***N*-Isopropylidene-*N'*-2-Nitrobenzenesulfonyl Hydrazine. A Reagent for Conversion of Alcohols to the Corresponding Monoalkyl Diazenes.**

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Supporting Information

General Procedures. All reactions were performed in oven-dried or flame-dried round bottomed flasks or modified Schlenk (Kjeldahl shape) flasks. 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).[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 rotary evaporators at ~20 Torr (house vacuum) at 25–35 °C, then at ~1 Torr (vacuum pump) unless otherwise indicated.

Materials. Commercial reagents and solvents were used as received with the following exceptions: Dichloromethane, diethyl ether, tetrahydrofuran, acetonitrile, toluene, and triethylamine were purified by the method of Grubbs et al. under positive argon pressure.[2] The molarity of *n*-butyllithium solutions was determined by titration using diphenylacetic acid as an indicator (average of three determinations).[3] Chlorobenzene was distilled over $CaCl_2$ under an argon atmosphere, 2,6-lutidene over CaH_2 under an argon atmosphere, and 2,2,2-trifluoroethanol over calcium sulfate and sodium

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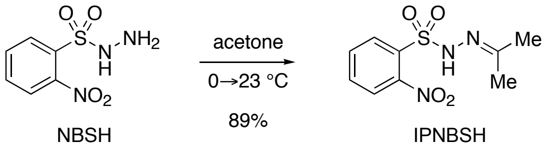
1. Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
2. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
3. Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.

bicarbonate under an argon atmosphere. Sodium hydride was purchased as a 60% dispersion in mineral oil, washed four times with hexanes and stored in a glove-box.

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with 400 and 500 MHz spectrometers. 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 7.27, CD_3CN: δ 1.96). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant(s) in Hertz, integration, assignment]. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with 400 and 500 MHz spectrometers 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 77.2). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant(s) in Hertz, assignment]. Infrared data were obtained with an FTIR and are reported as follows: [frequency of absorption (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak, br = broad), assignment]. Gas chromatography was performed on a HP-5 5% Phenyl Methyl Siloxane column.



<u>*N*-Isopropylidene-*N′*-2-nitrobenzenesulfonyl hydrazine (IPNBSH, eq 1):</u>[4]

A sample of NBSH[5] (1.14 g, 5.24 mmol, 1 equiv) was dissolved in acetone (8.0 mL) at 0 °C. After 30 min, the solvent was removed in vacuo and the residue was dissolved in acetone (4 mL). Slow addition of the acetone solution to a volume of hexanes (150 mL), collection of the fine powder by filtration, followed by sequential hexanes rinses (2 × 5 mL), and removal of volatiles by high vacuum provided triturated IPNBSH[4] as a white solid (1.20 g, 89%). mp: 139–140 °C (decomposition). TLC (66% ethyl acetate in hexanes), *Rf*: 0.7 (UV, CAM, anis). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): 8.30–8.28 (m, 1H), 7.87–7.85 (m, 2H) 7.79–7.77 (m, 2H), 1.96 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 20 °C): 158.9, 134.2, 133.5, 132.9, 132.0, 125.4, 25.5, 17.2. FTIR (thin film): 3264 (s), 1551 (s), 1375 (s), 1347 (m), 1177 (s). HRMS–ESI: calc'd for $C_9H_{12}N_3O_4S$ $[M+H]^+$: 258.0543, found: 258.0548.

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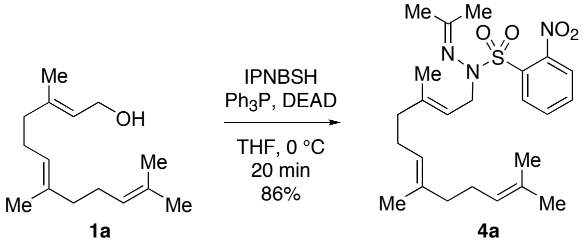
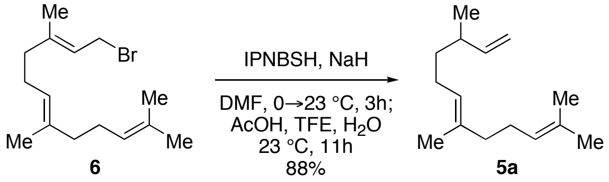
[4] Movassaghi, M.; Piizzi, G.; Siegel, D. S.; Piersanti, G. *Angew. Chem. Int. Ed.* **2006**, 45, 5859.

[5] (a) Dann, A. T.; Davies, W. *J. Chem. Soc.* **1929**, 1050 (b) Myers, A. G.; Zheng, B.; Movassaghi, M. *J. Org. Chem.* **1997**, *62*, 7507. (c) Myers, A. G.; Movassaghi M. In *e-Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed; John Wiley & Sons, 2003.



***N*-Isopropylidene-*N'*-((2E,6E)-3,7,11-trimethyl-dodeca-2,6,10-trienyl)-*N'*-2-nitrobenzene-sulfonyl hydrazide (4a, Scheme 2):**

DEAD (0.30 mL, 1.9 mmol, 1.2 equiv) was added drop-wise to a solution of IPNBSH (487 mg, 1.89 mmol, 1.20 equiv), *trans,trans*-farnesol (**1a**, 400 μL, 1.57 mmol, 1 equiv), and triphenylphosphine (496 mg, 1.89 mmol, 1.20 equiv) in anhydrous THF (30 mL) at 0 °C under an argon atmosphere. After 20 min, the volatiles were removed and the residue was purified by flash column chromatography on silica gel (30% ethyl acetate in hexanes) to afford the sulfonyl hydrazide **4a** (624 mg, 86%). TLC (40% ethyl acetate in hexanes), *Rf*: 0.4 (UV, $KMnO_4$). ^1H NMR (500 MHz, $CDCl_3$, 20 °C): 7.98–7.96 (m, 1H), 7.73–7.68 (m, 2H), 7.55–7.54 (m, 1H), 5.08–5.04 (m, 3H), 3.84 (d, 2H, *J* = 7.0), 2.12 (m, 3H), 2.11 (m, 3H), 2.07–2.01 (m, 4H), 1.98–1.94 (m, 4H), 1.68 (s, 3H), 1.62 (s, 3H), 1.60 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 20 °C): 182.8, 149.7, 142.5, 135.6, 134.1, 131.9, 131.5, 130.9, 128.3, 124.3, 123.7, 123.6, 117.0, 49.5, 39.9, 39.7, 26.6, 26.5, 25.9, 25.2, 21.2, 17.8, 16.5, 16.1. FTIR (thin film): 2918 (br s), 1644 (m), 1589 (m), 1547 (s), 1439 (s), 1372 (s). HRMS-ESI: calc'd for $C_{24}H_{36}N_3O_4S$ $[M+H]^+$: 462.2421, found: 462.2412.



***(E)*-3,7,11-Trimethyldodeca-1,6,10-triene (5a, eq 2):**[6]

A solution of IPNBSH (96 mg, 0.37 mmol, 1.3 equiv) in anhydrous DMF (1.5 mL) was added slowly to a suspension of sodium hydride (8.6 mg, 0.36 mmol, 1.2 equiv) in anhydrous DMF (1.5 mL) at 0 °C under an argon atmosphere to give an orange solution. After 1.5 h, *trans*,*trans*-farnesyl bromide (**6**, 81 μL, 0.30 mmol, 1 equiv) was added to the sodium amide solution and the resulting mixture was allowed to warm to 23 °C. After 3 h, excess base was quenched with glacial acetic acid (86 μL, 1.5 mmol, 5.0 equiv), and the reaction mixture was diluted by the addition of a mixture of trifluoroethanol and water (1:1, 1.5 mL). After 11 h, the reaction mixture was diluted with water (25 mL) and extracted with diethyl ether (3 × 25 mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated. The residue was purified by flash column chromatography on silica gel (100% ^{n}pentane) to afford the triene **5a** (54 mg, 88%). All spectroscopic data were in agreement with the literature.[6] TLC (40% ethyl acetate in hexanes), *Rf*: 0.8 (CAM, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$, 20 °C): 5.25–5.15 (m, 1H), 5.13–5.10 (m, 2H), 4.99 (t, 1H, *J* = 2.0 Hz), 4.94–4.91 (m, 2H), 2.14–1.98 (m, 7H), 1.69 (s, 3H), 1.61 (s, 3H), 1.60 (s, 3H), 1.36–1.33 (m, 2H), 0.99 (d, 3H, *J* = 8 Hz). ^{13}C NMR (500 MHz, $CDCl_3$, 20 °C): 145.0, 135.1, 131.5, 124.7, 124.6, 112.7, 39.9, 37.5, 36.9, 26.9, 25.9, 25.8, 20.4, 20.4, 17.9, 16.2. FTIR (thin film): 3077 (m), 2966 (s), 2915 (s), 2856 (s), 1640 (m), 1453 (s), 1376 (s). MS (*m/z*) $C_{15}H_{26}$ $[M]^+$: 206.

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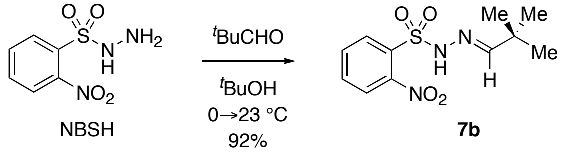
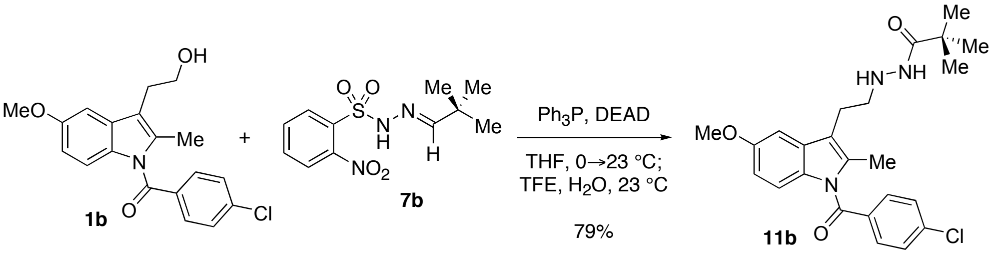
6. For prior syntheses of **5a**, see Saplay, K. M.; Sahni, R.; Damodaran, N. P.; Dev, S. *Tetrahedron* **1980**, *36*, 1455 and Myers, A. G.; Zheng, B. *Tetrahedron Lett.* **1996**, *37*, 4841.



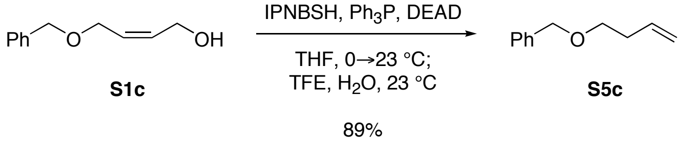
(*E*)-*N*'-(2,2-dimethyl-propylidene)-2-nitrobenzenesulfono-hydrazide (7b, Scheme 3):

NBSH (1.00 g, 4.62 mmol, 1 equiv) was dissolved in a solution of excess 2,2-dimethyl-propionaldehyde in ^{t}butanol (80% v/v, 8.0 mL) at 0 °C. After 30 min, the volatiles were removed under reduced pressure, and the residue was dissolved in dichloromethane (2 mL). Slow addition of this solution to a volume of hexanes (125 mL), collection of the resulting fine brown powder by filtration, followed by successive hexane rinses (2 × 5 mL) provided the hydrazone **7b** as a brown solid (1.16g, 92%). TLC (50% ethyl acetate in hexanes), R*f*: 0.8 (UV, CAM). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) δ: 8.24–8.21 (m, 1H), 7.91 (s, 1H), 7.86–7.76 (m, 3H), 7.26 (s, 1H), 0.99 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$, 20 °C) δ: 163.1, 134.4, 133.3, 132.6, 131.6, 125.1, 35.4, 27.2. FTIR (thin film): 3238 (s), 1548 (s), 1366 (s), 1321 (m), 1173 (s). HRMS-ESI (*m/z*): calcd for $C_{11}H_{15}N_3O_4S$ $[M+H]^+$: 286.0856, found: 286.0848.



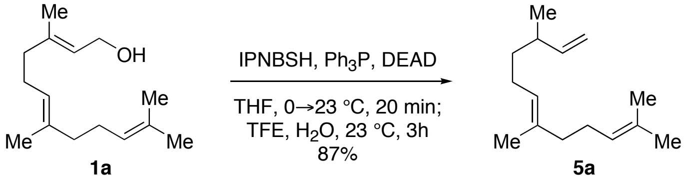
2,2-Dimethyl-propionic acid *N*'-{2-[1-(4-chloro-benzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl]-ethyl} hydrazide (11b, Scheme 3):

DEAD (78 μL, 0.50 mmol, 1.6 equiv) was added drop-wise to a solution of (*E*)-*N*'-(2,2-dimethyl-propylidene)-2-nitrobenzenesulfono-hydrazide (**7b**, 137 mg, 0.502 mmol, 1.63 equiv), *N*-(4-chlorobenzoyl)-3-(2-hydroxyethyl)-5-methoxy-2-methylindole (**1b**, 106 mg, 0.308 mmol, 1 equiv), and triphenylphosphine (133 mg, 0.505 mmol, 1.64 equiv) in anhydrous THF (3 mL) at 0 °C under an argon atmosphere. After 5 min, the reaction mixture was allowed to warm to 23 °C. After 30 min, a mixture of trifluoroethanol and water (1:1, 1.5 mL) was added to the reaction. After 11 h, the reaction mixture was partitioned between diethyl ether (25 mL) and water (10 mL). The organic layer was washed with water (3 × 10 mL), was dried over anhydrous sodium sulfate, was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (75% ethyl acetate in hexanes) to give the hydrazide **11b** (107 mg, 79%). TLC (75% ethyl acetate in hexanes), *Rf*: 0.3 (UV, CAM, anis). ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): 7.67–7.63 (m, 2H), 7.48–7.46 (m, 2H), 7.11 (s, 1H), 6.96–6.95 (d, 1H, J = 4.0 Hz), 6.91–6.89 (d, 1H, J = 8.0 Hz), 6.68–6.66 (dd, 1H, J = 8.0, 4.0 Hz), 4.77 (br s, 1H), 3.85 (s, 3H), 3.10–3.06 (t, 2H, J = 8.0 Hz), 2.87–2.83 (t, 2H, J = 8.0 Hz), 2.35 (s, 3H), 1.15 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$, 20 °C): 177.9, 168.4, 156.1, 139.2, 134.7, 134.2, 131.3, 130.7, 129.2, 117.3, 115.2, 111.4, 101.3, 99.9, 55.9, 51.7, 38.0, 27.3, 23.4, 13.5. FTIR (this film): 3305 (br m), 2960 (m), 1679 (s), 1478 (s), 1365 (s), 1325 (s). HRMS–ESI: calc'd for $C_{24}H_{29}ClN_3O_3$ $[M+H]^+$: 442.1897, found: 442.1900.



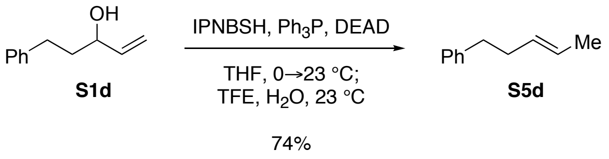
But-3-enyloxymethyl-benzene (S5c, Table 1, Entry 2):[7]

DEAD (66 µL, 0.42 mmol, 1.2 equiv) was added dropwise to a solution of IPNBSH (107 mg, 0.416 mmol, 1.20 equiv), *(Z)*-4-(benzyloxy)but-2-en-1-ol (**S1c**, 62 mg, 0.347 mmol, 1 equiv), and triphenylphosphine (109 mg, 0.417 mmol, 1.20 equiv) in anhydrous THF (3.5 mL) at 0 °C under an argon atmosphere. After 5 min, the reaction mixture was allowed to warm to 23 °C. After 2 h, a mixture of trifluoroethanol and water (1:1, 1.8 mL) was added to the reaction mixture. After 3 h, the reaction mixture was diluted with water (30 mL) and extracted with diethyl ether (3 × 30 mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated. The residue was purified by flash column chromatography on silica gel (4% diethyl ether in ^{n}pentane) to give **S5c** (50 mg, 89%). TLC (4% diethyl ether in pentane), *Rf*: 0.3 (anis). All spectroscopic data were in agreement with the literature.[7]



(E)-3,7,11-Trimethyldodeca-1,6,10-triene (5a, Table 1, entry 3):

DEAD (74 µL, 0.47 mmol, 1.2 equiv) was added drop-wise to a solution of IPNBSH (122 mg, 0.474 mmol, 1.21 equiv), *trans,trans*-farnesol (**1a**, 0.100 mL, 0.393 mmol, 1 equiv), and triphenylphosphine (124 mg, 0.473 mmol, 1.21 equiv) in anhydrous THF (9.0 mL) at 0 °C under an argon atmosphere. After 5 min, the reaction mixture was allowed to warm to 23 °C. After 20 min, a mixture of trifluoroethanol and water (1:1, 4.5 mL) was added to the reaction mixture to enable formation of the allylic diazene intermediate. After 3 h, the reaction mixture was partitioned between diethyl ether (25 mL) and water (25 mL), and the aqueous layer was extracted with diethyl ether (2 × 25 mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated. The residue was purified by flash column chromatography on silica gel (100% ^{n}pentane) to give triene **5a** (71 mg, 87%). See above for characterization data.[6]



(E)-5-Phenylpent-2-ene (S5d, Table 1, Entry 4):[8]

DEAD (55 µL, 0.35 mmol, 1.1 equiv)_was added drop-wise to a solution of IPNBSH (89 mg, 0.35 mmol, 1.1 equiv), 5-phenylpent-1-en-3-ol (**S1d**, 50 mg, 0.31 mmol, 1 equiv), and triphenylphosphine (91 mg, 0.35 mmol, 1.1 equiv) in anhydrous THF (2.9 mL) at 0 °C under an argon atmosphere. After 5 min, the reaction mixture was allowed to warm to 23 °C. After 2 h, a mixture of trifluoroethanol and water (1:1, 2.9 mL) was added to the reaction mixture to enable the formation of the intermediate allyl diazene. After 2 h, the reaction mixture was partitioned between diethyl ether (25 mL) and water (25 mL) and the aqueous layer was extracted with diethyl ether (2 × 25mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated. The residue was purified by flash column chromatography on silica gel (100%

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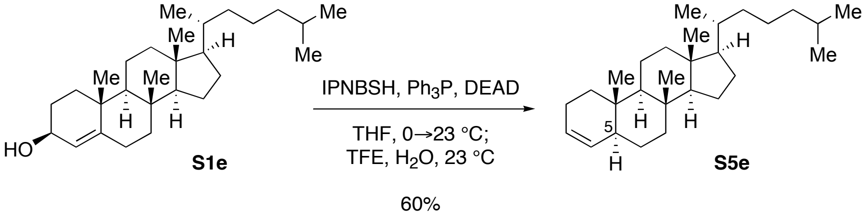
[7] For a prior synthesis of **S5c**, see Cleary, P. A.; Woerpel, K. A, *Org. Lett.*, **2005**, *7*, 5531.

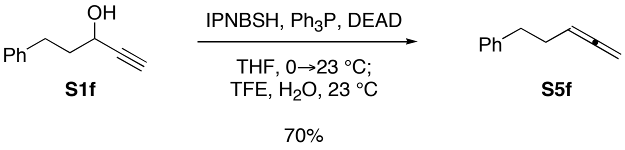
[8] For a prior synthesis of **S5d**, see Buss, A. D.; Warren, S. *J. Chem. Soc., Perkin Trans I,* **1985**, 2307 and Myers, A. G.; Zheng, B. *Tetrahedron Lett.* **1996**, *37*, 4841.

^{n}pentane) to give the alkene **S5d** (34 mg, 74%). TLC (pentane), *Rf*: 0.5 ($KMnO_4$). ^{1}H NMR (400 MHz) analysis revealed an *E*:*Z* ratio of 93:7. All spectroscopic data were in agreement with the literature.[8]



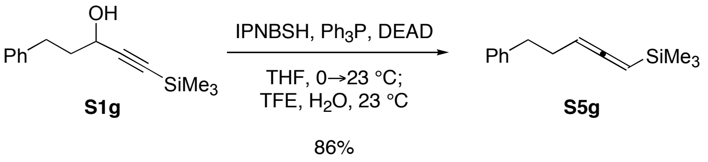
5α-Cholest-3-ene (S5e, Table 1, Entry 5):[9]

DEAD (45 μL, 0.28 mmol, 2.0 equiv) was added drop-wise to a solution of IPNBSH (72 mg, 0.28 mmol, 2.0 equiv), cholest-4-en-3β-ol (**S1e**, 54 mg, 0.14 mmol, 1 equiv), and triphenylphosphine (74 mg, 0.28 mmol, 2.0 equiv) in anhydrous THF (1.4 mL) at 0 °C under an argon atmosphere. After 5 min, the reaction mixture was allowed to warm to 23 °C. After 2 h, a mixture of trifluoroethanol and water (1:1, 0.7 mL) was added to the reaction mixture. After 2 h, the reaction mixture was diluted with water (25 mL) and extracted with diethyl ether (3 × 25mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated. The residue was purified by flash column chromatography on silica gel (100% hexanes) to give the alkene **S5e** (31 mg, 60%). TLC (Pentane), *Rf*: 0.8 (CAM). ^{1}H NMR (500 MHz) analysis revealed the presence of <8% of the C_5-diastereomers. All spectroscopic data were in agreement with the literature.[9]



5-Phenylpenta-1,2-diene (S5f, Table 1, Entry 6):[10]

DEAD (67.5 μL, 0.429 mmol, 1.20 equiv) was added drop-wise to a solution of IPNBSH (110 mg, 0.429 mmol, 1.20 equiv), 5-phenylpent-1-yn-3-ol (**S1f**, 57 mg, 0.36 mmol, 1 equiv), and triphenylphosphine (112 mg, 0.428 mmol, 1.20 equiv) in anhydrous THF (3.5 mL) at 0 °C under an argon atmosphere. After 5 min, the reaction mixture was allowed to warm to 23 °C. After 2 h, a mixture of trifluroethanol and water (1:1, 1.7 mL) was added to the reaction mixture to enable the formation of the propargylic diazene intermediate. After 2 h, the reaction mixture was partitioned between ^{n}pentane (25 mL) and water (25 mL). The organic layer was washed with water (2 × 25mL), was dried over anhydrous sodium sulfate, was filtered, and was concentrated. The residue was purified by flash column chromatography on silica gel (100% ^{n}pentane) to give the allene **S5f** (36 mg, 70%). TLC (100% ^{n}pentane), *Rf*: 0.6 (anis). All spectroscopic data were in agreement with the literature.[10]



Trimethyl-(5-phenylpenta-1,2-dienyl)-silane (S5g, Table 1, Entry 7):[11]

DEAD (43 μL, 0.27 mmol, 1.2 equiv) was added drop-wise to a solution of IPNBSH (69 mg, 0.27 mmol, 1.2 equiv), 5-phenyl-1-(trimethylsilyl)pent-1-yn-3-ol (**S1g**, 52 mg, 0.22, 1 equiv), and triphenylphosphine (71 mg, 0.27, 1.2 equiv) in anhydrous THF (2.2 mL) at 0 °C under an argon

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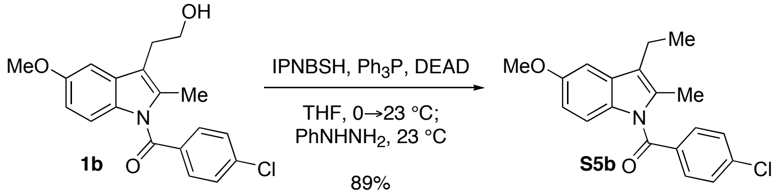
[9] For prior syntheses of **S5e**, see patent-JP,05-051329,A and Myers, A. G.; Zheng, B. *Tetrahedron Lett.* **1996**, *37*, 4841.

[10] For a prior synthesis of **S5f**, see Ohno, H.; Miyamura, K.; Tanaka, T. *J. Org. Chem.* **2002**, *67*, 1359.

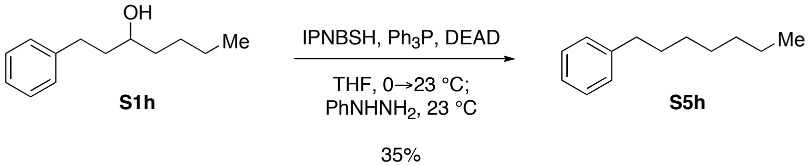
[11] For a prior synthesis of **S5g**, see Danheiser, R. L.; Carini, D. J., Fink, D. M., Basak, A. *Tetrahedron*, **1983**, *39*, 935.

atmosphere. After 5 min, the reaction mixture was allowed to warm to 23 °C. After 2 h, a mixture of trifluoroethanol and water (1:1, 1.1 mL) was added to the reaction mixture to enable the formation of the propargylic diazene intermediate. After 2.5 h, the reaction mixture was diluted with water (25 mL) and extracted with diethyl ether (3 × 25mL). The combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated. The residue was purified by flash column chromatography on silica gel (100% ^{n}pentane) to afford the allene **S5g** (41 mg, 86%). TLC (^{n}pentane), R*f*: 0.4 (UV, anis). All spectroscopic data were in agreement with the literature.[11]



1-(4-Chlorobenzoyl)-3-ethyl-5-methoxy-2-methyl-indole (S5b, Table 1, Entry 8):[12]

DEAD (44 µL, 0.28 mmol, 1.6 equiv) was added drop-wise to a solution of IPNBSH (71 mg, 0.28 mmol, 1.6 equiv), *N*-(4-chlorobenzoyl)-3-(2-hydroxyethyl)-5-methoxy-2-methylindole (**1b**, 59 mg, 0. 17 mmol, 1 equiv), and triphenylphosphine (73 mg, 0.28 mmol, 1.6 equiv) in anhydrous THF (1.7 mL) at 0 °C under an argon atmosphere. After 5 min, the reaction mixture was allowed to warm to 23 °C. After 30 min, phenylhydrazine (85 µL, 0.86 mmol, 5.0 equiv) was added via syringe and the mixture was kept at ambient temperature. After 4 h, the reaction mixture was diluted with diethyl ether (25 mL) and washed with water (25 mL). The aqueous layer was extracted with diethyl ether (2 × 25 mL), and the combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated. The residue was purified by flash column chromatography on silica gel (5% ethyl acetate in hexanes) to afford **S5b** (50 mg, 89%). TLC (5% ethyl acetate in hexanes), *Rf*: 0.3 (UV, CAM anis). All spectroscopic data were in agreement with the literature.[12]



1-Phenylheptane (S5h, Table 1, Entry 9):[12]

DEAD (290 µL, 1.84 mmol, 2.50 equiv) was added drop-wise to a solution of IPNBSH (474 mg, 1.84 mmol, 2.50 equiv), 1-phenylheptan-3-ol (**S1h**, 142 mg, 0.737 mmol, 1 equiv), and triphenylphosphine (485 mg, 1.85 mmol, 2.51 equiv) in anhydrous THF (5.2 mL) at 0 °C under an argon atmosphere. After 5 min, the reaction mixture was allowed to warm to 23 °C. After 20 h, phenyl hydrazine (360 µL, 3.67 mmol, 4.98 equiv) was added via syringe and the resulting mixture was kept at ambient temperature. After 13 h, the reaction mixture was partitioned between ^{n}pentane (25 mL) and water (25 mL). The organic layer was washed with water (4 × 25 mL), was dried over anhydrous sodium sulfate, was filtered, and was concentrated. The residue was purified by flash column chromatography (100% ^{n}pentane) to afford 1-heptylbenzene (**S5h**, 46 mg, 35%). TLC (30% EtOAc in hexanes), *Rf*: 0.9 (CAM). All spectroscopic data were in agreement with the literature.[12]

---

[12] For prior syntheses of **S5b** and **S5h**, see Myers, A. G.; Movassaghi, M.; Zheng, B. *J. Am. Chem. Soc.* **1997**, *119*, 8572.

Crystal Structure of IPNBSH.

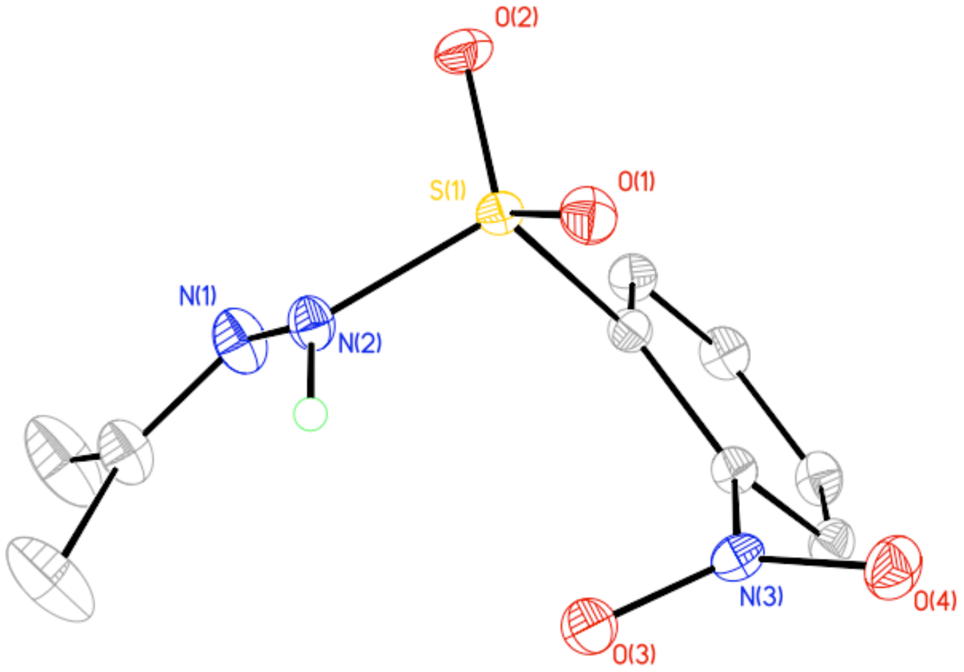


Table S1. Crystal data and structure refinement for IPNBSH.

Identification code	06182	
Empirical formula	C9 H11 N3 O4 S	
Formula weight	257.27	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.1746(3) Å	α= 90°.
	b = 15.1930(5) Å	β= 107.4690(10)°.
	c = 9.8516(3) Å	γ = 90°.
Volume	1167.11(7) Å^3	
Z	4	
Density (calculated)	1.464 Mg/m^3	
Absorption coefficient	0.285 mm^{-1}	
F(000)	536	
Crystal size	0.50 x 0.50 x 0.40 mm^3	
Theta range for data collection	2.55 to 29.57°.	
Index ranges	-10<=h<=11, -21<=k<=21, -13<=l<=13	
Reflections collected	22799	
Independent reflections	3274 [R(int) = 0.0201]	
Completeness to theta = 29.57°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8946 and 0.8707	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3274 / 1 / 159	
Goodness-of-fit on F^2	1.060	
Final R indices [I>2sigma(I)]	R1 = 0.0299, wR2 = 0.0848	
R indices (all data)	R1 = 0.0310, wR2 = 0.0858	
Largest diff. peak and hole	0.485 and -0.387 e.Å^{-3}	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for IPNBSH. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(4)	14328(1)	638(1)	10896(1)	19(1)
O(1)	10353(1)	1177(1)	10334(1)	16(1)
O(2)	8502(1)	2204(1)	8564(1)	19(1)
S(1)	9667(1)	1478(1)	8889(1)	13(1)
N(2)	8713(1)	623(1)	7983(1)	14(1)
N(1)	8126(1)	787(1)	6509(1)	20(1)
C(2)	7743(2)	110(1)	5704(1)	21(1)
C(1)	7901(2)	-824(1)	6199(1)	37(1)
C(3)	7091(2)	277(1)	4136(1)	42(1)
O(3)	12382(1)	-78(1)	9276(1)	17(1)
N(3)	13246(1)	580(1)	9726(1)	13(1)
C(4)	11421(1)	1759(1)	8265(1)	13(1)
C(5)	13012(1)	1342(1)	8763(1)	13(1)
C(6)	14415(1)	1592(1)	8345(1)	16(1)
C(8)	12641(1)	2704(1)	6852(1)	19(1)
C(9)	11247(1)	2452(1)	7304(1)	16(1)
C(7)	14214(1)	2279(1)	7368(1)	18(1)

Table S3. Bond lengths [Å] and angles [°] for IPNBSH.

O(4)-N(3)	1.2281(11)
O(1)-S(1)	1.4388(7)
O(2)-S(1)	1.4292(7)
S(1)-N(2)	1.6356(9)
S(1)-C(4)	1.7735(10)
N(2)-N(1)	1.4077(11)
N(1)-C(2)	1.2791(14)
C(2)-C(1)	1.4929(16)
C(2)-C(3)	1.4971(15)
O(3)-N(3)	1.2277(11)
N(3)-C(5)	1.4725(12)
C(4)-C(9)	1.3937(13)
C(4)-C(5)	1.3972(13)
C(5)-C(6)	1.3836(13)
C(6)-C(7)	1.3954(14)
C(8)-C(7)	1.3916(15)
C(8)-C(9)	1.3958(14)
O(2)-S(1)-O(1)	120.16(5)
O(2)-S(1)-N(2)	108.32(5)
O(1)-S(1)-N(2)	105.58(4)
O(2)-S(1)-C(4)	106.84(5)
O(1)-S(1)-C(4)	107.68(4)
N(2)-S(1)-C(4)	107.74(4)
N(1)-N(2)-S(1)	112.40(7)
C(2)-N(1)-N(2)	116.15(9)
N(1)-C(2)-C(1)	125.50(10)
N(1)-C(2)-C(3)	116.64(10)
C(1)-C(2)-C(3)	117.86(10)
O(3)-N(3)-O(4)	124.90(8)
O(3)-N(3)-C(5)	117.30(8)
O(4)-N(3)-C(5)	117.75(8)
C(9)-C(4)-C(5)	118.36(9)
C(9)-C(4)-S(1)	119.30(7)
C(5)-C(4)-S(1)	122.25(7)
C(6)-C(5)-C(4)	122.59(9)
C(6)-C(5)-N(3)	116.71(8)
C(4)-C(5)-N(3)	120.65(8)
C(5)-C(6)-C(7)	118.33(9)
C(7)-C(8)-C(9)	120.64(9)
C(4)-C(9)-C(8)	119.85(9)
C(8)-C(7)-C(6)	120.21(9)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters (Å^{2}x 10^3)for IPNBSH. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(4)	17(1)	23(1)	14(1)	2(1)	1(1)	2(1)
O(1)	17(1)	19(1)	12(1)	-1(1)	6(1)	-1(1)
O(2)	16(1)	17(1)	24(1)	-1(1)	7(1)	5(1)
S(1)	12(1)	13(1)	13(1)	-1(1)	5(1)	0(1)
N(2)	15(1)	14(1)	12(1)	1(1)	2(1)	-2(1)
N(1)	26(1)	19(1)	13(1)	2(1)	1(1)	-3(1)
C(2)	27(1)	19(1)	15(1)	1(1)	3(1)	-3(1)
C(1)	67(1)	18(1)	20(1)	-1(1)	3(1)	-3(1)
C(3)	72(1)	29(1)	14(1)	2(1)	-2(1)	-10(1)
O(3)	16(1)	14(1)	22(1)	1(1)	7(1)	-2(1)
N(3)	12(1)	15(1)	14(1)	2(1)	5(1)	2(1)
C(4)	13(1)	13(1)	13(1)	-1(1)	5(1)	-1(1)
C(5)	14(1)	12(1)	12(1)	1(1)	4(1)	-1(1)
C(6)	13(1)	17(1)	17(1)	0(1)	5(1)	-2(1)
C(8)	23(1)	16(1)	18(1)	3(1)	7(1)	-2(1)
C(9)	17(1)	14(1)	16(1)	2(1)	4(1)	1(1)
C(7)	18(1)	19(1)	18(1)	1(1)	7(1)	-5(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for IPNBSH.

	x	y	z	U(eq)
H(2)	9188(18)	134(8)	8292(15)	17
H(1A)	9116	-978	6588	56
H(1B)	7356	-1211	5395	56
H(1C)	7333	-895	6938	56
H(3A)	7065	913	3958	63
H(3B)	5930	36	3757	63
H(3C)	7850	-8	3665	63
H(6)	15489	1304	8713	19
H(8)	12514	3171	6186	22
H(9)	10183	2751	6958	19
H(7)	15154	2457	7053	22

Table S6. Hydrogen bonds for IPNBSH [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...O(3)	0.851(12)	2.518(13)	3.0751(11)	123.9(12)
N(2)-H(2)...O(1)#1	0.851(12)	2.374(13)	3.1702(11)	156.0(13)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y,-z+2

```
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tn                H1
at             3.001
np             63050
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fb          not used
bs                 2
tpwr              56
pw               8.9
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            -252.2
wp            6246.8
vs               120
sc                 0
wc               250
hzmm           24.99
is             33.57
rfl           4869.2
rfp           3633.1
th                 7
ins          100.000
nm  cdc  ph
```

```
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dn               C13
dpwr              30
dof                0
dm               nnn
dmm                w
dmf            10000
dseq
dres             1.0
homo               n
       PROCESSING
wtfile
proc              ft
fn            131072
math               f

werr
wexp
wbs
wnt              wft
```
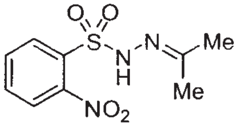
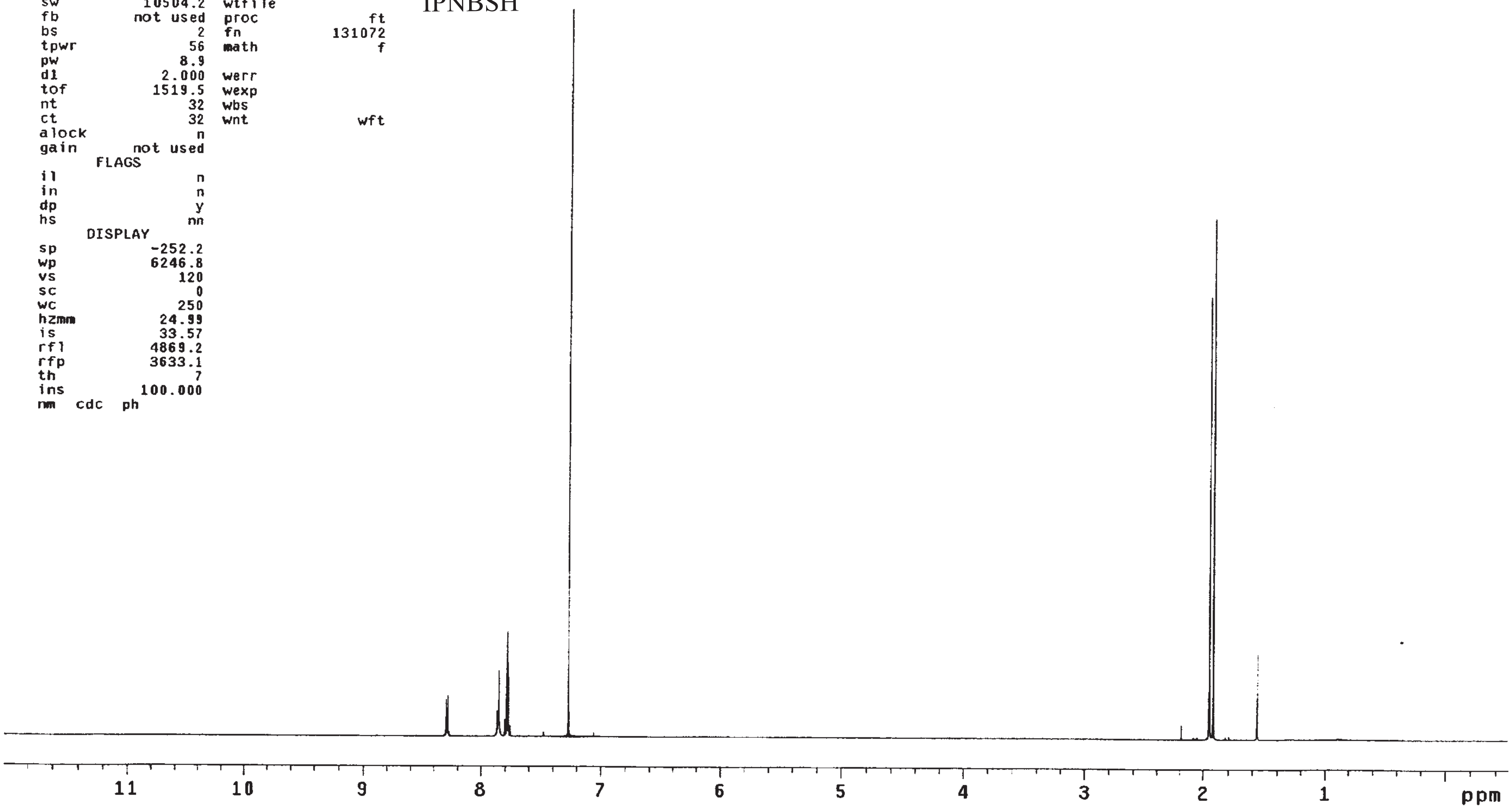
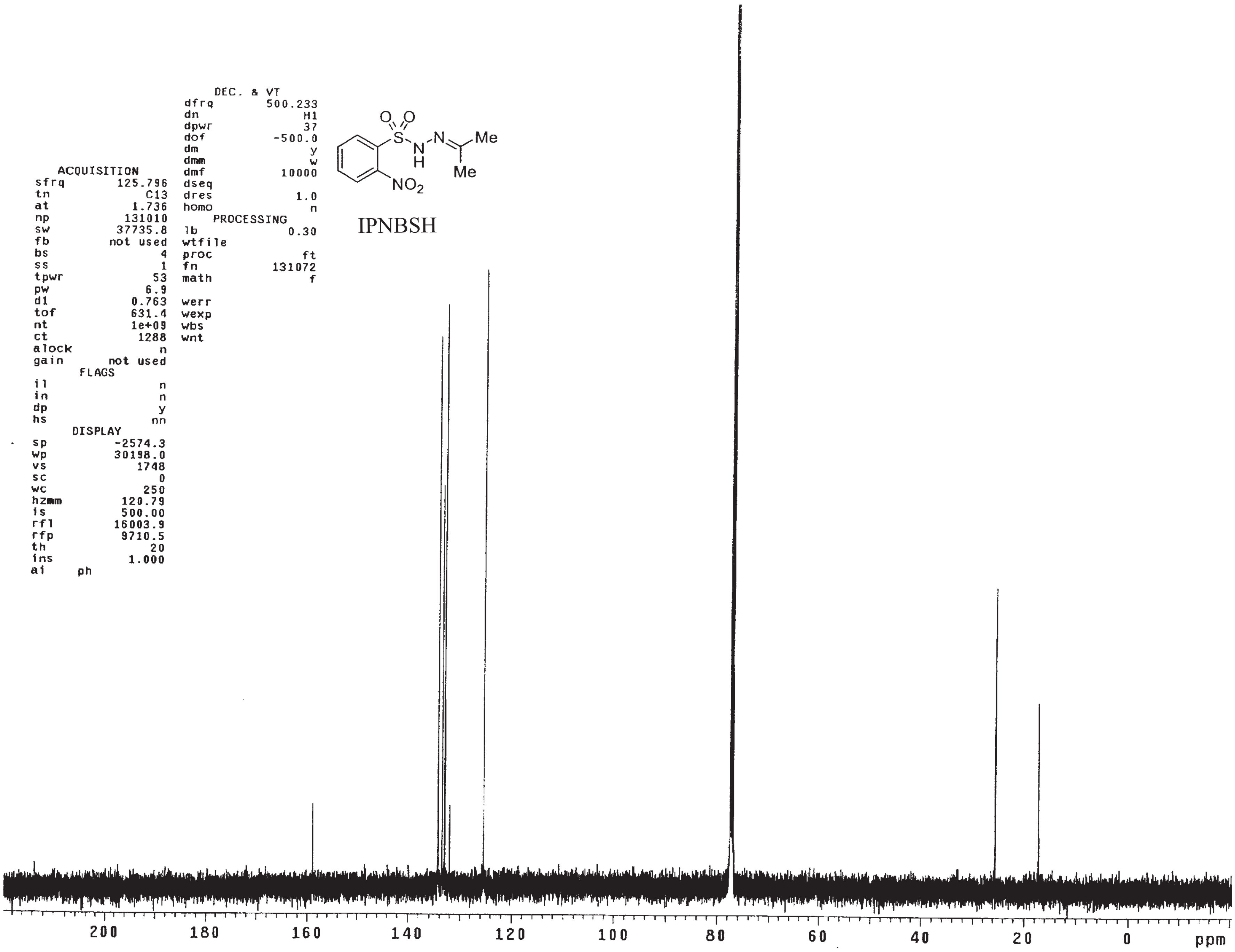



IPNBSH





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                          dm               y
                          dmm              w
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sfrq        125.796       dseq
tn              C13       dres           1.0
at            1.736       homo             n
np           131010          PROCESSING
sw          37735.8       lb            0.30
fb         not used       wtfile
bs                4       proc            ft
ss                1       fn          131072
tpwr             53       math             f
pw              6.9
d1            0.763       werr
tof           631.4       wexp
nt           1e+09        wbs
ct             1288       wnt
alock             n
gain       not used
       FLAGS
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in                n
dp                y
hs               nn
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wc              250
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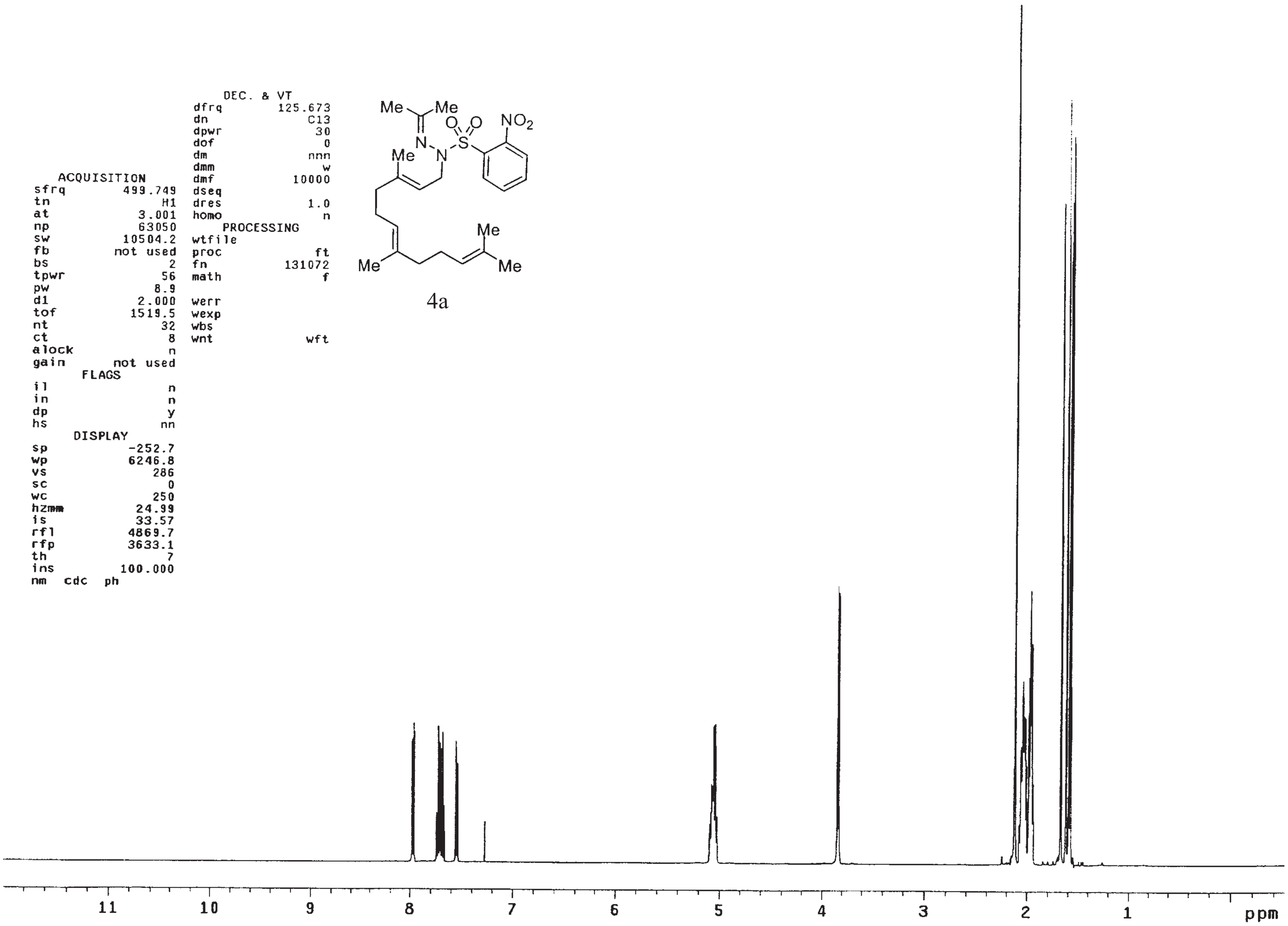
th               20
ins           1.000
ai     ph
```

IPNBSH



4a

```
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                      dm               nnn
                      dmm                w
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sfrq        499.749   dseq
tn               H1   dres             1.0
at            3.001   homo               n
np            63050      PROCESSING
sw          10504.2   wtfile
fb         not used   proc              ft
bs                2   fn            131072
tpwr             56   math               f
pw              8.9
d1            2.000   werr
tof          1519.5   wexp
nt               32   wbs
ct                8   wnt              wft
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
hs               nn
      DISPLAY
sp           -252.7
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vs              286
sc                0
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is            33.57
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th                7
ins         100.000
nm  cdc  ph
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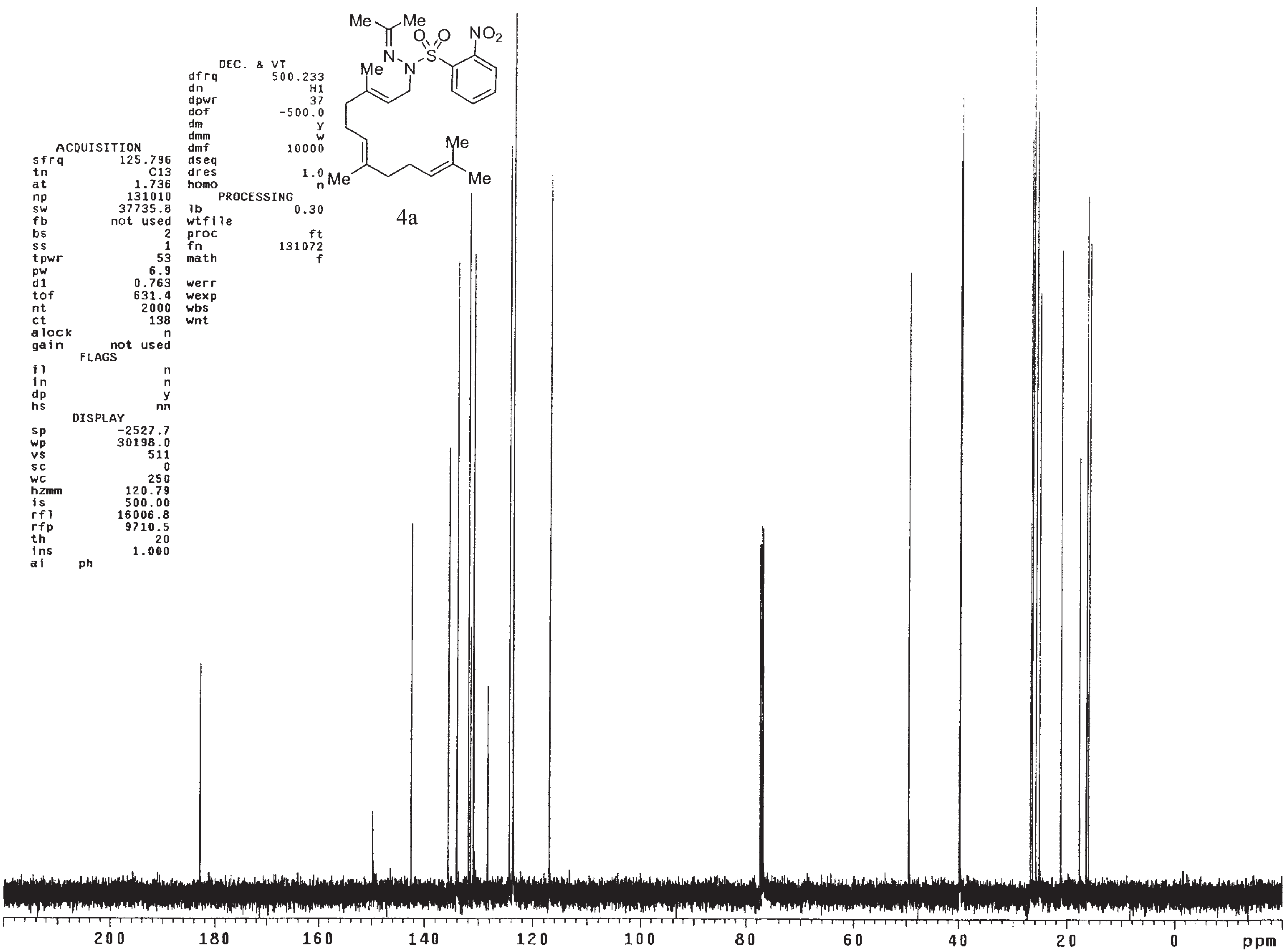

4a

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                       dmm                 w
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sfrq         125.796   dseq
tn               C13   dres              1.0
at             1.736   homo                n
np            131010        PROCESSING
sw           37735.8   lb               0.30
fb          not used   wtfile
bs                 2   proc               ft
ss                 1   fn             131072
tpwr              53   math                f
pw               6.9
d1             0.763   werr
tof            631.4   wexp
nt              2000   wbs
ct               138   wnt
alock              n
gain        not used
        FLAGS
il                 n
in                 n
dp                 y
hs                nn
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wp           30198.0
vs               511
sc                 0
wc               250
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rfl          16006.8
rfp           9710.5
th                20
ins            1.000
ai      ph
```

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                      dn            C13
                      dpwr           30
                      dof             0
                      dm            nnn
                      dmm             w
    ACQUISITION       dmf         10000
sfrq      499.749     dseq
tn             H1     dres          1.0
at          3.001     homo            n
np          63050        PROCESSING
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fb       not used     proc           ft
bs              2     fn         131072
tpwr           56     math            f
pw            8.9
d1          2.000     werr
tof        1519.5     wexp
nt             32     wbs
ct              0     wnt           wft
alock           n
gain     not used
      FLAGS
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in              n
dp              y
hs             nn
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wp         6246.8
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nm  cdc  ph
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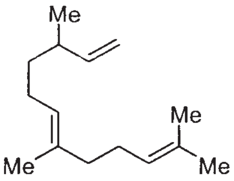
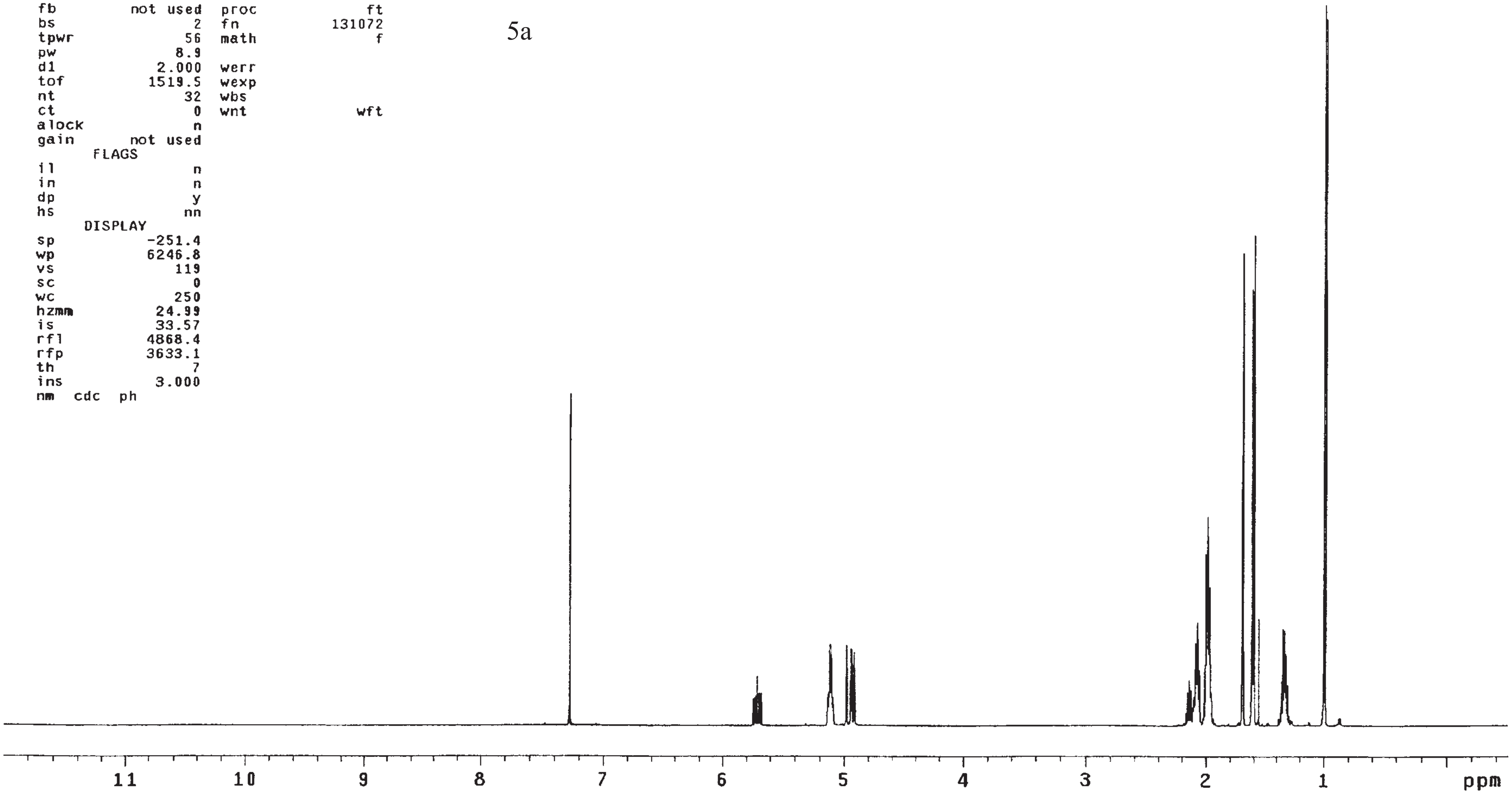


5a



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                     dmm               w
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sfrq       125.796   dseq
tn             C13   dres            1.0
at           1.736   homo              n
np          131010      PROCESSING
sw         37735.8   lb             0.30
fb        not used   wtfile
bs               1   proc             ft
ss               1   fn           131072
tpwr            53   math              f
pw             6.9
d1           0.763   werr
tof          631.4   wexp
nt           10000   wbs
ct               0   wnt
alock            n
gain      not used
     FLAGS
il               n
in               n
dp               y
hs              nn
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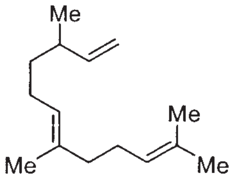
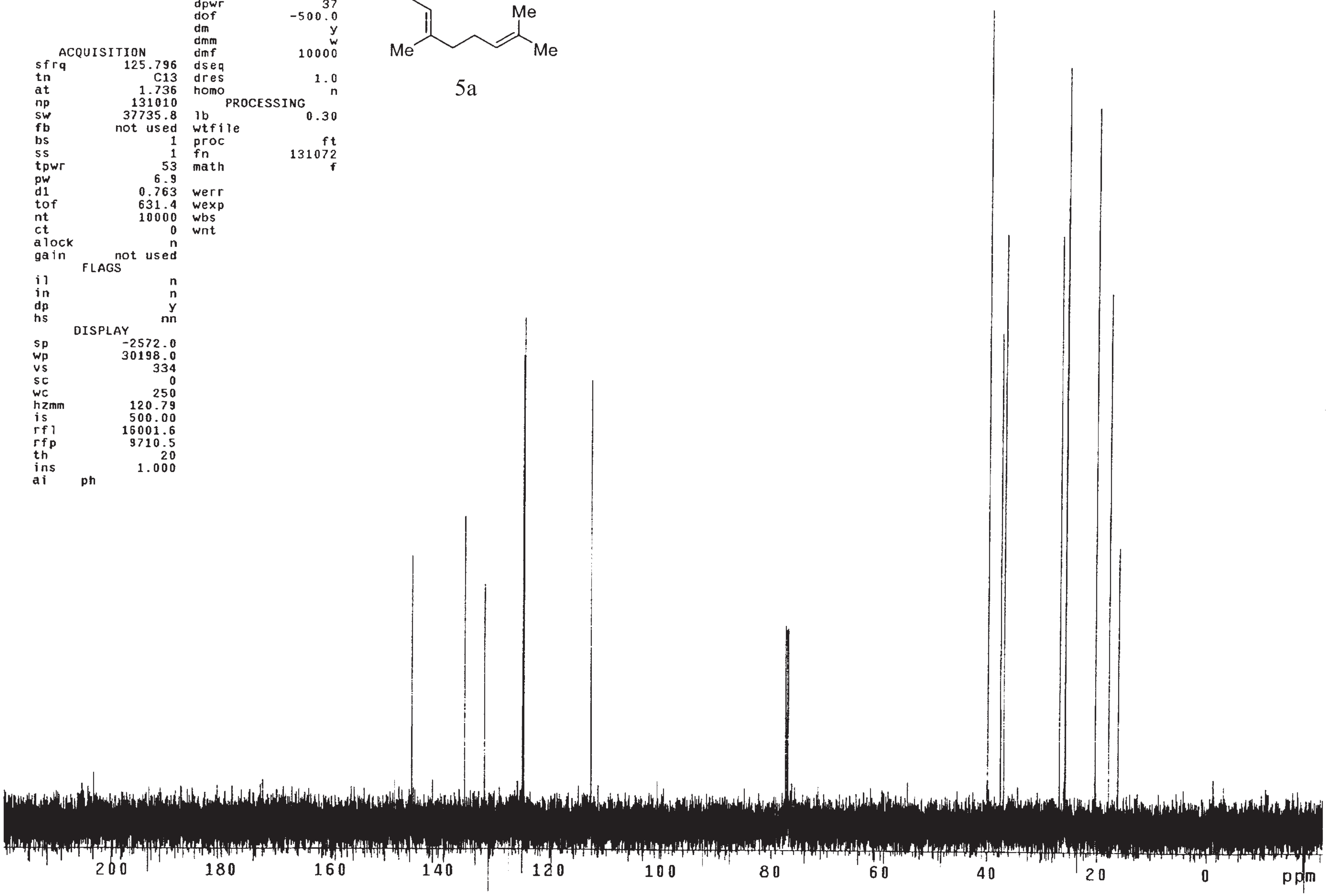
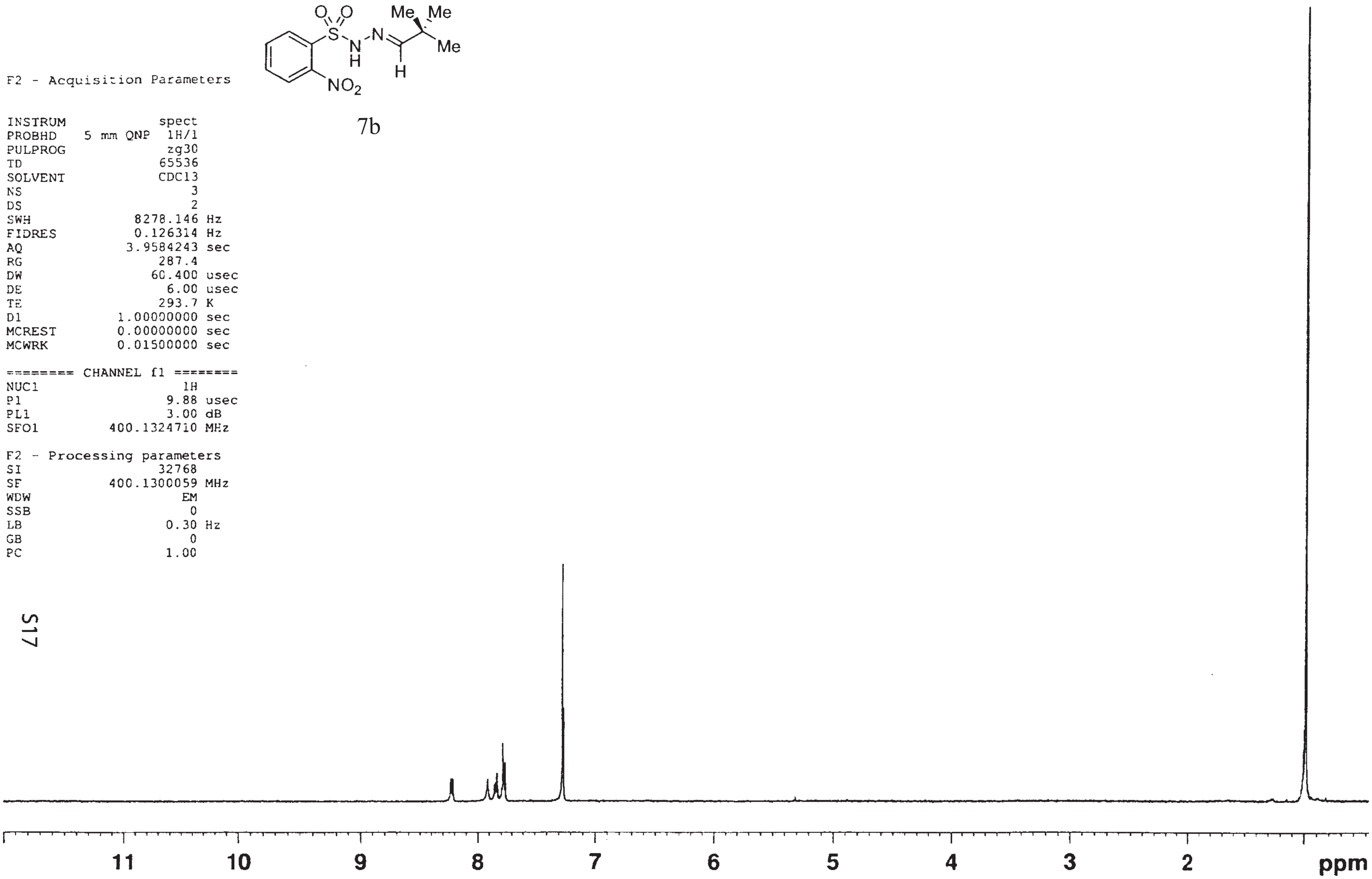


5a





7b

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F2 - Acquisition Parameters

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TD                   65536
SOLVENT              CDC13
NS                       3
DS                       2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                   287.4
DW                  60.400 usec
DE                    6.00 usec
TE                   293.7 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    9.88 usec
PL1                   3.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                   32768
SF             400.1300059 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

```
STANDARD CARBON PARAMETERS

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at          2.001       homo             n
np         125638          PROCESSING
sw        31397.2       lb            1.00
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bs              2       proc            ft
tpwr           58       fn          131072
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d1          3.000
tof             0       werr
nt          10000       wexp
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gain     not used
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in              n
dp              y
hs             nn
     DISPLAY
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wp        30158.7
vs           1419
sc              0
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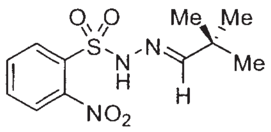

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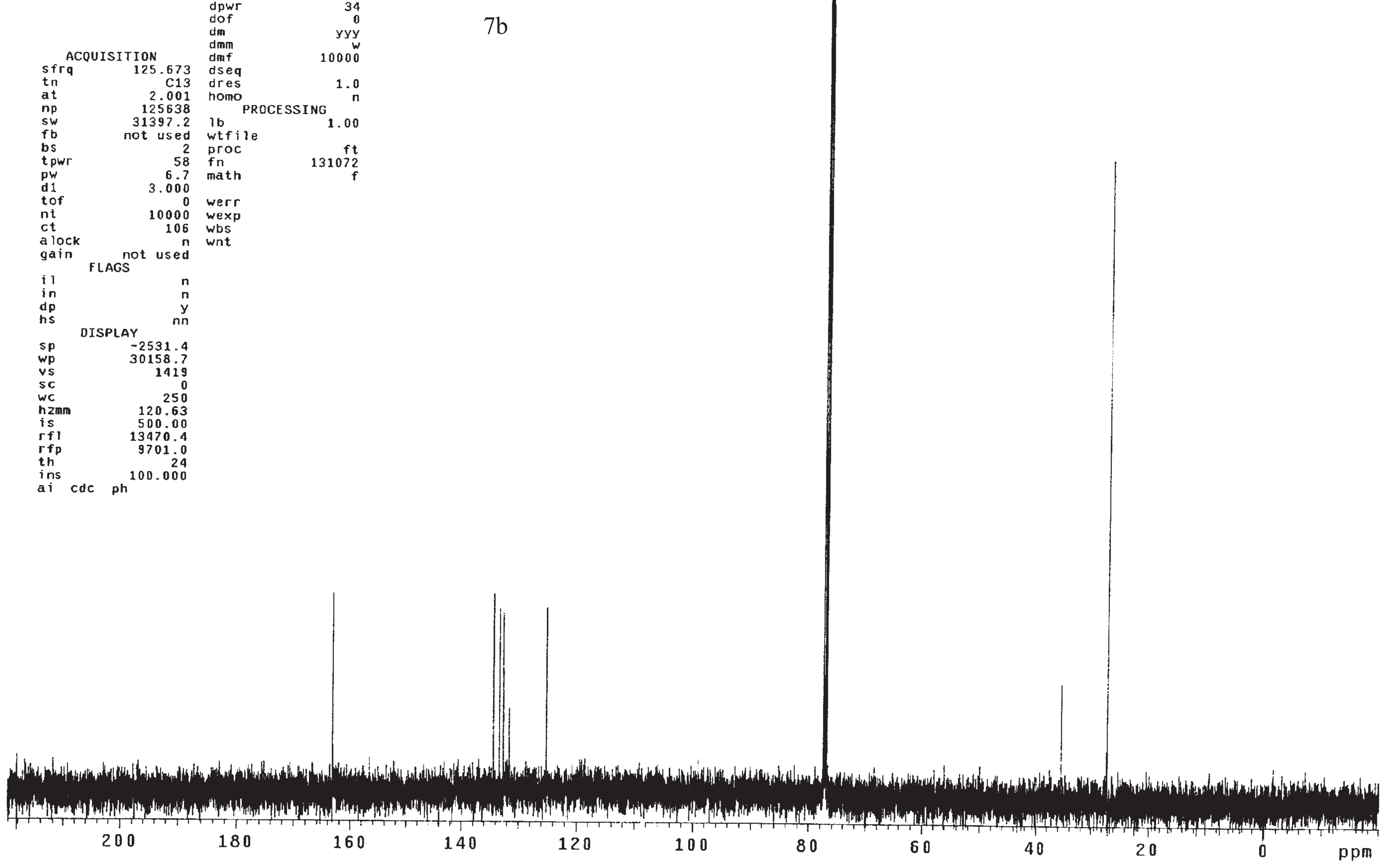

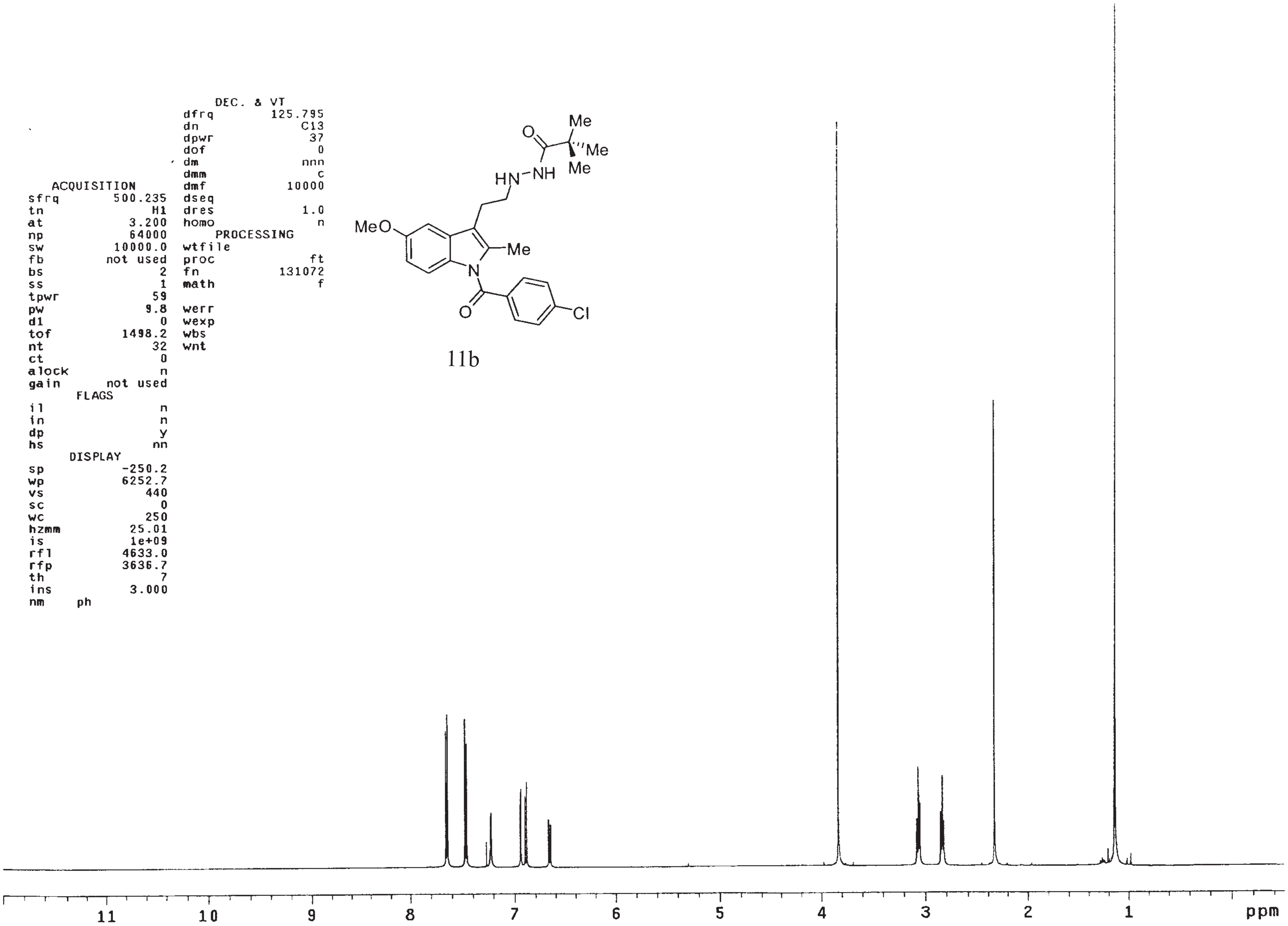

11b

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fb        not used   dmm               c
bs               2   dmf           10000
ss               1   dseq
tpwr            59   dres            1.0
pw             9.8   homo              n
d1               0        PROCESSING
tof         1498.2   wtfile
nt              32   proc             ft
ct               0   fn           131072
alock            n   math              f
gain      not used
      FLAGS          werr
il               n   wexp
in               n   wbs
dp               y   wnt
hs              nn
     DISPLAY
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wp          6252.7
vs             440
sc               0
wc             250
hzmm         25.01
is           1e+09
rfl         4633.0
rfp         3636.7
th               7
ins          3.000
nm    ph
```

```
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                              dn                 H1
                              dpwr               37
                              dof            -500.0
                              dm                  y
                              dmm                 w
      ACQUISITION             dmf             10000
sfrq         125.796          dseq
tn               C13          dres              1.0
at             1.736          homo                n
np            131010              PROCESSING
sw           37735.8          lb               0.30
fb          not used          wtfile
bs                 1          proc               ft
ss                 1          fn             131072
tpwr              53          math                f
pw               6.9
d1             0.763          werr
tof            631.4          wexp
nt             10000          wbs
ct                 0          wnt
alock              n
gain        not used
        FLAGS
il                 n
in                 n
dp                 y
hs                nn
       DISPLAY
sp           -2528.8
wp           30198.6
vs               232
sc                 0
wc               250
hzmm          120.79
is            500.00
rfl          16007.3
rfp           9710.5
th                20
ins            1.000
ai      ph
```
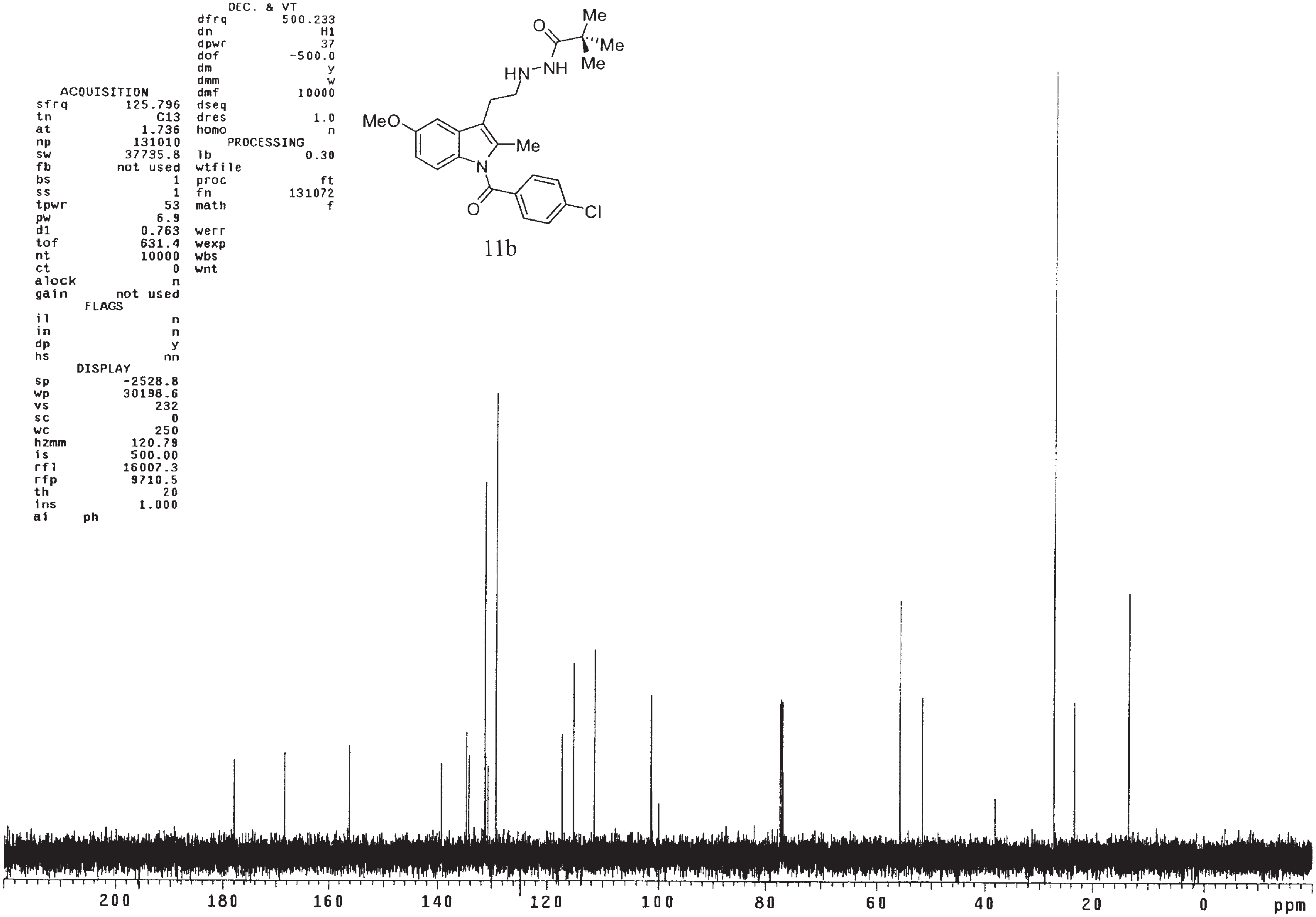
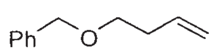
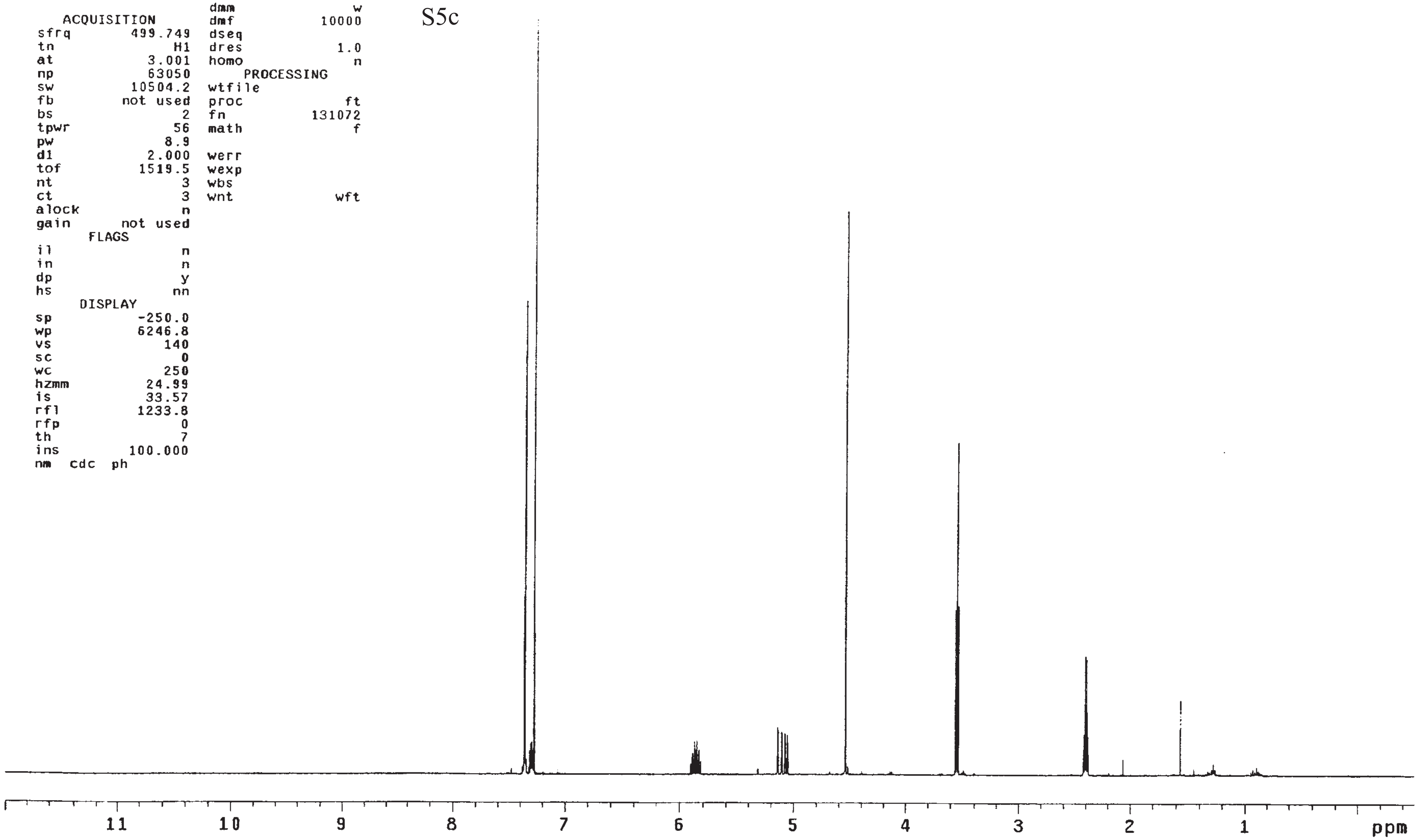



11b

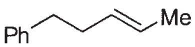


S5c

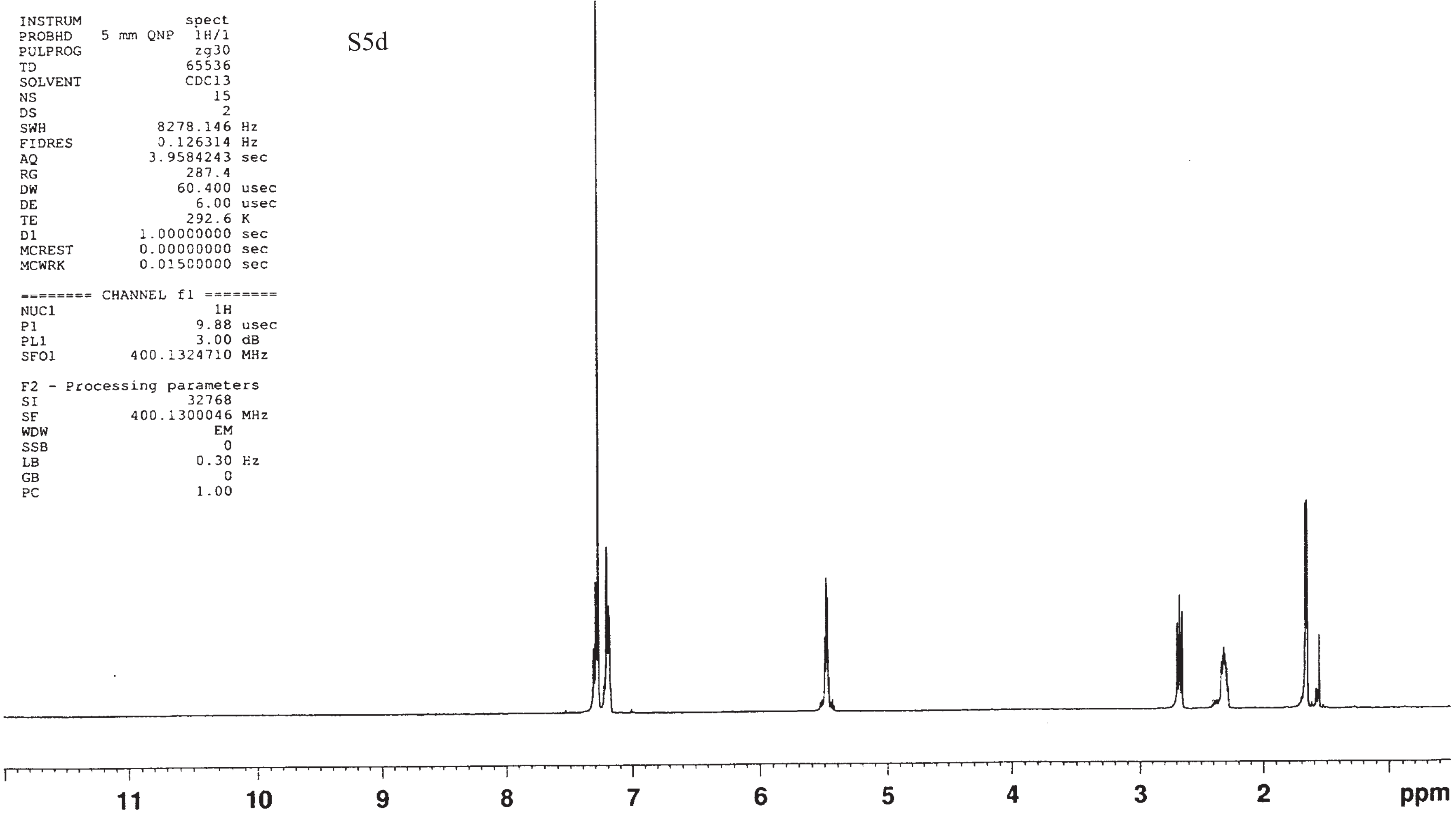


```
                            DEC. & VT
                        dfrq          125.673
                        dn                C13
                        dpwr               30
                        dof                 0
                        dm                nnn
                        dmm                 w
      ACQUISITION       dmf             10000
sfrq        499.749     dseq
tn               H1     dres              1.0
at            3.001     homo                n
np            63050         PROCESSING
sw          10504.2     wtfile
fb         not used     proc               ft
bs                2     fn             131072
tpwr             56     math                f
pw              8.9
d1            2.000     werr
tof          1519.5     wexp
nt                3     wbs
ct                3     wnt               wft
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
hs               nn
      DISPLAY
sp           -250.0
wp           6246.8
vs              140
sc                0
wc              250
hzmm          24.99
is            33.57
rfl          1233.8
rfp               0
th                7
ins         100.000
nm  cdc  ph
```

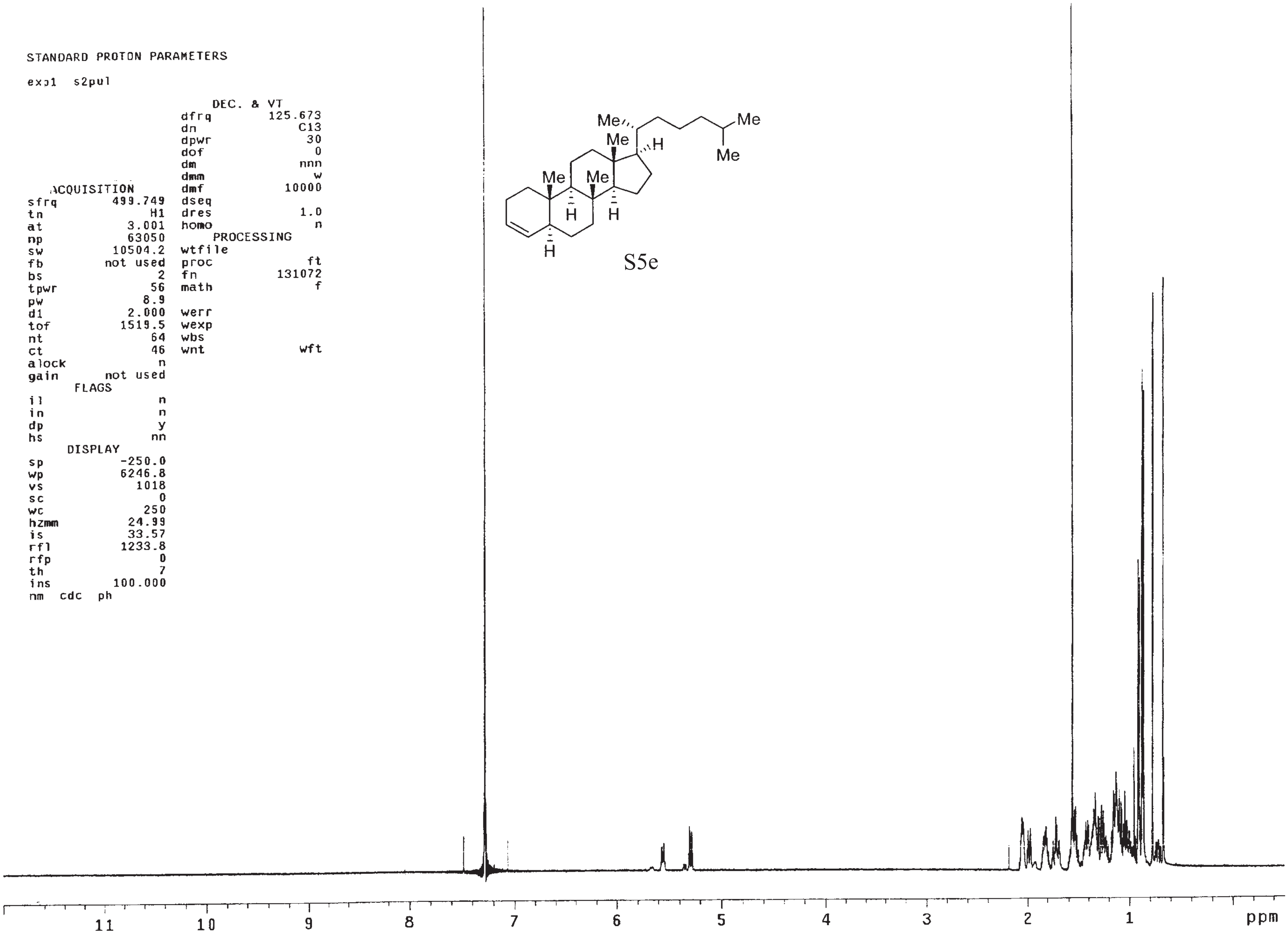
```
F2 - Acquisition Parameters

INSTRUM            spect
PROBHD   5 mm QNP  1H/1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    15
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 287.4
DW                60.400 usec
DE                  6.00 usec
TE                 292.6 K
D1            1.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.88 usec
PL1                 3.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300046 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



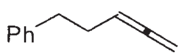
S5d



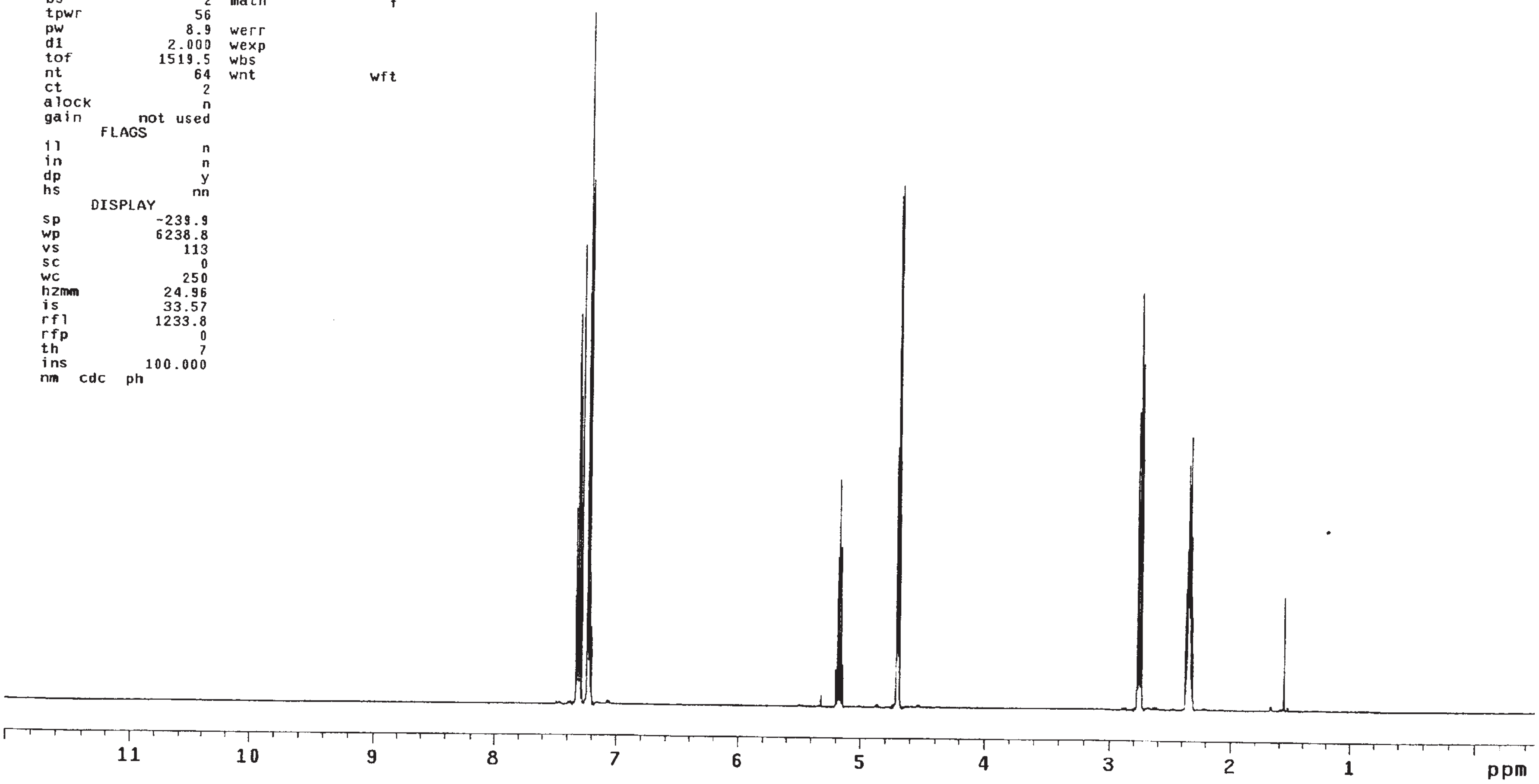
```
STANDARD PROTON PARAMETERS

exp1  s2pul

                          DEC. & VT
                     dfrq        125.673
                     dn              C13
                     dpwr             30
                     dof               0
                     dm              nnn
                     dmm               w
     ACQUISITION     dmf           10000
sfrq         499.749 dseq
tn                H1 dres            1.0
at             3.001 homo              n
np             63050      PROCESSING
sw           10504.2 wtfile
fb          not used proc             ft
bs                 2 fn           131072
tpwr              56 math              f
pw               8.9
d1             2.000 werr
tof           1519.5 wexp
nt                64 wbs
ct                46 wnt             wft
alock              n
gain        not used
       FLAGS
il                 n
in                 n
dp                 y
hs                nn
      DISPLAY
sp            -250.0
wp            6246.8
vs              1018
sc                 0
wc               250
hzmm           24.99
is             33.57
rfl           1233.8
rfp                0
th                 7
ins          100.000
nm  cdc  ph
```



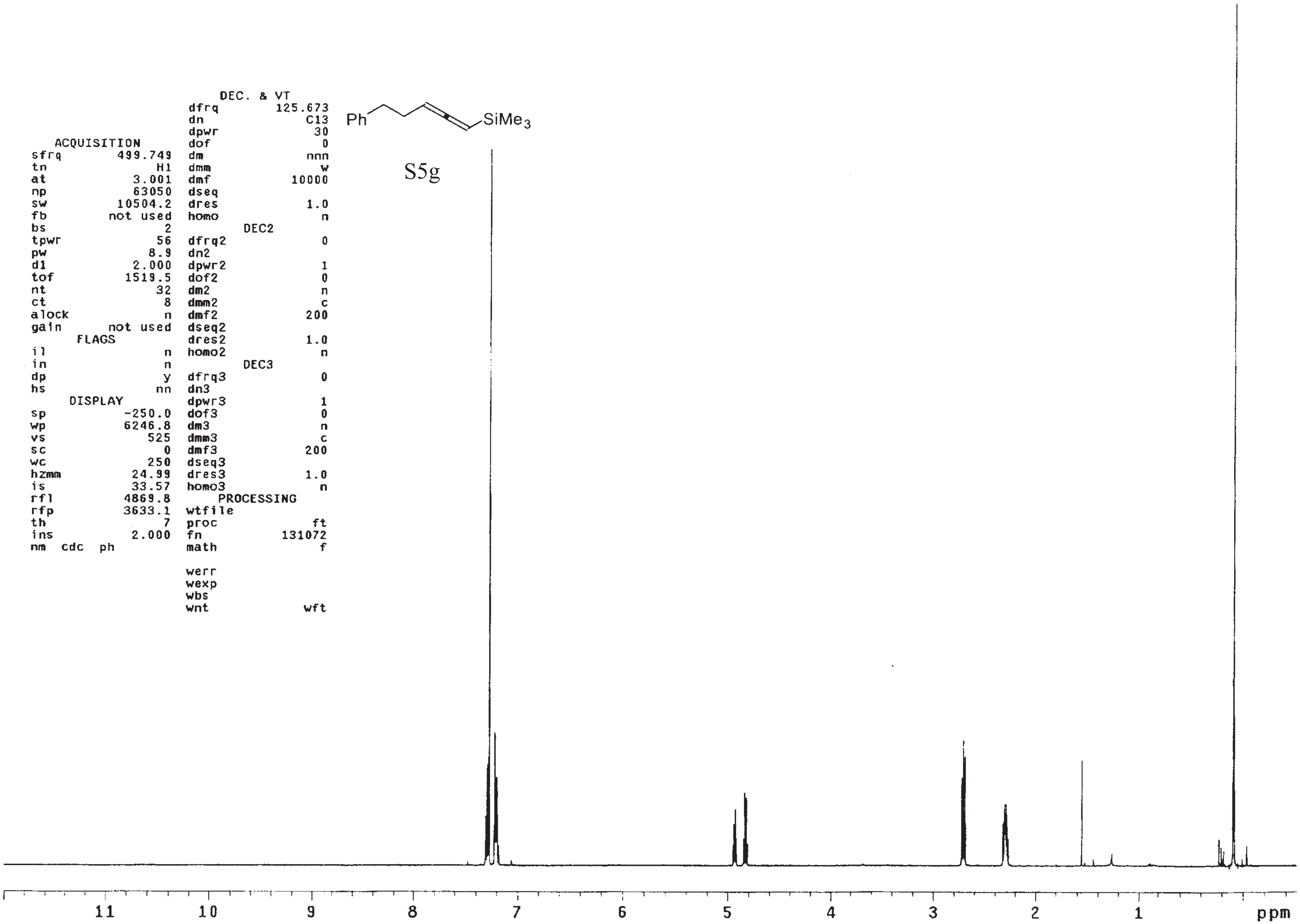
S5e



S5f

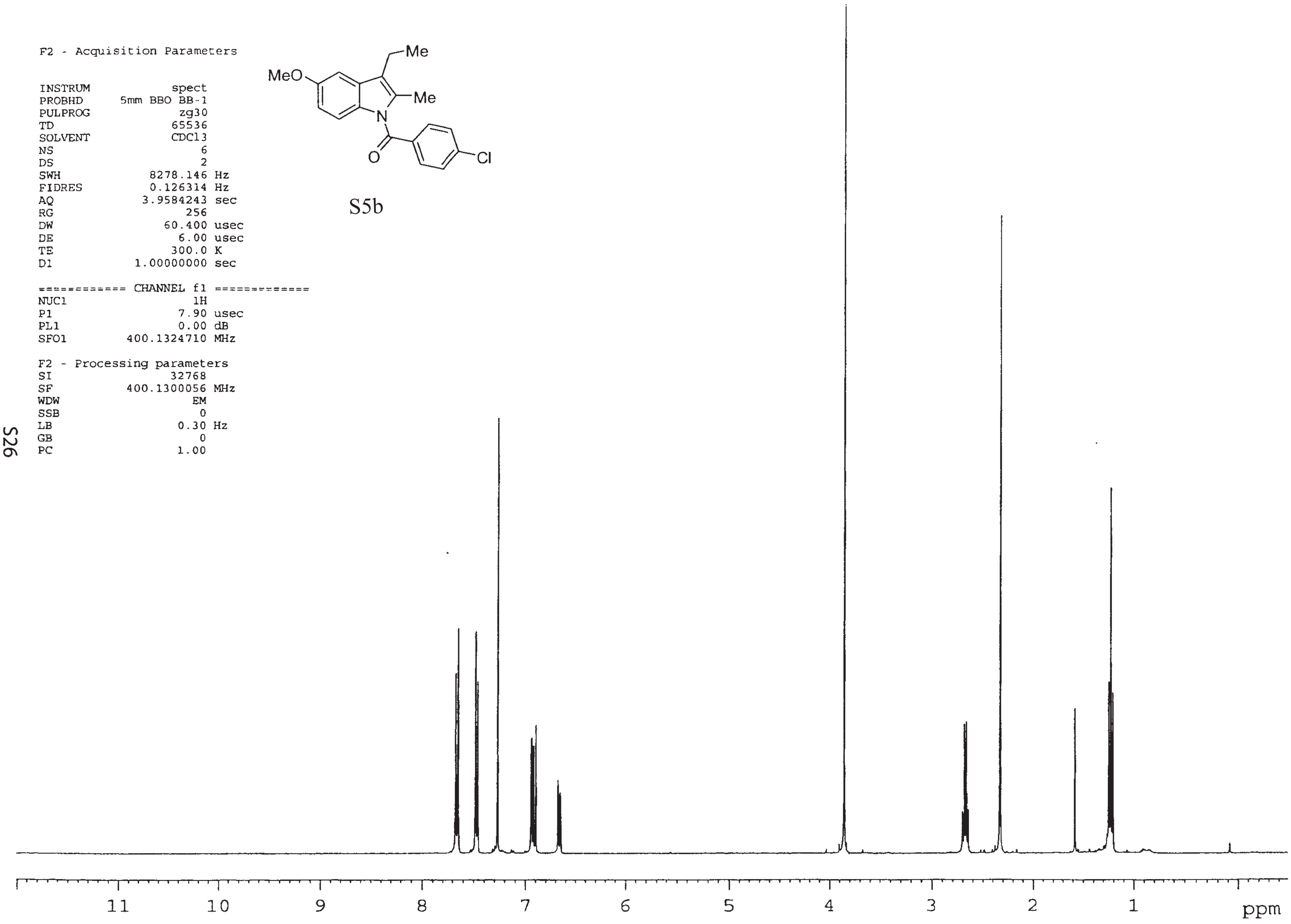


```
      ACQUISITION
sfrq        499.749
tn               H1
at            3.001
np            63050
sw          10504.2
fb         not used
bs                2
tpwr             56
pw              8.9
d1            2.000
tof          1519.5
nt               64
ct                2
alock             n
gain       not used
        FLAGS
il                n
in                n
dp                y
hs               nn
       DISPLAY
sp           -239.9
wp           6238.8
vs              113
sc                0
wc              250
hzmm          24.96
is            33.57
rfl          1233.8
rfp               0
th                7
ins         100.000
nm  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
     PROCESSING
wtfile
proc             ft
fn           131072
math              f

werr
wexp
wbs
wnt             wft
```



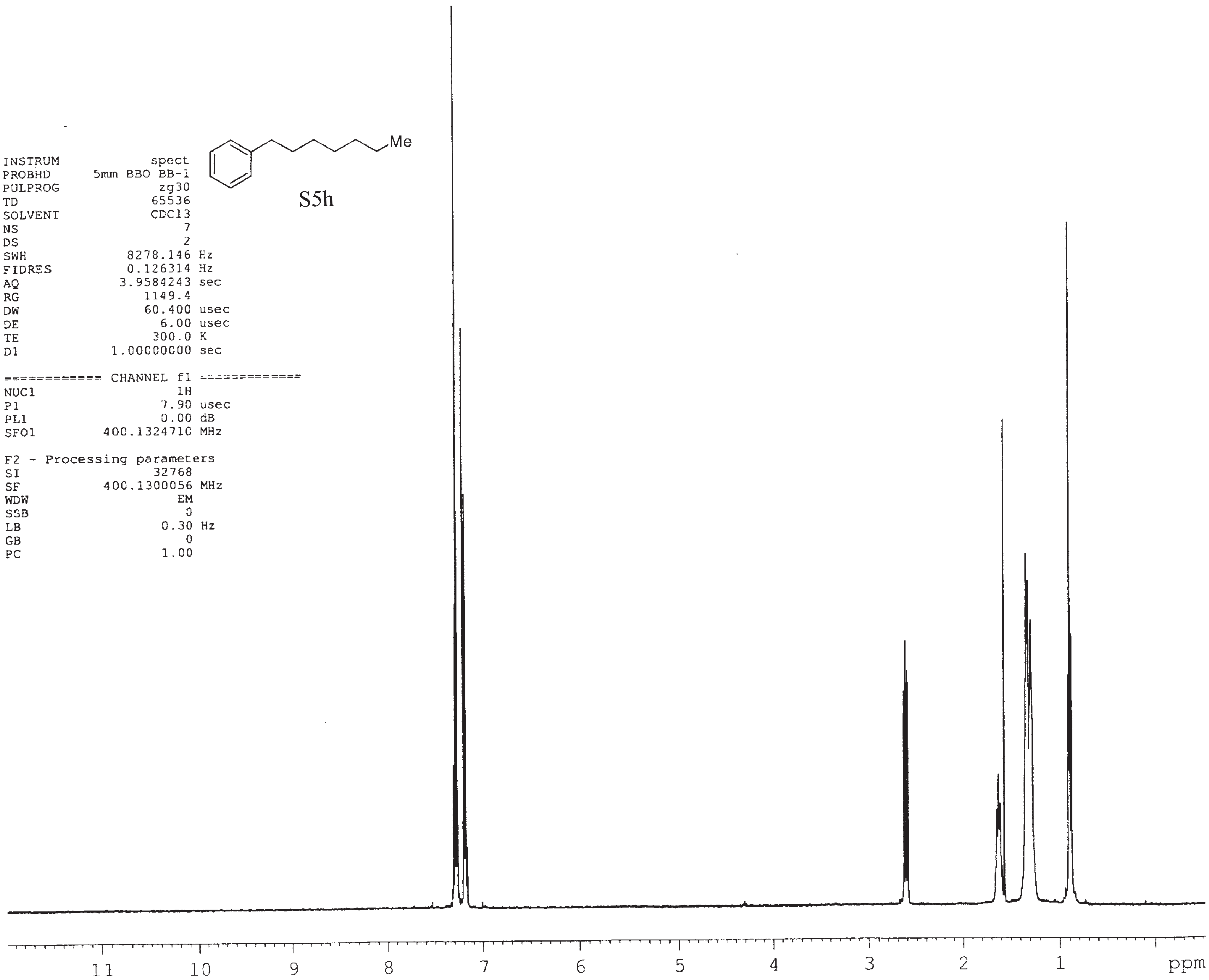
S5g

```
                          DEC. & VT
                      dfrq       125.673
                      dn             C13
                      dpwr            30
    ACQUISITION       dof              0
sfrq       499.749    dm             nnn
tn              H1    dmm              w
at           3.001    dmf          10000
np           63050    dseq
sw         10504.2    dres           1.0
fb        not used    homo             n
bs               2            DEC2
tpwr            56    dfrq2            0
pw             8.9    dn2
d1           2.000    dpwr2            1
tof         1519.5    dof2             0
nt              32    dm2              n
ct               8    dmm2             c
alock            n    dmf2           200
gain      not used    dseq2
      FLAGS           dres2          1.0
il               n    homo2            n
in               n            DEC3
dp               y    dfrq3            0
hs              nn    dn3
     DISPLAY          dpwr3            1
sp          -250.0    dof3             0
wp          6246.8    dm3              n
vs             525    dmm3             c
sc               0    dmf3           200
wc             250    dseq3
hzmm         24.99    dres3          1.0
is           33.57    homo3            n
rfl         4869.8        PROCESSING
rfp         3633.1    wtfile
th               7    proc            ft
ins          2.000    fn          131072
nm  cdc  ph           math             f

                      werr
                      wexp
                      wbs
                      wnt            wft
```



S5b

```
F2 - Acquisition Parameters

INSTRUM          spect
PROBHD      5mm BBO BB-1
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                   6
DS                   2
SWH           8278.146 Hz
FIDRES        0.126314 Hz
AQ           3.9584243 sec
RG                 256
DW              60.400 usec
DE                6.00 usec
TE               300.0 K
D1          1.00000000 sec

============ CHANNEL f1 =============
NUC1                1H
P1                7.90 usec
PL1               0.00 dB
SFO1       400.1324710 MHz

F2 - Processing parameters
SI               32768
SF         400.1300056 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```



S5h

```
INSTRUM              spect
PROBHD       5mm BBO BB-1
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      7
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                 1149.4
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec

============ CHANNEL f1 ============
NUC1                   1H
P1                   7.90 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300056 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```