Asymmetric Ni-Catalyzed Conjugate Allylation of Activated Enones

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Supplementary Material

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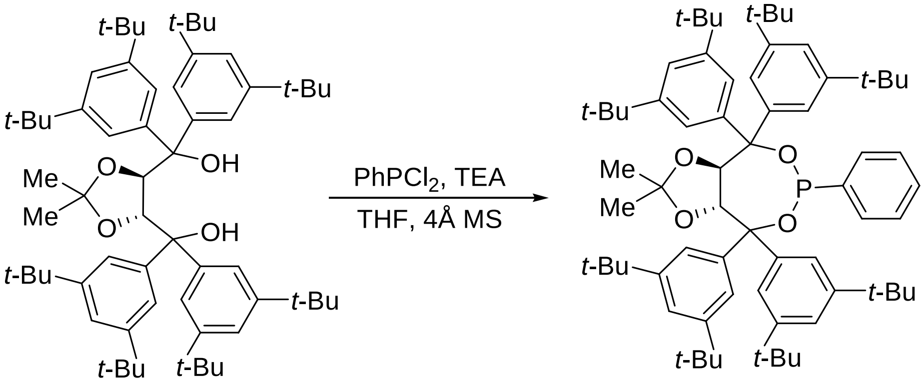
General. Melting points were determined using a Mel-Temp II melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on Gemini-500 (500 MHz), Gemini-400 (400 MHz), or Gemini-300 (300 MHz) spectrometers. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as an internal standard ($CDCl_3$: 7.24 ppm, C_6D_6: 7.15 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = hextet, br = broad, m = multiplet), and coupling constants (Hz). ^{13}C NMR was recorded on a Gemini-400 (100 MHz) instrument, or a Gemini-500 (125 MHz) instrument with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal standard ($CDCl_3$: 77.0 ppm, C_6D_6: 128.39 ppm). ^{19}F NMR was recorded on a Gemini-500 (470 MHz) instrument. Chemical shifts are reported in ppm and are referenced to a 0.05% solution of C_6F_6 (-63.72 ppm) in C_6D_6. ^{31}P NMR was recorded on a Gemini-300 (121 MHz) instrument with complete proton decoupling. Chemical shifts are reported in ppm and are referenced to 85% H_3PO_4 (0.0 ppm). Low-resolution mass spectrometry was performed by the Boston College, Department of Chemistry Mass Spectrometry Facility. Infrared (IR) spectra were obtained on a Nicolet 210 spectrophotometer. Optical rotations were measured using a Rudolf Research Analytical Autopol IV Polarimeter.

Liquid chromatography was performed using forced flow (flash chromatography) on silica gel (SiO_2, 40-63 μm) purchased from Silicycle. Thin layer chromatography (TLC) was performed on 250 μm silica gel plates from Silicycle or 200 μm neutral alumnia TLC plates from Sorbent Technologies. Visualization was achieved using UV light, phosphomolybdic acid in ethanol, or potassium permanganate in water, each followed by heating.

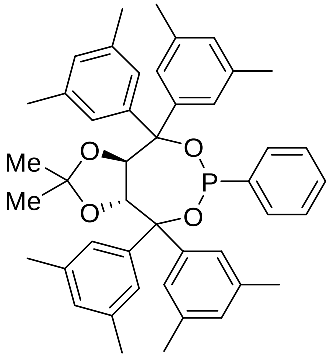
Analytical chiral gas-liquid chromatography (GLC) was performed on a Hewlett-Packard 6890 series chromatograph equipped with a CTC Analysis Combi Pal autosampler by Leap Technologies (Carrboro, NC), a split mode capillary injection system, a flame ionization detector, and a Supelco β-dex 120 column with helium as the carrier gas. Analytical achiral GLC was performed on a Hewlett-Packard 6890 series chromatograph equipped with a split mode capillary injection system, a flame ionization detector, and a Hewlett-Packard Ultra 1 capillary column (0.33 μm film thickness, 25 m length, 0.2mm ID) with helium as the carrier gas. Analytical chiral supercritical fluid chromatography (SFC) was performed on a Berger Instruments supercritical chromatograph equipped with an Alcott autosampler and a Knauer UV detector.

All reactions were conducted in oven or flame dried glassware under an inert atmosphere of nitrogen or argon. Toluene, d_8-toluene, and d_6-benzene were distilled over CaH_2 and degassed by freeze-pump-thaw cycles prior to use. Anhydrous tetrahydrofuran (THF), methylene chloride, and diethyl ether were purified using a Pure Solv MD-4 solvent purification system from Innovative Technology Inc. by passing the solvent through two activated alumina columns after being purged with Ar. Activated enone substrates used in the conjugate allylation were synthesized by the addition of the desired alkyl-substituted vinyl lithium to the Weinreb amide prepared from the desired cinnamic acid derivative and is described below. Note that the activated enones used in Table 1 and Table 3, entries 1, 3, and 4, were synthesized as previously described (Sieber, J. D.; Liu, S.; Morken, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 2214.). Bis(1,5-cyclooctadiene)nickel(0) was purchased from Strem Chemical Company. 5-fluoro-2-methylbenzaldehyde was purchased from Oakwood Chemicals and used without further purification. All other reagents were purchased from either Fisher or Aldrich Chemical Companies and used directly.

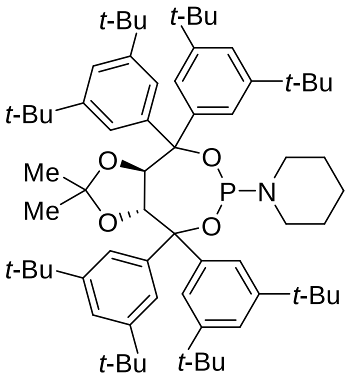
Ligand Synthesis.



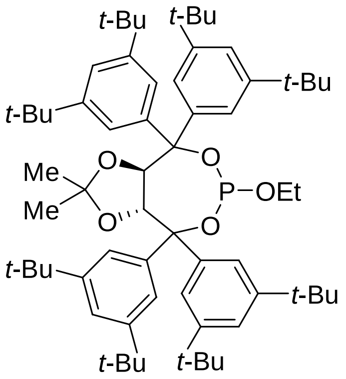
To a mixture of 0.898 g (0.981 mmol) of diol (synthesized from L-tartaric acid according to: Seebach, D.; Beck, A. K.; Keckel, A. *Angew. Chem. Int. Ed.* **2001**, *40*, 92.) and 4 Å molecular sieves in 3.9 mL of THF at 0 °C was added 0.32 ml (2.3 mmol) of triethylamine. Next, 150 µL (1.08 mmol) of dichlorophenylphosphine was added dropwise. The reaction was allowed to warm to room temperature and stirred here for 2 h. The reaction was diluted with Et_2O, filtered through celite, and concentrated under reduced pressure. Column chromatography (SiO_2, hexanes:EtOAc) afforded 0.726 g (73%) of phosphonite ligand as a white solid. mp 240-260 °C (decomp.). R_f = 0.40 (SiO_2, 30:1 hexanes:EtOAc); IR (CH_2Cl_2 solution): 3075 (m), 2968 (s), 2873 (s), 1797 (w), 1595 (s), 1482 (s), 1369 (s), 1249 (s), 1205 (s), 1167 (s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.96-8.30 (2H, m), 7.67 (2H, s), 7.55 (2H, s), 7.38-7.53 (5H, m), 7.26 (2H, d, *J* = 6.5 Hz), 7.21 (2H, d, *J* = 7.5 Hz), 7.14 (2H, s), 5.60 (1H, dd, *J* = 8.8 Hz, *J* = 3.5 Hz), 4.89 (1H, d, *J* = 8.8 Hz), 1.56 (3H, s) 1.20-1.33 (72H, m), 0.11 (3H, s); ^{13}C NMR ($CDCl_3$): δ 149.8, 149.5, 148.9, 148.8, 146.3, 145.6, 145.5, 142.6, 142.5, 141.6, 140.6, 130.5, 130.1, 129.9, 128.2, 128.1, 123.8, 122.3, 121.6, 120.7, 120.43, 120.38, 120.2, 84.39, 84.36, 84.24, 84.18, 84.09, 83.94, 83.17, 83.13, 35.02, 34.88, 34.77, 34.75, 31.53, 31.48, 31.45, 31.41, 28.09, 23.68. ^{31}P NMR ($CDCl_3$): δ 154.3. LRMS (ESI+) Calc'd for $C_{69}H_{97}O_4P$ $(M + Na + H)^+$: 1044.7 Found $(M + Na + H)^+$: 1044.6. $[\alpha]_D^{20}$ = -44° (*c* = 0.5, $CHCl_3$).



3,5-(Me)$_2$TADDOLPPh. Prepared in 62% yield. A white solid. mp 116-130 °C (sealed capillary, decomp.). R_f = 0.35 (SiO_2, 15:1 hexanes:EtOAc); IR (CH_2Cl_2 solution): 2991 (m), 2920 (s), 2865 (m), 1776 (w), 1599 (s), 1463 (s), 1379 (m), 1252 (m), 1214 (s), 1155 (s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.85-7.94 (2H, m), 7.54 (5H, s), 7.31 (2H, s), 7.12 (2H, s), 7.09 (2H, s), 6.96 (1H, s), 6.91 (2H, s), 6.86 (1H, s), 5.59 (1H, dd, *J* = 8.5 Hz, *J* = 5.5 Hz), 4.81 (1H, d, *J* = 8.5 Hz), 2.35 (6H, s), 2.32 (12H, s), 2.30 (6H, s), 1.62 (3H, s) 0.26 (3H, s); ^{13}C NMR ($CDCl_3$): δ 146.7, 146.1, 141.6, 141.3, 137.1, 136.8, 136.7, 136.2, 130.3, 129.9, 129.7, 129.1, 128.9, 128.7, 128.3, 128.2, 127.2, 126.3, 125.3, 125.2, 111.2, 84.14, 83.23, 83.16, 82.79, 82.55, 82.14, 27.97, 25.08, 21.67, 21.55. ^{31}P NMR ($CDCl_3$): δ 155.7. LRMS (ESI+) Calc'd for $C_{45}H_{49}O_4P$ $(M + Na)^+$: 707.3 Found $(M + Na)^+$: 706.7. $[\alpha]_D^{20}$ = -80° (*c* = 3.0, $CHCl_3$).

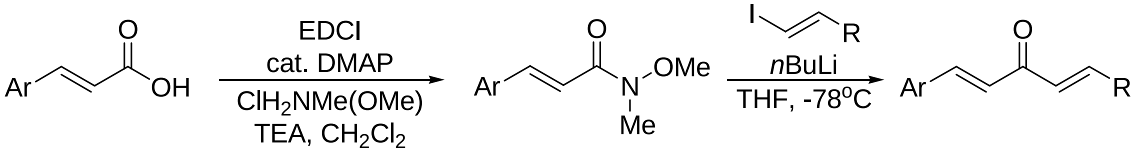


3,5-(^{t}Bu)$_2$TADDOLPNC$_5$H$_{10}$. Prepared according to: Woodward, A. R.; Burks, H. E.; Chan, L. M.; Morken, J. P. *Org. Lett.* **2005**, *7*, 5505 in 82% yield. A white solid. mp 192-200 ^{o}C (sealed capillary). R$_f$ = 0.33 (SiO$_2$, 30:1 hexanes:EtOAc); IR (CH$_2$Cl$_2$ solution): 3075 (w), 2966 (s), 2906 (m), 2865 (m), 1784 (w), 1599 (m), 1450 (m), 1358 (m), 1252 (m), 1201 (m), 1164 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.66 (4H, s), 7.44 (2H, br s), 7.27 (1H, s), 7.21-7.25 (3H, m), 7.17 (2H, s), 5.26 (1H, dd, J = 6.8 Hz, J = 1.6 Hz), 4.70 (1H, d, J = 6.8 Hz), 3.32-3.49 (4H, m), 1.60-1.75 (6H, m), 1.46 (3H, s), 1.31 (18H, s), 1.30 (18H, s), 1.28 (18H, s), 1.27 (18H, s), 0.09 (3H, s); ^{13}C NMR (CDCl$_3$): δ 149.5, 149.1, 148.7, 148.6, 146.5, 146.19, 146.17, 142.1, 141.2, 123.7, 122.0, 121.6, 120.5, 120.1, 120.0, 119.8, 109.7, 83.79, 83.62, 82.43, 82.35, 81.06, 45.10 (d, $^2J_{CP}$ = 20 Hz), 35.01, 34.94, 34.83, 31.56, 31.52, 28.02, 27.53 (d, $^3J_{CP}$ = 4.7 Hz), 25.50, 24.04. ^{31}P NMR (CDCl$_3$): δ 137.8. LRMS (ESI+) Calc'd for C$_{68}$H$_{102}$NO$_4$P (M)$^+$: 1027.8 Found (M)$^+$: 1027.8. $[\alpha]_D^{20}$ = -40^o (c = 3.0, CHCl$_3$).



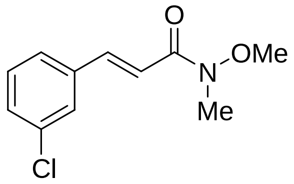
3,5-(^{t}Bu)$_2$TADDOLPOEt. Prepared according to: Woodward, A. R.; Burks, H. E.; Chan, L. M.; Morken, J. P. *Org. Lett.* **2005**, *7*, 5505 with EtOH as the trapping reagent in 75% yield. A white solid. mp 72-100 ^{o}C (sealed capillary). R$_f$ = 0.36 (SiO$_2$, 30:1 hexanes:EtOAc); IR (CH$_2$Cl$_2$ solution): 3075 (w), 2961 (s), 2902 (m), 2868 (m), 1788 (w), 1599 (m), 1476 (m), 1451 (m), 1392 (m), 1358 (m), 1248 (m), 1202 (m), 1168 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.55 (2H, s), 7.49 (2H, s), 7.36 (2H, s), 7.21-7.32 (6H, m), 5.20 (1H, d, J = 8.4 Hz), 5.07 (1H, d, J = 8.4 Hz), 4.30-4.42 (1H, m), 3.97-4.10 (1H, m), 1.18-1.36 (75H, m), 1.09 (3H, s), 0.31 (3H, s); ^{13}C NMR (CDCl$_3$): δ 149.7, 149.2, 148.9, 148.7, 145.7, 141.3, 140.9, 123.6, 123.3, 123.0 121.6, 121.4, 120.7, 120.3, 120.2, 120.1, 110.9, 84.21, 83.50, 83.27, 83.13, 82.51, 58.59, 34.92, 34.87, 34.83, 31.53, 31.27, 27.18, 25.17, 22.71, 17.10, 14.15. ^{31}P NMR (CDCl$_3$): δ 133.5. LRMS (ESI+) Calc'd for C$_{65}$H$_{97}$O$_5$P (M + Na)$^+$: 1011.7 Found (M + Na)$^+$: 1011.3. $[\alpha]_D^{20}$ = -68^o (c = 3.0, CHCl$_3$).

Representative procedure for the synthesis of activated enone substrates.

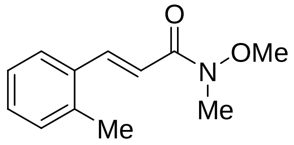


Amide synthesis: To 0.405 g (2.22 mmol) of *trans*-3-chlorocinnamic acid and 0.325 g (3.33 mmol) of *N*, *O*-dimethylhydroxylamine hydrochloride in 9 mL of CH$_2$Cl$_2$ was added 0.0542 g (0.444 mmol) of 4-(dimethylamino)pyridine (DMAP) followed by 0.638 g (3.33 mmol) of *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDCI). This mixture was put under N$_2$ and 0.44 mL (3.3 mmol) of triethylamine was added dropwise. After addition, the mixture was stirred overnight at ambient temperature. The final mixture was transferred to a separatory funnel, washed with water, then 1 M HCl (2x), and then saturated NaHCO$_3$. The organic layer was dried with anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. Silica gel chromatography (hexanes:EtOAc) afforded 0.435 g (87%) of the Weinreb amide as a white solid. All cinnamic acid derivatives were commercially available except for the acids required to prepare the benzyl-protected indole substrate, the *p*-trifluoromethylphenyl substituted substrate, and the 5-fluoro-2-methylphenyl substituted substrate. These Weinreb amides were prepared via Horner-Wadsworth-Emmons olefination between diethyl(*N*-methoxy-*N*-methylcarbamoylmethyl)phosphonate and 1-benzyl-1H-indole-3-carbaldehyde, *p*-trifluoromethylbenzaldehyde, or 5-fluoro-2-methylbenzaldehyde, respectively (Netz, D. F.; Seidel, J. L. *Tetrahedron Lett.* **1992**, *33*, 1957.*)*.

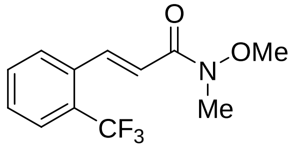
Vinyl lithium addition: To 0.426 g (1.90 mmol) of (*E*)-1-iodoheptene in 2 mL of THF at –78 ^{o}C was added 0.76 mL (1.9 mmol) of a 2.5 M solution of *n*-BuLi in hexane dropwise. This solution was stirred at this temperature for 30 min and then transferred via canula to a solution of 0.215 g (0.951 mmol) of (*E*)-3-(3-chlorophenyl)-*N*-methoxy-*N*-methylacrylamide in 10 mL of THF at –78 ^{o}C. After complete addition, TLC analysis showed complete consumption of the starting material after 15 min at –78 ^{o}C, so the reaction was subsequently quenched with satd. $NH_4Cl_{(aq)}$. The crude reaction was transferred to a separatory funnel with 1 M HCl and Et_2O. The organic layer was collected after shaking, and the aqueous layer was extracted with Et_2O (1x). The combined organics were washed with H_2O, then brine, and finally dried over anhydrous Na_2SO_4, and concentrated using reduced pressure. Silica gel chromatography (hexanes/EtOAc) of the crude mixture afforded 0.203 g (81%) of (1*E*, 4*E*)-1-(3-chlorophenyl)deca-1,4-dien-3-one as a light-yellow solid.



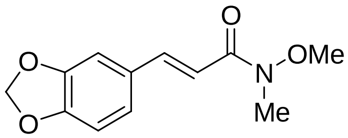
(*E*)-3-(3-chlorophenyl)-*N*-methoxy-*N*-methylacrylamide. A white solid. mp 48-52 ^{o}C. R_f = 0.29 (SiO_2, 2:1 Hexanes:EtOAc); IR (CH_2Cl_2 solution): 3069 (m), 2974 (m), 2930 (m), 2823 (m), 1659 (s), 1615 (s), 1564 (s), 1469 (s), 1425 (s), 1389 (s), 1199 (s) (m) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.62 (1H, d, *J* = 16 Hz), 7.52 (1H, s), 7.34-7.42 (1H, m), 7.22-7.32 (2H, m), 6.99 (1H, d, *J* = 16 Hz), 3.74 (3H, s), 3.27 (3H, s); ^{13}C NMR ($CDCl_3$): δ 166.3, 141.7, 136.9, 134.6, 129.9, 129.6, 127.4, 126.4, 117.1, 61.91, 32.45. LRMS (ESI+) Calc'd for $C_{11}H_{12}ClNO_2$ $(M)^+$: 225.1 Found $(M)^+$: 225.6.



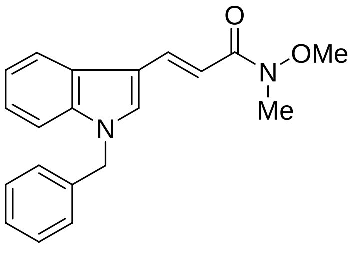
(*E*)-*N*-methoxy-*N*-methyl-3-*o*-tolylacrylamide. A colorless oil. R_f = 0.35 (SiO_2, 1:1 Hexanes:EtOAc); IR (neat): 3062 (w), 2968 (m), 2936 (m), 1659 (s), 1615 (s), 1464 (m), 1413 (m), 1388 (s), 1180 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.99 (1H, d, *J* = 16 Hz), 7.57 (1H, d, *J* = 8.0 Hz), 7.12-7.26 (3H, m), 6.92 (1H, d, *J* = 16 Hz), 3.72 (3H, s), 3.28 (3H, s), 2.41 (3H, s); ^{13}C NMR ($CDCl_3$): δ 166.8, 141.0, 137.5, 134.0, 130.5, 129.4, 126.1, 126.0, 116.8, 61.75, 32.39, 19.76. LRMS (ESI+) Calc'd for $C_{12}H_{15}NO_2$ $(M)^+$: 205.1 Found $(M)^+$: 205.6.



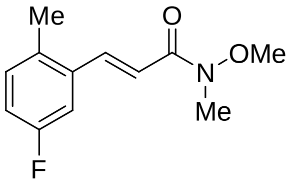
(*E*)-*N*-methoxy-*N*-methyl-3-(2-(trifluoromethyl)phenyl)acrylamide. A colorless oil. R_f = 0.15 (SiO_2, 3:1 Hexanes:EtOAc); IR (neat): 3075 (w), 2974 (m), 2936 (m), 2823 (w), 1841 (w), 1658 (s), 1627 (s), 1488 (s), 1381 (s), 1312 (s), 1287 (s), 1161 (s), 1123 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 8.06 (1H, app dq, *J* = 16 Hz, *J* = 2.4 Hz), 7.70 (1H, d, *J* = 8.0 Hz), 7.65 (1H, d, *J* = 8.0 Hz), 7.53 (1H, t, *J* = 8.0 Hz), 7.42 (1H, d, *J* = 8.0 Hz), 6.96 (1H, d, *J* = 16 Hz), 3.72 (3H, s), 3.28 (3H, s); ^{13}C NMR ($CDCl_3$): δ 165.9, 138.9, 134.3, 131.9, 129.0, 128.7 (q, $^2J_{CF}$ = 30 Hz), 127.9, 126.0 (q, $^3J_{CF}$ = 5.5 Hz), 123.9 (q, $^1J_{CF}$ = 272 Hz), 120.3, 61.88, 32.42. LRMS (APPI) Calc'd for $C_{12}H_{12}F_3NO_2$ $(M + H)^+$: 260.1 Found $(M + H)^+$: 260.1.



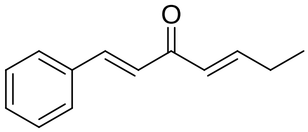
(*E*)-3-(benzo[*d*][1,3]diolol-5-yl)-*N*-methoxy-*N*-methylacrylamide. A white solid. mp 107-110 °C. R_f = 0.21 (SiO_2, 1:1 Hexanes:EtOAc); IR (CH_2Cl_2 solution): 2974 (m), 2936 (m), 2905 (m), 1841 (w), 1652 (s), 1614 (s), 1501 (s), 1444 (s), 1375 (s), 1255 (s), 1180 (m) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.59 (1H, d, *J* = 16 Hz), 7.03 (1H, s), 6.99 (1H, d, *J* = 8.0 Hz), 6.81 (1H, d, *J* = 16 Hz), 6.75 (1H, d, *J* = 8 Hz), 5.94 (2H, s), 3.70 (3H, s), 3.25 (3H, s); ^{13}C NMR ($CDCl_3$): δ 166.9, 149.0, 148.0, 142.9, 129.4, 124.0, 113.6, 108.3, 106.4, 101.3, 61.72, 32.44. LRMS (ESI+) Calc'd for $C_{12}H_{13}NO_4$ $(M)^+$: 235.1 Found $(M)^+$: 235.6.



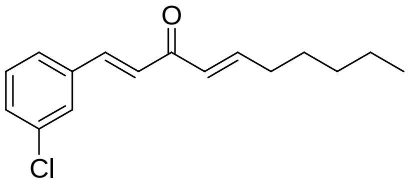
(*E*)-3-(1-benzyl-1*H*-indol-3-yl)-*N*-methoxy-*N*-methylacrylamide. A white solid. mp 42-46 °C. R_f = 0.14 (SiO_2, 2:1 Hexanes:EtOAc); IR (CH_2Cl_2 solution): 3106 (m), 3055 (m), 2968 (m), 2936 (m), 1651 (s), 1608 (s), 1526 (m), 1469 (s), 1381 (s), 1167 (m) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.96 (1H, d, *J* = 16 Hz), 7.90-8.0 (1H, m), 7.40 (1H, s), 7.20-7.34 (6H, m), 7.10 (2H, d, *J* = 6.4 Hz), 7.05 (1H, d, *J* = 16 Hz), 5.26 (2H, s), 3.79 (3H, s), 3.31 (3H, s); ^{13}C NMR ($CDCl_3$): δ 168.1, 137.4, 136.4, 136.2, 132.1, 128.7, 127.8, 126.7, 126.2, 122.8, 121.1, 120.4, 113.0, 110.7, 110.3, 61.59, 50.20, 32.51. LRMS (APPI) Calc'd for $C_{20}H_{20}N_2O_2$ $(M + H)^+$: 321.2 Found $(M + H)^+$: 321.2.



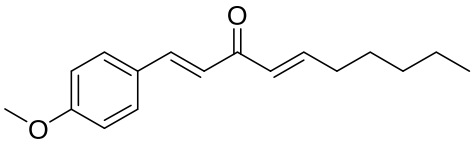
(*E*)-3-(5-fluoro-2-methylphenyl)-*N*-methoxy-*N*-methylacrylamide. The title compound was prepared via Horner-Wadsworth-Emmons olefination with 5-fluoro-2-methylbenzaldehyde in 78% yield. A white solid. mp 68-72 °C. R_f = 0.14 (SiO_2, 3:1 hexanes:EtOAc); IR (CH_2Cl_2 solution): 3075 (w), 2973 (m), 2936 (m), 1658 (s), 1620 (s), 1589 (m), 1495 (s), 1412 (m), 1381 (s), 1262 (m), 1179 (m) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.88 (1H, dd, *J* = 16 Hz, *J* = 1.6 Hz), 7.23 (1H, dd, *J* = 9.6 Hz, *J* = 2.4 Hz), 7.10 (1H, dd, *J* = 8.4 Hz, *J* = 5.6 Hz), 6.90 (1H, dt, *J* = 8.4 Hz, *J* = 2.4 Hz), 6.88 (1H, d, *J* = 16 Hz), 3.73 (3H, s), 3.27 (3H, s), 2.35 (3H, s); ^{13}C NMR ($CDCl_3$): δ 166.4, 161.1 (d, $^1J_{CF}$ = 242 Hz), 139.9, 135.6 (d, $^3J_{CF}$ = 7.0 Hz), 133.1, 131.9 (d, $^3J_{CF}$ = 7.8 Hz), 117.9, 116.2 (d, $^2J_{CF}$ = 20 Hz), 112.4 (d, $^2J_{CF}$ = 22 Hz), 61.84, 32.41. LRMS (APPI) Calc'd for $C_{12}H_{14}FNO_2$ $(M + H)^+$: 224.1 Found $(M + H)^+$: 224.1.



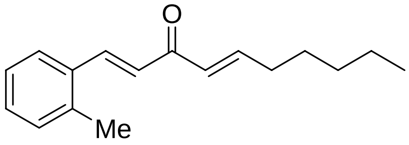
(1*E*, 4*E*)-1-phenylhepta-1,4-dien-3-one. Prepared in 90% yield from the Weinreb amide. A yellow oil. R_f = 0.29 (SiO_2, 10:1 Hexanes:EtOAc); IR (neat): 3031 (w), 2968 (m), 2936 (m), 2879 (w), 1659 (s), 1633 (s), 1602 (s), 1450 (m), 1349 (m), 1199 (m) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.63 (1H, d, *J* = 16 Hz), 7.56 (2H, m), 7.38 (3H, m), 7.05 (1H, dt, *J* = 16 Hz, *J* = 6.4 Hz), 6.97 (1H, d, *J* = 16 Hz), 6.42 (1H, d, *J* = 16 Hz), 2.30 (2H, p, *J* = 7.2 Hz), 1.11 (3H, t, *J* = 7.2 Hz) 1.10-1.40 (5H, m); ^{13}C NMR ($CDCl_3$): δ 189.4, 149.7, 143.0, 134.7, 130.2, 128.8, 128.23, 128.19, 124.6, 25.77, 12.30. LRMS (APPI) Calc'd for $C_{13}H_{14}O$ $(M + H)^+$: 187.1 Found $(M + H)^+$: 187.1.



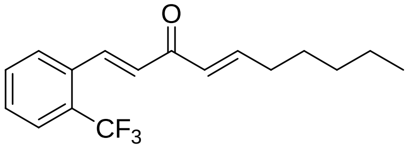
(1*E*, 4*E*)-1-(3-chlorophenyl)deca-1,4-dien-3-one. Prepared in 73% yield from the Weinreb amide. An off-white solid. mp 38-40 °C. R_f = 0.19 (SiO_2, 15:1 Hexanes:EtOAc); IR (CH_2Cl_2 solution): 3031, (w), 2955 (s), 2924 (s), 2854 (s), 2817 (w), 1948 (w), 1665 (s), 1602 (s), 1463 (m), 1419 (m), 1293 (m), 1199 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.52 (1H, d, *J* = 16 Hz), 7.52 (1H, m), 7.39 (1H, dt, *J* = 6.8 Hz, *J* = 2.0 Hz), 7.25-7.34 (2H, m), 6.99 (1H, dd, *J* = 16 Hz, *J* = 7.2 Hz), 6.94 (1H, d, *J* = 16 Hz), 6.74 (1H, dt, *J* = 16 Hz, *J* = 1.6 Hz), 2.25 (2H, q, *J* = 7.2 Hz), 1.48 (2H, p, *J* = 7.2 Hz), 1.24-1.38 (4H, m) 0.871 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (CDCl$_3$): δ 188.7, 148.8, 141.0, 136.6, 134.8, 130.03, 130.00, 129.3, 127.7, 126.5, 125.7, 32.700, 31.38, 27.81, 22.44, 13.96. LRMS (APPI) Calc'd for $C_{16}H_{19}ClO$ (M + H)$^+$: 263.1 Found (M + H)$^+$: 263.1.



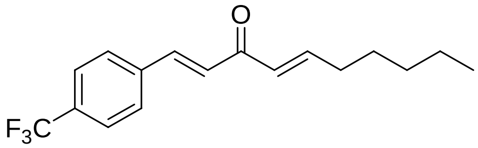
(1*E*, 4*E*)-1-(4-methoxyphenyl)deca-1,4-dien-3-one. Prepared in 90% yield from the Weinreb amide. A yellow oil. R_f = 0.11 (SiO$_2$, 10:1 Hexanes:EtOAc); IR (neat): 3006 (w), 2955 (m), 2930 (m), 2861 (m), 1659 (s), 1627 (s), 1590 (s), 1508 (s), 1420 (m), 1306 (m), 1256 (s), 1168 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.56 (1H, d, *J* = 16 Hz), 7.46 (2H, d, *J* = 8.8 Hz), 6.93 (1H, dt, *J* = 16 Hz, *J* = 7.2 Hz), 6.84 (2H, d, *J* = 8.8 Hz), 6.80 (1H, d, *J* = 16 Hz), 6.36 (1H, d, *J* = 16 Hz), 3.76 (3H, s), 2.20 (2H, q, *J* = 7.2 Hz), 1.44 (2H, p, *J* = 7.2 Hz), 1.20-1.36 (4H, m), 0.847 (3H, t, *J* = 6.8 Hz); ^{13}C NMR (CDCl$_3$): δ 188.9, 161.3, 147.6, 142.5, 129.8, 129.1, 127.3, 122.5, 114.2, 55.17, 32.52, 31.27, 27.78, 22.34, 13.87. LRMS (APPI) Calc'd for $C_{17}H_{22}O_2$ (M + H)$^+$: 259.2 Found (M + H)$^+$: 259.2.



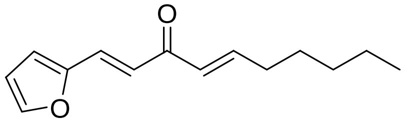
(1*E*, 4*E*)-1-*o*-tolyldeca-1,4-dien-3-one. Prepared in 89% yield from the Weinreb amide. A yellow oil. R_f = 0.25 (SiO$_2$, 15:1 Hexanes:EtOAc); IR (neat): 3025 (w), 2955 (s), 2930 (s), 2854 (m), 1658 (s), 1627 (s), 1596 (s), 1457 (m), 1319 (m), 1099 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.92 (1H, d, *J* = 16 Hz), 7.58 (1H, d, *J* = 7.6 Hz), 7.10-7.30 (3H, m), 6.99 (1H, dt, *J* = 16 Hz, *J* = 7.2 Hz), 6.89 (1H, d, *J* = 16 Hz), 6.39 (1H, dt, *J* = 16 Hz, *J* = 1.6 Hz), 2.41 (3H, s), 2.25 (2H, q, 7.2 Hz), 1.48 (2H, p, *J* = 7.6 Hz), 1.20-1.40 (4H, m), 0.88 (3H, t, *J* = 6.8 Hz); ^{13}C NMR (CDCl$_3$): δ 189.0, 148.2, 140.3, 137.9, 133.6, 130.6, 129.9, 129.5, 126.1, 125.5, 32.61, 31.31, 27.78, 22.38, 19.71, 13.90. LRMS (ESI+) Calc'd for $C_{17}H_{22}O$ (M)$^+$: 242.2 Found (M)$^+$: 242.7.



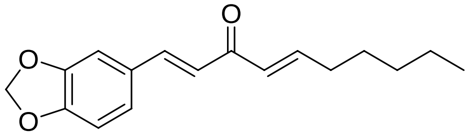
(1*E*, 4*E*)-1-(2-(trifluoromethyl)phenyl)deca-1,4-dien-3-one. Prepared in 79% yield from the Weinreb amide. A yellow oil. R_f = 0.22 (SiO$_2$, 16:1 Hexanes:EtOAc); IR (neat): 2955 (s), 2930 (s), 2867 (m), 1659 (s), 1633 (s), 1602 (s), 1489 (m), 1313 (s), 1162 (s), 1124 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.93 (1H, d, *J* = 16 Hz), 7.71 (1H, d, *J* = 8.0 Hz), 7.65 (1H, d, *J* = 8.0 Hz), 7.53 (1H, t, *J* = 8.0 Hz), 7.43 (1H, t, *J* = 8.0 Hz), 6.98 (1H, dt, *J* = 16 Hz, *J* = 7.2 Hz), 6.86 (1H, d, *J* = 16 Hz), 6.39 (1H, dt, *J* = 16 Hz, J = 1.6 Hz), 2.24 (2H, q, *J* = 6.8 Hz), 1.47 (2H, p, *J* = 7.2 Hz),1.22-1.36 (4H, m) 0.86 (3H, t, *J* = 6.8 Hz); ^{13}C NMR (CDCl$_3$): δ 188.9, 149.2, 138.1, 133.8, 132.0, 129.4, 128.9, 128.85 (q, $^{2}J_{CF}$ = 30 Hz), 128.6, 127.7, 126.0 (q, $^{3}J_{CF}$ = 5.4 Hz), 123.9 (q, $^{1}J_{CF}$ = 272 Hz), 32.68, 31.31, 27.76, 22.39, 13.88. LRMS (ESI+) Calc'd for $C_{17}H_{19}F_3O$ (M)$^+$: 296.1 Found (M)$^+$: 296.7.



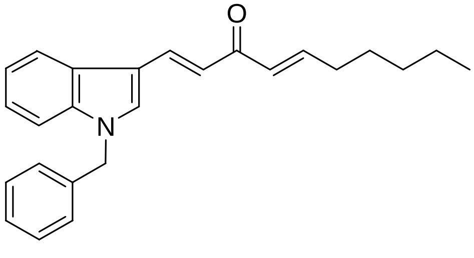
(1*E*, 4*E*)-1-(4-trifluoromethyl)phenyl)deca-1,4-dien-3-one. Prepared in 66% yield from the Weinreb amide. A yellow oil. R_f = 0.23 (SiO$_2$, 16:1 Hexanes:EtOAc); IR (neat): 3043 (w), 2961 (s), 2930 (s), 2861 (m), 1923 (w), 1665 (s), 1633 (s), 1469 (m), 1419 (m), 1319 (s), 1167 (s), 1135 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.65 (1H, d, *J* = 8.7 Hz), 7.63 (1H, d, *J* = 8.7 Hz), 7.62 (1H, d, *J* = 16 Hz), 7.02 (1H, d, *J* = 16 Hz), 7.02 (1H, dt, *J* = 16 Hz, *J* = 6.6 Hz), 6.41 (1H, d, *J* = 16 Hz), 2.28 (2H, q, *J* = 6.6 Hz), 1.50 (2H, p, *J* = 7.5 Hz),1.24-1.40 (4H, m) 0.89 (3H, t, *J* =6.6 Hz); ^{13}C NMR (CDCl$_3$): δ 188.7, 149.2, 140.8, 138.2, 131.6 (q, $^{2}J_{CF}$ = 32 Hz), 129.2, 128.3, 126.8, 125.8 (q, $^{3}J_{CF}$ = 3.1 Hz), 123.8 (q, $^{1}J_{CF}$ = 270 Hz), 32.76, 31.42, 27.85, 22.48, 13.93. LRMS (ESI+) Calc'd for $C_{17}H_{19}F_3O$ (M)$^+$: 296.1 Found (M)$^+$: 296.7.



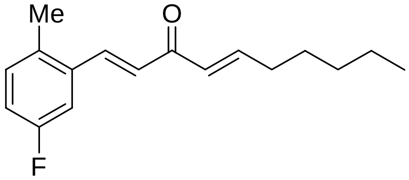
(1*E*, 4*E*)-1-(furan-2-yl)deca-1,4-dien-3-one. Prepared in 86% yield from the Weinreb amide. A yellow oil. R$_f$ = 0.15 (SiO$_2$, 15:1 Hexanes:EtOAc); IR (neat): 3124 (w), 3037 (w), 2955 (s), 2930 (s), 2861 (m), 1658 (s), 1633 (s), 1595 (s), 1482 (m), 1306 (m), 1217 (m), 1098 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.44 (1H, s), 7.36 (1H, d, *J* = 16 Hz), 6.93 (1H, dt, *J* = 16 Hz, *J* = 6.8 Hz), 6.85 (1H, d, *J* = 16 Hz), 6.60 (1H, d, *J* = 3.2 Hz), 6.42 (1H, m), 6.29 (1H, d, *J* = 16 Hz), 2.20 (2H, q, *J* = 6.8 Hz), 1.44 (2H, p, *J* = 6.8 Hz),1.17-1.36 (4H, m), 0.85 (3H, t, *J* =6.8 Hz); ^{13}C NMR (CDCl$_3$): δ 188.6, 151.4, 148.0, 144.6, 129.7,128.9, 121.8, 115.4, 112.4, 32.60, 31.31, 27.79, 22.39, 13.90. LRMS (APPI) Calc'd for $C_{14}H_{18}O_2$ (M + H)$^+$: 219.1 Found (M + H)$^+$: 219.1.



(1*E*, 4*E*)-1-(benzo[*d*][1,3]dioxol-5-yl)deca-1,4-dien-3-one. Prepared in 87% yield from the Weinreb amide. An off-white solid. mp = 40-44 °C. R$_f$ = 0.23 (SiO$_2$, 9:1 Hexanes:EtOAc); IR (CH$_2$Cl$_2$ solution): 2961 (s), 2930 (s), 2861 (s), 1658 (s), 1626 (s), 1589 (s), 1488 (s), 1444 (s), 1362 (m), 1255 (s), 1205 (m), 1098 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.51 (1H, d, *J* = 16 Hz), 7.04 (1H, s,), 7.01 (1H, d, *J* = 8.4 Hz), 6.94 (1H, dt, *J* = 16 Hz, *J* = 7.2 Hz), 6.77 (1H, d, *J* = 16 Hz), 6.77 (1H, d, *J* = 8.4 Hz), 6.36 (1H, dt, J = 16 Hz, J = 1.6 Hz), 5.96 (2H, s), 2.22 (2H, q, *J* = 7.2 Hz), 1.46 (2H, p, *J* = 7.2 Hz), 1.20-1.37 (4H, m) 0.86 (3H, t, *J* = 6.4 Hz); ^{13}C NMR (CDCl$_3$): δ 188.9, 149.6, 148.2, 147.9, 142.6, 129.25, 129.16, 124.8, 122.8, 108.5, 106.4, 101.5, 32.61, 31.35, 27.84, 22.41, 13.94. LRMS (APPI) Calc'd for $C_{17}H_{20}O_3$ (M + H)$^+$: 273.1 Found (M + H)$^+$: 273.1.



(1*E*, 4*E*)-1-(1-benzyl-1*H*-indol-3-yl)deca-1,4-dien-3-one. Prepared in 88% yield from the Weinreb amide. A yellow solid. mp 84-88 °C. R$_f$ = 0.21 (SiO$_2$, 5:1 Hexanes:EtOAc); IR (CH$_2$Cl$_2$ solution): 3106 (m), 3037 (w), 2961 (m), 2930 (m), 2854 (m), 1658 (m), 1627 (s), 1576 (s), 1526 (s), 1463 (m), 1387 (s), 1350 (m), 1281 (m), 1173 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.94-8.00 (1H, m), 7.91 (1H, d, *J* = 16 Hz), 7.44 (1H, s), 7.16-7.26 (6H, m), 7.13 (2H, dd, *J* = 7.6 Hz, *J* = 2 Hz), 6.99 (1H, dt, *J* = 16 Hz, *J* = 8.0 Hz), 6.99 (1H, d, *J* = 16 Hz), 6.44 (1H, dt, *J* = 16 Hz, *J* = 1.6 Hz), 5.30 (2H, s), 2.26 (2H, q, *J* = 8.0 Hz), 1.51 (2H, p, *J* = 7.2 Hz) 1.23-1.41 (4H, m), 0.90 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (CDCl$_3$): δ 189.2, 146.7, 137.7, 136.5, 136.0, 133.1, 133.0, 129.5, 128.9, 128.0, 126.9, 126.3, 123.1, 121.5, 120.7, 113.2, 110.5, 50.46, 32.65, 31.44, 27.98, 22.49, 14.01. LRMS (APPI) Calc'd for $C_{25}H_{27}NO$ (M + H)$^+$: 358.2 Found (M + H)$^+$: 358.2.



(1*E*, 4*E*)-1-(5-fluoro-2-methylphenyl)deca-1,4-dien-3-one. Prepared in 82% yield from the Weinreb amide. A yellow oil. R_f = 0.11 (SiO_2, 20:1 hexanes:EtOAc); IR (neat): 2955 (m), 2930 (s), 2861 (m), 1659 (s), 1627 (s), 1489 (s), 1338 (m), 1237 (m) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.83 (1H, dd, *J* = 16 Hz, *J* = 1.6 Hz), 7.26 (1H, dd, *J* = 9.6 Hz, *J* = 2.4 Hz), 7.12 (1H, dd, *J* = 8.4 Hz, *J* = 5.6 Hz), 6.99 (1H, dt, *J* = 16 Hz, *J* = 6.8 Hz), 6.95 (1H, dt, *J* = 8.4 Hz, *J* = 2.4 Hz), 6.86 (1H, d, *J* = 16 Hz), 6.36 (1H, dt, *J* = 16 Hz, *J* = 1.6 Hz), 2.37 (3H, s), 2.26 (2H, q, *J* = 6.8 Hz), 1.49 (2H, p, *J* = 7.2 Hz), 1.21-1.37 (4H, m), 0.88 (3H, t, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$): δ 188.8, 161.2 (d, $^1J_{CF}$ = 242 Hz), 148.8, 139.2, 135.4 (d, $^3J_{CF}$ = 7.8 Hz), 133.6, 132.0 (d, $^3J_{CF}$ = 7.8 Hz), 129.6, 126.3, 116.7 (d, $^2J_{CF}$ = 21 Hz), 112.4 (d, $^2J_{CF}$ = 22 Hz), 32.72, 31.38, 27.83, 22.45, 19.03, 13.96; ^{19}F NMR ($CDCl_3$): δ 93.28 (m). LRMS (APPI) Calc'd for $C_{17}H_{21}FO$ $(M + H)^+$: 261.2 Found $(M + H)^+$: 261.2.

Represenative procedure for the conjugate allylation catalyst survey (Table 1):

An oven-dried 2-dram vial equipped with a magnetic stir-bar was charged with 3.0 mg (0.011 mmol) of bis(1,5-cyclooctadiene)nickel, 11.8 mg (0.0218 mmol) of chiral ligand **6**, and 0.73 mL of THF in a dry-box under an argon atmosphere. The vial was capped and stirred for 45 min. Next, 22.0 mg (0.263 mmol) of allylboronic acid pinacol ester was added, followed by 25.0 mg (0.109 mmol) of (1*E*, 4*E*)-1-phenyldeca-1,4-dien-3-one. The vial was capped, taped with electrical tape, removed from the dry-box, and allowed to stir at ambient temperature for 8 h. After this time period, degassed water (N_2 sparge) was added and the mixture transferred to a separatory funnel with CH_2Cl_2. After swirling the layers, the organic layer was collected and the aqueous layer washed with CH_2Cl_2 (2x). The combined organic layers were dried with anhydrous Na_2SO_4, and volatiles were removed under reduced pressure. Analysis of the crude reaction mixture using ^1H NMR was used to determine the chemoselectivity of the reaction. Silica gel chromatography (hexanes/EtOAc) afforded 10.6 mg (36%) of the conjugate allylation product as a mixture of isomers.

Notes: Entry 1 was performed according to: Sieber, J. D.; Liu, S.; Morken, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 2214. Entry 2 uses 2.5 mol% $Pd_2(dba)_3$ and 6 mol% ligand and went for 24 h reaction time.

Representative procedure for the asymmetric conjugate allylation (Tables 2, 3, 5):

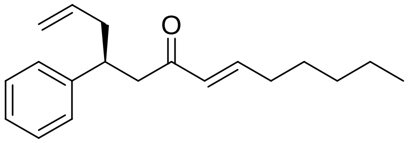
An oven-dried 2-dram vial equipped with a magnetic stir-bar was charged with 3.0 mg (0.011 mmol) of bis(1,5-cyclooctadiene)nickel, 22.4 mg (0.0219 mmol) of chiral ligand **14**, and 0.44 mL of toluene in a dry-box under an argon atmosphere. The vial was capped and stirred for 45 min. Next, 44.2 mg (0.263 mmol) of allylboronic acid pinacol ester was added followed by 50.0 mg (0.219 mmol) of (1*E*, 4*E*)-1-phenyldeca-1,4-dien-3-one. The vial was capped, taped with electrical tape, removed from the dry-box, and allowed to stir at ambient temperature. After this time period, degassed water (N_2 sparge) was added and the mixture transferred to a separatory funnel with CH_2Cl_2. After swirling the layers, the organic layer was collected and the aqueous layer washed with CH_2Cl_2 (2x). The combined organic layers were dried with anhydrous Na_2SO_4, and volatiles were removed under reduced pressure. Analysis of the crude reaction mixture using either ^1H NMR or GLC analysis was used to determine the chemoselectivity of the reaction. Silica gel chromatography (hexanes/EtOAc) afforded 43.7 mg (74%) of the conjugate allylation product.

Procedure for conjugate allylation with unactivated substrates (Scheme 3):

The conjugate allylation performed on benzylidene acetone, depicted in Scheme 3, was carried out using the same procedure as described for the asymmetric conjugate allylation in Table 2.

Conjugate allylation described in Table 4:

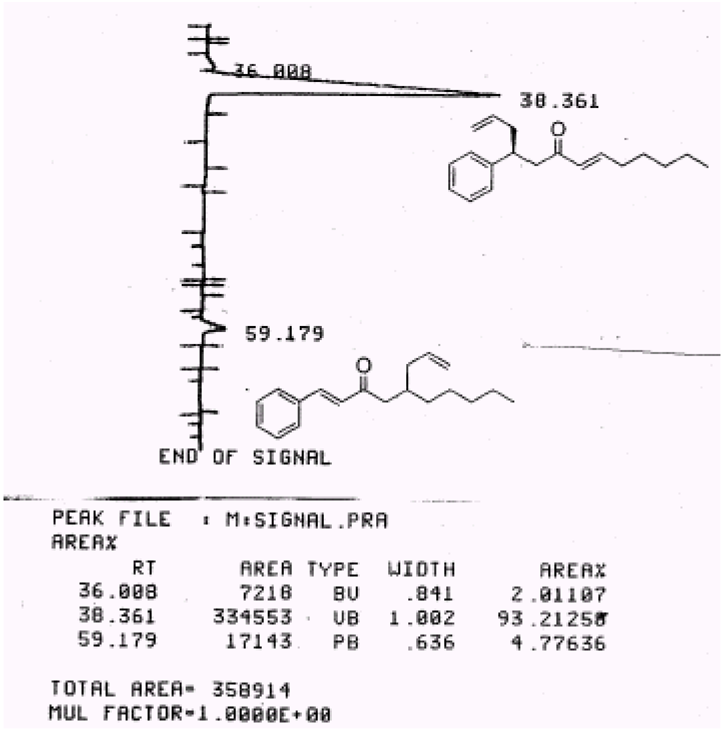
The conjugate allylation was performed as previously described (Sieber, J. D.; Liu, S.; Morken, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 2214). Note that for entry 4, the metal, ligand, and substrate were weighed into the vial, followed by dilution with THF, and lastly addition of allylboronic acid. Mixing $Ni(cod)_2$ and $P(O\text{-}o\text{-}{}^tBu)_3$ in THF under the previously described conditions led to a black solution which did not effect the conjugate allylation.



(*S*,*E*)-4-phenyltrideca-1,7-dien-6-one. An oil. R_f = 0.19 (SiO_2, 40:1 Hexanes:EtOAc); IR (neat): 3030 (m), 2926 (s), 1697 (s), 1667 (s), 1452 (m) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.14-7.24 (2H, m), 7.04-7.14 (3H, m), 6.65 (1H, dt, *J* = 16 Hz, *J* = 7.2 Hz), 5.92 (1H, d, *J* = 16 Hz), 5.56 (1H, ddt, *J* = 17 Hz, *J* = 10 Hz, *J* = 7.2 Hz), 4.82-4.94 (2H, m) 3.22 (1H, p, *J* = 7.2 Hz), 2.76 (1H, app dd, *J* = 16 Hz, *J* = 6.6 Hz), 2.75 (1H, app dd, *J* = 16 Hz, *J* = 7.6 Hz), 2.30 (2H, t, *J* = 7.2 Hz), 2.06 (2H, q, *J* = 6.8 Hz), 1.32 (2H, p, *J* = 7.2 Hz), 1.10-1.28 (4H, m), 0.796 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$): δ 199.1, 147.6, 144.2, 136.2, 130.5, 128.3, 127.5, 126.2, 116.6, 46.04, 40.99, 40.62, 32.39, 31.31, 27.74, 22.42, 13.97. LRMS (ESI+) Calc'd for $C_{19}H_{26}O$ $(M)^+$: 270.2 Found $(M)^+$: 270.7. $[\alpha]_D^{20}$ = +5.9 ° (*c* = 1.0, $CHCl_3$).

Proof of stereochemistry. Chemoselectivity was determined using achiral GLC. Enantioselectivities were determined by comparison with authentic racemic material prepared using either triphenylphosphine or triphenylphosphite as the achiral ligand in the conjugate allylation reaction. Absolute stereochemistry was determined by subjecting the conjugate allylation product to ring closing metathesis conditions using the Hoveyda-Grubbs second generation catalyst in CH_2Cl_2 to afford 5-phenyl-2-cycohexen-1-one (Sieber, J. D.; Liu, S.; Morken, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 2214.). The optical rotation was measured ($[\alpha]_D^{20}$ = +40° (*c* = 0.5, $CHCl_3$)) and compared to the known literature value (Hareau, G. P-J.; Koiwa, M.; Hikichi, S; Sato, F. *J. Am. Chem. Soc.* **1999**, *121*, 3640).

Achiral GLC (Ultra 1, Hewlett-Packard, 140 °C) analysis of the crude reaction mixture:



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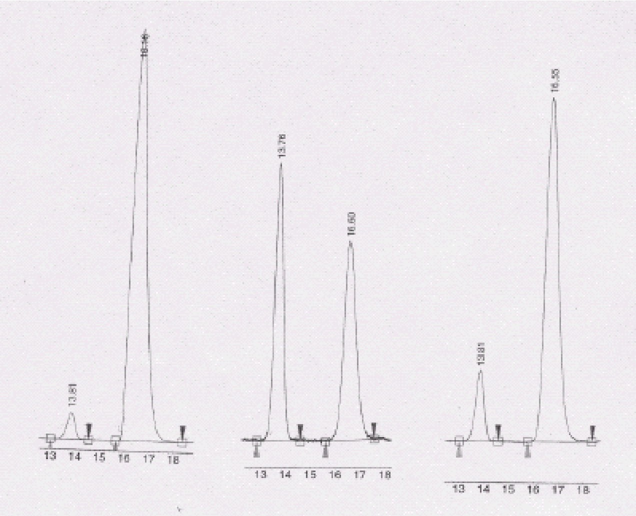
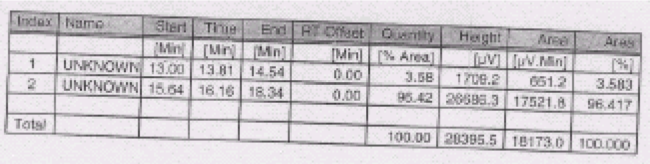
Chiral SFC (AD-H, Chiralpak, 150 bar, 50^{o}C, flow = 1.0 mL/min, 2.0 % MeOH) analysis of conjugate allylation product:



Allylation product

Racemic

Allylation product + racemic coinjection



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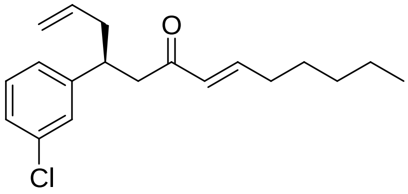
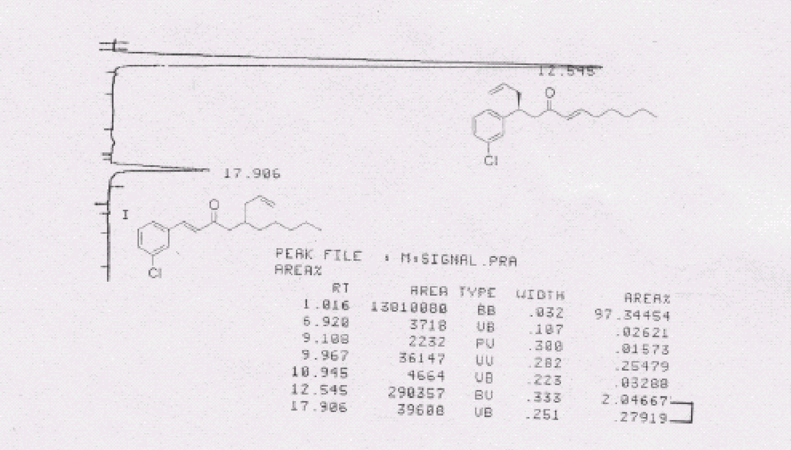
1	UNKNOWN	13.00	13.81	14.54	0.00	3.58	1709.2	651.2	3.583
2	UNKNOWN	15.64	16.16	18.34	0.00	96.42	26686.3	17521.8	96.417
Total						100.00	28395.5	18173.0	100.000



(*S,E*)-4-(3-chlorophenyl)trideca-1,7-dien-6-one. An oil. R_f(major) = 0.18 (SiO_2, 40:1 Hexanes:EtOAc), R_f(minor) = 0.24 (SiO_2, 40:1 Hexanes:EtOAc); IR (neat): 2957 (s), 2923 (s), 2853 (m), 1673 (s), 1624 (s), 1434 (m), 1367 (m) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.00-7.20 (4H, m), 6.74 (1H, dt, *J* = 16 Hz, *J* = 6.8 Hz), 5.99 (1H, d, *J* = 16 Hz), 5.54 (1H, ddt, *J* = 17 Hz, *J* = 10 Hz, *J* = 7.2 Hz), 4.87-5.03 (2H, m), 3.28 (1H, p, *J* = 7.2 Hz) 2.82 (1H, dd, *J* = 16 Hz, *J* = 6.0 Hz), 2.80 (1H, dd, *J* = 16 Hz, *J* = 7.6 Hz), 2.34 (2H, m), 2.14 (2H, q, *J* = 7.2 Hz), 1.40 (2H, p, *J* = 7.2 Hz), 1.15-1.35 (4H, m), 0.86 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$): δ 198.5, 147.9, 146.4, 135.7, 134.1, 130.4, 129.6, 127.5, 126.5, 125.9, 117.0, 45.65, 40.62, 40.48, 32.43, 31.33, 27.74, 22.43, 13.97. LRMS (ESI+) Calc'd for $C_{19}H_{25}ClO$ $(M)^+$: 304.2 Found $(M)^+$: 304.7. $[\alpha]_D^{20}$ = +4.4° (*c* = 2.5, $CHCl_3$).

Proof of stereochemistry. Chemoselectivity was determined using achiral GLC (Note: the starting material had the same retention time as the major isomer. The reported ratios are calculated assuming 95% conversion as evident by the appearance of no starting material in the crude ^1H NMR spectrum.). Enantioselectivities were determined by comparison with authentic racemic material prepared using either triphenylphosphine or triphenylphosphite as the achiral ligand in the conjugate allylation reaction. Absolute stereochemistry was determined by subjecting the conjugate allylation product to ring closing metathesis conditions using the Hoveyda-Grubbs second generation catalyst, in CH_2Cl_2, to afford 5-(*m*-chlorophenyl)-2-cycohexen-1-one (Sieber, J. D.; Liu, S.; Morken, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 2214.). The optical rotation was measured ($[\alpha]_D^{20}$ = +32° (*c* = 1.0, $CHCl_3$)) and compared to the known literature value (Chen, Q.; Kuriyama, M.; Soeta, T.; Hao, X.; Yamada, K. –I.; Tomioka, K. *Org. Lett.* **2005**, *7*, 4439).

Achiral GLC (Ultra 1, Hewlett-Packard, 180 °C) analysis of the crude reaction mixture:



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  12.545    290357   BU    .333    2.04667
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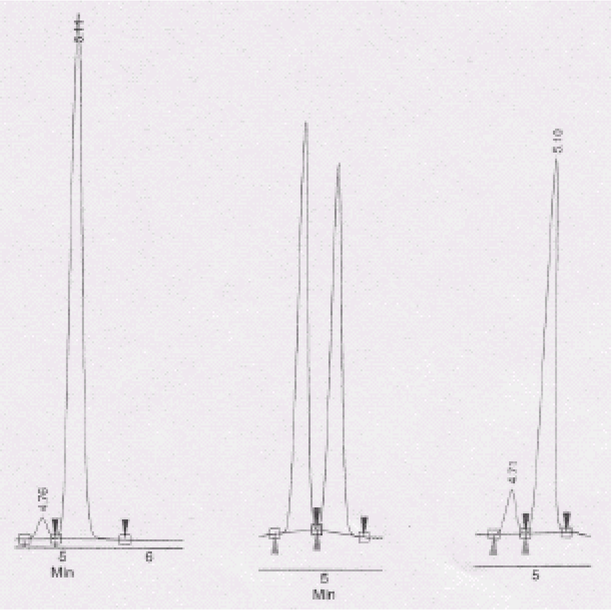
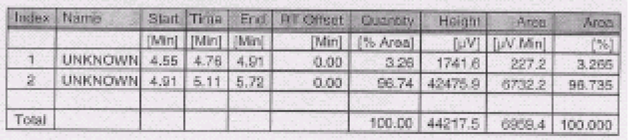
Chiral SFC (AD-H, Chiralpak, 150 bar, 50^{o}C, flow = 2.0 mL/min, 3.0 % MeOH) analysis of conjugate allylation product:



Allylation product

Racemic

Allylation product + racemic coinjection



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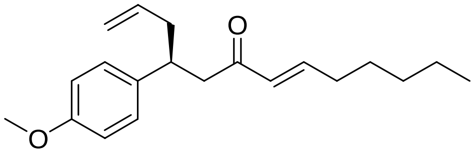
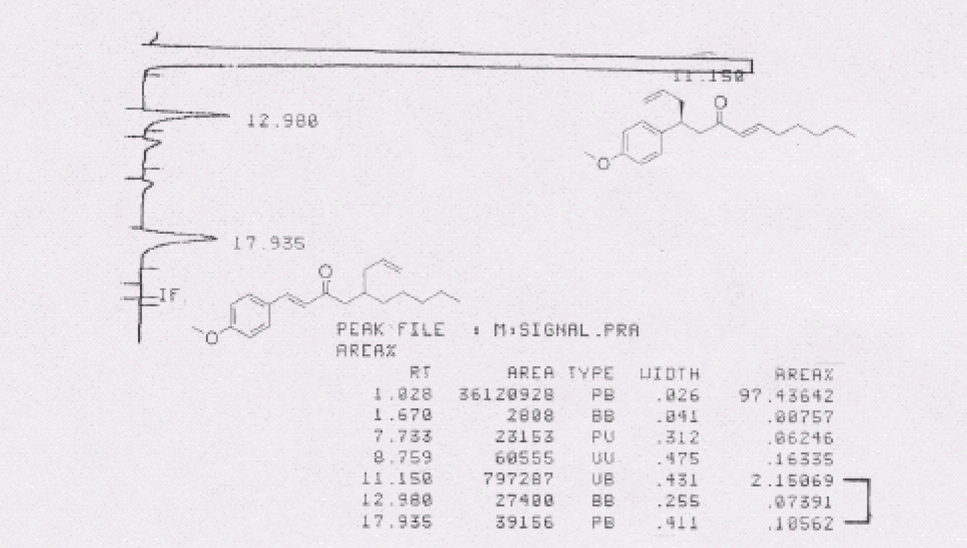
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV Min]	[%]
1	UNKNOWN	4.55	4.76	4.91	0.00	3.26	1741.6	227.2	3.265
2	UNKNOWN	4.91	5.11	5.72	0.00	96.74	42475.9	6732.2	96.735
Total						100.00	44217.5	6959.4	100.000



***(S,E)*-4-(4-methoxyphenyl)trideca-1,7-dien-6-one.** An oil. R_f = 0.18 (SiO_2, 17:1 pentane:Et_2O); IR (neat): 3074 (w), 2962 (s), 2924 (s), 2861 (s), 2055 (w), 1879 (w), 1671 (s), 1620 (s), 1514 (s), 1464 (m), 1243 (s), 1180 (s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.08 (2H, d, *J* = 8 Hz), 6.79 (2H, d, *J* = 8 Hz), 6.72 (1H, dt, *J* = 16 Hz, *J* = 7.2 Hz), 5.98 (1H, d, *J* = 16 Hz), 5.63 (1H, ddt, *J* = 17 Hz, *J* = 10 Hz, *J* = 6.8 Hz), 4.90-5.02 (2H, m) 3.75 (3H, s), 3.24 (1H, p, *J* = 7.6 Hz), 2.78 (2H, m), 2.34 (2H, t, *J* = 6.8 Hz), 2.13 (2H, q, *J* = 7.2 Hz), 1.39 (2H, p, *J* = 7.2 Hz), 1.18-1.34 (4 H, m), 0.863 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$): δ 199.3, 157.9, 147.5, 136.3, 136.2, 130.5, 128.3, 116.5, 113.7, 55.16, 46.33, 40.80, 40.28, 32.40, 31.33, 27.75, 22.42, 13.99. LRMS (ESI+) Calc'd for $C_{20}H_{28}O_2$ $(M)^+$: 300.2 Found $(M)^+$: 300.8. $[\alpha]_D^{20}$ = +9.5° (*c* = 3.0, $CHCl_3$).

Proof of stereochemistry. Chemoselectivity was determined using achiral GLC. Enantioselectivities were determined by comparison with authentic racemic material prepared using either triphenylphosphine or triphenylphosphite as the achiral ligand in the conjugate allylation reaction. Absolute stereochemistry was determined by subjecting the conjugate allylation product to ring closing metathesis conditions using the Hoveyda-Grubbs second generation catalyst, in CH_2Cl_2, to afford 5-(*p*-methoxyphenyl)-2-cycohexen-1-one (Sieber, J. D.; Liu, S.; Morken, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 2214.). Subsequent 1,4 reduction with Pd/C and H_2 (Chen, Q.; Kuriyama, M.; Soeta, T.; Hao, X.; Yamada, K. –I.; Tomioka, K. *Org. Lett.* **2005**, *7*, 4439.) gave the corresponding saturated cyclohexanone derivative. The optical rotation was measured ($[\alpha]_D^{20}$ = -12° (*c* = 1.0, $CHCl_3$)) and compared to the known literature value (Takaya, Y.; Ogasawara, M.; Hayashi, T. *Tetrahedron Lett.* **1999**, *40*, 6957.).

Achiral GLC (Ultra 1, Hewlett-Packard, 190 °C) analysis of the crude reaction mixture:



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   8.759     60555   UU    .475      .16335
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  12.980     27400   BB    .255      .07391
  17.935     39156   PB    .411      .10562
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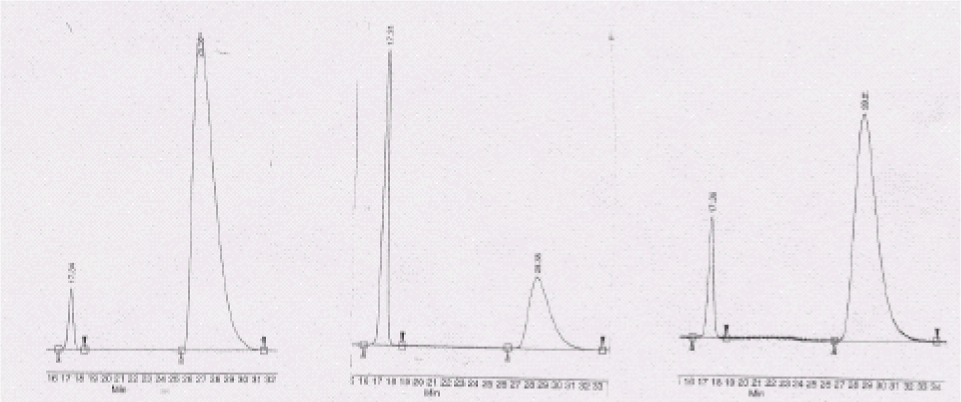
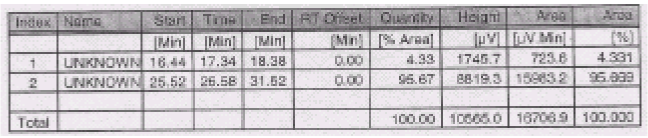
Chiral SFC (AD-H, Chiralpak, 150 bar, 50°C, flow = 1.0 mL/min, 3.0 % MeOH) analysis of conjugate allylation product:



Allylation product

Racemic

Allylation product+ racemic coinjection



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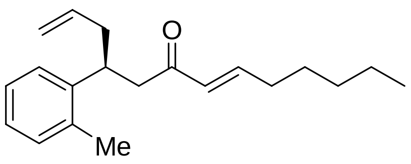
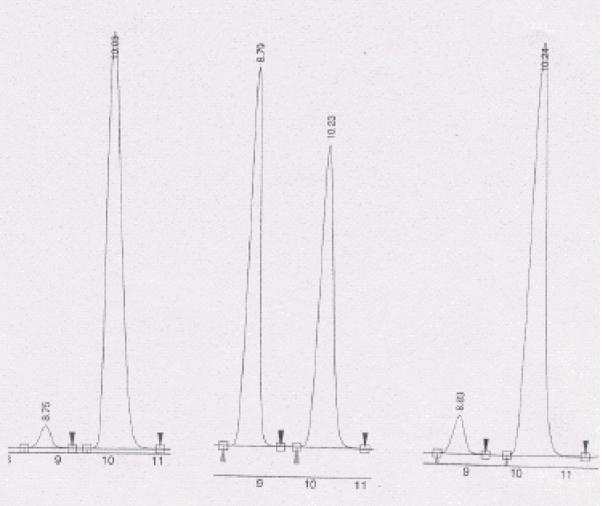
1	UNKNOWN	16.44	17.34	18.38	0.00	4.33	1745.7	723.6	4.331
2	UNKNOWN	25.52	26.58	31.52	0.00	95.67	8819.3	15983.2	95.669
Total						100.00	10565.0	16706.9	100.000



(*S*,*E*)-4-*o*-tolyltrideca-1,7-dien-6-one. An oil. R_f = 0.19 (SiO_2, 30:1 hexanes:EtOAc); IR (neat): 3069 (m), 3018 (m), 2930 (s), 2861 (s), 1829 (w), 1671 (s), 1627 (s), 1457 (m), 1262 (m) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.00-7.18 (4H, m), 6.73 (1H, dt, *J* = 16 Hz, *J* = 7.2 Hz), 5.99 (1H, dt, *J* = 16 Hz, *J* = 1.2 Hz), 5.63 (1H, ddt, *J* = 17 Hz, *J* = 10 Hz, *J* = 6.8 Hz), 4.88-5.02 (2H, m) 3.60 (1H, p, *J* = 6.8 Hz), 2.83 (2H, d, *J* = 6.8 Hz), 2.35 (5H, m), 2.13 (2H, q, *J* = 6.8 Hz), 1.39 (2H, p, *J* = 7.2 Hz), 1.18-1.35 (4 H, m), 0.87 (3H, t, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$): δ 199.2, 147.5, 142.5, 136.2, 135.9, 130.5, 130.3, 126.0, 125.9, 125.7, 116.5, 45.79, 40.44, 35.65, 32.40, 31.32, 27.76, 22.44, 19.84, 13.97. LRMS (ESI+) Calc'd for $C_{20}H_{28}O$ $(M)^+$: 284.2 Found $(M)^+$: 284.8. $[\alpha]_D^{20} = +6.4^o$ (*c* = 0.6, $CHCl_3$).

Proof of stereochemistry. Chemoselectivity was determined using ^{1}HNMR spectroscopy; the minor isomer was not observed in the crude ^{1}HNMR spectrum. Enantioselectivities were determined by comparison with authentic racemic material prepared using either triphenylphosphine or triphenylphosphite as the achiral ligand in the conjugate allylation reaction. Absolute stereochemistry was determined by subjecting the conjugate allylation product to ring closing metathesis conditions using the Hoveyda-Grubbs second generation catalyst, in CH_2Cl_2, to afford 5-(*o*-tolyl)-2-cycohexen-1-one (Sieber, J. D.; Liu, S.; Morken, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 2214.). Subsequent 1,4 reduction with Pd/C and H_2 (Chen, Q.; Kuriyama, M.; Soeta, T.; Hao, X.; Yamada, K. –I.; Tomioka, K. *Org. Lett.* **2005**, *7*, 4439.) gave the corresponding saturated cyclohexanone derivative. The optical rotation was measured ($[\alpha]_D^{20} = -37^o$ (*c* = 0.8, CCl_4)) and compared to the known literature value (Ek, M.; Ahlberg, P. *Acta. Chem. Scand. Ser. B* **1984**, *38*, 211.).

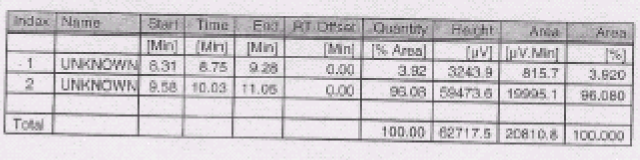
Chiral SFC (AD-H, Chiralpak, 150 bar, 50°C, flow = 1.0 mL/min, 3.0 % MeOH) analysis of conjugate allylation product:



Allylation product

Racemic

Allylation product + racemic coinjection



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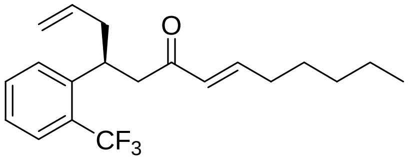
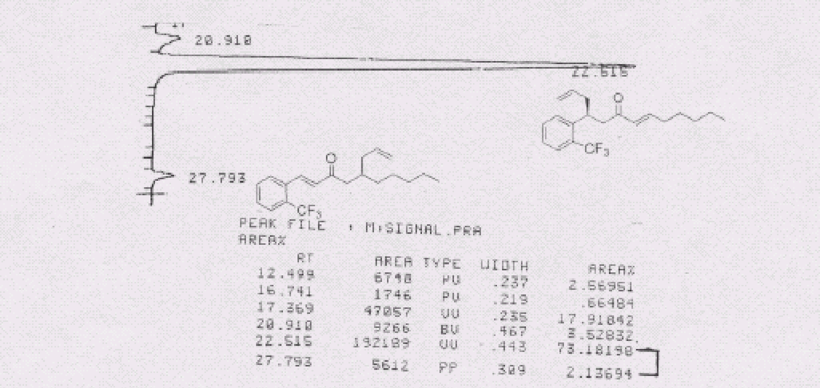
2	UNKNOWN	9.58	10.03	11.06	0.00	96.08	59473.6	19995.1	96.080
Total						100.00	62717.5	20810.8	100.000



(*S,E*)-4-(2-(trifluoromethyl)phenyl)trideca-1,7-dien-6-one. An oil. R_f = 0.18 (SiO_2, 30:1 hexanes:EtOAc); IR (neat): 2961 (s), 2930 (s), 2861 (s), 1828 (w), 1696 (s), 1457 (m), 1312 (s), 1155 (s), 1117 (s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.60 (1H, d, *J* = 8.0 Hz), 7.48 (1H, t, *J* = 7.5 Hz), 7.39 (1H, d, *J* = 8.0 Hz), 7.26 (1H, t, *J* = 7.5 Hz), 6.76 (1H, dt, *J* = 16 Hz, *J* = 7 Hz), 6.03 (1H, d, *J* = 16 Hz), 5.61 (1H, ddt, *J* = 17 Hz, *J* = 10 Hz, *J* = 7 Hz), 4.93 (1H, d, *J* = 17 Hz), 4.91 (1H, d, *J* = 10 Hz), 3.74 (1H, p, *J* = 7 Hz), 2.84 (1H, dd, *J* = 16 Hz, *J* = 7.5 Hz), 2.80 (1H, dd, *J* = 16 Hz, *J* = 6.0 Hz), 2.40 (2H, t, *J* = 7.5 Hz), 2.15 (2H, q, *J* = 7.0 Hz), 1.40 (2H, p, *J* = 7.5 Hz), 1.18-1.35 (4 H, m), 0.87 (3H, t, *J* = 7 Hz); ^{13}C NMR ($CDCl_3$): δ 198.3, 148.0, 143.3, 135.6, 131.8, 130.0, 128.5 (q, $^2J_{CF}$ = 29 Hz), 128.0, 126.2, 125.9 (q, $^3J_{CF}$ = 6.1 Hz), 124.4 (q, $^1J_{CF}$ = 272 Hz), 117.0, 46.45, 40.43, 36.08, 32.38, 31.28, 27.69, 22.39, 13.90. ^{19}F NMR ($CDCl_3$): δ -59.81. LRMS (ESI+) Calc'd for $C_{20}H_{25}F_3O$ $(M)^+$: 338.2 Found $(M)^+$: 338.8.

Proof of stereochemistry. Chemoselectivity was determined using achiral GLC. To determine the enantioselectivity, the title compound was subjected to ring-closing metathesis (RCM) conditions using the Hoveyda-Grubbs second generation catalyst, in CH_2Cl_2, to afford 5-(*o*-trifluoromethylphenyl)-2-cycohexen-1-one (Sieber, J. D.; Liu, S.; Morken, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 2214.). This derivative was then analyzed by chiral GLC. Stereochemical ratios were determined in comparison with authentic racemic material prepared using either triphenylphosphine or triphenylphosphite as the achiral ligand in the conjugate allylation reaction followed by RCM. Absolute stereochemistry was assumed to be analogous to the configuration determined for others.

Achiral GLC (Ultra 1, Hewlett-Packard, 150 °C) analysis of the crude reaction mixture:



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    20.910         9266   BV    .467       3.52832
    22.515       132189   VV    .443      73.18198
    27.793         5612   PP    .309       2.13694
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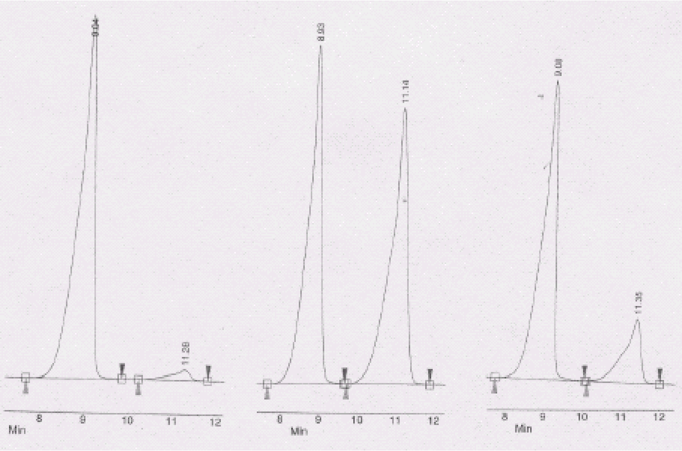
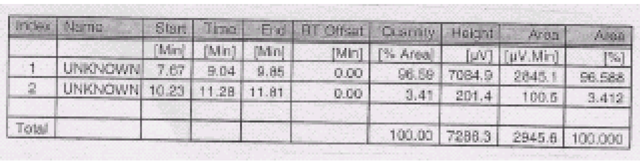
Chiral SFC ((R,R)-Whelk-O, Pirkle Covalent, 150 bar, 50°C, flow = 2.0 mL/min, 2.0 % MeOH) analysis of conjugate allylation-RCM product:





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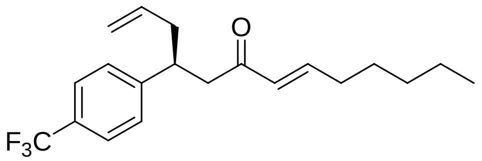
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	7.67	9.04	9.85	0.00	96.59	7084.9	2845.1	96.588
2	UNKNOWN	10.23	11.28	11.81	0.00	3.41	201.4	100.5	3.412
Total						100.00	7286.3	2945.6	100.000

Allylation-RCM product

Racemic

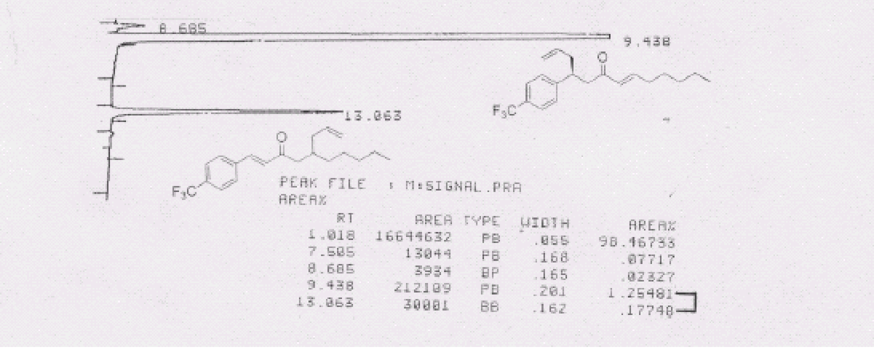
Allylation-RCM product + racemic coinjection



(S,E)-4-(4-(trifluoromethyl)phenyl)trideca-1,7-dien-6-one. An oil. R_f(major) = 0.19 (SiO_2, 30:1 hexanes:EtOAc), R_f(minor) = 0.24 (SiO_2, 30:1 hexanes:EtOAc); IR (neat): 2961 (s), 2930 (s), 2854 (m), 1702 (m), 1677 (s), 1620 (s), 1331 (s), 1167 (s), 1123 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.51 (2H, d, J = 8.0 Hz), 7.29 (2H, d, J = 8.0 Hz), 6.74 (1H, dt, J = 16 Hz, J = 7 Hz), 5.99 (1H, d, J = 16 Hz), 5.61 (1H, ddt, J = 17 Hz, J = 10 Hz, J = 7 Hz), 4.96 (1H, d, J = 17 Hz), 4.95 (1H, d, J = 10 Hz), 3.38 (1H, p, J = 7.5 Hz), 2.86 (1H, dd, J = 17 Hz, J = 7.0 Hz), 2.83 (1H, dd, J = 17 Hz, J = 7.5 Hz), 2.39 (1H, dd, J = 14 Hz, J = 7.0 Hz), 2.36 (1H, dd, J = 14 Hz, J =7.0 Hz), 2.14 (2H, q, J = 7.0 Hz), 1.39 (2H, p, J = 7.0 Hz), 1.20-1.33 (4 H, m), 0.86 (3H, t, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$): δ 198.5, 148.4, 148.0, 135.6, 130.4, 128.6 (q, $^2J_{CF}$ = 32 Hz), 127.9, 125.3 (q, $^3J_{CF}$ = 3.9 Hz), 124.2 (q, $^1J_{CF}$ = 271 Hz), 117.2, 45.60, 40.65, 40.39, 32.38, 31.30, 27.69, 22.36, 13.89. ^{19}F NMR ($CDCl_3$): δ -63.72. LRMS (ESI+) Calc'd for $C_{20}H_{25}F_3O$ $(M)^+$: 338.2 Found $(M)^+$: 338.8.

Proof of stereochemistry. Chemoselectivity was determined using achiral GLC. To determine the enantioselectivity, the title compound was subjected to ring-closing metathesis (RCM) conditions using the Hoveyda-Grubbs second generation catalyst, in CH_2Cl_2, to afford 5-(p-trifluoromethylphenyl)-2-cycohexen-1-one (Sieber, J. D.; Liu, S.; Morken, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 2214.). This derivative was then analyzed by chiral SFC. Stereochemical ratios were determined in comparison with authentic racemic material prepared using either triphenylphosphine or triphenylphosphite as the achiral ligand in the conjugate allylation reaction followed by RCM. Absolute stereochemistry was determined by comparing the optical rotation ($[\alpha]_D^{20}$ = +37^o (c = 1.0, $CHCl_3$)) of the RCM product to the known value (Chen, Q.; Kuriyama, M.; Soeta, T.; Hao, X.; Yamada, K. –I.; Tomioka, K. *Org. Lett.* **2005**, *7*, 4439).

Achiral GLC (Ultra 1, Hewlett-Packard, 170 ^{o}C) analysis of the crude reaction mixture:



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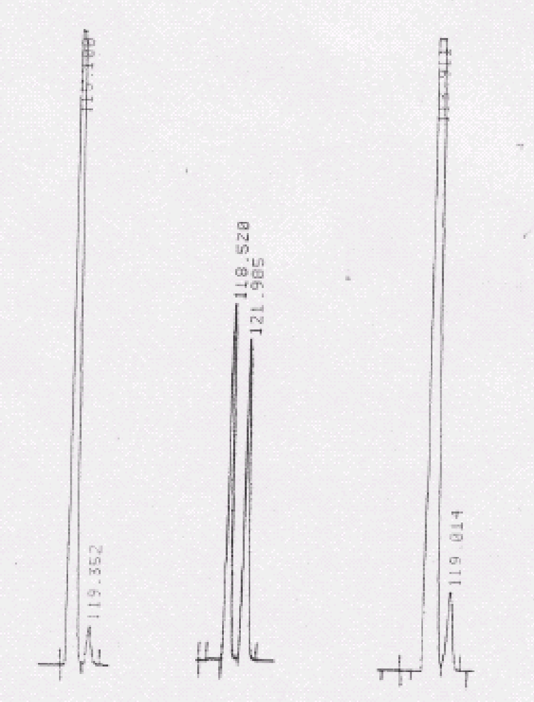
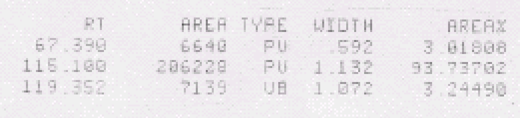
Chiral GLC (β-dex, Supelco, 130^{o}C) analysis of conjugate allylation-RCM product:



Allylation-RCM product   Racemic   Allylation-RCM product + racemic coinjection



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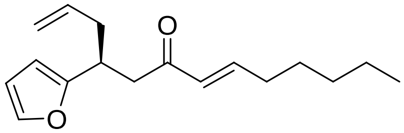
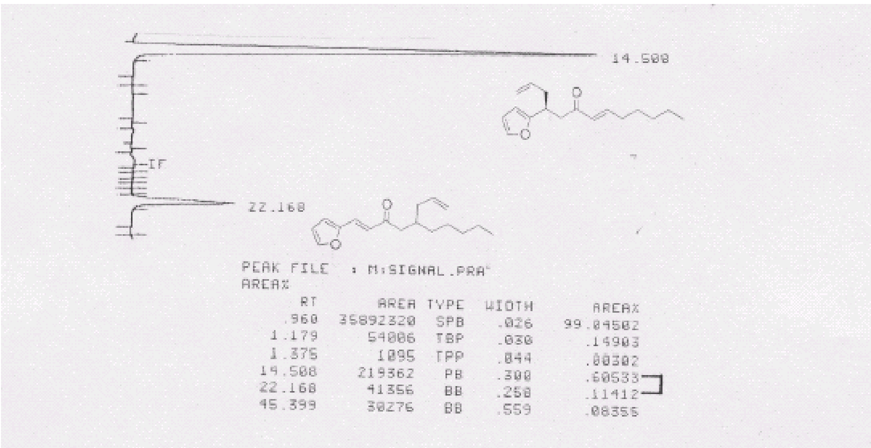


(*S*,*E*)-4-(furan-2-yl)trideca-1,7-dien-6-one. An oil. Isolated as an inseparable mixture of constitutional isomers. R_f = 0.16 (SiO_2, 30:1 Hexanes:EtOAc, both constitutional isomers); IR (neat): 3074 (w), 2955 (s), 2930 (s), 2854 (m), 1671 (s), 1626 (s), 1444 (m), 1362 (m) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.47 (1H, d, *J* = 3.2 Hz, minor), 7.28 (1H, d, *J* = 16 Hz, minor), 7.27 (1H, dd, *J* = 2.0 Hz, *J* = 1.2 Hz, major), 6.77 (1H, dt, *J* = 16 Hz, *J* = 7.2 Hz, major), 6.64 (1H, d, *J* = 2.0 Hz, minor), 6.61 (1H, d, *J* = 16 Hz, minor), 6.46 (1H, dd, *J* = 3.2 Hz, *J* = 2.0 Hz, minor), 6.23 (1H, dd, *J* = 3.2 Hz, *J* = 2.0 Hz, major), 6.03 (1H, dt, *J* = 16 Hz, *J* = 1.2 Hz, major), 5.98 (1H, d, *J* = 3.2 Hz, major), 5.67 (1H, ddt, *J* = 17 Hz, *J* = 10 Hz, *J* = 7.2 Hz, major), 4.94-5.04 (4H, m, major + minor), 3.43 (1H, p, *J* = 7.2 Hz, major), 2.87 (1H, dd. *J* = 16 Hz, *J* = 7.2 Hz, major), 2.75 (1H, dd, *J* = 16 Hz, *J* = 6.8 Hz, major), 2.53 (1H, dd, *J* = 16 Hz, *J* = 6.4 Hz, minor), 2.45 (1H, dd, *J* = 16 Hz, *J* = 5.6 Hz, minor), 2.28-2.46 (3H, m, major + minor), 1.42 (2H, p, *J* = 7.6 Hz, major), 1.18-1.35 (12H, m, major + minor), 0.87 (3H, t, *J* = 6.8 Hz, major), 0.85 (3H, t, *J* = 7.2 Hz, minor); ^{13}C NMR ($CDCl_3$): δ (major) 198.7, 157.1, 147.8, 140.9, 135.7, 130.4, 116.9, 109.9, 105.1, 43.06, 38.00, 34.27, 32.46, 31.34, 27.76, 22.45, 13.98. LRMS (ESI+) Calc'd for $C_{17}H_{24}O_2$ $(M)^+$: 260.2 Found $(M)^+$: 260.7.

Proof of stereochemistry. Chemoselectivity was determined using achiral GLC. Enantioselectivities were determined by comparison with authentic racemic material prepared using either triphenylphosphine or triphenylphosphite as the achiral ligand in the conjugate allylation reaction. Absolute stereochemistry was assumed to be analogous to the configuration determined for others.

Achiral GLC (Ultra 1, Hewlett-Packard, 145 °C) analysis of the crude reaction mixture:



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   22.168      41356   BB   .250     .11412
   45.399      30276   BB   .559     .08355
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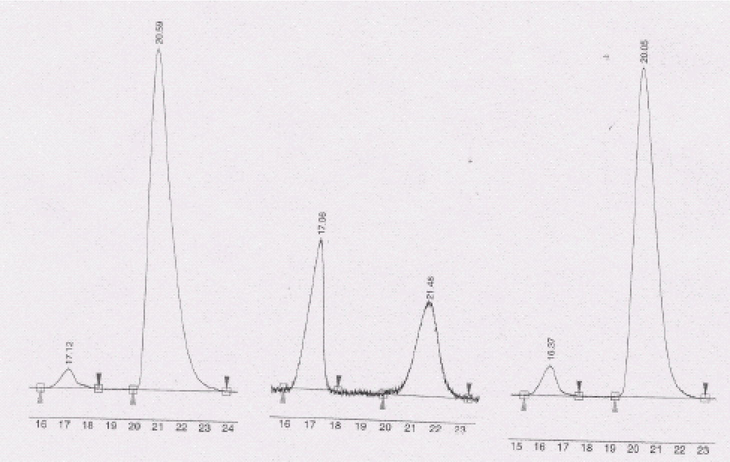
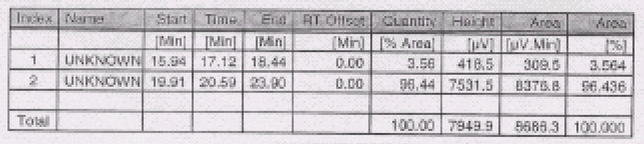
Chiral SFC (AD-H, Chiralpak, 150 bar, 50^{o}C, flow = 1.0 mL/min, 1.0 % MeOH) analysis of conjugate allylation product:



Allylation product

Racemic

Allylation product + racemic coinjection



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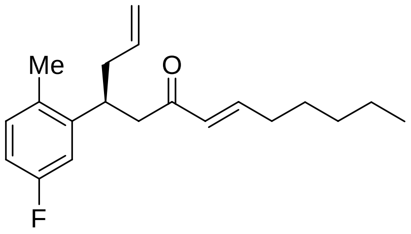
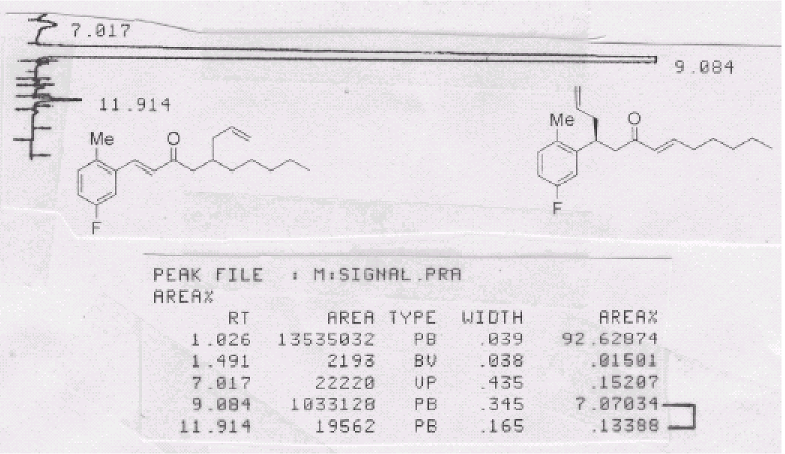
1	UNKNOWN	15.94	17.12	18.44	0.00	3.56	418.5	309.5	3.564
2	UNKNOWN	19.91	20.59	23.90	0.00	96.44	7531.5	8378.8	96.436
Total						100.00	7949.9	8688.3	100.000



(*S,E*)-4-(5-fluoro-2-methylphenyl)trideca-1,7-dien-6-one. An oil. R_f = 0.18 (SiO_2, 30:1 hexanes:EtOAc); IR (neat): 3075 (w), 3031 (w), 2955 (s), 2924 (s), 2861 (s), 1841 (w), 1697 (s), 1665 (s), 1621 (s), 1495 (s), 1457 (m), 1237 (m) cm^{-1}; ^1H NMR ($CDCl_3$): 7.03 (1H, dd, J = 8.4 Hz, J = 6.0 Hz), 6.68-6.85 (3H, m), 5.99 (1H, dt, J = 16 Hz, J = 1.6 Hz), 5.60 (1H, ddt, J = 17 Hz, J = 10 Hz, J = 6.8 Hz), 4.96 (1H, d, J = 17 Hz), 4.93 (1H, d, J = 10 Hz), 3.57 (1H, p, J = 7.2 Hz), 2.82 (1H, app dd, J = 16 Hz, J = 6.4 Hz), 2.78 (1H, app dd, J = 16 Hz, J = 7.2 Hz), 2.22-2.39 (5H, m), 2.13 (2H, q, J = 7.2 Hz), 1.40 (2H, p, J = 7.2 Hz), 1.17-1.34 (4H, m), 0.86 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$): δ 198.6, 161.4 (d, $^1J_{CF}$ = 241 Hz), 147.7, 144.7 (d, $^3J_{CF}$ = 6.2 Hz), 135.7, 131.42, 131.36 (d, $^3J_{CF}$ = 4.7 Hz), 130.4, 116.9, 112.5 (d, $^2J_{CF}$ = 21 Hz), 112.4 (d, $^2J_{CF}$ = 21 Hz), 45.43, 40.29, 35.73, 32.37, 31.28, 27.70, 22.39, 19.06, 13.91; ^{19}F NMR ($CDCl_3$): δ 93.93 (m). LRMS (ESI+) Calc'd for $C_{20}H_{27}FO$ $(M + Na)^+$: 325.2 Found $(M + Na)^+$: 324.7.

Proof of stereochemistry. GLC analysis of the crude reaction mixture was used to determine the chemoselectivity of the reaction (Note: the starting material had the same retention time as the major isomer. The reported ratios are calculated assuming 95% conversion as evident by the appearance of no starting material in the crude ^1H NMR spectrum.). The enantioselectivity was determined by measuring the enantiomeric excess of the cyclic enone after ring-closing metathesis (Scheme 2, eq 1) and is described below. Stereochemical ratios were determined in comparison with authentic racemic material prepared using either triphenylphosphine or triphenylphosphite as the achiral ligand in the conjugate allylation reaction followed by RCM.

Achiral GLC (Ultra 1, Hewlett-Packard, 180 °C) analysis of the crude reaction mixture:



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   9.084     1033128   PB    .345      7.07034
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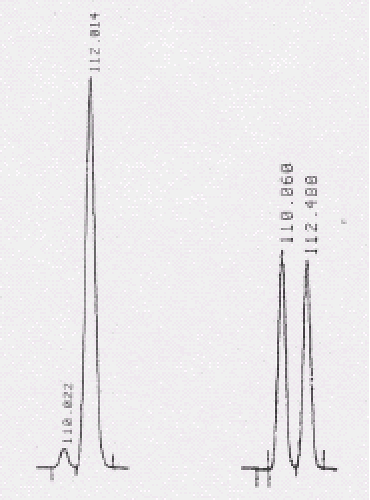
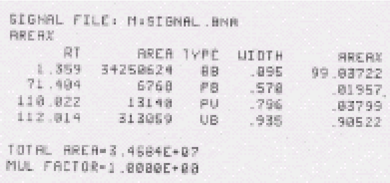
Chiral GLC (β-dex, Supelco, 135^{o}C) analysis of conjugate allylation-RCM product:



Allylation-RCM product

Racemic



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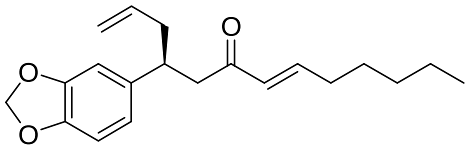
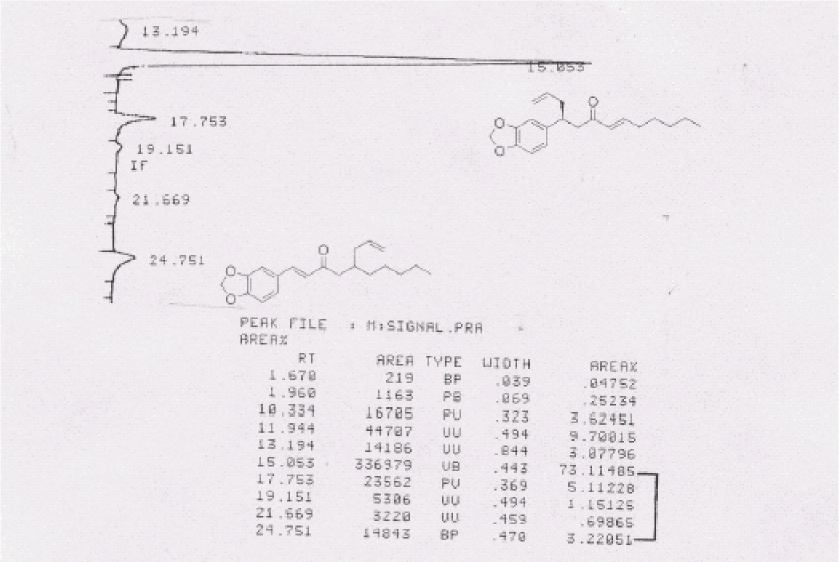


(*S,E*)-4-(benzo[*d*][1,3]dioxol-5-yl)trideca-1,7-dien-6-one. An oil. R_f = 0.27 (SiO_2, 15:1 pentane:Et_2O); IR (neat): 3075 (m), 2962 (s), 2930 (s), 2855 (s), 1841 (w), 1671 (s), 1627 (s), 1483 (s), 1444 (s), 1350 (m), 1243 (s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.55-6.80 (4H, m), 5.99 (1H, d, *J* = 16 Hz), 5.89 (2H, s), 5.62 (1H, ddt, *J* = 17 Hz, *J* = 10 Hz, *J* = 7.2 Hz), 4.90-5.05 (2H, m), 3.21 (1H, p, *J* = 7.2 Hz), 2.76 (2H, d, *J* = 6.8 Hz), 2.31 (2H, m), 2.13 (2H, q, *J* = 7.6 Hz), 1.40 (2H, p, *J* = 7.2 Hz), 1.16-1.36 (4H, m), 0.86 (3H, t, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$): δ 199.0, 147.6, 147.5, 145.8, 138.1, 136.2, 130.5, 120.5, 116.6, 108.1, 107.7, 100.8, 46.27, 40.84, 40.83, 32.41, 31.33, 27.76, 22.42, 13.96. LRMS (ESI+) Calc'd for $C_{20}H_{26}O_3$ $(M)^+$: 314.2 Found $(M)^+$: 314.8. $[\alpha]_D^{20} = +11^o$ (*c* = 3.0, $CHCl_3$).

Proof of stereochemistry. Chemoselectivity was determined using achiral GLC. Enantioselectivities were determined by comparison with authentic racemic material prepared using either triphenylphosphine or triphenylphosphite as the achiral ligand in the conjugate allylation reaction. Absolute stereochemistry was assumed to be analogous to the configuration determined for others.

Achiral GLC (Ultra 1, Hewlett-Packard, 190 °C) analysis of the crude reaction mixture:



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    11.944       44707   VV    .494      9.70015
    13.194       14186   VV    .044      3.07796
    15.053      336979   VB    .443     73.11485
    17.753       23562   PV    .369      5.11228
    19.151        5306   VV    .494      1.15126
    21.669        3220   VV    .459       .69865
    24.751       14843   BP    .470      3.22051
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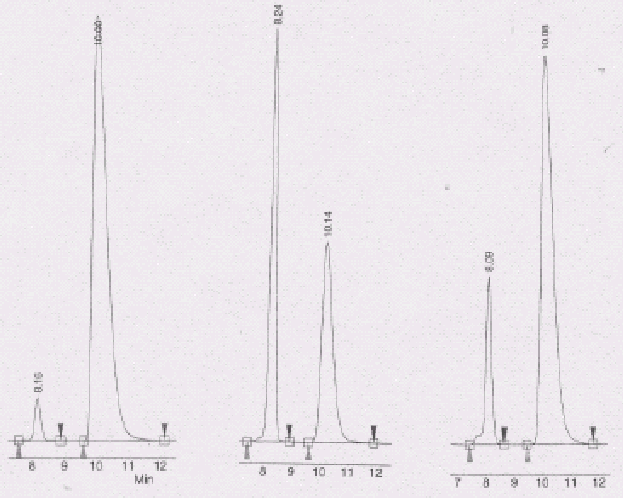
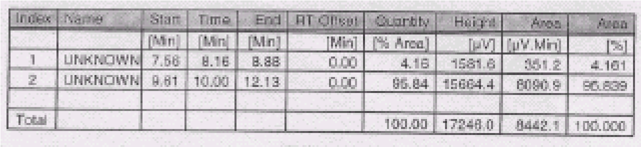
Chiral SFC (AD-H, Chiralpak, 150 bar, 50^{o}C, flow = 2.0 mL/min, 3.0 % MeOH) analysis of conjugate allylation product:



Allylation product

Racemic

Allylation product + racemic coinjection



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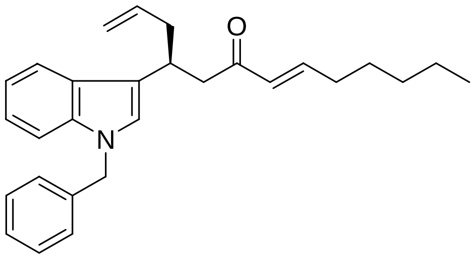
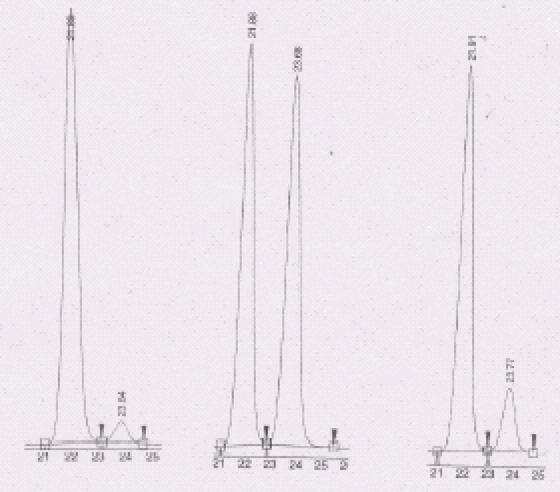
2	UNKNOWN	9.61	10.00	12.13	0.00	95.84	15664.4	8090.9	95.839
Total						100.00	17246.0	8442.1	100.000



(*S,E*)-4-(1-benzyl-1*H*-indol-3-yl)trideca-1,7-dien-6-one. An oil. R_f = 0.10 (SiO_2, 2:1 pentane:CH_2Cl_2); IR (neat): 3062 (m), 2924 (s), 2848 (s), 1697 (s), 1671 (s), 1463 (s), 1350 (s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.68 (1H, d, *J* = 7.5 Hz), 7.00-7.32 (8H, m), 6.91 (1H, s), 6.72 (1H, dt, *J* = 16 Hz, *J* = 6.8 Hz), 6.02 (1H, d, *J* = 16 Hz), 5.75 (1H, ddt, *J* = 17 Hz, *J* = 10 Hz, *J* = 7.2 Hz), 5.25 (2H, s), 5.00 (1H, d, *J* = 17 Hz), 4.95 (1H, d, *J* = 10 Hz), 3.66 (1H, p, *J* = 7.2 Hz), 2.97 (2H, dd, *J* = 16 Hz, *J* = 7.6 Hz), 2.93 (1H, dd, *J* =16 Hz, *J* = 7.6 Hz), 2.56 (1H, dd, *J* = 14 Hz, *J* = 6.8 Hz), 2.52 (1H, dd, *J* = 14 Hz, *J* = 6.4 Hz), 2.09 (2H, q, *J* = 6.8 Hz), 1.15-1.40 (6H, m), 0.87 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$): δ 199.8, 147.4, 137.6, 136.7, 130.5, 128.6, 127.4, 127.2, 126.5, 125.4, 121.6, 119.5, 118.9, 118.0, 116.3, 109.7, 49.84, 45.36, 39.74, 32.65, 32.38, 31.31, 27.68, 22.41, 13.97. LRMS (ESI+) Calc'd for $C_{28}H_{33}NO$ $(M)^+$: 399.3 Found $(M)^+$: 399.8. $[\alpha]_D^{20}$ = +15° (*c* = 3.5, $CHCl_3$).

Proof of stereochemistry. Chemoselectivity was determined using ^1H NMR spectroscopy; the minor isomer was not observed in the crude ^1H NMR spectrum. Enantioselectivities were determined by comparison with authentic racemic material prepared using either triphenylphosphine or triphenylphosphite as the achiral ligand in the conjugate allylation reaction. Absolute stereochemistry was assumed to be analogous to the configuration determined for others.

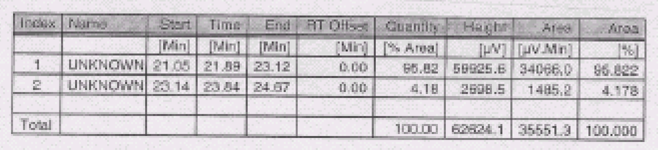
Chiral SFC (AS-H, Chiralpak, 150 bar, 50°C, flow = 1.0 mL/min, 4.0 % MeOH) analysis of conjugate allylation product:



Allylation product

Racemic

Allylation product + racemic coinjection



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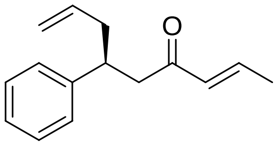
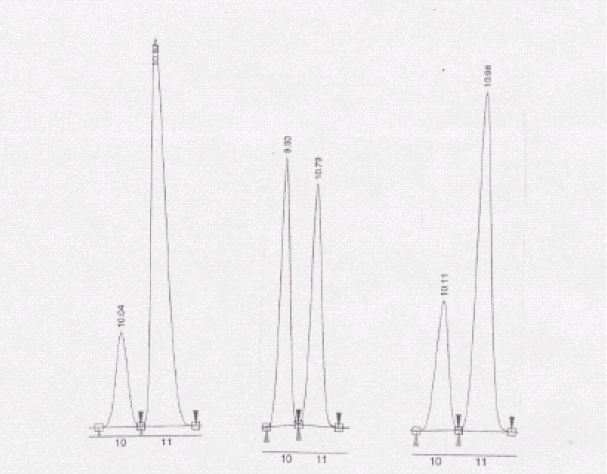
2	UNKNOWN	23.14	23.84	24.67	0.00	4.18	2698.5	1485.2	4.178
Total						100.00	62624.1	35551.3	100.000



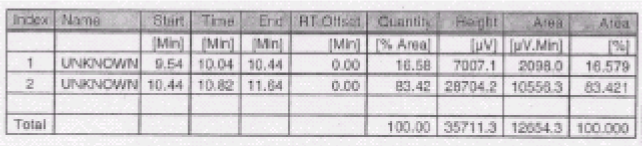
(*S*,*E*)-6-phenylnona-2,8-dien-4-one. An oil. R_f = 0.20 (SiO_2, 15:1 pentane:Et_2O); IR (neat): 3069 (m), 3024 (m), 2911 (m), 1697 (s), 1671 (s), 1627 (s), 1495 (m), 1439 (m) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.10-7.35 (5H, m), 6.76 (1H, dq, *J* = 16 Hz, *J* = 6.8 Hz), 6.03 (1H, dq, *J* = 16 Hz, *J* = 1.6 Hz), 5.63 (1H, ddt, *J* = 17 Hz, *J* = 10 Hz, *J* = 6.8 Hz), 4.86-5.05 (2H, m), 3.30 (1H, p, *J* = 7.2 Hz), 2.83 (1H, dd, *J* = 16 Hz, *J* = 6.8 Hz), 2.81 (1H, dd, *J* = 16 Hz, *J* = 7.2 Hz), 2.37 (2H, t, *J* = 7.2 Hz), 1.82 (3H, dd, *J* = 6.8 Hz, *J* = 1.6 Hz); ^{13}C NMR ($CDCl_3$): δ 198.7, 144.2, 142.4, 136.2, 132.1, 128.3, 127.5, 126.2, 116.6, 46.03, 40.85, 40.60, 18.18. LRMS (ESI+) Calc'd for $C_{15}H_{18}O$ $(M + Na)^+$: 237.1 Found $(M + Na)^+$: 236.7. $[\alpha]_D^{20}$ = +9.3° (*c* = 2.5, $CHCl_3$).

Proof of stereochemistry. Chemoselectivity was determined by ^1H NMR spectroscopy; the minor isomer was not observed in the crude ^1HNMR spectrum. Stereochemical ratios were determined in comparison with authentic racemic material prepared using either triphenylphosphine or triphenylphosphite as the achiral ligand in the conjugate allylation reaction. Absolute stereochemistry was determined by subjecting the conjugate allylation product to ring closing metathesis conditions using the Hoveyda-Grubbs second generation catalyst, in CH_2Cl_2, to afford 5-phenyl-2-cycohexen-1-one (Sieber, J. D.; Liu, S.; Morken, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 2214.). The optical rotation was measured ($[\alpha]_D^{20}$ = +37° (*c* = 0.5, $CHCl_3$)) and compared to the known literature value (Hareau, G. P-J.; Koiwa, M.; Hikichi, S; Sato, F. *J. Am. Chem. Soc.* **1999**, *121*, 3640).

Chiral SFC (AD-H, Chiralpak, 150 bar, 50°C, flow = 1.0 mL/min, 2.0 % MeOH) analysis of conjugate allylation product:



Allylation product   Racemic   Allylation product + racemic coinjection



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
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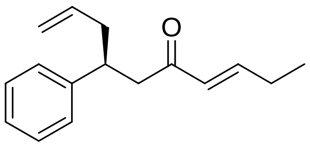
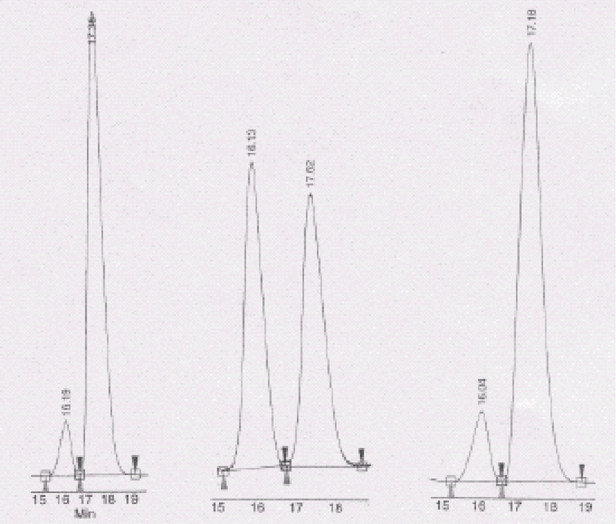
1	UNKNOWN	9.54	10.04	10.44	0.00	16.58	7007.1	2098.0	16.579
2	UNKNOWN	10.44	10.82	11.64	0.00	83.42	28704.2	10556.3	83.421
Total						100.00	35711.3	12654.3	100.000

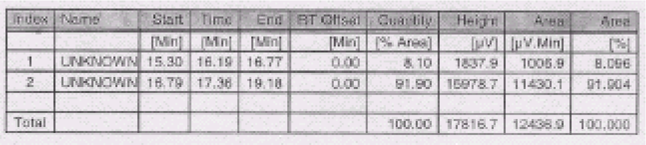


(*S,E*)-7-phenyldeca-3,9-dien-5-one. An oil. R_f = 0.22 (SiO_2, 20:1 Hexanes:EtOAc); IR (neat): 3068 (m), 3024 (m), 2968 (s), 2924 (s), 1948 (w), 1804 (w), 1697 (s), 1627 (s), 1451 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.12-7.32 (5H, m), 6.78 (1H, dt, *J* = 16 Hz, *J* = 6.8 Hz), 5.99 (1H, d, *J* = 16 Hz), 5.63 (1H, ddt, *J* = 17 Hz, *J* = 10 Hz, *J* = 6.8 Hz), 4.86-5.05 (2H, m) 3.29 (1H, p, *J* = 7.2 Hz), 2.84 (1H, app dd, *J* = 16 Hz, *J* = 6.8 Hz), 2.82 (1H, app dd, *J* = 16 Hz, *J* = 7.2 Hz), 2.37 (2H, t, *J* = 7.2 Hz), 2.16 (2H, p, *J* = 7.2 Hz), 1.00 (3H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$): δ 199.1, 148.7, 144.2, 136.2, 129.6, 128.3, 127.5, 126.3, 116.6, 46.12, 40.96, 40.63, 25.50, 12.25. LRMS (ESI+) Calc'd for $C_{16}H_{20}O$ $(M + Na)^+$: 251.2 Found $(M + Na)^+$: 250.7. $[\alpha]_D^{20} = +8.8^o$ (*c* = 1.0, $CHCl_3$).

Proof of stereochemistry. Chemoselectivity was determined by ^{1}H NMR spectroscopy; the minor isomer was not observed in the crude ^{1}HNMR spectrum. Stereochemical ratios were determined in comparison with authentic racemic material prepared using either triphenylphosphine or triphenylphosphite as the achiral ligand in the conjugate allylation reaction. Absolute stereochemistry was determined by subjecting the conjugate allylation product to ring closing metathesis conditions using the Hoveyda-Grubbs second generation catalyst, in CH_2Cl_2, to afford 5-phenyl-2-cycohexen-1-one (Sieber, J. D.; Liu, S.; Morken, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 2214.). The optical rotation was measured ($[\alpha]_D^{20} = +41^o$ (*c* = 0.5, $CHCl_3$)) and compared to the known literature value (Hareau, G. P.-J.; Koiwa, M.; Hikichi, S; Sato, F. *J. Am. Chem. Soc.* **1999**, *121*, 3640).

Chiral SFC (AD-H, Chiralpak, 150 bar, 50^{o}C, flow = 1.0 mL/min, 1.0 % MeOH) analysis of conjugate allylation product:



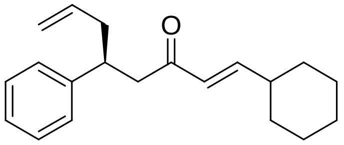


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	15.30	16.19	16.77	0.00	8.10	1837.9	1006.9	8.096
2	UNKNOWN	16.79	17.36	19.18	0.00	91.90	15978.7	11430.1	91.904
Total						100.00	17816.7	12436.9	100.000

Allylation product

Racemic

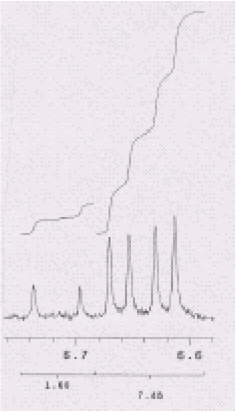
Allylation product + racemic coinjection



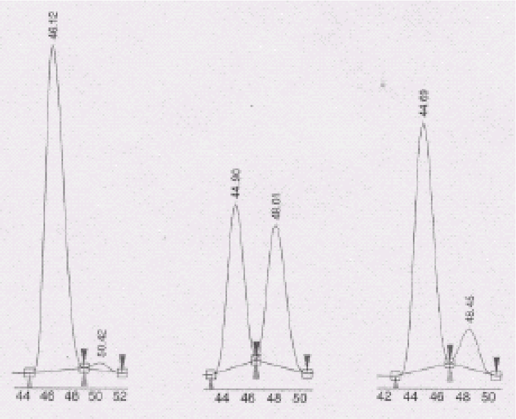
(*S*,*E*)-1-cyclohexyl-5-phenylocta-1,7-dien-3-one. An oil. Isolated as an inseparable mixture of constitutional isomers. R_f = 0.19 (SiO_2, 30:1 Hexanes:EtOAc, major+minor); IR (neat): 3069 (m), 3024 (m), 2924 (s), 2855 (s), 1948 (w), 1810 (w), 1700 (s), 1671 (s), 1627 (s), 1445 (s) cm^{-1}; ^1H NMR ($CDCl_3$), (only major isomer data shown, minor isomer has been characterized previously: Sieber, J. D.; Liu, S.; Morken, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 2214.): δ 7.10-7.30 (5H, m), 6.64 (1H, dd, *J* = 16 Hz, *J* = 6.8 Hz), 5.93 (1H, dd, *J* = 16 Hz, *J* = 1.2 Hz), 5.63 (1H, ddt, *J* = 17 Hz, *J* = 10 Hz, *J* = 6.8 Hz), 4.85-5.05 (2H, m) 3.28 (1H, p, *J* = 7.2 Hz), 2.83 (1H, dd, *J* = 16 Hz, *J* = 6.8 Hz), 2.81 (1H, dd, *J* = 16 Hz, *J* = 7.6 Hz), 2.37 (2H, t, *J* = 7.2 Hz), 2.05 (1H, m), 0.92-1.80 (10H, m); ^{13}C NMR ($CDCl_3$, major + minor isomers): δ 200.4, 199.4, 152.3, 144.2, 142.0, 137.4, 136.2, 134.6, 130.2, 128.8, 128.3, 128.2, 128.0, 127.5, 126.5, 126.2, 116.5, 116.2, 46.13, 42.58, 41.09, 40.59, 40.54, 40.44, 39.22, 35.91, 37.74, 30.09, 29.71, 26.72, 25.92, 25.69. LRMS (ESI+) Calc'd for $C_{20}H_{26}O$ $(M + Na)^+$: 305.2 Found $(M + Na)^+$: 304.8.

Proof of stereochemistry. Chemoselectivity was determined by ^{1}HNMR spectroscopy. Stereochemical ratios were determined in comparison with authentic racemic material prepared using either triphenylphosphine or triphenylphosphite as the achiral ligand in the conjugate allylation reaction. Absolute stereochemistry was determined by subjecting the conjugate allylation product to ring closing metathesis conditions using the Hoveyda-Grubbs second generation catalyst, in CH_2Cl_2, to afford 5-phenyl-2-cycohexen-1-one (Sieber, J. D.; Liu, S.; Morken, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 2214.). The optical rotation was measured ($[\alpha]_D^{20} = +45^o$ (c = 0.25, $CHCl_3$)) and compared to the known literature value (Hareau, G. P-J.; Koiwa, M.; Hikichi, S; Sato, F. *J. Am. Chem. Soc.* **1999**, *121*, 3640).

^{1}H NMR analysis of the crude reaction mixture (400 MHz, $CDCl_3$):



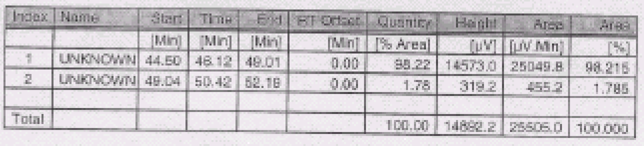
Chiral SFC (AS-H, Chiralpak, 150 bar, 50°C, flow = 0.5 mL/min, 1.0 % MeOH) analysis of conjugate allylation product:



Allylation product

Racemic

Allylation product + racemic coinjection



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV Min]	[%]
1	UNKNOWN	44.50	46.12	49.01	0.00	98.22	14573.0	25049.8	98.215
2	UNKNOWN	49.04	50.42	52.16	0.00	1.78	319.2	455.2	1.785
Total						100.00	14892.2	25505.0	100.000

Procedure for ring-closing methathesis (Scheme 2, eq 1):

(*S*)-5-(5-fluoro-2-methylphenyl)cyclohex-2-enone. To 237 mg (0.759 mmol) of (*S*,*E*)-4-(5-fluoro-2-methylphenyl)trideca-1,7-dien-6-one in a 20 mL scintillation vial with magnetic stir-bar, in a glove-box under an Ar atmosphere, was added a solution of 9.8 mg (0.0157 mmol) of the Hoveyda-Grubbs second generation catalyst in 16 mL of CH_2Cl_2. The vial was capped, taped, removed from the glove-box, and stirred at ambient temperature for 1 h. Next, 0.15 mL of *t*-butyl vinyl ether was added and stirring was continued for another 30 min. The reaction was concentrated using reduced pressure and purified using column chromatography (SiO_2, pentane:Et_2O) to afford 155 mg (97%) of the title compound as a colorless oil. R_f = 0.14 (SiO_2, 7:1 pentane:Et_2O); IR (neat): 3031 (m), 2930 (m), 1879 (w), 1678 (s), 1615 (m), 1584 (m), 1495 (s), 1388 (s), 1243 (s), 1161 (m) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.09 (1H, dd, J = 8.4 Hz, J = 6.0 Hz), 6.99-7.07 (1H, m), 6.91 (1H, dd, J = 10 Hz, J = 2.8 Hz), 6.81 (1H, dt, J = 8.0 Hz, J = 2.8 Hz), 6.01 (1H, dd, J = 11 Hz, J = 2.8 Hz), 3.45-3.58 (1H, m), 2.38-2.62 (4H, m); ^{13}C NMR ($CDCl_3$): δ 198.6, 161.4 (d, $^1J_{CF}$ = 242 Hz), 149.2, 143.0 (d, $^3J_{CF}$ = 6.2 Hz), 131.9 (d, $^3J_{CF}$ = 7.8 Hz), 130.6, 129.6, 113.2 (d, $^2J_{CF}$ = 21 Hz), 112.3 (d, $^2J_{CF}$ = 21 Hz), 44.16, 36.85, 32.48, 18.50; ^{19}F NMR: δ 95.10 (m). LRMS (APPI) Calc'd for $C_{13}H_{13}FO$ $(M + H)^+$: 205.1 Found $(M + H)^+$: 205.1.

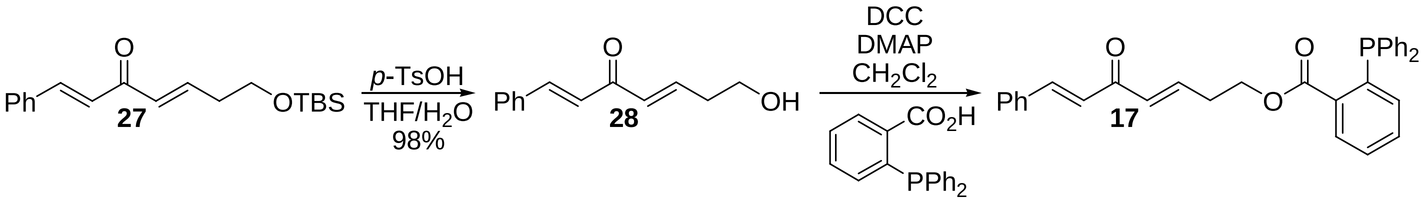
Procedure for Baeyer-Villiger/saponification (Scheme 2, eq 2):

1. Oxidation: For lead reference, see: Göttlich, R.; Yamakoshi, K.; Sasai, H.; Shibasaki, M. *Synlett* **1997**, 971. In a 2-dram vial with magnetic stir bar in a dry-box under Ar was weighed ~45 mg of crushed 4 Å molecular sieves. Next, 48.8 μL (0.049 mmol) of a 1.0 M solution of (±)-*trans*-1,2-diaminocyclohexane in CH_2Cl_2 was added by syringe followed by dilution with 0.43 mL of CH_2Cl_2. Next, 48.8 μL (0.049 mmol) of a 1.0 M solution of $SnCl_4$ in CH_2Cl_2 was added and the vial was capped with a septum, removed from the dry-box and cooled to 0 ^oC (ice/brine). TMS_2O_2 was added dropwise as a 1.0 M solution in CH_2Cl_2 (0.39 mL, 0.39 mmol). After stirring for 10 min at this temperature, 52.8 mg (0.195 mmol) of (*S)-E*-4-phenyltrideca-1,7-dien-6-one was added in 0.85 mL CH_2Cl_2 via canula. The reaction was subsequently warmed to room temperature and stirred for 15 h. Sodium sulfite (60 mg) was then added, and the reaction stirred for an additional 3 h. Finally, the reaction was filtered through a pad of silica gel using EtOAc and concentrated under reduced pressure. Silica gel chromatography (hexanes/EtOAc) of the crude material afforded 37.8 mg (68 %) of (*S*, *E*)-hept-1-enyl-3-phenylhex-5-enoate as a colorless oil along with 13.8 mg of unreacted starting material. R_f = 0.30 (30:1 Hexanes:EtOAc); IR (neat): 3080 (m), 3029 (m), 2958 (s), 2928 (s), 2856 (s), 1945 (w), 1750 (s), 1675 (m), 1447 (m), 1236 (m), 1160 (s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.25-7.32 (2H, m), 77.15-7.23 (3H, m), 6.95 (1H, dt, J = 12 Hz, J = 2 Hz), 5.64 (1H, ddt, J = 17 Hz, J = 10 Hz, J = 7.2 Hz), 5.33 (1H, dt, J = 12 Hz, J = 7.2 Hz), 4.91-5.05 (2H, m), 3.22 (1H, p, J = 7.6 Hz), 2.74 (1H, dd, J = 16 Hz, J = 6.8 Hz), 2.61 (1H, dd, J = 16 Hz, J = 8.4 Hz), 2.32-2.48 (2H, m), 1.93 (2H, q, J = 6.8 Hz), 1.17-1.39 (6H, m), 0.87 (3H, t, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$): δ 169.5, 143.3, 135.7, 135.2, 128.4, 127.3, 126.6, 117.0, 115.1, 41.55, 40.55, 40.28, 31.24, 27.16, 27.21, 22.45, 14.02. LRMS (ESI+) Calc'd for $C_{19}H_{26}O_2$ $(M + H)^+$: 287.2 Found $(M + H)^+$: 287.1. $[\alpha]_D^{20}$ = +15^o (c = 3.0, $CHCl_3$).

2. Saponification: To a solution of 27.4 mg (0.0957 mmol) of (*S*, *E*)-hept-1-enyl-3-phenylhex-5-enoate in 0.96 mL of a 3:1 THF:H_2O mixture at 0 ^oC was added LiOH•H_2O (8.0 mg, 0.19 mmol). The reaction was allowed to reach ambient temperature and stirring was continued for 20h. The reaction was acidified with 1 M HCl and extracted with EtOAc (3x). The organic layers were combined, washed with brine, and dried over anhydrous Na_2SO_4. Volatiles were removed under reduced pressure, and the product was purified using silica gel chromatography (1% AcOH in CH_2Cl_2/Et_2O, R_f = 0.25 in 1% AcOH in 20:1 CH_2Cl_2:Et_2O) to give 17.9 mg (98%) of 3-phenyl-hex-5-enoic acid after removal of AcOH by azeotropic distillation with toluene using a rotary evaporator followed by removal of toluene via azeotropic distillation with CH_2Cl_2. Spectral data was consistent with the literature (Allin, S. M.; Essat, M.; Pita, C. H.; Baird, R. D.; McKee, V.; Elsegood, M.; Edgar, M.; Andrews, D. M.; Shah, P.; Aspinall, I. *Org. Biomol. Chem.* **2005**, *3,* 809.).

Conjugate allylation procedure using substrate 17 (Scheme 4):

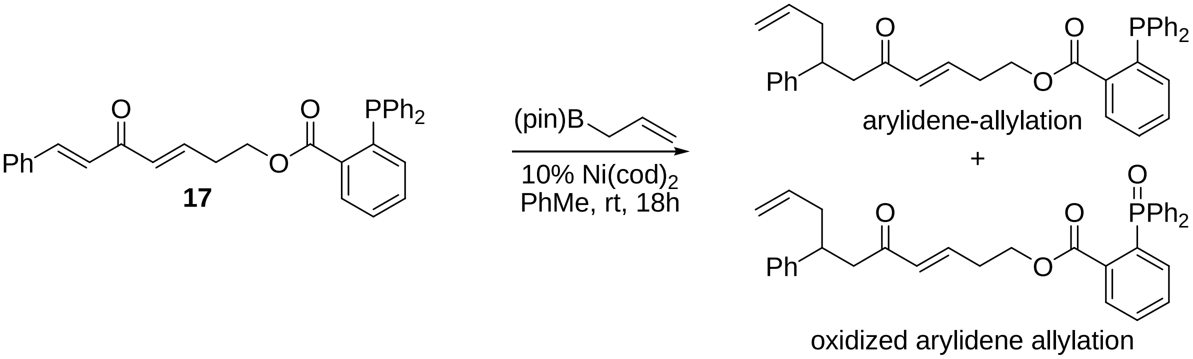
Synthesis of 17:



To a solution of 763 mg (2.41 mmol) of (1*E*, 4*E*)-7-(*t*-butyldimethylsilyloxy)-1-phenylhepta-1,4-dien-3-one, **27**, (prepared according to: Sieber, J. D.; Liu, S.; Morken, J. P. *J. Am. Chem. Soc.* **2007**, *129,* 2214.) in 12 mL of 3:1 THF:H_2O was added 458 mg (2.41 mmol) of *p*-toluenesulfonic acid monohydrate under a N_2 atmosphere. The starting material was consumed after 1h as evident by TLC analysis. H_2O was then added, followed by extraction with Et_2O. The combined organics were dried with anhydrous Na_2SO_4 and concentrated using reduced pressure. Silica gel chromatography (hexanes/EtOAc) of the crude material afforded 479 mg (98%) of **28** as a yellow oil. R_f = 0.30 (SiO_2, 1:2 hexanes:EtOAc); IR (neat): 3415 (s, br), 3058 (w), 2939 (m), 2878 (m), 1958 (w), 1659 (s), 1628 (s), 1598 (s), 1494 (m), 1449 (m), 1333 (s), 1308 (m) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.61 (1H, d, *J* = 16 Hz), 7.48-7.54 (2H, m), 7.31-7.37 (3H, m), 6.98 (1H, dt, *J* = 16 Hz, *J* = 7.0 Hz), 6.93 (1H, d, *J* = 16 Hz), 6.50 (1H, dt, *J* = 16 Hz, *J* = 1.6 Hz), 3.78 (2H, t, *J* = 6.2 Hz), 2.62-2.92 (1H, br s), 2.51 (2H, dq, *J* = 7.0 Hz, *J* = 1.6 Hz); ^{13}C NMR ($CDCl_3$): δ 189.1, 144.4, 143.4, 134.5, 130.9, 130.4, 128.8, 128.2, 124.5, 60.84, 35.87. LRMS (ES+) Calc'd for $C_{13}H_{14}O_2$ $(M + H)^+$: 203.1 Found $(M + H)^+$: 203.1.

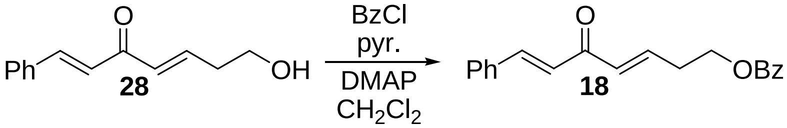
To 200 mg (0.968 mmol) of **28** in 1.9 mL of CH_2Cl_2 was added 386 mg (1.26 mmol) of *o*-diphenylphosphinobenzoic acid, 260 mg (1.26 mmol) of N, N'-dicyclohexylcarbodiimide (DCC), and 11.9 mg (0.0968 mmol) of 4-dimethylaminopyridine (DMAP) sequentially under N_2. This mixture was then allowed to stir at ambient temperature for 2h, and the reaction was then filtered through celite using CH_2Cl_2. Volatiles were removed under reduced pressure and the resultant oil purified by silica gel chromatography (hexanes/EtOAc) to afford 348 mg (73%) of **17** as a light-yellow solid. mp 140-145 °C. R_f = 0.20 (SiO_2, 4:1 hexanes:EtOAc); IR (CH_2Cl_2 solution): 3411 (br, m), 3058 (m), 2957 (m), 1967 (w), 1891 (w), 1717 (s), 1662 (s), 1628 (s), 1601 (s), 1433 (s), 1339 (m), 1275 (s), 1189 (s), 1122 (s) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.00-8.07 (1H, m), 7.63 (1H, d, *J* = 16 Hz), 7.51-7.59 (2H, m), 7.20-7.42 (16H, m), 6.96 (1H, d, *J* = 16 Hz), 6.89 (1H, dt, *J* = 16 Hz, *J* = 6.8 Hz), 6.46 (1H, d, *J* = 16 Hz), 4.32 (2H, t, *J* = 6.4 Hz), 2.55 (2H, q, *J* = 6.4 Hz); ^1H NMR (C_6D_6): δ 8.04-8.10 (1H, m), 7.70 (1H, d, *J* = 16 Hz), 7.32-7.46 (4H, m), 6.85-7.25 (14H, m), 6.81 (1H, d, *J* = 16 Hz), 6.73 (1H, dt, *J* = 16 Hz, *J* = 6.8 Hz), 6.16 (1H, d, *J* = 16 Hz), 3.94 (2H, t, *J* = 6.4 Hz), 2.00 (2H, q, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$): δ 188.7, 166.6, 143.3, 142.6, 140.3, 140.1, 137.8, 137.7, 134.7, 134.3, 133.9, 133.7, 132.0, 131.0, 130.6, 130.4, 128.8, 128.6, 128.5, 128.4, 128.3, 124.7, 63.11, 31.74. ^{13}C NMR (C_6D_6): δ 187.9, 167.0, 143.1, 142.5, 139.3, 139.2, 138.8, 135.2, 134.8, 134.6, 132.4, 131.9, 131.3, 130.5, 129.3, 129.1, 128.9, 128.8, 125.8, 63.67, 32.22. ^{31}P NMR (C_6D_6): δ -2.86. LRMS (ESI+) Calc'd for $C_{32}H_{27}O_3P$ $(M + H)^+$: 491.2 Found $(M + H)^+$: 491.1.

Conjugate Allylation of 17:

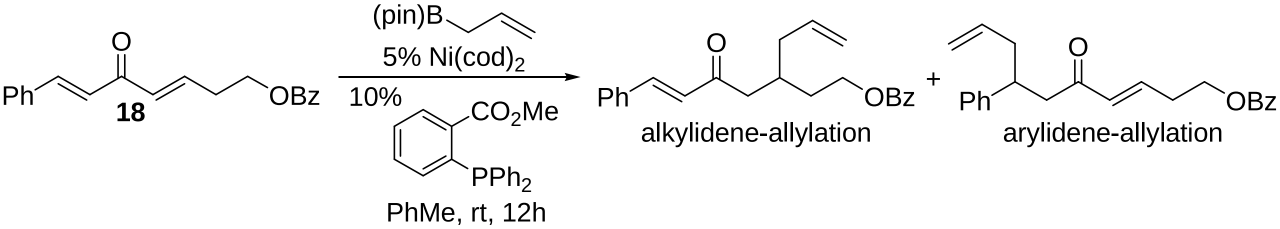


A 2-dram vial with magnetic stir-bar was charged with 2.2 mg (0.0082 mmol) of bis(1,5-cyclooctadiene)nickel and 40.0 mg (0.0815 mmol) of **17** in a dry-box. Toluene (0.41 mL) was then added followed by 16.4 mg (0.0978 mmol) of allylboronic acid pinacol ester. The vial was capped, sealed with electrical tape, removed from the dry-box, and stirred at ambient temperature for 18h. The reaction was quenched with the addition of 2 drops (18 Ga needle) of MeOH and subsequently concentrated under reduced pressure. Chemoselectivity was determined by ^{1}H NMR analysis of the crude mixture. Purification by flash chromatography (SiO_2, hexanes/EtOAc) afforded 17.1 mg of the conjugate allylation product along with 9.3 mg of oxidized material (combined yield = 60%). R_f (phosphine) = 0.17 (SiO_2, 6:1 hexanes:EtOAc); R_f (phosphine oxide) = 0.17 (SiO_2, 1:3 hexanes:EtOAc); IR (CH_2Cl_2 solution, phosphine): 3400 (br w), 3067 (m), 2919 (m), 28528 (m), 1953 (w), 1716 (s), 1670 (s), 1632 (m), 1429 (s), 1265 (s), 1243 (s), 1138 (s), 1113 (s) cm^{-1}; IR (CH_2Cl_2 solution, phosphine oxide): 3422 (br m), 3058 (m), 2928 (m), 2856 (m), 1966 (w), 1733 (s), 1661 (s), 1628 (m), 1433 (s), 1281 (s), 1256 (s), 1197 (s), 1121 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, phosphine): δ 7.95-8.02 (1H, m), 7.31-7.41 (2H, m), 7.26-7.31 (6H, m), 7.19-7.26 (6H, m), 7.10-7.18 (3H, m), 6.88-6.94 (1H, m), 6.63 (1H, dt, J = 16 Hz, J = 6.8 Hz), 6.01 (1H, d, J = 16 Hz), 5.61 (1H, ddt, J = 17 Hz, J = 10 Hz, J = 6.8 Hz), 4.88-4.99 (2H, m), 4.20 (2H, t, J = 6.4 Hz), 3.27 (1H, p, J = 7.2 Hz), 2.82 (2H, app d, J = 7.6 Hz), 2.40 (2H, q, J = 6.8 Hz), 2.36 (2H, t, J = 6.8 Hz); ^{1}H NMR ($CDCl_3$, phosphine oxide): δ 7.80-7.88 (1H, m), 7.52-7.68 (5H, m), 7.30-7.52 (8H, m), 7.10-7.29 (5H, m), 6.51 (1H, dt, J = 16 Hz, J = 6.8 Hz), 5.89 (1H, d, J = 16 Hz), 5.61 (1H, ddt, J = 17 Hz, J = 10 Hz, J = 7.2 Hz), 4.88-4.98 (2H, m), 4.00 (2H, t, J = 6.8 Hz), 3.26 (1H, p, J = 7.2 Hz), 2.74-2.86 (2H, m), 2.35 (2H, t, J = 7.2 Hz), 2.20 (2H, q, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, phosphine): δ 198.6, 166.6, 144.1, 142.1, 140.4, 140.1, 137.8, 137.7, 136.1, 134.3, 133.9, 133.7, 132.3, 132.0, 130.6, 128.6, 128.5, 128.4, 128.3, 128.2, 127.5, 126.3, 63.03, 46.20, 40.96, 40.63, 31.53. ^{31}P NMR ($CDCl_3$): δ -3.10 (phosphine), 32.72 (phosphine oxide). LRMS (ESI+) Calc'd for $C_{35}H_{33}O_3P$ $(M + H)^+$: 533.2 Found $(M + H)^+$: 533.1. LRMS (ESI+) Calc'd for $C_{35}H_{33}O_4P$ $(M + H)^+$: 549.2 Found $(M + H)^+$: 549.1.

Synthesis and Conjugate Allylation of 18:

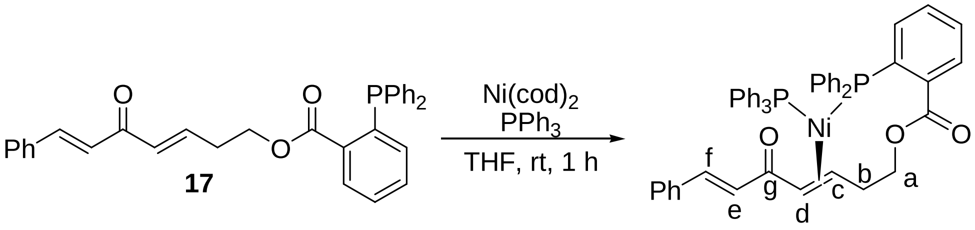


To a solution of 96.7 mg (0.478 mmol) of **28** in 1.9 mL of CH_2Cl_2 at 0 ^oC was added 0.10 mL of pyridine, 12 mg of DMAP, and 0.14 mL of benzoyl chloride, sequentially. Reaction progress was monitored by TLC, and after 1h at 0 ^oC, 0.05 mL of pyridine and 0.07 mL of benzoyl chloride was added. After an additional 30 min at 0 ^oC, starting material had been consumed as evident by TLC. Saturated $NaHCO_3$ was added, and the aqueous layer extracted with Et_2O (1x). The organic layer was washed with 1M HCl (2x) and dried with anhydrous Na_2SO_4. After removal of volatiles under reduced pressure, the crude material was purified by silica gel chromatography (hexanes/EtOAc) to afford 124 mg (86%) of **18** as an off-white solid. mp 60-66 ^oC. R_f = 0.13 (SiO_2, 6:1 hexanes:EtOAc); IR (CH_2Cl_2 solution): 3054 (m), 3025 (m), 2919 (m), 2848 (m), 1720 (s), 1661 (s), 1602 (s), 1450 (m), 1273 (s), 1188 (m) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.96-8.06 (1H, m), 7.63 (1H, d, *J* = 16 Hz), 7.49-7.59 (3H, m), 7.33-7.47 (5H, m), 7.02 (1H, dt, *J* = 16 Hz, *J* = 6.8 Hz), 6.94 (1H, d, *J* = 16 Hz), 6.57 (1H, d, *J* = 16 Hz), 4.48 (2H, t, *J* = 6.4 Hz), 2.75 (2H, q, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$): δ 188.7, 166.3, 143.5, 142.6, 134.6, 133.0, 131.0, 130.4, 129.9, 129.5, 128.9, 128.35, 128.26, 124.8, 62.84, 32.03. LRMS (ES+) Calc'd for $C_{20}H_{18}O_3$ $(M + H)^+$: 307.1 Found $(M + H)^+$: 307.1.



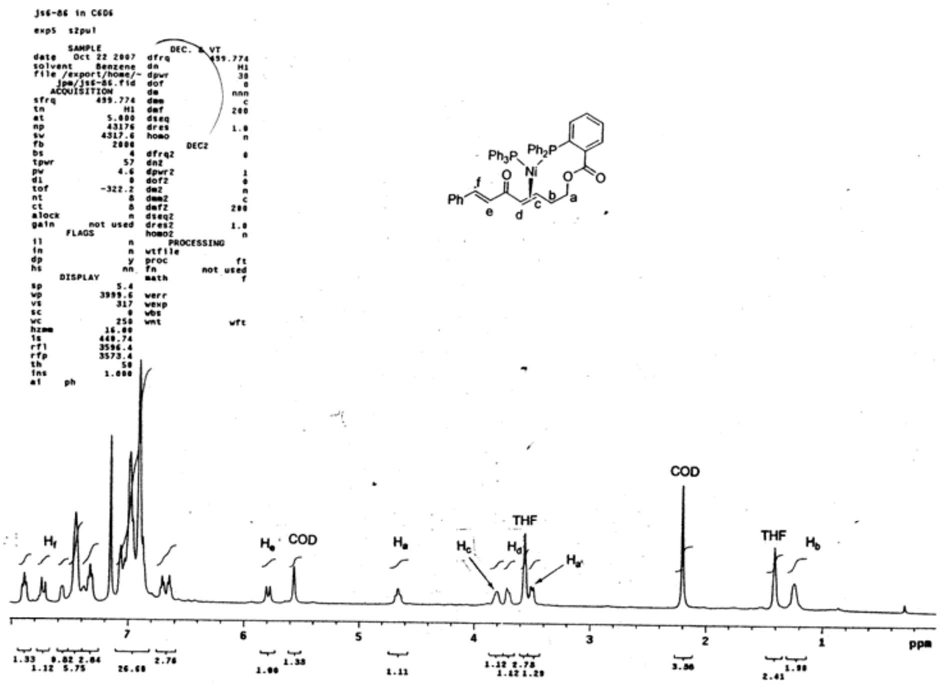
A dried vial with a stir-bar was charged with 2.0 mg (0.0074 mmol) of bis(1,5-cyclooctadiene)nickel, 4.7 mg (0.015 mmol) of ligand, and 0.98 mL of toluene under argon. To this solution was added 29.6 mg (0.176 mmol) of allylB(pin) and 45.0 mg (0.147 mmol) of **18**. The vial was sealed, removed from the dry-box, and allowed to stir at ambient for 12 h. After this time period, degassed water (N_2 sparge) was added and the mixture transferred to a separatory funnel with CH_2Cl_2. The organic layer was collected and the aqueous layer washed with CH_2Cl_2 (2x). The combined organic layers were dried with Na_2SO_4, and volatiles removed in vauo. Chemoselectivity was determined by ^1H NMR analysis of the crude mixture. Chromatography (hexanes/EtOAc) afforded 38.4 mg (75%) of the conjugate allylation product. Alkylidene allylation product: R_f = 0.23 (SiO_2, 6:1 hexanes:EtOAc); IR (CH_2Cl_2 solution): 3067 (m), 2915 (m), 2852 (m), 1961 (w), 1716 (s), 1666 (s), 1610 (s), 1450 (m), 1272 (s), 1117 (m) cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.01 (2H, d, *J* = 8 Hz), 7.28-7.61 (9H, m), 6.72 (1H, d, *J* = 16 Hz), 5.79 (1H, ddt, *J* = 17 Hz, *J* = 10 Hz, *J* = 7.2 Hz), 5.00-5.12 (2H, m), 4.30-4.45 (2H, m), 2.71 (1H, dd, *J* = 16 Hz, *J* = 6.8 Hz), 2.66 (1H, dd, *J* = 16 Hz, *J* = 6.8 Hz), 2.37 (1H, h, *J* = 6.4 Hz), 2.09-2.29 (2H, m), 1.72-1.92 (2H, m); ^{13}C NMR ($CDCl_3$): δ 199.3, 166.5, 142.5, 135.8, 134.4, 132.8, 130.4, 130.2, 129.5, 128.8, 128.3, 128.2, 126.3, 117.3, 63.00, 44.88, 38.26, 32.58, 31.23. LRMS (ESI+) Calc'd for $C_{23}H_{24}O_3$ $(M + H)^+$: 349.2 Found $(M + H)^+$: 349.1. Arylidene allylation product: R_f = 0.17 (SiO_2, 6:1 hexanes:EtOAc); IR (CH_2Cl_2 solution): 3071 (m), 3025 (m), 2919 (m), 2851 (m), 1720 (s), 1673 (s), 1636 (s), 1454 (m), 1272 (s), 1104 (m) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.96-8.04 (2H, m), 7.52-7.58 (1H, m), 7.38-7.46 (2H, m), 7.18-7.27 (2H, m), 7.10-7.18 (3H, m), 6.74 (1H, dt, J = 16 Hz, *J* = 6.8 Hz), 6.12 (1H, dt, *J* = 16 Hz, *J* = 2 Hz), 5.61 (1H, ddt, *J* = 17 Hz, *J* = 10 Hz, *J* = 6.8 Hz), 4.86-5.00 (2H, m), 4.37 (2H, t, *J* = 6.4 Hz), 3.27 (1H, p, *J* = 7.2 Hz), 2.85 (1H, dd, *J* = 17 Hz, *J* = 6.4 Hz), 2.82 (1H, dd, *J* = 17 Hz, *J* = 7.6 Hz), 2.61 (2H, q, *J* = 6.8 Hz), 2.36 (2H, t, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$): δ 198.6, 166.2, 144.0, 141.9, 136.1, 133.0, 132.4, 129.9, 129.5, 128.34, 128.32, 127.4, 126.3, 116.7, 62.71, 46.31, 41.00, 40.62, 31.80. LRMS (ESI+) Calc'd for $C_{23}H_{24}O_3$ (M + H)$^+$: 349.2 Found (M + H)$^+$: 349.1.

Synthesis and characterization of the Ni-enone complex (Scheme 5):

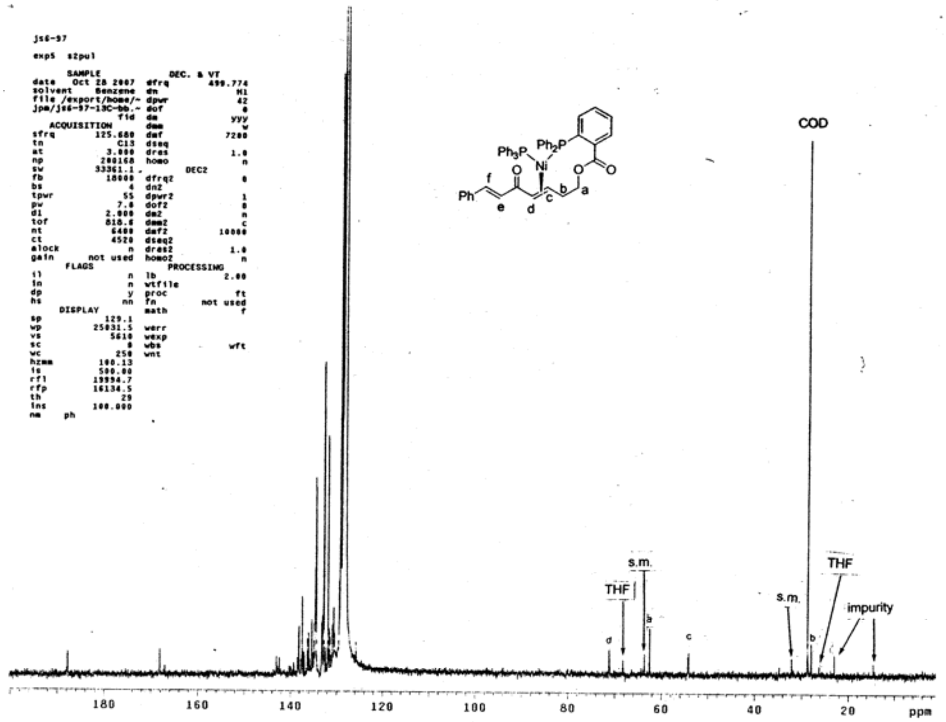


An oven dried 20 mL vial with magnetic stir-bar was charged with 27.5 mg (0.0999 mmol) of bis(1,5-cyclooctadiene)nickel, 49.0 mg (0.0999 mmol) of **17** and 1.0 mL of THF in a dry-box. After stirring for 5 min, a deep purple solution was formed, to which was then added 26.2 mg (0.0999 mmol) of triphenylphosphine. This mixture was then stirred for an additional 1 h providing a deep red solution. Volatile material was removed using reduced pressure in the dry-box. The residue was then triturated with degassed pentane (3x) and dried under vacuum to afford 88.1 mg of a deep red solid. mp 152-172 °C (sealed capillary, decomp.). ^{1}H NMR (C_6D_6): δ 7.89 (1H, t, J = 8.5 Hz), 7.73 (1H, d, J = 16 Hz, H$_f$), 7.34-7.60 (8H, m), 7.33 (2H, t, J = 8.5 Hz). 6.78-7.11 (27H, m), 6.71 (1H, t, J = 7.0 Hz), 6.64 (1H, t, J = 7.5 Hz), 5.80 (1H, d, J = 16 Hz, H$_e$), 4.66 (1H, br t, H$_a$), 3.80 (1H, m, H$_c$), 3.71 (1H, m, H$_d$), 3.50 (1H, d, J = 11 Hz, H$_{a'}$), 1.15-1.32 (2H, m, H$_b$); ^{13}C NMR (C_6D_6), diagnostic peaks: δ 187.8 (C$_g$), 168.1, 137.21 (C$_f$), 130.65 (C$_e$), 71.15 (C$_d$, d, $^2J_{CP}$ = 11 Hz), 62.52 (C$_a$), 54.23 (C$_c$, d, $^2J_{CP}$ = 20 Hz), 27.98 (C$_b$). Note that the aromatic region was too complex for further assignment. ^{31}P NMR (C_6D_6): δ 41.21 (d, $^2J_{PP}$ = 32 Hz), 28.59 (d, $^2J_{PP}$ = 32 Hz).

^1H and ^{13}C NMR in C_6D_6:



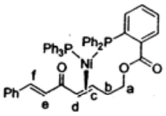
```
js6-86 in C6D6

exp5  s2pul

      SAMPLE                DEC. & VT
date   Oct 22 2007  dfrq        499.774
solvent    Benzene  dn               H1
file /export/home/~ dpwr             30
    jpm/js6-86.fid  dof               0
   ACQUISITION      dm              nnn
sfrq       499.774  dmm               c
tn              H1  dmf             200
at           5.000  dseq
np           43176  dres            1.0
sw          4317.6  homo              n
fb            2000        DEC2
bs               4  dfrq2             0
tpwr            57  dn2
pw             4.6  dpwr2             1
d1               0  dof2              0
tof         -322.2  dm2               n
nt               8  dmm2              c
ct               8  dmf2            200
alock            n  dseq2
gain      not used  dres2           1.0
     FLAGS          homo2             n
il               n     PROCESSING
in               n  wtfile
dp               y  proc             ft
hs              nn  fn         not used
    DISPLAY         math              f
sp             5.4
wp          3999.6  werr
vs             317  wexp
sc               0  wbs
wc             250  wnt             wft
hzmm         16.00
is          440.74
rfl         3596.4
rfp         3573.4
th              50
ins          1.000
ai     ph
```

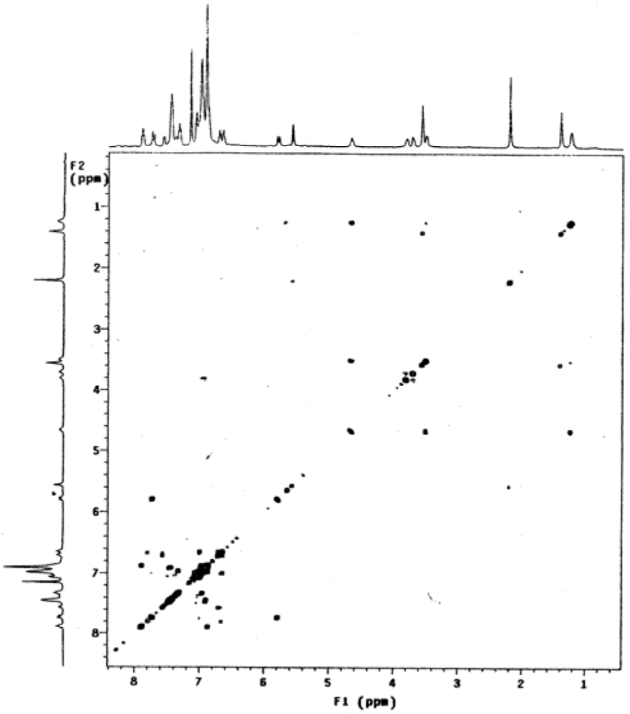


```
js6-97

exp5  s2pul

      SAMPLE               DEC. & VT
date   Oct 28 2007  dfrq       499.774
solvent    Benzene  dn              H1
file /export/home/~ dpwr            42
jpm/js6-97-13C-bb.~ dof              0
               fid  dm             yyy
   ACQUISITION      dmm              w
sfrq       125.680  dmf           7200
tn             C13  dseq
at           3.000  dres           1.0
np          200168  homo             n
sw         33361.1        DEC2
fb           18000  dfrq2            0
bs               4  dn2
tpwr            55  dpwr2            1
pw             7.0  dof2             0
d1           2.000  dm2              n
tof          818.6  dmm2             c
nt            6400  dmf2         10000
ct            4520  dseq2
alock            n  dres2          1.0
gain      not used  homo2            n
     FLAGS             PROCESSING
il               n  lb            2.00
in               n  wtfile
dp               y  proc            ft
hs              nn  fn        not used
    DISPLAY         math             f
sp           129.1
wp         25031.5  werr
vs            5610  wexp
sc               0  wbs            wft
wc             250  wnt
hzmm        100.13
is          500.00
rfl        19994.7
rfp        16134.5
th              29
ins        100.000
nm     ph
```

COSY in C_6D_6:

```
js6-86-gCOSY in C6D6

Pulse Sequence: gCOSY
 Solvent: Benzene
 Ambient temperature
File: js6-86gCOSY
INOVA-500  "nmr9"

 Relax. delay 1.000 sec
 Acq. time 0.237 sec
 Width     4317.6 Hz
 2D Width 4317.6 Hz
 16 repetitions
 512 increments
OBSERVE   H1, 499.7714019 MHz
DATA PROCESSING
 Sq. sine bell 0.119 sec
F1 DATA PROCESSING
 Sq. sine bell 0.030 sec
FT size 8192 x 8192
Total time 2 hr, 59 min, 6 sec
```





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js6-86-gCOSY in C6D6

Pulse Sequence: gCOSY
 Solvent: Benzene
 Ambient temperature
INOVA-500  "nmr9"

 Relax. delay 1.000 sec
 Acq. time 0.237 sec
 Width     4317.6 Hz
 2D Width 4317.6 Hz
 16 repetitions
 512 increments
OBSERVE   H1, 499.7714019 MHz
DATA PROCESSING
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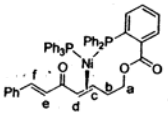
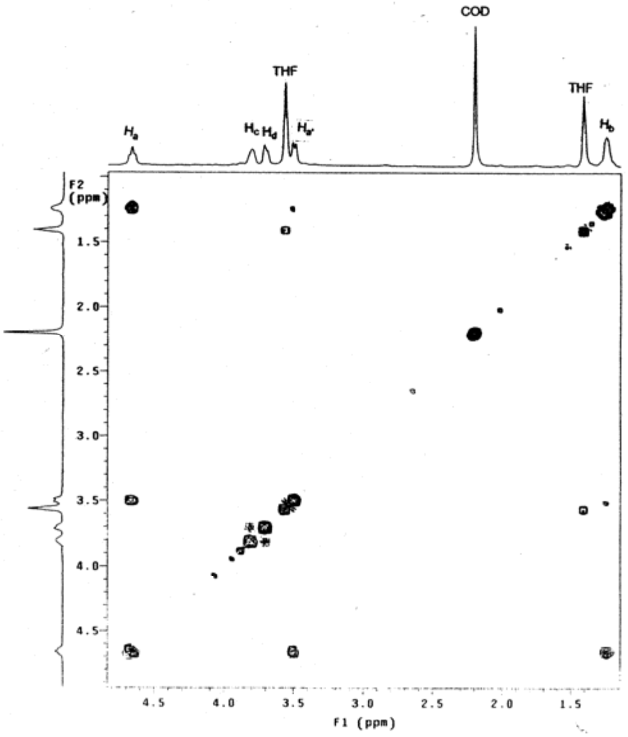
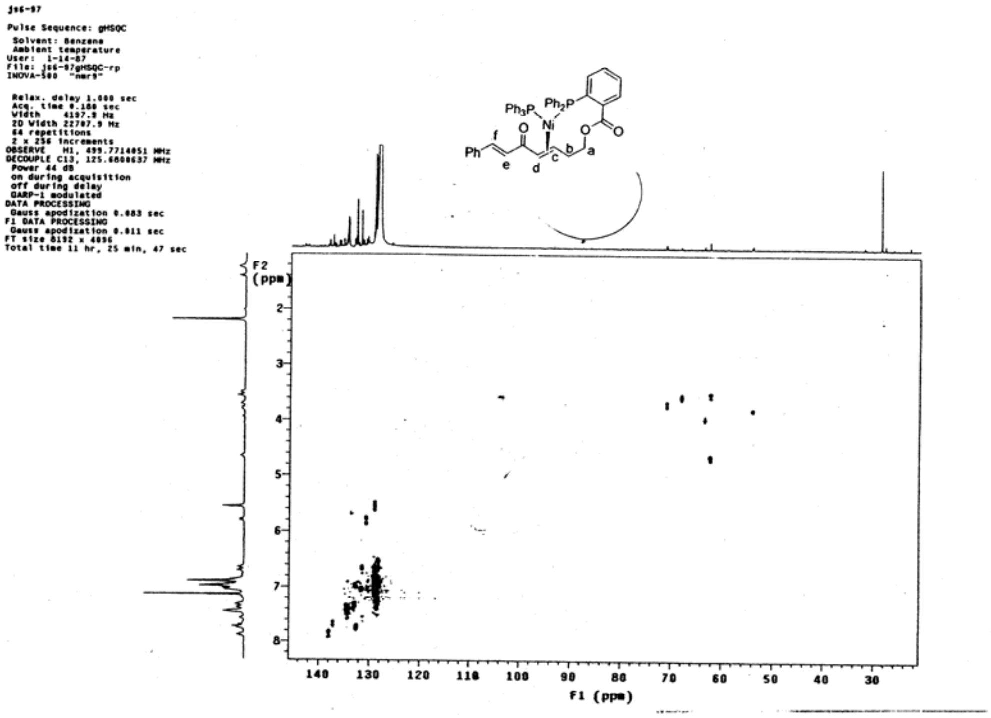
F1 DATA PROCESSING
 Sq. sine bell 0.030 sec
FT size 2048 x 2048
Total time 2 hr, 59 min, 6 sec
```





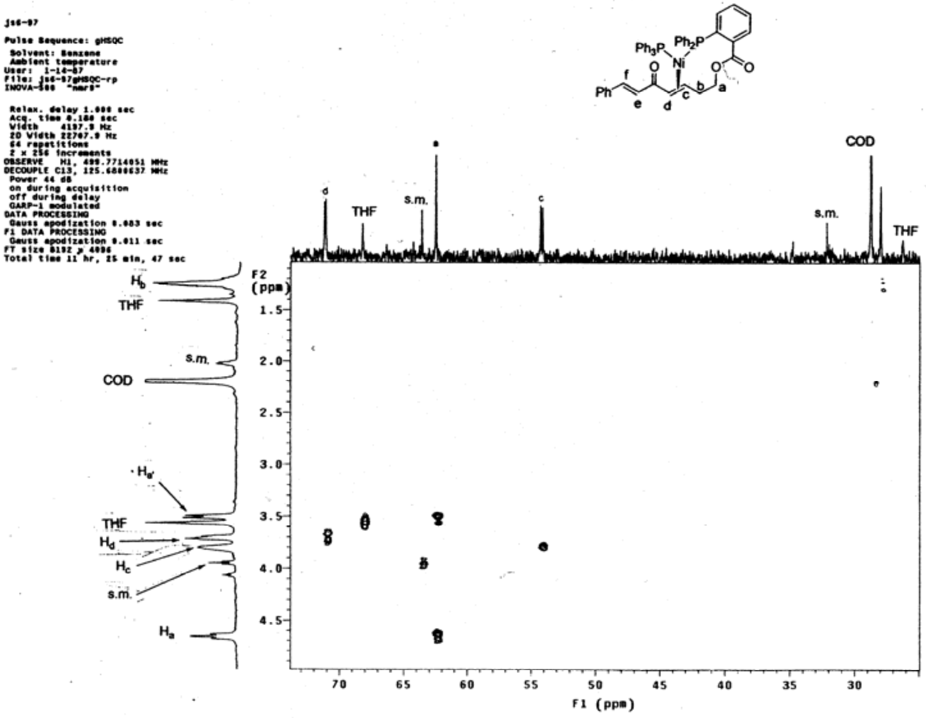
HSQC in C_6D_6:



```
js6-97

Pulse Sequence: gHSQC
 Solvent: Benzene
 Ambient temperature
User:  1-14-07
File: js6-97gHSQC-rp
INOVA-500  "nmr9"

 Relax. delay 1.000 sec
 Acq. time 0.100 sec
 Width     4197.9 Hz
 2D Width 22707.9 Hz
 64 repetitions
 2 x 256 increments
OBSERVE   H1, 499.7714051 MHz
DECOUPLE C13, 125.6800637 MHz
 Power 44 dB
 on during acquisition
 off during delay
 GARP-1 modulated
DATA PROCESSING
 Gauss apodization 0.083 sec
F1 DATA PROCESSING
 Gauss apodization 0.011 sec
FT size 8192 x 4096
Total time 11 hr, 25 min, 47 sec
```

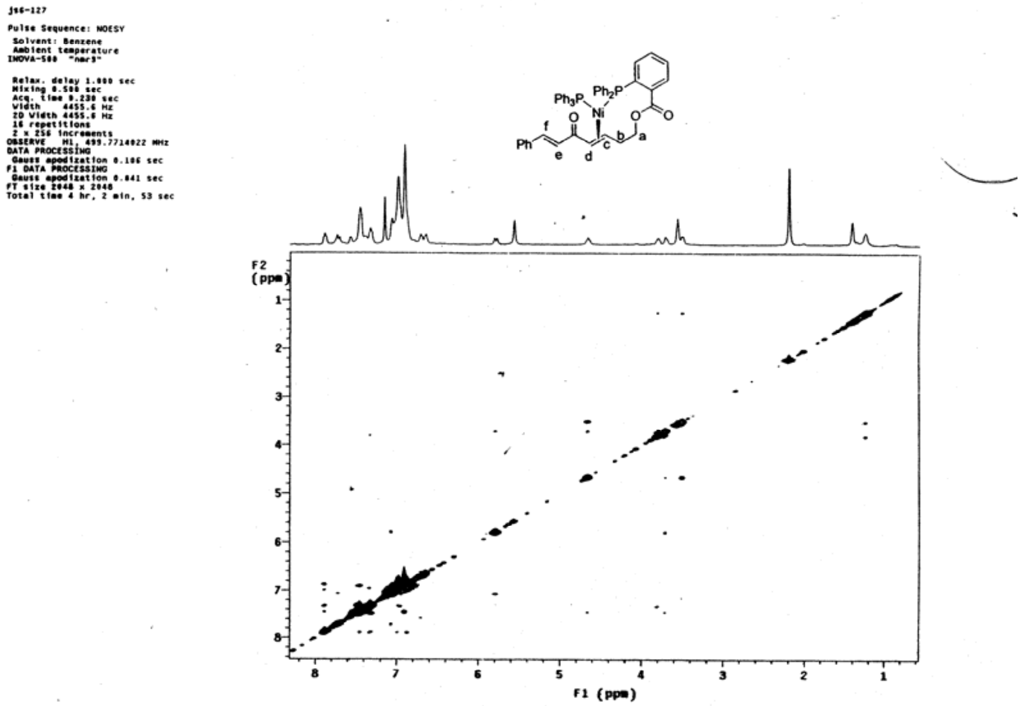


```
js6-97

Pulse Sequence: gHSQC
 Solvent: Benzene
 Ambient temperature
User:  1-14-07
File: js6-97gHSQC-rp
INOVA-500  "nmr9"

 Relax. delay 1.000 sec
 Acq. time 0.100 sec
 Width     4197.9 Hz
 2D Width 22707.9 Hz
 64 repetitions
 2 x 256 increments
OBSERVE   H1, 499.7714051 MHz
DECOUPLE C13, 125.6800637 MHz
 Power 44 dB
 on during acquisition
 off during delay
 GARP-1 modulated
DATA PROCESSING
 Gauss apodization 0.083 sec
F1 DATA PROCESSING
 Gauss apodization 0.011 sec
FT size 8192 x 4096
Total time 11 hr, 25 min, 47 sec
```

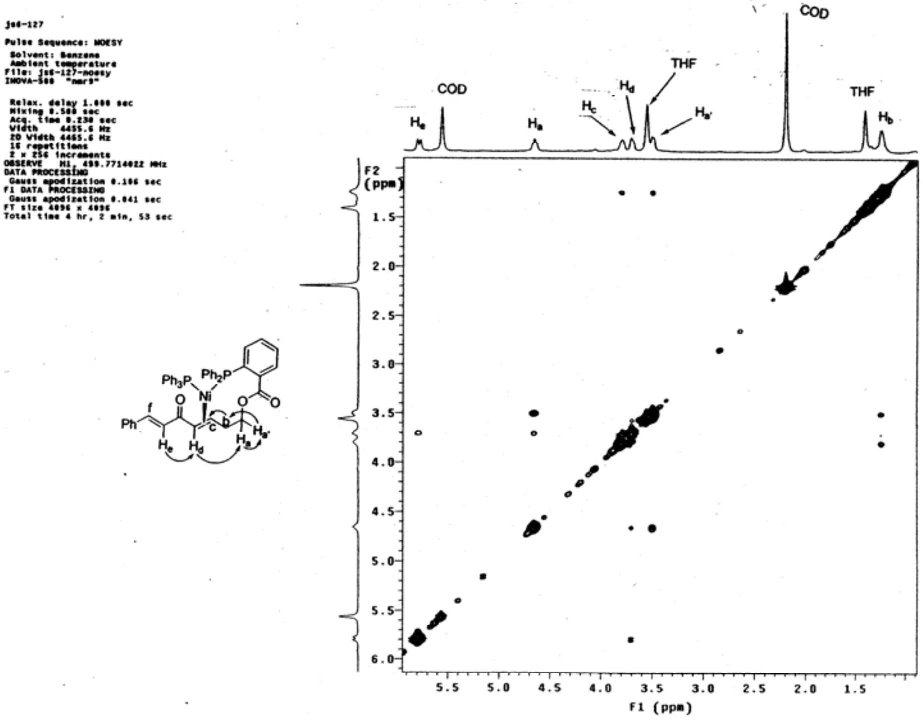
NOESYin C_6D_6:



```
js6-127

Pulse Sequence: NOESY
 Solvent: Benzene
 Ambient temperature
INOVA-500  "nmr9"

 Relax. delay 1.000 sec
 Mixing 0.500 sec
 Acq. time 0.230 sec
 Width    4455.6 Hz
 2D Width 4455.6 Hz
 16 repetitions
 2 x 256 increments
OBSERVE   H1, 499.7714022 MHz
DATA PROCESSING
 Gauss apodization 0.106 sec
F1 DATA PROCESSING
 Gauss apodization 0.041 sec
FT size 2048 x 2048
Total time 4 hr, 2 min, 53 sec
```



```
js6-127

Pulse Sequence: NOESY
 Solvent: Benzene
 Ambient temperature
File: js6-127-noesy
INOVA-500  "nmr9"

 Relax. delay 1.000 sec
 Mixing 0.500 sec
 Acq. time 0.230 sec
 Width    4455.6 Hz
 2D Width 4465.6 Hz
 16 repetitions
 2 x 256 increments
OBSERVE   H1, 499.7714022 MHz
DATA PROCESSING
 Gauss apodization 0.106 sec
F1 DATA PROCESSING
 Gauss apodization 0.041 sec
FT size 4096 x 4096
Total time 4 hr, 2 min, 53 sec
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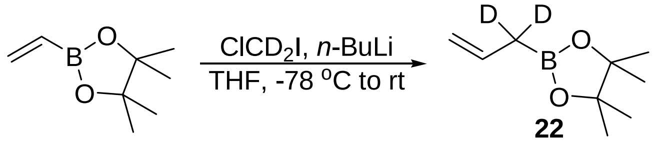
Deuterium Labelling Experiments (Scheme 7):

Synthesis of d_2-allylboronic acid pincacol ester (22):



For lead reference see: Sadhu, K. M.; Matteson, D. S. *Organometallics* **1985**, *4*, 1687. To 665 mg (4.32 mmol) of vinylboronic acid pinacol ester and 1.00 g (5.61 mmol) of d_2-chloroiodomethane (from Cambridge Isotopes or prepared from CD_2Cl_2 according to: Miyano, S.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2864.) in 17 mL of THF at –78 °C was added 2.07 mL (5.18 mmol) of 2.5 M *n*-BuLi in hexane dropwise. The reaction was then allowed to warm to room temperature and stirring continued overnight. The reaction was concentrated using reduced pressure. The residue was diluted with pentane and filtered through celite. Saturated NH_4Cl was added and the two layers were filtered through celite. The organic layer was collected and the aqueous layer extracted with pentane. The organic material was dried with $MgSO_4$ and concentrated using reduced pressure. Purification of the crude mixture using silica gel chromatography (pentane/CH_2Cl_2) gave 249 mg (34%) of **22** as a colorless oil that was contaminated with 8% of vinylboronic acid pinacol ester as determined by GLC analysis.

Conjugate allylation using **22**: The conjugate allylation was performed using the same procedure described for Table 1 with **22** in place of allylboronic acid pinacol ester. Chemoselectivity was determined using GLC analysis of the crude reaction mixture. ^{1}H NMR analysis of the crude material verified that deuterium scrambling of unreacted **22** did not occur under the reaction conditions. The product was purified using silica gel chromatography and the deuterium label ratios determined by ^{2}H NMR of the purified material.

Non-linear effects (Figure 1 and 2):

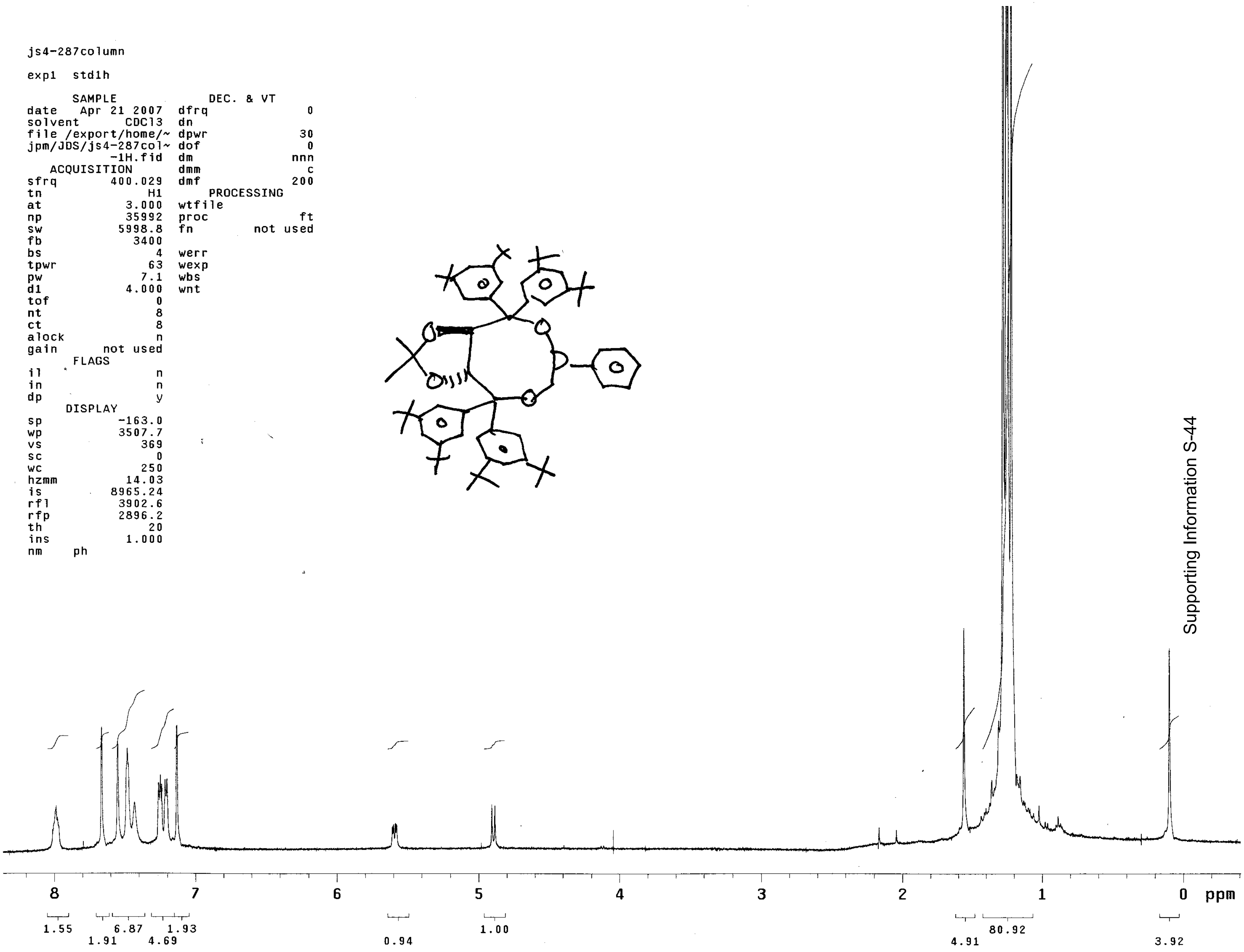
Effect of ligand optical purity on enantioselectivity:

An oven-dried 2-dram vial equipped with a magnetic stir-bar was charged with 3.0 mg (0.011 mmol) of bis(1,5-cyclooctadiene)nickel. The two enantiopodes of ligand were then added as 0.100 M stock solutions in toluene, using a gas-tight syringe, to make the desired optical purity of ligand for the reaction (0, 25, 50, and 75 % ee was examined). Next, 221 μL of toluene was added, and this mixtrure was stirred for 45 min. Next, 44.2 mg (0.263 mmol) of allylboronic acid pinacol ester was added followed by 50.0 mg (0.219 mmol) of (1*E*, 4*E*)-1-phenyldeca-1,4-dien-3-one. The vial was capped, taped with electrical tape, removed from the dry-box, and allowed to stir at ambient temperature for 20 h. After this time period, degassed water (N_2 sparge) was added and the mixture transferred to a separatory funnel with CH_2Cl_2. After swirling the layers, the organic layer was collected and the aqueous layer washed with CH_2Cl_2 (2x). The combined organic layers were dried with anhydrous Na_2SO_4, and volatiles were removed under reduced pressure. Analysis of the crude reaction mixture using GLC was used to determine the chemoselectivity of the reaction. Purification using silica gel chromatography (hexanes/EtOAc) afforded the conjugate allylation product. Enantioselectivity was determined using SFC analysis of the purified material.

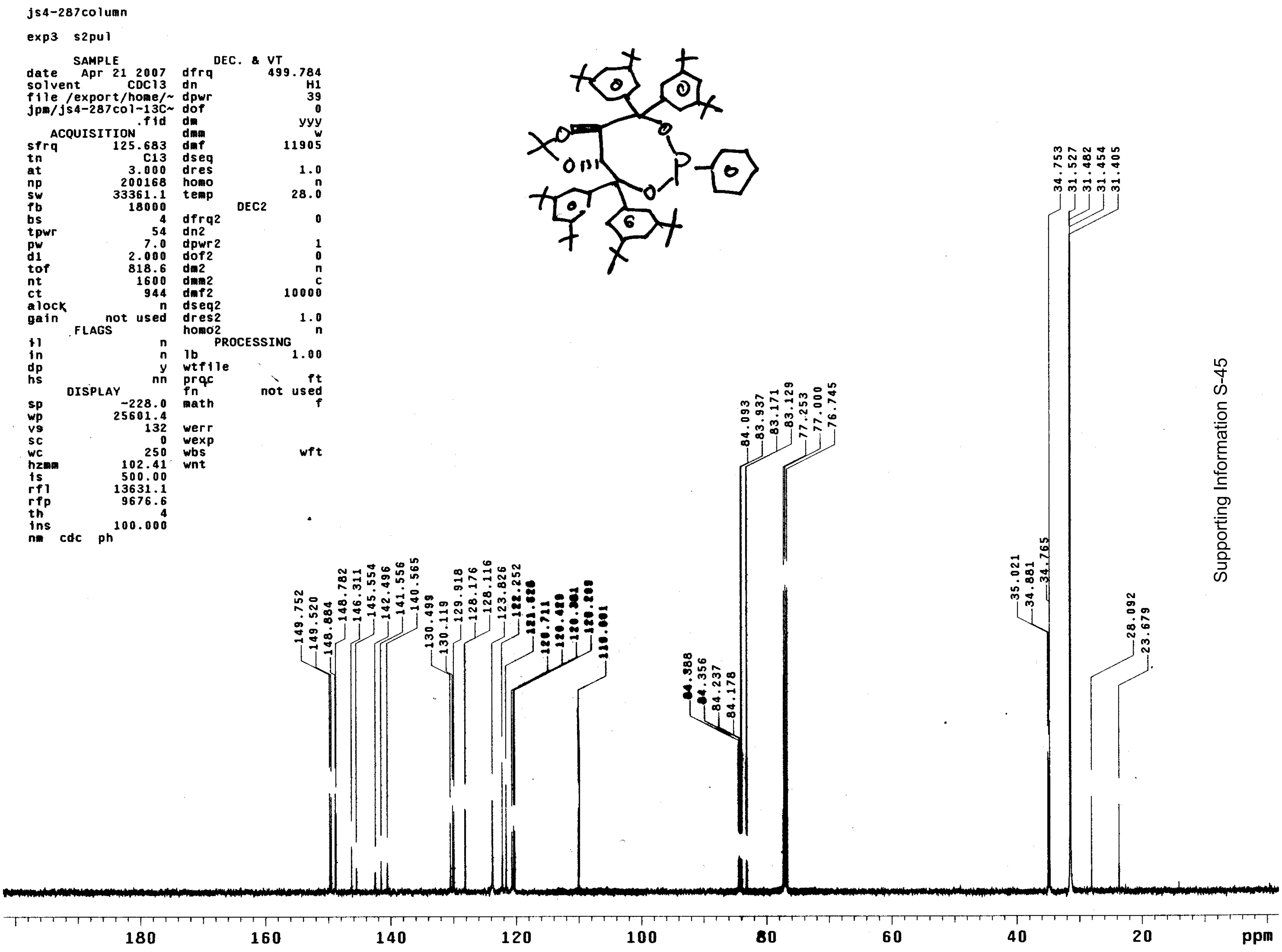
Effect of ligand optical purity and conversion:

Optically pure and racemic catalyst stock solutions, consisting of mixture of Ni(cod)$_2$ and ligand **14**, were prepared using 3.4 mg of Ni(cod)$_2$ and 24.5 mg of optically pure or racemic ligand **14** in 240 μL of d_8-toluene, respectively, and allowed to stand at room temperature for 45 min before use. To two oven-dried J-

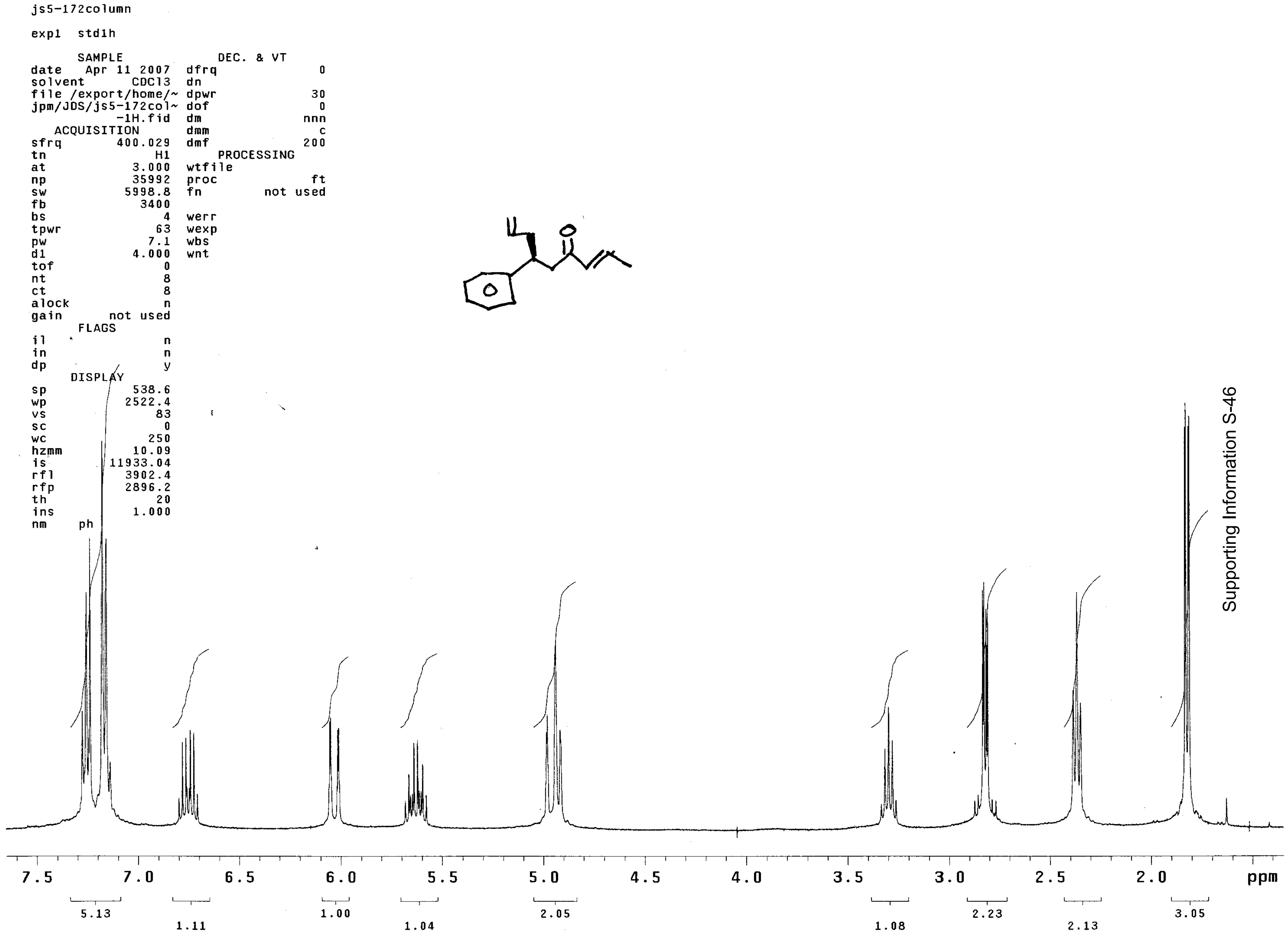
Young NMR tubes, in a dry-box, was added 350 μL of a 0.750 M stock solution of allylboronic acid pinacol ester in *d*$_8$-toluene to each tube. To one tube was added 175 μL of the optically pure catalyst stock solution, and to the other tube was added 175 μL of the racemic catalyst solution. Finally, 350 μL of a 0.500 M stock solution of substrate in *d*$_8$-toluene was added to each tube, and they were capped and inverted several times. The reactions were followed by ^{1}H NMR, and the ratio of starting material to product was used to calculate conversions. After complete consumption of starting material, the reactions were worked up as described for the conjugate allylation in Table 2.



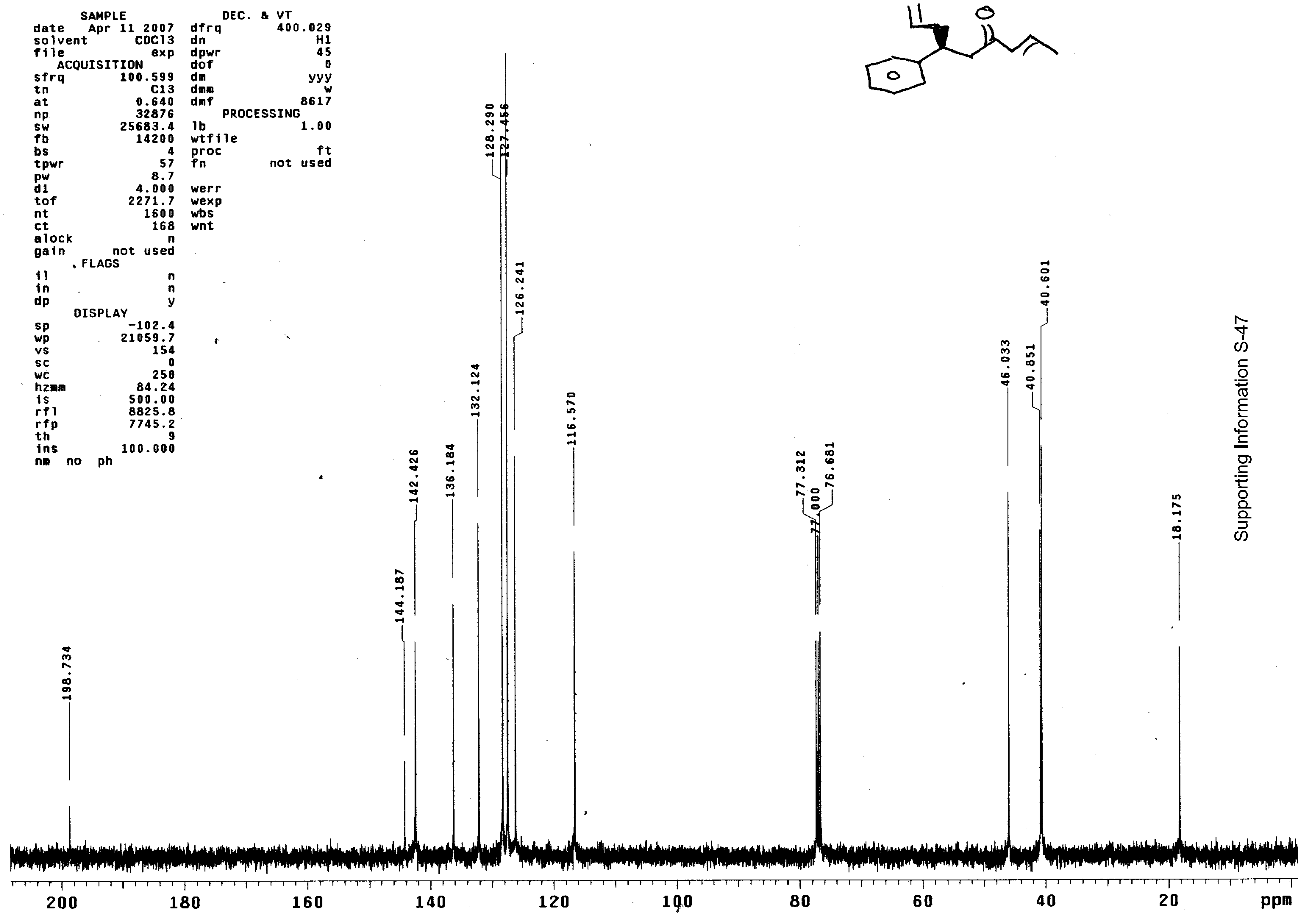
```
js4-287column

exp1  std1h

      SAMPLE              DEC. & VT
date   Apr 21 2007  dfrq              0
solvent      CDCl3  dn
file /export/home/~ dpwr             30
jpm/JDS/js4-287col~ dof               0
           -1H.fid  dm              nnn
   ACQUISITION      dmm               c
sfrq       400.029  dmf             200
tn              H1      PROCESSING
at           3.000  wtfile
np           35992  proc             ft
sw          5998.8  fn         not used
fb            3400
bs               4  werr
tpwr            63  wexp
pw             7.1  wbs
d1           4.000  wnt
tof              0
nt               8
ct               8
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp          -163.0
wp          3507.7
vs             369
sc               0
wc             250
hzmm         14.03
is         8965.24
rfl         3902.6
rfp         2896.2
th              20
ins          1.000
nm    ph
```



```
js4-287column

exp3  s2pul

      SAMPLE            DEC. & VT
date   Apr 21 2007  dfrq       499.784
solvent      CDCl3  dn              H1
file /export/home/~ dpwr            39
jpm/js4-287col-13C~ dof              0
               .fid dm             yyy
   ACQUISITION      dmm              w
sfrq       125.683  dmf          11905
tn             C13  dseq
at           3.000  dres           1.0
np          200168  homo             n
sw         33361.1  temp          28.0
fb           18000           DEC2
bs               4  dfrq2            0
tpwr            54  dn2
pw             7.0  dpwr2            1
d1           2.000  dof2             0
tof          818.6  dm2              n
nt            1600  dmm2             c
ct             944  dmf2         10000
alock            n  dseq2
gain      not used  dres2          1.0
      FLAGS         homo2            n
il               n        PROCESSING
in               n  lb            1.00
dp               y  wtfile
hs              nn  proc            ft
      DISPLAY       fn        not used
sp          -228.0  math             f
wp         25601.4
vs             132  werr
sc               0  wexp
wc             250  wbs            wft
hzmm        102.41  wnt
is          500.00
rfl        13631.1
rfp         9676.6
th               4
ins        100.000
nm  cdc  ph
```

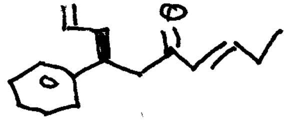


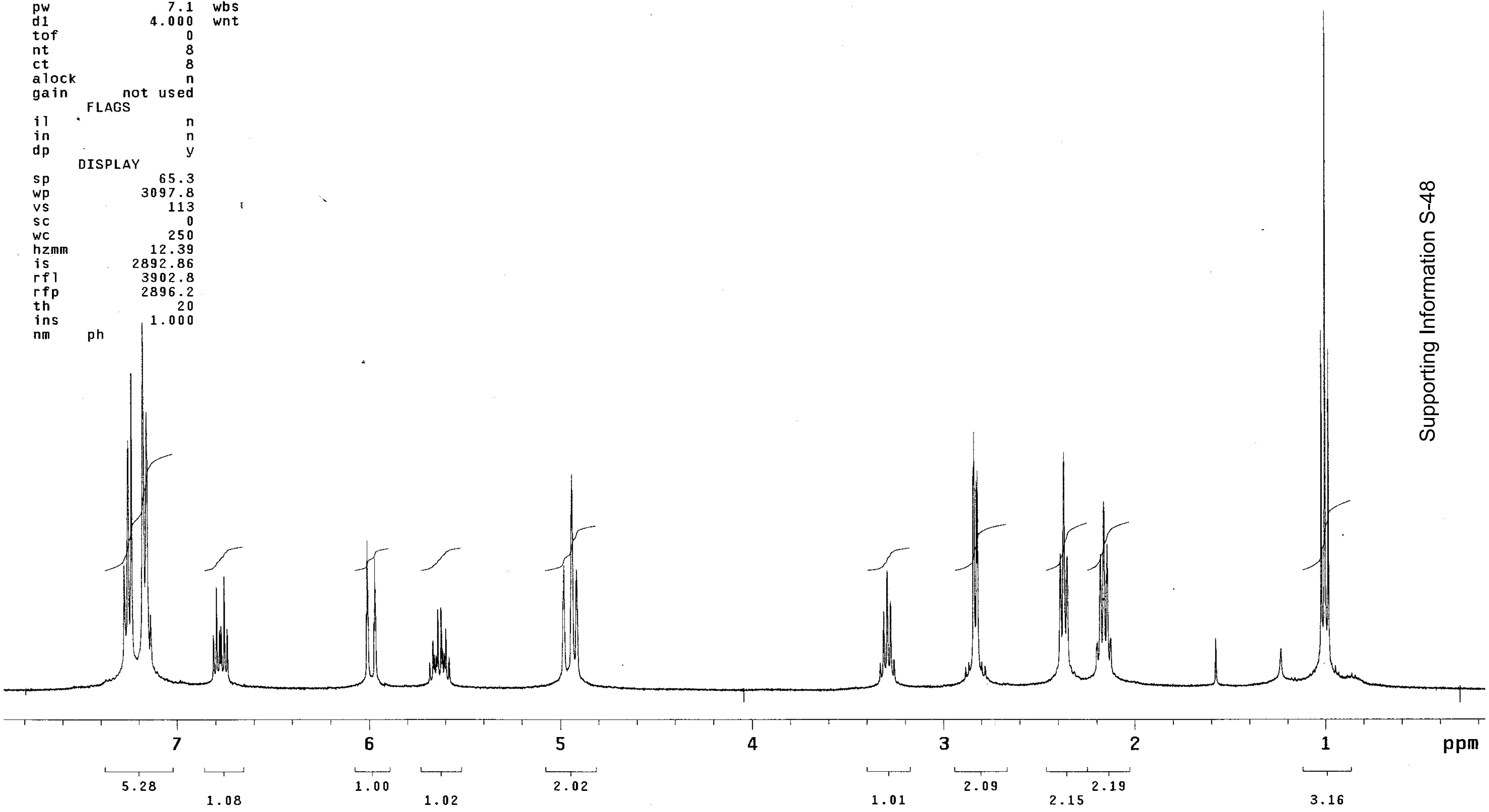
```
js5-172column

exp1  std1h

      SAMPLE                DEC. & VT
date   Apr 11 2007  dfrq             0
solvent      CDCl3  dn
file /export/home/~ dpwr            30
jpm/JDS/js5-172col~ dof              0
           -1H.fid  dm             nnn
   ACQUISITION      dmm              c
sfrq       400.029  dmf            200
tn              H1      PROCESSING
at           3.000  wtfile
np           35992  proc            ft
sw          5998.8  fn        not used
fb            3400
bs               4  werr
tpwr            63  wexp
pw             7.1  wbs
d1           4.000  wnt
tof              0
nt               8
ct               8
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
      DISPLAY
sp           538.6
wp          2522.4
vs              83
sc               0
wc             250
hzmm         10.09
is        11933.04
rfl         3902.4
rfp         2896.2
th              20
ins          1.000
nm    ph
```

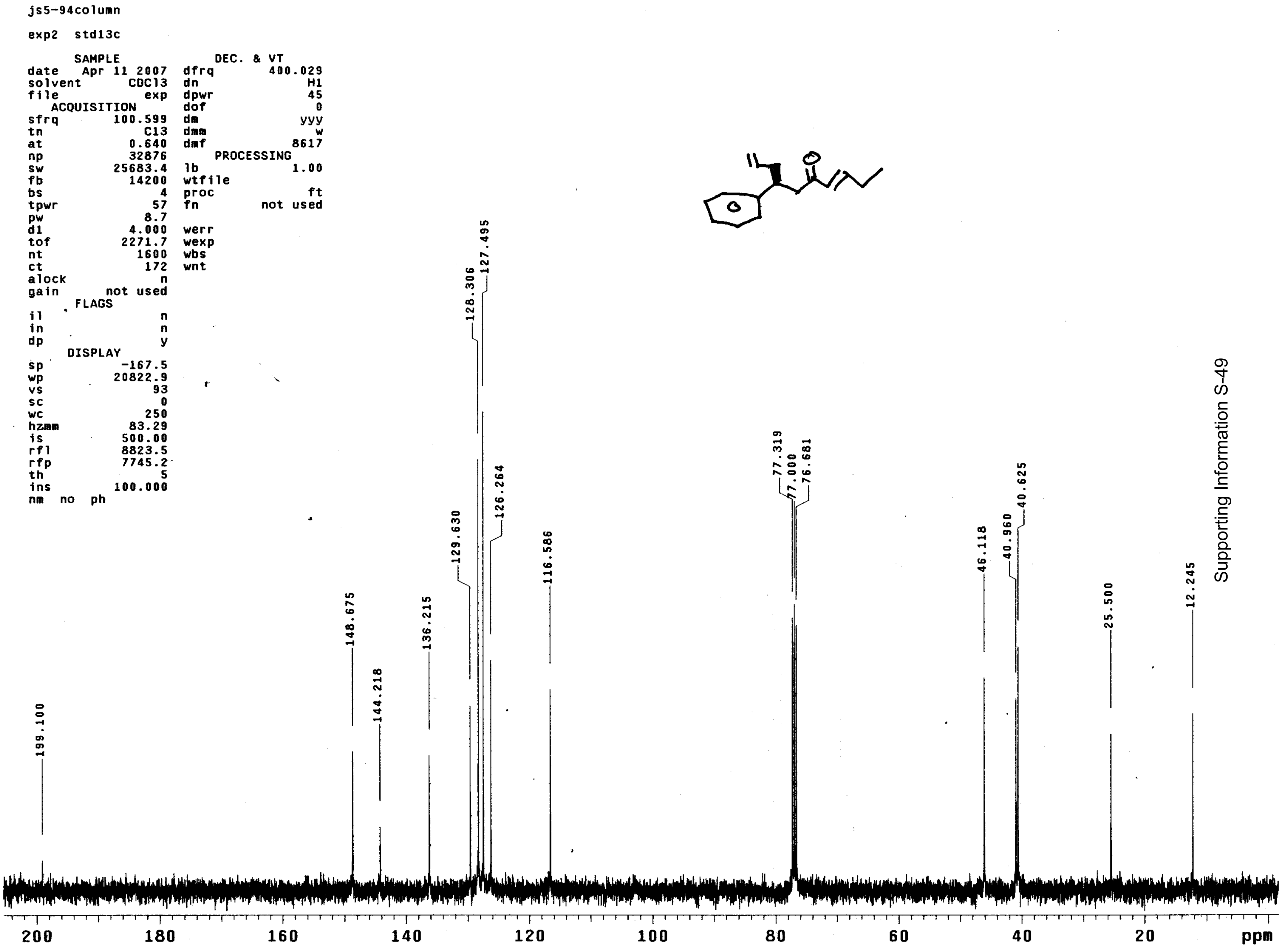


```
js5-172column

exp2  std13c

      SAMPLE                DEC. & VT
date   Apr 11 2007   dfrq        400.029
solvent      CDCl3   dn               H1
file           exp   dpwr             45
   ACQUISITION       dof               0
sfrq       100.599   dm              yyy
tn             C13   dmm               w
at           0.640   dmf            8617
np           32876        PROCESSING
sw         25683.4   lb             1.00
fb           14200   wtfile
bs               4   proc             ft
tpwr            57   fn         not used
pw             8.7
d1           4.000   werr
tof         2271.7   wexp
nt            1600   wbs
ct             168   wnt
alock            n
gain      not used
     FLAGS
il               n
in               n
dp               y
     DISPLAY
sp          -102.4
wp         21059.7
vs             154
sc               0
wc             250
hzmm         84.24
is          500.00
rfl         8825.8
rfp         7745.2
th               9
ins        100.000
nm  no  ph
```

```
js5-94column

exp1  std1h

      SAMPLE                DEC. & VT
date   Apr 11 2007  dfrq              0
solvent       CDCl3  dn
file /export/home/~ dpwr             30
jpm/JDS/js5-94col-~ dof               0
            1H.fid  dm              nnn
    ACQUISITION     dmm               c
sfrq        400.029 dmf             200
tn               H1      PROCESSING
at            3.000 wtfile
np            35992 proc             ft
sw           5998.8 fn         not used
fb             3400
bs                4 werr
tpwr             63 wexp
pw              7.1 wbs
d1            4.000 wnt
tof               0
nt                8
ct                8
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
      DISPLAY
sp             65.3
wp           3097.8
vs              113
sc                0
wc              250
hzmm          12.39
is          2892.86
rfl          3902.8
rfp          2896.2
th               20
ins           1.000
nm     ph
```

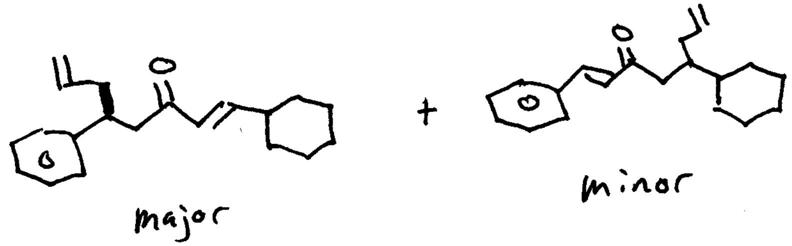


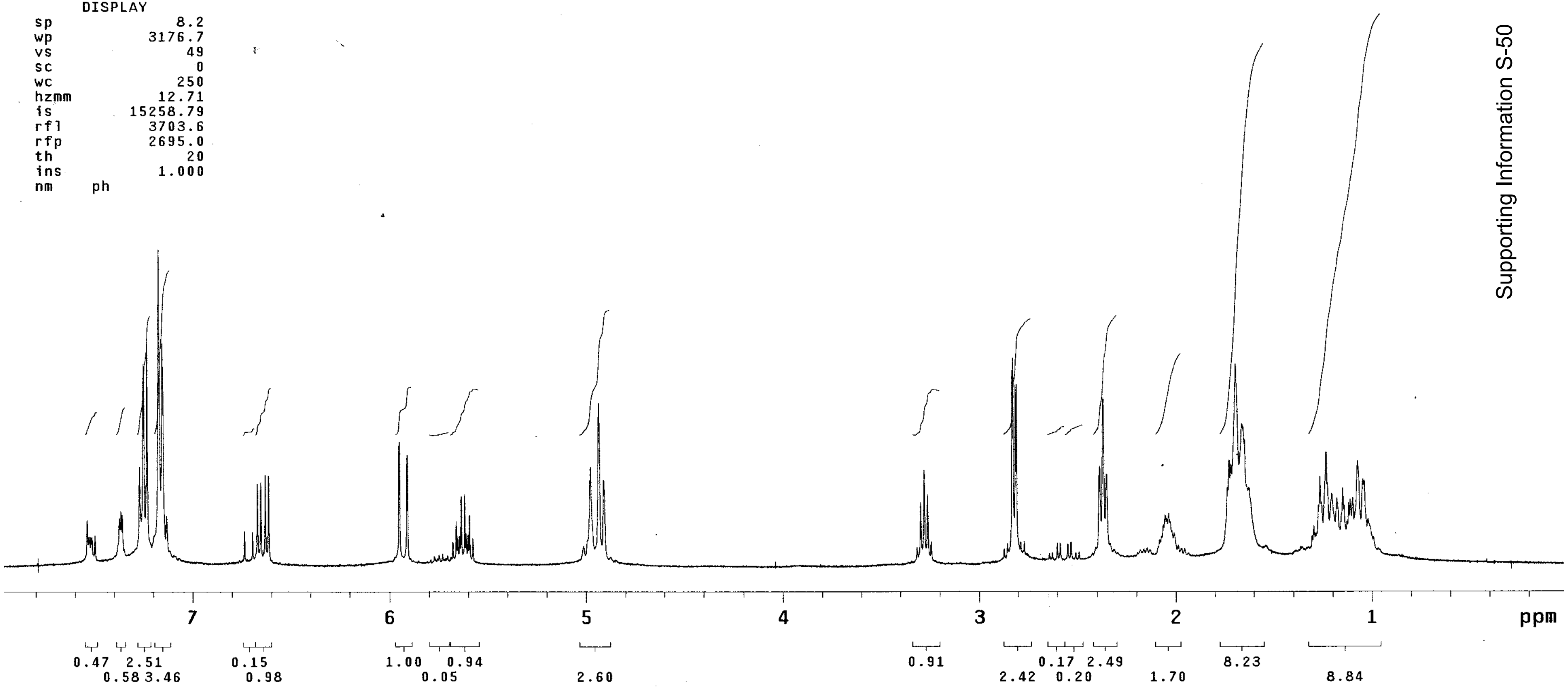




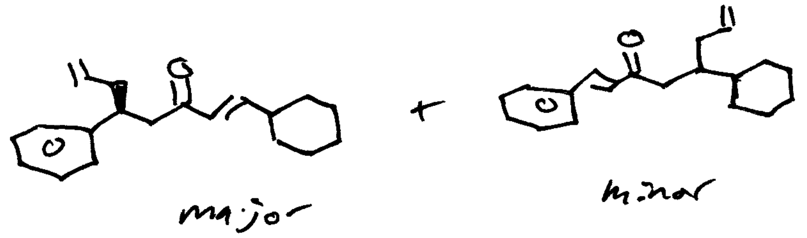
```
js5-94column

exp2  std13c

      SAMPLE              DEC. & VT
date   Apr 11 2007  dfrq        400.029
solvent       CDCl3  dn               H1
file            exp  dpwr             45
   ACQUISITION       dof               0
sfrq        100.599  dm              yyy
tn              C13  dmm               w
at            0.640  dmf            8617
np            32876       PROCESSING
sw          25683.4  lb             1.00
fb            14200  wtfile
bs                4  proc             ft
tpwr             57  fn         not used
pw              8.7
d1            4.000  werr
tof          2271.7  wexp
nt             1600  wbs
ct              172  wnt
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
     DISPLAY
sp           -167.5
wp          20822.9
vs               93
sc                0
wc              250
hzmm          83.29
is           500.00
rfl          8823.5
rfp          7745.2
th                5
ins         100.000
nm  no  ph
```

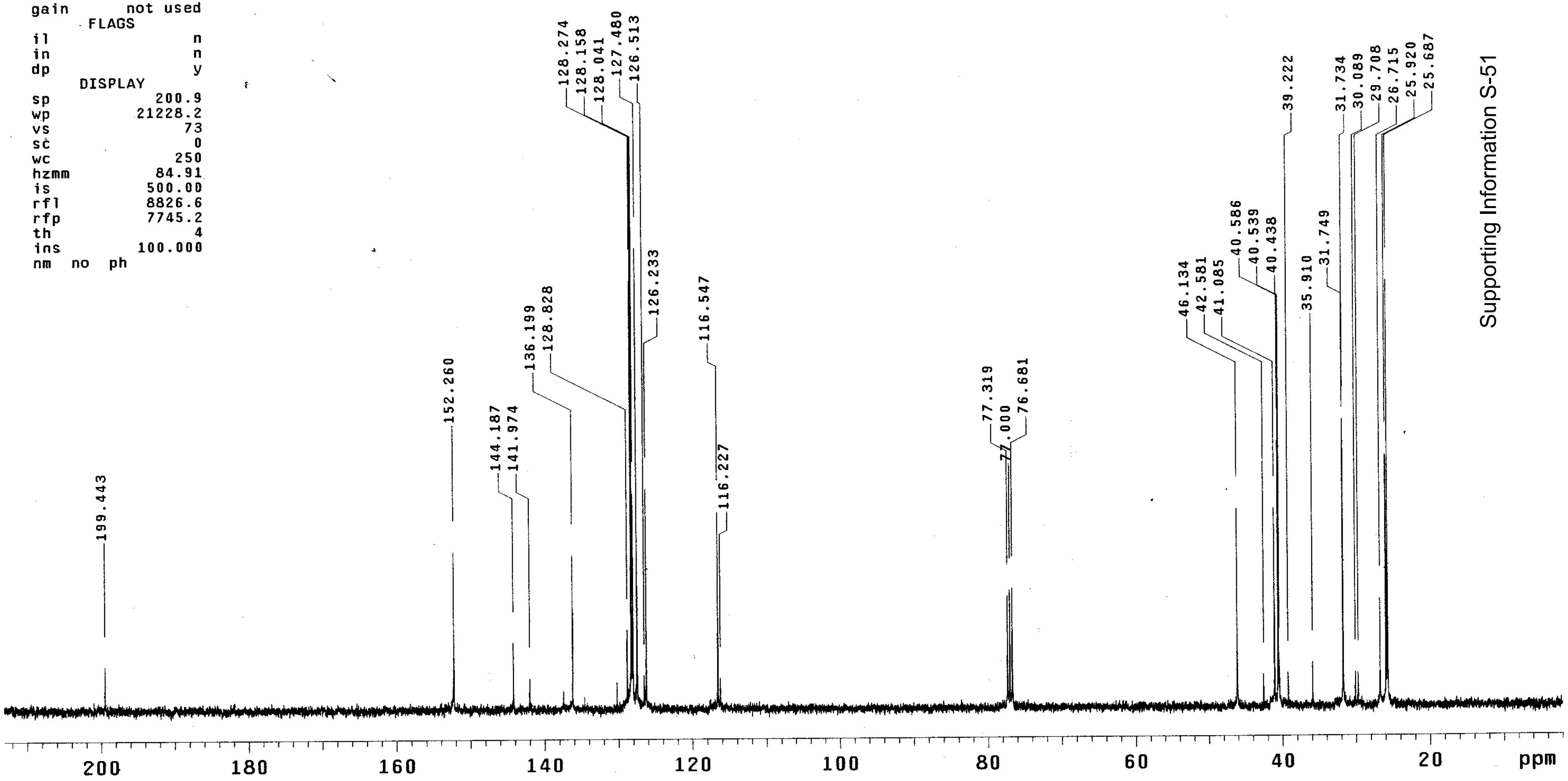
```
js5-173column

exp1  std1h

      SAMPLE                DEC. & VT
date   Apr 11 2007  dfrq              0
solvent      CDCl3  dn
file /export/home/~ dpwr             30
jpm/JDS/js5-173col~ dof               0
           -1H.fid  dm              nnn
    ACQUISITION     dmm               c
sfrq       400.029  dmf             200
tn              H1       PROCESSING
at           3.000  wtfile
np           35992  proc             ft
sw          5998.8  fn         not used
fb            3400
bs               4  werr
tpwr            63  wexp
pw             7.1  wbs
d1           4.000  wnt
tof              0
nt               8
ct               8
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp             8.2
wp          3176.7
vs              49
sc               0
wc             250
hzmm         12.71
is        15258.79
rfl         3703.6
rfp         2695.0
th              20
ins          1.000
nm     ph
```

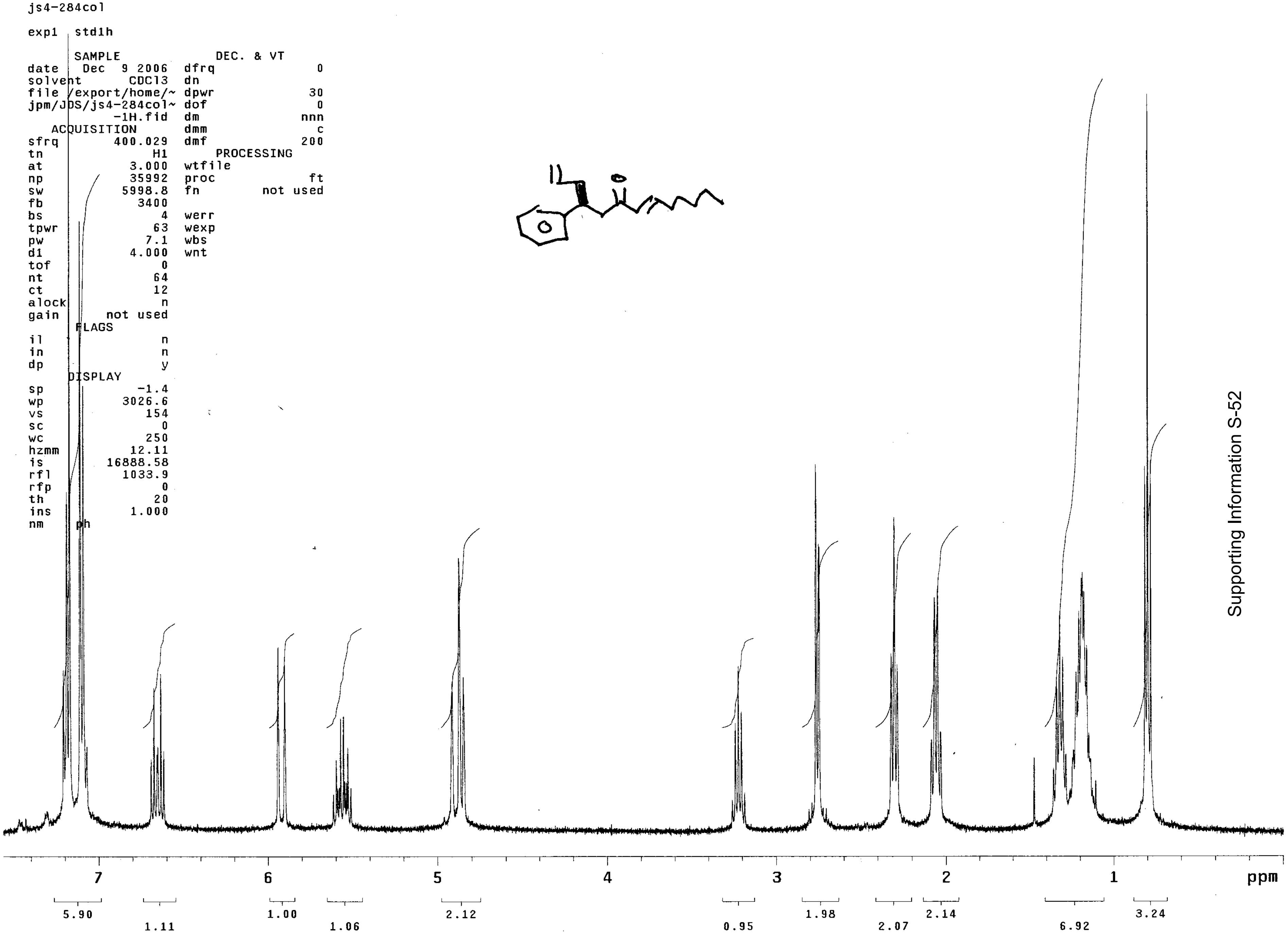




```
js5-173column

exp2  std13c

      SAMPLE               DEC. & VT
date   Apr 11 2007  dfrq       400.029
solvent       CDCl3  dn             H1
file /export/home/~ dpwr            45
jpm/JDS/js5-173col~ dof              0
         -13C.fid   dm             yyy
    ACQUISITION     dmm              w
sfrq        100.599 dmf           8617
tn              C13      PROCESSING
at            0.640 lb            1.00
np            32876 wtfile
sw          25683.4 proc            ft
fb            14200 fn        not used
bs                4
tpwr             57 werr
pw              8.7 wexp
d1            4.000 wbs
tof          2271.7 wnt
nt             1600
ct              192
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
       DISPLAY
sp            200.9
wp          21228.2
vs               73
sc                0
wc              250
hzmm          84.91
is           500.00
rfl          8826.6
rfp          7745.2
th                4
ins         100.000
nm  no  ph
```

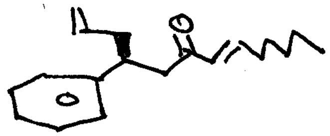


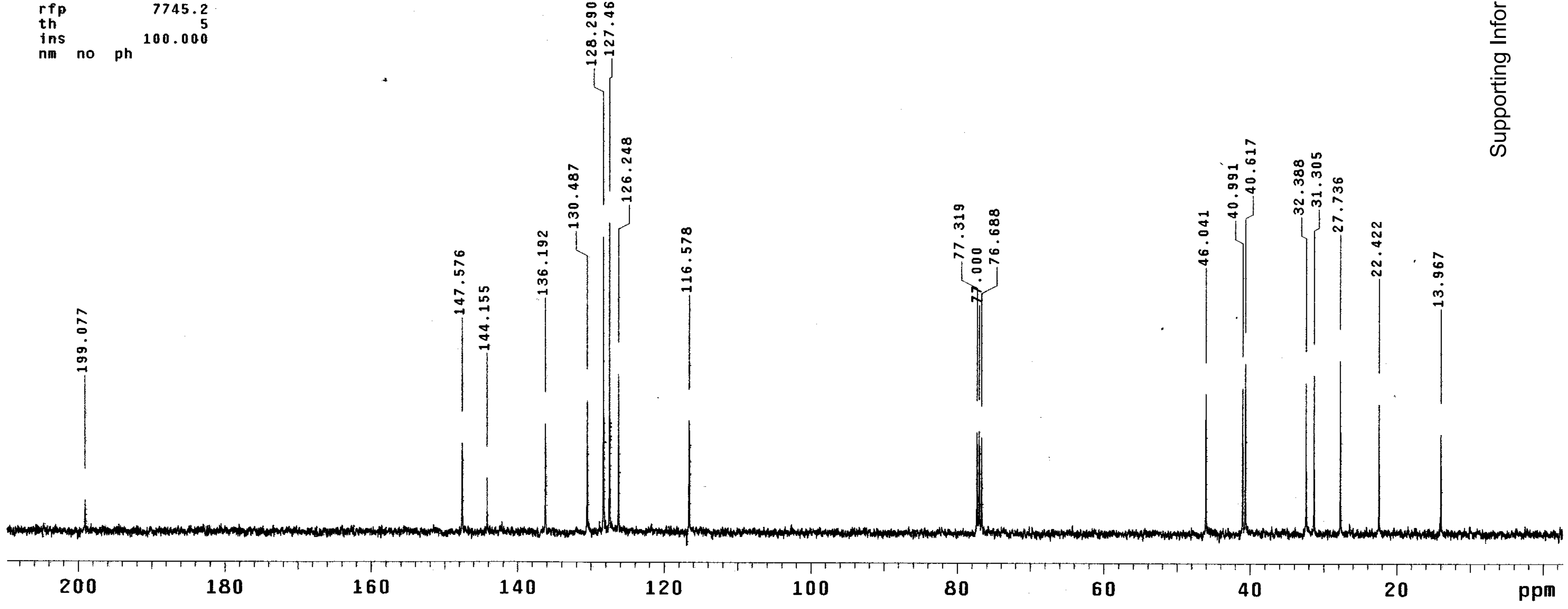




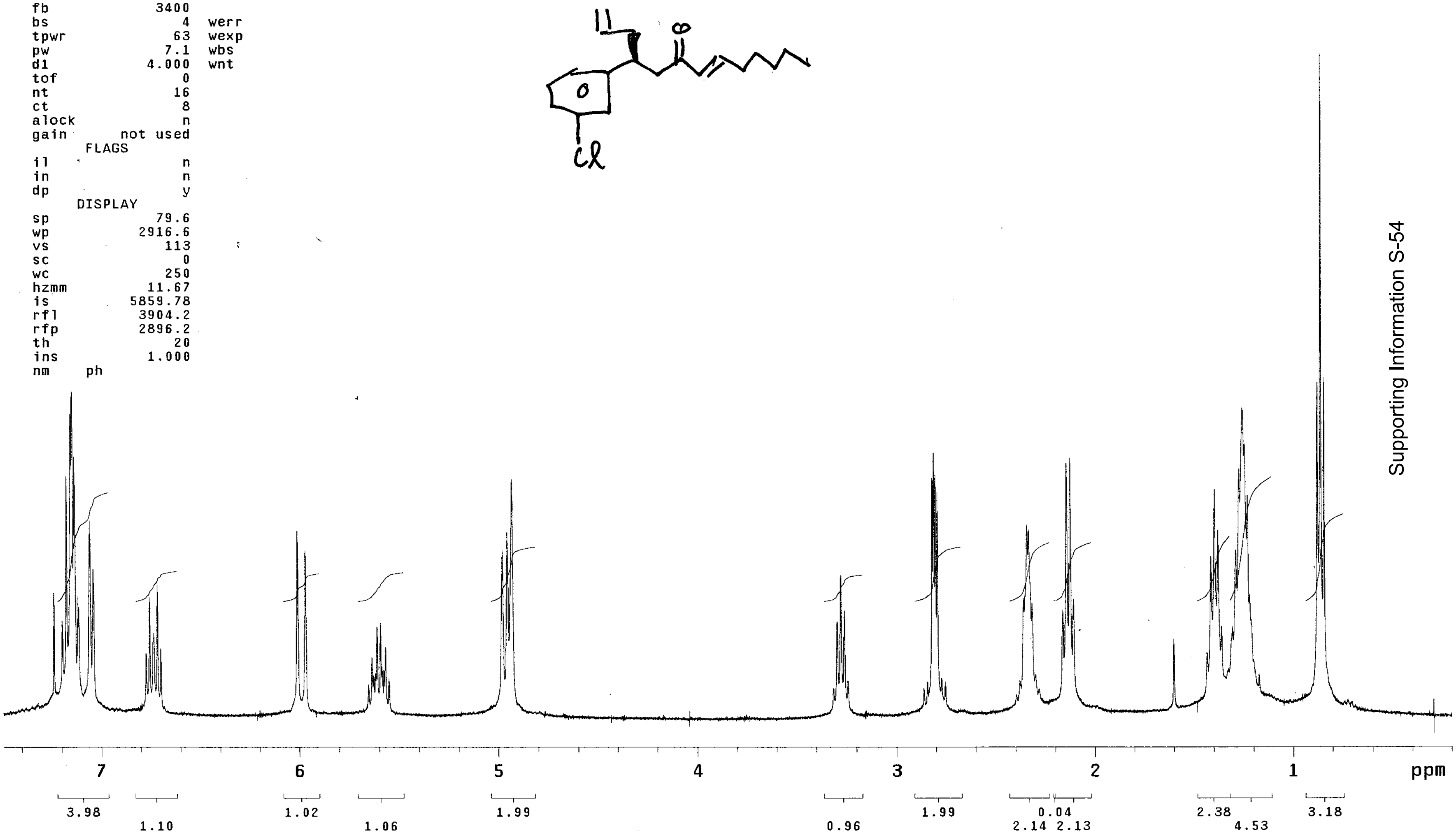
```
js4-284col

exp1  stdlh

        SAMPLE                DEC. & VT
date    Dec  9 2006   dfrq             0
solvent       CDCl3   dn
file /export/home/~   dpwr            30
jpm/JDS/js4-284col~   dof              0
            -1H.fid   dm             nnn
   ACQUISITION        dmm              c
sfrq        400.029   dmf            200
tn               H1        PROCESSING
at            3.000   wtfile
np            35992   proc            ft
sw           5998.8   fn        not used
fb             3400
bs                4   werr
tpwr             63   wexp
pw              7.1   wbs
d1            4.000   wnt
tof               0
nt               64
ct               12
alock             n
gain       not used
        FLAGS
il                n
in                n
dp                y
        DISPLAY
sp             -1.4
wp           3026.6
vs              154
sc                0
wc              250
hzmm          12.11
is         16888.58
rfl          1033.9
rfp               0
th               20
ins           1.000
nm      ph
```

```
js4-284col-13C

exp1  std13c

      SAMPLE              DEC. & VT
date   Dec  8 2006  dfrq        400.029
solvent       CDCl3  dn              H1
file            exp  dpwr            45
   ACQUISITION      dof              0
sfrq        100.599  dm             yyy
tn              C13  dmm              w
at            0.640  dmf           8617
np            32876       PROCESSING
sw          25683.4  lb            2.00
fb            14200  wtfile
bs               16  proc            ft
tpwr             57  fn        not used
pw              8.7
d1            4.000  werr
tof          2271.7  wexp
nt            40000  wbs
ct               64  wnt
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
     DISPLAY
sp           -272.5
wp          21363.0
vs               49
sc                0
wc              250
hzmm          85.45
is           500.00
rfl          8827.4
rfp          7745.2
th                5
ins         100.000
nm  no  ph
```

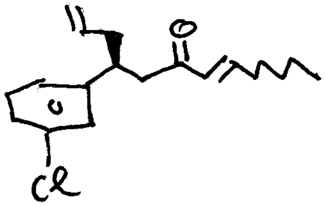


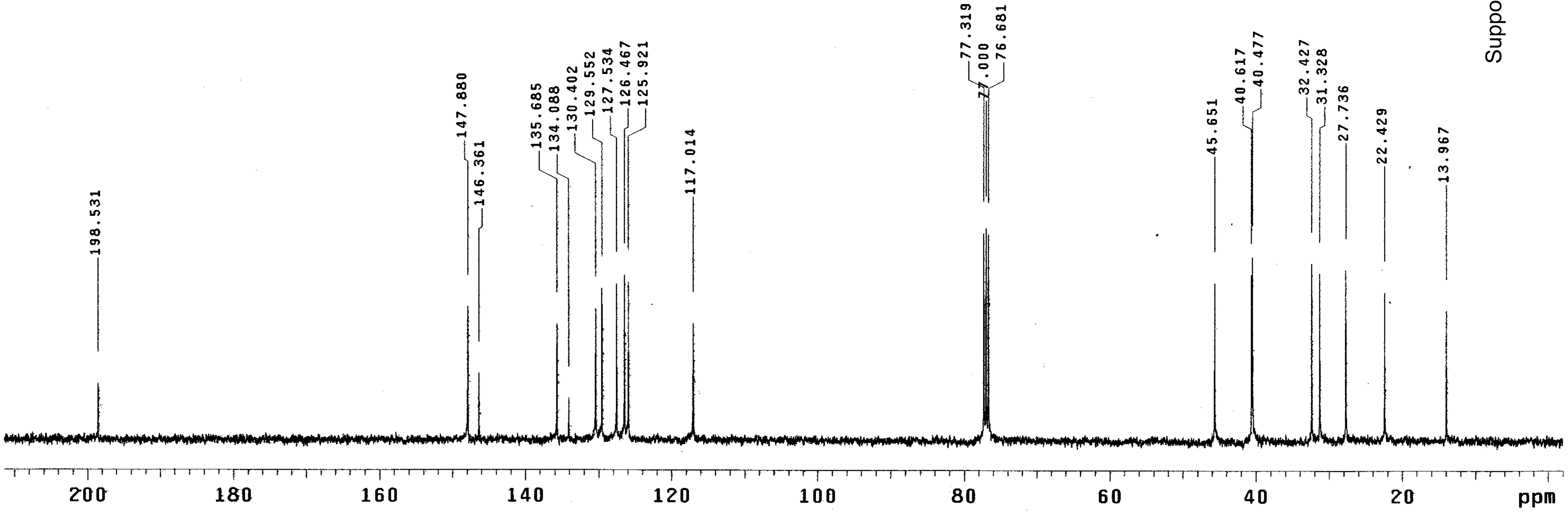


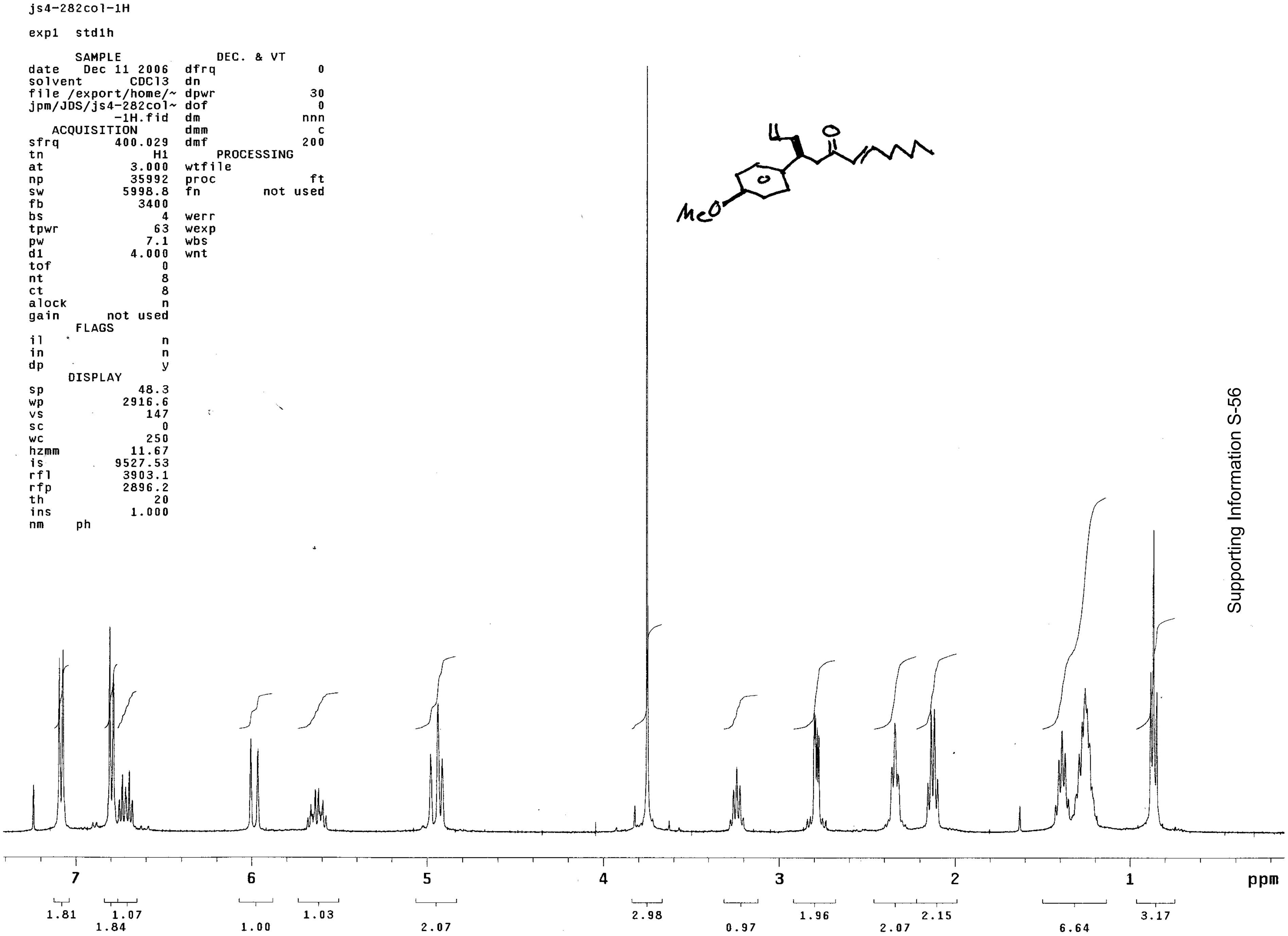
```
js4-285colmaj-1H

exp1  std1h

      SAMPLE                 DEC. & VT
date   Dec 15 2006  dfrq              0
solvent      CDCl3  dn
file /export/home/~ dpwr             30
jpm/JDS/js4-285col~ dof               0
        maj-1H.fid  dm              nnn
   ACQUISITION      dmm               c
sfrq       400.029  dmf             200
tn              H1       PROCESSING
at           3.000  wtfile
np           35992  proc             ft
sw          5998.8  fn         not used
fb            3400
bs               4  werr
tpwr            63  wexp
pw             7.1  wbs
d1           4.000  wnt
tof              0
nt              16
ct               8
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp            79.6
wp          2916.6
vs             113
sc               0
wc             250
hzmm         11.67
is         5859.78
rfl         3904.2
rfp         2896.2
th              20
ins          1.000
nm     ph
```



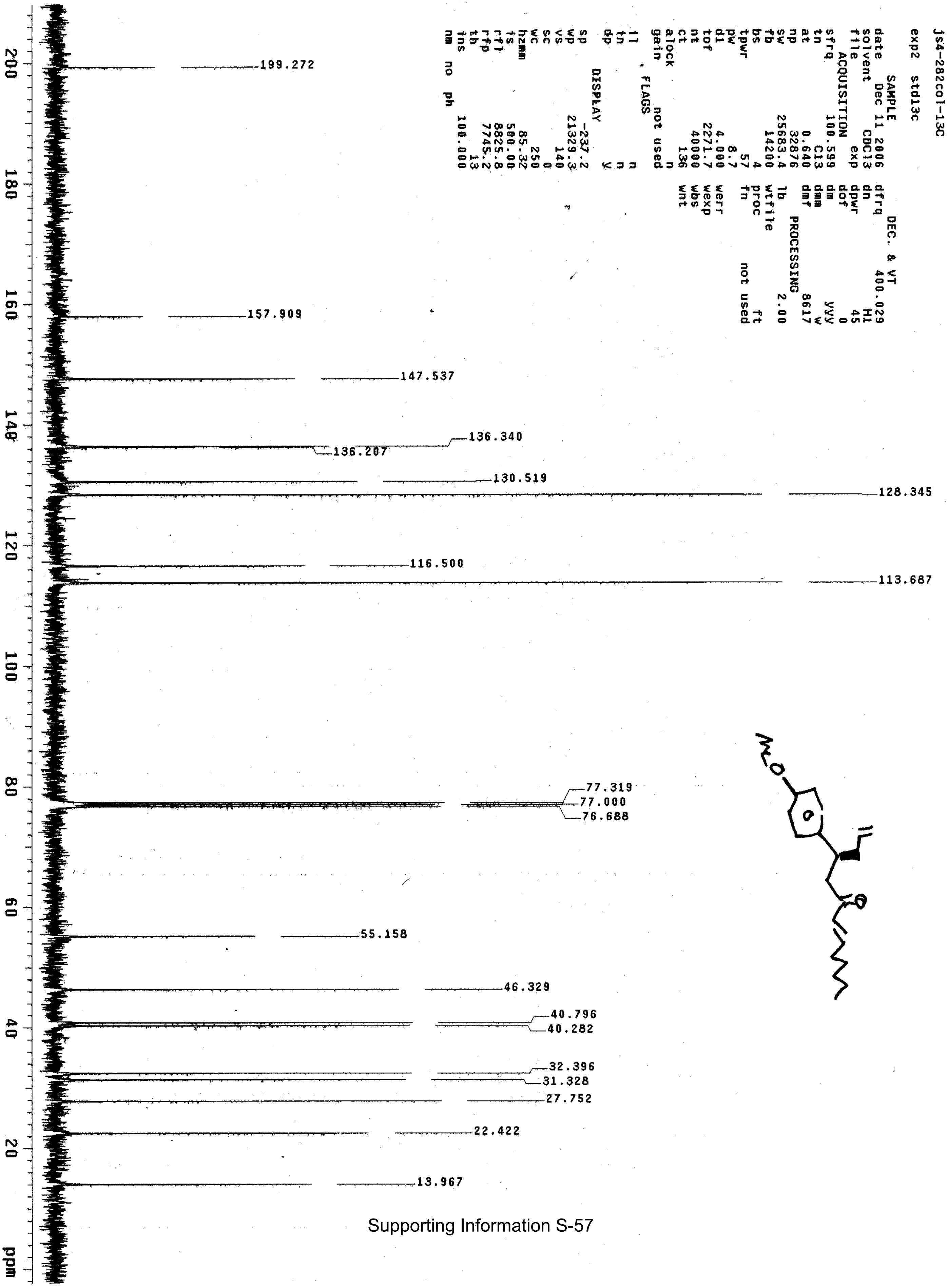
```
js4-285colmaj-13C

exp3  std13c

      SAMPLE              DEC. & VT
date   Dec 15 2006  dfrq        400.029
solvent      CDCl3  dn               H1
file           exp  dpwr             45
   ACQUISITION      dof               0
sfrq       100.599  dm              yyy
tn             C13  dmm               w
at           0.640  dmf            8617
np           32876        PROCESSING
sw         25683.4  lb             2.00
fb           14200  wtfile
bs               4  proc             ft
tpwr            57  fn         not used
pw             8.7
d1           4.000  werr
tof         2271.7  wexp
nt           40000  wbs
ct             292  wnt
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp          -202.7
wp         21464.1
vs              34
sc               0
wc             250
hzmm         85.86
is          500.00
rfl         8825.0
rfp         7745.2
th               6
ins        100.000
nm  no  ph
```

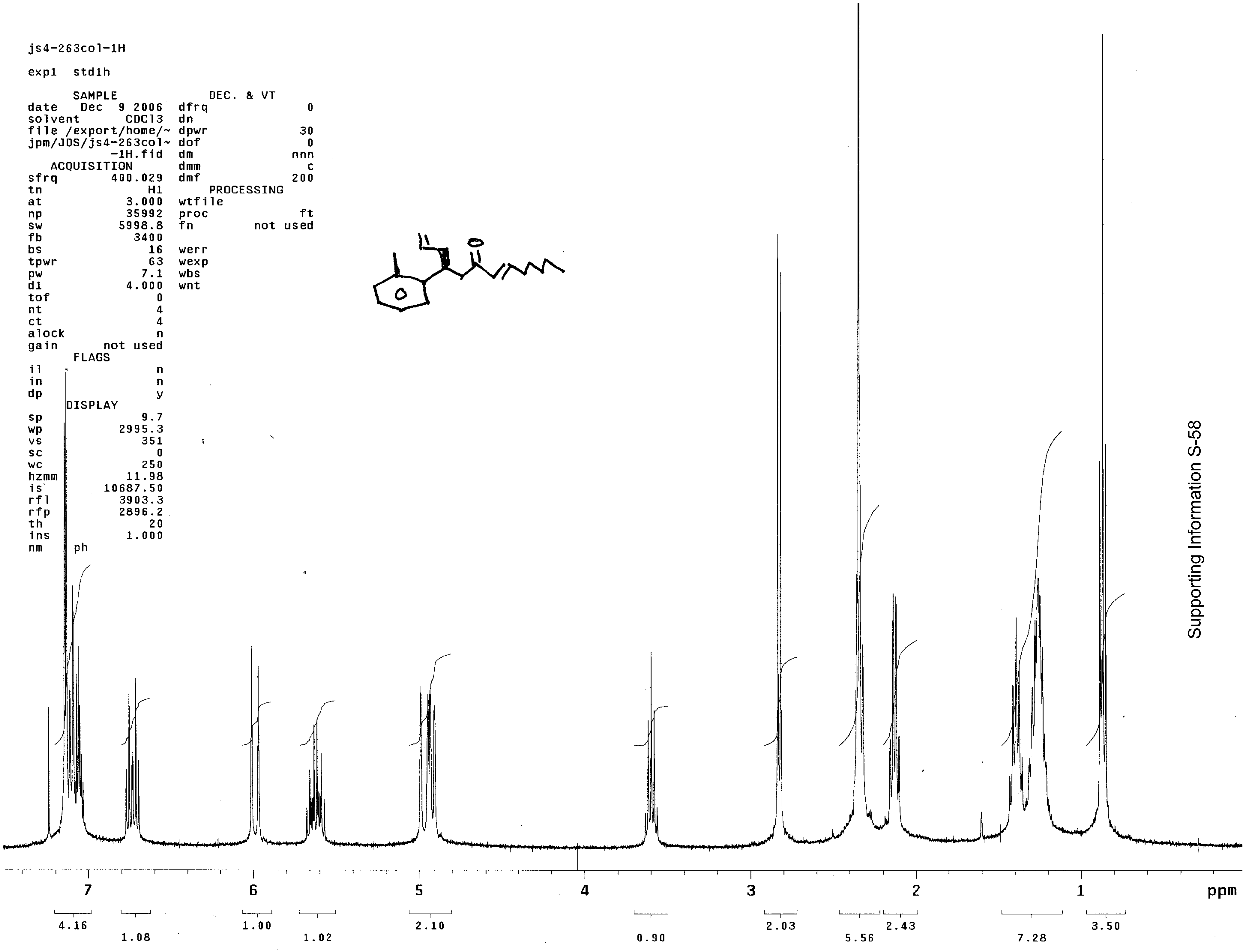






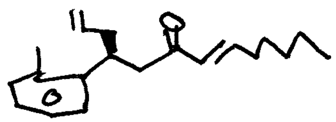
```
js4-282col-1H

exp1  std1h

      SAMPLE            DEC. & VT
date   Dec 11 2006  dfrq             0
solvent       CDCl3  dn
file /export/home/~ dpwr            30
jpm/JDS/js4-282col~ dof              0
          -1H.fid   dm             nnn
   ACQUISITION      dmm              c
sfrq        400.029 dmf            200
tn               H1       PROCESSING
at            3.000 wtfile
np            35992 proc            ft
sw           5998.8 fn        not used
fb             3400
bs                4 werr
tpwr             63 wexp
pw              7.1 wbs
d1            4.000 wnt
tof               0
nt                8
ct                8
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
     DISPLAY
sp             48.3
wp           2916.6
vs              147
sc                0
wc              250
hzmm          11.67
is          9527.53
rfl          3903.1
rfp          2896.2
th               20
ins           1.000
nm    ph
```

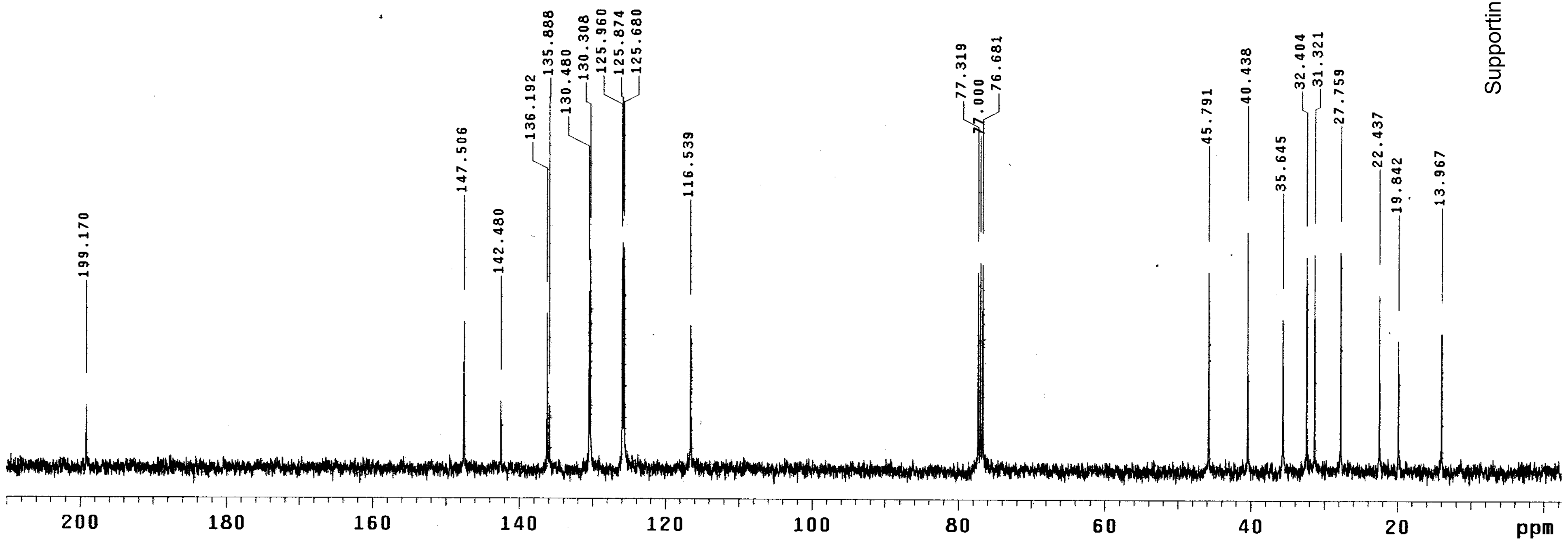

js4-282col-13C
exp2 std13c
SAMPLE
date Dec 11 2006
solvent CDCl3
file exp
ACQUISITION
sfrq 100.599
tn C13
at 0.640
np 32876
sw 25683.4
fb 14200
bs 4
tpwr 57
pw 8.7
d1 4.000
tof 2271.7
nt 40000
ct 136
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -237.2
wp 21329.3
vs 140
sc 0
wc 250
hzmm 85.32
is 500.00
rfl 8825.8
rfp 7745.2
th 13
ins 100.000
nm no ph
DEC. & VT
dfrq 400.029
dn H1
dpwr 45
dof 0
dm yyy
dmm w
dmf 8617
PROCESSING
lb 2.00
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
199.272
157.909
147.537
136.340
136.207
130.519
128.345
116.500
113.687
77.319
77.000
76.688
55.158
46.329
40.796
40.282
32.396
31.328
27.752
22.422
13.967
200
180
160
140
120
100
80
60
40
20
ppm
MeO



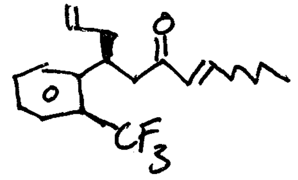
```
js4-263col-1H

exp1  std1h

       SAMPLE                DEC. & VT
date   Dec  9 2006  dfrq              0
solvent       CDCl3  dn
file /export/home/~ dpwr             30
jpm/JDS/js4-263col~ dof               0
           -1H.fid  dm              nnn
    ACQUISITION     dmm               c
sfrq        400.029 dmf             200
tn               H1      PROCESSING
at            3.000 wtfile
np            35992 proc             ft
sw           5998.8 fn         not used
fb             3400
bs               16 werr
tpwr             63 wexp
pw              7.1 wbs
d1            4.000 wnt
tof               0
nt                4
ct                4
alock             n
gain       not used
       FLAGS
il                n
in                n
dp                y
      DISPLAY
sp              9.7
wp           2995.3
vs              351
sc                0
wc              250
hzmm          11.98
is         10687.50
rfl          3903.3
rfp          2896.2
th               20
ins           1.000
nm      ph
```

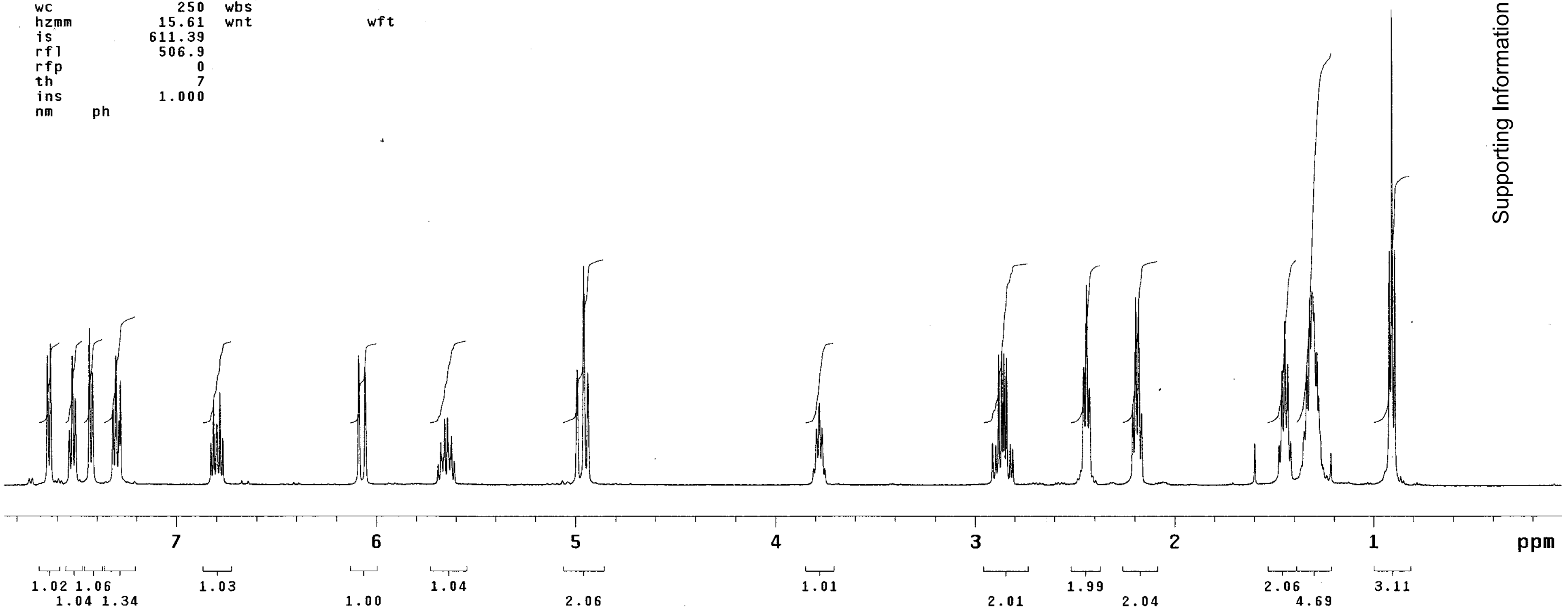
```
js4-263col-13C

exp2  std13c

        SAMPLE                DEC. & VT
date   Dec  9 2006   dfrq        400.029
solvent      CDCl3   dn               H1
file           exp   dpwr             45
    ACQUISITION      dof               0
sfrq       100.599   dm              yyy
tn             C13   dmm               w
at           0.640   dmf            8617
np           32876        PROCESSING
sw         25683.4   lb             2.00
fb           14200   wtfile
bs              16   proc             ft
tpwr            57   fn         not used
pw             8.7
d1           4.000   werr
tof         2271.7   wexp
nt           40000   wbs
ct              96   wnt
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
      DISPLAY
sp          -237.2
wp         21363.0
vs              38
sc               0
wc             250
hzmm         85.45
is          500.00
rfl         8825.8
rfp         7745.2
th               8
ins        100.000
nm  no  ph
```



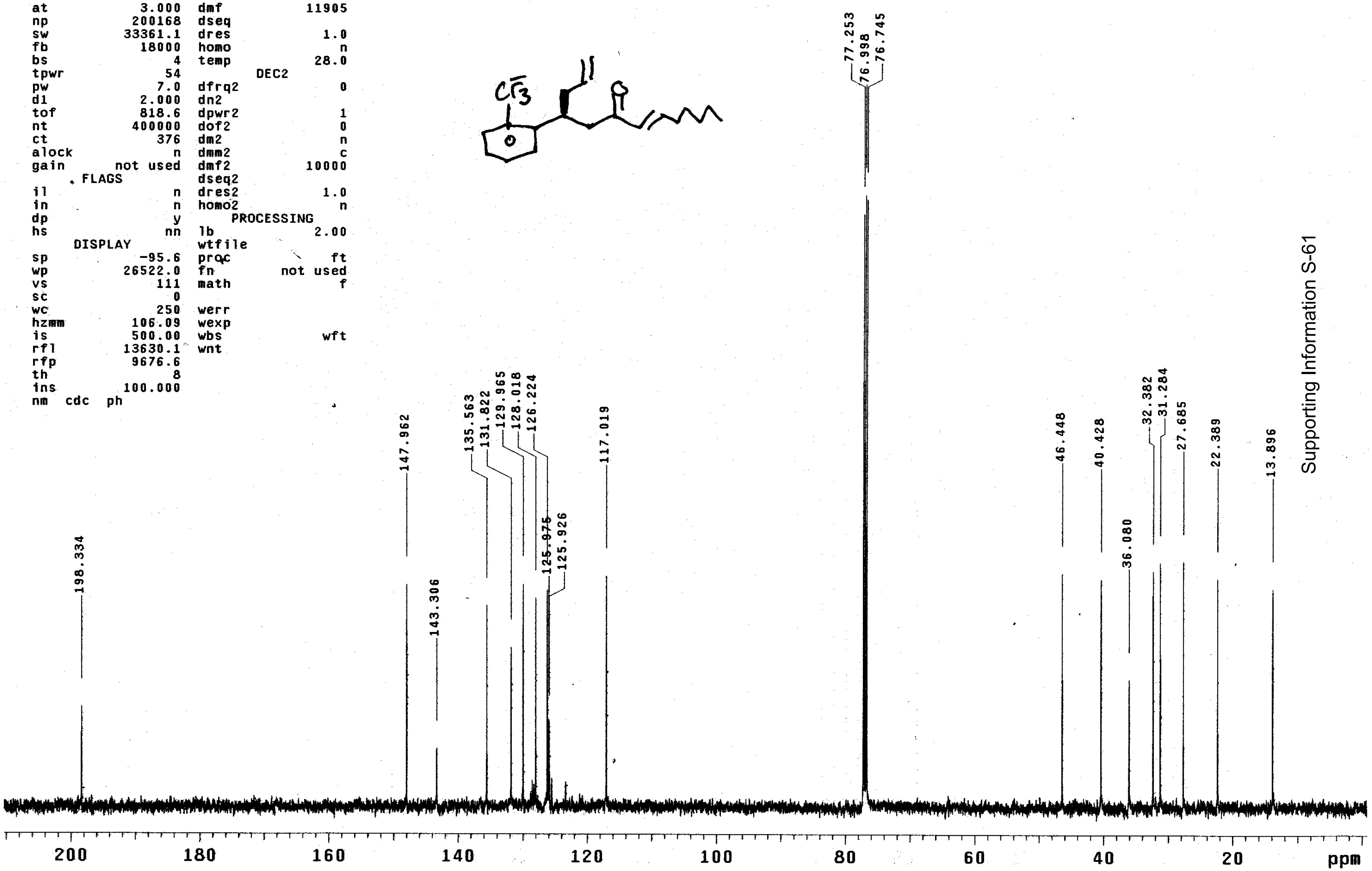


```
js4-292col

exp6  s2pul

      SAMPLE                   DEC. & VT
date   Dec  2 2006  dfrq          499.784
solvent       CDCl3  dn                  H1
file /export/home/~ dpwr                30
jpm/js4-292col.fid  dof                  0
   ACQUISITION      dm                 nnn
sfrq        499.784  dmm                 c
tn               H1  dmf               200
at            5.000  dseq
np            70058  dres              1.0
sw           7005.9  homo                n
fb             4000  temp             28.0
bs                4           DEC2
tpwr             56  dfrq2               0
pw              4.6  dn2
d1            4.000  dpwr2               1
tof           497.0  dof2                0
nt               16  dm2                 n
ct                8  dmm2                c
alock             n  dmf2              200
gain       not used  dseq2
      FLAGS          dres2             1.0
il                n  homo2               n
in                n       PROCESSING
dp                y  wtfile
hs               nn  proc               ft
     DISPLAY         fn           not used
sp             27.1  math                f
wp           3903.3
vs               75  wert
sc                0  wexp
wc              250  wbs
hzmm          15.61  wnt               wft
is           611.39
rfl           506.9
rfp               0
th                7
ins           1.000
nm     ph
```

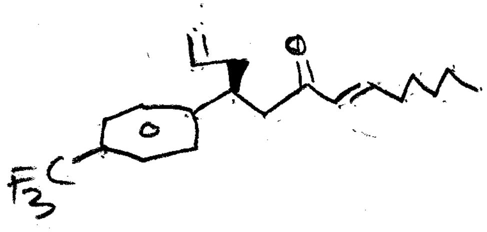


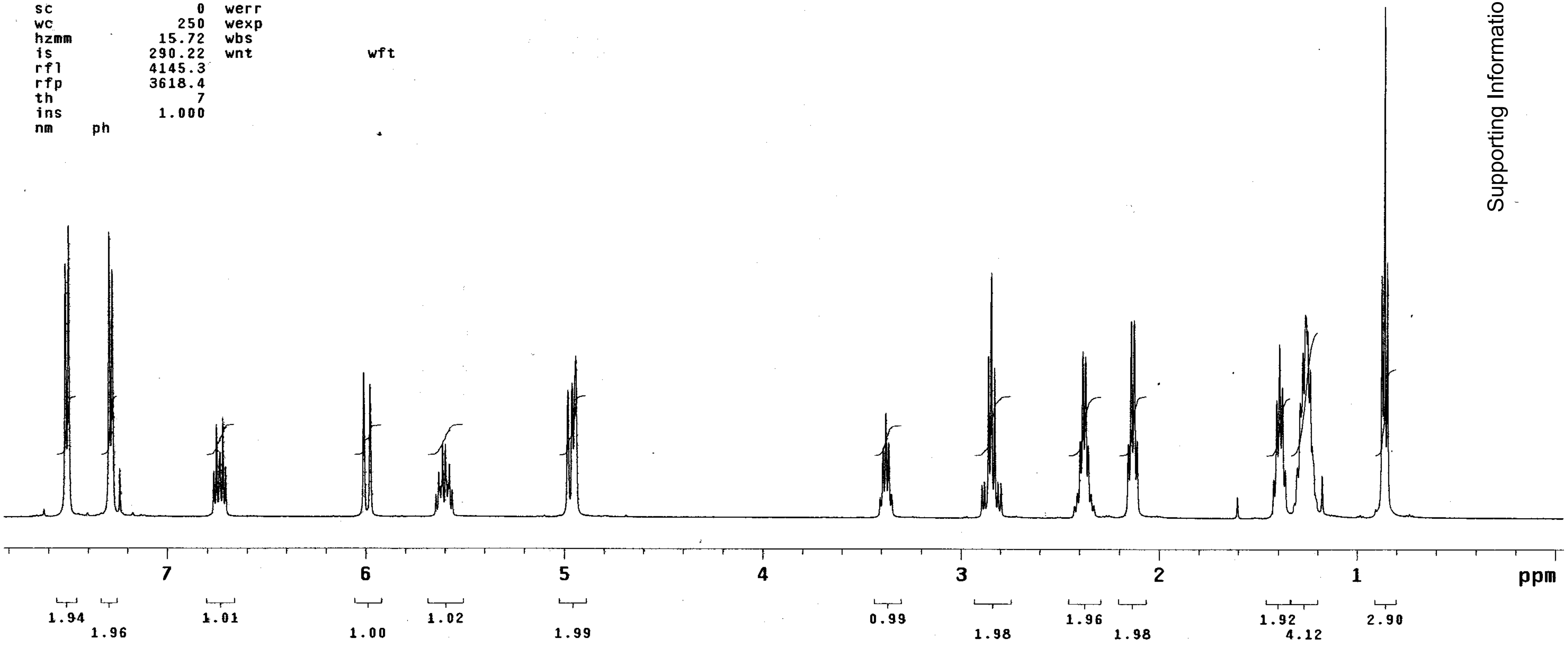


```
js4-292col-13c

exp1  s2pul

      SAMPLE              DEC. & VT
date   Dec  2 2006  dfrq       499.784
solvent      CDCl3  dn              H1
file           exp  dpwr            39
   ACQUISITION      dof              0
sfrq       125.683  dm             yyy
tn             C13  dmm              w
at           3.000  dmf          11905
np          200168  dseq
sw         33361.1  dres           1.0
fb           18000  homo             n
bs               4  temp          28.0
tpwr            54         DEC2
pw             7.0  dfrq2            0
d1           2.000  dn2
tof          818.6  dpwr2            1
nt          400000  dof2             0
ct             376  dm2              n
alock            n  dmm2             c
gain      not used  dmf2         10000
     FLAGS          dseq2
il               n  dres2          1.0
in               n  homo2            n
dp               y       PROCESSING
hs              nn  lb            2.00
     DISPLAY        wtfile
sp           -95.6  proc            ft
wp         26522.0  fn        not used
vs             111  math             f
sc               0
wc             250  werr
hzmm        106.09  wexp
is          500.00  wbs            wft
rfl        13630.1  wnt
rfp         9676.6
th               8
ins        100.000
nm  cdc  ph
```

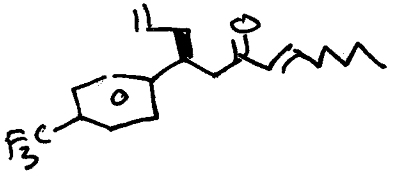


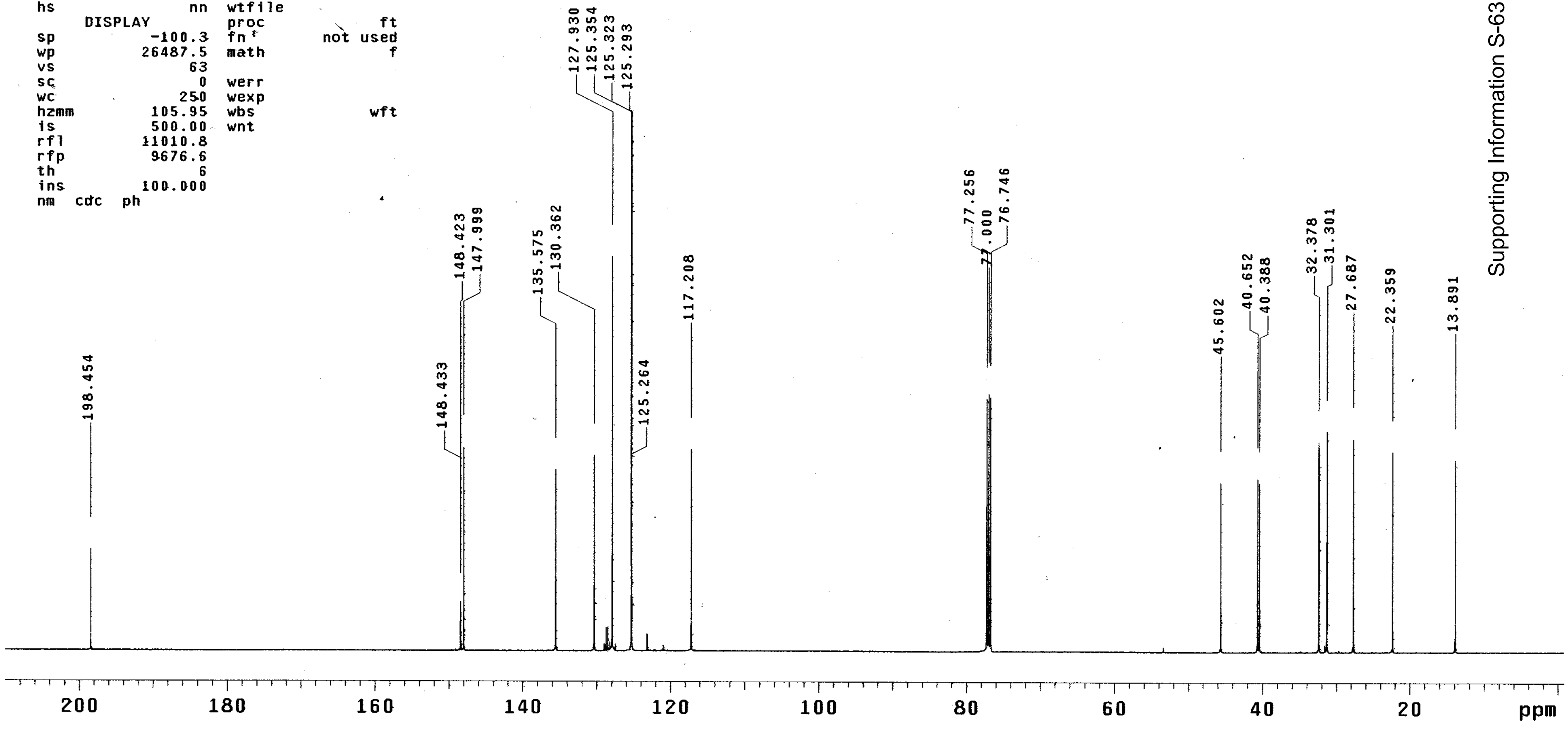
```
js5-1colmaj

exp1  s2pul

       SAMPLE                DEC. & VT
date   Dec  2 2006   dfrq         499.784
solvent       CDCl3   dn                H1
file            exp   dpwr              30
     ACQUISITION      dof                0
sfrq        499.784   dm               nnn
tn               H1   dmm                c
at            5.000   dmf              200
np            70058   dseq
sw           7005.9   dres             1.0
fb             4000   homo               n
bs                4   temp            28.0
tpwr             56             DEC2
pw              4.6   dfrq2              0
d1            4.000   dn2
tof           497.0   dpwr2              1
nt               16   dof2               0
ct                0   dm2                n
alock             n   dmm2               c
gain       not used   dmf2             200
       FLAGS          dseq2
il                n   dres2            1.0
in                n   homo2              n
dp                y        PROCESSING
hs               nn   wtfile
       DISPLAY        proc              ft
sp            -20.5   fn          not used
wp           3930.9   math               f
vs               81
sc                0   werr
wc              250   wexp
hzmm          15.72   wbs
is           290.22   wnt              wft
rfl          4145.3
rfp          3618.4
th                7
ins           1.000
nm      ph
```



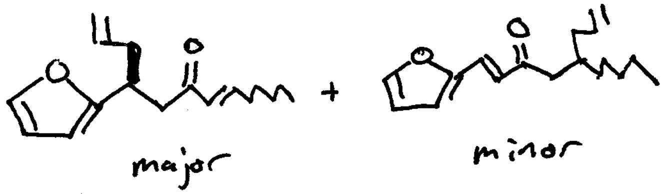


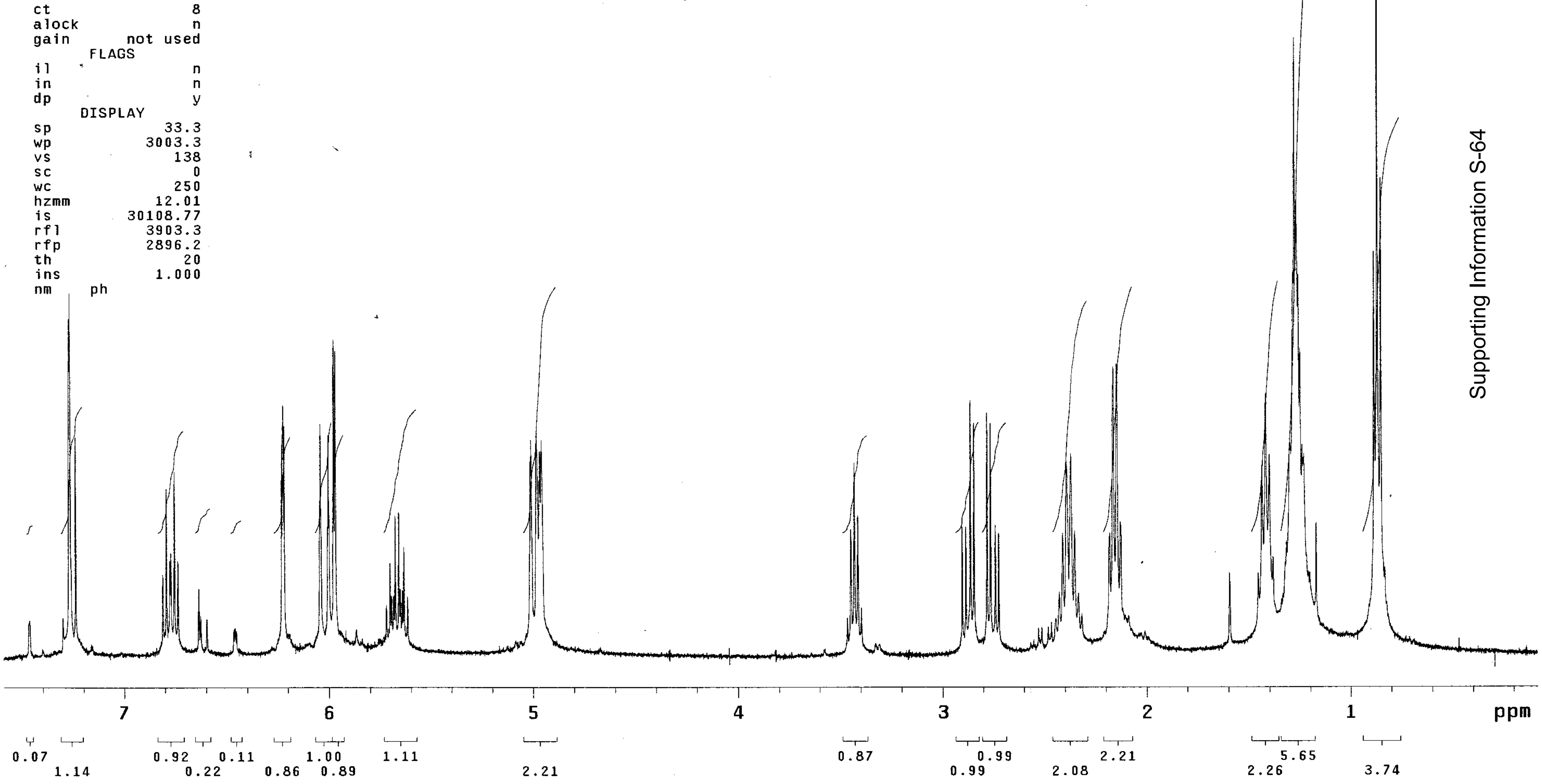
```
js5-1col-C

exp2  s2pul

      SAMPLE              DEC. & VT
date   Dec  5 2006  dfrq         499.784
solvent       CDCl3  dn                H1
file /export/home/~ dpwr               39
jpm/JS5-1col-C.fid  dof                 0
   ACQUISITION      dm                yyy
sfrq        125.684  dmm                w
tn              C13  dmf            11905
at            3.000  dseq
np           188754  dres             1.0
sw          31458.9  homo               n
fb            17000  temp            28.0
bs               16         DEC2
tpwr             54  dfrq2              0
pw              7.0  dn2
d1            2.000  dpwr2              1
tof          2486.7  dof2               0
nt            15000  dm2                n
ct            15000  dmm2               c
alock             n  dmf2           10000
gain       not used  dseq2
      FLAGS          dres2            1.0
il                n  homo2              n
in                n       PROCESSING
dp                y  lb              1.00
hs               nn  wtfile
     DISPLAY         proc              ft
sp           -100.3  fn          not used
wp          26487.5  math               f
vs               63
sc                0  werr
wc              250  wexp
hzmm         105.95  wbs              wft
is           500.00  wnt
rfl         11010.8
rfp          9676.6
th                6
ins         100.000
nm  cdc  ph
```



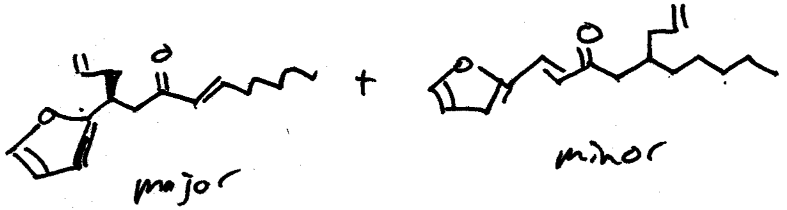


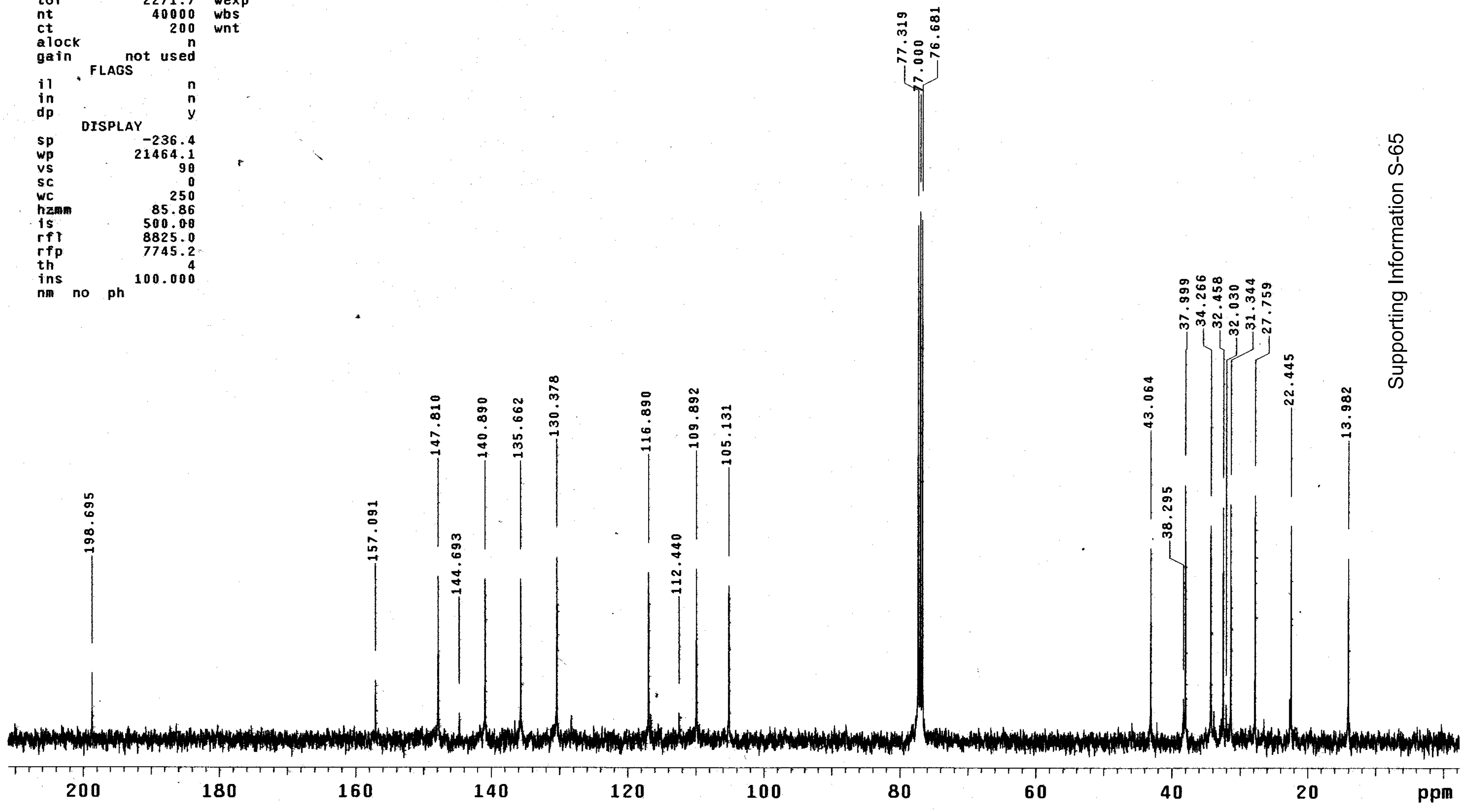
```
js5-2col-1H

exp1  std1h

      SAMPLE                DEC. & VT
date   Dec 22 2006  dfrq              0
solvent       CDCl3  dn
file /export/home/~  dpwr            30
jpm/JDS/js5-2col-1~  dof              0
              H.fid  dm             nnn
   ACQUISITION       dmm              c
sfrq        400.029  dmf            200
tn               H1       PROCESSING
at            3.000  wtfile
np            35992  proc            ft
sw           5998.8  fn        not used
fb             3400
bs                4  werr
tpwr             63  wexp
pw              7.1  wbs
d1            4.000  wnt
tof               0
nt               16
ct                8
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
     DISPLAY
sp             33.3
wp           3003.3
vs              138
sc                0
wc              250
hzmm          12.01
is         30108.77
rfl          3903.3
rfp          2896.2
th               20
ins           1.000
nm      ph
```

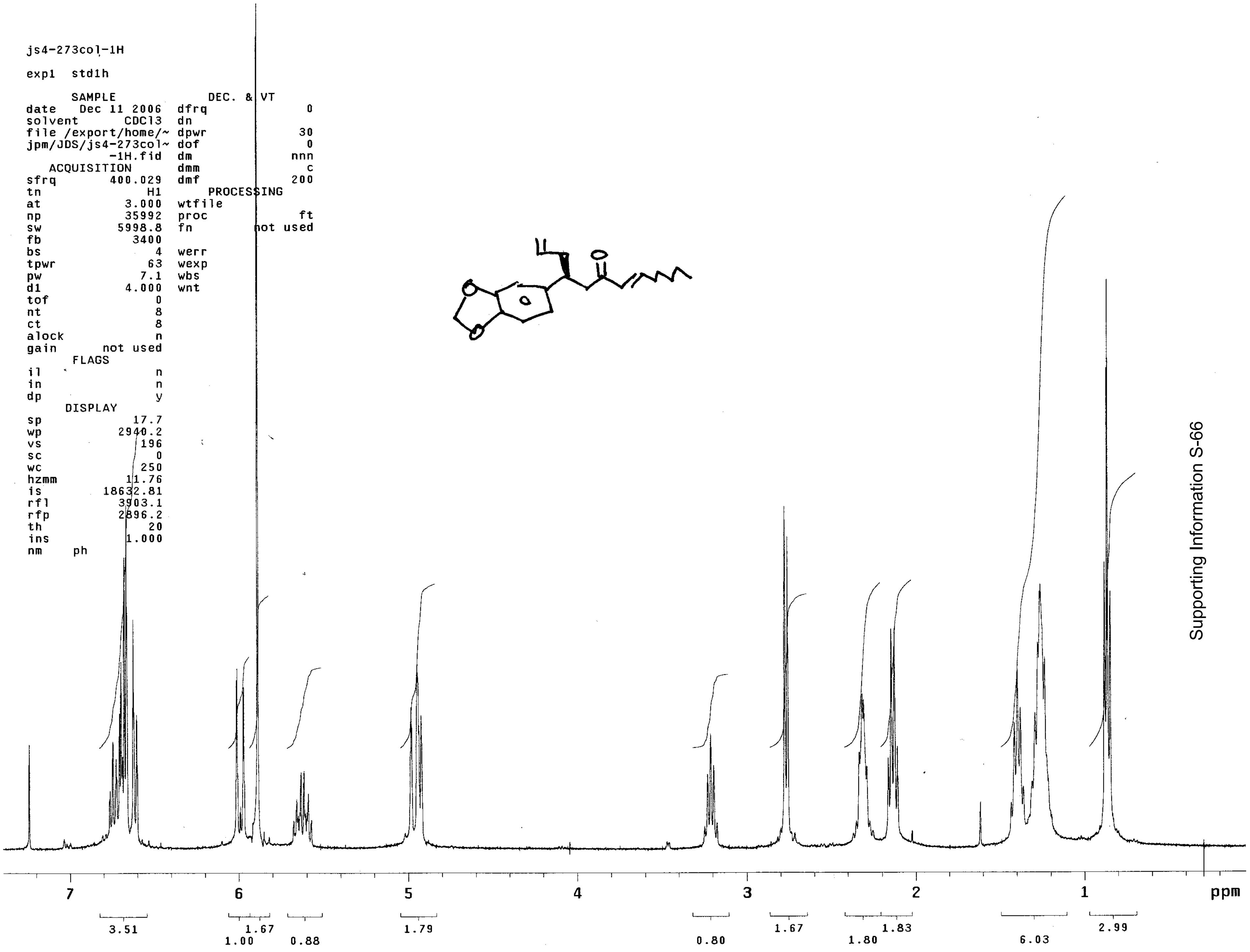




```
js5-2col-13C

exp2  std13c

      SAMPLE              DEC. & VT
date   Dec 22 2006  dfrq       400.029
solvent      CDCl3  dn              H1
file           exp  dpwr            45
   ACQUISITION      dof              0
sfrq       100.599  dm             yyy
tn             C13  dmm              w
at           0.640  dmf           8617
np           32876        PROCESSING
sw         25683.4  lb            2.00
fb           14200  wtfile
bs               4  proc            ft
tpwr            57  fn        not used
pw             8.7
d1           4.000  werr
tof         2271.7  wexp
nt           40000  wbs
ct             200  wnt
alock            n
gain      not used
     FLAGS
il               n
in               n
dp               y
     DISPLAY
sp          -236.4
wp         21464.1
vs              90
sc               0
wc             250
hzmm         85.86
is          500.00
rfl         8825.0
rfp         7745.2
th               4
ins        100.000
nm  no  ph
```

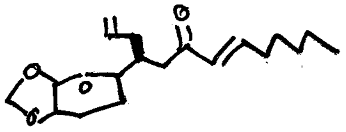


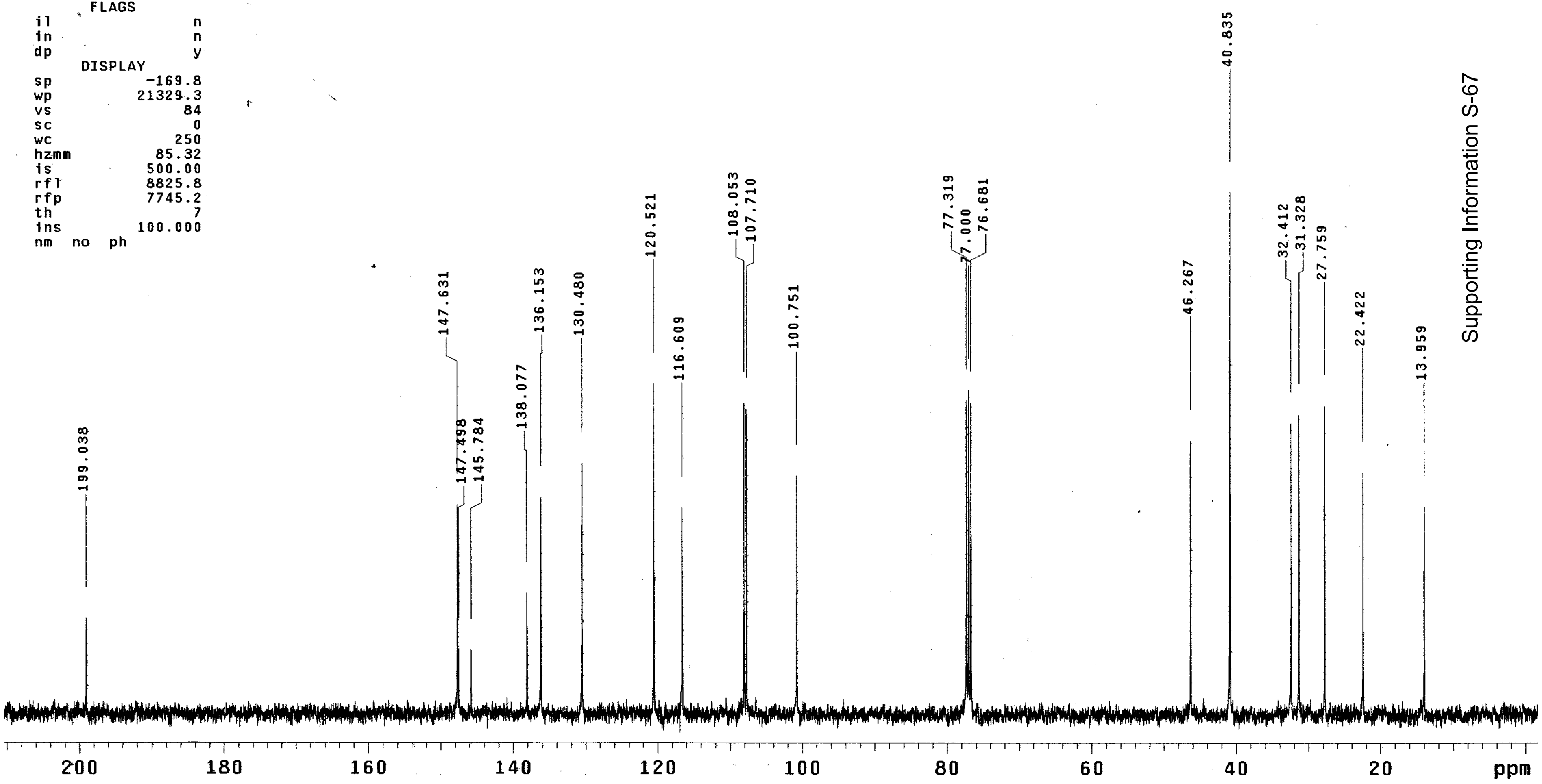




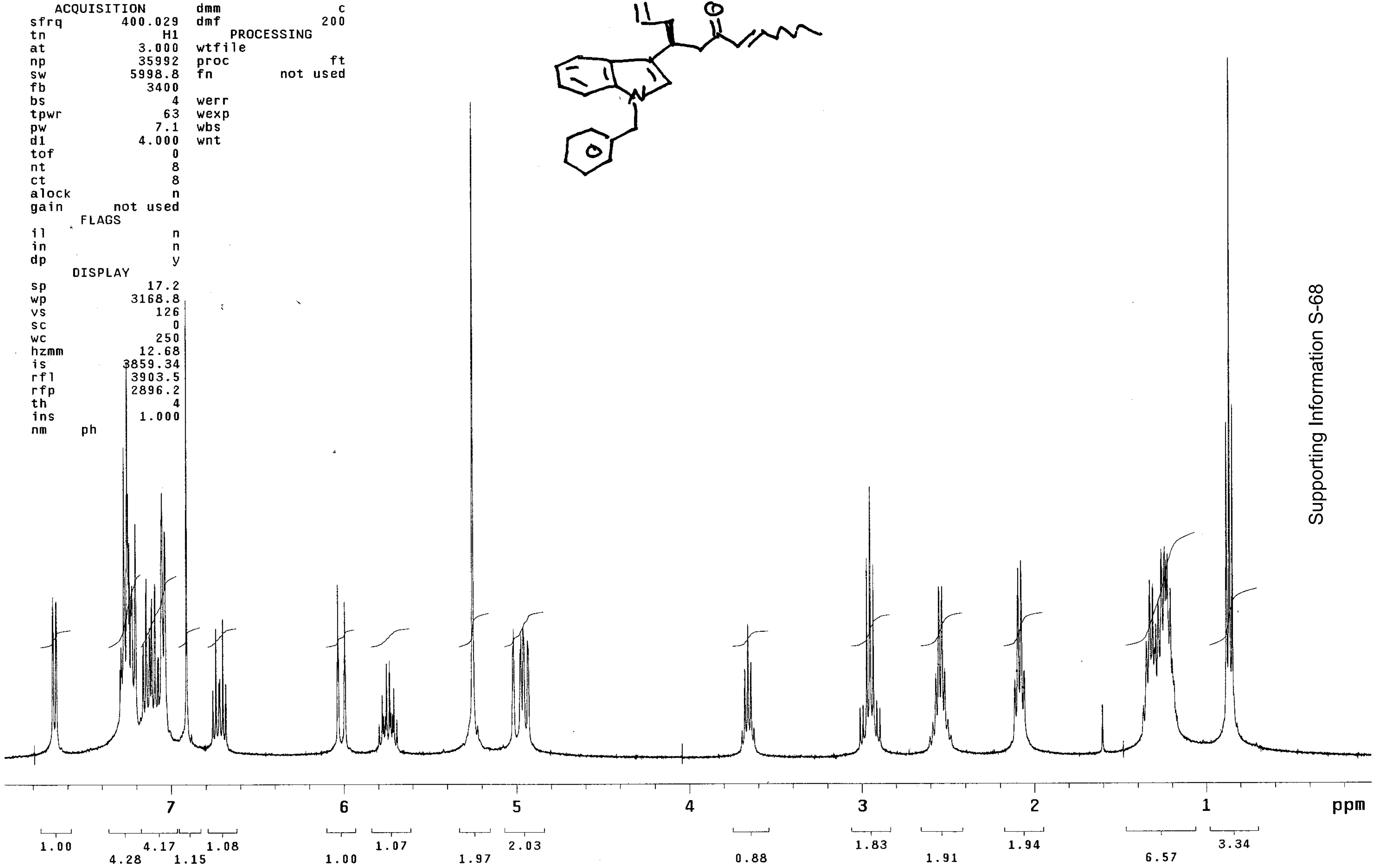
```
js4-273col-1H

exp1  std1h

      SAMPLE                  DEC. & VT
date   Dec 11 2006  dfrq                 0
solvent       CDCl3  dn
file /export/home/~ dpwr                30
jpm/JDS/js4-273col~ dof                  0
           -1H.fid  dm                 nnn
    ACQUISITION     dmm                  c
sfrq        400.029 dmf                200
tn               H1       PROCESSING
at            3.000 wtfile
np            35992 proc                ft
sw           5998.8 fn            not used
fb             3400
bs                4 werr
tpwr             63 wexp
pw              7.1 wbs
d1            4.000 wnt
tof               0
nt                8
ct                8
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
      DISPLAY
sp             17.7
wp           2940.2
vs              196
sc                0
wc              250
hzmm          11.76
is         18632.81
rfl          3903.1
rfp          2896.2
th               20
ins           1.000
nm     ph
```

```
js4-273col-13C

exp2  std13c

      SAMPLE               DEC. & VT
date   Dec 11 2006  dfrq        400.029
solvent      CDCl3  dn               H1
file           exp  dpwr             45
   ACQUISITION      dof               0
sfrq       100.599  dm              yyy
tn             C13  dmm               w
at           0.640  dmf            8617
np           32876        PROCESSING
sw         25683.4  lb             2.00
fb           14200  wtfile
bs               4  proc             ft
tpwr            57  fn         not used
pw             8.7
d1           4.000  werr
tof         2271.7  wexp
nt           40000  wbs
ct             168  wnt
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp          -169.8
wp         21329.3
vs              84
sc               0
wc             250
hzmm         85.32
is          500.00
rfl         8825.8
rfp         7745.2
th               7
ins        100.000
nm  no  ph
```

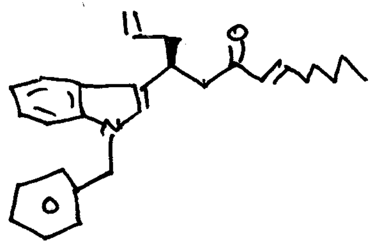


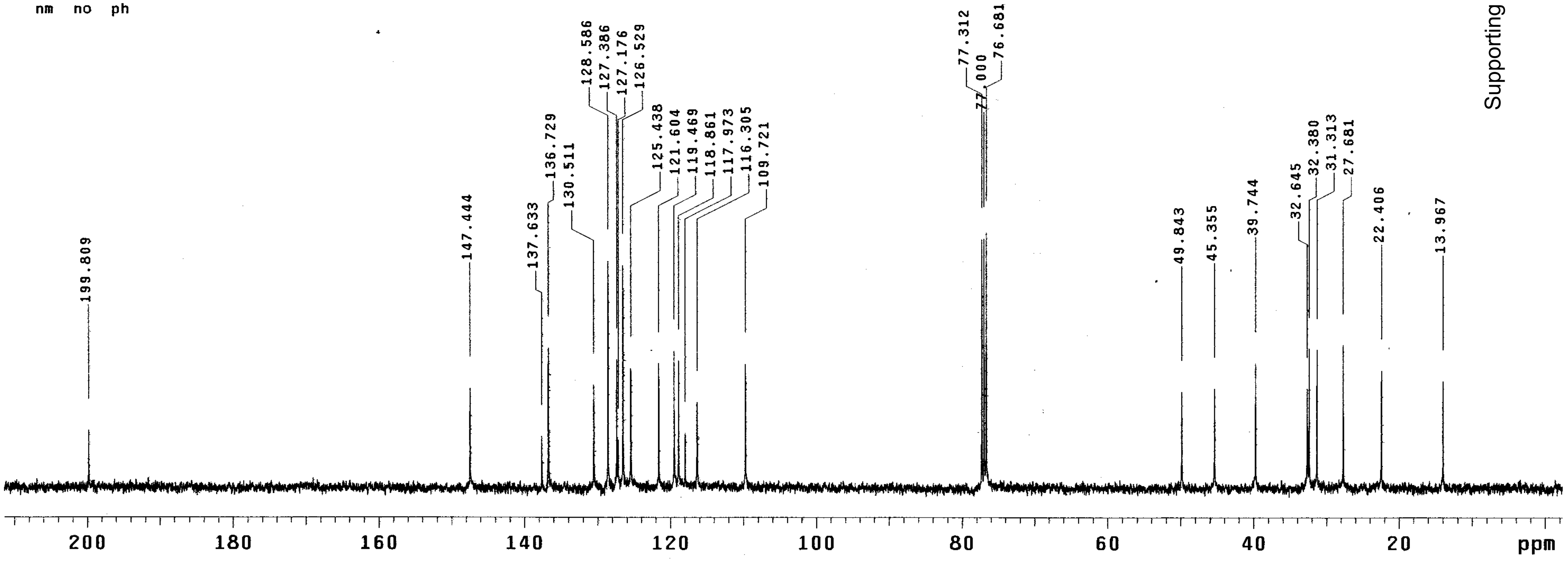


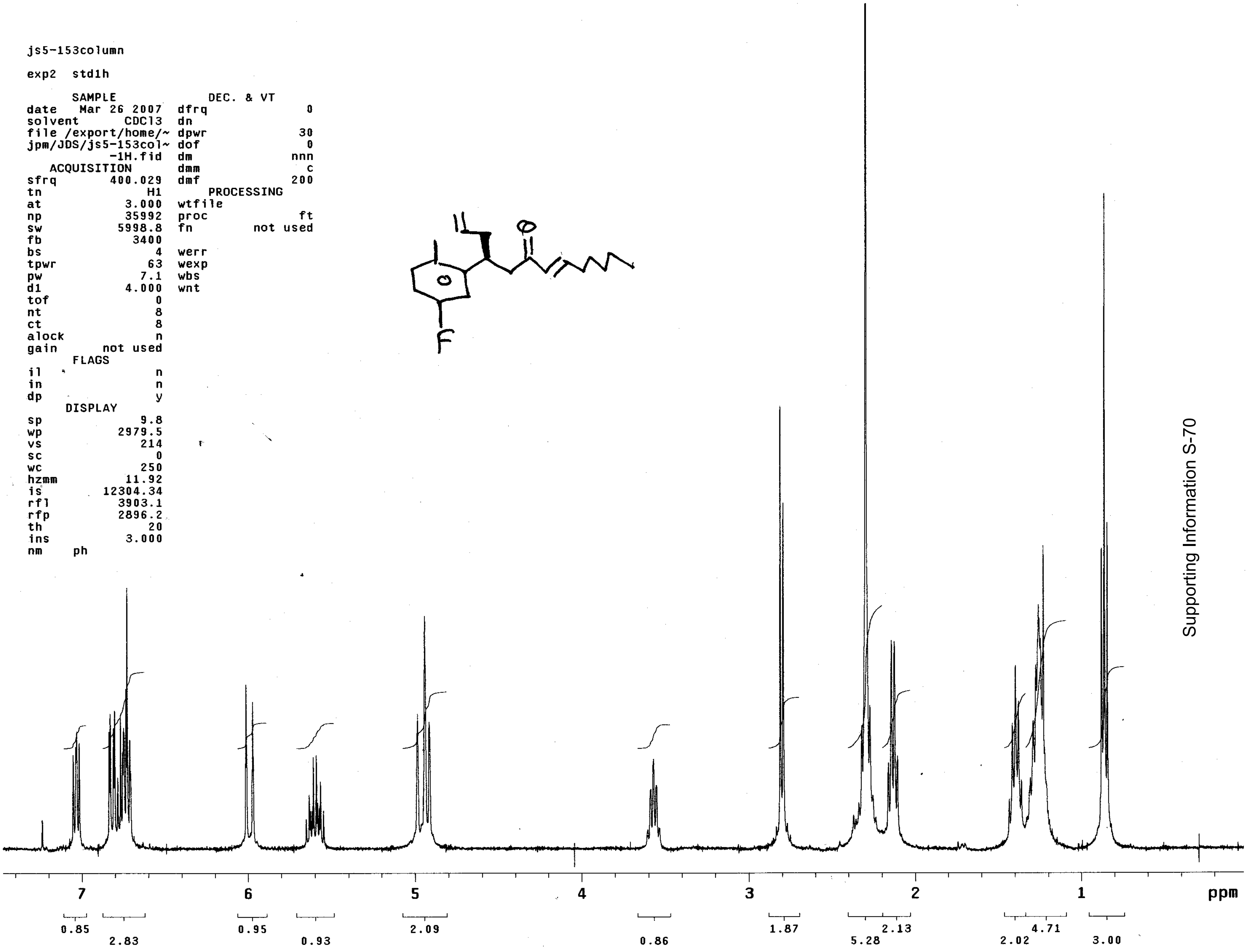
```
js4-280col-1H

exp1  std1h

      SAMPLE              DEC. & VT
date   Dec 22 2006  dfrq              0
solvent       CDCl3  dn
file /export/home/~  dpwr             30
jpm/JDS/js4-280col~  dof               0
          -1H.fid   dm               nnn
   ACQUISITION      dmm                c
sfrq        400.029  dmf              200
tn               H1       PROCESSING
at            3.000  wtfile
np            35992  proc              ft
sw           5998.8  fn          not used
fb             3400
bs                4  werr
tpwr             63  wexp
pw              7.1  wbs
d1            4.000  wnt
tof               0
nt                8
ct                8
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
      DISPLAY
sp             17.2
wp           3168.8
vs              126
sc                0
wc              250
hzmm          12.68
is          3859.34
rfl          3903.5
rfp          2896.2
th                4
ins           1.000
nm     ph
```



```
js4-280col-13C

exp2  std13c

      SAMPLE               DEC. & VT
date   Dec 22 2006  dfrq        400.029
solvent      CDCl3  dn               H1
file           exp  dpwr             45
   ACQUISITION      dof               0
sfrq       100.599  dm              yyy
tn             C13  dmm               w
at           0.640  dmf            8617
np           32876       PROCESSING
sw         25683.4  lb             2.00
fb           14200  wtfile
bs               4  proc             ft
tpwr            57  fn         not used
pw             8.7
d1           4.000  werr
tof         2271.7  wexp
nt            4000  wbs
ct              32  wnt
alock            n
gain      not used
     FLAGS
il               n
in               n
dp               y
    DISPLAY
sp          -240.4
wp         21497.8
vs              41
sc               0
wc             250
hzmm         85.99
is          500.00
rfl         8828.9
rfp         7745.2
th               5
ins        100.000
nm  no  ph
```

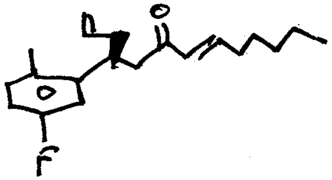


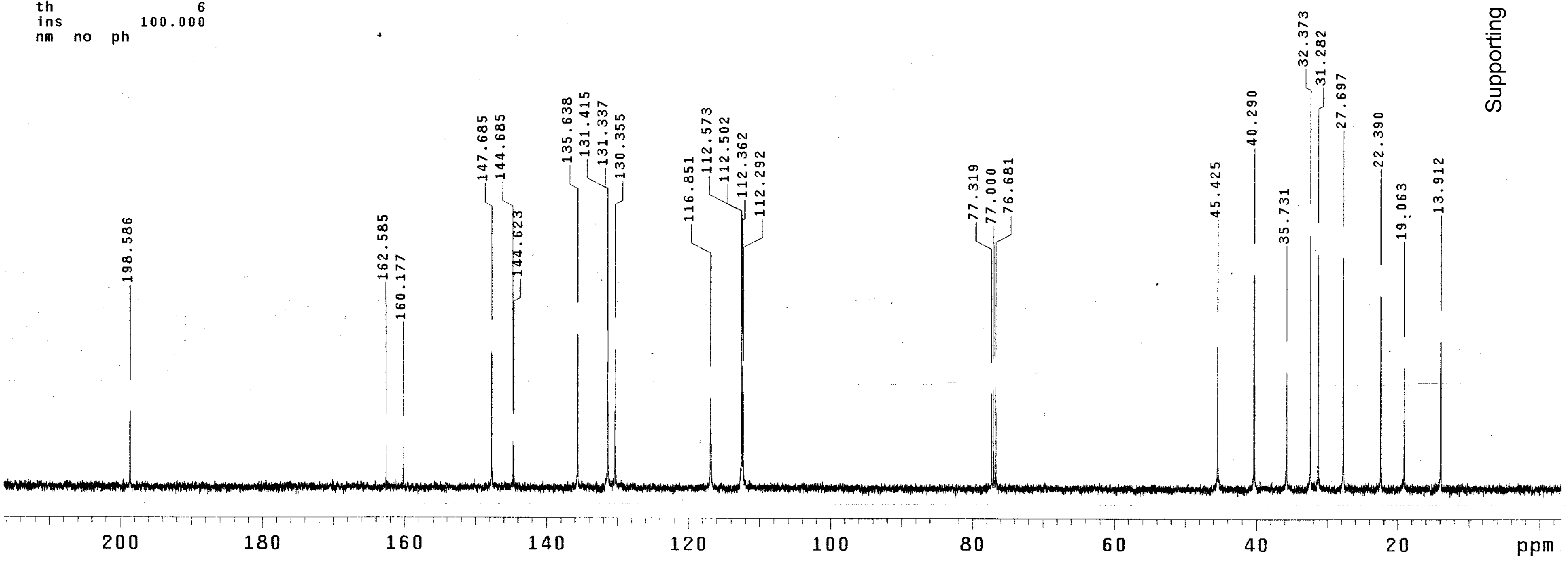


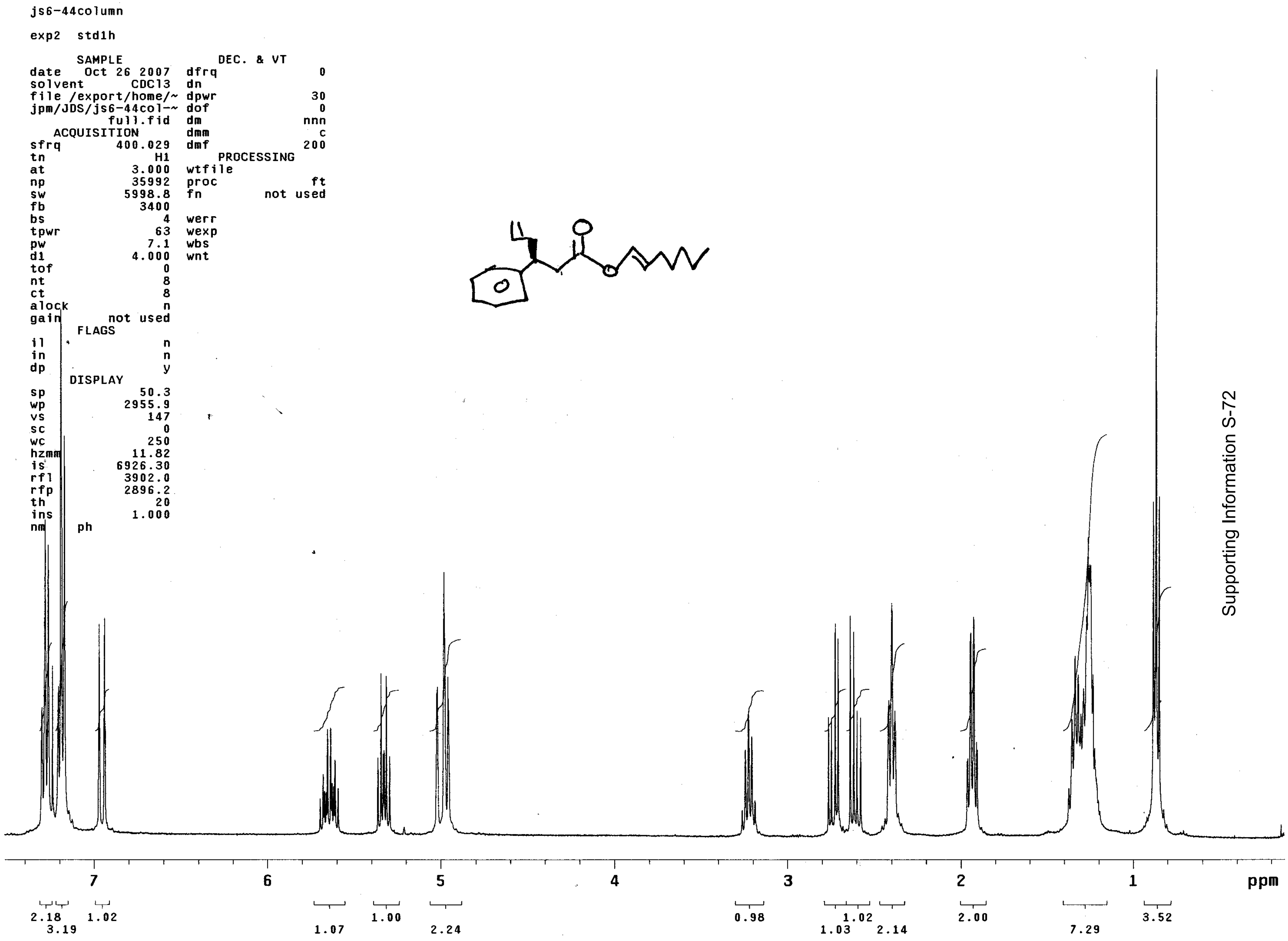


```
js5-153column

exp2  std1h

      SAMPLE              DEC. & VT
date   Mar 26 2007  dfrq            0
solvent      CDCl3  dn
file /export/home/~ dpwr           30
jpm/JDS/js5-153col~ dof             0
          -1H.fid   dm            nnn
   ACQUISITION      dmm             c
sfrq        400.029 dmf           200
tn               H1       PROCESSING
at            3.000 wtfile
np            35992 proc           ft
sw           5998.8 fn       not used
fb             3400
bs                4 werr
tpwr             63 wexp
pw              7.1 wbs
d1            4.000 wnt
tof               0
nt                8
ct                8
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
     DISPLAY
sp              9.8
wp           2979.5
vs              214
sc                0
wc              250
hzmm          11.92
is         12304.34
rfl          3903.1
rfp          2896.2
th               20
ins           3.000
nm    ph
```

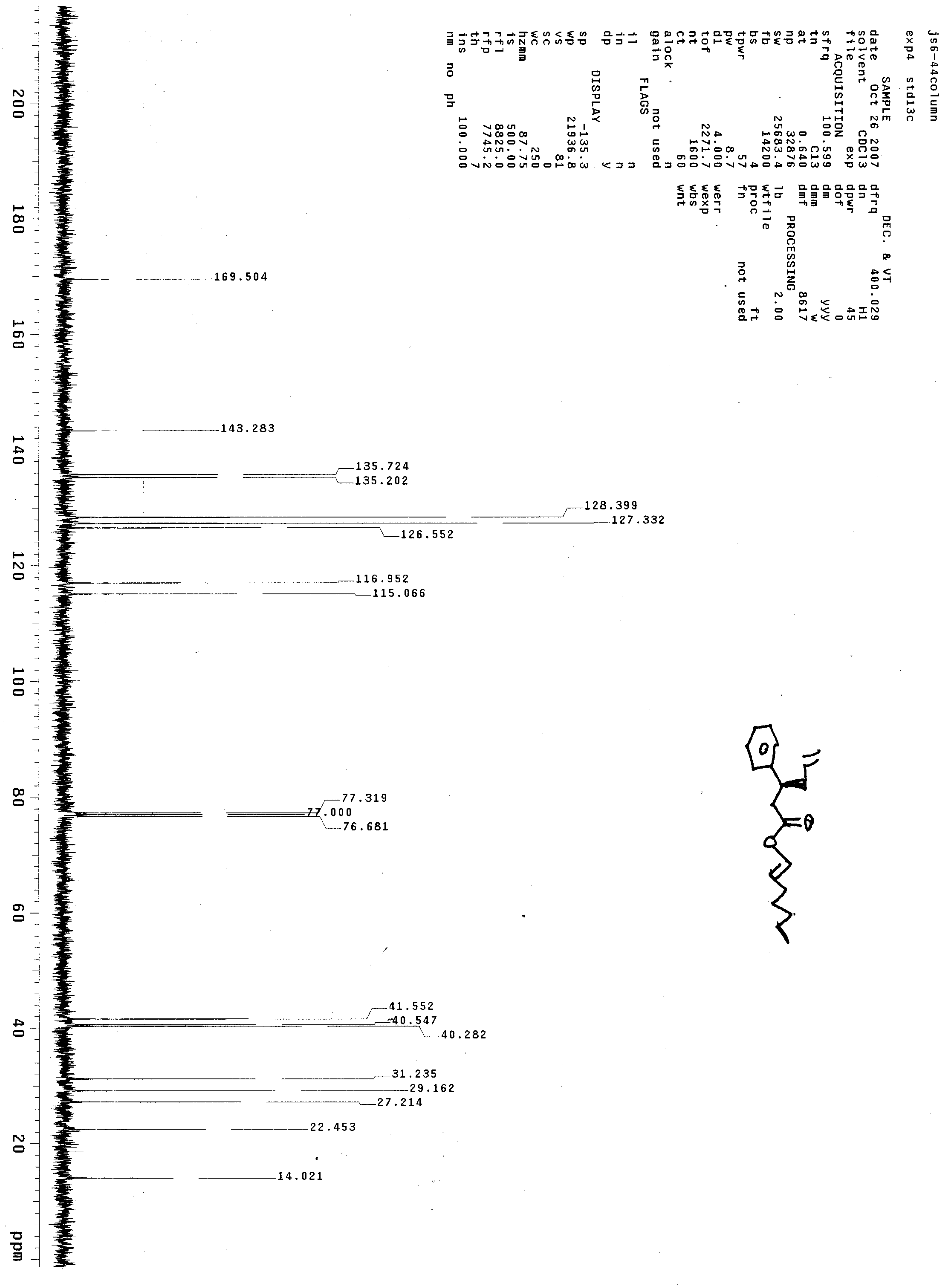
```
js5-153column

exp2  std13c

      SAMPLE              DEC. & VT
date   Mar 26 2007  dfrq         400.029
solvent       CDCl3  dn                H1
file /export/home/~ dpwr               45
jpm/JDS/js5-153col~ dof                 0
             -2.fid  dm               yyy
   ACQUISITION       dmm                w
sfrq        100.599  dmf             8617
tn              C13       PROCESSING
at            0.640  lb              1.00
np            32876  wtfile
sw          25683.4  proc              ft
fb            14200  fn          not used
bs                4
tpwr             57  werr
pw              8.7  wexp
d1            4.000  wbs
tof          2271.7  wnt
nt             1600
ct               40
alock             n
gain*      not used
      FLAGS
il                n
in                n
dp                y
     DISPLAY
sp           -308.6
wp          22071.6
vs               40
sc                0
wc              250
hzmm          88.29
is           500.00
rfl          8829.7
rfp          7745.2
th                6
ins         100.000
nm  no  ph
```

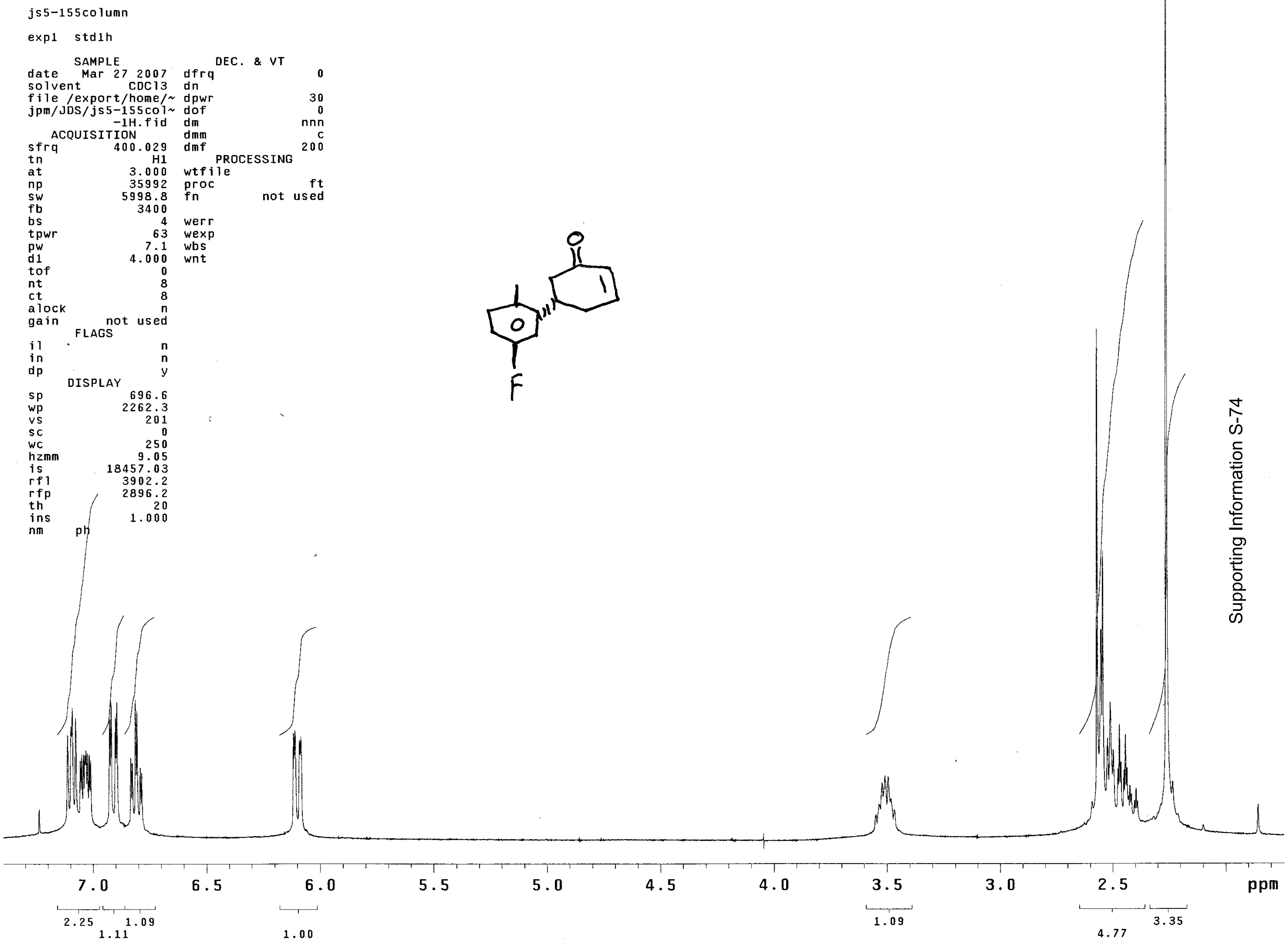






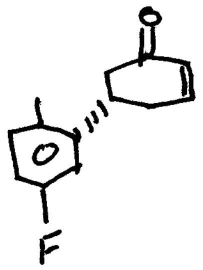
```
js6-44column

exp2  std1h

      SAMPLE                 DEC. & VT
date   Oct 26 2007  dfrq              0
solvent      CDCl3  dn
file /export/home/~ dpwr             30
jpm/JDS/js6-44col-~ dof               0
          full.fid  dm              nnn
    ACQUISITION     dmm               c
sfrq       400.029  dmf             200
tn              H1       PROCESSING
at           3.000  wtfile
np           35992  proc             ft
sw          5998.8  fn         not used
fb            3400
bs               4  werr
tpwr            63  wexp
pw             7.1  wbs
d1           4.000  wnt
tof              0
nt               8
ct               8
alock            n
gain      not used
       FLAGS
il               n
in               n
dp               y
       DISPLAY
sp            50.3
wp          2955.9
vs             147
sc               0
wc             250
hzmm         11.82
is         6926.30
rfl         3902.0
rfp         2896.2
th              20
ins          1.000
nm     ph
```

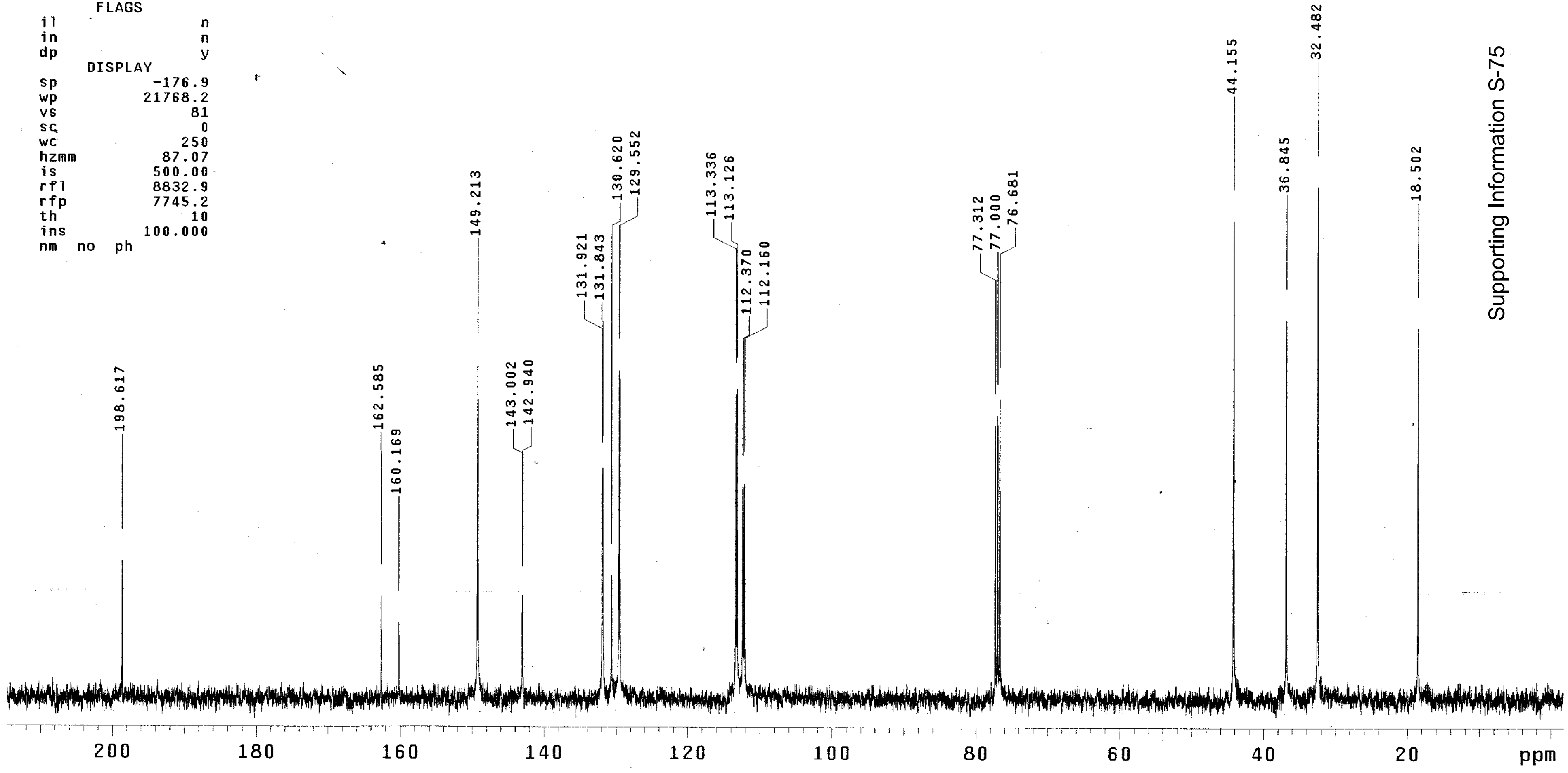

js6-44column
exp4 std13c
SAMPLE
date Oct 26 2007
solvent CDCl3
file exp
ACQUISITION
sfrq 100.599
tn C13
at 0.640
np 32876
sw 25683.4
fb 14200
bs 4
tpwr 57
pw 8.7
d1 4.000
tof 2271.7
nt 1600
ct 60
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -135.3
wp 21936.8
vs 81
sc 0
wc 250
hzmm 87.75
is 500.00
rfl 8825.0
rfp 7745.2
th 7
ins 100.000
nm no ph
DEC. & VT
dfrq 400.029
dn H1
dpwr 45
dof 0
dm yyy
dmm w
dmf 8617
PROCESSING
lb 2.00
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
169.504
143.283
135.724
135.202
128.399
127.332
126.552
116.952
115.066
77.319
77.000
76.681
41.552
40.547
40.282
31.235
29.162
27.214
22.453
14.021
200
180
160
140
120
100
80
60
40
20
ppm



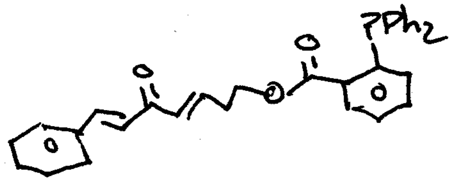
```
js5-155column

exp1  stdlh

      SAMPLE                DEC. & VT
date   Mar 27 2007  dfrq              0
solvent      CDCl3  dn
file /export/home/~ dpwr             30
jpm/JDS/js5-155col~ dof               0
           -1H.fid  dm              nnn
   ACQUISITION      dmm               c
sfrq       400.029  dmf             200
tn              H1       PROCESSING
at           3.000  wtfile
np           35992  proc             ft
sw          5998.8  fn         not used
fb            3400
bs               4  werr
tpwr            63  wexp
pw             7.1  wbs
d1           4.000  wnt
tof              0
nt               8
ct               8
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp           696.6
wp          2262.3
vs             201
sc               0
wc             250
hzmm          9.05
is        18457.03
rfl         3902.2
rfp         2896.2
th              20
ins          1.000
nm     ph
```

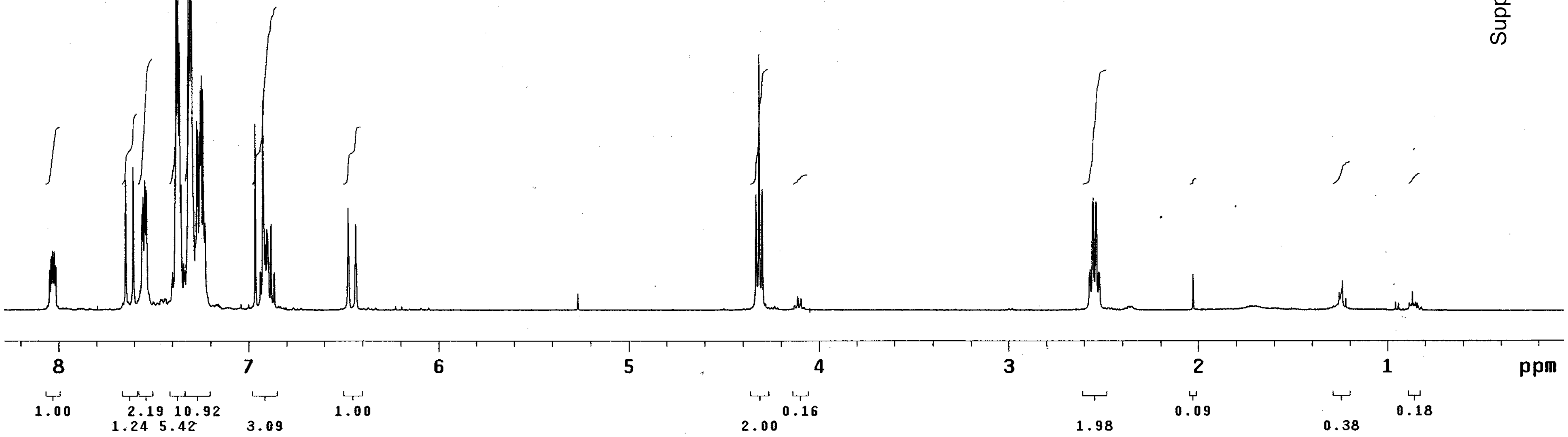
```
js5-155column

exp1  std13c

      SAMPLE              DEC. & VT
date   Mar 27 2007  dfrq        400.029
solvent       CDCl3  dn               H1
file /export/home/~ dpwr              45
jpm/JDS/js5-155col~ dof                0
         -13C.fid   dm               yyy
   ACQUISITION      dmm                w
sfrq        100.599 dmf             8617
tn              C13       PROCESSING
at            0.640 lb              2.00
np            32876 wtfile
sw          25683.4 proc              ft
fb            14200 fn          not used
bs                4
tpwr             57 werr
pw              8.7 wexp
d1            4.000 wbs
tof          2271.7 wnt
nt             1600
ct               60
alock             n
gain     not used
      FLAGS
il                n
in                n
dp                y
      DISPLAY
sp           -176.9
wp          21768.2
vs               81
sc                0
wc              250
hzmm          87.07
is           500.00
rfl          8832.9
rfp          7745.2
th               10
ins         100.000
nm  no  ph
```



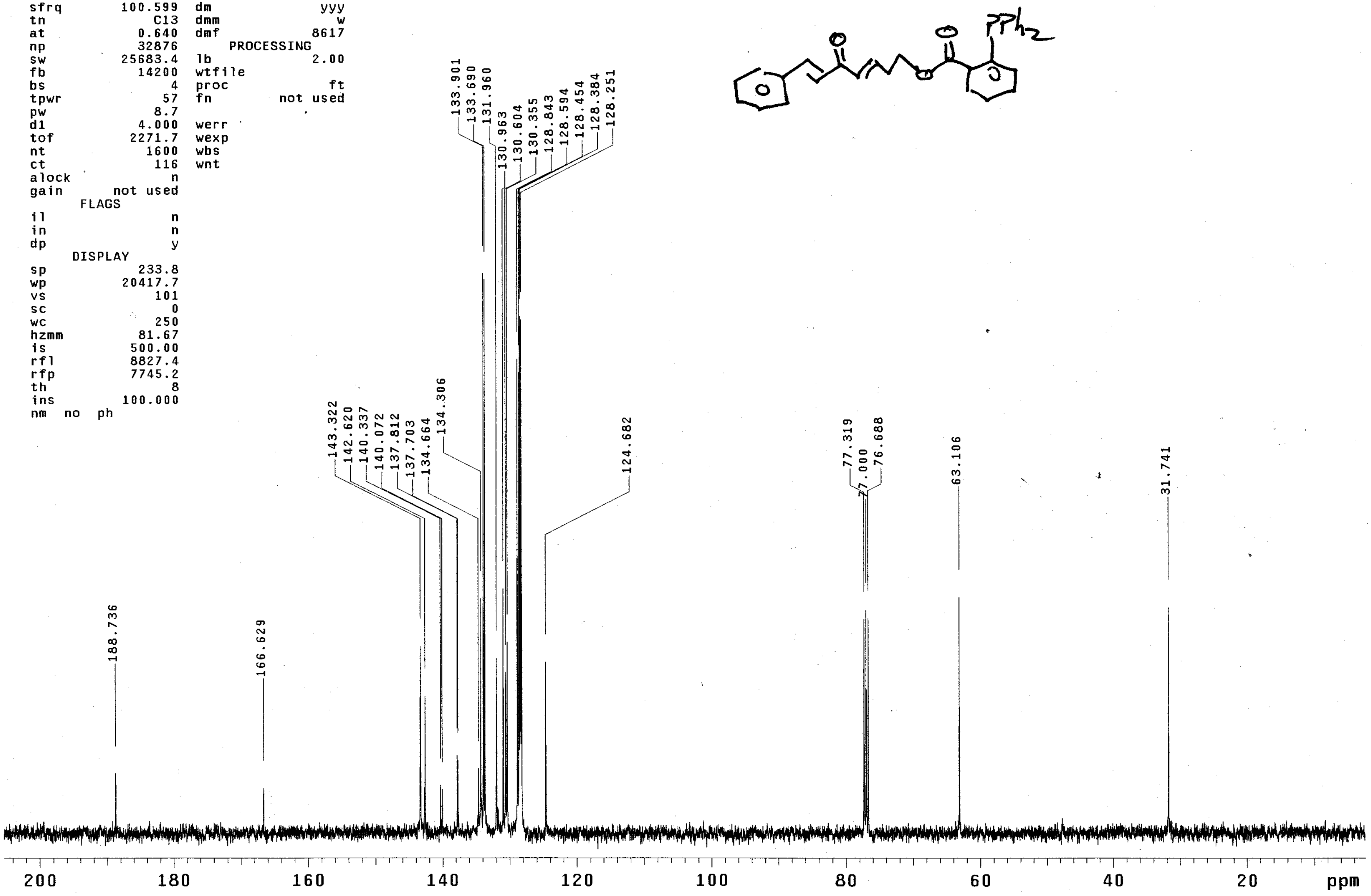


```
js5-261column

exp1  stdlh

     SAMPLE              DEC. & VT
date   Oct  9 2007  dfrq              0
solvent      CDCl3  dn
file /export/home/~ dpwr             30
jpm/JDS/js5-261col~ dof               0
        -full.fid   dm              nnn
   ACQUISITION      dmm               c
sfrq       400.029  dmf             200
tn              H1       PROCESSING
at           3.000  wtfile
np           35992  proc             ft
sw          5998.8  fn         not used
fb            3400
bs               4  werr
tpwr            63  wexp
pw             7.1  wbs
d1           4.000  wnt
tof              0
nt               8
ct               8
alock            n
gain     not used
      FLAGS
il               n
in               n
dp               y
      DISPLAY
sp            27.2
wp          3287.1
vs              63
sc               0
wc             250
hzmm         13.15
is        10936.49
rfl         3901.5
rfp         2896.2
th              20
ins          1.000
nm     ph
```

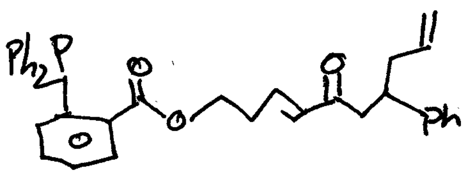


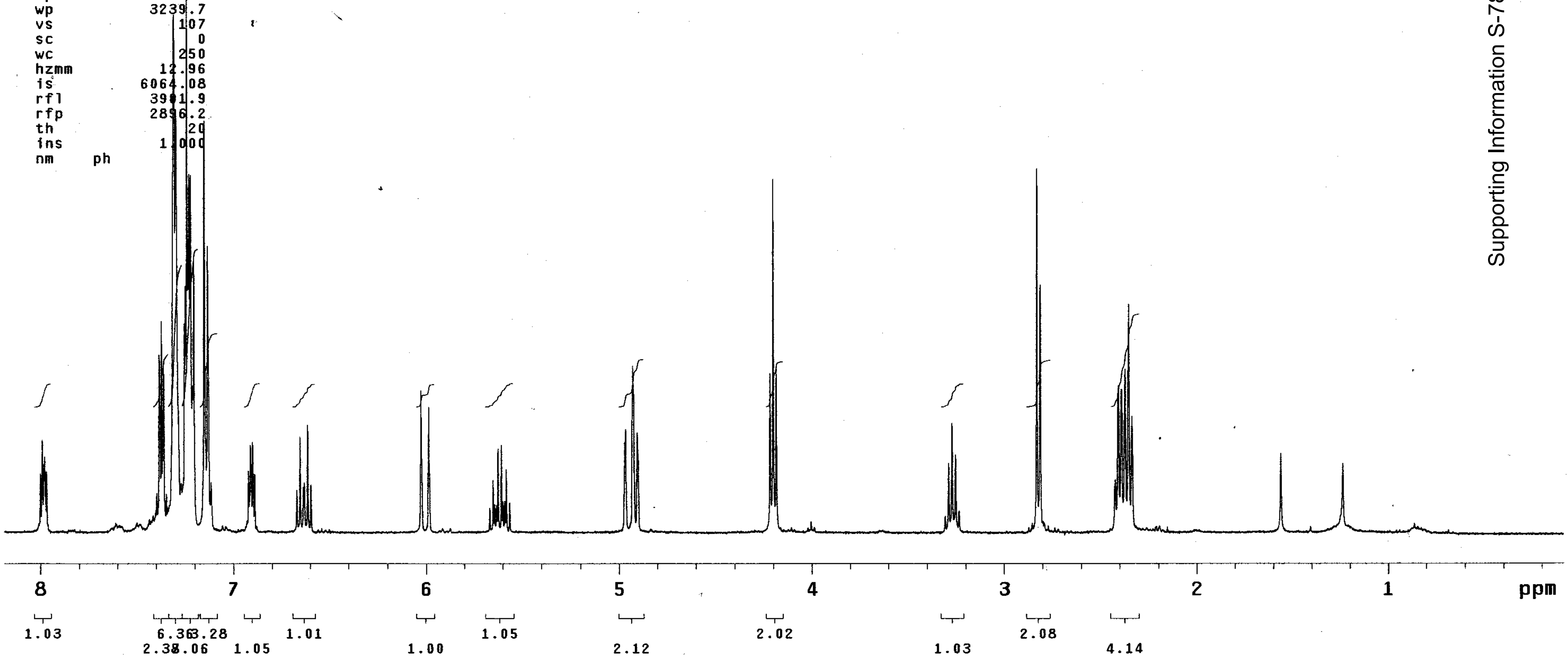


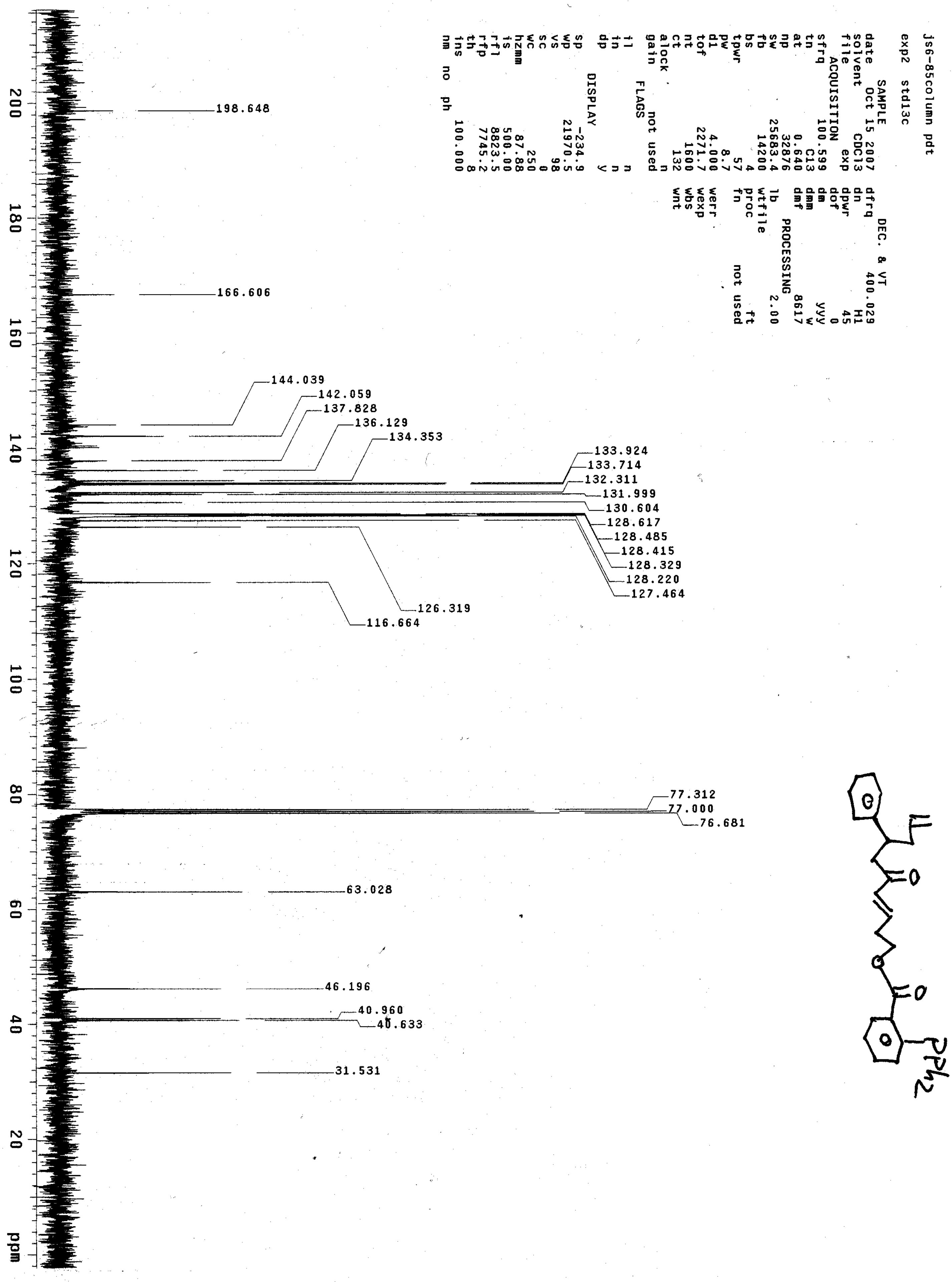
```
js5-261column

exp2  stdl3c

      SAMPLE              DEC. & VT
date   Oct  9 2007  dfrq        400.029
solvent      CDCl3  dn               H1
file           exp  dpwr             45
   ACQUISITION      dof               0
sfrq       100.599  dm              yyy
tn             C13  dmm               w
at           0.640  dmf            8617
np           32876       PROCESSING
sw         25683.4  lb             2.00
fb           14200  wtfile
bs               4  proc             ft
tpwr            57  fn         not used
pw             8.7
d1           4.000  werr
tof         2271.7  wexp
nt            1600  wbs
ct             116  wnt
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
      DISPLAY
sp           233.8
wp         20417.7
vs             101
sc               0
wc             250
hzmm         81.67
is          500.00
rfl         8827.4
rfp         7745.2
th               8
ins        100.000
nm  no  ph
```



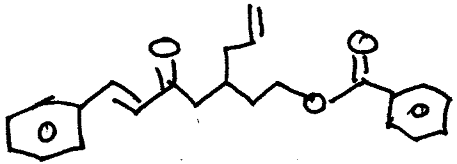
```
js6-85 column pdt

exp1  std1h

      SAMPLE              DEC. & VT
date   Oct 15 2007  dfrq              0
solvent      CDCl3  dn
file /export/home/~ dpwr             30
jpm/JDS/js6-85col.~ dof               0
               fid  dm              nnn
   ACQUISITION      dmm               c
sfrq       400.029  dmf             200
tn              H1       PROCESSING
at           3.000  wtfile
np           35992  proc             ft
sw          5998.8  fn         not used
fb            3400
bs               4  werr
tpwr            63  wexp
pw             7.1  wbs
d1           4.000  wnt
tof              0
nt              16
ct              12
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
      DISPLAY
sp            34.7
wp          3239.7
vs             107
sc               0
wc             250
hzmm         12.96
is         6064.08
rfl         3901.9
rfp         2896.2
th              20
ins          1.000
nm     ph
```

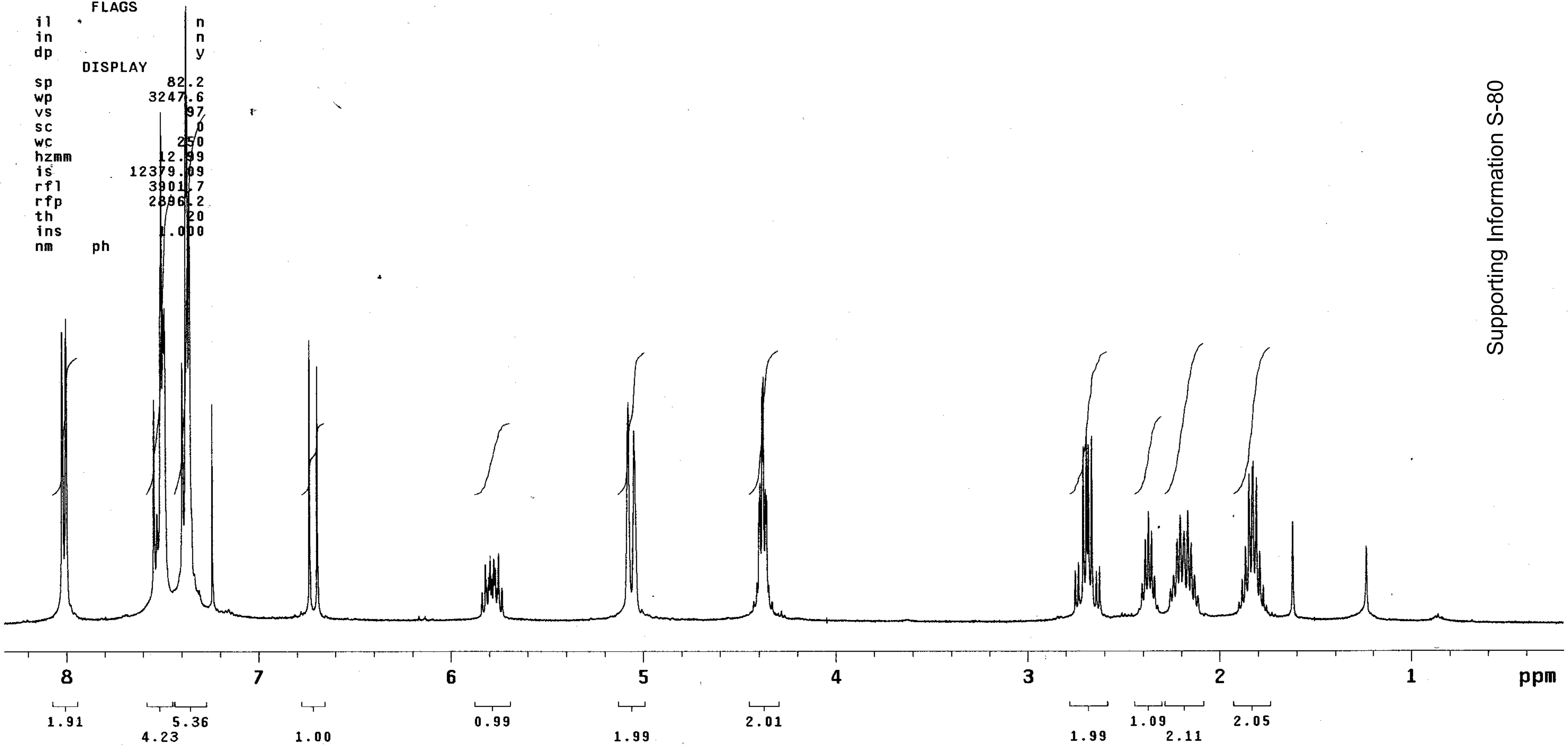




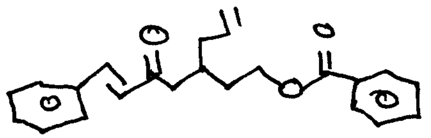

js6-85column pdt
exp2 std13c
SAMPLE
date Oct 15 2007
solvent CDCl3
file exp
ACQUISITION
sfrq 100.599
tn C13
at 0.640
np 32876
sw 25683.4
fb 14200
bs 4
tpwr 57
pw 8.7
d1 4.000
tof 2271.7
nt 1600
ct 132
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -234.9
wp 21970.5
vs 98
sc 0
wc 250
hzmm 87.88
is 500.00
rfl 8823.5
rfp 7745.2
th 8
ins 100.000
nm no ph
DEC. & VT
dfrq 400.029
dn H1
dpwr 45
dof 0
dm yyy
dmm w
dmf 8617
PROCESSING
lb 2.00
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
198.648
166.606
144.039
142.059
137.828
136.129
134.353
133.924
133.714
132.311
131.999
130.604
128.617
128.485
128.415
128.329
128.220
127.464
126.319
116.664
77.312
77.000
76.681
63.028
46.196
40.960
40.633
31.531
200
180
160
140
120
100
80
60
40
20
ppm
O
O
PPh2

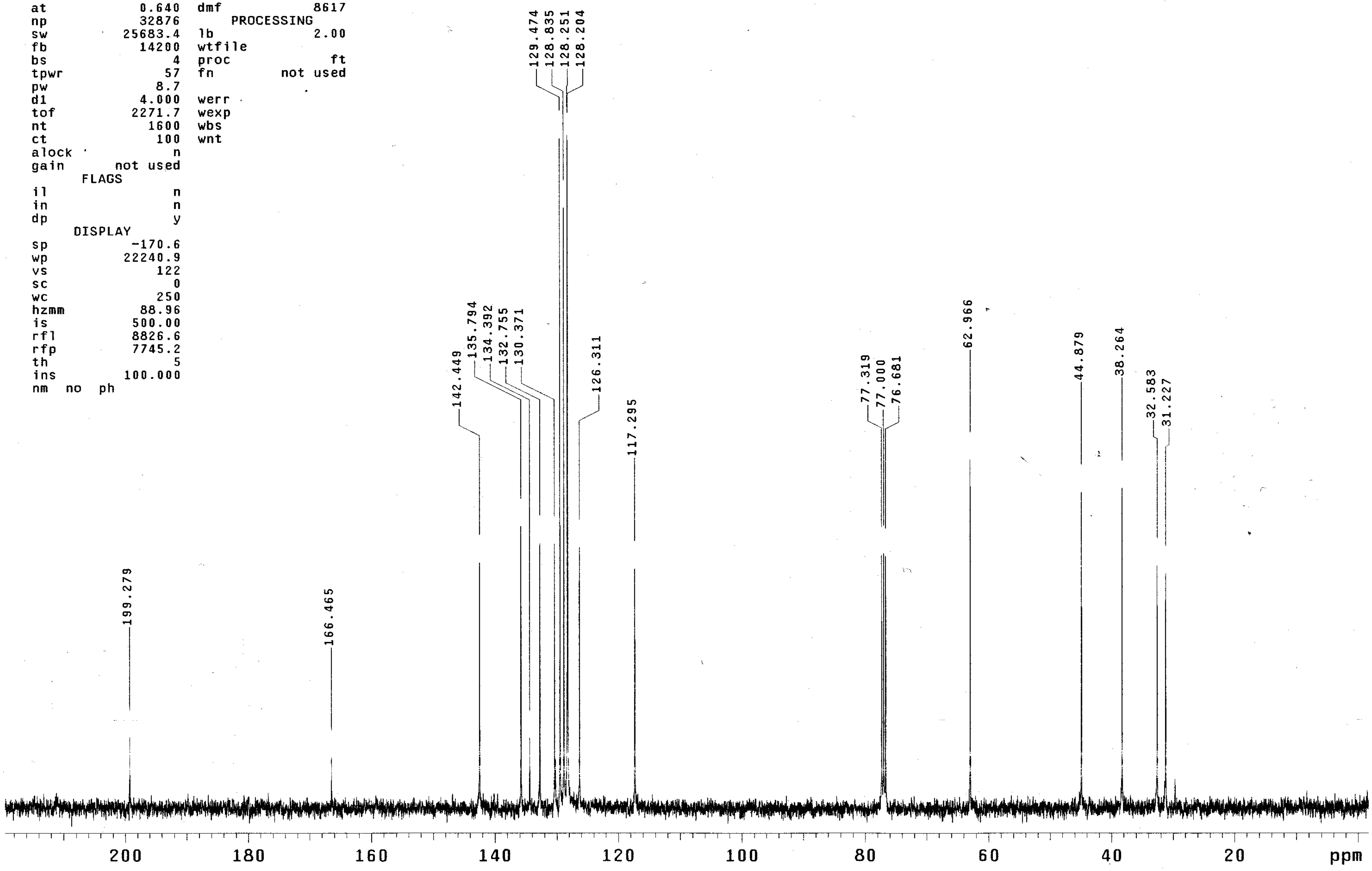
```
js6-101 column spot 1

expl  stdlh

      SAMPLE                 DEC. & VT
date   Oct 26 2007   dfrq               0
solvent       CDCl3   dn
file /export/home/~  dpwr              30
jpm/JDS/js6-101col~  dof                0
           spl.fid   dm               nnn
    ACQUISITION       dmm                c
sfrq        400.029   dmf              200
tn               H1        PROCESSING
at            3.000   wtfile
np            35992   proc              ft
sw           5998.8   fn          not used
fb             3400
bs                4   werr
tpwr             63   wexp
pw              7.1   wbs
d1            4.000   wnt
tof               0
nt               16
ct               16
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
     DISPLAY
sp             82.2
wp           3247.6
vs               97
sc                0
wc              250
hzmm          12.99
is         12379.09
rfl          3901.7
rfp          2896.2
th               20
ins           1.000
nm     ph
```



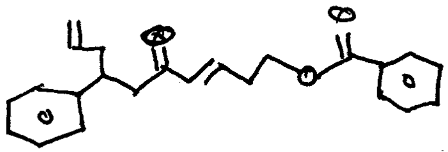


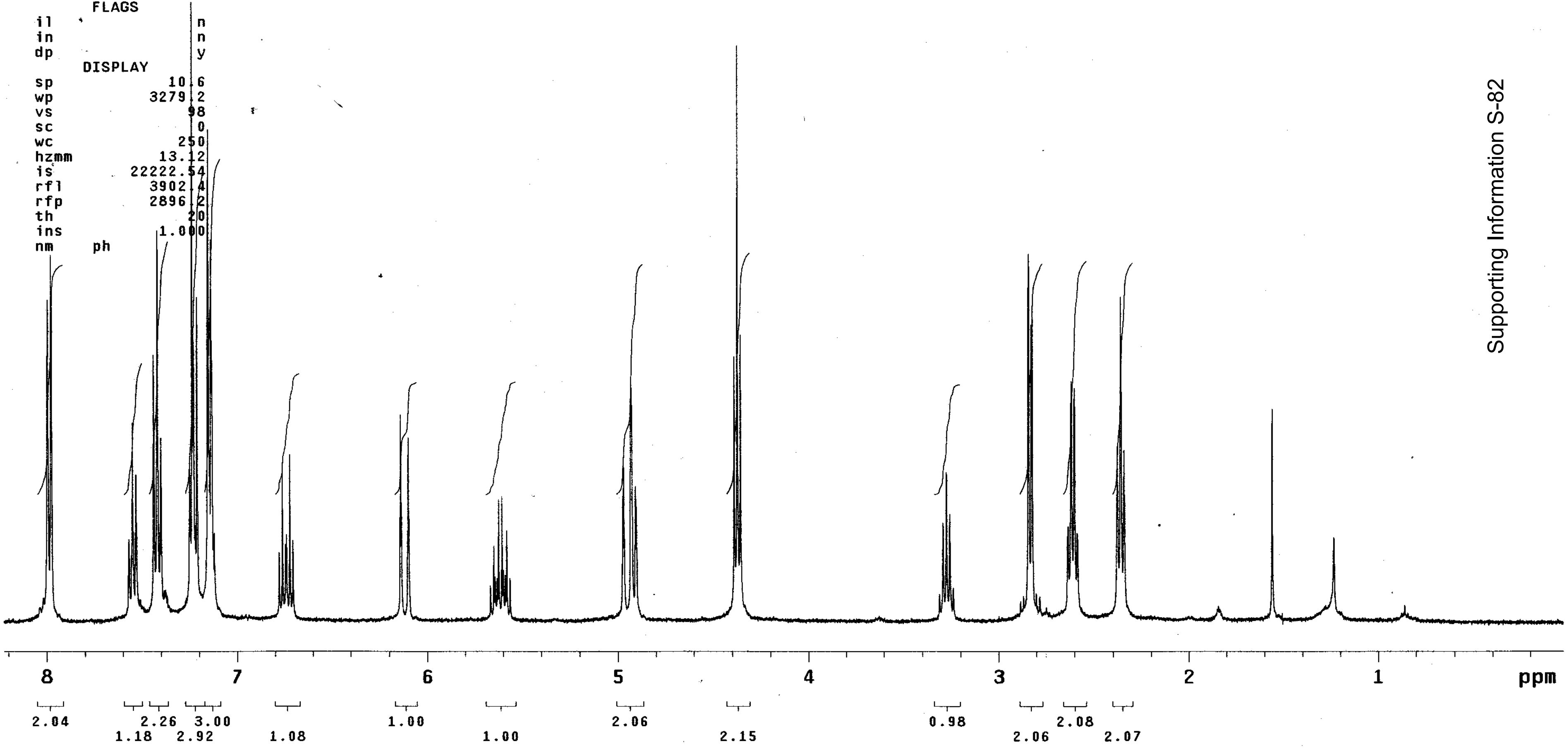
```
js6-104column spot 1

exp2  std13c

      SAMPLE                DEC. & VT
date   Oct 26 2007  dfrq        400.029
solvent       CDCl3  dn               H1
file            exp  dpwr             45
   ACQUISITION       dof               0
sfrq        100.599  dm              yyy
tn              C13  dmm               w
at            0.640  dmf            8617
np            32876       PROCESSING
sw          25683.4  lb             2.00
fb            14200  wtfile
bs                4  proc             ft
tpwr             57  fn         not used
pw              8.7
d1            4.000  werr
tof          2271.7  wexp
nt             1600  wbs
ct              100  wnt
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
     DISPLAY
sp           -170.6
wp          22240.9
vs              122
sc                0
wc              250
hzmm          88.96
is           500.00
rfl          8826.6
rfp          7745.2
th                5
ins         100.000
nm  no  ph
```

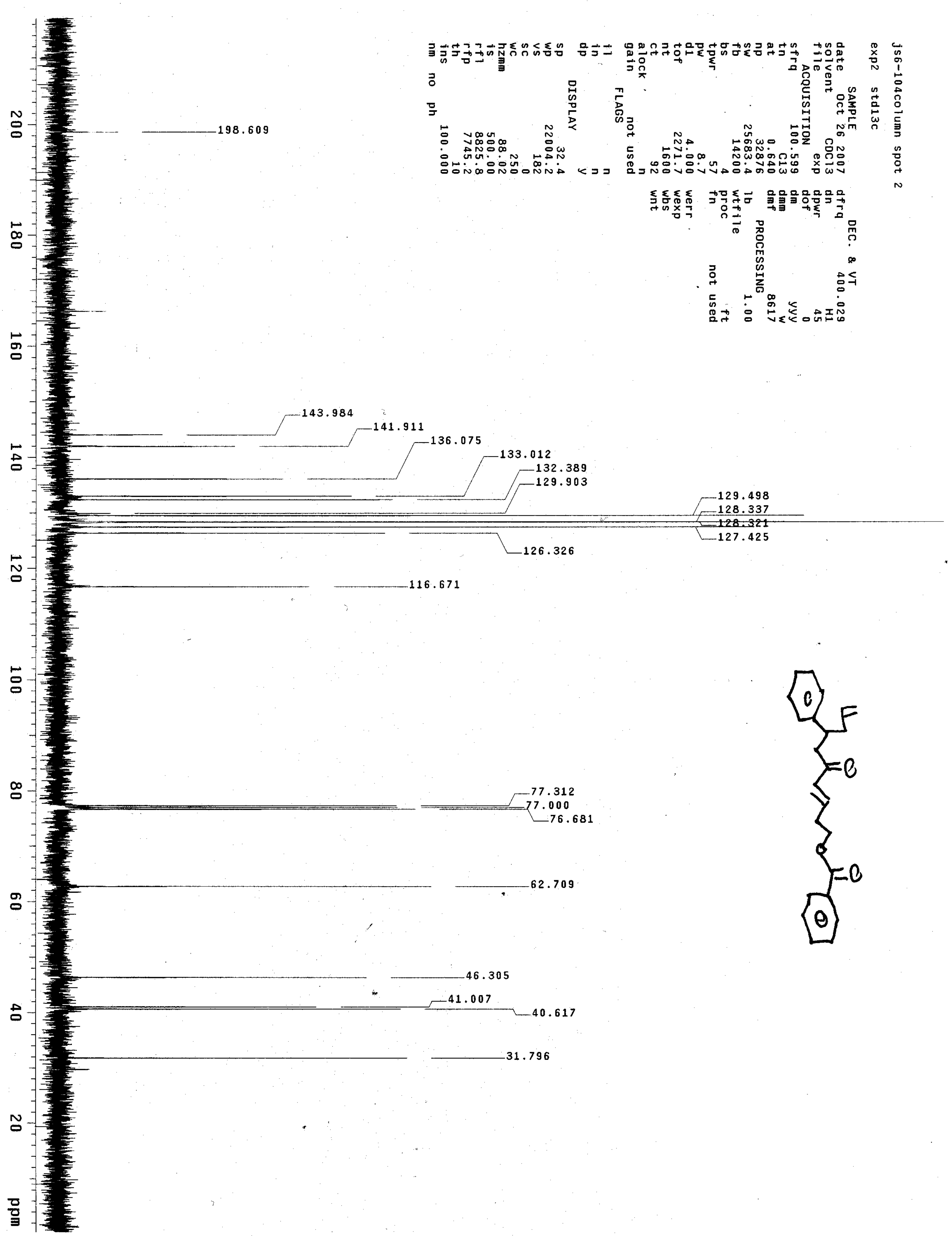




```
js6-101column spot 2

exp1  std1h

      SAMPLE              DEC. & VT
date   Oct 26 2007  dfrq             0
solvent      CDCl3  dn
file /export/home/~ dpwr            30
jpm/JDS/js6-101col~ dof              0
           sp2.fid  dm             nnn
   ACQUISITION      dmm              c
sfrq       400.029  dmf            200
tn              H1        PROCESSING
at           3.000  wtfile
np           35992  proc            ft
sw          5998.8  fn        not used
fb            3400
bs               4  werr
tpwr            63  wexp
pw             7.1  wbs
d1           4.000  wnt
tof              0
nt              16
ct               0
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp            10.6
wp          3279.2
vs              98
sc               0
wc             250
hzmm         13.12
is        22222.54
rfl         3902.4
rfp         2896.2
th              20
ins          1.000
nm     ph
```






js6-104column spot 2
exp2 std13c
SAMPLE
date Oct 26 2007
solvent CDCl3
file exp
ACQUISITION
sfrq 100.599
tn C13
at 0.640
np 32876
sw 25683.4
fb 14200
bs 4
tpwr 57
pw 8.7
d1 4.000
tof 2271.7
nt 1600
ct 92
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp 32.4
wp 22004.2
vs 182
sc 0
wc 250
hzmm 88.02
is 500.00
rfl 8825.8
rfp 7745.2
th 10
ins 100.000
nm no ph
DEC. & VT
dfrq 400.029
dn H1
dpwr 45
dof 0
dm yyy
dmm w
dmf 8617
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
198.609
143.984
141.911
136.075
133.012
132.389
129.903
129.498
128.337
128.321
127.425
126.326
116.671
77.312
77.000
76.681
62.709
46.305
41.007
40.617
31.796
200
180
160
140
120
100
80
60
40
20
ppm
F
O
O