Supporting Information

(Revised February 9, 2011)

Total Synthesis of (±)-Lysergic Acid, Lysergol, and Isolysergol by Palladium-Catalyzed Domino Cyclization of Amino Allenes Bearing a Bromoindolyl Group

Shinsuke Inuki, Shinya Oishi, Nobutaka Fujii,* and Hiroaki Ohno*

Graduate School of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

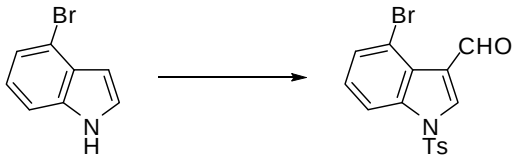
E-mail: hohno@pharm.kyoto-u.ac.jp; n-fujii@pharm.kyoto-u.ac.jp

Table of Contents

Experimental Section ····· 2
NMR Spectra ····· 20

Experimental Section

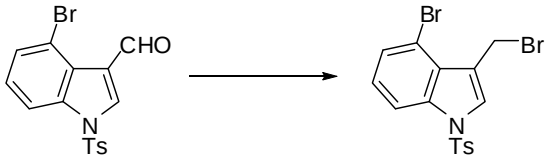
General Methods. All moisture-sensitive reaction were performed using syringe-septum cap techniques under an argon atmosphere and all glassware was dried in an oven at 80 °C for 2 h prior to use. Reactions at –78 °C employed a CO_2–MeOH bath. Melting points were measured by a hot stage melting point apparatus and are uncorrected. For flash chromatography, Wakosil C-300 was employed. ^{1}H NMR spectra were recording using a JEOR AL-400 or JEOL ECA-500 spectrometer, and chemical shifts are reported in δ (ppm) relative to TMS (in $CDCl_3$) as internal standard. ^{13}C NMR spectra were recorded using a JEOR AL-400 or JEOL ECA-500 spectrometer and referenced to the residual $CHCl_3$ signal. NOE spectra were recorded on 500 MHz instruments. Chemical shifts were reported in parts per million with the residual solvent peak used as an internal standard. ^{1}H NMR spectra are tabulated as follows: chemical shift, multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), number of protons, and coupling constant(s). Exact mass (HRMS) spectra were recorded on a JMS-HX/HX 110A mass spectrometer. Infrared (IR) spectra were obtained on a JASCO FT/IR-4100 FT-IR spectrometer with JASCO ATR PRO410-S. Microwave reaction was conducted in a sealed glass vessel (capacity 10 mL) using CEM Discover microwave reactor. The temperature was monitored using IR sensor mounted under the reaction vessel. For analytical HPLC, a Cosmosil 5C18-ARII column (4.6 × 250 mm, Nacalai Tesque Inc., Kyoto, Japan) was employed on a Shimadzu LC-10ADvp (Shimadzu Corp., Ltd., Kyoto, Japan). Preparative HPLC was performed using a Cosmosil 5C18-ARII column (20 × 250 mm, Nacalai Tesque Inc.) on a Shimadzu LC-6AD (Shimadzu Corp., Ltd.).



8 **S1**

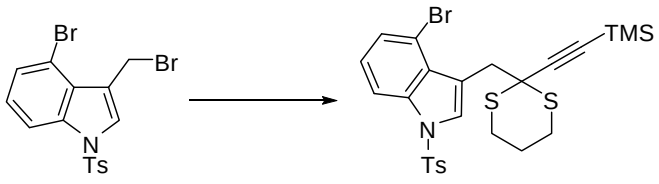
4-Bromo-1-tosyl-1*H*-indole-3-carbaldehyde (S1). The formylation of 4-bromoindole was carried out according to the method of Shea.[1] To a stirred DMF (6 mL) was added $POCl_3$ (0.98 mL, 10.5 mmol) at 0 °C under argon. The solution was stirred for 2 min, and then 4-bromoindole (940 mg, 4.7 mmol) in DMF (5 mL) was added. The mixture was stirred for 1 h neatoom temperature and was slowly quenched with KOH (2.66 g) in water (10 mL). The reaction mixture was left to cool overnight, and was then partitioned between EtOAc and saturated aqueous $NaHCO_3$. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure to give off a crude aldehyde as a white solid. To a stirred solution of this aldehyde in CH_2Cl_2 (40 mL) were added TsCl (1.08 g, 5.6 mmol), Et_3N (1.05 mL, 7.5 mmol) and DMAP (57.4 mg, 0.47 mmol) at 0 °C, and the mixture was stirred for 2 h at room temperature. The mixture was made acidic with 1N HCl, and whole was extracted with EtOAc. The extract was washed with brine, dried over

$MgSO_4$, and concentrated under pressure to give a white solid, which was purified by column chromatography over silica gel with *n*-hexane–EtOAc (7:1) to give **S1** (1.59 g, 90% yield). Recrystallization from *n*-hexane–chloroform gave essentially pure **S1** as colorless crystals: mp 176 °C; IR (neat): 1676 (C=O), 1381 (NSO_2), 1176 (NSO_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.38 (s, 3H), 7.24 (dd, *J* = 8.2, 8.2 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 2H), 8.00 (d, *J* = 8.2 Hz, 1H), 8.41 (s, 1H), 10.29 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 112.9, 113.9, 122.0, 126.1, 127.0, 127.3 (2C), 128.9, 130.4 (2C), 132.0, 134.1, 136.2, 146.4, 186.2. *Anal*. Calcd for $C_{16}H_{12}BrNO_3S$: C, 50.81; H, 3.20; N, 3.70. Found: C, 50.81; H, 3.16; N, 3.71.



S1 **9**

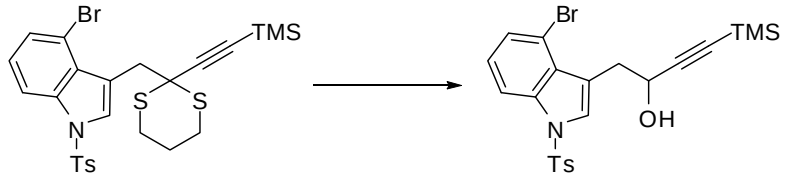
4-Bromo-3-(bromomethyl)-1-tosyl-1*H*-indole (9). To a stirred solution of the aldehyde **S1** (4.30 g, 11.4 mmol) in MeOH (300 mL) was added $NaBH_4$ (1.24 g, 32.7 mmol) at 0 °C. After stirring for 1.5 h at room temperature, H_2O was added, and the mixture was concentrated under reduced pressure. The residue was diluted with Et_2O, and the organic phase was separated and washed with brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give a crude alcohol as a white solid, which was used without further purification. To a stirred solution of this alcohol in CH_2Cl_2 (60 mL) was added Ph_3PBr_2 (5.30 g, 12.5 mmol) in CH_2Cl_2 (50 mL). The mixture was stirred overnight at room temperature. Concentration under reduced pressure gave an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (7:1) to give **9** (4.46 g, 89% yield). Recrystallization from *n*-hexane–chloroform gave pure **9** as colorless crystals: mp 157 °C; IR (neat): 1375 (NSO_2), 1173 (NSO_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.36 (s, 3H), 4.88 (s, 2H), 7.17 (dd, *J* = 8.1, 8.1 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.75 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.93 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 24.7, 112.9, 114.2, 119.6, 126.1, 127.0 (2C), 127.1, 127.9, 128.2, 130.1 (2C), 134.7, 136.3, 145.6. *Anal*. Calcd for $C_{16}H_{13}Br_2NO_2S$: C, 43.36; H, 2.96; N, 3.16. Found: C, 43.57; H, 2.75; N, 2.90.



9 **11**

4-Bromo-1-tosyl-3-[2-(trimethylsilylethynyl)-1,3-dithian-2-yl]methyl-1*H*-indole (11). To a stirred solution of the 2-(trimethylsilylethynyl)-1,3-dithiane **10** (38.3 mg, 0.177 mmol) in THF (1

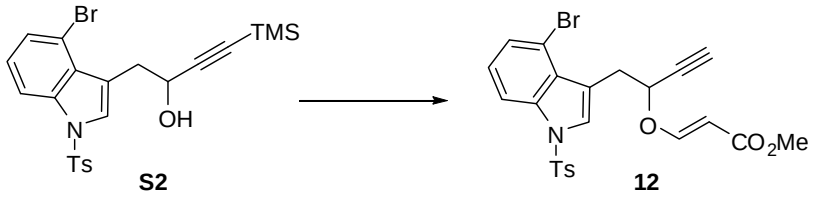
mL) was added *n*-BuLi (1.65 M solution in hexane; 0.12 mL, 0.195 mmol) at –40 °C under argon. After stirring for 1 h with warming to –20 °C, a solution of the bromide **9** (72.5 mg, 0.164 mmol) in THF (0.2 mL) was added to this reagent at –20 °C. The mixture was stirred for 2 h at this temperature and quenched with H_2O. The whole was extracted with Et_2O. The extract was washed with brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (7:1) to give **11** (90.6 mg, 96% yield). Recrystallization from MeCN gave pure **11** as colorless crystals: mp 138 °C; IR (neat): 2157 (C≡C), 1374 (NSO_2), 1173 (NSO_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.05 (s, 9H), 1.82-1.92 (m, 1H), 2.14-2.21 (m, 1H), 2.33 (s, 3H), 2.83 (ddd, *J* = 13.9, 3.3, 3.3 Hz, 2H), 3.29-3.37 (m, 2H), 3.78 (s, 2H), 7.07 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.94 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.00 (3C), 21.8, 25.8, 29.1 (2C), 36.7, 47.1, 93.1, 103.2, 113.1, 115.0, 116.1, 125.3, 127.2 (2C), 128.4, 128.6, 129.5, 130.1 (2C), 135.2, 136.1, 145.2. *Anal*. Calcd for $C_{25}H_{28}BrNO_2S_3Si$: C, 51.89; H, 4.88; N, 2.42. Found: C, 51.66; H, 4.78; N, 2.24.



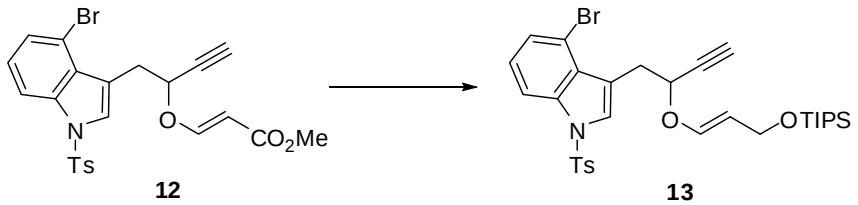
11 **S2**

(±)-1-(4-Bromo-1-tosyl-1*H*-indol-3-yl)-4-(trimethylsilyl)but-3-yn-2-ol (S2). To a stirred mixture of NCS (786 mg, 5.89 mmol) and $AgNO_3$ (1.03 g, 6.06 mmol) in MeCN (25 mL) and H_2O (5 mL) was added thioacetal **11**(1.00 g, 1.73 mmol) in MeCN (8 mL) at 0 °C. The mixture was stirred for 5 min at this temperature and quenched with saturated Na_2SO_3, saturated $NaHCO_3$ and brine (1:1:1). The mixture was filtered through a short pad of celite with EtOAc. The filtrate was extracted with Et_2O. The extract was washed with saturated Na_2SO_3, saturated $NaHCO_3$ and brine (1:1:1), brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give a yellow oily residue, which was used without further purification. To a stirred solution of the crude ketone in MeOH (50 mL) was added $CeCl_3 \cdot 7H_2O$ (838 mg, 2.25 mmol) at room temperature. After stirring for 10 min, $NaBH_4$ (118 mg, 3.11 mmol) was added to this solution at –20 °C. The mixture was stirred for 1 h at this temperature and quenched with H_2O. The mixture was concentrated under reduced pressure. The residue was diluted with Et_2O, and the extract was washed with brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (4:1) to give **S2** as a white amorphous solid (530 mg, 63% yield): IR (neat): 3540 (OH), 2172 (C≡C), 1373 (NSO_2), 1173 (NSO_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.16 (s, 9H), 1.90 (d, *J* = 5.1 Hz, 1H), 2.35 (s, 3H), 3.33 (dd, *J* = 14.0, 6.8 Hz, 1H), 3.42 (dd, *J* = 14.0, 6.8 Hz, 1H), 4.72 (ddd, *J* = 6.8, 6.8, 5.1 Hz, 1H), 7.11 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.0, 1H) , 7.59 (s, 1H), 7.73 (d,

J = 8.4 Hz, 2H), 7.94 (d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.00 (3C), 21.8, 34.6, 63.1, 90.8, 105.9, 113.1, 114.6, 117.8, 125.5, 127.1 (2C), 127.2, 128.1, 128.9, 130.2 (2C), 135.2, 136.5, 145.4; HRMS (FAB) calcd $C_{22}H_{23}BrNO_3SSi$: $[M - H]^-$, 488.0357; found: $[M - H]^-$, 488.0351.

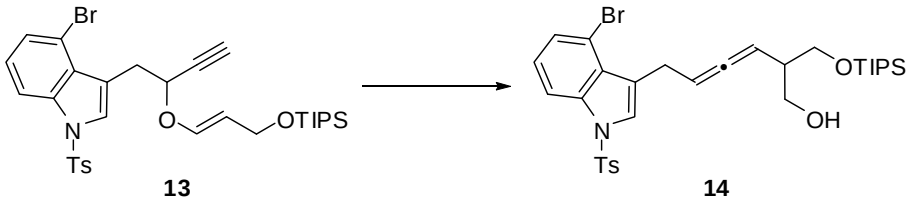


Methyl (±)-(*E*)-3-[1-(4-Bromo-1-tosyl-1*H*-indol-3-yl)but-3-yn-2-yloxy]acrylate (12). To a stirred solution of the alcohol **S2** (84.2 mg, 0.17 mmol) in THF (3 mL) was added TBAF (1.00 M solution in THF; 0.22 mL, 0.22 mmol) at 0 °C. The mixture was stirred for 1 h at this temperature and quenched with H_2O. The whole was extracted with EtOAc. The extract was washed with H_2O, brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give a pale yellow amorphous solid, which was used without further purification. To a stirred solution of this amorphous solid in Et_2O (1.5 mL) were added methyl propiolate (0.028 mL, 0.31 mmol) and Et_3N (0.043 mL, 0.31 mmol) at room temperature. The mixture was stirred overnight at room temperature. Concentration under pressure gave an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (4:1) to give **12** as a white amorphous solid (78.9 mg, 92% yield): IR (neat): 2122 (C≡C), 1709 (C=O), 1625 (C=C), 1373 (NSO_2), 1173 (NSO_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H), 2.59 (d, J = 2.1 Hz, 1H), 3.47 (dd, J = 13.9, 6.8 Hz, 1H), 3.53 (dd, J = 13.9, 6.8 Hz, 1H), 3.70 (s, 3H), 4.90 (ddd, J = 6.8, 6.8, 2.1 Hz, 1H), 5.38 (d, J = 12.4 Hz, 1H), 7.14 (dd, J = 8.0, 8.0 Hz, 1H), 7.22 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.0 Hz, 1H) , 7.55 (s, 1H), 7.57 (d, J = 12.4 Hz, 1H), 7.71 (d, J = 8.3 Hz, 2H), 7.97 (d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 32.2, 51.2, 71.0, 76.8, 79.6, 99.1, 113.1, 114.0, 116.2, 125.6, 126.8 (2C), 127.5, 127.9, 128.2, 130.0 (2C), 134.7, 136.4, 145.4, 159.9, 167.7; HRMS (FAB) calcd $C_{23}H_{19}BrNO_5S$: $[M - H]^-$, 500.0173; found: $[M - H]^-$, 500.0174.



(±)-(*E*)-4-Bromo-1-tosyl-3-{2-[3-(triisopropylsilyloxy)prop-1-enyloxy]but-3-ynyl}-1*H*-indole (13). To a stirred solution of the enol ether **12** (200 mg, 0.40 mmol) in Et_2O (6.5 mL) was added DIBAL-H (0.99 M solution in toluene; 1.0 mL, 1.0 mmol) at –78 °C. The mixture was stirred for 50 min at this temperature and quenched with 2N Rochelle salt. After stirring for 1.5 h, the whole was extracted with Et_2O. The extract was washed with brine and dried over $MgSO_4$. The filtrate was

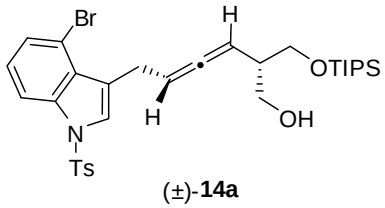
concentrated under reduced pressure to give a crude alcohol as a white amorphous solid, which was used without further purification. To a stirred solution of this alcohol in DMF (2.0 mL) were added imidazole (81.7 mg, 1.2 mmol) and TIPSCl (0.127 mL, 0.60 mmol) at 0 °C. After stirring overnight at room temperature, the mixture was diluted with Et_2O. The organic phase was separated and washed with H_2O, brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (15:1) to give **13** as a colorless oil (239 mg, 95% yield): IR (neat): 2116 (C≡C), 1665 (C=C), 1369 (NSO_2), 1173 (NSO_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.04-1.09 (m, 21H), 2.34 (s, 3H), 2.48 (d, *J* = 2.3 Hz, 1H), 3.37 (dd, *J* = 13.7, 6.9 Hz, 1H), 3.52 (dd, *J* = 13.7, 6.9 Hz, 1H), 4.19 (d, *J* = 6.3 Hz, 2H), 4.75 (ddd, *J* = 6.9, 6.9, 2.3 Hz, 1H), 5.19 (dt, *J* = 12.0, 6.3 Hz, 1H), 6.48 (d, *J* = 12.0 Hz, 1H), 7.11 (dd, *J* = 8.3, 8.3 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.57 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.1 (3C), 18.0 (6C), 21.6, 32.4, 61.0, 69.2, 75.3, 81.2, 107.2, 113.0, 114.2, 117.1, 125.4, 126.9 (2C), 127.3, 127.9, 128.6, 129.9 (2C), 134.9, 136.3, 145.2, 145.5; HRMS (FAB) calcd $C_{31}H_{39}BrNO_4SSi$: $[M - H]^-$, 628.1558; found: $[M - H]^-$, 628.1555.



(±)-(2*S*,a*R*)-6-(4-Bromo-1-tosyl-1*H*-indol-3-yl)-2-(triisopropylsilyloxymethyl)hexa-3,4-dien-1-ol (14a) and (±)-(2*R*,a*R*)-Isomer (14b).

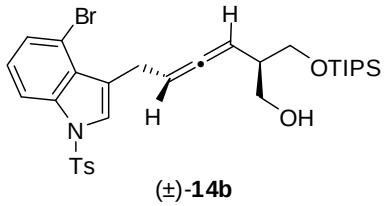
Microwave conditions (Table 1, entry 2): A solution of the silyl enol ether **13** (31 mg, 0.049 mmol) in $CHCl_3$ was heated under microwave irradiation at 120 °C for 12 min, then 150 °C for 12 min. The mixture was diluted with MeOH (0.4 mL), $NaBH_4$ (2.2 mg, 0.059 mmol) was added at room temperature. The mixture was stirred for 1 h at room temperature. Concentration under pressure gave an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (5:1) to give **14** as a colorless oil (25.4 mg, 82% yield, **a**:**b** = *ca.* 33:67).

Au-Catalyzed conditions (Table 1, entry 3): To a stirred solution of the silyl enol ether **13** (50 mg, 0.079 mmol) in CH_2Cl_2 (0.25 mL) was added $[(Ph_3PAu)_3O]BF_4$ (4.3 mg, 0.004 mmol) at room temperature. After stirring for 7.5 h at 40 °C, the mixture was diluted with MeOH (0.5 mL). $NaBH_4$ (3.6 mg, 0.095 mmol) was added at room temperature, and the mixture was stirred for 1 h at room temperature. Concentration under pressure gave an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (5:1) to give **14** as a colorless oil (39.1 mg, 78% yield, **a**:**b** = *ca.* 80:20). Both diastereomers were isolated by HPLC [5C18-ARII column, 254 nm, MeCN:H_2O = 86:14, 8 mL/min; for analytical HPLC: 1 mL/min, t_1 = 48.25 min (minor isomer), t_2 = 49.80 min (major isomer)].



(±)-**14a**

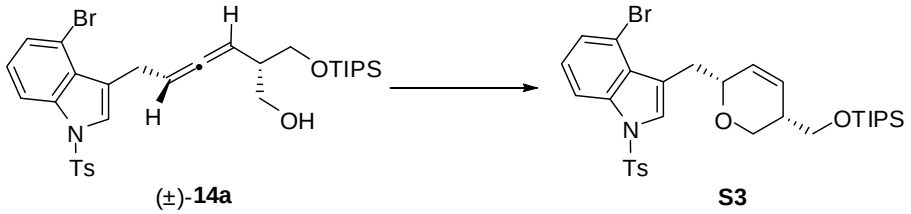
14a: IR (neat): 3456 (OH), 1963 (C=C=C), 1374 (NSO_2), 1173 (NSO_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.07-1.10 (m, 21H), 2.34 (s, 3H), 2.39-2.46 (m, 1H), 2.59 (dd, *J* = 6.3, 5.2 Hz, 1H), 3.52-3.72 (m, 5H), 3.78 (dd, *J* = 9.7, 4.6 Hz, 1H), 5.02 (ddd, *J* = 9.7, 6.3, 2.9 Hz, 1H), 5.45 (ddd, *J* = 13.1, 6.3, 2.3 Hz, 1H), 7.11 (dd, *J* = 8.5, 8.0 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.36 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.44 (s, 1H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.95 (dd, *J* = 8.5, 1.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.8 (3C), 17.9 (6C), 21.6, 26.5, 42.7, 65.9, 66.8, 89.8, 90.8, 112.9, 114.5, 121.8, 125.1, 125.4, 126.8 (2C), 127.7, 128.7, 129.9 (2C), 134.9, 136.5, 145.1, 204.7; HRMS (FAB) calcd $C_{31}H_{41}BrNO_4SSi$: $[M - H]^-$, 630.1714; found: $[M - H]^-$, 630.1707.



(±)-**14b**

14b: IR (neat): 3441 (OH), 1963 (C=C=C), 1375 (NSO_2), 1173 (NSO_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.02-1.07 (m, 21H), 2.35 (s, 3H), 2.38-2.46 (m, 1H), 2.60-2.67 (m, 1H), 3.55-3.72 (m, 5H), 3.78 (dd, *J* = 9.7, 4.0 Hz, 1H), 5.06 (ddd, *J* = 9.7, 6.3, 2.9 Hz, 1H), 5.44 (ddd, *J* = 13.2, 6.3, 2.3 Hz, 1H), 7.11 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.43 (s, 1H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.8 (3C), 17.9 (6C), 21.6, 26.5, 42.6, 66.0, 66.9, 89.8, 90.9, 112.9, 114.5, 121.8, 125.1, 125.4, 126.8 (2C), 127.7, 128.7, 129.9 (2C), 135.0, 136.5, 145.2, 204.7; HRMS (FAB) calcd $C_{31}H_{41}BrNO_4SSi$: $[M - H]^-$, 630.1714; found: $[M - H]^-$, 630.1705.

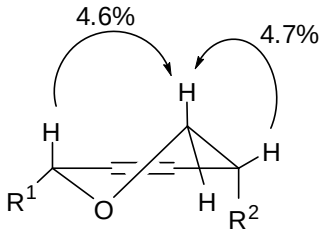
Determination of Relative Configuration of 14a:[2,3]



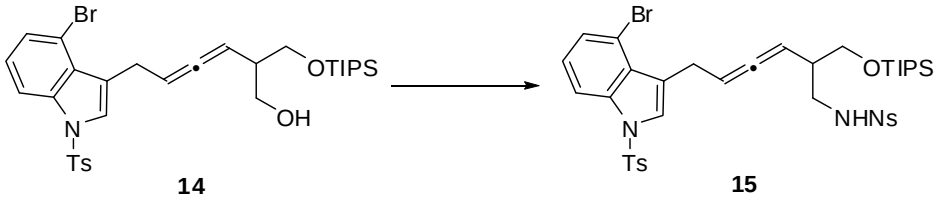
(±)-**14a** **S3**

(±)-4-Bromo-1-tosyl-3-{[(2*R*,5*S*)-5-(triisopropylsilyloxymethyl)-5,6-dihydro-2*H*-pyran-2-yl]methyl}-1*H*-indole (S3). To a stirred suspension of $AgBF_4$ (3.1 mg, 0.016 mmol) in toluene (2.5 mL) was added Ph_3PAuCl (7.8 mg, 0.016 mmol) at room temperature. After stirring rapidly for 5 min, the resulting mixture was filtered through a cotton plug. To a solution of allenol **14a** (20 mg, 0.032 mmol) in toluene (0.25 mL) was added the above filtrate (0.25 mL) at room temperature. The

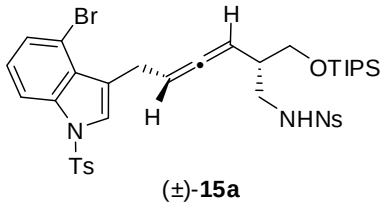
resulting mixture was stirred for 8.5 h at this temperature. Concentration under pressure gave an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (15:1) to give **S3** as a colorless oil (12.5 mg, 63% yield): IR (neat): 1598 (C=C), 1375 (NSO_2), 1173 (NSO_2); ^{1}H NMR (500 MHz, C_6D_6) δ 1.11-1.18 (m, 21H), 1.64 (s, 3H), 2.09-2.16 (br m, 1H), 3.16 (d, *J* = 6.3 Hz, 2H), 3.56 (dd, *J* = 11.2, 3.7 Hz, 1H), 3.72 (dd, *J* = 9.2, 5.4 Hz, 1H), 3.82 (dd, *J* = 9.2, 9.2 Hz, 1H), 4.15 (d, *J* = 11.2 Hz, 1H), 4.37-4.42 (m, 1H), 5.64 (d, *J* = 10.6 Hz, 1H), 5.70 (dd, *J* = 10.6, 4.3 Hz, 1H), 6.50 (d, *J* = 8.6 Hz, 2H), 6.71 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.72 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.0 (3C), 18.1 (6C), 21.6, 32.1, 38.3, 64.4, 73.5, 77.2, 113.0, 114.5, 119.4, 125.2, 126.4, 126.6, 126.9 (2C), 127.9, 129.0, 129.9 (2C), 131.0, 135.0, 136.5, 145.1; HRMS (FAB) calcd $C_{31}H_{41}BrNO_4SSi$: $[M + H]^+$, 630.1714; found: $[M + H]^+$, 630.1711.



Selected NOE cross peaks for pyran **S3**



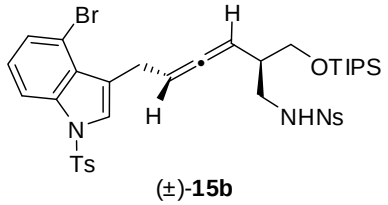
***N*-[(2*S*,a*R*)-6-(4-Bromo-1-tosyl-1*H*-indol-3-yl)-2-(triisopropylsilyloxymethyl)hexa-3,4-dienyl]-2-nitrobenzenesulfonamide (15a) and Its (±)-(2*R*,a*R*)-Isomer (15b).** To a stirred mixture of the allenol **14** (**a**:**b** = *ca.* 80:20) (300 mg, 0.48 mmol), $NsNH_2$ (317 mg, 1.57 mmol) and PPh_3 (630 mg, 2.40 mmol) in benzene (18 mL) was added diethyl azodicarboxylate (40% solution in toluene; 1.10 mL, 2.40 mmol) at room temperature, and the mixture was stirred for 1.5 h at this temperature. Concentration under pressure gave an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (3:1) to give **15** as a pale yellow amorphous solid (276 mg, 70% yield, **a**:**b** = 80:20).



(±)-**15a**

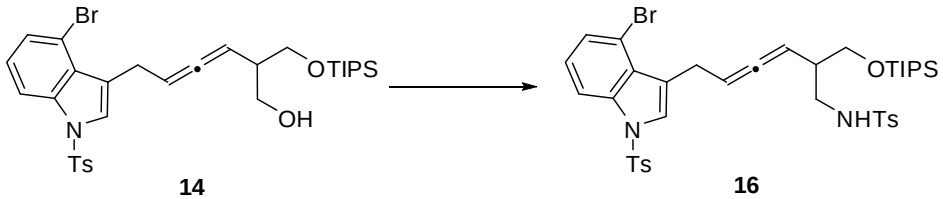
15a (major): IR (neat): 1962 (C=C=C), 1540 (NO_2), 1372 (NSO_2), 1172 (NSO_2); ^{1}H NMR (500

MHz, $CDCl_3$) δ 0.99-1.07 (m, 21H), 2.35 (s, 3H), 2.36-2.42 (m, 1H), 3.05 (ddd, *J* = 12.6, 6.3, 5.1 Hz, 1H), 3.27 (ddd, *J* = 12.6, 6.3, 5.3 Hz, 1H), 3.39 (dd, *J* = 10.3, 8.0 Hz, 1H), 3.56-3.70 (m, 2H), 3.61 (dd, *J* = 10.3, 4.6 Hz, 1H), 5.04 (ddd, *J* = 9.7, 6.3, 2.9 Hz, 1H), 5.49 (ddd, *J* = 13.2, 6.3, 2.3 Hz, 1H), 5.67 (t, *J* = 6.3 Hz, 1H), 7.10 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.38 (s, 1H), 7.64-7.70 (m, 2H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.79 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 8.09 (dd, *J* = 7.2, 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.8 (3C), 18.0 (6C), 21.6, 26.5, 41.5, 45.2, 65.1, 90.1, 91.8, 112.9, 114.4, 121.7, 125.0, 125.2, 125.5, 126.8 (2C), 127.7, 128.6, 130.0 (2C), 131.0, 132.6, 133.4, 133.8, 134.9, 136.5, 145.3, 148.0, 204.5; HRMS (FAB) calcd $C_{37}H_{45}BrN_3O_7S_2Si$: $[M - H]^-$, 814.1657; found: $[M - H]^-$, 814.1662.



(±)-**15b**

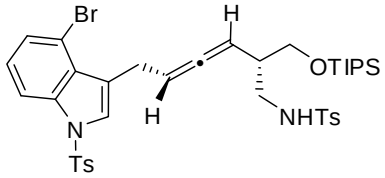
15b (minor): IR (neat): 1963 (C=C=C), 1541 (NO_2), 1372 (NSO_2), 1172 (NSO_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.99-1.05 (m, 21H), 2.31-2.34 (m, 1H), 2.35 (s, 3H), 3.10 (ddd, *J* = 12.6, 6.3, 5.7 Hz, 1H), 3.30 (ddd, *J* = 12.6, 6.3, 6.3 Hz, 1H), 3.40 (dd, *J* = 9.7, 7.4 Hz, 1H), 3.61 (dd, *J* = 9.7, 4.9 Hz, 1H), 3.61-3.64 (m, 2H), 5.00 (ddd, *J* = 9.7, 6.9, 3.4 Hz, 1H), 5.41 (ddd, *J* = 13.2, 6.9, 1.7 Hz, 1H), 5.65 (t, *J* = 6.3 Hz, 1H), 7.10 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.38 (s, 1H), 7.61-7.69 (m, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.77 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 8.09 (dd, *J* = 7.4, 1.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.8 (3C), 18.0 (6C), 21.6, 26.4, 41.6, 45.5, 65.1, 90.0, 91.5, 112.9, 114.5, 121.6, 125.1, 125.2, 125.4, 126.8 (2C), 127.7, 128.7, 130.0 (2C), 131.0, 132.6, 133.3, 133.8, 134.9, 136.5, 145.3, 148.0, 204.8; HRMS (FAB) calcd $C_{37}H_{45}BrN_3O_7S_2Si$: $[M - H]^-$, 814.1657; found: $[M - H]^-$, 814.1655.



14 **16**

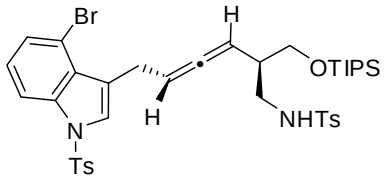
(±)-*N*-[(2*S*,a*R*)-6-(4-Bromo-1-tosyl-1*H*-indol-3-yl)-2-(triisopropylsilyloxymethyl)hexa-3,4-dien yl]-4-methylbenzenesulfonamide (16a) and Its (±)-(2*R*,a*R*)-Isomer (16b). To a stirred mixture of the allenol **14** (**a**:**b** = *ca.* 80:20; 150 mg, 0.24 mmol), FmocNHTs (308 mg, 0.78 mmol) and PPh_3 (312 mg, 1.19 mmol) in THF (4 mL) was added diethyl azodicarboxylate (0.54 mL, 1.19 mmol; 40% solution in toluene) at 0 °C, and the mixture was stirred for 3 h at room temperature. Concentration under pressure gave an oily residue, which was dissolved in DMF (7 mL). Piperidine (94 μL, 0.95 mmol) was added to the mixture at 0 °C. After stirring for 50 min at room temperature, the mixture was diluted with Et_2O and washed with H_2O, brine and dried over $MgSO_4$. The filtrate

was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (2:1) to give **16** as a yellow amorphous solid (136 mg, 73% yield, **a**:**b** = *ca.* 80:20).



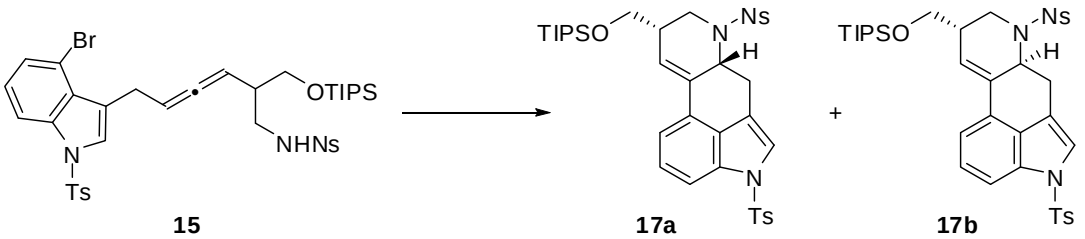
(±)-**16a**

16a (major): IR (neat): 1964 (C=C=C), 1374 (NSO_2), 1173 (NSO_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.98-1.04 (m, 21H), 2.29-2.34 (m, 1H), 2.34 (s, 3H), 2.40 (s, 3H), 2.98 (dd, *J* = 6.0, 6.0 Hz, 1H), 3.00 (dd, *J* = 6.0, 6.0 Hz, 1H), 3.36 (dd, *J* = 10.0, 8.3 Hz, 1H), 3.60 (dd, *J* = 10.0, 4.3 Hz, 1H), 3.60-3.64 (m, 2H), 4.96 (ddd, *J* = 9.1, 6.3, 2.9 Hz, 1H), 5.14 (t, *J* = 6.0 Hz, 1H), 5.44 (ddd, *J* = 13.2, 6.3, 2.3 Hz, 1H), 7.10 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.41 (s, 1H), 7.70-7.74 (m, 4H), 7.94 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.7 (3C), 17.9 (6C), 21.5, 21.6, 26.4, 40.5, 45.9, 66.4, 90.2, 91.6, 112.9, 114.4, 121.6, 125.1, 125.5, 126.8 (2C), 127.1 (2C), 127.7, 128.6, 129.6 (2C), 130.0 (2C), 134.9, 136.5, 137.0, 143.2, 145.2, 204.5; HRMS (FAB) calcd $C_{38}H_{48}BrN_2O_5S_2Si$: $[M - H]^-$, 783.1963; found: $[M - H]^-$, 783.1960.



(±)-**16b**

16b (minor): IR (neat): 1964 (C=C=C), 1374 (NSO_2), 1173 (NSO_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.94-1.04 (m, 21H), 2.27-2.33 (m, 1H), 2.35 (s, 3H), 2.41 (s, 3H), 2.99 (ddd, *J* = 6.3, 6.3, 1.7 Hz, 1H), 3.01 (ddd, *J* = 6.3, 6.3, 1.7 Hz, 1H), 3.35 (dd, *J* = 10.0, 7.7 Hz, 1H), 3.60 (dd, *J* = 10.0, 4.3 Hz, 1H), 3.61-3.65 (m, 2H), 4.94 (ddd, *J* = 9.7, 6.3, 2.9 Hz, 1H), 5.11 (t, *J* = 6.3 Hz, 1H), 5.42 (ddd, *J* = 13.2, 6.3, 2.3 Hz, 1H), 7.10 (dd, *J* = 8.2, 8.2 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.41 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.7 (3C), 17.9 (6C), 21.5, 21.6, 26.3, 40.5, 46.0, 66.4, 90.2, 91.5, 112.9, 114.4, 121.5, 125.1, 125.4, 126.8 (2C), 127.1 (2C), 127.7, 128.6, 129.6 (2C), 130.0 (2C), 134.9, 136.5, 137.0, 143.2, 145.2, 204.6; HRMS (FAB) calcd $C_{38}H_{48}BrN_2O_5S_2Si$: $[M - H]^-$, 783.1963; found: $[M - H]^-$, 783.1968.

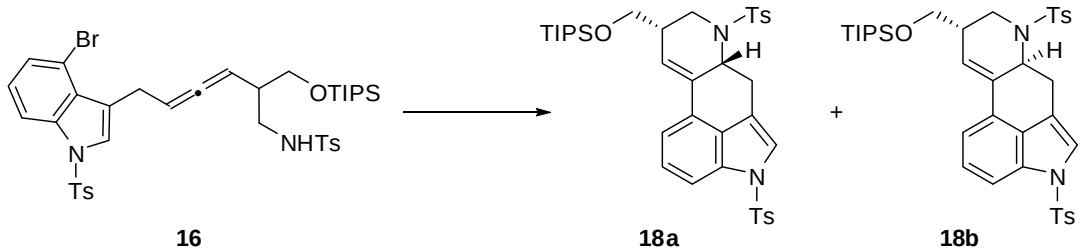


15 **17a** **17b**

(±)-(6a*R*,9*S*)-7-(2-Nitrophenylsulfonyl)-4-tosyl-9-(triisopropylsilyloxymethyl)-4,6,6a,7,8,9-hexahydroindolo[4,3-*fg*]quinoline (17a) and Its (±)-(6a*S*,9*S*)-Isomer (17b) (Table 2, Entry 3). To a stirred mixture of allenamide **15** (**a**:**b** = 80:20; 30 mg, 0.037 mmol) in DMF (0.6 mL) were added $Pd(PPh_3)_4$ (2.1 mg, 0.0018 mmol) and K_2CO_3 (15 mg, 0.11 mmol) at room temperature under argon, and the mixture was stirred for 3.5 h at 100 °C. The mixture was diluted with Et_2O and washed with H_2O, brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give a yellow oil which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (5:1) to give **17** as a yellow amorphous solid (22.3 mg, 83% yield, **a**:**b** = 73:27). Both diastereomers were isolated by PTLC with hexane–*i*-Pr_2O (3:1).

17a (major): IR (neat): 1596 (C=C), 1544 (NO_2), 1359 (NSO_2), 1178 (NSO_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97-1.04 (m, 21H), 2.36 (s, 3H), 2.40-2.48 (br m, 1H), 2.95 (dd, *J* = 13.7, 10.9 Hz, 1H), 2.99 (ddd, *J* = 14.9, 12.0, 2.3 Hz, 1H), 3.27 (dd, *J* = 14.9, 5.2 Hz, 1H), 3.55 (dd, *J* = 9.7, 8.0 Hz, 1H), 3.69 (dd, *J* = 9.7, 5.7 Hz, 1H), 4.10 (dd, *J* = 13.7, 5.2 Hz, 1H), 4.75-4.80 (m, 1H), 6.16 (s, 1H), 7.18-7.21 (m, 2H), 7.23-7.30 (m, 3H), 7.60-7.65 (m, 2H), 7.66-7.71 (m, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 7.4 Hz, 1H), 8.04 (dd, *J* = 8.0, 1.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.8 (3C), 17.9 (6C), 21.6, 29.7, 38.2, 43.0, 54.1, 64.9, 112.7, 115.6, 117.3, 120.5, 124.0, 124.3, 125.8, 126.8 (2C), 128.2, 130.0 (2C), 130.2, 131.0, 131.8, 133.4, 133.5, 133.6, 133.8, 135.4, 144.9, 147.9; HRMS (FAB) calcd $C_{37}H_{44}N_3O_7S_2Si$: $[M - H]^-$, 734.2395; found: $[M - H]^-$, 734.2392.

17b (minor): IR (neat): 1597 (C=C), 1542 (NO_2), 1359 (NSO_2), 1174 (NSO_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.94-1.01 (m, 21H), 2.36 (s, 3H), 2.53-2.58 (br m, 1H), 2.99 (ddd, *J* = 14.3, 12.0, 2.3 Hz, 1H), 3.12 (dd, *J* = 14.3, 5.0 Hz, 1H), 3.33 (dd, *J* = 9.7, 8.0 Hz, 1H), 3.35 (dd, *J* = 13.7, 3.4 Hz, 1H), 3.48 (dd, *J* = 9.7, 6.9 Hz, 1H), 3.97 (d, *J* = 13.7 Hz, 1H), 4.74 (dd, *J* = 12.0, 5.0 Hz, 1H), 6.31 (d, *J* = 5.2 Hz, 1H), 7.15 (d, *J* = 2.3 Hz, 1H), 7.18 (d, *J* = 6.9 Hz, 1H), 7.24 (d, *J* = 8.6 Hz, 2H), 7.28 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.62-7.72 (m, 3H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 8.14 (dd, *J* = 7.4, 1.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.9 (3C), 18.0 (6C), 21.6, 28.7, 39.5, 40.3, 53.9, 63.9, 112.7, 115.7, 117.2, 120.4, 123.1, 124.3, 125.8, 126.8 (2C), 128.2, 130.0 (2C), 130.6, 131.4, 131.9, 133.3, 133.6, 134.0, 134.1, 135.4, 144.9, 147.8; HRMS (FAB) calcd $C_{37}H_{44}N_3O_7S_2Si$: $[M - H]^-$, 734.2395; found: $[M - H]^-$, 734.2392.



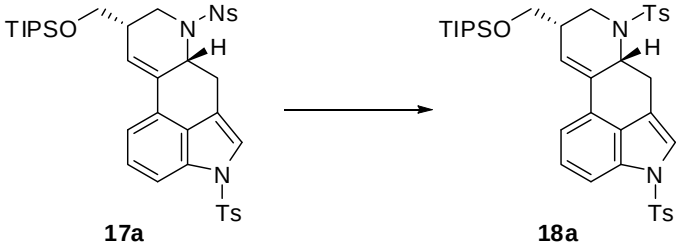
16 **18a** **18b**

(±)-(6a*R*,9*S*)-4,7-Ditosyl-9-(triisopropylsilyloxymethyl)-4,6,6a,7,8,9-hexahydroindolo[4,3-*fg*]quinoline (18a) and Its (±)-(6a*S*,9*S*)-Isomer (18b) (Table 2, Entry 12). To a stirred mixture of allenamide **16** (**a**:**b** = *ca.* 80:20; 30 mg, 0.038 mmol) in DMF (0.6 mL) were added $Pd(PPh_3)_4$ (2.2 mg, 0.0019 mmol) and K_2CO_3 (15.8 mg, 0.11 mmol) at room temperature under argon, and the mixture was stirred for 3 h at 120 °C. The mixture was diluted with Et_2O and washed with H_2O, brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give a yellow oil which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (6:1) to give **18** as a white amorphous solid (17.3 mg, 65% yield, **a**:**b** = 87:13). Both diastereomers were isolated by PTLC with hexane–*i*-Pr_2O (1:1).

18a (major): IR (neat): 1598 (C=C), 1376 (NSO_2), 1178 (NSO_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95-1.05 (m, 21H), 2.12-2.19 (br m, 1H), 2.35 (s, 3H), 2.39 (s, 3H), 2.84 (dd, *J* = 13.7, 10.6 Hz, 1H), 2.92 (ddd, *J* = 14.0, 12.0, 1.7 Hz, 1H), 3.33 (dd, *J* = 14.0, 5.4 Hz, 1H), 3.46 (dd, *J* = 9.6, 8.6 Hz, 1H), 3.63 (dd, *J* = 9.6, 5.4 Hz, 1H), 4.11 (dd, *J* = 13.7, 5.2 Hz, 1H), 4.67-4.73 (m, 1H), 6.07 (s, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 7.20-7.28 (m, 6H) , 7.67 (d, *J* = 8.0 Hz, 2H) , 7.77 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.9 (3C), 17.9 (6C), 21.5, 21.6, 30.0, 37.3, 42.9, 53.6, 65.0, 112.7, 115.5, 117.7, 120.5, 124.0, 125.7, 126.8 (2C), 126.9 (2C), 128.3, 129.8 (2C), 129.9 (2C), 130.2, 133.3, 133.4, 135.5, 138.0, 143.3, 144.8; HRMS (FAB) calcd $C_{38}H_{49}N_2O_5S_2Si$: $[M + H]^+$, 705.2852; found: $[M + H]^+$, 705.2850.

18b (minor): IR (neat): 1598 (C=C), 1377 (NSO_2), 1173 (NSO_2), ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.99-1.05 (m, 21H), 2.35 (s, 3H), 2.40 (s, 3H), 2.49-2.55 (br m, 1H), 2.87 (ddd, *J* = 14.3, 12.0, 1.7 Hz, 1H), 3.21 (dd, *J* = 13.2, 3.7 Hz, 1H), 3.30-3.39 (m, 3H), 3.89 (d, *J* = 13.2 Hz, 1H), 4.64 (dd, *J* = 11.5, 4.6 Hz, 1H), 6.29 (d, *J* = 5.2 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 7.18 (s, 1H), 7.22-7.29 (m, 5H) , 7.72 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.9 (3C), 18.0 (6C), 21.5, 21.6, 28.4, 39.5, 39.9, 53.7, 64.3, 112.7, 115.6, 117.6, 120.5, 123.6, 125.8, 126.8 (2C), 127.1 (2C), 128.3, 129.7 (2C), 129.9 (2C), 130.7, 133.3, 134.1, 135.5, 138.1, 143.2, 144.8; HRMS (FAB) calcd $C_{38}H_{49}N_2O_5S_2Si$: $[M + H]^+$, 705.2852; found: $[M + H]^+$, 705.2849.

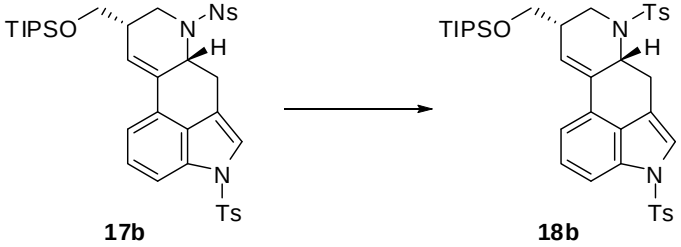
Determination of Relative Configuration of 18a:



17a **18a**

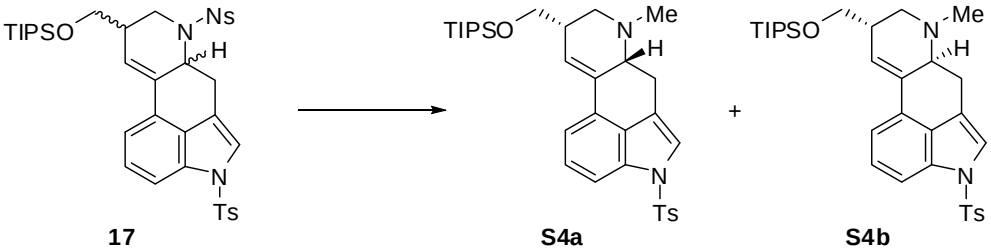
To a stirred mixture of **17a** (25 mg, 0.034 mmol) in DMF (0.2 mL) were added $LiOH·H_2O$ (14.3 mg 0.34 mmol) and $HSCH_2CO_2H$ (11.8 μL, 0.17 mmol) at 0 °C. After stirring for 1 h at room temperature, the mixture was diluted with EtOAc was washed with saturated $NaHCO_3$, brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give a crude amine as an oily residue, which was used without further purification. To a stirred solution of this amine in CH_2Cl_2 (0.25 mL) were added Et_3N (14.2 μL, 0.102 mmol) and TsCl (9.7 mg, 0.051 mmol) at 0 °C. After stirring for 2 h at room temperature, the mixture was diluted with EtOAc and washed with H_2O, brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (6:1) to give **18a** as a white amorphous solid (18.1 mg, 76% yield).

Determination of Relative Configuration of 18b:



17b **18b**

By a procedure identical with that described for synthesis of **18a** from **17a**, the nosylamide **17b** (24 mg, 0.033 mmol) was converted into **18b** as a white amorphous solid (13.8 mg, 59% yield).



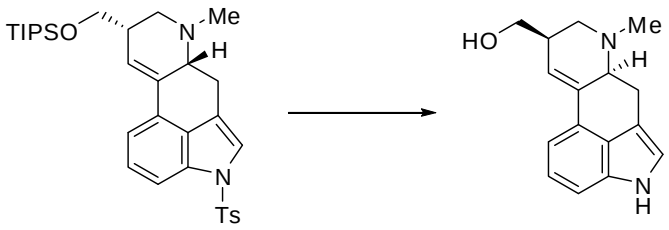
17 **S4a** **S4b**

(±)-(6a*R*,9*S*)-7-Methyl-4-tosyl-9-(triisopropylsilyloxymethyl)-4,6,6a,7,8,9-hexahydroindolo[4,3-*fg*]quinoline (S4a) and Its (±)-(6a*S*,9*S*)-Isomer (S4b). To a stirred mixture of **17** (**a**:**b** = 74:26) (136 mg, 0.19 mmol) in DMF (1.1 mL) were added $LiOH·H_2O$ (78 mg 1.9 mmol) and $HSCH_2CO_2H$ (64 μL, 0.92 mmol) at 0 °C. After stirring for 1 h at room temperature, the mixture was diluted with

EtOAc and washed with saturated $NaHCO_3$, brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give a crude amine as an oily residue, which was used without further purification. To a stirred solution of this amine in DMF (2.0 mL) were added K_2CO_3 (41 mg, 0.30 mmol) and MeI (15 μL, 0.24 mmol) at 0 °C. After stirring for 5 h at room temperature, the mixture was diluted with EtOAc and washed with saturated $NaHCO_3$, brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (5:1 to 3:1) to give **S4a** (53.4 mg, 52% yield) and **S4b** (16.7 mg, 16% yield) both as a brown amorphous solid.

S4a: IR (neat): 1599 (C=C), 1379 (NSO_2), 1177 (NSO_2), ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.03-1.09 (m, 21H), 2.33 (s, 3H), 2.46 (s, 3H), 2.48-2.53 (m, 3H), 2.95-3.04 (m, 2H), 3.37 (dd, *J* = 15.4, 5.4 Hz, 1H), 3.72 (dd, *J* = 9.3, 5.2 Hz, 1H), 3.78 (dd, *J* = 9.3, 9.0 Hz, 1H), 6.37 (d, *J* = 3.9 Hz, 1H), 7.16-7.21 (m, 1H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.23-7.29 (m, 2H), 7.72-7.76 (m, 1H), 7.74 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.0 (3C), 18.0 (6C), 21.5, 27.2, 39.2, 43.7, 53.0, 62.2, 65.0, 112.2, 116.1, 118.4, 119.7, 123.2, 125.8, 126.7 (2C), 128.6, 129.8 (2C), 129.9, 133.5, 135.0, 135.5, 144.6; HRMS (FAB) calcd $C_{32}H_{43}N_2O_3SSi$: $[M - H]^-$, 563.2769; found: $[M - H]^-$, 563.2770.

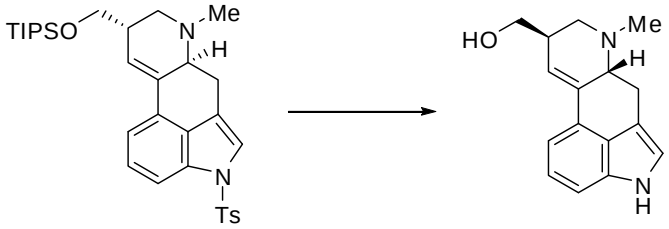
S4b: IR (neat): 1599 (C=C), 1379 (NSO_2), 1178 (NSO_2), ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.05-1.09 (m, 21H), 2.22 (dd, *J* = 10.7, 10.7 Hz, 1H), 2.33 (s, 3H), 2.50-2.58 (m, 4H), 2.82-2.93 (m, 1H), 2.98-3.01 (m, 1H), 3.07 (dd, *J* = 11.1, 5.0 Hz, 1H), 3.43 (dd, *J* = 15.1, 5.4 Hz, 1H), 3.65 (dd, *J* = 9.5, 7.6 Hz, 1H), 3.71 (dd, *J* = 9.5, 6.3 Hz, 1H), 6.38 (s, 1H), 7.19 (s, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.24-7.30 (m, 2H), 7.73-7.77 (m, 1H), 7.76 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.0 (3C), 18.0 (6C), 21.5, 27.0, 39.4, 44.0, 56.8, 62.5, 65.7, 112.2, 116.3, 118.1, 119.7, 123.9, 125.8, 126.7 (2C), 128.5, 129.6, 129.8, 133.5 (2C), 133.8, 135.6, 144.6; HRMS (FAB) calcd $C_{32}H_{43}N_2O_3SSi$: $[M - H]^-$, 563.2769; found: $[M - H]^-$, 563.2770.



S4a (±)-isolysergol (**3**)

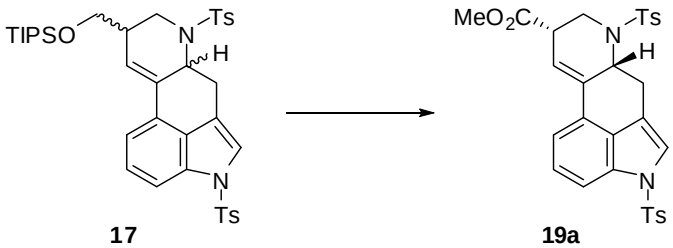
(±)-Isolysergol (3). To a stirred solution of **S4a** (8.3 mg, 0.015 mmol) in THF (0.33 mL) was added TBAF (1.00 M solution in THF; 18 μL, 0.018 mmol) at 0 °C. The mixture was stirred for 1 h at room temperature and quenched with H_2O. The whole was extracted with EtOAc. The extract was washed with H_2O, brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give a crude alcohol as a brown amorphous solid, which was used without further purification. To a stirred solution of this alcohol in MeOH (0.45 mL) was added Mg (3.6 mg, 0.15 mmol) at room temperature. The mixture was stirred for 2 h at this temperature. Concentration

under pressure gave an oily residue, which was purified by PTLC with EtOAc–MeOH (3:1) to give isolysergol **3** as a pale brown solid (3.8 mg, 99% yield): IR (neat): 3213 (OH), 1604 (C=C), The IR spectra was found to be identical with that of natural isolysergol.[4] ^{1}H NMR (500 MHz, $CDCl_3$–CD_3OD) δ 2.44-2.50 (m, 1H), 2.55 (s, 3H), 2.65 (ddd, *J* = 14.3, 11.5, 1.7 Hz, 1H), 2.85 (ddd, *J* = 11.5, 4.0, 1.7 Hz, 1H), 3.04 (d, *J* = 11.5 Hz, 1H), 3.14-3.19 (m, 1H), 3.53 (dd, *J* = 14.3, 5.7 Hz, 1H), 3.80 (ddd, *J* = 10.3, 3.6, 1.7 Hz, 1H), 3.96 (dd, *J* = 10.3, 3.4 Hz, 1H), 6.46 (d, *J* = 5.7 Hz, 1H), 6.89 (d, *J* = 1.7 Hz, 1H), 7.14-7.17 (m, 2H), 7.18-7.22 (m, 1H); The ^{1}H NMR spectra was found to be identical with that of synthesized isolysergol reported by Ninomiya and Naito.[5] ^{13}C NMR (125 MHz, $CDCl_3$–CD_3OD) δ 27.3, 36.3, 43.3, 57.4, 63.0, 66.0, 109.5, 109.9, 111.7, 118.2, 121.0, 122.9, 126.0, 128.0, 133.8, 136.7; HRMS (FAB) calcd $C_{16}H_{17}N_2O$: $[M - H]^-$, 253.1346; found: $[M - H]^-$, 253.1352.



S4b (±)-lysergol (**2**)

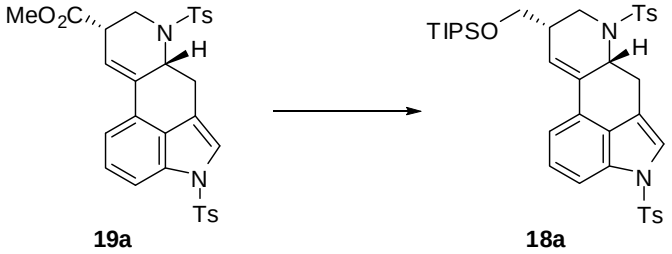
(±)-Lysergol (2). To a stirred solution of **S4b** (16.7 mg, 0.030 mmol) in THF (0.7 mL) was added TBAF (1.00 M solution in THF; 39 μL, 0.039 mmol) at 0 °C. The mixture was stirred for 1.5 h at room temperature and quenched with H_2O. The whole was extracted with EtOAc. The extract was washed with H_2O, brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give a crude alcohol as a brown amorphous solid, which was used without further purification. To a stirred solution of this alcohol in MeOH (0.85 mL) was added Mg (7.3 mg, 0.30 mmol) at room temperature. The mixture was stirred for 3 h at this temperature. Concentration under pressure gave an oily residue, which was purified by PTLC with EtOAc –MeOH (2:1) to give lysergol **2** as a pale brown solid (7.0 mg, 92% yield): IR (neat): 3427 (OH), 1606 (C=C), ^{1}H NMR (500 MHz, $CDCl_3$–CD_3OD) δ 2.36 (dd, *J* = 10.9, 10.9 Hz, 1H), 2.61 (s, 3H), 2.74 (ddd, *J* = 13.7, 12.0, 1.7 Hz, 1H), 2.85-2.93 (m, 1H), 3.17 (dd, *J* = 10.9, 5.2 Hz, 1H), 3.23-3.30 (m, 1H), 3.51-3.59 (m, 2H), 3.70 (dd, *J* = 10.9, 5.7 Hz, 1H), 6.41 (s, 1H), 6.94 (s, 1H), 7.13-7.18 (m, 2H), 7.20-7.25 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$–CD_3OD) δ 26.3, 38.1, 43.2, 56.5, 63.1, 64.6, 109.5 (2C), 111.6, 118.4, 121.0, 122.8, 125.8, 127.6, 133.9, 135.0; The IR, ^{1}H NMR and ^{13}C NMR spectra were found to be identical with those of natural lysergol. HRMS (FAB) calcd $C_{16}H_{17}N_2O$: $[M - H]^-$, 253.1346; found: $[M - H]^-$, 253.1349.



17 **19a**

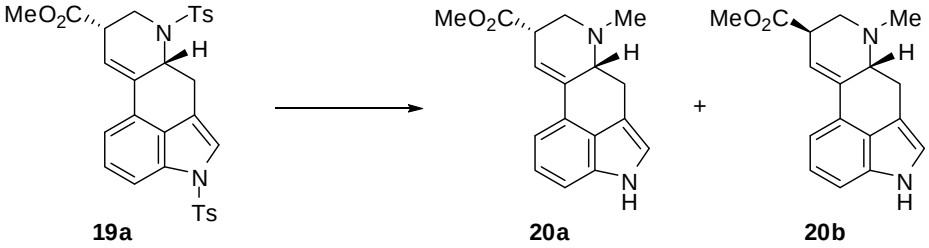
Methyl (±)-(6a*R*,9*S*)-4,7-ditosyl-4,6,6a,7,8,9-hexahydroindolo[4,3-*fg*]quinoline-9-carboxylate (19a). To a stirred solution of **17** (**a**:**b** = 74:26) (190 mg, 0.27 mmol) in THF (5 mL) was added TBAF (1.00 M solution in THF; 0.32 mL, 0.32 mmol) at 0 °C. The mixture was stirred for 40 min at room temperature and quenched with H_2O. The whole was extracted with EtOAc. The extract was washed with H_2O, brine and dried over $MgSO_4$. Concentration of the filtrate under reduced pressure followed by filtration through a short pad of SiO_2 with EtOAc give a crude alcohol. To a stirred solution of this alcohol in CH_2Cl_2 (10 mL) was added Dess-Martin periodinane (230 mg, 0.54 mmol) at 0 °C. After stirring for 30 min at this temperature, the mixture was warming to room temperature. The mixture was stirred for further 1 h at this temperature and filtrated through a short pad of SiO_2 with EtOAc to give a crude aldehyde. To a stirred mixture of the crude aldehyde and 2-methylbut-2-ene (1.66 mL, 16.2 mmol) in a mixed solvent of THF (2.9 mL) and *t*-BuOH (2.9 mL) were added $NaClO_2$ (117 mg, 1.30 mmol) and NaH_2PO_4 (155 mg, 1.30 mmol) at room temperature. After stirring for 1.5 h at room temperature, brine was added to the mixture. The whole was extracted with EtOAc. The extract was washed with brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give a crude carboxylic acid. To a stirred solution of this acid in a mixed solvent of toluene (1.7 mL) and MeOH (1.2 mL) was added $TMSCHN_2$ (2.00 M solution in Et_2O; 0.35 mL, 0.70 mmol) at 0 °C. The mixture was stirred for 30 min at room temperature. Concentration under pressure gave an oily residue, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (4:1) to give **19a** as a pale yellow amorphous solid (96.4 mg, 62% yield): IR (neat): 1736 (C=O), 1597 (C=C), 1347 (NSO_2), 1177 (NSO_2), ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.35 (s, 3H), 2.42 (s, 3H), 2.92 (ddd, J = 14.9, 12.0, 2.3 Hz, 1H), 3.03-3.08 (m, 1H), 3.19 (dd, J = 14.3, 10.9 Hz, 1H), 3.27 (dd, J = 14.9, 5.2 Hz, 1H), 3.70 (s, 3H), 4.26 (dd, J = 14.3, 5.2 Hz, 1H), 4.69-4.75 (m, 1H), 6.37 (s, 1H), 7.18-7.30 (m, 7H), 7.69 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 21.6, 29.4, 40.2, 40.8, 52.3, 53.0, 113.1, 115.9, 117.2, 120.4, 120.7, 125.8, 126.7 (4C), 128.3, 129.6, 129.9 (2C), 130.0 (2C), 133.4, 134.1, 135.4, 137.8, 143.7, 144.9, 171.2; HRMS (FAB) calcd for $C_{30}H_{29}N_2O_6S_2$: $[M + H]^+$, 577.1467; found: $[M + H]^+$, 577.1471.

Determination of Relative Configuration of 19a:



19a **18a**

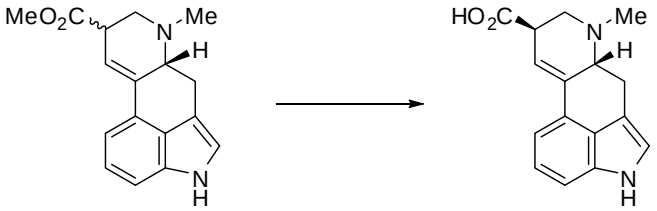
To a stirred solution of **19a** (5.0 mg, 0.0086 mmol) in MeOH (0.5 mL) was added $NaBH_4$ (1.63 mg, 0.043 mmol) at room temperature.[6] After stirring for 1 h at this temperature, H_2O was added, and the mixture was concentrated under reduced pressure. The residue was dissolved in EtOAc and washed with brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give a crude alcohol, which was used without further purification. To a stirred solution of this alcohol in DMF (0.2 mL) were added imidazole (16.6 mg, 0.24 mmol) and TIPSCl (0.026 mL, 0.12 mmol) at 0 °C. After stirring overnight at room temperature, the mixture was diluted with Et_2O and washed with H_2O, brine and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by PTLC with *n*-hexane–EtOAc (3:1) to give **18a** as a white amorphous solid (4.1 mg, 68% yield).



19a **20a** **20b**

(±)-Methyl Isolysergate (20a) and (±)-Methyl Lysergate (20b). To a stirred solution of **19a** (30 mg, 0.052 mmol) in THF (1.6 mL) was added sodium naphthalenide (0.67 M solution in THF; 0.78 mL, 0.52 mmol)[7] at −78 °C under argon. The mixture was stirred for 10 min at this temperature and quenched with saturated NH_4Cl. The mixture was made basic with saturated $NaHCO_3$. The whole was extracted with EtOAc. The extract was washed with brine and dried over $MgSO_4$. Concentration of the filtrate under reduced pressure gave a crude amine which was used without further purification. To a stirred solution of this amine in MeOH (3.0 mL) were added formalin (0.02 mL, 0.26 mmol), $NaBH_3CN$ (16.3 mg, 0.26 mmol) and AcOH (55 μL) at room temperature. After stirring for 1.5 h at this temperature, the mixture was quenched with saturated $NaHCO_3$. The mixture was concentrated under pressure followed by filtration through a short pad of SiO_2 with EtOAc. The filtrate was concentrated under reduced pressure to give a yellow solid, which was purified by flash chromatography over silica gel with *n*-hexane–EtOAc (1:10) to give **20a** and **20b** as a yellow solid (9.0 mg, 61% yield, **a**:**b** = 35:65). ^{1}H NMR spectra of **20a** and **20b** were in agreement with those reported by Hendrickson[8]: ^{1}H NMR (400 MHz, $CDCl_3$) of methyl

lysergate **20b** (major isomer): δ2.63 (s, 3H), 2.68-2.73 (m, 2H), 3.20-3.27 (m, 1H), 3.30 (dd, *J* = 11.6, 4.9 Hz, 1H), 3.53 (dd, *J* = 14.5, 5.5 Hz, 1H), 3.73-3.76 (m, 1H), 3.79 (s, 3H), 6.60 (s, 1H), 6.92 (t, *J* = 1.8 Hz, 1H), 7.16-7.25 (m, 3H), 7.92 (br s, 1H); methyl isolysergate **20a** (minor isomer): δ2.59 (s, 3H), 2.75-2.81 (m, 2H), 3.20-3.27 (m, 1H), 3.29-3.34 (m, 1H), 3.38 (dd, *J* = 11.6, 3.0 Hz, 1H), 3.44 (dd, *J* = 14.6, 5.4 Hz, 1H), 3.73 (s, 3H), 6.56 (d, *J* = 5.4 Hz, 1H), 6.91 (t, *J* = 1.8 Hz, 1H), 7.16-7.25 (m, 3H), 7.92 (br s, 1H); IR (neat): 3410 (NH), 1731 (C=O), 1604 (C=C); HRMS (FAB) calcd $C_{17}H_{17}N_2O_2$: $[M - H]^-$, 281.1296; found: $[M - H]^-$, 281.1304.



20 (±)-lysergic acid (**1**)

(±)-Lysergic Acid (1). The preparation of lysergic acid (**1**) was carried out according to the method of Hendrickson[8] and Szántay[9]: To solution of diastereomixture of methyl lysergate and isolysergate (20.6 mg, 0.073 mmol, **20a**:**b** = 35:65) in EtOH (0.68 mL) was added 1N NaOH (0.68 mL). The reaction mixture was stirred at 35 °C for 2 h. 0.1 N HCl solution was used to carefully adjust the pH to 6.2 and stirred for further 2 h at 0 °C while a solid material was formed. The precipitate was filtered off and washed with cold water and acetone to give **1** as a pale brown solid (10.6 mg, 54% yield). The IR, ^{1}H NMR and ^{13}C NMR spectra were in agreement with those reported by Hendrickson[8] and Szántay[9]: IR (neat): 3240 (OH), 1589 (C=O), ^{1}H NMR (500 MHz, C_5D_5N) δ 2.53 (s, 3H), 2.88-2.96 (m, 2H), 3.27-3.33 (m, 1H), 3.53 (dd, *J* = 11.2, 5.4 Hz, 1H), 3.64 (dd, *J* = 14.6, 5.4 Hz, 1H), 4.03-4.08 (m, 1H), 7.20-7.26 (m, 2H), 7.30 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 11.68 (s, 1H); ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 2.47 (s, 3H), 2.48-2.51 (m, 2H), 2.96-3.02 (m, 1H), 3.13 (dd, *J* = 11.5, 5.2 Hz, 1H), 3.46 (dd, *J* = 14.6, 5.4 Hz, 1H), 3.47-3.52 (m, 1H), 6.47 (br s, 1H), 7.01-7.08 (m, 3H), 7.18 (d, *J* = 7.4 Hz, 1H), 10.70 (br s, 1H); ^{13}C NMR (125 MHz, C_5D_5N) δ27.8, 43.2, 43.9, 56.0, 63.7, 110.4, 110.5, 112.2, 119.8, 120.1, 127.3, 128.8, 135.8, 136.7, 175.0 (one of the sp^2 carbons was overlapped with C_5D_5N solvent peaks); ^{13}C NMR [125 MHz, $(CD_3)_2SO$] δ26.6, 41.7, 43.2, 54.6, 62.5, 108.8, 109.9, 111.0, 118.7, 119.3, 122.3, 125.9, 127.3, 133.8, 135.4, 173.4; HRMS (FAB) calcd $C_{16}H_{17}N_2O_2$: $[M - H]^-$, 269.1290; found: $[M - H]^-$, 269.1289.

Reference:

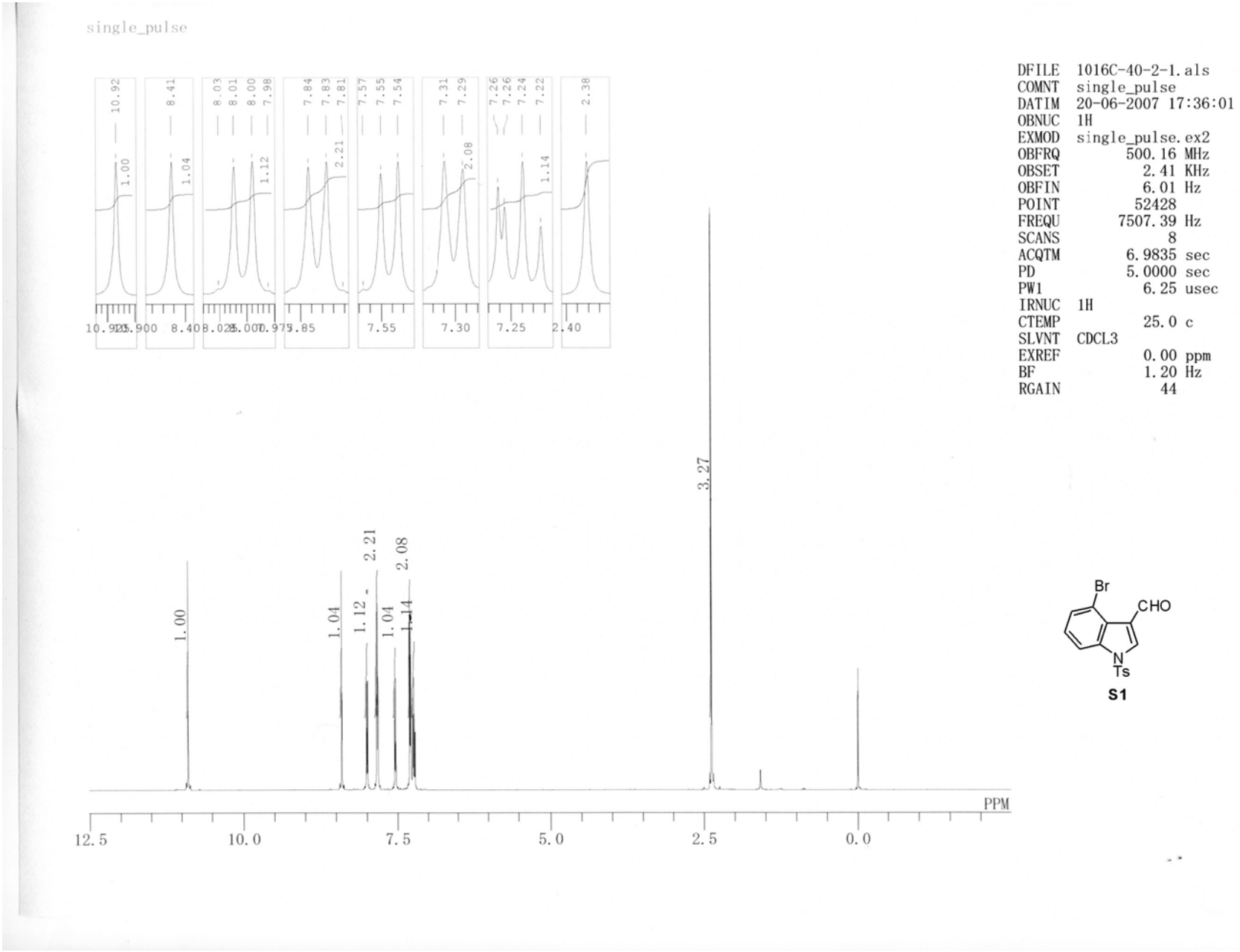
(1) Lauchli, R.; Shea, K. J. *Org. Lett.* **2006**, *8*, 5287-5289.

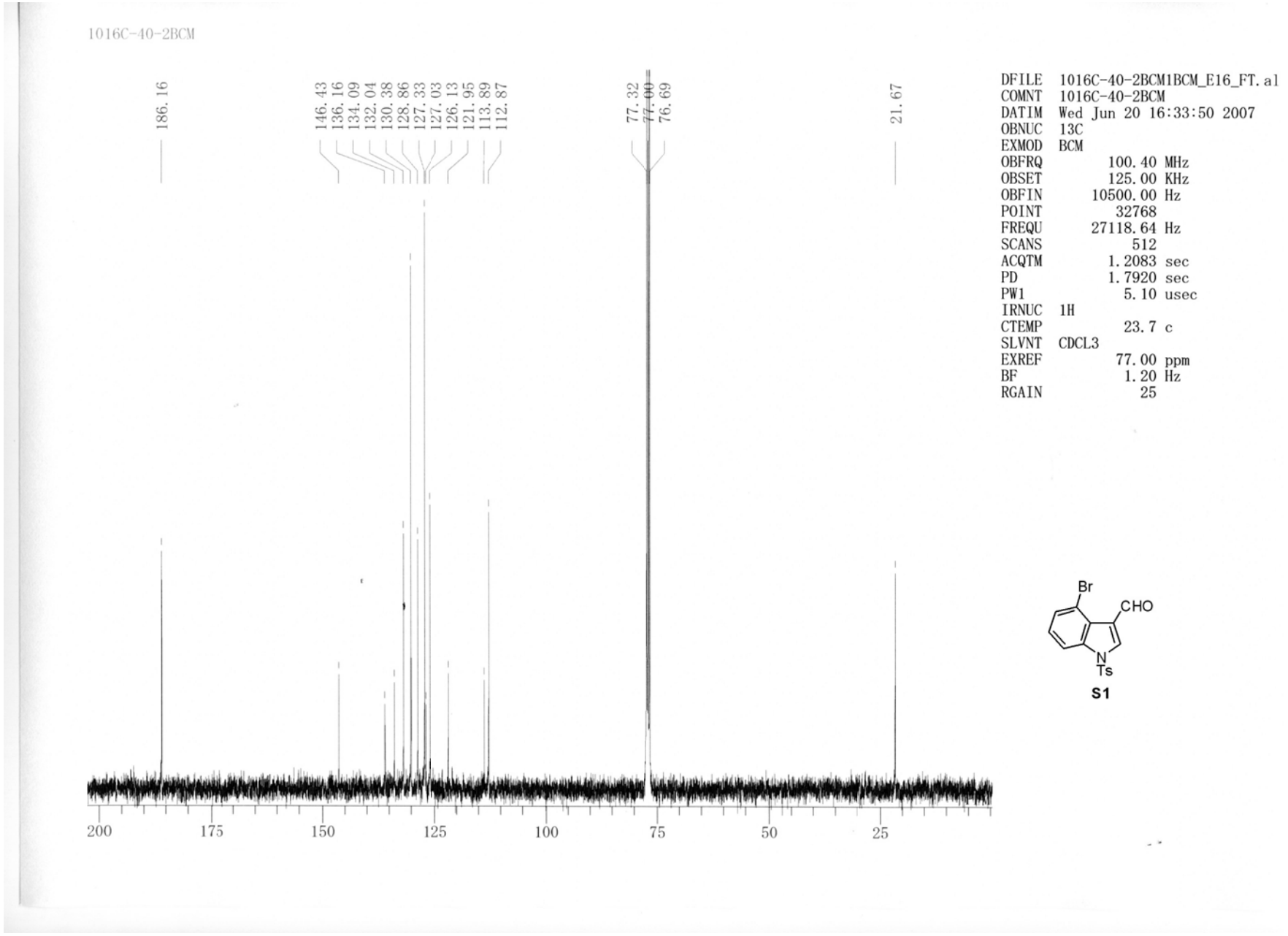
(2) Sherry, B. D.; Toste, F. D. *J. Am. Chem. Soc*. **2004**, *126*, 15978-15979.

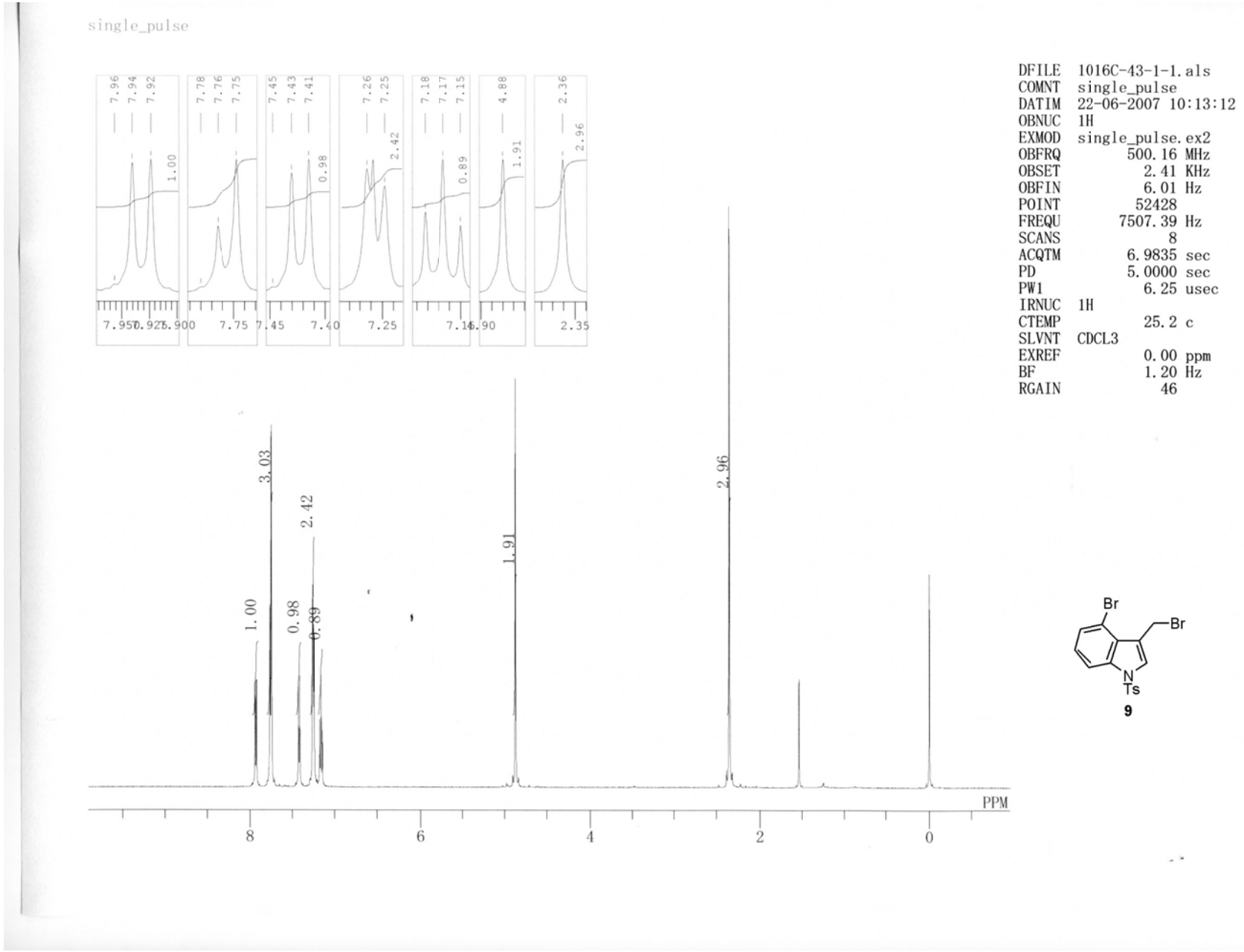
(3) Gockel, B.; Krause, N. *Org. Lett*. **2006**, *8*, 4485-4488.

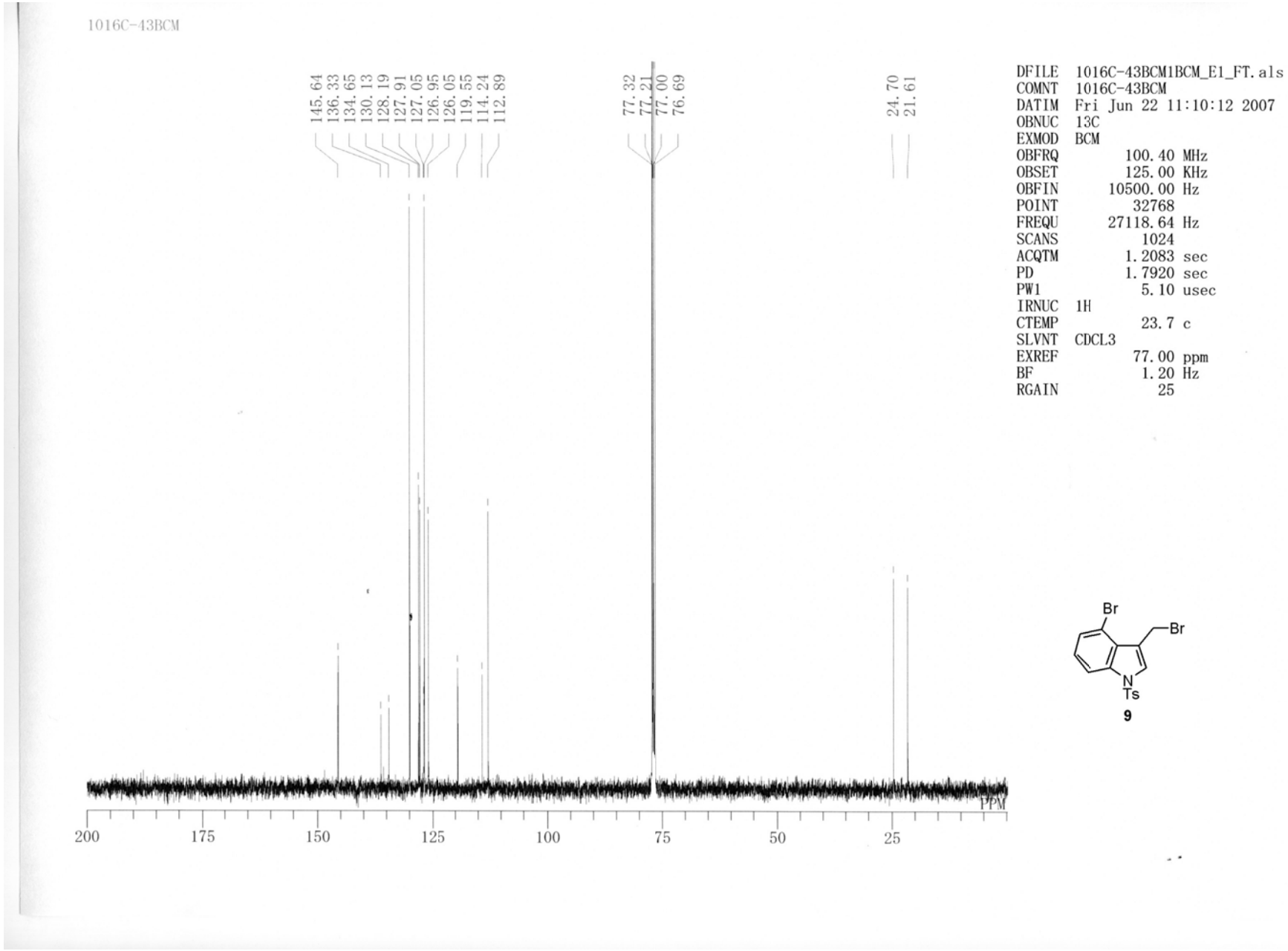
(4) Agurell, S. *Acta Pharm. Suecica* **1966**, *3*, 7-10.

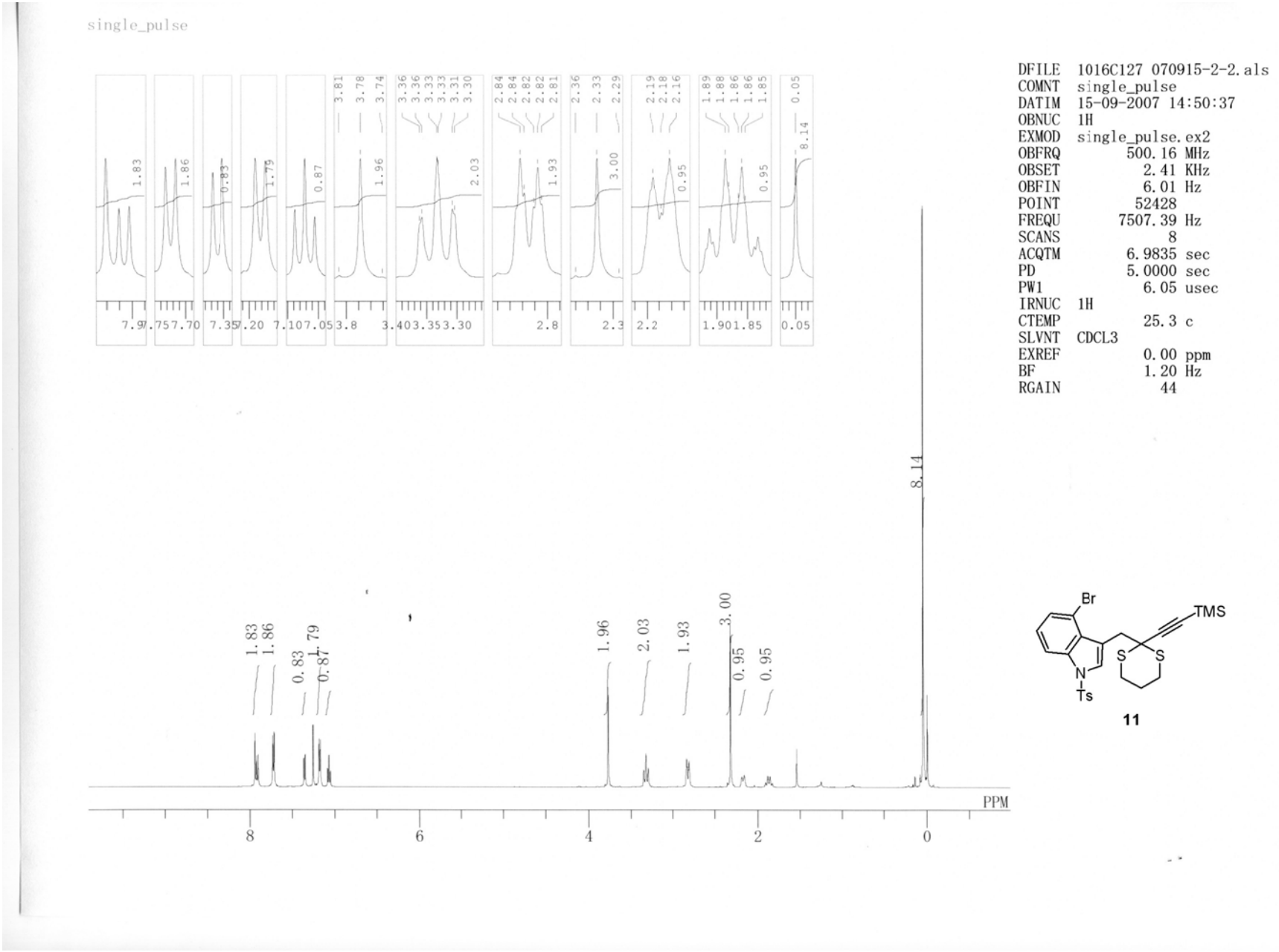
(5) Ninomiya, I.; Hashimoto, C.; Kiguchi, T.; Naito, T.; Barton, D. H. R.; Lusinchi, X.; Milliet, P. *J. Chem. Soc., Perkin Trans. 1* **1990**, 707-713.
(6) Ballabio, M.; Sbraletta, P.; Mantegani, S.; Brambilla, E. *Tetrahedron* **1992**, *48*, 4555-4566.
(7) Hong, S.; Yang, J.; Weinreb, S. M. *J. Org. Chem.* **2006**, *71*, 2078-2089.
(8) Hendrickson, J. B.; Wang, J. *Org. Lett*. **2004**, *6*, 3-5.
(9) Moldvai, I.; Temesvári-Major, E.; Incze, M.; Szentirmay, É.; Gács-Baitz, E.; Szántay, C. *J. Org. Chem*. **2004**, *69*, 5993-6000.

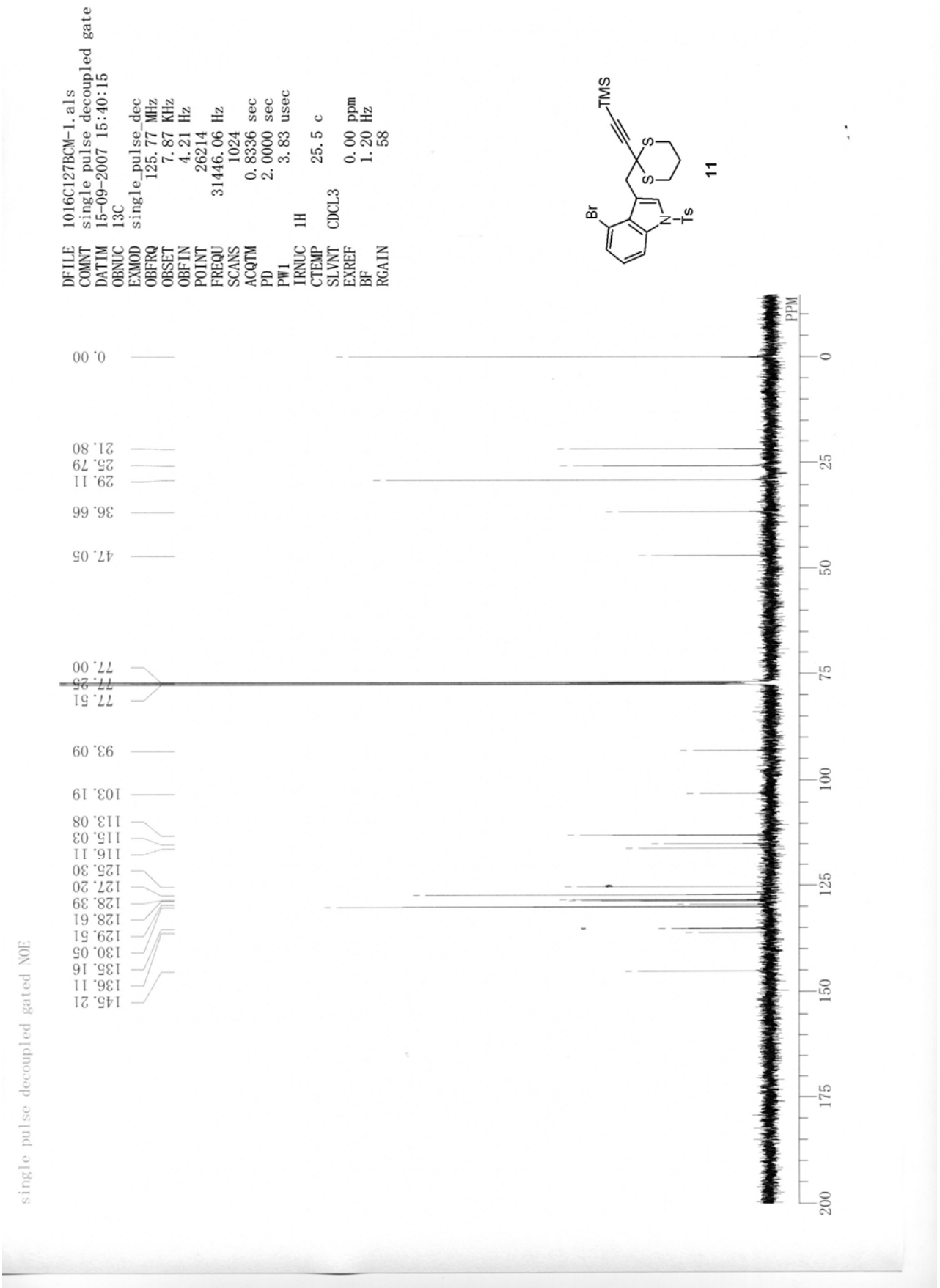

single_pulse
DFILE 1016C-40-2-1.als
COMNT single_pulse
DATIM 20-06-2007 17:36:01
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 52428
FREQU 7507.39 Hz
SCANS 8
ACQTM 6.9835 sec
PD 5.0000 sec
PW1 6.25 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 44
10.92
8.41
8.03
8.01
8.00
7.98
7.84
7.83
7.81
7.57
7.55
7.54
7.31
7.29
7.26
7.26
7.24
7.22
2.38
1.00
1.04
1.12
2.21
2.08
1.14
3.27
PPM
12.5
10.0
7.5
5.0
2.5
0.0
Br
CHO
N
Ts
S1

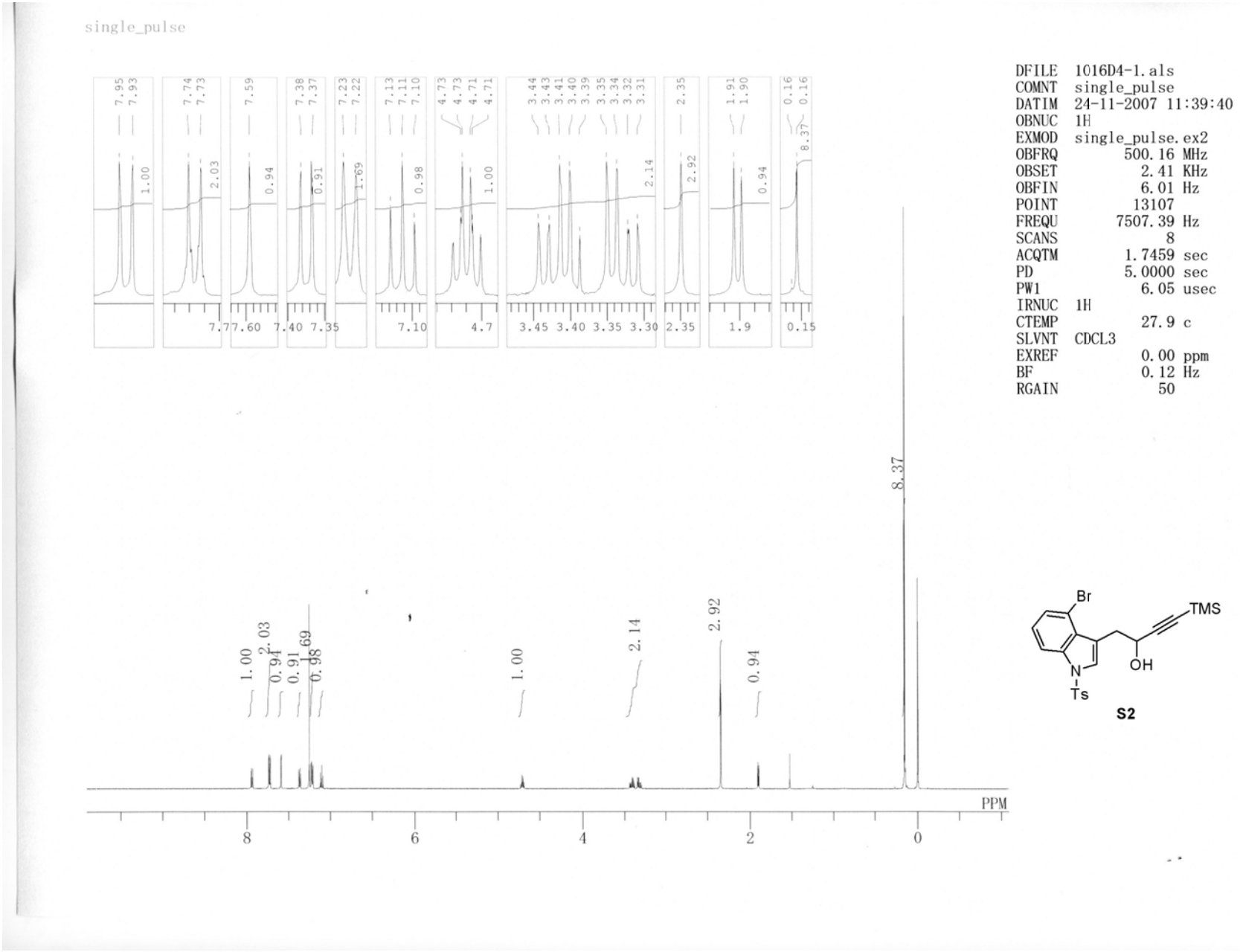

1016C-40-2BCM
186.16
146.43
136.16
134.09
132.04
130.38
128.86
127.33
127.03
126.13
121.95
113.89
112.87
77.32
77.00
76.69
21.67
DFILE 1016C-40-2BCM1BCM_E16_FT.al
COMNT 1016C-40-2BCM
DATIM Wed Jun 20 16:33:50 2007
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 512
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 5.10 usec
IRNUC 1H
CTEMP 23.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 25
200
175
150
125
100
75
50
25
Br
CHO
N
Ts
S1

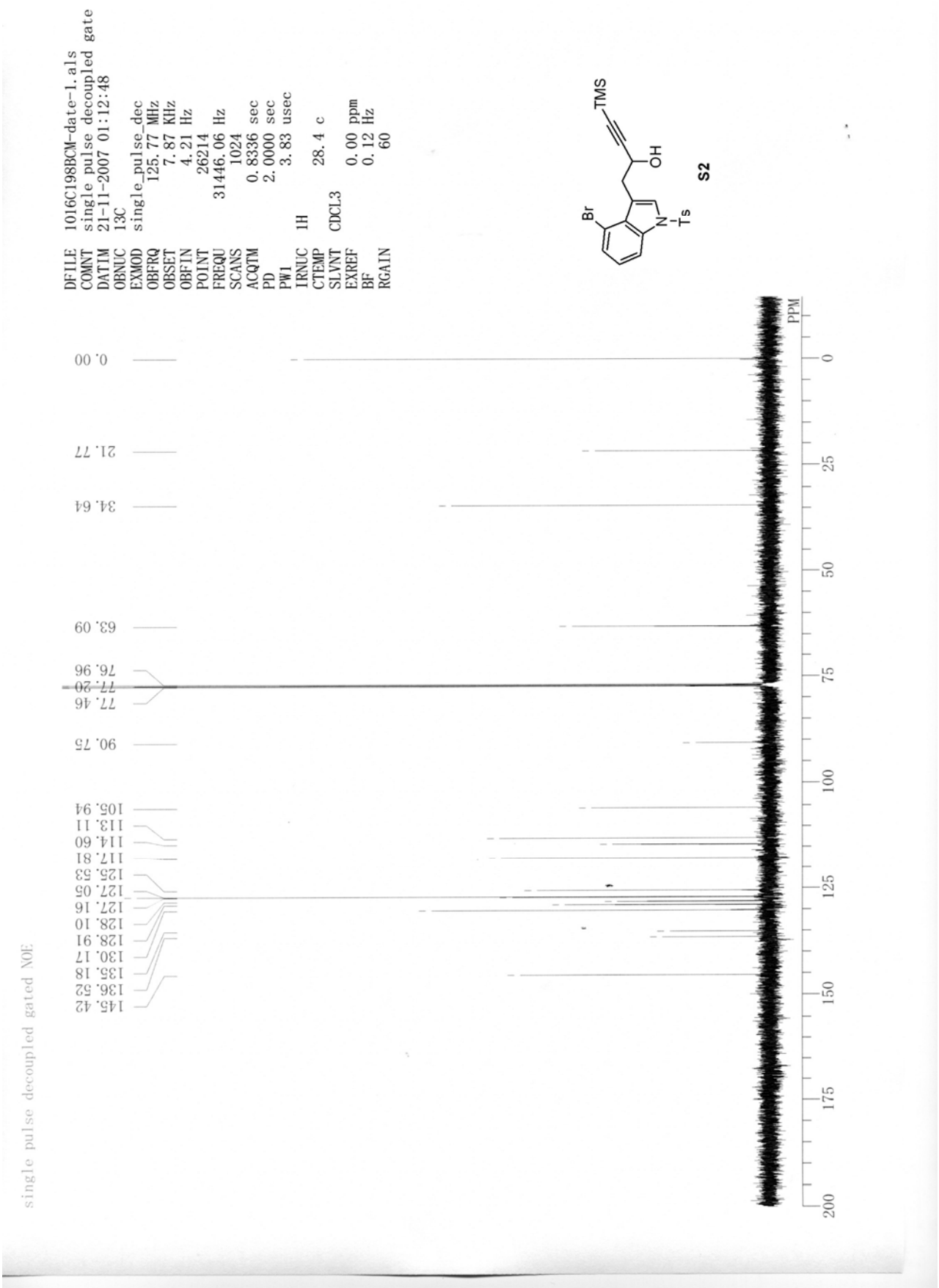

single_pulse
DFILE 1016C-43-1-1.als
COMNT single_pulse
DATIM 22-06-2007 10:13:12
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 52428
FREQU 7507.39 Hz
SCANS 8
ACQTM 6.9835 sec
PD 5.0000 sec
PW1 6.25 usec
IRNUC 1H
CTEMP 25.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 46
7.96
7.94
7.92
1.00
7.78
7.76
7.75
7.45
7.43
7.41
0.98
7.26
7.25
2.42
7.18
7.17
7.15
0.89
4.88
1.91
2.36
2.96
3.03
2.42
1.91
2.96
1.00
0.98
0.89
PPM
8
6
4
2
0
Br
Br
N
Ts
9

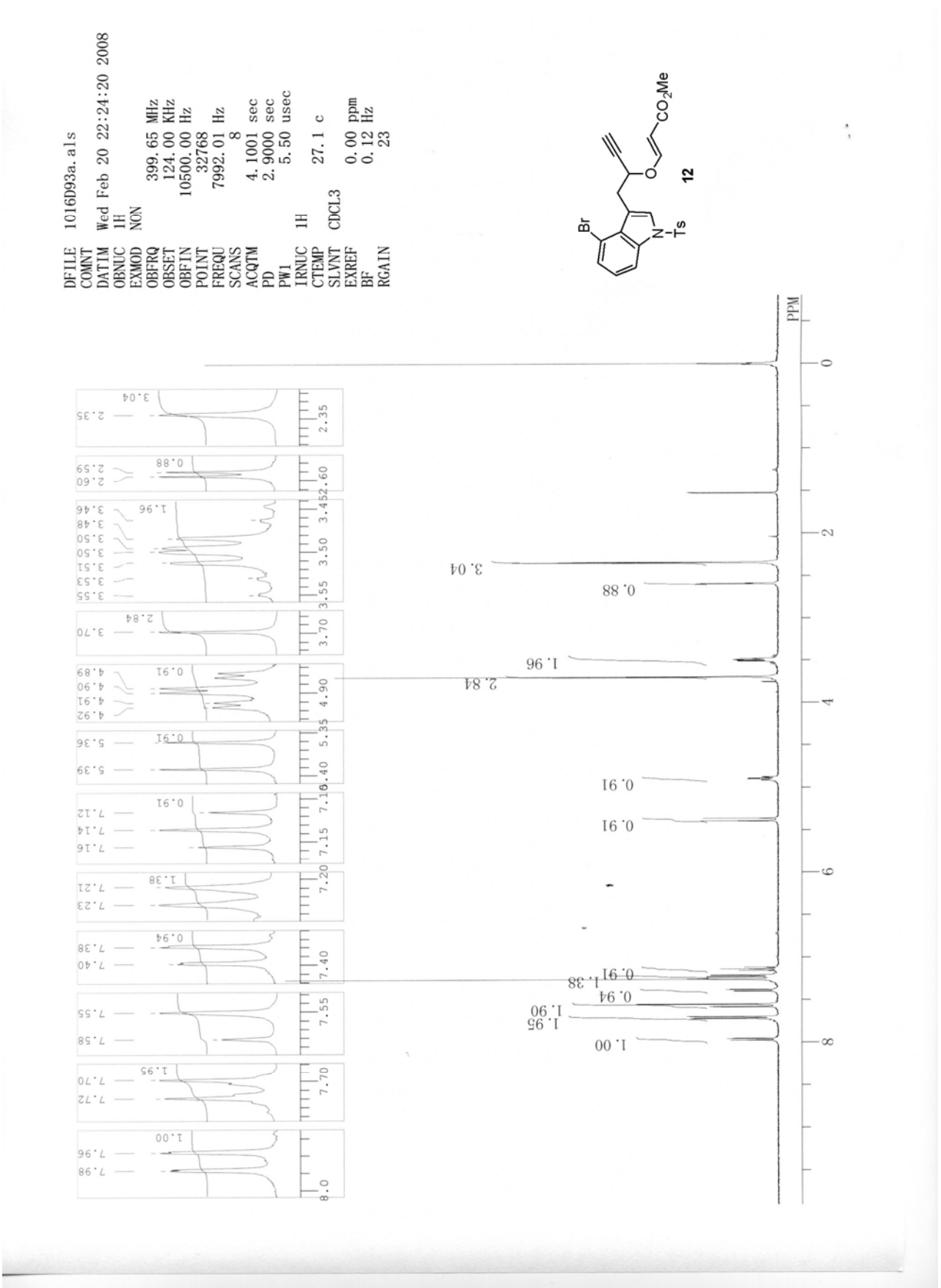

1016C-43BCM
145.64
136.33
134.65
130.13
128.19
127.91
127.05
126.95
126.05
119.55
114.24
112.89
77.32
77.21
77.00
76.69
24.70
21.61
DFILE 1016C-43BCM1BCM_E1_FT.als
COMNT 1016C-43BCM
DATIM Fri Jun 22 11:10:12 2007
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 1024
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 5.10 usec
IRNUC 1H
CTEMP 23.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 25
Br
Br
N
Ts
9
200
175
150
125
100
75
50
25
PPM

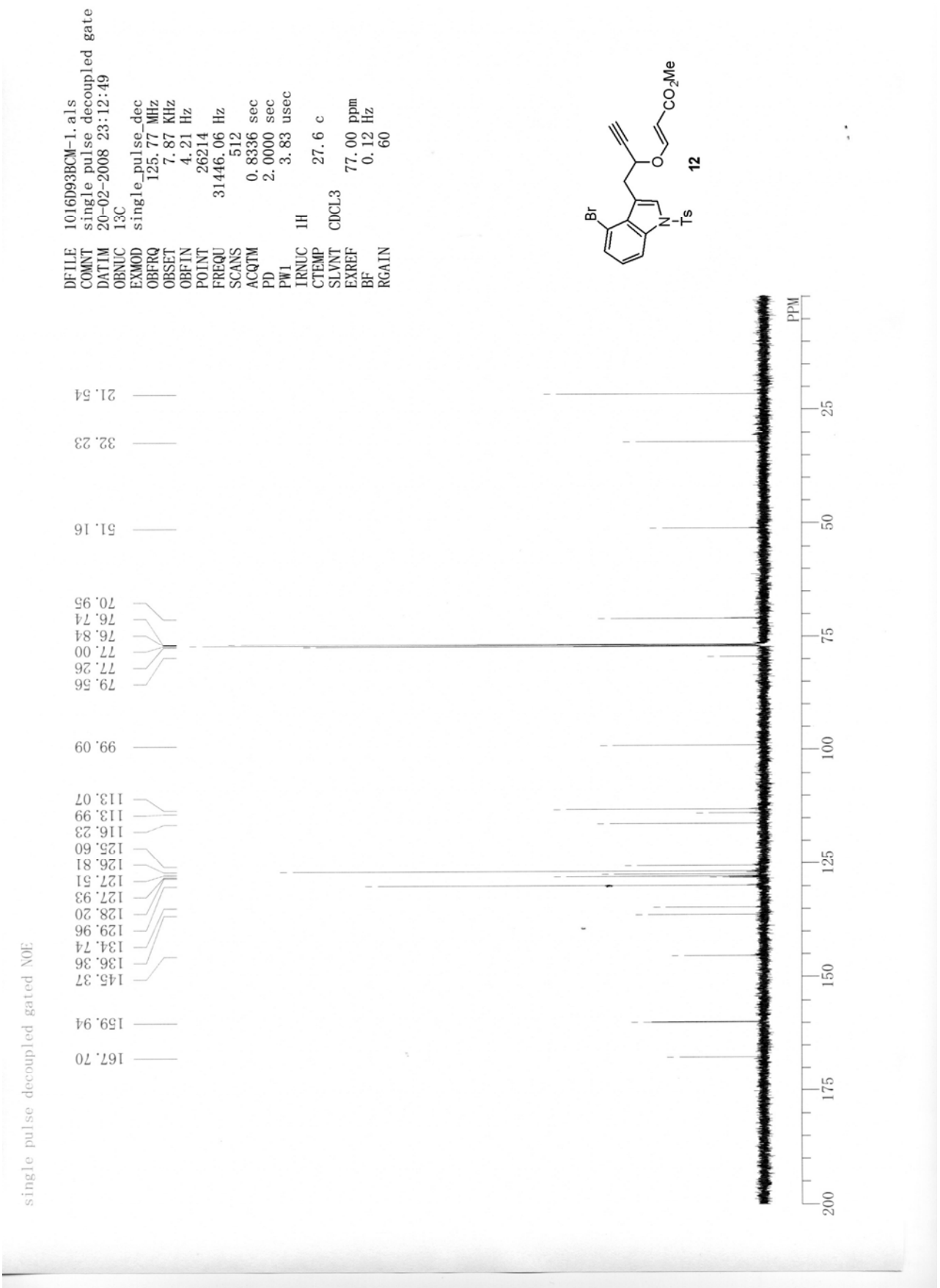

single_pulse
DFILE 1016C127 070915-2-2.als
COMNT single_pulse
DATIM 15-09-2007 14:50:37
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 52428
FREQU 7507.39 Hz
SCANS 8
ACQTM 6.9835 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 25.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 44
1.83
1.86
0.83
1.79
0.87
1.96
2.03
1.93
3.00
0.95
0.95
8.14
PPM
Br
TMS
S
S
N
Ts
11

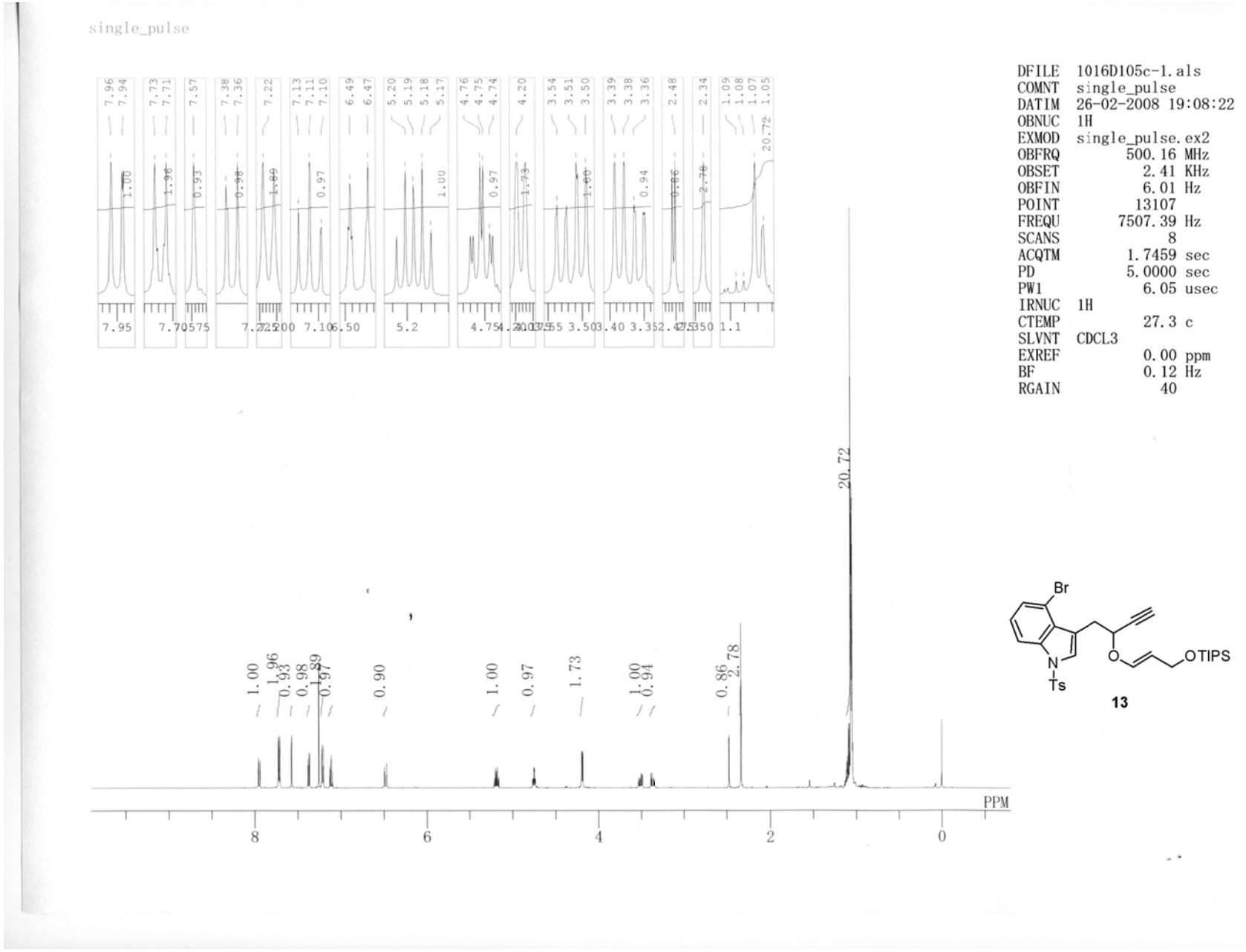

DFILE 1016C127BCM-1.als
COMNT single pulse decoupled gate
DATIM 15-09-2007 15:40:15
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 1024
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 25.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 58
TMS
Br
Ts
11
single pulse decoupled gated NOE
PPM

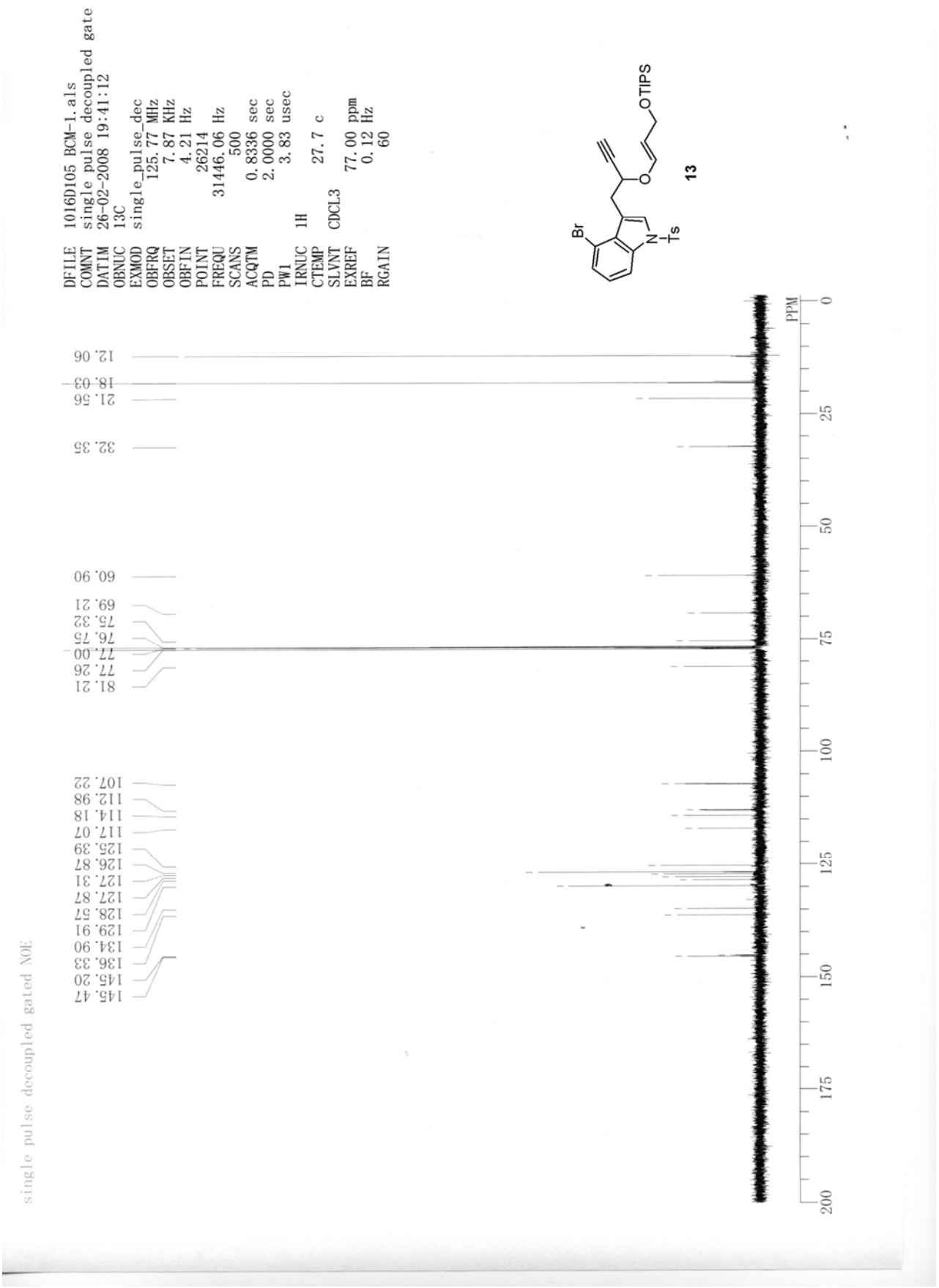

single_pulse
DFILE 1016D4-1.als
COMNT single_pulse
DATIM 24-11-2007 11:39:40
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 27.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50
PPM
Br
TMS
OH
N
Ts
S2

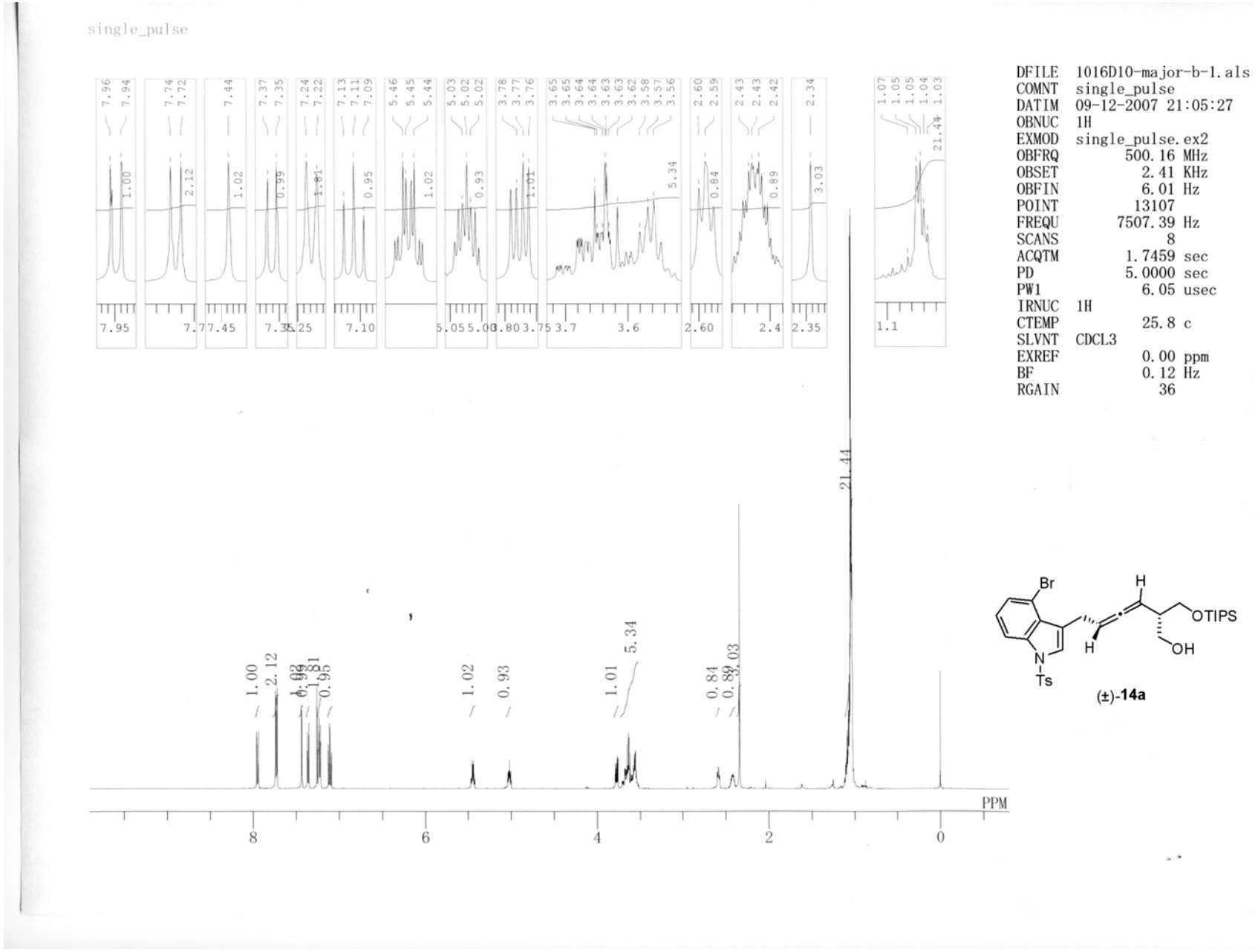

DFILE 1016C198BCM-date-1.als
COMNT single pulse decoupled gate
DATIM 21-11-2007 01:12:48
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 1024
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 28.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 60
TMS
OH
Br
N
Ts
S2
0.00
21.77
34.64
63.09
76.96
77.20
77.46
90.75
105.94
113.11
114.60
117.81
125.53
127.05
127.16
128.10
128.91
130.17
135.18
136.52
145.42
PPM
0
25
50
75
100
125
150
175
200
single pulse decoupled gated NOE

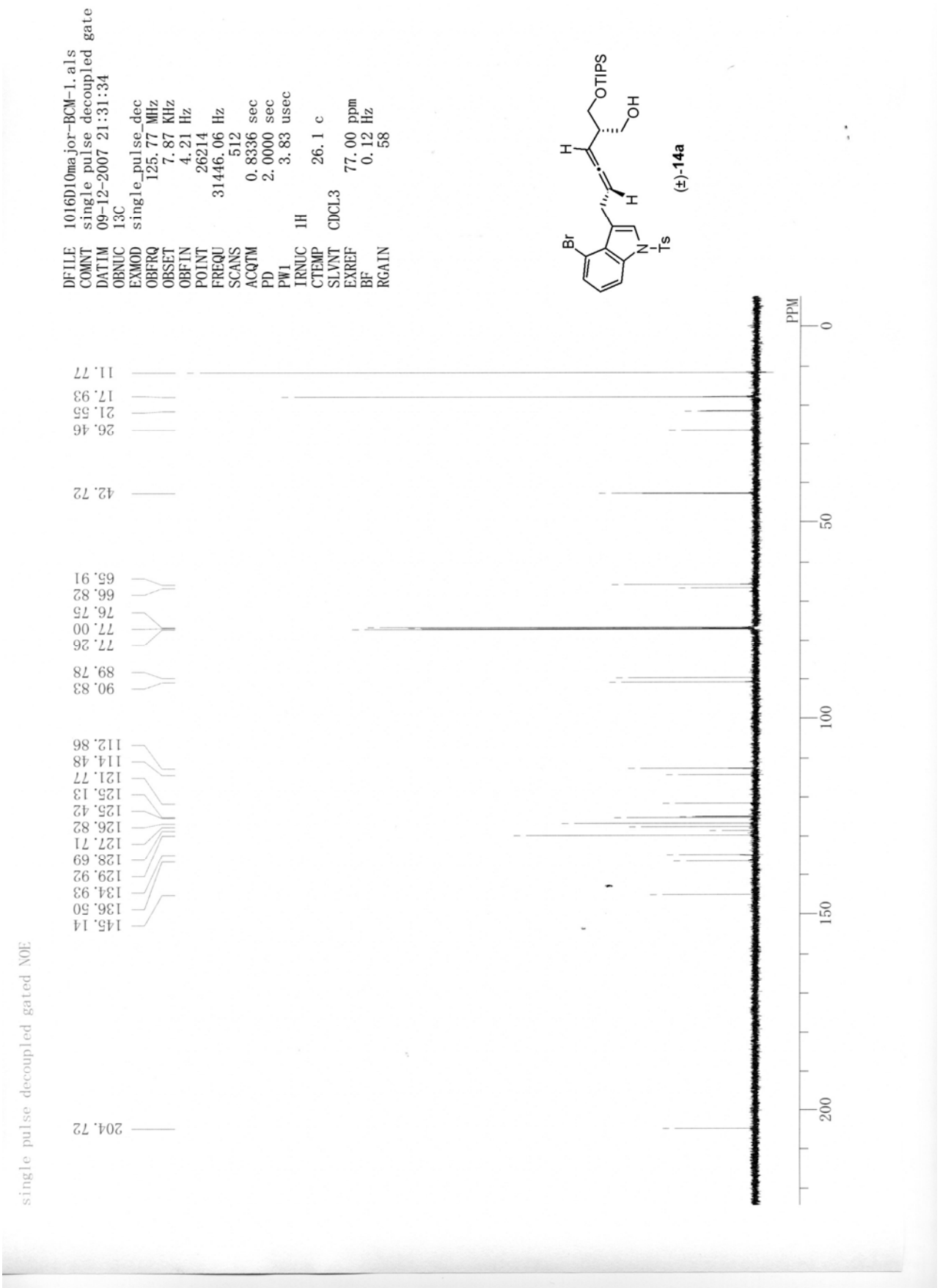

DFILE 1016D93a.als
COMNT
DATIM Wed Feb 20 22:24:20 2008
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7992.01 Hz
SCANS 8
ACQTM 4.1001 sec
PD 2.9000 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 27.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 23
Br
N
Ts
O
CO2Me
12
PPM
0
2
4
6
8
3.04
0.88
1.96
2.84
0.91
0.91
1.38
0.94
1.90
1.95
1.00

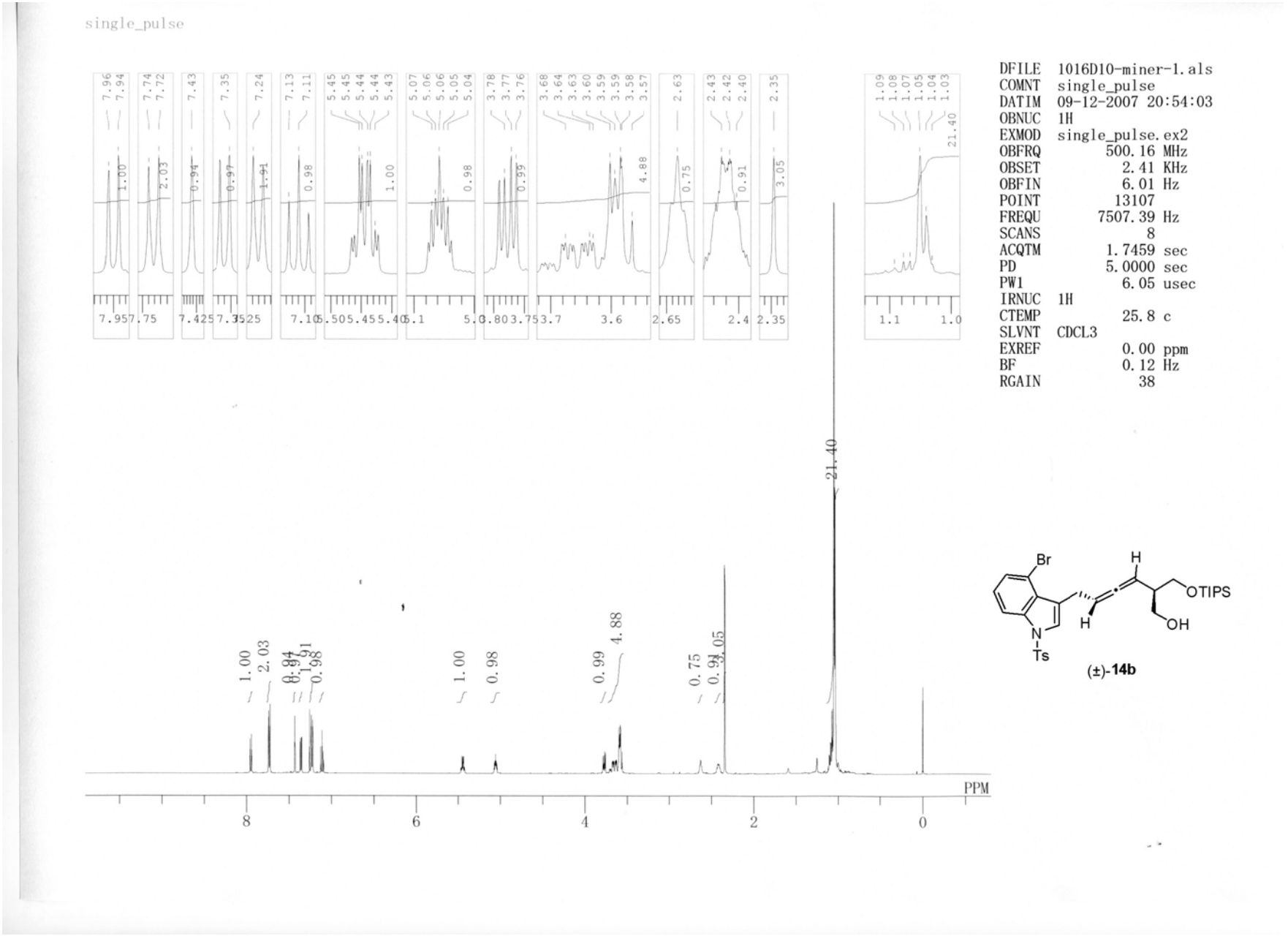

DFILE 1016D93BCM-1.als
COMNT single pulse decoupled gate
DATIM 20-02-2008 23:12:49
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 512
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 27.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
single pulse decoupled gated NOE
21.54
32.23
51.16
70.95
76.74
76.84
77.00
77.26
79.56
99.09
113.07
113.99
116.23
125.60
126.81
127.51
127.93
128.20
129.96
134.74
136.36
145.37
159.94
167.70
PPM
Br
Ts
CO2Me
12

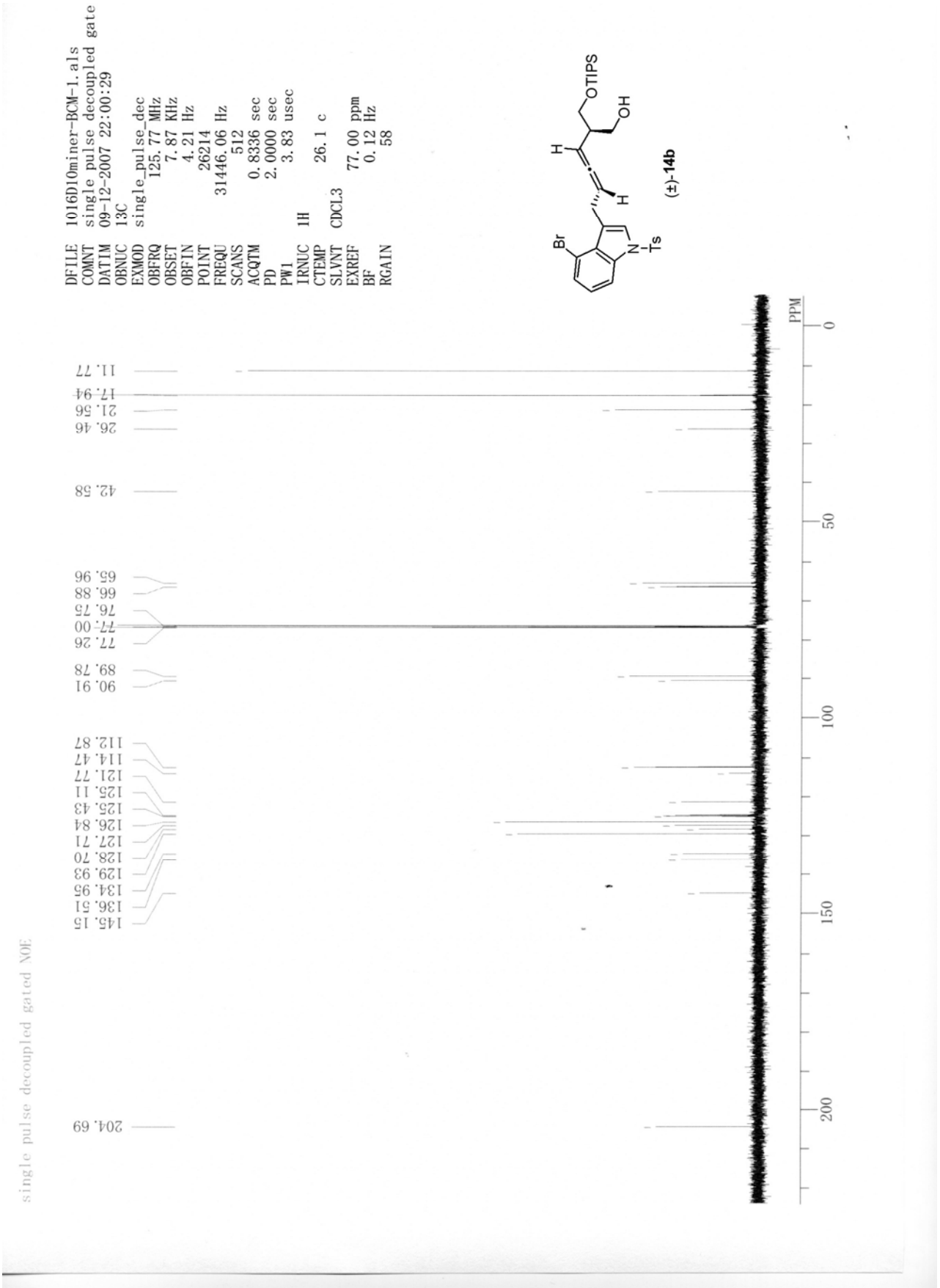

single_pulse
DFILE 1016D105c-1.als
COMNT single_pulse
DATIM 26-02-2008 19:08:22
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 27.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40
PPM
Br
N
Ts
O
OTIPS
13

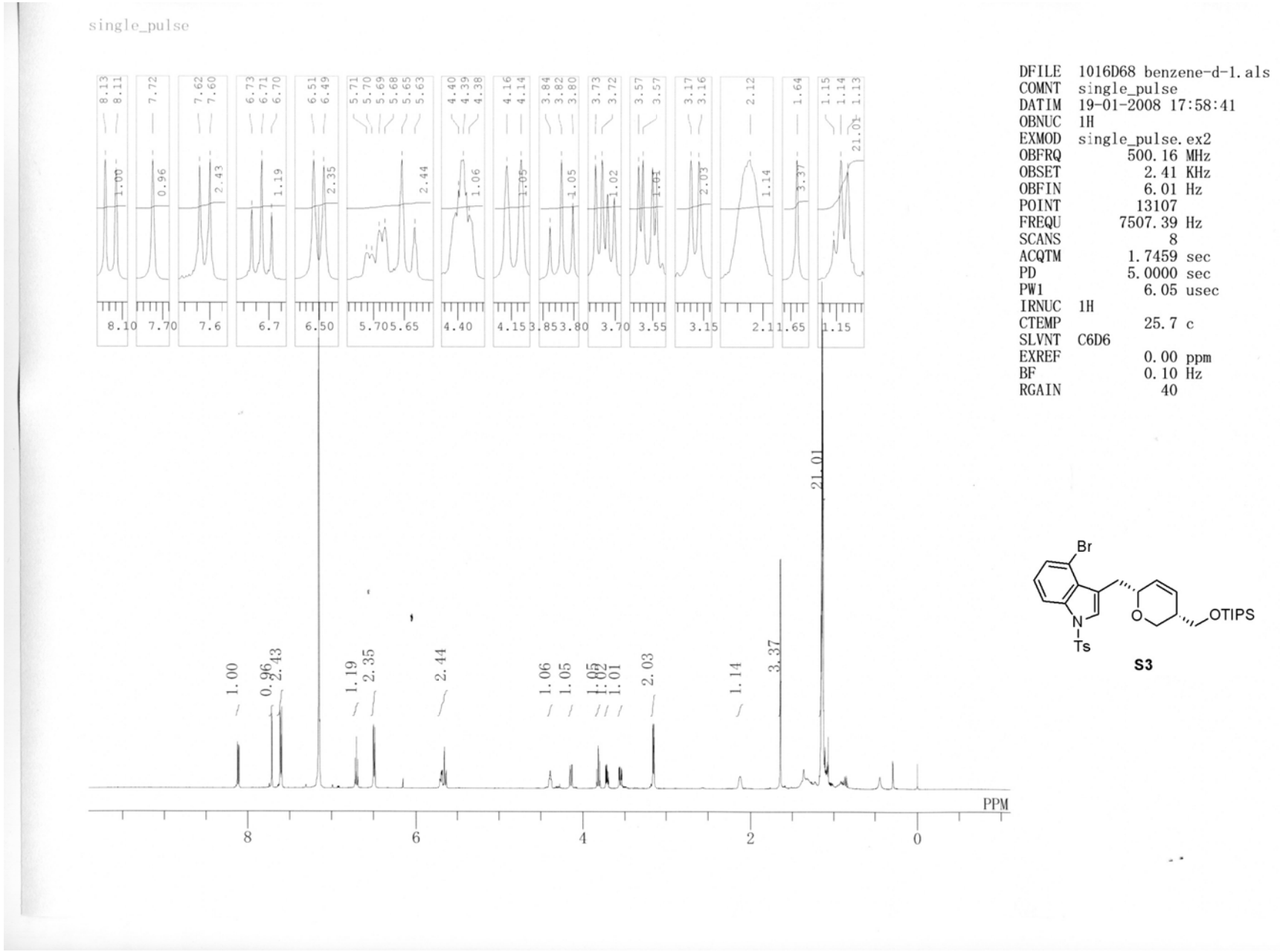

DFILE 1016D105 BCM-1.als
COMNT single pulse decoupled gate
DATIM 26-02-2008 19:41:12
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 500
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 27.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
single pulse decoupled gated NOE
PPM
Br
OTIPS
Ts
13

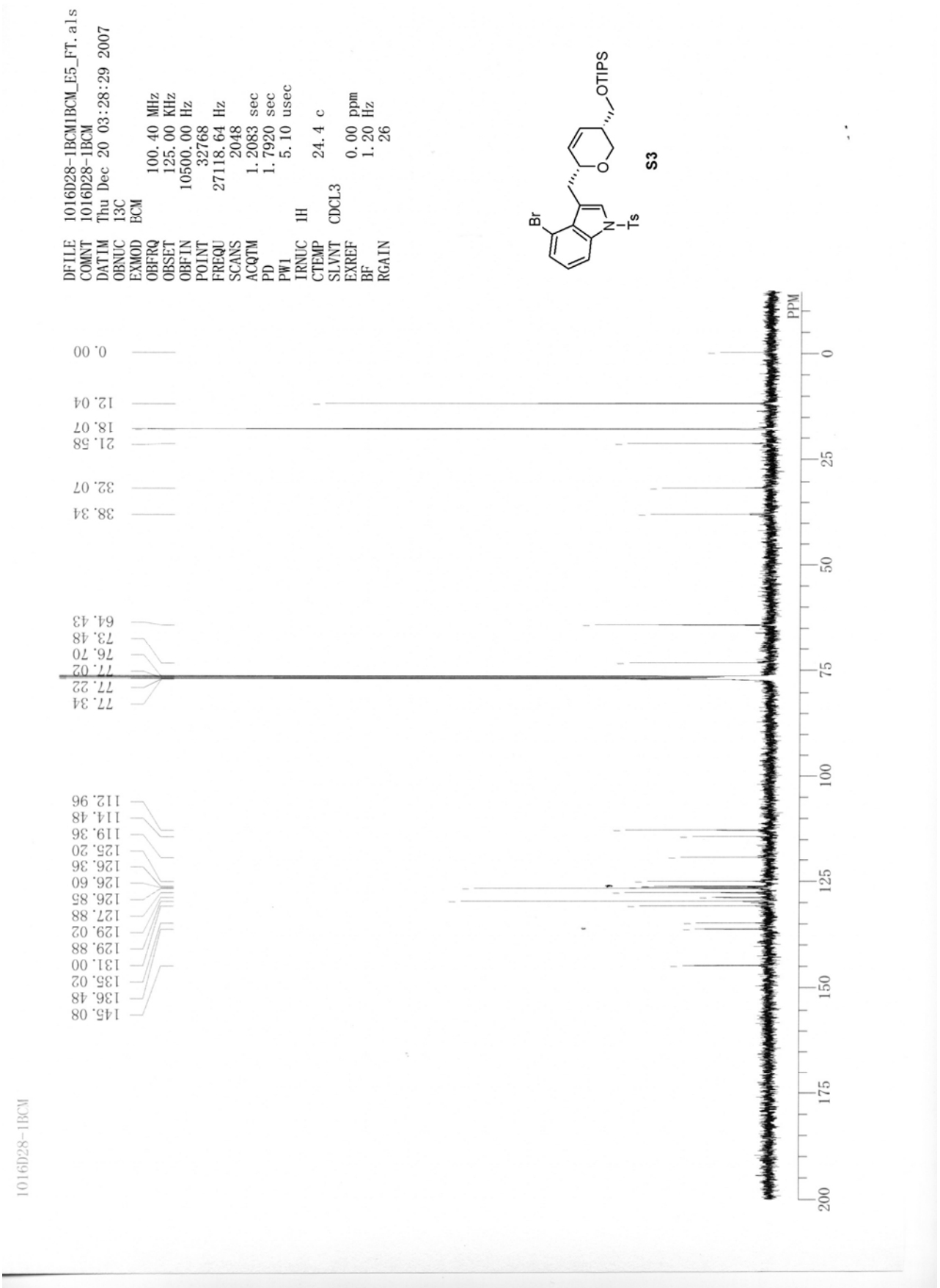

single_pulse
DFILE 1016D10-major-b-1.als
COMNT single_pulse
DATIM 09-12-2007 21:05:27
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 25.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 36
PPM
Br
H
OTIPS
H
OH
N
Ts
(±)-14a

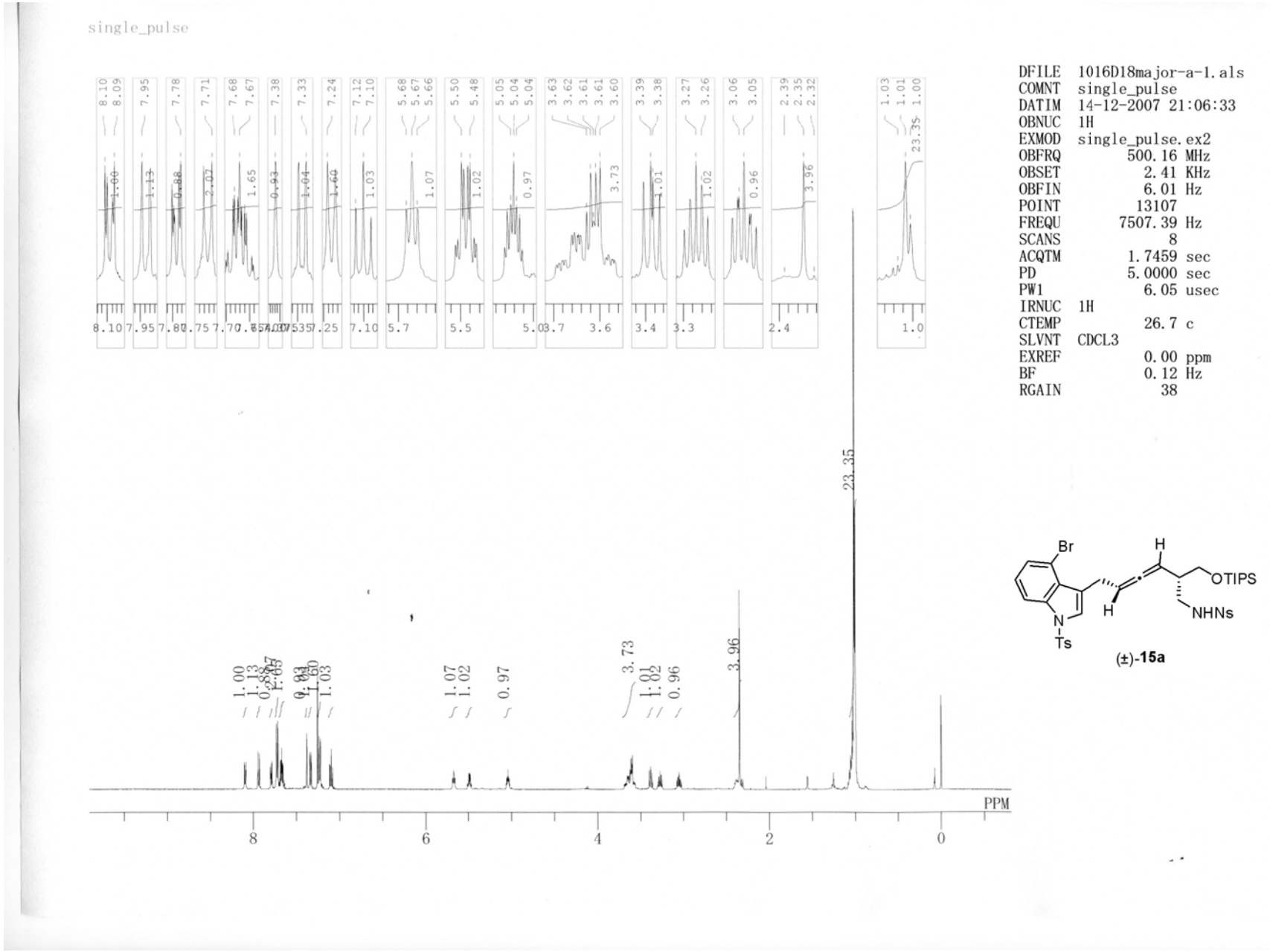

DFILE 1016D10major-BCM-1.als
COMNT single pulse decoupled gate
DATIM 09-12-2007 21:31:34
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 512
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 26.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 58
OTIPS
OH
H
H
Br
N
Ts
(±)-14a
11.77
17.93
21.55
26.46
42.72
65.91
66.82
76.75
77.00
77.26
89.78
90.83
112.86
114.48
121.77
125.13
125.42
126.82
127.71
128.69
129.92
134.93
136.50
145.14
204.72
PPM
0
50
100
150
200
single pulse decoupled gated NOE

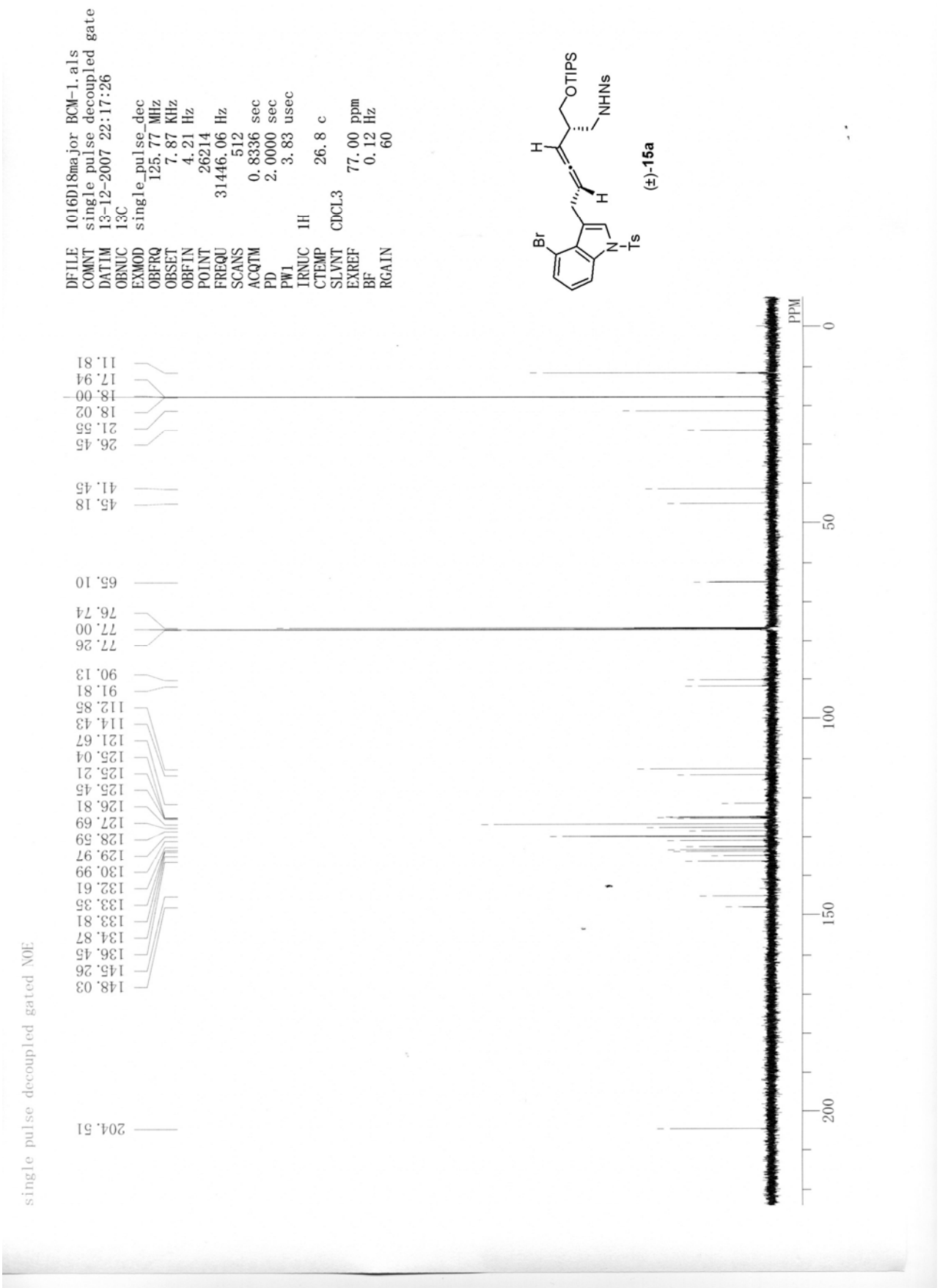

single_pulse
DFILE 1016D10-miner-1.als
COMNT single_pulse
DATIM 09-12-2007 20:54:03
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 25.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 38
PPM
Br
H
OTIPS
H
OH
N
Ts
(±)-14b

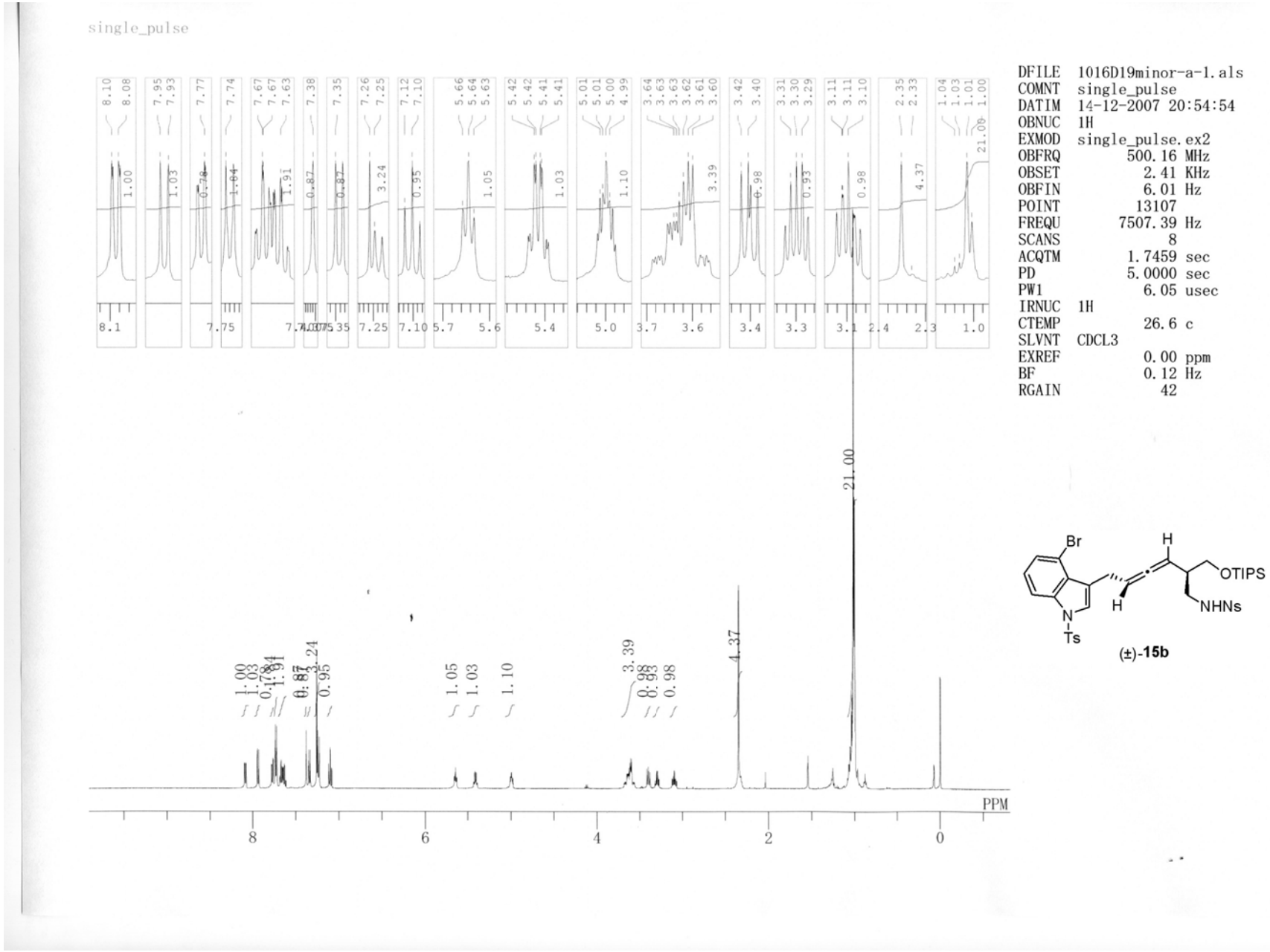

DFILE 1016D10miner-BCM-1.als
COMNT single pulse decoupled gate
DATIM 09-12-2007 22:00:29
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 512
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 26.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 58
OTIPS
OH
H
H
Br
N
Ts
(±)-14b
single pulse decoupled gated NOE
PPM
0
50
100
150
200
11.77
17.94
21.56
26.46
42.58
65.96
66.88
76.75
77.00
77.26
89.78
90.91
112.87
114.47
121.77
125.11
125.43
126.84
127.71
128.70
129.93
134.95
136.51
145.15
204.69

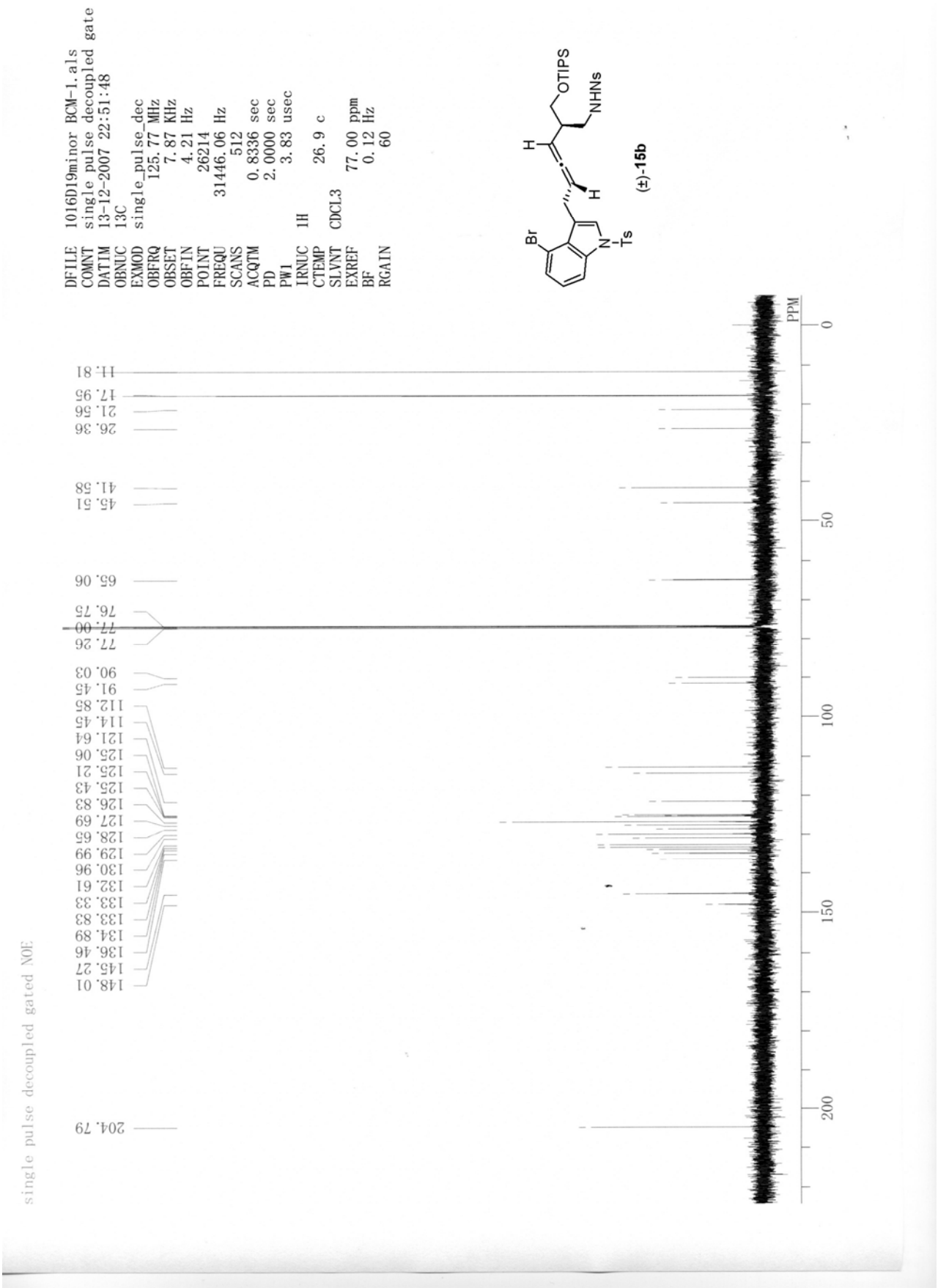

single_pulse
DFILE 1016D68 benzene-d-1.als
COMNT single_pulse
DATIM 19-01-2008 17:58:41
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 25.7 c
SLVNT C6D6
EXREF 0.00 ppm
BF 0.10 Hz
RGAIN 40
PPM
Br
N
Ts
O
OTIPS
S3

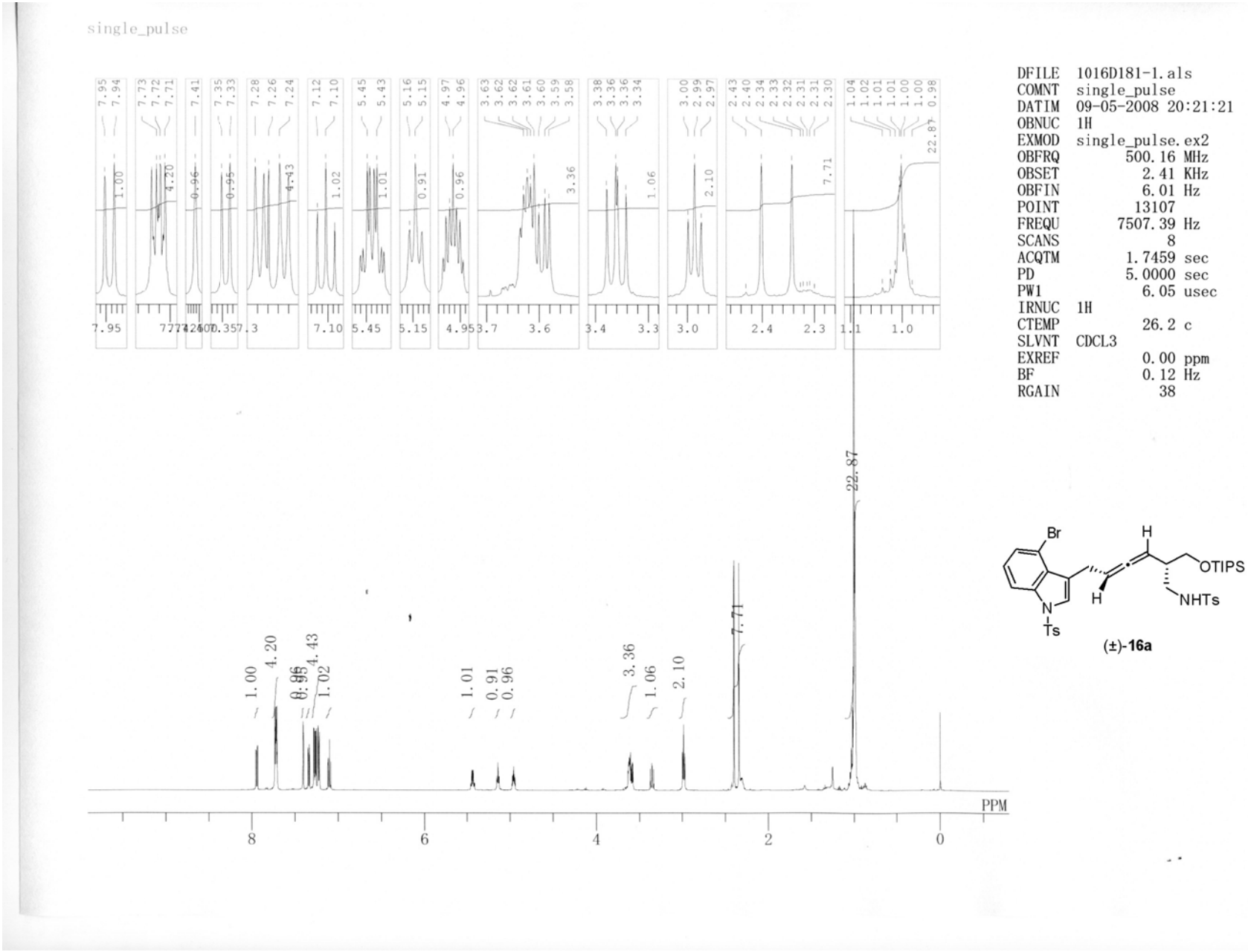

DFILE 1016D28-1BCM1BCM_E5_FT.als
COMNT 1016D28-1BCM
DATIM Thu Dec 20 03:28:29 2007
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 2048
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 5.10 usec
IRNUC 1H
CTEMP 24.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 26
OTIPS
Br
N
Ts
S3
PPM
0.00
12.04
18.07
21.58
32.07
38.34
64.43
73.48
76.70
77.02
77.22
77.34
112.96
114.48
119.36
125.20
126.36
126.60
126.85
127.88
129.02
129.88
131.00
135.02
136.48
145.08
1016D28-1BCM

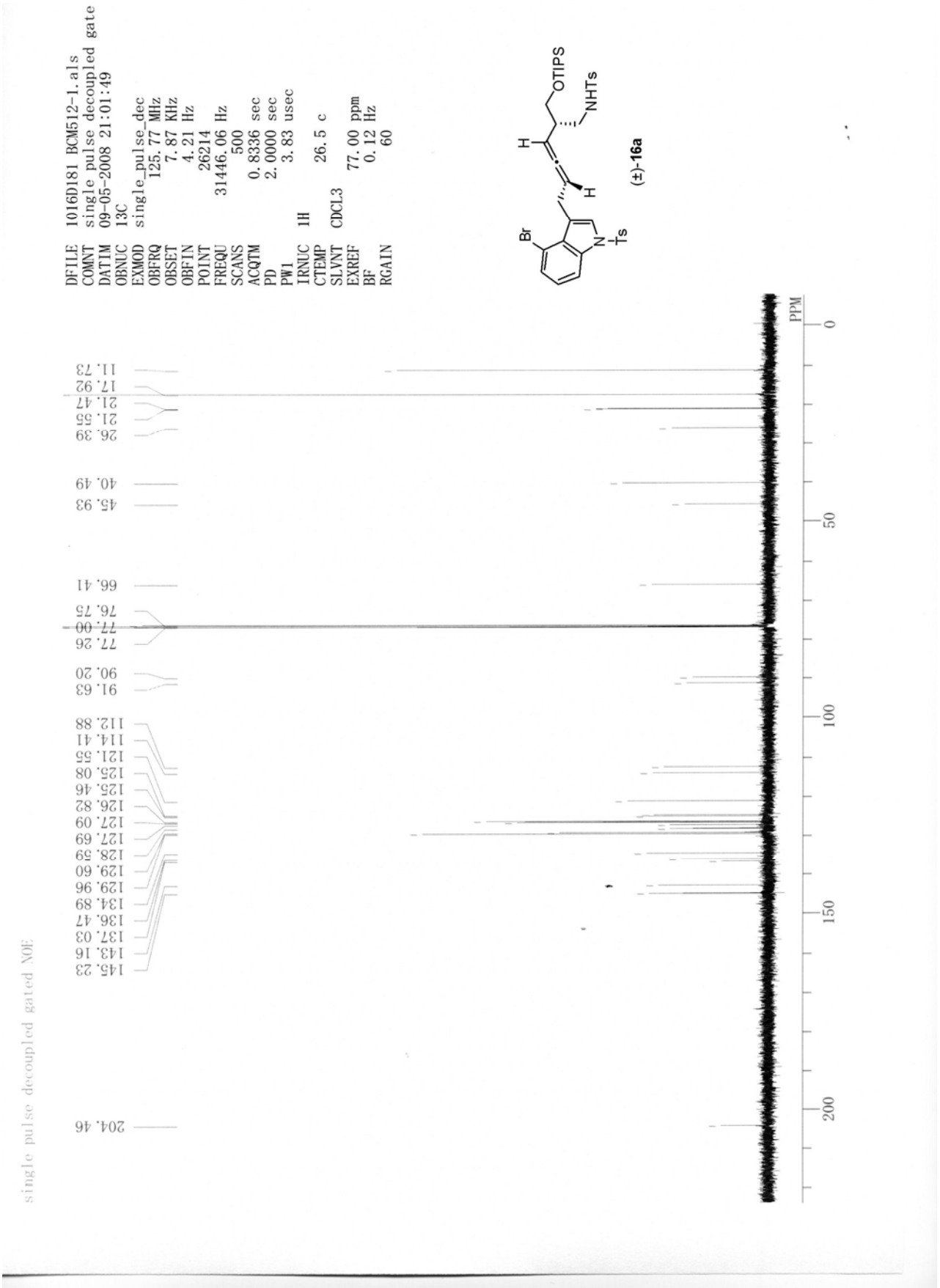

single_pulse
DFILE 1016D18major-a-1.als
COMNT single_pulse
DATIM 14-12-2007 21:06:33
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 26.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 38
PPM
Br
H
OTIPS
H
NHNs
N
Ts
(±)-15a

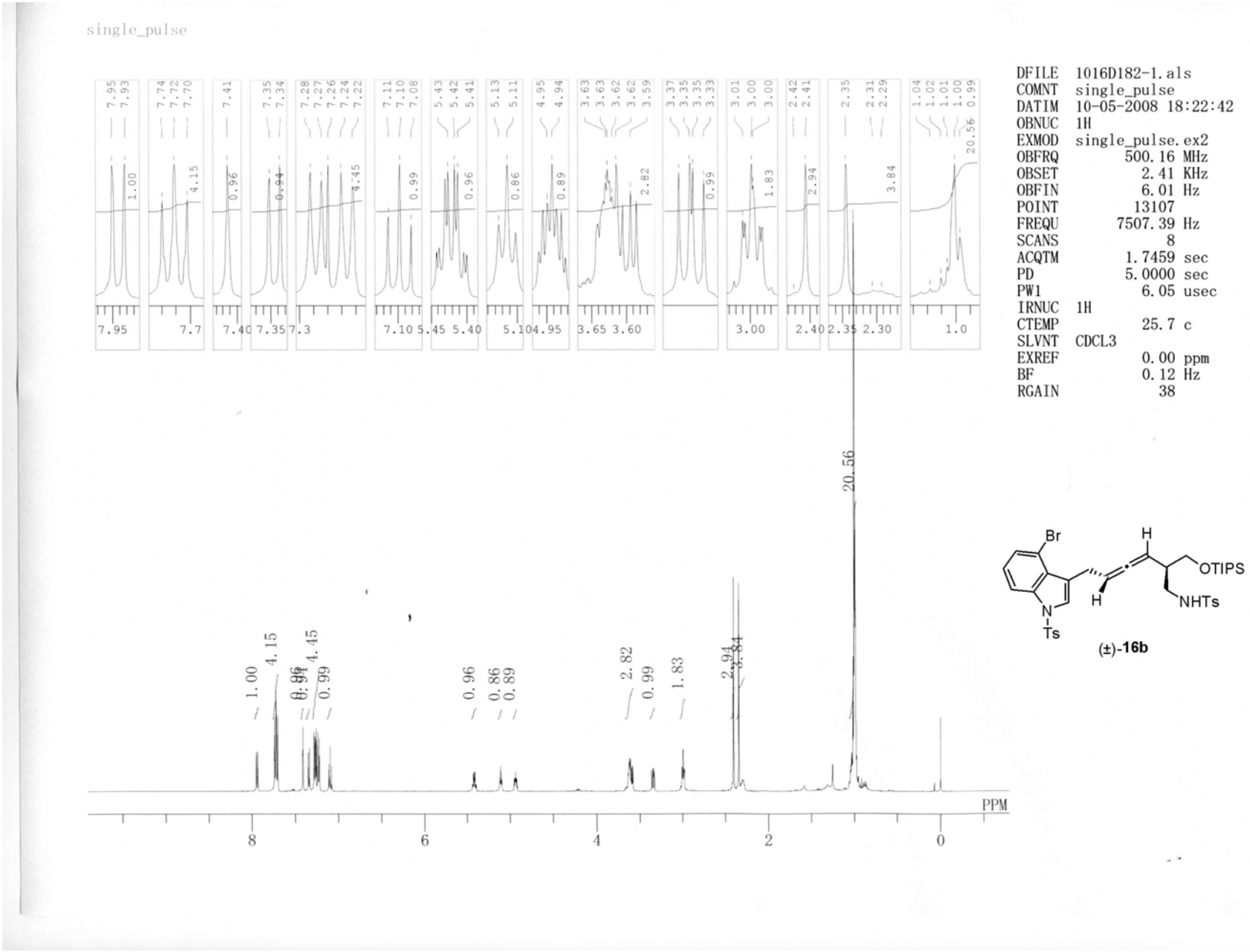

DFILE 1016D18major BCM-1.als
COMNT single pulse decoupled gate
DATIM 13-12-2007 22:17:26
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 512
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 26.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
OTIPS
NHNs
H
H
Br
N
Ts
(±)-15a
single pulse decoupled gated NOE
PPM
0
50
100
150
200
11.81
17.94
18.00
18.02
21.55
26.45
41.45
45.18
65.10
76.74
77.00
77.26
90.13
91.81
112.85
114.43
121.67
125.04
125.21
125.45
126.81
127.69
128.59
129.97
130.99
132.61
133.35
133.81
134.87
136.45
145.26
148.03
204.51

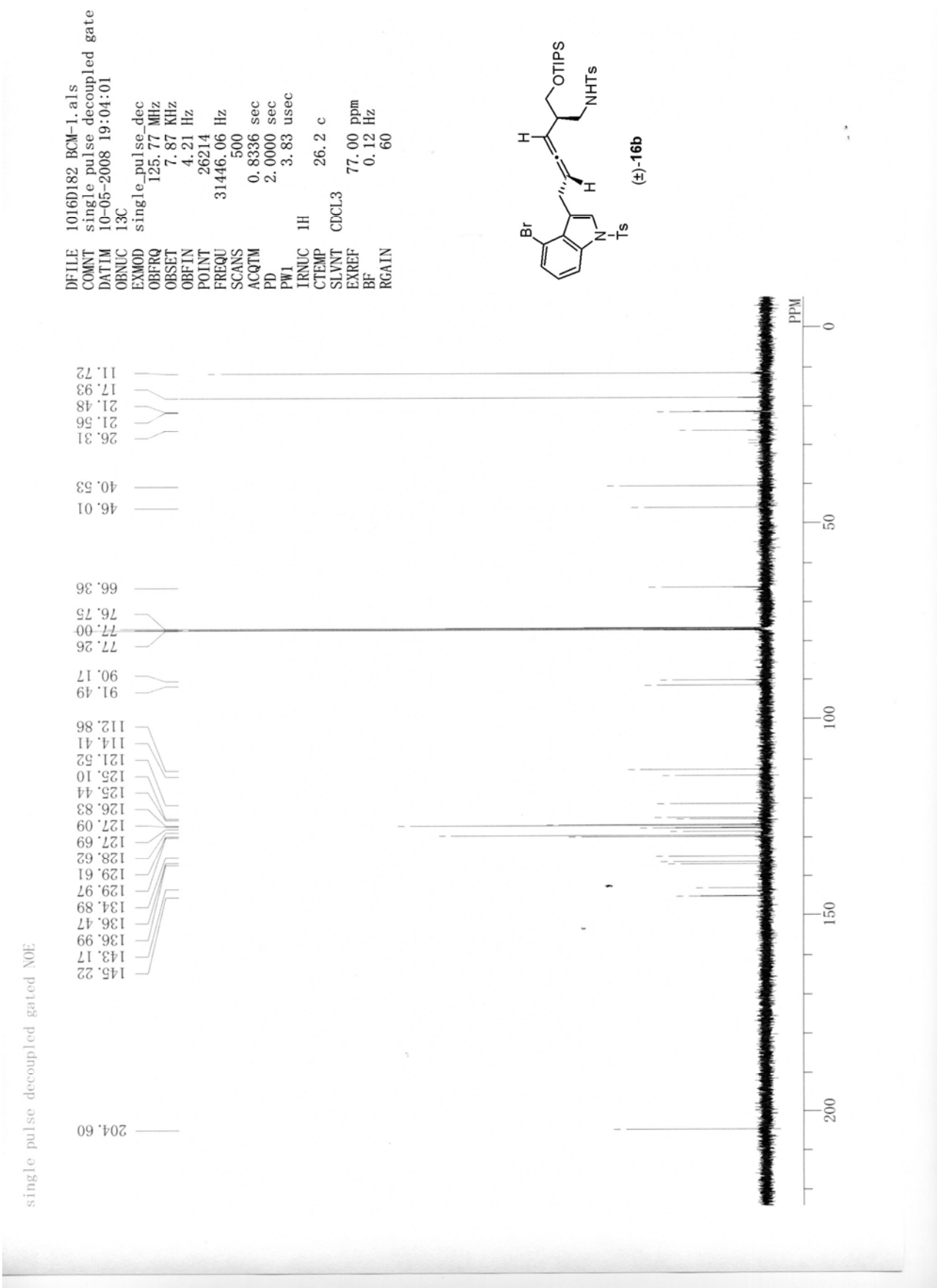

single_pulse
DFILE 1016D19minor-a-1.als
COMNT single_pulse
DATIM 14-12-2007 20:54:54
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 26.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 42
PPM
Br
H
OTIPS
H
NHNs
N
Ts
(±)-15b

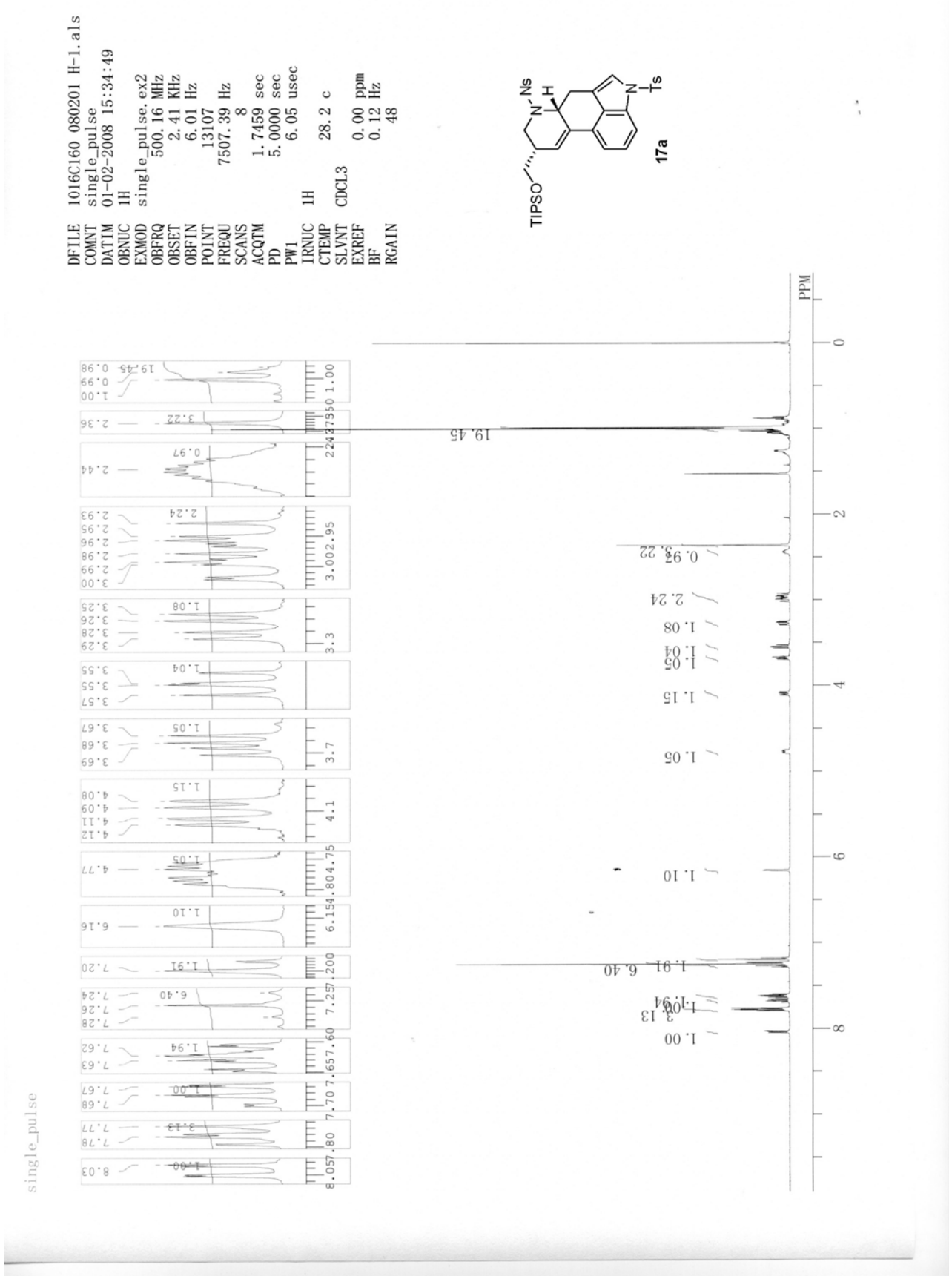

DFILE 1016D19minor BCM-1.als
COMNT single pulse decoupled gate
DATIM 13-12-2007 22:51:48
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 512
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 26.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
OTIPS
NHNs
H
H
Br
N
Ts
(±)-15b
11.81
17.95
21.56
26.36
41.58
45.51
65.06
76.75
77.00
77.26
90.03
91.45
112.85
114.45
121.64
125.06
125.21
125.43
126.83
127.69
128.65
129.99
130.96
132.61
133.33
133.83
134.89
136.46
145.27
148.01
204.79
PPM
0
50
100
150
200
single pulse decoupled gated NOE

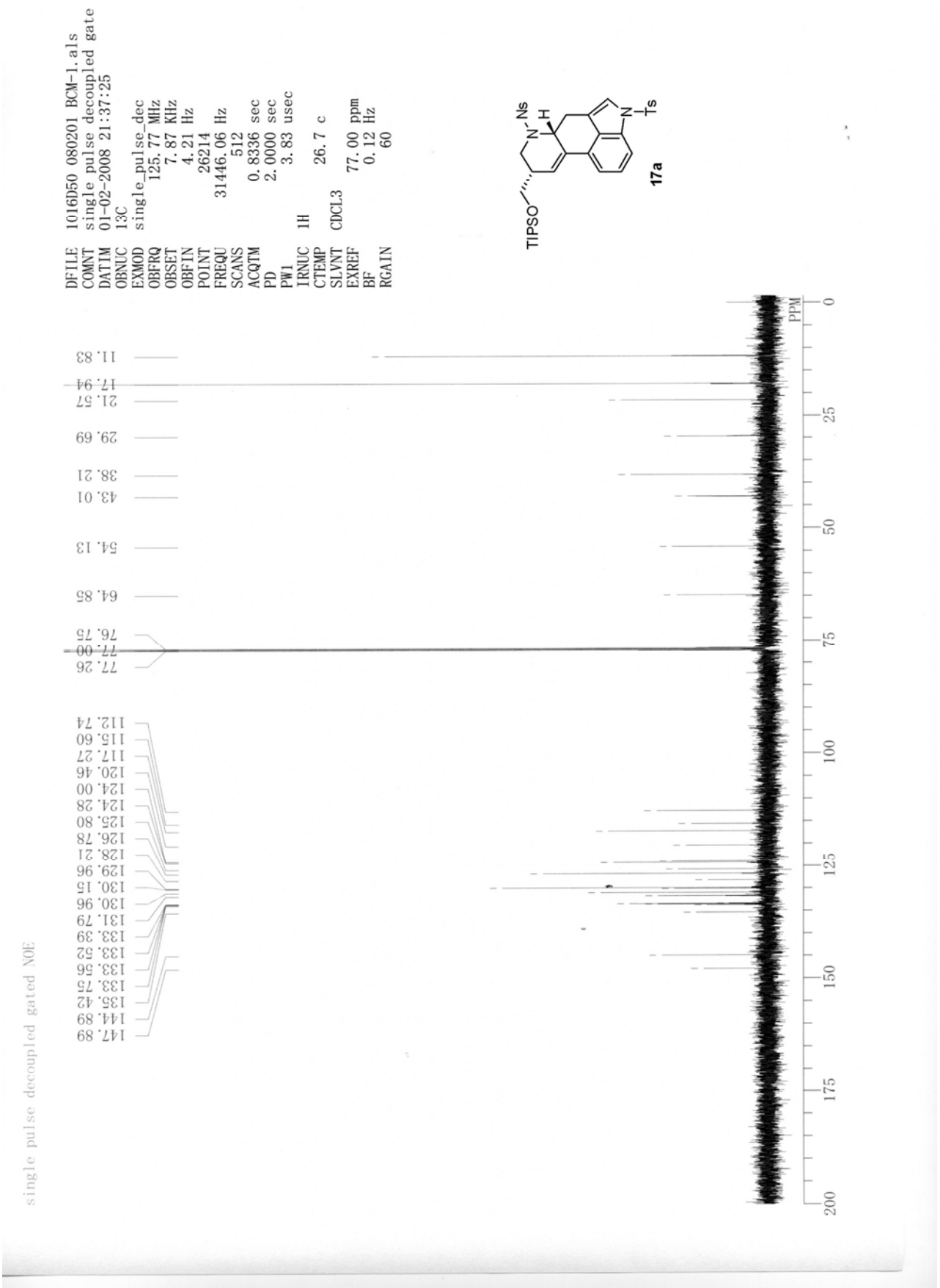

single_pulse
DFILE 1016D181-1.als
COMNT single_pulse
DATIM 09-05-2008 20:21:21
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 26.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 38
Br
H
OTIPS
H
NHTs
N
Ts
(±)-16a
PPM

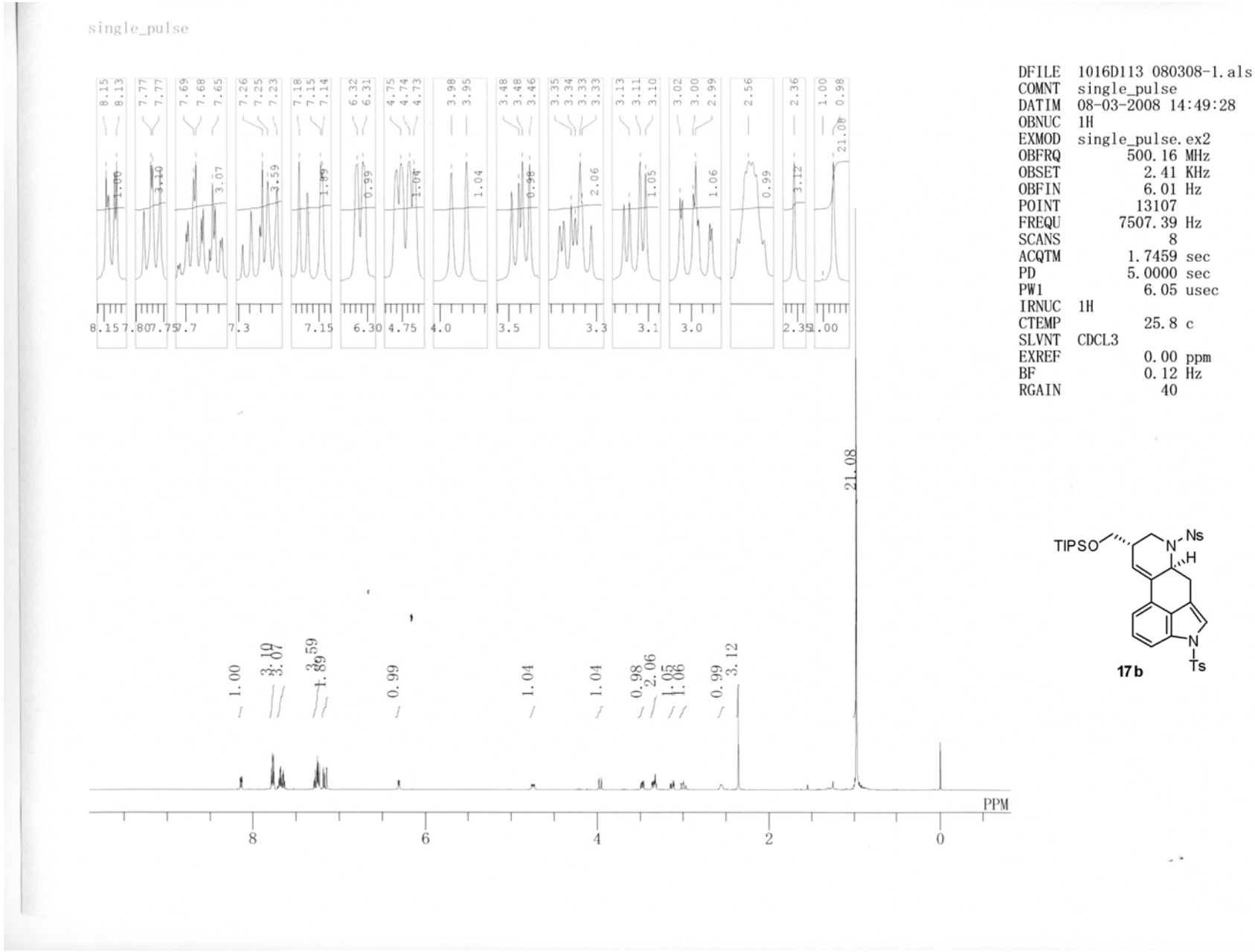

DFILE 1016D181 BCM512-1.als
COMNT single pulse decoupled gate
DATIM 09-05-2008 21:01:49
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 500
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 26.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
OTIPS
NHTs
H
H
Br
N
Ts
(±)-16a
11.73
17.92
21.47
21.55
26.39
40.49
45.93
66.41
76.75
77.00
77.26
90.20
91.63
112.88
114.41
121.55
125.08
125.46
126.82
127.09
127.69
128.59
129.60
129.96
134.89
136.47
137.03
143.16
145.23
204.46
PPM
0
50
100
150
200
single pulse decoupled gated NOE

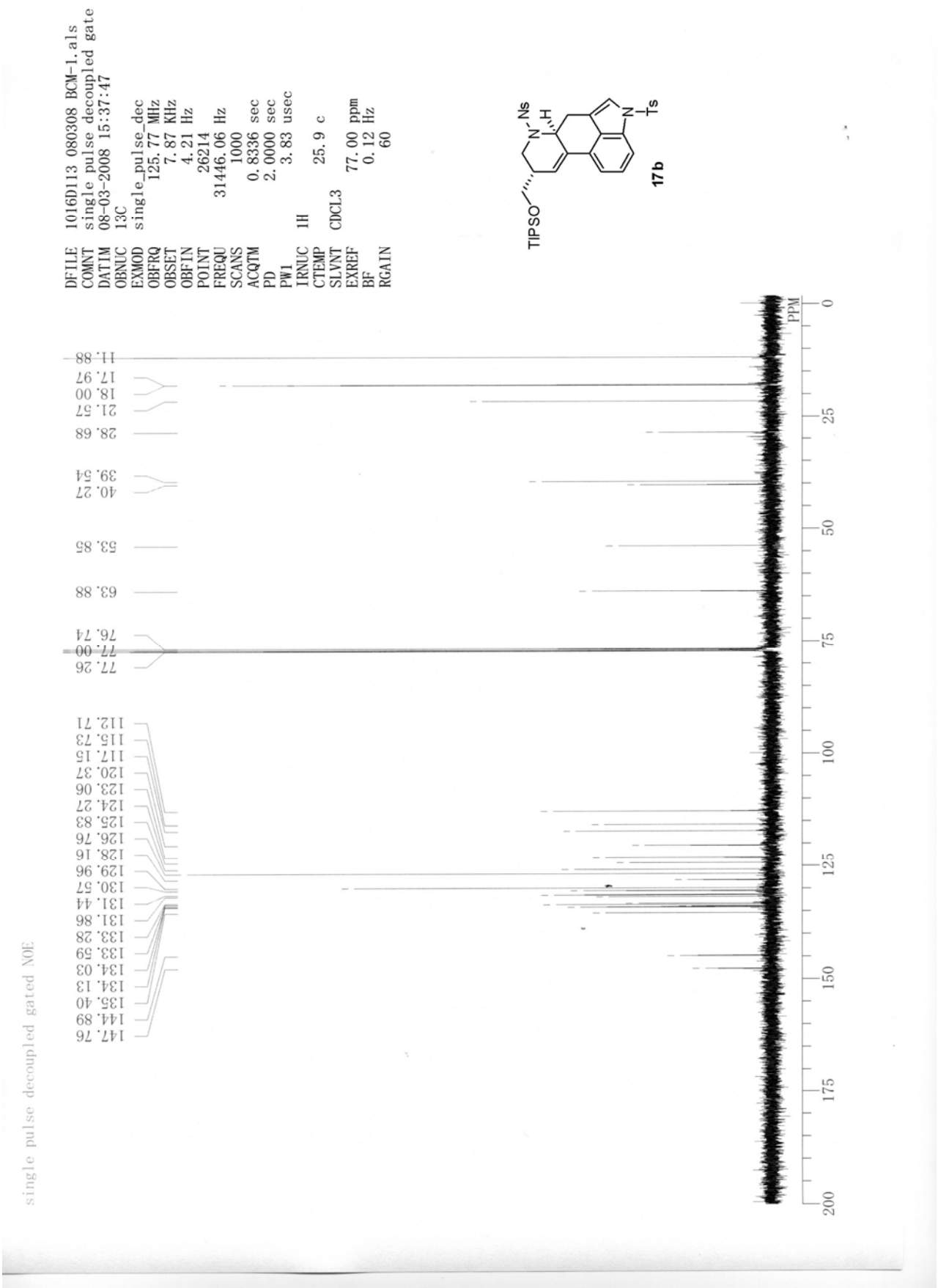

single_pulse
DFILE 1016D182-1.als
COMNT single_pulse
DATIM 10-05-2008 18:22:42
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 25.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 38
PPM
Br
H
OTIPS
H
NHTs
N
Ts
(±)-16b

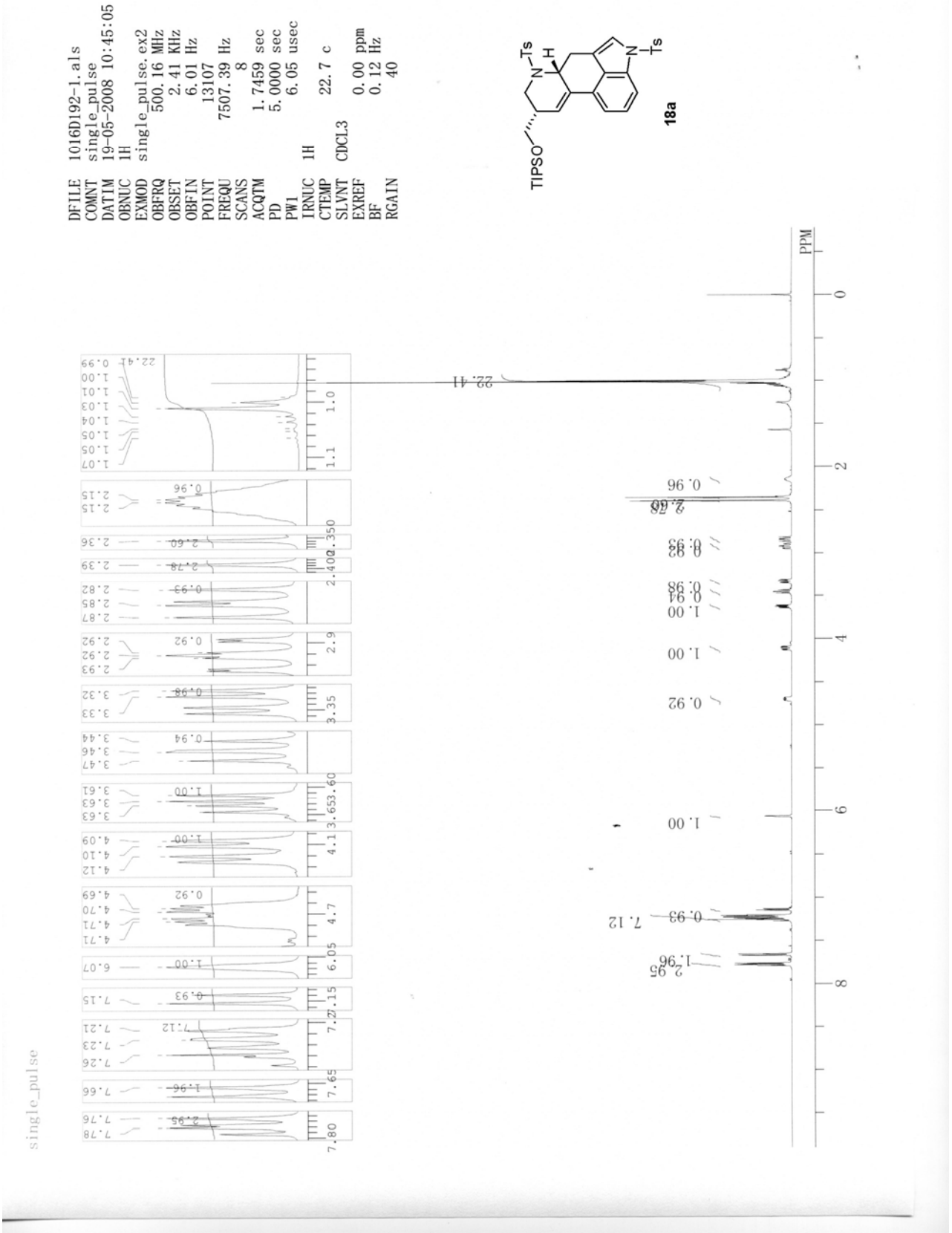

DFILE 1016D182 BCM-1.als
COMNT single pulse decoupled gate
DATIM 10-05-2008 19:04:01
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 500
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 26.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
OTIPS
NHTs
H
H
Br
N
Ts
(±)-16b
11.72
17.93
21.48
21.56
26.31
40.53
46.01
66.36
76.75
77.00
77.26
90.17
91.49
112.86
114.41
121.52
125.10
125.44
126.83
127.09
127.69
128.62
129.61
129.97
134.89
136.47
136.99
143.17
145.22
204.60
PPM
0
50
100
150
200
single pulse decoupled gated NOE

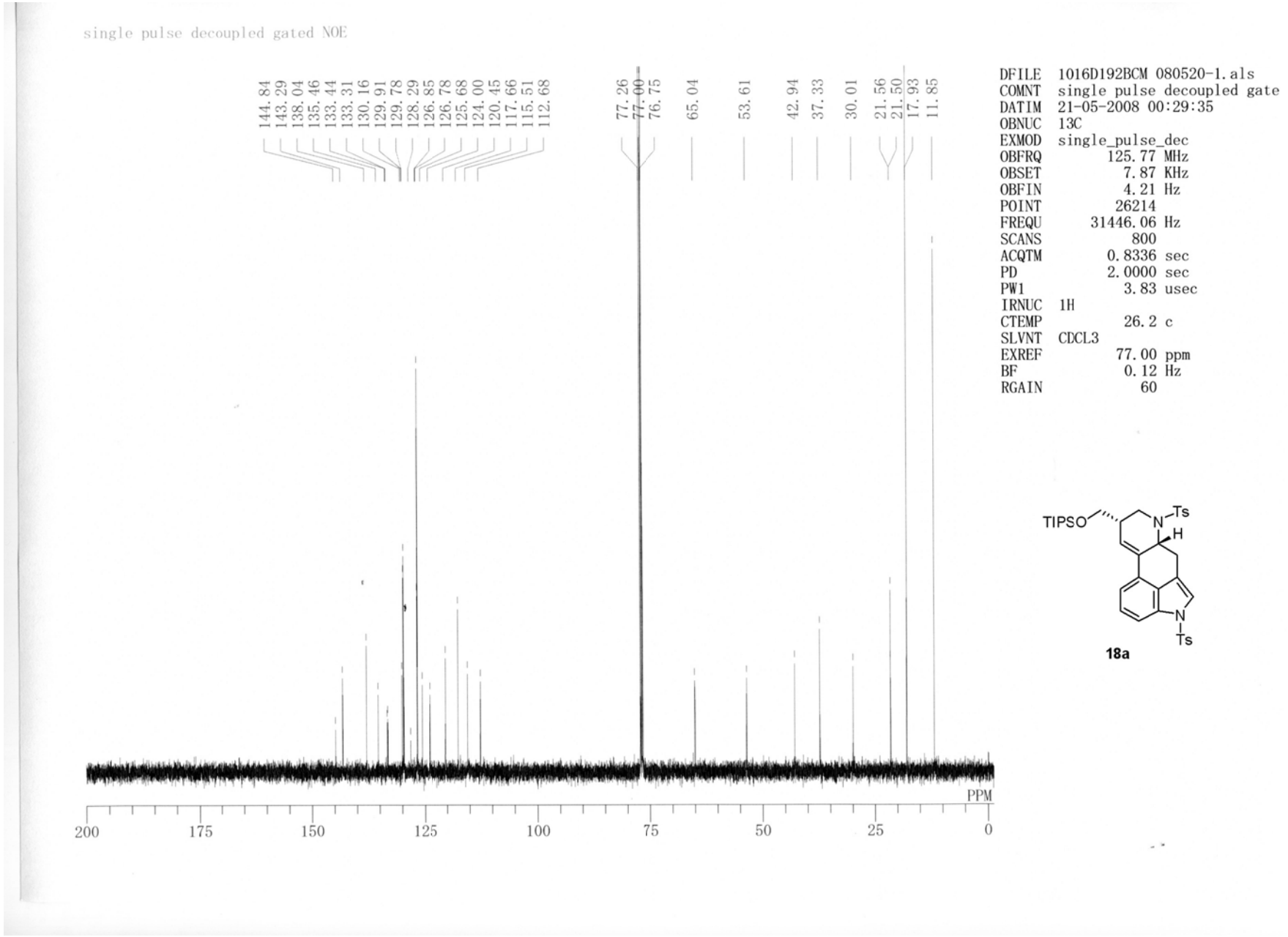

DFILE 1016C160 080201 H-1.als
COMNT single_pulse
DATIM 01-02-2008 15:34:49
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 28.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 48
TIPSO
Ns
Ts
17a
PPM
single_pulse

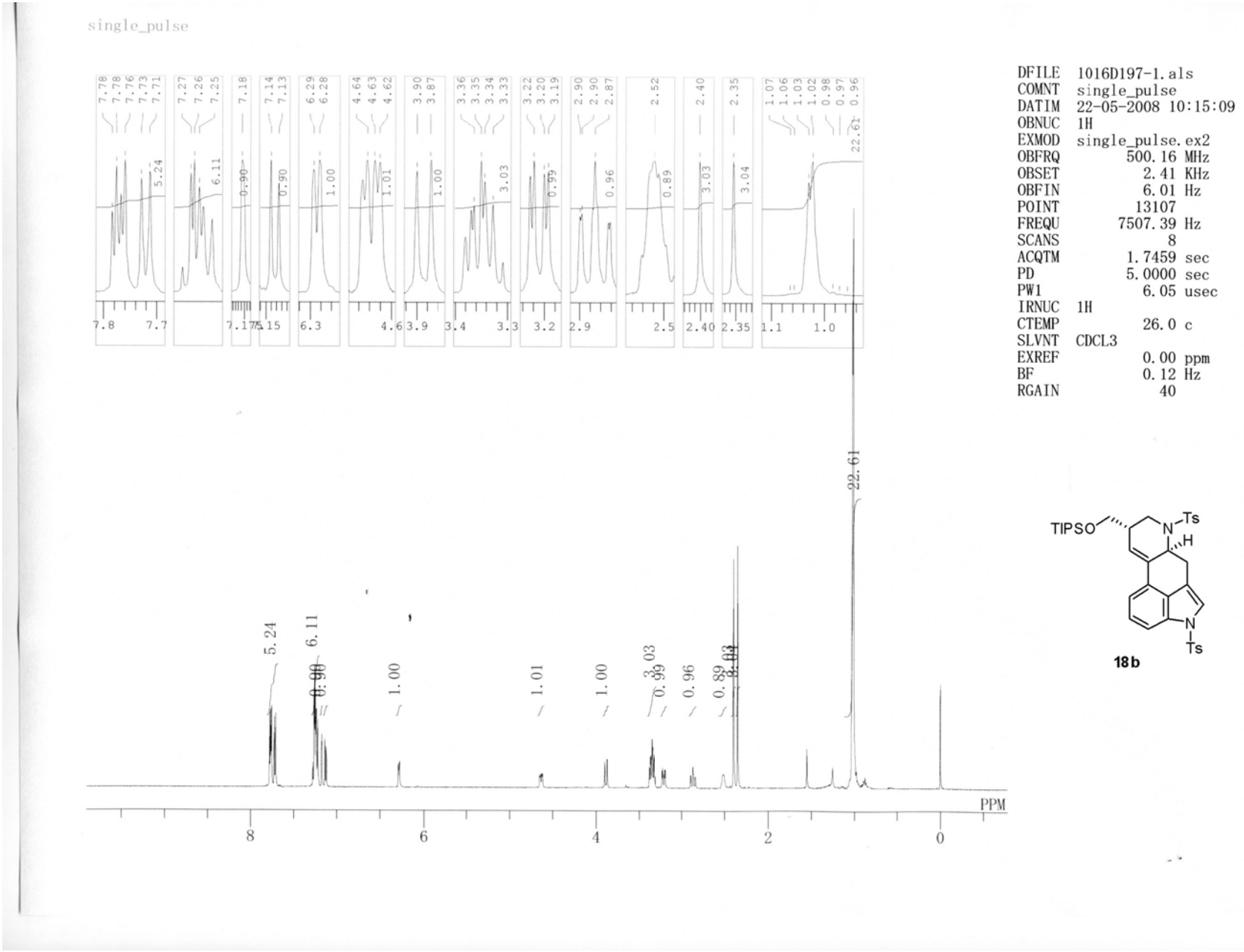

DFILE 1016D50 080201 BCM-1.als
COMNT single pulse decoupled gate
DATIM 01-02-2008 21:37:25
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 512
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 26.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
TIPSO
Ns
Ts
17a
single pulse decoupled gated NOE
PPM

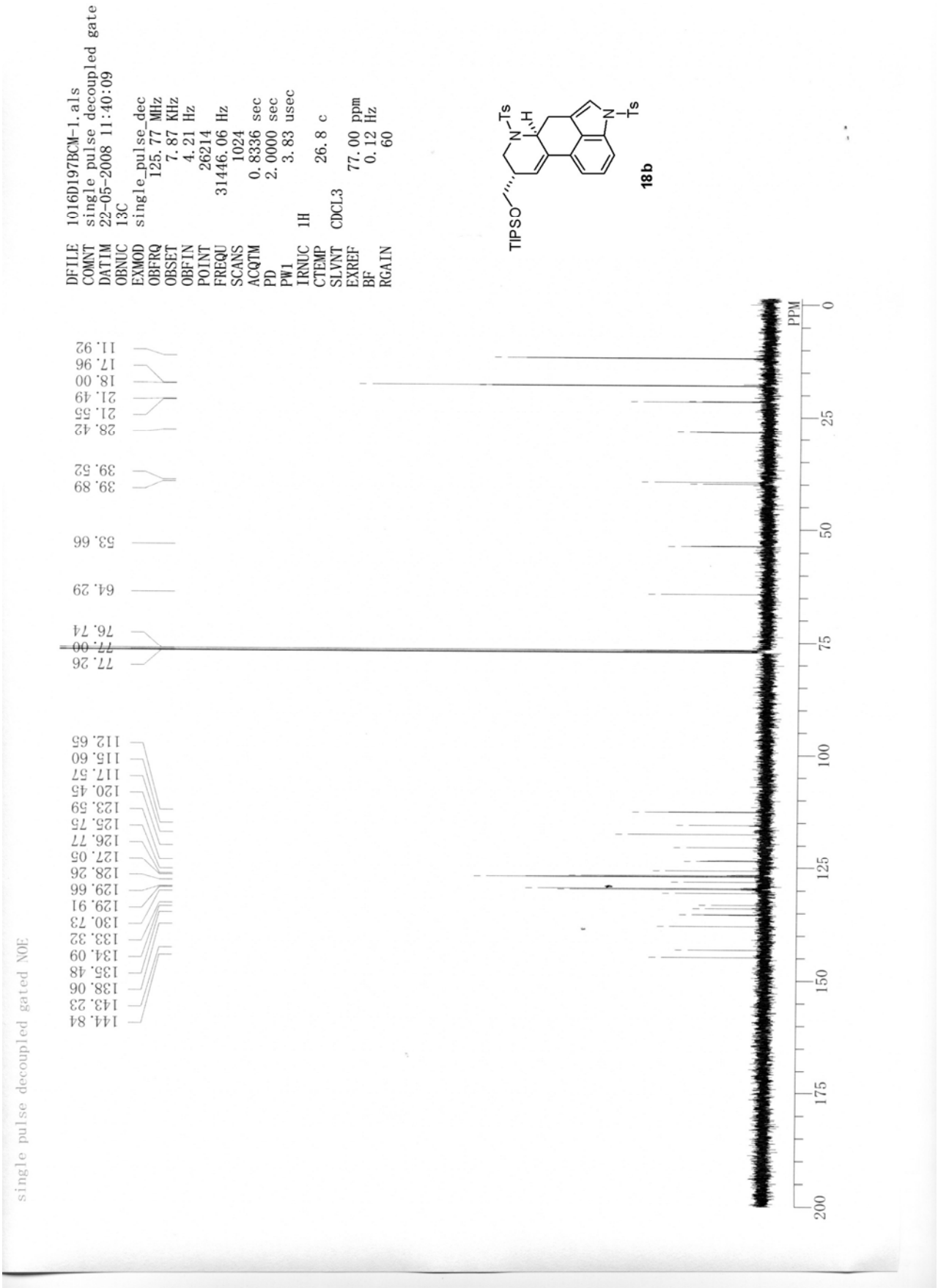

single_pulse
DFILE 1016D113 080308-1.als
COMNT single_pulse
DATIM 08-03-2008 14:49:28
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 25.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40
TIPSO
N
Ns
H
N
Ts
17b
PPM

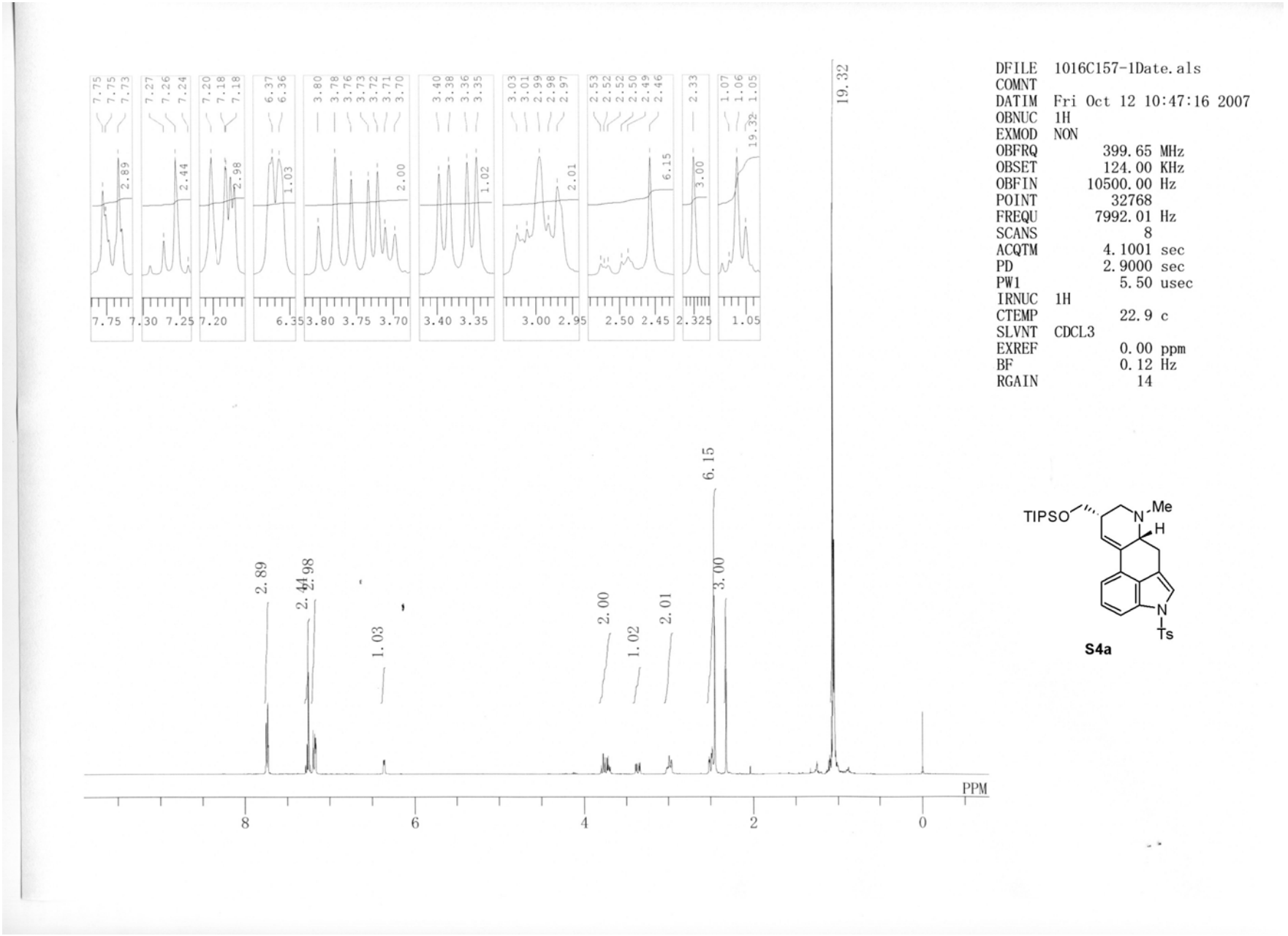

DFILE 1016D113 080308 BCM-1.als
COMNT single pulse decoupled gate
DATIM 08-03-2008 15:37:47
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 1000
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 25.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
TIPSO
Ns
Ts
17b
PPM
single pulse decoupled gated NOE

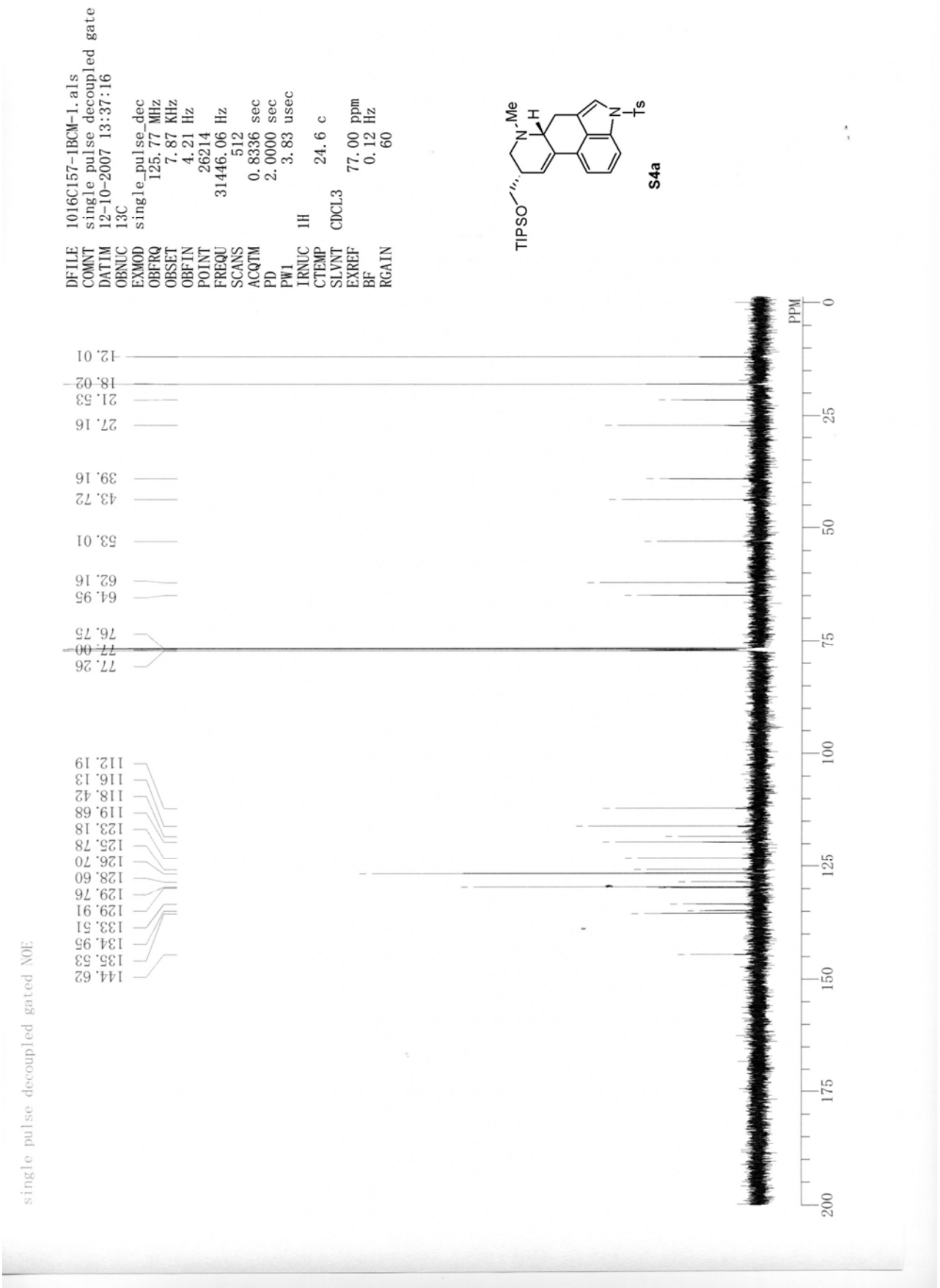

DFILE 1016D192-1.als
COMNT single_pulse
DATIM 19-05-2008 10:45:05
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 22.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40
TIPSO
Ts
N
H
N
Ts
18a
single_pulse
PPM

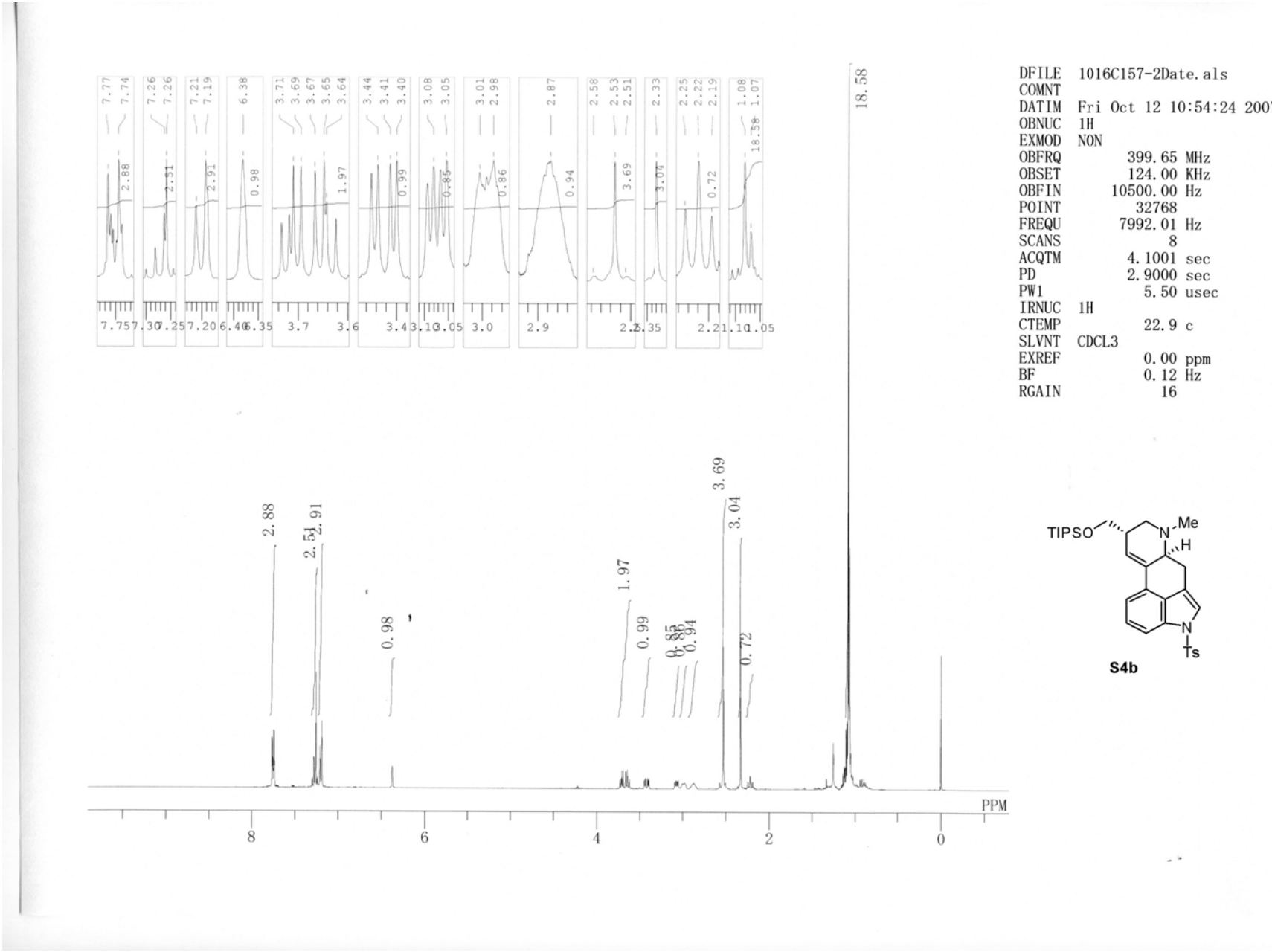

single pulse decoupled gated NOE
144.84
143.29
138.04
135.46
133.44
133.31
130.16
129.91
129.78
128.29
126.85
126.78
125.68
124.00
120.45
117.66
115.51
112.68
77.26
77.00
76.75
65.04
53.61
42.94
37.33
30.01
21.56
21.50
17.93
11.85
DFILE 1016D192BCM 080520-1.als
COMNT single pulse decoupled gate
DATIM 21-05-2008 00:29:35
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 800
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 26.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
TIPSO
N
Ts
H
N
Ts
18a
PPM
200
175
150
125
100
75
50
25
0

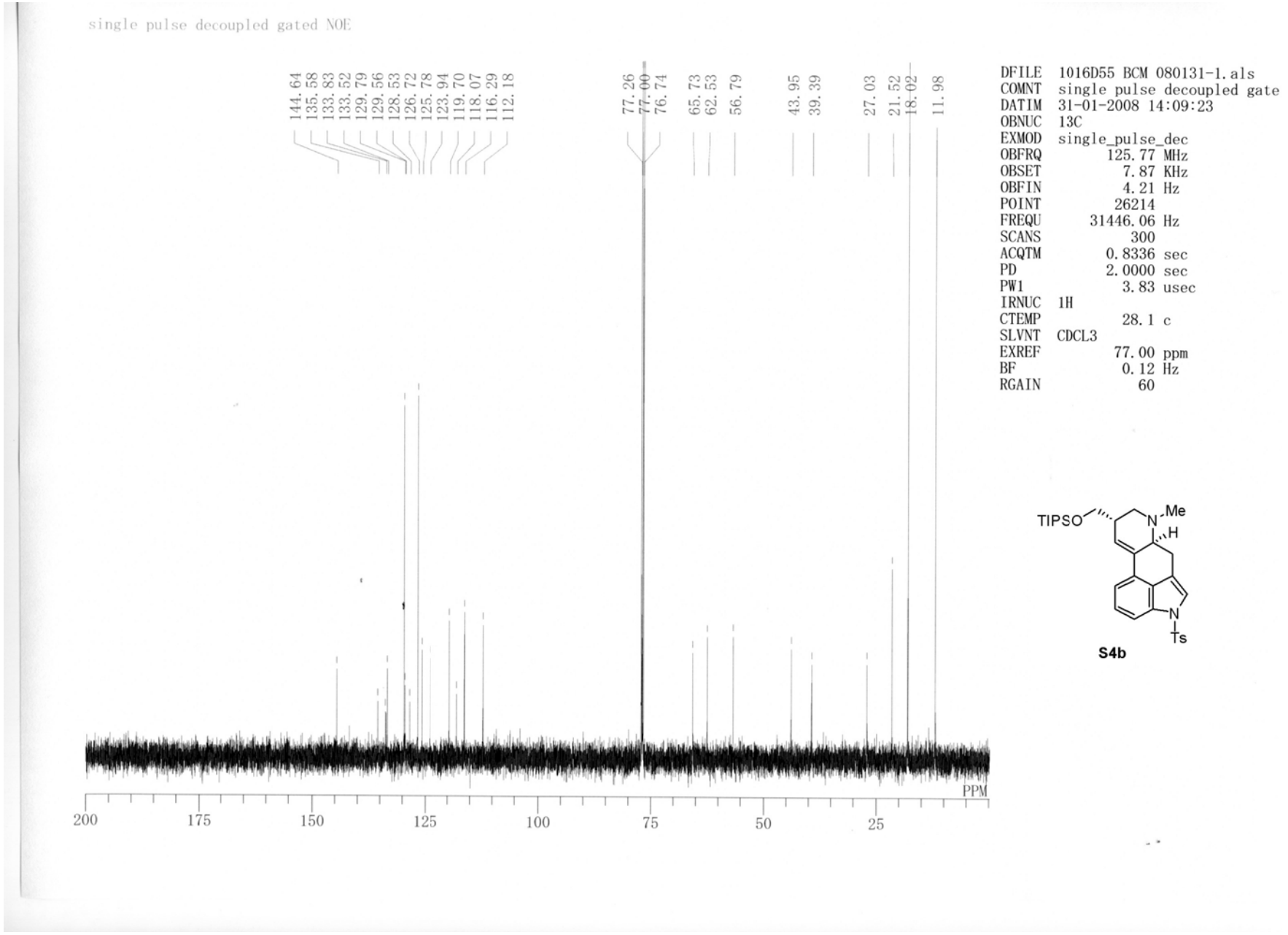

single_pulse
DFILE 1016D197-1.als
COMNT single_pulse
DATIM 22-05-2008 10:15:09
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 26.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40
TIPSO
Ts
N
H
N
Ts
18b
PPM

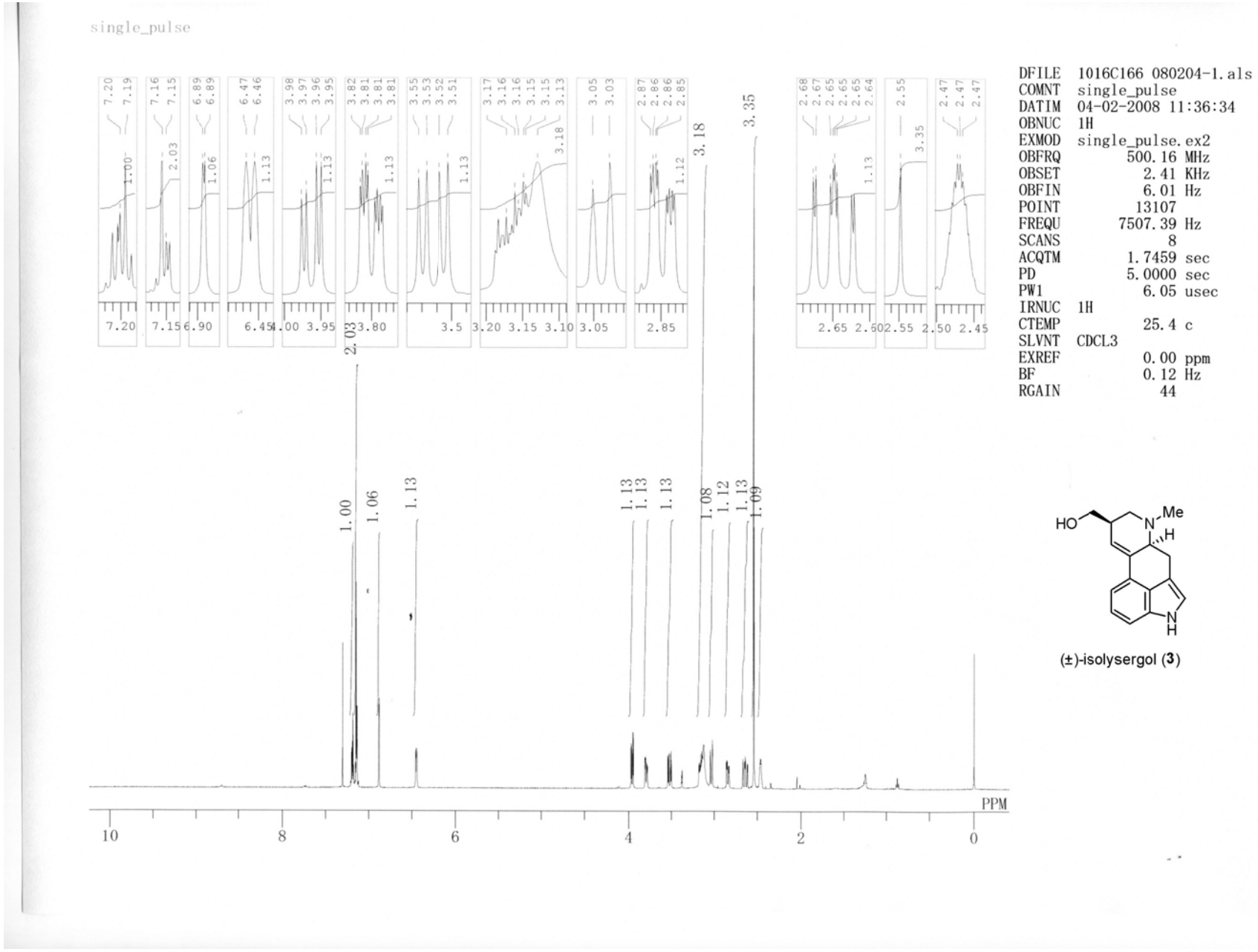

DFILE 1016D197BCM-1.als
COMNT single pulse decoupled gate
DATIM 22-05-2008 11:40:09
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 1024
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 26.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
TIPSO
Ts
H
Ts
18b
single pulse decoupled gated NOE
11.92
17.96
18.00
21.49
21.55
28.42
39.52
39.89
53.66
64.29
76.74
77.00
77.26
112.65
115.60
117.57
120.45
123.59
125.75
126.77
127.05
128.26
129.66
129.91
130.73
133.32
134.09
135.48
138.06
143.23
144.84
PPM
0
25
50
75
100
125
150
175
200


DFILE 1016C157-1Date.als
COMNT
DATIM Fri Oct 12 10:47:16 2007
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7992.01 Hz
SCANS 8
ACQTM 4.1001 sec
PD 2.9000 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 22.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 14
TIPSO
N
Me
H
N
Ts
S4a
PPM

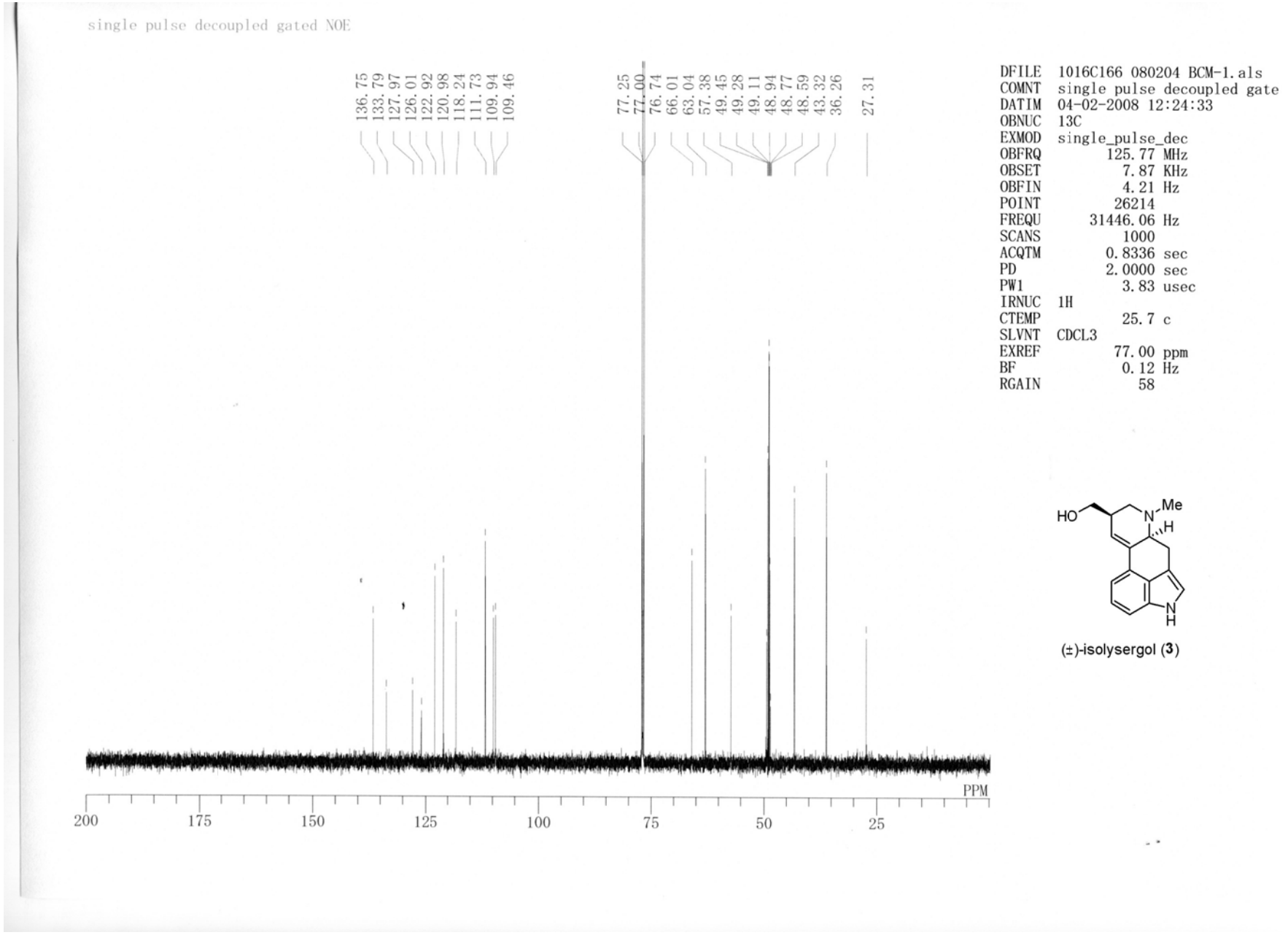

DFILE 1016C157-IBCM-1.als
COMNT single pulse decoupled gate
DATIM 12-10-2007 13:37:16
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 512
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 24.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
TIPSO
Me
H
N
N
Ts
S4a
single pulse decoupled gated NOE
PPM

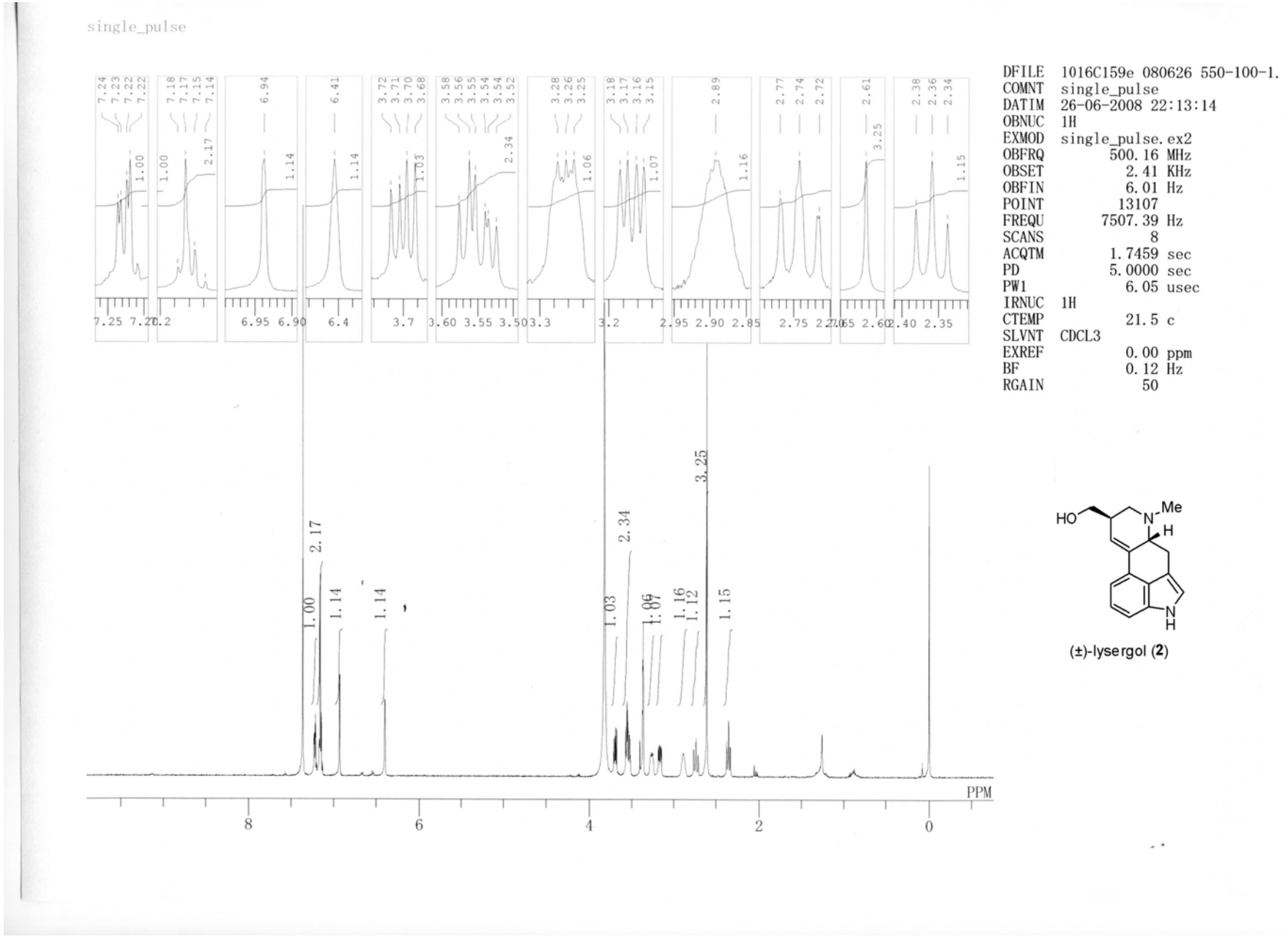

DFILE 1016C157-2Date.als
COMNT
DATIM Fri Oct 12 10:54:24 2007
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7992.01 Hz
SCANS 8
ACQTM 4.1001 sec
PD 2.9000 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 22.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 16
TIPSO
N
Me
H
N
Ts
S4b
PPM

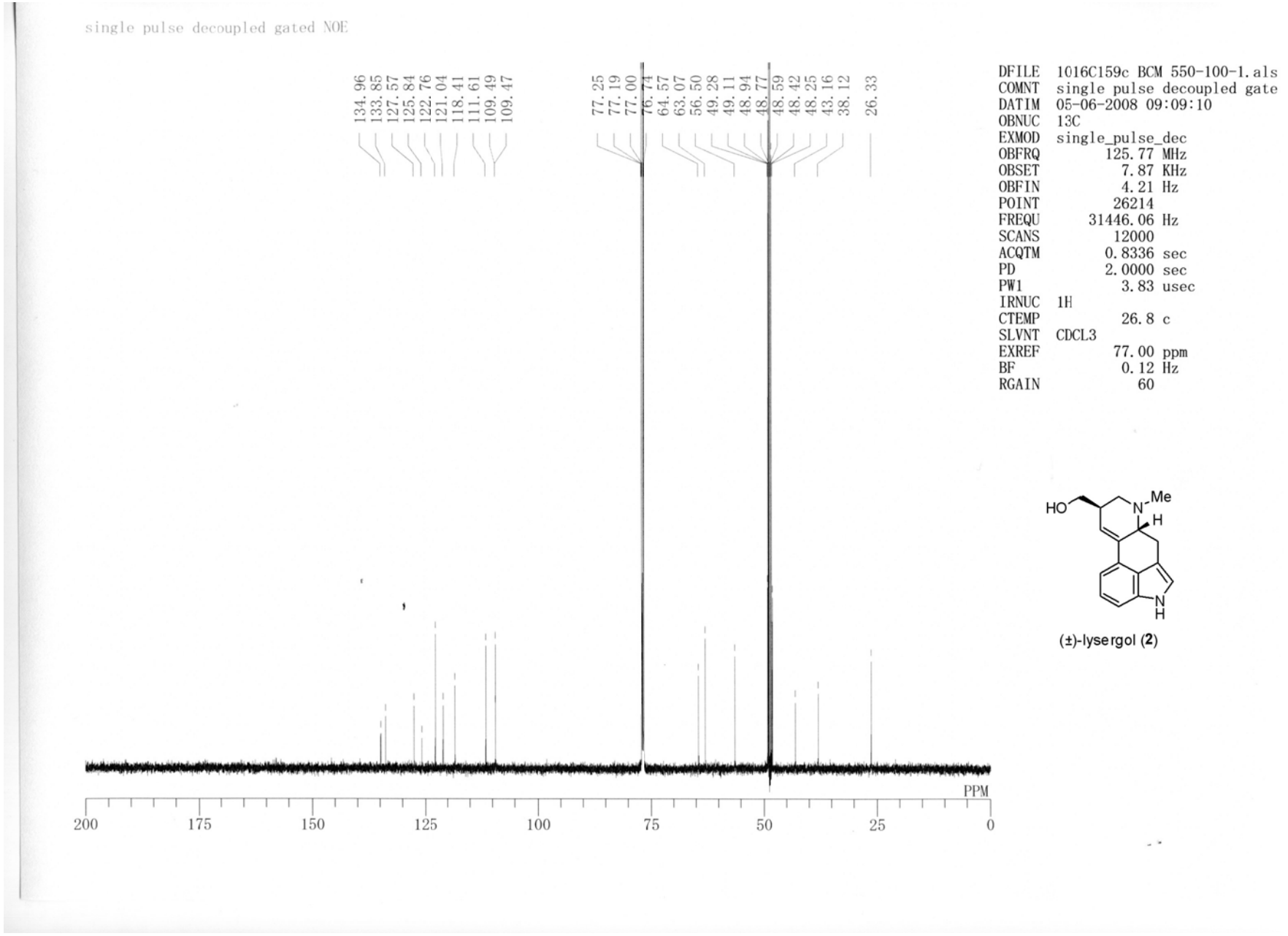

single pulse decoupled gated NOE
144.64
135.58
133.83
133.52
129.79
129.56
128.53
126.72
125.78
123.94
119.70
118.07
116.29
112.18
77.26
77.00
76.74
65.73
62.53
56.79
43.95
39.39
27.03
21.52
18.02
11.98
DFILE 1016D55 BCM 080131-1.als
COMNT single pulse decoupled gate
DATIM 31-01-2008 14:09:23
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 300
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 28.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
TIPSO
N
Me
H
N
Ts
S4b
PPM
200
175
150
125
100
75
50
25

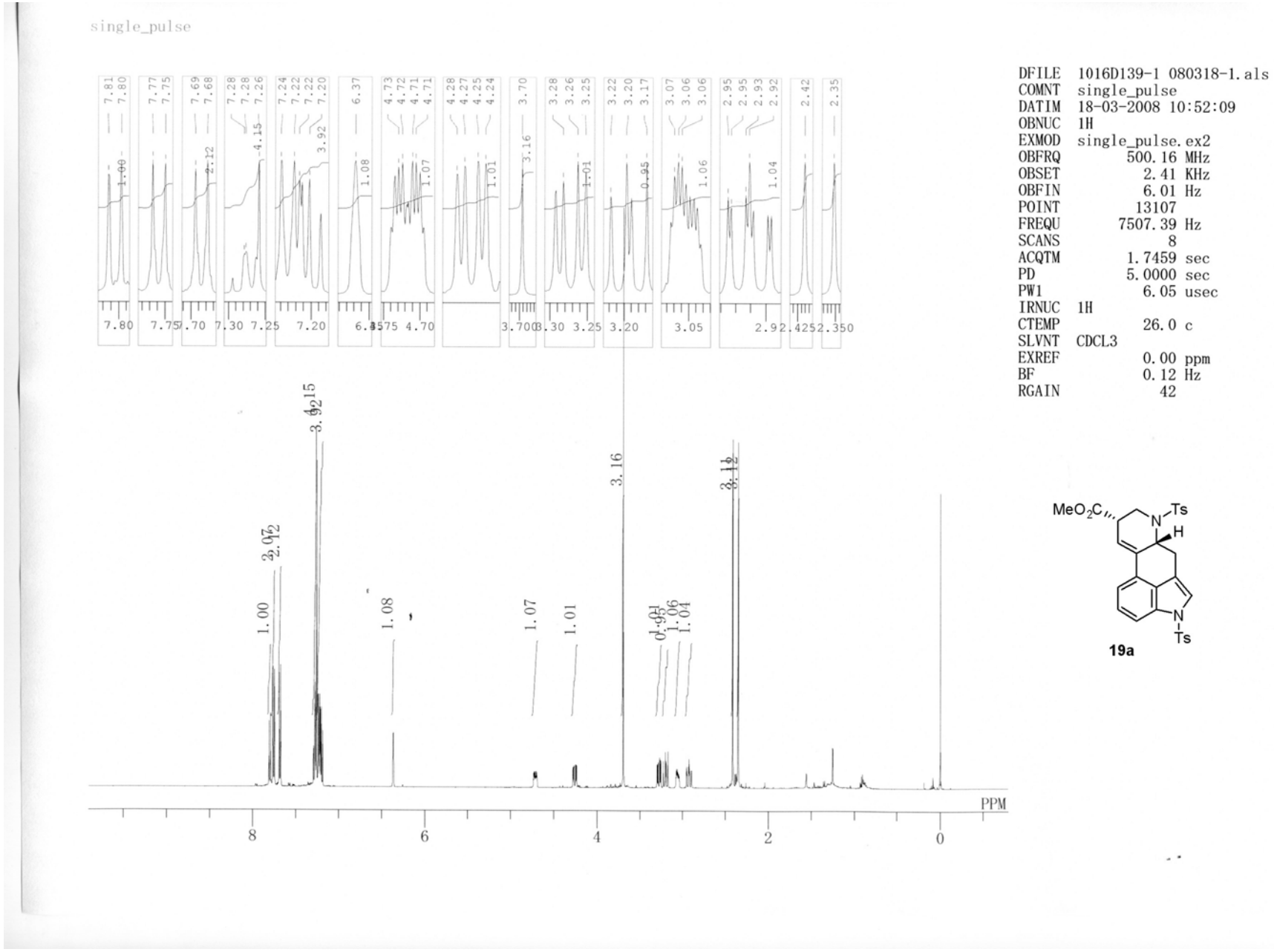


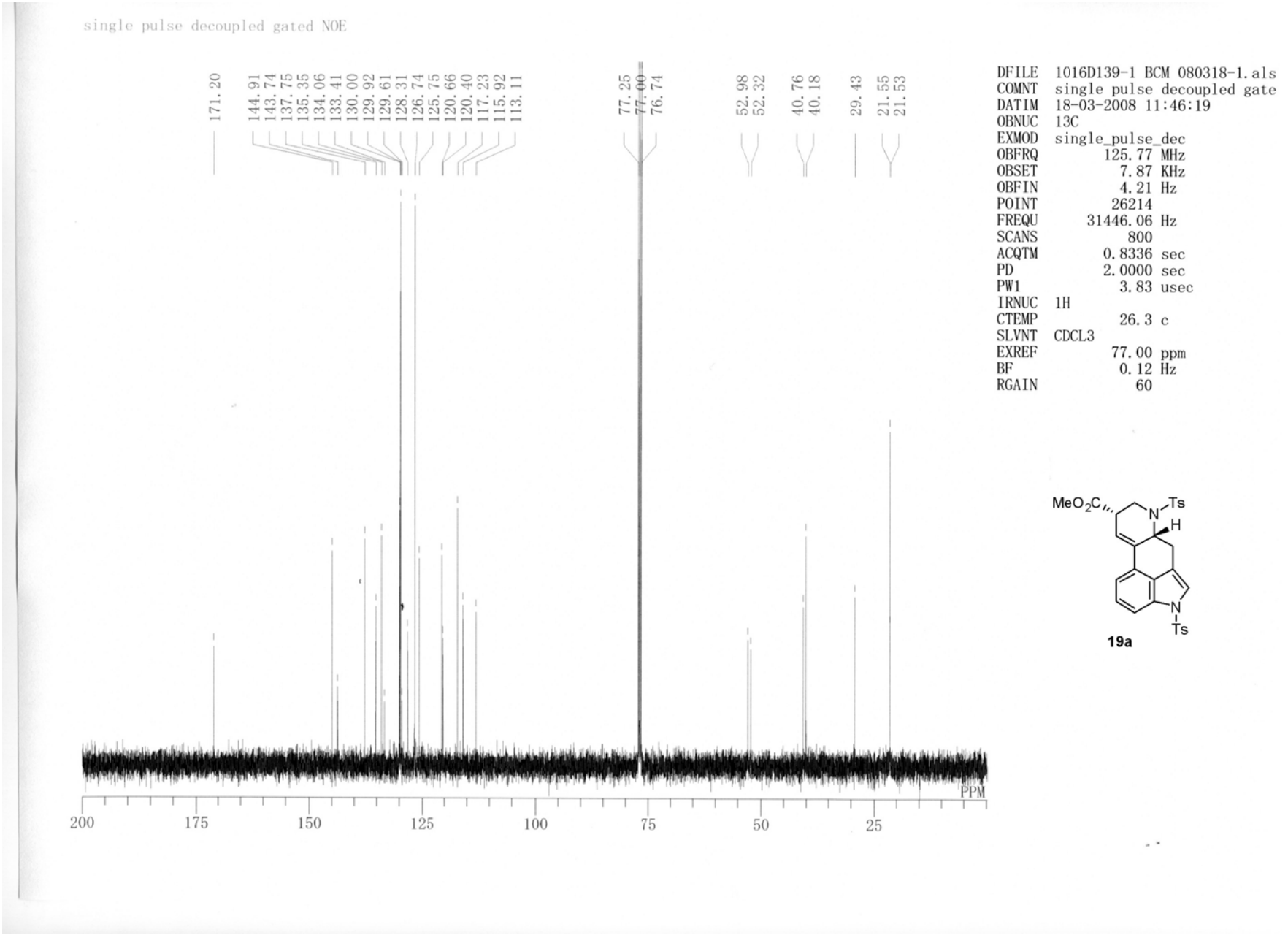
(±)-isolysergol (**3**)

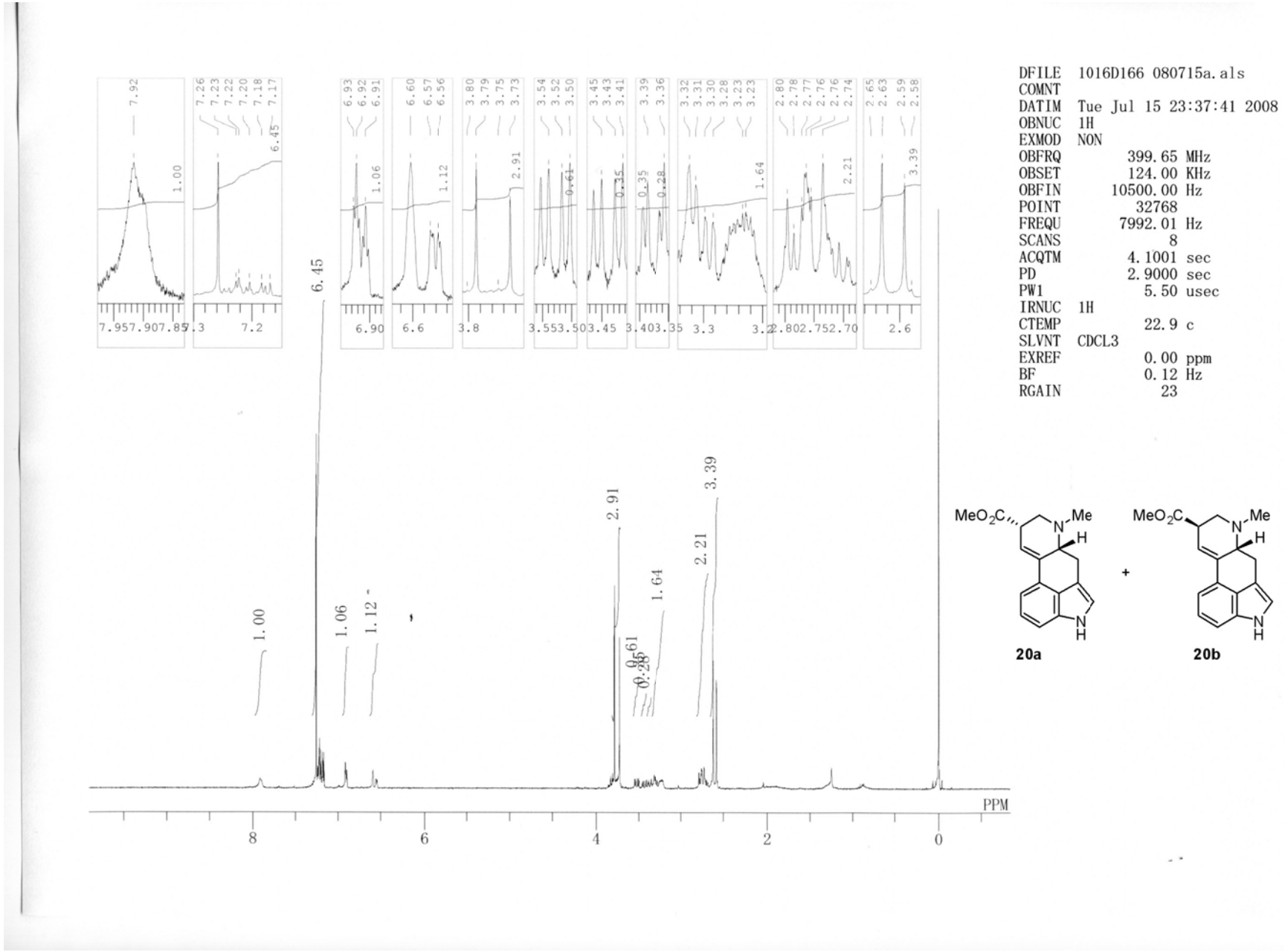

single pulse decoupled gated NOE
136.75
133.79
127.97
126.01
122.92
120.98
118.24
111.73
109.94
109.46
77.25
77.00
76.74
66.01
63.04
57.38
49.45
49.28
49.11
48.94
48.77
48.59
43.32
36.26
27.31
DFILE 1016C166 080204 BCM-1.als
COMNT single pulse decoupled gate
DATIM 04-02-2008 12:24:33
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 1000
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 25.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 58
HO
N
Me
H
N
H
(±)-isolysergol (3)
PPM
200
175
150
125
100
75
50
25

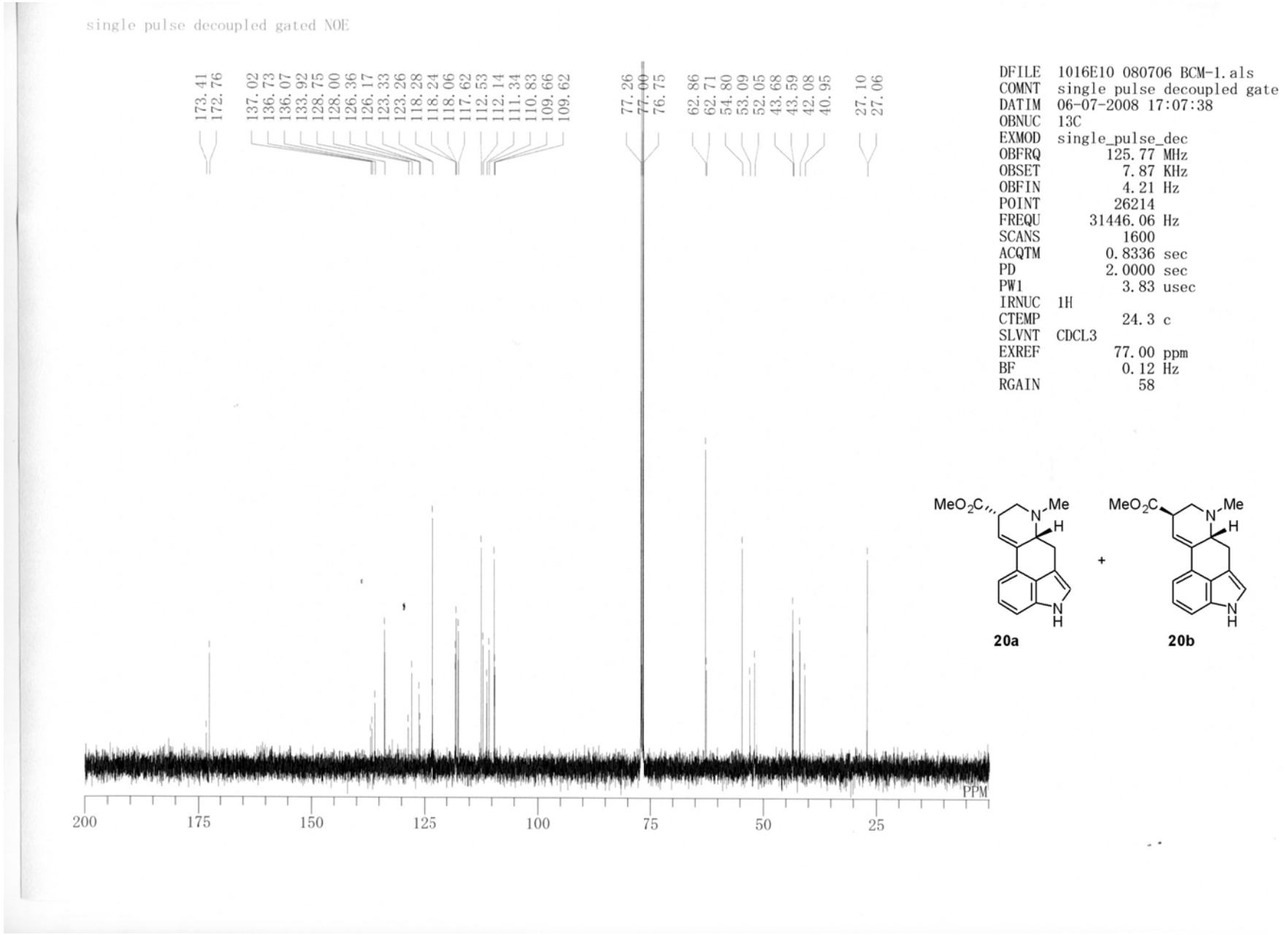

single_pulse
DFILE 1016C159e 080626 550-100-1.
COMNT single_pulse
DATIM 26-06-2008 22:13:14
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 21.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50
PPM
HO
N
Me
H
N
H
(±)-lysergol (2)


single pulse decoupled gated NOE
134.96
133.85
127.57
125.84
122.76
121.04
118.41
111.61
109.49
109.47
77.25
77.19
77.00
76.74
64.57
63.07
56.50
49.28
49.11
48.94
48.77
48.59
48.42
48.25
43.16
38.12
26.33
DFILE 1016C159c BCM 550-100-1.als
COMNT single pulse decoupled gate
DATIM 05-06-2008 09:09:10
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 12000
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 26.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
HO
N
Me
H
N
H
(±)-lysergol (2)
PPM
200
175
150
125
100
75
50
25
0

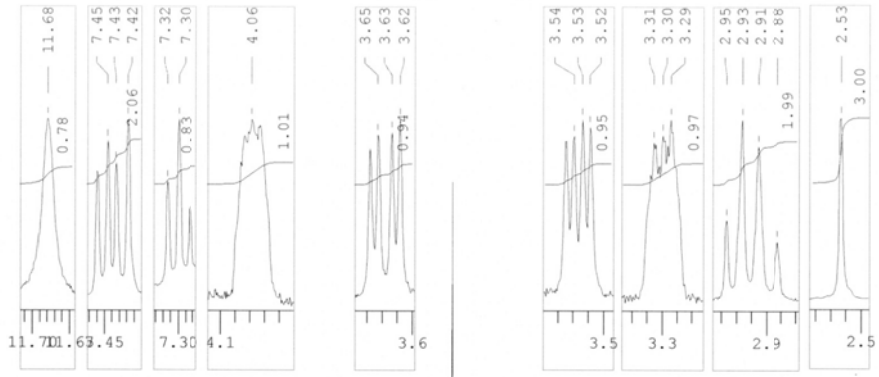

single_pulse
DFILE 1016D139-1 080318-1.als
COMNT single_pulse
DATIM 18-03-2008 10:52:09
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 8
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 26.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 42
PPM
MeO2C
N
Ts
H
19a

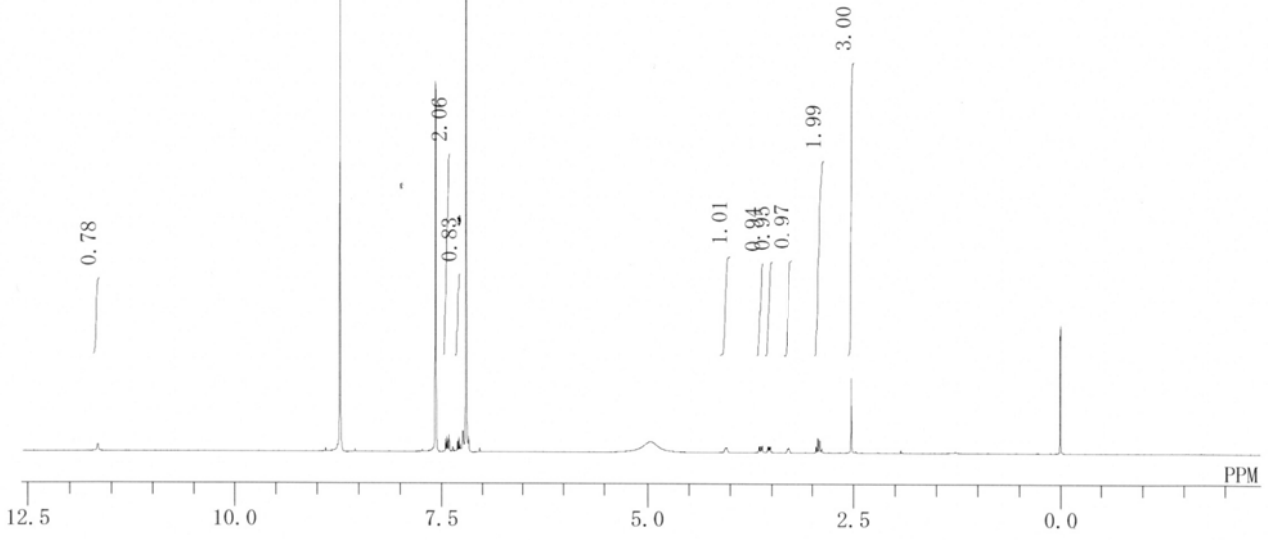

single pulse decoupled gated NOE
171.20
144.91
143.74
137.75
135.35
134.06
133.41
130.00
129.92
129.61
128.31
126.74
125.75
120.66
120.40
117.23
115.92
113.11
77.25
77.00
76.74
52.98
52.32
40.76
40.18
29.43
21.55
21.53
DFILE 1016D139-1 BCM 080318-1.als
COMNT single pulse decoupled gate
DATIM 18-03-2008 11:46:19
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 800
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 26.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60
MeO2C
N
Ts
H
N
Ts
19a
PPM
200
175
150
125
100
75
50
25


DFILE 1016D166 080715a.als
COMNT
DATIM Tue Jul 15 23:37:41 2008
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7992.01 Hz
SCANS 8
ACQTM 4.1001 sec
PD 2.9000 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 22.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 23
MeO2C
N
Me
H
N
H
20a
+
MeO2C
N
Me
H
N
H
20b
PPM

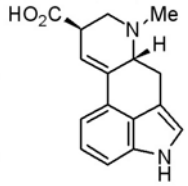

single pulse decoupled gated NOE
173.41
172.76
137.02
136.73
136.07
133.92
128.75
128.00
126.36
126.17
123.33
123.26
118.28
118.24
118.06
117.62
112.53
112.14
111.34
110.83
109.66
109.62
77.26
77.00
76.75
62.86
62.71
54.80
53.09
52.05
43.68
43.59
42.08
40.95
27.10
27.06
DFILE 1016E10 080706 BCM-1.als
COMNT single pulse decoupled gate
DATIM 06-07-2008 17:07:38
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 1600
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 24.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 58
MeO2C
N
Me
H
N
H
20a
+
MeO2C
N
Me
H
N
H
20b
PPM
200
175
150
125
100
75
50
25

single_pulse

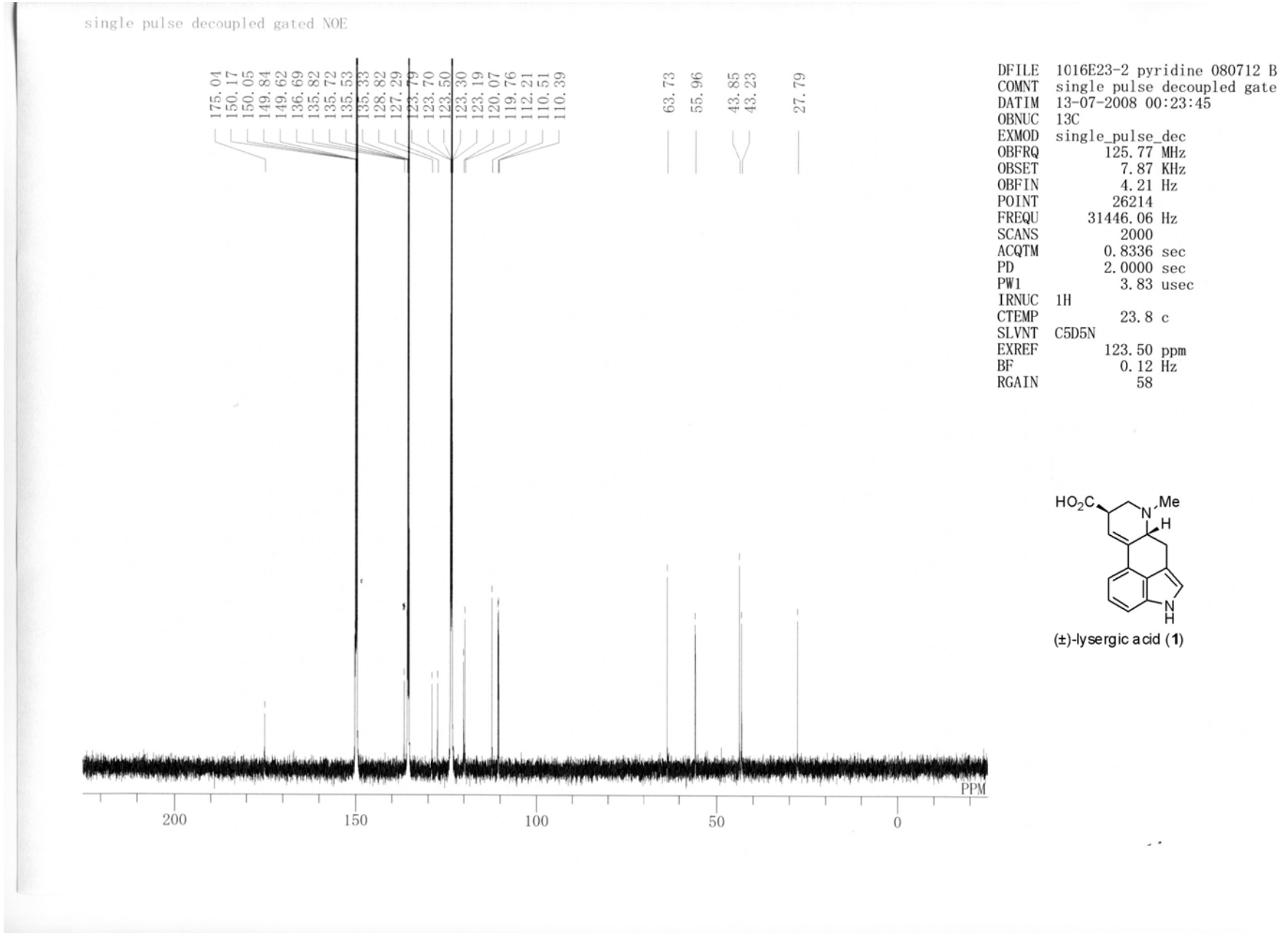




DFILE 1016E23-2a pyridine-1.als
COMNT single_pulse
DATIM 12-07-2008 15:55:15
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.39 Hz
SCANS 32
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 24.8 c
SLVNT C5D5N
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 48



(±)-lysergic acid (**1**)


single pulse decoupled gated NOE
175.04
150.17
150.05
149.84
149.62
136.69
135.82
135.72
135.53
135.33
128.82
127.29
123.79
123.70
123.50
123.30
123.19
120.07
119.76
112.21
110.51
110.39
63.73
55.96
43.85
43.23
27.79
DFILE 1016E23-2 pyridine 080712 B
COMNT single pulse decoupled gate
DATIM 13-07-2008 00:23:45
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 2000
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.83 usec
IRNUC 1H
CTEMP 23.8 c
SLVNT C5D5N
EXREF 123.50 ppm
BF 0.12 Hz
RGAIN 58
HO2C
N
Me
H
N
H
(±)-lysergic acid (1)
PPM
200
150
100
50
0