Supporting information for:

Vicinal stereocontrol during nucleophilic addition to arene chromium tricarbonyl complexes: Formal synthesis of (±) *erythro* Juvabione

Anthony J. Pearson*, Harinandini Paramahamsan, James D. Dudones

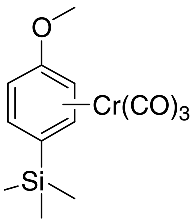
Department of Chemistry, Case Western Reserve University, 10900 Euclid Avenue, Cleveland, OH 44106

anthony.pearson@case.edu

General procedures: All reactions involving chromium tricarbonyl complexes were performed using oven-dried (125 ºC) glassware under anhydrous, oxygen free argon atmosphere. All reactions were performed in freshly distilled (under nitrogen) solvents and monitored by TLC on silica gel. The TLC plates were visualized with UV light and/or with phosphomolybdic acid solution in ethanol. Reactions performed at -60 ºC were maintained at that temperature using ethanol bath and Neslab Cryotrol. Flash chromatography was performed on silica gel with mesh 170-400 under nitrogen pressure. NMR spectra were recorded on a Varian Gemini 200 (200 MHz) or Varian Gemini 300 (300 MHz) or Varian 600 (600 MHz) spectrometer. FTIR spectra were recorded as neat oils or KBr pellet on a Nicolet Impact 400 FTIR spectrometer. High resolution mass spectra (HRMS) of compounds were recorded in-house using a Kratos MS25A instrument by either EI (Electron Ionization) or FAB (Fast Ion Bombardment). Capillary GC was carried out using HP5890 Series II Gas Chromatograph. The melting points were measured on a Thomas Hoover apparatus and are uncorrected. The purity of new compounds was assessed from their ^{1}H and ^{13}C NMR spectra. 4-Methoxy trimethylsilylbenzene was prepared by the literature procedure.[1] Chromium complexes are previously reported in the literature and were prepared from the corresponding arenes by Pauson and Mahaffy procedure of refluxing the arene with chromium hexacarbonyl in dibutyl ether and THF mixture.[2] *endo*-2-Naphthyl isoborneol was prepared from D(+) Camphor by addition of naphthylmagnesium bromide in THF in the presence of anhydrous cerium chloride.[3]

Experimental parameters for Capillary GC on HP5890 Series II Gas Chromatograph:
Column: 25 m HP 5MS capillary column
Carrier gas: Helium at 45 psi
Injector temperature: 200 ºC
Detector temperature: 300 ºC
Run time: 26 minutes

η⁶-(4-methoxytrimethylsilylbenzene)chromium tricarbonyl (3)



Yield: 92%; *R*$_f$: 0.44 (4:1 hexane/ethyl acetate); FAB HRMS *m/z* 316.0218 (M^+), calculated for $C_{13}H_{16}O_4SiCr$ 316.0223; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.55 (2H, d, *J* = 6.4 Hz), 5.09 (2H, d, *J* = 6.4 Hz), 3.73 (3H, s), 0.27 (9H, s); ^{13}C NMR and APT (50 MHz, $CDCl_3$) δ 233.7, 144.4, 100.0, 93.6, 77.9, 55.3, -1.3; FTIR (KBr) ν_{max} 1961, 1869 cm^{-1}

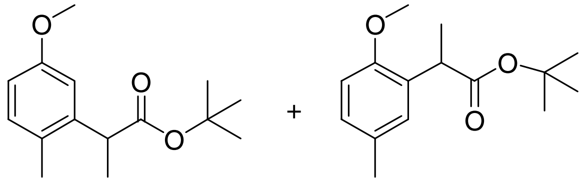
General Procedure for Nucleophilic Addition/Electrophilic Addition/Demetallation Sequence:

To a solution of diisopropylamine (1.7 mL, 12.5 mmol, 5 equiv) in anhydrous THF (12.5 mL) at 0 ºC was added dropwise *n*-butyllithium (1.6M in hexanes; 5.0 mL, 12.5 mmol, 5 equiv). After 15 minutes, the resulting LDA solution was cooled to -78 ºC and a solution of *tert*-butyl propionate (1.9 mL, 2.5 mmol, 5 equiv) in THF (12.5 mL) was added dropwise. After an additional 30 minutes a solution of the arene tricarbonyl chromium complex (2.5 mmol, 1 equiv) in 12.5 mL of THF was added, followed immediately by the addition of anhydrous HMPA (5.4 mL, 31 mmol, 12.5 equiv). The resulting heterogeneous, yellow reaction mixture was warmed to -60 ºC and maintained at this temperature for the duration of the reaction. After 4 hours trifluoroacetic acid (5.2 mL, 67.5 mmol, 27 equiv) was added in one portion and the reaction mixture immediately turned to a deep red color. After 0.5 hours the reaction mixture was removed from the cooling bath and diluted with aqueous concentrated ammonia (5 mL). Finally, after an additional 0.5 hours the now heterogeneous green reaction mixture was diluted with additional aqueous concentrated ammonia and extracted with ether. The combined ether extracts were washed with water, dried ($MgSO_4$), then filtered and concentrated *in vacuo* to give a green oil. Integration of the ^{1}H NMR spectrum of the crude product indicated the diastereomer ratio. The product was then purified by column chromatography.

General Procedure for Nucleophilic Addition/Oxidation Sequence:

The reaction was performed as described above with the following procedural change. After 4 hours of reaction time after the arene complex has been added, a solution of iodine (4 equiv) in THF was added and the red solution was stirred at room temperature for 3 hours. The solution was diluted with diethyl ether and washed with 5% aqueous sodium bisulfite, brine and water, then dried ($MgSO_4$), and solvent was evaporated. The crude product was analyzed by ^{1}H NMR spectroscopy and capillary GC to determine the ratio of the *ortho* and *meta* regioisomers.

***tert*-Butyl 2-(5-methoxy-2-methylphenyl)propionate + *tert*-Butyl 2-(2-methoxy-5-methylphenyl)propionate (5)** *75:25*



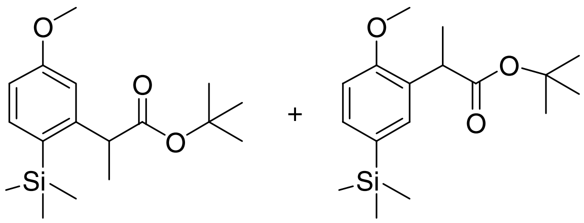
Combined yield: (0.42 g, 67%); R_f: 0.31 (95:5 hexane/ethyl acetate); EI HRMS *m/z* (M^+) 250.1574, calculated for $C_{15}H_{22}O_3$ 250.1569; Ratio of regioisomers from capillary GC: 76:24; Retention times: *Ortho* isomer t_R = 15.64 min, *Meta* isomer t_R = 16.01 min

Data for major *meta* isomer ^{1}H NMR (300 MHz, C_6D_6) δ 7.14 (1H, d, J = 2.6 Hz), 6.93 (1H, d, J = 8.3 Hz), 6.64 (1H, dd, J = 8.3 Hz, 2.7 Hz), 3.78 (1H, q, J = 7.1 Hz), 3.35 (3H, s), 2.18 (3H, s), 1.39 (3H, d, J = 7.0 Hz), 1.29 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.1, 158.2, 140.9, 131.2, 127.9, 112.2, 112.1, 80.6, 55.4, 42.6, 28.1, 18.8, 17.9

Data for minor isomer ***tert*-Butyl 2-(2-methoxy-5-methylphenyl) propionate (5)** ^{1}H NMR (300 MHz, C_6D_6) δ 7.20 (1H, s), 6.88 (1H, d, J = 8.1 Hz), 6.48 (1H, d, J = 8.1 Hz), 4.19 (1H, q, J = 7.3 Hz), 3.31 (3H, s), 2.14 (3H, s), 1.55 (3H, d, J = 7.1 Hz), 1.35 (9H, s); ^{13}C NMR (75

MHz, C_6D_6) δ 174.0, 155.1, 130.6, 129.8, 129.0, 128.3, 110.7, 79.4, 55.0, 40.5, 28.0, 20.7, 18.0

tert-Butyl 2-(5-methoxy-2-trimethylsilylphenyl)propionate + _tert_-Butyl 2-(2-methoxy-5-trimethylsilylphenyl)propionate (6) ***96:4***

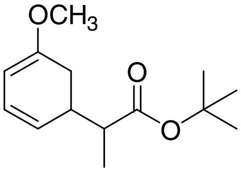


Combined yield: (0.59 g, 76%); R_f: 0.42 (95:5 hexane/ethyl acetate); EI HRMS *m/z* (M^+) 308.1789, calculated for $C_{17}H_{28}O_3Si$ 308.1808; Ratio of regioisomers from capillary GC: 93:7; Retention times: *Ortho* isomer t_R = 17.52 min *Meta* isomer t_R = 18.17 min

Data for major *meta* isomer ^{1}H NMR (300 MHz, C_6D_6) δ 7.39 (1H, d, *J* = 8.3 Hz), 7.29 (1H, d, *J* = 2.3 Hz), 6.72 (1H, dd, *J* = 8.3 Hz, 2.6 Hz), 3.93 (1H, q, *J* = 7.0 Hz), 3.36 (3H, s), 1.47 (3H, d, *J* = 6.9 Hz), 1.28 (9H, s) 0.36 (9H, s); ^{13}C NMR (50 MHz, C_6D_6) δ 173.6, 161.7, 149.9, 136.5, 129.1, 112.5, 112.4, 80.0, 54.6, 46.3, 27.9, 20.5, 0.7

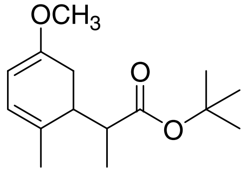
Data for minor *ortho* isomer ^{1}H NMR (300 MHz, C_6D_6) δ 7.64 (1H, s), 7.36 (1H, dd, *J* = 8.0, 1.7 Hz), 6.59 (1H, d, *J* = 8.2 Hz), 4.23 (1H, q, *J* = 7.0 Hz), 3.33 (3H, s), 1.55 (3H, d, *J* = 6.9 Hz), 1.25 (9H, s) 0.27 (9H, s); ^{13}C NMR (50 MHz, C_6D_6) δ 173.6, 161.7, 149.9, 133.5, 133.1, 127.9, 110.5, 79.5, 54.8, 40.7, 28.1, 18.2, -0.7

tert-Butyl 2-(5-methoxycyclohexa-2,4-dien-1-yl)propanoate + 1,3-isomeric diene mixture (7)



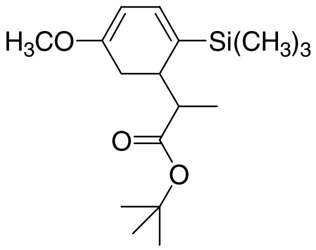
Pale yellow oil. Combined yield: (0.56 g, 72%); R_f: 0.73 (4:1 hexane/ethyl acetate); FAB HRMS *m/z* 310.1966 (M^+), calculated for $C_{17}H_{30}O_3Si$ 310.1964.

tert-Butyl 2-(2-methyl-5-methoxycyclohexa-2,4-dien-1-yl)propanoate + isomeric dienes (8)



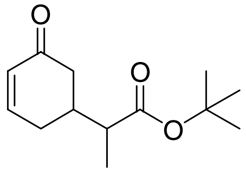
Pale yellow oil. Combined yield: (0.35 g, 55%); R_f: 0.46 (9:1 hexane/ethyl acetate); EI HRMS *m/z* (M^+) 252.1723, calculated for $C_{15}H_{24}O_3$ 252.1725.

tert-Butyl 2-(2-trimethylsilyl-5-methoxycyclohexa-2,4-dien-1-yl)propanoate (9)



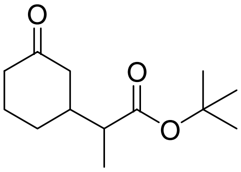
Pale yellow oil. Yield: (0.70 g, 90%); R_f: 0.73 (4:1 hexane/ethyl acetate); FAB HRMS *m/z* 310.1966 (M^+), calculated for $C_{17}H_{30}O_3Si$ 310.1964; ^1H NMR (300 MHz, $CDCl_3$) δ6.30 (1H, d, $J = 6.1$ Hz), 4.91 (1H, dd, $J = 6.1$ Hz, 2.2 Hz), 3.57 (3H, s), 3.02-2.97 (1H, m), 2.52-2.36 (m, 2H), 2.13 (1H, dd, $J = 2.3$ Hz, 17.5 Hz), 1.46 (9H, s), 0.98 (3H, d, $J = 7.1$ Hz), 0.12 (9H, s); ^{13}C NMR and APT (50 MHz, $CDCl_3$) δ 174.6, 159.5, 134.6, 129.6, 93.0, 80.0, 54.7, 44.9, 37.2, 28.0, 27.8, 10.1, -0.6; FTIR (Neat on NaCl plate) ν_{max} 1726, 1645 cm^{-1}.

tert-Butyl 2-(5-oxocyclohex-2-en-1-yl)propanoate (10-*erythro*)



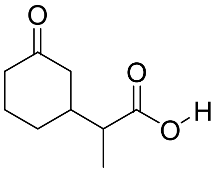
A solution of the cyclohexadiene **9** (1.5 g, 5.4 mmol, 1 equiv) in 10 mL of diethyl ether, and *para*-toluenesulfonic acid monohydrate (1.54 g, 8.1 mmol, 1.5 equiv) was stirred at room temperature until all the starting diene had been consumed, according to TLC (3h). The reaction mixture was then diluted with aqueous saturated $NaHCO_3$ (5 mL) and extracted with diethyl ether. The combined ether extracts were washed with brine, dried (Na_2SO_4), and the solvent was removed *in vacuo*. Purification by column chromatography (4:1 hexane/ethyl acetate) afforded the title compound as a pale yellow oil (1.10 g, 94%); R_f: 0.34 (4:1 hexane/ethyl acetate); FAB HRMS *m/z* (MH^+) 225.1487, calculated for $C_{17}H_{30}O_3Si$ 225.1491; ^{1}H NMR (200 MHz, $CDCl_3$) δ6.98 (1H, ddd, *J* = 6.7 Hz, 3.8 Hz, 1.6 Hz), 6.04 (1H, dd, *J* = 6.7 Hz, 0.7 Hz), 2.55 (1H, dd, *J* = 10.3 Hz, 0.6 Hz), 2.45-2.13 (5H, m), 1.46 (9H, s), 1.14 (3H, d, *J* = 3.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 199.2, 174.2, 149.7, 129.7, 80.8, 44.9, 41.6, 37.9, 29.9, 28.2, 14.4; FTIR (Neat on NaCl plate) ν_{max} 1683 cm^{-1}.

***tert*-Butyl 2-(3-oxocyclohexyl)propanoate (11-*erythro*)**



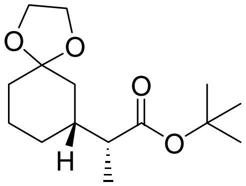
Erythro*-10** (0.45 g, 2 mmol) was hydrogenated in 10 mL ethyl acetate solution over 10% Pd-C (0.02g, 0.2 mmol) at room temperature under atmospheric pressure for 4 hours. After removal of the catalyst by filtration through a celite pad, the solvent was distilled *in vacuo*. The residue was chromatographed on silica gel (hexane/ethyl acetate (3:1)) to afford the title compound **11-*erythro as a colorless oil (0.35 g, 78%); R_f: 0.50 (3:1 hexane/ethyl acetate); EI HRMS *m/z* (MH^+) 227.1651, calculated for $C_{13}H_{22}O_3$ 227.1647; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40-2.29 (2H, m), 2.26-2.15 (2H, m), 2.10-1.90 (3H, m), 1.87-1.76 (1H, br m), 1.63-1.52 (2H, m), 1.41 (9H, s), 1.05 (3H, d, *J* = 7.2 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 211.1, 174.6, 80.5, 45.5, 44.9, 41.6, 41.3, 29.2, 28.1, 25.1, 14.0; FTIR (Neat on NaCl) ν_{max} 1723 cm^{-1}.

2-(3-Oxocyclohexyl)propanoic acid (12-*erythro*)



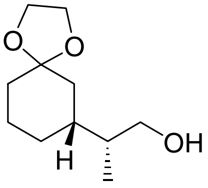
Keto-ester **11-*erythro*** (0.32 g, 1.41 mmol) was dissolved in 3 mL of 100% formic acid and the solution was stirred at room temperature for 3 hours. The solution was then concentrated *in vacuo* to give an oil, which was chromatographed on silica gel (methylene chloride/methanol (98:2)). The combined fractions after evaporation of solvent yielded a white crystalline solid (0.17 g, 72%); R_f: 0.30 (98:2 methylene chloride/methanol); Mp: 75-77 ºC; EI HRMS *m/z* (M^+) 170.0943, calculated for $C_9H_{14}O_3$ 170.0943; ^1H NMR (200 MHz, $CDCl_3$) δ 9.43 (1H, br s), 2.45-2.21 (4H, m), 2.20-2.01 (3H, m), 2.00-1.83 (2H, m), 1.18 (3H, d, $J = 7.0$ Hz) ; ^{13}C NMR (50 MHz, $CDCl_3$) δ 211.6, 180.9, 44.6, 44.4, 41.2, 41.1, 29.1, 25.2, 13.6; Three small signals corresponding to the **12-*threo*** keto acid were observed at δ 45.6, 27.9, 13.8; FTIR (Neat on NaCl plate) ν_{max} 3452, 1720 cm^{-1}.

***tert*-Butyl 2-(1,4-dioxaspiro[4.5]dec-7-yl)propanoate (13-*erythro*)**



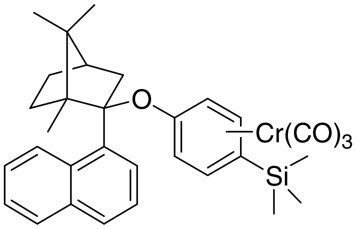
To keto-ester **11** (0.23g, 1 mmol, 1 equiv) was added ethylene glycol (0.08 g, 1.2 mmol, 1.2 equiv), 20 mL of dry benzene and a few crystals of *para*-toluenesulfonic acid. The mixture was refluxed with azeotropic removal of water (Dean-Stark trap) for 3 hours, after which the cooled reaction mixture was washed with half-saturated $NaHCO_3$, dried ($MgSO_4$) and concentrated *in vacuo* to afford **13-*erythro***. The crude material was purified by column chromatography (4:1 hexane/ethyl acetate) to afford a colorless oil (0.23 g, 88%); R_f: 0.46 (4:1 hexane/ethyl acetate); EI HRMS *m/z* (M^+) 270.1831, calculated for $C_{15}H_{26}O_4$ 270.1827; ^1H NMR (200 MHz, $CDCl_3$) δ 3.90 (4H, s), 2.21-2.07 (1H, m), 1.96-1.51 (4H, m), 1.41 (9H, s), 1.36-0.88 (5H, m), 1.04 (3H, d, $J = 7.0$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 175.3, 109.3), 79.9, 64.3, 64.2, 45.8, 38.5, 38.3, 34.8, 29.4, 28.2, 23.1, 14.1; FTIR (Film on NaCl plate) ν_{max} 1727 cm^{-1}.

2-(1,4-dioxaspiro[4.5]dec-7-yl)propan-1-ol (14-*erythro*)



In a round bottom flask under nitrogen atmosphere was placed 0.015g (0.4 mmol, 2 equiv) of lithium aluminium hydride in 0.5 mL of freshly distilled THF, and the reaction flask was cooled in an ice bath. **13-*erythro*** (0.053g, 0.2 mmol, 1 equiv) in 0.6 mL of THF was added dropwise to the reaction vessel and the mixture was stirred for 1 hour, after which 2.5 mL of ethyl acetate was added dropwise at 0 ºC. The solution was diluted with 3 mL of diethyl ether and washed with brine and dried (Na_2SO_4) and solvent removed *in vacuo*. Column chromatography (1:1 hexane/ethyl acetate) gave **14-*erythro*** as a colorless liquid (0.02 g, 52%); R_f: 0.5 (1:1 hexane/ethyl acetate); EI HRMS *m/z* (M^+) 200.1413, calculated for $C_{11}H_{20}O_3$ 200.1412; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.94 (4H, s), 3.60 (1H, dd, J_{AB} = 10.7 Hz, 5.8 Hz), 3.44 (1H, dd, J_{AB} = 10.6 Hz, 6.7 Hz), 1.77-1.52 (7H, m), 1.50-1.20 (3H, m), 1.10-0.99 (1H, m), 0.88 (3H, d, J = 6.8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 109.7, 66.2, 64.4, 64.2, 40.4, 37.6, 37.0, 34.9, 29.6, 23.5, 13.4; FTIR (Thin film on NaCl plate) ν_{max} 3563 (broad) cm^{-1}.

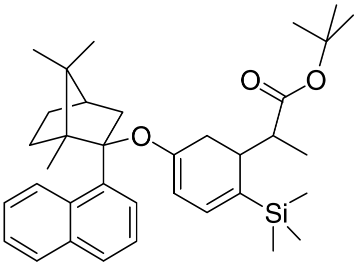
η^6-{4-[[(1*R*,2*S*)-1,7,7-Trimethyl-2-(1-naphthyl)bicyclo[2.2.1]hept-2-yl]oxy]trimethylsilylbenzene}chromium tricarbonyl (16)



To a heterogeneous mixture of potassium hydride (20 % dispersion in mineral oil; 0.90 g, 4.5 mmol, 1.5 equiv, washed thrice with freshly distilled diethyl ether to remove the mineral oil), in anhydrous diethyl ether (12 mL) at 0 ºC under argon, was added a solution of 2-naphthyl isoborneol (0.93 g, 3.3 mmol, 1.1 equiv), in diethyl ether (6 mL), dropwise so that the hydrogen gas effervescence is not too vigorous. One hour after the hydrogen gas evolution had stopped, a solution of η^6-(4-fluoro(trimethylsilyl)benzene)chromium tricarbonyl (0.91 g, 3 mmol, 1 equiv) in ether (9 mL) was added dropwise. The S_NAr reaction was complete after 4 hours as indicated by complete disappearance of starting fluoro complex on the TLC plate. The dark brown mixture was carefully quenched by slow addition of 5% aqueous hydrochloric acid. The aqueous phase was then extracted with ether (3 x 25 mL) and the combined ether extracts were washed with water, dried ($MgSO_4$), then filtered and concentrated *in vacuo* to give a yellow solid which on recrystallization from 1:1 mixture of hexane/dichloromethane gave yellow rhombic crystals which was washed with cold hexane

(1.30 g, 77%); R_f: 0.39 (20:1 hexane/ether); FAB HRMS *m/z* 564.1788 (M^+), calculated for $C_{32}H_{36}O_4SiCr$ 564.1782; ^1H NMR (300 MHz, $CDCl_3$) δ 8.49-8.46 (1H, m), 7.83-7.75 (3H, m), 7.49-7.28 (3H, m), 5.33 (1H, dd, *J* = 6.9 Hz, 1.5 Hz), 5.17 (1H, dd, *J* = 6.9 Hz, 2.3 Hz), 4.95 (1H, dd, *J* = 6.9 Hz, 1.5 Hz), 4.74 (1H, dd, *J* = 6.9 Hz, 2.3 Hz), 2.95 (1H, dt, *J* = 14.7 Hz, 3.2 Hz), 2.64 (1H, d, *J* = 14.7 Hz), 2.12 (1H, t, *J* = 4.2 Hz), 1.85-1.74 (1H, m), 1.48-1.34 (1H, m), 1.38 (3H, s), 1.25-1.04 (1H, m), 1.14 (3H, s), 0.97 (3H, s), 0.82-0.78 (1H, m), 0.09 (9H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 234.0, 141.0, 136.5, 135.0, 131.8, 130.0, 128.9, 128.8, 126.0, 125.7, 125.4, 124.3, 99.7, 98.4, 97.7, 93.8, 82.7, 81.3, 56.9, 51.4, 45.8, 41.9, 31.2, 25.7, 22.0, 21.2, 14.0, -1.5; FTIR (KBr) ν_{max} 1961, 1869 cm^{-1}.

***tert*-Butyl [5-[[(1R,2S)-1,7,7-trimethyl-2-(1-naphthyl)bicyclo[2.2.1]hept-2-yl]oxy]2-trimethylsilylcyclohexa-2,4-dien-1-yl] propionate (17b)**



Nucleophilic addition to complex **16** followed by protonation and decomplexation followed the general procedure. Yield: 76% (based on recovered starting complex **16**); R_f: 0.30 (20:1 hexane/ether); EI HRMS *m/z* 558.3498 (M^+), calculated for $C_{36}H_{50}O_3Si$ 558.3529; Data for major diastereomer: ^1H NMR (600 MHz, C_6D_6) δ 9.21 (1H, d, *J* = 9.0 Hz), 7.65-7.58 (3H, m), 7.50 (1H, d, *J* = 7.2 Hz), 7.27 (1H, t, *J* = 8.1 Hz), 7.21 (1H, t, *J* = 7.8 Hz), 5.87 (1H, d, *J* = 6.6 Hz), 4.57 (1H, dd, *J* = 2.1 Hz, 6.3 Hz), 3.22 (1H, dt, *J* = 10.8 Hz, 3.0 Hz), 2.65 (1H, dd, *J* = 3.6 Hz, 18.0 Hz), 2.59-2.47 (2H, m), 2.40 (1H, d, *J* = 15.0 Hz), 1.73 (1H, t, *J* = 3.9 Hz), 1.46-1.37 (1H, m), 1.41 (9H, s), 1.26-1.18 (1H, m), 1.23 (3H, s), 1.17 (3H, s), 1.05-0.95 (3H, m), 0.88 (3H, d, *J* = 7.2 Hz), 0.81 (3H, s), 0.07 (9H,s); ^{13}C NMR (50 MHz, C_6D_6) δ 174.5, 152.2, 139.0, 135.7, 135.4, 133.3, 129.7, 129.5, 129.1, 128.3, 126.0, 125.7, 125.2, 124.2, 100.3, 94.3, 79.3, 56.5, 51.3, 46.0, 44.9, 42.8, 38.7, 31.0, 29.1, 28.1, 26.0, 22.1, 21.5, 14.3, 10.8, -0.5; FTIR (Thin film on NaCl plate) ν_{max} 1725, 1644, 1563 cm^{-1}.

References:

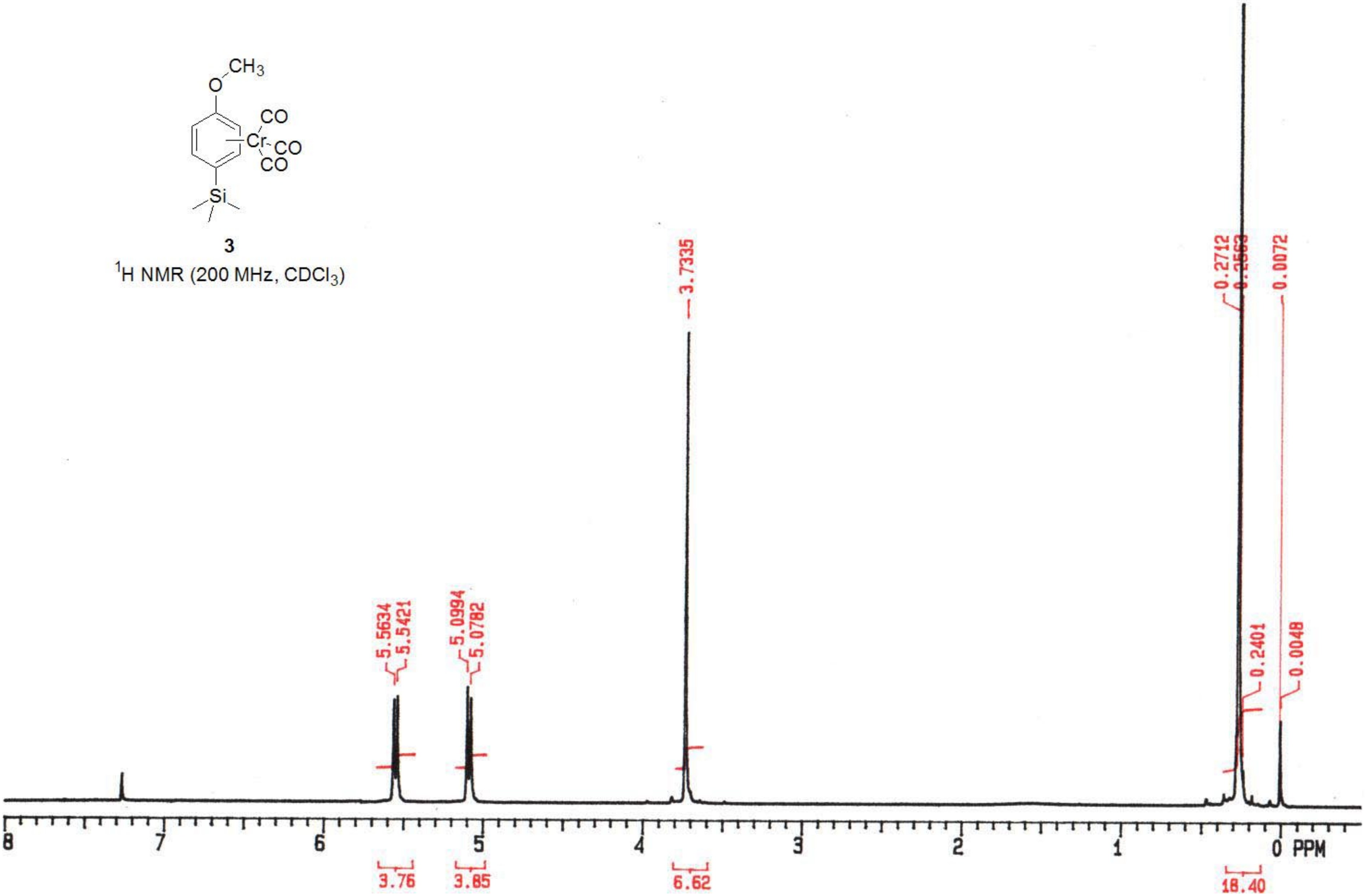
1) Moerlein, S. M. *J. Organomet. Chem.* **1987**, 319, 29-39.

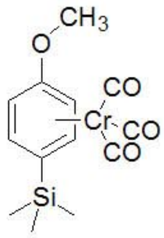
2) Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Syn.* **1979**, *19*, 154-158.

3) Dimitrov, V.; Bratovanov, S.; Simova, S.; Kostova, K. *Tetrahedron Lett.* **1994**, *35*, 6713.

3

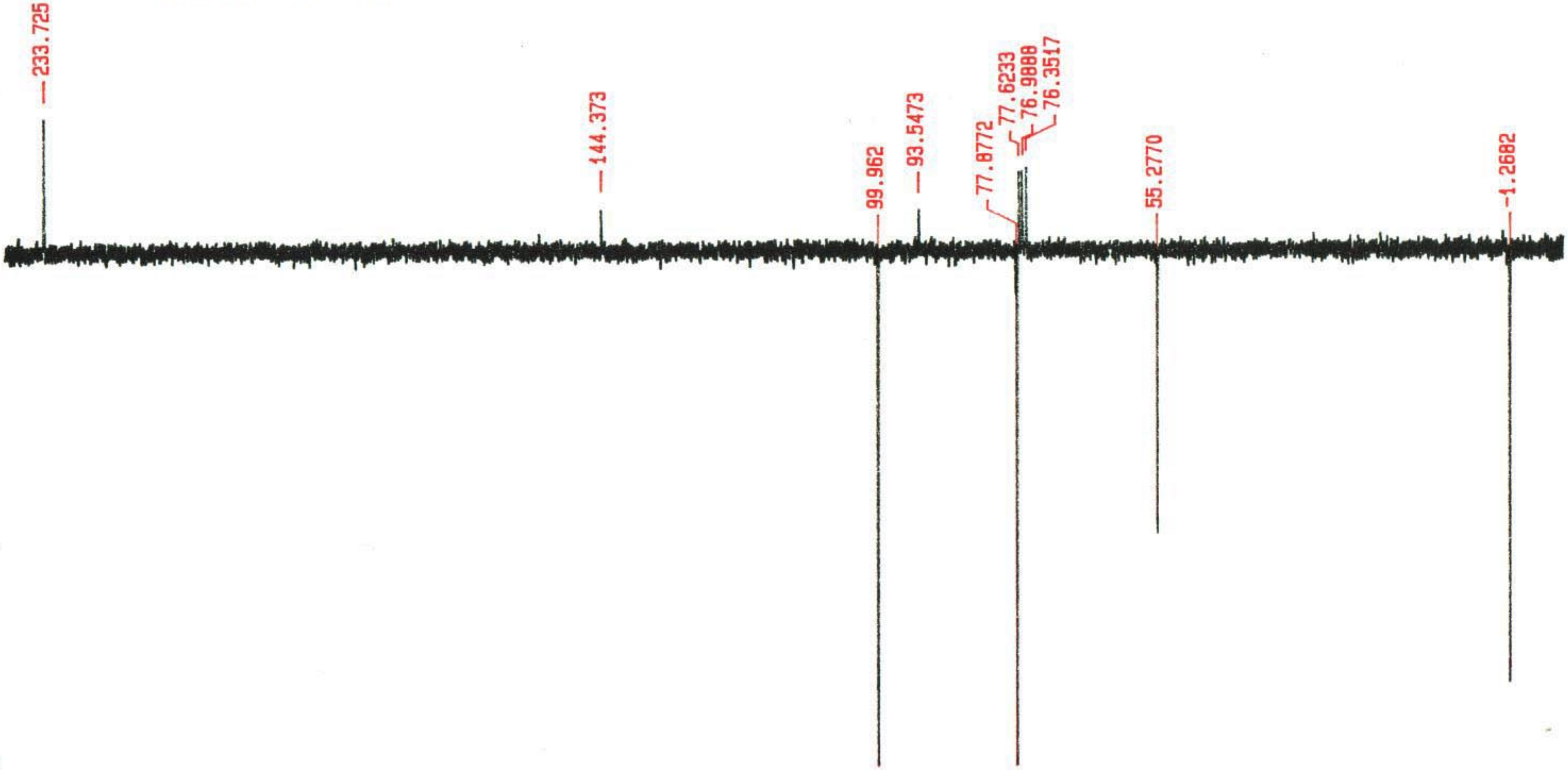
^{1}H NMR (200 MHz, $CDCl_3$)

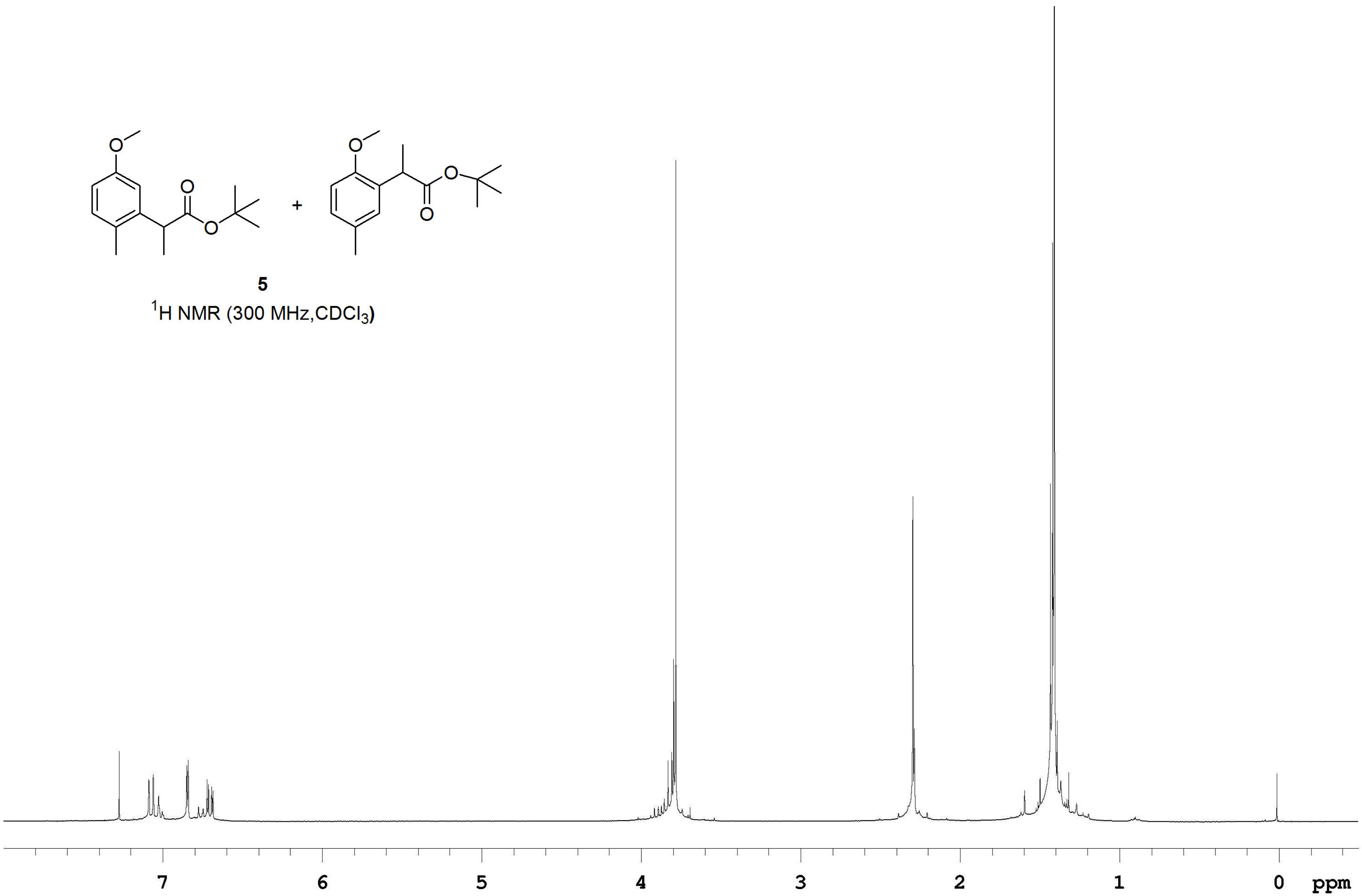




3

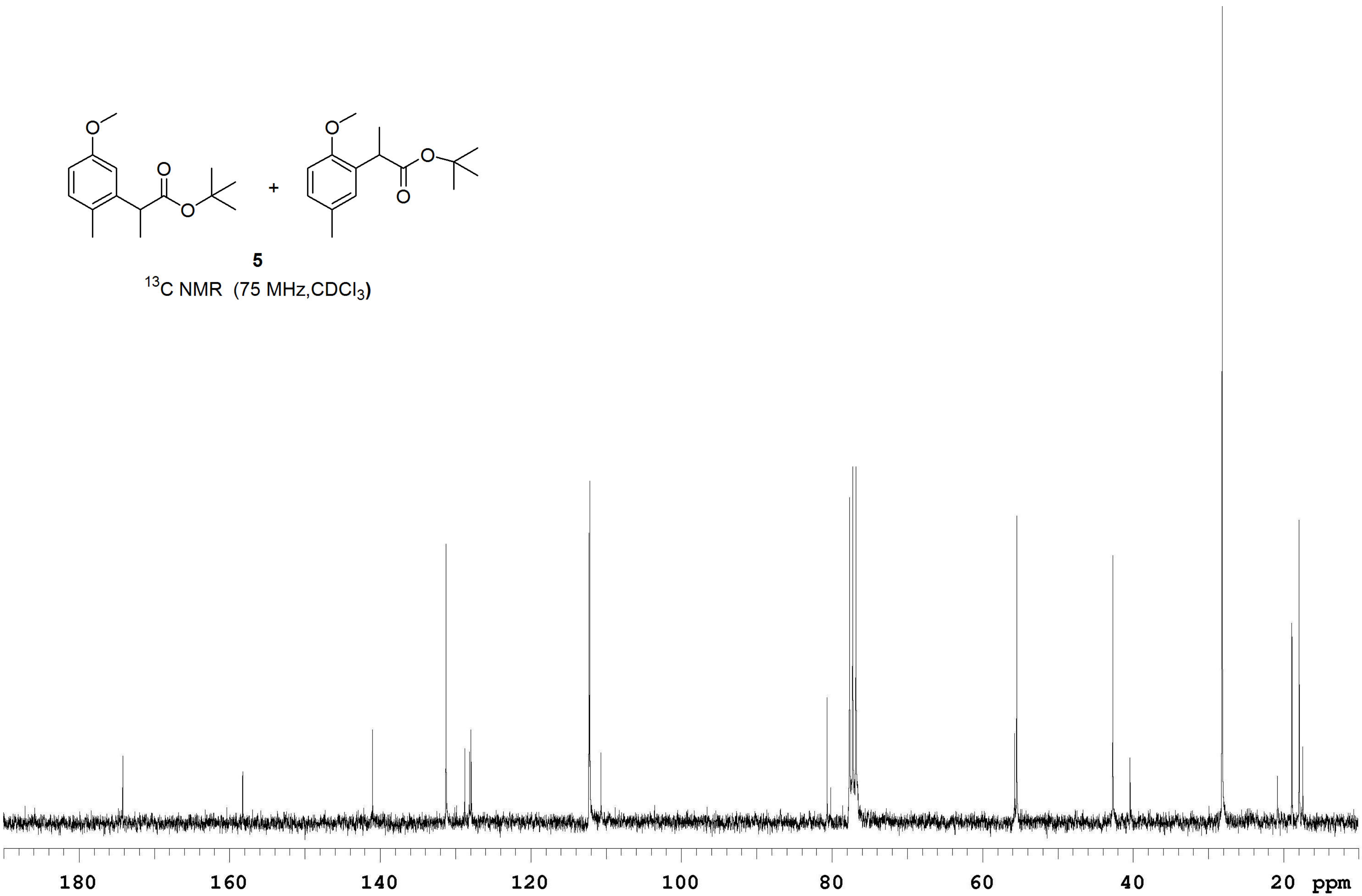
^{13}C NMR 50 MHz, CDCl$_3$)





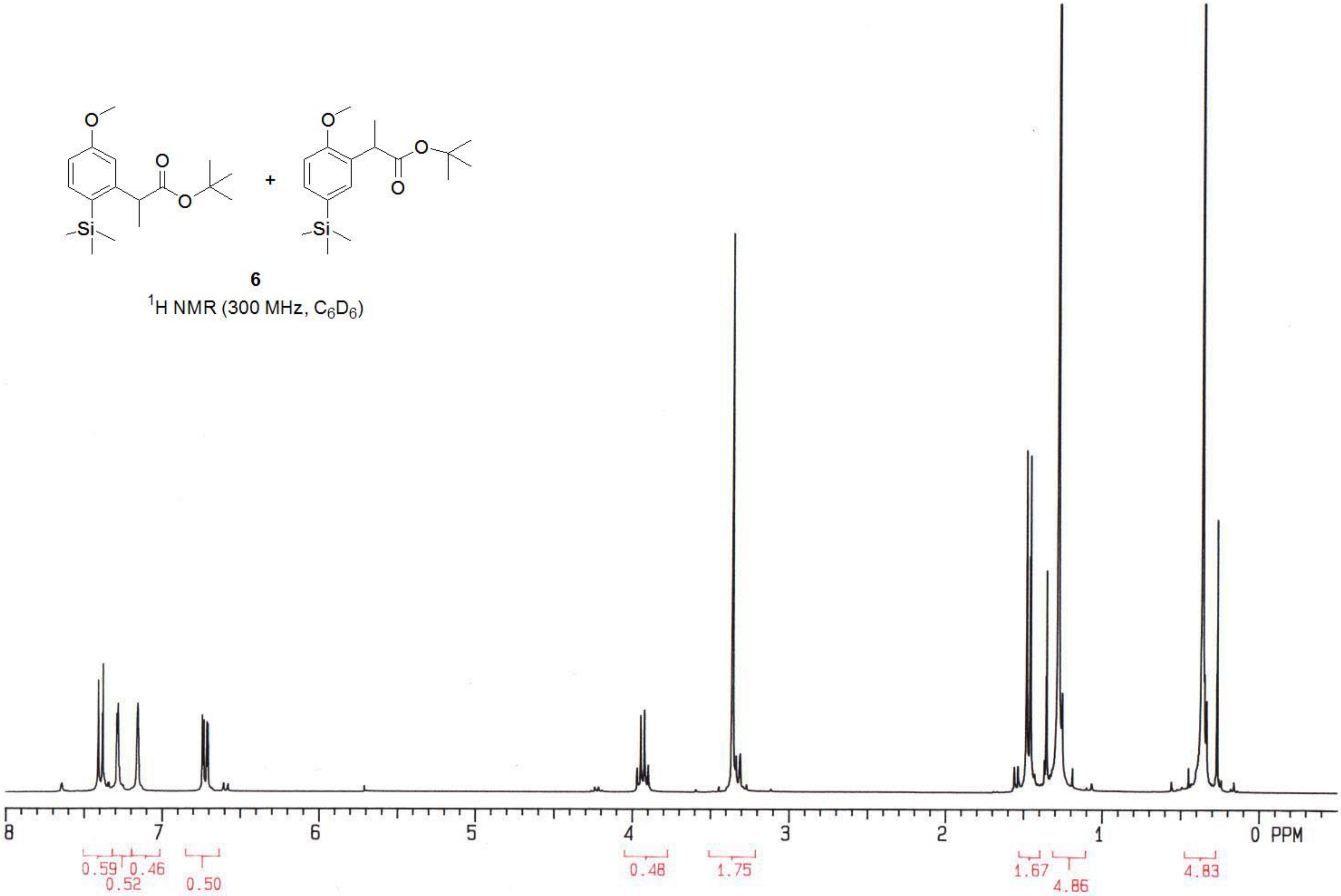
5

^{1}H NMR (300 MHz,CDCl$_3$)



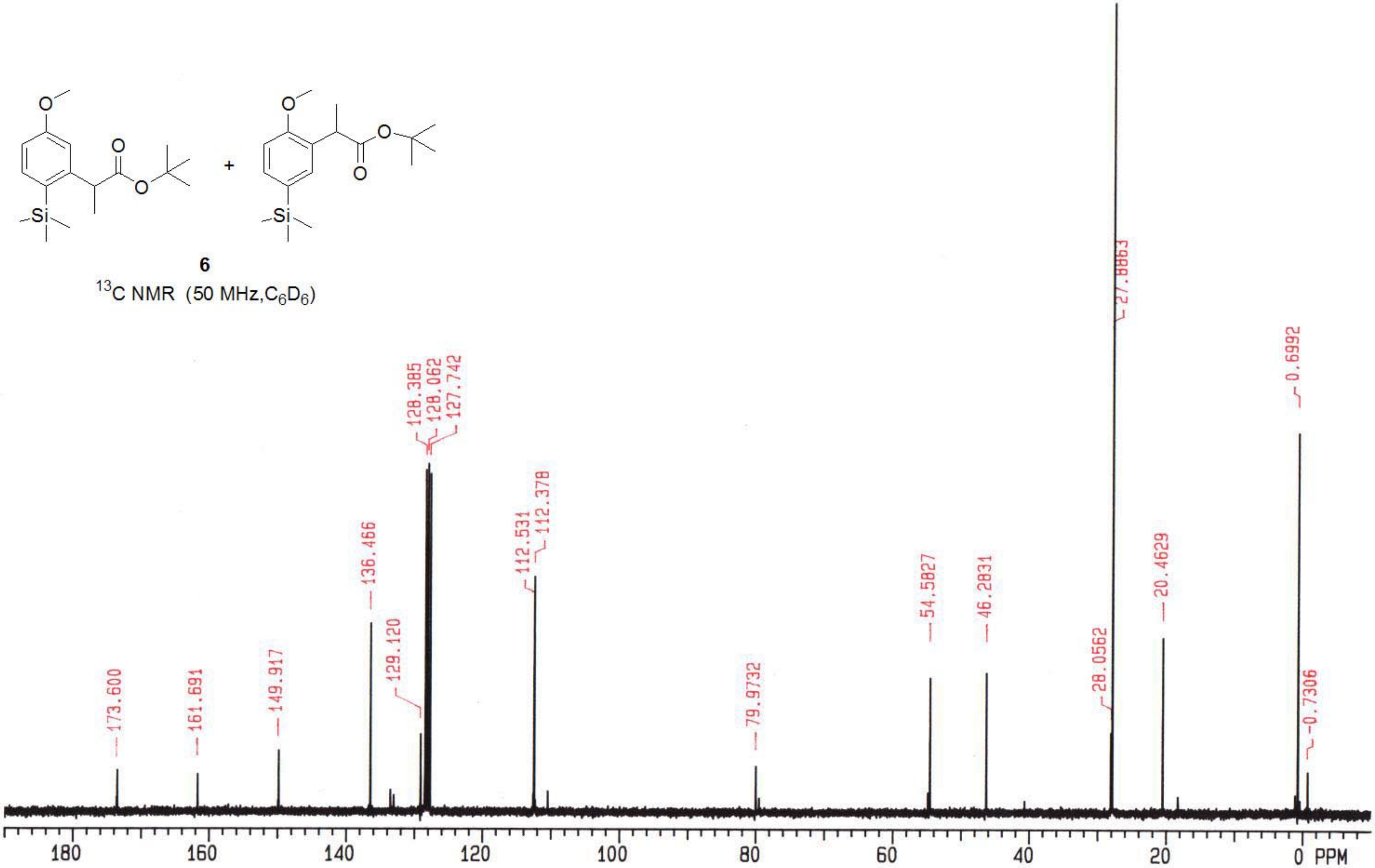
5

^{13}C NMR (75 MHz,CDCl$_3$)



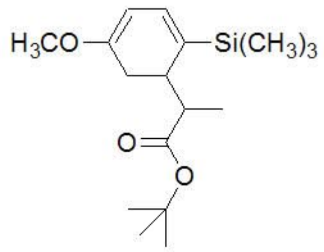
6

^{1}H NMR (300 MHz, C_6D_6)



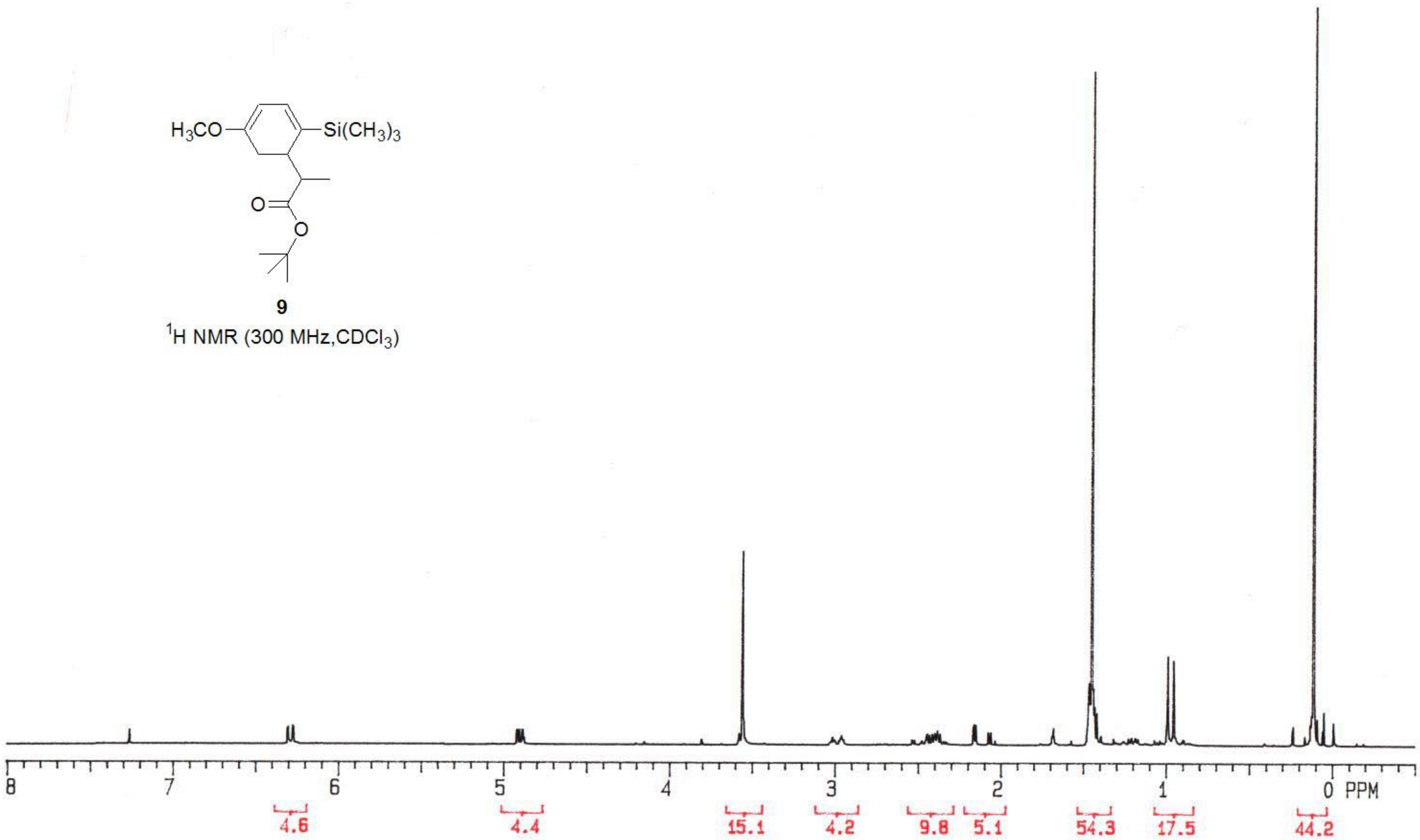
6

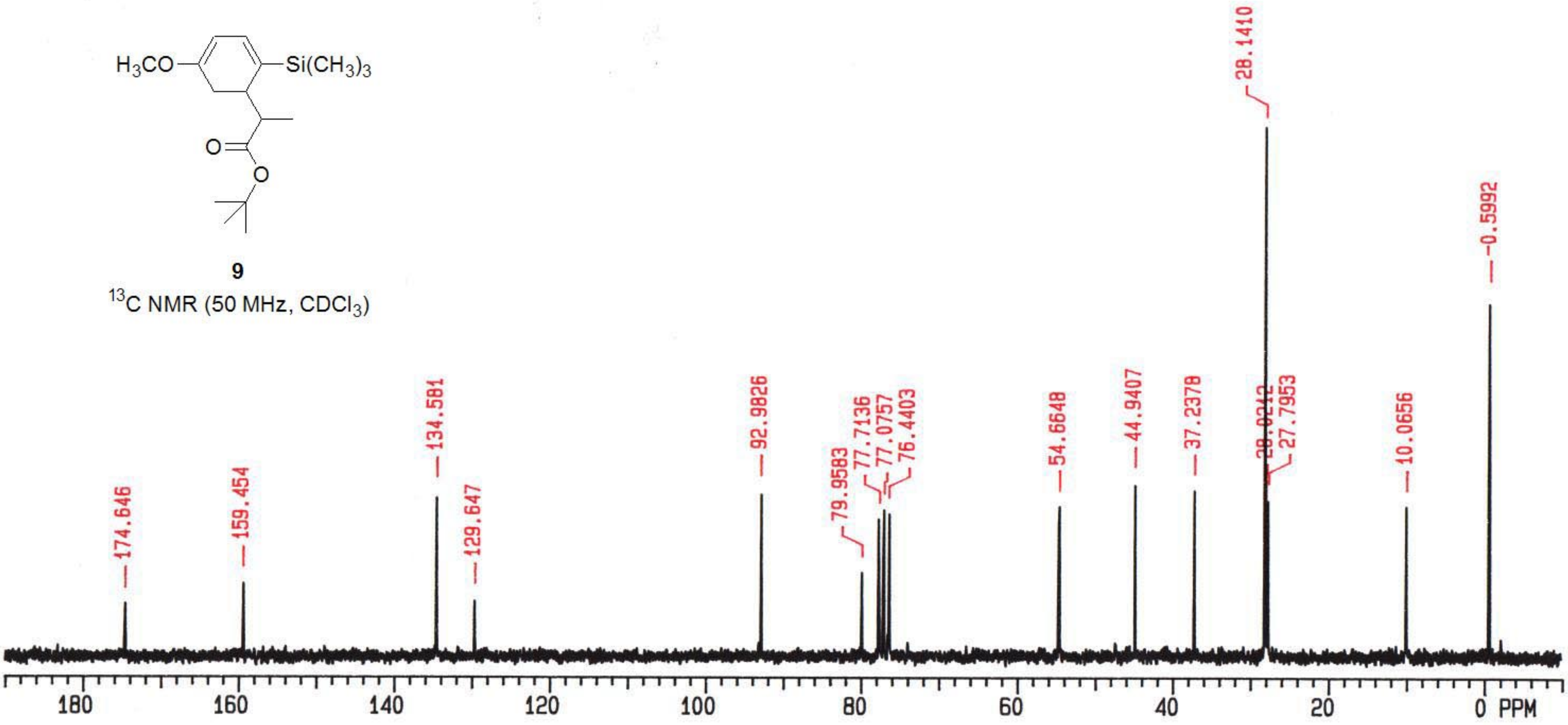
^{13}C NMR (50 MHz, C_6D_6)



9

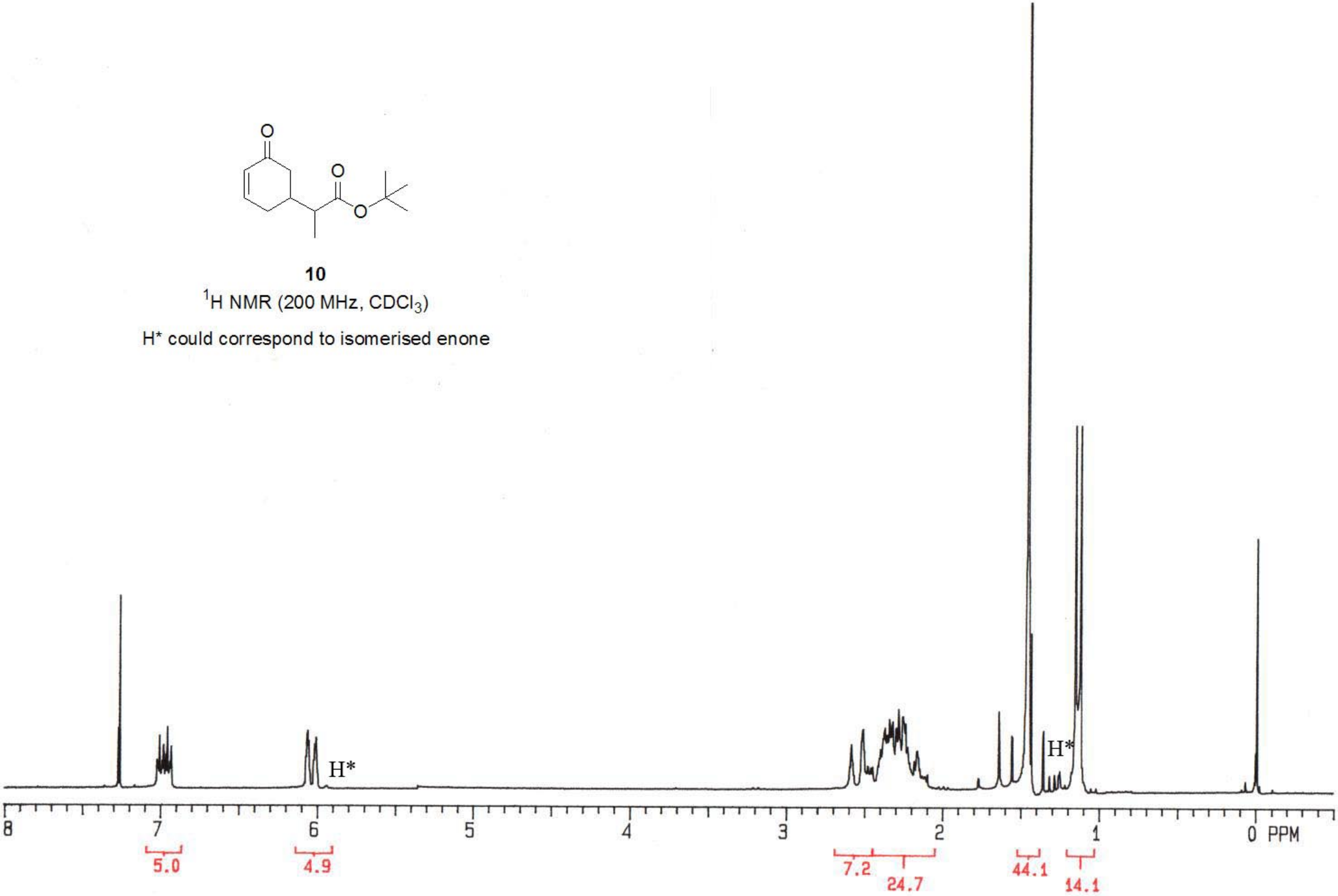
^{1}H NMR (300 MHz,CDCl$_3$)





9

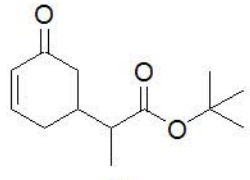
^{13}C NMR (50 MHz, $CDCl_3$)



10

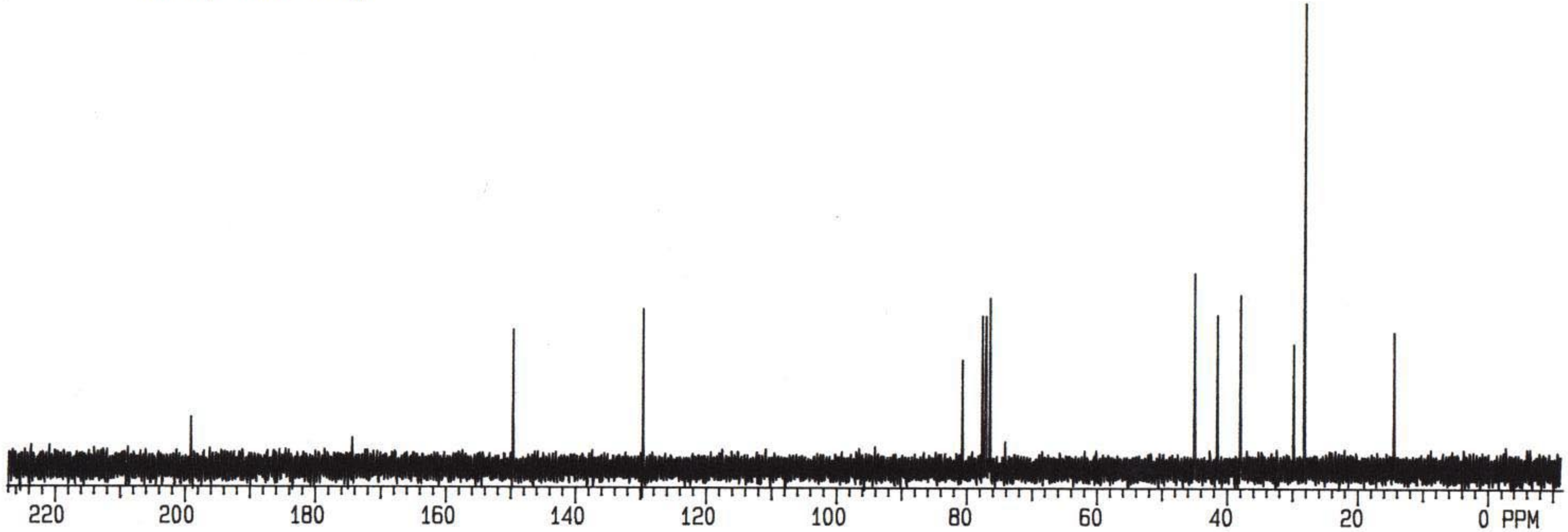
^{1}H NMR (200 MHz, CDCl$_3$)

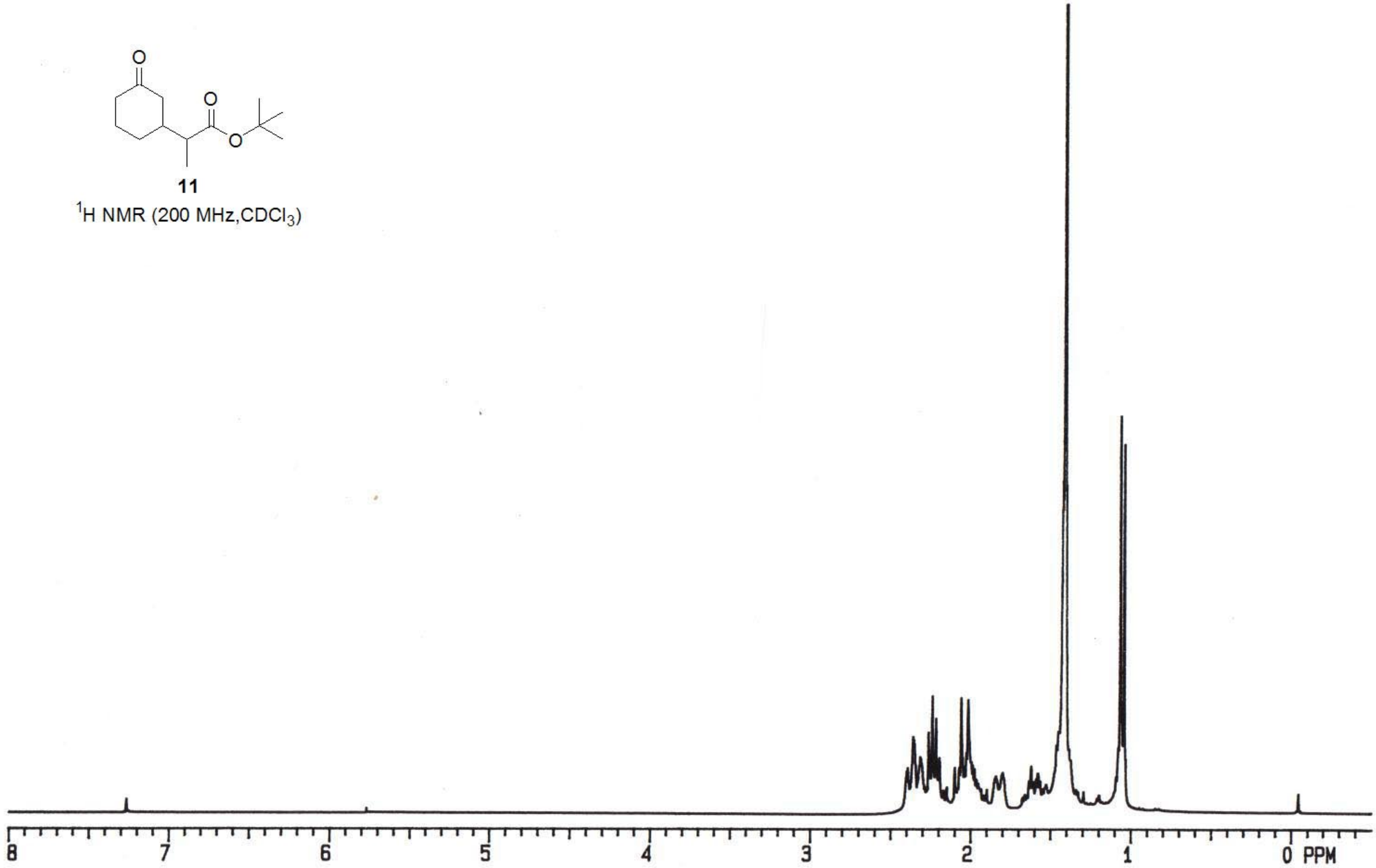
H* could correspond to isomerised enone



10

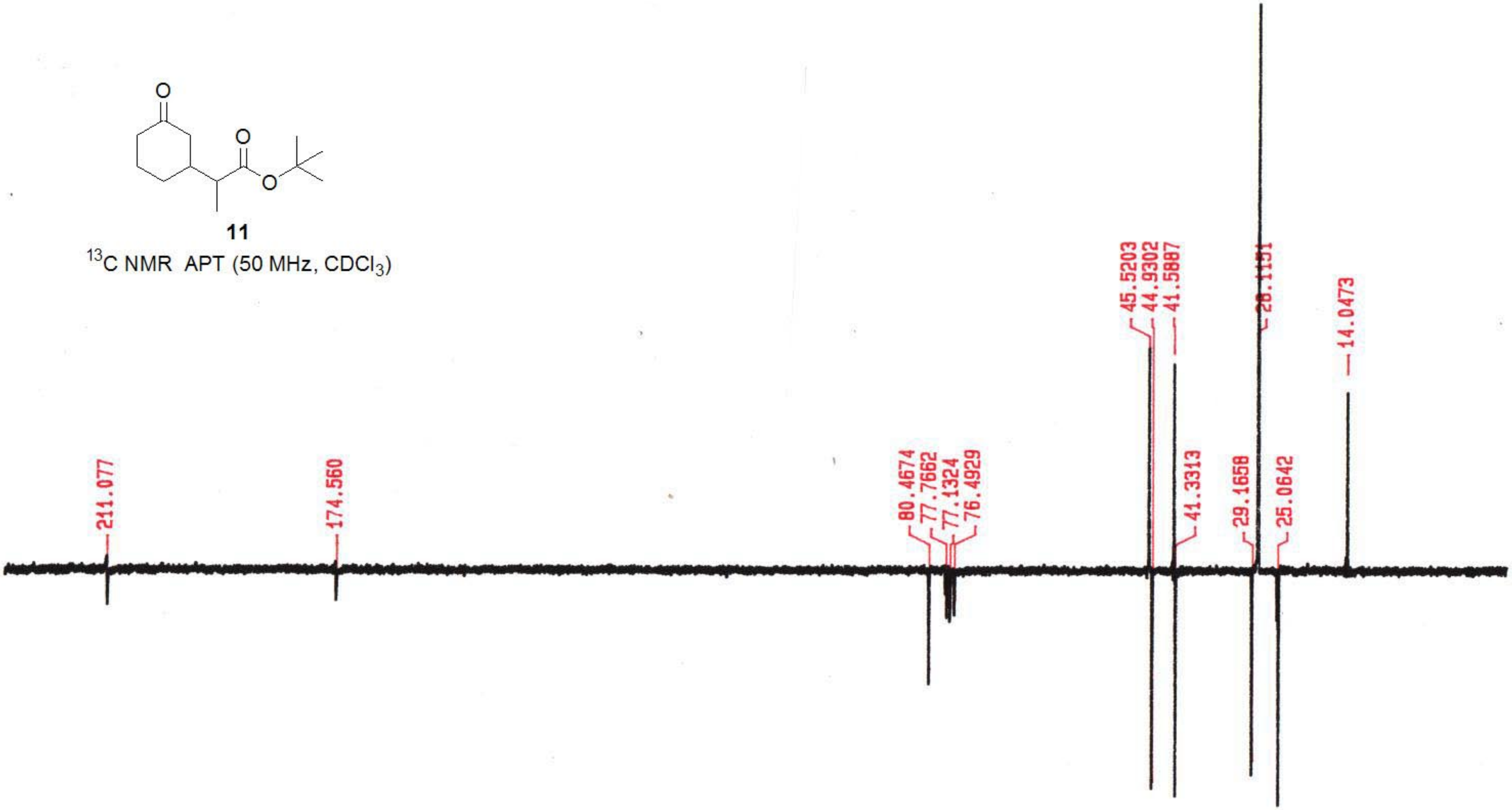
^{13}C NMR (50 MHz, CDCl$_3$)





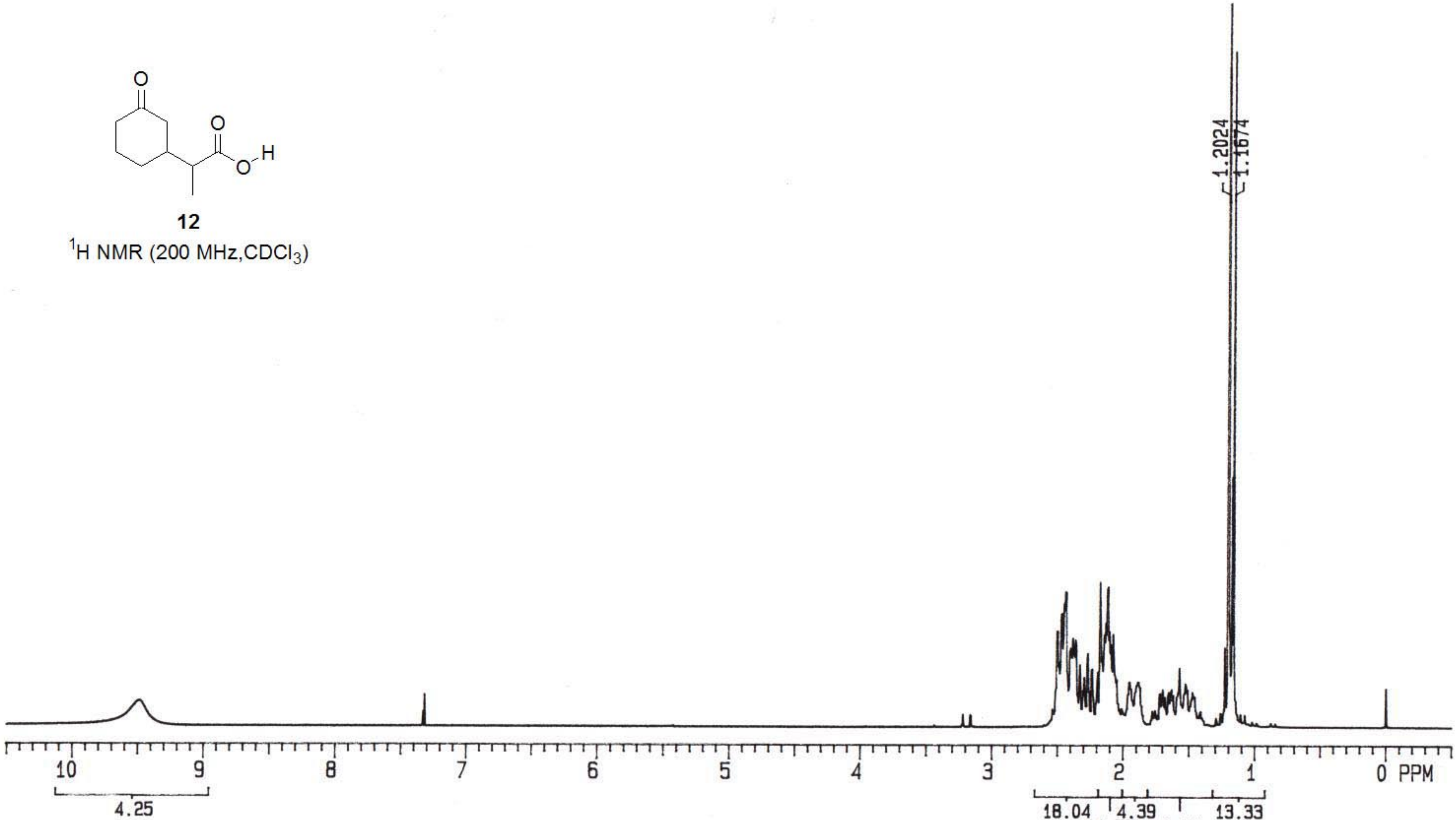
11

^{1}H NMR (200 MHz,CDCl$_3$)



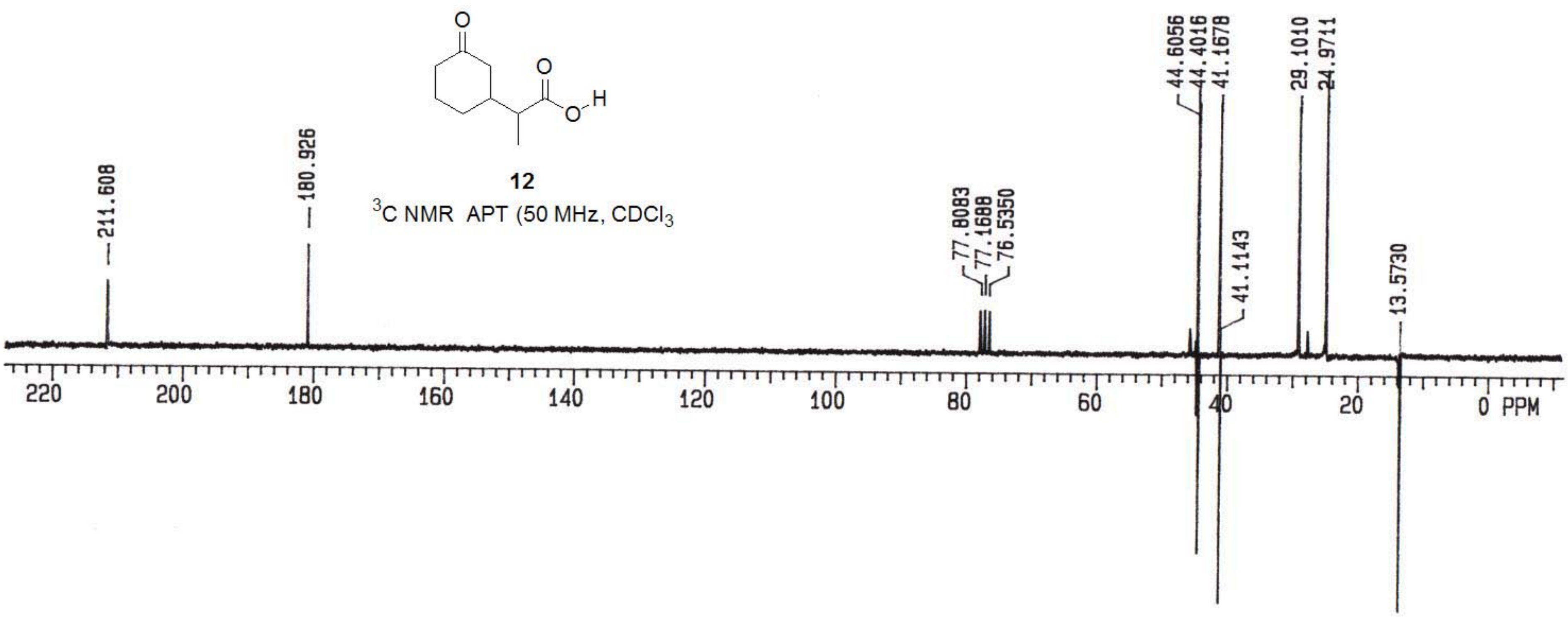
11

^{13}C NMR APT (50 MHz, $CDCl_3$)



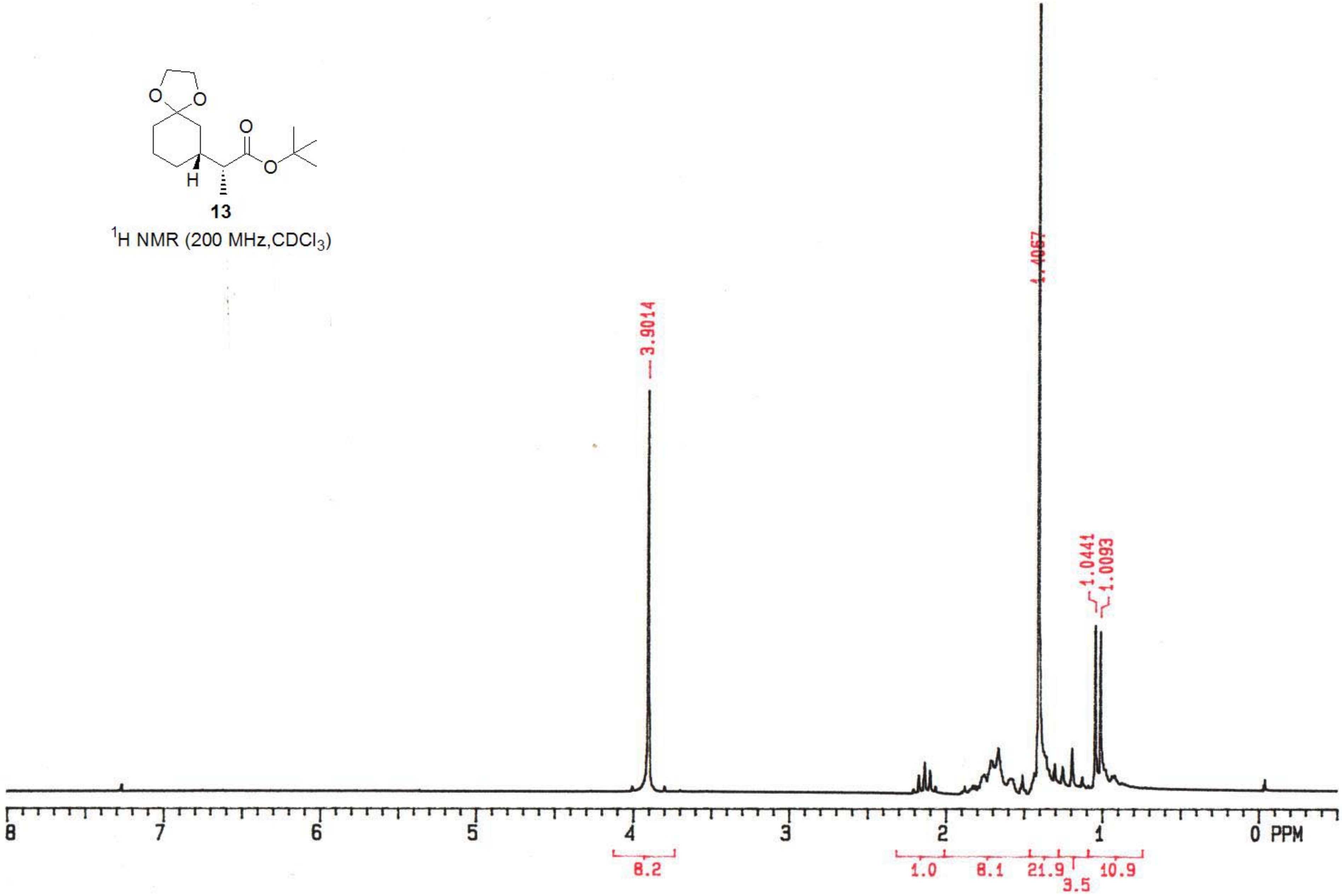
12

^{1}H NMR (200 MHz,CDCl$_3$)



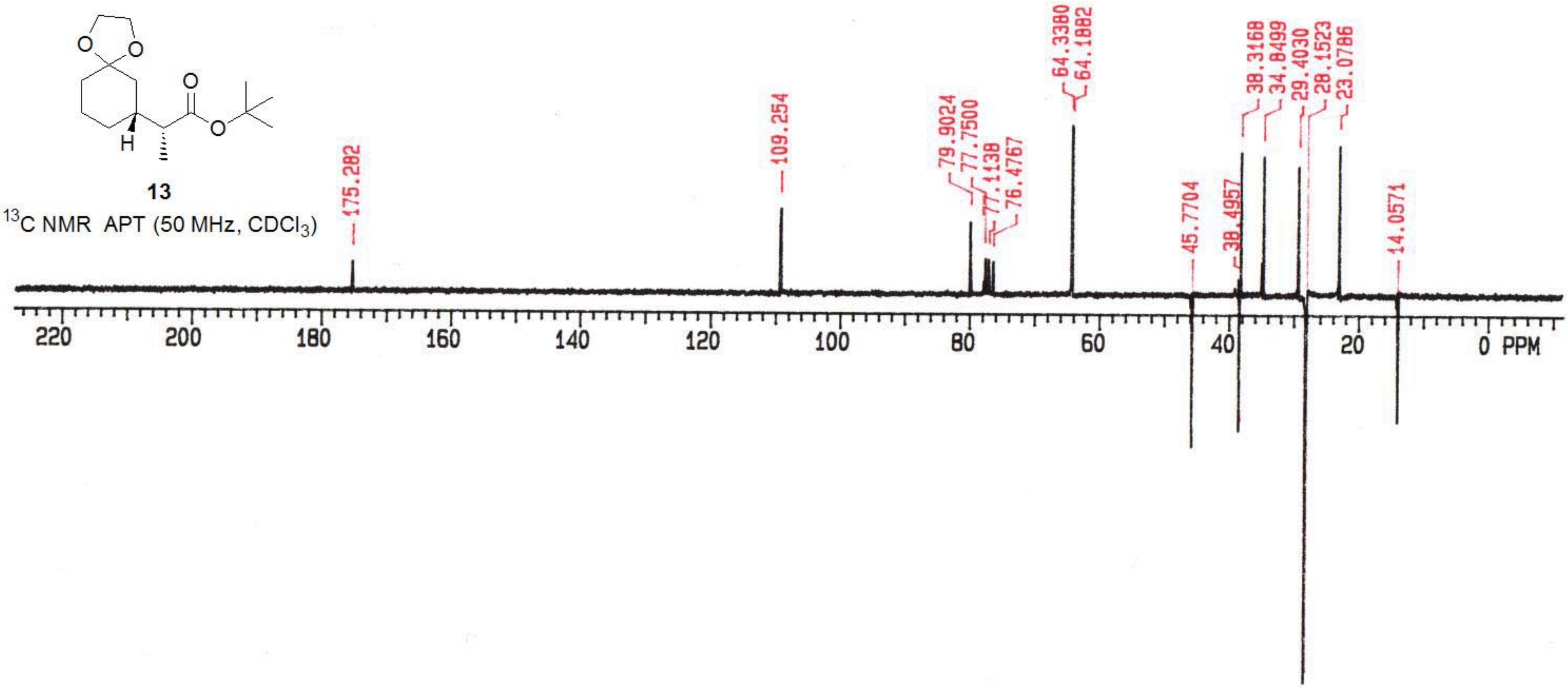
12

^{3}C NMR APT (50 MHz, $CDCl_3$



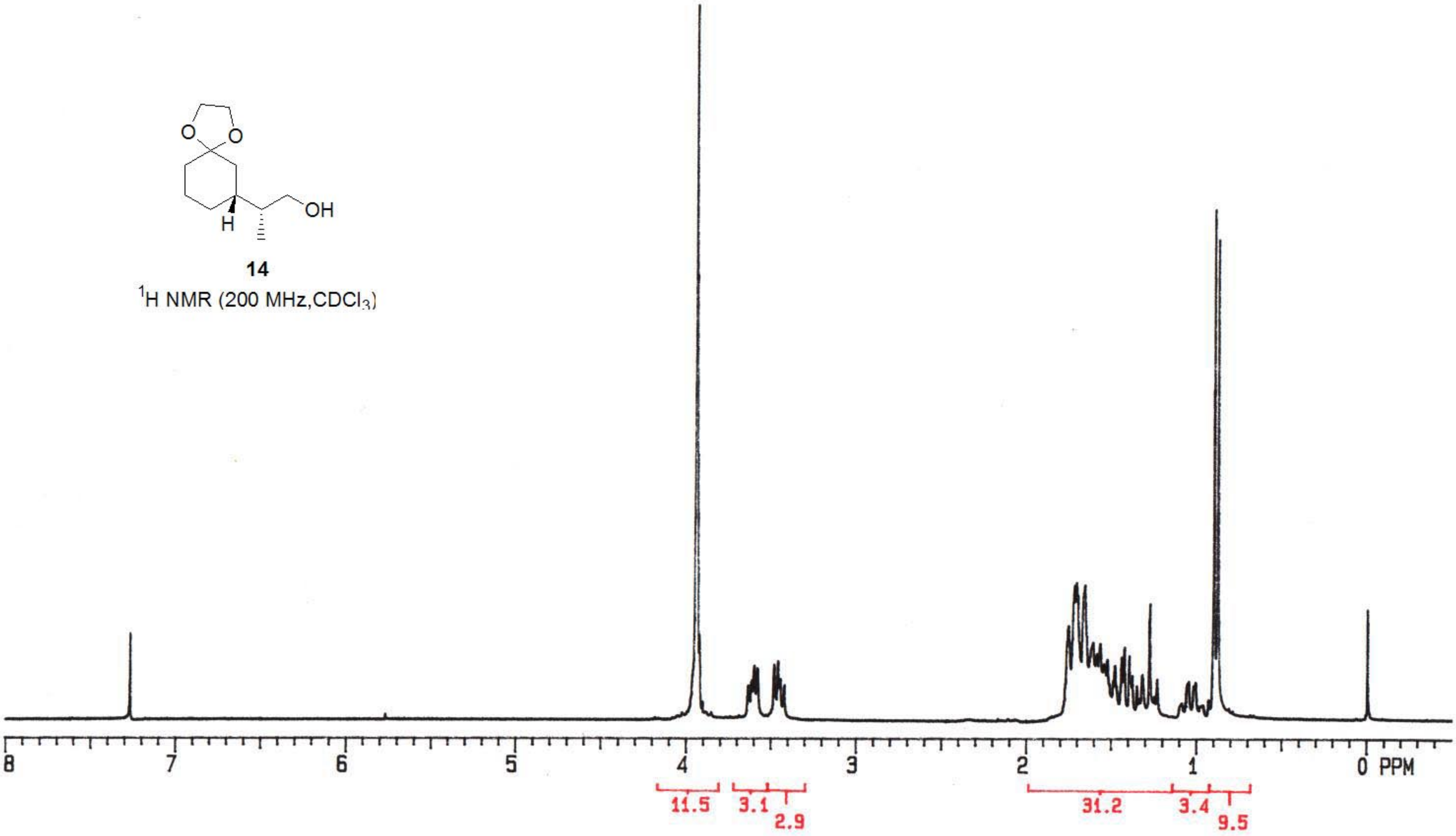
13

^{1}H NMR (200 MHz,CDCl$_3$)



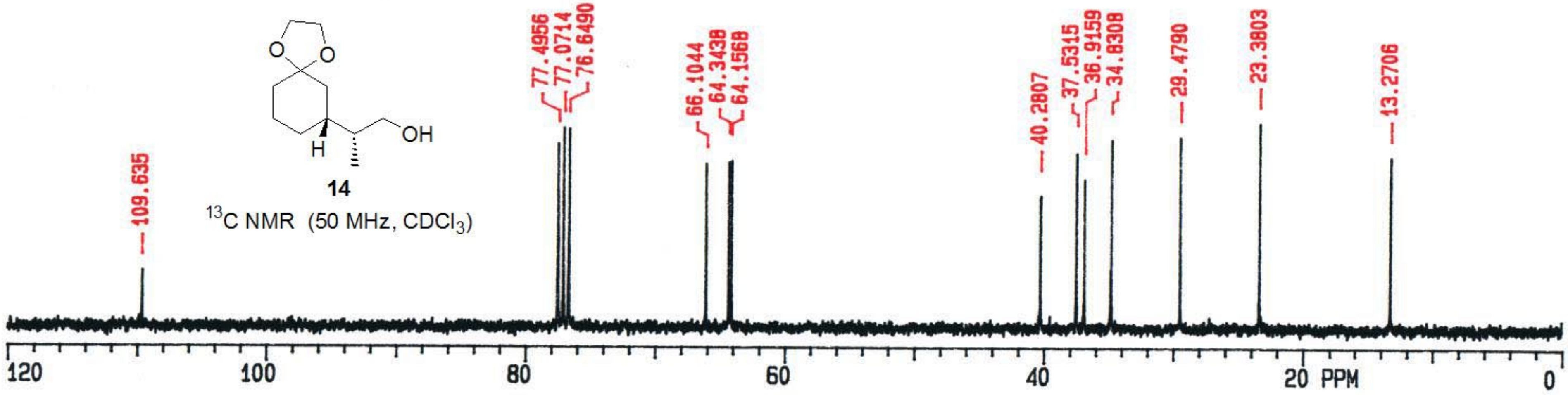
13

^{13}C NMR APT (50 MHz, CDCl$_3$)



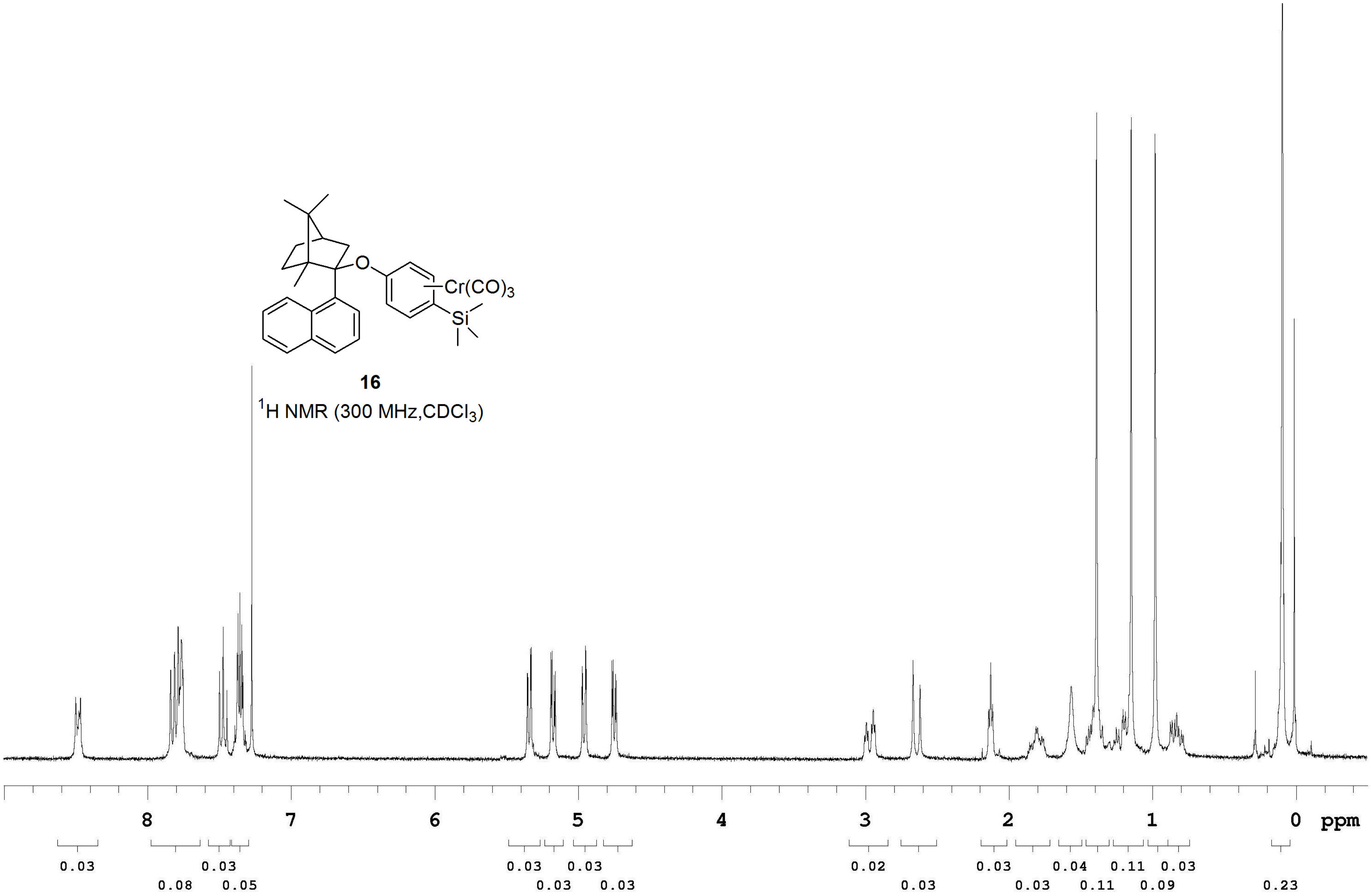
14

^{1}H NMR (200 MHz,CDCl$_3$)



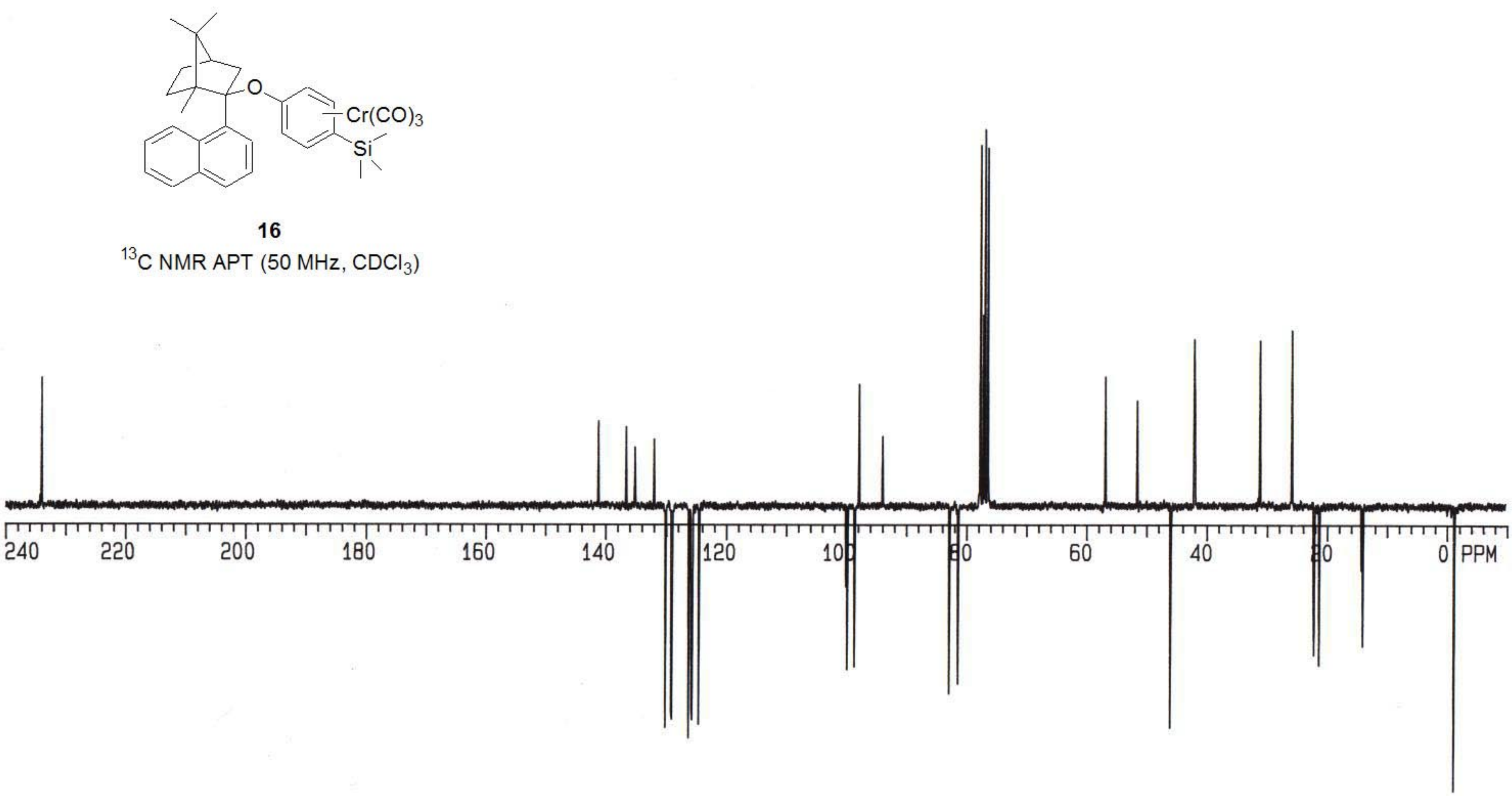
14

^{13}C NMR (50 MHz, $CDCl_3$)



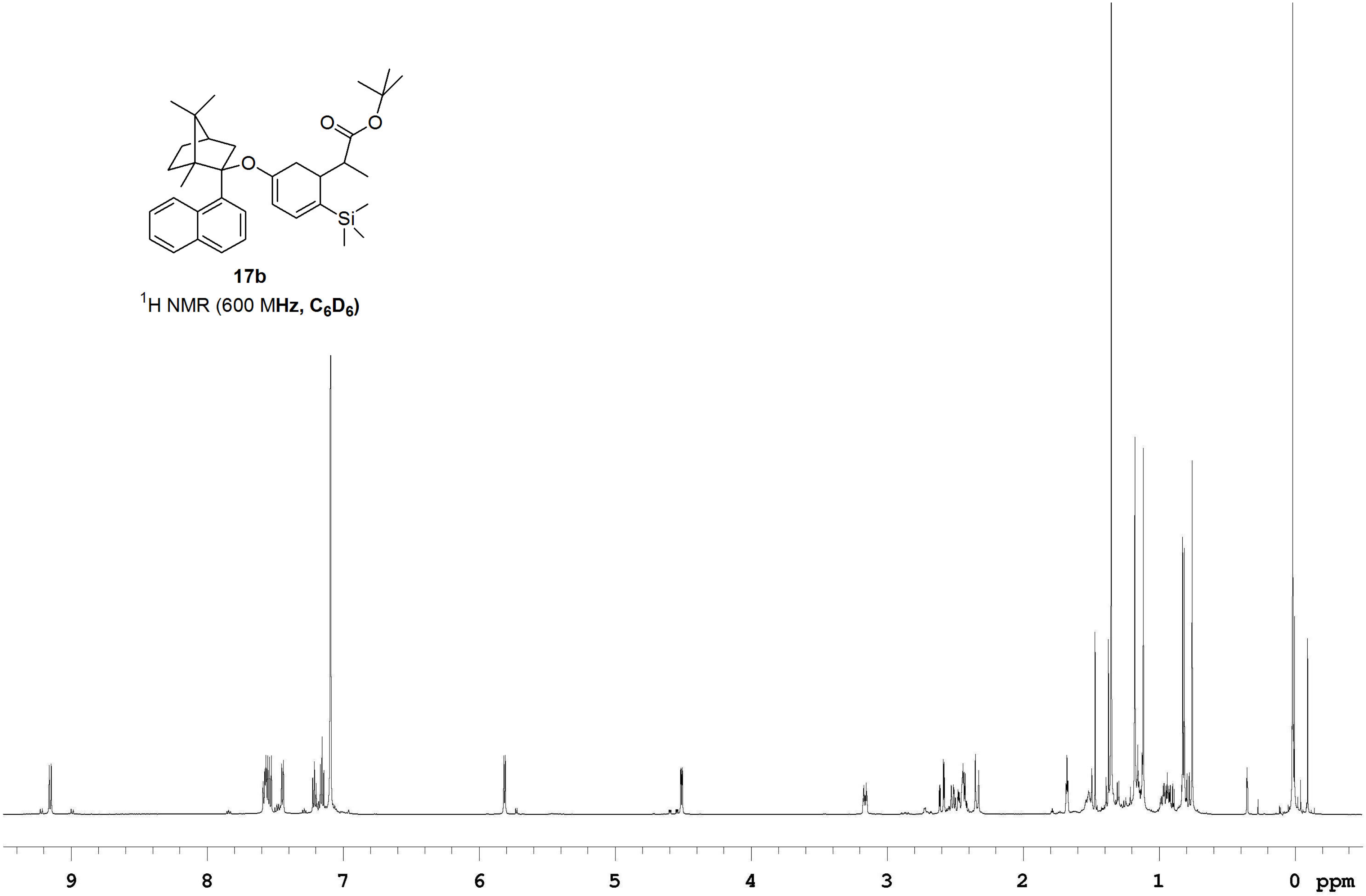
16

^{1}H NMR (300 MHz,CDCl$_3$)



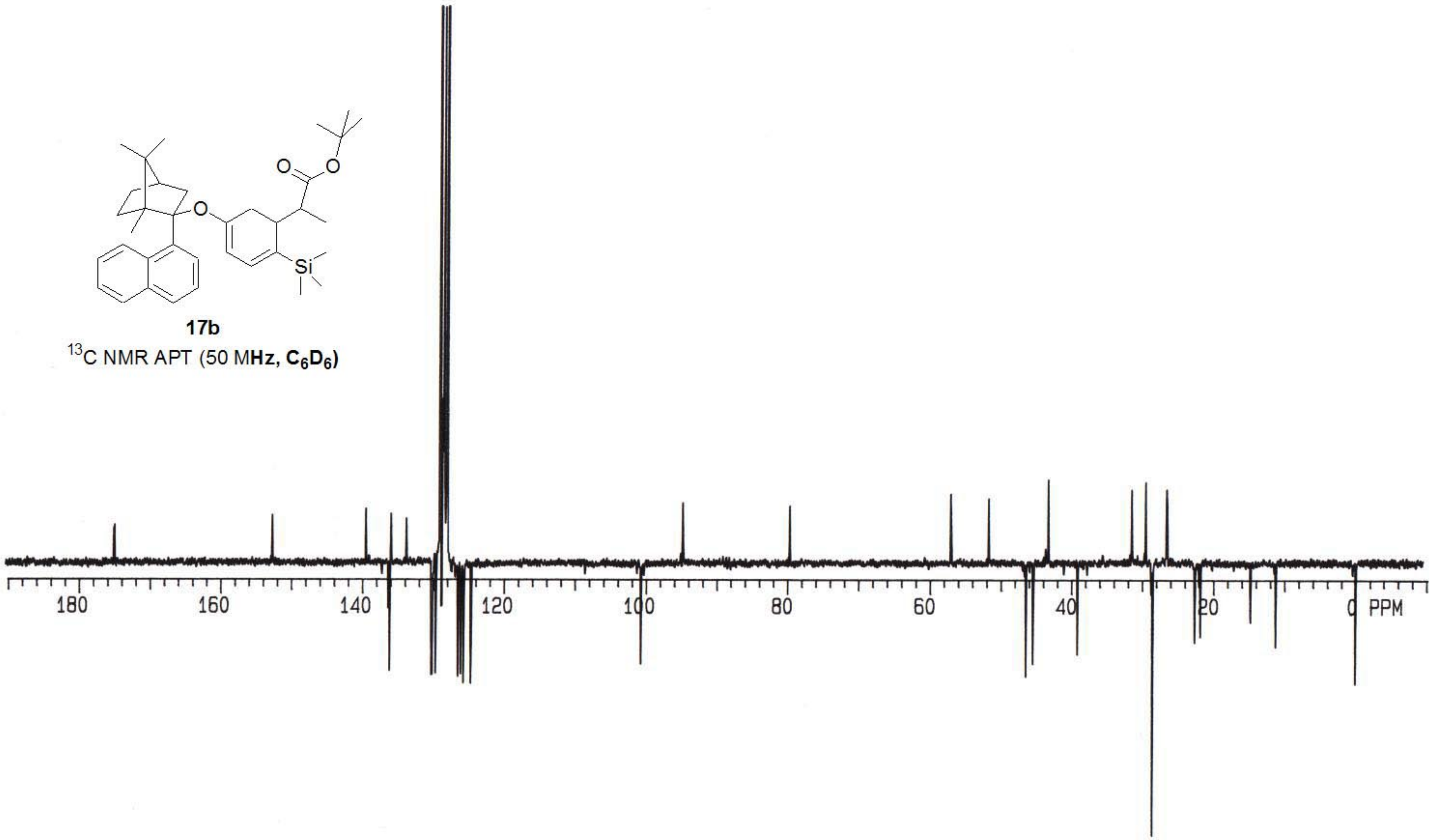
16

^{13}C NMR APT (50 MHz, $CDCl_3$)



17b

^{1}H NMR (600 M**Hz, C_6D_6)**



17b

^{13}C NMR APT (50 MHz, C_6D_6)