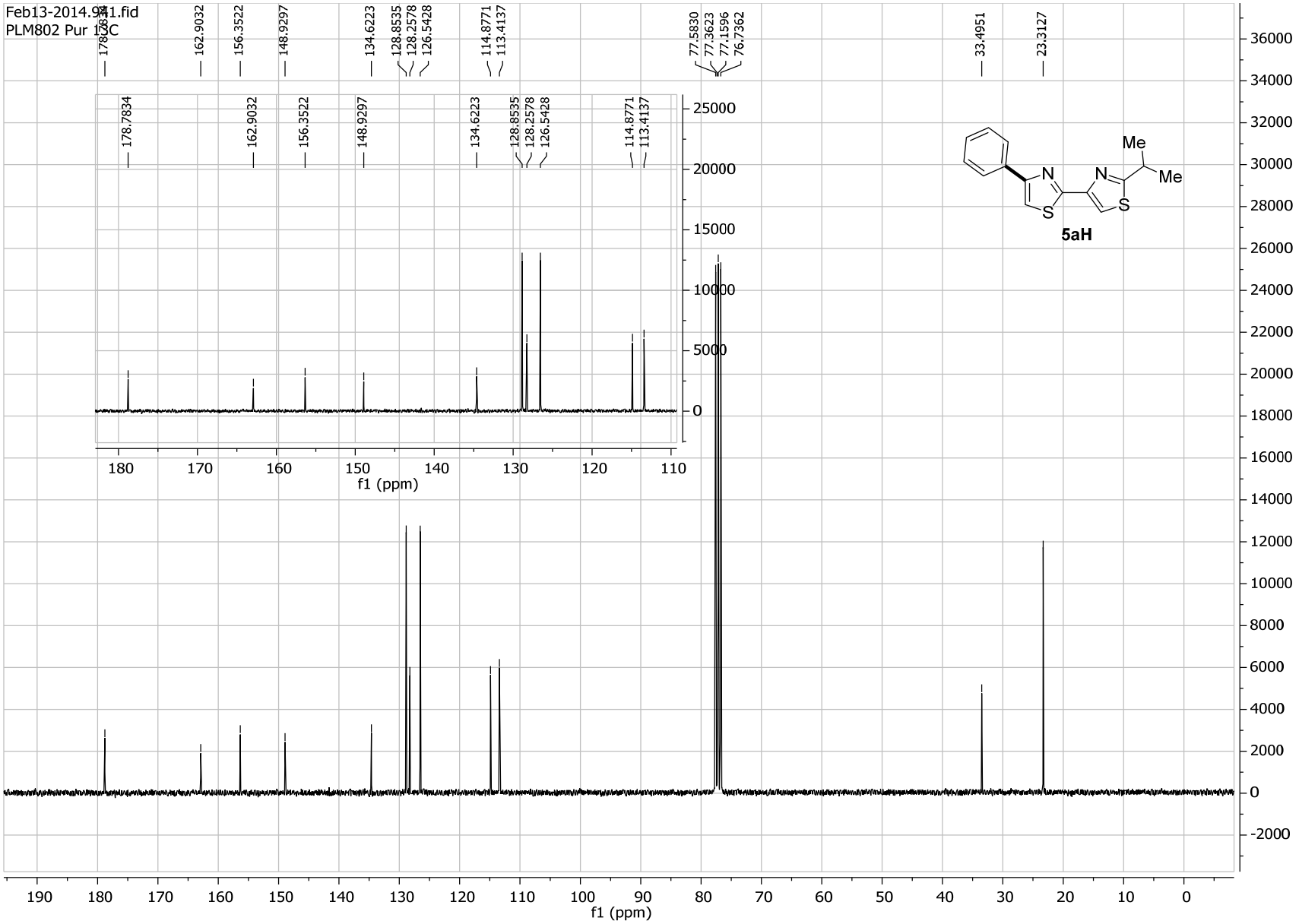

9.4237
8.5456
8.5034
8.1194
7.9419
3.4148
3.3919
3.3690
3.3462
3.3235
3.3019
1.4488
1.4258
1.00
1.24
0.92
1.03
1.02
1.25
6.65
f1 (ppm)
Me
Me
5aF

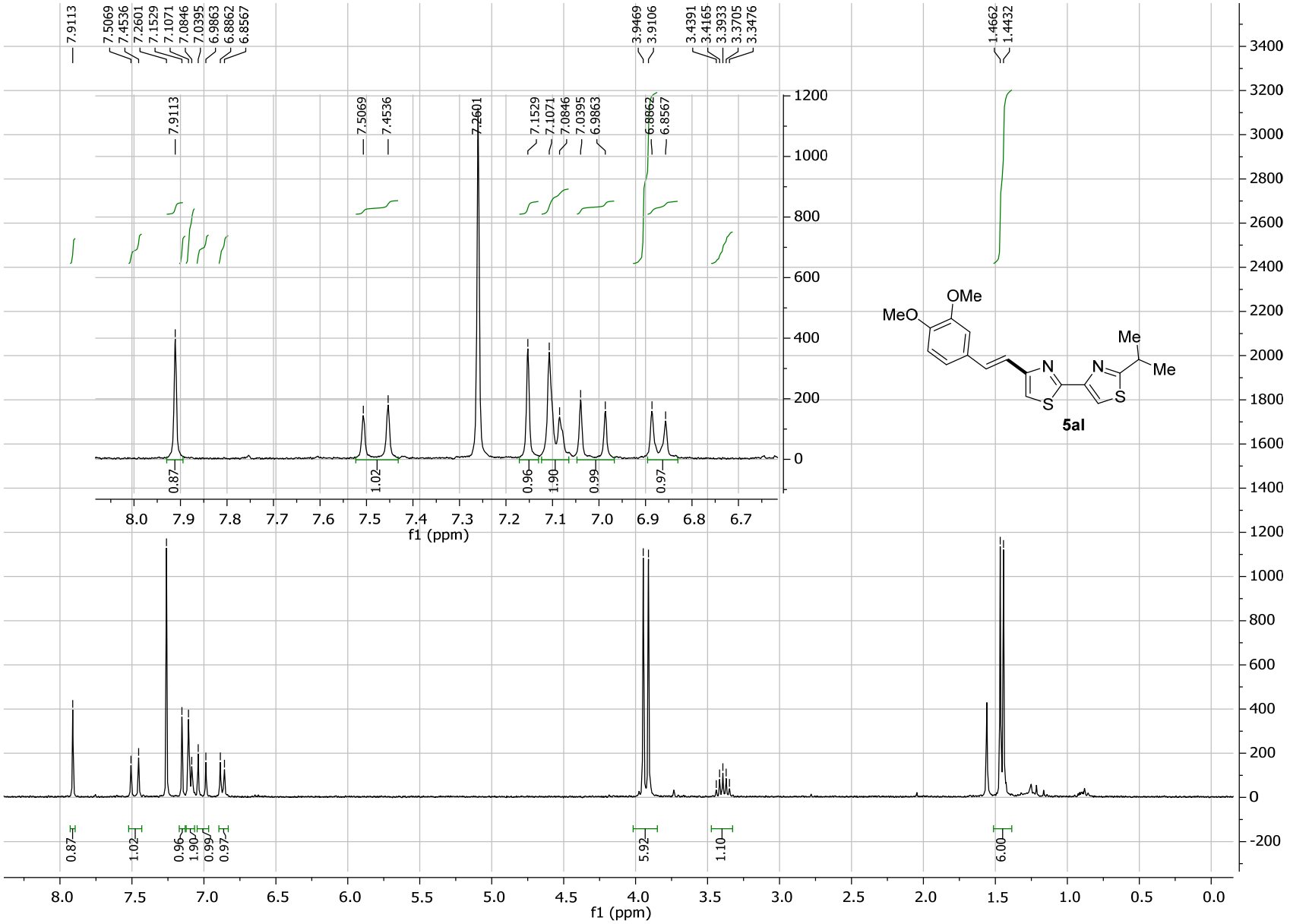

179.0109
163.8588
153.4936
148.4659
148.1330
144.0847
143.6470
143.1557
119.4033
115.4861
77.5835
77.3639
77.1602
76.7367
33.4923
23.2765
f1 (ppm)
Me
Me
N
N
N
N
S
S
5aF

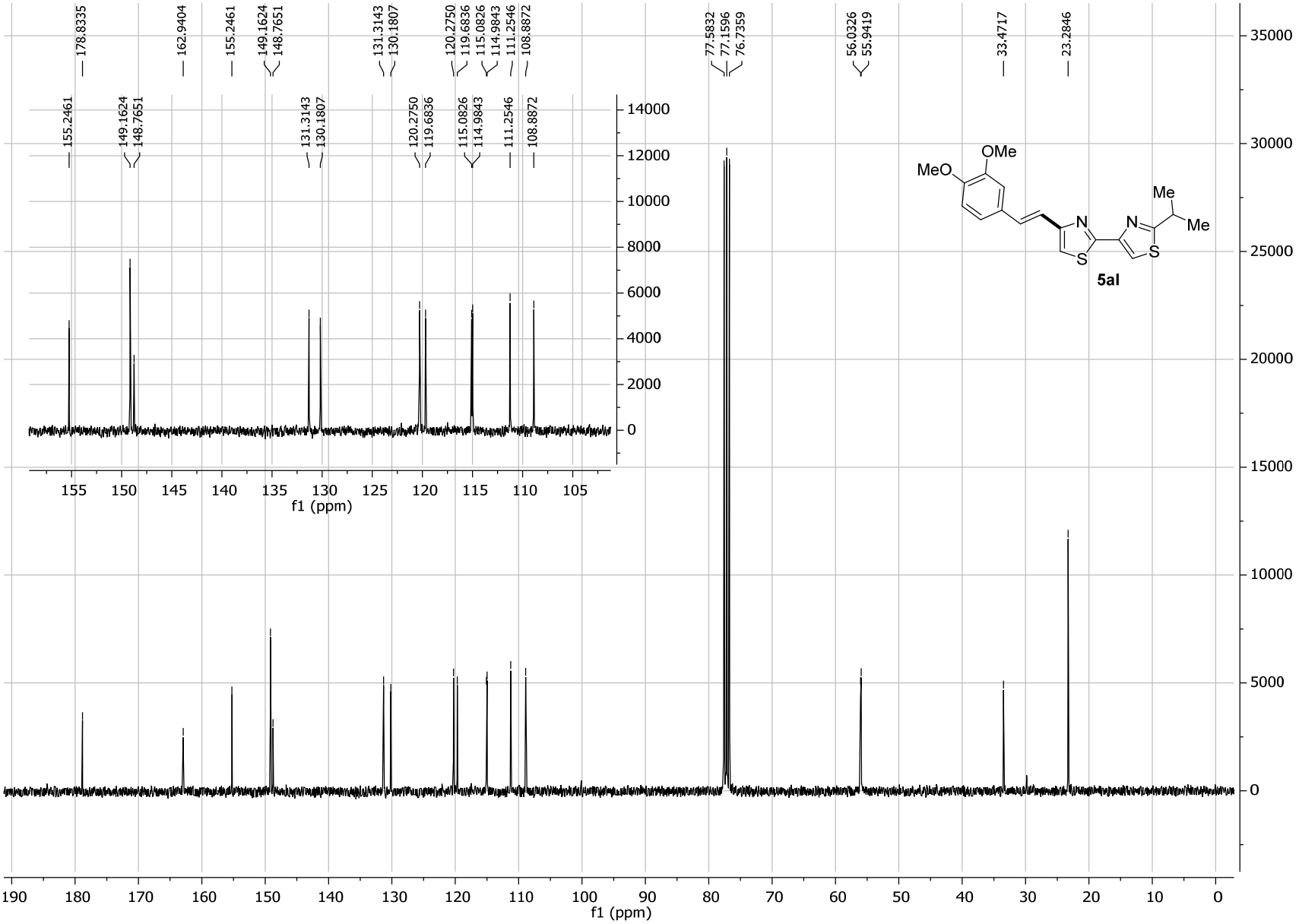

Feb20-2013.7.30.fid
PLM792 Pur
8.1911
8.1448
7.9344
7.2600
4.4864
4.4626
4.4388
4.4151
3.4205
3.3975
3.3745
3.3515
3.3285
1.4580
1.4350
1.4316
1.4077
EtO2C
N
S
N
N
S
S
Me
Me
5aG
f1 (ppm)
f1 (ppm)
0.89
0.87
0.89
2.00
1.09
9.17


Feb20-2013.738.fid
PLM792 Pur
179.0768
163.6089
163.5794
161.6046
149.1933
148.0416
148.0092
127.9239
117.9314
115.8057
77.5839
77.1604
76.7371
61.6938
33.4778
23.2433
14.5121
f1 (ppm)
EtO2C
N
S
N
N
S
S
Me
Me
5aG


Feb13-2014-PM02-H1
PLM802 Pur
7.9948
7.9900
7.9835
7.9663
7.9344
7.4927
7.4720
7.4665
7.4483
7.4436
7.4227
7.3781
7.3739
7.3697
7.3568
7.3496
7.3252
7.2603
3.4447
3.4217
3.3987
3.3757
3.3528
1.4727
1.4497
2.04
0.92
0.92
1.99
1.00
1.03
5.93
f1 (ppm)
Me
Me
N
N
S
S
5aH


Feb13-2014.941.fid
PLM802 Pur 13C
178.7834
162.9032
156.3522
148.9297
134.6223
128.8535
128.2578
126.5428
114.8771
113.4137
77.5830
77.3623
77.1596
76.7362
33.4951
23.3127
f1 (ppm)
Me
Me
N
N
S
S
5aH


7.9113
7.5069
7.4536
7.2601
7.1529
7.1071
7.0846
7.0395
6.9863
6.8862
6.8567
3.9469
3.9106
3.4391
3.4165
3.3933
3.3705
3.3476
1.4662
1.4432
0.87
1.02
0.96
1.90
0.99
0.97
5.92
1.10
6.00
f1 (ppm)
OMe
MeO
Me
Me
N
S
5al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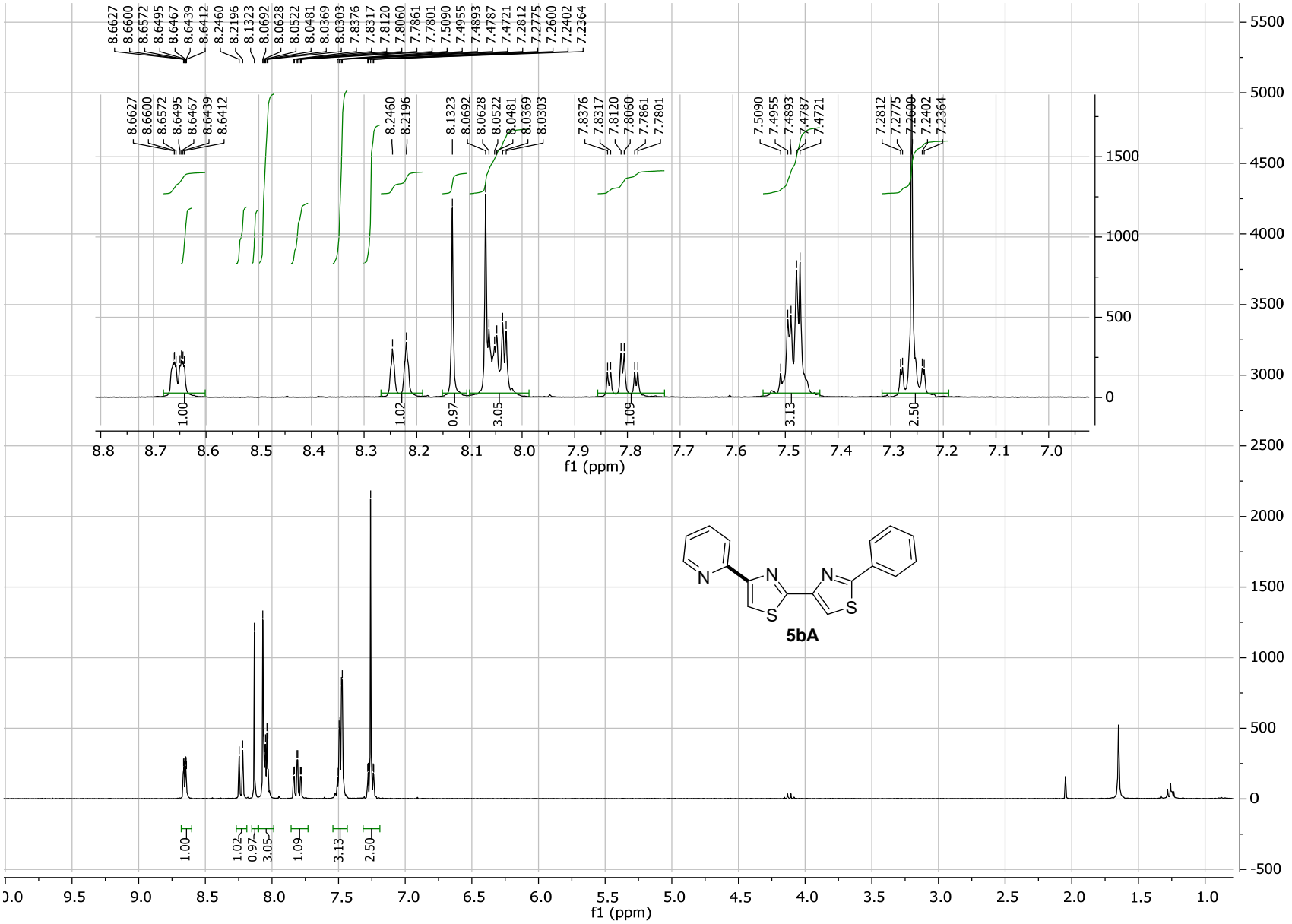
155.2461
149.1624
148.7651
131.3143
130.1807
120.2750
119.6836
115.0826
114.9843
111.2546
108.8872
77.5832
77.1596
76.7359
56.0326
55.9419
33.4717
23.2846
OMe
MeO
N
S
N
S
Me
Me
5al
f1 (ppm)
f1 (ppm)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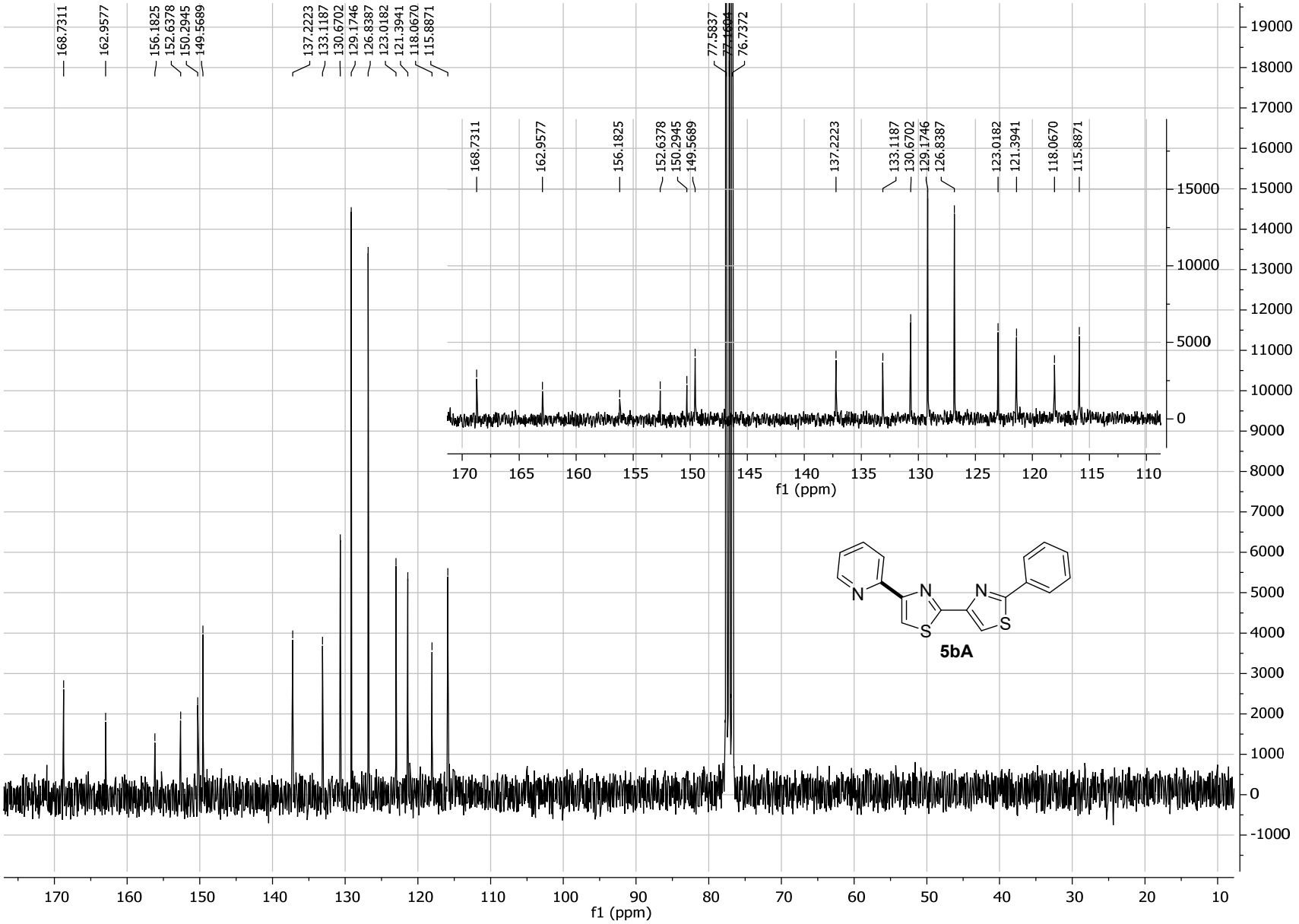
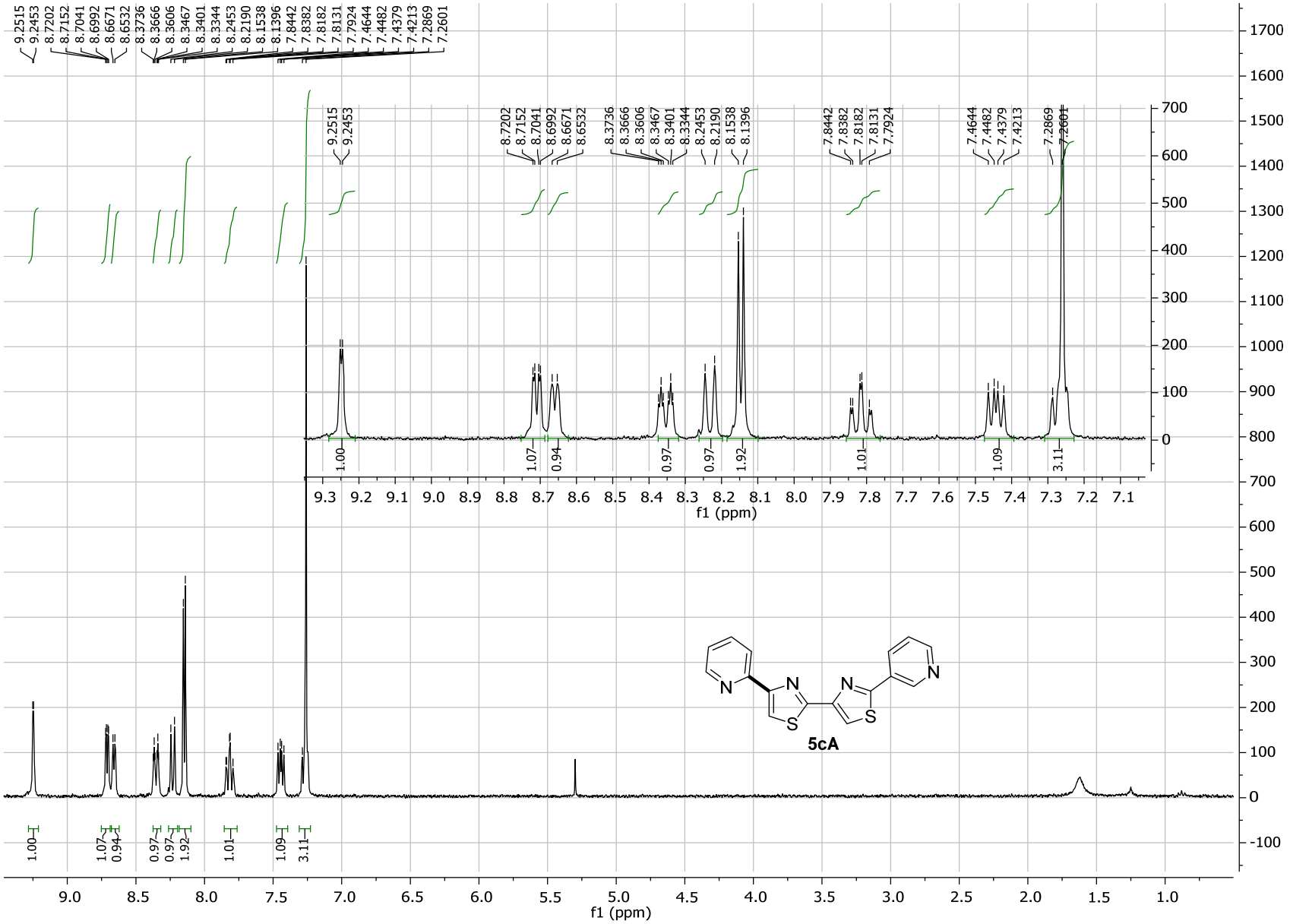
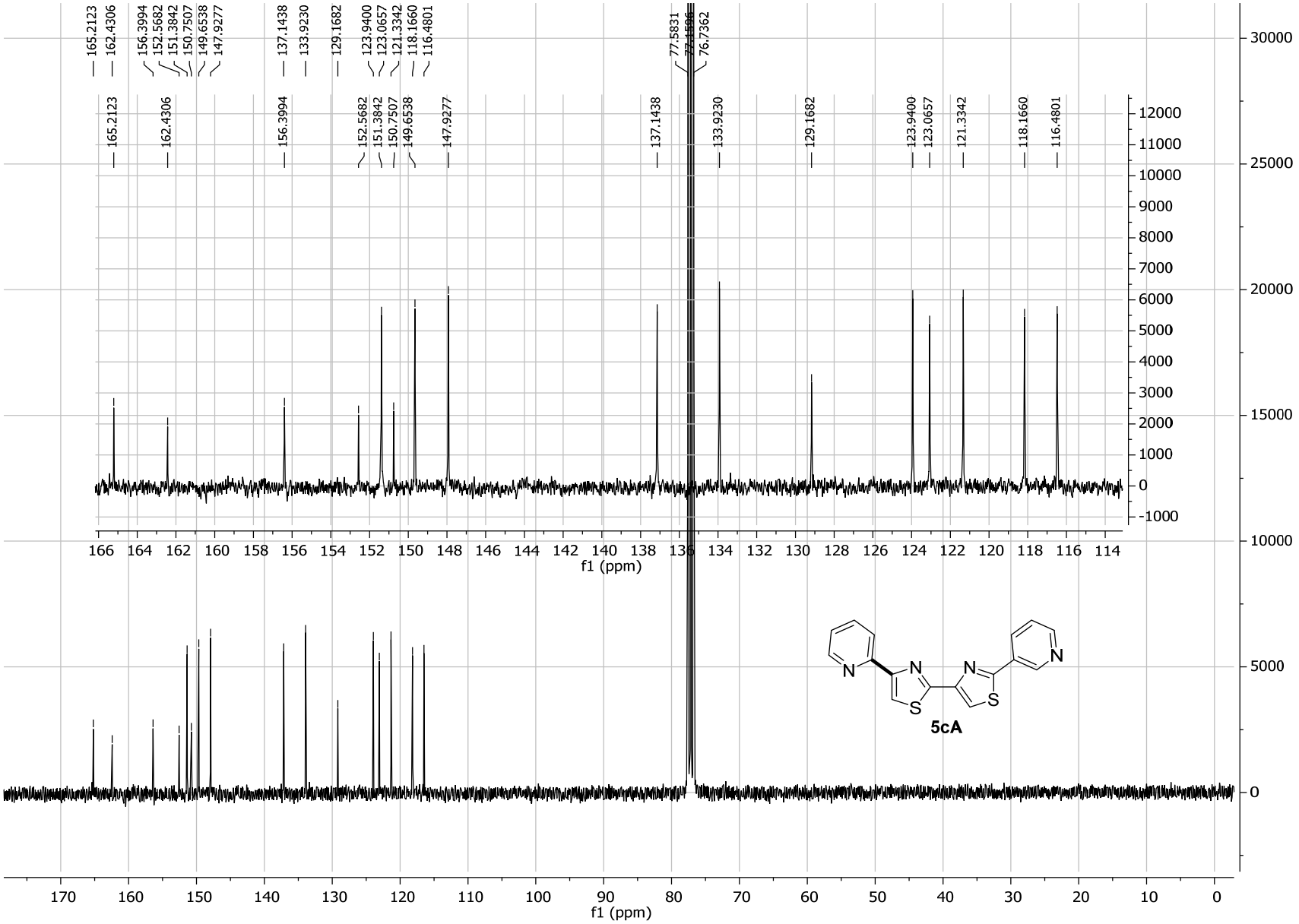
8.6600
8.6572
8.6495
8.6467
8.6439
8.6412
8.2460
8.2196
8.1323
8.0692
8.0628
8.0522
8.0481
8.0369
8.0303
7.8376
7.8317
7.8120
7.8060
7.7861
7.7801
7.5090
7.4955
7.4893
7.4787
7.4721
7.2812
7.2775
7.2600
7.2402
7.2364
1.00
1.02
0.97
3.05
1.09
3.13
2.50
f1 (ppm)
5bA


168.7311
162.9577
156.1825
152.6378
150.2945
149.5689
137.2223
133.1187
130.6702
129.1746
126.8387
123.0182
121.3941
118.0670
115.8871
77.5837
77.1804
76.7372
f1 (ppm)
N
N
N
S
S
5bA


9.2515
9.2453
8.7202
8.7152
8.7041
8.6992
8.6671
8.6532
8.3736
8.3666
8.3606
8.3467
8.3401
8.3344
8.2453
8.2190
8.1538
8.1396
7.8442
7.8382
7.8182
7.8131
7.7924
7.4644
7.4482
7.4379
7.4213
7.2869
7.2601
1.00
1.07
0.94
0.97
0.97
1.92
1.01
1.09
3.11
f1 (ppm)
5cA


165.2123
162.4306
156.3994
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151.3842
150.7507
149.6538
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137.1438
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129.1682
123.9400
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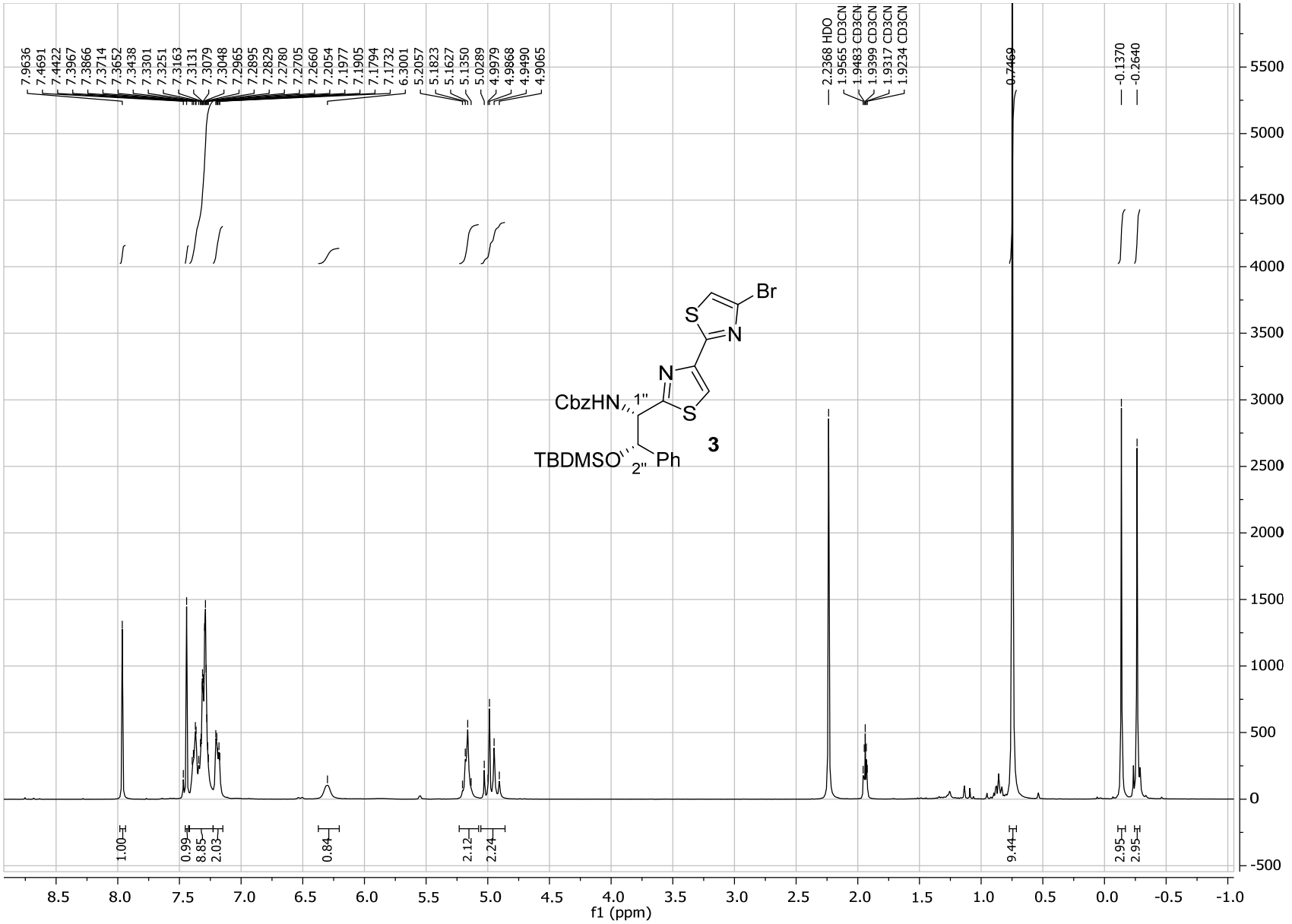
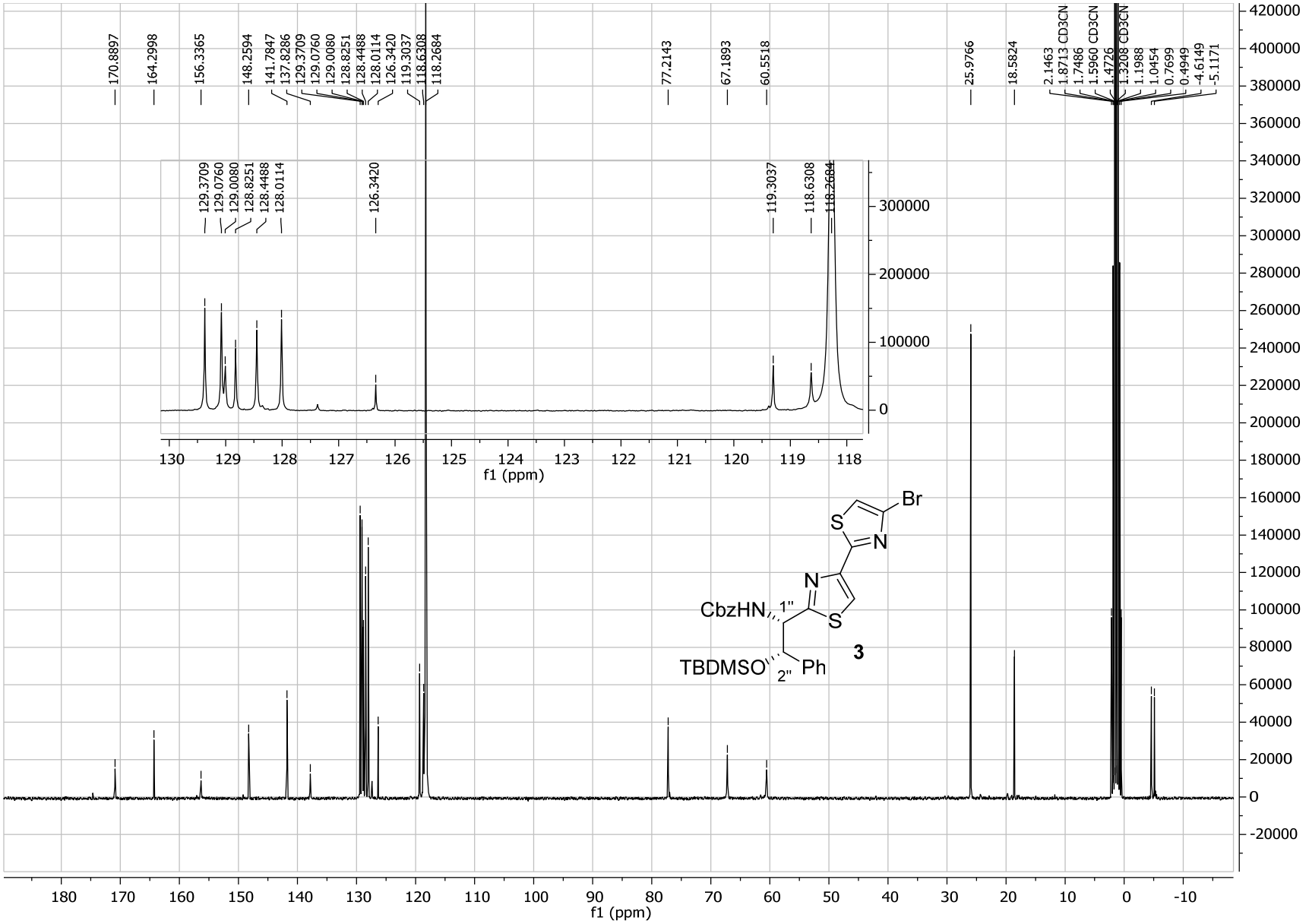
121.3342
118.1660
116.4801
77.5831
77.1596
76.7362
f1 (ppm)
5cA


7.9636
7.4691
7.4422
7.3967
7.3866
7.3714
7.3652
7.3438
7.3301
7.3251
7.3163
7.3131
7.3079
7.3048
7.2965
7.2895
7.2829
7.2780
7.2705
7.2660
7.2054
7.1977
7.1905
7.1794
7.1732
6.3001
5.2057
5.1823
5.1627
5.1350
5.0289
4.9979
4.9868
4.9490
4.9065
2.2368 HDO
1.9565 CD3CN
1.9483 CD3CN
1.9399 CD3CN
1.9317 CD3CN
1.9234 CD3CN
0.7469
-0.1370
-0.2640
Br
S
N
N
S
CbzHN
1"
TBDMSO
2"
Ph
3
1.00
0.99
8.85
2.03
0.84
2.12
2.24
9.44
2.95
2.95
f1 (ppm)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156.3365
148.2594
141.7847
137.8286
129.3709
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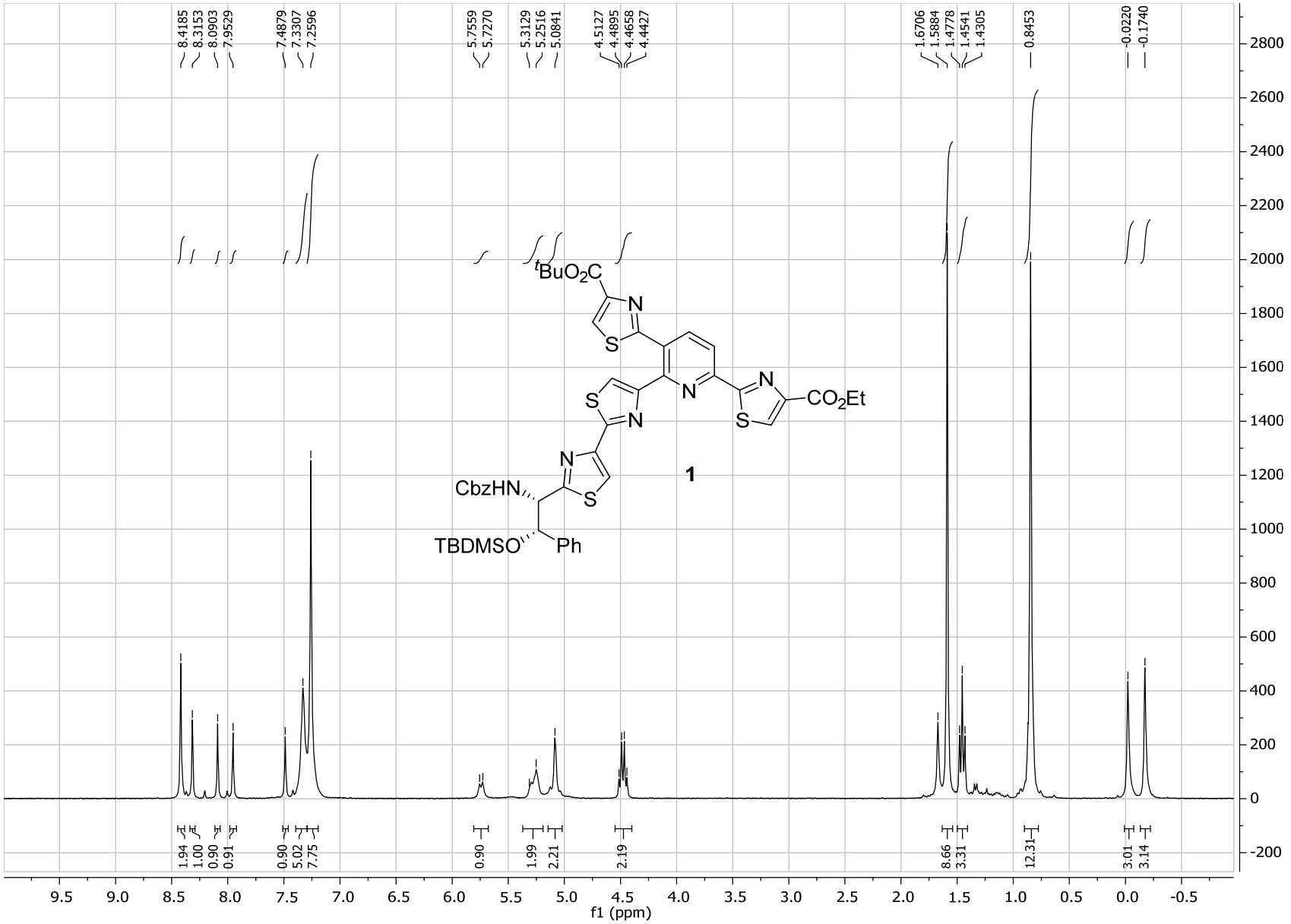
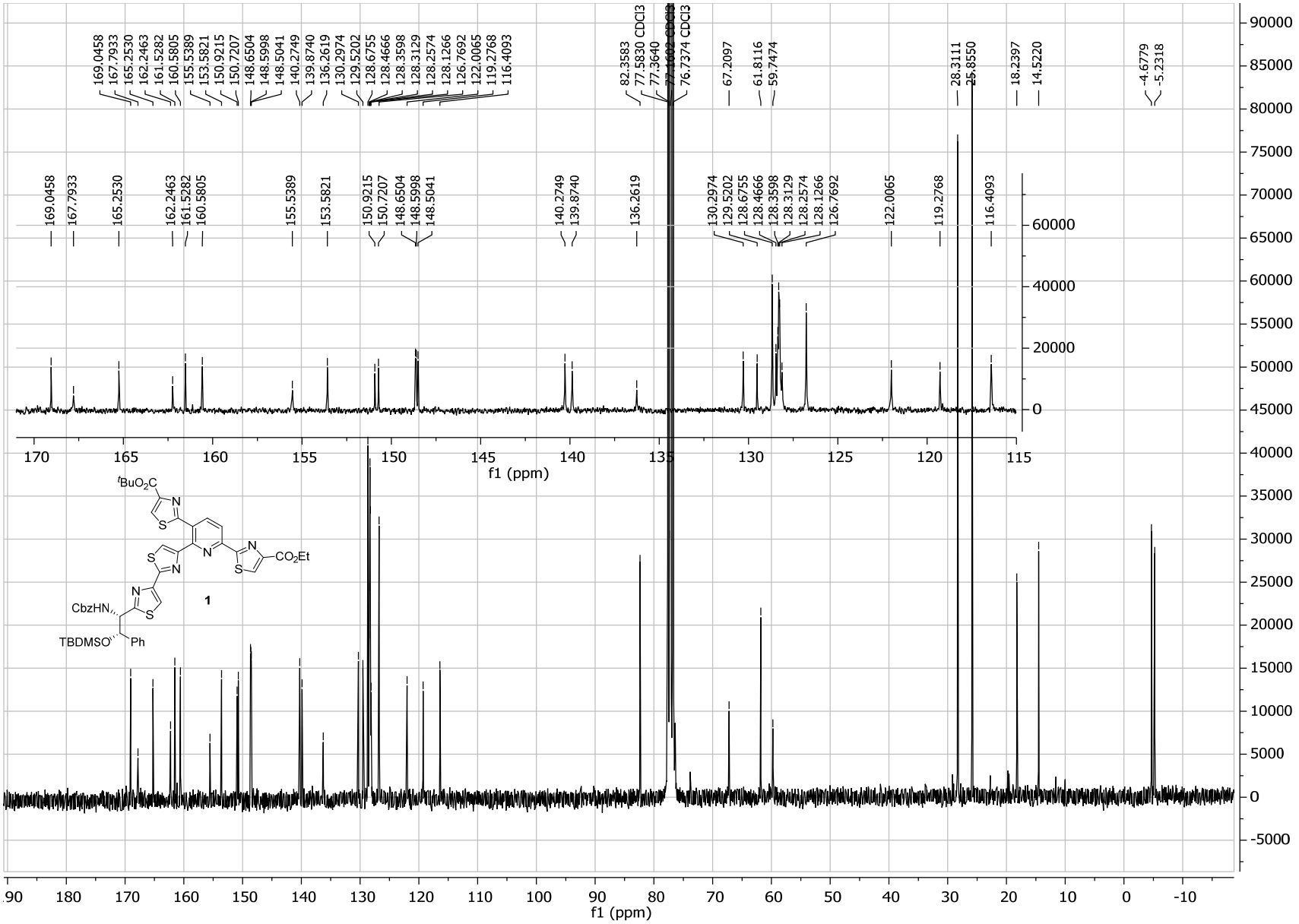
129.0080
128.8251
128.4488
128.0114
126.3420
119.3037
118.6308
118.2684
77.2143
67.1893
60.5518
25.9766
18.5824
2.1463
1.8713 CD3CN
1.7486
1.5960 CD3CN
1.4726
1.3208 CD3CN
1.1988
1.0454
0.7699
0.4949
-4.6149
-5.1171
f1 (ppm)
Br
S
N
N
S
CbzHN
1"
TBDMSO
2"
Ph
3


8.4185
8.3153
8.0903
7.9529
7.4879
7.3307
7.2596
5.7559
5.7270
5.3129
5.2516
5.0841
4.5127
4.4895
4.4658
4.4427
1.6706
1.5884
1.4778
1.4541
1.4305
0.8453
-0.0220
-0.1740
1.94
1.00
0.90
0.91
0.90
5.02
7.75
0.90
1.99
2.21
2.19
8.66
3.31
12.31
3.01
3.14
f1 (ppm)
1


169.0458
167.7933
165.2530
162.2463
161.5282
160.5805
155.5389
153.5821
150.9215
150.7207
148.6504
148.5998
148.5041
140.2749
139.8740
136.2619
130.2974
129.5202
128.6755
128.4666
128.3598
128.3129
128.2574
128.1266
126.7692
122.0065
119.2768
116.4093
82.3583
77.5830 CDCl3
77.3640
77.1602 CDCl3
76.7374 CDCl3
67.2097
61.8116
59.7474
28.3111
25.8550
18.2397
14.5220
-4.6779
-5.2318
f1 (ppm)
1
CbzHN
TBDMSO
Ph
CO2Et