SUPPORTING INFORMATION

Alkynes as Masked Ylides: Gold Catalysed Intermolecular Reactions of Propargylic Carboxylates with Thioethers.

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General Experimental

All reactions were carried out under Ar in flame-dried glassware. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF (Na), Et_2O (Na), CH_2Cl_2 (P_4O_{10}), Et_3N (CaH_2), toluene (Na). Anhydrous $ClCH_2CH_2Cl$ was purchased from Aldrich.

Flash chromatography: Fluorochem silica gel 60 (40-63 μ). IR: Perkin–Elmer Paragon 1600 FTIR spectrometer spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS and HRMS (EI): VG-ZabSpec, MS and HRMS (ES): Micromass LCT. Melting points: Kofler hot stage. Elemental analyses: Carlo Erba EA1110. All commercially available compounds (Fluka, Lancaster, Aldrich) were used as received. NMR: Spectra were recorded on Bruker AC300, AV300 and Bruker AV400 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_C \equiv 77.0$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H \equiv 7.26$ ppm; CD_2Cl_2: $\delta_C \equiv 53.8$ ppm; residual CH_2Cl_2 in CD_2Cl_2: $\delta_H \equiv 5.32$ ppm). ***Where indicated, the signal assignments in the NMR spectra are unambiguous***; the numbering scheme is arbitrary and is shown in the inserts. The assignments are based upon 1D and 2D spectra recorded using the following pulse sequences from the Bruker standard pulse program library: PENDANT, DEPT 45, DEPT 135; Gradient COSY 90; Gradient HSQC for ^1J(C,H) = 145 Hz; Gradient HMBC for correlations via ^nJ(C,H). HPLC was performed on a Dionex Summit instrument: %ee determined by HPLC (Chiralpak AD column, 2-propanol : hexane = 5 : 95)

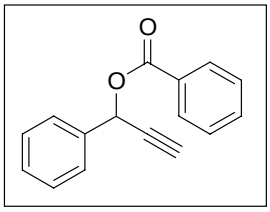
Starting Materials

All the propargylic carboxylate derivatives were prepared using the following standard procedure from the propargylic alcohol.

Acylation Reaction: General Procedure (GP 1). The acylating reagent (1.2 eq.) is added to a solution of triethylamine (1.4 eq.) and propargylic alcohol (1 eq.) in dichloromethane (4 ml/mmol) at 0 °C under Ar. The reaction mixture is stirred 1-2 h and then treated with sat. $NH_4Cl_{(aq)}$, then with brine and extracted with ethyl acetate. Removal of solvent under reduced pressure affords a residue which is purified by flash chromatography in ethyl acetate/hexanes to afford the analytically pure propargylic carboxylates.

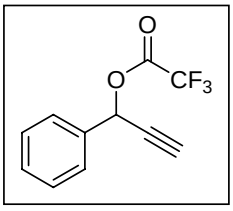
The following compounds were prepared by this method:

1-Phenylprop-2-ynyl benzoate



colourless crystals (4.66 mmol, 83% yield); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.08 (m, 2 H), 7.64-7.65 (m, 3 H), 7.47-7.39 (m, 5 H), 6.70 (d, *J* 2.2, 1 H), 2.70 (d, *J* 2.2, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 165.2, 136.5, 133.3, 129.8 (2 C), 129.5, 129.0, 128.7 (2 C), 128.3 (2 C), 127.6 (2 C), 80.2, 75.6, 65.8; IR (NaCl): *v* = 3300, 1723, 1105, 1095, 739, 705; HR-MS (ES-TOF): *m/z*: calcd for $C_{16}H_{12}O_2Na$: 259.0735, found 259.0730 [*M*+*Na*].

1-Phenylprop-2-ynyl 2,2,2-trifluoroacetate

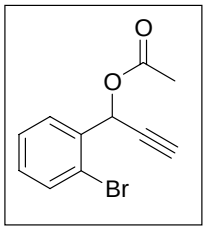


colourless oil (8.10 mmol, quant.); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.57 (m, 2 H), 7.44 (m, 3 H), 6.52 (d, *J* 2.3, 1 H), 2.82 (d, *J* 2.3, 1 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 156.4 (q, *J* 43.1), 134.1, 130.0, 129.0 (2 C), 128.0 (2 C), 114.3 (q, *J* 285.8), 77.9, 77.7, 69.5; IR (NaCl): *v* = 3300, 1789, 1372, 1226, 1172, 1147, 891, 760, 696; MS(EI) 228 (M^+, 31%), 159 (5), 131 (22), 115 (100).

1-(2-bromophenyl)prop-2-ynyl acetate

n-BuLi (2.5 M solution in hexanes, 3.2 mL, 8.5 mmol) was added to a solution of ethynyltrimethylsilane (1.2 mL, 8.5 mmol) in anhydrous THF (20 mL) at -78 °C under Ar. The reaction was stirred at -78 °C for 20 min before the addition of the *o*-bromobenzaldehyde (0.7 mL, 6 mmol). The resulting mixture was allowed to warm to 0 °C and was stirred for 2 h. The reaction mixture was quenched with aqueous NH_4Cl, and extracted with ethyl acetate.

The combined organic phases were washed with brine, dried over Na_2SO_4 and filtered. After evaporation of the filtrate, the residue was treated with K_2CO_3 (12 mmol) in methanol (20 mL). The mixture was stirred at RT until hydrolysis was complete. The reaction mixture was quenched with aqueous NH_4Cl, and extracted with diethyl ether. The combined organic phases were washed with brine, dried over Na_2SO_4 and filtered. After evaporation of the filtrate, the desired propargylic carboxylate was prepared according to **GP 1**:



colourless solid (1.29 g, 5.09 mmol, 85%); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.79 (dd, *J* 7.7 and 1.7, 1 H), 7.59 (dd, *J* 7.7 and 1.3, 1 H), 7.39 (ddd, *J* 7.7, 7.6 and 1.3, 1 H), 7.25 (ddd, *J* 7.7, 7.6 and 1.7, 1 H), 6.68 (d, *J* 2.3, 1 H), 2.67 (d, *J* 2.3, 1 H), 2.14 (s, 3 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 169.3, 135.4, 133.1, 130.6, 129.5, 127.7, 123.3, 79.3, 75.8, 64.8, 20.7; IR (NaCl): *v* = 3300, 1744, 1371, 1225, 1021, 960, 739, 705; HR-MS (ES-TOF): *m/z*: calcd for $C_{11}H_{19}O_2NaBr$: 274.9684, found 274.9678 [*M+Na*].

All the thioether derivatives were prepared by alkylation of the corresponding thiol using a modified variant of the method reported by Ono.[1]

Alkylation Reaction: General Procedure (GP 3).

To a mixture of thiol (9.8 mmol) and DBU (10.8 mmol) in toluene (30 mL) at 0 °C under Ar was slowly added allyl bromide (10.8 mmol). The reaction mixture was then stirred at RT for 1-3 h and was treated with aqueous NH_4Cl, then with brine and was extracted with ethyl acetate. The combined organic phases were dried over Na_2SO_4, filtered, and the solvent removed under reduce pressure to give the crude sulfide. The residue was purified through silica gel flash column chromatography (hexanes/ethyl acetate) or by distillation to give the desired sulfide.

The following compounds were prepared by this method:

Allyl phenylsulfide

(Quant. yield). Spectroscopic data were identical to those reported in literature.[2]

Allyl (p-tolyl)sulfide

(Quant. yield). Spectroscopic data were identical to those reported in literature.[3]

Allyl (4-methoxyphenyl)sulfide

(95% yield). Spectroscopic data were identical to those reported in literature.[4]

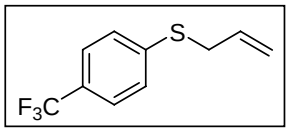
Allyl (2-bromophenyl)sulfide

(82% yield). Spectroscopic data were identical to those reported in literature.[5]

Propargyl phenylsulfide

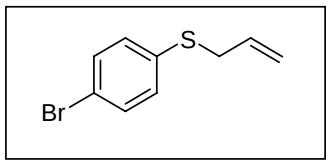
(Quant. yield). Spectroscopic data were identical to those reported in literature.[6]

Allyl(4-(trifluoromethyl)phenyl)sulfide



Colourless oil (quant. yield); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.51 (d, *J* 8.2, 2 H), 7.37 (d, *J* 8.2, 2 H), 5.88 (ddt, *J* 16.9, 10.0 and 6.7, 1 H), 5.24 (dq, *J* 16.9 and 1.3, 1 H), 5.15 (dq, *J* 10.0 and 1.1, 1 H), 3.62 (ddd, *J* 6.7, 1.3 and 1.1, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 141.6, 132.7, 130.8 (q, *J* 33), 128.0 (2 C), 127.4, 125.5 (2 C), 124.1 (q, *J* = 272 Hz), 118.3, 35.8; IR (NaCl): *v* = 3086, 2982, 2919, 1607, 1402, 1328, 1165, 1124, 1096, 1064, 1014, 924, 824, 734; MS(EI) 218 (M^+, 100%).

Alyl(4-bromophenyl)sulfide



The title compound was obtained according to the general procedure as a colourless oil (quant. yield); ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.39 (d, *J* 8.3, 2 H), 7.20 (d, *J* 8.3, 2 H), 5.85 (m, 1 H), 5.10 (m, 2 H), 3.52 (d, *J* 6.8, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 135.0, 133.0, 131.6 (2 C), 131.2 (2 C), 119.9, 117.8, 37.0; IR (NaCl): *v* = 3081, 3009, 2978, 2916, 1636, 1473, 1092, 1008, 920, 807, 734; MS(EI) 229 (M^+, 100%)

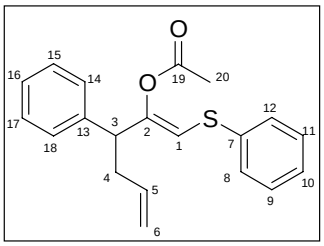
Products

General Procedure for the Gold-Catalyzed Rearrangement-Coupling Reaction (Table 2)

AuCl (1.4 μmol, 5 mol%) was added to a solution of the propargylic carboxylate (0.29 mmol) and the thioether in 1,2-DCE (0.1 M). The resulting mixture was stirred at 70 °C under an atmosphere until the reaction was complete (GC/MS and TLC). The crude mixture was rapidly filtered under a plug of silica and the solvent was evaporated. The residue was either purified by flash chromatography (hexane/ethyl acetate, 95/5) to give the enol acetate derivative in analytically pure form, or the crude mixture was dissolved in MeOH (2 mL) and K_2CO_3 (2 eq) was added. The mixture was stirred at RT until hydrolysis was complete and quenched with aqueous NH_4Cl, and extracted with diethyl ether. The combined organic phases were washed with brine, dried over Na_2SO_4 and filtered. After evaporation of the solvent, the residue was purified through silica gel flash chromatography (hexanes / ethyl acetate, 95/5) to yield to the desired compounds.

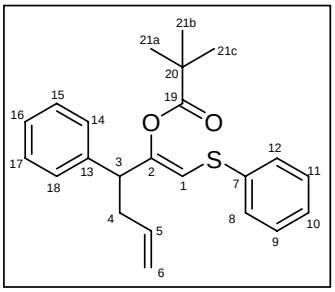
The following compounds were prepared by this method:

(*Z*)-3-Phenyl-1-(phenylthio)hexa-1,5-dien-2-yl acetate, 9a



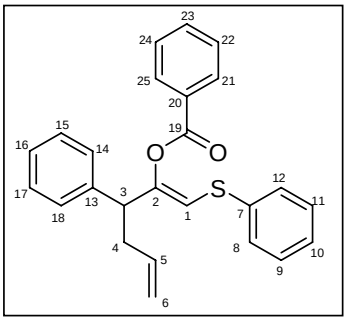
Pale yellow oil; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.35-7.20 (m, 10 H, H-Ar), 5.95 (d, *J* 0.8, 1 H, H-1), 5.71 (ddt, *J* 17.0, 10.2 and 6.8, 1 H, H-5), 5.07 (ddt, *J* 17.0, 1.5 and 1.5, 1 H, H-6a), 5.01 (ddt, *J* 10.2, 1.5 and 1.5, 1 H, H-6b), 3.67 (t, *J* 7.6, 1 H, H-3), 2.71 (m, 1 H, H-4a), 2.55 (m, 1 H, H-4b), 2.11 (s, 3 H, H-20); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 167.7 (C-19), 151.6 (C-2), 139.9 (C-13), 135.6 (C-5), 135.3 (C-7), 129.2 (2 C), 129.0 (2 C), 128.5 (2 C), 128.2 (2 C), 127.0, 126.6, 116.9 (C-6), 111.9 (C-1), 49.8 (C-3), 37.1 (C-4), 20.5 (C-20); IR (NaCl): *v* = 3060, 3027, 2978, 2921, 1759, 1582, 1479, 1440, 1368, 1194, 1134, 1024, 1012, 916, 742, 702, 692; HR-MS (ES-TOF): *m/z*: calcd for $C_{20}H_{20}O_2NaS$: 347.1082, found 347.1086 [*M+Na*].

(Z)-3-Phenyl-1-(phenylthio)hexa-1,5-dien-2-yl pivalate, 9b



Colourless solid; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.35-7.20 (m, 10 H, H-Ar), 5.96 (s, 1 H, H-1), 5.71 (m, 1 H, H-5), 5.02 (m, 2 H, H-6), 3.70 (t, *J* 7.5, 1 H, H-3), 2.71 (m, 1 H, H-4a), 2.54 (m, 1 H, H-4b), 1.17 (s, 9 H, H-21); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 175.4 (C-19), 151.5 (C-2), 140.1 (C-13), 135.7 (C-5, C-7), 129.2 (2 C), 129.0 (2 C), 128.3 (4 C), 127.0, 126.5, 116.8 (C-6), 111.8 (C-1), 49.7 (C-3), 39.1 (C-20), 37.1 (C-4), 27.0 (C-21); IR (NaCl): *v* = 3063, 3029, 2976, 2933, 2872, 1746, 1479, 1115, 1026, 918, 739, 702; HR-MS (ES-TOF): *m/z*: calcd for $C_{23}H_{26}O_2NaS$: 389.1551, found 389.1548 [*M+Na*].

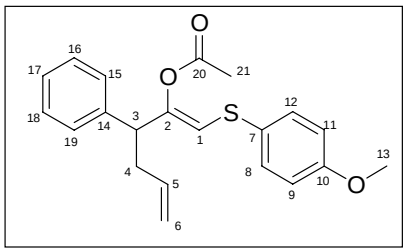
(*Z*)-3-Phenyl-1-(phenylthio)hexa-1,5-dien-2-yl benzoate, 9c



Colourless solid; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, *J* 7.9, 2 H, H-21, H-25), 7.58 (t, *J* 7.4, 1 H, H-23), 7.43 (t, *J* 7.9, 2 H, H-22, H-24), 7.33-7.19 (m, 10 H, H-Ar), 6.05 (s, 1 H, H-1), 5.77 (m, 1 H, H-5), 5.08 (dd, *J* 17.1 and 1.3, 1H, H-6a), 5.01 (dd, *J* 10.2 and 1.3, 1 H, H-6b), 3.82 (t, *J* 7.5, 1 H, H-3), 2.80 (m, 1 H, H-4a), 2.63 (m, 1 H, H-4b); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 163.5 (C-19), 151.7 (C-2), 140.0 (C-13), 135.6 (C-5), 135.4 (C-7), 133.4, 130.1 (2 C), 129.1 (2 C), 129.1 (C-20), 129.0 (2 C), 128.5 (2 C), 128.4 (2 C), 128.2 (2 C), 127.0, 126.5, 116.9 (C-6), 112.3 (C-1), 50.0 (C-3), 37.1 (C-4); IR (NaCl):

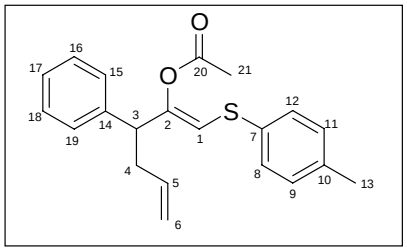
v = 3062, 3029, 2921, 2851, 1735, 1244, 1081, 1063, 705; HR-MS (ES-TOF): *m/z*: calcd for $C_{25}H_{22}O_2NaS$: 409.1238, found 409.1249 [*M+Na*].

(*Z*)-1-(4-Methoxyphenylthio)-3-phenylhexa-1,5-dien-2-yl acetate, 9d



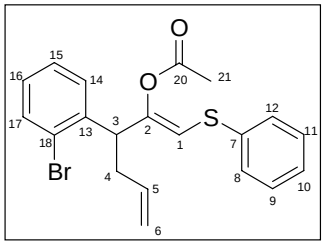
Pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.32-7.21 (m, 7 H, H-Ar), 6.84 (m, 2 H, H-Ar), 5.85 (s, 1 H, H-1), 5.69 (m, 1 H, H-5), 5.00 (m, 2 H, H-6), 3.79 (s, 3 H, H-13), 3.62 (t, *J* 7.7, 1 H, H-3), 2.67 (m, 1 H, H-4a), 2.52 (m, 1 H, H-4b), 2.10 (s, 3 H, H-21); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 167.8 (C-20), 159.1 (C-10), 149.7 (C-2), 140.0 (C-14), 135.6 (C-5), 132.2 (2 C), 128.4 (2 C), 128.2 (2 C), 127.0, 125.4 (C-7), 116.8 (C-6), 114.7 (2 C), 113.9 (C-1), 55.3 (C-13), 49.7 (C-3), 37.1 (C-4), 20.5 (C-21); IR (NaCl): *v* = 3063, 3027, 3003, 2937, 2836, 1758, 1494, 1287, 1247, 1194, 1030, 703; HR-MS (ES-TOF): *m/z*: calcd for $C_{21}H_{22}O_3NaS$: 377.1187, found 377.1172 [*M+Na*].

(*Z*)-3-Phenyl-1-(p-tolylthio)hexa-1,5-dien-2-yl acetate, 9e



Pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.32-7.22 (m, 7 H, H-Ar), 7.10 (d, *J* 8.1, 2 H, H-Ar), 5.91 (s, 1 H, H-1), 5.71 (m, 1 H, H-5), 5.00 (m, 2 H, H-6), 3.65 (t, *J* 7.6, 1 H, H-3), 2.69 (m, 1 H, H-4a), 2.53 (m, 1 H; H-4b), 2.31 (s, 3 H, H-13), 2.10 (s, 3 H, H-21); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 167.8 (C-20), 150.7 (C-2), 140.0 (C-14), 136.8 (C-10), 135.6 (C-5), 131.6 (C-7), 129.7 (4 C), 128.4 (2 C), 128.2 (2 C), 127.0, 116.8 (C-6), 112.8 (C-1), 49.8 (C-3), 37.1 (C-4), 20.8 (C-13), 20.5 (C-21); IR (NaCl): *v* = 3062, 3027, 2977, 2921, 2864, 1759, 1493, 1368, 1194, 1133, 1016, 806, 702; HR-MS (ES-TOF): *m/z*: calcd for $C_{21}H_{22}O_2NaS$: 361.1238, found 361.1247 [*M+Na*].

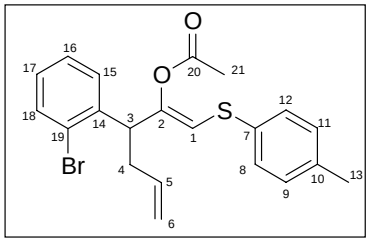
(*Z*)-3-(2-Bromophenyl)-1-(phenylthio)hexa-1,5-dien-2-yl acetate, 9i



Pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.57 (d, *J* 8.1, 1 H, H-Ar), 7.37-7.26 (m, 7 H, H-Ar), 7.10 (m, 1 H, H-Ar), 6.05 (s, 1 H, H-1), 5.75 (m, 1 H, H-5), 5.07 (m, 1 H, H-6a), 5.02 (m, 1 H, H-6b), 4.31 (t, *J* 7.6, 1 H, H-3), 2.71 (m, 1 H, H-4a), 2.55 (m, 1 H, H-4b), 2.12 (s, 3 H, H-21); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 167.6 (C-20), 150.0 (C-2), 139.1(C-13), 135.2 (C-7), 134.9 (C-5), 133.0, 129.2 (2 C), 129.0 (2 C), 128.8, 128.5, 127.6, 126.6, 125.4 (C-18), 117.2 (C-6),

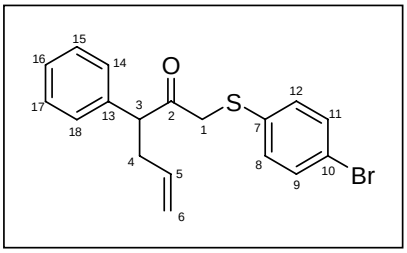
112.7 (C-1), 48.0 (C-3), 36.6 (C-4), 20.5 (C-21); IR (NaCl): *v* = 3060, 2922, 2851, 1761, 1479, 1469, 1439, 1368, 1191, 1136, 1024, 740, 690; HR-MS (ES-TOF): *m/z*: calcd for $C_{20}H_{19}BrO_2NaS$: 425.0187, found 425.0201 [M+Na].

(*Z*)-3-(2-Bromophenyl)-1-(p-tolylthio)hexa-1,5-dien-2-yl acetate, 9j



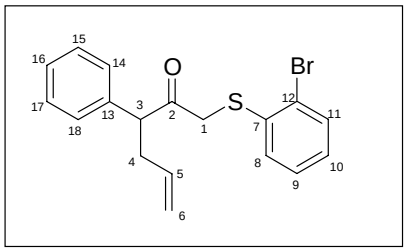
Pale yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, *J* 7.8, 1 H, H-Ar), 7.29 (m, 4 H, H-Ar), 7.09 (m, 3 H, H-Ar), 6.01 (s, 1 H, H-1), 5.74 (m, 1 H, H-5), 5.06 (m, 1 H, H-6a), 5.01 (m, 1 H, H-6b), 4.29 (t, *J* 7.4, 1 H, H-3), 2.68 (m, 1 H, H-4a), 2.55 (m, 1 H, H-4b), 2.33 (s, 3 H, H-13), 2.11 (s, 3 H, H-21); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 167.5 (C-20), 149.1 (C-2), 139.1 (C-14), 136.7 (C-10), 134.9 (C-5), 132.9, 131.4 (C-7), 129.7 (4 C), 128.7, 128.4, 127.5, 125.3 (C-19), 117.1 missing one C (C-6), 113.5 (C-1), 47.9 (C-3), 36.5 (C-4), 20.9 (C-13), 20.4 (C-21); IR (NaCl): *v* = 3069, 2978, 2920, 1761, 1492, 1469, 1439, 1368, 1193, 1136, 1023, 806, 758, 734; HR-MS (ES-TOF): *m/z*: calcd for $C_{21}H_{21}BrO_2NaS$: 439.0343, found 439.0352 [*M*+*Na*].

1-(4-Bromophenylthio)-3-phenylhex-5-en-2-one, 10f



Pale yellow solid; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.34-7.26 (m, 5 H, H-Ar), 7.16 (m, 2 H-Ar), 7.05 (m, 2 H-Ar), 5.59 (m, 1 H, H-5), 4.99 (m, 1 H, H-6a), 4.91 (m, 1 H, H-6b), 4.04 (t, *J* 7.5, 1 H, H-3), 3.62 (d, *J* 15.4, 1 H, H-1a), 3.56 (d, *J* 15.4, 1 H, H-1b), 2.75 (m, 1 H, H-4a), 2.43 (m, 1 H, H-4b); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 203.2 (C-2), 137.5 (C-13), 135.3 (C-5), 133.8 (C-7), 132.0 (2 C), 131.2 (2 C), 129.1 (2 C), 128.4 (2 C), 127.6, 120.7 (C-10), 117.0 (C-6), 56.4 (C-3), 42.9 (C-1), 36.5 (C-4); IR (NaCl): *v* = 3056, 2893, 1709, 1474, 1092, 1007, 810, 738, 702; MS(EI) 362 (M^+, 7%), 360 (M^+, 7%), 203 (9), 201 (9), 172 (7), 131 (100).

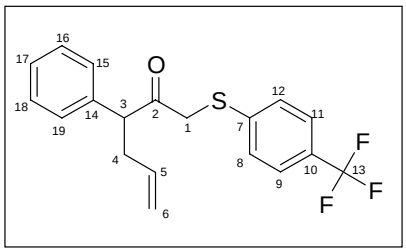
1-(2-Bromophenylthio)-3-phenylhex-5-en-2-one, 10g



Pale yellow solid; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.51 (dd, *J* 7.8 and 1.3, 1 H, H-Ar), 7.32-7.16 (m, 5 H, H-Ar), 7.14-7.00 (m, 2 H, H-Ar), 5.58 (m, 1 H, H-5), 4.93 (dd, *J* 17.1 and 1.3, 1 H, H-6a), 4.89 (dd, *J* 10.1 and 1.3, 1 H, H-6b), 4.11 (t, *J* 7.5, 1 H, H-3), 3.69 (d, *J* 15.5, 1 H, H-1a), 3.63 (d, *J* 15.5, 1 H, H-1b), 2.75 (m, 1 H, H-4a), 2.44 (m, 1 H, H-4b); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 203.4 (C-2), 137.5 (C-13), 135.9 (C-7), 135.2 (C-5), 133.0, 129.1, 129.0 (2 C),

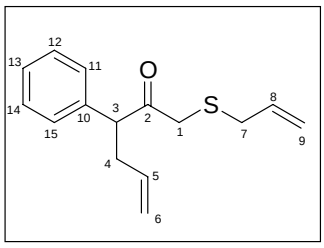
128.4 (2 C), 127.8, 127.6, 127.4, 123.7 (C-12), 116.9 (C-6), 56.2 (C-3), 41.9 (C-1), 36.4 (C-4); IR (NaCl): ν = 3061, 3027, 2977, 2917, 1710, 1450, 1428, 1020, 746, 701; HR-MS (ES-TOF): *m/z*: calcd for $C_{18}H_{17}BrNaOS$: 383.0081, found 383.0092 [*M*+*Na*].

3-Phenyl-1-(4-(trifluoromethyl)phenylthio)hex-5-en-2-one, 10h



Pale yellow solid; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.42 (d, *J* 8.4, 2 H, H-Ar), 7.32-7.18 (m, 7 H, H-Ar), 5.58 (m, 1 H, H-5), 4.98 (dd, *J* 17.1 and 1.4, 1 H, H-6a), 4.92 (d, *J* 10.4, 1 H, H-6b), 4.06 (t, *J* 7.4, 1 H, H-3), 3.74 (d, *J* 15.8, 1 H, H-1a), 3.66 (d, *J* 15.8, 1 H, H-1b), 2.77 (m, 1 H, H-4a), 2.43 (m, 1 H, H-4b); ^{13}C-NMR (75 MHz, $CDCl_3$): C-10 and C-13 are not observed δ = 203.0 (C-2), 140.2 (C-7), 137.4 (C-14), 135.1 (C-5), 129.1 (2 C), 128.3 (2 C), 127.9 (2 C), 127.7, 125.7 (q, *J* 2.7, 2 C), 117.0 (C-6), 56.5 (C-3), 41.8 (C-1), 36.5 (C-4); IR (NaCl): ν = 3065, 3029, 2923, 2852, 1712, 1606, 1328, 1167, 1125, 1096, 1064, 1013, 701; HR-MS (EI): *m/z*: calcd for $C_{19}H_{17}F_3OS$: 350.0952, found 350.0968.

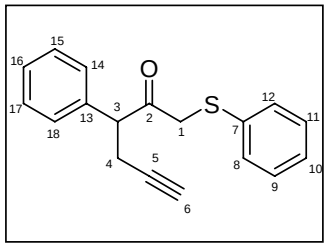
1-(Allylthio)-3-phenylhex-5-en-2-one, 10k



Colourless oil; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.35-7.21 (m, 5 H, H-Ar), 5.67 (m, 2 H, H-5, H-8), 5.01 (m, 4 H, H-6, H-9), 4.08 (t, *J* 7.5, 1 H, H-3), 3.15 (d, *J* 14.8, 1 H, H-1a), 3.10 (d, *J* 14.8, 1 H, H-1b), 3.00 (m, 2 H, H-7), 2.79 (m, 1 H, H-4a), 2.47 (m, 1 H, H-4b); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 203.7 (C-2), 137.9 (C-10), 135.5, 132.6, 128.9 (2 C), 128.3 (2 C), 127.4, 118.2, 116.7, 56.0 (C-3), 38.4 (C-1), 36.6 (C-4), 34.4 (C-7); IR (NaCl): ν = 3079, 3027, 2978, 2917, 1704, 1640, 1493, 1453, 992, 920, 753, 701; HR-MS (ES-TOF): *m/z*: calcd for $C_{15}H_{18}NaOS$: 269.0976, found 269.0968 [*M*+*Na*].

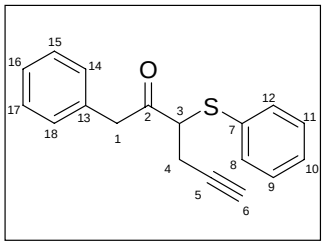
1-(Phenylthio)-3-phenylhex-5-yn-2-one, 16 / 1-phenyl-3-(phenylthio)hex-5-yn-2-one, 17 (Scheme 6)

Prepared using $AuCl_3$; Isolated as a 1 : 1.6 mixture of isomers **16** : **17**; HPLC separation was performed using a Phenomenex SEMI-PREP Luna 10u C18 column, size 250 mm × 10 mm, acetonitrile / water = 70 : 30 (3 mL/min).



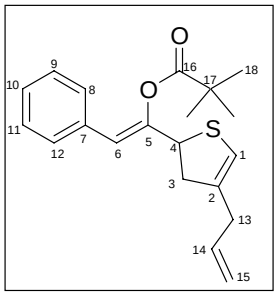
16-Colourless solid; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.33-7.16 (m, 10 H, H-Ar), 4.29 (t, *J* 7.4, 1 H, H-3), 3.65 (d, *J* = 15.2, 1 H, H-1a), 3.59 (d, *J* 15.2, 1 H, H-1b), 2.84 (ddd, *J* 16.8, 7.4 and 2.6,

1 H, H-4a), 2.54 (ddd, *J* 16.8, 7.4 and 2.6, 1 H, H-4b), 1.86 (t, *J* 2.6, 1 H, H-6); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 202.7 (C-2), 136.7 (C-13), 134.5 (C-7), 129.9 (2 C), 129.1 (2 C), 129.0 (2 C), 128.3 (2 C), 128.0, 126.9, 81.7 (C-5), 69.8 (C-6), 55.0 (C-3), 42.9 (C-1), 22.0 (C-4); IR (NaCl): *v* = 3289, 1708, 1482, 1454, 1086, 1069, 750, 670, 632; HR-MS (ES-TOF): *m/z*: calcd for $C_{18}H_{16}NaOS$: 303.0820, found 303.0809 [*M+Na*].



17-Colourless oil; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.42-7.18 (m, 10 H, H-Ar), 4.01 (d, *J* 15.4, 1 H, H-1a), 3.95 (d, *J* 15.4, 1 H, H-1b), 3.83 (dd, *J* 7.6 and 7.4, 1 H, H-3), 2.63 (ddd, *J* 17.2, 7.4 and 2.6, 1 H, H-4a), 2.48 (ddd, *J* 17.2, 7.6 and 2.6, 1 H, H-4b), 2.04 (t, *J* 2.6, 1 H, H-6); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 201.6 (C-2), 134.5 (2 C), 133.6 (C-13), 130.6 (C-7), 129.6 (2 C), 129.2 (2 C), 129.1, 128.7 (2 C), 127.1, 80.7 (C-5), 70.7 (C-6), 53.8 (C-3), 47.5 (C-1), 20.2 (C-4); IR (NaCl): *v* = 3291, 3061, 3029, 2917, 1712, 1496, 1439, 1341, 1091, 1025, 750, 693, 643; HR-MS (ES-TOF): *m/z*: calcd for $C_{18}H_{16}NaOS$: 303.0820, found 303.0810 [*M+Na*].

(*Z*)-1-(4-Allyl-2,3-dihydrothiophen-2-yl)-2-phenylvinyl pivalate, 19 (Scheme 7)



Colourless solid; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.35-7.20 (m, 5 H, H-Ar), 6.33 (br s, 1 H, H-6), 5.82 (m, 1 H, H-14), 5.74 (br s, 1 H, H-1), 5.10 (m, 2 H, H-15), 4.59 (dd, *J* 8.6 and 7.9, 1 H, H-4), 2.85 (m, 4 H, H-3, H-13), 1.25 (s, 9 H, H-18); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 175.7 (C-16), 147.9 (C-5), 135.1 (C-14), 133.9 (C-7), 133.4 (C-2), 128.5 (2 C), 128.1 (2 C), 127.4 (C-10), 117.9 (C-1), 116.9 (C-6), 116.6 (C-15), 51.7 (C-4), 41.9 (C-3), 39.1 (C-17), 36.0 (C-13), 27.1 (C-18); IR (NaCl): *v* = 3057, 3027, 2976, 2933, 1745, 1480, 1112, 1030, 920, 739, 699; HR-MS (ES-TOF): *m/z*: calcd for $C_{20}H_{24}NaO_2S$: 351.1395, found 351.1400 [*M+Na*].

References

[1] N. Ono, H. Miyake, T. Saito, A. Kaji, *Synthesis* 1980, 952.
[2] M. Piffl, J. Weston, W. Günter, *J. Org. Chem.* 2000, **65**, 5942.
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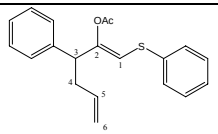
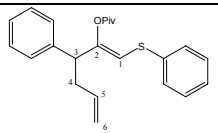
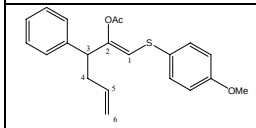
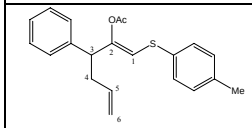
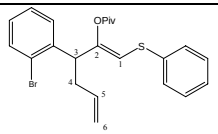
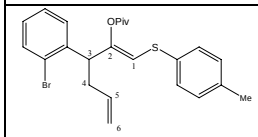
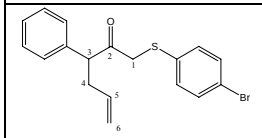
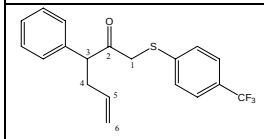
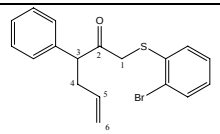
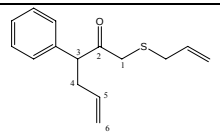
[4] J. Ham, I. Yang, H. Kang, *J. Org. Chem.* 2004, **69**, 3236.
[5] X. Arnau, M. Moreno-Mañas, R. Pleixats, *Tetrahedron* 1993, **49**, 11019.
[6] A. Linden, L. Krueger, J.-E.Bäckvall, *J. Org. Chem.* 2003, **68**, 5890.

NMR Comparison Tables

Compounds	Resonance (ppm) for assigned protons and carbons							
	1	**2**	**3**	**4**	**5**	**6**	**C(Ph)**	**C(SPh)**
	5.95 111.9	- 151.6	3.67 49.8	2.71/2.54 37.1	5.72 135.6	5.05/5.00 116.9	- 139.9	- 135.3
	5.96 111.8	- 151.5	3.69 49.7	2.71/2.54 37.1	5.72 135.7	5.04/4.99 116.8	- 140.1	- 135.7
	5.86 113.9	- 149.7	3.62 49.7	2.69/2.51 37.1	5.69 135.6	5.02/4.97 116.8	- 140.0	- 125.4
	5.91 112.8	- 150.7	3.65 49.8	2.69/2.50 37.1	5.72 135.6	5.03/4.98 116.8	- 140.0	- 131.6
	6.05 112.7	- 150.0	4.31 48.0	2.71/2.56 36.6	5.74 134.9	5.07/5.02 117.2	- 139.1	- 135.2
	6.01 113.5	- 149.1	4.29 47.9	2.68/2.55 36.5	5.74 134.9	5.06/5.01 117.1	- 139.1	- 131.4

Compounds	Resonance (ppm) for assigned protons and carbons							
	1	**2**	**3**	**4**	**5**	**6**	**C(Ph)**	**C(SPh)**
	3.63/3.57 42.9	- 203.2	4.04 56.4	2.75/2.43 36.5	5.59 135.3	4.99/4.91 117.0	- 137.5	- 133.8
	3.74/3.66 41.8	- 203.4	4.06 56.5	2.77/2.43 36.5	5.58 135.1	4.98/4.92 117.0	- 137.4	- 140.2
	3.69/3.63 41.9	- 203.0	4.11 56.2	2.75/2.44 36.4	5.58 135.2	4.97/4.90 116.9	- 137.5	- 135.9
	3.15/3.10 38.4	- 203.7	4.08 56.0	2.79/2.47 36.6	5.67 135.5 132.6	5.01 118.2 116.7	- 137.9	- -

HPLC data (Scheme 5)

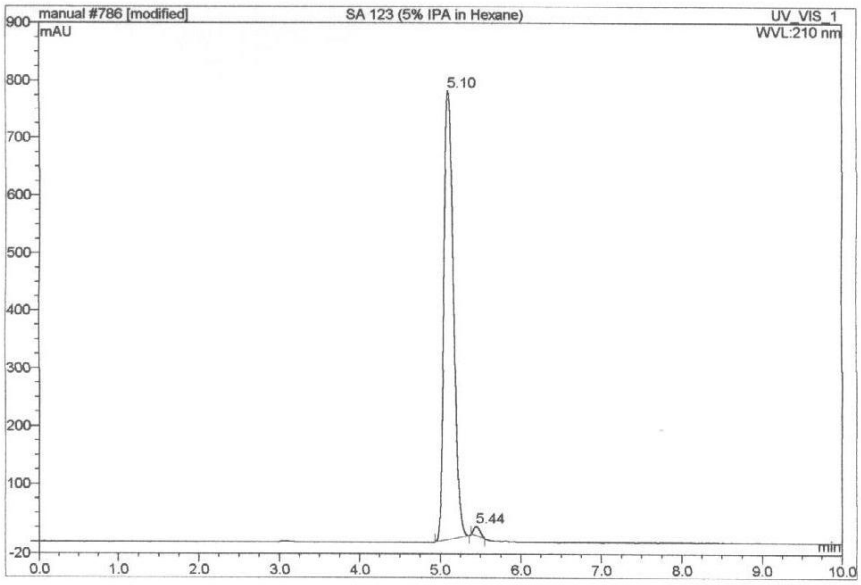
(*R*)-1-phenylprop-2-ynyl benzoate, (*R*)-6

Operator: Timebase:HPLC1_1 Sequence:manual

Page 786-1
30/8/07 9:30 AM

786 SA 123 (5% IPA in Hexane)

Sample Name:	**SA 123 (5% IPA in Hexane)**	*Injection Volume:*	**20.0**
Vial Number:	**1**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**210**
Control Program:		*Bandwidth:*	**1**
Quantif. Method:	**default**	*Dilution Factor:*	**1.0000**
Recording Time:	**30/8/07 8:37**	*Sample Weight:*	**1.0000**
Run Time (min):	**12.61**	*Sample Amount:*	**1.0000**



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	5.10	n.a.	779.037	106.997	98.66	n.a.	BMB
2	5.44	n.a.	15.490	1.450	1.34	n.a.	BMB*
Total:			794.527	108.447	100.00	0.000	

relarea/Integration

Chromeleon (c) Dionex 1999
Version 6.11 Build 490

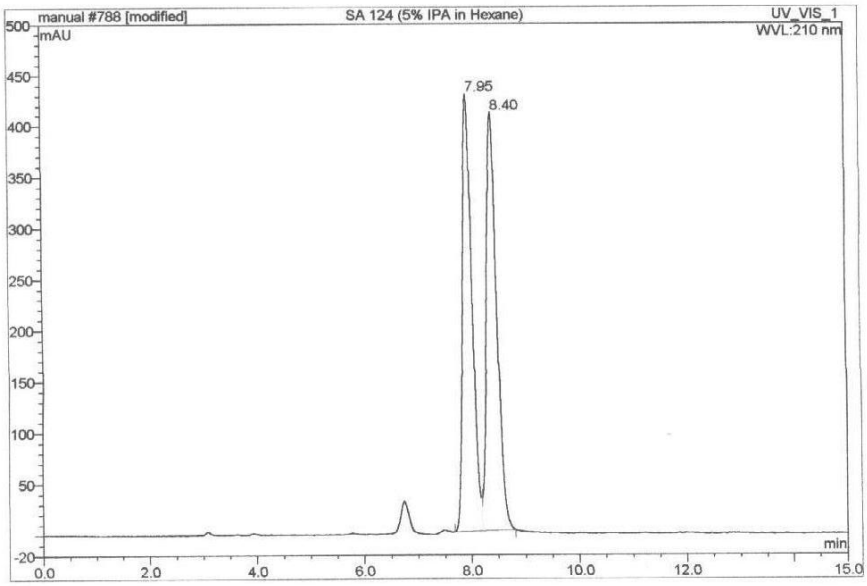
(Z)-1-(4-methoxyphenylthio)-3-phenylhexa-1,5-dien-2-yl acetate, 9c [from (*R*)-6]

Operator: Timebase:HPLC1_1 Sequence:manual

Page 788-1
30/8/07 9:56 AM

788 SA 124 (5% IPA in Hexane)

Sample Name:	**SA 124 (5% IPA in Hexane)**	*Injection Volume:*	**20.0**
Vial Number:	**1**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**210**
Control Program:		*Bandwidth:*	**1**
Quantif. Method:	**default**	*Dilution Factor:*	**1.0000**
Recording Time:	**30/8/07 9:12**	*Sample Weight:*	**1.0000**
Run Time (min):	**16.47**	*Sample Amount:*	**1.0000**



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.95	n.a.	428.079	87.804	49.03	n.a.	BM
2	8.40	n.a.	408.928	91.296	50.97	n.a.	MB
Total:			837.007	179.100	100.00	0.000	

relarea/Integration

Chromeleon (c) Dionex 1999
Version 6.11 Build 490

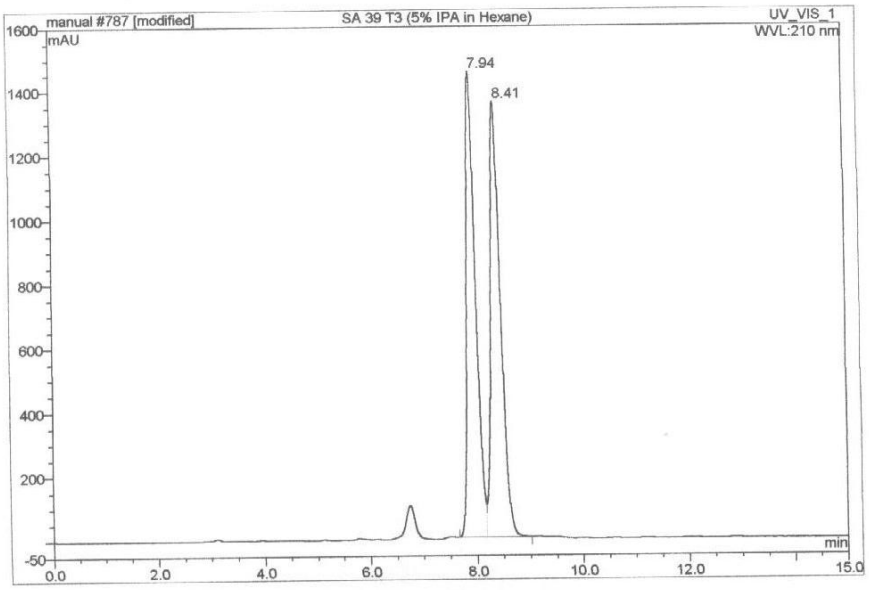
(Z)-1-(4-methoxyphenylthio)-3-phenylhexa-1,5-dien-2-yl acetate, 9c [From racemic 6]

Operator: Timebase:HPLC1_1 Sequence:manual

Page 787-1
30/8/07 9:54 AM

787 SA 39 T3 (5% IPA in Hexane)

Sample Name:	**SA 39 T3 (5% IPA in Hexane)**	*Injection Volume:*	**20.0**
Vial Number:	**1**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**210**
Control Program:		*Bandwidth:*	**1**
Quantif. Method:	**default**	*Dilution Factor:*	**1.0000**
Recording Time:	**30/8/07 8:51**	*Sample Weight:*	**1.0000**
Run Time (min):	**17.66**	*Sample Amount:*	**1.0000**

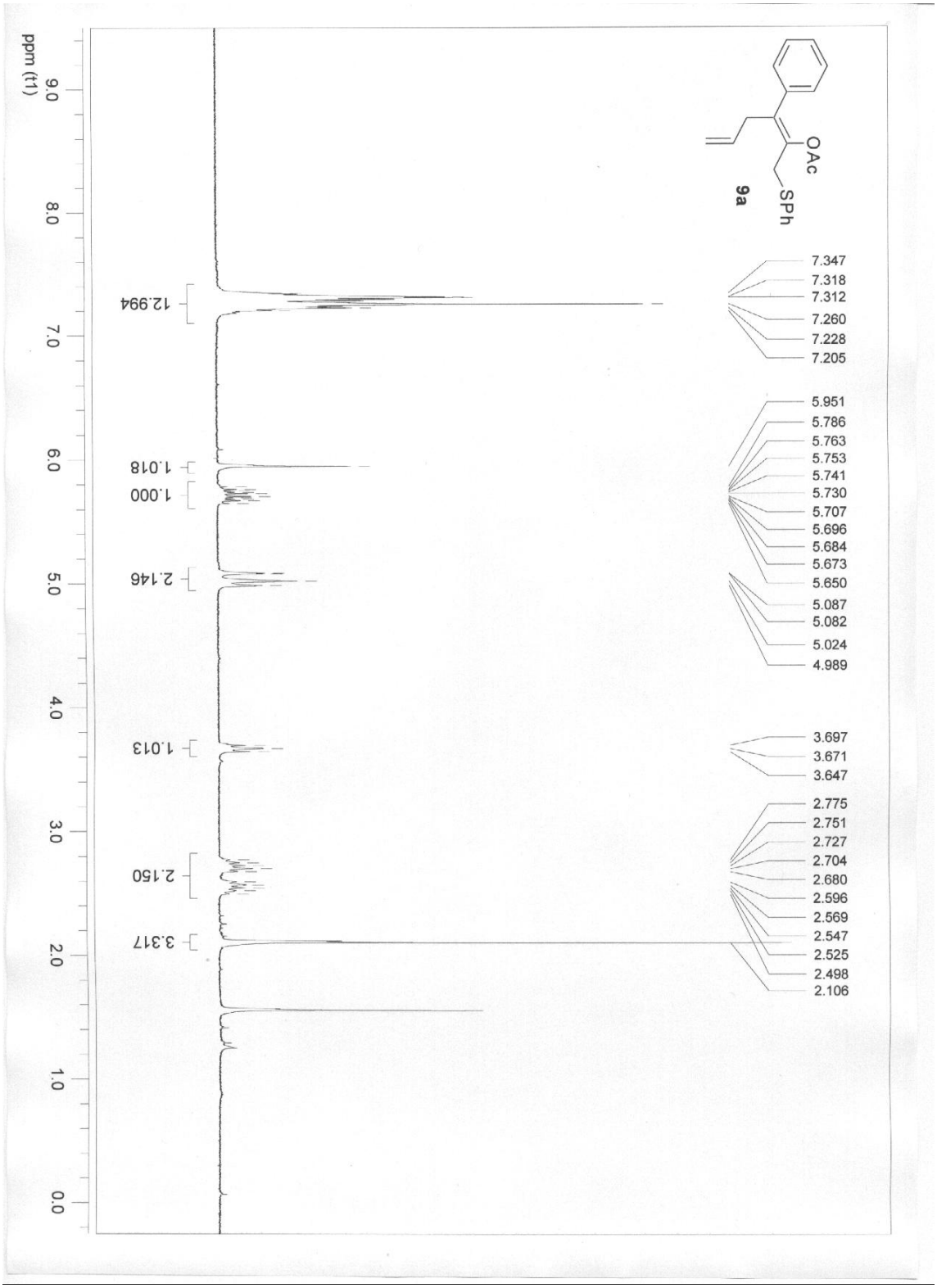


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.94	n.a.	1453.993	288.367	49.07	n.a.	BM
2	8.41	n.a.	1356.902	299.324	50.93	n.a.	MB
Total:			2810.895	587.690	100.00	0.000	

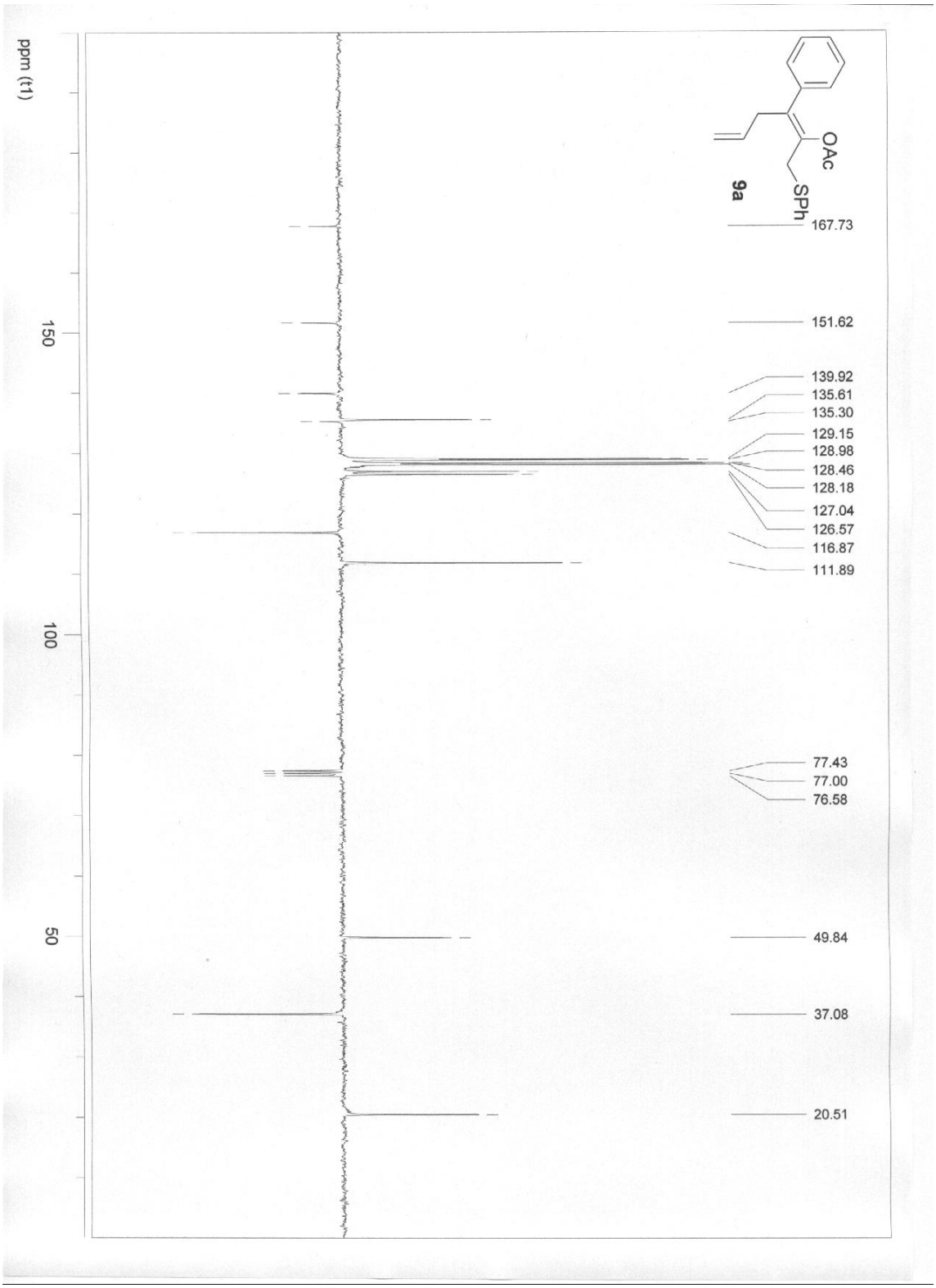
relarea/Integration

Chromeleon (c) Dionex 1999
Version 6.11 Build 490

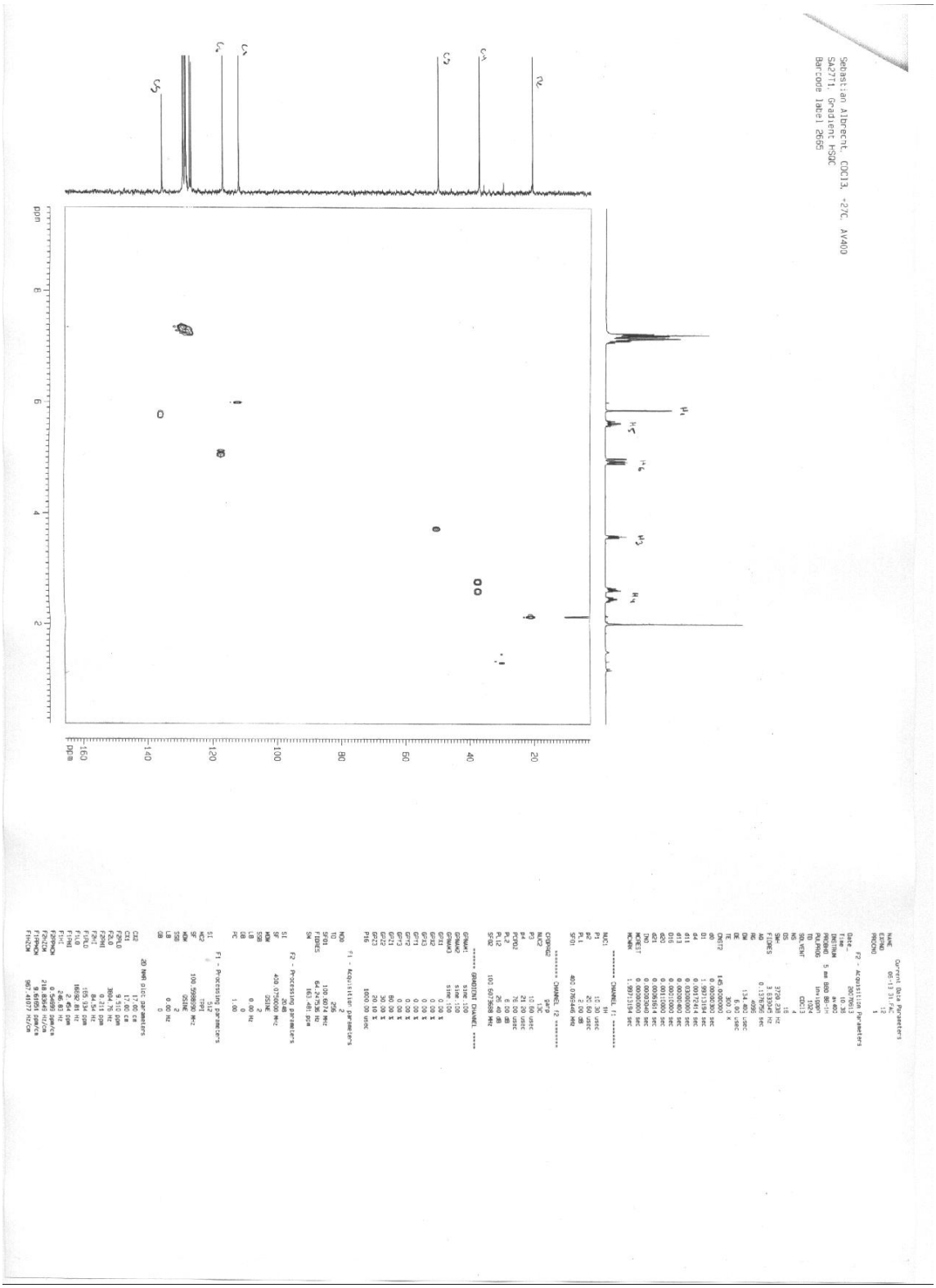
NMR Spectra



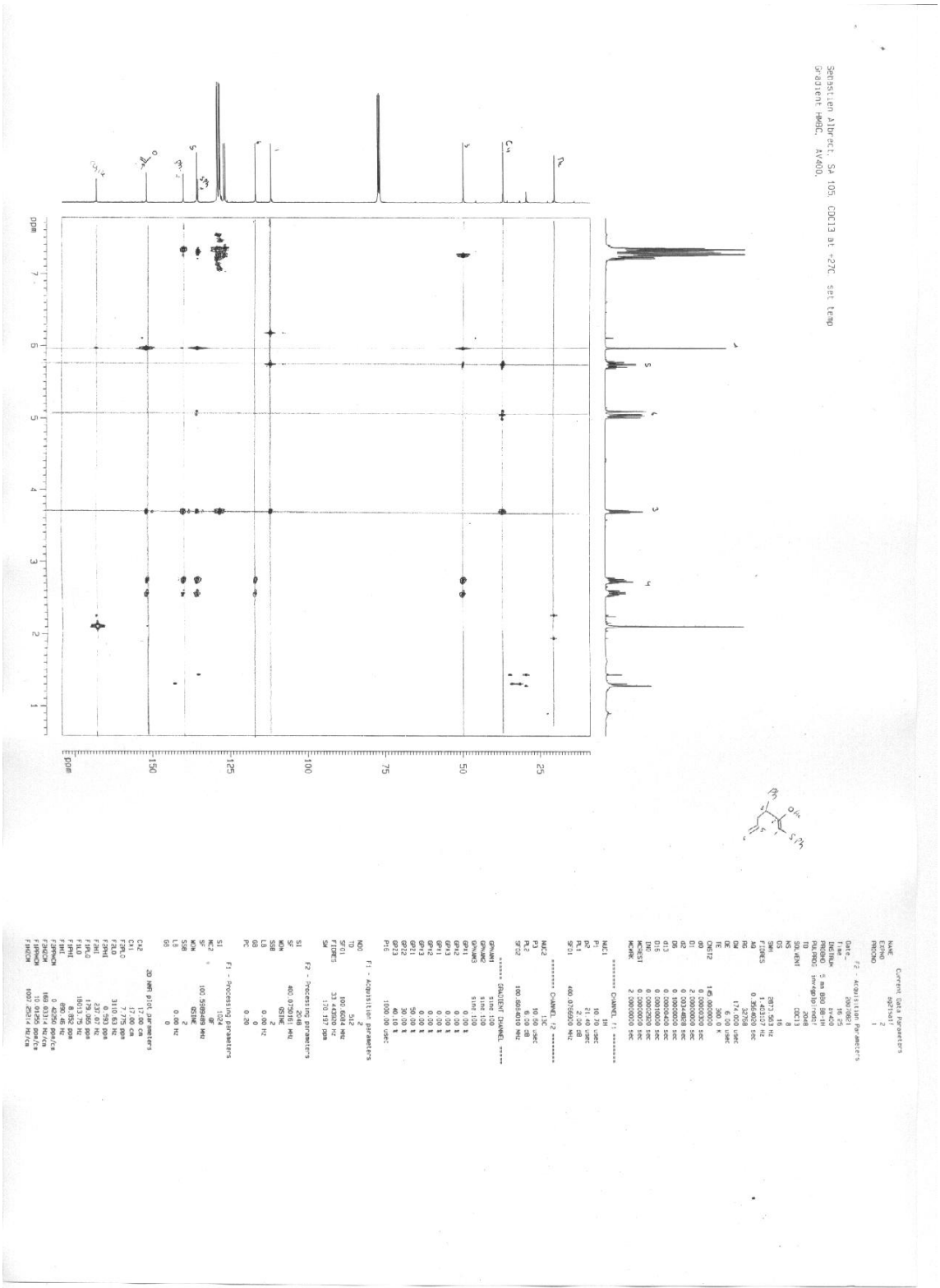
^{1}H-NMR (300 MHz, $CDCl_3$) of **9a**



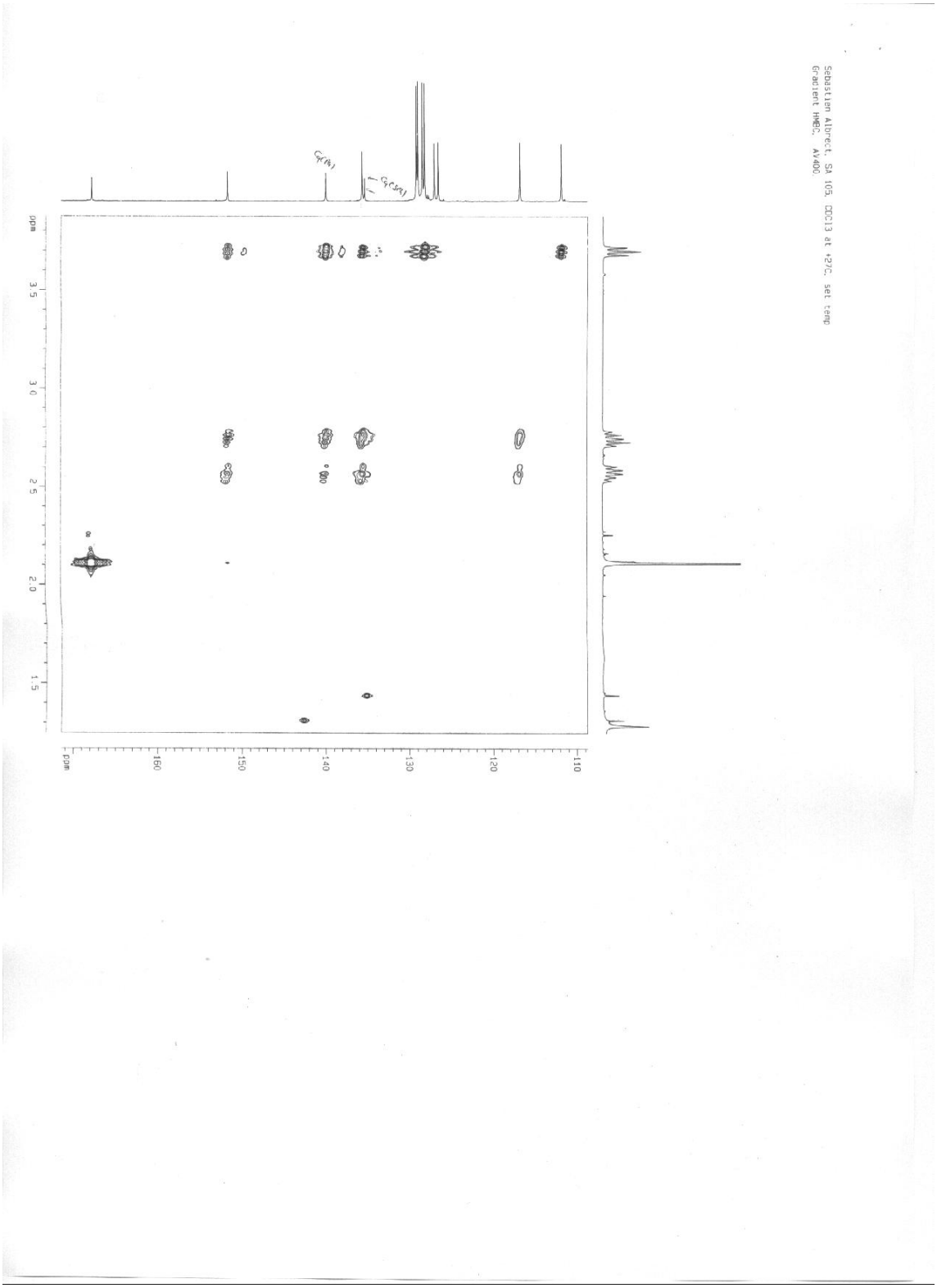
^{13}C-NMR (75 MHz, $CDCl_3$) of **9a**



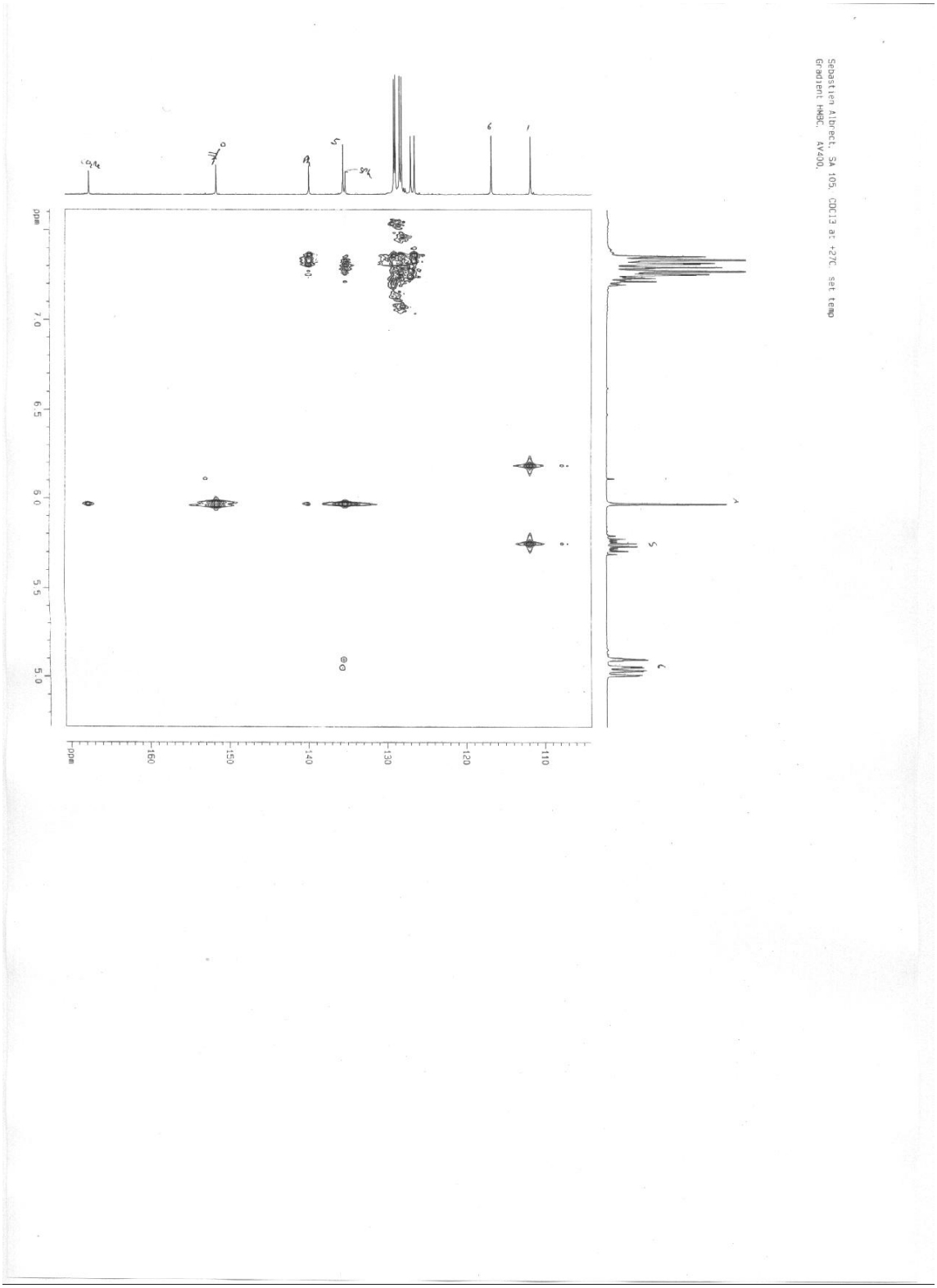
HSQC of **9a**


Sebastien Albrecht, SA 105, CDCl3 at +27C set temp
Gradient HMBC, AV400.
ppm
150
125
100
75
50
25

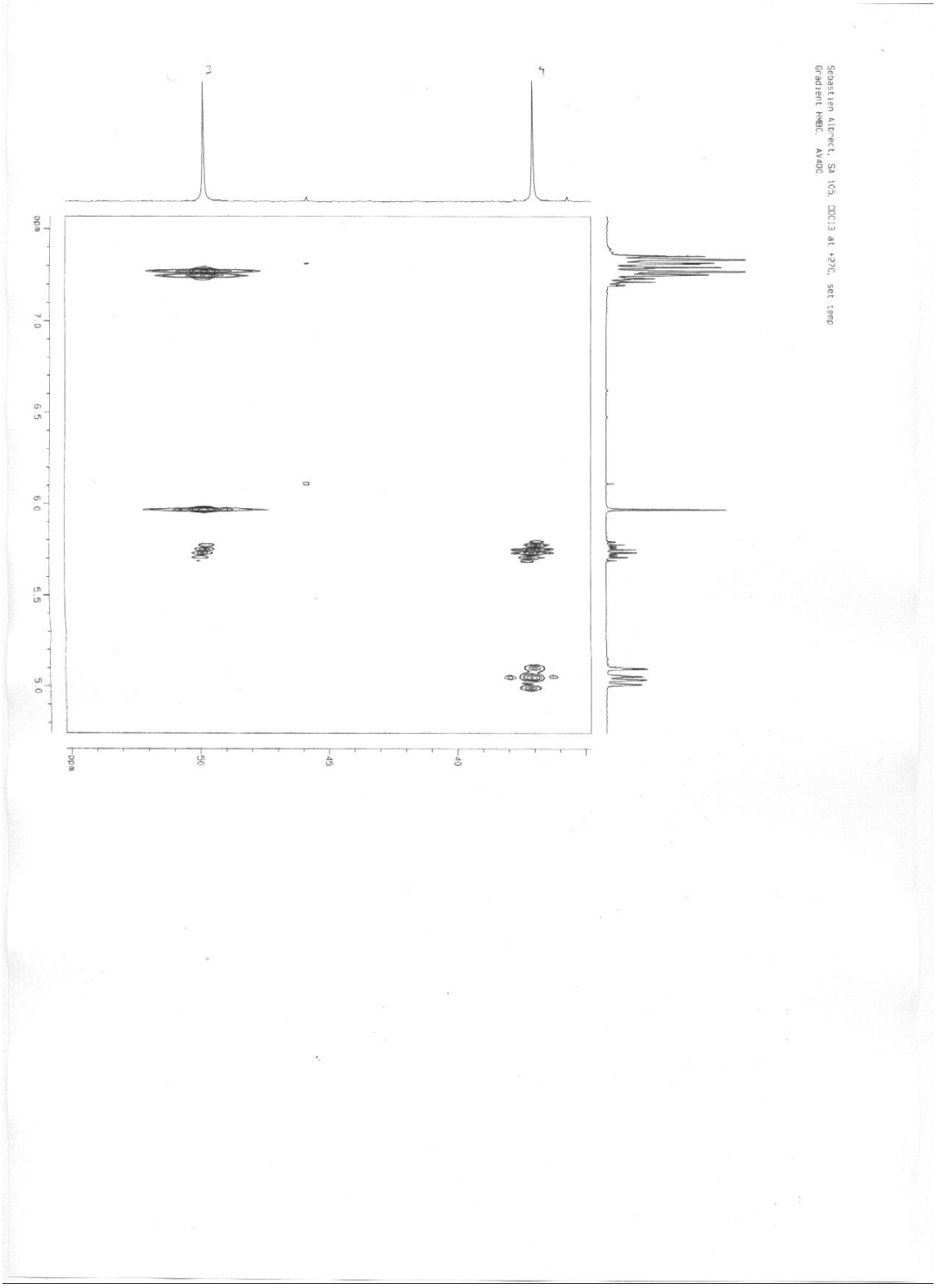
HMBC of **9a**


Sebastien Albrecht, SA 105, CDCl3 at +27C, set temp
Gradient HMBC, AV400
ppm
3.5
3.0
2.5
2.0
1.5
ppm
160
150
140
130
120
110

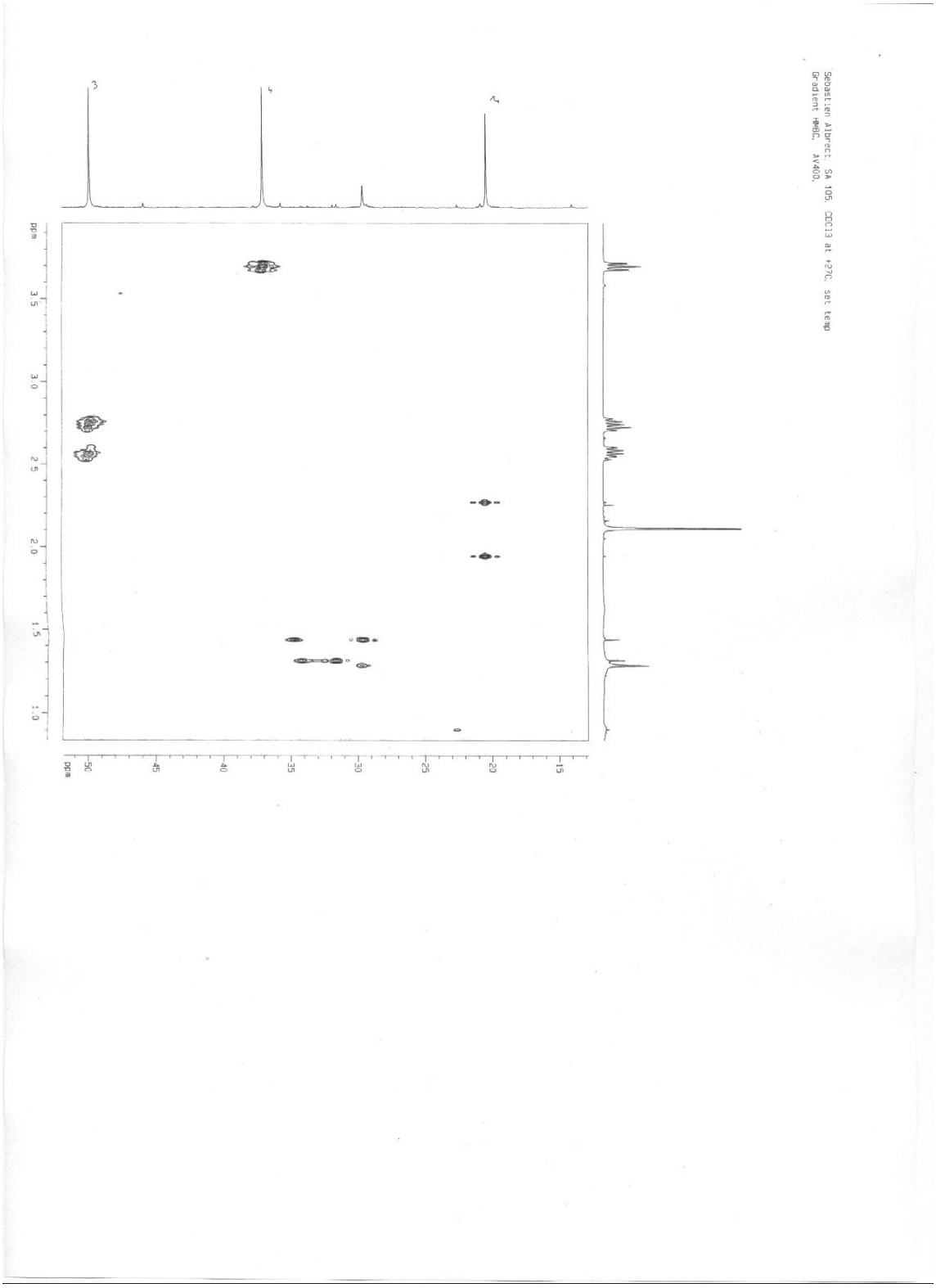
HMBC of **9a**


Sebastien Albrecht, SA 105, CDCl3 at +27C set temp
Gradient HMBC, 4V400,
ppm
7.0
6.5
6.0
5.5
5.0
ppm
160
150
140
130
120
110

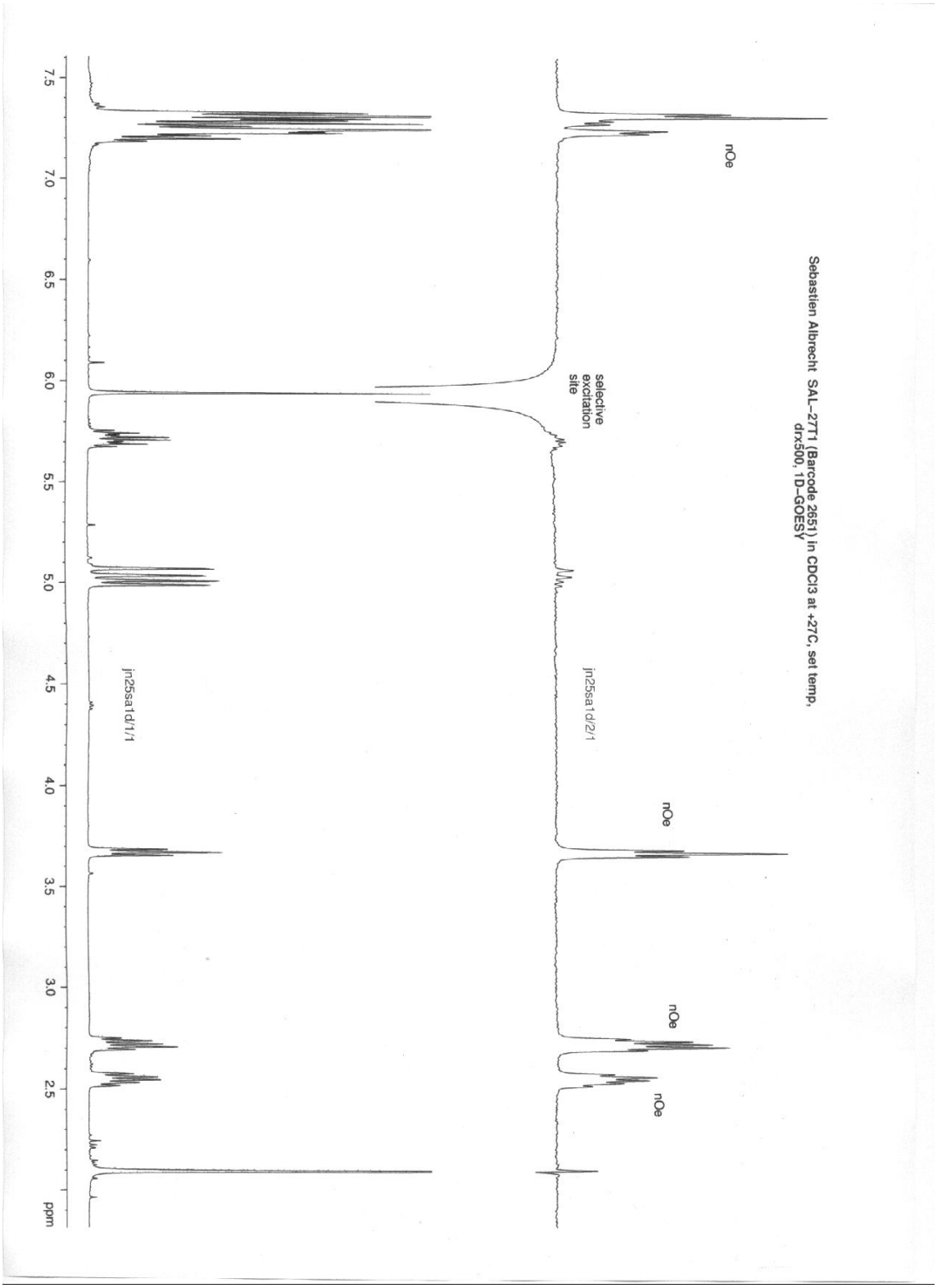
HMBC of **9a**


Sebastien Albrect, SA 105, CDCl3 at +27C, set temp
Gradient HMBC, AV400
ppm
7.0
6.5
6.0
5.5
5.0
ppm
50
45
40

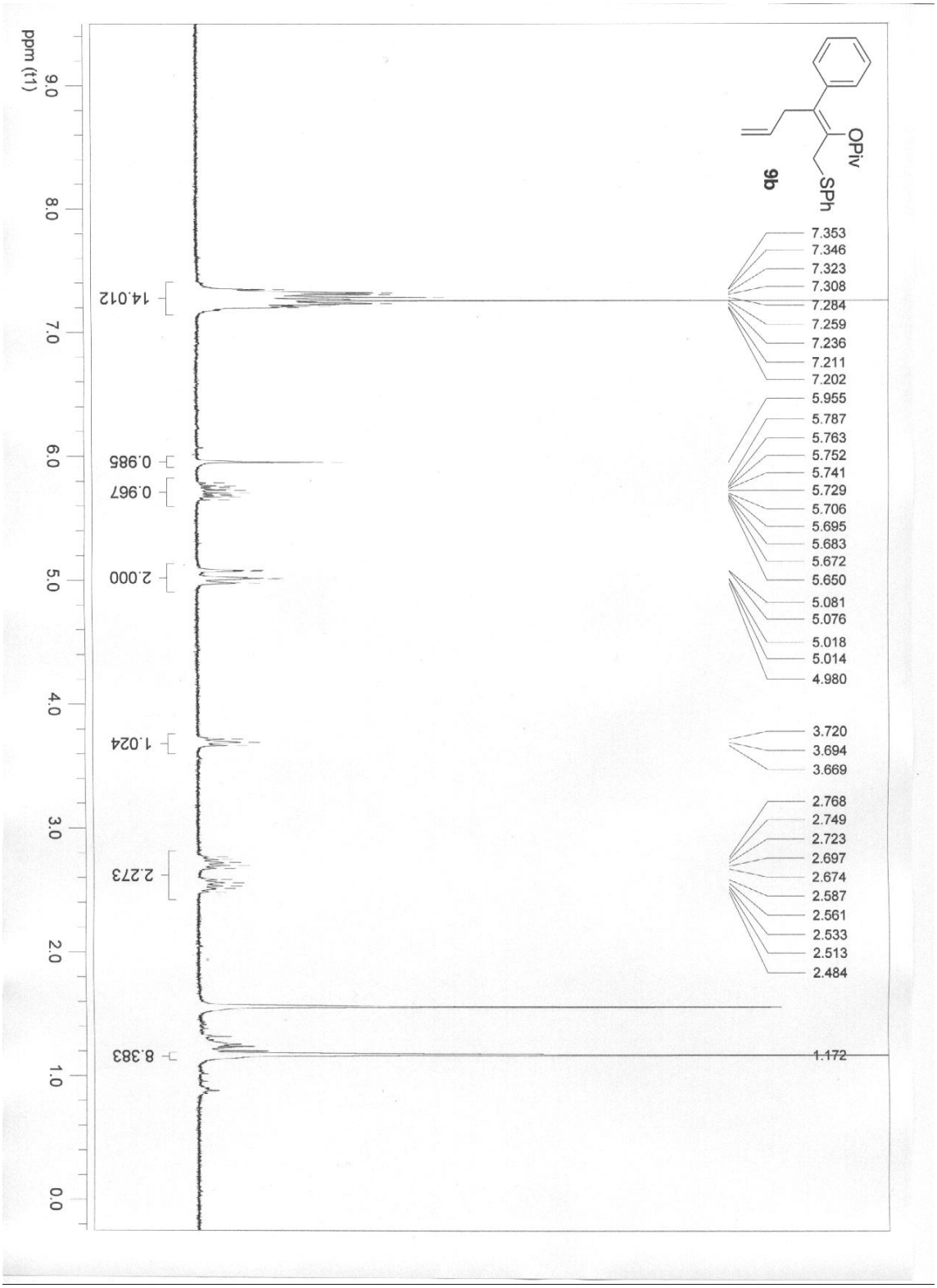
HMBC of **9a**


Sebastien Albrect SA 105 CDCl3 at +27C set temp
Gradient HMBC Av400
3
5
2
ppm
3.5
3.0
2.5
2.0
1.5
1.0
ppm
50
45
40
35
30
25
20
15

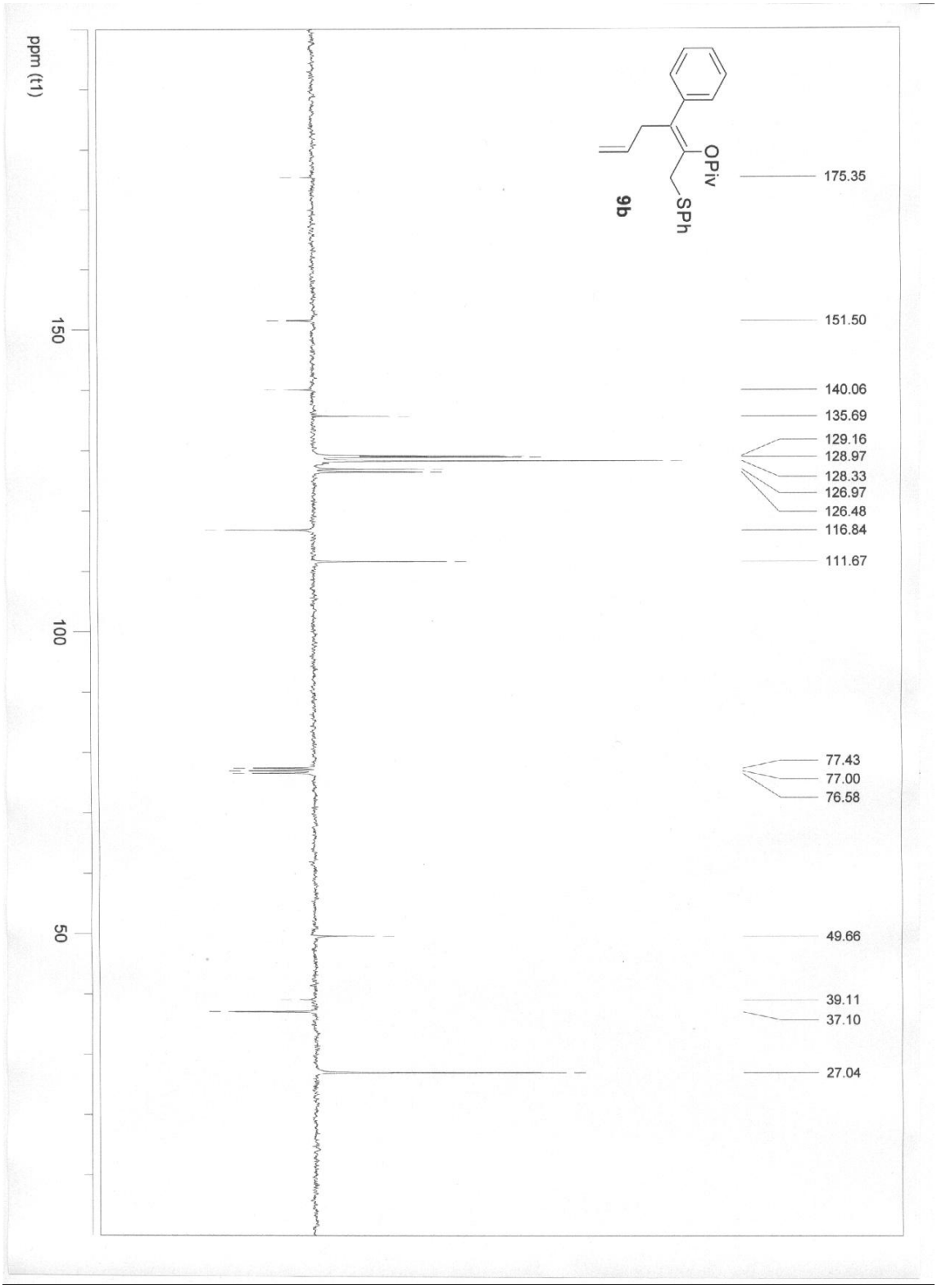
HMBC of **9a**


Sebastien Albrecht SAL-27T1 (Barcode 2651) in CDCl3 at +27C, set temp,
drx500, 1D-GOESY
selective
excitation
site
nOe
nOe
nOe
nOe
jn25sa1d'1/1
jn25sa1d/2/1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm

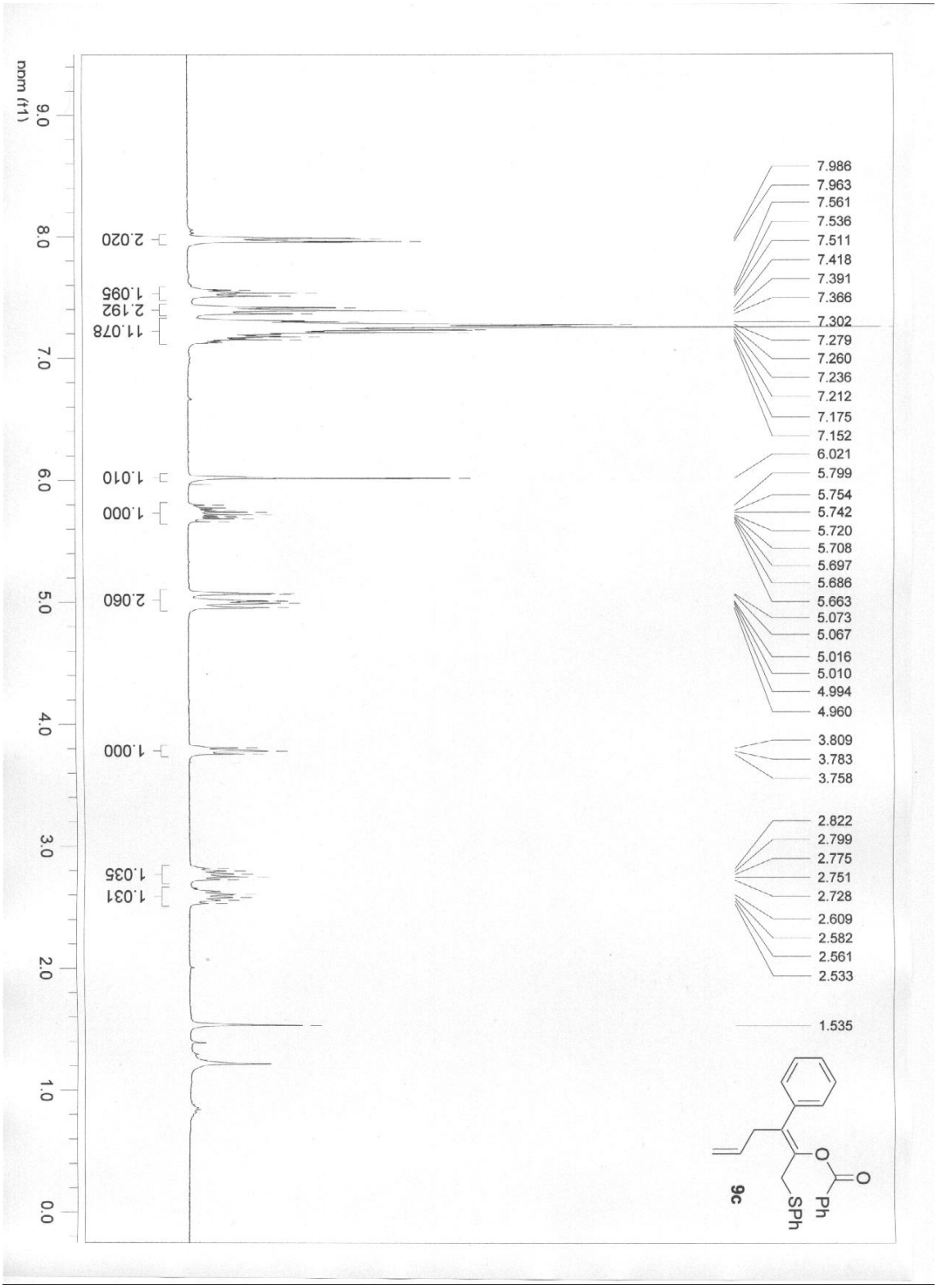
NOE of **9a**



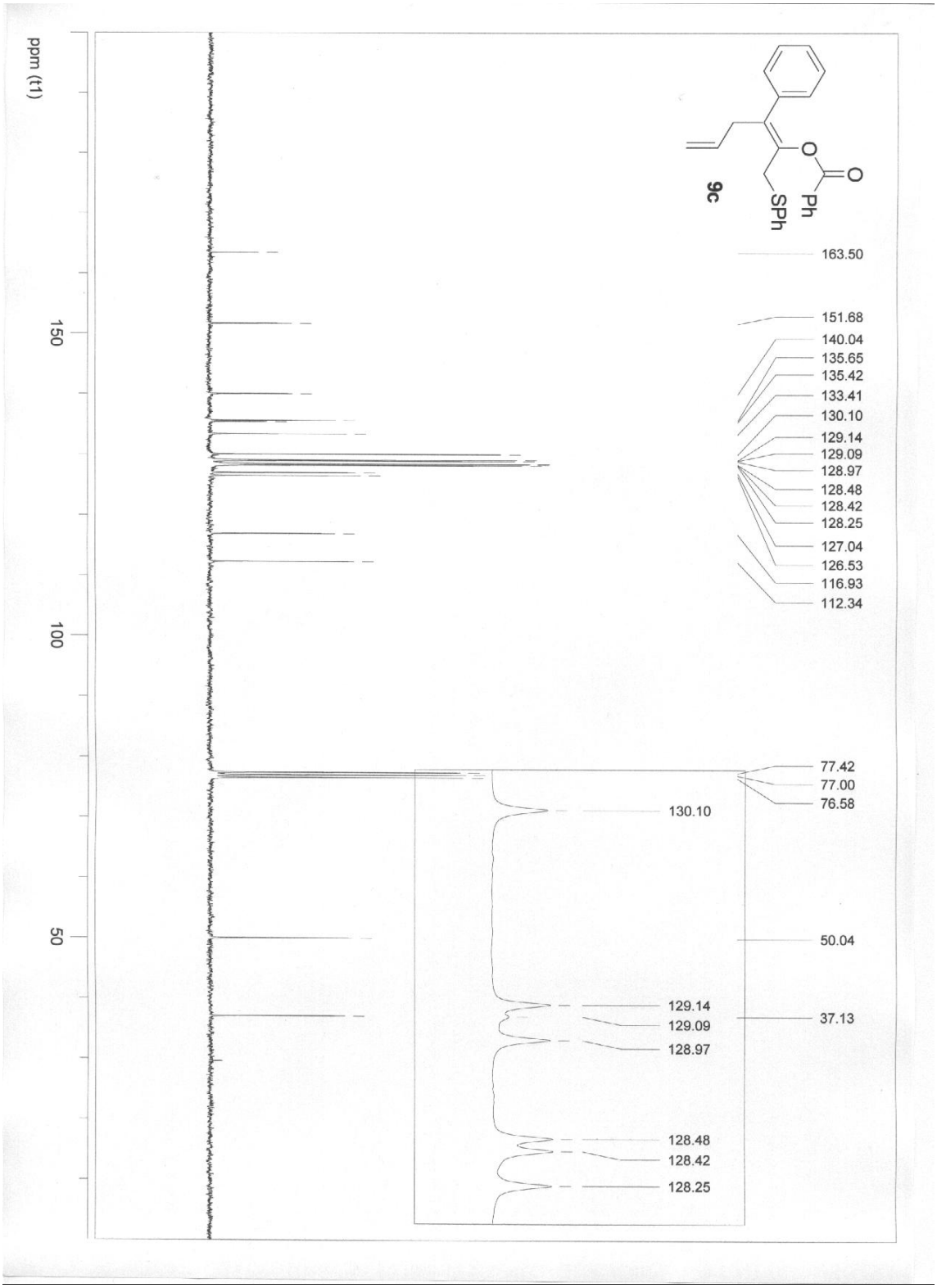
^{1}H-NMR (300 MHz, $CDCl_3$) of **9b**



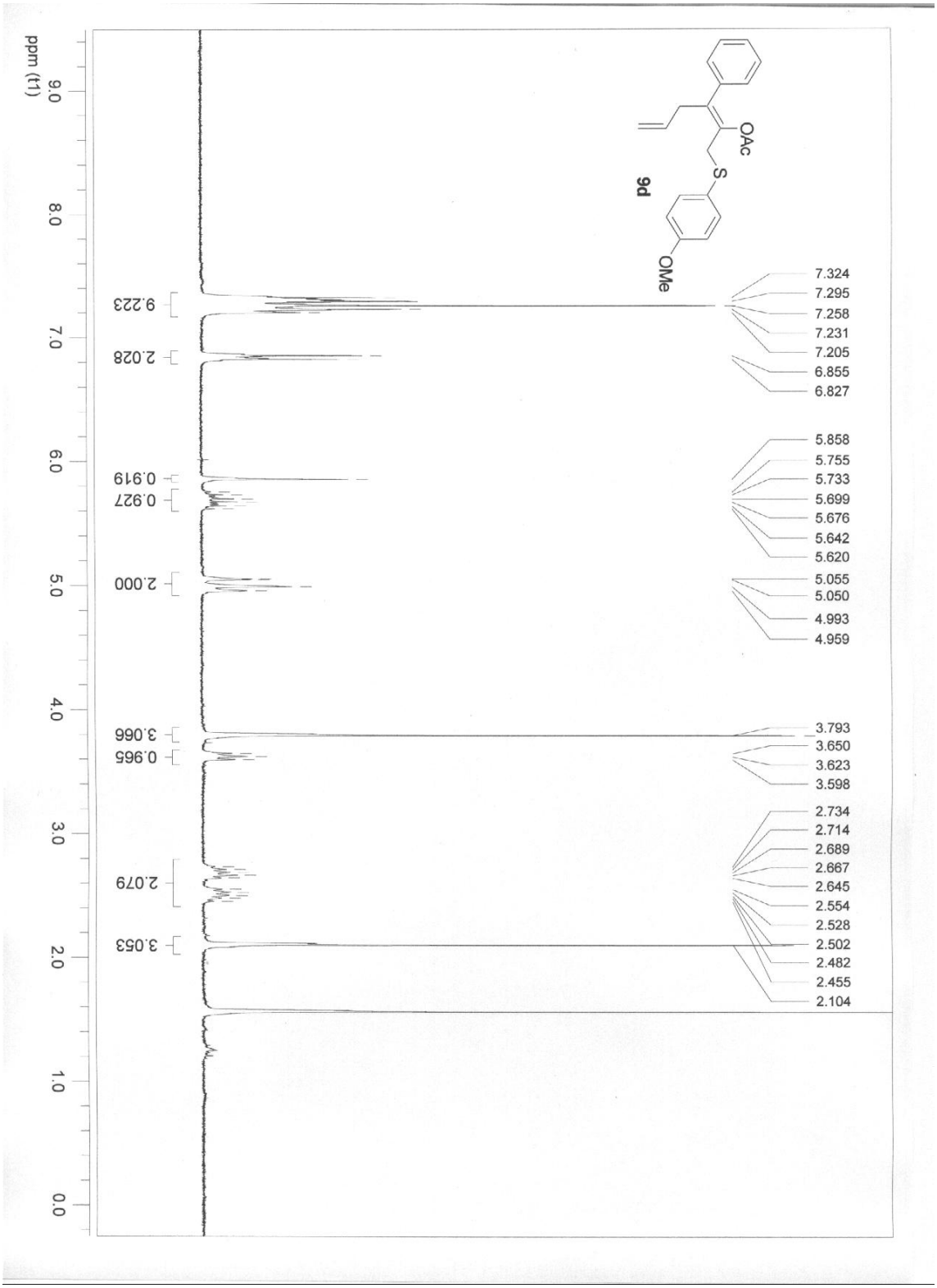
^{13}C-NMR (75 MHz, $CDCl_3$) of **9b**



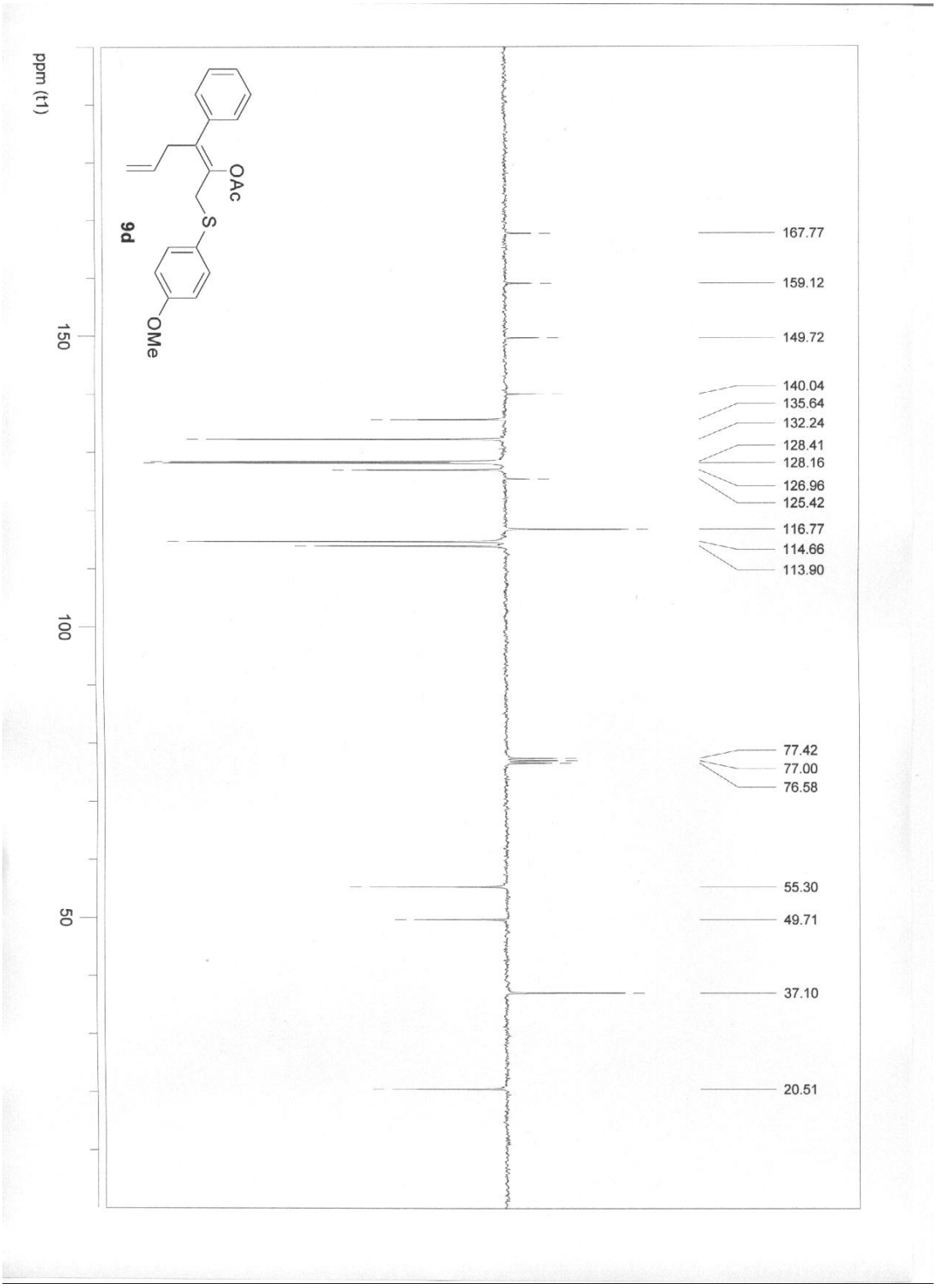
^{1}H-NMR (300 MHz, $CDCl_3$) of **9c**



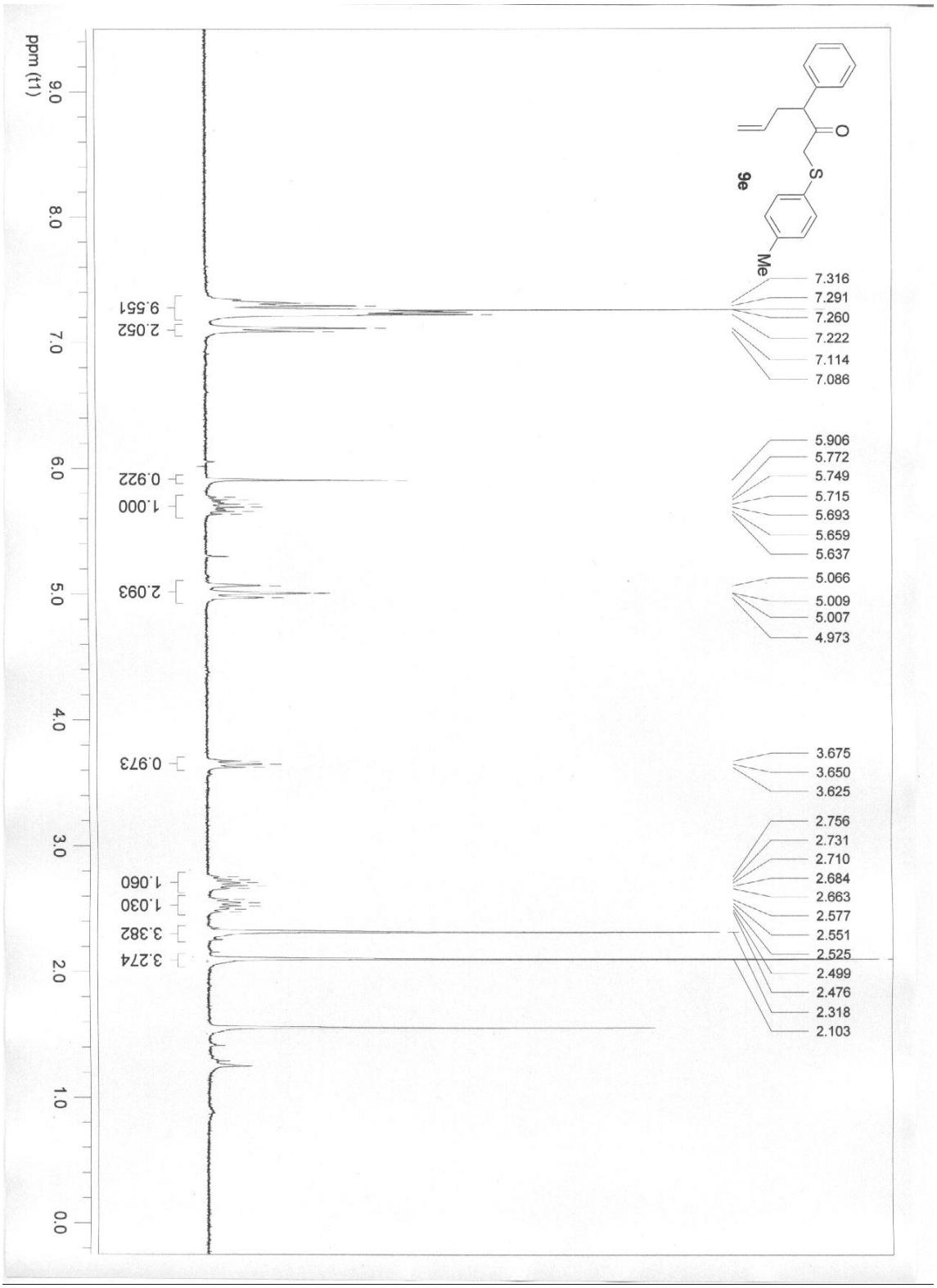
^{13}C-NMR (75 MHz, $CDCl_3$) of **9c**



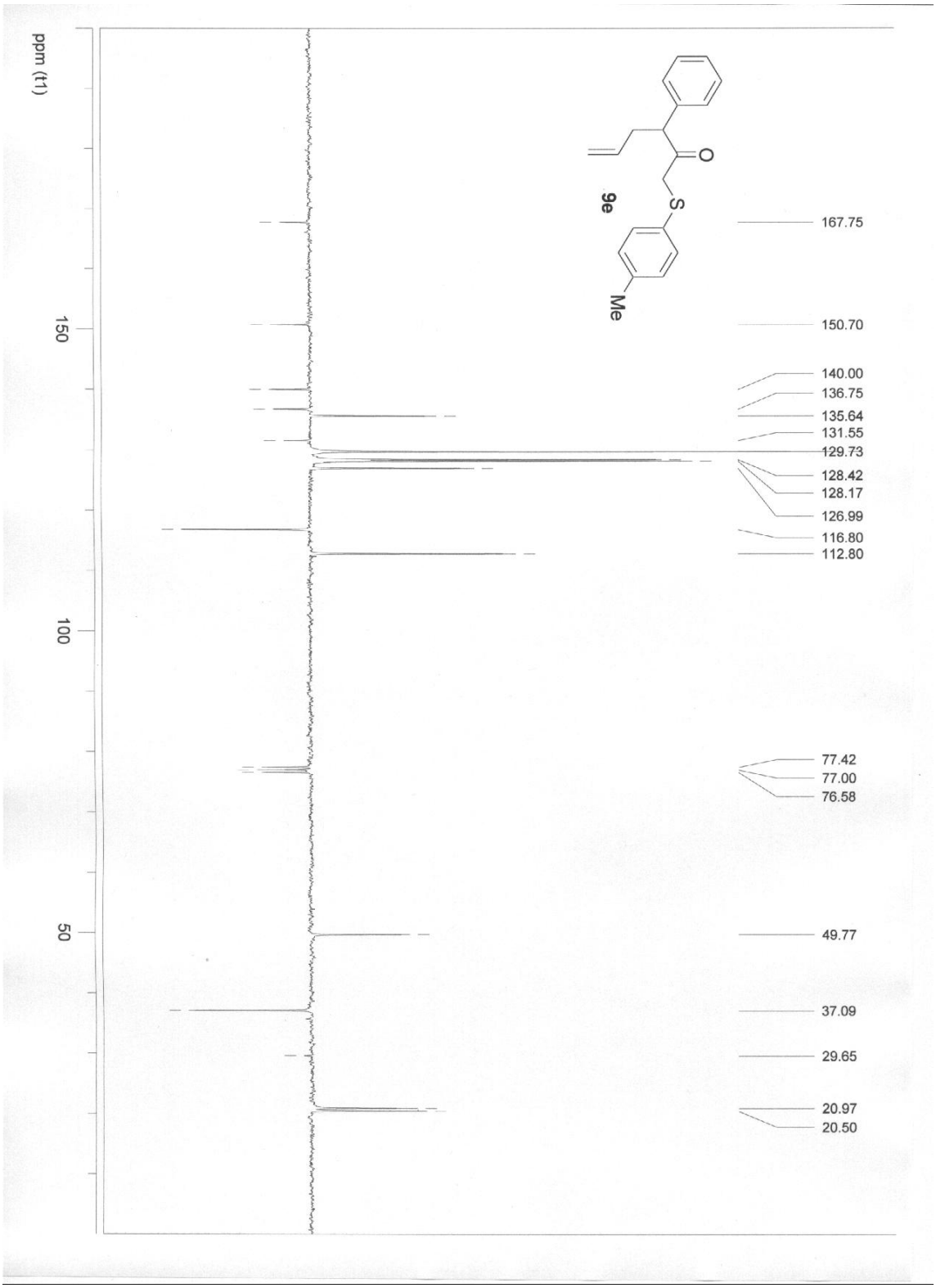
^{1}H-NMR (300 MHz, $CDCl_3$) of **9d**



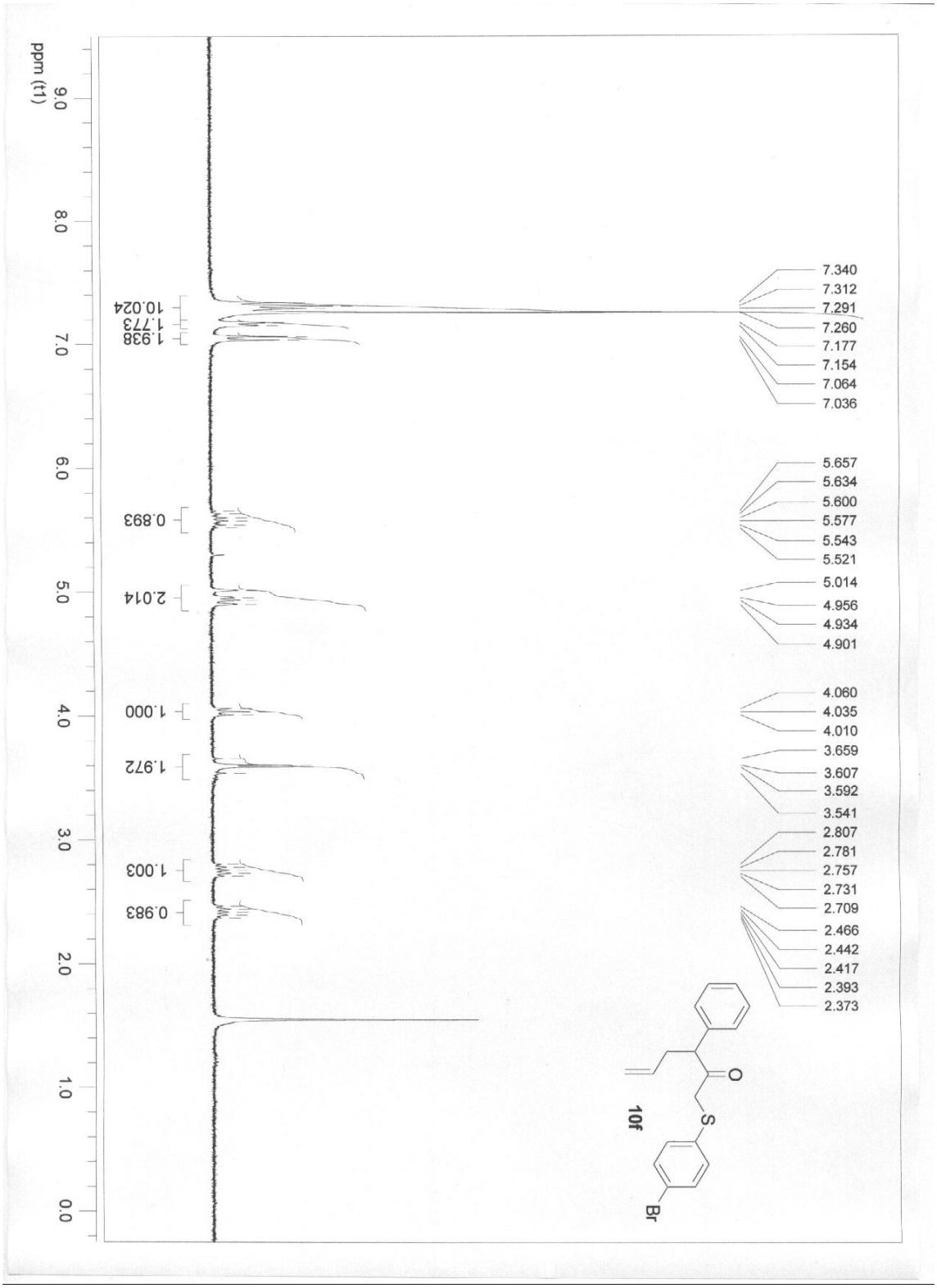
^{13}C-NMR (75 MHz, $CDCl_3$) of **9d**



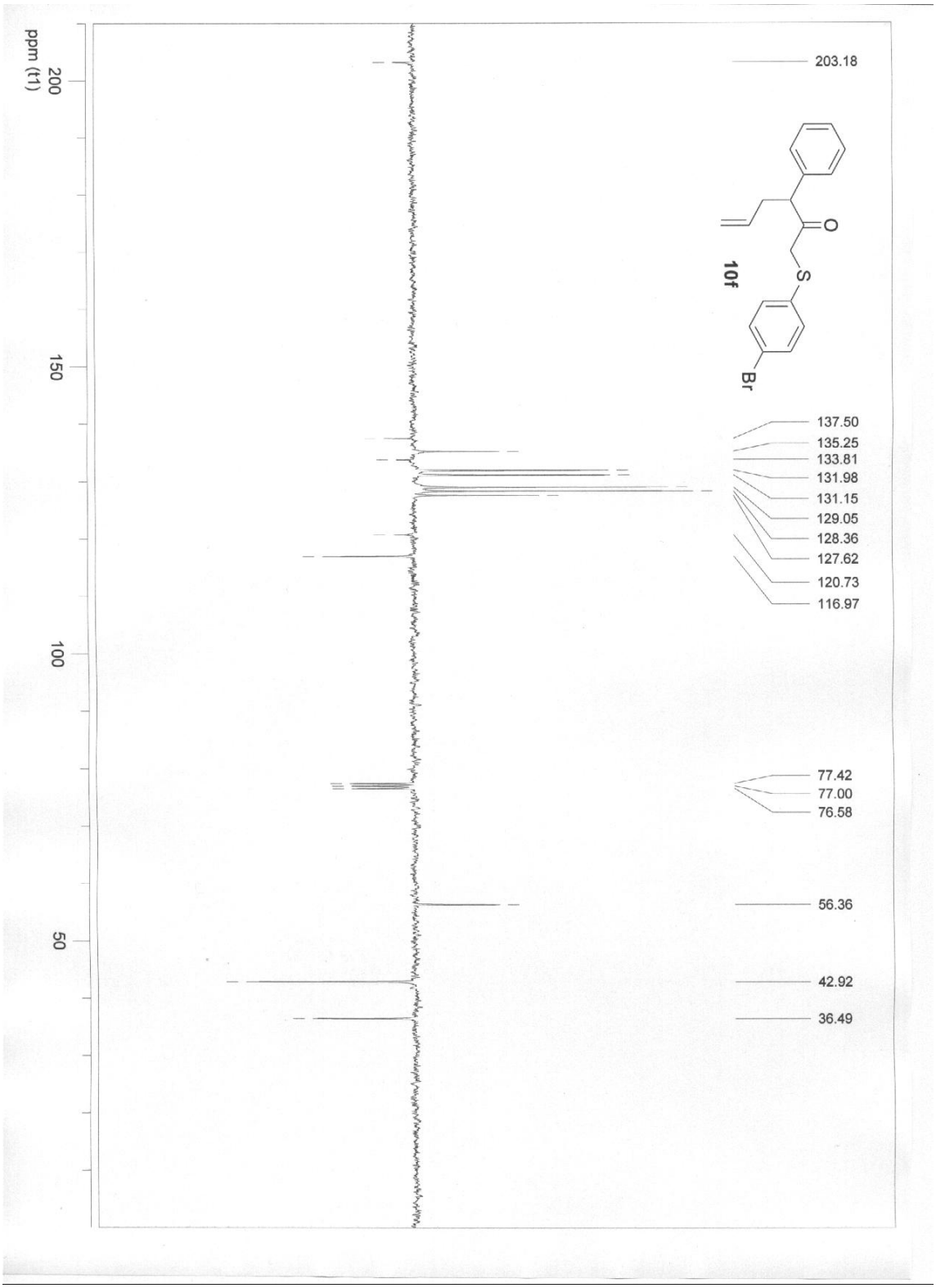
^{1}H-NMR (300 MHz, $CDCl_3$) of **9e**



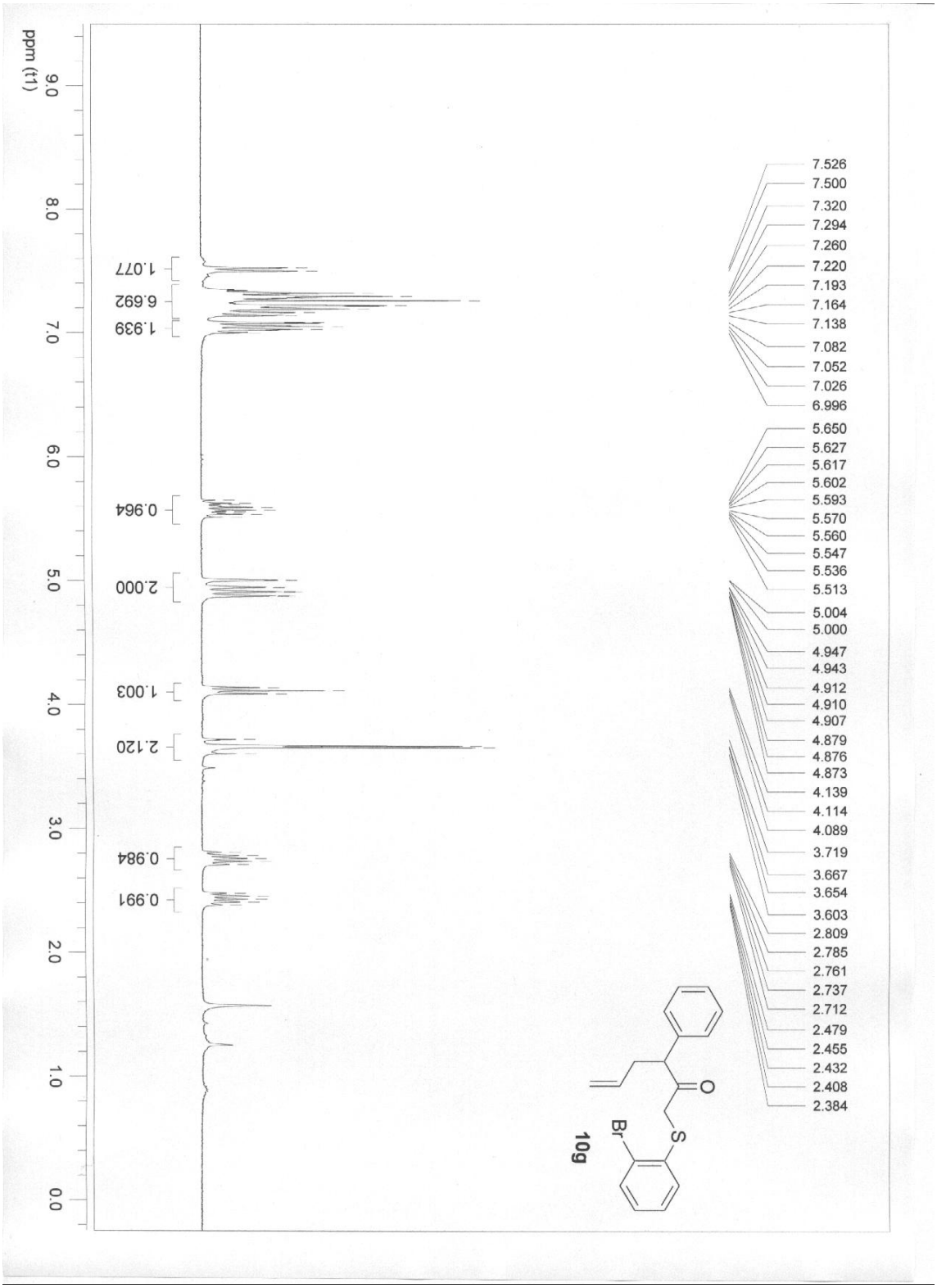
^{13}C-NMR (75 MHz, $CDCl_3$) of **9e**



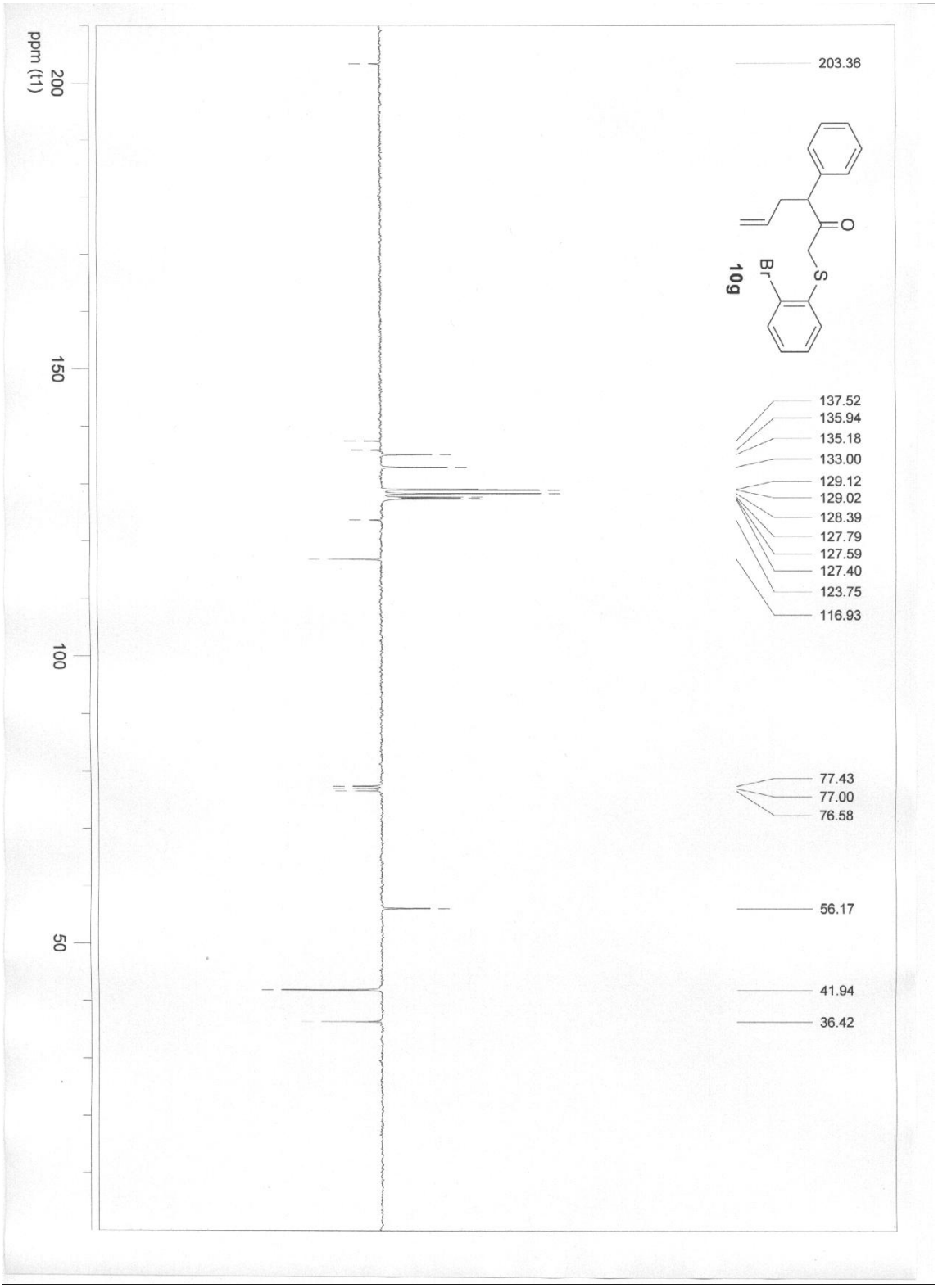
^{1}H-NMR (300 MHz, $CDCl_3$) of **10f**



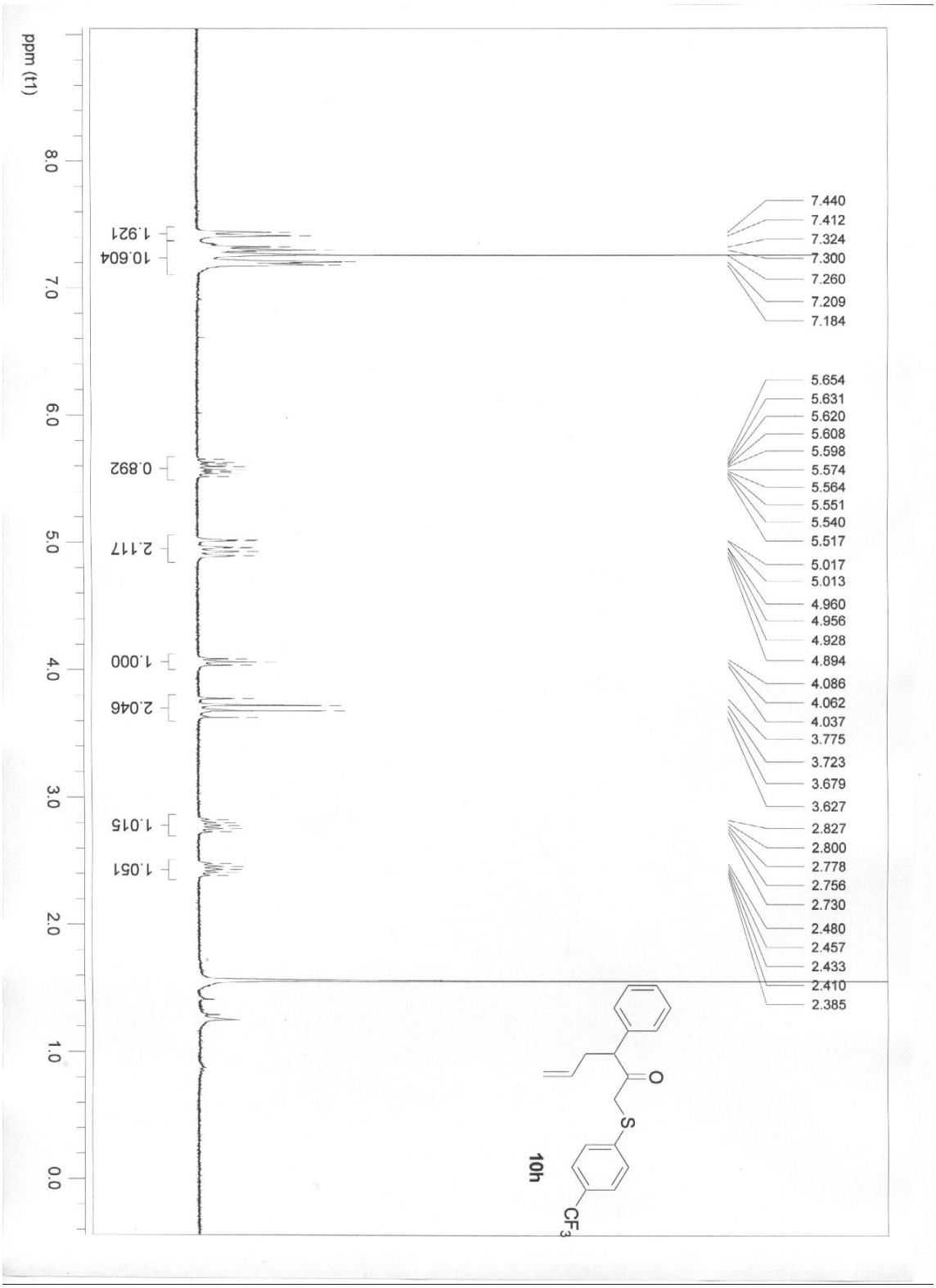
^{13}C-NMR (75 MHz, $CDCl_3$) of **10f**



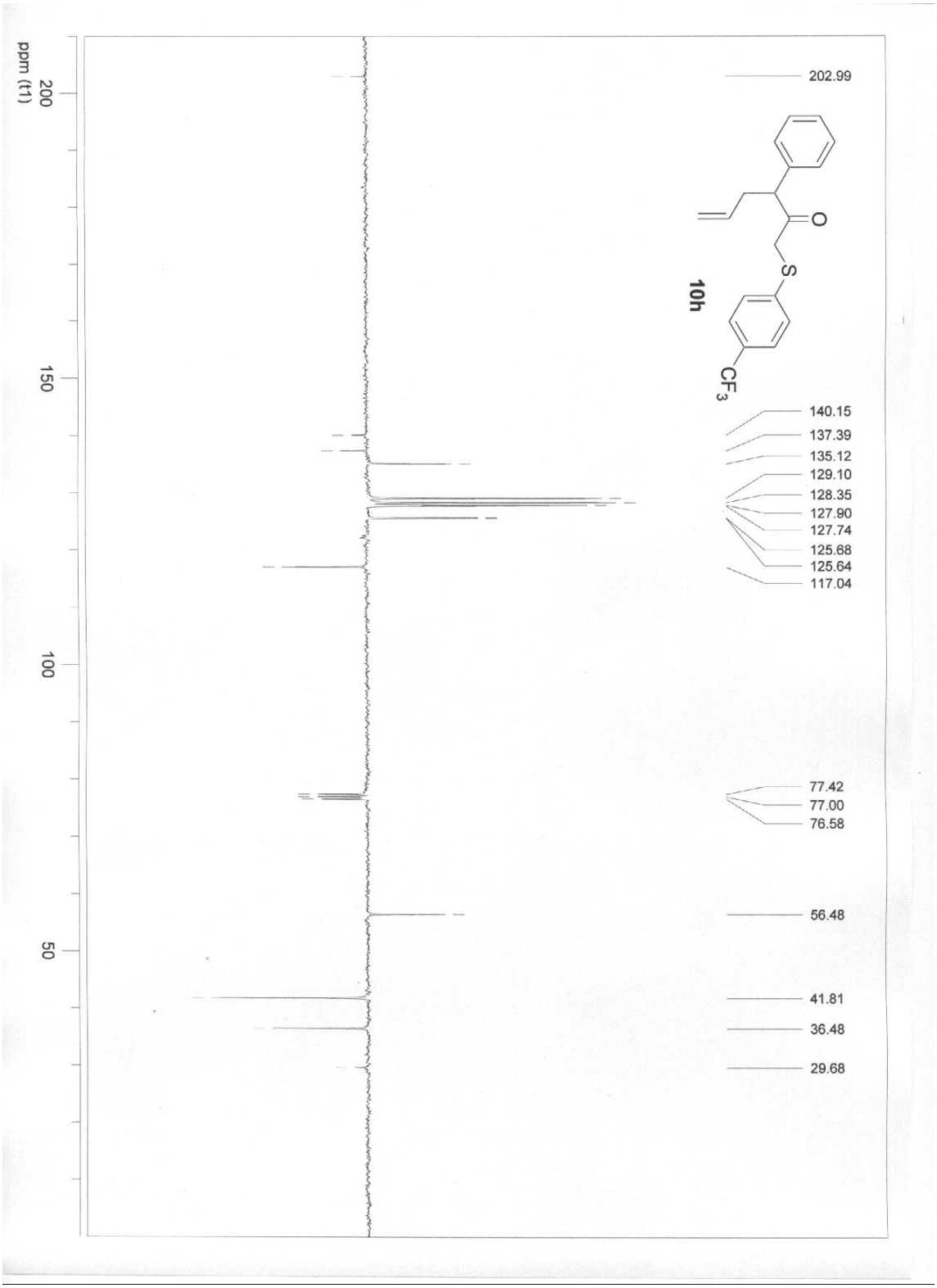
^{1}H-NMR (300 MHz, $CDCl_3$) of **10g**



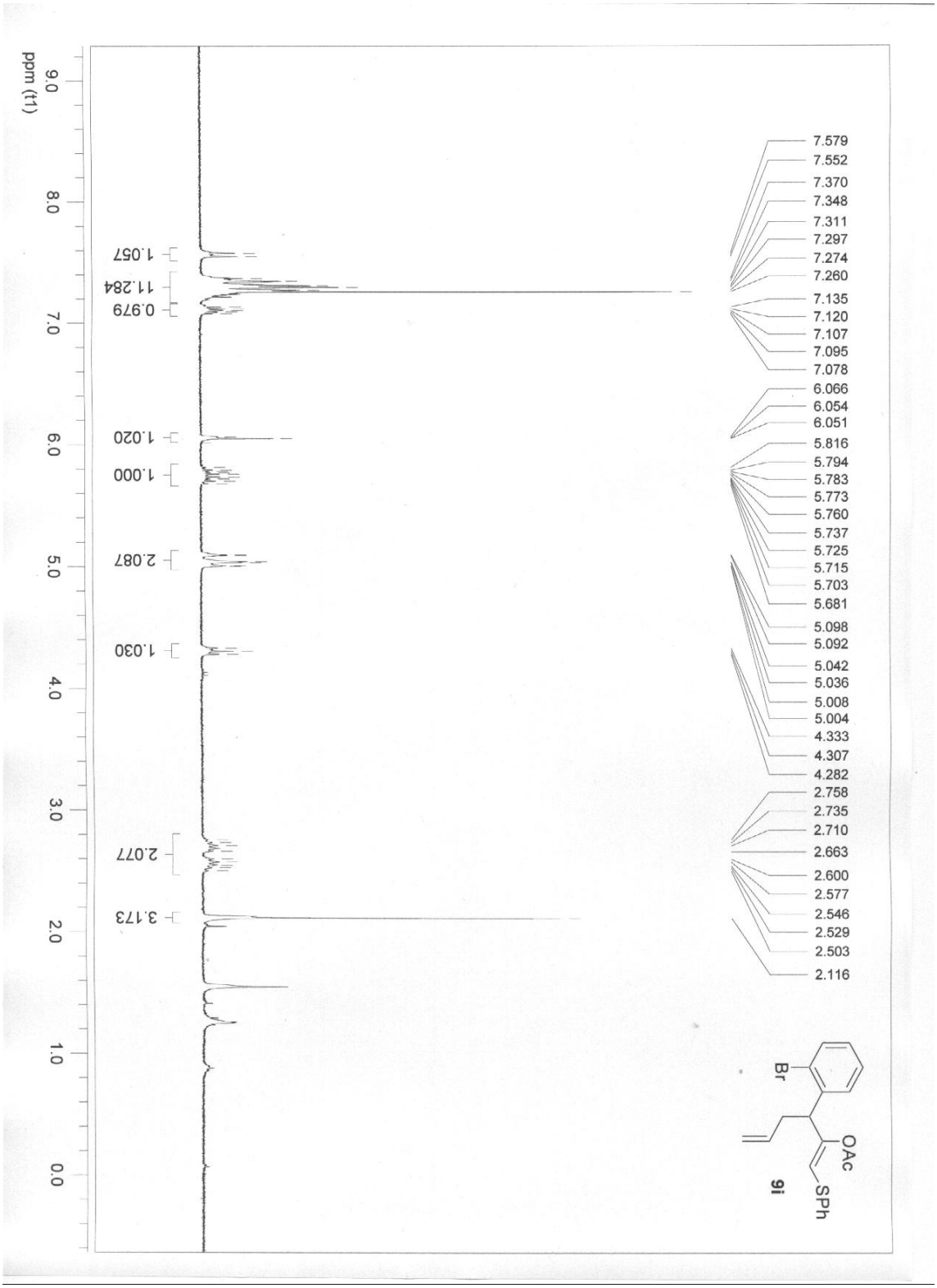
^{13}C-NMR (75 MHz, $CDCl_3$) of **10g**



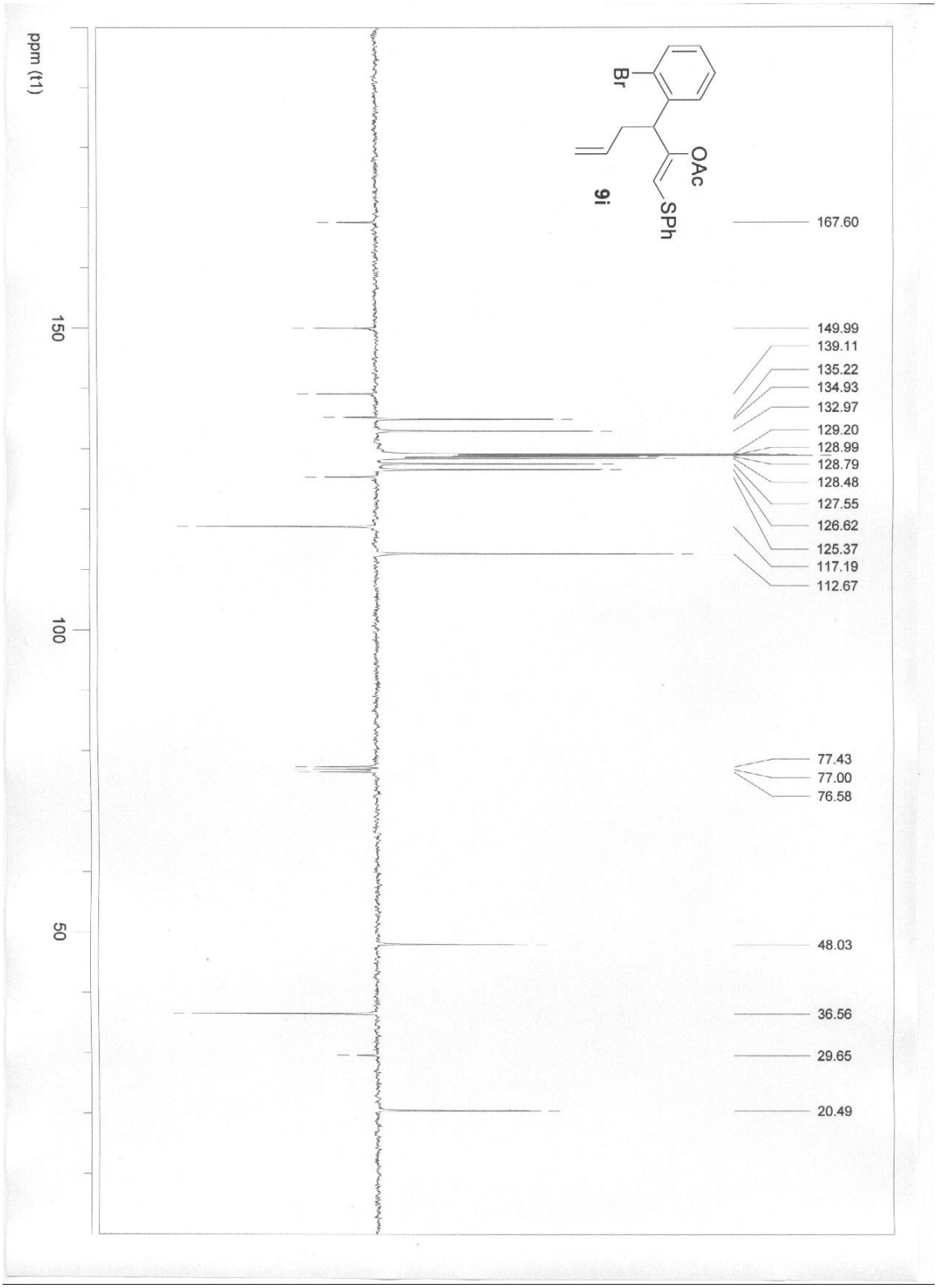
^{1}H-NMR (300 MHz, $CDCl_3$) of **10h**



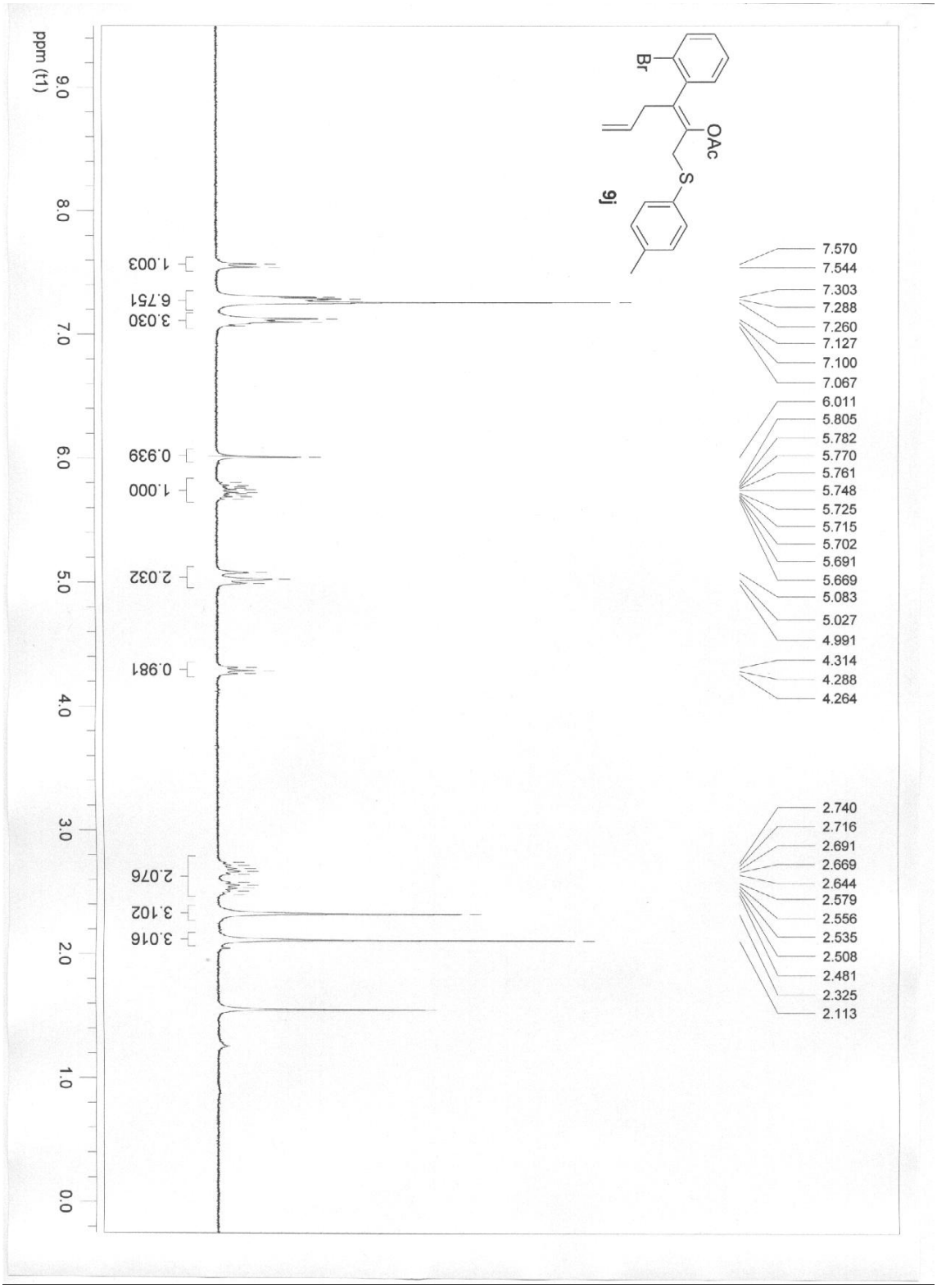
^{13}C-NMR (75 MHz, $CDCl_3$) of **10h**



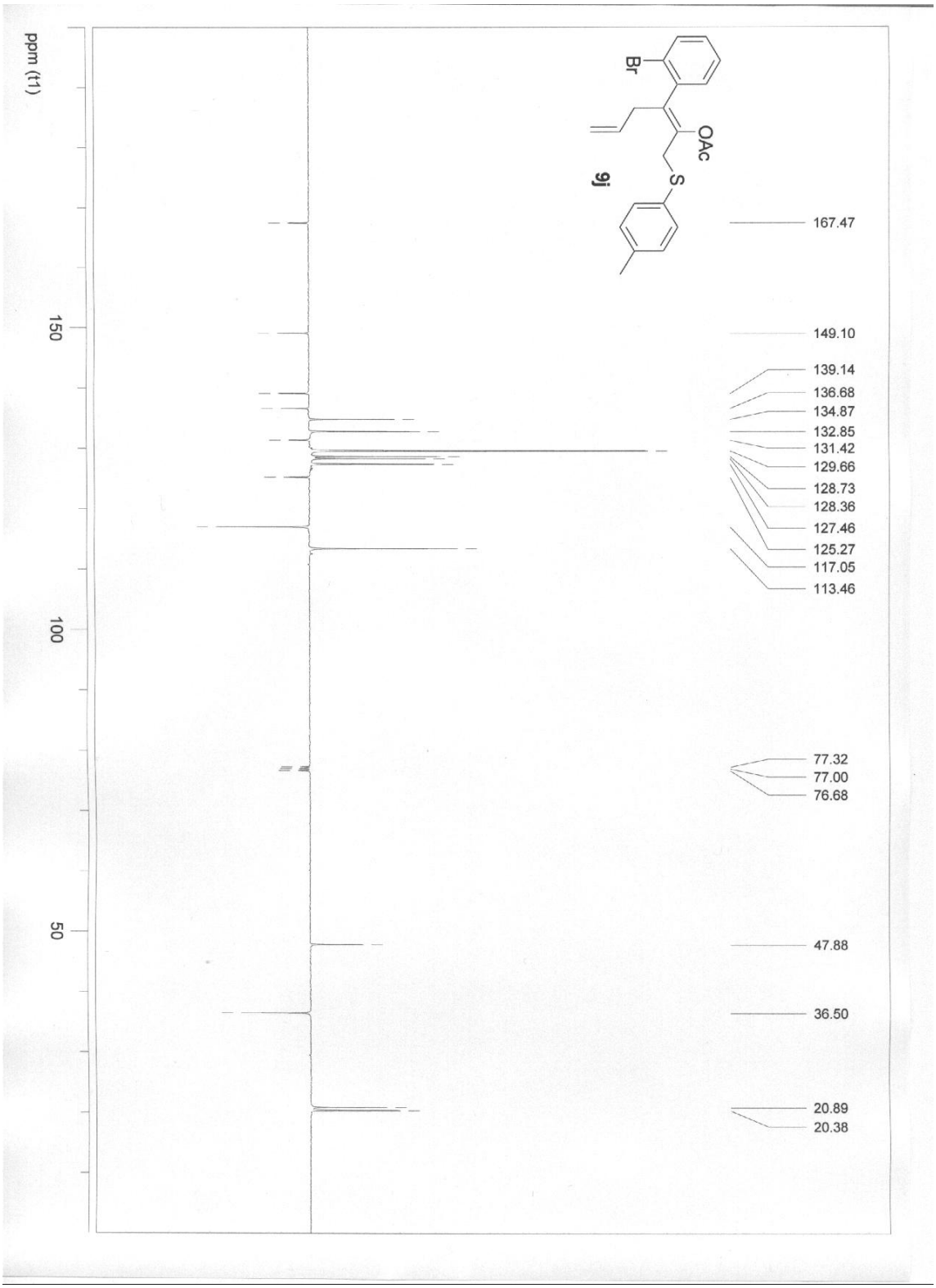
^{1}H-NMR (300 MHz, $CDCl_3$) of **9i**



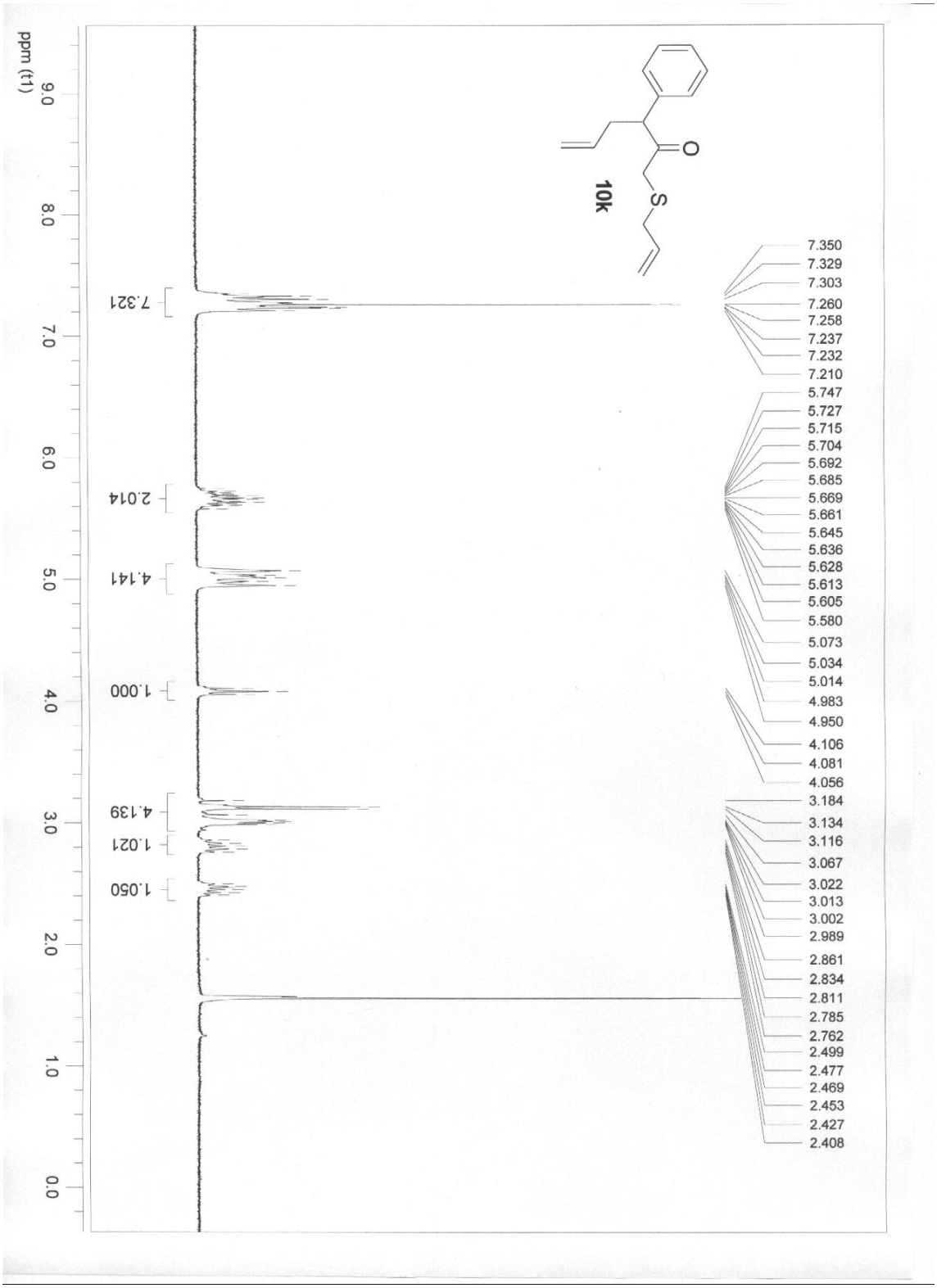
^{13}C-NMR (75 MHz, $CDCl_3$) of **9i**



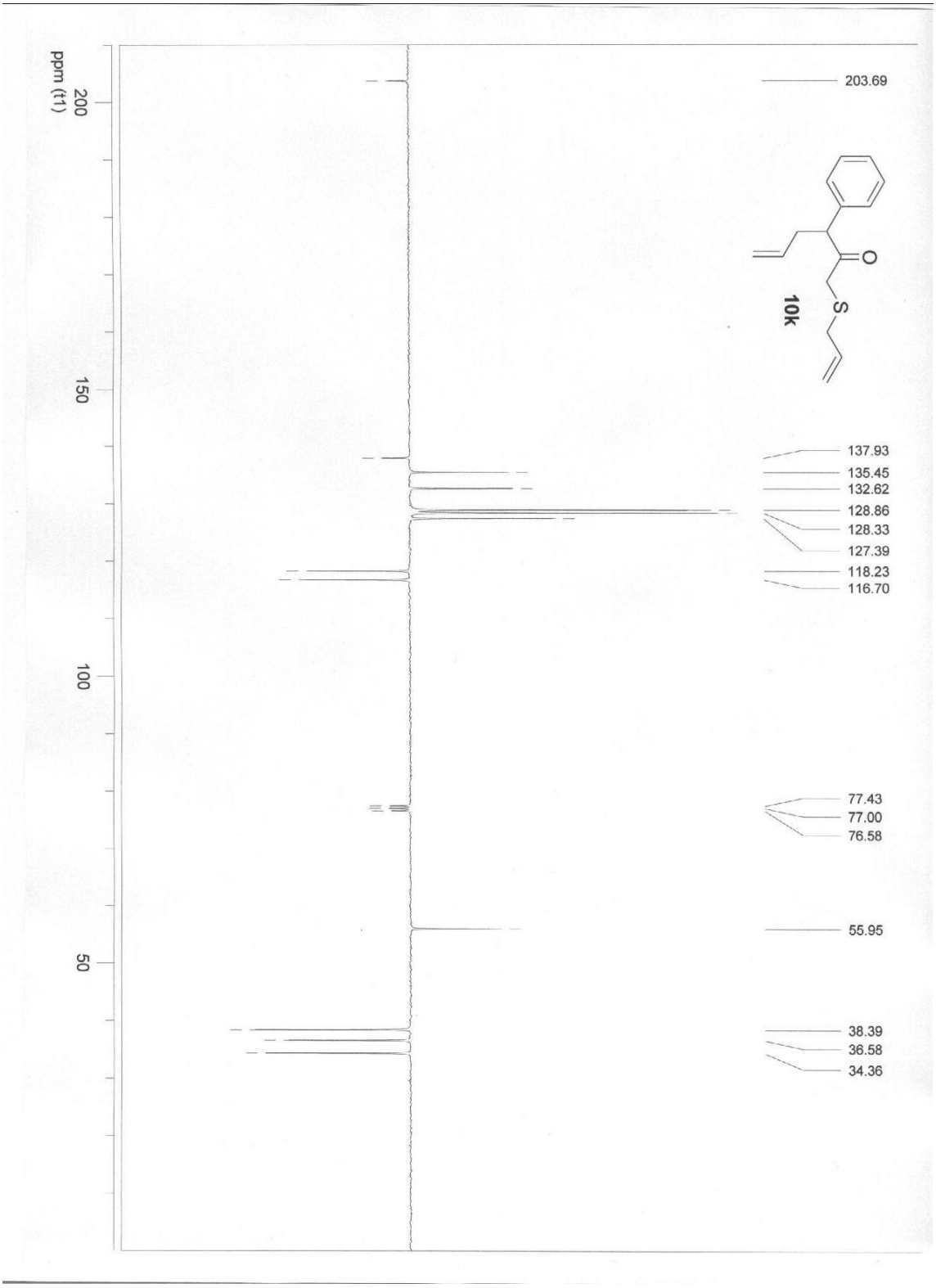
^{1}H-NMR (300 MHz, $CDCl_3$) of **9j**



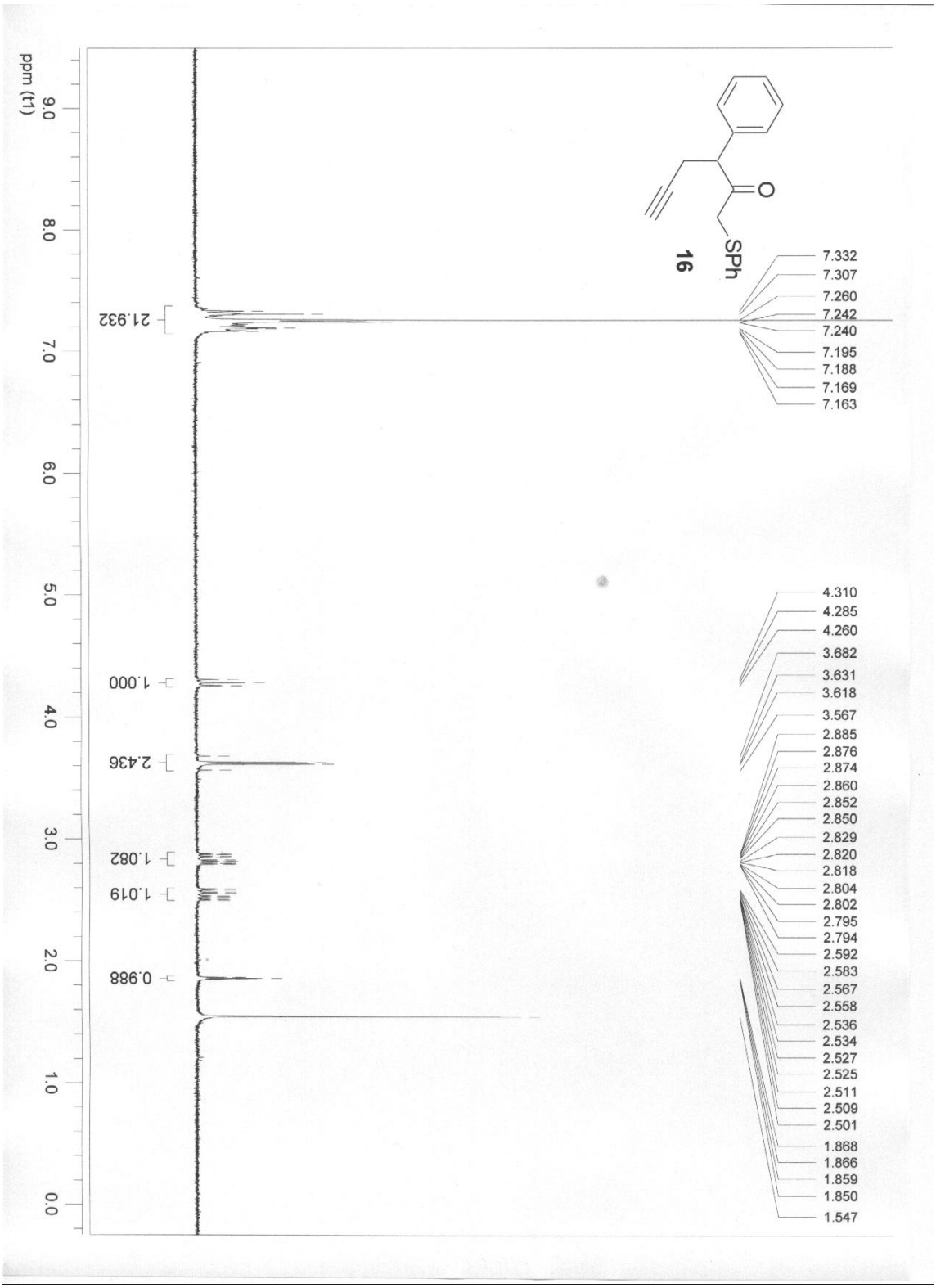
^{13}C-NMR (75 MHz, $CDCl_3$) of **9j**



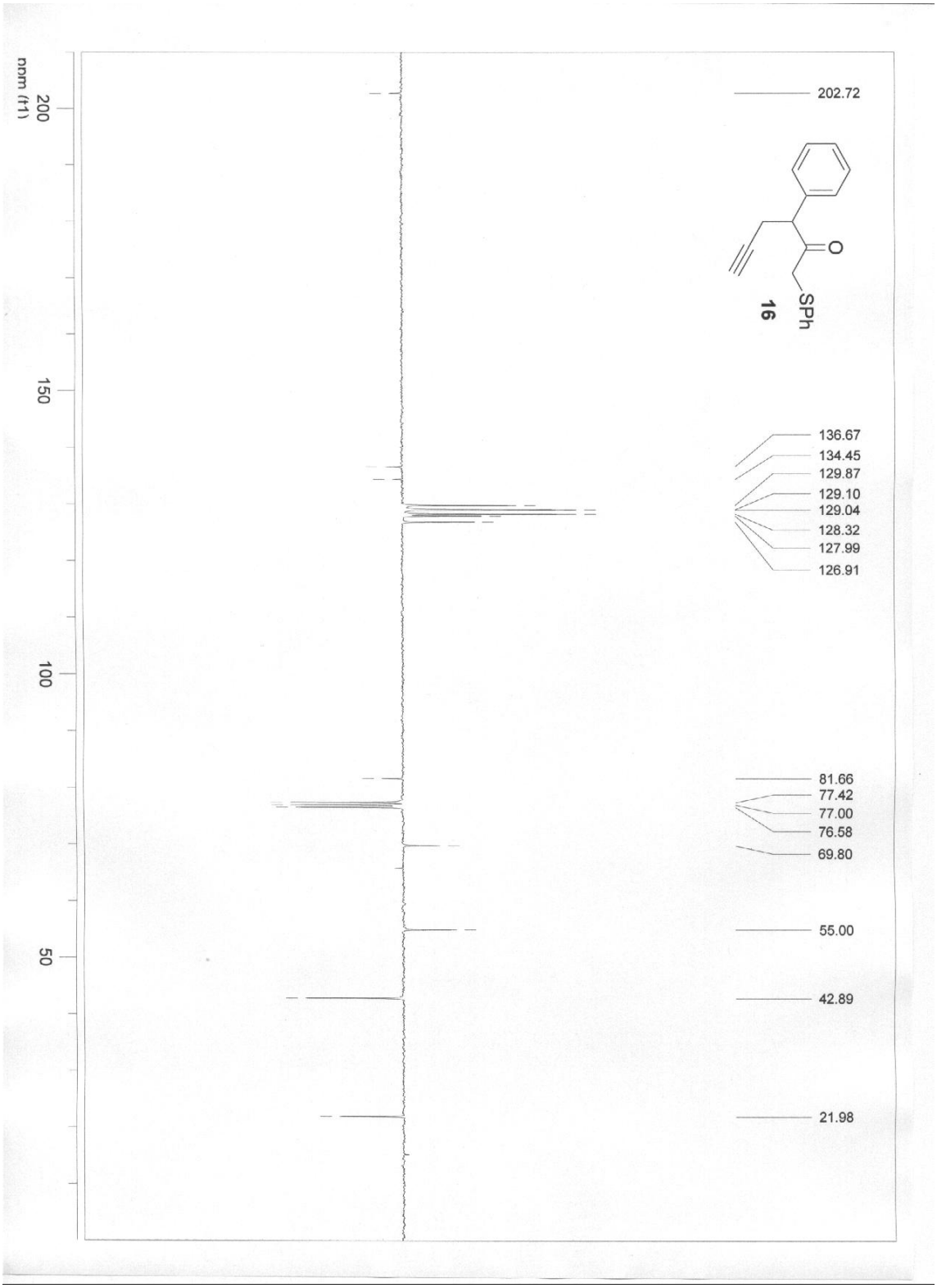
^{1}H-NMR (300 MHz, $CDCl_3$) of **10k**



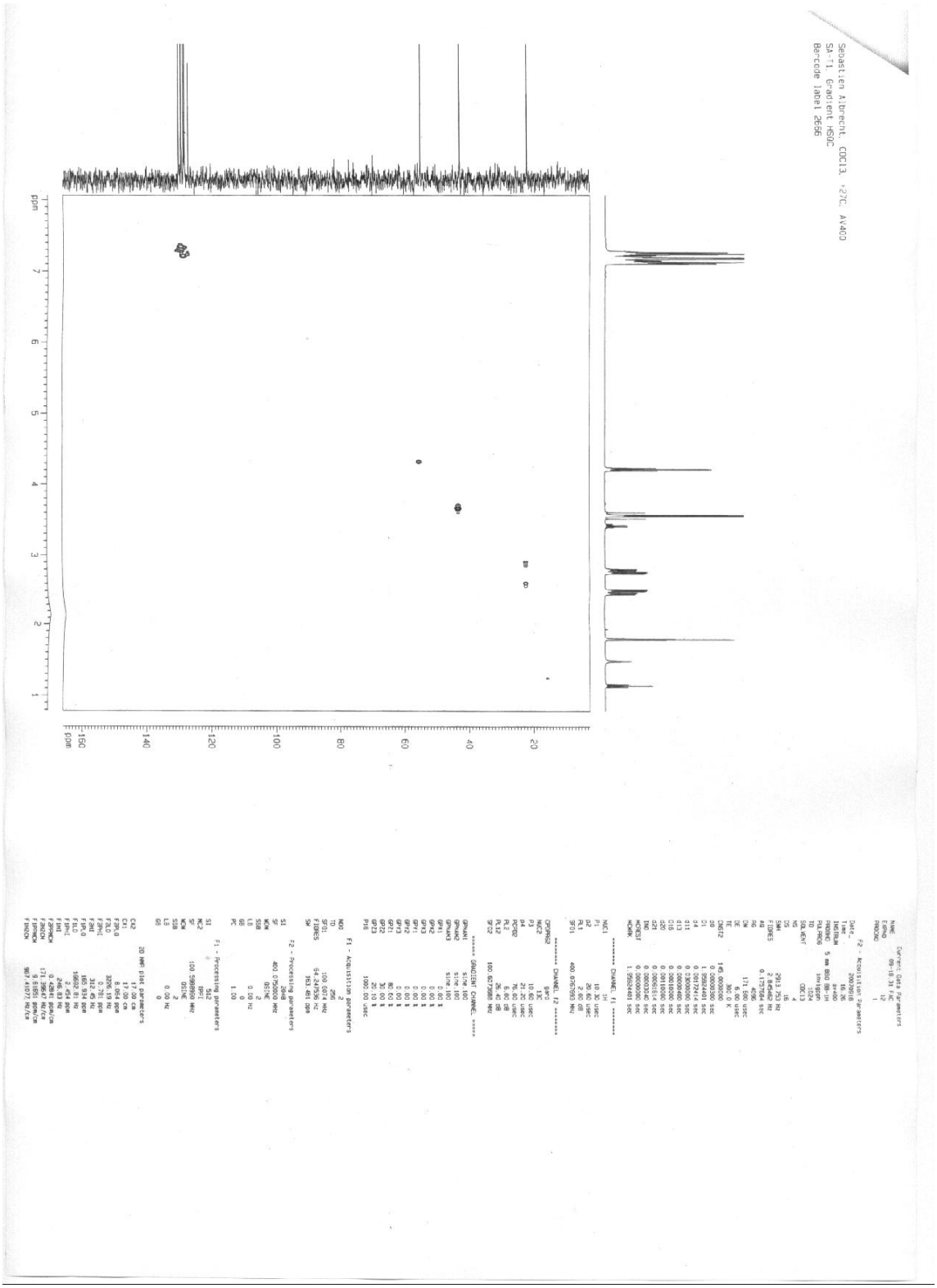
^{13}C-NMR (75 MHz, $CDCl_3$) of **10k**



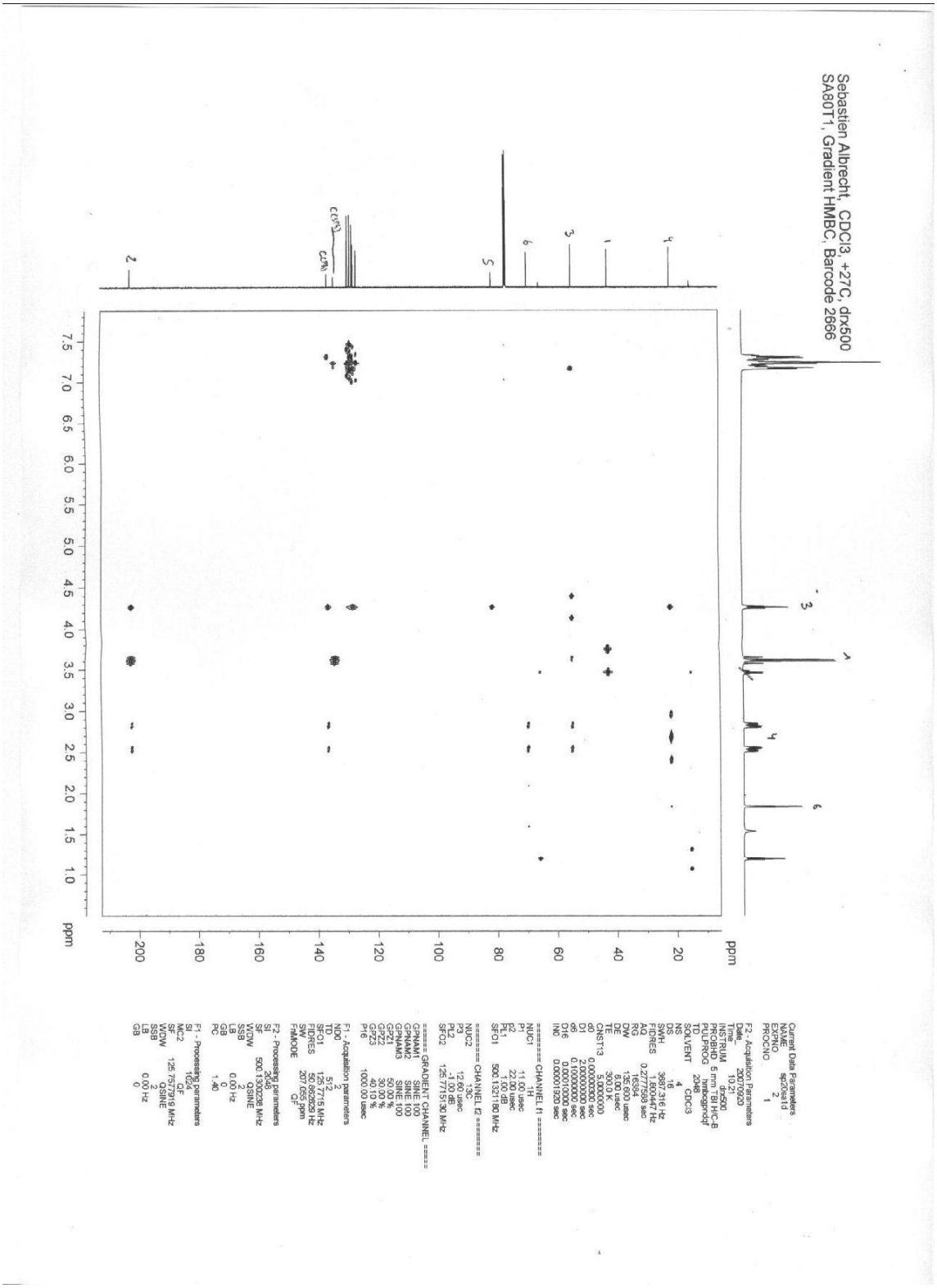
^{1}H-NMR (300 MHz, $CDCl_3$) of **16**



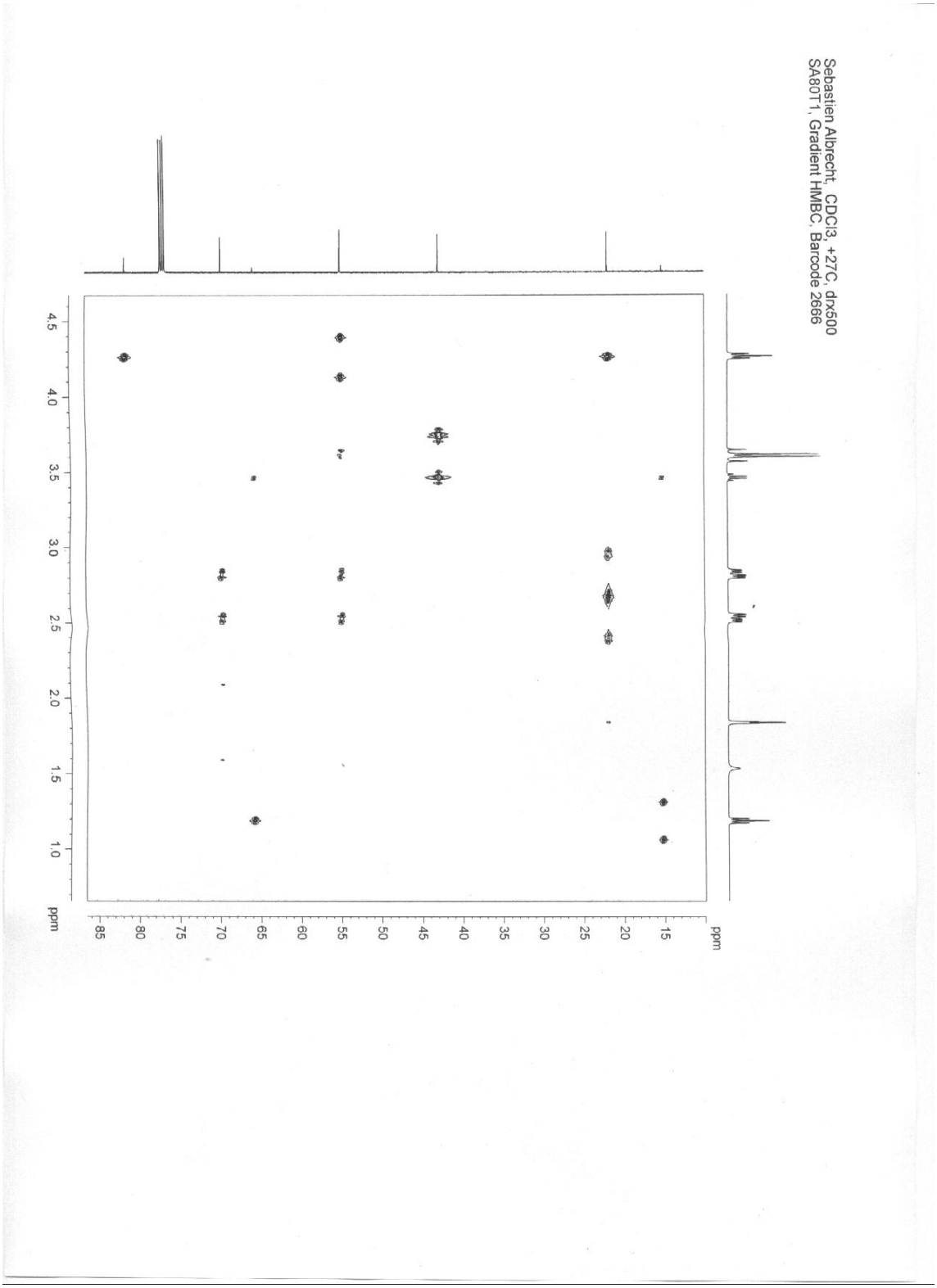
^{13}C-NMR (75 MHz, $CDCl_3$) of **16**



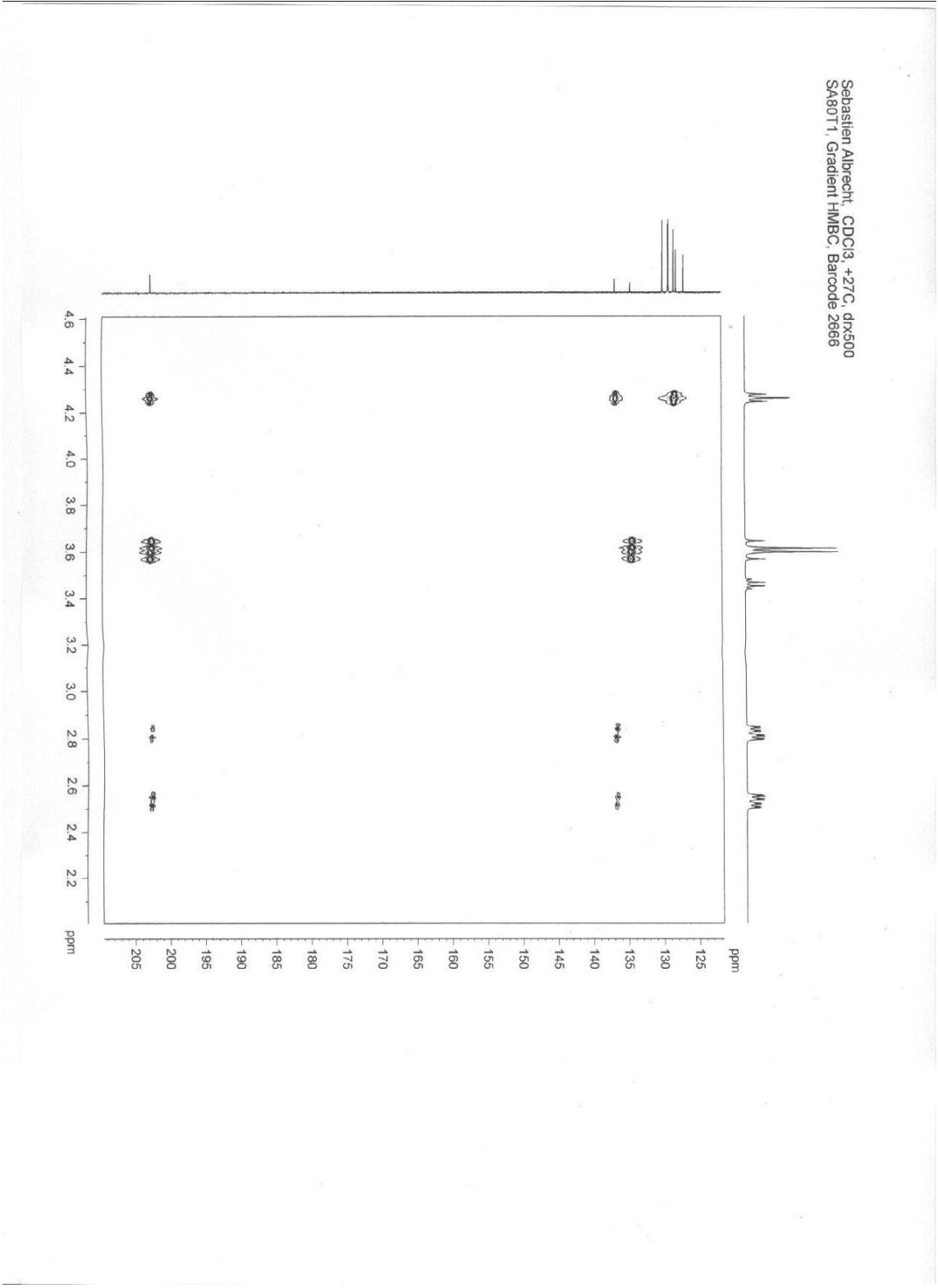
HSQC of **16**


Sebastien Albrecht, CDCl3, +27C, drx500
SA80T1, Gradient HMBC, Barcode 2666
ppm
ppm

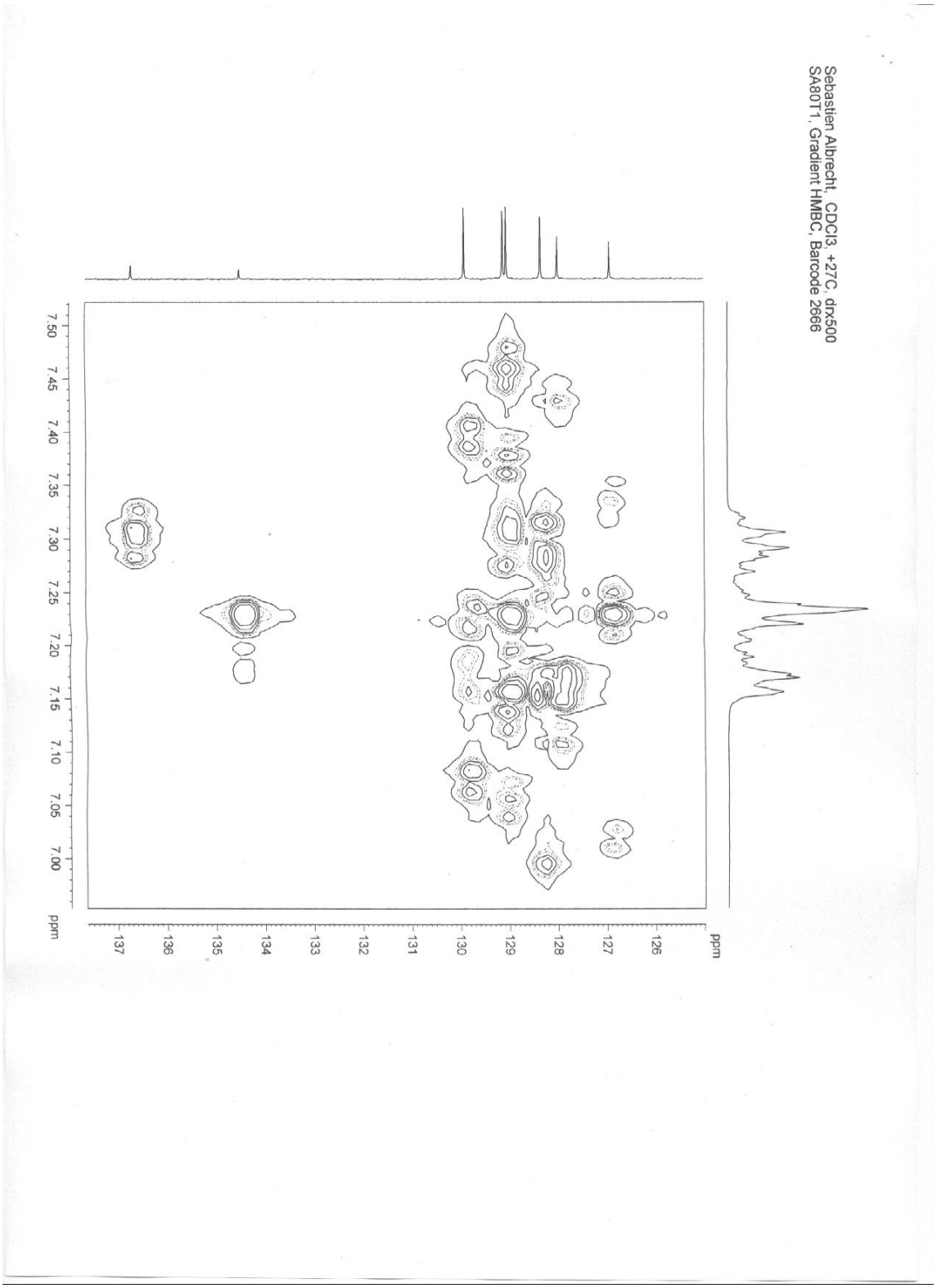
HMBC of **16**


Sebastien Albrecht, CDCl3, +27C, drx500
SA80T1, Gradient HMBC, Barcode 2666
ppm
ppm

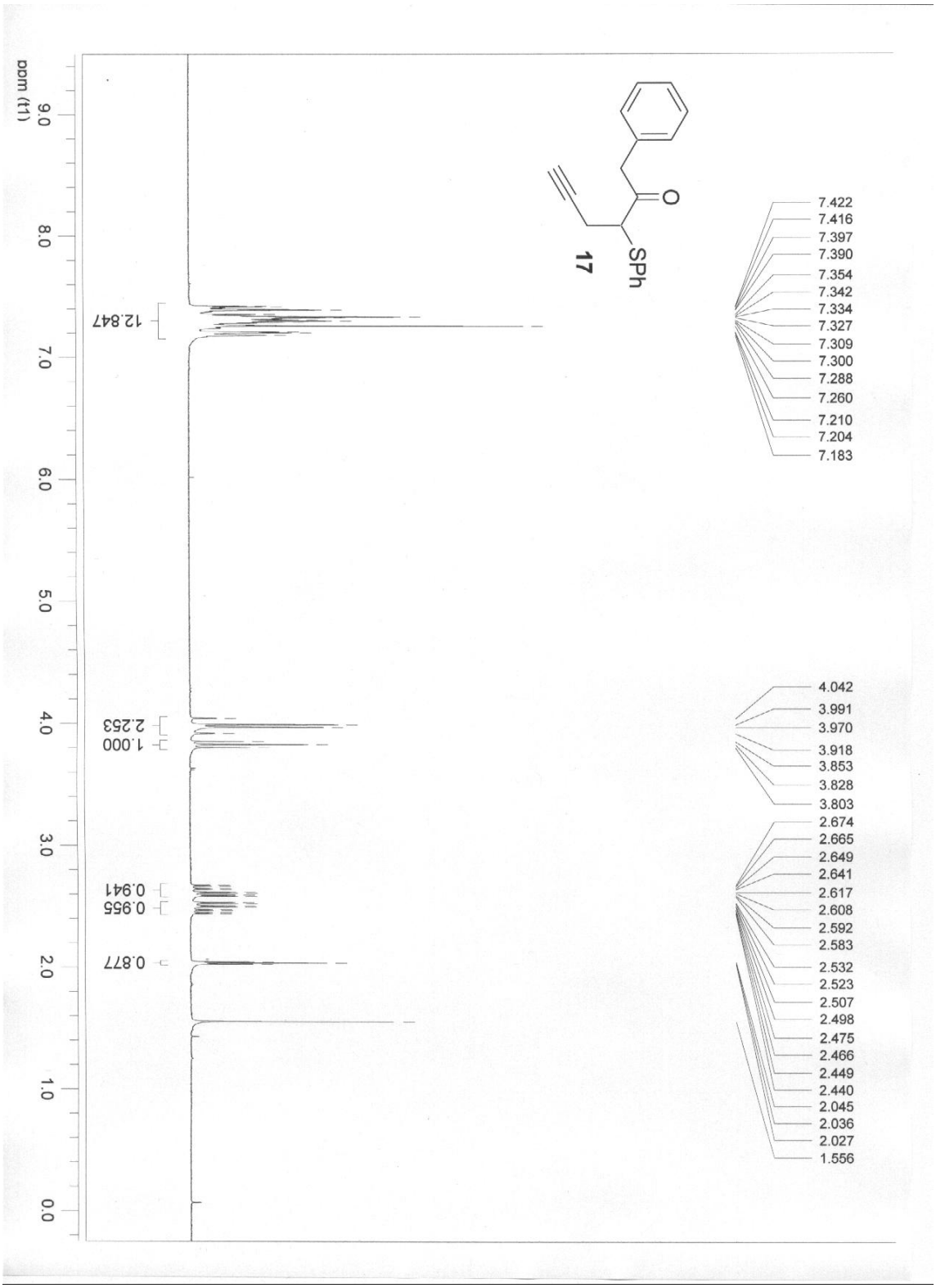
HMBC of **16**


Sebastien Albrecht, CDCl3, +27C, drx500
SA80T1, Gradient HMBC, Barcode 2666
ppm
ppm

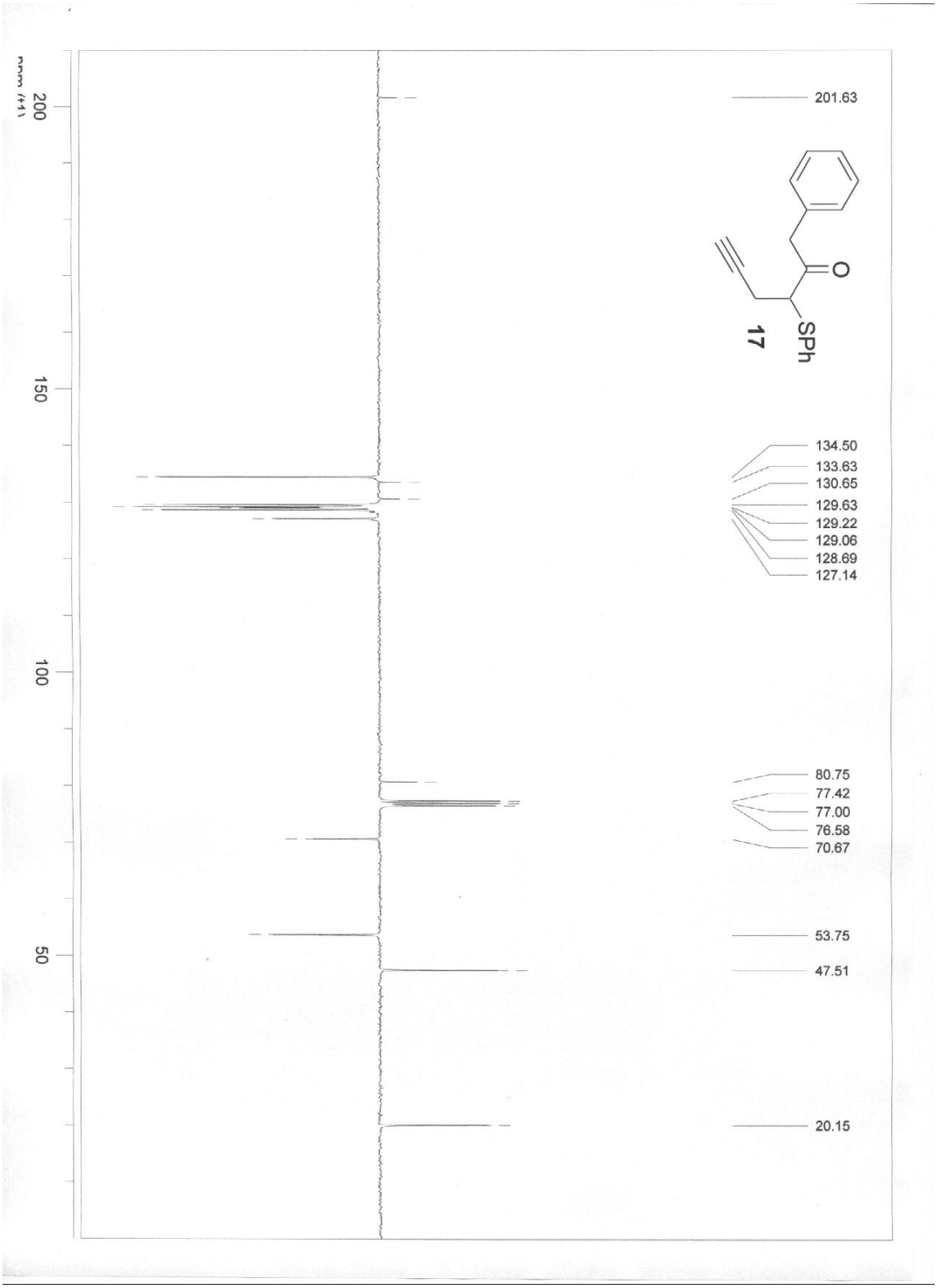
HMBC of **16**


Sebastien Albrecht, CDCl3, +27C, drx500
SA80T1, Gradient HMBC, Barcode 2666
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
7.00
ppm
137
136
135
134
133
132
131
130
129
128
127
126
ppm

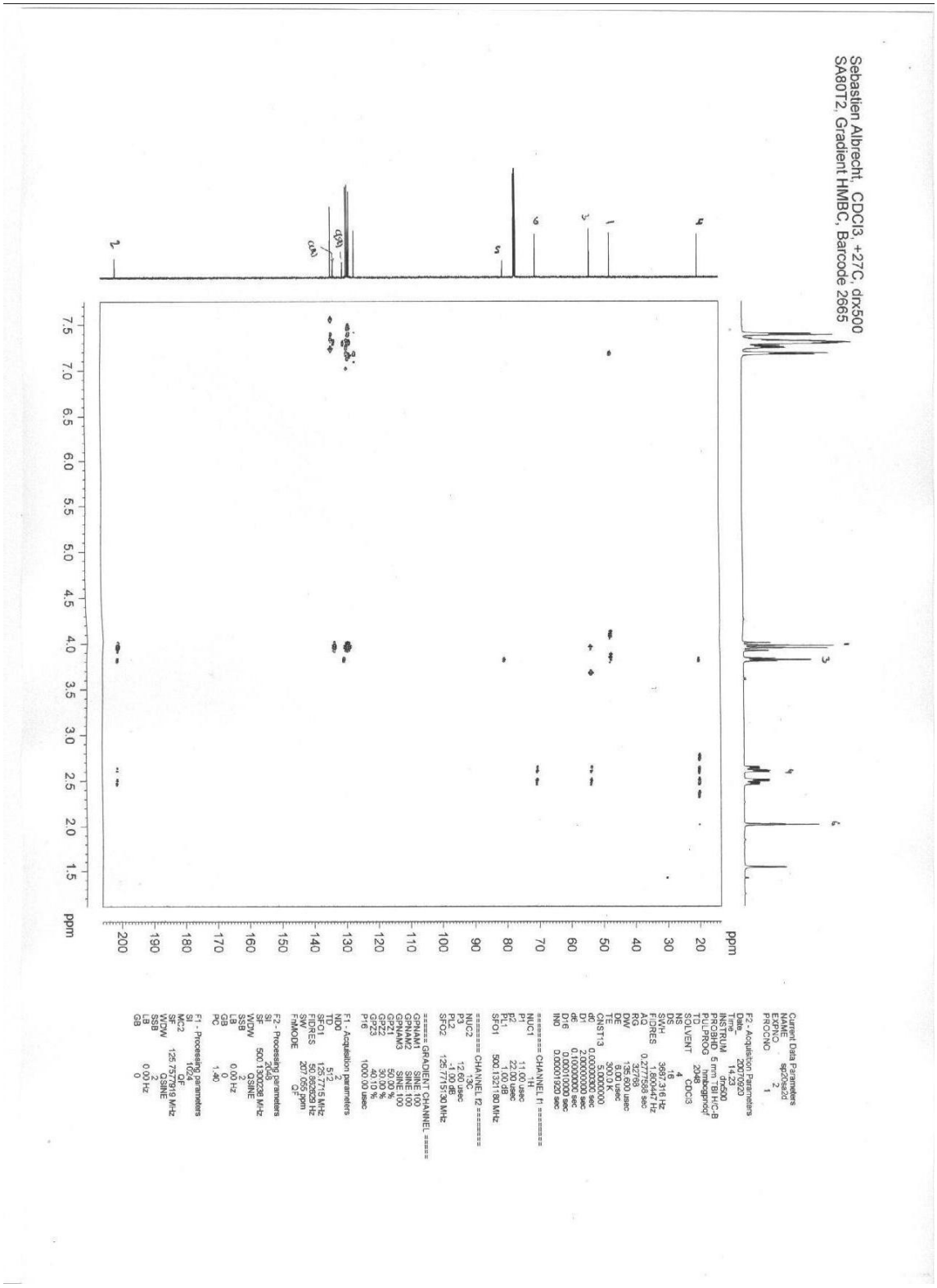
HMBC of **16**



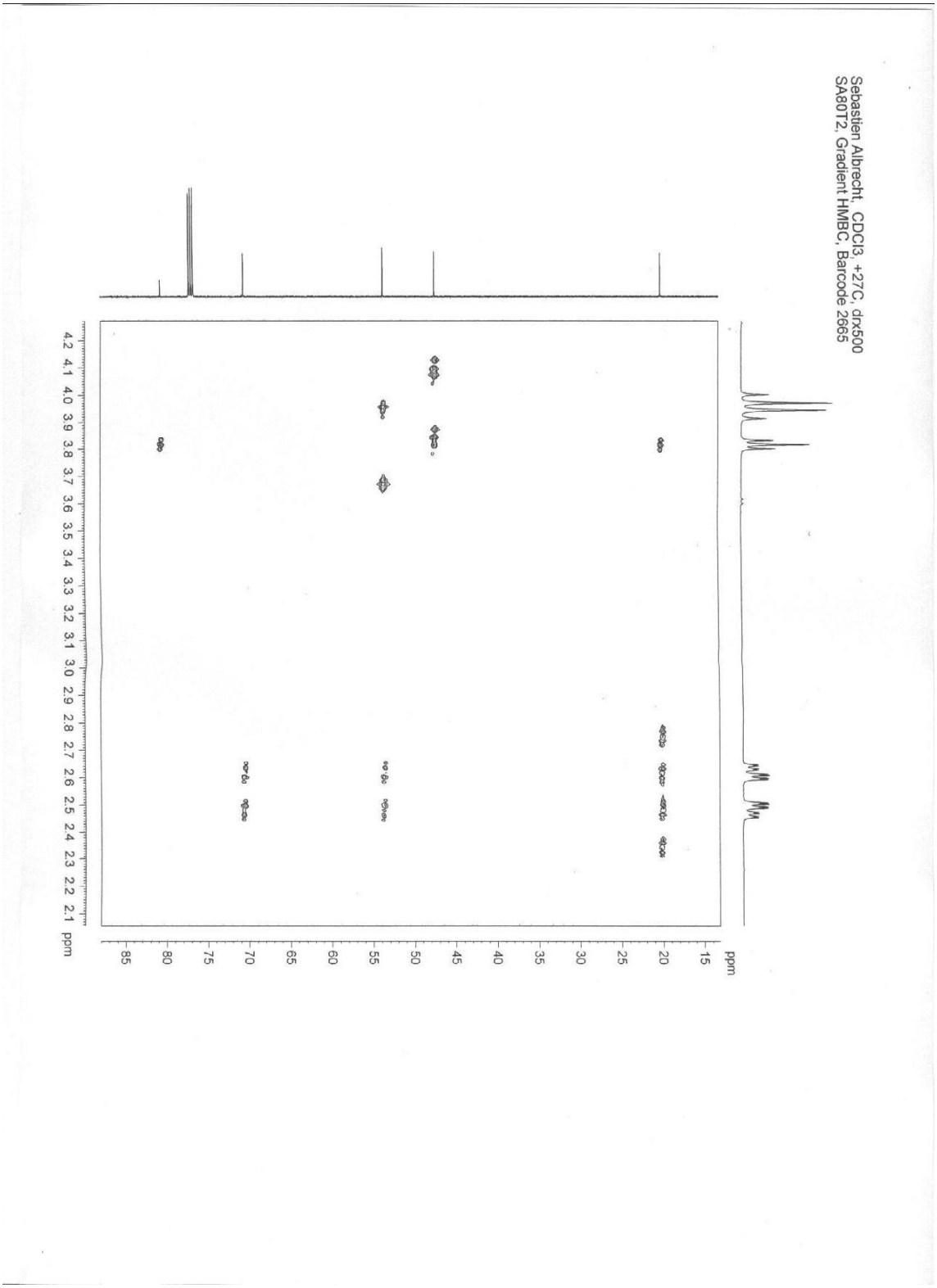
^{1}H-NMR (300 MHz, $CDCl_3$) of **17**



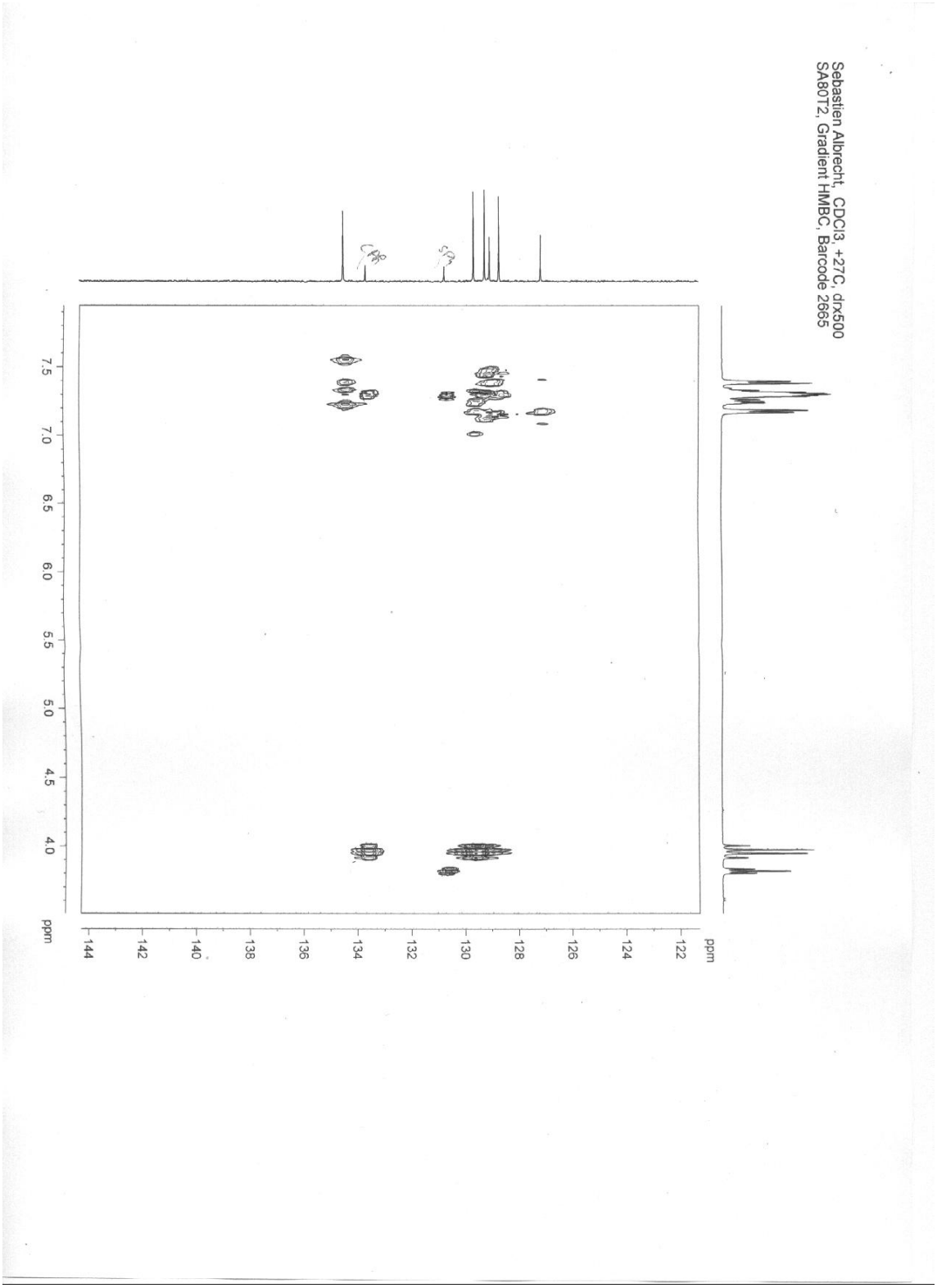
^{13}C-NMR (75 MHz, $CDCl_3$) of **17**


Sebastien Albrecht, CDCl3, +27C, drx500
SA80T2, Gradient HMBC, Barcode 2665
ppm

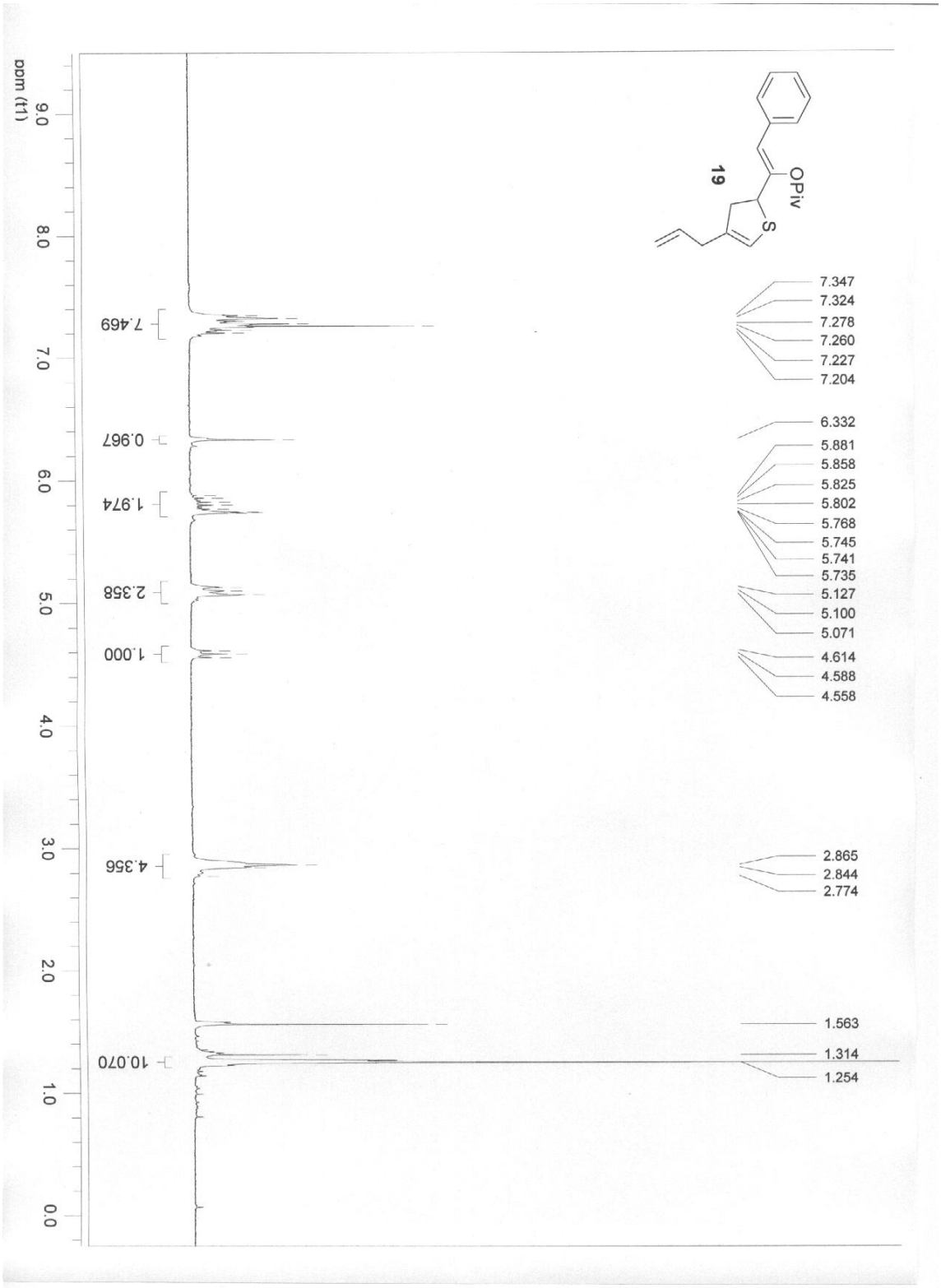
HMBC of **17**


Sebastien Albrecht, CDCl3, +27C, drx500
SA80T2, Gradient HMBC, Barcode 2665
ppm
ppm

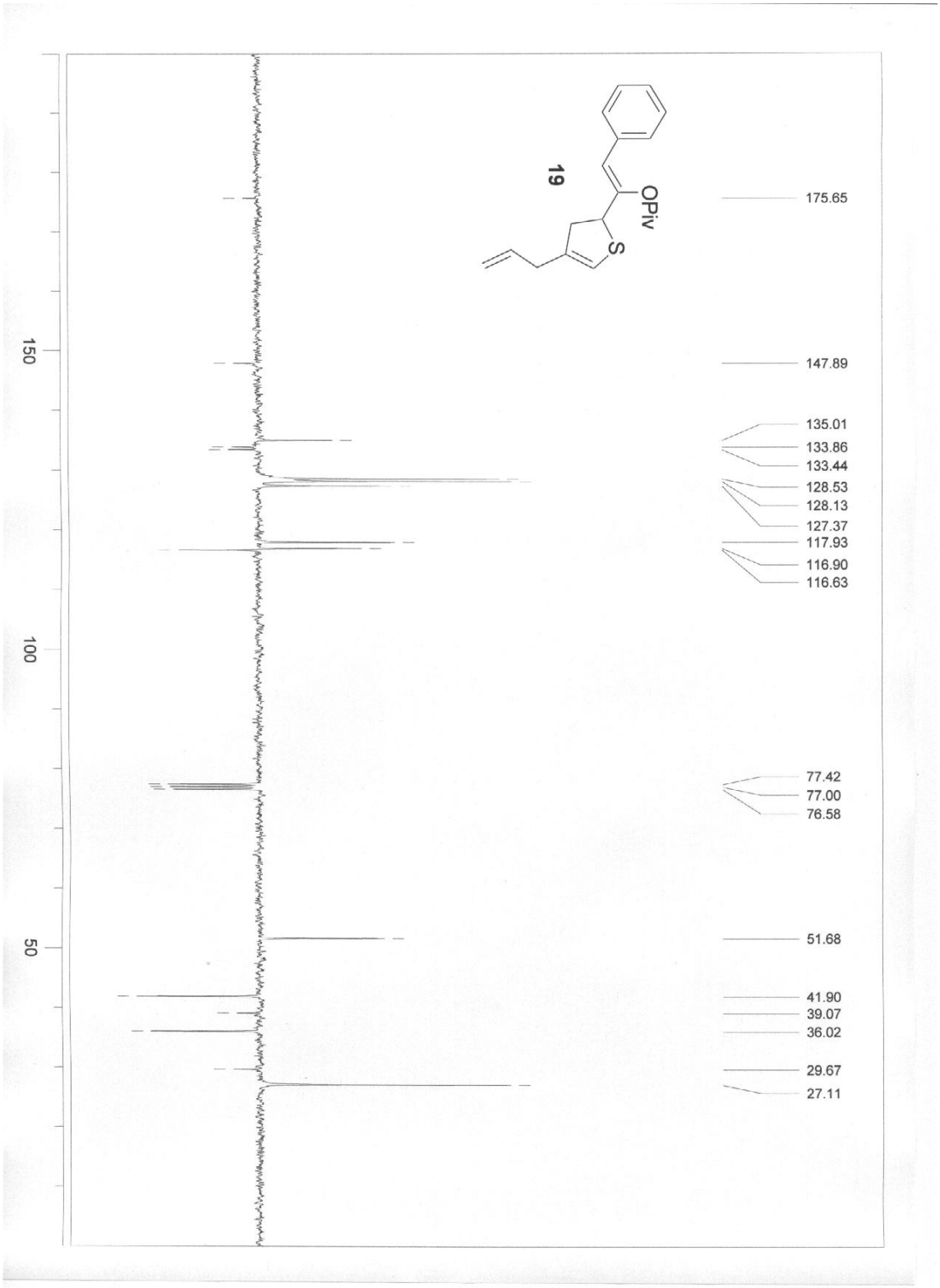
HMBC of **17**


Sebastien Albrecht, CDCl3, +27C, drx500
SA80T2, Gradient HMBC, Barcode 2665
ppm
ppm

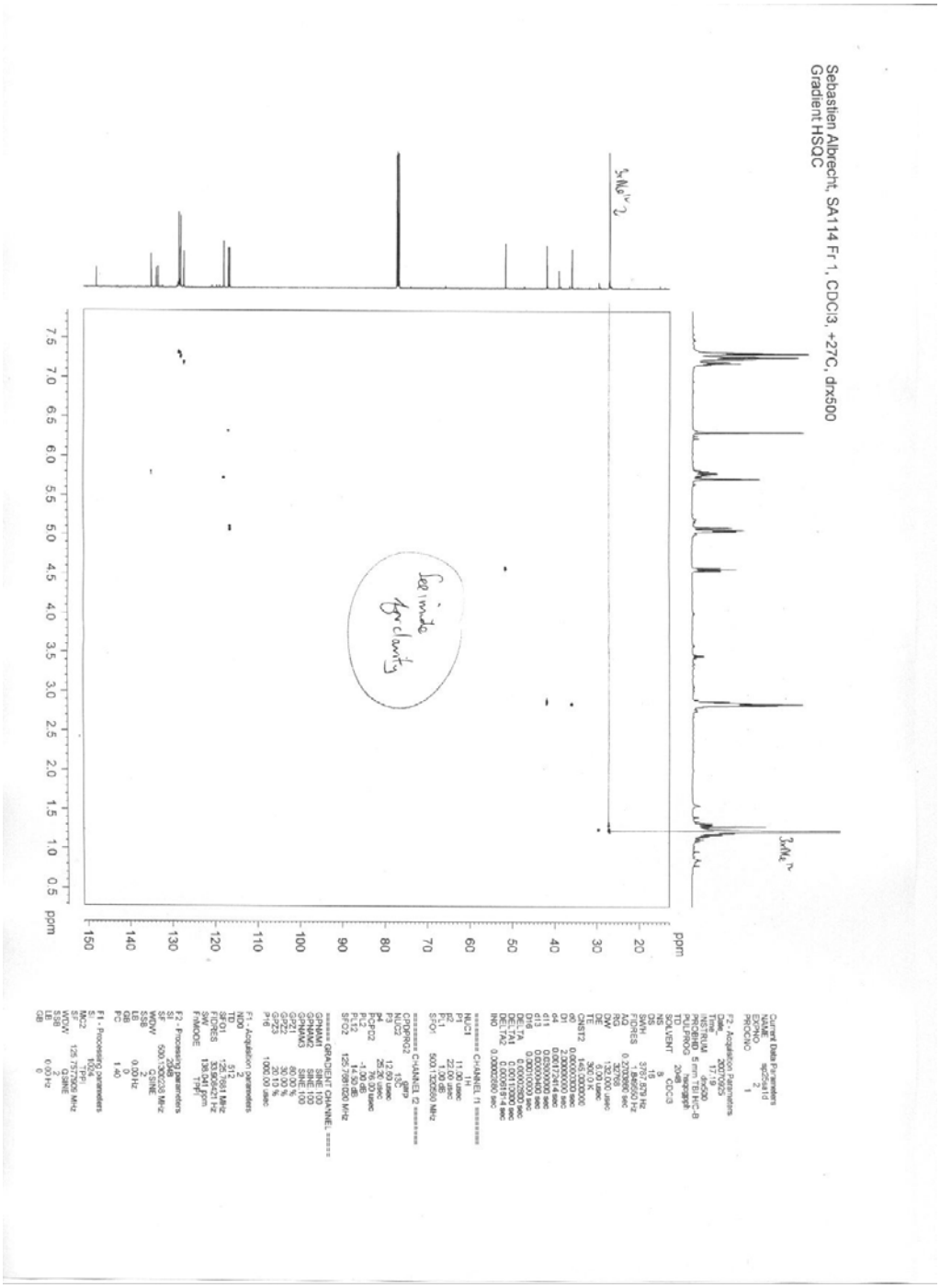
HMBC of **17**



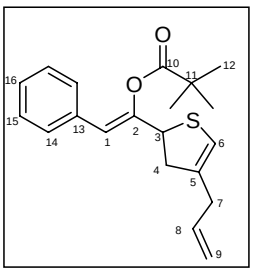
^{1}H-NMR (300 MHz, $CDCl_3$) of **19**



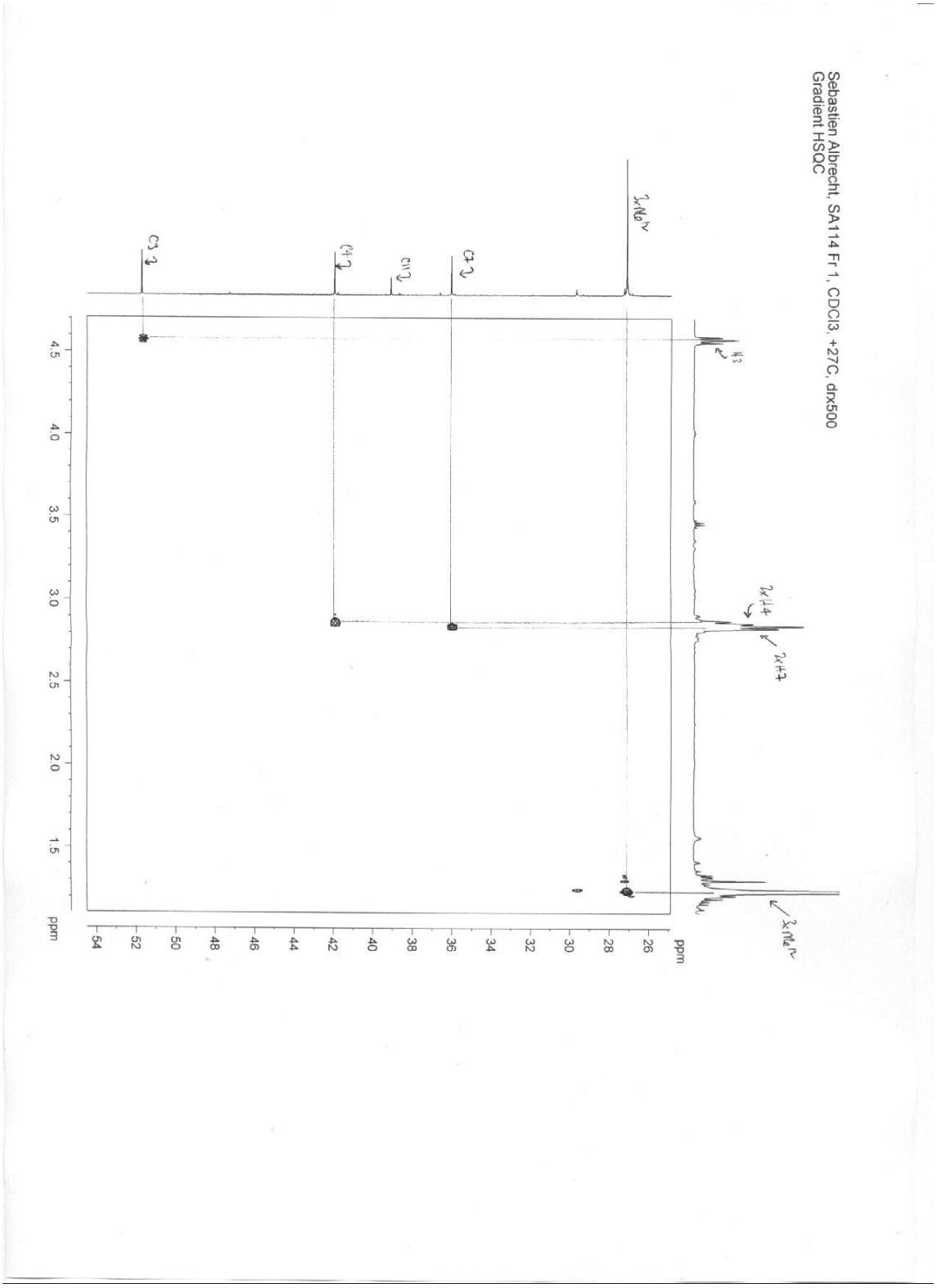
^{13}C-NMR (75 MHz, $CDCl_3$) of **19**



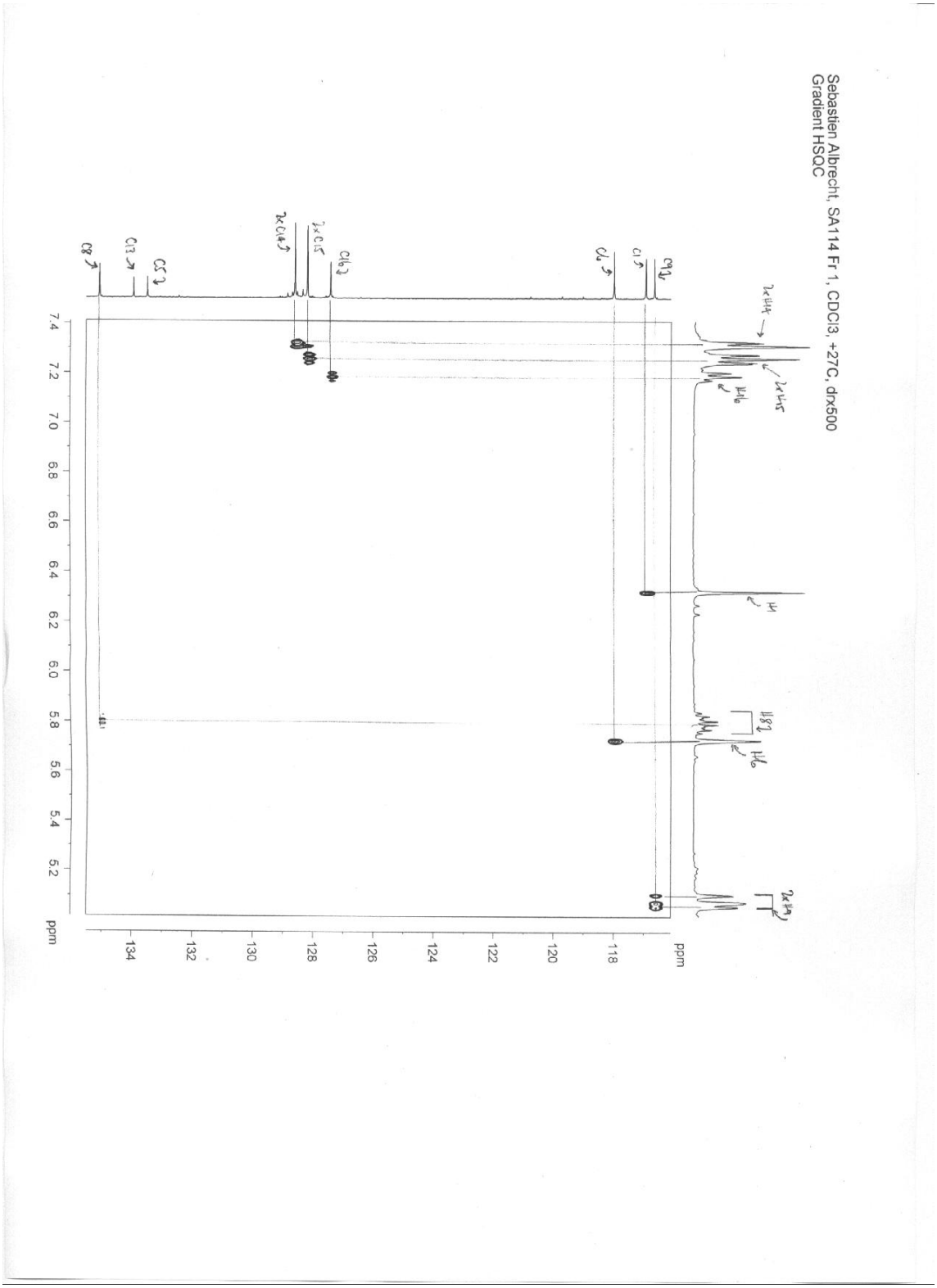
HSQC of **19**



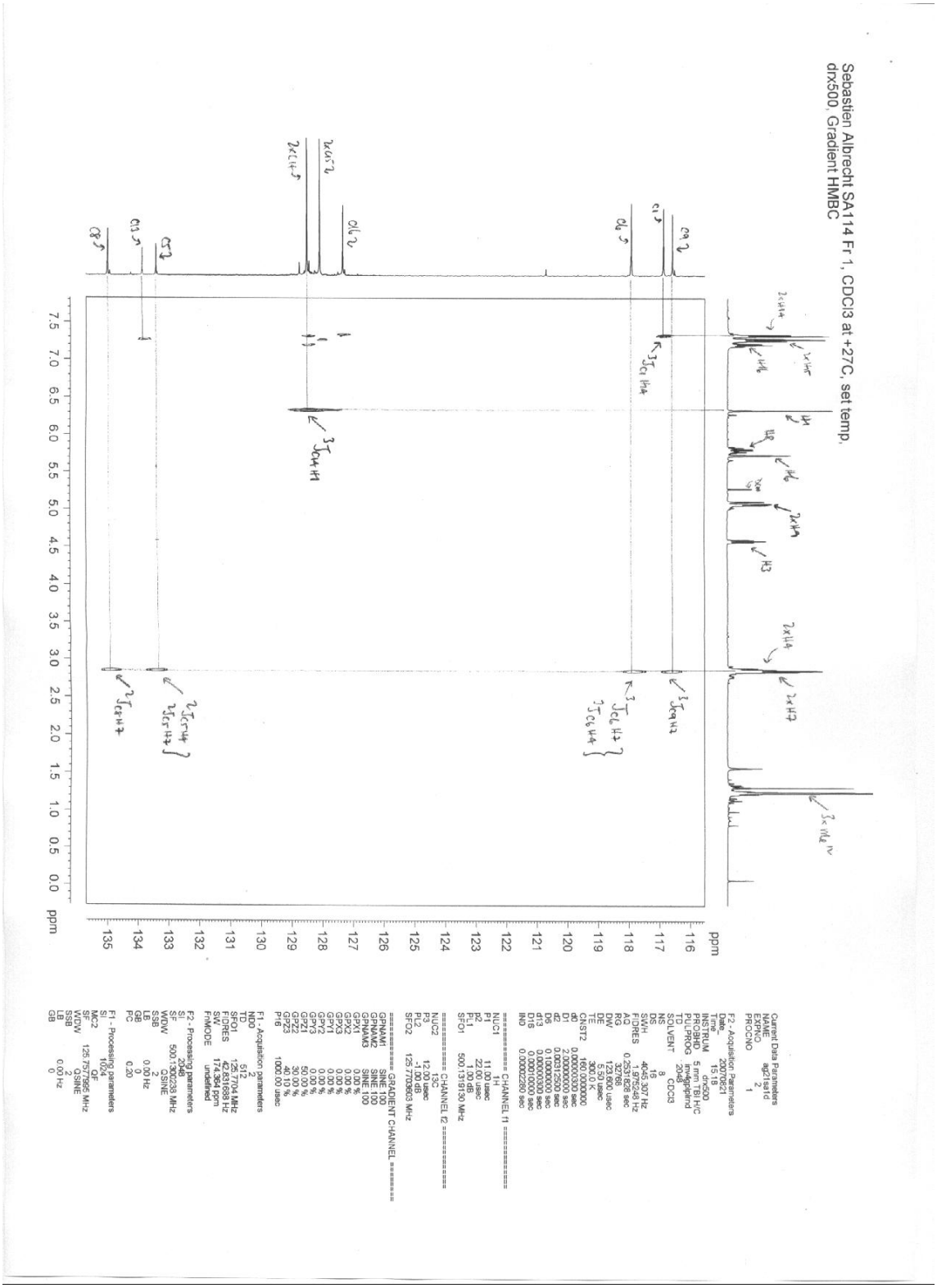
Note: Assignment on the following spectra uses the numbering scheme as follows:


Sebastien Albrecht, SA114 Fr 1, CDCl3, +27C, drx500
Gradient HSQC
C3
C4
C11
C2
3xMe
H3
2xH4
2xH2
3xMe
ppm
ppm

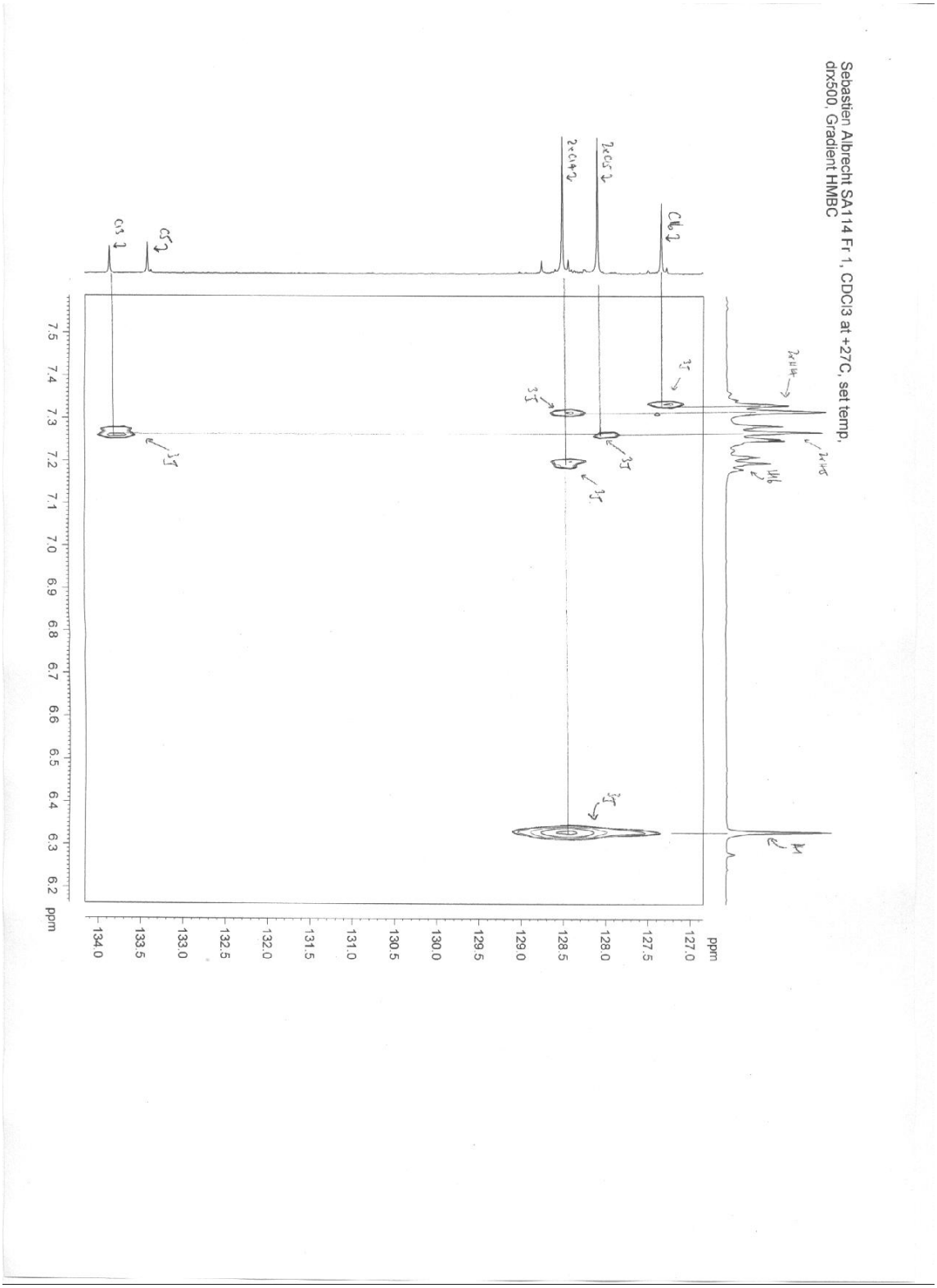
HSQC of **19**


Sebastien Albrecht, SA114 Fr 1, CDCl3, +27C, drx500
Gradient HSQC
ppm
ppm

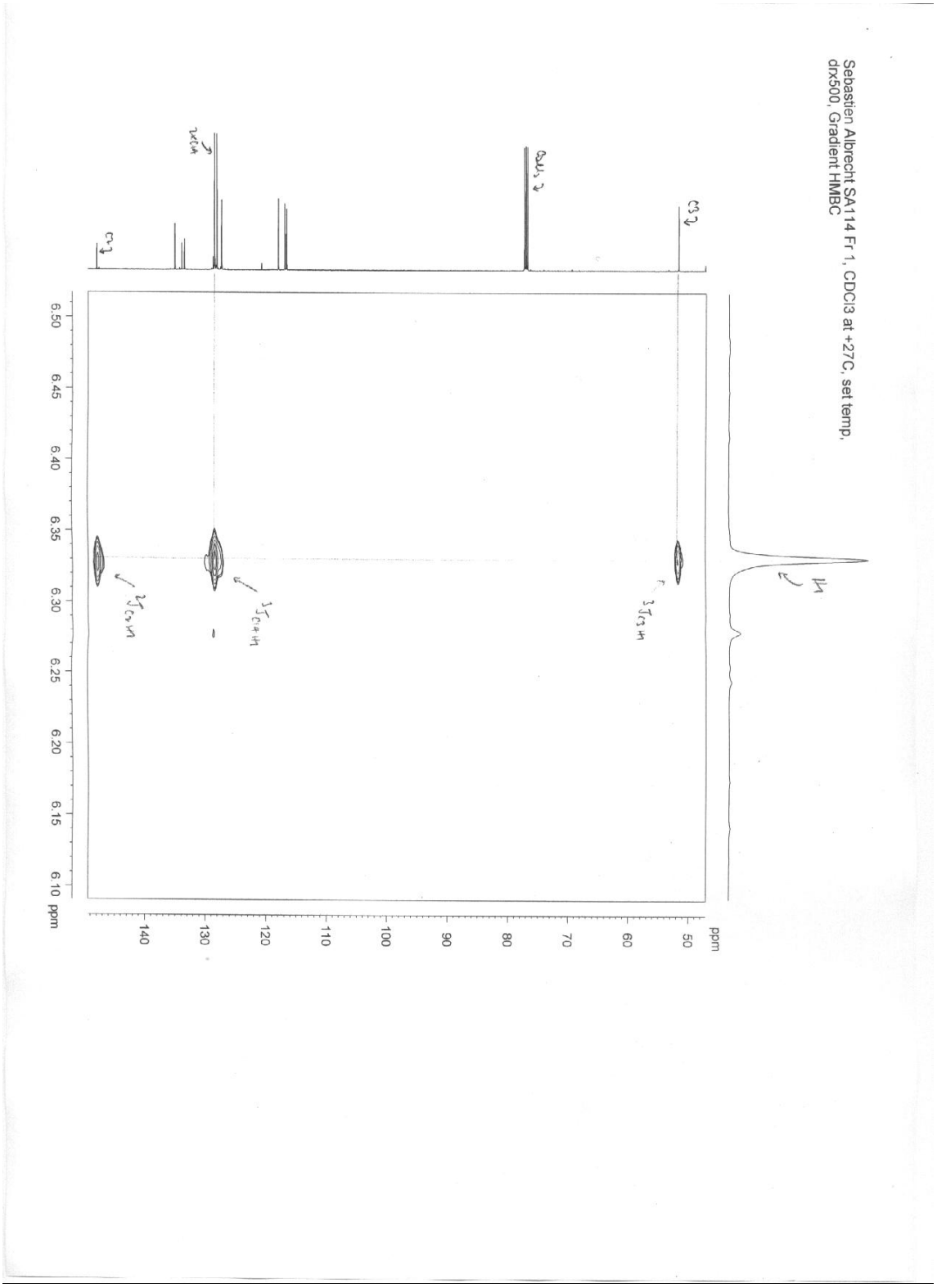
HSQC of **19**


Sebastien Albrecht SA114 Fr 1, CDCl3 at +27C, set temp.
drx500, Gradient HMBC
ppm

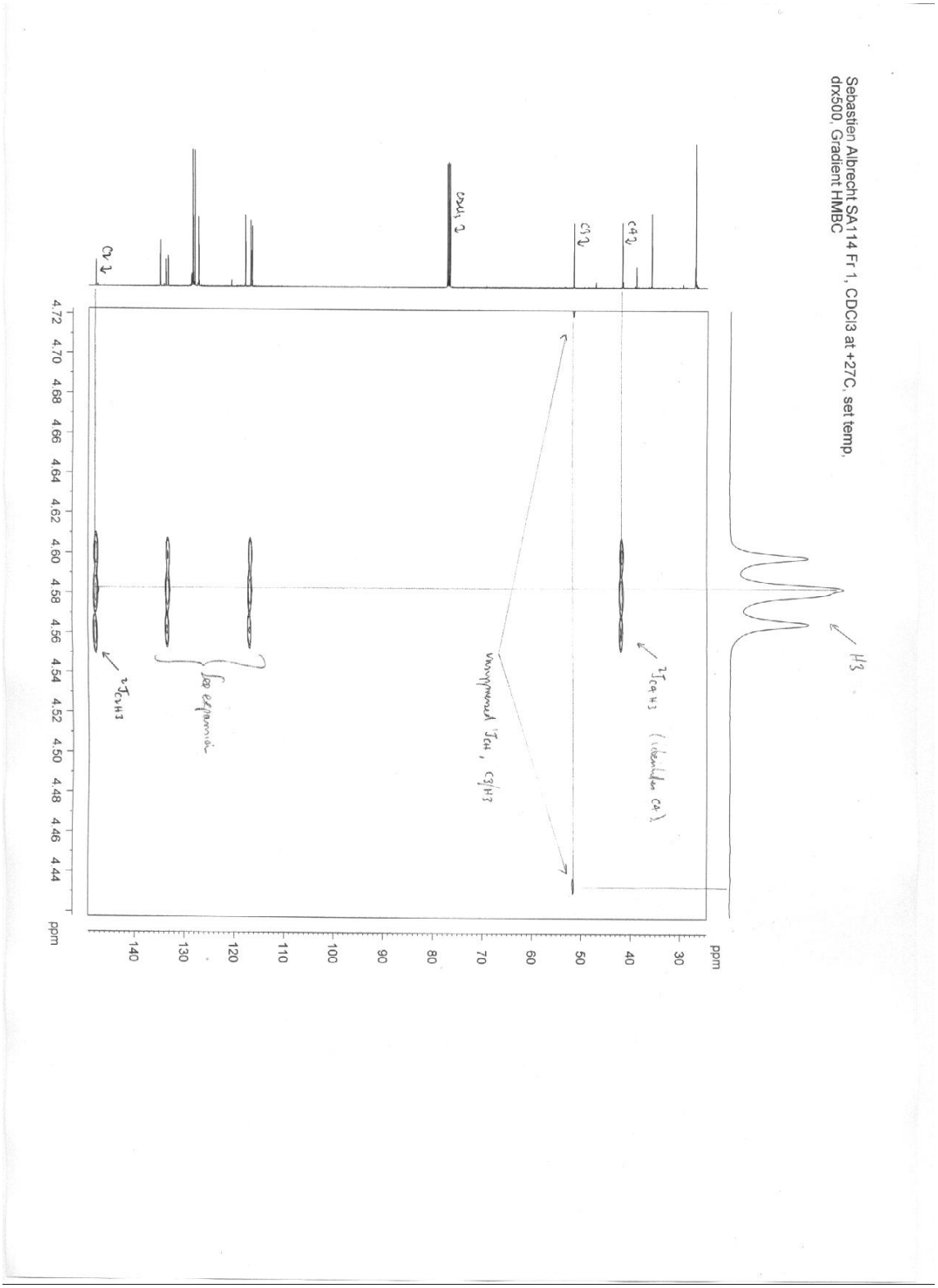
HMBC of **19**


Sebastien Albrecht SA114 Fr 1, CDCl3 at +27C, set temp,
drx500, Gradient HMBC
ppm
ppm

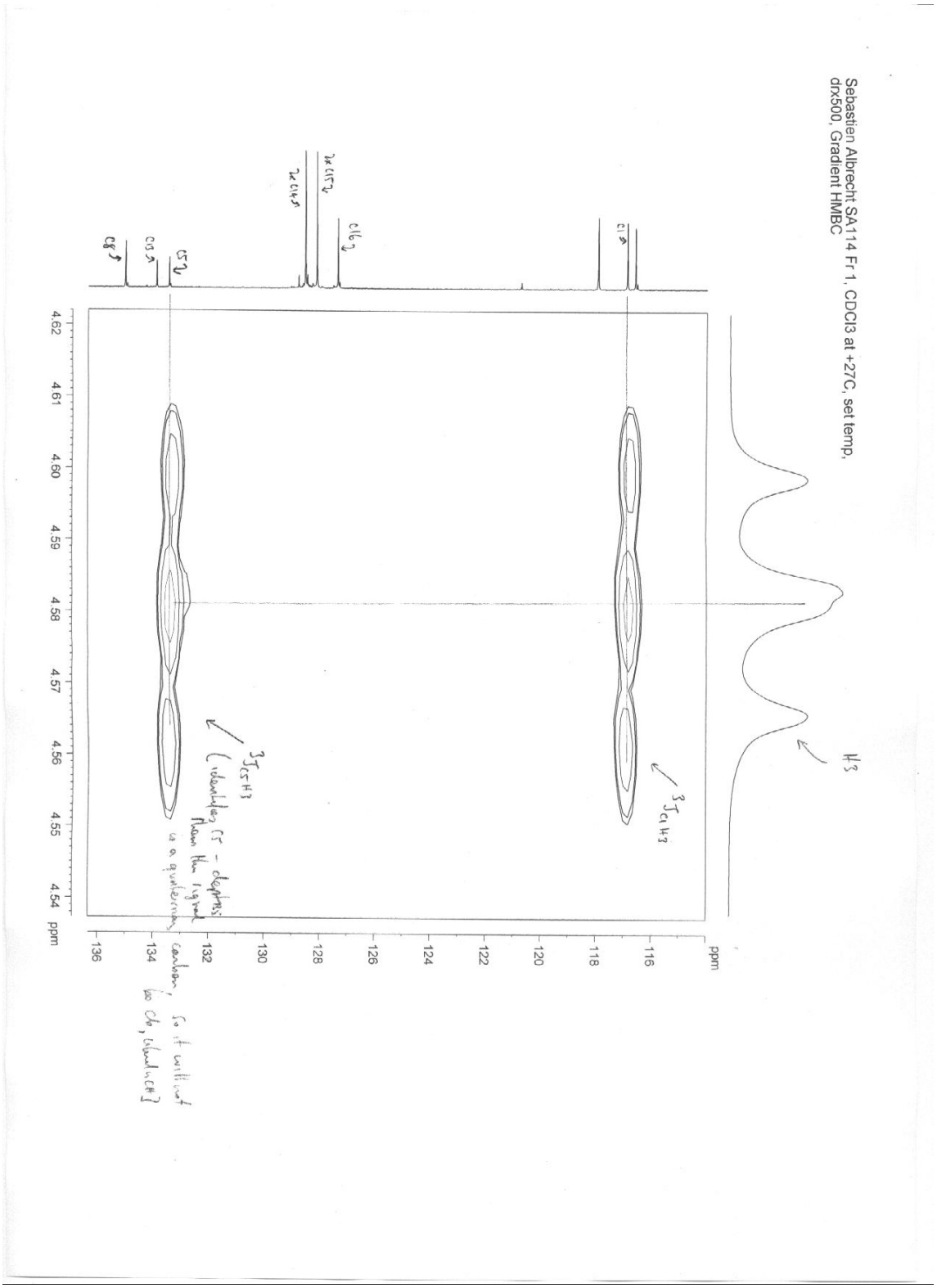
HMBC of **19**


Sebastien Albrecht SA114 Fr 1, CDCl3 at +27C, set temp,
drx500, Gradient HMBC
6.50
6.45
6.40
6.35
6.30
6.25
6.20
6.15
6.10
ppm
140
130
120
110
100
90
80
70
60
50
ppm

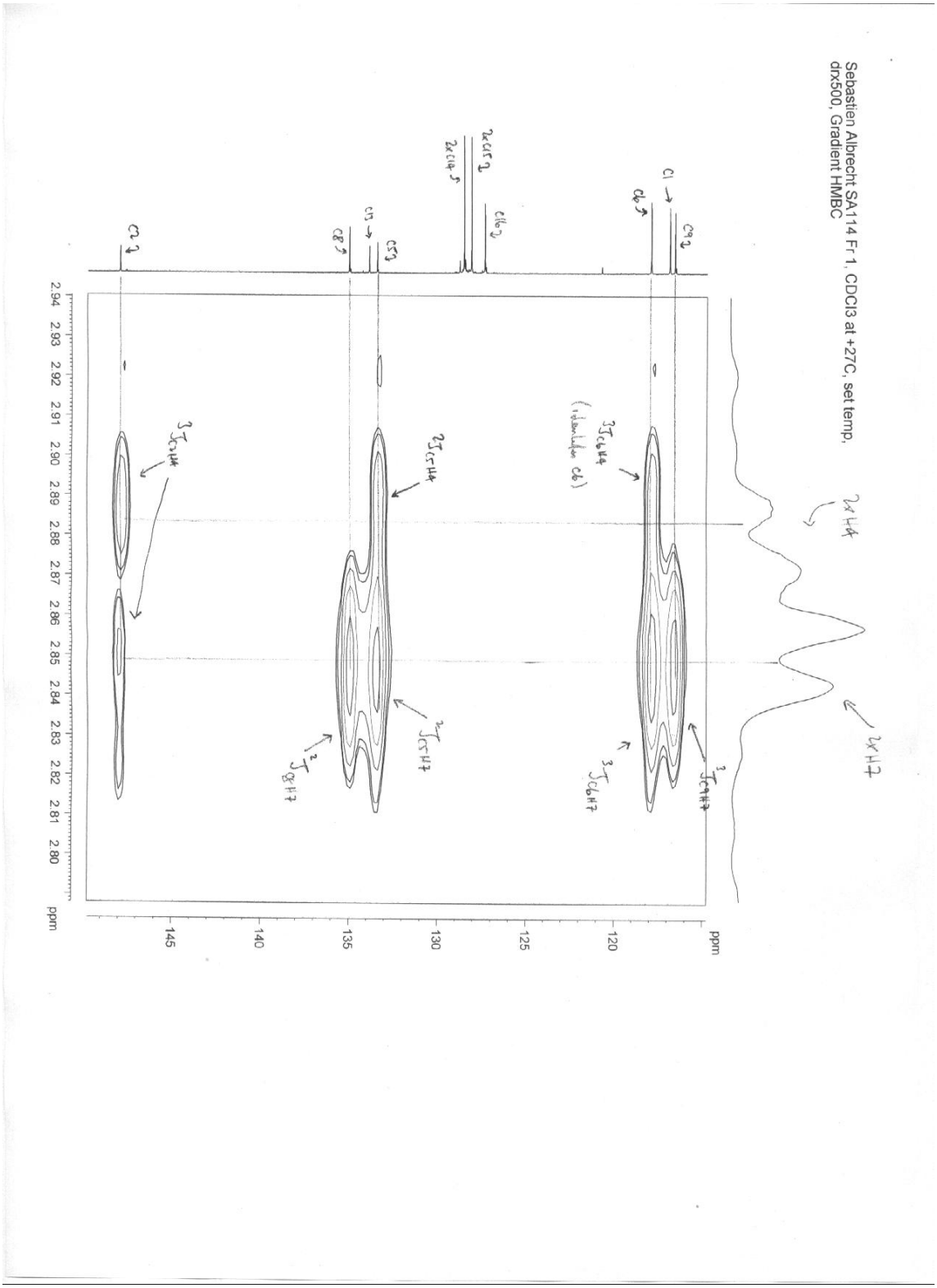
HMBC of **19**


Sebastien Albrecht SA114 Fr 1, CDCl3 at +27C, set temp,
drx500, Gradient HMBC
H3
ppm
ppm

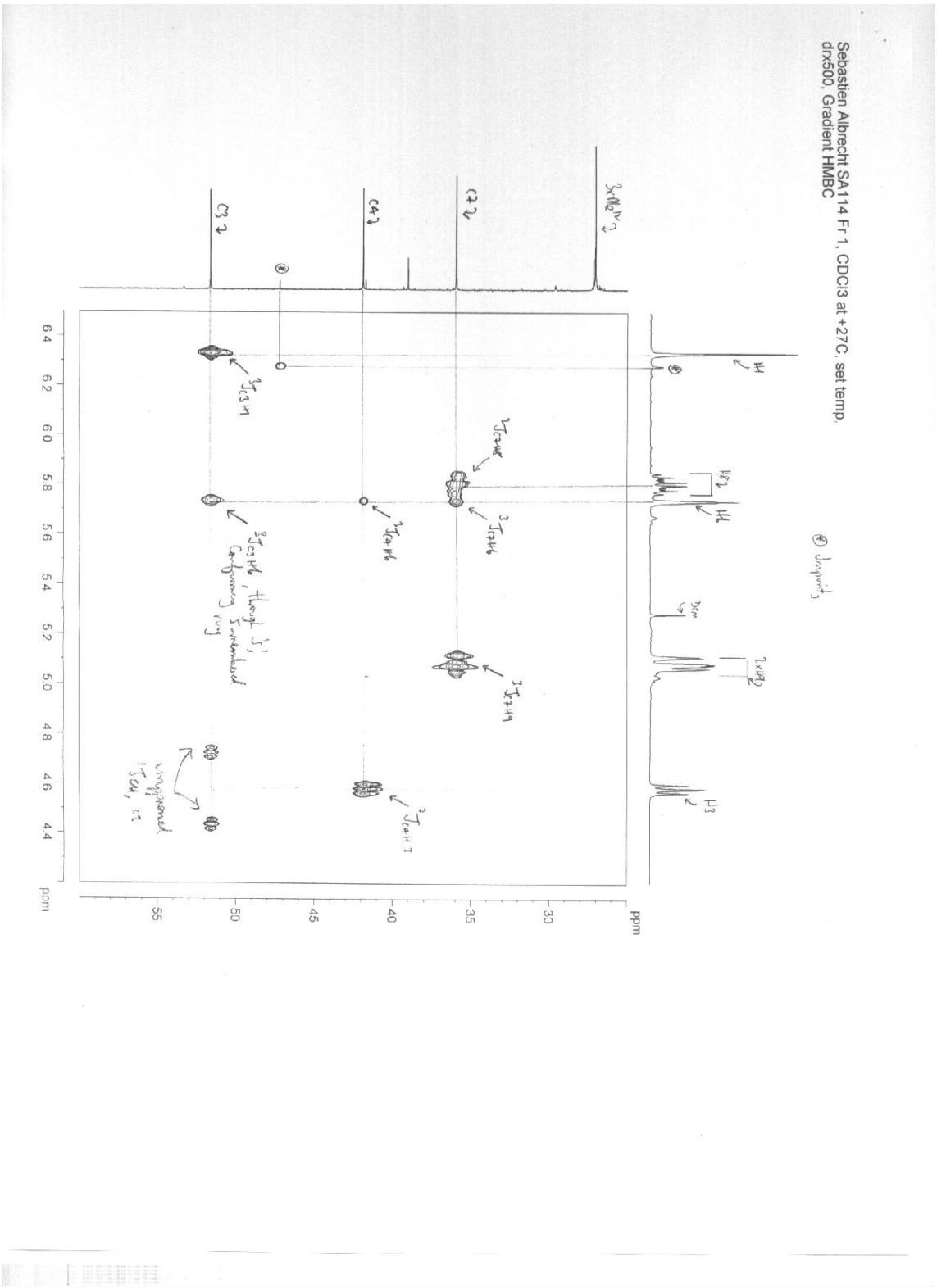
HMBC of **19**


Sebastien Albrecht SA114 Fr 1, CDCl3 at +27C, set temp,
drx500, Gradient HMBC
H3
ppm
ppm

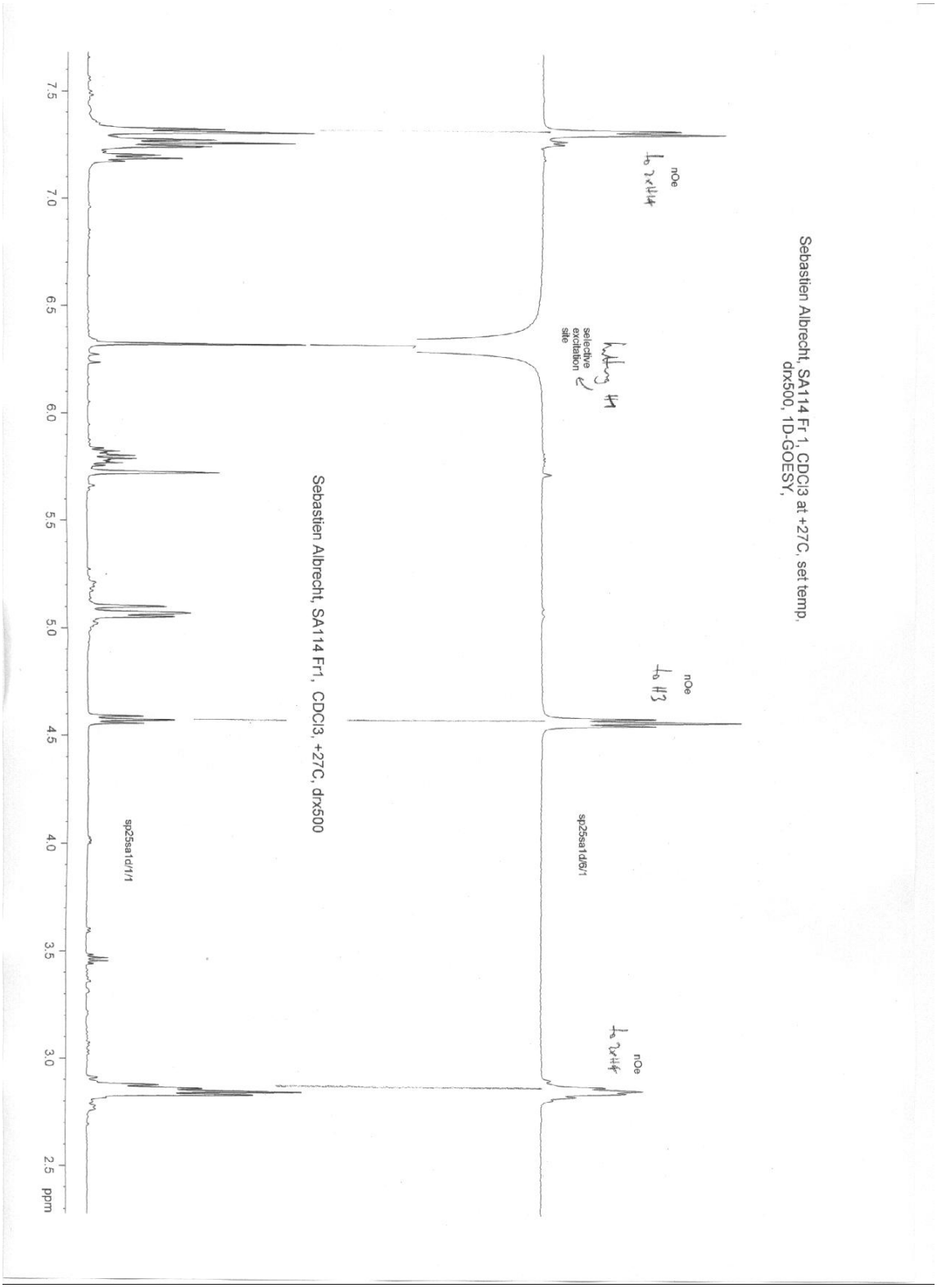
HMBC of **19**


Sebastien Albrecht SA114 Fr 1, CDCl3 at +27C, set temp, drx500, Gradient HMBC
ppm
ppm

HMBC of **19**


Sebastien Albrecht SA114 Fr 1, CDCl3 at +27C, set temp.
drx500, Gradient HMBC
ppm
ppm

HMBC of **19**


Sebastien Albrecht, SA114 Fr 1, CDCl3 at +27C, set temp,
drx500, 1D-GOESY,
nOe
selective excitation site
nOe
nOe
Sebastien Albrecht, SA114 Fr1, CDCl3, +27C, drx500
sp25sa1d5/1
sp25sa1d/1/1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm

nOe of **19**