Supporting Information

Direct catalytic enantioselective Mannich-type reaction of dichloroacetonitrile using chiral bis(imidazoline)-Pd catalysts

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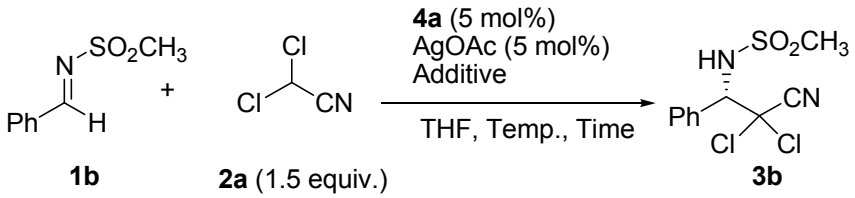
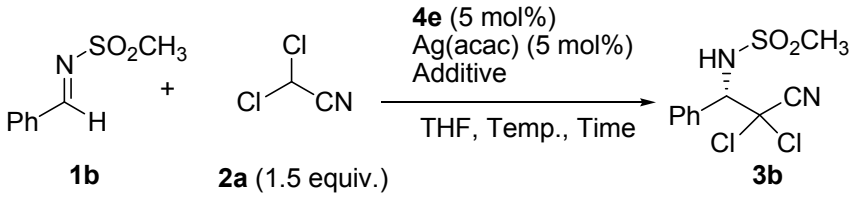
General Methods:

All reactions were performed in oven-dried glassware under a positive pressure of nitrogen. Solvents were transferred via syringe and were introduced into the reaction vessels through a rubber septum. All reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica-gel (60-F254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or *p*-anisaldehyde in ethanol/heat. Column chromatography was carried out on a column packed with silica-gel 60N spherical neutral size 63-210 μm. Optical rotations were measured on a JASCO P-2200. ^{1}H NMR (300 MHz), ^{19}F NMR (282 MHz) and ^{13}C NMR (75.5 MHz) spectra for solution in $CDCl_3$ were recorded on a Varian Gemini-300 and Bruker Avance 500. Chemical shifts (δ) are expressed in ppm downfield from internal TMS, $CHCl_3$ or C_6F_6. Infrared spectra were recorded on a JASCO FT/IR-4600 spectrometer with ZnSe ATR unit. HRMS were recorded on a Waters SYNAPT G2 (ESI). HPLC analyses were performed on a JASCO PU-2080 Plus using 4.6 x 250 mm DAICEL CHIRALPAK IA-3®, IC®, ID, IE-3® column.

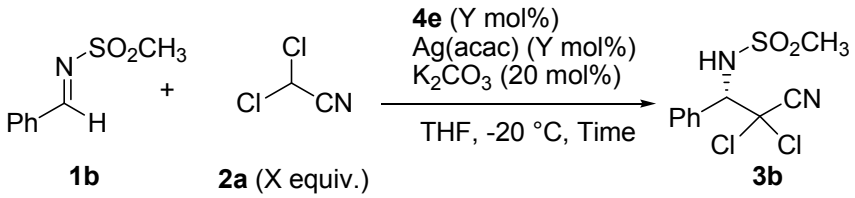
Table S1. Reaction condition



Entry	Additive	Temp. (°C)	Time (h)	Yield (%)	Ee (%)
1	-	r.t.	21	16	53
2	K_2CO_3 (20 mol%)	r.t.	21	99	53
3	K_2CO_3 (20 mol%)	0	20	99	59



Entry	Additive	Temp. (°C)	Time (h)	Yield (%)	Ee (%)
1	K_2CO_3 (20 mol%)	-20	24	99	91
2	K_2CO_3 (20 mol%)	-40	24	75	92
3	K_2CO_3 (20 mol%)	-60	144	30	94
4	Cs_2CO_3 (20 mol%)	-60	144	55	84
5	HFIP (100 mol%)	-20	12	56	91



Entry	X (equiv.)	Y (mol%)	Time (h)	Yield (%)	Ee (%)
1	1.5	5	24	99	91
2	1.5	2	96	59	91
3	3.0	2	24	96	91
4	3.0	1	72	trace	-

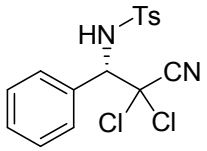
Synthesis of palladium-pincer complex with phebim:

Catalysts **4a-e** were synthesized by using previous our method.[1]

General procedure for the reaction of dichloroacetonitrile with *N*-sulfonylimines catalyzed by chiral phebim-Pd(II) complexes:

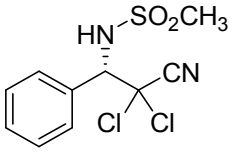
2a (8 μL, 0.0996 mmol), *N*-sulfonylimine **1b** (12.2 mg, 0.0664 mmol), and K_2CO_3 (1.8 mg, 0.0133 mmol) were added to the mixture of Ag(acac) (0.7 mg, 3.32 μmol), **4e** (3.2 mg, 3.32 μmol) in THF (0.5 mL) at −20 ºC. After disappearance of *N*-sulfonylimine **1a** monitored by TLC, it was passed through celite with THF. Filtration and removal of solvent under reduced pressure gave a residue, which was purified by column chromatography (Benzene/CH_3CN=95/5) giving **3a** (20.7 mg, 99%) as a white solid.

(3*S*)-2,2-Dichloro-3-phenyl-3-(toluenesulfonyl)aminopropionitrile (3a)



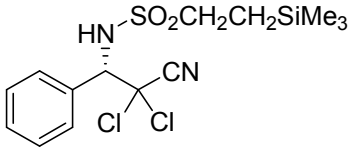
$[\alpha]_D^{25}$ +12.3 (*c* 0.24, $CHCl_3$, 47% ee); mp = 207.9-208.3 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 3H), 5.06 (d, *J* = 10.5 Hz, 1H), 6.17-5.96 (m, 1H), 7.09 (d, *J* = 7.2 Hz, 2H), 7.29-7.23 (m, 5H), 7.56 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.6, 67.6, 71.6, 114.2, 127.2, 128.7, 128.8. 129.6, 130.0, 132.2, 136.5, 144.2; IR (ATR) 3250, 3010, 2949, 2249, 1512, 1444, 1329, 1166, 923, 758, 703 cm^{-1}; HRMS (ESI, positive) m/z calcd for $C_{16}H_{14}Cl_2N_2NaO_2S$ [M+Na^+]: 391.0050, found 391.0049; HPLC (DAICEL CHIRALPAK IC®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 225 nm) tR = 12.0 min (minor), 13.7 min (major).

(3*S*)-2,2-Dichloro-3-phenyl-3-(methanesulfonyl)aminopropionitrile (3b)



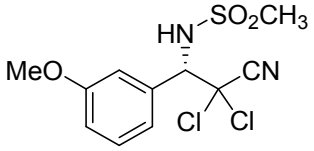
$[\alpha]_D^{25}$ +44.5 (*c* 0.24, $CHCl_3$, 91% ee); mp = 123.2-123.8 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.88 (s, 3H), 5.23 (d, *J* = 9.9 Hz 1H), 6.14-6.11 (m, 1H), 7.53-7.42 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 42.6, 67.4, 71.7, 114.3, 128.8, 129.2, 130.6, 132.7; IR (ATR) 3243, 2924, 2853, 2249, 1584, 1457, 1440, 1325, 1165, 980, 757, 734 cm^{-1}; HRMS (ESI, positive) m/z calcd for $C_{10}H_{10}Cl_2N_2NaO_2S$ [M+Na^+]: 314.9737, found 314.9736; HPLC (DAICEL CHIRALPAK IC®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 225 nm) tR = 11.9 min (major), 13.3 min (minor).

(3*S*)-2,2-Dichloro-3-phenyl-3-{2-(trimethylsilyl)ethanesulfonyl}aminopropionitrile (3d)



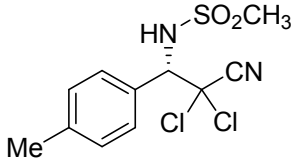
$[\alpha]_D^{25}$ +29.2 (*c* 0.547, $CHCl_3$, 90% ee); mp = 95.2-95.8 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.02 (s, 9H), 1.04-0.90 (m, 2H), 3.09-2.90 (m, 2H), 5.33 (d, *J* = 10.0 Hz, 1H), 6.24 (d, *J* = 10.0 Hz, 1H), 7.70-7.61 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ −2.1, 10.4, 50.9, 67.4, 71.9, 114.4, 128.9, 129.0, 129.2, 130.5, 133.2; IR (ATR) 3262, 2956, 2923, 2307, 1460, 1316, 1253, 1149, 840, 795, 751 cm^{-1}; HRMS (ESI, positive) m/z calcd for $C_{14}H_{20}Cl_2N_2NaO_2SSi$ [M+Na$^+$]: 401.0290, found 401.0272; HPLC (DAICEL CHIRALPAK IC®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 225 nm) tR = 9.0 min (major), 10.6 min (minor).

(3*S*)-2,2-Dichloro-3-(3-methoxyphenyl)-3-(methanesulfonyl)aminopropionitrile (**3e**)



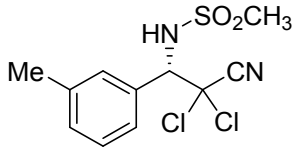
$[\alpha]_D^{25}$ +50.1 (*c* 0.437, $CHCl_3$, 90% ee); mp = 138.7-139.5 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.89 (s, 3H), 3.83 (s, 3H), 5.18 (d, *J* = 10.2 Hz, 1H), 6.13 (d, *J* = 10.2 Hz, 1H), 7.09-6.98 (m, 3H), 7.40-7.34 (m, 1H); ^{13}C NMR (75.5MHz, $CDCl_3$) δ 42.6, 55.6, 67.4, 71.6, 114.4, 114.5, 115.9, 120.9, 130.3, 134.2,160.0; IR (ATR) 3244, 2946, 2929, 2310, 1494, 1328, 1159, 982, 777, 701 cm^{-1}; HRMS (ESI, positive) m/z calcd for $C_{11}H_{12}Cl_2N_2NaO_3S$ [M+Na$^+$]: 344.9843, found 344.9836; HPLC (DAICEL CHIRALPAK IC®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 225 nm) tR = 10.6 min (major), 12.8 min (minor).

(3*S*)-2,2-Dichloro-3-(4-methylphenyl)-3-(methanesulfonyl)aminopropionitrile (3f)



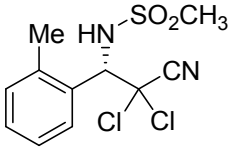
$[\alpha]_D^{25}$ +44.1 (*c* 0.503, $CHCl_3$, 83% ee); mp = 144.7-145.5 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.86 (s, 3H), 5.18 (d, *J* = 9.9 Hz, 1H), 6.06 (d, *J* = 9.9 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.4, 42.6, 67.2, 71.8, 114.4, 128.7, 129.7, 129.9, 140.8; IR (ATR) 3266, 2957, 2926, 2248, 1489, 1455, 1327, 973, 768, 721 cm^{-1}; HRMS (ESI, positive) m/z calcd for $C_{11}H_{12}Cl_2N_2O_2SNa$ [M+Na$^+$]: 328.9894, found 328.9901; HPLC (DAICEL CHIRALPAK IC®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 225 nm) tR = 14.4 min (major), 17.8 min (minor).

(3*S*)-2,2-Dichloro-3-(3-methylphenyl)-3-(methanesulfonyl)aminopropionitrile (3g)



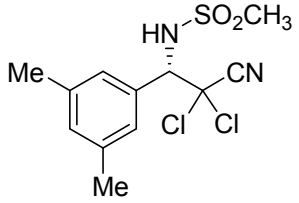
$[\alpha]_D^{25}$ +50.7 (*c* 0.50, $CHCl_3$, 93% ee); mp = 98.0-98.8 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.88 (s, 3H), 5.18 (d, *J* = 9.9 Hz, 1H), 5.17 (d, *J* = 9.9 Hz, 1H), 6.03 (d, *J* = 9.9 Hz, 1H), 7.36-7.26 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.6, 42.6, 67.4, 71.7, 114.4, 125.7, 129.1, 129.5, 131.3, 132.7, 139.2; HRMS (ESI, positive) m/z calcd for $C_{11}H_{12}Cl_2N_2NaO_2S$ [M+Na^+]: 328.9894, found 328.9901; HPLC (DAICEL CHIRALPAK IC®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 225 nm) tR = 12.7 min (major), 15.7 min (minor).

(3*S*)-2,2-Dichloro-3-(2-methylphenyl)-3-(methanesulfonyl)aminopropionitrile (3h)



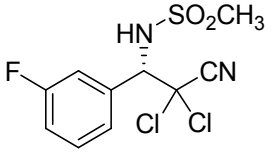
$[\alpha]_D^{25}$ +66.7 (*c* 0.467, $CHCl_3$, 87% ee); mp = 140.7-141.5 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.54 (s, 3H), 2.87 (s, 3H), 5.60 (d, *J* = 9.9 Hz, 1H), 5.84 (br, 1H), 7.37-7.26 (m, 3H), 7.55 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 20.3, 42.7, 62.6, 72.7, 114.4, 126.3, 127.2, 130.3, 131.6, 132.5, 137.7; IR (ATR) 3260, 2970, 2925, 2250, 1492, 1435, 1336, 957, 750, 725 cm^{-1}; HRMS (ESI, positive) m/z calcd for $C_{11}H_{12}Cl_2N_2NaO_2S$ [M+Na^+]: 328.9894, found 328.9899; HPLC (DAICEL CHIRALPAK IE-3®, Hexane:*i*PrOH = 90:10, 1.0 mL/min, 225 nm) tR = 11.9 min (major), 14.2 min (minor).

(3*S*)-2,2-Dichloro-3-(3,5-dimethylphenyl)-3-(methanesulfonyl)aminopropionitrile (3i)



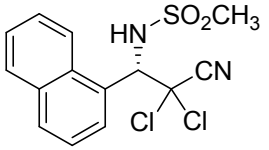
$[\alpha]_D^{25}$ +37.6 (*c* 0.23, $CHCl_3$, 94% ee); mp = 153.2-154.0 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 6H), 2.90 (s, 3H) , 5.12 (d, *J* = 9.9 Hz, 1H) , 5.86 (d, *J* = 9.9 Hz, 2H) , 7.08 (s, 2H), 7.36 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.5, 42.6, 50.3, 67.5, 71.8, 114.4, 126.4, 128.5, 132.2, 132.8, 139.0; IR (ATR) 3255, 2954, 2925, 2250, 1497, 1489, 1333, 979, 770, 710 cm^{-1}; HRMS (ESI, positive) m/z calcd for $C_{12}H_{14}Cl_2N_2NaO_2S$ [M+Na^+]: 343.0051, found 343.0051; HPLC (DAICEL CHIRALPAK IC®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 225 nm) tR = 10.6 min (major), 14.4 min (minor).

(3*S*)-2,2-Dichloro-3-(3-fluoromophenyl)-3-(methanesulfonyl)aminopropionitrile (3j)



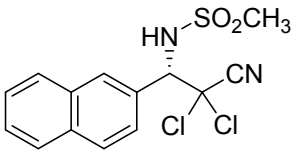
$[\alpha]_D^{25}$ +37.2 (*c* 0.343, $CHCl_3$, 80% ee); mp = 119.2-119.8 ºC; ^1H NMR (300 MHz, $CDCl_3$) δ 2.96 (s, 3H), 5.24 (d, *J* = 10.5 Hz, 1H), 6.15 (d, *J* = 10.5 Hz, 1H), 7.32-7.15 (m, 3H), 7.48-7.41 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −113.4; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 42.7, 66.8 (d, $J_{C\text{-}F}$ = 1.7 Hz), 71.3, 114.2, 116.0 (d, $J_{C\text{-}F}$ = 23.3 Hz), 117.7 (d, $J_{C\text{-}F}$ = 21.0 Hz), 128.6 (d, $J_{C\text{-}F}$ = 3.3 Hz), 130.9 (d, $J_{C\text{-}F}$ = 8.3 Hz), 163.8 (d, $J_{C\text{-}F}$ = 251.7 Hz); IR (ATR) 3245, 2955, 2925, 2250, 1490, 1454, 1340, 1153, 970, 767, 743 cm^{-1}; HRMS (ESI, positive) m/z calcd for $C_{10}H_9Cl_2FN_2NaO_2S$ [M+Na^+]: 332.9643, found 332.9649; HPLC (DAICEL CHIRALPAK IC®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 225 nm) tR = 7.9 min (major), 8.6 min (minor).

(3*S*)-2,2-Dichloro-3-(1-naphthyl)-3-(methanesulfonyl)aminopropionitrile (3k)



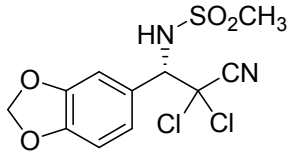
$[\alpha]_D^{25}$+40.4 (*c* 0.453, $CHCl_3$, 93% ee); mp = 163.2-163.7 ºC; ^1H NMR (300 MHz, $CDCl_3$) δ 2.80 (s, 3H), 6.12 (d, *J* = 9.6 Hz, 1H), 6.25 (d, *J* = 9.6 Hz, 1H), 7.71-7.65 (m, 2H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.96-7.91 (m, 1H), 8.21 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 42.6, 61.2, 71.9, 114.5, 122.6, 125.2, 125.4, 126.8, 127.9, 129.4, 130.1, 131.3, 131.6, 133.8; IR (ATR) 3253, 2961, 2925, 2253, 1513, 1332, 1160, 974, 775, 738 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{12}Cl_2N_2NaO_2S$ [M+Na^+]: 364.9894, found 364.9894; HPLC (DAICEL CHIRALPAK IC®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 225 nm) tR = 15.2 min (major), 17.4 min (minor).

(3*S*)-2,2-Dichloro-3-(2-naphthyl)-3-(methanesulfonyl)aminopropionitrile (3l)



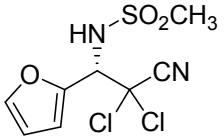
$[\alpha]_D^{25}$ +45.0 (*c* 0.387, $CHCl_3$, 85% ee); ^1H NMR (300 MHz, $CDCl_3$) δ 2.89 (s, 3H), 5.42-5.39 (m, 1H), 6.28 (d, *J* = 9.9 Hz, 1H), 7.60-7.53 (m, 3H), 7.93-7.85 (m, 3H), 7.99 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 42.7, 67.6, 71.8, 114.4, 124.9, 127.3, 127.8, 127.9, 128.6, 129.3, 129.4, 130.0, 132.8, 134.0; IR (ATR) 3267, 3025, 2931, 2248, 1510, 1436, 1325, 1156, 975, 809, 747 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{12}Cl_2N_2NaO_2S$ [M+Na^+]: 364.9894, found 364.9895; HPLC (DAICEL CHIRALPAK IC®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 225 nm) tR = 15.5 min (major), 21.3 min (minor).

(3*S*)-2,2-Dichloro-3-(3,4-methylenedioxyphenyl]-3-(methanesulfonyl)aminopropionitrile (3m)



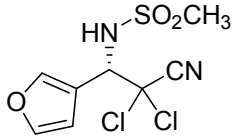
$[\alpha]_D^{25}$ +40.8 (*c* 0.583, $CHCl_3$, 94% ee); mp = 138.1-138.9 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.92 (s, 3H), 5.13 (d, *J* = 9.9 Hz, 1H), 6.09-5.93 (m, 3H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.98-6.96 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 42.6, 67.2, 71.8, 102.0, 108.5, 108.7, 114.4, 123.4, 126.3, 148.4, 149.4; IR (ATR) 3230, 2960, 2924, 2250, 1492, 1326, 1159, 932, 768, 730 cm^{-1}; HRMS (ESI, positive) m/z calcd for $C_{11}H_{10}Cl_2N_2NaO_4S$ [M+Na$^+$]: 358.9636, found 358.9637; HPLC (DAICEL CHIRALPAK IC®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 225 nm) tR = 14.0 min (major), 17.9 min (minor).

(3*S*)-2,2-Dichloro-3-(2-furyl)-3-(methanesulfonyl)aminopropionitrile (3n)



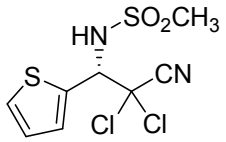
$[\alpha]_D^{25}$ +37.2 (*c* 0.353, $CHCl_3$, 80% ee); mp = 110.4-111.1 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.01 (s, 3H), 5.35 (d, *J* = 9.9 Hz, 1H), 5.72 (d, *J* = 9.9 Hz, 1H), 6.51-6.43 (m, 1H), 6.70-6.60 (m, 1H), 7.56-7.47 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 42.4, 62.0, 70.5, 111.3, 112.5, 114.1, 144.5, 145.2; IR (ATR) 3255, 2957, 2932, 2215, 1644, 1440, 1323, 1156, 978, 790, 755 cm^{-1}; HRMS (ESI) m/z calcd for $C_8H_8Cl_2N_2NaO_3S$ [M+Na$^+$]: 304.9530, found 304.9530; HPLC (DAICEL CHIRALPAK IC®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 225 nm) tR = 10.9 min (major), 13.5 min (minor).

(3*S*)-2,2-Dichloro-3-(3-furyl)-3-(methanesulfonyl)aminopropionitrile (**3o**)



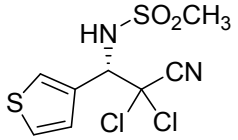
$[\alpha]_D^{25}$ +37.4 (*c* 0.397, $CHCl_3$, 93% ee); mp = 154.1-154.6 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.02 (s, 3H), 5.35 (d, *J* = 10.2 Hz, 1H), 5.73 (d, *J* = 10.2 Hz, 1H), 6.61 (s, 1H), 7.52-7.45 (m, 1H), 7.72-7.64 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 42.8, 60.9, 71.6, 109.1, 114.5, 118.9, 142.6, 144.5; IR (ATR) 3250, 2958, 2930, 2250, 1586, 1323, 1155, 1110, 784, 748, 675 cm^{-1}; HRMS (ESI) m/z calcd for $C_8H_8Cl_2N_2NaO_3S$ [M+Na$^+$]: 304.9530, found 304.9530; HPLC (DAICEL CHIRALPAK IC®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 225 nm) tR = 10.3 min (major), 11.5 min (minor).

(3*S*)-2,2-Dichloro-3-(2-thienyl)-3-(methanesulfonyl)aminopropionitrile (3p)



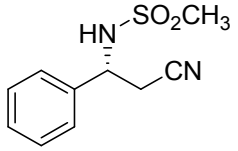
$[\alpha]_D^{25}$ +48.3 (*c* 0.367, $CHCl_3$, 93% ee); mp = 152.2-152.8 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.95 (s, 3H), 5.53-5.56 (br, 2H), 7.08-7.11 (m, 1H), 7.34-7.35 (m, 1H), 7.45-7.47 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 42.6, 63.8, 71.6, 114.3, 127.5, 128.3, 130.1, 134.8; IR (ATR) 3255, 2943, 2928, 2248, 1578, 1448, 1325, 976, 773, 720 cm^{-1}; HRMS (ESI) m/z calcd for $C_8H_8Cl_2N_2NaO_2S_2$ [M+Na^+]: 320.9302, found 320.9313; HPLC (DAICEL CHIRALPAK IC®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 225 nm) tR = 12.4 min (major), 13.5 min (minor).

(3*S*)-2,2-Dichloro-3-(3-thienyl)-3-(methanesulfonyl)aminopropionitrile (3q)



$[\alpha]_D^{25}$ +52.0 (*c* 0.44, $CHCl_3$, 93% ee); mp = 154.4-155.4 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.92 (s, 3H), 5.38-5.33 (m, 1H), 6.08 (br, 1H), 7.28-7.27 (m, 1H), 7.45-7.42 (m, 1H), 7.58-7.57 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 42.5, 63.6, 71.5, 114.4, 126.6, 127.0, 127.6, 133.4; IR (ATR) 3253, 2936, 2852, 2338, 1528, 1441, 1324, 977, 773, 670 cm^{-1}; HRMS (ESI) m/z calcd for $C_8H_8Cl_2N_2NaO_2S_2$ [M+Na^+]: 320.9302, found 320.9313; HPLC (DAICEL CHIRALPAK IC®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 225 nm) tR = 10.3 min (major), 11.3 min (minor).

(3*R*)-3-Phenyl-3-(methanesulfonyl)aminopropionitrile (5)

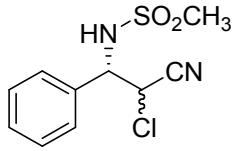


A mixture of **3b** (17.6 mg, 0.06 mmol), $CrCl_2$ (44.2 mg, 0.36 mmol) in THF (0.6 mL) was stirred for 8 h under nitrogen atmosphere. The reaction mixture was diluted with AcOEt and water, aqueous $NaHCO_3$. The mixture was extracted with AcOEt and washed with water, and dried over Na_2SO_4. Filtration and removal of solvent under reduced pressure gives a residue, which was purified by column chromatography (hexane/AcOEt = 70:30) to give compound **5** as a white solid (10 mg, 74%).

$[\alpha]_D^{25}$ +34.8 (*c* 0.257, $CHCl_3$, 89% ee); mp = 88.4-89.0 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.84 (s, 3H), 2.88-2.97 (m, 2H), 4.96-5.06 (td, *J* = 7.2, 6.6 Hz, 1H), 5.38-5.55 (br, 1H), 7.37-7.48 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 26.9, 42.2, 54.3, 116.8, 126.4, 129.5, 129.7, 138.0; IR (ATR) 3276, 2970, 2925, 2252, 1497, 1337, 1142, 980, 760, 703 cm^{-1}; HRMS (ESI, positive) m/z calcd for $C_{10}H_{12}N_2NaO_2S$

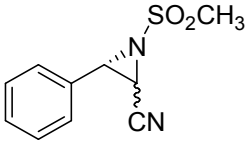
[M+Na$^+$]: 247.0517, found 247.0518; HPLC (DAICEL CHIRALPAK IC®, Hexane:*i*PrOH = 70:30, 1.0 mL/min, 210 nm) tR = 24.4 min (major), 28.4 min (minor).

(2*R*,3*S*)- and (2*S*,3*S*) -2-Chloro-3-phenyl-3-(methanesulfonyl)aminopropionitrile (6)



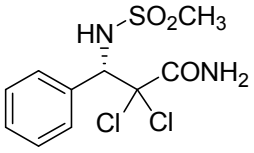
A mixture of **3b** (35.2 mg, 0.12 mmol), $CrCl_2$ (44.2 mg, 0.36 mmol) in THF (1.2 mL) was stirred for 1 h under nitrogen atmosphere. The mixture was diluted with AcOEt and washed with water, and dried over Na_2SO_4. Filtration and removal of solvent under reduced pressure gives a residue, which was purified by column chromatography (hexane/AcOEt = 70:30) to give compound **6** as a white solid (31 mg, 97%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.92 (s, 3H), 4.82-4.89 (m, 1H), 4.96-5.06 (m, 1H), 7.44-7.46 (m, 5H); ^{13}C NMR (75.5MHz, $CDCl_3$) δ 42.3, 42.5, 47.4, 47.5, 60.1, 60.6, 114.8, 115.2, 127.3, 127.5, 129.5, 129.6, 134.3, 134.5; IR (ATR) 3283, 3023, 2963, 2300, 1457, 1320, 1162, 907, 774, 702 cm^{-1}; HRMS (ESI) m/z calcd for $C_{10}H_{11}ClN_2NaO_2S$ [M+Na$^+$]: 281.0128, found 281.0127; HPLC (DAICEL CHIRALPAK IC® and IE-3®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 225 nm) tR = 33.6 min (major enantiomer for major-diastereomer), 40.5 min (minor enantiomer for minor-diastereomer), 42.6 min (major enantiomer for minor-diastereomer), 46.8 min (minor enantiomer for major-diastereomer).

(2*R*,3*S*)- and (2*S*,3*S*)-1-(Methanesulfonyl)-3-phenylaziridine-2-carbonitrile (7)



A mixture of **6** (29.8 mg, 0.115 mmol), K_2CO_3 (31.8, 0.23 mmol) in acetone (1.8 mL) was stirred at r.t. for 15 h under nitrogen atmosphere. Removal of solvent under reduced pressure gives a residue, which was purified by column chromatography (hexane/AcOEt = 75:25) to give compound **7** as a colorless oil (25.6 mg, 91%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 3.19 (d, *J* = 3.9 Hz, 1H, minor-isomer), 3.24 (s, 3H), 3.63 (d, *J* = 6.9 Hz, 1H, major-isomer), 4.08 (d, *J* = 6.9 Hz, 1H, major-isomer), 4.26 (d, *J* = 3.9 Hz, 1H, minor-isomer), 7.31-7.44 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 31.0, 31.8, 40.3, 41.2, 44.2, 46.5, 113.2, 113.5, 126.6, 127.4, 129.1, 129.3, 129.7, 130.0, 131.4; IR (ATR) 3029, 2935, 2250, 1606, 1498, 1326, 1153, 794, 716, 697 cm^{-1}; HRMS (ESI, positive) m/z calcd for $C_{10}H_{10}N_2NaO_2S$ [M+Na$^+$]: 245.0361, found 245.0366; HPLC (DAICEL CHIRALPAK ID®, Hexane:*i*PrOH = 80:20, 1.0 mL/min, 225 nm) tR = 11.7 min (major enantiomer for major-diastereomer), 13.8 min (minor enantiomer for major-diastereomer), 11.8 min (major enantiomer for minor-diastereomer), 22.7 min (minor enantiomer for minor-diastereomer).

(3*S*)-2,2-Dichloro-3-phenyl-3-(methanesulfonyl)aminopropanamide (8)



A mixture of **3b** (13.7 mg, 0.0467 mmol), acetaldoxime (8.4 μL, 0.14 mmol), and $InCl_3 \cdot 4H_2O$ (0.7 mg, 0.00234 mmol) in toluene (0.3 mL) was heated to 40 ºC for 18 h under nitrogen atmosphere. Removal of solvent under reduced pressure gives a residue, which was purified by column chromatography (hexane/AcOEt = 40:60) to give compound **8** as a white solid (13.0 mg, 90%).

$[\alpha]_D^{25}$ +47.2 (*c* 0.317, $CHCl_3$, 91% ee); mp = 178.2-179.0 ºC; ^{1}H NMR (300 MHz, CD_3OD) δ 2.67 (s, 3H), 4.87-4.92 (m, 3H), 7.32-7.38 (m, 3H), 7.56-7.58 (m, 2H); ^{13}C NMR (75.5 MHz, CD_3OD) δ 42.0, 66.6, 89.1, 129.2, 130.0, 130.8, 136.8, 169.1; IR (ATR) 3296, 2976, 2930, 2309, 1455, 1309, 1150, 927, 770, 707 cm^{-1}; HRMS (ESI, positive) m/z calcd for $C_{10}H_{12}Cl_2N_2NaO_3S$ [M+Na^+]: 332.9843, found 332.9843; HPLC (DAICEL CHIRALPAK IC®, Hexane:*i*PrOH = 70:30, 1.0 mL/min, 225 nm) tR = 16.7 min (minor), 27.8 min (major).

MO Calculations:

The Cartesian Coordination of **4e**-Pd and **2a** using Gaussian 09 B3LYP/LANL2DZ was shown in Table S2.

Table S2.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	0.036650	-0.553132	-0.034230
2	7	0	0.017983	1.557680	-0.040647
3	8	0	-3.977376	-4.722837	-0.325200
4	7	0	-1.959371	-0.962565	-0.331509
5	7	0	-3.699841	-2.412244	-0.463651
6	6	0	-3.063148	0.971992	-1.582873
7	6	0	0.092984	-5.278904	-0.026990
8	6	0	-2.749546	0.611463	-2.922587
9	6	0	0.058817	-2.502661	-0.027678
10	6	0	-4.444417	-3.596512	-0.606031
11	6	0	-3.128381	-0.057222	-0.454549
12	6	0	-2.298217	-2.245682	-0.309868
13	6	0	-1.168733	-3.200860	-0.162222
14	6	0	-6.646724	-0.142989	0.032266
15	6	0	-5.443601	-0.759933	0.479498
16	6	0	-3.363520	2.329562	-1.272943
17	6	0	-5.267537	-1.024353	1.870213
18	6	0	-7.656167	0.166854	0.966981
19	6	0	-3.332210	3.293504	-2.296841
20	6	0	-6.307031	-0.700489	2.764173
21	6	0	-4.353481	-1.046362	-0.555136
22	6	0	-5.861454	-3.464475	-1.139782
23	6	0	-7.512303	-0.108818	2.338323
24	6	0	-2.727267	1.613363	-3.914996
25	6	0	-3.003625	2.961423	-3.624638
26	6	0	-1.141891	-4.616361	-0.150301
27	8	0	4.150107	-4.618749	0.282590
28	7	0	2.037038	-0.914254	0.277830
29	7	0	3.807898	-2.319822	0.454513
30	6	0	3.041656	1.037176	1.573752

31	6	0	3.284208	2.409035	1.276920
32	6	0	4.579105	-3.486416	0.598317
33	6	0	3.178141	0.020427	0.440435
34	6	0	2.407405	-2.188261	0.267381
35	6	0	1.302829	-3.170733	0.110411
36	6	0	5.393209	-0.887419	-1.837529
37	6	0	5.531314	-0.623139	-0.442511
38	6	0	2.698929	0.656203	2.901122
39	6	0	6.710041	0.018888	0.033451
40	6	0	6.445978	-0.539045	-2.706422
41	6	0	2.587345	1.652946	3.892551
42	6	0	7.734048	0.352706	-0.876776
43	6	0	4.424949	-0.938159	0.566476
44	6	0	5.975510	-3.326864	1.176678
45	6	0	7.627944	0.077480	-2.251633
46	6	0	3.161215	3.367483	2.298748
47	6	0	2.799400	3.015166	3.612449
48	6	0	1.311218	-4.586187	0.097869
49	1	0	0.106348	-6.365452	-0.027797
50	1	0	-3.193647	0.488171	0.488275
51	1	0	-6.167419	-0.910036	3.823400
52	1	0	-4.785308	-0.961769	-1.552522
53	1	0	-2.473097	1.333045	-4.935890
54	1	0	-2.060651	-5.179722	-0.224931
55	1	0	6.335557	-0.749142	-3.768983
56	1	0	2.311110	1.357003	4.903326
57	1	0	2.243580	-5.127052	0.172600
58	1	0	3.255734	0.576278	-0.495127
59	1	0	4.831772	-0.846651	1.573692
60	6	0	0.003661	2.757449	-0.023685
61	6	0	0.132693	4.114465	0.033529
62	1	0	-6.243226	-4.474850	-1.297090
63	1	0	-6.512968	-2.940143	-0.433898
64	1	0	-5.882600	-2.917955	-2.090504
65	1	0	6.633774	-2.775818	0.497889
66	1	0	5.954143	-2.793846	2.135054
67	1	0	6.378730	-4.329354	1.331064
68	1	0	3.315833	4.415652	2.053376

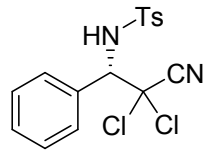
69	1	0	8.630286	0.842276	-0.501293
70	1	0	-3.538162	4.331484	-2.046154
71	1	0	-8.571328	0.637517	0.613647
72	17	0	-0.538591	4.970318	1.531971
73	17	0	-0.094107	5.086484	-1.522447
74	6	0	-6.894673	0.217497	-1.427825
75	1	0	-6.123207	0.886253	-1.828633
76	1	0	-6.931246	-0.669131	-2.076933
77	1	0	-7.856852	0.729475	-1.530753
78	6	0	-4.005355	-1.643084	2.457326
79	1	0	-3.897824	-2.700173	2.184511
80	1	0	-3.092517	-1.129729	2.134302
81	1	0	-4.036214	-1.589562	3.550587
82	6	0	-8.605910	0.234546	3.332595
83	1	0	-8.268385	1.001268	4.043436
84	1	0	-9.499920	0.617965	2.828543
85	1	0	-8.901111	-0.644786	3.920385
86	6	0	-2.401635	-0.808284	-3.350707
87	1	0	-1.427210	-1.116415	-2.952516
88	1	0	-3.136990	-1.551452	-3.017268
89	1	0	-2.349944	-0.871742	-4.443120
90	6	0	-3.697449	2.795418	0.137967
91	1	0	-2.845192	2.663648	0.817220
92	1	0	-3.937359	3.862961	0.136164
93	1	0	-4.557431	2.263326	0.565745
94	6	0	-2.915204	4.034321	-4.692806
95	1	0	-2.035004	4.670037	-4.523679
96	1	0	-2.828549	3.599959	-5.695505
97	1	0	-3.795906	4.689701	-4.680119
98	6	0	2.408020	-0.780611	3.315276
99	1	0	1.458711	-1.132581	2.892800
100	1	0	3.185127	-1.487321	2.997954
101	1	0	2.332566	-0.851311	4.405920
102	6	0	3.650374	2.893467	-0.118717
103	1	0	2.820385	2.741961	-0.820459
104	1	0	3.852510	3.968392	-0.102706
105	1	0	4.539712	2.390747	-0.522129
106	6	0	2.611282	4.080148	4.676024

107	1	0	3.462381	4.773063	4.706671
108	1	0	1.713701	4.677639	4.464495
109	1	0	2.495324	3.639326	5.673012
110	6	0	6.915658	0.381358	1.499564
111	1	0	6.120519	1.032429	1.882822
112	1	0	6.956016	-0.505661	2.147941
113	1	0	7.863735	0.913923	1.626141
114	6	0	4.158403	-1.531051	-2.455207
115	1	0	4.067700	-2.591445	-2.189013
116	1	0	3.227934	-1.038695	-2.150535
117	1	0	4.212586	-1.472182	-3.547293
118	6	0	8.735758	0.448782	-3.219829
119	1	0	8.405808	1.230702	-3.917713
120	1	0	9.619521	0.824782	-2.692583
121	1	0	9.044607	-0.414957	-3.823297

References

1) a) K. Hyodo, S. Nakamura, K. Tsuji, T. Ogawa, Y. Funahashi, N. Shibata, *Adv. Synth. Catal.* **2011**, *353*, 3385–3390; b) K. Hyodo, S. Nakamura, N. Shibata, *Angew. Chem. Int. Ed.* **2012**, *51*, 10337–10341.

^{1}H-NMR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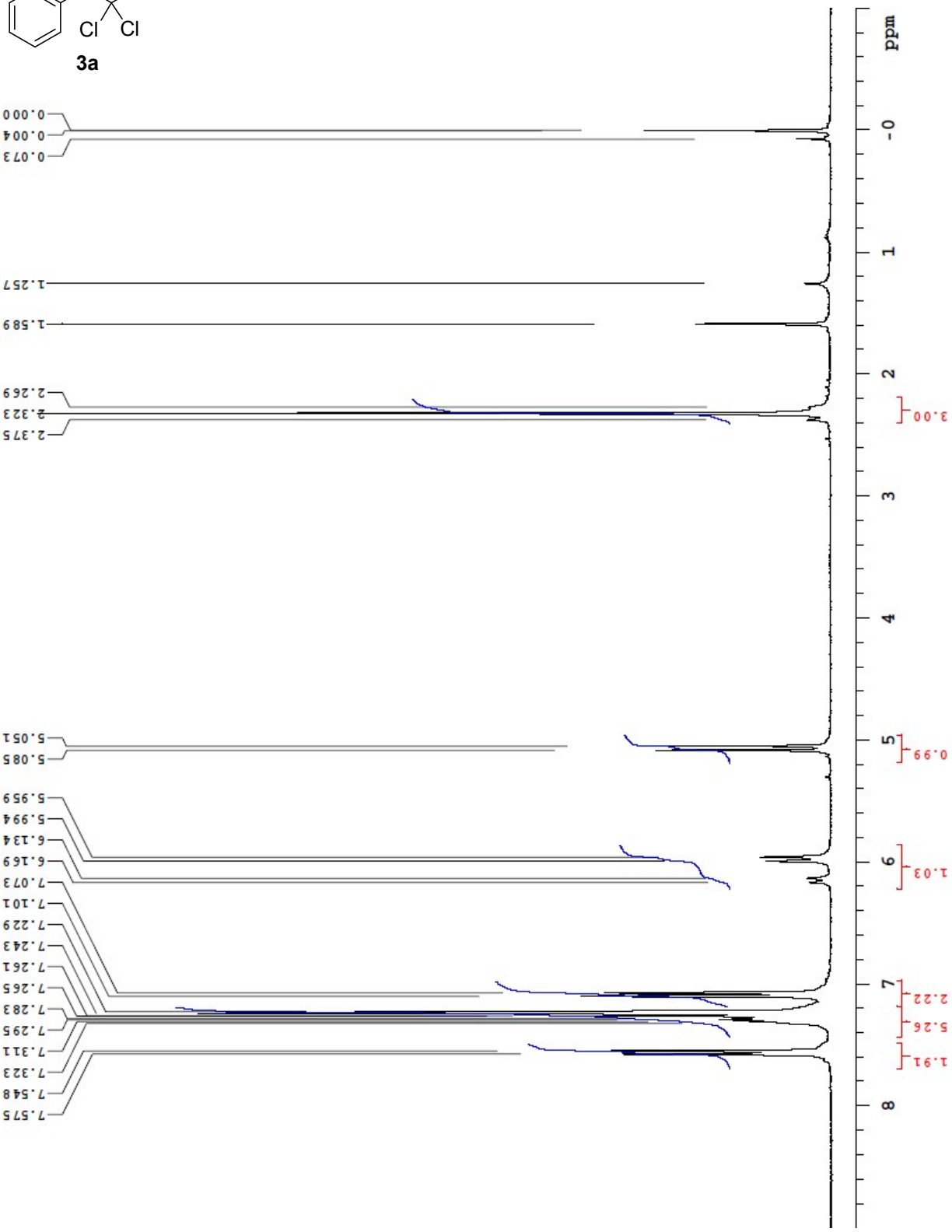
Ts
CN
Cl
Cl

3a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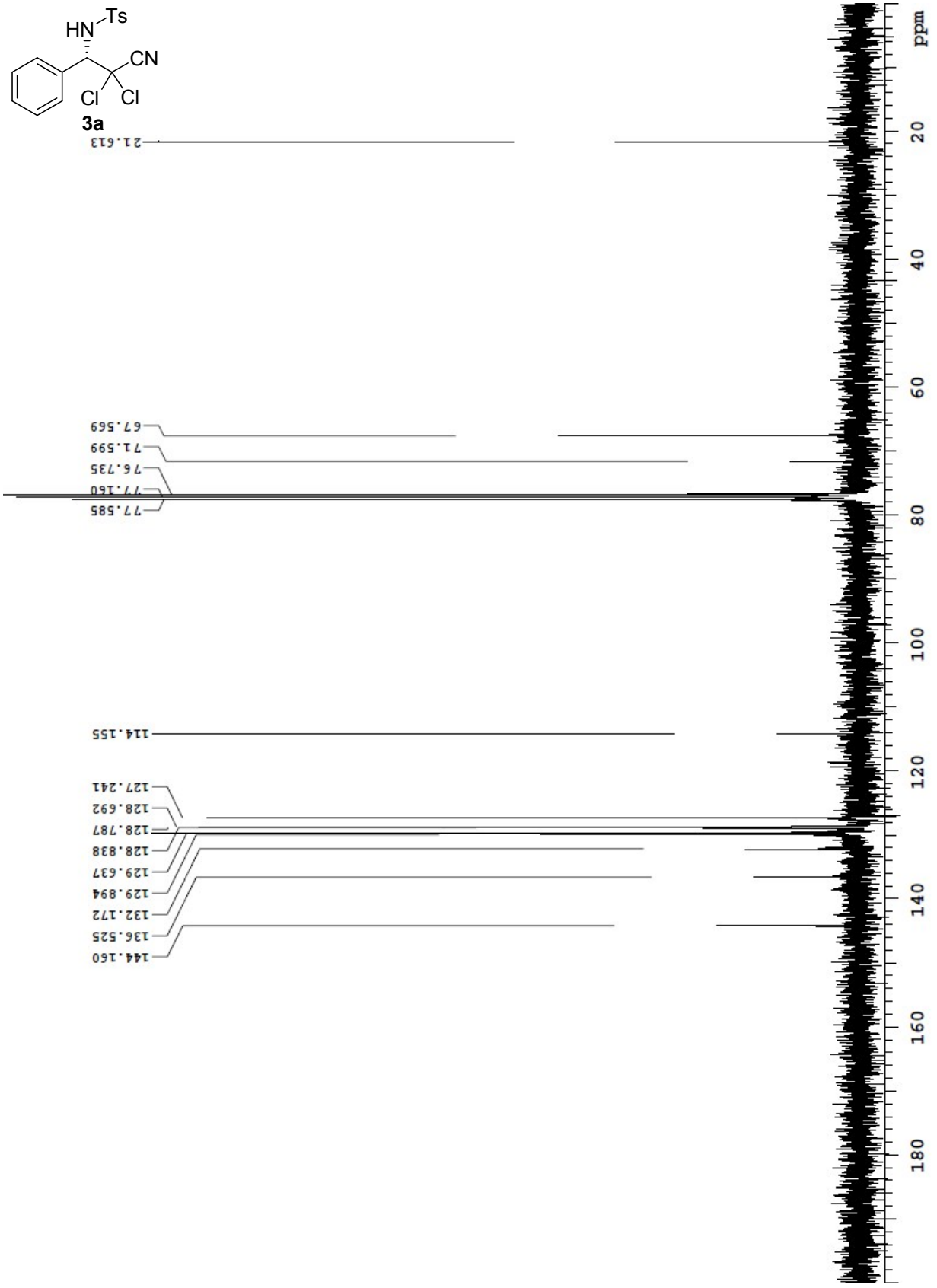
7.265
7.283
7.295
7.311
7.323
7.548
7.575
ppm
3.00
0.99
1.03
2.22
5.26
1.91

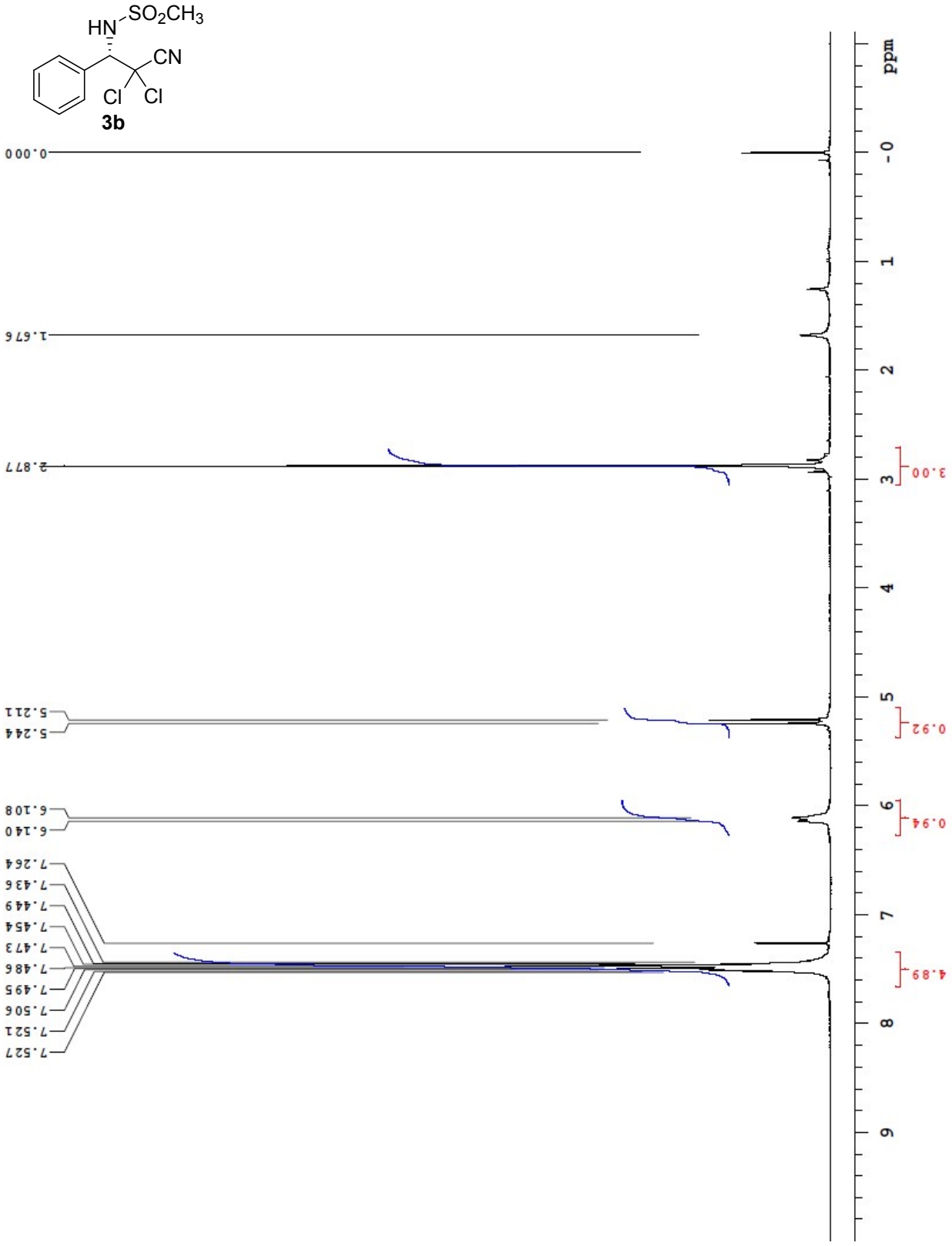
^{13}C-NMR

HN
Ts
CN
Cl
Cl

3a


21.613
67.569
71.599
76.735
77.160
77.585
114.155
127.241
128.692
128.787
128.838
129.637
129.894
132.172
136.525
144.160
ppm
20
40
60
80
100
120
140
160
180

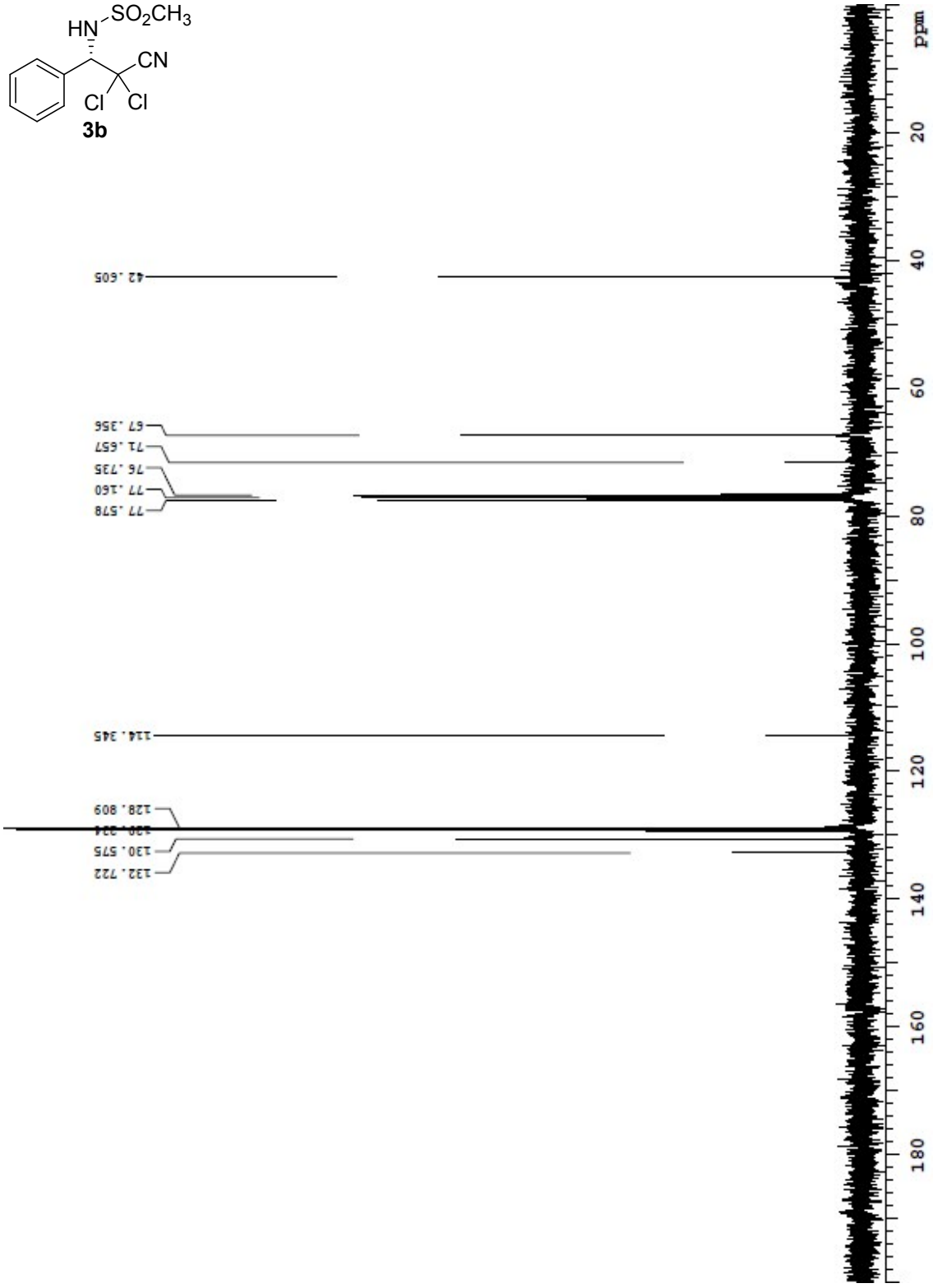
^{1}H-NMR


HN
SO2CH3
CN
Cl
Cl
3b
0.000
1.676
2.877
5.211
5.244
6.108
6.140
7.264
7.436
7.449
7.454
7.473
7.486
7.495
7.506
7.521
7.527
3.00
0.92
0.94
4.89
ppm

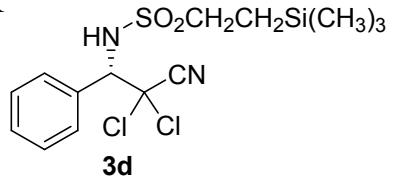
^{13}C-NMR

HN
SO2CH3
CN
Cl
Cl

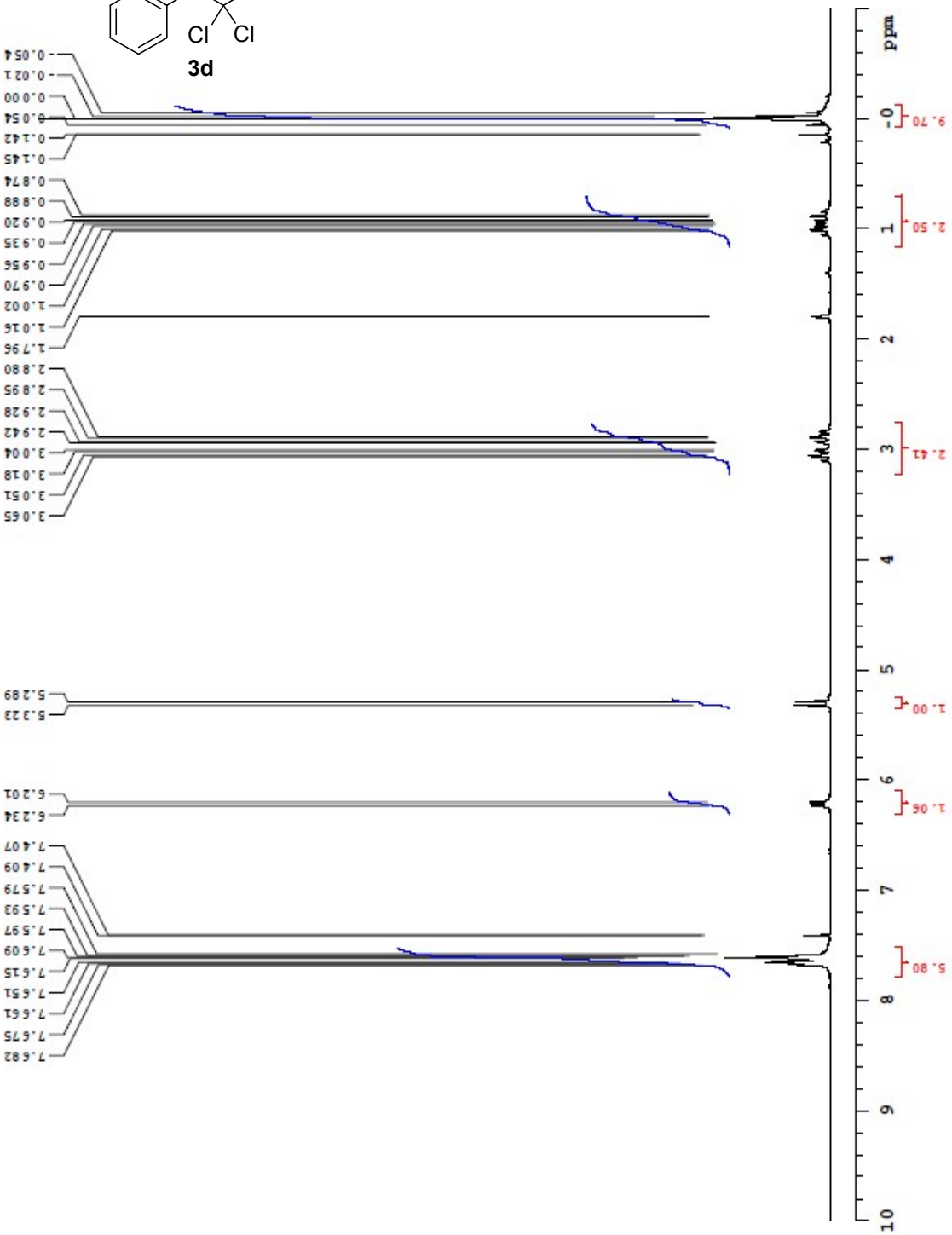
3b


42.605
67.356
71.657
76.735
77.160
77.578
114.345
128.809
130.575
132.722
ppm
20
40
60
80
100
120
140
160
180

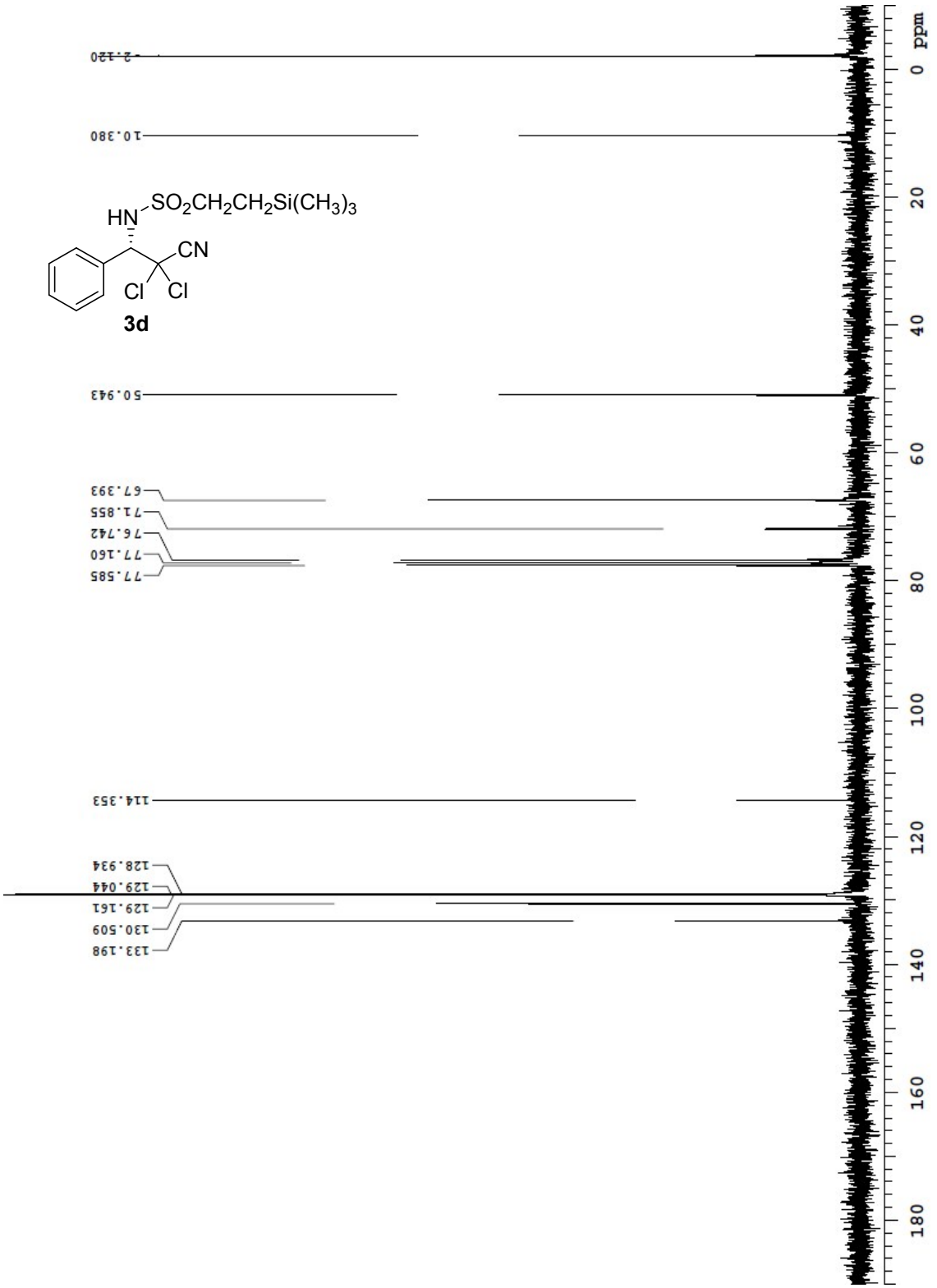
^{1}H-NMR


HN
SO2CH2CH2Si(CH3)3
CN
Cl
Cl

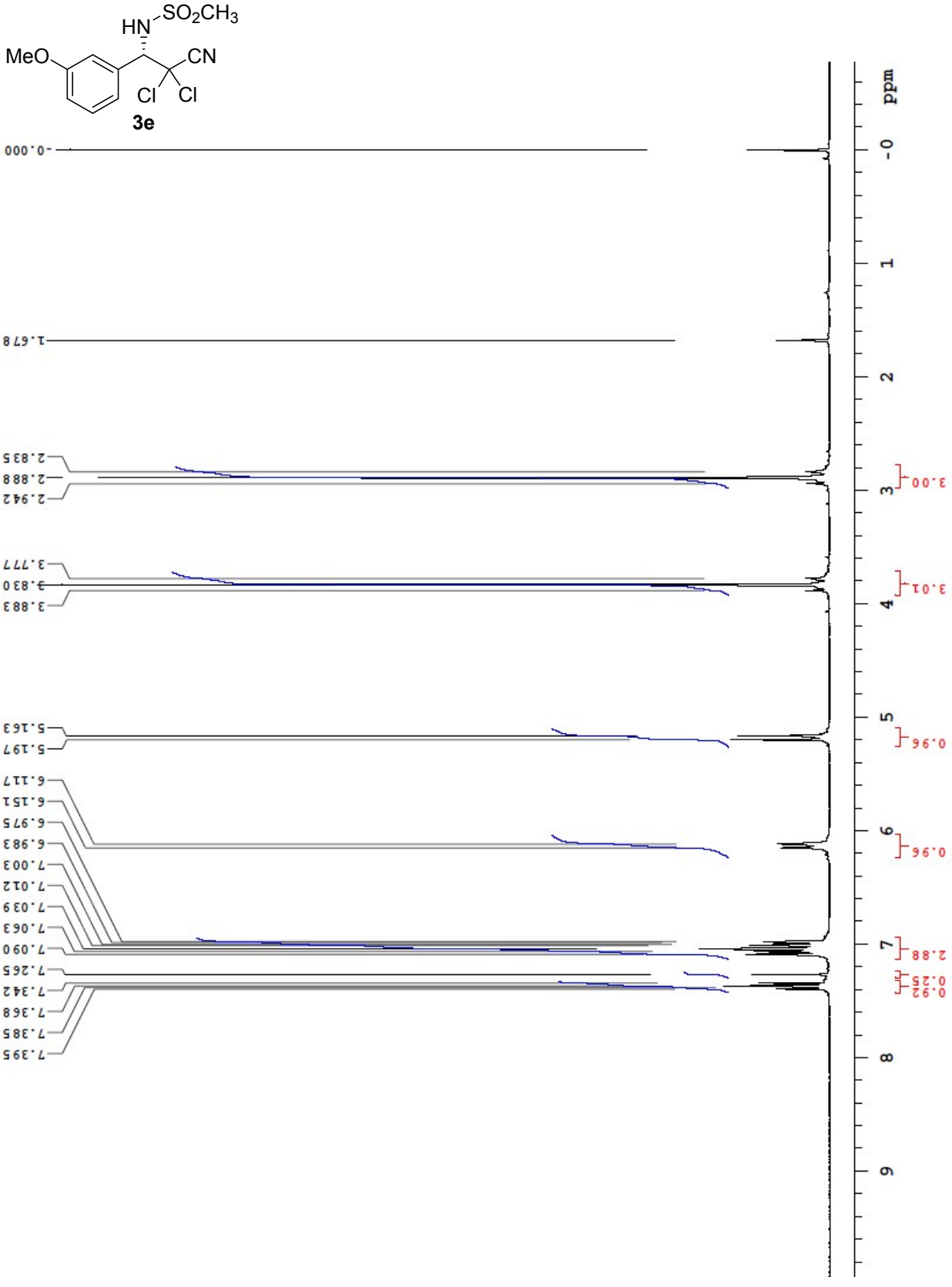
3d


0.054
0.021
0.000
0.054
0.142
0.145
0.874
0.888
0.920
0.935
0.956
0.970
1.002
1.016
1.796
2.880
2.895
2.928
2.942
3.004
3.018
3.051
3.065
5.289
5.323
6.201
6.234
7.407
7.409
7.579
7.593
7.597
7.609
7.615
7.651
7.661
7.675
7.682
ppm
9.70
2.50
2.41
1.00
1.06
5.80

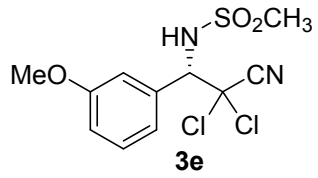
^{13}C-NMR


HN
SO2CH2CH2Si(CH3)3
CN
Cl
Cl
3d
2.120
10.380
50.943
67.393
71.855
76.742
77.160
77.585
114.353
128.934
129.044
129.161
130.509
133.198
0 ppm
20
40
60
80
100
120
140
160
180

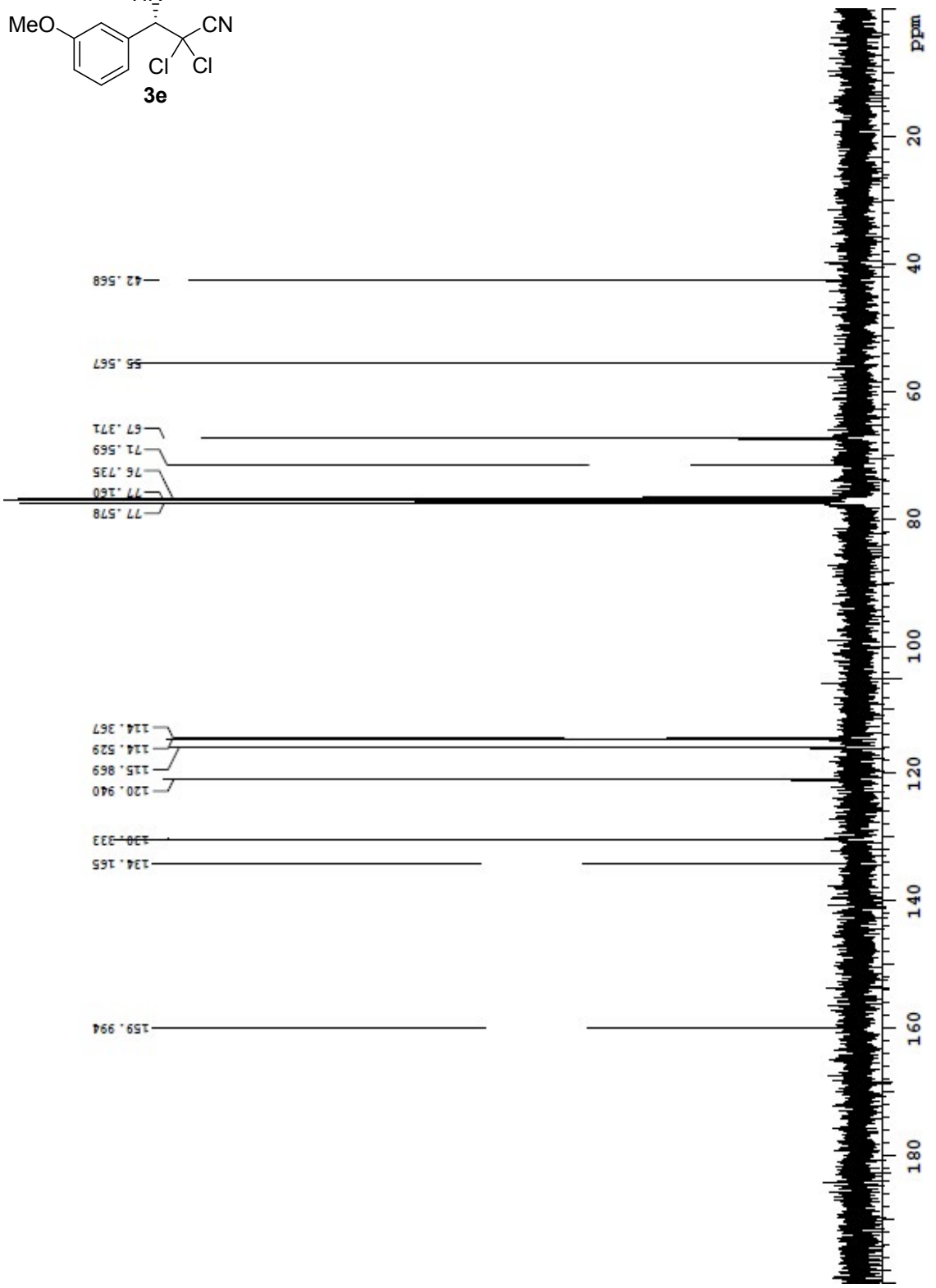
^{1}H-NMR


HN
SO2CH3
MeO
CN
Cl
Cl
3e
ppm
0.000
1.678
2.835
2.888
2.942
3.777
3.830
3.883
5.163
5.197
6.117
6.151
6.975
6.983
7.003
7.012
7.039
7.063
7.090
7.265
7.342
7.368
7.385
7.395
3.00
3.01
0.96
0.96
2.88
0.25
0.92

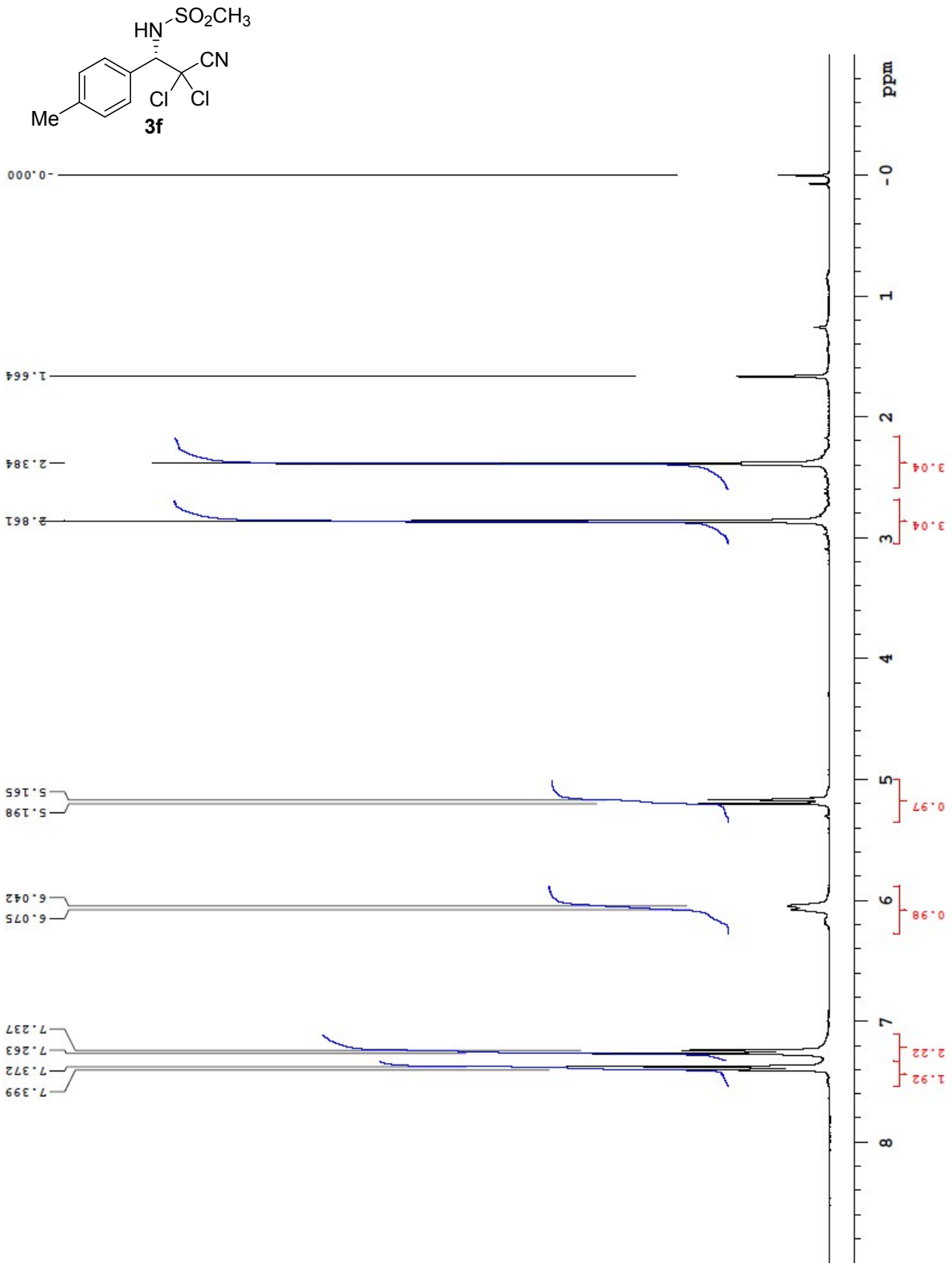
^{13}C-NMR


HN
SO2CH3
MeO
CN
Cl
Cl

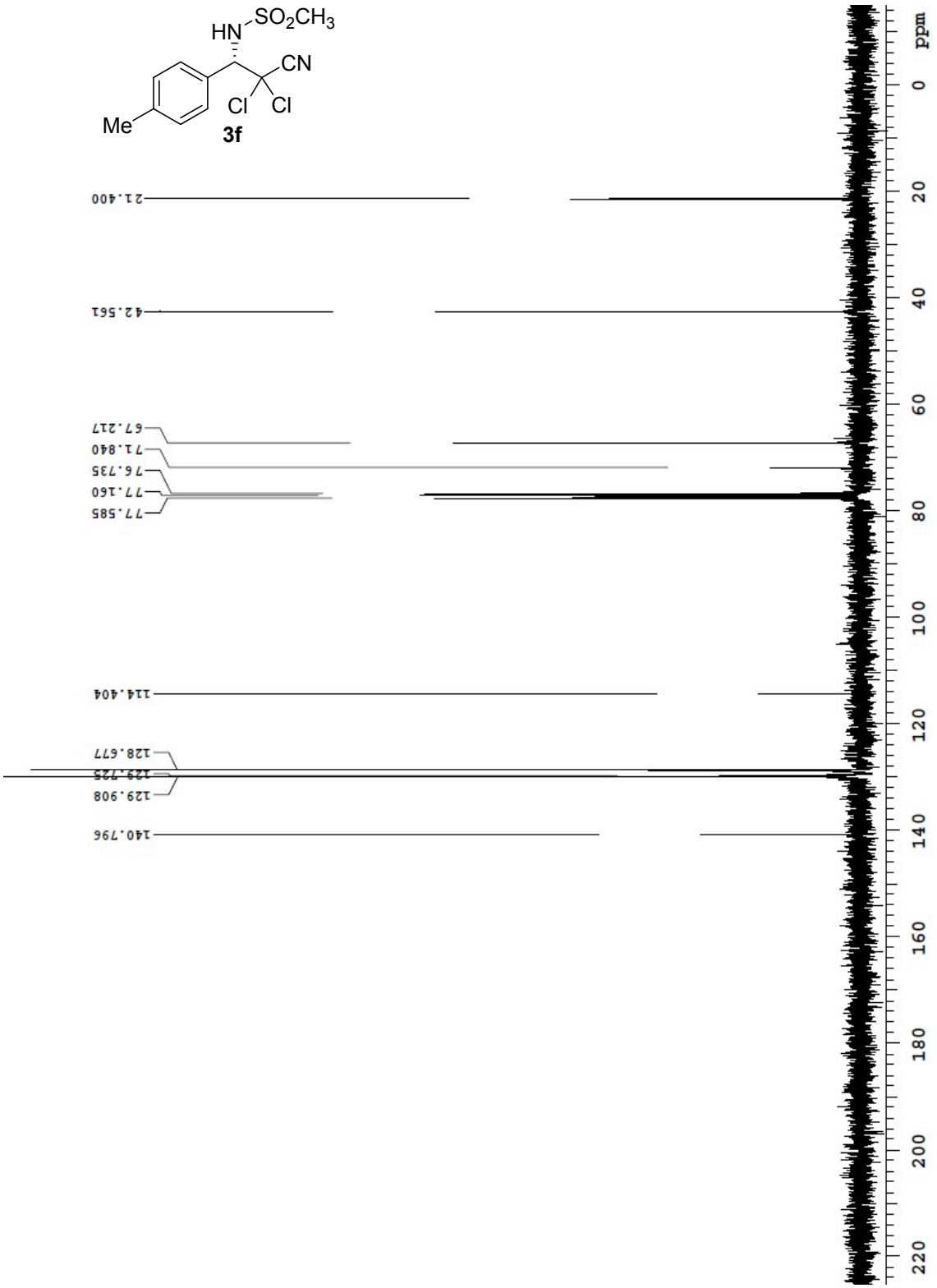
3e


42.568
55.567
67.371
71.569
76.735
77.160
77.578
114.367
114.529
115.869
120.940
130.033
134.165
159.994
ppm
20
40
60
80
100
120
140
160
180

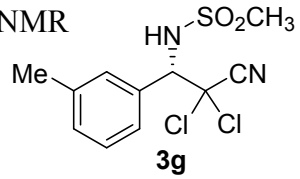
^{1}H-NMR


HN
SO2CH3
CN
Cl
Cl
Me
3f
ppm
0.000
1.664
2.384
2.861
5.165
5.198
6.042
6.075
7.237
7.263
7.372
7.399
3.04
3.04
0.97
0.98
2.22
1.92

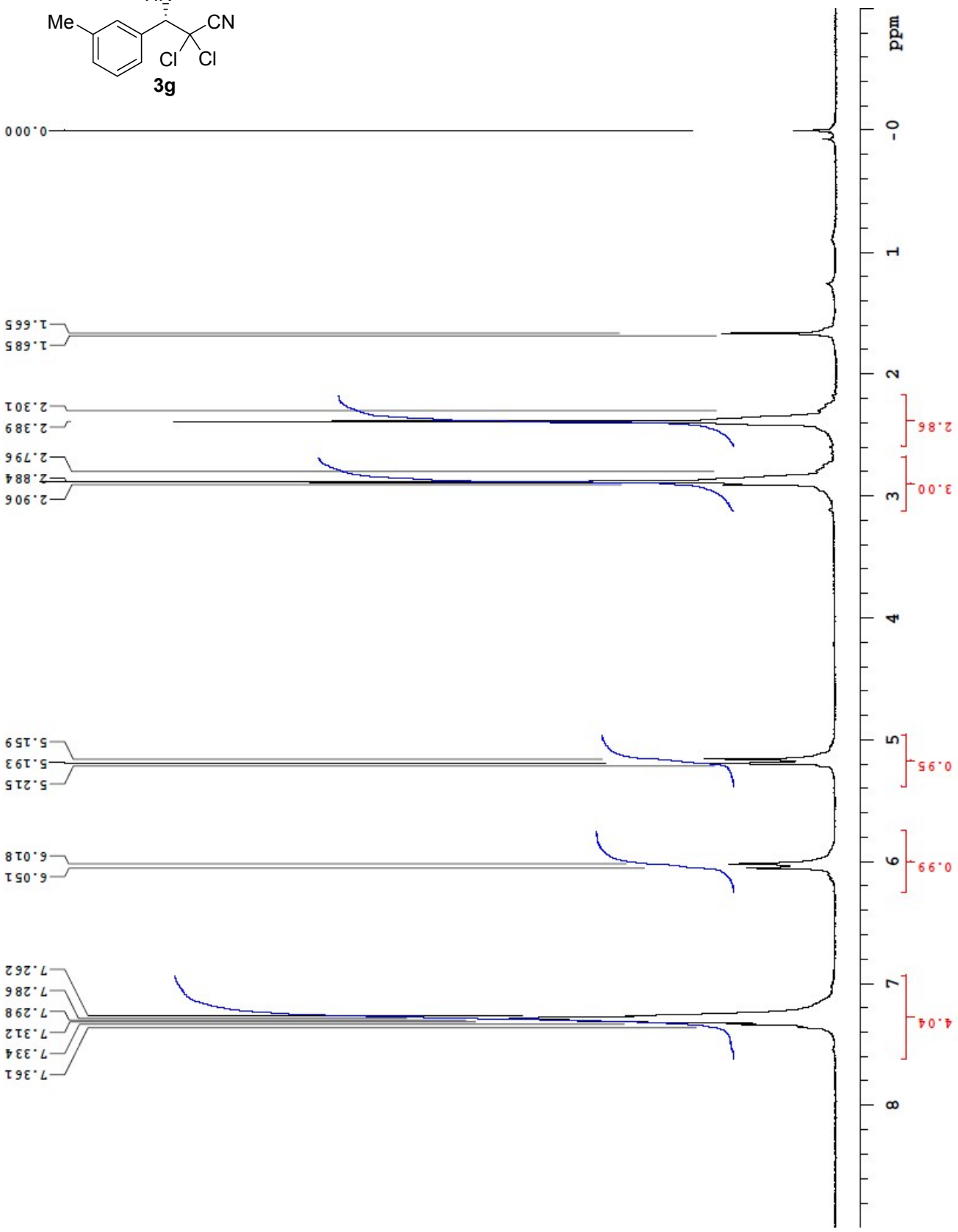
^{13}C-NMR


HN
SO2CH3
CN
Cl
Cl
Me
3f
21.400
42.561
67.217
71.840
76.735
77.160
77.585
114.404
128.677
129.725
129.908
140.796
ppm
0
20
40
60
80
100
120
140
160
180
200
220

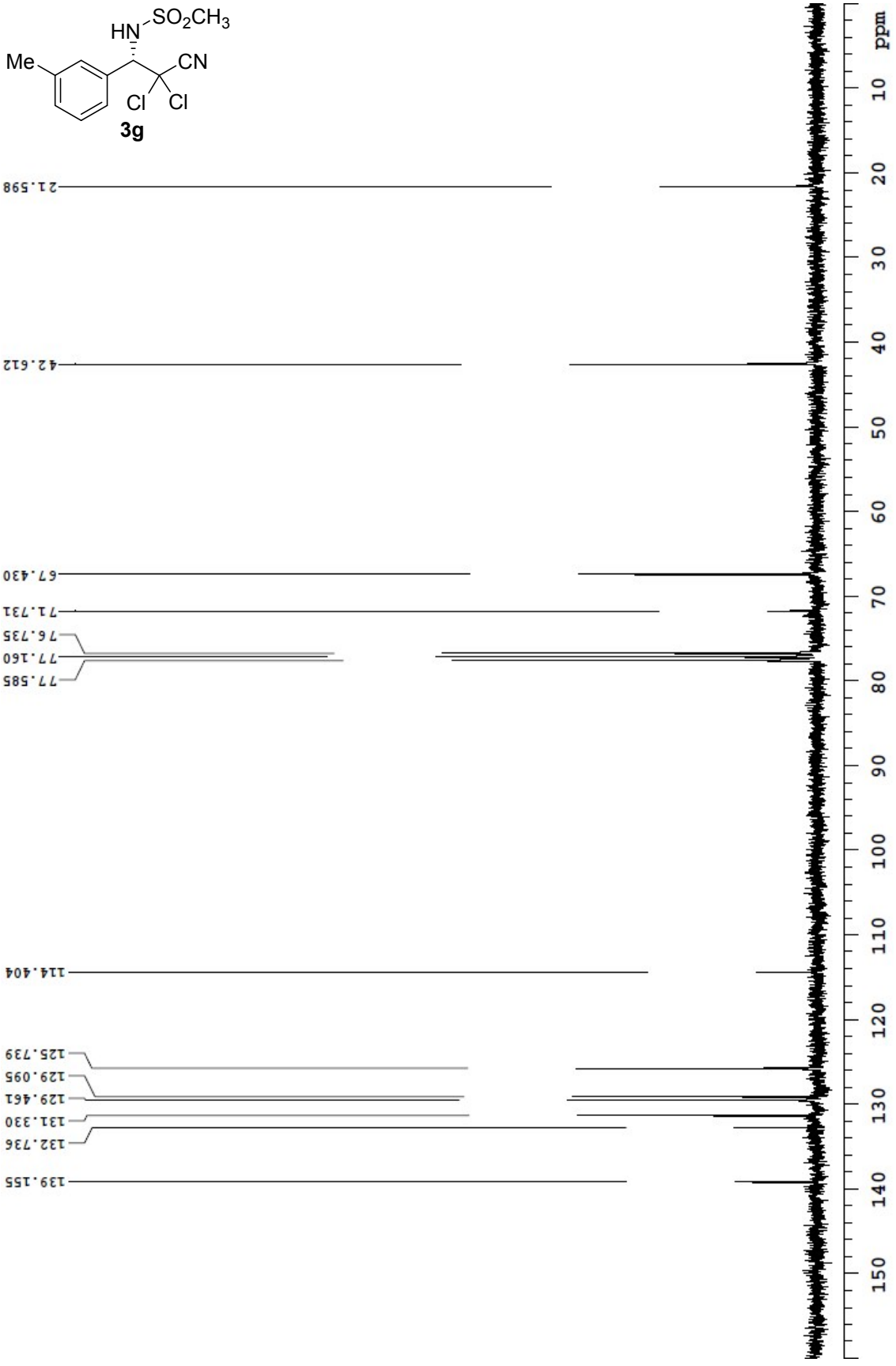
^{1}H-NMR


HN
SO2CH3
Me
CN
Cl
Cl

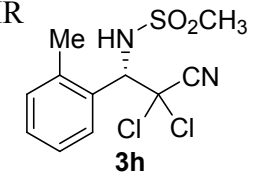
3g


0.000
1.665
1.685
2.301
2.389
2.796
2.884
2.906
5.159
5.193
5.215
6.018
6.051
7.262
7.286
7.298
7.312
7.334
7.361
ppm
2.86
3.00
0.95
0.99
4.04

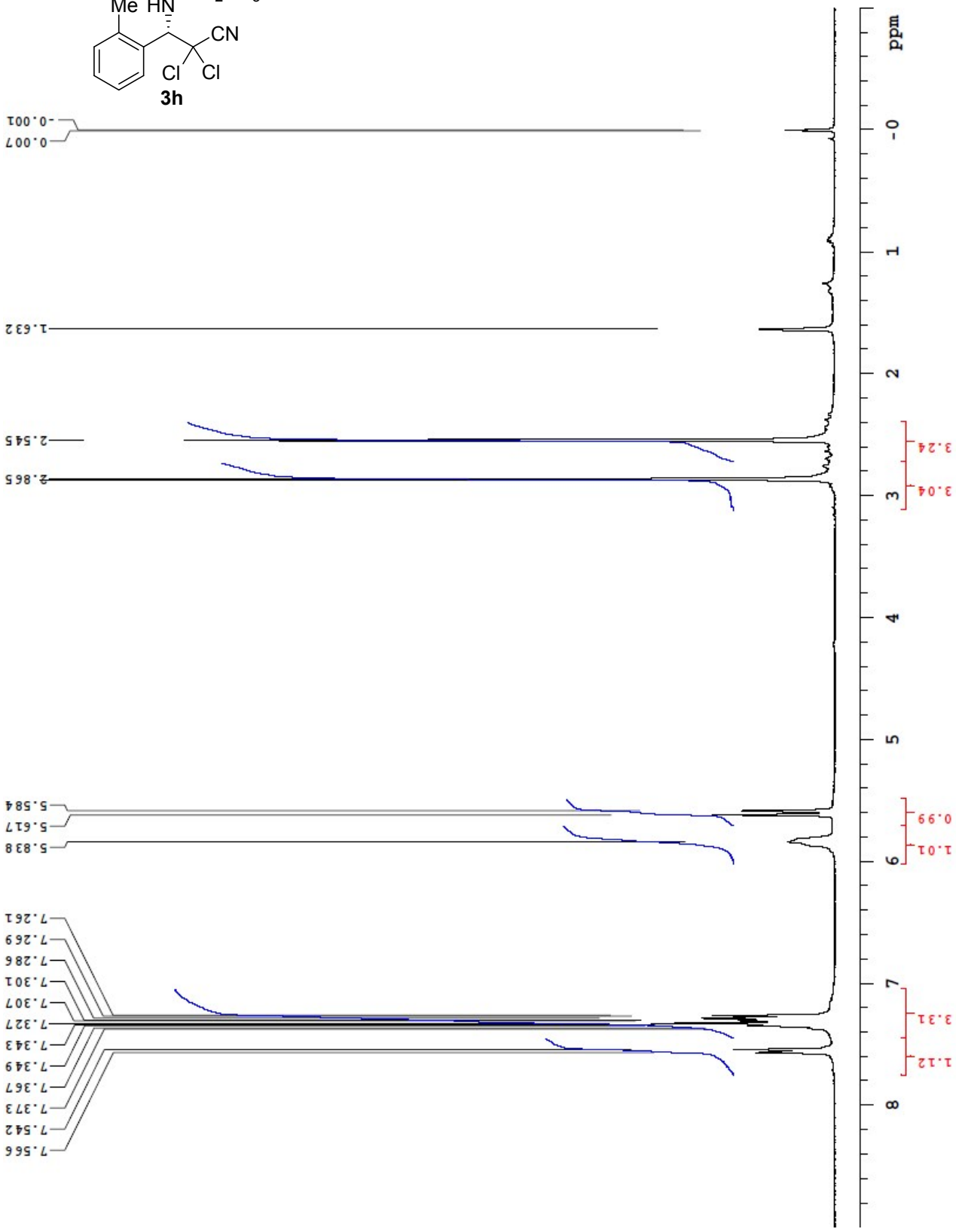
^{13}C-NMR


HN
SO2CH3
Me
CN
Cl
Cl
3g
21.598
42.612
67.430
71.731
76.735
77.160
77.585
114.404
125.739
129.095
129.461
131.330
132.736
139.155
ppm

^{1}H-NMR


Me
HN
SO2CH3
CN
Cl
Cl

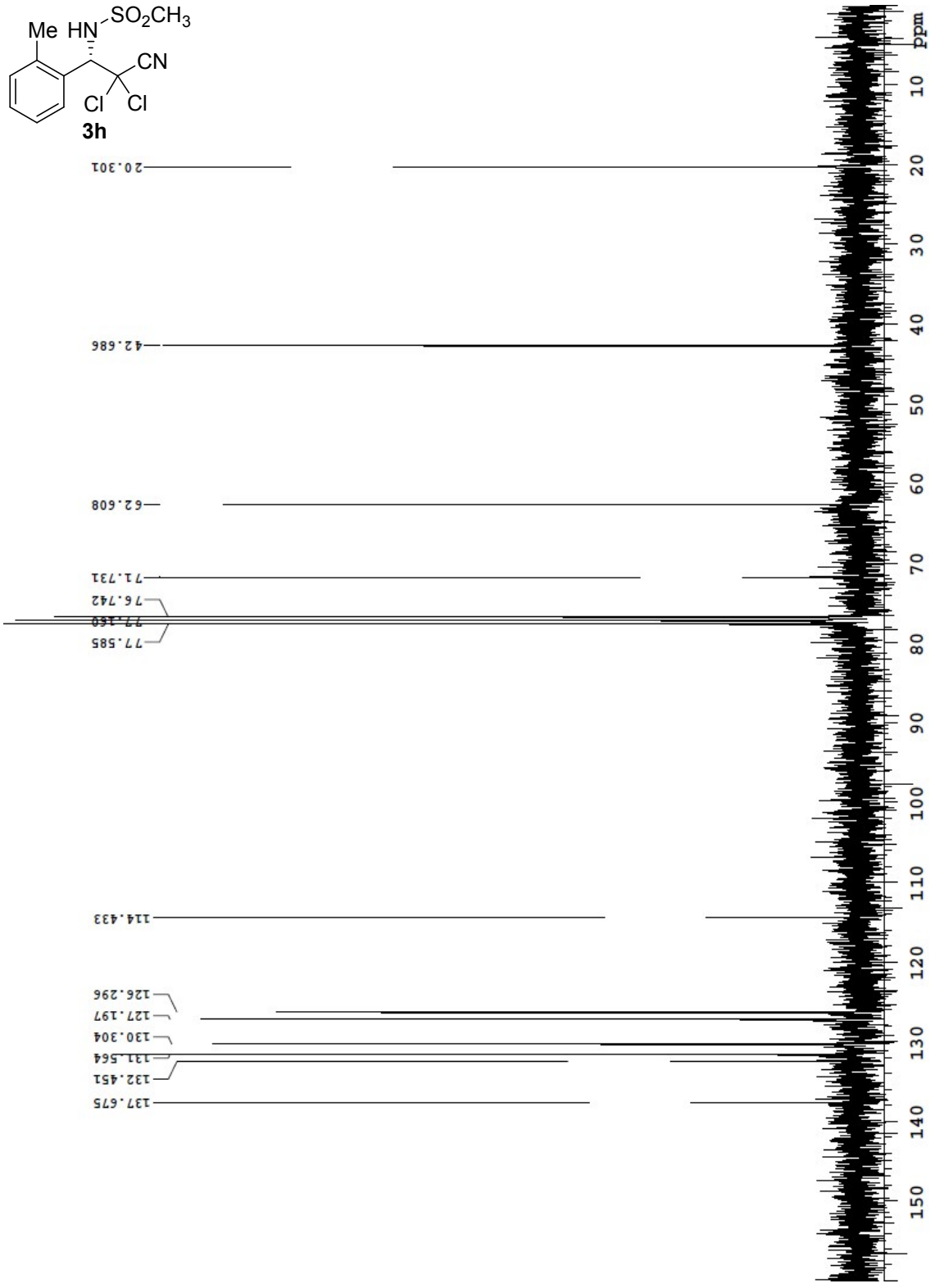
3h


-0.001
0.007
1.632
2.545
2.865
5.584
5.617
5.838
7.261
7.269
7.286
7.301
7.307
7.327
7.343
7.349
7.367
7.373
7.542
7.566
3.24
3.04
0.99
1.01
3.31
1.12
ppm

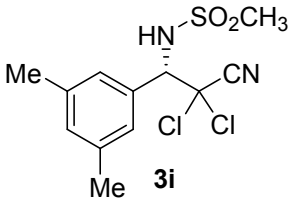
^{13}C-NMR

Me
HN
SO2CH3
CN
Cl
Cl

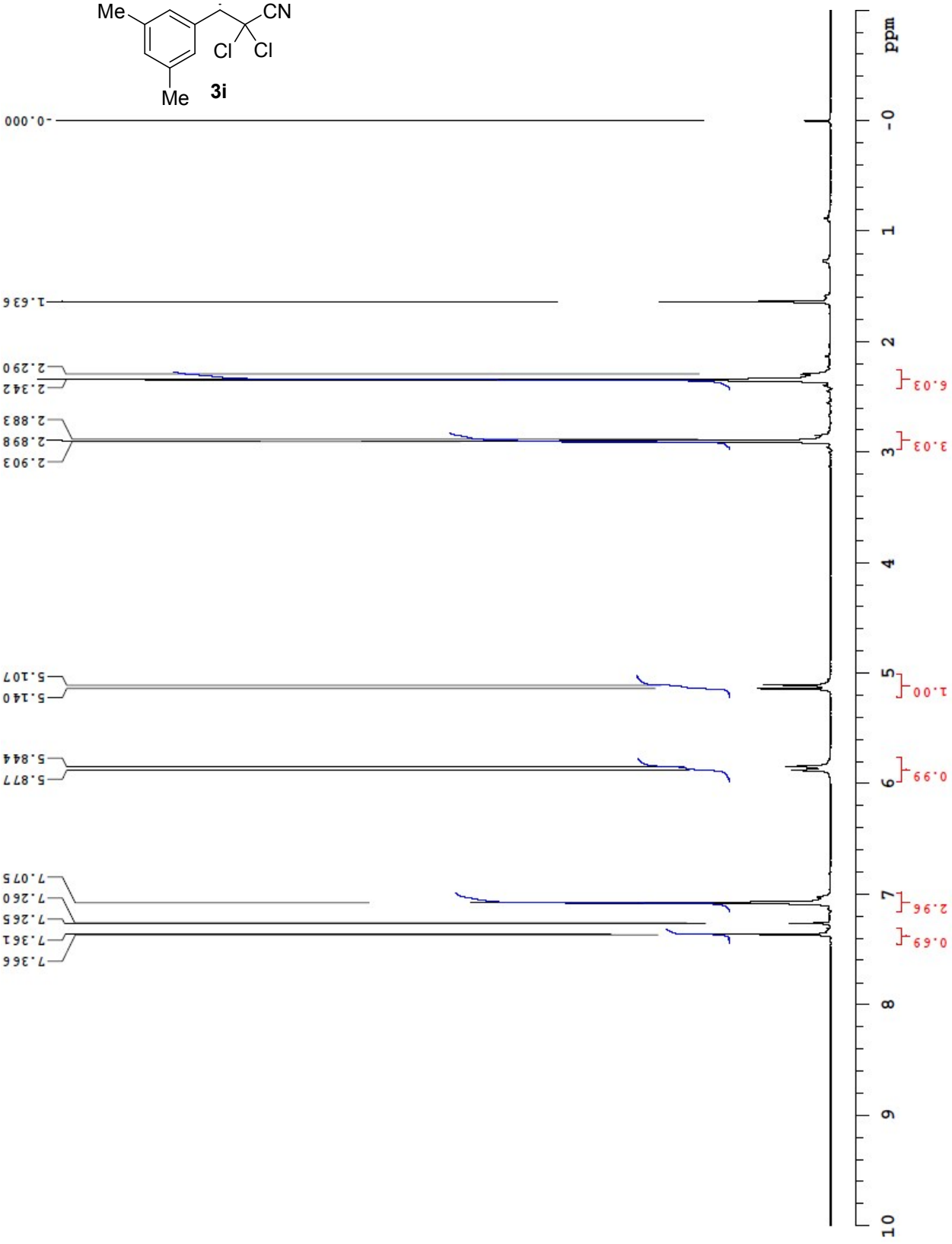
3h


20.301
42.686
62.608
71.731
76.742
77.160
77.585
114.433
126.296
127.197
130.304
131.564
132.451
137.675
ppm

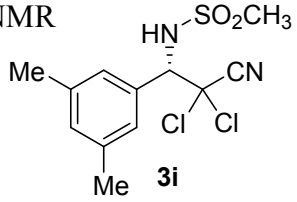
^{1}H-NMR


HN
SO2CH3
Me
CN
Cl
Cl
Me

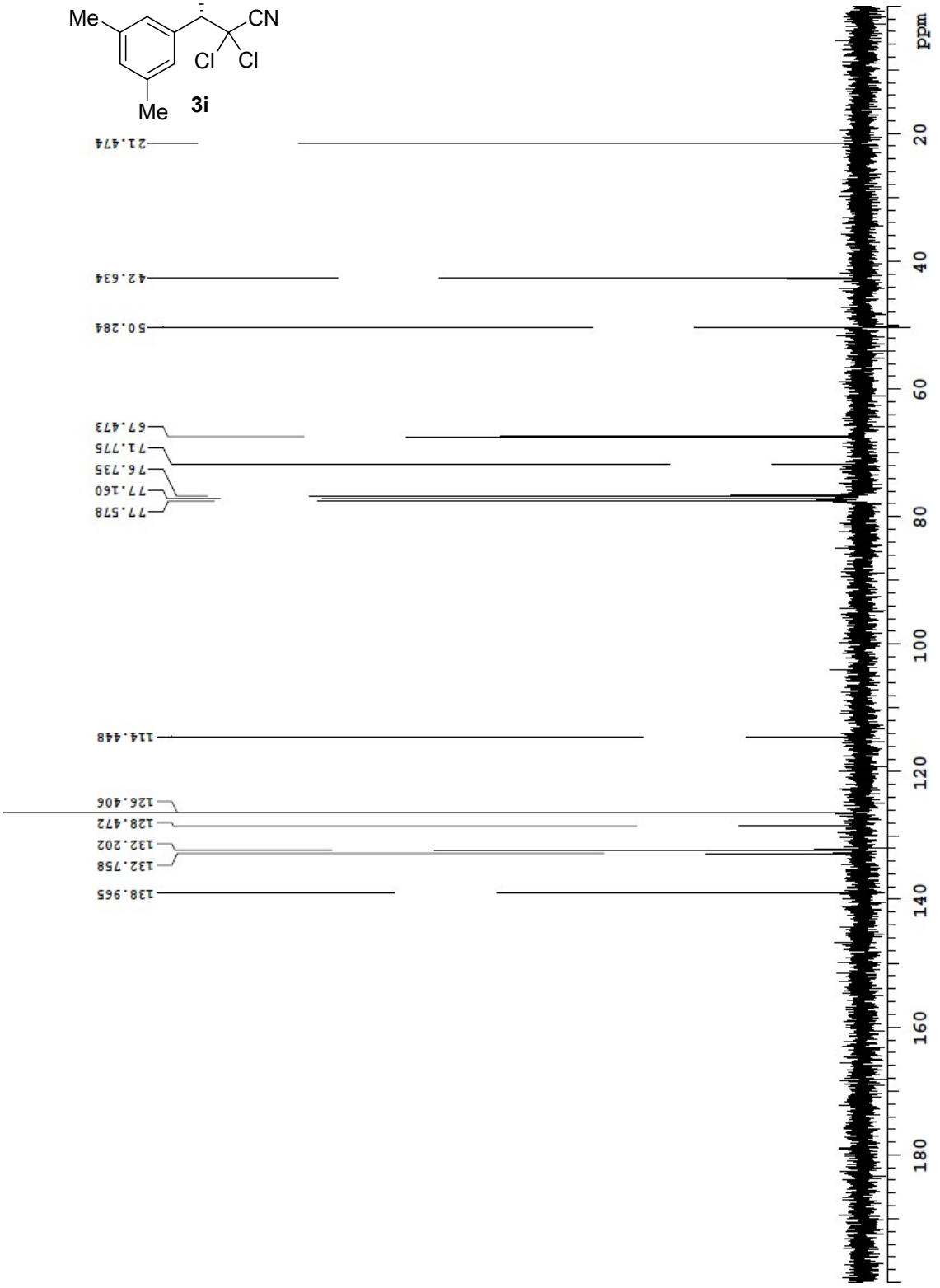
3i


0.000
1.636
2.290
2.342
2.883
2.898
2.903
5.107
5.140
5.844
5.877
7.075
7.260
7.265
7.361
7.366
ppm
6.03
3.03
1.00
0.99
2.96
0.69

^{13}C-NMR


HN
SO2CH3
Me
CN
Cl
Cl
Me

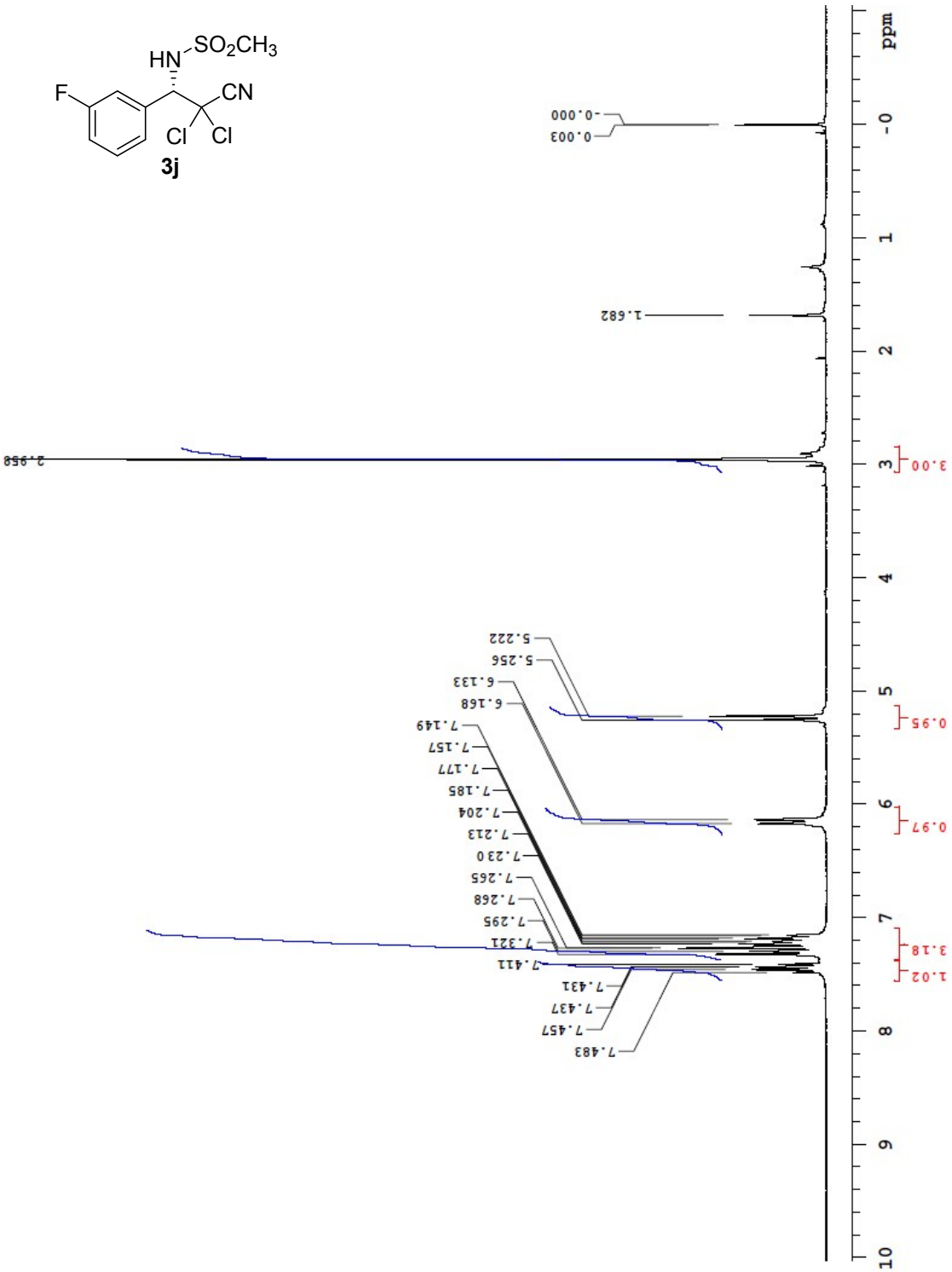
3i


21.474
42.634
50.284
67.473
71.775
76.735
77.160
77.578
114.448
126.406
128.472
132.202
132.758
138.965
ppm
20
40
60
80
100
120
140
160
180

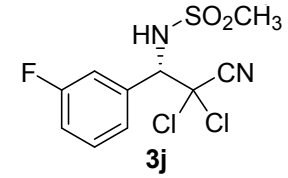
^{1}H-NMR

HN
SO2CH3
F
CN
Cl
Cl

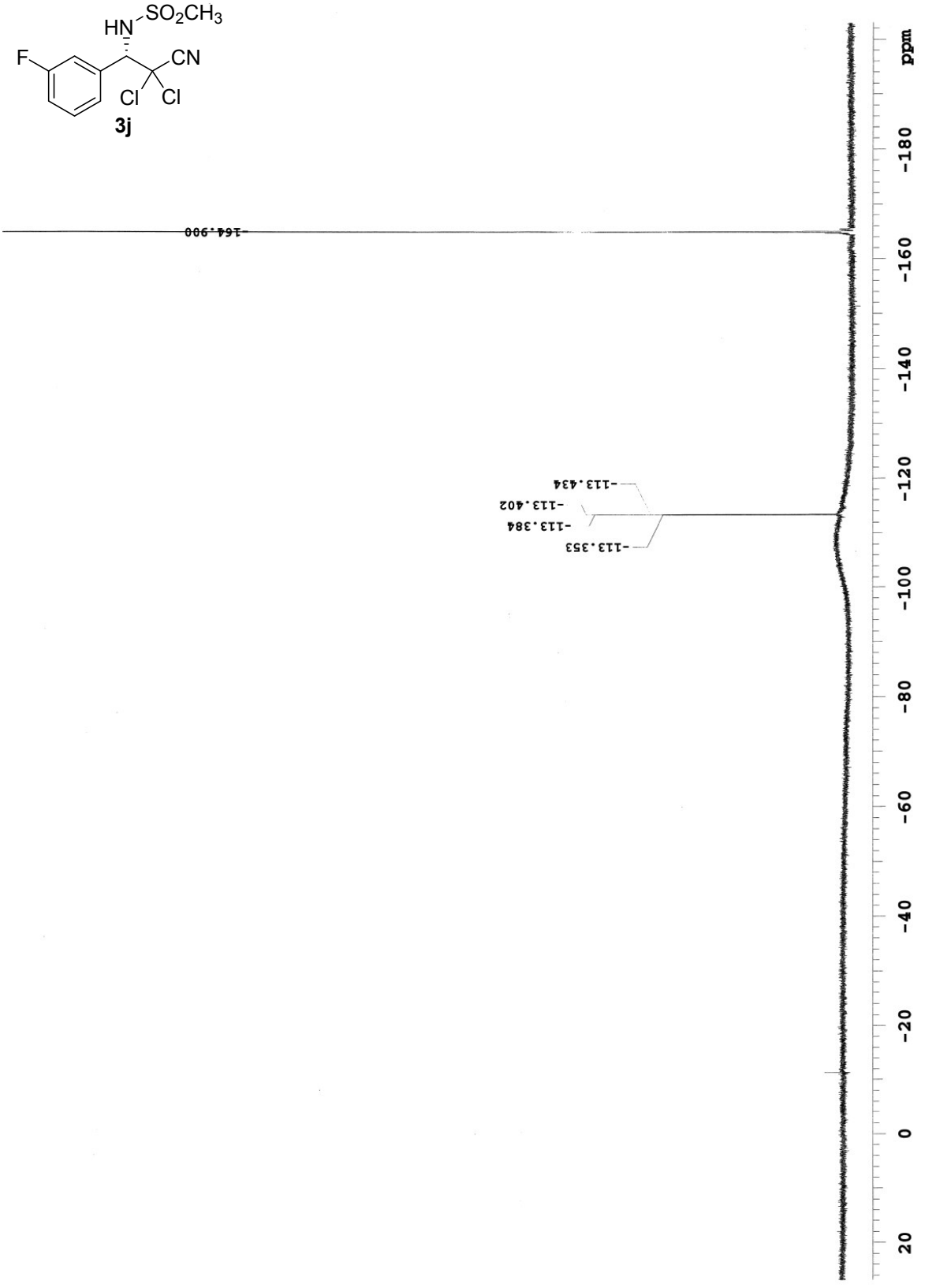
3j


ppm
-0.000
0.003
1.682
2.958
3.00
5.222
5.256
6.133
6.168
7.149
7.157
7.177
7.185
7.204
7.213
7.230
7.265
7.268
7.295
7.321
7.411
7.431
7.437
7.457
7.483
0.95
0.97
3.18
1.02

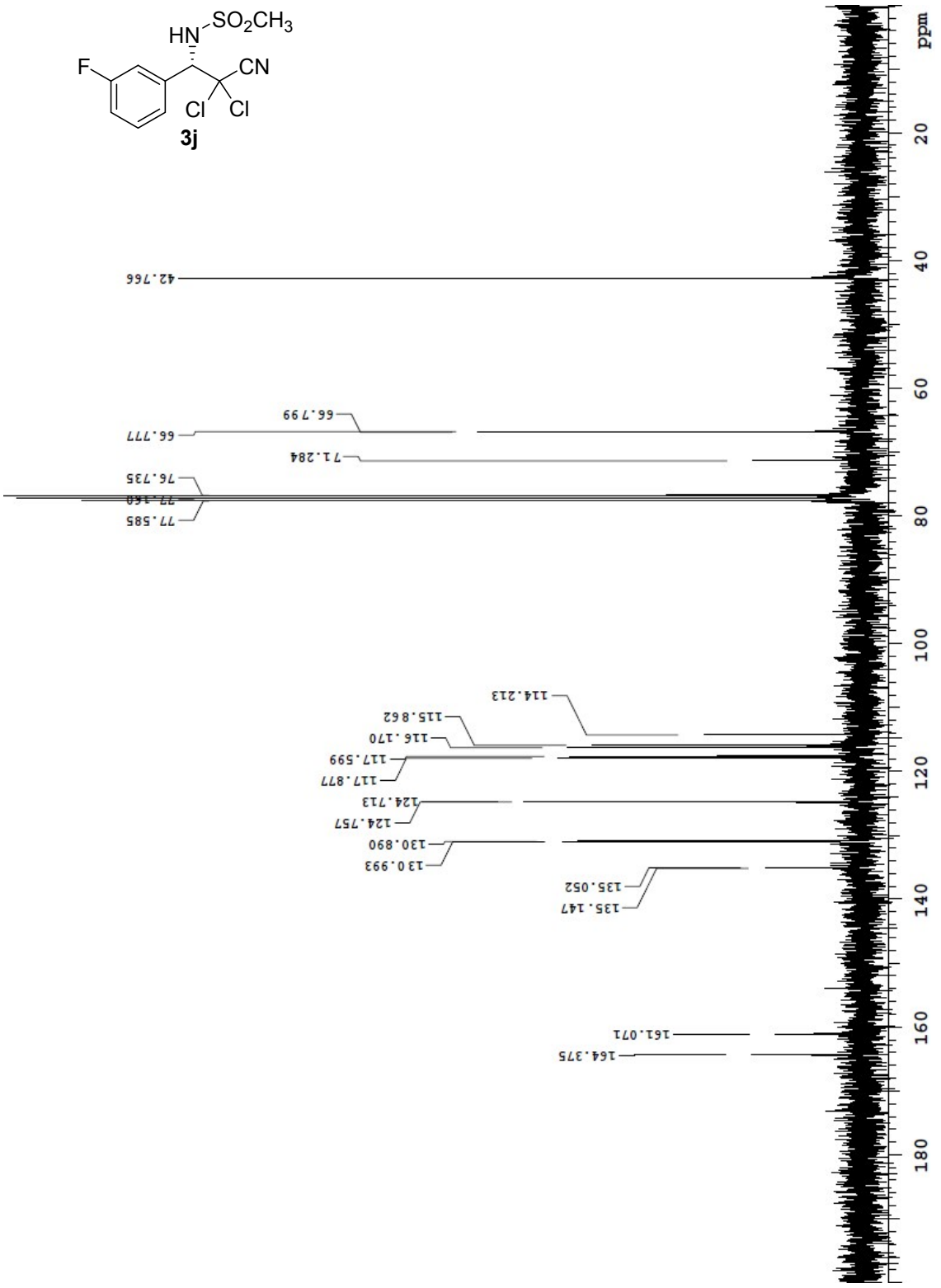
^{19}F-NMR


HN
SO2CH3
F
CN
Cl
Cl

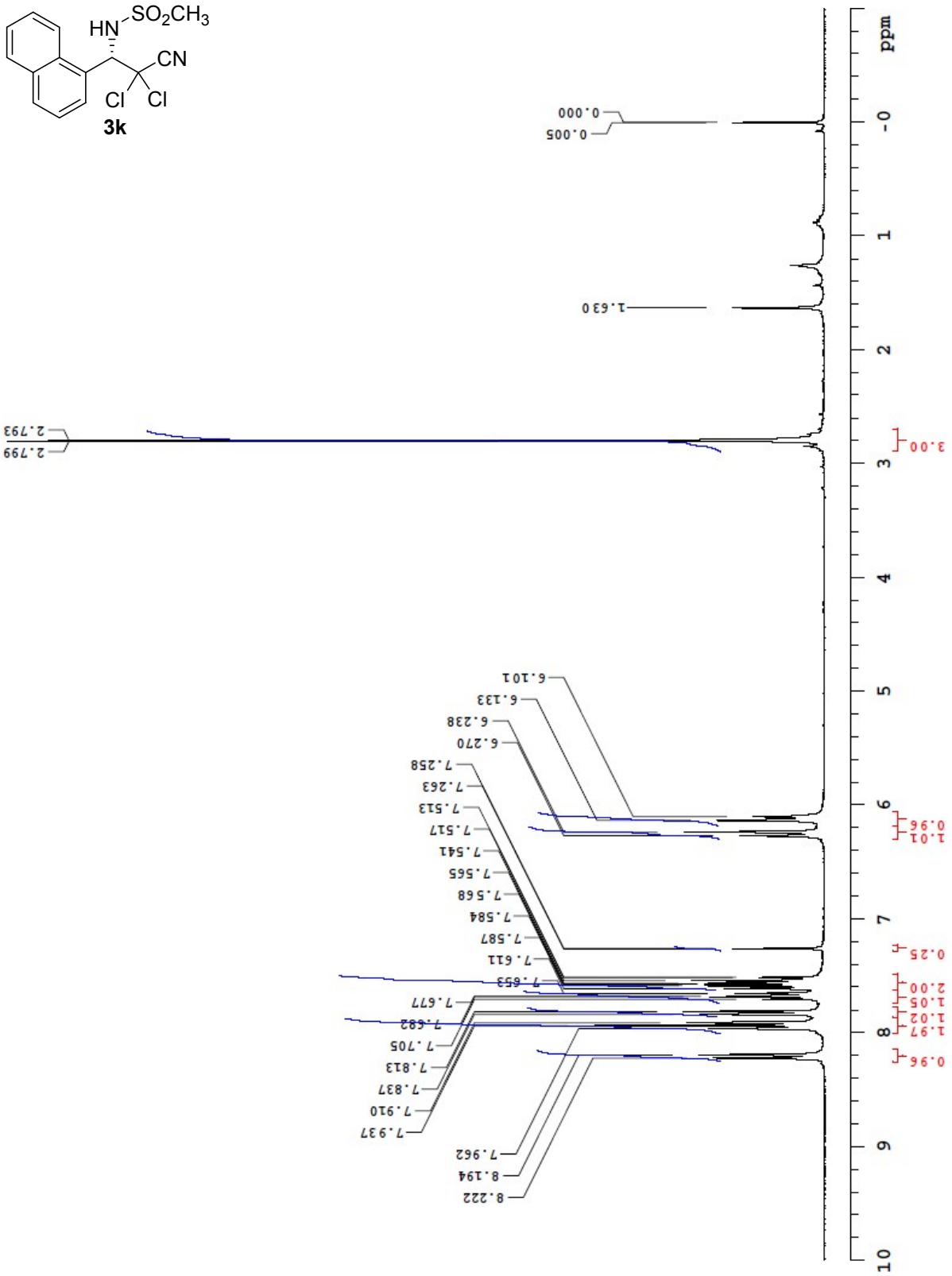
3j


-164.900
-113.434
-113.402
-113.384
-113.353
ppm
-180
-160
-140
-120
-100
-80
-60
-40
-20
0
20

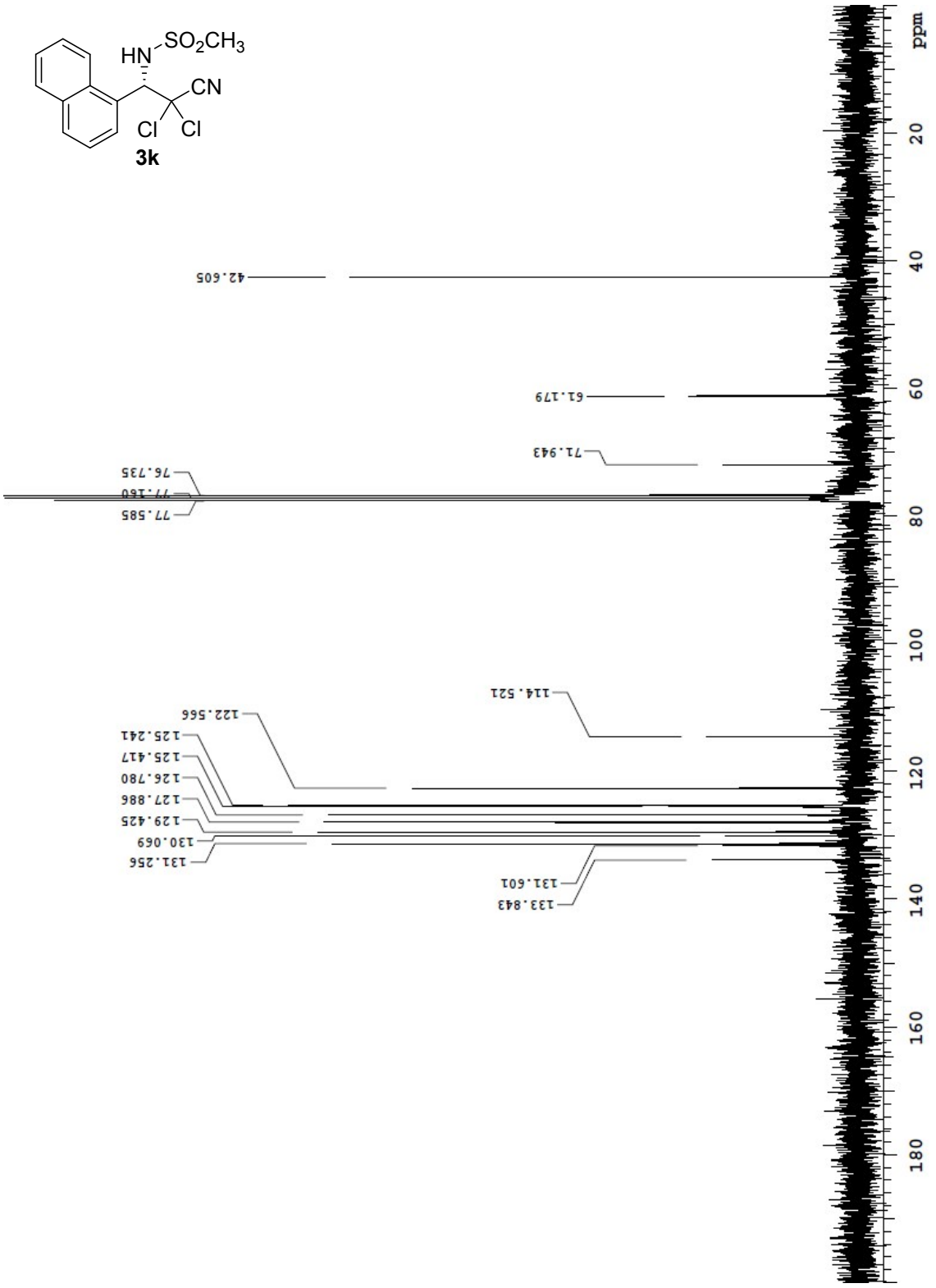
^{13}C-NMR


HN
SO2CH3
F
CN
Cl
Cl
3j
ppm
20
40
60
80
100
120
140
160
180
42.766
66.799
66.777
71.284
76.735
77.160
77.585
114.213
115.862
116.170
117.599
117.877
124.713
124.757
130.890
130.993
135.052
135.147
161.071
164.375

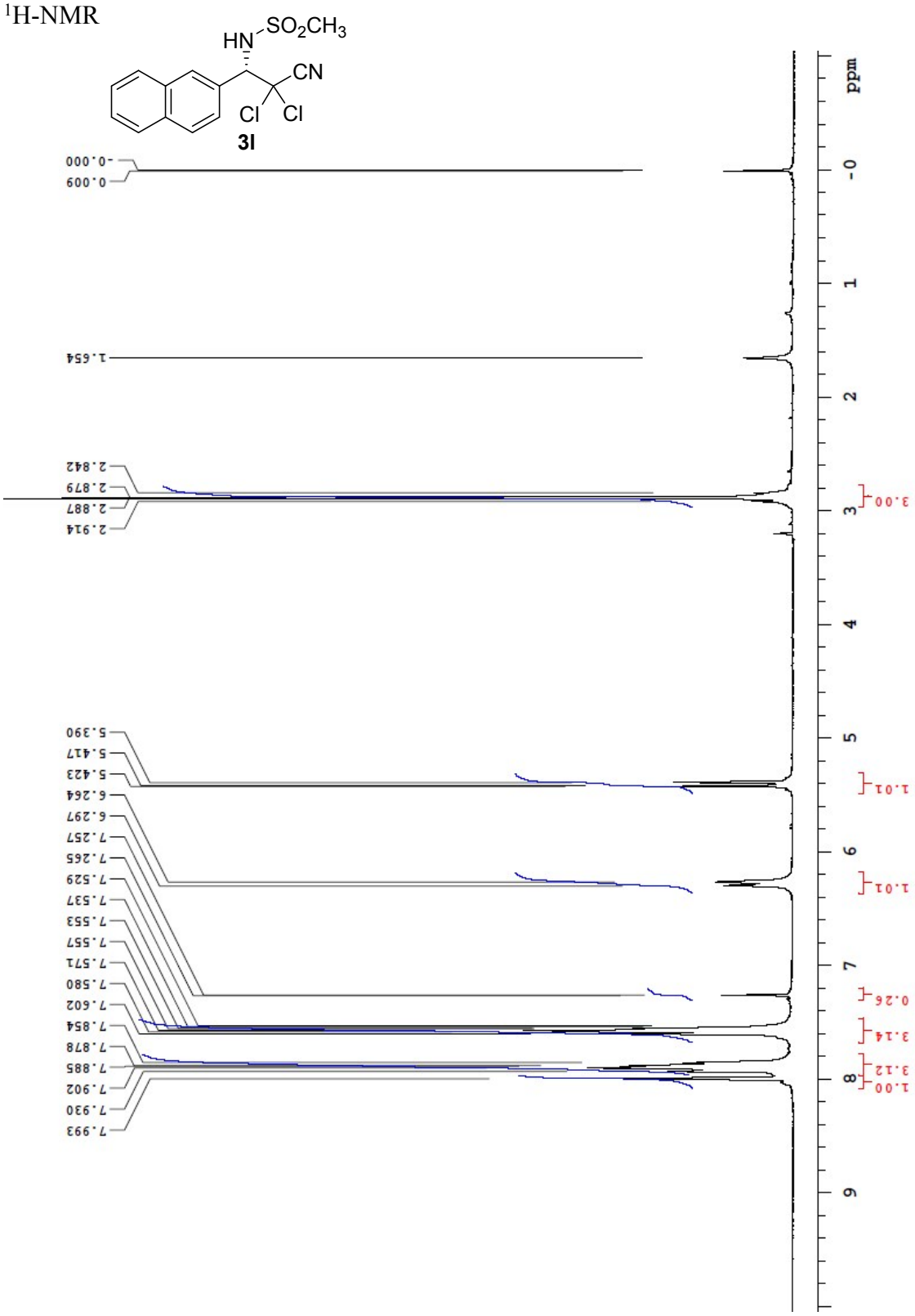
^{1}H-NMR


HN
SO2CH3
CN
Cl
Cl
3k
ppm
0.005
0.000
1.630
2.799
2.793
6.101
6.133
6.238
6.270
7.258
7.263
7.513
7.517
7.541
7.565
7.568
7.584
7.587
7.611
7.653
7.677
7.682
7.705
7.813
7.837
7.910
7.937
7.962
8.194
8.222
3.00
1.01
0.96
0.25
2.00
1.05
1.02
1.97
0.96

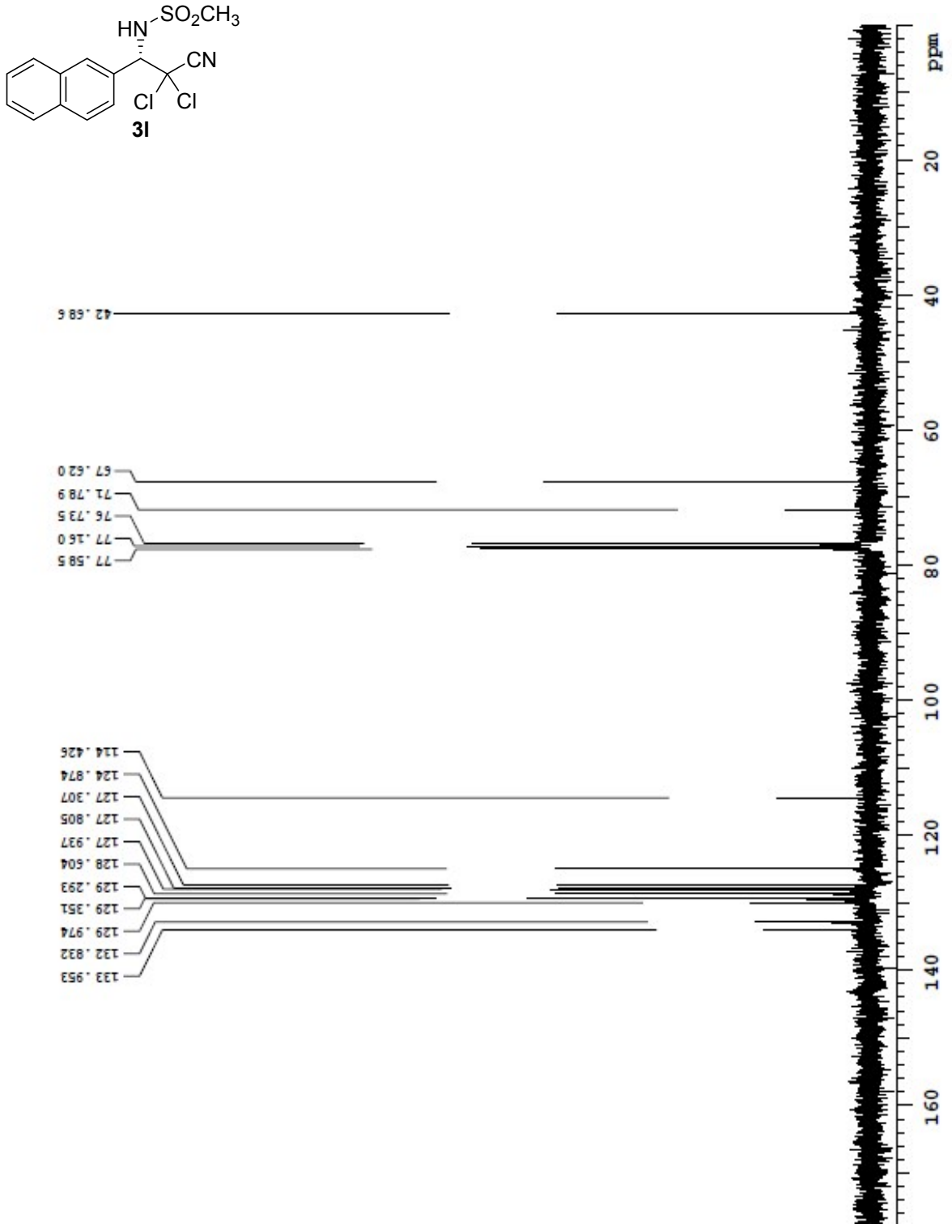
^{13}C-NMR


HN
SO2CH3
CN
Cl
Cl
3k
42.605
61.179
71.943
76.735
77.160
77.585
114.521
122.566
125.241
125.417
126.780
127.886
129.425
130.069
131.256
131.601
133.843
ppm
20
40
60
80
100
120
140
160
180

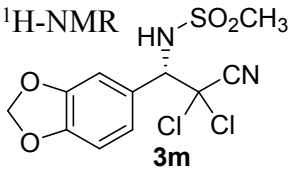
^{1}H-NMR


HN
SO2CH3
CN
Cl
Cl
3l
-0.000
0.009
1.654
2.842
2.879
2.887
2.914
5.390
5.417
5.423
6.264
6.297
7.257
7.265
7.529
7.537
7.553
7.557
7.571
7.580
7.602
7.854
7.878
7.885
7.902
7.930
7.993
3.00
1.01
1.01
0.26
3.14
3.12
1.00
ppm

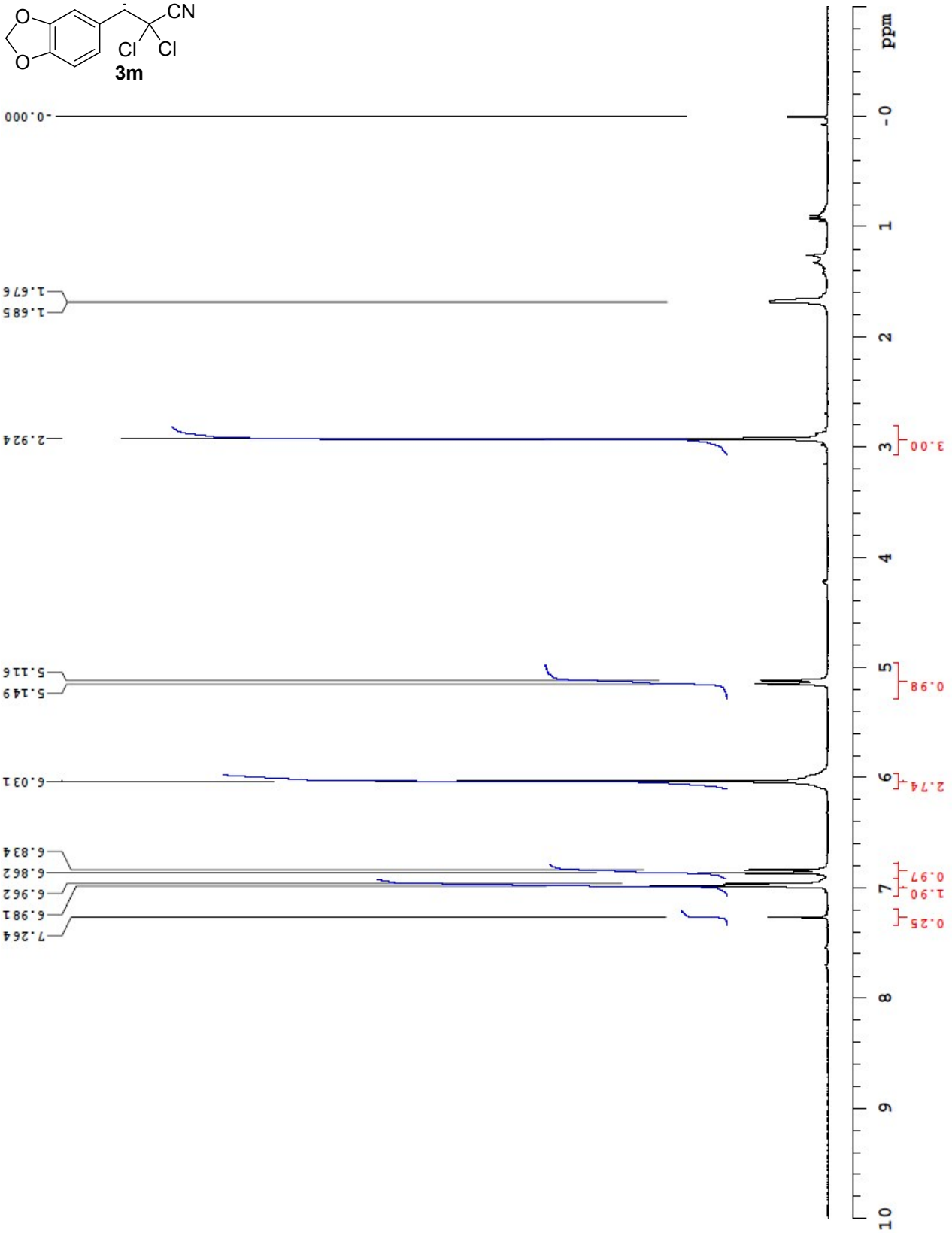
^{13}C-NMR


HN
SO2CH3
CN
Cl
Cl
3l
ppm
20
40
60
80
100
120
140
160
42.685
67.620
71.789
76.735
77.160
77.585
114.426
124.874
127.307
127.805
127.937
128.604
129.293
129.351
129.974
132.832
133.953

^{1}H-NMR


HN
SO2CH3
CN
Cl
Cl
O
O

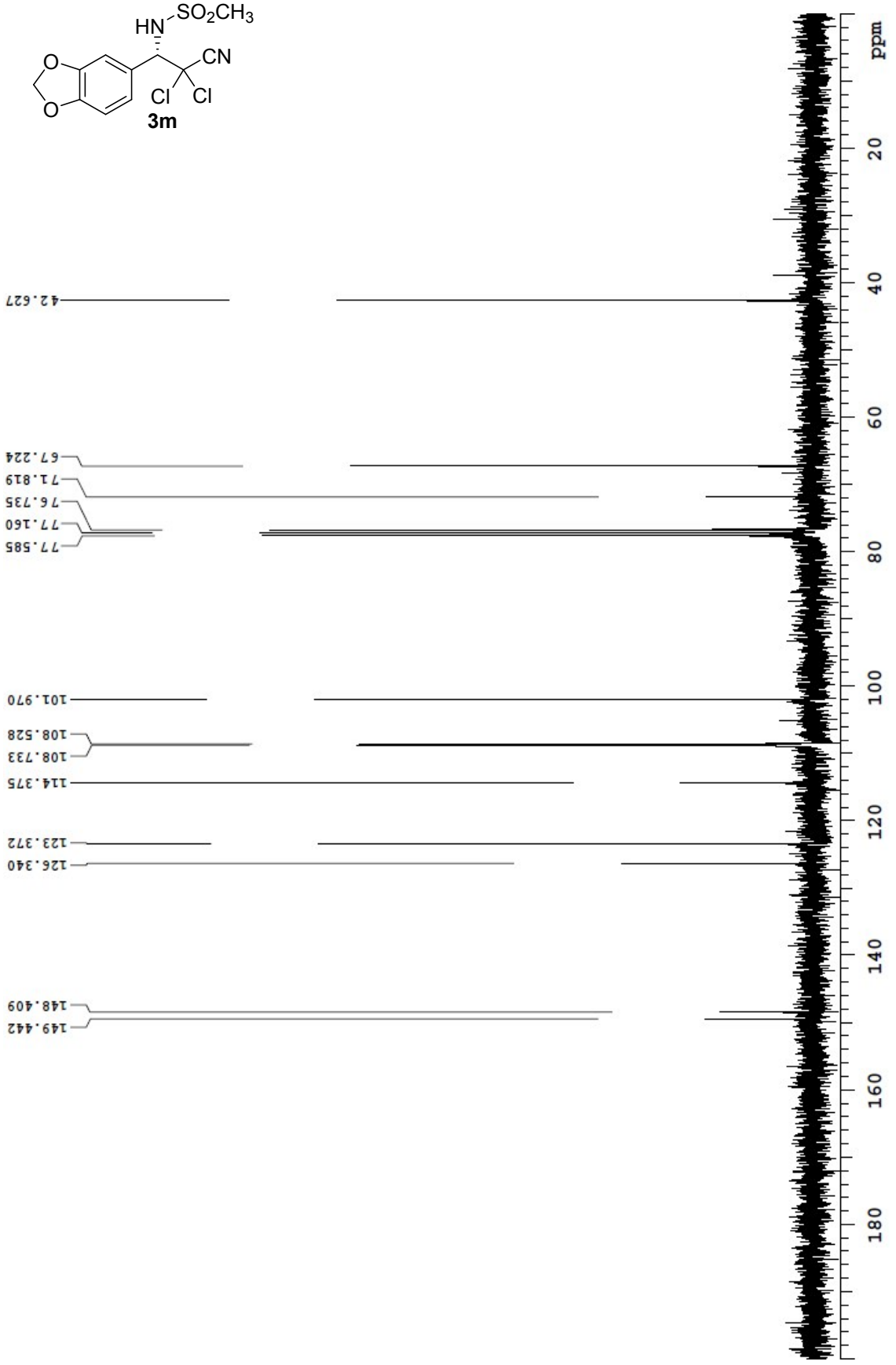
3m


-0.000
1.676
1.685
2.924
5.116
5.149
6.031
6.834
6.862
6.962
6.981
7.264
3.00
0.98
2.74
0.97
1.90
0.25
ppm

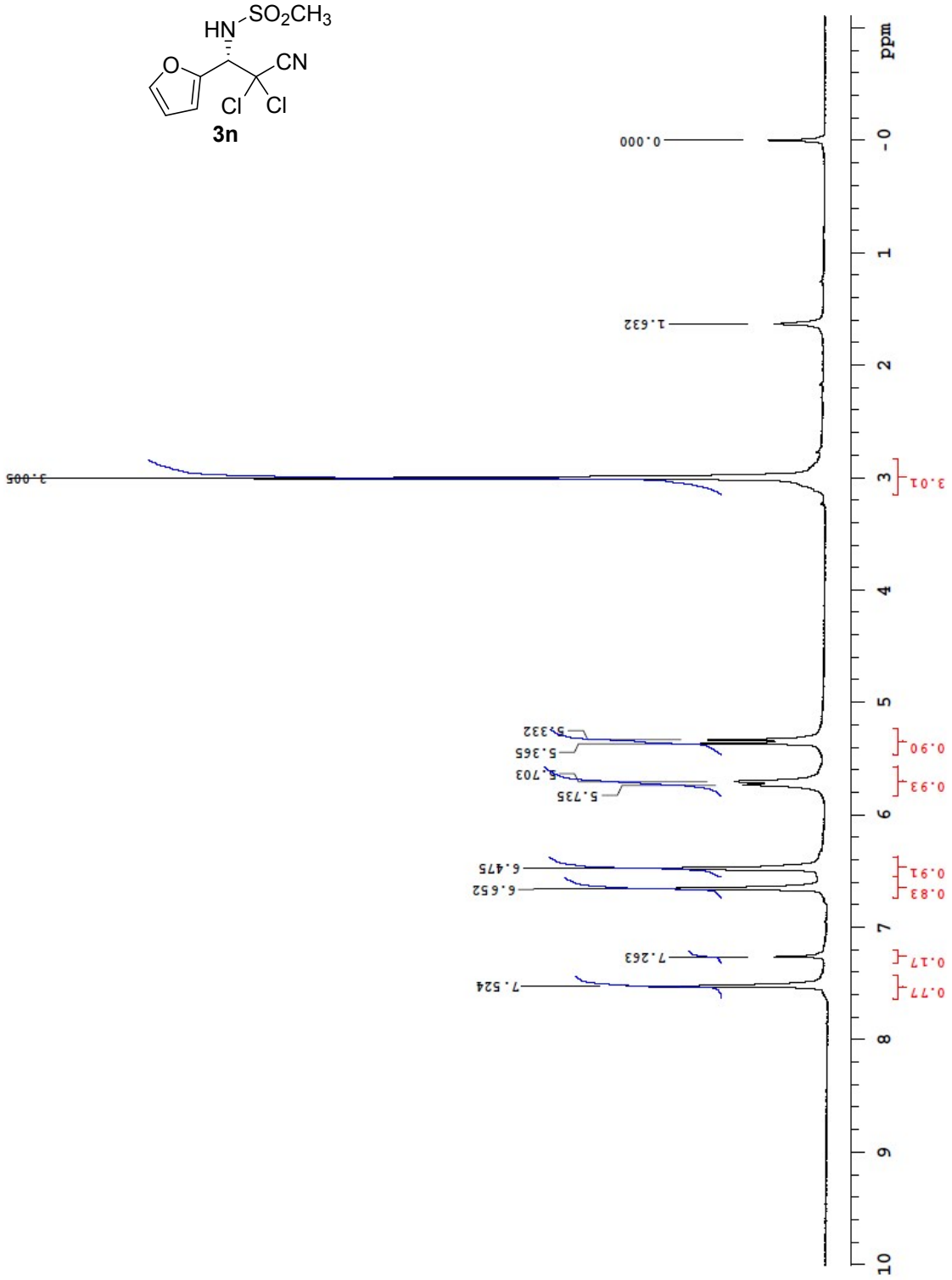
^{13}C-NMR

HN
SO2CH3
CN
Cl
Cl
O
O

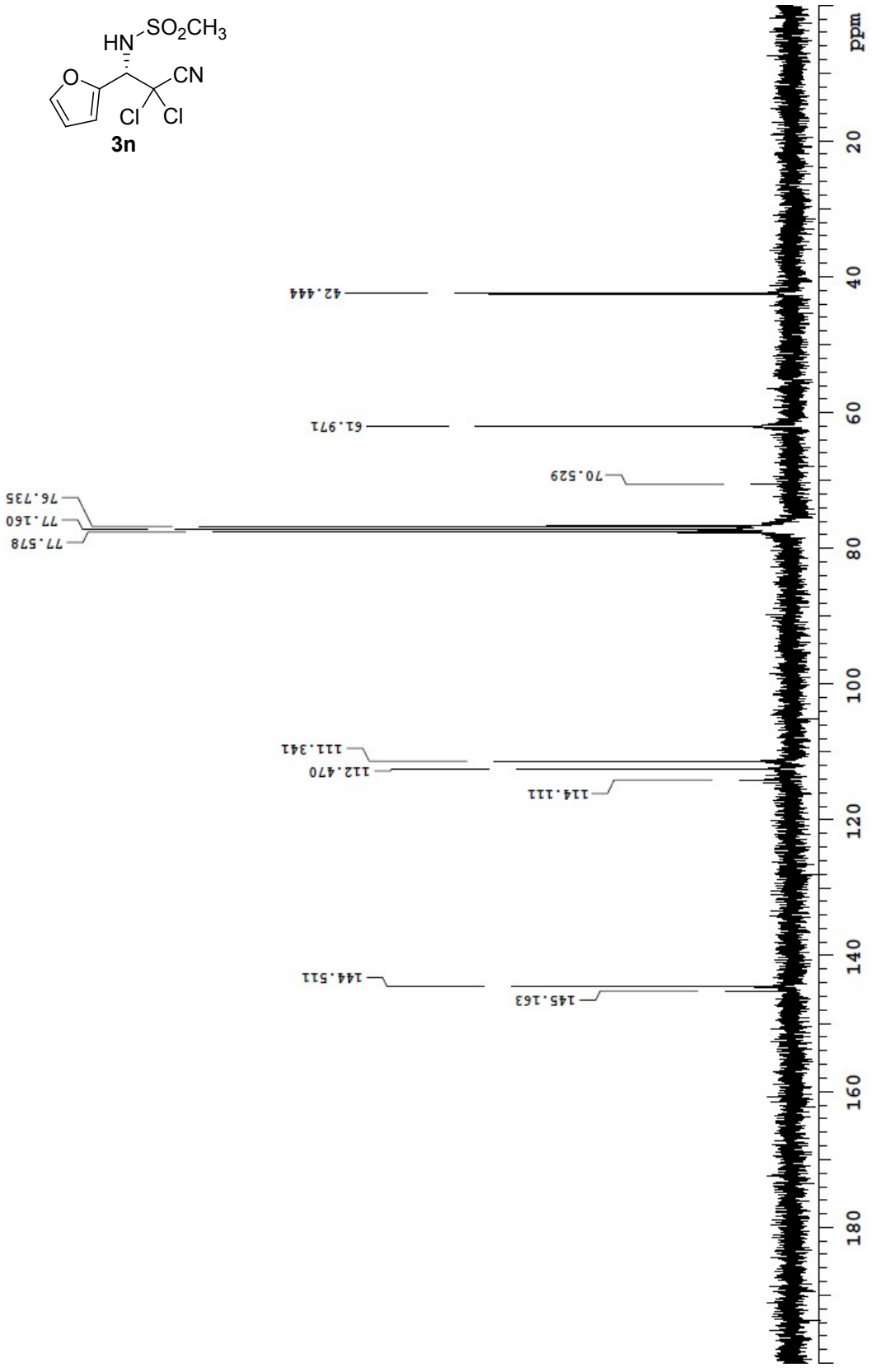
3m


42.627
67.224
71.819
76.735
77.160
77.585
101.970
108.528
108.733
114.375
123.372
126.340
148.409
149.442
ppm
20
40
60
80
100
120
140
160
180

^{1}H-NMR


HN
SO2CH3
O
CN
Cl
Cl
3n
0.000
1.632
3.005
5.332
5.365
5.703
5.735
6.475
6.652
7.263
7.524
3.01
0.90
0.93
0.91
0.83
0.17
0.77
ppm

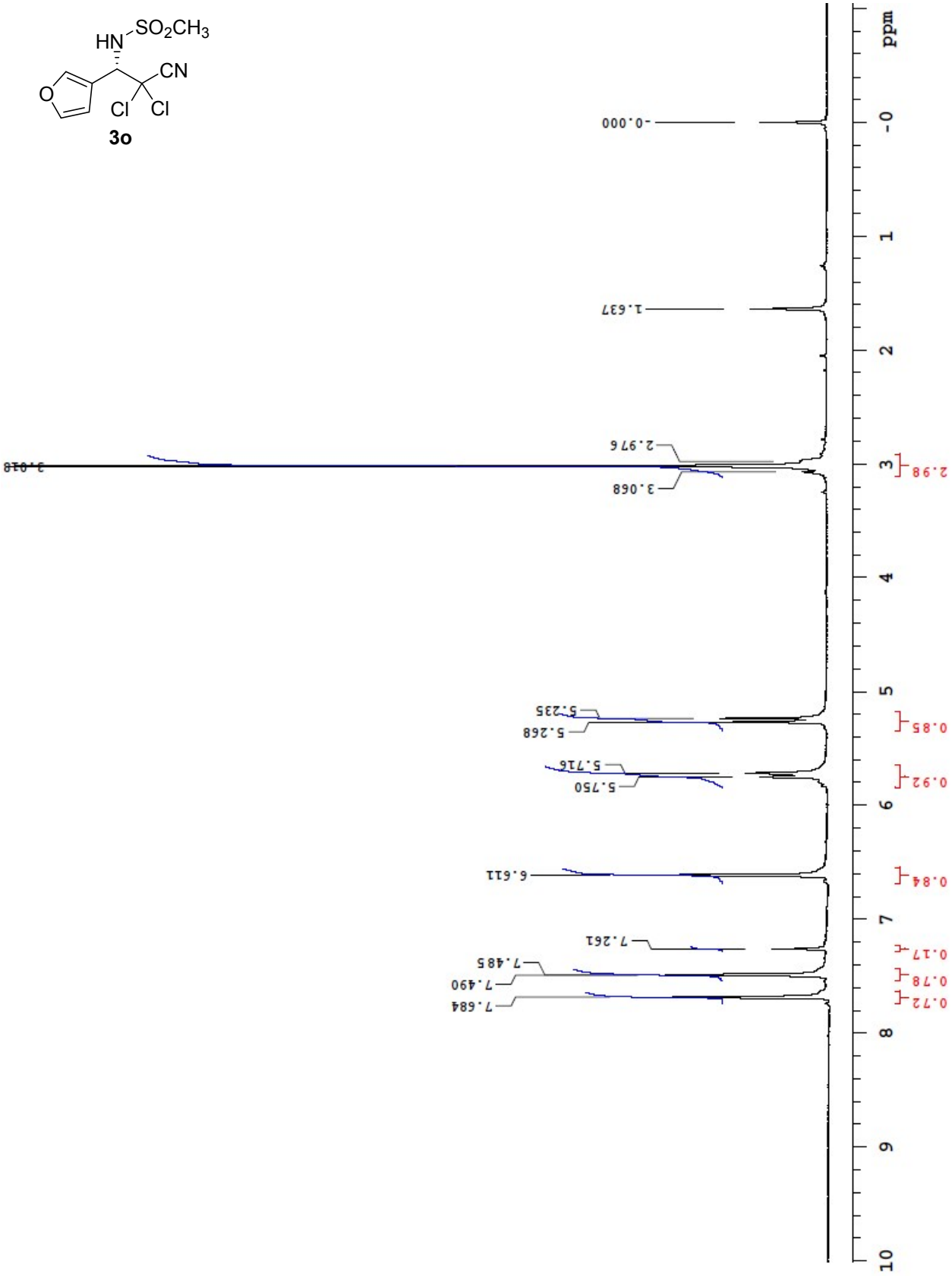
^{13}C-NMR


HN
SO2CH3
O
CN
Cl
Cl
3n
42.444
61.971
70.529
76.735
77.160
77.578
111.341
112.470
114.111
144.511
145.163
ppm
20
40
60
80
100
120
140
160
180

^{1}H-NMR

HN
SO2CH3
CN
O
Cl
Cl

3o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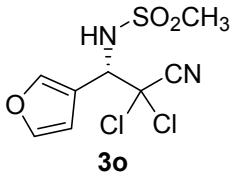
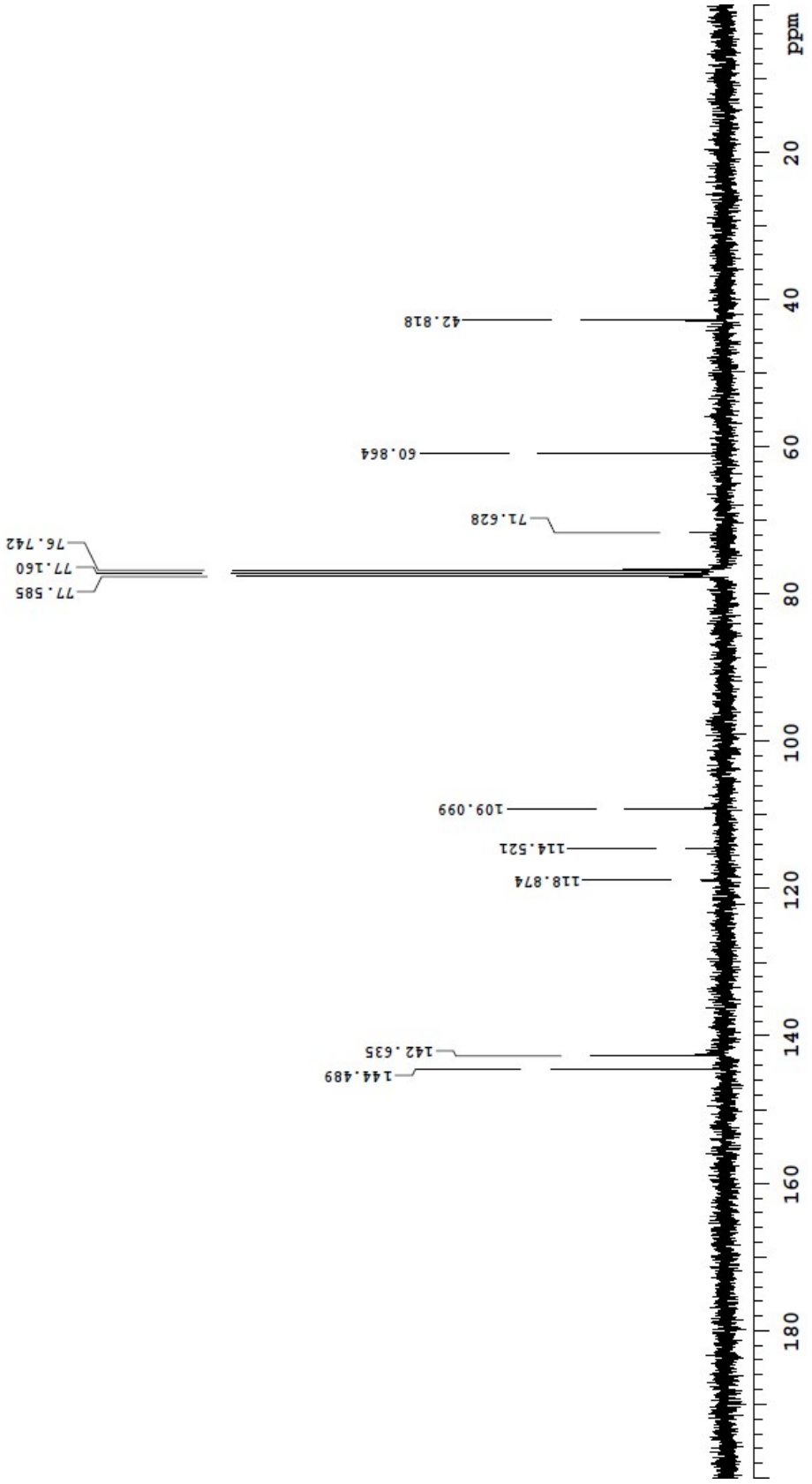
-0.000
1.637
2.976
3.018
3.068
5.235
5.268
5.716
5.750
6.611
7.261
7.485
7.490
7.684
2.98
0.85
0.92
0.84
0.17
0.78
0.72

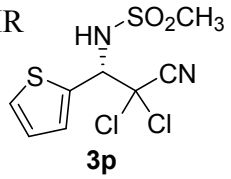
^{13}C-NMR


HN
SO2CH3
CN
O
Cl
Cl

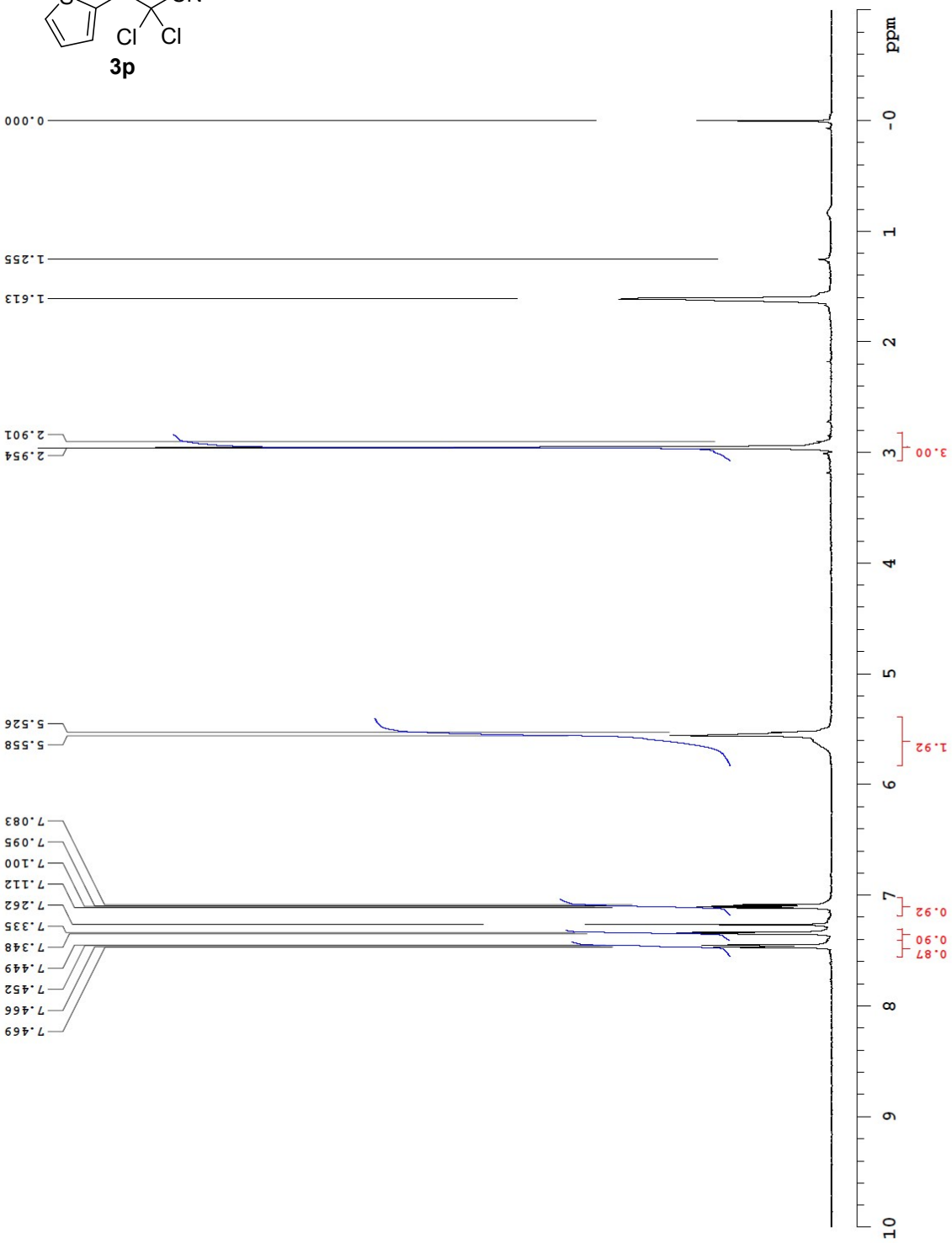
3o


42.818
60.864
71.628
76.742
77.160
77.585
109.099
114.521
118.874
142.635
144.489
ppm
20
40
60
80
100
120
140
160
180

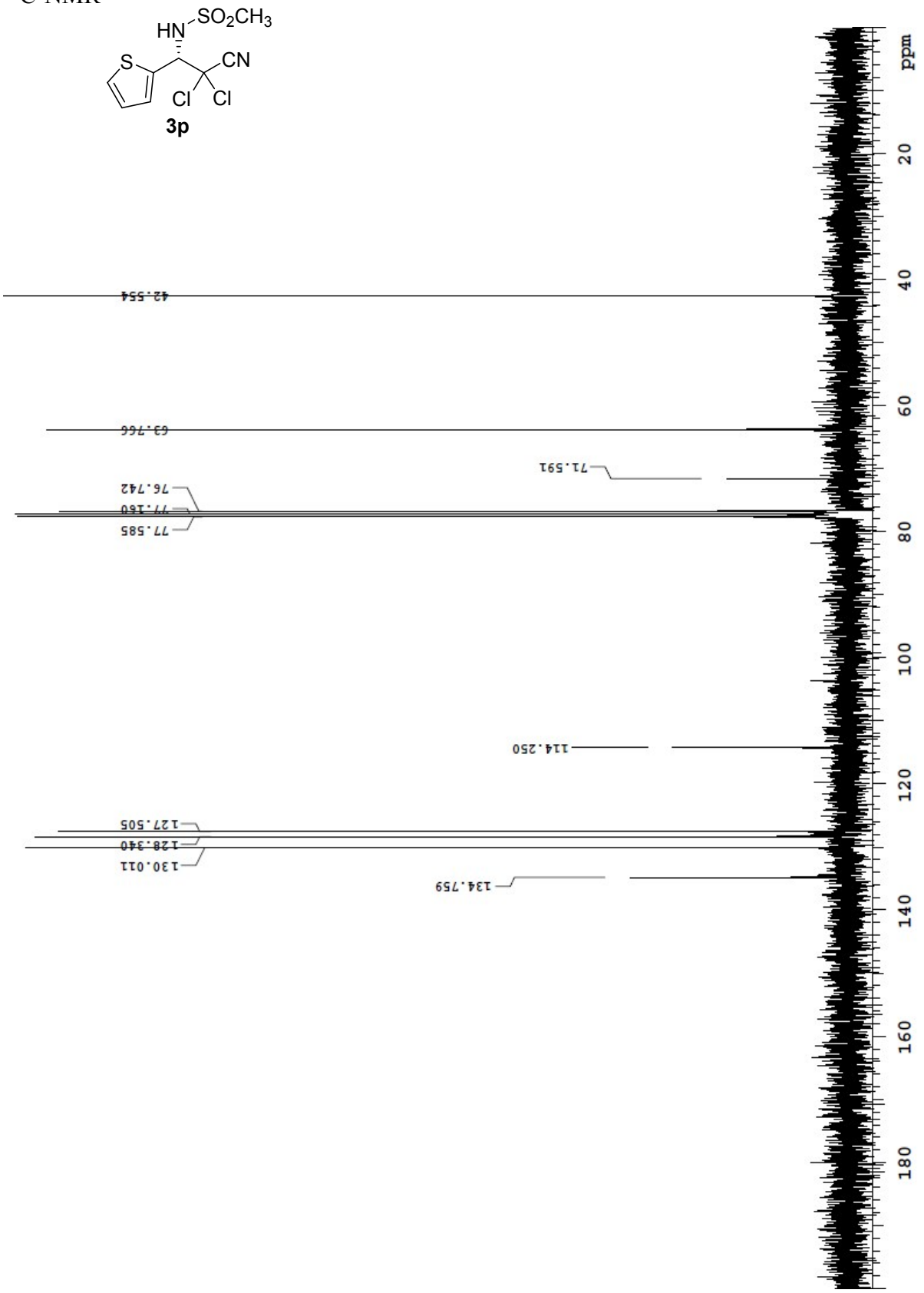
^{1}H-NMR


HN
SO2CH3
S
CN
Cl
Cl

3p


0.000
1.255
1.613
2.901
2.954
5.526
5.558
7.083
7.095
7.100
7.112
7.262
7.335
7.348
7.449
7.452
7.466
7.469
3.00
1.92
0.92
0.90
0.87
ppm

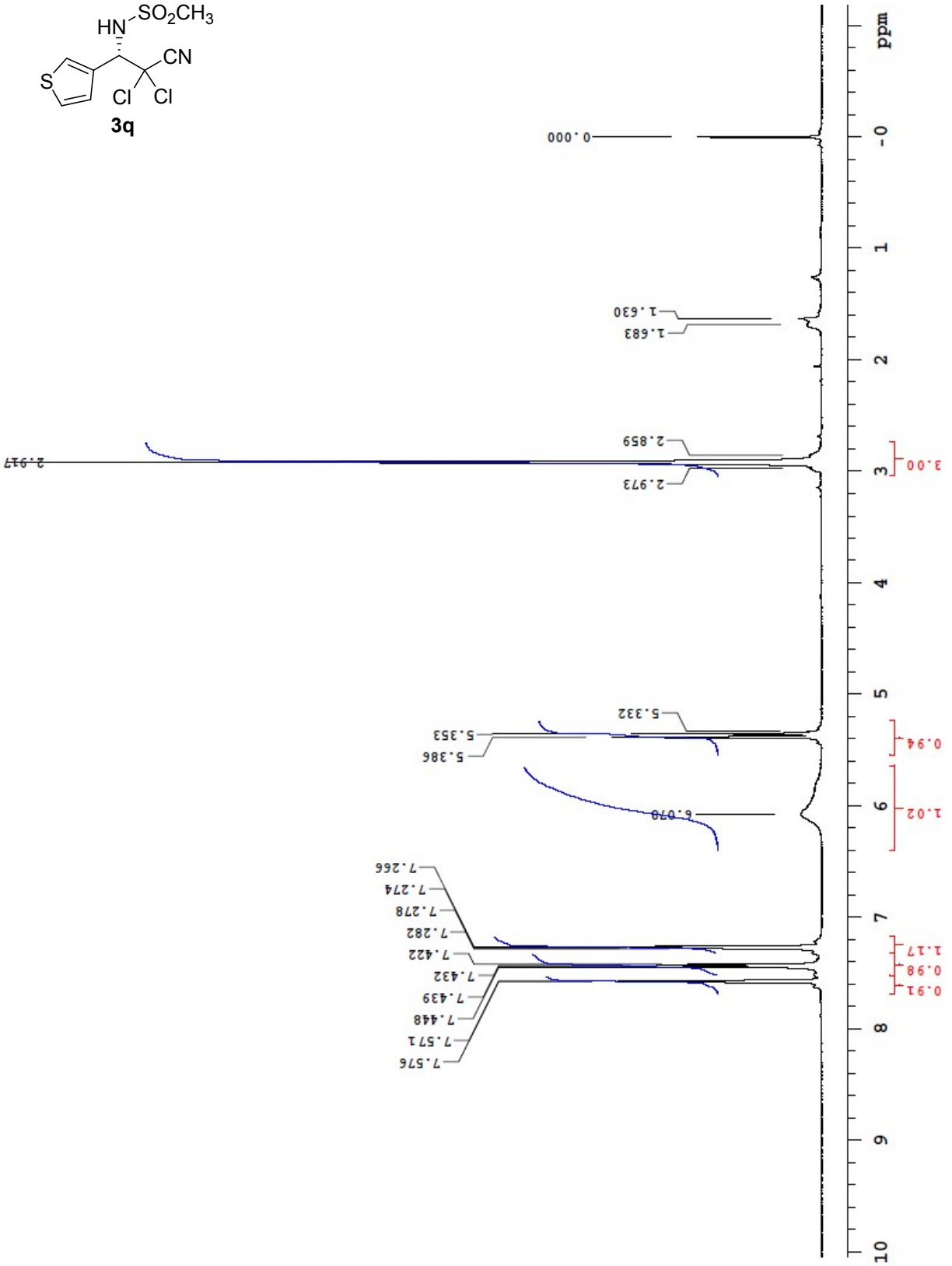
^{13}C-NMR


HN
SO2CH3
S
CN
Cl
Cl
3p
42.554
63.766
71.591
76.742
77.160
77.585
114.250
127.505
128.340
130.011
134.759
ppm
20
40
60
80
100
120
140
160
180

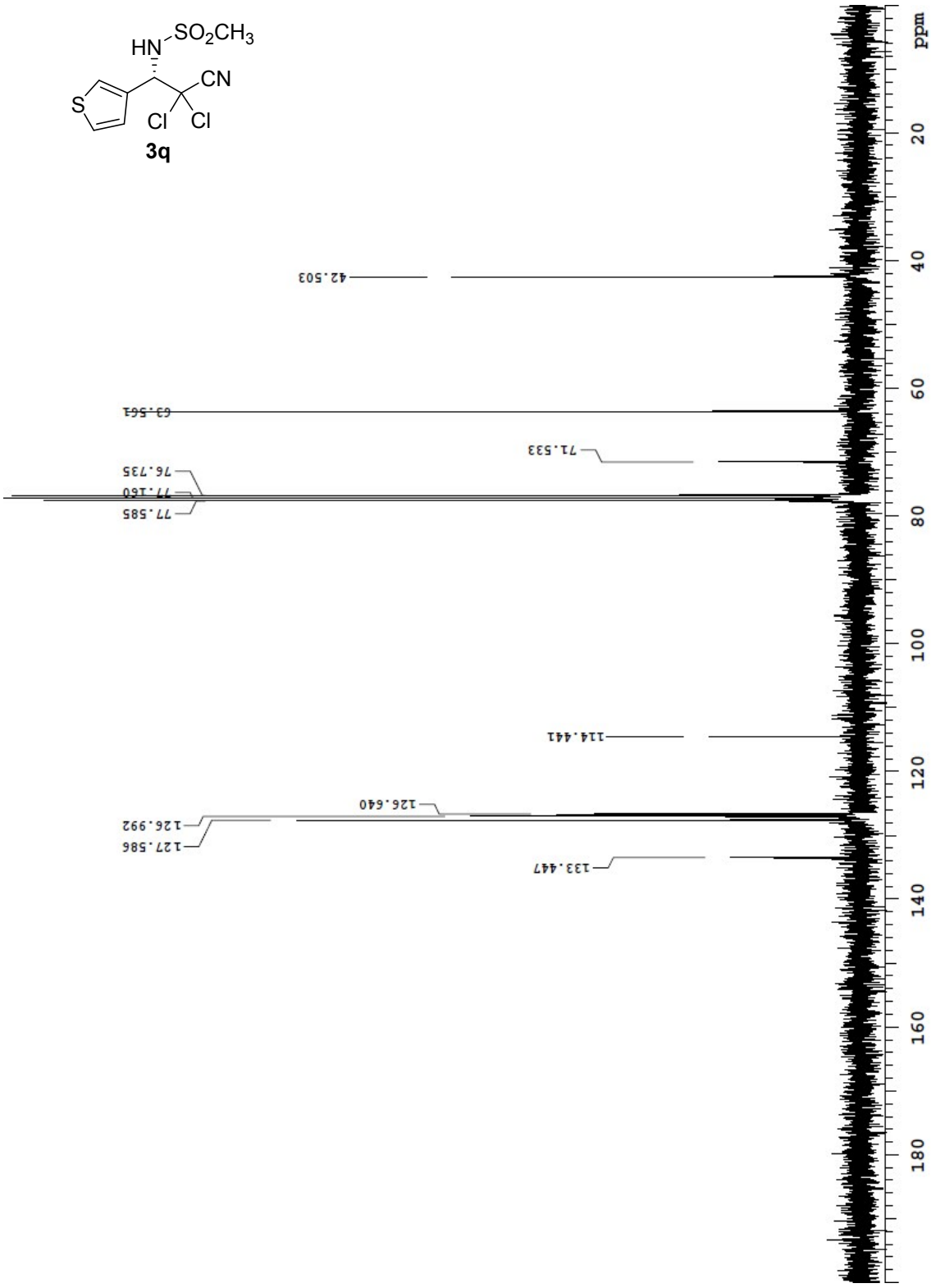
^{1}H-NMR

HN
SO2CH3
CN
S
Cl
Cl

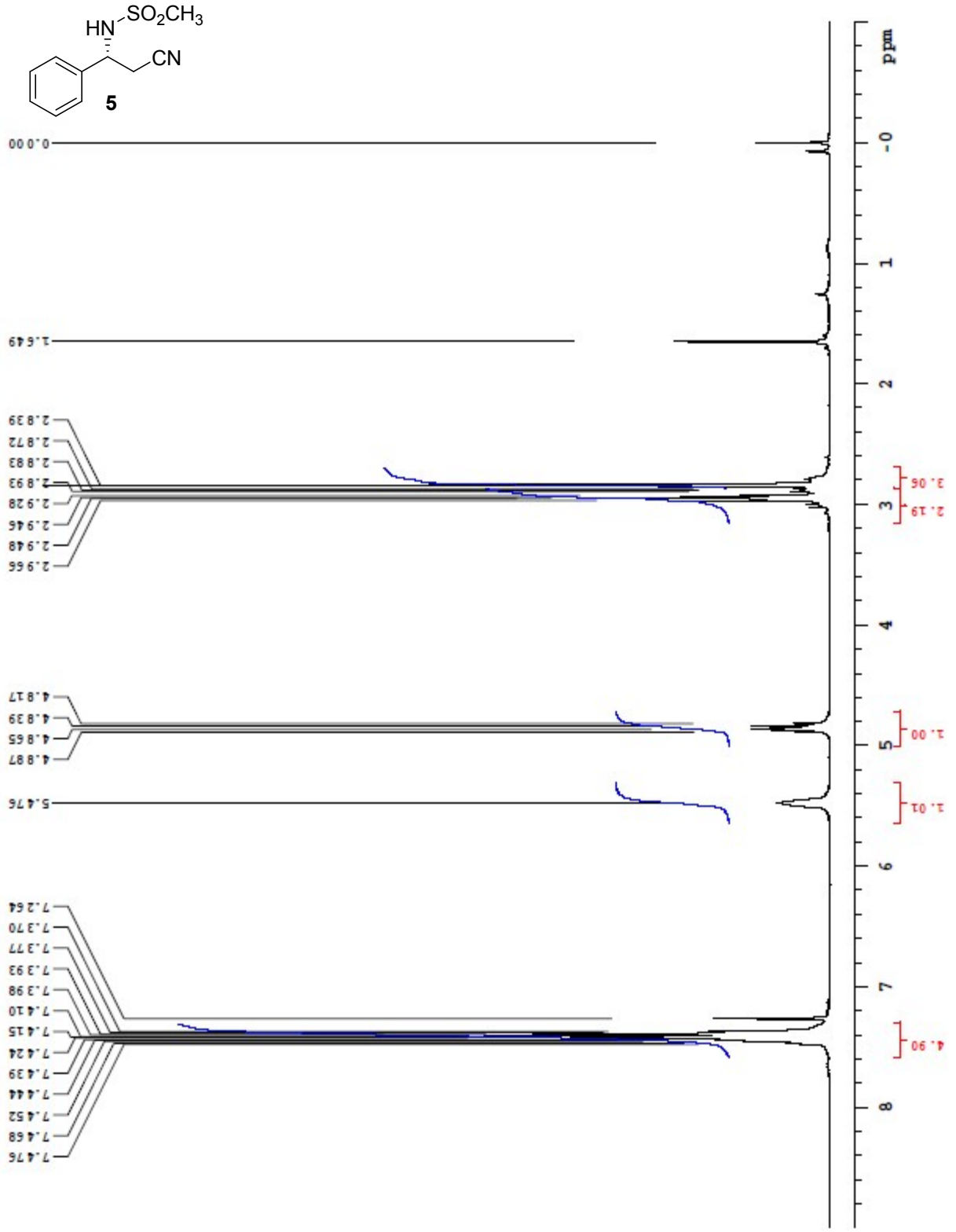
3q


0.000
1.630
1.683
2.859
2.917
2.973
3.00
5.332
5.353
5.386
0.94
6.070
1.02
7.266
7.274
7.278
7.282
7.422
7.432
7.439
7.448
7.571
7.576
0.91
0.98
1.17
ppm

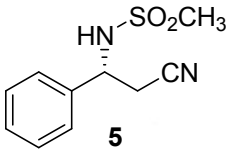
^{13}C-NMR


HN
SO2CH3
CN
S
Cl
Cl
3q
42.503
63.561
71.533
76.735
77.160
77.585
114.441
126.640
126.992
127.586
133.447
ppm
20
40
60
80
100
120
140
160
180

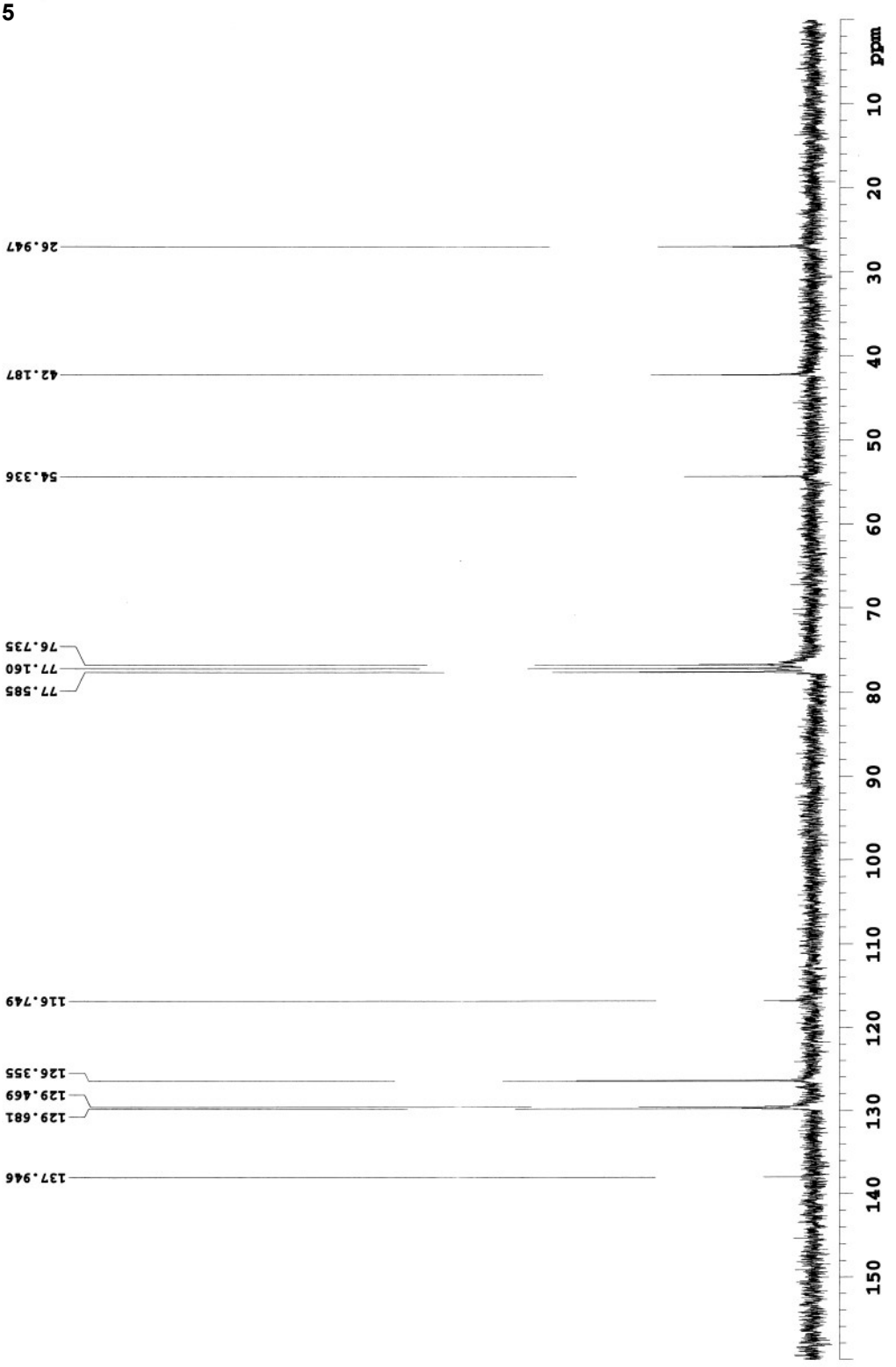
^{1}H-NMR


HN
SO2CH3
CN
5
0.000
1.649
2.839
2.872
2.883
2.893
2.928
2.946
2.948
2.966
4.817
4.839
4.865
4.887
5.476
7.264
7.370
7.377
7.393
7.398
7.410
7.415
7.424
7.439
7.444
7.452
7.458
7.476
3.06
2.19
1.00
1.01
4.90
ppm

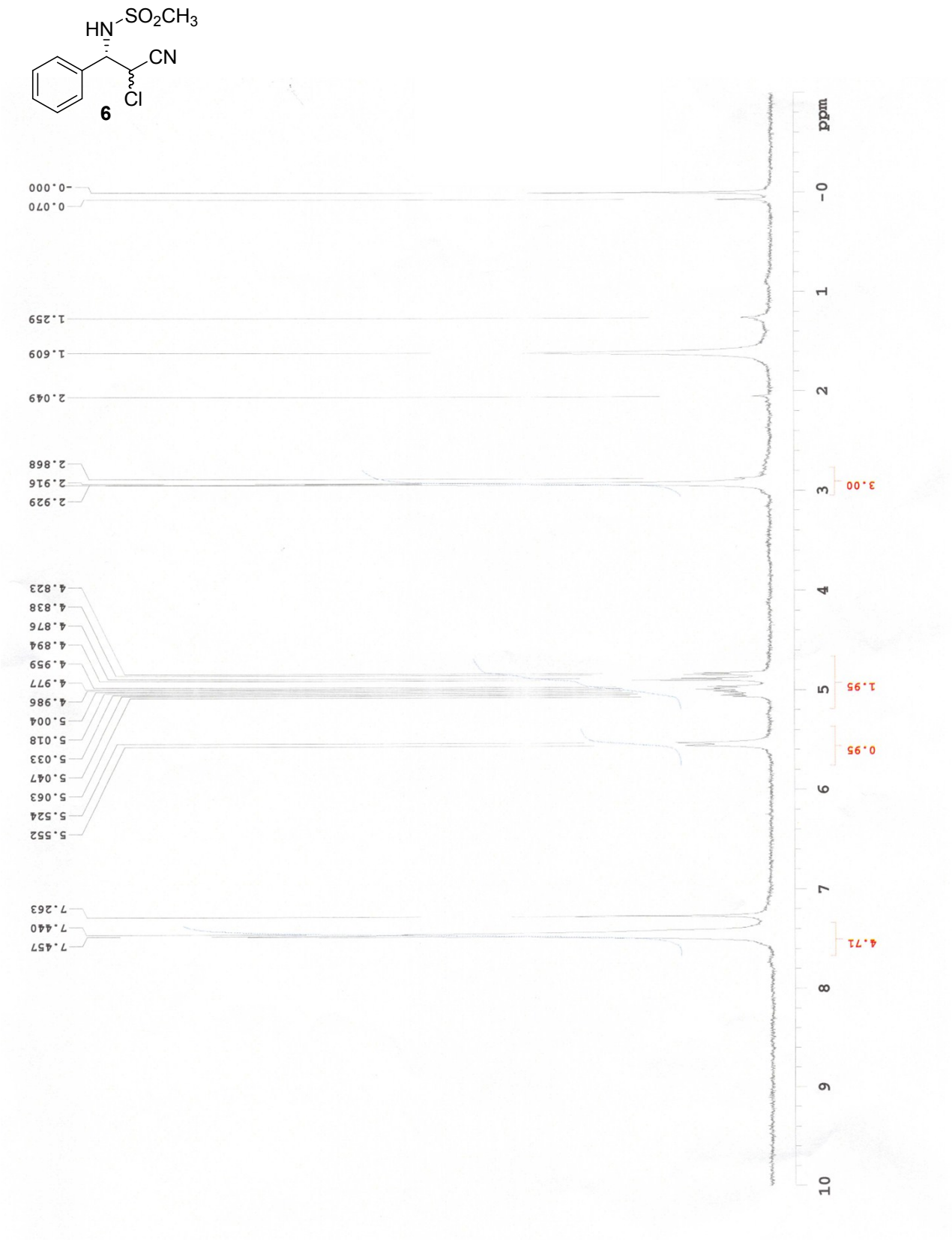
^{13}C-NMR


HN
SO2CH3
CN

5


26.947
42.187
54.336
76.735
77.160
77.585
116.749
126.355
129.469
129.681
137.946
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150

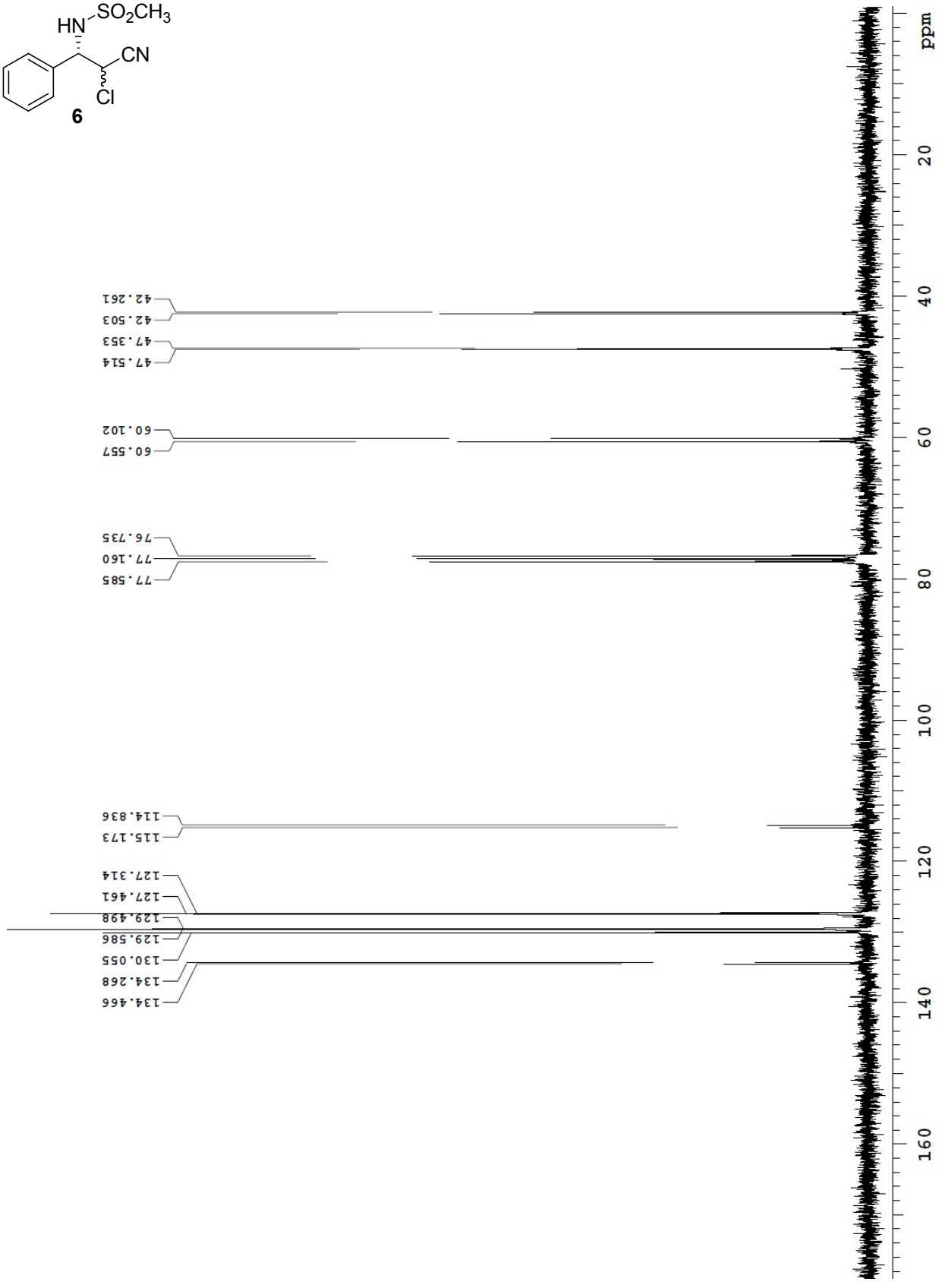
^{1}H-NMR


HN
SO2CH3
CN
Cl
6
-0.000
0.070
1.259
1.609
2.049
2.868
2.916
2.929
4.823
4.838
4.876
4.894
4.959
4.977
4.986
5.004
5.018
5.033
5.047
5.063
5.524
5.552
7.263
7.440
7.457
ppm
3.00
1.95
0.95
4.71

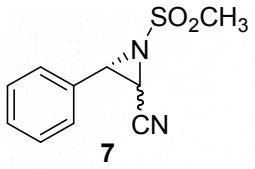
^{13}C-NMR

HN
SO2CH3
CN
Cl

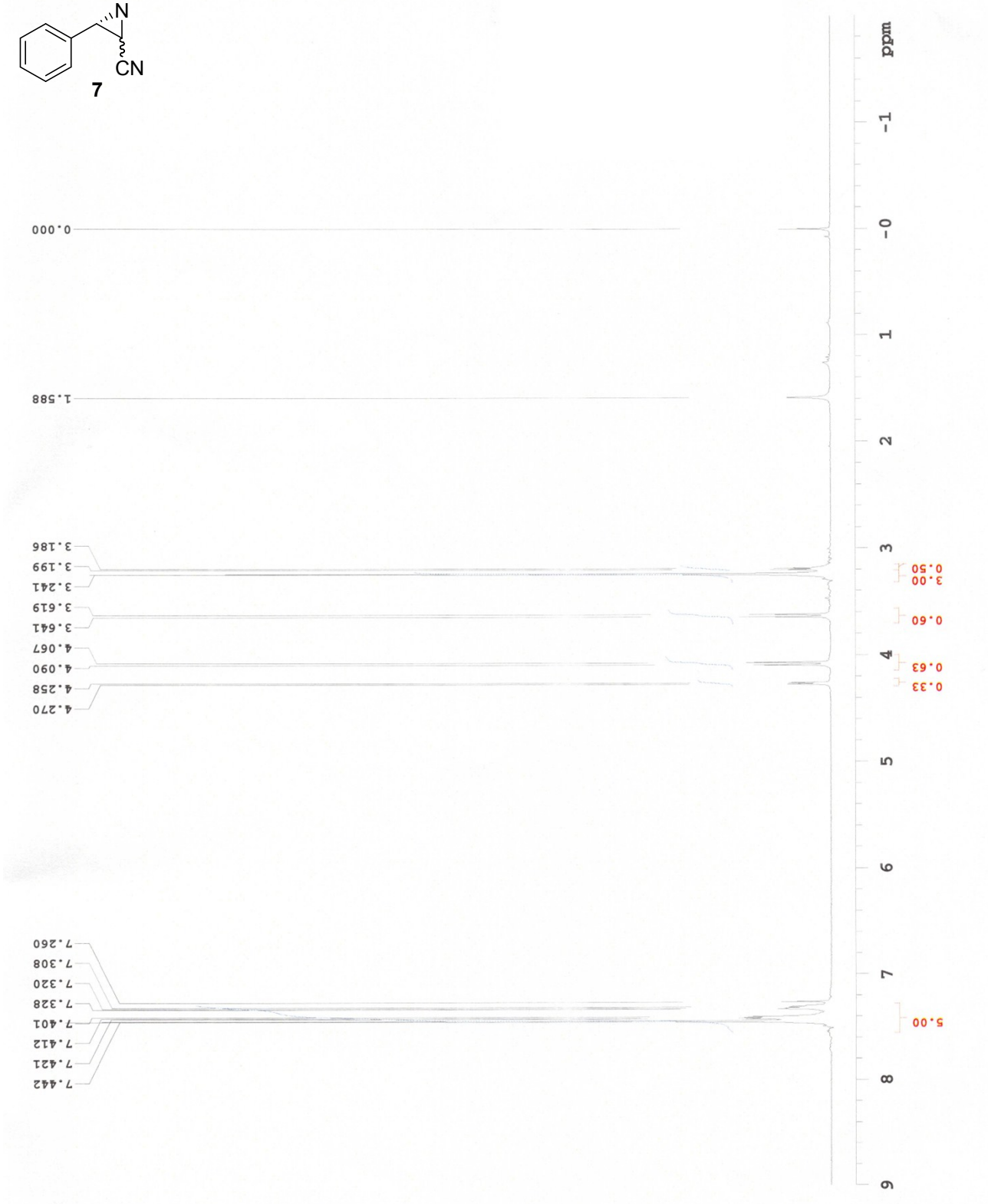
6


42.261
42.503
47.353
47.514
60.102
60.557
76.735
77.160
77.585
114.836
115.173
127.314
127.461
129.498
129.586
130.055
134.268
134.466
ppm
20
40
60
80
100
120
140
160

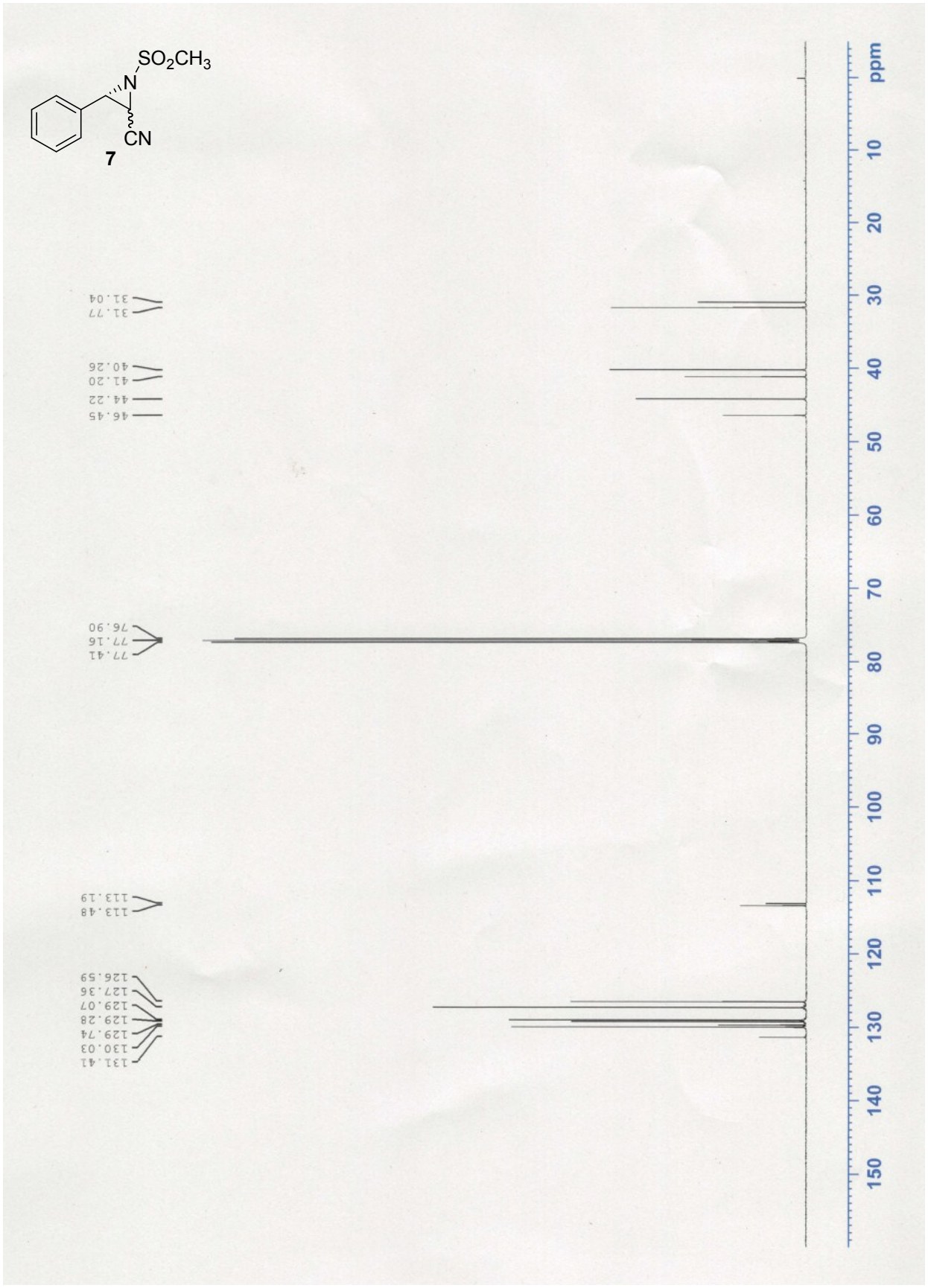
^{1}H-NMR


SO2CH3
N
CN

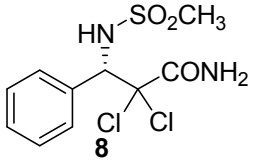
7


0.000
1.588
3.186
3.199
3.241
3.619
3.641
4.067
4.090
4.258
4.270
7.260
7.308
7.320
7.328
7.401
7.412
7.421
7.442
0.50
3.00
0.60
0.63
0.33
5.00
ppm

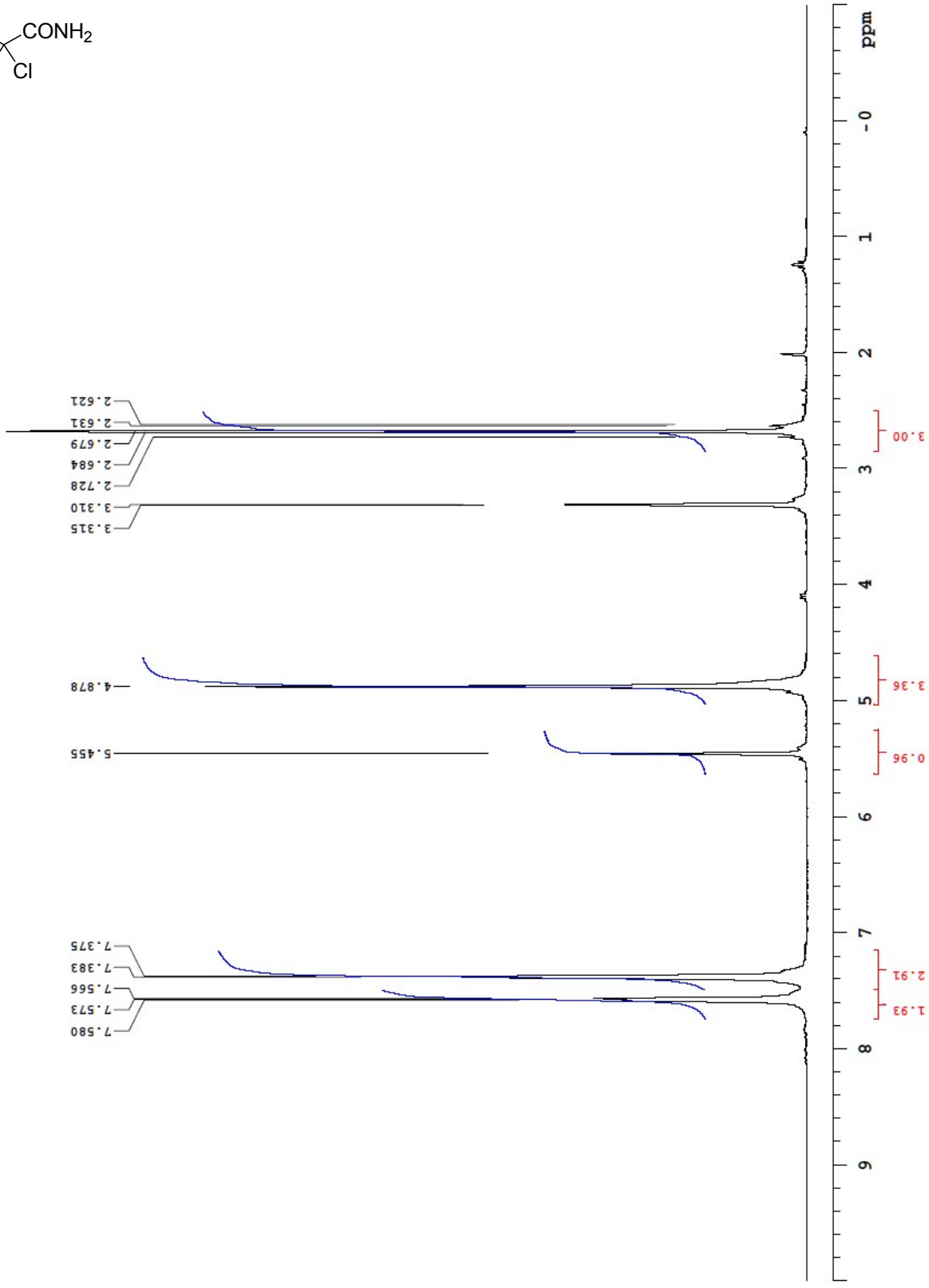
^{13}C-NMR


SO2CH3
N
CN
7
31.04
31.77
40.26
41.20
44.22
46.45
76.90
77.16
77.41
113.19
113.48
126.59
127.36
129.07
129.28
129.74
130.03
131.41
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150

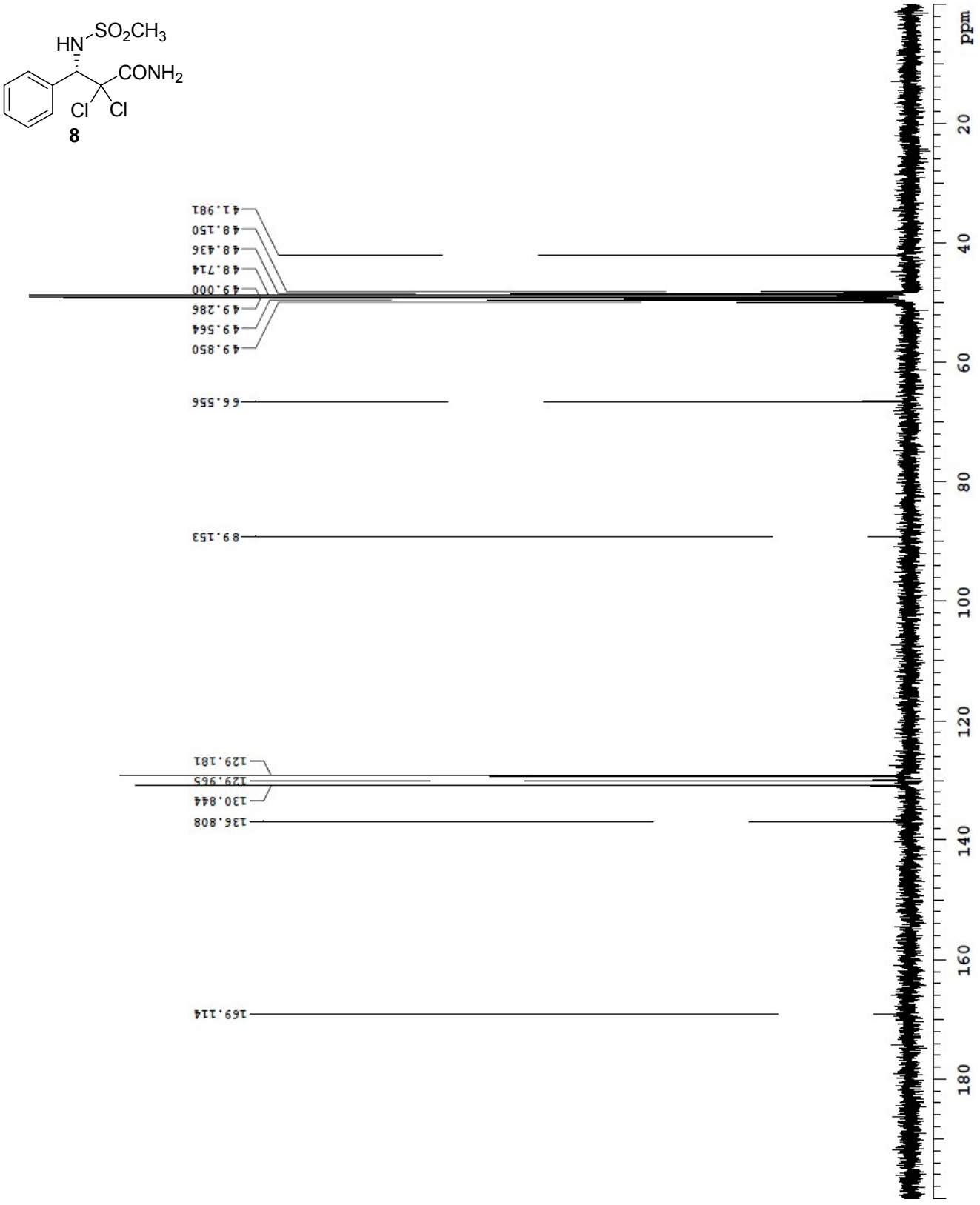
^{1}H-NMR


HN
SO2CH3
CONH2
Cl
Cl

8

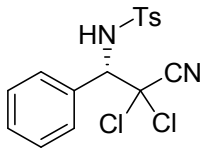

ppm
2.621
2.631
2.679
2.684
2.728
3.310
3.315
4.878
5.455
7.375
7.383
7.566
7.573
7.580
3.00
3.36
0.96
2.91
1.93

^{13}C-NMR

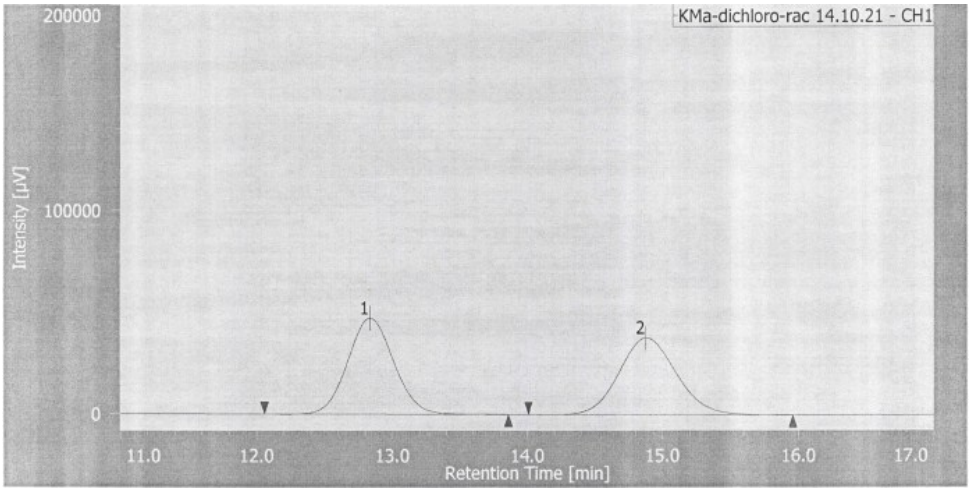

HN
SO2CH3
CONH2
Cl
Cl
8
41.981
48.150
48.436
48.714
49.000
49.286
49.564
49.850
66.556
89.153
129.181
129.965
130.844
136.808
169.114
ppm
20
40
60
80
100
120
140
160
180

HPLC Chart

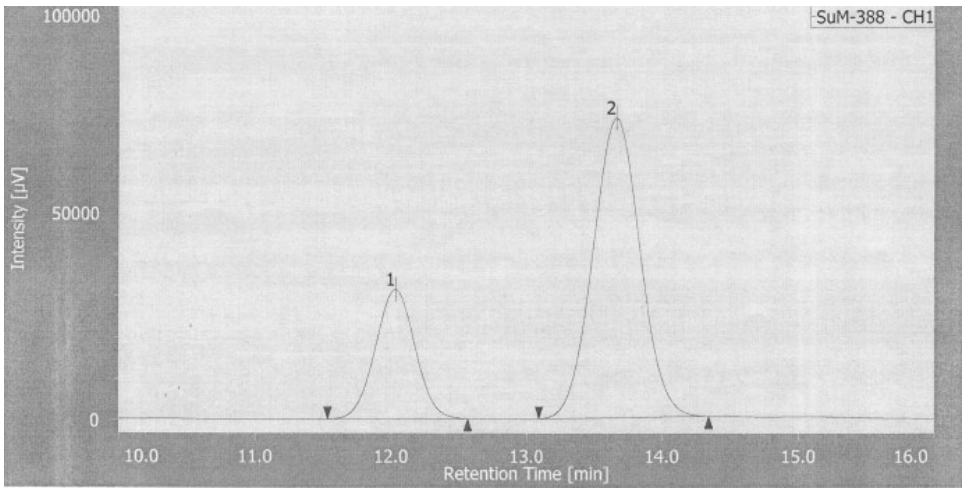
(3*S*)-3-Phenyl-2,2-dichloro-3-(toluenesulfonyl)aminopropionitrile (3a)



racemic-**3a**



(*S*)-**3a**



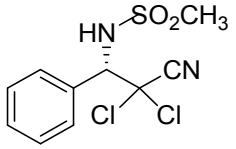
racemic-**3a**

Peak	tR (min)	Area (%)
1	12.8	50.1
2	14.9	49.9

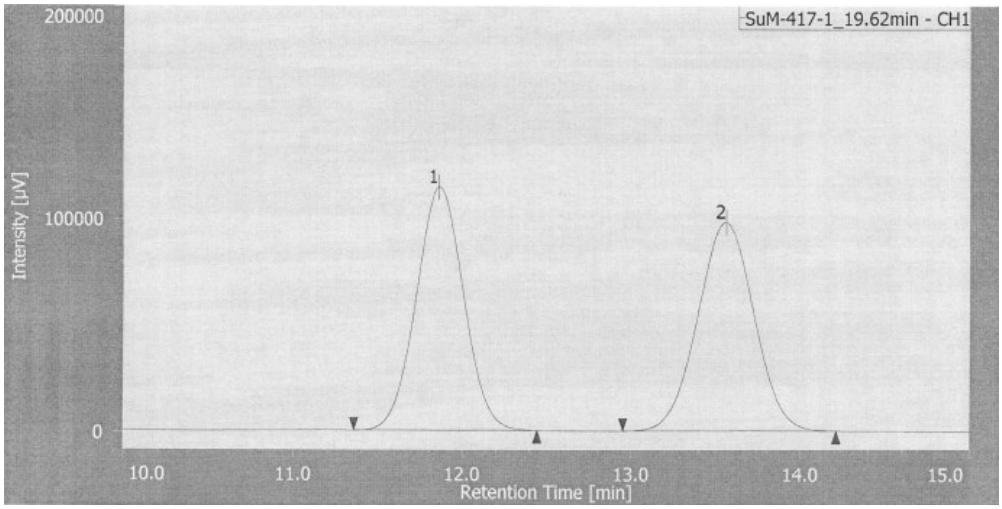
(*S*)-**3a**

Peak	tR (min)	Area (%)
1	12.0	26.6
2	13.7	73.4

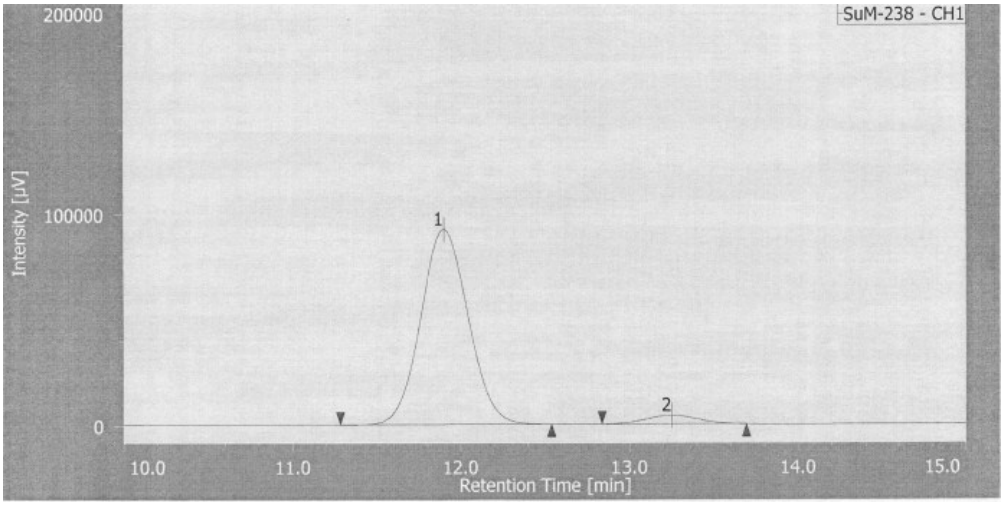
(3S) -2,2-Dichloro -3-phenyl -3-(methanesulfonyl)aminopropionitrile (3b)



racemic-**3b**



(*S*)-**3b**



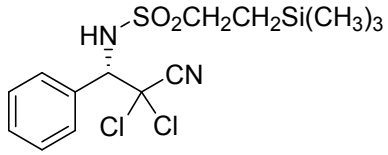
racemic-**3b**

Peak	tR (min)	Area (%)
1	11.9	49.9
2	13.6	50.1

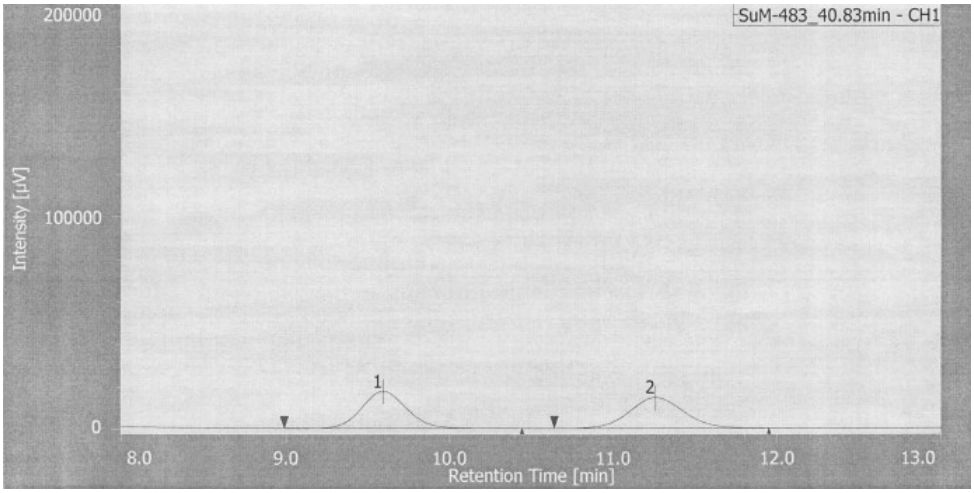
(*S*)-**3b**

Peak	tR (min)	Area (%)
1	11.99	95.5
2	13.3	4.2

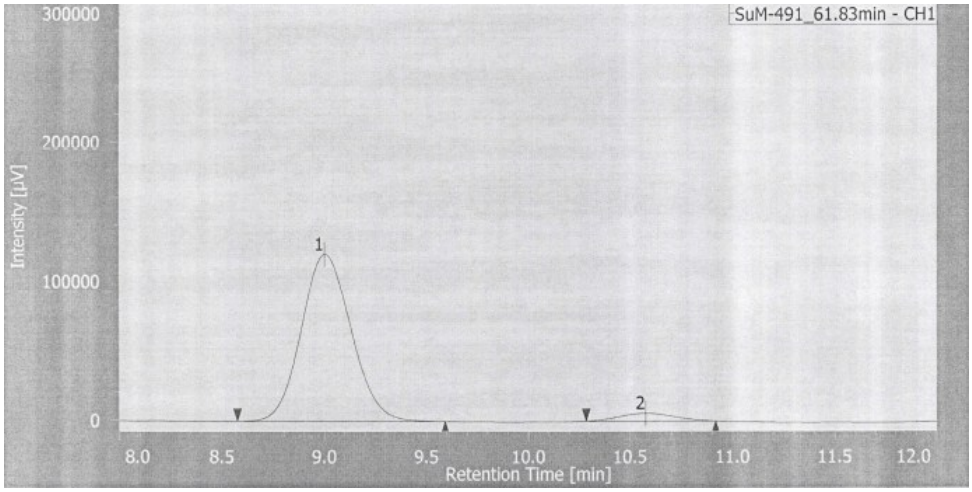
(3S) -2,2-Dichloro -3-phenyl -3-{2-(trimethylsilyl)ethanesulfonyl}aminopropionitrile (3d)



racemic-**3d**



(*S*)-**3d**



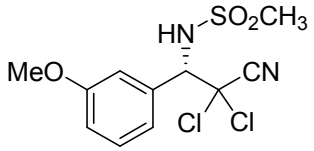
racemic-**3d**

Peak	tR (min)	Area (%)
1	9.6	50.0
2	11.3	50.0

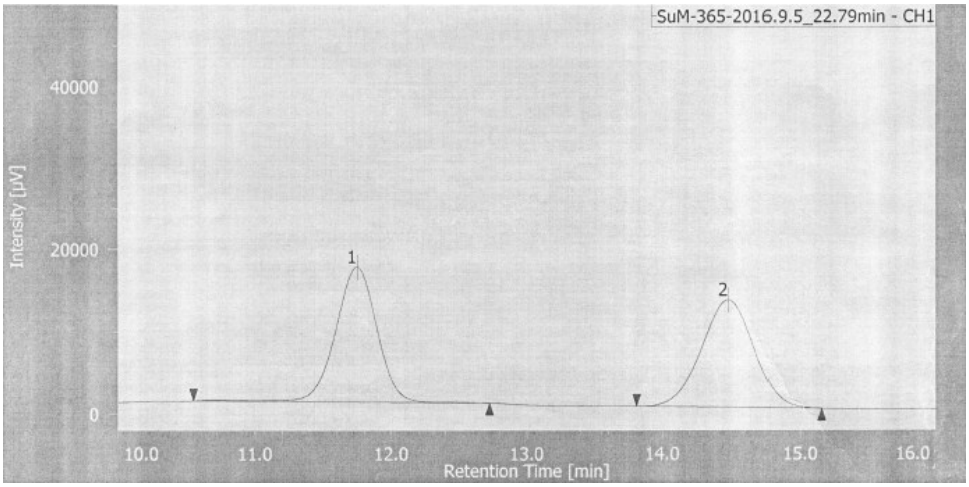
(*S*)-**3d**

Peak	tR (min)	Area (%)
1	9.0	95.2
2	10.6	4.8

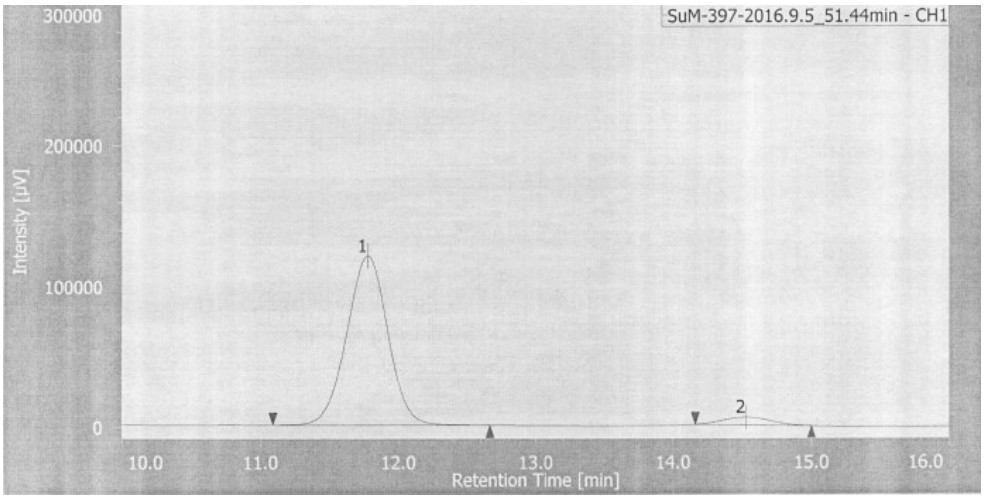
(3*S*) -2,2-Dichloro -3-(3-methoxyphenyl) -3-(methanesulfonyl)aminopropionitrile (3e)



racemic-**3e**



(*S*)-**3e**



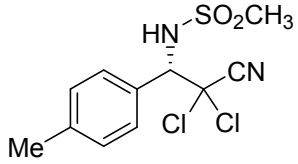
racemic-**3e**

Peak	tR (min)	Area (%)
1	11.8	50.1
2	14.5	49.9

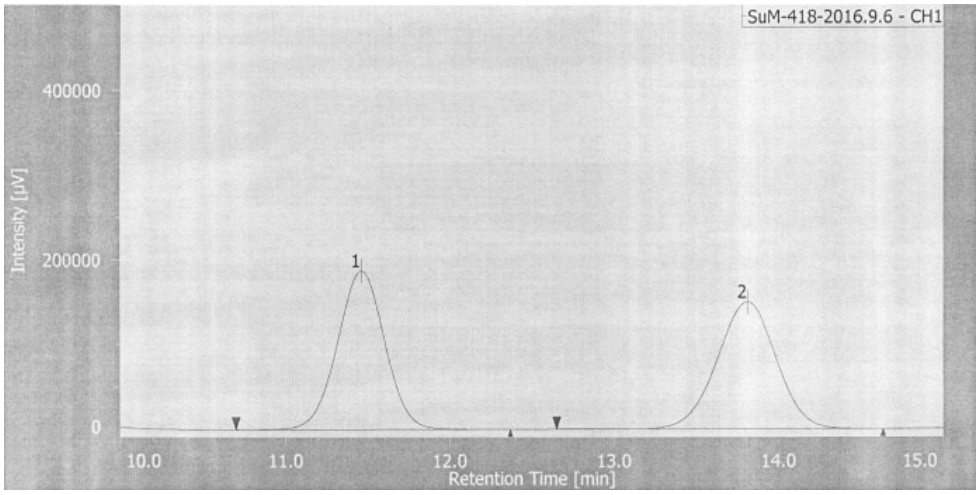
(*S*)-**3e**

Peak	tR (min)	Area (%)
1	11.8	94.8
2	14.5	5.2

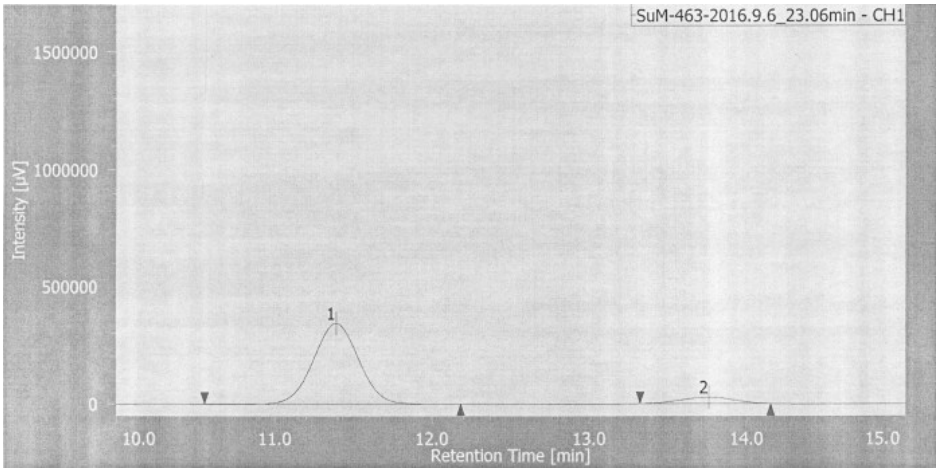
(3*S*) -2,2-Dichloro -3-(4-methyl) -3-(methanesulfonyl)aminopropionitrile (3f)



racemic-**3f**



(*S*)-**3f**



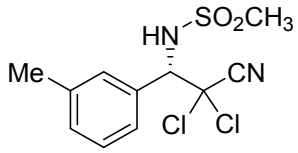
racemic-**3f**

Peak	tR (min)	Area (%)
1	11.5	50.2
2	13.8	49.8

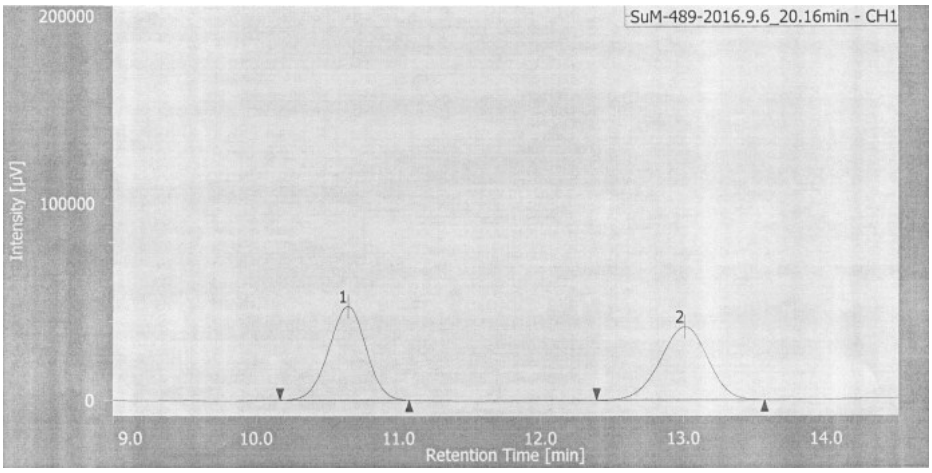
(*S*)-**3f**

Peak	tR (min)	Area (%)
1	11.4	91.6
2	13.8	8.4

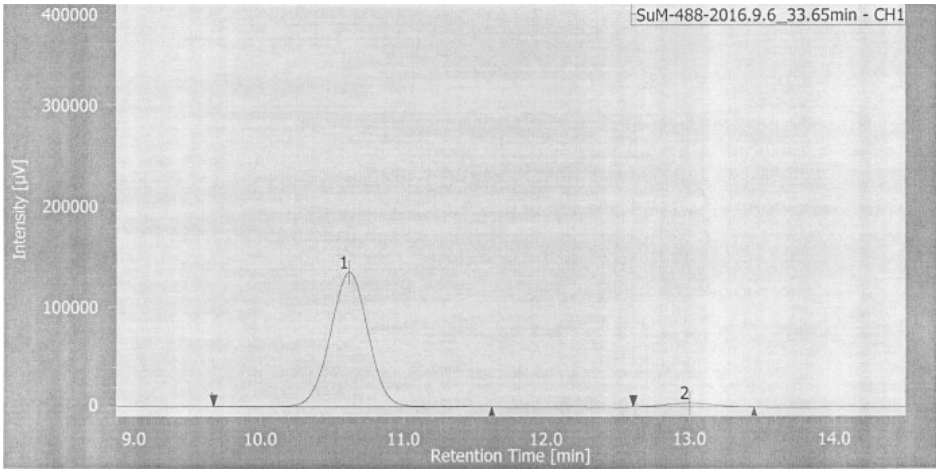
(3*S*) -2,2-Dichloro -3-(3-methyl) -3-(methanesulfonyl)aminopropionitrile (3g)



racemic-**3g**



(*S*)-**3g**



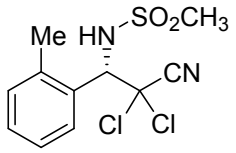
racemic-**3g**

Peak	tR (min)	Area (%)
1	10.6	50.2
2	13.0	49.8

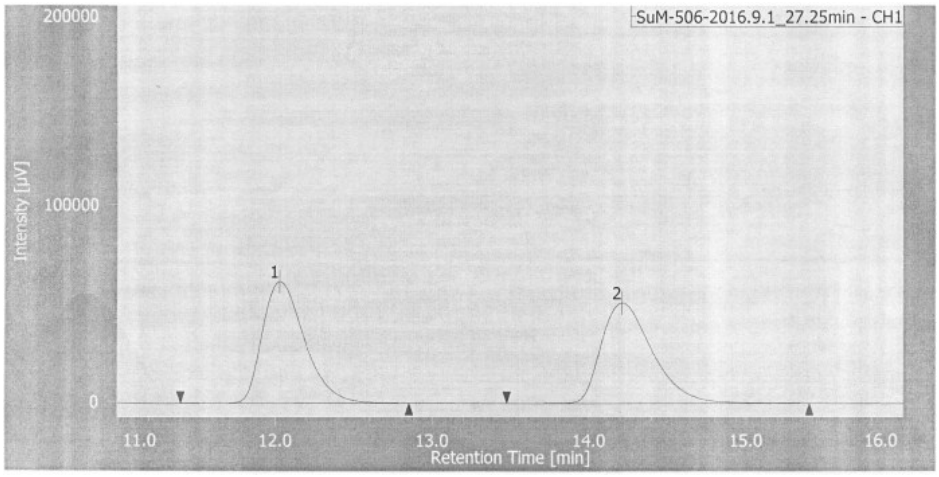
(*S*)-**3g**

Peak	tR (min)	Area (%)
1	10.6	96.5
2	13.0	3.5

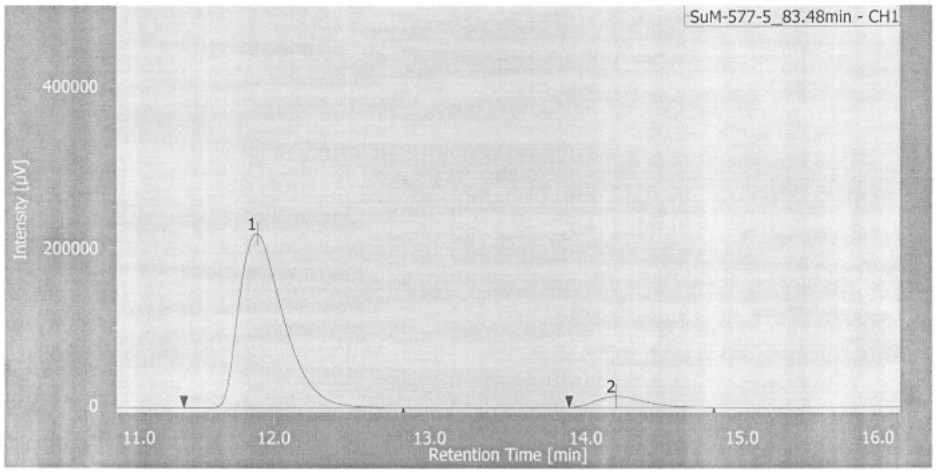
(3*S*) -2,2-Dichloro -3-(2-methyl) -3-(methanesulfonyl)aminopropionitrile (3h)



racemic-**3h**



(*S*)-**3h**



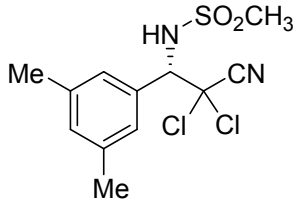
racemic-**3h**

Peak	tR (min)	Area (%)
1	12.0	49.9
2	14.2	50.1

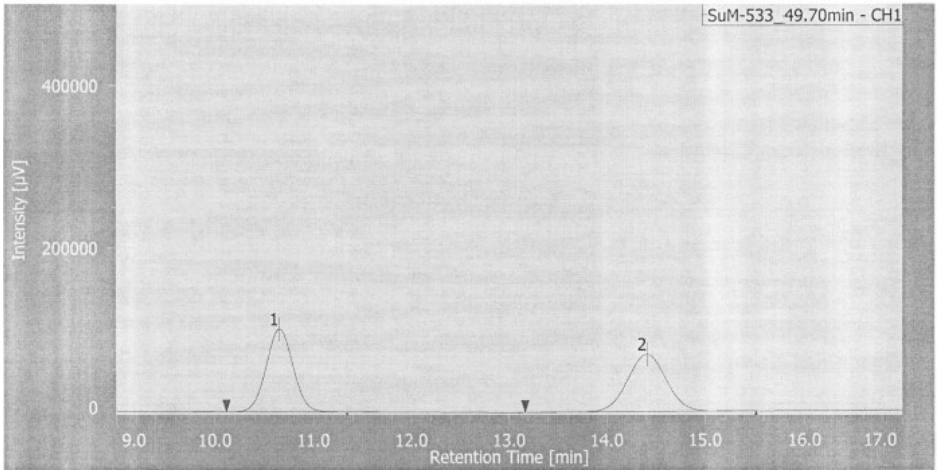
(*S*)-**3h**

Peak	tR (min)	Area (%)
1	11.9	93.4
2	14.2	6.6

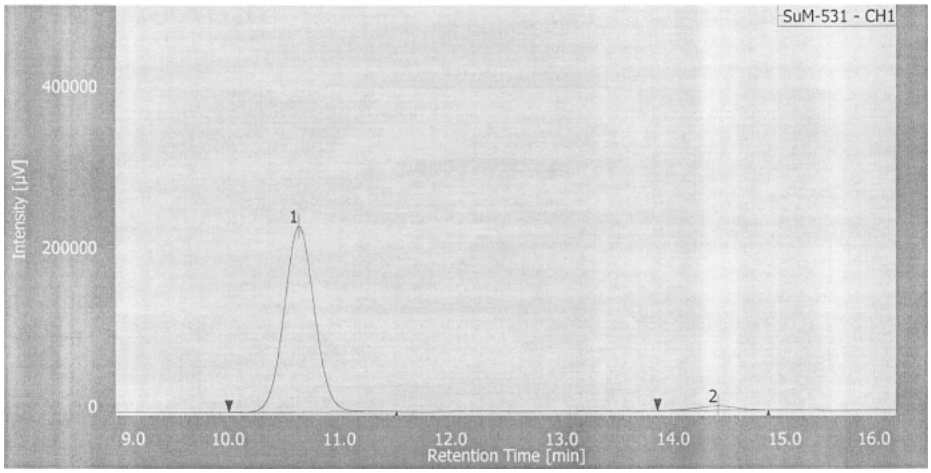
(3*S*) -2,2-Dichloro -3-(3,5-dimethylphenyl) -3-(methanesulfonyl)aminopropionitrile (3i)



racemic-**3i**



(*S*)-**3i**



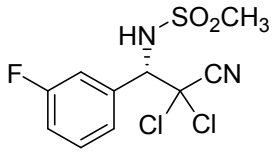
racemic-**3i**

Peak	tR (min)	Area (%)
1	10.6	50.1
2	14.4	49.9

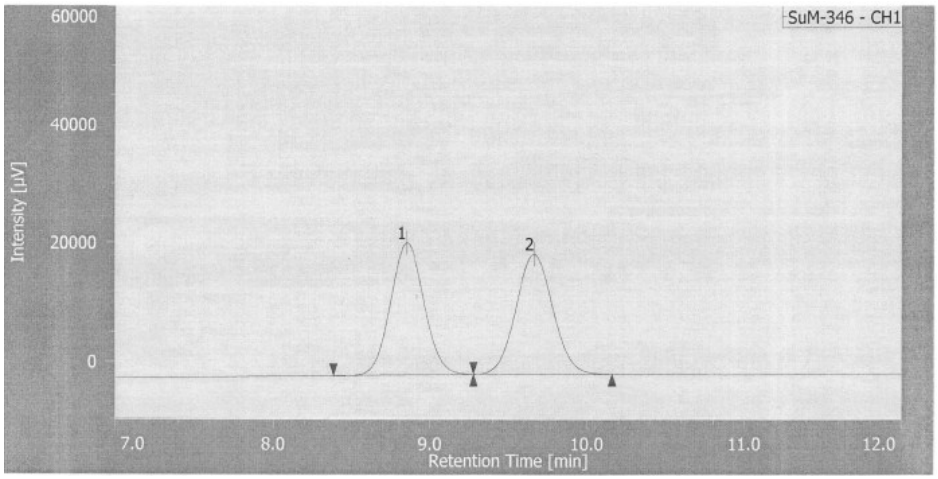
(*S*)-**3i**

Peak	tR (min)	Area (%)
1	10.6	96.9
2	14.4	3.1

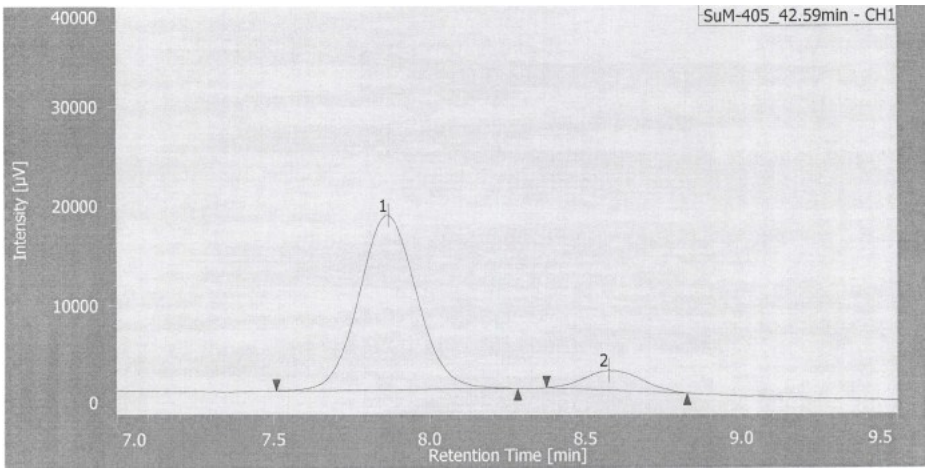
(3*S*) -2,2-Dichloro -3-(3-fluoromophenyl) -3-(methanesulfonyl)aminopropionitrile (3j)



racemic-**3j**



(*S*)-**3j**



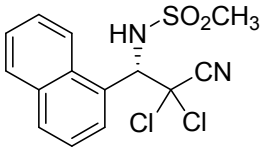
racemic-**3j**

Peak	tR (min)	Area (%)
1	8.9	50.0
2	9.7	50.0

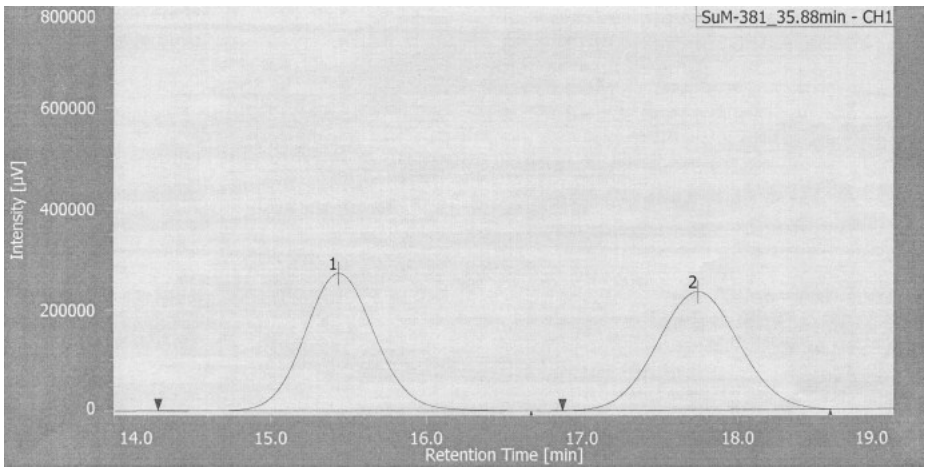
(*S*)-**3j**

Peak	tR (min)	Area (%)
1	7.9	89.9
2	8.6	10.1

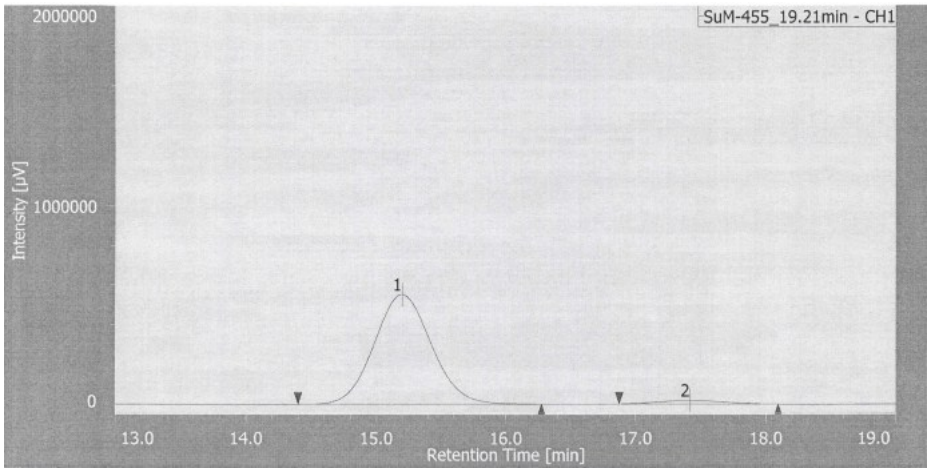
(3*S*)-2,2-Dichloro-3-(1-naphthyl)-3-(methanesulfonyl)aminopropionitrile (3k)



racemic-**3k**



(*S*)-**3k**



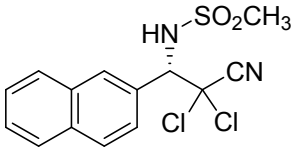
racemic-**3k**

Peak	tR (min)	Area (%)
1	15.4	49.9
2	17.7	50.1

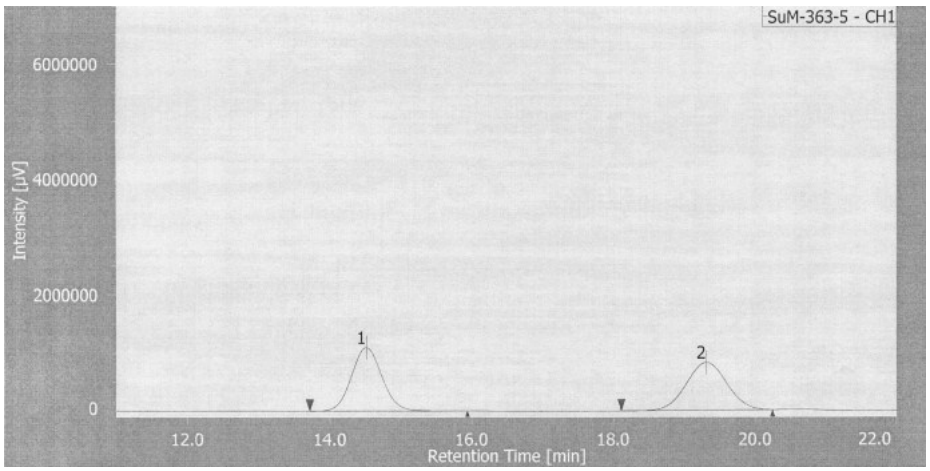
(*S*)-**3k**

Peak	tR (min)	Area (%)
1	15.2	96.7
2	17.4	3.3

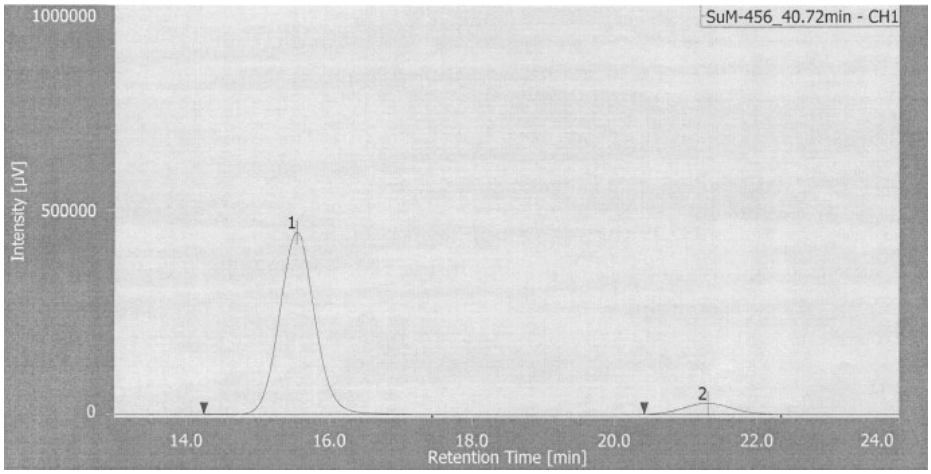
(3*S*)-2,2-Dichloro-3-(2-naphthyl)-3-(methanesulfonyl)aminopropionitrile (3l)



racemic-**3l**



(*S*)-**3l**



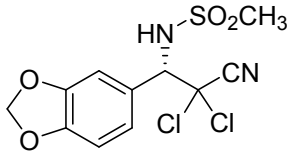
racemic-**3l**

Peak	tR (min)	Area (%)
1	14.5	49.9
2	19.3	50.1

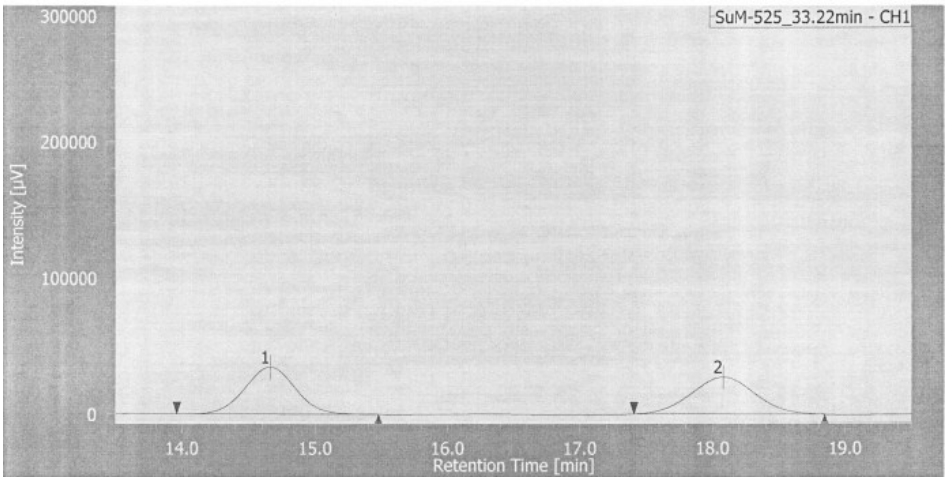
(*S*)-**3l**

Peak	tR (min)	Area (%)
1	15.5	92.5
2	21.3	7.5

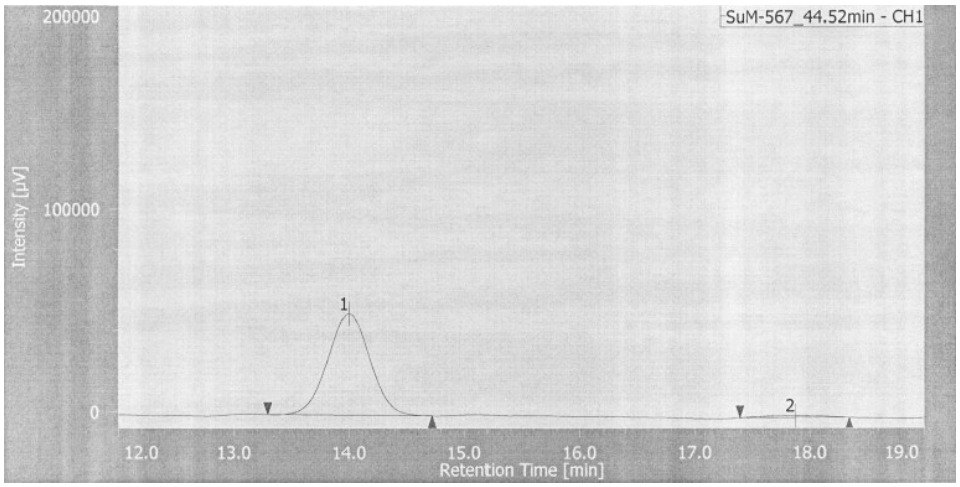
(3*S*) -2,2-dichloro-3-(4,5-Methylenedioxyphenyl) -3-(methanesulfonyl)aminopropionitrile (3m)



racemic-**3m**



(*S*)-**3m**



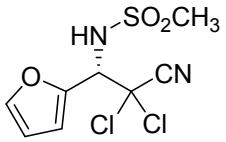
racemic-**3m**

Peak	tR (min)	Area (%)
1	14.6	50.1
2	18.1	49.9

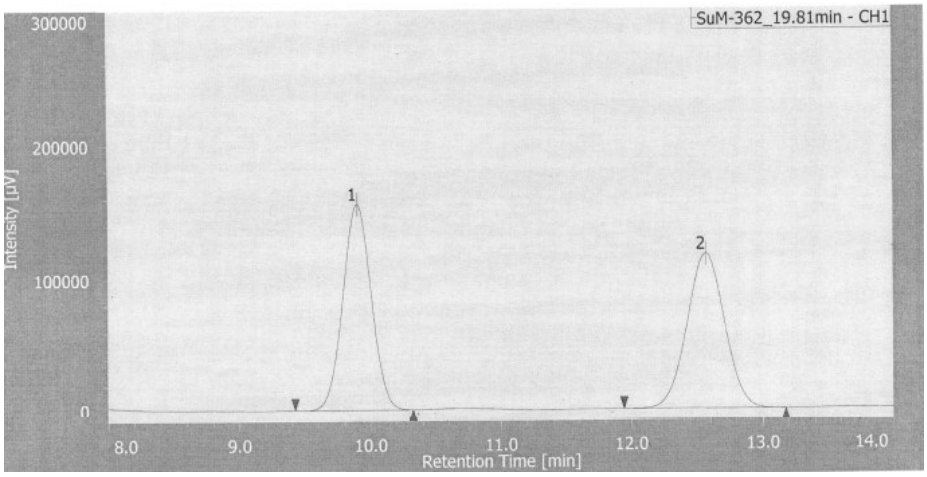
(*S*)-**3m**

Peak	tR (min)	Area (%)
1	14.0	97.1
2	17.9	2.9

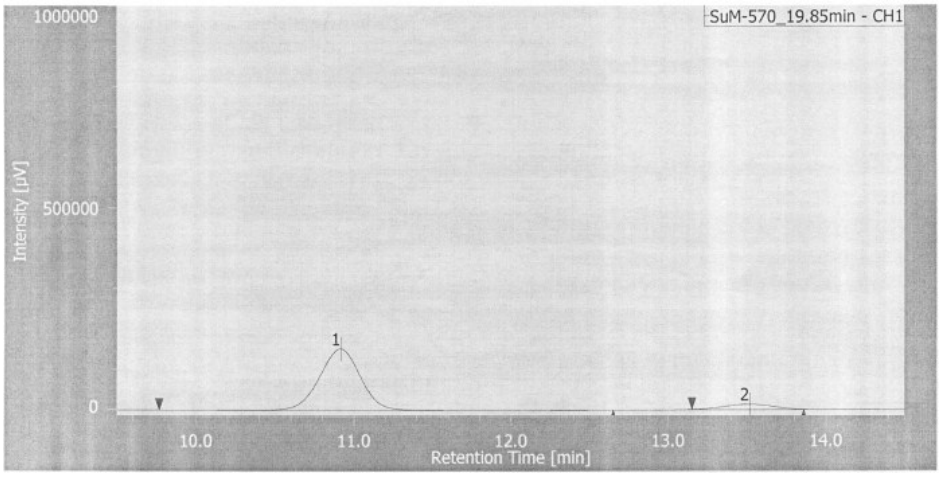
(3*S*)-2,2-Dichloro-3-(2-furyl)-3-(methanesulfonyl)aminopropionitrile (3n)



racemic-**3n**



(*S*)-**3n**



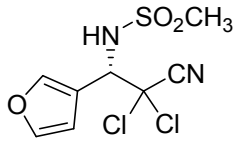
racemic-**3n**

Peak	tR (min)	Area (%)
1	9.9	50.0
2	12.6	50.0

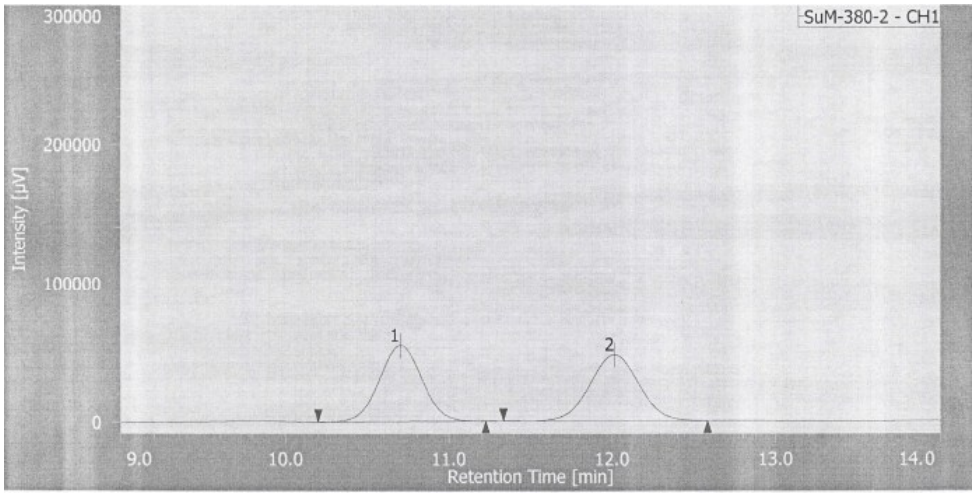
(*S*)-**3n**

Peak	tR (min)	Area (%)
1	10.9	89.9
2	13.5	10.1

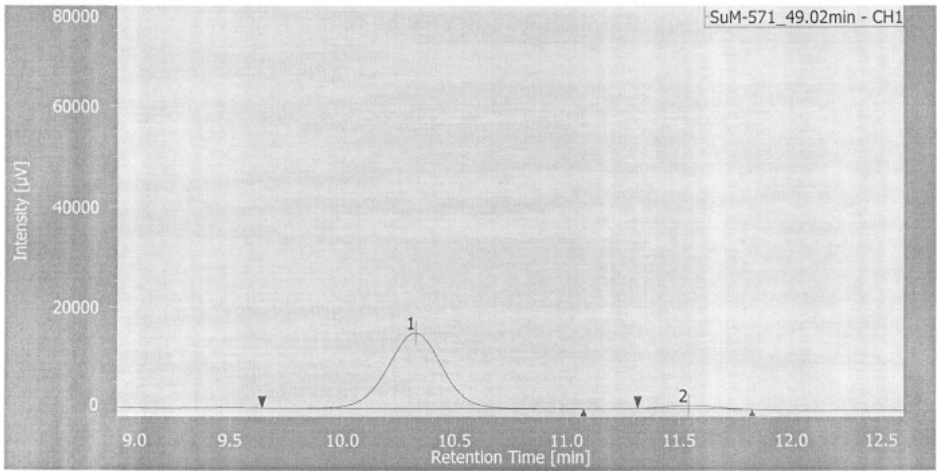
(3*S*)-2,2-Dichloro-3-(3-furyl)-3-(methanesulfonyl)aminopropionitrile (3o)



racemic-**3o**



(*S*)-**3o**



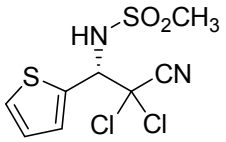
racemic-**3o**

Peak	tR (min)	Area (%)
1	10.7	50.0
2	12.0	49.9

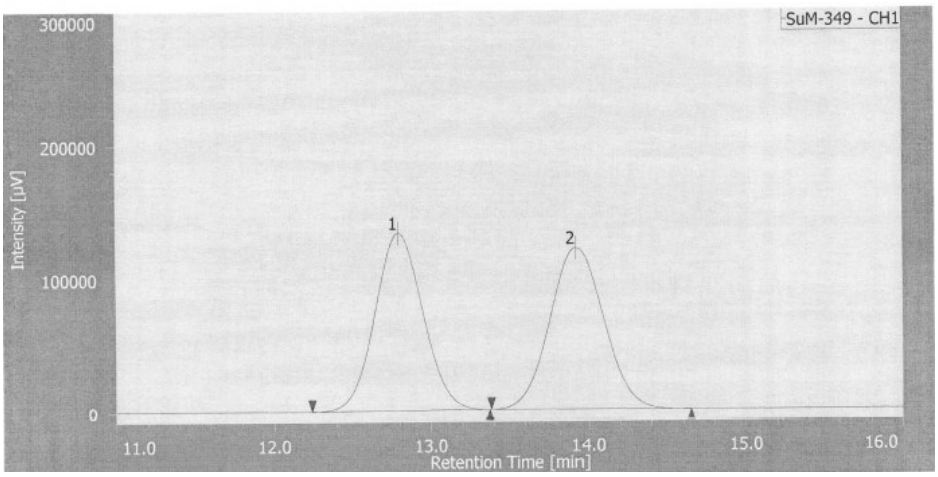
(*S*)-**3o**

Peak	tR (min)	Area (%)
1	10.3	96.4
2	11.5	3.6

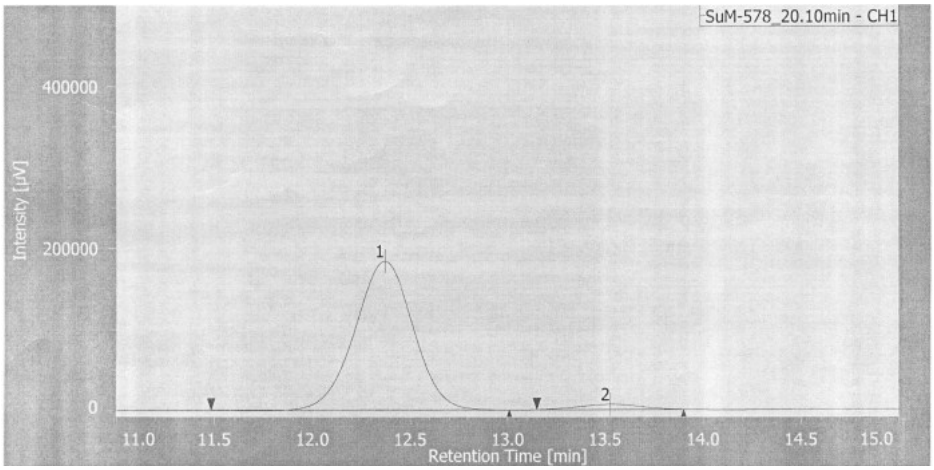
(3*S*)-2,2-Dichloro-3-(2-thienyl)-3-(methanesulfonyl)aminopropionitrile (3p)



racemic-**3p**



(*S*)-**3p**



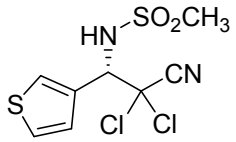
racemic-**3p**

Peak	tR (min)	Area (%)
1	12.8	50.0
2	13.9	50.0

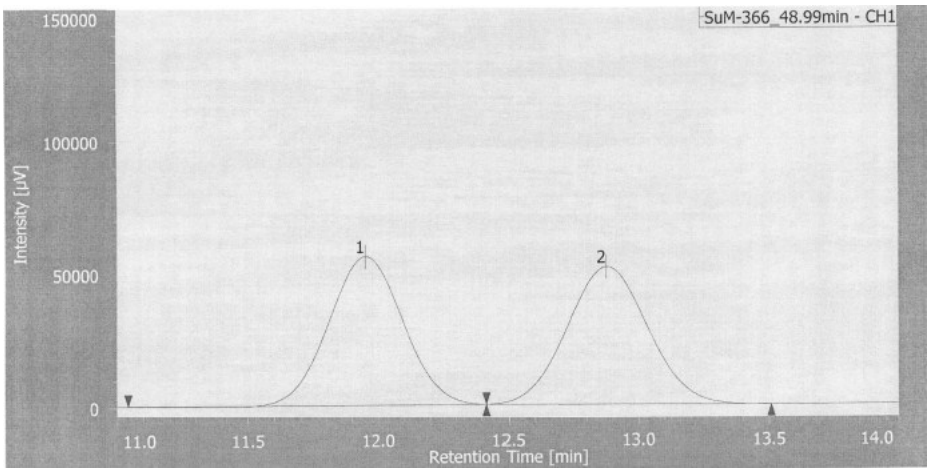
(*S*)-**3p**

Peak	tR (min)	Area (%)
1	12.4	96.5
2	13.5	3.5

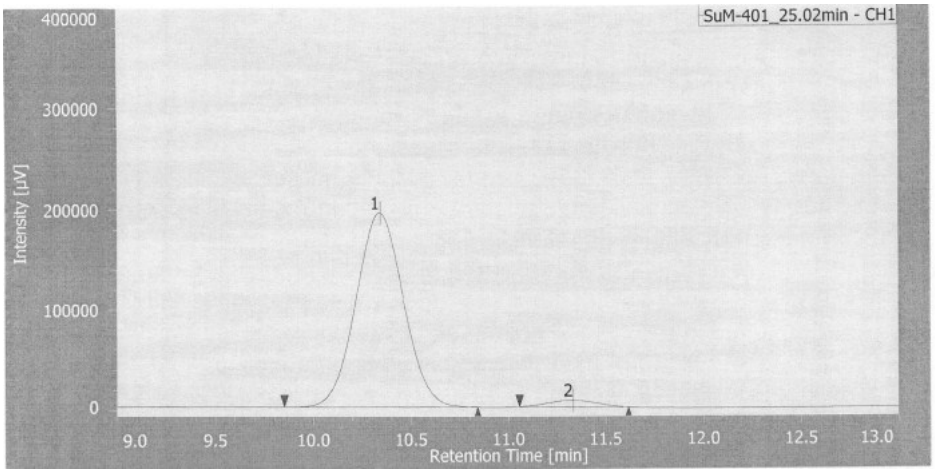
(3*S*)-2,2-Dichloro-3-(3-thienyl)-3-(methanesulfonyl)aminopropionitrile (3q)



racemic-**3q**



(*S*)-**3q**



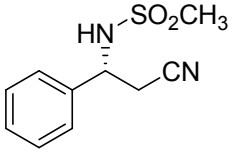
racemic-**3q**

Peak	tR (min)	Area (%)
1	12.0	49.8
2	12.9	50.2

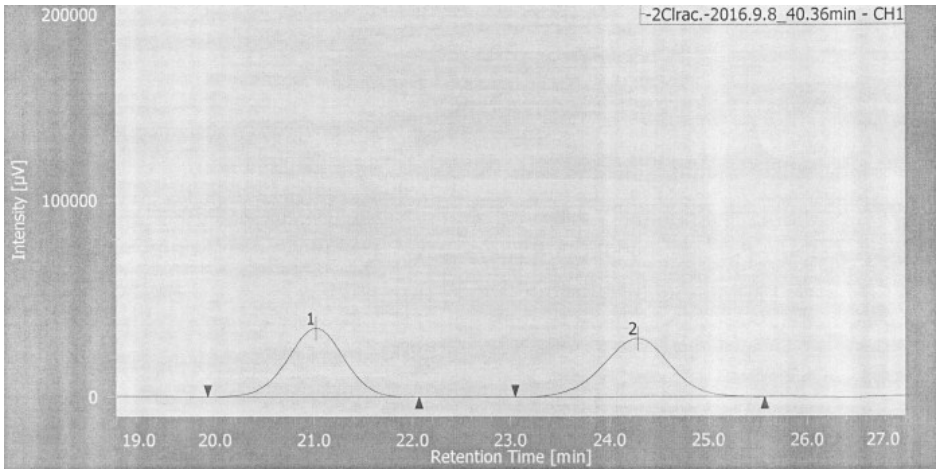
(*S*)-**3q**

Peak	tR (min)	Area (%)
1	10.3	96.7
2	11.3	3.3

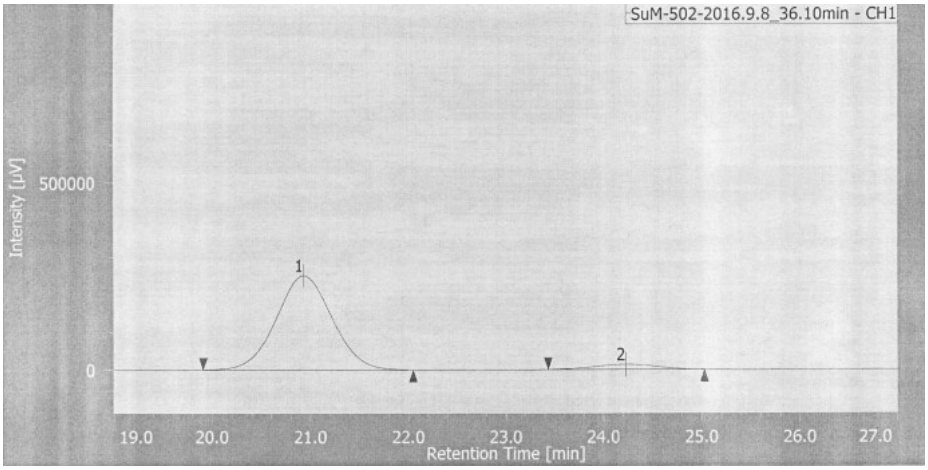
(3*R*)-3-Phenyl-3-(methanesulfonyl)aminopropionitrile (5)



racemic-**5**



(*R*)-**5**



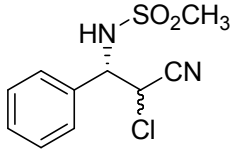
racemic-**5**

Peak	tR (min)	Area (%)
1	21.0	50.1
2	24.3	49.9

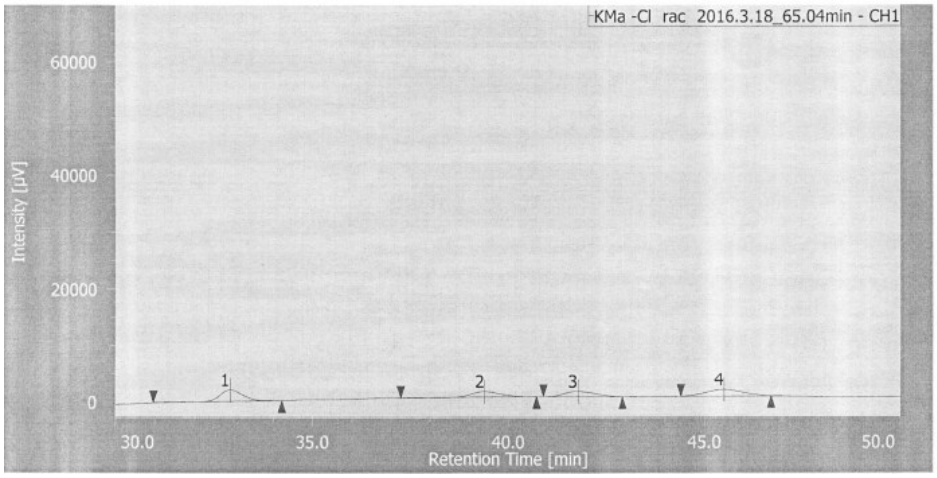
(*R*)-**5**

Peak	tR (min)	Area (%)
1	20.9	94.4
2	24.2	5.6

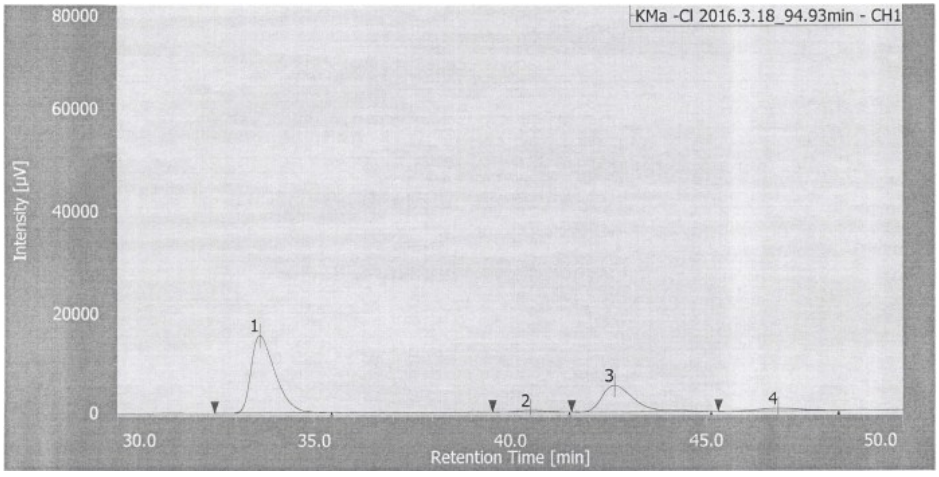
(3*S*) -2-Chloro -3-phenyl-3-(methanesulfonyl)aminopropionitrile (6)



racemic-**6**



(*S*)-**6**



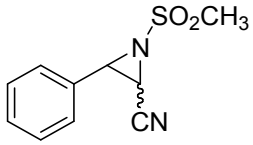
racemic-**6**

Peak	tR (min)	Area (%)
1	32.9	30.2
2	39.4	19.4
3	41.8	19.8
4	45.5	30.7

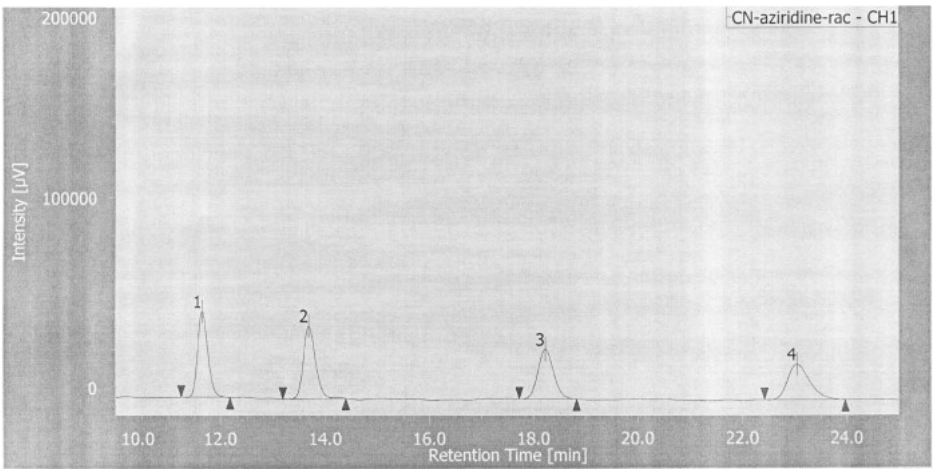
(*S*)-**6**

Peak	tR (min)	Area (%)
1	33.6	64.5
2	40.5	1.7
3	42.6	29.8
4	46.8	4.0

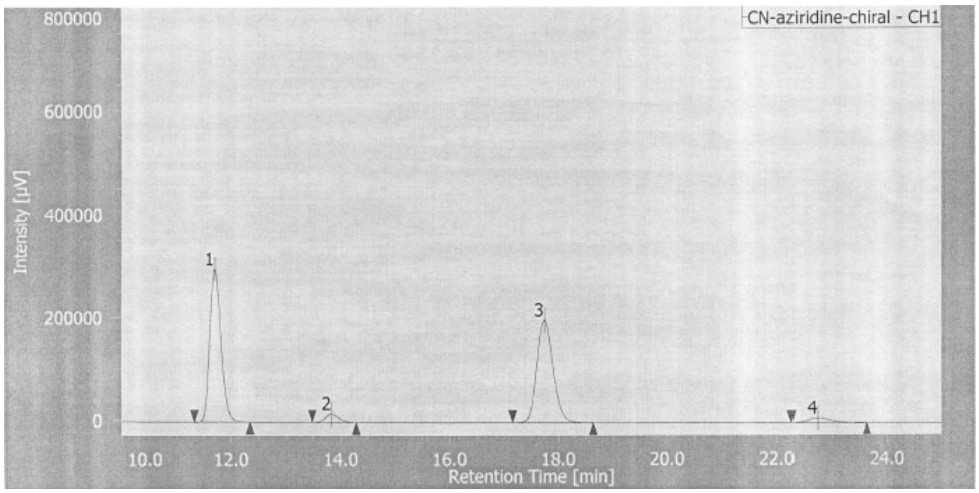
(2*R*,3*S*)- and (2*S*,3*S*)-1-(methanesulfonyl)-3-phenylaziridine-2-carbonitrile (7)



racemic-**7**



(*S*)-**7**



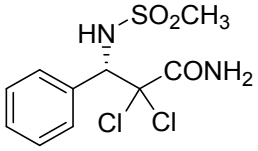
racemic-**7**

Peak	tR (min)	Area (%)
1	11.7	26.5
2	13.7	26.8
3	18.2	23.5
4	23.0	23.3

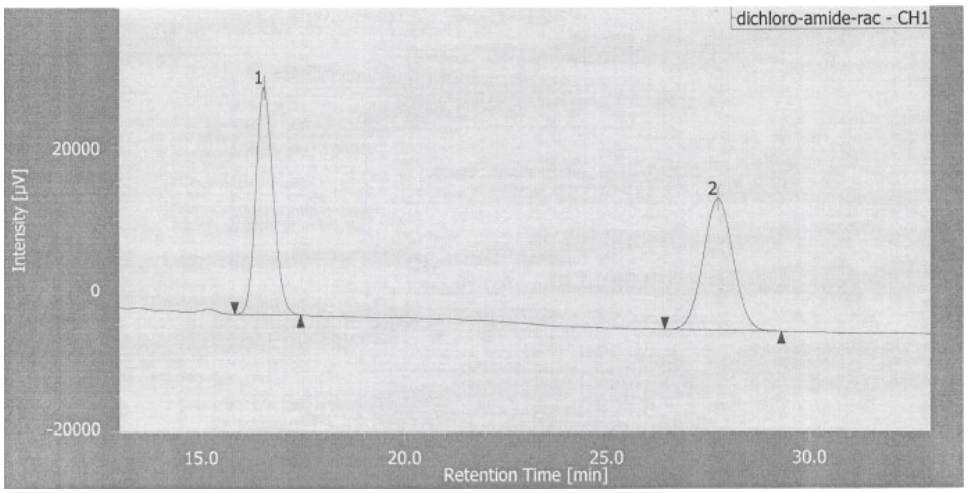
(*S*)-**7**

Peak	tR (min)	Area (%)
1	11.7	47.6
2	13.8	3.0
3	17.8	46.6
4	22.7	2.8

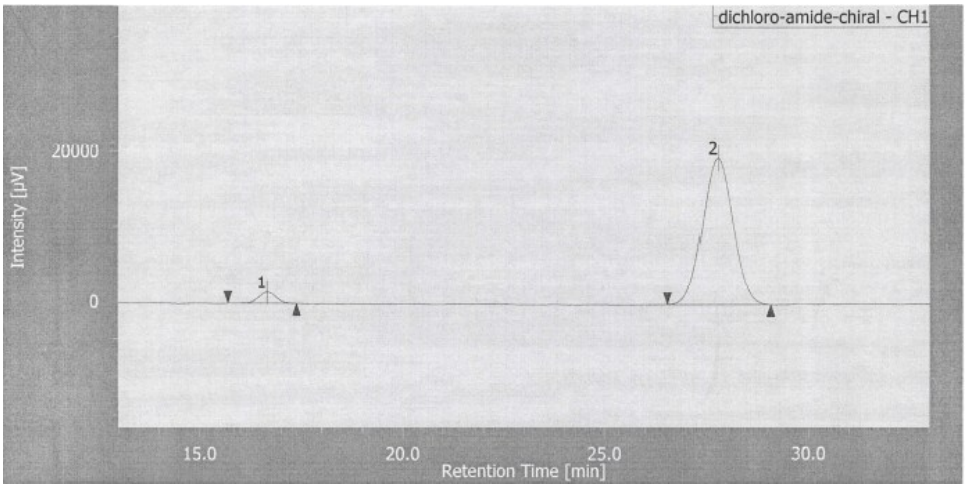
(3*S*)-3-Phenyl-2,2-dichloro-3-(methanesulfonyl) aminopropionamide (8)



racemic-**8**



(*S*)-**8**



racemic-**8**

Peak	tR (min)	Area (%)
1	16.5	50.0
2	27.8	50.0

(*S*)-**8**

Peak	tR (min)	Area (%)
1	16.7	4.4
2	27.8	95.6