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Synthesis of Cyclopropanes via Organoiron Methodology: Preparation and Rearrangement of Divinylcyclopropanes

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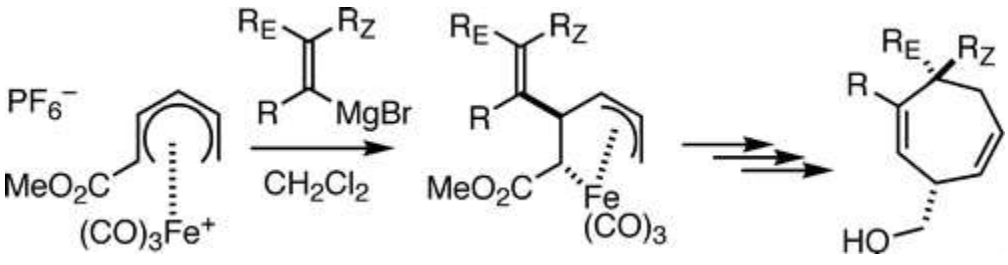
Abstract



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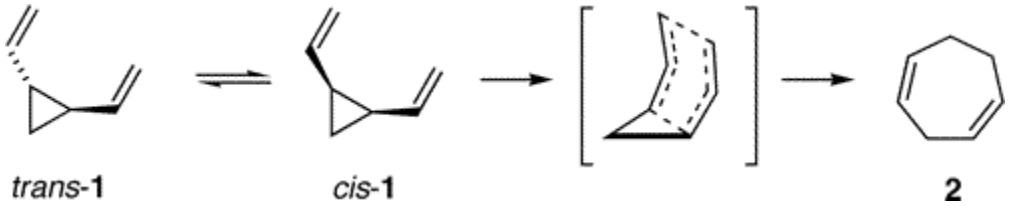
Addition of alkenyl Grignard reagents to (1-methoxycarbonylpentadienyl)iron(1+) cation generates the corresponding (2-alkenylpent-3-en-1,5-diyl)iron complexes. Oxidatively induced-reductive elimination of these complexes gives divinylcyclopropanes which can undergo subsequent Cope rearrangement to give 1,4-cycloheptadienes.

The Cope rearrangement of *cis*-divinylcyclopropane (*cis*-**1**), which occurs at <35 °C, is known to afford 1,4-cycloheptadiene (**2**, Scheme 1).[1] A variety of methods exist for the preparation of divinylcyclopropanes. Among these are oxo-sulfonium ylide cyclopropanation of enals followed by Wittig olefination of the resultant cyclopropanecarboxaldehyde,[2] reaction of 2-metalated vinylcyclopropanes with 3-alkoxy-2-cycloalken-1-ones followed by hydrolysis/dehydration,[3] and rhodium-catalyzed cyclopropanation of vinyldiazomethanes.[4]



Scheme 1

The addition of stabilized carbon nucleophiles to (1-methoxycarbonylpentadienyl)iron(1+) cation (**3**) is known to afford stable (pentenediyl)iron complexes (**4**), which undergo oxidatively induced-reductive elimination to give vinylcyclopropanecarboxylates (**5**, Scheme 2).[5] We have utilized this methodology to prepare 2-(2`-carboxycyclo-propyl)glycines (**6**)[5a] and the C9−C16 alkenyl cyclopropane segment (**7**) of ambruticin.[5b] We herein report on the preparation and rearrangement of divinylcyclopropanes via this methodology.

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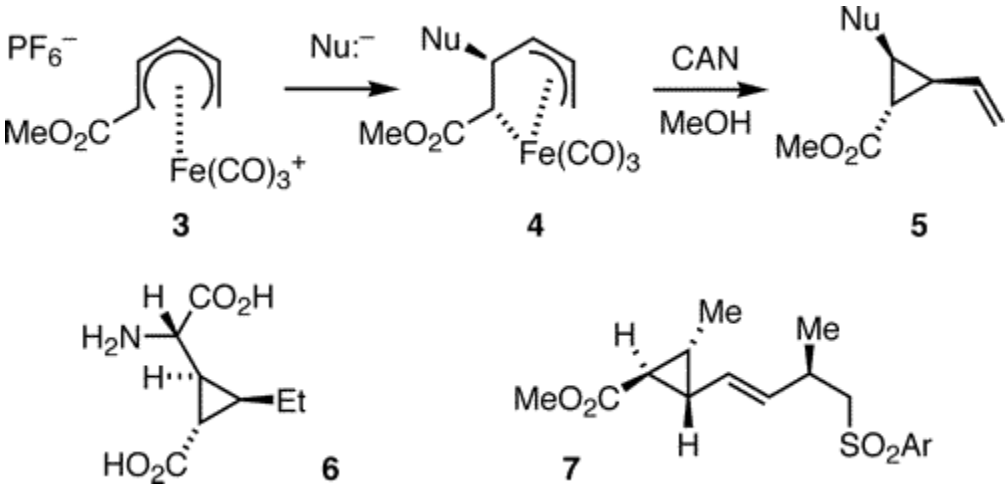

Scheme 2

Reaction of cation **3** with vinylmagnesium chloride, in CH_2Cl_2, gave the corresponding (2-alkenyl-3-pentene-1,5-diyl)iron complexes **4a** (Scheme 3). Use of CH_2Cl_2 as solvent is crucial for addition of Grignard reagents at C2; use of 1,2-dichloroethane, toluene, THF, dioxane, or mixtures led to diminished yields of **4a**. The structure of pentenediyl complex **4a** was assigned on the basis of its NMR spectral data. In particular, a ^{13}C NMR signal at δ 11.4 ppm and a ^{1}H NMR signal at δ 0.24 (d) ppm are characteristic of a carbon σ-bonded to iron and its attached proton.[5]

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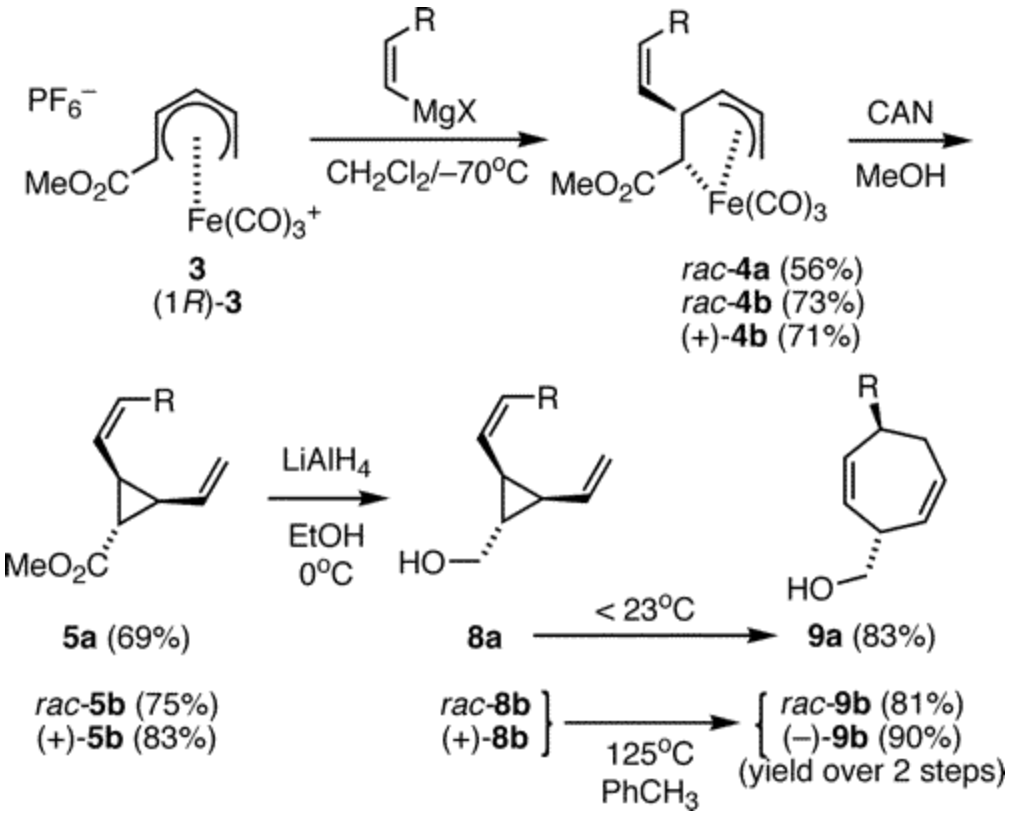

Scheme 3 [a]

[a] **a**, R = H; **b**, R = Me.

Oxidative decomplexation of **4a** with excess CAN/methanol gave *cis*-divinylcyclopropane **5a**. This compound rearranges at 40−60 °C to give the known (3-methoxycarbonyl)-1,4-cycloheptadiene.[6] Alternatively, reduction of the cyclopropanecarboxylate (LAH/ether) gave the rearranged (2,6-cycloheptadien-1-yl)methanol **9a**. Presumably, the intermediate divinylcyclopropane **8a** rapidly rearranges at <23 °C. It is known that the presence of an electron-withdrawing group strengthens the distal cyclopropane ring bond, and this should have an effect on the rate of the Cope rearrangement.

In a similar fashion, reaction of *rac*-**3** with the Grignard reagent prepared from *cis*-1-propenyl bromide gave *rac*-**4b**. Oxidative decomplexation of **4b** gave *rac*-**5b**, which upon reduction gave the cyclopropylcarbinol *rac*-**8b**. In comparison to the parent divinylcyclopropane **8a**, the *cis*-alkenyl cyclopropane **8b** is stable at ambient temperatures and only rearranges at elevated temperature (125 °C) to give a single cycloheptadiene *rac*-**9b**.[7] This methodology

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can be extended to the enantioselective preparation of cycloheptadienes. Thus reaction of (1*R*)-**3**[8] with *cis*-1-propenyl Grignard reagent gave (+)-**4b**, which upon oxidative decomplexation gave the optically active divinylcyclopropane (+)-**5b**. Reduction of (+)-**5b** gave (+)-**8b** which, upon rearrangement at elevated temperature, gave (−)-**9b**. Both (+)-**4b** and (+)-**5b** were determined to be >95% ee on the basis of ^{1}H NMR spectroscopy in the presence of a chiral lanthanide shift reagent, while the (*S*)-Mosher's ester of (−)-**9b** was determined to be >95% de.

In a similar fashion, reaction of **3** with the Grignard reagents derived from 2-bromo-1-propene, α-bromostyrene, 1-bromo-2-methylpropene, and 1-bromocyclopentene gave the corresponding (pentenediyl)iron complexes **4c**−**f** (Table 1). Oxidative decomplexation of **4c** gave the divinylcyclopropane **5c** along with the rearranged cycloheptadiene product (ca. 2.5:1, 88% yield). Reduction of this mixture gave the (2,6-cycloheptadien-1-yl)methanol **9c** (Cope rearrangement occurs at <23 °C). In comparison, oxidative decomplexation of (pentenediyl)iron complexes **4d** or **4e**, which contain an electron-rich alkenyl group, gave diminished yield of divinylcyclopropane. Further experimentation indicated that this diminished yield was due to secondary oxidation of the divinylcyclopropane product by CAN. For this reason, we explored alternative oxidation conditions, the most successful of which was the use of alkaline hydrogen peroxide at low temperature (conditions B). While the chemical yields under conditions B were good, the products consisted of a mixture of *cis*- and *trans*-divinylcyclopropanes, as evidenced by NMR spectroscopy. These mixtures could be converted into a single cycloheptadiene product by the standard reduction/Cope rearrangement conditions. Monitoring of this reaction by VT NMR spectroscopy indicated that the *cis*-divinylcyclopropane rearranges at temperatures lower than those of the trans isomer; rearrangement of the trans isomer presumably occurs via isomerization to the cis isomer via a diradical opening of the cyclopropane ring.[1]

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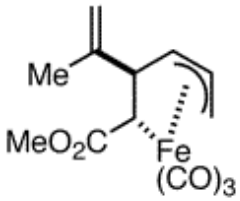
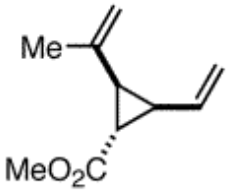
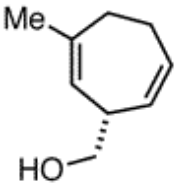
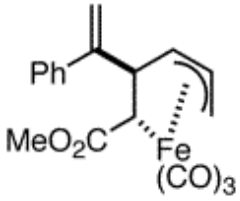
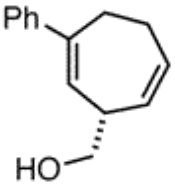
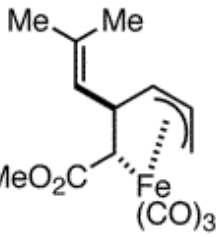
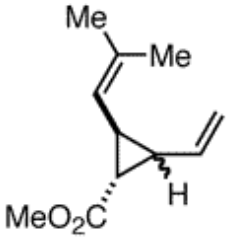
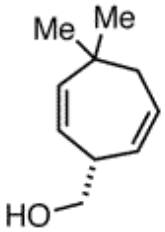
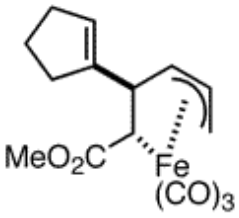
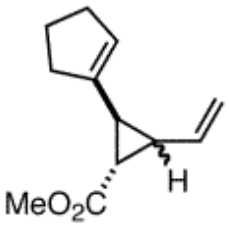
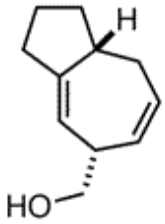
Table 1. Preparation of (Pentendiyl)iron Complexes, Divvinylcyclopropanes, and Cycloheptadienes

pentenediyl complex	oxidation conditions[a]	divinyl-cyclopropane	Cope conditions[a]	1,4-cyclo-heptadiene
 **4c** (42-52%)	**A**	 **5c**[c]	**C**	 **6c** (82%)[b]
 **4d** (38-49%)	**A**	not observed	**C**	 **6d** (33%)[b]
 **4e** (71-76%)	**A** **B**	 **5e** (11%, *cis* only) **5e/e'** (63-84%)[d]	**D**	 **6e** (80%)[b]
 **4f** (50%)	**B**	 **5f** (85%)[e]	**E**	 **6f** (76%)[b]

[a] Decomplexation conditions: A = excess CAN/MeOH/23 °C; B = H_2O_2/MeOH/−45 °C; C = LAH, then rearrangement at or below 23 °C; D = LAH, then rearrangement at 195 °C; E = LAH, then rearrangement at 210 °C.[b] Yield over three steps (decomplexation, LAH reduction, and Cope rearrangement).[c] Obtained as a mixture with the cycloheptadiene 2.5:1).[d] Divinylcyclopropane obtained as a mixture of cis and trans isomers (1:1).[e] Divinylcyclopropane obtained as a mixture of cis and trans isomers (ca. 1:2.5).

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Generation of the mixture of *cis*- and *trans*-divinylcyclopropanes (**5**/**5`**) is rationalized due to the difference in the oxidizing agent involved. For the (pentenediyl)iron complex **4e** (Scheme 3), treatment with CAN is presumed to involve single electron oxidation to afford a $17e^-$ intermediate, which undergoes rapid reductive elimination to give the *cis*-divinylcyclopropane **5e**. Alternatively, treatment of **4e** with alkaline hydrogen peroxide proceeds via nucleophilic attack on coordinated CO, and decarbonylation, to generate a $16e^-$ intermediate. Reductive elimination from the $16e^-$ intermediate is slower, and a competitive reaction is a π−σ−π rearrangement that migrates the iron from one face to the opposite face of the pentenediyl ligand. Notably, the ratio of **5e**:**5e`** produced from decomplexation with H_2O_2/HO^- varies depending on the reaction temperature. In summary, a synthesis of divinylcyclopropanes from (pentadienyl)iron(1+) cations has been developed. The divinylcyclopropane products undergo Cope rearrangement to afford cycloheptadienes. The overall yields for this 4-step transformation (ca. 38−61%) are comparable to other literature methods and preparation of enantiomerically pure cycloheptadienes has been demonstrated. Applications of this methodology to the synthesis of hydroazulene containing natural products will be reported in due course.

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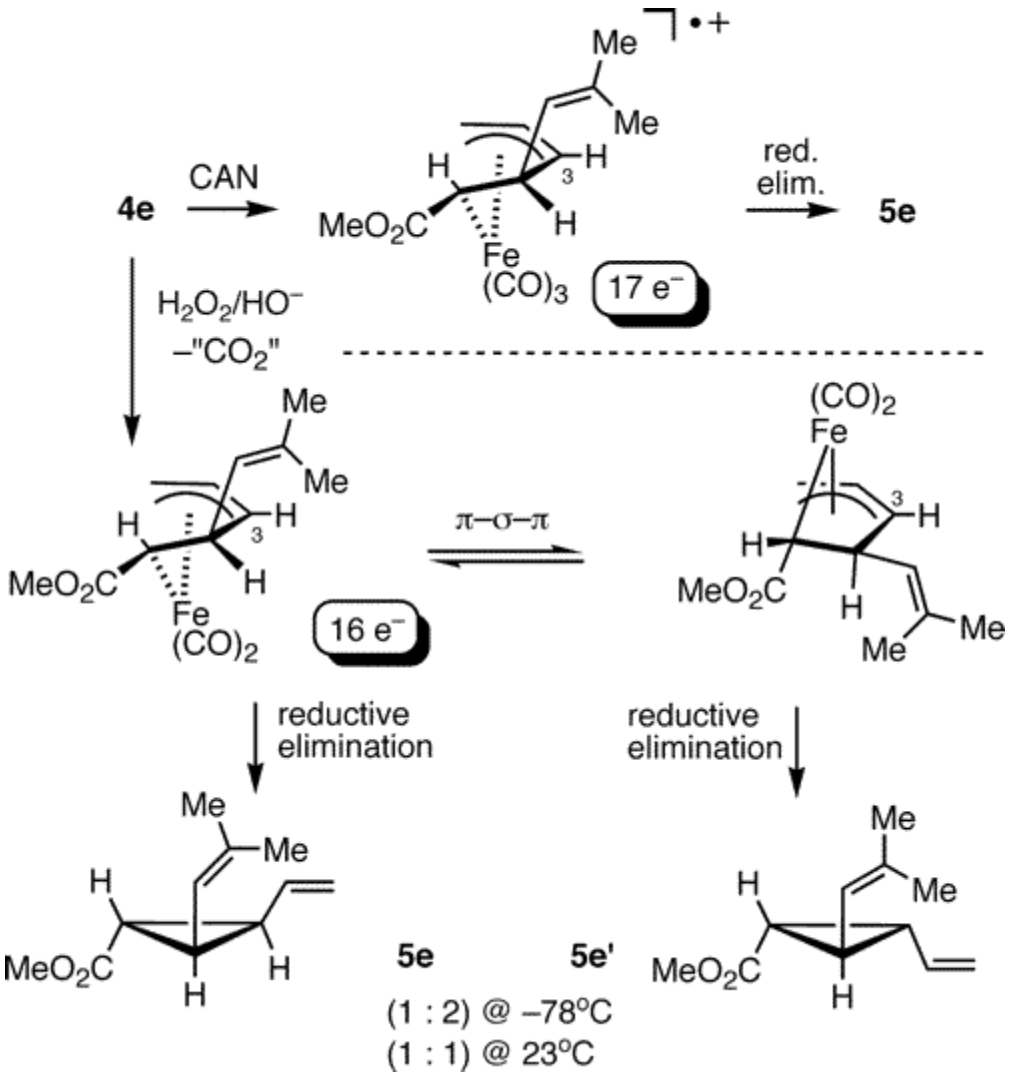

Scheme 4

Acknowledgment

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Chief; John Wiley & Sons: New York, 1992; Vol. 41, pp 1−133. (d) Piers, E. In *Comprehensive Organic Synthesis*; Trost, B. M., Editor-in-Chief; Pergammon Press: New York, 1991; Vol. 5, pp 971−998.

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Supporting Information Available

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Synthesis of Cyclopropanes via Organoiron Methodology: Preparation and Rearrangement of Divinylcyclopropanes

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Supporting Material

Experimental procedures	S1-S11
^{1}H NMR spectrum of **9a**	S12
^{13}C NMR spectrum of **9a**	S13
^{1}H NMR spectrum of **5b**	S14
^{13}C NMR spectrum of **5b**	S15
^{13}C NMR spectrum of **8b**	S16
^{1}H NMR spectrum of **9b**	S17
^{13}C NMR spectrum of **9b**	S18
^{1}H NMR spectrum of **9c**	S19
^{13}C NMR spectrum of **9c**	S20
^{1}H NMR spectrum of **9d**	S21
^{13}C NMR spectrum of **9d**	S22
^{1}H NMR spectrum of **5e**	S23
^{13}C NMR spectrum of **5e**	S24
^{1}H NMR spectrum of **9e**	S25
^{13}C NMR spectrum of **9e**	S26
^{1}H NMR spectrum of **9f**	S27
^{13}C NMR spectrum of **9f**	S28

Experimental Section[1]

Reaction of (±)-3 with vinyl Grignard: To a stirring mixture of *rac*-**3**[2] (1.640 g, 4.000 mmol) in anhydrous CH_2Cl_2 (40 mL) under nitrogen at –70 °C, was added a solution of vinylmagnesium chloride in THF (3.75 mL, 1.6 M, 6.0 mmol). The dark reaction mixture was stirred for 1 h, quenched with saturated aqueous NH_4Cl (5 mL), and warmed to room temperature. The mixture was poured onto water (25 mL), the layers were separated, and the aqueous phase extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phases were dried ($MgSO_4$), filtered through a short

bed of SiO_2 and concentrated. Immediate column chromatography (SiO_2, hexanes-ethyl acetate = 40:1) afforded *rac*-**4a** (0.659 g, 2.26 mmol, 56%) as an orange oil that crystallized upon cooling. mp 36-38 °C; IR (KBr) 3090, 2955, 2066, 1992, 1694, 1165 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (d, J = 8.5 Hz, 1H), 2.39 (ddd, J = 0.9, 2.3, 12.2 Hz, 1H), 3.55 (ddd, J = 1.5, 2.3, 8.4 Hz, 1H), 3.69 (s, 3H), 3.71-3.82 (m, 1H), 4.47 (dddd, J = 1.2, 1.2, 7.0, 7.6 Hz, 1H), 4.67 (dddd, J = 0.5, 6.7, 8.5, 12.2 Hz, 1H), 4.77-4.81 (m, 1H), 4.82-4.85 (m, 1H), 5.38 (ddd, J = 5.4, 10.1, 17.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 11.4, 41.9, 51.7, 54.4, 63.5, 98.2, 112.7, 141.2, 180.5, 203.8, 210.3, 210.7. Anal. Calcd for $C_{12}H_{12}FeO_5$: C, 49.35; H, 4.14. Found: C, 49.55; H, 4.19.

Reaction of *rac*-3 with *cis*-1-propenyl Grignard: The reaction of *rac*-**3** (1.64 g, 4.00 mmol) in anhydrous CH_2Cl_2 (40 mL) with *cis*-1-propenylmagnesium bromide (6.0 mL, 1.0 M in THF, freshly prepared from *cis*-1-bromo-1-propene) was carried out in a fashion similar to the preparation of **4a**. Column chromatography (SiO_2, hexanes-ethyl acetate = 40:1) afforded *rac*-**4b** (0.887 g, 2.90 mmol, 73%) as a crystalline orange solid. mp 56-59 °C; IR (KBr) 3009, 2953, 2065, 2003, 1977, 1688, 1163 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.09 (d, J = 8.1 Hz, 1H), 1.54 (dd, J = 1.8, 7.0 Hz, 3H), 2.44-2.50 (m, 1H), 3.57-3.63 (m, 1H), 3.68 (s, 3H), 3.94-4.05 (m, 1H), 4.48-4.61 (m, 2H), 4.81-4.91 (m, 1H), 5.05-5.17 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.4, 13.7, 36.9, 51.6, 54.5, 65.6, 97.3, 123.0, 135.9, 180.5, 203.9, 210.7, 210.8. Anal. Calcd for $C_{13}H_{14}FeO_5$: C, 51.01; H, 4.61. Found: C, 50.89; H, 4.61.

Reaction of (1*R*)-3 with *cis*-1-propenyl Grignard: The reaction of (1*R*)-**3** (1.51 g, 3.68 mmol) with *cis*-1-propenylmagnesium bromide was carried out in a fashion similar to the reaction of *rac*-**3** with *cis*-1-propenylmagnesium bromide. Column chromatography (SiO_2, hexanes-ethyl acetate = 40:1) afforded **(+)-4b** (0.800 g, 2.61 mmol, 71%) as an orange crystalline solid. $[\alpha]_D^{20}$ = +589 (c = 0.248, $CHCl_3$); mp 44-47 °C. The ^1H NMR spectrum of (+)-**4b** was identical to that

of *rac*-**4b**. Analysis by ^{1}H NMR spectroscopy in the presence of a chiral shift reagent [(+)-Eu(hfc)$_3$, $CDCl_3$] indicated that the product was >95% ee.

Reaction of (±)-3 with isopropenyl Grignard (4c): The reaction of *rac*-**3** (1.640 g, 4.000 mmol) in anhydrous CH_2Cl_2 (40 mL) with isopropenylmagnesium bromide (0.5 M in THF) was carried out in a fashion similar to the preparation of **4a**. Immediate column chromatography (SiO_2, hexanes-ethyl acetate = 30:1) afforded **4c** (0.631 g, 2.06 mmol, 52%) as an orange oil which crystallized on standing. mp 46-48 °C; IR (KBr) 3078, 2950, 2066, 2009, 1976, 1690, 1159 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.27 (d, J = 9.0 Hz, 1H), 1.50 (br s, 3H), 2.27 (ddd, J = 1.0, 2.2, 12.0 Hz, 1H), 3.50 (ddd, J = 1.5, 2.2, 8.5 Hz, 1H), 3.58-3.67 (m, 1H), 3.70 (s, 3H), 4.43-4.49 (m, 1H), 4.54-4.57 (m, 1H), 4.59-4.62 (m, 1H), 4.74 (dddd, J = 0.5, 7.0, 8.3, 12.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 12.7, 19.6, 45.2, 51.7, 54.5, 64.0, 98.4, 108.8, 147.4, 180.8, 204.0, 210.2, 210.8. Anal. Calcd for $C_{13}H_{14}FeO_5$: C, 51.01; H, 4.61. Found: C, 50.57; H, 4.58.

Reaction of *rac*-3 with α-styryl Grignard (4d): The reaction of *rac*-**3** (1.64 g, 4.00 mmol) in anhydrous CH_2Cl_2 (40 mL) with α-styrylmagnesium bromide (1.0 M in THF, 6.0 mL, 6.0 mmol, freshly prepared from α-bromostyrene) was carried out in a fashion similar to the preparation of **4a**. Column chromatography (SiO_2, hexanes-ethyl acetate gradient = 40:1 → 20:1) gave **4d** (0.719 g, 1.95 mmol, 49%) as a yellow-orange crystalline solid. mp 90-93 °C; IR (KBr) 3029, 2948, 2065, 1994, 1684, 1435, 1227, 1163, 908, 777 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.26 (d, J = 8.5 Hz, 1H), 2.26 (ddd, J = 0.9, 2.4, 12.0 Hz, 1H), 3.46 (ddd, J = 1.5, 2.4, 8.3 Hz, 1H), 3.61 (s, 3H), 4.27-4.36 (m, 1H), 4.51-4.58 (m, 1H), 4.72 (dddd, J = 0.6, 6.7, 8.5, 12.1 Hz, 1H), 4.93 (dd, J = 0.9, 2.0 Hz, 1H), 5.07 (dd, J = 0.9, 2.0 Hz, 1H), 7.19-7.30 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 12.1, 42.4, 51.6, 54.2, 63.5, 97.9, 111.7, 127.3, 127.7, 128.3, 139.3, 152.2, 180.7, 204.0, 210.0, 210.8. Anal. Calcd for $C_{18}H_{16}FeO_5$: C, 58.72; H, 4.38. Found: C, 58.83; H, 4.53.

Reaction of *rac*-3 with 2-methyl-1-propenyl Grignard (4e): The reaction of *rac*-**3** (1.640 g, 4.000 mmol) in anhydrous CH_2Cl_2 (40 mL) 2-methyl-1-propenylmagnesium bromide (0.5 M in THF, 12.0 mL, 6.0 mmol) was carried out in a fashion similar to the preparation of **4a**. Immediate column chromatography (SiO_2, hexanes-ethyl acetate = 40:1) afforded **4e** (0.904 g, 2.82 mmol, 71%) as a yellow crystalline solid. mp 64-65 °C; IR (KBr) 2983, 2948, 2910, 2855, 2058, 2000, 1943, 1692, 1432, 1365, 1160, 890, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.08 (d, J = 8.1 Hz, 1H), 1.54 (s, 3H), 1.55 (s, 3H), 2.42-2.51 (m, 1 H) 3.55-3.61 (m, 1H), 3.67 (s, 3H), 3.87 (br q, $J \approx$ 8.1 Hz, 1H), 4.47-4.64 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 14.2, 18.6, 25.7, 38.0, 51.6, 54.4, 66.4, 97.1, 130.6, 131.1, 180.6, 204.0, 210.7, 211.0. Anal. Calcd for $C_{14}H_{16}FeO_5$: C, 52.53; H, 5.03. Found: C, 52.35; H, 5.24.

Reaction of *rac*-3 with 1-cyclopentenyl Grignard (4f): The reaction of *rac*-**3** (1.64 g, 4.00 mmol) in anhydrous CH_2Cl_2 (40 mL) with 1-cyclopentenylmagnesium bromide (1.0 M in THF, freshly prepared from 1-bromocyclopentene) was carried out in a fashion similar to the preparation of **4a**. Immediate column chromatography (SiO_2, hexanes-ethyl acetate = 40:1) afforded *rac*-**4f** (0.661 g, 1.99 mmol, 50%) as a yellow crystalline solid. mp 86-94 °C; IR (KBr) 2951, 2846, 2067, 2009, 1975, 1690, 1161 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.29 (d, J = 8.8 Hz, 1H), 1.67-1.82 (m, 2H), 1.93-2.11 (m, 2H), 2.11-2.24 (m, 2H), 2.39 (dd, J = 1.9, 12.0 Hz, 1H), 3.522 (ddd, J = 1.7, 2.0, 8.4 Hz, 1H), 3.64-3.75 (m, 1H and s, 3H), 4.46-4.54 (m, 2H), 4.65 (ddd, J = 6.9, 8.4, 12.0 Hz, 1H), 5.16 (pseudo h, J = 2.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 12.0, 23.5, 32.11, 32.14, 40.6, 51.7, 54.5, 64.3, 98.2, 123.0, 147.2, 180.8, 204.0, 210.5, 210.9. Anal. Calcd for $C_{15}H_{16}O_5Fe$: C, 54.24; H, 4.86. Found: C, 54.33; H, 4.93.

Oxidative decomplexation of 4a with CAN (Conditions A): To a stirring solution of **4a** (0.595 g, 1.71 mmol) in absolute methanol (20 mL) was added in portions CAN (6 x 1.13 g, 99%, 12.2

mmol) over a period of 25 min. After stirring for 10 min after the last addition, the red mixture was poured onto brine (25 mL) and extracted with ethyl acetate (3 x 25 mL). The combined extracts were washed sequentially with: water (3 x 25 mL), saturated aqueous sodium bicarbonate (25 mL) and brine (25 mL). The organic phase was then dried ($MgSO_4$). Analysis of an aliquot by ^{1}H NMR spectroscopy typically indicated the presence of kinetically unstable cyclopropane **5a** along with varying amounts of the Cope rearrangement product 3-methoxycarbonyl-1,4-cycloheptadiene. The organic phase (i.e. the ethyl acetate extracts) was heated in an oil bath at 55-60 °C for 45 min, cooled to room temperature, and carefully concentrated at 20 °C. Column chromatography (SiO_2, hexanes-ethyl acetate = 20:1) gave 3-methoxycarbonyl-1,4-cycloheptadiene (0.215 g, 1.41 mmol, 69%) as a volatile colorless oil. The ^{1}H NMR spectrum was identical with the literature[3] spectral data.

5a: ^{1}H NMR ($CDCl_3$) δ 1.86 (t, J = 4.9 Hz, 1H), 2.27-2.35 (m, 2H), 3.70 (s, 3H), 5.12 (dd, J = 1.7, 10.3 Hz, 2H), 5.24 (ddd, J = 0.6, 1.8, 17.0 Hz, 2H), 5.49-5.62 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 28.2, 31.8, 52.2, 117.4, 133.8, 173.1.

3-methoxycarbonyl-1,4-cycloheptadiene: IR (neat) 3028, 2951, 2907, 2836, 1743, 1644, 1435, 1266, 1171, 1030, 822, 796; ^{1}H NMR ($CDCl_3$) δ 2.13-2.39 (m, 4H), 3.74 (s, 3H), 4.17-4.25 (m, 1H), 5.77-5.93 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 26.2, 44.8, 52.5, 127.1, 132.4, 173.8.

General Procedure for Oxidative decomplexation (CAN)/reduction/Cope rearrangement sequence. Cyclohepta-2,6-dienylmethanol (9a): To a stirring solution of **4a** (0.500 g, 1.71 mmol) in absolute methanol (17 mL) was added in portions CAN (6 x 0.95 g, 99%, 10.3 mmol) over a period of 14 min. Shortly after the last addition and cessation of effervescence, the red mixture was poured onto brine (20 mL) and extracted with ethyl acetate (4 x 20 mL). The combined extracts were washed sequentially with: water (3 x 20 mL), saturated aqueous sodium

bicarbonate (20 mL) and brine (20 mL). The organic phase was dried ($MgSO_4$) and carefully concentrated at 20 °C to give a volatile yellow oil. The oil was dissolved in ether (~1.0 mL) and added dropwise to a stirring solution of $LiAlH_4$ in ether (3.0 mL, 1.0 M, 3.0 mmol) at 0 °C. Additional ether (~2.0 mL) was used to insure a quantitative transfer of the crude **5a**. The solution was stirred at 0 °C for 3 h, then quenched with saturated aqueous sodium bicarbonate (5 mL). After warming to room temperature and diluting with 2 M NaOH (10 mL), the mixture was extracted with ether (4 x 15 mL). The combined extracts were dried ($MgSO_4$) and concentrated to give an oil. Analysis of this oil by ^{1}H NMR spectroscopy did not indicate the presence of intermediate **8a**. Column chromatography (SiO_2, hexanes-ethyl acetate = 4:1) of the crude material provided **9a** as a colorless oil (0.177 g, 1.43 mmol, 83%). IR (neat) 3346 (br), 3014, 2906, 1646, 1449, 1430, 1033, 817, 784, 736 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.52 (br s, 1H), 2.12-2.25 (m, 2H), 2.27-2.40 (m, 2H), 3.29-3.40 (m, 1H), 3.67 (app. d, J = 6.0 Hz, 2H), 5.51-5.59 (m, 2H), 5.84-5.93 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 26.9, 42.3, 67.1, 130.2, 132.3. GC/MS *m/z* 124. Anal. Calcd for $C_8H_{12}O{\cdot}0.3H_2O$: C, 74.15; H, 9.80. Found: C, 74.05; H, 9.66.

***trans*-(4-Methylcyclohepta-2,6-dienyl)methanol (*rac*-9b)**: The decomplexation of *rac*-**4b** (0.295 g, 0.801 mmol) with CAN/MeOH was carried out in a fashion similar to the above procedure, to give crude *rac*-**5b** as a volatile yellow oil. The crude divinylcyclopropane carboxylate was reduced with $LiAlH_4$/ether, in a fashion similar to that above, to give *rac*-**8b** as a colorless oil. The crude divinylcyclopropylmethanol was dissolved in toluene (10 mL) and heated in a sealed reaction tube at 115-125 °C for 90 min. After cooling to ambient temperature, purification by column chromatography (SiO_2, hexanes-ethyl acetate gradient = 10:1 → 4:1) gave *rac*-**9b** as a colorless oil (0.155 g, 1.12 mmol, 81%). IR (neat) 3334, 3009, 2955, 2928, 2871, 1655, 1456, 1372, 1026, 828, 775, 731, 674 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.04 (d, J = 7.0 Hz,

3H), 1.50 (br s, 1H), 2.07-2.29 (m, 2H), 2.39-2.53 (m, 1H), 3.19-3.29 (m, 1H), 3.68 (app. d, $J \approx$ 6.0 Hz, 2H), 5.43 (dddd, J = 1.4, 2.1, 4.1, 11.8 Hz, 1H), 5.59-5.68 (m, 2H), 5.91 (dddd, J = 2.3, 5.3, 7.3, 11.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 22.9, 32.6, 34.8, 42.5, 66.9, 127.3, 131.1, 131.2, 138.8; GC/MS *m/z* 138. Anal. Calcd for $C_9H_{14}O \cdot 0.2H_2O$: C, 76.23; H, 10.23. Found: C, 76.33; H, 10.12.

For the purposes of characterization, the crude divinylcyclopropane carboxylate could be purified by column chromatography (SiO_2, hexanes-ethyl acetate = 20:1) to give *rac*-**5b** (75%) as a pale yellow oil). **5b:** IR (neat) 3085, 3025, 2952, 2857, 1728, 1637, 1441, 1284, 1211, 1168, 912, 810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.72 (dd, J = 1.8, 6.8 Hz, 3H), 1.75 (dd, J = 4.8, 4.8 Hz, 1H), 2.27-2.36 (m, 1H), 2.43 (ddt, J = 1.2, 4.9, 9.2 Hz, 1H), 3.70 (s, 3H), 5.05-5.15 (m, 2H), 5.23 (ddd, J = 0.6, 1.8, 17.0 Hz, 1H), 5.47-5.68 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.7, 26.8, 29.2, 31.8, 52.2, 117.2, 125.6, 127.9, 134.3, 173.4. Anal. Calcd for $C_{10}H_{14}O_2 \cdot 0.25H_2O$: C, 70.35; H, 8.56. Found: C, 70.24; H, 8.42.

Similarly, the kinetically stable divinylcyclopropyl methanol could be obtained by chromatographic purification (SiO_2, hexanes-ethyl acetate = 20:1) of the crude material, giving *rac*-**8b** (73%) as a volatile pale yellow oil. **8b:** ^{1}H NMR ($CDCl_3$) δ 1.23-1.34 (m, 1H), 1.63-1.72 (overlapped m, 1H), 1.65 (br s, 1H), 1.70 (dd, J = 1.7, 6.8 Hz, 3H), 1.73-1.82 (m, 1H), 3.60 (app. d, J = 6.7 Hz, 2H), 5.01 (ddd, J = 0.6, 1.8, 10.3 Hz, 1H), 5.07-5.17 (m, 2H), 5.47-5.62 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.6, 22.6, 27.8, 30.8, 66.0, 115.0, 125.6, 128.0, 136.8.

((1*S*,4*S*)-4-methylcyclohepta-2,6-dienyl)methanol ((-)-9b): The decomplexation of **(+)-4b** (0.475 g, 1.55 mmol) with CAN/MeOH was carried out in a fashion similar to that for *rac*-**4b**, to give crude **(+)-5b** as a volatile yellow oil. The oil was then reduced with $LiAlH_4$/ether in a fashion similar to that for the racemic material, to give (+)-**8b** as a colorless oil. The oil was

dissolved in toluene (10 mL) and heated under nitrogen in a sealed reaction tube at 125 °C for 90 min. After cooling to ambient temperature, purification by column chromatography (SiO_2, hexanes-ethyl acetate = 10:1 → 4:1) provided **(–)-9b** as a colorless oil (0.178 g, 1.29 mmol, 83%). Intermediates **(+)-5b** (83%, 1 step) and **(+)-8b** (90%, 1 step) were isolated, purified (SiO_2, hexanes-ethyl acetate = 10:1 and SiO_2, hexanes-ethyl acetate = 4:1 respectively), and characterized in separate experiments.

(+)-5b: $[\alpha]_D^{20}$ = +28.2 (c = 0.410, $CHCl_3$). The ^1H NMR spectrum of (+)-**5b** was identical with that of *rac*-**5b**. This compound was determined to be optically pure by comparison of the ^1H NMR spectrum ($CDCl_3$) in the presence of (+)-Eu(hfc)$_3$ with that of the racemic material.

(+)-8b: $[\alpha]_D^{20}$ = +89.0 (c = 0.352, $CHCl_3$). The ^1H NMR spectrum of (+)-**8b** was identical with that of *rac*-**8b**.

(–)-9b: $[\alpha]_D^{20}$ = –7.2 (c = 0.448, $CHCl_3$). The ^1H NMR spectrum of (–)-**9b** was identical with that of *rac*-**9b**. This compound was determined to be optically pure by comparison of the ^1H NMR spectrum (C_6D_6) of the (*S*)-MTPA esters derived from both **(–)-9b** and *rac*-**9b**. In the case of diastereomeric esters derived from *rac*-**9b**, separation of signals could be observed for the allylic methyl groups.

(3-Methylcyclohepta-2,6-dienyl)methanol (9c): Decomplexation (conditions A)/reduction/Cope rearrangement of **4c** (0.315 g, 1.03 mmol) according to the above procedure, followed by column chromatography (SiO_2, hexanes-ethyl acetate = 4:1) of the crude material provided **9c** as a colorless oil (0.116 g, 0.839 mmol, 82%). IR (neat) 3342, 3011, 2910, 1652, 1445, 1375, 1078, 1023, 811 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.49 (br s, 1H), 1.76 (t, J = 1.6 Hz, 3H), 1.99-2.10 (m, 1H), 2.10-2.35 (m, 2H), 2.36-2.48 (m, 1H), 3.26-3.36 (m, 1H), 3.65 (app. d, J = 6.3 Hz, 2H), 5.33-5.38 (m, 1H), 5.54 (qdd, J = 1.3, 3.9, 11.3 Hz, 1H), 5.80 (ddddd, J = 0.6, 2.4,

5.0, 5.5, 11.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 26.0, 26.1, 31.7, 40.8, 67.3, 124.6, 130.2, 131.5, 140.0. GC/MS *m/z* 138. Anal. Calcd for $C_9H_{14}O \cdot 0.25H_2O$: C, 75.75; H, 10.24. Found: C, 75.73; H, 10.11.

(3-Phenylcyclohepta-2,6-dienyl)methanol (9d): Decomplexation (CAN)/reduction/Cope rearrangement of **4d** (0.295 g, 0.801 mmol) according to the above procedure, followed by column chromatography (SiO_2, hexanes-ethyl acetate = 4:1) of the crude material provided **9d** as a pale yellow oil (0.053 g, 0.265 mmol, 33%). IR (neat) 3352, 3019, 2811, 1598, 1494, 1444, 1081, 1028, 758, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.62 (br s, 1H), 2.22-2.48 (m, 2H), 2.65 (qddd, *J* = 0.8, 3.5, 6.5, 14.7 Hz, 1H), 2.99 (tddd, *J* = 1.2, 3.5, 11.0, 14.7 Hz, 1H), 3.52-3.61 (m, 1H), 3.76 (app. d, *J* ≈ 6.5 Hz, 2H), 5.49-5.57 (m, 1H), 5.75-5.84 (m, 1H), 5.96 (qd, *J* = 1.0, 4.4 Hz, 1H), 7.20-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 26.9, 30.0, 40.9, 67.2, 125.8, 126.9, 128.3, 128.5, 129.6, 131.5, 143.1, 143.4; GC/MS *m/z* 200. Anal. Calcd for $C_{14}H_{16}O \cdot 0.5H_2O$: C, 80.35; H, 8.19. Found: C, 80.38; H, 7.85.

Attempted oxidative decomplexation (CAN) of 4e. Attempted oxidative decomplexation of **4e** in methanol gave a complex mixture of unidentifiable products. Attempted oxidative decomplexation of **4e** (0.456 g, 1.42 mmol) with CAN using CH_3CN as solvent, followed by purification by column chromatography (SiO_2, hexanes-ethyl acetate = 20:1) gave **5e** (0.028 g, 0.155 mmol, 11%) as a pale yellow, volatile oil. IR (neat) 3085, 2926, 2855, 1730, 1638, 1444, 1284, 1213, 1159, 985, 902 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.69 (dd, *J* = 4.8, 4.8 Hz, 1H), 1.71 (s, 3H), 1.72 (s, 3H), 2.23-2.37 (m, 2H), 3.69 (s, 3H), 4.87 (qdd, *J* = 1.5, 1.5, 8.5 Hz, 1H), 5.10 (ddd, *J* = 0.6, 1.8, 10.3 Hz, 1H), 5.22 (ddd, *J* = 0.8, 1.8, 17.2 Hz, 1H), 5.47-5.60 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 18.8, 26.0, 27.8, 29.3, 31.8, 52.1, 117.0, 119.7, 134.7, 136.4, 173.6. Exposure of **5e** to excess CAN in methanol resulted in decomposition into unidentifiable products.

General Procedure for Oxidative decomplexation (H_2O_2/HO^-)/reduction/Cope rearrangement sequence. (4,4-Dimethylcyclohepta-2,6-dienyl)methanol (9e): To a stirring solution of complex **4e** (0.780 g, 2.44 mmol) in absolute methanol (50 mL) and 30% aqueous H_2O_2 (15 mL) at –78 °C under nitrogen, was added a methanolic solution of NaOH (0.59 g, 15 mmol NaOH dissolved in a minimal volume of methanol). The mixture was stirred at –78 °C for 30 min, the cold bath was removed, and the mixture stirred for an additional 30 min while warming to room temperature. During this period, the reaction bubbled and became brown. The muddy mixture was diluted with water (50 mL) and extracted with ether (4 x 50 mL). The combined extracts were washed with water (3 x 50 mL) followed by brine (50 mL). The organic phase was dried ($MgSO_4$) and concentrated to give a volatile yellow oil. The ^{1}H NMR spectrum indicated the residue to contain a mixture of *cis* and *trans*-divinylcyclopropane carboxylates (**5e**:**5e'** ≈ 1:2.2). The crude mixture (**5e**:**5e'**) was reduced with $LiAlH_4$ in ether (4.2 mL, 1.0 M, 4.2 mmol) at 0 °C in a fashion similar to that above to give a tan oil. Analysis of the residue by ^{1}H NMR spectroscopy indicated that it consisted of a mixture of *cis* and *trans*-divinylcyclopropylmethanols (1:2.2). None of the rearrangement product was observed. The mixture of divinylcyclopropylmethanols was dissolved in mesitylene (12 mL) and heated under nitrogen in a sealed reaction tube at 195-200 °C for 1 h. After cooling to ambient temperature, purification by column chromatography (SiO_2, hexanes-ethyl acetate gradient = 10:1 → 4:1) provided **9e** as a pale yellow oil (0.296 g, 1.94 mmol, 80%). IR (neat) 3337 (br), 3001, 2955, 2866, 1653, 1469, 1375, 1359, 1079, 1031, 807, 746, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.02 (s, 3H), 1.05 (s, 3H), 1.46 (br s, 1H), 2.08 (dddd, J = 1.1, 1.1, 6.8, 14.1 Hz, 1H), 2.38 (dd, J = 6.5, 14.2 Hz, 1H), 3.21-3.31 (m, 1H), 3.66 (app. d, $J \approx$ 6.1 Hz, 2H), 5.28 (ddd, J = 1.3, 3.3, 12.0 Hz, 1H), 5.46 (ddd, J = 1.3, 2.6, 12.0 Hz, 1H), 5.74 (dddd, J = 1.3, 1.3, 4.1, 10.6 Hz, 1H), 5.85 (dtd, J =

2.0, 6.5, 10.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 29.7, 30.9, 35.3, 39.9, 41.5, 66.9, 125.1, 130.2, 132.7, 142.2; GC/MS *m/z* 152. Anal. Calcd for $C_{10}H_{16}O \cdot 0.1H_2O$: C, 77.97; H, 10.60. Found: C, 77.73; H, 10.55.

3-Hydroxymethylene-bicyclo[5.3.0]dec-1,4-diene (9f): Decomplexation (H_2O_2)/reduction of **4f** (0.657 g, 1.98 mmol) according to the above procedure, followed by Cope rearrangement in mesitylene at 210-220 °C, and purification by column chromatography (SiO_2, hexanes-ethyl acetate gradient = 10:1 → 4:1) gave **9f** as a colorless oil (0.248 g, 1.51 mmol, 76% for 3 steps). IR (neat) 3338 (br), 3000, 2948, 2869, 1062, 1026 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.24-1.36 (m, 1H), 1.48 (br s, 1H), 1.49-1.61 (m, 1H), 1.63-1.76 (m, 1H), 1.85-1.99 (m, 1H), 2.01-2.14 (m, 1H), 2.16-2.27 (m, 1H), 2.30-2.42 (m, 2H), 2.75-2.89 (m, 1H), 3.22-3.33 (m, 1H), 3.64 (pseudo dd, *J* = 2.7, 5.6, 2H), 5.39-5.49 (m, 2H), 5.73-5.82 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 25.6, 34.0, 34.9, 35.1, 41.3, 42.4, 67.7, 120.1, 128.8, 131.0, 150.7.

[1] For general experimental instrumentations and conditions, see: Yun, Y. K.; Godula, K.; Cao, Y.; Donaldson, W. A. *J. Org. Chem.* **2003**, *68*, 901-910.
[2] Tao, C.; Donaldson, W. A. *J. Org. Chem.* **1993**, *58*, 2134-2143.
[3] Pikulik, I.; Childs, R. F. *Can. J. Chem.* **1997**, *55*, 251-258.

STANDARD 1H OBSERVE

Archive directory: /export/home/general/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
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Mercury-300BB "mercury300"

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Pulse 45.0 degrees
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DATA PROCESSING
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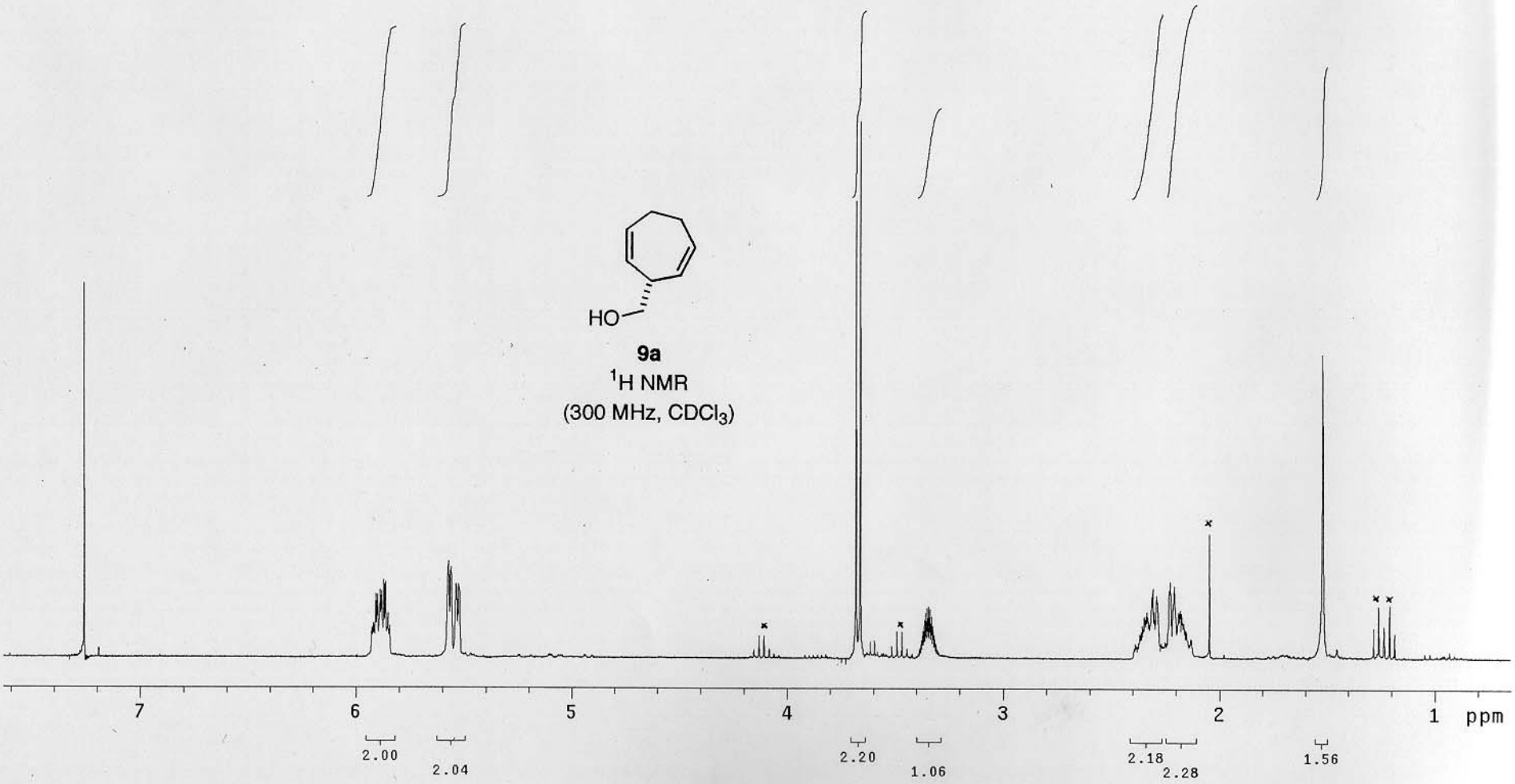
Total time 0 min, 46 sec



9a

^{1}H NMR

(300 MHz, $CDCl_3$)

13C OBSERVE

Archive directory: /export/home/general/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"

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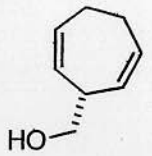
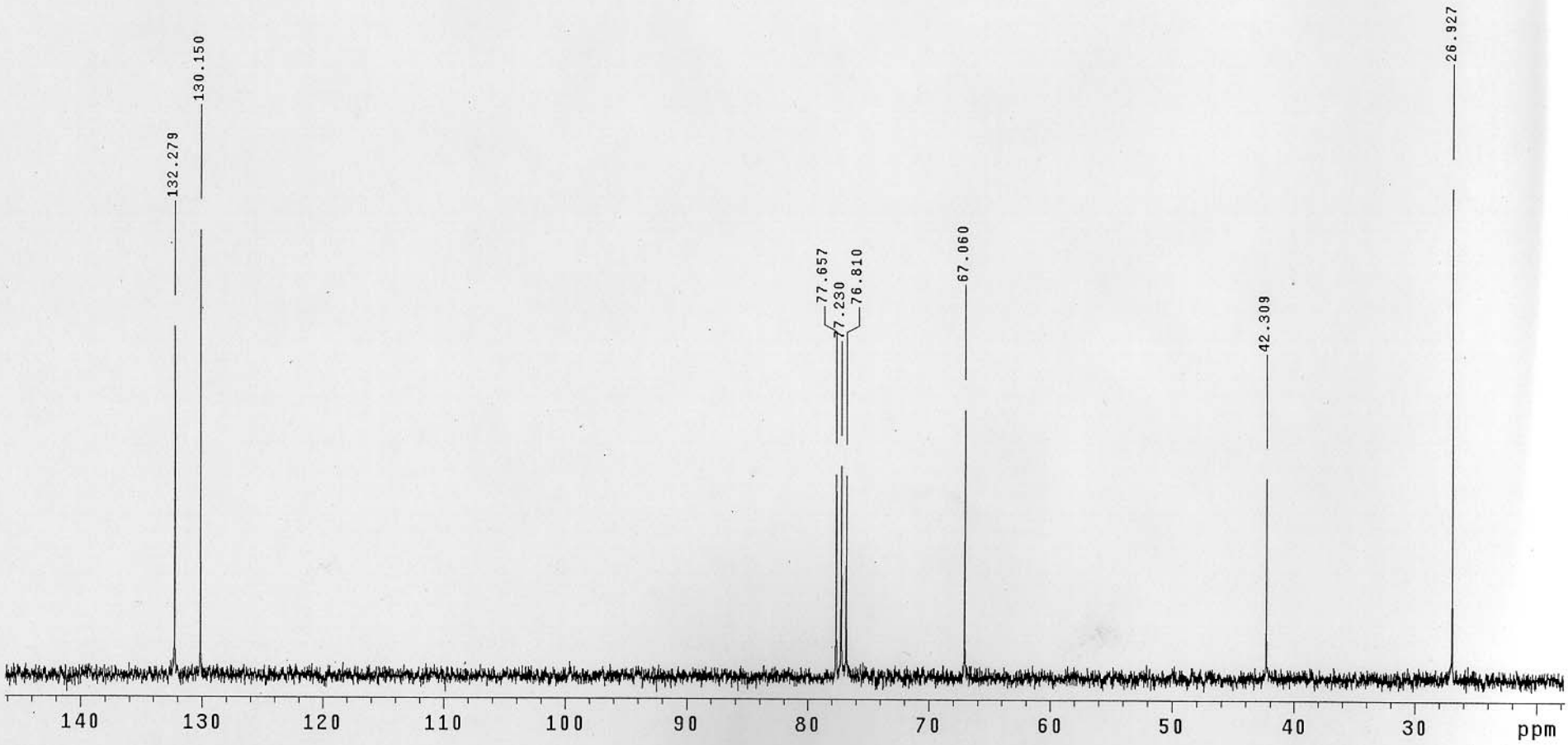
256 repetitions
OBSERVE C13, 75.4703358 MHz
DECOUPLE H1, 300.1417937 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 8 min, 59 sec



9a

^{13}C NMR

(75 MHz, $CDCl_3$)



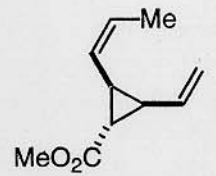
STANDARD 1H OBSERVE

Archive directory: /export/home/general/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: nw485chrom
Mercury-300BB "mercury300"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 4803.1 Hz
8 repetitions
OBSERVE H1, 300.1403284 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 46 sec



5b

^{1}H NMR

(300 MHz, $CDCl_3$)

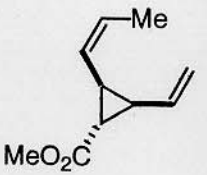
13C OBSERVE

Archive directory: /export/home/general/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"

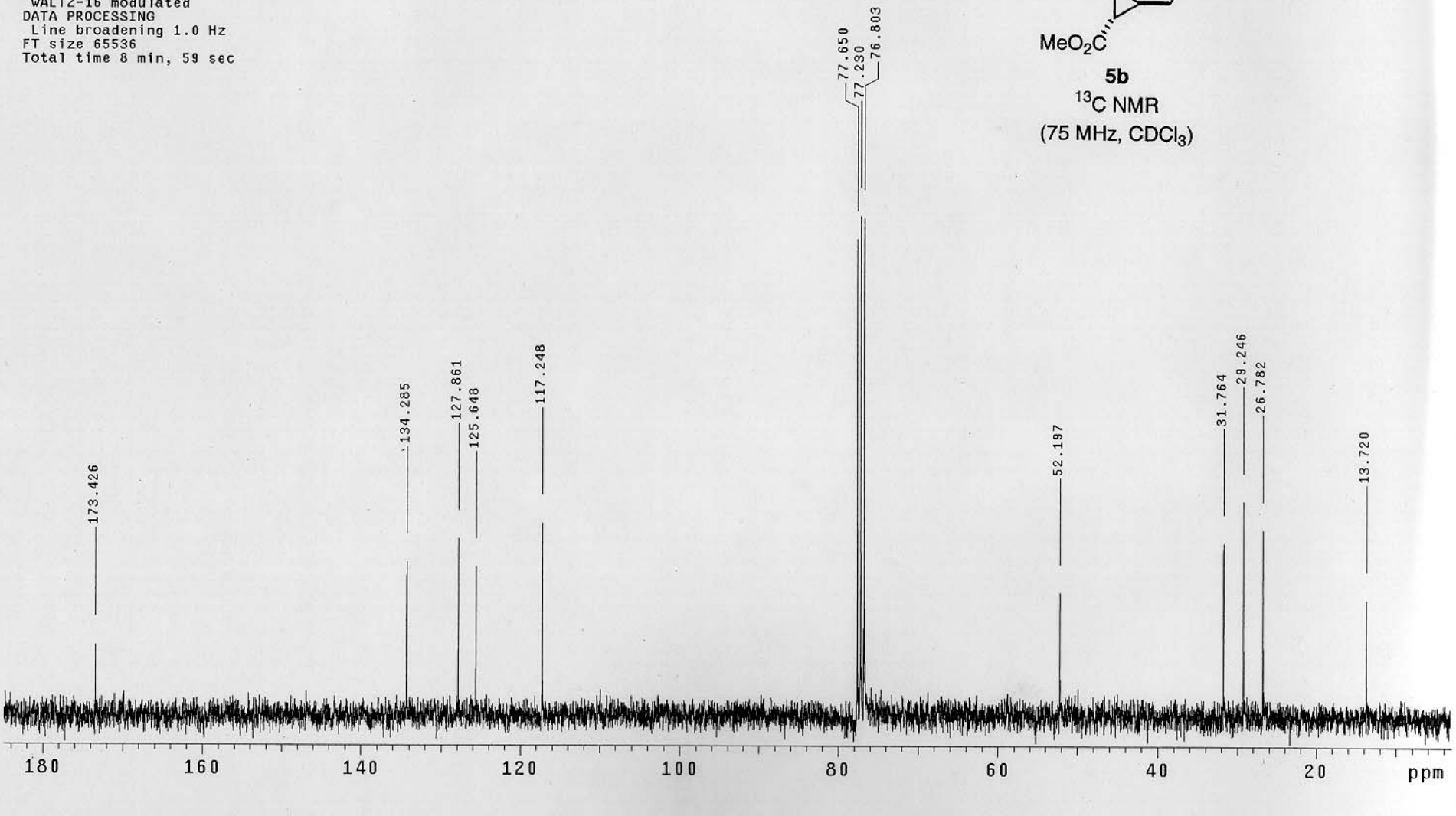
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 18867.9 Hz
128 repetitions
OBSERVE C13, 75.4703347 MHz
DECOUPLE H1, 300.1417937 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 8 min, 59 sec



5b

^{13}C NMR

(75 MHz, $CDCl_3$)

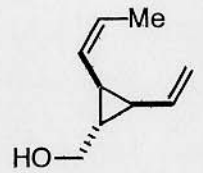


13C OBSERVE

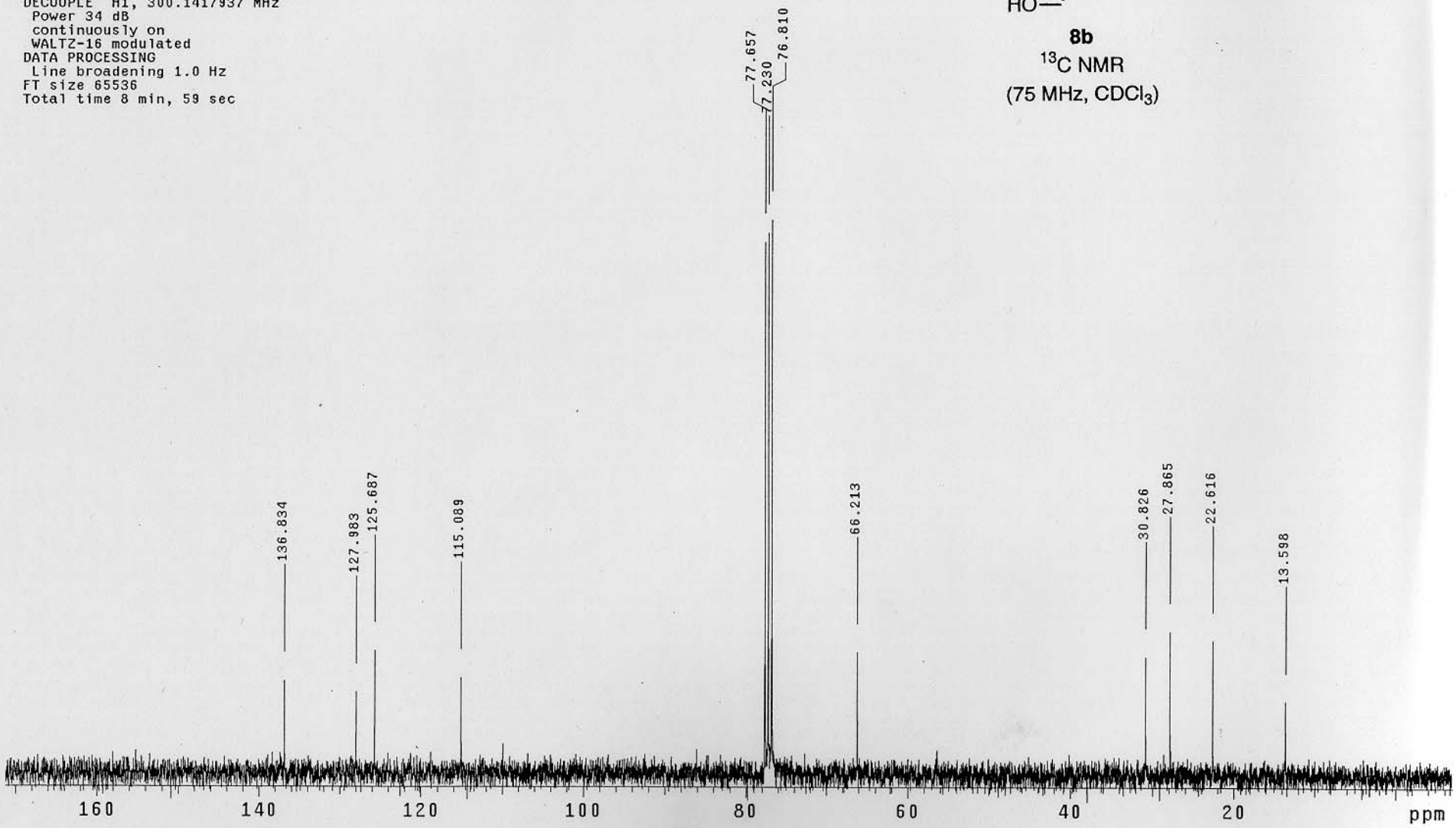
Archive directory: /export/home/general/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 18867.9 Hz
256 repetitions
OBSERVE C13, 75.4703335 MHz
DECOUPLE H1, 300.1417937 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 8 min, 59 sec



8b
^{13}C NMR
(75 MHz, $CDCl_3$)

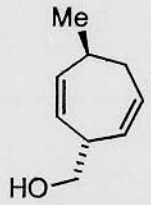


STANDARD 1H OBSERVE

Archive directory: /export/home/general/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 4803.1 Hz
8 repetitions
OBSERVE H1, 300.1403273 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 46 sec



9b

^{1}H NMR

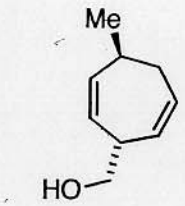
(300 MHz, $CDCl_3$)

13C OBSERVE

Archive directory: /export/home/general/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"

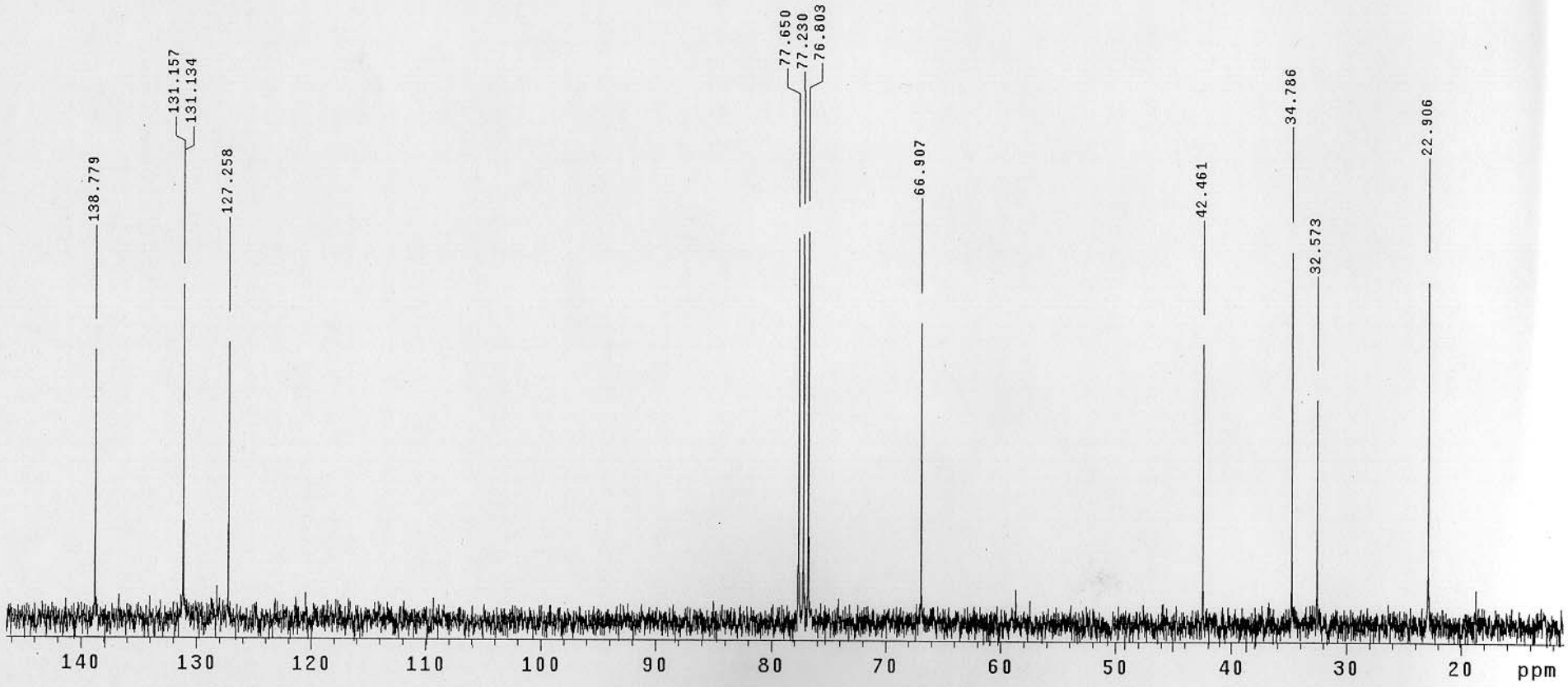
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 18867.9 Hz
160 repetitions
OBSERVE C13, 75.4703364 MHz
DECOUPLE H1, 300.1417937 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 8 min, 59 sec



9b

^{13}C NMR

(75 MHz, $CDCl_3$)

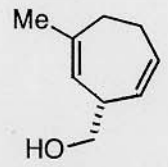


STANDARD 1H OBSERVE

Archive directory: /export/home/general/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 4803.1 Hz
8 repetitions
OBSERVE H1, 300.1403280 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 46 sec



9c

^{1}H NMR

(300 MHz, $CDCl_3$)

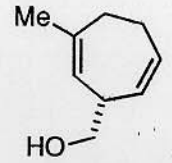
13C OBSERVE

Archive directory: /export/home/general/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"

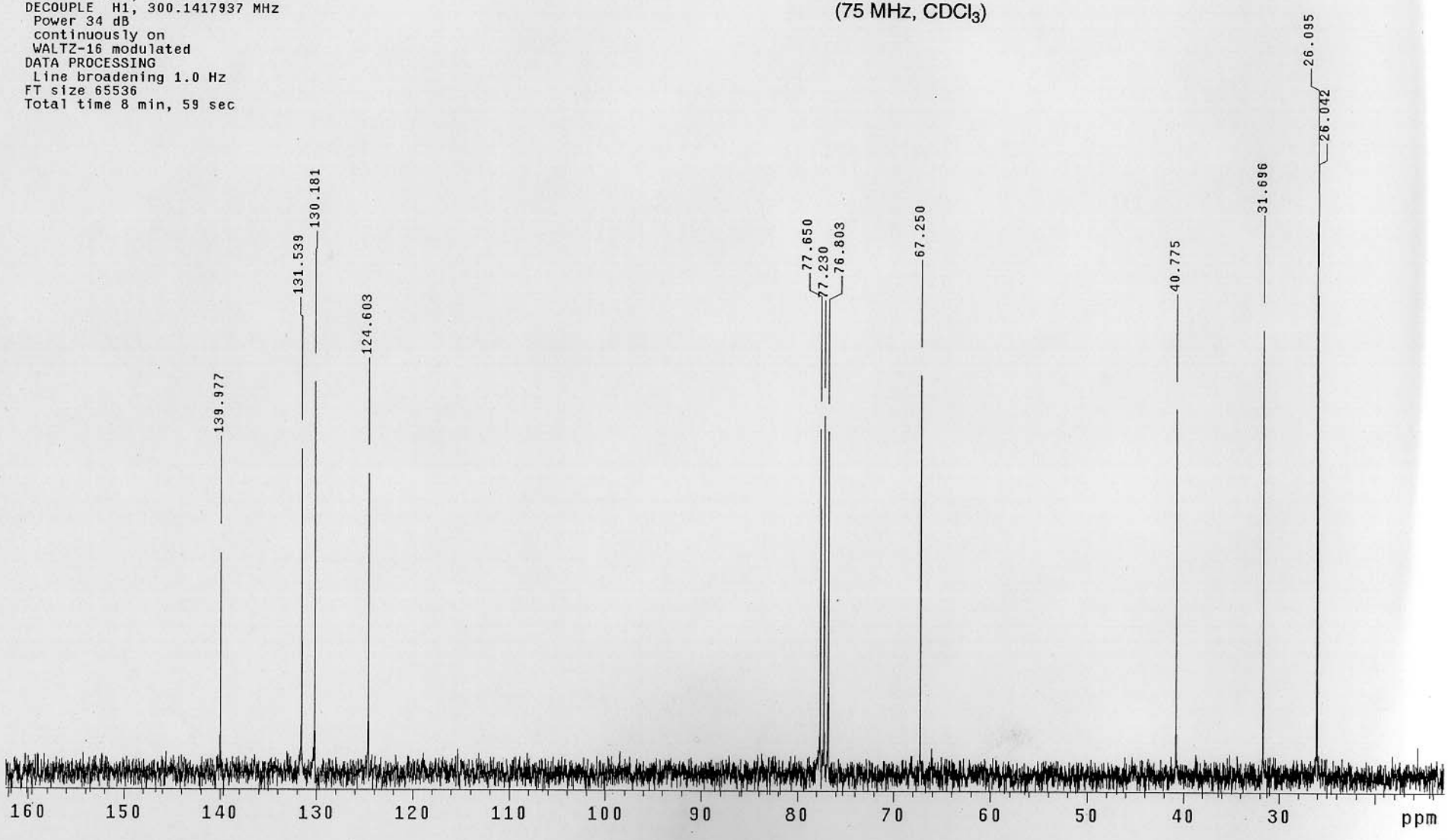
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 18867.9 Hz
256 repetitions
OBSERVE C13, 75.4703358 MHz
DECOUPLE H1, 300.1417937 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 8 min, 59 sec



9c

^{13}C NMR

(75 MHz, $CDCl_3$)

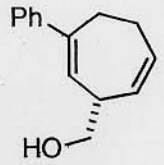


STANDARD 1H OBSERVE

Archive directory: /export/home/general/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"

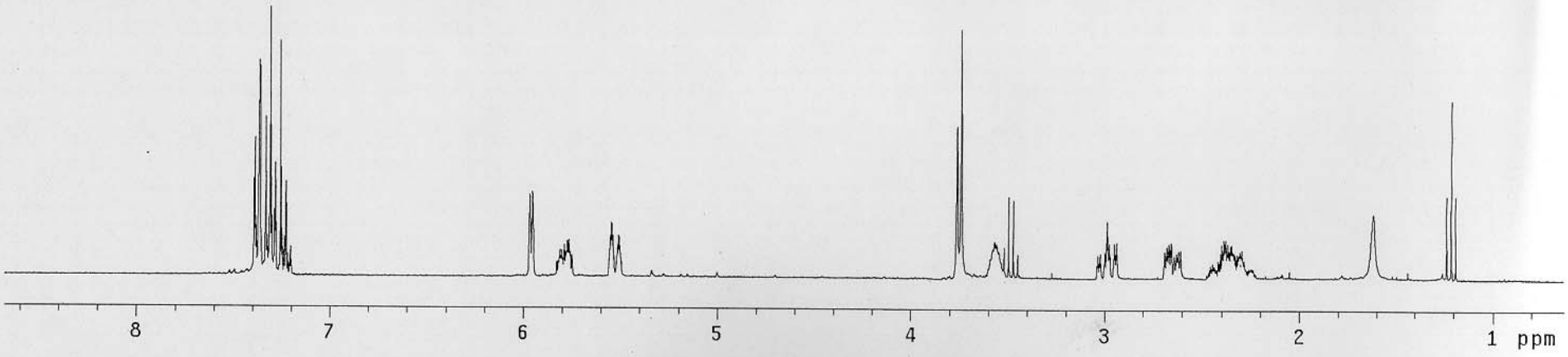
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 4803.1 Hz
8 repetitions
OBSERVE H1, 300.1403280 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 46 sec



9d

^{1}H NMR

(300 MHz, $CDCl_3$)



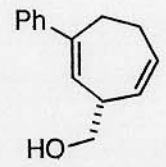
13C OBSERVE

Archive directory: /export/home/general/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"

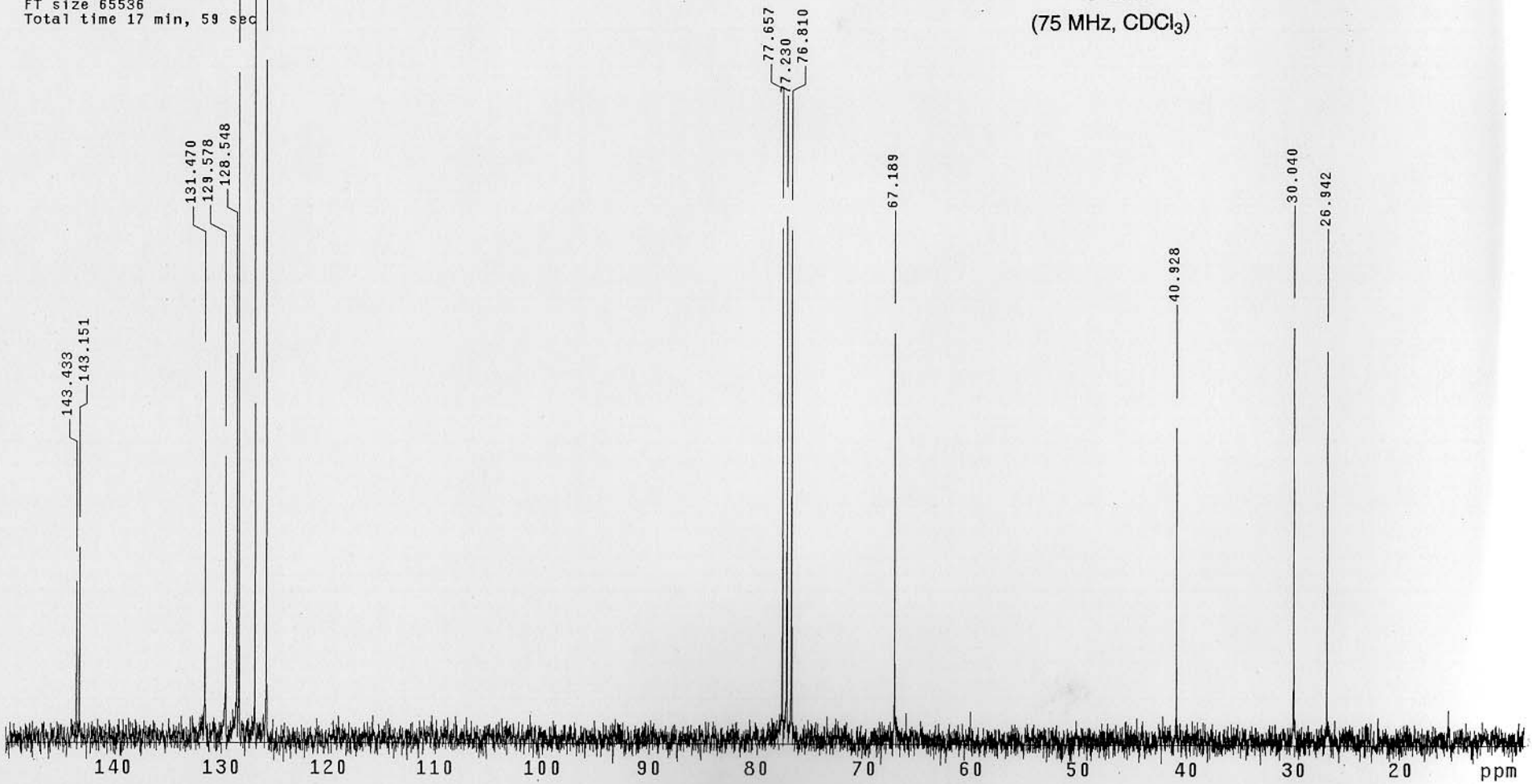
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 18867.9 Hz
512 repetitions
OBSERVE C13, 75.4703353 MHz
DECOUPLE H1, 300.1417937 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 59 sec



9d

^{13}C NMR

(75 MHz, $CDCl_3$)



S12

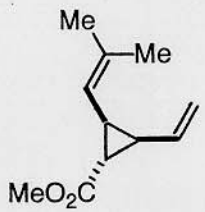
STANDARD 1H OBSERVE

Archive directory: /export/home/general/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 4803.1 Hz
8 repetitions
OBSERVE H1, 300.1403284 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 46 sec



5e

^{1}H NMR

(300 MHz, $CDCl_3$)

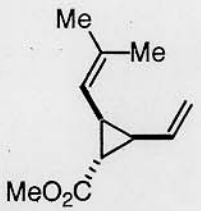
13C OBSERVE

Archive directory: /export/home/general/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
File: nw489chromC13
Mercury-300BB "mercury300"

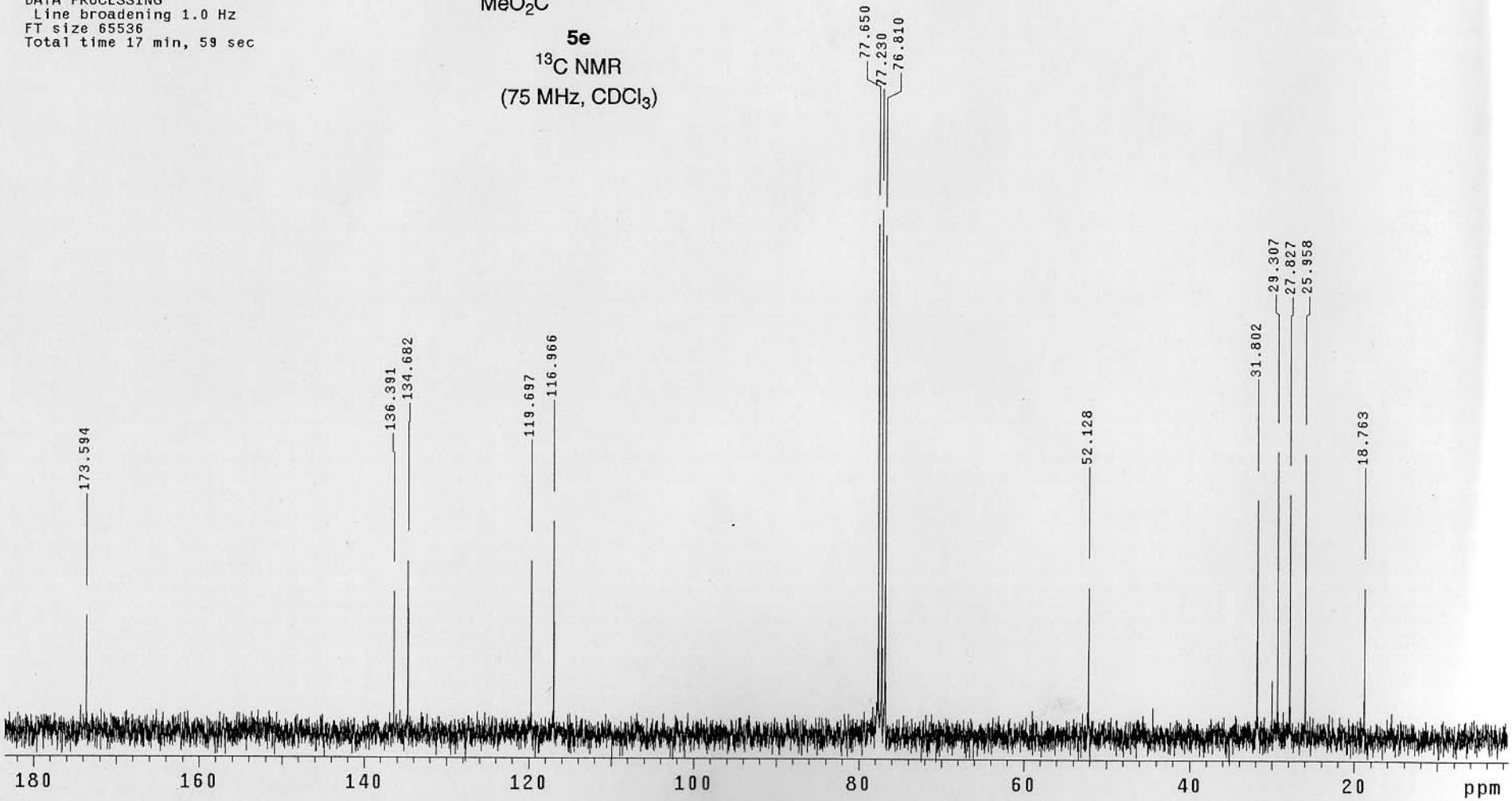
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 18867.9 Hz
128 repetitions
OBSERVE C13, 75.4703341 MHz
DECOUPLE H1, 300.1417937 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 59 sec



5e

^{13}C NMR

(75 MHz, $CDCl_3$)

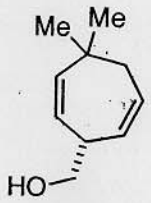


STANDARD 1H OBSERVE

Archive directory: /export/home/general/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 4803.1 Hz
8 repetitions
OBSERVE H1, 300.1403273 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 46 sec



9e
^{1}H NMR
(300 MHz, $CDCl_3$)

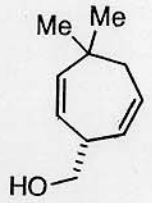
13C OBSERVE

Archive directory: /export/home/general/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"

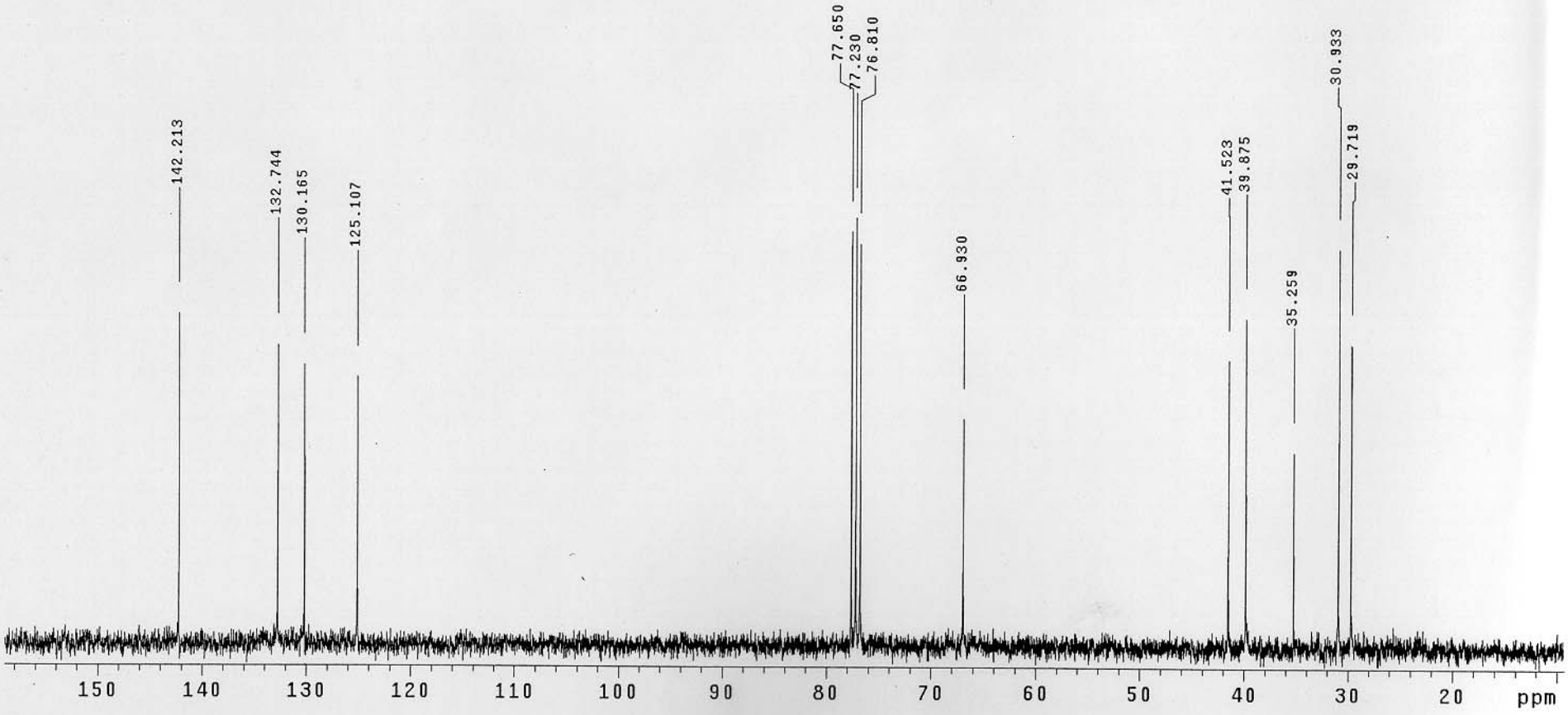
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 18867.9 Hz
256 repetitions
OBSERVE C13, 75.4703358 MHz
DECOUPLE H1, 300.1417937 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 59 sec



9e

^{13}C NMR

(75 MHz, $CDCl_3$)

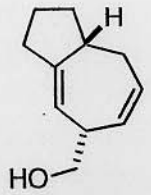


STANDARD 1H OBSERVE

Archive directory: /export/home/general/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"

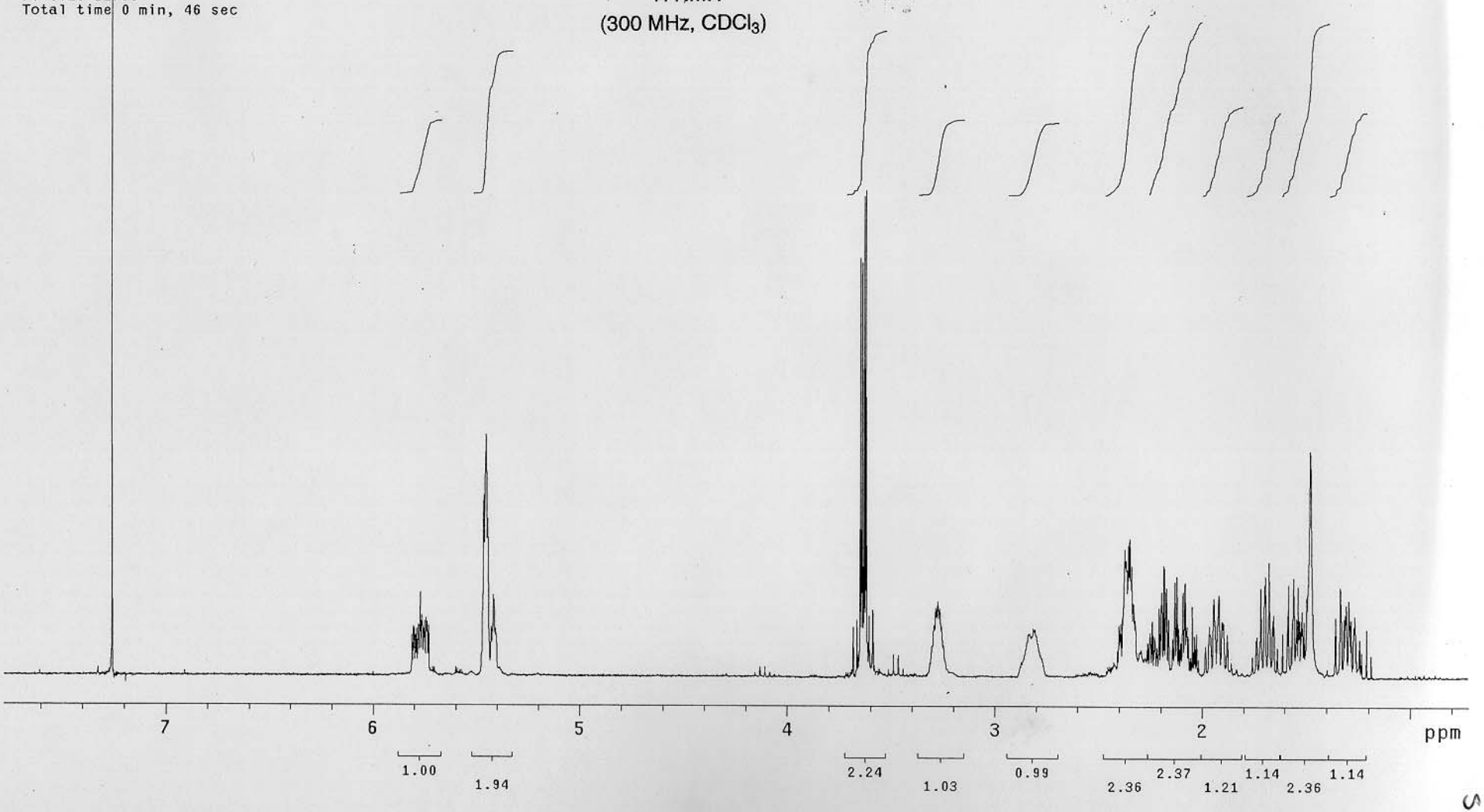
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 4803.1 Hz
8 repetitions
OBSERVE H1, 300.1403278 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 46 sec



9f

^{1}H NMR

(300 MHz, $CDCl_3$)

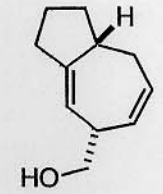


13C OBSERVE

Archive directory: /export/home/general/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "mercury300"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 18867.9 Hz
256 repetitions
OBSERVE C13, 75.4703353 MHz
DECOUPLE H1, 300.1417937 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 8 min, 59 sec



9f

^{13}C NMR

(75 MHz, $CDCl_3$)