Directed Heterodimerization: Stereocontrolled Fragment Assembly via Solvent-Caged Unsymmetrical Diazene Fragmentation

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Supporting Information

Contents:

General Procedures. All reactions were performed in oven-dried or flame-dried round bottomed flasks, modified Schlenk (Kjeldahl shape) flasks, or glass pressure vessels. The flasks were fitted with rubber septa and reactions were conducted under a positive pressure of argon. Stainless steel syringes or cannulae were used to transfer air- and moisture-sensitive liquids. Flash column chromatography was performed as described by Still et al. using silica gel (60-Å pore size, 32–63 µm, standard grade, Sorbent Technologies) or non-activated alumina gel (80–325 mesh, chromatographic grade, EM Science).[1] Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel or neutral alumina gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light and/or by exposure to an ethanolic phosphomolybdic acid (PMA), an acidic solution of *p*-anisaldehyde (anis), an aqueous solution of ceric ammonium molybdate (CAM), an aqueous solution of potassium permanganate ($KMnO_4$) or an ethanolic solution of ninhydrin followed by heating (<1 min) on a hot plate (~250 °C). Organic solutions were concentrated on Büchi R-200 rotary evaporators at ~10 Torr (house vacuum) at 25–35 °C, then at ~0.5 Torr (vacuum pump) unless otherwise indicated.

Materials. Commercial reagents and solvents were used as received with the following exceptions: Dichloromethane, diethyl ether, tetrahydrofuran, acetonitrile, methanol and toluene were purchased from J.T. Baker (Cycletainer^{TM}) and were purified by the method of Grubbs et al. under positive argon pressure.[2] *tert*-Butanol was distilled from calcium hydride and stored sealed under an argon atmosphere. *N*-Chlorosuccinimide (NCS) was recrystallized from benzene.

Instrumentation. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded with a Varian inverse probe 500 INOVA spectrometer. Chemical shifts are recorded in parts per million from internal tetramethylsilane on the δ scale and are referenced from the residual protium in the NMR solvent ($CHCl_3$: δ 7.24, CD_2HCN: 1.94, $CD_3SO_2CD_2H$: 2.50). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constant(s) in Hertz, integration, assignment]. Carbon-13 nuclear magnetic resonance spectra were recorded with a Varian 500 INOVA spectrometer and are recorded in parts per million from internal tetramethylsilane on the δ scale and are referenced from the carbon resonances of the solvent ($CDCl_3$: δ 77.23; CD_3CN: 118.79, DMSO-*d*$_6$: 39.51). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constant(s) in Hertz, assignment]. Fluorine-19 nuclear magnetic resonance spectra were recorded with a Varian 300 INOVA spectrometer and are recorded in parts per million on the δ scale and are referenced from the fluorine resonances of trifluorochloromethane (CF_3Cl δ 0.00). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constant(s) in Hertz, integration, assignment]. Chiral HPLC analysis was performed on an Agilent Technologies 1100 Series system. Preparative HPLC was performed on a Waters system with the 1525 Binary HPLC Pump, 2489 UV/Vis Detector, SFO System Fluidics Organizer, and 2767 Sample Manager components. Infrared data were obtained with a Perkin-Elmer 2000 FTIR and are reported as follows: [frequency of absorption (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak, br = broad), assignment]. We thank Dr. Li Li at the Massachusetts Institute of Technology Department of Chemistry instrumentation facility for obtaining mass spectroscopic data.

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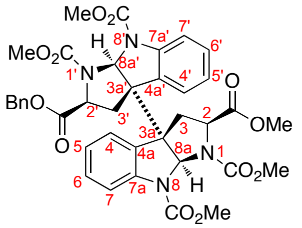
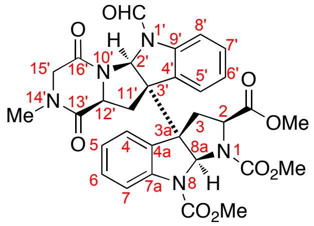
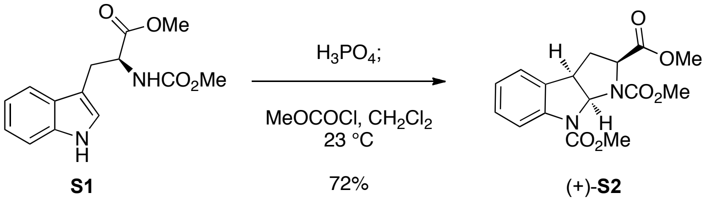
[1] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

[2] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

Positional Numbering System. In assigning the ^{1}H and ^{13}C NMR data of all intermediates en route to dimers *meso*-**2**, (+)-**3**, (+)-**4b**, (+)-**4d**, (+)-**4e**, (+)-**4f**, (+)-**4h**, (+)-**4i**, and (+)-**15** we have employed a uniform numbering system.



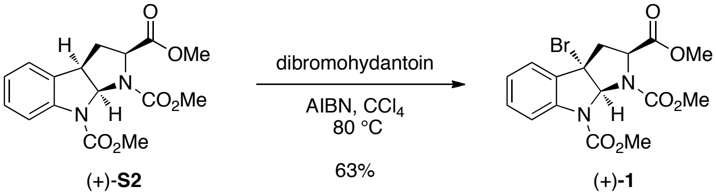




(+)-(2*R*,3a*R*,8a*R*)-Trimethyl3,3a-dihydropyrrolo[2,3-b]indole-1,2,8(2*H*,8a*H*)tricarboxylate (S2):

A fine suspension of indole **S1** (20.0 g, 75.7 mmol, 1 equiv) in aqueous phosphoric acid (225 mL) was stirred vigorously. After 5 h, the homogenous solution was added drop-wise to a vigorously stirred mixture of dichloromethane (600 mL) and an aqueous solution of sodium carbonate (9% wt/wt, 600 mL). The pH of the aqueous layer was monitored through the addition, and once all the sodium carbonate had been neutralized, another portion of solid sodium carbonate was added. This slow addition was continued until all the acid had been neutralized (6 × 55 g of sodium carbonate added). The mixture was extracted with diethyl ether (1 L), and the organic layer was dried over anhydrous sodium sulfate, filtered and concentrated to afford a foamy white solid (18.3 g, 92%). A solution of methylchloroformate (26.5 mL, 345 mmol, 5.00 equiv) in CH_2Cl_2 (100 mL) was slowly added over 2 h to a solution of the hexahydropyrroloindole (18.3 g, 69.2 mmol, 1 equiv), DMAP (216 mg, 1.77 mmol, 0.0260 equiv) and pyridine (28.0 mL, 346 mmol, 5.00 equiv) in CH_2Cl_2 (900 mL) at 0 ºC. After 1 h, the reaction mixture was allowed to warm to 23 ºC. After 5 h, 10% aqueous copper (II) sulfate solution (1 L) was added to the reaction mixture, and the aqueous and organic layers were separated. The organic layer was washed with water (2 × 1 L) and brine (500 mL), was dried over anhydrous sodium sulfate and filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 60→80% EtOAc in hexanes; SiO_2: 12.5 × 7.5 cm) on silica gel to give hexahydropyrroloindole derivative (+)-**S2** ($[\alpha]^{24}_{D}$ = + 16 (*c* 0.32, CH_2Cl_2)) as a white solid (16.6 g, 72%).

^{1}H NMR (500 MHz, $CDCl_3$, 50 °C) δ:	7.61 (d, *J* = 8.0 Hz, 1H, $C_7\mathbf{H}$), 7.17 (t, *J* = 8.0 Hz, 1H, $C_6\mathbf{H}$), 7.07 (d, *J* = 7.5 Hz, 1H, $C_4\mathbf{H}$), 6.95 (t, *J* = 7.5 Hz, 1H, $C_5\mathbf{H}$), 6.40 (d, *J* = 7.0 Hz, 1H, $C_{8a}\mathbf{H}$), 4.60 (d, *J* = 9.0 Hz, 1H, $C_2\mathbf{H}$), 3.98 (t, *J* = 6.5 Hz, 1H, $C_{3a}\mathbf{H}$), 3.84 (s, 3H, $NCO_2C\mathbf{H}_3$), 3.71 (s, 3H, $NCO_2C\mathbf{H}_3$), 3.10 (s, 3H, $CO_2C\mathbf{H}_3$), 2.61 (d, *J* = 13.0 Hz, 1H, $C_3\mathbf{H}_a$), 2.53–2.47 (m, 1H, $C_3\mathbf{H}_b$).
^{13}C NMR (125 MHz, $CDCl_3$, 50 °C) δ:	171.7 ($\mathbf{C}O_2CH_3$), 155.1 ($N\mathbf{C}O_2CH_3$), 154.1 ($N\mathbf{C}O_2CH_3$), 142.9 ($\mathbf{C}_{7a}$), 131.2 ($\mathbf{C}_{4a}$), 128.8 ($\mathbf{C}_6$), 124.2 ($\mathbf{C}_5$), 123.6 ($\mathbf{C}_4$), 116.8 ($\mathbf{C}_7$), 77.4 ($\mathbf{C}_{8a}$), 59.7 ($\mathbf{C}_2$), 53.0 ($NCO_2\mathbf{C}H_3$), 52.9 ($NCO_2\mathbf{C}H_3$), 52.1 ($CO_2\mathbf{C}H_3$), 45.3 ($\mathbf{C}_{3a}$), 34.3 ($\mathbf{C}_3$).
FTIR (neat) cm^{-1}:	3000 (w), 2954 (w), 1714 (s), 1484 (m), 1449 (m), 1397 (m), 1271 (m).
HRMS (ESI):	calc'd for $C_{16}H_{19}N_2O_6$ $[M+H]^+$: 335.1238, found: 335.1249.
TLC (60% EtOAc in hexanes), *R*$_f$:	0.34 (UV).



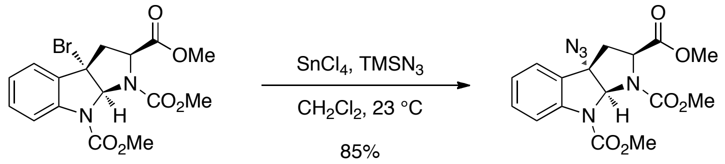
(+)-**S2**

(+)-**1**

(+)-(2*R*,3a*S*,8a*R*)-Trimethyl 3a-bromo-3,3a-dihydropyrrolo[2,3-b]indole-1,2,8(2*H*,8a*H*)-tricarboxylate (1):

Dibromohydantoin (1.98 g, 6.92 mmol, 1.00 equiv) and AIBN (114 mg, 0.694 mmol, 0.010 equiv) were added to a degassed solution of hexahydropyrroloindole (+)-**S2** (2.31 g, 6.92 mmol, 1 equiv) in carbon tetrachloride (140 mL), and the reaction mixture was heated to reflux. After 1 hour, the reaction mixture was allowed to cool to room temperature. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 40→50% EtOAc in hexanes; SiO_2: 15 × 5.0 cm) on silica gel to give bromide (+)-**1** ($[\alpha]^{24}_{D}$ = + 104 (*c* 0.61, CH_2Cl_2)) as a white solid (1.81 g, 63%).

^{1}H NMR (500 MHz, CD_3CN, 60 °C) δ:	7.63 (d, *J* = 8.0 Hz, 1H, $C_7\mathbf{H}$), 7.41 (d, *J* = 8.0 Hz, 1H, $C_4\mathbf{H}$), 7.36 (t, *J* = 8.5 Hz, 1H, $C_6\mathbf{H}$), 7.12 (t, *J* = 7.5 Hz, 1H, $C_5\mathbf{H}$), 6.39 (s, 1H, $C_{8a}\mathbf{H}$), 4.59 (d, 1H, *J* = 9.5 Hz, $C_2\mathbf{H}$), 3.89 (s, 3H, $NCO_2C\mathbf{H}_3$), 3.70 (s, 3H, $NCO_2C\mathbf{H}_3$), 3.32 (d, *J* = 13.0 Hz, 1H, $C_3\mathbf{H}_a$), 3.18 (dd, *J* = 13.0, 9.5 Hz, 1H, $C_3\mathbf{H}_b$), 3.17 (s, 3H, $CO_2C\mathbf{H}_3$).
^{13}C NMR (125 MHz, CD_3CN, 60 °C) δ:	171.9 ($\mathbf{C}O_2CH_3$), 156.0 ($N\mathbf{C}OCH_3$), 155.4 ($N\mathbf{C}OCH_3$), 143.6 ($\mathbf{C}_{7a}$), 134.3 ($\mathbf{C}_{4a}$), 132.6 ($\mathbf{C}_6$), 126.1 ($\mathbf{C}_5$), 125.9 ($\mathbf{C}_4$), 118.8 ($\mathbf{C}_7$), 86.6 ($\mathbf{C}_{8a}$), 62.7 ($\mathbf{C}_{3a}$), 61.5 ($\mathbf{C}_2$), 54.5 ($NCO_2\mathbf{C}H_3$), 54.2 ($NCO_2\mathbf{C}H_3$), 53.3 ($CO_2\mathbf{C}H_3$), 44.4 ($\mathbf{C}_3$).
FTIR (neat) cm^{-1}:	3002 (w), 2954 (w), 1717 (s), 1481 (m), 1447 (s), 1393 (s).
HRMS (ESI):	calc'd for $C_{16}H_{18}BrN_2O_6$ $[M+H]^+$: 413.0343, found: 413.0348.
TLC (40% EtOAc in hexanes), R_f:	0.20 (UV).

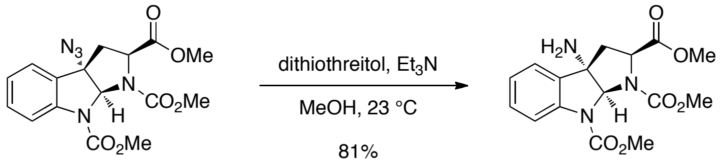


(+)-**1** (+)-**S3**

(+)-(2*R*,3a*S*,8a*R*)-Trimethyl 3a-azido-3,3a-dihydropyrrolo[2,3-b]indole-1,2,8(2*H*,8a*H*)-tricarboxylate (S3):

Tin (IV) chloride (510 µL, 4.4 mmol, 1.0 equiv) was added to a solution of trimethylsilylazide (11.7 mL, 88.2 mmol, 20.0 equiv) and bromide (+)-**1** (1.81 g, 4.39 mmol, 1 equiv) in CH_2Cl_2 (44 mL) via syringe. After 12 hours, the reaction mixture was cooled to 0 °C, and excess acid was quenched by addition of aqueous saturated sodium bicarbonate solution (12 mL). The reaction mixture was diluted with water (20 mL) and extracted with dichloromethane (2 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate and filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 50% EtOAc in hexanes; SiO_2: 15 × 4.0 cm) on silica gel to give azide (+)-**S3** ($[\alpha]^{24}_{D} = +47$ (*c* 0.79, CH_2Cl_2)) as a white solid (1.4 g, 85%).

^1H NMR (500 MHz, CD_3CN, 50 °C) δ:	7.72 (d, $J = 8.0$ Hz, 1H, $C_7\mathbf{H}$), 7.43 (t, $J = 7.5$ Hz, 1H, $C_6\mathbf{H}$), 7.39 (d, $J = 7.5$ Hz, 1H, $C_4\mathbf{H}$), 7.17 (t, $J = 7.5$ Hz, 1H, $C_5\mathbf{H}$), 6.12 (s, 1H, $C_{8a}\mathbf{H}$), 4.67 (d, 1H, $J = 9.0$ Hz, $C_2\mathbf{H}$), 3.86 (s, 3H, $NCO_2C\mathbf{H}_3$), 3.69 (s, 3H, $NCO_2C\mathbf{H}_3$), 3.18 (s, 3H, $CO_2C\mathbf{H}_3$), 2.90 (d, $J = 13.0$ Hz, 1H, $C_3\mathbf{H}_a$), 2.73 (dd, $J = 13.0, 9.5$ Hz, 1H, $C_3\mathbf{H}_b$).
^{13}C NMR (125 MHz, CD_3CN, 50 °C) δ:	172.1 ($\mathbf{C}O_2CH_3$), 156.2 ($N\mathbf{C}OCH_3$), 155.2 ($N\mathbf{C}OCH_3$), 144.9 ($\mathbf{C}_{7a}$), 132.9 ($\mathbf{C}_{4a}$), 129.5 ($\mathbf{C}_6$), 125.8 ($\mathbf{C}_5$), 125.5 ($\mathbf{C}_4$), 118.6 ($\mathbf{C}_7$), 83.0 ($\mathbf{C}_{8a}$), 75.7 ($\mathbf{C}_{3a}$), 61.0 ($\mathbf{C}_2$), 54.3 ($NCO_2\mathbf{C}H_3$), 54.1 ($NCO_2\mathbf{C}H_3$), 53.3 ($CO_2\mathbf{C}H_3$), 38.9 ($\mathbf{C}_3$).
FTIR (neat) cm^{-1}:	2955 (w), 2105 (s), 1721 (s), 1482 (m), 1448 (s), 1392 (m), 1263 (m).
HRMS (ESI):	calc'd for $C_{16}H_{18}N_5O_6$ $[M+H]^+$: 376.1252, found: 376.1262.
TLC (45% EtOAc in hexanes), R_f:	0.19 (UV, CAM).

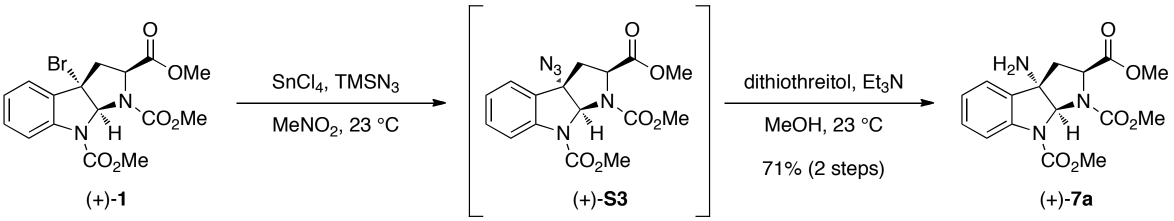


(+)-**S3** (+)-**7a**

<u>(+)-(2*R*,3a*S*,8a*R*)-Trimethyl 3a-amino-3,3a-dihydropyrrolo[2,3-b]indole-1,2,8(2*H*,8a*H*)-tricarboxylate (7a):</u>

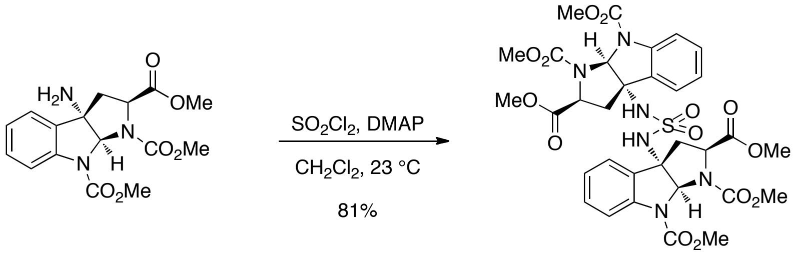
Triethylamine (435 μL, 3.11 mmol, 6.23 equiv) was added via syringe to a solution of azide (+)-**S3** (187 mg, 0.499 mmol, 1 equiv) and dithiothreitol (456 mg, 2.96 mmol, 5.93 equiv) in methanol (6 mL). After 20 min, the reaction mixture was diluted with CH_2Cl_2 (20 mL) and washed with aqueous saturated sodium bicarbonate solution (10 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous sodium sulfate, and filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 35% iPrOH in hexanes→7% iPrOH in CH_2Cl_2→5% MeOH in CH_2Cl_2; SiO_2: 18.5 × 2.5 cm) on silica gel to give amine (+)-**7a** ($[\alpha]^{23}_{D}$ = + 18 (*c* 1.4, CH_2Cl_2)) as a white solid (142 mg, 81%).

^{1}H NMR (500 MHz, $CDCl_3$, 50 °C) δ:	7.68 (d, *J* = 8.0 Hz, 1H, C$_7$**H**), 7.26 (t, *J* = 8.5 Hz, 1H, C$_6$**H**), 7.24 (d, *J* = 7.5 Hz, 1H, C$_4$**H**), 7.02 (t, *J* = 7.5 Hz, 1H, C$_5$**H**), 5.92 (s, 1H, C$_{8a}$**H**), 4.64 (d, *J* = 9.5 Hz, 1H, C$_2$**H**), 3.87 (s, 3H, NCO$_2$C**H**$_3$), 3.73 (s, 3H, NCO$_2$C**H**$_3$), 3.15 (s, 3H, CO$_2$C**H**$_3$), 2.77 (d, *J* = 13.0 Hz, 1H, C$_3$**H**$_a$), 2.47 (dd, *J* = 12.5, 9.0 Hz, 1H, C$_3$**H**$_b$), 1.63 (br-s, 2H, N**H**$_2$).
^{13}C NMR (125 MHz, $CDCl_3$, 50 °C) δ:	171.2 (**C**O$_2$CH$_3$), 155.2 (N**C**OCH$_3$), 154.4 (N**C**OCH$_3$), 142.6 (**C**$_{7a}$), 133.9 (**C**$_{4a}$), 130.2 (**C**$_6$), 124.0 (**C**$_5$), 123.5 (**C**$_4$), 117.1 (**C**$_7$), 84.2 (**C**$_{8a}$), 68.6 (**C**$_{3a}$), 59.8 (**C**$_2$), 53.1 (NCO$_2$**C**H$_3$), 53.1 (NCO$_2$**C**H$_3$), 52.2 (CO$_2$**C**H$_3$), 41.5 (**C**$_3$).
FTIR (neat) cm^{-1}:	3364 (br-w), 3002 (w), 2955 (w), 1713 (s), 1483 (m), 1450 (s), 1394 (m).
HRMS (ESI):	calc'd for $C_{16}H_{20}N_3O_6$ $[M+H]^+$: 350.1347, found: 350.1347.
TLC (10% MeOH in CH_2Cl_2), R_f:	0.39 (UV).



(+)-(2*R*,3a*S*,8a*R*)-Trimethyl 3a-azido-3,3a-dihydropyrrolo[2,3-b]indole-1,2,8(2*H*,8a*H*)-tricarboxylate (7a):

Tin (IV) chloride (57 μL, 0.49 mmol, 2.0 equiv) was added to a solution of trimethylsilylazide (165 μL, 1.2 mmol, 5.1 equiv) and bromide (+)-**1** (101 mg, 0.25 mmol, 1 equiv) in nitromethane (1.2 mL) via syringe. After 48 hours, the reaction mixture was cooled to 0 °C, and excess acid was quenched by addition of aqueous saturated sodium bicarbonate solution (2 mL). The reaction mixture was diluted with water (10 mL) and extracted with dichloromethane (2 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate and filtered. The volatiles were removed under reduced pressure to afford the crude azide (+)-**S3** (113 mg). Triethylamine (102 μL, 0.730 mmol, 3.0 equiv) was added via syringe to a solution of crude azide (+)-**S3** (113 mg) and dithiothreitol (113 mg, 0.733 mmol, 3.0 equiv) in methanol (1.2 mL). After 3 hours, the reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed with aqueous saturated sodium bicarbonate solution (20 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous sodium sulfate, and filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 35% iPrOH in hexanes→8% iPrOH in CH_2Cl_2→5% MeOH in CH_2Cl_2; SiO_2: 13 × 1.5 cm) on silica gel to give amine (+)-**7a** as a white solid (61 mg, 71%). See page S7 for spectroscopic data for amine (+)-**7a**.



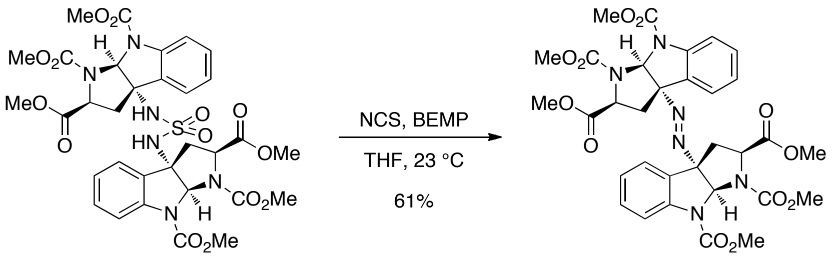
(+)-**7a**

(+)-**6a**

(+)-Homodimeric sulfamide 6a (Scheme 2):

Sulfuryl chloride (7 µL, 0.087 mmol, 0.51 equiv) was added drop-wise to a solution of amine (+)-**7a** (59 mg, 0.17 mmol, 1 equiv) and DMAP (0.8 mg, 0.007 mmol, 0.04 equiv) in CH_2Cl_2 (5.0 mL) at 0 °C. After 5 min, triethylamine (59 µL, 0.42 mmol, 2.5 equiv) was added to the reaction mixture. After 30 min, the reaction was allowed to warm to 23 °C. After 12 hours, excess acid was quenched by addition of saturated sodium bicarbonate solution (1 mL). The reaction mixture was diluted with water and extracted with CH_2Cl_2 (3 × 20 mL). The organic layer was washed with brine (10 mL), dried over anhydrous sodium sulfate and filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 4% MeOH in CH_2Cl_2; SiO_2: 10 × 1.5 cm) on silica gel to give sulfamide (+)-**6a** ($[\alpha]^{24}_{D}$ = + 67 (*c* 0.91, CH_2Cl_2)) as a white solid (52 mg, 81%).

^{1}H NMR (500 MHz, CD_3CN, 60 °C) δ:	7.62 (d, *J* = 8.0 Hz, 2H, $C_7\mathbf{H}$), 7.32 (t, *J* = 7.5 Hz, 2H, $C_6\mathbf{H}$), 7.21 (d, *J* = 7.5 Hz, 2H, $C_4\mathbf{H}$), 7.01 (t, *J* = 7.5 Hz, 2H, $C_5\mathbf{H}$), 6.34 (s, 2H, $C_{8a}\mathbf{H}$), 5.83 (s, 2H, $N\mathbf{H}SO_2$), 4.61 (d, *J* = 9.5 Hz, 2H), 3.82 (s, 6H, $NCO_2C\mathbf{H}_3$), 3.68 (br-s, 6H, $NCO_2C\mathbf{H}_3$), 3.12 (s, 6H, $CO_2C\mathbf{H}_3$), 2.95 (dd, *J* = 13.0, 9.5 Hz, 2H, $C_3\mathbf{H}_a$), 2.71 (dd, *J* = 13.0 Hz, 2H, $C_3\mathbf{H}_b$).
^{13}C NMR (125 MHz, CD_3CN, 60 °C) δ:	172.3 ($\mathbf{C}O_2CH_3$), 156.4 ($N\mathbf{C}O_2CH_3$), 155.3 ($N\mathbf{C}O_2CH_3$), 145.1 ($\mathbf{C}_{7a}$), 132.2 ($\mathbf{C}_6$), 131.4 ($\mathbf{C}_{4a}$), 126.8 ($\mathbf{C}_4$), 125.1 ($\mathbf{C}_5$), 118.5 ($\mathbf{C}_7$), 81.6 ($\mathbf{C}_{8a}$), 71.7 ($\mathbf{C}_{3a}$), 60.4 ($\mathbf{C}_2$), 54.2 ($NCO_2\mathbf{C}H_3$), 54.1 ($NCO_2\mathbf{C}H_3$), 53.2 ($CO_2\mathbf{C}H_3$), 39.5 ($\mathbf{C}_3$).
FTIR (neat) cm^{-1}:	3238 (br-m), 2956 (m), 1716 (s), 1484 (s), 1451 (s), 1396 (s).
HRMS (ESI):	calc'd for $C_{32}H_{36}N_6NaO_{14}S$ $[M+Na]^+$: 783.1902, found: 783.1905.
TLC (4% MeOH in CH_2Cl_2), R_f:	0.22 (UV, CAM).

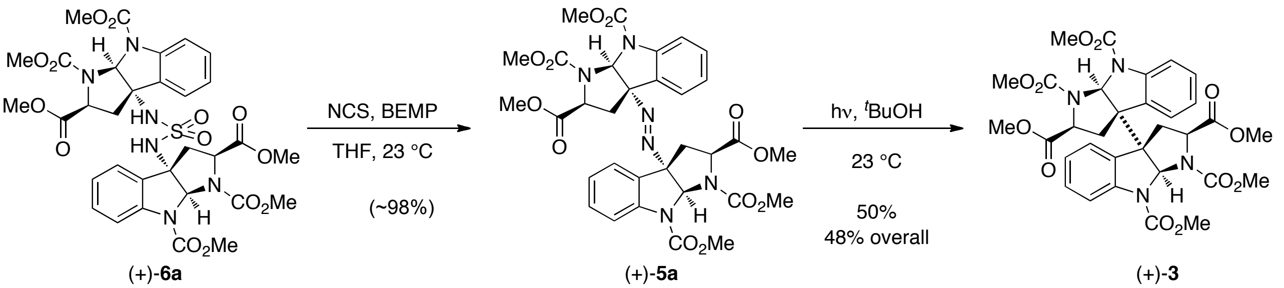


(+)-**6a** (+)-**5a**

(+)-Homodimeric diazene 5a (Scheme 2):

A solution of sulfamide (+)-**6a** (32 mg, 0.042 mmol, 1 equiv) in THF (1.1 mL) was added to resin-bound BEMP (284 mg, 2.2 g/mmol on 200-400 mesh polystyrene resin, 0.625 mmol, 15 equiv) via cannula. After 1 h, a solution of NCS (67 mg, 0.50 mmol, 12 equiv) in THF (1 mL) was added to the reaction mixture. After 5 min, an additional portion of resin-bound BEMP (284 mg, 0.625 mmol, 15 equiv) was added as a solid, and the reaction vessel was purged with argon. After 15 min, the reaction mixture was diluted with ethyl acetate (20 mL) and filtered. The resin was washed with ethyl acetate (2 × 10 mL). The filtrate was washed with aqueous saturated sodium thiosulfate solution (2 × 10 mL) and brine (10 mL). The organic layer was dried over anhydrous sodium sulfate and filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 15% acetone in CH_2Cl_2; SiO_2: 6.0 × 1.5 cm) on silica gel to afford diazene (+)-**5a** ($[\alpha]^{24}_{D} = +18$ (*c* 0.19, CH_2Cl_2)) as a pale yellow solid (18 mg, 61%).

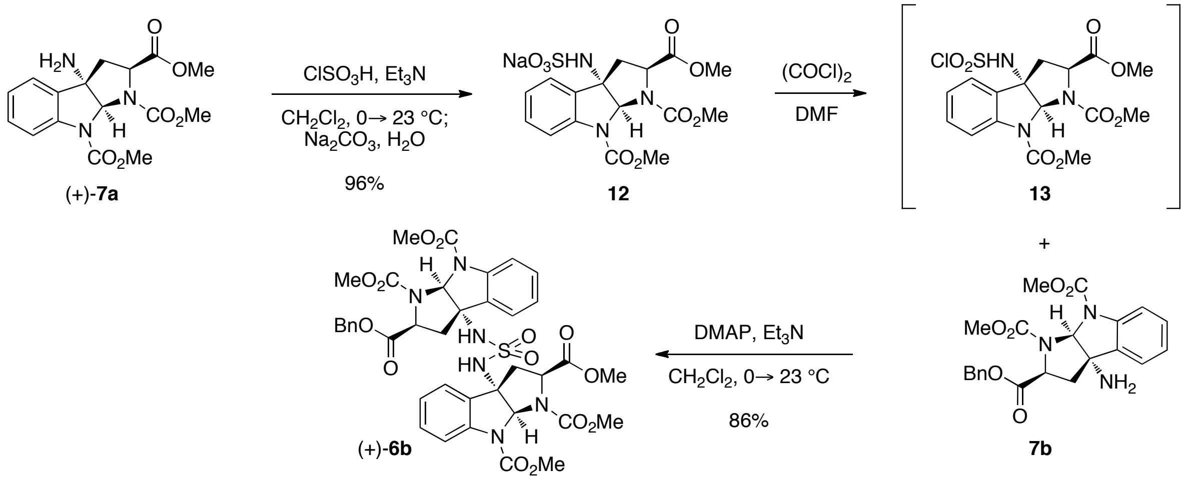
^{1}H NMR (500 MHz, CD_3CN, 20 °C) δ:	7.60 (d, *J* = 8.5 Hz, 1H, $C_7\mathbf{H}$), 7.31 (t, *J* = 7.5 Hz, 1H, $C_6\mathbf{H}$), 7.11 (d, *J* = 7.5 Hz, 1H, $C_4\mathbf{H}$), 7.03 (t, *J* = 8.0 Hz, 1H, $C_5\mathbf{H}$), 6.43 (s, 1H, $C_{8a}\mathbf{H}$), 4.70 (d, *J* = 8.5 Hz, 1H, $C_2\mathbf{H}$), 3.79 (s, 3H, $NCO_2C\mathbf{H}_3$), 3.67 (s, 3H, $NCO_2C\mathbf{H}_3$), 3.16 (s, 3H, $CO_2C\mathbf{H}_3$), 2.80 (d, *J* = 12.5 Hz, 1H, $C_3\mathbf{H}_a$), 2.71 (dd, *J* = 13.0, 9.0 Hz, 1H, $C_3\mathbf{H}_b$).
^{13}C NMR (125 MHz, CD_3CN, 20 °C) δ:	172.2 ($\mathbf{C}O_2CH_3$), 156.2 ($N\mathbf{C}O_2CH_3$), 154.9 ($N\,\mathbf{C}O_2CH_3$), 144.8 ($\mathbf{C}_{7a}$), 131.8 ($\mathbf{C}_6$), 130.0 ($\mathbf{C}_{4a}$), 126.2 ($\mathbf{C}_4$), 125.0 ($\mathbf{C}_5$), 118.0 ($\mathbf{C}_7$), 88.3 ($\mathbf{C}_{8a}$), 79.8 ($\mathbf{C}_{3a}$), 60.7 ($\mathbf{C}_2$), 54.0 ($NCO_2\mathbf{C}H_3$), 53.9 ($NCO_2\mathbf{C}H_3$), 53.1 ($CO_2\mathbf{C}H_3$), 37.5 (C_3).
FTIR (neat) cm^{-1}:	2955 (w), 1712 (s), 1483 (m), 1449 (m), 1393 (m), 1342 (w), 1261 (w).
HRMS (ESI):	calc'd for $C_{32}H_{35}N_6O_{12}$ $[M+H]^+$: 695.2307, found: 695.2303.
TLC (20% acetone in CH_2Cl_2), R_f:	0.30 (UV, CAM).



(+)-Homodimer 3 (Scheme 2):

A solution of sulfamide (+)-**6a** (19 mg, 0.025 mmol, 1 equiv) in THF (1.5 ml) was added to resin-bound BEMP (180 mg, 2.2 g/mmol on 200-400 mesh polystyrene resin, 0.395 mmol, 15.8 equiv) via cannula. After 1 h, a solution of NCS (42 mg, 0.31 mmol, 12 equiv) in THF (1 mL) was added to the reaction mixture. After 5 min, an additional portion of resin-bound BEMP (180 mg, 0.395 mmol, 15.8 equiv) was added as a solid. After 10 min, the reaction mixture was diluted with ethyl acetate (10 mL) and filtered. The resin was washed with ethyl acetate (2 × 10 mL). The filtrate was washed with aqueous saturated sodium thiosulfate solution (3 × 10 mL) and brine (10 mL). The organic layer was dried over anhydrous sodium sulfate and filtered. The volatiles were removed under reduced pressure and the resulting diazene (+)-**5a** (17 mg, ~98%) was used crude for photolysis. A degassed solution of diazene (+)-**5a** (17 mg, 0.024 mmol, 1 equiv) in *tert*-butanol (2.5 mL) in a Pyrex® vessel was irradiated using a medium pressure 450W mercury lamp (>280 nm). After 5 h, the volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 15% acetone in CH_2Cl_2; SiO_2: 5 × 0.75 cm) on silica gel to give dimer (+)-**3** (8.0 mg, 50%, 48% overall) as white solid ($[\alpha]^{24}_{D} = +81$ (*c* 0.30, CH_2Cl_2)). This compound was determined to be of >98% ee by chiral HPLC analysis (Chirapak AS-H, 20% ^{i}PrOH / 80% hexanes, 1.0 ml/min, 220 nm, t_R (minor, not observed) = 25.8 min, t_R (major) = 59.4 min).

^{1}H NMR (500 MHz, CD_3CN, 60 °C) δ:	7.62 (d, *J* = 8.0 Hz, 2H, $C_7\mathbf{H}$), 7.33-7.27 (m, 4H), 7.02 (t, *J* = 7.5, 2H, $C_5\mathbf{H}$), 5.57 (s, 2H, $C_{8a}\mathbf{H}$), 4.53 (d, *J* = 9.0 Hz, 2H, $C_2\mathbf{H}$), 3.78 (s, 6H, $NCO_2C\mathbf{H}_3$), 3.54 (s, 6H, $NCO_2C\mathbf{H}_3$), 3.13 (s, 6H, $CO_2C\mathbf{H}_3$), 2.92 (dd, *J* = 13.5, 9.5 Hz, 2H, $C_3\mathbf{H}_a$), 2.78 (d, *J* = 13.0 Hz, 2H, $C_3\mathbf{H}_b$).
^{13}C NMR (125 MHz, CD_3CN, 60 °C) δ:	172.5 ($\mathbf{C}O_2CH_3$), 156.0 ($N\mathbf{C}O_2CH_3$), 154.8 ($N\mathbf{C}O_2CH_3$), 145.0 ($\mathbf{C}_{7a}$), 132.2 ($\mathbf{C}_{4a}$), 131.6 ($\mathbf{C}_6$), 126.5 ($\mathbf{C}_5$), 124.8 ($\mathbf{C}_4$), 117.9 ($\mathbf{C}_7$), 80.7 ($\mathbf{C}_{8a}$), 61.2 ($\mathbf{C}_{3a}$), 60.8 ($\mathbf{C}_2$), 54.1 ($NCO_2\mathbf{C}H_3$), 53.9 ($NCO_2\mathbf{C}H_3$), 53.2 ($CO_2\mathbf{C}H_3$), 36.4 ($\mathbf{C}_3$).
FTIR (neat) cm^{-1}:	2955 (w), 2917 (w), 1717 (s), 1482 (m), 1448 (m), 1395 (m).
HRMS (ESI):	calc'd for $C_{32}H_{35}N_4O_{12}$ $[M+H]^+$: 667.2246, found: 667.2240.
TLC (15% acetone in CH_2Cl_2), R_f:	0.20 (UV, CAM).



(+)-Heterodimeric sulfamide 6b (Scheme 3):

Chlorosulfonic acid (16 μL, 0.25 mmol, 2.0 equiv) was added drop-wise via syringe to a solution of triethylamine (72 μL, 0.52 mmol, 4.1 equiv) in CH_2Cl_2 (1.5 mL) at 0 °C. After 5 min, a solution of amine (+)-**7a** (44 mg, 0.13 mmol, 1 equiv) in CH_2Cl_2 (1.5 mL) was added via syringe. After 5 min, the reaction mixture was allowed to warm to 23 °C. After 1 h, the reaction mixture was transferred to a separatory funnel and washed three times with a solution of sodium carbonate (40 mg, 0.38 mmol, 3 equiv) in water (10 mL). The combined aqueous layers were concentrated. The white residue was suspended in ethanol (30 mL) and sonicated for 30 min. The suspension was filtered and the washed with ethanol (3 × 5 mL). The volatiles were removed under reduced pressure to afford the sulfamate **12** as a white solid (55 mg, 96%). The crude sulfamate was dried by azeotropic distillation with benzene (3 × 5 mL) and used without further purification. Oxalyl chloride (104 μL, 1.22 mmol, 10 equiv) and DMF (0.5 μL, 0.006 mmol, 0.05 equiv) were added to a suspension of crude sulfamate **12** (55 mg, 0.12 mmol, 2.3 equiv) in CH_2Cl_2 (2.5 mL). After 1 h, volatiles were removed under reduced pressure, and the solid was dissolved in benzene (5 mL) and concentrated under reduced pressure. A solution of amine **7b** (23 mg, 0.053 mmol, 1 equiv) and DMAP (1.3 mg, 0.011 mmol, 0.02 equiv) in CH_2Cl_2 (1.5 mL) was added via syringe at 0 °C to sulfamate **12** in CH_2Cl_2 (1.5 ml). After 5 min, triethylamine (45 μL, 0.32 mmol, 6.1 equiv) was added to the reaction mixture, and the reaction mixture was allowed to warm to room temperature. After 12 h, the reaction mixture was concentrated under reduced pressure. The resulting residue was diluted with ethyl acetate (20 mL) and was washed with DI water (10 mL). The aqueous layer was extracted with ethyl acetate (2 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous sodium sulfate and filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 50% acetone in hexanes; SiO_2: 10 × 1.25 cm) on silica gel to give sulfamide (+)-**6b** ($[\alpha]^{24}_{D}$ = + 45.4 (*c* 0.37, CH_2Cl_2)) as a white solid (38 mg, 86%).

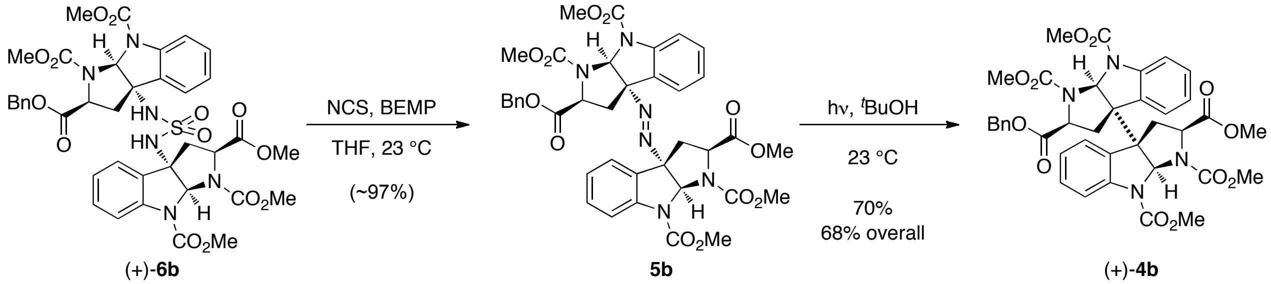
^{1}H NMR (500 MHz, CD_3CN, 65 °C) δ: 7.64 (d, *J* = 8.2 Hz, 1H, $C_{7'}\mathbf{H}$), 7.58 (d, *J* = 8.2, 1H, $C_7\mathbf{H}$), 7.38–7.28 (m, 5H, $Ph\mathbf{H}_{meta}$, $Ph\mathbf{H}_{para}$, $C_{6'}\mathbf{H}$, $C_6\mathbf{H}$), 7.20 (d, *J* = 7.6 Hz, 1H, $C_{4'}\mathbf{H}$), 7.17–7.16 (m, 3H, $Ph\mathbf{H}_{ortho}$, $C_4\mathbf{H}$), 7.00 (t, *J* = 7.5 Hz, 1H, $C_{5'}\mathbf{H}$), 6.96 (t, *J* = 7.5 Hz, 1H, $C_5\mathbf{H}$), 6.41 (s, 2H, $C_{8a'}\mathbf{H}$, $C_{8a}\mathbf{H}$), 5.66 (s, 2H, $N\mathbf{H}SO_2$), 4.68 (d, *J* = 9.6 Hz, 1H, $C_2\mathbf{H}$), 4.65 (d, *J* = 12.5 Hz, 1H, $PhC\mathbf{H}_a$), 4.63 (d, *J* = 9.6 Hz, 1H, $C_{2'}\mathbf{H}$), 4.44 (d, *J* = 12.5, 1H, $PhC\mathbf{H}_b$), 3.82 (s, 6H $NCO_2C\mathbf{H}_3$), 3.70 (s, 3H, $NCO_2C\mathbf{H}_3$), 3.69 (s, 3H, $NCO_2C\mathbf{H}_3$), 3.14 (s, 3H, $CO_2C\mathbf{H}_3$), 2.96 (app dt, J = 12.1 Hz, J = 9.8 Hz, 2H, $C_{3a}\mathbf{H}_a$, $C_{3'}\mathbf{H}_a$), 2.71 (d, J = 12.1 Hz, 2H, $C_3\mathbf{H}_b$, $C_{3'}\mathbf{H}_b$)

^{13}C NMR (125 MHz, CD_3CN, 65 °C) δ: 171.0 ($\mathbf{C}O_2Bn$), 171.2 ($\mathbf{C}O_2CH_3$), 156.0 ($N\mathbf{C}O_2CH_3$) 155.1 ($N\mathbf{C}O_2CH_3$). 144.7 ($\mathbf{C}_{4a'}$), 144.6 ($\mathbf{C}_{4a}$), 137.0 ($\mathbf{C}_{Ph\text{-}\mathit{ipso}}$), 131.8 ($\mathbf{C}_{6'}$), 131.8 ($\mathbf{C}_6$), 131.0 ($\mathbf{C}_{7a'}$), 130.9 ($\mathbf{C}_{7a}$), 129.7 ($\mathbf{C}_{Ph}$), 129.4 ($\mathbf{C}_{Ph}$), 129.2 ($\mathbf{C}_{Ph}$) 126.3 ($\mathbf{C}_{4'}$), 126.2 ($\mathbf{C}_4$) 124.8 ($\mathbf{C}_{5'}$), 124.7 ($\mathbf{C}_5$), 118.1 ($\mathbf{C}_7$), 118.1 ($\mathbf{C}_{7'}$) 81.3 ($\mathbf{C}_{8a'}$), 81.2 ($\mathbf{C}_{8a}$), 71.3 ($C_{3a}$), 71.3 ($\mathbf{C}_{3a'}$) 67.8 ($\mathbf{C}H_2Ph$), 60.2 ($\mathbf{C}_2$), 60.0 ($\mathbf{C}_{2'}$), 53.8 ($NCO_2\mathbf{C}H_3$), 53.7 ($NCO_2\mathbf{C}H_3$), 52.8 ($CO_2\mathbf{C}H_3$), 39.2 ($\mathbf{C}_3$), 39.1 ($\mathbf{C}_{3'}$)

FTIR (neat) cm^{-1}: 3238 (br), 2954 (w), 2955(w), 1721 (s), 1484 (m), 1604 (w), 1484 (m), 1450 (m).

HRMS (ESI): calc’d for $C_{38}H_{41}N_6O_{14}S$ $[M+H]^+$ = 837.2396
found: 837.2396

TLC (50% acetone in hexnes), R_f: 0.30 (UV, CAM).



(+)-Heterodimer 4b (Scheme 3):

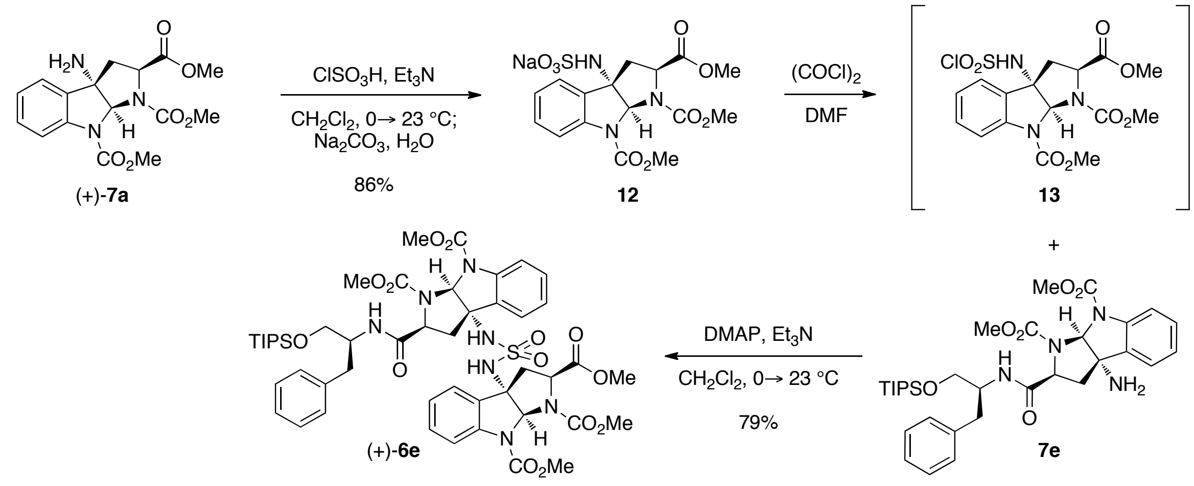
A solution of sulfamide (+)-**6b** (10 mg, 0.012 mmol, 1 equiv) in THF (500 μL) was added to resin-bound BEMP (83 mg, 2.2 g/mmol on 200-400 mesh polystyrene resin, 0.18 mmol, 15 equiv) via cannula. After 1 h, a solution of NCS (20 mg, 0.15 mmol, 12 equiv) in THF (500 μL) was added to the reaction mixture. After 5 min, an additional portion of resin-bound BEMP (83 mg, 0.18 mmol, 15 equiv) was added as a solid. After 10 min, the reaction mixture was diluted with ethyl acetate (10 mL) and filtered. The resin was washed with ethyl acetate (2 × 10 mL). The filtrate was washed with aqueous saturated sodium thiosulfate solution (3 × 10 mL) and brine (10 mL). The organic layer was dried over anhydrous sodium sulfate and filtered. The volatiles were removed under reduced pressure and the resulting diazene **5b** (9 mg, ~97%) was used crude for photolysis. A degassed solution of diazene **5b** (6 mg, 0.008 mmol, 1 equiv) in *tert*-butanol (1.0 mL) in a Pyrex® vessel was irradiated using a medium pressure 450W mercury lamp (>280 nm) After 5 h, the volatiles were removed under reduced pressure. Analysis of the residue by HPLC showed only heterodimer (+)-**4b** and no observable amounts of homodimers (+)-**3** and (+)-**15** (Chiralpak OD-H, 25% ^{i}PrOH / 75% hexanes, 0.8 mL/min, t_R (homodimer (+)-**3**, not observed) = 20.7 min, t_R (heterodimer (+)-**4b**) = 24.7 min, t_R (homodimer (+)-**15**, not observed) = 28.1 min). The residue was purified by flash column chromatography (eluent: 3% ^{i}PrOH in CH_2Cl_2) on silica gel to afford heterodimer(+)-**4b** (7 mg, 56%). The residue was purified by flash column chromatography (eluent: 3% iPrOH in CH_2Cl_2; SiO_2: 5 × 1.0 cm) on silica gel to give dimer (+)-**4b** (4 mg, 70%, 68% overall) as a pale yellow solid ($[\alpha]^{24}_D$ = + 37 (*c* 0.16, CH_2Cl_2)).

^{1}H NMR (500 MHz, CD_3CN, 60 °C) δ:	7.57 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.34–7.24 (m, 7H), 7.17 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.03–6.97 (m, 2H), 5.59 (s, 1H), 5.57 (s, 1H), 4.64 (d, *J* = 12.5 Hz, 1H, PhC**H**$_a$), 4.58 (d, *J* = 9.5 Hz, 1H), 4.52 (d, *J* = 9.0 Hz, 1H), 4.39 (d, *J* = 12.5 Hz, 1H, PhC**H**$_b$), 3.78 (s, 3H, NCO_2C**H**$_3$), 3.77 (s, 3H, NCO_2C**H**$_3$), 3.54 (s, 3H, NCO_2C**H**$_3$), 3.52 (s, 3H, NCO_2C**H**$_3$), 3.13 (s, 3H, CO_2C**H**$_3$), 2.97–2.90 (m, 2H), 2.80 (d, *J* = 8.5 Hz, 1H), 2.77 (d, *J* = 8.0 Hz, 1H).
^{13}C NMR (125 MHz, CD_3CN, 60 °C) δ:	172.5, 171.9, 156.0 (N**C**O_2CH_3), 154.8 (N**C**O_2CH_3), 145.0, 144.9, 137.4, 132.2, 132.0, 131.6, 130.1, 129.8, 129.6, 126.5, 126.4, 125.9, 124.9, 124.8, 118.0, 117.9, 80.7, 80.7, 68.2 (PH**C**H_2), 61.2, 61.1, 60.9, 60.7, 54.1 (NCO_2**C**H_3), 53.9 (NCO_2**C**H_3), 53.2 (CO_2**C**H_3), 36.4, 36.4.

FTIR (neat) cm^{-1}: 2955 (w), 1718 (s), 1482 (m), 1448 (m), 1395 (m).

HRMS (ESI): calc'd for $C_{38}H_{38}N_4NaO_{12}$ $[M+Na]^+$: 765.2378, found: 765.2345.

TLC (3% iPrOH in CH_2Cl_2), R_f: 0.23 (UV).



General procedure for C_{sp3}–N, C_{sp3}–N' sulfamide synthesis–heterodimeric sulfamide (+)-6e (Table 1):

Chlorosulfonic acid (11 μL, 0.16 mmol, 2.0 equiv) was added drop-wise via syringe to a solution of triethylamine (45 μL, 0.33 mmol, 4.1 equiv) in CH_2Cl_2 (700 μL) at 0 °C. After 5 min, a solution of amine (+)-**7a** (28 mg, 0.081 mmol, 1.0 equiv) in CH_2Cl_2 (2.0 mL) was added via cannula. After 5 min, the reaction mixture was allowed to warm to 23 °C. After 1 h, the reaction mixture was transferred to a separatory funnel and washed three times with a solution of sodium carbonate (28 mg, 0.24 mmol, 3 equiv) in water (10 mL). The combined aqueous layers were concentrated. The white residue was suspended in ethanol (20 mL). The suspension was filtered and the washed with ethanol (3 × 5 mL). The volatiles were removed under reduced pressure to afford the sulfamate **12** as a white solid (31 mg, 86%). The crude sulfamate was dried by azeotropic distillation with benzene (3 × 5 mL) and used without further purification. Oxalyl chloride (61 μL, 0.70 mmol, 10 equiv) and DMF (0.5 μL, 0.006 mmol, 0.01 equiv) were added to a suspension of crude sulfamate **12** (31 mg, 0.070 mmol, 2.3 equiv) in CH_2Cl_2 (1.5 mL). After 1 h, volatiles were removed under reduced pressure, and the solid was dissolved in benzene (5 mL) and concentrated under reduced pressure. A solution of amine **7e** (19 mg, 0.030 mmol, 1 equiv) and DMAP (0.7 mg, 0.006 mmol, 0.02 equiv) in CH_2Cl_2 (1.0 mL) was added via cannula at 0 °C. After 5 min, triethylamine (17 μL, 0.12 mmol, 4.1 equiv) was added to the reaction mixture, and the reaction mixture was allowed to warm to room temperature. After 12 h, the reaction mixture was diluted with ethyl acetate (10 mL) and was washed with DI water (10 mL). The aqueous layer was extracted with ethyl acetate (2 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous sodium sulfate and filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 5% iPrOH in CH_2Cl_2; SiO_2: 10 × 1.25 cm) on silica gel to give sulfamide (+)-**6e** ($[\alpha]^{24}_{D}$ = + 11 (*c* 0.17, CH_2Cl_2)) as a white solid (24 mg, 79%).

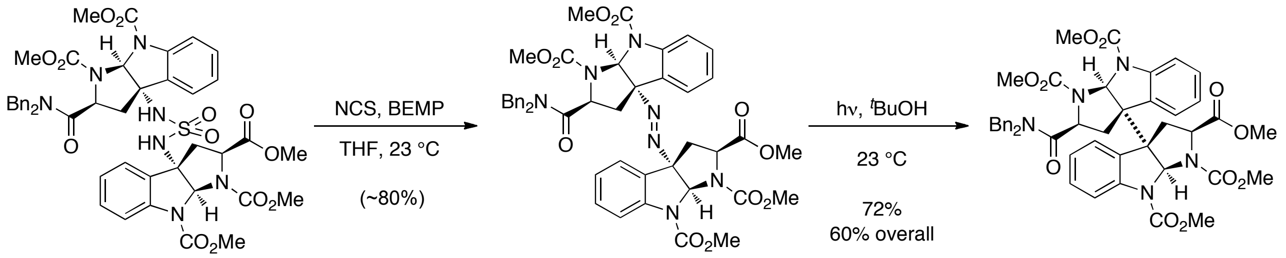
^{1}H NMR (500 MHz, CD_3CN, 50 °C) δ: 7.69 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.34–7.29 (m, 2H), 7.26–7.16 (m, 5H), 7.07–6.97 (m, 4H), 6.54 (s, 1H, $C_{8a'}$**H**), 6.39 (s, 1H, C_{8a}**H**), 6.32 (d, *J* = 8.5 Hz, 1H, CON**H**), 5.73 (br-s, 1H, N**H**SO_2), 5.65 (br-s, 1H, N**H**SO_2), 4.62 (d, *J* = 8.5 Hz, 1H, C_2**H**), 4.55 (d, *J* = 9.0 Hz, 1H, $C_{2'}$**H**), 3.85 (s, 3H, NCO_2C**H_3**), 3.84 (s, 3H, NCO_2C**H_3**), 3.73 (s, 3H, NCO_2C**H_3**), 3.70 (s, 3H, NCO_2C**H_3**), 3.60–3.54 (m, 1H, CONHC**H**), 3.39 (dd, *J* = 10.0, 4.0 Hz, 1H, C**H_a**OSi), 3.35 (dd, *J* = 10.0, 3.5 Hz, 1H, C**H_b**OSi), 3.13 (s, 3H, CO_2C**H_3**), 2.95 (dd, *J* = 12.5, 9.0 Hz, 1H), 2.89–2.82 (m, 2H), 2.71 (d, *J* = 13.0 Hz, 1H, $C_3\mathbf{H}_a$), 2.24 (dd, *J* = 13.5, 9.5 Hz, 1H, $C\mathbf{H}_a$Ph), 2.06 (dd, *J* = 13.0, 5.0 Hz, 1H, $C\mathbf{H}_b$Ph), 1.05–1.02 (m, 21H).

^{13}C NMR (125 MHz, CD_3CN, 60 °C) δ: 172.3 ($\mathbf{C}O_2CH_3$), 170.7 ($\mathbf{C}$ONH), 157.7 ($N\mathbf{C}O_2CH_3$), 156.4 ($N\mathbf{C}O_2CH_3$), 155.5 ($N\mathbf{C}O_2CH_3$), 155.5 ($N\mathbf{C}O_2CH_3$), 145.1, 144.4, 140.3, 132.2, 132.1, 131.8, 131.5, 130.8, 130.0, 127.9, 127.0, 126.7, 125.4, 125.2, 118.7, 118.5, 83.1 ($\mathbf{C}_{8a'}$), 81.6 ($\mathbf{C}_{8a}$), 72.4 ($\mathbf{C}_{3a}$), 71.7 ($\mathbf{C}_{3a'}$), 64.0 ($\mathbf{C}H_2OSi$), 62.8 ($\mathbf{C}_{2'}$), 60.4 ($\mathbf{C}_2$), 54.5 ($NCO_2\mathbf{C}H_3$), 54.2 ($NCO_2\mathbf{C}H_3$), 54.2 ($NCO_2\mathbf{C}H_3$), 54.1 ($NCO_2\mathbf{C}H_3$), 53.8 (CONH$\mathbf{C}$H), 53.2 ($CO_2\mathbf{C}H_3$), 39.6 ($\mathbf{C}_{3'}$), 39.5 ($\mathbf{C}_3$), 37.9 (Ph$\mathbf{C}H_2$), 19.1 ($SiCH(\mathbf{C}H_3)_2$), 13.6 ($Si\mathbf{C}H(CH_3)_2$).

FTIR (neat) cm^{-1}: 3419 (w), 2954 (w), 2866 (w), 1718 (s), 1484 (m), 1448 (s), 1392 (m).

HRMS (ESI): calc’d for $C_{49}H_{65}N_7NaO_{14}SSi$ $[M+Na]^+$ = 1058.3972
found: 1058.3964

TLC (5% iPrOH in CH_2Cl_2), R_f: 0.26 (UV, CAM).



6d **5d** (+)-**4d**

(+)-Heterodimer 4d (Table 1, entry 1):

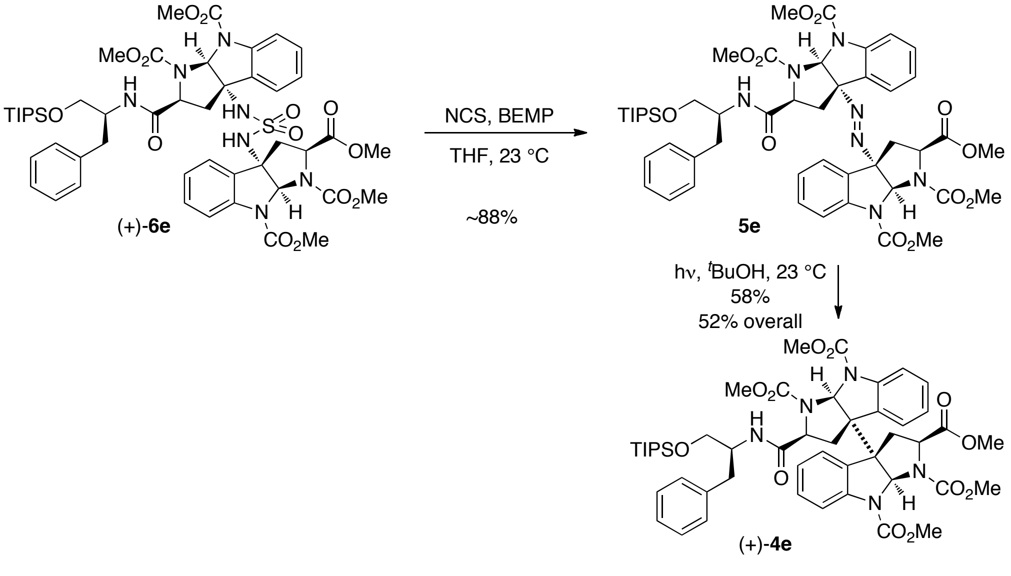
A solution of sulfamide **6d** (11 mg, 0.012 mmol, 1 equiv) in THF (300 μL) was added to resin-bound BEMP (40 mg, 2.2 g/mmol on 200-400 mesh polystyrene resin, 0.088 mmol, 7.5 equiv) via cannula. After 1 h, a solution of NCS (10 mg, 0.071 mmol, 6.0 equiv) in THF (200 μL) was added to the reaction mixture. After 5 min, an additional portion of resin-bound BEMP (40 mg, 0.088 mmol, 7.5 equiv) was added as a solid. After 10 min, the reaction mixture was diluted with ethyl acetate (10 mL) and filtered. The resin was washed with ethyl acetate (2 × 10 mL). The filtrate was washed with aqueous saturated sodium thiosulfate solution (2 × 10 mL) and brine (10 mL). The organic layer was dried over anhydrous sodium sulfate and filtered. The volatiles were removed under reduced pressure and the resulting diazene **5d** (8.3 mg, ~80%) was used crude for photolysis. A degassed solution of diazene **5d** (8.3 mg, 0.010 mmol, 1 equiv) in *tert*-butanol (1.0 mL) in a Pyrex® vessel was irradiated using a medium pressure 450W mercury lamp. After 5 h, the volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 50% acetone in hexanes; SiO_2: 6.5 × 1.25 cm) on silica gel to give dimer (+)-**4d** (6 mg, 72%, 60% overall) as a yellow solid ($[\alpha]^{23}_{D}$ = + 40 (*c* 0.34, CH_2Cl_2)).

^{1}H NMR (500 MHz, CD_3CN, 60 °C) δ:	7.63–7.59 (m, 4H), 7.40–7.24 (m, 11H), 7.04 (app. dt, *J* = 8.0, 1.0 Hz, 1H), 6.98 (app. dt, *J* = 7.5, 1.0 Hz, 1H), 6.94 (br-d, *J* = 7.0 Hz, 1H), 5.66 (s, 1H, $C_{8a'}\mathbf{H}$), 5.60 (s, 1H, $C_{8a}\mathbf{H}$), 4.81 (d, *J* = 10.5 Hz, 1H, $C_{2'}\mathbf{H}$), 4.74 (d, *J* = 13.5 Hz, 1H, $CONC_a\mathbf{H}_a$), 4.68 (d, *J* = 16.5 Hz, 1H, $CONC_b\mathbf{H}_a$), 4.53 (d, *J* = 9.5 Hz, 1H, $C_2\mathbf{H}$), 4.23 (d, *J* = 18.0 Hz, 1H, $CONC_b\mathbf{H}_b$), 3.82 (s, 3H, $NCO_2C\mathbf{H}_3$), 3.82 (s, 3H, $NCO_2C\mathbf{H}_3$), 3.71 (d, *J* = 12.5 Hz, 1H, $CONC_a\mathbf{H}_b$), 3.58 (s, 3H, $NCO_2C\mathbf{H}_3$), 3.58 (s, 3H, $NCO_2C\mathbf{H}_3$), 3.15 (s, 3H, $CO_2C\mathbf{H}_3$), 3.08 (dd, *J* = 13.5, 11.0 Hz, 1H, $C_{3'}\mathbf{H}_a$), 2.92 (dd, *J* = 13.5, 9.5 Hz, 1H, $C_3\mathbf{H}_a$), 2.72 (d, *J* = 13.5 Hz, 1H, $C_3\mathbf{H}_b$), 2.54 (d, *J* = 14.0 Hz, 1H, $C_{3'}\mathbf{H}_b$).
^{13}C NMR (125 MHz, CD_3CN 60 °C) δ:	172.5 ($\mathbf{C}O_2CH_3$), 171.6 ($\mathbf{C}ON$), 156.0 ($N\mathbf{C}O_2CH_3$), 155.1 ($N\mathbf{C}O_2CH_3$), 154.8 ($N\mathbf{C}O_2CH_3$), 145.0, 145.0, 133.7 ($\mathbf{C}_{4a'}$), 132.4 ($\mathbf{C}_{4a}$), 132.0, 131.6, 131.5, 131.0, 130.4, 130.1, 129.8, 129.2, 128.9, 128.6, 126.2, 126.5 125.6, 124.8, 124.7, 117.9, 117.8, 81.1 ($\mathbf{C}_{8a'}$), 80.7 ($\mathbf{C}_{8a}$), 61.2, 61.2, 60.7 ($\mathbf{C}_2$), 60.1 ($\mathbf{C}_{2'}$), 54.1 ($NCO_2\mathbf{C}H_3$), 54.0 ($NCO_2\mathbf{C}H_3$), 53.9 ($NCO_2\mathbf{C}H_3$), 53.7 ($NCO_2\mathbf{C}H_3$), 53.2 ($CO_2\mathbf{C}H_3$), 50.8 ($N\mathbf{C}_bH_2$), 49.7 ($N\mathbf{C}_aH_2$), 37.2 ($\mathbf{C}_{3'}$), 36.8 ($\mathbf{C}_3$).

FTIR (neat) cm^{-1}: 2953 (w), 1720 (s), 1674 (m), 1482 (s), 1446 (s), 1394 (m).

HRMS (ESI): calc'd for $C_{45}H_{46}N_5O_{11}$ $[M+H]^+$: 832.3188, found: 832.3159.

TLC (50% acetone in hexanes), R_f: 0.23 (UV, CAM)

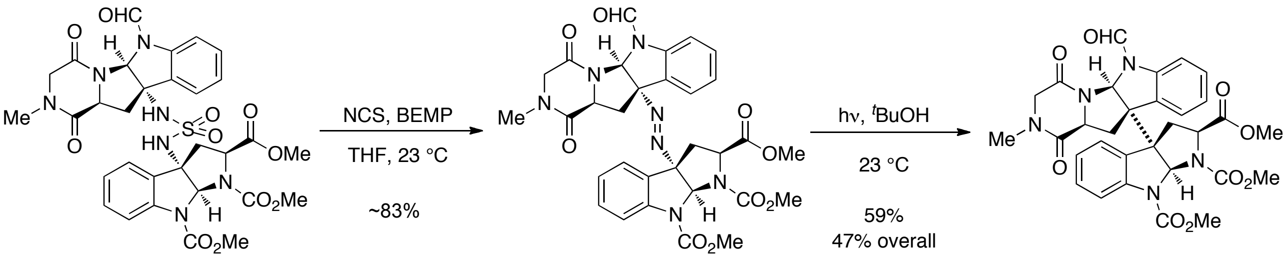


(+)-Heterodimer 4e (Table 1, entry 2):

A solution of sulfamide **6e** (21 mg, 0.020 mmol, 1 equiv) in THF (800 μL) was added to resin-bound BEMP (69 mg, 2.2 g/mmol on 200-400 mesh polystyrene resin, 0.15 mmol, 7.6 equiv) via cannula. After 1 h, a solution of NCS (16 mg, 0.12 mmol, 6.0 equiv) in THF (300 μL) was added to the reaction mixture. After 5 min, an additional portion of resin-bound BEMP (69 mg, 0.15 mmol, 7.6 equiv) was added as a solid. After 10 min, the reaction mixture was diluted with ethyl acetate 5 mL) and filtered. The resin was washed with ethyl acetate (3 × 5 mL). The filtrate was washed with aqueous saturated sodium thiosulfate solution (2 × 10 mL) and brine (10 mL). The organic layer was dried over anhydrous sodium sulfate and filtered. The volatiles were removed under reduced pressure and the resulting diazene **5e** (17 mg, ~88%) was used crude for photolysis. A degassed solution of diazene **5e** (17 mg, 0.018 mmol, 1 equiv) in *tert*-butanol (1.8 mL) in a Pyrex® vessel was irradiated using a medium pressure 450W mercury lamp. After 5 h, the volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 40% ^{i}PrOH in hexanes; SiO_2: 7.0 × 1.25 cm) on silica gel to give dimer (+)-**4e** (10 mg, 59%, 52% overall) as a pale yellow solid ($[\alpha]^{23}_D$ = + 8.6 (*c* 0.16, CH_2Cl_2)).

^{1}H NMR (500 MHz, CD_3CN 70 °C) δ: 7.66 (d, *J* = 8.0 Hz, 1H, C_7**H**), 7.59 (d, *J* = 8.0 Hz, 1H, $C_{7'}$**H**), 7.35 (d, *J* = 7.0 Hz, 1H, $C_{4'}$**H**), 7.30–7.18 (m, 6H), 7.06 (d, *J* = 7.5 Hz, 2H, CH_2Ph-*o*-**H**), 6.99 (t, *J* = 7.5 Hz, 2H), 6.19 (d, *J* = 8.0 Hz, 1H, N**H**), 5.82 (s, 1H, $C_{8a'}$**H**), 5.63 (s, 1H, C_{8a}**H**), 4.55 (d, *J* = 9.0 Hz, 1H, C_2**H**), 4.47 (d, *J* = 10.0 Hz, 1H $C_{2'}$**H**), 3.81 (s, 3H, NCO_2C**H_3**), 3.80 (s, 3H, NCO_2C**H_3**), 3.59–3.52 (m, 1H, COC**H**NH), 3.56 (s, 3H, NCO_2C**H_3**), 3.54 (s, 3H, NCO_2C**H_3**), 3.35 (app t, *J* = 4.5 Hz, 2H, C**H_2**OSi), 3.14 (s, 3H, CO_2C**H_3**), 2.98–2.94 (m, 2H), 2.85–2.76 (m, 2H), 2.20 (dd, *J* = 13.0, 9.0 Hz, 1H, C**H_a**Ph), 2.11 (dd, *J* = 14.0 Hz, 5.0 Hz, 1H C**H_b**Ph), 1.05–1.01 (m, 21H, SiC**H**$(CH_3)_2$, (SiCH(C**H_3**$)_2$).

^{13}C NMR (125 MHz, CD_3CN, 60 °C) δ:	172.5 ($\mathbf{C}O_2CH_3$), 171.0 ($\mathbf{C}ONH$), 157.3 ($N\mathbf{C}O_2CH_3$), 156.0 ($N\mathbf{C}O_2CH_3$), 154.8 ($N\mathbf{C}O_2CH_3$), 154.7 ($N\mathbf{C}O_2CH_3$), 145.0 ($\mathbf{C}_{7a}$), 144.1 ($\mathbf{C}_{7a'}$), 140.2, 132.7, 132.3, 131.5, 131.4, 130.9, 130.0, 127.9, 126.7 ($\mathbf{C}_{4'}$), 126.3, 125.2, 124.9, 118.0 ($\mathbf{C}_{7}$), 118.0 ($\mathbf{C}_{7'}$), 81.9 ($\mathbf{C}_{8a'}$), 80.8 ($\mathbf{C}_{8a}$), 63.9 ($\mathbf{C}H_2OSi$), 63.3 ($\mathbf{C}_{2'}$), 61.6, 61.5, 60.8 ($\mathbf{C}_{2}$), 54.3, 54.1, 54.1, 53.9, 53.8, 53.2 ($CO_2\mathbf{C}H_3$), 37.8 ($\mathbf{C}H_2Ph$), 36.6 ($\mathbf{C}_{3}$), 36.3 ($\mathbf{C}_{3'}$), 19.1 ($SiCH(\mathbf{C}H_3)_2$), 13.6 ($Si\mathbf{C}H(CH_3)_2$).
FTIR (neat) cm^{-1}:	3421 (w), 2954 (w), 2866 (w), 1719 (s), 1482 (m), 1446 (s), 1392 (m).
HRMS (ESI):	calc’d for $C_{49}H_{64}N_5O_{12}Si$ $[M+H]^+$: 942.4315, found: 942.4320.
TLC (80% EtOAc in hexanes), R_f:	0.26 (UV, CAM)

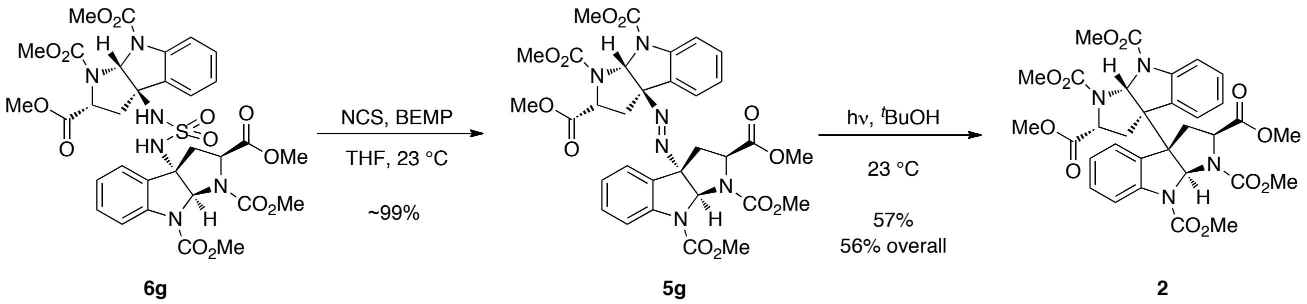


6f **5f** (+)-**4f**

(+)-Heterodimer 4f (Table 1, entry 3):

A solution of sulfamide **6f** (11 mg, 0.015 mmol, 1 equiv) in THF (750 μL) was added to resin-bound BEMP (51 mg, 2.2 g/mmol on 200-400 mesh polystyrene resin, 0.11 mmol, 7.5 equiv) via cannula. After 1 h, a solution of NCS (12 mg, 0.089 mmol, 6.0 equiv) in THF (250 μL) was added to the reaction mixture. After 5 min, an additional portion of resin-bound BEMP (51 mg, 0.11 mmol, 7.5 equiv) was added as a solid. After 10 min, the reaction mixture was diluted with ethyl acetate (10 mL) and filtered. The resin was washed with ethyl acetate (3 × 5 mL). The filtrate was washed with aqueous saturated sodium thiosulfate solution (2 × 10 mL) and brine (10 mL). The organic layer was dried over anhydrous sodium sulfate and filtered. The volatiles were removed under reduced pressure and the resulting diazene **5f** (8.0 mg, ~83%) was used crude for photolysis. A degassed solution of diazene **5f** (8.0 mg, 0.012 mmol, 1 equiv) in *tert*-butanol (1.2 mL) in a Pyrex® vessel was irradiated using a medium pressure, 450W mercury lamp (>280 nm). After 5 h, the volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 15% ^{i}PrOH in CH_2Cl_2; SiO_2: 9.0 × 1.0 cm) on silica gel to give dimer (+)-**4f** (4.4 mg, 59%, 47% overall) as a white solid ($[\alpha]^{24}_{D}$ = + 39 (*c* 0.28, CH_2Cl_2)).

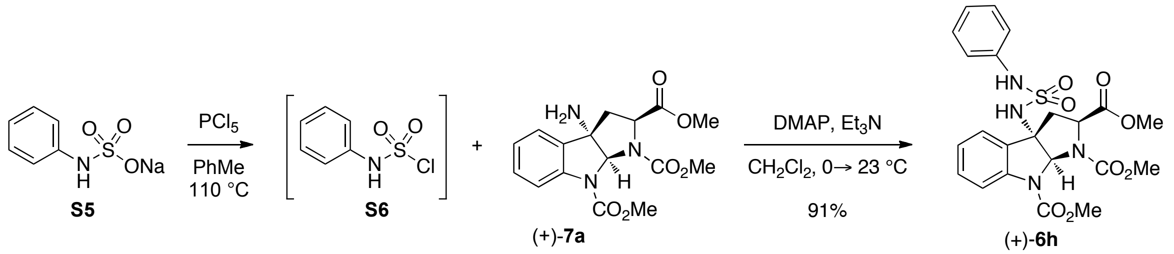
^{1}H NMR (500 MHz, CD_3CN, 60 °C) δ:	8.85 (s, 1H, NC**H**O), 7.68 (d, *J* = 8.5 Hz, 1H, C_7**H**), 7.46 (d, *J* = 8.0 Hz, 1H, $C_{8'}$**H**), 7.41 (d, *J* = 8.0 Hz, 1H, $C_{5'}$**H**), 7.31 (d, *J* = 7.0 Hz, IH, C_4**H**), 7.19 (t, *J* = 8.0 Hz, 2H, C_6**H**, $C_{7'}$**H**), 7.05 (t, *J* = 7.5, 1H, $C_{6'}$**H**), 6.95 (t, *J* = 7.5 Hz, 1H, C_5**H**), 6.01 (s, 1H, C_{8a}**H**), 5.72 (s, 1H, $C_{2'}$**H**), 4.60 (dd, *J* = 7.0, 3.5 Hz, 1H, C_2**H**), 4.25 (t, *J* = 8.5 Hz, 1H, $C_{11'}$**H**), 4.02 (d, *J* = 18.0 Hz, 1H, $C_{15'}$**H**$_a$), 3.84 (s, 3H, NCO_2C**H**$_3$), 3.63 (s, 3H, NCO_2C**H**$_3$), 3.63 (d, *J* = 17.0 Hz, 1H, $C_{15'}$**H**$_b$), 3.12 (s, 3H, CO_2C**H**$_3$), 2.94–2.88 (m, 4H, C_3**H**$_a$, C_3**H**$_b$, $C_{12'}$**H**$_a$, $C_{12'}$**H**$_b$), 2.73 (s, 3H, NC**H**$_3$).
^{13}C NMR (125 MHz, CD_3CN, 60 °C) δ:	172.6 (**C**O_2CH_3), 169.0 (**C**$_{16'}$), 168.5 (**C**$_{13'}$), 163.5 (N**C**HO), 156.1 (N**C**O_2CH_3), 154.9 (N**C**O_2CH_3), 144.7 (**C**$_{7a}$), 141.5 (**C**$_{9'}$), 135.4 (**C**$_{4'}$), 132.0 (**C**$_{4a}$), 131.5 (**C**$_{7'}$), 130.9 (**C**$_6$), 126.5 (**C**$_{5'}$), 126.3 (**C**$_{6'}$), 126.2 (**C**$_4$), 125.0 (**C**$_5$), 118.3 (**C**$_{8'}$), 118.0 (**C**$_7$), 81.1 (**C**$_{8a}$), 80.7 (**C**$_{2'}$), 61.3 (**C**$_{3a}$), 60.9 (**C**$_{3'}$), 60.7 (**C**$_2$), 58.7 (**C**$_{11'}$), 55.3 (**C**$_{15'}$), 54.3 (NCO_2**C**H_3), 54.0 (NCO_2**C**H_3), 53.2 (CO_2**C**H_3), 37.1 (**C**$_3$), 35.1 (**C**$_{12'}$), 34.2 (N**C**H_3).
FTIR (neat) cm^{-1}:	2955 (w), 2917 (w), 2849 (w), 1717 (s), 1685 (s), 1483 (m), 1448 (s), 1340 (s).
HRMS (ESI):	calc'd for $C_{31}H_{31}N_5NaO_9$ $[M+Na]^+$: 640.2014, found: 640.2026.
TLC (15% iPrOH in CH_2Cl_2), R_f:	0.20 (UV, CAM)



meso-Dimer 2 (Table 1, entry 4):

A solution of sulfamide **6g** (30 mg, 0.042 mmol, 1 equiv) in THF (2 mL) was added to resin-bound BEMP (289 mg, 2.2 g/mmol on 200-400 mesh polystyrene resin, 0.636 mmol, 15 equiv) via cannula. After 1 h, a solution of NCS (67 mg, 0.51 mmol, 12 equiv) in THF (2 mL) was added to the reaction mixture. After 5 min, an additional portion of resin-bound BEMP (289 mg, 0.636 mmol, 15 equiv) was added as a solid. After 10 min, the reaction mixture was diluted with ethyl acetate (10 mL) and filtered. The resin was washed with ethyl acetate (3 × 10 mL). The filtrate was washed with aqueous saturated sodium thiosulfate solution (2 × 10 mL) and brine (10 mL). The organic layer was dried over anhydrous sodium sulfate and filtered. The volatiles were removed under reduced pressure and the resulting diazene **5g** (29 mg, ~99%) was used crude for photolysis. A degassed solution of diazene **5g** (29 mg, 0.042 mmol, 1 equiv) in *tert*-butanol (4.2 mL) in a Pyrex® vessel was irradiated using a medium pressure, 450W mercury lamp (>280 nm). After 5 h, the volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 30% acetone in CH_2Cl_2; SiO_2: 8.0 × 1.25 cm) on silica gel to give dimer **2** (16 mg, 57%, 56% overall).

^{1}H NMR (500 MHz, DMSO-d_6, 145 °C) δ:	7.43 (d, J = 8.0 Hz, 2H, C_7**H**), 7.21 (t, J = 8.0 Hz, 2H, C_6**H**), 6.84 (t, J = 7.5, 2H, C_5**H**), 6.54 (d, J =8.0 Hz, 2H, C_4**H**), 6.07 (s, 2H, C_{8a}**H**), 4.65 (d, J = 9.0 Hz, 2H, C_2**H**), 3.66 (s, 6H, $NCO_2C\mathbf{H}_3$), 3.65 (s, 6H, $NCO_2C\mathbf{H}_3$), 3.05 (s, 6H, $CO_2C\mathbf{H}_3$), 2.78 (dd, J = 13.0, 9.0 Hz, 2H, $C_3\mathbf{H}_a$), 2.66 (d, J = 12.5 Hz, 2H, $C_3\mathbf{H}_b$).
^{13}C NMR (125 CD_3CN, 60 °C°C) δ:	172.6 ($\mathbf{C}O_2CH_3$), 156.4 ($N\mathbf{C}O_2CH_3$), 155.5 ($N\mathbf{C}O_2CH_3$), 145.2 ($\mathbf{C}_{7a}$), 132.2, 131.4, 126.8, 125.2, 118.4 ($\mathbf{C}_7$), 81.7 ($\mathbf{C}_{8a}$), 60.4 ($\mathbf{C}_{3a}$), 54.2 ($\mathbf{C}_2$), 54.2 ($NCO_2\mathbf{C}H_3$), 54.1 ($NCO_2\mathbf{C}H_3$), 53.2 ($CO_2\mathbf{C}H_3$), 39.6 ($\mathbf{C}_3$).
FTIR (neat) cm^{-1}:	2955 (w), 1710 (s), 1483 (m), 1449 (m), 1395 (m), 1351 (s).
HRMS (ESI):	calc'd for $C_{32}H_{35}N_4O_{12}$ [M+H]$^+$: 667.2246, found: 667.2249.
TLC (30% acetone in CH_2Cl_2), R_f:	0.30 (UV, CAM)



General procedure for C_{sp3}–N, C_{sp2}–N' sulfamide synthesis–heterodimeric sulfamide (+)-6h (Table 1, entry 5):

Phosphorous pentachloride (154 mg, 0.739 mmol, 2.5 equiv) was added to a heterogeneous mixture of sulfamate **S5**[3] (160 mg, 0.82 mmol, 2.7 equiv) in toluene (16 ml) and heated to reflux. After 12 h the reaction was allowed to cool to room temperature and the solvent was removed under reduced pressure. The resulting light brown solid was dissolved in benzene (5 mL) and concentrated under reduced pressure; this process was repeated once more. A solution of amine (+)-**7a** (103 mg, 0.030 mmol, 1 equiv) and DMAP (7.0 mg, 0.06 mmol, 0.2 equiv) in CH_2Cl_2 (4.0 mL) was added via cannula at 0 °C. After 5 min, triethylamine (260 μL, 1.86 mmol, 6.2 equiv) was added to the reaction mixture, and the reaction mixture was allowed to warm to room temperature. After 4 h, the reaction mixture was concentrated under reduced pressure and the resulting residue was diluted with ethyl acetate (30 mL) and was washed with DI water (10 mL). The aqueous layer was extracted with ethyl acetate (2 × 10 mL). The combined organic layers were washed with brine (10 mL), were dried over anhydrous sodium sulfate, and were filtered. The volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 25%→40% acetone in hexanes) on silica gel to give sulfamide (+)-**6h** ($[\alpha]^{24}_{D}$ = + 60.3 (*c* 0.27, CH_2Cl_2)) as a white solid (138 mg, 91%).

^{1}H NMR (500 MHz, CD_3CN, 60 °C) δ:	7.62 (d, *J* = 8.1 Hz, 1H, $C_7\mathbf{H}$), 7.34–7.29 (m, 3H, Ph$\mathbf{H}_{meta}$, Ph$\mathbf{H}_{para}$), 7.13 (d, *J* = 3.8 Hz, 1H, $C_4\mathbf{H}$), 7.12 (t, *J* = 7.4 Hz, 1H, $C_6\mathbf{H}$), 7.04 (d, *J* = 8.6 Hz, 2H, Ph$\mathbf{H}_{ortho}$), 7.00 (t, *J* = 7.5 Hz, 1H, $C_5\mathbf{H}$), 6.76 (bs, 2H, N$\mathbf{H}SO_2$), 6.37 (s, 1H, $C_{8a}\mathbf{H}$), 4.65 (d, *J* = 9.3 Hz, 1H, $C_2\mathbf{H}$), 3.80 (s, 3H, $NCO_2C\mathbf{H}_3$), 3.68 (s, 3H, $NCO_2C\mathbf{H}_3$), 3.13 (s, 3H, $CO_2C\mathbf{H}_3$), 2.99 (dd, *J* = 13.0 Hz, 9.4 Hz, 1H, $C_3\mathbf{H}_a$), 2.74 (d, *J* = 13.0 Hz, 1H, $C_3\mathbf{H}_b$).
^{13}C NMR (125 MHz, CD_3CN, 60 °C) δ:	171.8 ($\mathbf{C}O_2CH_3$), 156.0 ($N\mathbf{C}O_2CH_3$), 155.0 ($N\mathbf{C}O_2CH_3$), 144.7 ($\mathbf{C}_{7a}$), 138.9 (Ph$\mathbf{C}_{ipso}$), 131.8 (Ph$\mathbf{C}_{para}$), 130.6 ($\mathbf{C}_{4a}$), 130.3 (Ph$\mathbf{C}_{meta}$), 126.2 ($\mathbf{C}_4$), 125.1 ($\mathbf{C}_6$), 124.8 ($\mathbf{C}_5$), 120.5 (Ph$\mathbf{C}_{ortho}$), 118.0 ($\mathbf{C}_7$), 81.8 ($\mathbf{C}_{8a}$), 71.2 ($\mathbf{C}_{3a}$), 60.0 ($\mathbf{C}_2$), 53.7 ($NCO_2\mathbf{C}H_3$), 53.6 ($NCO_2\mathbf{C}H_3$), 52.8 ($CO_2\mathbf{C}H_3$), 39.5 ($\mathbf{C}_3$).
FTIR (neat) cm^{-1}:	3255 (br), 2955 (w), 1715 (s), 1602 (w) 1484 (m), 1451 (m), 1397 (m).
HRMS (ESI):	calc'd for $C_{22}H_{25}N_4O_8S$ $[M+H]^+$ = 505.1388 found: 505.1385.
TLC (50% acetone in hexanes), R_f:	0.42 (UV, CAM).

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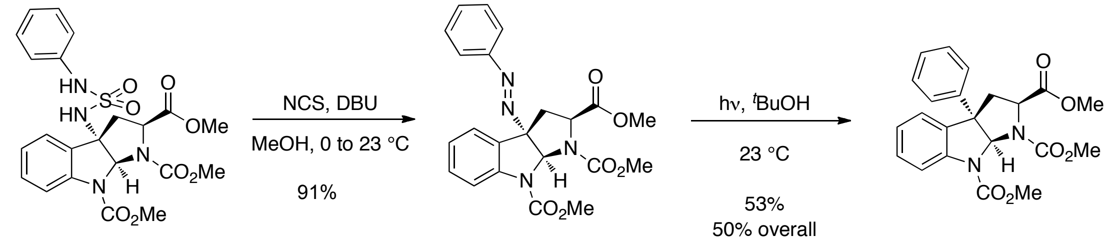
[3] For preparation of **S5**, see Audrieth, L. F.; Sveda, M. *J. Org. Chem.* **1944**, *9*, 89.

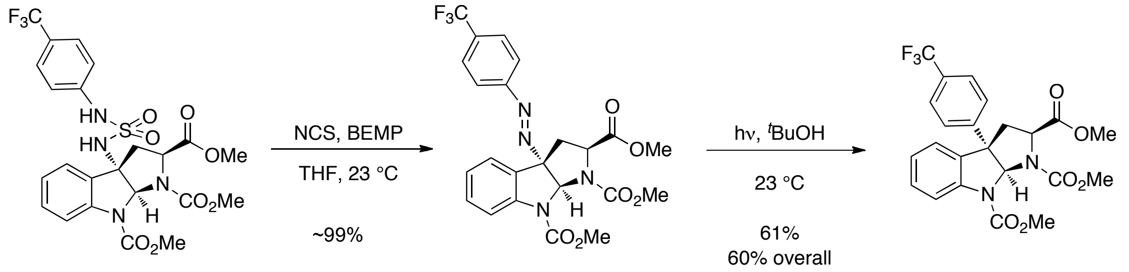


(+)-**6h** **5h** (+)-**4h**

(+)-(2*S*,3a*S*,8a*S*)-Trimethyl 3a-phenyl-3,3a-dihydropyrrolo[2,3-*b*]indole-1,2,8(2*H*,8a*H*)-tricarboxylate (4h, Table 1, entry 5):

DBU (33 μL, 0.22 mmol, 4.4 equiv) was added to a solution of sulfamide (+)-**6h** (25 mg, 0.050 mmol, 1 equiv) in MeOH (23 mL) and agitated by vigorous stirring. After 10 min, the reaction vessel was covered in aluminum foil and cooled to 0 °C. After 10 min, a solution of NCS (15 mg, 0.11 mmol, 2.2 equiv) in MeOH (2 mL) was added dropwise via syringe. The reaction mixture was allowed to warm to room temperature. After 3 h, the mixture was cooled to 0 °C and excess oxidant was quenched by addition of saturated aqueous sodium thiosulfate solution (3 mL) and the resulting mixture was allowed to warm to room temperature. The heterogeneous mixture was filtered, and the filter cake was washed with ethyl acetate (25 mL). The biphasic filtrate was concentrated under reduced pressure to allow the removal of the volatile organics. The resulting solution was diluted with diethyl ether (50 mL) and the aqueous layer separated. The organic layer was washed with water (2 × 5 mL) and brine (10 mL). The organic layer was dried over anhydrous sodium sulfate and filtered. The volatiles were removed under reduced pressure and the resulting crude diazene **5h** (20 mg, 91%) was used directly in the next step. A degassed solution of diazene **5h** (20 mg, 0.046 mmol, 1 equiv) in *tert*-butanol (5 mL) in a Pyrex® vessel was placed in a Rayonet photochemical reactor and irradiated with 300 nm lamps. After 12 h, the volatiles were removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (eluent: 15% acetone in hexanes; SiO_2: 6.0 × 0.5 cm) to give dimer (+)-**4h** (10 mg 53%, 50% overall) as a white solid ($[\alpha]^{24}_{D}$ = +100 (*c* 0.55, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_3CN, 60 °C) δ:	7.65 (d, *J* = 8.1 Hz, 1H, C_7**H**), 7.35–7.32 (m, 2H, Ph$\mathbf{H}_{ortho}$), 7.29–7.25 (m, 4H, C_6**H**, Ph$\mathbf{H}_{meta}$, Ph$\mathbf{H}_{para}$), 7.19 (ddd, *J* = 7.6 Hz, 1.3 Hz, 0.5 Hz, 1H C_4**H**), 7.04 (app dt, *J* = 7.5 Hz, 1.1 Hz, 1H, C_5**H**), 6.37 (s, 1H, C_{8a}**H**), 4.74 (dd, *J* = 8.9 Hz, 1.1 Hz, 1H, C_2**H**), 3.84 (s, 3H, $NCO_2C\mathbf{H}_3$), 3.70 (s, 3H, $NCO_2C\mathbf{H}_3$), 3.19 (s, 3H, $CO_2C\mathbf{H}_3$), 3.08 (dd, *J* = 13.4 Hz, 1.1 Hz, 1H, $C_3\mathbf{H}_a$), 3.02 (dd, *J* = 13.1 Hz, 8.9 Hz, 1H, $C_3\mathbf{H}_b$).
^{13}C NMR (125 MHz, CD_3CN, 60 °C) δ:	172.4 ($\mathbf{C}O_2CH_3$), 156.1 ($N\mathbf{C}O_2CH_3$), 155.0 ($N\mathbf{C}O_2CH_3$), 143.6 ($\mathbf{C}_{1'}$), 143.5 (C_{7a}), 136.1 ($\mathbf{C}_{4a}$), 130.2 ($\mathbf{C}_6$), 130.2 (Ph$\mathbf{C}_{ortho}$), 128.7 (Ph$\mathbf{C}_{para}$), 126.8 (Ph$\mathbf{C}_{meta}$), 125.8 ($\mathbf{C}_4$), 124.9 ($\mathbf{C}_5$), 118.0 ($\mathbf{C}_7$), 84.7 ($\mathbf{C}_{8a}$), 61.3 ($\mathbf{C}_2$), 60.8 ($\mathbf{C}_{3a}$), 53.8 ($NCO_2\mathbf{C}H_3$), 53.5 ($NCO_2\mathbf{C}H_3$), 52.7 ($CO_2\mathbf{C}H_3$), 40.3 ($\mathbf{C}_3$).
FTIR (neat) cm^{-1}:	2953 (w), 2360 (w), 1711 (s), 1482 (m), 1447 (m), 1446 (m), 1392 (m), 1322 (m).
HRMS (ESI):	calc'd for $C_{22}H_{22}N_2NaO_6$ $[M+Na]^+$: 433.1370, found: 433.1366
TLC (50% acetone in hexanes), R_f:	0.60 (UV, CAM)

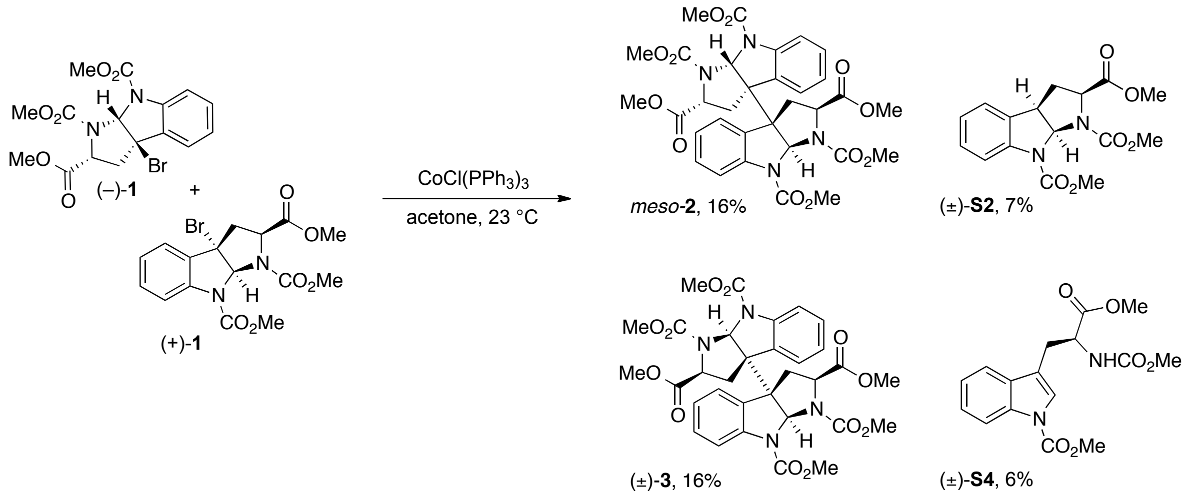


6i **5i** **(+)-4i**

(+)-(2*S*,3a*S*,8a*S*)-Trimethyl 3a-(4-(trifluoromethyl)phenyl)-3,3a-dihydropyrrolo[2,3-*b*]indole-1,2,8(2*H*,8a*H*)-tricarboxylate (4i, Table 1, entry 6):

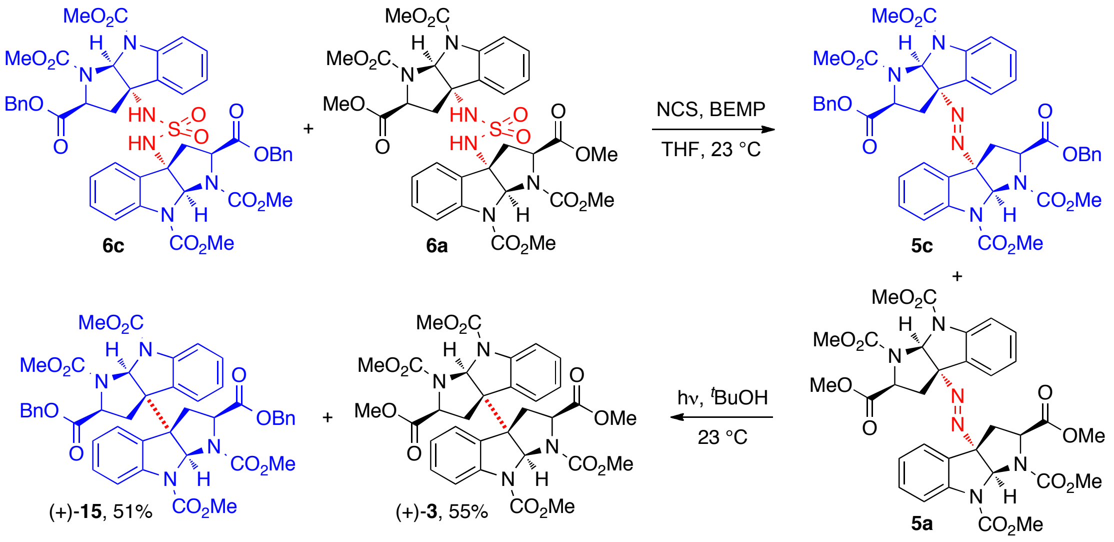
A solution of sulfamide **6i** (7.3 mg, 0.013 mmol, 1 equiv) in THF (300 μL) was added to resin-bound BEMP (44 mg, 2.2 g/mmol on 200-400 mesh polystyrene resin, 0.10 mmol, 7.6 equiv) via cannula. After 1 h, a solution of NCS (10 mg, 0.076 mmol, 6.0 equiv) in THF (150 μL) was added to the reaction mixture. After 5 min, an additional portion of resin-bound BEMP (44 mg, 0.10 mmol, 7.6 equiv) was added as a solid. After 10 min, the reaction mixture was diluted with ethyl acetate (10 mL) and filtered. The resin was washed with ethyl acetate (3 × 5 mL). The filtrate was washed with aqueous saturated sodium thiosulfate solution (2 × 10 mL) and brine (10 mL). The organic layer was dried over anhydrous sodium sulfate and filtered. The volatiles were removed under reduced pressure and the resulting diazene **5i** (6.8 mg, ~99%) was used crude for photolysis. A degassed solution of diazene **5i** (4.3 mg, 0.0085 mmol, 1 equiv) in *tert*-butanol (850 μL) in a Pyrex® vessel was irradiated using medium pressure 450W mercury lamp (>280 nm). After 72 h, the volatiles were removed under reduced pressure and the residue was purified by flash column chromatography (eluent: 40% acetone in hexanes; SiO_2: 6 × 0.5 cm) on silica gel to give dimer (+)-**4i** (2.5 mg, 61%, 60% overall) as a white solid ($[\alpha]^{24}_{D}$ = + 77 (*c* 0.12, CH_2Cl_2)).

^{1}H NMR (500 MHz, CD_3CN, 60 °C) δ:	7.67 (d. J = 8.0 Hz, 1H, $C_7\mathbf{H}$), 7.64 (d, J = 8.0 Hz, 2H, CF_3-*o*-**H**), 7.45 (d, J = 8.0 Hz, 2H, CF_3-*m*-**H**), 7.30 (t, J = 7.5 Hz, 1H, $C_6\mathbf{H}$), 7.20 (d, J = 7.5 Hz, 1H, $C_4\mathbf{H}$), 7.06 (t, J = 7.0 Hz, 1H, $C_5\mathbf{H}$), 6.41 (s, 1H, $C_{8a}\mathbf{H}$), 4.76 (d, J = 8.5 Hz, 1H, $C_2\mathbf{H}$), 3.85 (s, 3H, $NCO_2C\mathbf{H}_3$), 3.70 (s, 3H, $NCO_2C\mathbf{H}_3$), 3.20 (s, 3H, $CO_2C\mathbf{H}_3$), 3.11 (d, J = 13.0 Hz, 1H, $C_3\mathbf{H}_a$), 3.04 (dd, J = 13.0 Hz, 9.0 Hz, 1H, $C_3\mathbf{H}_b$).
^{13}C NMR (125 MHz, CD_3CN, 60 °C) δ:	172.7 ($\mathbf{C}O_2CH_3$), 156.4 ($N\mathbf{C}O_2CH_3$), 155.3 ($N\mathbf{C}O_2CH_3$), 148.4 (CF_3-*p*-**C**) , 144.0 ($\mathbf{C}_{7a}$), 135.7 ($\mathbf{C}_{4a}$), 131.0 (CF_3-*m*-**C**), 130.6 (q, J = 32.0 Hz, CF_3-*i*-**C**), 128.2 ($\mathbf{C}_6$), 127.5 (q, J = 4.0 Hz, CF_3-*o*-**C**), 126.3 ($\mathbf{C}_5$), 126.0 (q, J = 271.7 Hz, $\mathbf{C}F_3$), 125.5 ($\mathbf{C}_4$), 118.7 ($\mathbf{C}_7$), 84.9 ($\mathbf{C}_{8a}$), 61.6 ($\mathbf{C}_2$), 61.1 ($\mathbf{C}_{3a}$), 54.3 ($NCO_2\mathbf{C}H_3$), 54.0 ($NCO_2\mathbf{C}H_3$), 53.2 ($CO_2\mathbf{C}H_3$), 40.6 ($\mathbf{C}_3$).
^{19}F NMR (282 MHz, CD_3CN, 20 °C) δ:	–63.55 ($ArC\mathbf{F}_3$).
FTIR (neat) cm^{-1}:	2956 (w), 1709 (s), 1483 (m), 1449 (m), 1395 (m), 1325 (s).
HRMS (ESI):	calc'd for $C_{23}H_{22}F_3N_2O_6$ $[M+H]^+$: 479.1424, found: 479.1427.
TLC (40% acetone in hexanes), R_f:	0.32 (UV)



Mechanistic study 1: Equation 1, undirected synthesis of dimers *meso*-2 and (±)-3:

A solid sample of freshly prepared tristriphenylphosphine cobalt chloride (96 mg, 0.11 mmol, 1.5 equiv) was rapidly added to a degassed (argon purge 15 min) solution of (–)-**1** (15 mg, 0.036 mmol, 0.50 equiv) and (+)-**1** (15 mg, 0.036 mmol, 0.50 equiv) in acetone (750 μL) under argon atmosphere. After 20 min the reaction mixture was quenched with saturated ammonium chloride (2 ml) and diluted with ethyl acetate (50 ml). The aqueous layer was separated and the organic layer was washed with saturated ammonium chloride (4 × 5 ml) water (1 × 5 ml) and brine (1 × 10 ml). The resulting organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. ^{1}H NMR of the unpurified reaction mixture in CD_3CN revealed a 22% yield of *meso*-**2** and 17% of (±)-**3** based on mesitylene as an internal standard**.** The crude mixture was purified by reverse phase preparative HPLC (Waters X-bridge preparative HPLC column 19 × 250 mm C-18, 5 μm; 25% MeCN / 75% H_2O 5 min, linear gradient to 40% MeCN / 60% H_2O 30 min; 20 mL/min, t_R ((±)-**S2**) = 16.9 min, t_R ((±)-**3**) = 24.8 min, t_R (*meso*-**2**) = 26.9 min, t_R ((±)-**S4**) = 30.0 min). Isolated yield of *meso*-**2** (3.8 mg, 16%), (±)-**3** (3.8 mg, 16%), (±)-**S2** (1.3 mg, 6%), and (±)-**S4** (1.6 mg, 7%). See page S23 for spectroscopic data for *meso*-**2**, page S11 for spectroscopic data for dimer **3**, and page S4 for spectroscopic data for **S2**.



Mechanistic study 2: Equation 2, directed synthesis of homodimers (+)-3 and (+)-15:

A solution of sulfamide **6c** (7.9 mg, 8.7 μmol, 1 equiv) and sulfamide **6a** (6.6 mg, 8.7 μmol, 1 equiv) in THF (700 μL) was added to resin-bound BEMP (59 mg, 2.2 g/mmol on 200-400 mesh polystyrene resin, 0.13 mmol, 15 equiv) via cannula. After 1 h, a solution of NCS (14 mg, 0.097 mmol, 11 equiv) in THF (350 μL) was added to the reaction mixture. After 5 min, an additional portion of resin-bound BEMP (59 mg, 0.13 mmol, 15 equiv) was added as a solid. After 10 min, the reaction mixture was diluted with ethyl acetate (10 mL) and filtered. The resin was washed with ethyl acetate (3 × 5 mL). The filtrate was washed with aqueous saturated sodium thiosulfate solution (2 × 10 mL) and brine (10 mL). The organic layer was dried over anhydrous sodium sulfate and filtered. The volatiles were removed under reduced pressure and the resulting mixture of diazenes **5c** and **5a** (12 mg) was used crude for photolysis. A degassed solution of diazenes **5c** and **5a** (12 mg) in *tert*-butanol (1.5 mL) in a Pyrex® vessel was irradiated using a medium pressure, 450W mercury lamp (>280 nm). After 5 h, the volatiles were removed under reduced pressure. The residue was filtered through a plug of silica gel (eluent: $CH_2Cl_2 \rightarrow {}^iPrOH$; SiO_2: 1.0 cm × 0.5 cm) to afford the crude mixture of dimers (+)-**15** and (+)-**3** (11 mg). HPLC[4] analysis of the residue showed only homodimers (+)-**15** and (+)-**3** and no observable amount of heterodimer (+)-**4b** (Chiralpak OD-H, 30% ^{i}PrOH / 70% hexanes, 0.6 mL/min, t_R (homodimer **3**) = 21.6 min, t_R (heterodimer (+)-**4b**, not observed) = 26.1 min, t_R (homodimer (+)-**15**) = 30.4 min). The residue was purified by flash column chromatography (eluent: 20→50% acetone in hexanes; SiO_2: 6.0 × 1.0 cm) on silica gel to afford homodimer (+)-**3** (3.2 mg, 55%) and homodimer (+)-**15** (3.7 mg, 51%) ($[\alpha]^{24}_D$ = + 154 (*c* 0.29, CH_2Cl_2)). See page S11 for spectroscopic data for dimer (+)-**3**.

Spectroscopic data for dimer (+)-**15**:

^{1}H NMR (500 MHz, CD_3CN, 60 °C) δ: 7.55 (d, *J* = 8.0 Hz, 2H, C_7**H**), 7.37-7.24 (m, 10H), 7.18–7.16 (m, 3H), 6.98 (td, *J* = 7.5, 1.0 Hz, 2H, C_5**H**), 5.58 (s, 2H, C_{8a}**H**), 4.64 (d, *J* = 12.0 Hz, 2H, PhC**H**$_a$), 4.57 (d, *J* = 9.0 Hz, 2H, C_2**H**), 4.39 (d, *J* = 12.5 Hz, 2H, PhC**H**$_b$), 3.77 (s, 6H, NCO_2C**H**$_3$), 3.51 (s, 6H,

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[4] ^{1}H NMR analysis of the crude reaction mixture was of limited utility due to our appreciation for the resonance overlap of compounds **3**, **4b**, and **15** when analyzed independently.

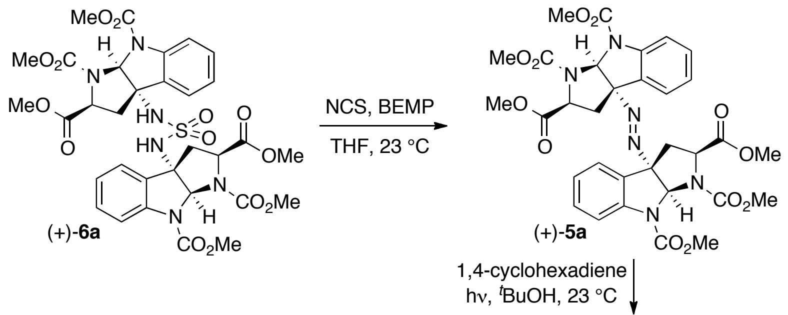
$NCO_2C\mathbf{H}_3$), 2.95 (dd, J = 13.5, 9.5 Hz, 2H, $C_3\mathbf{H}_a$), 2.79 (d, J = 13.0 Hz, 2H, $C_3\mathbf{H}_b$).

^{13}C NMR (125 MHz, CD_3CN, 60 °C) δ: 171.9 ($\mathbf{C}O_2CH_2Ph$), 156.0 ($N\mathbf{C}O_2CH_3$), 154.8 ($N\mathbf{C}O_2CH_3$), 144.9 ($\mathbf{C}_{7a}$), 137.5, 132.2 ($\mathbf{C}_{4a}$), 131.6 ($\mathbf{C}_6$), 130.1, 129.8, 129.6, 126.4 ($\mathbf{C}_5$), 124.9 ($\mathbf{C}_4$), 118.0 ($\mathbf{C}_7$), 80.7 ($\mathbf{C}_{8a}$), 68.2 ($Ph\mathbf{C}H_2$), 61.1 ($\mathbf{C}_{3a}$), 60.9 ($\mathbf{C}_2$), 54.1 ($NCO_2\mathbf{C}H_3$), 53.9 ($NCO_2\mathbf{C}H_3$), 36.4 ($\mathbf{C}_3$).

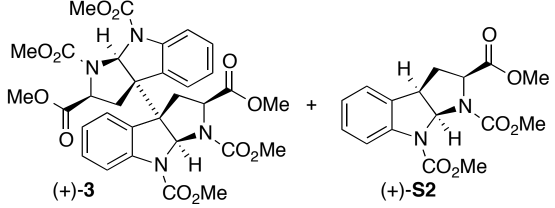
FTIR (neat) cm^{-1}: 2955 (w), 1720 (s), 1482 (m), 1448 (m), 1394 (m).

HRMS (ESI): calc'd for $C_{44}H_{43}N_4O_{12}$ $[M+H]^+$: 819.2872, found: 819.2884.

TLC (40% acetone in hexanes), R_f: 0.25 (UV, CAM).



cyclohexadiene (equiv)	NMR ratio **3**:**S2**	% yield **3**	% yield **S2**
5	1.9:1	45	21
20	1.7:1	41	20

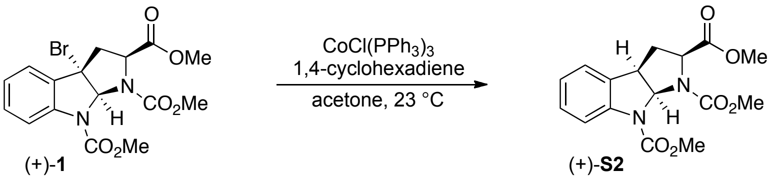


Mechanistic study 3: Diazene fragmentation in the presence of hydrogen atom donor (5.0 equiv):

A solution of sulfamide (+)-**6a** (13 mg, 0.017 mmol, 1 equiv) in THF (1 mL) was added to resin-bound BEMP (116 mg, 0.255 mmol, 15.0 equiv) via syringe. After 1 h, a solution of NCS (27 mg, 0.20 mmol, 12 equiv) in THF (0.5 mL) was added to the reaction mixture. After 5 min, an additional portion of resin-bound BEMP (116 mg, 0.255 mmol, 15.0 equiv) was added as a solid. After 10 min, the reaction mixture was diluted with ethyl acetate (10 mL) and filtered. The resin was washed with ethyl acetate (3 × 5 mL). The filtrate was washed with aqueous saturated sodium thiosulfate solution (2 × 10 mL) and brine (10 mL). The organic layer was dried over anhydrous sodium sulfate and filtered. The volatiles were removed under reduced pressure and the resulting diazene (+)-**5a** (12 mg) was used crude for photolysis. A degassed solution of diazene (+)-**5a** (12 mg, 0.017 mmol, 1 equiv) and 1,4-cyclohexadiene (8.0 µL, 0.085 mmol, 5.0 equiv) in *tert*-butanol (1.7 mL) in a Pyrex® vessel was irradiated using a medium pressure, 450W mercury lamp (>280 nm). After 5 h, the volatiles were removed under reduced pressure. ^{1}H NMR analysis of the residue showed a 1.9:1 mixture of the dimer (+)-**3** and the reduced product (+)-**S2**. The residue was purified by flash column chromatography (eluent: 40% acetone in hexanes; SiO_2: 6.0 × 1.0 cm) on silica gel to afford dimer (+)-**3** (5 mg, 45%) and reduced tricycle (+)-**S2** (2.4 mg, 21%). For full characterization and spectroscopic data for dimer (+)-**3** and tricycle (+)-**S2** see page S11 and S4, respectively.

Diazene fragmentation in the presence of hydrogen atom donor (20 equiv):

A solution of sulfamide (+)-**6a** (14 mg, 0.018 mmol, 1 equiv) in THF (1 mL) was added to resin-bound BEMP (125 mg, 0.276 mmol, 15.3 equiv) via syringe. After 1 h, a solution of NCS (30 mg, 0.22 mmol, 12 equiv) in THF (0.5 mL) was added to the reaction mixture. After 5 min, an additional portion of resin-bound BEMP (125 mg, 0.276 mmol, 15.3 equiv) was added as a solid. After 10 min, the reaction mixture was diluted with ethyl acetate (10 mL) and filtered. The resin was washed with ethyl acetate (3 × 5 mL). The filtrate was washed with aqueous saturated sodium thiosulfate solution (2 × 10 mL) and brine (10 mL). The organic layer was dried over anhydrous sodium sulfate and filtered. The volatiles were removed under reduced pressure and the resulting diazene (+)-**5a** (13 mg) was used crude for photolysis. A degassed solution of diazene **5a** (13 mg, 0.018 mmol, 1 equiv) and 1,4-cyclohexadiene (35 µL, 0.085 mmol, 20 equiv) in *tert*-butanol (1.8 mL) in a Pyrex® vessel was irradiated using a medium pressure, 450W mercury lamp (>280 nm). After 5 h, the volatiles were removed under reduced pressure. ^{1}H NMR analysis of the residue showed a 1.7:1 mixture of the dimer (+)-**3** and the reduced product (+)-**S2**. The residue was purified by flash column chromatography (eluent: 40% acetone in hexanes; SiO_2: 6.0 × 1.0 cm) on silica gel to afford dimer (+)-**3** (5 mg, 41%) and reduced tricycle (+)-**S2** (2.4 mg, 20%). For full characterization and spectroscopic data for dimer (+)-**3** and tricycle (+)-**S2** see page S11 and S4, respectively.



(+)-**1** (+)-**S2**

1,4-cyclohexadiene (equiv)	% yield **S2**
5	54
20	82

Cobalt mediated dimerization in the presence of hydrogen atom donor (5.0 equiv):

A solid sample of freshly prepared tristriphenylphosphine cobalt chloride (63 mg, 0.072 mmol, 1.5 equiv) was rapidly added to a degassed (argon purge 15 min) solution of (+)-**1** (30 mg, 0.073 mmol, 1 equiv) and 1,4-cyclohexadiene (34 μL, 0.11 mmol, 5.0 equiv) in acetone (750 μL) under argon atmosphere. After 20 min the reaction mixture was quenched with saturated ammonium chloride (2 mL) and diluted with ethyl acetate (50 mL). The aqueous layer was separated and the organic layer was washed with saturated ammonium chloride (4 × 5 mL) water (1 × 5 mL) and brine (1 × 10 mL). The resulting organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. ^{1}H NMR of the unpurified reaction mixture in CD_3CN revealed (+)-**S2** as the major product (dimer (+)-**3** was not observed). The crude residue was purified by flash column chromatography (eluent: 50% ethyl acetate in hexanes) on silica gel to afford (+)-**S2** (13 mg, 54%). For full characterization and spectroscopic data for tricycle (+)-**S2** see page S4.

Cobalt mediated dimerization in the presence of hydrogen atom donor (20 equiv):

A solid sample of freshly prepared tristriphenylphosphine cobalt chloride (63 mg, 0.072 mmol, 1.5 equiv) was rapidly added to a degassed (argon purge 15 min) solution of (+)-**1** (20 mg, 0.048 mmol, 1 equiv) and 1,4-cyclohexadiene (91 μL, 0.85 mmol, 20 equiv) in acetone (500 μL) under argon atmosphere. After 20 min the reaction mixture was quenched with saturated ammonium chloride (2 mL) and diluted with ethyl acetate (50 mL). The aqueous layer was separated and the organic layer was washed with saturated ammonium chloride (4 × 5 mL) water (1 × 5 mL) and brine (1 × 10 mL). The resulting organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. ^{1}H NMR of the unpurified reaction mixture in CD_3CN revealed (+)-**S2** as the major product (dimer (+)-**3** was not observed). The crude residue was purified by flash column chromatography (eluent: 50% ethyl acetate in hexanes) on silica gel to afford (+)-**S2** (13 mg, 82%). For full characterization and spectroscopic data for tricycle (+)-**S2** see page S4.

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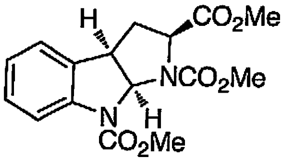

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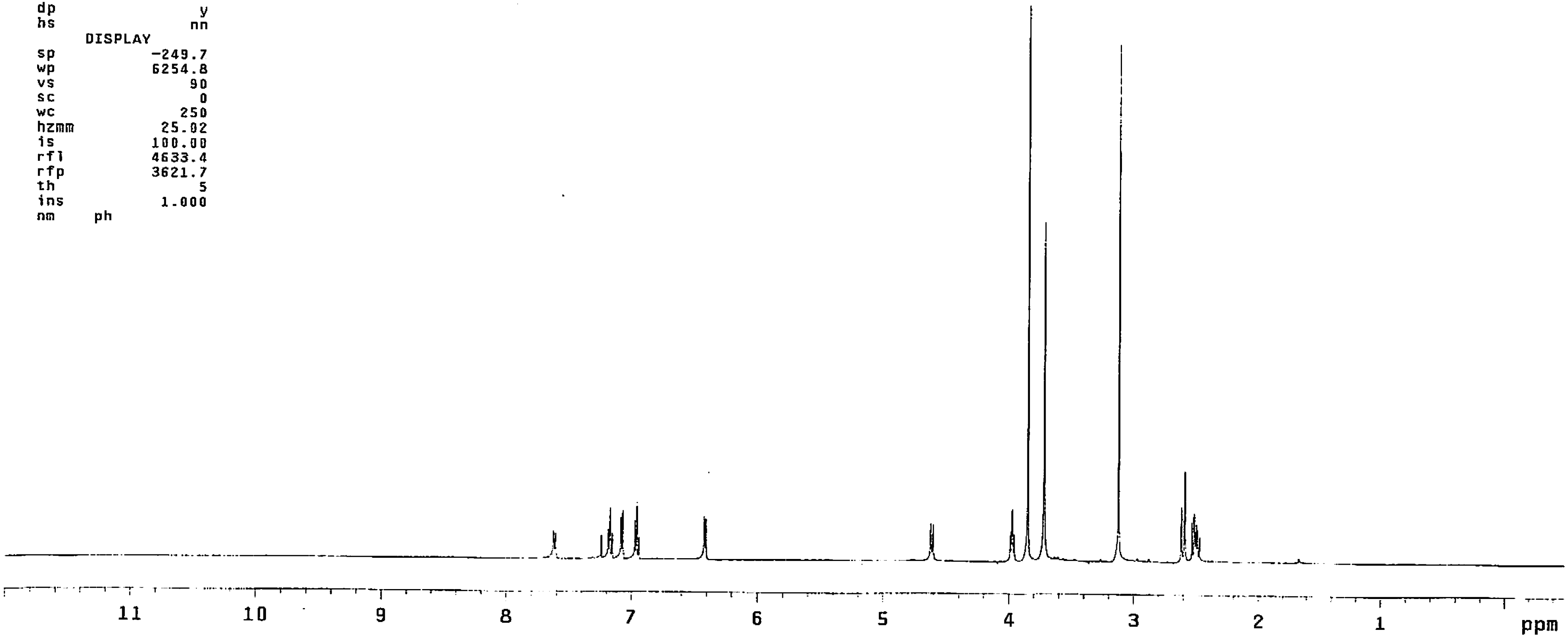

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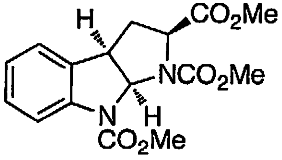

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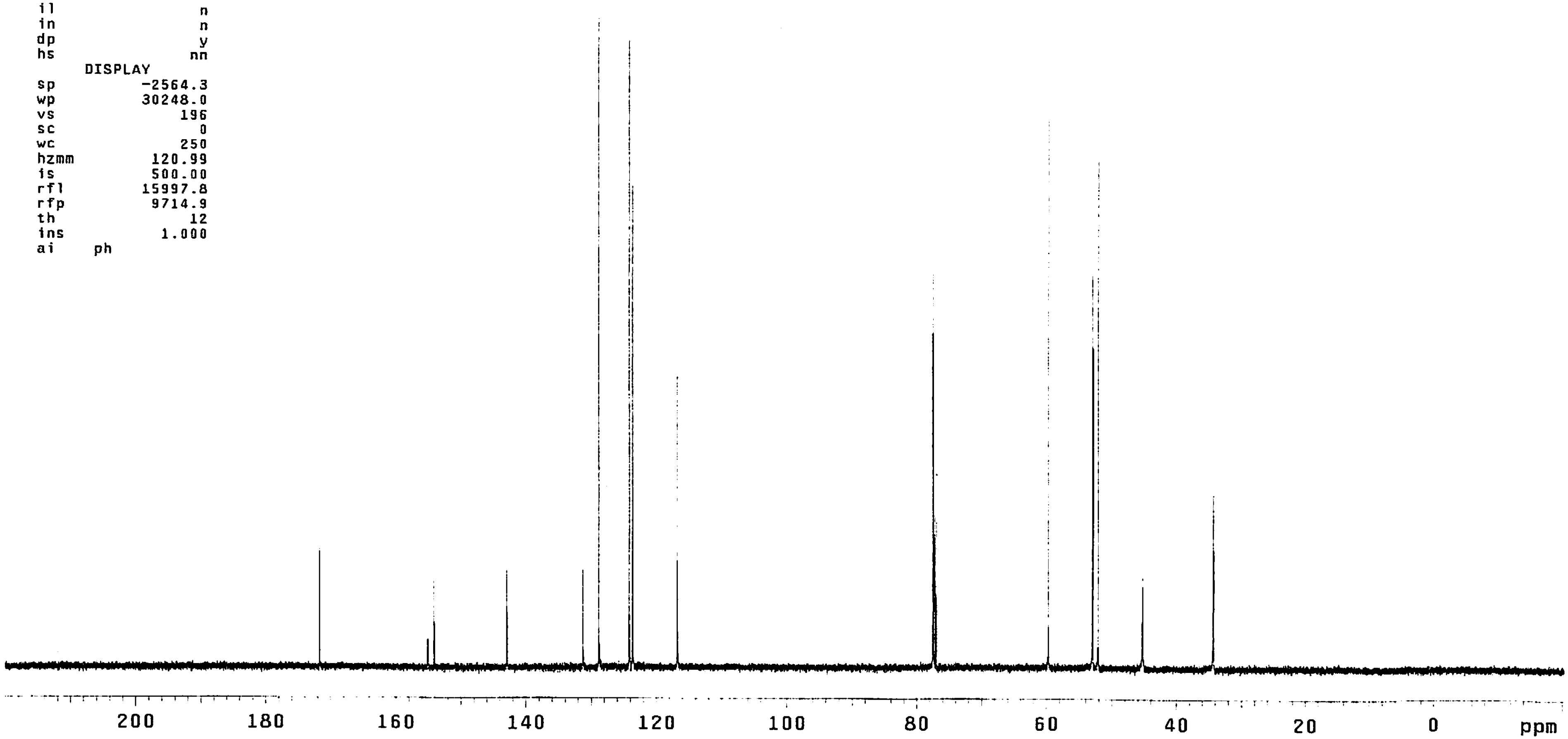

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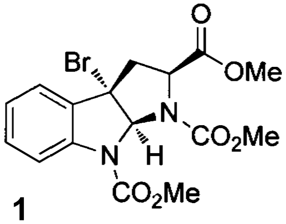
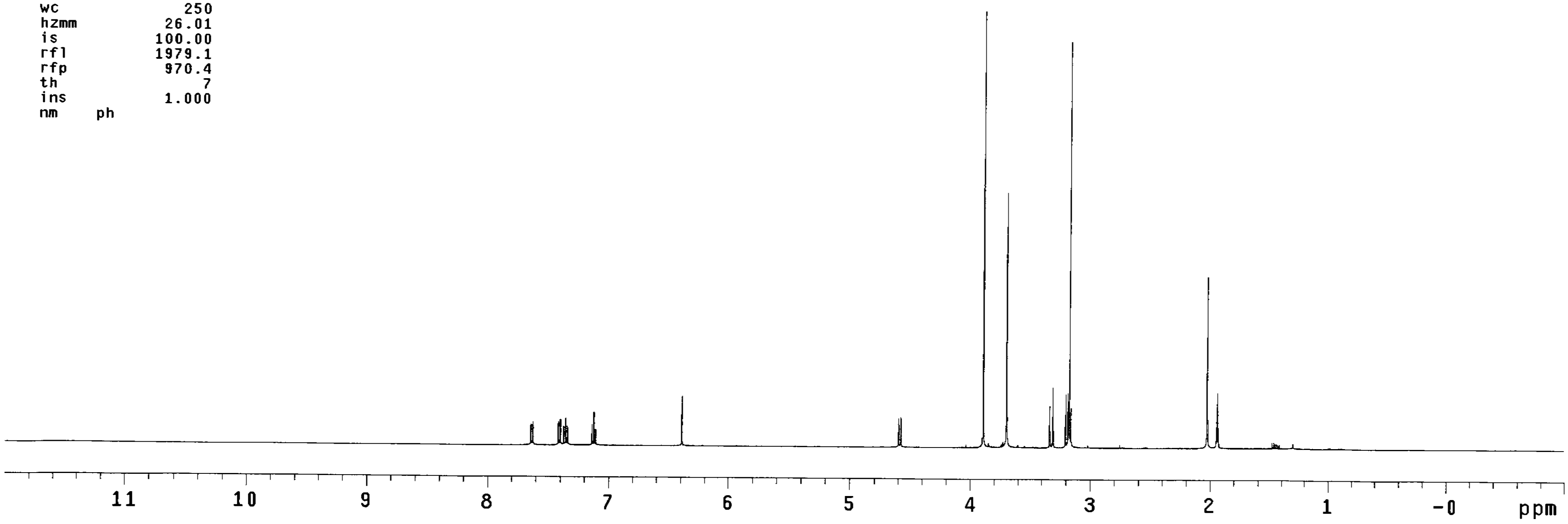
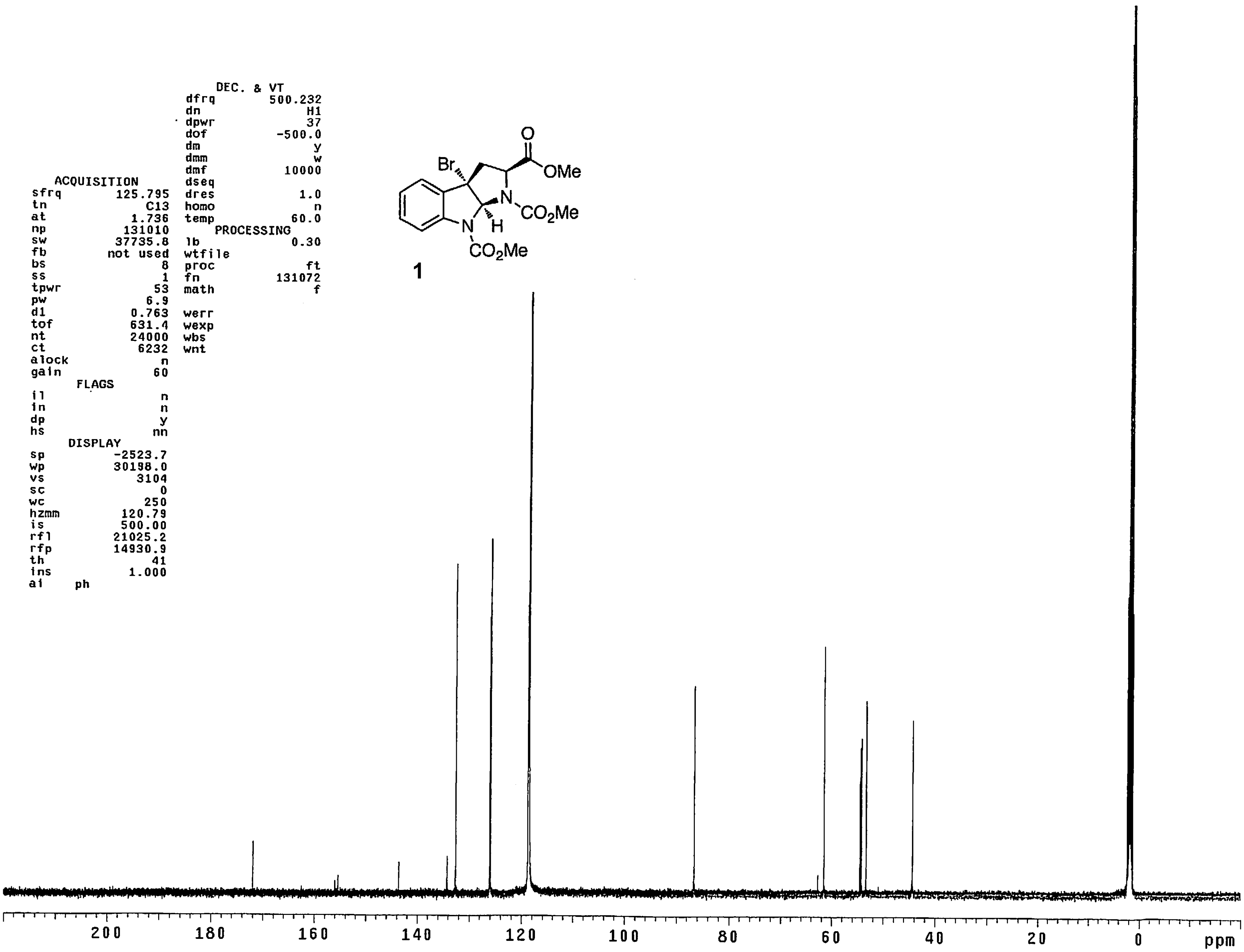
nm     ph
```



1

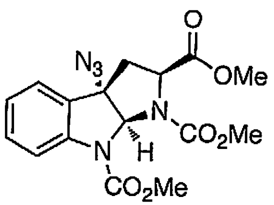




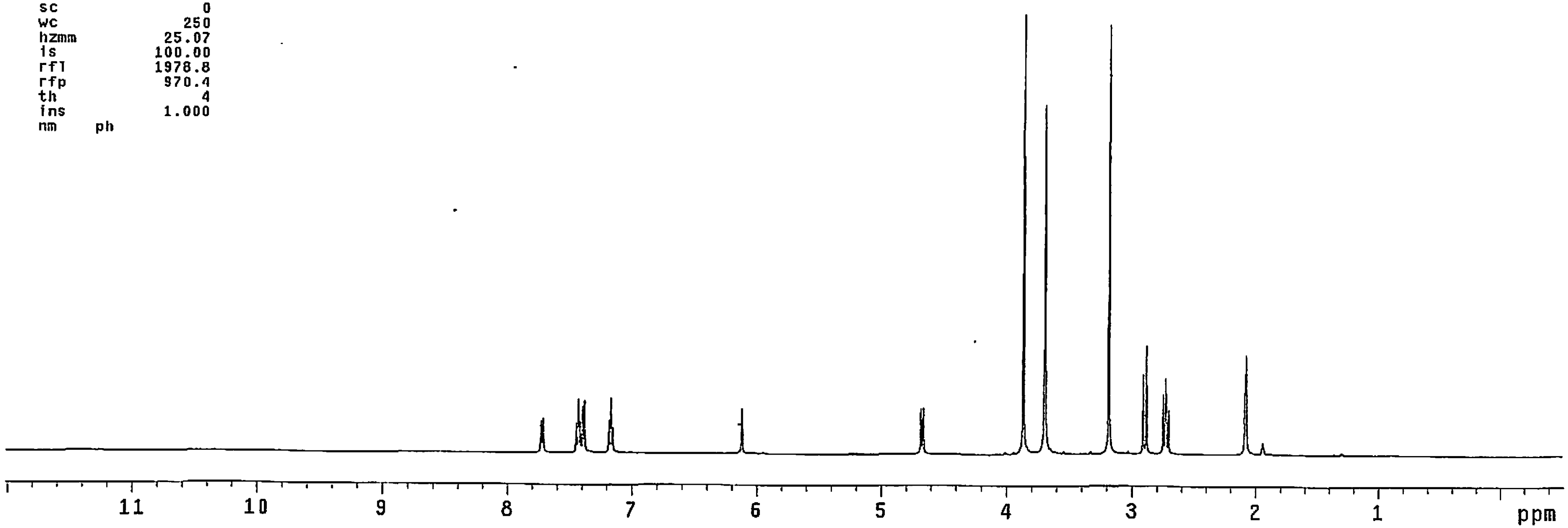
```
     ACQUISITION                  DEC. & VT
sfrq        125.795      dfrq         500.232
tn              C13      dn                H1
at            1.736      dpwr              37
np           131010      dof           -500.0
sw          37735.8      dm                 y
fb         not used      dmm                w
bs                8      dmf            10000
ss                1      dseq
tpwr             53      dres             1.0
pw              6.9      homo               n
d1            0.763      temp            60.0
tof           631.4          PROCESSING
nt            24000      lb              0.30
ct             6232      wtfile
alock             n      proc              ft
gain             60      fn            131072
        FLAGS            math               f
il                n
in                n      werr
dp                y      wexp
hs               nn      wbs
       DISPLAY           wnt
sp          -2523.7
wp          30198.0
vs             3104
sc                0
wc              250
hzmm         120.79
is           500.00
rfl         21025.2
rfp         14930.9
th               41
ins           1.000
ai    ph
```

1

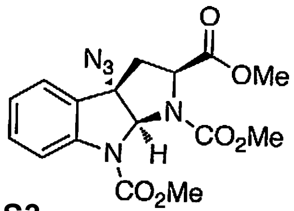
```
                                  DEC. & VT
                        dfrq           125.795
                        dn                 C13
                        dpwr                37
                        dof                  0
                        dm                 nnn
                        dmm                  c
     ACQUISITION        dmf              10000
sfrq          500.234   dseq
tn                 H1   dres               1.0
at              3.200   homo                 n
np              64000   temp              50.0
sw            10000.0       PROCESSING
fb           not used   wtfile
bs                  4   proc                ft
ss                  1   fn              131072
tpwr               58   math                 f
pw                9.0
d1                  0   werr
tof            1498.2   wexp
nt                128   wbs
ct                 20   wnt
alock               n
gain         not used
        FLAGS
il                  n
in                  n
dp                  y
hs                 nn
       DISPLAY
sp             -259.3
wp             6267.9
vs                 71
sc                  0
wc                250
hzmm            25.07
is             100.00
rfl            1978.8
rfp             970.4
th                  4
ins             1.000
nm    ph
```



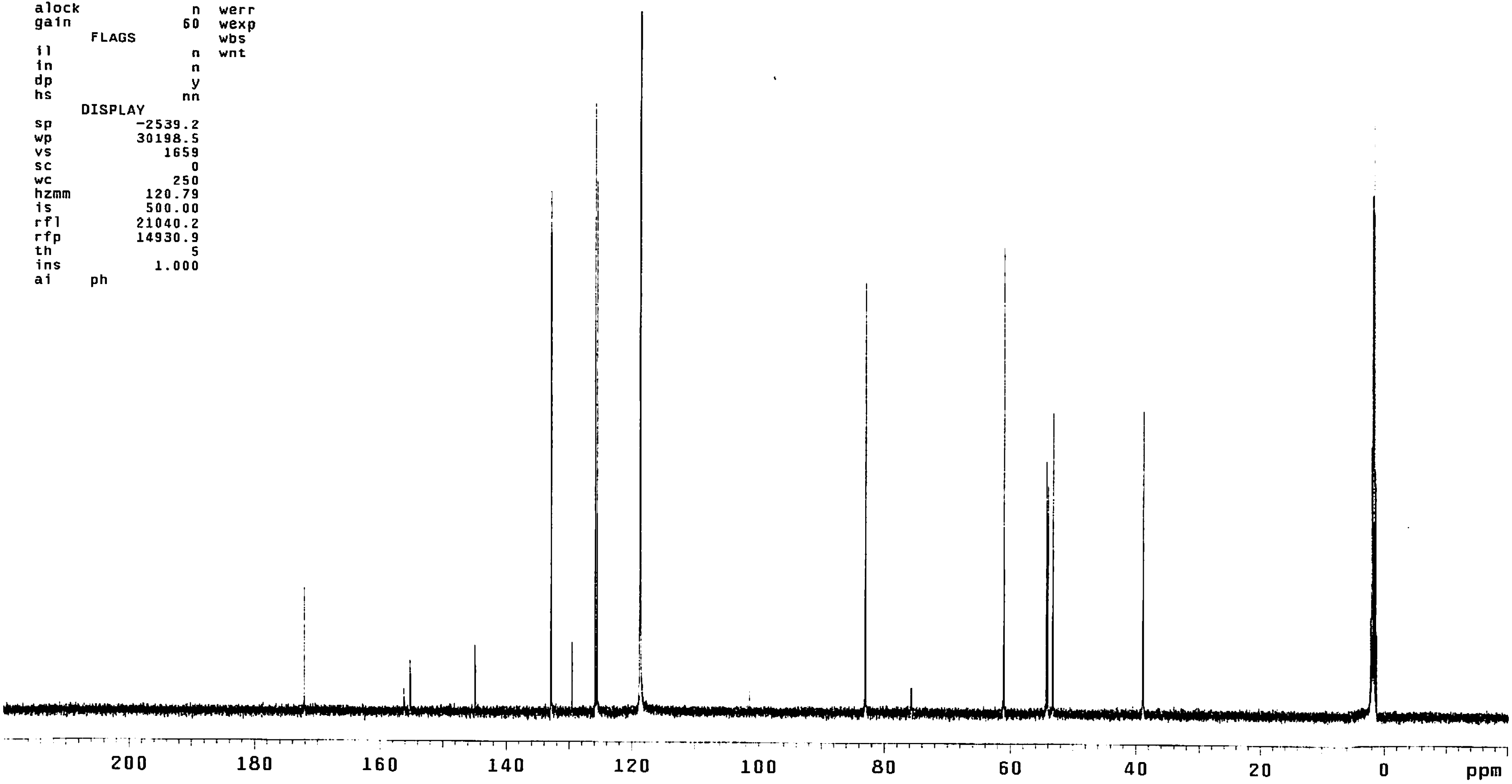
S3



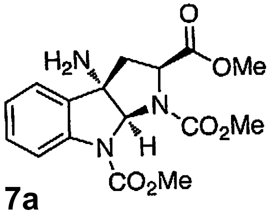
```
                                        DEC. & VT
                                dfrq          500.232
                                dn                 H1
                                dpwr               37
      ACQUISITION               dof            -500.0
sfrq          125.795           dm                  y
tn                C13           dmm                 w
at              1.736           dmf             10000
np             131010           dseq
sw            37735.8           dres              1.0
fb           not used           homo                n
bs                  8           temp             50.0
ss                  1               PROCESSING
tpwr               53           lb               0.30
pw                6.9           wtfile
d1              0.763           proc               ft
tof             631.4           fn             131072
nt              24000           math                f
ct               1448
alock               n           werr
gain               60           wexp
          FLAGS                 wbs
il                  n           wnt
in                  n
dp                  y
hs                 nn
        DISPLAY
sp            -2539.2
wp            30198.5
vs               1659
sc                  0
wc                250
hzmm           120.79
is             500.00
rfl           21040.2
rfp           14930.9
th                  5
ins             1.000
ai     ph
```



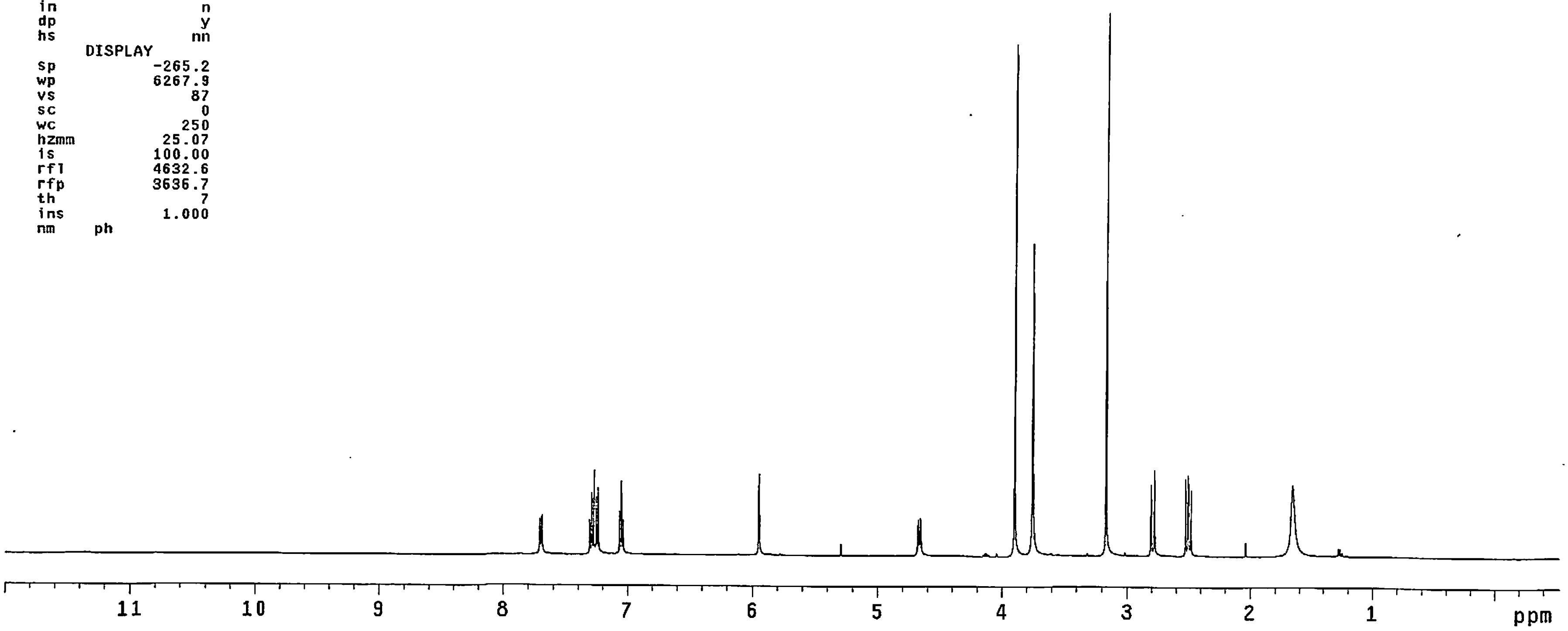
S3

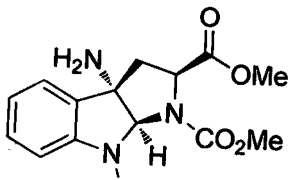


```
                             DEC. & VT
                         dfrq       125.794
                         dn             C13
                         dpwr            37
                         dof              0
                         dm             nnn
                         dmm              c
     ACQUISITION         dmf          10000
sfrq         500.231     dseq
tn                H1     dres           1.0
at             3.200     homo             n
np             64000     temp          50.0
sw           10000.0        PROCESSING
fb          not used     wtfile
bs                 4     proc            ft
ss                 1     fn          131072
tpwr              58     math             f
pw               9.0
d1                 0     werr
tof           1498.2     wexp
nt               128     wbs
ct                39     wnt
alock              n
gain        not used
       FLAGS
il                 n
in                 n
dp                 y
hs                nn
      DISPLAY
sp            -265.2
wp            6267.9
vs                87
sc                 0
wc               250
hzmm           25.07
is            100.00
rfl           4632.6
rfp           3636.7
th                 7
ins            1.000
nm     ph
```



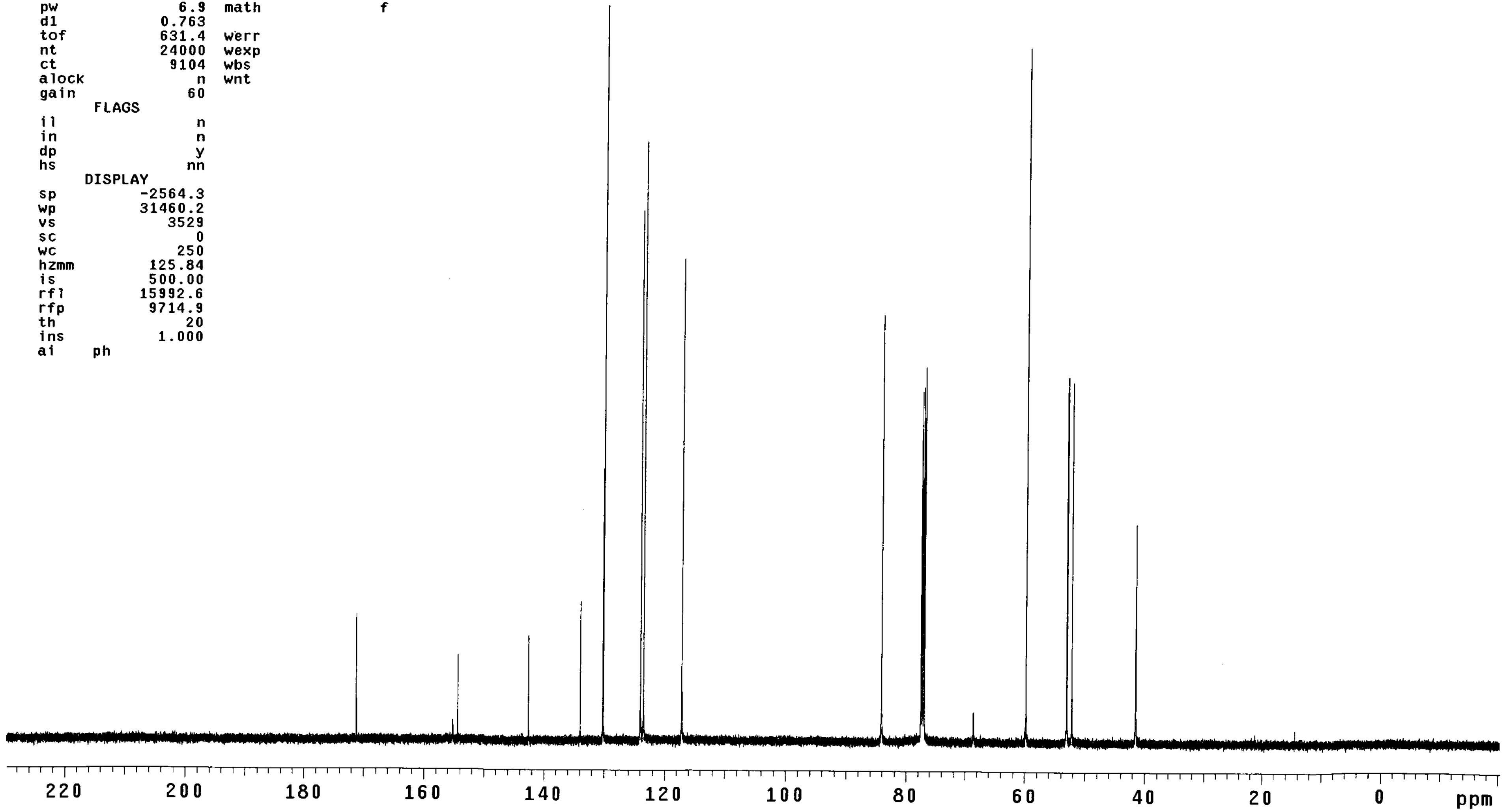
7a

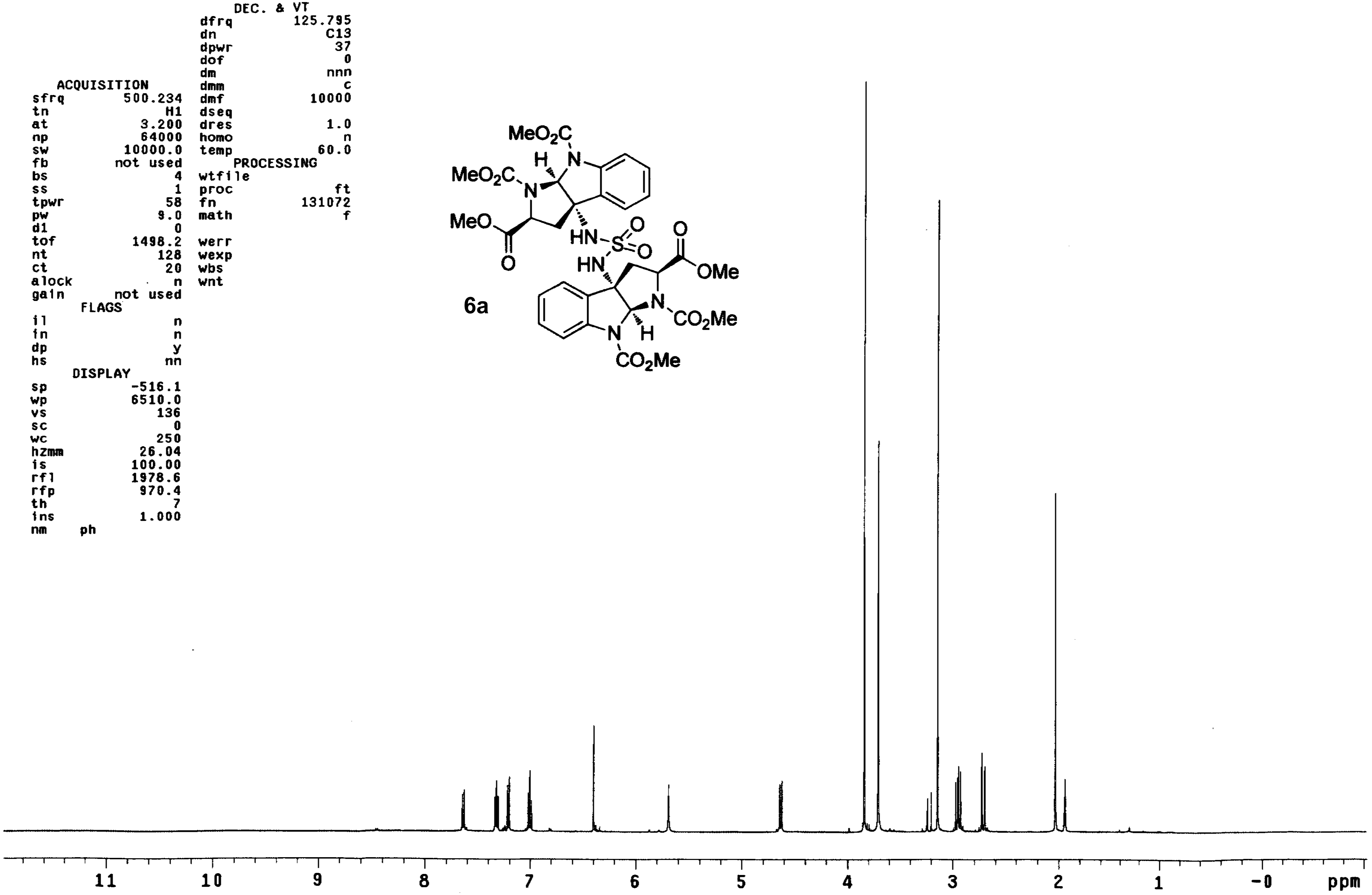




7a

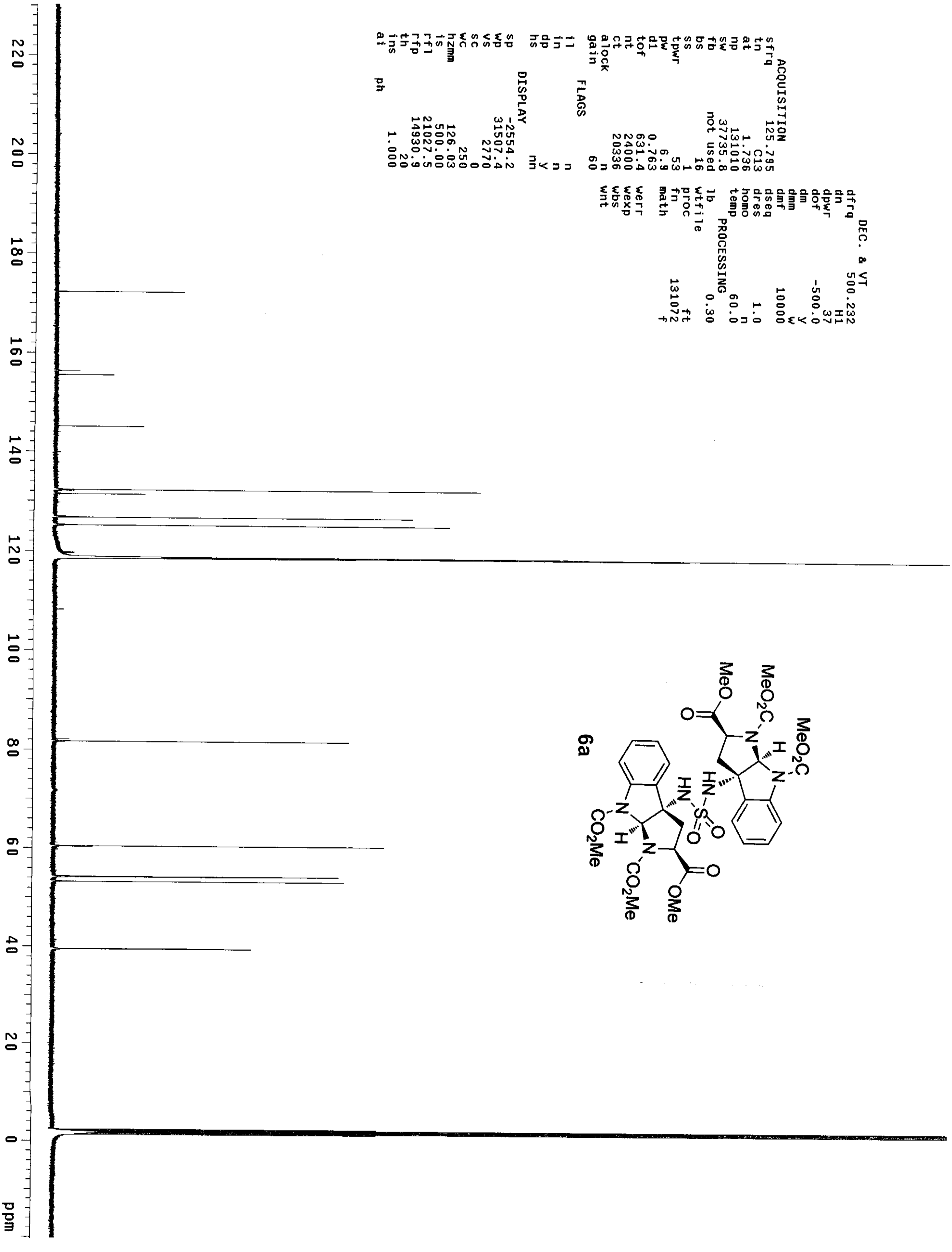
```
                              DEC. & VT
                       dfrq          500.229
                       dn                 H1
                       dpwr               37
                       dof            -500.0
                       dm                  y
                       dmm                 w
      ACQUISITION      dmf             10000
sfrq         125.795   dseq
tn               C13   dres              1.0
at             1.736   homo                n
np            131010   temp             50.0
sw           37735.8      PROCESSING
fb          not used   lb               0.30
bs                 8   wtfile
ss                 1   proc               ft
tpwr              53   fn             131072
pw               6.9   math                f
d1             0.763
tof            631.4   werr
nt             24000   wexp
ct              9104   wbs
alock              n   wnt
gain              60
      FLAGS
il                 n
in                 n
dp                 y
hs                nn
      DISPLAY
sp           -2564.3
wp           31460.2
vs              3529
sc                 0
wc               250
hzmm          125.84
is            500.00
rfl          15992.6
rfp           9714.9
th                20
ins            1.000
ai    ph
```





```
                              DEC. & VT
                        dfrq       125.795
                        dn             C13
                        dpwr            37
                        dof              0
                        dm             nnn
     ACQUISITION        dmm              c
sfrq         500.234    dmf          10000
tn                H1    dseq
at             3.200    dres           1.0
np             64000    homo             n
sw           10000.0    temp          60.0
fb          not used       PROCESSING
bs                 4    wtfile
ss                 1    proc            ft
tpwr              58    fn          131072
pw               9.0    math             f
d1                 0
tof           1498.2    werr
nt               128    wexp
ct                20    wbs
alock              n    wnt
gain        not used
       FLAGS
il                 n
in                 n
dp                 y
hs                nn
       DISPLAY
sp            -516.1
wp            6510.0
vs               136
sc                 0
wc               250
hzmm           26.04
is            100.00
rfl           1978.6
rfp            970.4
th                 7
ins            1.000
nm     ph
```

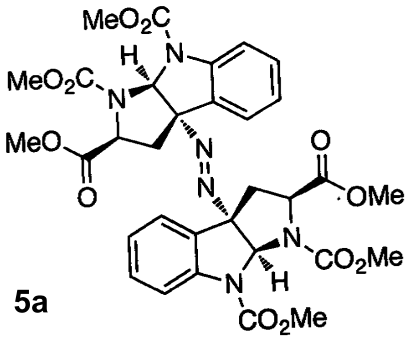
6a

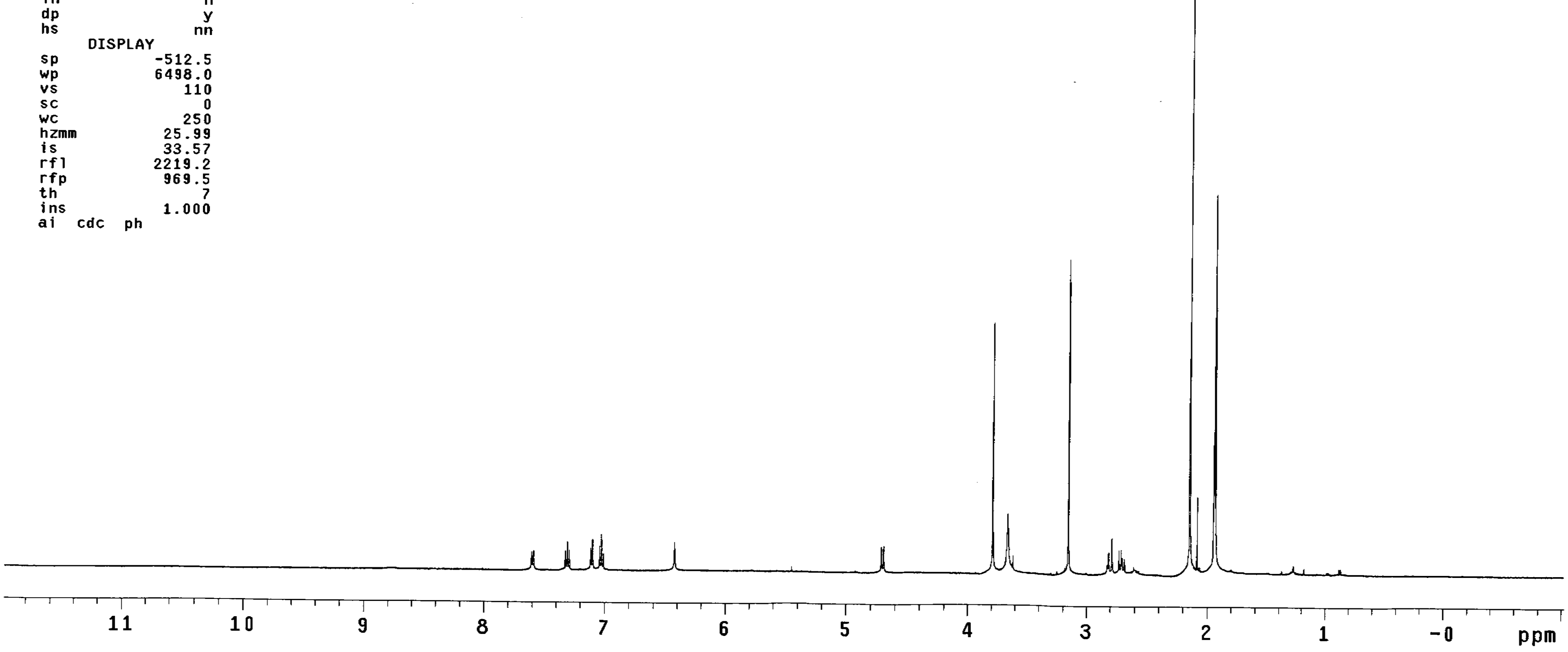


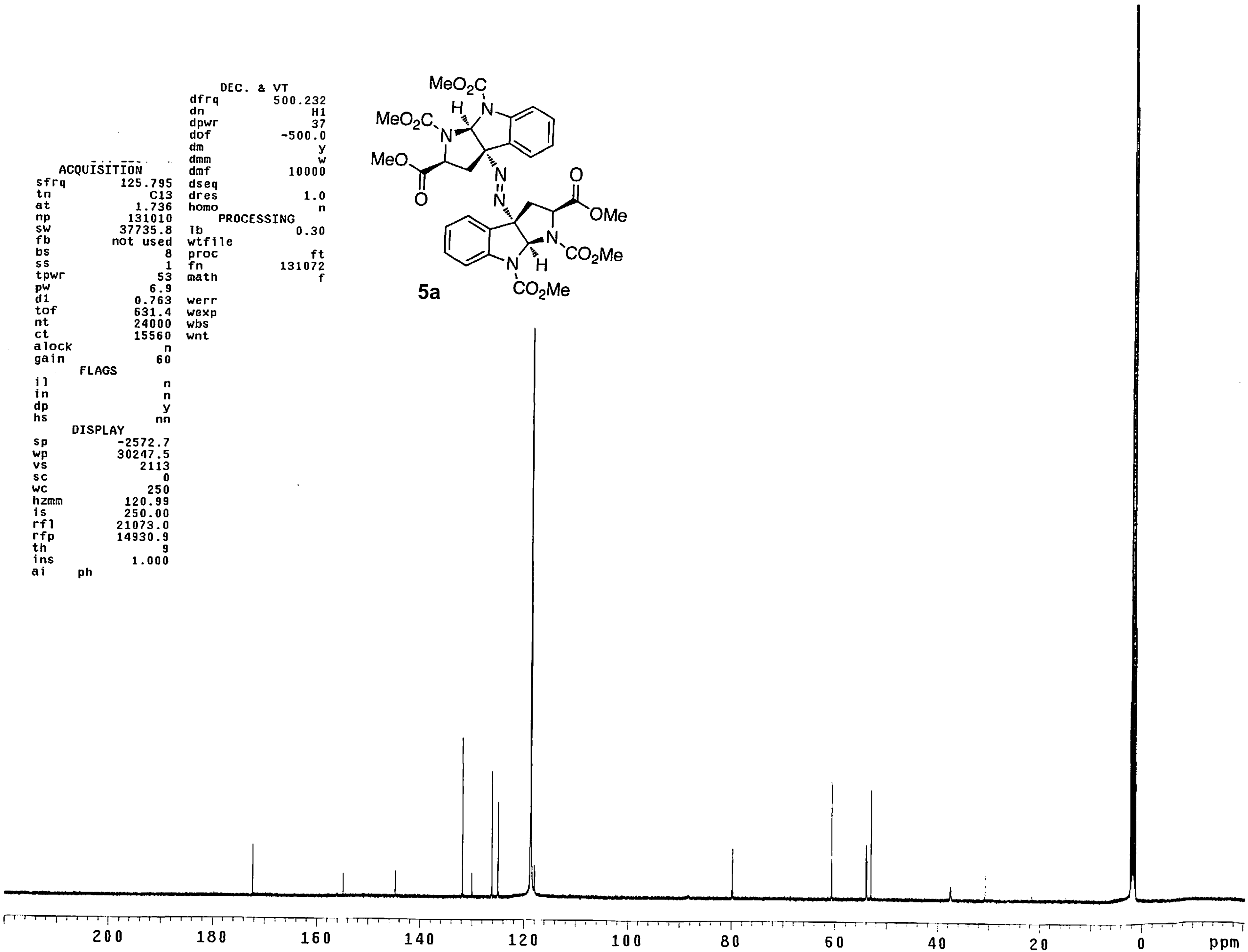
6a

```
      ACQUISITION              DEC. & VT
sfrq        125.795      dfrq        500.232
tn              C13      dn               H1
at            1.736      dpwr             37
np           131010      dof          -500.0
sw          37735.8      dm                y
fb         not used      dmm               w
bs               16      dmf           10000
ss                1      dseq
tpwr             53      dres            1.0
pw              6.9      homo              n
d1            0.763      temp           60.0
tof           631.4          PROCESSING
nt            24000      lb             0.30
ct            20336      wtfile
alock             n      proc             ft
gain             60      fn           131072
         FLAGS           math              f
il                n
in                n      werr
dp                y      wexp
hs               nn      wbs
        DISPLAY          wnt
sp          -2554.2
wp         31507.4
vs             2770
sc                0
wc              250
hzmm         126.03
is           500.00
rfl         21027.5
rfp         14930.9
th               20
ins           1.000
ai     ph
```

```
                                     DEC. & VT
                           dfrq          125.673
                           dn                C13
                           dpwr               30
                           dof                 0
                           dm                nnn
                           dmm                 w
      ACQUISITION          dmf             10000
sfrq          499.748      dseq
tn                 H1      dres              1.0
at              3.001      homo                n
np              63050         PROCESSING
sw            10504.2      wtfile
fb           not used      proc               ft
bs                  4      fn             262144
tpwr               60      math                f
pw                8.6
d1              2.000      werr
tof            1519.5      wexp
nt                128      wbs
ct                 16      wnt               wft
alock               n
gain         not used
        FLAGS
il                  n
in                  n
dp                  y
hs                 nn
       DISPLAY
sp             -512.5
wp             6498.0
vs                110
sc                  0
wc                250
hzmm            25.99
is              33.57
rfl            2219.2
rfp             969.5
th                  7
ins             1.000
ai   cdc   ph
```


5a

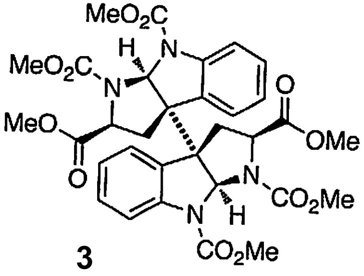




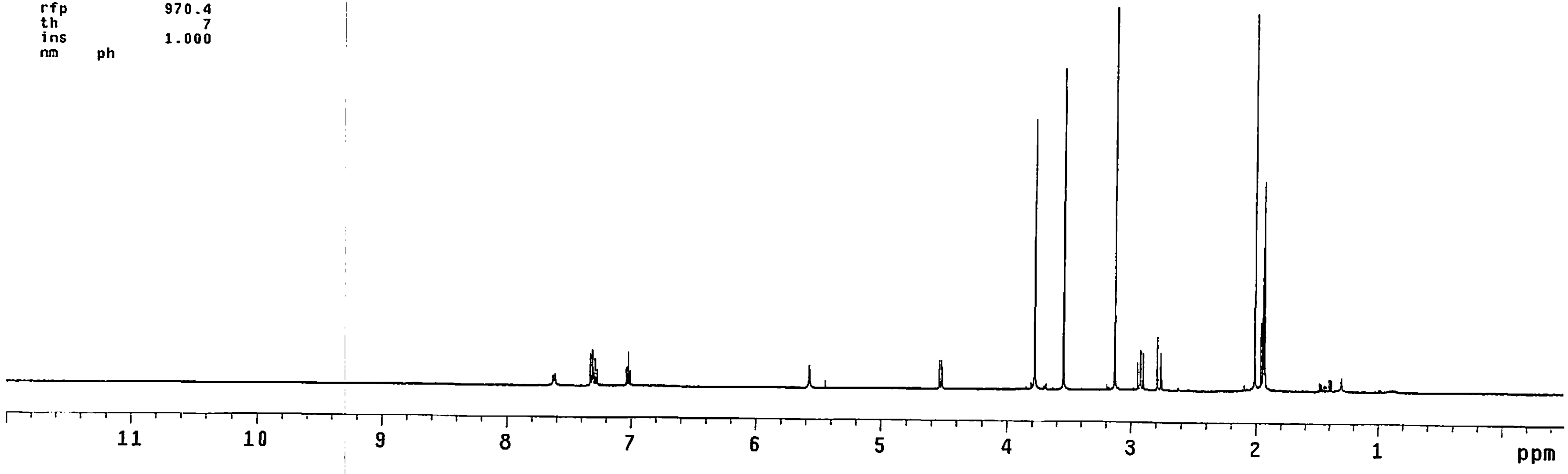
5a

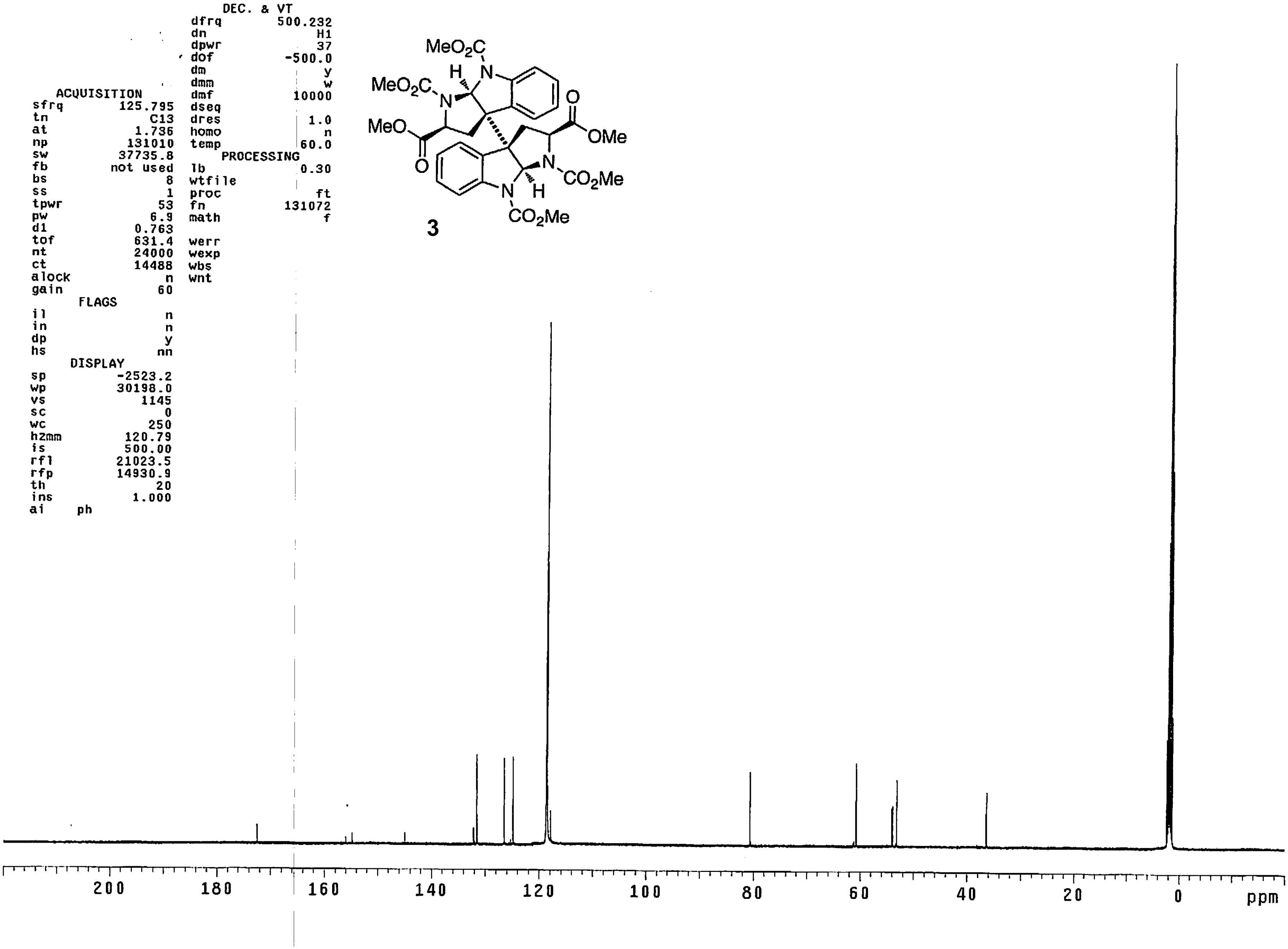
```
     ACQUISITION              DEC. & VT
sfrq       125.795    dfrq       500.232
tn             C13    dn              H1
at           1.736    dpwr            37
np          131010    dof         -500.0
sw         37735.8    dm               y
fb        not used    dmm              w
bs               8    dmf          10000
ss               1    dseq
tpwr            53    dres           1.0
pw             6.9    homo             n
d1           0.763         PROCESSING
tof          631.4    lb            0.30
nt           24000    wtfile
ct           15560    proc            ft
alock            n    fn          131072
gain            60    math             f
       FLAGS
il               n    werr
in               n    wexp
dp               y    wbs
hs              nn    wnt
      DISPLAY
sp         -2572.7
wp         30247.5
vs            2113
sc               0
wc             250
hzmm        120.99
is          250.00
rfl        21073.0
rfp        14930.9
th               9
ins          1.000
ai    ph
```

```
                                    DEC. & VT
                          dfrq          125.795
                          dn                C13
                          dpwr               38
                          dof                 0
                          dm                nnn
                          dmm                 c
     ACQUISITION          dmf             10000
sfrq          500.234     dseq
tn                 H1     dres              1.0
at              3.200     homo                n
np              64000     temp             60.0
sw            10000.0           PROCESSING
fb           not used     wtfile
bs                  4     proc               ft
ss                  1     fn             131072
tpwr               58     math                f
pw                9.0
d1                  0     werr
tof            1498.2     wexp
nt                128     wbs
ct                 24     wnt
alock               n
gain         not used
      FLAGS
il                  n
in                  n
dp                  y
hs                 nn
      DISPLAY
sp             -250.1
wp             6252.7
vs                 61
sc                  0
wc                250
hzmm            25.01
is             100.00
rfl            1978.9
rfp             970.4
th                  7
ins             1.000
nm      ph
```



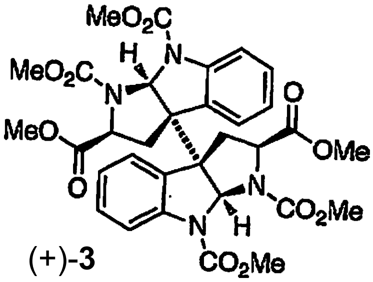
3



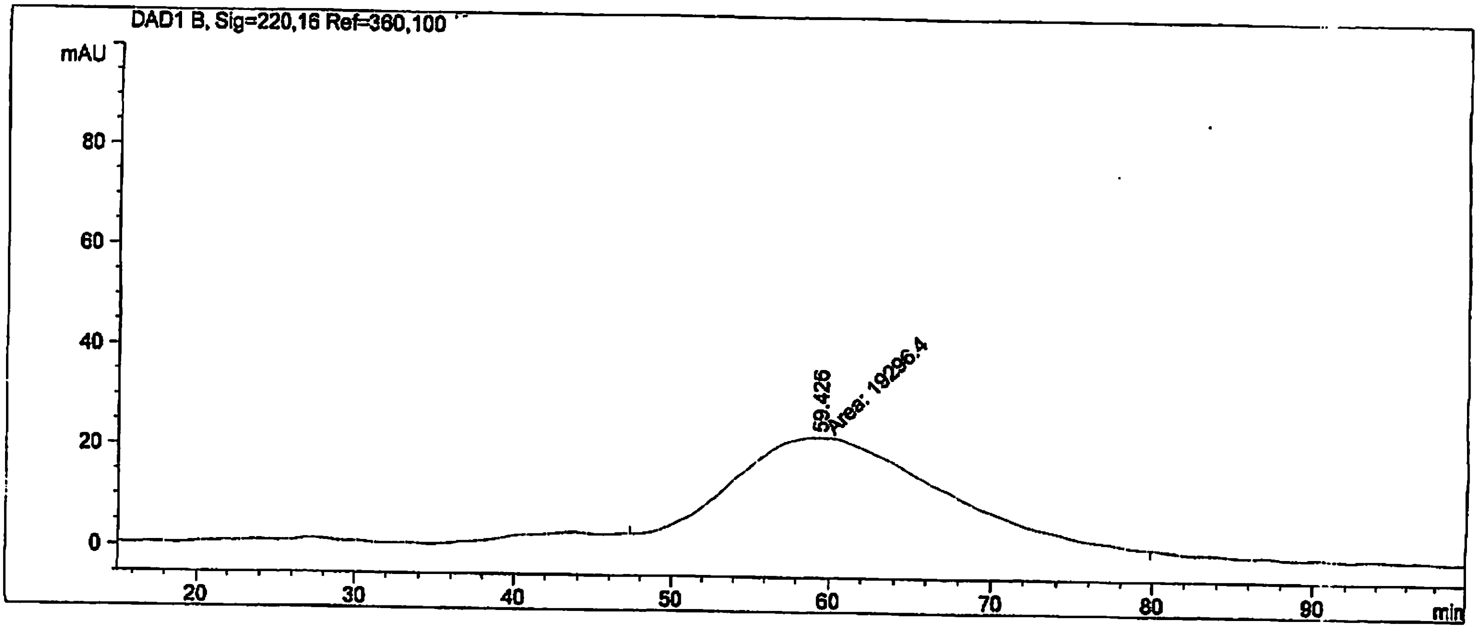


3

```
                                       DEC. & VT
                                 dfrq        500.232
                                 dn               H1
                                 dpwr             37
      ACQUISITION                dof          -500.0
sfrq         125.795             dm                y
tn               C13             dmm               w
at             1.736             dmf           10000
np            131010             dseq
sw           37735.8             dres            1.0
fb          not used             homo              n
bs                 8             temp           60.0
ss                 1                  PROCESSING
tpwr              53             lb             0.30
pw               6.9             wtfile
d1             0.763             proc             ft
tof            631.4             fn           131072
nt             24000             math              f
ct             14488
alock              n             werr
gain              60             wexp
        FLAGS                    wbs
il                 n             wnt
in                 n
dp                 y
hs                nn
       DISPLAY
sp           -2523.2
wp           30198.0
vs              1145
sc                 0
wc               250
hzmm          120.79
is            500.00
rfl          21023.5
rfp          14930.9
th                20
ins            1.000
ai     ph
```



(+)-3



```
=====================================================================
                       Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

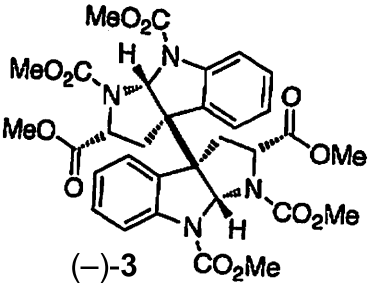
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  59.426 MM    15.1926 1.92964e4   21.16857 100.0000

Totals :                   1.92964e4   21.16857

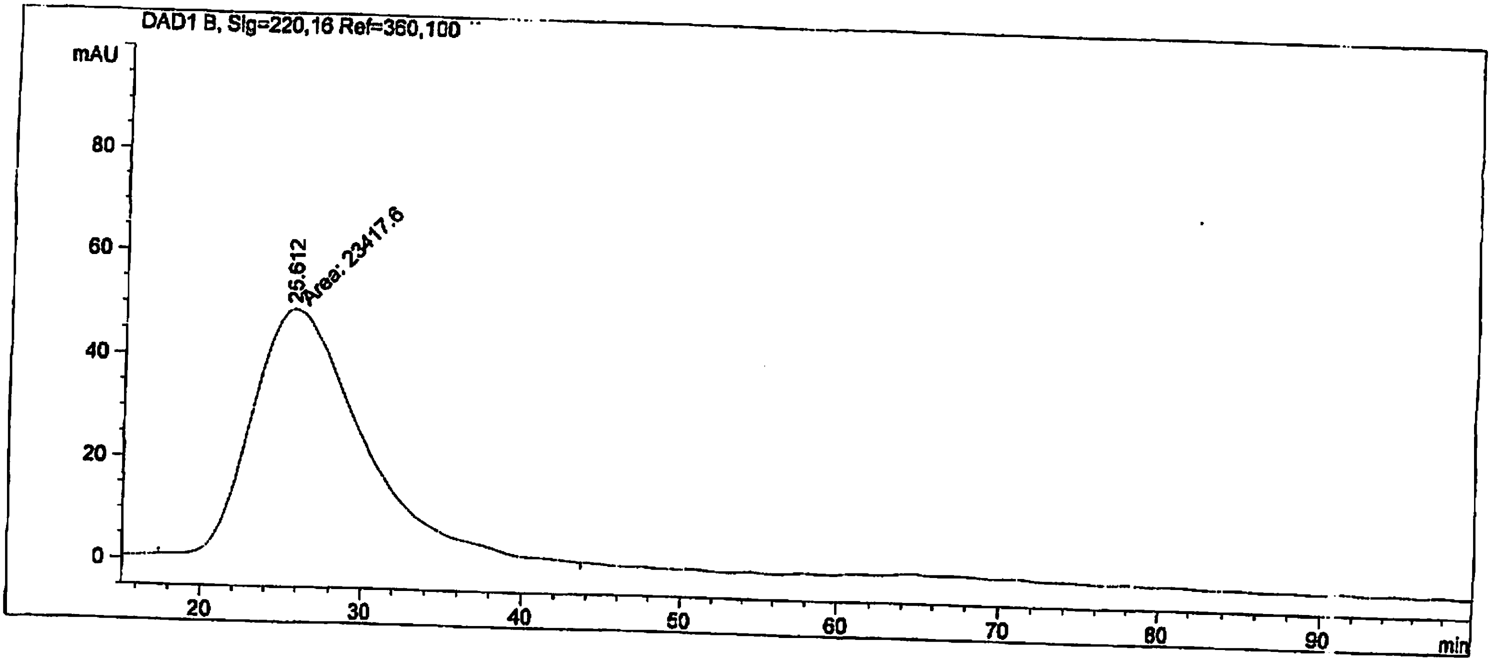
 Results obtained with enhanced integrator!
=====================================================================
                       Summed Peaks Report
=====================================================================

Signal 1: DAD1 B, Sig=220,16 Ref=360,100
=====================================================================
                    Final Summed Peaks Report
=====================================================================

Signal 1: DAD1 B, Sig=220,16 Ref=360,100
```



(−)-3



```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

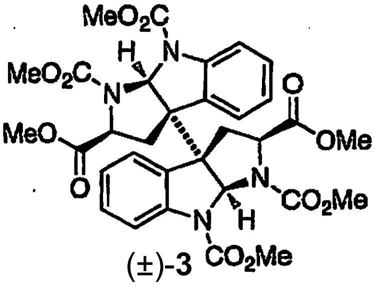
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  25.612 MM    8.0918 2.34176e4   48.23330 100.0000

Totals :                  2.34176e4   48.23330

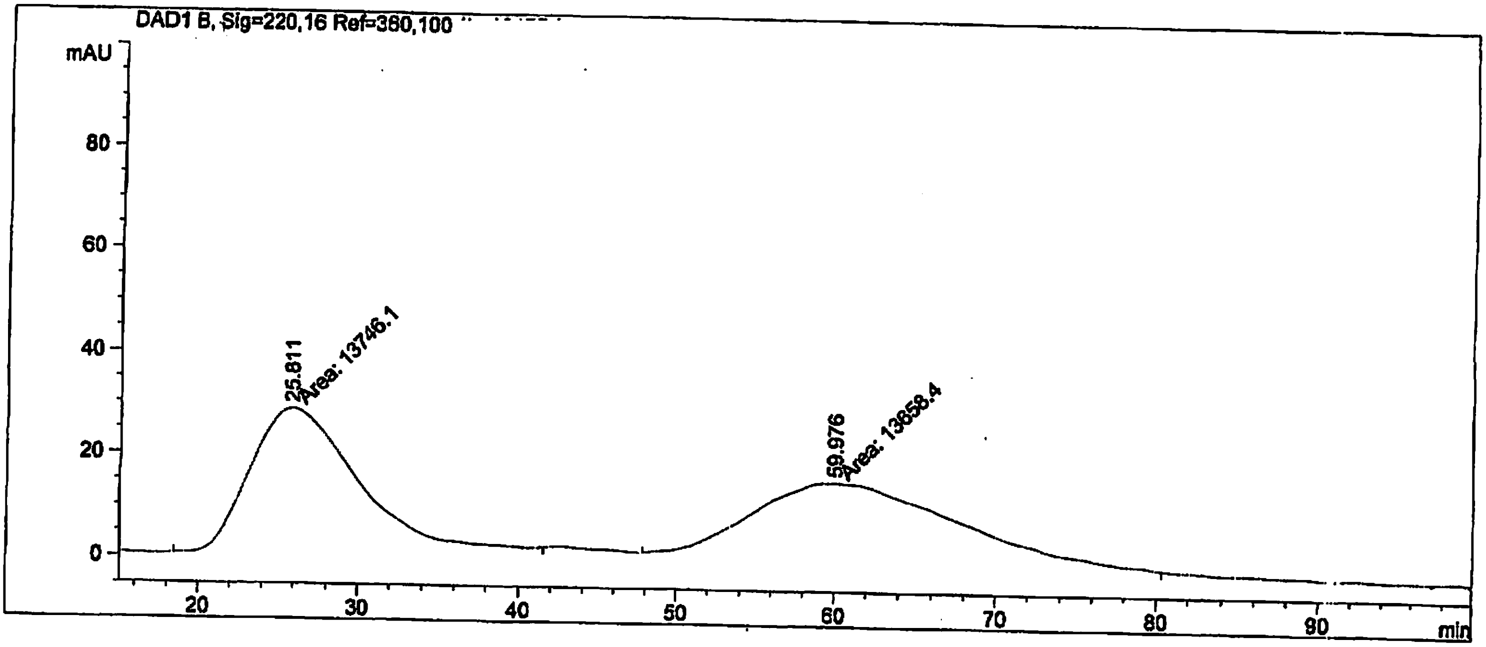
Results obtained with enhanced integrator!
=====================================================================
                         Summed Peaks Report
=====================================================================

Signal 1: DAD1 B, Sig=220,16 Ref=360,100
=====================================================================
                      Final Summed Peaks Report
=====================================================================

Signal 1: DAD1 B, Sig=220,16 Ref=360,100
```



(±)-3



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By                 :      Signal
Multiplier                :      1.0000
Dilution                  :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

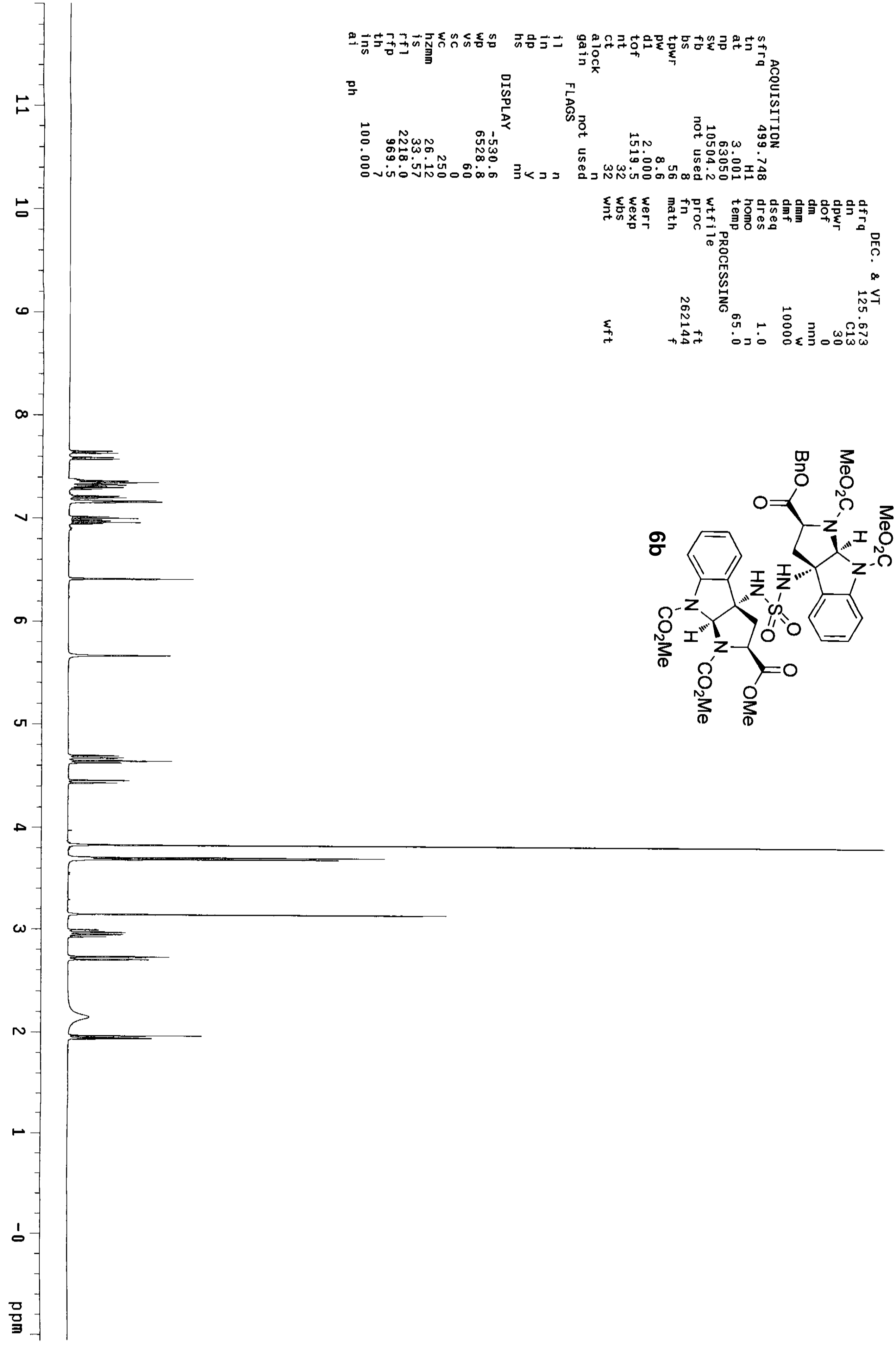
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  25.811 MM    8.0687 1.37461e4   28.39389  50.1600
   2  59.976 MM   15.0646 1.36584e4   15.11094  49.8400

Totals :                  2.74046e4   43.50483

 Results obtained with enhanced integrator!
=====================================================================
                        Summed Peaks Report
=====================================================================

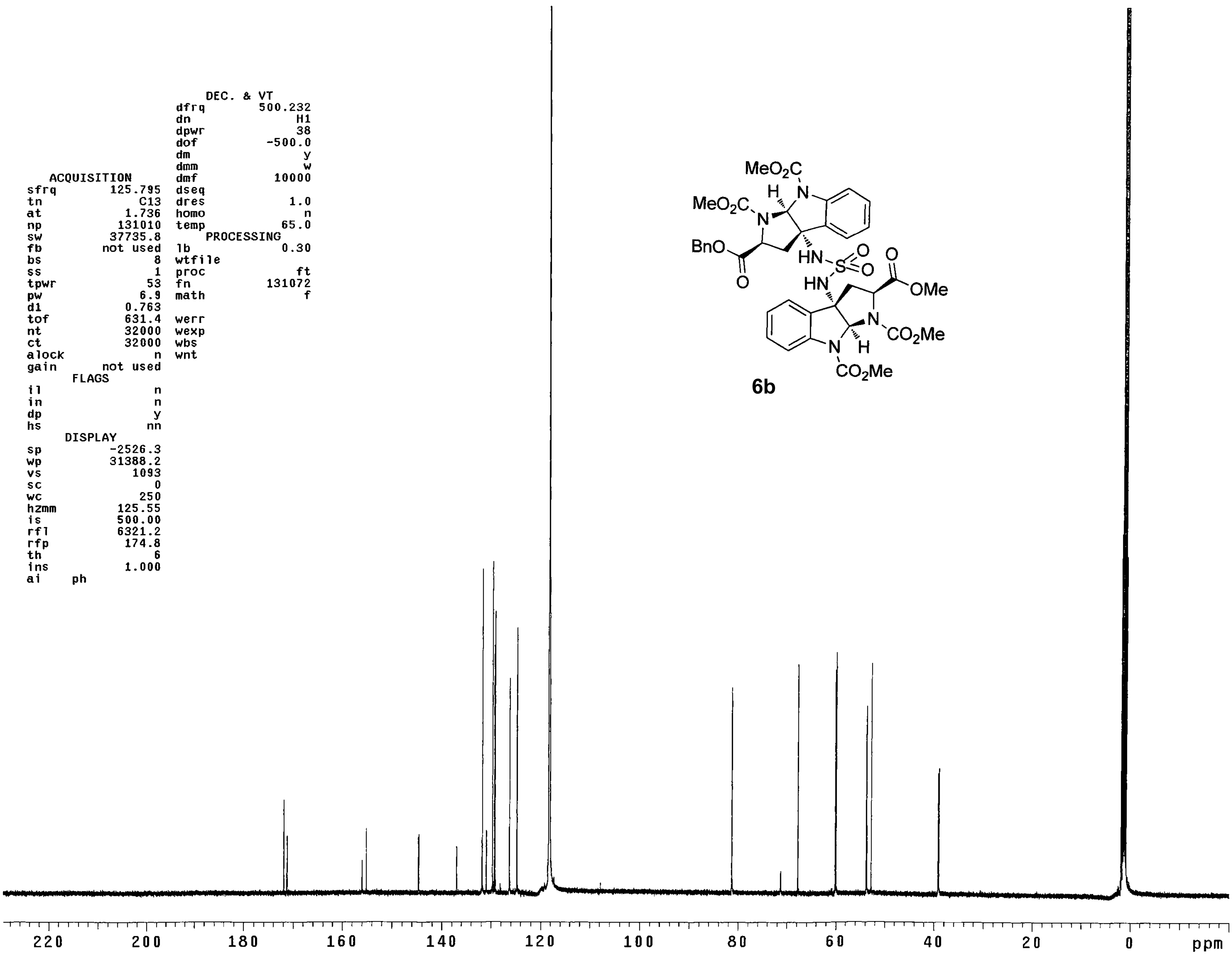
Signal 1: DAD1 B, Sig=220,16 Ref=360,100
=====================================================================
                     Final Summed Peaks Report
=====================================================================

Signal 1: DAD1 B, Sig=220,16 Ref=360,100
```

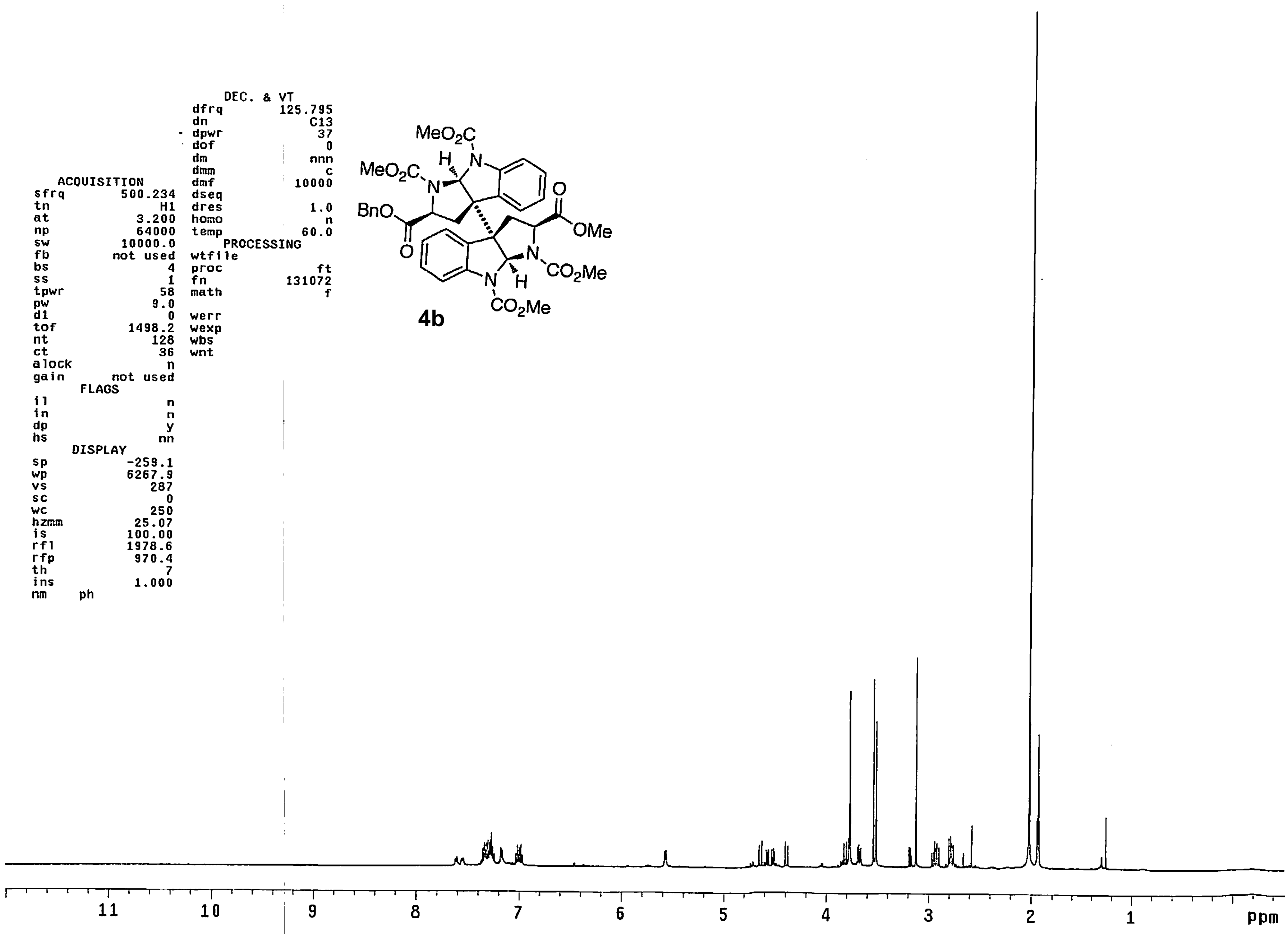

ACQUISITION
sfrq 499.748
tn H1
at 3.001
np 63050
sw 10504.2
fb not used
bs 8
tpwr 56
pw 8.6
d1 2.000
tof 1519.5
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -530.6
wp 6528.8
vs 60
sc 0
wc 250
hzmm 26.12
is 33.57
rfl 2218.0
rfp 969.5
th 7
ins 100.000
ai ph
DEC. & VT
dfrq 125.673
dn C13
dpwr 30
dof 0
dm nnn
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 65.0
PROCESSING
wtfile
proc ft
fn 262144
math f
werr
wexp
wbs
wnt wft
MeO2C
MeO2C
BnO
O
N
H
N
HN
S
O
O
HN
N
H
N
CO2Me
O
OMe
CO2Me
11
10
9
8
7
6
5
4
3
2
1
-0
ppm

6b

```
                              DEC. & VT
                         dfrq        500.232
                         dn               H1
                         dpwr             38
                         dof          -500.0
                         dm                y
                         dmm               w
     ACQUISITION         dmf           10000
sfrq         125.795     dseq
tn               C13     dres            1.0
at             1.736     homo              n
np            131010     temp           65.0
sw           37735.8        PROCESSING
fb          not used     lb             0.30
bs                 8     wtfile
ss                 1     proc             ft
tpwr              53     fn           131072
pw               6.9     math              f
d1             0.763
tof            631.4     werr
nt             32000     wexp
ct             32000     wbs
alock              n     wnt
gain        not used
      FLAGS
il                 n
in                 n
dp                 y
hs                nn
      DISPLAY
sp           -2526.3
wp           31388.2
vs              1093
sc                 0
wc               250
hzmm          125.55
is            500.00
rfl           6321.2
rfp            174.8
th                 6
ins            1.000
ai     ph
```

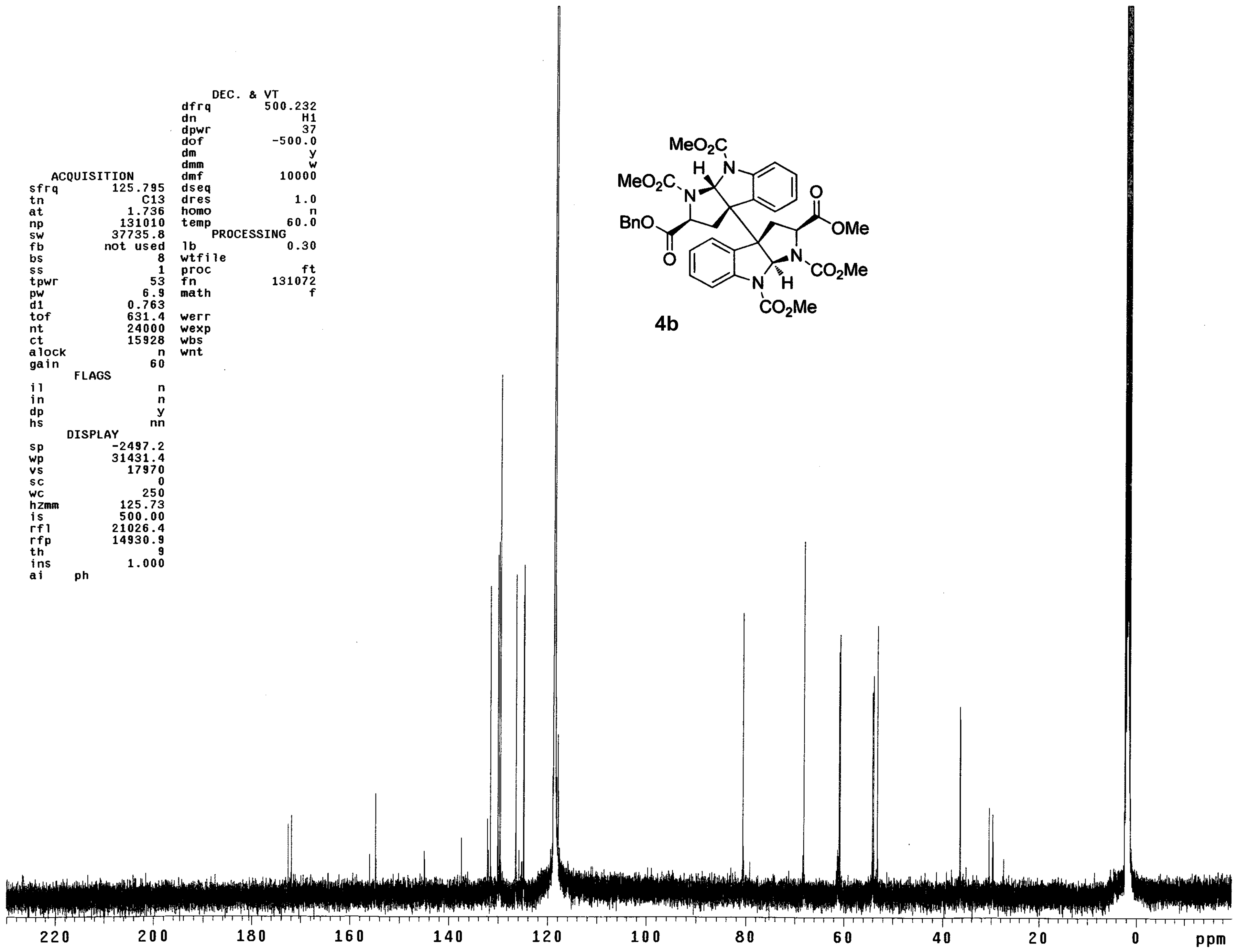


6b



4b

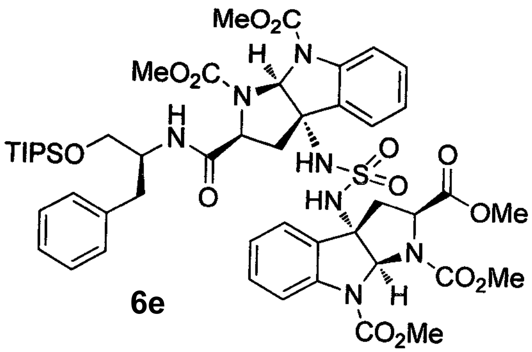
```
        ACQUISITION            DEC. & VT
sfrq        500.234     dfrq        125.795
tn               H1     dn              C13
at            3.200     dpwr             37
np            64000     dof               0
sw          10000.0     dm              nnn
fb         not used     dmm               c
bs                4     dmf           10000
ss                1     dseq
tpwr             58     dres            1.0
pw              9.0     homo              n
d1                0     temp           60.0
tof          1498.2        PROCESSING
nt              128     wtfile
ct               36     proc             ft
alock             n     fn           131072
gain       not used     math              f
        FLAGS
il                n     werr
in                n     wexp
dp                y     wbs
hs               nn     wnt
        DISPLAY
sp           -259.1
wp           6267.9
vs              287
sc                0
wc              250
hzmm          25.07
is           100.00
rfl          1978.6
rfp           970.4
th                7
ins           1.000
nm     ph
```



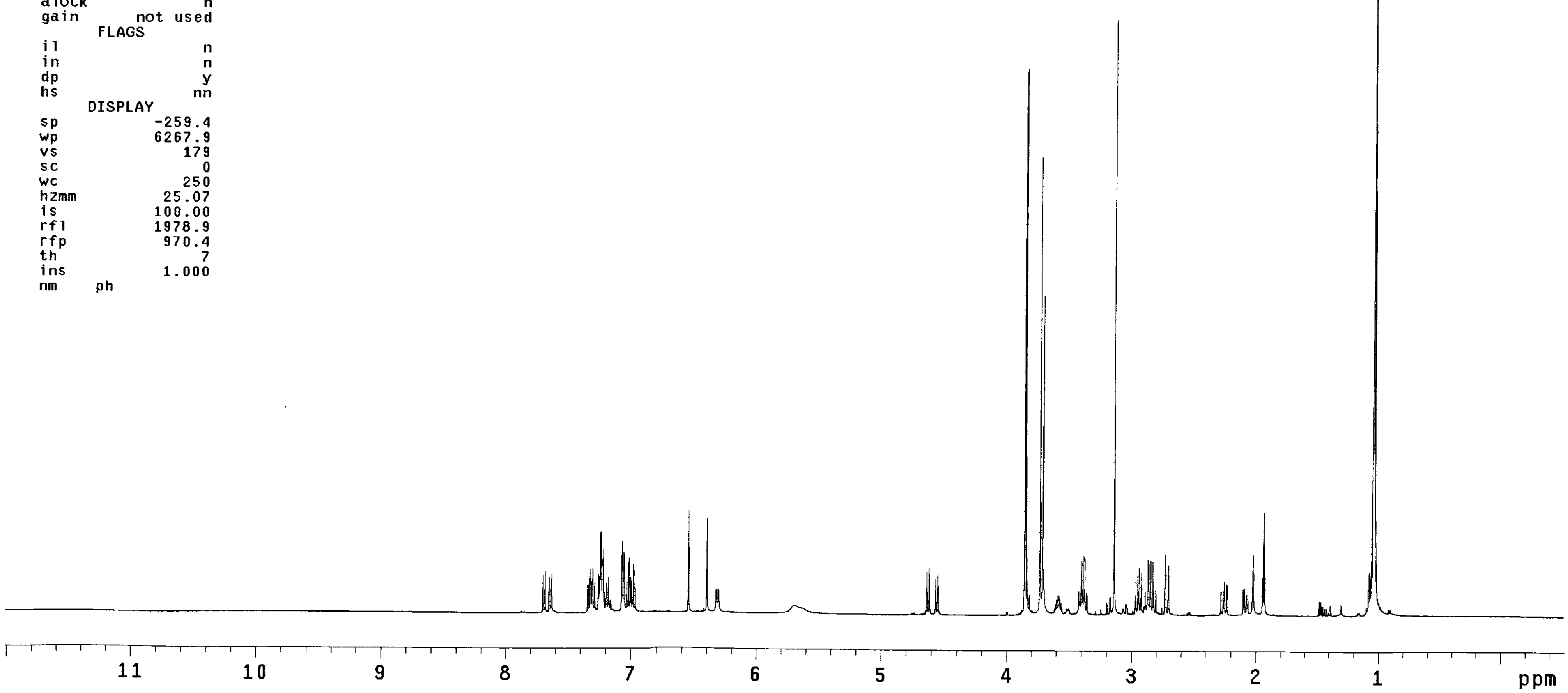
4b

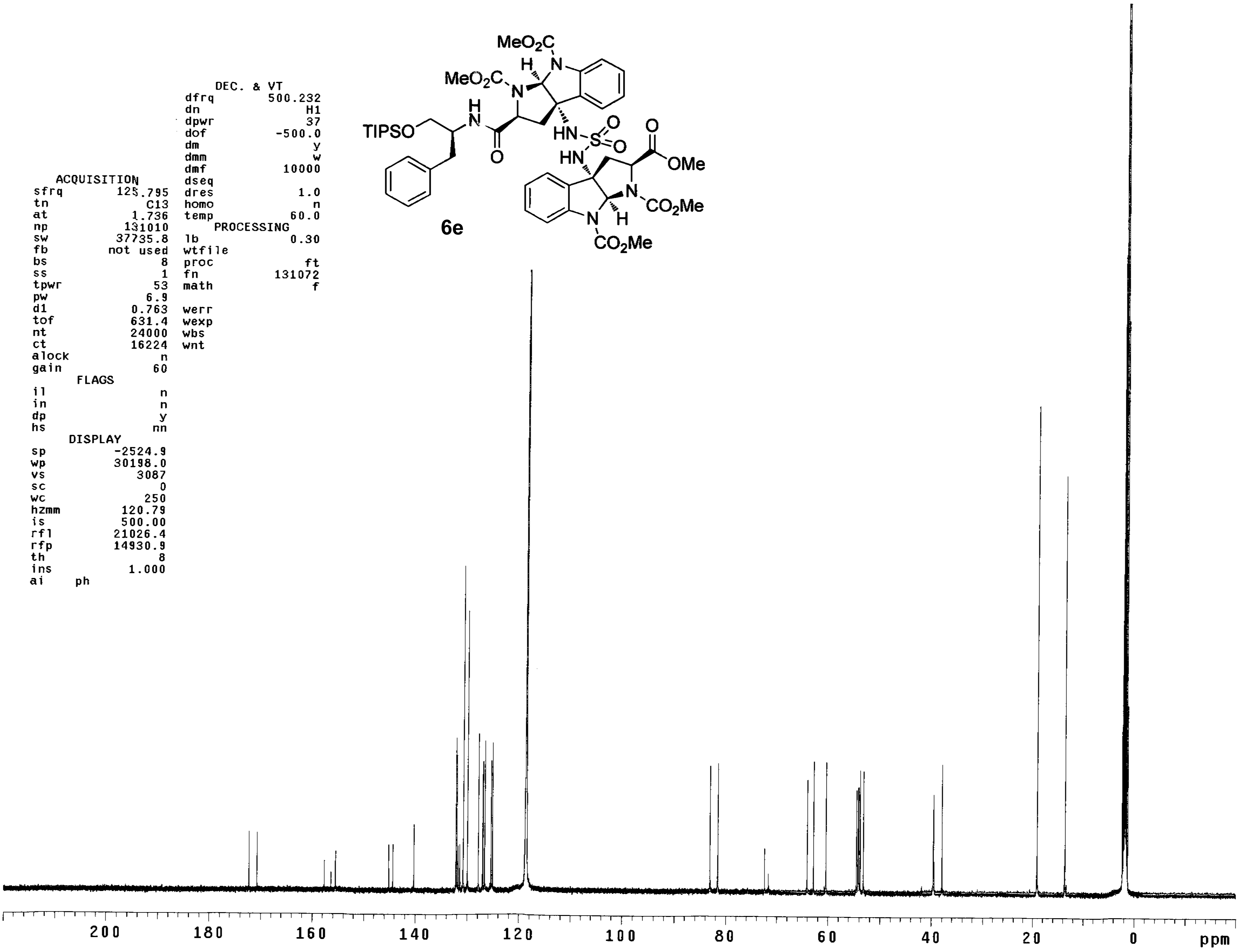
```
          ACQUISITION                DEC. & VT
sfrq          125.795      dfrq          500.232
tn                C13      dn                 H1
at              1.736      dpwr               37
np             131010      dof            -500.0
sw            37735.8      dm                  y
fb           not used      dmm                 w
bs                  8      dmf             10000
ss                  1      dseq
tpwr               53      dres              1.0
pw                6.9      homo                n
d1              0.763      temp             60.0
tof             631.4            PROCESSING
nt              24000      lb               0.30
ct              15928      wtfile
alock               n      proc               ft
gain               60      fn             131072
            FLAGS          math                f
il                  n
in                  n      werr
dp                  y      wexp
hs                 nn      wbs
           DISPLAY         wnt
sp            -2497.2
wp            31431.4
vs              17970
sc                  0
wc                250
hzmm           125.73
is             500.00
rfl           21026.4
rfp           14930.9
th                  9
ins             1.000
ai     ph
```

```
                              DEC. & VT
                        dfrq        125.795
                        dn              C13
                        dpwr             37
                        dof               0
                        dm              nnn
                        dmm               c
     ACQUISITION        dmf           10000
sfrq         500.234    dseq
tn                H1    dres            1.0
at             3.200    homo              n
np             64000    temp           60.0
sw           10000.0        PROCESSING
fb          not used    wtfile
bs                 4    proc             ft
ss                 1    fn           131072
tpwr              58    math              f
pw               9.0
d1                 0    werr
tof           1498.2    wexp
nt               128    wbs
ct                36    wnt
alock              n
gain        not used
        FLAGS
il                 n
in                 n
dp                 y
hs                nn
       DISPLAY
sp            -259.4
wp            6267.9
vs               179
sc                 0
wc               250
hzmm           25.07
is            100.00
rfl           1978.9
rfp            970.4
th                 7
ins            1.000
nm    ph
```



6e

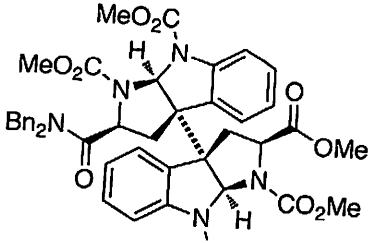




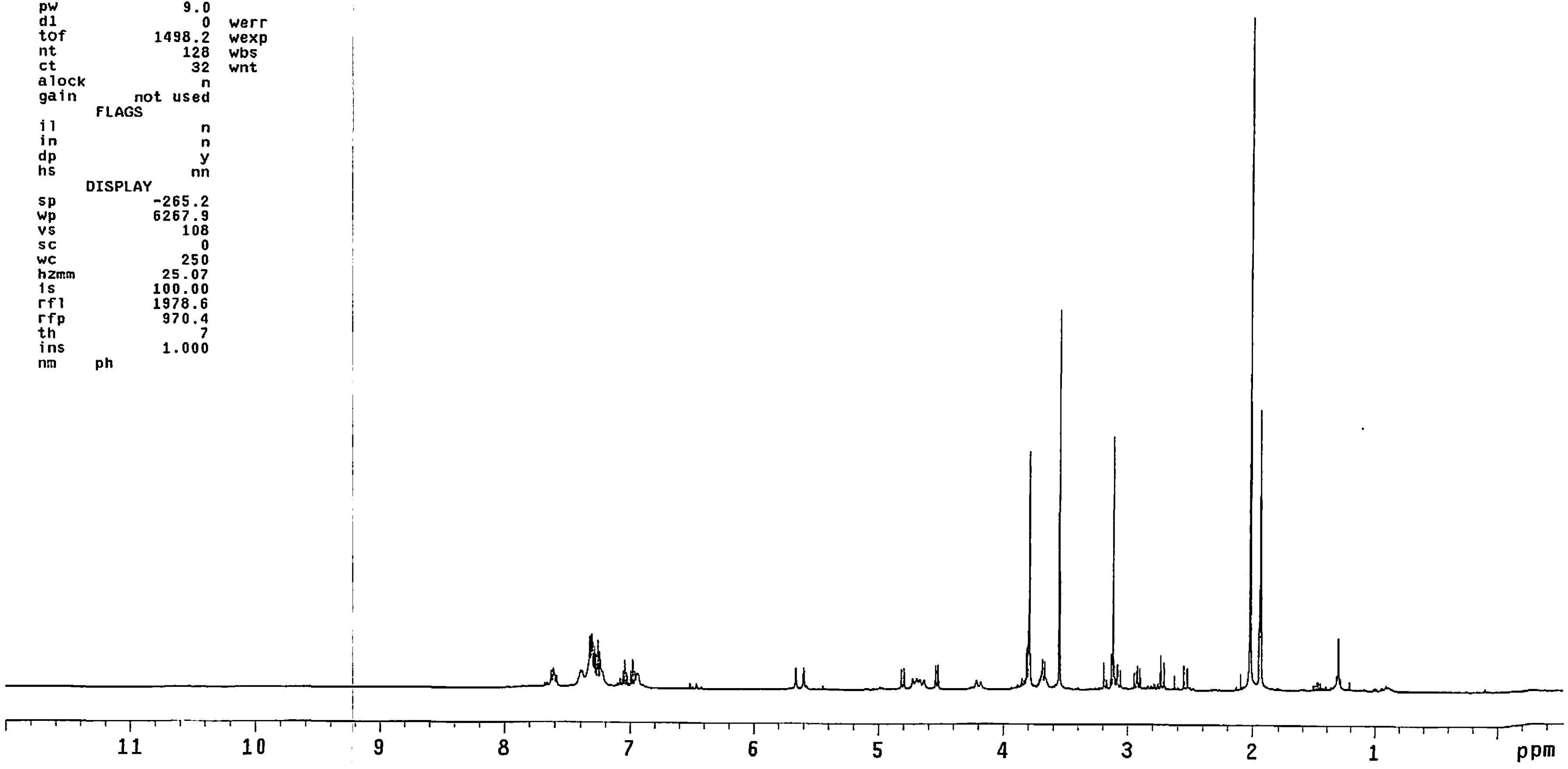
6e

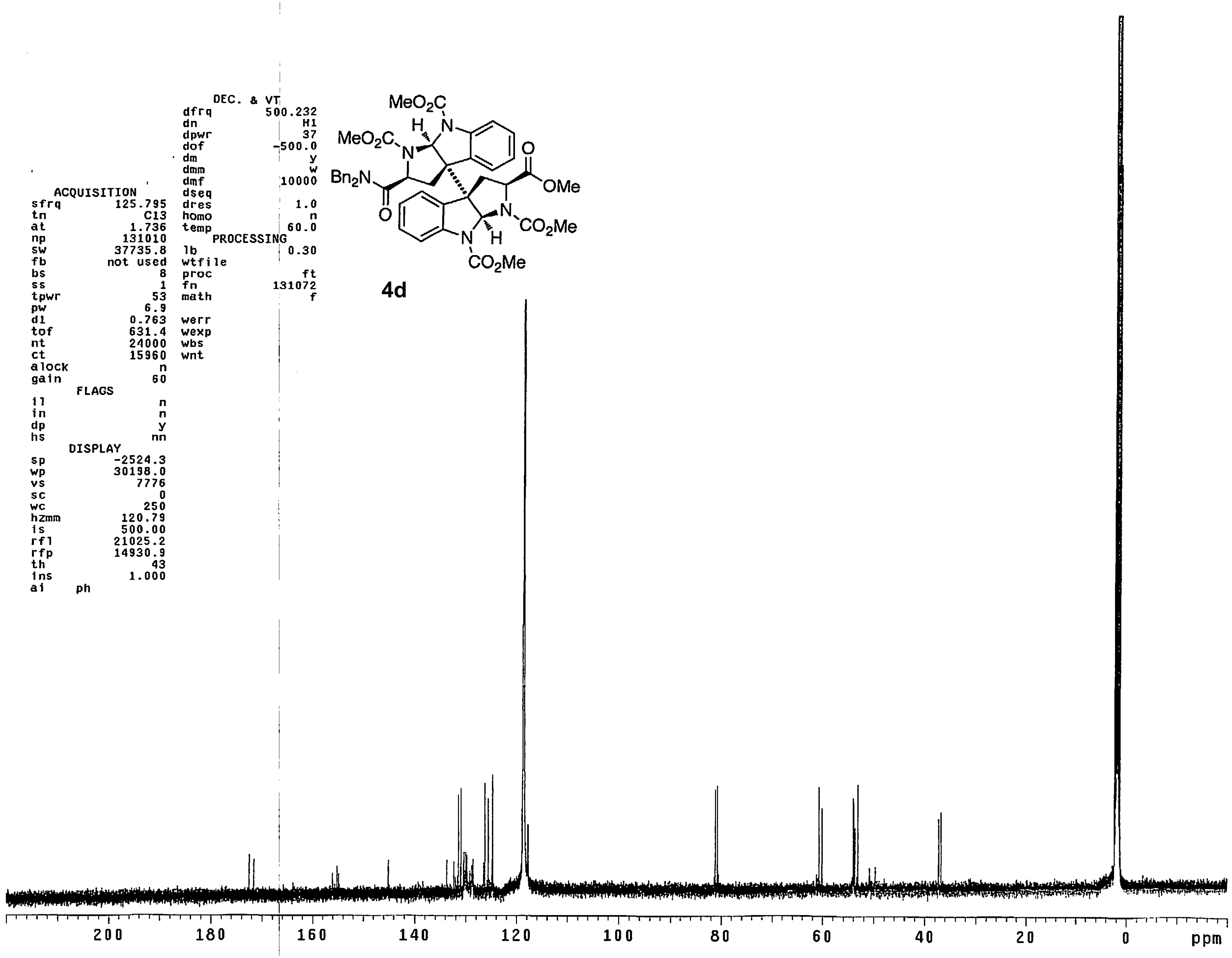
```
                              DEC. & VT
                              dfrq        500.232
                              dn               H1
                              dpwr             37
                              dof          -500.0
                              dm                y
                              dmm               w
                              dmf           10000
   ACQUISITION                dseq
sfrq          125.795         dres            1.0
tn                C13         homo              n
at              1.736         temp           60.0
np             131010            PROCESSING
sw            37735.8         lb             0.30
fb           not used         wtfile
bs                  8         proc             ft
ss                  1         fn           131072
tpwr               53         math              f
pw                6.9
d1              0.763         werr
tof             631.4         wexp
nt              24000         wbs
ct              16224         wnt
alock               n
gain               60
      FLAGS
il                  n
in                  n
dp                  y
hs                 nn
     DISPLAY
sp            -2524.9
wp            30198.0
vs               3087
sc                  0
wc                250
hzmm           120.79
is             500.00
rfl           21026.4
rfp           14930.9
th                  8
ins             1.000
ai     ph
```

```
                                DEC. & VT
                           dfrq         125.795
                           dn               C13
                           dpwr              37
                           dof                0
                           dm               nnn
                           dmm                c
      ACQUISITION          dmf            10000
sfrq           500.234     dseq
tn                  H1     dres             1.0
at               3.200     homo               n
np               64000     temp            60.0
sw             10000.0          PROCESSING
fb            not used     wtfile
bs                   4     proc              ft
ss                   1     fn            131072
tpwr                58     math               f
pw                 9.0
d1                   0     werr
tof             1498.2     wexp
nt                 128     wbs
ct                  32     wnt
alock                n
gain          not used
       FLAGS
il                   n
in                   n
dp                   y
hs                  nn
      DISPLAY
sp              -265.2
wp              6267.9
vs                 108
sc                   0
wc                 250
hzmm             25.07
is              100.00
rfl             1978.6
rfp              970.4
th                   7
ins              1.000
nm     ph
```



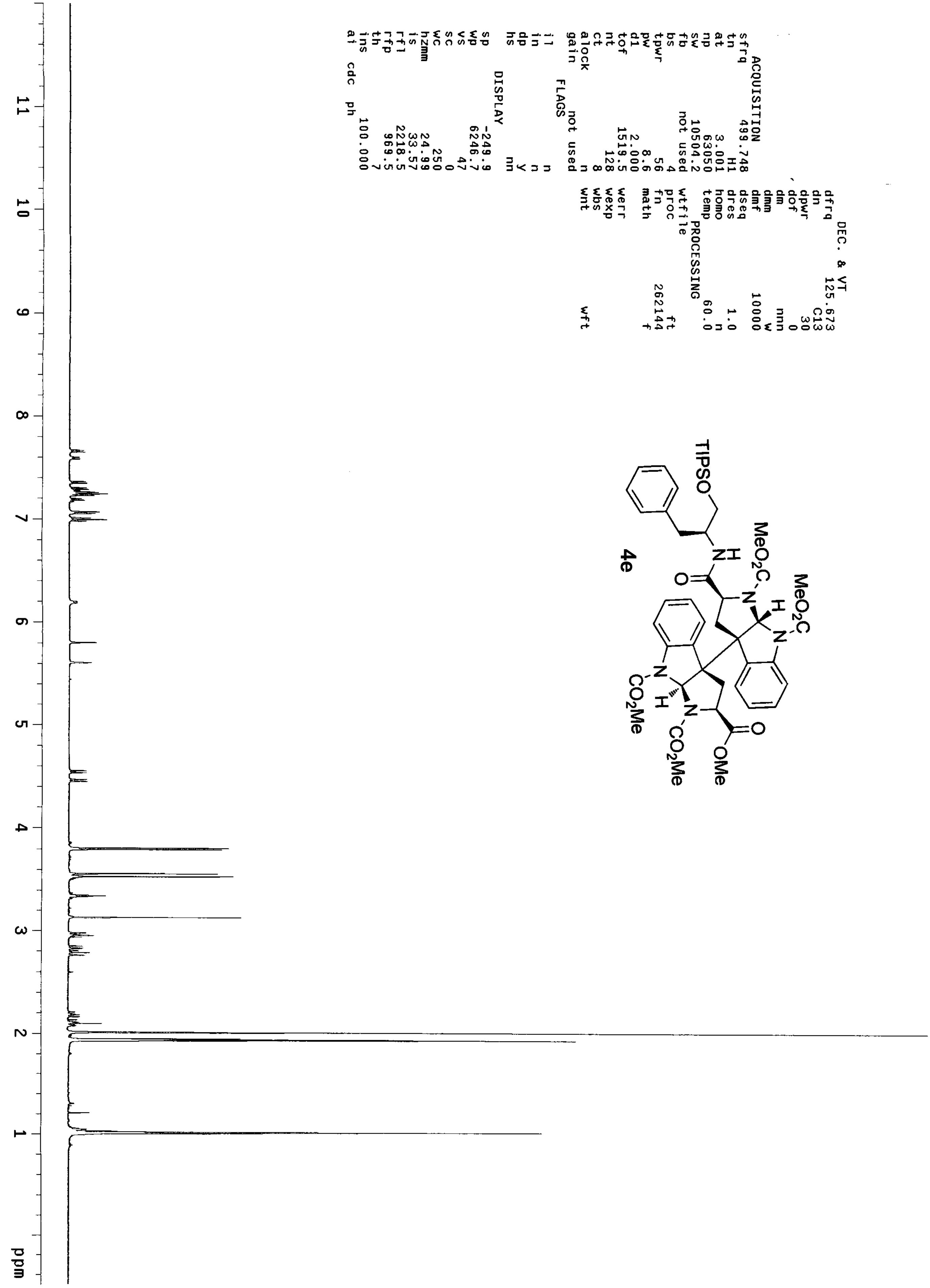
4d

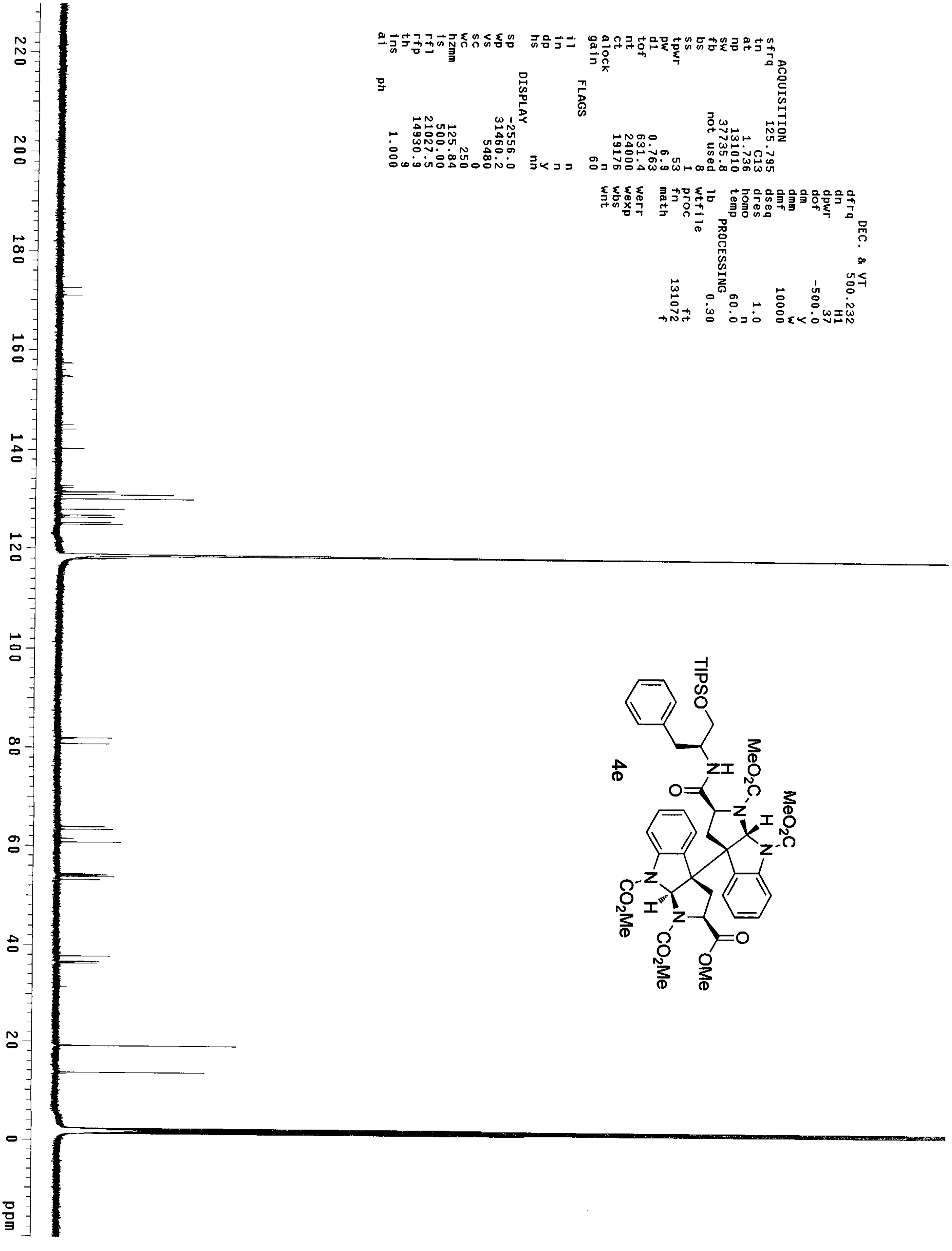




```
                         DEC. & VT
                     dfrq       500.232
                     dn              H1
                     dpwr            37
                     dof         -500.0
                     dm               y
                     dmm              w
      ACQUISITION    dmf          10000
sfrq       125.795   dseq
tn             C13   dres           1.0
at           1.736   homo             n
np          131010   temp          60.0
sw         37735.8       PROCESSING
fb        not used   lb            0.30
bs               8   wtfile
ss               1   proc            ft
tpwr            53   fn          131072
pw             6.9   math             f
d1           0.763
tof          631.4   werr
nt           24000   wexp
ct           15960   wbs
alock            n   wnt
gain            60
       FLAGS
il               n
in               n
dp               y
hs              nn
      DISPLAY
sp         -2524.3
wp         30198.0
vs            7776
sc               0
wc             250
hzmm        120.79
is          500.00
rfl        21025.2
rfp        14930.9
th              43
ins          1.000
ai    ph
```

4d


ACQUISITION
sfrq 499.748
tn H1
at 3.001
np 63050
sw 10504.2
fb not used
bs 4
tpwr 56
pw 8.6
d1 2.000
tof 1519.5
nt 128
ct 8
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -249.9
wp 6246.7
vs 47
sc 0
wc 250
hzmm 24.99
is 33.57
rfl 2218.5
rfp 969.5
th 7
ins 100.000
ai cdc ph
DEC. & VT
dfrq 125.673
dn C13
dpwr 30
dof 0
dm nnn
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 60.0
PROCESSING
wtfile
proc ft
fn 262144
math f
werr
wexp
wbs
wnt wft
TIPSO
MeO2C
MeO2C
H
N
N
O
H
N
N
H
N
CO2Me
CO2Me
O
OMe
4e
11
10
9
8
7
6
5
4
3
2
1
ppm



ACQUISITION
sfrq 125.795
tn C13
at 1.736
np 131010
sw 37735.8
fb not used
bs 8
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 631.4
nt 24000
ct 19176
alock n
gain 60

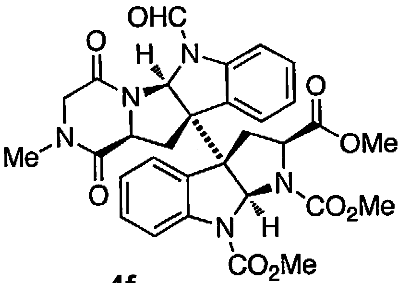
FLAGS
il n
in n
dp y
hs nn

DISPLAY
sp -2556.0
wp 31460.2
vs 5480
sc 0
wc 250
hzmm 125.84
is 500.00
rfl 21027.5
rfp 14930.9
th 9
ins 1.000
ai ph

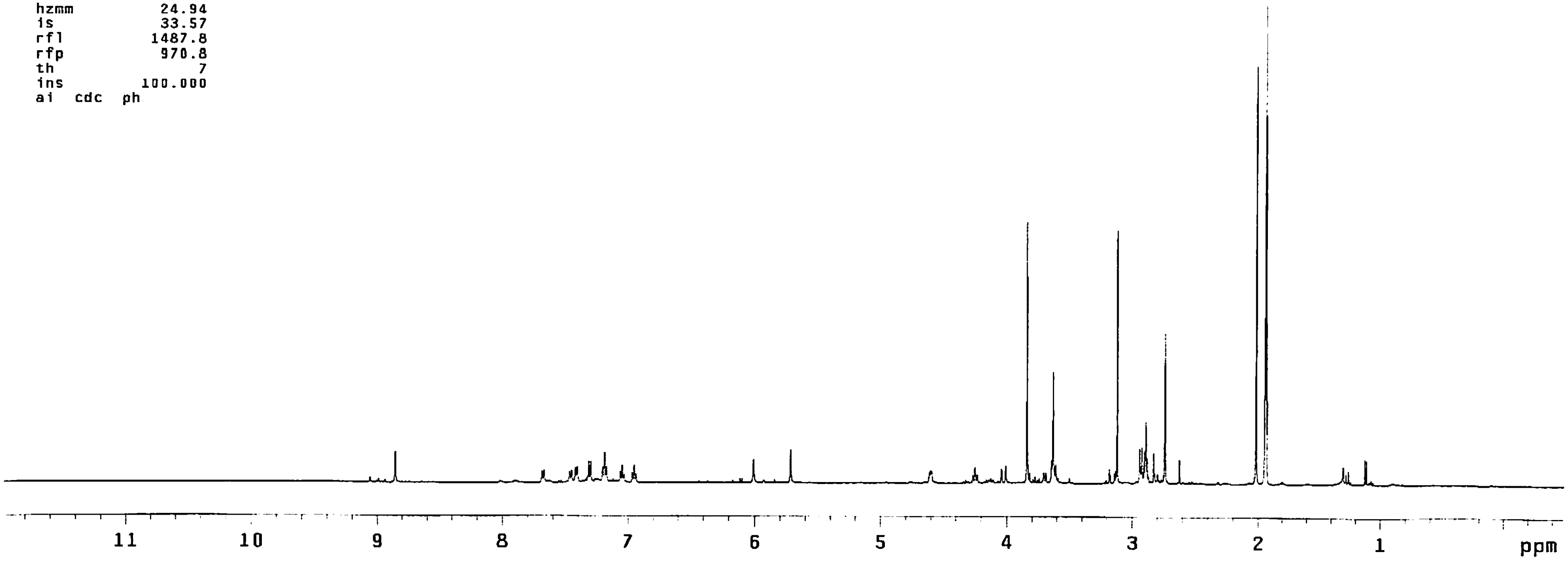
DEC. & VT
dfrq 500.232
dn H1
dpwr 37
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 60.0

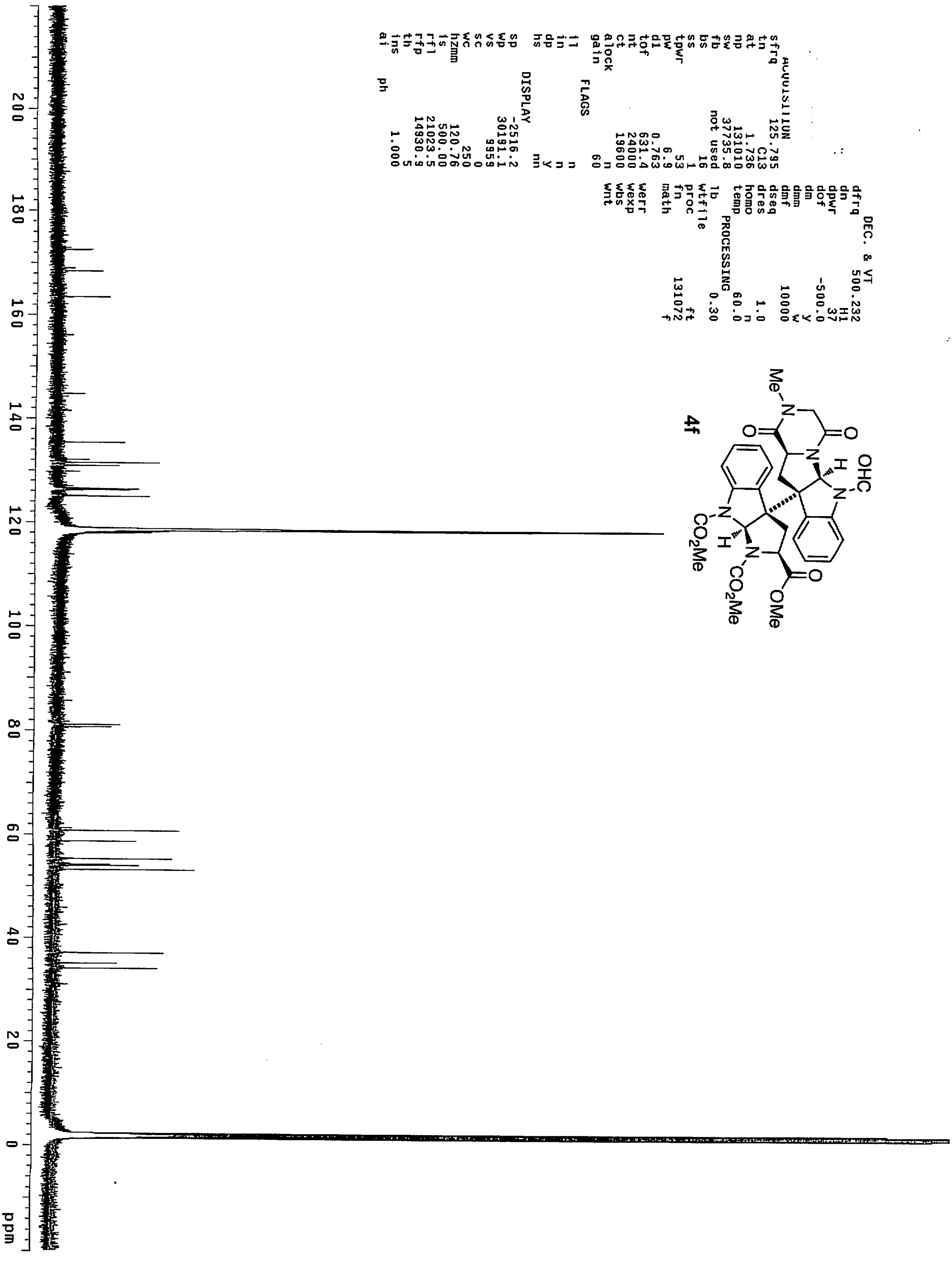
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt

```
                                   DEC. & VT
                          dfrq          125.846
                          dn                C13
                          dpwr               30
    ACQUISITION           dof                 0
sfrq         500.438      dm                nnn
tn                H1      dmm                 c
at             4.999      dmf               200
np            120102      dseq
sw           12012.0      dres              1.0
fb          not used      homo                n
bs                 4      temp             60.0
tpwr              56          PROCESSING
pw               8.0      wtfile
d1             0.100      proc               ft
tof           3003.2      fn             262144
nt               128      math                f
ct                12
alock              n      werr
gain        not used      wexp
      FLAGS               wbs
il                 n      wnt               wft
in                 n
dp                 y
hs                nn
      DISPLAY
sp            -248.5
wp            6234.8
vs                40
sc                 0
wc               250
hzmm           24.94
is             33.57
rfl           1487.8
rfp            970.8
th                 7
ins          100.000
ai   cdc   ph
```

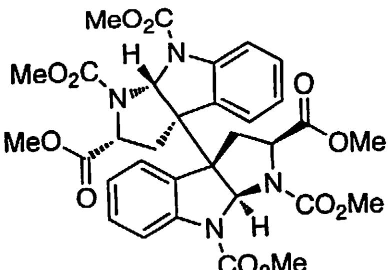


4f

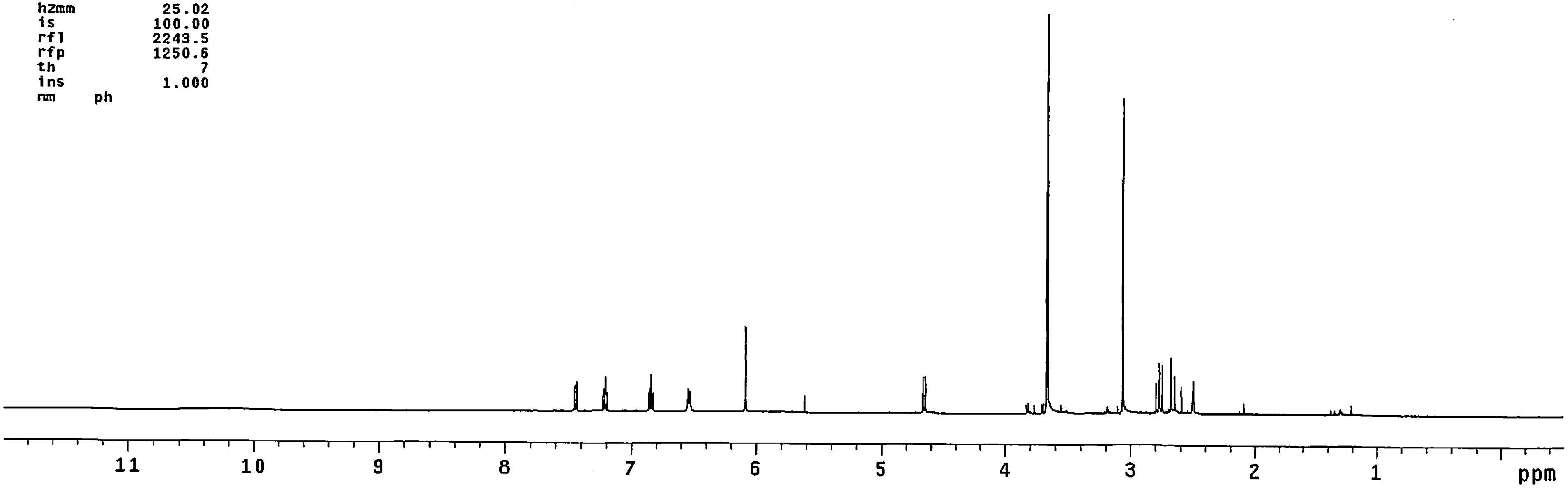


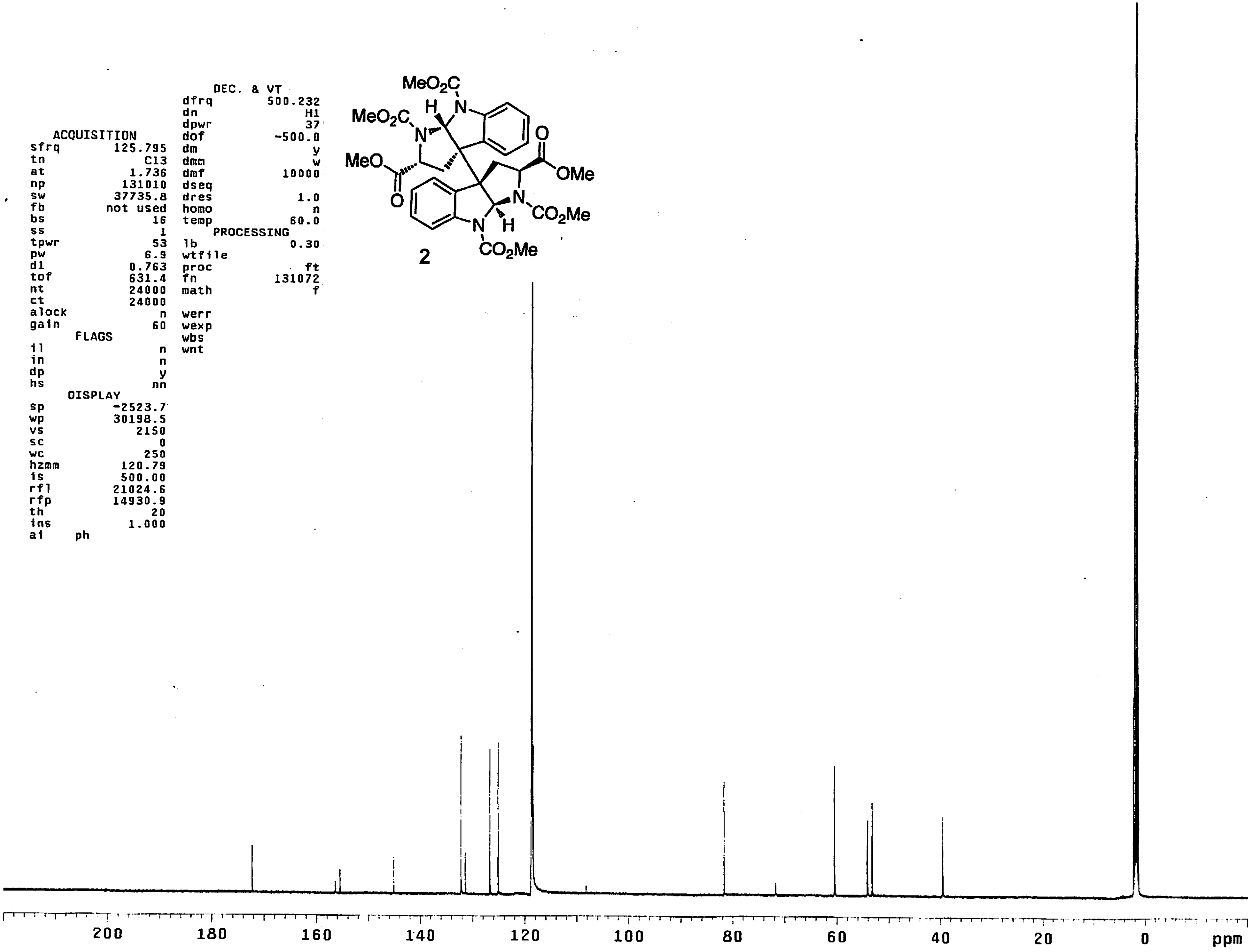

ACQUISITION
sfrq 125.795
tn C13
at 1.736
np 131010
sw 37735.8
fb not used
bs 16
ss 1
tpwr 53
pw 6.9
d1 0.763
tof 631.4
nt 24000
ct 19600
alock n
gain 60
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2516.2
wp 30191.1
vs 9959
sc 0
wc 250
hzmm 120.76
is 500.00
rfl 21023.5
rfp 14930.9
th 5
ins 1.000
ai ph
DEC. & VT
dfrq 500.232
dn H1
dpwr 37
dof -500.0
dm y
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 60.0
PROCESSING
lb 0.30
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
OHC
N
H
N
O
Me
N
O
N
H
N
CO2Me
N
CO2Me
O
OMe
4f
200
180
160
140
120
100
80
60
40
20
0
ppm

```
                                   DEC. & VT
                              dfrq          125.795
                              dn                C13
                              dpwr               37
                              dof                 0
                              dm                nnn
                              dmm                 c
       ACQUISITION            dmf             10000
sfrq          500.234         dseq
tn                 H1         dres              1.0
at              3.200         homo                n
np              64000         temp            145.0
sw            10000.0              PROCESSING
fb           not used         wtfile
bs                  4         proc               ft
ss                  1         fn             131072
tpwr               58         math                f
pw                9.0
d1                  0         werr
tof            1498.2         wexp
nt                128         wbs
ct                 12         wnt
alock               n
gain         not used
        FLAGS
il                  n
in                  n
dp                  y
hs                 nn
       DISPLAY
sp             -257.0
wp             6254.7
vs                 64
sc                  0
wc                250
hzmm            25.02
is             100.00
rfl            2243.5
rfp            1250.6
th                  7
ins             1.000
nm     ph
```



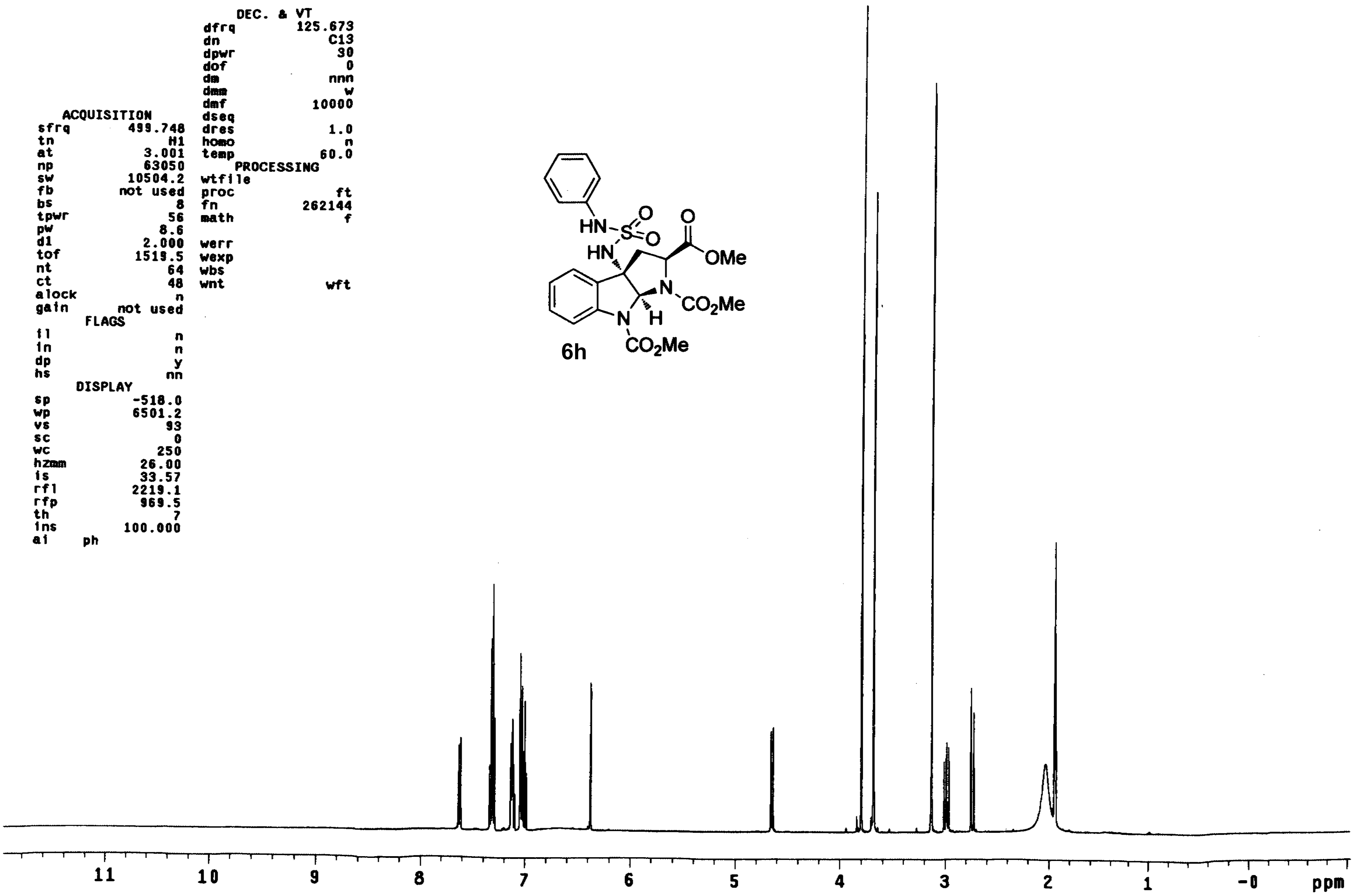
2





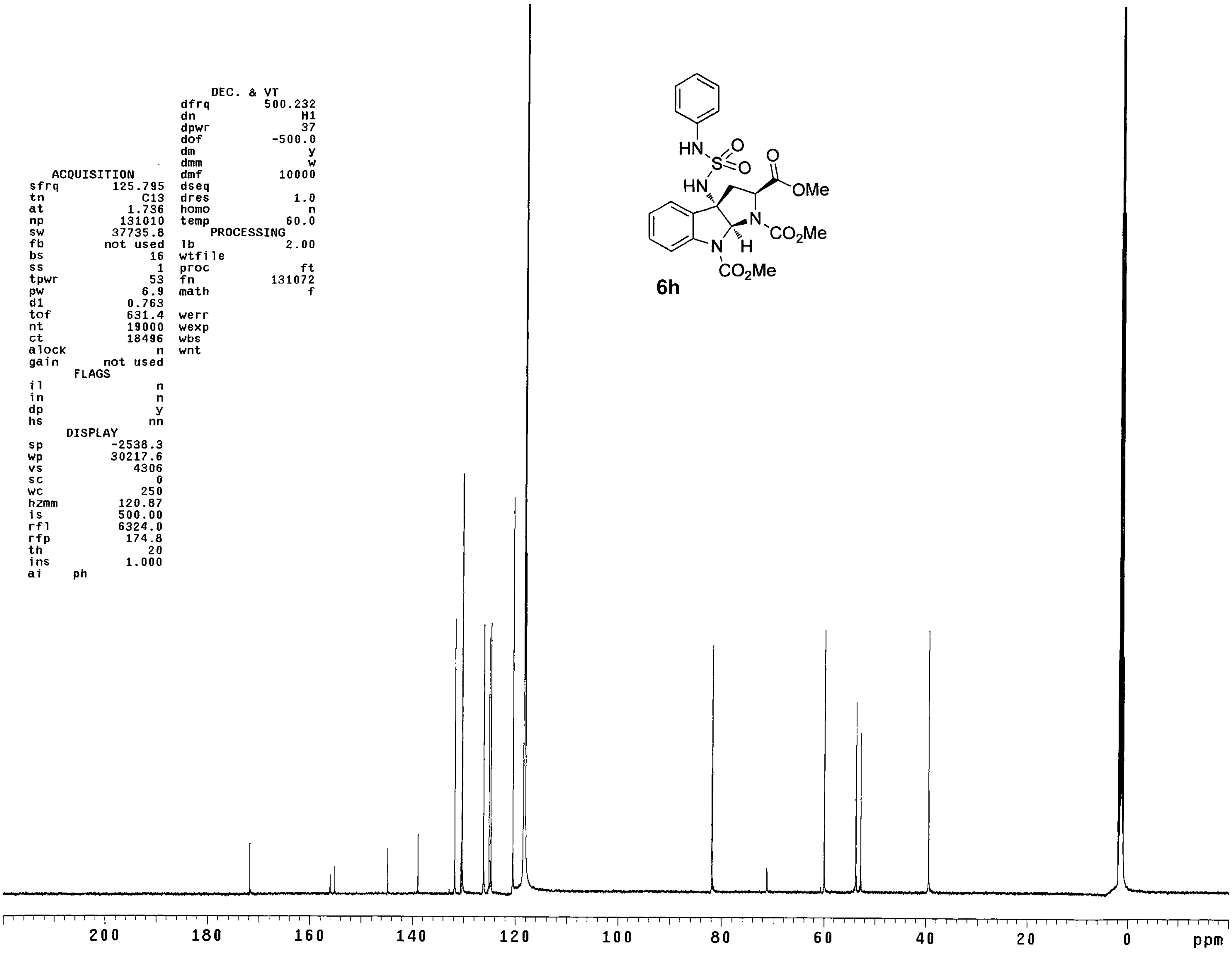
2

```
      ACQUISITION                    DEC. & VT
sfrq        125.795       dfrq          500.232
tn              C13       dn                 H1
at            1.736       dpwr               37
np           131010       dof            -500.0
sw          37735.8       dm                  y
fb         not used       dmm                 w
bs               16       dmf             10000
ss                1       dseq
tpwr             53       dres              1.0
pw              6.9       homo                n
d1            0.763       temp             60.0
tof           631.4             PROCESSING
nt            24000       lb               0.30
ct            24000       wtfile
alock             n       proc               ft
gain             60       fn             131072
         FLAGS            math                f
il                n
in                n       werr
dp                y       wexp
hs               nn       wbs
        DISPLAY           wnt
sp          -2523.7
wp          30198.5
vs             2150
sc                0
wc              250
hzmm         120.79
is           500.00
rfl         21024.6
rfp         14930.9
th               20
ins           1.000
ai     ph
```



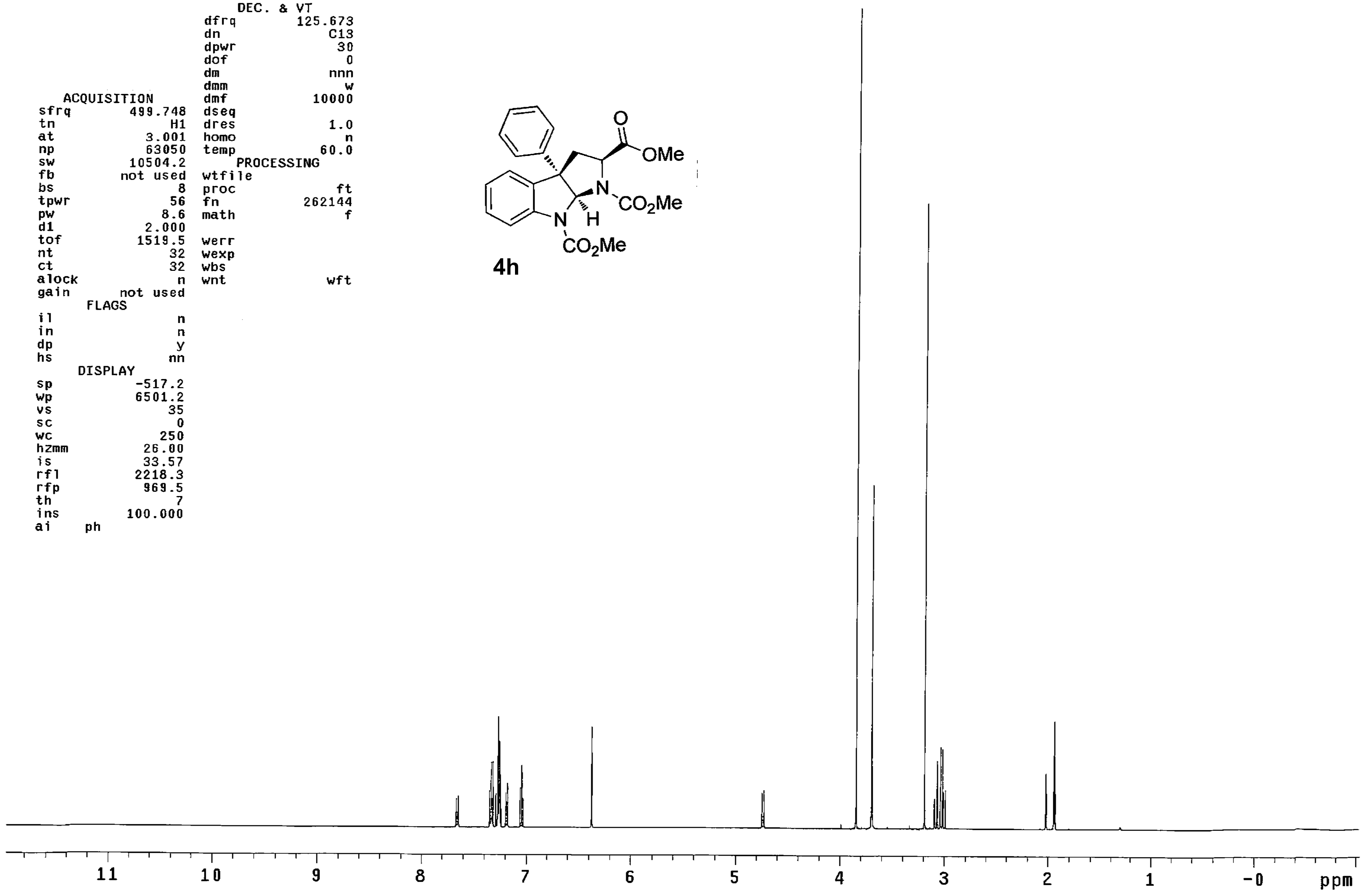
6h

```
      ACQUISITION              DEC. & VT
sfrq         499.748    dfrq          125.673
tn                H1    dn                C13
at             3.001    dpwr               30
np             63050    dof                 0
sw           10504.2    dm                nnn
fb          not used    dmm                 w
bs                 8    dmf             10000
tpwr              56    dseq
pw               8.6    dres              1.0
d1             2.000    homo                n
tof           1519.5    temp             60.0
nt                64        PROCESSING
ct                48    wtfile
alock              n    proc               ft
gain        not used    fn             262144
        FLAGS           math                f
il                 n
in                 n    werr
dp                 y    wexp
hs                nn    wbs
       DISPLAY          wnt               wft
sp            -518.0
wp            6501.2
vs                93
sc                 0
wc               250
hzmm           26.00
is             33.57
rfl           2219.1
rfp            969.5
th                 7
ins          100.000
ai     ph
```



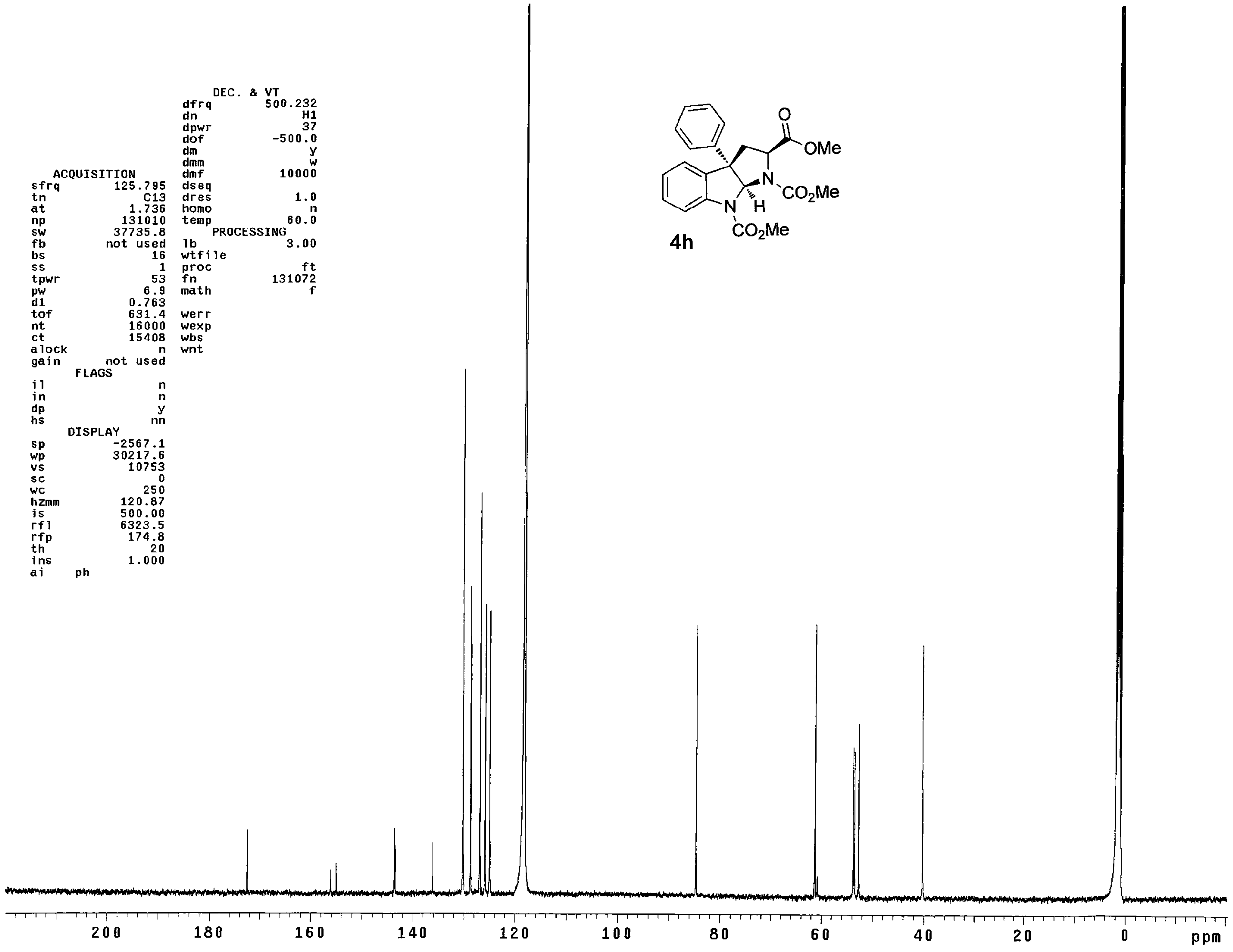
6h

```
   ACQUISITION                    DEC. & VT
sfrq       125.795   dfrq          500.232
tn             C13   dn                 H1
at           1.736   dpwr               37
np          131010   dof            -500.0
sw         37735.8   dm                  y
fb        not used   dmm                 w
bs              16   dmf             10000
ss               1   dseq
tpwr            53   dres              1.0
pw             6.9   homo                n
d1           0.763   temp             60.0
tof          631.4        PROCESSING
nt           19000   lb               2.00
ct           18496   wtfile
alock            n   proc               ft
gain      not used   fn             131072
      FLAGS          math                f
il               n
in               n   werr
dp               y   wexp
hs              nn   wbs
      DISPLAY        wnt
sp         -2538.3
wp         30217.6
vs            4306
sc               0
wc             250
hzmm        120.87
is          500.00
rfl         6324.0
rfp          174.8
th              20
ins          1.000
ai    ph
```



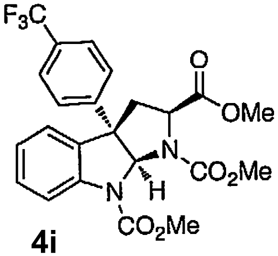
```
   ACQUISITION          DEC. & VT
sfrq      499.748   dfrq       125.673
tn             H1   dn             C13
at          3.001   dpwr            30
np          63050   dof              0
sw        10504.2   dm             nnn
fb       not used   dmm              w
bs              8   dmf          10000
tpwr           56   dseq
pw            8.6   dres           1.0
d1          2.000   homo             n
tof        1519.5   temp          60.0
nt             32      PROCESSING
ct             32   wtfile
alock           n   proc            ft
gain     not used   fn          262144
      FLAGS         math             f
il              n
in              n   werr
dp              y   wexp
hs             nn   wbs
     DISPLAY        wnt            wft
sp         -517.2
wp         6501.2
vs             35
sc              0
wc            250
hzmm        26.00
is          33.57
rfl        2218.3
rfp         969.5
th              7
ins       100.000
ai    ph
```

4h



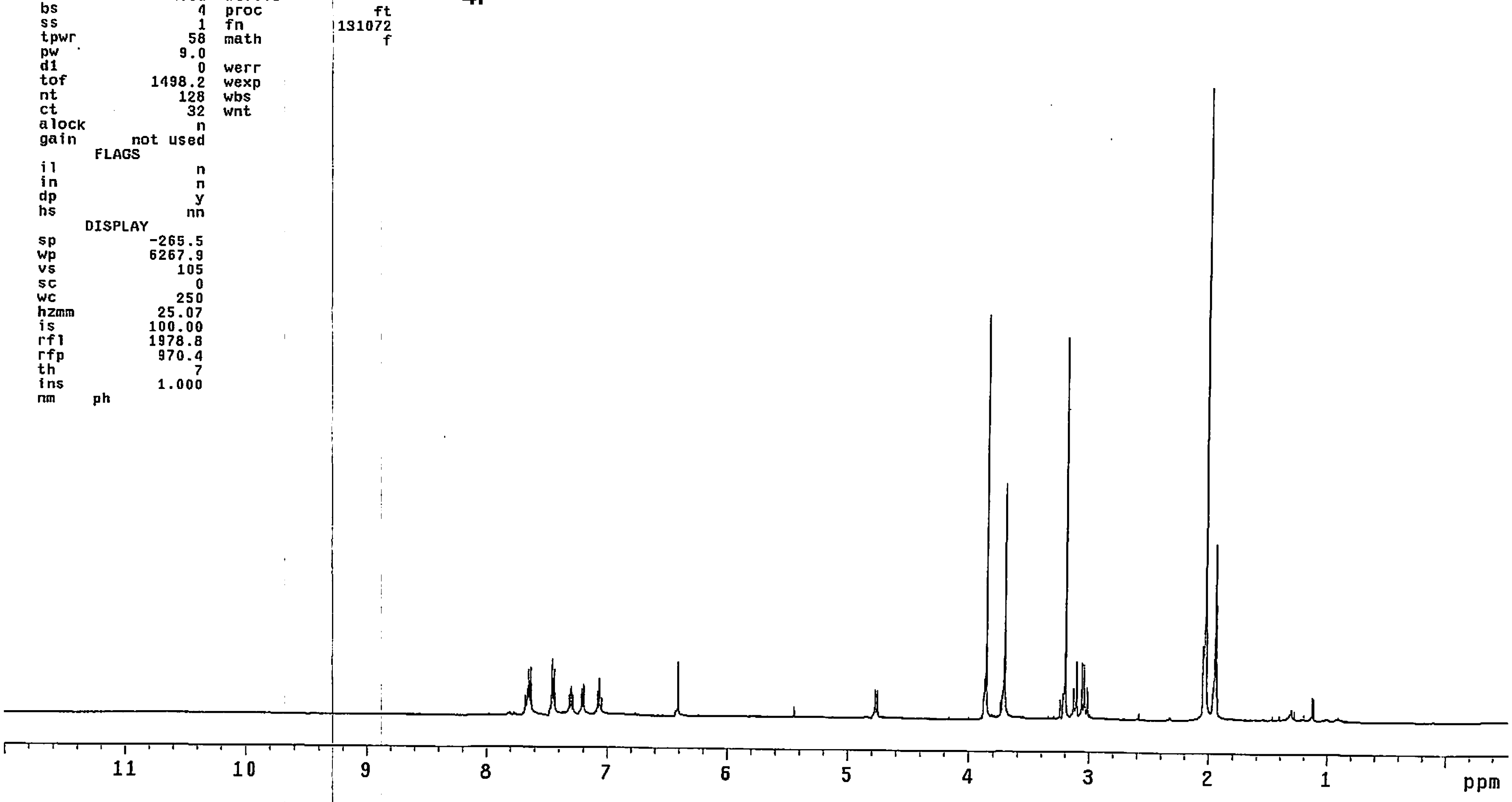
```
     ACQUISITION              DEC. & VT
sfrq       125.795    dfrq        500.232
tn             C13    dn               H1
at           1.736    dpwr             37
np          131010    dof          -500.0
sw         37735.8    dm                y
fb        not used    dmm               w
bs              16    dmf           10000
ss               1    dseq
tpwr            53    dres            1.0
pw             6.9    homo              n
d1           0.763    temp           60.0
tof          631.4         PROCESSING
nt           16000    lb             3.00
ct           15408    wtfile
alock            n    proc             ft
gain      not used    fn           131072
       FLAGS          math              f
il               n
in               n    werr
dp               y    wexp
hs              nn    wbs
      DISPLAY         wnt
sp         -2567.1
wp         30217.6
vs           10753
sc               0
wc             250
hzmm        120.87
is          500.00
rfl         6323.5
rfp          174.8
th              20
ins          1.000
ai    ph
```

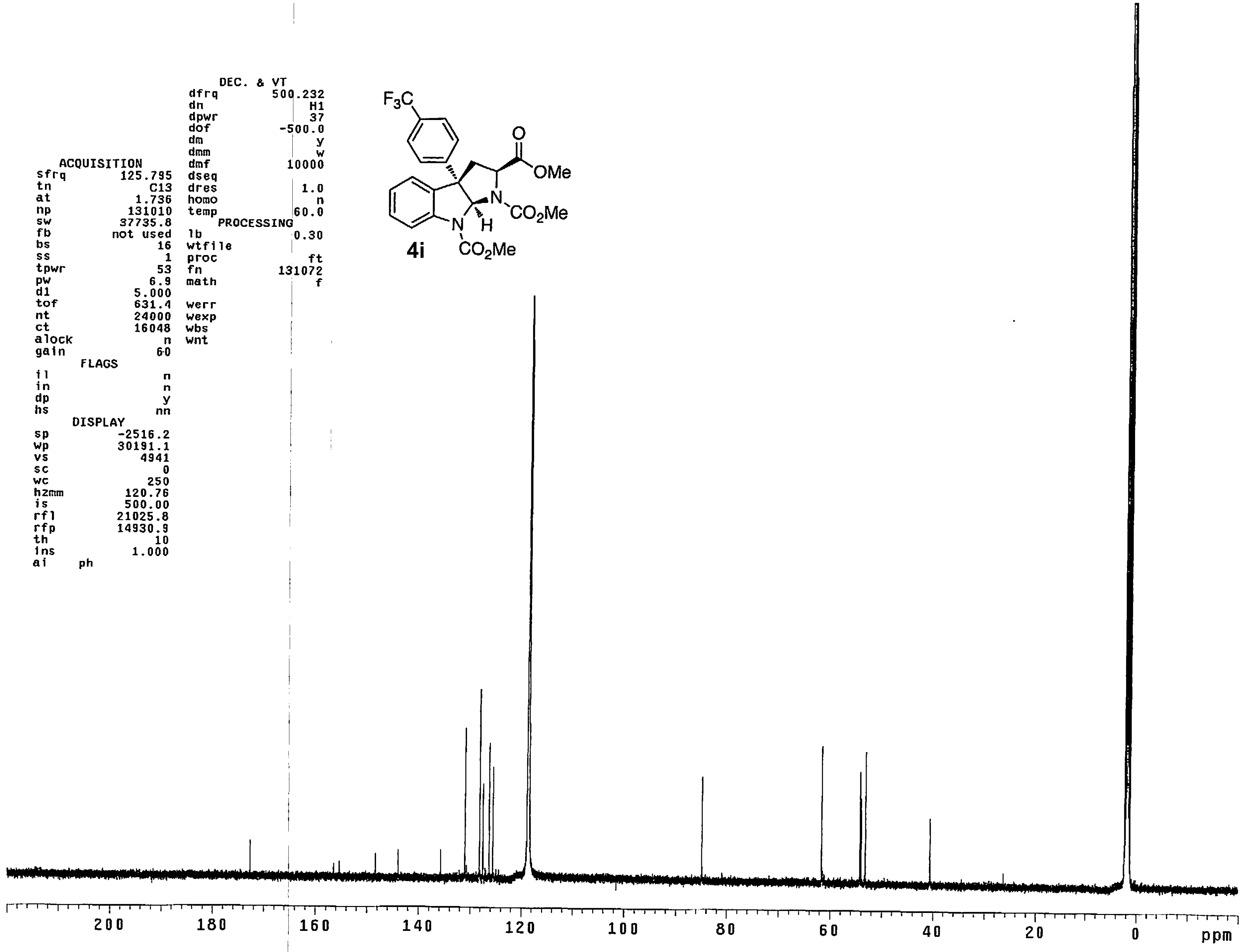
4h



4i

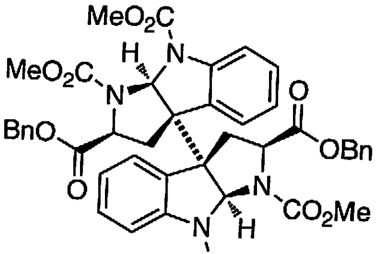
```
                            DEC. & VT
                     dfrq          125.795
                     dn                C13
                     dpwr               37
                     dof                 0
                     dm                nnn
                     dmm                 c
    ACQUISITION      dmf             10000
sfrq       500.234   dseq
tn              H1   dres              1.0
at           3.200   homo                n
np           64000   temp             60.0
sw         10000.0       PROCESSING
fb        not used   wtfile
bs               4   proc               ft
ss               1   fn             131072
tpwr            58   math                f
pw             9.0
d1               0   werr
tof         1498.2   wexp
nt             128   wbs
ct              32   wnt
alock            n
gain      not used
       FLAGS
il               n
in               n
dp               y
hs              nn
      DISPLAY
sp          -265.5
wp          6267.9
vs             105
sc               0
wc             250
hzmm         25.07
is          100.00
rfl         1978.8
rfp          970.4
th               7
ins          1.000
nm    ph
```





```
                                DEC. & VT
                        dfrq          500.232
                        dn                 H1
                        dpwr               37
                        dof            -500.0
                        dm                  y
       ACQUISITION      dmm                 w
sfrq          125.795   dmf             10000
tn                C13   dseq
at              1.736   dres              1.0
np             131010   homo                n
sw            37735.8   temp             60.0
fb           not used      PROCESSING
bs                 16   lb               0.30
ss                  1   wtfile
tpwr               53   proc               ft
pw                6.9   fn             131072
d1              5.000   math                f
tof             631.4
nt              24000   werr
ct              16048   wexp
alock               n   wbs
gain               60   wnt
        FLAGS
il                  n
in                  n
dp                  y
hs                 nn
       DISPLAY
sp            -2516.2
wp            30191.1
vs               4941
sc                  0
wc                250
hzmm           120.76
is             500.00
rfl           21025.8
rfp           14930.9
th                 10
ins             1.000
ai     ph
```

```
                              DEC. & VT
                       dfrq          125.795
                       dn                C13
                       dpwr               37
                       dof                 0
                       dm                nnn
                       dmm                 c
    ACQUISITION        dmf             10000
sfrq        500.234    dseq
tn               H1    dres              1.0
at            3.200    homo                n
np            64000    temp             60.0
sw          10000.0        PROCESSING
fb         not used    wtfile
bs                4    proc               ft
ss                1    fn             131072
tpwr             58    math                f
pw              9.0
d1                0    werr
tof          1498.2    wexp
nt              128    wbs
ct                4    wnt
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
hs               nn
      DISPLAY
sp           -264.7
wp           6267.9
vs               32
sc                0
wc              250
hzmm          25.07
is           100.00
rfl          1971.1
rfp           970.4
th                7
ins           1.000
nm    ph
```



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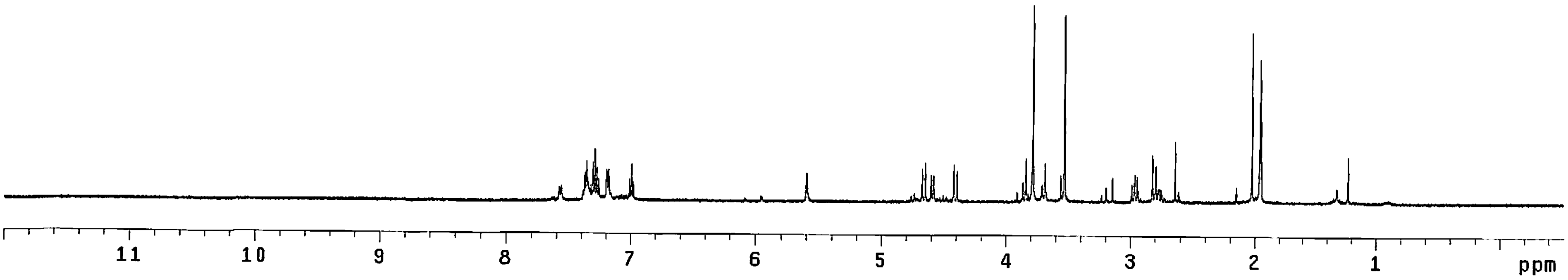
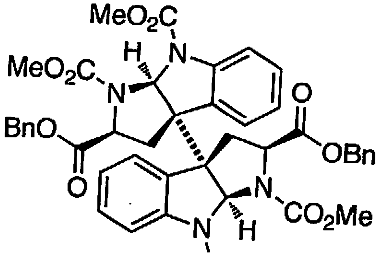
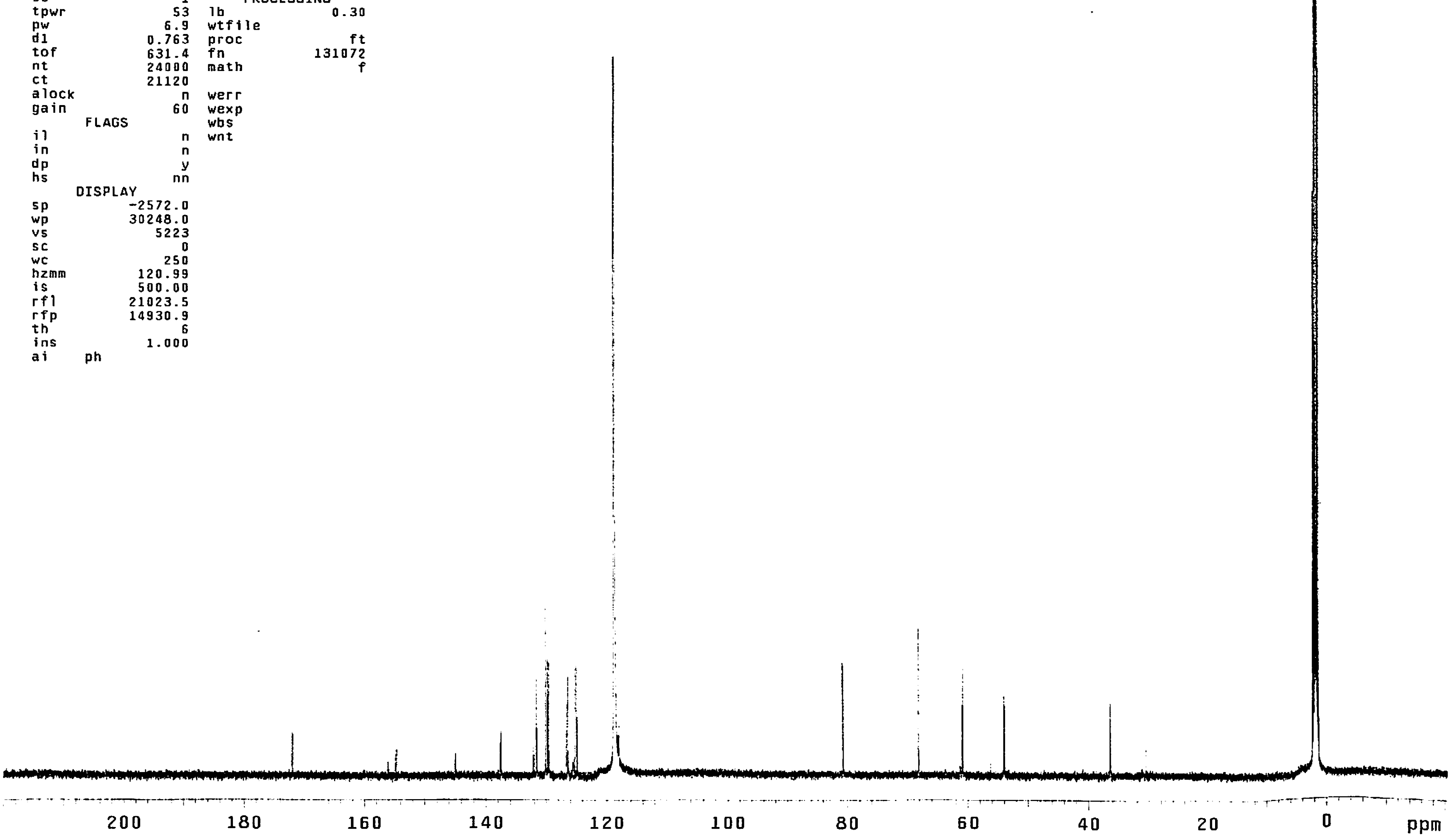
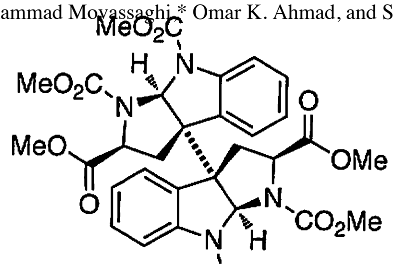




15

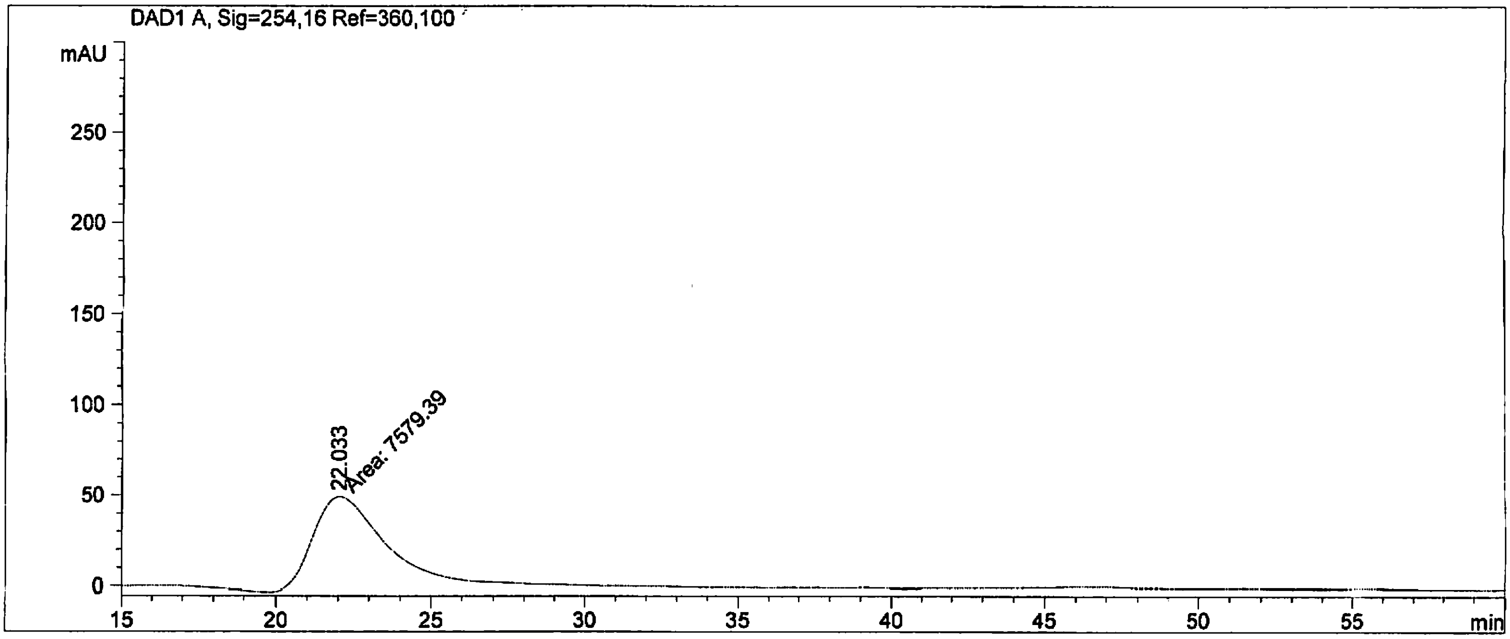
```
       ACQUISITION              DEC. & VT
sfrq        125.795     dfrq          500.232
tn              C13     dn                 H1
at            1.736     dpwr               37
np           131010     dof            -500.0
sw          37735.8     dm                  y
fb         not used     dmm                 w
bs               16     dmf             10000
ss                1     dseq
tpwr             53     dres              1.0
pw              6.9     homo                n
d1            0.763     temp             60.0
tof           631.4           PROCESSING
nt            24000     lb               0.30
ct            21120     wtfile
alock             n     proc               ft
gain             60     fn             131072
         FLAGS          math                f
il                n
in                n     werr
dp                y     wexp
hs               nn     wbs
        DISPLAY         wnt
sp          -2572.0
wp          30248.0
vs             5223
sc                0
wc              250
hzmm         120.99
is           500.00
rfl         21023.5
rfp         14930.9
th                6
ins           1.000
ai     ph
```





3

Pure sample of the weakly UV-active product **3**



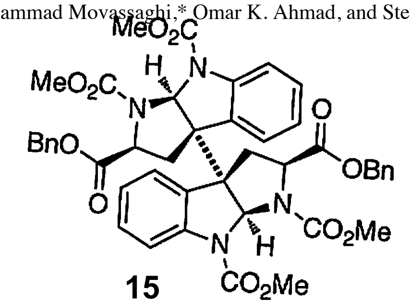
```
=====================================================================
                      External Standard Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs
=====================================================================
                         Summed Peaks Report
=====================================================================

Signal 1: DAD1 A, Sig=254,16 Ref=360,100
=====================================================================
                      Final Summed Peaks Report
=====================================================================

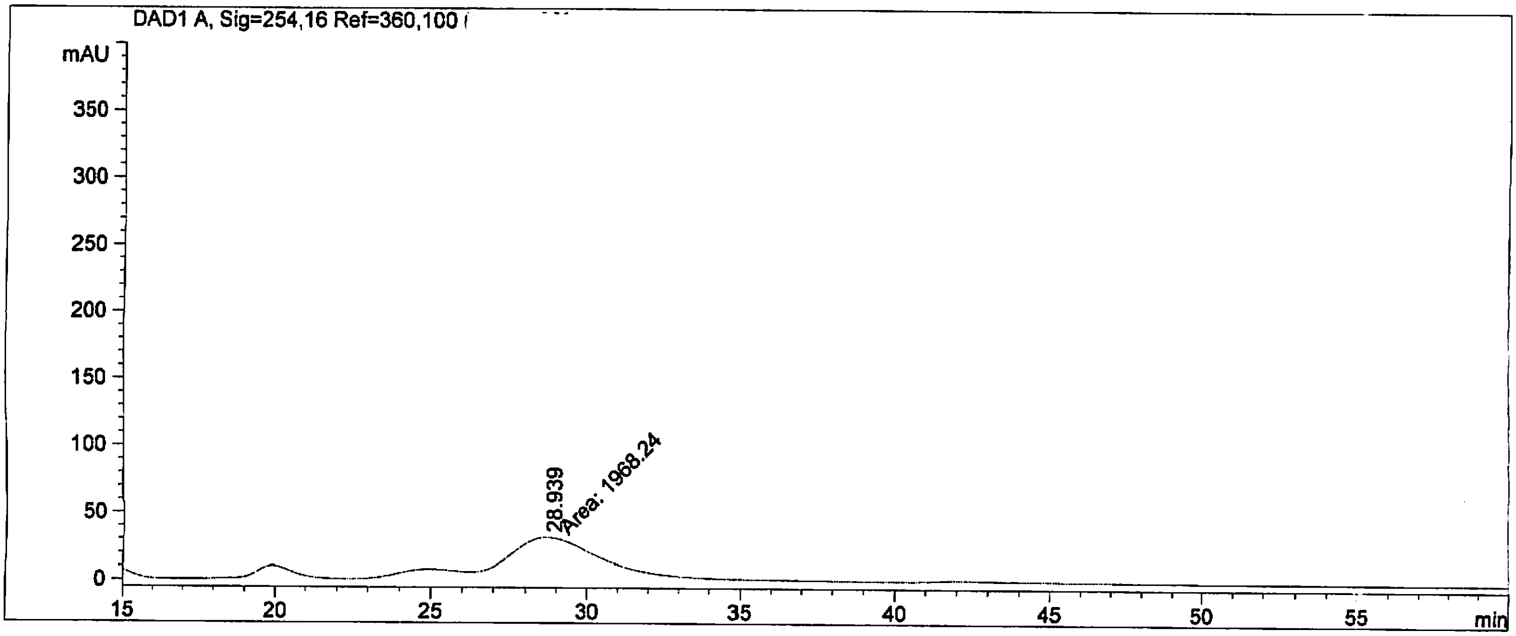
Signal 1: DAD1 A, Sig=254,16 Ref=360,100
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```



15

Pure sample of the weakly UV-active product **15**



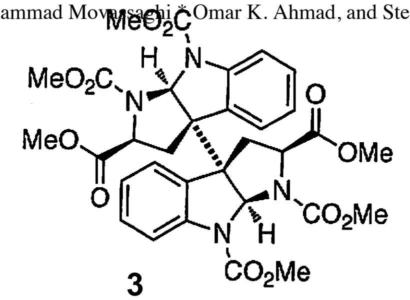
```
=====================================================================
                     External Standard Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs
=====================================================================
                        Summed Peaks Report
=====================================================================

Signal 1: DAD1 A, Sig=254,16 Ref=360,100
=====================================================================
                     Final Summed Peaks Report
=====================================================================

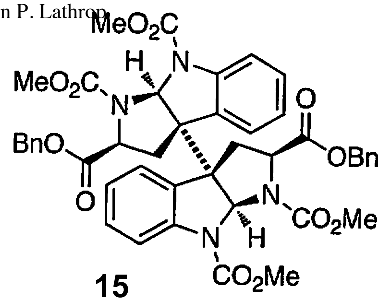
Signal 1: DAD1 A, Sig=254,16 Ref=360,100
=====================================================================
                       Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```



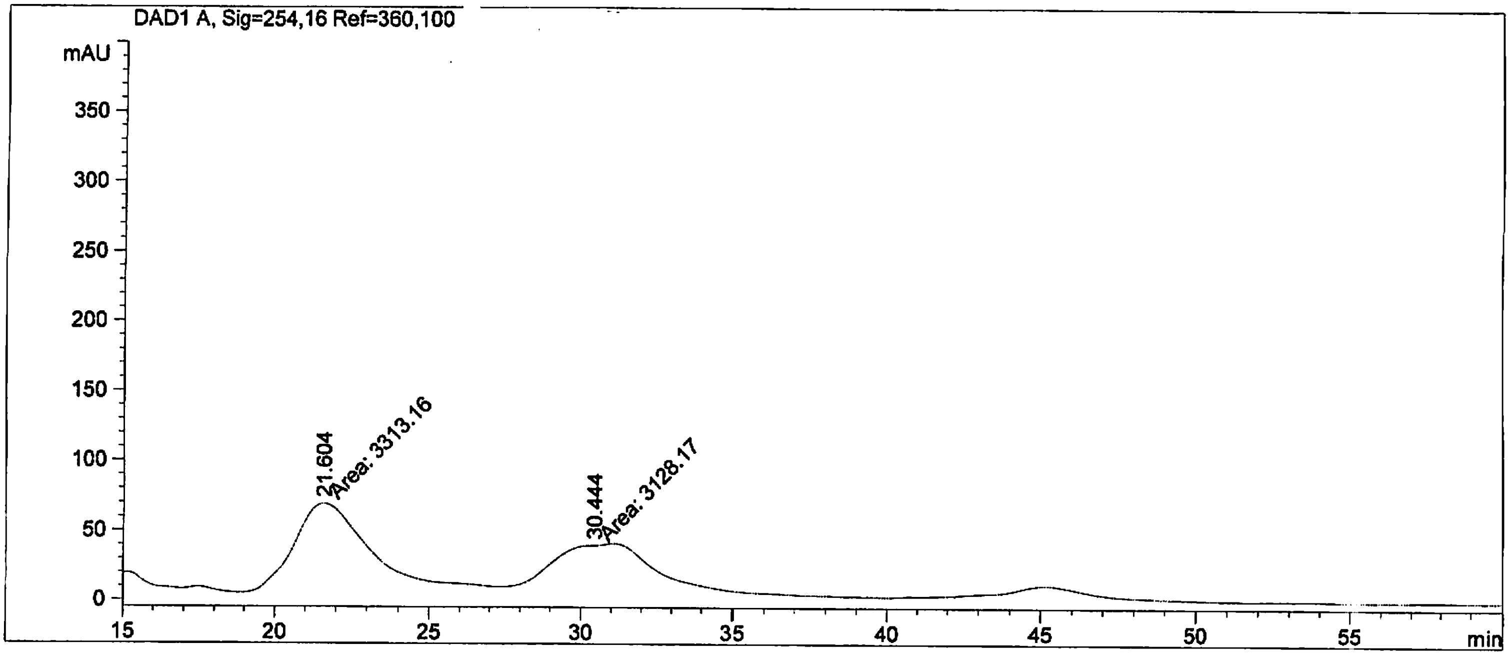
3

+



15

Product mixture prior to purification



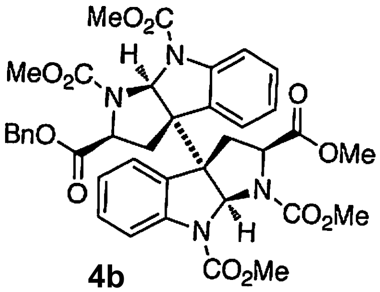
```
=====================================================================
                    External Standard Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs
=====================================================================
                       Summed Peaks Report
=====================================================================

Signal 1: DAD1 A, Sig=254,16 Ref=360,100
=====================================================================
                    Final Summed Peaks Report
=====================================================================

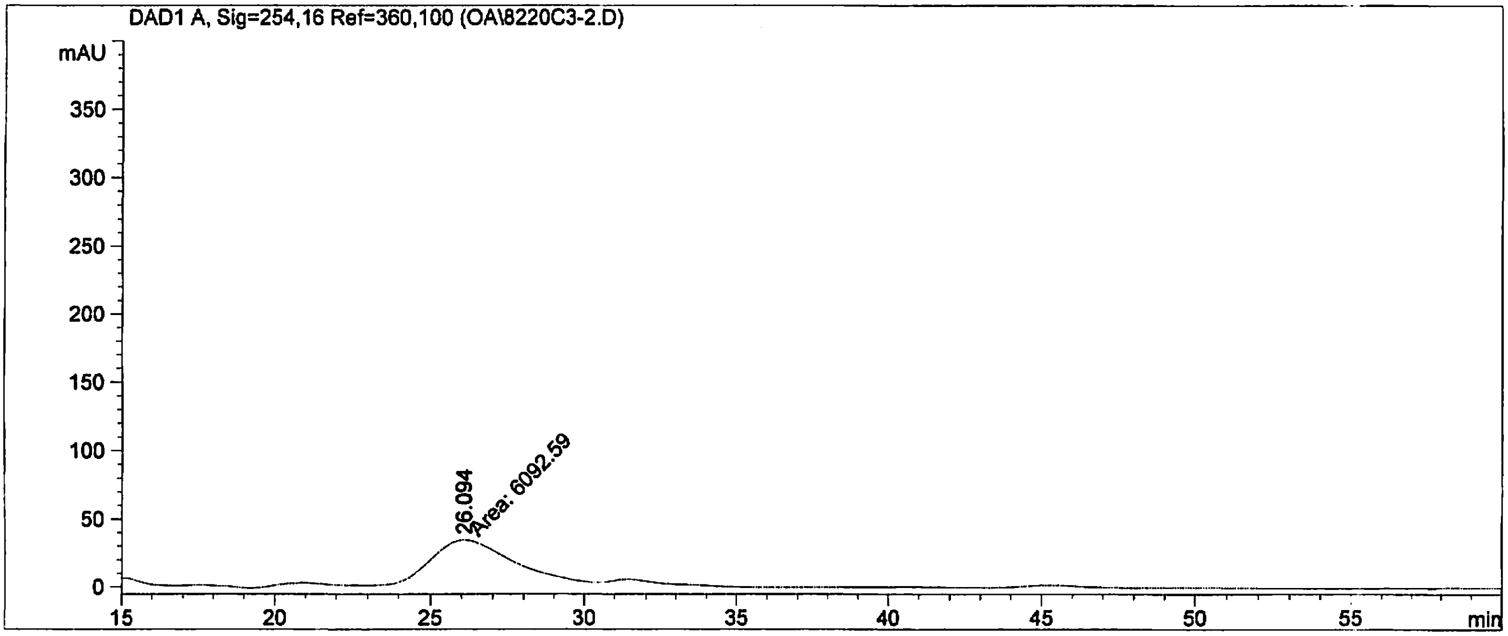
Signal 1: DAD1 A, Sig=254,16 Ref=360,100
=====================================================================
                       Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```



4b

Pure sample of the weakly UV-active product **4b**



```
=====================================================================
                          External Standard Report
=====================================================================

Sorted By                 :       Signal
Multiplier                :       1.0000
Dilution                  :       1.0000
Use Multiplier & Dilution Factor with ISTDs
=====================================================================
                             Summed Peaks Report
=====================================================================

Signal 1: DAD1 A, Sig=254,16 Ref=360,100
=====================================================================
                          Final Summed Peaks Report
=====================================================================

Signal 1: DAD1 A, Sig=254,16 Ref=360,100
=====================================================================
                             Area Percent Report
=====================================================================

Sorted By                 :       Signal
Multiplier                :       1.0000
Dilution                  :       1.0000
Use Multiplier & Dilution Factor with ISTDs
```