Strategies for Expanding Structural Diversity Available from Olefin Isomerization-Claisen Rearrangement Reactions

Supporting Information

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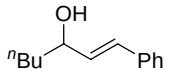
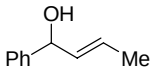
General Information: Unless otherwise stated all reactions were performed in dry glassware under an atmosphere of oxygen free nitrogen using standard inert atmosphere techniques for the manipulation of solvents and reagents. Anhydrous solvents were obtained by passing through successive alumina columns on a solvent purification system. $[IrCl(C_8H_{14})_2]_2$[1] and PCy_3 were stored and weighed out in a glove box. Acetone was distilled from Drierite and stored under dry nitrogen. Pinacolborane was purchased from Aldrich, distilled under partial vacuum, and stored under nitrogen in a freezer. Chemical shifts are reported relative to residual C**H**Cl_3 (7.27 ppm) for ^{1}H, and **C**DCl_3 (77.0 ppm) or **C**D_3CN (1.39 ppm) for ^{13}C NMR spectra. Reactions conducted using microwave irradiation were performed using a CEM Discover microwave reactor with internal temperature monitoring using an integrated infrared detector.

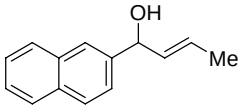


1-Phenyl-hept-1-en-3-ol (7a):[2] To 1.90 mL (2.00 g, 15.1 mmol) of cinnamaldehyde in 15 mL of Et_2O at –78°C was added 10.4 mL (16.6 mmol) of *n*-butyl lithium in hexanes (1.6 M) *via* syringe. The mixture was stirred at –78 °C for 30 min, then quenched carefully with sat. aq. NH_4Cl. The aqueous layer was extracted with Et_2O (3x), the combined organic layers were dried over Na_2SO_4, filtered and the crude product mixture was concentrated *in vacuo*. Purification by flash chromatography on SiO_2 (7.5:1 hexanes/EtOAc) yielded 2.57 g (89 %) of the title compound as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46-7.22 (m, 5H), 6.58 (d, J = 16.0 Hz, 1H), 6.23 (dd, J = 15.9, 6.8 Hz, 1H), 4.29 (q, J = 6.5 Hz, 1H), 1.69-1.50 (m, 2H), 1.49-1.30 (m, 4H), 0.93 (t, J = 6.7 Hz, 3H).

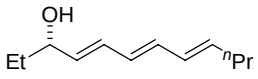
[1] Onderdelinden, A. L.; van der Ent, A. *Inorg. Chim. Acta* **1972**, *6*, 420.
[2] Trost, B. M.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 2027.



1-Phenyl-but-2-en-1-ol (7b):[3] To 4.74 g (3.18 mL, 30.2 mmol) of bromobenzene in 200 mL of Et_2O at –78°C was added 35.5 mL (60.4 mmol) of *tert*-butyllithium in pentane (1.7 M). Following 1 h, 2.51 mL (2.12 g, 30.2 mmol) of crotonaldehyde was added slowly *via* syringe, and the mixture was stirred an additional 20 min. The reaction was quenched carefully with water and slowly raised to ambient temperature. The aqueous layer was extracted with Et_2O (3x), the combined organic layers were dried over Na_2SO_4, filtered and the crude product mixture was concentrated *in vacuo*. The crude product was used as isolated: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.27 (m, 5H), 5.85-5.67 (m, 2H), 5.18 (br. dd, *J* = 6.4, 3.2 Hz, 1H), 1.85 (d, *J* = 3.5 Hz, 1H), 1.73 (d, *J* = 5.5 Hz, 3H).



1-Naphthalen-2-yl-but-2-en-1-ol (7c):[4] To 1.2 g (49 mol) of mechanically activated Mg(0) was added 15 mL of THF and I_2 (cat., in 0.5 mL of THF). Initiation was afforded by brief warming with a heatgun (brown → clear/white color shift), after which 0.010 kg (48 mmol) of 2-bromonapthalene in 10 mL of THF was carefully added over 30 min to maintain a gentle reflux. The mixture was refluxed 15 min longer with a heatgun, then stirred at ambient temperature for 1 h. In a separate flask, 4.8 mL (4.1 g) of crotonaldehyde was dissolved in 19 mL of THF and the temperature reduced to –78°C. The active Grignard reagent was added *via* syringe over 15 min and after 1 h, the reaction was quenched carefully with sat. aq. NH_4Cl and raised to ambient temperature. The aqueous layer was extracted with Et_2O (3x), the combined organic layers were dried over Na_2SO_4, filtered and the crude product mixture was concentrated *in vacuo*. The product was purified by flash chromatography on SiO_2 (6:1 hexanes/EtOAc) to afford 7.5 g (79%) of the product as a highly viscous, yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86-7.82 (m, 4H), 7.51-7.45 (m, 3H), 5.90-5.73 (m, 2H), 5.35 (d, *J* = 5.1 Hz, 1H), 2.00 (s, 1H), 1.76 (d, *J* = 5.6 Hz, 3H).

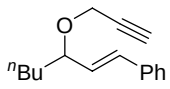


(*S*,4*E*,6*E*,8*E*)-Dodeca-4,6,8-trien-3-ol (7d): Both the trienal aldehyde and MIB ligand were prepared according to literature procedures.[5,6] To a solution of 41 mg (0.17 mmol) of MIB in 3.3 mL toluene was added 6.6 mL (6.6 mmol) of Et_2Zn in hexanes (1.0 M) at ambient temperature. Following 30 min, the flask was immersed in an ice bath and 0.50 g (3.3 mmol) of the aldehyde was added dropwise by syringe. The reaction was stirred at 0 °C for 30 min, then quenched carefully with sat. aq. Rochelle's salt and stirred vigorously for 30 min while warming to ambient temperature. The aqueous layer was extracted with EtOAc (3x), the combined organic layers were dried over Na_2SO_4, filtered, and the crude product mixture was concentrated *in vacuo*. Purification by flash chromatography on SiO_2 (6:1 hexanes/EtOAc) yielded 0.43 g (73%) of the title compound as a clear oil. Separation of the enantiomers by chiral HPLC (Daicel Chiracel^{TM} OD-H column, flow rate 1.0 ml/min, 2.0% *i*-PrOH, 98.0% hexanes) provided the enantiomeric ratio: (*S*)-**7d** (Tr = 12.1): (*R*)-**7d** (Tr = 13.3) 94.5:5.5 (89% ee): $[\alpha]_D$ = +24.0° (c 1.24, $CHCl_3$); IR (thin film) 3354, 3015, 2961, 1636, 1436, 995 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.26-6.18 (m, 2H), 6.11 (dd, *J* = 15.0, 10.4 Hz, 1H), 6.07 (dd, *J* = 15.0, 10.6 Hz, 1H), 5.73 (dt, *J* = 14.5, 7.1 Hz, 1H), 5.66 (dd, *J* = 15.2, 6.9 Hz, 1H), 4.11-4.06 (m, 1H), 2.09 (q, *J* = 7.2 Hz, 2H), 1.65-1.51 (m, 2H), 1.46-1.39 (m, 3H), 0.93 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.6, 135.0, 133.4, 130.9, 130.3, 129.6, 74.0, 34.8, 30.1, 22.4, 13.6, 9.6; MS (EI) *m/z* 180 (M^+), 162, 147, 133, 119, 105, 91; HRMS (EI) *m/z* calculated for $C_{12}H_{20}O_1$ (M^+): 180.1514, found 180.1506.

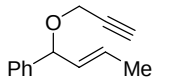
General Procedure A for Preparing Propargylic Ethers 5a-d: To 0.080 g (2.0 mmol) of sodium hydride (60% dispersion in mineral oil, pre-washed 3x with pentane) was added 1.4 mL of THF. The solution was cooled to 0 °C, and the allylic alcohol (1.0 mmol) was added *via* syringe or Pasteur pipette. The reaction was stirred at 0 °C for ~15 min, then warmed slowly to ambient temperature. At this time, a condenser was attached to the reaction vessel and the reaction mixture was heated to reflux for 30 min, whereupon 0.30 g (2.0 mmol) of propargyl

[3] Pocker, Y.; Hill, M. J. *J. Am. Chem. Soc.* **1969**, *91*, 3243.
[4] Dishington, A. P.; Douthwaite, R. E.; Mortlock, A.; Muccioli, A. B.; Simpkins, N. S. *J. Chem. Soc., Perkin Trans. 1*, **1997**, 323.
[5] Ishida, A.; Mukaiyama, T. *Bull. Chem. Soc. Japan* **1977**, *50*, 1161.
[6] Nugent, W. A. *Chem. Commun.* **1999**, 1369.

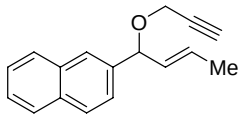
bromide in toluene (80%/wt) was added carefully through the condenser. Following 1 h at reflux, the solution was cooled to ambient temperature and quenched carefully with H_2O. The aqueous layer was extracted with Et_2O (3x), the combined organic layers were dried over $MgSO_4$, and the solvent was filtered and removed *in vacuo*. The product was purified as indicated.



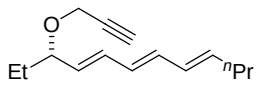
(3-Prop-2-ynyloxy-hept-1-enyl)benzene (5a): The general procedure **A** was followed employing 1.14 g (6.00 mmol) of allylic alcohol **7a**. Purification by flash chromatography on SiO_2 (40:1 hexanes/EtOAc) afforded 1.03 g (75%) of the product as a red-orange oil. Further purification was accomplished by distillation at low pressure (~100°C): IR (thin film) 3301, 3027, 2956, 2116, 1494, 1071, 969, 750, 693 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.43-7.24 (m, 5H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.03 (dd, *J* = 15.9, 8.3 Hz, 1H), 4.23 (dd, *J* = 15.6, 2.1 Hz, 1H), 4.08 (dd, *J* = 15.5, 2.1 Hz, 1H), 4.05 (q, *J* = 6.7 Hz, 1H), 2.42 (t, *J* = 2.2 Hz, 1H), 1.78-1.69 (m, 1H), 1.65-1.53 (m, 1H), 1.49-1.32 (m, 4H), 0.91 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.3, 133.0, 129.3, 128.5, 127.7, 126.4, 80.2, 79.6, 73.8, 55.0, 35.2, 27.4, 22.5, 13.9; MS (EI) *m/z* 228 (M^+), 198, 189, 171, 131, 85, 57; HRMS (EI) *m/z* calculated for $C_{16}H_{20}O$: 228.1514, found 228.1508.



(1-Prop-2-ynyloxy-but-2-enyl)benzene (5b): The general procedure **A** was followed employing 889 mg (6.00 mmol) of allylic alcohol **7b**. The product was purified by flash chromatography on SiO_2 (40:1 hexanes/EtOAc) to afford 939 mg (84%) of the product as a red-orange oil: IR (thin film) 3295, 3029, 2916, 2116, 1493, 1451, 1062, 968, 755, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.39-7.26 (m, 5H), 5.78 (dq, *J* = 15.3, 6.2 Hz, 1H), 5.60 (ddq, *J* = 15.3, 7.2, 1.3 Hz, 1H), 4.98 (d, *J* = 7.4 Hz, 1H), 4.17 (dd, *J* = 15.7, 2.4 Hz, 1H), 4.09 (dd, *J* = 15.7, 2.4 Hz, 1H), 2.42 (t, *J* = 2.4 Hz, 1H), 1.74 (dd, *J* = 6.4, 1.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.7, 131.1, 129.1, 128.3, 127.5, 126.8, 80.8, 79.9, 74.1, 54.7, 17.1; MS (EI) *m/z* 186 (M^+), 171, 147, 131, 105, 91, 77, 69; HRMS (EI) *m/z* calculated for $C_{13}H_{14}O$: 186.1045, found 186.1039.

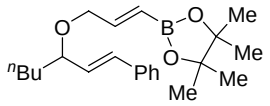


2-(1-Prop-2-ynyloxy-but-2-enyl)naphthalene (5c): The general procedure **A** was followed employing 1.42 g (7.16 mmol) of allylic alcohol **7c**, 0.480 g (12.0 mmol) of NaH, and 1.79 g (12.0 mmol) of propargyl bromide. Purification by flash chromatography on SiO_2 (50:1→25:1 hexanes/EtOAc) afforded 1.23 g (73%) of the product as a viscous, red-orange oil. Further purification was accomplished by distillation at low pressure (~120°C): IR (thin film) 3293, 3056, 2854, 2116, 1508, 1440, 1062, 967, 750 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.86-7.82 (m, 4H), 7.50-7.45 (m, 3H), 5.83 (dq, *J* = 15.2, 6.2 Hz, 1H), 5.68 (ddq, *J* = 15.4, 7.2, 1.4 Hz, 1H), 5.15 (d, *J* = 7.2 Hz, 1H), 4.22 (dd, *J* = 15.6, 2.3 Hz, 1H), 4.12 (dd, *J* = 15.8, 2.3 Hz, 1H), 2.45 (t, *J* = 2.4 Hz, 1H), 1.75 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.0, 133.2, 133.0, 131.0, 129.5, 128.2, 127.9, 127.6, 126.0, 125.8, 125.7, 124.8, 81.0, 79.9, 74.3, 55.0, 17.7; MS (EI) *m/z* 236 (M^+), 221, 197, 179, 155, 141, 127; HRMS (EI) *m/z* calculated for $C_{17}H_{16}O$: 236.1201, found 236.1201.

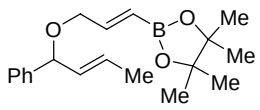


(*S*,4*E*,6*E*,8*E*)-3-(Prop-2-ynyloxy)dodeca-4,6,8-triene (5d): The general procedure **A** was followed employing 2.1 g (12 mmol) of trienyl alcohol **7d** with 1.5 h heating time. Purification by flash chromatography on SiO_2 (50:1 hexanes/EtOAc) afforded 2.2 g (83%) of the product as a yellow oil: $[\alpha]_D$ = –141 (c 1.32, $CHCl_3$); IR (thin film) 3307, 3016, 2962, 2116, 1636, 1463, 1072, 997, 663 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 6.27-6.04 (m, 4H), 5.75 (dt, *J* = 14.6, 7.0 Hz, 1H), 5.44 (dd, *J* = 15.4, 8.4 Hz, 1H), 4.17 (dd, *J* = 15.6, 2.3 Hz, 1H), 4.01 (dd, *J* = 15.7, 2.3 Hz, 1H), 3.84 (dt, *J* = 8.3, 6.5 Hz, 1H), 2.39 (t, *J* = 2.3 Hz, 1H), 2.09 (q, *J* = 7.2 Hz, 2H), 1.72-1.61 (m, 1H), 1.60-1.48 (m, 1H), 1.48-1.37 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.91 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.0, 133.8 (2C), 131.8, 130.2, 129.4, 80.9. 80.4, 73.6, 55.1, 34.9, 28.4, 22.4, 13.6, 9.7; MS (EI) *m/z* 218 (M^+), 189, 162, 133, 119, 107, 91, 79; HRMS (EI) *m/z* calculated for $C_{15}H_{22}O_1$ (M^+): 218.1671, found 218.1665.

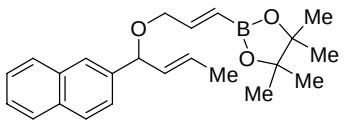
General Procedure B for Preparing Vinyl Boronic Esters 6a-d:[7] The alkyne (1.0 equiv) was added to a suspension of $Cp_2Zr(H)Cl$[8] (0.05 equiv) in CH_2Cl_2 (3.0 M) at 0 °C in a microwave reaction vessel. Pinacolborane (1.1 equiv) was added and the resulting suspension was warmed directly to ambient temperature, then heated at 100 °C in a microwave reactor for 45 min. The solvent was removed *in vacuo* and the residue purified by flash chromatography on Iatrobeads 6RS-8060 silica gel.



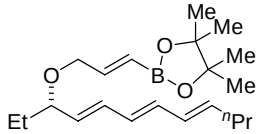
2-{(1*E*)-3-[(*E*)-1-Phenylhept-1-en-3-yloxy]prop-1-enyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6a): General Procedure **B** was followed employing 1.00 g of 1-[(*E*)-3-(prop-2-ynyloxy)hept-1-enyl]benzene (4.38 mmol). Purification by flash chromatography (5 % EtOAc/hexanes) gave 1.18 g (75 %) of the title compound as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-7.20 (m, 5H), 6.66 (dt, *J* = 18, 4.6 Hz, 1H), 6.49 (d, *J* = 16 Hz, 1H), 6.05 (dd, *J* = 16, 8.0 Hz, 1H), 5.73 (dt, *J* = 18, 1.8 Hz, 1H), 4.15 (ddd, *J* = 15, 4.4, 1.9 Hz, 1H), 3.96 (ddd, *J* = 15, 4.8, 1.8 Hz, 1H), 3.85 (dt, *J* = 6.5, 7.3 Hz, 1H), 1.78-1.50 (m, 2H), 1.27 (s, 12H), 1.40-1.24 (m, 4H), 0.89 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.8, 136.5, 132.0, 130.5, 128.4, 127.5, 126.3, 118.6 (br), 83.0, 80.4, 69.5, 35.5, 27.4, 24.6, 22.6, 14.0; MS (EI) *m/z* 356 (M^+), 341, 326, 299, 270, 257, 199, 173, 167, 155, 143, 131, 117, 105, 91, 85, 77, 67, 57; HRMS *m/z* calculated for $C_{22}H_{33}{}^{11}BO_3$: 356.2523, found 356.2523.



2-{(1*E*)-3-[(*E*)-1-Phenylbut-2-enyloxy]prop-1-enyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6b): General Procedure **B** was followed employing 1.14 g of 1-[(*E*)-1-(prop-2-ynyloxy)but-2-enyl]benzene (6.14 mmol). Purification by flash chromatography (5 % EtOAc/hexanes) gave 1.60 g (83 %) of the title compound as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.20 (m, 5H), 6.67 (dt, *J* = 18, 4.5 Hz, 1H), 5.76 (dt, *J* = 16, 1.8 Hz, 1H), 5.70 (ddq, *J* = 15, 5.9, 0.6 Hz, 1H), 5.57 (ddq, *J* = 15, 7.2. 1.2 Hz, 1H), 4.74 (d, *J* = 7.0 Hz, 1H), 4.07 (ddd, *J* = 15, 4.5, 1.8 Hz, 1H), 4.00 (ddd, *J* = 15, 4.5, 1.8 Hz, 1H), 1.70 (dd, *J* = 6.3, 1.3 Hz, 3H), 1.27 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.4, 141.5, 132.0, 128.2, 128.0, 127.2, 126.5, 118.9 (br), 83.0, 81.8, 69.3, 24.6, 17.6; MS (EI) *m/z* 314 (M^+), 299, 284, 271, 256, 230, 214, 208, 199, 169, 147, 131, 119, 91, 85, 69, 59; HRMS *m/z* calculated for $C_{19}H_{27}{}^{11}BO_3$: 314.2053, found 314.2060.



2-{(1*E*)-3-[(*E*)-1-(Naphthalen-2-yl)but-2-enyloxy]prop-1-enyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6c): General Procedure **B** was followed employing 1.00 g of 2-[(*E*)-1-(prop-2-ynyloxy)but-2-enyl]naphthalene (4.23 mmol). Purification by flash chromatography (8 % EtOAc/hexanes) gave 1.19 g (77 %) of the title compound as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (m, 4H), 7.46 (m, 3H), 6.70 (dt, *J* = 18, 4.5 Hz, 1H), 5.81-5.61 (m, 3H), 4.92 (d, *J* = 6.6 Hz, 1H), 4.11 (ddd, *J* = 15, 4.5, 1.8 Hz, 1H), 4.05 (ddd, *J* = 15, 4.5, 1.9 Hz, 1H), 1.72 (d, *J* = 5.8 Hz, 3H), 1.27 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.4, 138.9, 133.1, 132.8, 131.8, 128.2, 128.0, 127.8, 127.5, 125.8, 125.6, 125.2, 124.7, 118.8 (br), 83.0, 81.9, 69.3, 24.6, 17.6; MS (EI) *m/z* 364 (M^+), 349, 280, 197, 181, 169, 155, 141, 127, 115, 101, 85, 69, 59; HRMS *m/z* calculated for $C_{23}H_{29}{}^{11}BO_3$: 364.2210, found 364.2228.

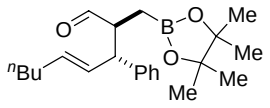


2-{(1*E*)-3-[(*S*,4*E*,6*E*,8*E*)-Dodeca-4,6,8-trien-3-yloxy]prop-1-enyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6d): General Procedure **B** was followed employing 0.88 g of (*S*,4*E*,6*E*,8*E*)-3-(prop-2-ynyloxy)dodeca-4,6,8-triene (4.0 mmol), heating at 80 °C for 45 min. Purification by flash chromatography (22:1 hexanes/EtOAc) gave 0.75 g (55%) of the title compound as a colorless oil: $[\alpha]_D$ = –14.2 (c 1.22, $CHCl_3$); IR (thin film) 2976, 1644, 1463, 1354, 1146, 996, 850, 628 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.64 (dt, *J* = 18.1, 4.5 Hz, 1H), 6.24-6.04 (m, 4H), 5.72 (dt, *J* = 14.9, 7.1 Hz, 1H), 5.71 (d, *J* = 18.0 Hz, 1H), 5.48 (dd, *J* = 14.4, 8.1 Hz, 1H), 4.10 (ddd, *J* = 14.7, 4.2, 1.7 Hz, 1H), 3.91 (ddd, *J* = 14.7, 4.7, 1.6 Hz, 1H), 3.66 (dt, *J* = 7.8, 6.5 Hz, 1H), 2.08 (q, *J* = 7.1, 2H), 1.70-1.62 (m, 1H), 1.56-1.49 (m, 1H), 1.46-1.38 (m, 2H), 1.27 (s, 12H), 0.91 (t, *J* = 7.5 Hz, 3H), 0.89 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.9, 135.6, 133.3, 133.2, 132.8, 130.3, 129.6,

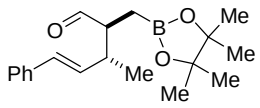
[7] A modification of the procedure described by: Pereira, S.; Srebnik, M. *Organometallics* **1995**, *14*, 3127-3128.
[8] Buchwald, S.; LaMaire, S.; Nielsen, R.; Watson, B.; King, S. *Org. Synth., Coll. Vol. IX* **1994**, 162.

118.6 (br), 83.1, 81.5, 69.6, 34.9, 28.6, 24.8, 22.4, 13.6, 9.7; MS (EI) *m/z* 346 (M^+), 317, 288, 248, 187, 179, 163, 107; HRMS (EI) *m/z* calculated for $C_{21}H_{35}BO_3$ (M^+): 346.2679, found 346.2679.

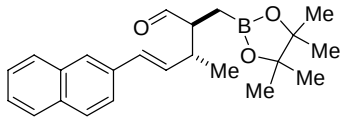
General Procedure C for Preparing β-Boronic Aldehydes 8 a-d: Note that distillation of propargylic ethers **5a-c** benefits the reproducibility of iridium catalyzed isomerizations. A solution of $[(^cC_8H_{14})_2IrCl]_2$ (1.0 mol%, 0.02 equiv Ir) and PCy_3 (6.0 mol%, 0.06 equiv) in anhydrous CH_2Cl_2 or 1,2-dichloroethane (1,2-DCE) was added to a solution of $NaBPh_4$ (2.0 mol%, 0.02 equiv) in and equal volume of CH_2Cl_2/acetone (25:1) or 1,2-DCE/acetone (25:1) (0.67M final concentration in substrate **6**) and the resulting yellow solution stirred for 5 min at ambient temperature. Allyl borolane **6** (1.0 equiv) was added and the reaction stirred for 90 min at ambient temperature whereupon PPh_3 (6.0 mol%, 0.06 equiv) was added and the resulting solution heated at (40 or 80 °C) for the indicated time. The solvent was removed *in vacuo* and the residue purified by flash chromatography on Iatrobeads 6RS-8060 silica gel. Diastereomeric ratios were determined by integration of the specified resonances from 300 MHz ^{1}H-NMR. Satisfactory mass spectral data could not be obtained for compounds **8a-d**; copies of ^{1}H and ^{13}C spectra are provided and mass spectral data is provided for all compounds derived from **8**.



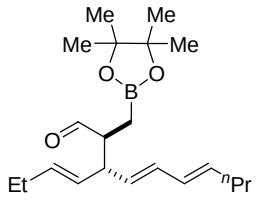
R*-(E,2R,3S)-2-[(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-3-phenylnon-4-enal (8a): General Procedure **C** (1,2-DCE, 80 °C) was followed employing 1.15 g of 2-((1E)-3-((E)-1-phenylhept-1-en-3-yloxy)prop-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.23 mmol) and a reaction time of 2.5 hours. Purification by flash chromatography (6 % EtOAc/hexanes) on Iatrobeads gave 0.772 g (67 %) of the title compound as a colorless oil (C**H**O, *anti:syn* = 92:8): ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.77 (d, *J* = 1.8 Hz, 1H), 7.35-7.25 (m, 2H), 7.25-7.15 (m, 3H), 5.67 (ddt, *J* = 15, 8.7, 1.2 Hz, 1H), 5.53 (dt, *J* = 15, 6.6 Hz, 1H), 3.53 (t, *J* = 8.6 Hz, 1H), 2.94 (m, 1H), 2.00 (m, 2H), 1.21 (s, 6H), 1.35-1.19 (m, 4H), 1.18 (s, 6H), 0.87 (m, 3H), 0.80 (dd, *J* = 16, 9.6 Hz, 1H), 0.68 (dd, *J* = 16, 5.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.1, 142.1, 132.9, 129.9, 128.4, 127.8, 126.4, 83.0, 52.6, 51.1, 32.1, 31.3, 24.7, 24.5, 22.0, 13.8, 9.7 (br).



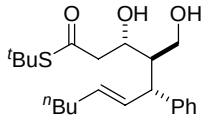
R*-(E,2R,3S)-3-Methyl-2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-5-phenylpent-4-enal (8b): General Procedure **C** (CH_2Cl_2, 40 °C) was followed employing 0.500 g of 2-((1E)-3-((E)-1-phenylbut-2-enyloxy)prop-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.59 mmol) and a reaction time of 4 hours. Purification by flash chromatography (8 % EtOAc/hexanes) on Iatrobeads gave 0.326 g (65 %) of the title compound as a colorless oil (vinyl C**H**, *syn:anti* = 92:8): ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.76 (d, *J* = 0.8 Hz, 1H), 7.36-7.20 (m, 5H), 6.42 (d, *J* = 16 Hz, 1H), 6.19 (dd, *J* = 16, 7.5 Hz, 1H), 2.85 (m, 1H), 2.70 (m, 1H), 1.24 (s, 6H), 1.21 (s, 6H), 1.12 (d, *J* = 6.9 Hz, 1H), 1.00 (dd, *J* = 16, 10 Hz, 1H), 0.82 (dd, *J* = 16, 5.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.8, 137.1, 132.7, 130.1, 128.4, 127.1, 126.0, 83.1, 53.2, 37.8, 24.7, 24.5, 16.4, 6.7 (br).



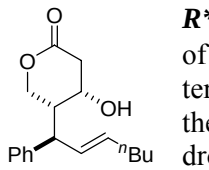
R*-(E,2R,3S)-3-Methyl-2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-5-(naphthalen-2-yl)pent-4-enal (8c): General Procedure **C** (CH_2Cl_2, 40 °C) was followed employing 0.264 g of 2-((1E)-3-((E)-1-(naphthalen-2-yl)but-2-enyloxy)prop-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.723 mmol) and a reaction time of 4 hours. Purification by flash chromatography (10 % EtOAc/hexanes) on Iatrobeads gave 0.159 g (61 %) of the title compound as a colorless oil (C**H**O, *syn:anti* = 91:9). Slow evaporation from pentane at −22 °C afforded crystals which were suitable for X-Ray analysis: ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.79 (d, *J* = 0.9 Hz, 1H), 7.80-7.75 (m, 3H), 7.69 (s, 1H), 7.56 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.48-7.39 (m, 2H), 6.58 (d, *J* = 16 Hz, 1H), 6.32 (dd, *J* = 16, 7.5 Hz, 1H), 2.91 (m, 1H), 2.76 (m, 1H), 1.24 (s, 6H), 1.21 (s, 6H), 1.16 (d, *J* = 6.9 Hz, 3H), 1.04 (dd, *J* = 16, 10 Hz, 1H), 0.86 (dd, *J* = 16, 5.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.7, 134.5, 133.5, 133.1, 132.7, 130.2, 128.0, 127.7, 127.5, 126.1, 125.7, 125.5, 123.4, 83.1, 53.2, 37.9, 24.7, 24.5, 16.4, 6.9 (br).



(2*S*,3*S*,4*E*,6*E*)-3-[(*E*)-But-1-enyl]-2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]deca-4,6-dienal (8d): General Procedure **C** (1,2-DCE, 80 °C) was followed employing 0.67 g of 2-{(1*E*)-3-[(*S*,4*E*,6*E*,8*E*)-dodeca-4,6,8-trien-3-yloxy]prop-1-enyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.9 mmol) and a reaction time of 5 hours. Purification by flash chromatography (18:1 hexanes:EtOAc) on Iatrobeads gave 0.39 g (58%) of the title compound as an orange oil (C**H**O, = 88:7:5): $[\alpha]_D$ = +24.7 (c 1.47, $CHCl_3$); IR (thin film) 2963, 2725, 1724, 1461, 1371, 1146, 989, 847 cm^{-1}; ^1H NMR (300 MHz, C_6D_6): δ 9.68 (d, *J* = 0.8 Hz, 1H), 6.03 (dd, *J* = 14.4, 10.4 Hz, 1H), 5.95 (dd, *J* = 14.4, 10.3 Hz, 1H), 5.51 (dd, *J* = 14.3, 7.0 Hz, 1H), 5.46-5.33 (m, 2H), 5.29 (dd, *J* = 15.4, 7.3 Hz, 1H), 3.00 (q, *J* = 7.0 Hz, 1H), 2.70 (br dt, *J* = 9.9, 5.9 Hz, 1H), 1.97-1.80 (m, 2H), 1.36-1.23 (m, 1H), 1.17 (dd, *J* = 16.0, 10.0 Hz, 1H), 1.10 (s, 6H), 1.09 (s, 6H), 0.96 (dd, *J* = 16.0, 4.8 Hz, 1H), 0.83 (t, *J* = 7.4 Hz, 3H), 0.82 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.9, 134.5, 133.9, 131.9, 130.9, 130.0, 128.4, 83.2, 52.5, 47.7, 34.7, 25.6, 24.8, 24.7, 22.4, 13.7 (B-**C** = *unobserved*).



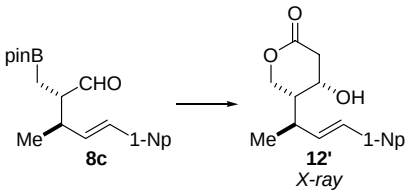
***R**-3-Hydroxy-4-hydroxymethyl-5-phenylundec-6-enethioic acid S-tert-butyl ester (11):** To 0.15 g (0.42 mmol) of β-boronic aldehyde **8a** (92:8 *syn : anti*) in 4.2 mL CH_2Cl_2 was added 112 mg (0.547 mmol) of (1-tert-butylsulfanyl-vinyloxy)-trimethyl-silane,[9] and the flask was immersed in a –78 °C bath. To the mixture was added 0.63 mL (0.63 mmol) of dimethylaluminum chloride in hexanes (1.0 M) dropwise and the reaction was stirred for 1 h at –78 °C. The reaction was quenched with 10% w/w citric acid in MeOH and slowly raised to ambient temperature. Water was added to form a biphasic mixture, and the aqueous layer was extracted with Et_2O (3x). The combined organic layers were dried over Na_2SO_4, filtered, and the solvent removed. The crude borane was passed through a plug of silica (5:1 hexanes:EtOAc) and isolated *in vacuo*. The compound mixture was then subject to 12 mL of a 2 : 1 : 1 CH_2Cl_2 : aq. 1M NaOH : 30% HOOH solution for 1.5 h. Following this time, the aqueous layer was extracted with CH_2Cl_2 (3x), and the combined organic layers were dried over Na_2SO_4. The solvent was filtered and removed *in vacuo*. Purification by flash chromatography on SiO_2 (5:1 hexanes/EtOAc) yielded 95 mg (60%) of the product as a clear, viscous oil: IR (thin film) 3364, 3027, 2960, 1679, 1454, 1364, 1054, 969, 758, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.33-7.17 (m, 5H), 5.68-5.52 (m, 2H), 4.55 (dq, *J* = 9.6, 3.3 Hz, 1H), 3.79 (dt, *J* = 11.6, 2.6 Hz, 1H), 3.74 (dd, *J* = 10.9, 8.4 Hz, 1H), 3.33 (ddd, *J* = 11.8, 8.0, 3.8 Hz, 1H), 3.31 (d, *J* = 4.1 Hz, 1H), 2.95 (dd, *J* = 15.6, 9.6 Hz, 1H), 2.67 (dd, *J* = 15.7, 3.3 Hz, 1H), 2.62 (dd, *J* = 8.0, 2.6 Hz, 1H), 2.03 (q, *J* = 6.7 Hz, 2H), 1.64-1.56 (m, 1H), 1.49 (s, 9H), 1.40-1.24 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.2, 143.6, 132.6, 131.6, 128.6, 127.8, 126.2, 69.8, 60.5, 50.3, 48.5, 48.0, 47.6, 32.2, 31.4, 29.7, 22.1, 13.8; MS (EI) *m/z* 360 (M^+-H_2O), 304, 173, 117, 91; HRMS (EI) *m/z* calculated for $C_{22}H_{32}O_2S$ (M^+-H_2O): 360.2123, found 360.2128.



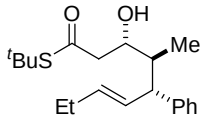
***R**-4-Hydroxy-5-(1-phenyl-hept-2-enyl)tetrahydropyran-2-one (12):** To 0.050 g (0.14 mmol) of β-boronic aldehyde **8a** (92:8 *syn : anti*) in 1.4 mL CH_2Cl_2 was added 37 mg (0.18 mmol) of (1-tert-butylsulfanyl-vinyloxy)-trimethyl-silane,[9] and the flask was immersed in a –78 °C bath. To the mixture was added 0.21 mL (0.21 mmol) of dimethylaluminum chloride in hexanes (1.0 M) dropwise and the reaction was stirred for 1 h at –78°C. The reaction was quenched at –78 °C by addition of H_2O and slowly raised to ambient temperature. The aqueous layer was extracted with Et_2O (3x) and the combined organic layers were dried over Na_2SO_4. Filtration of the organic extracts followed by removal of the solvent *in vacuo* left a residue that was immediately subject to 4 mL of a 2:1:1 MeOH: aq. 1M NaOH: 30% HOOH solution for 1 h. Following this time, the solution was acidified with aq. 1M HCl to ~pH 0.5 and stirred for 2 h. The aqueous layer was then extracted with Et_2O (3x) and the combined organic layers were dried over Na_2SO_4, filtered and the crude product mixture was concentrated *in vacuo*. Purification of the crude product mixture by flash chromatography on SiO_2 (7:3 hexanes/EtOAc) afforded 29 mg (71%) of the title compound as a clear, viscous oil. Separation of the diastereomers by GC-MS provided the diastereomer ratio: 2.7 % (T_r = 19.26), 97.3 % (T_r = 19.38). IR (thin film) 3431, 3028, 2957, 2926, 1720, 1188, 1064, 982, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.36-7.16 (m, 5H), 5.69-5.54 (m, 2H), 4.48-4.35 (m, 1H), 4.32 (t, *J* = 11.5 Hz, 1H), 3.81 (dd, *J* = 11.6, 4.9 Hz, 1H), 3.25 (dd, *J* = 10.9, 8.3 Hz, 1H), 2.79 (dd, *J* = 18.2, 2.9 Hz, 1H), 2.72 (dd, *J* = 18.2, 3.9 Hz, 1H), 2.24 (tdd, *J* = 11.6, 4.9, 1.6 Hz, 1H), 2.02 (q, *J* = 6.8 Hz, 2H), 1.36-1.25 (m, 4H), 0.88 (t, *J* = 7.0 Hz,

[9] Evans, D. A.; Scheidt, K. A.; Johnston, J. N.; Willis, M. C. *J. Am. Chem. Soc.* **2001**, *123*, 4480.

1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.3, 141.7, 133.1, 130.3, 128.9, 127.2, 126.9, 68.3, 63.4, 47.5, 41.8, 39.3, 32.1, 31.3, 22.2, 13.8; MS (EI) *m/z* 270 (M^+-H_2O), 210, 173, 117, 91; HRMS (EI) *m/z* calculated for $C_{18}H_{22}O_2$ (M^+-H_2O): 270.1620, found 270.1623. An X-ray structure determination for a related compound is provided below.

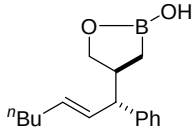


***R**-4-Hydroxy-5-(3-naphthalen-2-yl-1-phenyl-allyl)tetrahydro-pyran-2-one (12′):** To 0.17 mg (0.48 mmol) of β-boronic aldehyde **8c** (91:9 *syn : anti*) (1 mmol) in 4.8 mL CH_2Cl_2 was added 127 mg (0.621 mmol) of (1-tert-butylsulfanyl-vinyloxy)-trimethyl-silane,[9] and the flask was immersed in a –78 °C bath. To the mixture was added 0.72 mL (0.71 mmol) of dimethylaluminum chloride in hexanes (1.0 M) dropwise and the reaction was stirred for 1 h at –78°C. The reaction was quenched at –78 °C with 10% w/w citric acid in MeOH and slowly raised to ambient temperature. Water was added to form a biphasic mixture and the aqueous layer was extracted with Et_2O (3x). The combined organic layers were dried over Na_2SO_4, filtered and the solvent removed. The crude borane was passed through a plug of silica (5:1 hexanes:EtOAc) and isolated *in vacuo*. The product mixture was then subject to 12 mL of a 2:1:1 CH_2Cl_2: aq. 1M NaOH: 30% HOOH solution for 1.5 h. Following this time, the aqueous layer was extracted with CH_2Cl_2 (3x), and the organic layers were dried over Na_2SO_4. The layers were filtered and the solvent removed *in vacuo*. The crude product was then treated with 12 mL 1M NaOH in MeOH for 1 h at ambient temperature, then acidified to ~ pH 2 with aq. 1M HCl and stirred for an additional 1 h. The reaction was then diluted with water and the aqueous layer was extracted with Et_2O (3x). The combined organic layers were dried over Na_2SO_4, filtered, and the crude product mixture concentrated *in vacuo*. Remaining solvents were removed under high vacuum. Purification by flash chromatography on SiO_2 (3:2 hexanes/EtOAc) gave 54 mg (38%) of the product as a white foam. Recrystallization from hexanes/EtOAc (slow evaporation) gave crystals suitable for X-ray analysis: m.p. 117-119°C; IR (KBr) 3362, 3053, 2965, 1709, 1195, 1041, 971 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81-7.43 (m, 7H), 6.66 (d, *J* = 15.8 Hz, 1H), 6.21 (dd, *J* = 15.8, 9.3 Hz, 1H), 4.54 (t, *J* = 11.1 Hz, 1H), 4.47 (dd, *J* = 10.9, 5.7 Hz, 1H), 4.35-4.30 (m, 1H), 2.73 (dd, *J* = 18.1, 2.8 Hz, 1H), 2.65 (dd, *J* = 18.1, 3.7 Hz, 1H), 2.51 (tq, *J* = 9.2, 6.8 Hz, 1H), 1.87 (td, *J* = 9.7, 5.9 Hz, 1H), 1.18 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.1, 134.2, 133.5, 133.0, 132.8, 130.8, 128.2, 127.8, 127.6, 126.3, 125.9 (2C), 123.3, 68.3, 63.9, 42.5, 39.4, 36.0, 18.6; MS (EI) *m/z* 296 (M^+), 278, 181; HRMS (EI) *m/z* calculated for $C_{19}H_{20}O_3$ (M^+): 296.1412, found 296.1401.



***R**-3-Hydroxy-4-methyl-5-phenylnon-6-enethioic acid S-tert-butyl ester:** To 0.100 g (0.494 mmol) of aldehyde **13**[10] in 5 mL CH_2Cl_2 was added 131 mg (0.641 mmol) of (1-tert-butylsulfanyl-vinyloxy)-trimethyl-silane, and the flask was immersed in a –78 °C bath. To the mixture was added 0.74 mL (0.74 mmol) of dimethylaluminum chloride in hexanes (1.0 M) dropwise and the reaction was stirred for 1 h at –78 °C. The reaction was quenched by addition of 10% w/v citric acid in MeOH and slowly raised to ambient temperature; stirring was continued for 1 h. The reaction was diluted with water and the aqueous layer was extracted with Et_2O (3x). The combined organic layers were dried over Na_2SO_4, filtered and the crude product mixture was concentrated *in vacuo*. Remaining solvents were removed under high vacuum. Purification *via* flash chromatography on SiO_2 (10:1 hexanes/EtOAc) afforded 143 mg (86%) of the product as a clear, viscous oil. Separation of the diastereomers by GC-MS provided the diastereomer ratio: 97.8 % (T_r = 17.70), 2.2 % (T_r = 17.77): IR (thin film) 3485, 3026, 2964, 1678, 1454, 1364, 969, 753, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32-7.14 (m, 5H), 5.63-5.52 (m, 2H), 4.42 (ddd, *J* = 9.5, 3.1, 2.2 Hz, 1H), 3.23 (dd, *J* = 10.4, 8.6 Hz, 1H), 2.77 (dd, *J* = 15.5, 9.5 Hz, 1H), 2.54 (dd, *J* = 15.5, 3.2 Hz, 1H), 2.03 (qd, *J* = 7.4, 4.7 Hz, 2H), 1.73 (ddq, *J* = 10.5, 6.9, 2.2 Hz, 1H), 1.49 (s, 9H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.68 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.3, 144.5, 133.4, 131.5, 128.5, 127.8, 126.0, 68.3, 52.8, 49.9, 48.4, 42.4, 29.8, 25.5, 13.7, 10.9; MS (ESI) *m/z* 357 (M^++Na); HRMS (ESI) *m/z* calculated for $NaC_{20}H_{30}O_2S$ (M^++Na): 357.1864, found 357.1847.

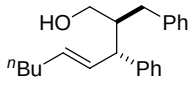
[10] Nelson, S. G.; Bungard, C. J.; Wang, K. *J. Am. Chem. Soc.* **2003**, *125*, 13000.



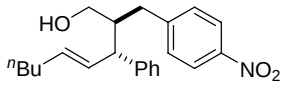
Cyclic borinic acid (14): To a solution of 1.1 g (3.1 mmol) boronic aldehyde **8a** in 31 mL pentane at –78 °C is slowly added 3.7 mL (3.7 mmol) $^{i}Bu_2AlH$ in pentane (1.0M). The reaction is stirred at –78 °C for 30 min, then quenched slowly with H_2O and warmed to ambient temperature. The cloudy biphasic mixture is extracted with Et_2O (3x) and the combined organic extracts are dried over Na_2SO_4. (NOTE: emulsions can form in large-scale reductions; 1M HCl can be added dropwise until the salts dissolve or a florsil plug can be utilized following extraction to alleviate this problem.) Following filtration, the solvents are removed *in vacuo* to afford the crude borinic acid. Purification of the product via flash chromatography on SiO_2 (3:1 hexanes:EtOAc) afforded 0.46 g (55%) of the product as a clear, viscous oil that was used directly in subsequent transformations.

General Procedure D for Suzuki Cross Coupling Reactions of 14: CEM microwave tubes with snap-on septa were utilized for all coupling reactions and were found to be convenient alternatives to Schlenk tubes for low temperature applications. For reproducible results, it is essential to remove all atmospheric oxygen from the borane/pre-catalyst mixture *via* high vacuum prior to introduction of the solvent. Degassed solvents are required to give optimal yields for large-scale applications.

A mixture of 11 mg (0.05 mmol, 5 mol%) of palladium acetate, 39 mg (0.15 mmol) of triphenylphosphine and the borinic acid **14** (1.0 mmol) are placed in a CEM microwave tube.[11] The tube is sealed with Teflon tape and the atmosphere is removed under vacuum for 30 min. The reaction vessel is backfilled with nitrogen 3x, following which time 2 mL of ^{t}amyl alcohol is added.[12] To the stirring solution is immediately added the aryl bromide (2.1 mmol) followed by 0.92 mL of aq. 1.3M sodium carbonate. The reaction is stirred for 60 min at ambient temperature followed by heating at 80°C for the indicated period of time (yellow → white suspension or clear solution). Upon completion, the reaction is diluted with water, the biphasic mixture is transferred to a seperatory funnel and the aqueous layer is extracted 3x with EtOAc. The combined organics are dried over Na_2SO_4, filtered, and the solvent is removed *in vacuo*. The crude alcohol is purified as specified. Representative isolated diastereomeric ratios were determined by GC-MS [HP-1 (12 m x 0.20 mm), pressure 21 kPa, method: 70 °C for 2.00 min, ramp @ 10 °C/min to 300 °C, hold for 60 min].



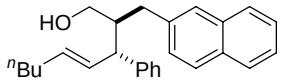
***R**-(*E*,2*S*,3*R*)-2-Benzyl-3-phenylnon-4-en-1-ol (15a):** General Procedure **D** was followed employing 75 mg (0.27 mmol) of borinic acid **14**, 3.1 mg (0.014 mmol) of palladium acetate, 11 mg (0.042 mmol) of triphenylphosphine, 0.060 mL (0.090 g, 0.57 mmol) of bromobenzene, 0.25 mL of aq. 1.3M sodium carbonate, and a reaction time of 5.5 h. Purification by flash chromatography (6:1 hexanes:EtOAc) on SiO_2 gave 54 mg (67 %) of the title compound as a colorless oil. Separation of the diastereomers by GC-MS provided the diastereomer ratio: 4.5 % (T_r = 18.80), 95.5 % (T_r =18.97): IR (thin film) 3389, 3026, 2926, 1601, 1494, 1453, 1030, 970, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.09 (m, 10H), 5.69 (dd, *J* = 15.2, 8.8 Hz, 1H), 5.58 (dt, *J* = 15.1, 6.1 Hz, 1H), 3.70 (dd, *J* = 11.2, 4.0 Hz, 1H), 3.55 (dd, *J* = 11.3, 4.2 Hz, 1H), 3.34 (t, *J* = 9.1 Hz, 1H), 2.55 (dd, *J* = 13.8, 4.8 Hz, 1H), 2.46 (dd, *J* = 13.7. 9.7 Hz, 1H), 2.14 (m, 1H), 2.03 (q, *J* = 6.8 Hz, 2H), 1.33 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.0, 140.9, 132.0, 131.9, 129.0, 128.6, 128.3, 127.9, 126.2, 125.8, 62.1, 51.2, 47.7, 35.2, 32.2, 31.5, 22.2, 13.9; MS (EI) *m/z* 308 (M^+), 290, 233, 199, 173, 117, 91; HRMS (EI) *m/z* calculated for $C_{22}H_{28}O$: 308.2140, found 308.2147.



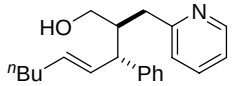
***R**-(*E*,2*S*,3*R*)-2-(4-Nitrobenzyl)-3-phenylnon-4-en-1-ol (15b):** General Procedure **D** was followed employing 75 mg (0.27 mmol) of borinic acid **14**, 3.1 mg (0.014 mmol) of palladium acetate, 11 mg (0.042 mmol) of triphenylphosphine, 0.12 g (0.57 mmol) of 1-bromo-4-nitrobenzene, 0.25 mL of aq. 1.3M sodium carbonate, and a reaction time of 15 h. Purification by flash chromatography (5:1 hexanes:EtOAc) on SiO_2 gave 79 mg (81%) of the title compound as a colorless oil. Separation of the diastereomers by GC-MS provided the diastereomer ratio: 1.2 % (T_r = 22.58), 98.8 % (T_r = 22.74): IR (thin film) 3441, 3027, 2927, 1600, 1518, 1345, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.8 Hz, 2H), 7.38 – 7.21 (m, 7H), 5.66 (dd, *J* = 15.2, 8.3 Hz, 1H), 5.58 (dt, *J* = 15.1, 6.0 Hz, 1H), 3.71 (dt, *J* = 11.1, 4.3 Hz, 1H), 3.50 (ddd, *J* = 11.0, 5.6, 3.9 Hz, 1H), 3.32 (t, *J* = 9.1 Hz, 1H), 2.68 (dd, *J* = 13.6, 9.5 Hz, 1H), 2.58 (dd, *J* = 13.6, 4.7 Hz, 1H), 2.14 (m, 1H), 2.03 (q, *J* = 6.7 Hz, 2H), 1.31 (m, 4H), 0.88 (t, *J* = 7.3 Hz, 3H); ^{13}C

[11] General procedure: Huff, B. E.; Koenig, T. M.; Mitchell, D.; Staszak, M. A. *Org. Synth., Coll. Vol. X* **1995**, 102.
[12] Solvent system: Kirchoff, J. H.; Netherton, M. R.; Hills, I. D.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 13662.

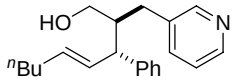
NMR (75 MHz, $CDCl_3$): δ 149.2, 146.4, 143.5, 132.4, 131.5, 129.9, 128.8, 127.8, 126.5, 123.5, 61.5, 51.3, 47.5, 35.1, 32.2, 31.5, 22.2, 13.9; MS (EI) *m/z* 353 (M^+), 278, 253, 199, 174, 131, 115; HRMS (EI) *m/z* calculated for $C_{22}H_{27}NO_3$: 353.1991, found 353.2002.



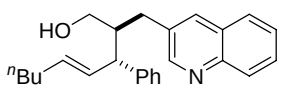
***R**-(*E*,2*S*,3*R*)-2-[(Naphthalen-3-yl)methyl]-3-phenylnon-4-en-1-ol (15c):** General Procedure **D** was followed employing 75 mg (0.27 mmol) of borinic acid **14**, 3.1 mg (0.014 mmol) of palladium acetate, 11 mg (0.042 mmol) of triphenylphosphine, 0.12 g (0.57 mmol) of 2-bromonapthalene, 0.25 mL of aq. 1.3M sodium carbonate, and a reaction time of 1.5 h. Purification by flash chromatography (8:1 hexanes:EtOAc) on SiO_2 gave 63 mg (67%) of the title compound as a colorless oil. Separation of the diastereomers by GC-MS provided the diastereomer ratio: 1.4 % (T_r = 23.15), 98.6 % (T_r = 23.39): IR (thin film) 3382, 3025, 2926, 1600, 1452, 1028, 969, 815, 747, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.81-7.73 (m, 3H), 7.54 (s, 1H), 7.48-7.21 (m, 8H), 5.71 (dd, *J* = 15.2, 9.1 Hz, 1H), 5.60 (dt, *J* = 15.2, 6.4 Hz, 1H), 3.73 (dt, *J* = 11.1, 5.6 Hz, 1H), 3.57 (dt, *J* = 10.9, 5.9 Hz, 1H), 3.39 (t, *J* = 9.0 Hz, 1H), 2.71 (dd, *J* = 13.7, 5.1 Hz, 1H), 2.64 (dd, *J* = 13.6, 9.2 Hz, 1H), 2.29–2.18 (m, 1H), 2.04 (q, *J* = 6.7 Hz, 2H), 1.41-1.27 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.0, 138.4, 133.5, 132.1, 132.0, 131.8, 128.6, 127.9, 127.8, 127.6, 127.5, 127.4, 127.3, 126.3, 125.9, 125.1, 62.0, 51.3, 47.6, 35.3, 32.2, 31.5, 22.2, 13.9; MS (EI) *m/z* 358 (M^+), 340, 283, 269, 255, 199, 173, 142, 117; HRMS (EI) *m/z* calculated for $C_{26}H_{30}O$: 358.2297, found 358.2300.



***R**-(*E*,2*S*,3*R*)-3-Phenyl-2-[(pyridin-2-yl)methyl]non-4-en-1-ol (15d):** General Procedure **D** was followed employing 75 mg (0.27 mmol) of borinic acid **14**, 3.1 mg (0.014 mmol) of palladium acetate, 11 mg (0.042 mmol) of triphenylphosphine, 0.090 g (0.57 mmol) of 2-bromopyridine, 0.25 mL of aq. 1.3M sodium carbonate, and a reaction time of 48 h. Purification by flash chromatography (2:1 → 1:1 hexanes:EtOAc) on SiO_2 gave 0.030 g (36%) of the title compound as a light yellow oil: IR (thin film) 3373, 3025, 2925, 1593, 1569, 1472, 969, 756, 701 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.48 (d, *J* = 4.8 Hz, 1H), 7.55 (td, *J* = 7.7, 1.7 Hz, 1H), 7.35-7.10 (m, 6H), 6.85 (d, *J* = 7.8 Hz, 1H), 5.56 (dd, *J* = 15.2, 7.6 Hz, 1H), 5.47 (dt, *J* = 15.1, 5.9 Hz, 1H), 5.08 (br. s, 1H), 3.69 (dd, *J* = 11.6, 4.2 Hz, 1H), 3.61 (dd, *J* = 11.6, 6.0 Hz, 1H), 3.21 (dd, *J* = 10.4, 8.2 Hz, 1H), 2.80 (dd, *J* = 14.1, 4.2 Hz, 1H), 2.69 (dd, *J* = 14.1, 7.8 Hz, 1H), 2.35 (dddt, *J* = 10.3, 8.1, 6.0, 4.2 Hz, 1H), 1.97 (q, *J* = 6.5 Hz, 2H), 1.35-1.23 (m, 4H), 0.86 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.3, 148.5, 144.1, 136.7, 132.1, 131.7, 128.6, 128.0, 126.2, 124.0, 121.2, 63.5, 51.3, 45.0, 38.4, 32.2, 31.5, 22.2, 13.9; MS (EI) *m/z* 309 (M^+), 278, 174, 169, 136, 118, 106, 91; HRMS (EI) *m/z* calculated for $C_{21}H_{27}NO$: 309.2093, found 309.2106.

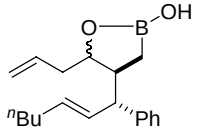


***R**-(*E*,2*S*,3*R*)-3-Phenyl-2-[(pyridin-3-yl)methyl]non-4-en-1-ol (15e):** General Procedure **D** was followed employing 75 mg (0.27 mmol) of borinic acid **14**, 3.1 mg (0.014 mmol) of palladium acetate, 11 mg (0.042 mmol) of triphenylphosphine, 55 μL (0.090 g, 0.57 mmol) of 3-bromopyridine, 0.25 mL of aq. 1.3M sodium carbonate, and a reaction time of 20 h. Purification by flash chromatography (1:1 hexanes:EtOAc → 2:1 EtOAc:hexanes) on SiO_2 gave 66 mg (78%) of the title compound as a light yellow oil: IR (thin film) 3276, 3027, 2925, 1597, 1577, 1424, 1029, 968, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.42 (dd, *J* = 4.8, 1.5 Hz, 1H), 8.34 (d, *J* = 1.9 Hz, 1H), 7.40 (dt, *J* = 7.8, 1.9 Hz, 1H), 7.37-7.21 (m, 5H), 7.17 (dd, *J* = 7.8, 5.0 Hz, 1H), 5.66 (dd, *J* = 15.2, 8.5 Hz, 1H), 5.56 (dt, *J* = 15.1, 6.2 Hz, 1H), 3.70 (dt, *J* = 11.2, 4.9 Hz, 1H), 3.53 (dt, *J* = 10.8, 4.5 Hz, 1H), 3.33 (t, *J* = 9.0 Hz, 1H), 2.59-2.47 (m, 2H), 2.18-2.06 (m, 1H), 2.02 (q, *J* = 6.7 Hz, 2H), 1.49 (t, *J* = 5.0 Hz, 1H), 1.39-1.22 (m, 4H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.4, 147.2, 143.7, 136.6, 136.4, 132.2, 131.6, 128.7, 127.8, 126.3, 123.2, 61.2, 50.9, 47.3, 32.2, 32.0, 31.5, 22.2, 13.9; MS (EI) *m/z* 309 (M^+), 173, 117, 91; HRMS (EI) *m/z* calculated for $C_{21}H_{27}NO$: 309.2093, found 309.2099.

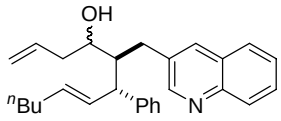


***R**-(*E*,2*S*,3*R*)-3-Phenyl-2-[(quinolin-3-yl)methyl]non-4-en-1-ol (15f):** General Procedure **D** was followed employing 75 mg (0.27 mmol) of borinic acid **14**, 3.1 mg (0.014 mmol) of palladium acetate, 11 mg (0.042 mmol) of triphenylphosphine, 78 μL (0.12 g, 0.57 mmol) of 3-bromoquinoline, 0.25 mL of aq. 1.3M sodium carbonate, and a reaction time of 12 h. Purification by flash chromatography (3:2 hexanes:EtOAc) on SiO_2 gave 85 mg (89%) of the title compound as a

yellow oil: IR (thin film) 3290, 3026, 2925, 1601, 1574, 1495, 1452, 1034, 967, 787, 752, 701 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.66 (d, *J* = 2.2 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 1.8 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H) , 7.66 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.52 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.34-7.22 (m, 5H), 5.69 (dd, *J* = 15.2, 8.6 Hz, 1H), 5.59 (dt, *J* = 15.2, 5.9 Hz, 1H), 3.74 (dt, *J* = 11.0, 4.8 Hz, 1H), 3.60 (dt, *J* = 11.0, 5.3 Hz, 1H), 3.38 (t, *J* = 9.1 Hz, 1H), 2.76 (dd, *J* = 13.8, 8.7 Hz, 1H), 2.70 (dd, *J* = 14.0, 5.2 Hz, 1H), 2.28-2.18 (m, 1H), 2.03 (q, *J* = 6.7 Hz, 2H), 1.60 (t, *J* = 5.4 Hz, 1H), 1.40-1.23 (m, 4H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.3, 146.7, 143.7, 135.2, 133.7, 132.3, 131.6, 129.1, 128.8, 128.6, 128.0, 127.9, 127.3, 126.5, 126.4, 61.4, 51.1, 47.4, 32.2 (2C), 31.5, 22.2, 13.9; MS (EI) *m/z* 359 (M^+), 342, 328, 262, 173, 142, 117, 91; HRMS (EI) *m/z* calculated for $C_{25}H_{29}NO$: 359.2249, found 359.2258.

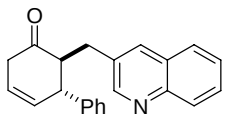


Cyclic homoallylic borinic acid (16): To a solution of 0.96 g (2.7 mmol) boronic aldehyde **8a** in 27 mL Et_2O at –78°C is slowly added 3.2 mL (3.2 mmol) allylmagnesium bromide in Et_2O (1.0M). The reaction is stirred at –78°C for 1 h, then quenched slowly with H_2O and warmed to ambient temperature. The cloudy biphasic mixture is extracted with Et_2O (3x) and the combined organic extracts are dried over Na_2SO_4. Following filtration, the solvents are removed *in vacuo* to afford the crude boronic alcohol. Purification of the product via flash chromatography on SiO_2 (4:1 hexanes:EtOAc) afforded 0.67 g (78%) of the product as a clear, viscous oil.



***R**-(*E*,4*R*,5*S*,6*R*)-6-Phenyl-5-[(quinolin-3-yl)methyl]dodeca-1,7-dien-4-ol + *R**-(*E*,4*S*,5*S*,6*R*)-6-phenyl-5-[(quinolin-3-yl)methyl]dodeca-1,7-dien-4-ol (17):** General Procedure **D** was followed employing 0.75 g (2.4 mmol) of borinic acid **16**, 27 mg (0.12 mmol) of palladium acetate, 94 mg (0.36 mmol) of triphenylphosphine, 0.65 mL (1.0 g, 5.0 mmol) of 3-bromoquinoline, 2.2 mL of aq. 1.3M sodium carbonate, and a reaction time of 7 h. Purification by flash chromatography (2:1 hexanes:EtOAc) on SiO_2 gave 0.54 g (58%) of the title compound as a yellow oil (d.r. 2:1 by 300 MHz ^1H-NMR, aryl C**H**): *Diastereomer A* - IR (thin film) 3336, 3062, 2955, 1639, 1600, 1573, 1495, 1451, 1049, 750 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.52 (d, *J* = 2.1 Hz, 1H), 8.03 (d, *J* = 8.3 Hz, 1H), 7.65-7.58 (m, 3H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.22-7.09 (m, 5H), 5.84-5.76 (m, 1H), 5.70 (dd, *J* = 15.0, 9.3 Hz, 1H), 5.53 (dt, *J* = 14.9, 6.5 Hz, 1H), 5.17 (d, *J* = 11.7 Hz, 1H), 5.16 (d, *J* = 14.5 Hz, 1H), 3.95-3.88 (m, 1H), 3.39 (t, *J* = 9.0 Hz, 1H), 2.98 (dd, *J* = 14.3, 6.0 Hz, 1H), 2.61 (dd, *J* = 14.2, 6.7 Hz, 1H), 2.53-2.42 (m, 2H), 2.30-2.18 (m, 1H), 2.02 (q, *J* = 6.7 Hz, 2H), 1.68 (d, *J* = 4.3 Hz, 1H), 1.39-1.26 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, CD_3CN): δ 153.3, 147.4, 145.6, 137.0, 136.6, 135.5, 133.4, 132.9, 129.7, 129.3 (2C), 129.2, 128.9, 128.4, 127.3, 127.0, 117.2, 71.3, 53.2, 49.9, 41.6, 32.9, 32.4, 31.2, 22.9, 14.2; MS (EI) *m/z* 399 (M^+), 381, 358, 340, 191, 173, 142, 117; HRMS (EI) *m/z* calculated for $C_{28}H_{33}NO$: 399.2570, found 399.2562.

Diastereomer B - ^1H NMR (300 MHz, $CDCl_3$): δ 8.52 (d, *J* = 2.1 Hz, 1H), 8.03 (d, *J* = 8.3 Hz, 1H), 7.65-7.58 (m, 3H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.22-7.09 (m, 5H), 5.84-5.76 (m, 1H), 5.70 (dd, *J* = 15.0, 9.3 Hz, 1H), 5.53 (dt, *J* = 14.9, 6.5 Hz, 1H), 5.17 (d, *J* = 11.7 Hz, 1H), 5.16 (d, *J* = 14.5 Hz, 1H), 3.95-3.88 (m, 1H), 3.39 (t, *J* = 9.0 Hz, 1H), 2.98 (dd, *J* = 14.3, 6.0 Hz, 1H), 2.61 (dd, *J* = 14.2, 6.7 Hz, 1H), 2.53-2.42 (m, 2H), 2.30-2.18 (m, 1H), 2.02 (q, *J* = 6.7 Hz, 2H), 1.68 (d, *J* = 4.3 Hz, 1H), 1.39-1.26 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H); MS (EI) *m/z* 399 (M^+), 381, 358, 340, 191, 173, 142, 117; HRMS (EI) *m/z* calculated for $C_{28}H_{33}NO$: 399.2610, found 399.2562.



***R**-(5*R*,6*S*)-5-phenyl-6-[(quinolin-3-yl)methyl]cyclohex-3-enone (19):** To a solution of 32 mg (0.08 mmol) of alcohol **17** in 8 mL CH_2Cl_2 was added a solution of 3.4 mg (0.0040 mmol) Grubbs II catalyst (**18**) in 8 mL CH_2Cl_2 via cannula. The reaction was stirred at ambient temperature for 3 h, then quenched with 15 μL of DMSO[13] and left for 12 h. The crude reaction mixture was concentrated and the residue was purified by flash chromatography on SiO_2 (2:1 EtOAc:hexanes). The purified RCM product was immediately oxidized using 51 mg (0.12 mmol) of Dess-Martin periodinane in CH_2Cl_2 (1 mL) for 30 min (0 °C → rt).[14,15] The crude ketone is passed through a plug of florsil (1:1 hexanes:EtOAc eluent) to remove heterogeneous impurities and the filtrate was concentrated. Purifying the

[13] Ahn, Y. M.; Yang, K.; Georg, G. I. *Org. Lett.* **2001**, *3*, 1411.
[14] Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155.
[15] Boeckman Jr., R. K; Shao, P.; Mullins, J. J. *Org. Synth., Coll. Vol. X* **1995**, 696.

crude product mixture by flash chromatography on SiO_2 (2:1 hexanes:EtOAc) gave 12 mg (48%) of the title compound as a viscous yellow oil: IR (thin film) 3029, 2924, 1716, 1678, 1602, 1571, 1494, 787, 751, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.52 (d, *J* = 1.5 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 1.3 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.64 (td, *J* = 7.0, 1.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.41-7.22 (m, 5H), 5.87-5.82 (m, 2H), 3.62 (dt, *J* = 9.5, 2.4 Hz, 1H), 3.27 (dd, *J* = 13.8, 8.7 Hz, 1H), 3.15-3.09 (m, 2H), 2.95 (dm, *J* = ~15.8 Hz, 1H), 2.75 (dd, *J* = 13.8, 3.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.4, 152.0, 146.5, 142.3, 135.7, 133.1, 131.2, 129.1, 128.8 (3C), 128.0, 127.4 (2C), 126.6, 124.1, 57.5, 50.5, 40.5, 30.2; MS (EI) *m/z* 313 (M^+), 222, 182, 143, 130, 115; HRMS (EI) *m/z* calculated for $C_{22}H_{19}NO$: 313.1467, found 313.1464.

X-ray Structure Determinations for Compounds **8c** and **12′**

I. Compound 8c

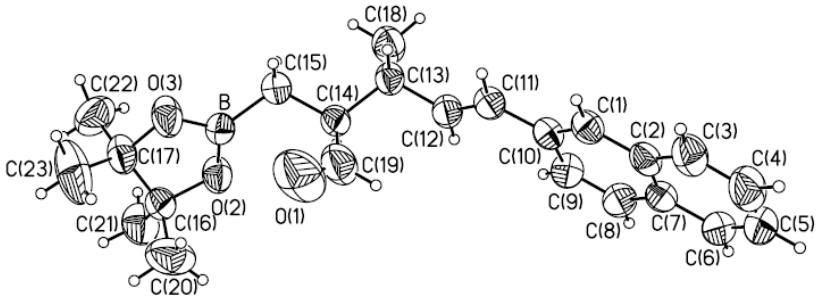


Figure S1. *R-(*E*,2*R*,3*S*)-2-[(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-3-phenylnon-4-enal (8c)**

Table 1. Crystal data and structure refinement for compound **8c**.

Empirical formula	$C_{23}H_{29}BO_3$	
Formula weight	364.27	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pca2(1)	
Unit cell dimensions	a = 12.5986(6) Å	α= 90°.
	b = 8.2876(4) Å	β= 90°.
	c = 20.2572(10) Å	γ = 90°.
Volume	2115.10(18) $Å^3$	
Z	4	
Density (calculated)	1.144 Mg/m^3	
Absorption coefficient	0.073 mm^{-1}	
F(000)	784	
Crystal size	0.29 x 0.21 x 0.21 mm^3	
Theta range for data collection	2.01 to 27.50°.	
Index ranges	-16<=h<=16, -10<=k<=10, -26<=l<=26	
Reflections collected	19669	
Independent reflections	2500 [R(int) = 0.0238]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9848 and 0.9791	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2500 / 1 / 249	
Goodness-of-fit on F^2	1.247	
Final R indices [I>2sigma(I)]	R1 = 0.0481, wR2 = 0.1299	
R indices (all data)	R1 = 0.0567, wR2 = 0.1360	
Largest diff. peak and hole	0.224 and -0.127 $e.Å^{-3}$	

II. Compound 12′

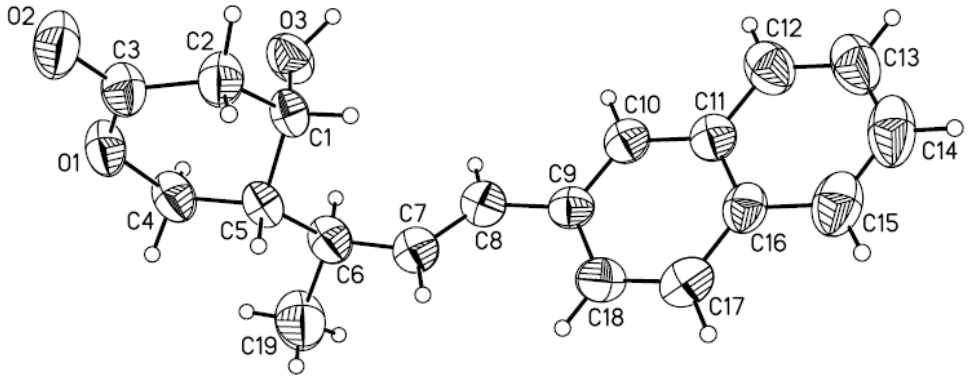


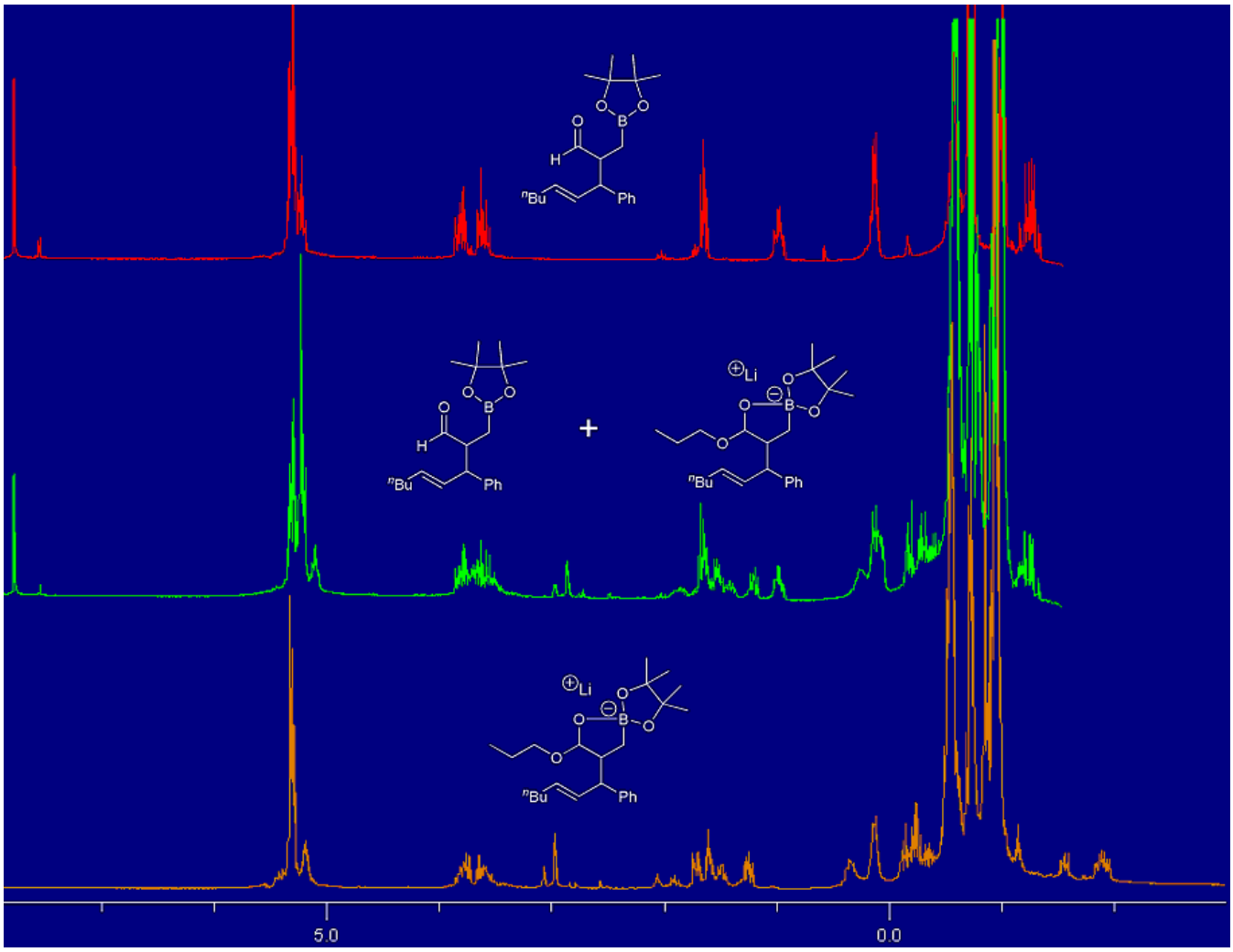
Figure S2. *R-(4*S*,5*R*)-Tetrahydro-4-hydroxy-5-[(*R*,*E*)-4-(naphthalen-3-yl)but-3-en-2-yl]pyran-2-one (12′)**

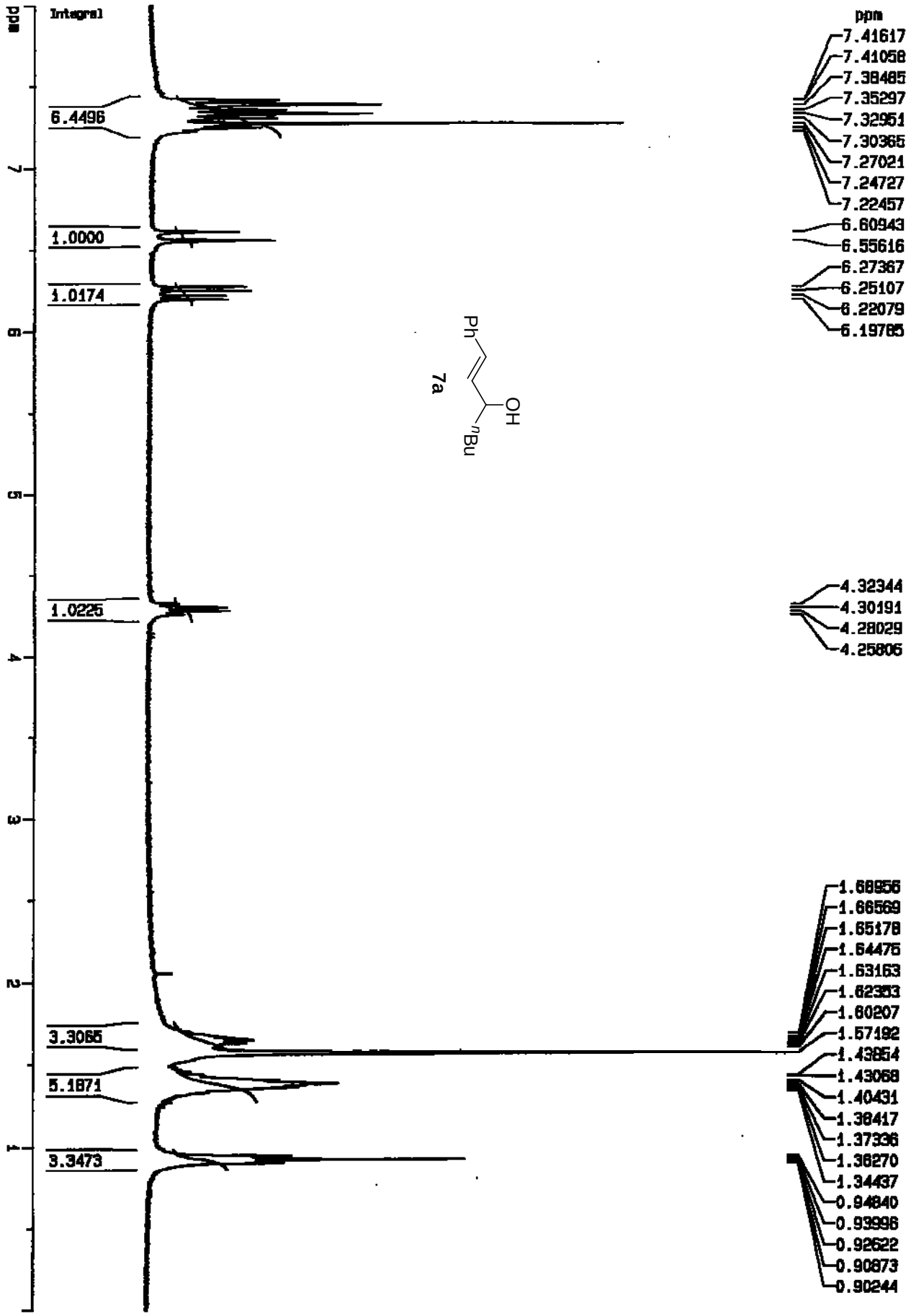
Table 2. Crystal data and structure refinement for compound **12′**.

Empirical formula	$C_{19}H_{20}O_3$	
Formula weight	314.36	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.3590(5) Å	α= 90°.
	b = 21.7109(10) Å	β= 106.2630(10)°.
	c = 16.1006(7) Å	γ = 90°.
Volume	3476.2(3) $Å^3$	
Z	8	
Density (calculated)	1.201 Mg/m^3	
Absorption coefficient	0.080 mm^{-1}	
F(000)	1336	
Crystal size	0.27 x 0.21 x 0.08 mm^3	
Theta range for data collection	1.62 to 25.00°.	
Index ranges	-12<=h<=12, -25<=k<=25, -19<=l<=19	
Reflections collected	27806	
Independent reflections	6121 [R(int) = 0.0685]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	None	
Max. and min. transmission	0.9937 and 0.9788	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6121 / 0 / 432	
Goodness-of-fit on F^2	1.079	
Final R indices [I>2sigma(I)]	R1 = 0.0764, wR2 = 0.1658	
R indices (all data)	R1 = 0.1535, wR2 = 0.1899	
Largest diff. peak and hole	0.176 and -0.129 $e.Å^{-3}$	

^{1}H-NMR Study of LiO^{n}Pr Addition to β-Boronic Aldehyde **8a**

*Note: Spectra taken in d_8-THF at high concentration (~45 mg / 1 mL), hence chemical shifts were not standardized.

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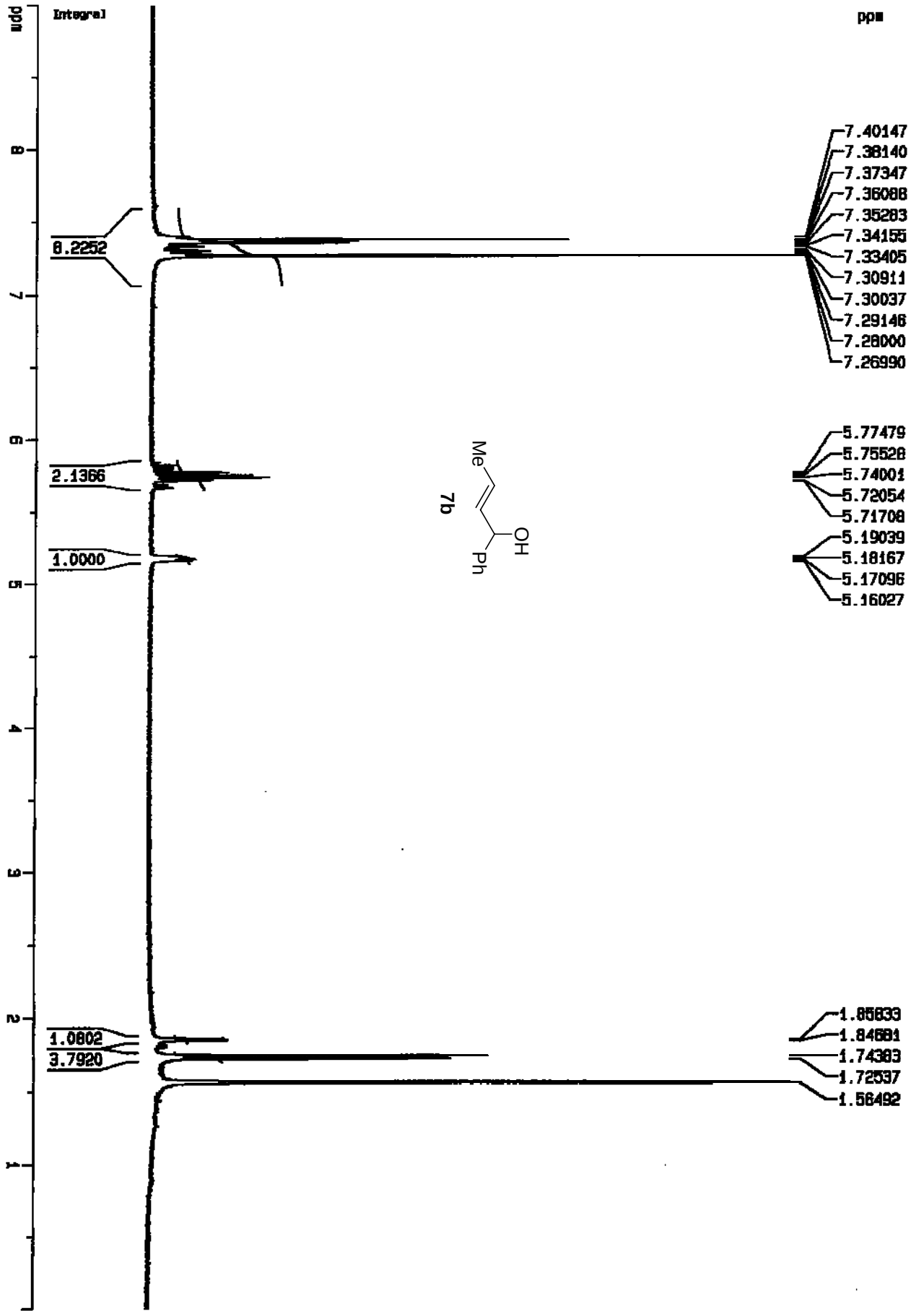
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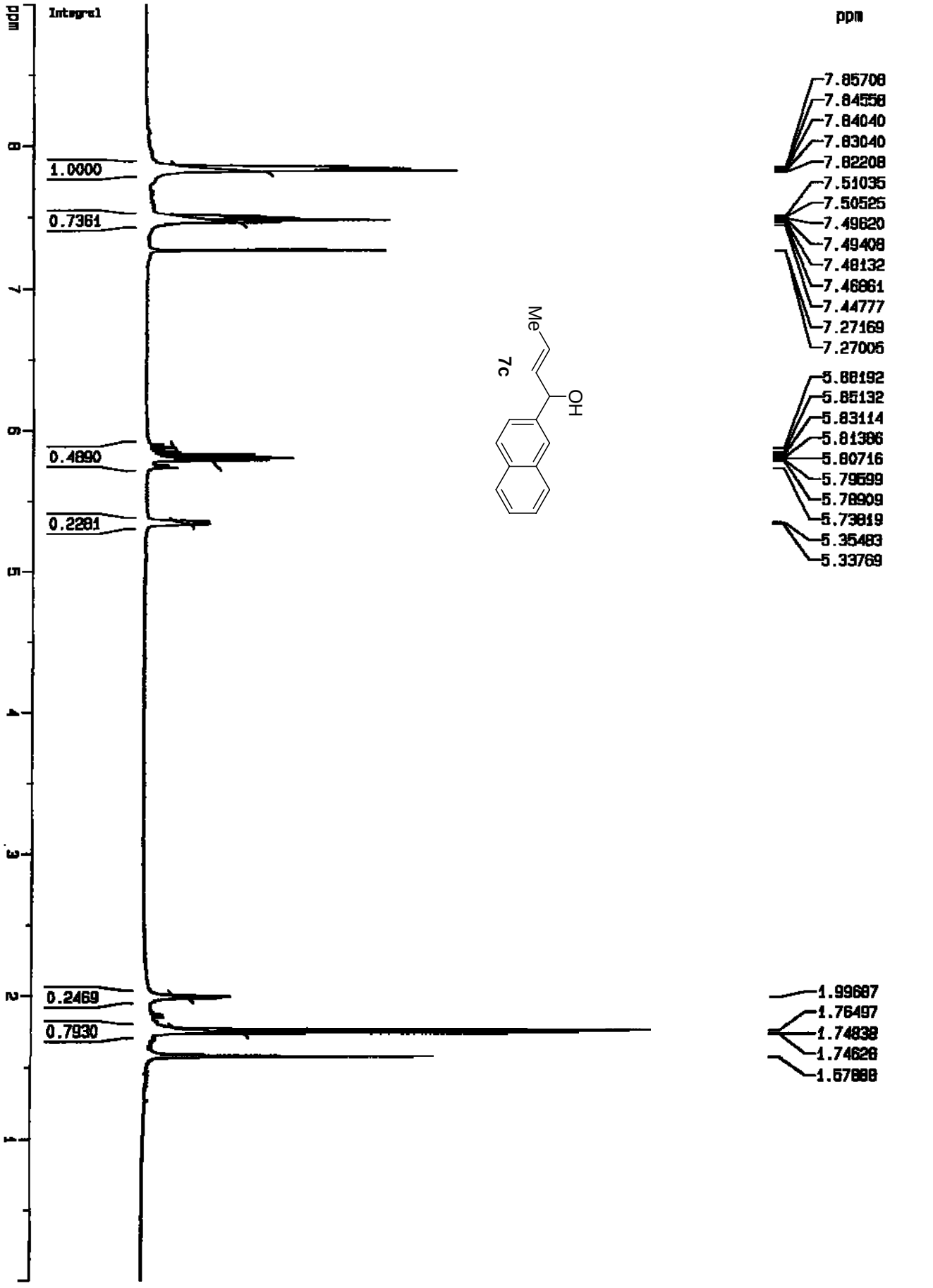
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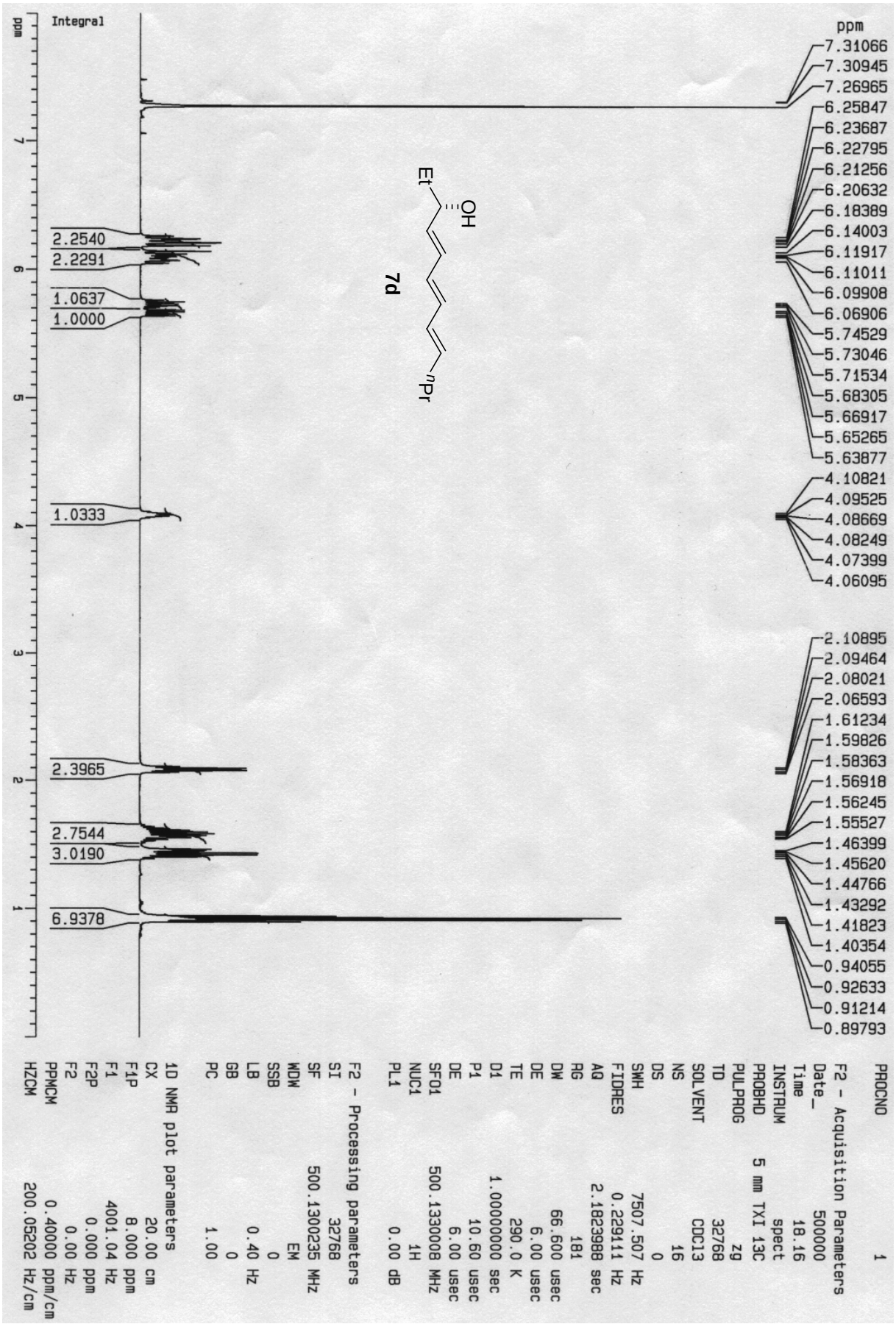
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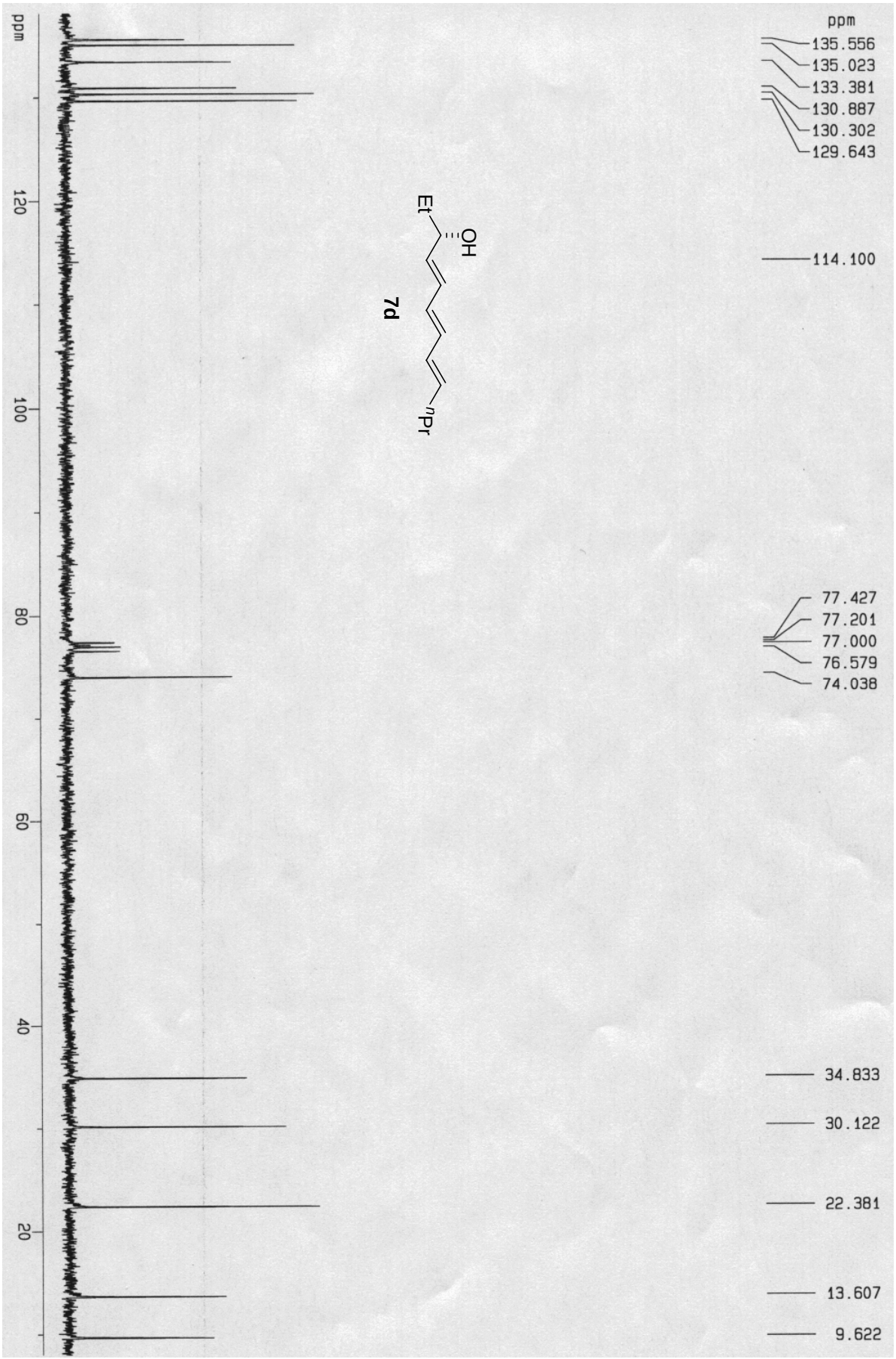
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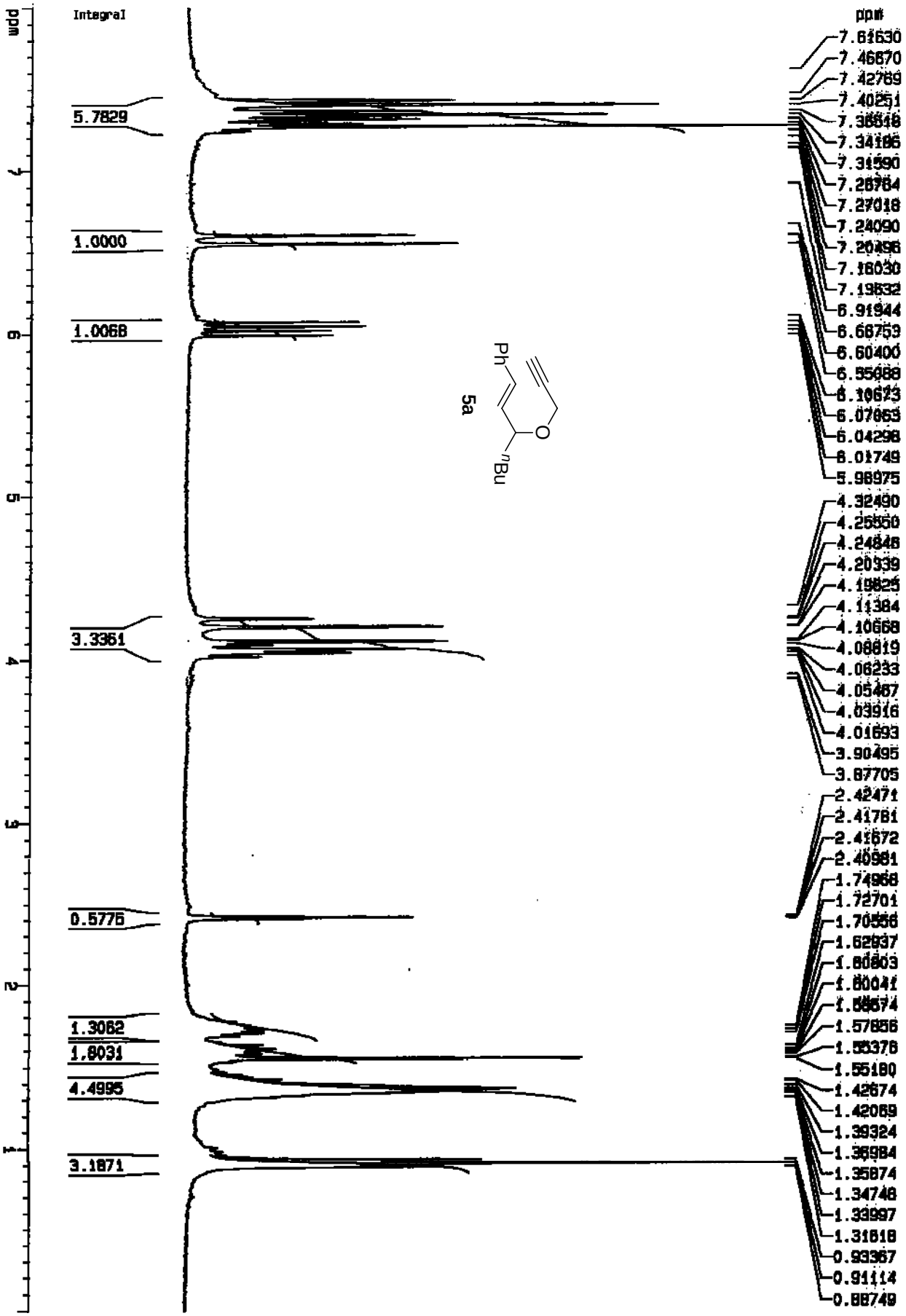
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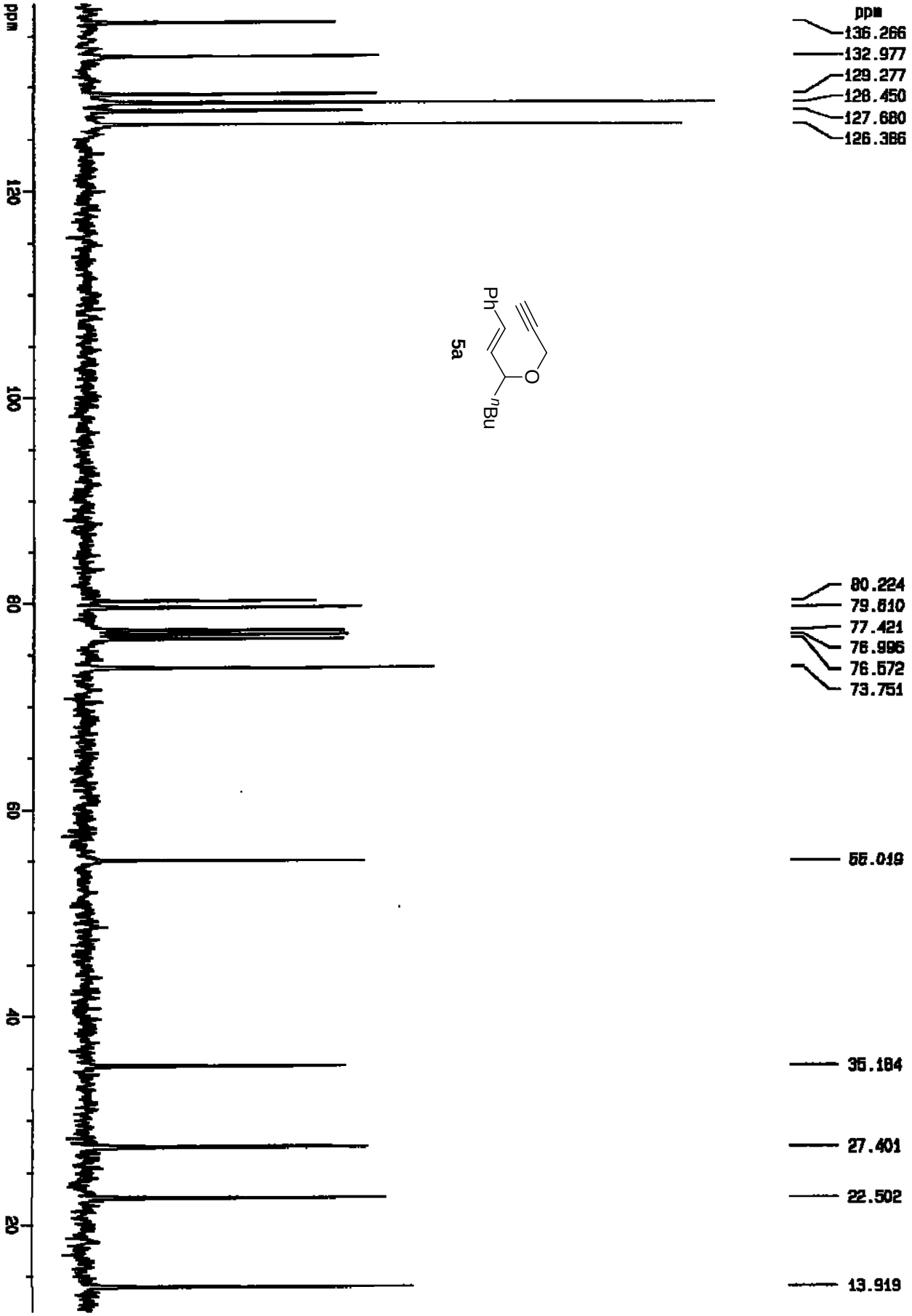
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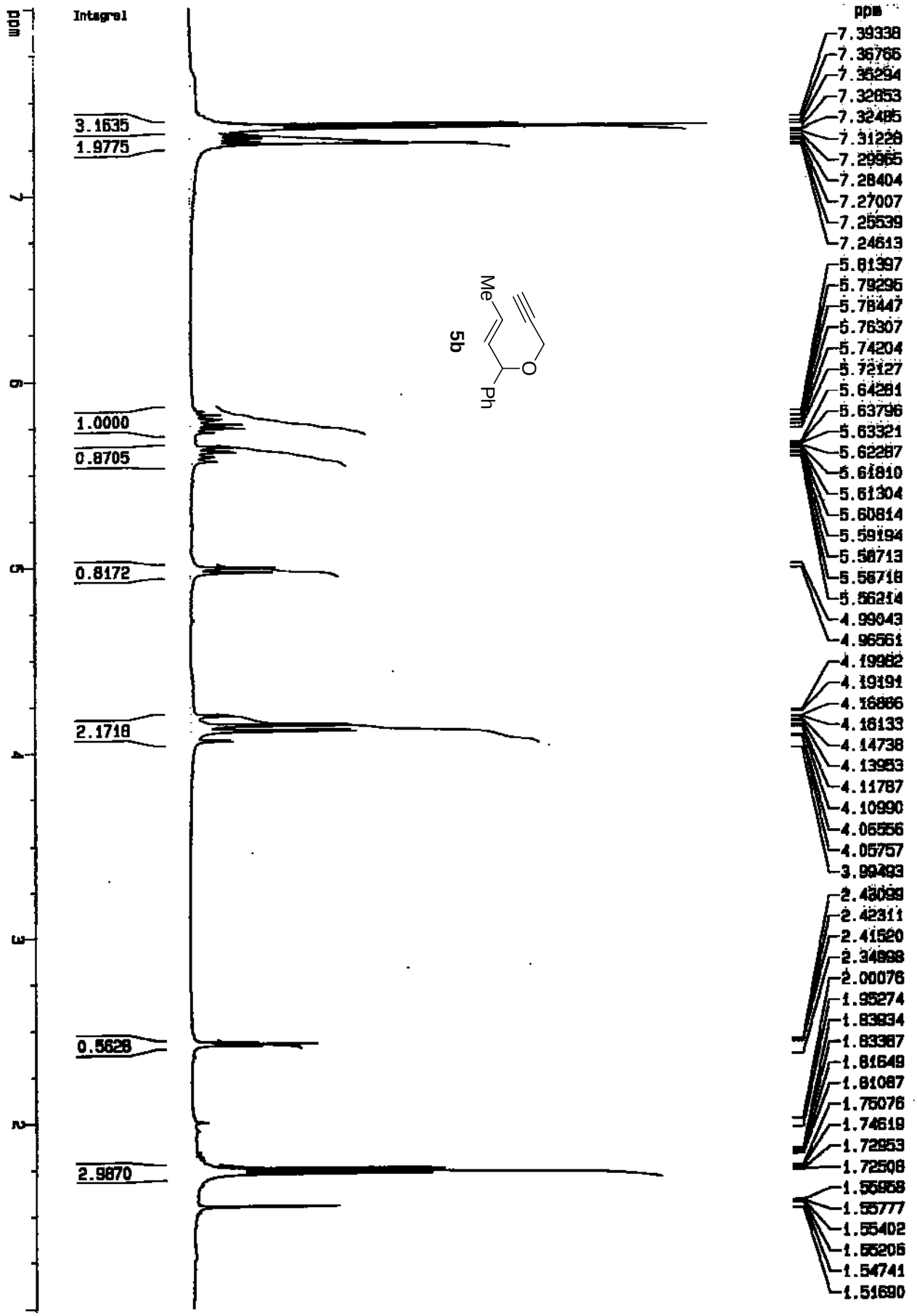
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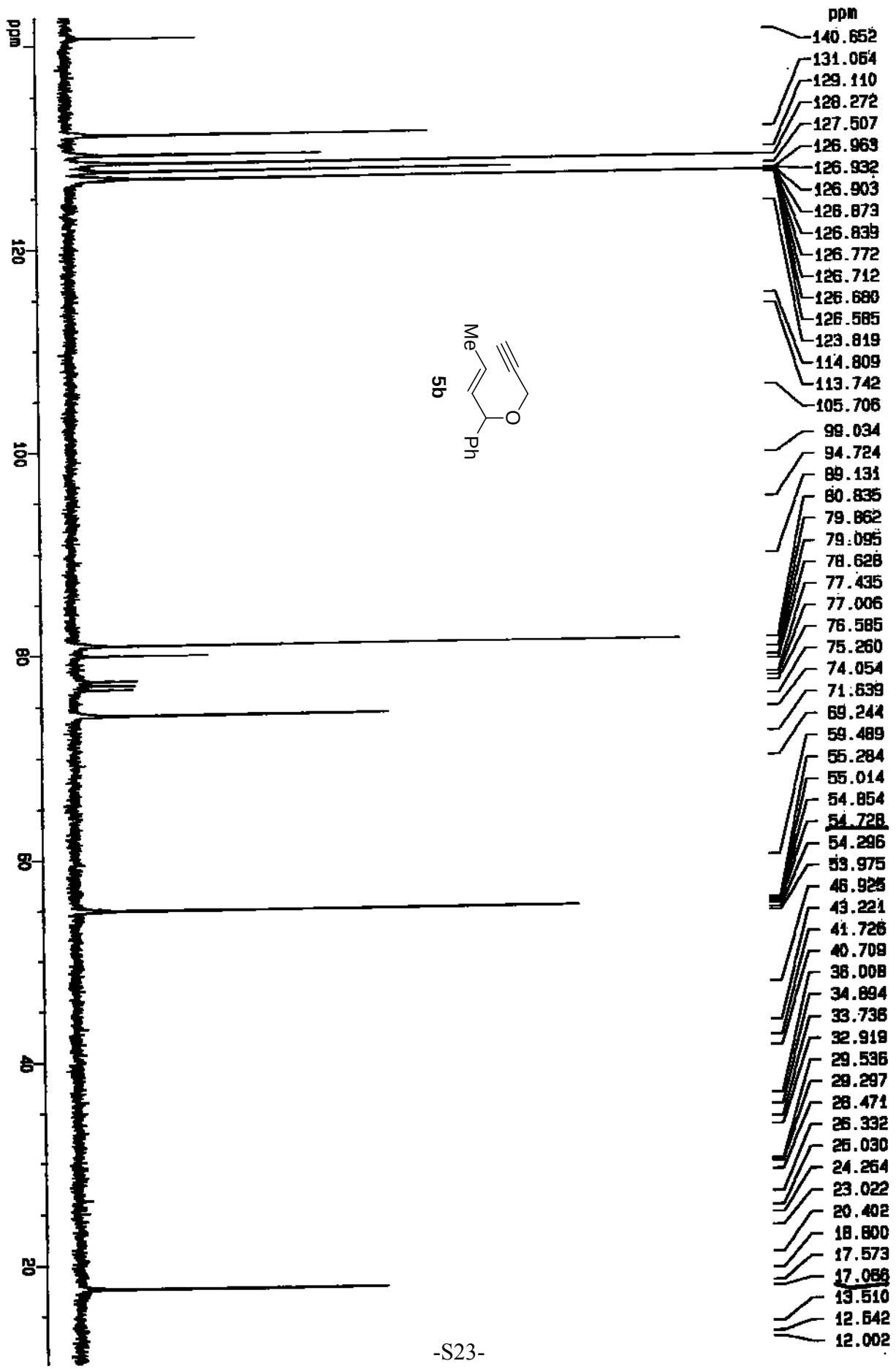
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32.919
29.536
29.297
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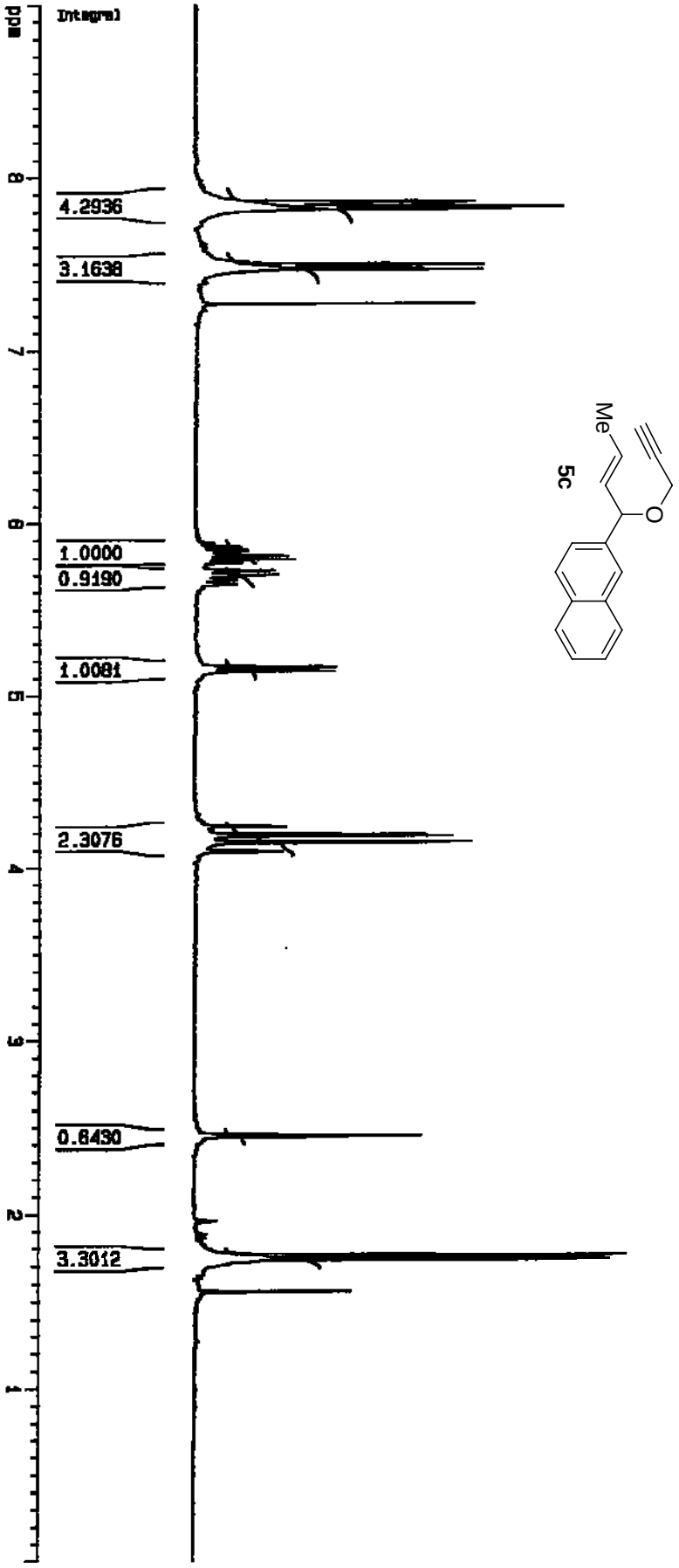
12.002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Me
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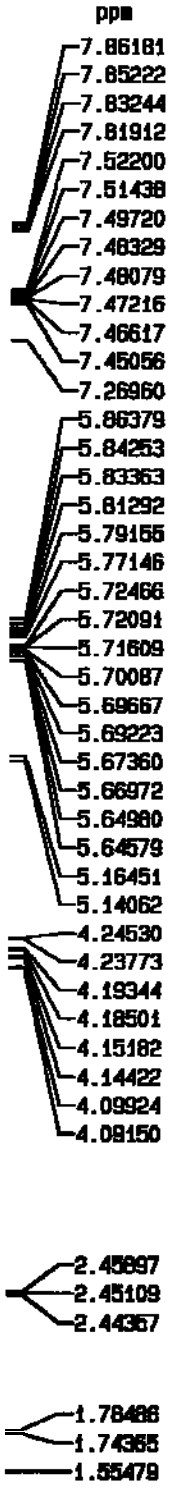
5c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7.47216
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7.45056
7.26960
5.86379
5.84253
5.83363
5.81292
5.79155
5.77146
5.72466
5.72091
5.71609
5.70087
5.69667
5.69223
5.67360
5.66972
5.64980
5.64579
5.16451
5.14062
4.24530
4.23773
4.19344
4.18501
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4.09150
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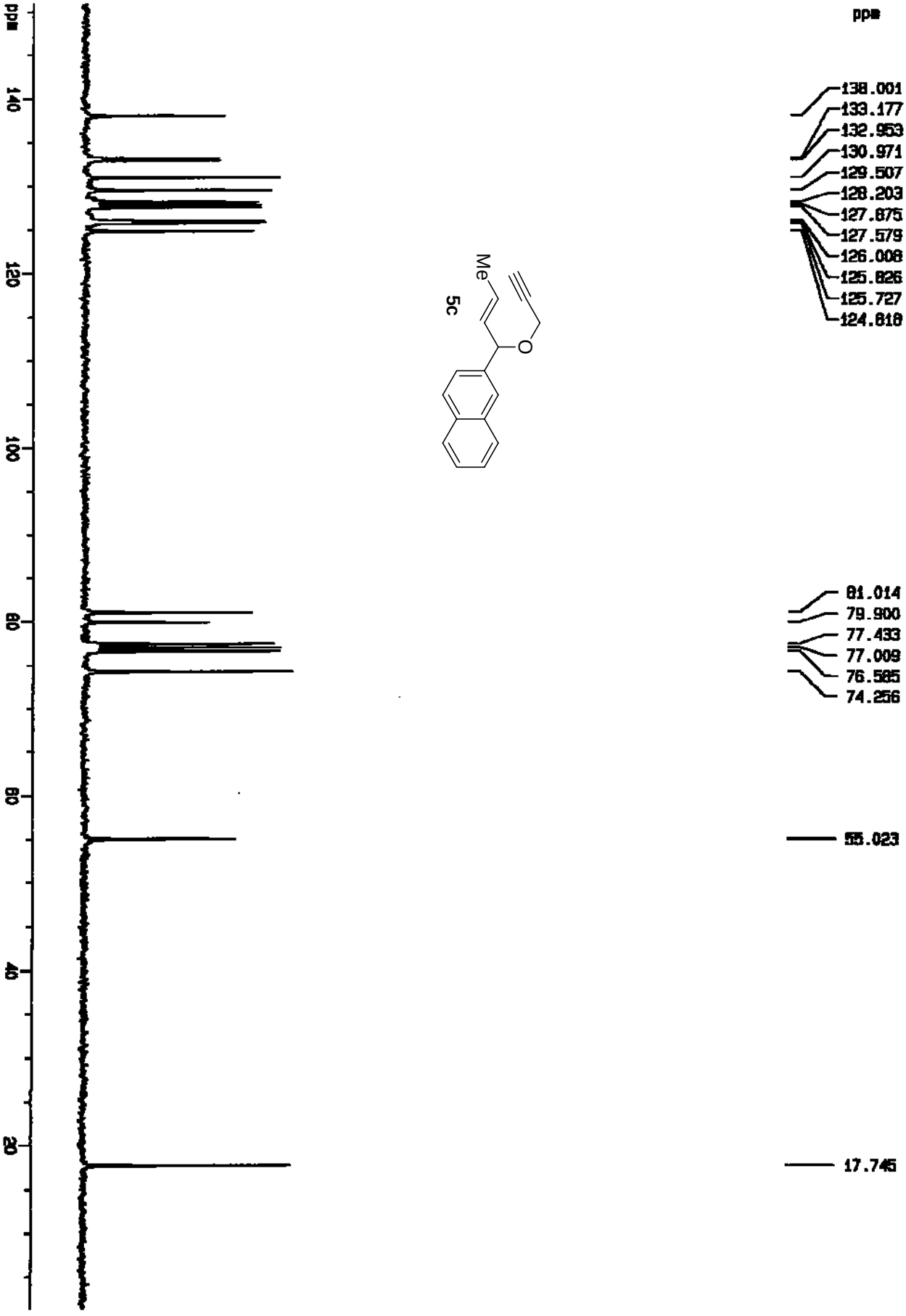
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O
5c
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127.875
127.579
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124.818
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77.009
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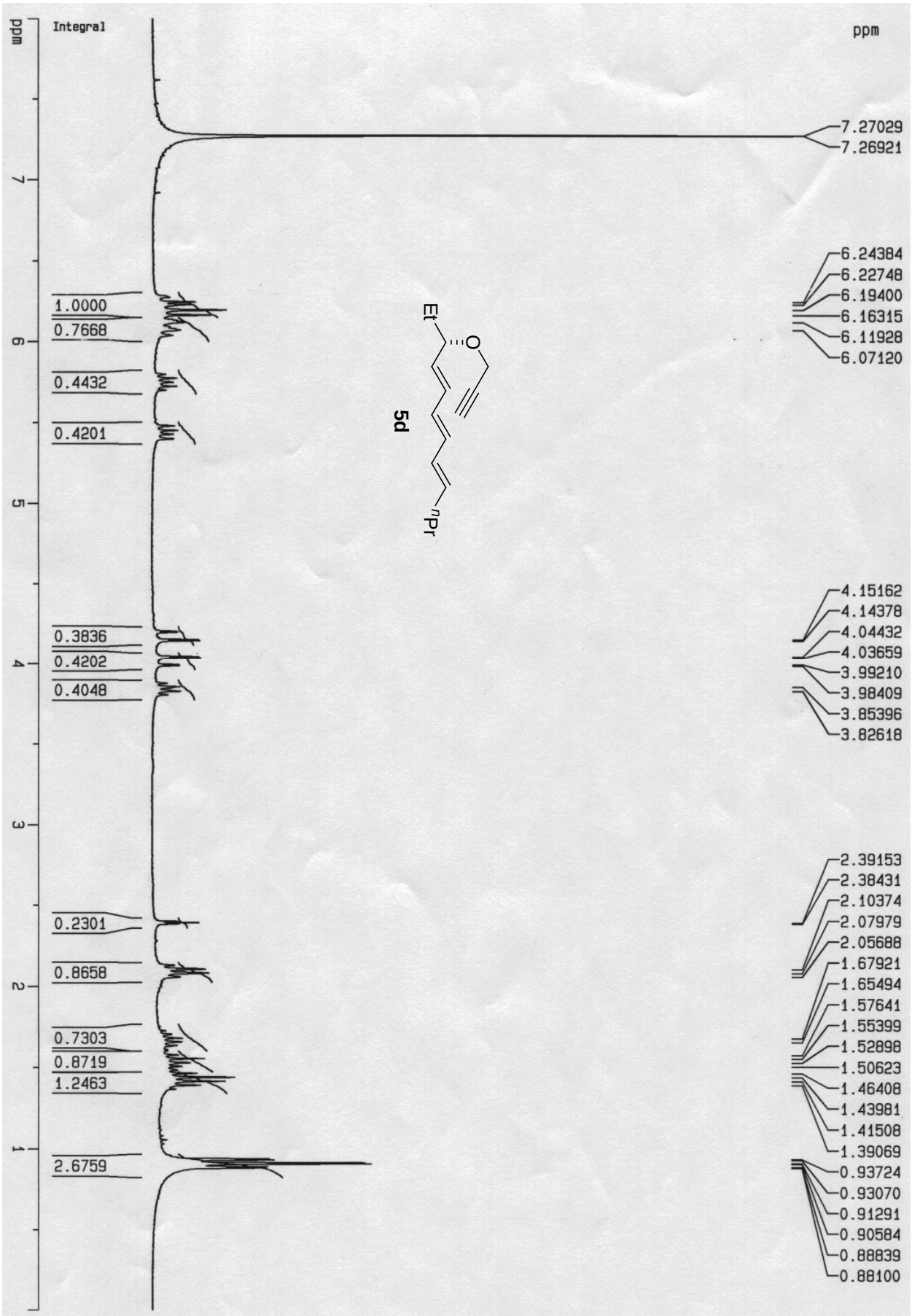
55.023
17.745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4.14378
4.04432
4.03659
3.99210
3.98409
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3.82618
2.39153
2.38431
2.10374
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1.65494
1.57641
1.55399
1.52898
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0.93070
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0.90584
0.88839
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1.0000
0.7668
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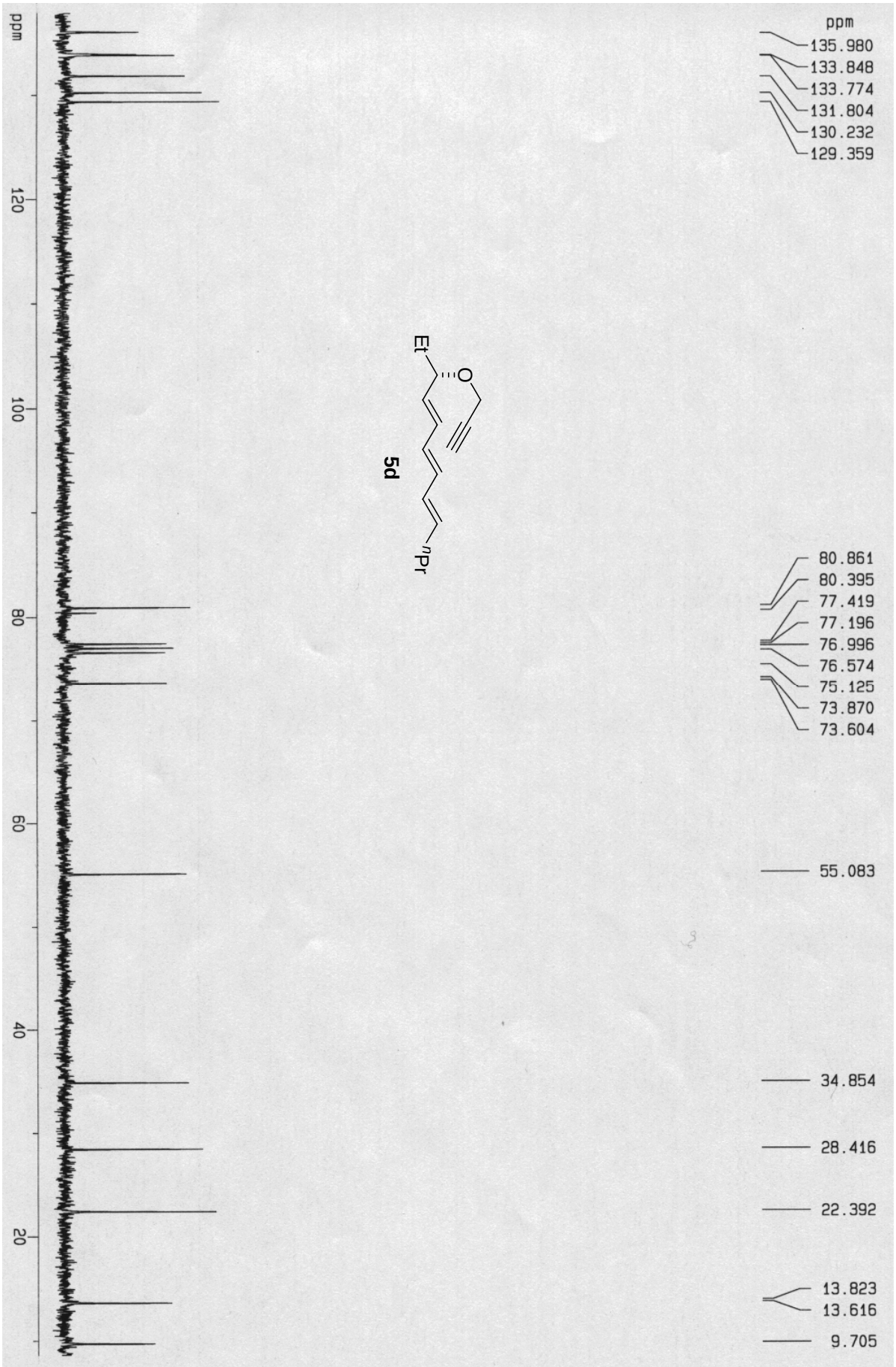
Et
O
nPr
5d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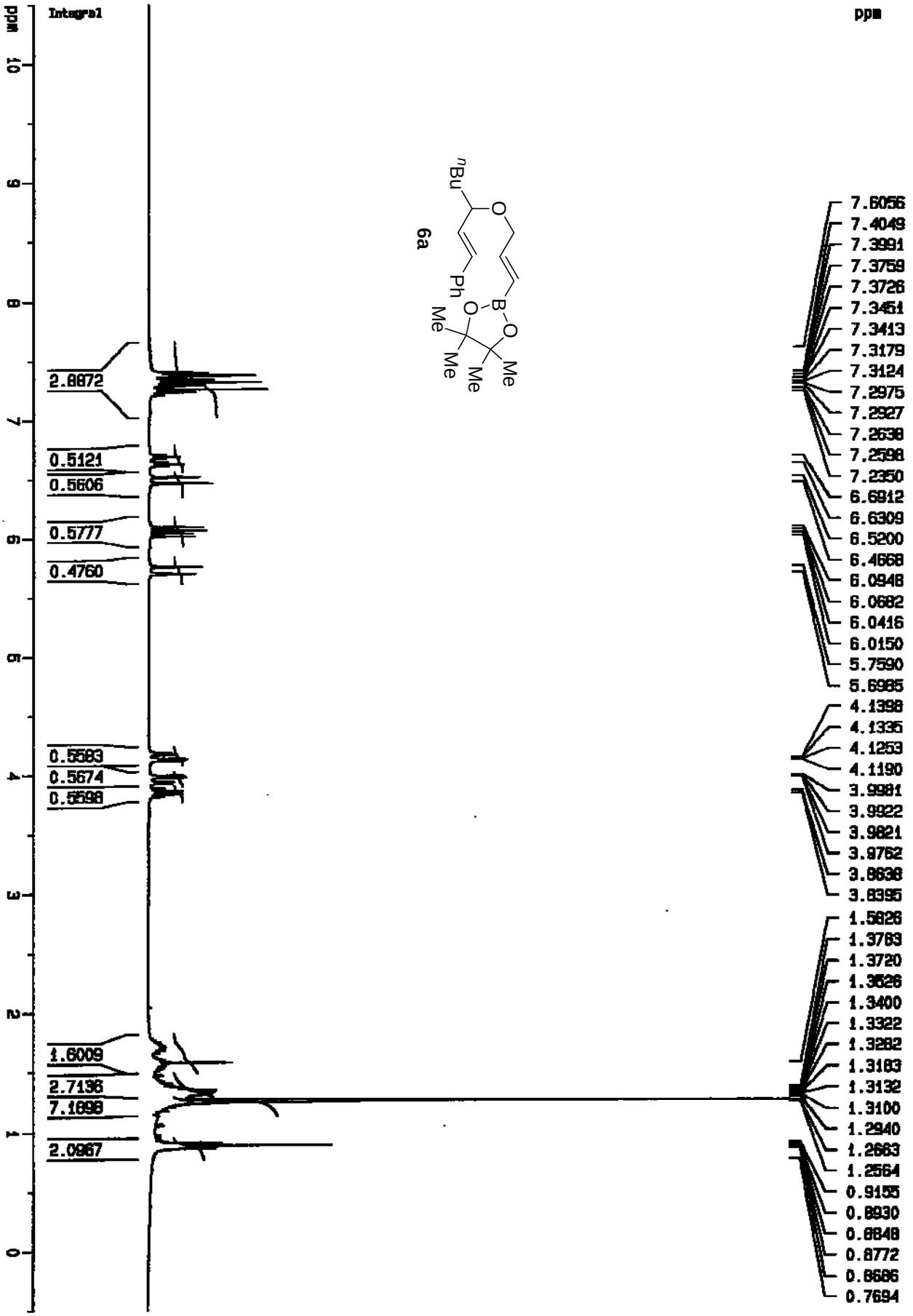
13.616
9.705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2.0967
nBu
O
Ph
O
B
O
Me
Me
Me
Me
6a
7.6056
7.4049
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7.3726
7.3451
7.3413
7.3179
7.3124
7.2975
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7.2598
7.2350
6.6912
6.6309
6.5200
6.4668
6.0948
6.0682
6.0416
6.0150
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5.6985
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4.1335
4.1253
4.1190
3.9981
3.9922
3.9821
3.9762
3.8638
3.8395
1.5826
1.3763
1.3720
1.3626
1.3400
1.3322
1.3282
1.3183
1.3132
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0.8848
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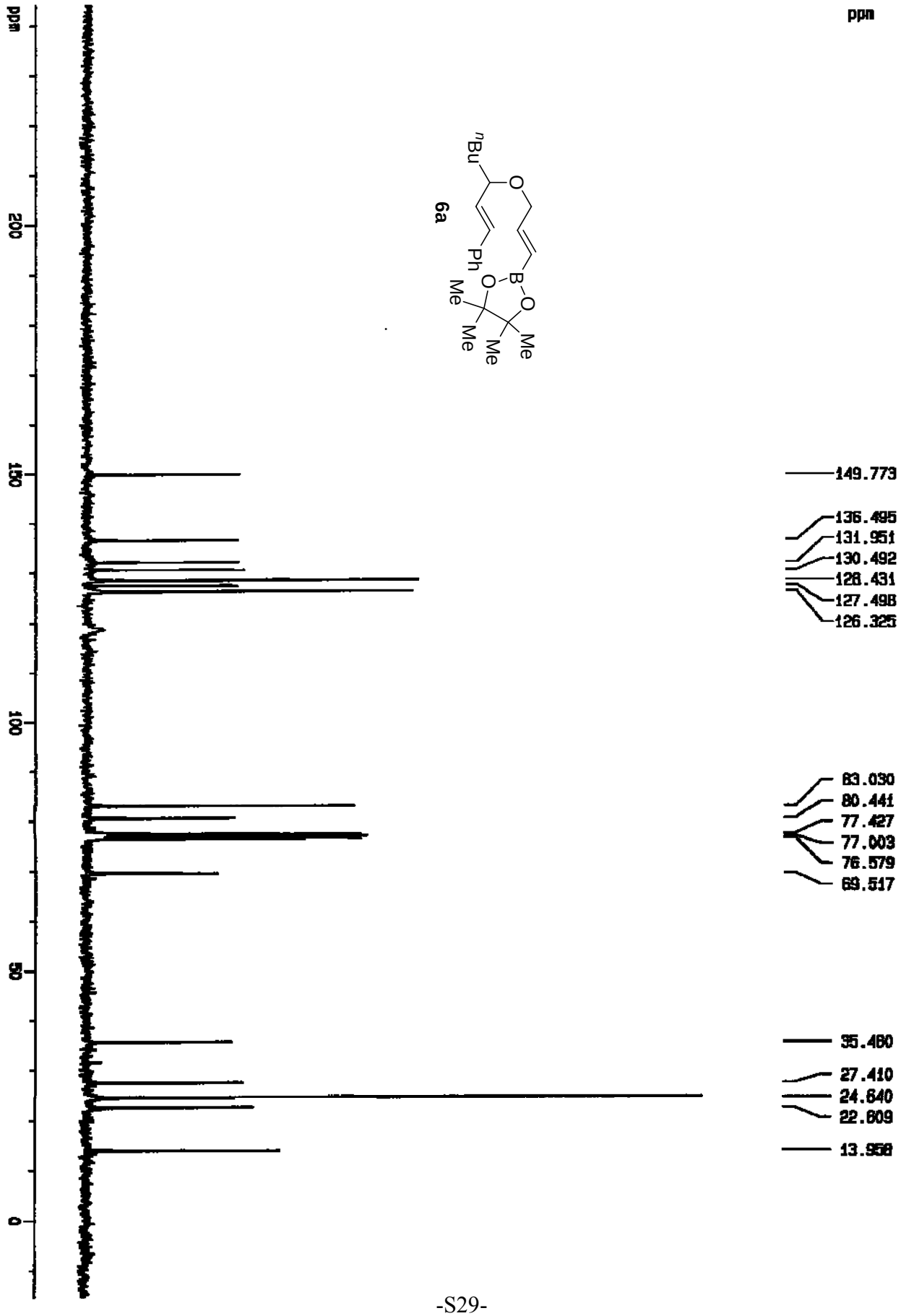
0.8686
0.7694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6a
nBu
Ph
Me
Me
Me
Me
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127.498
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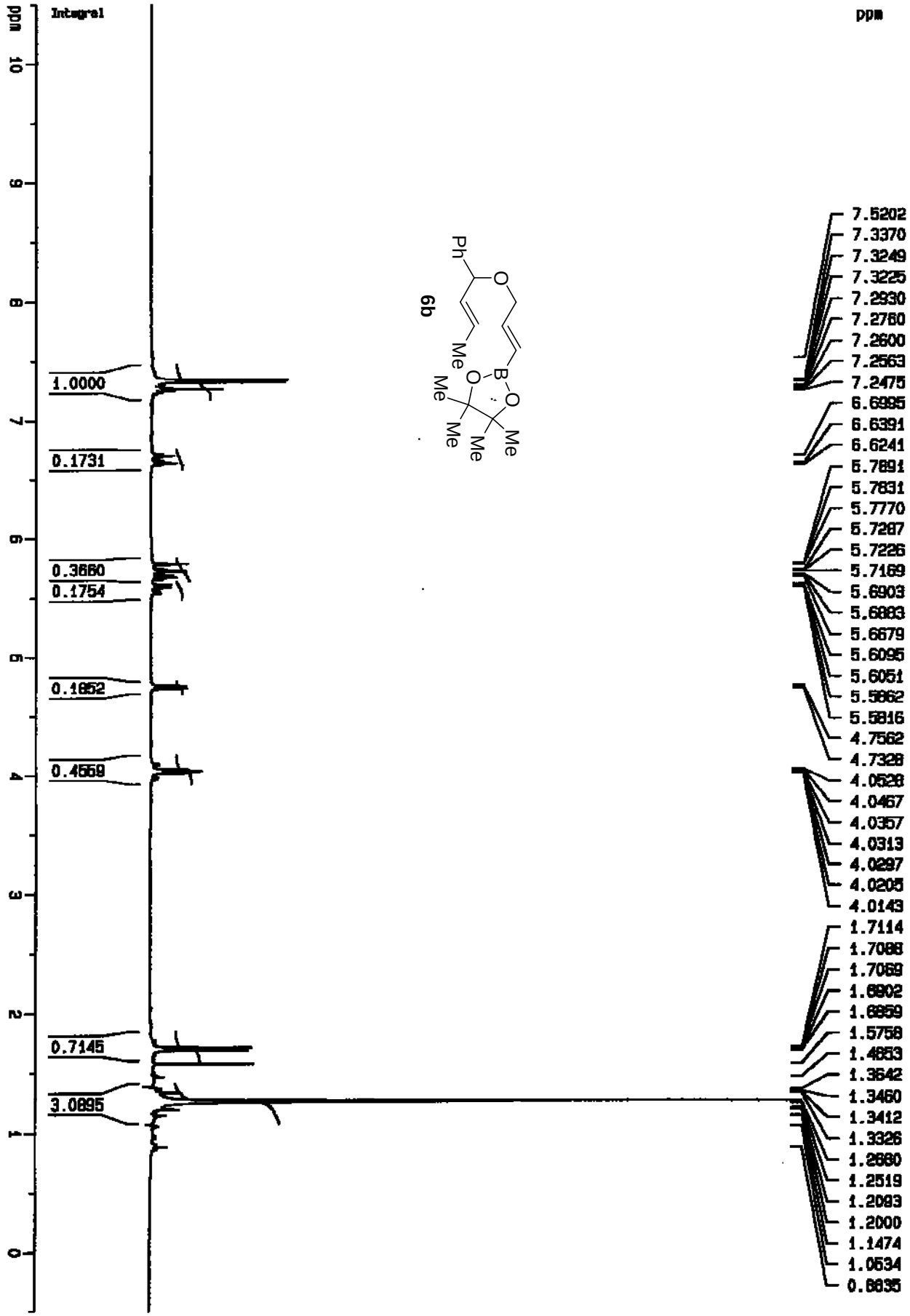
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Ph
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Me
O
B
O
Me
Me
Me
Me
6b
7.5202
7.3370
7.3249
7.3225
7.2930
7.2760
7.2600
7.2563
7.2475
6.6995
6.6391
6.6241
5.7891
5.7831
5.7770
5.7287
5.7226
5.7169
5.6903
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5.6051
5.5862
5.5816
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4.7328
4.0528
4.0467
4.0357
4.0313
4.0297
4.0205
4.0143
1.7114
1.7088
1.7069
1.6902
1.6859
1.5758
1.4853
1.3642
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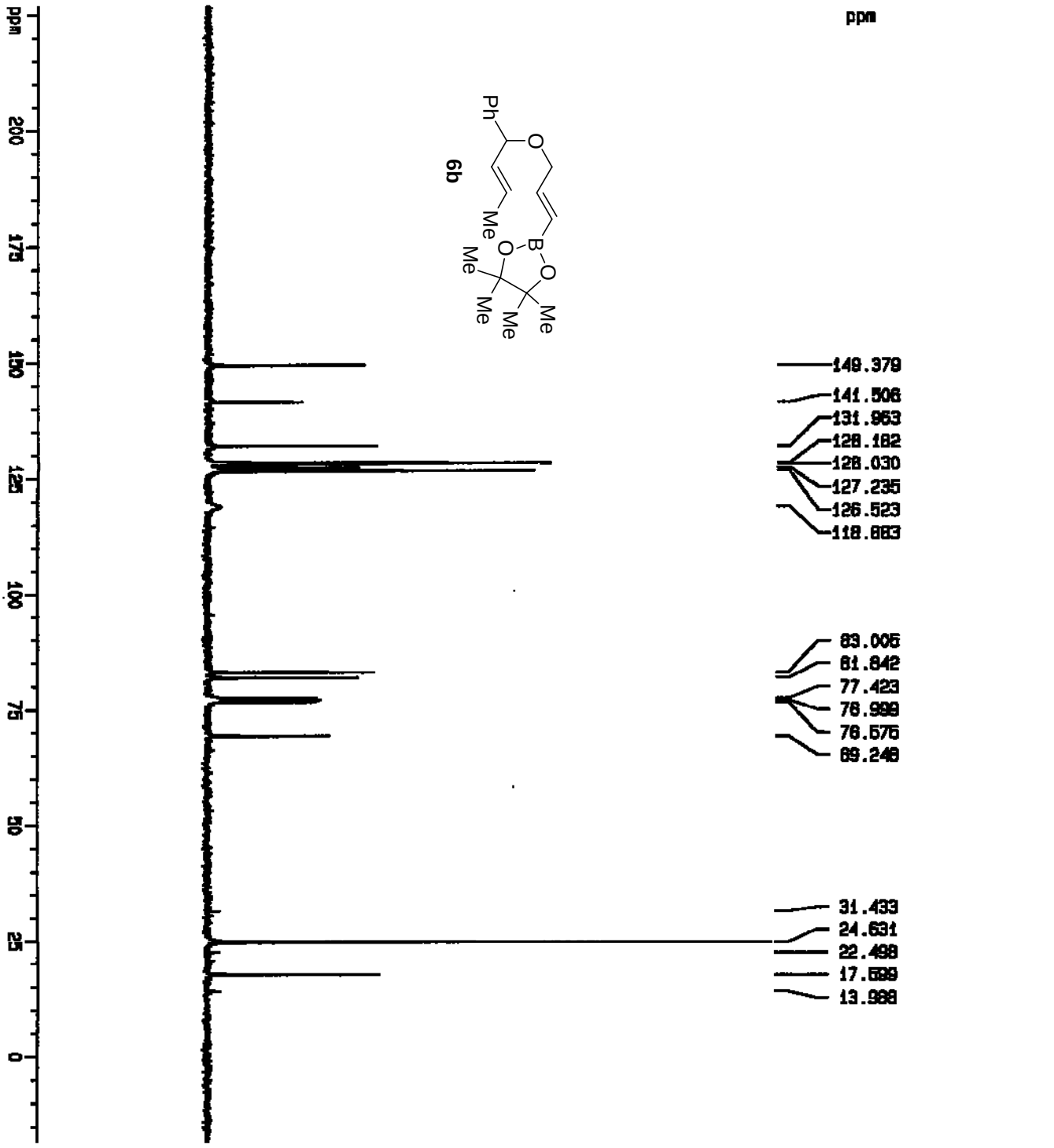
0.8835



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PROCNO 1

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TD 16384
SOLVENT CDCl3
NS 402
DS 0
SWH 18518.518 Hz
FIDRES 1.130281 Hz
AQ 0.442400 sec
RG 1024.0
DW 27.000 usec
DE 6.00 usec
TE 300.0 K
D1 0.00000000 sec
D3 0.00100000 sec

CHANNEL f1
NUC1 13C
P1 4.00 usec
PL1 0.00 dB
SFO1 75.5007008 MHz

CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 120.00 dB
PL12 12.00 dB
SFO2 300.2318914 MHz

F2 - Processing parameters
SI 32768
SF 75.4650000 MHz
WDW EM
SSB 0
LB 4.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
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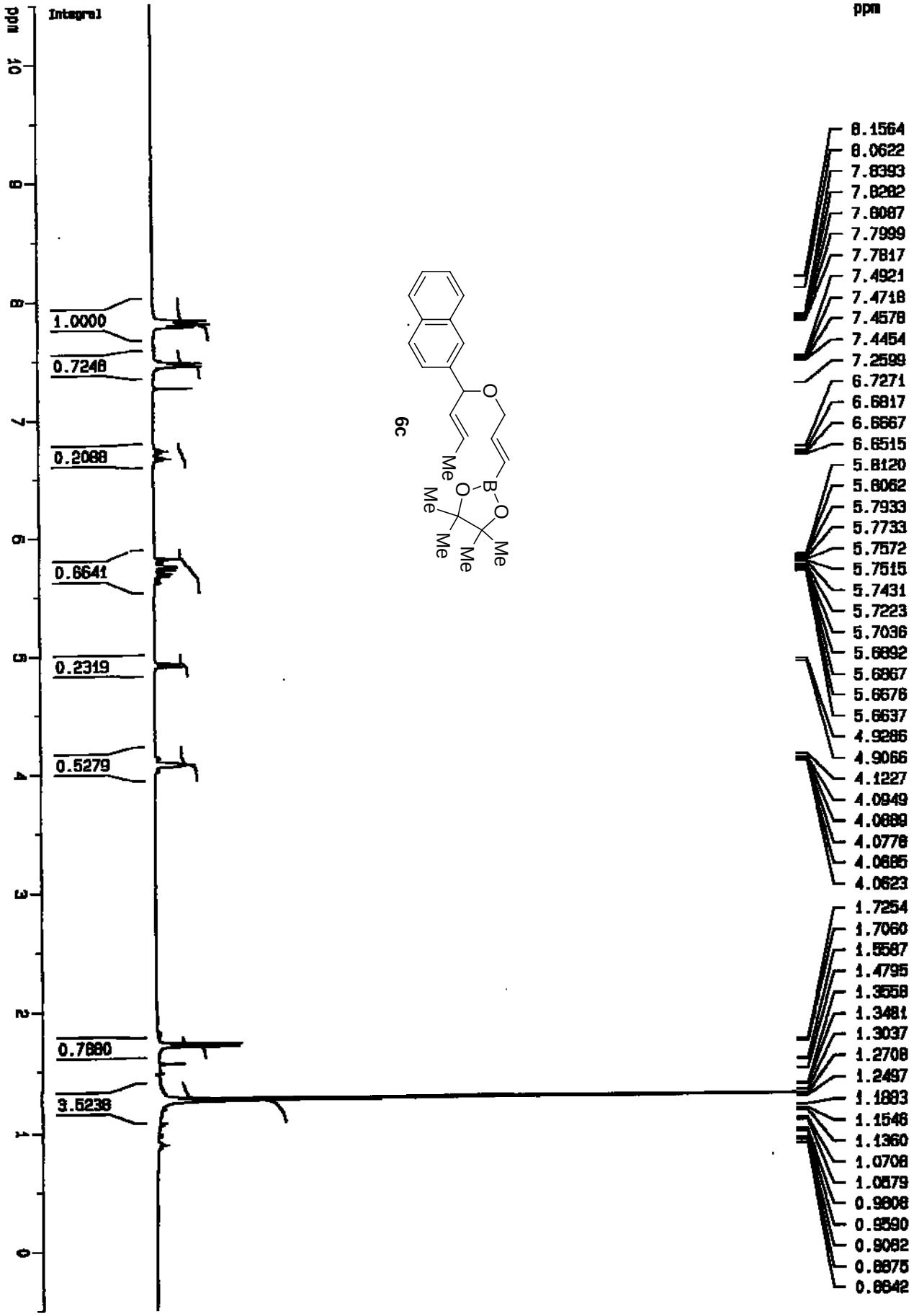
F1 17140.06 Hz
F2P -19.258 ppm
F2 -1378.48 Hz
PPMCM 12.26507 ppm/cm
HZCM 925.82568 Hz/cm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6c
Me
Me
Me
Me
Me
O
O
B
O
8.1564
8.0622
7.8393
7.8282
7.8087
7.7999
7.7817
7.4921
7.4718
7.4578
7.4454
7.2599
6.7271
6.6817
6.6667
6.6515
5.8120
5.8062
5.7933
5.7733
5.7572
5.7515
5.7431
5.7223
5.7036
5.6892
5.6867
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4.9066
4.1227
4.0949
4.0889
4.0778
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4.0623
1.7254
1.7060
1.5587
1.4795
1.3558
1.3481
1.3037
1.2708
1.2497
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1.1360
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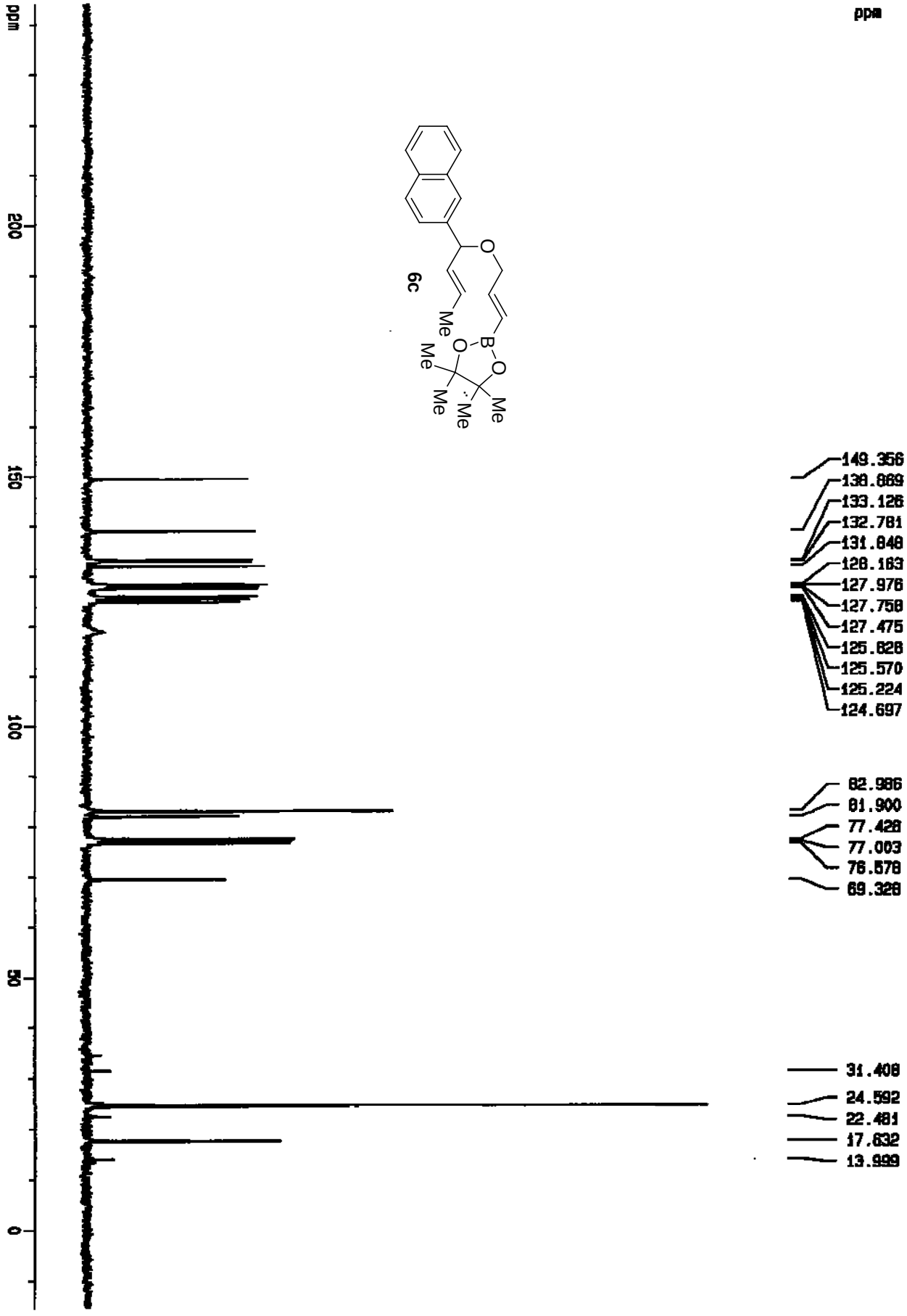
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150
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50
0
6c
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Me
O
B
O
Me
Me
Me
Me
O
ppm
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131.848
128.163
127.976
127.758
127.475
125.828
125.570
125.224
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77.428
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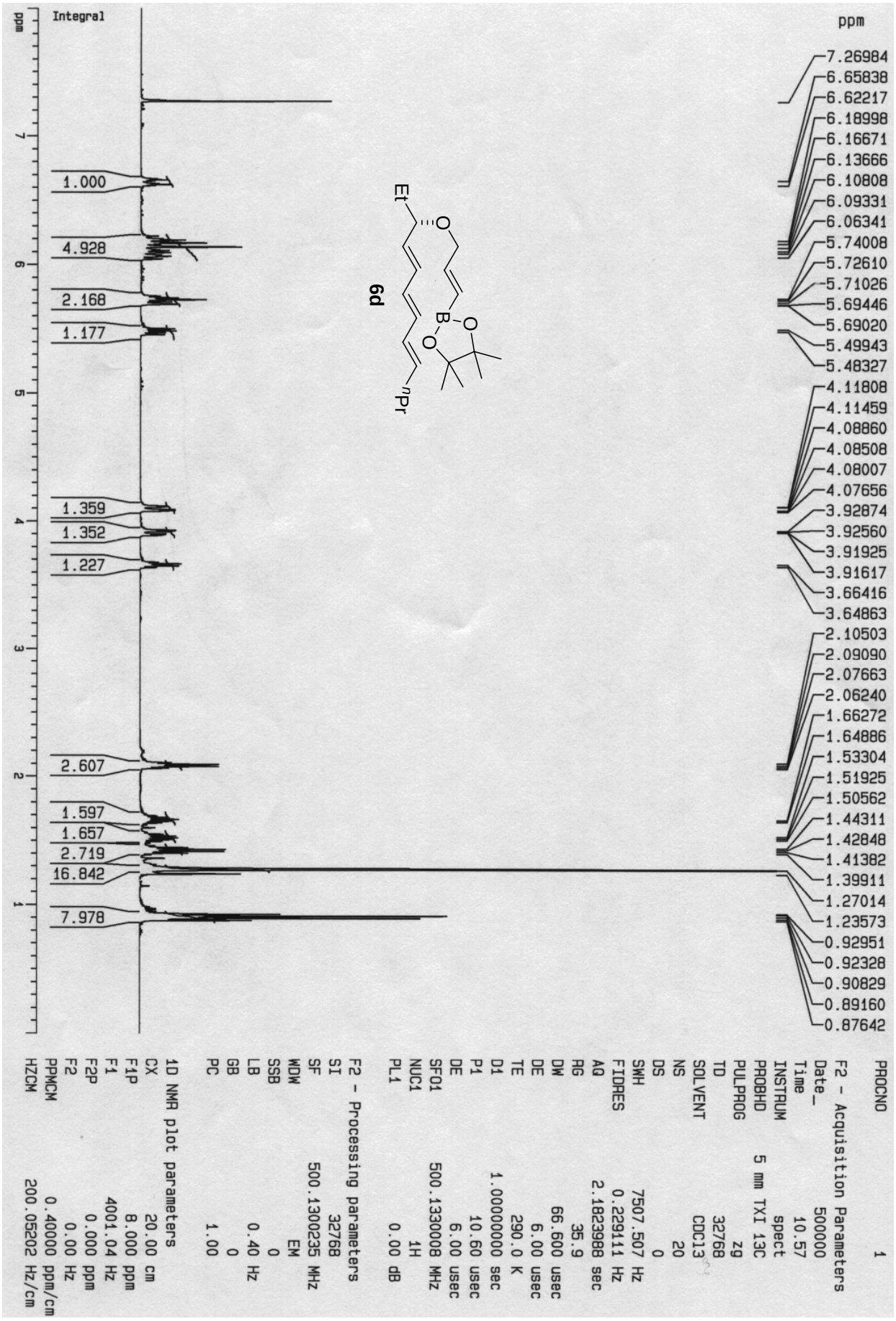
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7.978
Et
nPr
6d
ppm
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6.65838
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6.18998
6.16671
6.13666
6.10808
6.09331
6.06341
5.74008
5.72610
5.71026
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5.49943
5.48327
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4.11459
4.08860
4.08508
4.08007
4.07656
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3.91925
3.91617
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3.64863
2.10503
2.09090
2.07663
2.06240
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1.53304
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1.50562
1.44311
1.42848
1.41382
1.39911
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1.23573
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0.92328
0.90829
0.89160
0.87642
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Time 10.57
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PULPROG zg
TD 32768
SOLVENT CDCl3
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SWH 7507.507 Hz
FIDRES 0.229111 Hz
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RG 35.9
DW 66.600 usec
DE 6.00 usec
TE 290.0 K
D1 1.00000000 sec
P1 10.60 usec
DE 6.00 usec
SFO1 500.1330008 MHz
NUC1 1H
PL1 0.00 dB
F2 - Processing parameters
SI 32768
SF 500.1300235 MHz
WDW EM
SSB 0
LB 0.40 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
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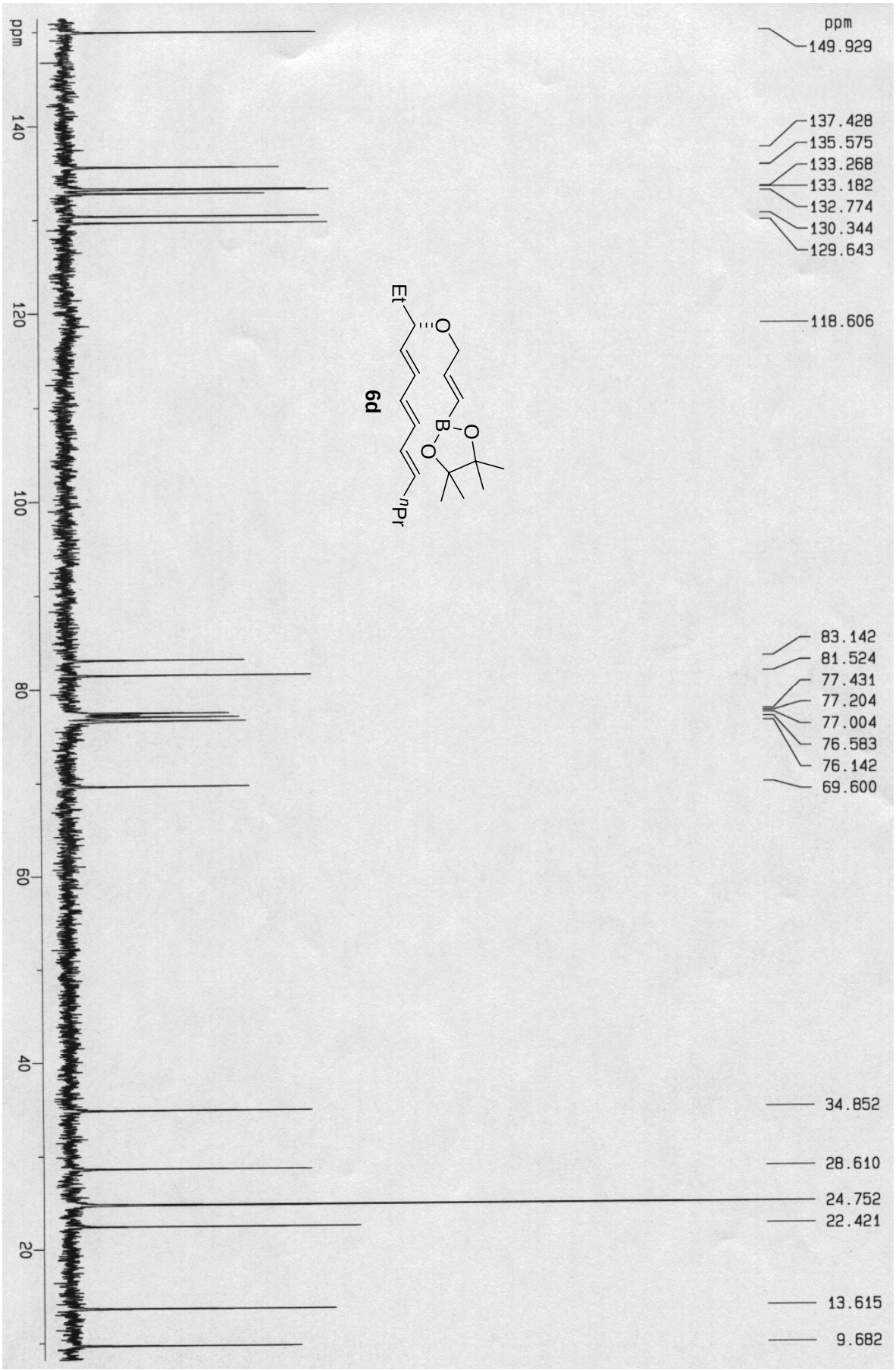
F1 4001.04 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.40000 ppm/cm
HZCM 200.05202 Hz/cm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ppm
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133.268
133.182
132.774
130.344
129.643
118.606
83.142
81.524
77.431
77.204
77.004
76.583
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28.610
24.752
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Et
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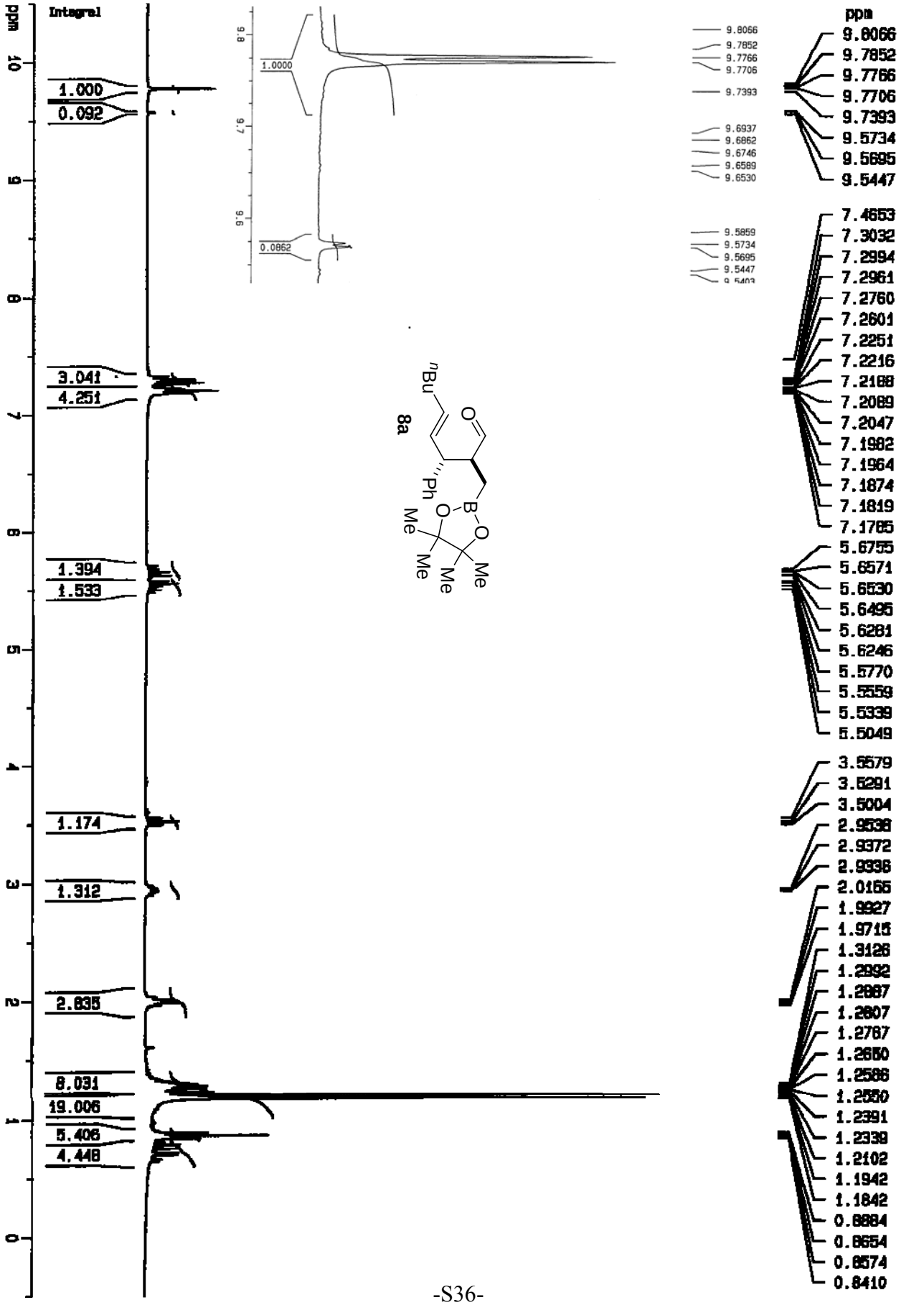
nPr
6d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8a
nBu
Ph
Me
Me
Me
Me
O
O
B
O
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9.7393
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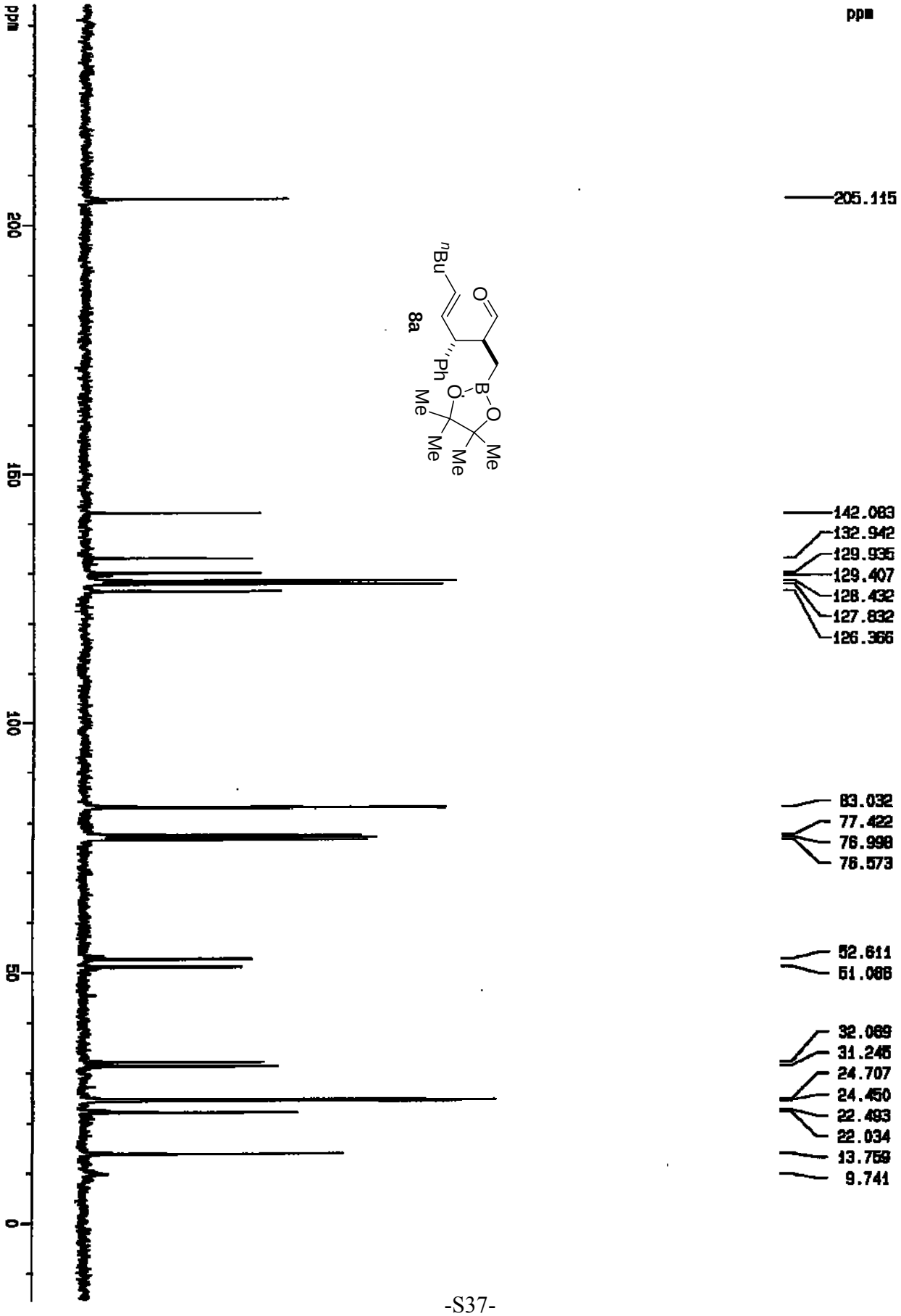
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Me
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128.432
127.832
126.366
83.032
77.422
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76.573
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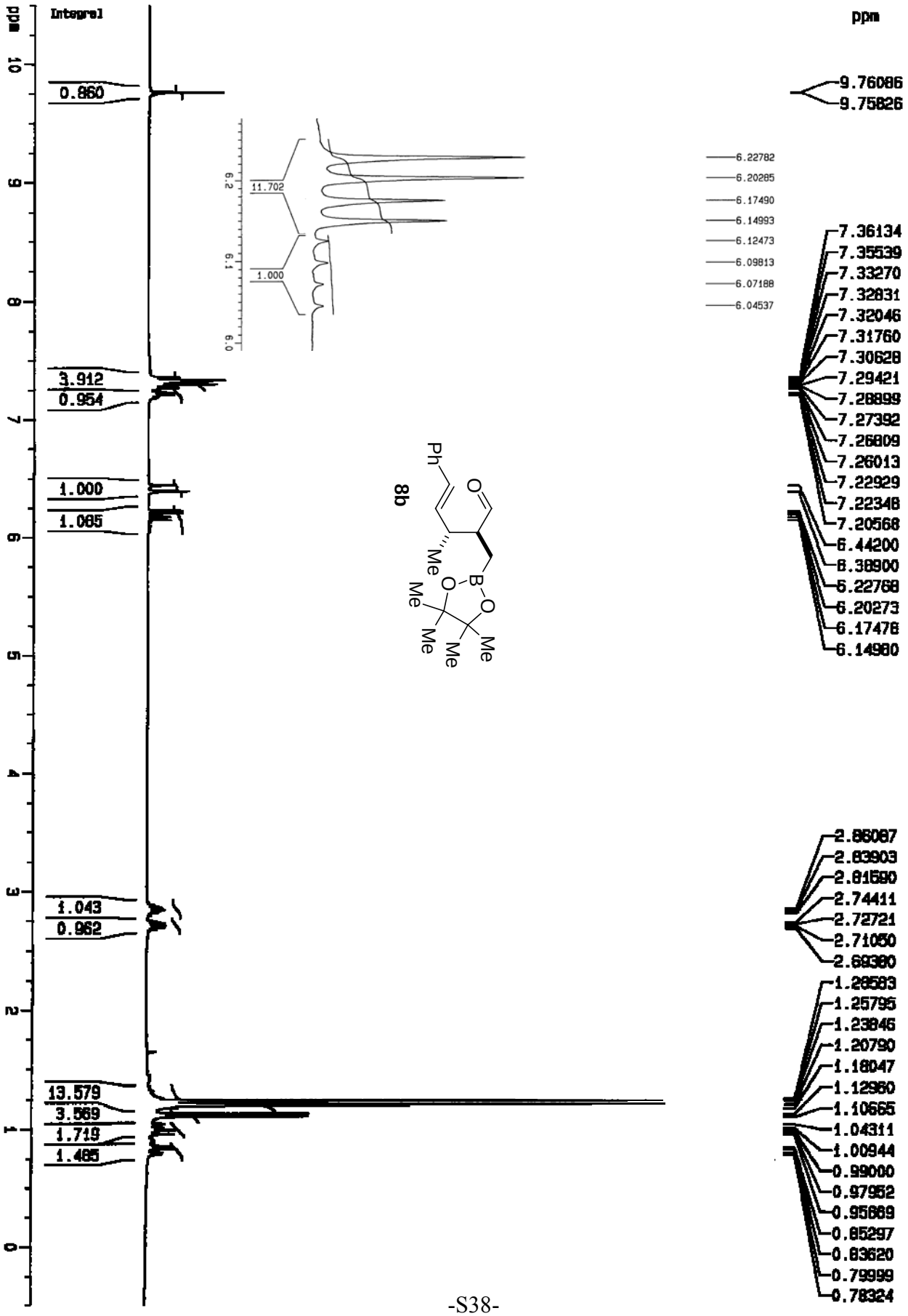
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7.32046
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Me
B
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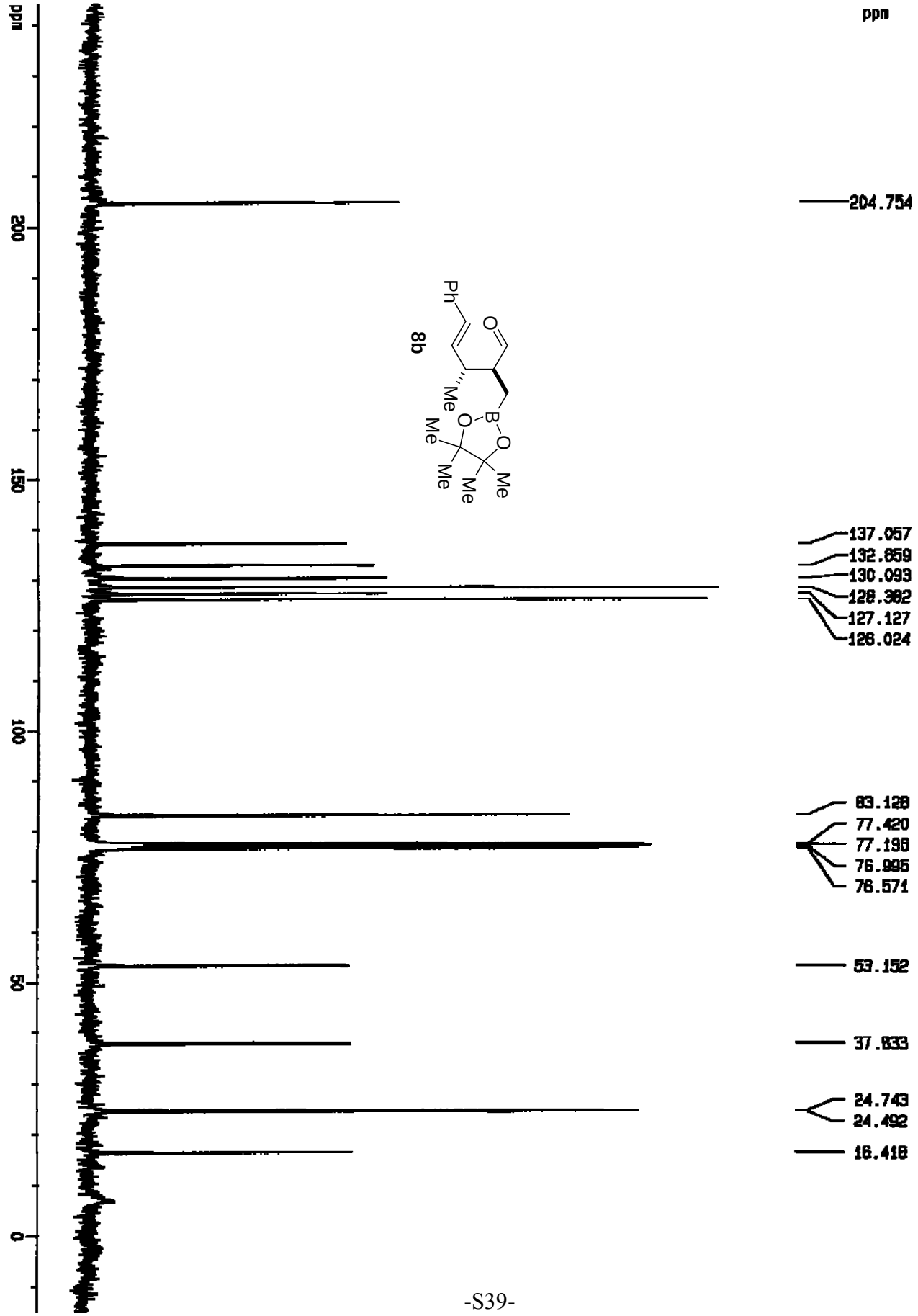
Me
Me
Me
8b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O
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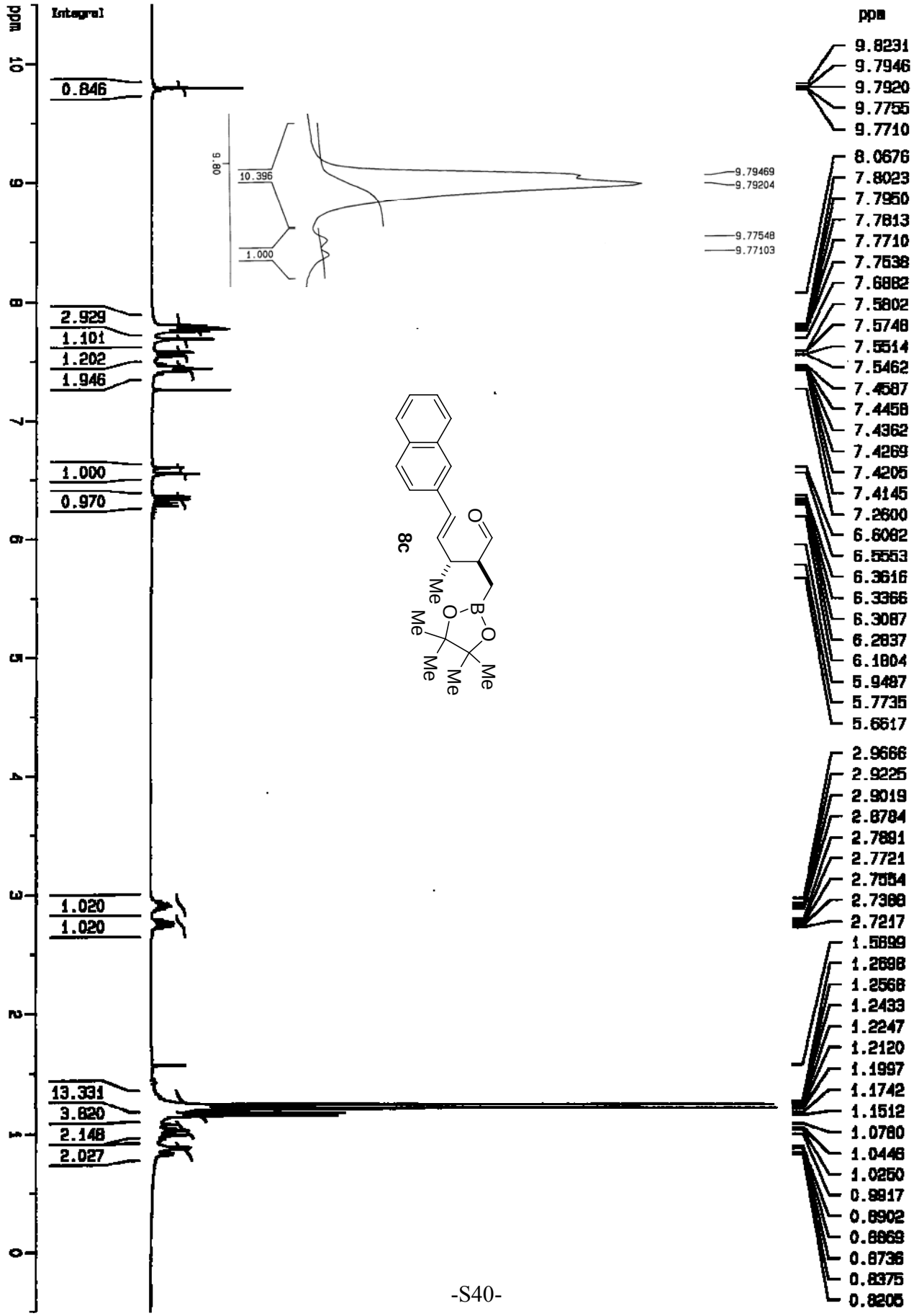
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1.020
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3.820
2.148
2.027
9.79469
9.79204
9.77548
9.77103
8c
O
B
O
Me
Me
Me
Me
Me
ppm
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9.7710
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7.7638
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7.4145
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6.5553
6.3616
6.3366
6.3087
6.2837
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5.7735
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2.9019
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2.7217
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1.2568
1.2433
1.2247
1.2120
1.1997
1.1742
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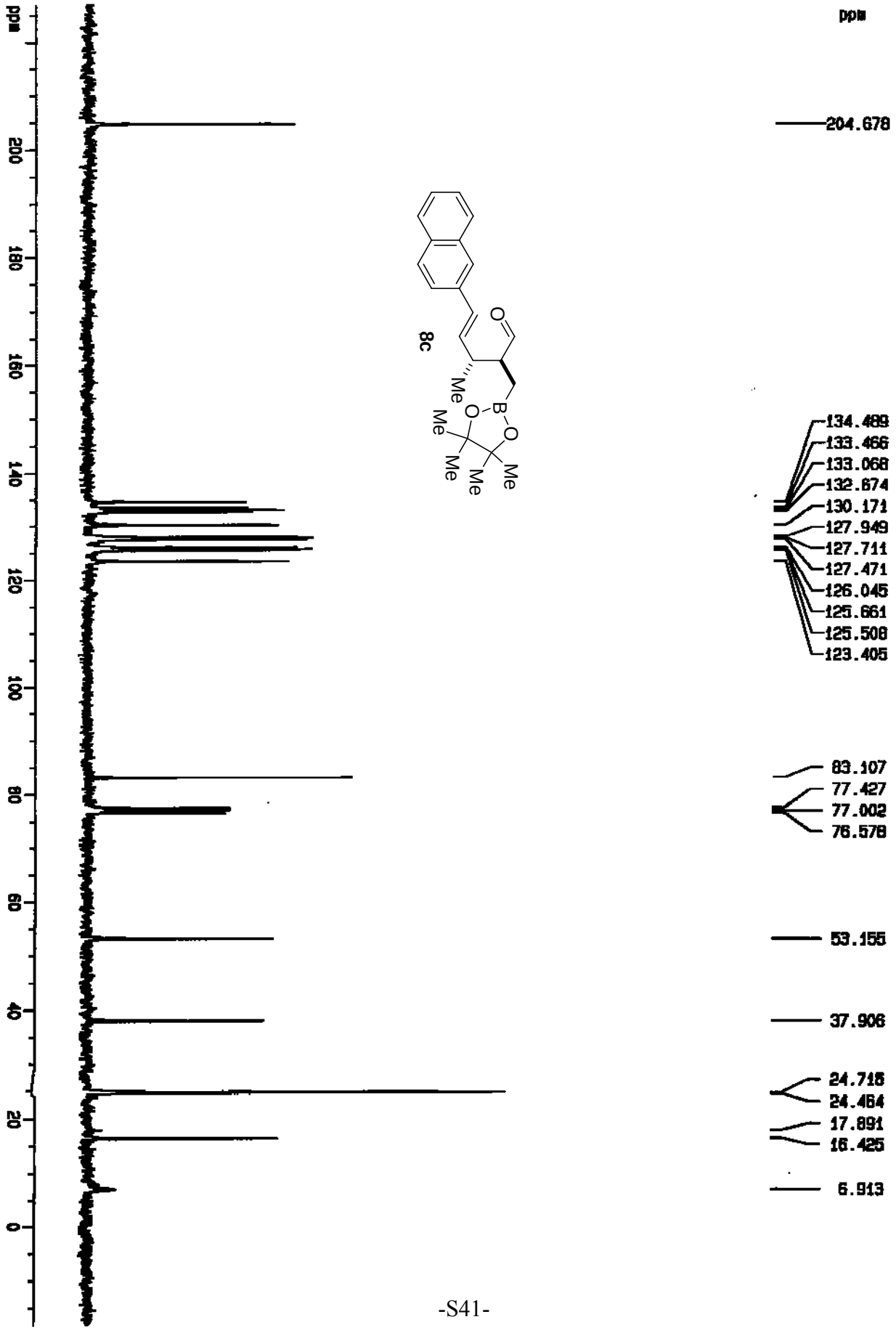
0.8205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83.107
77.427
77.002
76.578
53.155
37.906
24.715
24.464
17.891
16.425
6.913
8c
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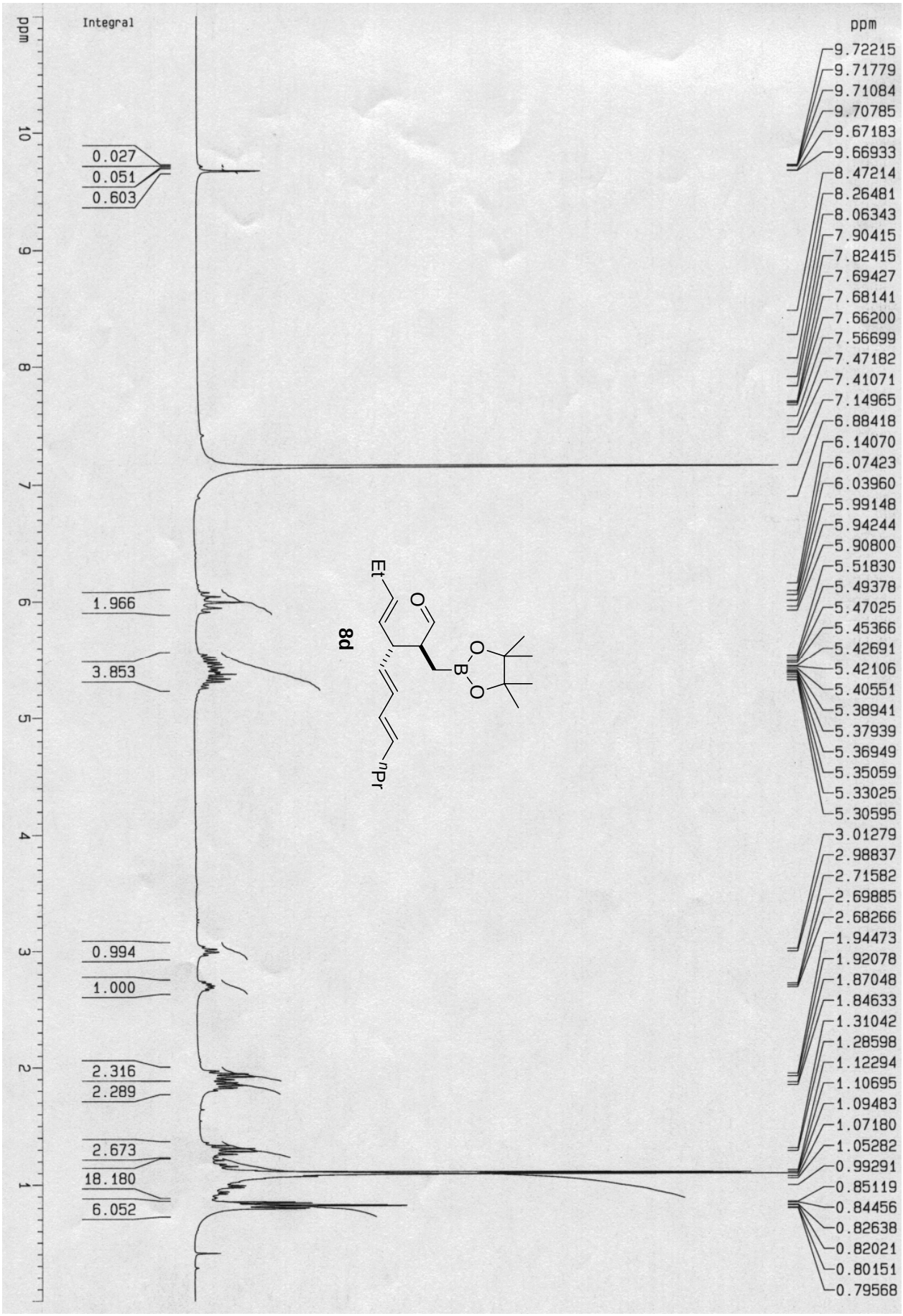
Me
Me
O
B
O
Me
Me
Me


Integral
ppm
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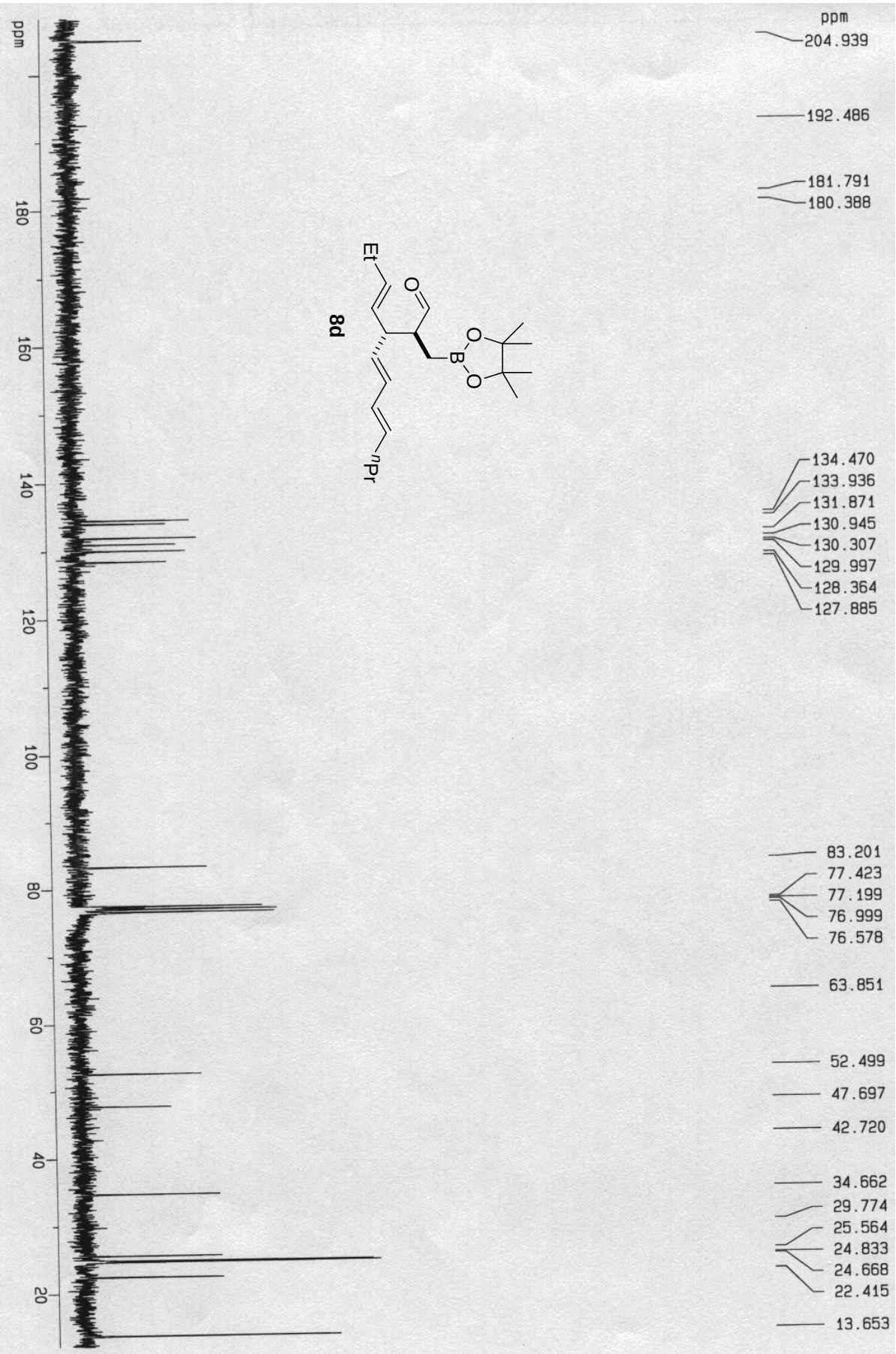
1.966
3.853
0.994
1.000
2.316
2.289
2.673
18.180
6.052
8d
Et
O
O
B
O
nPr
9.72215
9.71779
9.71084
9.70785
9.67183
9.66933
8.47214
8.26481
8.06343
7.90415
7.82415
7.69427
7.68141
7.66200
7.56699
7.47182
7.41071
7.14965
6.88418
6.14070
6.07423
6.03960
5.99148
5.94244
5.90800
5.51830
5.49378
5.47025
5.45366
5.42691
5.42106
5.40551
5.38941
5.37939
5.36949
5.35059
5.33025
5.30595
3.01279
2.98837
2.71582
2.69885
2.68266
1.94473
1.92078
1.87048
1.84633
1.31042
1.28598
1.12294
1.10695
1.09483
1.07180
1.05282
0.99291
0.85119
0.84456
0.82638
0.82021
0.80151
0.79568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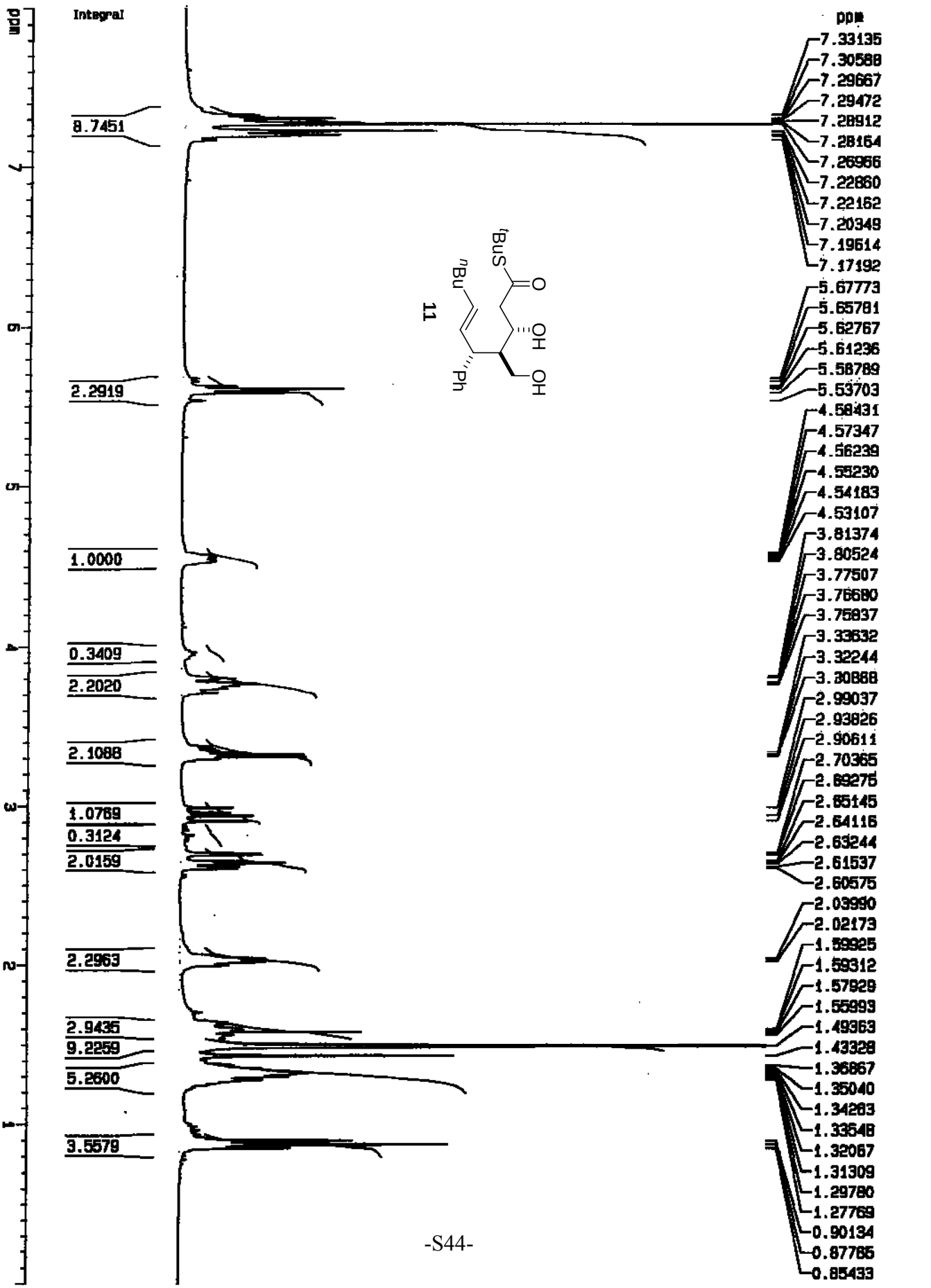
134.470
133.936
131.871
130.945
130.307
129.997
128.364
127.885
83.201
77.423
77.199
76.999
76.578
63.851
52.499
47.697
42.720
34.662
29.774
25.564
24.833
24.668
22.415
13.653
Et
O
O
B
O
nPr
8d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ppm
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1.0000
0.3409
2.2020
2.1088
1.0769
0.3124
2.0159
2.2963
2.9435
9.2259
5.2600
3.5579
7.33135
7.30588
7.29667
7.29472
7.28912
7.28164
7.26966
7.22860
7.22162
7.20349
7.19614
7.17192
5.67773
5.65781
5.62767
5.61236
5.58789
5.53703
4.58431
4.57347
4.56239
4.55230
4.54183
4.53107
3.81374
3.80524
3.77507
3.76680
3.75837
3.33632
3.32244
3.30888
2.99037
2.93826
2.90611
2.70365
2.69275
2.65145
2.64116
2.63244
2.61537
2.60575
2.03990
2.02173
1.59925
1.59312
1.57929
1.55993
1.49363
1.43328
1.36867
1.35040
1.34263
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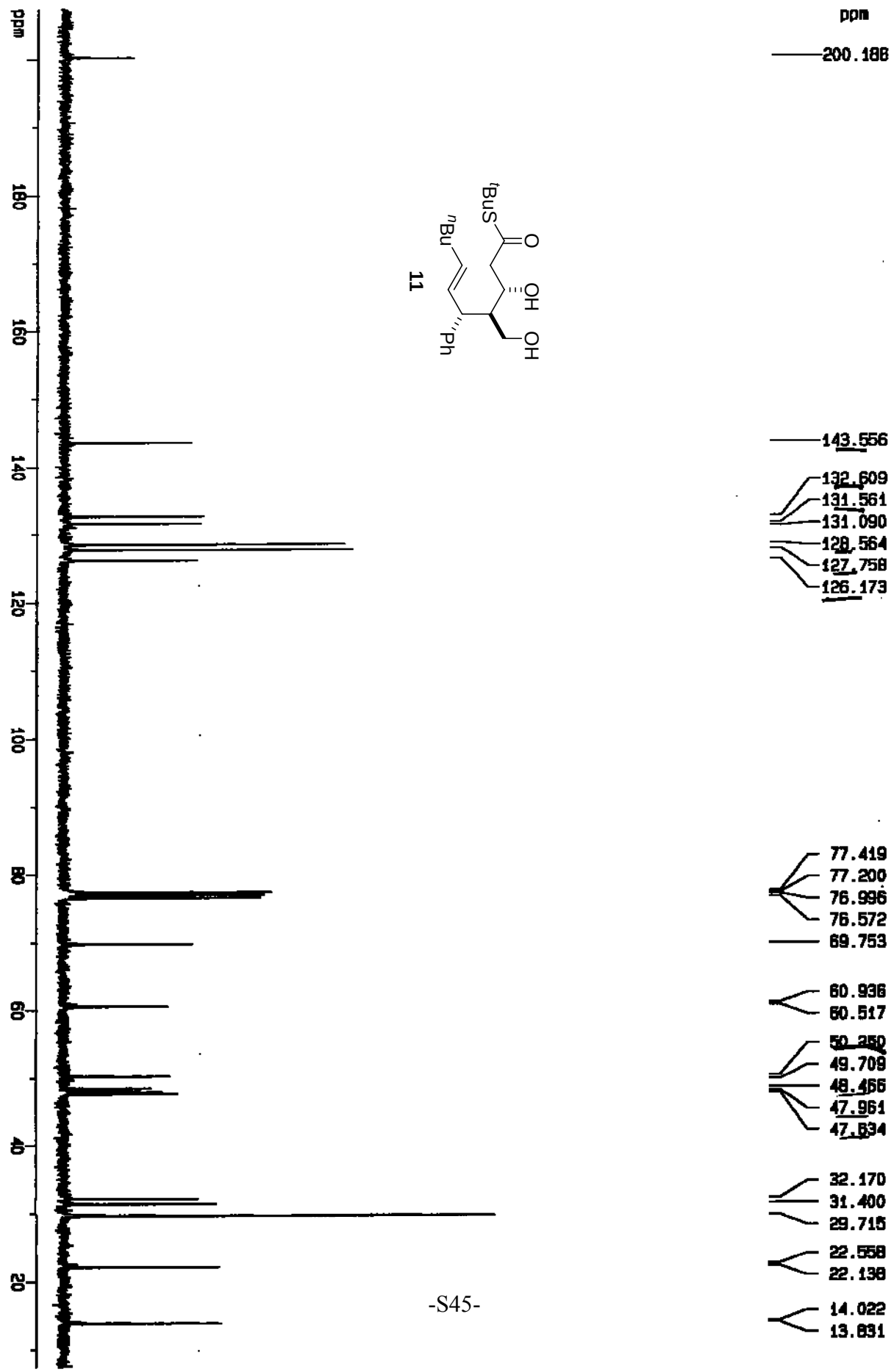
1.32067
1.31309
1.29780
1.27769
0.90134
0.87765
0.85433

11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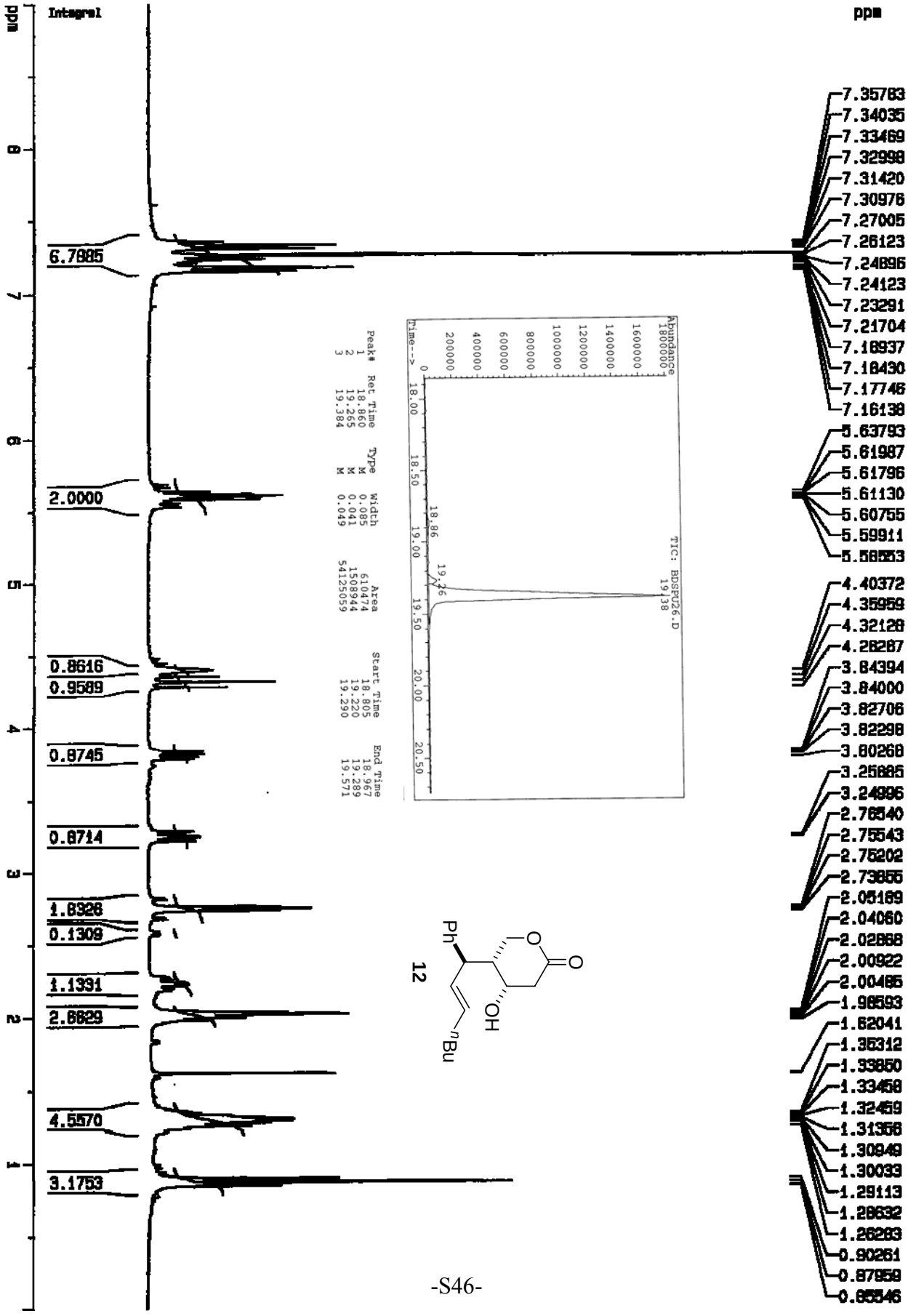
131.561
131.090
128.564
127.758
126.173
77.419
77.200
76.996
76.572
69.753
60.936
60.517
50.250
49.709
48.466
47.961
47.634
32.170
31.400
29.715
22.558
22.138
14.022
13.831
11
OH
OH
Ph
Bu
Bu


Integral
ppm
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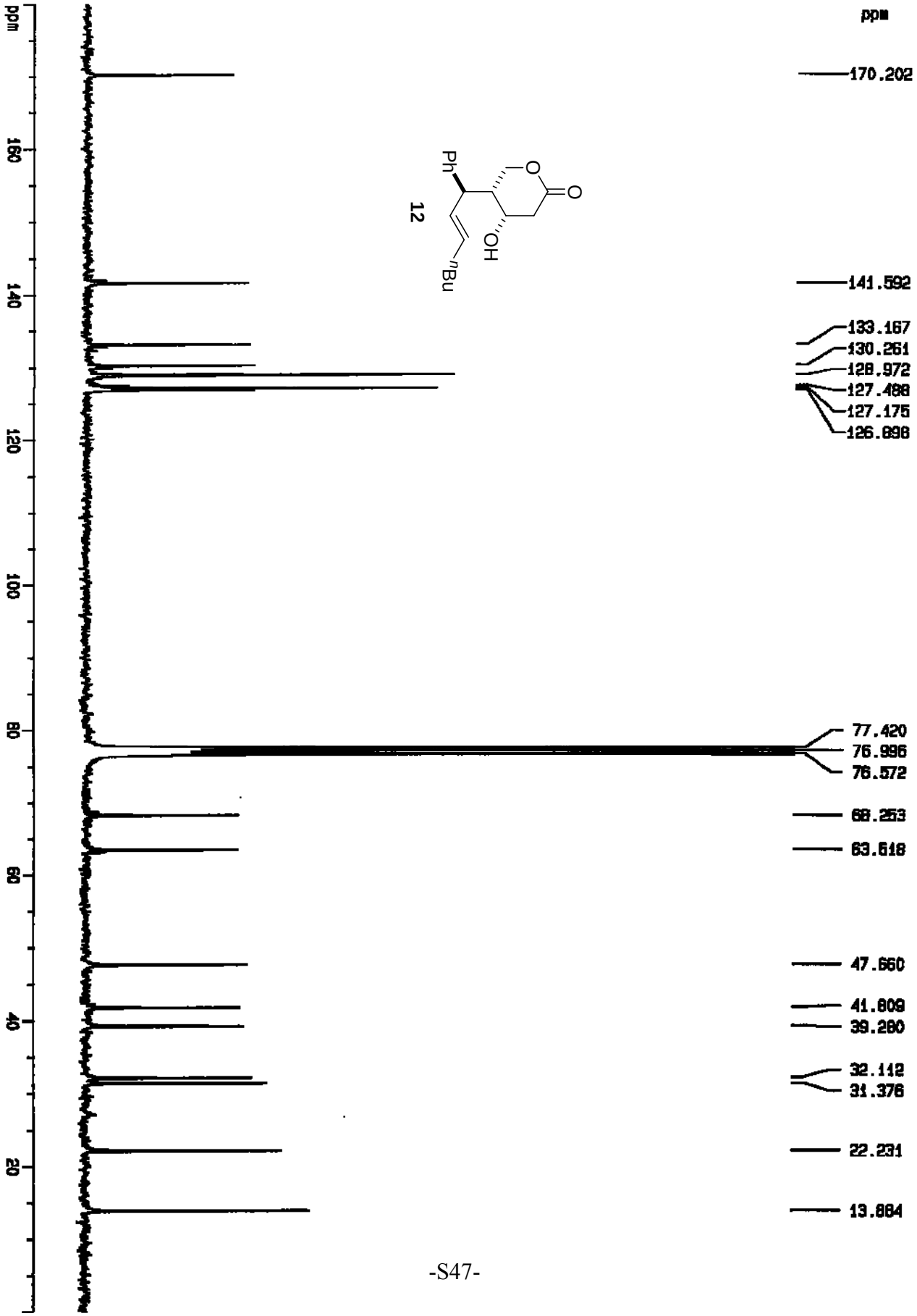
0.9589
0.8745
0.8714
1.8328
0.1309
1.1391
2.8629
4.5570
3.1753
7.35783
7.34035
7.33469
7.32998
7.31420
7.30976
7.27005
7.26123
7.24896
7.24123
7.23291
7.21704
7.18937
7.18430
7.17746
7.16138
5.63793
5.61987
5.61796
5.61130
5.60755
5.59911
5.58553
4.40372
4.35959
4.32128
4.28287
3.84394
3.84000
3.82706
3.82298
3.80268
3.25885
3.24996
2.76540
2.75543
2.75202
2.73855
2.05169
2.04060
2.02868
2.00922
2.00485
1.98593
1.62041
1.36312
1.33850
1.33458
1.32459
1.31356
1.30949
1.30033
1.29113
1.28632
1.26283
0.90261
0.87959
0.85546
Abundance
TIC: BDSPU26.D
Peak# Ret Time Type Width Area Start Time End Time
1 18.860 M 0.085 610474 18.805 18.967
2 19.265 M 0.041 1508944 19.220 19.289
3 19.384 M 0.049 54125059 19.290 19.571
Ph
O
O
OH
nBu
12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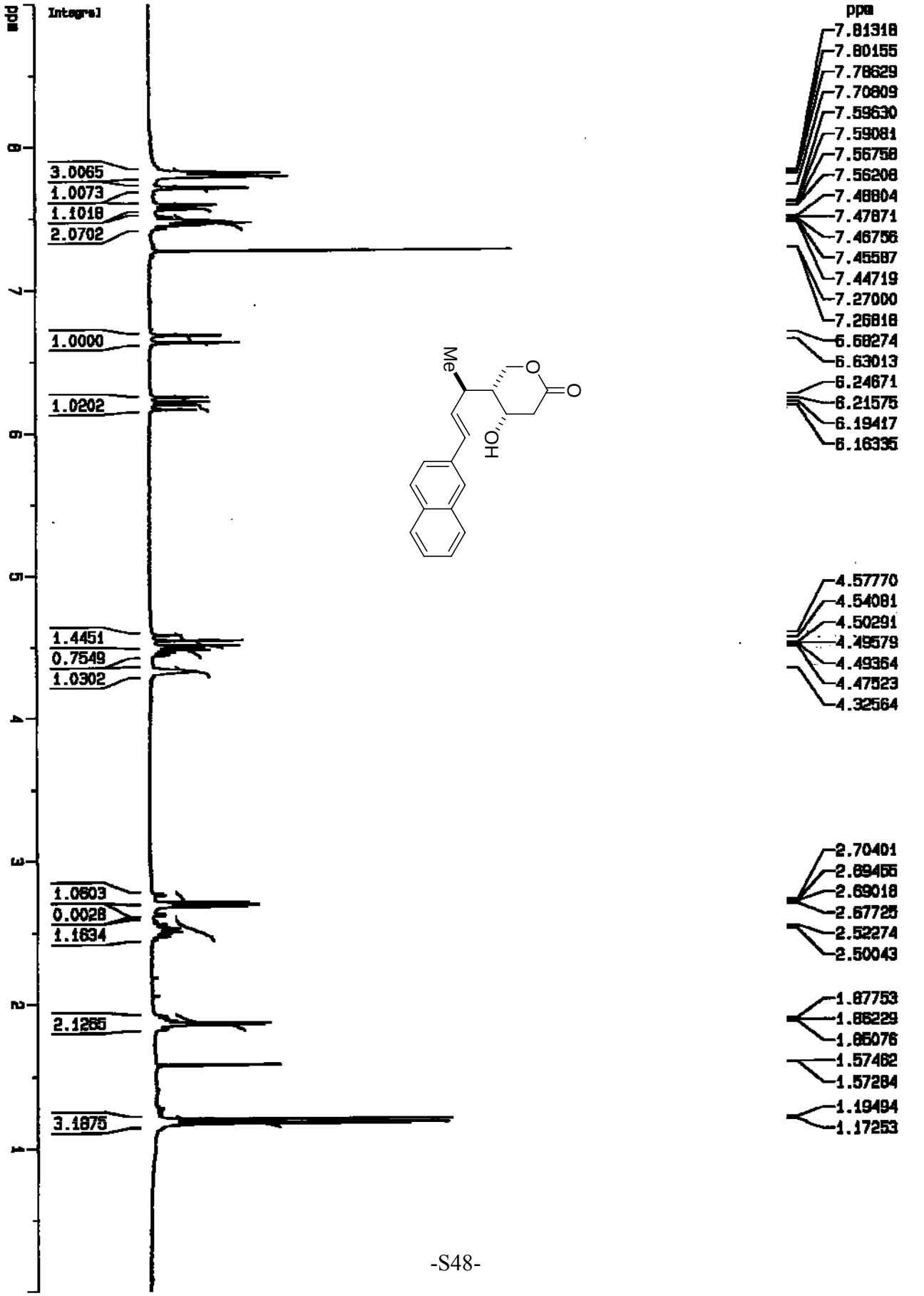
133.167
130.261
128.972
127.488
127.175
126.898
77.420
76.996
76.572
68.253
63.618
47.660
41.809
39.280
32.112
31.376
22.231
13.884
12
Ph
OH
nBu
O
O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Integral
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1.1018
2.0702
1.0000
1.0202
1.4451
0.7549
1.0302
1.0603
0.0028
1.1634
2.1265
3.1875
Me
O
O
HO
7.81318
7.80155
7.78629
7.70809
7.59630
7.59081
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7.56208
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7.47871
7.46756
7.45587
7.44719
7.27000
7.26818
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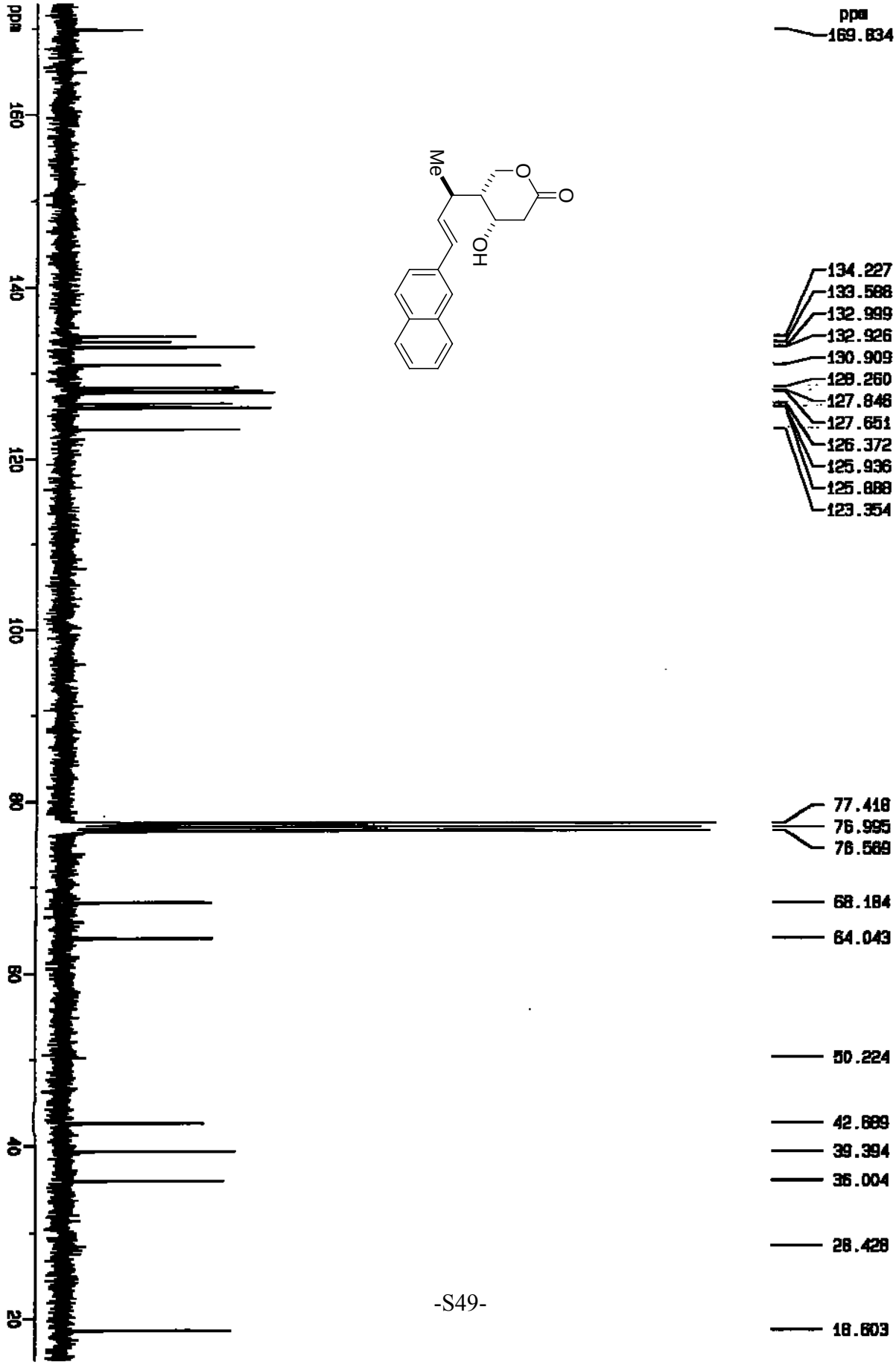
6.63013
6.24671
6.21575
6.19417
6.16335
4.57770
4.54081
4.50291
4.49579
4.49364
4.47523
4.32564
2.70401
2.69455
2.69018
2.67725
2.52274
2.50043
1.87753
1.86229
1.85076
1.57462
1.57284
1.19494
1.17253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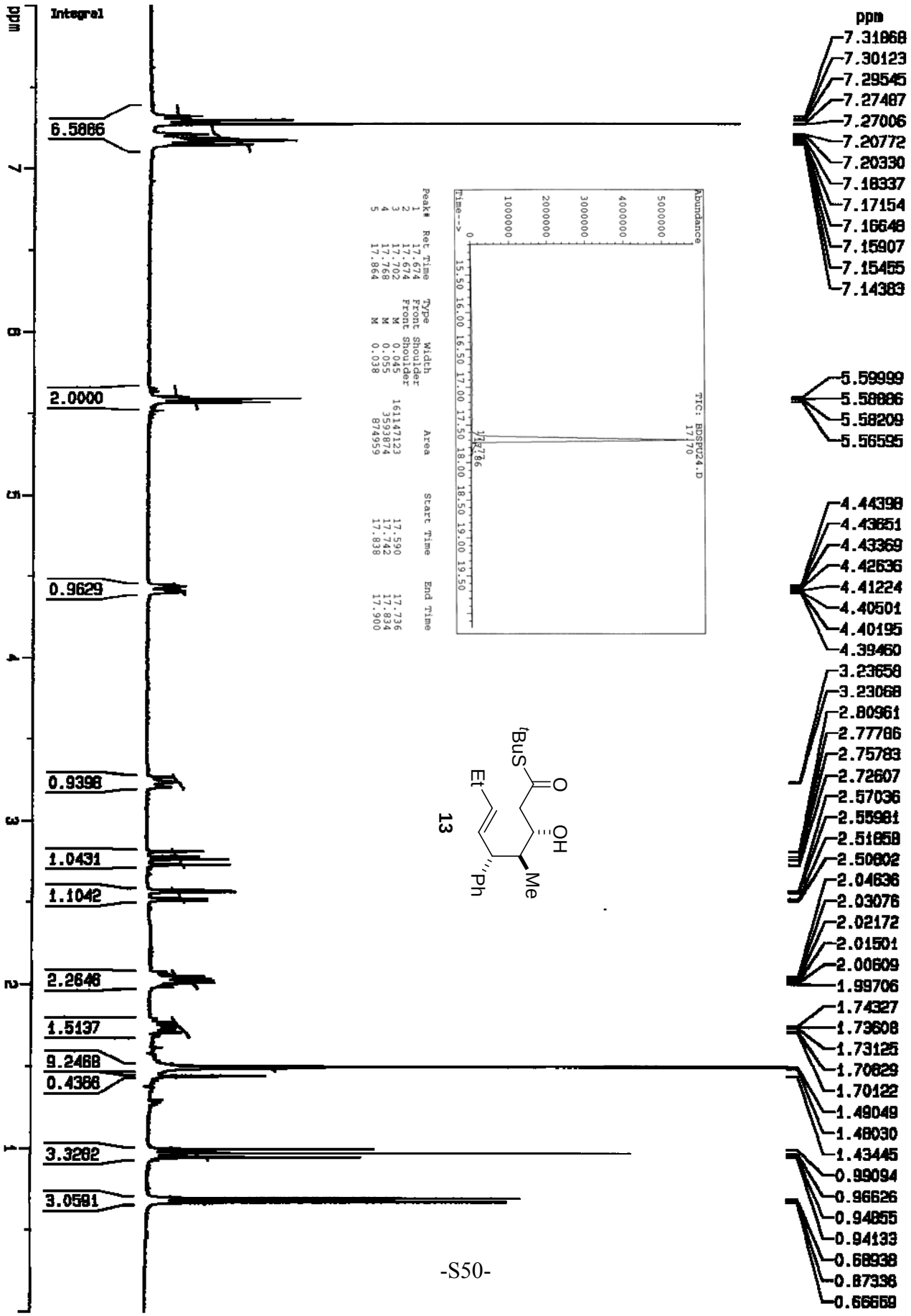
140
120
100
80
60
40
20
Me
O
O
HO
ppm
169.834
134.227
133.588
132.999
132.926
130.909
128.260
127.846
127.651
126.372
125.936
125.888
123.354
77.418
76.995
76.569
68.184
64.043
50.224
42.689
39.394
36.004
28.428
18.603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Integral
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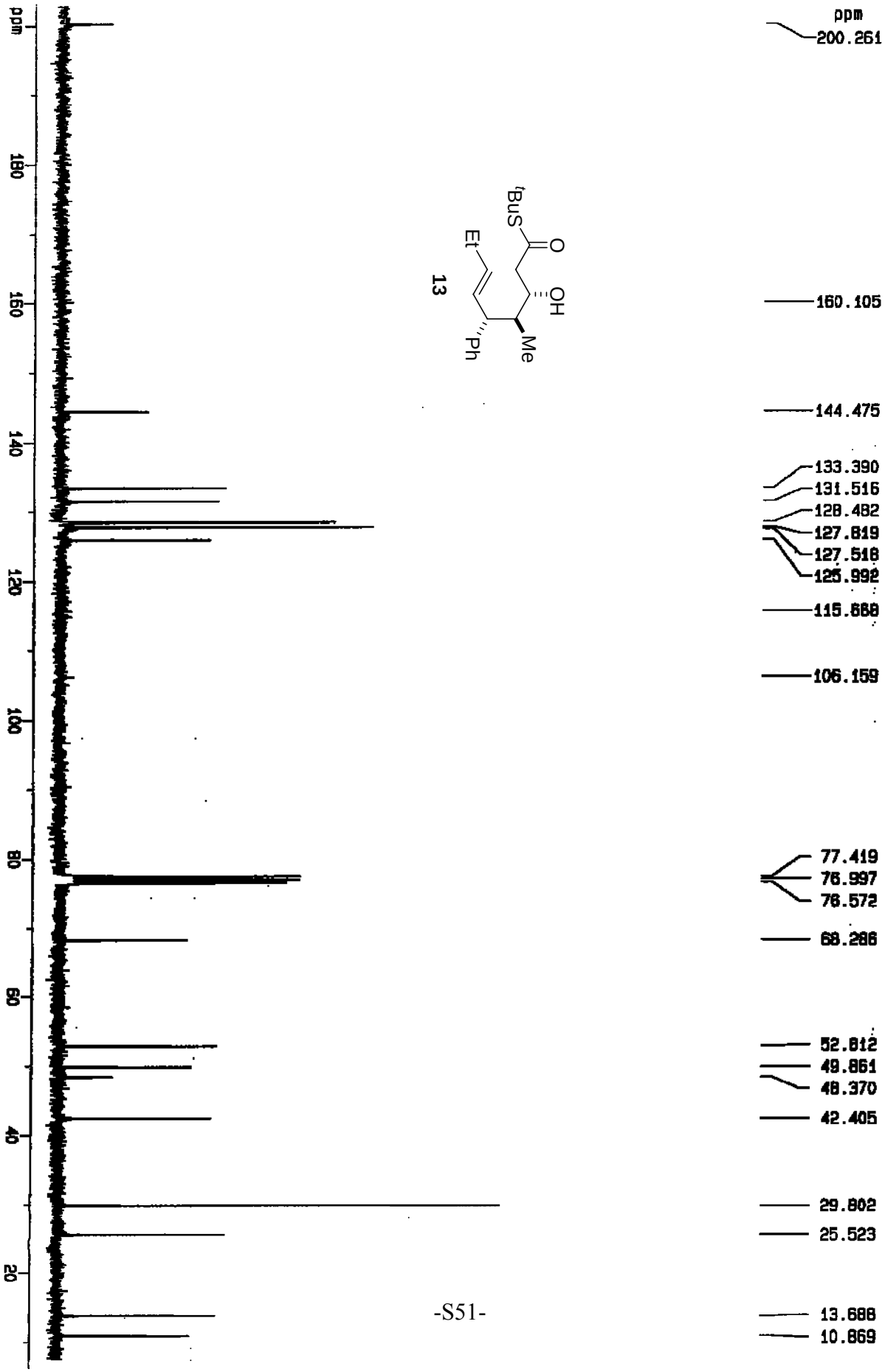
2.0000
0.9629
0.9398
1.0431
1.1042
2.2646
1.5137
9.2468
0.4366
3.3282
3.0591
ppm
7.31868
7.30123
7.29545
7.27487
7.27006
7.20772
7.20330
7.18337
7.17154
7.16648
7.15907
7.15455
7.14383
5.59999
5.58886
5.58209
5.56595
4.44398
4.43651
4.43369
4.42636
4.41224
4.40501
4.40195
4.39460
3.23658
3.23068
2.80961
2.77786
2.75783
2.72607
2.57036
2.55981
2.51858
2.50602
2.04636
2.03076
2.02172
2.01501
2.00609
1.99706
1.74327
1.73608
1.73125
1.70629
1.70122
1.49049
1.48030
1.43445
0.99094
0.96626
0.94855
0.94133
0.68938
0.87336
0.66659
Abundance
TIC: BDSHU24.D
Time-->
Peak# Ret Time Type Width Area Start Time End Time
1 17.674 Front Shoulder 17.590 17.736
2 17.674 Front Shoulder 17.742 17.834
3 17.702 M 0.045 161147123 17.838 17.900
4 17.768 M 0.055 3593874
5 17.864 M 0.038 874959
tBuS
O
OH
Et
Me
Ph
13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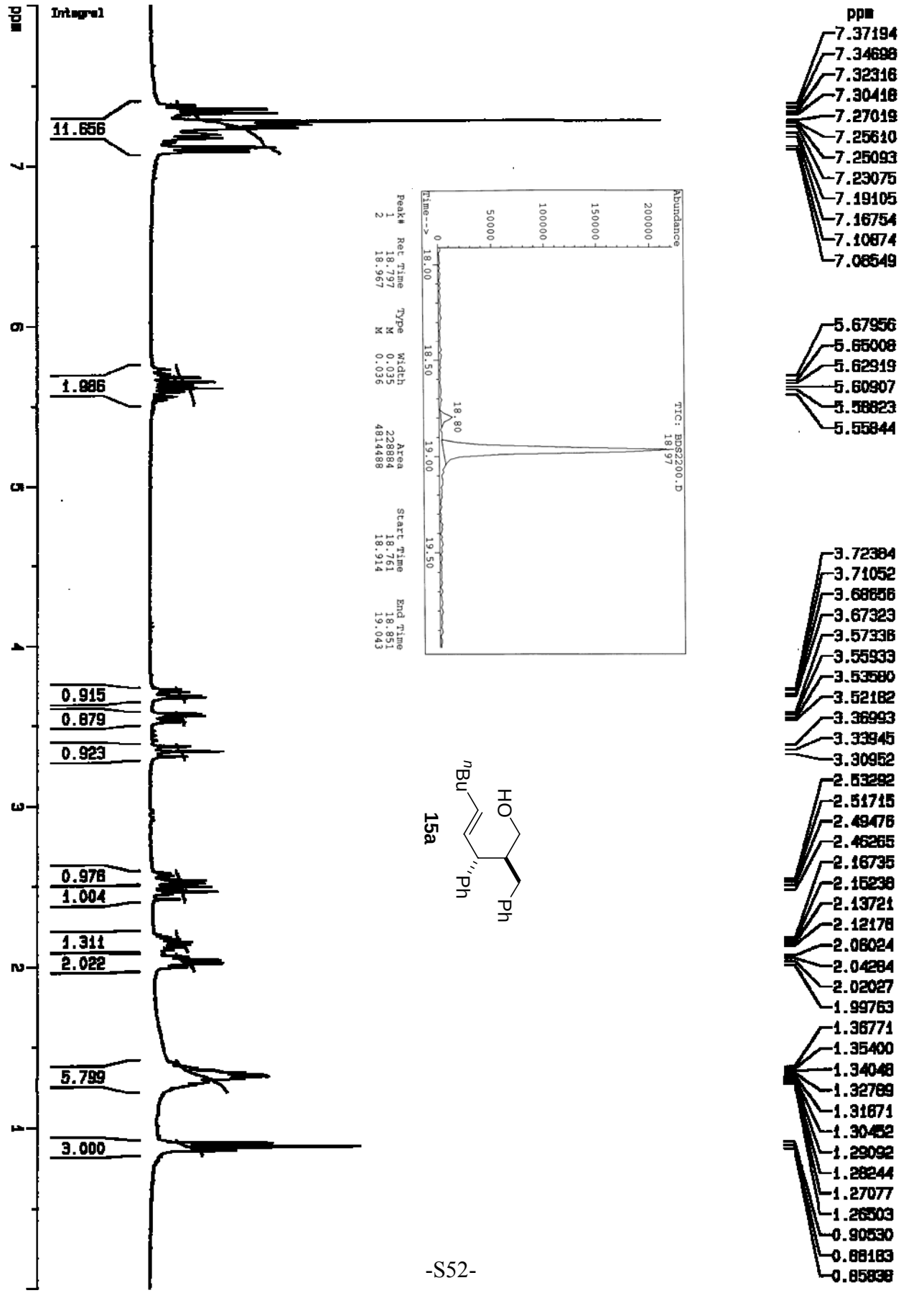
128.482
127.819
127.518
125.992
115.688
106.159
77.419
76.997
76.572
68.286
52.812
49.861
48.370
42.405
29.802
25.523
13.688
10.869
13
tBuS
O
OH
Et
Ph
Me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Integral
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0.879
0.923
0.976
1.004
1.311
2.022
5.799
3.000
Abundance
TIC: BDS2200.D
Peak# Ret Time Type Width Area Start Time End Time
1 18.797 M 0.035 228884 18.761 18.851
2 18.967 M 0.036 4814488 18.914 19.043
15a
nBu
HO
Ph
Ph
7.37194
7.34698
7.32316
7.30418
7.27019
7.25610
7.25093
7.23075
7.19105
7.16754
7.10874
7.08549
5.67956
5.65008
5.62919
5.60907
5.58823
5.55844
3.72384
3.71052
3.68656
3.67323
3.57336
3.55933
3.53580
3.52182
3.36993
3.33945
3.30952
2.53292
2.51715
2.49476
2.46265
2.16735
2.15238
2.13721
2.12178
2.08024
2.04284
2.02027
1.99763
1.36771
1.35400
1.34048
1.32789
1.31671
1.30452
1.29092
1.28244
1.27077
1.26503
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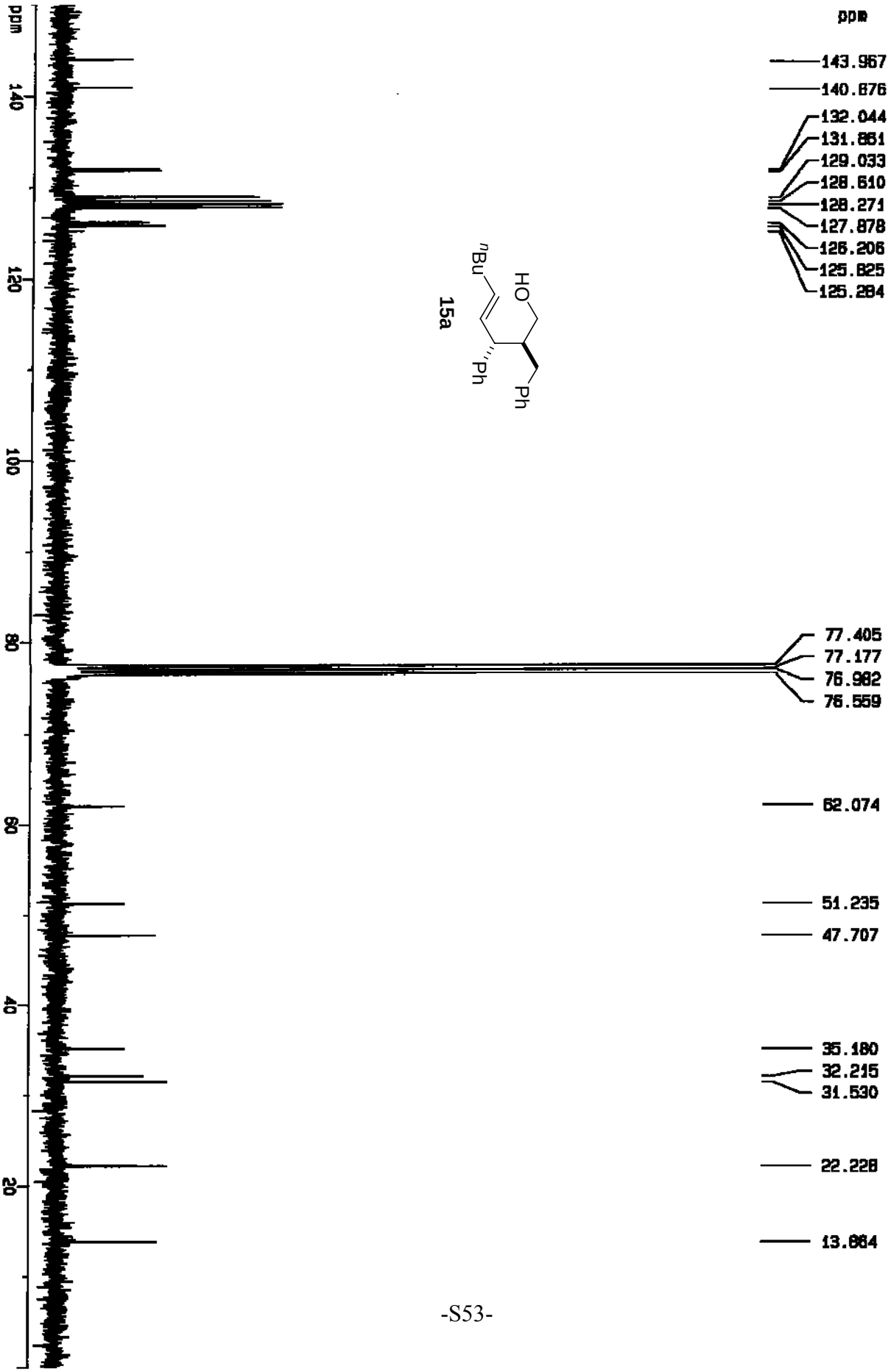
0.88183
0.85838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140
120
100
80
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20
ppm
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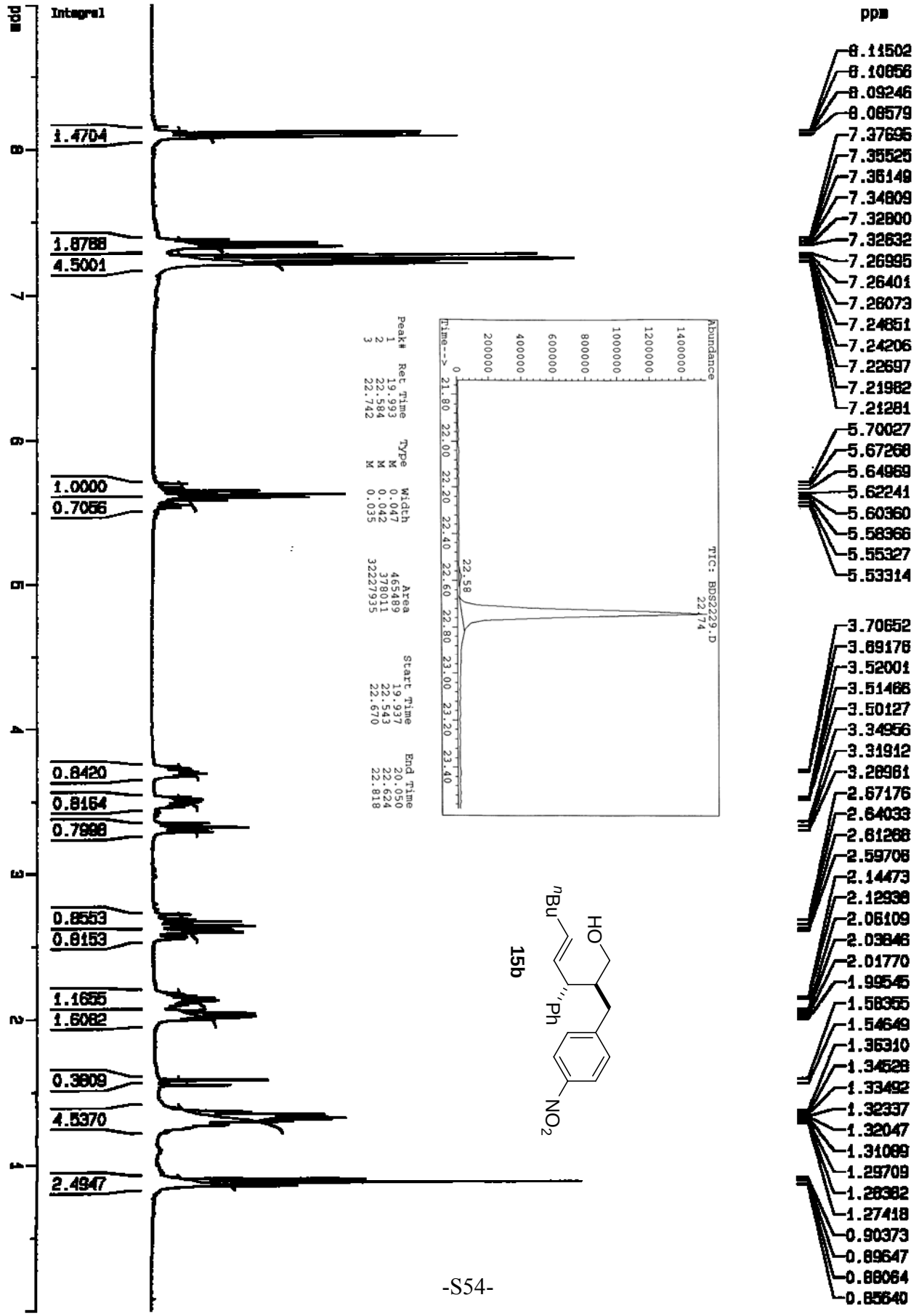
129.033
128.610
128.271
127.878
126.206
125.825
125.284
77.405
77.177
76.982
76.559
62.074
51.235
47.707
35.180
32.215
31.530
22.228
13.864
15a
HO
nBu
Ph
Ph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Integral
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1.0000
0.7056
0.8420
0.8164
0.7998
0.8553
0.8153
1.1655
1.6082
0.3809
4.5370
2.4947
Abundance
TIC: BDS2229.D
22.58
Time-->
Peak# Ret Time Type Width Area Start Time End Time
1 19.993 M 0.047 465489 19.937 20.050
2 22.584 M 0.042 378011 22.543 22.624
3 22.742 M 0.035 32227935 22.670 22.818
8.11502
8.10856
8.09246
8.08579
7.37695
7.35525
7.36149
7.34809
7.32800
7.32632
7.26995
7.26401
7.26073
7.24851
7.24206
7.22697
7.21982
7.21281
5.70027
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5.64969
5.62241
5.60360
5.58366
5.55327
5.53314
3.70652
3.69176
3.52001
3.51466
3.50127
3.34956
3.31912
3.28961
2.67176
2.64033
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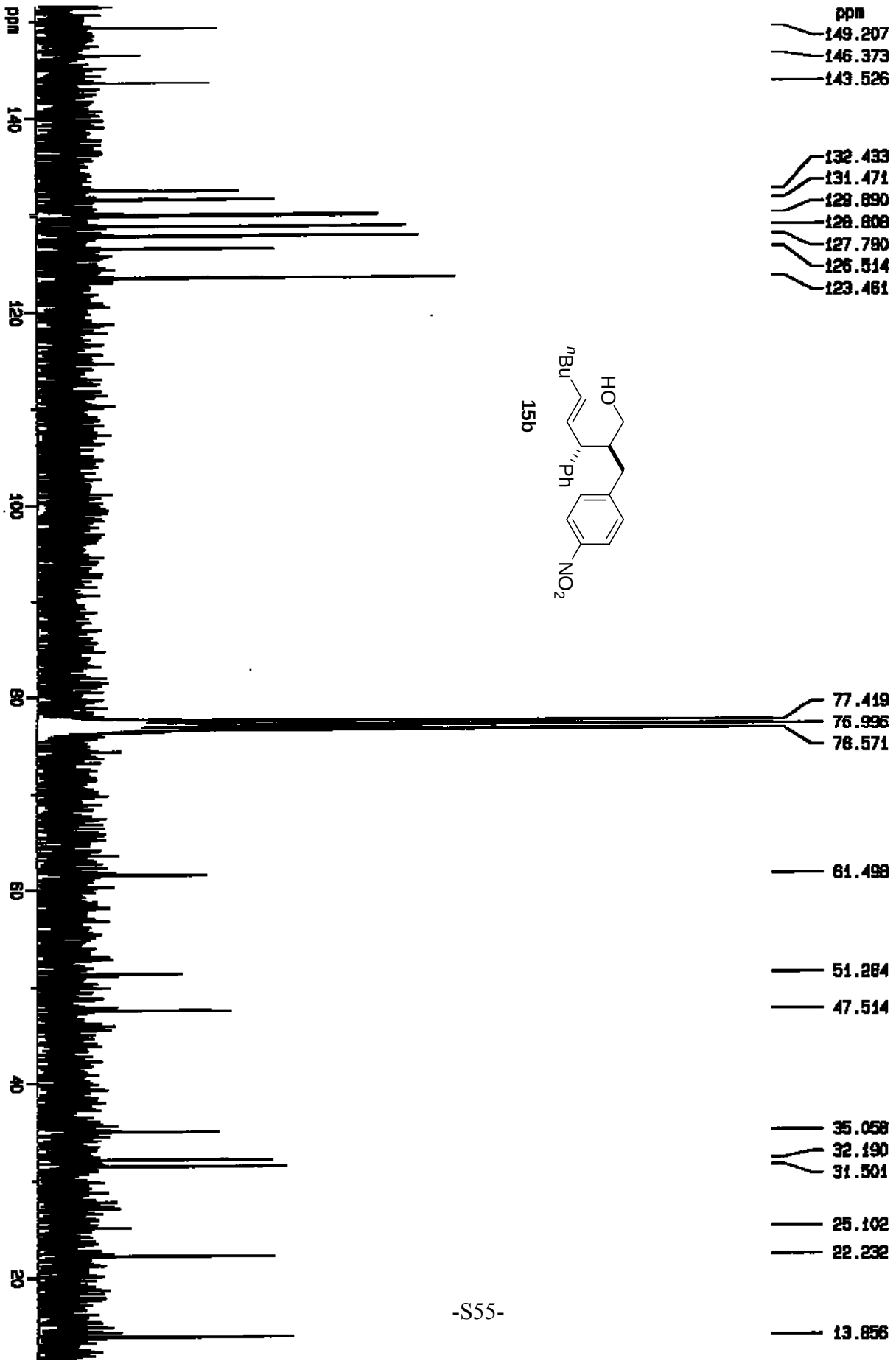
2.59706
2.14473
2.12938
2.06109
2.03646
2.01770
1.99545
1.58355
1.54649
1.36310
1.34528
1.33492
1.32337
1.32047
1.31089
1.29709
1.28382
1.27418
0.90373
0.89647
0.88064
0.85640
15b
HO
nBu
Ph
NO2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120
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80
60
40
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149.207
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143.526
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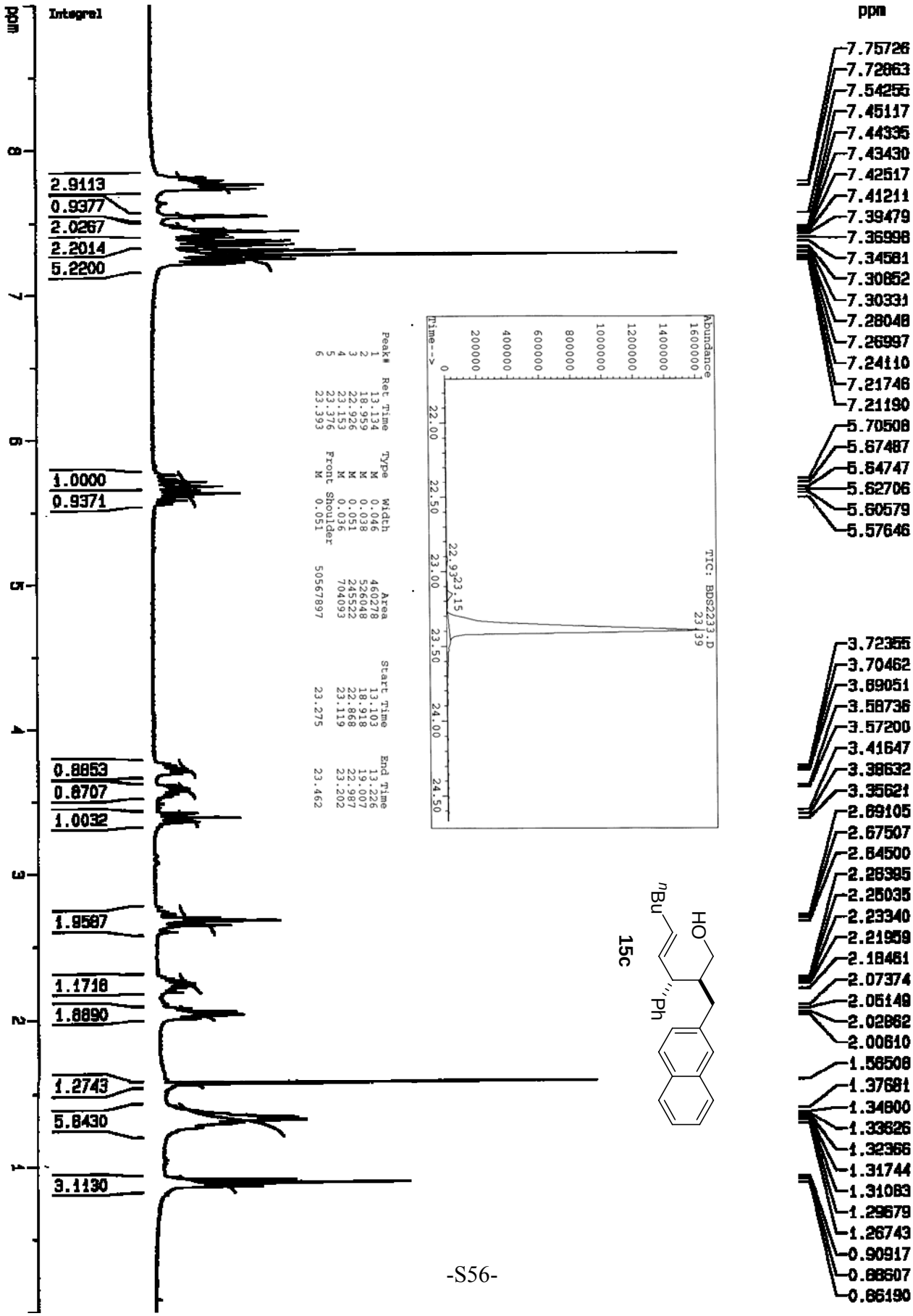
131.471
129.890
128.808
127.790
126.514
123.461
77.419
76.996
76.571
61.498
51.264
47.514
35.058
32.190
31.501
25.102
22.232
13.856
15b
nBu
HO
Ph
NO2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Integral
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2.0267
2.2014
5.2200
1.0000
0.9371
0.8853
0.8707
1.0032
1.9587
1.1718
1.8890
1.2743
5.8430
3.1130
Abundance
TIC: BDS2233.D
22.93
23.15
Time-->
Peak# Ret Time Type Width Area Start Time End Time
1 13.134 M 0.046 460278 13.103 13.226
2 18.959 M 0.038 526048 18.918 19.007
3 22.926 M 0.051 245522 22.868 22.987
4 23.153 M 0.036 704093 23.119 23.202
5 23.376 Front Shoulder
6 23.393 M 0.051 50567897 23.275 23.462
15c
7.75726
7.72863
7.54255
7.45117
7.44335
7.43430
7.42517
7.41211
7.39479
7.36998
7.34581
7.30852
7.30331
7.28048
7.26997
7.24110
7.21746
7.21190
5.70508
5.67487
5.64747
5.62706
5.60579
5.57646
3.72355
3.70462
3.69051
3.58736
3.57200
3.41647
3.38632
3.35621
2.69105
2.67507
2.64500
2.28395
2.25035
2.23340
2.21959
2.18461
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2.05149
2.02862
2.00610
1.56508
1.37681
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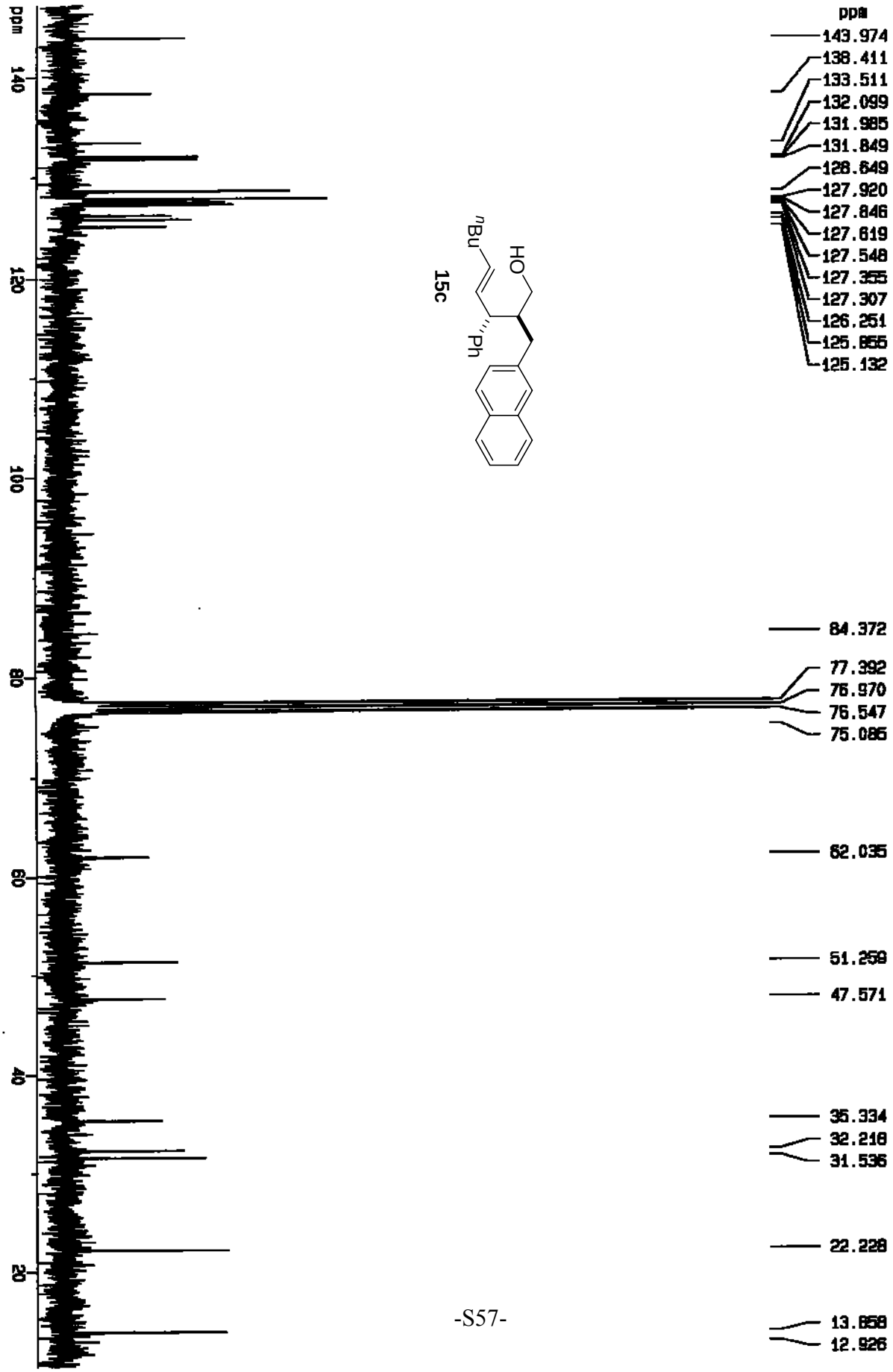
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80
60
40
20
ppm
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131.985
131.849
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127.920
127.846
127.619
127.548
127.355
127.307
126.251
125.855
125.132
84.372
77.392
76.970
76.547
75.085
62.035
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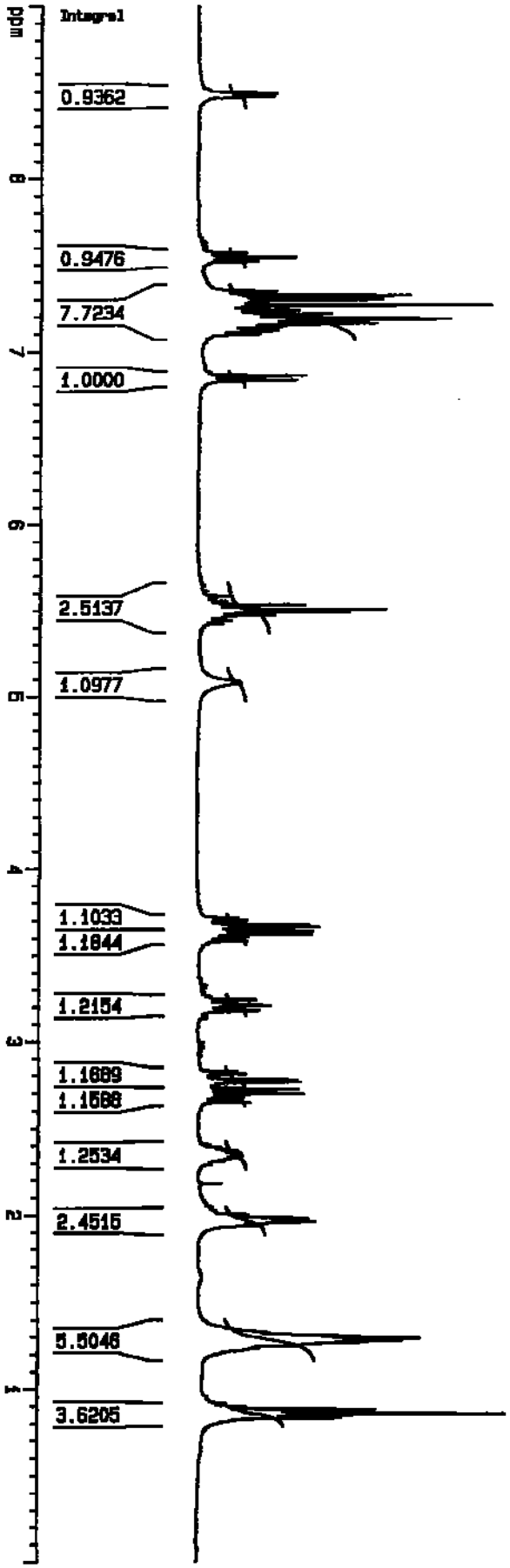
47.571
35.334
32.218
31.536
22.228
13.858
12.926
15c
nBu
HO
Ph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1.1844
1.2154
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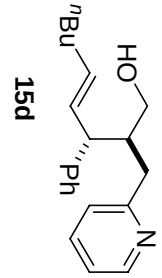
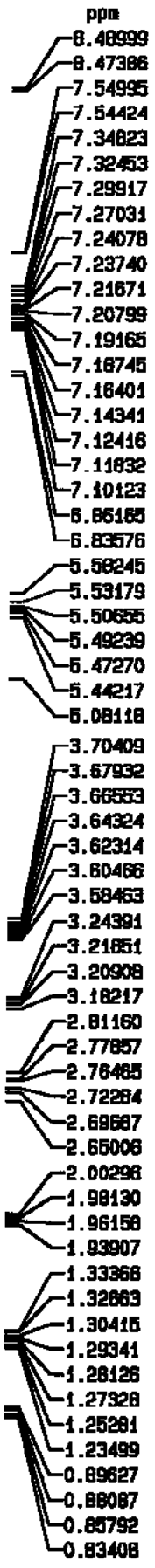
1.1588
1.2534
2.4515
5.5046
3.6205


HO
nBu
Ph
N

15d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7.21671
7.20799
7.19165
7.18745
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7.14341
7.12416
7.11832
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5.53179
5.50655
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5.47270
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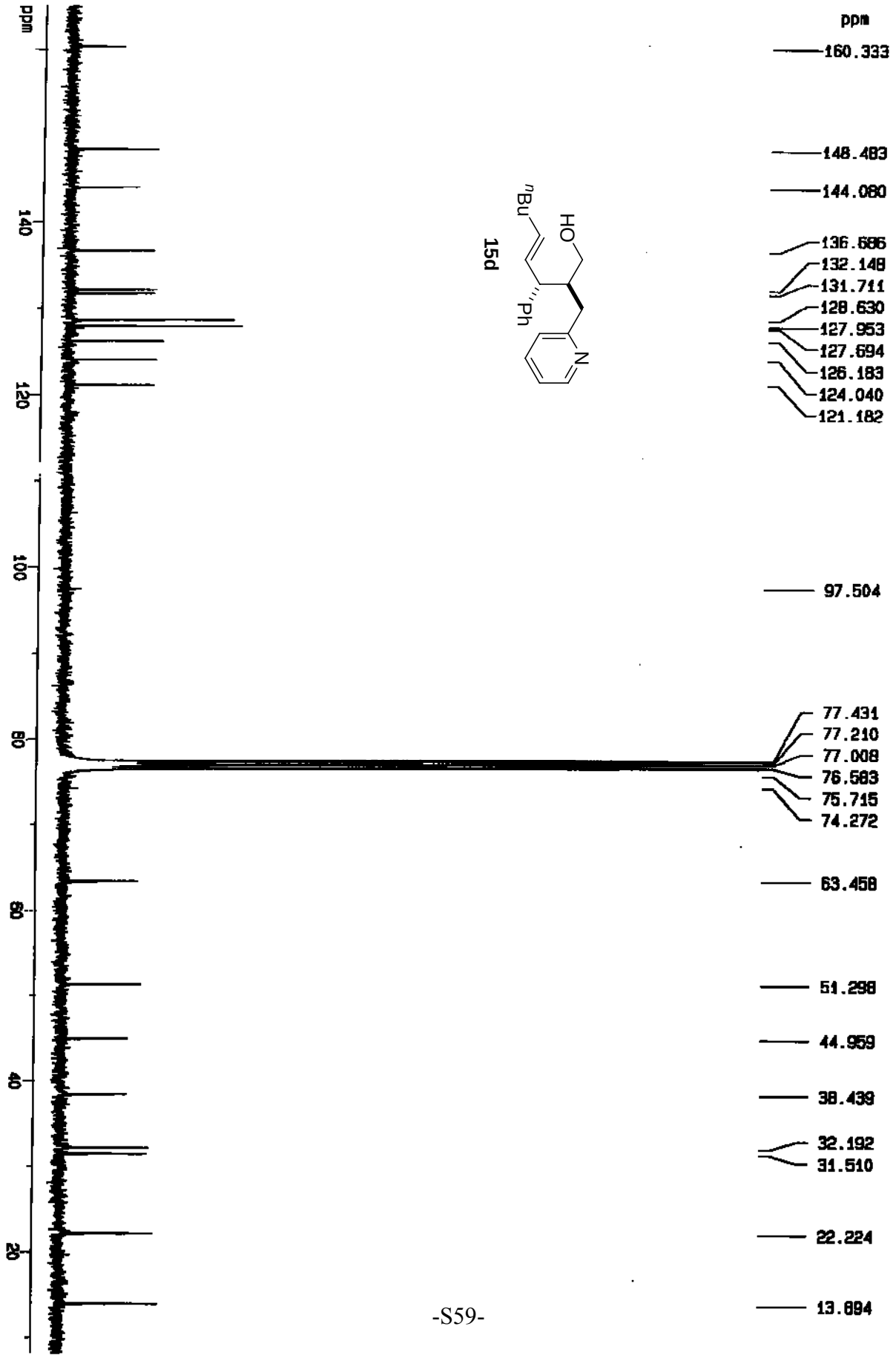
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97.504
77.431
77.210
77.008
76.583
75.715
74.272
63.458
51.298
44.959
38.439
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22.224
13.894
15d
HO
nBu
Ph
N
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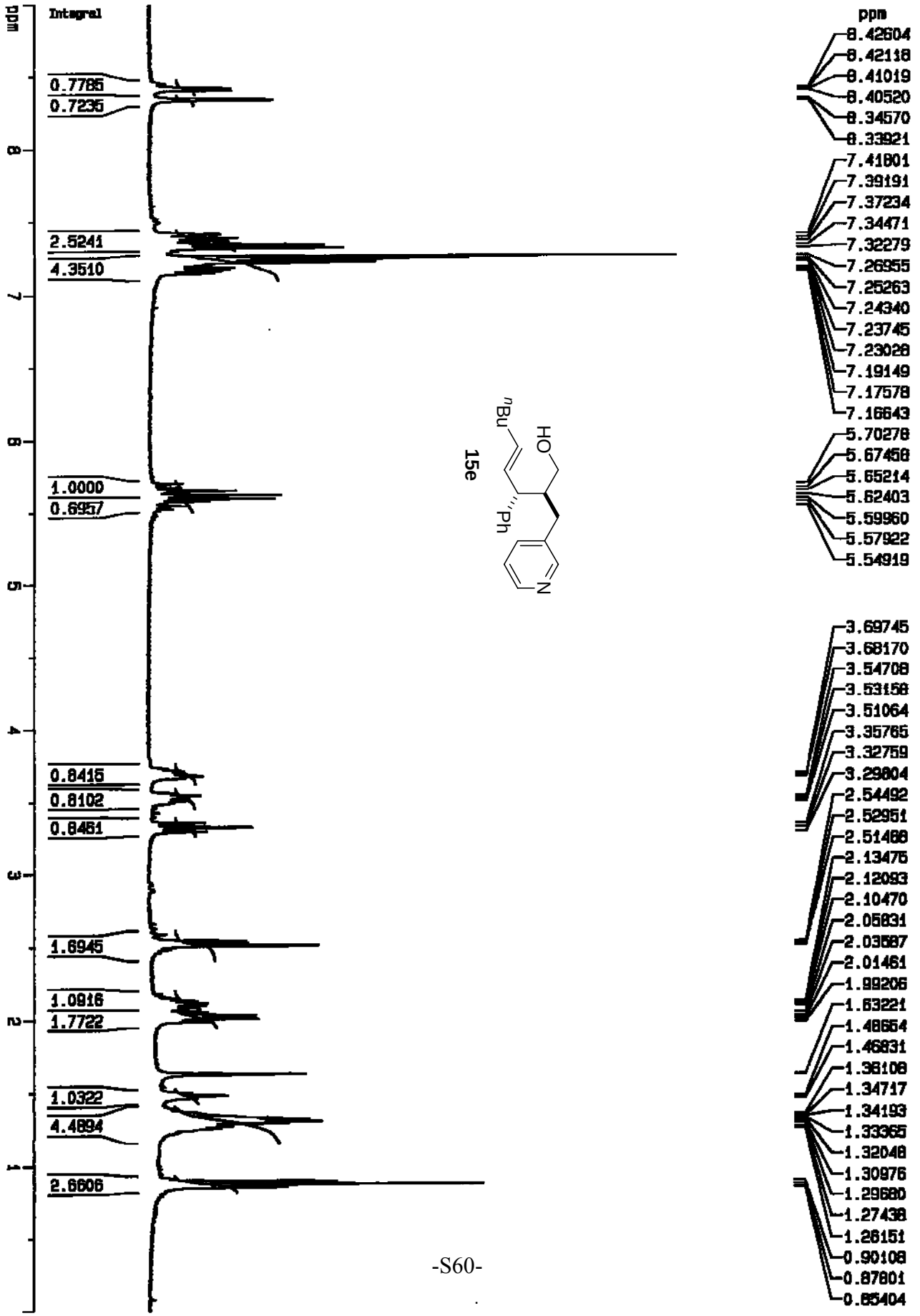
100
80
60
40
20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4.4894
2.6606
15e
nBu
HO
Ph
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8.40520
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7.37234
7.34471
7.32279
7.26955
7.25263
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7.23745
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3.53158
3.51064
3.35765
3.32759
3.29804
2.54492
2.52951
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2.12093
2.10470
2.05831
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2.01461
1.99206
1.63221
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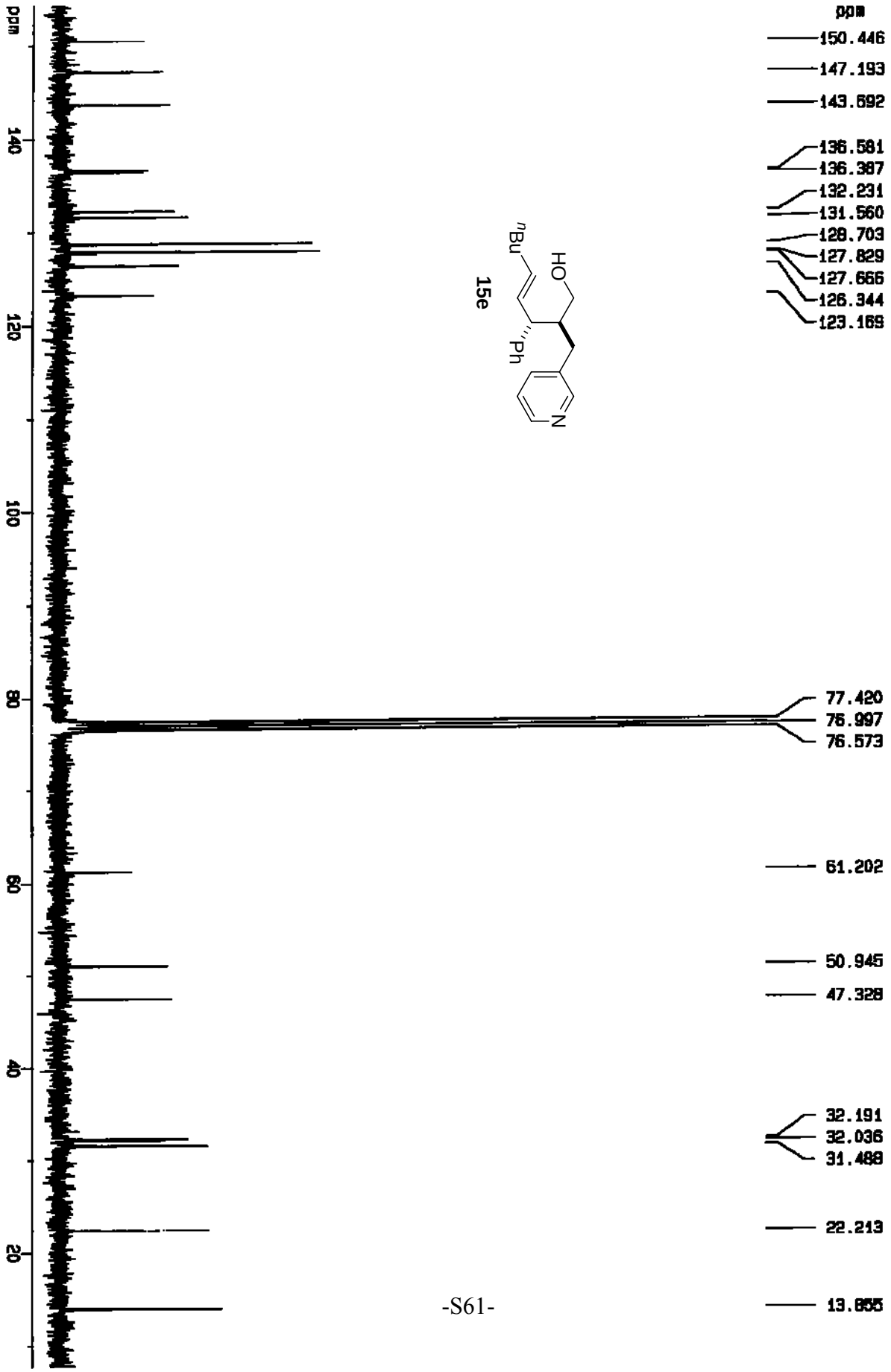
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76.997
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32.191
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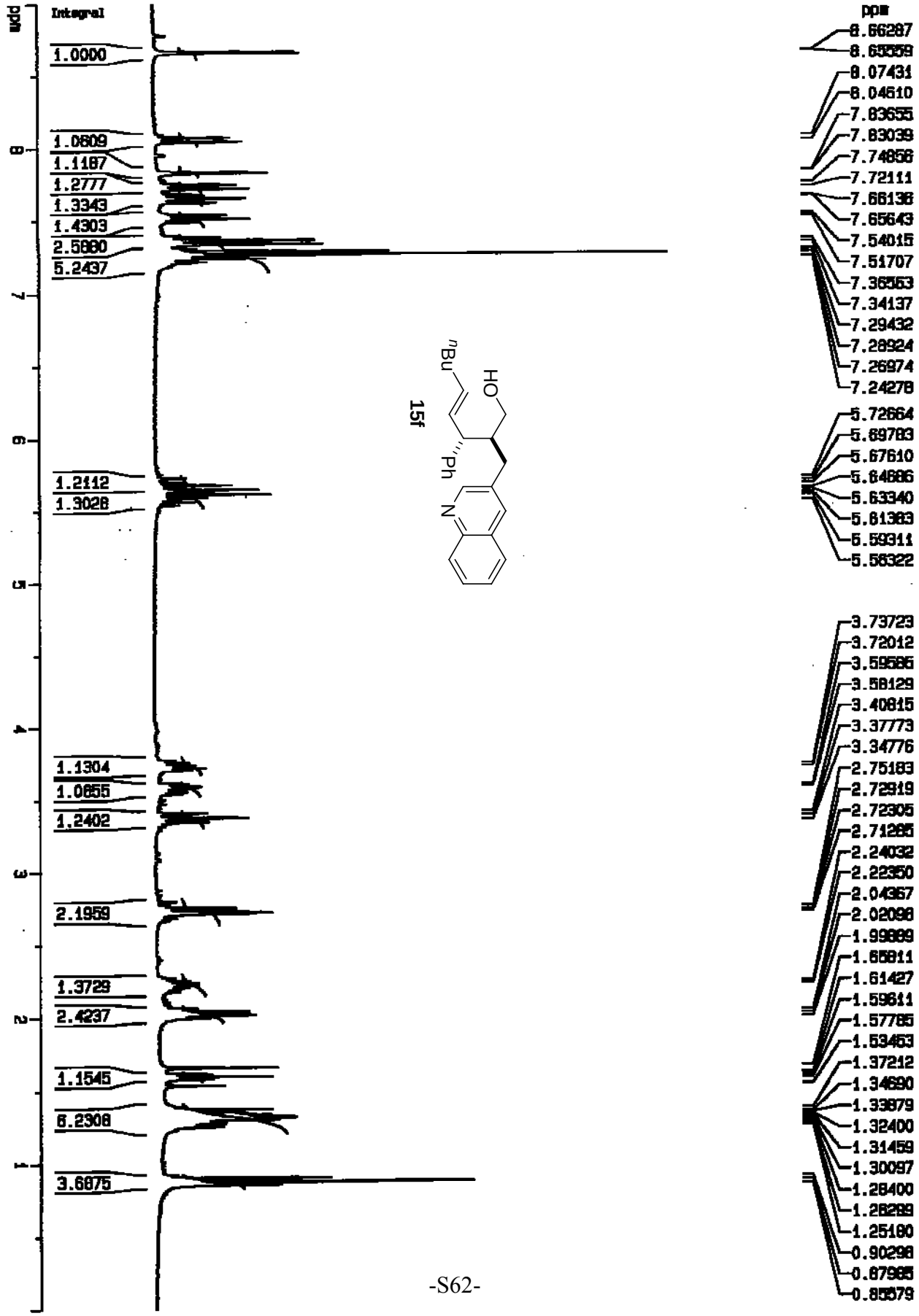
Ph
N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1.0855
1.2402
2.1959
1.3729
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1.1545
6.2308
3.6875
8
7
6
5
4
3
2
1
nBu
HO
Ph
N
15f
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8.04610
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7.83039
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7.36563
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5.69783
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5.64886
5.63340
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1.34690
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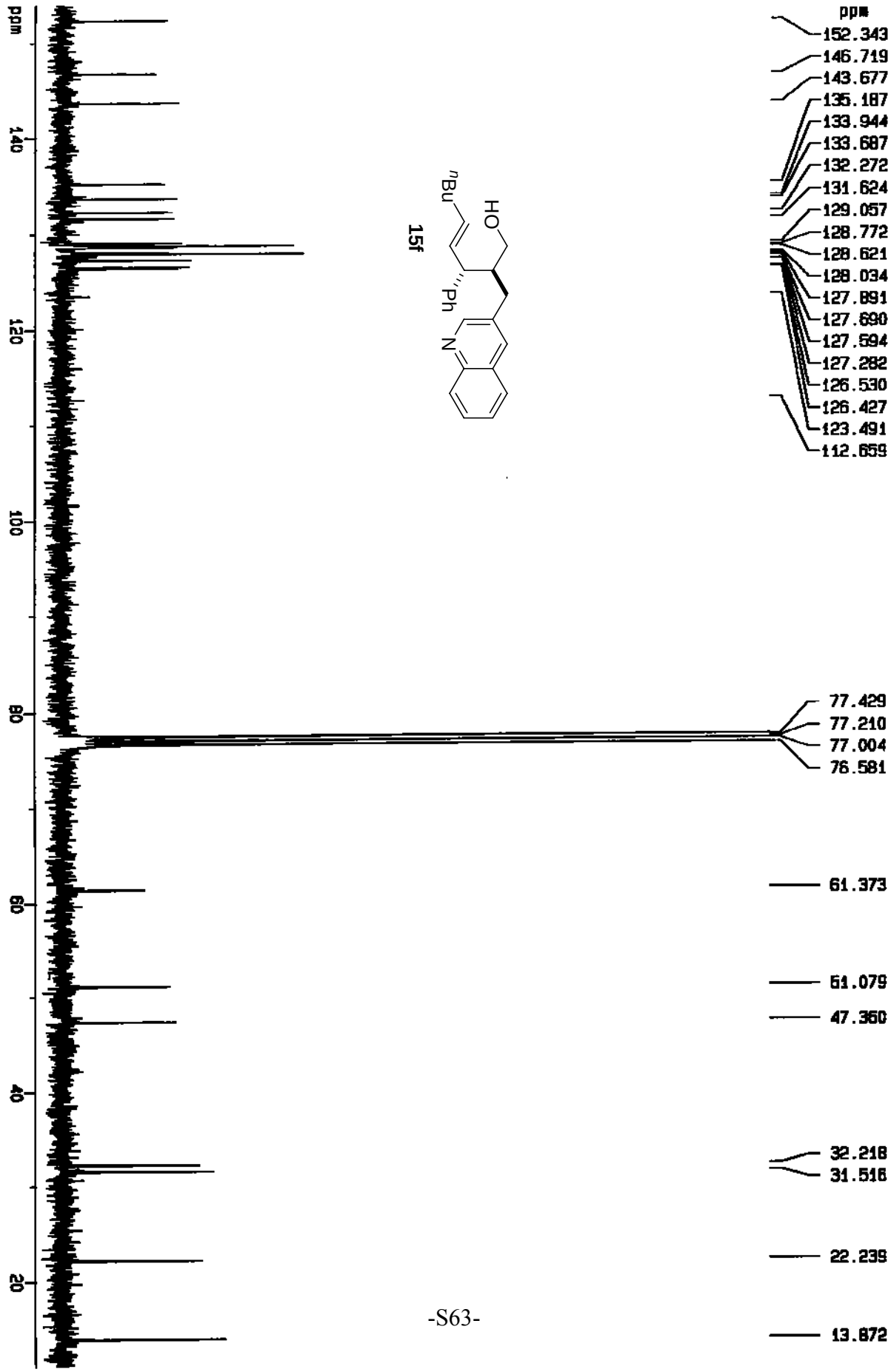
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80
60
40
20
15f
nBu
HO
Ph
N
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133.687
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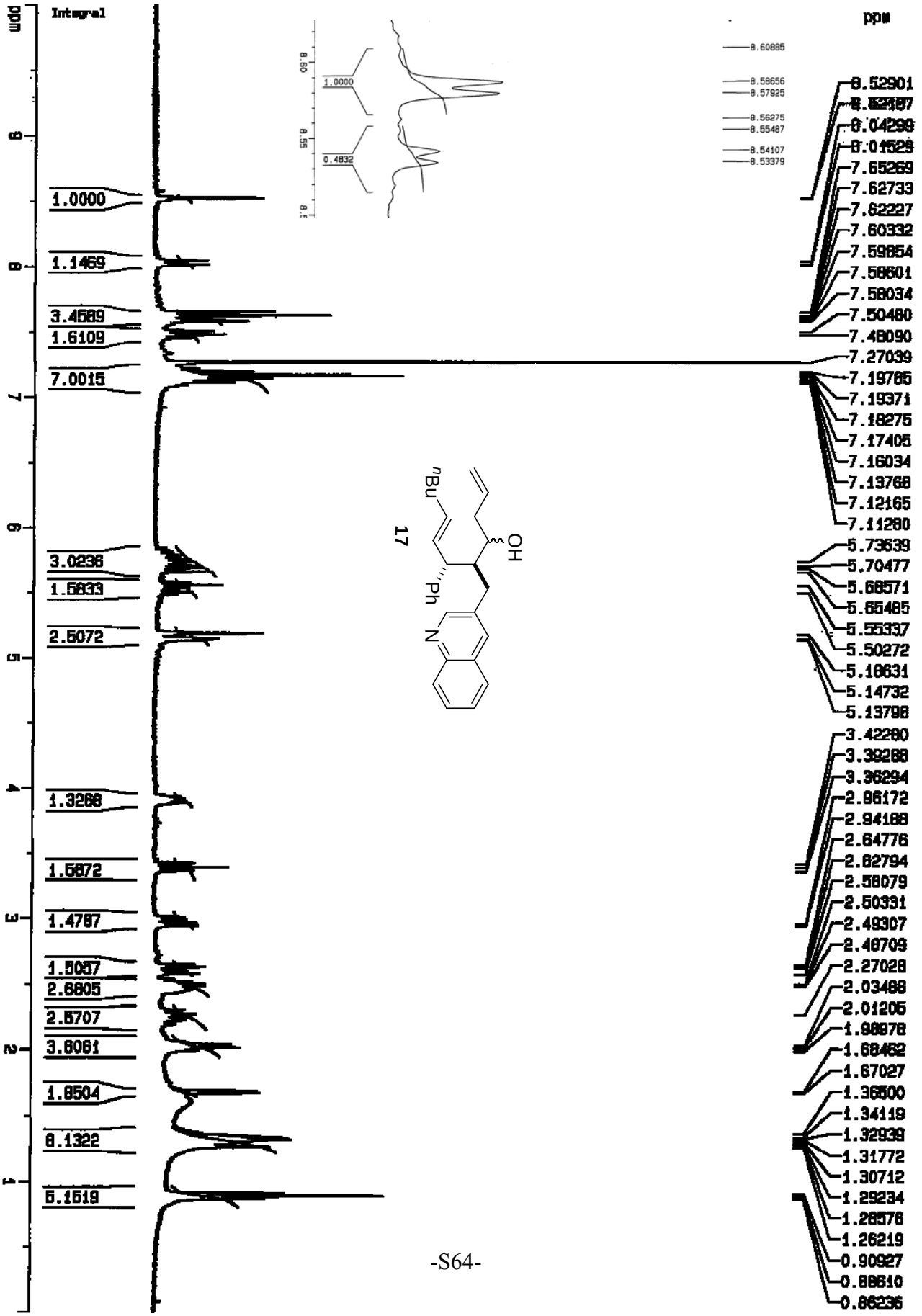
13.872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2.6605
2.5707
3.6061
1.8504
8.1322
5.1519
1.0000
0.4832
8.60885
8.58656
8.57925
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8.55487
8.54107
8.53379
8.52901
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7.58601
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7.50480
7.48090
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2.58079
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2.01205
1.98978
1.68462
1.67027
1.36500
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1.32939
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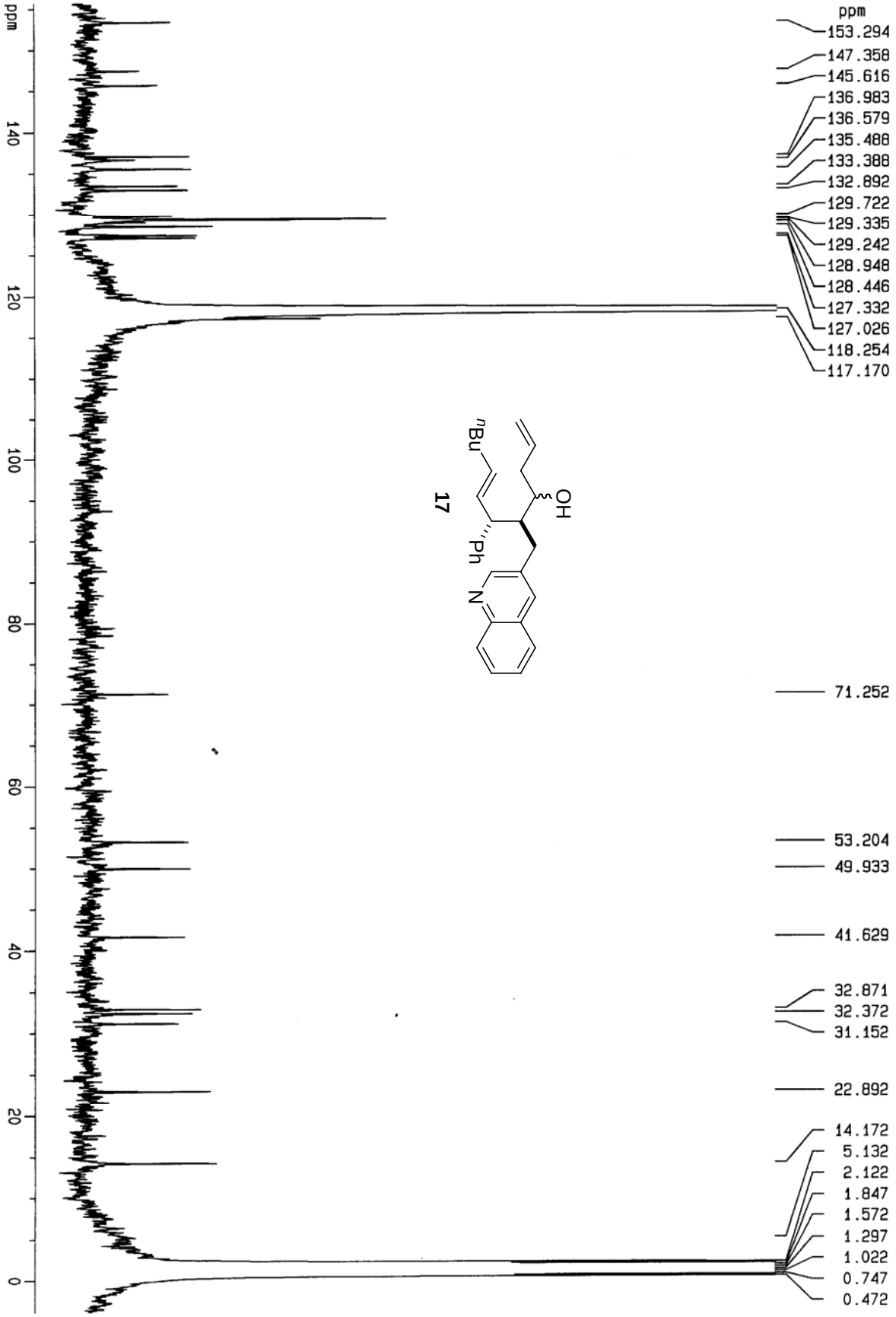
OH
Ph
N
17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129.242
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128.446
127.332
127.026
118.254
117.170
71.252
53.204
49.933
41.629
32.871
32.372
31.152
22.892
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5.132
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1.572
1.297
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Ph
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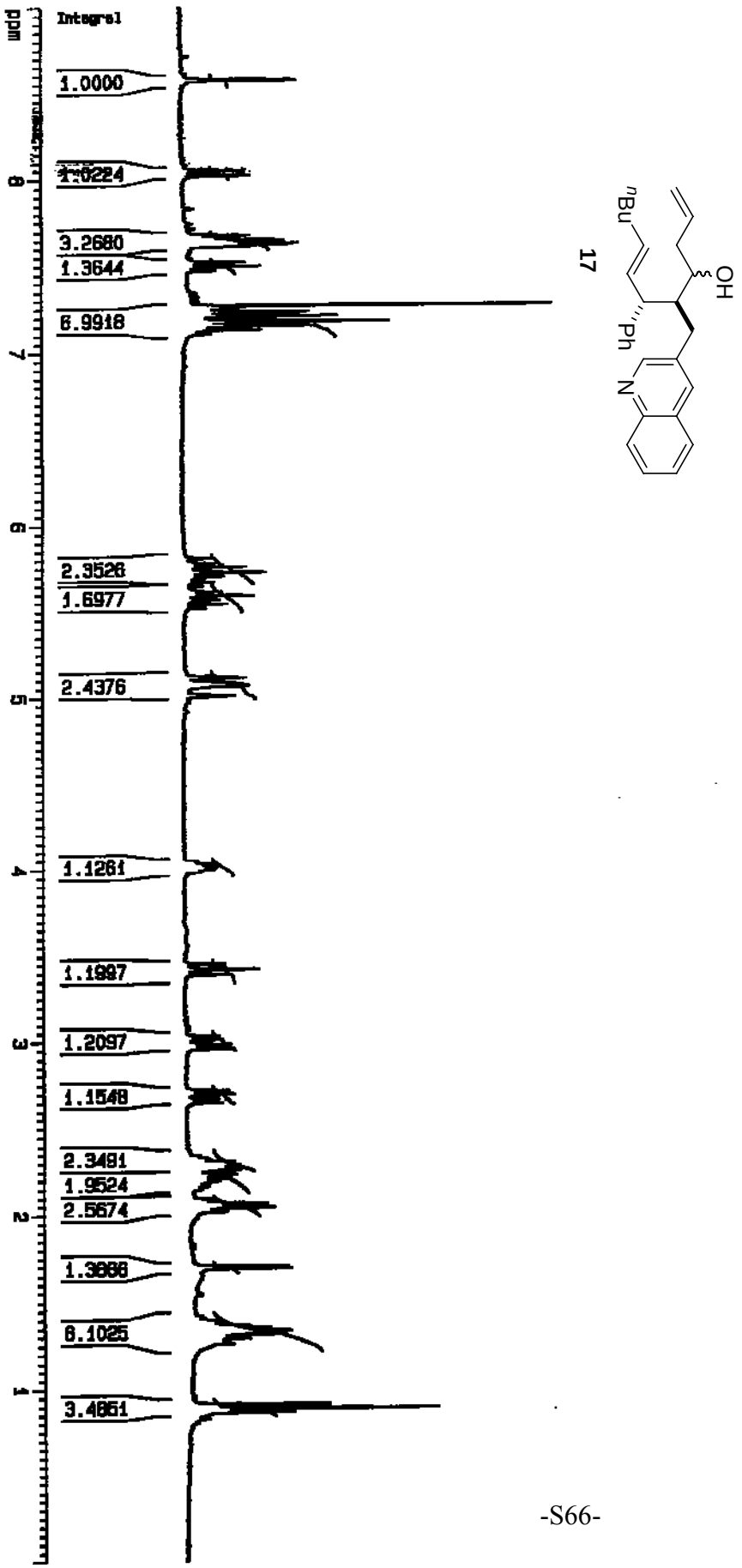
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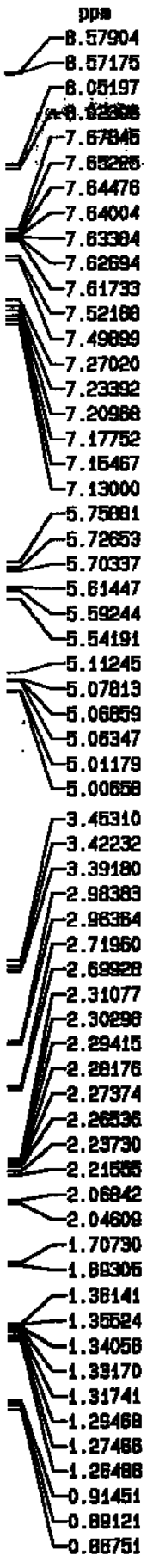
3.4861

17
nBu
Ph
N
OH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5.06347
5.01179
5.00658
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3.42232
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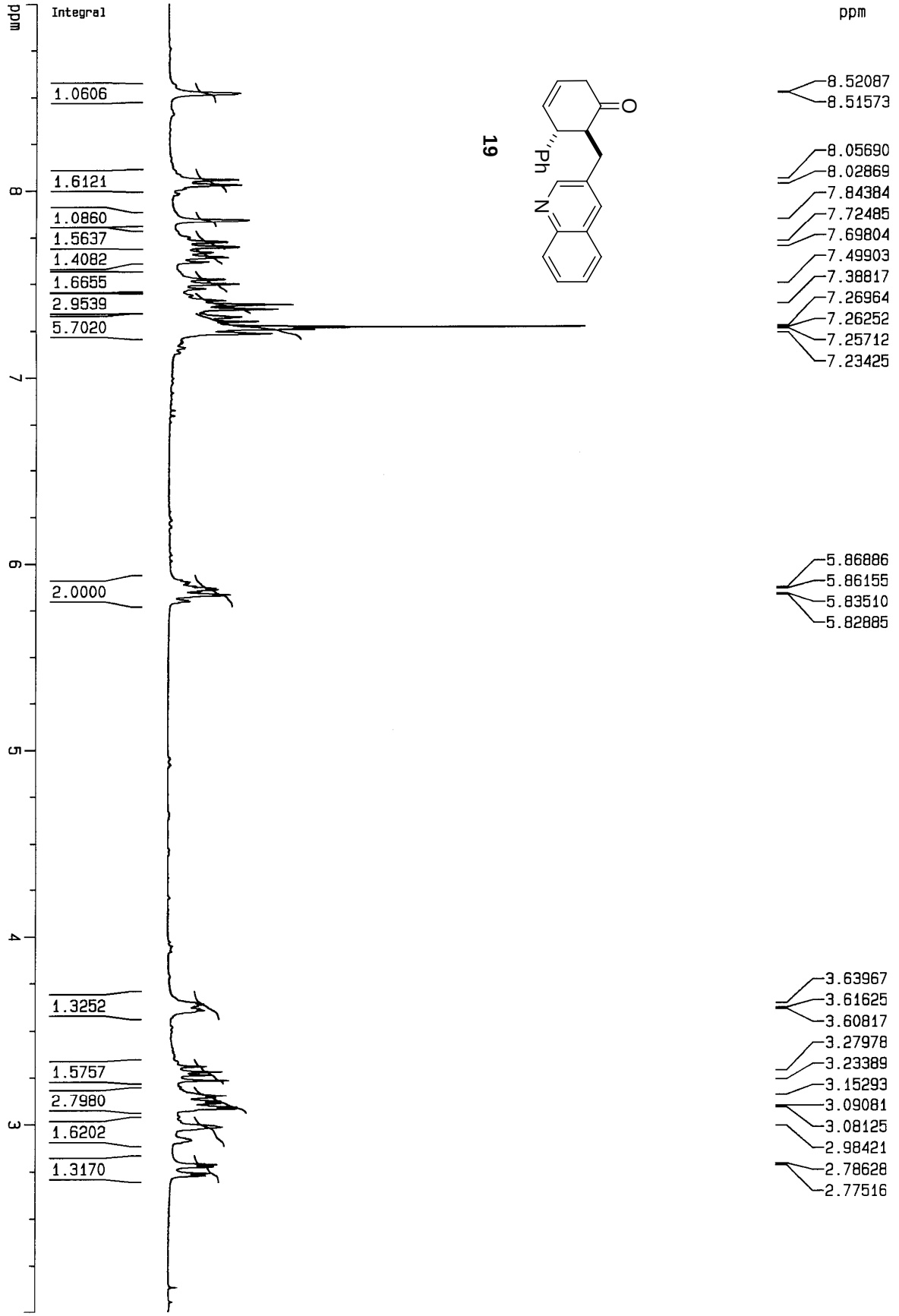
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1.3170
19
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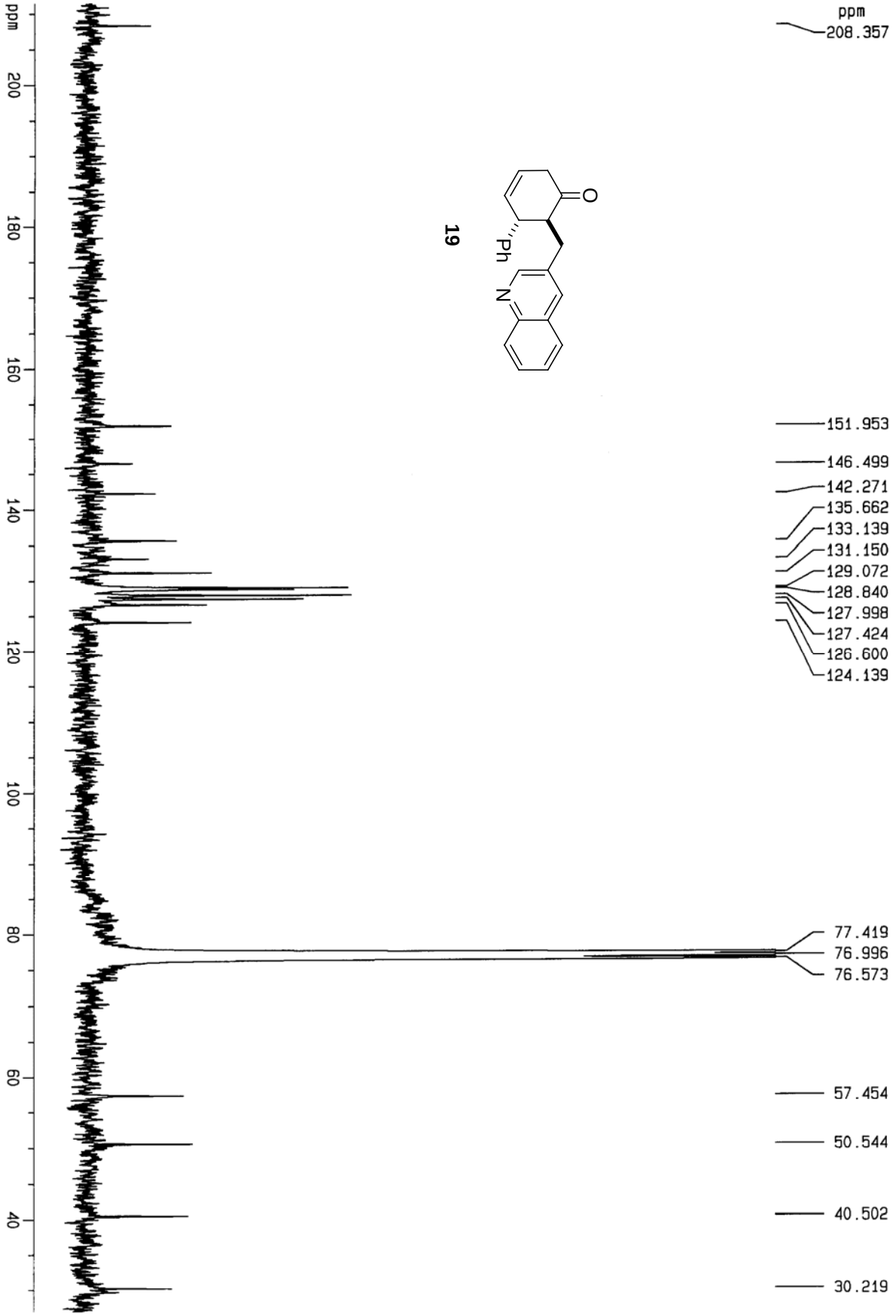
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77.419
76.996
76.573
57.454
50.544
40.502
30.219
19
O
Ph
N