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Supporting Information

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Supporting Information:

Catalytic Enantioselective 1,6-Conjugate Addition of Grignard Reagents to Linear Dienoates

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Experimental Section

General procedures: Thin-layer chromatography (TLC) was performed on commercial Kieselgel 60F_{254} silica gel plates and compounds were visualized with $KMnO_4$ reagent. Flash chromatography was performed on silica gel. Drying of solutions was performed with $MgSO_4$. Concentration of solutions was conducted with a rotary evaporator. Progress of the reactions and conversion were determined by GC-MS (GC, HP6890; MS, HP5973) with an HP5 column (Agilent Technologies, Palo Alto, CA). Enantio- and regioselectivities were determined by capillary GC analysis (HP6890, CP-Chiralsil-Dex-CB (25 m x 0.25 mm); Shimadzu GC-17A, CP-Chiraldex-B-PM (30 m x 0.25 mm)) using flame ionization detection or HPLC analysis ((*R,R*)-Whelk-01, 4.6 x 250 mm, 5 m, 40 °C, 0.5 mL/min, 205 nm; chiralcel OD-H, 4.6 x 250 mm, 5 m, 40 °C, 0.5 mL/min, 205 nm) (in comparison to authentic samples of racemates of 1,6- and 1,4-addition products). Optical rotations were measured in CH_2Cl_2 on a Schmidt + Haensch polarimeter (Polartronic MH8) with a 10 cm cell (c given in g/100 mL), a trace contamination (~2%) of 1,4-addition product was present; which in all cases was inseparable by column chromotography. Absolute configurations were determined by comparison of retention times on chiral GC-spectra (2-methylbutanoic acid) or optical rotation of compounds previously published. ^{1}H NMR spectra were recorded at 400 MHz with $CDCl_3$ as solvent (Varian AMX400 spectrometer). ^{13}C NMR spectra were obtained at 100.59 MHz in $CDCl_3$. The nature of the carbon was determined from APT ^{13}C NMR experiments. Chemical shifts were determined relative to the residual solvent peaks ($CHCl_3$, δ = 7.26 for hydrogen atoms, δ = 77.0 for carbon atoms). The following abbreviations are used to indicate signal multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; br, broad; m, multiplet. High resolution mass spectra were determined on a AEI-MS-902 mass spectrometer by EI (70ev) measurements.

All reactions were conducted under N_2 atmosphere using standard Schlenk techniques. CH_2Cl_2 was distilled from CaH_2 under N_2 prior to use. CuBr•SMe_2 was purchased from Aldrich. (+)-(*S,R*)- reversed Josiphos was generously donated by Solvias. (-)-(*R,S*)- reversed Josiphos was purchased from Aldrich. Grignard reagents were purchased from Aldrich (MeMgBr, EtMgBr, *i*BuMgBr and PhMgBr) or prepared from the corresponding alkyl bromides and magnesium turnings in anhydrous Et_2O following standard procedures. Grignard reagents were titrated using *s*BuOH and catalytic amounts of 1,10- phenanthroline before use.

Ethyl sorbate (**4**) was purchased from Aldrich, before use this substrate was purified by column chromatography (10% Et_2O/pentane) to remove antioxidant and polymer. (*2E,4E*)-ethyl hepta-2,4-dienoate (**17a**), (*2E,4E*)-ethyl nona-2,4-dienoate (**17b**) and (*2E,4E*)-ethyl 6-methylhepta-2,4-dienoate (**17c**) were prepared from the corresponding enaldehydes (purchased from Aldrich), via Horner-Emmons reaction (triethylphosphonoacetate was purchased from Aldrich) according or analogous to a well established protocol.[1] (*2E,4E*)-ethyl 7-methylocta-2,4-dienoate (**17d**), (*2E,4E*)-ethyl 7-phenylhepta-2,4-dienoate (**17e**), (*2E,4E*)-ethyl 6-(*tert*-butyldiphenylsilyloxy)hexa-2,4-dienoate (**17f**) and (*2E,4E*)-ethyl 6-(benzyloxy)hexa-2,4-dienoate (**17g**) were prepared from the corresponding aldehyde (purchased from Aldrich), via Horner-Emmons reaction with (*2E*)-triethylphosphonocrotonate according or analogous to a well established protocol.[2] Triethylphosphono-crotonate was purchased from Aldrich (90% technical grade) and purified by column chromatography (gradient 25% Et_2O/pentane to 100% Et_2O) to give pure (*2E*)-triethylphosphonocrotonate. (*2E,4E*)-S-ethyl hepta-2,4-dienethioate (**22**) was prepared from (*E*)-pent-2-enal (purchased from Aldrich), via a Wittig reaction according to a well established protocol.[3]

$RuCl_3$•$3H_2O$, DIBAL-H (1.0 M solution in CH_2Cl_2), $LiAlH_4$ and NMe_3 were purchased from Aldrich. $NaIO_4$ was purchased from Merck. Et_2O was distilled from benzophenone-ketyl under nitrogen prior to use. Chlorosulfonic acid was purchased from Aldrich and distilled under nitrogen prior to use.

Experimental data for substrates:

(*2E,4E*)-ethyl hepta-2,4-dienoate (**17a**) data are in accordance with data described in ref 1.

(*2E,4E*)-ethyl nona-2,4-dienoate (**17b**)
colorless oil; ^{1}H NMR δ 7.24- 7.15 (m, 1H), 6.15-6.00 (m, 2H), 5.71 (d, *J* = 15.3 Hz, 1H), 4.13 (qd, *J* = 7.1 Hz, 1.1 Hz, 2H), 2.10 (q, *J* = 6.6 Hz, 2H) , 1.27 (m, 7H), 0.84 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR δ 167.0 (C), 144.8 (CH), 144.4 (CH), 128.2 (CH), 119.0 (CH), 59.9 (CH_2), 32.5 (CH_2), 30.7 (CH_2), 22.1 (CH_2), 14.1 (CH_3), 13.7 (CH_3); MS *m/z* 182 (M^+, 68), 125 (M-*n*Bu, 100), 97 (C_7H_{13}, 48); HRMS calcd. for $C_{11}H_{18}O_2$ 182.1307, found 182.1316.

(*2E,4E*)-ethyl 6-methylhepta-2,4-dienoate (**17c**) data are in accordance with data described in ref 4.

(*2E,4E*)-ethyl 7-methylocta-2,4-dienoate (**17d**) data are in accordance with data described in ref 2. Additional data: MS *m/z* 182 (M^+, 100), 127 (88), 125 (M-*i*Bu, 91), 67 (C_5H_7, 94); HRMS calcd. for $C_{11}H_{18}O_2$ 182.1307, found 182.1311.

(*2E,4E*)-ethyl 7-phenylhepta-2,4-dienoate (**17e**)
colorless oil; ^{1}H NMR δ 7.34-7.14 (m, 6H), 6.27-6.08 (m, 2H), 5.79 (d, *J* = 15.1 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.75 (t, *J* = 8.0 Hz, 2H), 2.56-2.43 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR δ 167.2 (C), 144.8 (CH), 143.1 (CH), 141.1 (C), 128.9 (CH), 128.4 (CH), 128.4 (CH), 126.0 (CH), 119.6 (CH), 60.2 (CH_2), 35.1 (CH_2), 34.7 (CH_2), 14.3 (CH_3); MS *m/z* 230 (M^+, 10), 91 (C_7H_7, 100); HRMS calcd. for $C_{15}H_{18}O_2$ 230.1307, found 230.1308.

(*2E,4E*)-ethyl 6-(tert-butyldiphenylsilyloxy)hexa-2,4-dienoate (**17f**)
colorless oil; ^{1}H NMR δ 7.70-7.65 (m, 4H), 7.48-7.36 (m, 6H), 7.31 (dd, *J* = 11.2 Hz, 15.3 Hz, 1H), 6.59-6.42 (m, 1H), 6.16 (dt, *J* = 15.2 Hz, 4.2 Hz, 1H), 5.89 (d, *J* = 15.2 Hz, 1H), 4.34-4.30 (m, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.08 (s, 9H); ^{13}C NMR δ 166.9 (C), 143.9 (CH), 141.2 (CH), 135.3 (CH), 133.1 (C), 129.7 (CH), 127.7 (CH), 126.8 (CH), 120.8 (CH), 63.5 (CH_2), 60.1 (CH_2), 26.7 (CH_3), 19.1 (C), 14.2

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[1] S. Mann, S. Carillon, O. Breyne, C. Duhayon, L. Hamon, A. Marquet, *Eur. J. Org. Chem.* **2002**, 736-744.

[2] J. M. Takacs, F. Clement, J. Zhu, S. V. Chandramouli, X. Gong, *J. Am. Chem. Soc.* **1997**, *119*, 5804 – 5817.

[3] Described for reaction of aldehyde with $Ph_3PCHCOSEt$ (procedure D, 16 h reaction time): R. Des Mazery, M. Pullez, F. López, S. R. Harutyunyan, A. J. Minnaard, B. L. Feringa, *J. Am. Chem. Soc.* **2005**, *127*, 9966-9967.

[4] B. Bennacer, D. Trubuil, C. Rivalle, D. S. Grierson, *Eur. J. Org. Chem.* **2003**, 4561-4568.

(CH_3); MS *m/z* 394 (M^+, 27), 337 (M-*t*Bu, 100), 227 (TBDPSOEt-*t*Bu, 41), 199 (TBDPSOH-*t*Bu, 66); HRMS calcd. for $C_{24}H_{30}O_3Si$ 394.1964, found 394.1982.

(*2E*,*4E*)-ethyl 6-(benzyloxy)hexa-2,4-dienoate (**17g**)
colorless oil; ^{1}H NMR δ 7.45-7.27 (m, 6H), 6.42 (m, 1H), 6.18 (dt, *J* = 14.8 Hz, 5.0 Hz, 1H), 5.89 (dd, *J* = 15.4 Hz, 0.5 Hz, 1H), 4.54 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.13 (d, *J* = 5.3 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR δ 166.9 (C), 143.6 (CH), 138.5 (CH), 137.8 (C), 129.1 (CH), 128.4 (CH), 127.7 (CH), 127.7 (CH), 121.4 (CH), 72.5 (CH_2), 69.5 (CH_2), 60.3 (CH_2), 14.2 (CH_3); MS *m/z* 246 (M^+, 1), 91 (C_7H_7, 100); HRMS calcd. for $C_{15}H_{18}O_3$ 246.1256, found 246.1256.

(*2E*,*4E*)-*S*-ethyl hepta-2,4-dienethioate (**22**)
colorless oil; ^{1}H NMR δ 7.17 (dd, *J* = 15.2 Hz, 10.6 Hz, 1H), 6.22 (dt, *J* = 15.1 Hz, 6.4 Hz, 1H), 6.15-6.01 (m, 2H), 2.93 (q, *J* = 7.4 Hz, 2H), 2.23-2.12 (m, 2H), 1.26 (t, *J* = 7.4 Hz, 3H), 1.03 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR δ 190.1 (C), 147.5 (CH), 140.9 (CH), 127.2 (CH), 126.4 (CH), 26.2 (CH_2), 23.1 (CH_2), 14.8 (CH_3), 12.8 (CH_3); MS *m/z* 170 (M^+, 16), 109 (M - SEt, 100), 81 (M - COSEt, 66); HRMS calcd. for $C_9H_{14}OS$ 170.0765, found 170.0773.

General procedure for the enantioselective 1,6-conjugate addition:[5]
(exemplified for the addition of EtMgBr to **4**)
In a dried Schlenk tube equipped with septum and stirring bar under nitrogen, CuBr•SMe_2 (5.14 mg, 25 µmol, 5.0 mol%) and (*R,S*)-reversed Josiphos (15.46 mg, 26 µmol, 5.25 mol%) were dissolved in dry CH_2Cl_2 (2 mL). After 5 min stirring at room temperature the mixture was cooled to -70 °C and EtMgBr (Aldrich, 3.0M solution in Et_2O, 0.33 mL, 1.0 mmol, 2.0 equiv.) was added. After stirring for an additional 10 min, a solution of **4** (70.1 mg, 0.5 mmol, 1.0 equiv.) in dry CH_2Cl_2 (additional 0.5 mL) was added with syringe pump over 2 h. The reaction mixture was stirred overnight (16 h including addition) at -70 °C and subsequently EtOH (0.1 mL) and an aq. NH_4Cl-solution (1 M, 0.5 mL) were added. The mixture was warmed to RT and an additional 5 mL of the NH_4Cl-solution and 5 mL of CH_2Cl_2 were added and the layers were separated. After extraction with CH_2Cl_2 (2 x 5 mL), the combined organic extracts were dried and carefully concentrated to a yellow oil. Flash chromatography (5% Et_2O/pentane) yielded **5** as a colorless[6] oil.

(*R*)-(-)-(*E*)-ethyl 5-methylhept-3-enoate (**5**)
[84% yield, 95% ee, regioselectivity 1,6:1,4 = 98:2, $[\alpha]_D^{20}$ = -20.0 (c = 2.0, CH_2Cl_2); colorless oil]; ^{1}H NMR δ 5.56-5.34 (m, 2H), 4.12 (qd, *J* = 7.1 Hz , 1.3 Hz, 2H), 3.00 (dd, *J* = 6.4 Hz, 0.8 Hz, 2H), 2.10-1.95 (m, 1H), 1.35-1.17 (m, 5H), 0.96 (dd, *J* = 6.8 Hz, 1.3 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR δ 172.3 (C), 140.3 (CH), 120.0 (CH), 60.4 (CH_2), 38.3 (CH), 38.2 (CH_2), 29.5 (CH_2), 20.0 (CH_3), 14.2 (CH_3), 11.6 (CH_3); MS (GC/MS) *m/z* 170 (M^+, 4), 82 (C_6H_{10}, 55), 55 (C_3H_3O, 100); HRMS calcd. for $C_{10}H_{18}O_2$ 170.1307, found 170.1315. Enantioselectivity was determined by chiral GC analysis for 2-methylbutanoic acid,[7] column: Chiraldex-B-PM, 60 °C, retention times (min): 42.8 (minor), 45.5 (major). Regioselectivity was determined by chiral GC analysis, column: Chiraldex-B-PM, 60 °C, retention times (min): 95.2 (1,4-product, major), 100.5 (1,4 product, minor), 104.3 (1,6-product).

(*S*)-(+)-(*E*)-ethyl 5-methylhept-3-enoate (**5**)
[95% ee, regioselectivity 1,6:1,4 = 99:1, $[\alpha]_D^{20}$ = 20.2 (c = 1.0, CH_2Cl_2); colorless oil]; . Enantioselectivity was determined by chiral GC analysis for 2-methylbutanoic acid,[7] column: Chiraldex-B-PM, 60 °C, retention times (min): 41.5 (major), 49.0 (minor). Regioselectivity was determined by chiral GC analysis, column: Chiraldex-B-PM, 60 °C, retention times (min): 102.8 (1,4-product, major), 108.4 (1,6-product).

(-)-(*E*)-ethyl 5-methylnon-3-enoate (**15a**)
[85% yield, 97% ee, regioselectivity 1,6:1,4 = 99:1, $[\alpha]_D^{20}$ = -12.0 (c = 1.0, CH_2Cl_2); colorless oil]; ^{1}H NMR δ 5.55-5.32 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.00 (d, *J* = 5.8 Hz, 2H), 2.17-2.03 (m, 1H), 1.34-1.14 (m, 9H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.86 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR δ 172.2 (C), 140.6 (CH), 119.8 (CH), 60.4 (CH_2), 38.2 (CH_2), 36.6 (CH), 36.5 (CH_2), 29.4 (CH_2), 22.7 (CH_2), 20.4 (CH_3), 14.2 (CH_3), 14.1 (CH_3); MS (GC/MS) *m/z* 198 (M^+, 5), 110 (C_8H_{14}, 100), 69 (C_4H_5O, 70), 55 (C_3H_3O, 76); HRMS calcd. for $C_{12}H_{22}O_2$ 198.1620, found 198.1613. Regio- and enantioselectivity were determined by chiral GC analysis, column: Chiraldex-B-PM, 80 °C, retention times (min): 80.9 (1,4-product, major), 85.8 (1,4-product, minor), 95.1 (1,6-product, minor), 96.0 (1,6-product, major).

(-)-(*E*)-ethyl 5-methylnona-3,8-dienoate (**15b**)
[57% yield, 92% ee, regioselectivity 1,6:1,4 = 97:3, $[\alpha]_D^{20}$ = -17.6 (c = 1.0, CH_2Cl_2, for 88% ee); colorless oil]; ^{1}H NMR δ 5.76 (ddt, *J* = 16.9 Hz, 10.2 Hz, 6.7 Hz, 1H), 5.55-5.31 (m, 2H), 5.02-4.86 (m, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.99 (d, *J* = 6.5 Hz, 2H), 2.20-2.07 (m, 1H), 2.06-1.91 (m, 2H), 1.34 (q, *J* = 7.5 Hz, 2H), 1.23 (td, *J* = 7.13 Hz, 0.5 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR δ 172.1 (C), 140.0 (CH), 138.8 (CH), 120.3 (CH), 114.2 (CH_2), 60.4 (CH_2), 38.1 (CH_2), 36.1 (CH), 35.9 (CH_2), 31.4 (CH_2), 20.3 (CH_3), 14.1 (CH_3); MS *m/z* 196 (M^+, 1), 108 (C_8H_{12}, 56), 81 (C_5H_5O, 100), 67 (C_5H_7, 59), 55 (C_3H_3O, 57); HRMS calcd. for $C_{12}H_{20}O_2$ 196.1463, found 196.1464. Regio- and enantioselectivity were determined by chiral GC analysis, column: Chiraldex-B-PM, 80 °C, retention times (min): 83.8 (1,4-product, major), 88.3 (1,4-product, minor), 97.0 (1,6-product, minor), 98.5 (1,6-product, major).

(-)-(*E*)-ethyl 5,6-dimethylhept-3-enoate (**15c**)
[54% yield, 72% ee, regioselectivity 1,6:1,4 = 99:1, $[\alpha]_D^{20}$ = -17.6 (c = 1.0, CH_2Cl_2); colorless oil]; ^{1}H NMR δ 5.57-5.36 (m, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.01 (d, *J* = 5.5 Hz, 2H), 2.04-1.87 (m, 1H), 1.56-1.44 (m, 1H), 1.25 (td, *J* = 7.1 Hz, 0.7 Hz, 3H) 0.94 (d, *J* = 6.8 Hz, 3H), 0.87-0.78 (m, 6H); ^{13}C NMR δ 172.3 (C), 138.9 (CH), 120.7 (CH), 60.4 (CH_2), 42.9 (CH_2), 38.2 (CH), 32.8 (CH_2), 19.8 (CH_3), 19.6 (CH_3), 17.2 (CH_3), 14.2 (CH_3); MS (GC/MS) *m/z* 184 (M^+, 10), 96 (C_6H_8O, 91), 68 (C_4H_4O, 88), 55 (C_3H_3O, 100); HRMS calcd. for $C_{11}H_{20}O_2$ 184.1463, found 184.1461.

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[5] 0.5 g scale synthesis was performed via the same procedure using CuBr•SMe_2 (14.7 mg, 71 µmol, 2.0 mol%) and (*R,S*)-reversed Josiphos (44.5 mg, 75 µmol, 2.1 mol%) in dry CH_2Cl_2 (10 mL); EtMgBr (Aldrich, 3.0 M solution in Et_2O, 1.8 mL, 5.4 mmol, 1.5 equiv.); **4** (500 mg, 3.6 mmol, 1.0 equiv.) in dry CH_2Cl_2 (additional 4.0 mL).

[6] Occasionally the product is polluted with a yellow coloured side product undetectable by GC/MS or NMR.

[7] a) R. Hoen, J. A. F. Boogers, H. Bernsmann, A. J. Minnaard, A. Meetsma, T. D. Tiemersma-Wegman, A. H. M. de Vries, J. G. de Vries, B. L. Feringa, *Angew. Chem.* **2005**, *117*, 4281-4284, *Angew. Chem. Int. Ed.* **2005**, *44*, 4209-4212. b) Acid was obtained by Ru-catalysed $NaIO_4$-oxidation.

Regio- and enantioselectivity were determined by chiral GC analysis, column: Chiraldex-B-PM, 70 °C, retention times (min): 92.9 (1,4-product, major), 99.0 (1,6-product, minor), 100.0 (1,6-product, major).

(-)-(*E*)-ethyl 5-ethylnon-3-enoate (**18a**)[8]
[88% yield, 96% ee, regioselectivity 1,6:1,4 = 99:1, $[\alpha]_D^{20}$ = -0.2 (c = 1.0, CH_2Cl_2); colorless oil]; ^{1}H NMR δ 5.55-5.37 (m, 1H), 5.30-5.21 (m, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.01 (dd, *J* = 6.9 Hz, 1.3 Hz, 2H), 1.91-1.77 (m, 1H), 1.44-1.15 (m, 11H), 0.92-0.76 (m, 6H); ^{13}C NMR δ 172.2 (C), 139.0 (CH), 121.4 (CH), 60.4 (CH_2), 44.4 (CH), 38.2 (CH_2), 34.5 (CH_2), 29.4 (CH_2), 27.9 (CH_2), 22.8 (CH_2), 14.2 (CH_3), 14.1 (CH_3), 11.6 (CH_3); MS *m/z* 212 (M^+, 28), 124 (C_9H_{16}, 100), 67 (C_5H_7, 54), 55 (C_3H_3O, 57); HRMS calcd. for $C_{13}H_{24}O_2$ 212.1776, found 212.1786. Regio- and enantioselectivity were determined by chiral GC analysis, column: Chiraldex-B-PM, 80 °C, retention times (min): 42.7 (1,4-product, major), 43.3 (1,4-product, minor), 46.4 (1,6-product, minor), 47.0 (1,6-product, major).

(+)-(*E*)-ethyl 5-ethylnon-3-enoate (**18a**)[8]
[80% yield, 93% ee, regioselectivity 1,6:1,4 = 99:1, $[\alpha]_D^{20}$ = 0.2 (c = 1.0, CH_2Cl_2); colorless oil]; data was in accordance to (-)-**18a**. Regio- and enantioselectivity were determined by chiral GC analysis, column: Chiraldex-B-PM, 80 °C, retention times (min): 43.0 (1,4-product, major), 46.0 (1,6-product, major), 47.0 (1,6-product, minor).

(-)-(*E*)-ethyl 5-ethyl-6-methylhept-3-enoate (β,γ- **18c**) and
(-)-(*E*)-ethyl 5-ethyl-6-methylhept-2-enoate (α,β-**19c**)
[82% yield, 79% ee, regioselectivity 1,6:1,4 = 96:4, $[\alpha]_D^{20}$ = -1.0 (c = 1.0, CH_2Cl_2); colorless oil]; ^{1}H NMR δ 5.51-5.36 (m ,1H), 5.33-5.25 (m, 0.7H), 5.12 (ddd, *J* = 15.4 Hz, 8.2 Hz, 1.2 Hz, 0.3H), 4.10 (m, 2H), 3.04 (dd, *J* = 6.9 Hz, 1.3 Hz, 0.9H, β,γ-), 2.40-2.16 (m, *J* = 1.1H, α,β-), 1.72-1.52 (m, 2H), 1.51-1.35 (m, 1H), 1.33-1.14 (m, 5H), 0.98-0.92 (dd, *J* = 6.7 Hz, 2.9 Hz, 2H), 0.89-0.75 (m, 8H); ^{13}C NMR δ 172.9 (C, β,γ-), 172.3 (C, α,β-), 138.6 (CH, β,γ-), 136.6 (CH, α,β-), 129.0 (CH, β,γ-), 122.6 (CH, α,β-), 60.4 (CH_2, α,β-), 60.0 (CH_2, β,γ-), 51.1 (CH, α,β-), 41.2 (CH, β,γ-), 40.6 (CH_2, β,γ-), 38.3 (CH_2, α,β-), 31.4 (CH, α,β-), 31.0 (CH, β,γ-), 27.8 (CH_2, β,γ-), 24.9 (CH_2, α,β-), 22.7 (CH_3, α,β-), 22.6 (CH_3, α,β-), 20.7 (CH_3, β,γ-), 18.9 (CH_3, β,γ-), 14.3 (CH_3, α,β-), 14.2 (CH_3, β,γ-), 12.1 (CH_3, β,γ-), 11.5 (CH_3, α,β-); MS (GC/MS) *m/z* α,β-unsaturated product 198 (M^+, 3), 110 ($C_7H_{10}O$, 100), 95 (C_6H_7O, 62), 69 (C_5H_7, 48), β,γ-unsaturated product 198 (M^+, 5), 110 ($C_7H_{10}O$, 56), 81 (C_5H_5O, 100); HRMS calcd. for $C_{12}H_{22}O_2$ 198.1620, found 198.1627. Regio- and enantioselectivity were determined by chiral GC analysis, column: Chiraldex-B-PM, 75 °C, retention times (min): 54.6 (α,β-unsaturated-1,6-product, minor), 55.3 (α,β-unsaturated-1,6-product, major), 104.2 (1,4-product, minor), 107.2 (β,γ-unsaturated 1,6-product, minor), 108.5 (β,γ-unsaturated-1,6-product, major), 114.1 (1,4-product, major).

(+)-(*E*)-ethyl 5-ethyl-7-methyloct-3-enoate (**18d**)
[77% yield, 97% ee, regioselectivity 1,6:1,4 = 98:2, $[\alpha]_D^{20}$ = 9.5 (c = 1.0, CH_2Cl_2); colorless oil]; ^{1}H NMR δ 5.46 (dtd, *J* = 15.3 Hz, 7.0 Hz, 0.6 Hz, 1H), 5.22 (ddt, *J* = 15.3 Hz, 9.0 Hz, 1.3 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.01 (dd, *J* = 7.0 Hz, 1.3 Hz, 2H), 2.01-1.86, (m, 1H), 1.62-1.05 (m, 8H), 0.92-0.65 (m, 9H) (spectrum contains traces of α,β-unsaturated 1,6-product δ 2.38-2.16 (m)); ^{13}C NMR δ 172.2 (C), 139.0 (CH), 121.4 (CH), 60.4 (CH_2), 44.3 (CH_2), 42.3 (CH), 38.2 (CH_2), 28.2 (CH_2), 25.3 (CH_3), 23.5 (CH_3), 21.8 (CH_3), 14.1 (CH_3), 11.6 (CH_3); MS (GC/MS) *m/z* 212 (M^+, 1), 97 (C_7H_{13}, 84), 95 (C_6H_7O, 100), 81 (C_5H_50, 64), 55 (C_3H_3O, 69); HRMS calcd. for $C_{13}H_{24}O_2$ 212.1776, found 212.1768. Regio- and enantioselectivity were determined by chiral GC analysis, column: Chiraldex-B-PM, 75 °C (isothermic), retention times (min): 125.1 (1,4-product, minor), 134.5 (1,4-product, major), 144.4 (1,6-product, minor), 149.4 (1,6-product, major).

(+)-(*E*)-ethyl 5-ethyl-7-phenylhept-3-enoate (**18e**)
[73% yield, 90% ee, regioselectivity 1,6:1,4 = 98:2, $[\alpha]_D^{20}$ = 4.1 (c = 1.0, CH_2Cl_2); colorless oil]; ^{1}H NMR δ 7.38-7.10 (m, 5H), 5.58 (dt, *J* = 15.3 Hz, 7.0 Hz, 1H), 5.36 (dd, *J* = 8.9 Hz, 15.3 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.10 (dd, *J* = 6.9 Hz, 1.0 Hz, 2H), 2.82-2.43 (m, 2H), 2.03-1.90 (m, 1H), 1.80-1.20 (m, 7H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR δ 172.0 (C), 142.6 (C), 138.3 (CH), 128.3 (CH), 128.1 (CH), 125.4 (CH), 122.3 (CH), 60.4 (CH_2), 43.9 (CH), 38.1 (CH_2), 36.5 (CH_2), 33.4 (CH_2), 27.8 (CH_2), 14.1 (CH_3), 11.5 (CH_3); MS *m/z* 260 (M^+, 28), 104 (C_8H_8, 79), 91 (C_7H_7, 100); HRMS calcd. for $C_{17}H_{24}O_2$ 260.1776, found 260.1768. Enantioselectivity was determined by chiral HPLC analysis, column: Whelk (99.9% heptane/*i*PrOH), 40 °C, retention times (min): 23.5 (major), 25.0 (minor). Regioselectivity was determined by chiral GC analysis, column: Chiraldex-B-PM, 170 °C, retention times (min): 26.4 (1,4-product), 27.6 (1,6-product).

(-)-(*E*)-ethyl 5-[(*tert*-butyldiphenylsilyloxy)methyl]hept-3-enoate (**18f**)
[82% yield, 73% ee, regioselectivity 1,6:1,4 = 96:4, $[\alpha]_D^{20}$ = -8.5 (c = 0.8, CH_2Cl_2); colorless oil]; ^{1}H NMR δ 7.68- 7.61 (m, 4H), 7.46-7.34 (m, 6H), 5.61-5.50 (m, 1H), 5.42-5.31 (m, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.56 (d, *J* = 6.1 Hz, 2H), 3.02 (dd, *J* = 6.9 Hz, 1.3 Hz, 2H), 2.18-2.08 (m, 1H), 1.33-1.18 (m, 5H), 1.04 (s, 9H), 0.83 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR δ 172.0 (C), 135.8 (CH), 135.6 (CH), 133.9 (C), 129.4 (CH), 127.5 (CH), 123.0 (CH), 67.0 (CH_2), 60.5 (CH_2), 47.0 (CH), 38.4 (CH_2), 26.8 (CH_3), 23.8 (CH_2), 19.3 (C), 14.2 (CH_3), 11.5 (CH_3); MS *m/z* 423 (M^+-H, 0.3), 368 (57), 367 (M- *t*Bu, 100), 227 (TBDPSOEt-*t*Bu, 58), 199 (TBDPSOH-*t*Bu, 50); HRMS calcd. for $C_{22}H_{27}O_3Si$ 367.1729 (Mass -*t*Bu), found 367.1729. Regio- and enantioselectivity were determined by chiral HPLC analysis for (*E*)-5-((tert-butyldiphenylsilyloxy)methyl)hept-3-en-1-ol,[9] column: chiralcel OD-H (99% heptane/*i*PrOH), 40 °C, retention times (min): 19.6 (1,4-product), 20.7 (1,6-product, minor), 21.9 (1,6-product, major).

(-)-(E)-ethyl 5-(benzyloxymethyl)hept-3-enoate (**18g**)
[69% yield, 90% ee, regioselectivity 1,6:1,4 = >95:5, $[\alpha]_D^{20}$ = -12.3 (c = 1.0, CH_2Cl_2); colorless oil]; ^{1}H NMR δ 7.39-7.23 (m, 5H), 5.61 (dtd, *J* = 7.7 Hz, 6.9 Hz, 0.8 Hz, 1H), 5.40 (ddt, *J* = 15.5 Hz, 8.4 Hz, 1.3 Hz, 1H), 4.50 (s, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.39 (d, *J* = 6.4 Hz, 2H), 3.05 (dd, *J* = 6.9 Hz, 1.3 Hz, 2H), 2.34-2.21 (m, 1H), 1.64-1.49 (m, 1H), 1.34-1.17 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR δ 172.0 (C), 138.5 (C), 135.6 (CH), 128.2 (CH), 127.5 (CH), 127.4 (CH), 123.0 (CH), 73.6 (CH_2), 72.9 (CH_2), 60.5 (CH_2), 44.5 (CH), 38.2 (CH_2), 24.2 (CH_2), 14.2 (CH_3), 11.4 (CH_3); MS *m/z* 276 (M^+, 2), 188 ($C_{13}H_{16}O$, 47), 155 ($C_9H_{15}O_2$, 36), 91 (C_7H_7, 100); HRMS calcd. for $C_{17}H_{24}O_3$ 276.1725, found 276.1728. Enantioselectivity was determined by chiral HPLC analysis for (*E*)-5-(benzyloxymethyl)hept-3-en-1-ol,[9] column: chiralcel OD-H (99% heptane/*i*PrOH), 40 °C, retention times (min): 45.1 (1,6-product, minor), 48.9 (1,6-product, major). Regioselectivity was determined by NMR.

(*S*)-(+)-(*E*)-*S*-ethyl 5-methylhept-3-enethioate (**23**)

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[8] R.Takeuchi, Y. Akiyama, *J. Organomet. Chem.* **2002**, *651*, 137-145.

[9] Alcohol was obtained by DIBAL-H reduction. Reaction was performed for both racemic and chiral s22Et.

[85% yield, 93% ee, regioselectivity 1,6:1,4 = 99:1, $[\alpha]_D^{20}$ = 11.9 (c = 1.0, CH_2Cl_2); colorless oil]; ^{1}H NMR δ 5.52-5.39 (m, 2H), 3.23-3.15 (m, 2H), 2.85 (q, *J* = 7.4 Hz, 2H), 2.13-1.97 (m, 1H), 1.37-1.14 (m, 5H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.85 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR δ 198.5 (C), 142.0 (CH), 119.6 (CH), 47.6 (CH_2), 38.4 (CH), 29.5 (CH_2), 23.3 (CH_2), 19.8(CH_3), 14.7 (CH_3), 11.7 (CH_3); MS (GC/MS) *m/z* 186 (M^+, 0.2), 97 (C_7H_{13}, 37), 55 (C_3H_3O, 100); HRMS calcd. for $C_{10}H_{18}OS$ 186.1078, found 186.1084. Enantioselectivity was determined by chiral GC analysis for 2-methylbutanoic acid,[7] column: Chiraldex-B-PM, 60 °C, retention times (min): 41.5 (major), 47.8 (minor). Regioselectivity was determined by chiral GC analysis, column: Chiraldex-B-PM, 100 °C, retention times (min): 30.1 (1,4-product, minor), 30.6 (1,4-product, major), 32.5 (1,6-product).

(*R*)-(-)-(*E*)-ethyl 5,9-dimethyldeca-3,8-dienoate (**24**)
[34% yield (0.5 g scale, 2% catalyst, 1.2 equiv. Grignard reagent), 86% ee, regioselectivity 1,6:1,4 = 97:3, $[\alpha]_D^{20}$ = -14.1 (c = 1.0, CH_2Cl_2); colorless oil]; ^{1}H NMR δ 5.55-5.32 (m, 2H), 5.12-5.01 (m, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.00 (d, *J* = 6.2 Hz, 2H), 2.19-2.04 (m, 1H), 2.01-1.86 (m, 2H), 1.61 (d, *J* = 36.2 Hz, 6H), 1.36-1.16 (m, 5H), 0.96 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR δ 172.1 (C), 140.3 (CH), 131.2 (C), 124.5 (CH), 120.1 (CH), 60.4 (CH_2), 38.2 (CH_2), 36.9 (CH_2), 36.2 (CH), 25.7 (CH_2), 25.6 (CH_3), 20.4 (CH_3), 17.6 (CH_3), 14.1 (CH_3); MS *m/z* 224 (M^+, 15), 181 ($C_{11}H_{17}O_2$, 51), 82 (C_6H_{10}, 100), 69 (C_4H_5O, 56); HRMS calcd. for $C_{14}H_{24}O_2$ 224.1776, found 224.1767. Regio- and enantioselectivity was determined by chiral GC analysis, column: Chiralsil-Dex-CB, 105 °C, retention times (min): 81.3 (1,4-product, major), 94.2 (1,6-product, minor), 94.7 (1,6-product, major).

Synthesis of (*R*)-(-)-(*E*)-5,9-dimethyldeca-3,8-dien-1-ol (25):[10]
In a dried Schlenk tube equipped with septum and stirring bar under nitrogen, **24** (150 mg, 0.67 mmol, 1.0 equiv.) was dissolved in dry Et_2O (6.5 mL). The mixture was cooled to 0 °C and $LiAlH_4$ (56 mg, 1.48 mmol, 2.2 equiv.) was added in small portions. After stirring for 1 h at 0 °C the reaction was quenched with a 5% aq. HCl solution to a pH of 5. Et_2O (5 mL) and H_2O (5 mL) were added and the layers were separated. After extraction with Et_2O (2x 5 mL), the combined organic extracts were washed with H_2O and brine (10 mL), dried and carefully concentrated to a colorless oil. Flash chromatography (10% Et_2O/pentane) yielded **25** as a colorless oil.

Experimental data:
[93% yield, $[\alpha]_D^{20}$ = -21.1 (c = 1.0, CH_2Cl_2); colorless oil]; ^{1}H NMR δ 5.46-5.27 (m, 2H), 5.12-5.03 (m, 1H), 3.61 (t, *J* = 6.3 Hz, 2H), 2.25 (q, *J* = 6.4 Hz, 2H), 2.17-2.03 (m, 1H), 1.98-1.88 (m, 2H), 1.70-1.54 (m, 6H), 1.28 (q, *J* = 7.0 Hz, 3H), 0.96 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR δ 140.1 (C), 131.2 (CH), 124.6 (CH), 124.0 (CH), 62.0 (CH_2), 37.0 (CH_2), 36.4 (CH), 36.0 (CH_2), 25.8 (CH_2), 25.7 (CH_3), 20.7 (CH_3), 17.6 (CH_3); MS *m/z* 182 (M^+, 9), 82 (C_6H_{10}, 100), 69 (C_5H_9, 91), 55 (C_4H_7, 80); HRMS calcd. for $C_{12}H_{22}O$ 182.1671, found 182.1678.

Synthesis of (*R*)-(-)-Trimethylammonium (*E*)-5,9-dimethyldeca-3,8-dienyl sulphate (26):[11]
In a dried Schlenk tube equipped with septum and stirring bar under nitrogen, **25** (60 mg, 0.33 mmol, 1.0 equiv.) was dissolved in dry Et_2O (0.5 mL). The mixture was cooled to -5 °C and $ClSO_3H$ (22 µL, 0.33 mmol, 1.0 equiv.) was added dropwise. After stirring for 2 h at -5 °C the reaction was quenched with NMe_3 at -5 °C (45% aq. solution, 0.2 mL). Then H_2O (2 mL) and Et_2O (2 mL) were added and the solution was stirred for 2 min and decanted. This was repeated once with 2 mL Et_2O. The aqueous layer was concentrated to a slightly yellow oil. Flash chromatography (10% MeOH/$CHCl_3$) yielded **26** as a colorless oil.

Experimental data:
[55% yield, $[\alpha]_D^{20}$ = -10.5 (c = 0.7, $CHCl_3$); lit.[11] = -17.0 (c = 1.89, $CHCl_3$) ; colorless oil];

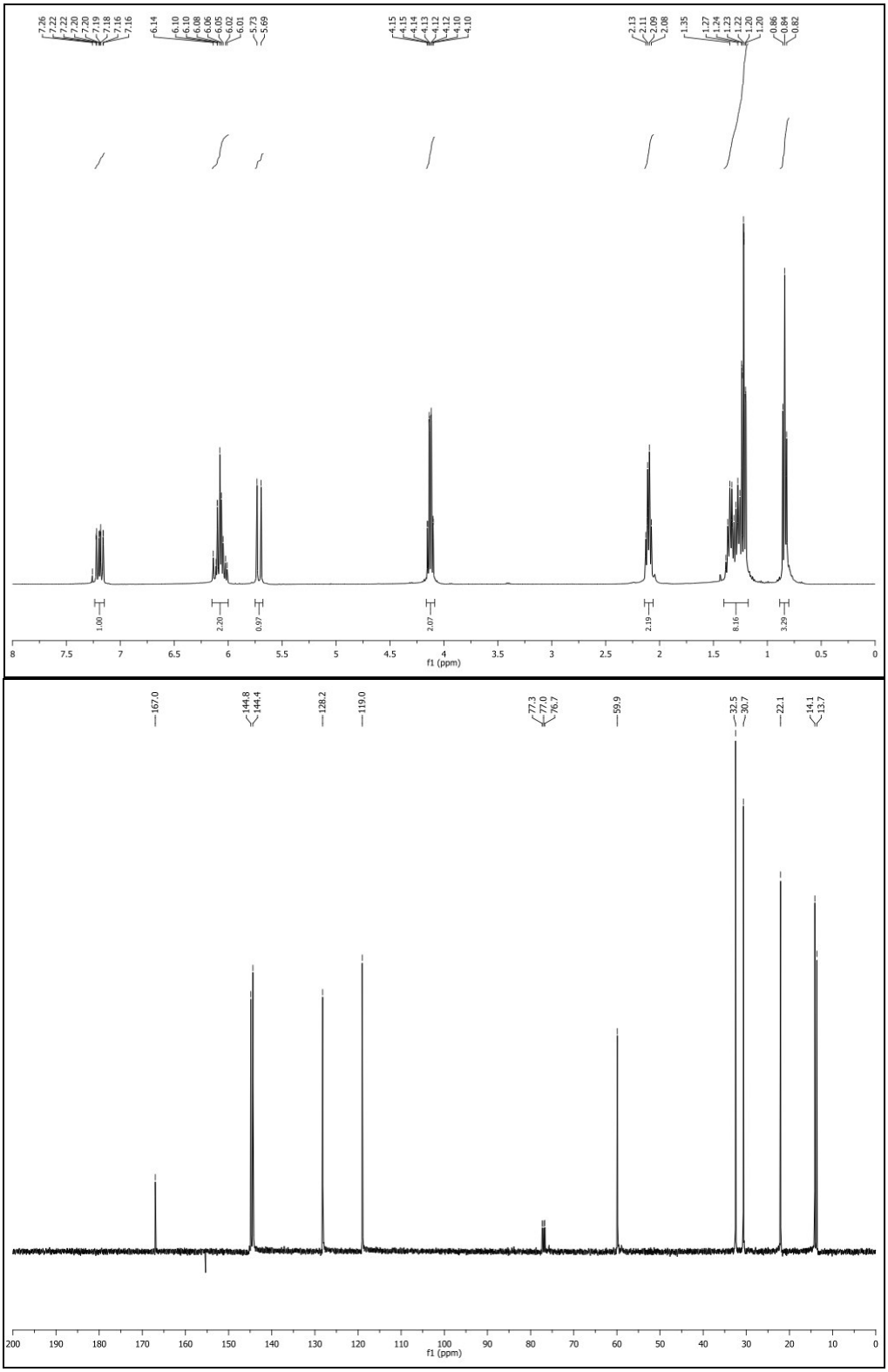
	^{1}H NMR			^{13}C NMR	
position:	natural:	synthetic:	position:	natural:	synthetic:
1	4.02 (t, 7.3)	4.04 (t, 7.3, 2H)	1	67.8 CH_2	68.4 CH_2
2	2.37 (m)	2.35 (dd, 7.1, 13.0 Hz, 2H)	2	32.6 CH_2	32.5 CH_2
3	5.36 (dt, 15.4, 6.1)	5.44-5.25 (m, 2H)	3	123.1 CH	123.1 CH
4	5.38 (dd, 15.4, 7.0)		4	139.1 CH	139.2 CH
5	2.06 (m)	2.04 (dt, 13.5, 6.7 Hz, 1H)	5	36.2 CH	36.2 CH
6	1.27 (m)	1.31-1.17 (m, 2H)	6	36.9 CH_2	37.0 CH_2
7	1.92 (m)	1.90 (dd, 7.5, 15.2 Hz, 2H)	7	25.6 CH_2	25.7 CH_2
8	5.07 (t, 6.5)	5.05 (m, 1H)	8	124.5 CH	124.6 CH
10	1.58 (s)	1.56 (s, 3H)	9	131.1 C	131.1 C
11	0.94 (d, 6.6)	0.92 (d, 6.7 Hz, 3H)	10	17.6 CH_3	17.7 CH_3
12	1.67 (s)	1.65 (d, 0.9 Hz, 3H)	11	20.5 CH_3	20.4 CH_3
NH	9.75 (brs)	9.39 (brs, 1H)	12	25.5 CH_3	25.7 CH_3
N-CH_3	2.96 (d, 3.7)	2.93 (d, 5.1 Hz, 5H)	N-CH_3	45.3 CH_3	45.7 CH_3
	Impurity:	3.94 (brs)			

[10] N. F. Langille, J. S. Panek, *Org. Lett.* **2004**, *6*, 3203-3206.

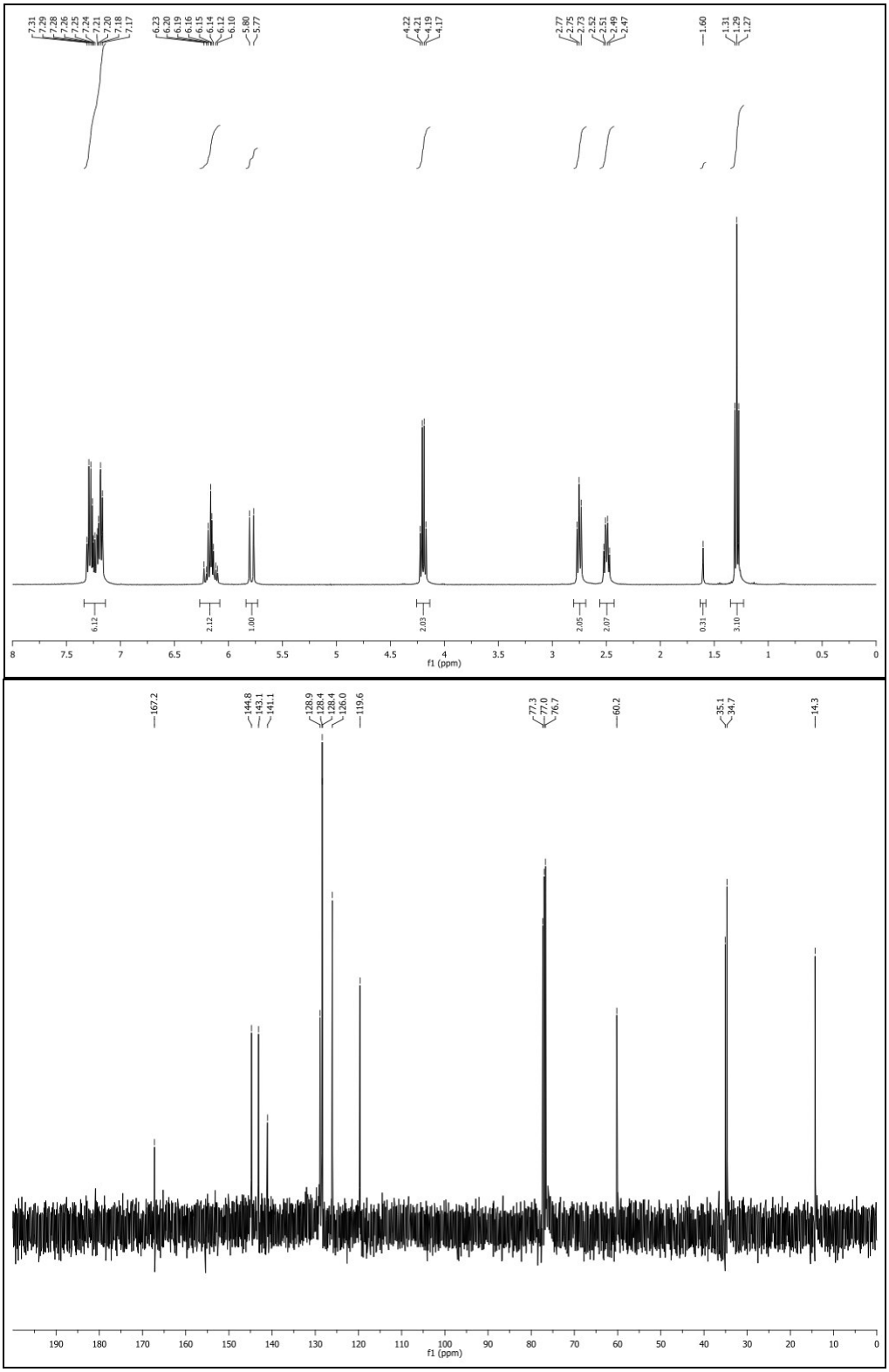
[11] L. Chen, Y. Fang, X. Luo, H. He, T. Zhu, H. Liu, Q. Gu, W. Zhu, *J. Nat. Prod.* **2006**, *69*, 1787-1789.

Supporting information 2

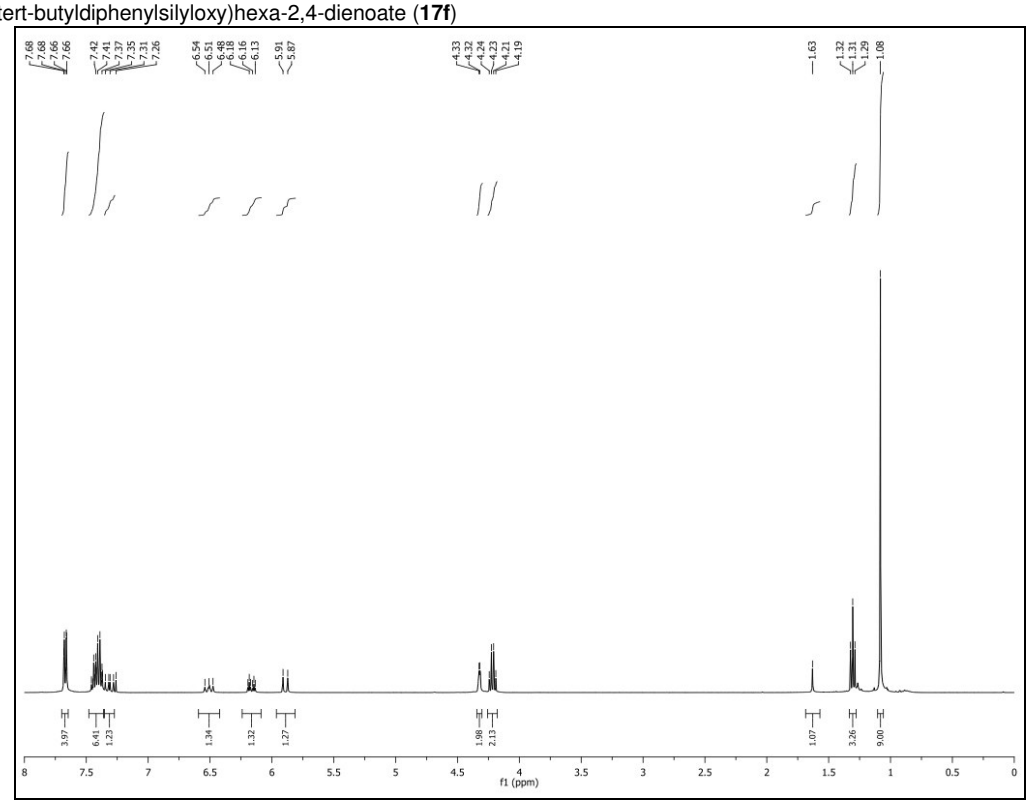
Please note: the peak in ^{13}C around 156 ppm is an artefact.
(*2E*,*4E*)-ethyl nona-2,4-dienoate (**17b**)

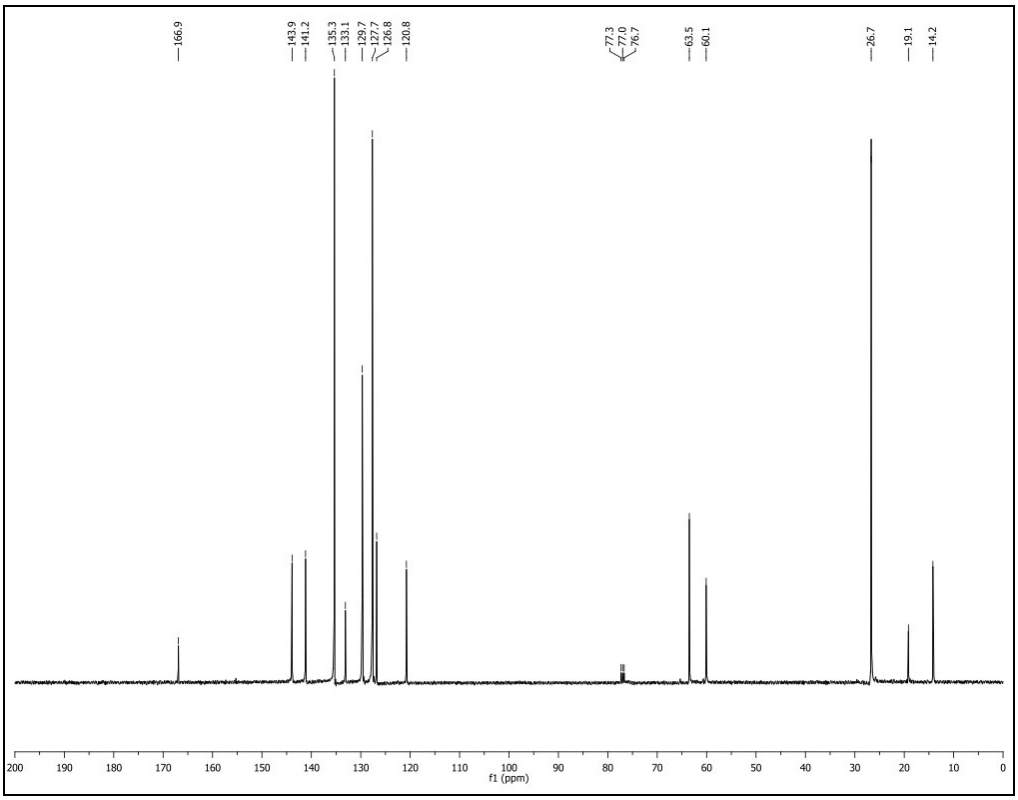


(*2E*,*4E*)-ethyl 7-phenylhepta-2,4-dienoate (**17e**)

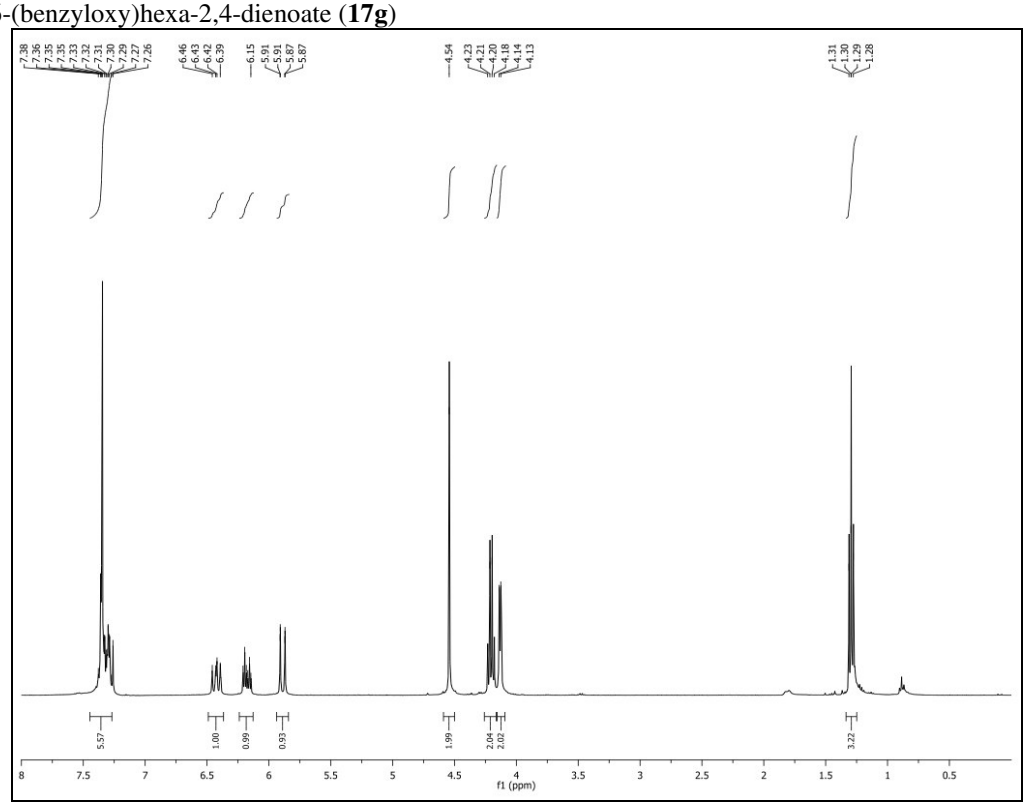


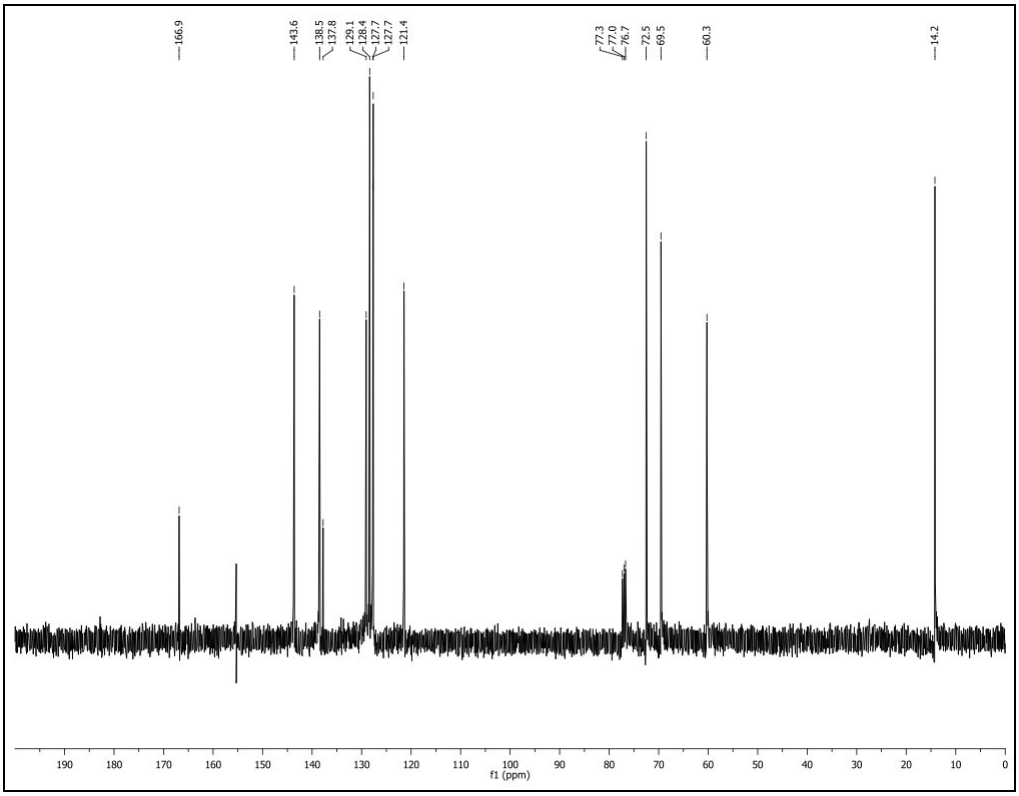
(*2E*,*4E*)-ethyl 6-(tert-butyldiphenylsilyloxy)hexa-2,4-dienoate (**17f**)



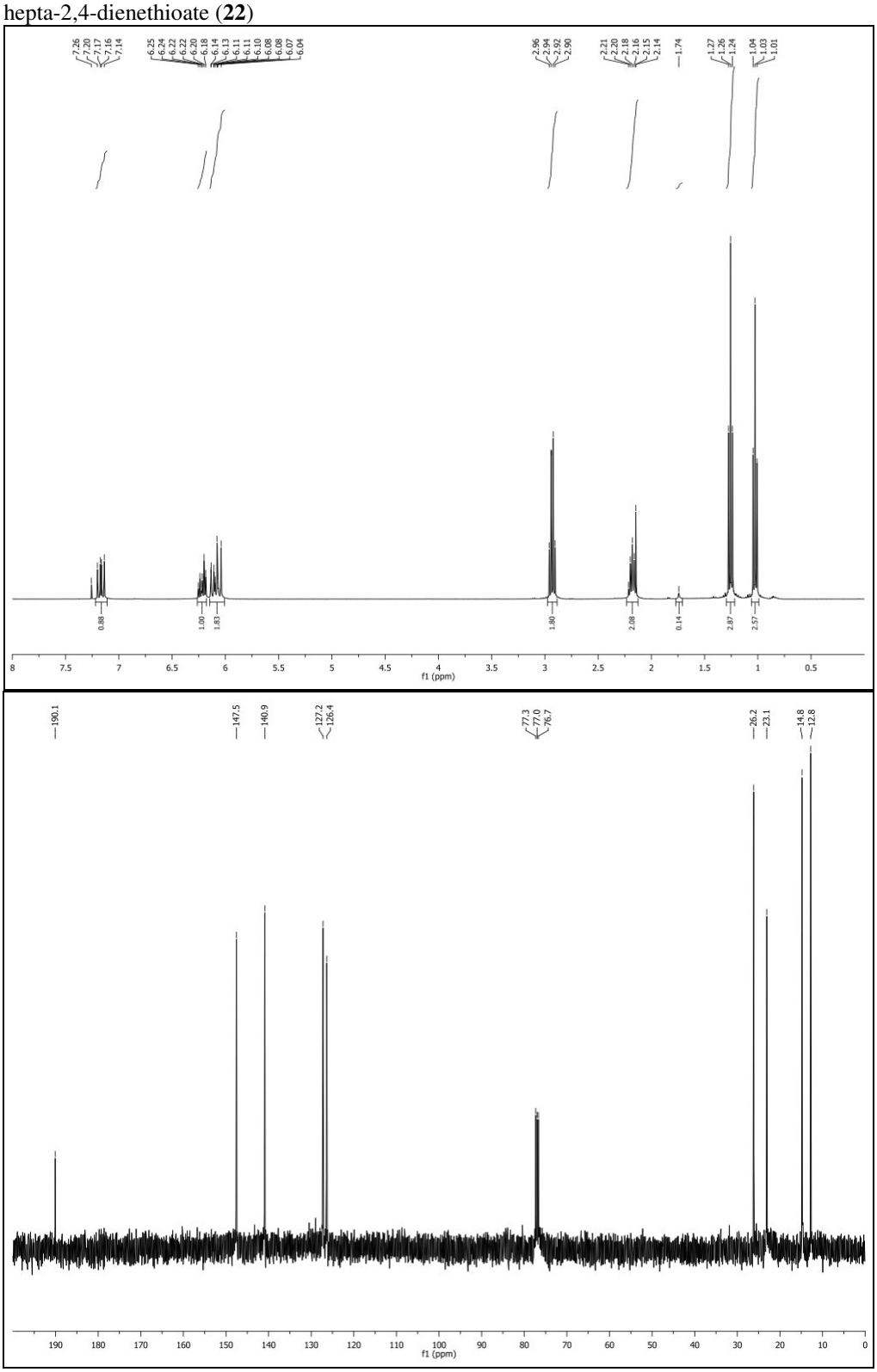


(*2E*,*4E*)-ethyl 6-(benzyloxy)hexa-2,4-dienoate (**17g**)

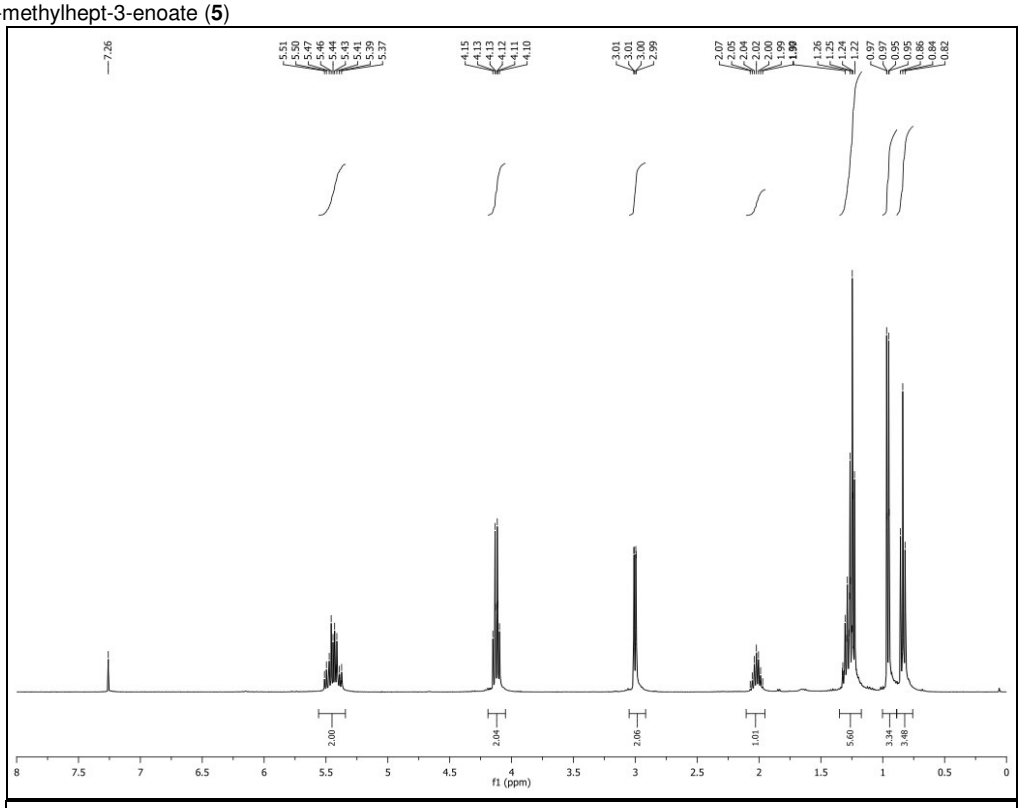


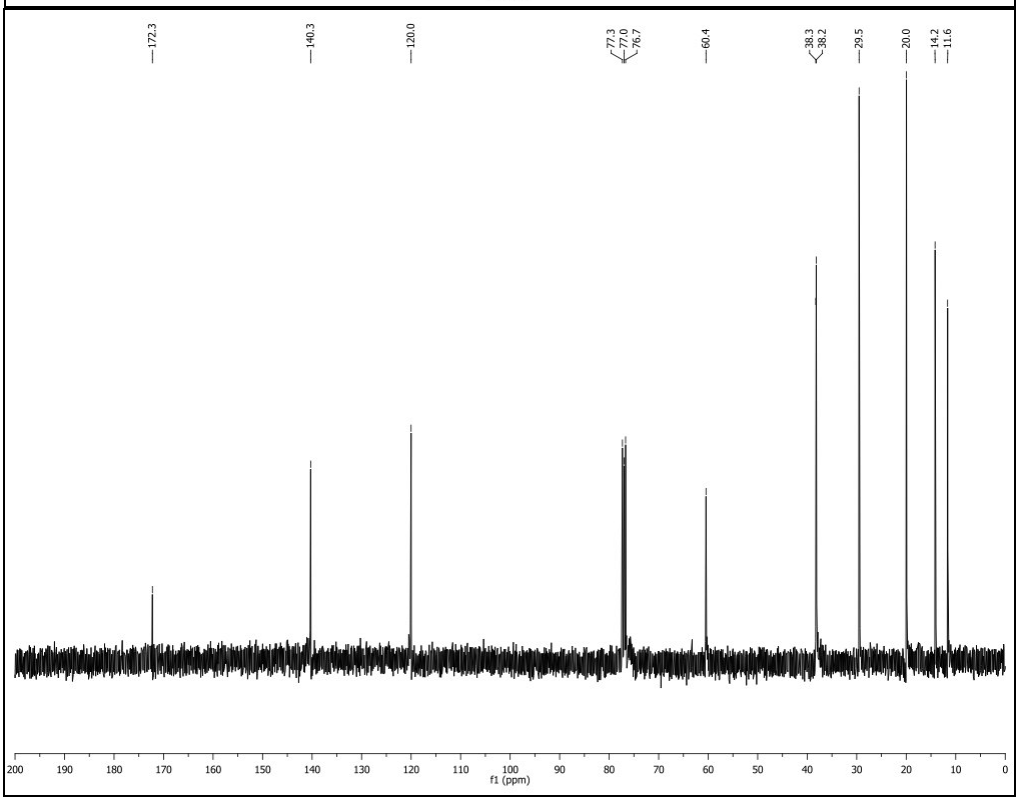


(*2E*,*4E*)-*S*-ethyl hepta-2,4-dienethioate (**22**)



(*R*)-(-)-(*E*)-ethyl 5-methylhept-3-enoate (**5**)





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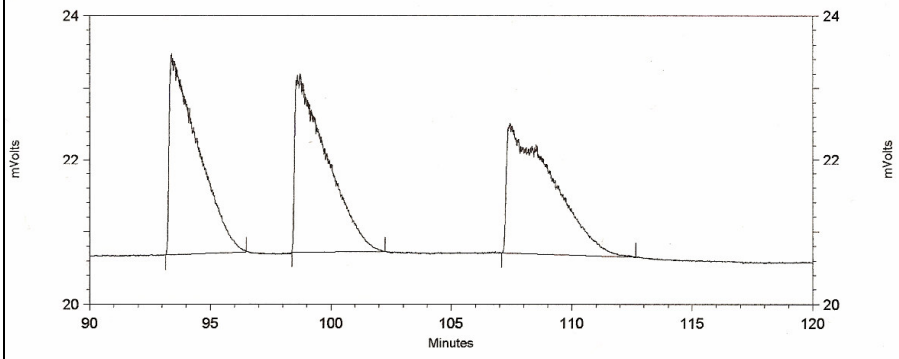

TDHMS1Et Cu -80

FID1 Results

Retention Time	Area	Area %
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98.730	224539	32.77
107.430	234894	34.28
Totals	685275	100.00

Area % Report

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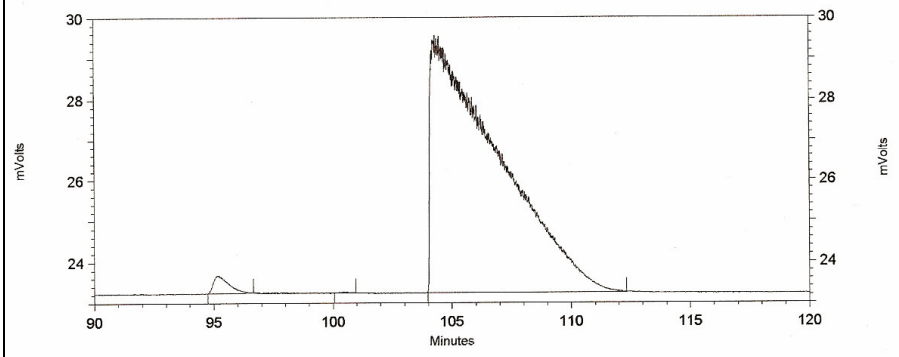

FID1 Results

Retention Time	Area	Area %
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100.470	952	0.08
104.310	1236777	98.37
Totals	1257327	100.00

Area % Report

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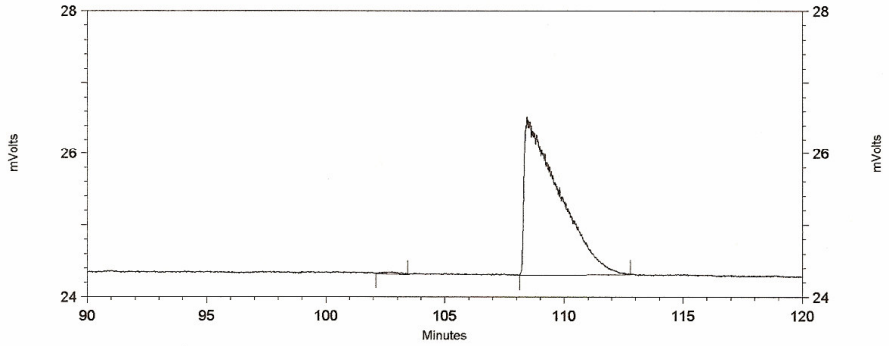

FID1 Results

Retention Time	Area	Area %
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108.443	220439	99.36
Totals	221855	100.00

Stereoselectivity

Area % Report

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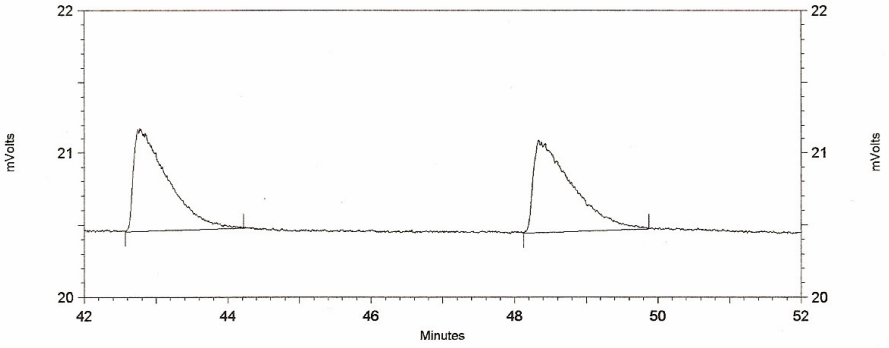
Printed: 07/30/2007 01:47:49 PM

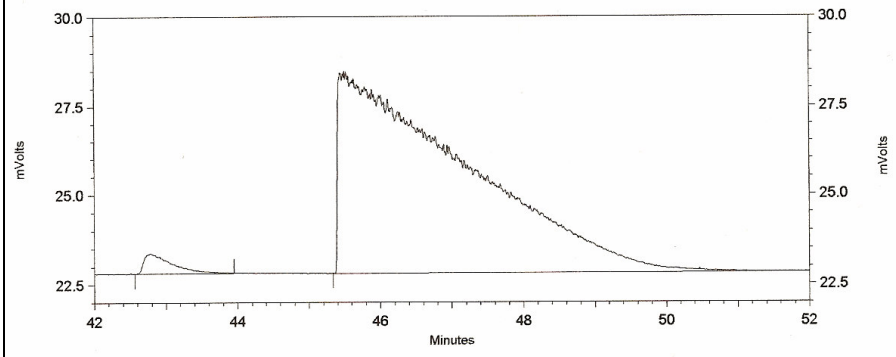


FID1 Results

Retention Time	Area	Area %
42.777	23462	49.71
48.340	23740	50.29
Totals	47202	100.00

Area % Report

Method Name: C:\CLASS-VP\Enterprise\Projects\Default\Method\A1_F_tdhsepCOOH2-80.met
Data: C:\CLASS-VP\Data\A1_15032007\A1_15032007_01
User: System
Acquired: 3/15/2007 7:21:45 PM
Printed: 07/30/2007 01:49:02 PM



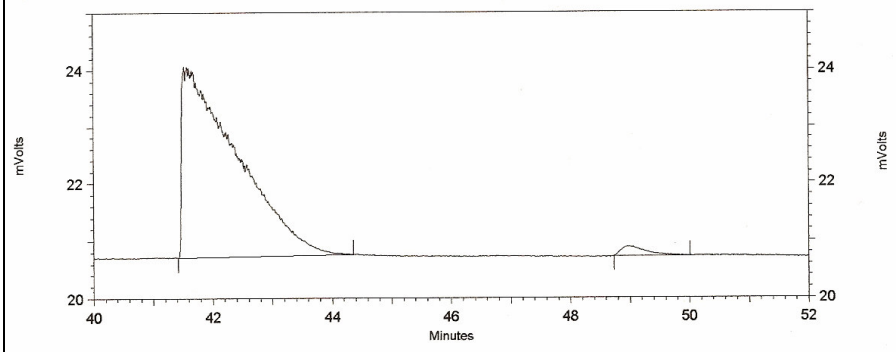
FID1 Results

Retention Time	Area	Area %
42.777	16051	2.26
45.503	694045	97.74
Totals	710096	100.00

Page 1 of 1

Area % Report

Method Name: C:\CLASS-VP\Enterprise\Projects\Default\Method\A1_F_tdhsepCOOH2-80.met
Data: C:\CLASS-VP\Data\A1_09062007\A1_09062007_03
User: System
Acquired: 6/9/2007 7:08:01 PM
Printed: 07/30/2007 01:49:49 PM

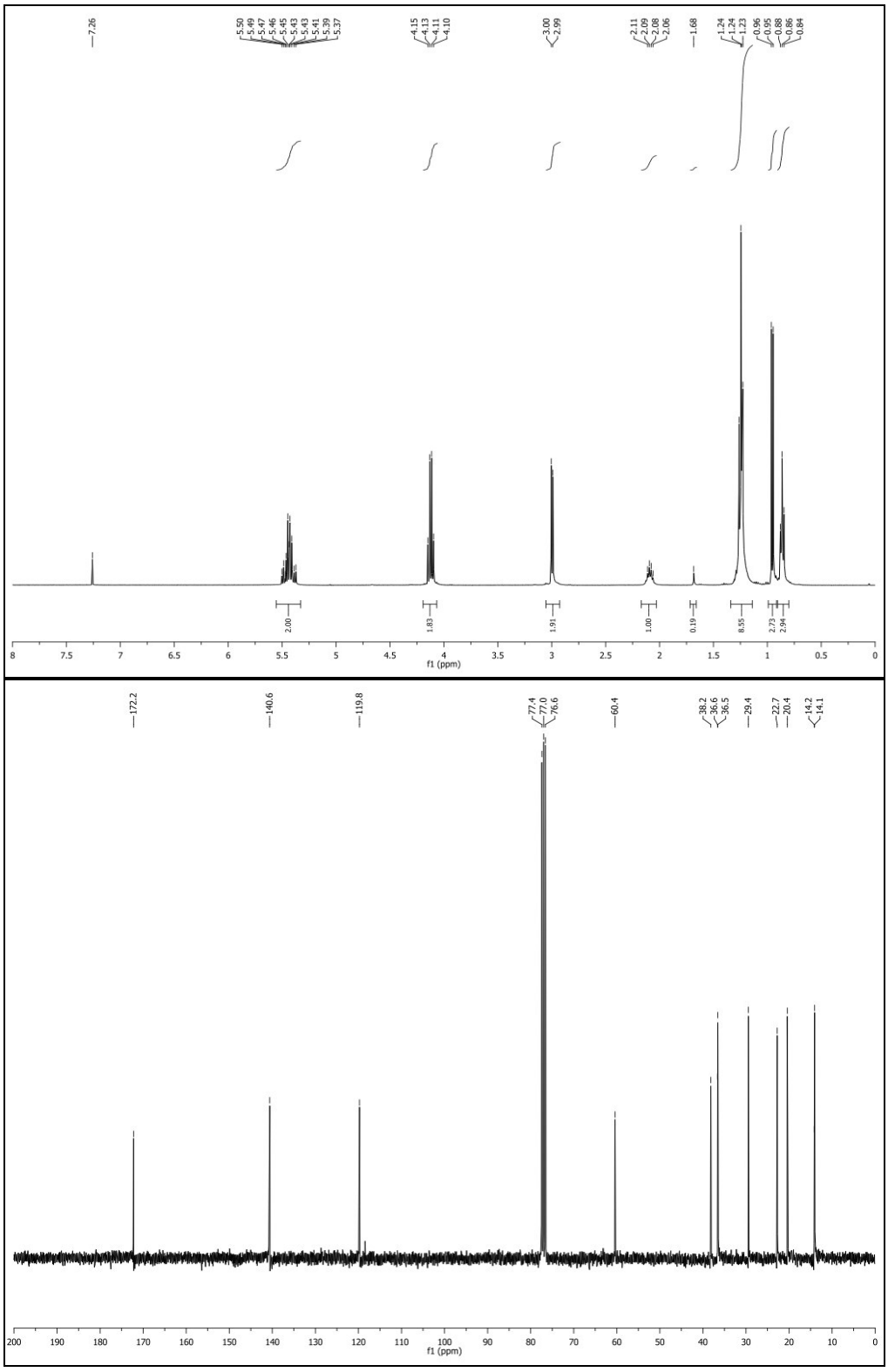


FID1 Results

Retention Time	Area	Area %
41.527	212908	97.78
48.953	4839	2.22
Totals	217747	100.00

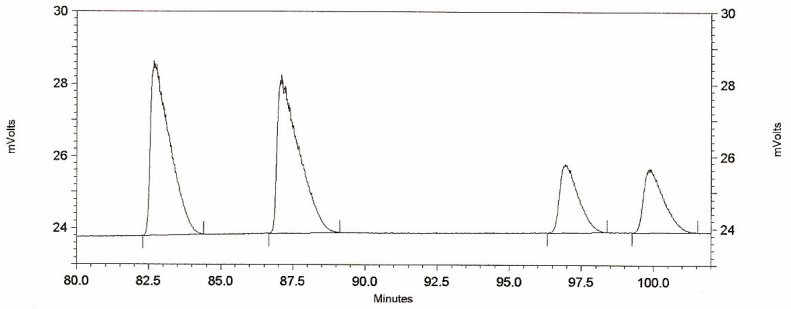
For ee: 96%

(-)-(*E*)-ethyl 5-methylnon-3-enoate (**15a**)



Area % Report

Method Name: C:\CLASS-VP\Enterprise\Projects\Default\Method\A1_F_tdhsepS1Bu2-80.met
Data: C:\CLASS-VP\Data\2006\A1_13072006\A1_13072006_tdh3
User: System
Acquired: 7/13/2006 9:35:35 PM
Printed: 07/30/2007 02:05:52 PM

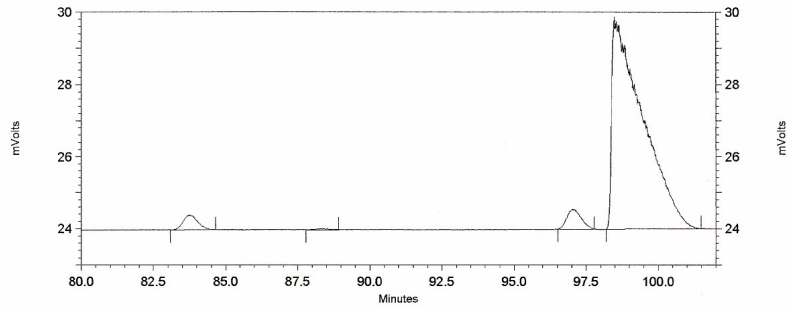


FID1 Results

Retention Time	Area	Area %
82.670	221976	36.20
87.097	223678	36.48
96.930	83939	13.69
99.870	83612	13.64
Totals	613205	100.00

Area % Report

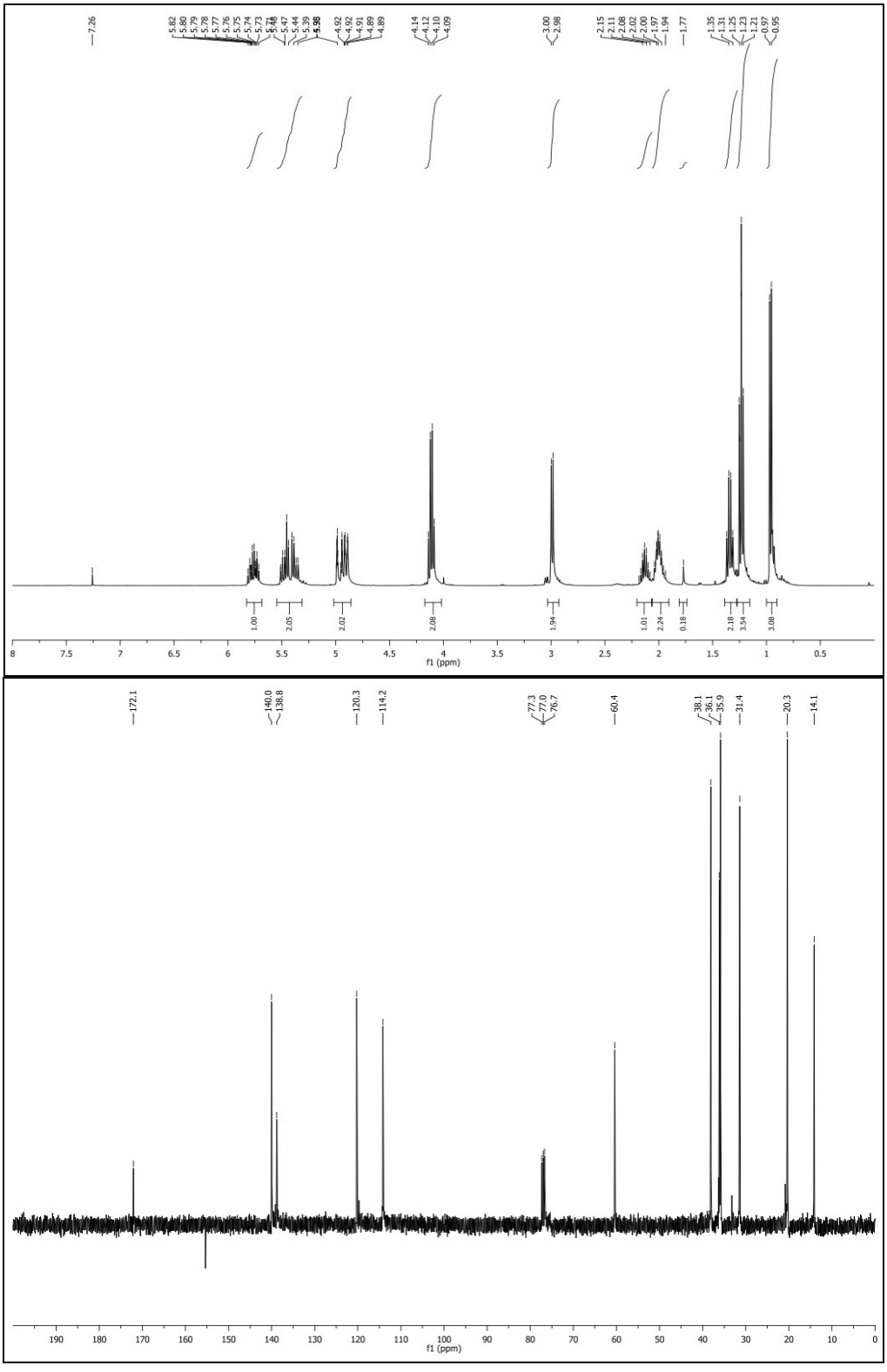
Method Name: C:\CLASS-VP\Enterprise\Projects\Default\Method\A1_F_tdhsepS1Bu2-80.met
Data: C:\CLASS-VP\Data\2006\A1_13072006\A1_13072006_tdh4
User: System
Acquired: 7/13/2006 11:46:25 PM
Printed: 07/30/2007 02:04:59 PM



FID1 Results

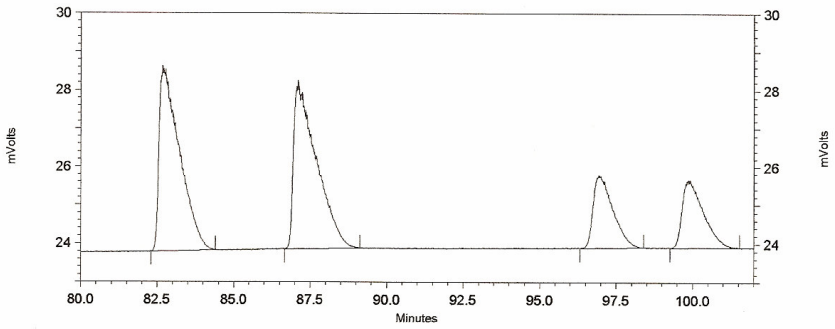
Retention Time	Area	Area %
83.767	14425	3.08
88.273	1307	0.28
97.040	18983	4.05
98.487	433479	92.59
Totals	468194	100.00

(-)-(*E*)-ethyl 5-methylnona-3,8-dienoate (**15b**)



Area % Report

Method Name: C:\CLASS-VP\Enterprise\Projects\Default\Method\A1_F_tdhsepS1Bu2-80.met
Data: C:\CLASS-VP\Data\2006\A1_13072006\A1_13072006_tdh3
User: System
Acquired: 7/13/2006 9:35:35 PM
Printed: 07/30/2007 02:05:52 PM

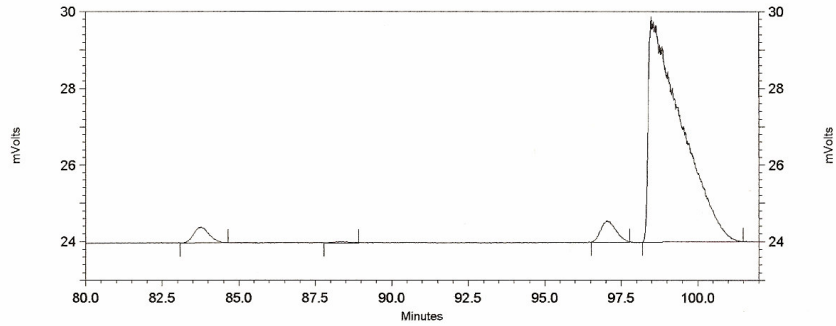


FID1 Results

Retention Time	Area	Area %
82.670	221976	36.20
87.097	223678	36.48
96.930	83939	13.69
99.870	83612	13.64
Totals	613205	100.00

Area % Report

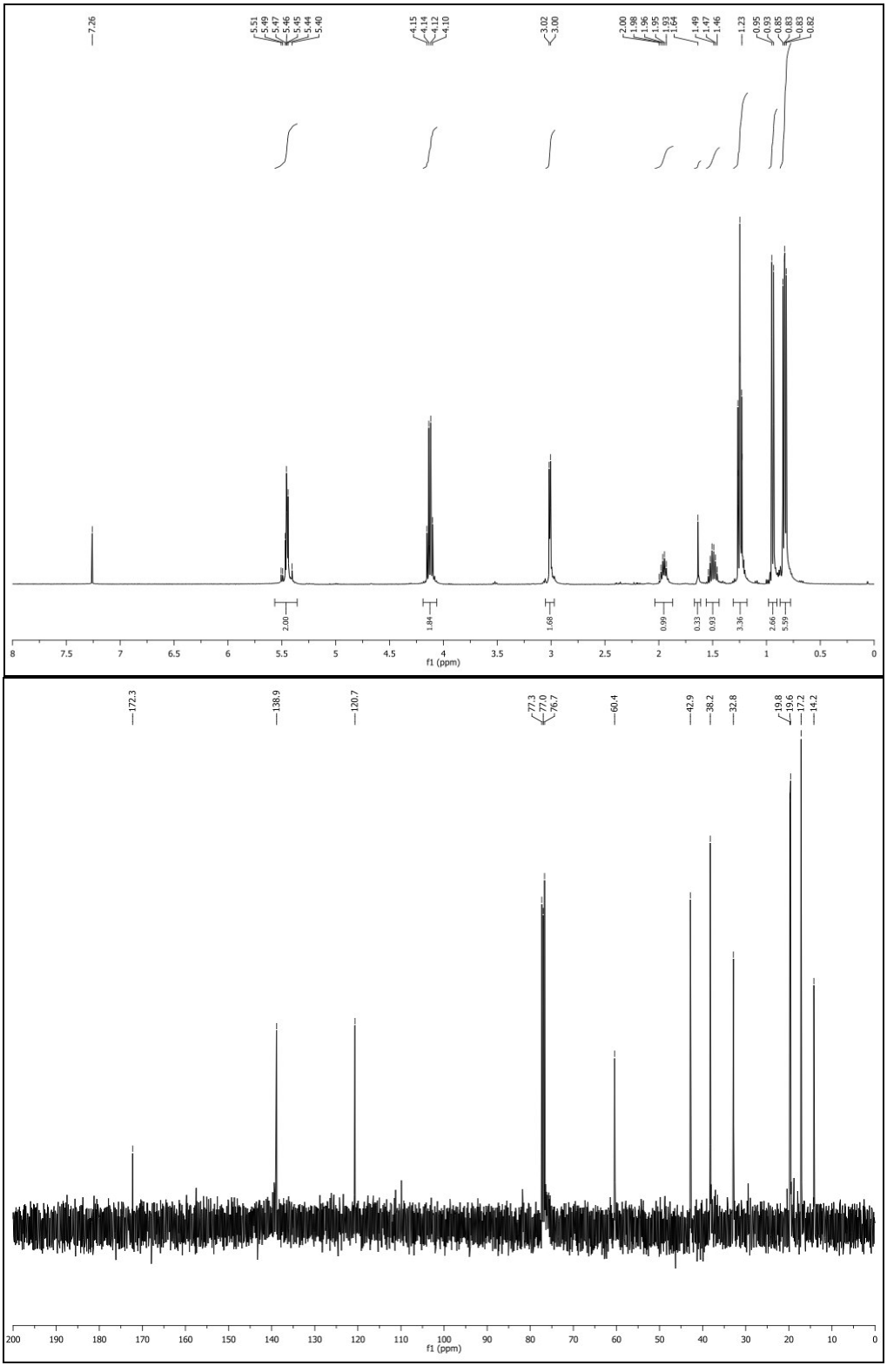
Method Name: C:\CLASS-VP\Enterprise\Projects\Default\Method\A1_F_tdhsepS1Bu2-80.met
Data: C:\CLASS-VP\Data\2006\A1_13072006\A1_13072006_tdh4
User: System
Acquired: 7/13/2006 11:46:25 PM
Printed: 07/30/2007 02:04:59 PM



FID1 Results

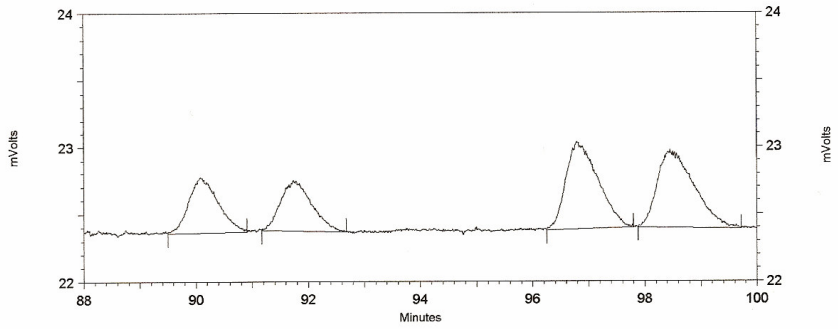
Retention Time	Area	Area %
83.767	14425	3.08
88.273	1307	0.28
97.040	18983	4.05
98.487	433479	92.59
Totals	468194	100.00

(-)-(*E*)-ethyl 5,6-dimethylhept-3-enoate (**15c**)



Area % Report

Method Name: C:\CLASS-VP\Enterprise\Projects\Default\Method\A1_F_tdhsepS1iPr-70.met
Data: C:\CLASS-VP\Data\2006\A1_10072006\A1_10072006_tdh5
User: System
Acquired: 7/10/2006 11:46:27 PM
Printed: 07/30/2007 01:58:44 PM



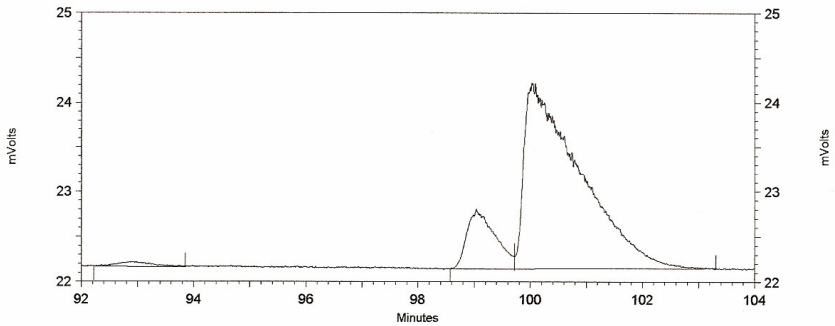
FID1 Results

Retention Time	Area	Area %
90.077	14875	18.35
91.737	14295	17.63
96.797	25855	31.89
98.457	26054	32.13

Totals		
	81079	100.00

Area % Report

Method Name: C:\CLASS-VP\Enterprise\Projects\Default\Method\A1_F_tdhsepS1iPr-70.met
Data: C:\CLASS-VP\Data\A1_14052007\A1_18052007_01
User: System
Acquired: 5/18/2007 12:36:57 PM
Printed: 07/30/2007 02:00:32 PM

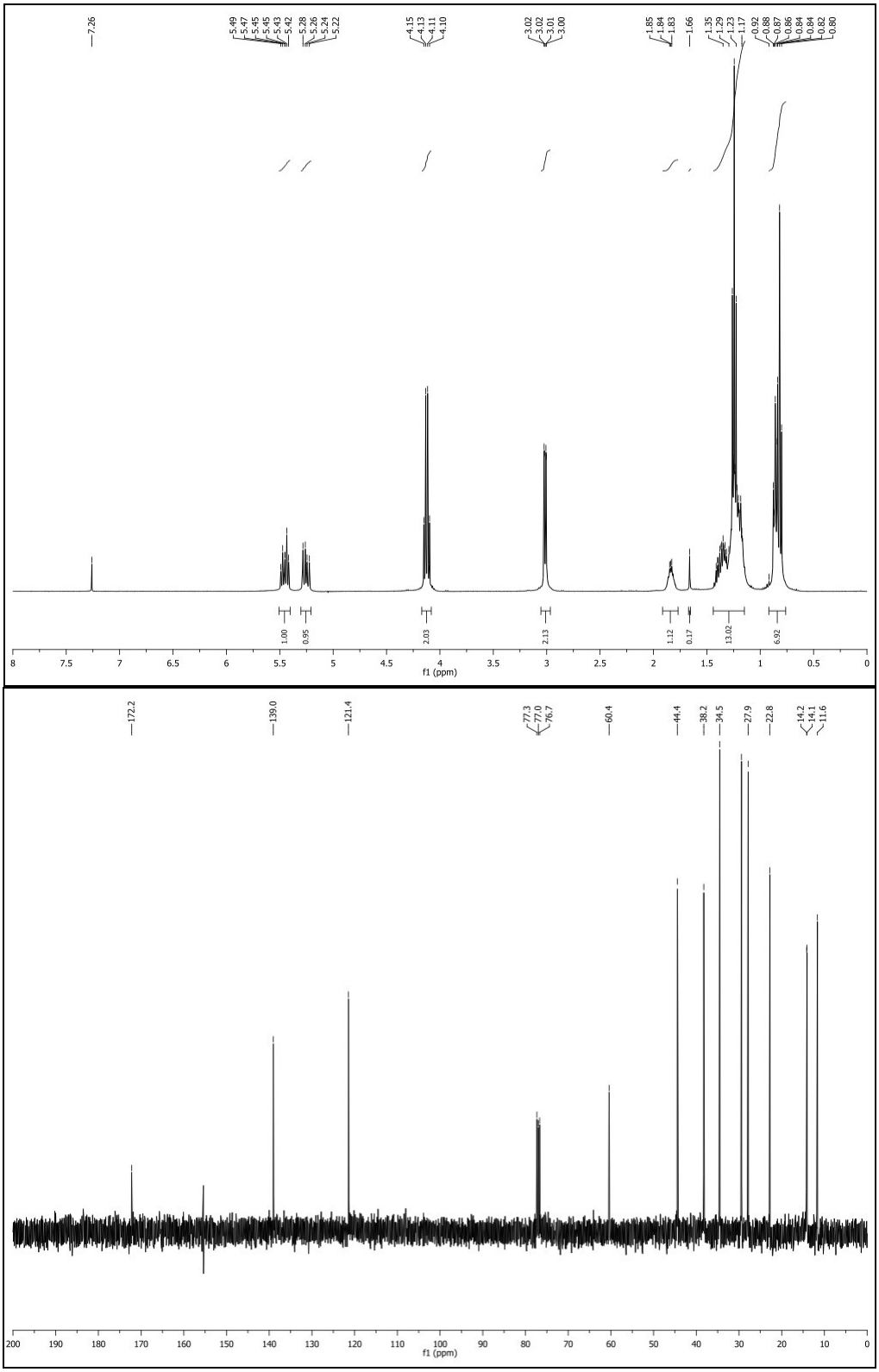


FID1 Results

Retention Time	Area	Area %
92.857	2372	1.41
99.033	23067	13.70
100.027	142948	84.89

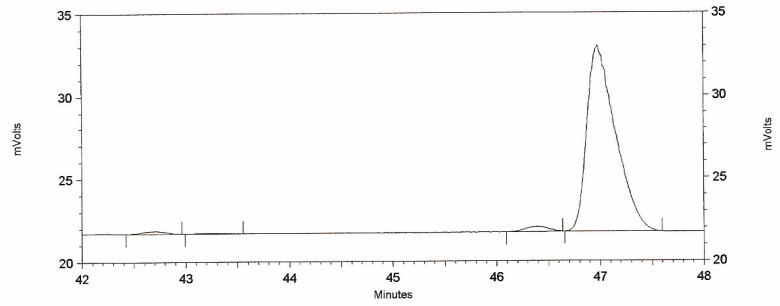
Totals		
	168387	100.00

(-)-(*E*)-ethyl 5-ethylnon-3-enoate (**18a**)



Area % Report

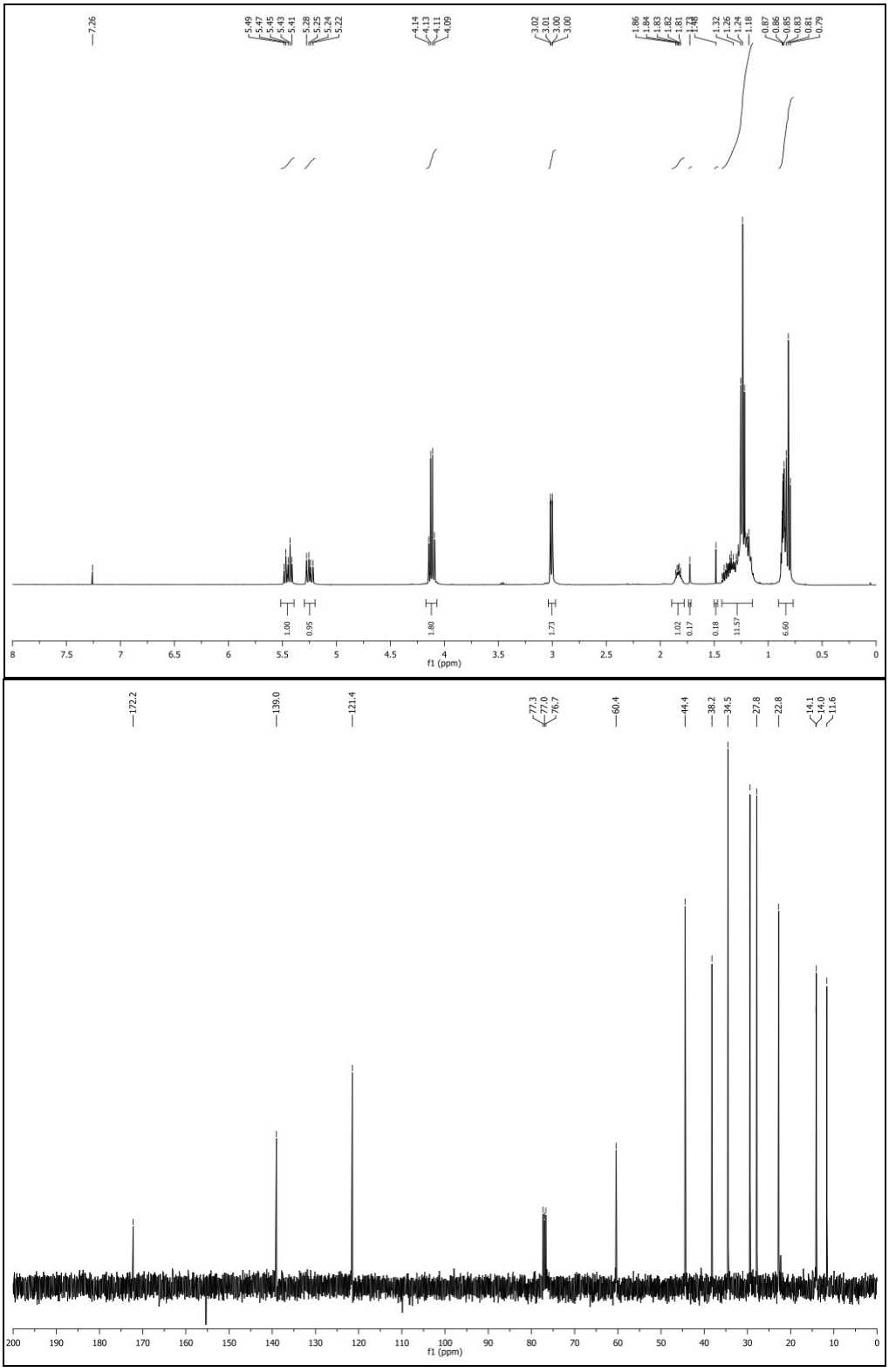
Method Name: C:\CLASS-VP\Enterprise\Projects\Default\Method\A1_F_tdhsepS2Bu1-100.met
Data: C:\CLASS-VP\Data\2006\A1_21072006\A1_21072006_tdh3
User: System
Acquired: 7/21/2006 3:56:21 PM
Printed: 07/30/2007 02:20:59 PM



FID1 Results

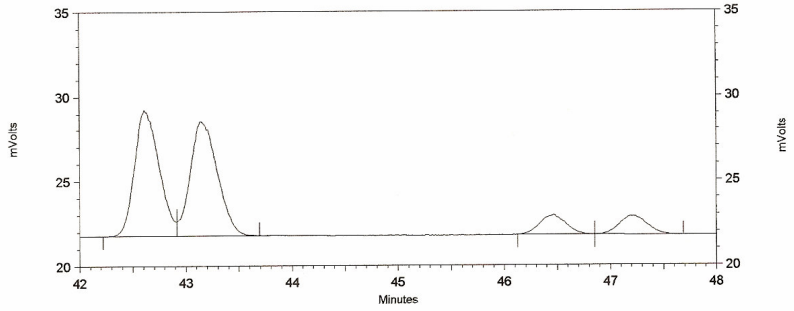
Retention Time	Area	Area %
42.707	2627	1.17
43.267	702	0.31
46.403	4755	2.12
46.980	215937	96.39
Totals	224021	100.00

(+)-(*E*)-ethyl 5-ethylnon-3-enoate (**18a**)



Area % Report

Method Name: C:\CLASS-VP\Enterprise\Projects\Default\Method\A1_F_tdhsepS2Bu1-100.met
Data: C:\CLASS-VP\Data\2006\A1_21072006\A1_21072006_tdh1
User: System
Acquired: 7/21/2006 1:14:19 PM
Printed: 07/30/2007 02:22:48 PM

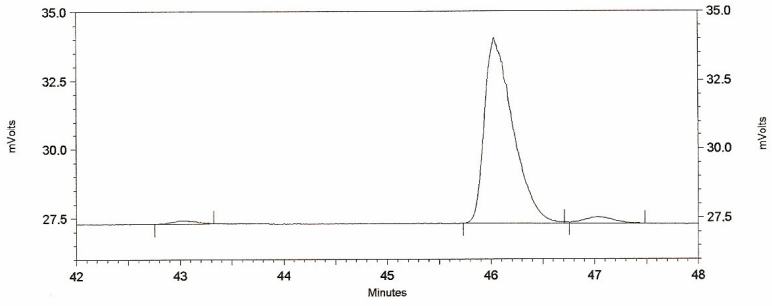


FID1 Results

Retention Time	Area	Area %
42.610	119730	43.03
43.137	119008	42.77
46.467	19645	7.06
47.193	19894	7.15
Totals	278277	100.00

Area % Report

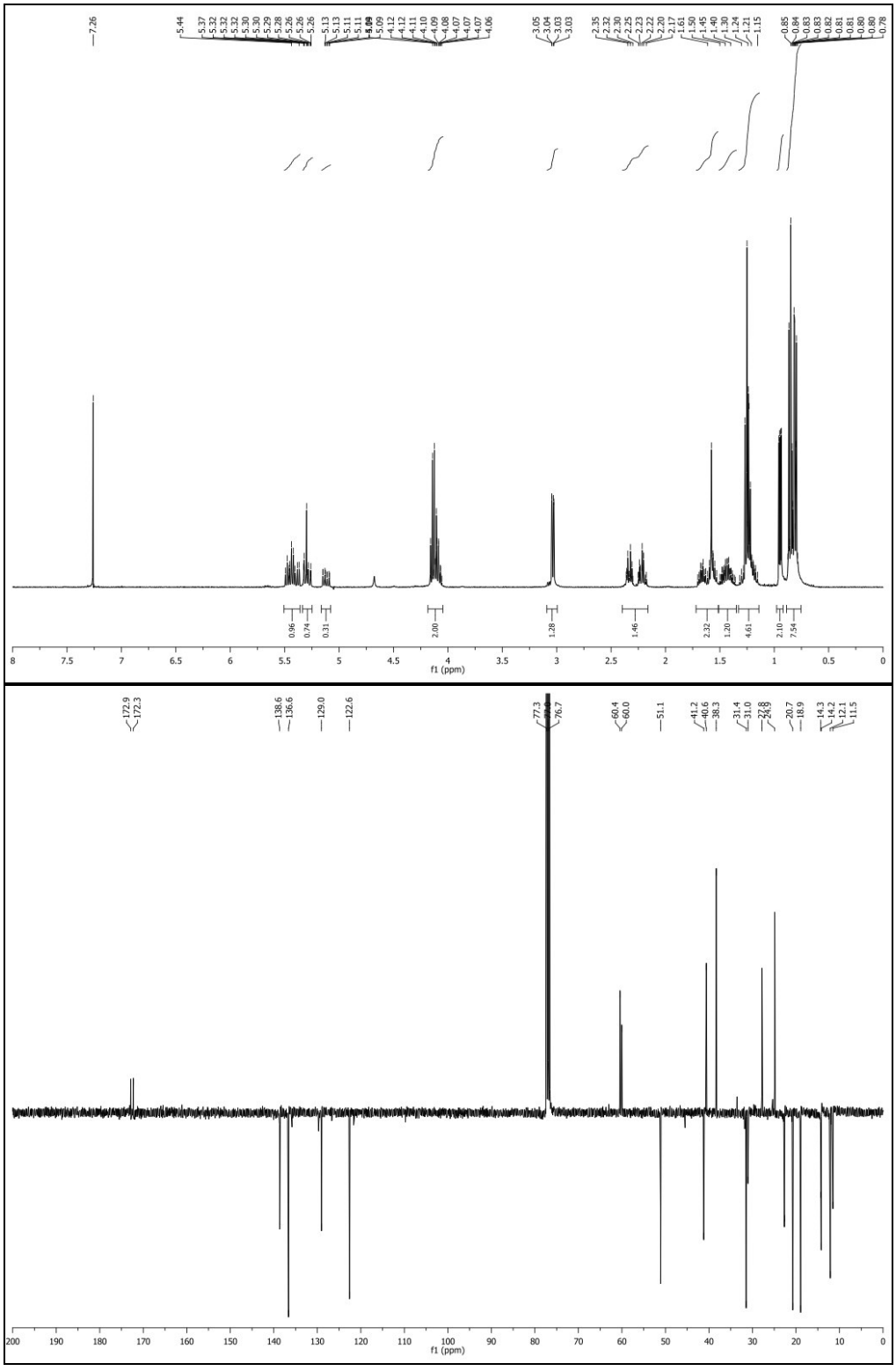
Method Name: C:\CLASS-VP\Enterprise\Projects\Default\Method\A1_F_tdhsepS2Bu1-100.met
Data: C:\CLASS-VP\Data\2006\A1_09102006\A1_12102006_01
User: System
Acquired: 10/12/2006 9:43:44 AM
Printed: 07/30/2007 02:23:49 PM



FID1 Results

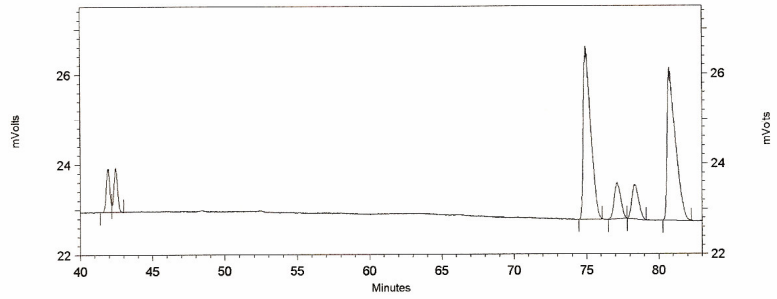
Retention Time	Area	Area %
42.993	1867	1.39
46.030	128063	95.13
47.027	4689	3.48
Totals	134619	100.00

(-)-(*E*)-ethyl 5-ethyl-6-methylhept-3-enoate (β,γ- **18c**) and (-)-(*E*)-ethyl 5-ethyl-6-methylhept-2-enoate (α,β-**19c**)



Area % Report

Method Name: C:\CLASS-VP\Enterprise\Projects\Default\Method\A1_F_tdhsepS1Bu2-80.met
Data: C:\CLASS-VP\Data\2006\A1_20072006\A1_20072006_tdh7
User: System
Acquired: 7/21/2006 6:31:50 AM
Printed: 07/30/2007 02:27:24 PM

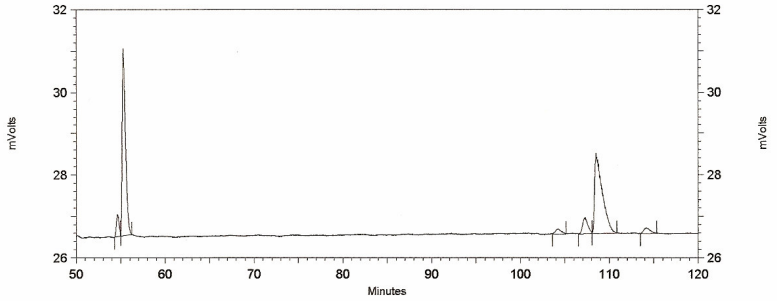


FID1 Results

Retention Time	Area	Area %
41.947	16278	4.61
42.443	16458	4.66
74.937	135021	38.20
77.123	25011	7.08
78.313	25100	7.10
80.727	135616	38.37
Totals	353484	100.00

Area % Report

Method Name: C:\CLASS-VP\Enterprise\Projects\Default\Method\A1_F_tdhsepS14Et-75.met
Data: C:\CLASS-VP\Data\2006\A1_16102006\A1_16102006_03
User: System
Acquired: 10/17/2006 11:36:19 AM
Printed: 07/30/2007 02:31:35 PM

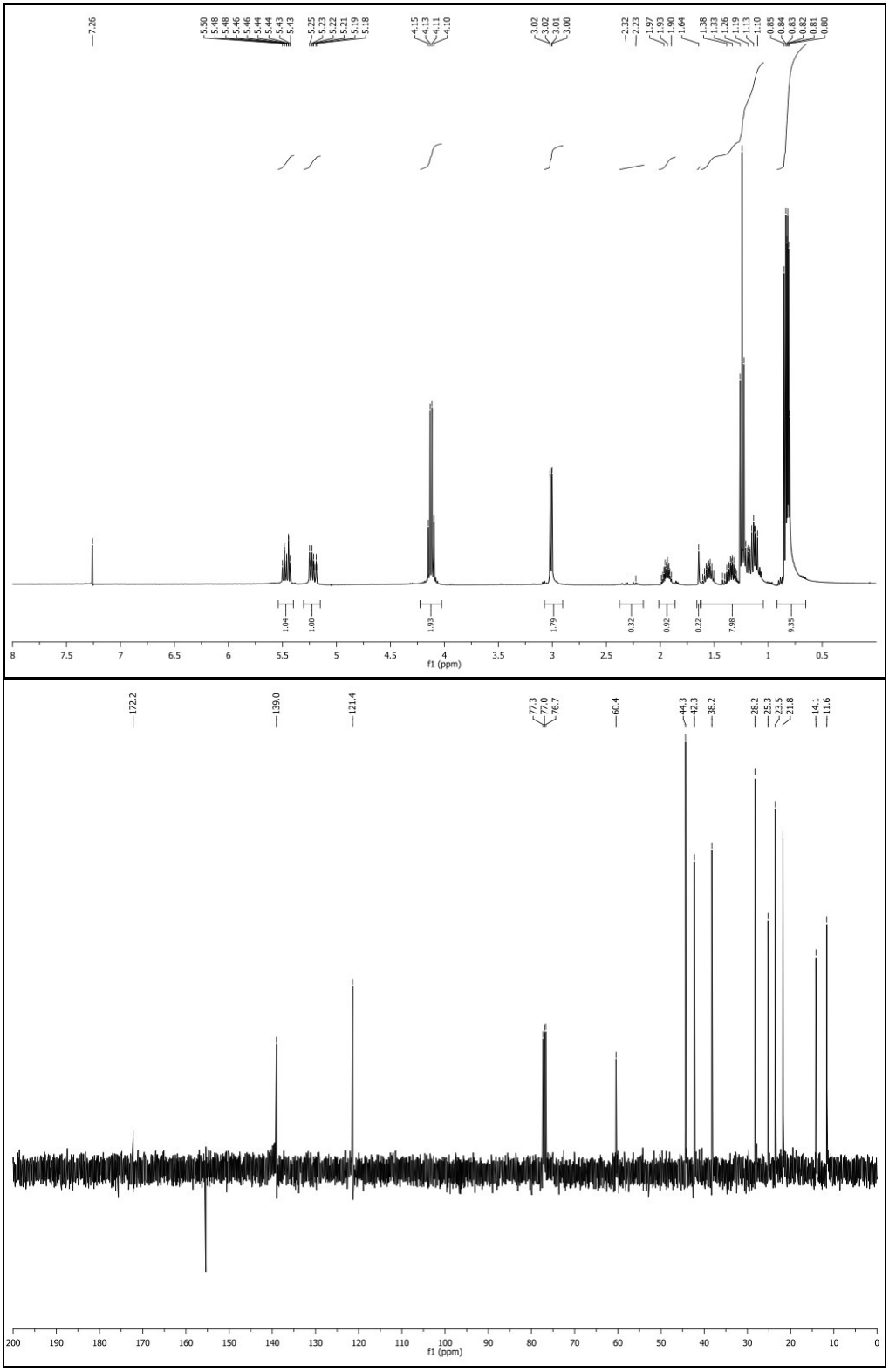


FID1 Results

Retention Time	Area	Area %
54.617	10753	3.96
55.267	114982	42.35
104.210	5495	2.02
107.190	15855	5.84
108.490	117494	43.28
114.133	6907	2.54
Totals	271486	100.00

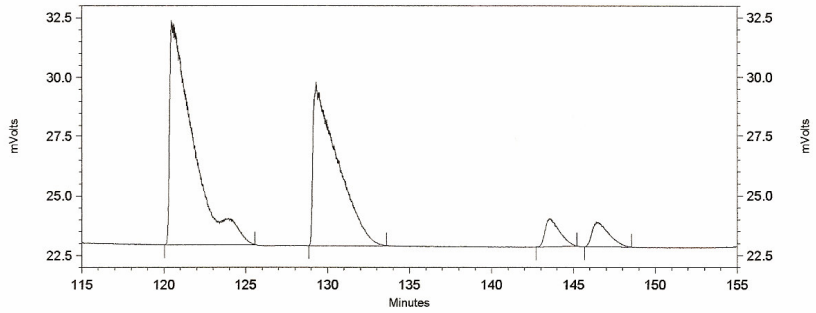
ee α,β-: 83%; ee β,γ-: 77%

(+)-(*E*)-ethyl 5-ethyl-7-methyloct-3-enoate (**18d**)



Area % Report

Method Name: C:\CLASS-VP\Enterprise\Projects\Default\Method\A1_F_tdhsepS23Et-75.met
Data: C:\CLASS-VP\Data\2006\A1_02102006\A1_02102006_tdh6
User: System
Acquired: 10/2/2006 9:54:58 PM
Printed: 07/30/2007 02:38:26 PM



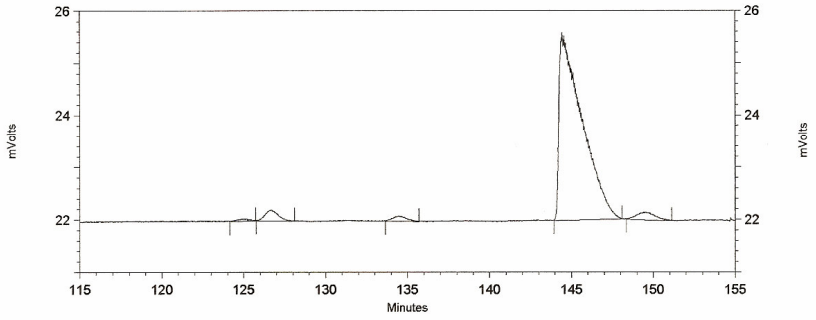
FID1 Results

Retention Time	Area	Area %
120.470	918771	52.15
129.303	696741	39.55
143.637	73137	4.15
146.400	73131	4.15

Totals	1761780	100.00

Area % Report

Method Name: C:\CLASS-VP\Enterprise\Projects\Default\Method\A1_F_tdhsepS23Et-75.met
Data: C:\CLASS-VP\Data\A1_19072007\A1_23072007_02
User: System
Acquired: 7/23/2007 3:43:10 PM
Printed: 07/30/2007 02:40:25 PM

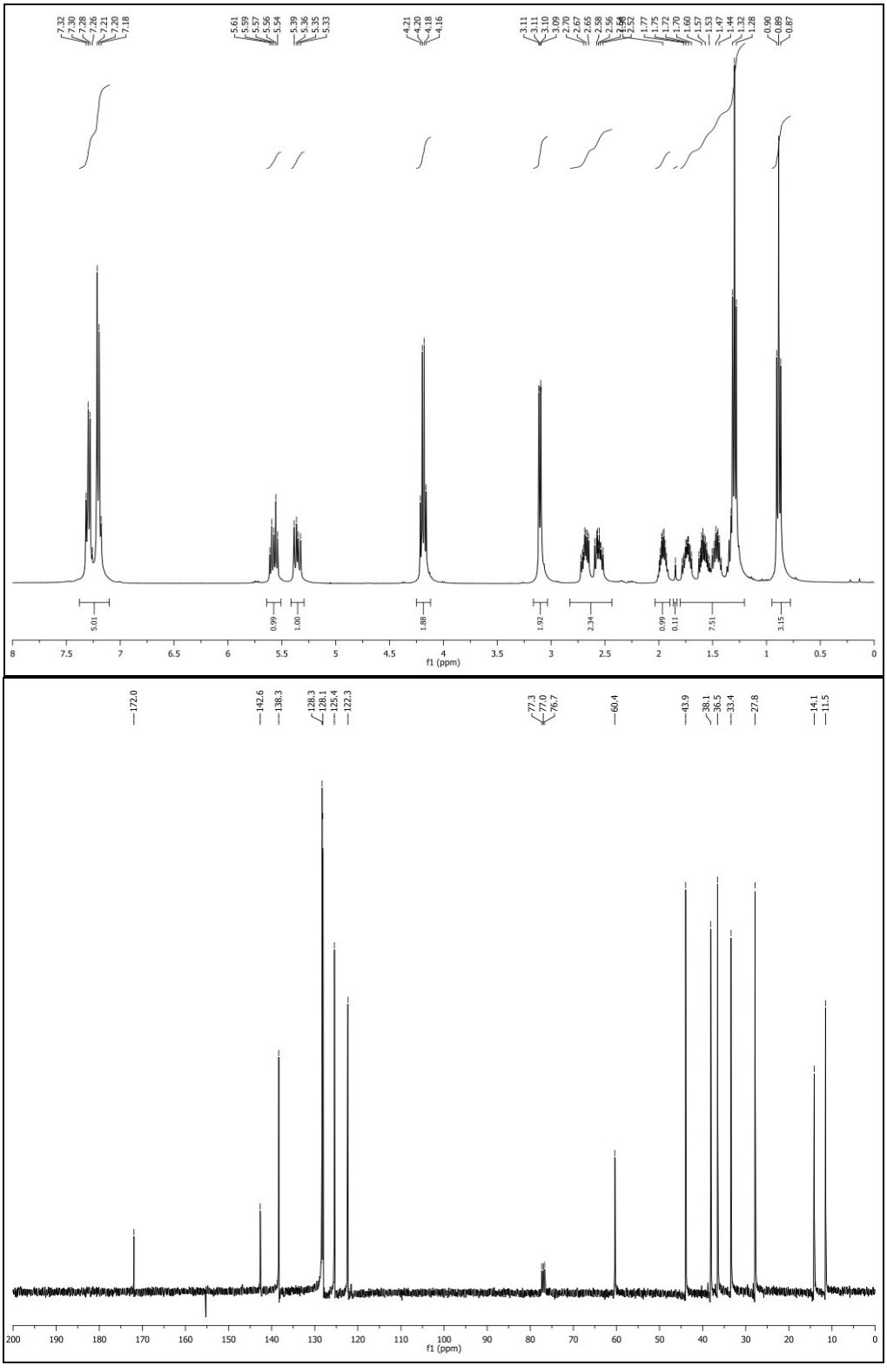


FID1 Results

Retention Time	Area	Area %
125.130	2114	0.56
126.657	11671	3.08
134.520	6155	1.62
144.443	347872	91.66
149.437	11727	3.09

Totals	379539	100.00

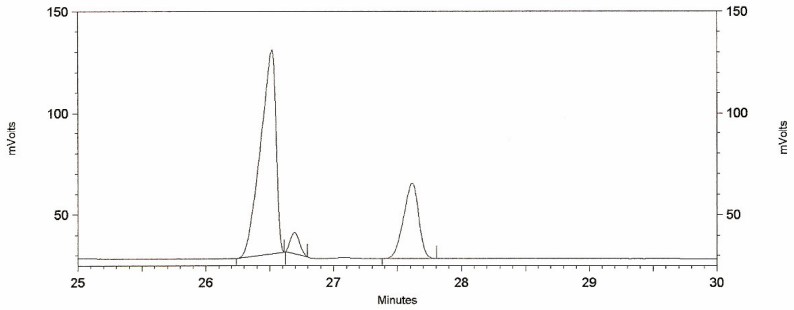
(+)-(*E*)-ethyl 5-ethyl-7-phenylhept-3-enoate (**18e**)



Regioselectivity:

Area % Report

Method Name: C:\CLASS-VP\Enterprise\Projects\Default\Method\A1_F_tdhsepS22Et.met
Data: C:\CLASS-VP\Data\2006\A1_04102006\A1_04102006_tdh5
User: System
Acquired: 10/4/2006 5:20:33 PM
Printed: 07/30/2007 02:34:58 PM

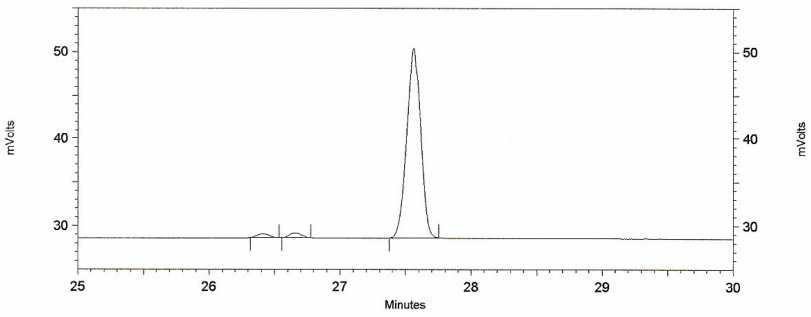


FID1 Results

Retention Time	Area	Area %
26.517	845545	70.47
26.693	52106	4.34
27.610	302223	25.19
Totals	1199874	100.00

Area % Report

Method Name: C:\CLASS-VP\Enterprise\Projects\Default\Method\A1_F_tdhsepS22Et.met
Data: C:\CLASS-VP\Data\2006\A1_04102006\A1_04102006_tdh6
User: System
Acquired: 10/4/2006 7:49:30 PM
Printed: 07/30/2007 02:34:28 PM

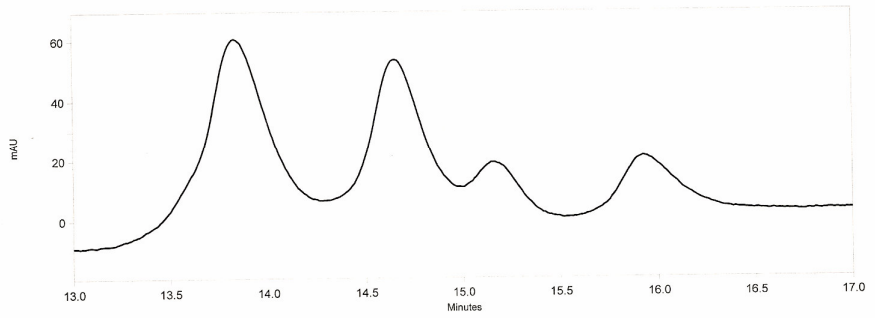


FID1 Results

Retention Time	Area	Area %
26.407	2679	1.61
26.657	3382	2.03
27.563	160641	96.36
Totals	166702	100.00

Stereoselectivity:

Sample ID: tdhs21 rac whelk999-01
Data Name: F:\NP-HPLC backup 2007 may 08\!Data from 2006 and before\09102006\09102006_95
User: System
Method Name: C:\CLASS-VP\Methods\Algemeen\Chiralcel OD-H\ODH 90_10 30min.met
Vial # : 55
Inj. Vol : 6 ul
Sample Amt: 1
Acquired: 10/14/2006 3:10:11 AM
Printed: 7/30/2007 3:11:30 PM



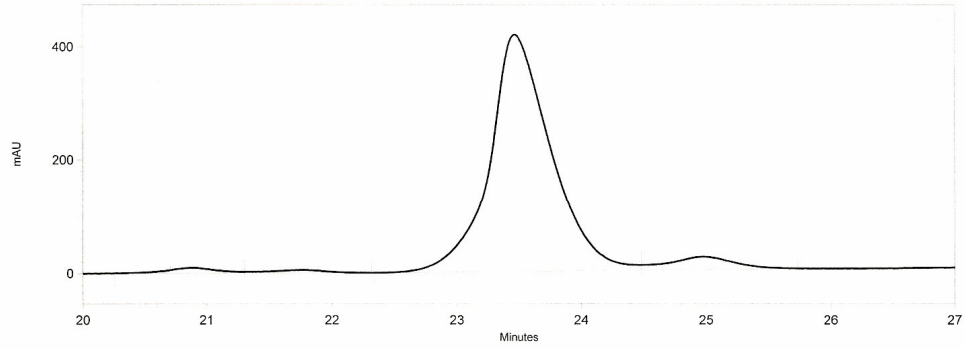
1: 205 nm, 8 nm

Pk #	Name	Retention Time	Area	Area Percent

Peak: 1

Peak: 1 Peak: 2

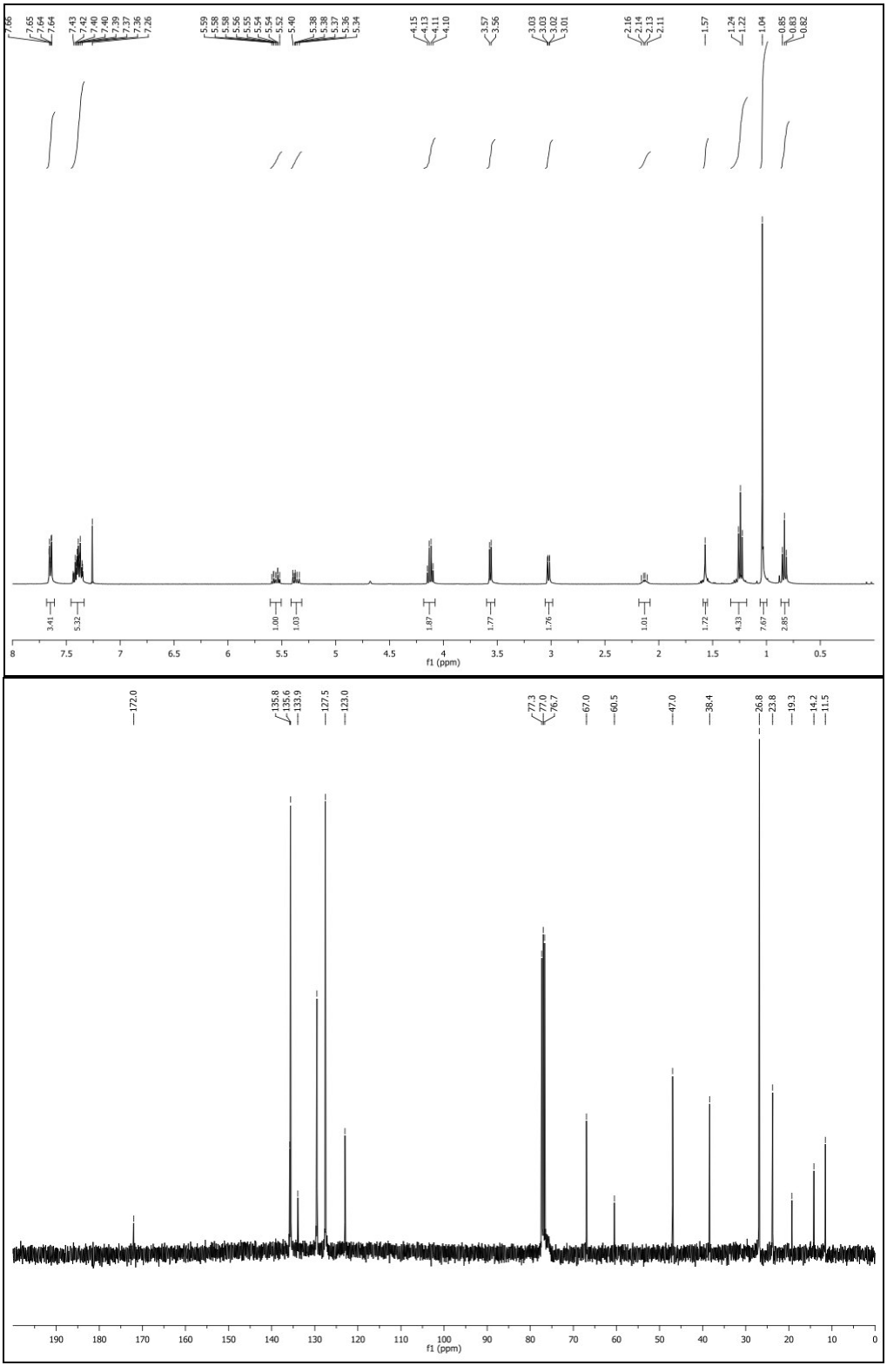
Sample ID: tdhs21Et
Data Name: F:\NP-HPLC backup 2007 may 08\!Data from 2006 and before\10112006\10112006_08
User: System
Method Name: C:\CLASS-VP\Methods\Algemeen\Chiralcel OD-H\ODH 90_10 30min.met
Vial # : 24
Inj. Vol : 2 ul
Sample Amt: 1
Acquired: 11/10/2006 8:40:15 PM
Printed: 7/30/2007 3:10:40 PM



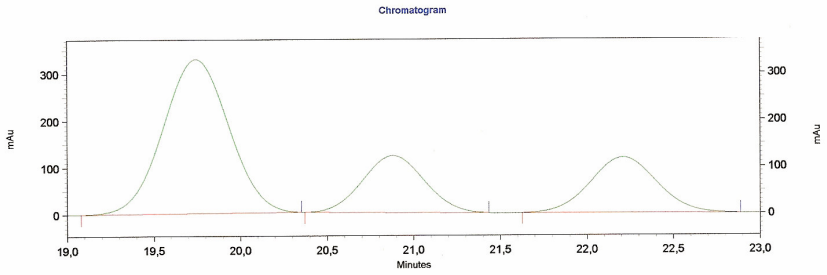
1: 205 nm, 8 nm

Pk #	Name	Retention Time	Area	Area Percent
1	1	20.896	258522	1.65
2	2	21.781	154779	0.99
3		22.261	797	0.01
4	3	23.467	14414927	92.13
5	4	24.971	817297	5.22
Totals			15646322	100.00

(-)-(*E*)-ethyl 5-[(*tert*-butyldiphenylsilyloxy)methyl]hept-3-enoate (**18f**)



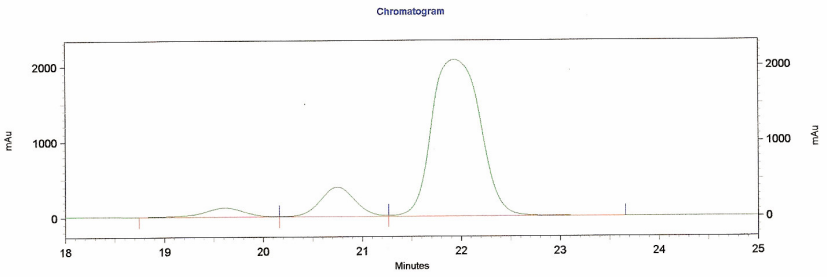
Sample ID : thms22Et derOH rac ODH 99-1
Vial# : 31
Sample amount : 1
Inj. volume : 3
Acquired : 30-7-2007 14:40:32
Data Name : D:\DATA\20070622\20070622_18
Method Name :
C:\CLASS-VP\Enterprise\Projects\Default\Method\General\Chiralpak AS-H\AS-H 90_10 45 min.met
Sequence Name :
C:\CLASS-VP\Enterprise\Projects\Default\Sequence\20070726.seq



1: 215 nm,
2 nm Results

Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 19,744 Minutes	19,744	8685926	58,429
2	Peak @ 20,880 Minutes	20,880	3022914	20,335
3	Peak @ 22,208 Minutes	22,208	3157005	21,237
Totals			14865845	100,000

Sample ID : thms22Et derOH sel ODH 99-1
Vial# : 32
Sample amount : 1
Inj. volume : 3
Acquired : 25-6-2007 9:20:50
Data Name : D:\DATA\20070622\20070622_19
Method Name :
C:\CLASS-VP\Enterprise\Projects\Default\Method\General\Chiralpak AS-H\AS-H 90_10 45 min.met
Sequence Name :
C:\CLASS-VP\Enterprise\Projects\Default\Sequence\20070726.seq

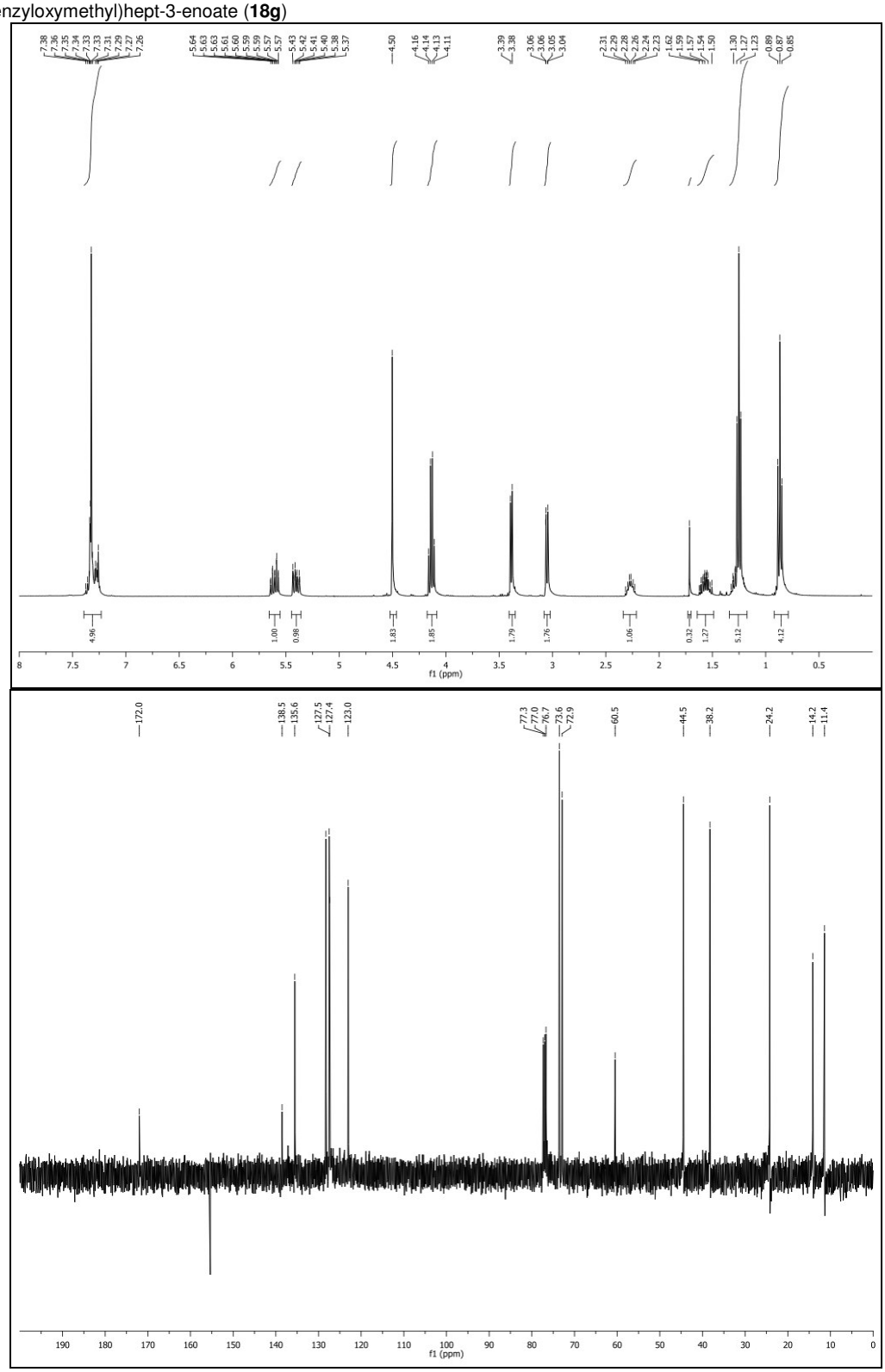


1: 215 nm,
2 nm Results

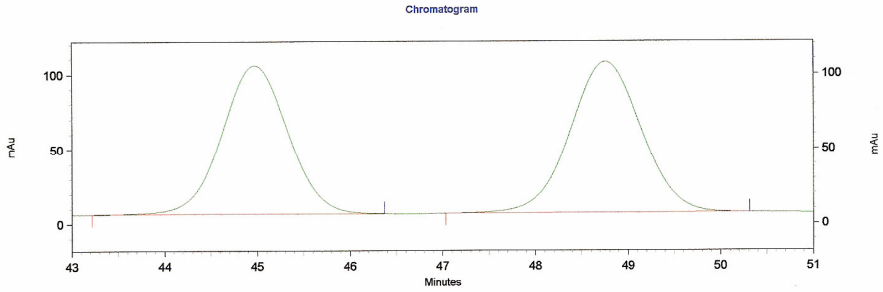
Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 19,612 Minutes	19,612	3402035	4,082
2	Peak @ 20,748 Minutes	20,748	9550931	11,459
3	Peak @ 21,932 Minutes	21,932	70396255	84,459
Totals			83349221	100,000

for ee: 76%

(-)-(E)-ethyl 5-(benzyloxymethyl)hept-3-enoate (**18g**)



Sample ID : tdhs21 et rac odh 99-1
Vial# : 47
Sample amount : 1
Inj. volume : 2
Acquired : 30-7-2007 14:51:10
Data Name : D:\DATA\20070726\20070726_02
Method Name :
C:\CLASS-VP\Enterprise\Projects\Default\Method\General\Chiralpak AS-H\AS-H 90_10 45 min.met
Sequence Name :
C:\CLASS-VP\Enterprise\Projects\Default\Sequence\20070726.seq



1: 210 nm,
2 nm Results

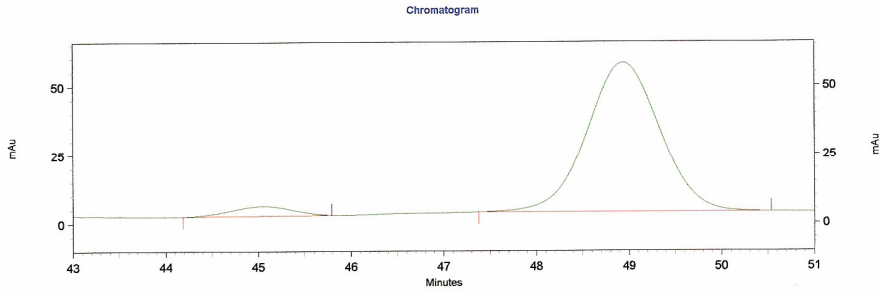
Pk #	Name	Retention Time	Area	Area Percent

Spectrum Report

Spectra of all named detected peaks

(The peak spectrum is defined as the peak apex spectrum)

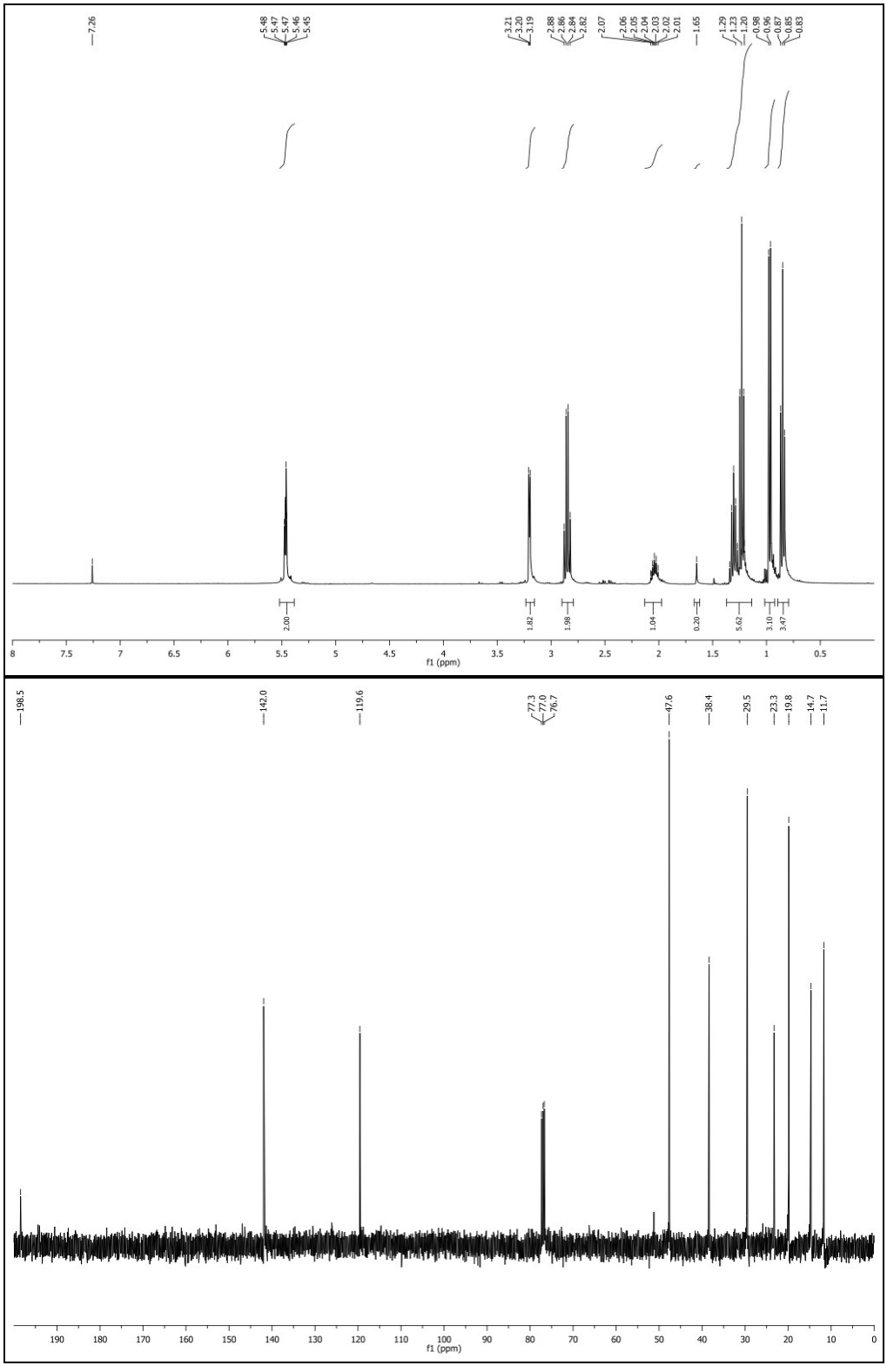
Sample ID : tdhs21 et sel odh 99-1
Vial# : 48
Sample amount : 1
Inj. volume : 2
Acquired : 26-7-2007 13:28:02
Data Name : D:\DATA\20070726\20070726_03
Method Name :
C:\CLASS-VP\Enterprise\Projects\Default\Method\General\Chiralpak AS-H\AS-H 90_10 45 min.met
Sequence Name :
C:\CLASS-VP\Enterprise\Projects\Default\Sequence\20070726.seq



1: 215 nm,
2 nm Results

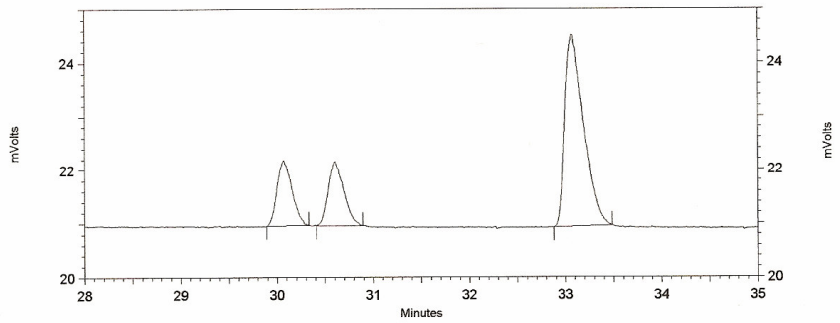
Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 45,052 Minutes	45,052	160988	5,125
2	Peak @ 48,940 Minutes	48,940	2979942	94,875
Totals			3140930	100,000

(*S*)-(+)-(*E*)-*S*-ethyl 5-methylhept-3-enethioate (**23**)



Area % Report

Method Name: C:\CLASS-VP\Enterprise\Projects\Default\Method\A1_F_tdhsepS21Et100.met
Data: C:\CLASS-VP\Data\A1_08062007\A1_08062007_02
User: System
Acquired: 6/8/2007 9:52:49 AM
Printed: 07/30/2007 02:11:13 PM

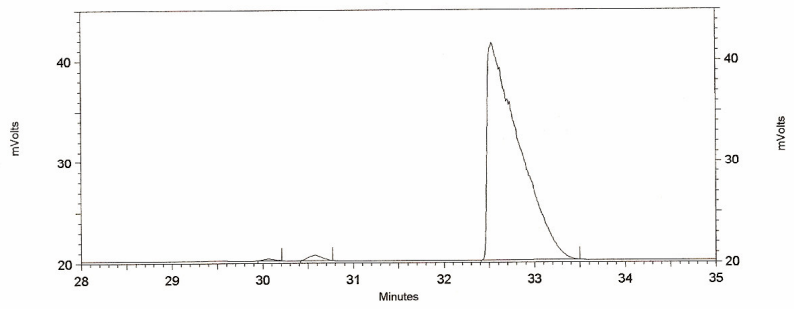


FID1 Results

Retention Time	Area	Area %
30.070	13171	17.63
30.603	13443	17.99
33.070	48110	64.38
Totals	74724	100.00

Area % Report

Method Name: C:\CLASS-VP\Enterprise\Projects\Default\Method\A1_F_tdhsepS21Et100.met
Data: C:\CLASS-VP\Data\A1_08062007\A1_08062007_03
User: System
Acquired: 6/8/2007 12:34:11 PM
Printed: 07/30/2007 02:12:08 PM

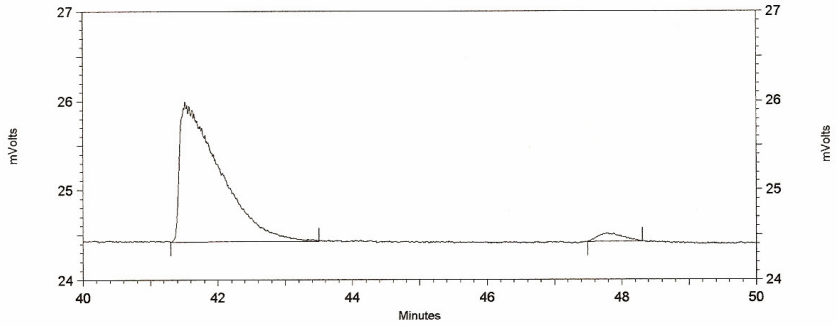


FID1 Results

Retention Time	Area	Area %
30.070	1372	0.26
30.570	5278	1.00
32.530	522085	98.74
Totals	528735	100.00

Area % Report

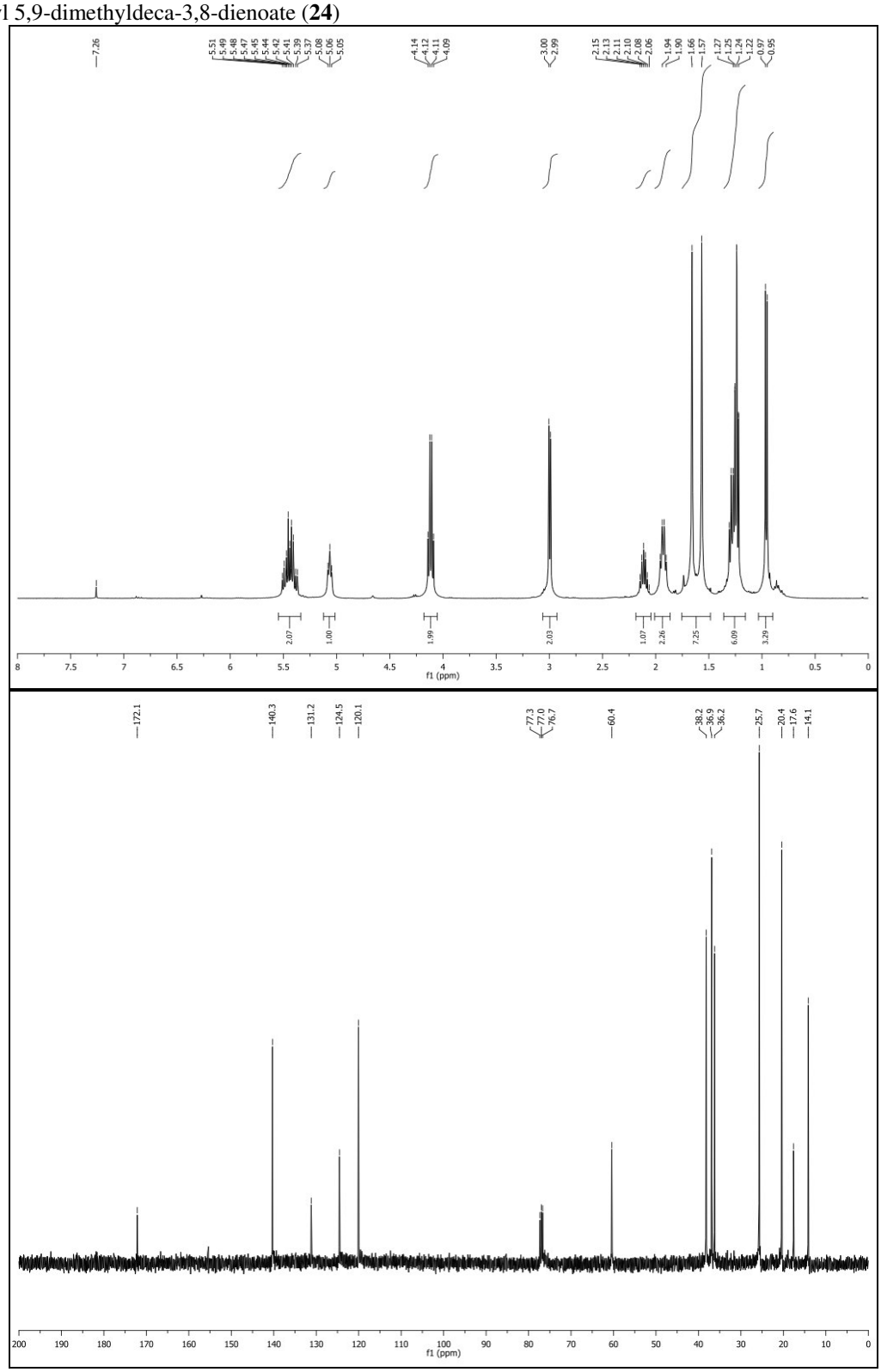
Method Name: C:\CLASS-VP\Enterprise\Projects\Default\Method\A1_F_tdhsepCOOH2-80.met
Data: C:\CLASS-VP\Data\2006\A1_23062006\A1_23062006_tdh1
User: System
Acquired: 6/23/2006 1:30:31 PM
Printed: 07/30/2007 02:18:35 PM



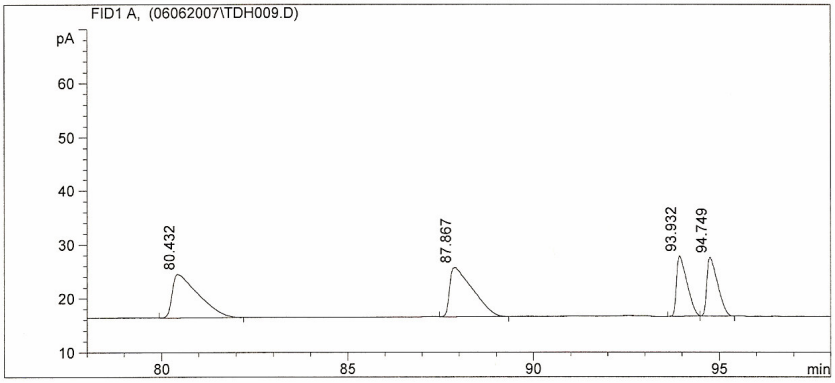
FID1 Results

Retention Time	Area	Area %
41.513	64277	96.48
47.780	2346	3.52
Totals	66623	100.00

(*R*)-(-)-(*E*)-ethyl 5,9-dimethyldeca-3,8-dienoate (**24**)



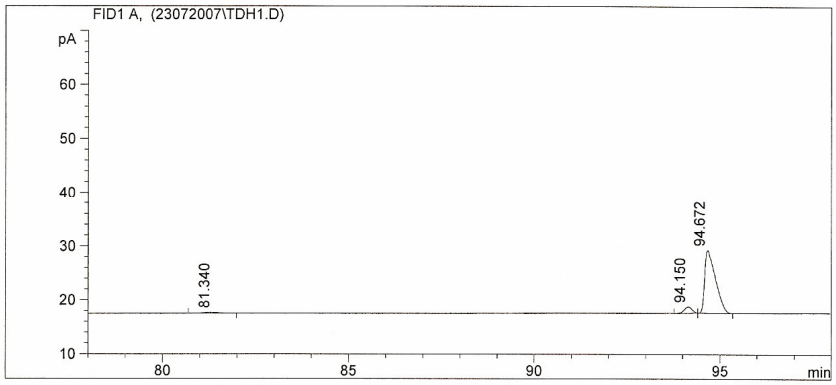
```
Instrument Name : GC02
Sample name     : TDHs1TSrac 105
Data File       : C:\HPCHEM\1\DATA\06062007\TDH009.D

Injection Date  : 6-6-2007 22:12:36          Seq Line   :          1
Report Style    : FRONT.frp                  Vial No.   :         27
Acq Operator    : Tim                        Inj. Vol.  :      3 µl

Method          : TDH2_F.M
Analysis Method : C:\HPCHEM\1\METHODS\BR50R3_F.M

Sample info     : Chiralsil DEX CB
```



Signal 1: FID1 A,

Peak #	RT [min]	Type	Name	Width [min]	Area	Area %	Response	Amount
1	80.432	MM		0.811	396.943	32.491	0.000	0.000
2	87.867	MM		0.709	390.071	31.929	0.000	0.000
3	93.932	MM		0.323	217.014	17.764	0.000	0.000
4	94.749	MM		0.332	217.656	17.816	0.000	0.000

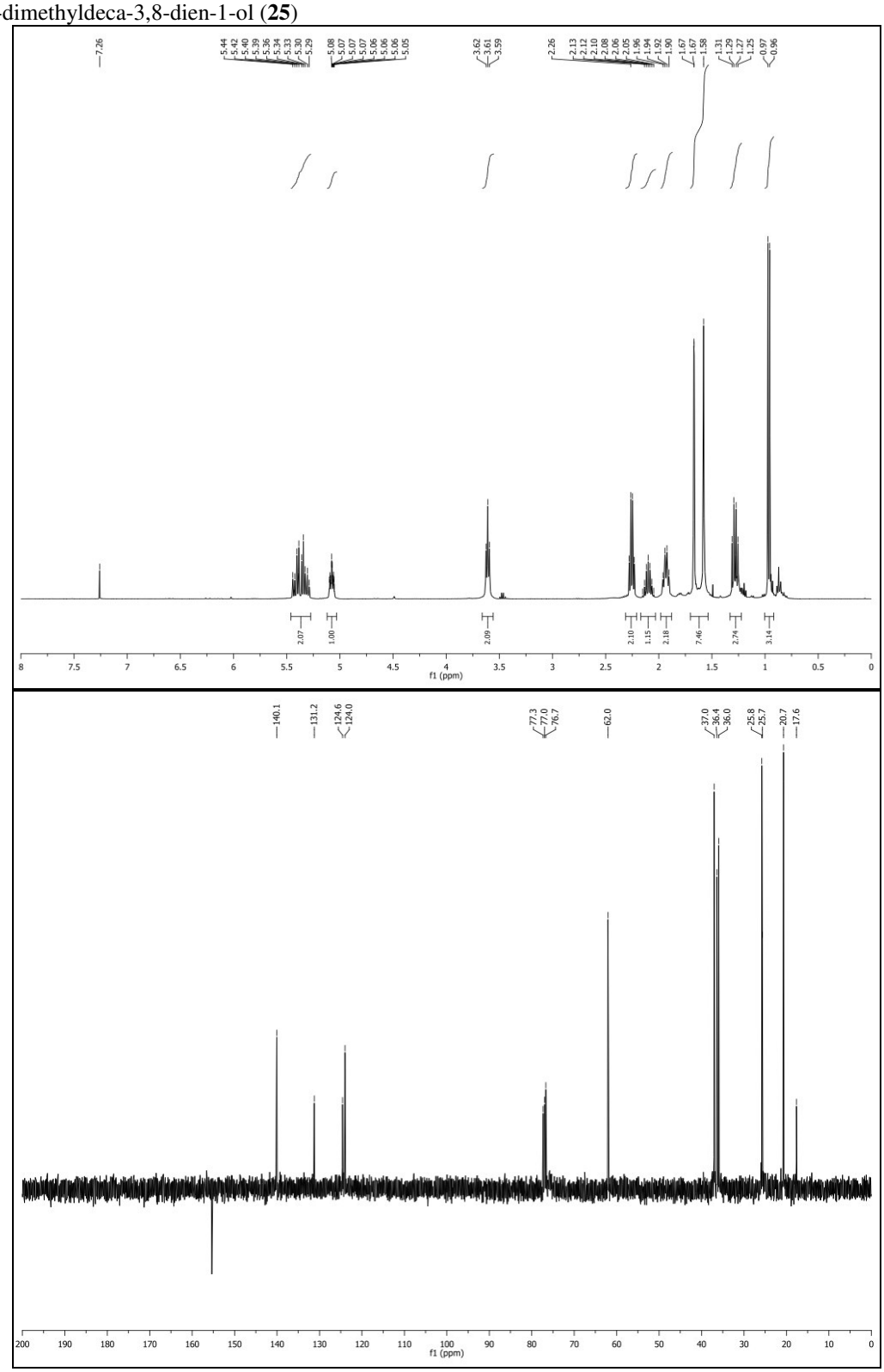
```
Instrument Name : GC02
Sample name     : TDH1TS
Data File       : C:\HPCHEM\1\DATA\23072007\TDH1.D

Injection Date  : 23-7-2007 12:10:28         Seq Line   :          1
Report Style    : FRONT.frp                  Vial No.   :         26
Acq Operator    : Tim                        Inj. Vol.  :      1 µl

Method          : TDH2_F.M
Analysis Method : C:\HPCHEM\1\METHODS\BR50R3_F.M

Sample info     : Chiralsil DEX CB
```



Signal 1: FID1 A,

Peak #	RT [min]	Type	Name	Width [min]	Area	Area %	Response	Amount
1	81.340	MM		0.646	7.834	3.027	0.000	0.000
2	94.150	MM		0.243	17.042	6.585	0.000	0.000
3	94.672	MM		0.335	233.927	90.388	0.000	0.000

(*R*)-(-)-(*E*)-5,9-dimethyldeca-3,8-dien-1-ol (**25**)



(*R*)-(-)-Trimethylammonium (*E*)-5,9-dimethyldeca-3,8-dienyl sulphate (**26**)