Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Dynamic Kinetic Resolution in the Stereoselective Synthesis of 4,5-Diaryl Cyclic Sulfamidates by Using Chiral Rhodium-Catalyzed Asymmetric Transfer Hydrogenation

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General

All commercial reagents were used as obtained commercially unless otherwise noted. Reactions were performed using oven dried glassware under an atmosphere of nitrogen. Dichloromethane (DCM) was dried with CaH and distilled prior to use. Flash column chromatography was carried out on Fuji Chromatorex silica gel (38-75 μm). Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} plates. Visualization of the developed chromatogram was accomplished with UV light and by staining with ethanolic phosphomolybdic acid (PMA) solution followed by heating.

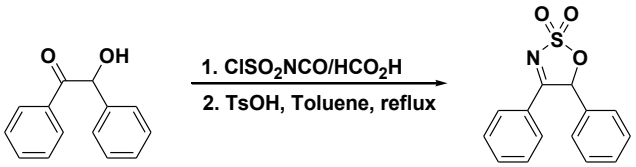
Nuclear magnetic resonance (NMR) spectra were recorded using Bruker 500 MHz NMR instrument (^{1}H NMR at 500 MHz and ^{13}C NMR at 125 MHz) or Bruker 300 MHz NMR instrument (^{1}H NMR at 300 MHz and ^{13}C NMR at 75 MHz). ^{1}H NMR data are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, coupling constants (Hz). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High performance liquid chromatography (HPLC) was carried out on a Perkin Elmer series 200 HPLC equipped with a Chiralcel OD-H or Chiralcel AD-H column. Specific rotations were measured on a Rudolph Autopol IV (Automatic polarimeter). High-resolution mass spectra and elemental analysis were obtained from the center for chemical analysis in Korea Research Institute of Chemical Technology.

The formic acid/triethylamine (molar ratio = 5/2) azeotrope was prepared by the distillation of the mixtures, according to the literature procedure.[1]

(1*R*,2*S*)-(-)-2-Amino-1,2-diphenylethanol (99%), (1*S*,2*R*)-(+)-2-Amino-1,2-diphenylethanol (99%), and (1*R*,2*R*)-(+)-2-Amino-1,2-diphenylethanol (99.5%) were purchased from Aldrich Chemistry.

Chiral catalysts, (*R,R*)-Rh-**1**:[2] RhCl[(*R,R*)-TsDPEN]Cp*, (*R,R*)-Ir-**2**:[3] IrCl[(*R,R*)-TsDPEN]Cp*, (*R,R*)-Ru-**3**:[4] RuCl[(*R,R*)-TsDPEN](η^6-*p*-cymene), were prepared according to the literature procedures.

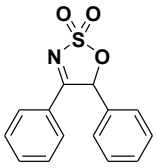
1. General procedure for the synthesis of cyclic imine (6) from benzoin



Benzoin 6a

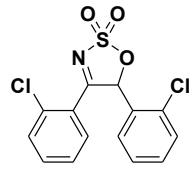
Formic acid (420 μL, 11.0 mmol) was added dropwise to neat chlorosulfonyl isocyanate (960 μL, 11.0 mmol) at 0 ^{0}C with rapid stirring. Vigorous gas evolution was observed during the addition process. The resulting viscous suspension was stirred for 5min at 0 ^{0}C during which time the mixture solidified. DMA (*N,N*-dimethyl acetamide, 11 mL) was added and the solution was stirred for 30min at room temperature. The reaction mixture was cooled to 0 ^{0}C and a solution of benzoin (1g, 7.3 mmol) in DMA (7 ml) was added dropwise. After stirring at room temperature for 1-2 h, the reaction mixture was diluted with EtOAc (30 mL) and washed with brine. The solvent was removed to provide the mixture of cyclic imine (**6a**), uncyclized sulfamidate ketone, and byproduct, α-chloride ketone. Then *p*-toluenesulfonic acid (0.1 eq) and toluene were added, and the reaction mixture was heated to reflux temperature for 1-2 h with azeotropic removal of water (This step can be carried out in the air without special handling). The solvent was evaporated, and the residue was purified by column chromatography to give the desired imine (**6a**). This procedure was applied to the synthesis of **6a**~**6m** except for **6b**.

4,5-Diphenyl-5*H*-[1,2,3]oxathiazole 2,2-dioxide (6a)



White solid, yield: 73%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85-7.84 (d, 2H, J = 3.6 Hz), 7.83 (t, 1H, J = 1.2 Hz), 7.61-7.39 (m, 7H), 6.67 (ds, 1H, J = 1.5 Hz).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.4, 135.3, 132.8, 131.0, 130.4, 129.9, 129.4, 128.7, 127.3, 89.9.; HRMS (EI): m/z calcd for $C_{14}H_{11}NO_3S$ 273.0457, found 273.0455.

4,5-Bis-(2-chloro-phenyl)-5*H*-[1,2,3]oxathiazole 2,2-dioxide (6b)

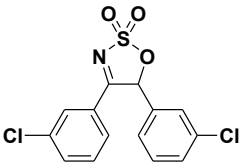


The yield of **6b** from 1,2-bis-(2-chloro-phenyl)-2-hydroxy-ethanone and $ClSO_2NH_2$ according to the general procedure for the synthesis of **6a** was very low. Therefore **6b** was prepared by another method: 1,2-bis-(2-chloro-phenyl)-2-hydroxy-ethanone (300 mg, 1.1 mmol) and $NH_2SO_2NH_2$ (154 mg, 1.6 mmol) in 3 mL of xylene were refluxed for 3 hr. The reaction mixture was concentrated to dryness and the residue was diluted with EtOAc. The solution was washed

with water and then brine. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was purified by silica gel column chromatography (hexane/EtOAc = 10/1) to give 138 mg (40%) of **6b**.

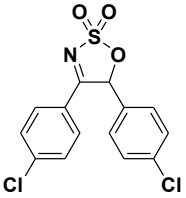
White solid, yield: 40%, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, 1H, *J* = 7.8 Hz), 7.35-7.52 (m, 6H), 7.24-7.30 (m, 2H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.17, 134.68, 134.43, 133.86, 132.14, 131.66, 131.38, 130.47, 129.77, 128.95, 128.00, 127.48, 127.10, 87.34.; HRMS (EI): m/z calcd for $C_{14}H_9Cl_2NO_3S$ 340.9680, found 340.9705.

4,5-Bis-(3-chloro-phenyl)-5*H*-[1,2,3]oxathiazole 2,2-dioxide (6c)



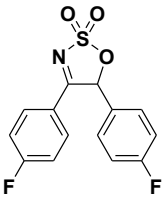
White solid, yield: 66%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (m, 1H), 7.64-7.58 (m, 2H), 7.47-7.37 (m, 4H), 7.30-7.26 (m, 1H), 6.58 (ds, 1H, *J* = 2.1 Hz).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.7, 136.0, 135.98, 135.5, 134.0, 131.5, 131.4, 130.1, 128.7, 128.6, 128.3, 126.7, 88.6.; HRMS (EI): m/z calcd for $C_{14}H_9Cl_2NO_3S$ 340.9680, found 340.9702.

4,5-Bis-(4-chloro-phenyl)-5*H*-[1,2,3]oxathiazole 2,2-dioxide (6d)



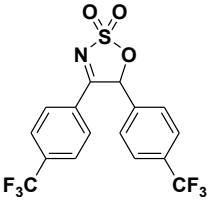
White solid, yield: 66%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79-7.74 (m, 2H), 7.44-7.32 (m, 6H), 6.64 (ds, 1H, *J* = 3.9 Hz).; ^{13}C NMR (75 MHz, $CDCl_3$) 175.1, 142.4, 137.6, 131.6, 130.9, 130.4, 130.0, 130.0, 125.4, 88.7.; HRMS (EI): m/z calcd for $C_{14}H_9Cl_2NO_3S$ 340.9680, found 340.9700.

4,5-Bis-(4-fluoro-phenyl)-5*H*-[1,2,3]oxathiazole 2,2-dioxide (6e)



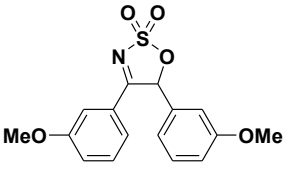
White solid, yield: 67%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89-7.84 (m, 2H), 7.42-7.38 (m, 2H), 7.16-7.10 (m, 4H), 6.64 (s, 1H).; ^{13}C NMR (125 MHz, DMSO) 177.2, 167.2, (165.1), 164.1, (162.1), 133.6, (133.5), 131.2, (131.1), 129.2, (129.17), 123.3, (123.25), 117.0, (116.9), 116.86, (116.7), 89.1.; HRMS (EI): m/z calcd for $C_{14}H_9F_2NO_3S$ 309.0271, found 309.0270.

4,5-Bis-(4-trifluoromethyl-phenyl)-5*H*-[1,2,3]oxathiazole 2,2-dioxide (6f)



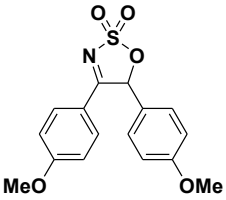
White solid, yield: 52%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97-7.94 (m, 2H), 7.73-7.71 (m, 4H), 7.57-7.55 (m, 2H), 6.77 (ds, 1H, *J* = 3.0 Hz).; ^{13}C NMR (75 MHz, $CDCl_3$) 177.3, 136.4, 134.5, (134.1, 133.7, 131.6, 131.1. (130.7), 130.2, 129.6, 126.8, (126.7), 126.4, (126.35), 125.4, (125.0), 121.8, (121.4), 89.0.; HRMS (EI): m/z calcd for $C_{16}H_9F_6NO_3S$ 409.0207, found 409.0217.

4,5-Bis-(3-methoxy-phenyl)-5*H*-[1,2,3]oxathiazole 2,2-dioxide (6g)



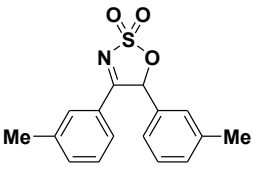
White solid, yield: 87%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.37-7.26 (m, 3H), 7.13-7.12 (m, 1H), 7.01-7.69 (m, 3H), 6.59 (s, 1H), 3.80 (s, 3H), 3.78 (s, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) 176.3, 160.6, 160.0, 134.1, 131.0, 130.3, 128.4, 123.0, 122.1, 120.8, 116.5, 114.2, 113.9, 89.9, 55.6, 55.5.; HRMS (EI): m/z calcd for $C_{16}H_{15}NO_5S$ 333.0671, found 333.0674.

4,5-Bis-(4-methoxy-phenyl)-5*H*-[1,2,3]oxathiazole 2,2-dioxide (6h)



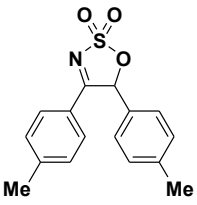
White solid, yield: 56%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94-7.91 (m, 2H), 7.41-7.38 (m, 2H), 6.90-6.86 (m, 4H), 6.29 (s, 1H), 3.87 (s, 3H), 3.77 (s, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) 190.1, 164.0, 160.2, 131.6, 129.9, 128.4, 127.2, 114.6, 114.1, 62.2, 55.6, 55.4.; HRMS (EI): m/z calcd for $C_{16}H_{15}NO_5S$ 333.0671, found 333.0675.

4,5-Bis-(3-methyl-phenyl)-5*H*-[1,2,3]oxathiazole 2,2-dioxide (6i)



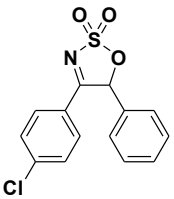
White solid, yield: 60%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.55-7.52 (d, 1H, J = 7.8 Hz), 7.40-7.37 (d, 1H, J = 7.8 Hz), 7.33-7.19 (m, 5H), 6.60 (s, 1H), 2.34 (s, 6H).; ^{13}C NMR (75 MHz, $CDCl_3$) 176.7, 139.9, 139.5, 136.2, 132.8, 131.8, 130.8, 129.7, 129.2, 129.1, 127.6, 127.2, 125.8, 90.1, 21.5, 21.4.; HRMS (EI): m/z calcd for $C_{16}H_{15}NO_3S$ 301.0773, found 301.0780.

4,5-Bis-(4-methyl-phenyl)-5*H*-[1,2,3]oxathiazole 2,2-dioxide (6j)



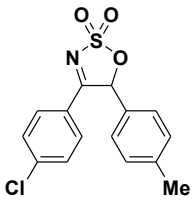
White solid, yield: 67%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74-7.71 (d, 2H, J = 8.4 Hz), 7.29-7.19 (m, 6H), 6.61 (s, 1H), 2.38 (s, 3H), 2.34 (s, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) 176.3, 146.8, 141.3, 130.5, 130.5, 130.1, 130.1, 128.6, 124.6, 88.8, 22.1, 21.5.; HRMS (EI): m/z calcd for $C_{16}H_{15}NO_3S$ 301.0773, found 301.0776.

4-(4-Chloro-phenyl)-5-phenyl-5*H*-[1,2,3]oxathiazole 2,2-dioxide (6k)



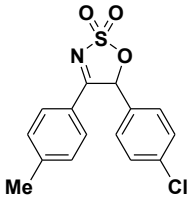
White solid, yield: 80%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80-7.76 (m, 2H), 7.45-7.32 (m, 7H), 6.64 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 175.3, 142.1, 132.5, 131.6, 131.2, 130.1, 129.9, 128.7, 125.7, 89.7.; HRMS (EI): m/z calcd for $C_{14}H_{10}ClNO_3S$ 307.0070, found 307.0078.

4-(4-Chloro-phenyl)-5-(4-methyl-phenyl)-5*H*-[1,2,3]oxathiazole 2,2-dioxide (6l)



White solid, yield: 60%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79-7.76 (m, 2H), 7.40-7.37 (m, 2H), 7.28-7.20 (m, 4H), 6.60 (s, 1H), 2.35 (s, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) 175.6, 142.0, 141.6, 131.6, 130.7, 129.8, 129.4, 128.6, 125.7, 89.8, 21.4.; HRMS (EI): m/z calcd for $C_{15}H_{12}ClNO_3S$ 321.0226, found 321.0230.

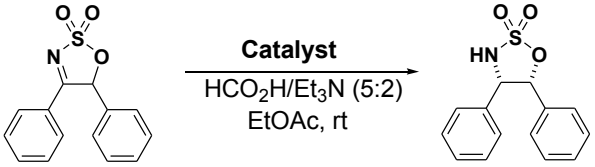
4-(4-Methyl-phenyl)-5-(4-chloro-phenyl)-5*H*-[1,2,3]oxathiazole 2,2-dioxide (6m)



White solid, yield: 88%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72-7.69 (d, 2H, J = 8.4 Hz), 7.40-7.32 (m, 4H), 7.24-7.21 (d, 2H, J = 8.1 Hz), 6.64 (s, 1H), 2.38 (s, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) 175.8, 147.1, 137.1, 131.4, 130.3, 130.2, 031.0, 129.9, 124.1, 88.6, 22.0.; HRMS (EI): m/z calcd for $C_{15}H_{12}ClNO_3S$ 321.0226, found 321.0230.

2. Optimization of the ATH-DKR reaction of 6a

2-1. ATH-DKR reaction of **6a** with various catalysts[a]



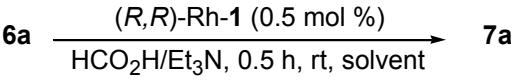
Entry	catalyst		rxn time (h)	yield (%)[b]	dr (*cis/trans*)[c]	ee(%)[d]	config[e]
1	(*R,R*)-Rh-**1**	0.5 mol %	0.5	99.0	>20:1	98.0	4*S*,5*R*
2	(*R,R*)-Ir-**2**	0.5 mol %	1	91.1	>20:1	28.2	4*S*,5*R*
3	(*R,R*)-Ru-**3**	0.5 mol %	12	85.5	>20:1	89.5	4*S*,5*R*
4	(*R,R*)-Rh-**1**	0.1 mol %	3	>99[f]	>20:1	99.0	4*S*,5*R*
5	(*R,R*)-Rh-**1**	0.05 mol %	15	94[f]	>20:1	98.0	4*S*,5*R*

[a] **6a** (0.1 mmol) in 1.0 mL of EtOAc with 0.1 mL of HCO_2H/Et_3N (5:2) azeotropic mixture, catalyst (0.5 ~ 0.1 mol %) at 25 ^{0}C. [b] Isolated yields. [c] Only a single diastereomer was detected in the ^{1}H-NMR of the crude reaction mixture. [d] ee was determined by chiral HPLC. [e] Determined by X-ray crystallography. [f] Determined by ^{1}H-NMR analysis.

Imine **6a** (0.25 mmol) and RhCl[(*R,R*)-TsDPEN]Cp*, (*R,R*)-Rh-**1**, (0.5 mol %) were place in round bottom flask. To this mixture, solvent (2.5 mL) was added and then an azeotropic mixture

of HCO_2H/Et_3N (molar ratio = 5/2, 250 μL) were added via a syringe. After stirring at room temperature for 0.5 h, the reaction mixture was diluted with EtOAc (5 mL) and washed with water (3 × 3 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and evaporated. The analysis of crude ^{1}H-NMR showed no imine **6a** was remained. % ee was determined by chiral HPLC analysis. (Chiralcel AD-H, 20% isopropanol/hexanes, 1.0 mL/min, 215 nm, tr(major) = 7.8 min, tr(minor) = 9.0 min)

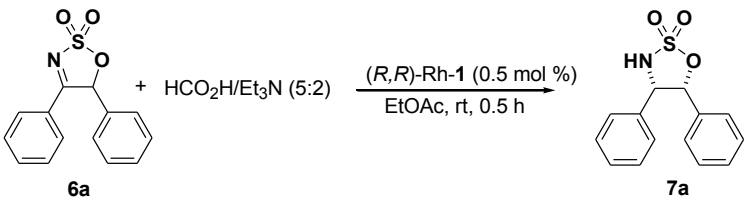
2-2. ATH-DKR reaction of 6a in various solvents[a]



Entry	solvent	convn(%)[b]	dr[c]	ee(%)[d]	config[e]
1	EtOAc	>99	>20:1	98.0	4*S*,5*R*
2	CH_2Cl_2	>99	>20:1	88.2	4*S*,5*R*
3	THF	>99	>20:1	96.1	4*S*,5*R*
4	DMF	>99	>20:1	83.5	4*S*,5*R*
5	MeOH	66[f]	>20:1	93.7	4*S*,5*R*
6	Toluene	>99	>20:1	81.1	4*S*,5*R*
7	CH_3CN	>99	>20:1	92.8	4*S*,5*R*
8	neat (no solvent)[g]	>99(89)[h]	>20:1	96.6	4*S*,5*R*

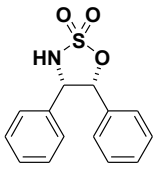
[a] **6a** (0.1 mmol) in 1 mL of solvent with 0.1 mL HCO_2H/Et_3N (5:2) azeotropic mixture, (*R,R*)-Rh-**1** 0.5 mol %, at 25 ^{0}C for 0.5 h. [b]Determined by ^{1}H-NMR analysis. [c]Only a single diastereomer was detected in the ^{1}H-NMR of the crude reaction mixture. [d]e.e. was determined by HPLC analysis. [e]Determined by X-ray crystallography. [f]Reaction time: 2 h. [g]**6a**:HCO_2H:Et_3N = 1:2:2. [h]Isolated yield in parentheses.

3. General procedure for asymmetric transfer hydrogenation of imines (6):



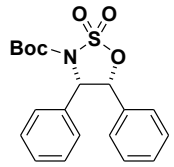
Imine **6a** (136.7 mg, 0.5 mmol) and RhCl[(*R,R*)-TsDPEN]Cp*, (*R,R*)-Rh-**1**, (1.6 mg, 0.5 mol %) were placed in round bottom flask. To this mixture, EtOAc (5 mL) was added and then an azeotropic mixture of HCO_2H/Et_3N (molar ratio = 5/2, 500 μL) were added via a syringe. After stirring at room temperature for 0.5 h, the reaction mixture was diluted with EtOAc (5 mL) and washed with water (3 × 3 mL). The organic layer was dried over anhydrous $MgSO_4$ and then the residue was purified by column chromatography on silica gel to give the desired cyclic sulfamidate **7a**. (For all compounds in Table 2, only a single diastereomer was detected in the ^{1}H-NMR of the respective crude reaction mixture.)

4,5-Diphenyl-[1,2,3]oxathiazolidine 2,2-dioxide, (4*S*,5*R*)-7a



White solid, yield: 99%; 98.0% ee (Chiralcel AD-H, 20% isopropanol/hexanes, 1.0 mL/min, 215 nm, tr(major) = 7.8 min, tr(minor) = 9.0 min); $[\alpha]_D^{19}$ = -9.3 (c 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19-7.11 (m, 6H), 7.00-6.97 (m, 4H), 6.11 (d, 1H, *J* = 6.0 Hz), 5.29 (t, 1H, *J* = 6 Hz), 5.24 (br, s, 1H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.8, 132.3, 129.1, 128.9, 128.6, 128.3, 127.5, 126.5, 87.4, 64.8.; HRMS (EI): m/z calcd for $C_{14}H_{13}NO_3S$ 275.0616, found 275.0637.; Anal. Calcd for $C_{14}H_{13}NO_3S$: C, 61.07; H, 4.76; N, 5.09; S, 11.65; found: C, 60.34; H, 4.83; N, 5.00; S, 11.48.

(4*S*,5*R*)-*N-Boc*-4,5-diphenyl)-[1,2,3]oxathiazolidine 2,2-dioxide, (4*S*,5*R*)-*N-Boc*-7a:

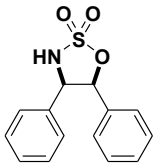


To a solution of (4*S,5R*)-**7a** (39 mg, 0.14 mmol) and di-*tert*-butyldicarbonate (61.1 mg, 0.28 mmol) in dichloromethane (1 mL) was added catalytic amount of DMAP (0.001 mmol), and the mixture was stirred for 1 h at room temperature. Then, the reaction mixture was diluted with dichloromethane (5 ml) and washed with saturated aqueous $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, and evaporated. The residue was purified by flash chromatography on silica gel (Hex/EtOAc=3:1) to give 44.6 mg (85% yield) of (4*S,5R*)-*N-Boc*-**7a**.

White solid, 97.6% ee (Chiralpak OD-H, 5% isopropanol/ hexanes, 1.0 mL/min, 215 nm, t_r(minor) = 9.7 min, t_r(major) = 11.3 min); $[\alpha]_D^{30}$ = -145.9 (*c* 0.30, $CHCl_3$);^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12-7.21 (m, 6H), 7.04-7.07 (m, 2H), 6.92-6.94 (m, 2H), 6.17 (d, 1H, *J* = 6.0 Hz), 5.43 (d, 1H, J = 6.0 Hz), 1.49 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ148.2, 133.5, 130.5, 129.3, 128.5, 128.4, 128.3, 127.2, 126.3, 85.7, 83.3, 66.6, 27.9. HRMS (EI): m/z calcd for $C_{19}H_{21}NO_5S$ 375.1140, found 375.1132.

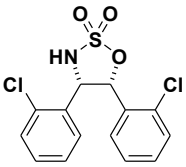
This product is identical with the (4*S*,5*R*)-**14**, which is derived from (1*S*,2*R*)-**11**, judged from ^{1}H-NMR, ^{13}C-NMR, optical rotation, and ciral HPLC (See 7-1).

4,5-Diphenyl-[1,2,3]oxathiazolidine 2,2-dioxide, (4*R*,5*S*)-7a



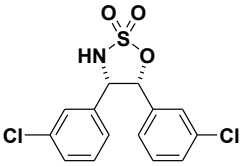
This compound was prepared from imine **6a** by using essentially the same reaction procedure for **(4*S*,5*R*)-7a** but, instead using the (*S,S*)-Rh-**1** catalyst. White solid, yield: 99%; 97.4% ee (Chiralcel AD-H, 20% isopropanol/hexanes, 1.0 mL/min, 215 nm, tr(minor) = 7.1 min, tr(major) = 8.1 min); $[\alpha]_D^{19}$ = +8.0 (c 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17-7.15 (m, 6H), 7.00 (br, s, 4H), 6.11 (d, 1H, *J* = 5.9 Hz), 5.29 (t, 1H, *J* = 5.4 Hz), 5.24 (br, s, 1H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.8, 132.3, 129.1, 128.9, 128.6, 128.3, 127.5, 126.5, 87.4, 64.8.; HRMS (EI): m/z calcd for $C_{14}H_{13}NO_3S$ 275.0616, found 275.0616.

4,5-Bis-(2-chloro-phenyl)-[1,2,3]oxathiazolidine 2,2-dioxide, (4*S*,5*R*)-7b



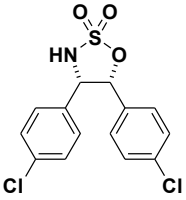
White solid, yield: 99%; 21.8% ee (Chiralcel AD-H, 20% isopropanol/hexanes, 1.0 mL/min, 215 nm, tr(major) = 5.0 min, tr(minor) = 5.7 min); $[\alpha]_D^{22}$ = -16.3 (c 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CHCl_3$) δ 7.53-7.54 (m, 1H), 7.03-7.22 (m, 6H), 7.02-7.03 (m, 1H), 6.64 (d, 1H, *J* = 6.1 Hz), 5.96 (t, 1H, *J* = 5.8 Hz), 5.28 (d, 1H, *J* = 5.4 Hz).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.71, 133.04, 131.73, 130.38, 130.01, 129.39, 129.24, 129.10, 128.34, 127.00, 126.46, 83.08, 59.89.; Anal. Calcd for $C_{14}H_{11}Cl_2NO_3S$: C, 48.85; H, 3.22; N, 4.07; S, 9.32; found: C, 49.32; H, 3.22; N, 3.91; S, 9.15.

4,5-Bis-(3-chloro-phenyl)-[1,2,3]oxathiazolidine 2,2-dioxide, (4*S*,5*R*)-7c



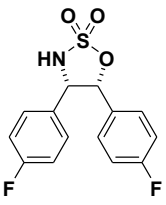
White solid, yield: 99%; 99.9% ee (Chiralcel AD-H, 5% isopropanol/hexanes, 1.0 mL/min, 215 nm, tr(major) = 33.6 min, tr(minor) = 37.9 min); $[\alpha]_D^{22}$ = -19.7 (c 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CHCl_3$) δ 7.26-6.89 (m, 8H), 6.05 (br, s, 1H), 5.25 (br, s, 2H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ135.6, 134.6, 134.5, 133.8, 129.8, 129.6, 129.4, 129.1, 127.5, 126.5, 125.4, 124.4, 85.7, 63.8.; Anal. Calcd for $C_{14}H_{11}Cl_2NO_3S$: C, 48.85; H, 3.22; N, 4.07; S, 9.32; found: C, 49.04; H, 3.30; N, 3.95; S, 9.23.

4,5-Bis-(4-chloro-phenyl)-[1,2,3]oxathiazolidine 2,2-dioxide, (4S,5*R*)-7d



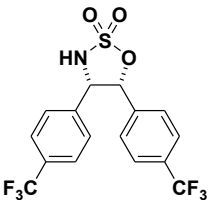
White solid, yield: 99%; 99.4% ee (Chiralcel AD-H, 20% isopropanol/hexanes, 1.0 mL/min, 215 nm, tr(major) = 7.3 min, tr(minor) = 8.9 min); $[\alpha]_D^{22}$ = -36.8 (c 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17-7.13 (m, 4H), 6.98-6.91 (m, 4H), 6.08 (d, 1H, *J* = 6.3 Hz), 5.62 (br, s, 1H), 5.26 (br, s, 1H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.5, 135.2, 132.2, 130.5, 129.0, 128.9, 128.8, 127.9, 86.4, 64.1.; Anal. Calcd for $C_{14}H_{11}Cl_2NO_3S$: C, 48.85; H, 3.22; N, 4.07; S, 9.32; found: C, 48.65; H, 3.29; N, 3.76; S, 9.10.

4,5-Bis-(4-fluoro-phenyl)-[1,2,3]oxathiazolidine 2,2-dioxide, (4*S*,5*R*)-7e



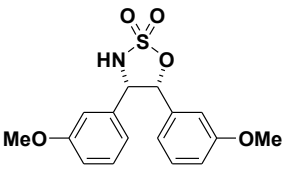
White solid, yield: 94%; 98.5% ee (Chiralcel AD-H, 20% isopropanol/hexanes, 1.0 mL/min, 215 nm, tr(major) = 6.9 min, tr(minor) = 8.4 min); $[\alpha]_D^{21}$ = -20.0 (c 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04-6.83 (m, 8H), 6.15 (d, 1H, *J* = 4.8 Hz), 6.08 (d, 1H, *J* = 6.3 Hz), 5.26 (d, 1H, *J* = 6.1 Hz).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7, (164.5), 161.4, (161.2), 129.8, (129.79), 129.4, (129.3), 128.5, (128.4), 128.0, (127.99), 116.3, (115.7), 115.69, (115.5, 115.4), 86.8, 64.1.; HRMS (ESI): m/z calcd for $C_{14}H_{11}F_2NO_3S$ 311.0428, found 311.0385.

4,5-Bis-(4-trifluoromethyl-phenyl)-[1,2,3]oxathiazolidine 2,2-dioxide, (4*S*,5*R*)-7f



White solid, yield: 99%; 99.0% ee (Chiralcel AD-H, 20% isopropanol/hexanes, 1.0 mL/min, 215 nm, tr(major) = 5.3 min, tr(minor) = 6.7 min); $[\alpha]_D^{24}$ = -28.0 (c 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.43 (m, 4H), 7.18-7.12 (m, 4H), 6.21 (d, 1H, *J* = 6.3 Hz), 5.37 (br, s, 2H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.5, 135.6, 131.7, (131.4, 131.2), 127.8, 126.7, (126.68), 125.6, (125.56, 125.53, 125.50), 125.46, 125.4, (125.4, 125.37), 124.6, 124.5, (122.4, 122.37), 85.7, 63.9.; HRMS (ESI): m/z calcd for $C_{16}H_{11}F_6NO_3S$ 411.0364, found 411.0329.

4,5-Bis-(3-methoxy-phenyl)-[1,2,3]oxathiazolidine 2,2-dioxide, (4*S*,5*R*)-7g



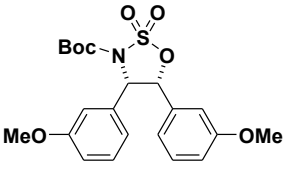
White solid, yield: 99%; 94.4% ee (Chiralcel AD-H, 20% isopropanol/hexanes, 1.0 mL/min, 215 nm, tr(major) = 10.4 min, tr(minor) = 11.7 min); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11-7.05 (m, 2H), 6.76-6.70 (m, 2H), 6.64 (d, 2H, *J* = 7.5 Hz), 6.53-6.48 (m, 2H), 6.04 (d, 1H, *J* = 6.1 Hz) 5.23 (d, 1H, *J* = 6.1 Hz), 3.61 (s, 3H), 3.60 (s, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 159.5, 159.5, 135.3, 133.8, 129.6, 129.4, 119.9, 118.9, 115.4, 115.0, 112.6, 111.5, 87.2, 64.7, 55.3.

This compound was unstable under silica-gel column chromatography purification and converted to the corresponding *N-Boc* derivative, *N-Boc*-(4*S*,5*R*)-**7g**, which is sufficiently stable under silica-gel column chromatographic purification.

(4*S*,5*R*)-*N-Boc*-4,5-bis-(3-methoxy-phenyl)-[1,2,3]oxathiazolidine 2,2-dioxide, (4*S*,5*R*)-*N-Boc*-7g:

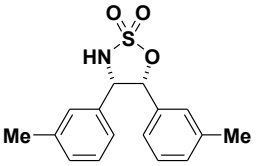
To a solution of (4*S*,5*R*)-**7g** (47 mg, 0.14 mmol) and di-*tert*-butyldicarbonate (61.1 mg, 0.28 mmol) in dichloromethane (1 mL) was added catalytic amount of DMAP (0.001 mmol), and the

mixture was stirred for 1 h at room temperature. Then, the reaction mixture was diluted with dichloromethane (5 ml) and washed with saturated aqueous $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, and evaporated. The residue was purified by flash chromatography on silica gel (Hex/EtOAc=3:1) to give 38.4 mg (63% yield) of (4*S,*5*R*)-*N*-*Boc*-**7g**.



White solid, yield: 63%; 98.3% ee (Chiralcel OD-H, 20% isopropanol/hexanes, 1.0 mL/min, 215 nm, tr(minor) = 6.6 min, tr(major) = 9.7min); $[\alpha]_D^{20}$ -124.2 (c 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CHCl_3$) δ 7.13-7.07 (m, 2H), 6.76-6.58 (m, 5H), 6.37 (s, 1H), 6.11 (d, 1H, *J* = 5.5 Hz), 5.39 (d, 1H, *J* = 5.5 Hz), 3.64 (s, 3H), 3.56 (s, 3H), 1.49 (s, 9H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 159.5, 148.3, 135.2, 132.0, 129.6, 129.5, 119.6, 118.8, 116.0, 114.7, 112.5, 111.2, 85.1, 83.3, 77.4, 66.6, 55.3, 28.0.; HRMS (EI): m/z calcd for $C_{21}H_{25}NO_7S$ 435.1352, found 435.1351.

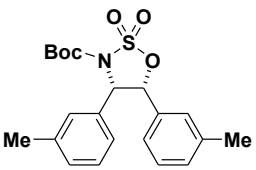
4,5-Bis-(3-methyl-phenyl)-[1,2,3]oxathiazolidine 2,2-dioxide, (4*S*,5*R*)-7i



White solid, yield: 99%; 88.5% ee (Chiralcel AD-H, 5% isopropanol/hexanes, 0.8 mL/min, 215 nm, tr(major) = 31.0 min, tr(minor) = 33.0 min); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06-6.97 (m, 4H), 6.80-6.76 (m, 4H), 6.02 (t, 1H, *J* = 3.0 Hz), 5.21 -5.20 (d, 2H, *J* = 3.5 Hz), 2.18 (s, 6H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.2, 138.0, 133.6, 132.2, 129.7, 129.5 128.3, 128.2, 128.1, 127.2, 124.6, 123.6, 87.6, 64.8, 21.3, 14.3.

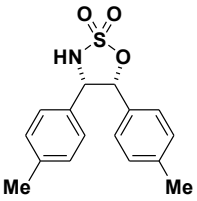
This compound was unstable under silica-gel column chromatography purification and converted to the corresponding N-Boc derivative, *N*-*Boc*-(4*S*,5*R*)-**7i**, which is sufficiently stable under silica-gel column chromatographic purification.

(4*S*,5*R*)-*N*-*Boc*-4,5-bis-(3-methyl-phenyl)-[1,2,3]oxathiazolidine 2,2-dioxide, (4*S*,5*R*)-*N*-*Boc*-7i: Prepared as essentially the same procedure for (4*S,*5*R*)-*N*-*Boc*-**7g** from (4*S,*5*R*)-**7g**.



White solid, yield: 64.3%; 91.3% ee (Chiralcel OD-H, 10% isopropanol/hexanes, 1.0 mL/min, 215 nm, tr(minor) = 5.5 min, tr(major) = 6.5min); $[\alpha]_D^{20}$ = -155.27 (c 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CHCl_3$) δ 7.06-6.96 (m, 4H), 6.87-6.67 (m, 4H), 6.09 (d, 1H, *J* = 5.6 Hz), 5.36 (d, 1H, *J* = 5.6 HZ), 2.17 (s, 3H), 2.14 (s, 3H), 1.49 (s, 9H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 138.0, 137.9, 130.4, 130.0, 129.2, 128.1, 128.0, 127.9, 127.1, 124.3, 123.5, 85.2, 83.5, 66.6, 27.9, 27.4, 21.2, 21.1.; HRMS (EI): m/z calcd for $C_{21}H_{25}NO_5S$ 403.1453, found 403.1447.

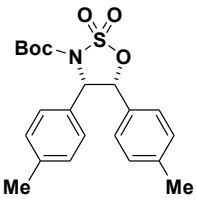
4,5-Bis-(4-methyl-phenyl)-[1,2,3]oxathiazolidine 2,2-dioxide, (4*S*,5*R*)-7j



White solid, yield: 99%; 87.0% ee (Chiralcel AD-H, 10% isopropanol/hexanes, 1.0 mL/min, 215 nm, tr(major) = 14.2 min, tr(minor) = 16.9 min); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97 (d, 4H, *J* = 4.9 Hz), 6.88-6.86 (m, 4H), 6.03 (d, 1H, *J* = 3.7 Hz), 5.20 (t, 1H, *J* = 3.5 Hz), 4.88 (br, s, 1H), 2.34 (s, 6H).

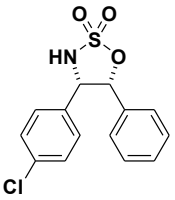
This compound was unstable under silica-gel column chromatography purification and converted to the corresponding N-Boc derivative, *N-Boc*-(4*S*,5*R*)-**7j**, which is sufficiently stable under silica-gel column chromatographic purification.

(4*S*,5*R*)-*N-Boc*-4,5-bis-(4-methyl-phenyl)-[1,2,3]oxathiazolidine 2,2-dioxide, (4*S*,5*R*)-*N-Boc*-7j: Prepared as essentially the same procedure for (4*S,*5*R*)-*N-Boc*-**7g** from (4*S,*5*R*)-**7g**.



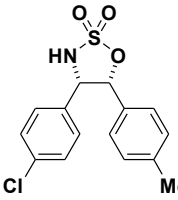
White solid, yield: 30%; 93.1% ee (Chiralcel AD-H, 10% isopropanol/hexanes, 1.0 mL/min, 215 nm, tr(major) = 7.0 min, tr(minor) = 10.3 min); $[\alpha]_D^{20}$ = -133.6 (c 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CHCl_3$) δ 6.96-6.94 (m, 6H), 6.81-6.79 (m, 2H), 6.11 (d, 1H, *J* = 5.3 Hz), 5.37 (d, 1H, *J* = 5.2 Hz), 2.25 (s, 6H), 1.53 (s, 9H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.4, 139.4, 138.4, 130.7, 129.2, 129.1, 127.6, 127.3, 126.6, 85.6, 83.9, 66.7, 28.0, 27.6, 21.3.; HRMS (EI): m/z calcd for $C_{21}H_{25}NO_5S$ 403.1453, found 403.1447.

4-(4-Chloro-phenyl)-5-phenyl-[1,2,3]oxathiazolidine 2,2-dioxide, (4*S*,5*R*)-7k



White solid, yield: 98%; 96.7% ee (Chiralcel OD-H, 30% isopropanol/hexanes, 1.0 mL/min, 215 nm, tr(minor) = 8.8 min, tr(major) = 16.5 min); $[\alpha]_D^{18}$ = -48.6 (c 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-7.09 (m, 5H), 6.99-6.94 (m, 4H), 6.12 (d, 1H, *J* = 6.2 Hz), 5.45 (d, 1H, *J* = 5.0 Hz) 5.25 (t, 1H, *J* = 5.7 Hz).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.4, 133.1, 132.5, 129.3, 128.6, 128.0, 127.8, 126.5, 86.3, 62.4.; Anal. Calcd for $C_{14}H_{12}ClNO_3S$: C, 54.28; H, 3.90; N, 4.52; S, 10.35; found: C, 54.26; H, 3.94; N, 4.51; S, 10.35.

4-(4-Chloro-phenyl)-5-(4-methyl-phenyl)-[1,2,3]oxathiazolidine 2,2-dioxide, (4*S*,5*R*)-7l



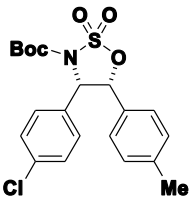
White solid, yield: 99%; 99.9% ee (Chiralcel AD-H, 10% isopropanol/hexanes, 1.0 mL/min, 215 nm, tr(major) = 13.6 min, tr(minor) = 18.2 min); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14-7.11 (m, 2H), 6.98-6.95 (m, 4H), 6.86-6.85 (m, 2H), 6.07 (d, 1H, *J* = 3.7 Hz), 5.44 (br, s, 1H) 5.20 (t, 1H, *J* = 3.4 Hz), 2.26 (s, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.3, 134.7, 132.8,

129.2, 129.0, 128.8, 128.7, 126.5, 87.4, 64.3, 21.3.

This compound was unstable under silica-gel column chromatography purification and converted to the corresponding N-Boc derivative, *N-Boc*-(4*S*,5*R*)-**7l**, which is sufficiently stable under silica-gel column chromatographic purification.

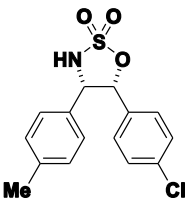
(4*S*,5*R*)-*N-Boc*-4-(4-chloro-phenyl)-5-(4-methyl-phenyl)-[1,2,3]oxathiazolidine 2,2-dioxide, (4*S*,5*R*)-*N-Boc*-7l:

Prepared as essentially the same procedure for (4*S,*5*R*)-*N-Boc*-**7g** from (4*S,*5*R*)-**7g**.



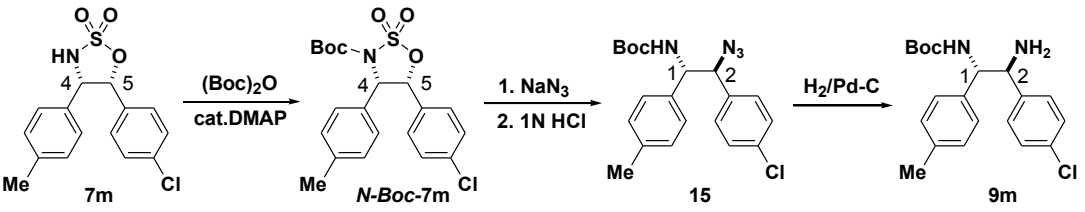
White solid, yield: 55%; 98.5% ee (Chiralcel AD-H, 10% isopropanol/hexanes, 1.0 mL/min, 215 nm, tr(major) = 7.9 min, tr(minor) = 12.7 min); $[\alpha]_D^{21}$ = -174.5 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CHCl_3$) δ 7.17-7.14 (m, 2H), 7.02-6.97 (m, 4H), 6.82-6.79 (m, 2H), 6.12 (d, 1H, *J* = 5.4 Hz), 5.38 (d, 1H, *J* = 5.3 Hz), 2.25 (s, 3H), 1.49 (s, 9H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 139.8, 134.7, 132.5, 129.3, 128.8, 128.76, 127.3, 126.3, 86.0, 83.5, 66.1, 28.0, 21.3.; HRMS (EI): m/z calcd for $C_{20}H_{22}ClNO_5S$ 423.0907, found 423.0914.

4-(4-Methyl-phenyl)-5-(4-chloro-phenyl)-[1,2,3]oxathiazolidine 2,2-dioxide, (4*S*,5*R*)-7m



White solid, yield: 94%; 99.9% ee (Chiralcel AD-H, 20% isopropanol/hexanes, 1.0 mL/min, 215 nm, tr(major) = 15.7 min, tr(minor) = 17.0 min); $[\alpha]_D^{21}$ = +22.8 (c 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15-6.87 (m, 8H), 6.03 (d, 1H, *J* = 4.5 Hz), 5.23 (br, m, 2H), 2.25 (s, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.1, 135.0, 131.1, 130.3, 129.5, 128.5, 128.0, 127.3, 86.8, 64.4, 21.2.; Anal. Calcd for $C_{15}H_{14}ClNO_3S$: C, 55.64; H, 4.36; N, 4.33; S, 9.90; found: C, 55.20; H, 4.34; N, 3.94; S, 9.68.

4. Synthesis of (1*S*,2*S*)-2-Amino-2-(4-chlorophenyl)-1-(*N-Boc*-amino)-1-(4-methylphenyl) ethane, (1*S*,2*S*)-9m



4-1. (4*S*,5*R*)-*N*-*Boc*-4-(4-methyl-phenyl)-5-(4-chloro-phenyl)-[1,2,3]oxathiazolidine 2,2-dioxide, (4*S*,5*R*)-*N*-*Boc*-7m:

To a solution of (4*S*,5*R*)-**7m** (45.4 mg, 0.14 mmol, 97.5 % ee) and di-*tert*-butyldicarbonate (61.1 mg, 0.28 mmol) in dichloromethane (1 mL) was added catalytic amount of DMAP, and the mixture was stirred for 1 h at room temperature. Then, the reaction mixture was diluted with dichloromethane (5 ml) and washed with saturated aqueous $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, and evaporated. The residue was purified by flash chromatography on silica gel (Hex/EtOAc=3:1) to give 50.9 mg (86% yield) of (4*S*,5*R*)-*N*-*Boc*-**7m**.

White solid, yield: 86%; $[\alpha]_D^{19}$ = -163.94 (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16-7.13 (d, 2H, *J* = 8.4 Hz), 7.01-6.86 (m, 6H), 6.11 (d, 1H, *J* = 5.7Hz), 5.9 (d, 1H, *J* = 5.7 Hz), 2.26 (s, 3H), 1.48 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.8, 138.5, 135.2, 129.4, 129.2, 128.5, 127.8, 127.1, 85.1, 82.7, 66.2, 27.8, 27.4, 21.1.; HRMS (EI): m/z calcd for $C_{20}H_{22}ClNO_5S$ 423.0907, found 423.0911.

4-2. (1*S*,2*S*)-*N*-*Boc*-2-azido-2-(4-chloro-phenyl)-1-(4-methyl-phenyl)-ethyl amine, 15:

NaN_3 (76.7 mg, 1.18 mmol, 5.0 equiv) was added in a single portion to a solution of (4*S*,5*R*)-*N*-*Boc*-4-(4-methyl-phenyl)-5-(4-chloro-phenyl)-[1,2,3]oxathiazolidine 2,2-dioxide ((4*S*,5*R*)-*N*-*Boc*-**7m**) (110 mg, 0.26 mmol, 1.0 equiv) in DMF (2 ml) at 25 °C. The resulting mixture was warmed to 60 °C and stirred for 5 h. Upon completion, the reaction mixture was cooled to rt and contents were diluted with Et_2O (3 mL), treated with 1*N* aqueous HCl (3 mL), and allowed to stir for an additional 12 h at 25 °C. Once this operation was complete, the reaction mixture was poured into saturated $NaHCO_3$ solution and extracted with Et_2O. The combined organic layers were then washed with water, dried ($MgSO_4$), and concentrated. The resultant light yellow solid was purified by flash column chromatography (silica gel, EtOAc/hexanes, 3:1).

White solid, yield: 94%; $[\alpha]_D^{20}$ = + 85.96 (*c* 0.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.04 (m, 8H), 5.22 (d, 1H, *J* = 8.4 Hz), 4.90 (br, s, 1H), 4.82 (br, s, 1H), 2.31 (s, 3H), 1.35 (s, 9H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.1, 137.7, 135.9, 135.4, 134.4, 129.3, 129.1, 128.9, 126.9, 80.1, 69.7, 58.7, 28.4, 21.2.; HRMS (EI): m/z calcd for $C_{20}H_{23}ClN_4O_2$ 386.1510, found 386.1565.

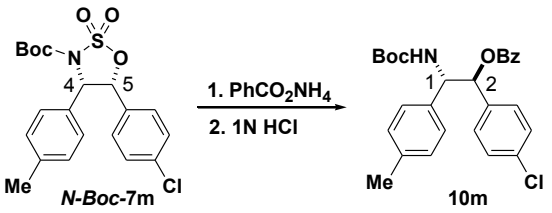
4-3. (1*S*,2*S*)-2-Amino-2-(4-chlorophenyl)-1-(*N*-*Boc*-amino)-1-(4-methylphenyl) ethane, (1*S*,2*S*)-9m

A mixture of (1*S*,2*S*)-*N*-*Boc*-2-azido-2-(4-chloro-phenyl)-1-(4-methyl-phenyl)-ethyl amine, **15**, (60.1 mg, 0.16 mmol) and 10% palladium on carbon (60.0 mg) in MeOH (1 ml) was stirred

under an atmosphere of H_2 for 12 h. The reaction mixture was filtered over Celite and washed three times with dichloromethane. After concentration of the solution under reduced pressure, the crude product was purified by silica gel column chromatography (EtOAc/hexane, 1:1).

White solid, yield: 71%; $[\alpha]_D^{18}$ = - 6.3 (c = 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.11 (m, 8H), 5.75 (d, 1H, *J* = 7.2 Hz), 4.82 (br, s, 1H), 4.32 (d, 1H, *J* = 3 Hz), 2.32 (s, 3H), 1.32 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.7, 142.4, 138.1, 136.9, 129.3, 128.4, 127.5, 127.0, 126.5, 79.3, 77.4, 60.1, 28.4, 21.2.; Anal. Calcd for $C_{20}H_{25}ClN_2O_2$: C, 66.56; H, 6.98; N, 7.76; found: C, 66.72; H, 7.13; N, 7.93.

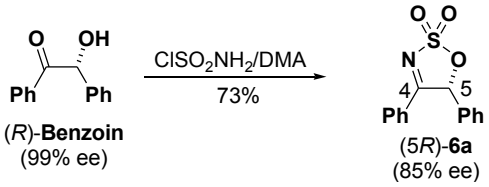
5. Synthesis of (1*S*,2*S*)-1-(*N*-*Boc*-amino)-1-(4-methylphenyl)-2-(4-chlorophenyl)-2-benzoyloxy ethane, (1*S*,2*S*)-10m



Ammonium benzoate (33.4 mg, 0.24 mmol) was added to a solution of (4*S*,5*R*)-*N*-*Boc*-**7m** (50.9 mg, 0.12 mmol) in dry DMF (1 ml). The solution was heated to 60 ^oC for 12 h. The solvent was evaporated, and the residue was re-dissolved in dichloromethane (3 mL) and 1*N* HCl (3 mL) was added. The reaction mixture was stirred at room temperature for 6 h, before the pH was adjusted to 8 with saturated aqueous $NaHCO_3$ solution. The layers were separated and the aqueous layer was extracted three times with dichloromethane. The combined organic layer was washed with H_2O and brine. After drying over $MgSO_4$, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica-gel (EtOAc/hexane, 5:1).

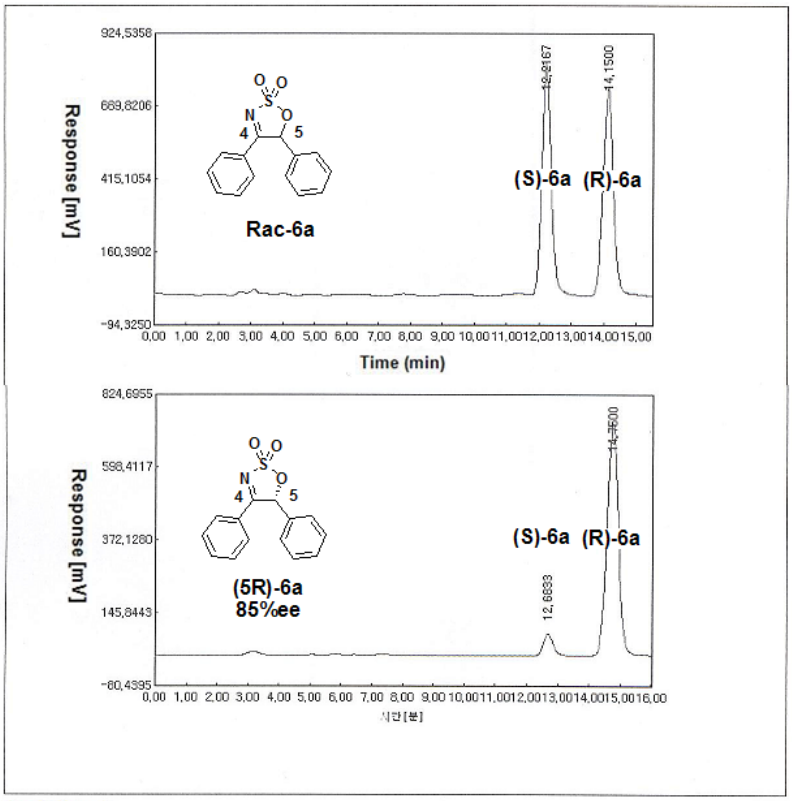
White solid, yield: 85%; $[\alpha]_D^{19}$ = -24.5 (c 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, 2H, *J* = 7.4 Hz), 7.58-7.55 (m, 1H), 7.46-7.43 (m, 2H), 7.23-7.18 (m, 4H), 7.07-7.02 (m, 4H), 6.16 (d, 1H, *J* = 7.1 Hz), 5.21 (br, m, 2H), 2.29 (s, 3H), 1.29 (s, 9H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 155.1, 137.7, 136.0, 134.1, 133.3, 129.9, 129.7, 129.3, 128.7, 128.5, 128.5, 127.3, 79.8, 78.0, 58.9, 29.7, 28.2, 21.1.; Anal. Calcd for $C_{27}H_{28}ClNO_4$: C, 69.59; H, 6.06; N, 3.01; found: C, 69.06; H, 6.18; N, 2.78.

6. Synthesis of (5*R*)-4,5-diphenyl-5H-[1,2,3]oxathiazole 2,2-dioxide [(5*R*)-6a]:



(*R*)-**Benzoin** (99% ee) → (5*R*)-**6a** (85% ee)

To the solution of (*R*)-benzoin (25 mg, 0.12 mmol, 99% ee) in DMA (*N,N*-dimethyl acetamide, 0.3 mL) was added chlorosulfamide ($ClSO_2NH_2$, 1.5 eq.). The reaction mixture was stirred at room temperature for 2 h, the reaction mixture was diluted with EtOAc (1 mL) and washed with brine. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed. The residue was re-dissolved in toluene (3 mL) and catalytic amount of PTSA (*p*-toluenesulfonic acid) was added. The reaction mixture was heated for 10 min at 110 ^{o}C and cooled to room temperature. The solvent was removed and the residue was purified by column chromatography to give the desired imine (*5R*)-**6a**. ^{1}H NMR & ^{13}C NMR spectra of (*5R*)-**6a** are same as those of racemic-**6a**. White solid, yield: 73%; 85% ee (Chiralcel AD-H, 20% isopropanol/hexanes, 1.0 mL/min, 215 nm, t_r(minor) = 12.7 min, t_r(major) = 14.8 min.).



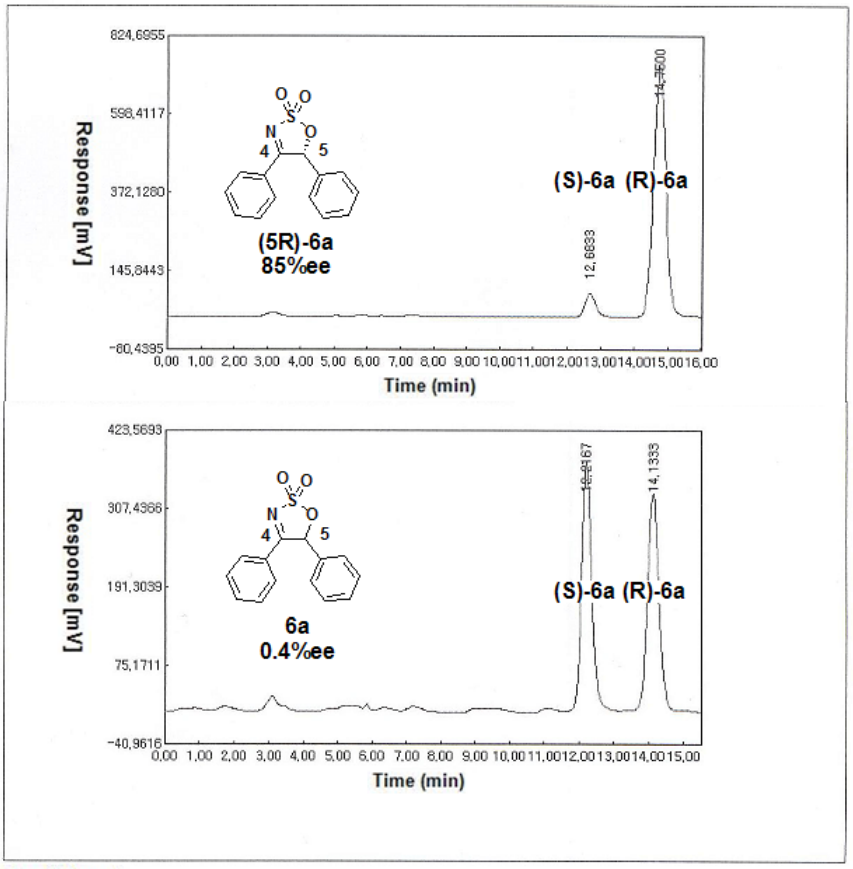
Result Report

Peak #	Time (min)	Area [mV*s]	BL	wide (sec)	Area %
1	12.6833	1479.7453	BB	65.0000	7.3136
2	14.7500	18752.9540	BB	99.0000	92.6864
Total		20232.6992			

6-1. Racemization of (5*R*)-4,5-diphenyl-5H-[1,2,3]oxathiazole 2,2-dioxide [(5*R*)-6a] in the presence of HCO_2H/Et_3N:

(*5R*)-**6a** (5 mg, 0.02 mmol, 85% ee) was dissolved in 0.2 mL of EtOAc and HCO_2H/Et_3N (5:2 azeotropic mixture, 0.02 mL) was added in one portion. After stirring for 30 min at room temperature, the reaction mixture was diluted with EtOAc (0.5 mL) and water (1 mL) was added. The organic layer was separated, dried over anhydrous $MgSO_4$ and evaporated to give crude **6a** (Recovery yield >99%). The optical purity of **6a** was completely lost and racemic **6a** (0.4% ee) was recovered (determined by chiral HPLC analysis).

Chiralcel AD-H, 20% isopropanol/hexanes, 1.0 mL/min, 215 nm, t_r(major) = 12.3 min, t_r(minor) = 14.1 min.



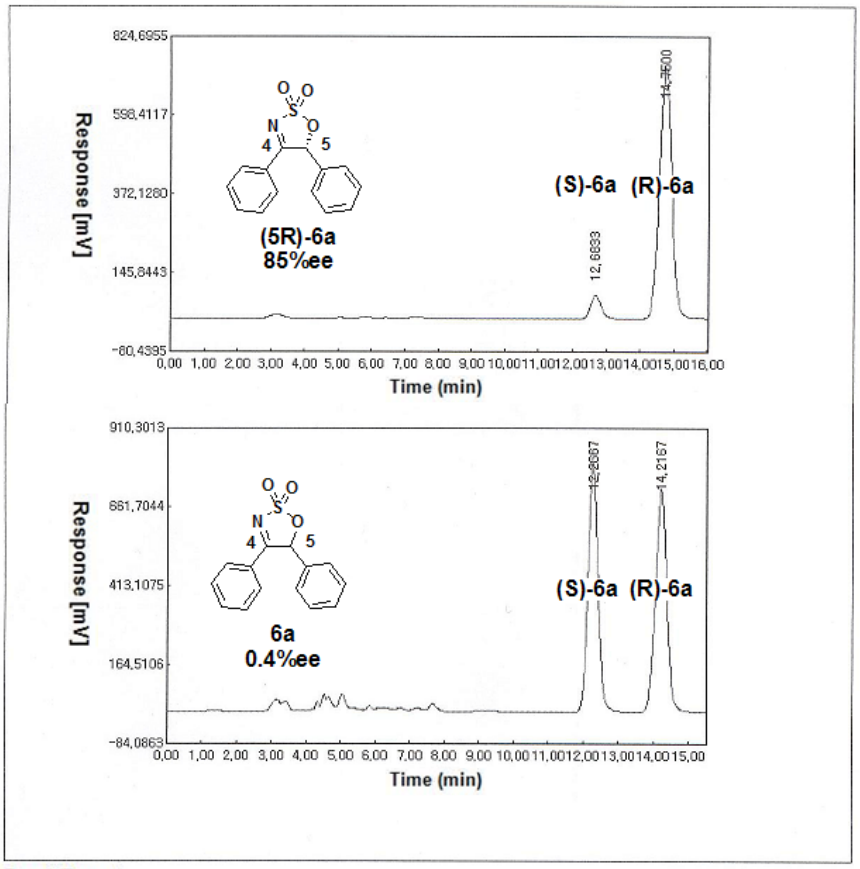
Result Report

Peak #	Time (min)	Area [mV*s]	BL	wide (sec)	Area %
1	12.2167	7540.7053	BB	79.0000	50.2144
2	14.1333	7476.3250	VB	73.0000	49.7856
Total		15017.0303			

6-2. Racemization of (5*R*)-4,5-diphenyl-5H-[1,2,3]oxathiazole 2,2-dioxide [(5*R*)-6a] in the presence of Et_3N:

(*5R*)-**6a** (5 mg, 0.02 mmol, 85% ee) was dissolved in 0.2 mL of EtOAc and Et_3N (0.02 mL) was added in one portion. After stirring for 30 min at room temperature, the reaction mixture was diluted with EtOAc (0.5 mL) and water (1 mL) was added. The organic layer was separated, dried over anhydrous $MgSO_4$ and evaporated to give crude **6a** (Recovery yield >99%). The optical purity of **6a** was completely lost and racemic **6a** (0.4% ee) was recovered (determined by chiral HPLC analysis).

Chiralcel AD-H, 20% isopropanol/hexanes, 1.0 mL/min, 215 nm, t_r(minor) = 12.3 min, t_r(major) = 14.2 min.

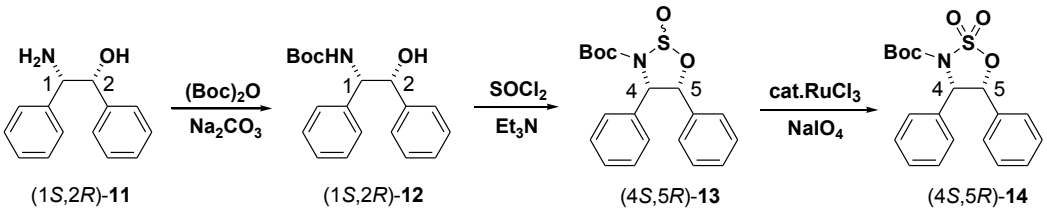


Result Report

Peak #	Time (min)	Area [mV*s]	BL	wide (sec)	Area %
1	12.2667	16392.2789	BB	86.0000	49.7907
2	14.2167	16530.1185	BB	91.0000	50.2093
Total		32922.3984			

7. Synthesis of *cis*- and *trans*-4,5-diphenyl cyclic sulfamidates

7-1. (4*S*,5*R*)-*N*-*Boc*-4,5-Diphenyl-[1,2,3]oxathiazolidine 2,2-dioxide, (4*S*,5*R*)-**14**[5]



(1*S*,2*R*)-**11** (1*S*,2*R*)-**12** (4*S*,5*R*)-**13** (4*S*,5*R*)-**14**

To a stirred mixture of (1*S*,2*R*)-1-amino-1,2-diphenyl-2-ethanol, (1*S*,2*R*)-**11**, (500 mg, 2.3 mmol) and sodium carbonate (496 mg, 4.7 mmol) in a mixture of THF/H_2O (3:1, 28 mL) at 0 ^oC, di-*tert*-butyl dicarbonate (563 mg, 2.6 mmol) was added and stirred at 0 ^oC for 1 h and then at room temperature for another 2 h. The reaction mixture was diluted with H_2O (30 mL) and extracted with ethyl acetate (20 mL x 3) The combined organic layer was washed with brine and dried over anhydrous $MgSO_4$. It was filtered and solvent was removed under vacuum to give a waxy solid **12** which was used for next step without further purification.

To a stirred solution of (1*S*,2*R*)-**12** and triethylamine (978 μL, 7.0 mmol) in 20 mL of dry dichloromethane at -40 ^oC was added $SOCl_2$ (171 μL, 2.3 mmol). After being stirred for 1h, the reaction mixture was quenched with water (20 mL) at -40 ^oC and was allowed to warm to room temperature, then H_2O (20 mL) was added. The aqueous phase was extracted with dichloromethane (20 mL x 2). The combined organic phase was washed with brine and dried over $MgSO_4$, and evaporated to afford a crude mixture of *endo*- and *exo*-isomer of sulfamidites (4*S*,5*R*)-**13** which was used for next step without further purification.

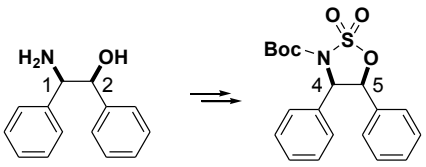
To an ice-cold solution of the sulfamidites (4*S*,5*R*)-**13** in a mixed solvent of CH_3CN (8.0 mL), CH_2Cl_2 (4.5 mL), and water (9.5 mL) was added ruthenium(III) chloride (catalytic amount) and then $NaIO_4$ (217.0 mg, 3.5 mmol) in portions at 0 ^oC. The mixture was stirred at 0 ^oC for 4 h, and water (20 mL) was added. The organic layer was separated and the aqueous phase was extracted with ether (20 mL x 3). The combined organic layer was washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash chromatography to afford white solid of (4*S*,5*R*)-**14**. The overall yield over three steps from (1*S*,2*R*)-**11** was 84.7% (731.0 mg).

(4*S*,5*R*)-**14**: White solid, 97.3% ee (Chiralpak OD-H, 5% isopropanol/ hexanes, 1.0 mL/min, 215 nm, t_r(minor) = 9.8 min, t_r(major) = 11.2 min); $[\alpha]_D^{22}$ = -148.0 (*c* 0.30, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07-7.23 (m, 6H), 7.04-7.05 (m, 2H), 6.92-6.94 (m, 2H), 6.16 (d, 1H, *J* = 5.7 Hz), 5.43 (d, 1H, J = 5.7 Hz), 1.49 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ148.2, 133.5, 130.5, 129.3, 128.5, 128.4, 128.3, 127.2, 126.3, 85.7, 83.3, 66.6, 27.9. HRMS (EI): m/z calcd

for $C_{19}H_{21}NO_5S$ 375.1140, found 375.1131.

This product is identical with the (4*S*,5*R*)-*N*-*Boc*-**7a**, which is derived from the major ATH product of **6a** with (*R,R*)-Rh-**1** catalyst, judged from ^{1}H-NMR, ^{13}C-NMR, optical rotation, and ciral HPLC (See 3, (4*S*,5*R*)-*N*-*Boc*-**7a**).

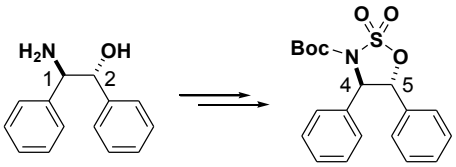
7-2. (4*R*,5*S*)-*N*-*Boc*-4,5-Diphenyl-[1,2,3]oxathiazolidine 2,2-dioxide, (4*R*,5*S*)-**14**



(1*R*,2*S*)-**11** (4*R*,5*S*)-**14**

Prepared from (1*R*,2*S*)-1-amino-1,2-diphenyl-2-ethanol, (1*R*,2*S*)-**11**.
Overall yield 78.2% from (1*R*,2*S*)-**11**.
White solid, 96.8% ee (Chiralpak OD-H, 5% isopropanol/ hexanes, 1.0 mL/min, 215 nm, t_r(major) = 9.7 min, t_r(minor) = 11.3 min); $[\alpha]_D^{22}$ = +153.1 (*c* 0.30, $CHCl_3$);^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12-7.23 (m, 6H), 7.05-7.07 (m, 2H), 6.92-6.94 (m, 2H), 6.17 (d, 1H, *J* = 6.0 Hz), 5.43 (d, 1H, J = 5.4 Hz), 1.49 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ148.2, 133.5, 130.5, 129.3, 128.5, 128.4, 128.3, 127.2, 126.3, 85.7, 83.4, 66.6, 27.9. HRMS (EI): m/z calcd for $C_{19}H_{21}NO_5S$ 375.1140, found 375.1135.

7-3. (4*R*,5*R*)-*N*-*Boc*-4,5-Diphenyl-[1,2,3]oxathiazolidine 2,2-dioxide, (4*R*,5*R*)-**14**



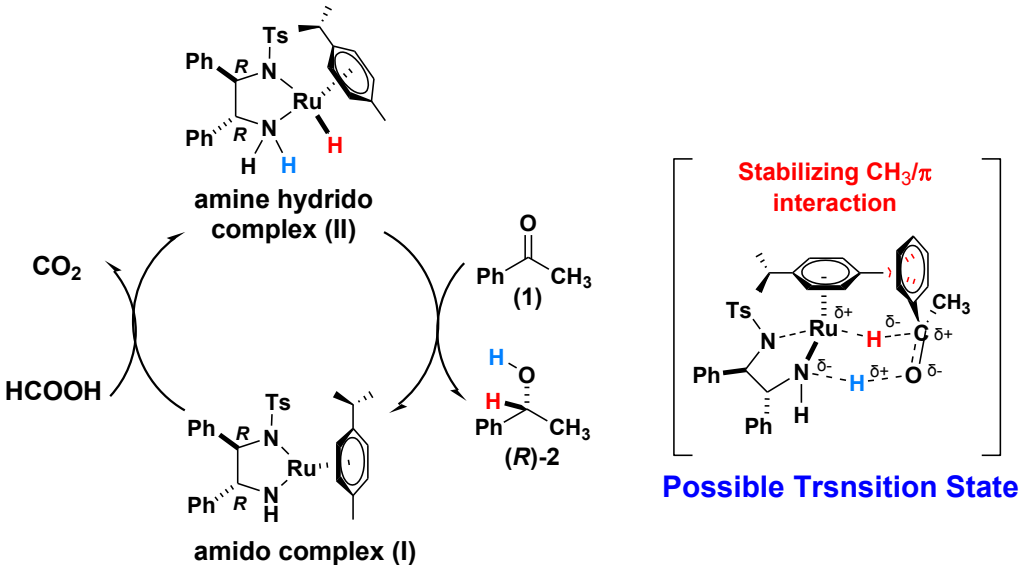
(1*R*,2*R*)-**11** (4*R*,5*R*)-**14**

Prepared from (1*R*,2*R*)-1-amino-1,2-diphenyl-2-ethanol, (1*R*,2*R*)-**11**.
Overall yield 82.2% from (1*R*,2*R*)-**11**.
White solid ; $[\alpha]_D^{22}$ = +61.3 (*c* 0.30, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.44 (m, 6H), 7.23-7.28 (m, 4H), 5.49 (d, 1H, *J* = 8.7 Hz), 5.16 (d, 1H, J = 9.0 Hz), 1.36 (s, 9H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.2, 135.1, 131.9, 130.3, 129.2, 129.1, 129.0, 127.2, 126.8, 85.7, 85.4, 68.6, 27.7.; Anal. Calcd for $C_{19}H_{21}NO_5S$: C, 60.78; H, 5.64; N, 3.73; O, 21.31; S, 8.54. Found: C, 61.14; H, 5.76; N, 3.75; O, 19.65; S, 9.08.

8. Plausible mechanism and possible transition state for ATH of cyclic sulfamidate imine with the Rh catalyst [(*R*,*R*)-Rh-1] to the corresponding cyclic sulfamidate.

Kinetic studies and isotope labeling experiments as well as computational analysis for the asymmetric transfer hydrogen (ATH) reaction of ketone with 2-propanol or formic acid/triethyl amine as hydrogen sources promoted by the chiral Ru catalyst (*R*,*R*)-RuCl[TsDPEN](*p*-cymene) (Ru-**3**) revealed that the reaction takes place reversibly through a six-membered pericyclic transition state.[6-10] The NH unit forms a hydrogen bond with the carbonyl oxygen atom to stabilize the transition state. The proposed mechanism of the chiral Ru catalyst Ru-**3** for the transfer hydrogenation of acetophenone (**1**) involves a concerted transfer of proton and hydride from amine hydrido complexe (**II**) to the substrate in a cyclic six-membered transition state to give the (*R*)-1-phenylethanol (**2**) and amido complexe (**I**) as shown in Figure S-1.

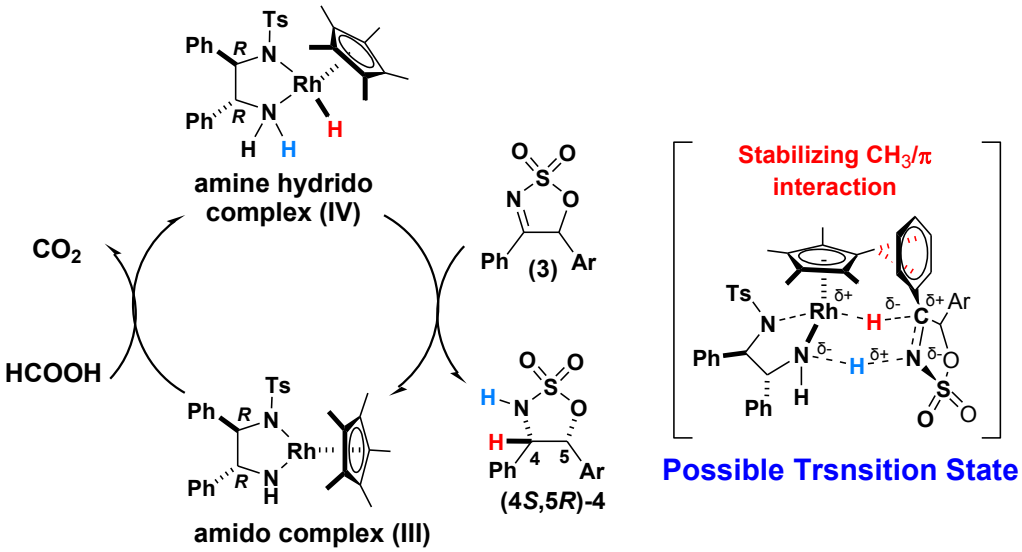
Figure S-1. Interconversion of the amido (**I**) and the amine hydrido Ru complex (**II**) in the ATH of acetophenone to 1-phenylethanol (**2**) *via* possible six-membered transition state (Modified from ref. 6).



The origin of stereoselectivity in the transfer hydrogenation catalyzed by Ru-**3** has been ascribed not only to the chiral diamine ligand but also to the contribution of polyalkylated arenes to the stabilization of the $C(sp_2)H/\pi$ or $C(sp_3)H/\pi$ attractive interactions between arene ligands and phenyl group of ketone developed in the transition state. Although the stereodetermining transition state structure is determined integrally by combining various steric and electronic factors, the secondary interaction between nonreacting sites (the $C(sp_2)H/\pi$ or

$C(sp_3)H/\pi$ attractive interactions) is particularly important in generating the asymmetric sense of the ATH of ketone.

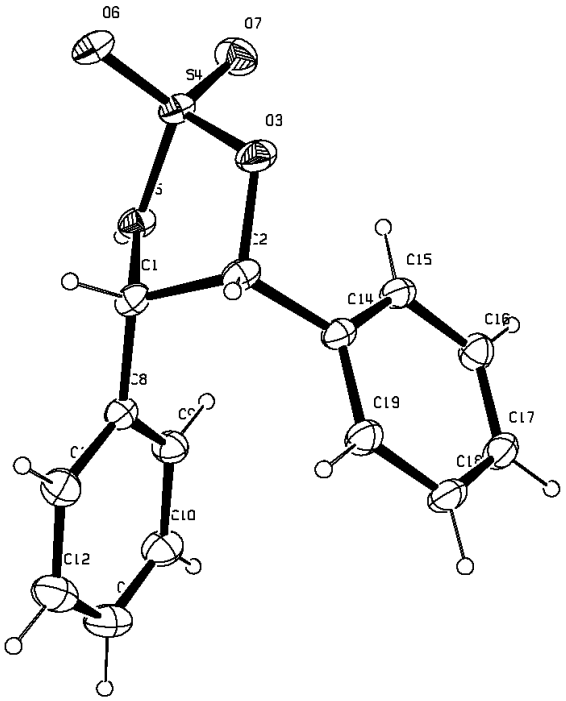
Figure S-2. Plausible mechanism and possible transition state for ATH of cyclic sulfamidate imine (**3**) with the Rh catalyst [(*R,R*)-Rh-**1**] to the corresponding cyclic sulfamidate (4*S*,5*R*)-**4**.



The chiral Rh catalyst [(*R,R*)-Rh-**1**], (*R,R*)-RhCl[TsDPEN]Cp*, is isoelectronic with the chiral Ru complex (Ru-**3**) and imine is also isoelectronic with ketone. Therefore, essentially the same mechanism for ATH of ketone with Ru-**3** catalyst could be applied to the ATH of cyclic sulfamidate imine (**3**) with Rh-**1** catalyst to the corresponding cyclic sulfamidate [(4*S*,5*R*)-**4**] as shown in Figure S-2.

9. X-ray crystallography analysis data of (4*S*,5*R*)-7a

CCDC-803456 contains the supplementary crystallographic data for (4*S*,5*R*)-**7a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.



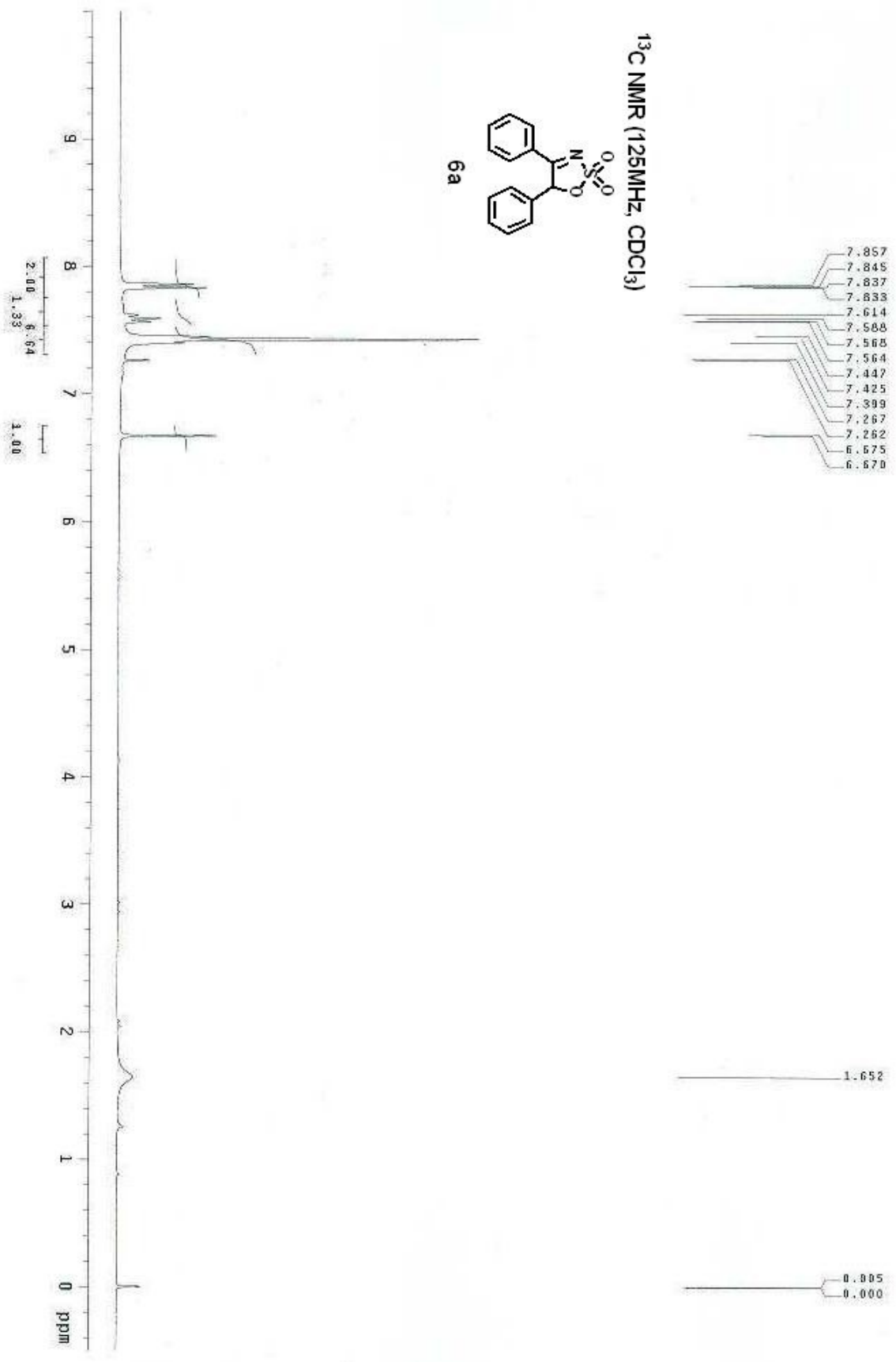
Crystal data for (4*S*,5*R*)-7a.

Identification code	20100309_0m	
Empirical formula	C14 H13 N O3 S	
Formula weight	275.31	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 5.72190(10) Å	α= 90°.
	b = 14.5983(4) Å	β= 90°.
	c = 15.3184(4) Å	γ = 90°.
Volume	1279.55(5) Å^3	
Z	4	

Density (calculated)	1.429 Mg/m^3
Absorption coefficient	0.256 mm^{-1}
F(000)	576
Crystal size	0.32 x 0.20 x 0.05 mm^3
Theta range for data collection	2.66 to 28.30°.
Index ranges	-7<=h<=7, -16<=k<=19, -20<=l<=19
Reflections collected	7449
Independent reflections	3142 [R(int) = 0.0295]
Completeness to theta = 28.30°	99.2 %
Absorption correction	Multi-scan
Max. and min. transmission	0.9873 and 0.9226
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3142 / 0 / 172
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0420, wR2 = 0.0979
R indices (all data)	R1 = 0.0587, wR2 = 0.1077
Absolute structure parameter	-0.02(10)
Largest diff. peak and hole	0.282 and -0.287 $e.Å^{-3}$

10. References

1. K. Narita and M. Sekiya, *Chem. Pharm. Bull*., 1977, **25**, 135.
2. J. Mao and D. C. Baker, *Org. Lett.,* 1999, **1**, 841.
3. K. Mashima, T. Abe and K. Tani, *Chem. Lett.,* 1998, **27**, 1199.
4. K.-J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya and R. Noyori, *Angew. Chem. Int. Ed. Eng.,* 1997, **36**, 285.
5. R. Guo, S. Lu, X. Chen, C.-W. Tsang, W. Jia, C. Sui-Seng, D. Amoroso and K. Abdur-Rashid, *J. Org. Chem.,* 2010, **75**, 937.
6. T. Ikariya and A. J. Blacker, *Acc. Chem. Res.,* 2007, **40**, 1300.
7. S. Gladiali and E. Alberico, *Chem. Soc. Rev.,* 2006, **35**, 226.
8. J. S. M. Samec, J.-E. Backvall, P. G. Andersson and P. Brandt, *Chem. Soc. Rev.,* 2006, **35**, 237.
9. T. Ikariya, K. Murata, and R. Noyori, *Org. Biomol. Chem.* 2006, **4**, 393.
10. R. Noyori, M. Yamakawa and S. Hashiguchi, *J. Org. Chem.,* 2001, **66**, 7931.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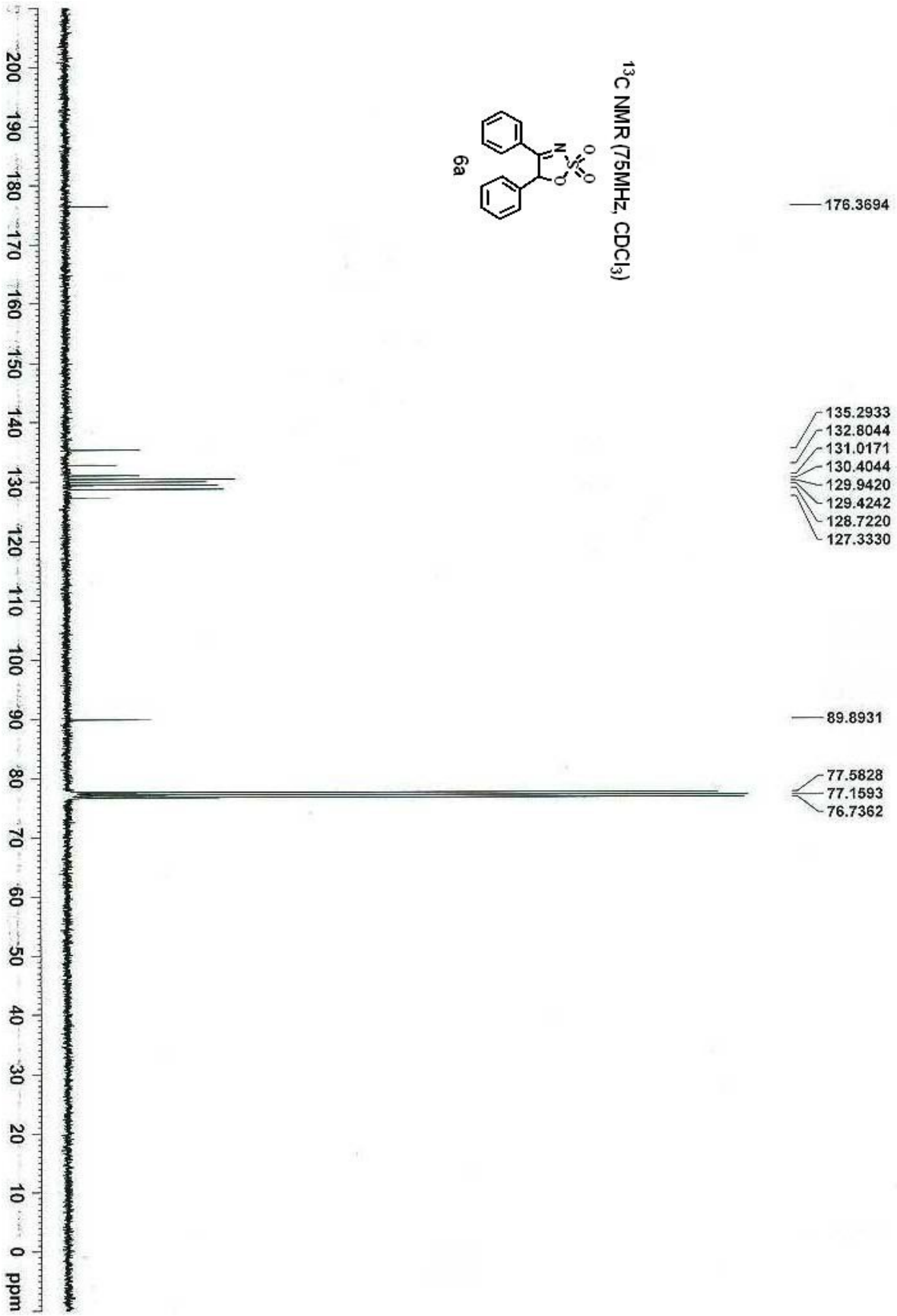
7.845
7.837
7.833
7.614
7.588
7.568
7.564
7.447
7.425
7.399
7.267
7.262
6.675
6.670
1.652
0.005
0.000
2.00
6.64
1.33
1.00
ppm


^{13}C NMR (75MHz, CDCl$_3$)
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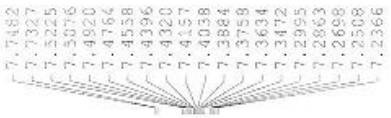
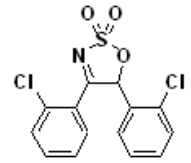
132.8044
131.0171
130.4044
129.9420
129.4242
128.7220
127.3330
89.8931
77.5828
77.1593
76.7362
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm



^{1}H NMR (500MHz, $CDCl_3$)



6b

NAME KSY_1118_2Cl_im
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PROCNO 1
Date_ 20110118
Time 14.56
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FIDRES 0.114555 Hz
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RG 256
DW 66.600 usec
DE 6.00 usec
TE 293.3 K
D1 1.00000000 sec
TD0 1

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SF 500.1300000 MHz
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LB 0.30 Hz
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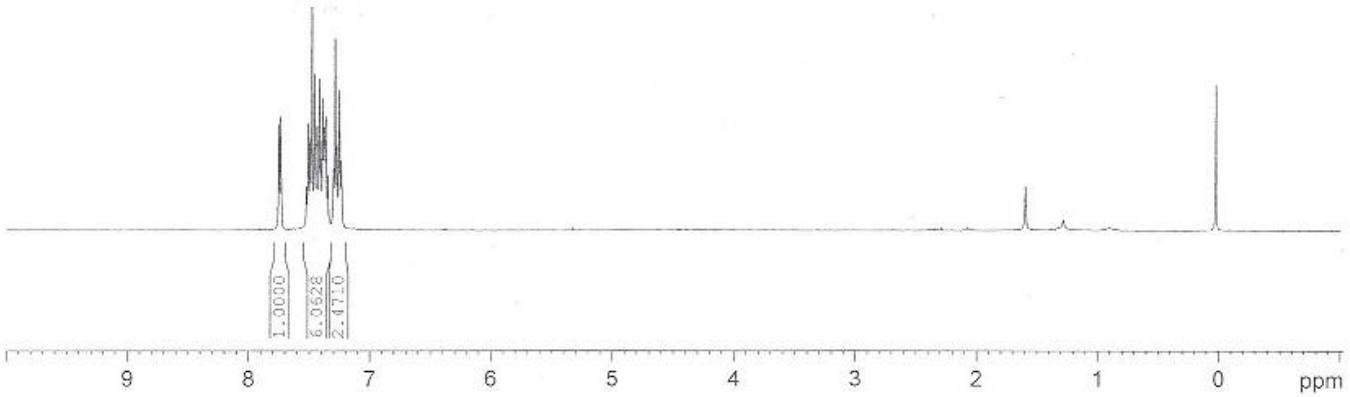
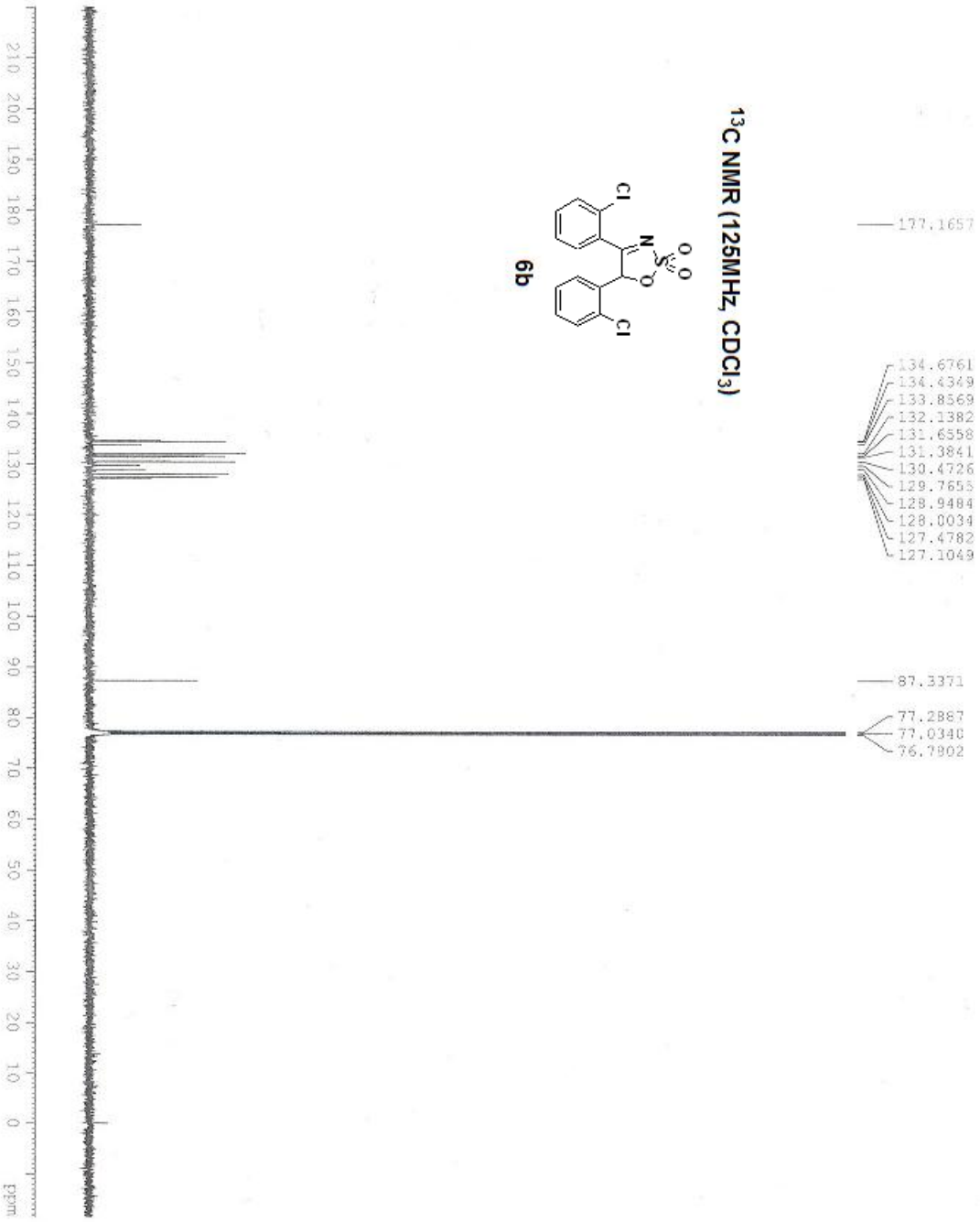
PC 1.00



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EXPNO                             1
PROCNO                            1
Date_                       20110118
Time                          15.27
INSTRUM                       spect
PROBHD     5 mm DUL 13C-1
PULPROG                   zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                              512
DS                                2
SWH                       35211.270 Hz
FIDRES                        0.537281 Hz
AQ                        0.9306754 sec
RG                             90.5
DW                        14.200 usec
DE                         6.00 usec
TE                            294.1 K
D1                        2.00000000 sec
D11                       0.03000000 sec
TD0                               1

======== CHANNEL f1 ========
NUC1                         13C
P1                         8.00 usec
PL1                        1.40 dB
PL1W                 70.60439201 W
SFO1                 125.7726799 MHz

======== CHANNEL f2 ========
CPDPRG2                    waltz16
NUC2                         1H
PCPD2                     100.00 usec
PL2                        -1.90 dB
PL12                       16.00 dB
PL13                       19.00 dB
PL2W                 27.23316002 W
PL12W                 0.44167015 W
PL13W                 0.22135943 W
SFO2                 500.1320005 MHz
SI                           32768
SF                   125.7577890 MHz
WDW                              EM
SSB                               0
LB                         1.00 Hz
GB                                0
PC                             1.40
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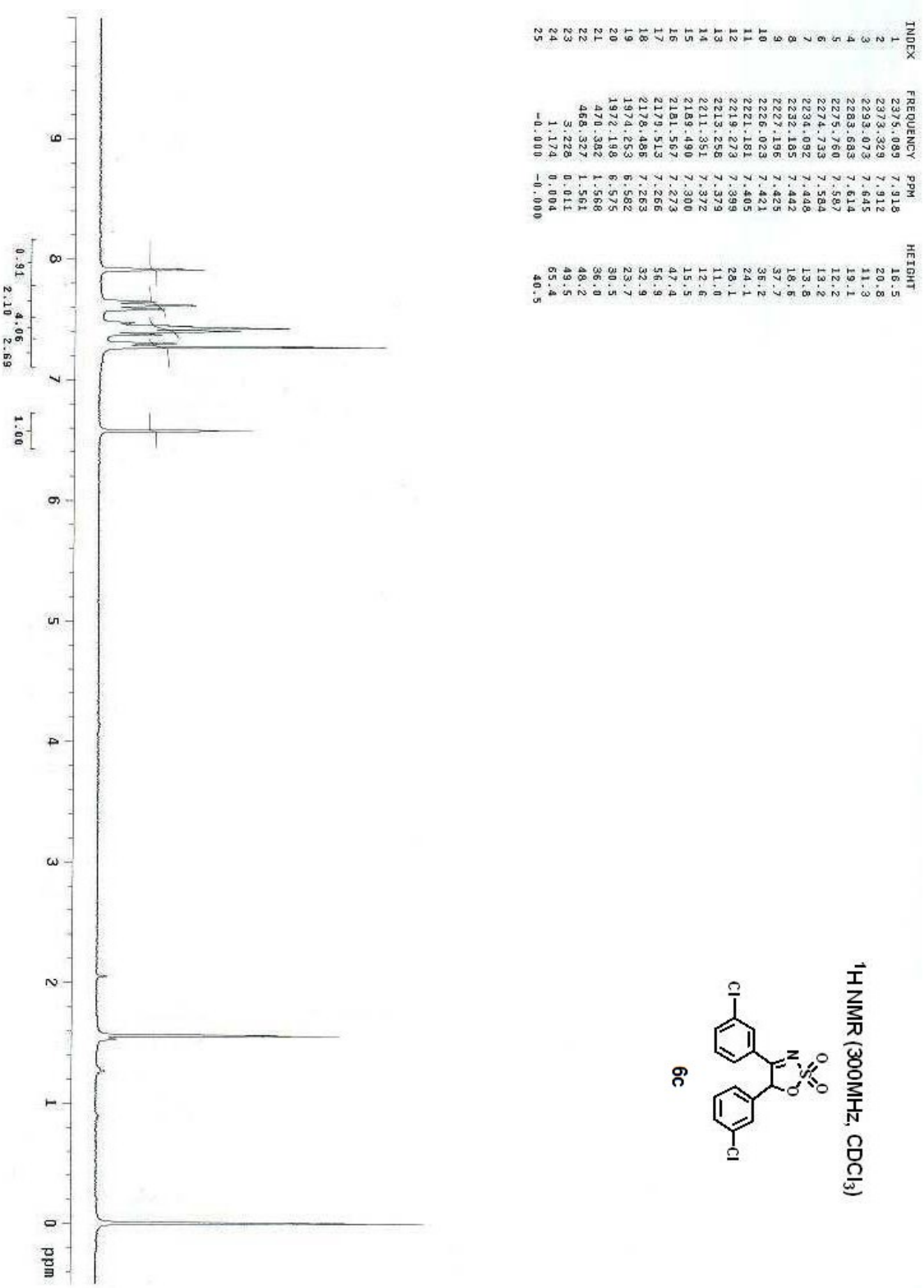
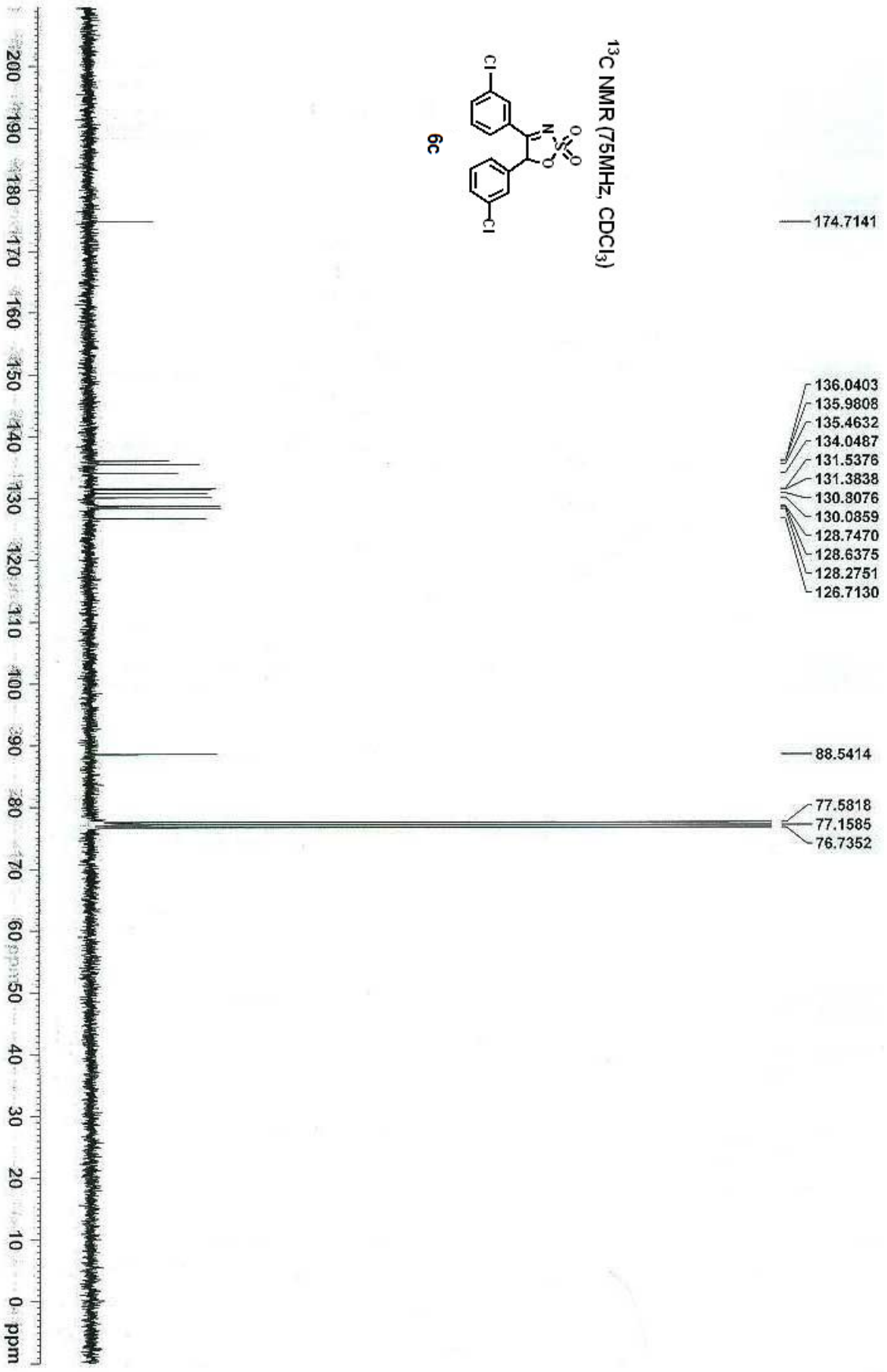
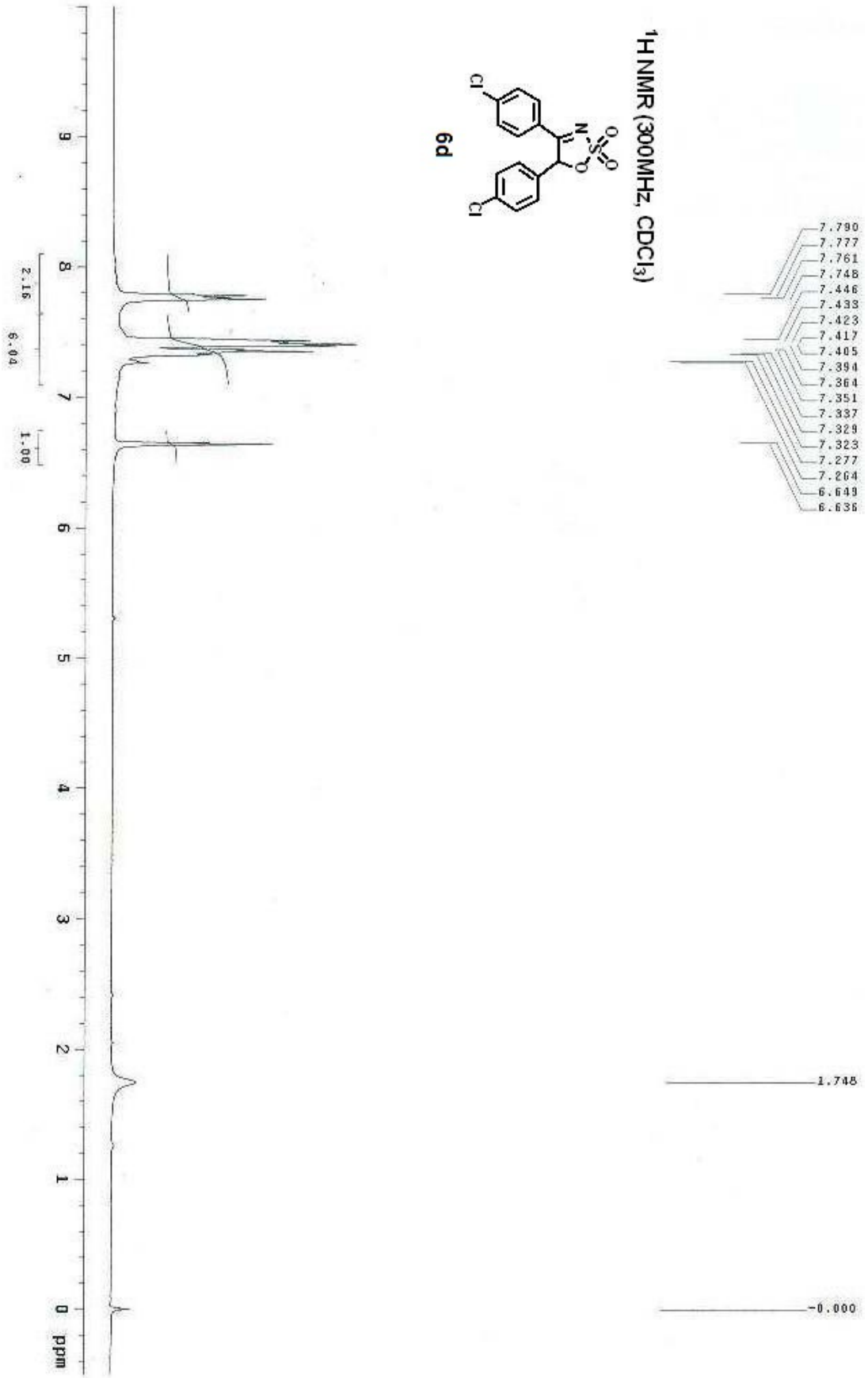
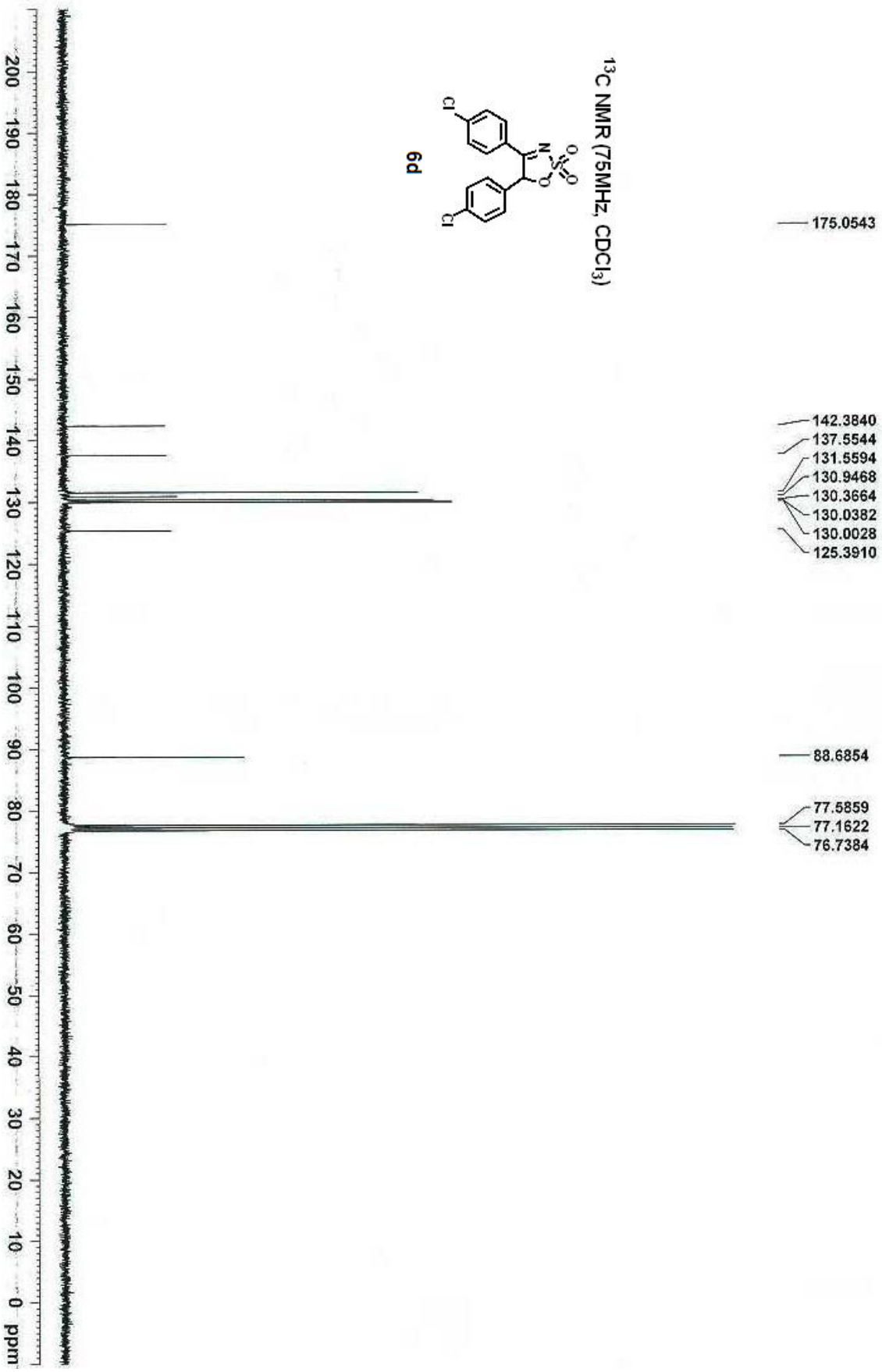


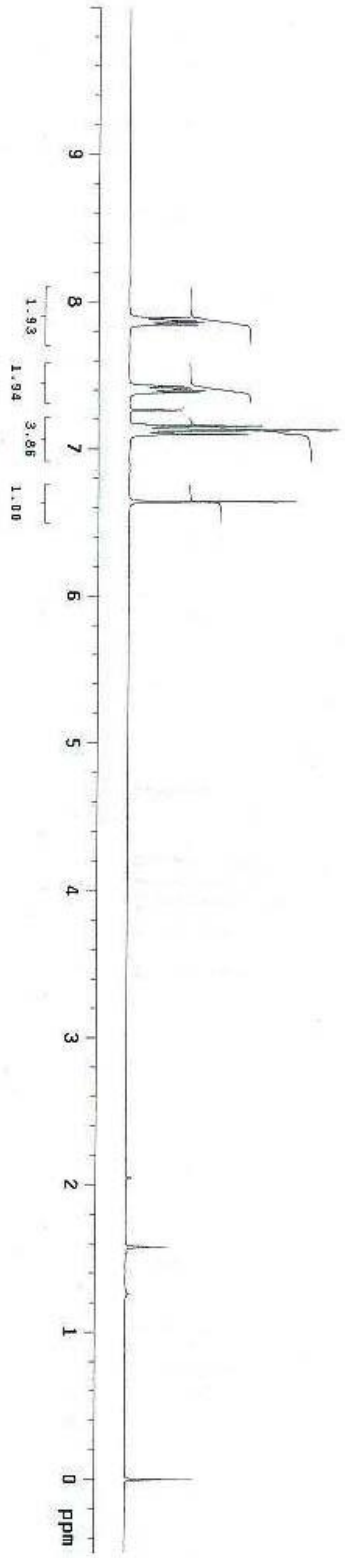
^{1}H NMR (300MHz, $CDCl_3$)

6c


^{13}C NMR (75MHz, CDCl$_3$)
6c
Cl
Cl
174.7141
136.0403
135.9808
135.4632
134.0487
131.5376
131.3838
130.8076
130.0859
128.7470
128.6375
128.2751
126.7130
88.5414
77.5818
77.1585
76.7352
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

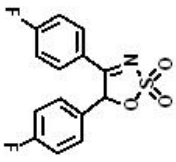

6d
^{1}H NMR (300MHz, CDCl$_3$)
7.790
7.777
7.761
7.748
7.446
7.438
7.423
7.417
7.405
7.394
7.364
7.351
7.337
7.329
7.323
7.277
7.264
6.649
6.636
2.16
6.04
1.00
1.748
-0.000
ppm


^{13}C NMR (75MHz, CDCl$_3$)
6d
Cl
Cl
175.0543
142.3840
137.5544
131.5594
130.9468
130.3664
130.0382
130.0028
125.3910
88.6854
77.5859
77.1622
76.7384
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

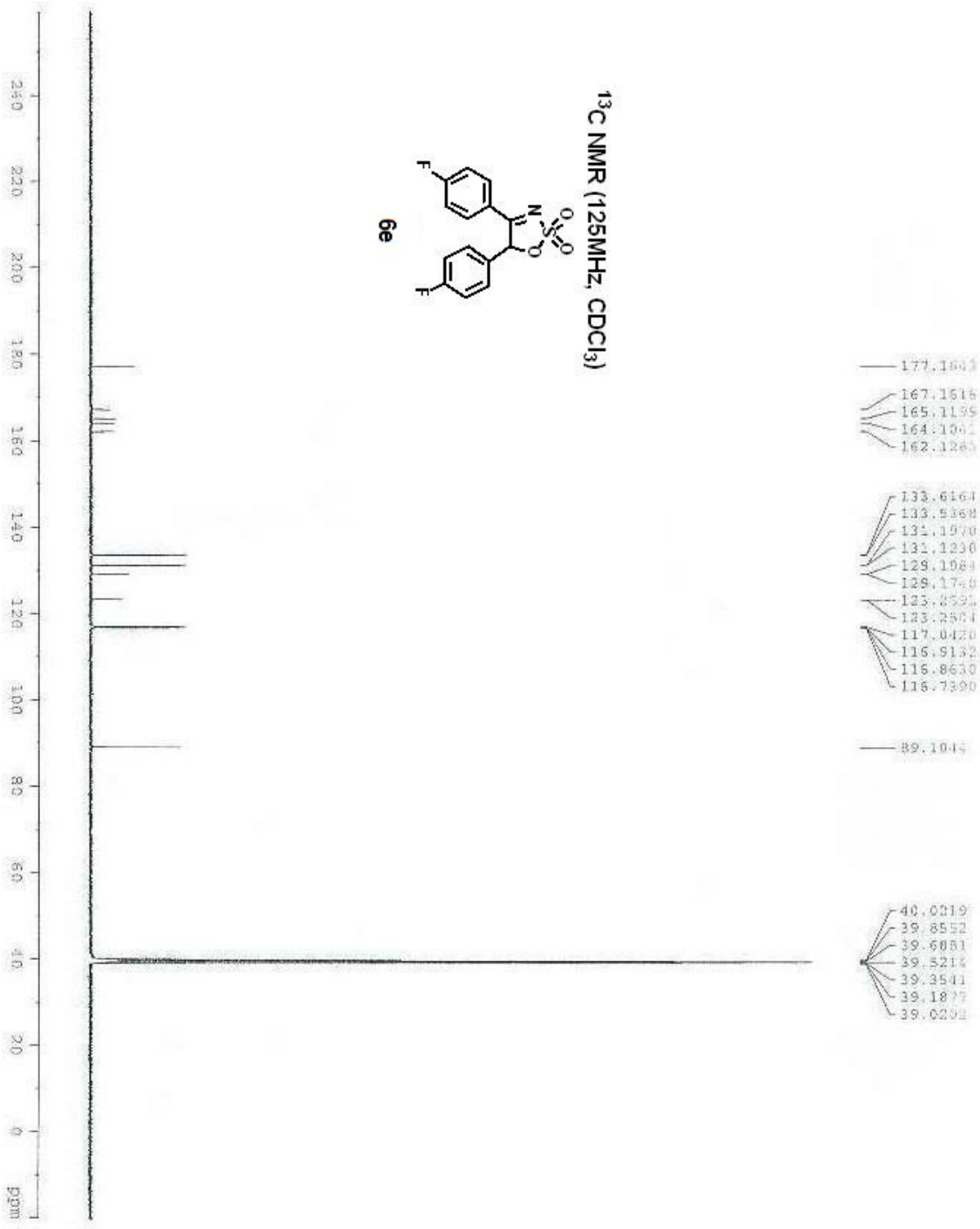


INDEX	FREQUENCY	PPM	HEIGHT
1	2367.753	7.894	10.0
2	2362.471	7.876	11.0
3	2360.711	7.870	8.0
4	2358.657	7.864	12.2
5	2353.921	7.846	11.3
6	2228.370	7.429	8.9
7	2223.382	7.413	10.1
8	2221.621	7.407	7.8
9	2219.714	7.400	12.6
10	2214.725	7.384	11.6
11	2178.632	7.263	8.7
12	2147.234	7.159	21.7
13	2145.180	7.152	9.8
14	2138.725	7.130	34.0
15	2132.269	7.109	7.4
16	2130.215	7.102	19.3
17	1982.006	6.641	27.3
18	472.729	1.576	6.9
19	0.000	0.000	11.1

^{1}H NMR (300MHz, $CDCl_3$)



6e


^{13}C NMR (125MHz, CDCl$_3$)
6e
F
F
N
O
O
O
S
177.1603
167.1616
165.1159
164.1041
162.1265
133.6164
133.5368
131.1970
131.1230
129.1084
129.1740
123.8592
123.2504
117.0420
116.9152
116.8630
116.7390
89.1046
40.0219
39.8552
39.6881
39.5214
39.3541
39.1877
39.0208
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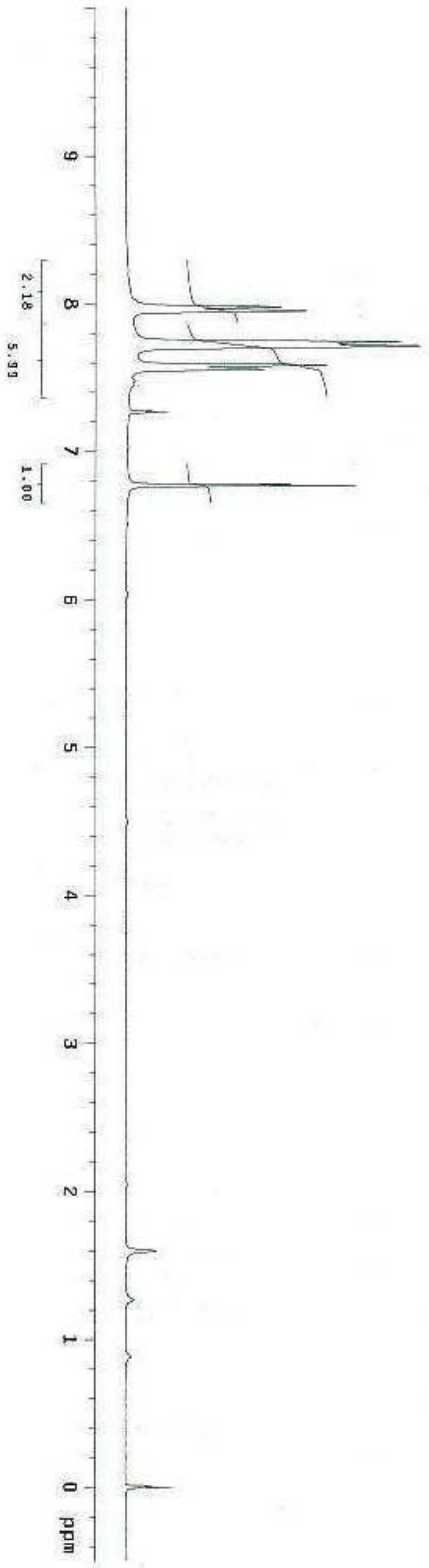
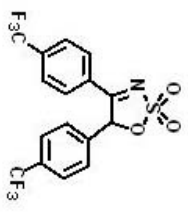
EXPNO 2
PROCNO 1
Date_ 20101027
Time 11.57
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 512
DS 2
SWH 35211.270 Hz
FIDRES 0.537281 Hz
AQ 1149.4 sec
RG 0.9306754
DW 14.200 usec
DE 6.00 usec
TE 297.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 1.40 dB
PL1W 70.60439301 W
SFO1 125.7728799 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -1.90 dB
PL12 16.00 dB
PL13 19.00 dB
PL2W 27.23316002 W
PL12W 0.44167015 W
PL13W 0.32135963 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7578448 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

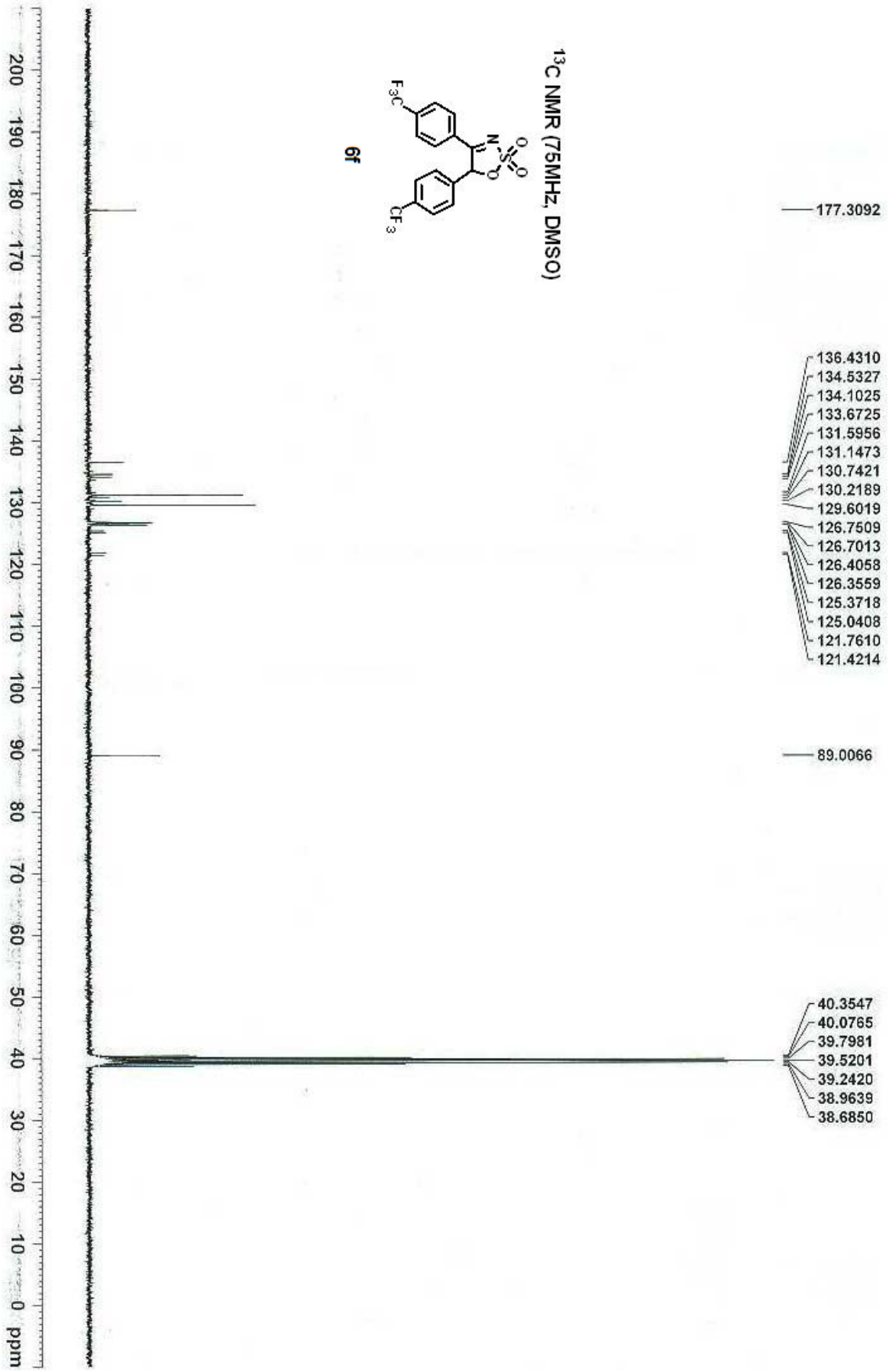


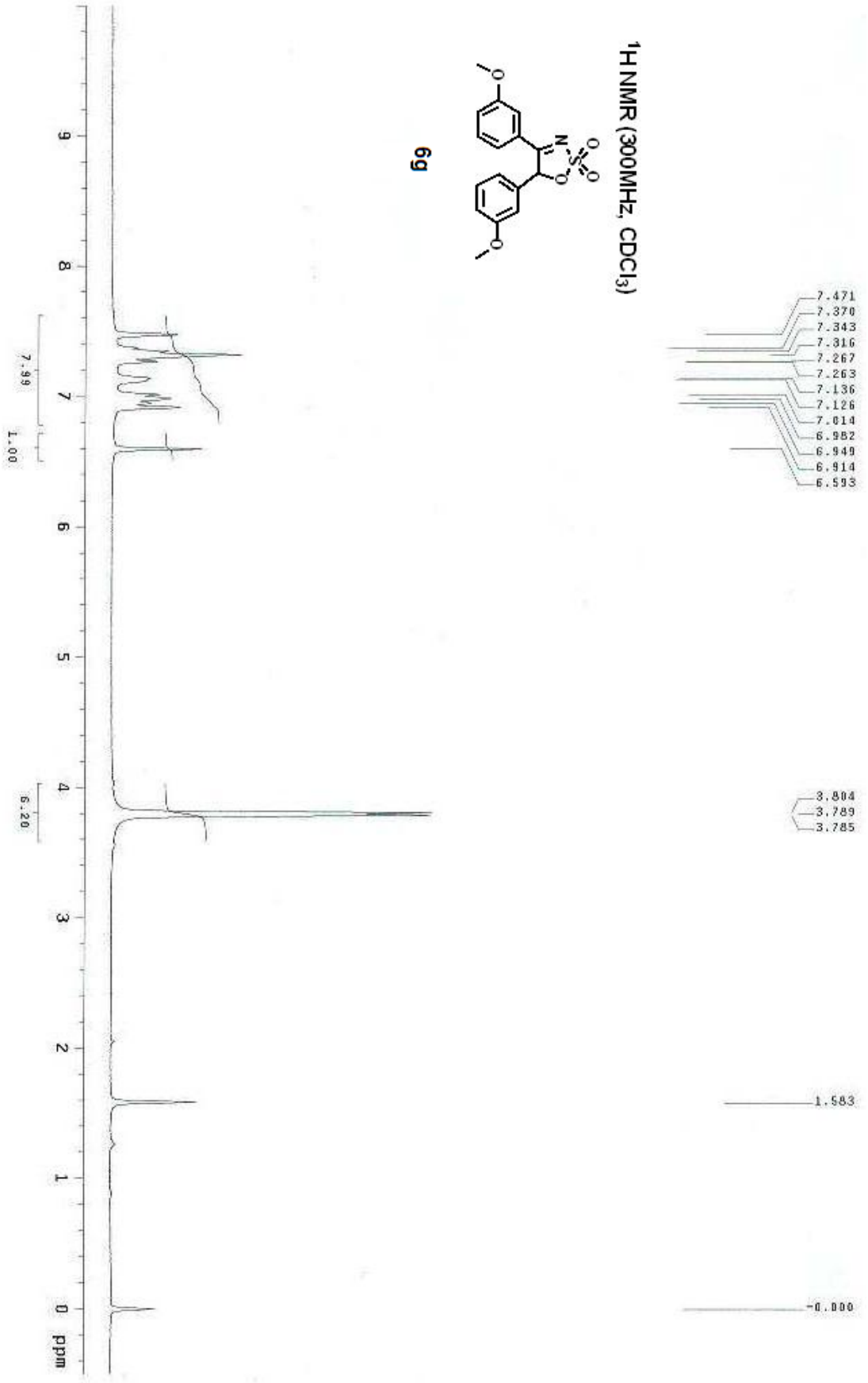
INDEX	FREQUENCY	PPM	HEIGHT
1	2392.989	7.978	25.0
2	2392.402	7.976	25.3
3	2384.186	7.949	29.4
4	2321.390	7.739	44.6
5	2318.602	7.730	35.2
6	2318.015	7.728	35.1
7	2316.108	7.722	35.5
8	2312.734	7.710	47.8
9	2273.413	7.579	32.5
10	2265.197	7.552	22.4
11	2181.860	7.274	4.1
12	2178.779	7.264	6.7
13	2033.380	6.779	26.8
14	2030.299	6.769	37.3
15	478.745	1.596	5.1
16	3.081	0.010	4.4
17	-0.000	-0.000	7.5

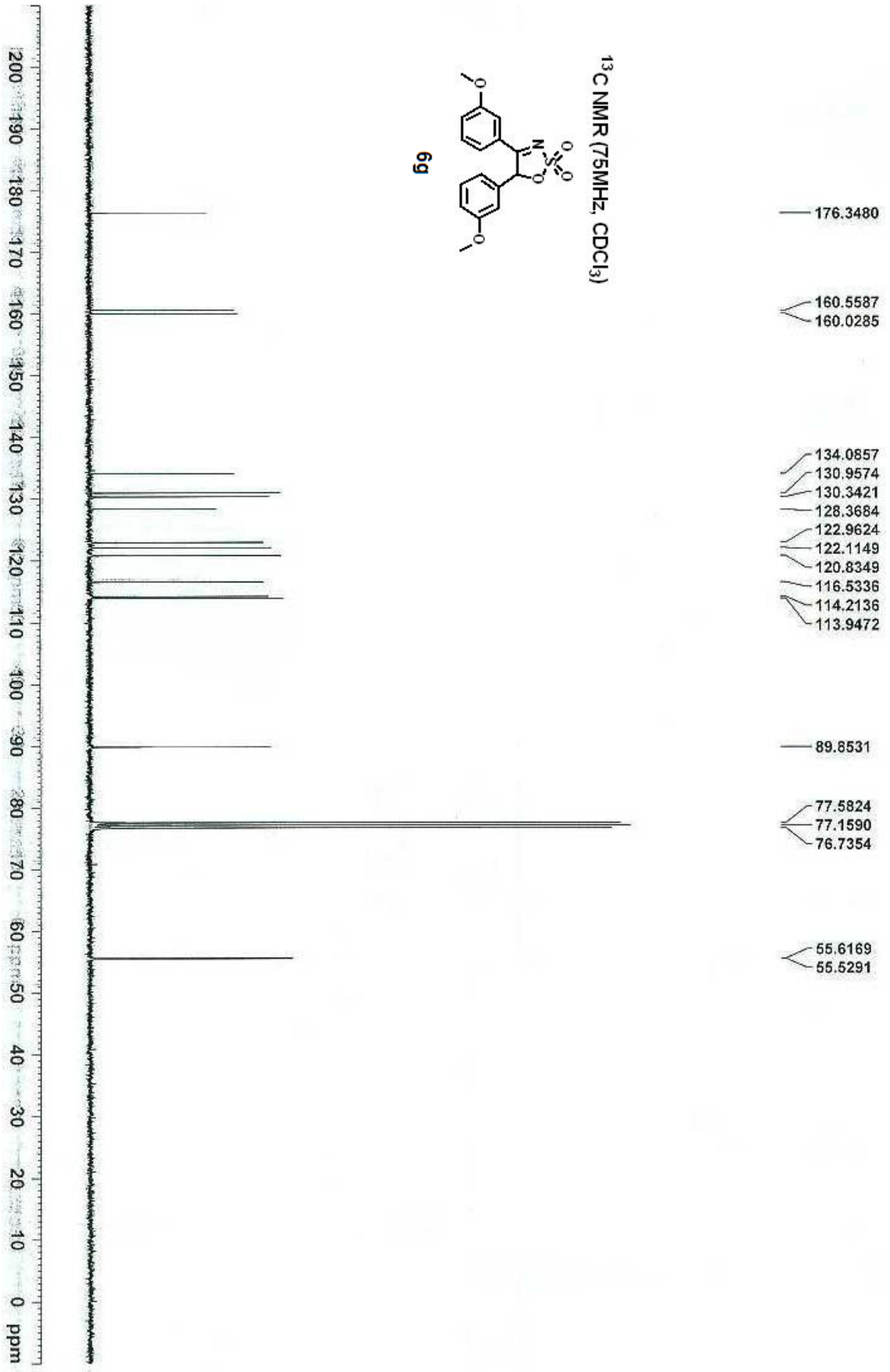
^{1}H NMR (300MHz, $CDCl_3$)

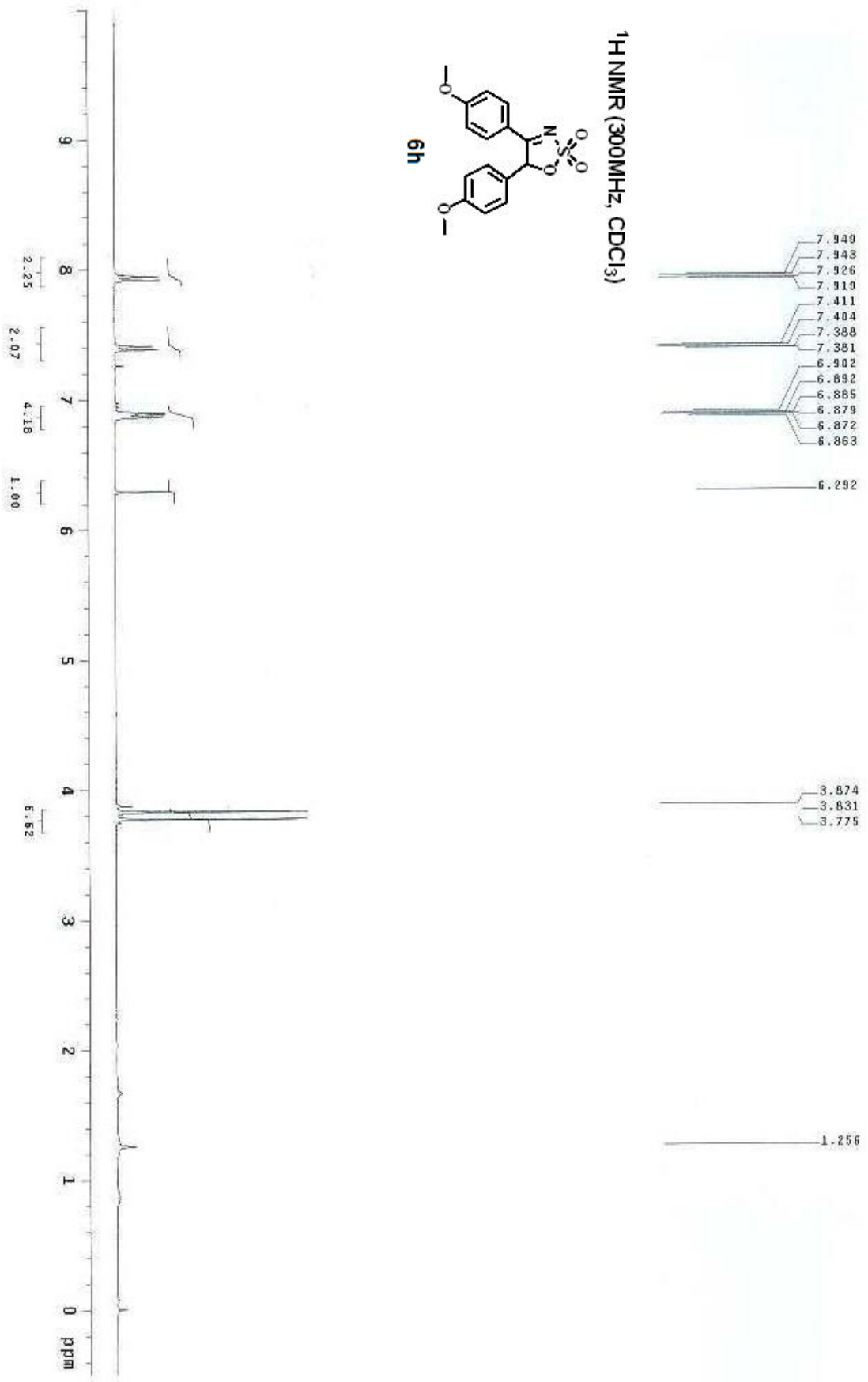


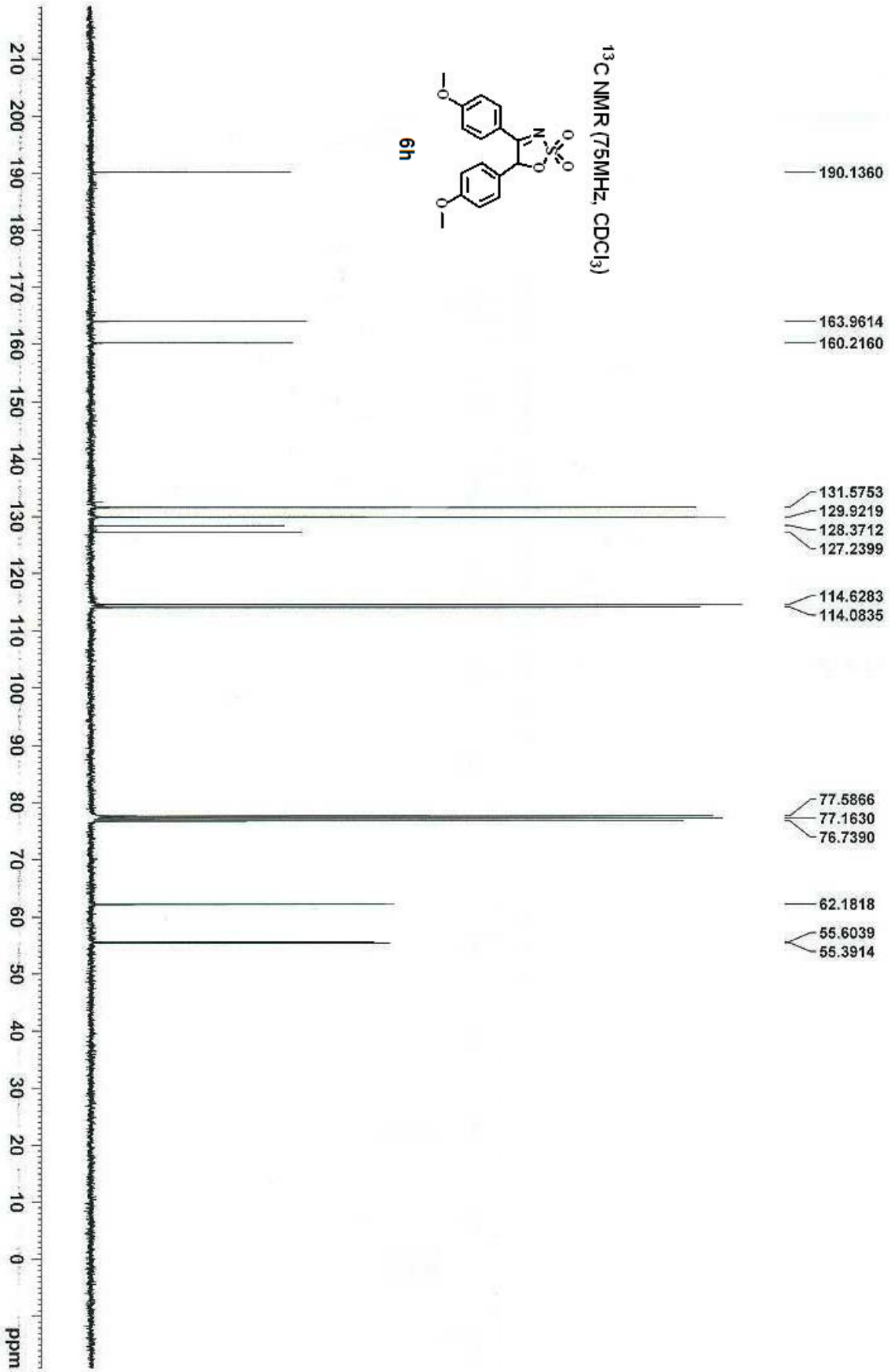
6f

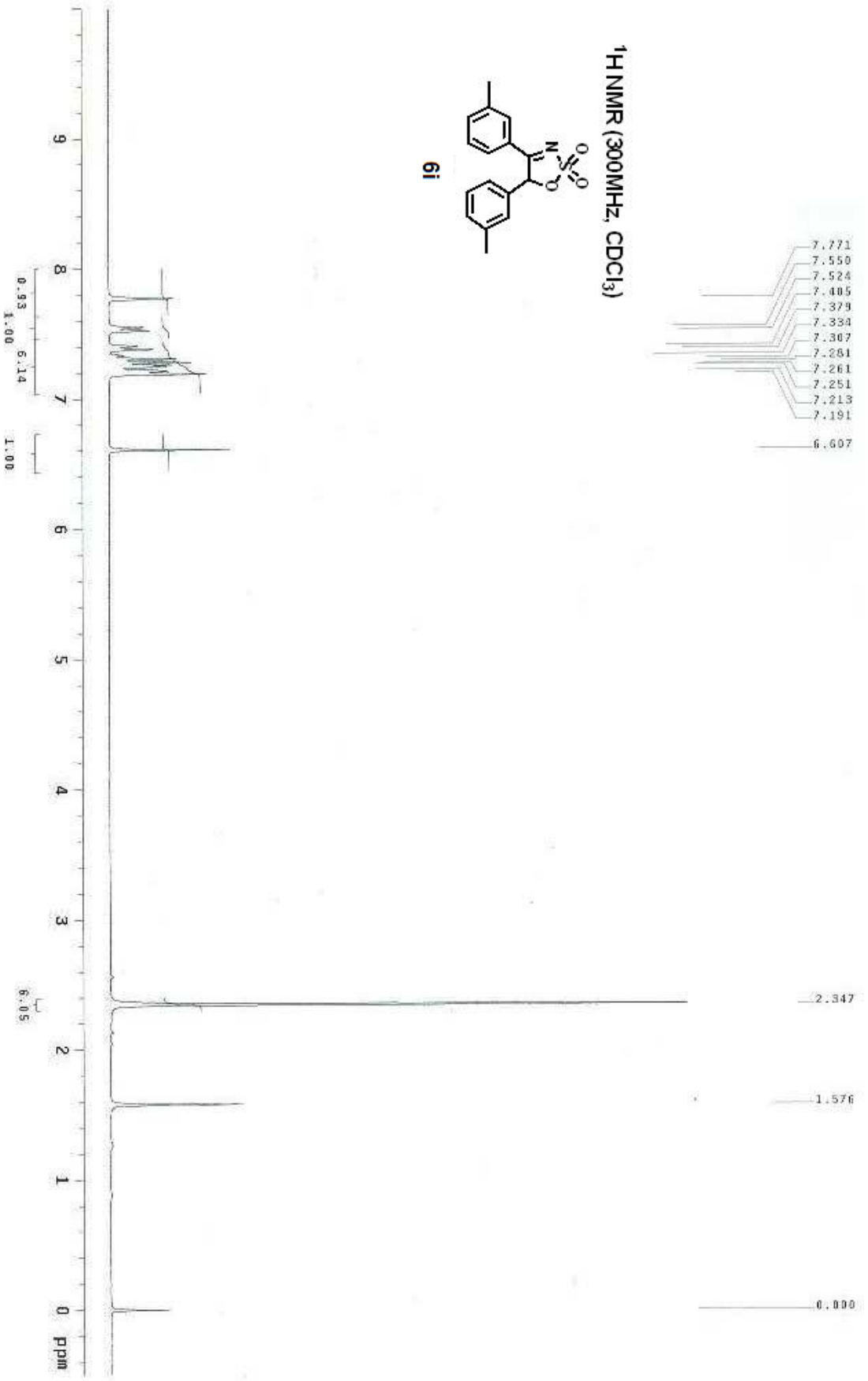

^{13}C NMR (75MHz, DMSO)
6f
177.3092
136.4310
134.5327
134.1025
133.6725
131.5956
131.1473
130.7421
130.2189
129.6019
126.7509
126.7013
126.4058
126.3559
125.3718
125.0408
121.7610
121.4214
89.0066
40.3547
40.0765
39.7981
39.5201
39.2420
38.9639
38.6850
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

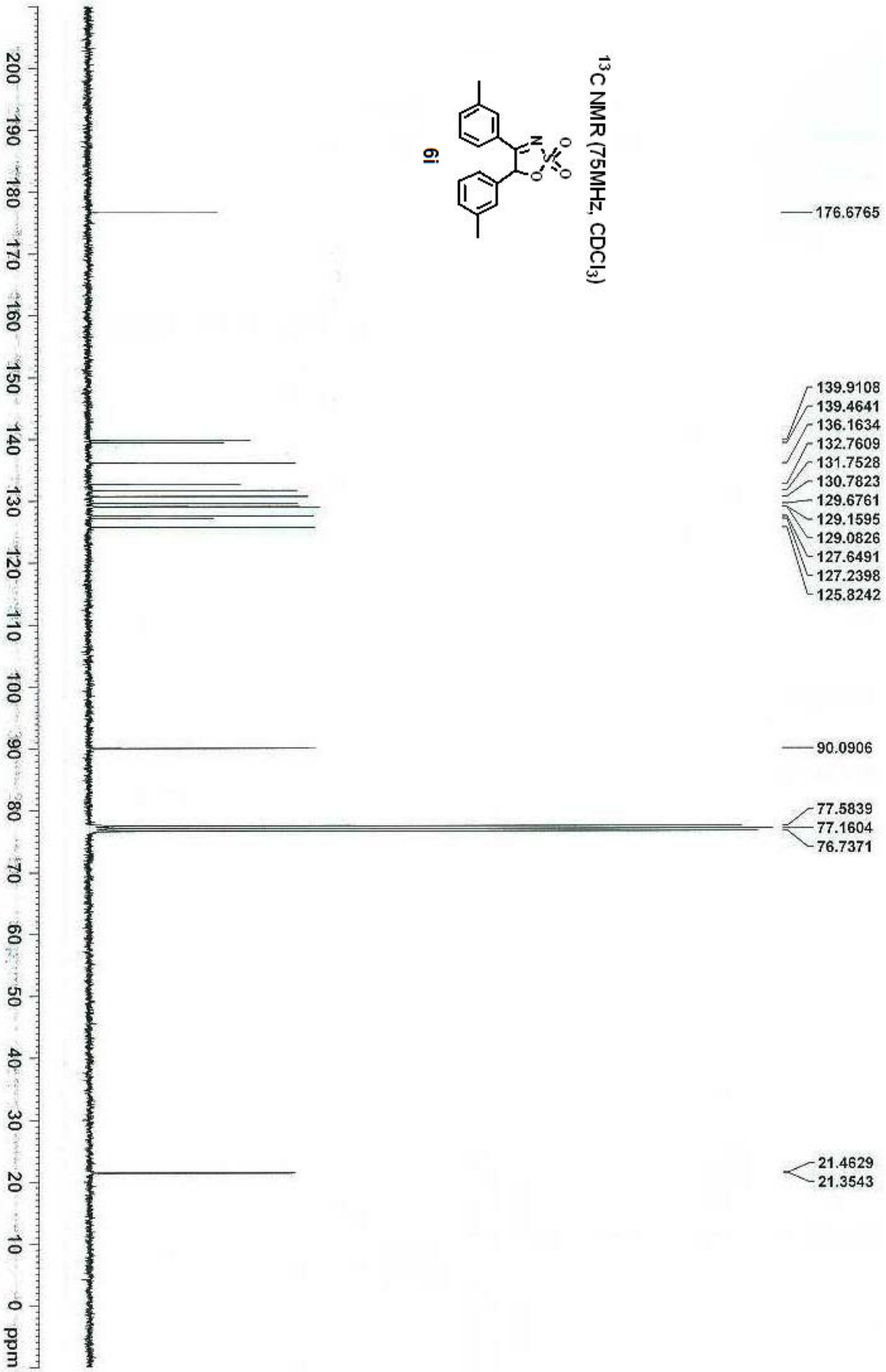

^{1}H NMR (300MHz, CDCl$_3$)
6g
7.471
7.370
7.343
7.316
7.267
7.263
7.136
7.126
7.014
6.982
6.949
6.914
6.593
3.804
3.789
3.785
1.583
0.000
7.99
1.00
6.20
ppm

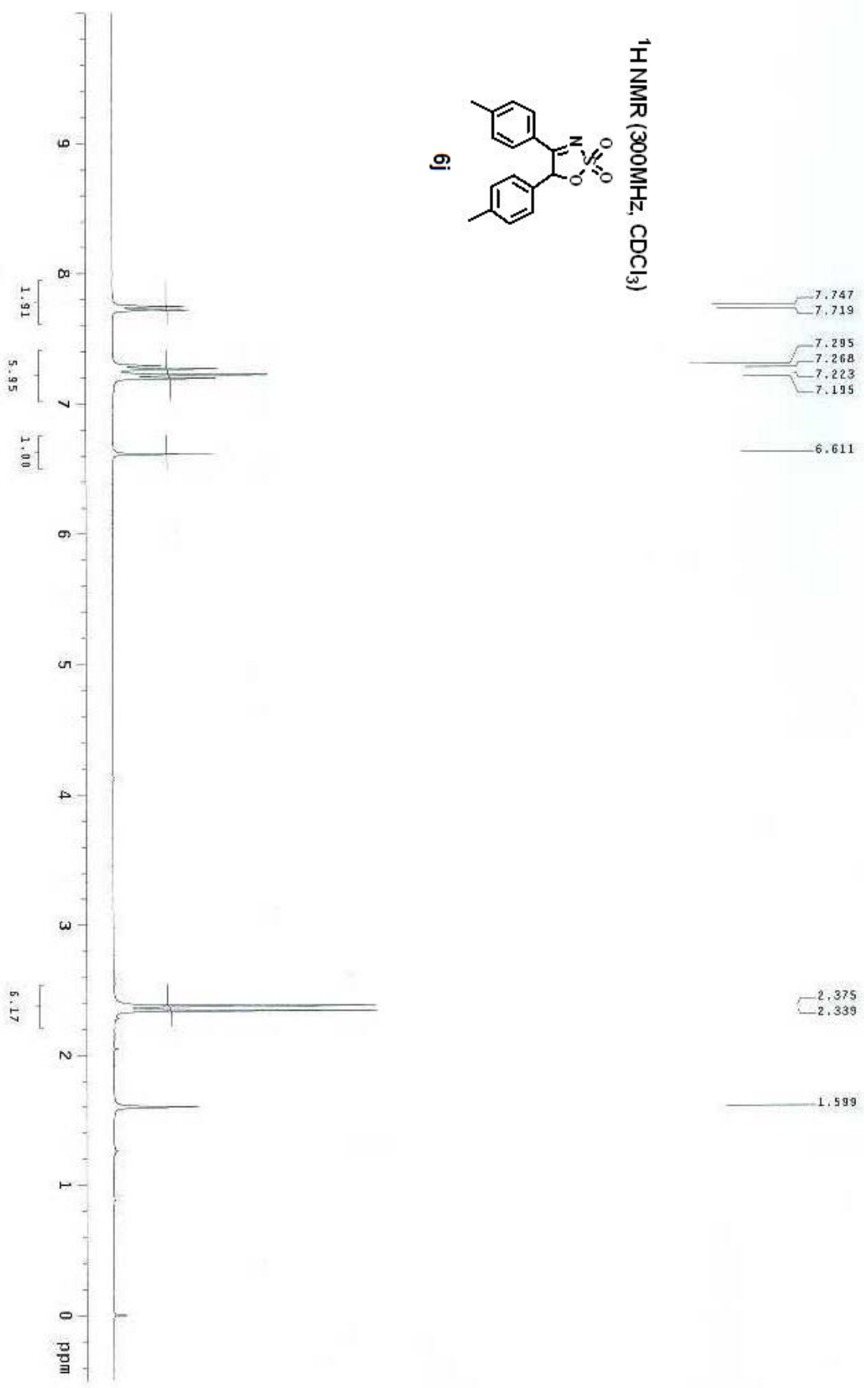

^{13}C NMR (75MHz, $CDCl_3$)
6g
176.3480
160.5587
160.0285
134.0857
130.9574
130.3421
128.3684
122.9624
122.1149
120.8349
116.5336
114.2136
113.9472
89.8531
77.5824
77.1590
76.7354
55.6169
55.5291
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

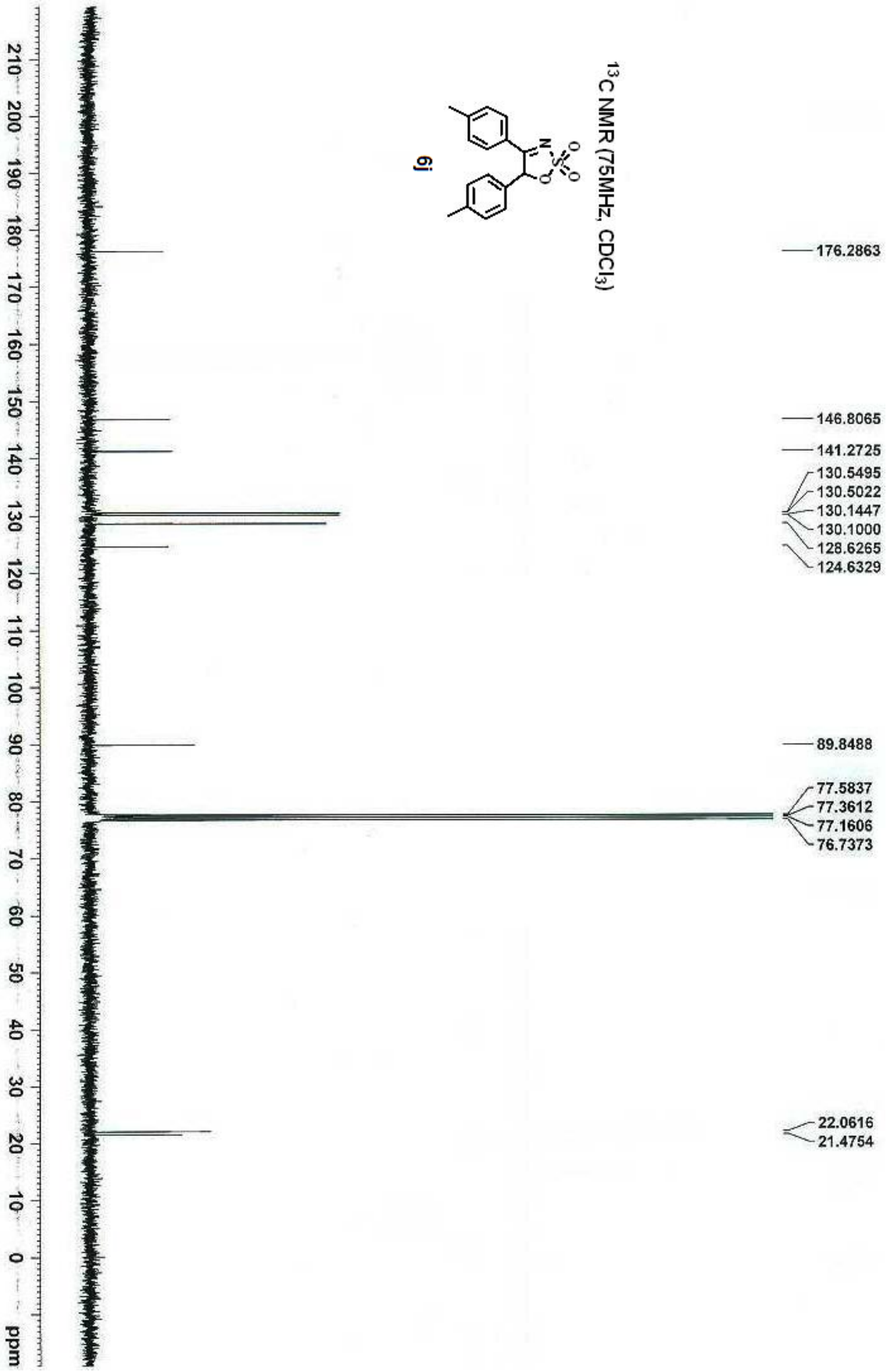

6h
^{1}H NMR (300MHz, CDCl$_3$)
7.949
7.943
7.926
7.919
7.411
7.404
7.388
7.381
6.902
6.892
6.885
6.879
6.872
6.863
6.292
3.874
3.831
3.775
1.256
2.25
2.07
4.18
1.00
5.62
ppm

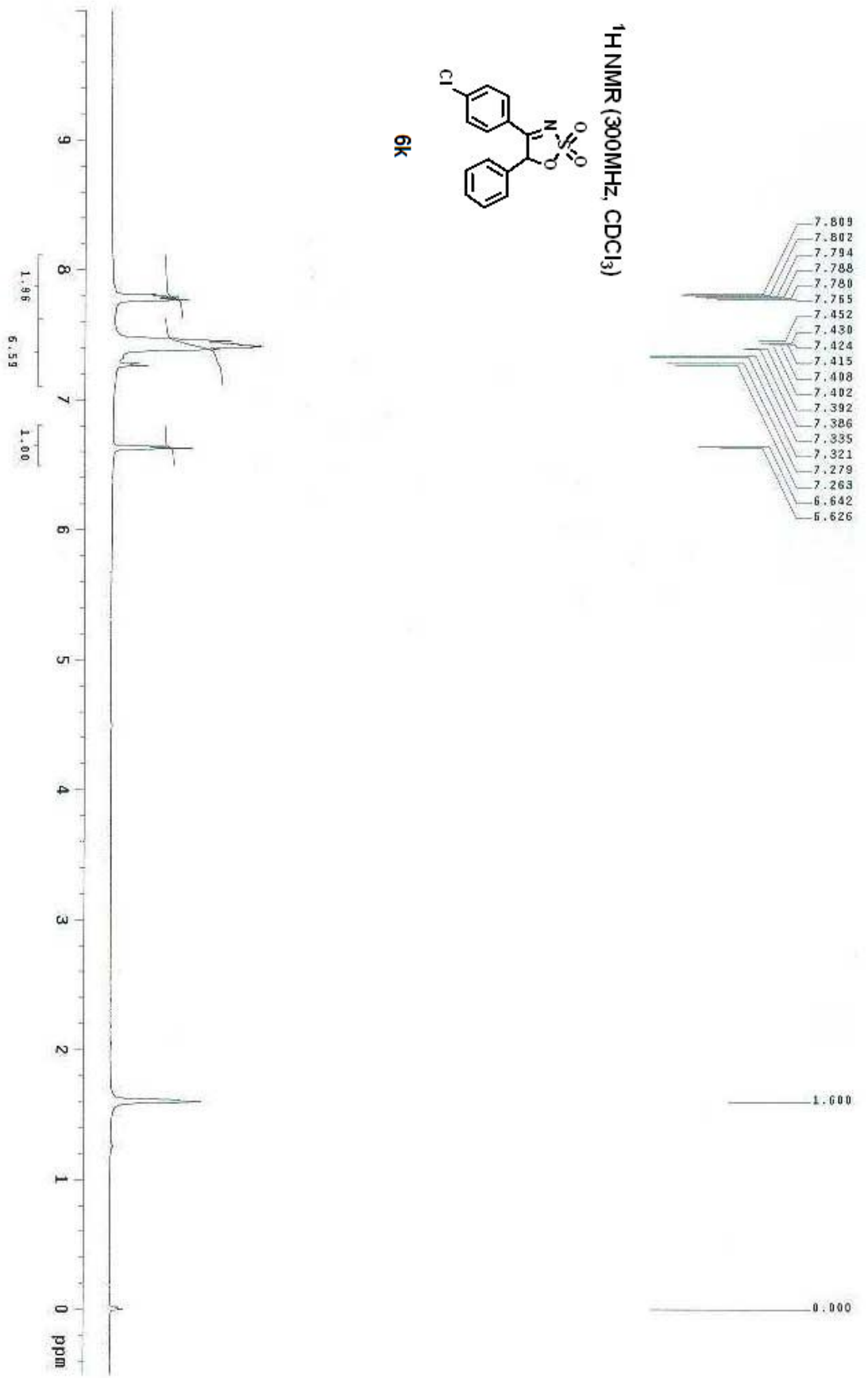

^{13}C NMR (75MHz, CDCl$_3$)
6h
190.1360
163.9614
160.2160
131.5753
129.9219
128.3712
127.2399
114.6283
114.0835
77.5866
77.1630
76.7390
62.1818
55.6039
55.3914
ppm


1H NMR (300MHz, CDCl3)
6i
7.771
7.550
7.524
7.405
7.379
7.334
7.307
7.284
7.261
7.251
7.213
7.191
6.607
2.347
1.576
0.000
ppm


^{13}C NMR (75MHz, CDCl$_3$)
6i
176.6765
139.9108
139.4641
136.1634
132.7609
131.7528
130.7823
129.6761
129.1595
129.0826
127.6491
127.2398
125.8242
90.0906
77.5839
77.1604
76.7371
21.4629
21.3543
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


¹H NMR (300MHz, CDCl₃)
6j
7.747
7.719
7.295
7.268
7.223
7.195
6.611
2.375
2.339
1.599
1.91
5.55
1.00
5.17
ppm


^{13}C NMR (75MHz, CDCl$_3$)
6j
176.2863
146.8065
141.2725
130.5495
130.5022
130.1447
130.1000
128.6265
124.6329
89.8488
77.5837
77.3612
77.1606
76.7373
22.0616
21.4754
ppm


1H NMR (300MHz, CDCl3)
6k
Cl
7.809
7.802
7.794
7.788
7.780
7.765
7.452
7.430
7.424
7.415
7.408
7.402
7.392
7.386
7.335
7.321
7.279
7.263
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6.626
1.000
0.000
1.96
6.59
1.00
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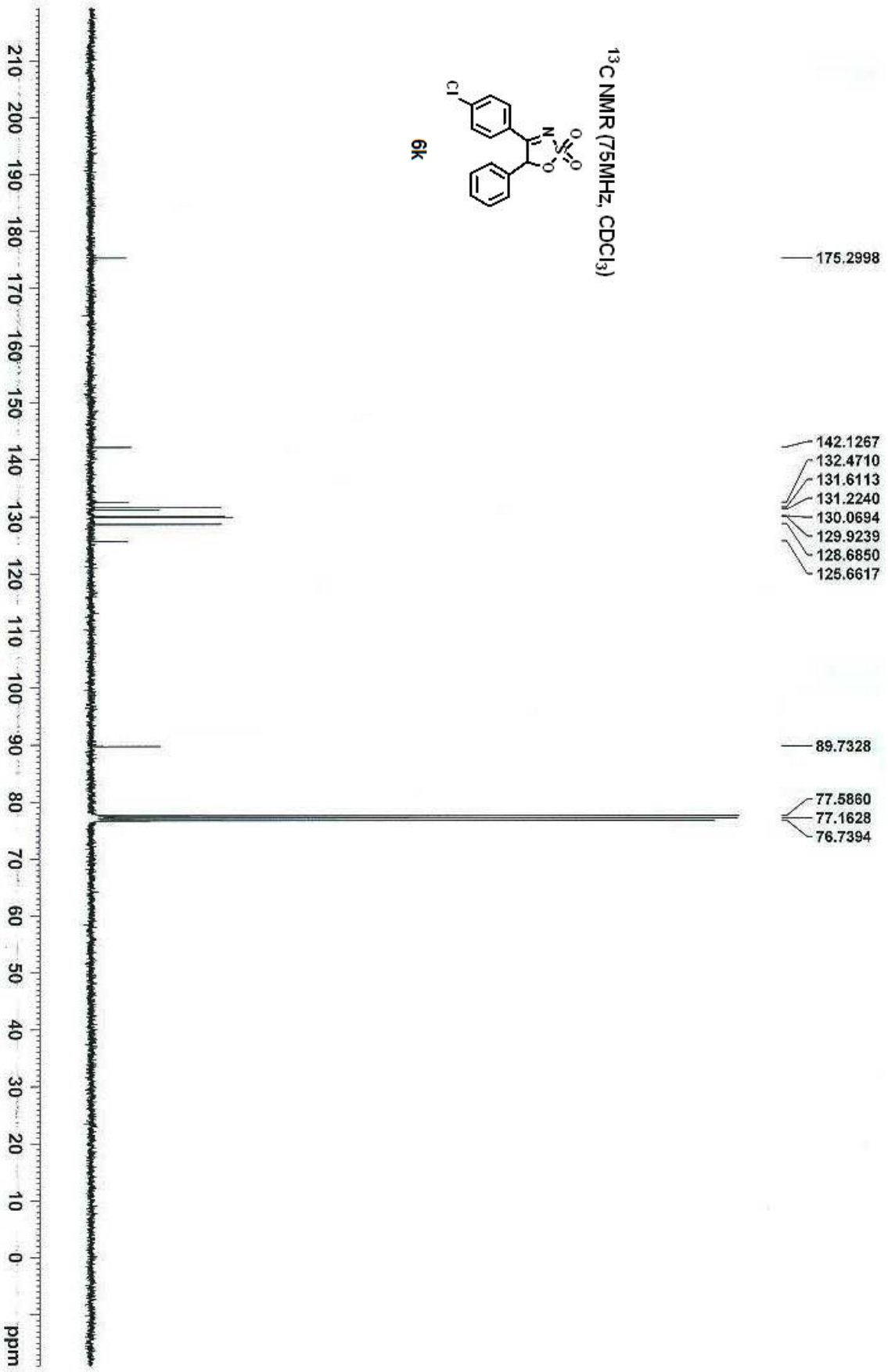
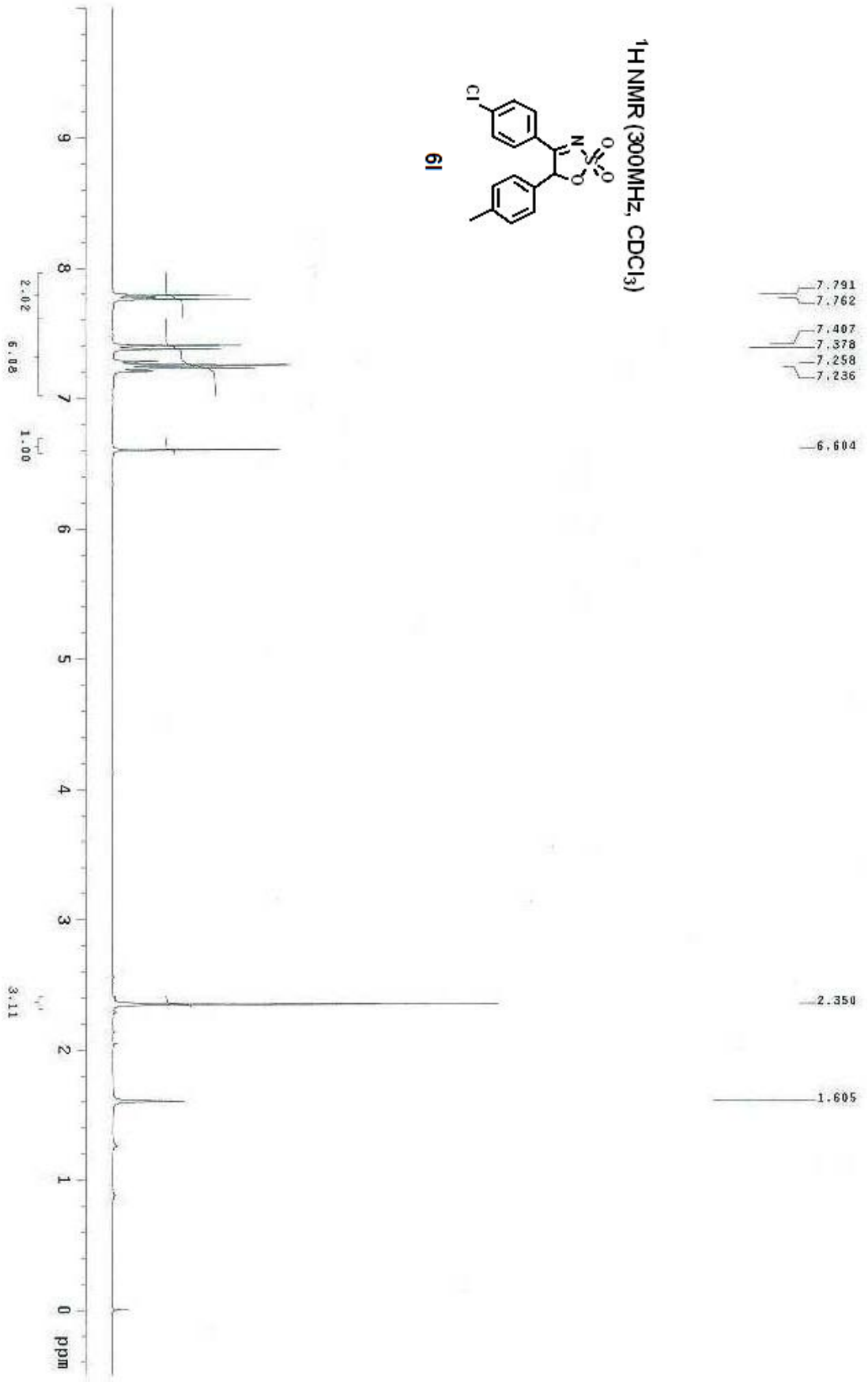
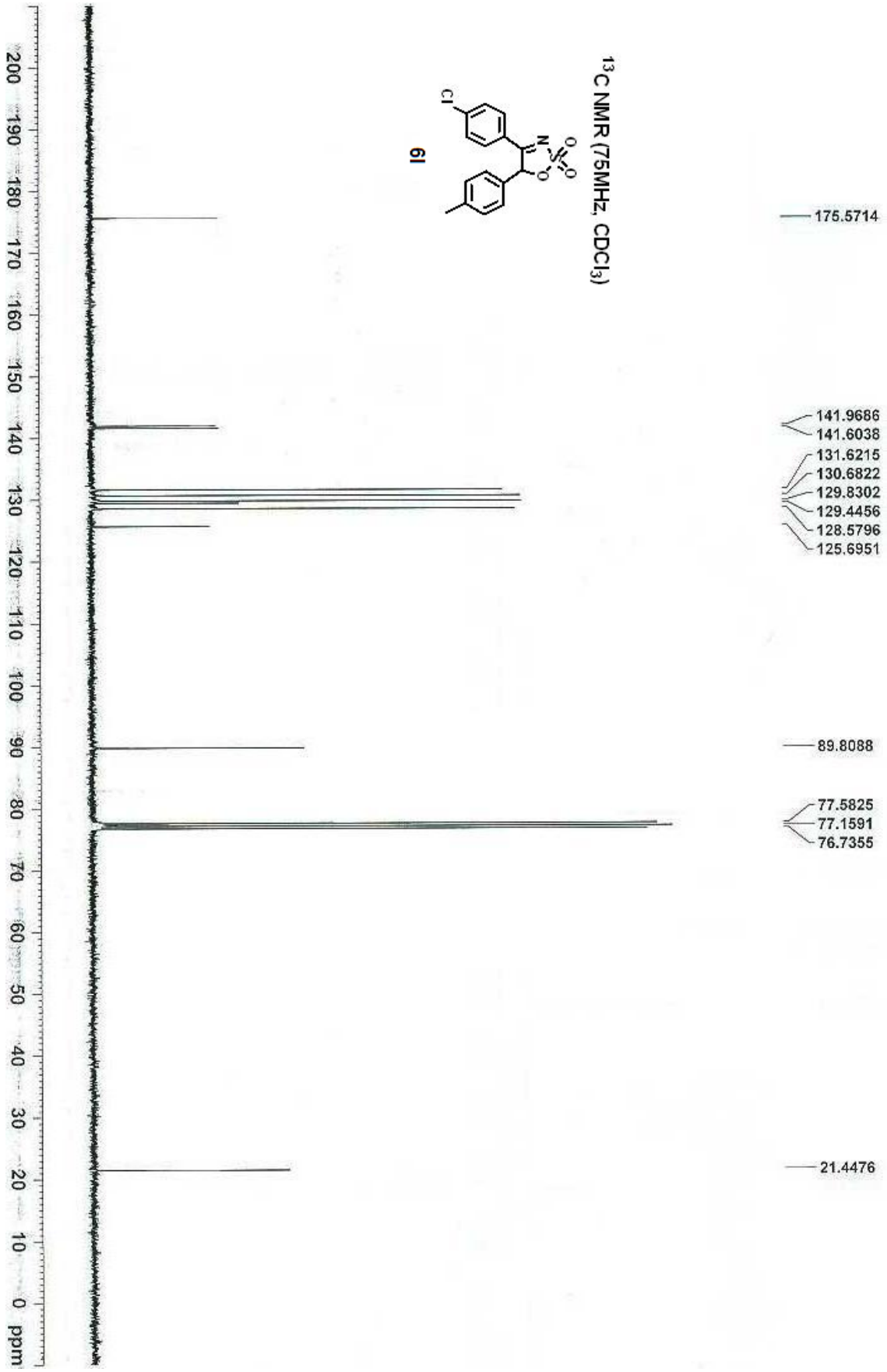
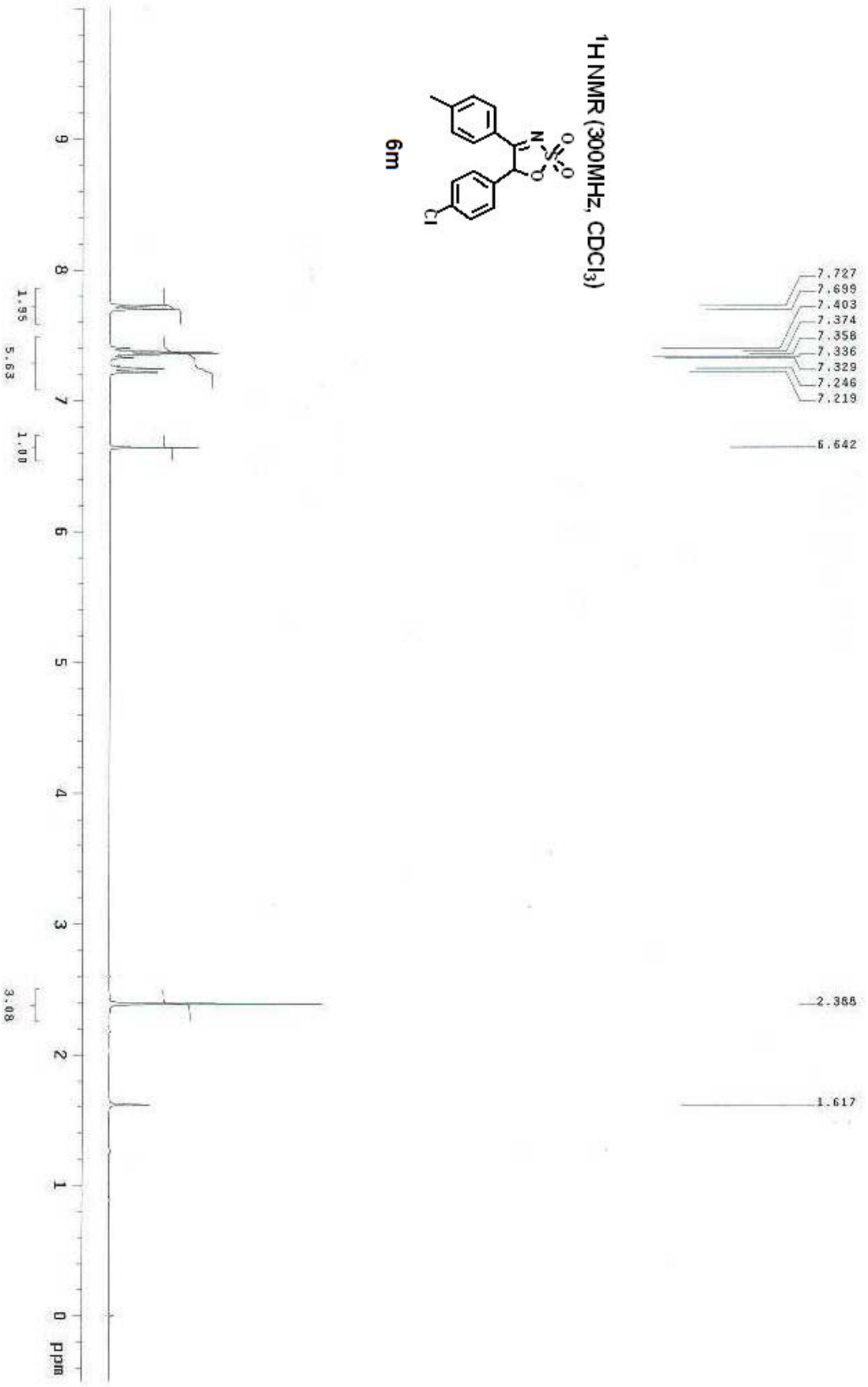

^{13}C NMR (75MHz, CDCl$_3$)
6k
Cl
N
O
S
O
O
175.2998
142.1267
132.4710
131.6113
131.2240
130.0694
129.9239
128.6850
125.6617
89.7328
77.5860
77.1628
76.7394
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


^{1}H NMR (300MHz, CDCl$_3$)
6l
Cl
O
S
O
N
O
7.791
7.762
7.407
7.378
7.258
7.236
6.604
2.350
1.605
2.02
6.08
1.00
3.11
9
8
7
6
5
4
3
2
1
0
ppm


^{13}C NMR (75MHz, CDCl$_3$)
6l
175.5714
141.9686
141.6038
131.6215
130.6822
129.8302
129.4456
128.5796
125.6951
89.8088
77.5825
77.1591
76.7355
21.4476
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


6m
^{1}H NMR (300MHz, CDCl$_3$)
7.727
7.699
7.403
7.374
7.358
7.336
7.329
7.246
7.219
6.642
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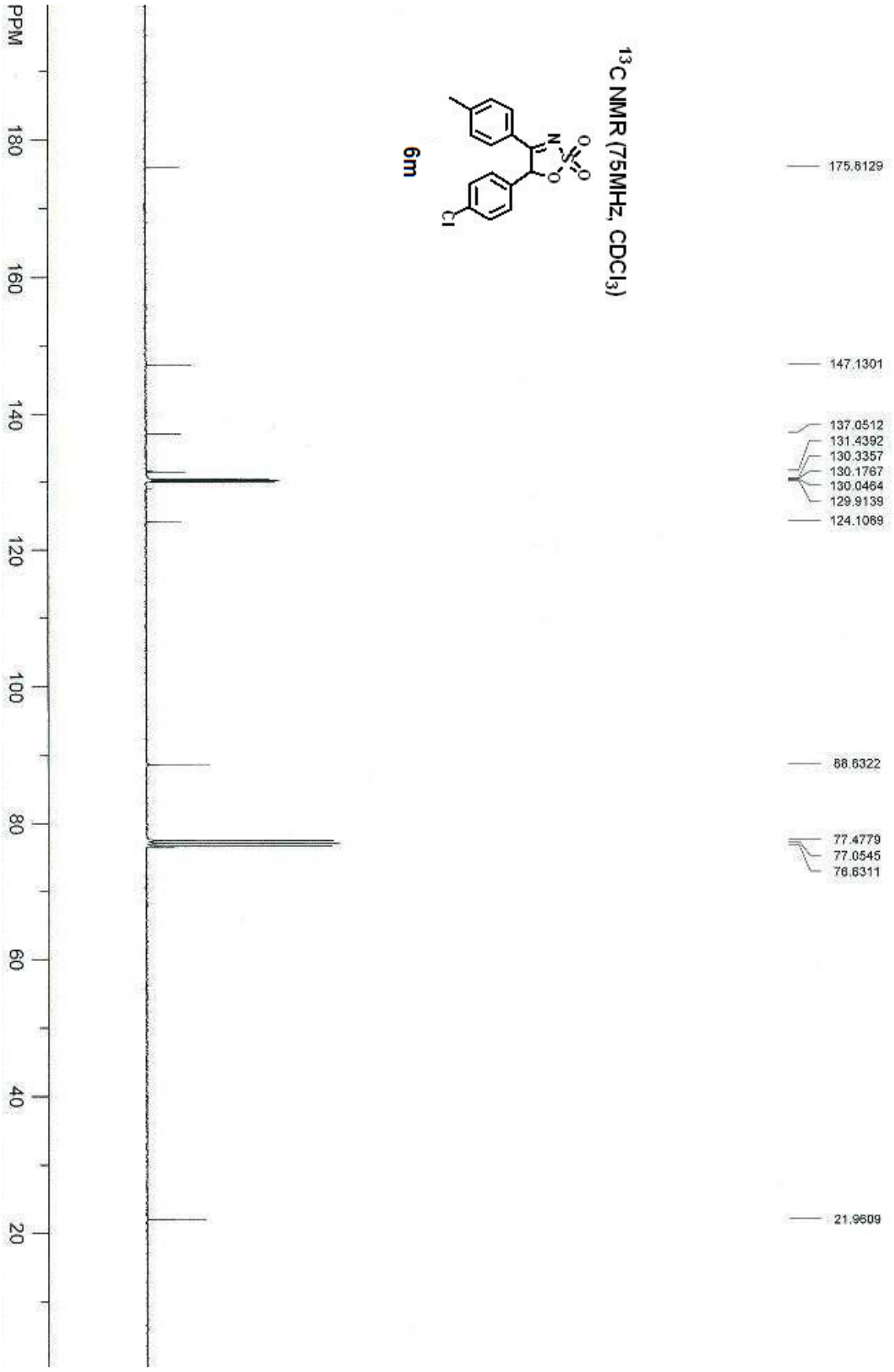
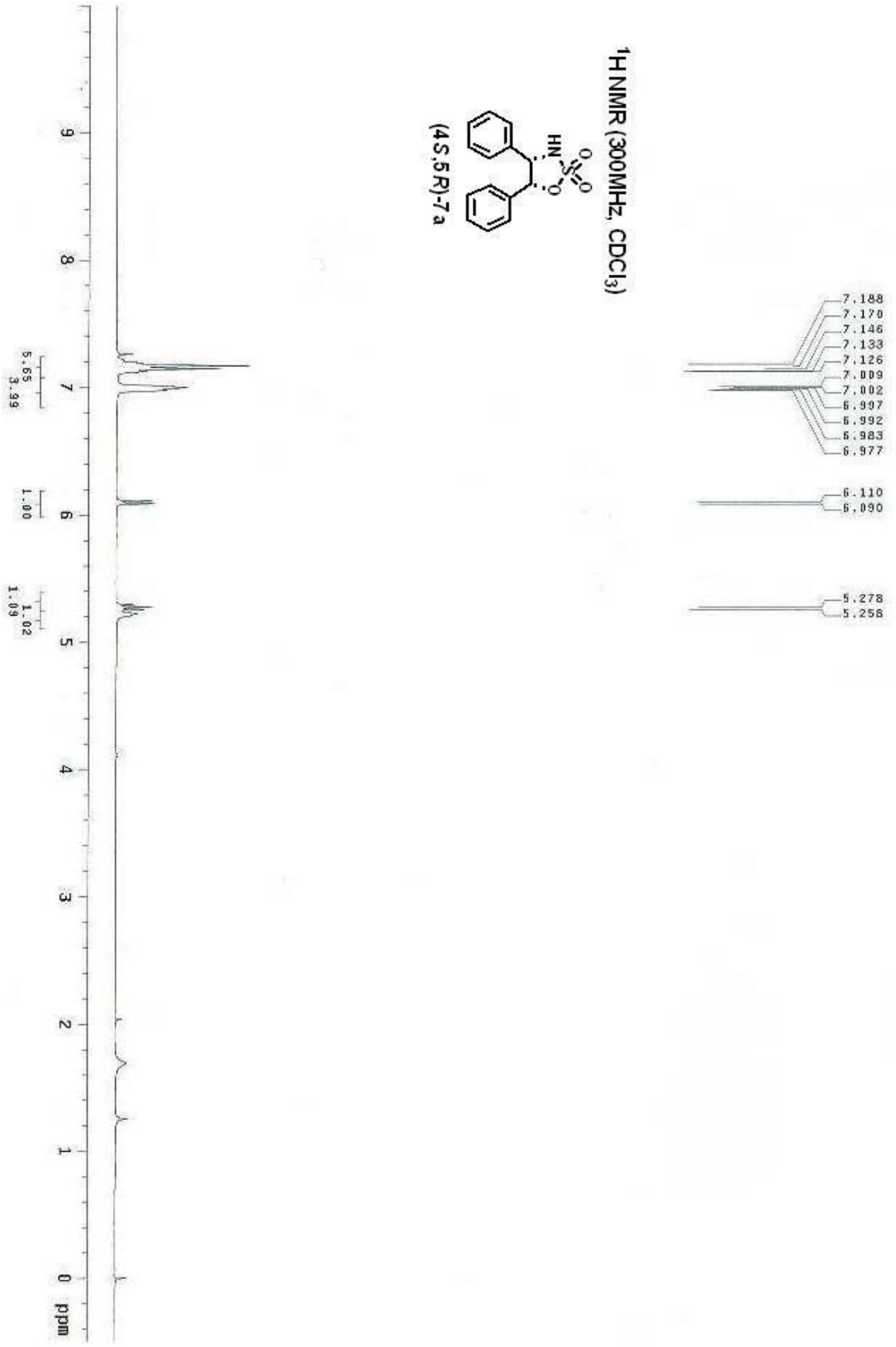
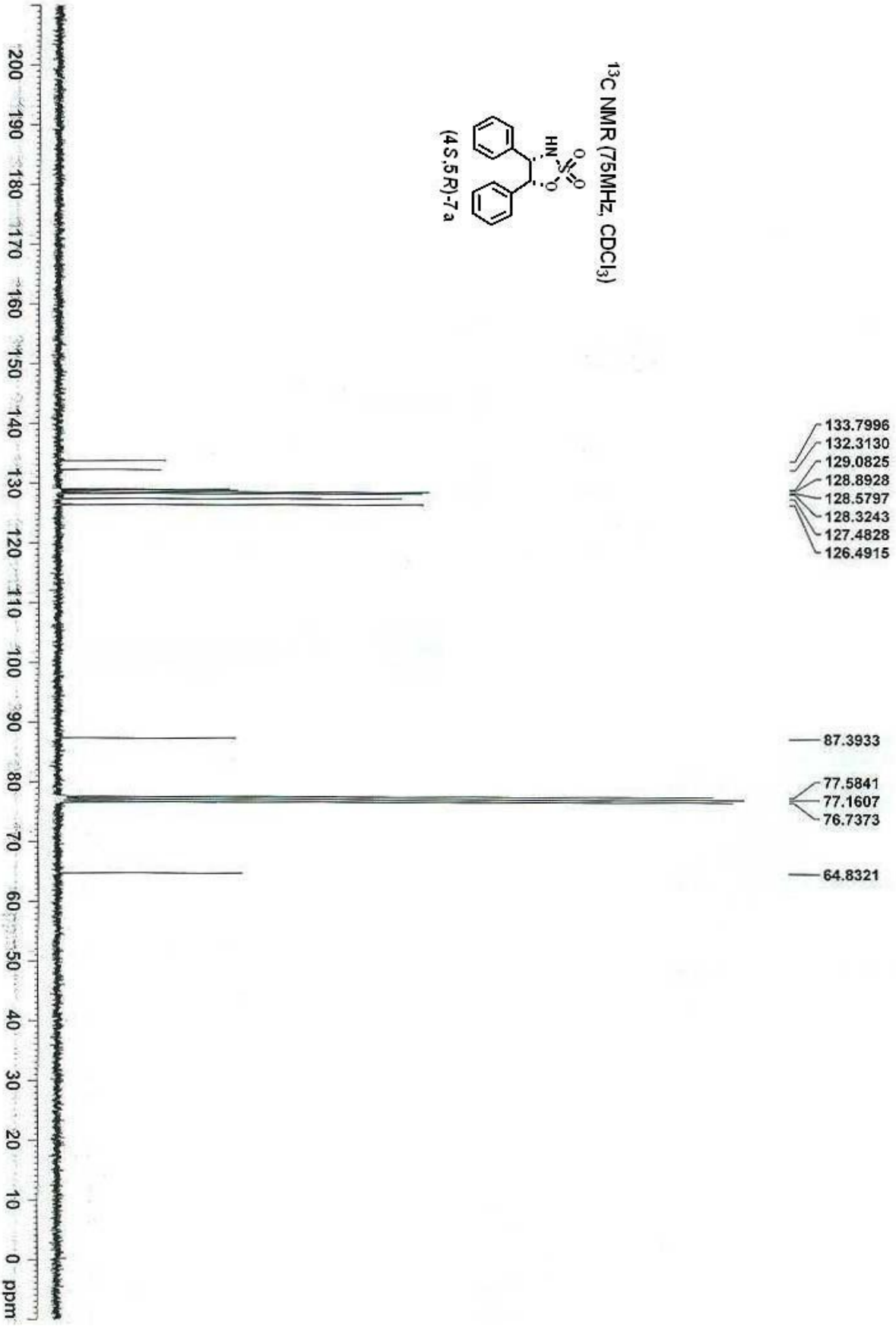
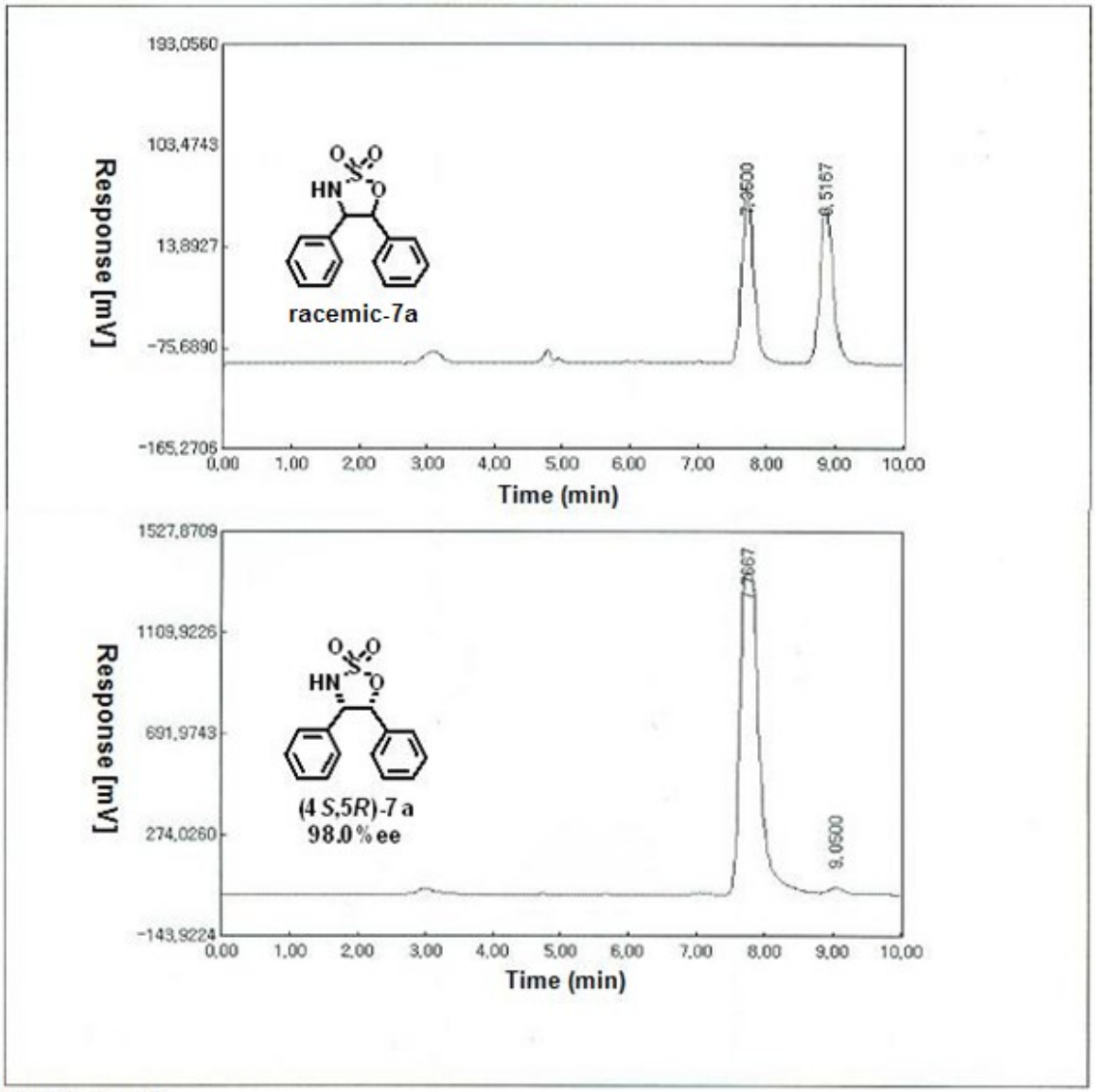
1.617
1.95
5.63
1.00
3.08
ppm


^{13}C NMR (75MHz, CDCl$_3$)
6m
PPM
180
160
140
120
100
80
60
40
20
175.8129
147.1301
137.0512
131.4392
130.3357
130.1767
130.0464
129.9139
124.1089
88.6322
77.4779
77.0545
76.6311
21.9609

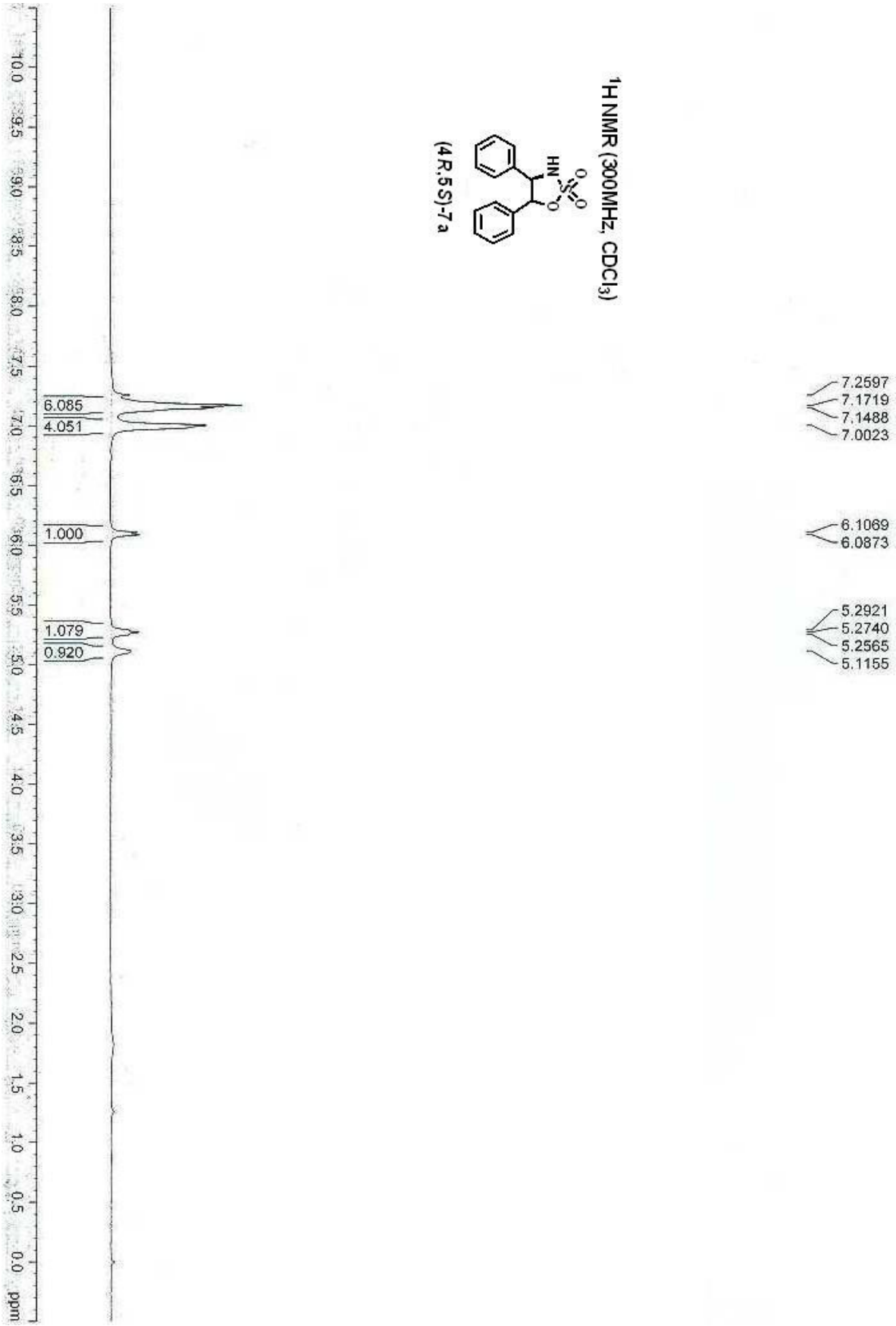

^{1}H NMR (300MHz, CDCl$_3$)
(4S,5R)-7a
HN
O
S
O
O
7.188
7.170
7.146
7.133
7.126
7.009
7.002
6.997
6.992
6.983
6.977
6.110
6.090
5.278
5.258
5.65
3.99
1.00
1.02
1.09
9
8
7
6
5
4
3
2
1
0
ppm

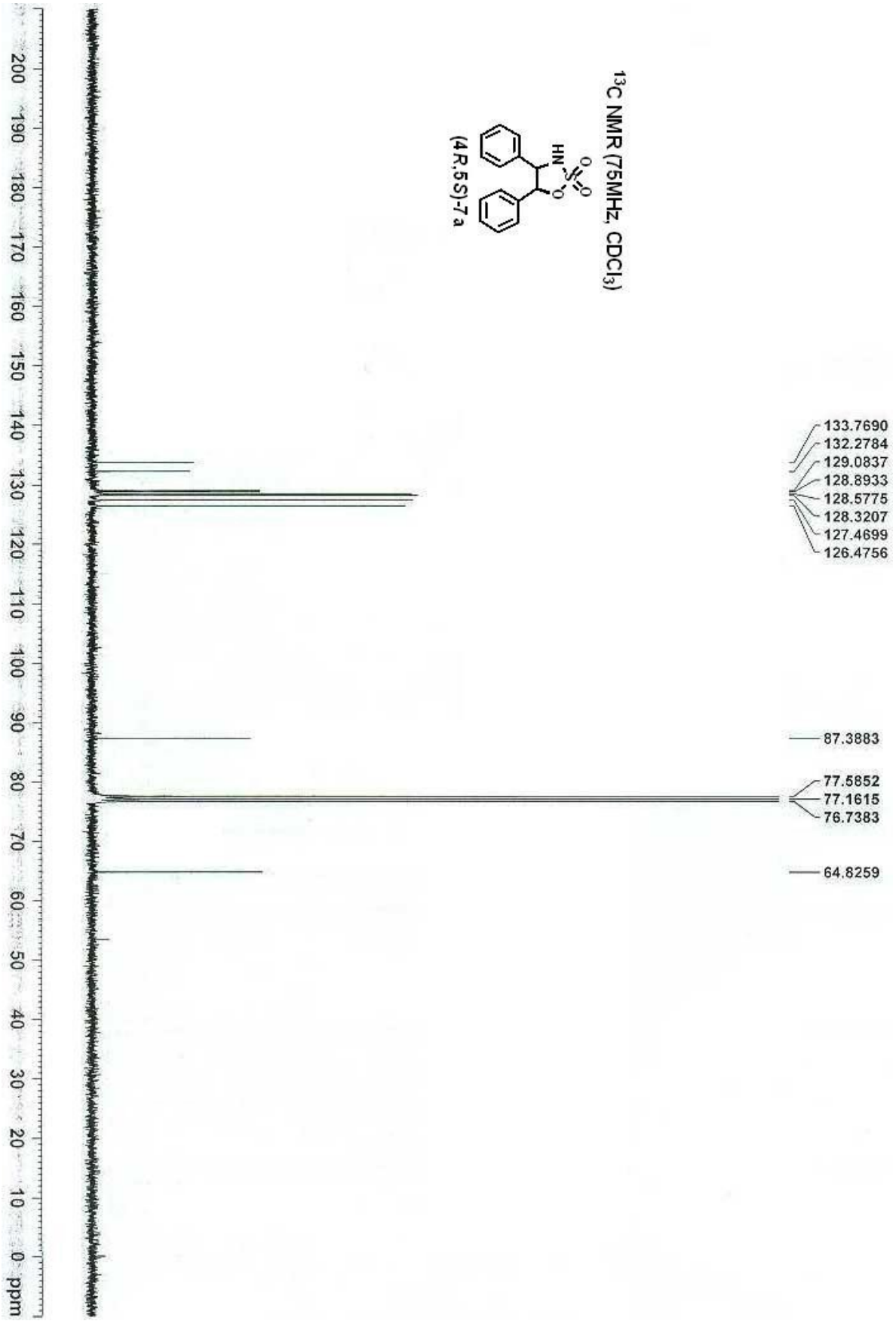

^{13}C NMR (75MHz, CDCl$_3$)
(4S,5R)-7a
HN
O
O
133.7996
132.3130
129.0825
128.8928
128.5797
128.3243
127.4828
126.4915
87.3933
77.5841
77.1607
76.7373
64.8321
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

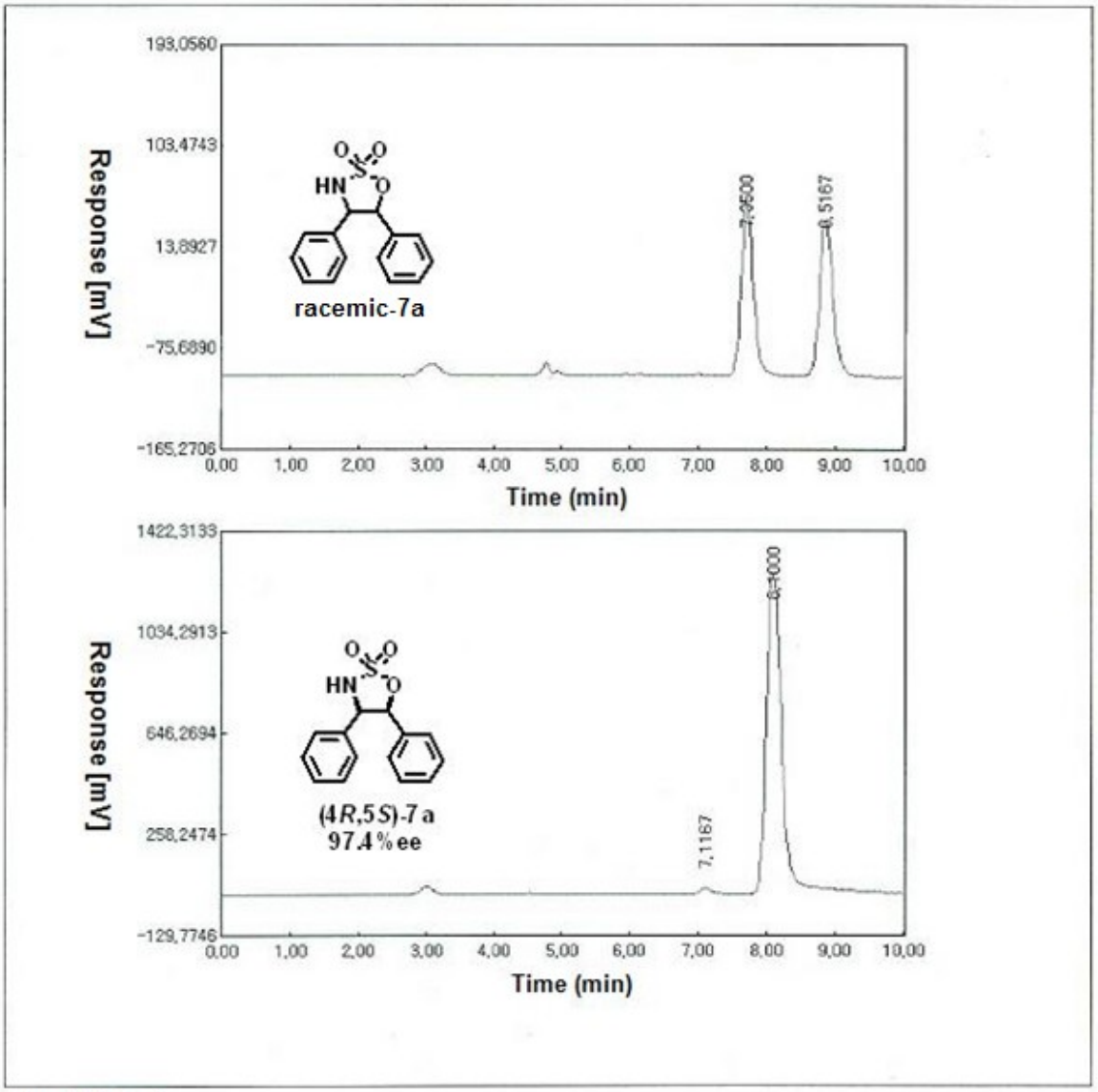


Result Report

Peak #	Time (min)	Area [mV*s]	BL	wide (sec)	Area %
1	3.0000	194.3282	BB	20.0000	0.7233
2	7.7667	26405.3896	BB	61.0000	98.2787
3	9.0500	268.1618	BB	23.0000	0.9981
Total		26867.8809			

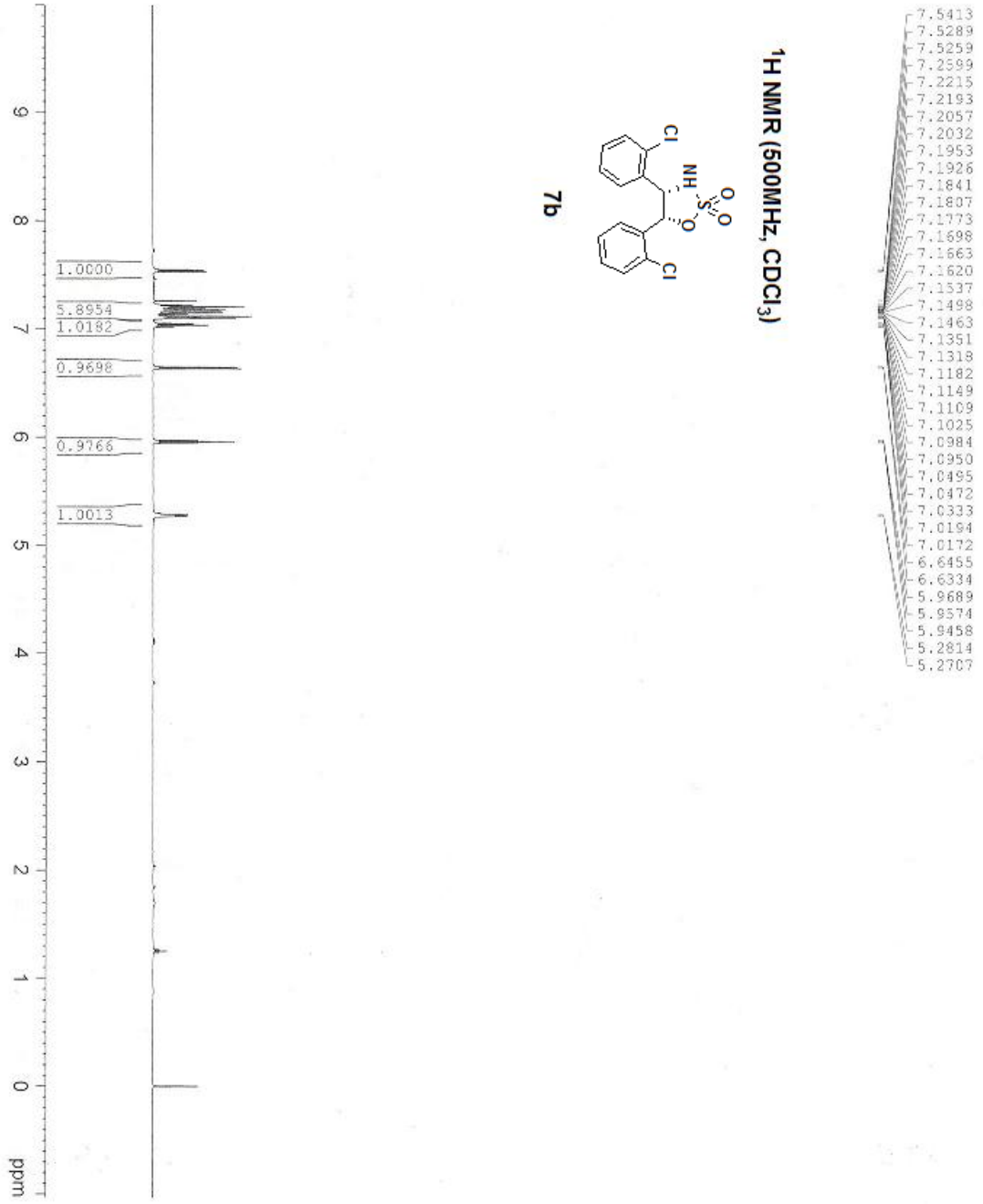

^{1}H NMR (300MHz, CDCl$_3$)
(4R,5S)-7a
HN
O
S
O
O
7.2597
7.1719
7.1488
7.0023
6.1069
6.0873
5.2921
5.2740
5.2565
5.1155
6.085
4.051
1.000
1.079
0.920
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


^{13}C NMR (75MHz, CDCl$_3$)
(4R,5S)-7a
HN
O
S
O
O
133.7690
132.2784
129.0837
128.8933
128.5775
128.3207
127.4699
126.4756
87.3883
77.5852
77.1615
76.7383
64.8259
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

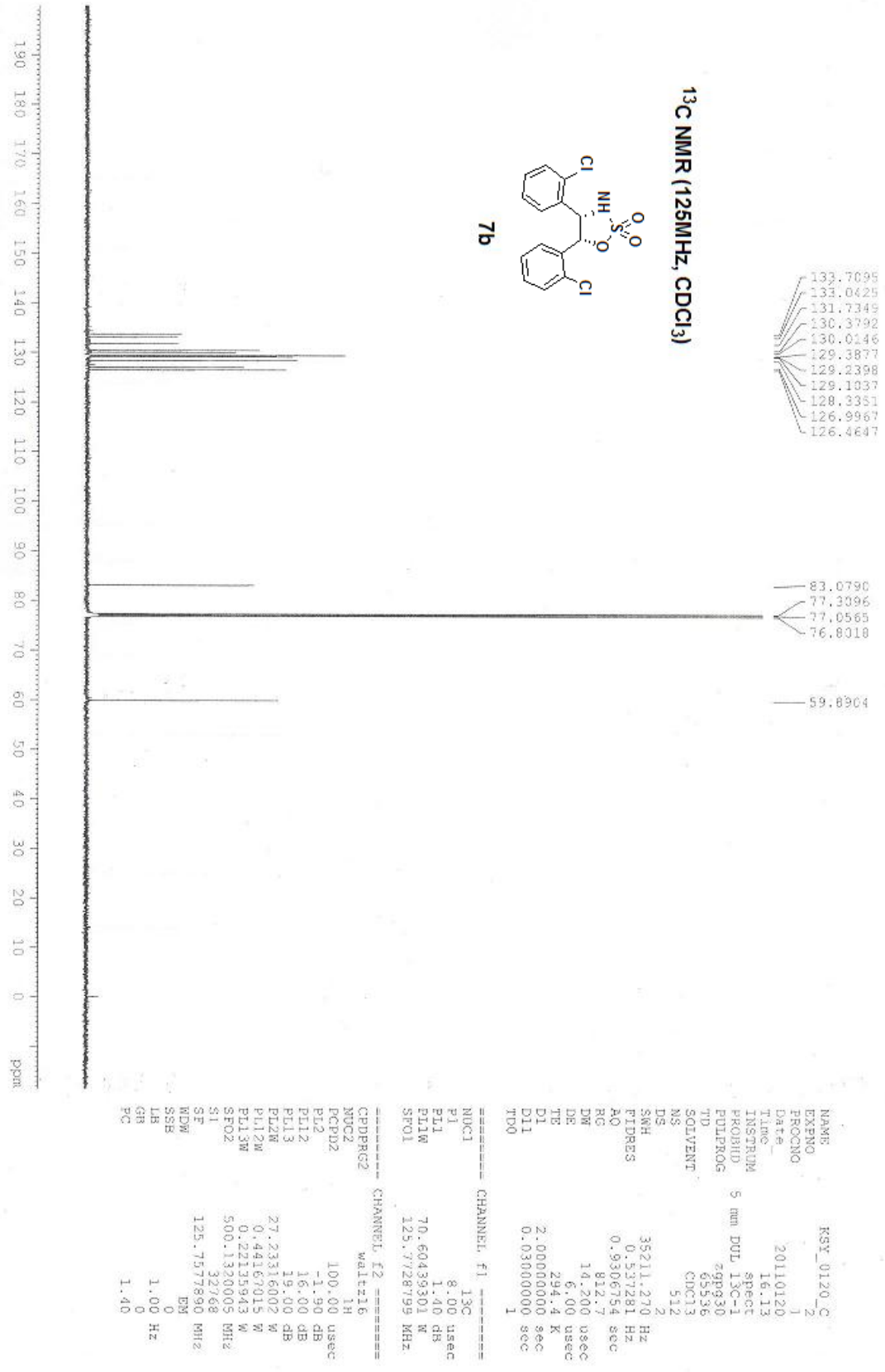


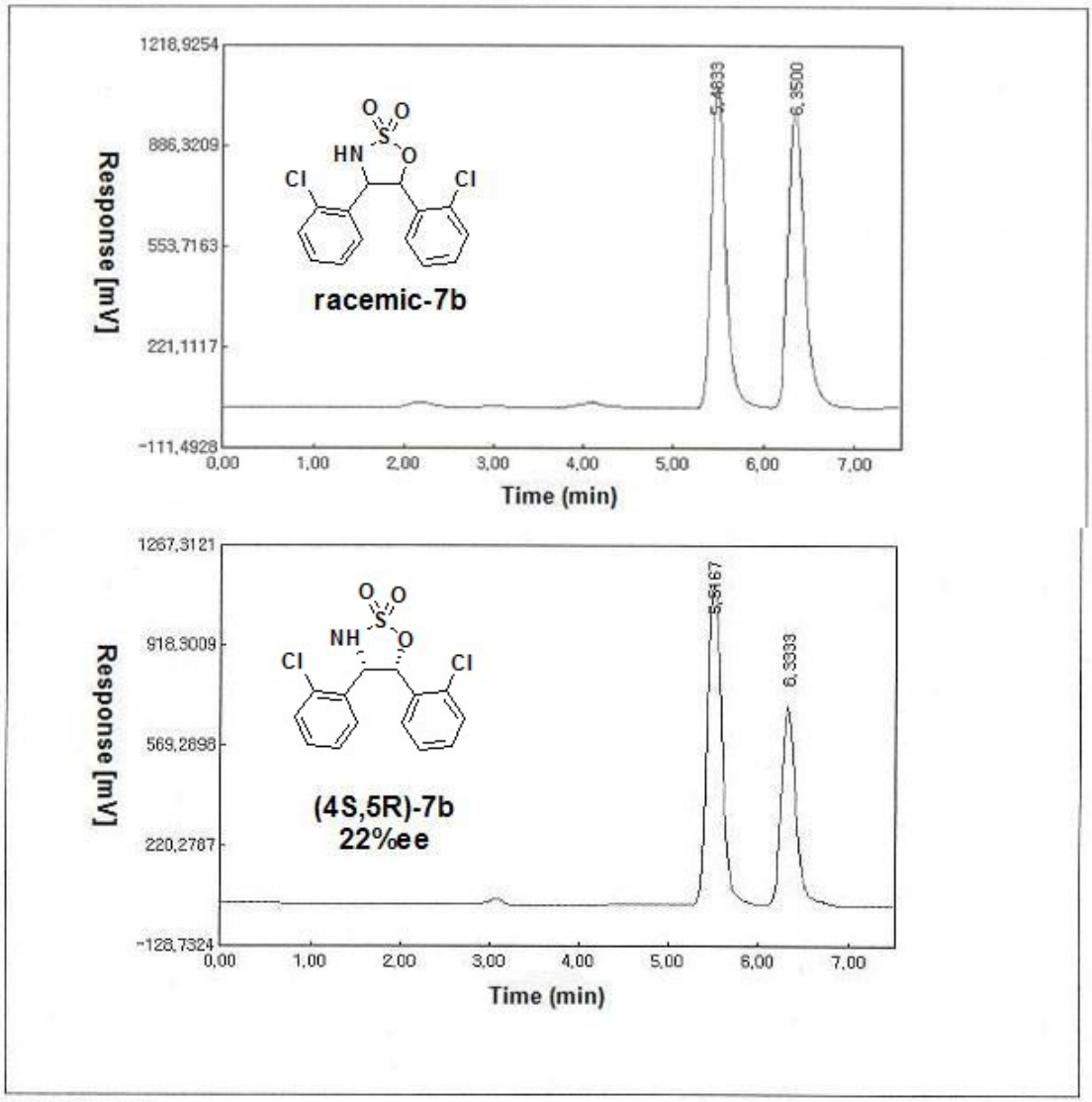
Result Report

Peak #	Time (min)	Area [mV*s]	BL	wide (sec)	Area %
1	3.0167	359.5693	BB	26.0000	1.8540
2	7.1167	250.6404	BB	23.0000	1.2924
3	8.1000	18783.5336	BB	52.0000	96.8536
Total		19393.7441			



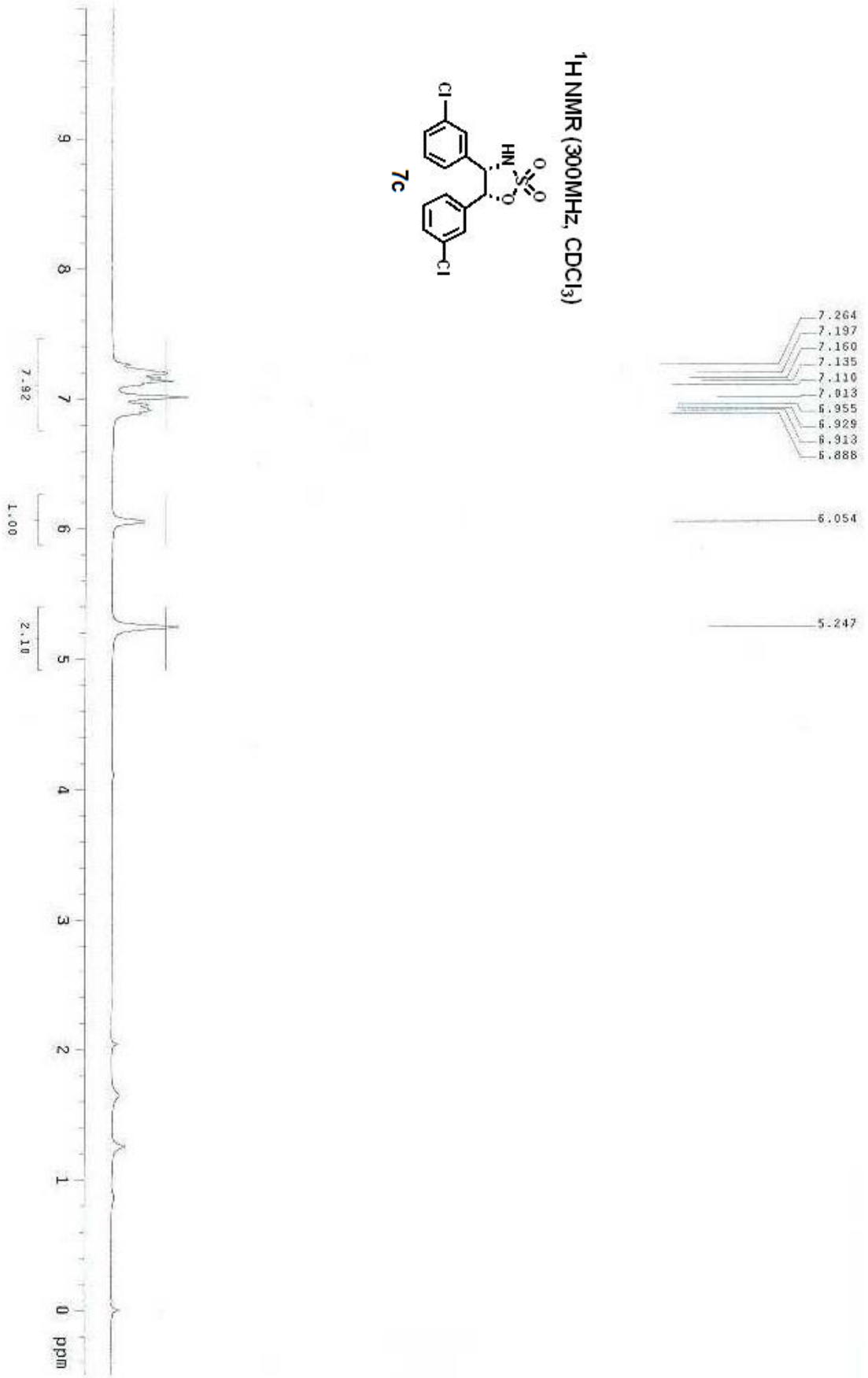

```
NAME                 KSY_0121_2
EXPNO                         4
PROCNO                        1
Date_              20110121
Time                      16.20
INSTRUM                    spect
PROBHD  5 mm DUL 13C-1
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                            4
DS                            2
SWH                  7507.507 Hz
FIDRES               0.114555 Hz
AQ                4.3648143 sec
RG                          128
DW                     66.600 usec
DE                      6.00 usec
TE                      294.3 K
D1                1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                        1H
P1                      9.80 usec
PL1                    -1.90 dB
PL1W             27.23316002 W
SFO1          500.1332508 MHz
SI                        32768
SF            500.1300136 MHz
WDW                        EM
SSB                         0
LB                   0.30 Hz
GB                          0
PC                       1.00
```

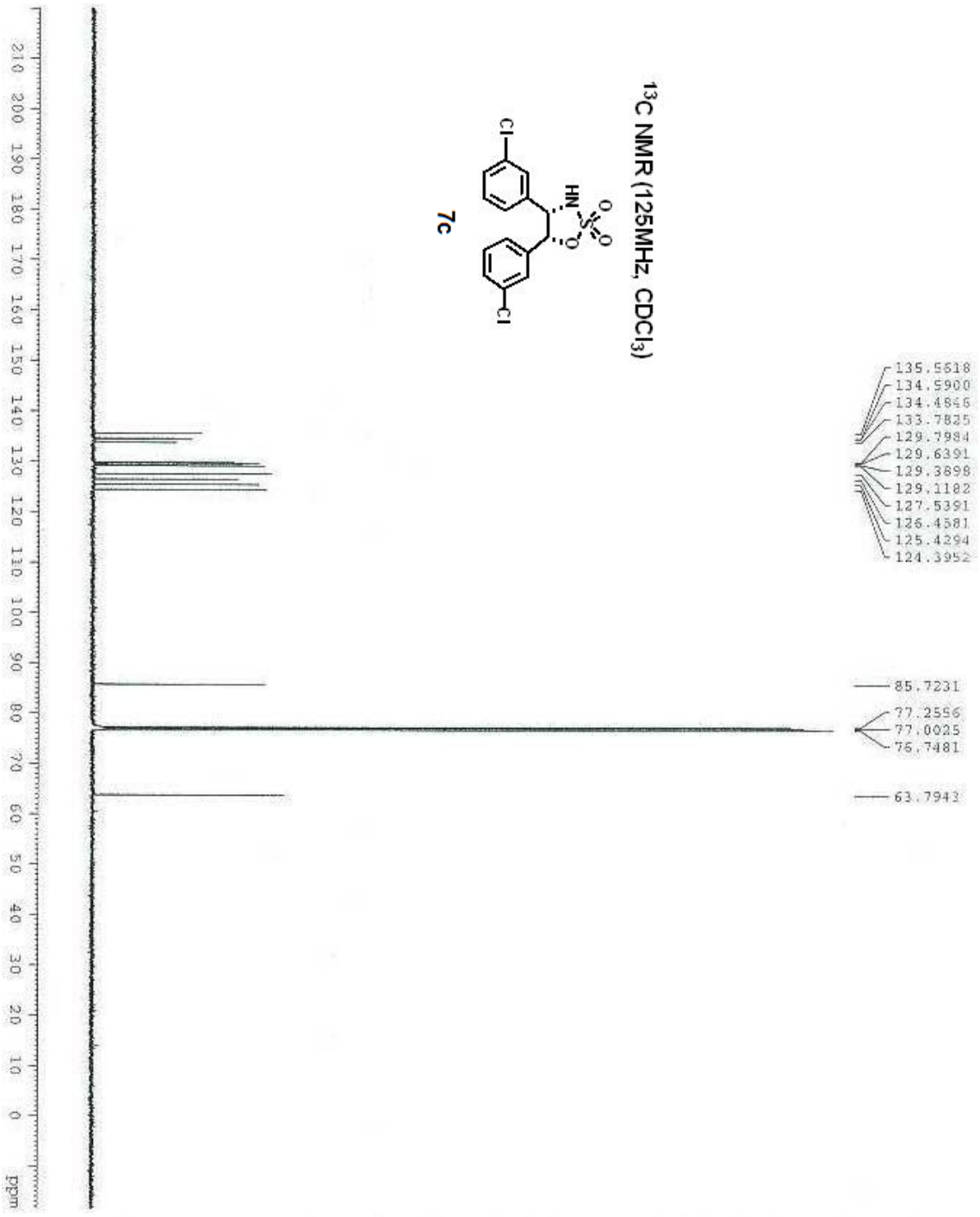

13C NMR (125MHz, CDCl3)
7b
Cl
NH
S
O
O
O
Cl
133.7095
133.0425
131.7349
130.3792
130.0146
129.3877
129.2398
129.1037
128.3351
126.9967
126.4647
83.0790
77.3096
77.0565
76.8018
59.8904
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
NAME RSY_0120_C
EXPNO 2
PROCNO 1
Date_ 20110120
Time 16.13
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 2
SWH 35211.270 Hz
FIDRES 0.537281 Hz
AQ 0.9306754 sec
RG 812.7
DW 14.200 usec
DE 6.00 usec
TE 294.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 1.40 dB
PL1W 70.60439301 W
SFO1 125.7728799 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -1.90 dB
PL12 16.00 dB
PL13 19.00 dB
PL2W 27.23316002 W
PL12W 0.44167015 W
PL13W 0.22135943 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



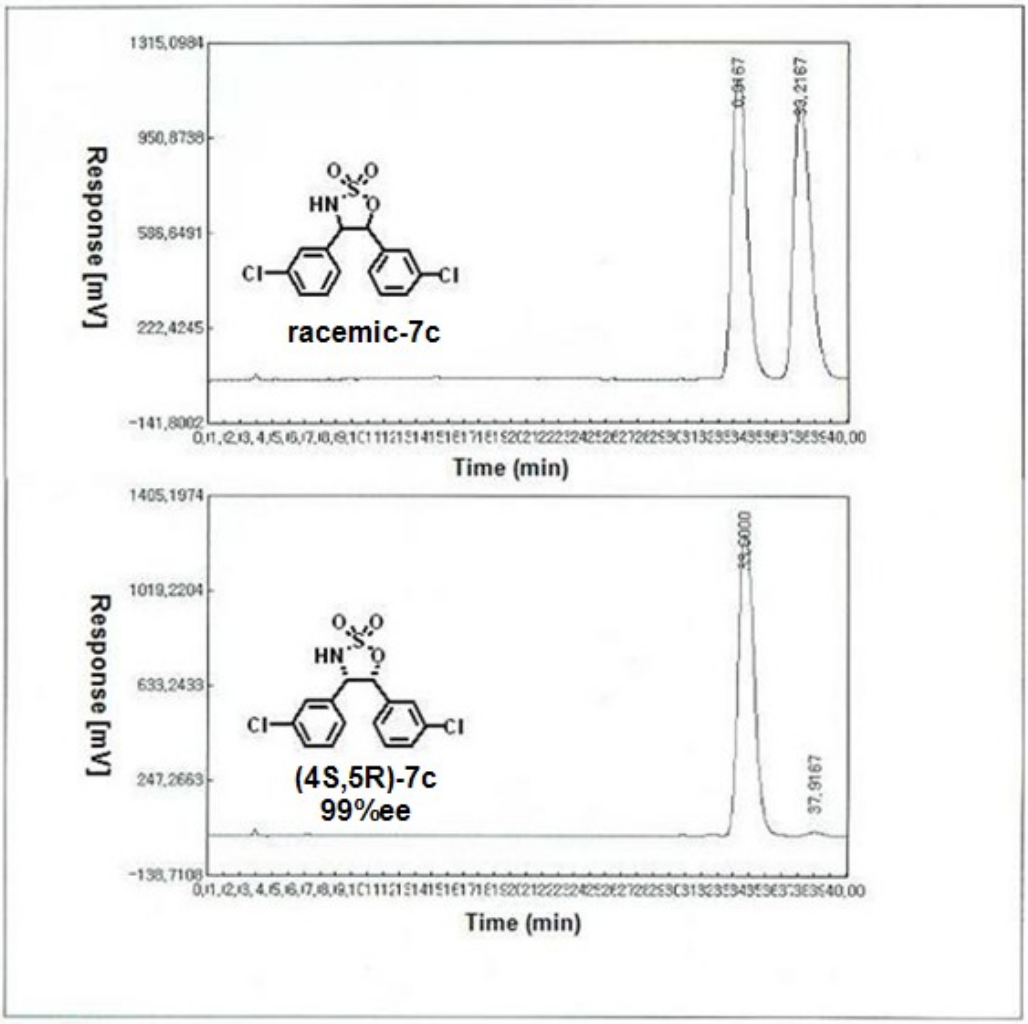
Result Report

Peak #	Time (min)	Area [mV*s]	BL	wide (sec)	Area %
1	5.5167	12825.3085	VV	48.0000	60.8924
2	6.3333	8236.9532	VB	65.0000	39.1076
Total		21062.2617			


1H NMR (300MHz, CDCl3)
7c
Cl
HN
O
S
O
O
Cl
7.264
7.197
7.160
7.135
7.110
7.013
6.955
6.929
6.913
6.888
6.054
5.247
7.92
1.00
2.10
9
8
7
6
5
4
3
2
1
0
ppm

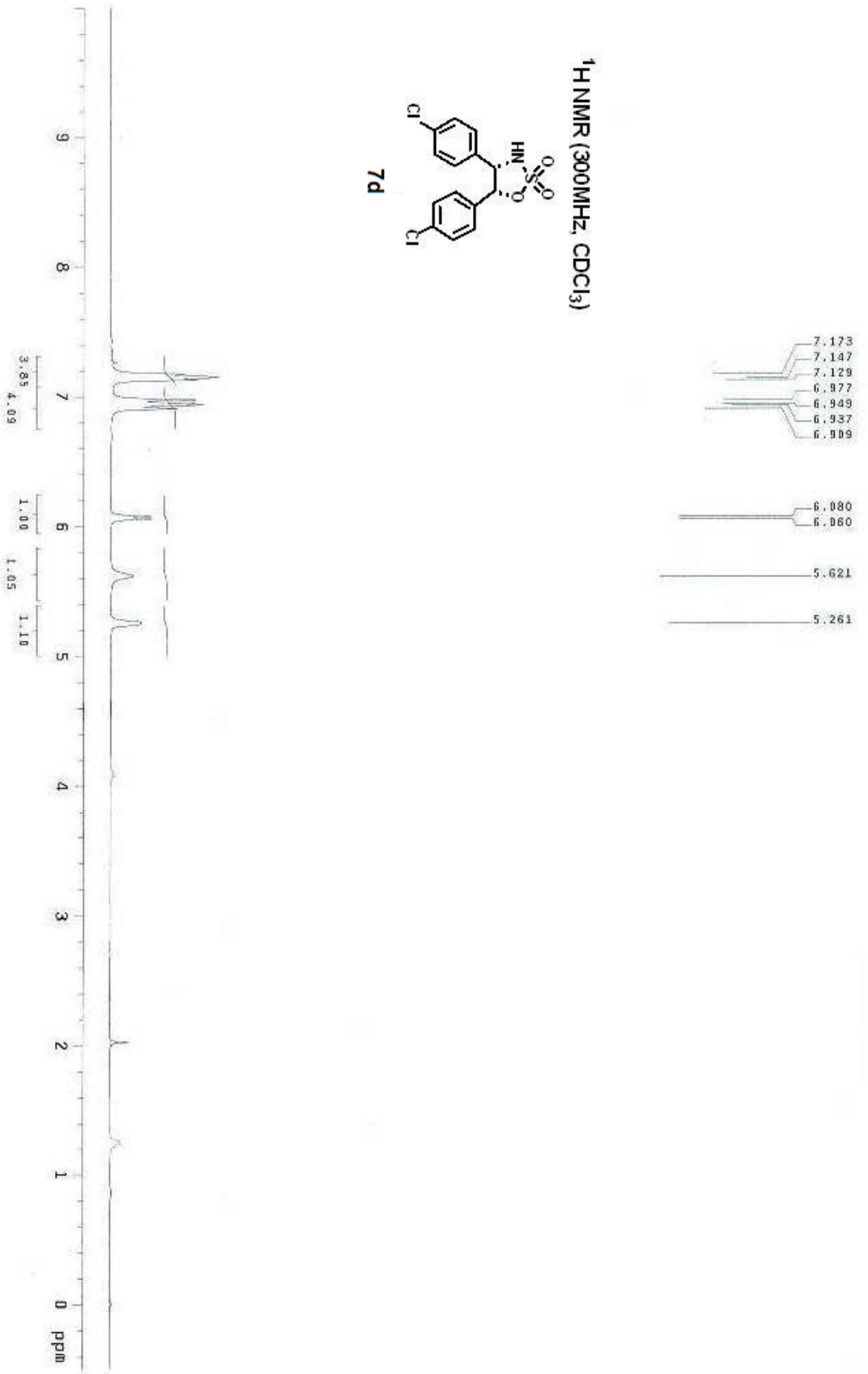


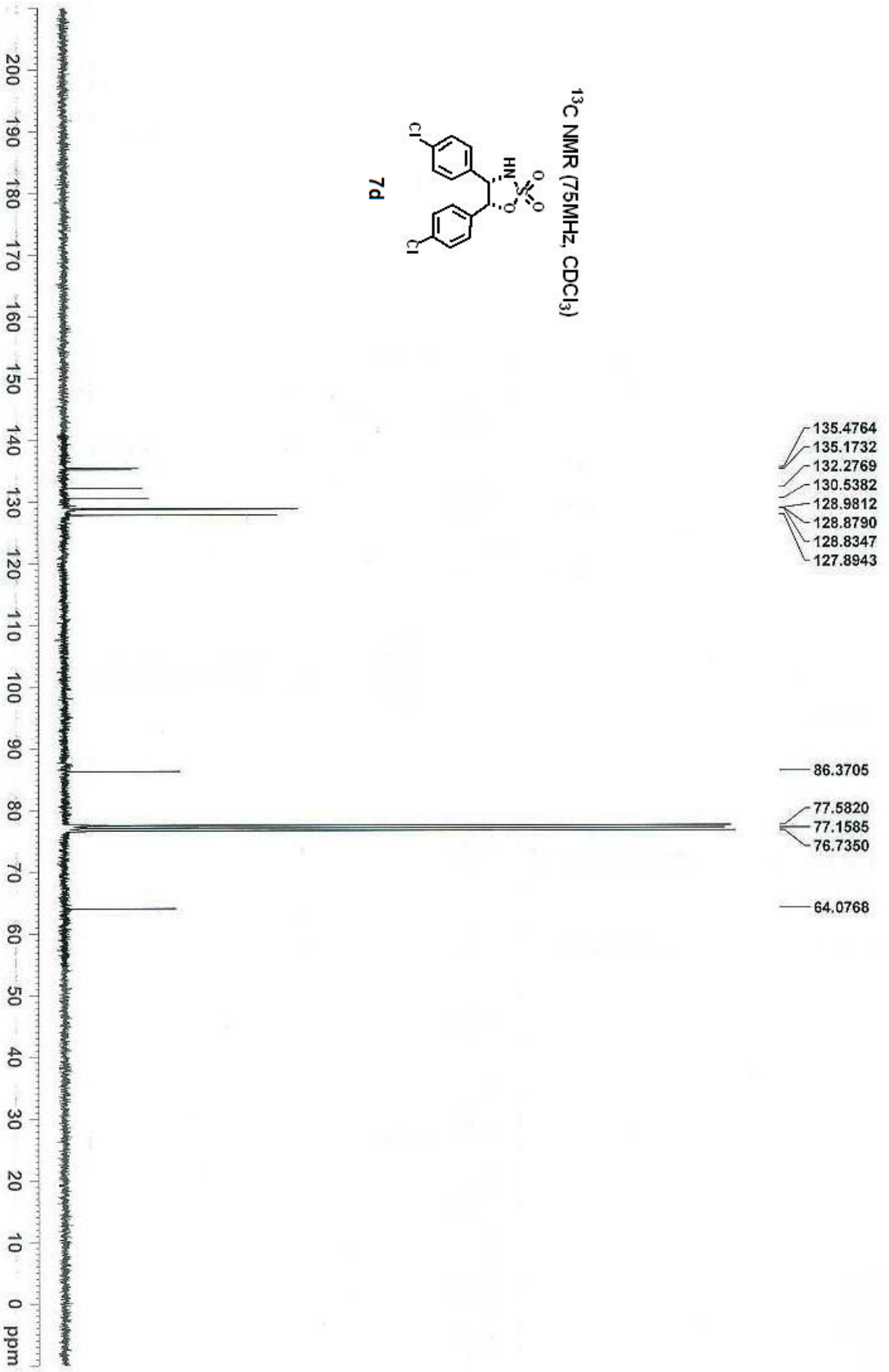

```
NAME                                    HUA_3C1
EXPNO                                         1
PROCNO                                        1
Date_                               20101105
Time                                    16.38
INSTRUM                                 spect
PROBHD                  5 mm DUL 13C-1
PULPROG                             zgpg30
TD                                  65536
SOLVENT                             CDCl3
NS                                    512
DS                                      2
SWH                             35211.270 Hz
FIDRES                              0.537281 Hz
AQ                              0.9306754 sec
RG                                    512
DW                                 14.200 usec
DE                                  6.00 usec
TE                                297.5 K
D1                              2.00000000 sec
D11                             0.03000000 sec
TD0                                     1

======== CHANNEL f1 ========
NUC1                                  13C
P1                                 8.00 usec
PL1                                1.40 dB
PL1W                         70.60439301 W
SFO1                        125.7728799 MHz

======== CHANNEL f2 ========
CPDPRG2                           waltz16
NUC2                                  1H
PCPD2                             100.00 usec
PL2                               -1.90 dB
PL12                              16.00 dB
PL13                              19.00 dB
PL2W                         27.23316002 W
PL12W                         0.41167015 W
PL13W                         0.22135943 W
SFO2                        500.1320005 MHz
SI                                  32768
SF                          125.7577946 MHz
WDW                                    EM
SSB                                     0
LB                                 1.00 Hz
GB                                      0
PC                                 1.40
```

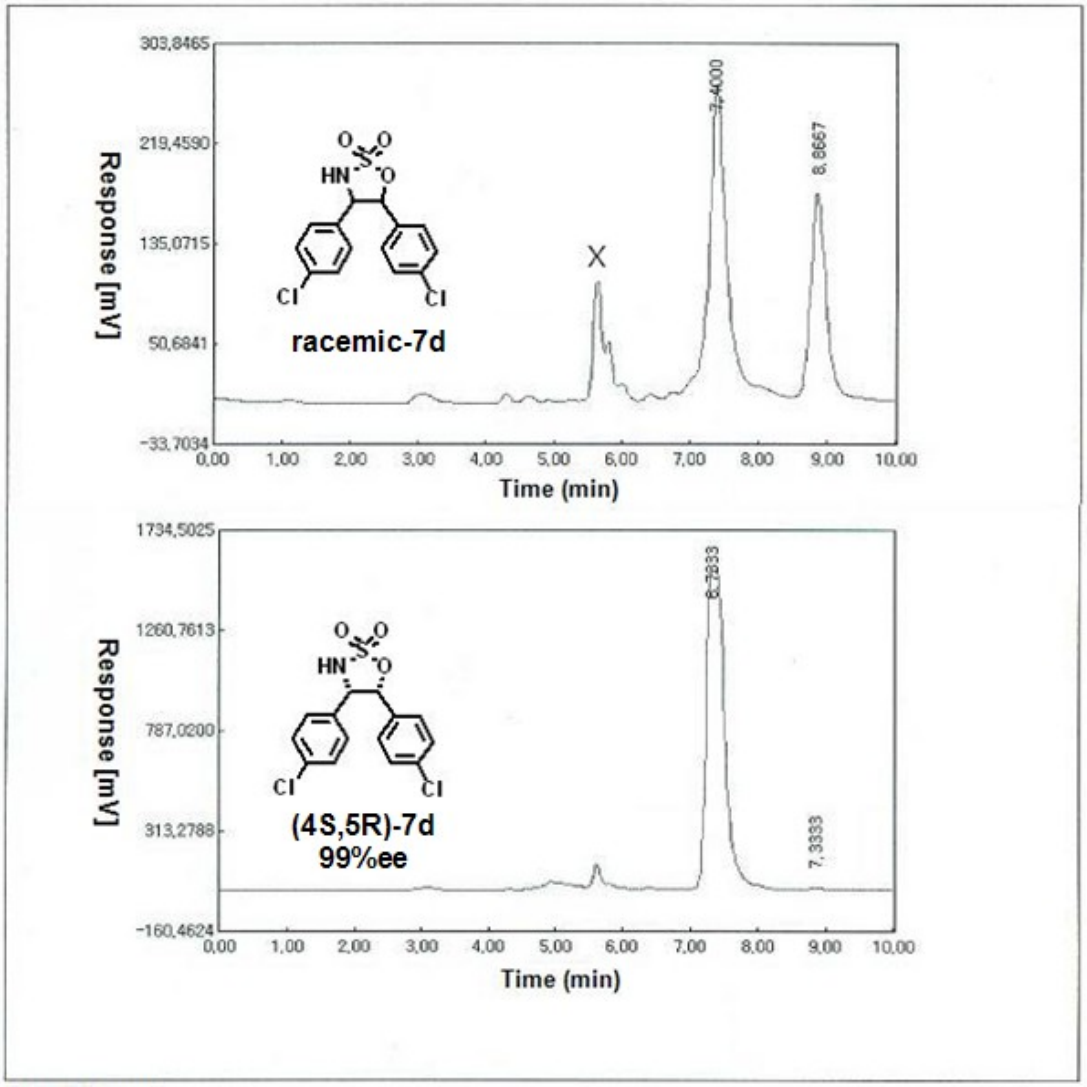


Result Report

Peak #	Time (min)	Area [mV*s]	BL	wide (sec)	Area %
1	2.7167	13.5374	BB	13.0000	0.0157
2	2.9500	218.4371	BB	21.0000	0.2536
3	3.7667	39.5275	BB	15.0000	0.0459
4	6.2000	24.3187	BB	15.0000	0.0282
5	33.6000	85791.2412	BB	193.0000	99.6159
6	37.9167	34.9975	BB	29.0000	0.0406
Total		86122.0625			

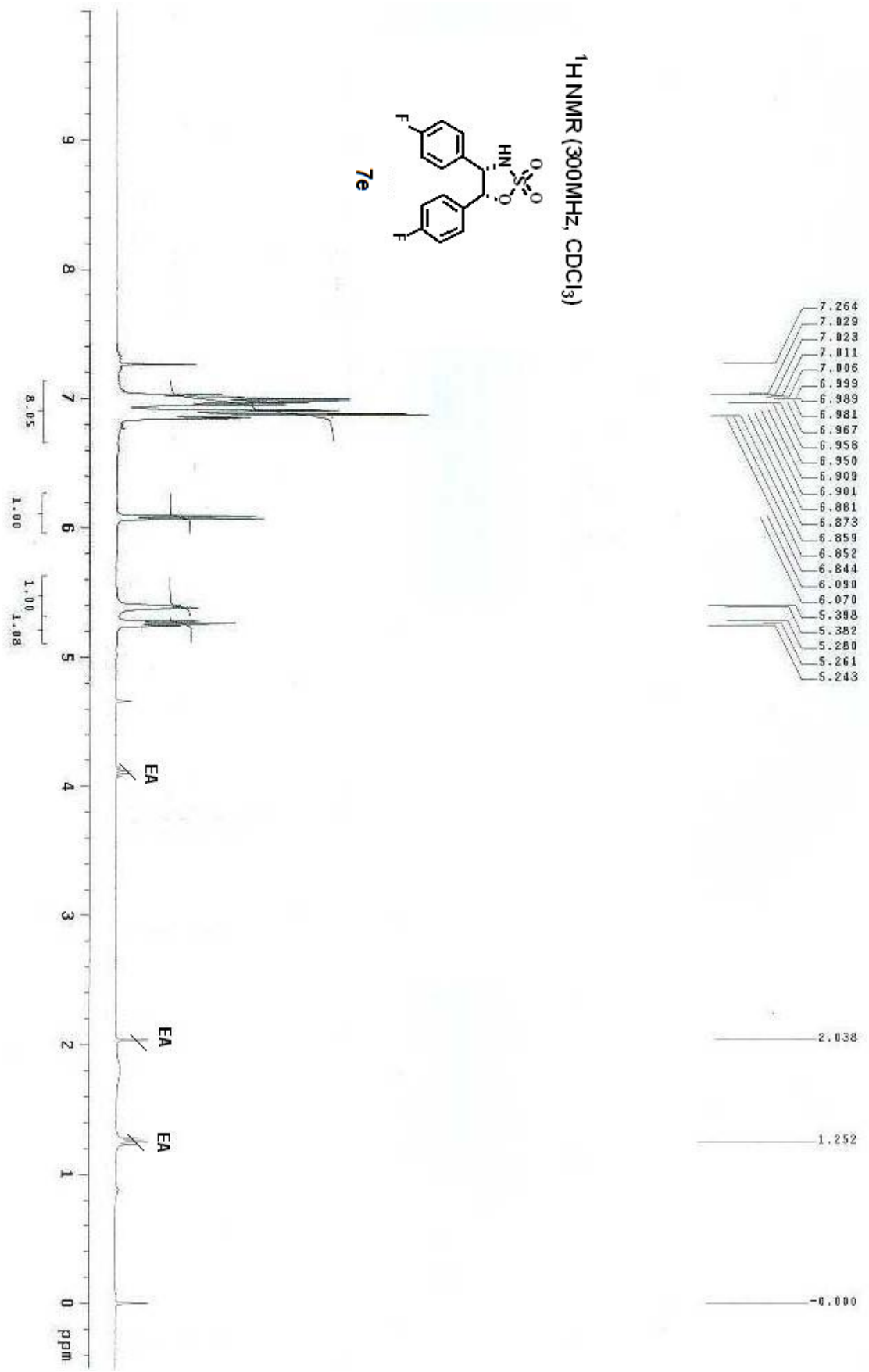

7d
Cl
HN
O
S
O
O
Cl
^{1}H NMR (300MHz, CDCl$_3$)
7.173
7.147
7.129
6.977
6.949
6.937
6.909
6.080
6.060
5.621
5.261
3.85
4.09
1.00
1.05
1.10
9
8
7
6
5
4
3
2
1
0
ppm

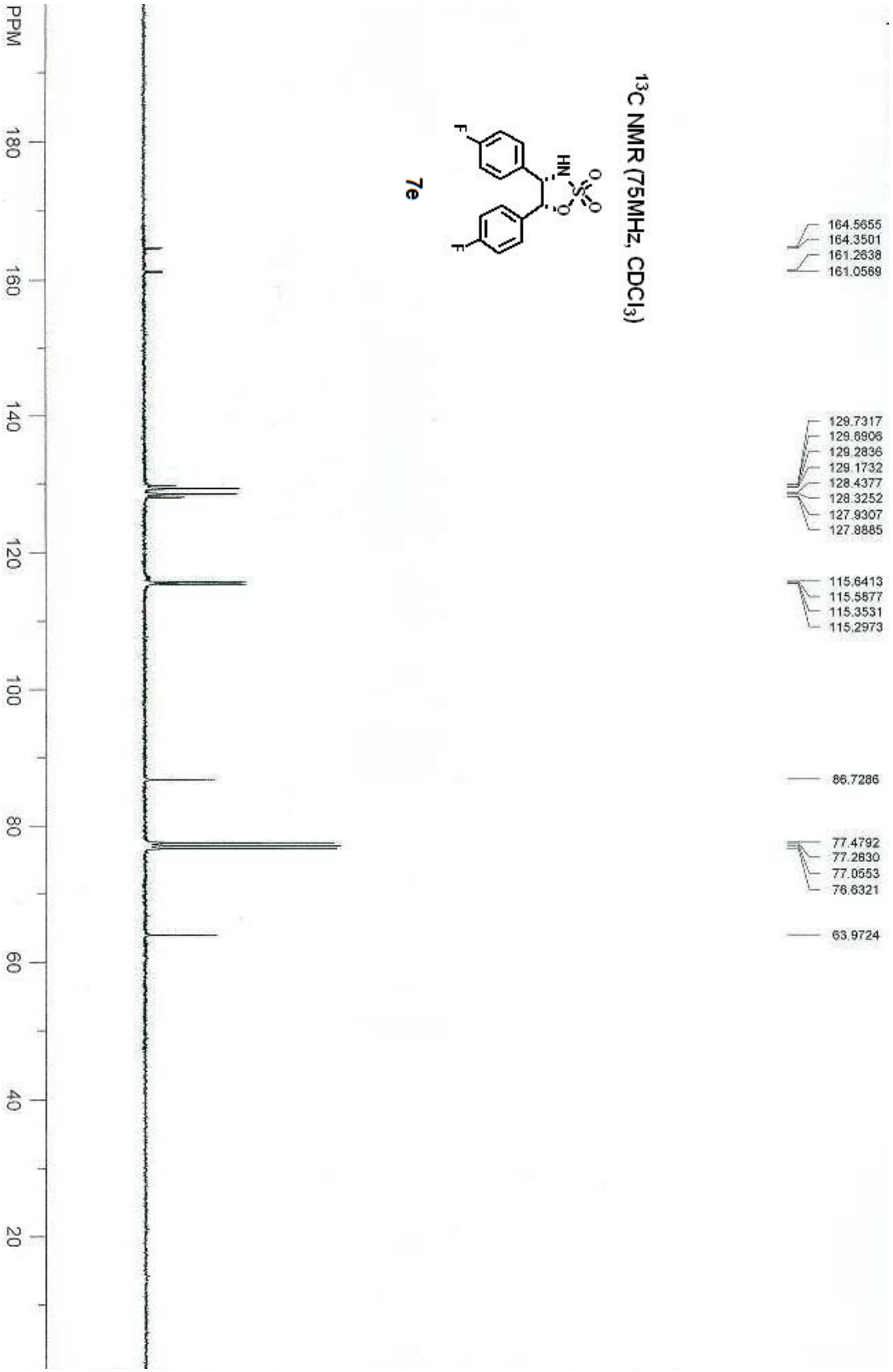

^{13}C NMR (75MHz, CDCl$_3$)
7d
Cl
NH
O
S
O
O
Cl
135.4764
135.1732
132.2769
130.5382
128.9812
128.8790
128.8347
127.8943
86.3705
77.5820
77.1585
76.7350
64.0768
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

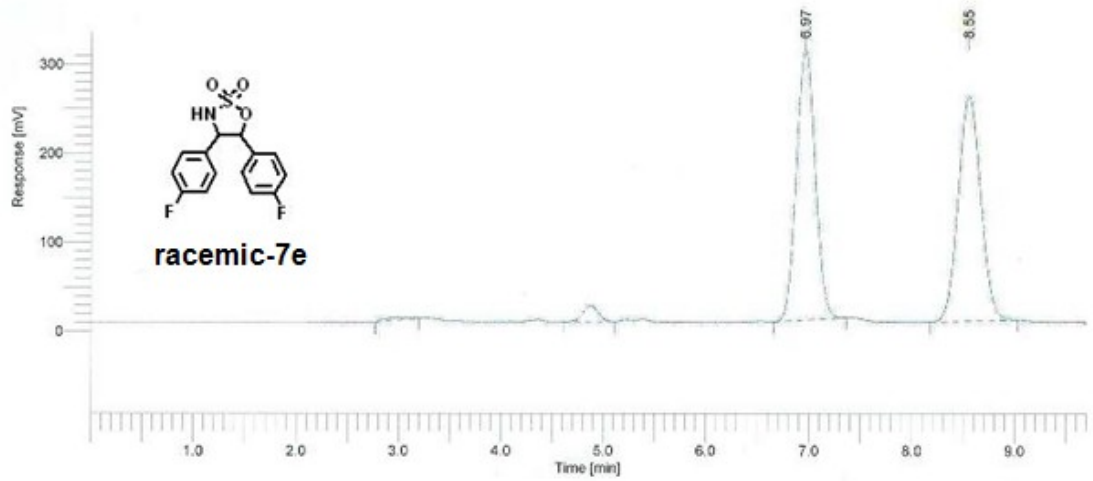


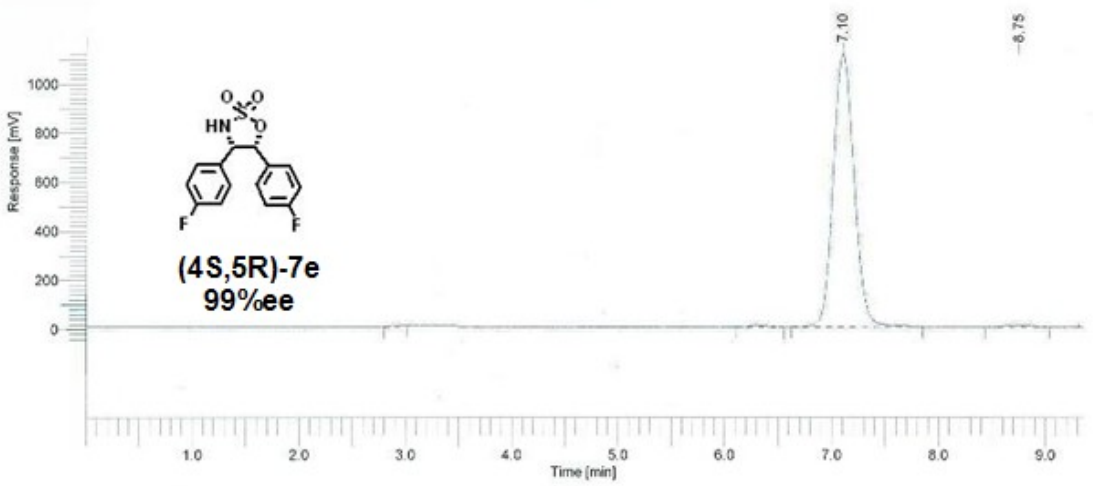
Result Report

Peak #	Time (min)	Area [mV*s]	BL	wide (sec)	Area %
15	7.3333	29716.4006	VB	93.0000	90.6248
16	8.8667	96.1782	BB	29.0000	0.2933
Total		29812.57			


^{1}H NMR (300MHz, CDCl$_3$)
7e
F
HN
O
S
O
O
F
7.264
7.029
7.023
7.011
7.006
6.999
6.989
6.981
6.967
6.956
6.950
6.909
6.901
6.881
6.873
6.859
6.852
6.844
6.090
6.070
5.398
5.382
5.280
5.261
5.243
2.038
1.252
-0.000
EA
EA
EA
8.05
1.00
1.00
1.08
9
8
7
6
5
4
3
2
1
0
ppm

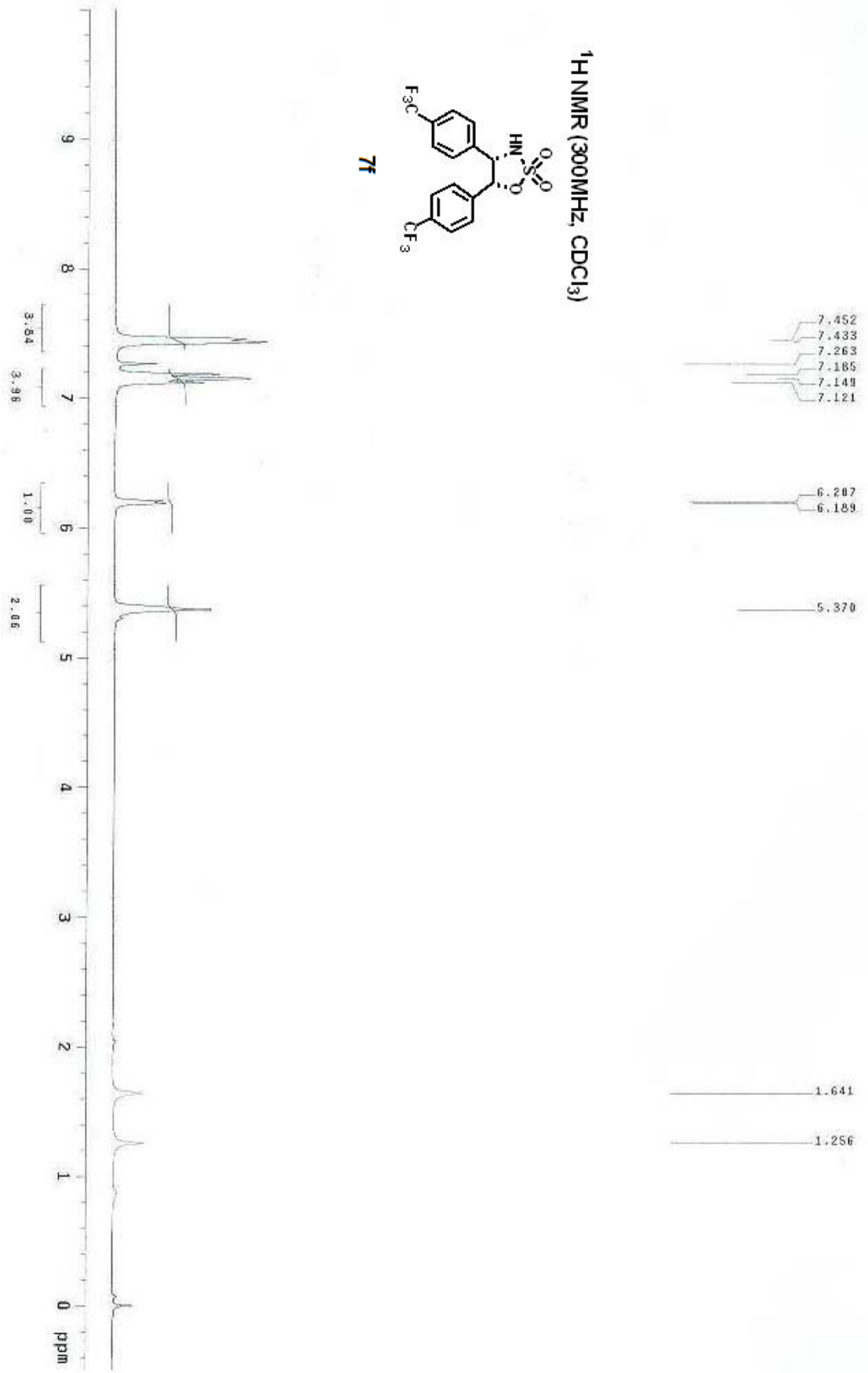

^{13}C NMR (75MHz, CDCl$_3$)
7e
F
HN
O
S
O
O
F
PPM
180
160
140
120
100
80
60
40
20
164.5655
164.3501
161.2638
161.0569
129.7317
129.6906
129.2836
129.1732
128.4377
128.3252
127.9307
127.8885
115.6413
115.5877
115.3531
115.2973
86.7286
77.4792
77.2630
77.0553
76.6321
63.9724

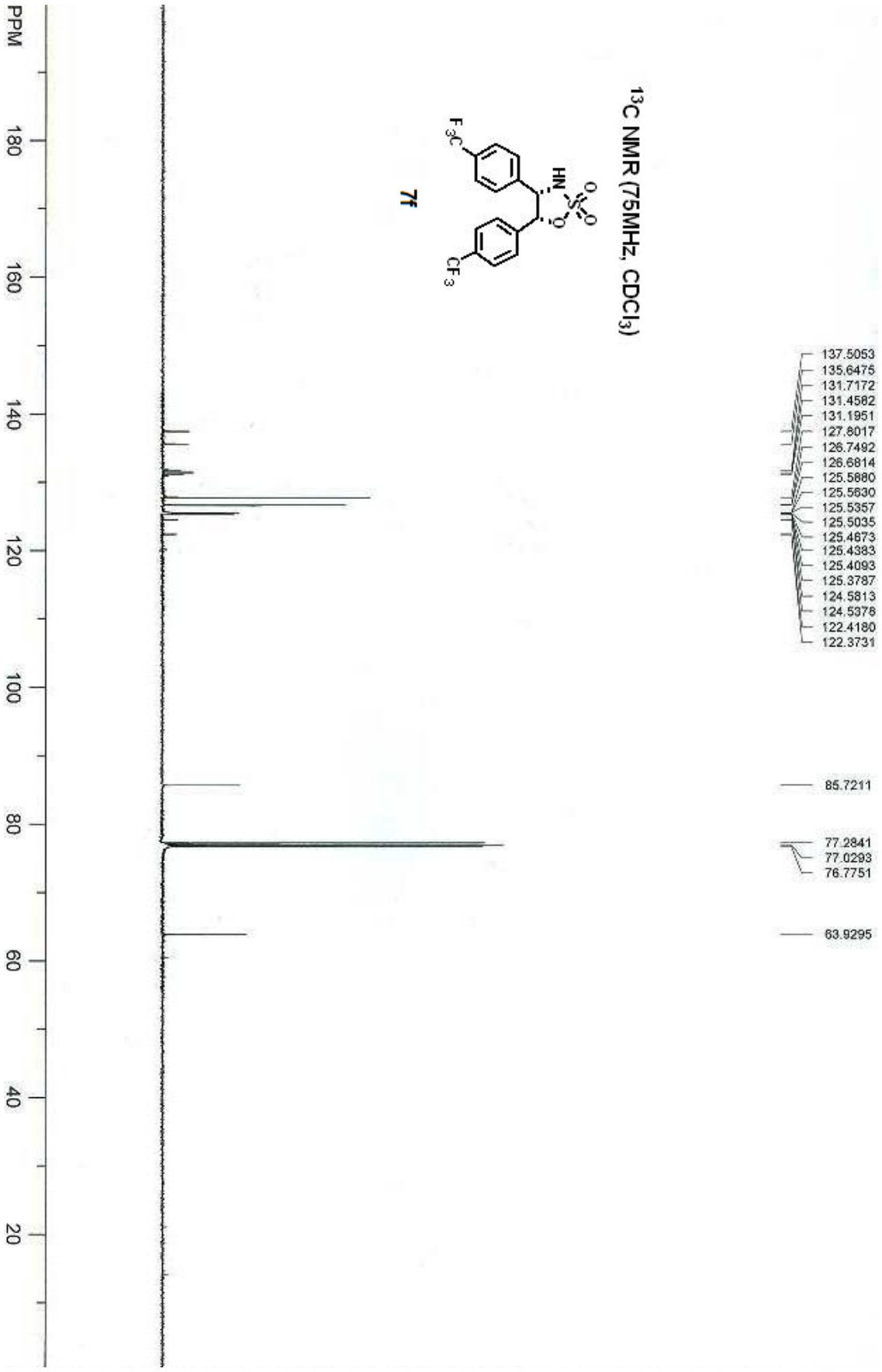


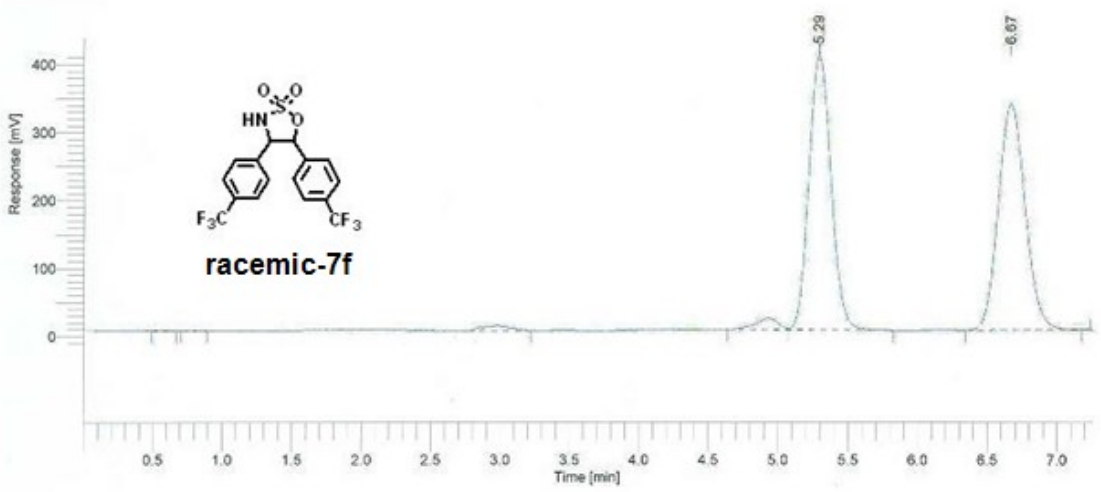


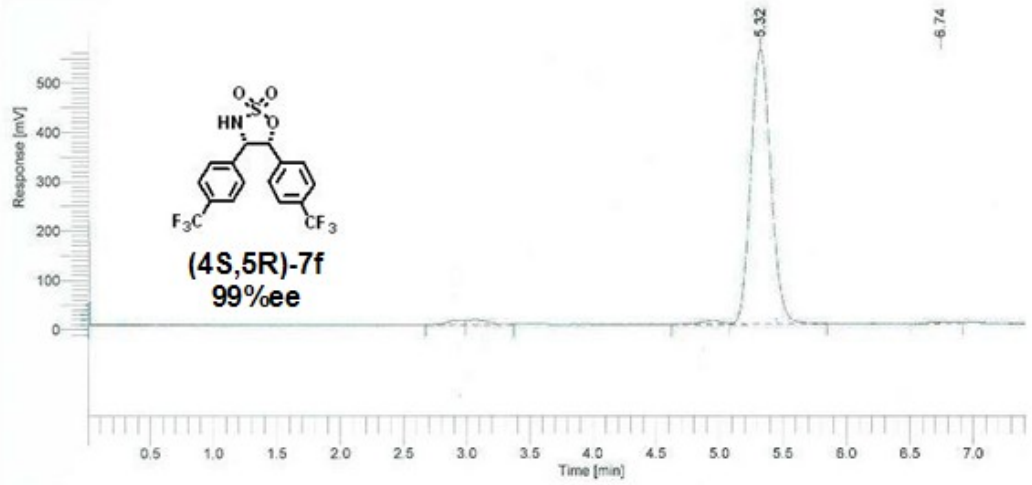
DEFAULT REPORT

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	2.963	18534.03	1572.13	0.12	0.12	BB	11.7891
2	6.313	63666.71	5734.35	0.42	0.42	BB	11.1027
3	7.103	15106941.86	1.11e+06	98.72	98.72	BB	13.5884
4	8.750	114290.90	7568.49	0.75	0.75	BB	15.1009
		15303433.51	1.13e+06	100.00	100.00		


^{1}H NMR (300MHz, CDCl$_3$)
7f
F$_3$C
CF$_3$
HN
O
S
O
O
7.452
7.433
7.263
7.185
7.149
7.121
6.207
6.189
5.370
1.641
1.256
3.84
3.96
1.00
2.06
9
8
7
6
5
4
3
2
1
0
ppm

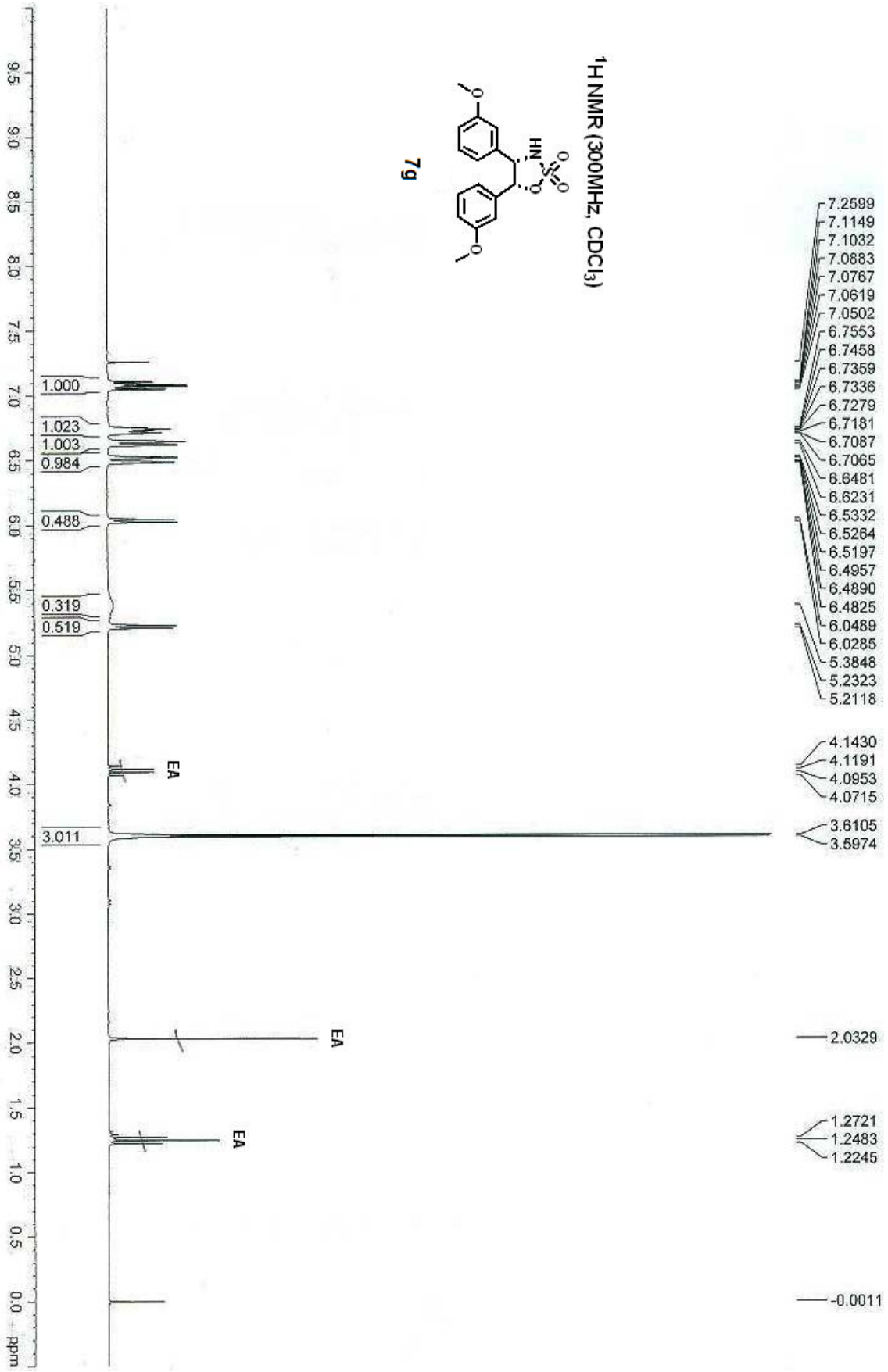

^{13}C NMR (75MHz, CDCl$_3$)
7f
F$_3$C
CF$_3$
HN
PPM
180
160
140
120
100
80
60
40
20
137.5053
135.6475
131.7172
131.4562
131.1951
127.8017
126.7492
126.6814
125.5680
125.5630
125.5357
125.5035
125.4673
125.4383
125.4093
125.3787
124.5813
124.5376
122.4180
122.3731
85.7211
77.2841
77.0293
76.7751
63.9295

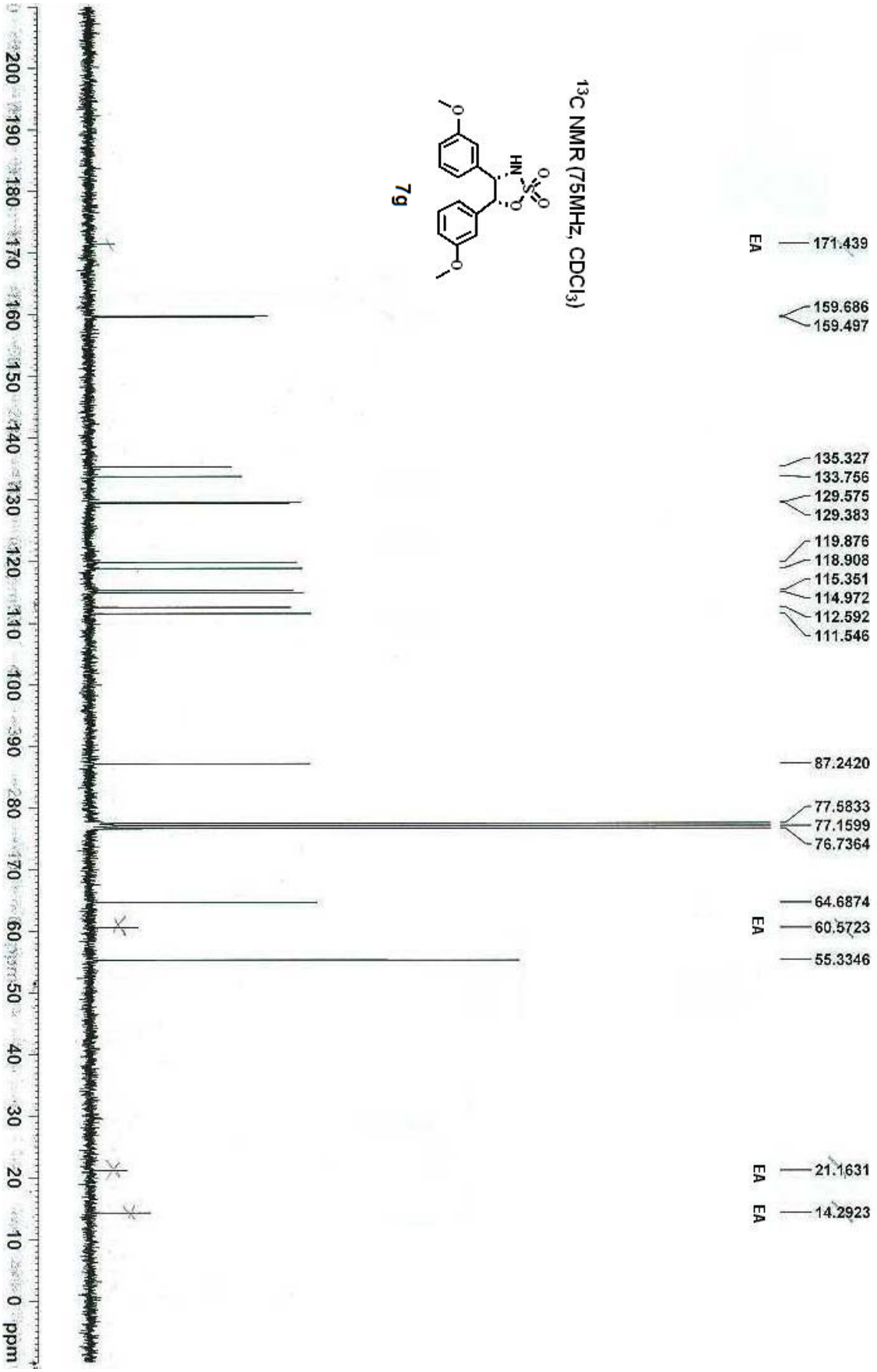


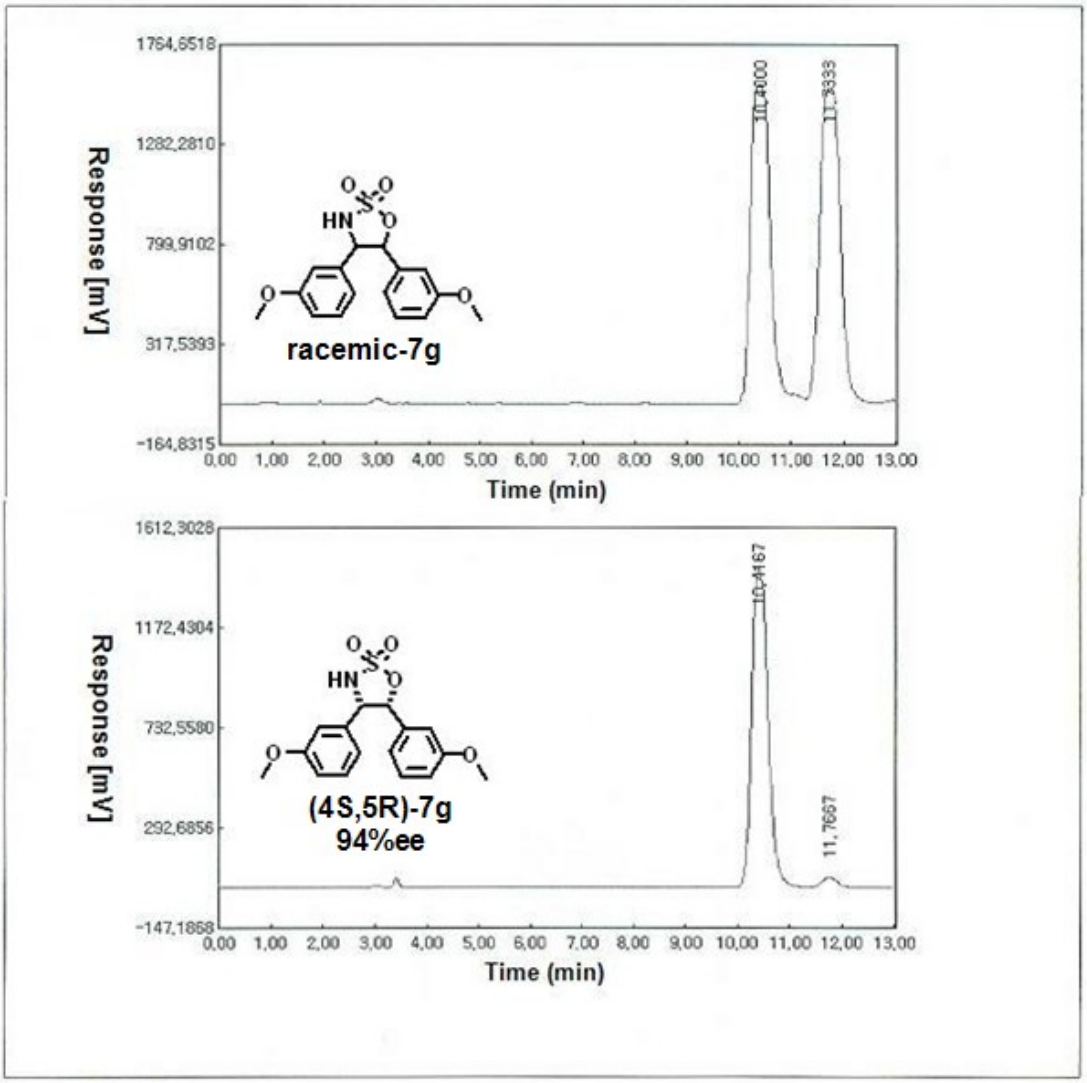


DEFAULT REPORT

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	2.947	71098.60	8377.91	1.11	1.11	BV	8.4864
2	3.061	98241.21	9391.54	1.53	1.53	VB	10.4606
3	4.945	78118.03	6764.65	1.22	1.22	BV	11.5480
4	5.318	6116483.54	557026.75	95.49	95.49	VB	10.9806
5	6.736	29786.12	2501.80	0.47	0.47	BB	11.9059
6	7.920	11502.55	2305.73	0.18	0.18	BB	4.9887
		6405230.06	586368.38	100.00	100.00		

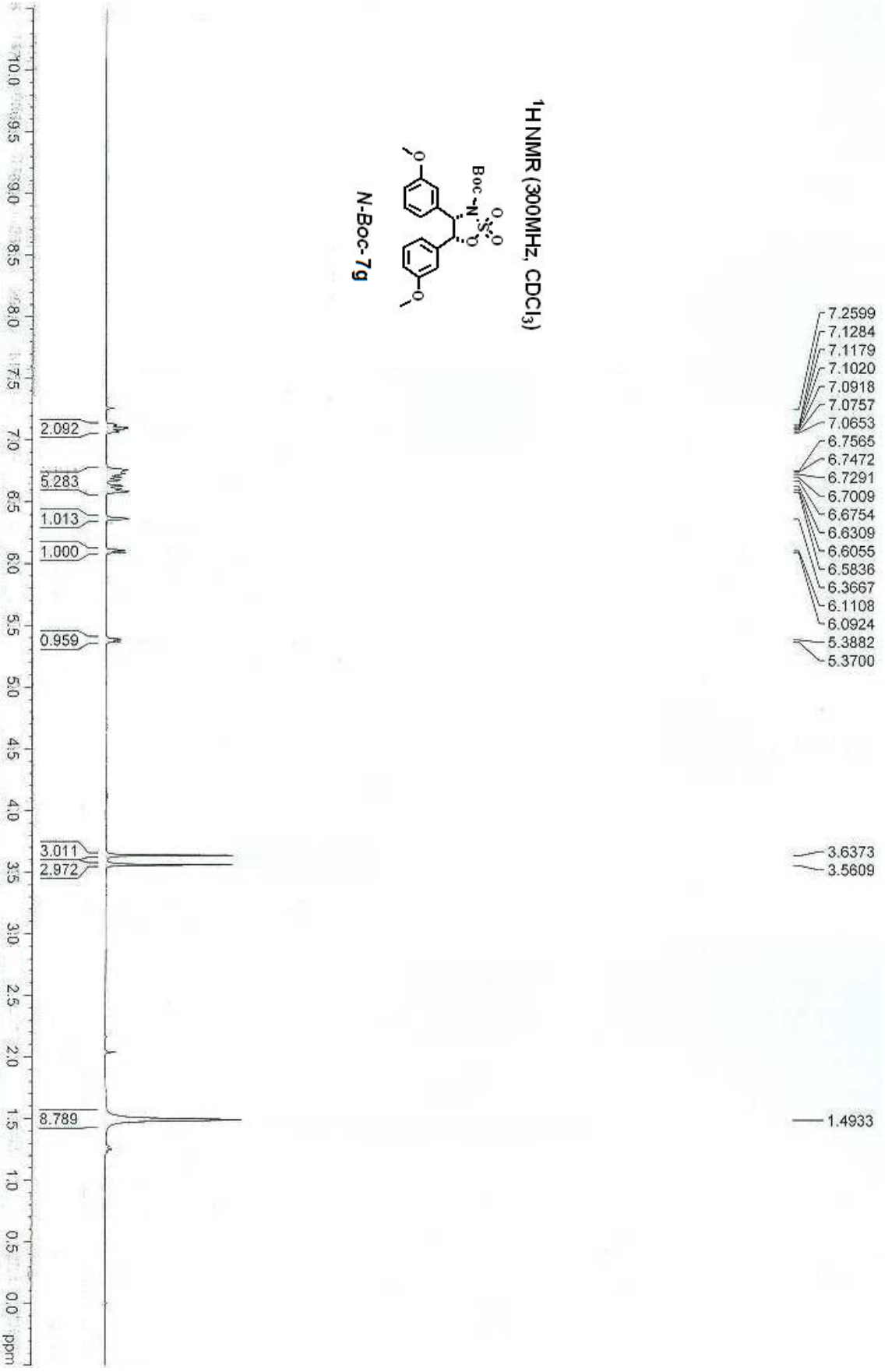

1H NMR (300MHz, CDCl3)
7g
7.2599
7.1149
7.1032
7.0883
7.0767
7.0619
7.0502
6.7553
6.7458
6.7359
6.7336
6.7279
6.7181
6.7087
6.7065
6.6481
6.6231
6.5332
6.5264
6.5197
6.4957
6.4890
6.4825
6.0489
6.0285
5.3848
5.2323
5.2118
4.1430
4.1191
4.0953
4.0715
3.6105
3.5974
2.0329
1.2721
1.2483
1.2245
-0.0011
1.000
1.023
1.003
0.984
0.488
0.319
0.519
3.011
EA
EA
EA
ppm

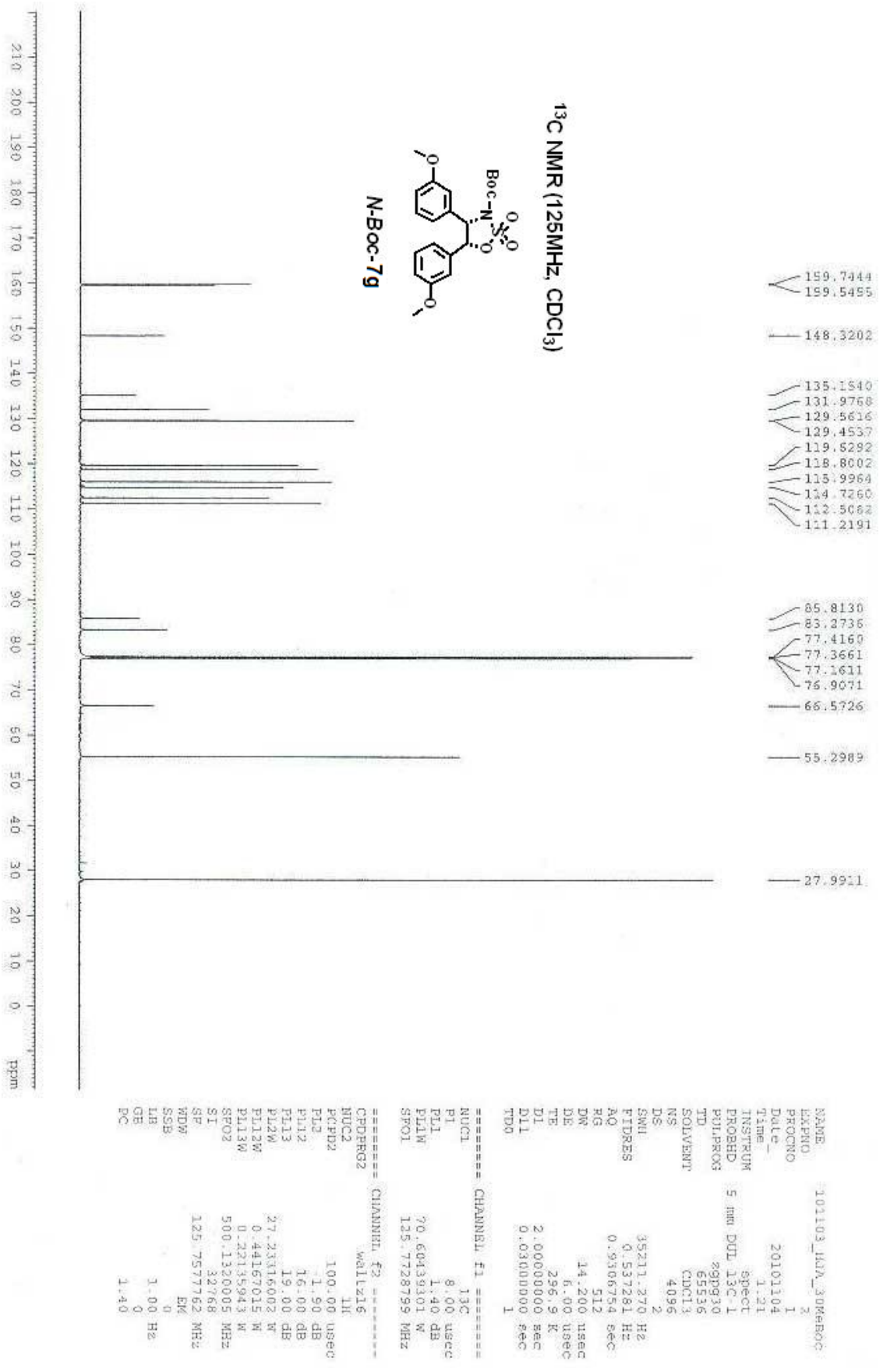

^{13}C NMR (75MHz, $CDCl_3$)
7g
171.439
159.686
159.497
135.327
133.756
129.575
129.383
119.876
118.908
115.351
114.972
112.592
111.546
87.2420
77.5833
77.1599
76.7364
64.6874
60.5723
55.3346
21.1631
14.2923
EA
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

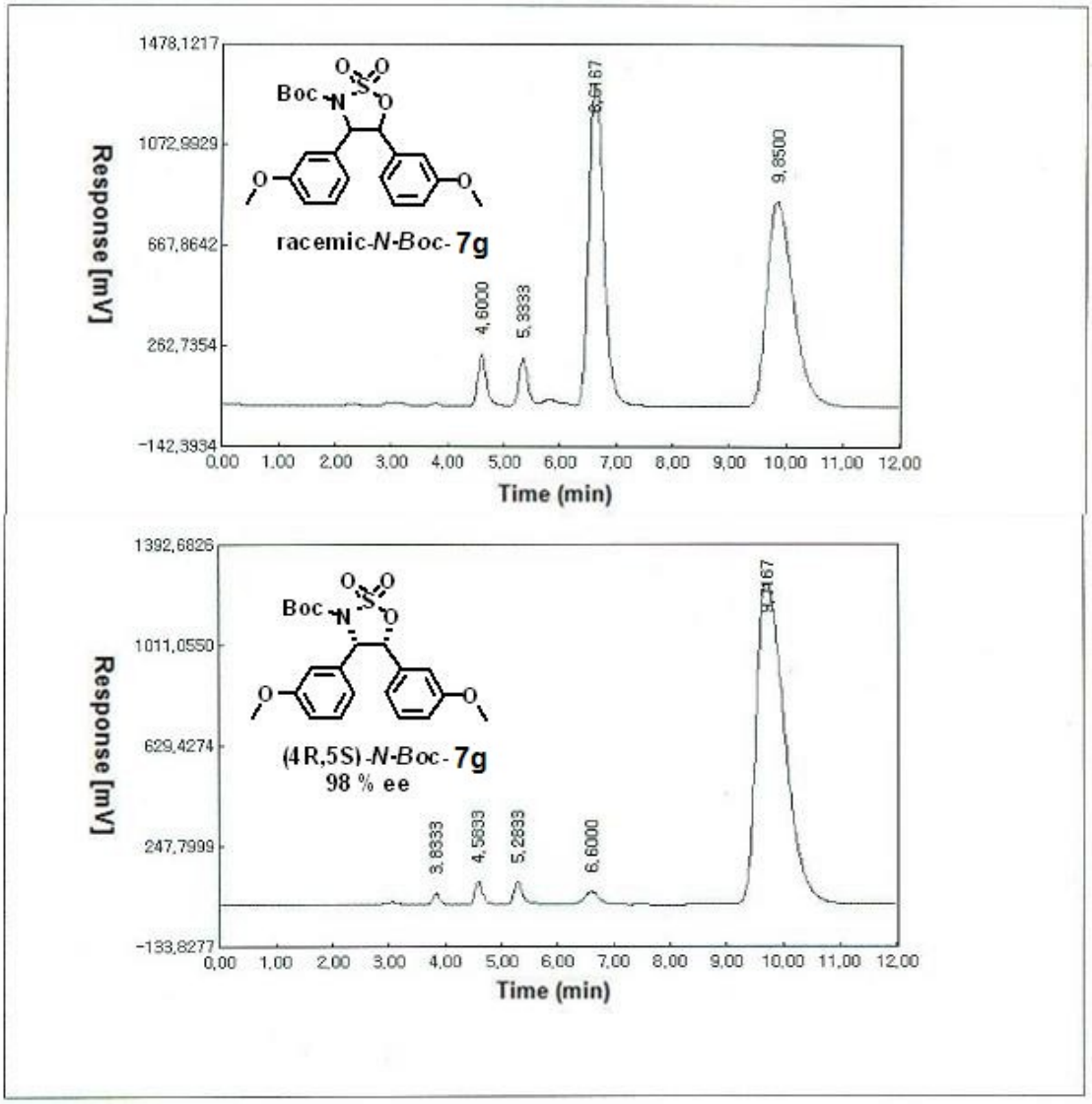


Result Report

Peak #	Time (min)	Area [mV*s]	BL	wide (sec)	Area %
1	10.4167	31640.5137	VB	88.0000	97.2023
2	11.7667	910.6725	BB	55.0000	2.7977
Total		32551.1855			

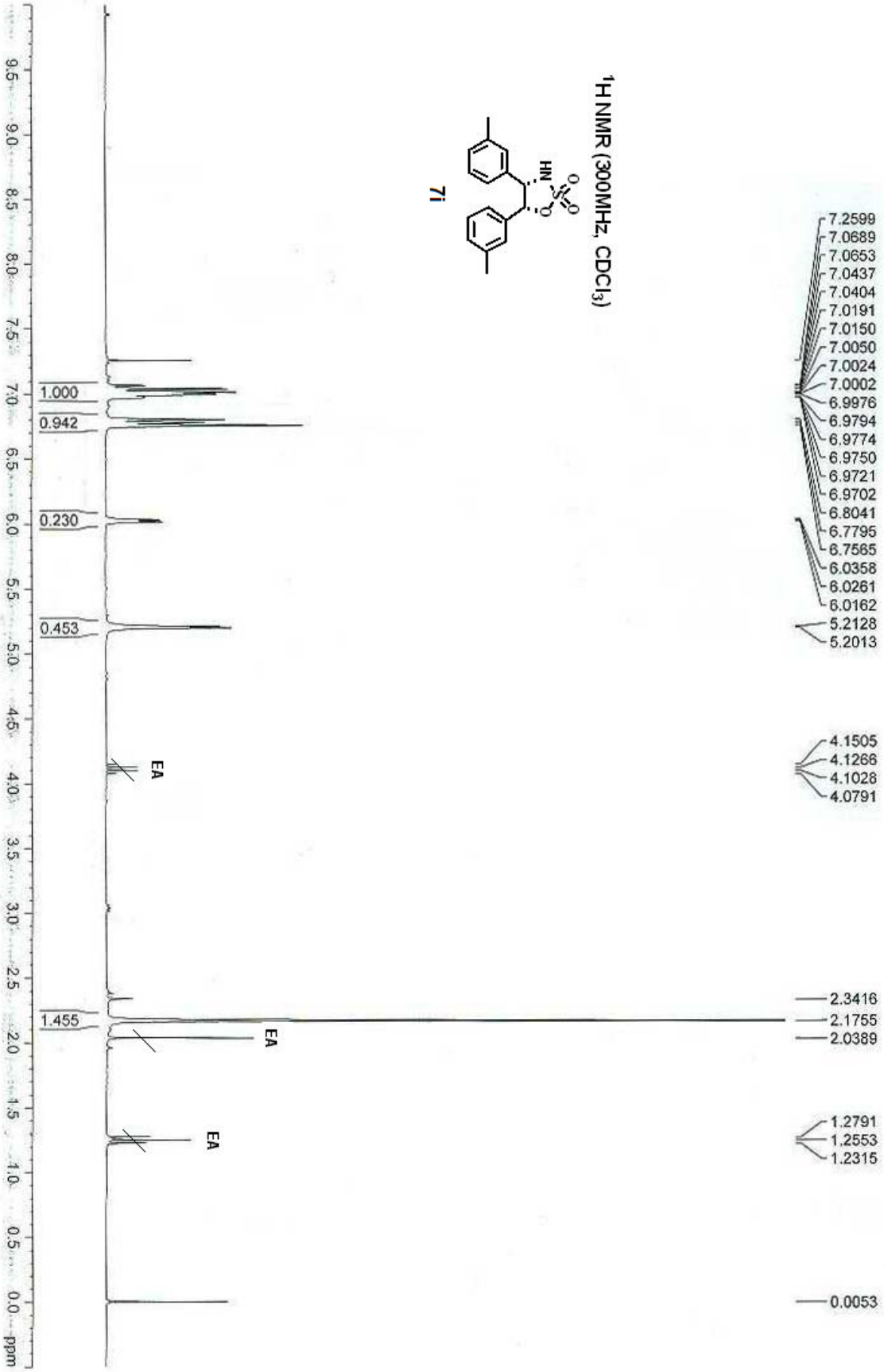

^{1}H NMR (300MHz, CDCl$_3$)
N-Boc-7g
7.2599
7.1284
7.1179
7.1020
7.0918
7.0757
7.0653
6.7565
6.7472
6.7291
6.7009
6.6754
6.6309
6.6055
6.5836
6.3667
6.1108
6.0924
5.3882
5.3700
3.6373
3.5609
1.4933
2.092
5.283
1.013
1.000
0.959
3.011
2.972
8.789
ppm

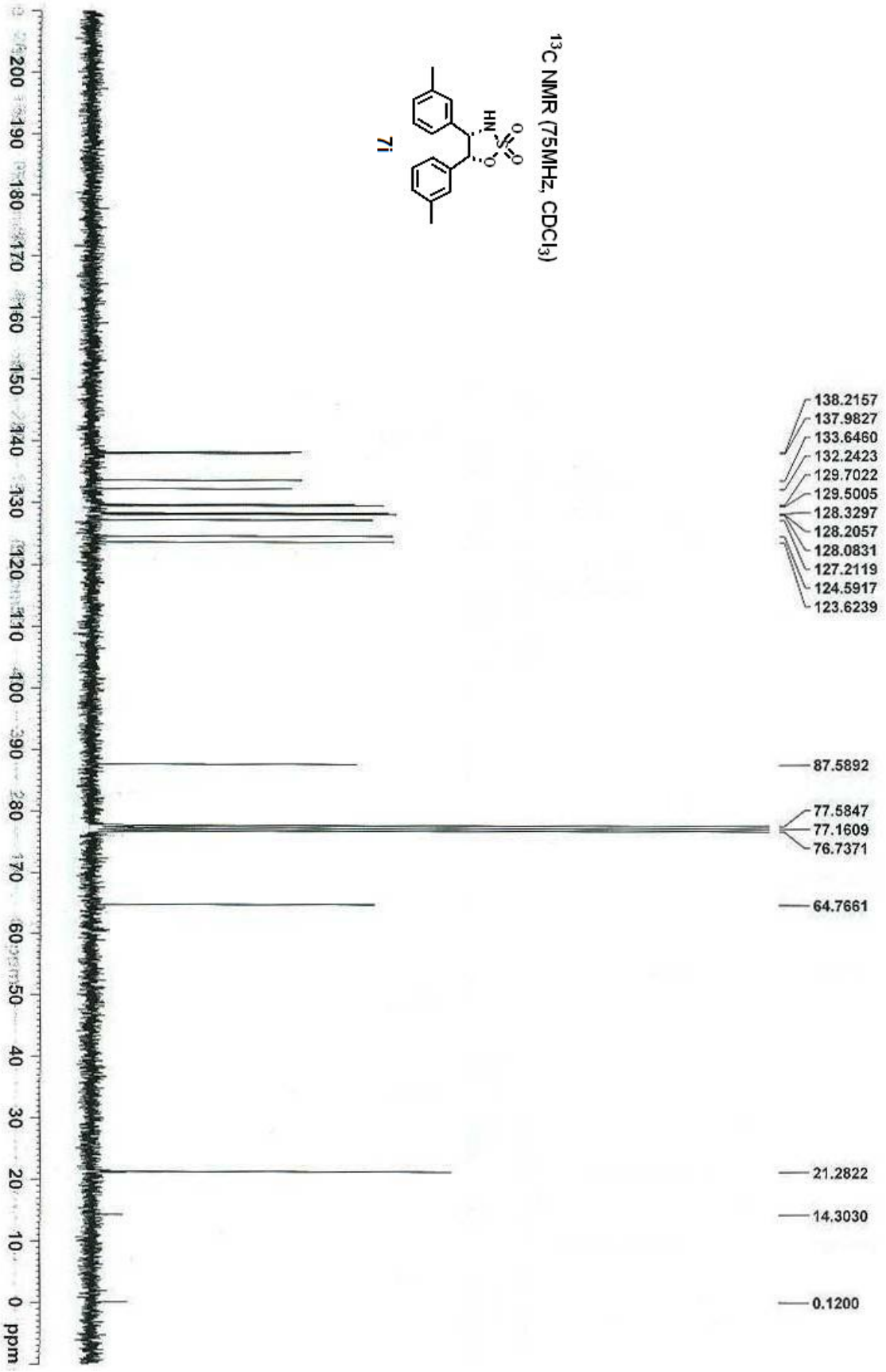

13C NMR (125MHz, CDCl3)
N-Boc-7g
159.7444
159.5455
148.3202
135.1540
131.9768
129.5616
129.4537
119.5292
118.8002
115.9964
114.7260
112.5082
111.2191
85.8130
83.2736
77.4160
77.3661
77.1611
76.9071
66.5726
55.2989
27.9911
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
NAME 101103_HJA_30MeBOC
EXPNO 3
PROCNO 1
Date_ 20101104
Time 1.21
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 4096
DS 2
SWH 35211.270 Hz
FIDRES 0.537281 Hz
AQ 0.9306754 sec
RG 512
DW 14.200 usec
DE 6.00 usec
TE 296.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 1.40 dB
PL1W 70.60439301 W
SFO1 125.7728799 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -1.90 dB
PL12 16.00 dB
PL13 19.00 dB
PL2W 27.23316002 W
PL12W 0.44167015 W
PL13W 0.22135943 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7577762 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

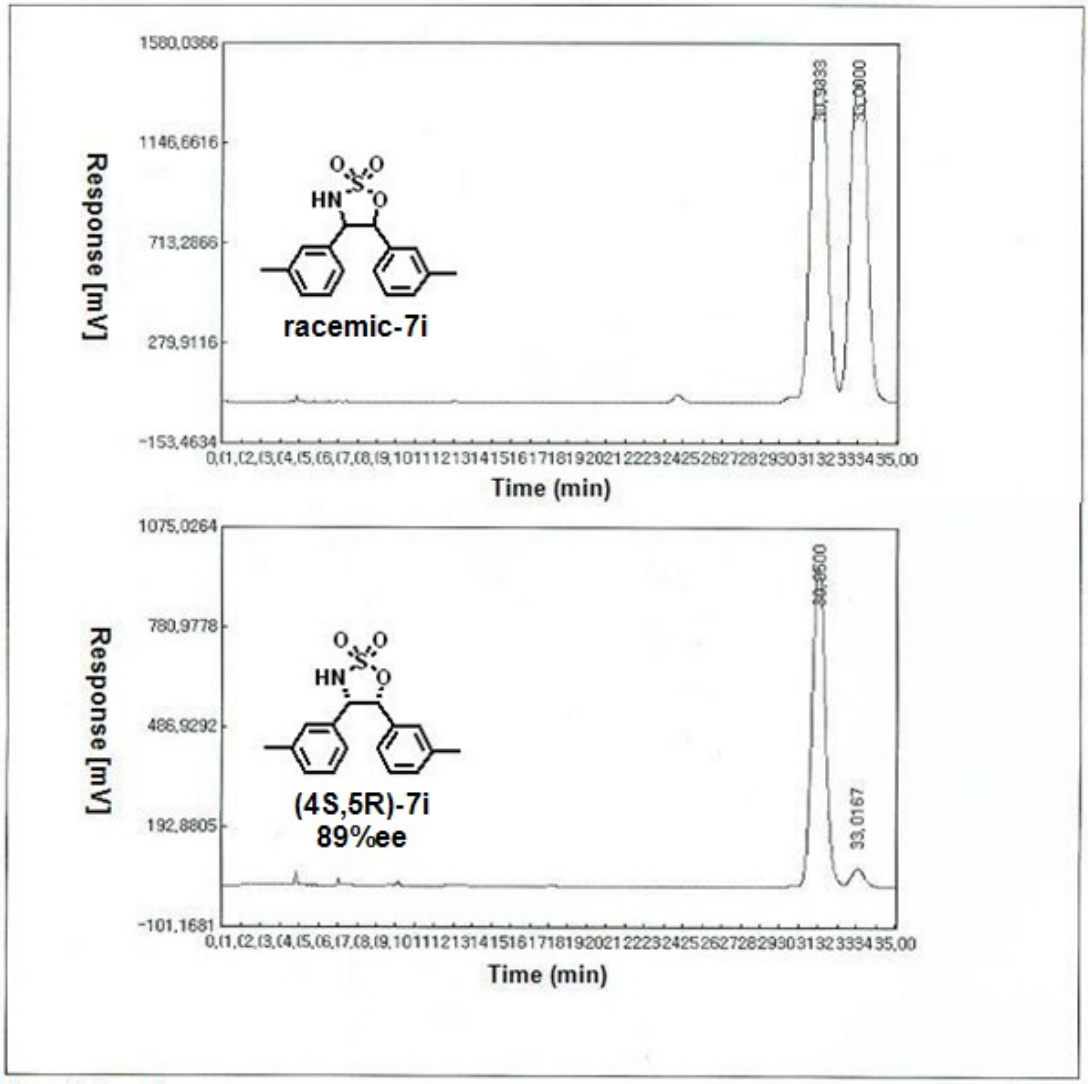


Result Report

Peak #	Time (min)	Area [mV•s]	BL	wide (sec)	Area %
1	3.8333	291.6175	BB	16.0000	0.6644
2	4.5833	717.9036	BB	20.0000	1.6355
3	5.2833	753.4113	BB	21.0000	1.7164
4	6.6000	362.9644	BB	20.0000	0.8269
5	9.7167	41768.3730	BB	81.0000	95.1568
Total		43894.2695			

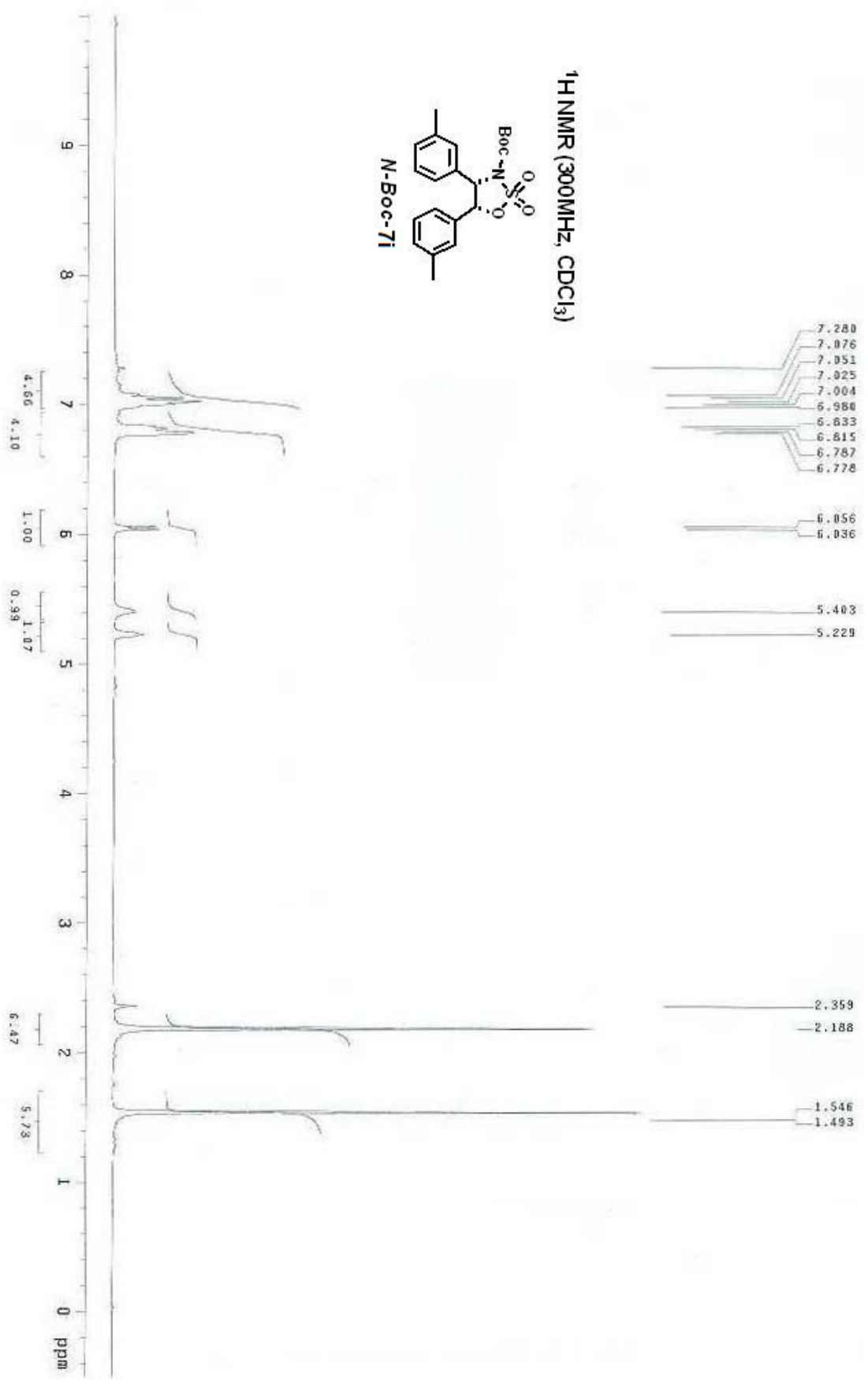

^{1}H NMR (300MHz, CDCl$_3$)
7i
7.2599
7.0689
7.0653
7.0437
7.0404
7.0191
7.0150
7.0050
7.0024
7.0002
6.9976
6.9794
6.9774
6.9750
6.9721
6.9702
6.8041
6.7795
6.7565
6.0358
6.0261
6.0162
5.2128
5.2013
4.1505
4.1266
4.1028
4.0791
2.3416
2.1755
2.0389
1.2791
1.2553
1.2315
0.0053
1.000
0.942
0.230
0.453
1.455
EA
EA
EA
ppm

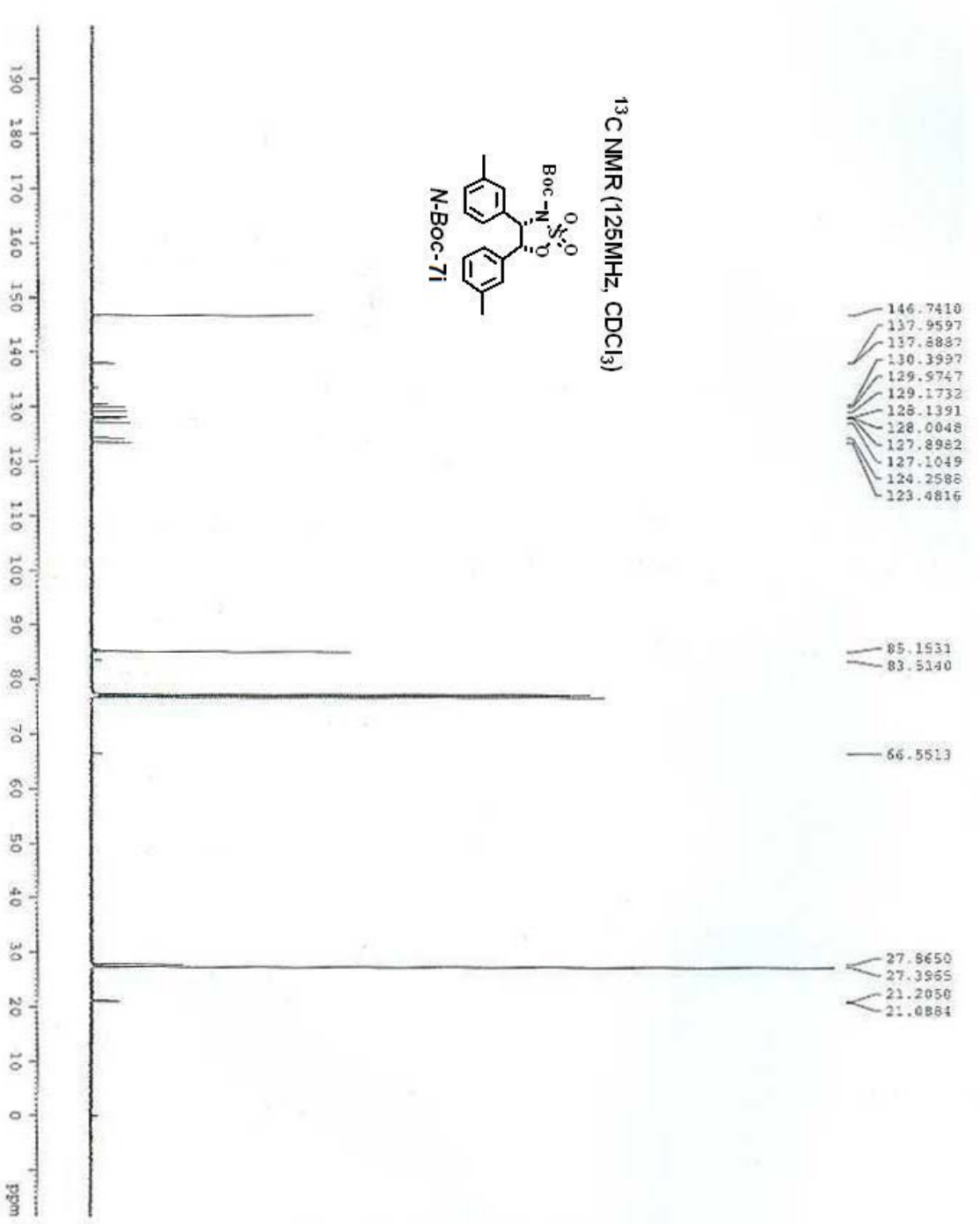

^{13}C NMR (75MHz, $CDCl_3$)
7i
HN
O
S
O
O
138.2157
137.9827
133.6460
132.2423
129.7022
129.5005
128.3297
128.2057
128.0831
127.2119
124.5917
123.6239
87.5892
77.5847
77.1609
76.7371
64.7661
21.2822
14.3030
0.1200
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

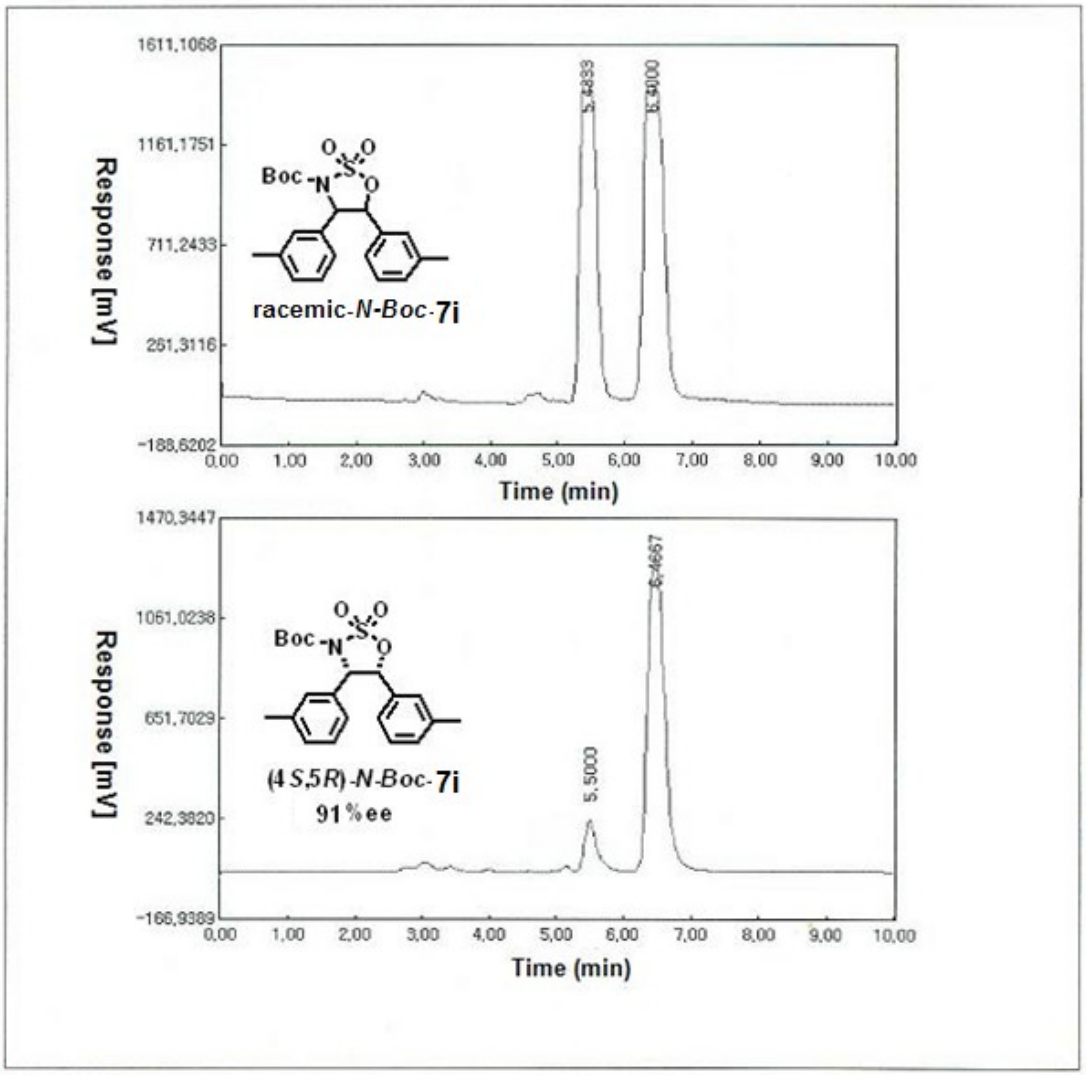


Result Report

Peak #	Time (min)	Area [mV*s]	BL	wide (sec)	Area %
1	30.9500	46127.0592	BV	141.0000	94.2734
2	33.0167	2801.9863	VB	126.0000	5.7266
Total		48929.0430			

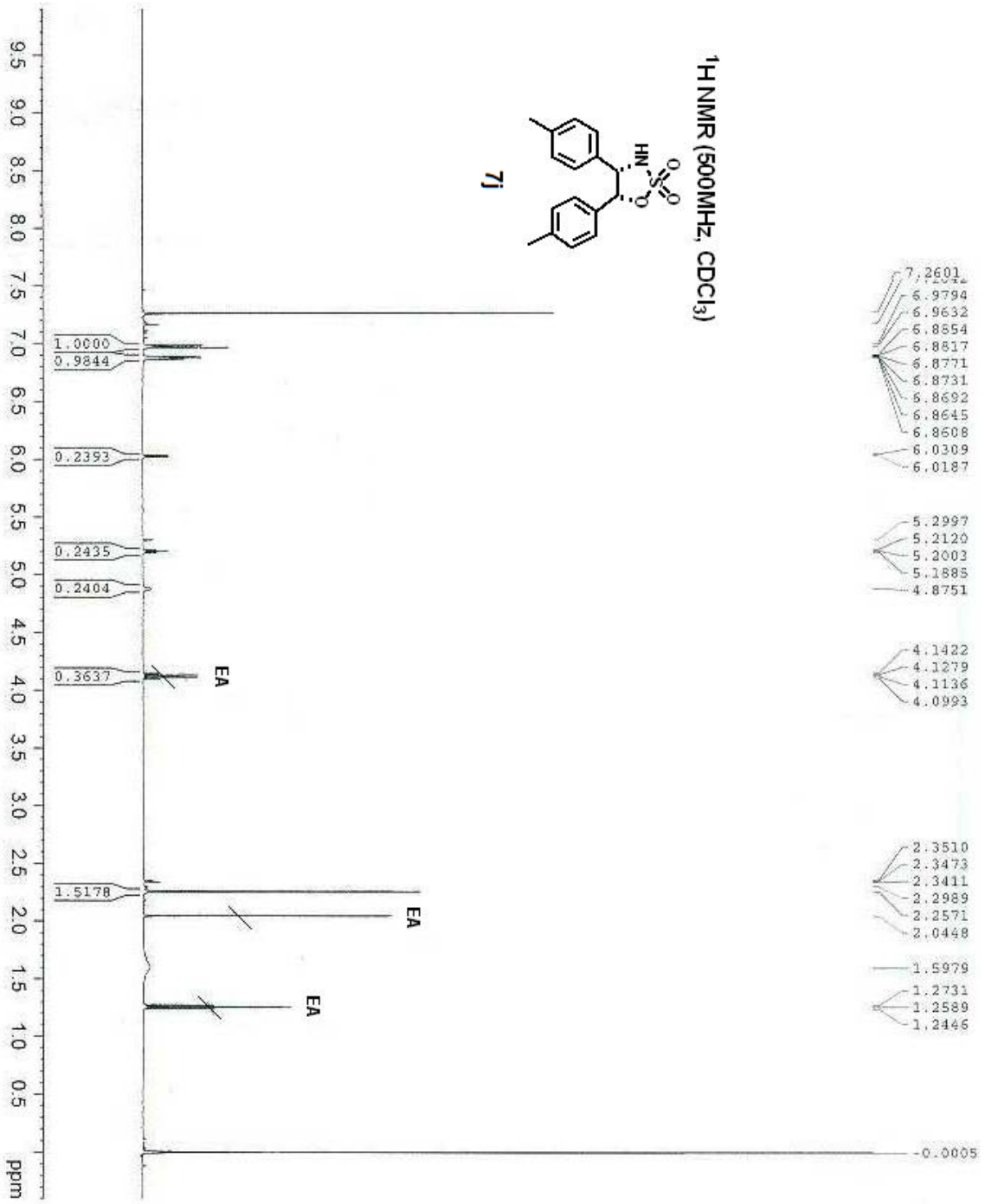

¹H NMR (300MHz, CDCl₃)
N-Boc-7i
Boc
7.280
7.076
7.051
7.025
7.004
6.980
6.833
6.815
6.787
6.778
6.056
6.036
5.403
5.229
2.359
2.188
1.546
1.493
4.66
4.10
1.00
0.99
1.07
6.47
5.73
ppm


^{13}C NMR (125MHz, CDCl$_3$)
N-Boc-7i
Boc
146.7410
137.9597
137.8882
130.3997
129.9747
129.1732
128.1391
128.0048
127.8982
127.1049
124.2588
123.4816
85.1931
83.5140
66.5513
27.9650
27.3965
21.2050
21.0884
ppm



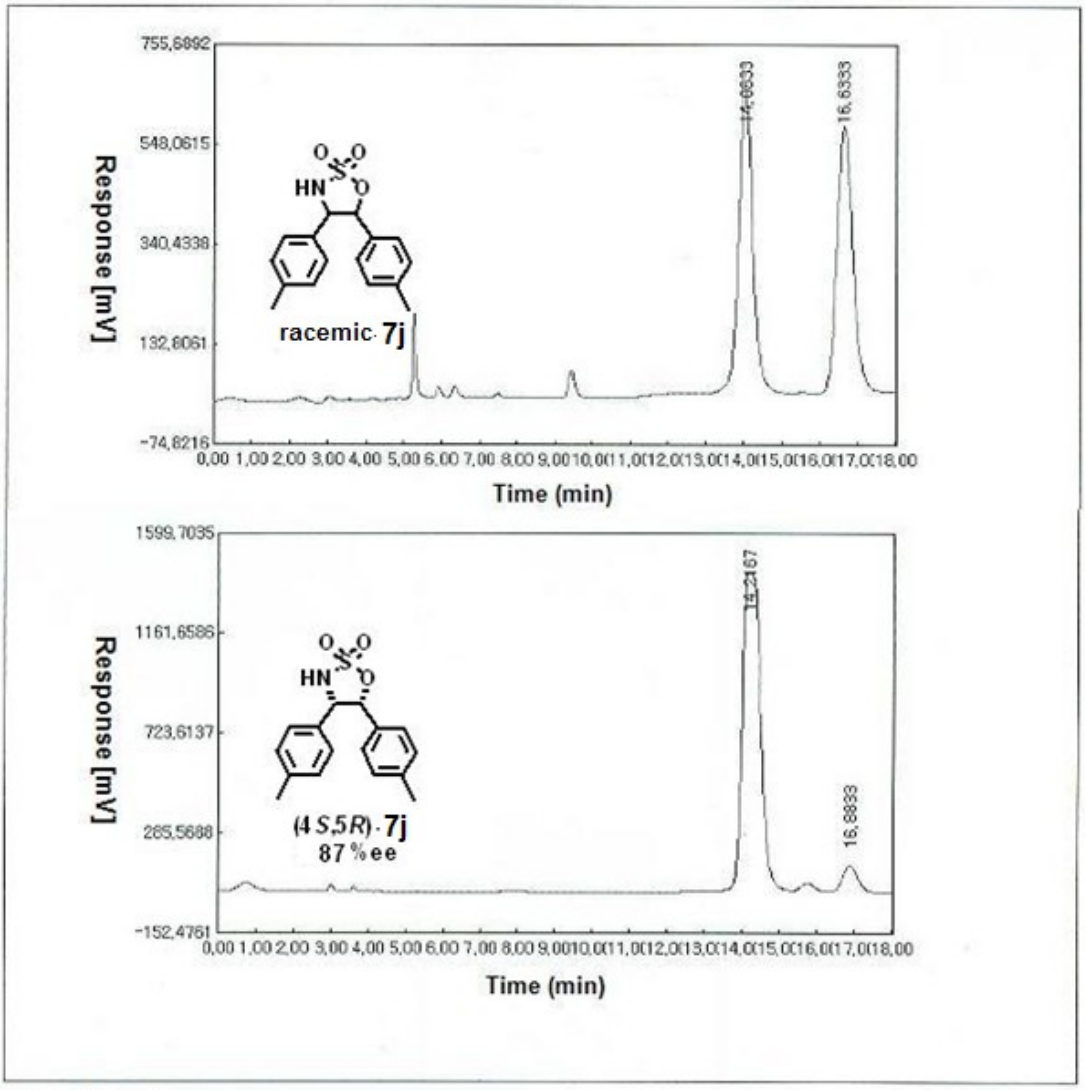
Result Report

Peak #	Time (min)	Area [mV*s]	BL	wide (sec)	Area %
1	5.5000	906.9436	BB	12.0000	4.3252
2	6.4667	20061.6528	BB	32.0000	95.6748
Total		20968.5957			



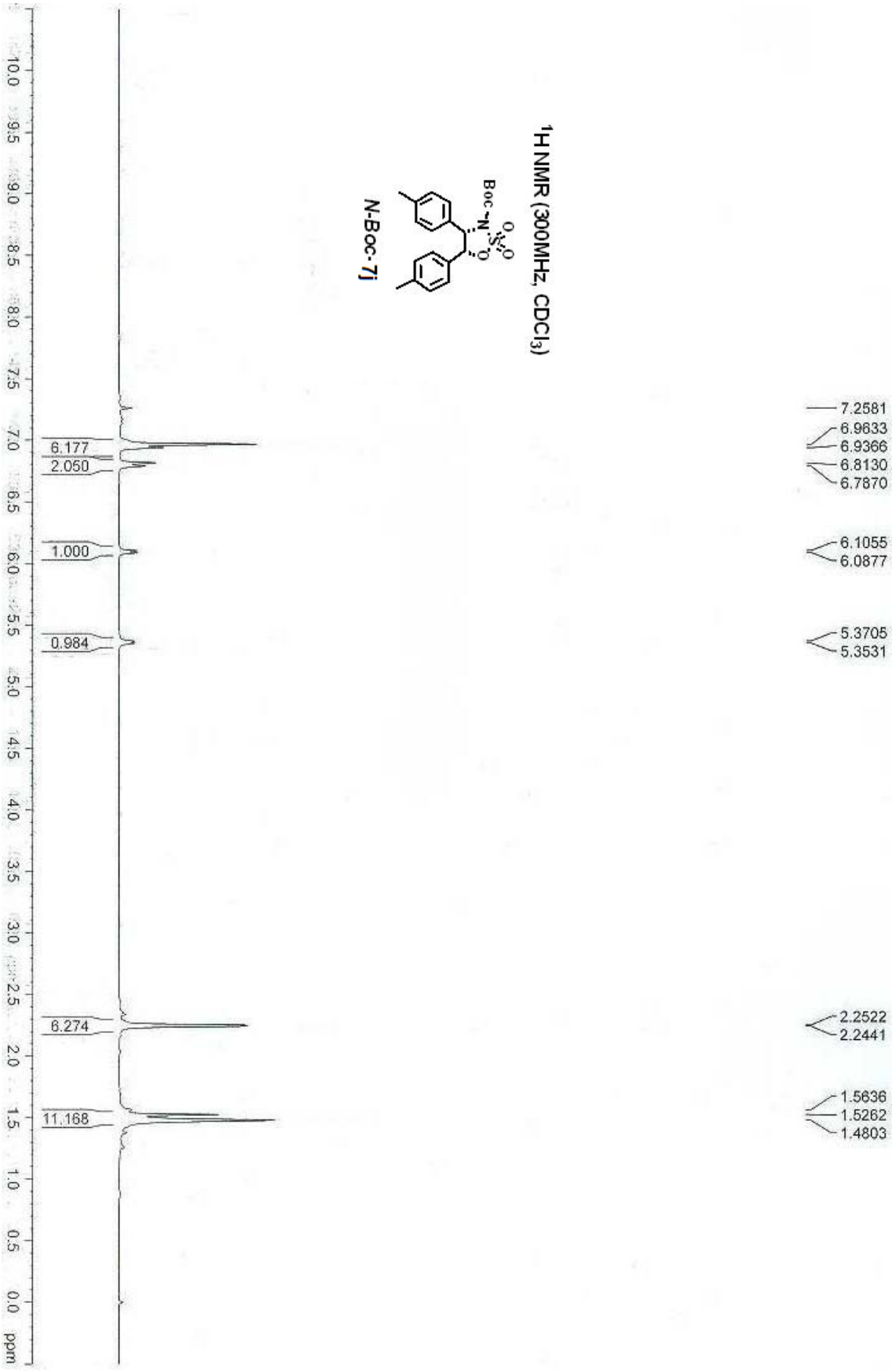
NAME RSY_1007_4Mecrude
EXPNO 1
PROCNO 1
Date_ 20101007
Time_ 12.40
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 7507.507 Hz
FIDRES 0.114555 Hz
AQ 4.3648143 sec
RG 574.7
DW 66.600 usec
DE 6.00 usec
TE 296.9 K
D1 1.00000000 sec
TD0 1

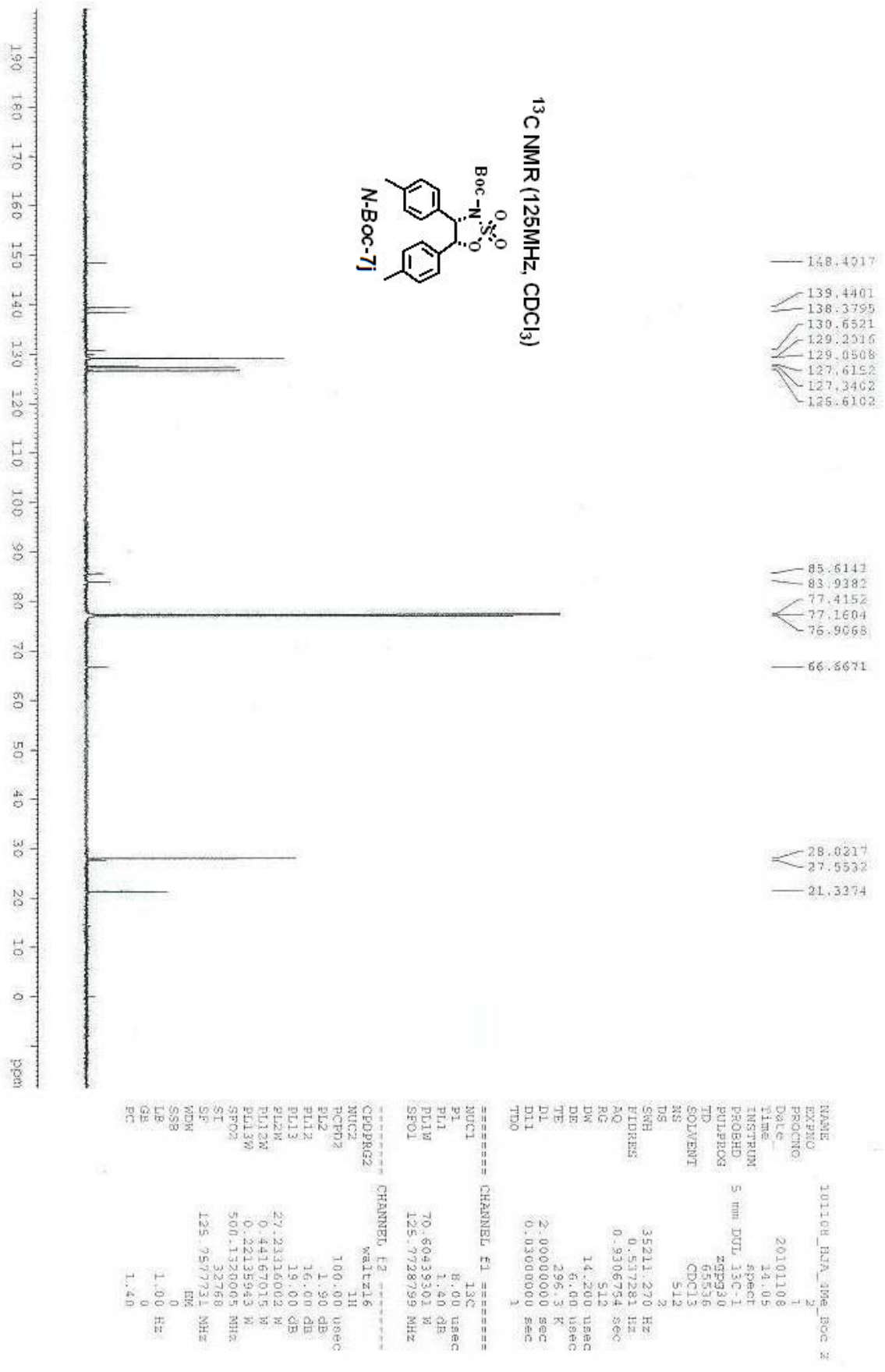
======== CHANNEL f1 ========
NUC1 1H
P1 9.80 usec
PL1 -1.90 dB
PL1W 27.23316002 W
SFO1 500.1332508 MHz
SI 32768
SF 500.1300134 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



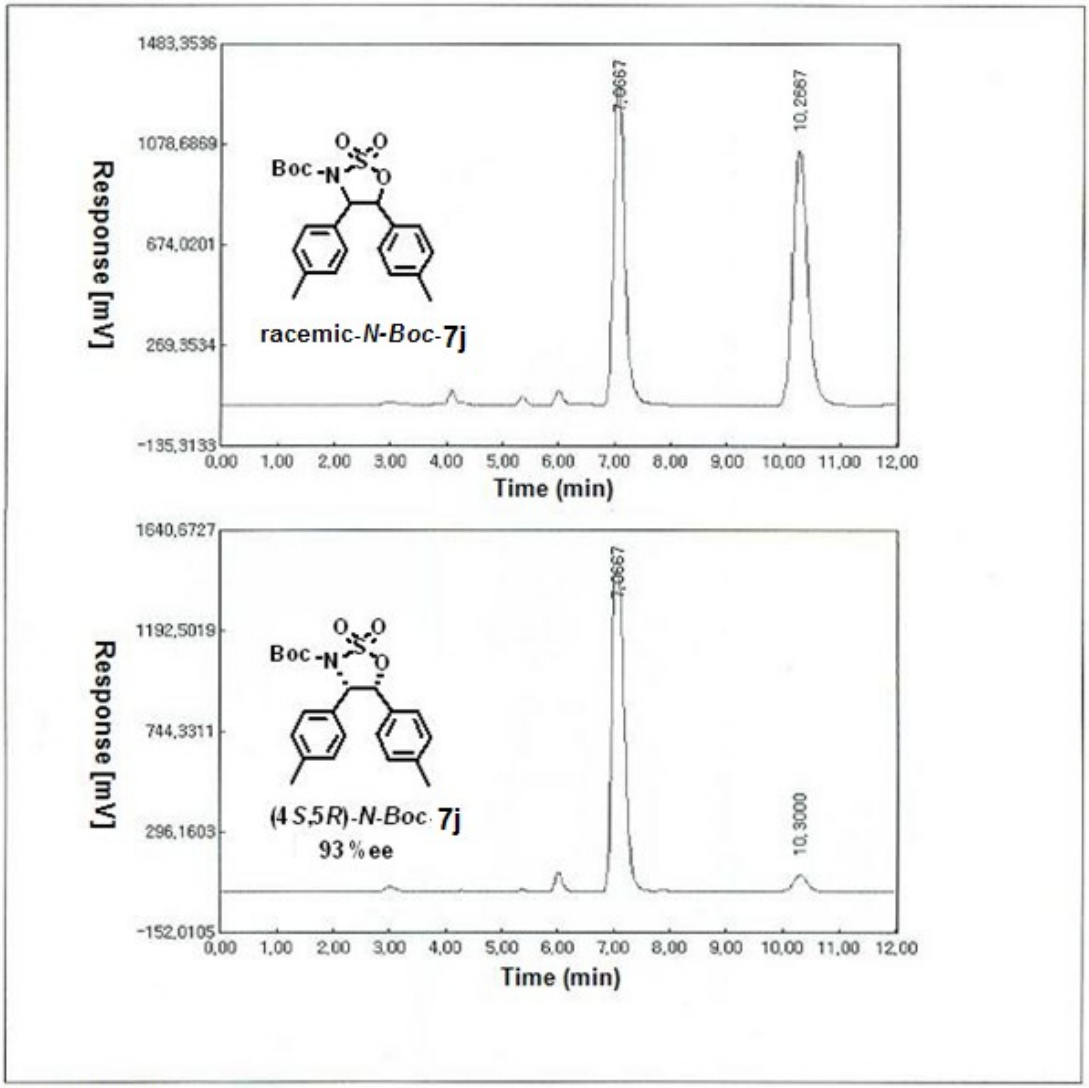
Result Report

Peak #	Time (min)	Area [mV*s]	BL	wide (sec)	Area %
1	14.2167	47825.1201	BV	115.0000	93.4941
2	16.8833	3327.9649	BB	85.0000	6.5059
Total		51153.0859			


^{1}H NMR (300MHz, CDCl$_3$)
N-Boc-7j
7.2581
6.9633
6.9366
6.8130
6.7870
6.1055
6.0877
5.3705
5.3531
2.2522
2.2441
1.5636
1.5262
1.4803
6.177
2.050
1.000
0.984
6.274
11.168
ppm

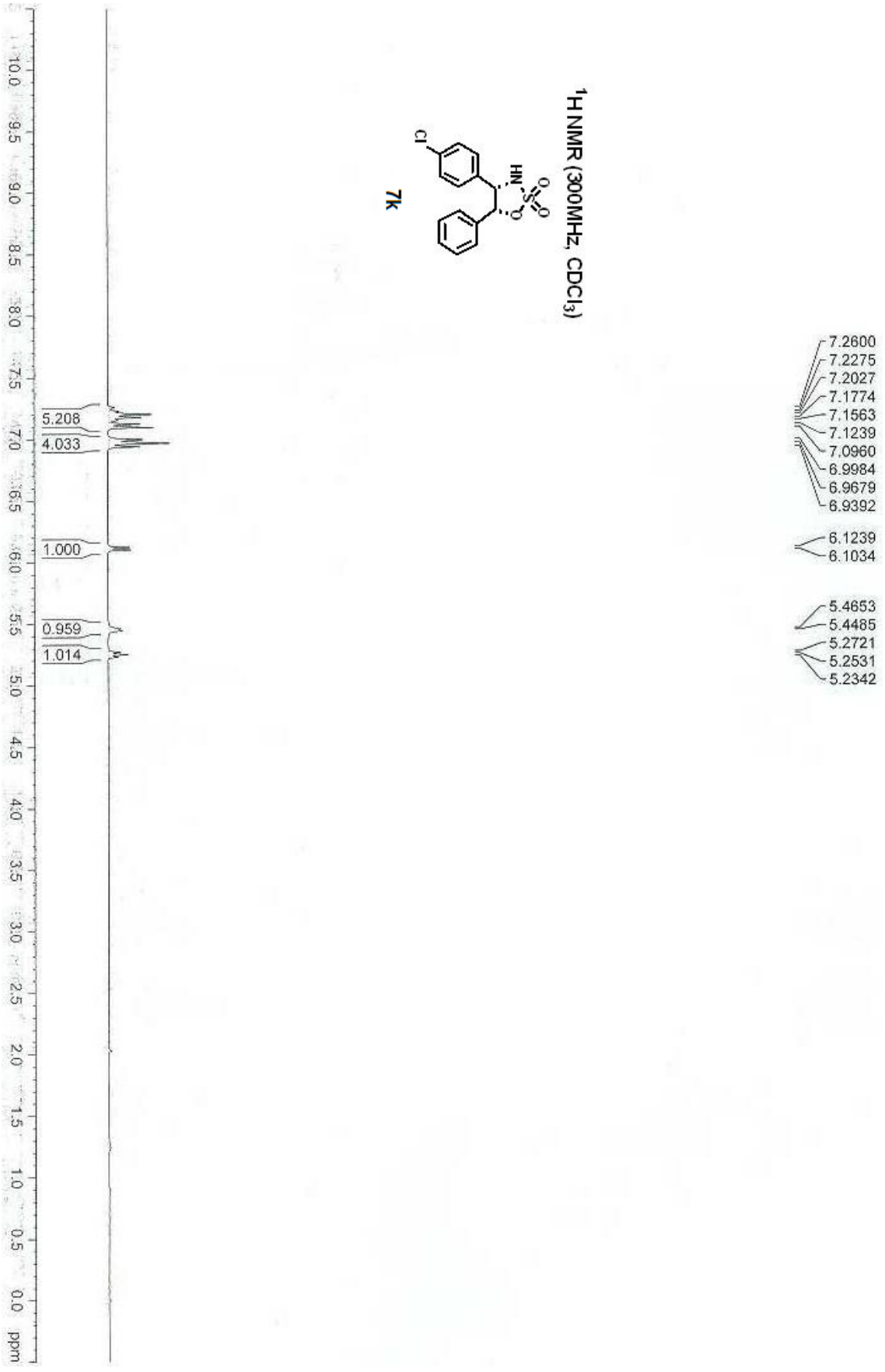


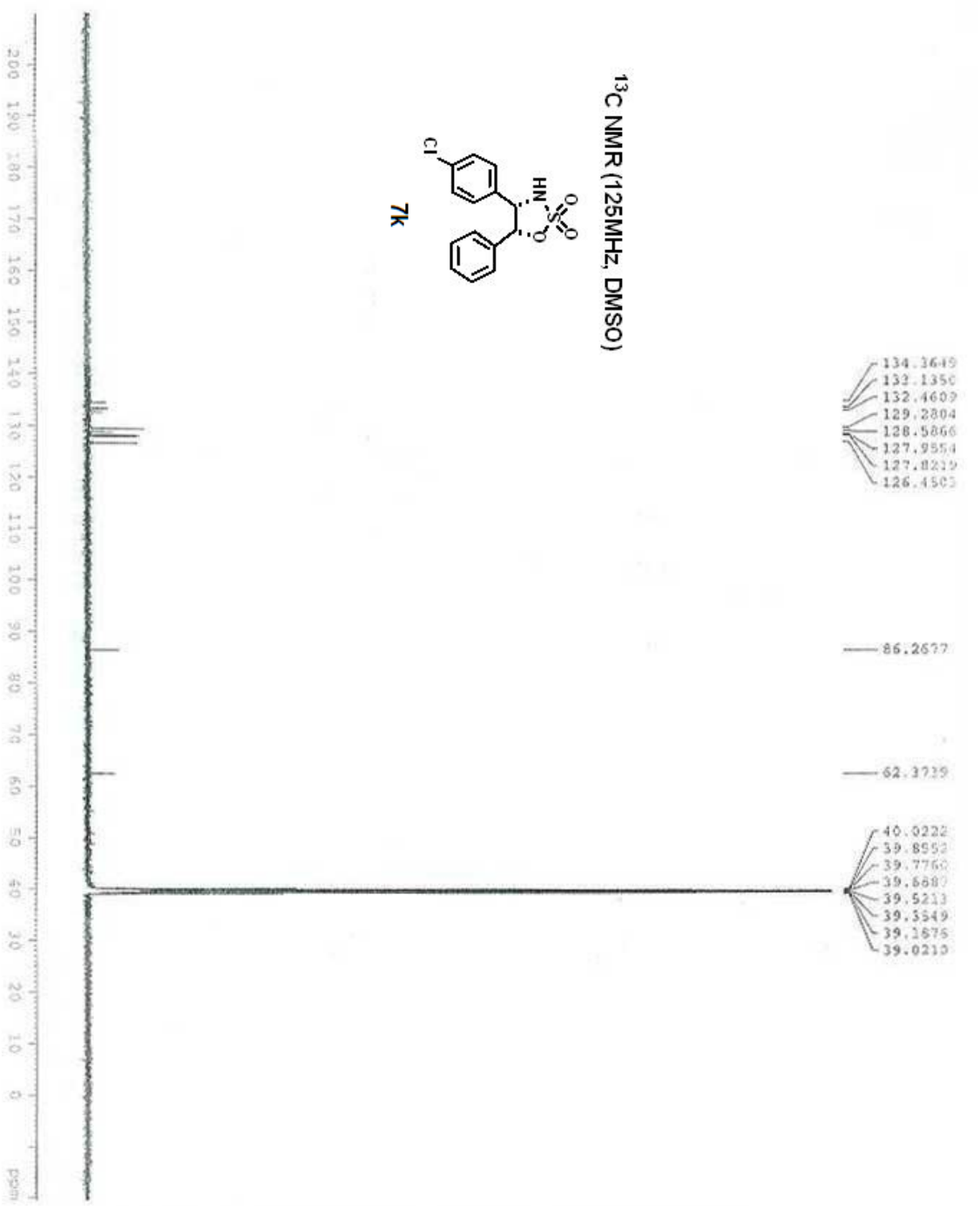

```
NAME                 101108_HJA_1Me_Boc 2
EXPNO                   2
PROCNO                  1
Date_                20101108
Time                 14.05
INSTRUM                spect
PROBHD     5 mm DUL 13C-1
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     512
DS                       2
SWH                35211.270 Hz
FIDRES              0.537281 Hz
AQ                  0.9306754 sec
RG                     512
DW                  14.200 usec
DE                   6.00 usec
TE                  296.3 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   13C
P1                   8.00 usec
PL1                  1.40 dB
PL1W            70.60439301 W
SFO1            125.7728799 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                   1H
PCPD2               100.00 usec
PL2                  1.90 dB
PL12                16.00 dB
PL13                19.00 dB
PL2W            27.23316002 W
PL12W            0.44167015 W
PL13W            0.22135943 W
SFO2            500.1320005 MHz
SI                   32768
SF              125.7577731 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



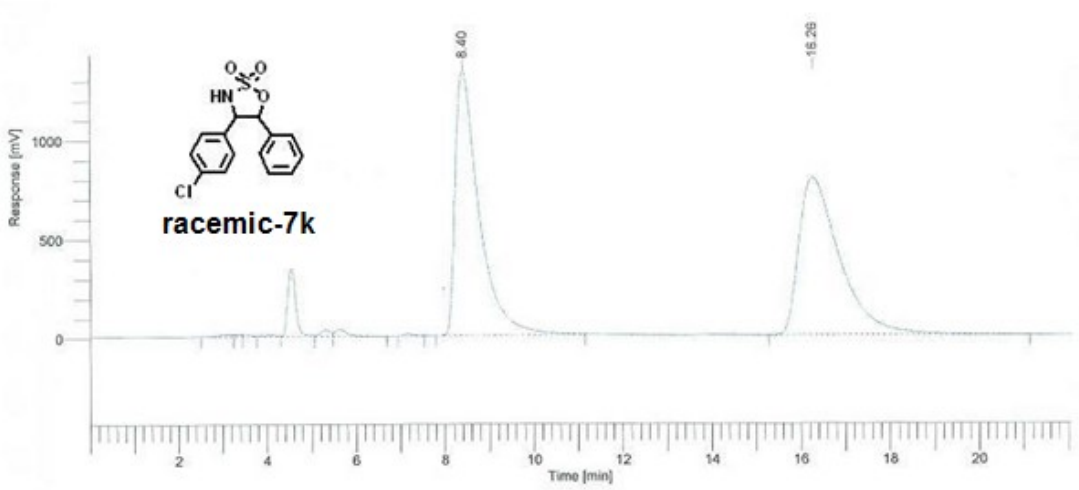
Result Report

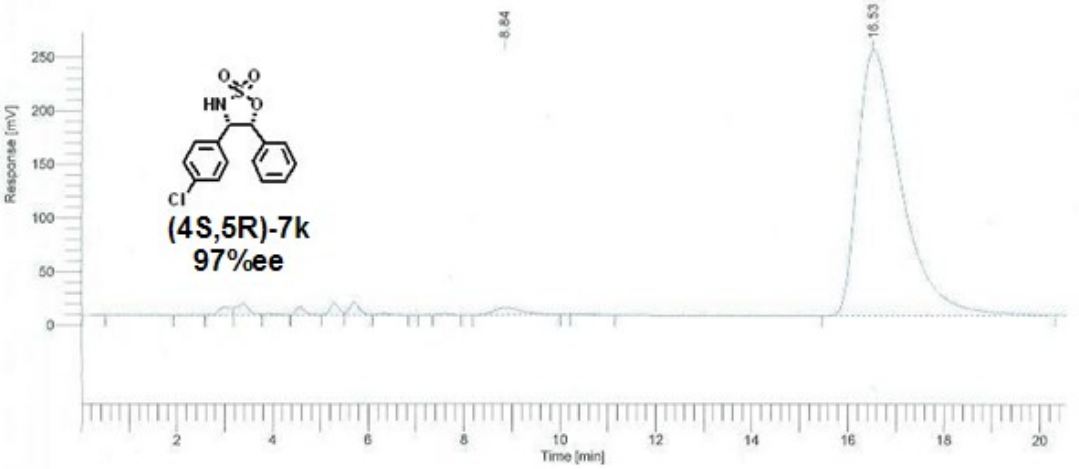
Peak #	Time (min)	Area [mV*s]	BL	wide (sec)	Area %
1	6.0167	708.4693	BB	19.0000	2.8773
2	7.0667	23085.1137	BB	40.0000	93.7545
3	10.3000	829.3597	BB	25.0000	3.3682
Total		24622.9414			


^{1}H NMR (300MHz, CDCl$_3$)
7k
Cl
HN
O
S
O
O
7.2600
7.2275
7.2027
7.1774
7.1563
7.1239
7.0960
6.9984
6.9679
6.9392
6.1239
6.1034
5.4653
5.4485
5.2721
5.2531
5.2342
5.208
4.033
1.000
0.959
1.014
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
ppm



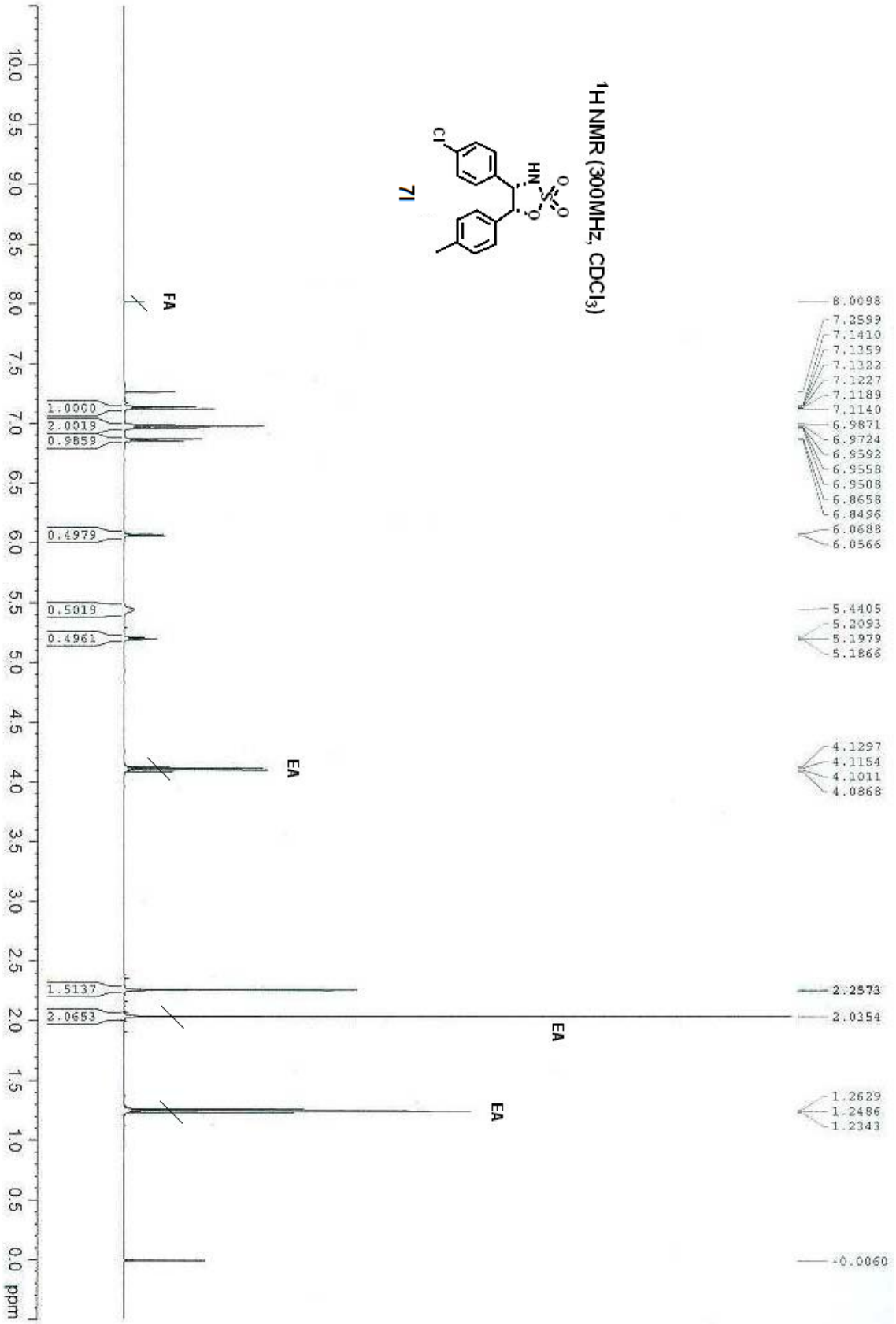

```
NAME                 101027_4Cl_YR_amino
EXPNO                       2
PROCNO                      1
Date_               20101027
Time                   11.27
INSTRUM                spect
PROBHD     5 mm PUL 13C.1
PULPROG             zgpg30
TD                     65536
SOLVENT               DMSO
NS                      512
DS                        2
SWH                35211.270 Hz
FIDRES              0.537281 Hz
AQ                  0.9306754 sec
RG                     1290.2
DW                  14.200 usec
DE                   6.00 usec
TE                   297.0 K
D1                  2.00000000 sec
D11                 0.03000000 sec
PD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                    8.00 usec
PL1                   1.40 dB
PL1W            70.60439301 W
SFO1            125.7728799 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                100.00 usec
PL2                   -1.90 dB
PL12                  16.00 dB
PL13                  19.00 dB
PL2W            27.23316002 W
PL12W            0.44167015 W
PL13W            0.22135943 W
SFO2            500.1320005 MHz
SI                      32768
SF                125.7578474 MHz
WDW                        EM
SSB                         0
LB                   1.00 Hz
GB                          0
PC                       1.40
```

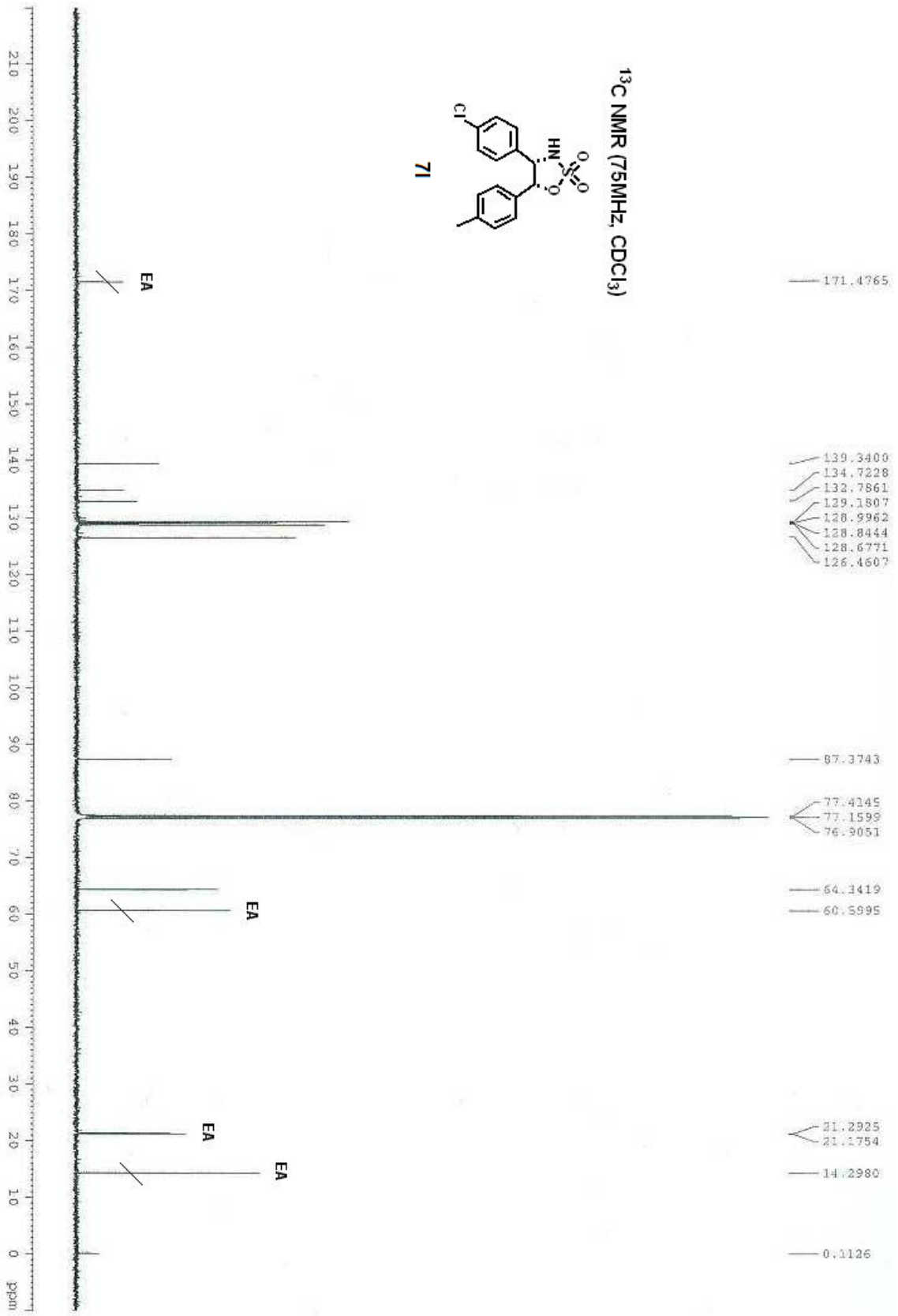


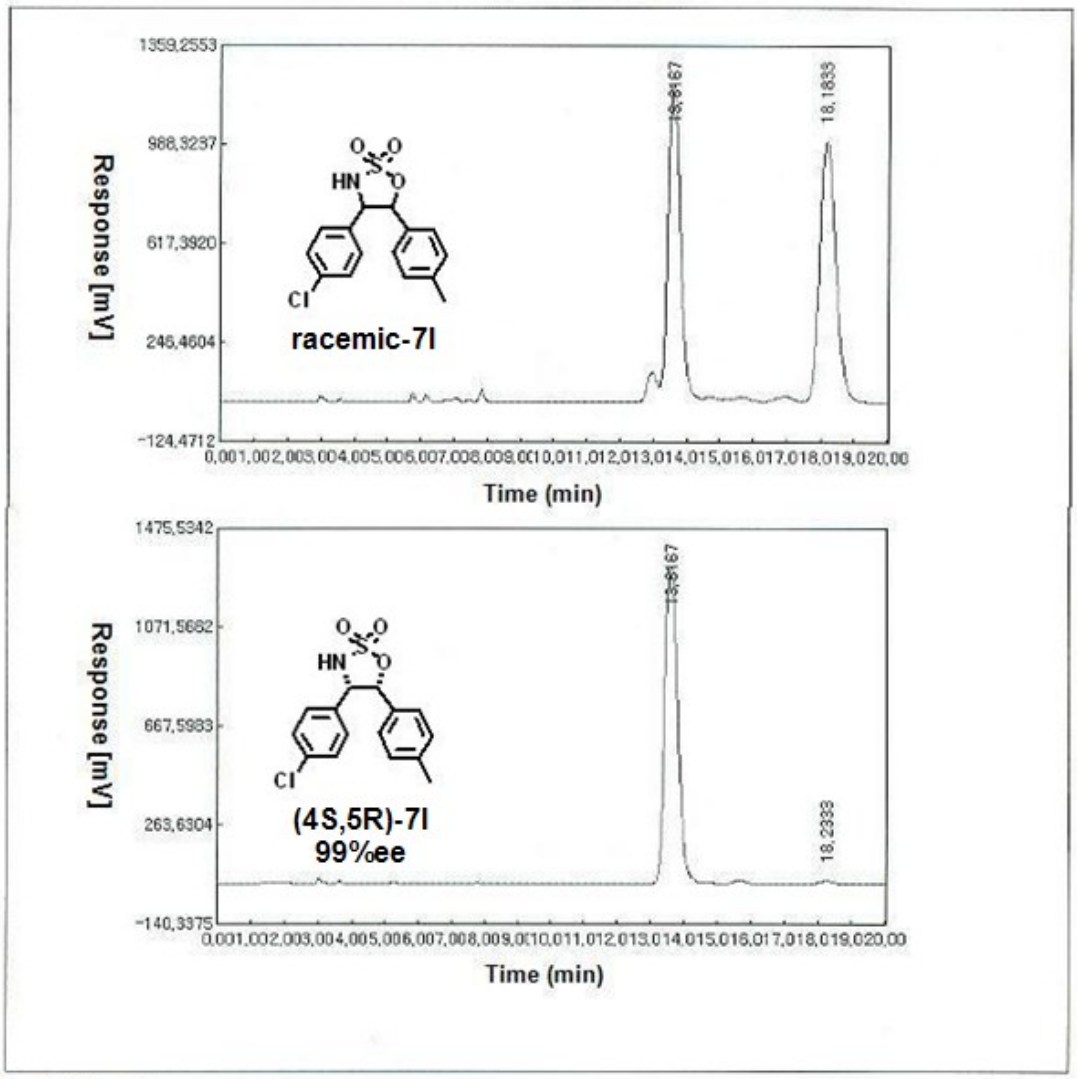


DEFAULT REPORT

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	0.376	3168.87	129.29	0.02	0.02	BB	24.5101
2	2.320	10539.38	438.92	0.06	0.06	BV	24.0122
3	2.999	138832.13	7595.09	0.83	0.83	VV	18.2792
4	3.389	204482.60	11038.20	1.22	1.22	VV	18.5250
5	3.895	28580.87	1331.90	0.17	0.17	VB	21.4587
6	4.570	98751.93	7613.16	0.59	0.59	BV	12.9712
7	5.282	147629.99	11036.17	0.88	0.88	VV	13.3769
8	5.695	169779.42	12031.01	1.01	1.01	VV	14.1118
9	6.296	22306.44	1402.10	0.13	0.13	VB	15.9093
10	7.216	2737.36	281.66	0.02	0.02	BV	9.7187
11	7.570	16393.70	957.87	0.10	0.10	VB	17.1147
12	8.845	267007.80	6663.42	1.59	1.59	BB	40.0707
13	10.503	12995.13	474.94	0.08	0.08	BB	27.3615
14	16.529	15667018.50	247738.93	93.31	93.31	BB	63.2400
		16790224.10	308732.67	100.00	100.00		

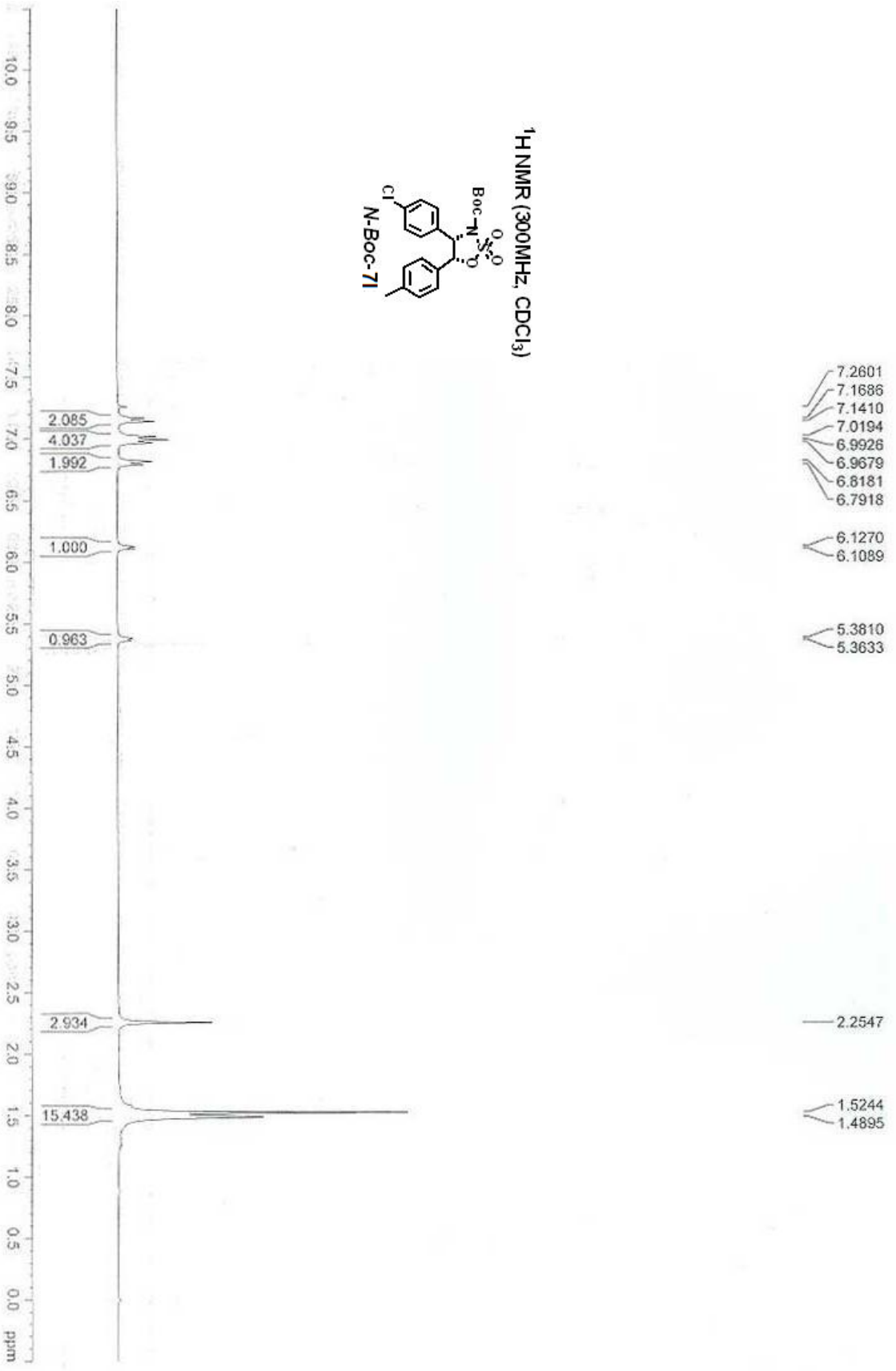

1H NMR (300MHz, CDCl3)
7l
Cl
HN
O
O
O
S
FA
EA
EA
EA
1.0000
2.0019
0.9859
0.4979
0.5019
0.4961
1.5137
2.0653
8.0098
7.2599
7.1410
7.1359
7.1322
7.1227
7.1189
7.1140
6.9871
6.9724
6.9592
6.9558
6.9508
6.8658
6.8496
6.0688
6.0566
5.4405
5.2093
5.1979
5.1866
4.1297
4.1154
4.1011
4.0868
2.2573
2.0354
1.2629
1.2486
1.2343
-0.0060
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 ppm

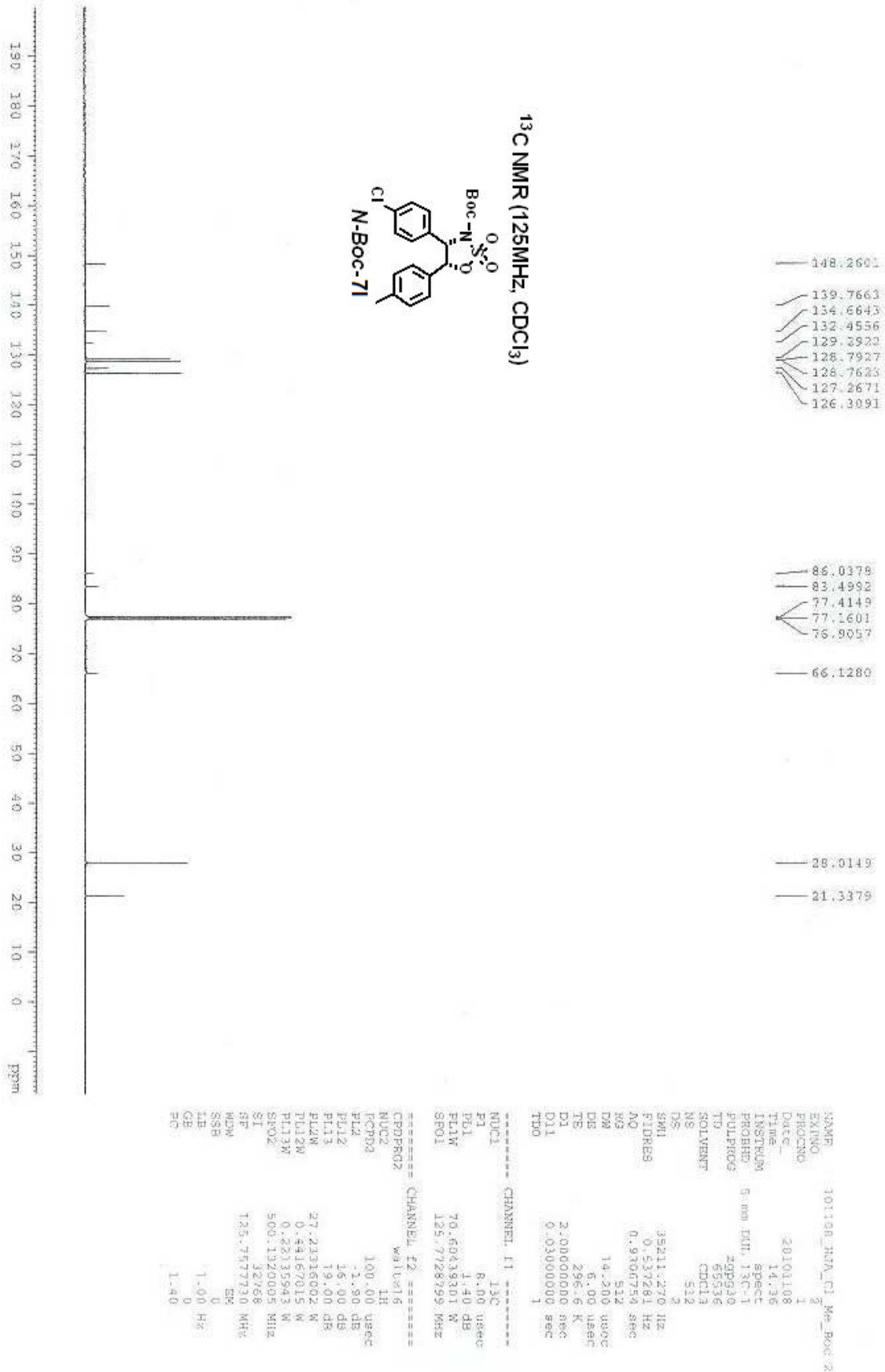

^{13}C NMR (75MHz, CDCl$_3$)
7l
Cl
HN
S
O
O
O
EA
EA
EA
EA
171.4765
139.3400
134.7228
132.7861
129.1807
128.9962
128.8444
128.6771
126.4607
87.3743
77.4145
77.1599
76.9051
64.3419
60.5995
21.2925
21.1754
14.2980
0.1126
ppm

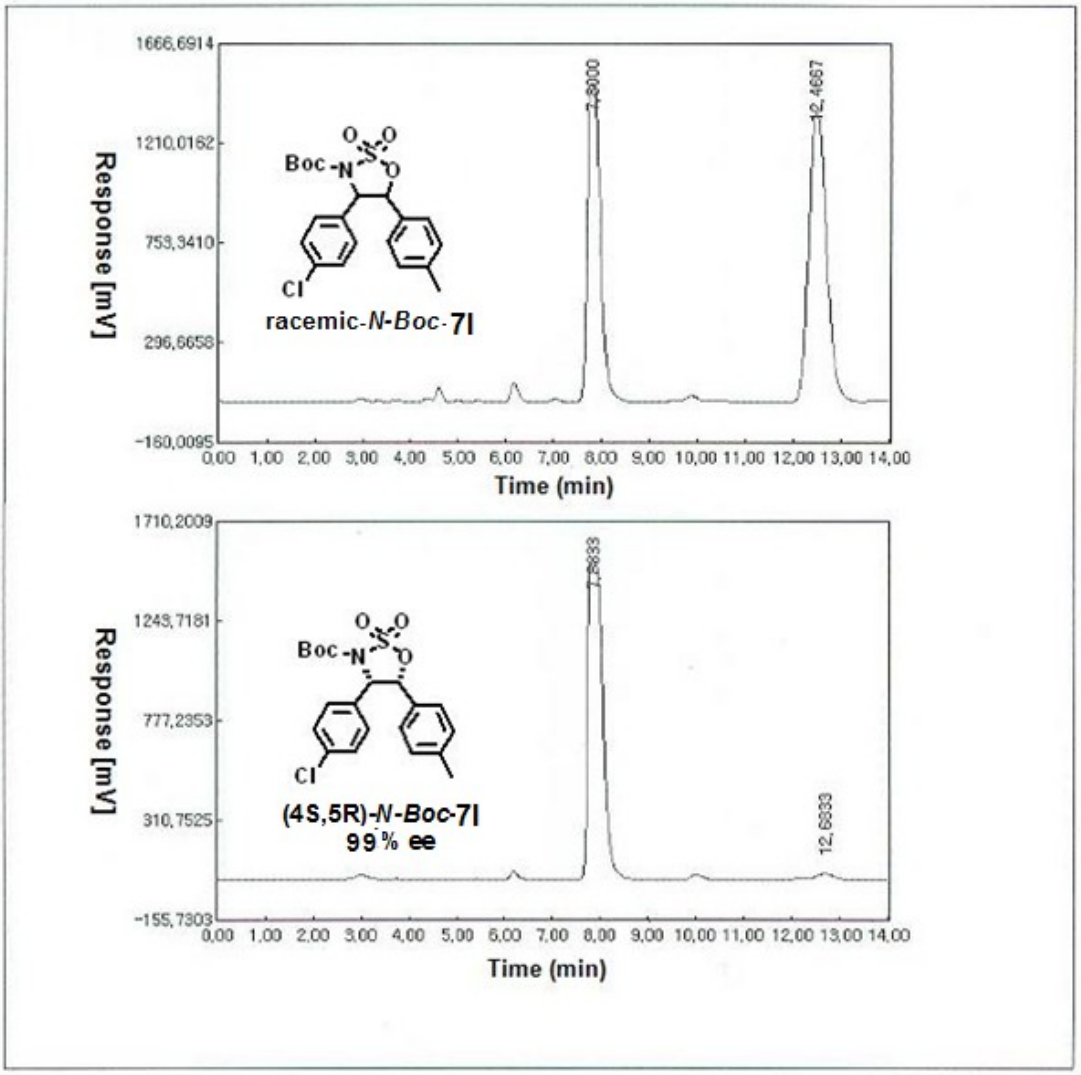


Result Report

Peak #	Time (min)	Area [mV*s]	BL	wide (sec)	Area %
1	3.0333	183.8998	BB	30.0000	0.4958
2	13.6167	36150.6770	BB	93.0000	97.4654
3	15.6667	363.9467	BB	65.0000	0.9812
4	18.2333	392.2732	BB	67.0000	1.0576
Total		37090.7969			

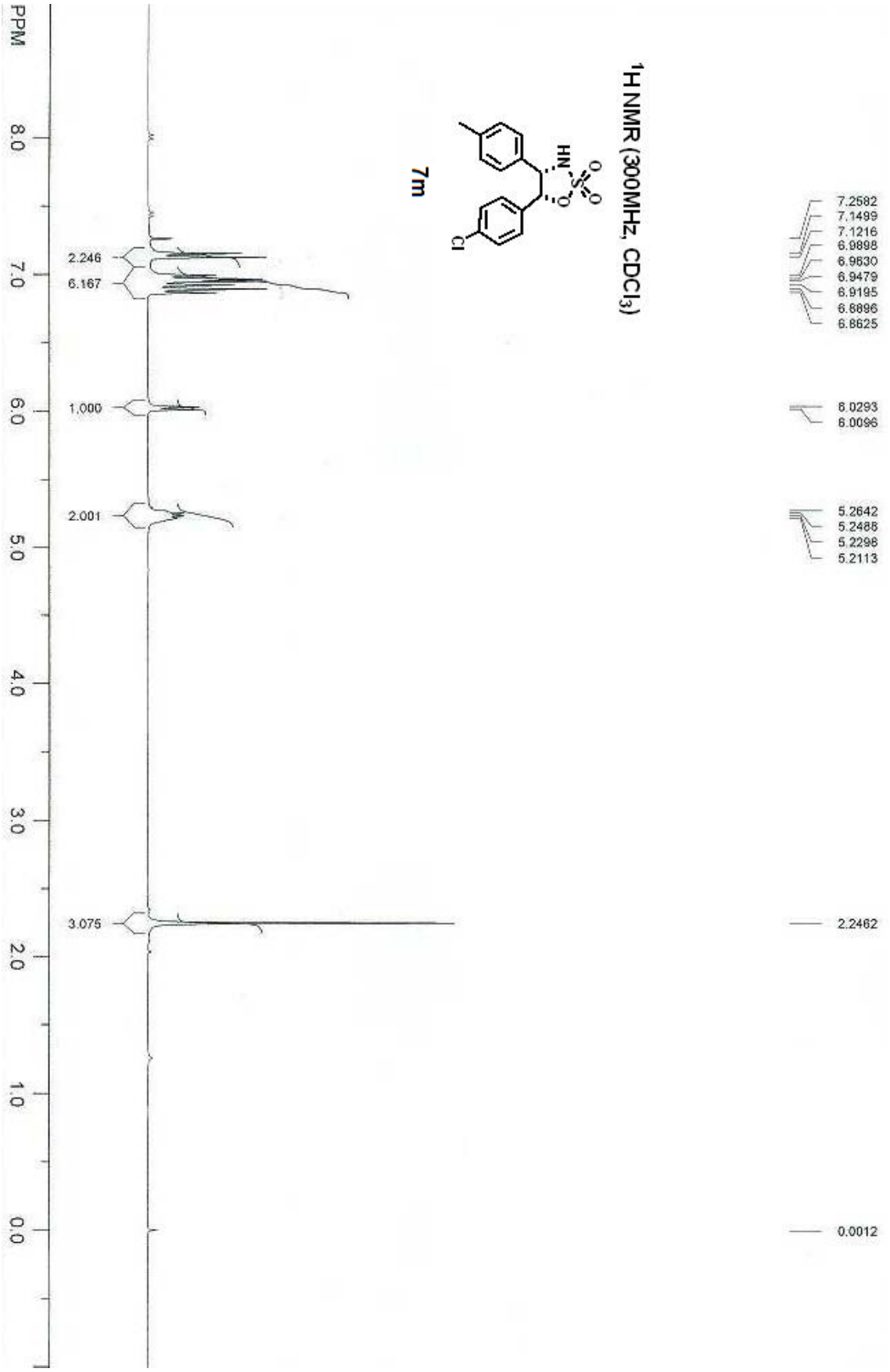

^{1}H NMR (300MHz, CDCl$_3$)
N-Boc-7l
Cl
Boc
7.2601
7.1686
7.1410
7.0194
6.9926
6.9679
6.8181
6.7918
6.1270
6.1089
5.3810
5.3633
2.2547
1.5244
1.4895
2.085
4.037
1.992
1.000
0.963
2.934
15.438
ppm

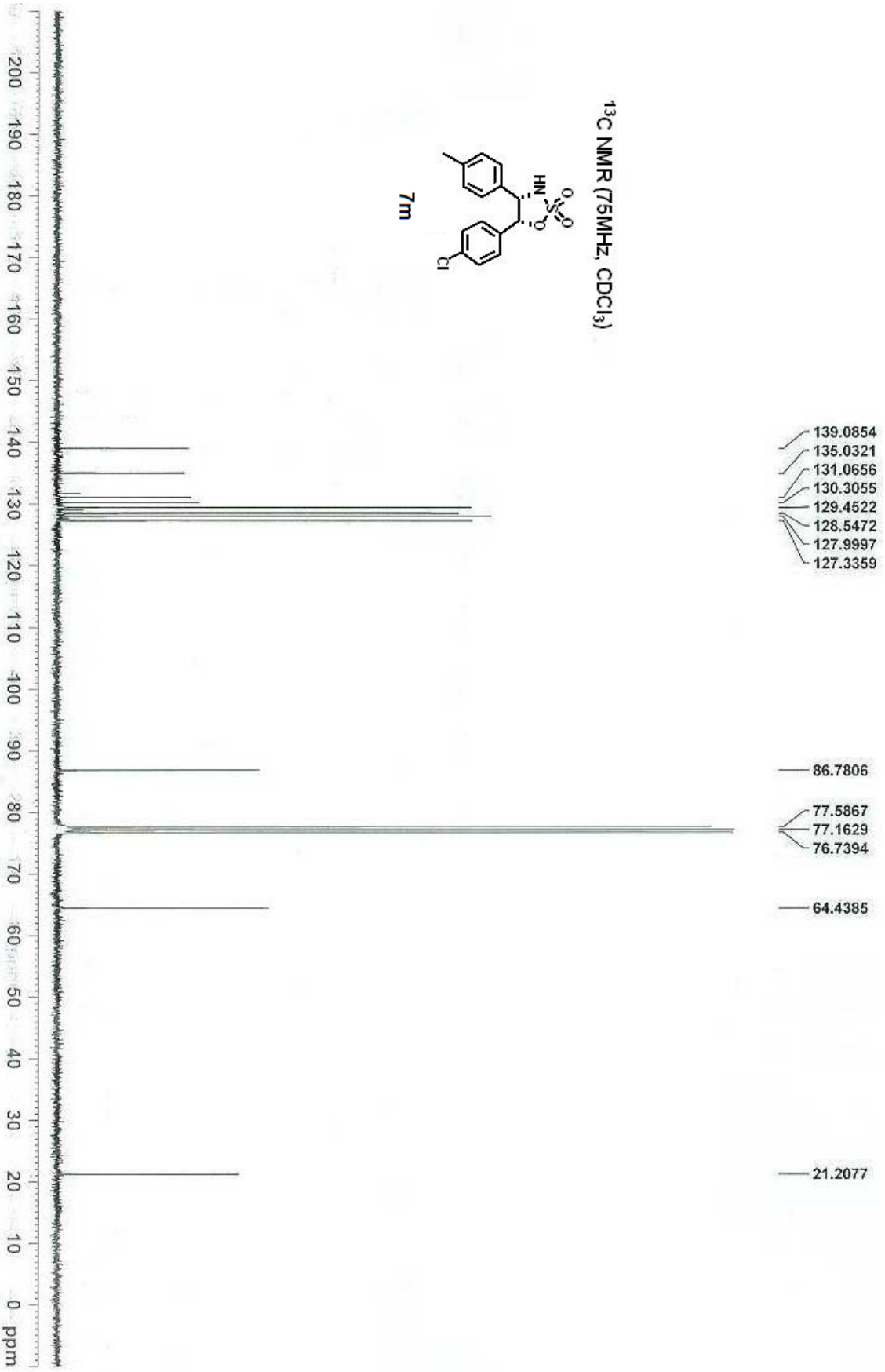

13C NMR (125MHz, CDCl3)
N-Boc-7l
Cl
Boc-N
148.2601
139.7663
134.6643
132.4556
129.2922
128.7927
128.7623
127.2671
126.3091
86.0379
83.4992
77.4149
77.1601
76.9057
66.1280
28.0149
21.3379
ppm

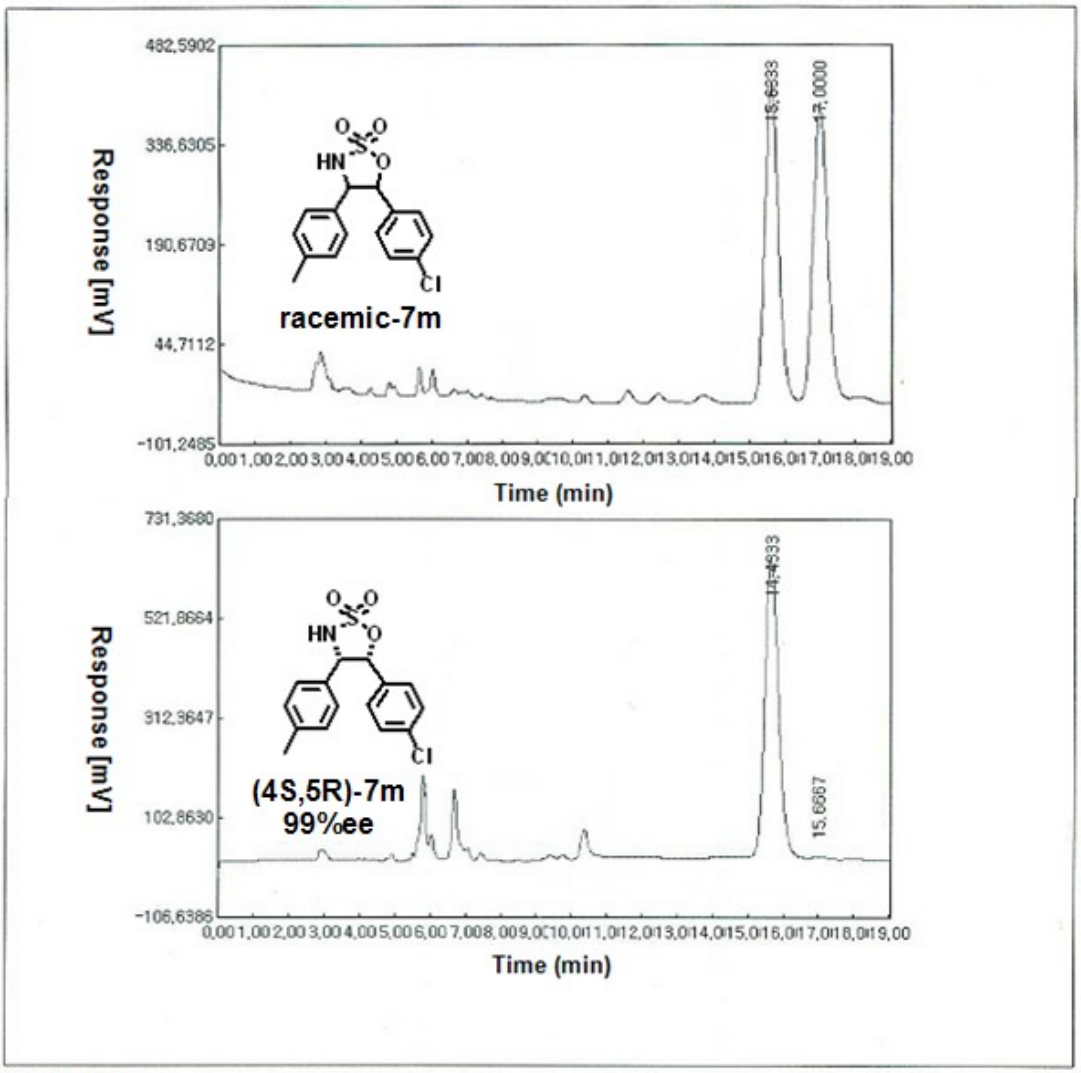


Result Report

Peak #	Time (min)	Area [mV*s]	BL	wide (sec)	Area %
1	3.0000	241.5256	BB	26.0000	0.7116
2	6.2000	334.0131	BB	21.0000	0.9841
3	7.8833	32865.1483	BB	59.0000	96.8293
4	10.0167	249.1193	BB	24.0000	0.7340
5	12.6833	251.5202	BB	27.0000	0.7410
Total		33941.3281			

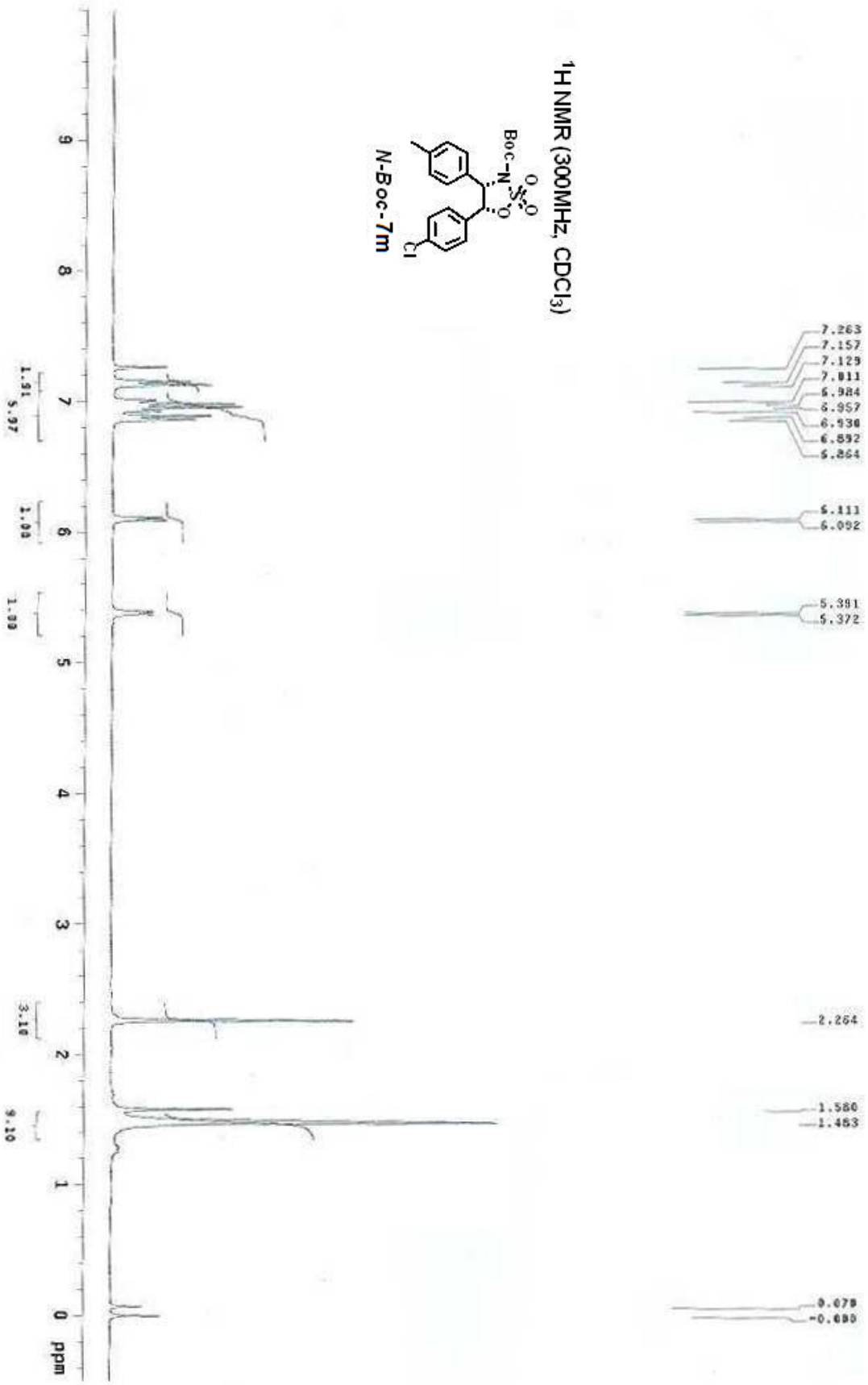

^{1}H NMR (300MHz, CDCl$_3$)
7m
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2.246
6.167
1.000
2.001
3.075
7.2582
7.1499
7.1216
6.9898
6.9830
6.9479
6.9195
6.8896
6.8625
6.0293
6.0096
5.2642
5.2488
5.2298
5.2113
2.2462
0.0012

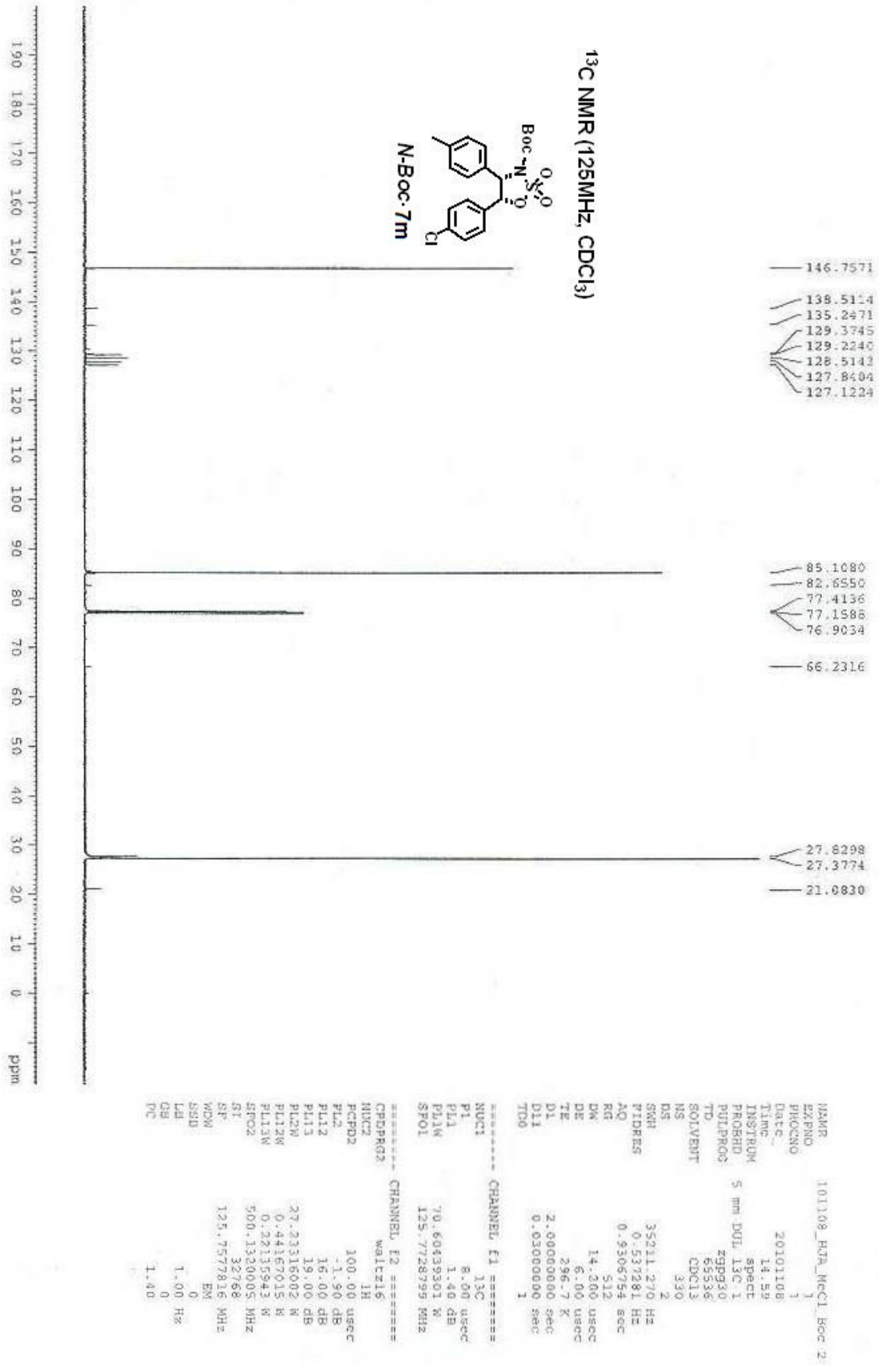

^{13}C NMR (75MHz, CDCl$_3$)
7m
HN
O
O
O
Cl
139.0854
135.0321
131.0656
130.3055
129.4522
128.5472
127.9997
127.3359
86.7806
77.5867
77.1629
76.7394
64.4385
21.2077
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



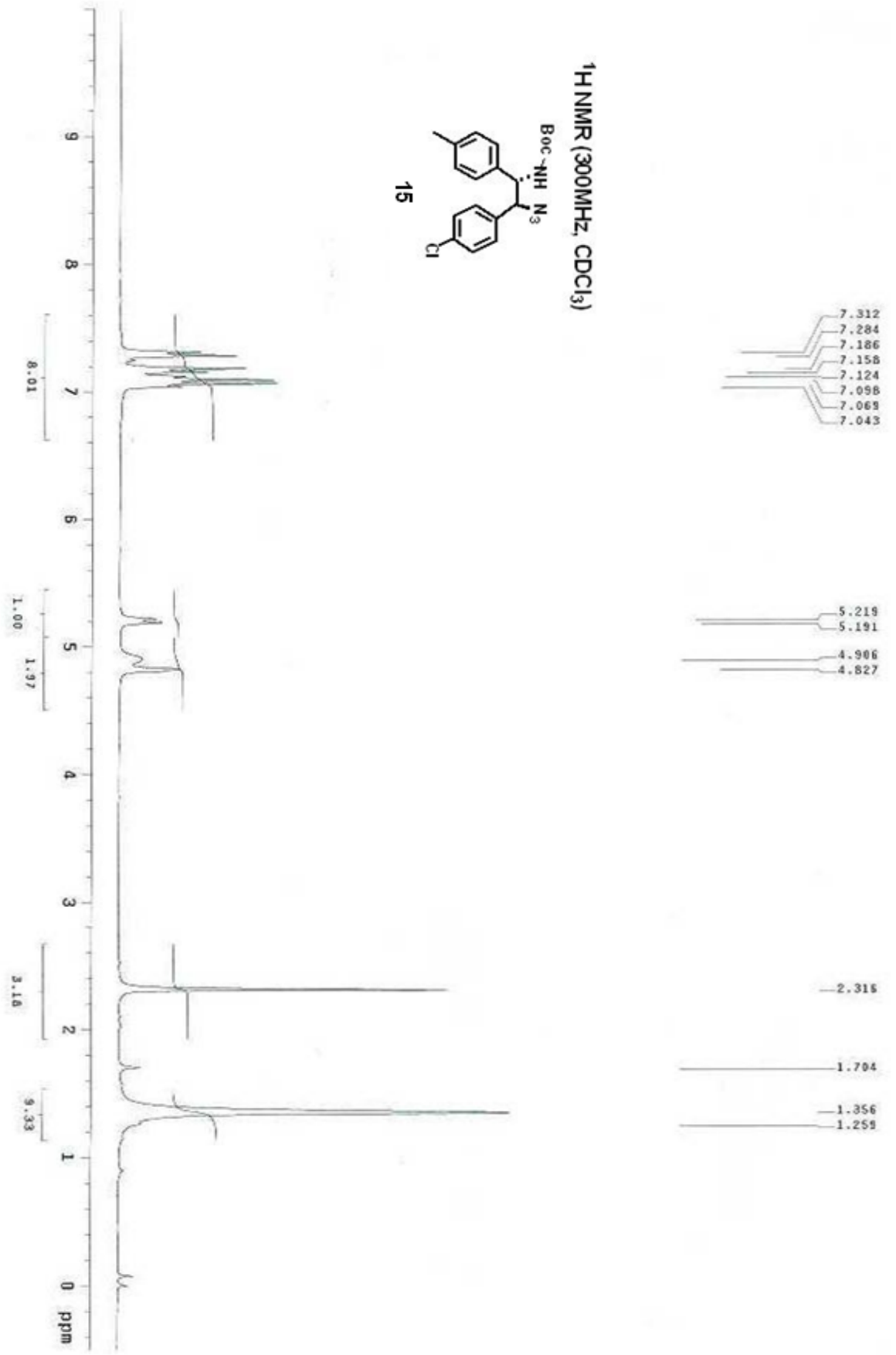
Result Report

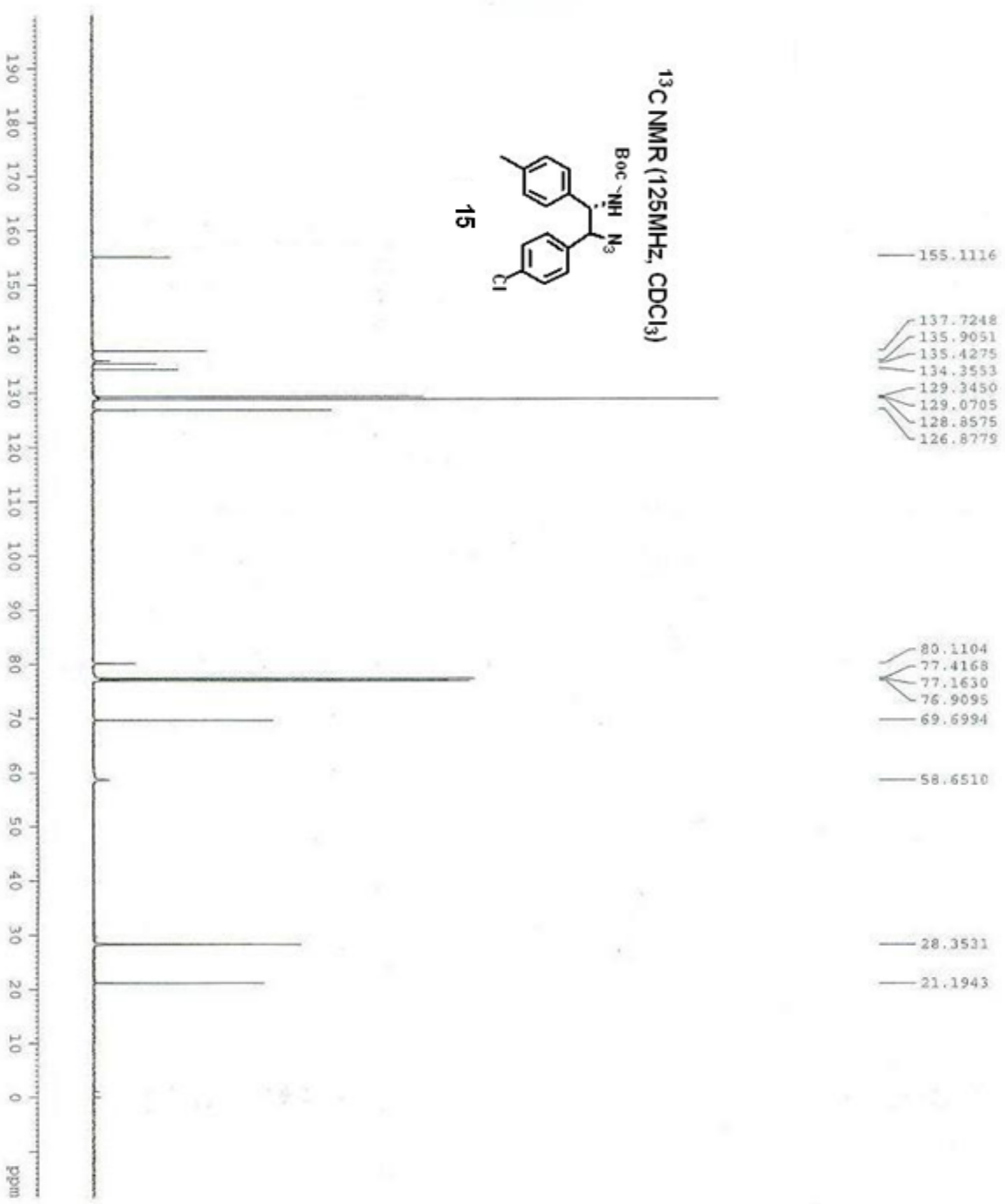
Peak #	Time (min)	Area [mV*s]	BL	wide (sec)	Area %
26	15.6667	17431.5022	BB	101.0000	73.1587
27	17.0000	5.1808	BB	17.0000	0.0217
28	17.9500	4.6992	BB	20.0000	0.0197
Total		23826.9727			


^{1}H NMR (300MHz, CDCl$_3$)
N-Boc-7m
7.263
7.157
7.129
7.011
6.984
6.957
6.930
6.892
6.864
6.111
6.092
5.381
5.372
2.264
1.586
1.463
0.079
-0.000
ppm

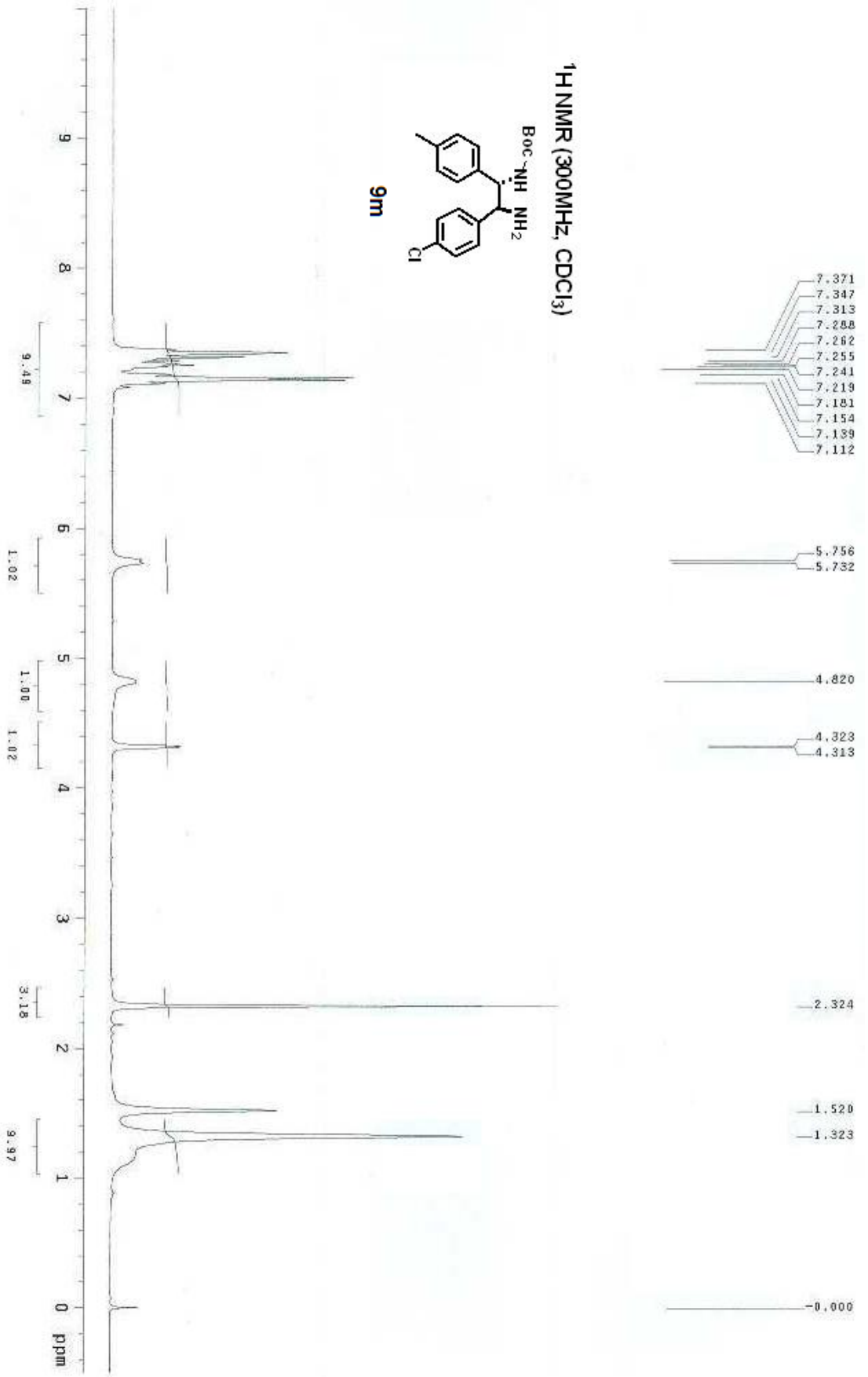


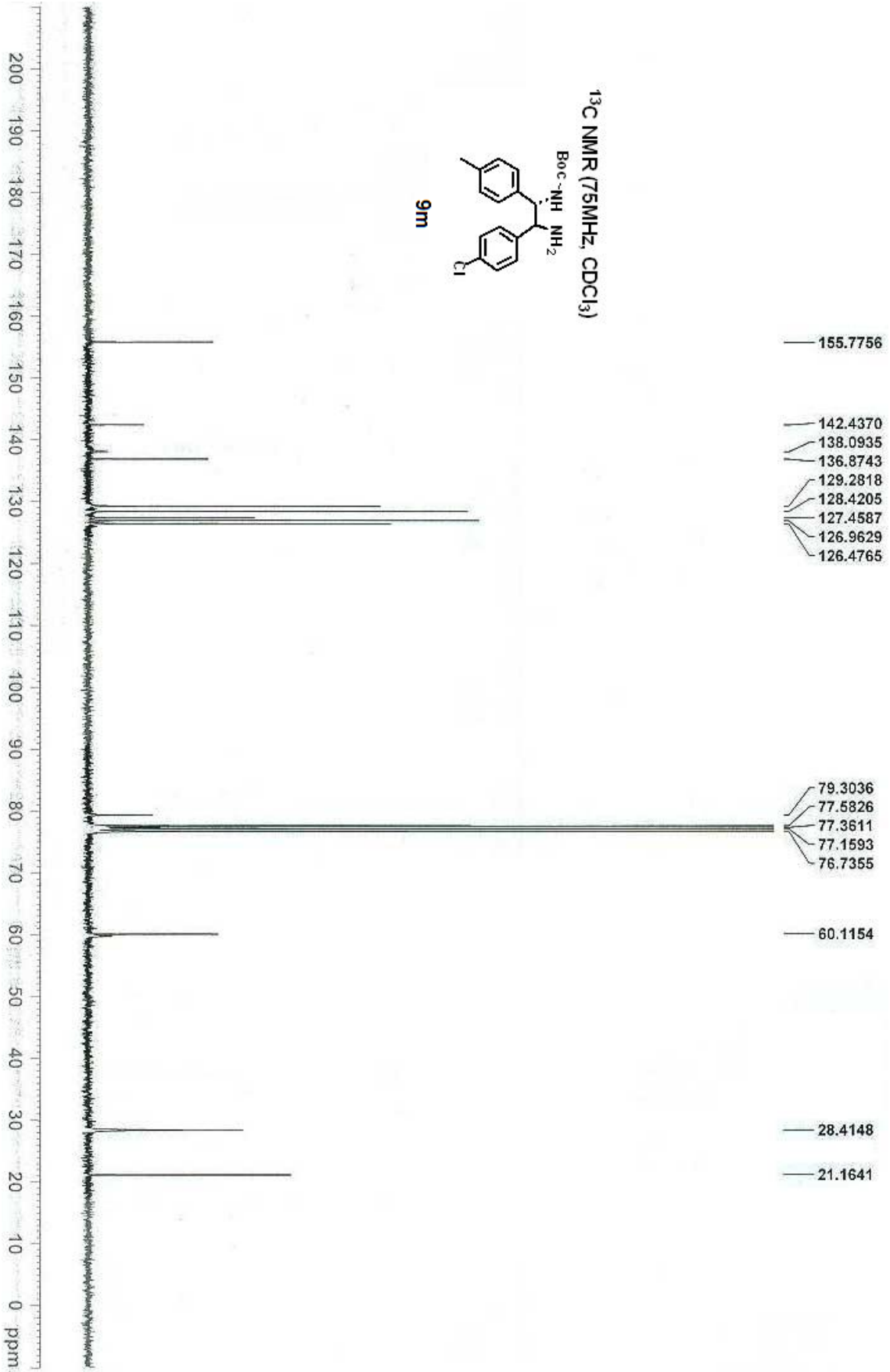

```
NAME                    101108_RJA_McCl_Boc_2
EXPNO                   1
PROCNO                  1
Date_                   20101108
Time                    14.59
INSTRUM                 spect
PROBHD     5 mm DUL 13C 1
PULPROG                 zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                      330
DS                      2
SWH                     35211.270 Hz
FIDRES                  0.537281 Hz
AQ                      0.9306754 sec
RG                      512
DW                      14.200 usec
DE                      6.00 usec
TE                      296.7 K
D1                      2.00000000 sec
D11                     0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                    13C
P1                      8.00 usec
PL1                     1.40 dB
PL1W                    70.60439301 W
SFO1                    125.7728799 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                    1H
PCPD2                   100.00 usec
PL2                     -1.90 dB
PL12                    16.00 dB
PL13                    19.00 dB
PL2W                    27.23316602 W
PL12W                   0.44167015 W
PL13W                   0.22135843 W
SFO2                    500.1320005 MHz
SI                      32768
SF                      125.7577816 MHz
WDW                     EM
SSB                     0
LB                      1.00 Hz
GB                      0
PC                      1.40
```

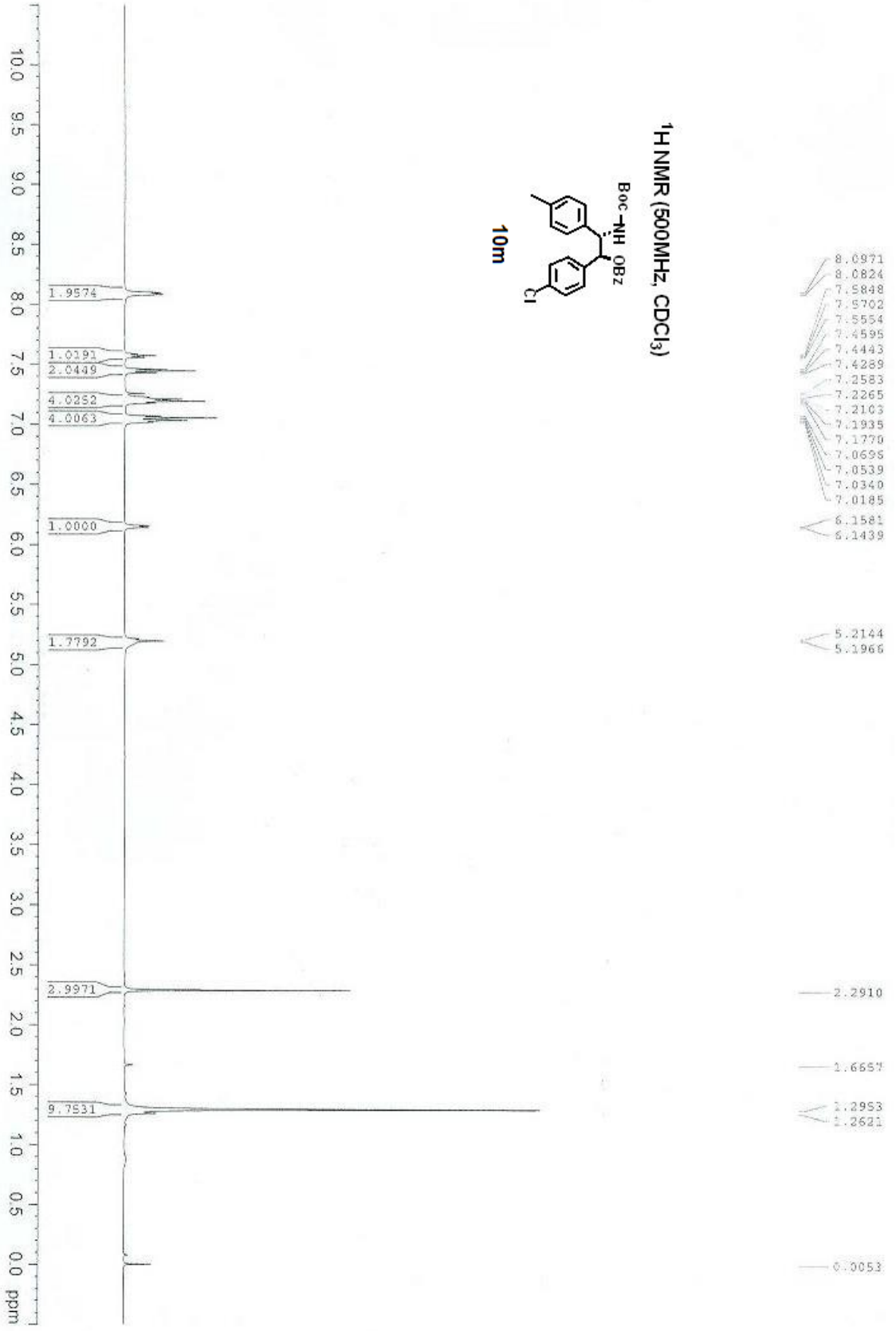

1H NMR (300MHz, CDCl3)
Boc-NH N3
Cl
15
7.312
7.284
7.186
7.158
7.124
7.098
7.069
7.043
5.219
5.191
4.906
4.827
2.315
1.704
1.356
1.259
8.01
1.00
1.97
3.18
9.33
ppm

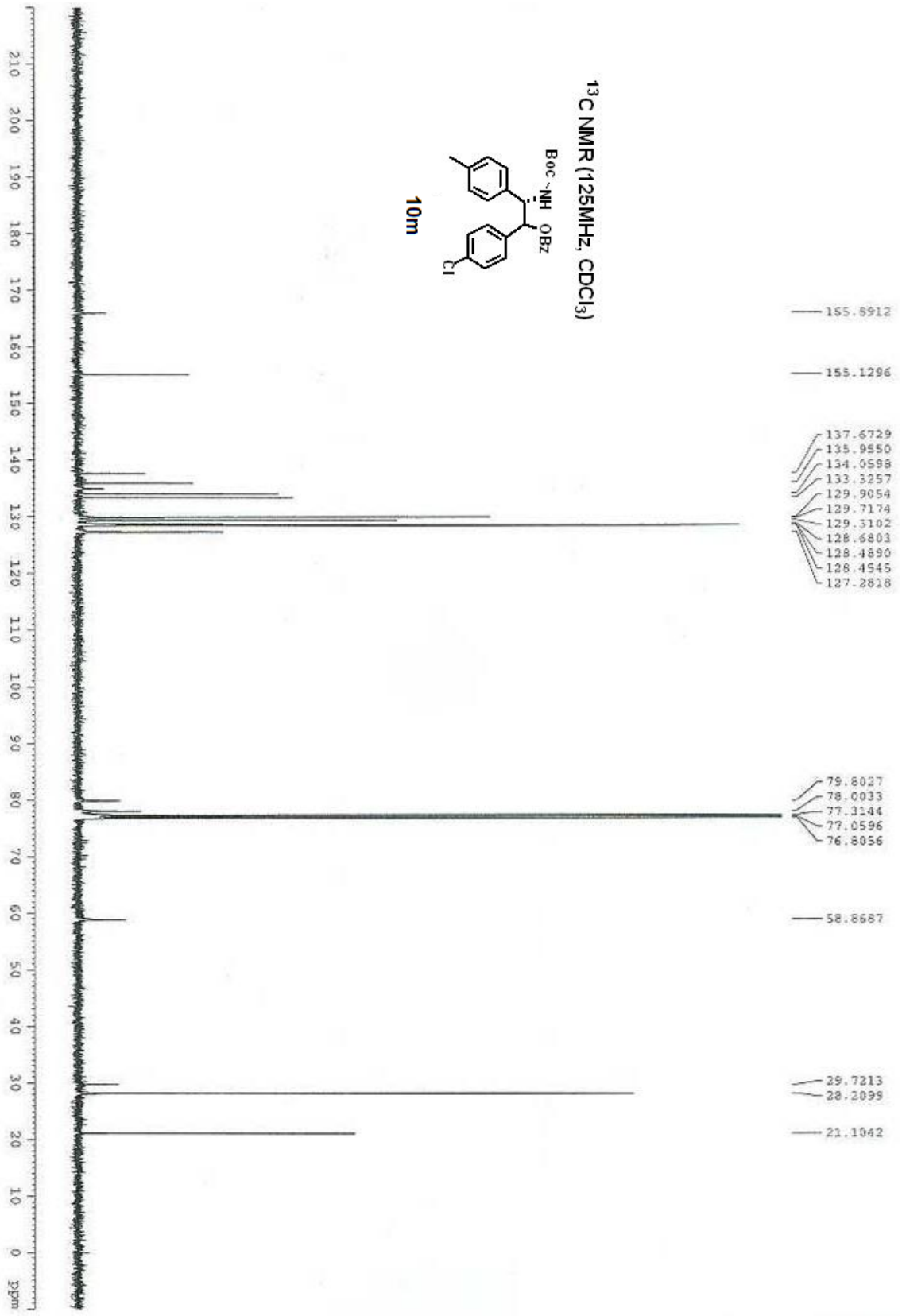



```
NAME                 101011_HJA01
EXPNO                         2
PROCNO                        1
Date_                  20101011
Time_                     12.59
INSTRUM                   spect
PROBHD     5 mm DUL 13C-1
PULPROG                zgpg30
TD                        65536
SOLVENT                  CDCl3
NS                         1024
DS                            2
SWH                  35211.270 Hz
FIDRES                0.537281 Hz
AQ                    0.9306754 sec
RG                          512
DW                       14.200 usec
DE                        6.00 usec
TE                       296.9 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                        13C
P1                        8.00 usec
PL1                       1.40 dB
PL1W                70.69439301 W
SFO1               125.7728799 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                   100.00 usec
PL2                      -1.90 dB
PL12                     16.00 dB
PL13                     19.00 dB
PL2W                27.23316002 W
PL12W                0.44167015 W
PL13W                0.22135943 W
SFO2               500.1320005 MHz
SI                        32768
SF                 125.7577785 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```


^{1}H NMR (300MHz, CDCl$_3$)
9m
Boc-NH
NH$_2$
Cl
7.371
7.347
7.313
7.288
7.262
7.255
7.241
7.219
7.181
7.154
7.139
7.112
5.756
5.732
4.820
4.323
4.313
2.324
1.520
1.323
0.000
9.49
1.02
1.00
1.02
3.18
9.97
ppm


^{13}C NMR (75MHz, CDCl$_3$)
9m
Boc-NH
NH$_2$
Cl
155.7756
142.4370
138.0935
136.8743
129.2818
128.4205
127.4587
126.9629
126.4765
79.3036
77.5826
77.3611
77.1593
76.7355
60.1154
28.4148
21.1641
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


^{1}H NMR (500MHz, CDCl$_3$)
10m
Boc–NH
OBz
Cl
8.0971
8.0824
7.5848
7.5702
7.5554
7.4595
7.4443
7.4289
7.2583
7.2265
7.2103
7.1935
7.1770
7.0695
7.0539
7.0340
7.0185
6.1581
6.1439
5.2144
5.1966
2.2910
1.6657
1.2953
1.2621
0.0053
1.9574
1.0191
2.0449
4.0252
4.0063
1.0000
1.7792
2.9971
9.7531
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 ppm


^{13}C NMR (125MHz, CDCl$_3$)
10m
Boc-NH
OBz
Cl
155.8912
155.1296
137.6729
135.9550
134.0598
133.3257
129.9054
129.7174
129.3102
128.6803
128.4890
128.4545
127.2818
79.8027
78.0033
77.3144
77.0596
76.8056
58.8687
29.7213
28.2099
21.1042
ppm