Supporting Information

Addition of ArSSAr to Dienes via Intramolecular C-C Bond Formation Initiated by a Catalytic Amount of ArS^+

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General Remarks.

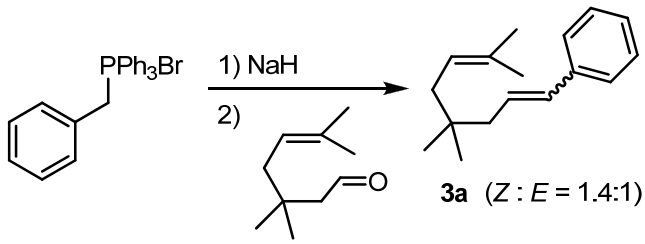
GC analysis was performed on a SHIMADZU GC-2014 gas chromatograph equipped with a flame ionization detector and a fused silica capillary column (column, CBPI; 0.25mm x 25 m). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Varian MERCURY plus-400 (^{1}H 400 MHz, ^{13}C 100 MHz) or JEOL ECA-600P (^{1}H 600 MHz, ^{13}C 150 MHz) spectrometer with Me_4Si as an internal standard unless otherwise noted. EI mass spectra were recorded on JMS-SX102A spectrometer. FAB mass spectra were recorded on JMX-HX110A spectrometer. Thin-layer chromatography (TLC) was carried out by using Merck precoated silica gel F_{254} plates (thickness 0.25 mm). Flash chromatography was carried out on a column of silica gel (Kanto Chem. Co., Silica Gel N, spherical, neutral, 40-100 μm). Gel permeation chromatography (GPC) was carried out on Japan Analytical Industry LC-908 equipped with JAIGEL-1H and 2H using $CHCl_3$ as eluent. High performance liquid chromatography (HPLC) was carried out on Shimadu LC-10 equipped with YMC 12S05-2520WT and SL12S05-2546WT. All reactions were carried out under Ar atmosphere unless otherwise noted.

Materials.

$Bu_4NB(C_6F_5)_4$ was prepared from Bu_4NBr (35.1 g, 109 mmol) and aqueous solution of $NaB(C_6F_5)_4$ (10 wt%, 499 g, 71.1 mmol) in water (100 mL). The mixture was diluted with EtOAc and was washed with water. After drying over $MgSO_4$ and removal of solvent, the precipitate was recrystallized from $CHCl_3$/hexane and was dried at 50 ^oC/1 mmHg overnight to give $Bu_4NB(C_6F_5)_4$ (65.1 g, 70.6 mmol, 99%). Dichloromethane was washed with water, distilled from P_2O_5, redistilled from dried K_2CO_3 to remove a trace amount of acid, and was stored over molecular sieves 4A. ArSSAr (Ar = *p*-FC_6H_4) was prepared according to the procedure in the literature,[1] and was identified by the comparison of its spectral data with that of authentic sample.[2] ArSSAr (Ar = *p*-$MeOC_6H_4$) was prepared according to the procedure in the literature[1]: TLC R_f 0.33 (hexane/EtOAc 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 6H), 6.80-6.85 (m, 4H), 7.36-7.42 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 114.6, 128.4, 132.6, 159.9; LRMS (EI) m/z 278 (M^+), 139 (M^+-S(*p*-$MeOC_6H_4$)); HRMS (EI) calcd for $C_{14}H_{14}O_2S_2$ (M^+) 278.0435, found 278.0436.

Synthesis of Dienes.

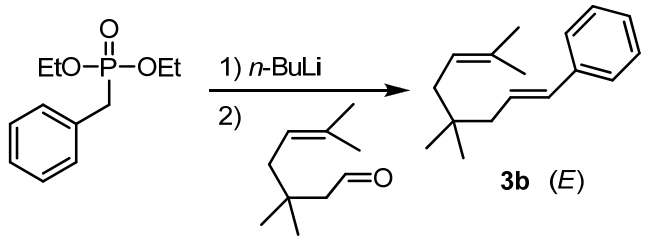
(4,4,7-Trimethylocta-1,6-dienyl)benzene (3a).



3,3,6-trimethylhept-5-enal was prepared according to the procedure in the literature[3]: TLC R_f 0.37 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (s, 6H), 1.59 (s, 3H), 1.73 (d, J = 1.2 Hz, 3H), 2.01 (d, J = 7.6 Hz, 2H), 2.24 (d, J = 3.2 Hz, 2H), 5.15-5.22 (m, 1H), 9.83 (t, J = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9, 26.0, 27.4, 34.7, 40.9, 54.5, 120.0, 134.3, 203.7; LRMS (EI) m/z 153 (M^+-H); HRMS (EI) calcd for $C_{10}H_{18}O$ (M^+) 154.1358, found 154.1362.

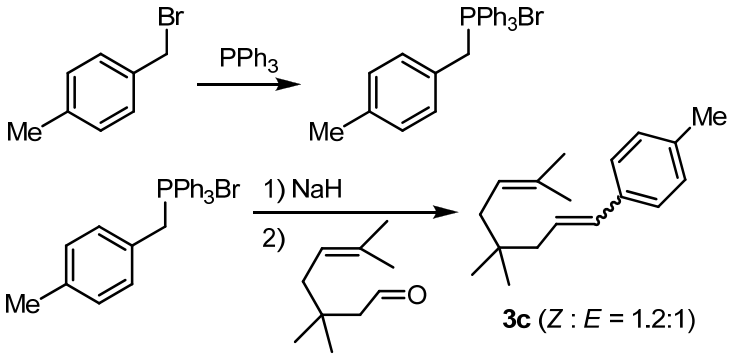
To a solution of benzyltriphenylphosphonium bromide (6.91 g, 16 mmol) in DMF (40 mL) was added NaH (55% in oil, 693 mg, 16 mmol) at 0 °C. The mixture was stirred at 0 °C for 2 h. Then 3,3,6-trimethylhept-5-enal (811 mg, 5.3 mmol) in DMF (20 mL) was added slowly, and the mixture was stirred at room temperature for 3 h. The reaction mixture was partitioned between ether and saturated brine. The organic phase was separated and washed with saturated brine and dried over $MgSO_4$. After removal of the solvent, the crude product was purified via flash chromatography (hexane) followed by GPC to give the title compound (**3a**) (769 mg, 3.4 mmol, 64%). This compound was obtained as a mixture of *E*/*Z* isomers (*Z* : *E* = 1.4:1 by ^{1}H NMR analysis): TLC R_f 0.54 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (s, 6H, *Z* isomer), 0.90 (s, 6H, *E* isomer), 1.57 (s, 3H, *Z* isomer), 1.61 (s, 3H, *E* isomer), 1.66 (d, J = 1.2 Hz, 3H, *Z* isomer), 1.74 (d, J = 1.2 Hz, 3H, *E* isomer), 1.90 (d, J = 7.6 Hz, 2H, *Z* isomer), 1.93 (d, J = 7.6 Hz, 2H, *E* isomer), 2.09 (dd, J = 7.6, 1.2 Hz, 2H, *E* isomer), 2.25 (dd, J = 7.6, 2.0 Hz, 2H, *Z* isomer), 5.08-5.14 (m, 1H, *Z* isomer), 5.19-5.26 (m, 1H, *E* isomer), 5.76 (dt, J = 12.0, 7.6 Hz, 1H, *Z* isomer), 6.25 (dt, J = 15.6, 7.6 Hz, 1H, *E* isomer), 6.36 (d, J = 15.6 Hz, 1H, *E* isomer), 6.49 (dt, J = 12.0, 2.0 Hz, 1H, *Z* isomer), 7.16-7.37 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 17.9 and 18.0, 26.0 and 26.1, 26.8 and 26.9, 34.8 and 35.1, 39.9 and 40.0, 40.2 and 45.4, 121.10 and 121.14, 126.0 and 128.0, 126.3 and 128.5, 126.8 and 128.8, 128.1 and 129.7, 130.0 and 131.9, 132.88 and 132.92, 138.0 and 138.0; LRMS (EI) m/z 228 (M^+), 159 (M^+-CH_2CH=$C(CH_3)_2$), 111 (M^+-CH_2CH=CHPh); HRMS (EI) calcd for $C_{17}H_{24}$ (M^+) 228.1878, found 228.1878.

(4,4,7-Trimethylocta-1,6-dienyl)benzene (3b).



To a solution of diethylbenzylphosphonate (24.3 g, 106.5 mmol) in THF (200 mL) was added *n*-BuLi (1.65 M in hexane, 67 mL, 110.6 mmol) at -78 ^{o}C. The mixture was stirred at -78 °C for 1 h and then the solution of 3,3,6-trimethylhept-5-enal (1.26 g, 8.2 mmol) in THF (20 mL) was added slowly. The mixture was warmed gradually to room temperature and was stirred for 3.5 h. The reaction mixture was partitioned between ether and saturated aqueous $NaHCO_3$. The organic phase was separated and washed with saturated brine and dried over $MgSO_4$. After removal of the solvent, the crude product was purified via flash chromatography (hexane) followed by GPC to give the title compound (**3b**) (819.1 mg, 3.6 mmol, 44%, purity ca. 98% by GC analysis): TLC R_f 0.54 (hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.89 (s, 6H), 1.61 (s, 3H), 1.74 (d, J = 1.1 Hz, 3H), 1.93 (d, J = 7.6 Hz, 2H), 2.09 (dd, J = 7.6, 1.0 Hz, 2H), 5.20-5.25 (m, 1H), 6.25 (dt, J = 15.8, 7.6 Hz, 1H), 6.36 (d, J = 15.8 Hz, 1H), 7.16-7.36 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 18.0, 26.1, 26.9, 35.1, 40.2, 45.4, 121.1, 126.0, 126.8, 128.0, 128.5, 131.9, 132.9, 138.0; LRMS (EI) m/z 228 (M^+); HRMS (EI) calcd for $C_{17}H_{24}$ (M^+) 228.1878, found 228.1880.

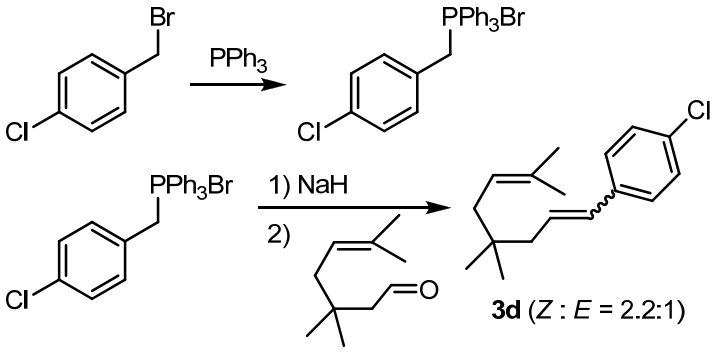
1-Methyl-4-(4,4,7-trimethylocta-1,6-dienyl)benzene (3c).



To a solution of *p*-methylbenzylbromide (9.5 g, 51.3 mmol) in CH_3CN (100 mL) was added triphenylphosphine (13.5 g, 51.5 mmol). Then the mixture was stirred at reflux condition over night. The removal of the solvent gave *p*-methylbenzyltriphenylphosphonium bromide (21.8 g, 48.7 mmol, ca. 95%), and this material was used for the subsequent reaction without further purification. To a solution of *p*-methylbenzyltriphenylphosphonium bromide (7.0 g, ca. 15.6 mmol) in DMF (80 mL) was added NaH (55% in oil, 749 mg, 17.2 mmol) at 0 ^{o}C. The mixture was stirred at 0 °C for 2.5 h. Then, 3,3,6-trimethylhept-5-enal (925 mg, 6.0 mmol) in DMF (18 mL)

was added slowly, and the mixture was stirred at room temperature over night. The reaction mixture was partitioned between ether and saturated brine. The organic phase was separated and washed with saturated brine and dried over $MgSO_4$. After removal of the solvent, the crude product was purified via flash chromatography (hexane) followed by GPC to give the title compound (**3c**) (980 mg, 4.0 mmol, 67%). This compound was obtained as a mixture of *E*/*Z* isomers (*Z* : *E* = 1.2:1 by ^{1}H NMR analysis): TLC R_f 0.36 (hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.87 (s, 6H, *Z* isomer), 0.89 (s, 6H, *E* isomer), 1.58 (s, 3H, *Z* isomer), 1.60 (s, 3H, *E* isomer), 1.67 (s, 3H, *Z* isomer), 1.73 (s, 3H, *E* isomer), 1.91 (t, *J* = 8.9 Hz, 2H, *E* and *Z* isomers), 2.08 (d, *J* = 7.6 Hz, 2H, *E* isomer), 2.24 (dd, *J* = 7.3, 1.7 Hz, 2H, *Z* isomer), 2.32 (s, 3H, *E* isomer), 2.34 (s, 3H, *Z* isomer), 5.10-5.14 (m, 1H, *Z* isomer), 5.20-5,24 (m, 1H, *E* isomer), 5.71 (dt, *J* = 11.7, 7.3 Hz, 1H, *Z* isomer), 6.19 (dt, *J* = 15.5, 7.6 Hz, 1H, *E* isomer), 6.32 (d, *J* = 15.5 Hz, 1H, *E* isomer), 6.45 (d, *J* = 11.7 Hz, 1H, *Z* isomer), 7.09-7.26 (m, 5H, *E* and *Z* isomers); ^{13}C NMR (150 MHz, $CDCl_3$): δ 17.9 and 18.0, 21.12 and 21.16, 26.0 and 26.1, 26.8 and 26.9, 34.8 and 35.1, 39.98 and 40.0, 40.2 and 45.4, 121.16 and 121.20, 125.9 and 127.0, 128.7 and 128.8, 129.1 and 129.2, 129.8 and 131.7, 132.8 and 132.9, 135.1 and 135.2, 136.0 and 136.5; LRMS (EI) m/z 242 (M^+), 227 (M^+-CH_3), 173 (M^+-$CH_2CH{=}C(CH_3)_2$); HRMS (EI) calcd for $C_{18}H_{26}$ (M^+) 242.2035, found 242.2033.

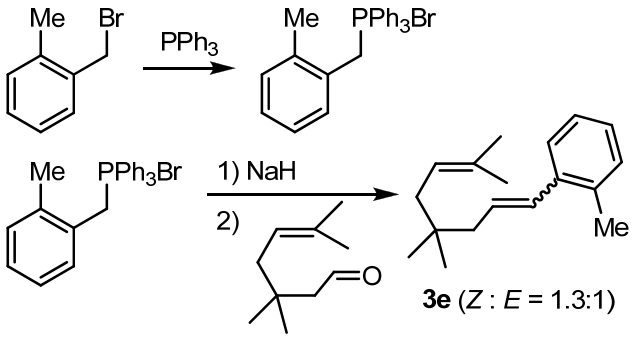
1-Chloro-4-(4,4,7-trimethylocta-1,6-dienyl)benzene (3d).



To a solution of *p*-chlorobenzylbromide (20.8 g, 101 mmol) in CH_3CN (100 mL) was added triphenylphosphine (27.3 g, 104 mmol). Then the mixture was stirred at reflux condition over night. The removal of the solvent gave *p*-chlorobenzyltriphenylphosphonium bromide (45.8 g, 98 mmol, ca. 97%), and this material was used for the subsequent reaction without further purification. To a solution of *p*-chlorobenzyltriphenylphosphonium bromide (8.3 g, ca. 17.7 mmol) in DMF (70 mL) was added NaH (55% in oil, 788 mg, 18.1 mmol) at 0 ^{o}C. The mixture was stirred at 0 °C for 1.5 h. Then, 3,3,6-trimethylhept-5-enal (1.02 g, 6.6 mmol) in DMF (17 mL) was added slowly, and the mixture was stirred at room temperature over night. The reaction mixture was partitioned between ether and saturated aqueous $NaHCO_3$. The organic phase was separated and washed with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$. After removal of the solvent, the crude product was purified via flash chromatography

(hexane) followed by GPC to give the title compound (**3d**) (1.17 g, 4.5 mmol, 68%). This compound was obtained as a mixture of *E*/*Z* isomers (*Z* : *E* = 2.2:1 by ^{1}H NMR analysis): TLC R_f 0.60 (hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.87 (s, 6H, *Z* isomer), 0.90 (s, 6H, *E* isomer), 1.57 (s, 3H, *Z* isomer), 1.60 (s, 3H, *E* isomer), 1.67 (s, 3H, *Z* isomer), 1.73 (s, 3H, *E* isomer), 1.89 (d, *J* = 7.6 Hz, 2H, *Z* isomer), 1.92 (d, *J* = 7.6 Hz, 2H, *E* isomer), 2.08 (dd, *J* = 7.2, 0.7 Hz, 2H, *E* isomer), 2.19 (dd, *J* = 7.6, 1.7 Hz, 2H, *Z* isomer), 5.07-5.13 (m, 1H, *Z* isomer), 5.19-5.24 (m, 1H, *E* isomer), 5.77 (dt, *J* = 11.7, 7.6 Hz, 1H, *Z* isomer), 6.22 (dt, *J* = 15.8, 7.2 Hz, 1H, *E* isomer), 6.30 (d, *J* = 15.8 Hz, 1H, *E* isomer), 6.43 (d, *J* = 11.7 Hz, 1H, *Z* isomer), 7.18-7.29 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 17.9 and 18.0, 26.0 and 26.1, 26.8 and 26.9, 34.8 and 35.1, 39.87 and 39.93, 40.2 and 45.4, 120.96 and 121.03, 127.1 and 128.2, 128.6 and 130.1, 128.81 and 128.84, 130.5 and 130.7, 132.0 and 132.3, 132.97 and 133.04, 136.36 and 136.44; LRMS (EI) m/z 262 (M^+), 193 (M^+-CH_2CH=$C(CH_3)_2$); HRMS (EI) calcd for $C_{17}H_{23}Cl_1$ (M^+) 262.1488, found 262.1488.

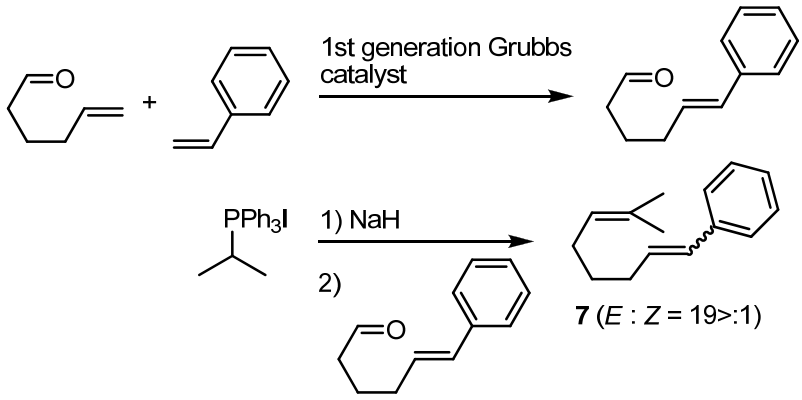
1-Methyl-2-(4,4,7-trimethylocta-1,6-dienyl)benzene (3e).



To a solution of *o*-methylbenzylbromide (20.3 g, 110 mmol) in CH_3CN (100 mL) was added triphenylphosphine (28.8 g, 110 mmol). Then the mixture was stirred at reflux condition over night. The removal of the solvent gave *o*-methylbenzyltriphenylphosphonium bromide (46.4 g, 104 mmol, ca. 95%), and this material was used for the subsequent reaction without further purification. To a solution of *o*-methylbenzyltriphenylphosphonium bromide (9.0 g, ca. 20.1 mmol) in DMF (70 mL) was added NaH (55% in oil, 915 mg, 21 mmol) at 0 ^{o}C. The mixture was stirred at 0 °C for 1 h. Then, 3,3,6-trimethylhept-5-enal (933 mg, 6.0 mmol) in DMF was added slowly, and the mixture was stirred at room temperature for 5 h. The reaction mixture was partitioned between ether and saturated brine. The organic phase was separated and washed with saturated brine and dried over $MgSO_4$. After removal of the solvent, the crude product was purified via flash chromatography (hexane) followed by GPC to give the title compound (**3e**) (1.15 g, 4.7 mmol, 78%). This compound was obtained as a mixture of *E*/*Z* isomers (*Z* : *E* = 1.3:1 by ^{1}H NMR analysis): TLC R_f 0.52 (hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.82 (s, 6H, *Z* isomer), 0.91 (s, 6H, *E* isomer), 1.56 (s, 3H, *Z* isomer), 1.61 (s, 3H, *E* isomer), 1.65 (d, *J* = 1.0 Hz, 3H, *Z* isomer), 1.74 (d, *J* = 0.7 Hz,

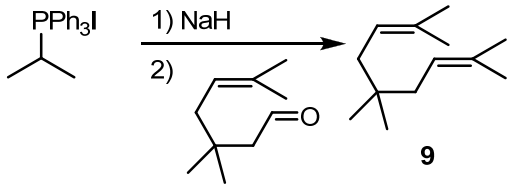
3H, *E* isomer), 1.85 (d, *J* = 7.6 Hz, 2H, *Z* isomer), 1.93 (d, *J* = 7.9 Hz, 2H, *E* isomer), 2.06 (dd, *J* = 7.6, 1.7 Hz, 2H, *Z* isomer), 2.12 (dd, *J* = 7.6, 1.0 Hz, 2H, *E* isomer), 2.24 (s, 3H, *Z* isomer), 2.33 (s, 3H, *E* isomer), 5.02-5.18 (m, 1H, *Z* isomer), 5.20-5.27 (m, 1H, *E* isomer), 5.80 (dt, *J* = 11.7, 7.6 Hz, 1H, *Z* isomer), 6.10 (dt, *J* = 15.4, 7.6 Hz, 1H, *E* isomer), 6.50 (d, *J* = 11.7 Hz, 1H, *Z* isomer), 6.54 (d, *J* = 15.4 Hz, 1H, *E* isomer), 7.09-7.17 (m, 4H, *Z* isomer and 3H, *E* isomer), 7.41 (d, *J* = 7.6 Hz, 1H, *E* isomer); ^{13}C NMR (150 MHz, $CDCl_3$): δ 17.8 and 18.0, 19.9 and 19.9, 26.0 and 26.1, 26.8 and 26.9, 34.7 and 35.0, 39.7 and 39.8, 40.3 and 45.7, 121.2 and 121.2, 125.1 and 125.1, 125.6 and 126.0, 126.6 and 126.7, 129.2 and 129.4, 129.5 and 129.6, 129.9 and 130.1, 132.7 and 132.9, 134.9 and 136.2, 137.0 and 137.3; LRMS (EI) m/z 242 (M^+), 173 (M^+-CH_2CH=$C(CH_3)_2$); HRMS (EI) calcd for $C_{18}H_{26}$ (M^+) 242.2035, found 242.2036.

(7-Methylocta-1,6-dienyl)benzene (7).



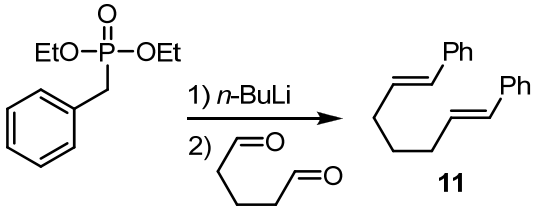
(*E*)-6-Phenyl-5-hexenal was prepared according to the procedure in the literature using 1st generation Grubbs catalyst.[4] To a solution of isopropyltriphenylphosphonium iodide (7.5 g, 17.3 mmol) in DMF was added NaH (55% in oil, 847 mg, 19.4 mmol) at 0 ^{o}C. The mixture was stirred at 0 °C for 1.5 h. Then, (*E*)-6-phenyl-5-hexenal (836 mg, 4.8 mmol) in DMF (20 mL) was added slowly, and the mixture was stirred at room temperature over night. The reaction mixture was partitioned between ether and saturated brine. The organic phase was separated and washed with saturated brine and dried over $MgSO_4$. After removal of the solvent, the crude product was purified via flash chromatography (hexane) followed by GPC to give the title compound (**7**) (298 mg, 1.5 mmol, 31%). This compound was obtained as a mixture of *E*/*Z* isomers (*E* : *Z* = 19>:1 by ^{1}H NMR analysis): TLC R_f 0.34 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$, *E* isomer) δ 1.51 (quintet, *J* = 7.6 Hz, 1H), 1.61 (d, *J* = 0.4 Hz, 3H), 1.70 (d, *J* = 1.2 Hz, 3H), 2.03 (q, *J* = 7.6 Hz, 1H), 2.21 (qd, *J* = 7.6, 1.2 Hz, 1H), 5.10-5.18 (m, 1H), 6.23 (dt, *J* = 15.6, 7.6 Hz, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 7.16-7.22 (m, 1H), 7.24-7.36 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, *E* isomer) δ 17.7, 25.8, 27.5, 29.5, 32.6, 124.4, 125.9, 126.7, 128.4, 129.8, 131.0, 131.7, 137.9; LRMS (EI) m/z 200 (M^+); HRMS (EI) calcd for $C_{15}H_{20}$ (M^+) 200.1565, found 200.1568.

2,5,5,8-Tetramethylnona-2,7-diene (9).



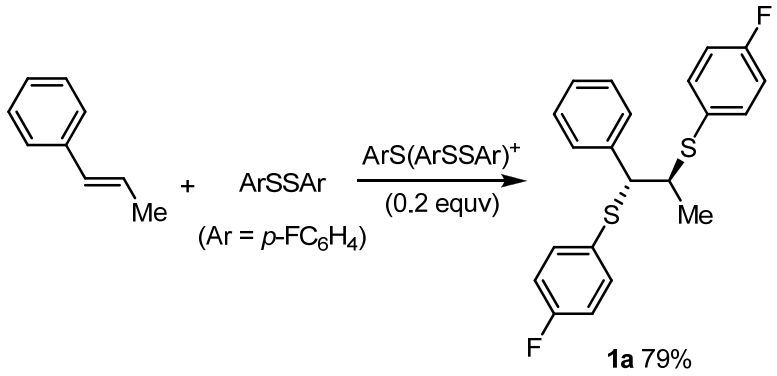
To a solution of isopropyltriphenylphosphonium iodide (5.15 g, 11.9 mmol) in DMF (23 mL) was added NaH (55% in oil, 570 mg, 13.1 mmol) at 0 °C. The mixture was stirred at 0 °C for 1.5 h. Then, 3,3,6-trimethylhept-5-enal (1.07 g, 6.9 mmol) was added slowly, and the mixture was stirred at room temperature for 0.5 h. The reaction mixture was partitioned between ether and saturated brine. The organic phase was separated and washed with saturated brine and dried over $MgSO_4$. After removal of the solvent, the crude product was purified via flash chromatography (hexane) followed by GPC to give the title compound (**9**) (820 mg, 4.5 mmol, 65%): TLC R_f 0.84 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (s, 6H), 1.59 (d, J = 0.8 Hz, 6H), 1.72 (d, J = 1.2 Hz, 6H), 1.86 (d, J = 7.6 Hz, 4H), 5.15-5.22 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.8, 26.1, 26.7, 35.3, 40.1, 121.5, 132.5; LRMS (EI) m/z 180 (M^+), 111 (M^+-CH_2CH=$C(CH_3)_2$); HRMS (EI) calcd for $C_{13}H_{24}$ (M^+) 180.1878, found 180.1877.

(*E*)-1-Phenyl-(*E*)-7-phenyl-1,6-heptadiene (11).



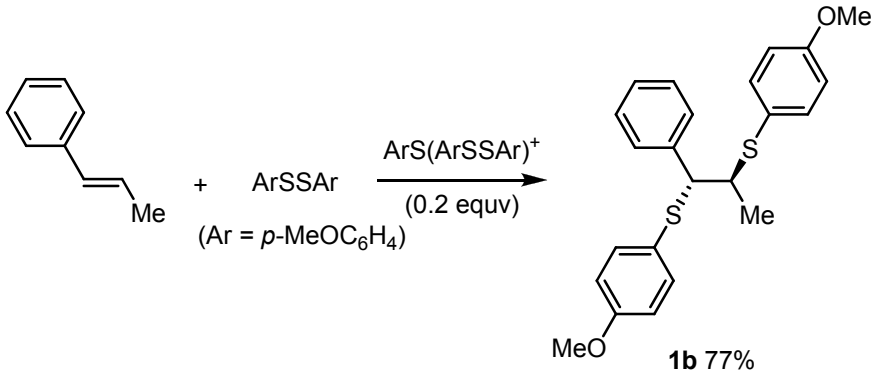
To a solution of diethylbenzylphosphonate (11.6 g, 51 mmol) in THF (120 mL) was added *n*-BuLi (1.59 M in hexane, 36 mL, 57 mmol) at -78 °C. The mixture was stirred at -78 °C for 3.5 h and then the solution of glutaraldehyde (2.13 g, 21.3 mmol) in THF (15 mL) was added slowly. The mixture was warmed gradually to room temperature and stirred for 9 h. The reaction mixture was partitioned between ether and saturated brine. The organic phase was separated, and washed with saturated brine, and dried over $MgSO_4$. After removal of the solvent, the crude product was purified via flash chromatography (hexane/EtOAc 100:1) followed by GPC to give the title compound (**11**) (288 mg, 1.2 mmol, 6 %): TLC R_f 0.37 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.66 (quintet, J = 7.6 Hz, 2H), 2.28 (qd, J = 7.6, 1.2 Hz, 4H), 6.24 (dt, J = 16.0, 7.6 Hz, 2H), 6.40 (d, J = 16.0 Hz, 2H), 7.16-7.22 (m, 2H), 7.25-7.37 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.0, 32.5, 125.9, 126.8, 128.5, 130.2, 130.6, 137.8; LRMS (EI) m/z 248 (M^+); HRMS (EI) calcd for $C_{19}H_{20}$ (M^+) 248.1565, found 248.1568.

A Typical Procedure for Addition of ArSSAr to (*E*)-*β*-Methylstyrene Using a Catalytic Amount of ArS(ArSSAr)$^+$.



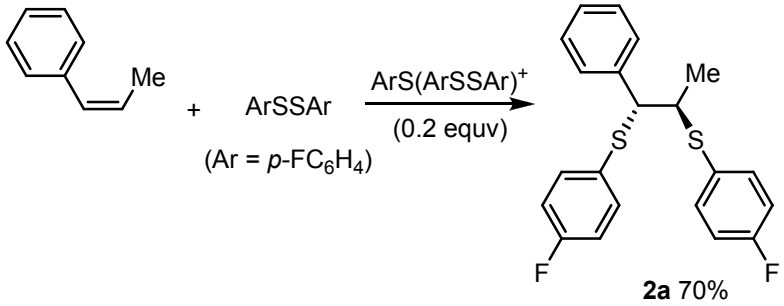
The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode and a platinum plate cathode (40 mm x 20 mm). In the anodic chamber was placed a solution of ArSSAr (Ar = *p*-FC_6H_4) (258.5 mg, 1.02 mmol) in 0.1 M $Bu_4NB(C_6F_5)_4/CH_2Cl_2$ (8.0 mL). In the cathodic chamber were placed 0.1 M $Bu_4NB(C_6F_5)_4/CH_2Cl_2$ (8.0 mL) and trifluoromethanesulfonic acid (15.4 mg, 0.103 mmol). The constant current electrolysis (8 mA) was carried out at -78 ^oC with magnetic stirring until 0.06 F/mol of electricity was consumed. After the electrolysis, the temperature in the anodic chamber containing electrogenerated $ArS(ArSSAr)^+B(C_6F_5)_4^-$ (0.06 mmol) was changed at -50 ^oC. Then, to the anodic chamber containing electrogenerated $ArS(ArSSAr)^+B(C_6F_5)_4^-$, was added (*E*)-*β*-methylstyrene (36.4 mg, 0.308 mmol) and the mixture was stirred for 0.5 h at -50 ^oC. The reaction was quenched with Et_3N (1 mL). The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (2 x 3 cm) of silica gel to remove $Bu_4NB(C_6F_5)_4$. The silica gel was washed with ether (150 mL). The crude product was purified via flash chromatography (hexane/EtOAc 20:1) to give 1-methyl-2-phenyl-2-(4-fluorophenylthio)ethyl(4-fluorophenyl)sulfide (**1a**) (90.8 mg, 0.244 mmol, 79%); ^1H NMR (400 MHz, $CDCl_3$) δ 1.42 (d, *J* = 6.8 Hz, 3H), 3.55 (dq, *J* = 6.8, 6.8 Hz, 1H), 4.17 (d, *J* = 6.8 Hz, 1H), 6.80-6.88 (m, 2H), 6.92-7.00 (m, 2H), 7.10-7.28 (m, 7H), 7.30-7.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 50.4, 60.7, 115.8 (d, *J* = 21.9 Hz), 116.0 (d, *J* = 21.4 Hz), 127.4, 128.2, 128.6, 129.61 (d, *J* = 3.1 Hz), 129.64 (d, *J* = 2.8 Hz), 135.0 (d, *J* = 8.0 Hz), 135.6 (d, *J* = 8.3 Hz), 139.9, 162.3 (d, *J* = 245.9 Hz), 162.5 (d, *J* = 246.4 Hz); LRMS (FAB) m/z 372 (M^+); HRMS (FAB) calcd for $C_{21}H_{18}F_2S_2$ (M^+) 372.0818, found 372.0833.

1-Methyl-2-phenyl-2-(4-methoxyphenylthio)ethyl(4-methoxyphenyl)sulfide (1b).



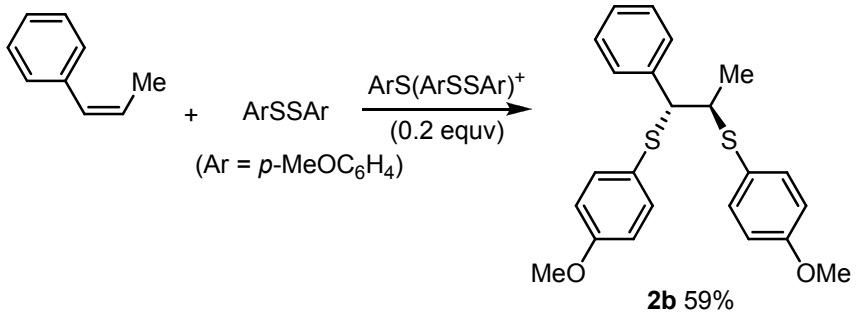
Prepared from ArSSAr (Ar = *p*-$MeOC_6H_4$) (277.9 mg, 0.998 mmol) and (*E*)-*β*-methylstyrene (36.6 mg, 0.310 mmol) with 0.06 F/mol of electricity and purified via GPC to give the title compound (**1b**) (94.9 mg, 0.239 mmol, 77%): TLC R_f 0.27 (hexane/EtOAc 10:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.41 (d, *J* = 6.8 Hz, 3H), 3.48 (dq, *J* = 6.8, 6.8 Hz, 1H), 3.73 (s, 3H), 3.79 (s, 3H), 4.10 (d, *J* = 6.8 Hz, 1H), 6.66-6.70 (m, 2H), 6.78-6.82 (m, 2H), 7.10-7.14 (m, 2H), 7.17-7.26 (m, 5H), 7.30-7.34 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.2, 50.3, 55.20, 55.28, 60.9, 114.2, 114.4, 124.9, 125.0, 127.1, 128.0, 128.7, 135.3, 136.0, 140.6, 159.4, 159.6; LRMS (EI) m/z 396 (M^+), 257 (M^+-S(*p*-$MeOC_6H_4$)); HRMS (EI) calcd for $C_{23}H_{24}O_2S_2$ (M^+) 396.1218, found 396.1219.

1-Methyl-2-phenyl-2-(4-fluorophenylthio)ethyl(4-fluorophenyl)sulfide (2a).



Prepared from ArSSAr (Ar = *p*-FC_6H_4) (254.9 mg, 1.00 mmol) and (*Z*)-*β*-methylstyrene (36.0 mg, 0.305 mmol) with 0.06 F/mol of electricity and purified via flash chromatography (hexane/EtOAc 20:1) to give the title compound (**2a**) (80.2 mg, 0.215 mmol, 70%): TLC R_f 0.23 (hexane/EtOAc 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (d, *J* = 7.2 Hz, 3H), 3.51 (dq, *J* = 7.2, 7.2 Hz, 1H), 4.14 (d, *J* = 7.2 Hz, 1H), 6.84-6.90 (m, 2H), 6.94-7.02 (m, 2H), 7.16-7.30 (m, 7H), 7.31-7.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.7, 48.2, 58.7, 115.9 (d, *J* = 21.4 Hz), 116.1 (d, *J* = 21.4 Hz), 127.6, 128.0, 129.0, 129.2 (d, *J* = 3.6 Hz), 129.5 (d, *J* = 3.6 Hz), 135.0 (d, *J* = 7.9 Hz), 135.5 (d, *J* = 7.9 Hz), 138.0, 162.4 (d, *J* = 246.4 Hz), 162.5 (d, *J* = 246.8 Hz); LRMS (EI) m/z 372 (M^+), 245 (M^+-S(*p*-FC_6H_4)); HRMS (EI) calcd for $C_{21}H_{18}F_2S_2$ (M^+) 372.0818, found 372.0815.

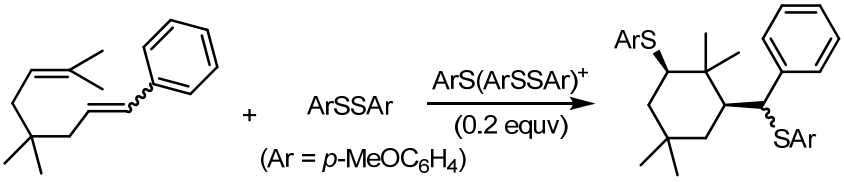
1-Methyl-2-phenyl-2-(4-methoxyphenylthio)ethyl(4-methoxyphenyl)sulfide (2b).



2b 59%

Prepared from ArSSAr (Ar = *p*-$MeOC_6H_4$) (282.4 mg, 1.01 mmol) and (*Z*)-*β*-methylstyrene (34.5 mg, 0.292 mmol) with 0.06 F/mol of electricity and purified via GPC to give the title compound (**2b**) (68.0 mg, 0.171 mmol, 59%): TLC R_f 0.16 (hexane/EtOAc 20:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (d, *J* = 6.8 Hz, 3H), 3.47 (dq, *J* = 6.8, 6.8 Hz, 1H), 3.77 (s, 3H), 3.81 (s, 3H), 4.12 (d, *J* = 6.8 Hz, 1H), 6.68-6.83 (m, 4H), 7.14-7.31 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.2, 48.0, 55.2, 55.3, 58.6, 114.3, 114.5, 124.7, 125.0, 127.3, 127.8, 129.2, 135.0, 135.6, 138.4, 159.3, 159.5; LRMS (EI) m/z 396 (M^+); HRMS (EI) calcd for $C_{23}H_{24}O_2S_2$ (M^+) 396.1218, found 396.1218.

A Typical Procedure for Addition of ArSSAr to Dienes via Intramolecular C-C Bond Formation Using a Catalytic Amount of ArS(ArSSAr)$^+$ (Method A).



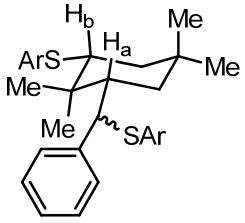
3a (*Z* : *E* = 1.4:1)

5a 77%
(diastereomer ratio 1.1:1)

The anodic oxidation was carried out in an H-type divided cell as described above. In the anodic chamber was placed a solution of ArSSAr (Ar = *p*-$MeOC_6H_4$) (282.6 mg, 1.02 mmol mmol) in 0.1 M $Bu_4NB(C_6F_5)_4/CH_2Cl_2$ (8.0 mL). In the cathodic chamber were placed 0.1 M $Bu_4NB(C_6F_5)_4/CH_2Cl_2$ (8.0 mL) and trifluoromethanesulfonic acid (16.6 mg, 0.111 mmol). The constant current electrolysis (8 mA) was carried out at -78 ^{o}C with magnetic stirring until 0.06 F/mol of electricity was consumed. After the electrolysis, the temperature in the anodic chamber containing electrogenerated $ArS(ArSSAr)^+B(C_6F_5)_4^-$ (0.06 mmol) was changed at 0 ^{o}C. Then, to the anodic chamber containing electrogenerated $ArS(ArSSAr)^+B(C_6F_5)_4^-$, was added (4,4,7-trimethylocta-1,6-dienyl)benzene (**3a**) (69.9 mg, 0.306 mmol), and the mixture was stirred for 0.5 h at 0 ^{o}C. The reaction was quenched with Et_3N (1 mL). The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (2 x 3 cm) of silica gel to remove $Bu_4NB(C_6F_5)_4$. The silica gel was washed with ether (150 mL). The crude product was purified via GPC to give 1-(4-methoxyphenylthio)-2,2,5,5-tetramethyl-3-(phenyl(4-methoxyphenylthio)methyl)-

cyclohexane (**5a**) (120.0 mg, 0.237 mmol, 77%). This compound was characterized as a mixture of two diasteromers (1.1:1 by ^{1}H NMR analysis). The stereochemistry was determined by the proton-proton coupling constant and proton homonuclear NOE experiments: TLC R_f 0.28 (hexane/EtOAc 10:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.47 (s, 3H) and 1.22 (s, 3H), 0.69 (s, 3H) and 0.83 (s, 3H), 0.94 (s, 3H) and 0.97 (s, 3H), 1.33 (s, 3H) and 1.36 (s, 3H), 1.36-1.74 (m, 7H, which means mixture of two diastereomers), 1.86-1.96 (m, 3H, which means mixture of two diastereomers), 2.74 (dd, J = 13.0, 4.4 Hz, 1H) and 2.80 (dd, J = 13.1, 4.1 Hz, 1H), 3.71 (s, 3H) and 3.75 (s, 3H), 3.76 (s, 3H) and 3.78 (s, 3H), 4.28 (d, J = 2.0 Hz, 1H) and 4.54 (d, J = 3.1 Hz, 1H), 6.64-6.82 (m, 4H), 7.02-7.33 (m, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.8 and 15.7, 24.6 and 25.1, 27.4 and 28.2, 31.7 and 31.8, 32.9 and 33.1, 36.2 and 36.6, 39.97 and 40.09, 43.8 and 44.0, 48.0 and 50.8, 55.16 and 55.21, 55.2 and 55.2, 56.2 and 56.5, 59.2 and 59.5, 114.2 and 114.3, 114.4 and 114.4, 125.9 and 126.2, 126.3 and 126.9, 127.1 and 127.3, 127.6 and 127.9, 128.1 and 129.8, 134.1 and 134.1, 134.5 and 135.5, 140.8 and 145.7, 158.8 and 158.9, 159.1 and 159.4; LRMS (EI) m/z 506 (M^+), 367 (M^+-S(p-$MeOC_6H_4$)); HRMS (EI) calcd for $C_{31}H_{38}O_2S_2$ (M^+) 506.2313, found 506.2318.

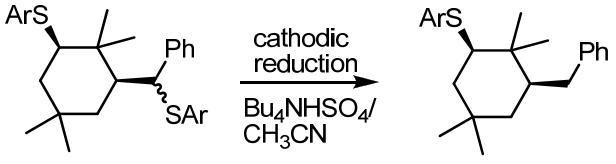
NOE Data for **5a**:



(Ar = p-$MeOC_6H_4$)

Signal Irradiated	NOE's observed
H_b (diastereomer 1)	H_a (8.1 %)
H_a (diastereomer 1)	H_b (5.6 %)
H_b (diastereomer 2)	H_a (8.5 %)
H_a (diastereomer 2)	H_b (8.9 %)

1-(4-Methoxyphenylthio)-2,2,5,5-tetramethyl-3-benzylcyclohexane (6): Cathodic Reduction of 1-(4-Methoxyphenylthio)-2,2,5,5-tetramethyl-3-(phenyl(4-methoxyphenylthio)methyl)cyclohexane (5a).[5]

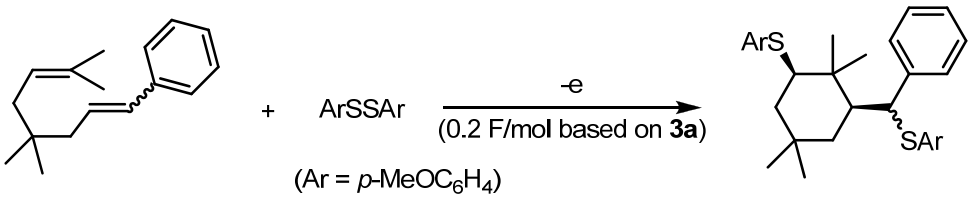


5a (Ar = p-$MeOC_6H_4$) **6** 70% (single diastereomer)

The cathodic reduction was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt cathode and a platinum plate anode (10 mm x 10 mm). In the cathodic chamber was placed a solution of 1-(4-methoxyphenylthio)-2,2,5,5-tetramethyl-3-(phenyl(4-methoxyphenylthio)methyl)-cyclohexane (**5a**) (116.5 mg, 0.230 mmol, a mixture of two diastereomers) in 0.2 M Bu_4NHSO_4/CH_3CN (4.0 mL). In the anodic chamber was placed 0.2 M Bu_4NHSO_4/CH_3CN (4.0 mL). The constant current electrolysis (25 mA) was carried out

at 0 °C with magnetic stirring (5.2 F/mol of electricity) until starting material (**5a**) was consumed completely. After the electrolysis, the reaction was quenched with Et_3N (1 mL). The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (2 x 3 cm) of silica gel to remove Bu_4NHSO_4. The silica gel was washed with ether (150 mL). The crude product was purified via flash chromatography (hexane/EtOAc 90:1) and ^1H NMR analysis using CH_2Br_2 as an internal standard indicated that 1-(4-methoxyphenylthio)-2,2,5,5-tetramethyl-3-benzyl-cyclohexane (**6**) was formed in 70 % yield as a single diastereomer: TLC R_f 0.48 (hexane/EtOAc 10:1); ^1H NMR (600 MHz, $CDCl_3$) δ 0.66 (s, 3H), 0.81 (s, 3H), 0.92 (s, 3H), 1.01-1.10 (m, 2H), 1.40 (s, 3H), 1.50-1.62 (m, 3H), 2.06 (dd, J = 13.4, 11.0 Hz, 1H), 2.93 (dd, J = 12.0, 5.2 Hz, 1H), 2.99 (dd, J = 13.4, 2.4 Hz, 1H), 3.80 (s, 3H), 6.81-6.85 (m, 2H), 7.08-7.13 (m, 2H), 7.14-7.18 (m, 1H), 7.23-7.28 (m, 2H), 7.33-7.38 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.3, 24.7, 27.7, 31.4, 32.8, 37.3, 38.6, 39.8, 44.1, 45.8, 55.3, 58.9, 114.4, 125.6, 127.5, 128.2, 128.9, 134.1, 142.0, 158.8; LRMS (EI) m/z 368 (M^+); HRMS (EI) calcd for $C_{24}H_{32}O_1S_1$ (M^+) 368.2174, found 368.2174.

A Typical Procedure for Cyclization Using a Catalytic Amount of Electricity (Method B, *In-Cell Electrolysis*).

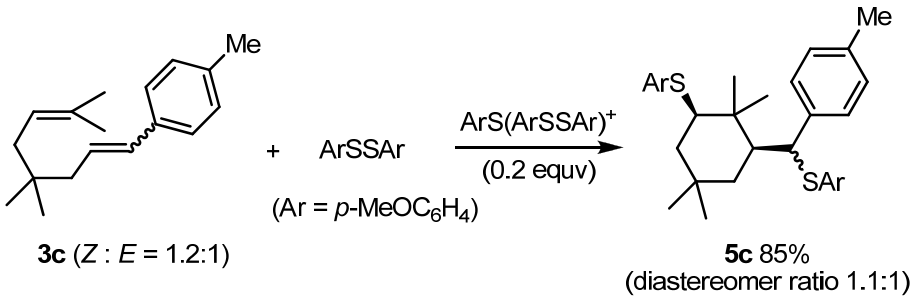


3a (*Z* : *E* = 1.4:1)

5a 82%
(diastereomer ratio 1.1:1)

The anodic oxidation was carried out in an H-type divided cell as described above. In the anodic chamber was placed a solution of (4,4,7-trimethylocta-1,6-dienyl)benzene (**3a**) (70.1 mg, 0.307 mmol) and ArSSAr (Ar = *p*-$MeOC_6H_4$) (280.0 mg, 1.01 mmol) in 0.1 M $Bu_4NB(C_6F_5)_4/CH_2Cl_2$ (8.0 mL). In the cathodic chamber were placed 0.1 M $Bu_4NB(C_6F_5)_4/CH_2Cl_2$ (8.0 mL) and trifluoromethanesulfonic acid (15.0 mg, 0.10 mmol). The constant current electrolysis (8 mA) was carried out at 0 °C with magnetic stirring until 0.20 F/mol of electricity (based on **3a**) was consumed. The mixture was stirred for 0.5 h at 0 °C, and then the reaction was quenched with Et_3N (1 mL). The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (2 x 3 cm) of silica gel to remove $Bu_4NB(C_6F_5)_4$. The silica gel was washed with ether (150 mL). The crude product was purified via GPC to give **5a** (128.0 mg, 0.253 mmol, 82%). This compound was characterized as a mixture of two diasteromers (1.1:1 by ^1H NMR analysis).

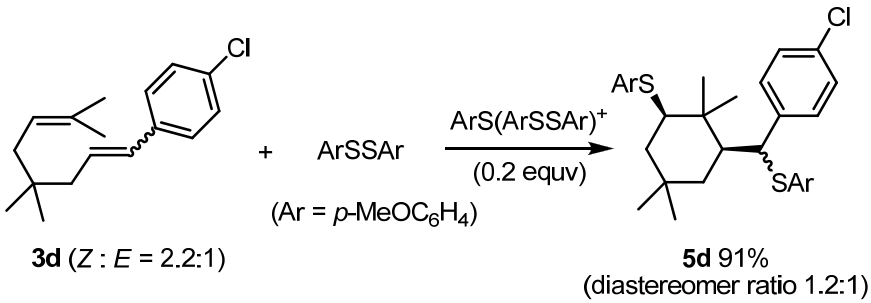
1-(4-Methoxyphenylthio)-2,2,5,5-tetramethyl-3-((4-methylphenyl)(4-methoxyphenyl thio)methyl)cyclohexane (5c).



3c (*Z* : *E* = 1.2:1) **5c** 85% (diastereomer ratio 1.1:1)

Prepared from ArSSAr (Ar = *p*-$MeOC_6H_4$) (281.4 mg, 1.01 mmol) and 1-methyl-4-(4,4,7-trimethylocta-1,6-dienyl)benzene (**3c**) (72.5 mg, 0.299 mmol) with 0.06 F/mol of electricity (method A, reaction temperature: 0 °C), and purified via GPC to give **3c** (132.6 mg, 0.255 mmol, 85%, purity ca. 95%). This compound was characterized as a mixture of two diasteromers (1.1:1 by ^{1}H NMR analysis): TLC R_f 0.33 (hexane/EtOAc 5:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.47 (s, 3H) and 1.21 (s, 3H), 0.69 (s, 3H) and 0.82 (s, 3H), 0.94 (s, 3H) and 0.96 (s, 3H), 1.30 (s, 3H) and 1.35 (s, 3H), 1.40-1.93 (m, 5H), 2.72 (dd, *J* = 12.7, 4.1 Hz, 1H) and 2.80 (dd, *J* = 13.0, 4.1 Hz, 1H), 3.71 (s, 3H) and 3.77 (s, 3H), 3.77 (s, 3H) and 3.78 (s, 3H), 4.26 (d, *J* = 1.7 Hz, 1H) and 4.54 (d, *J* = 2.8 Hz, 1H), 6.66-6.82 (m, 4H), 7.00-7.32 (m, 8H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.9 and 15.6, 21.0 and 21.1, 24.6 and 25.2, 27.4 and 28.2, 31.7 and 31.8, 32.9 and 33.2, 36.1 and 36.6, 39.9 and 40.1, 43.9 and 44.0, 47.9 and 51.0, 55.2 and 55.3, 55.3 and 55.3, 55.7 and 56.2, 59.3 and 59.5, 114.2 and 114.3, 114.4 and 114.4, 126.1 and 126.5, 127.2 and 127.4, 127.5 and 128.6, 128.8 and 129.6, 134.1 and 134.1, 134.3 and 135.4, 135.8 and 136.6, 137.6 and 142.7, 158.2 and 158.8, 159.0 and 159.4; LRMS (EI) m/z 520 (M^+), 381 (M^+-S(*p*-$MeOC_6H_4$)); HRMS (EI) calcd for $C_{32}H_{40}O_2S_2$ (M^+) 520.2470, found 520.2468.

1-(4-Methoxyphenylthio)-2,2,5,5-tetramethyl-3-((4-chlorophenyl)(4-methoxyphenylt hio)methyl)cyclohexane (5d).

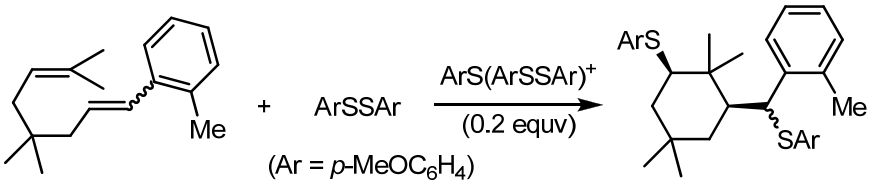


3d (*Z* : *E* = 2.2:1) **5d** 91% (diastereomer ratio 1.2:1)

Prepared from ArSSAr (Ar = *p*-$MeOC_6H_4$) (280.2 mg, 1.01 mmol) and 1-chloro-4-(4,4,7-trimethylocta-1,6-dienyl)benzene (**3d**) (78.6 mg, 0.299 mmol) with 0.06 F/mol of electricity (method A, reaction temperature: 0 °C), and purified via GPC to give **5d** (147.6 mg, , 0.273 mmol, 91%). This compound was characterized as a mixture

of two diasteromers (1.2:1 by ^{1}H NMR analysis): TLC R_f 0.38 (hexane/EtOAc 10:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.48 (s, 3H) and 1.22 (s, 3H), 0.68 (s, 3H) and 0.84 (s, 3H), 0.94 (s, 3H) and 0.96 (s, 3H), 1.34 (s, 3H) and 1.34 (s, 3H), 1.25-1.96 (m, 5H), 2.75 (dd, J = 13.1, 4.1 Hz, 1H) and 2.79 (dd, J = 13.1, 4.1 Hz, 1H), 3.72 (s, 3H) and 3.76 (s, 3H), 3.77 (s, 3H) and 3.78 (s, 3H), 4.25 (d, J = 2.0 Hz, 1H) and 4.48 (d, J = 3.1 Hz, 1H), 6.66-6.82 (m, 4H), 7.03-7.33 (m, 8H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.0 and 15.7, 24.6 and 25.1, 27.5 and 28.3, 31.7 and 31.8, 32.9 and 33.1, 36.4 and 36.5, 40.0 and 40.1, 43.8 and 43.9, 48.0 and 50.9, 55.19 and 55.23, 55.2 and 55.2, 55.5 and 56.0, 59.2 and 59.4, 114.3 and 114.4, 114.5 and 114.5, 125.4 and 125.7, 127.0 and 127.2, 128.0 and 128.3, 129.0 and 131.1, 131.9 and 132.6, 134.2 and 134.2, 134.6 and 135.5, 139.5 and 144.2, 158.88 and 158.90, 159.2 and 159.6; LRMS (EI) m/z 540 (M^+), 401 (M^+-S(p-$MeOC_6H_4$)); HRMS (EI) calcd for $C_{31}H_{37}Cl_1O_2S_2$ (M^+) 540.1923, found 540.1923.

1-(4-Methoxyphenylthio)-2,2,5,5-tetramethyl-3-((2-methylphenyl)(4-methoxyphenyl thio)methyl)cyclohexane (5e).

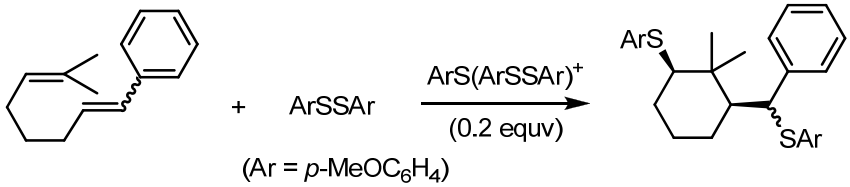


3e (Z : E = 1.3:1)

5e 84%
(diastereomer ratio 2.2:1)

Prepared from ArSSAr (Ar = p-$MeOC_6H_4$) (277.6 mg, 0.997 mmol) and 1-methyl-2-(4,4,7-trimethylocta-1,6-dienyl)benzene (**3e**) (71.7 mg, 0.296 mmol) with 0.06 F/mol of electricity (method A, reaction temperature: 0 °C), and purified via GPC to give **5e** (129.2 mg, 0.248 mmol, 84%). This compound was characterized as a mixture of two diasteromers (2.2:1 by ^{1}H NMR analysis): TLC R_f 0.30 (hexane/EtOAc 10:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.52 (s, 3H) and 1.20 (s, 3H), 0.74 (s, 3H) and 0.80 (s, 3H), 0.95 (s, 3H) and 0.98 (s, 3H), 1.26 (s, 3H) and 1.36 (s, 3H), 1.40-1.96 (m, 5H), 1.97 (br s, 3H) and 2.21 (s, 3H), 2.74 (dd, J = 12.7, 4.1 Hz, 1H) and 2.80 (dd, J = 12.7, 4.1 Hz, 1H), 3.72 (s, 3H) and 3.76 (s, 3H), 3.77 (s, 3H) and 3.78 (s, 3H), 4.54 (br s, 1H) and 4.70 (d, J = 3.8 Hz, 1H), 6.60-7.70 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.7 and 15.8, 19.6 and 20.4, 24.68 and 24.74, 28.2 and 28.3, 31.8 and 31.9, 33.0 and 33.2, 37.1 and 37.4, 39.7 and 40.3, 43.9 and 44.0, 48.2 and 49.3, 50.7 and 51.5, 55.18 and 55.18, 55.23 and 55.23, 59.5 and 59.6, 114.1 and 114.2, 114.4 and 114.4, 125.7 and 125.8, 126.1 and 126.2, 126.6 and 127.2, 127.4 and 128.7, 129.6 and 129.9, 130.4 and 132.6, 134.1 and 134.4, 134.1 and 135.5, 135.5 and 136.2, 139.8 and 143.7, 158.8 and 158.8, 159.4 and 159.6; LRMS (EI) m/z 520 (M^+), 381 (M^+-S(p-$MeOC_6H_4$)); HRMS (EI) calcd for $C_{32}H_{40}O_2S_2$ (M^+) 520.2470, found 520.2476.

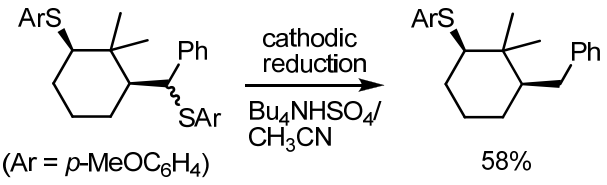
1-(4-Methoxyphenylthio)-2,2-dimethyl-3-(phenyl(4-methoxyphenylthio)methyl)cyclohexane (8).



7 (*E* : *Z* = 19>:1) **8** 58% (diastereomer ratio 12.1:1.8:1)

Prepared from ArSSAr (Ar = *p*-$MeOC_6H_4$) (282.5 mg, 1.01 mmol) and (7-methylocta-1,6-dienyl)benzene (**7**) (59.2 mg, 0.296 mmol) with 0.06 F/mol of electricity (method A, reaction temperature: 0 °C), and purified via GPC to give **8** (81.7 mg, 0.171 mmol, 58%, purity ca. 95%). This compound was characterized as a mixture of three diasteromers (12.1:1.8:1 by ^1H NMR analysis). The stereochemistry of the major isomer was determined by the further transformation (*vide infra*) due to the overlapping of signals: TLC R_f 0.30 (hexane/EtOAc 10:1); ^1H NMR (600 MHz, $CDCl_3$, major isomer) δ 1.03-1.13 (m, 1H), 1.29 (s, 3H), 1.40 (s, 3H), 1.63-1.97 (m, 6H), 2.60 (dd, *J* = 12.7, 4.1 Hz, 1H), 3.72 (s, 3H), 3.77 (s, 3H), 4.33 (d, *J* = 1.7 Hz, 1H), 6.63-6.82 (m, 4H), 7.00-7.37 (m, 9H); ^{13}C NMR (150Hz, $CDCl_3$, major isomer) δ 16.5, 23.5, 27.2, 28.5, 30.9, 40.3, 55.2, 55.3, 55.8, 56.5, 63.2, 114.2, 114.4, 126.3, 127.1, 127.8, 128.2, 129.8, 134.2, 134.9, 145.7, 158.98, 159.05; LRMS (EI) m/z 478 (M^+); HRMS (EI) calcd for $C_{29}H_{34}O_2S_2$ (M^+) 478.2000, found 478.1998.

This compound was further transformed by the cathodic reduction in order to determine the stereochemistry of the major isomer completely.

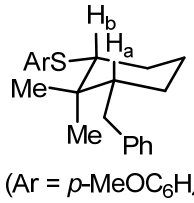


(Ar = *p*-$MeOC_6H_4$) 58%
(diastereomer ratio 12.1:1.8:1)
8

The cathodic reduction was carried out in an H-type divided cell as described above. In the cathodic chamber was placed a solution of 1-(4-methoxyphenylthio)-2,2-dimethyl-3-(phenyl(4-methoxyphenylthio)methyl)cyclohexane (**8**) (92.1 mg, 0.192 mmol, a mixture of three diastereomers) in 0.2 M Bu_4NHSO_4/CH_3CN (4.0 mL). In the anodic chamber was placed 0.2 M Bu_4NHSO_4/CH_3CN (4.0 mL). The constant current electrolysis (25 mA) was carried out at 0 °C with magnetic stirring (6.5 F/mol of electricity) until starting material (**8**) was consumed completely. After the electrolysis, the reaction was quenched with Et_3N (1

mL). The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (2 x 3 cm) of silica gel to remove Bu_4NHSO_4. The silica gel was washed with ether (150 mL). The crude product was purified via flash chromatography (hexane/EtOAc 20:1) and ^{1}H NMR analysis using $(Cl_2CH)_2$ as an internal standard indicated that 1-(4-methoxyphenylthio)-2,2-dimethyl-3-benzyl-cyclohexane was formed in 58 % yield. The stereochemistry of the major isomer was determined by the proton-proton coupling constant and proton homonuclear NOE experiments: TLC R_f 0.46 (hexane/EtOAc 10:1); ^{1}H NMR (600 MHz, $CDCl_3$, major isomer) δ 0.97 (s, 3H), 0.97-1.03 (m, 1H), 1.06-1.17 (m, 1H), 1.34 (tt, J = 11.0, 2.4 Hz, 1H), 1.37-1.42 (m, 1H), 1.43 (s, 3H), 1.56-1.65 (m, 2H), 1.80-1.85 (m, 1H), 2.09 (dd, J = 13.0, 11.0 Hz, 1H), 2.70 (dd, J = 12.4, 4.1 Hz, 1H), 3.00 (dd, J = 13.0, 2.4 Hz, 1H), 3.79 (s, 3H), 6.81-6.85 (m, 2H), 7.10-7.30 (m, 5H), 7.37-7.40 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, major isomer) δ 15.1, 26.6, 26.6, 27.9, 31.1, 37.4, 38.8, 50.8, 55.3, 62.9, 114.4, 125.6, 127.2, 128.1, 129.1, 134.9, 142.2, 159.0; LRMS (EI) m/z 340 (M^+); HRMS (EI) calcd for $C_{22}H_{28}O_1S_1$ (M^+) 340.1861, found 340.1862.

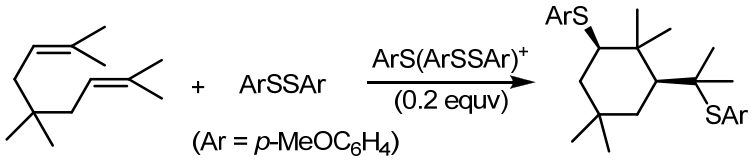
NOE Data for 1-(4-methoxyphenylthio)-2,2-dimethyl-3-benzylcyclohexane:



(Ar = *p*-MeOC$_6$H$_4$)

Signal Irradiated	NOE's observed
H_a	H_b (10.0 %)
H_b	H_a (7.4 %)

1-(4-Methoxyphenylthio)-2,2,5,5-tetramethyl-3-(dimethyl(4-methoxyphenylthio)methyl)cyclohexane (10).

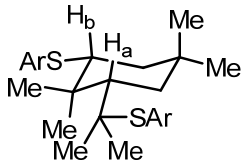


9 **10** 77%

Prepared from ArSSAr (Ar = *p*-MeOC$_6$H$_4$) (283.2 mg, 1.02 mmol) and 2,5,5,8-tetramethylnona-2,7-diene (**9**) (54.4 mg, 0.302 mmol) with 0.06 F/mol of electricity (method A, reaction temperature: -78 ^{o}C), and purified via GPC to give **10** (106.6 mg, 0.232 mmol, 77%). This compound was obtained as a single diastereomer. The stereochemistry was determined by the proton-proton coupling constant and proton homonuclear NOE experiments: TLC R_f 0.21 (hexane/EtOAc 20:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.88 (s, 3H), 0.97 (s, 3H), 1.03 (s, 3H), 1.24 (s, 3H), 1.42 (s, 3H), 1.45 (s, 3H), 1.46 (t, J = 13.0 Hz, 1H), 1.56-1.68 (m, 3H), 2.02 (d, J = 13.0 Hz, 1H), 2.81 (dd, J = 13.1, 4.4 Hz, 1H), 3.80 (s, 3H), 3.82 (s, 3H), 6.82 (d, J = 8.2 Hz, 2H), 6.85 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 16.5,

24.3, 27.0, 30.3, 31.5, 32.4, 33.1, 38.9, 41.4, 44.8, 50.5, 55.26, 55.29, 56.0, 61.5, 113.9, 114.5, 123.7, 127.6, 134.1, 139.2, 158.8, 160.3; LRMS (EI) m/z 458 (M^+); HRMS (EI) calcd for $C_{27}H_{38}O_2S_2$ (M^+) 458.2313, found 458.2311.

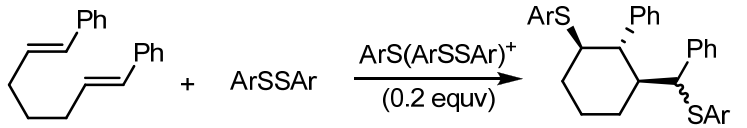
NOE Data for **10**:



Signal Irradiated	NOE's observed
H_a	H_b (8.2 %)

(Ar = *p*-$MeOC_6H_4$)

1-(4-Methoxyphenylthio)-2-phenyl-3-(phenyl(4-methyoxyphenylthio)methyl)cyclohexane (12).



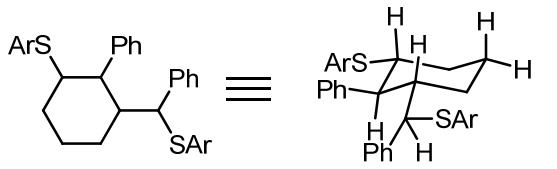
(Ar = *p*-$MeOC_6H_4$)

11

12 84%
(diastereomer ratio 11.5:1.1:1)

Prepared from ArSSAr (Ar = *p*-$MeOC_6H_4$) (281.5 mg, 1.01 mmol) and (*E*)-1-phenyl-(*E*)-7-phenyl-1,6-heptadiene (**11**) (74.8 mg, 0.301 mmol) with 0.06 F/mol of electricity (method A, reaction temperature: 33 °C), and purified via GPC. ^{1}H NMR analysis using $(Cl_2CH)_2$ as an internal standard indicated that the title compound (**12**) was formed in 84 % yield. This compound was characterized as a mixture of three diasteromers (11.5:1.1:1 by ^{1}H NMR analysis). Analytical sample was further purified by HPLC (hexane/EtOAc 20:1) to obtain three compounds (diastereomer **12-1**, **12-2** and **12-3**).

Diastereomer **12-1** (main diastereomer)



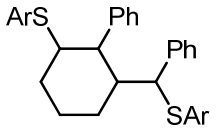
diastereomer 12-1

(Ar = *p*-$MeOC_6H_4$)

The stereochemistry was determined based on the proton-proton coupling constants because proton homonuclear NOE experiments could not provide clear results due to the overlapping of signals: TLC R_f 0.23 (hexane/EtOAc 10:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.14 (qt, *J* = 13.4, 3.4 Hz, 1H), 1.38 (qd, *J* = 13.4, 3.4 Hz, 1H), 1.44-1.52 (m, 1H), 1.72-1.80 (m, 2H), 1.98 (tt, *J* = 11.3, 2.4 Hz, 1H), 2.01-2.08 (m, 1H), 3.07 (td, *J* =

11.3, 3.4 Hz, 1H), 3.12 (t, J = 11.3 Hz, 1H), 3.65 (s, 3H), 3.76 (s, 3H), 3.80 (d, J = 2.4 Hz, 1H), 6.55-6.58 (m, 2H), 6.72-6.76 (m, 2H), 6.92-6.96 (m, 2H), 7.09-7.13 (m, 1H), 7.15-7.21 (m, 6H), 7.27-7.30 (m, 1H), 7.33-7.42 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 25.4, 26.0, 34.6, 52.4, 53.3, 54.6, 55.1, 55.2, 57.9, 114.08, 114.13, 125.0, 126.0, 126.5, 127.0, 127.9, 128.5, 133.2, 133.2, 136.0, 136.0, 142.2, 142.6, 158.6, 159.2; LRMS (EI) m/z 526 (M^+), 387 (M^+-S(p-$MeOC_6H_4$)); HRMS (EI) calcd for $C_{33}H_{34}O_2S_2$ (M^+) 526.2000, found 526.2000.

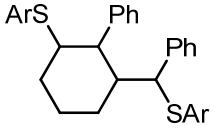
Diastereomer **12-2** (second diastereomer)



diastereomer 12-2
(Ar = p-$MeOC_6H_4$)

The stereochemistry was not determined: TLC R_f 0.23 (hexane/EtOAc 10:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.75 (br d, J = 14.1 Hz, 1H), 1.86-2.10 (m, 4H), 2.57-2.64 (m, 1H), 2.69 (br d, J = 3.5 Hz, 1H), 2.96-3.04 (m, 1H), 3.29 (br s, 1H), 3.60 (d, J = 11.3 Hz, 1H), 3.70 (s, 3H), 3.79 (s, 3H), 6.56-6.61 (m, 4H), 6.73-6.80 (m, 4H), 6.90-6.95 (m, 2H), 6.96-7.00 (m, 2H), 7.01-7.05 (m, 1H), 7.08-7.14 (m, 3H), 7.25-7.30 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.0, 25.1, 26.9, 38.9, 46.2, 53.5, 55.2, 55.3, 59.5, 113.9, 114.4, 124.8, 125.7, 126.2, 126.3, 127.5, 127.9, 128.6, 130.0, 135.5, 136.1, 141.0, 142.3, 159.3, 159.3; LRMS (EI) m/z 526 (M^+), 387 (M^+-S(p-$MeOC_6H_4$)); HRMS (EI) calcd for $C_{33}H_{34}O_2S_2$ (M^+) 526.2000, found 526.2003.

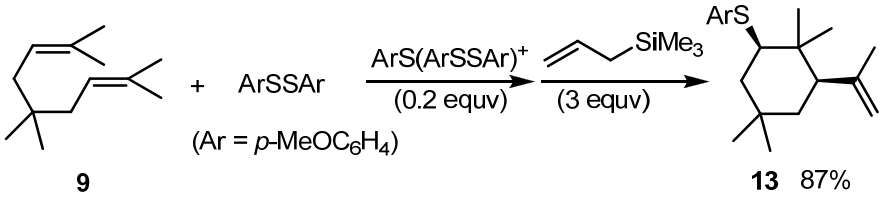
Diastereomer **12-3** (third diastereomer)



diastereomer 12-3
(Ar = p-$MeOC_6H_4$)

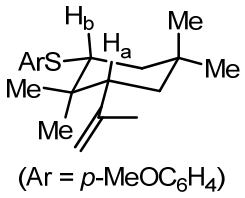
The stereochemistry was not determined: TLC R_f 0.23 (hexane/EtOAc 10:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.00-1.35 (m, 3H), 1.80-1.87 (m, 1H), 1.88-1.94 (m, 1H), 2.10-2.18 (m, 2H), 2.42-2.48 (m, 1H), 2.73-2.80 (m, 1H), 3.73 (s, 3H), 3.81 (s, 3H), 3.96 (d, J = 2.0 Hz, 1H), 6.63-6.67 (m, 2H), 6.73-6.78 (m, 2H), 6.93-7.02 (m, 4H), 7.10-7.17 (m, 4H), 7.22-7.32 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 26.0, 26.1, 34.8, 46.8, 52.8, 55.2, 55.3, 55.5, 56.6, 114.0, 114.3, 125.4, 126.8, 127.2, 127.7, 127.7, 128.3, 129.6, 129.6, 135.5, 135.6, 138.0, 142.1, 159.1, 159.4; LRMS (EI) m/z 526 (M^+), 387 (M^+-S(p-$MeOC_6H_4$)); HRMS (EI) calcd for $C_{33}H_{34}O_2S_2$ (M^+) 526.2000, found 526.2000.

(4-Methoxyphenylthio)-2,2,5,5-tetramerhyl-3-(prop-1-en-2-yl)cyclohexane (**13**).



Prepared from ArSSAr (Ar = *p*-$MeOC_6H_4$) (278.9 mg, 1.00 mmol) and 2,5,5,8-tetramethylnona-2,7-diene (**9**) (55.8 mg, 0.309 mmol) with 0.06 F/mol of electricity (method A, reaction temperature: -78 ^oC) and allyltrimethylsilane (114.3 mg, 1.00 mmol, reaction temperature was gradually increased from -78 ^oC to room temperature for 0.5 h.). Then, the reaction was quenched by the addition of Et_3N (1 mL). This compound was purified via GPC to give **13** (86.1 mg, 0.270 mmol, 87%). This compound was obtained as a single diastereomer. The stereochemistry was determined by the proton-proton coupling constant and proton homonuclear NOE experiments: TLC R_f 0.45 (hexane/EtOAc 10:1); ^1H NMR (600 MHz, $CDCl_3$) δ 0.97 (s, 3H), 0.916 (s, 3H), 0.919 (s, 3H), 1.11 (dt, J = 13.6, 2.6 Hz, 1H), 1.18 (s, 3H), 1.53-1.61 (m, 3H), 1.74 (t, J = 0.7 Hz, 3H), 2.06 (dd, J = 13.6, 2.6 Hz, 1H), 2.90 (dd, J = 11.7, 5.5 Hz, 1H), 3.80 (s, 3H), 4.65-4.67 (m, 1H), 4.86-4.88 (m, 1H), 6.80-6.85 (m, 2H), 7.33-7.38 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.3, 24.2, 25.1, 28.6, 31.7, 33.0, 39.0, 40.9, 44.0, 50.8, 55.3, 59.3, 113.3, 114.4, 127.6, 134.1, 147.1, 158.8; LRMS (EI) m/z 318 (M^+); HRMS (EI) calcd for $C_{20}H_{30}O_1S_1$ (M^+) 318.2017, found 318.2015.

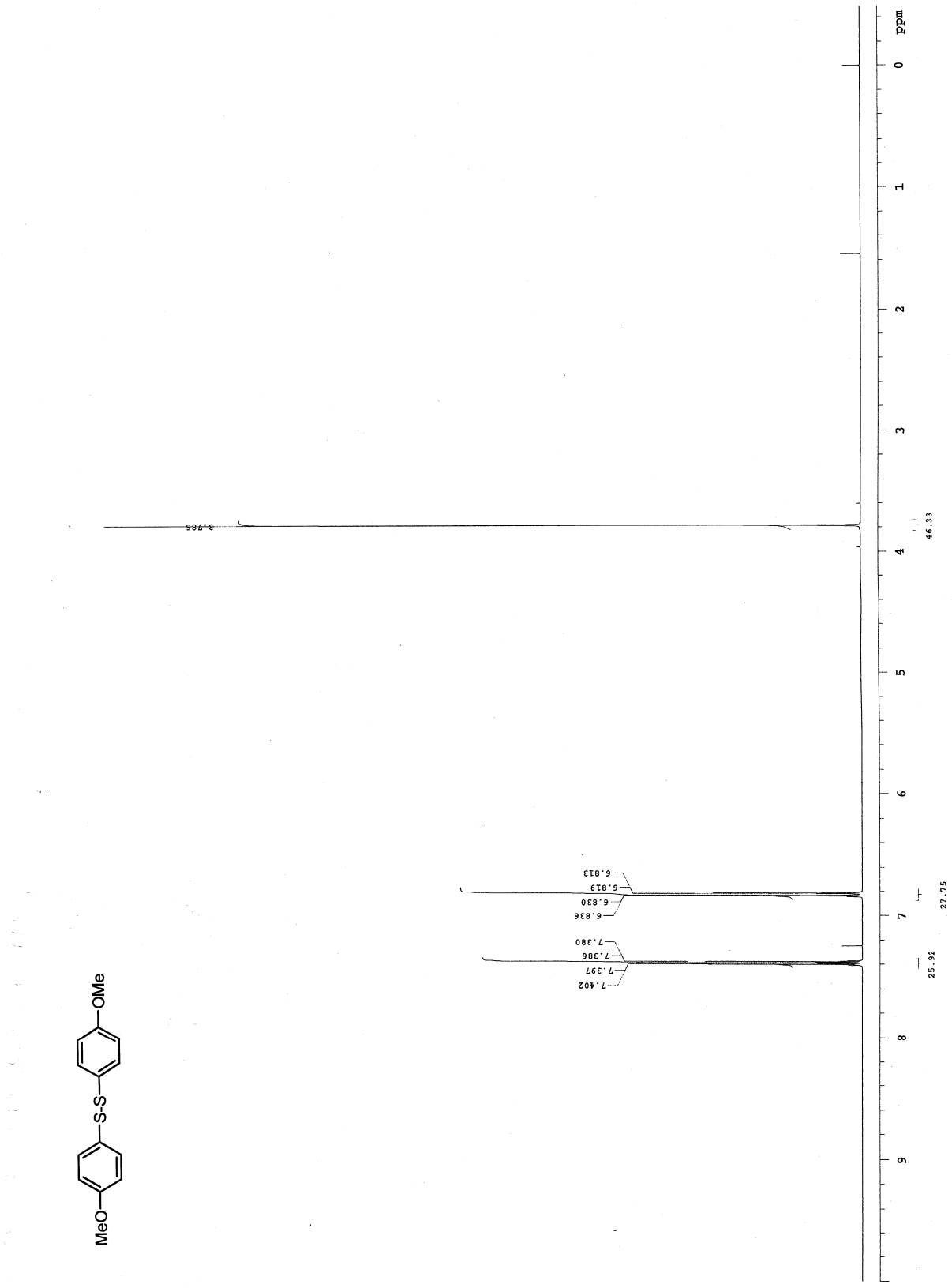
NOE Data for **13**:



Signal Irradiated	NOE's observed
H_a	H_b (10.3%)
H_b	H_a (8.4%)

References

1. R. Leino, J. E. Lönnqvist, *Tetrahedron Lett.,* 2004, **45**, 8489.
2. D. P. Becker, C. I. Villamil, T. E. Barta, L. J. Bedell, T. L. Boehm, G. A. DeCrescenzo, J. N. Freskos, D. P. Getman, S. Hockerman, R. Heintz, S. C. Howard, M. H. Li, J. J. McDonald, C. P. Carron, C. L. Funckes-Shippy, P. P. Mehta, G. E. Munie, C. A. Swearingen, *J. Med. Chem.,* 2005, **48***,* 6713.
3. N. H. Andersen, D. W. Ladner, *Snthetic Commun.,* 1978, **8**, 449.
4. K. Yoshikai, T. Hayama, K. Nishimura, K. Yamada, K. Tomioka, *J. Org. Chem.,* 2005, **70**, 681.
5. N. S. Ltter, E. Steckhan, *Tetrahedron,* 1987, **43**, 2475.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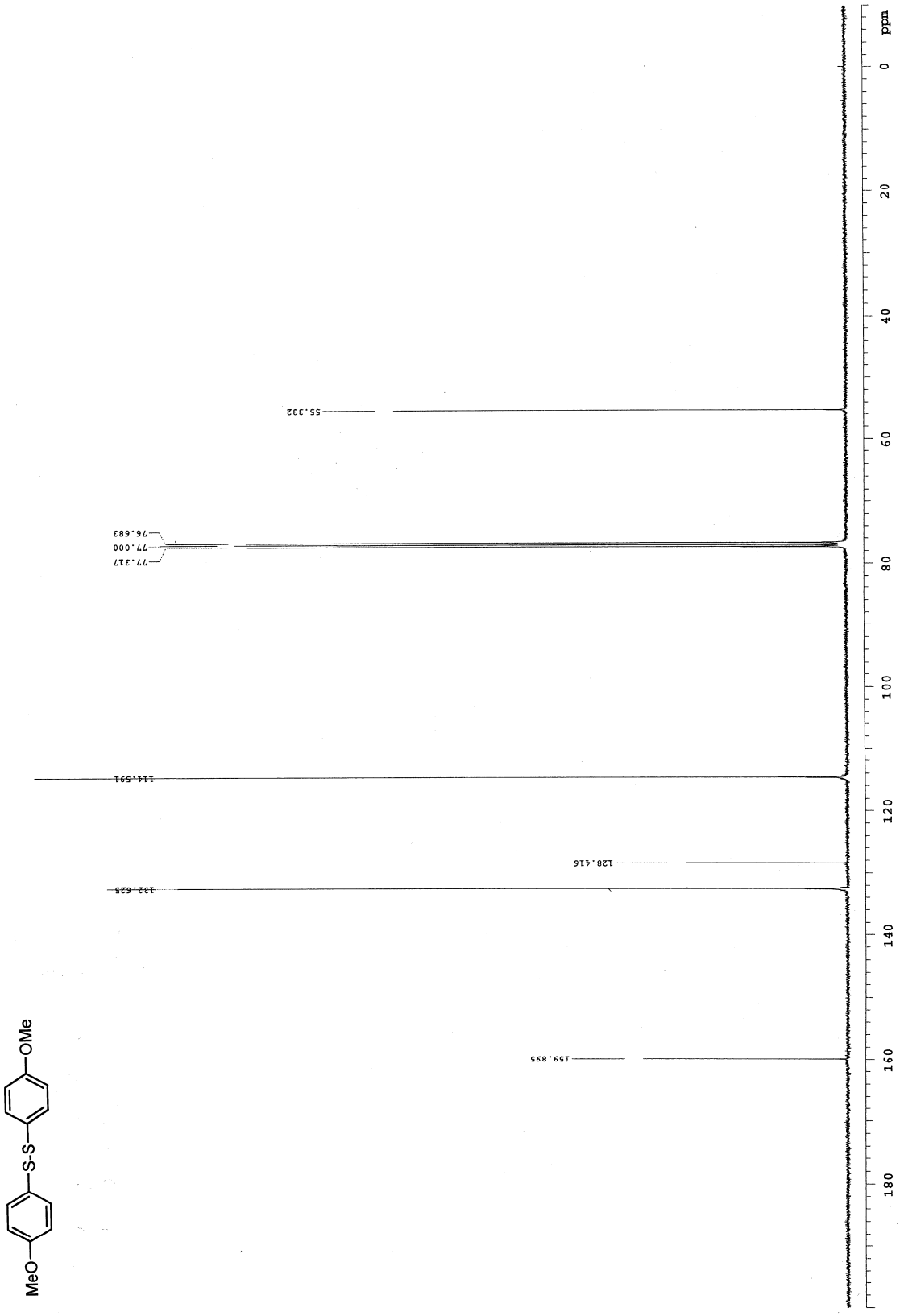
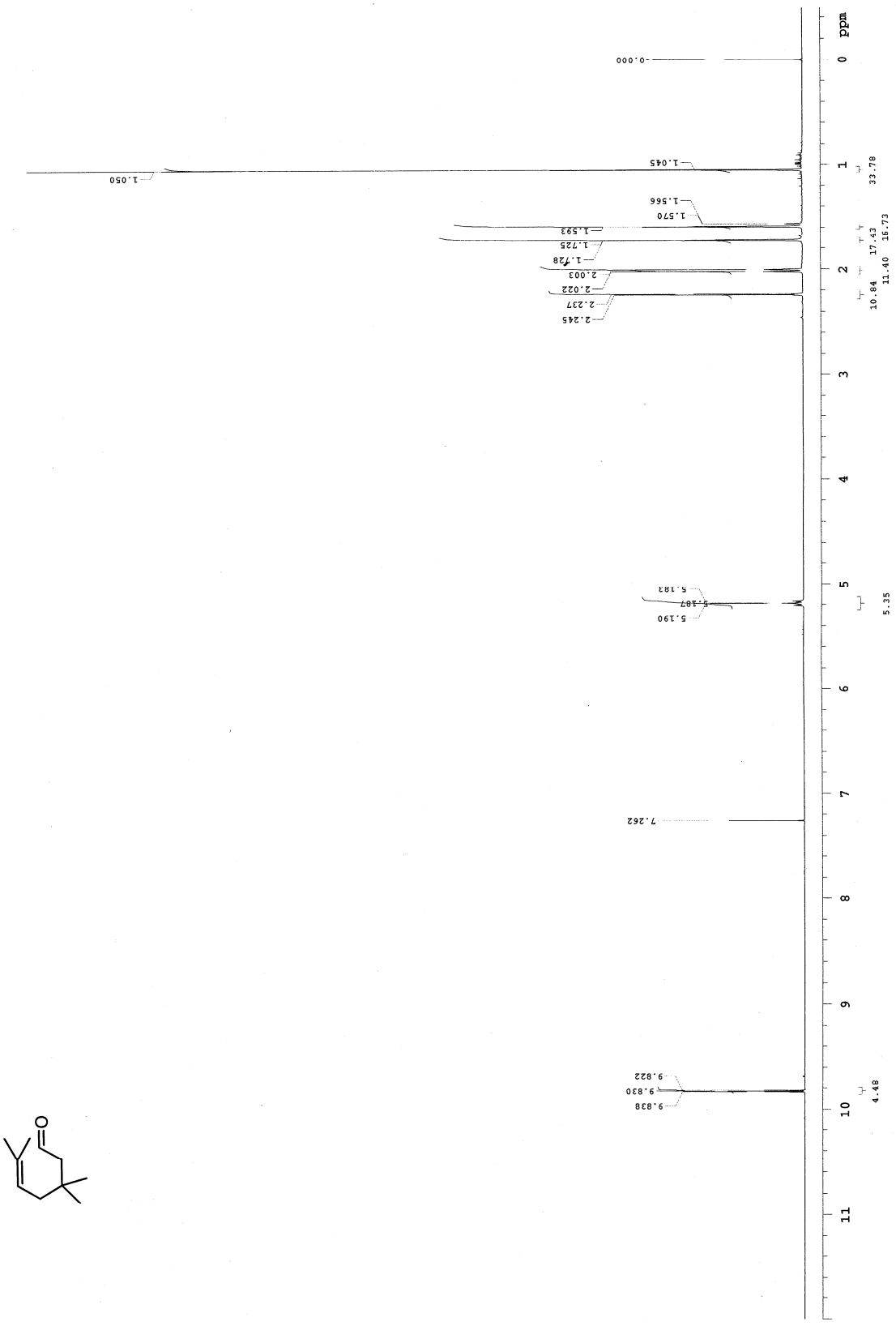
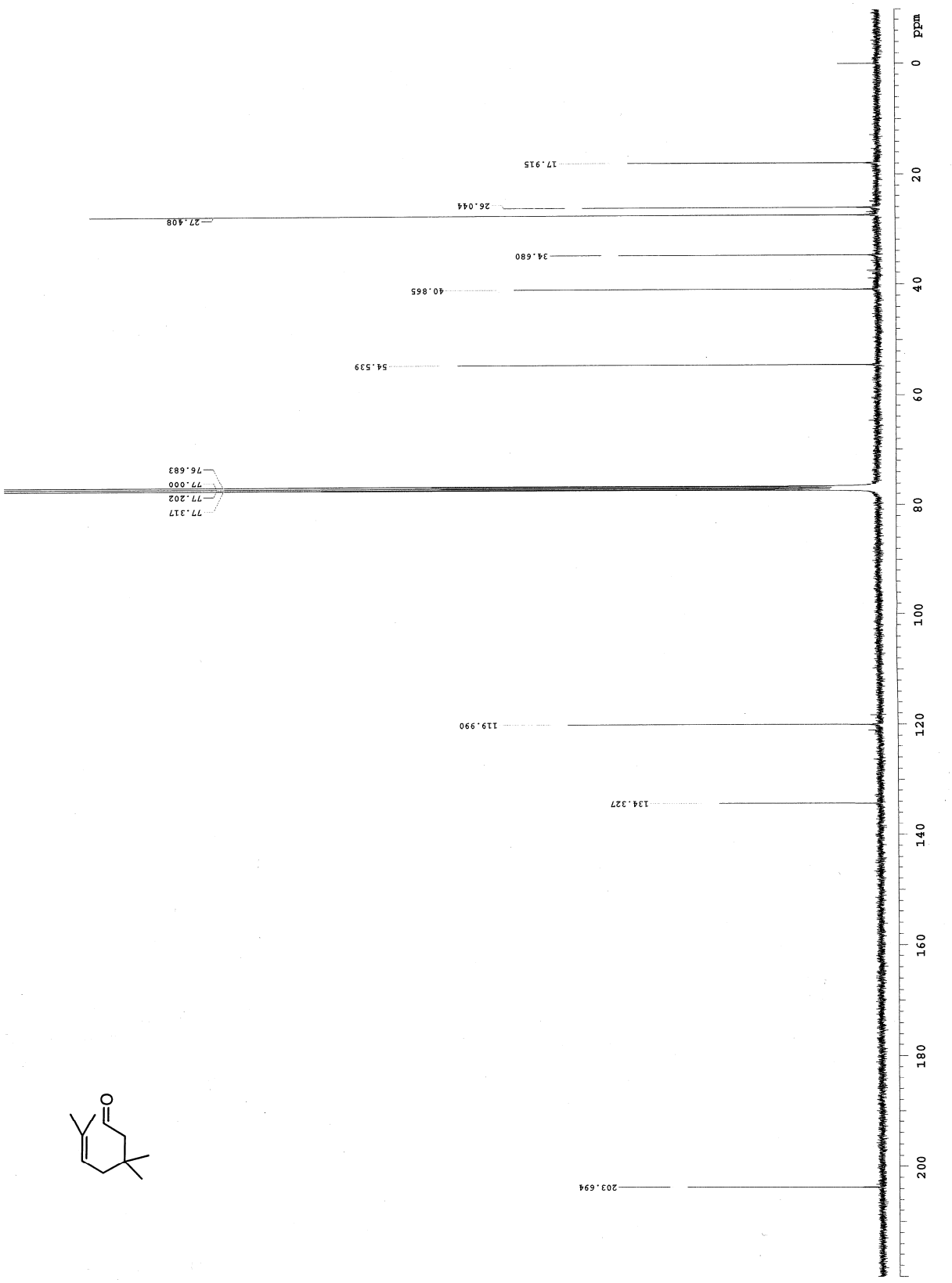
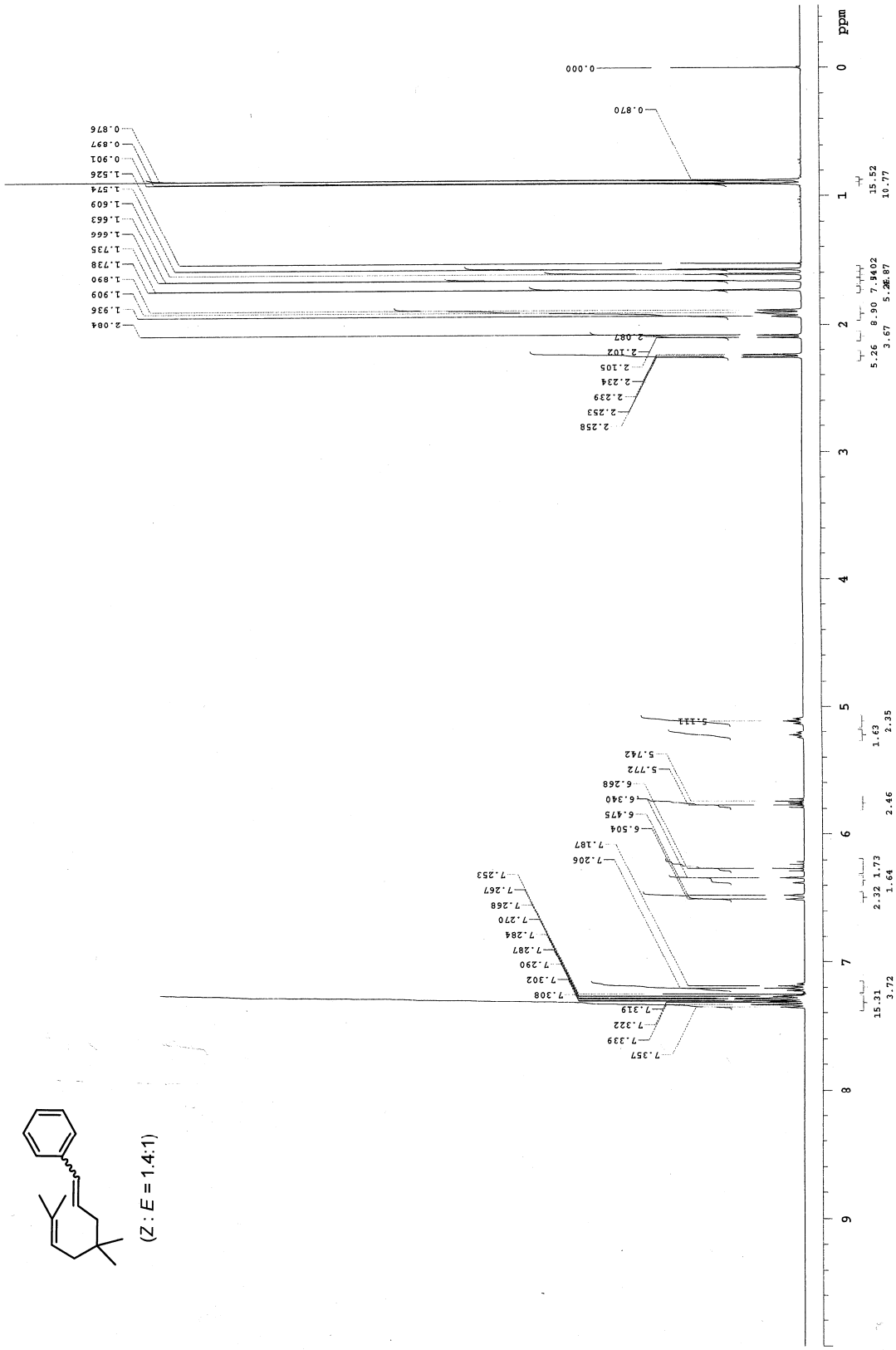
1
2
3
4
5
6
7
8
9
3.785
6.813
6.819
6.830
6.836
7.380
7.386
7.397
7.402
46.33
27.75
25.92
OMe
S-S
MeO

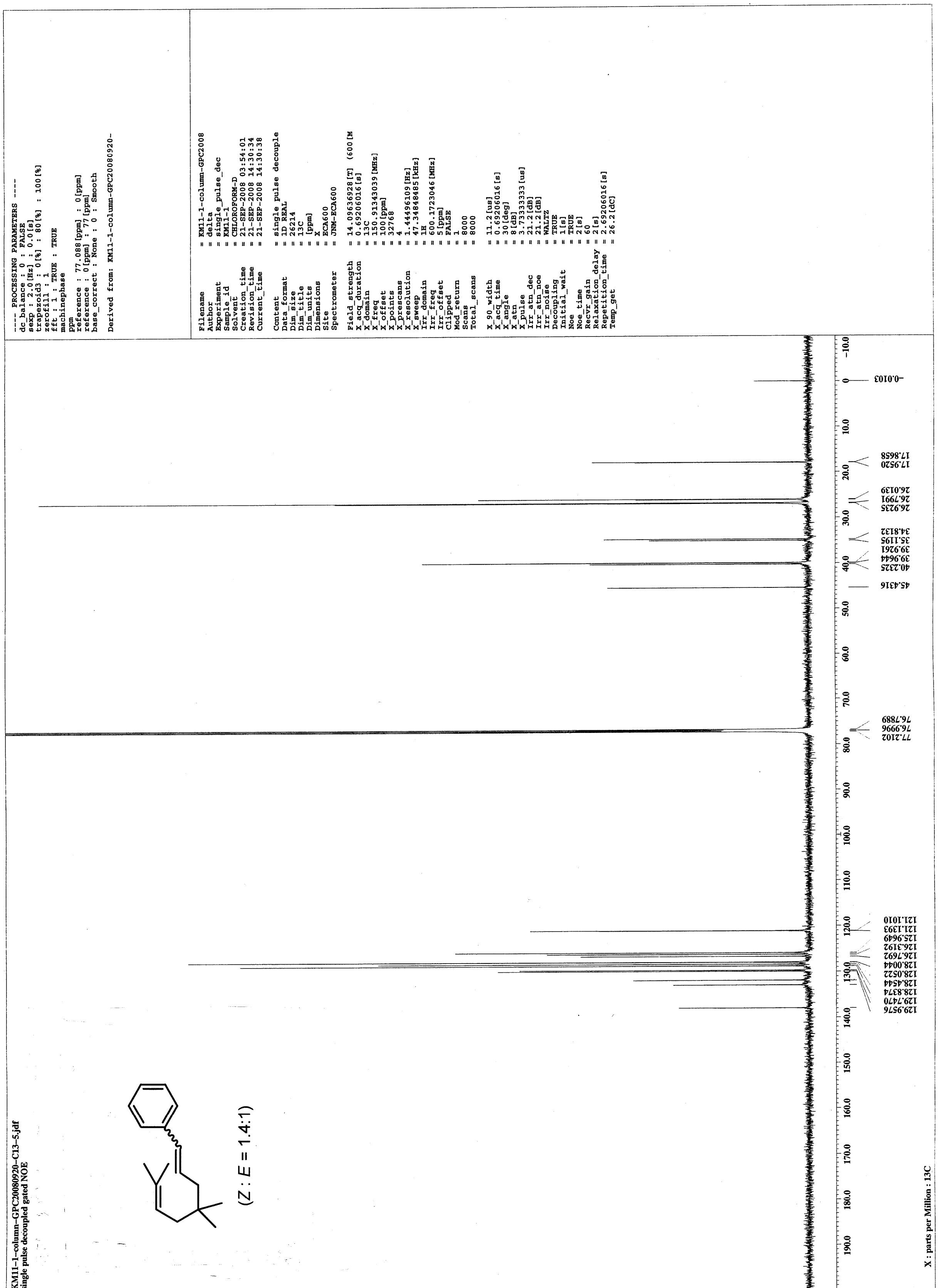

55.332
76.683
77.000
77.317
114.591
128.416
132.625
159.895
ppm
0
20
40
60
80
100
120
140
160
180
OMe
S-S
MeO

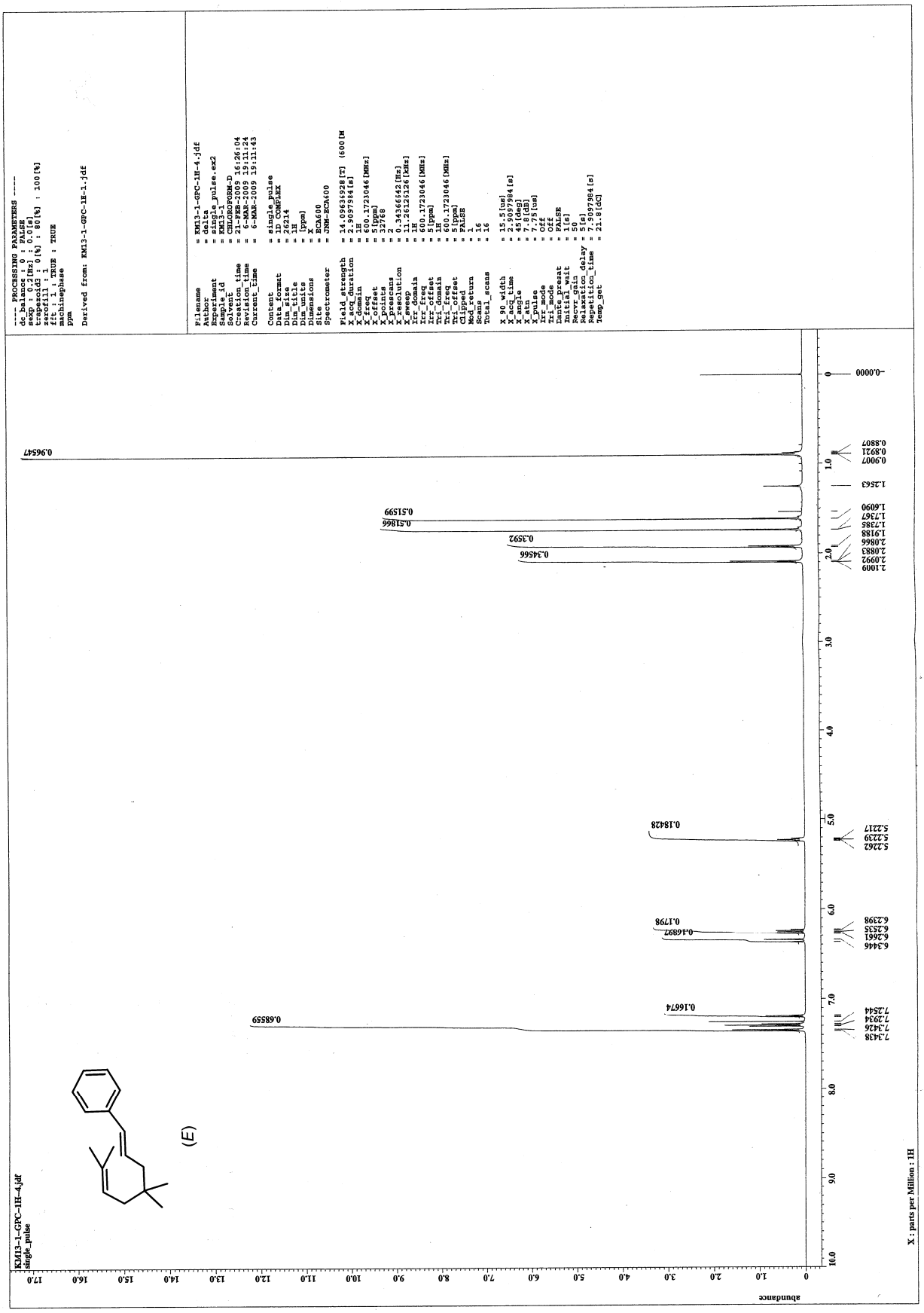

ppm
0.000
1.045
1.050
1.566
1.570
1.593
1.725
1.728
2.003
2.022
2.237
2.245
5.183
5.187
5.190
7.262
9.822
9.830
9.838
33.78
17.43
16.73
11.40
10.84
5.35
4.48

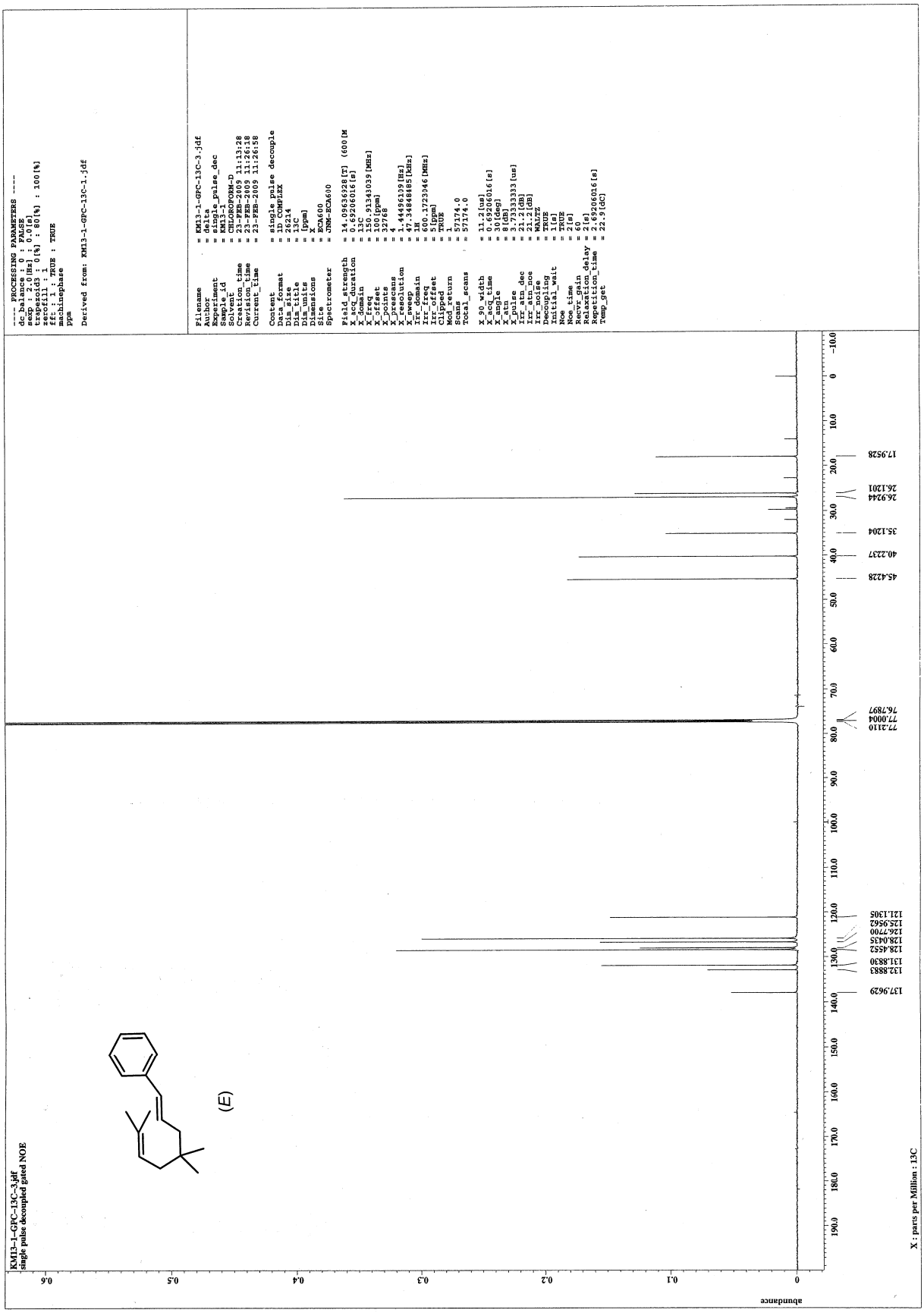

ppm
0
20
40
60
80
100
120
140
160
180
200
17.915
26.044
27.408
34.680
40.865
54.539
76.683
77.000
77.202
77.317
119.990
134.327
203.694

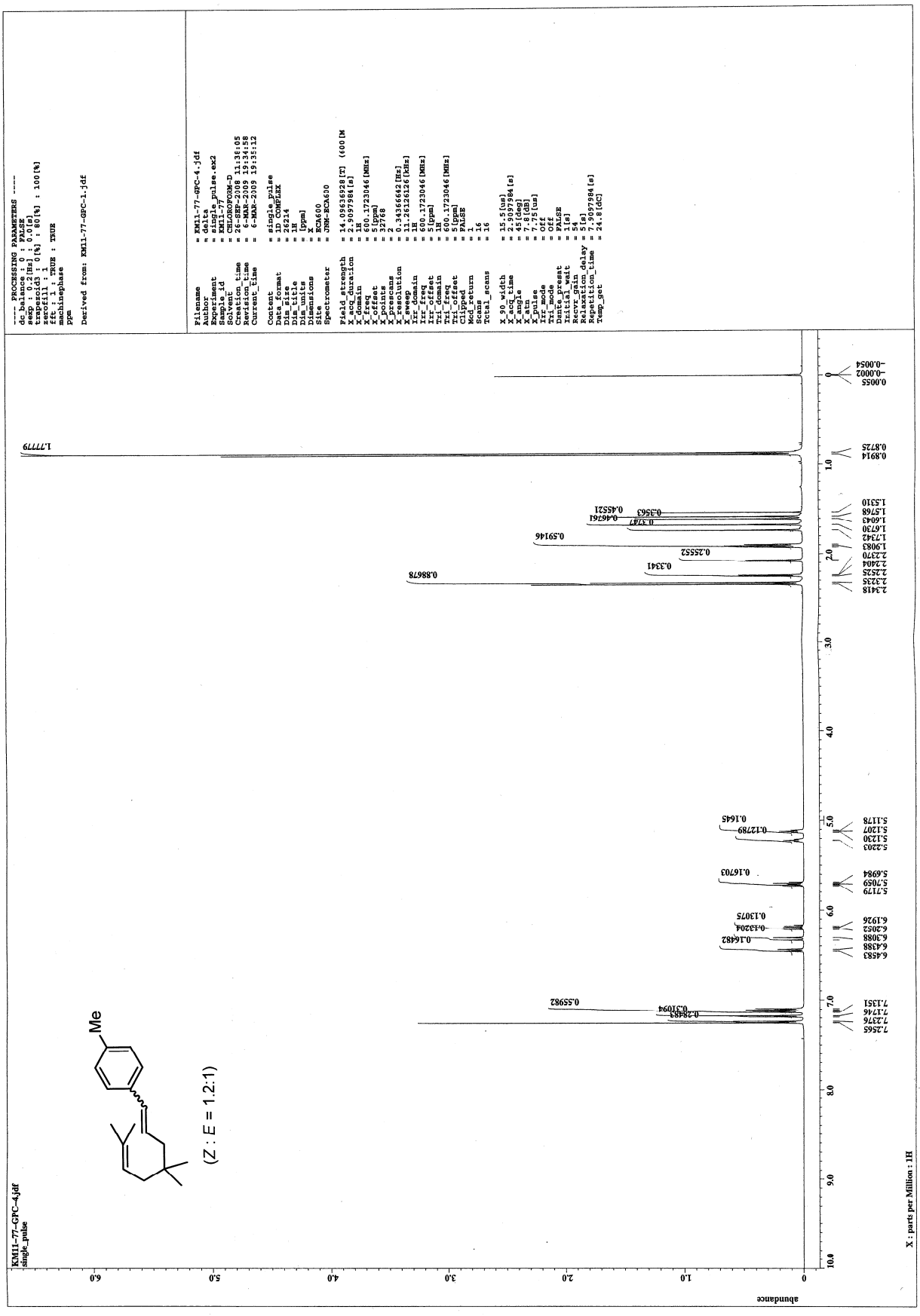

ppm
0.000
0.870
0.876
0.897
0.901
1.526
1.574
1.609
1.663
1.666
1.735
1.738
1.890
1.909
1.936
2.084
2.087
2.102
2.105
2.234
2.239
2.253
2.258
5.111
5.742
5.772
6.268
6.340
6.475
6.504
7.187
7.206
7.253
7.267
7.268
7.270
7.284
7.287
7.290
7.302
7.308
7.319
7.322
7.339
7.357
15.52
10.77
8.90
5.26
3.67
1.63
2.35
2.46
2.32
1.73
1.64
15.31
3.72

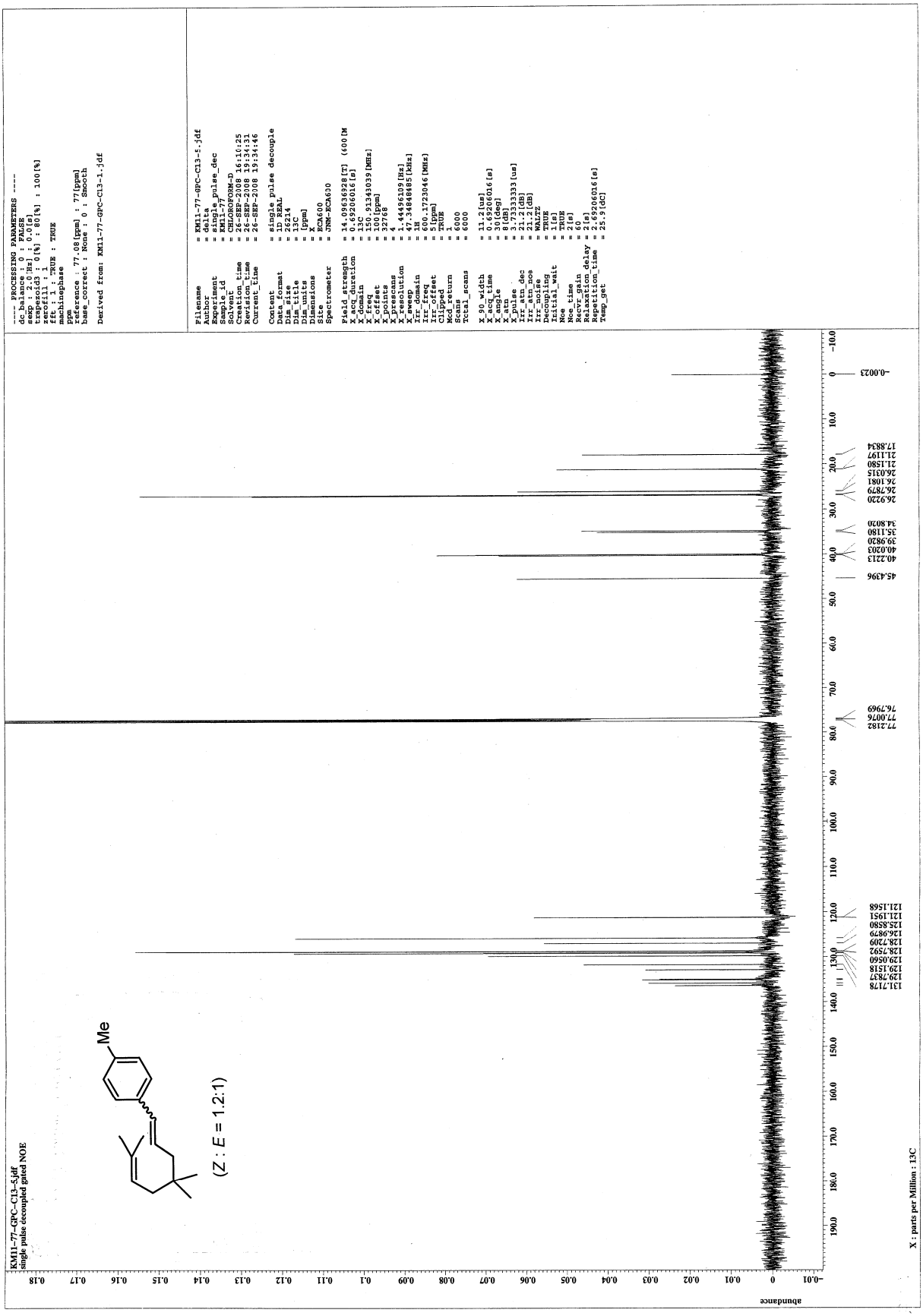
(*Z* : *E* = 1.4:1)

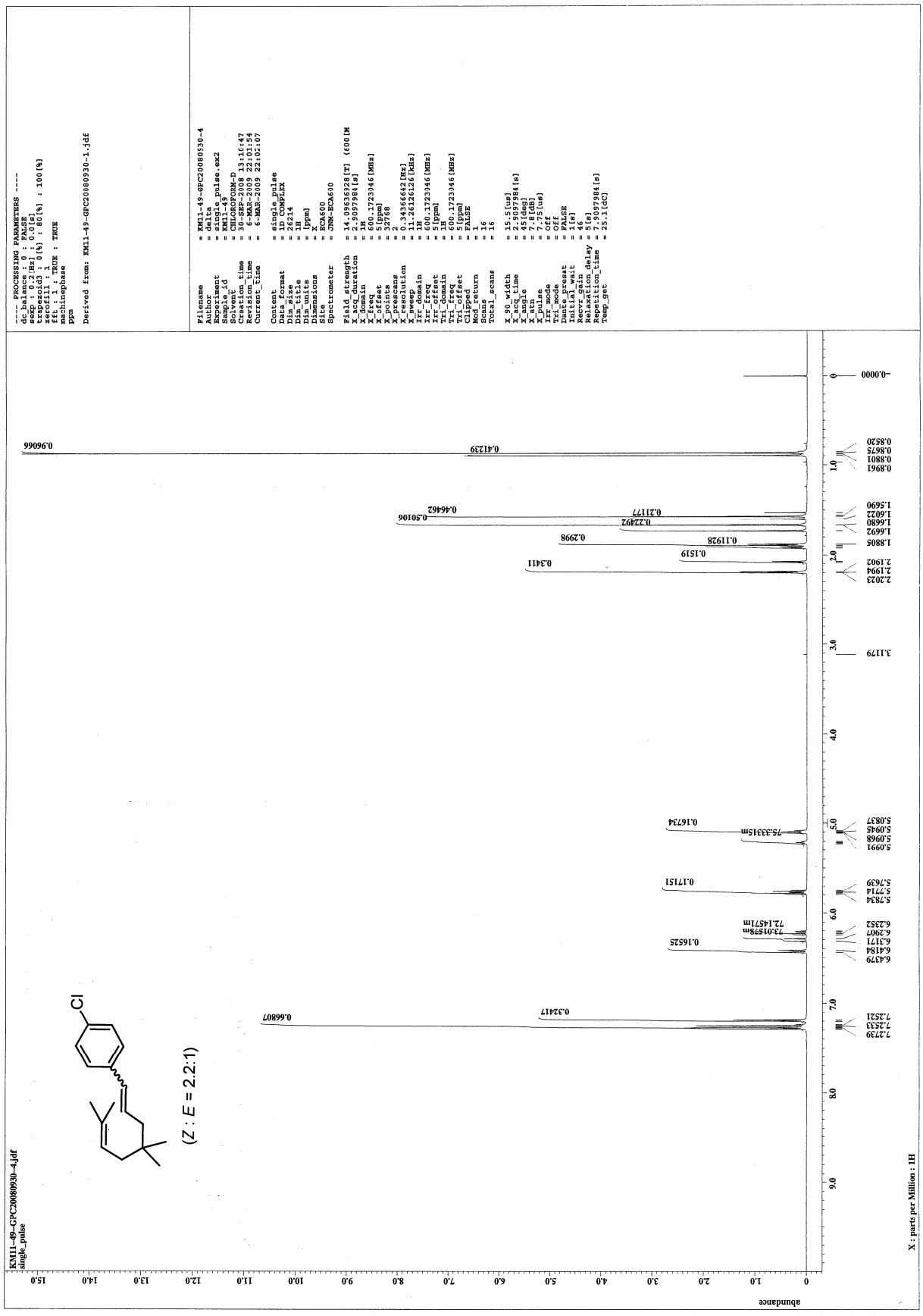


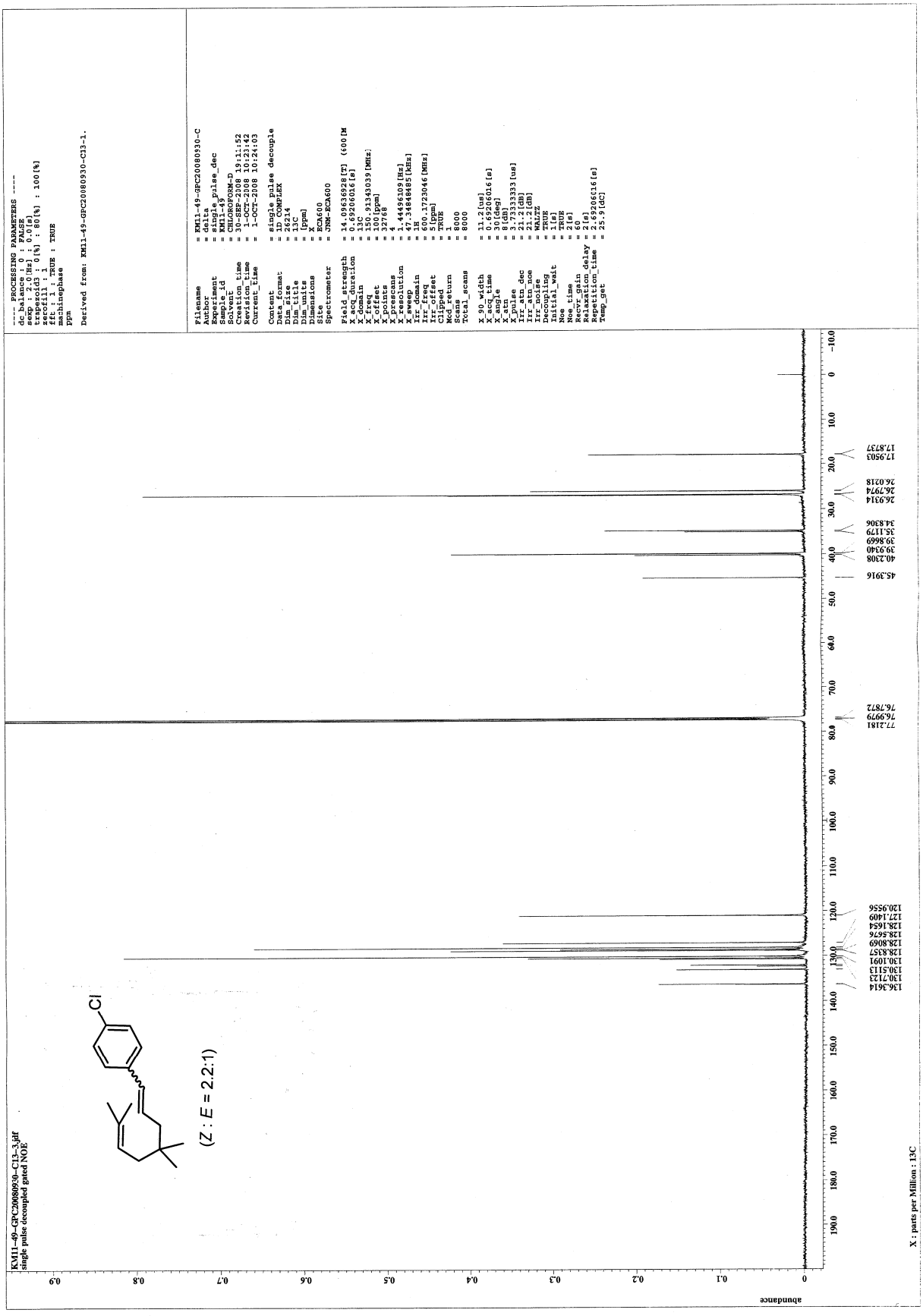

KM13-1-GPC-1H-4.jdf
single_pulse
(E)
X : parts per Million : 1H
abundance
0.96547
0.51866
0.51599
0.35920
0.34566
0.18428
0.16892
0.16674
0.68559
-0.0000

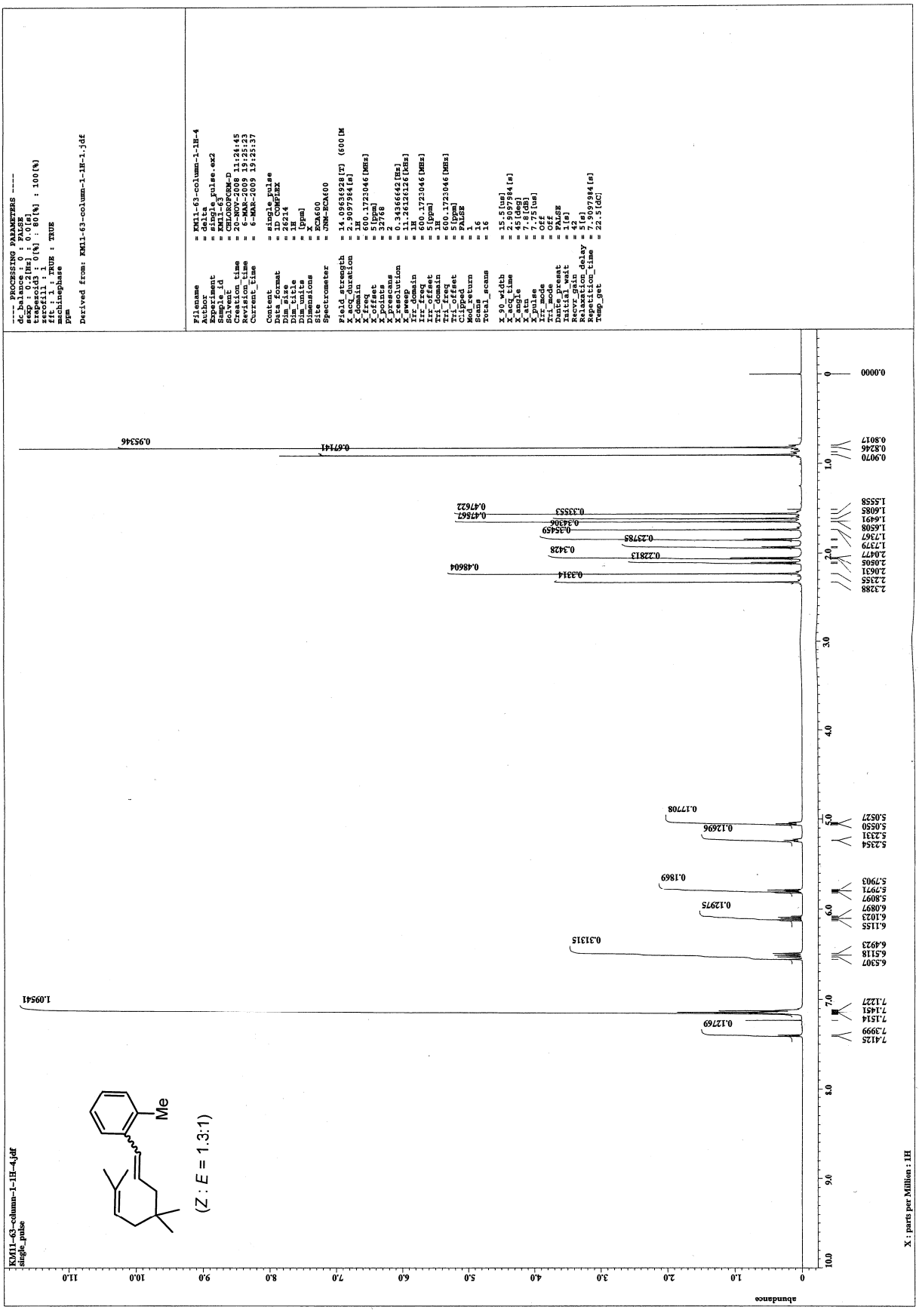

KM13-1-GPC-13C-3.jdf
single pulse decoupled gated NOE
(E)
abundance
X : parts per Million : 13C
17.9528
26.9244
26.1201
35.1204
40.2237
45.4228
77.3110
77.0004
76.7897
121.1305
125.9562
126.7700
128.0435
128.4552
131.8830
132.8883
137.9629

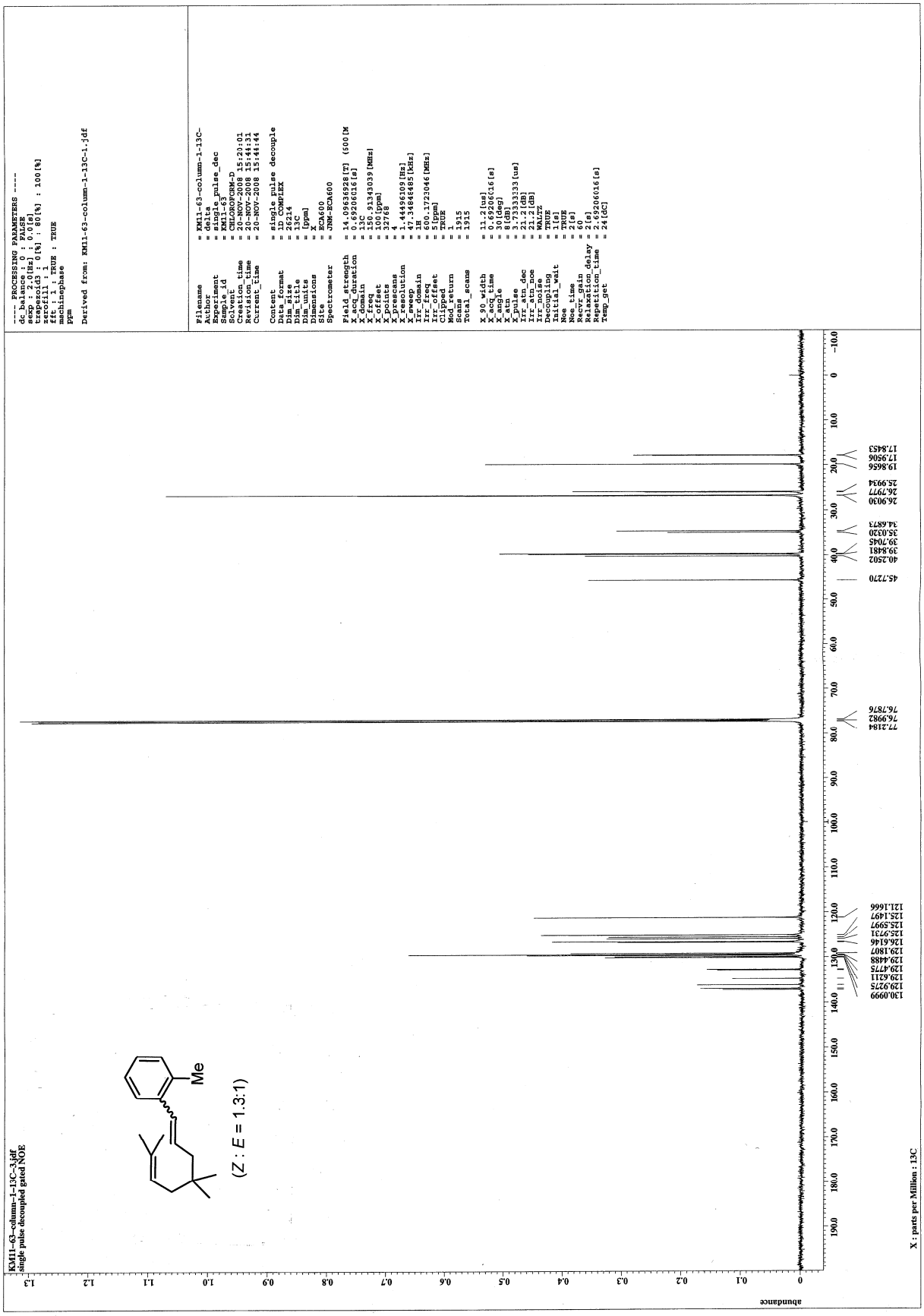

Me
(Z : E = 1.2:1)
KM11-77-GPC-4.jdf
single_pulse
abundance
X : parts per Million : 1H

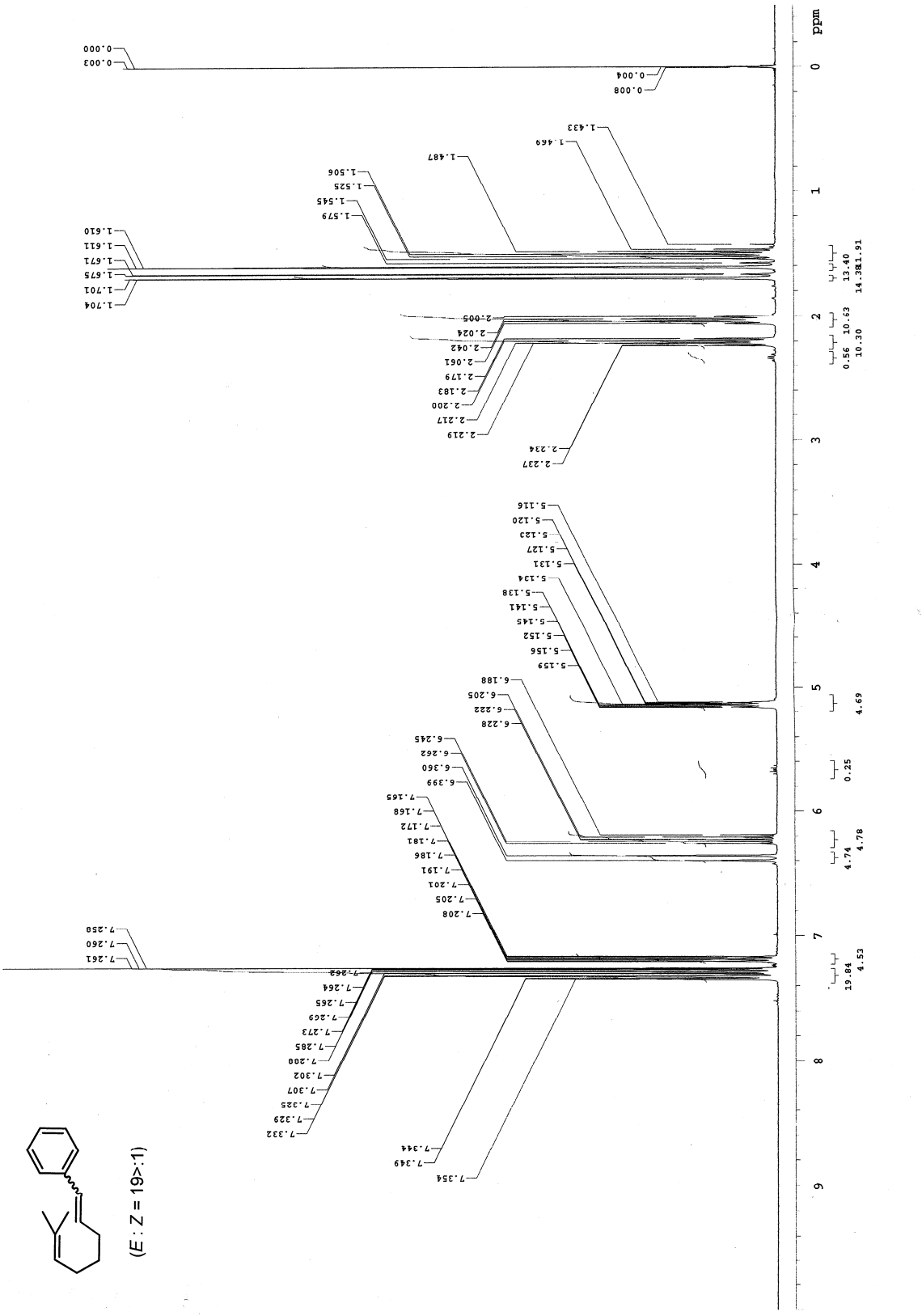

KM11-77-GPC-C13-5.jdf
single pulse decoupled gated NOE
Me
(Z : E = 1.2:1)
X : parts per Million : 13C
abundance
77.2182
77.0076
76.7969
45.4396
40.2213
40.0203
39.9820
35.1180
34.8020
26.9220
26.7879
26.1081
26.0315
21.1580
21.1197
17.8834
-0.0023
131.7178
129.7837
129.1518
128.9560
128.7592
128.7209
126.9879
125.8580
121.1951
121.1568

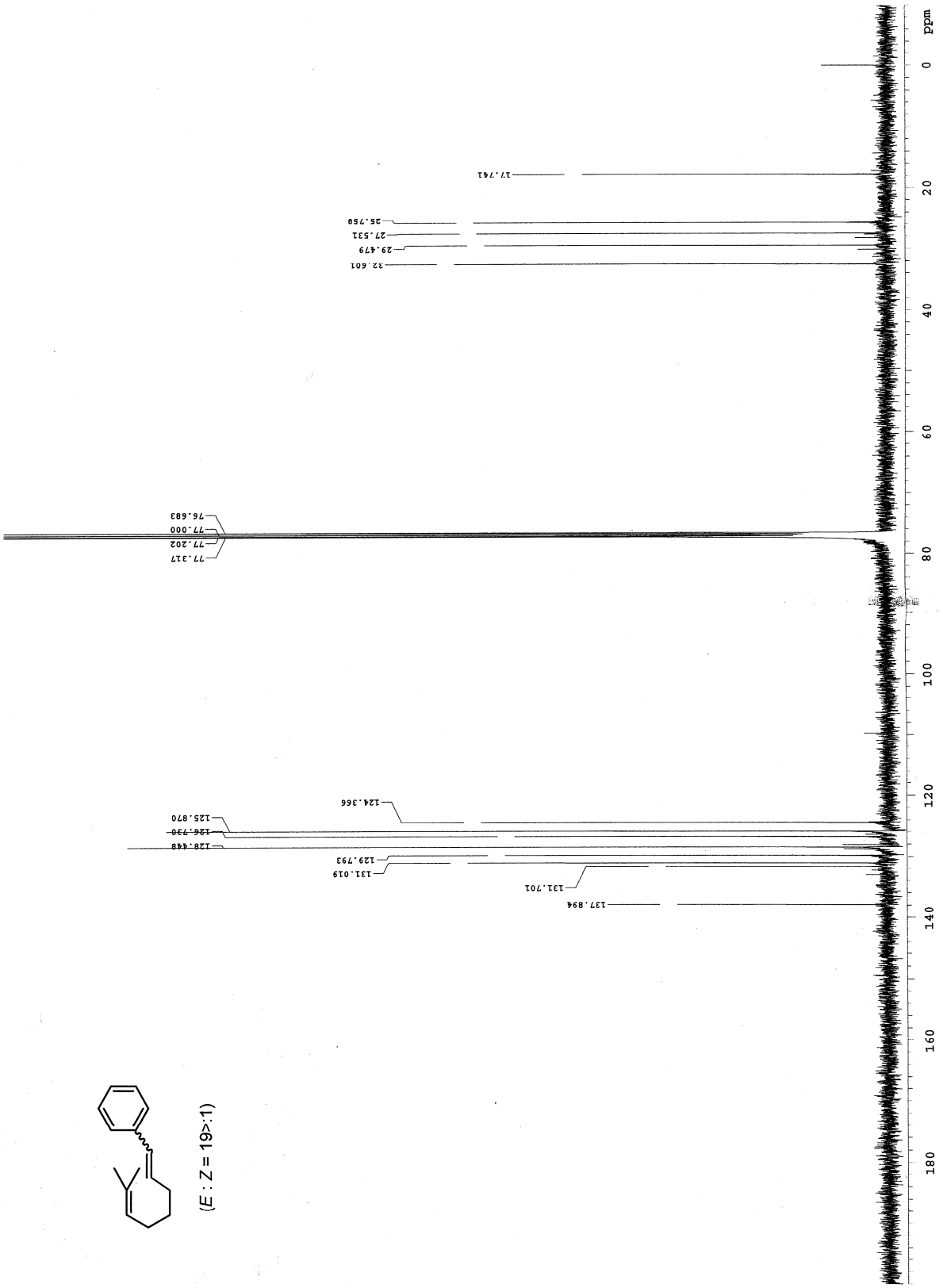

(Z : E = 2.2:1)
Cl
KM11-49-GPC20080930-4.jdf
single_pulse
abundance
X : parts per Million : 1H


KM11-49-GPC20080930-C13-3.jnf
single pulse decoupled gated NOE
Cl
(Z : E = 2.2:1)
abundance
X : parts per Million : 13C
17.9503
17.8737
26.9314
26.7974
26.0218
34.8306
35.1179
39.8669
39.9340
40.2308
45.3916
76.9979
76.7872
77.2181
120.9556
127.1409
128.1654
128.5676
128.8069
128.8357
130.1091
130.5115
130.7123
136.3614

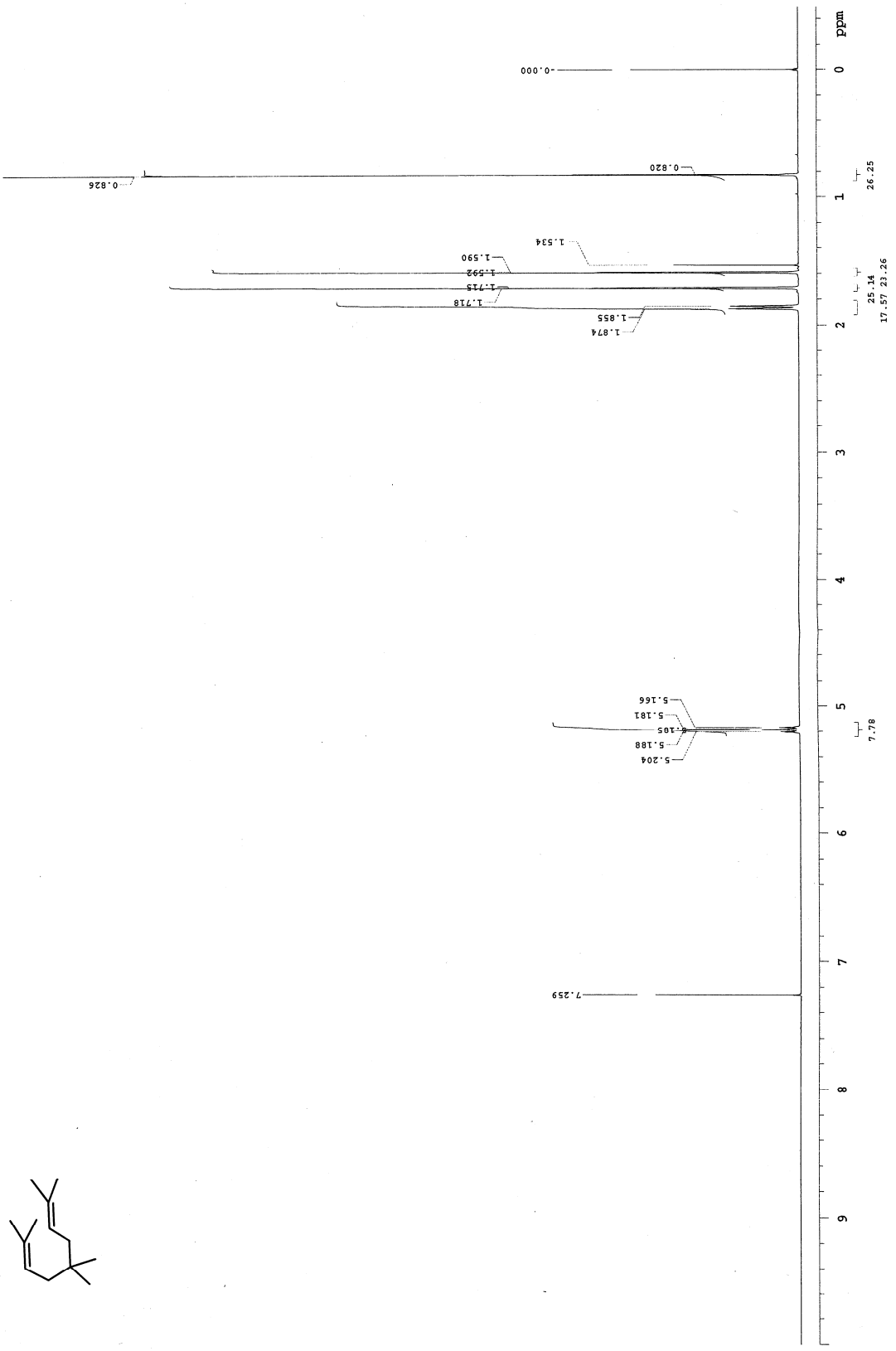

Me
(Z : E = 1.3:1)
KM11-63-column-1-1H-4.jdf
single_pulse
X : parts per Million : 1H
abundance

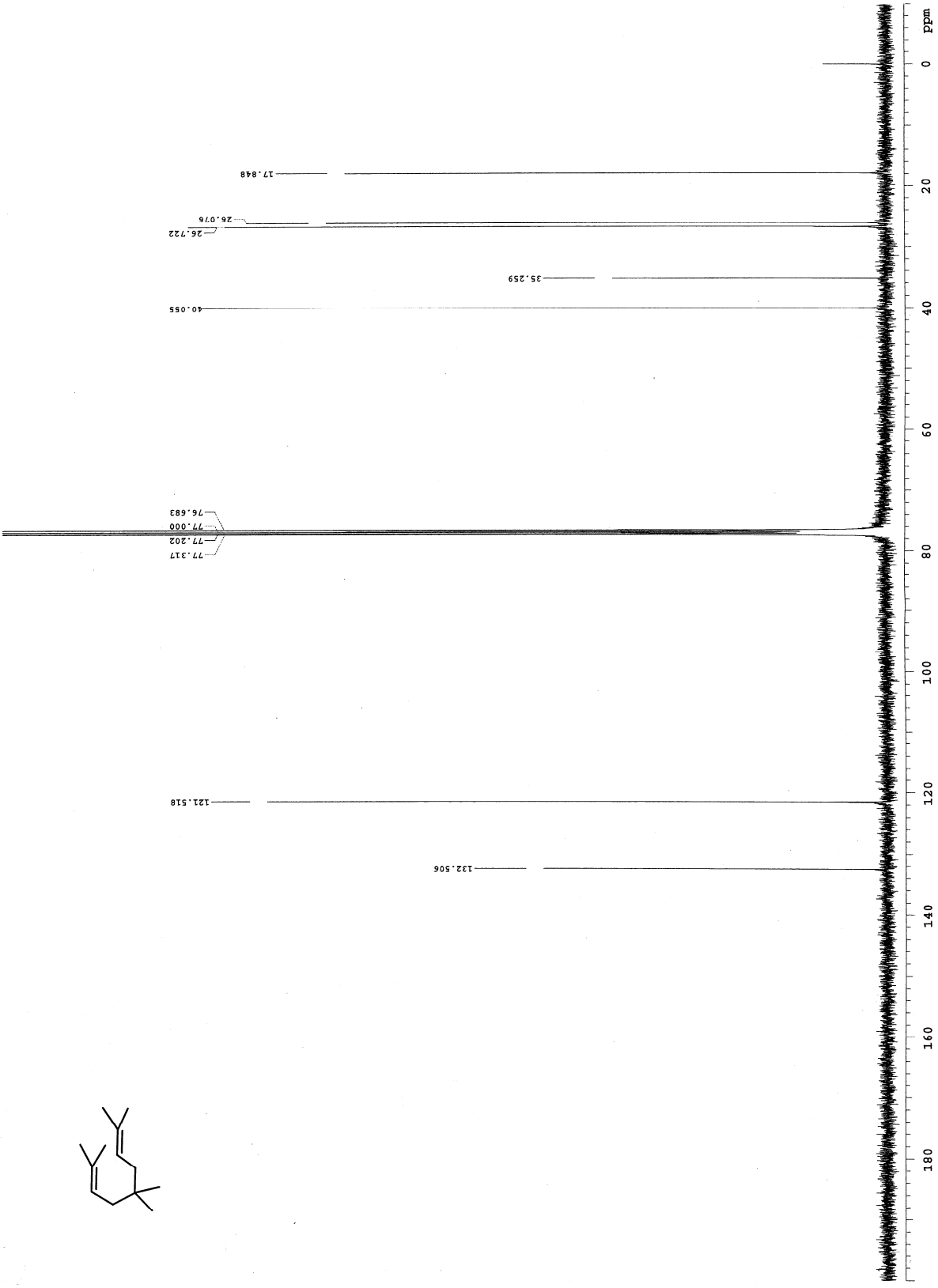

KM11-63-column-1-13C-3.jdf
single pulse decoupled gated NOE
Me
(Z : E = 1.3:1)
X : parts per Million : 13C
abundance
45.7270
77.2184
76.9982
76.7876
40.2502
39.8481
39.7045
35.0320
34.6873
26.9030
26.7977
25.9934
19.8656
17.9506
17.8453
130.0999
129.9275
129.6211
129.4775
129.1807
128.4488
126.6146
125.9731
125.5997
125.1497
121.1666

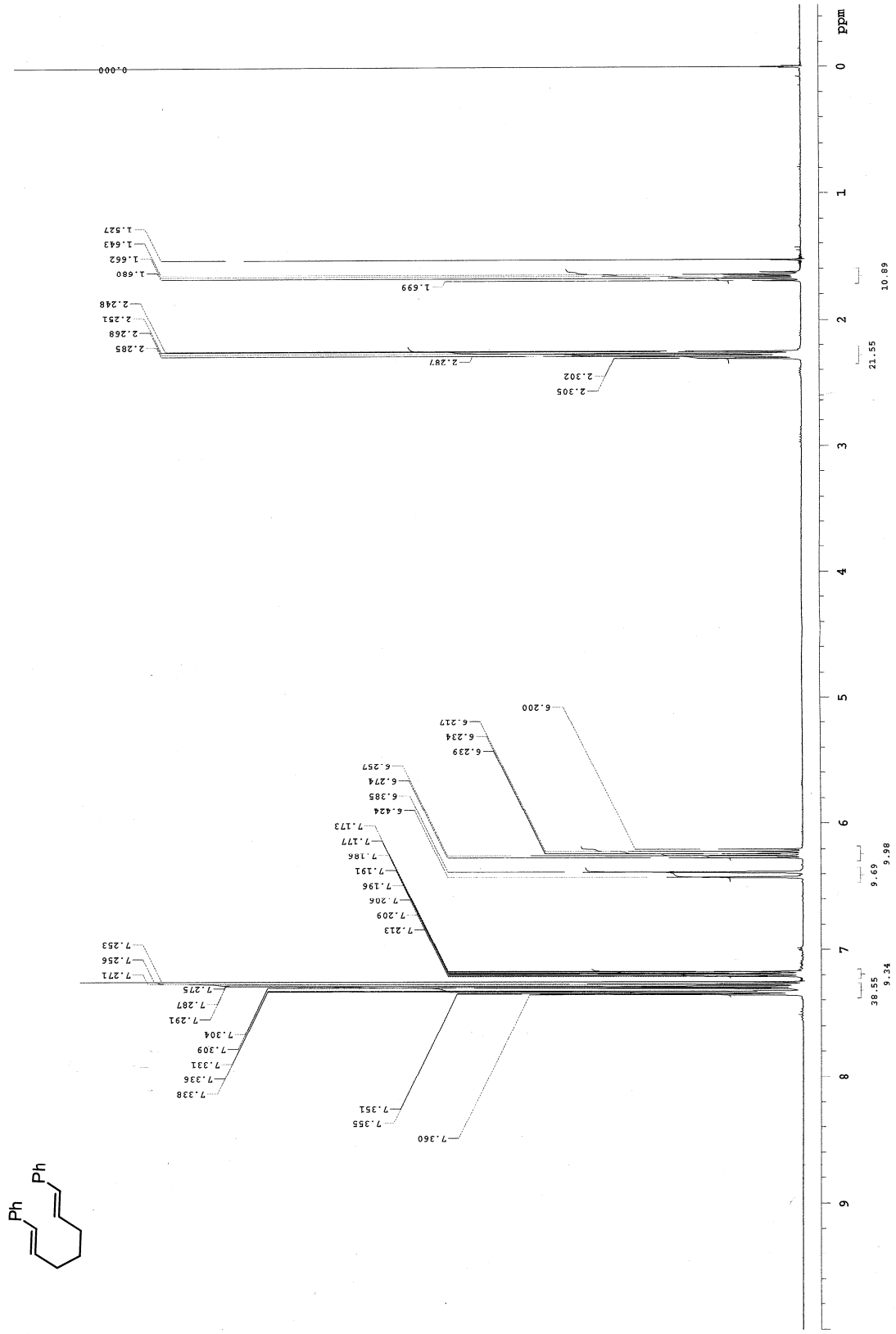

(E : Z = 19>:1)

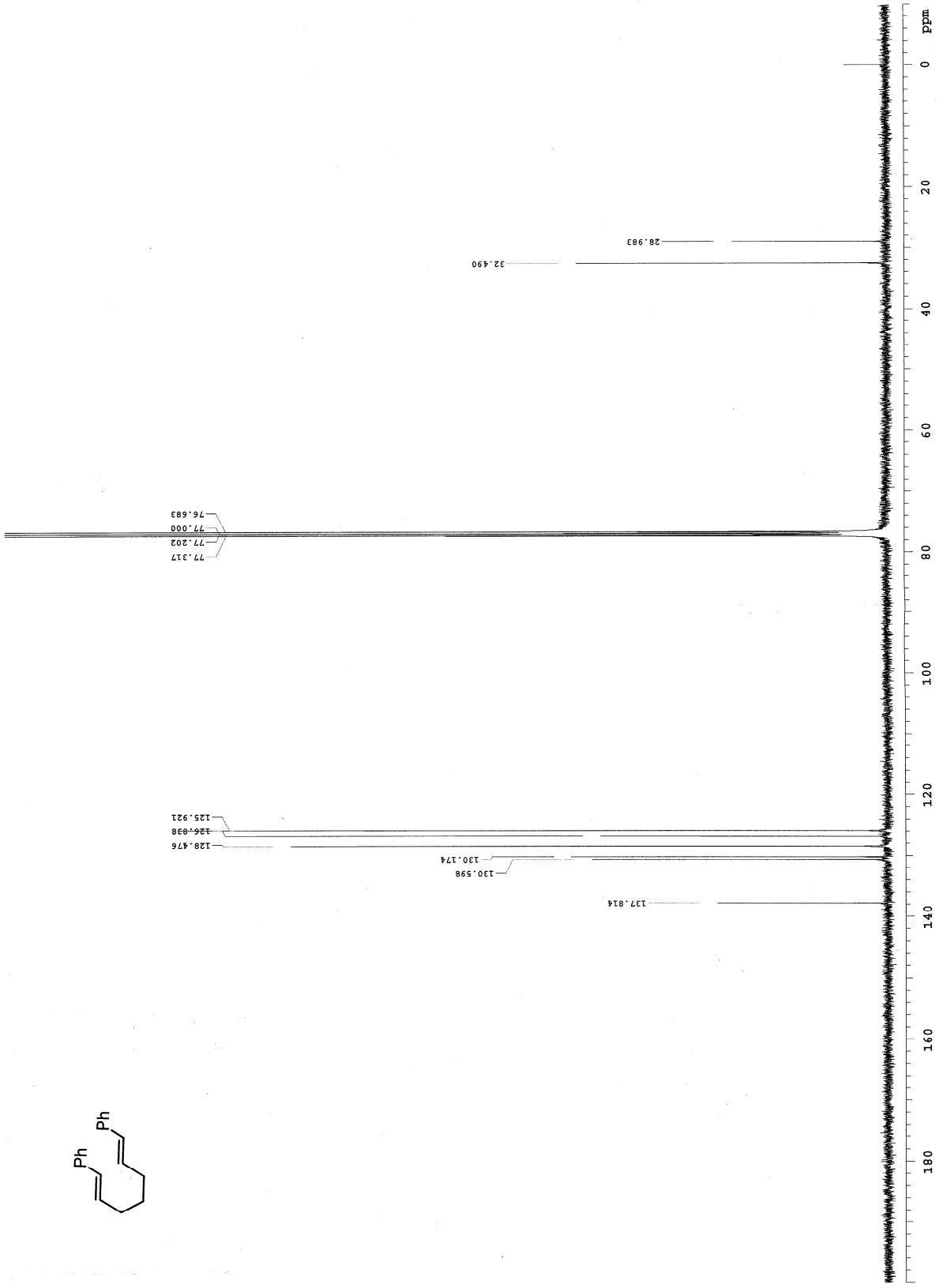

ppm
0
20
40
60
80
100
120
140
160
180
17.741
25.758
27.531
29.479
32.601
76.683
77.000
77.202
77.317
124.366
125.870
126.730
128.448
129.793
131.019
131.701
137.894

(*E* : *Z* = 19>:1)


ppm
0
1
2
3
4
5
6
7
8
9
0.000
0.820
0.826
1.534
1.590
1.592
1.715
1.718
1.855
1.874
5.166
5.181
5.185
5.188
5.204
7.259
26.25
25.14
17.57
23.26
7.78


ppm
0
20
40
60
80
100
120
140
160
180
17.848
26.076
26.722
35.259
40.055
76.683
77.000
77.202
77.317
121.518
132.506


0.000
1.527
1.643
1.662
1.680
1.699
2.248
2.251
2.268
2.285
2.287
2.302
2.305
6.200
6.217
6.234
6.239
6.257
6.274
6.385
6.424
7.173
7.177
7.186
7.191
7.196
7.206
7.209
7.213
7.253
7.256
7.271
7.275
7.287
7.291
7.304
7.309
7.331
7.336
7.338
7.351
7.355
7.360
Ph
Ph
ppm
0
1
2
3
4
5
6
7
8
9
10.89
21.55
9.98
9.69
9.34
38.55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32.490
76.683
77.000
77.202
77.317
125.921
126.038
128.476
130.174
130.598
137.814
ppm
0
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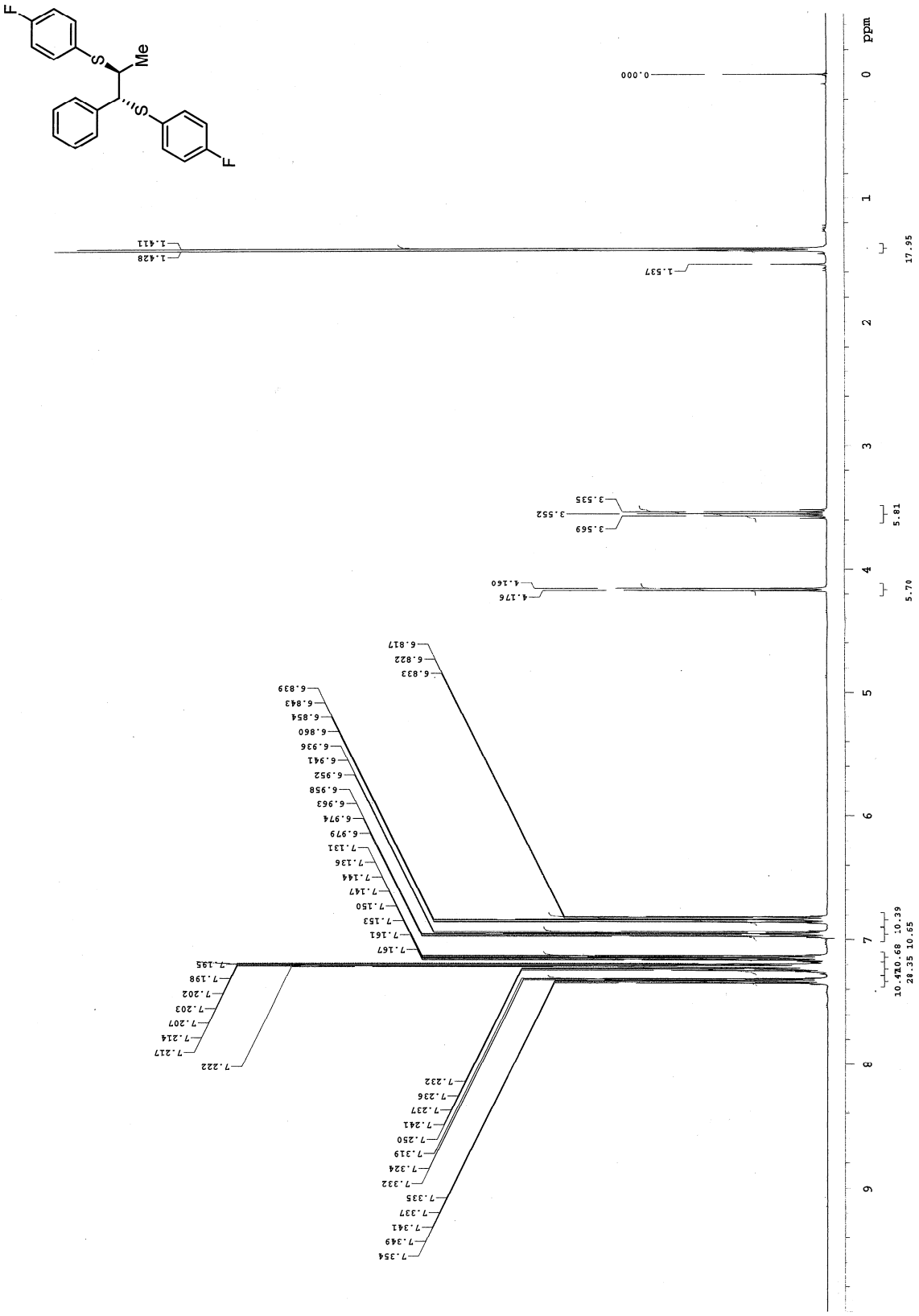
40
60
80
100
120
140
160
180
Ph
Ph


F
S
Me
S
F
0.000
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1.428
1.537
3.535
3.552
3.569
4.160
4.176
6.817
6.822
6.833
6.839
6.843
6.854
6.860
6.936
6.941
6.952
6.958
6.963
6.974
6.979
7.131
7.136
7.144
7.147
7.150
7.153
7.161
7.167
7.195
7.198
7.202
7.203
7.207
7.214
7.217
7.222
7.232
7.236
7.237
7.241
7.250
7.319
7.324
7.332
7.335
7.337
7.341
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7.354
ppm
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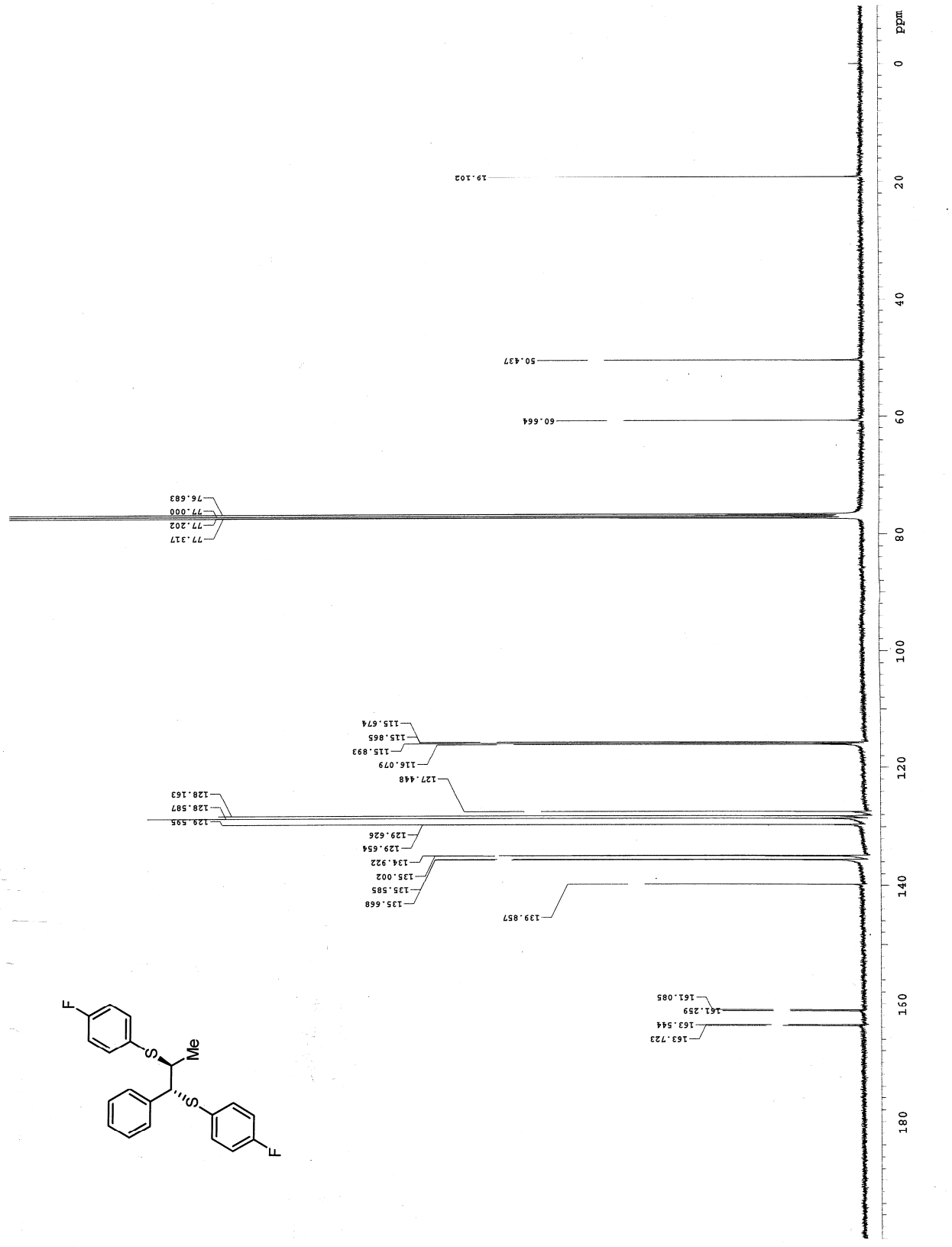
5.70
10.39
10.68
10.41
28.35
10.65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60
80
100
120
140
160
180
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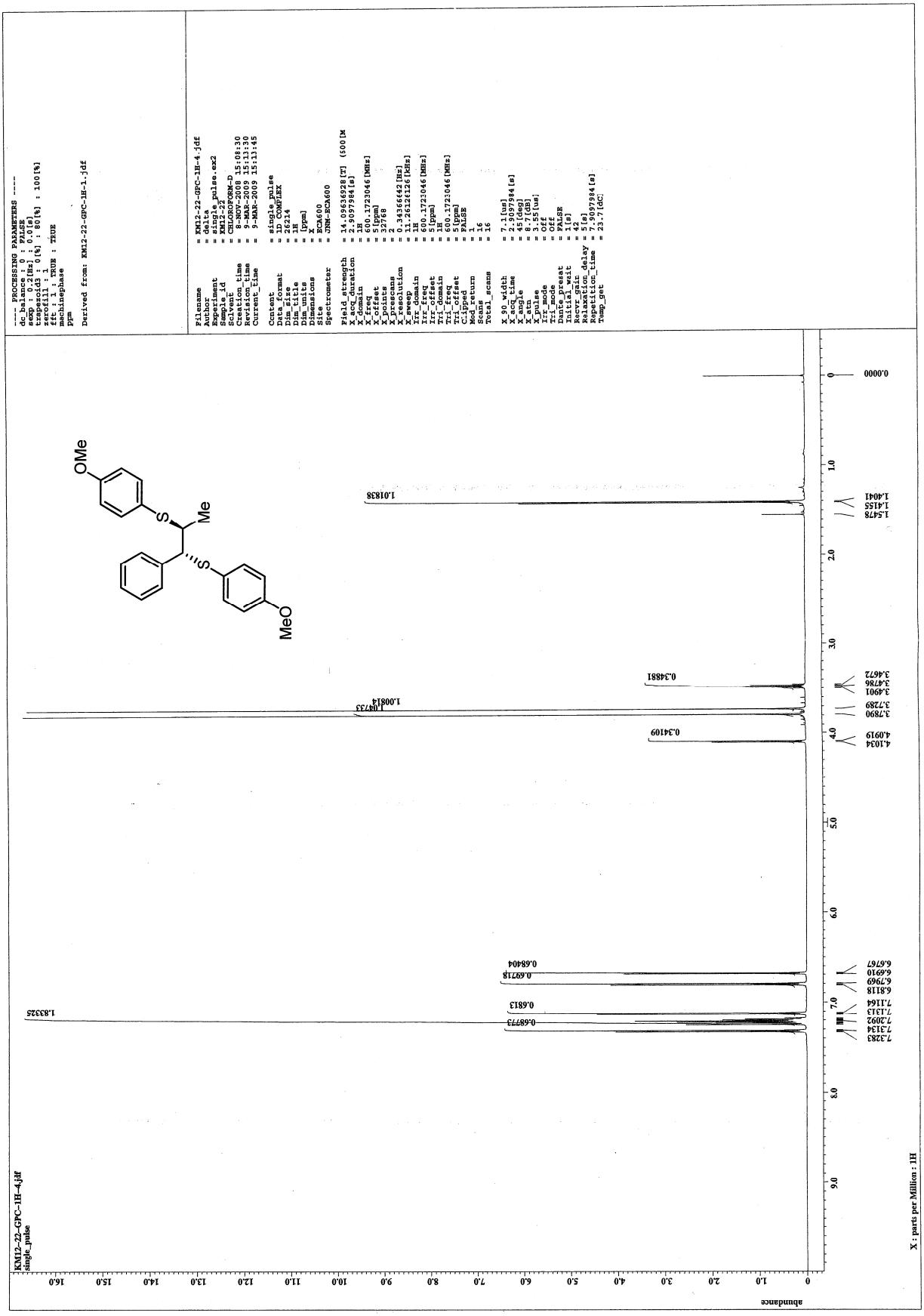
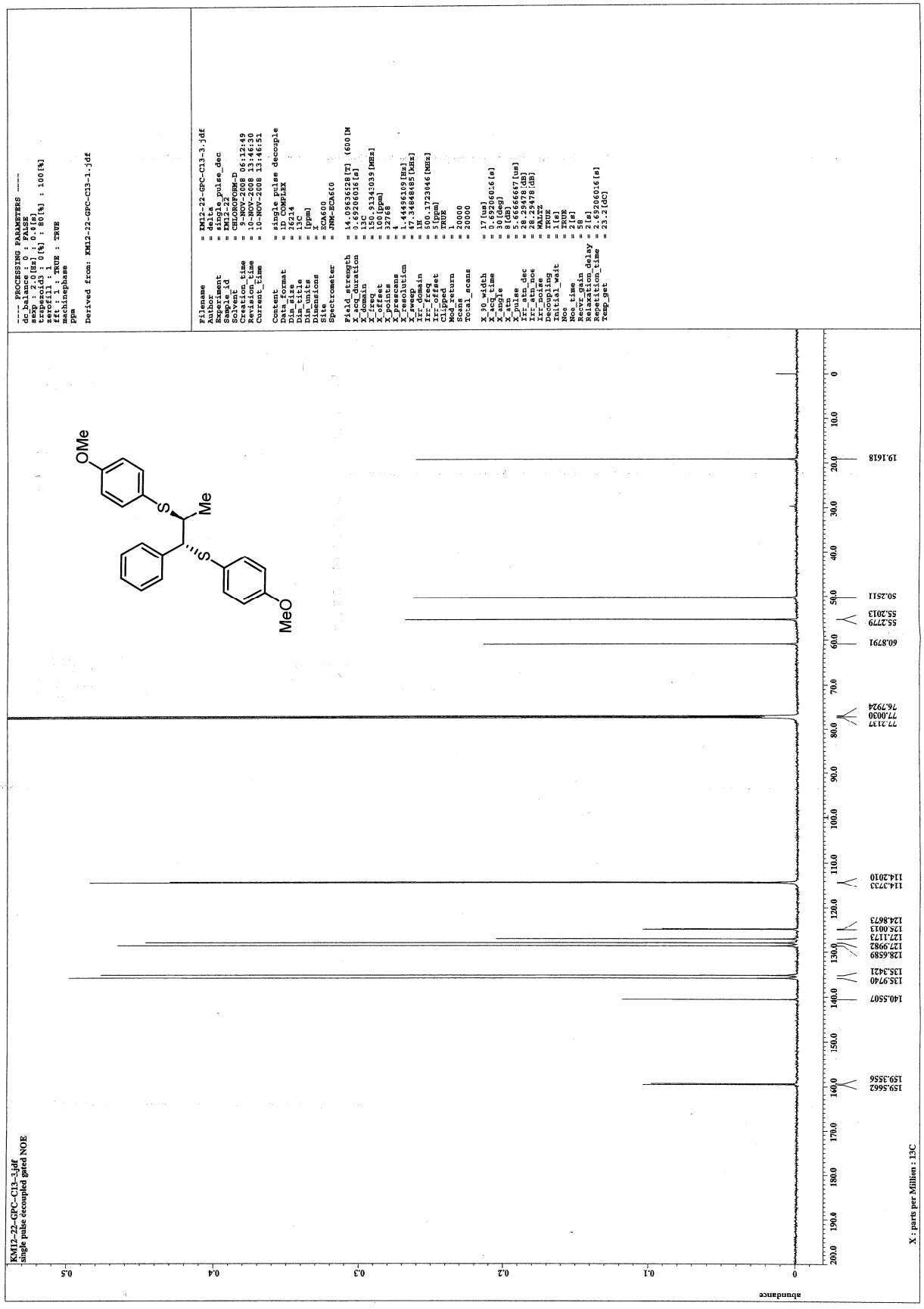
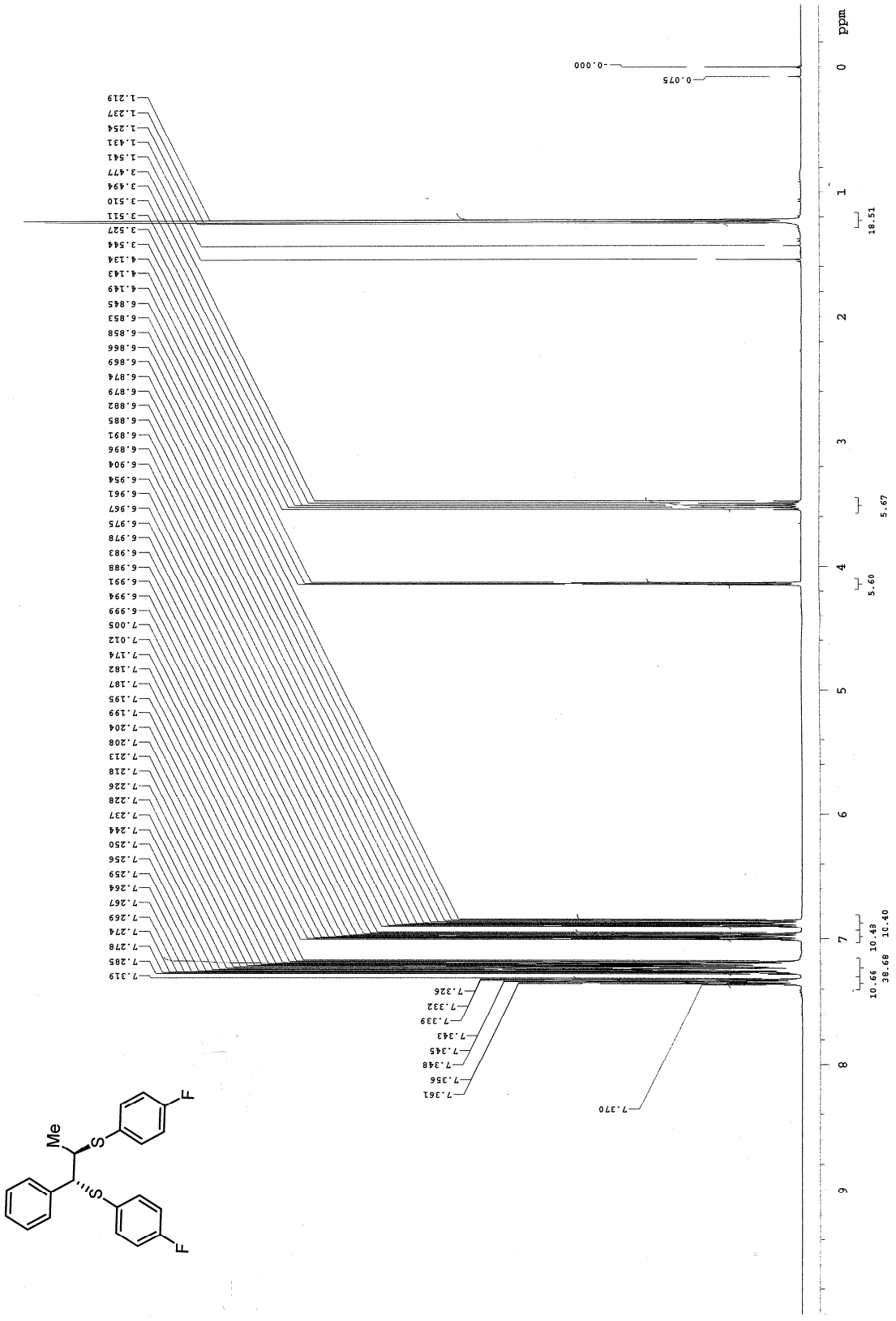
50.437
60.664
76.683
77.000
77.202
77.317
115.674
115.865
115.893
116.079
127.448
128.163
128.587
129.595
129.626
129.654
134.922
135.002
135.585
135.668
139.857
161.085
161.259
163.544
163.723
F
S
Me
S
F


OMe
Me
MeO
KM12-22-GPC-1H-4.jdf
single_pulse
X : parts per Million : 1H
abundance


OMe
S
Me
S
MeO
KM12-22-GPC-C13-3.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C
abundance
159.5662
159.3556
140.5507
135.9740
135.3421
128.6589
127.9982
127.1173
125.0013
124.8673
114.3733
114.2010
77.3137
77.0030
76.7924
60.8791
55.2779
55.2013
50.2511
19.1618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1.254
1.431
1.541
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3.510
3.511
3.527
3.544
4.134
4.143
4.149
6.845
6.853
6.858
6.866
6.869
6.874
6.879
6.882
6.885
6.891
6.896
6.904
6.954
6.961
6.967
6.975
6.978
6.983
6.988
6.991
6.994
6.999
7.005
7.012
7.174
7.182
7.187
7.195
7.199
7.204
7.208
7.213
7.218
7.226
7.228
7.237
7.244
7.250
7.256
7.259
7.264
7.267
7.269
7.274
7.278
7.285
7.319
7.326
7.332
7.339
7.343
7.345
7.348
7.356
7.361
7.370
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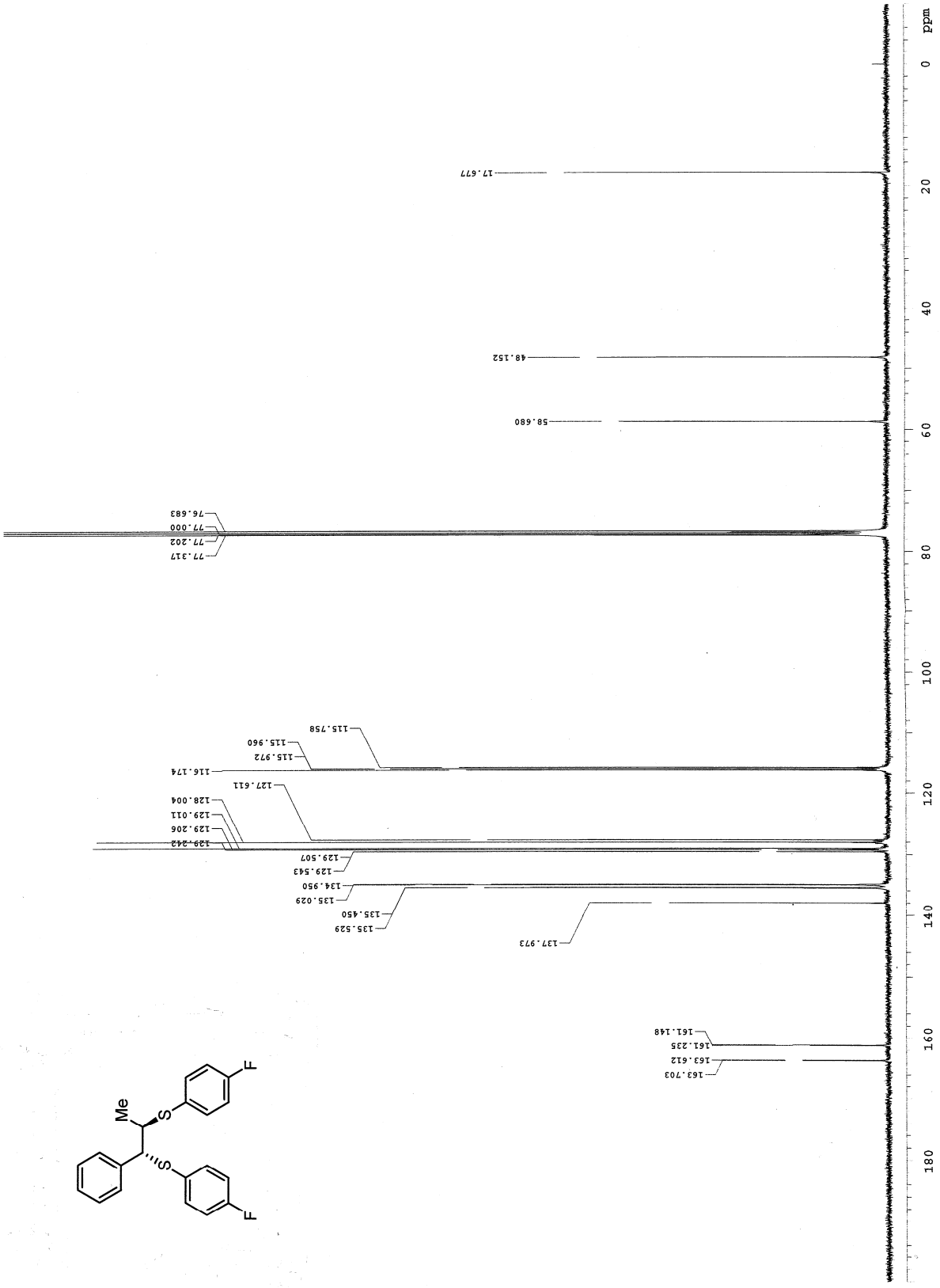
5.67
5.60
10.48
10.40
10.66
38.68
Me
S
S
F
F


ppm
0
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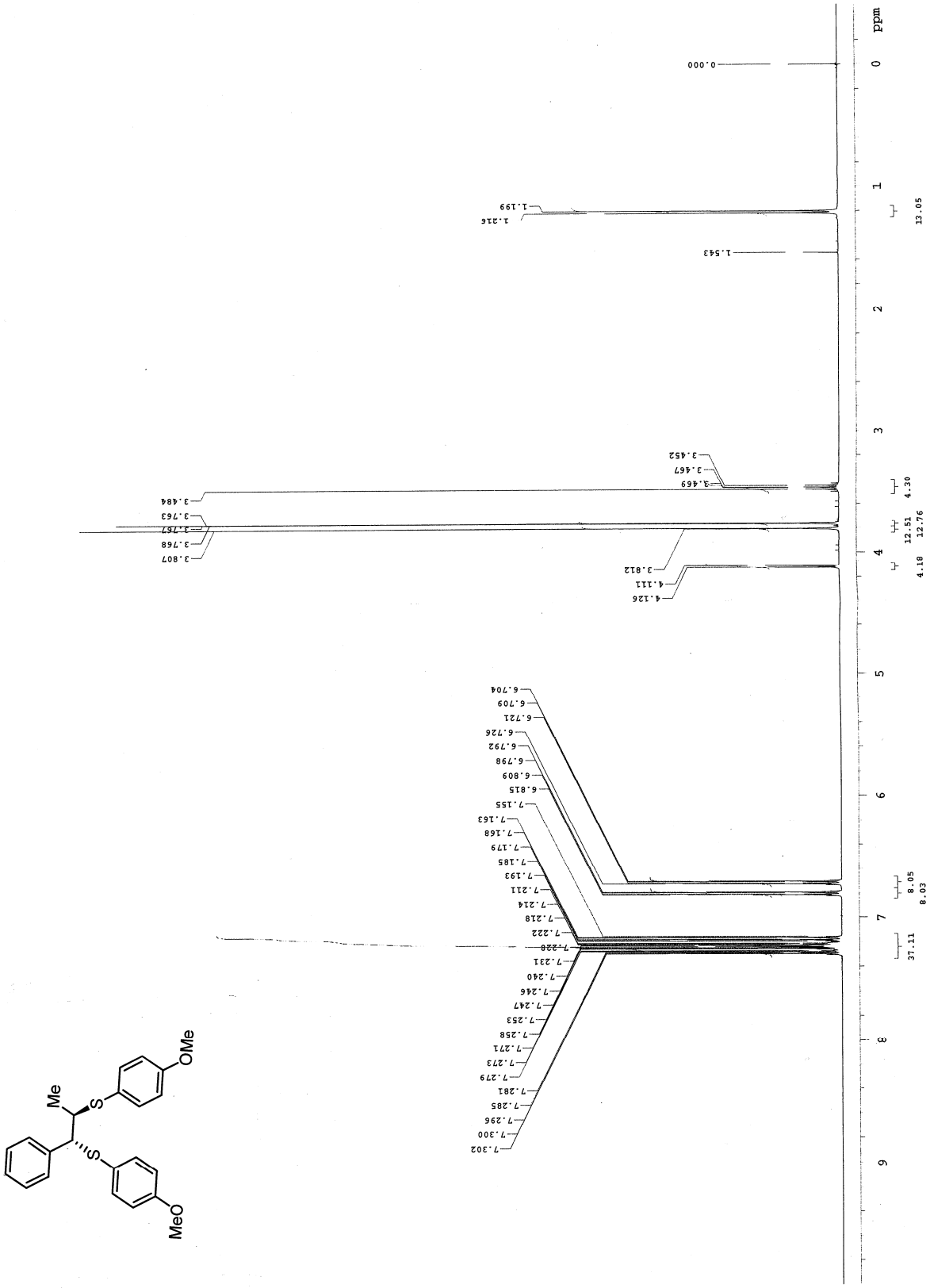
40
60
80
100
120
140
160
180
17.677
48.152
58.680
76.683
77.000
77.202
77.317
115.758
115.960
115.972
116.174
127.611
128.004
129.011
129.206
129.242
129.507
129.543
134.950
135.029
135.450
135.529
137.973
161.148
161.235
163.612
163.703
Me
S
S
F
F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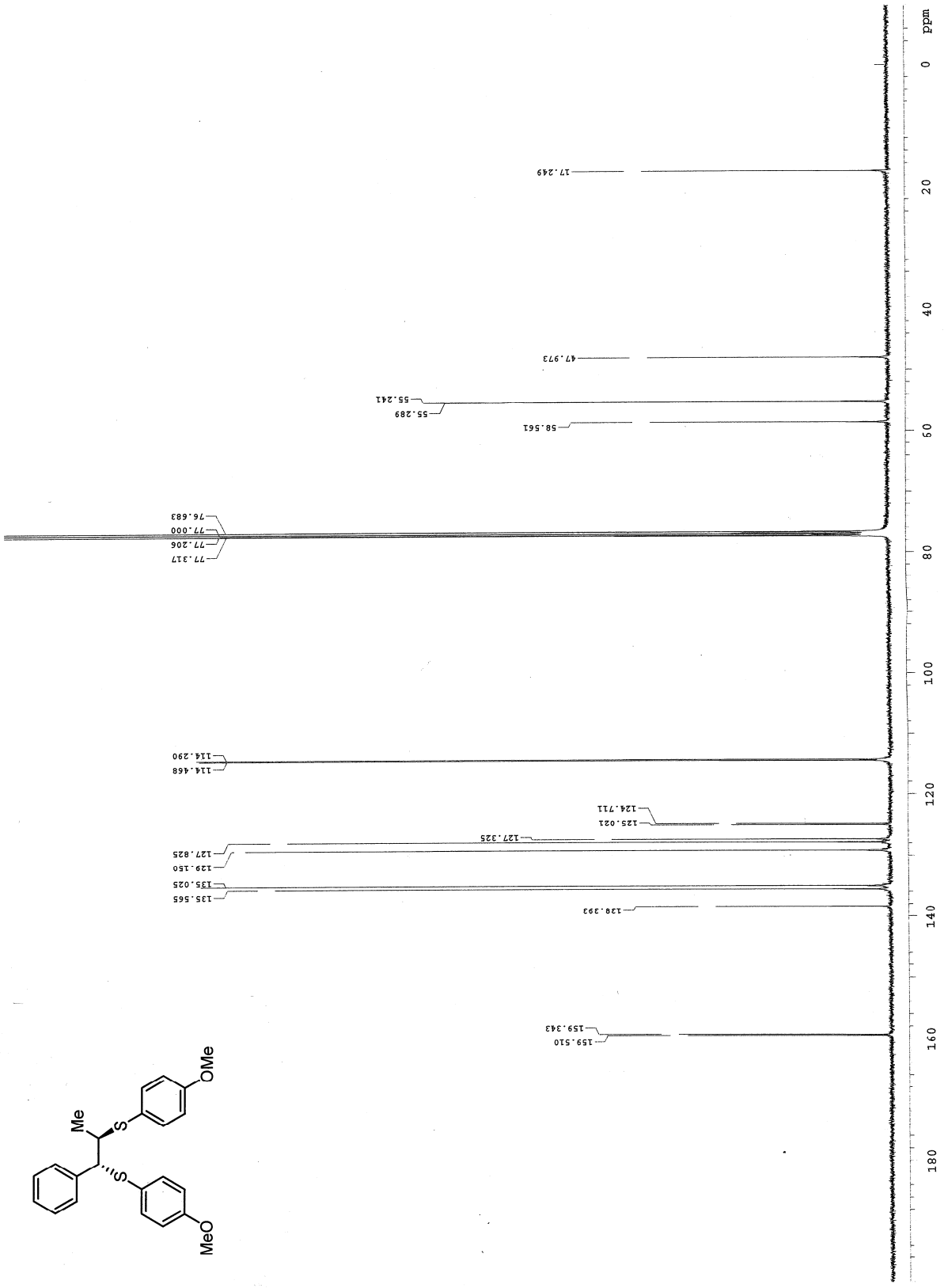
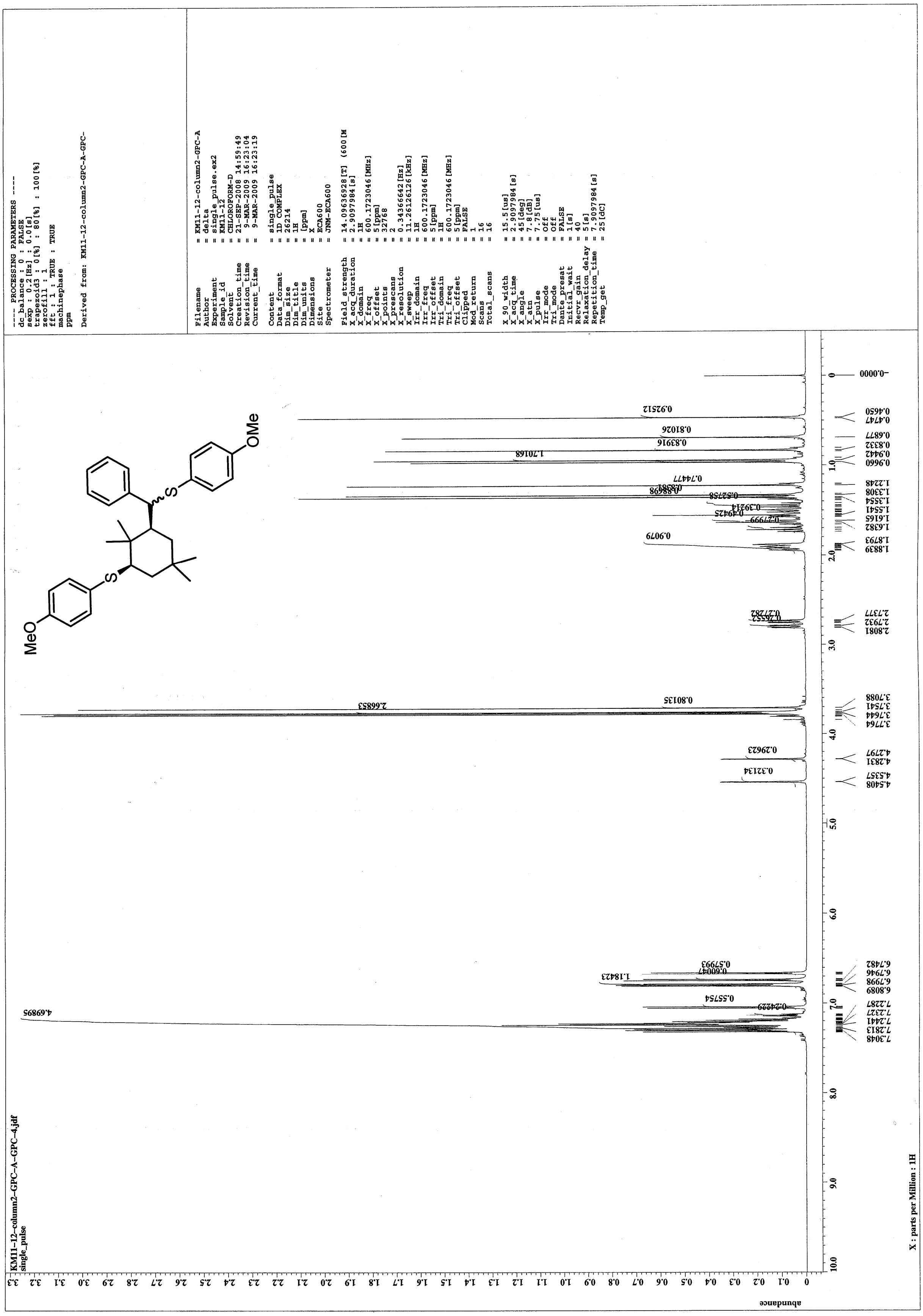
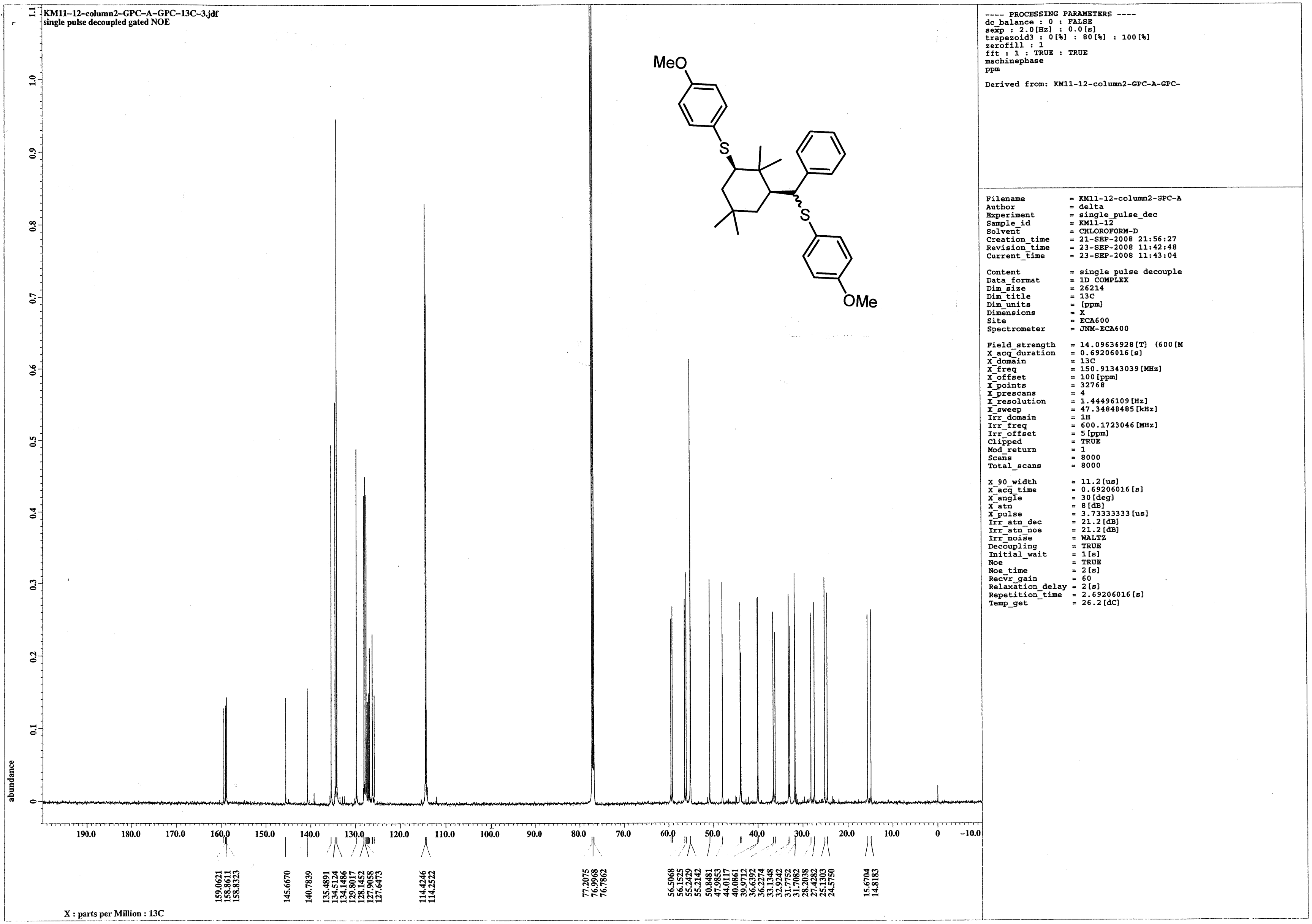
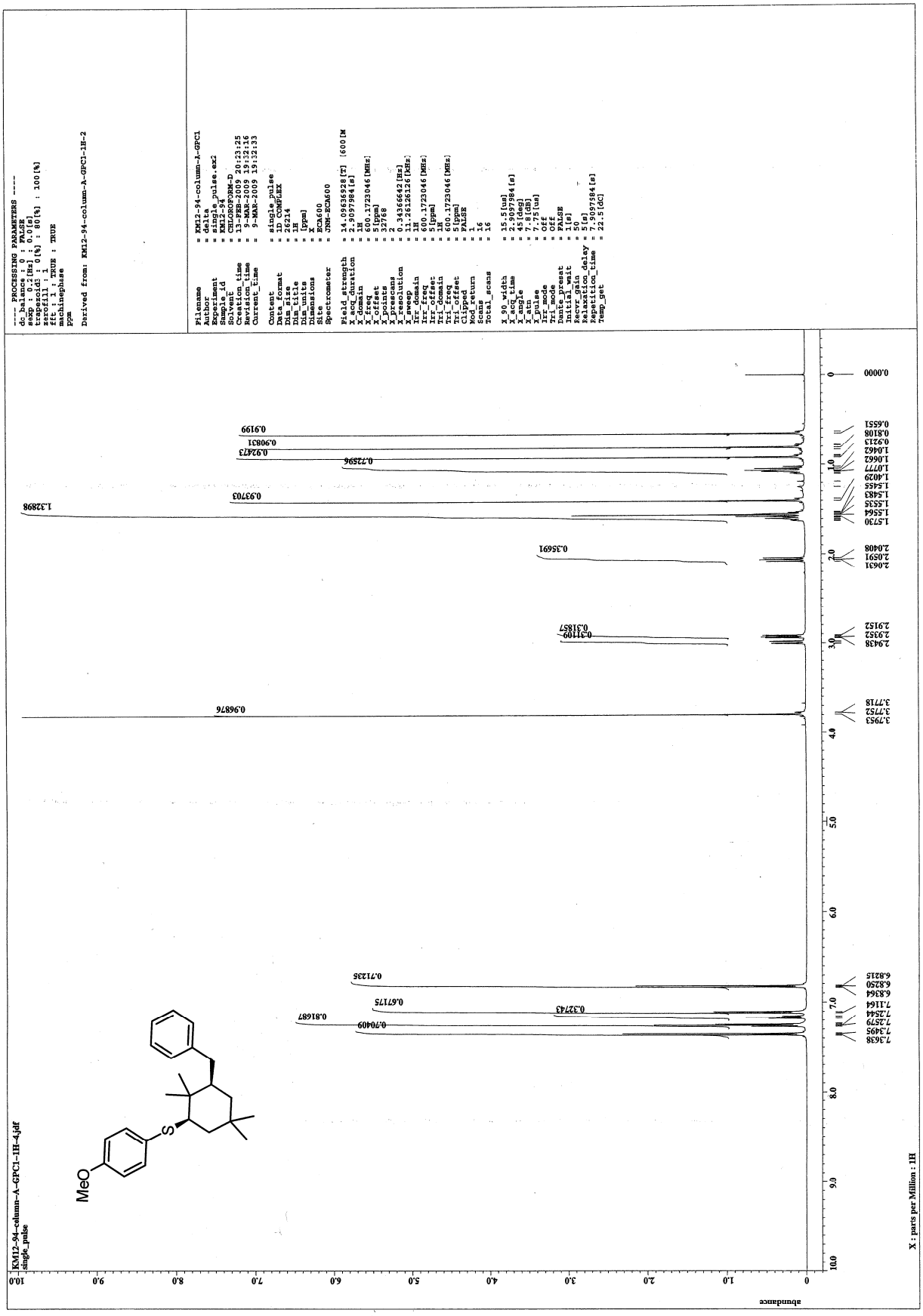
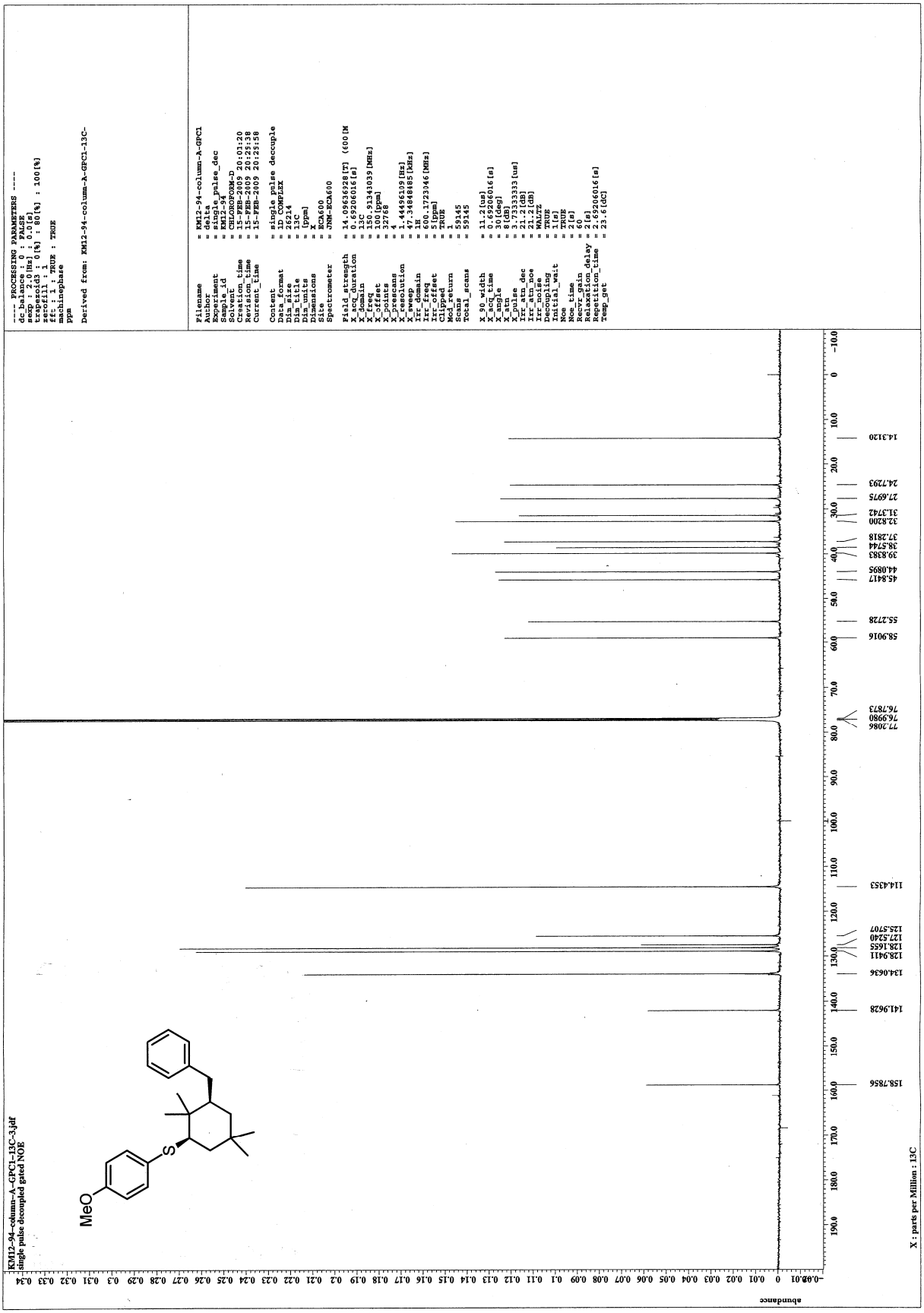
3
4
5
6
7
8
9
0.000
1.199
1.316
1.543
3.452
3.467
3.469
3.484
3.763
3.767
3.768
3.807
3.812
4.111
4.126
6.704
6.709
6.721
6.726
6.792
6.798
6.809
6.815
7.155
7.163
7.168
7.179
7.185
7.193
7.211
7.214
7.218
7.222
7.228
7.231
7.240
7.246
7.247
7.253
7.258
7.271
7.273
7.279
7.281
7.285
7.296
7.300
7.302
13.05
4.30
12.51
12.76
4.18
8.05
8.03
37.11
Me
S
S
OMe
MeO

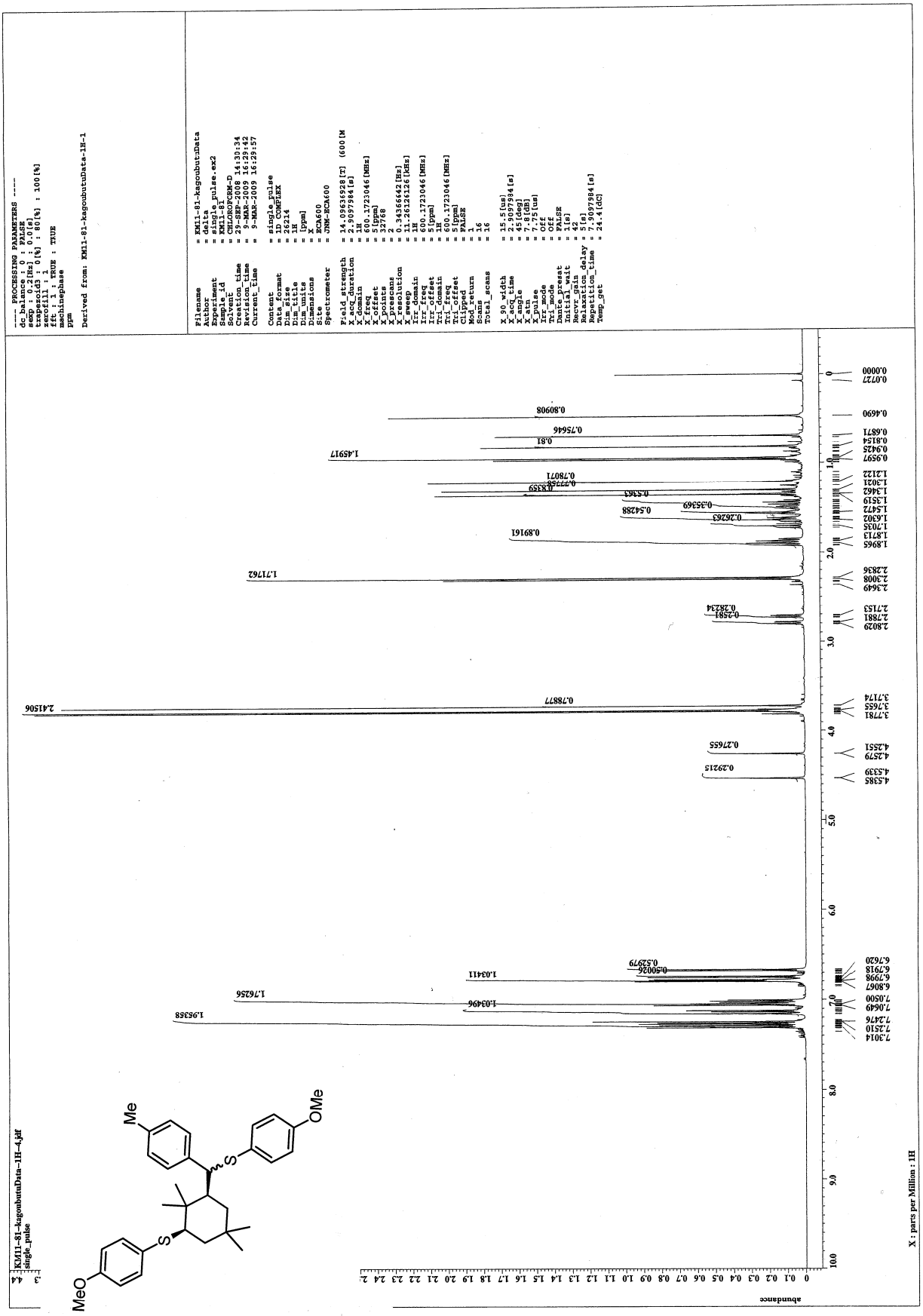

17.249
47.973
55.241
55.289
58.561
76.683
77.000
77.206
77.317
114.290
114.468
124.711
125.021
127.325
127.825
129.150
135.025
135.565
138.393
159.343
159.510
ppm
0
20
40
50
80
100
120
140
160
180
Me
OMe
MeO

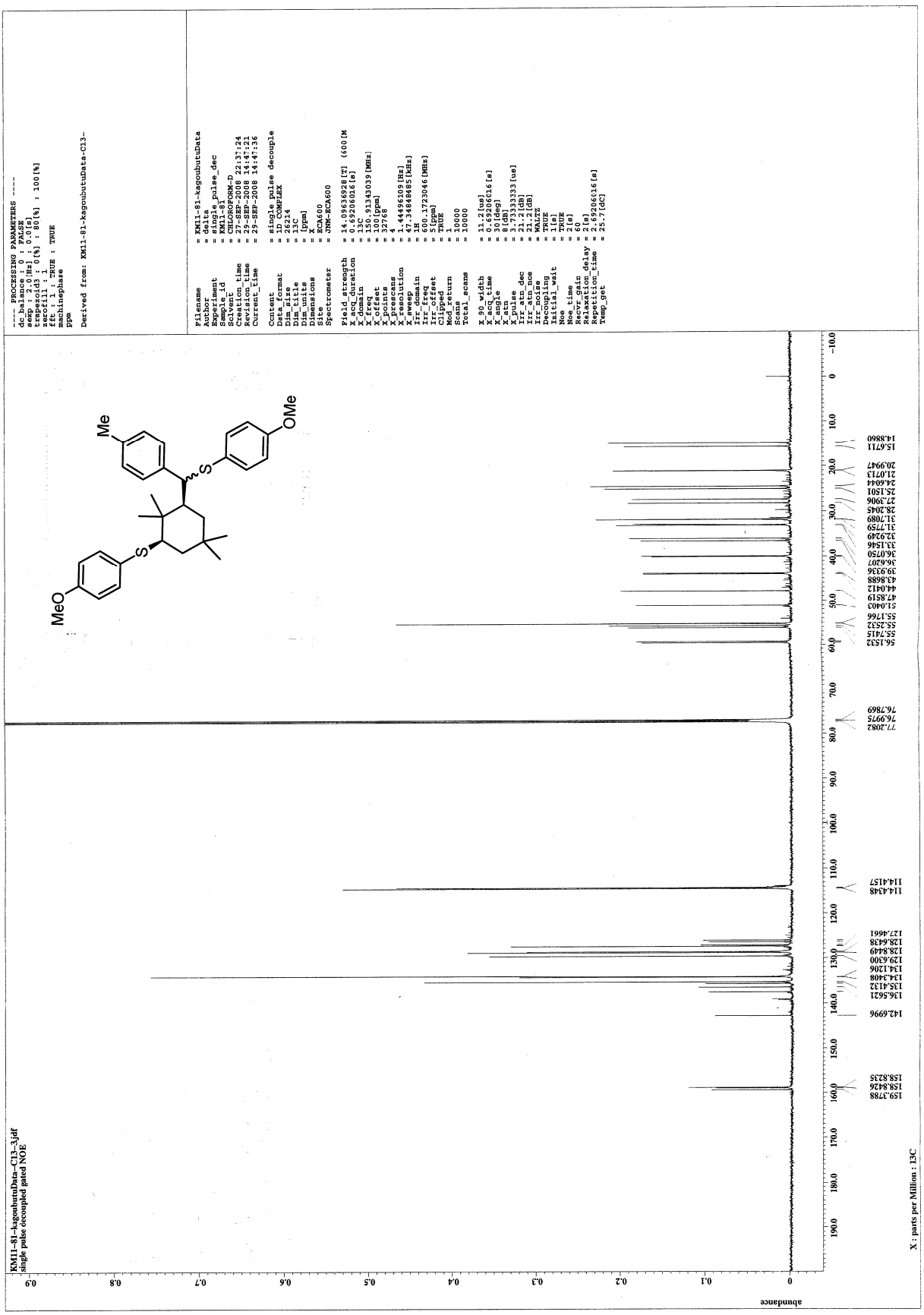


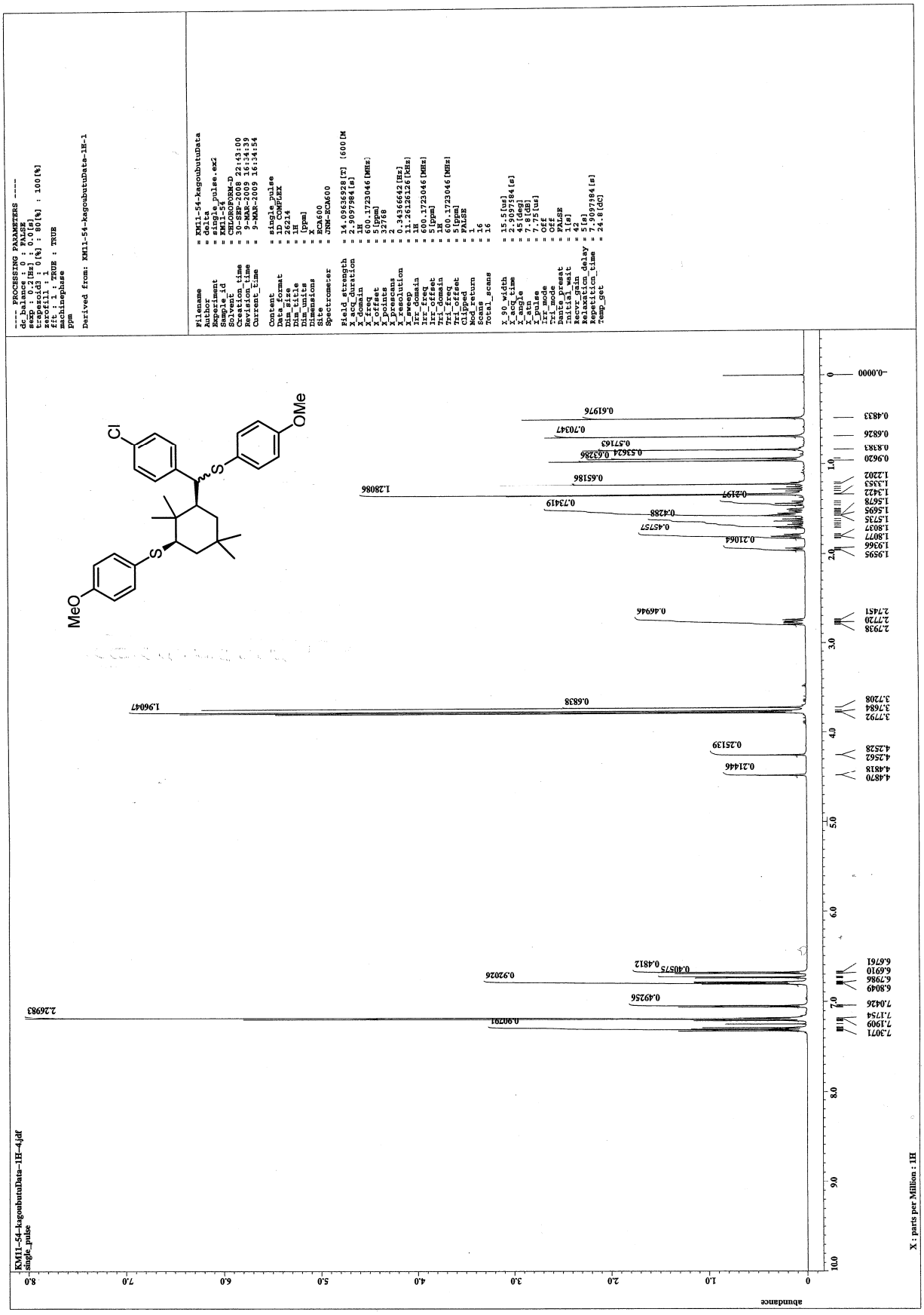


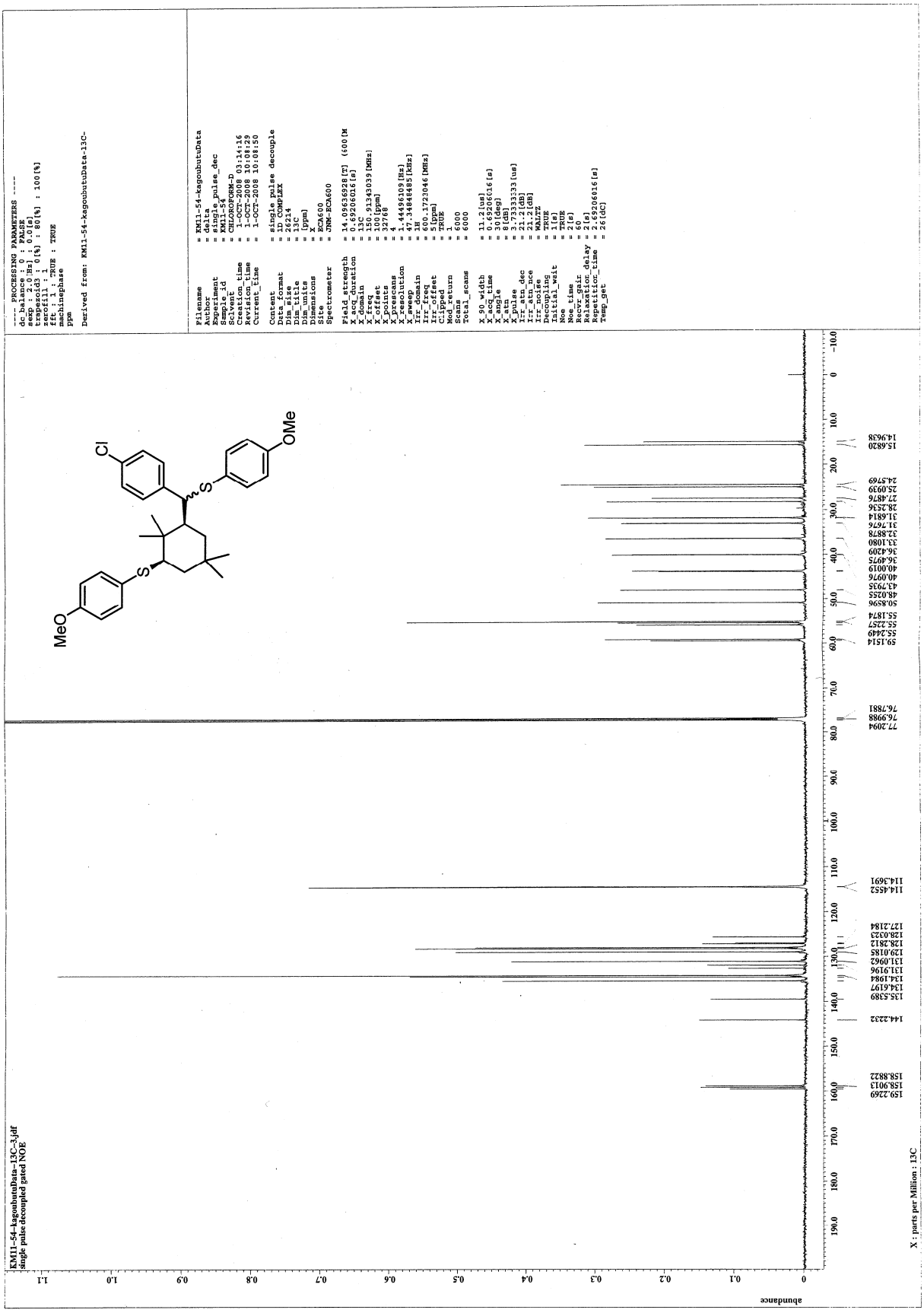

MeO
S
KM12-94-column-A-GPC1-1H-4.jdf
single_pulse
X : parts per Million : 1H
abundance

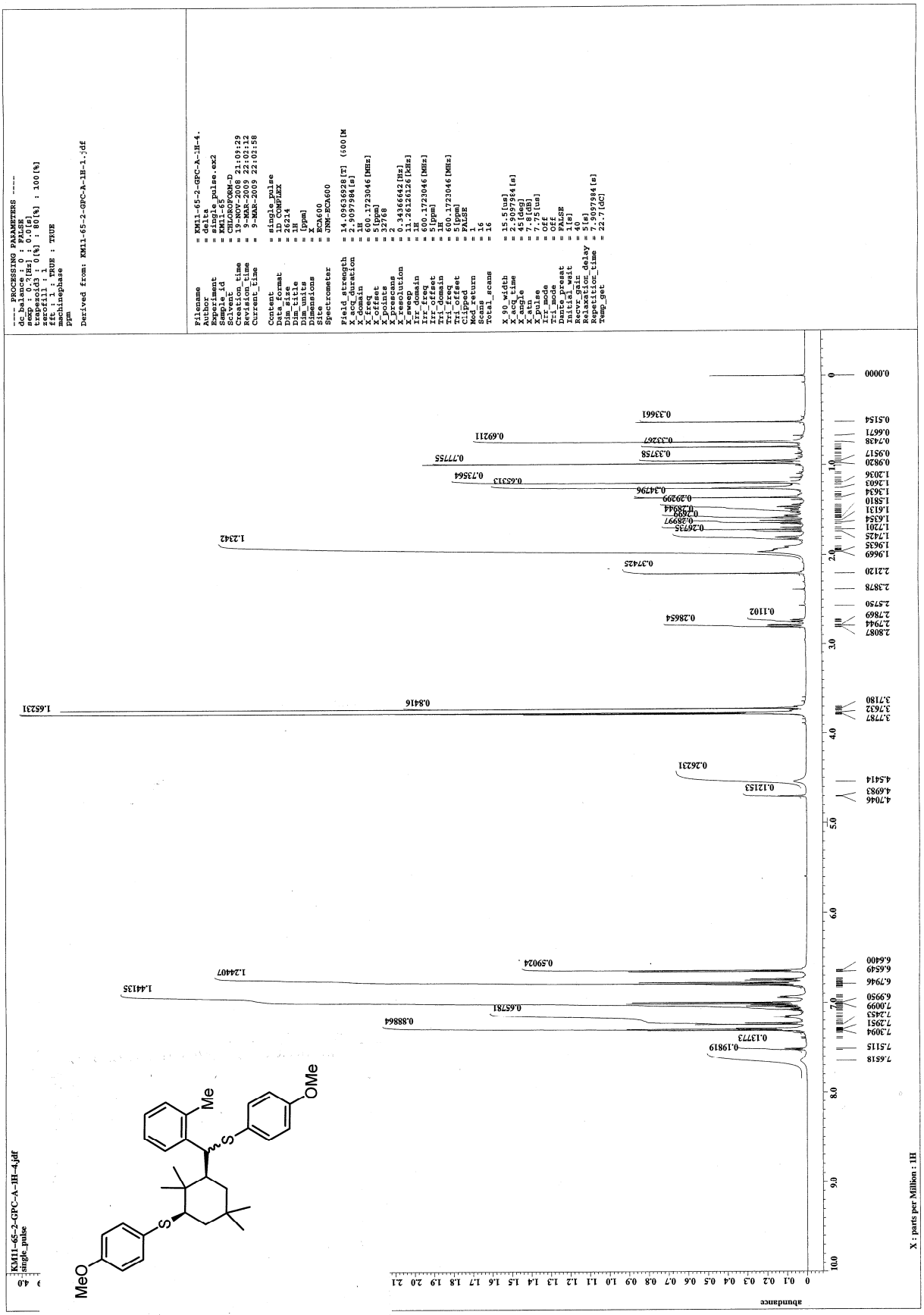

KM12-94-column-A-GPC1-13C-3.jdf
single pulse decoupled gated NOE
MeO
S
X : parts per Million : 13C
abundance
14.3120
24.7293
27.6975
31.3742
32.8200
37.2818
38.5744
39.8383
44.0895
45.8417
55.2728
58.9016
76.7873
76.9980
77.2086
114.4353
125.5707
127.5240
128.1625
128.9411
134.0636
141.9628
158.7856

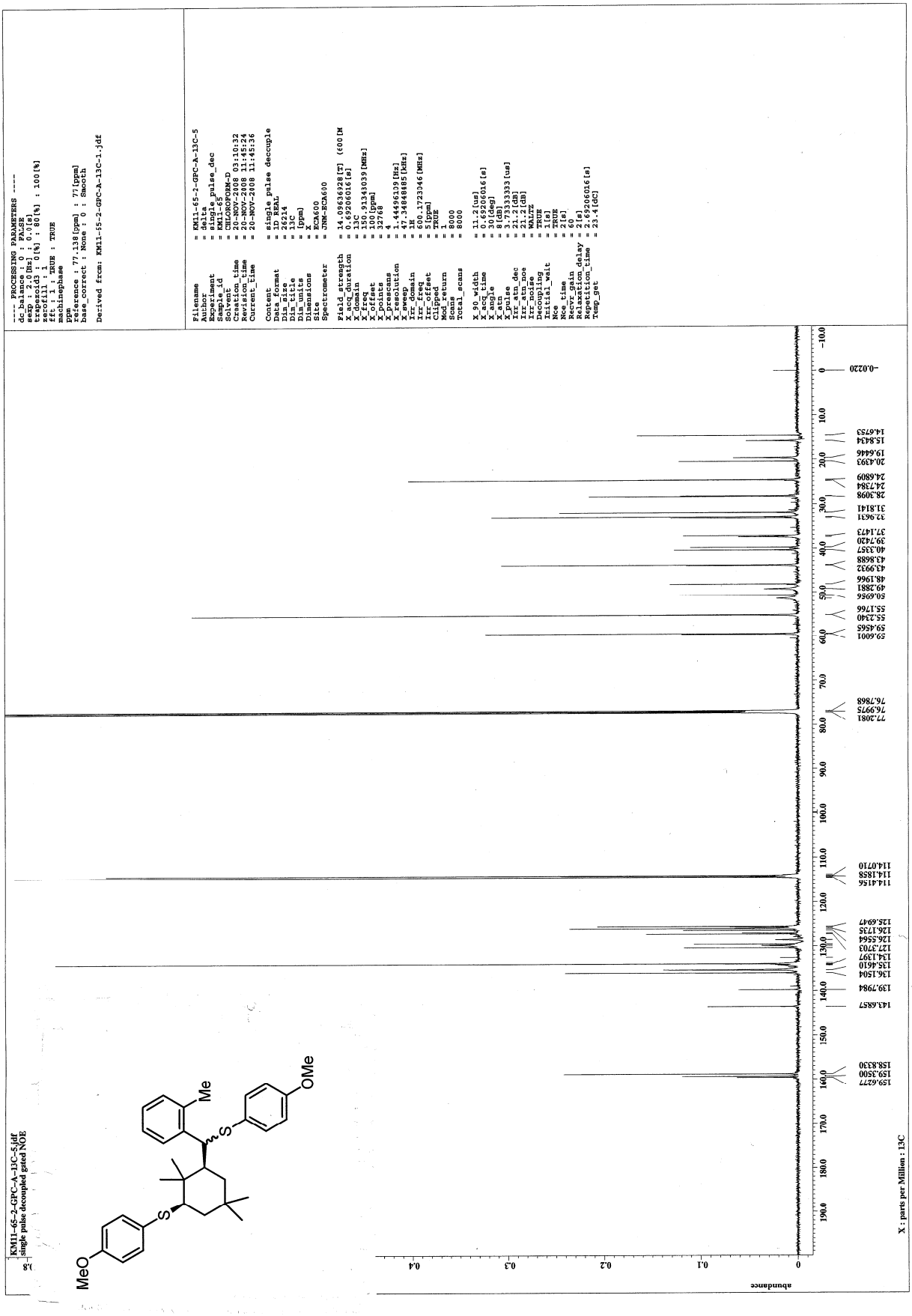

Me
OMe
MeO
S
S
X : parts per Million : 1H
abundance

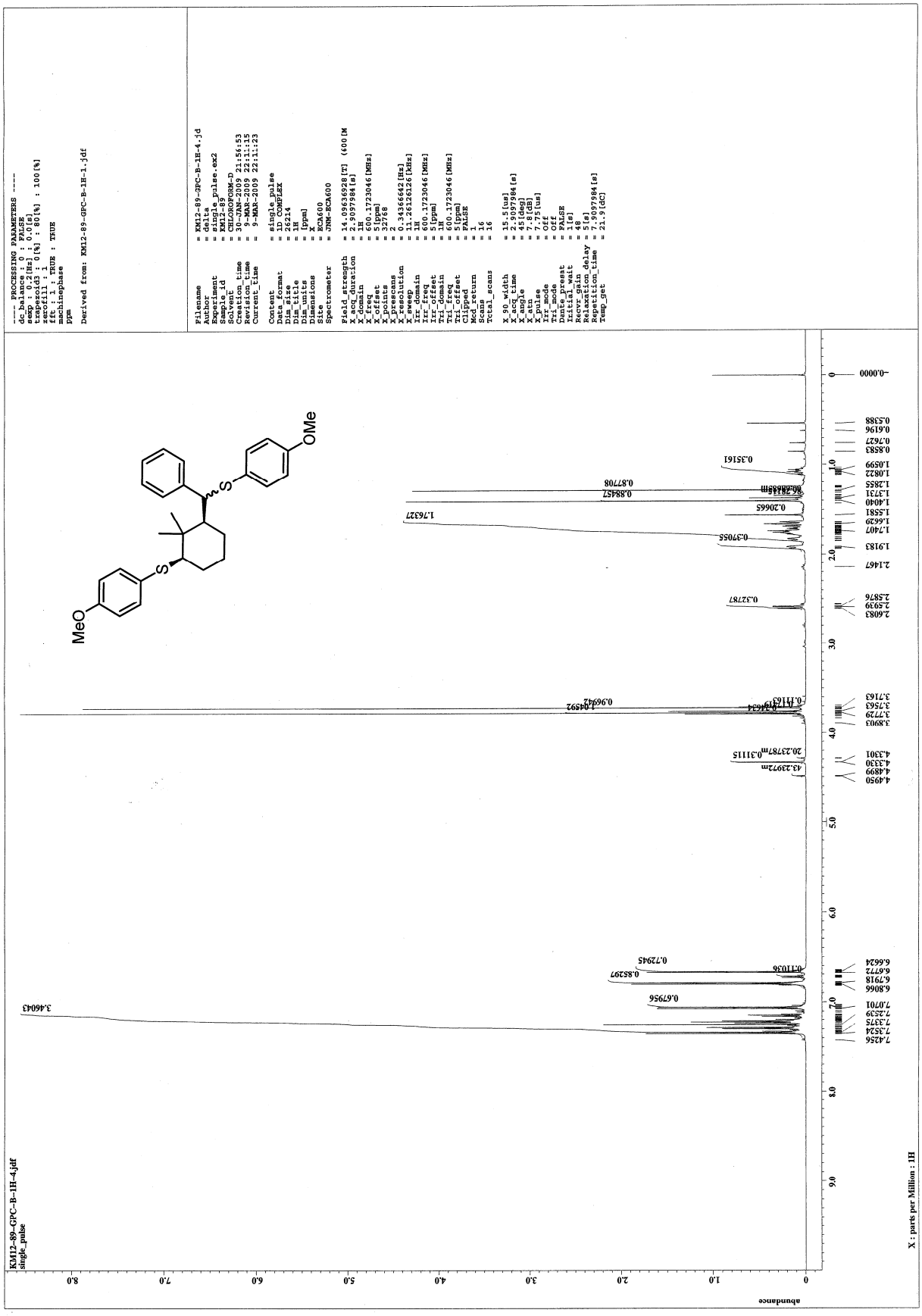

KM11-81-kagoubutuData-C13-3.jdf
single pulse decoupled gated NOE
abundance
X : parts per Million : 13C
MeO
OMe
Me
S
S

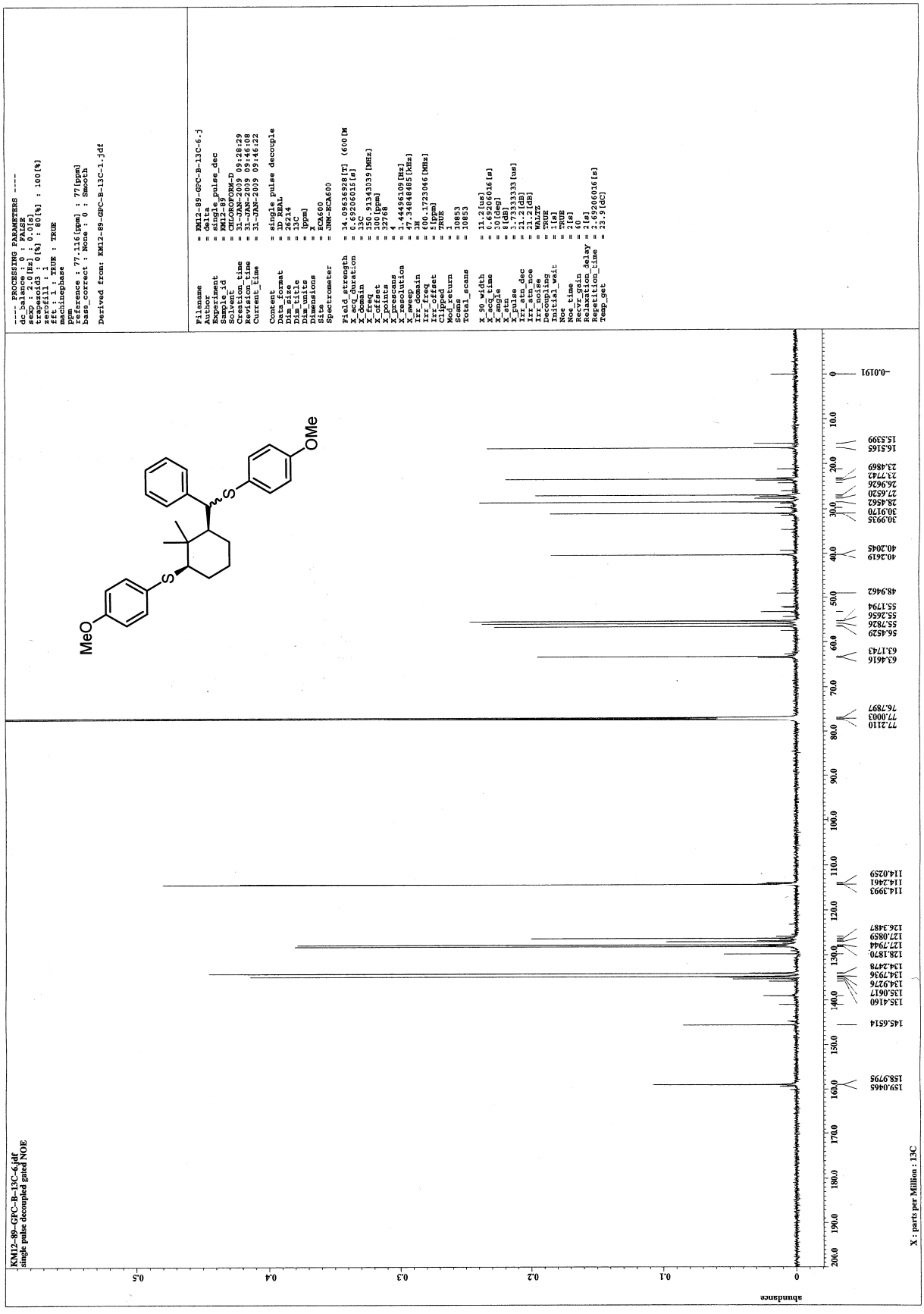

OMe
Cl
MeO
S
S
X : parts per Million : 1H
abundance

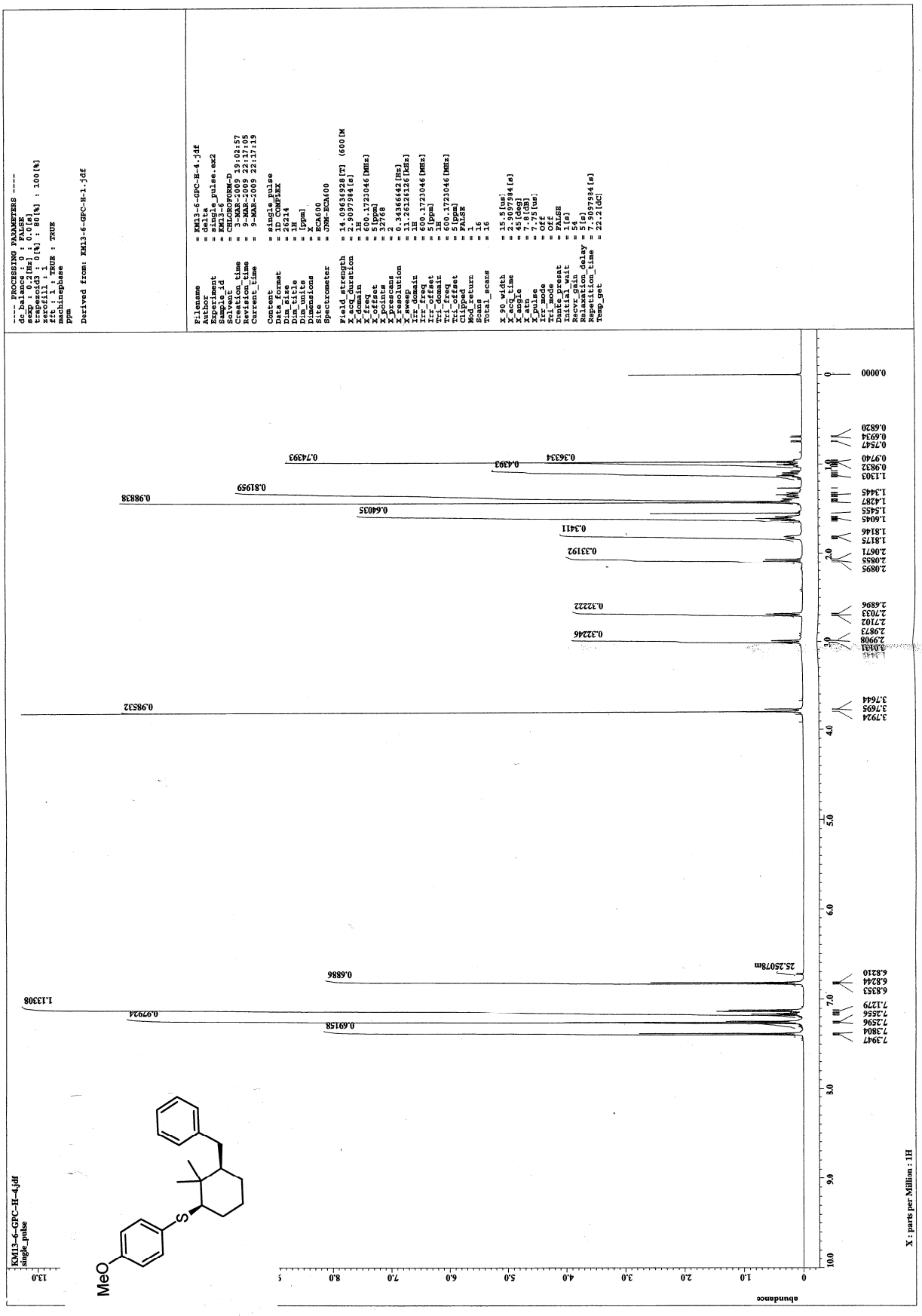

KM11-54-kagoubutuData-13C-3.jdf
Single pulse decoupled gated NOE
abundance
X : parts per Million : 13C
MeO
OMe
Cl
S
S

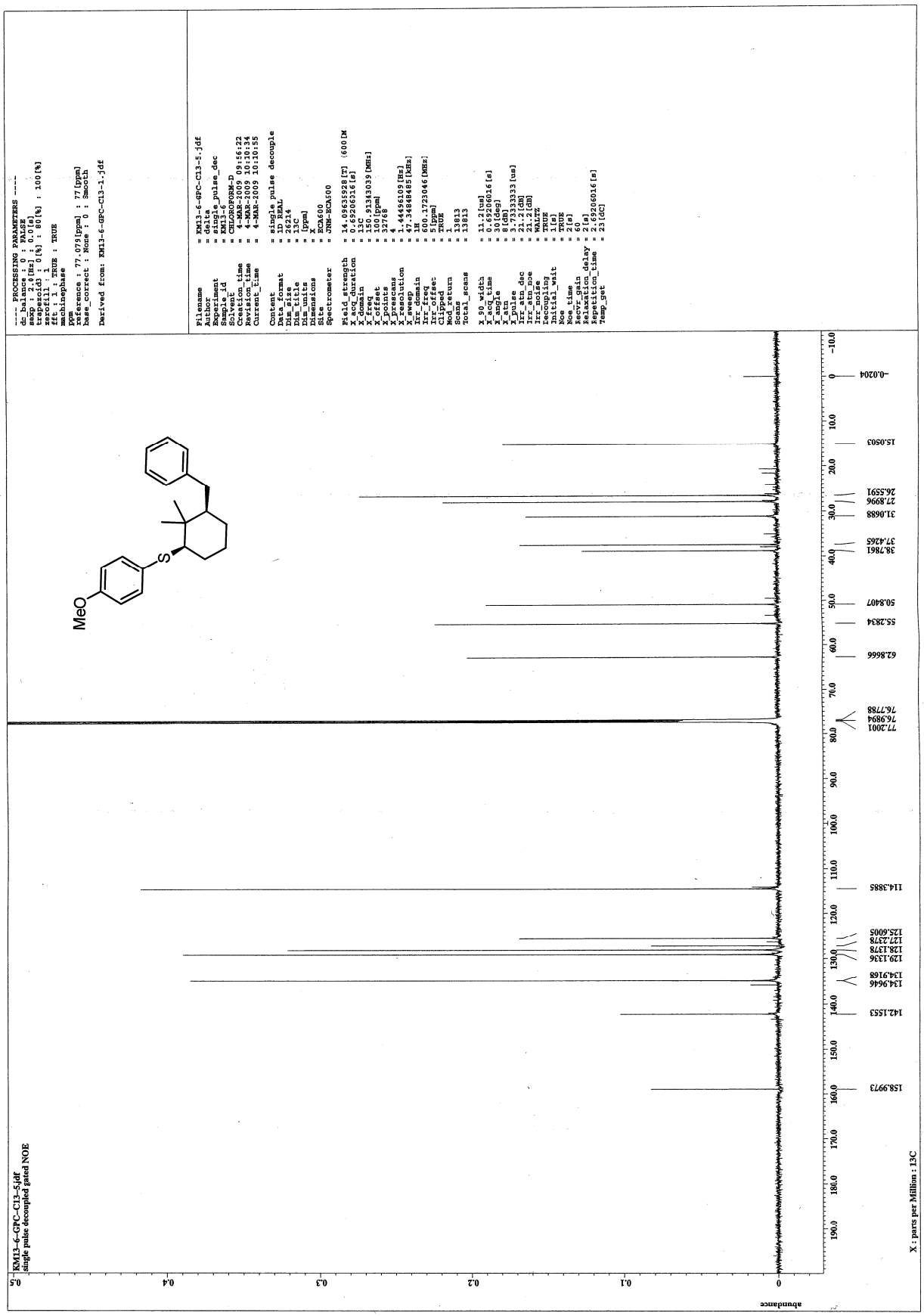

MeO
Me
S
S
OMe
abundance
X : parts per Million : 1H

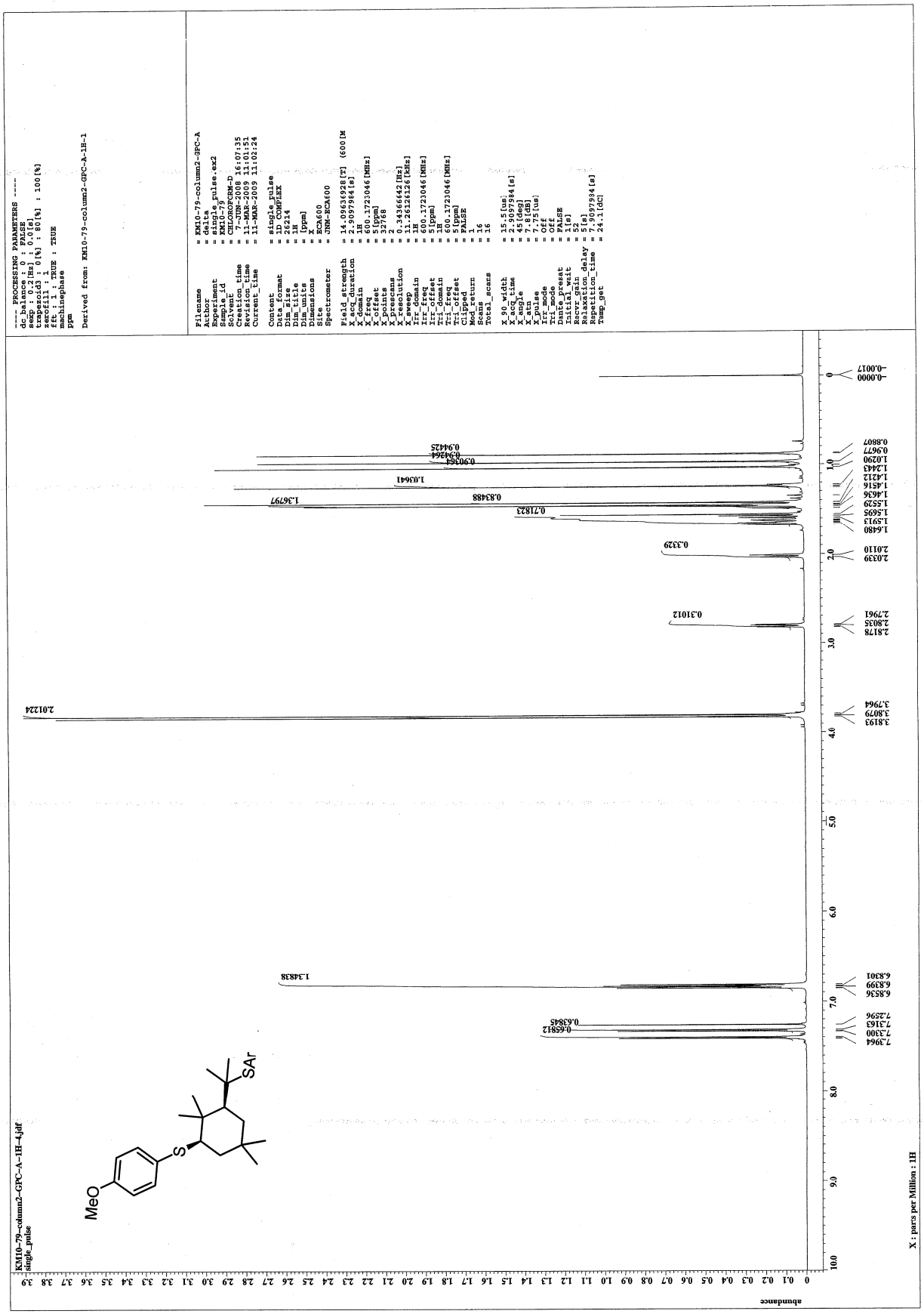

KM11-65-2-GPC-A-13C-5.jdf
single pulse decoupled gated NOE
MeO
Me
S
S
OMe
X : parts per Million : 13C
abundance

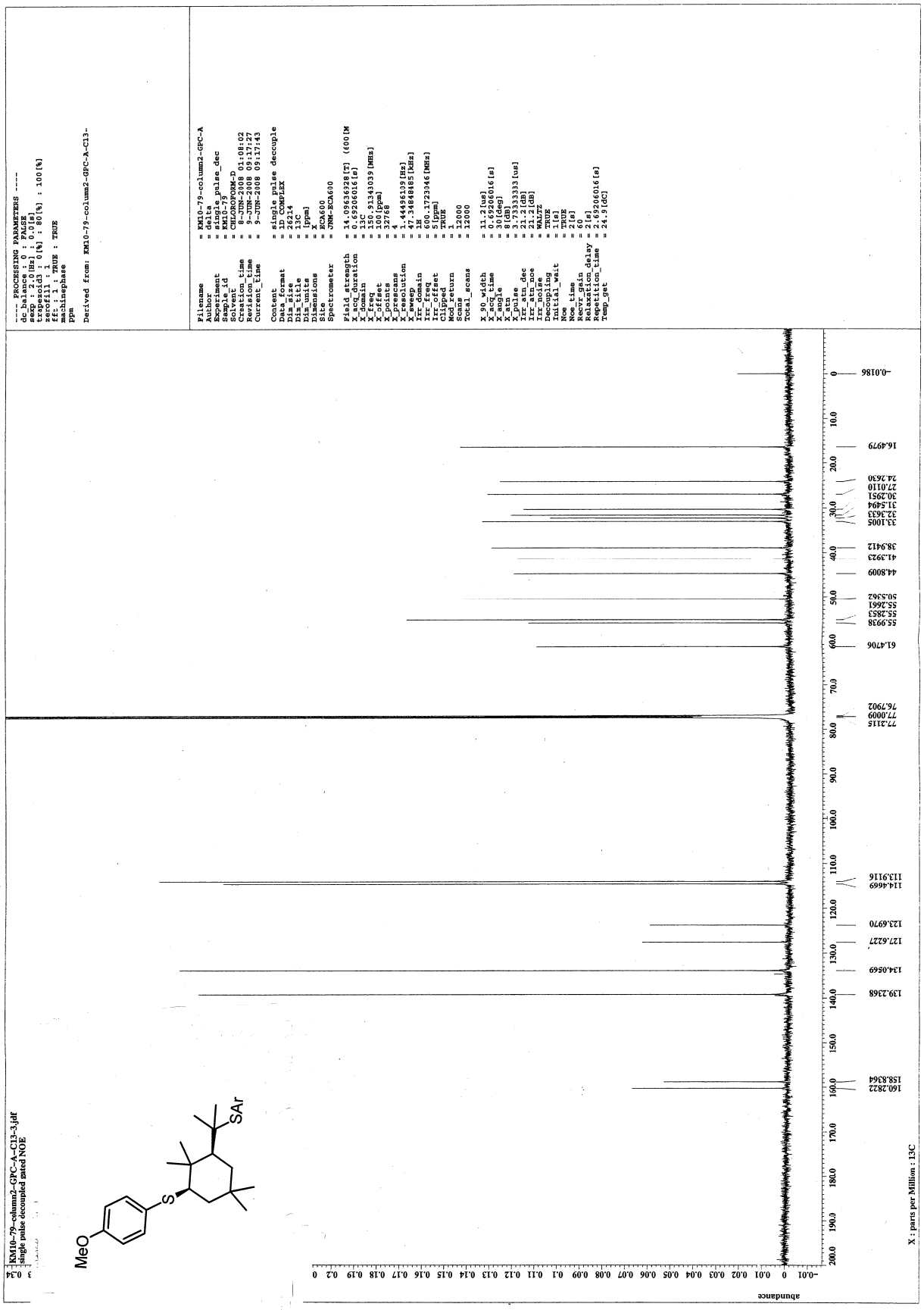

MeO
OMe
KM12-89-GPC-B-1H-4.jdf
single_pulse
X : parts per Million : 1H
abundance

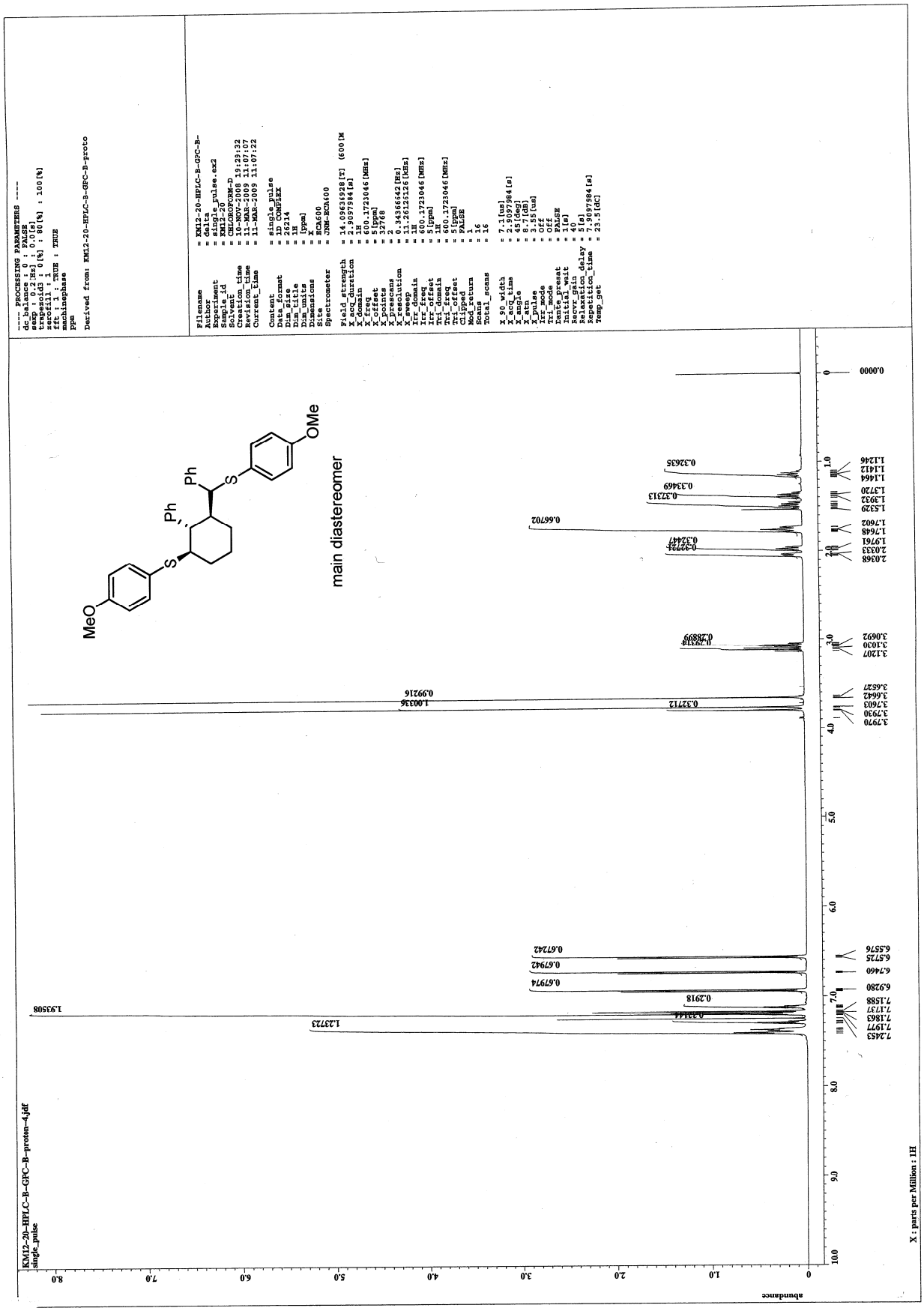

MeO
OMe
KM12-89-GPC-B-13C-6.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C
abundance

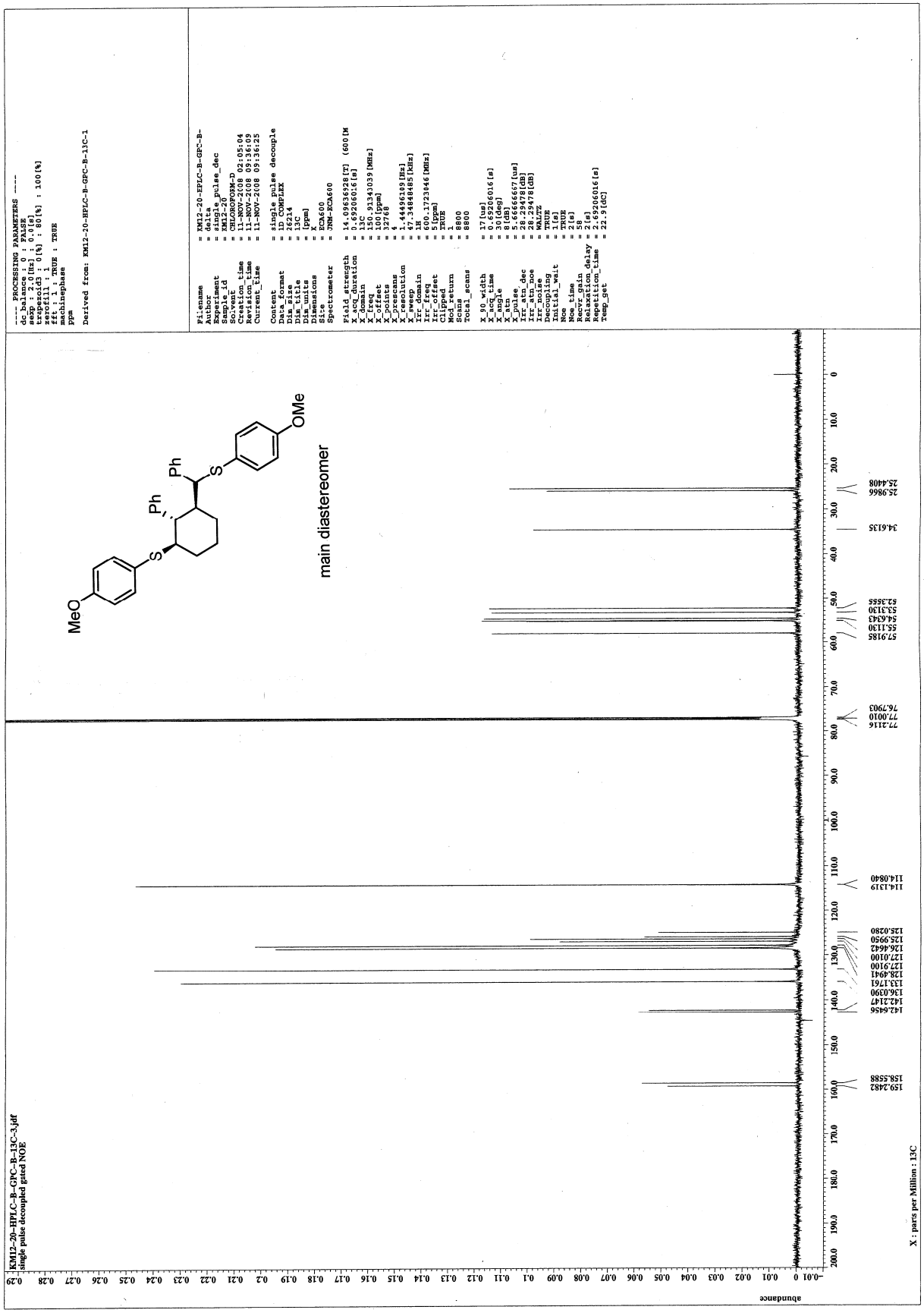

MeO
S
X : parts per Million : 1H
abundance

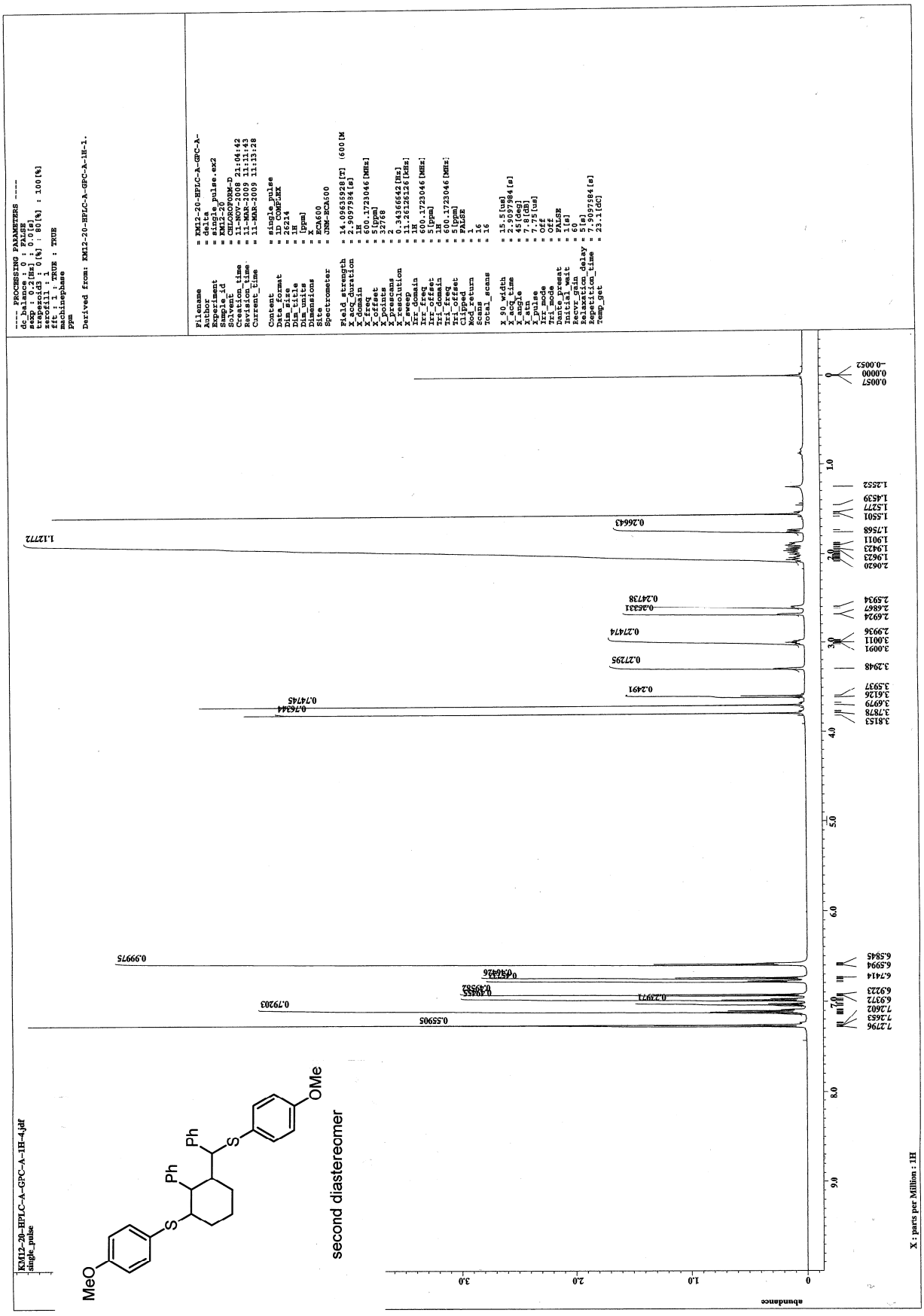

KM13-6-GPC-C13-5.jdf
single pulse decoupled gated NOE
MeO
S
X : parts per Million : 13C
abundance

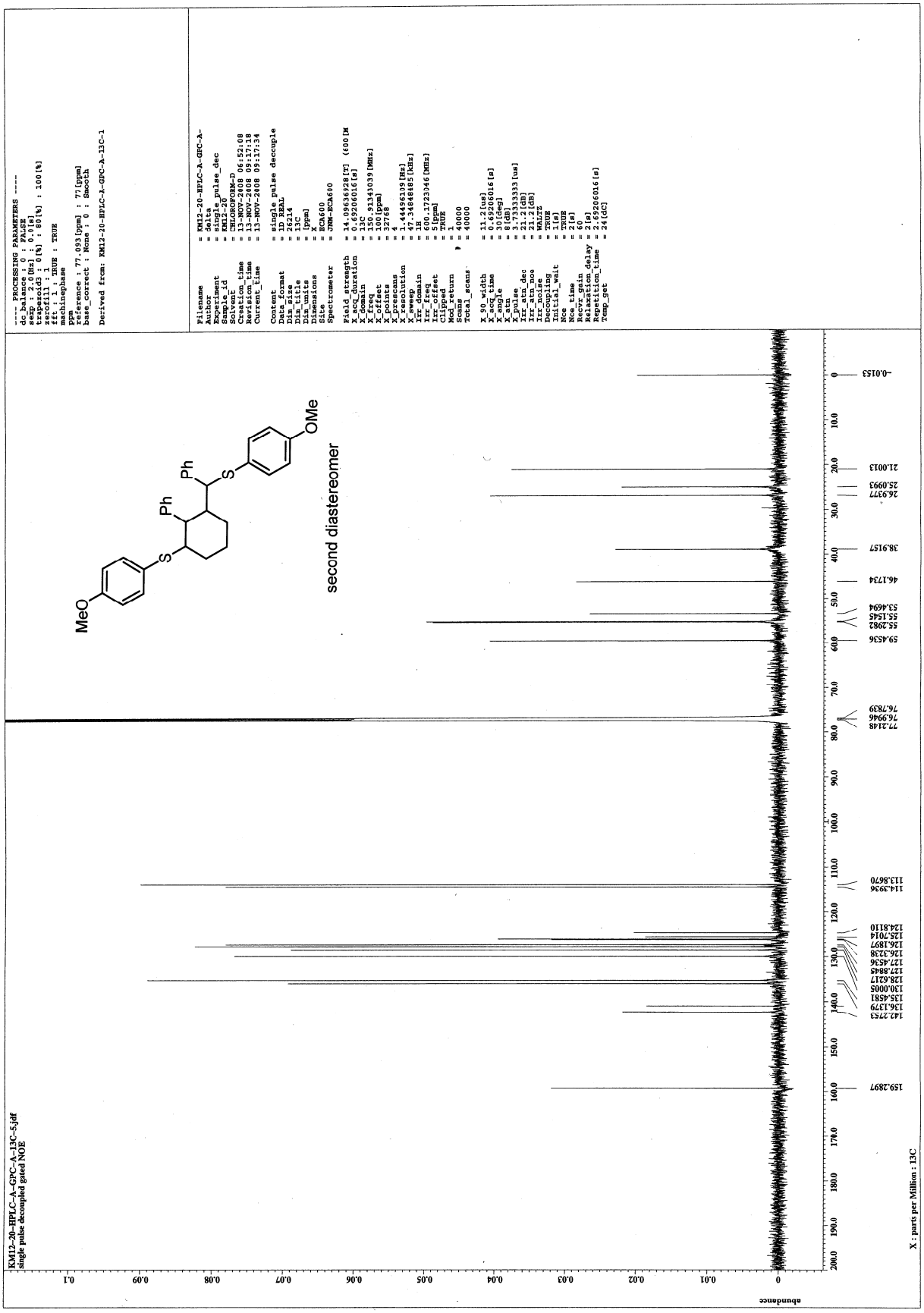

KM10-79-column2-GPC-A-1H-4.jdf
single_pulse
MeO
S
SAr
X : parts per Million : 1H
abundance
2.01224
1.36838
0.63845
0.63812
0.33229
0.31012
1.36797
0.83488
0.71823
1.03641
0.90364
0.94425

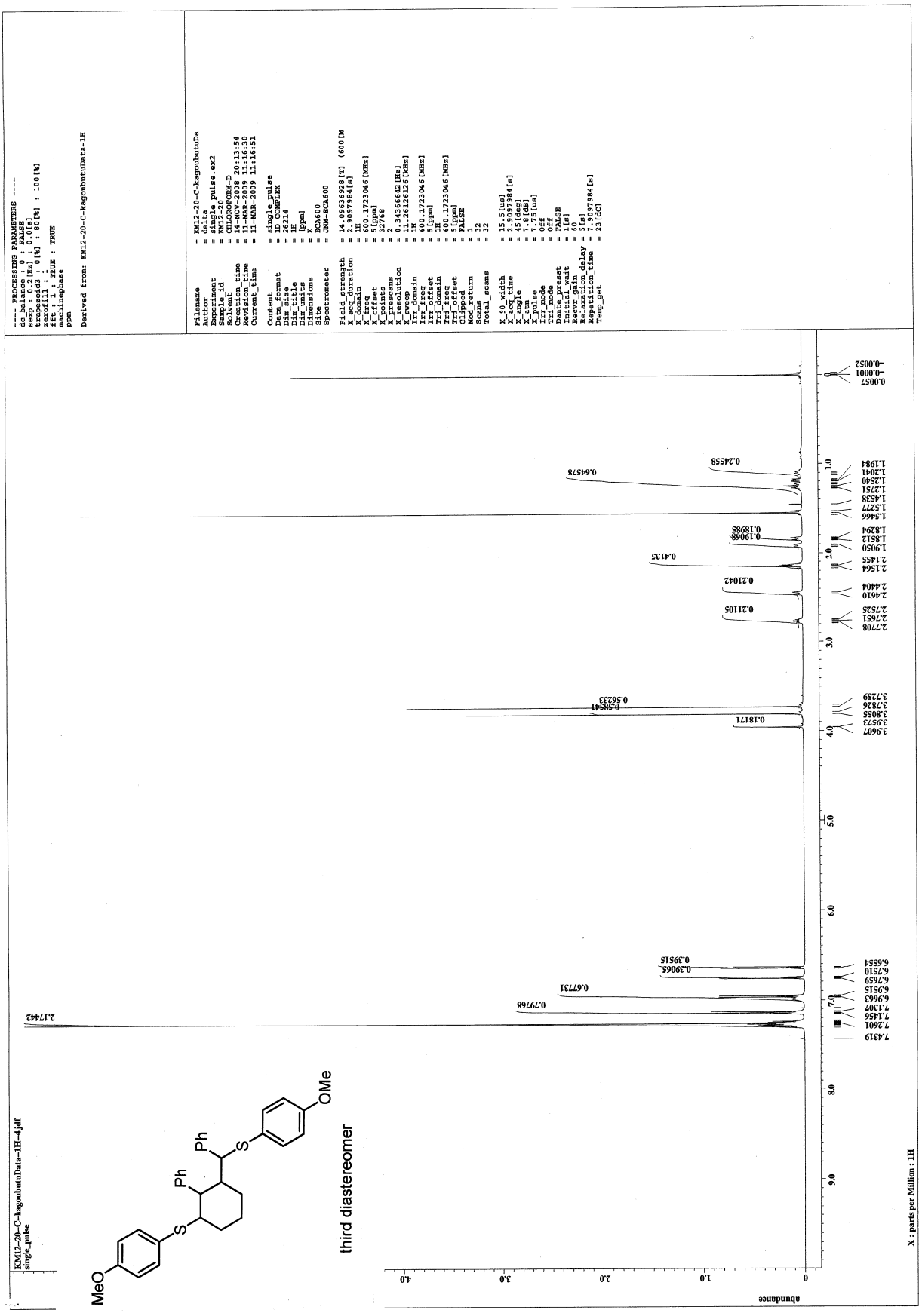

KM10-79-column2-GPC-A-C13-3.jdf
single pulse decoupled gated NOE
MeO
S
SAr
X : parts per Million : 13C
abundance

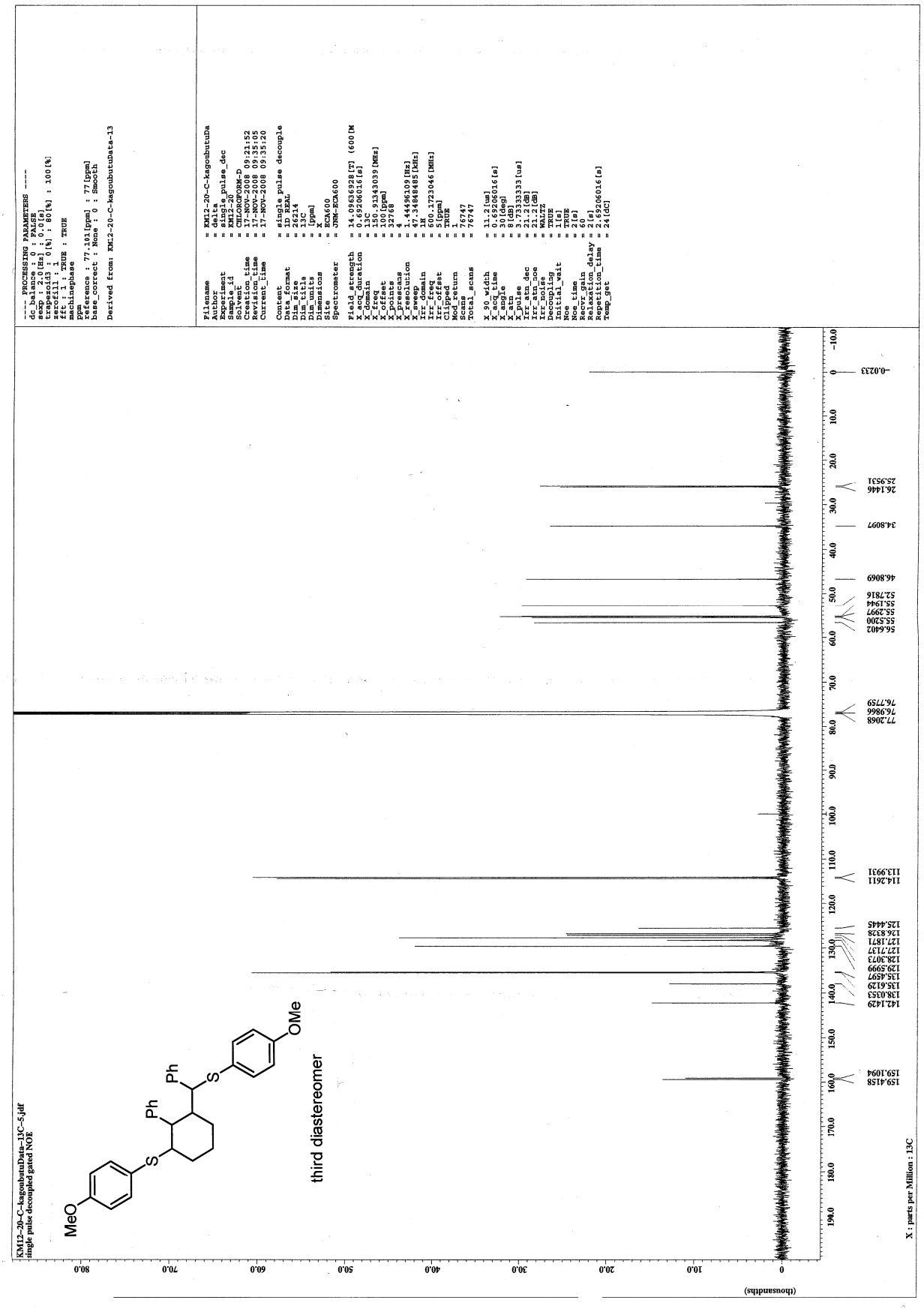

main diastereomer
MeO
OMe
Ph
Ph
S
S
KM12-20-HPLC-B-GPC-B-proton-4.jdf
single_pulse
X : parts per Million : 1H
abundance

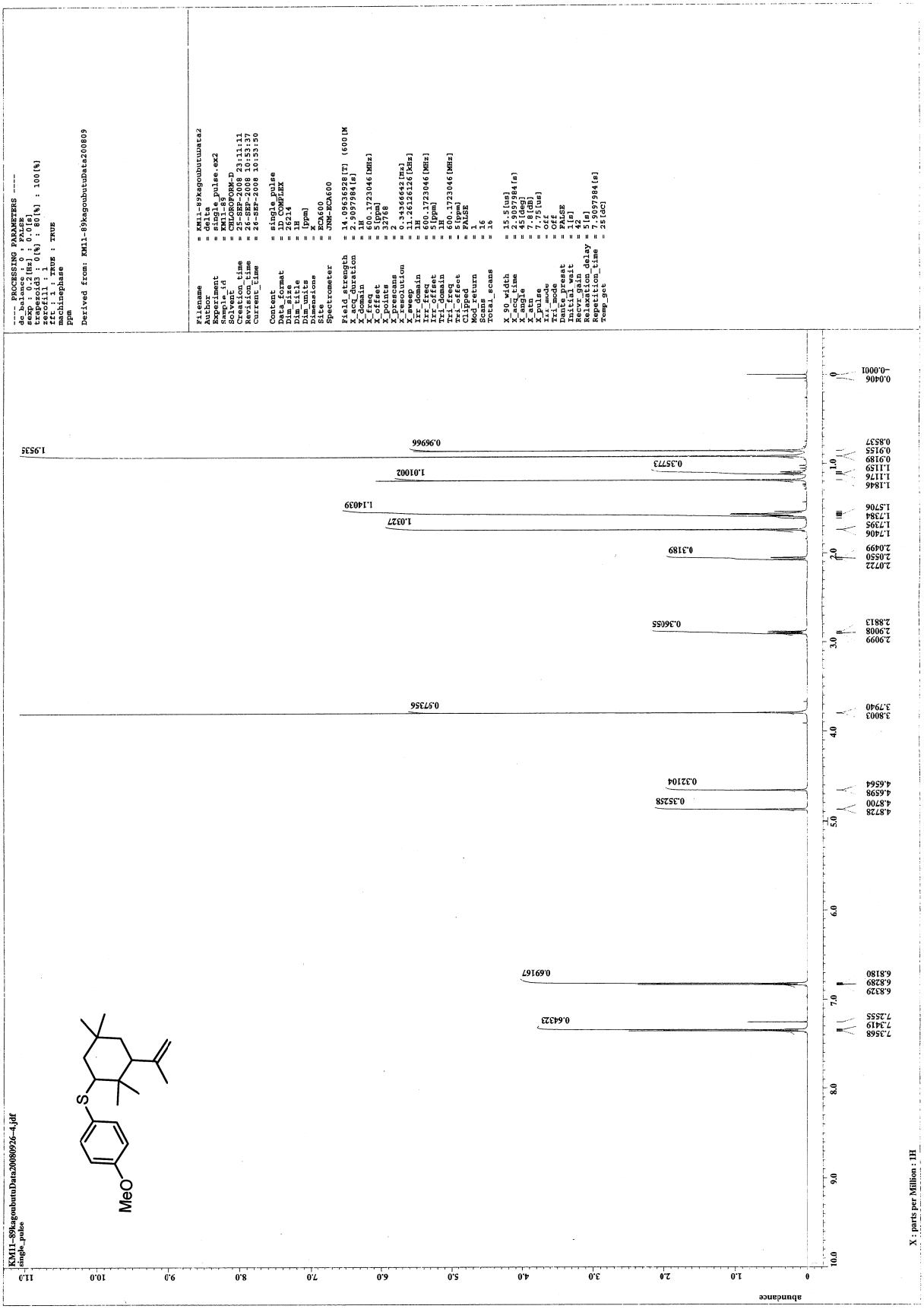

KM12-20-HPLC-B-GPC-B-13C-3.jdf
single pulse decoupled gated NOE
MeO
Ph
Ph
S
S
OMe
main diastereomer
X : parts per Million : 13C
abundance

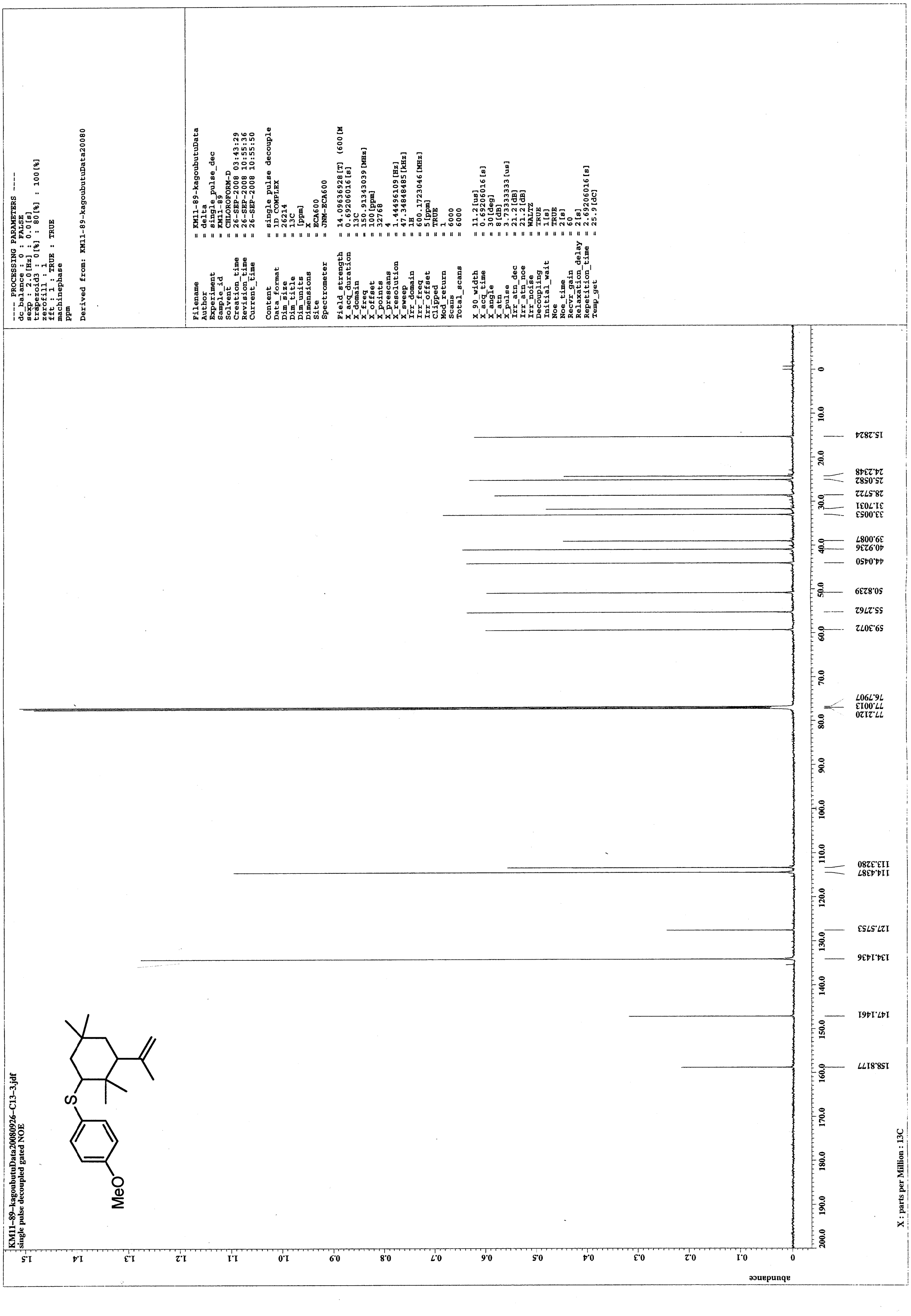

KM12-20-HPLC-A-GPC-A-1H-4.jdf
single_pulse
MeO
S
Ph
Ph
S
OMe
second diastereomer
X : parts per Million : 1H
abundance


KM12-20-HPLC-A-GPC-A-13C-5.jdf
single pulse decoupled gated NOE
second diastereomer
MeO
OMe
Ph
Ph
S
S
X : parts per Million : 13C
abundance


MeO
Ph
Ph
S
S
OMe
third diastereomer
abundance
X : parts per Million : 1H


KM12-20-C-kagonbutuData-13C-5.jdf
single pulse decoupled gated NOE
MeO
S
Ph
Ph
S
OMe
third diastereomer
X : parts per Million : 13C
(thousandths)
-0.0233
25.9531
26.1446
34.8097
46.8069
52.7816
55.1944
55.2997
55.5200
56.6402
76.7759
76.9866
77.2068
113.9931
114.2611
125.4445
127.1871
127.7137
128.3073
128.5999
135.4597
135.6129
138.0353
142.1429
159.1094
159.4158


MeO
S
abundance
X : parts per Million : 1H


KM11-89-kagoubutuData20080926-C13-3.jdf
single pulse decoupled gated NOE
MeO
S
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
Derived from: KM11-89-kagoubutuData20080
Filename = KM11-89-kagoubutuData
Author = delta
Experiment = single_pulse_dec
Sample_id = KM11-89
Solvent = CHLOROFORM-D
Creation_time = 26-SEP-2008 03:43:29
Revision_time = 26-SEP-2008 10:55:36
Current_time = 26-SEP-2008 10:55:50
Content = single pulse decouple
Data_format = 1D COMPLEX
Dim_size = 26214
Dim_title = 13C
Dim_units = [ppm]
Dimensions = X
Site = ECA600
Spectrometer = JNM-ECA600
Field_strength = 14.09636928[T] (600[M
X_acq_duration = 0.69206016[s]
X_domain = 13C
X_freq = 150.91343039[MHz]
X_offset = 100[ppm]
X_points = 32768
X_prescans = 4
X_resolution = 1.44496109[Hz]
X_sweep = 47.34848485[kHz]
Irr_domain = 1H
Irr_freq = 600.1723046[MHz]
Irr_offset = 5[ppm]
Clipped = TRUE
Mod_return = 1
Scans = 6000
Total_scans = 6000
X_90_width = 11.2[us]
X_acq_time = 0.69206016[s]
X_angle = 30[deg]
X_atn = 8[dB]
X_pulse = 3.73333333[us]
Irr_atn_dec = 21.2[dB]
Irr_atn_noe = 21.2[dB]
Irr_noise = WALTZ
Decoupling = TRUE
Initial_wait = 1[s]
Noe = TRUE
Noe_time = 2[s]
Recvr_gain = 60
Relaxation_delay = 2[s]
Repetition_time = 2.69206016[s]
Temp_get = 25.9[dC]
158.8177
147.1461
134.1436
127.5753
114.4387
113.3280
77.2120
77.0013
76.7907
59.3072
55.2762
50.8239
44.0450
40.9236
39.0087
33.0053
31.7031
28.5722
25.0582
24.2348
15.2824
abundance
X : parts per Million : 13C