

Regioselective Transfer Hydrodeuteration of Alkenes with an HD Surrogate Using $\text{B}(\text{C}_6\text{F}_5)_3$ Catalysis

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Supporting Information

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1. General Information

Reagents and Solvents

Standard solvents and reagents were obtained from *ABCR*, *Acros*, *Alfa Aesar*, *Merck*, *Sigma-Aldrich* or *Tokyo Chemical Industry* (TCI). $\text{B}(\text{C}_6\text{F}_5)_3$ was purchased from *Boulder Scientific Company*, sublimed prior to use, and stored in a glovebox. Et_3SiCl and Et_3SiH were dried over CaH_2 and distilled prior to use. For reactions performed outside a glovebox: Et_2O and THF were dried over potassium/benzophenone and freshly distilled prior to use; CH_2Cl_2 was dried over CaH_2 and freshly distilled prior to use; anhydrous DMF (99.8%, extra dry, over molecular sieves, AcroSeal[®]) was purchased from *Acros Organics* and used as received. For reactions performed inside a glovebox: 1,2- $\text{C}_6\text{H}_4\text{F}_2$ (98%) was purchased from *ABCR*, dried over CaH_2 , distilled, degassed by three freeze-pump-thaw cycles, and stored in a glovebox over thermally activated 4 Å molecular sieves. CH_2Cl_2 was dried over CaH_2 , distilled, degassed by three freeze-pump-thaw cycles, and stored in a glovebox over thermally activated 4 Å molecular sieves. PhMe and C_6H_6 were dried over sodium/benzophenone, distilled, degassed by three freeze-pump-thaw cycles, and stored in a glovebox over thermally activated 4 Å molecular sieves. Brine refers to a saturated solution of NaCl in deionized H_2O .

Reactions

Reactions were performed using standard Schlenk techniques or in an *MBraun* glovebox as indicated and under a static pressure of nitrogen. Glassware for reactions performed outside the glovebox was dried under vacuum using a heat gun. Glassware for reactions performed inside a glovebox was dried overnight in a 120 °C oven and plastic syringes were dried overnight in a 60 °C oven before being transferred into the glovebox. All reactions were stirred with magnetic followers. All stated temperatures refer to external bath temperatures.

Chromatography

Flash column chromatography was performed on *Grace* 60 (40–63 µm, 230–400 mesh, ASTM) silica gel according to the method reported by W. C. Still and co-workers.¹ Technical grade solvents were distilled prior to use. TLC analyses were performed on *Alugram*[®] Xtra SIL G/UV₂₅₄ silica gel 60 pre-coated aluminium-backed plates with layer thickness of 200 µm. Product spots were visualised under UV light ($\lambda_{\text{max}} = 254 \text{ nm}$) and/or by staining with a potassium permanganate solution.

Nuclear Magnetic Resonance (NMR) Spectroscopy

All spectra were recorded in CDCl_3 , C_6D_6 or 9:1 $\text{CHCl}_3:\text{CDCl}_3$ on *Bruker* AV500 or AV700 instruments with the deuterated solvent acting as internal deuterium lock. ^1H NMR spectra were recorded at 500 or 700 MHz, ^2H NMR at 77 MHz, ^{13}C NMR spectra at 126 or 175 MHz with broadband proton decoupling and ^{19}F NMR spectra at 377 MHz without proton decoupling as stated. The residual protic solvent signal acted as an internal reference for ^1H NMR and the deuterated solvent carbon signal acted as an internal reference for ^2H NMR and ^{13}C NMR (CHCl_3 : ^1H NMR = 7.26 ppm, CDCl_3 : ^{13}C NMR = 77.16 ppm; $\text{C}_6\text{D}_5\text{H}$: ^1H NMR = 7.16 ppm, C_6D_6 : ^{13}C NMR = 128.06 ppm; 9:1 $\text{CHCl}_3:\text{CDCl}_3$: ^2H NMR = 7.26 Hz). ^{19}F NMR spectra were not externally referenced. Chemical shifts are reported to 0.01 ppm for ^1H NMR and ^2H NMR spectra and to 0.1 ppm for ^{13}C NMR and ^{19}F spectra. Peaks that are within 0.01 ppm for ^1H NMR or 0.1 ppm for ^{13}C NMR but are still distinguishable are reported to 0.001 ppm and 0.01 ppm, respectively. Coupling constants are quoted to the nearest 0.1 Hz for ^1H NMR and ^{13}C NMR. The multiplicity of a signal is reported as follows: s–singlet, d–doublet, t–triplet, q–quartet, quint.–quintet, sept.–septet, m–multiplet, br.–

broad, app.–apparent, or combinations thereof. Structural assignments were made with the aid of COSY, HMQC, and HMBC experiments.

Infrared Spectroscopy

Fourier-transform infrared (FTIR) spectra were recorded from neat samples on a *Jasco* FT/IR-4100 spectrometer equipped with an ATR unit. Selected absorption maxima are given in wavenumbers (cm^{-1}).

Mass Spectrometry

High resolution mass spectra (HRMS) were obtained from the *Analytical Facility* at the *Institut für Chemie, Technische Universität Berlin*.

Melting Points

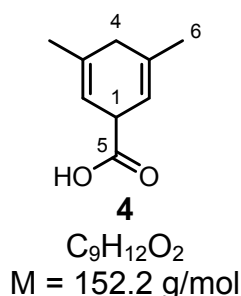
Melting points (M.P.) were obtained from recrystallized samples using a *Stuart Scientific* SMP20 instrument and are uncorrected. The solvent used for recrystallisation is quoted in parentheses.

Compound Naming and Numbering

Compound names were generated by the computer program *Chemdraw* according to the guidelines specified by the International Union of Pure and Applied Chemistry (IUPAC). Atom numbering within compounds was usually assigned on the basis of that in the given name although sometimes it was altered to ensure consistency across similar classes of compounds.

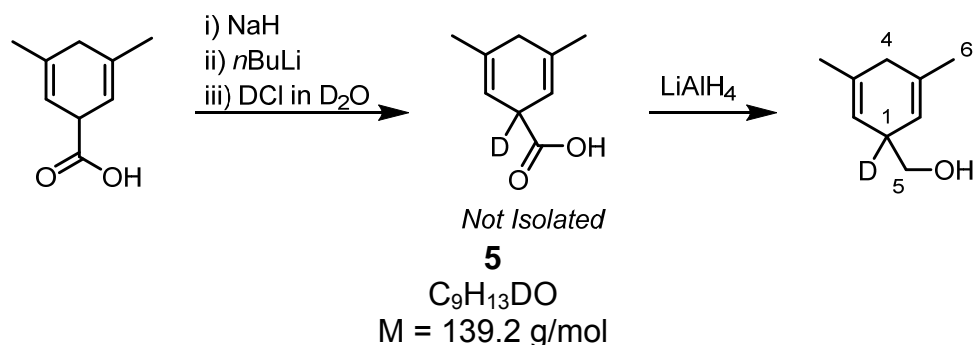
2. Synthesis of Surrogates

3,5-Dimethylcyclohexa-2,5-diene-1-carboxylic acid (4)



A 3-neck round bottom flask fitted with a dry-ice condenser was flushed with dry N_2 for 10 min before being placed in a dry-ice/acetone bath (-78°C). NH_3 (ca. 40 mL) was condensed through a KOH filled drechsel bottle. A small piece of Li wire was added to ensure the NH_3 was dry (blue colour) before a solution of 3,4-dimethylbenzoic acid (2.00 g, 13.3 mmol) in THF (8 mL + 2 mL rinse) was added. Li wire (minimum 184 mg, 26.6 mmol, 2 equiv) was added portionwise until a deep blue colour was achieved. [Nb. Li wire was not accurately weighed out, rather it was titrated in]. The dry-ice was removed from the cold bath and the reaction allowed to stir in the remaining acetone for 45 min (external bath temperature rose to -50°C in this time). If the blue colour had faded by this time, further Li wire was added and the blue colour maintained for at least 15 min. The reaction was quenched at -50°C by dropwise addition of MeOH (2.15 mL, 53.2 mmol, 4 equiv) [Caution: quenching is exothermic and drop rate should not exceed 1 drop/second for the *entire* duration of MeOH addition. The blue colour of the reaction fades by the end of MeOH addition]. The reaction was then removed from the cold bath and placed in a room temperature water bath to facilitate the evaporation of NH_3 [Caution: Stench]. The reaction was diluted first by dropwise addition of HCl (37%, aq.) until $\text{pH} < 0$ was achieved and then with Et_2O . The layers were separated, the aqueous phase was extracted with Et_2O ($\times 2$) and the combined organic layers were dried over anhydrous MgSO_4 , filtered and concentrated *in vacuo* to afford the title compound as a pale yellow solid (2.02 g, 13.3 mmol, quant.) which was used without further purification.

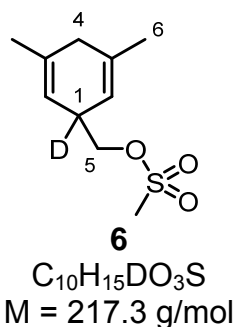
$R_f = 0.43$ (pentane:EtOAc 4:1). **M.P.** = $112\text{--}114^\circ\text{C}$ (Et_2O). **^1H NMR** (500 MHz, C_6D_6): δ = 1.48 (s, 6H, 6 \times H-6), 2.04 (dd, J = 21.8, 8.2 Hz, 1H, H-4), 2.12 (dd, J = 21.9, 7.4 Hz, 1H, H-4), 3.63–3.71 (m, 1H, H-1) and 5.55 ppm (s, 2H, 2 \times H-2). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (125 MHz, C_6D_6): δ = 22.9 (2C, 2 \times C-6), 35.7 (C-4), 44.4 (C-1), 116.5 (2C, 2 \times C-2), 133.9 (2C, 2 \times C-3) and 180.0 ppm (C-5). **IR** (ATR): ν = 2846, 1689, 1283, 1220, 904 and 700 cm^{-1} . **HRMS** (APCI) for $\text{C}_9\text{H}_{11}\text{O}^-$ [$\text{M}-\text{H}$] $^-$: calculated 151.0765, found 151.0764 (Δ = 0.7 ppm).

(3,5-Dimethylcyclohexa-2,5-dien-1-yl-1-*d*)methanol (5)

A solution of acid **4** (1.94 g, 12.8 mmol) in THF (10 mL + 5 mL rinse) was added dropwise to a suspension of NaH (60 wt %, 562 mg, 14.0 mmol, 1.1 equiv) in THF (145 mL, total 0.08 M) at 0 °C and the reaction then stirred for 1.5 h. The reaction was then cooled to –78 °C and *n*BuLi (2.5 M in hexanes, 10.2 mL, 25.5 mmol, 2 equiv) was added dropwise *via* syringe pump over 1 h. The resulting orange solution was stirred for 100 min at –78 °C before being warmed to 0 °C. The reaction was quenched by dropwise addition of DCl (35 wt % in D₂O, 4.2 mL, 51.0 mmol, 4 equiv) and the resulting mixture stirred at room temperature for 1 h. The organic solvent was removed directly under reduced pressure and the aqueous phase was then extracted with Et₂O (×2). The combined organic layers were dried over anhydrous MgSO₄ and concentrated *in vacuo* to afford the intermediate acid which was used directly without further purification.

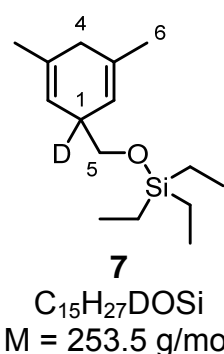
A solution of the intermediate acid in THF (8 mL + 2 mL rinse) was added dropwise *via* a dropping funnel to a suspension of LiAlH₄ (730 mg, 19.2 mmol, 1.5 equiv) in THF (22 mL, total 0.4 M) at 0 °C. The reaction was removed from the cold bath and stirred overnight at room temperature before being diluted with Et₂O (ca. 20 mL) and cooled to 0 °C. The reaction was quenched by sequential dropwise addition of H₂O (730 μL, 1 mL/g LiAlH₄), NaOH (15 wt %, 730 μL, 1 mL/g LiAlH₄) and H₂O (2.19 mL, 3 mL/g LiAlH₄) before being stirred vigorously for 10 min. MgSO₄ was added and the reaction stirred vigorously for a further 15 min before being filtered. The filter cake was washed several times with Et₂O and the filtrate then concentrated *in vacuo* before being purified by flash column chromatography (SiO₂, 4:1 pentane:Et₂O) to afford the title compound as a colourless oil (1.50 g, 10.8 mmol, 84% over 2 steps).

$R_f = 0.2$ (4:1 pentane:Et₂O). ¹H NMR (500 MHz, CDCl₃): δ = 1.73 (s, 6H, 6 × H-6), 2.48 (s, 2H, 2 × H-4), 3.54 (s, 2H, 2 × H-5) and 5.36 ppm (s, 2H, 2 × H-2). ²H NMR (77 MHz, 9:1 CHCl₃:CDCl₃): δ = 2.90 ppm (bs, D-1). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 23.2 (2C, 2 × C-6), 36.3 (C-4), 40.4 (t, *J* = 19.4 Hz, C-1), 66.6 (C-5), 120.0 (2C, 2 × C-2) and 134.4 ppm (2C, 2 × C-3). IR (ATR): ν = 3327, 2991, 2862, 1435, 1088, 1042, 1010 and 928 cm^{–1}. HRMS (ESI) for C₉H₁₄DO⁺ [M+H]⁺: calculated 140.1180, found 140.1178 (Δ = 1.4 ppm).

(3,5-Dimethylcyclohexa-2,5-dien-1-yl-1-*d*)methyl methanesulfonate (6)

A solution of alcohol **5** (50.0 mg, 0.362 mmol) and Et_3N (110 μL , 0.793 mmol, 2.2 equiv) in CH_2Cl_2 (1.8 mL, 0.2 M) was cooled to -78°C and methylsulfonyl chloride (56 μL , 0.73 mmol, 2 equiv) was then added dropwise. The reaction was stirred at -78°C for 1 h before being quenched by dropwise addition of MeOH. The reaction was directly concentrated *in vacuo* and purified by flash column chromatography (SiO_2 , 3:2 pentane: Et_2O) to afford the title compound as a colourless oil (73.2 mg, 0.337 mmol, 93%).

$R_f = 0.38$ (pentane: Et_2O 3:2). $^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 1.72$ (s, 6H, 6 \times H-6), 2.48 (s, 2H, 2 \times H-4), 2.99 (s, 3H, SO_2CH_3), 4.04 (s, 2H, 2 \times H-5) and 5.36 ppm (s, 2H, 2 \times H-2). $^2\text{H NMR}$ (77 MHz, 9:1 CHCl_3 : CDCl_3): $\delta = 3.11$ ppm (bs, D-1). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): $\delta = 23.0$ (2C, 2 \times C-6), 36.1 (C-4), 37.3 (SO_2CH_3), 73.5 (C-5), 117.8 (2C, 2 \times C-2) and 134.7 ppm (2C, 2 \times C-3). A signal for C-1 could not be identified. IR (ATR): $\nu = 1348$, 1169, 947 and 797 cm^{-1} . HRMS (ESI) for $\text{C}_{10}\text{H}_{15}\text{DNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: calculated 240.0775, found 240.0774 ($\Delta = 0.4 \text{ ppm}$)

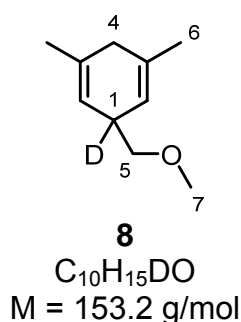
((3,5-dimethylcyclohexa-2,5-dien-1-yl-1-*d*)methoxy)triethylsilane (7)

A solution of alcohol **5** (139 mg, 1.00 mmol), imidazole (204 mg, 3.00 mmol, 3 equiv) and *N,N*-dimethylaminopyridine (12.2 mg, 0.100 mmol, 10 mol %) in CH_2Cl_2 (5 mL, 0.2 M) was cooled to 0°C and chlorotriethylsilane (251 μL , 1.50 mmol, 1.5 equiv) was then added dropwise. The reaction was removed from the cold bath and stirred at room temperature for 2.5 h before being quenched by addition of NaHCO_3 (sat., aq.). The layers were separated and the aqueous phase was extracted with CH_2Cl_2 ($\times 2$). The combined organic layers were washed with brine, dried over anhydrous MgSO_4 , filtered and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2 , 99:1—97:3 pentane: Et_2O) to afford the title compound as a colourless oil (228 mg, 0.899 mmol, 90%).

Contains approximately 6% of the corresponding aromatised compound as determined by ^1H NMR.

R_f = 0.33 (pentane). ^1H NMR (500 MHz, CDCl_3): δ = 0.60 (q, J = 8.0 Hz, 6H, 3 \times SiCH_2CH_3), 0.96 (t, J = 8.0 Hz, 9 H, 3 \times SiCH_2CH_3), 1.70 (s, 6H, 6 \times H-6), 2.46 (s, 2H, 2 \times H-4), 3.45 (s, 2H, 2 \times H-5) and 5.43 ppm (2H, 2 \times H-2). ^2H NMR (77 MHz, 9:1 CHCl_3 : CDCl_3): δ = 2.85 ppm (bs, D-1). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ = 4.60 (3C, 3 \times SiCH_2CH_3), 6.90 (3C, 3 \times SiCH_2CH_3), 23.2 (2C, 2 \times C-6), 36.5 (C-4), 40.6 (t, J = 19.5 Hz, C-1), 68.0 (C-5), 120.6 (2C, 2 \times C-2) and 132.5 ppm (2C, 2 \times C-3). IR (ATR): ν = 2954, 2875, 1102, 1004, 789 and 724 cm^{-1} . HRMS (EI) for $\text{C}_{15}\text{H}_{27}\text{DOSi}^+$ $[\text{M}]^+$: calculated 253.1967, found 253.1961 (Δ = 2.4 ppm).

3-(Methoxymethyl)-1,5-dimethylcyclohexa-1,4-diene-3-*d* (8)



To a suspension of NaH (60 wt %, 360 mg, 9.00 mmol, 1.5 equiv) in DMF (24 mL) at 0 $^{\circ}\text{C}$ was added a solution of alcohol **5** (834 mg, 6.00 mmol) in DMF (4 mL + 2 mL rinse, total 0.2 M) dropwise. The reaction was stirred for 1 h at 0 $^{\circ}\text{C}$ before iodomethane (560 μL , 9.00 mmol, 1.5 equiv) was added. The reaction was then stirred at 40 $^{\circ}\text{C}$ for 16 h before being cooled to room temperature and quenched by dropwise addition of H_2O (10 mL). The reaction mixture was diluted with Et_2O and the layers were separated. The aqueous phase was extracted with Et_2O ($\times 2$) and the combined organic layers were washed with brine ($\times 2$), dried over anhydrous MgSO_4 , filtered, and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2 , 29:1 pentane: Et_2O) to afford the title compound as a colourless oil (868 mg, 5.67 mmol, 94%).

The isolated material sometimes contained up to 6% of the corresponding aromatised compound due to their similar retention times on flash column chromatography. The aromatised compound had no impact on subsequent reactivity and the surrogate was therefore used without further purification. The desired compound was found to begin eluting slightly before the aromatised compound so a small quantity was isolated in higher purity (ca. 99% by ^1H NMR) to aid unambiguous characterisation.

R_f = 0.4 (19:1 pentane: Et_2O). ^1H NMR (500 MHz, CDCl_3): δ = 1.71 (s, 6H, 6 \times H-6), 2.46 (s, 2H, 2 \times H-4), 3.25 (s, 2H, 2 \times H-5), 3.35 (s, 3H, 3 \times H-7) and 5.40 ppm (s, 2H, 2 \times H-2). ^2H NMR (77 MHz, 9:1 CHCl_3 : CDCl_3): δ = 2.95 ppm (bs, D-1). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ = 22.3 (2C, 2 \times C-6), 36.3 (C-4), 38.1 (t, J = 19.4 Hz, C-1), 59.1 (C-7), 77.8 (C-5), 120.5 (2C, 2 \times C-2) and 132.7 ppm (2C, 2 \times C-3). IR (ATR): ν = 2862, 1446, 1114 and 929 cm^{-1} . HRMS (APCI) for $\text{C}_9\text{H}_{12}\text{D}^+$ $[\text{M}+\text{H}-\text{MeOH}]^+$: calculated 122.1075, found 122.1071 (Δ = 3.3 ppm).

3. Synthesis of Starting Materials

General Procedures:

GP1: Grignard Addition and Elimination from Commercial Grignard Reagents

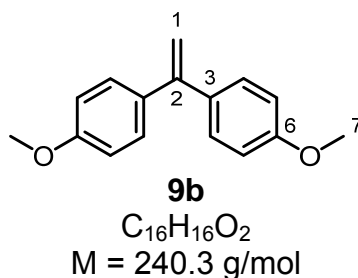
To a solution of the given ketone or acid chloride in THF (0.2 M) at 0 °C was added the given Grignard reagent dropwise. The reaction was then stirred at room temperature for the given period of time before being quenched with the given quantity of H₂SO₄ and stirred overnight at room temperature. The reaction was then diluted with H₂O and Et₂O and the layers were separated. The aqueous phase was extracted with Et₂O (×2) and the combined organic layers were washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo* before being purified by flash column chromatography to afford the title compound.

GP2: Grignard Addition and Elimination from Freshly Prepared PhMgBr

A 2-neck round bottomed flask fitted with a short Vigreux column was charged with the given quantity of Mg and a single small crystal of I₂. THF (1 M wrt. PhBr) was added followed by approximately a quarter of the given quantity of PhBr. The reaction was then initiated by gentle heating with a heat gun. Once an exotherm could be detected the remaining PhBr was added dropwise. The reaction was then stirred at 80 °C for 2 h before being cooled to room temperature. The reaction was diluted with THF (end concentration 0.5 M wrt. PhBr) and cooled to 0 °C before the given ketone was added dropwise. The reaction was then stirred at room temperature for the given period of time before being quenched with the given quantity of H₂SO₄ and stirred overnight at room temperature. The reaction was then diluted with H₂O and Et₂O and the layers were separated. The aqueous phase was extracted with Et₂O (×2) and the combined organic layers were washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo* before being purified by flash column chromatography to afford the title compound.

GP3: Wittig Methylenation

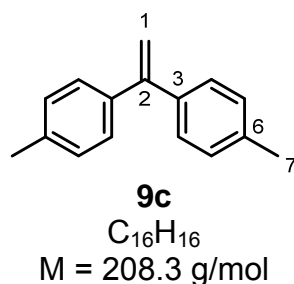
To a suspension of methyltriphenylphosphonium bromide in Et₂O (0.2 M) at 0 °C was added *n*BuLi dropwise. The reaction was stirred at 0 °C for 1 h before the given ketone was added dropwise (if a liquid) or as a single portion (if a solid) and the reaction then stirred at room temperature overnight. The reaction was then diluted with H₂O and Et₂O and the layers were separated. The aqueous phase was extracted with Et₂O (×2) and the combined organic layers were washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo* before being purified by flash column chromatography to afford the title compound.

4,4'-(Ethene-1,1-diyl)bis(methoxybenzene) (9b)

Prepared according to **GP1** using 4,4'-dimethoxybenzophenone (242 mg, 1.00 mmol) and MeMgBr (3 M in Et₂O, 660 μ L, 2.00 mmol, 2 equiv) with stirring for 2 h before adding H₂SO₄ (160 μ L, 3.00 mmol, 3 equiv). No flash column chromatography was required. After work up the title compound was isolated as a white solid (240 mg, 1.00 mmol, quant.).

Data were consistent with that reported.²

$R_f = 0.45$ (95:5 pentane:Et₂O). **M.P.** = 142–144 °C (Et₂O). **¹H NMR** (500 MHz, CDCl₃): δ = 3.82 (s, 6H, 6 \times H-7), 5.30 (s, 2H, 2 \times H-1), 6.85–6.89 (m, 4H, 4 \times H-5) and 7.26–7.30 ppm (m, 4H, 4 \times H-4). **¹³C{¹H} NMR** (125 MHz, CDCl₃): δ = 55.4 (2C, 2 \times C-7), 111.8 (C-1), 113.6 (4C, 4 \times C-5), 129.6 (4C, 4 \times C-4), 134.5 (2C, 2 \times C-3), 149.1 (C-2) and 159.4 ppm (2C, 2 \times C-6).

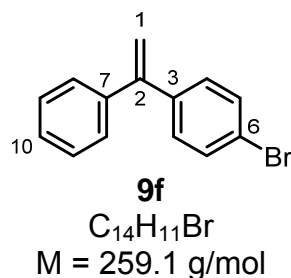
4,4'-(Ethene-1,1-diyl)bis(methylbenzene) (9c)

Prepared according to **GP1** using 4,4'-dimethylbenzophenone (210 mg, 1.00 mmol) and MeMgBr (3 M in Et₂O, 660 μ L, 2.00 mmol, 2 equiv) with stirring for 6 h before adding H₂SO₄ (160 μ L, 3.00 mmol, 3 equiv). Flash column chromatography (SiO₂, pentane) of the crude material afforded the title compound as a colourless oil (163 mg, 0.783 mmol, 78%).

Data were consistent with that reported.²

$R_f = 0.35$ (pentane). **¹H NMR** (500 MHz, CDCl₃): δ = 2.41 (s, 6H, 6 \times H-7), 5.42 (s, 2H, 2 \times H-1), 7.16–7.20 (m, 4H, 4 \times H-5) and 7.27–7.30 ppm (m, 4H, 4 \times H-4). **¹³C{¹H} NMR** (125 MHz, CDCl₃): δ = 21.3 (2C, 2 \times C-7), 113.1 (C1), 128.3 (4C, 4 \times C-4), 129.0 (4C, 4 \times C-5), 137.6 (2C, 2 \times C-6), 139.0 (2C, 2 \times C-3) and 149.9 ppm (C-2).

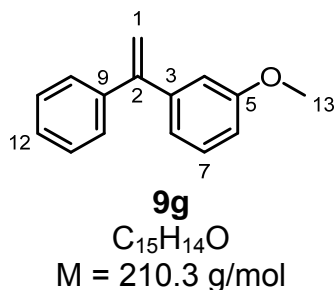
R_f = 0.4 (pentane). **¹H NMR** (500 MHz, CDCl₃): δ = 5.40 (s, 2H, 2 × H-1), 7.00–7.06 (m, 4H, 4 × H-5) and 7.27–7.32 ppm (m, 4H, 4 × H-4). **¹³C{¹H} NMR** (125 MHz, CDCl₃): δ = 114.3 (C-1), 115.3 (d, *J* = 21.5 Hz, 4C, 4 × C-5), 130.0 (d, *J* = 8.1 Hz, 4C, 4 × C-4), 137.5 (d, *J* = 3.1 Hz, 2C, 2 × C-3), 148.2 (C-2) and 162.7 ppm (d, *J* = 246.8 Hz, 2C, 2 × C-6). **¹⁹F NMR** (471 MHz, CDCl₃): δ = –114.4 ppm.

1-Bromo-4-(1-phenylvinyl)benzene (9f)

Prepared according to **GP3** using 4-bromobenzophenone (391 mg, 1.50 mmol), MePPh_3Br (803 mg, 2.25 mmol, 1.5 equiv) and $n\text{BuLi}$ (2.5 M in hexanes, 480 μL , 1.80 mmol, 1.2 equiv). Flash column chromatography (SiO_2 , pentane) of the crude material afforded the title compound as a colourless oil (316 mg, 1.22 mmol, 81%).

Data were consistent with that reported.⁴

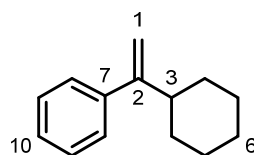
$R_f = 0.5$ (pentane). $^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 5.47$ (d, $J = 1.0$ Hz, 1H, H-1), 5.49 (d, $J = 1.0$ Hz, 1H, H-1), 7.21–7.24 (m, 2H, 2 \times H-5), 7.30–7.38 (m, 5H, 2 \times H-8, 2 \times H-9 and H-10) and 7.45–7.49 ppm (m, 2H, 2 \times H-4). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): $\delta = 114.9$ (C-1), 121.9 (C-6), 128.1 (C-10), 128.3 (2C, 2 \times C-8 or 2 \times C-9), 128.4 (2C, 2 \times C-8 or 2 \times C-9), 130.0 (2C, 2 \times C-5), 131.5 (2C, 2 \times C-4), 140.6 (C-3), 141.1 (C-7) and 149.2 ppm (C-2).

1-Methoxy-3-(1-phenylvinyl)benzene (9g)

Prepared according to **GP2** using Mg (168 mg, 7.00 mmol, 3.5 equiv), bromobenzene (630 μL , 6.00 mmol, 3 equiv) and 3-methoxyacetophenone (275 μL , 2.00 mmol) with stirring for 18 h before adding H_2SO_4 (426 μL , 8.00 mmol, 4 equiv). Flash column chromatography (SiO_2 , pentane) of the crude material afforded the title compound as a colourless oil (373 mg, 1.77 mmol, 88%).

Data were consistent with that reported.²

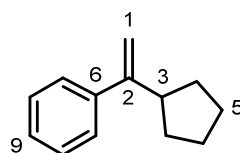
$R_f = 0.63$ (95:5 pentane: Et_2O). $^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 3.80$ (s, 3H, 3 \times H-13), 5.48 (app. q, $J = 1.1$ Hz, 2H, 2 \times H-1), 6.87–6.92 (2H, H-4 and H-6), 6.93–6.96 (1H, H-8), 7.26 (t, $J = 7.9$ Hz, 1H, H-7) and 7.30–7.39 ppm (m, 5H, 2 \times H-10, 2 \times H-11 and H-12). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): $\delta = 55.4$ (C-13), 113.3 (C-6), 114.1 (C-4), 114.5 (C-1), 121.0 (C-8), 127.8 (C-12), 128.3 (2C, 2 \times C-10 or 2 \times C-11), 128.4 (2C, 2 \times C-10 or 2 \times C-11), 129.2 (C-7), 141.5 (C-9), 143.1 (C-3), 150.1 (C-2) and 159.6 ppm (C-5).

(1-Cyclohexylvinyl)benzene (9h)**9h**C₁₄H₁₈

M = 186.3 g/mol

Prepared according to **GP3** using cyclohexyl phenyl ketone (188 mg, 1.00 mmol), MePPh₃Br (536 mg, 1.50 mmol, 1.5 equiv) and *n*BuLi (2.5 M in hexanes, 560 μ L, 1.40 mmol, 1.4 equiv). Flash column chromatography (SiO₂, pentane) of the crude material afforded the title compound as a colourless oil (173 mg, 0.929 mmol, 92%).

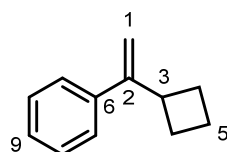
R_f = 0.6 (pentane). ¹H NMR (500 MHz, CDCl₃): δ = 1.17–1.30 (m, 3H, 2 \times H-4 and H-6), 1.32–1.43 (m, 2H, 2 \times H-5), 1.72–1.79 (m, 1H, H-6), 1.80–1.86 (m, 2H, 2 \times H-5), 1.86–1.93 (m, 2H, 2 \times H-4), 2.43–2.50 (m, 1H, H-3), 5.05 (t, *J* = 1.4 Hz, 1H, H-1), 5.18 (dd, *J* = 1.4, 0.6 Hz, 1H, H-1), 7.27–7.32 (m, 1H, H-10) and 7.33–7.39 ppm (m, 4H, 2 \times H-8 and 2 \times H-9). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 26.6 (C-6), 27.0 (2C, 2 \times C-5), 32.9 (2C, 2 \times C-4), 42.7 (C-3), 110.5 (C-1), 126.8 (2C, 2 \times C-8), 127.1 (C-10), 128.2 (2C, 2 \times C-9), 143.1 (C-7) and 155.2 ppm (C-2). IR (ATR): ν = 2919, 2849, 1445, 752 and 697 cm⁻¹. HRMS (EI) for C₁₄H₁₈⁺ [M]⁺: calculated 186.1394, found 186.1403 (Δ = 4.8 ppm).

(1-Cyclopentylvinyl)benzene (9i)**9i**C₁₃H₁₆

M = 172.3 g/mol

Prepared according to **GP3** using cyclopentyl phenyl ketone (331 μ L, 2.00 mmol), MePPh₃Br (1.07 g, 3.00 mmol, 1.5 equiv) and *n*BuLi (2.5 M in hexanes, 960 μ L, 1.20 mmol, 1.2 equiv). Flash column chromatography (SiO₂, pentane) of the crude material afforded the title compound as a colourless oil (297 mg, 1.72 mmol, 86%).

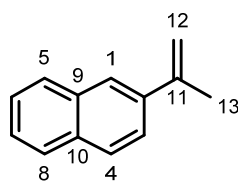
R_f = 0.55 (pentane). ¹H NMR (500 MHz, CDCl₃): δ = 1.34–1.45 (m, 2H, 2 \times H-4), 1.52–1.62 (m, 2H, 2 \times H-5), 1.62–1.72 (m, 2H, 2 \times H-5), 1.79–1.88 (m, 2H, 2 \times H-4), 2.91 (quint. *J* = 8.3 Hz, 1H, H-3), 5.02 (t, *J* = 1.4 Hz, 1H, H-1), 5.12 (t, *J* = 1.1 Hz, 1H, H-1), 7.17–7.22 (m, 1H, H-9), 7.23–7.28 (m, 2H, 2 \times H-8) and 7.30–7.34 ppm (m, 2H, 2 \times H-7). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 25.0 (2C, 2 \times C-5), 32.3 (2C, 2 \times C-4), 44.7 (C-3), 110.2 (C-1), 126.7 (2C, 2 \times C-7), 127.1 (C-9), 128.2 (2C, 2 \times C-8), 143.4 (C-6) and 153.1 ppm (C-2). IR (ATR): ν = 2949, 2866, 1492, 891, 773 and 698 cm⁻¹. HRMS (EI) for C₁₃H₁₆⁺ [M]⁺: calculated 172.1247, found 172.1247 (Δ = 0.0 ppm).

(1-Cyclobutylvinyl)benzene (9j)**9j** $C_{12}H_{14}$

M = 158.2 g/mol

Prepared according to **GP3** using cyclobutyl phenyl ketone (305 μ L, 2.00 mmol), MePPh₃Br (1.07 g, 3.00 mmol, 1.5 equiv) and *n*BuLi (2.5 M in hexanes, 960 μ L, 2.40 mmol, 1.2 equiv). Flash column chromatography (SiO₂, pentane) of the crude material afforded the title compound as a colourless oil (298 mg, 1.88 mmol, 94%).

R_f = 0.6 (pentane). **¹H NMR** (500 MHz, CDCl₃): δ = 1.74–1.86 (m, 1H, H-5), 1.93–2.05 (m, 3H, 2 \times H-4 and H-5), 2.18–2.28 (m, 2H, 2 \times H-4), 3.43–3.53 (m, 1H, H-3), 5.06 (t, J = 1.4 Hz, H-1), 5.36 (t, J = 1.2 Hz, H-1), 7.24–7.29 (m, 1H, H-9), 7.30–7.35 (m, 2H, 2 \times H-8) and 7.36–7.41 ppm (m, 2H, 2 \times H-7). **¹³C{¹H} NMR** (125 MHz, CDCl₃): δ = 17.9 (C-5), 28.6 (2C, 2 \times C-4), 39.8 (C-3), 109.9 (C-1), 126.2 (2C, 2 \times C-7), 127.3 (C-9), 128.3 (2C, 2 \times C-8), 140.9 (C-6) and 152.2 ppm (C-2). **IR** (ATR): ν = 2971, 2936, 1493, 889, 772 and 700 cm⁻¹. **HRMS** (EI) for C₁₂H₁₄⁺ [M]⁺: calculated 158.1090, found 158.1090 (Δ = 0.0 ppm).

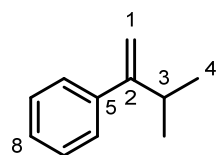
2-(Prop-1-en-2-yl)naphthalene (9k)**9k** $C_{13}H_{12}$

M = 168.2 g/mol

Prepared according to **GP1** using 2-naphthoyl chloride (381 mg, 2.00 mmol) and MeMgBr (3 M in Et₂O, 2 mL, 6.00 mmol, 3 equiv) with stirring for 3 h before adding H₂SO₄ (426 μ L, 8.00 mmol, 4 equiv). Flash column chromatography (SiO₂, pentane) of the crude material afforded the title compound as a colourless oil (55.8 mg, 0.332 mmol, 16%).

Data were consistent with that reported.⁵

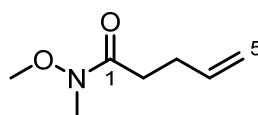
R_f = 0.4 (pentane). **¹H NMR** (500 MHz, CDCl₃): δ = 2.29 (d, J = 1.5, 0.8 Hz, 3H, 3 \times H-13), 5.21 (quint., J = 1.5 Hz, 1H, H-12), 5.54 (q, J = 0.6 Hz, 1H, H-12), 7.34–7.50 (m, 2H, H-6 and H-7), 7.68 (dd, J = 8.6, 1.9 Hz, 1H, H-3), 7.80 (d, J = 8.9 Hz, H-4), 7.81–7.87 (m, 2H, H-5 and H-8) and 7.86 ppm (d, J = 1.7 Hz, 1H, H-1). **¹³C{¹H} NMR** (125 MHz, CDCl₃): δ = 22.0 (C-13), 113.2 (C-12), 124.0 (C-3), 124.4 (C-1), 126.0 (C-6 or C-7), 126.3 (C-6 or C-7), 127.6 (C-4), 127.8 (C-5 or C-8), 128.4 (C-5 or C-8), 133.0 (C-10), 133.5 (C-9), 138.5 (C-11) and 143.2 ppm (C-2).

(3-Methylbut-1-en-2-yl)benzene (9I)**9I** $C_{11}H_{14}$

M = 146.2 g/mol

Prepared according to **GP3** using isobutyrophenone (300 μ L, 2.00 mmol), MePPh₃Br (1.07 g, 3.00 mmol, 1.5 equiv) and *n*BuLi (2.5 M in hexanes, 1.12 mL, 2.80 mmol, 1.4 equiv). Flash column chromatography (SiO₂, pentane) of the crude material afforded the title compound as a colourless oil (228 mg, 1.56 mmol, 78%).

R_f = 0.6 (pentane). 1H NMR (500 MHz, CDCl₃): δ = 1.13 (d, J = 6.8 Hz, 6H, 6 \times H-4), 2.81–2.91 (m, 1H, H-3), 5.06 (t, J = 1.3 Hz, 1H, H-1), 5.17 (dd, J = 1.2, 0.6 Hz, 1H, H-1), 7.26–7.30 (m, 1H, H-8) and 7.21–7.39 (m, 4H, 2 \times H-6 and 2 \times H-7). $^{13}C\{^1H\}$ NMR (125 MHz, CDCl₃): δ = 22.2 (2C, 2 \times C-4), 32.5 (C-3), 110.1 (C-1), 126.8 (2C, 2 \times C-6 or 2 \times C-7), 127.2 (C-8), 128.3 (2C, 2 \times C-6 or 2 \times C-7), 143.0 (C-5) and 156.0 ppm (C-2). IR (ATR): ν = 2960, 1492, 1460, 894, 775 and 697 cm⁻¹. HRMS (EI) for $C_{11}H_{14}^+$ [M]⁺: calculated 146.1090, found 146.1087 (Δ = 2.1 ppm).

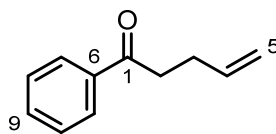
N-Methoxy-N-methylpent-4-enamide (S1)**S1** $C_7H_{13}NO_2$

M = 143.2 g/mol

To a suspension of *N,O*-dimethylhydroxylamine hydrochloride (429 mg, 4.40 mmol, 1.1 equiv) in CH₂Cl₂ (20 mL, 0.2 M) at room temperature were sequentially added 4-pentenoic acid (410 μ L, 4.00 mmol), Et₃N (2.23 mL, 16.0 mmol, 4 equiv) and thionyl chloride (321 μ L, 4.40 mmol, 1.1 equiv). The reaction was stirred at room temperature for 2 days. The reaction mixture was filtered through Celite®, eluting with CH₂Cl₂, before being washed with HCl (2 M, aq.) and NaOH (1 M, aq.). The organic phase was dried over anhydrous MgSO₄, filtered and concentrated *in vacuo* before being purified by flash column chromatography (SiO₂, 7:3 pentane:Et₂O) to afford the title compound as a colourless oil (299 mg, 2.09 mmol, 52%).

Data were consistent with that reported.⁶

R_f = 0.25 (7:3 pentane:Et₂O). 1H NMR (500 MHz, CDCl₃): δ = 2.35–2.41 (m, 2H, 2 \times H-3), 2.52 (t, J = 7.5 Hz, 2H, 2 \times H-2), 3.17 (s, 3H, NCH₃), 3.67 (s, 3H, OCH₃), 4.98 (ddt, J = 10.2, 2.5, 0.9 Hz, H-5_{cis}), 5.06 (dq, J = 17.2, 1.7 Hz, 1H, H-5_{trans}) and 5.86 ppm (ddt, J = 17.0, 10.3, 6.5 Hz, 1H, H-4). $^{13}C\{^1H\}$ NMR (125 MHz, CDCl₃): δ = 28.7 (C-3), 31.3 (C-2), 32.3 (NCH₃), 61.4 (OCH₃), 115.3 (C-5), 137.6 (C-4) and 174.0 ppm (C-1).

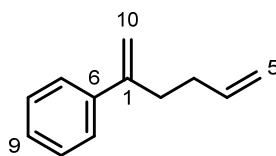
1-Phenylpent-4-en-1-one (S2)**S2**C₁₁H₁₂O

M = 160.2 g/mol

A 2-neck round bottomed flask fitted with a short vigreux column was charged with the given quantity of Mg and a single small crystal of I₂. THF (4 mL) was added followed by approximately a quarter of the bromobenzene (total 366 μ L, 3.50 mmol, 2 equiv). The reaction was then initiated by gentle heating with a heat gun. Once an exotherm could be detected the remaining bromobenzene was added dropwise. The reaction was then stirred at 80 °C for 2 h before being cooled to room temperature. The reaction was cooled to 0 °C before a solution of weinreb amide **S1** (250 mg, 1.75 mmol) in THF (4 mL) was added dropwise. The reaction was then stirred at 0 °C for 2 h before being quenched by addition of NH₄Cl (sat. aq.). The mixture was then diluted with H₂O and Et₂O and the layers were separated. The aqueous phase was extracted with Et₂O (\times 2) and the combined organic layers were washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo* before being purified by flash column chromatography (SiO₂, 29:1 pentane:Et₂O) to afford the title compound as a colourless oil (260 mg, 1.62 mmol, 92%).

Data were consistent with that reported.⁷

R_f = 0.4 (19:1 pentane:Et₂O). ¹H NMR (500 MHz, CDCl₃): δ = 2.46–2.54 (m, 2H, 2 \times H-3), 3.08 (t, J = 7.4 Hz, 2H, 2 \times H-2), 5.01 (ddt, J = 10.2, 2.6, 0.8 Hz, 1H, H-5_{cis}), 5.09 (dq, J = 17.1, 1.7 Hz, 1H, H-5_{trans}), 5.91 (ddt, J = 17.0, 10.4, 6.6 Hz, 1H, H-4), 7.43–7.49 (m, 2H, 2 \times H-8), 7.53–7.58 (m, 1H, H-9) and 7.94–7.99 ppm (m, 2H, 2 \times H-7). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 28.3 (C-3), 37.9 (C-2), 115.4 (C-5), 128.1 (2C, 2 \times C-7), 128.7 (2C, 2 \times C-8), 133.1 (C-9), 137.1 (C-6), 137.4 (C-4) and 199.5 ppm (C-1).

Hexa-1,5-dien-2-ylbenzene (9m)**9m**C₁₂H₁₄

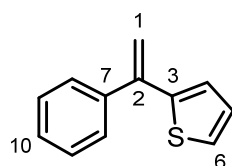
M = 158.2 g/mol

Prepared according to **GP3** using ketone **S2** (200 mg, 1.25 mmol), MePPh₃Br (669 mg, 1.88 mmol, 1.5 equiv) and *n*BuLi (2.5 M in hexanes, 600 μ L, 1.50 mmol, 1.2 equiv). Flash column chromatography (SiO₂, pentane) of the crude material afforded the title compound as a colourless oil (149 mg, 0.942 mmol, 75%).

R_f = 0.55 (pentane). ¹H NMR (500 MHz, CDCl₃): δ = 2.20–2.28 (m, 2H, 2 \times H-3), 2.59–2.64 (m, 2H, 2 \times H-2), 4.99 (ddt, J = 10.2, 2.0, 1.2 Hz, 1H, H-5_{cis}), 5.03 (dq, J = 17.1, 1.7 Hz, 1H, H-5_{trans}), 5.09 (q, J = 1.3 Hz, 1H, H-10), 5.29–5.31 (m, 1H, H-10), 5.86 (ddt, J =

17.0, 10.3, 6.6 Hz, 1H, H-4), 7.26–7.31 (m, 1H, H-9), 7.32–7.37 (m, 2H, 2 × H-8) and 7.40–7.44 ppm (m, 2H, 2 × H-7). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ = 32.6 (C-3), 34.9 (C-2), 112.6 (C-10), 114.9 (C-5), 126.3 (2C, 2 × C-7), 127.5 (C-9), 128.4 (2C, 2 × C-8), 138.3 (C-4), 141.4 (C-6) and 148.1 ppm (C-1). IR (ATR): ν = 3078, 2932, 1492, 995, 893, 774 and 699 cm^{-1} . HRMS (EI) for $\text{C}_{12}\text{H}_{14}^+$ $[\text{M}]^+$: calculated 158.1090, found 158.1087 (Δ = 1.9 ppm).

2-(1-Phenylvinyl)thiophene (9n)



9n

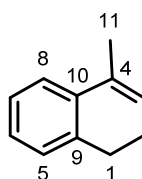
$\text{C}_{12}\text{H}_{10}\text{S}$

$M = 186.3 \text{ g/mol}$

Prepared according to **GP3** using 2-benzoyl thiophene (282 mg, 1.50 mmol), MePPh_3Br (803 mg, 2.25 mmol, 1.5 equiv) and $n\text{BuLi}$ (2.5 M in hexanes, 720 μL , 1.20 mmol, 1.2 equiv). In a modification to the described procedure the reaction was stirred for 2 h at 0 °C before addition of the ketone. Flash column chromatography (SiO_2 , pentane) of the crude material afforded the title compound as a colourless oil (203 mg, 1.09 mmol, 71%).

$R_f = 0.4$ (pentane). ^1H NMR (500 MHz, CDCl_3): δ = 5.27 (d, $J = 0.6 \text{ Hz}$, 1H, H-1), 5.61 (d, $J = 0.7 \text{ Hz}$, 1H, H-1), 6.93 (d, $J = 3.6, 1.1 \text{ Hz}$, 1H, H-4), 6.99 (dd, $J = 5.1, 3.6 \text{ Hz}$, 1H, H-5), 7.25 (dd, $J = 5.1, 1.2 \text{ Hz}$, 1H, H-6), 7.35–7.41 (m, 3H, 2 × H-8 and H-10) and 7.44–7.48 ppm (m, 2H, 2 × H-9). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ = 113.8 (C-1), 125.2 (C-6), 126.6 (C-4), 127.4 (C-5), 128.2 (C-10), 128.3 (2C, 2 × C-8 or 2 × C-9), 128.4 (2C, 2 × C-8 or 2 × C-9), 141.2 (C-7), 143.5 (C-2) and 144.9 ppm (C-3). IR (ATR): ν = 2967, 1491, 1445 and 690 cm^{-1} . HRMS (APCI) for $\text{C}_{12}\text{H}_{11}\text{S}^+$ $[\text{M}+\text{H}]^+$: calculated 187.0576, found 187.0578 (Δ = 1.1 ppm).

4-Methyl-1,2-dihydronaphthalene (9o)



9o

$\text{C}_{11}\text{H}_{12}$

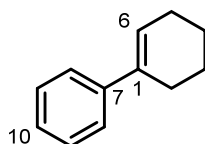
$M = 144.2 \text{ g/mol}$

Prepared according to **GP1** using α -tetralone (133 μL , 1.00 mmol), MeMgBr (3 M in Et_2O , 660 μL , 2.00 mmol, 2 equiv) with stirring for 20 h before adding H_2SO_4 (160 μL , 3.00 mmol, 3 equiv). Flash column chromatography (SiO_2 , pentane) of the crude material afforded the title compound as a colourless oil (109 mg, 0.756 mmol, 75%).

Data were consistent with that reported.⁸

R_f = 0.5 (pentane). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ = 2.09 (q, J = 1.7 Hz, 3H, 3 \times H-11), 2.25–2.31 (m, 2H, 2 \times H-2), 2.9 (t, J = 8.0 Hz, 2H, 2 \times H-1), 5.86–5.90 (m, 1H, H-3), 7.13–7.20 (m, 2H, H-5 and H-8) and 7.21–7.28 ppm (m, 2H, H-6 and H-7). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ = 19.4 (C-11), 23.3 (C-2), 28.5 (C-1), 122.9 (C-6 or C-7), 125.5 (C-3), 126.5 (C-6 or C-7), 126.8 (C-5 or C-8), 127.5 (C-5 or C-8), 132.3 (C-10), 136.0 (C-4) and 136.4 ppm (C-9). IR (ATR): ν = 2928, 2881, 2828, 1485, 1435, 810, 793 and 729 cm^{-1} . HRMS (EI) for $\text{C}_{11}\text{H}_{12}^+ [\text{M}]^+$: calculated 144.0934, found 144.0928 (Δ = 4.2 ppm).

2,3,4,5-Tetrahydro-1,1'-biphenyl (9p)



9p

$\text{C}_{12}\text{H}_{14}$

M = 158.2 g/mol

Prepared according to **GP2** using Mg (106 mg, 4.40 mmol, 2.2 equiv), bromobenzene (419 μL , 4.00 mmol, 2 equiv) and cyclohexanone (208 μL , 2.00 mmol) with stirring for 15 h before adding H_2SO_4 (320 μL , 6.00 mmol, 3 equiv). Flash column chromatography (SiO_2 , pentane) of the crude material afforded the title compound as a colourless oil (196 mg, 1.24 mmol, 61%).

Data were consistent with that reported.⁹

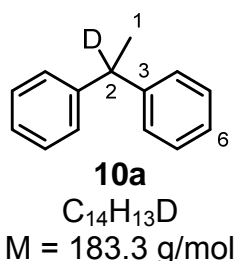
R_f = 0.68 (pentane). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ = 1.65–1.73 (m, 2H, 2 \times H-4), 1.78–1.85 (m, 2H, 2 \times H-3), 2.20–2.27 (m, 2H, 2 \times H-5), 2.41–2.47 (m, 2H, 2 \times H-2), 6.15 (sept., J = 1.9 Hz, 1H, H-6), 7.21–7.25 (m, 1H, H-10), 7.30–7.35 (m, 2H, 2 \times H-9) and 7.38–7.43 ppm (m, 2H, 2 \times H-8). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ = 22.3 (C-4), 23.2 (C-3), 26.0 (C-5), 27.5 (C-2), 124.9 (C-6), 125.1 (2C, 2 \times C-9), 126.6 (C-10), 128.3 (2C, 2 \times C-8), 136.7 (C-1) and 142.8 ppm (C-7).

4. Synthesis of Hydrodeuterated Products

GP4: Transfer Hydrodeuteration of Alkenes

In a nitrogen filled glove box the given alkene (0.2 mmol) and surrogate **8** (0.26 mmol, 1.3 equiv) [in instances where the surrogate contained a small quantity of the aromatised byproduct the purity is given as a wt %] were sequentially weighed into a 2 mL GC vial and a magnetic follower was then added. In a separate 2 mL GC vial, $\text{B}(\text{C}_6\text{F}_5)_3$ (2.6 mg, 5.0 μmol , 2.5 mol %) was dissolved in 1,2- $\text{C}_6\text{H}_4\text{F}_2$ (500 μL , 0.4 M) before being transferred to the reaction vial *via* pipette. The GC vial was fitted with a cap and the reaction stirred in the glove box at room temperature for 16 h. The reaction was then removed from the glove box and filtered through Celite®, eluting with Et_2O , and concentrated *in vacuo*. If desired, CH_2Br_2 (14 μL , 1 equiv) could be added at this stage and the reaction analysed by ^1H NMR. Otherwise, the crude reaction mixture was purified by flash column chromatography (SiO_2) to afford the title compound.

(Ethane-1,1-diyl-1-*d*)dibenzene (**10a**)



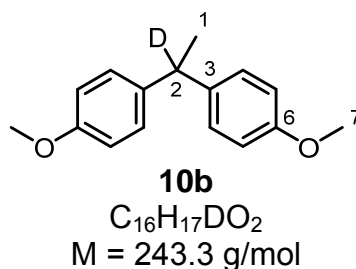
On 0.200 mmol scale:

Prepared according to **GP4** using alkene **9a** (36.0 mg, 0.200 mmol) and surrogate **8** (39.8 mg, 0.260 mmol, 1.3 equiv). Flash column chromatography (SiO_2 , pentane) of the crude material afford the title compound as a colourless oil (32.8 mg, 0.179 mmol, 90%).

On 1.00 mmol scale:

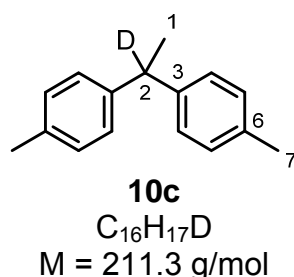
In a nitrogen filled glove box alkene **9a** (180 mg, 1.00 mmol) and surrogate **8** (99 wt %, 201 mg, 1.30 mmol, 1.3 equiv) were sequentially weighed into a 5 mL screw cap vial, dissolved in 1,2- $\text{C}_6\text{H}_4\text{F}_2$ (2 mL) and a magnetic follower was then added. In a separate 2 mL GC vial, $\text{B}(\text{C}_6\text{F}_5)_3$ (25.6 mg, 50.0 μmol , 5 mol %) was dissolved in 1,2- $\text{C}_6\text{H}_4\text{F}_2$ (500 μL , total 0.4 M) before being transferred to the reaction vial *via* pipette. The vial was fitted with a cap and the reaction stirred in the glove box at room temperature for 16 h. The reaction was then removed from the glove box and filtered through Celite®, eluting with Et_2O , and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography (SiO_2 , pentane) to afford the title compound as a colourless oil (156 mg, 0.852 mmol, 85%).

$R_f = 0.35$ (pentane). ^1H NMR (500 MHz, CDCl_3): $\delta = 1.69$ (s, 3H, 3 \times H-1), 7.20–7.26 (2H, 2 \times H-6), 7.26–7.30 (m, 4H, 4 \times H-5) and 7.30–7.36 ppm (m, 4H, 4 \times H-4). ^2H NMR (77 MHz, 9:1 $\text{CHCl}_3:\text{CDCl}_3$): $\delta = 4.17$ ppm (bs, D-2). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): $\delta = 21.9$ (C-1), 44.5 (t, $J = 19.5$ Hz, C-2), 126.2 (2C, 2 \times C-6), 127.7 (4C, 4 \times C-5), 128.5 (4C, 4 \times C-4) and 126.5 ppm (2C, 2 \times C-3). IR (ATR): $\nu = 3022, 1599, 1491, 1444, 1026, 747$ and 694 cm^{-1} . HRMS (EI) for $\text{C}_{14}\text{H}_{13}\text{D}^+$ $[M]^+$: calculated 183.1153, found 183.1147 ($\Delta = 3.2$ ppm).

4,4'-(Ethane-1,1-diyl-1-*d*)bis(methoxybenzene) (10b)

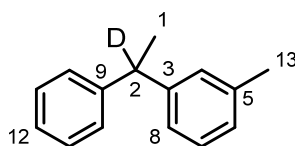
Prepared according to **GP4** using alkene **9b** (48.0 mg, 0.200 mmol) and surrogate **8** (95 wt %, 41.9 mg, 0.260 mmol, 1.3 equiv). Flash column chromatography (SiO_2 , 99:1→97:3 pentane:Et₂O) of the crude material afford the title compound as a colourless oil (46.9 mg, 0.193 mmol, 96%).

$R_f = 0.25$ (pentane). **M.P.** = 75–77 °C (pentane). **¹H NMR** (500 MHz, CDCl₃): δ = 1.59 (s, 3H, 3 × H-1), 3.78 (s, 6H, 6 × H-7), 6.83 (dt, J = 9.5, 2.5 Hz, 4H, 4 × H-5) and 7.13 ppm (dt, J = 9.6, 2.6 Hz, 4H, 4 × H-4). **²H NMR** (77 MHz, 9:1 CHCl₃:CDCl₃): δ = 4.07 ppm (bs, D-2). **¹³C{¹H} NMR** (125 MHz, CDCl₃): δ = 22.3 (C-1), 42.8 (t, J = 19.1 Hz, C-2), 55.4 (2C, 2 × C-7), 113.8 (4C, 4 × C-5), 128.5 (4C, 4 × C-4), 139.1 (2C, 2 × C-3) and 157.9 ppm (2C, 2 × C-6). **IR** (ATR): ν = 2959, 1604, 1503, 1235, 1172, 1024, 819 and 749 cm⁻¹. **HRMS** (EI) for $C_{16}H_{17}DO^+$ [$M-C_7H_7O$]⁺: calculated 136.0867, found 136.0868 (Δ = 0.7 ppm).

4,4'-(Ethane-1,1-diyl-1-*d*)bis(methylbenzene) (10c)

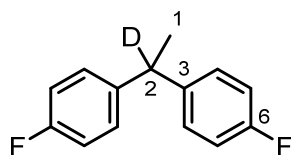
Prepared according to **GP4** using alkene **9c** (41.6 mg, 0.200 mmol) and surrogate **8** (94 wt %, 42.3 mg, 0.260 mmol, 1.3 equiv). Flash column chromatography (SiO_2 , pentane) of the crude material afford the title compound as a colourless oil (40.7 mg, 0.193 mmol, 96%).

$R_f = 0.3$ (pentane). **¹H NMR** (500 MHz, CDCl₃): δ = 1.63 (s, 3H, 3 × H-1), 2.33 (s, 6H, 6 × H-7) and 7.13 ppm (app. q, J = 7.6 Hz, 8H, 4 × H-4 and 4 × H-5). **²H NMR** (77 MHz, 9:1 CHCl₃:CDCl₃): δ = 4.11 ppm (bs, D-2). **¹³C{¹H} NMR** (125 MHz, CDCl₃): δ = 21.1 (2C, 2 × C-7), 22.0 (C-1), 43.7 (t, J = 19.4 Hz, C-2), 127.5 (4C, 4 × C-4), 129.2 (4C, 4 × C-5), 135.5 (2C, 2 × C-6) and 143.7 ppm (2C, 2 × C-3). **IR** (ATR): ν = 2964, 1510 and 801 cm⁻¹. **HRMS** (EI) for $C_{16}H_{17}D^+$ [M]⁺: calculated 211.1466, found 211.1459 (Δ = 3.3 ppm).

1-Methyl-3-(1-phenylethyl-1-*d*)benzene (10d)**10d** $C_{15}H_{15}D$ $M = 197.3 \text{ g/mol}$

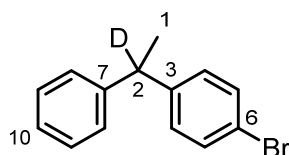
Prepared according to **GP4** using alkene **9d** (38.9 mg, 0.200 mmol) and surrogate **8** (99 wt %, 40.0 mg, 0.260 mmol, 1.3 equiv). Flash column chromatography (SiO_2 , pentane) of the crude material afford the title compound as a colourless oil (35.8 mg, 0.181 mmol, 90%).

$R_f = 0.35$ (pentane). 1H NMR (500 MHz, $CDCl_3$): $\delta = 1.66$ (s, 3H, 3 \times H-1), 2.35 (s, 3H, 3 \times H-13), 7.02–7.09 (m, 3H, H-4, H-6 and H-8), 7.19–7.24 (m, 2H, H-7 and H-12), 7.25–7.29 (m, 2H, 2 \times H-10) and 7.29–7.34 ppm (m, 2H, 2 \times H-11). 2H NMR (77 MHz, 9:1 $CHCl_3:CDCl_3$): $\delta = 4.13$ ppm (bs, D-2). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 21.6$ (C-13), 21.9 (C-1), 44.4 (t, $J = 19.5$ Hz, C-2), 124.7 (C-8), 126.1 (C-12), 126.9 (C-6), 127.7 (2C, 2 \times C-10), 128.4 (C-7), 128.46 (2C, 2 \times C-11), 128.54 (C-4), 138.0 (C-5), 146.4 (C-3) and 146.6 ppm (C-9). IR (ATR): $\nu = 2965, 1601, 1490, 1445, 763$ and 695 cm^{-1} . HRMS (EI) for $C_{15}H_{15}D^+ [M]^+$: calculated 197.1309, found 197.1310 ($\Delta = 0.5$ ppm).

4,4'-(Ethane-1,1-diyl-1-*d*)bis(fluorobenzene) (10e)**10e** $C_{14}H_{11}DF_2$ $M = 219.3 \text{ g/mol}$

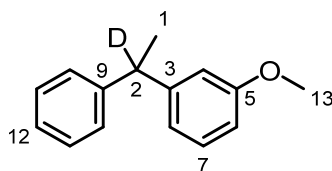
Prepared according to **GP4** using alkene **9e** (43.2 mg, 0.200 mmol) and surrogate **8** (95 wt %, 41.9 mg, 0.260 mmol, 1.3 equiv). Flash column chromatography (SiO_2 , pentane) of the crude material afford the title compound as a colourless oil (21.2 mg, 96.7 μmol , 48%).

$R_f = 0.3$ (pentane). 1H NMR (500 MHz, $CDCl_3$): $\delta = 1.60$ (s, 3H, 3 \times H-1), 6.94–7.00 (m, 4H, 4 \times H-5) and 7.11–7.18 ppm (m, 4H, 4 \times H-4). 2H NMR (77 MHz, 9:1 $CHCl_3:CDCl_3$): $\delta = 4.13$ ppm (bs, D-2). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 22.2$ (C-1), 43.0 (t, $J = 19.1$ Hz, C-2), 115.3 (d, $J = 21.1$ Hz, 4C, 4 \times C-5), 129.0 (d, $J = 7.7$ Hz, 4C, 4 \times C-4), 141.9 (2C, 2 \times C-3) and 161.5 ppm (d, $J = 244.2$ Hz, 2C, 2 \times C-6). ^{19}F NMR (471 MHz, $CDCl_3$): $\delta = -177.2$ ppm. IR (ATR): $\nu = 1503, 1219, 1157$ and 817 cm^{-1} . HRMS (EI) for $C_{14}H_{11}DF_2^+ [M]^+$: calculated 219.0960, found 219.0964 ($\Delta = 1.8$ ppm).

1-Bromo-4-(1-phenylethyl-1-*d*)benzene (10f)**10f** $C_{14}H_{12}DBr$ $M = 262.2 \text{ g/mol}$

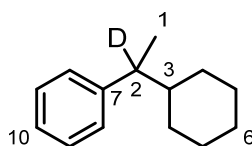
Prepared according to **GP4** using alkene **9f** (51.8 mg, 0.200 mmol) and surrogate **8** (94 wt %, 42.3 mg, 0.260 mmol, 1.3 equiv). Flash column chromatography (SiO_2 , pentane) of the crude material afford the title compound as a colourless oil (26.1 mg, 99.5 μmol , 50%).

$R_f = 0.35$ (pentane). $^1\text{H NMR}$ (500 MHz, $CDCl_3$): $\delta = 1.61$ (s, 3H, 3 \times H-1), 7.10 (dt, $J = 9.1, 2.3$ Hz, 2H, 2 \times H-4), 7.18–7.22 (m, 3H, 2 \times H-8 or 2 \times H-9, and H-10), 7.27–7.32 (m, 2H, 2 \times H-8 or 2 \times H-9) and 7.41 ppm (dt, $J = 9.2, 2.3$ Hz, 2H, 2 \times H-5). $^2\text{H NMR}$ (77 MHz, 9:1 $CHCl_3:CDCl_3$): $\delta = 4.12$ ppm (bs, D-2). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, $CDCl_3$): $\delta = 21.7$ (C-1), 44.0 (t, $J = 19.6$ Hz, C-2), 120.0 (C-6), 126.4 (C-10), 127.6 (2C, 2 \times C-8 or 2 \times C-9), 128.6 (2C, 2 \times C-8 or 2 \times C-9), 129.5 (2C, 2 \times C-4), 131.6 (2C, 2 \times C-5), 145.5 (C-3) and 145.8 ppm (C-7). IR (ATR): $\nu = 2965, 1486, 1075, 1008, 818, 736$ and 686 cm^{-1} . HRMS (EI) for $C_{14}H_{12}DBr^+ [M]^+$: calculated 261.0257, found 261.0258 ($\Delta = 0.4$ ppm).

1-Methoxy-3-(1-phenylethyl-1-*d*)benzene (10g)**10g** $C_{15}H_{15}DO$ $M = 213.3 \text{ g/mol}$

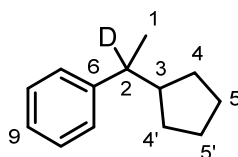
Prepared according to **GP4** using alkene **9g** (42.0 mg, 0.200 mmol) and surrogate **8** (94 wt %, 42.3 mg, 0.260 mmol, 1.3 equiv). Flash column chromatography (SiO_2 , pentane) of the crude material afford the title compound as a colourless oil (37.6 mg, 88% mass recovery) containing 6 mol % alkene **9g** (94 wt %, 0.166 mmol, 82%). Traces of an unknown side-product were also present.

$R_f = 0.55$ (pentane). $^1\text{H NMR}$ (500 MHz, $CDCl_3$): $\delta = 1.65$ (s, 3H, 3 \times H-1), 3.79 (s, 3H, 3 \times H-13), 6.75 (ddd, $J = 8.2, 2.6, 0.9$ Hz, 1H, H-6), 6.80–6.82 (m, 1H, H-4), 6.85 (dq, $J = 7.6, 0.9$ Hz, 1H, H-8) and 7.18–7.33 ppm (m, 6H, H-7, 2 \times H-10, 2 \times H-11 and H-12). $^2\text{H NMR}$ (77 MHz, 9:1 $CHCl_3:CDCl_3$): $\delta = 4.13$ ppm (bs, D-2). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, $CDCl_3$): $\delta = 21.8$ (C-1), 44.5 (t, $J = 19.7$ Hz, C-2), 55.3 (C-13), 111.1 (C-6), 113.9 (C-4), 120.2 (C-8), 126.2 (C-12), 127.7 (2C, 2 \times C-10 or 2 \times C-11), 128.5 (2C, 2 \times C-10 or 2 \times C-11), 129.4 (C-7), 146.3 (C-9), 148.1 (C-3) and 159.8 ppm (C-5). IR (ATR): $\nu = 2963, 1595, 1485, 1446, 1261, 1166, 1040, 766$ and 695 cm^{-1} . HRMS (EI) for $C_{15}H_{15}DO^+ [M]^+$: calculated 213.1258, found 213.1251 ($\Delta = 3.3$ ppm)

(1-Cyclohexylethyl-1-d)benzene (10h)**10h** $C_{11}H_{15}D$ $M = 189.3 \text{ g/mol}$

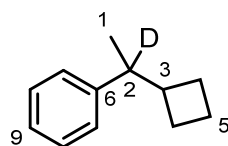
Prepared according to **GP4** using alkene **9h** (37.6 mg, 0.200 mmol) and surrogate **8** (95 wt %, 41.9 mg, 0.260 mmol, 1.3 equiv). Flash column chromatography (SiO_2 , pentane) of the crude material afford the title compound as a colourless oil (34.9 mg, 0.184 mmol, 92%).

$R_f = 0.6$ (pentane). 1H NMR (500 MHz, $CDCl_3$): $\delta = 0.78\text{--}0.87$ (m, 1H, H-4), 0.90–1.00 (m, 1H, H-4), 1.06–1.18 (m, 2H, H-5 and H-6), 1.18–1.29 (m, 4H, 3 \times H-1 and H-5), 1.35–1.49 (m, 2H, H-3 and H-4), 1.59–1.67 (m, 2H, H-5 and H-6), 1.72–1.79 (m, 1H, H-5), 1.85–1.92 (m, 1H, H-4), 7.13–7.21 (m, 3H, 2 \times H-8 and H-10) and 7.26–7.31 ppm (m, 2H, 2 \times H-9). 2H NMR (77 MHz, 9:1 $CHCl_3:CDCl_3$): $\delta = 2.45$ ppm (bs, D-2). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 18.8$ (C-1), 26.67 (C-5 or C-6), 26.71 (2C, 2 \times C-5 or C-5 and C-6), 30.8 (C-4), 31.6 (C-4), 44.3 (C-3), 45.6 (t, $J = 19.2$ Hz, C-2), 125.8 (C-10), 127.8 (2C, 2 \times C-8), 128.1 (2C, 2 \times C-9) and 147.2 ppm (C-7). IR (ATR): $\nu = 2919, 1849, 1445, 752$ and 697 cm^{-1} . HRMS (EI) for $C_{11}H_{15}D^+ [M]^+$: calculated 189.1622, found 189.1621 ($\Delta = 0.5$ ppm).

(1-Cyclopentylethyl-1-d)benzene (10i)**10i** $C_{13}H_{17}D$ $M = 175.3 \text{ g/mol}$

Prepared according to **GP4** using alkene **9i** (34.8 mg, 0.200 mmol) and surrogate **8** (99 wt %, 40.0 mg, 0.260 mmol, 1.3 equiv). Flash column chromatography (SiO_2 , pentane) of the crude material afford the title compound as a colourless oil (26.3 mg, 0.150 mmol, 75%).

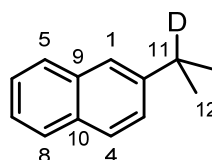
$R_f = 0.6$ (pentane). 1H NMR (500 MHz, $CDCl_3$): $\delta = 0.96\text{--}1.07$ (m, 1H, H-4), 1.18–1.29 (m, 4H, 3 \times H-1 and H-4'), 1.35–1.49 (m, 2H, H-4 and H-5), 1.50–1.60 (m, 2H, H-5 and H-5'), 1.61–1.71 (m, 1H, H-5'), 1.86–2.00 (m, 2H, H-3 and H-4'), 7.15–7.21 (m, 3H, 2 \times H-7 and H-9) and 7.25–7.30 ppm (m, 2H, 2 \times H-8). 2H NMR (77 MHz, 9:1 $CHCl_3:CDCl_3$): $\delta = 2.43$ ppm (bs, D-2). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 21.5$ (C-1), 25.3 (C-5 or C-5'), 25.5 (C-5 or C-5'), 31.5 (C-4'), 31.9 (C-4), 45.8 (t, $J = 19.3$ Hz, C-2), 47.6 (C-3), 125.8 (C-9), 127.4 (2C, 2 \times C-7), 128.3 (2C, 2 \times C-8) and 148.1 ppm (C-6). IR (ATR): $\nu = 2950, 2865, 1491, 1446, 794$ and 697 cm^{-1} . HRMS (EI) for $C_{13}H_{17}D^+ [M]^+$: calculated 175.1466, found 175.1468 ($\Delta = 1.1$ ppm).

(1-Cyclobutylethyl-1-*d*)benzene (10j)**10j**C₁₂H₁₅D

M = 161.3 g/mol

Prepared according to **GP4** using alkene **9j** (31.6 mg, 0.200 mmol) and surrogate **8** (95 wt %, 41.9 mg, 0.260 mmol, 1.3 equiv). Flash column chromatography (SiO₂, pentane) of the crude material afford the title compound as a colourless oil (14.5 mg, 89.9 μmol, 45%).

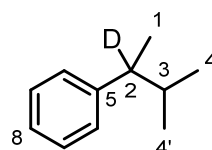
R_f = 0.45 (pentane). ¹H NMR (500 MHz, CDCl₃): δ = 1.14 (s, 3H, 3 × H-1), 1.55–1.66 (m, 1H, H-4), 1.70–1.84 (m, 4H, 2 × H-4 and 2 × H-5), 2.07–2.17 (m, 1H, H-4), 2.42 (quint., *J* = 7.5 Hz, 1H, H-3), 7.14–7.20 (m, 3H, 2 × H-7 and H-9) and 7.25–7.30 ppm (m, 2H, 2 × H-8). ²H NMR (77 MHz, 9:1 CHCl₃:CDCl₃): δ = 2.61 ppm (bs, D-2). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 17.6 (C-5), 19.0 (C-1), 27.3 (C-4), 27.6 (C-4), 42.8 (C-3), 46.3 (t, *J* = 19.2 Hz, C-2), 125.9 (C-9), 127.3 (2C, 2 × C-7), 128.3 (2C, 2 × C-8) and 146.2 ppm (C-6). IR (ATR): ν = 2958, 1491, 1444, 756 and 696 cm⁻¹. HRMS (EI) for C₁₂H₁₅D⁺ [*M*]⁺: calculated 161.1309, found 161.1311 (Δ = 1.2 ppm)

2-(Propan-2-yl-2-*d*)naphthalene (10k)**10k**C₁₃H₁₃D

M = 171.3 g/mol

Prepared according to **GP4** using alkene **9k** (33.6 mg, 0.200 mmol) and surrogate **8** (94 wt %, 42.3 mg, 0.260 mmol, 1.3 equiv). Flash column chromatography (SiO₂, pentane) of the crude material afford the title compound as a colourless oil (7.2 mg, 42 μmol, 21%).

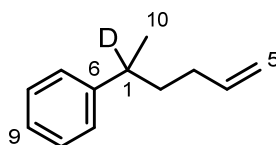
R_f = 0.5 (pentane). ¹H NMR (500 MHz, CDCl₃): δ = 1.35 (t, *J* = 0.9 Hz, 6H, 6 × H12), 7.38–7.47 (m, 3H, H-3, H-6 and H-7), 7.65 (d, *J* = 1.6 Hz, 1H, H-1) and 7.77–7.82 ppm (m, 3H, H-4, H-5 and H-8). ²H NMR (77 MHz, 9:1 CHCl₃:CDCl₃): δ = 3.07 ppm (bs, D-11). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 24.0 (2C, 2 × C-12), 33.9 (t, *J* = 19.4 Hz, C-11), 124.2 (C-1), 125.2 (C-6 or C-7), 125.87 (C-3 or C-6 or C-7), 125.94 (C-3 or C-6 or C-7), 127.7 (2C, C-5 and C-8), 128.0 (C-4), 132.2 (C-10), 133.8 (C-9) and 146.4 ppm (C-2). IR (ATR): ν = 2956, 1457, 852, 815 and 742 cm⁻¹. HRMS (EI) for C₁₃H₁₃D⁺ [*M*]⁺: calculated 171.1152, found 171.1153 (Δ = 0.6 ppm).

(3-Methylbutan-2-yl-2-*d*)benzene (10l)

10l
 $C_{11}H_{15}D$
 $M = 149.3 \text{ g/mol}$

Prepared according to **GP4** using alkene **9l** (29.2 mg, 0.200 mmol) and surrogate **8** (95 wt %, 41.9 mg, 0.260 mmol, 1.3 equiv). After work up and concentration under reduced pressure (not lower than 300 mbar), CH_2Br_2 (14 μ L, 0.20 mmol, 1 equiv) was added and the crude material was subjected to 1H NMR analysis. A yield of 91% with reference to CH_2Br_2 was calculated. Flash column chromatography (SiO_2 , pentane) of the crude material afford the title compound as a colourless oil (11.7 mg, 78.4 μ mol, 39%) [Note: Volatile].

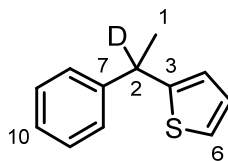
$R_f = 0.6$ (pentane). 1H NMR (500 MHz, $CDCl_3$): $\delta = 0.76$ (d, $J = 6.7$ Hz, 3H, 3 \times H-4), 0.94 (d, $J = 6.7$ Hz, 3H, 3 \times H-4'), 1.23 (s, 3H, 3 \times H-1), 1.77 (sept., $J = 6.7$ Hz, 1H, H-3), 7.14–7.21 (m, 3H, 2 \times H-6 and H-8) and 7.26–7.30 ppm (m, 2H, 2 \times H-7). 2H NMR (77 MHz, 9:1 $CHCl_3:CDCl_3$): $\delta = 2.42$ ppm (bs, D-2). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 18.8$ (C-1), 20.3 (C-4'), 21.3 (C-4), 34.5 (C-3), 46.5 (t, $J = 19.4$ Hz, C-2), 125.8 (C-8), 127.8 (2C, 2 \times C-6), 128.2 (2C, 2 \times C-7) and 147.2 ppm (C-5). IR (ATR): $\nu = 2957, 1446, 763$ and 697 cm^{-1} . HRMS (EI) for $C_{11}H_{15}^+ [M]^+$: calculated 149.1309, found 149.1302 ($\Delta = 4.7$ ppm)

(Hex-5-en-2-yl-2-*d*)benzene (10m)

10m
 $C_{12}H_{15}D$
 $M = 161.3 \text{ g/mol}$

Prepared according to **GP4** using alkene **9m** (31.6 mg, 0.200 mmol) and surrogate **8** (99 wt %, 40.0 mg, 0.260 mmol, 1.3 equiv). Flash column chromatography (SiO_2 , pentane) of the crude material afford the title compound as a colourless oil (13.4 mg, 83.1 μ mol, 41%).

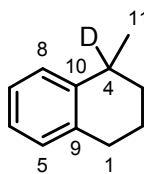
$R_f = 0.4$ (pentane). 1H NMR (500 MHz, $CDCl_3$): $\delta = 1.25$ (s, 2H, 3 \times H-10), 1.61–1.74 (m, 2H, 2 \times H-2), 1.90–2.03 (m, 2H, 2 \times H-3), 4.91–5.00 (m, 2H, 2 \times H-5), 5.78 (qt, $J = 14.8, 6.7$ Hz, 1H, H-4), 7.16–7.21 (m, 3H, 2 \times H-7 and H-9) and 7.27–7.32 ppm (m, 2H, 2 \times H-8). 2H NMR (77 MHz, 9:1 $CHCl_3:CDCl_3$): $\delta = 2.71$ ppm (bs, D-1). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 22.3$ (C-10), 32.0 (C-3), 37.5 (C-2), 39.0 (t, $J = 19.5$ Hz, C-1), 114.5 (C-5), 126.0 (C-9), 127.2 (2C, 2 \times C-7), 128.5 (2C, 2 \times C-8), 139.0 (C-4) and 147.5 ppm (C-6). IR (ATR): $\nu = 2921, 1446, 907, 754$ and 697 cm^{-1} . HRMS (EI) for $C_{12}H_{15}D^+ [M]^+$: calculated 161.1309, found 161.1301 ($\Delta = 5.0$ ppm)

2-(1-Phenylethyl-1-*d*)thiophene (10n)**10n**C₁₂H₁₁DS

M = 189.3 g/mol

Prepared according to **GP4** using alkene **9n** (37.2 mg, 0.200 mmol) and surrogate **8** (94 wt %, 42.3 mg, 0.260 mmol, 1.3 equiv). Flash column chromatography (SiO₂, pentane) of the crude material afford the title compound as a colourless oil (33.4 mg, 0.176 mmol, 88%).

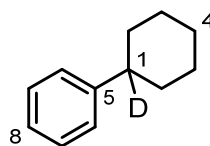
R_f = 0.4 (pentane). ¹H NMR (500 MHz, CDCl₃): δ = 1.73 (s, 3H, 3 × H-1), 6.83 (dd, *J* = 3.5, 1.2 Hz, 1H, H-4), 6.95 (dd, *J* = 5.1, 3.5 Hz, 1H, H-5), 7.17 (dd, *J* = 5.1, 1.2 Hz, 1H, H-6), 7.23–7.27 (m, 1H, H-10) and 7.28–7.36 ppm (m, 4H, 2 × H-8 and 2 × H-9). ²H NMR (77 MHz, 9:1 CHCl₃:CDCl₃): δ = 4.36 ppm (bs, D-2). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 23.4 (C-1), 40.5 (t, *J* = 19.7 Hz, C-2), 123.6 (C-6), 123.7 (C-4), 126.6 (2C, C-5 and C-10), 127.4 (2C, 2 × C-8), 128.6 (2C, 2 × C-9), 146.1 (C-7) and 150.8 ppm (C-3). IR (ATR): ν = 2967, 1491, 1445 and 690 cm⁻¹. HRMS (EI) for C₁₂H₁₁DS⁺ [M]⁺: calculated 189.0717, found 189.0714 (Δ = 1.6 ppm)

1-Methyl-1,2,3,4-tetrahydronaphthalene-1-*d* (10o)**10o**C₁₁H₁₃D

M = 147.2 g/mol

Prepared according to **GP4** using alkene **9o** (28.8 mg, 0.200 mmol) and surrogate **8** (95 wt %, 41.9 mg, 0.260 mmol, 1.3 equiv). Flash column chromatography (SiO₂, pentane) of the crude material afford the title compound as a colourless oil (20.5 mg, 0.139 mmol, 70%).

R_f = 0.5 (pentane). ¹H NMR (500 MHz, CDCl₃): δ = 1.30 (s, 3H, 3 × H-11), 1.51–1.58 (m, 1H, H-3), 1.69–1.80 (m, 1H, H-2), 1.84–1.97 (m, 2H, H-2 and H-3), 2.70–2.84 (m, 2H, 2 × H-1), 7.05–7.16 (m, 3H, H-5, H-6 and H-7) and 7.20–7.23 ppm (m, 1H, H-8). ²H NMR (77 MHz, 9:1 CHCl₃:CDCl₃): δ = 2.92 ppm (bs, D-4). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 20.5 (C-2), 22.9 (C-11), 30.1 (C-1), 31.5 (C-3), 32.1 (t, *J* = 19.5 Hz, C-4), 125.5 (C-6 or C-7), 125.7 (C-6 or C-7), 128.2 (C-8), 129.1 (C-5), 137.0 (C-9) and 142.2 ppm (C-10). IR (ATR): ν = 2925, 1487, 1445 and 745 cm⁻¹. HRMS (EI) for C₁₁H₁₃D⁺ [M]⁺: calculated 147.1151, found 147.1153 (Δ = 1.4 ppm).

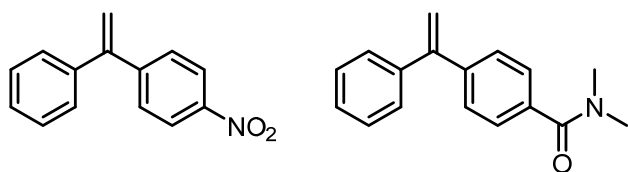
(Cyclohexyl-1-*d*)benzene (10p)**10p** $\text{C}_{12}\text{H}_{15}\text{D}$ $M = 161.3 \text{ g/mol}$

Prepared according to **GP4** using alkene **9p** (31.6 mg, 0.200 mmol) and surrogate **8** (99 wt %, 40.0 mg, 0.260 mmol, 1.3 equiv). Flash column chromatography (SiO_2 , pentane) of the crude material afford the title compound as a colourless oil (4.3 mg, 27 μmol , 13%). Alkene **9p** (16.5 mg, 0.104 mmol, 52%) could also be recovered.

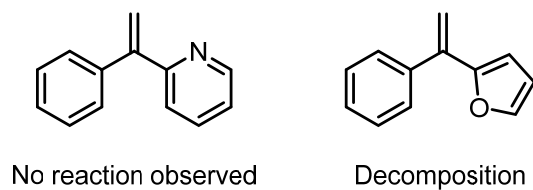
$R_f = 0.63$ (pentane). $^1\text{H NMR}$ (700 MHz, CDCl_3): $\delta = 1.21\text{--}1.30$ (m, 1H, H-4), 1.35–1.47 (m, 4H, 2 \times H-2 and 2 \times H-3), 1.72–1.78 (m, 1H, H-4), 1.81–1.91 (m, 4H, 2 \times H-2 and 2 \times H-3), 7.16–7.20 (m, 1H, H-8), 7.20–7.23 (m, 2H, 2 \times H-6) and 7.27–7.31 ppm (m, 2H, 2 \times H-7). $^2\text{H NMR}$ (77 MHz, 9:1 $\text{CHCl}_3:\text{CDCl}_3$): $\delta = 2.49$ ppm (bs, D-1). $^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3): $\delta = 26.3$ (C-4), 27.1 (2C, 2 \times C-3), 34.5 (2C, 2 \times C-2), 44.2 (t, $J = 19.1$ Hz, C-1), 125.9 (C-8), 126.9 (2C, 2 \times C-6), 128.4 (2C, 2 \times C-7) and 148.2 ppm (C-5). IR (ATR): $\nu = 2920, 2848, 1445, 749$ and 695 cm^{-1} . HRMS (EI) for $\text{C}_{12}\text{H}_{15}\text{D}^+ [M]^+$: calculated 161.1309, found 161.1314 ($\Delta = 3.1$ ppm)

5. Unsuccessful Substrates

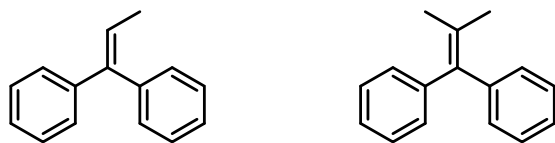
Electron-withdrawing groups: No reaction observed



Heterocycles:



Tri- and tetra-substituted alkenes: No reaction observed



Aliphatic substituted alkenes:

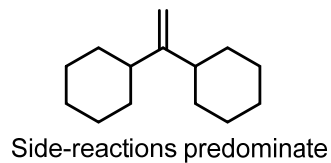
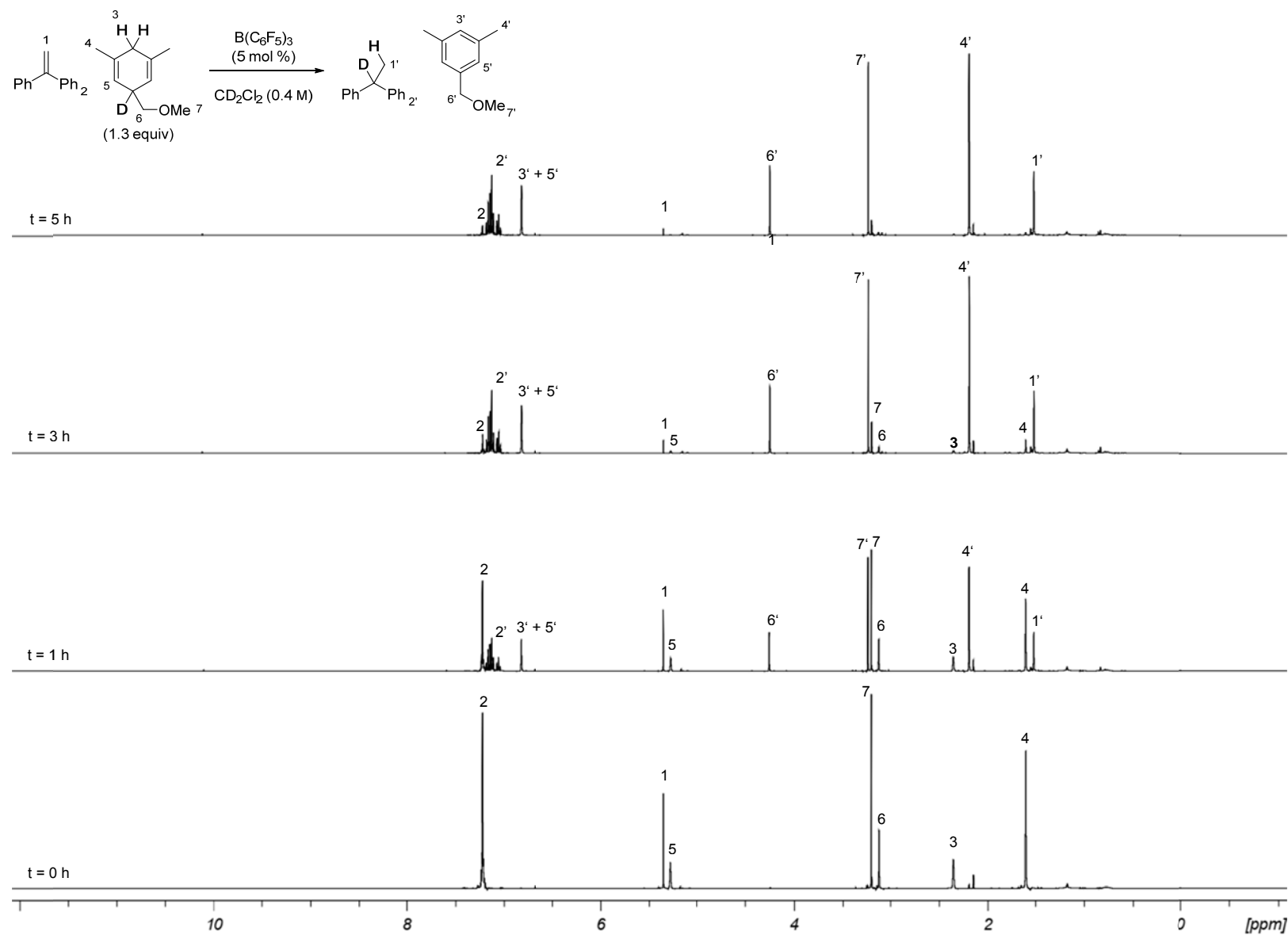
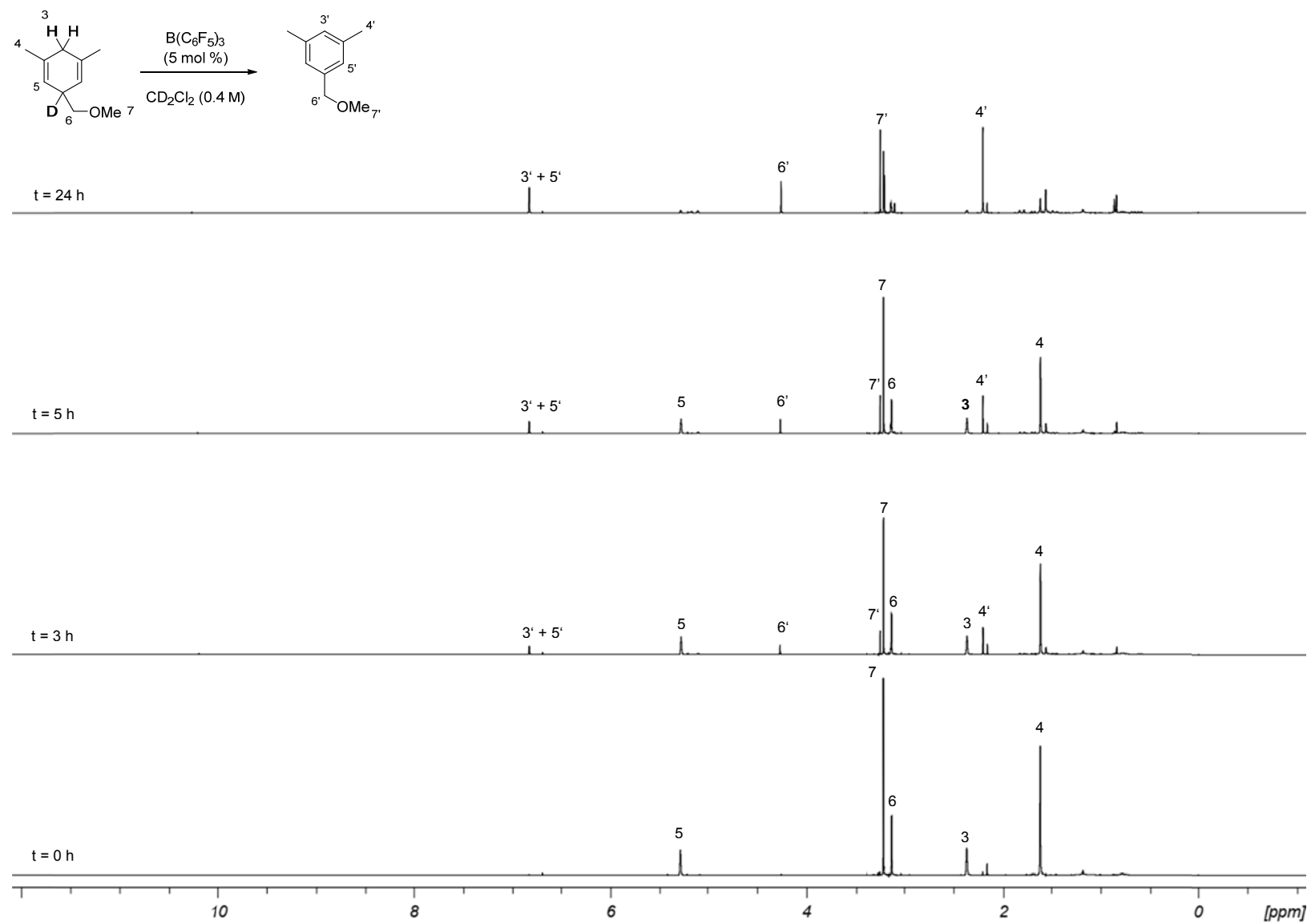


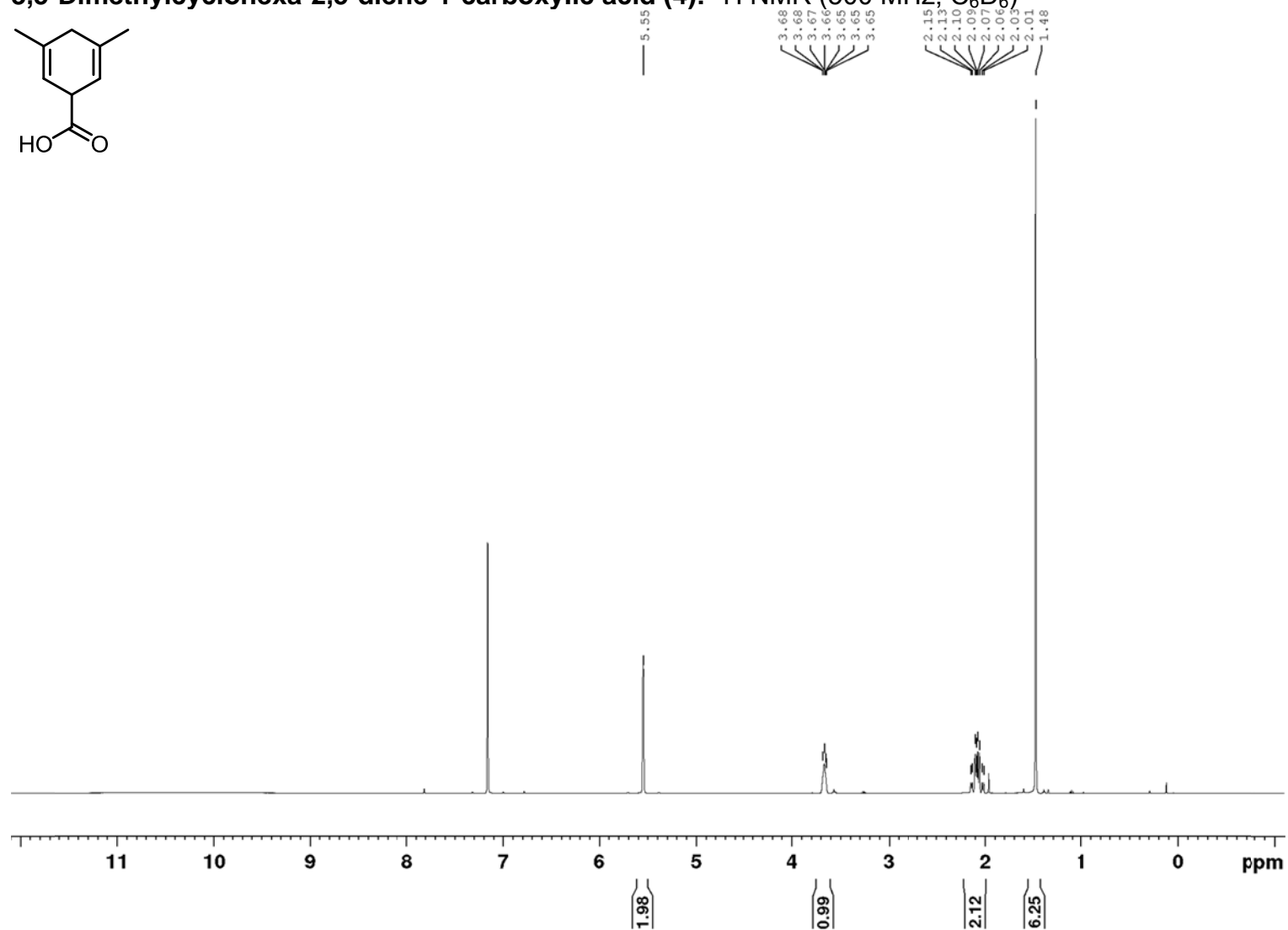
Figure S1 Unsuccessful Substrates

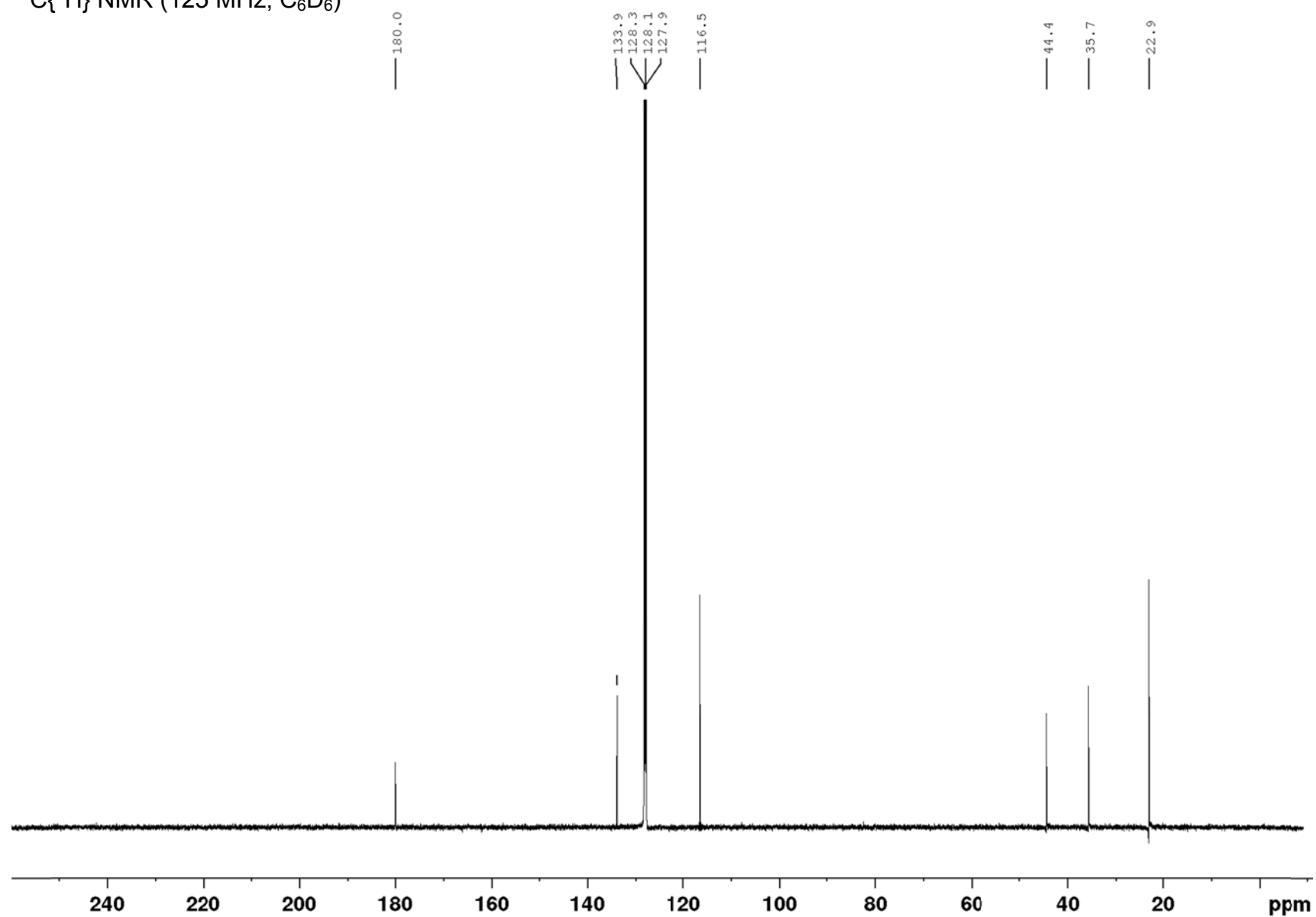
6. *In-situ* NMR Monitoring Experiments



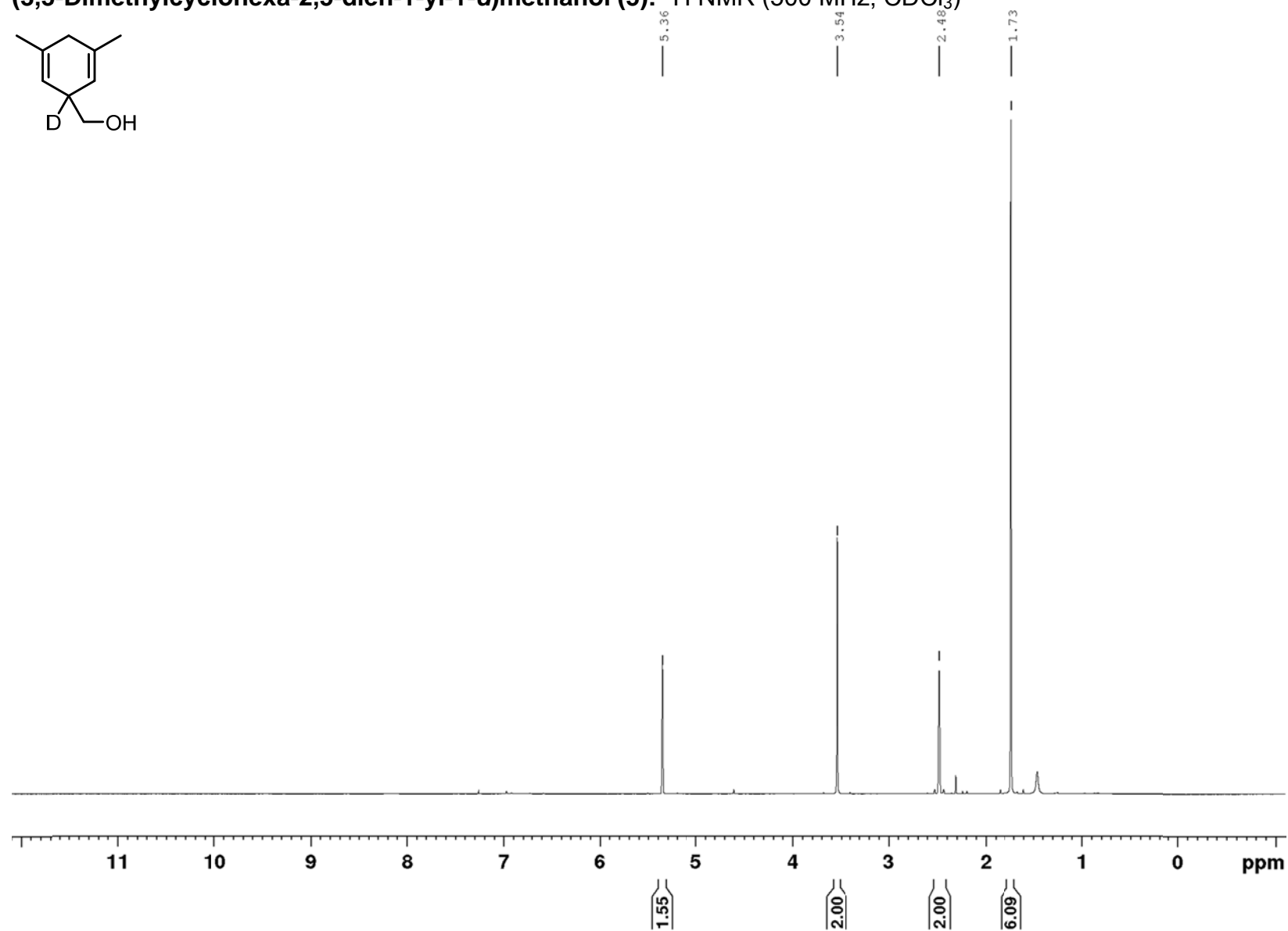
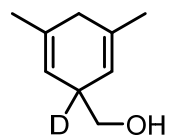


7. NMR Spectra

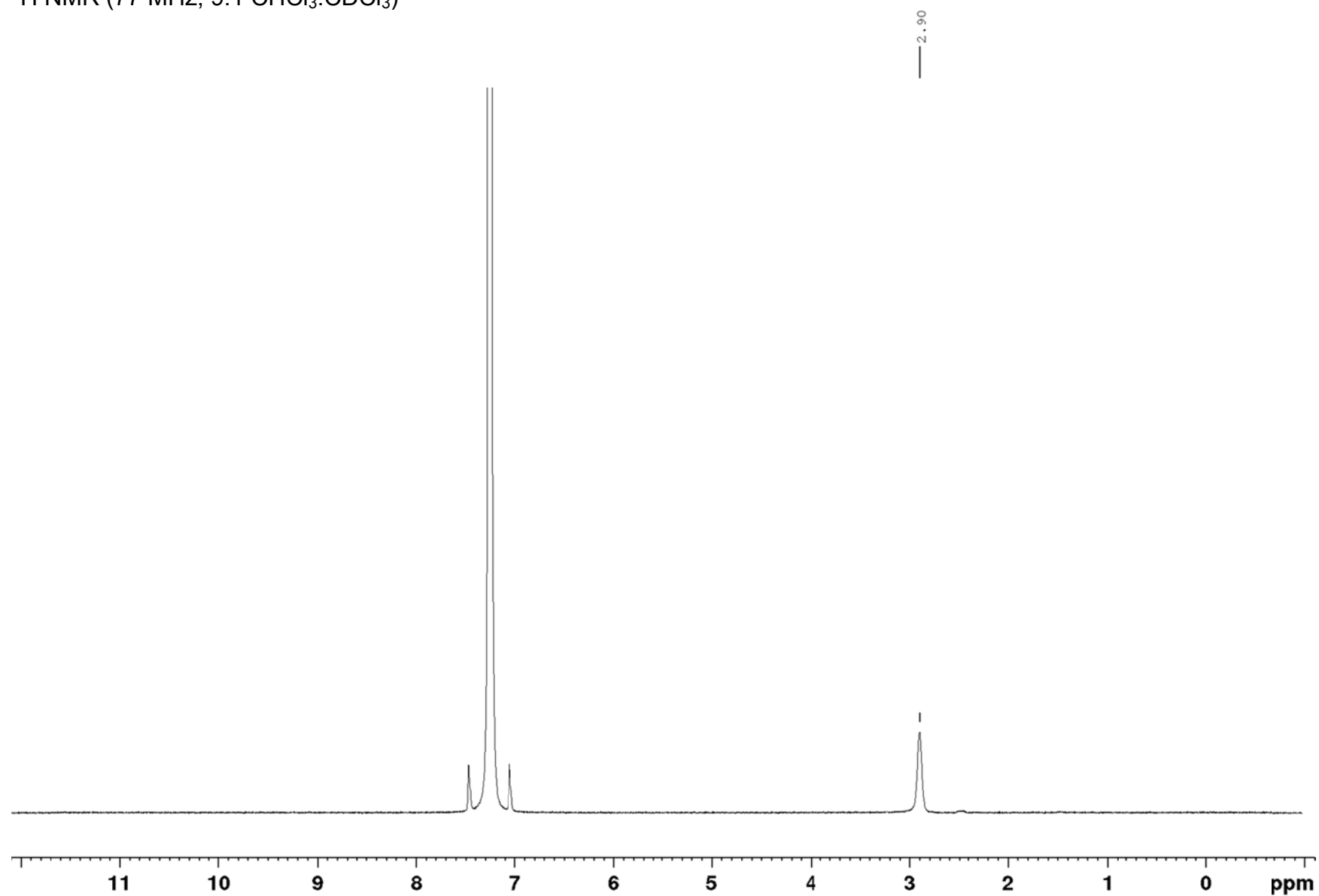
3,5-Dimethylcyclohexa-2,5-diene-1-carboxylic acid (**4**): ^1H NMR (500 MHz, C_6D_6)

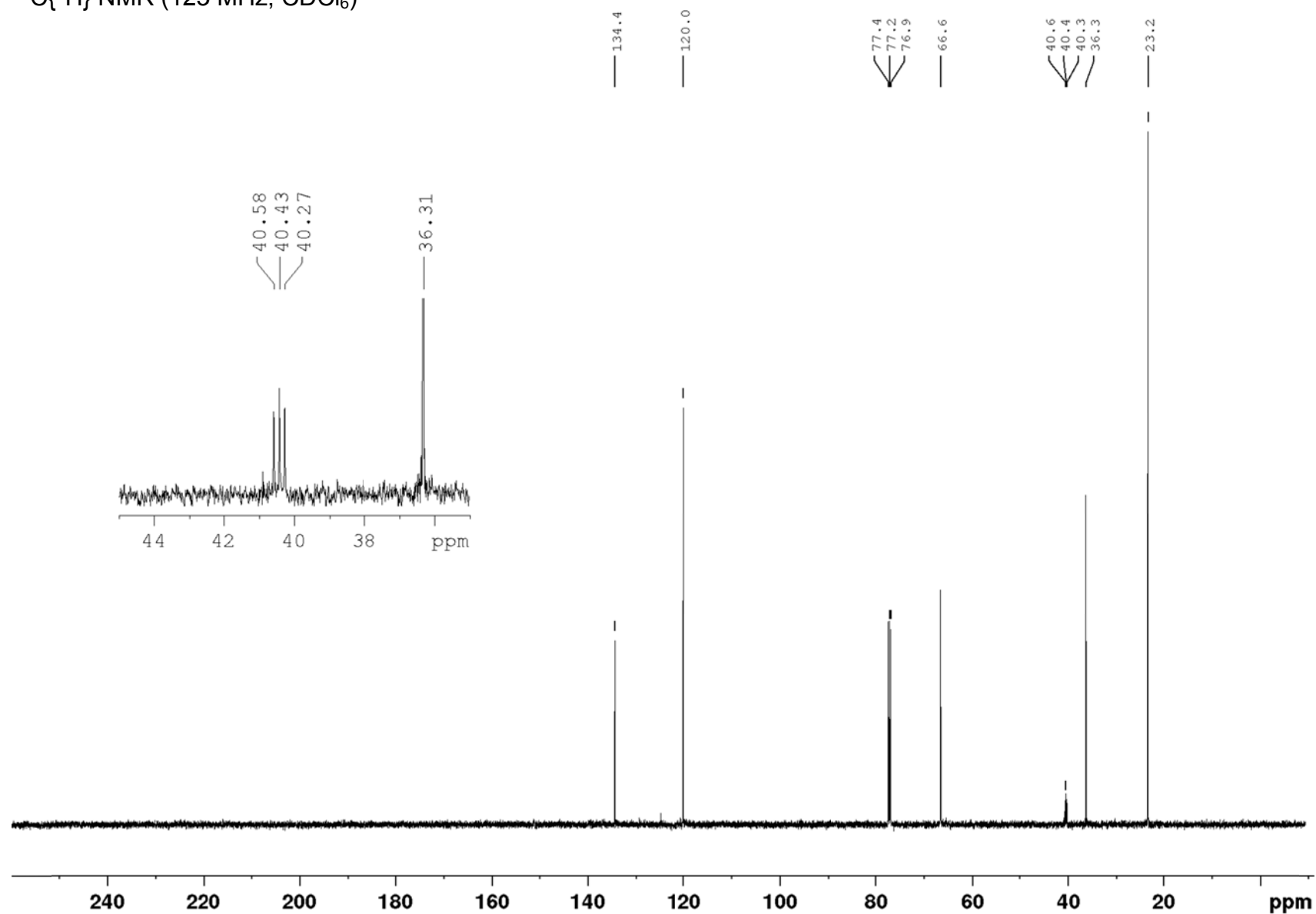
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6)

(3,5-Dimethylcyclohexa-2,5-dien-1-yl-1-*d*)methanol (**5**): ^1H NMR (500 MHz, CDCl_3)

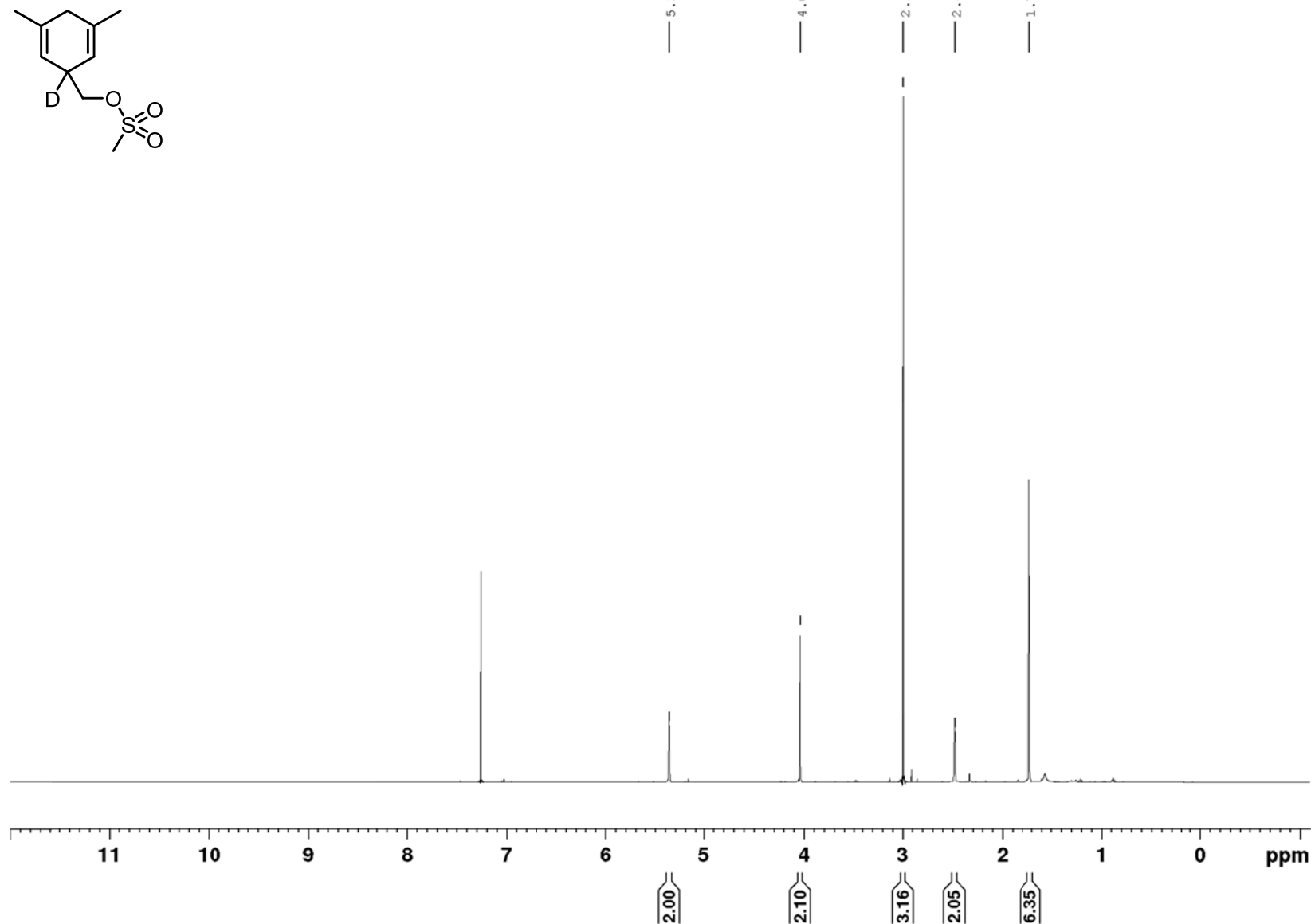


^2H NMR (77 MHz, 9:1 $\text{CHCl}_3:\text{CDCl}_3$)

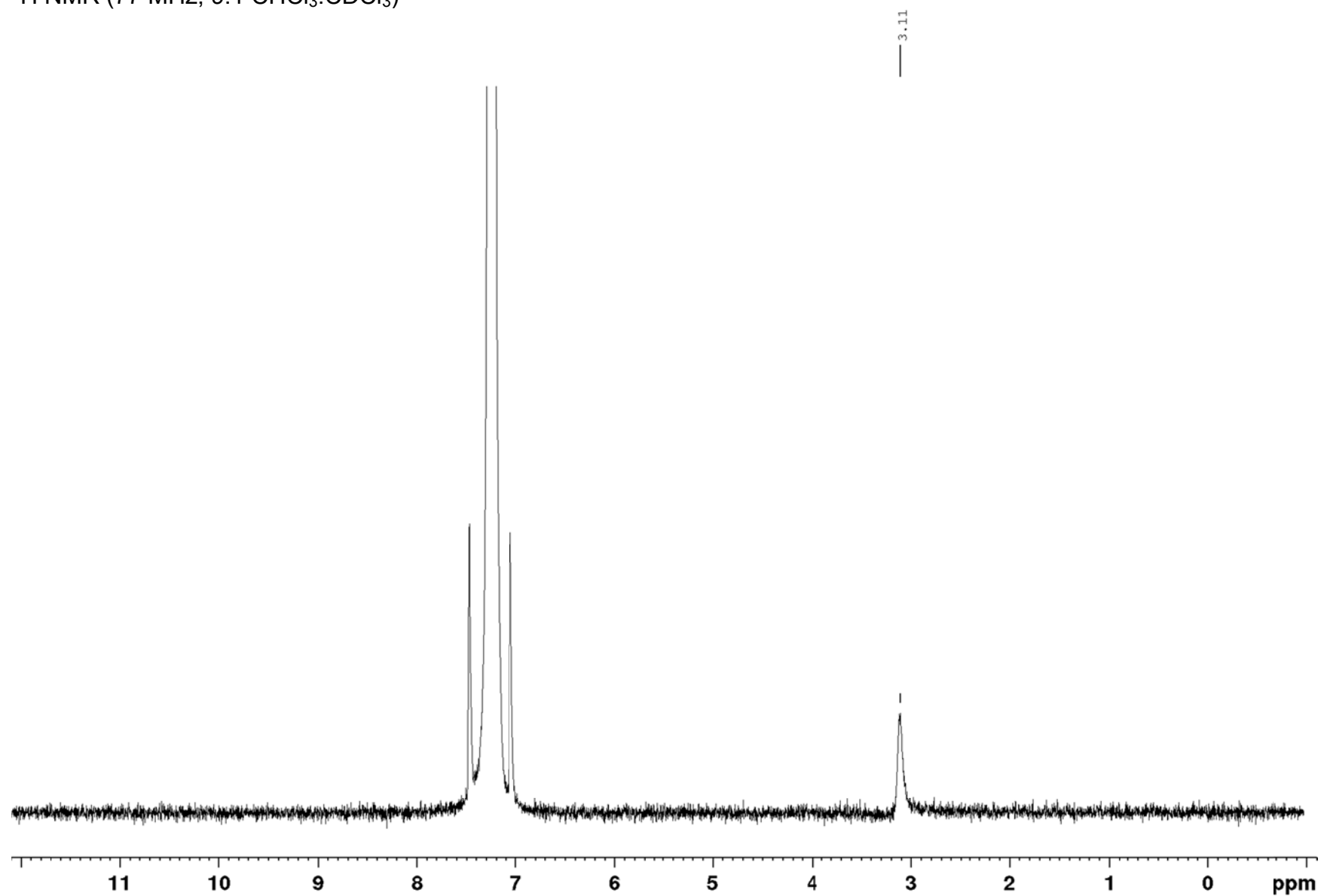


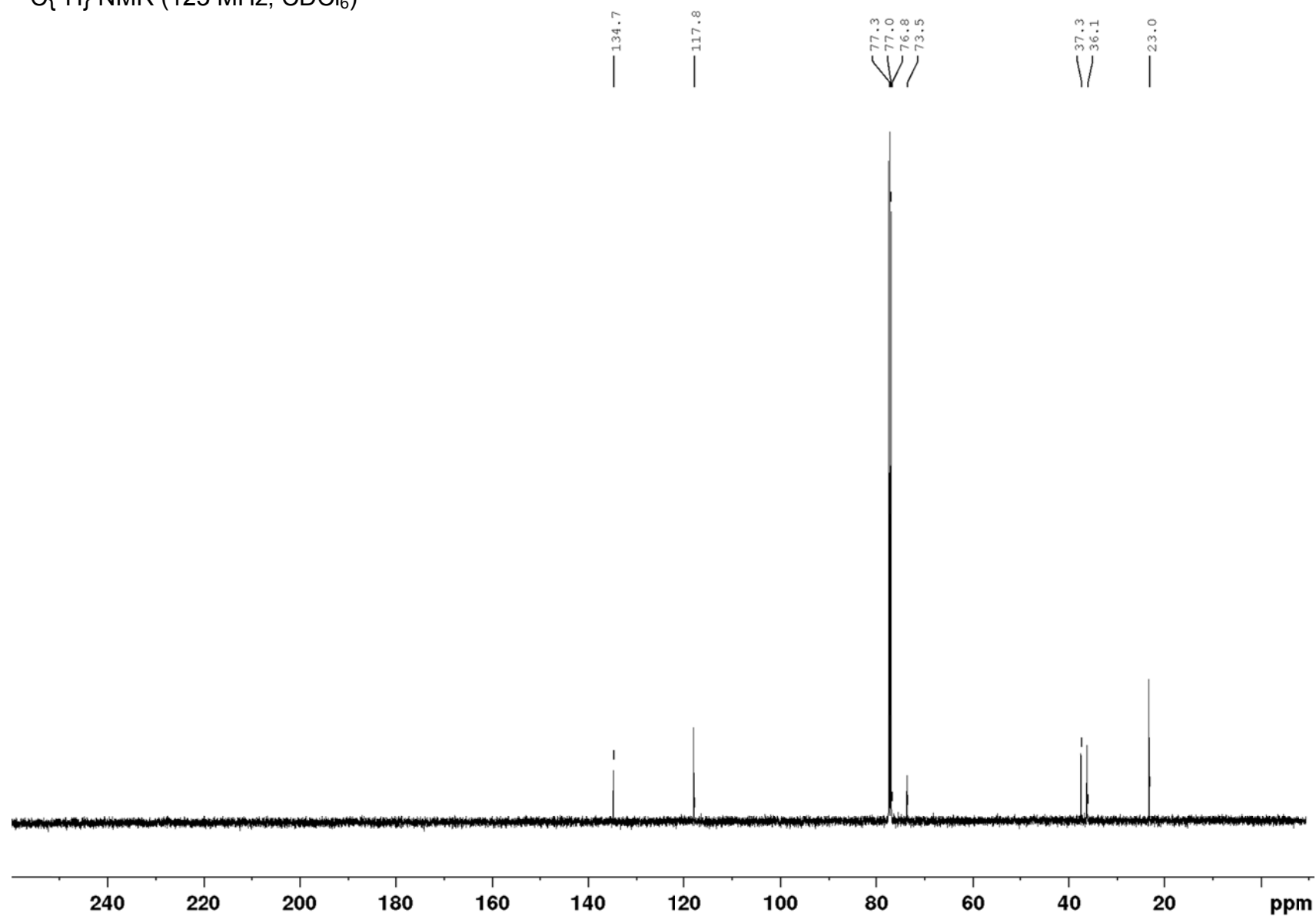
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

(3,5-dimethylcyclohexa-2,5-dien-1-yl-1-*d*)methyl methanesulfonate (**6**): ^1H NMR (500 MHz, CDCl_3)

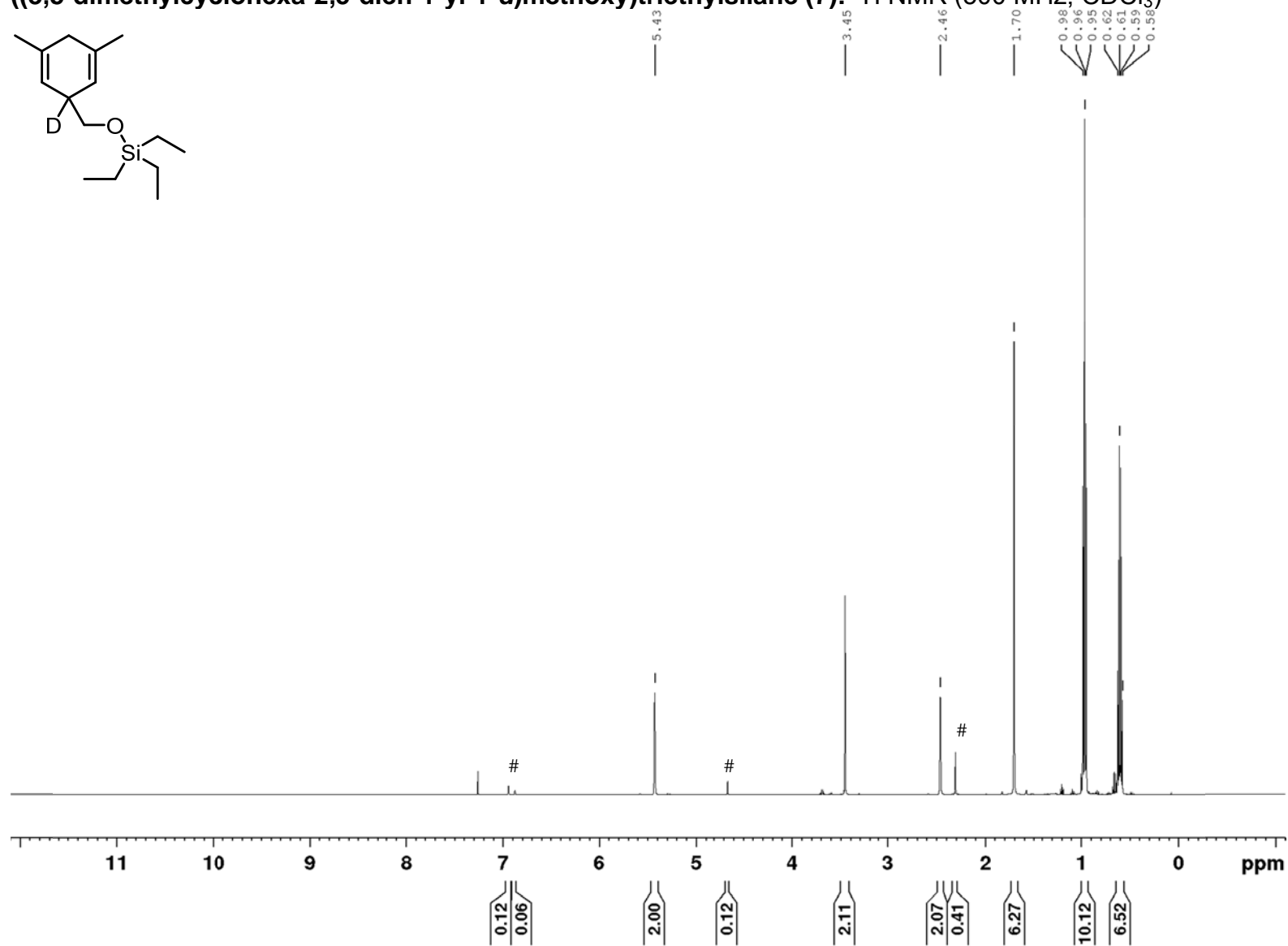


^2H NMR (77 MHz, 9:1 $\text{CHCl}_3:\text{CDCl}_3$)



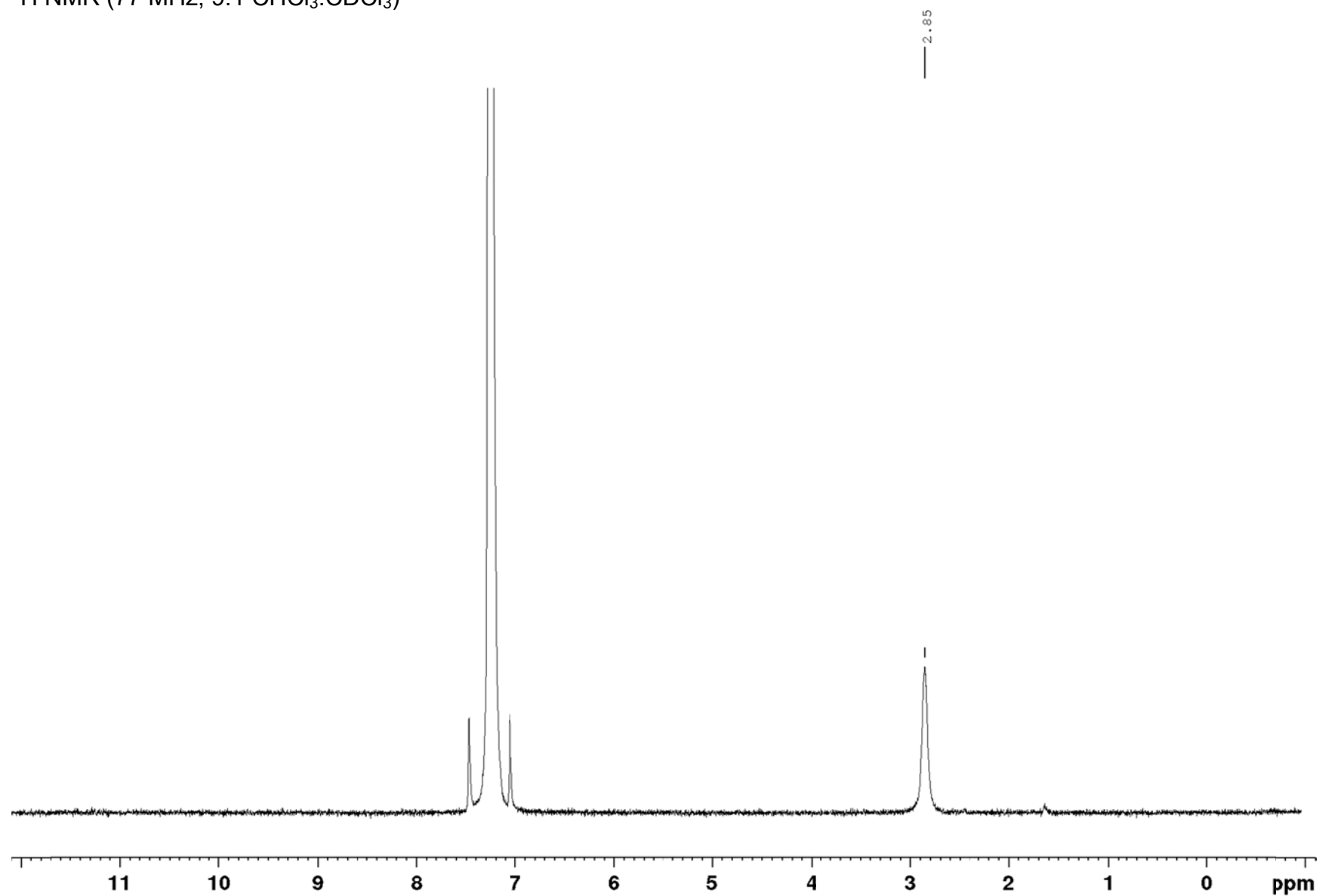
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

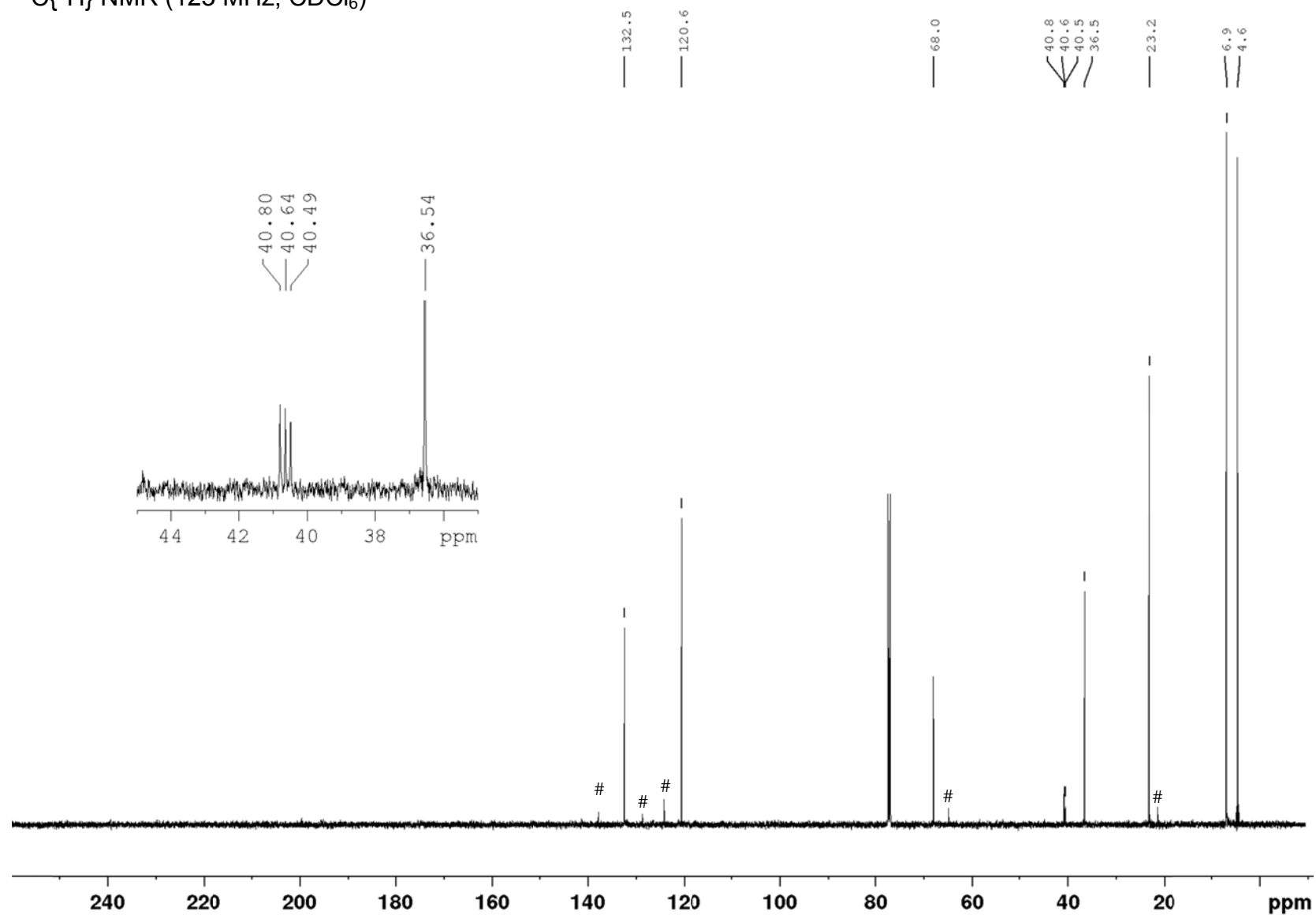
((3,5-dimethylcyclohexa-2,5-dien-1-yl-1-*d*)methoxy)triethylsilane (7): ^1H NMR (500 MHz, CDCl_3)



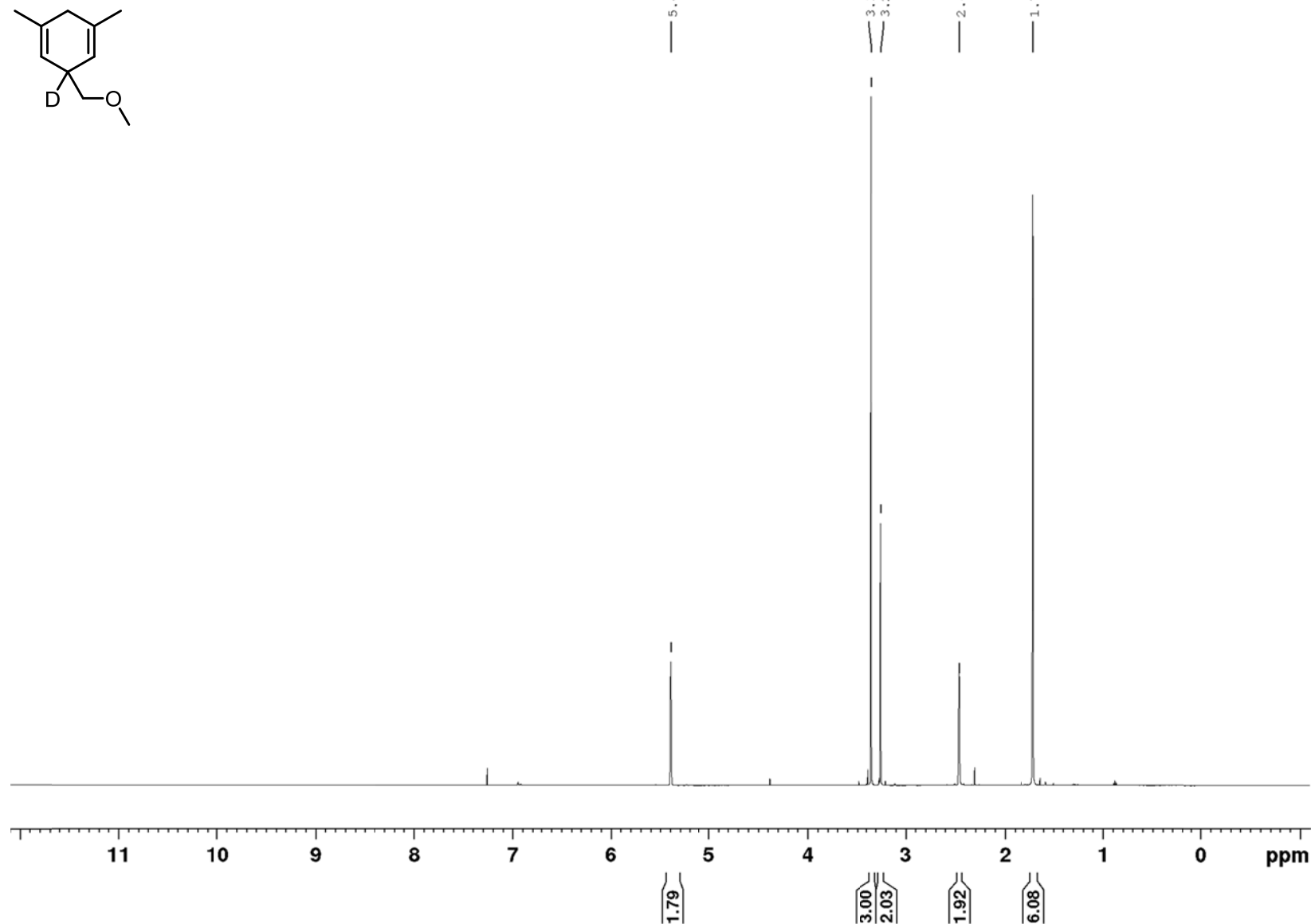
#Peaks corresponding to the aromatised compound

^2H NMR (77 MHz, 9:1 $\text{CHCl}_3:\text{CDCl}_3$)

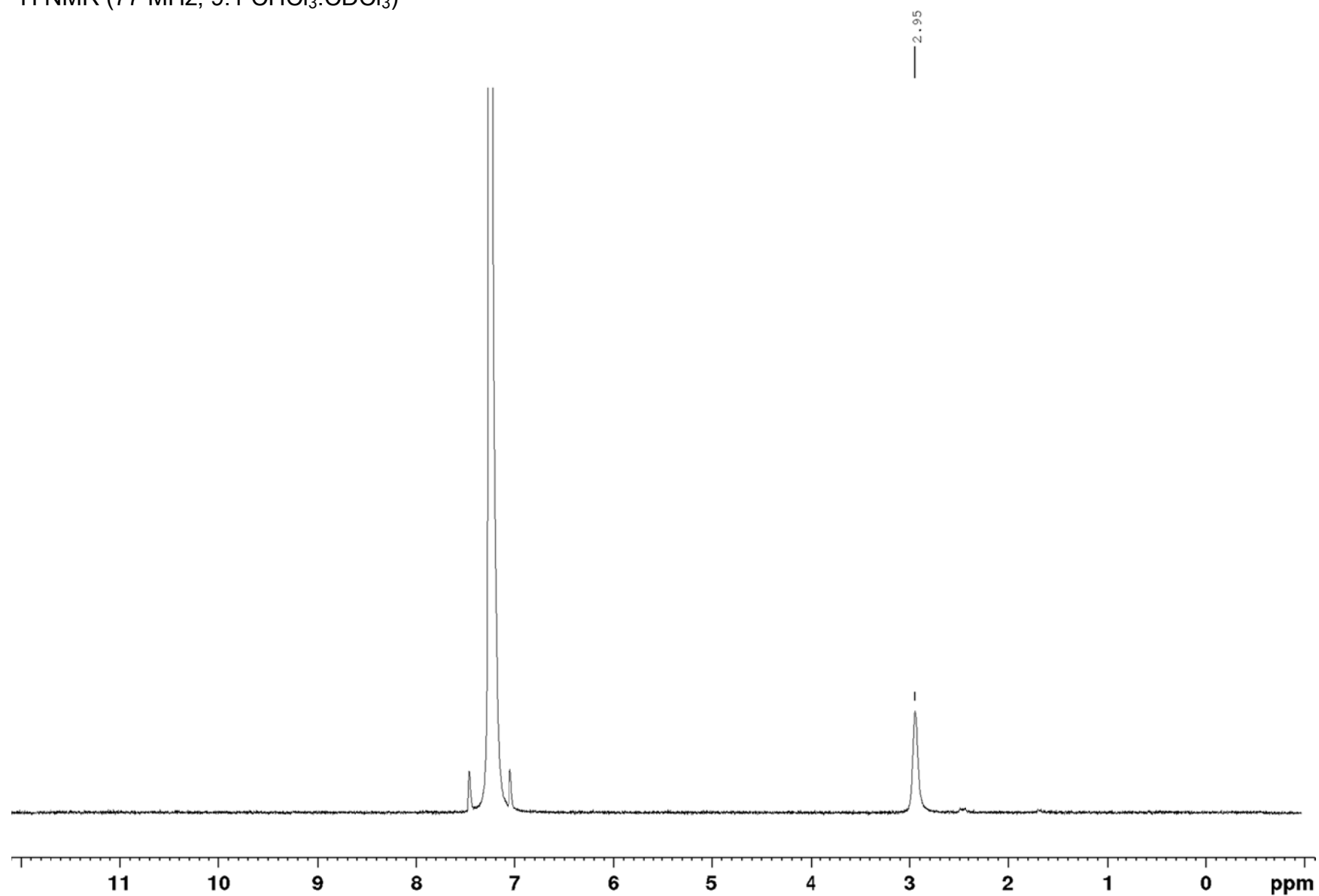


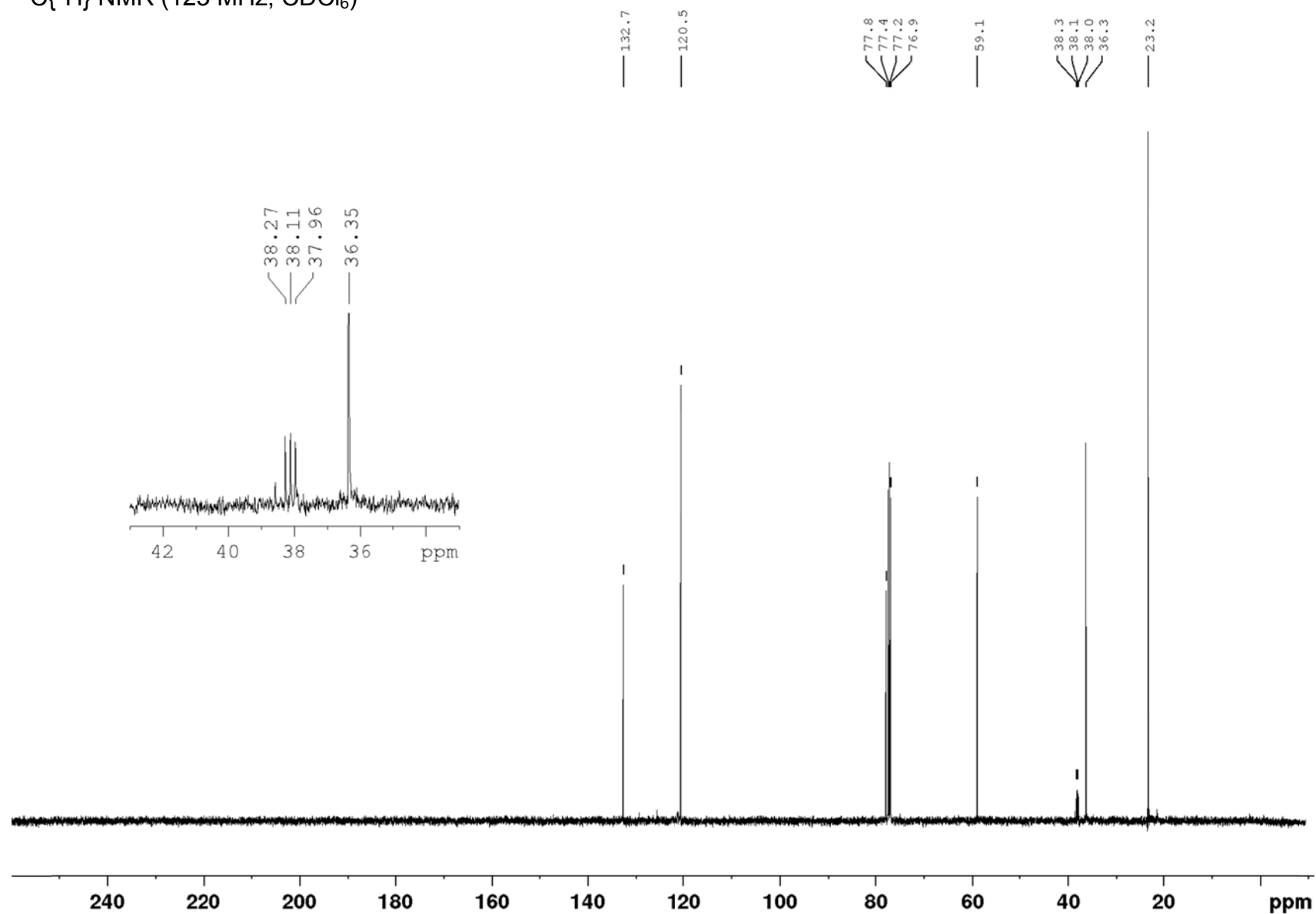
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

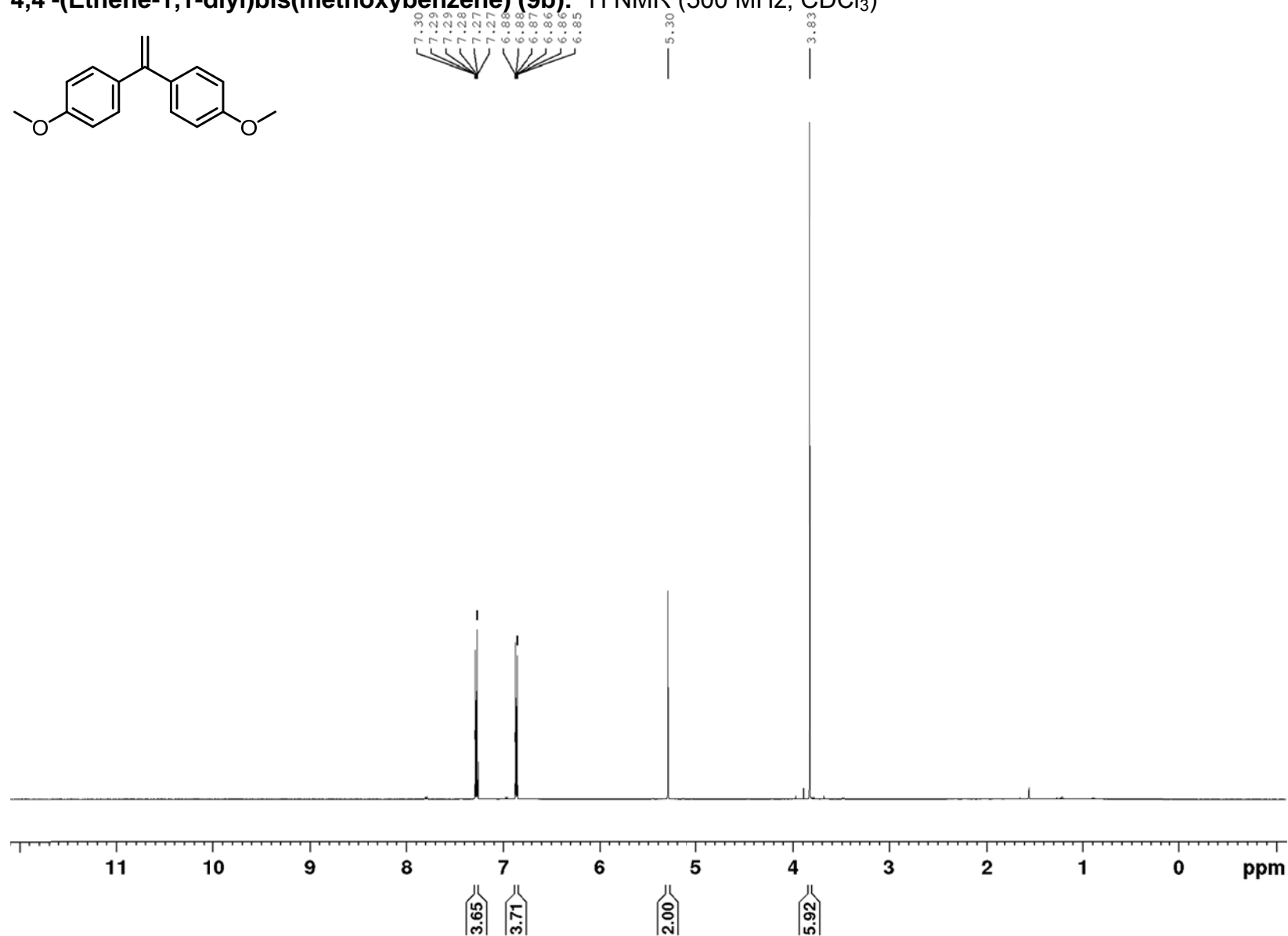
#Peaks corresponding to the aromatised compound

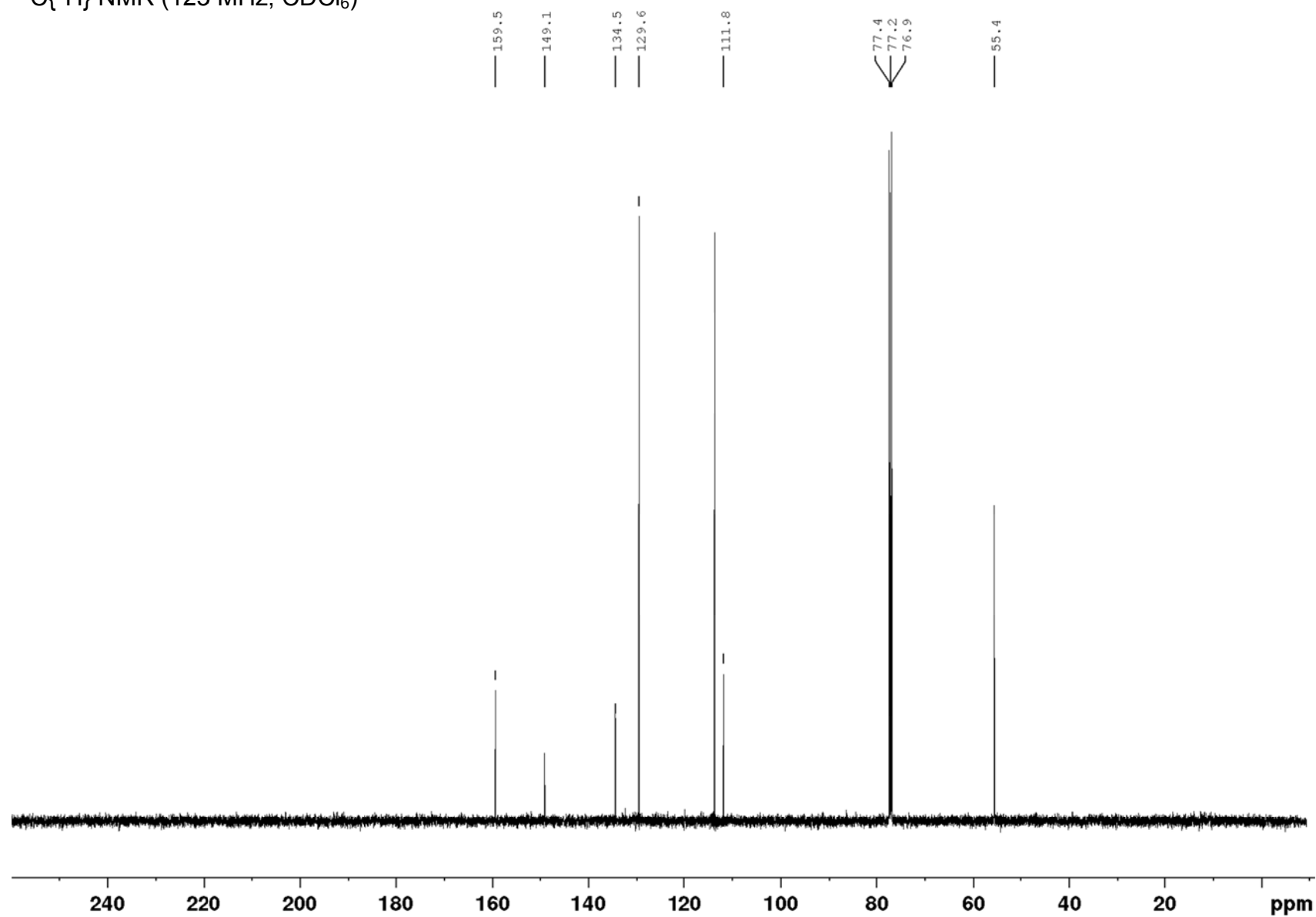
3-(Methoxymethyl)-1,5-dimethylcyclohexa-1,4-diene-3-*d* (8): ^1H NMR (500 MHz, CDCl_3)

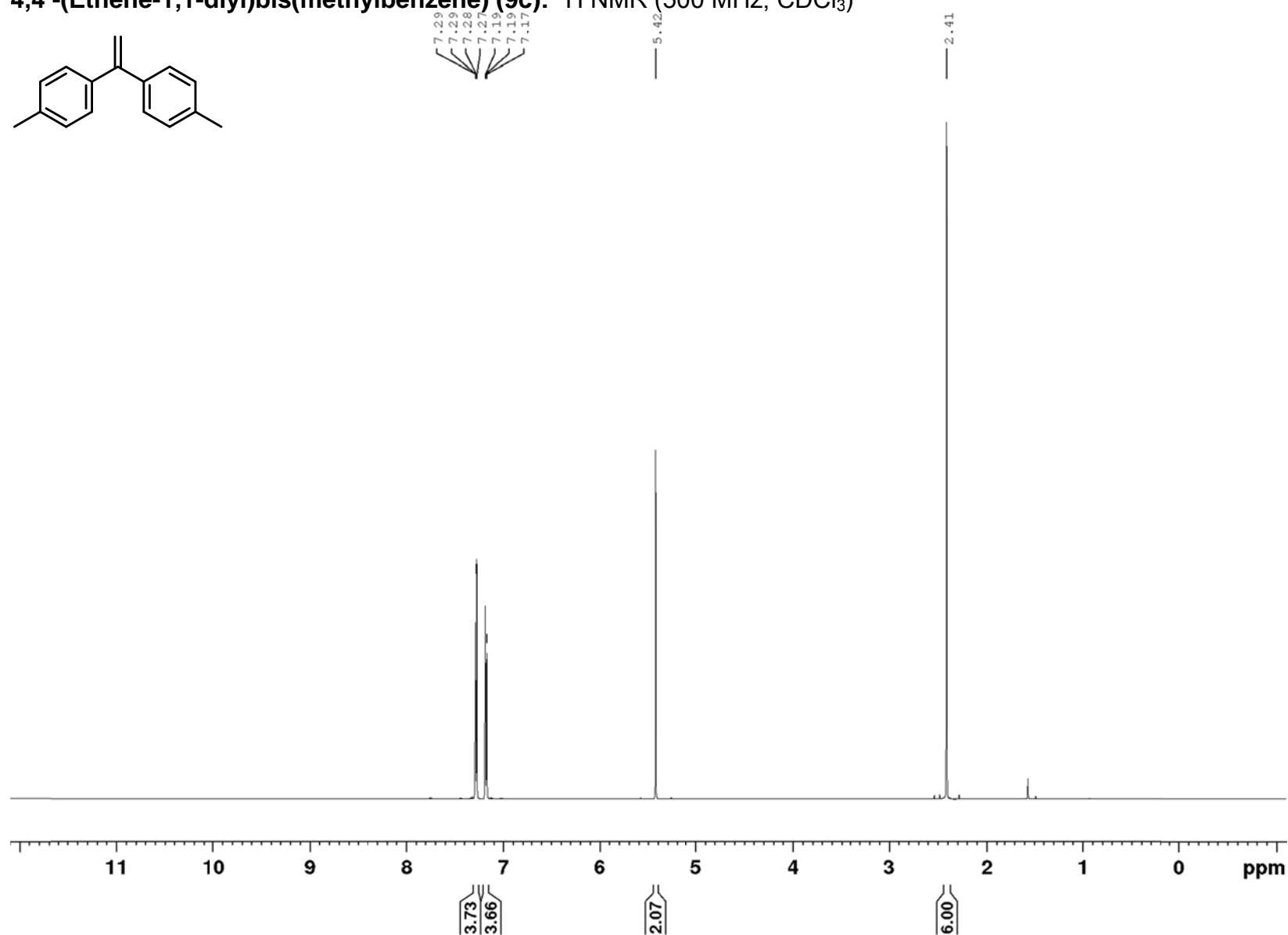
^2H NMR (77 MHz, 9:1 $\text{CHCl}_3:\text{CDCl}_3$)

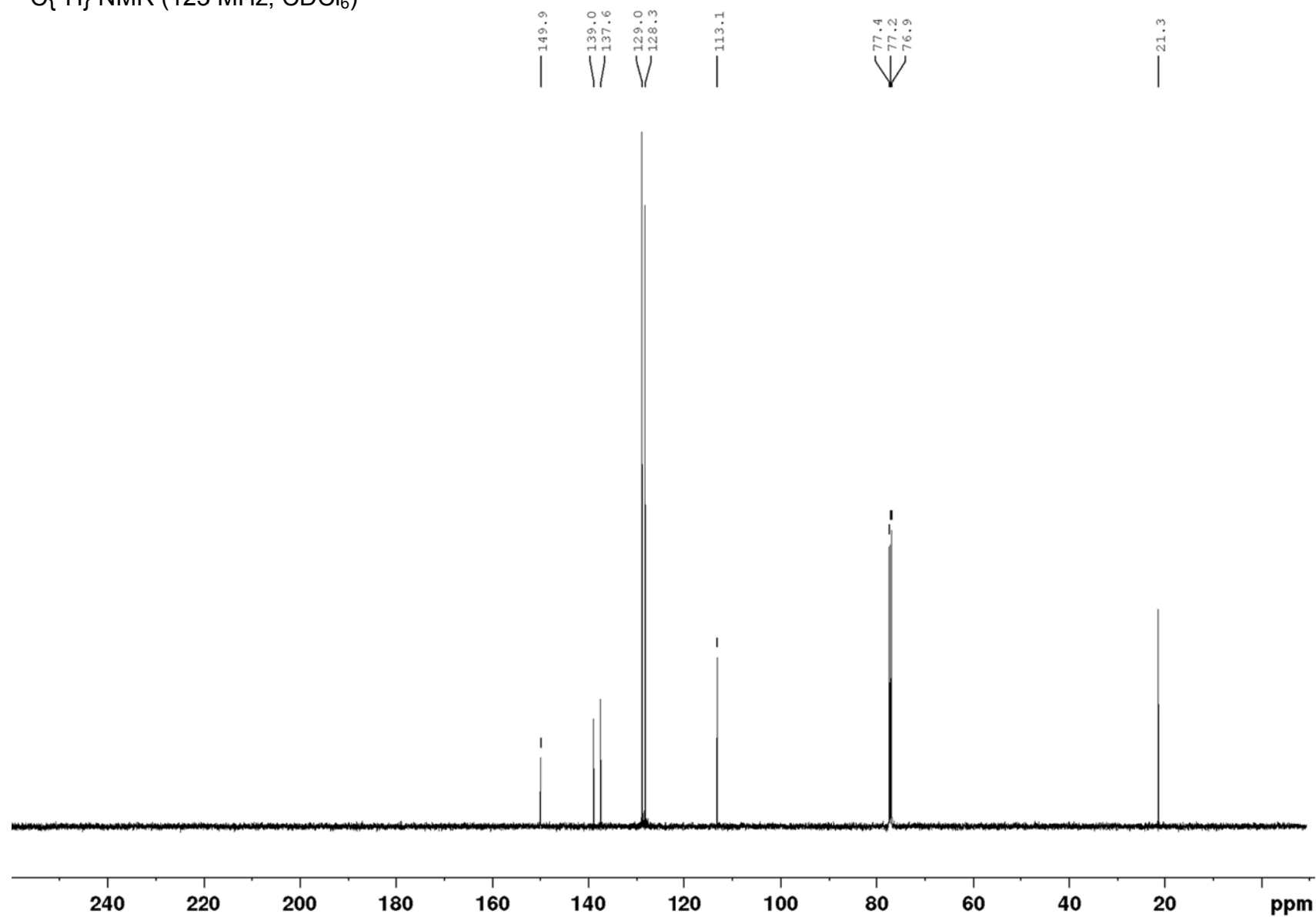


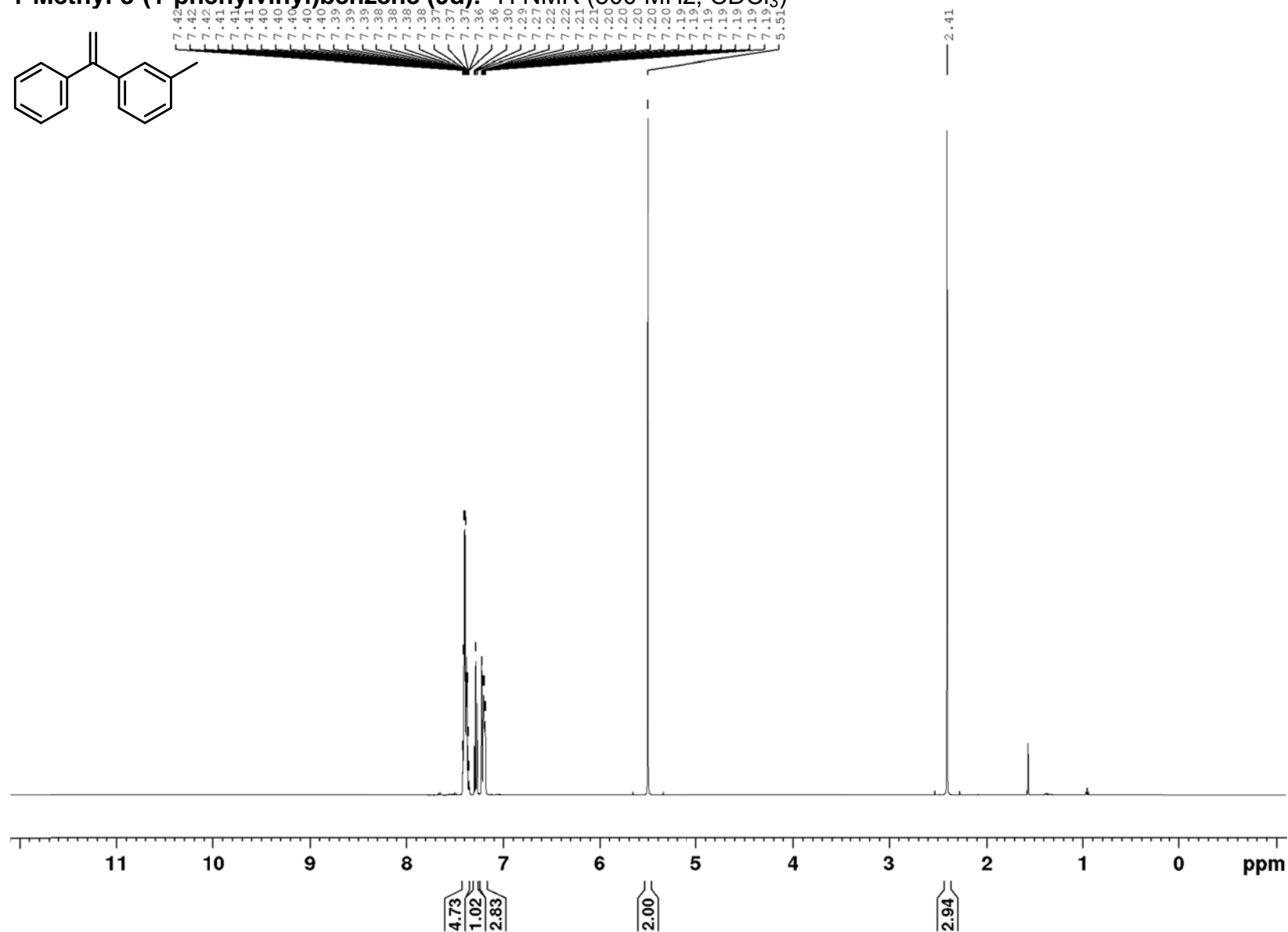
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

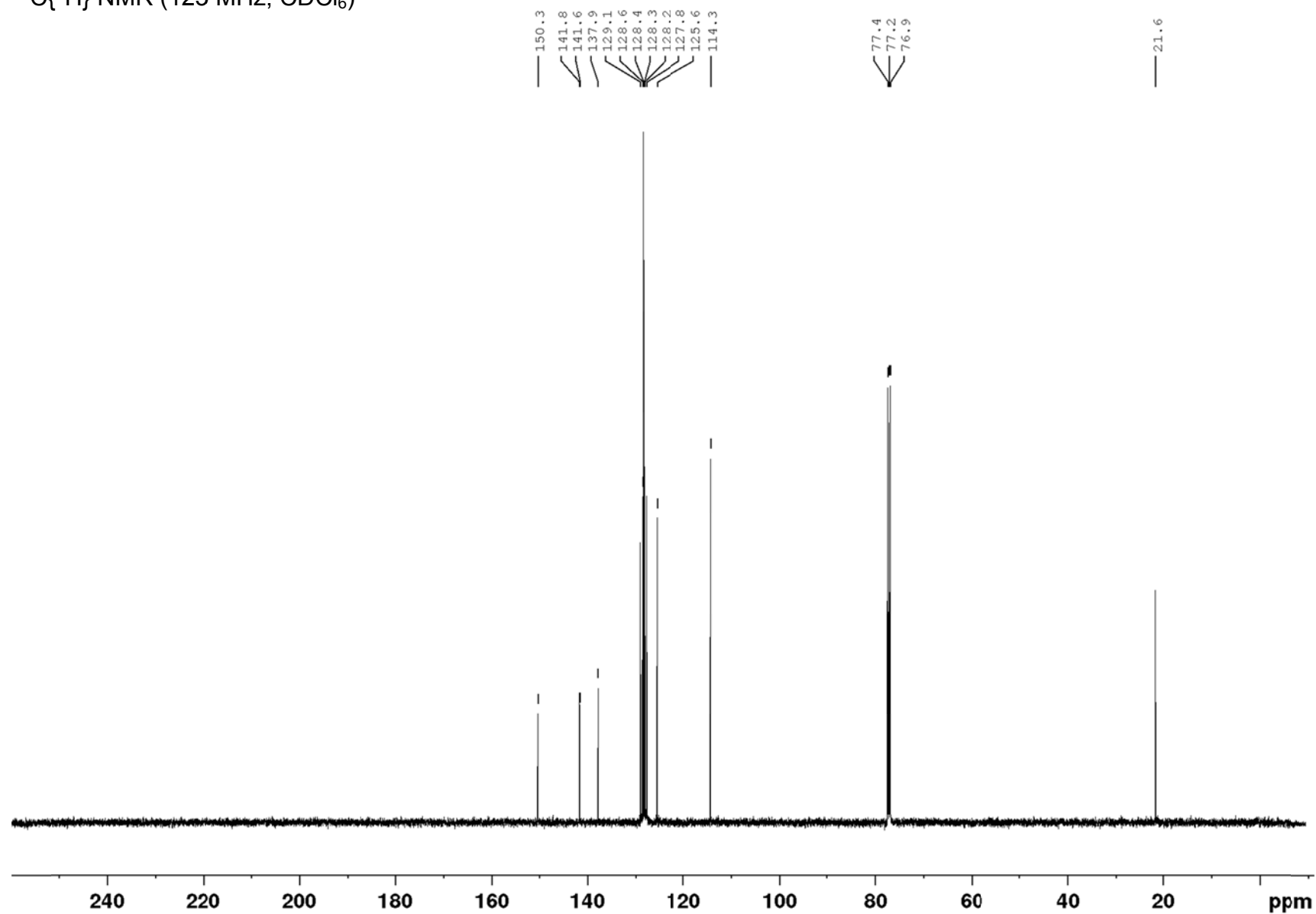
4,4'-(Ethene-1,1-diyl)bis(methoxybenzene) (9b): ^1H NMR (500 MHz, CDCl_3)

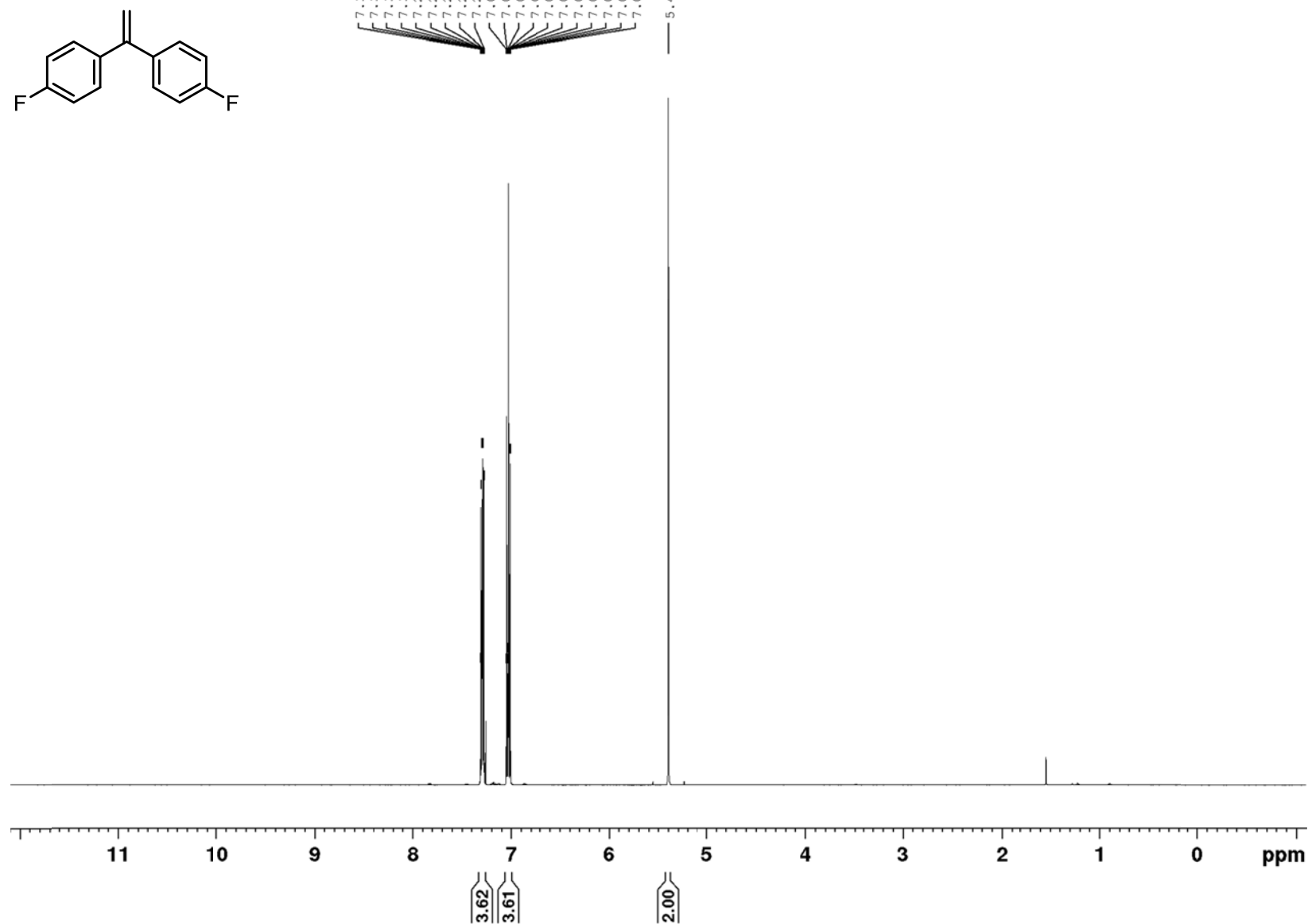
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

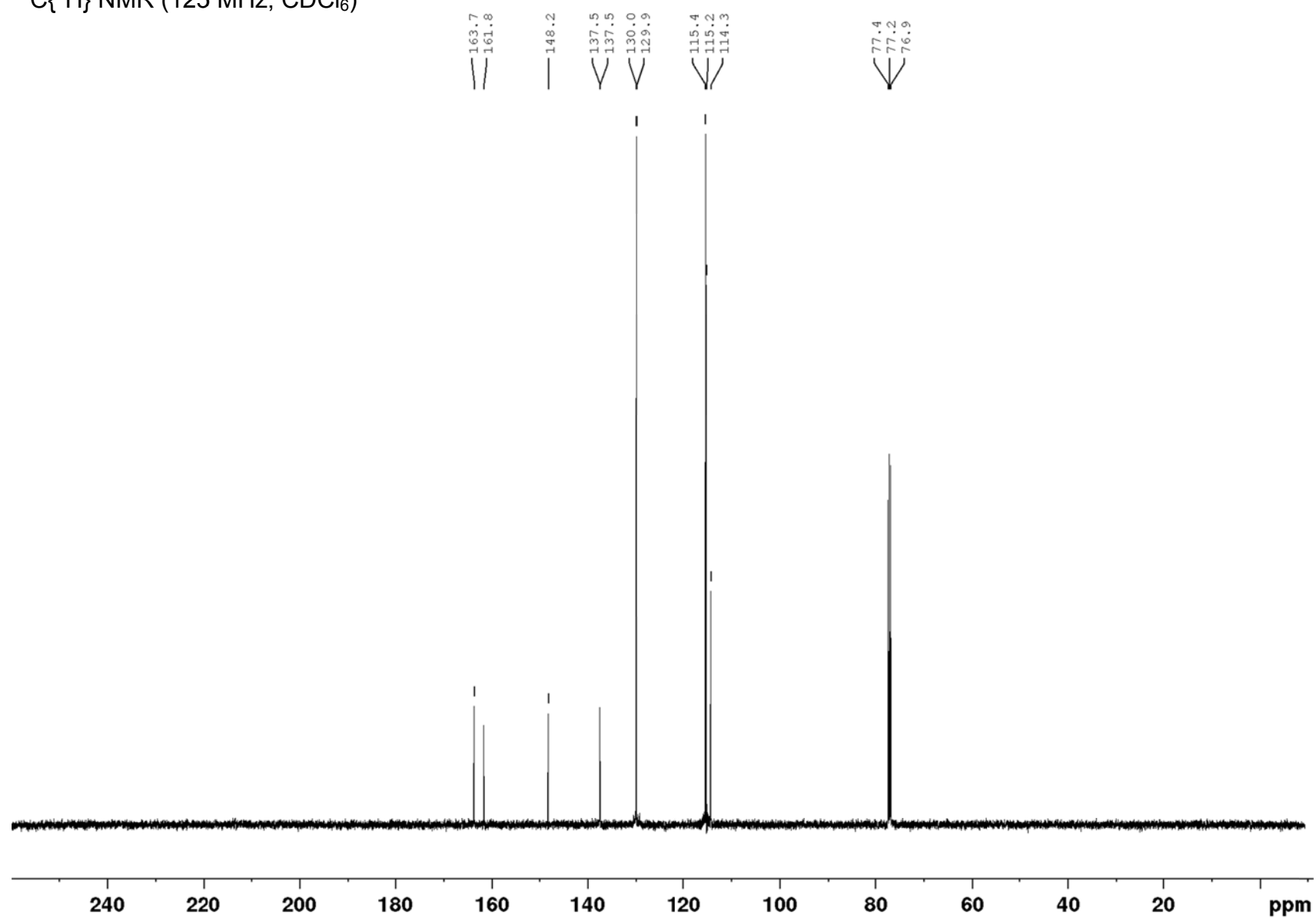
4,4'-(Ethene-1,1-diyl)bis(methylbenzene) (9c): ^1H NMR (500 MHz, CDCl_3)

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

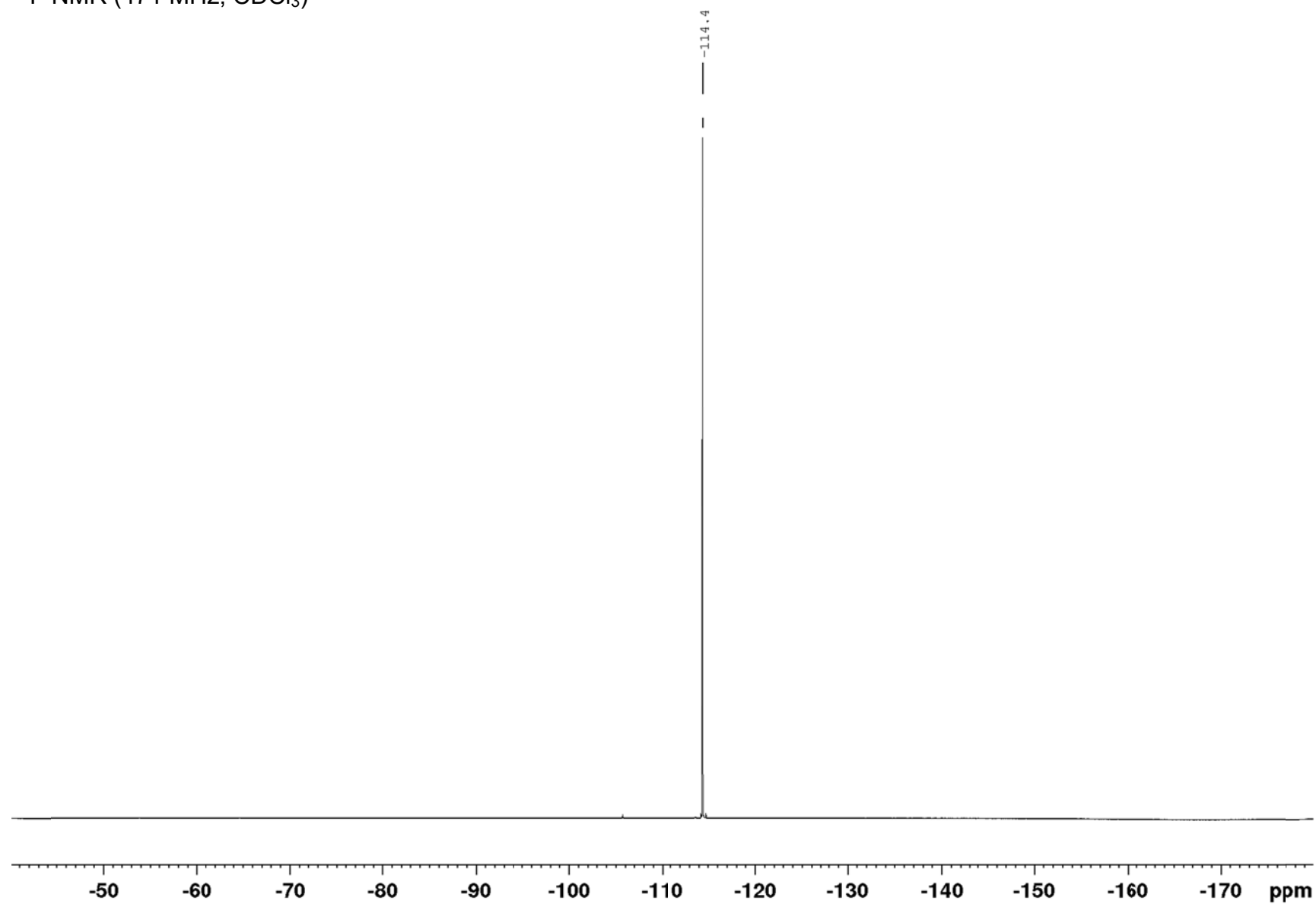
1-Methyl-3-(1-phenylvinyl)benzene (9d): ^1H NMR (500 MHz, CDCl_3)

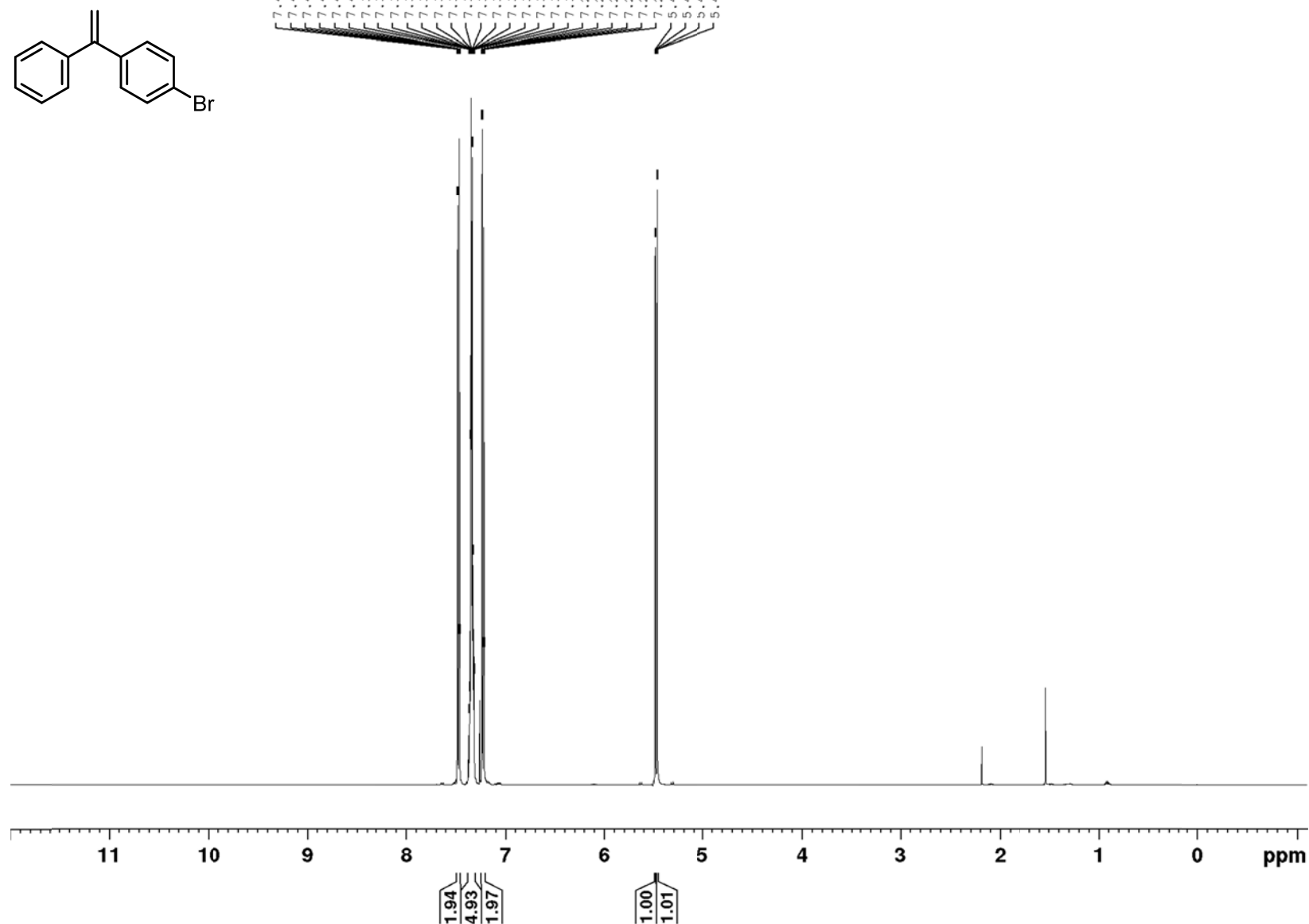
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

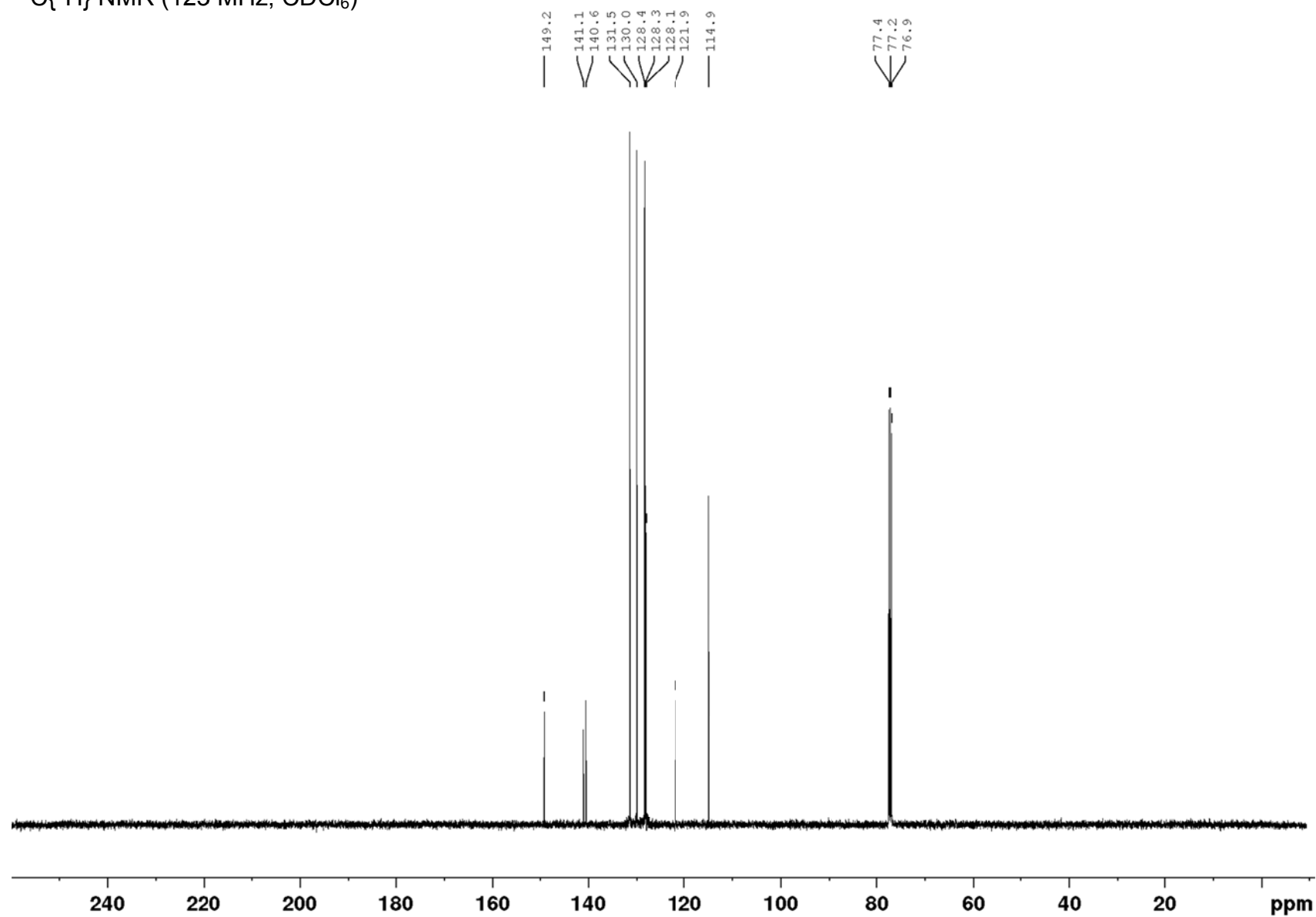
4,4'-(Ethene-1,1-diyl)bis(fluorobenzene) (9e): ^1H NMR (500 MHz, CDCl_3)

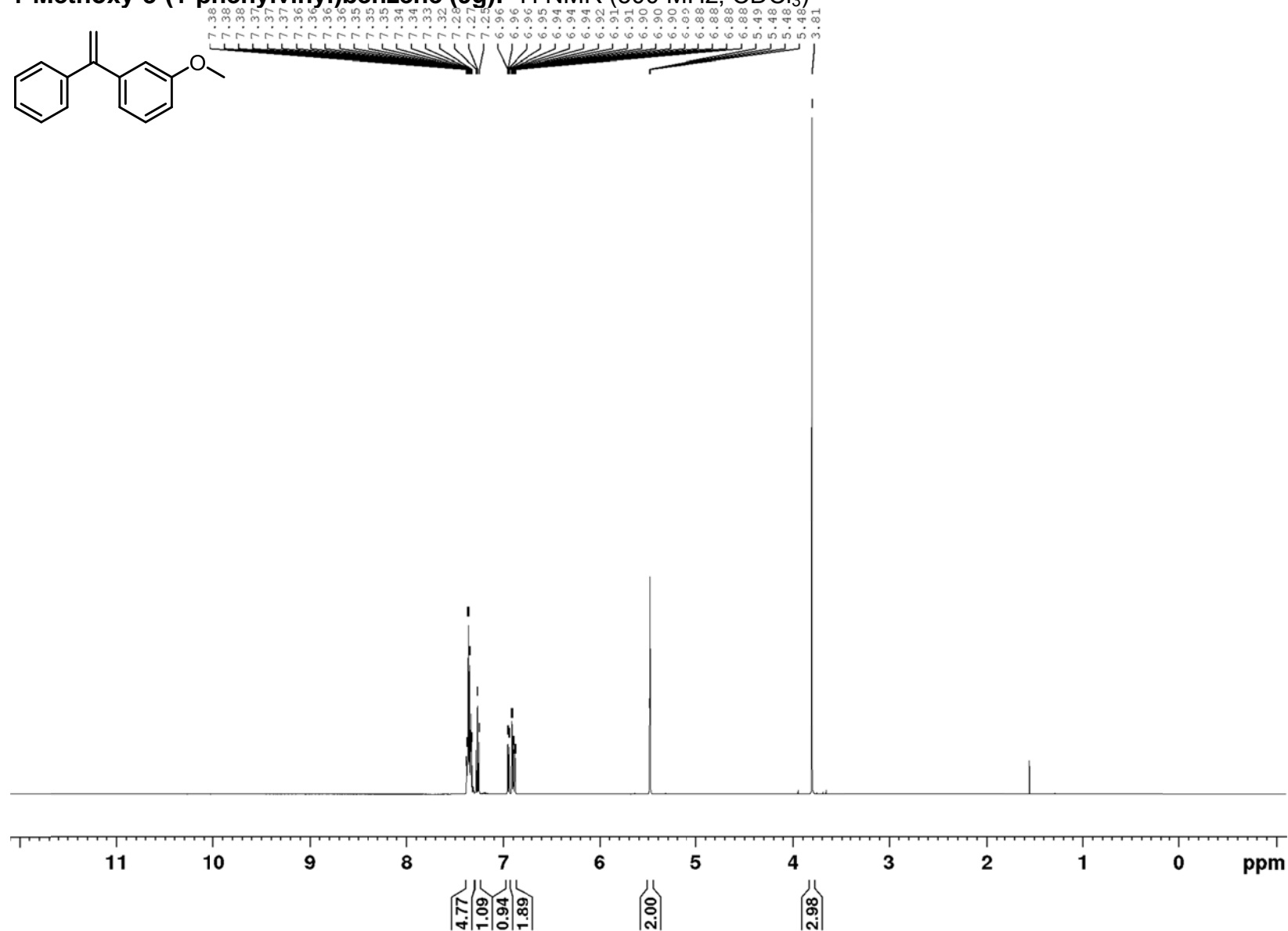
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

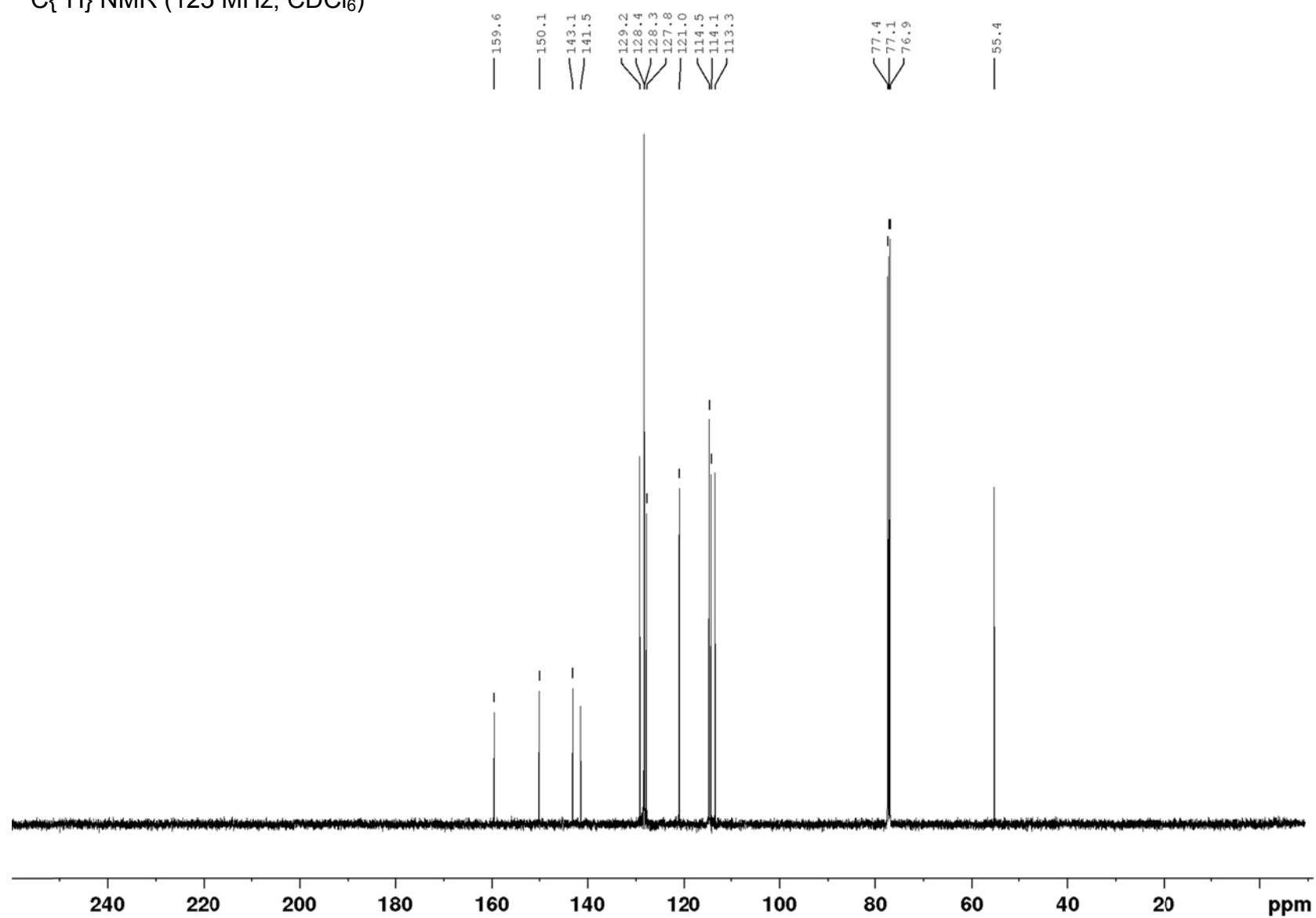
^{19}F NMR (471 MHz, CDCl_3)



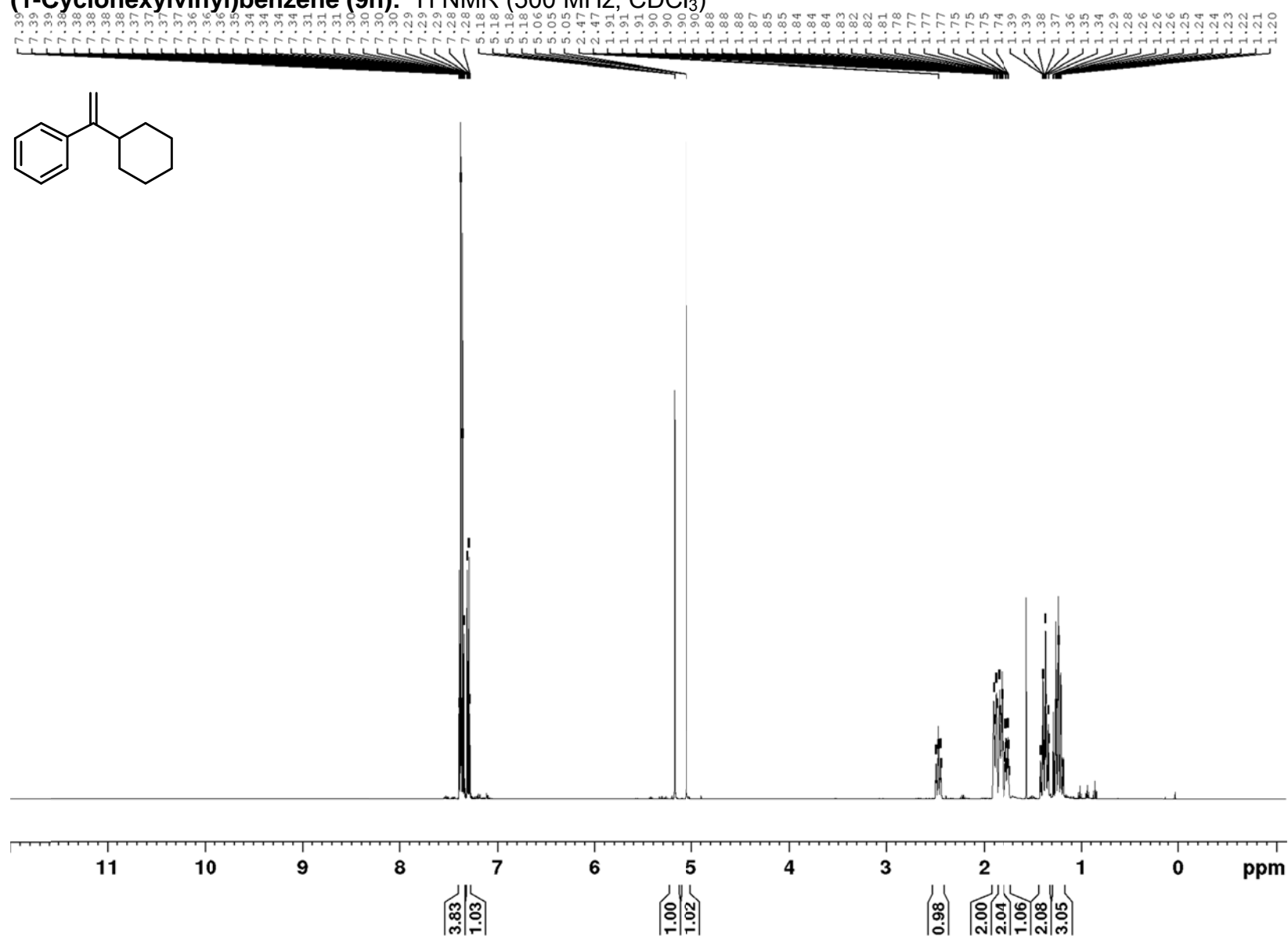
1-Bromo-4-(1-phenylvinyl)benzene (9f): ^1H NMR (500 MHz, CDCl_3)

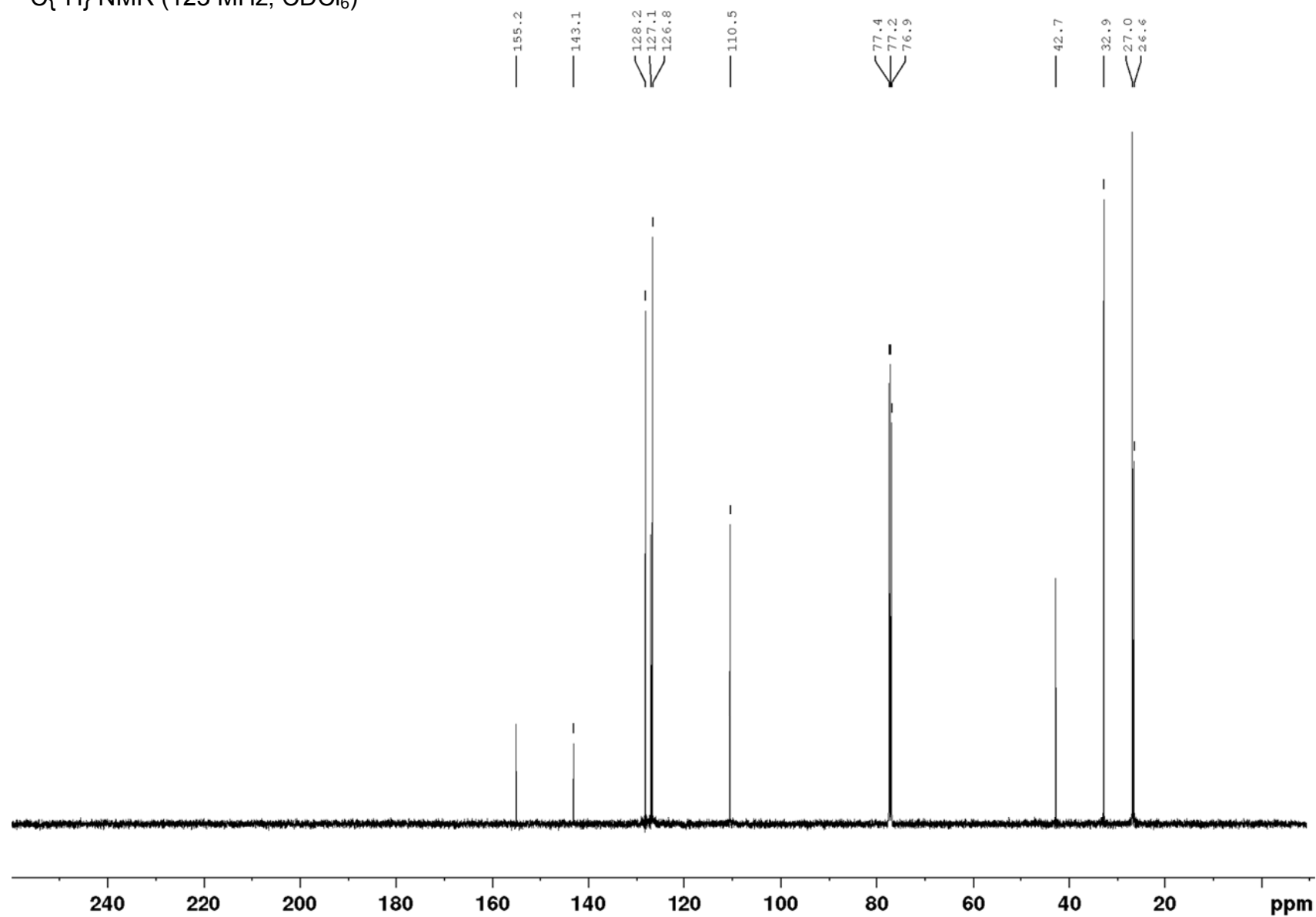
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

1-Methoxy-3-(1-phenylvinyl)benzene (9g): ^1H NMR (500 MHz, CDCl_3)

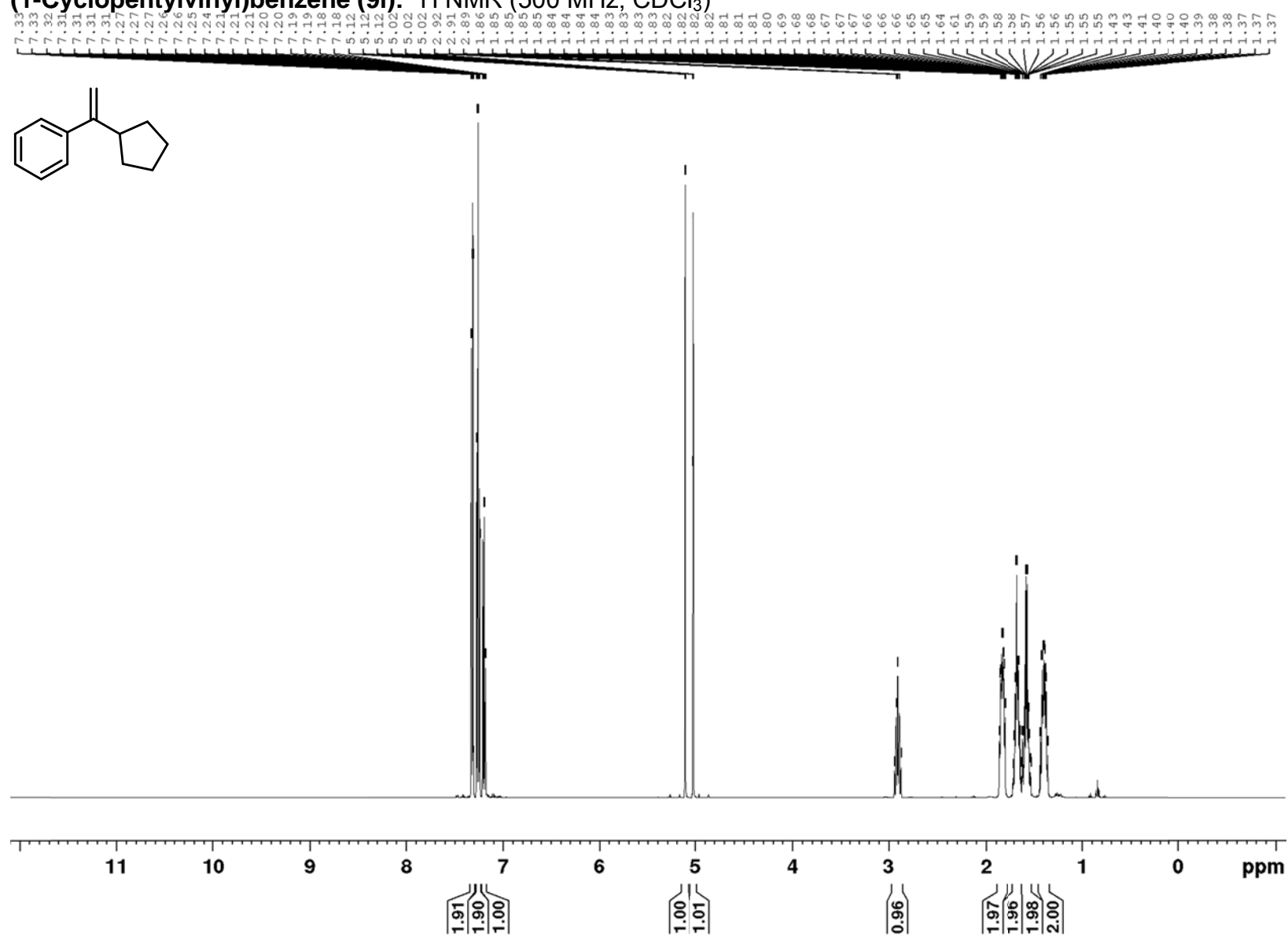
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

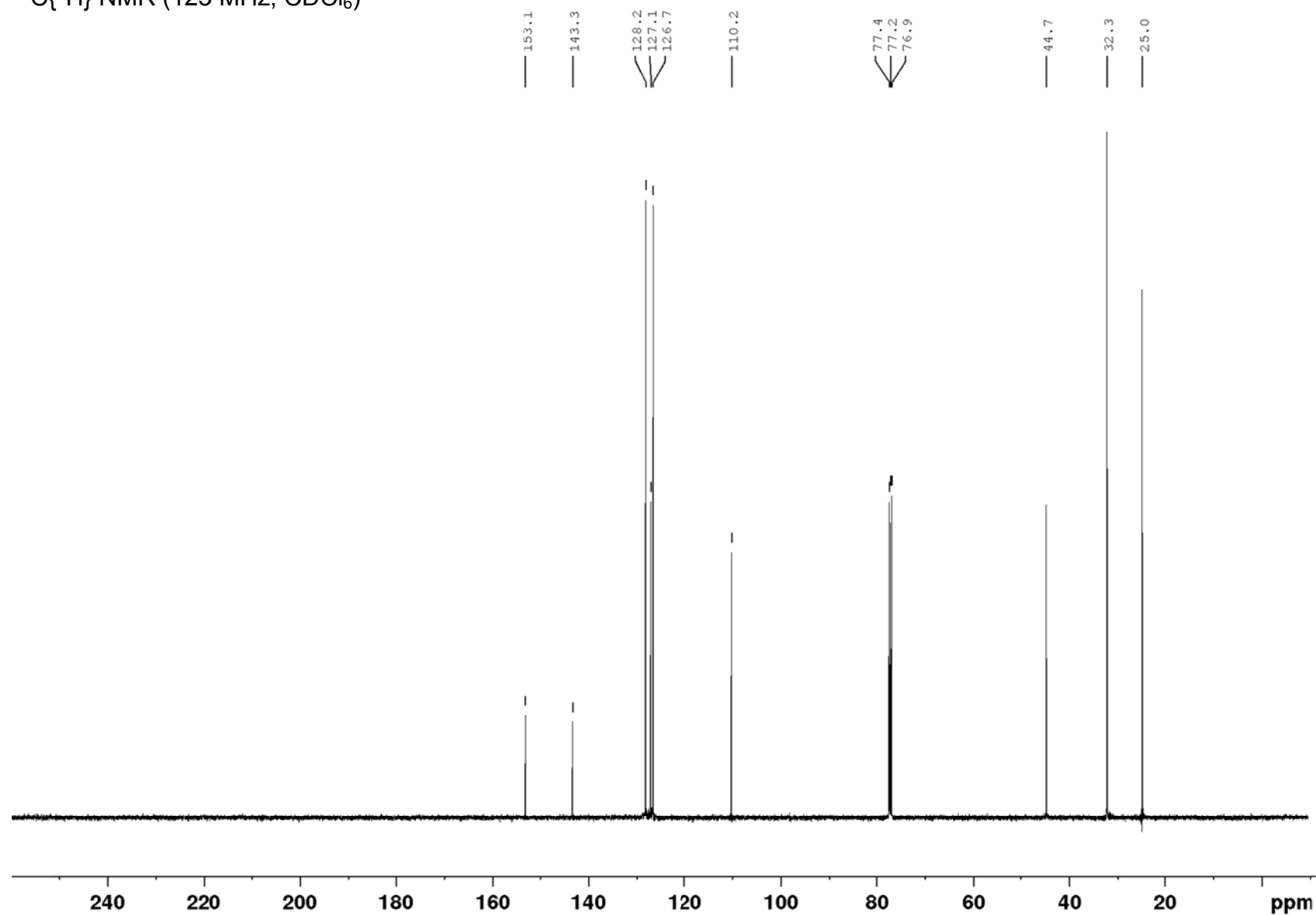
(1-Cyclohexylvinyl)benzene (9h): ^1H NMR (500 MHz, CDCl_3)

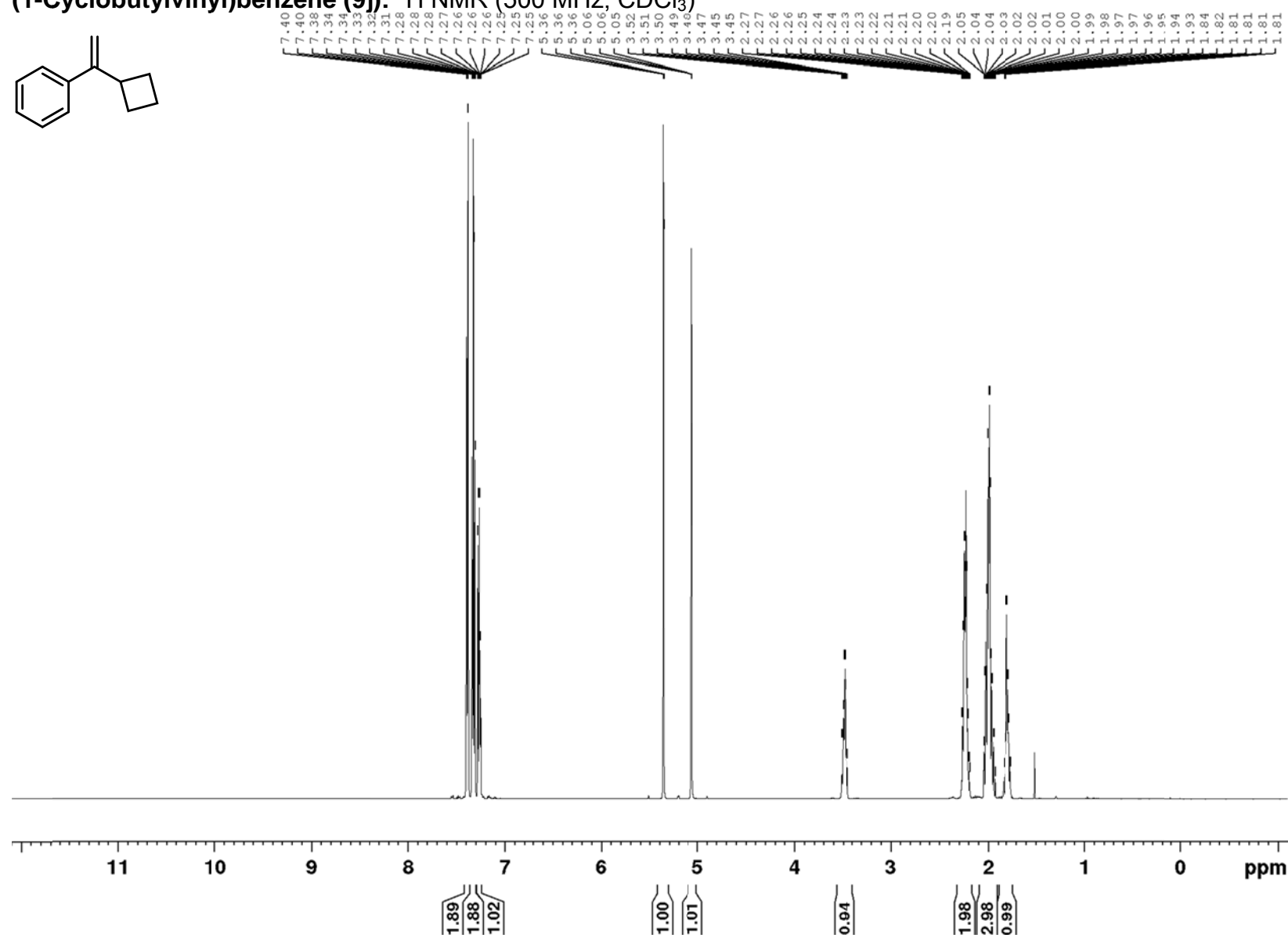
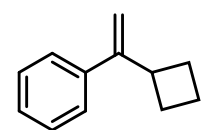


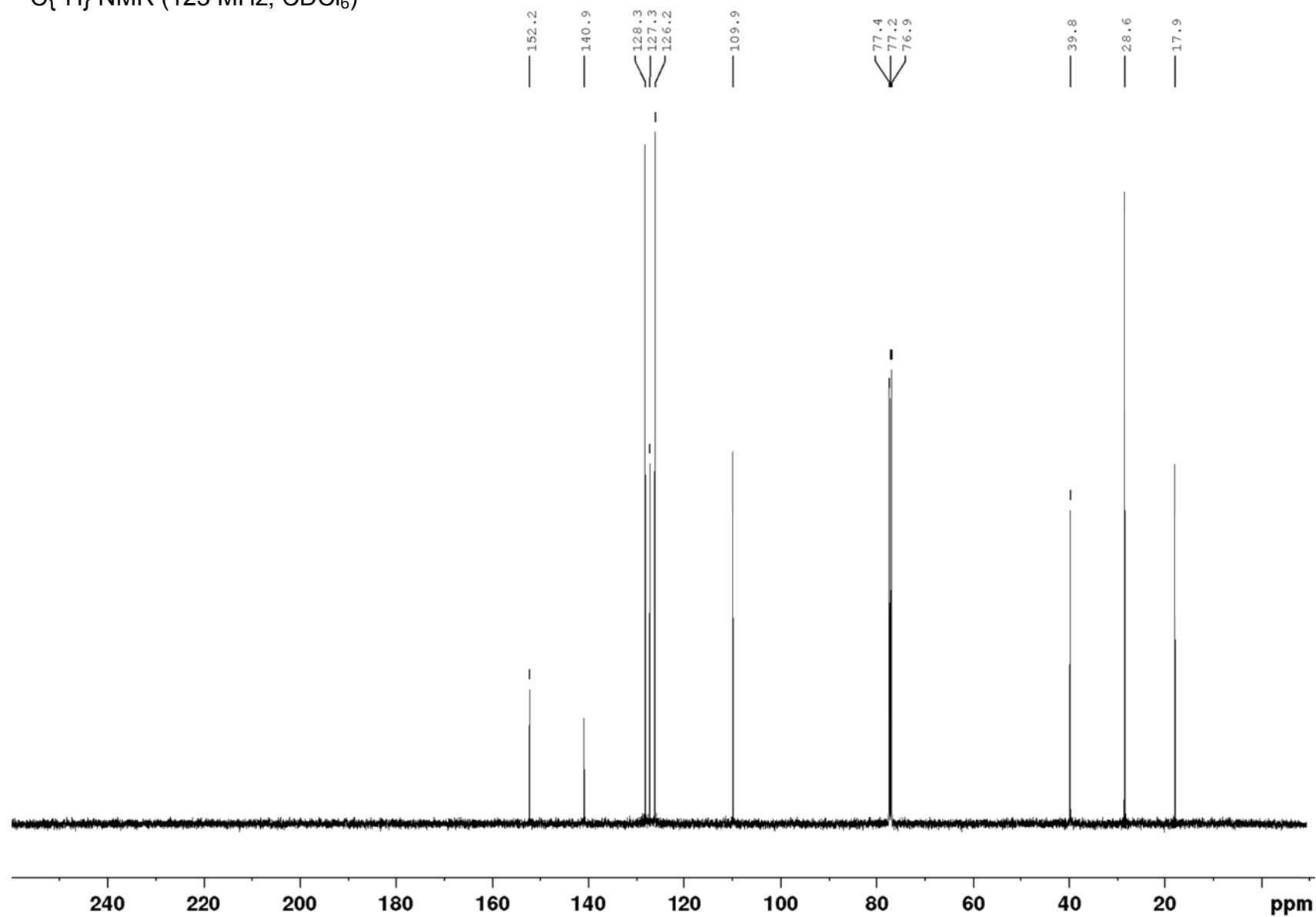
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

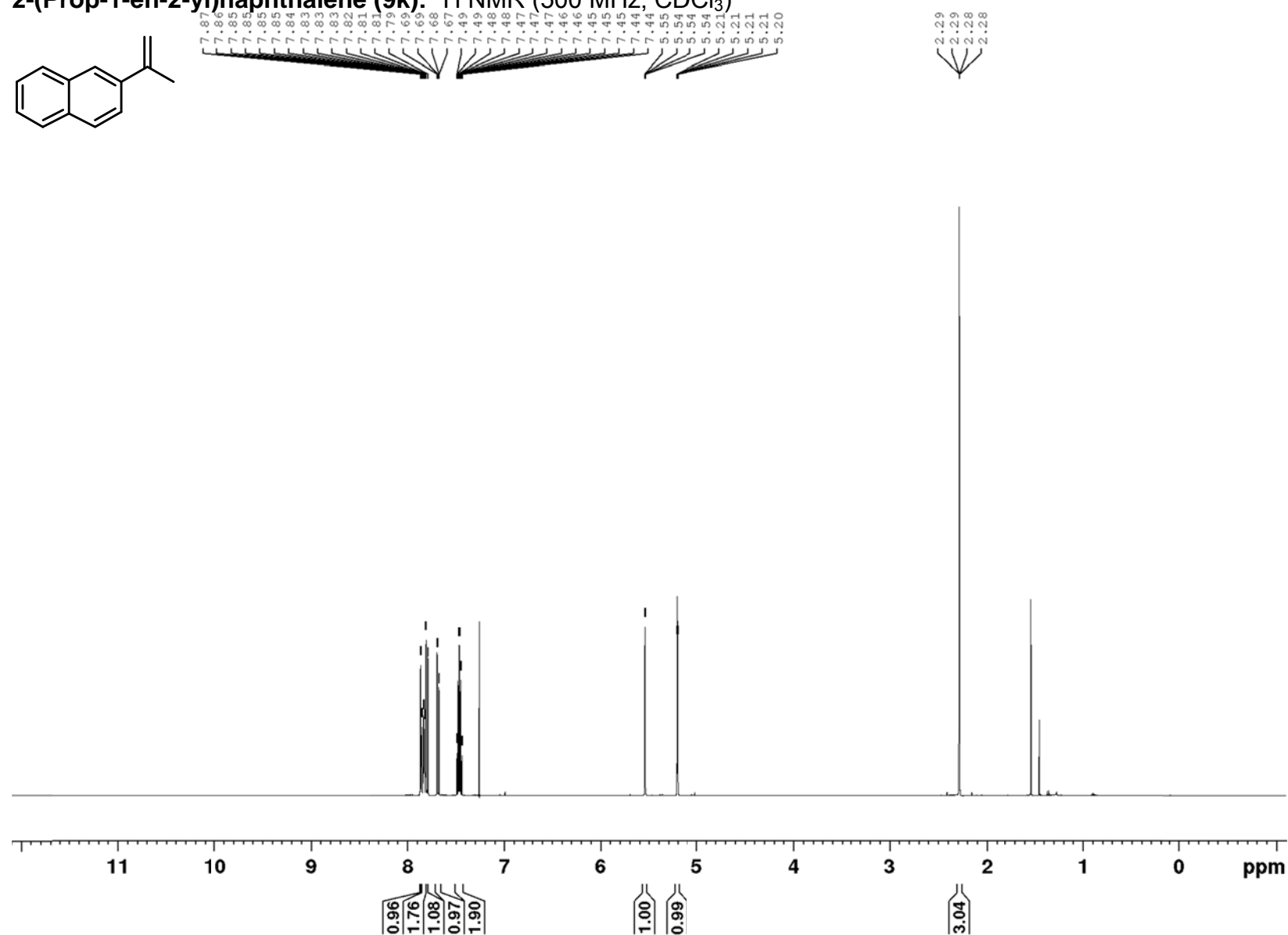
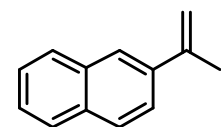
(1-Cyclopentylvinyl)benzene (9i): ^1H NMR (500 MHz, CDCl_3)

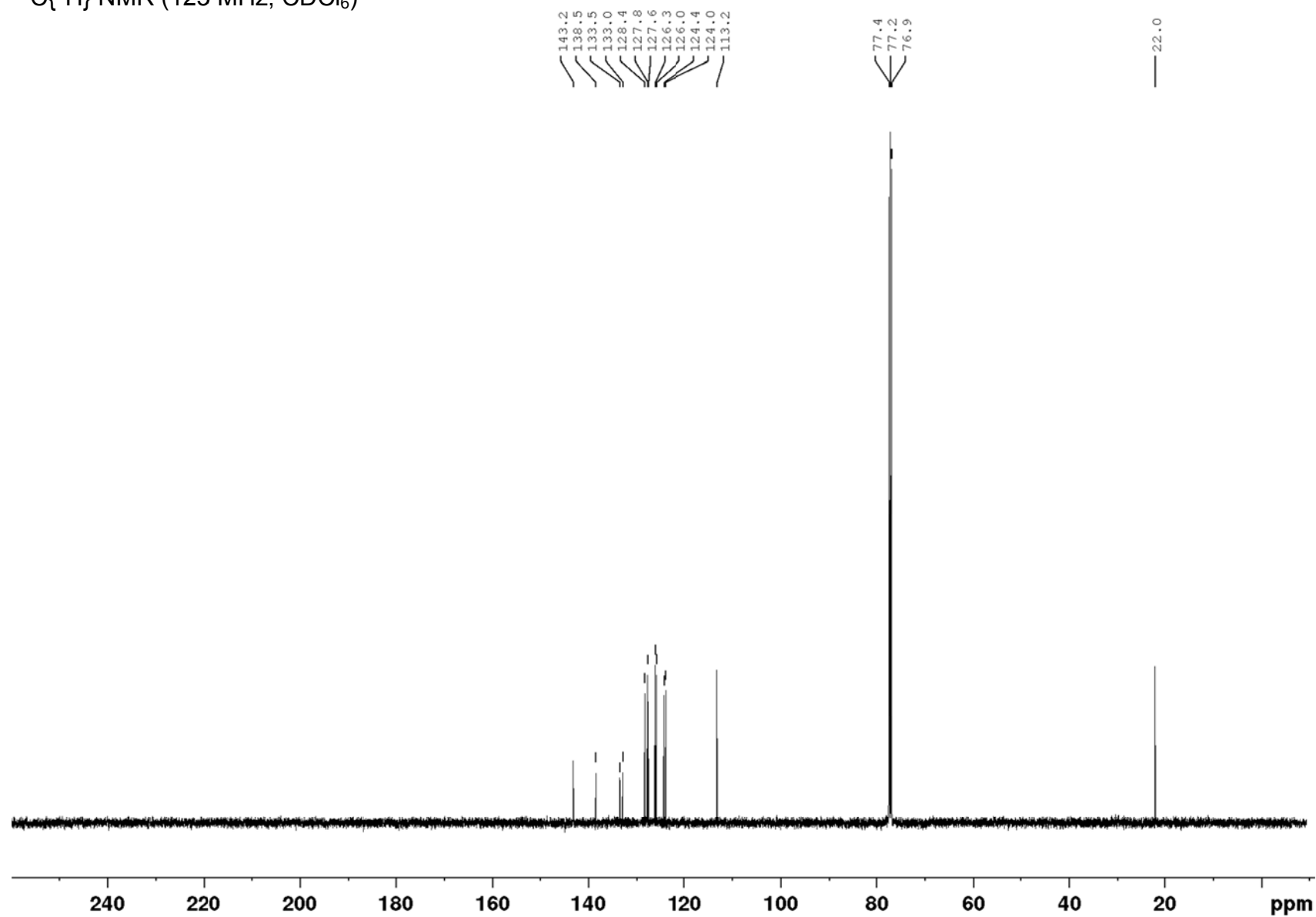


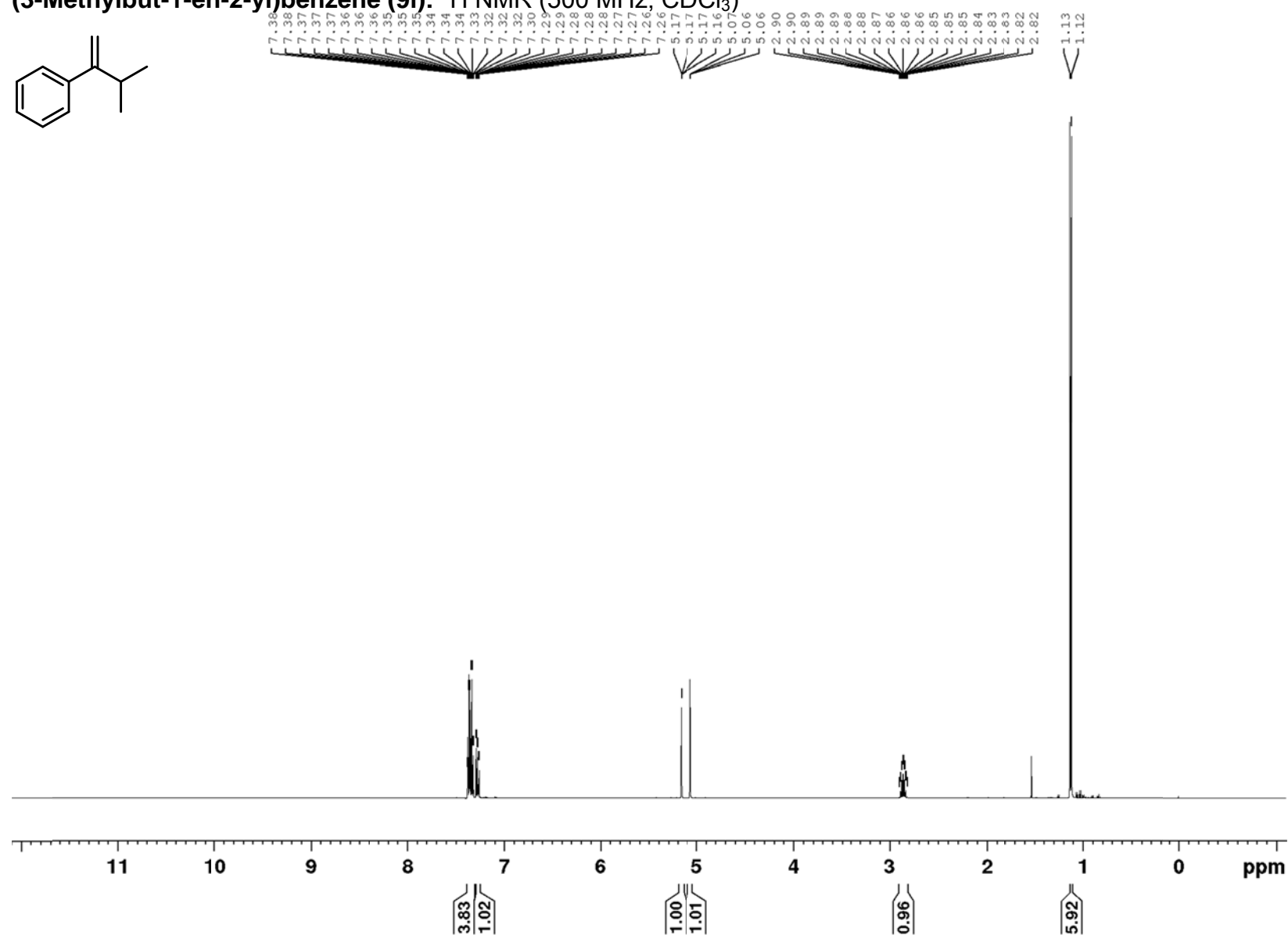
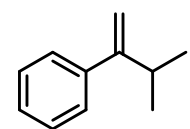
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

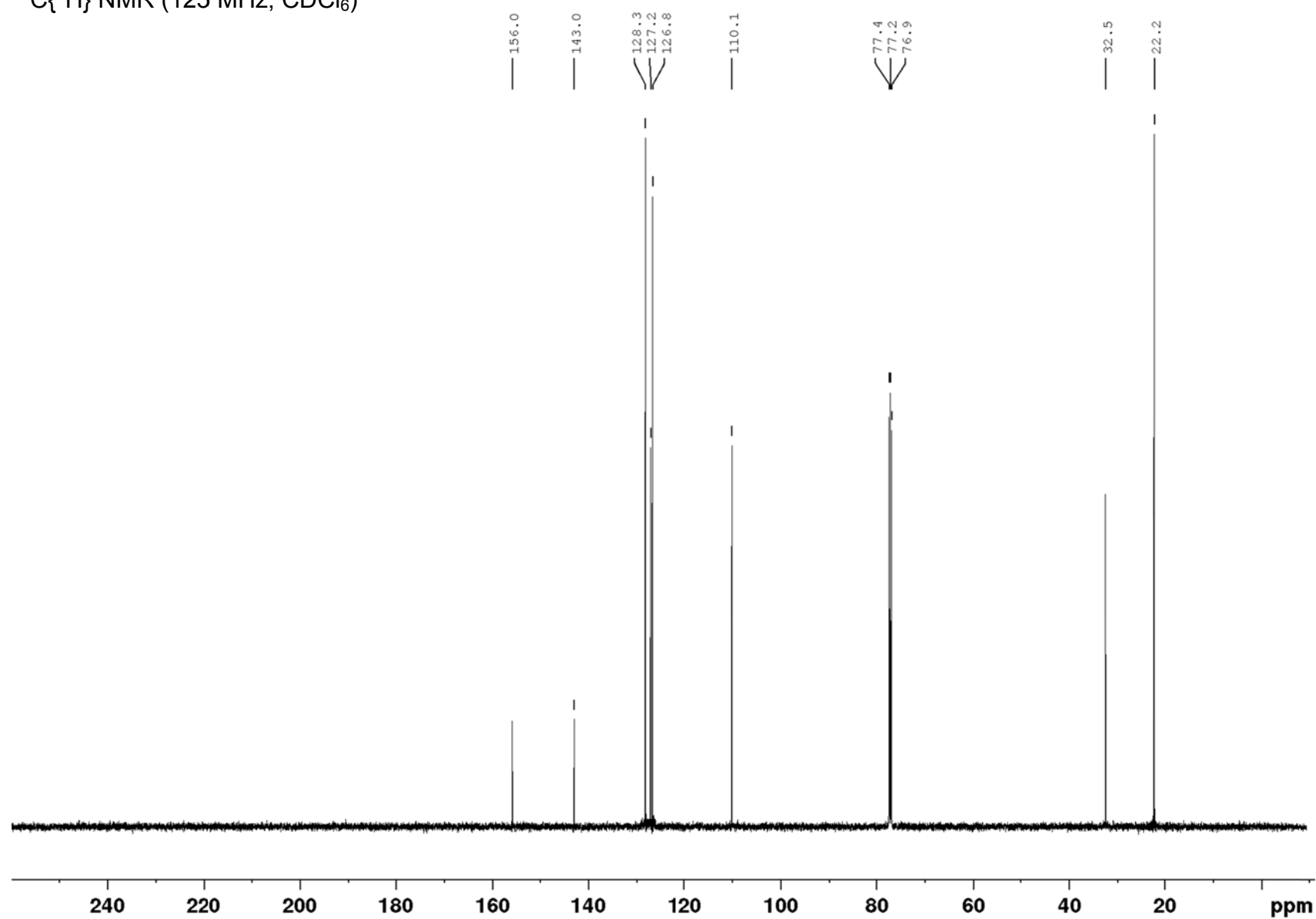
(1-Cyclobutylvinyl)benzene (9j): ^1H NMR (500 MHz, CDCl_3)

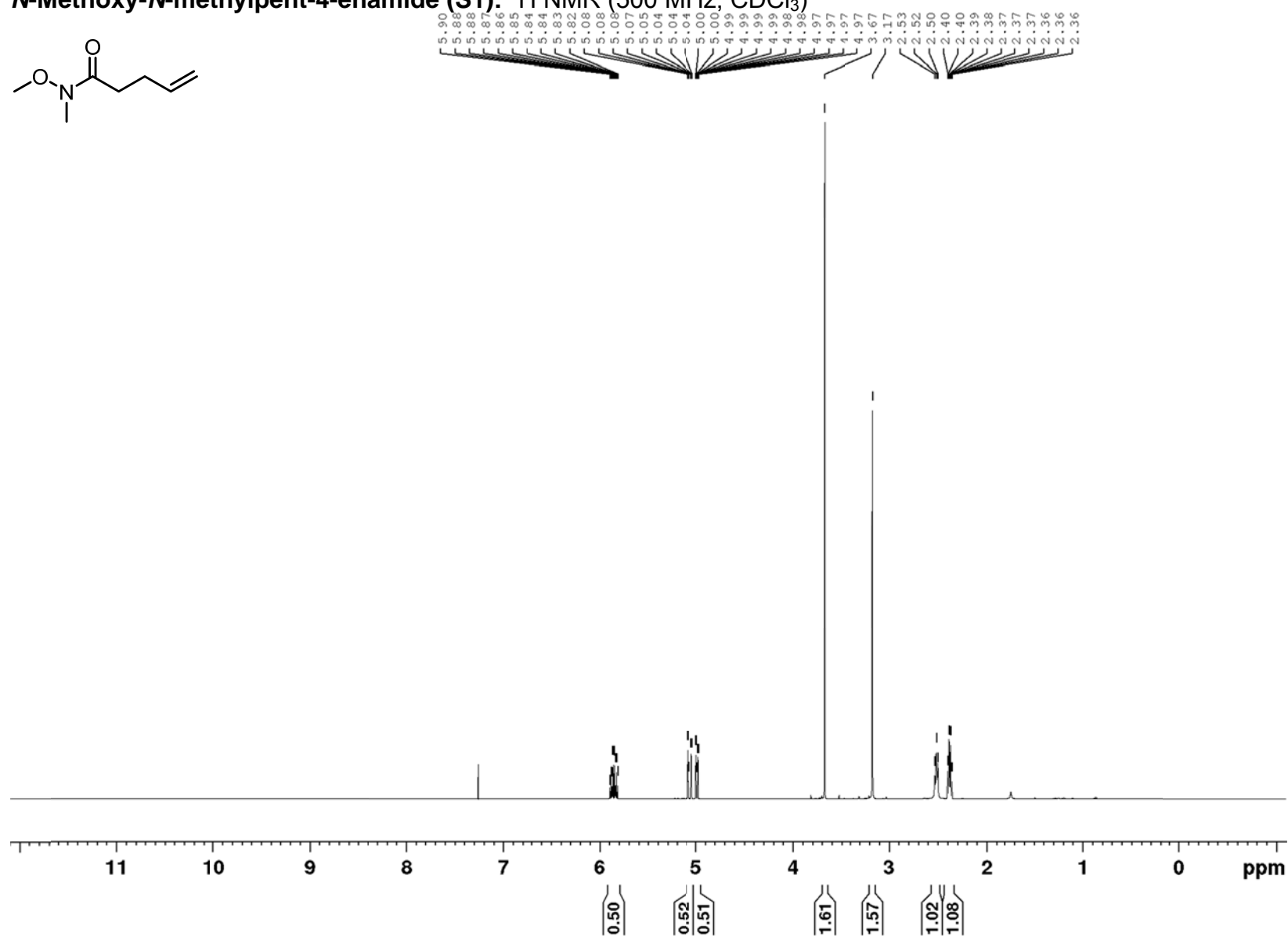
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

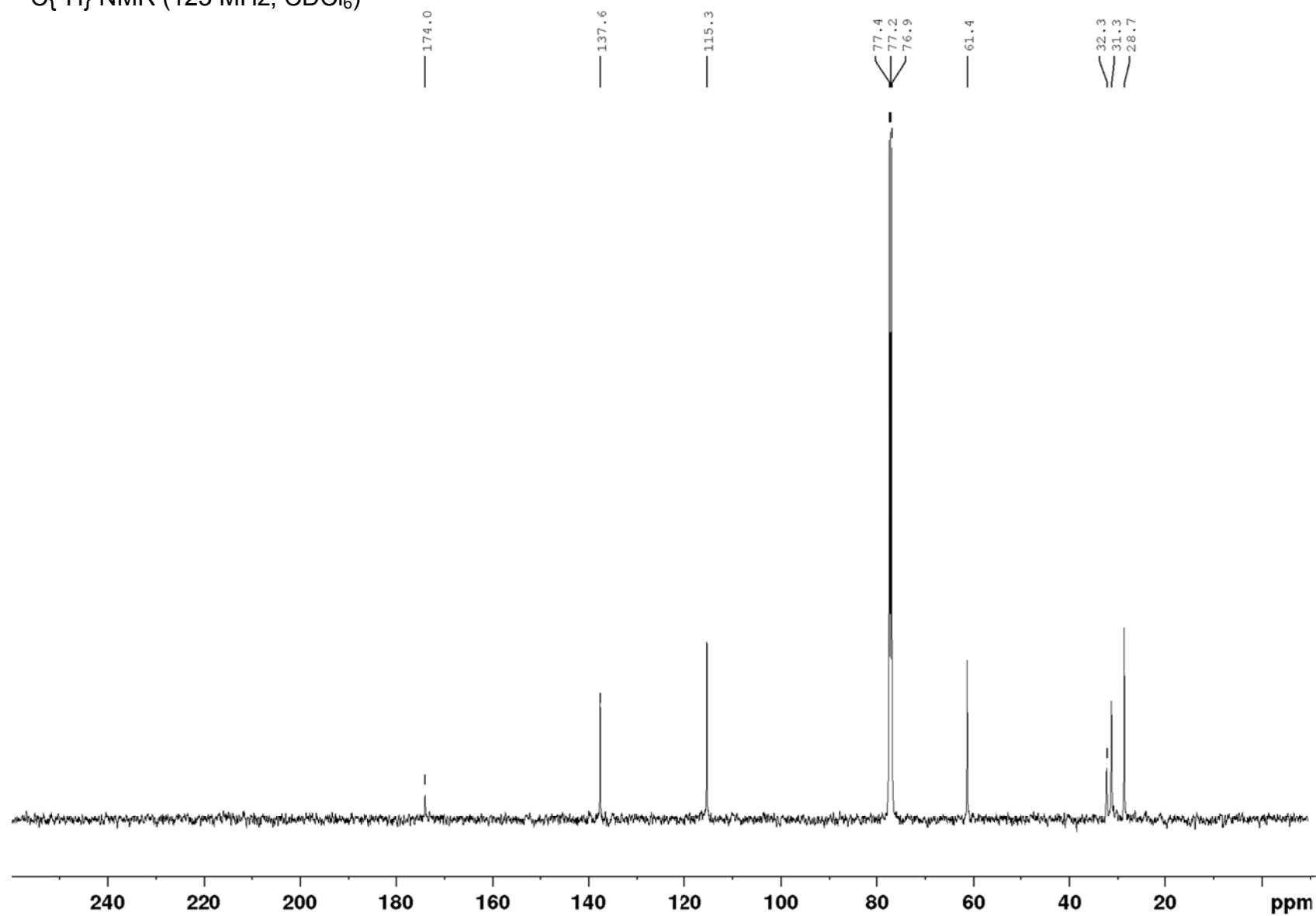
2-(Prop-1-en-2-yl)naphthalene (9k): ^1H NMR (500 MHz, CDCl_3)

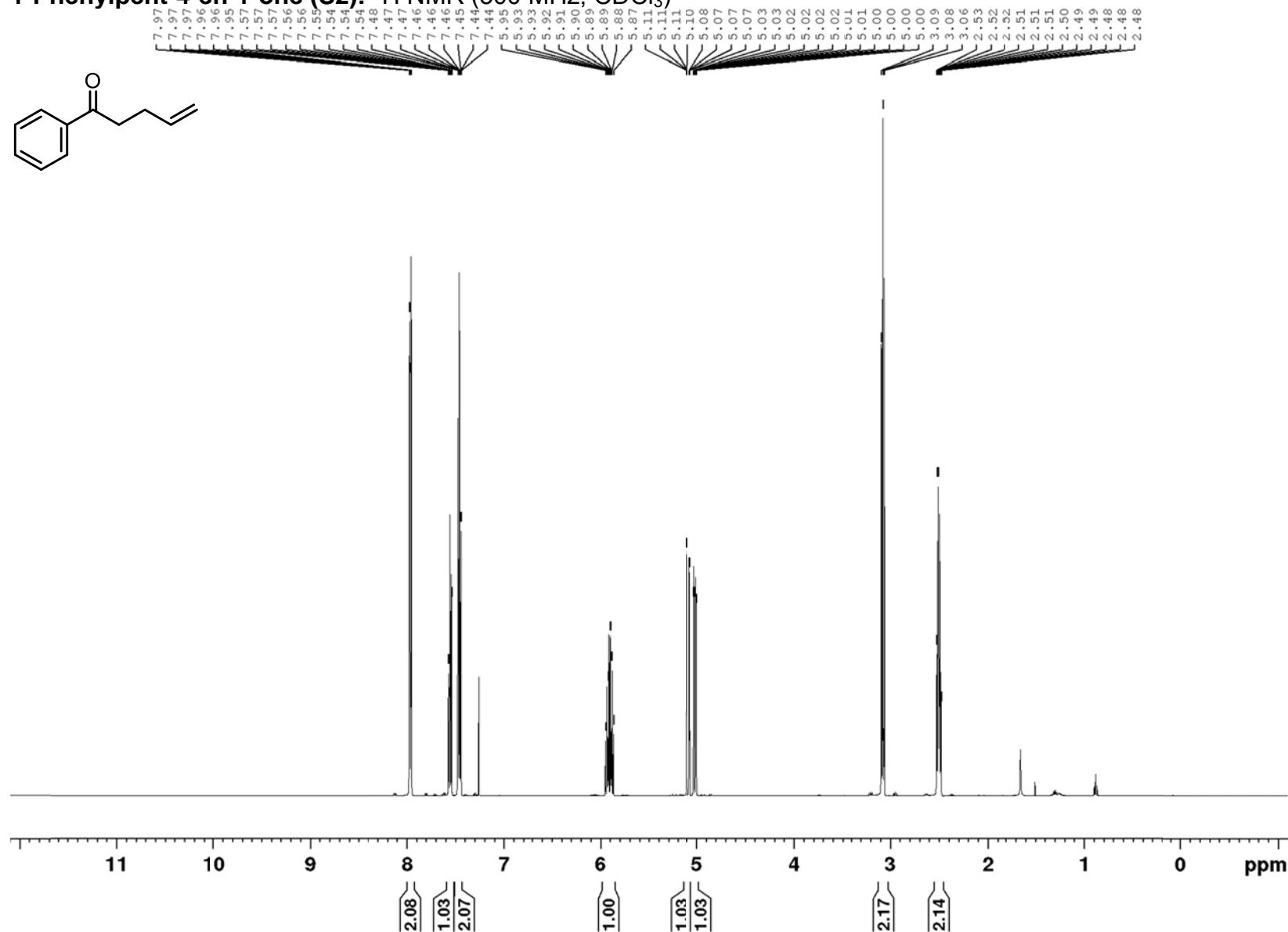
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

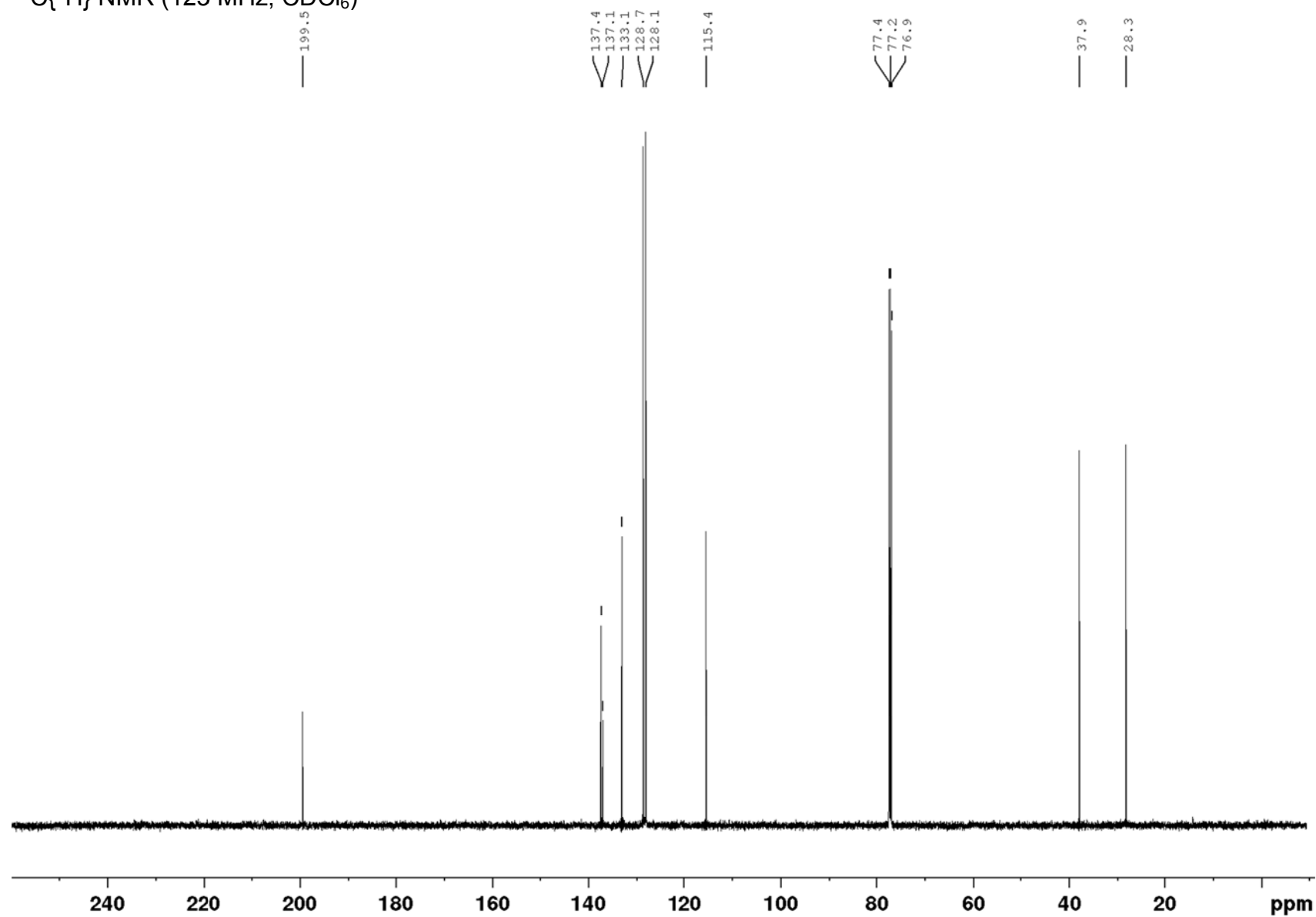
(3-Methylbut-1-en-2-yl)benzene (9l): ^1H NMR (500 MHz, CDCl_3)

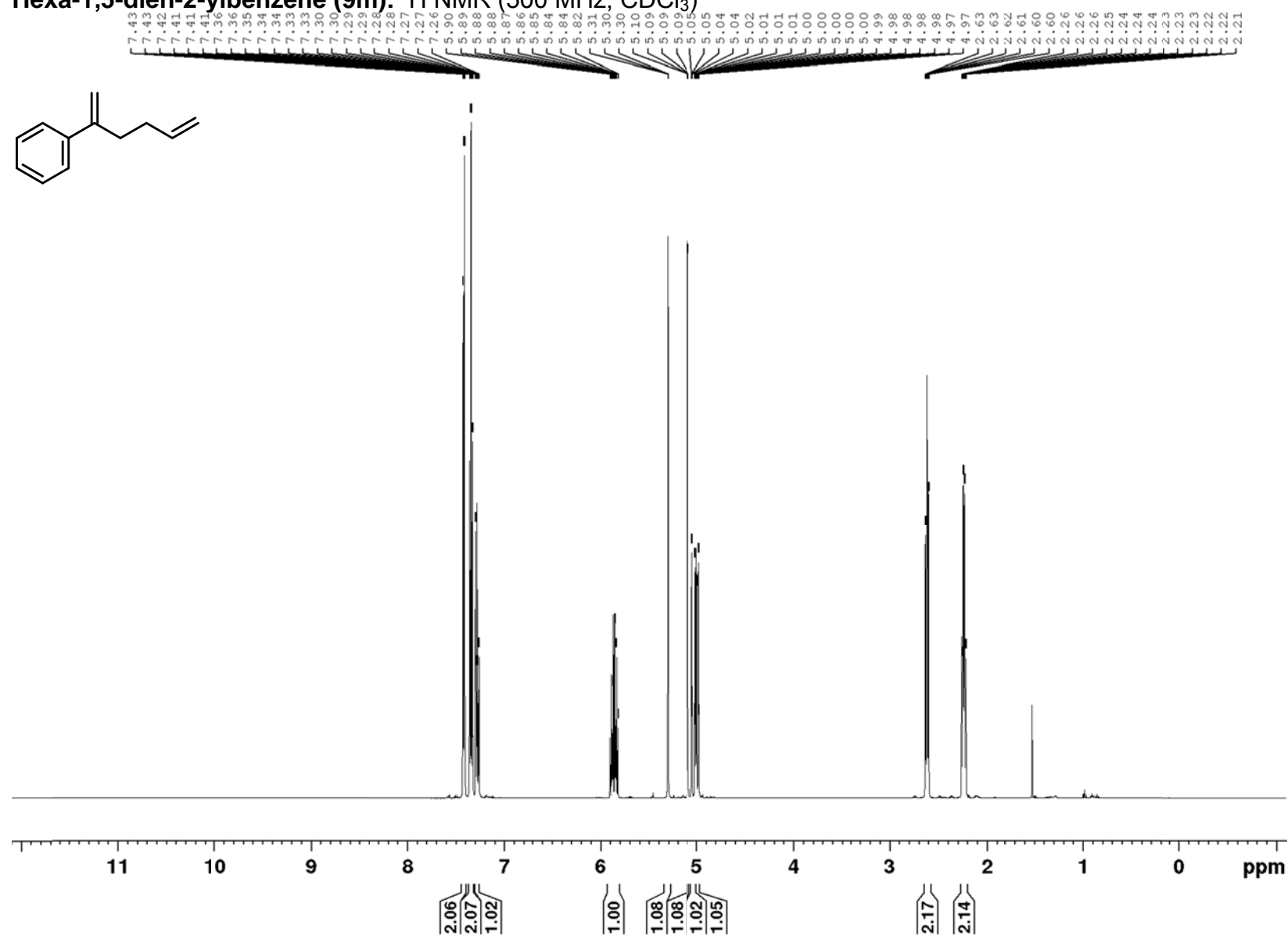
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

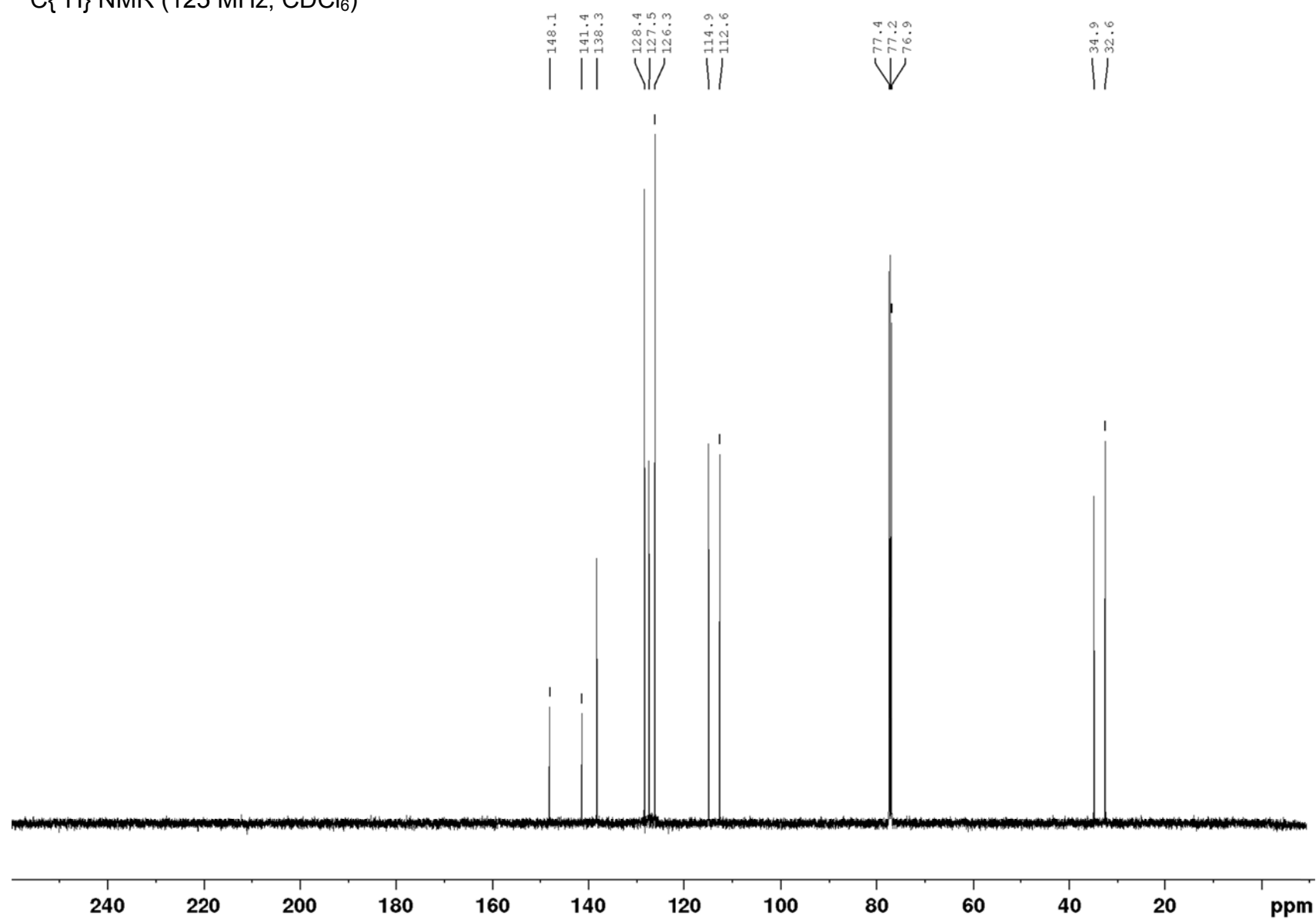
***N*-Methoxy-*N*-methylpent-4-enamide (S1):** ^1H NMR (500 MHz, CDCl_3)

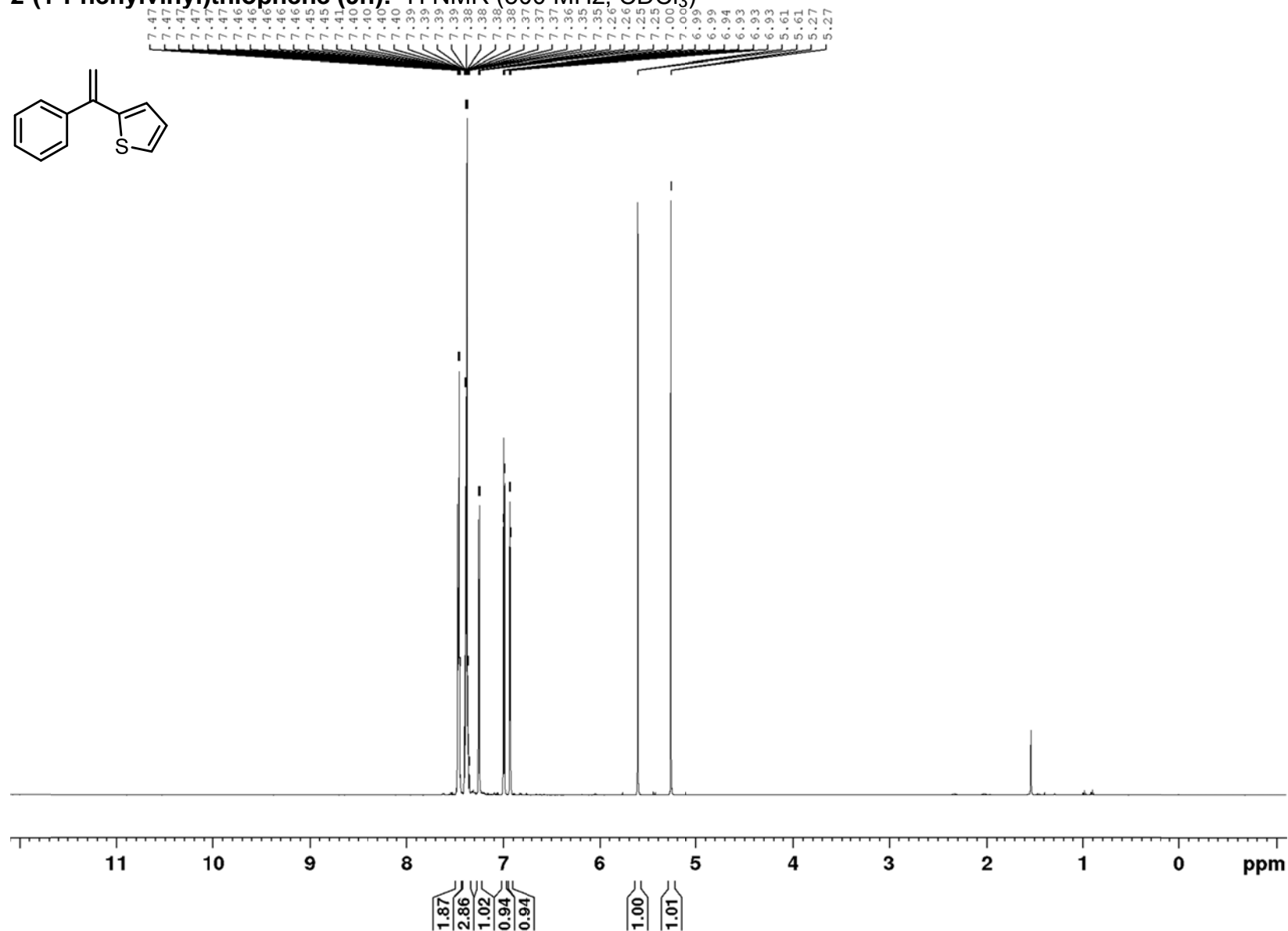
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

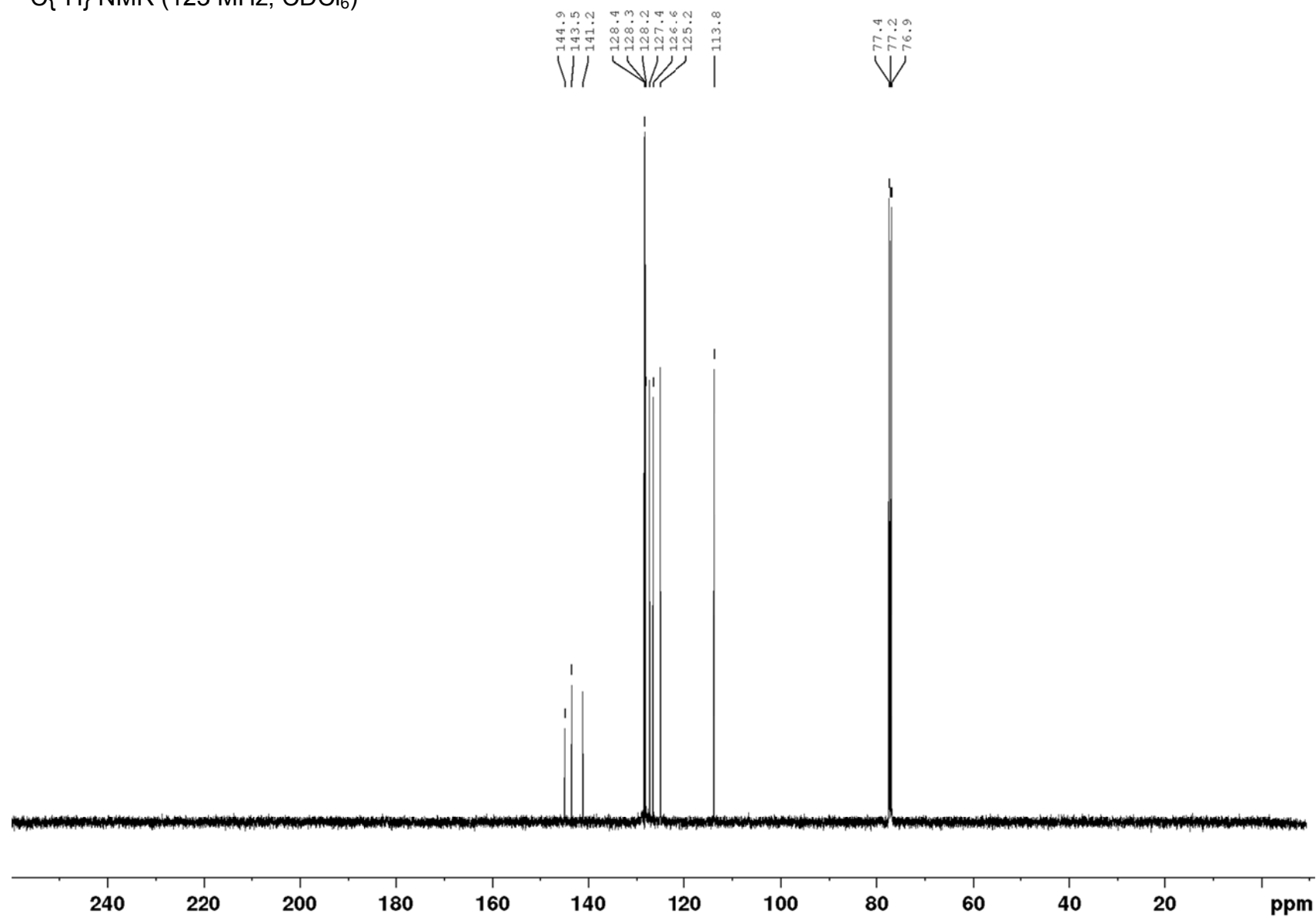
1-Phenylpent-4-en-1-one (S2): ^1H NMR (500 MHz, CDCl_3)

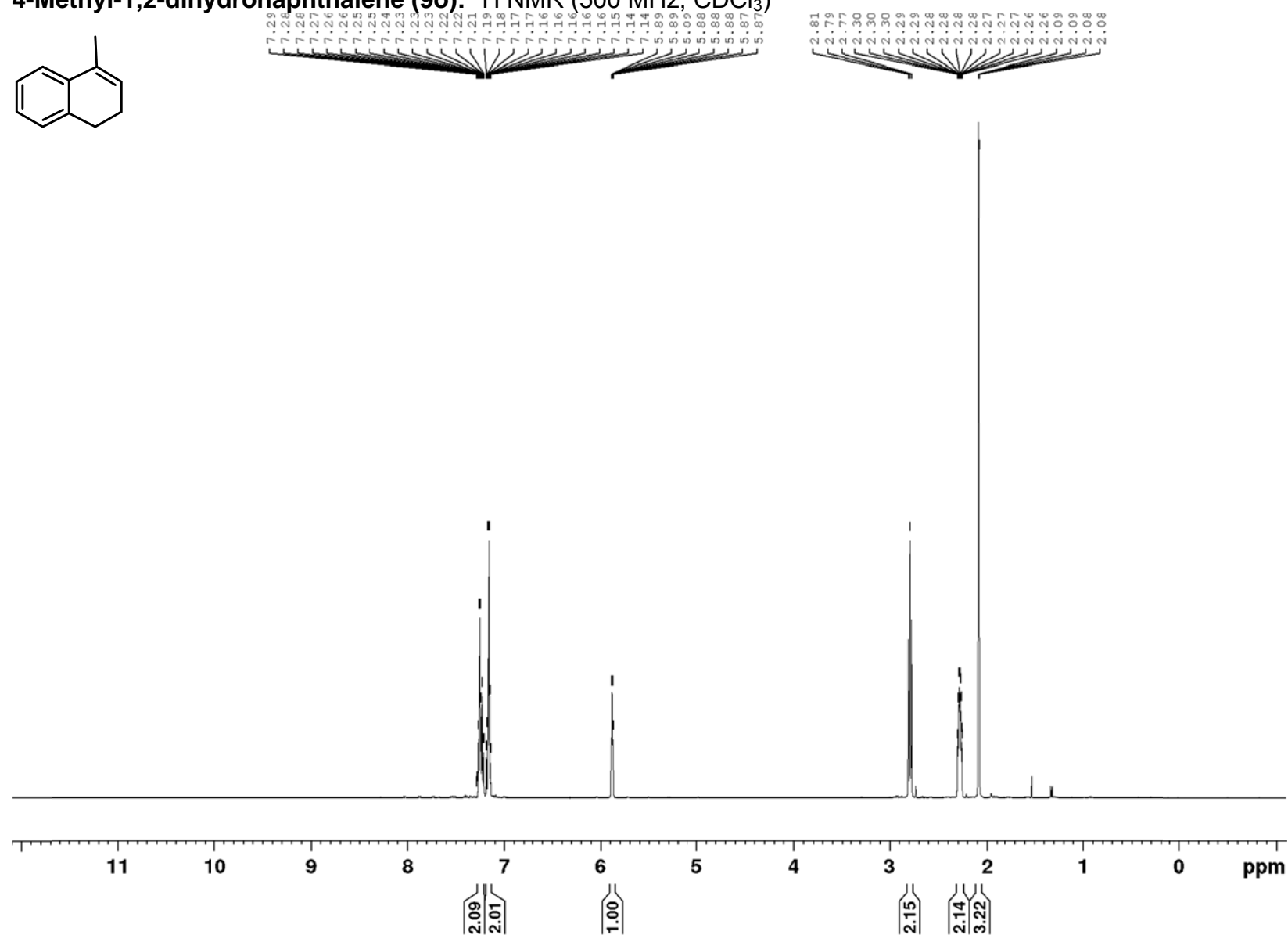
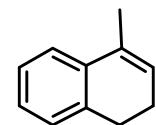
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

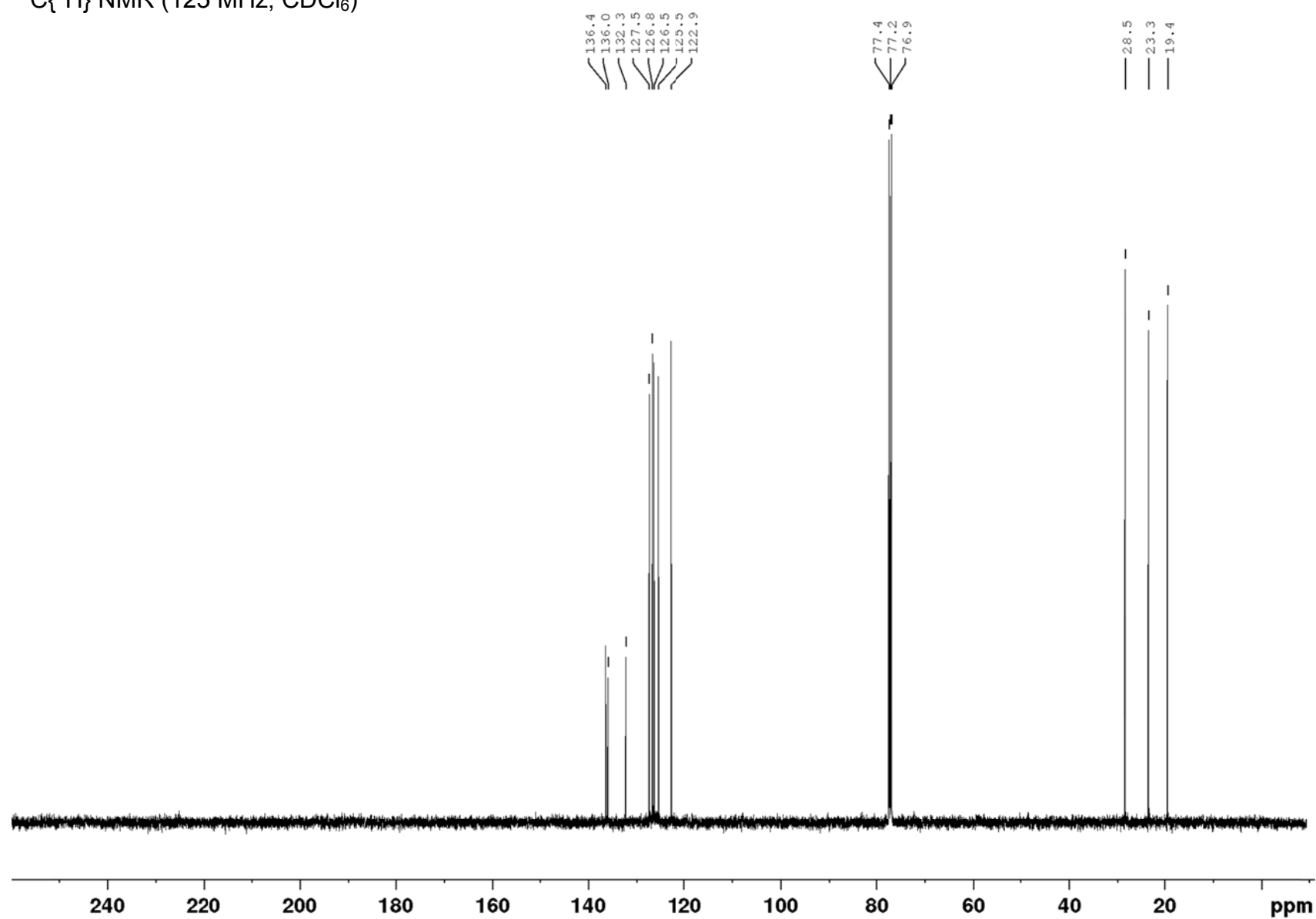
Hexa-1,5-dien-2-ylbenzene (9m): ^1H NMR (500 MHz, CDCl_3)

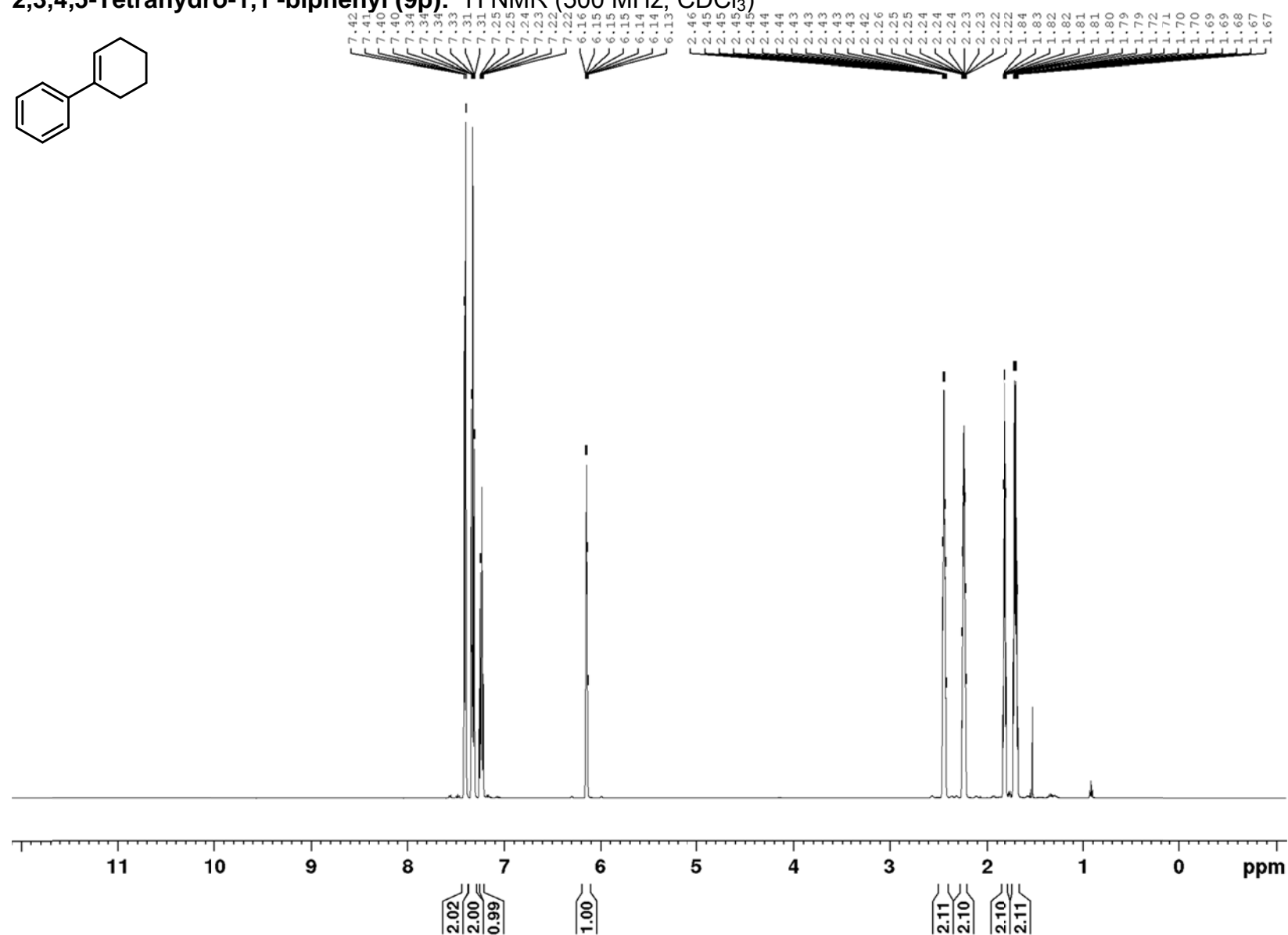
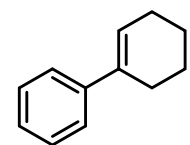
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

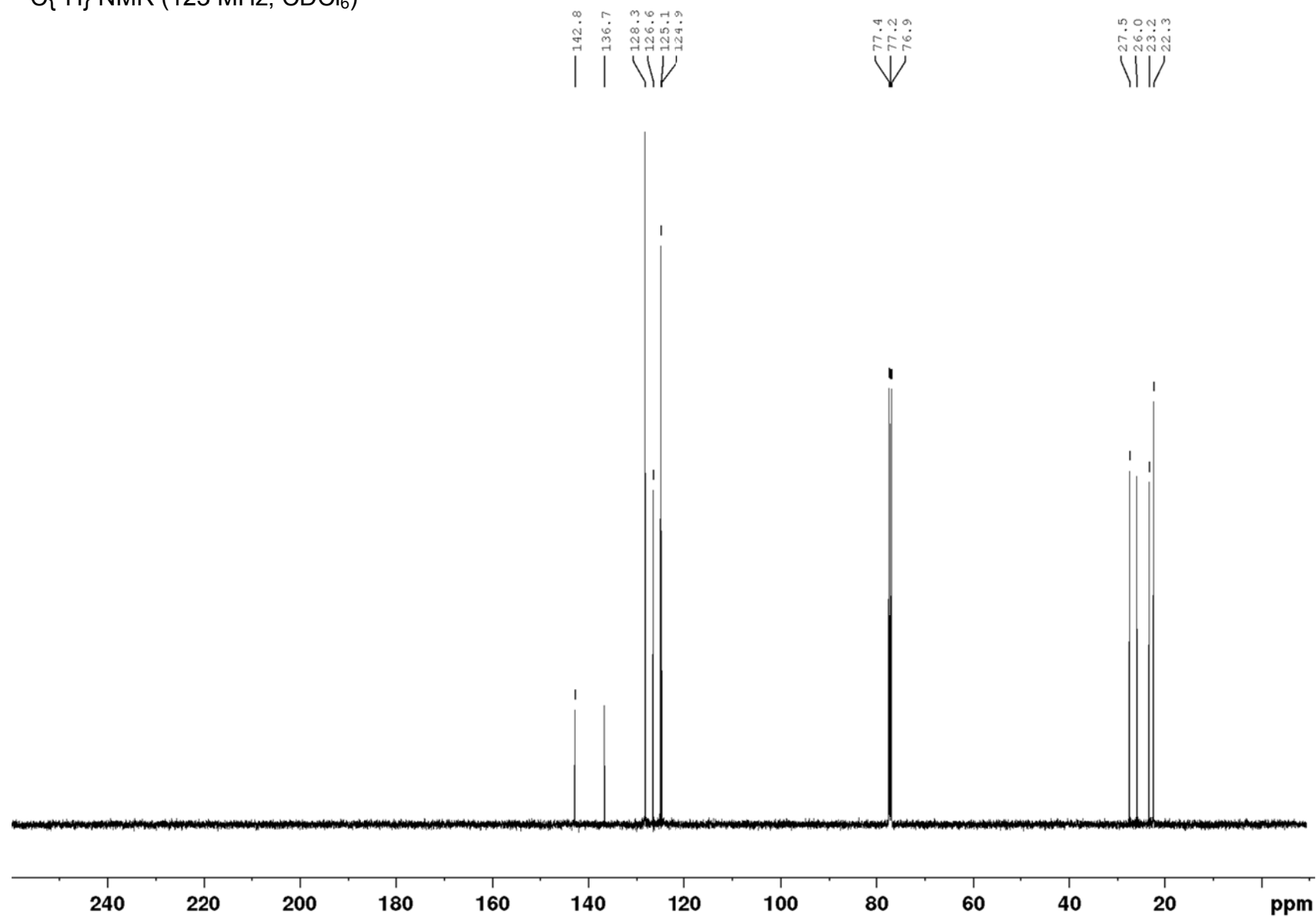
2-(1-Phenylvinyl)thiophene (9n): ^1H NMR (500 MHz, CDCl_3)

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

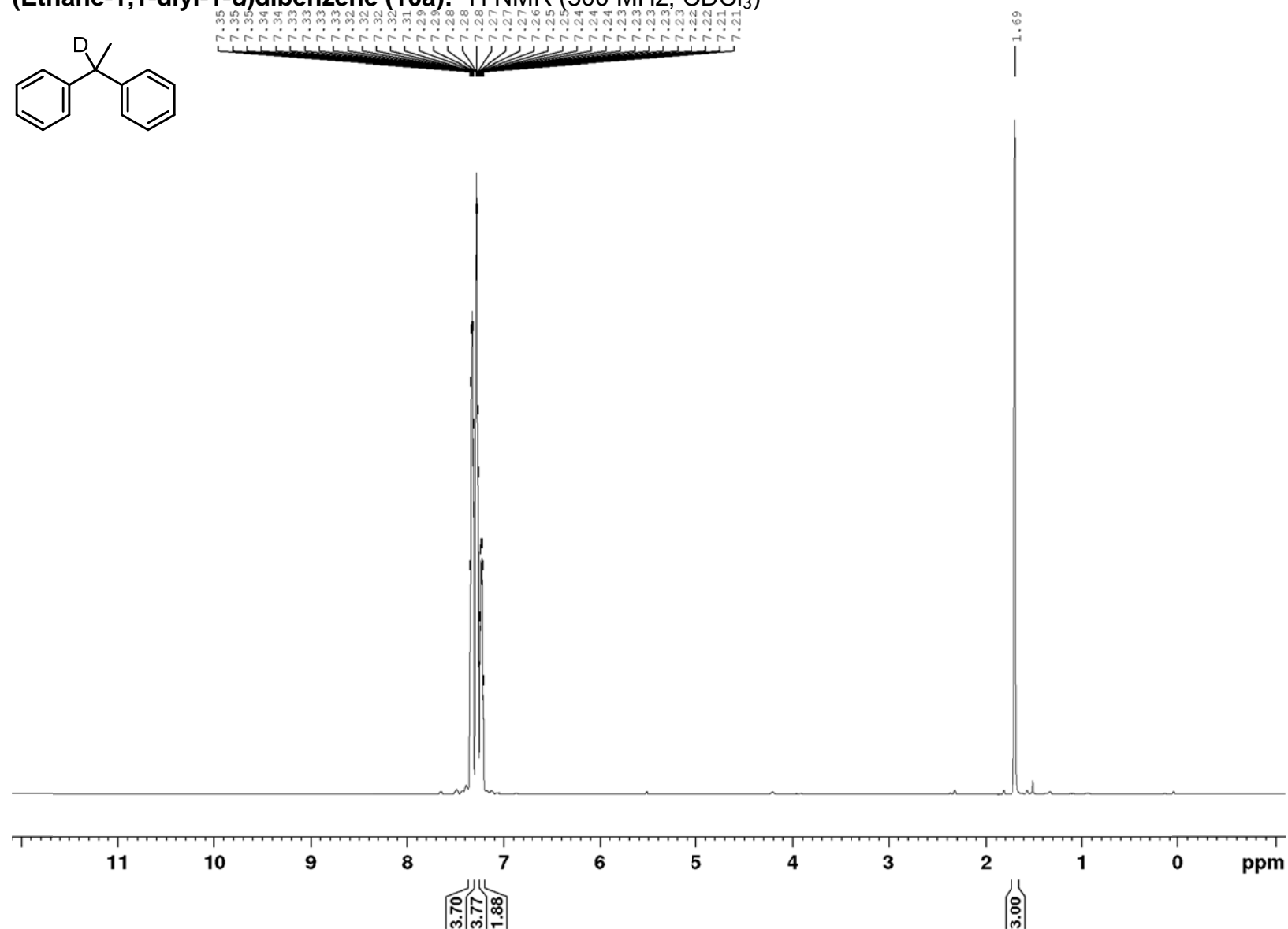
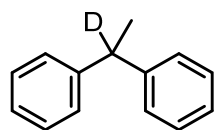
4-Methyl-1,2-dihydronaphthalene (9o): ^1H NMR (500 MHz, CDCl_3)

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

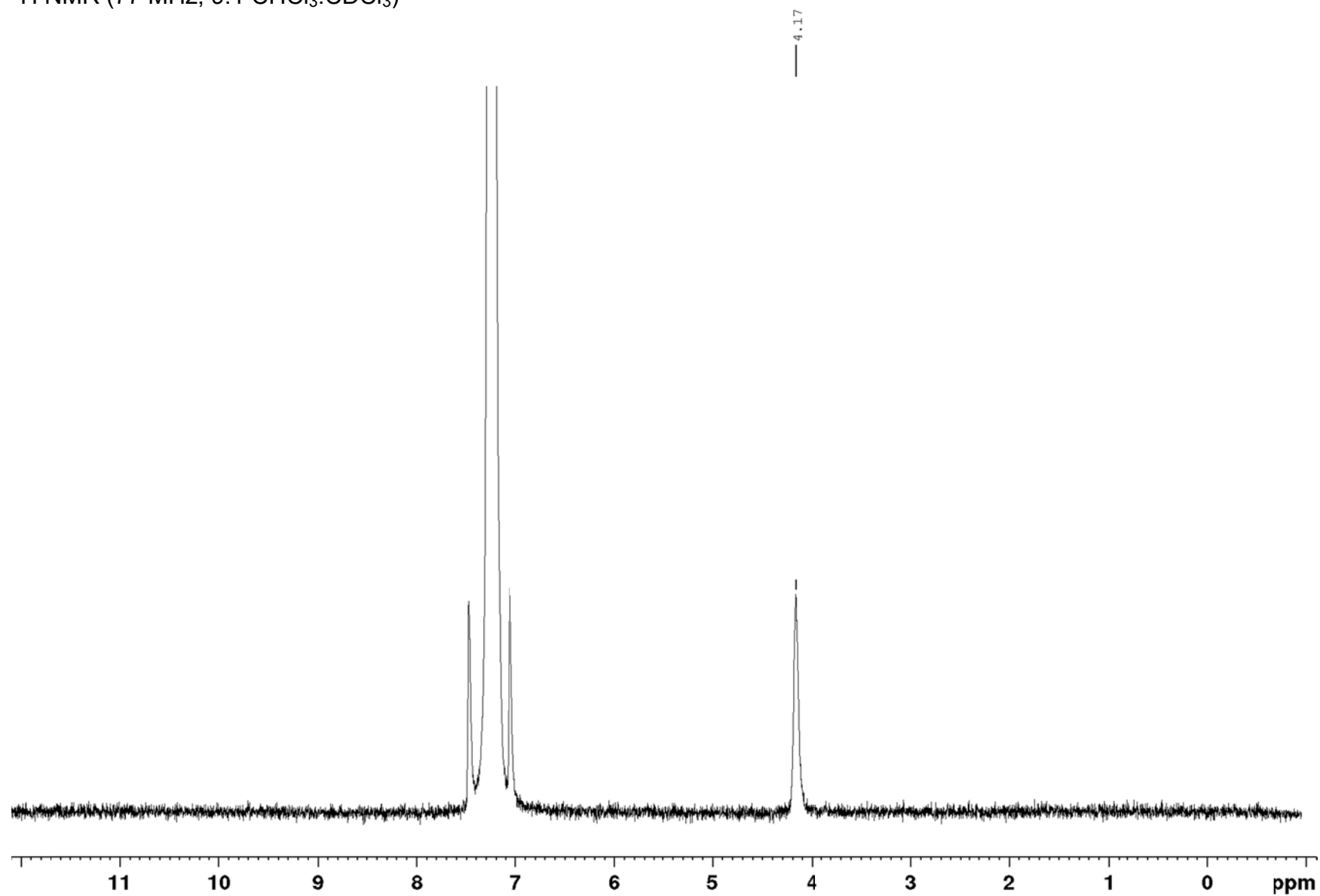
2,3,4,5-Tetrahydro-1,1'-biphenyl (9p): ^1H NMR (500 MHz, CDCl_3)

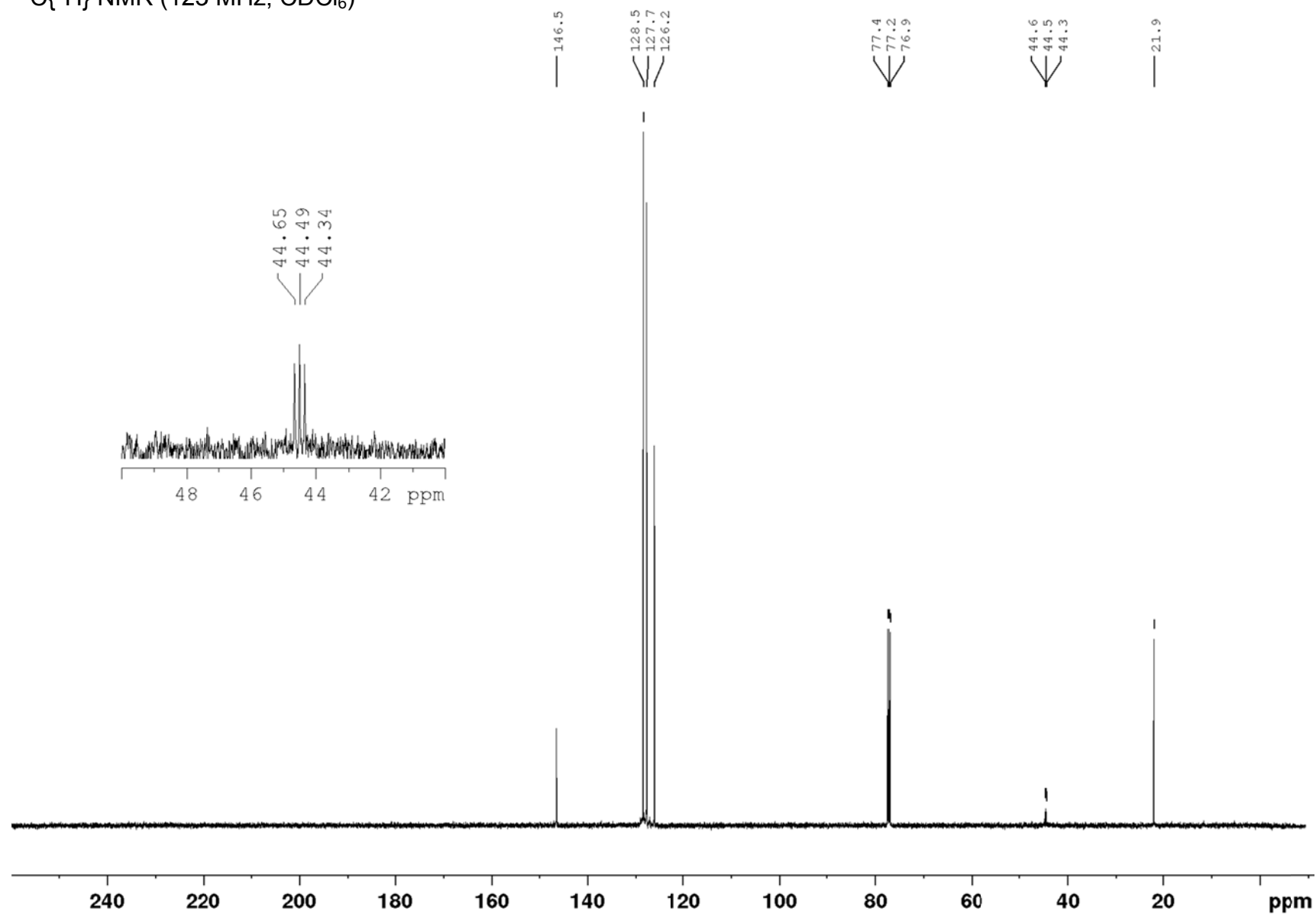
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

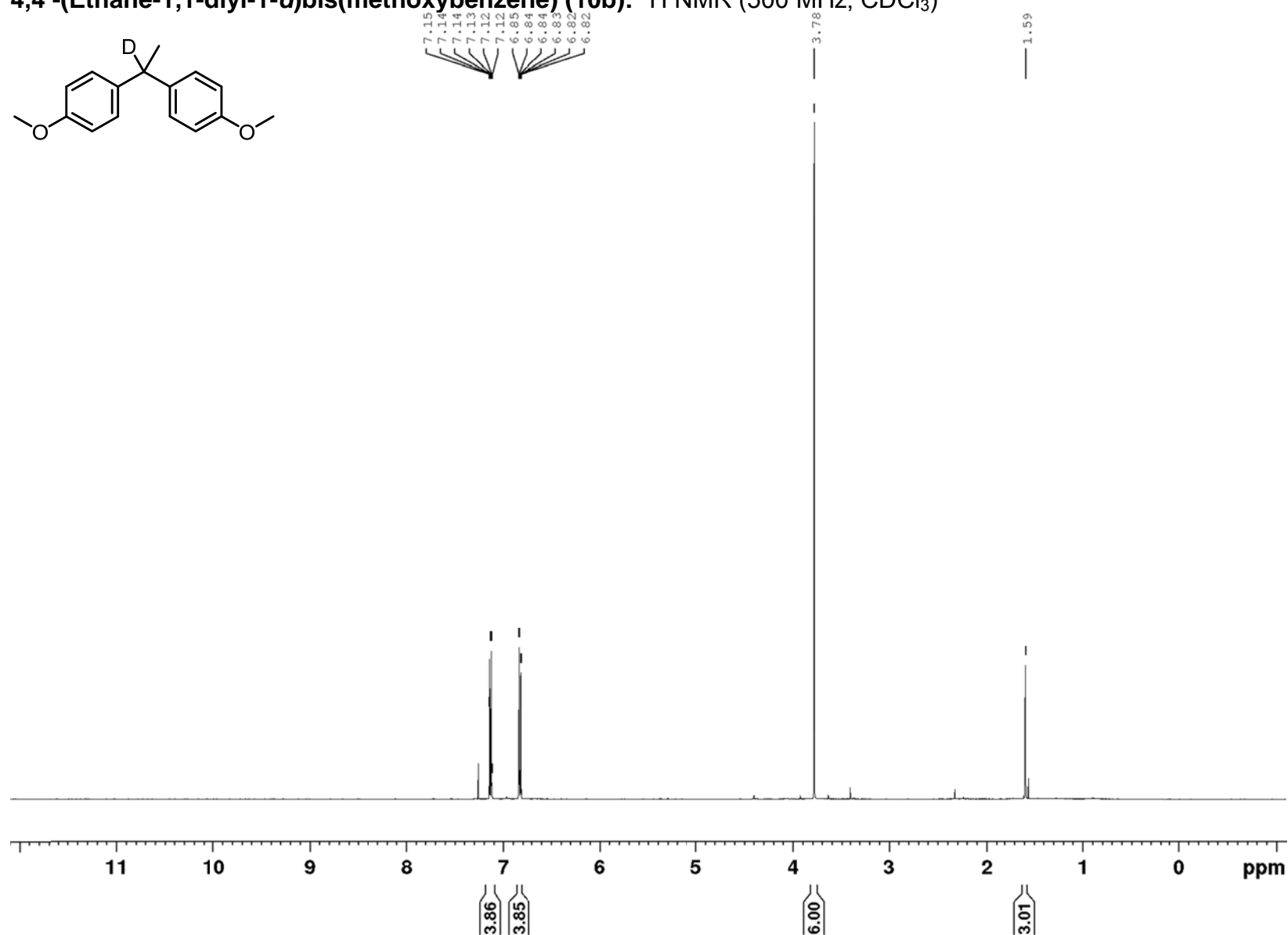
(Ethane-1,1-diyl-1-*d*)dibenzene (10a): ^1H NMR (500 MHz, CDCl_3)



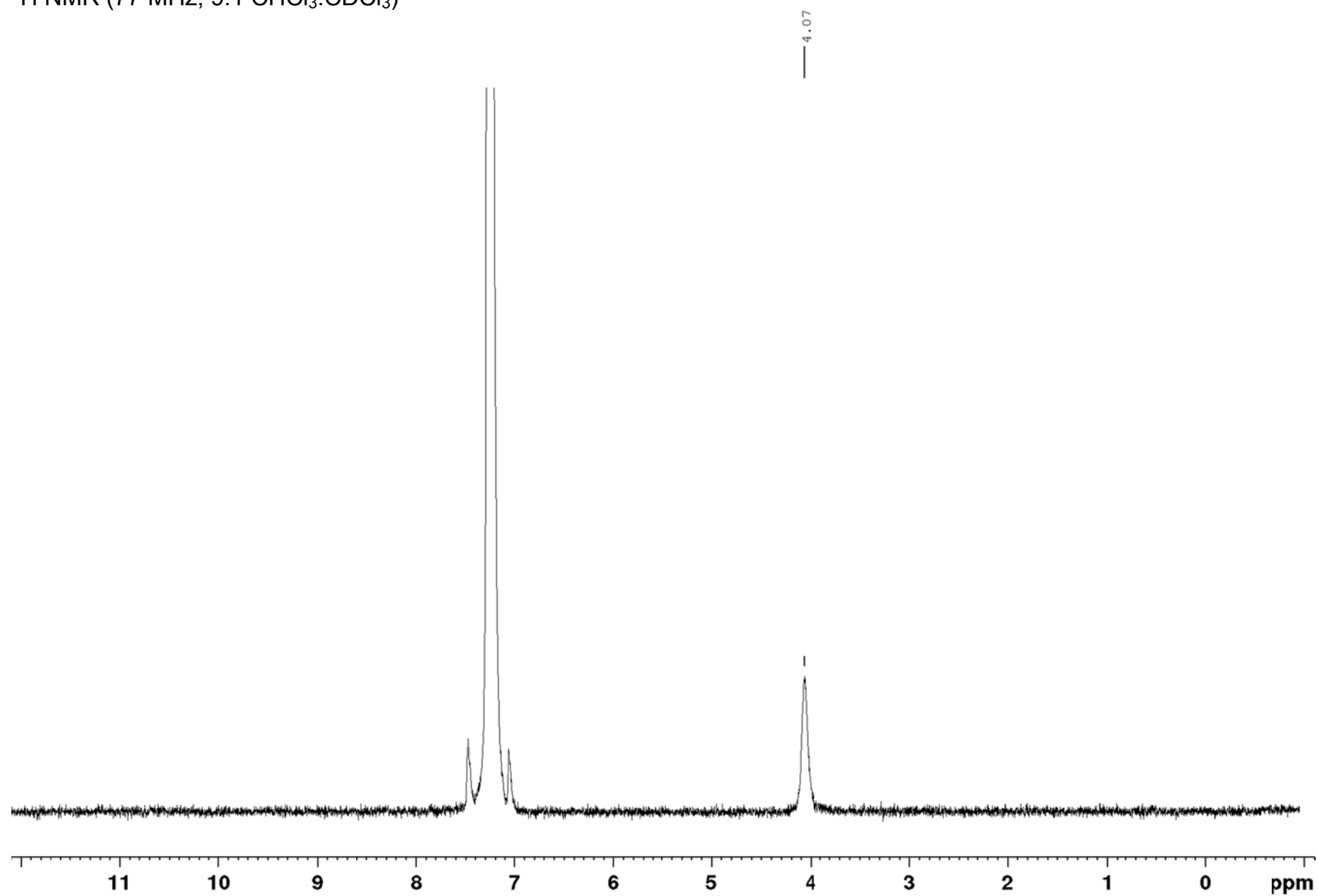
^2H NMR (77 MHz, 9:1 $\text{CHCl}_3:\text{CDCl}_3$)

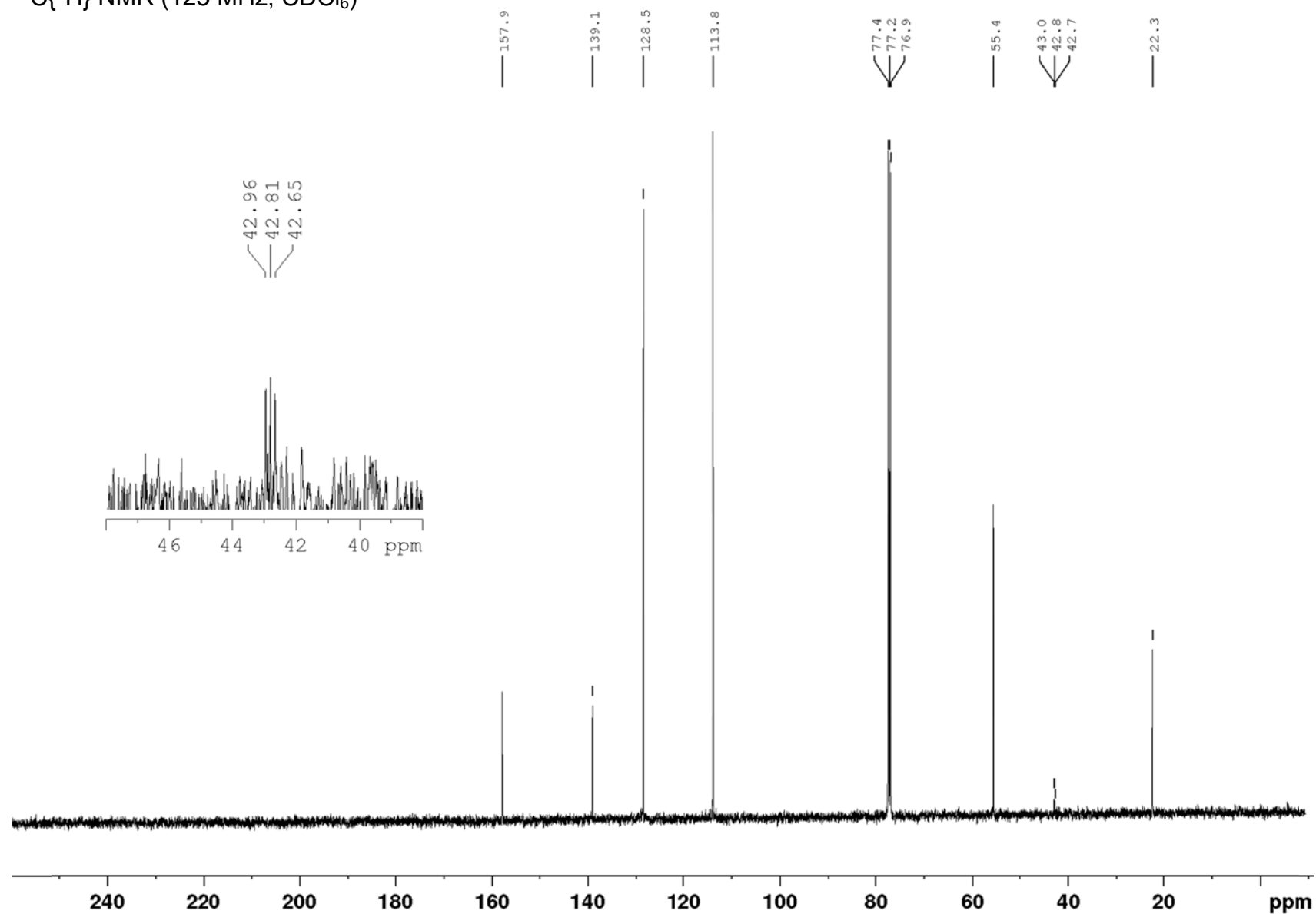


$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

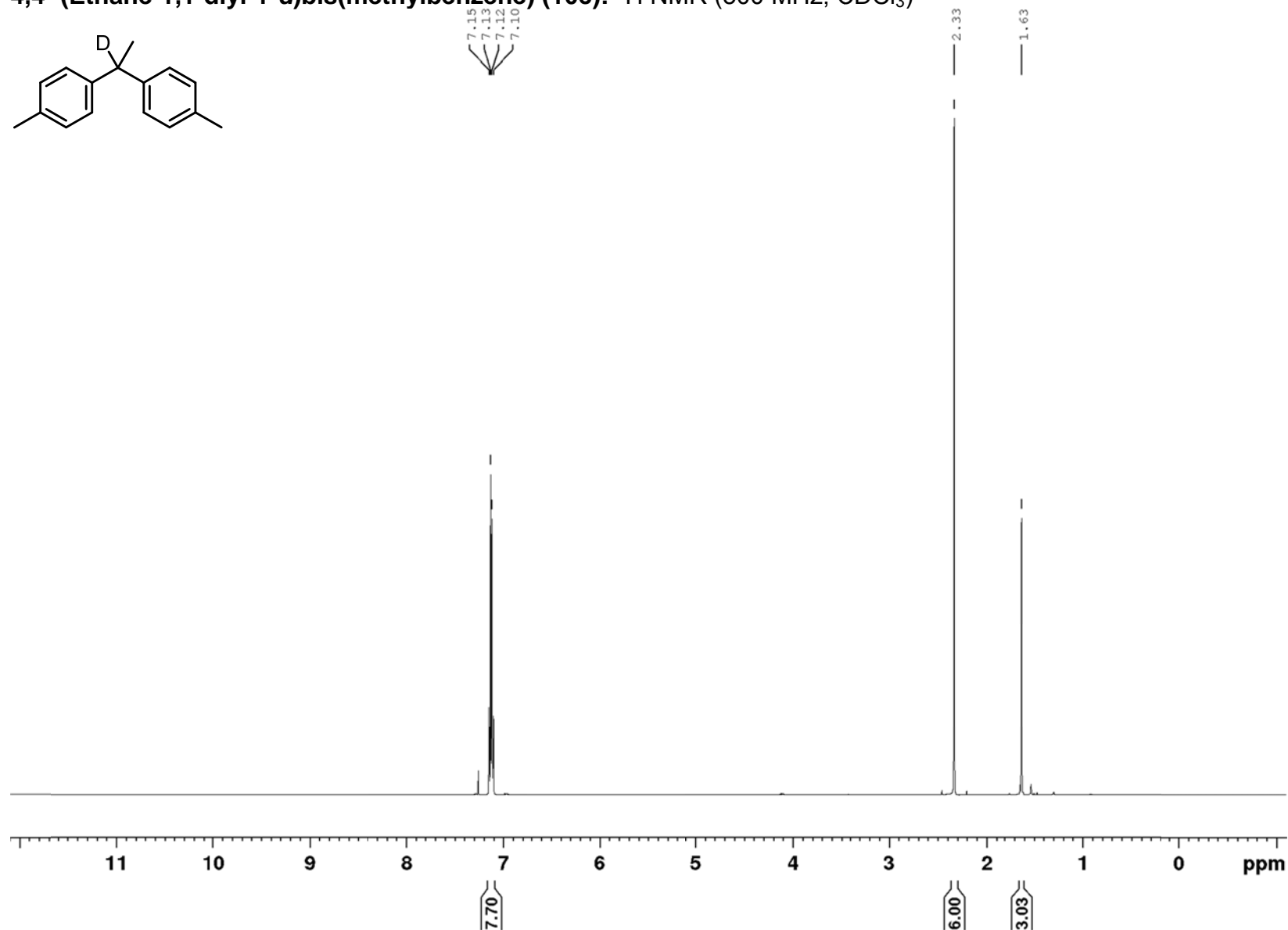
4,4'-(Ethane-1,1-diyl-1-*d*)bis(methoxybenzene) (10b): ^1H NMR (500 MHz, CDCl_3)

^2H NMR (77 MHz, 9:1 $\text{CHCl}_3:\text{CDCl}_3$)

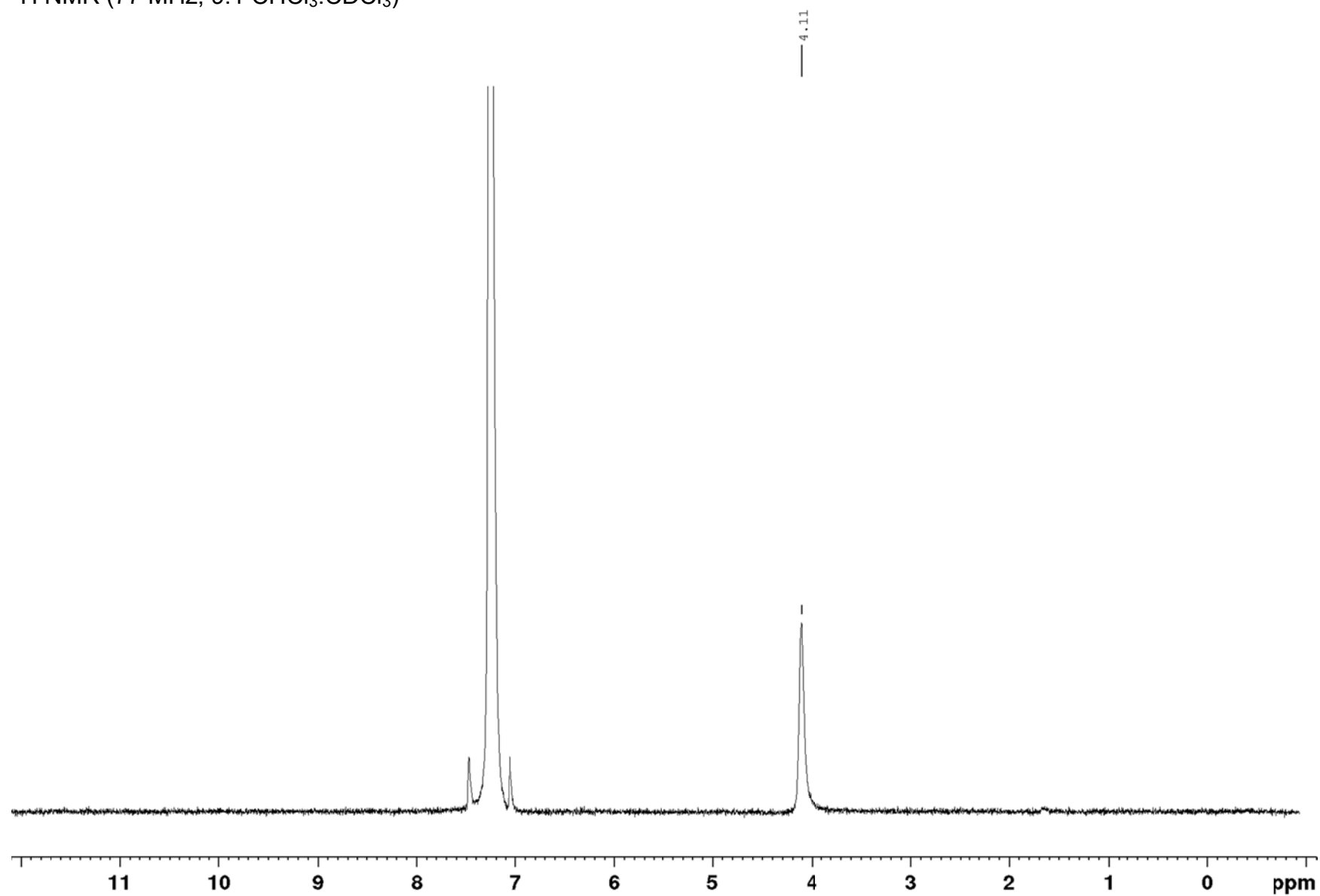


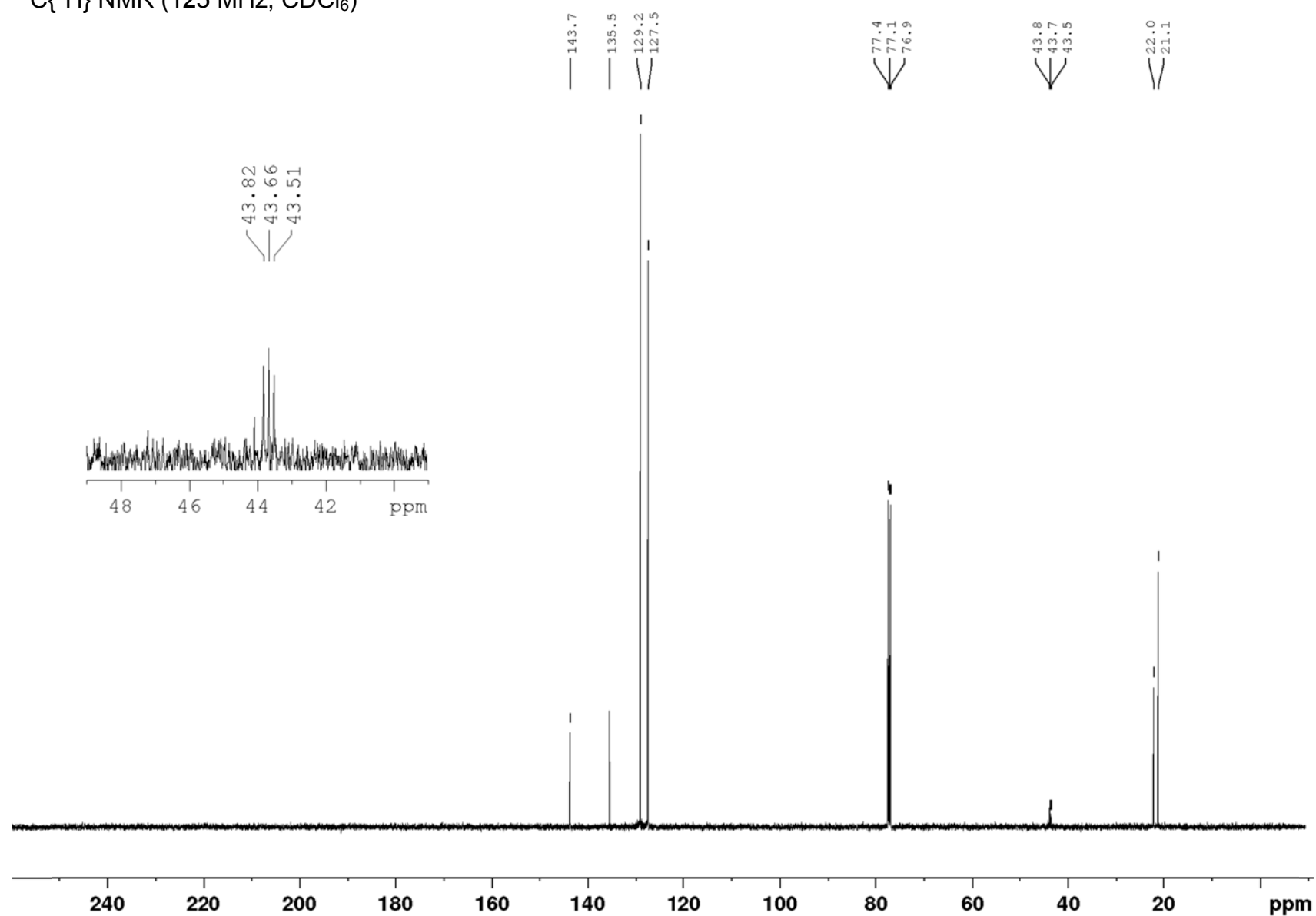
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

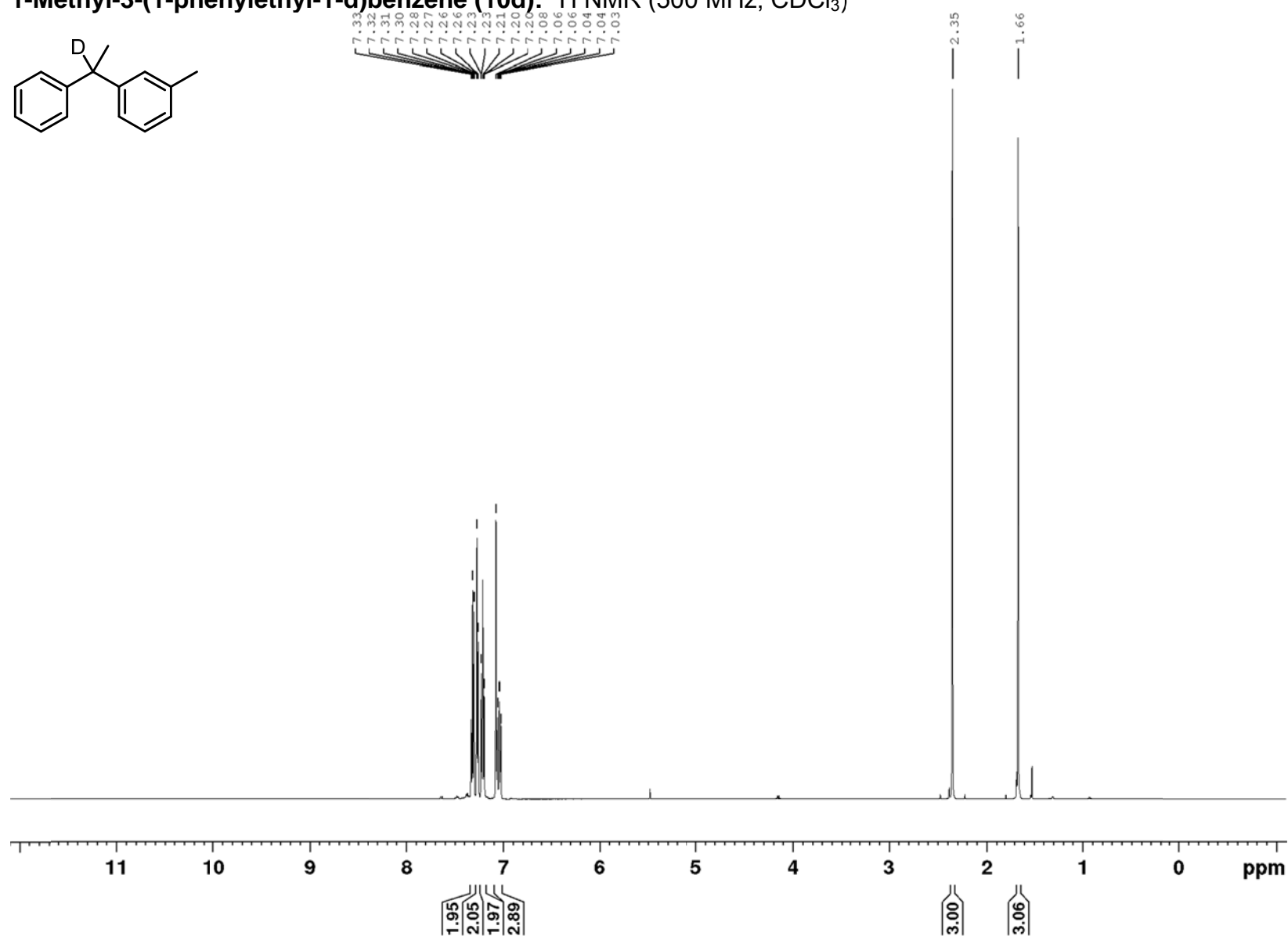
4,4'-(Ethane-1,1-diyl-1-*d*)bis(methylbenzene) (10c): ^1H NMR (500 MHz, CDCl_3)



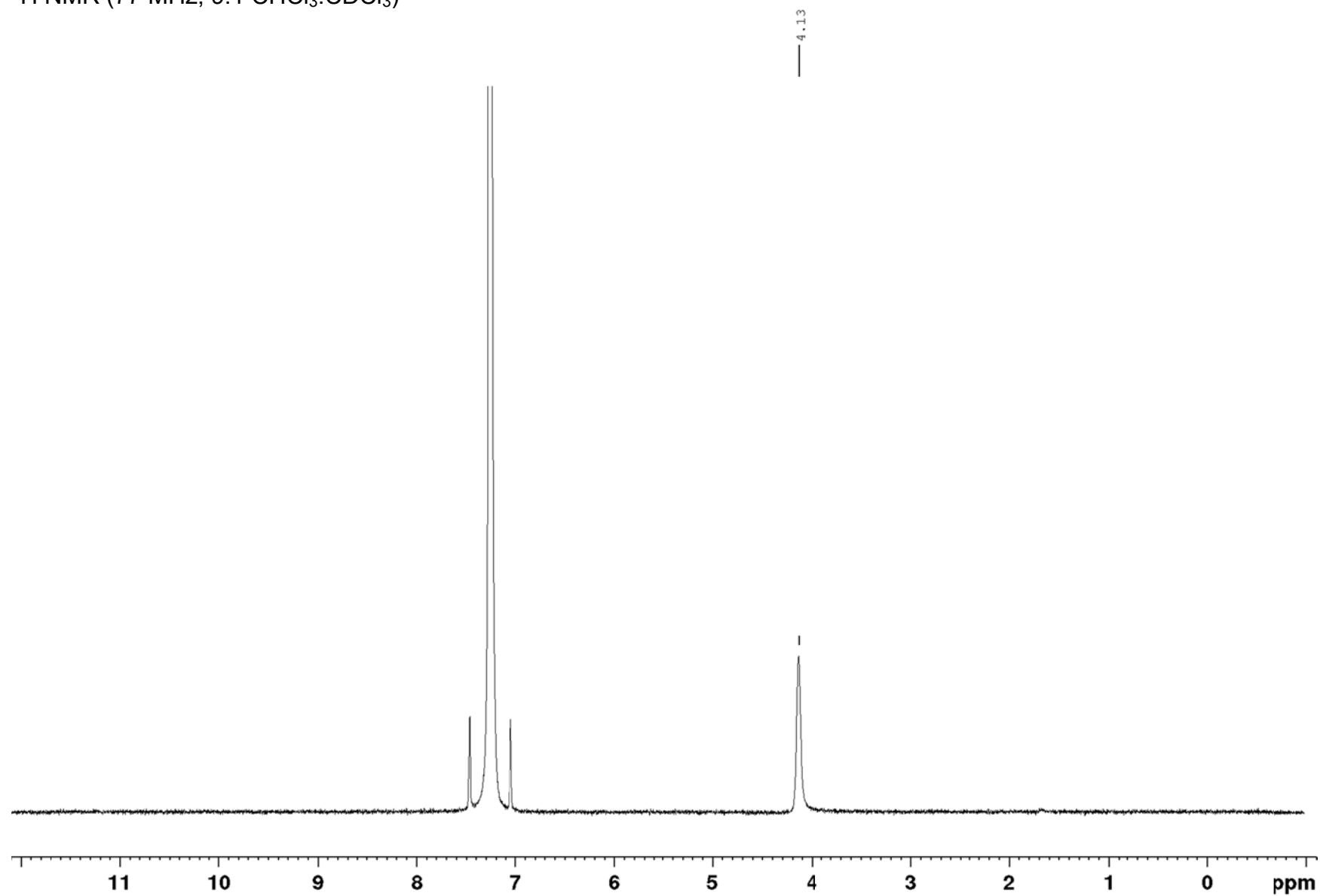
^2H NMR (77 MHz, 9:1 $\text{CHCl}_3:\text{CDCl}_3$)

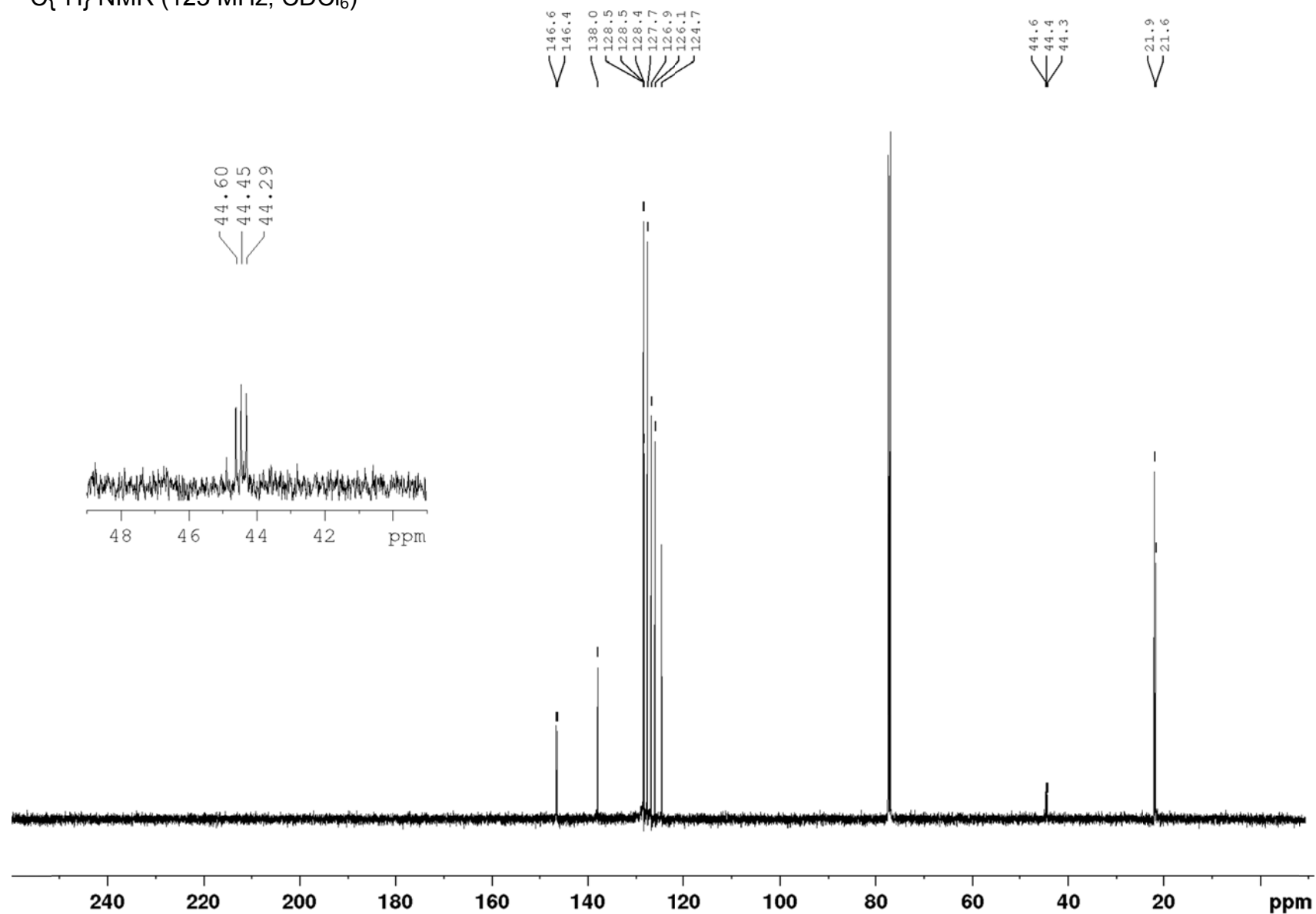


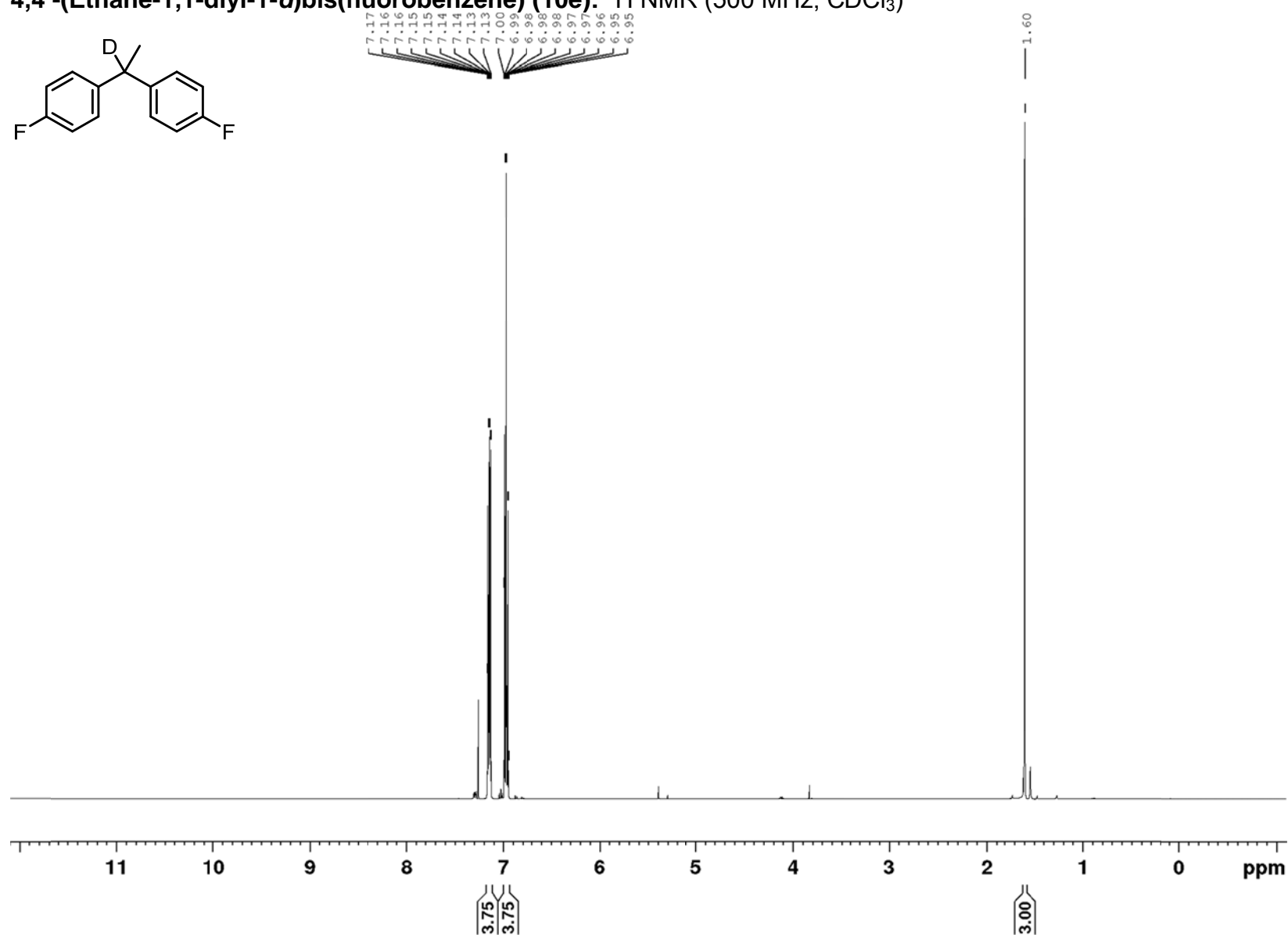
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

1-Methyl-3-(1-phenylethyl-1-d)benzene (10d): ^1H NMR (500 MHz, CDCl_3)

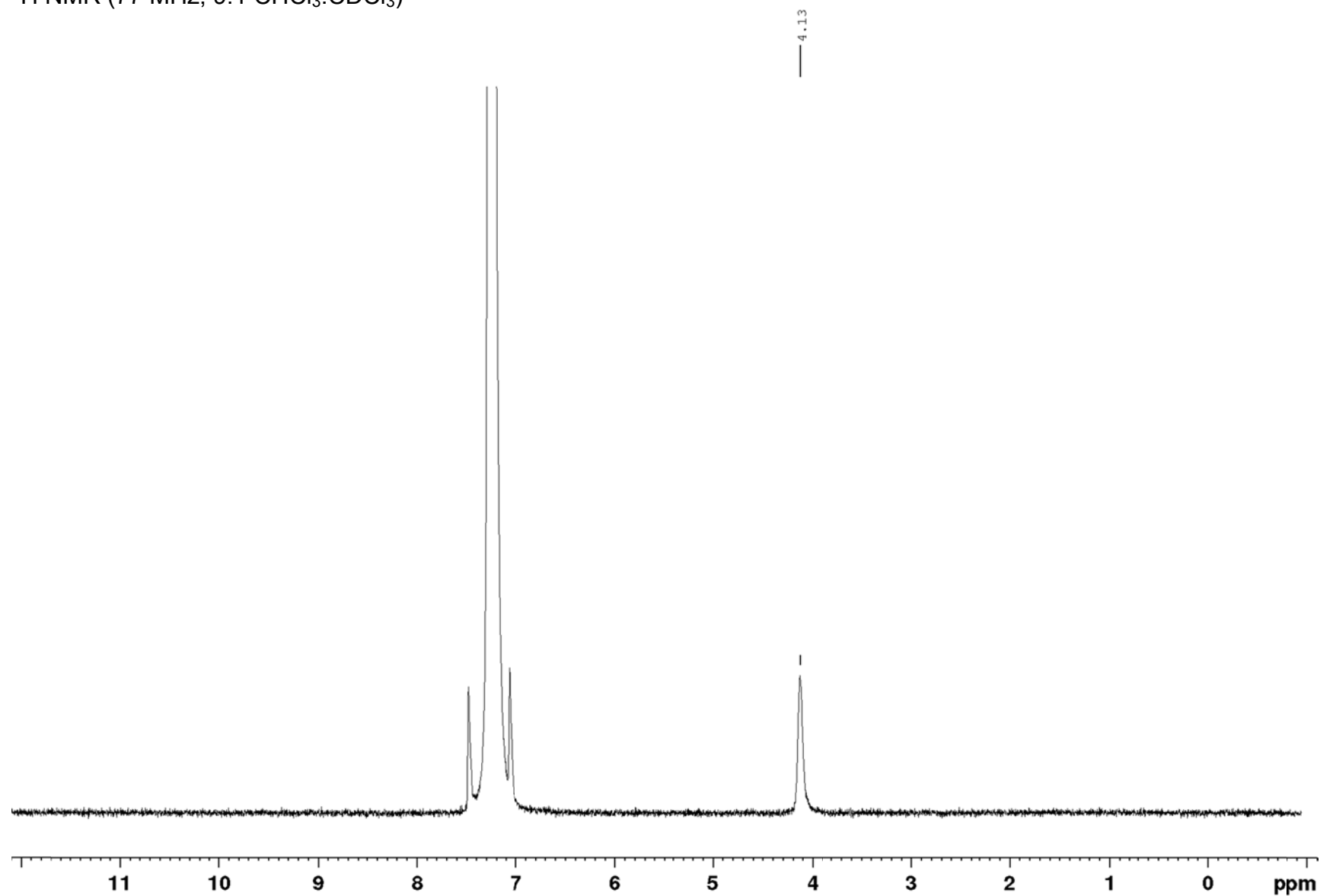
^2H NMR (77 MHz, 9:1 $\text{CHCl}_3:\text{CDCl}_3$)

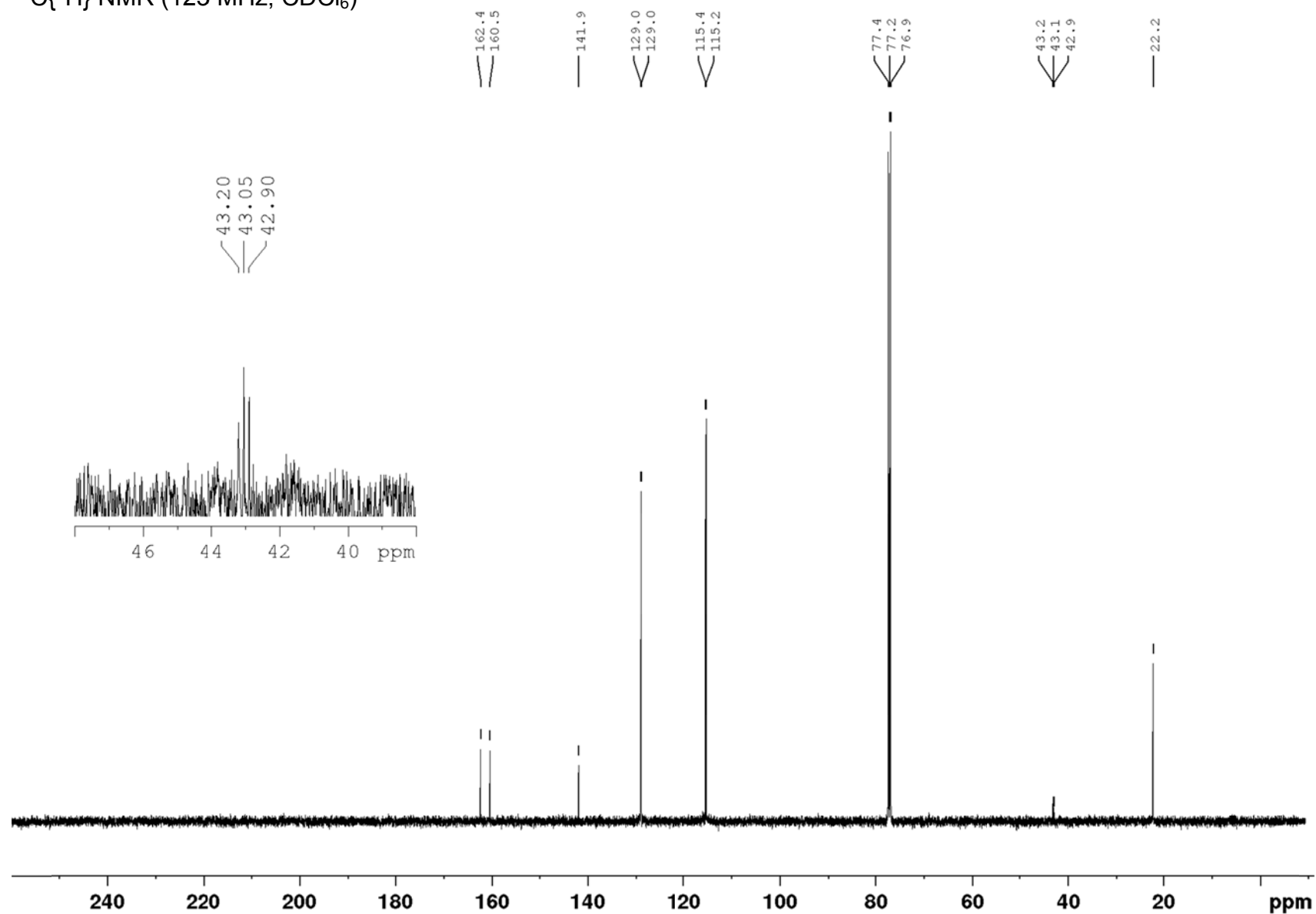


$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

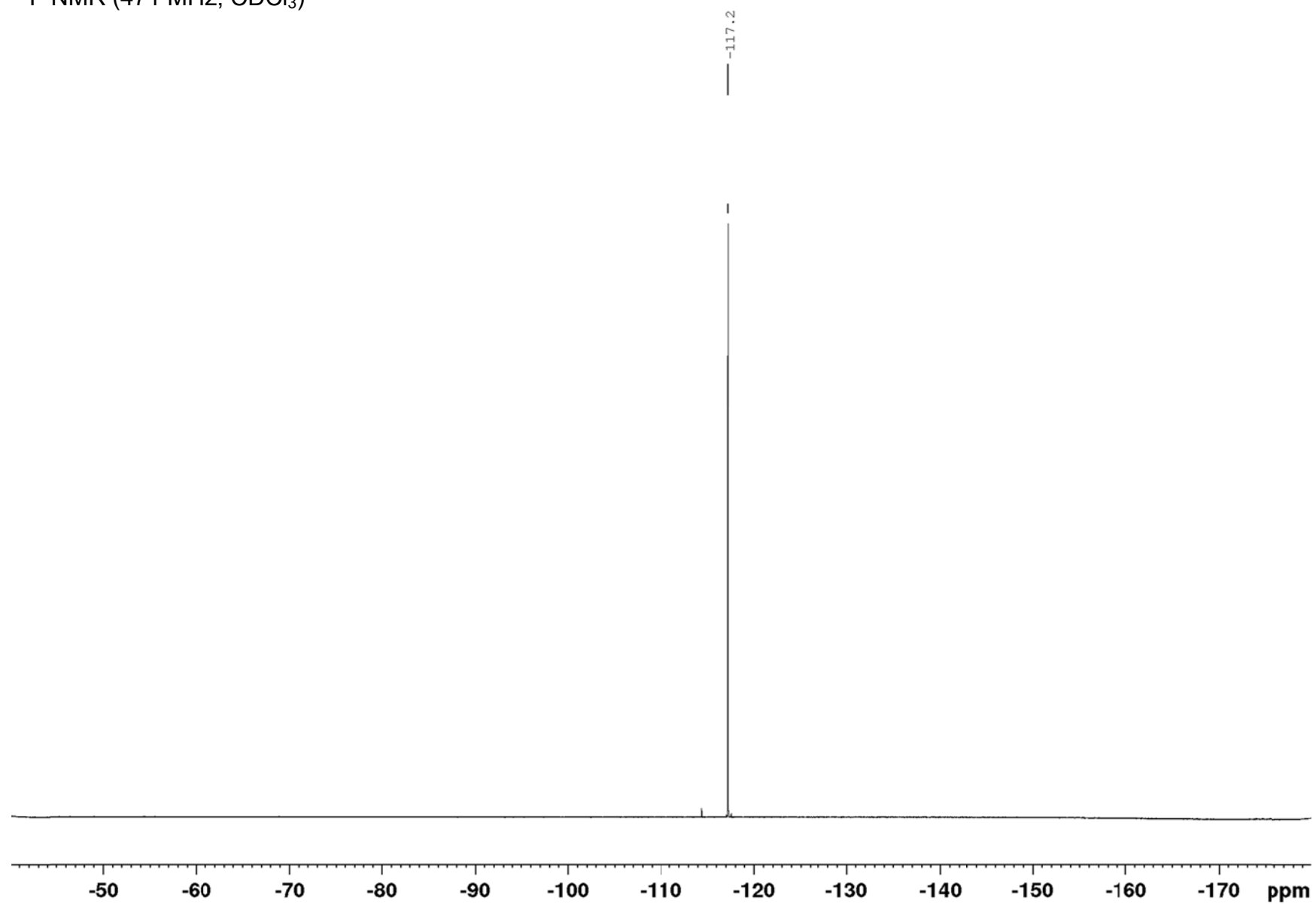
4,4'-(Ethane-1,1-diyl-1-*d*)bis(fluorobenzene) (10e): ^1H NMR (500 MHz, CDCl_3)

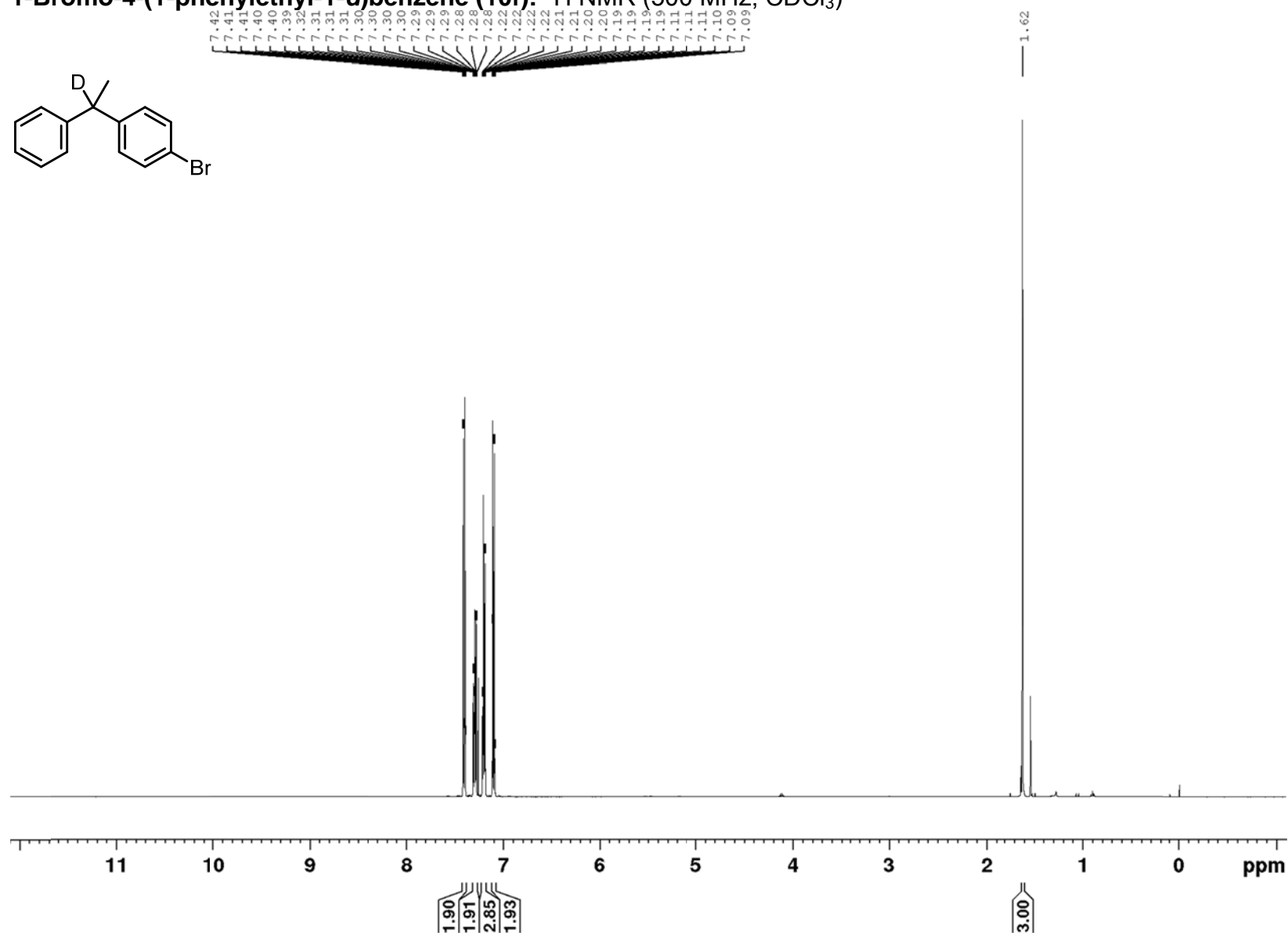
^2H NMR (77 MHz, 9:1 $\text{CHCl}_3:\text{CDCl}_3$)



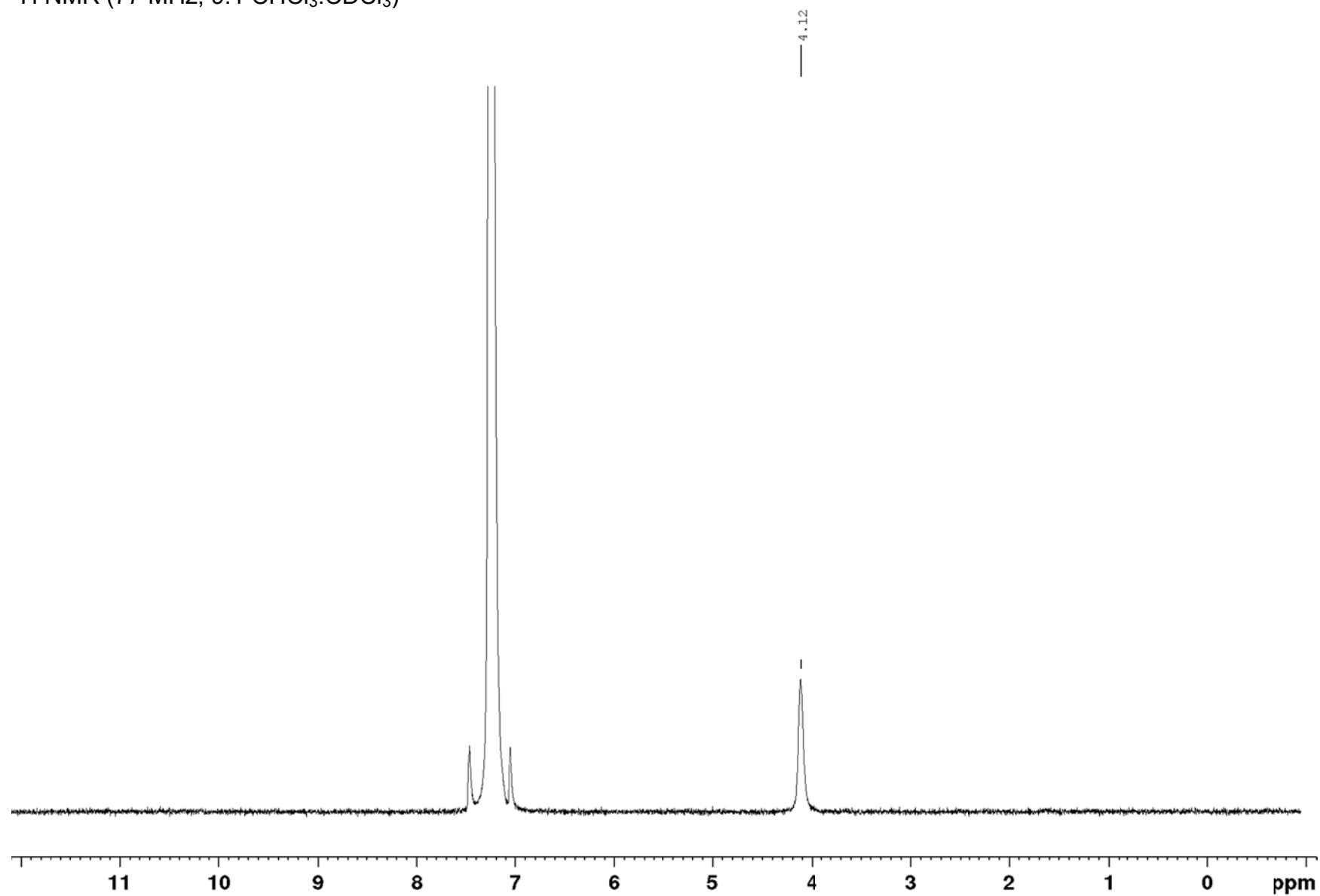
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

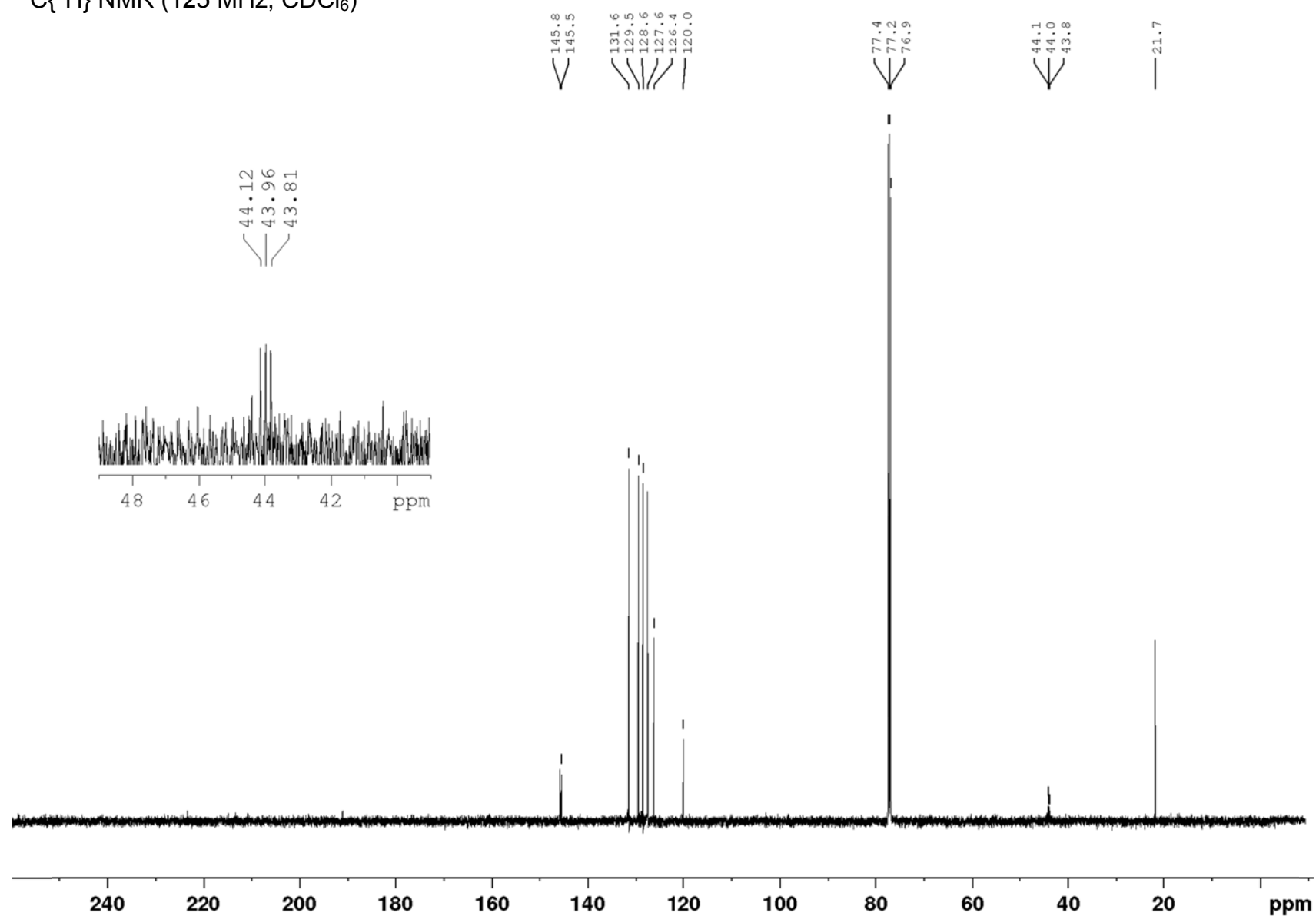
^{19}F NMR (471 MHz, CDCl_3)

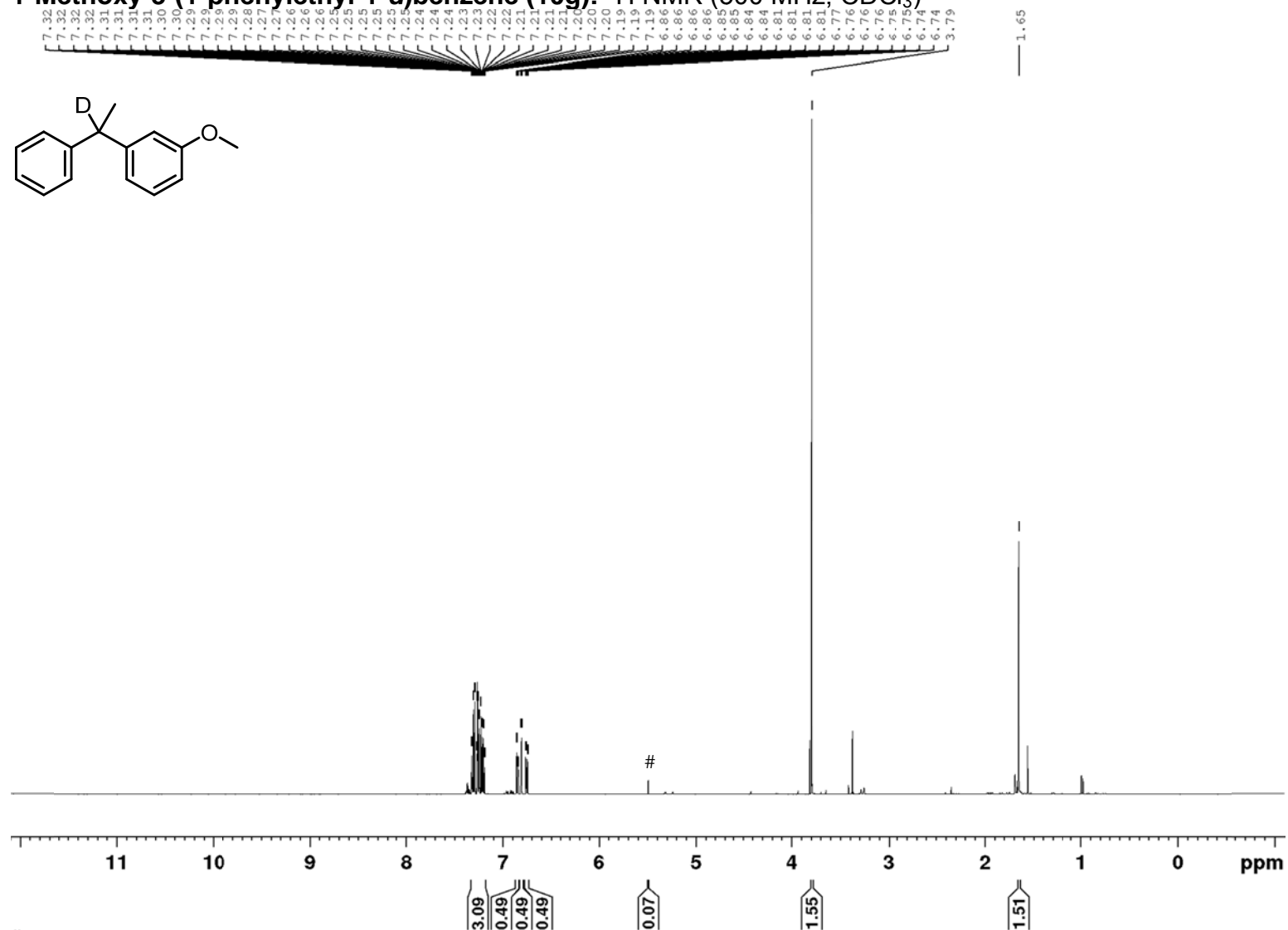


1-Bromo-4-(1-phenylethyl-1-*d*)benzene (10f): ^1H NMR (500 MHz, CDCl_3)

^2H NMR (77 MHz, 9:1 $\text{CHCl}_3:\text{CDCl}_3$)

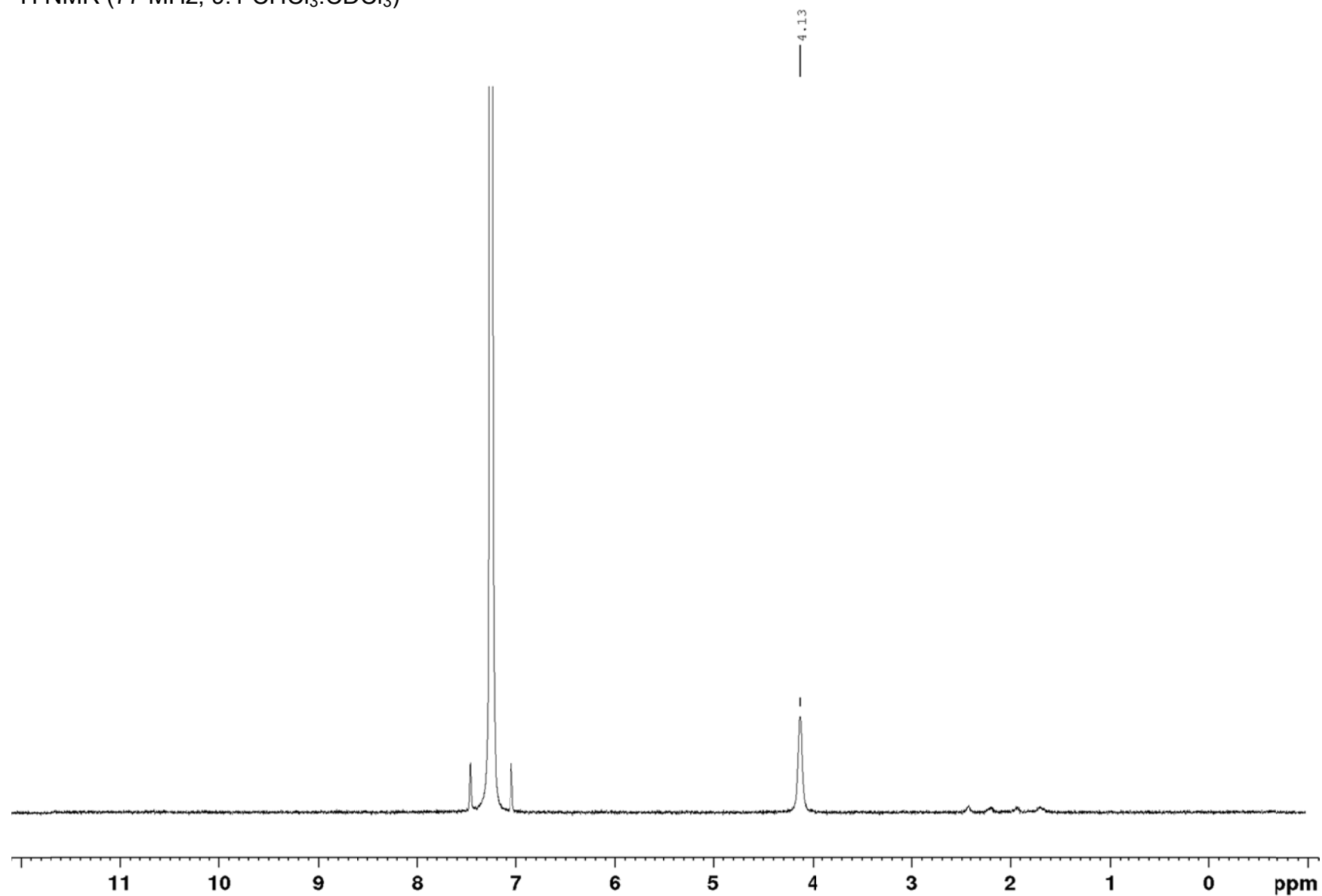


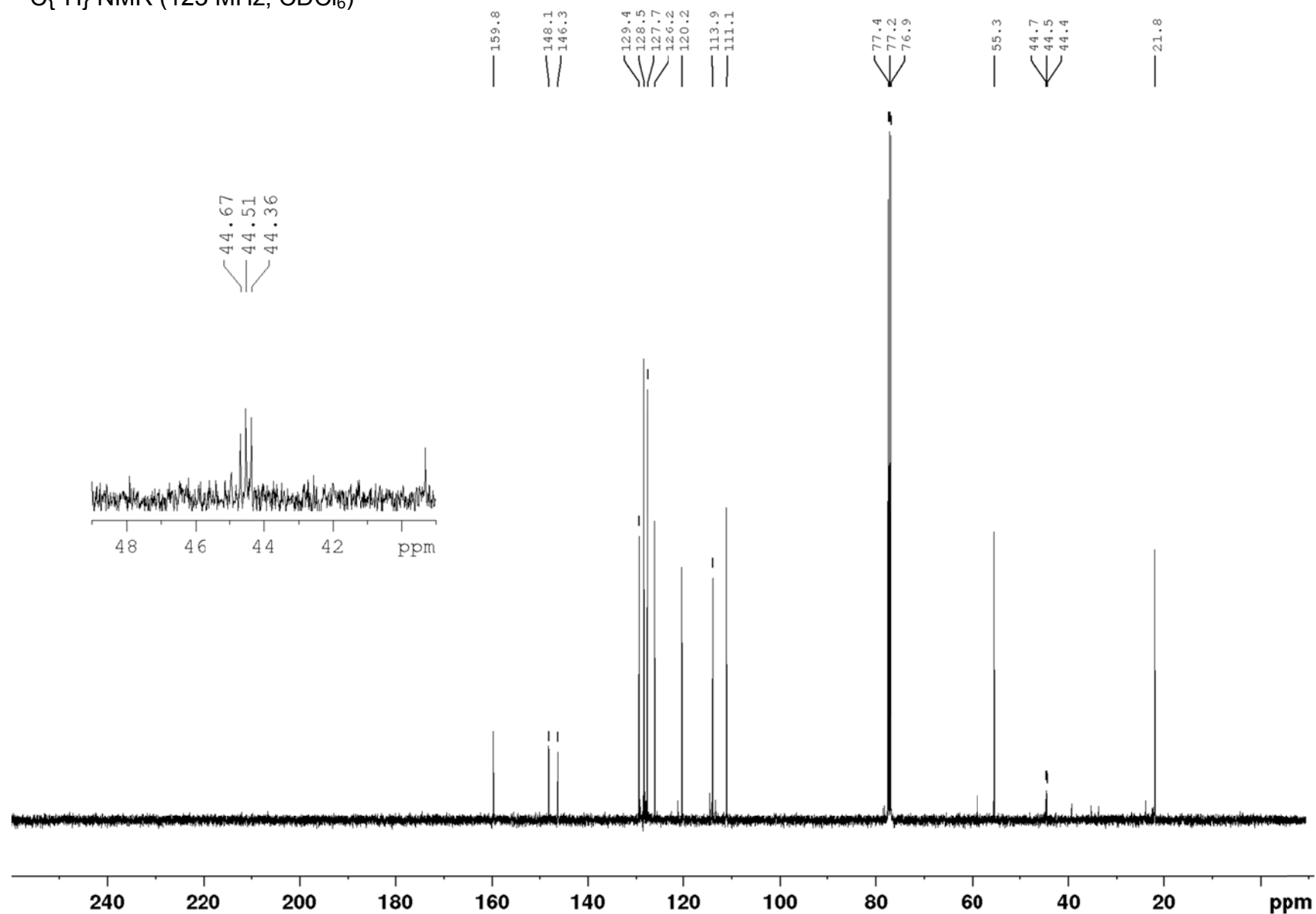
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

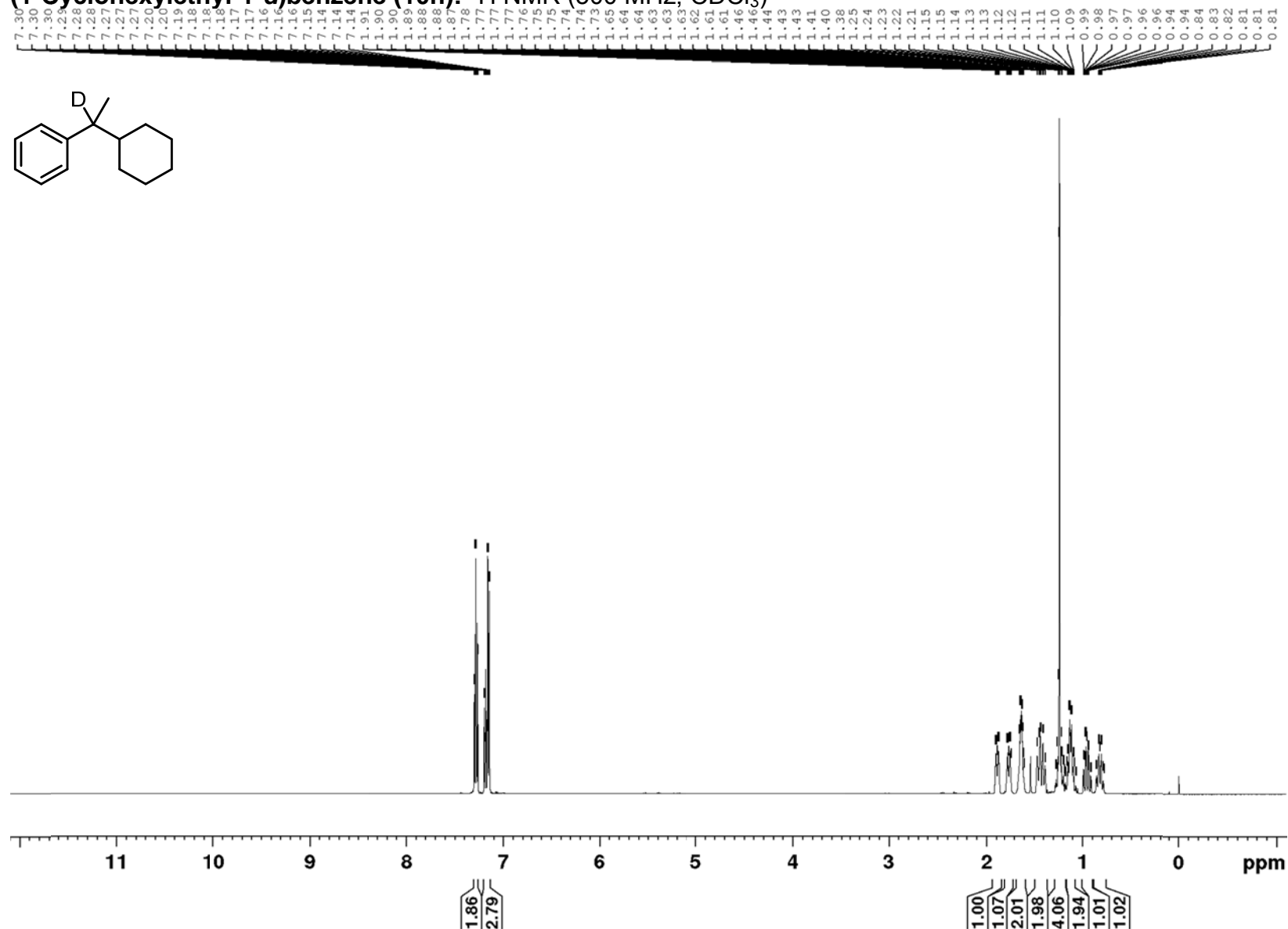
1-Methoxy-3-(1-phenylethyl-1-*d*)benzene (10g): ^1H NMR (500 MHz, CDCl_3)

#Peak corresponds to unreacted starting material

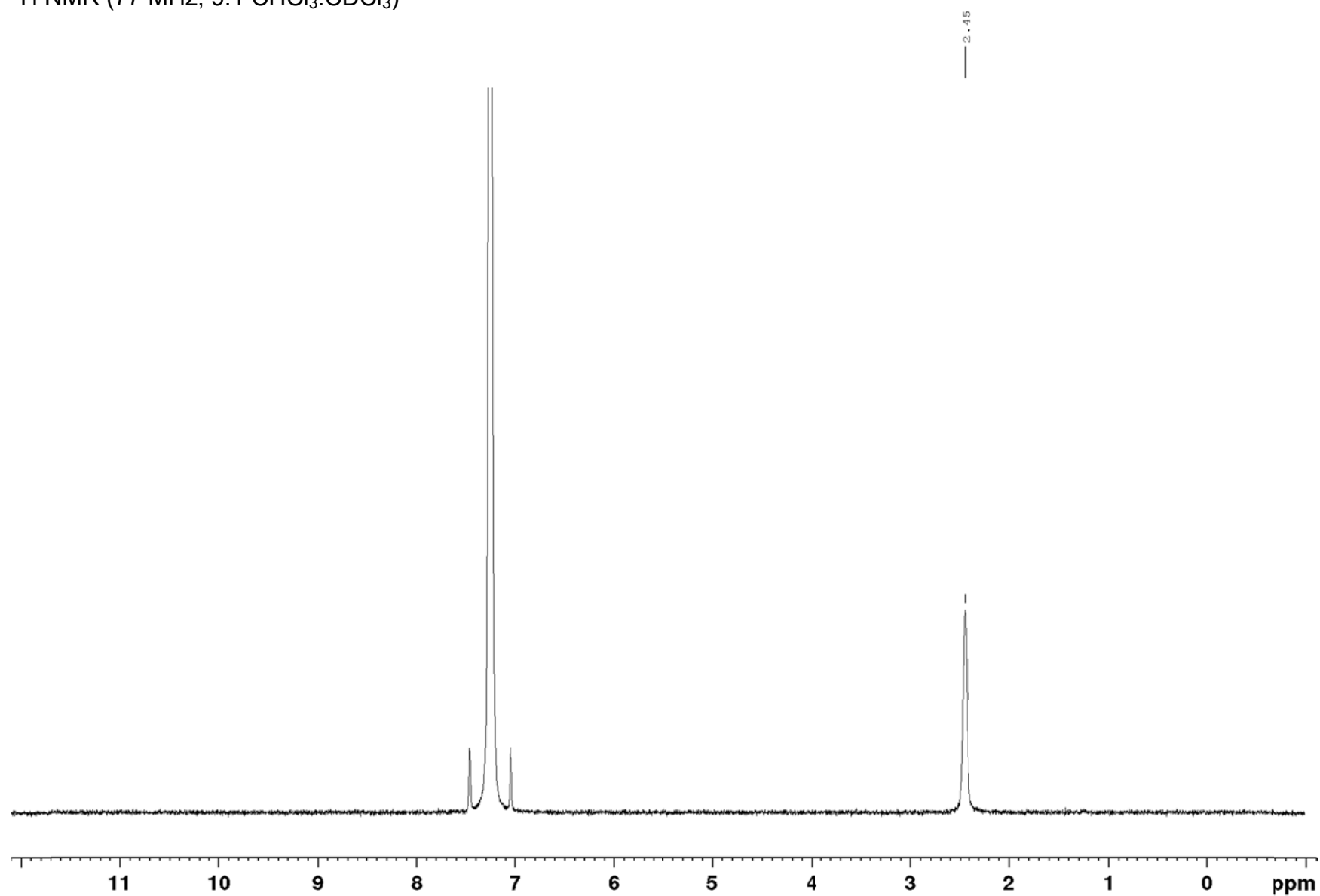
^2H NMR (77 MHz, 9:1 $\text{CHCl}_3:\text{CDCl}_3$)

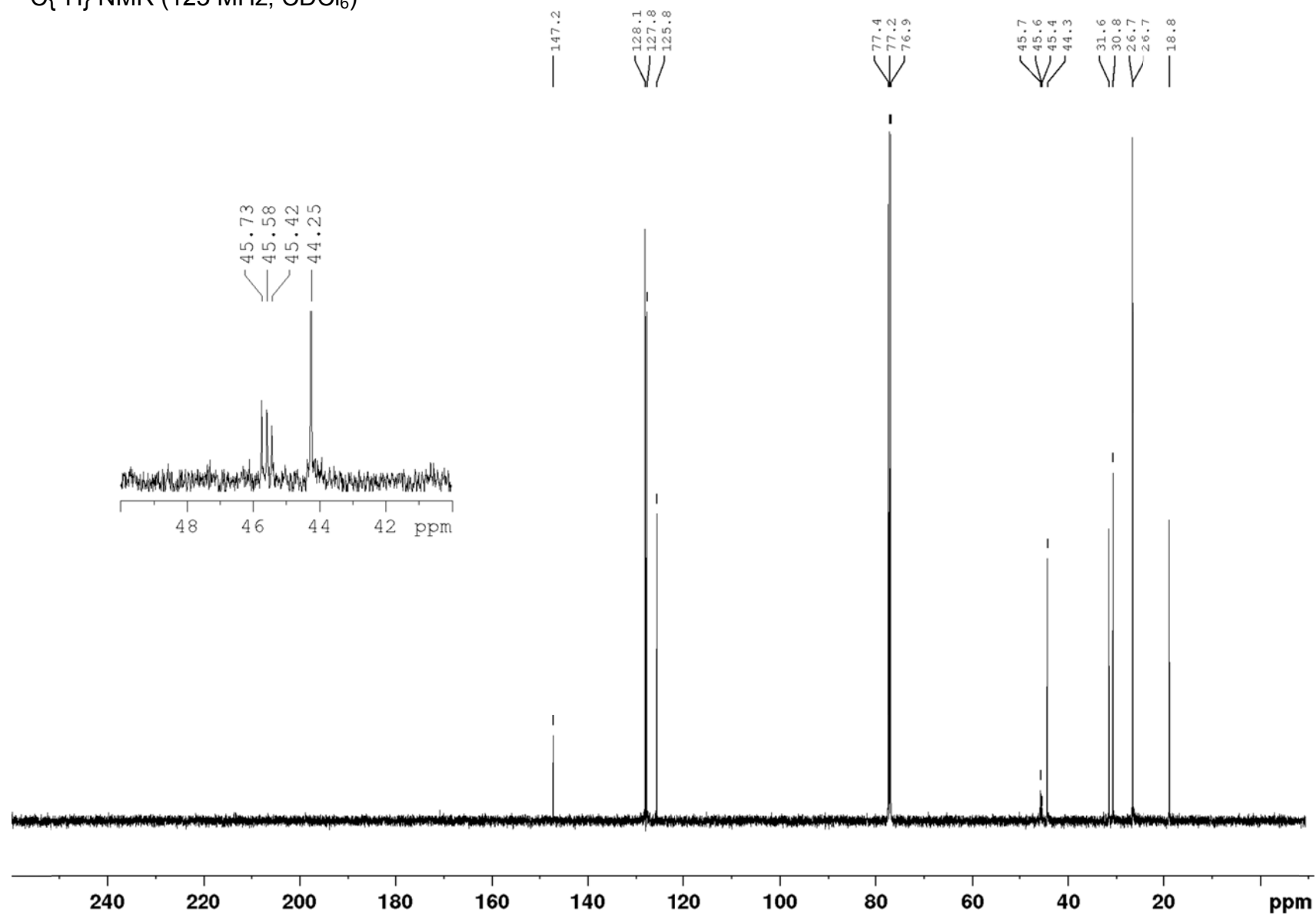


$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

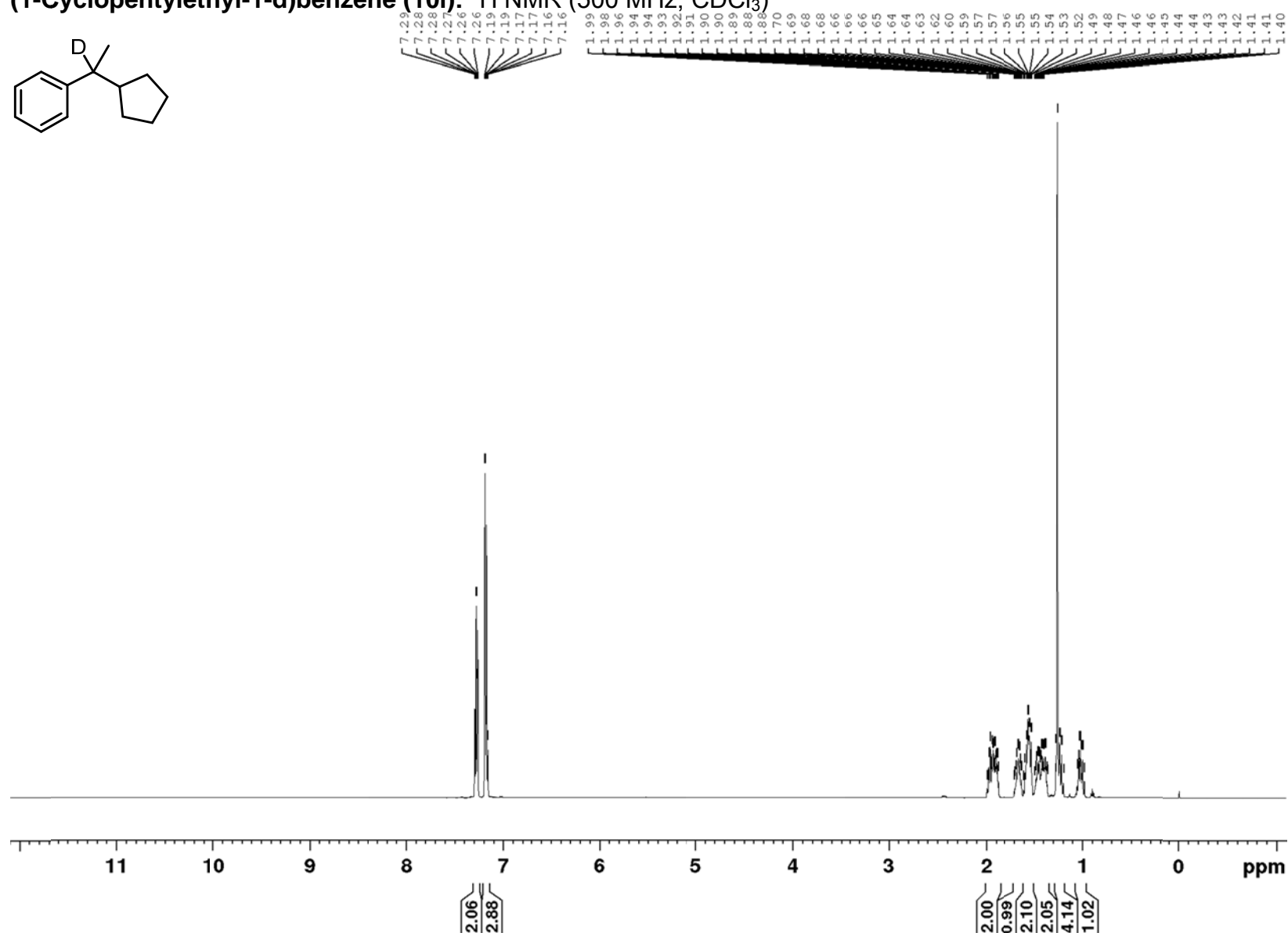
(1-Cyclohexylethyl-1-*d*)benzene (10h): ^1H NMR (500 MHz, CDCl_3)

^2H NMR (77 MHz, 9:1 $\text{CHCl}_3:\text{CDCl}_3$)

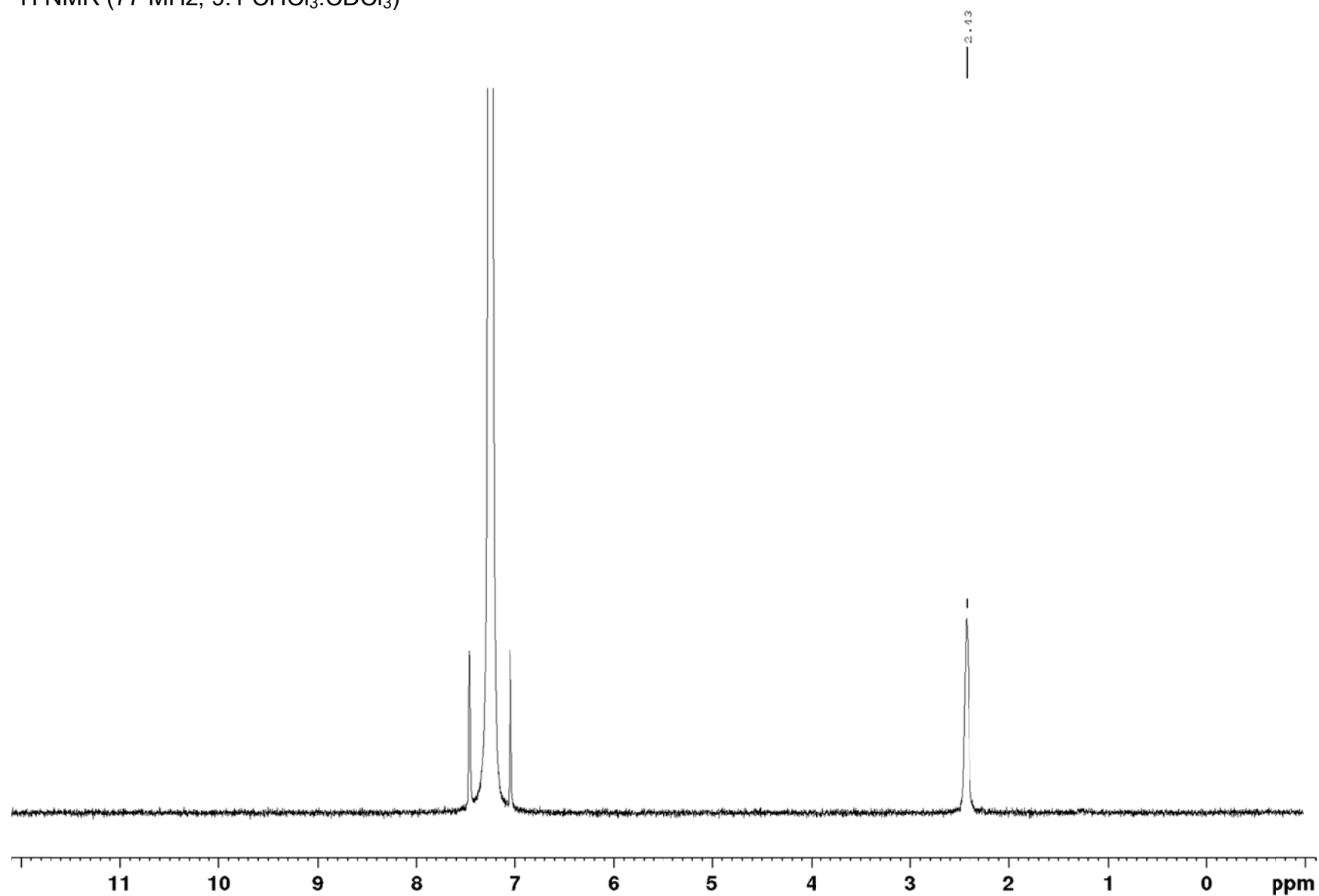


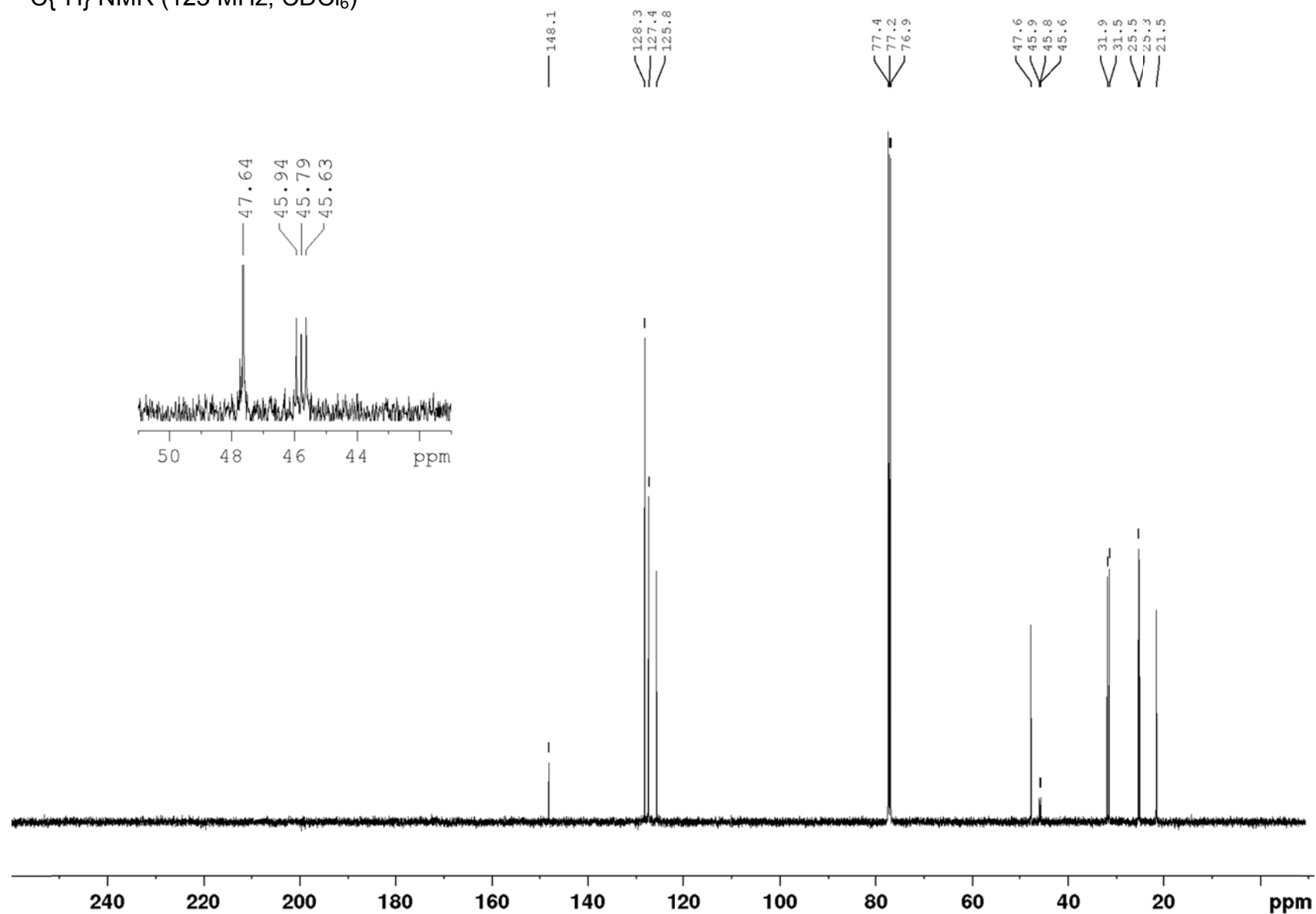
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

(1-Cyclopentylethyl-1-d)benzene (**10i**): ^1H NMR (500 MHz, CDCl_3)

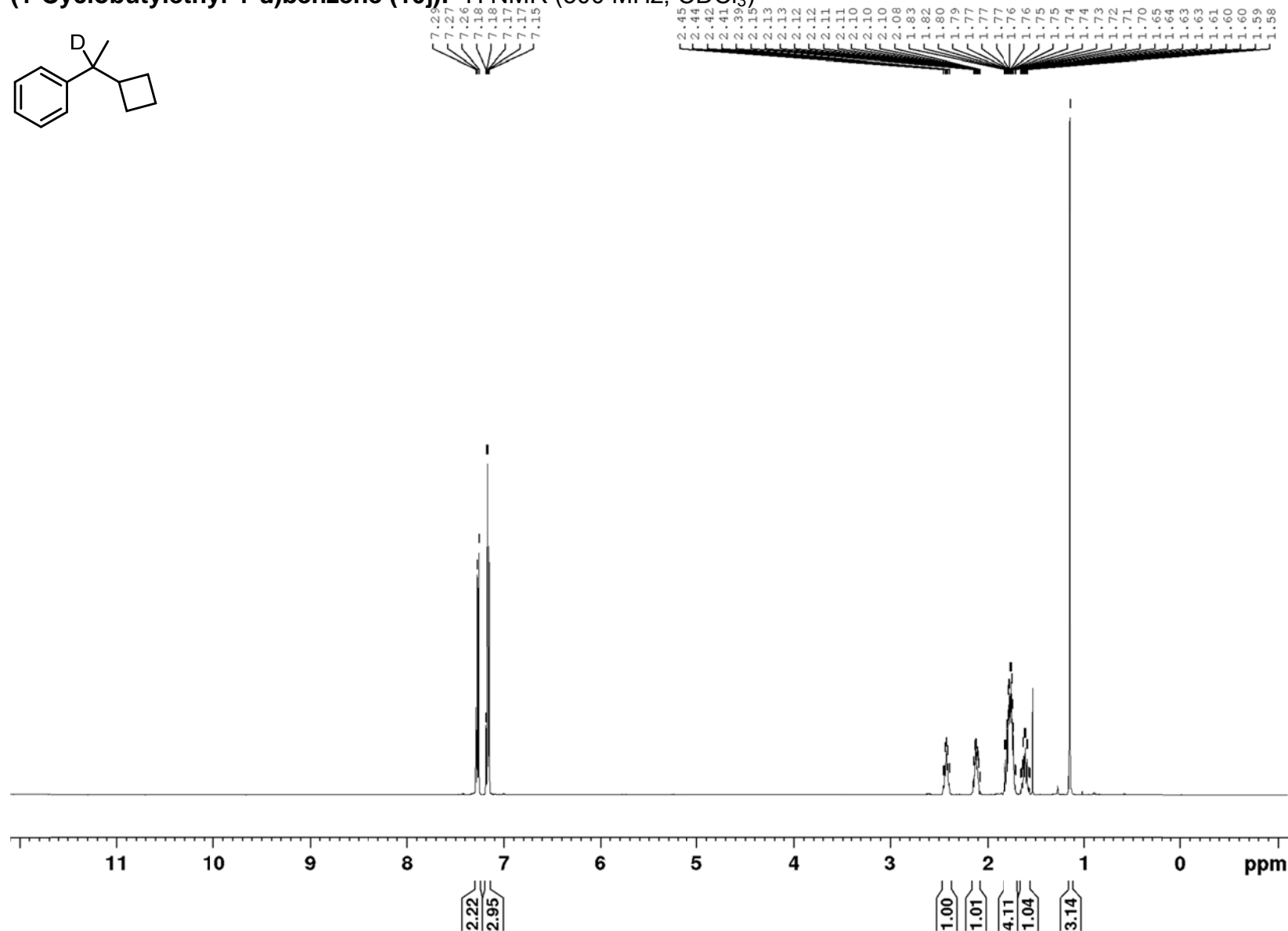


^2H NMR (77 MHz, 9:1 $\text{CHCl}_3:\text{CDCl}_3$)

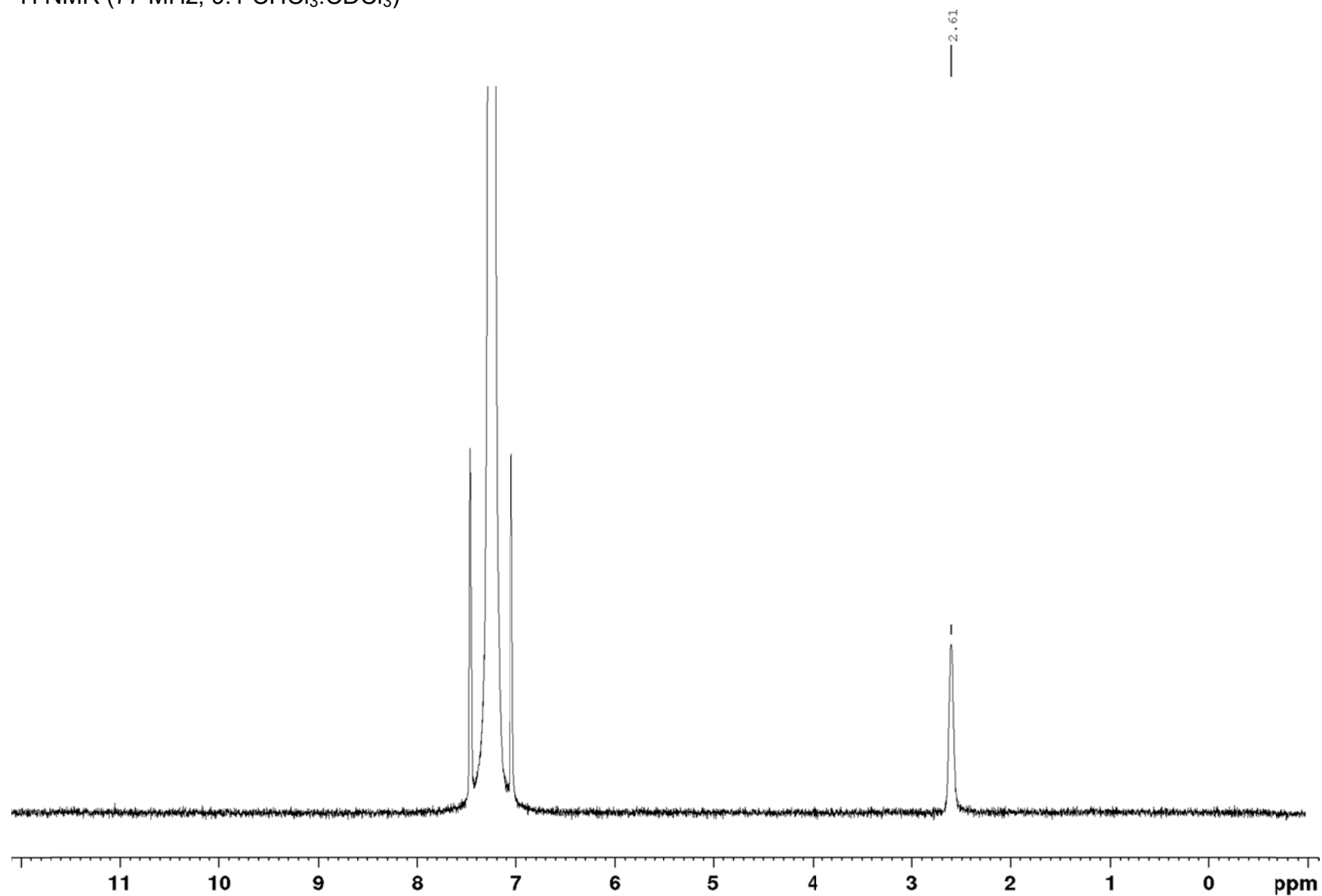


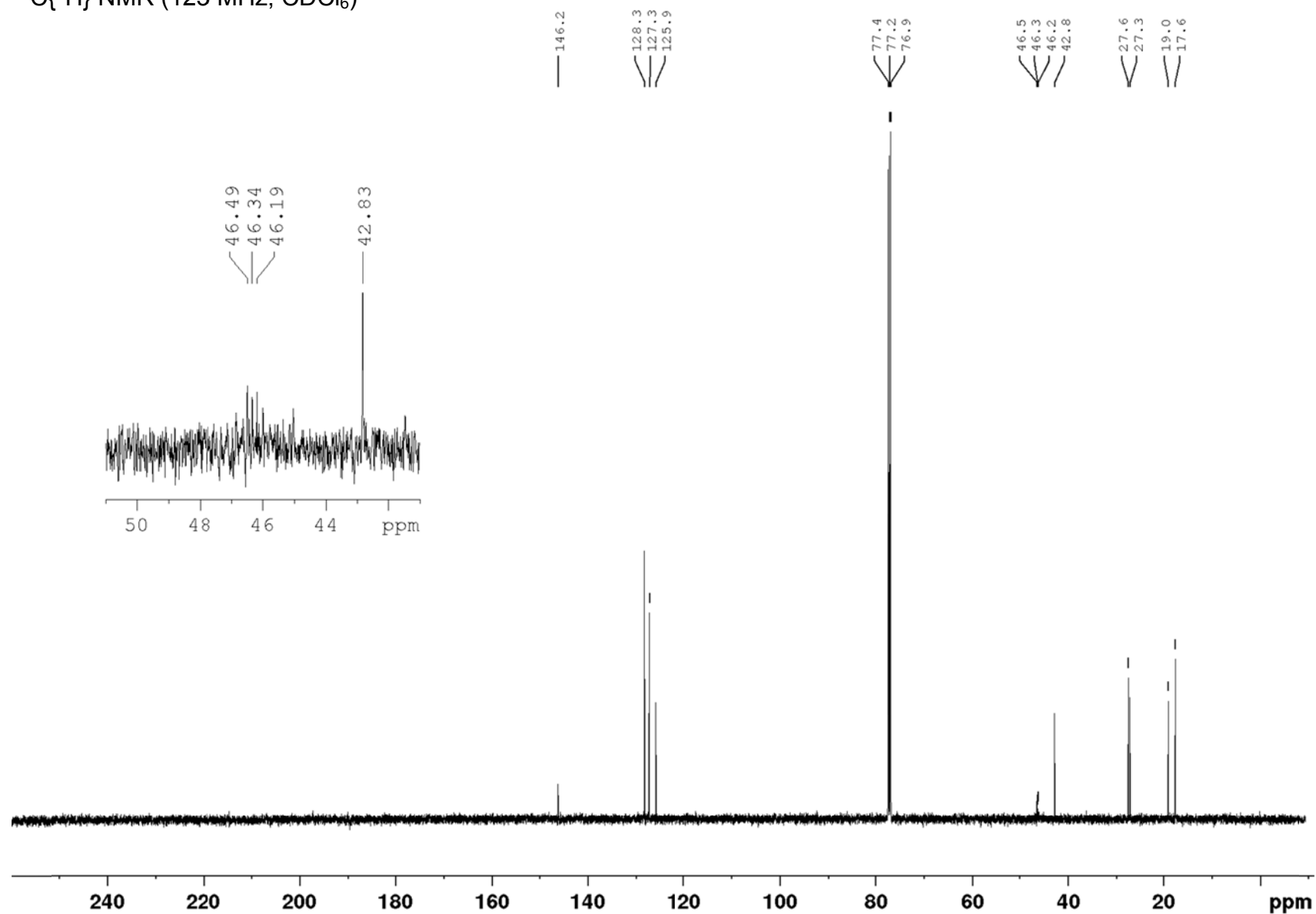
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

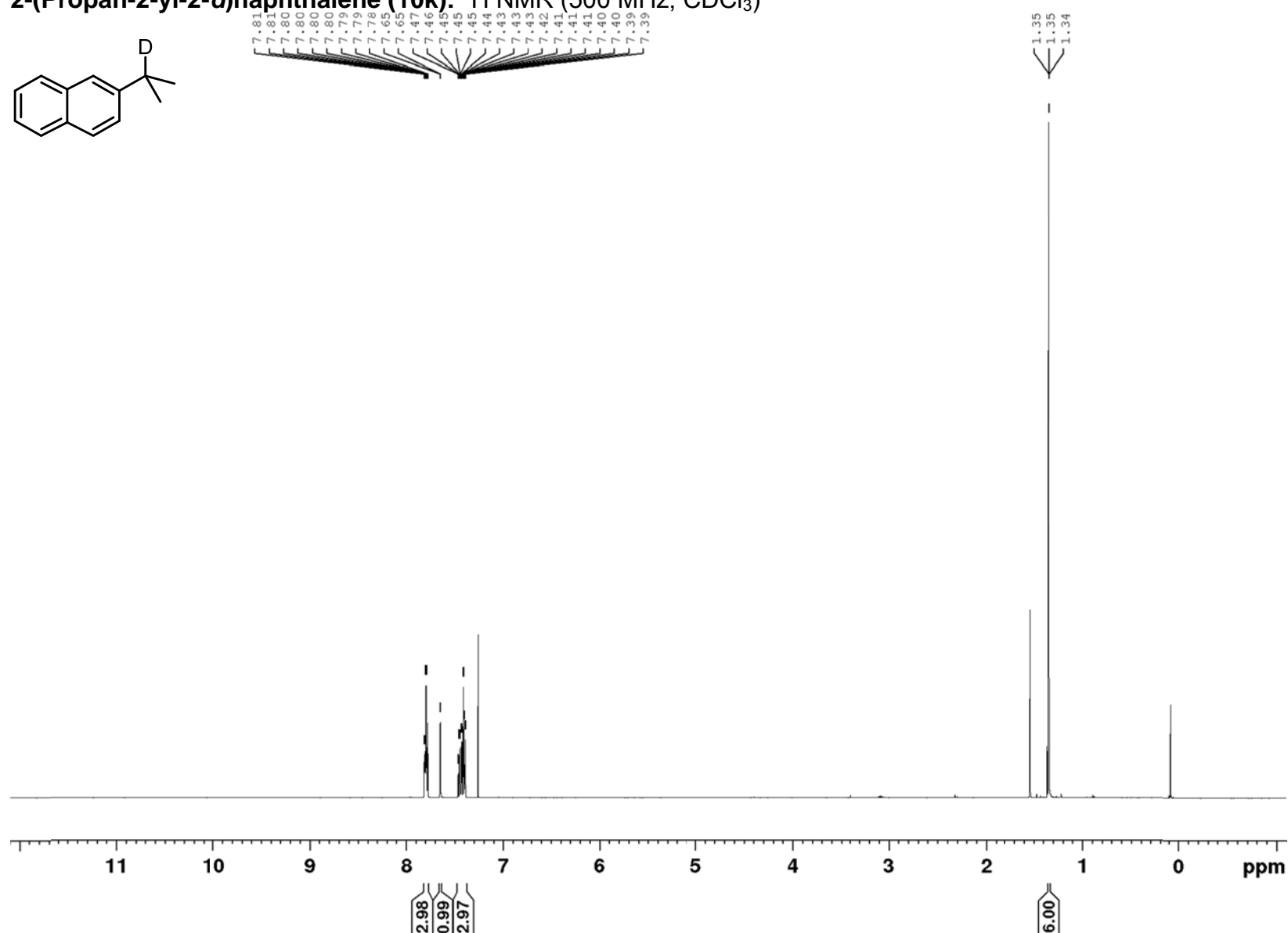
(1-Cyclobutylethyl-1-*d*)benzene (10j): ^1H NMR (500 MHz, CDCl_3)



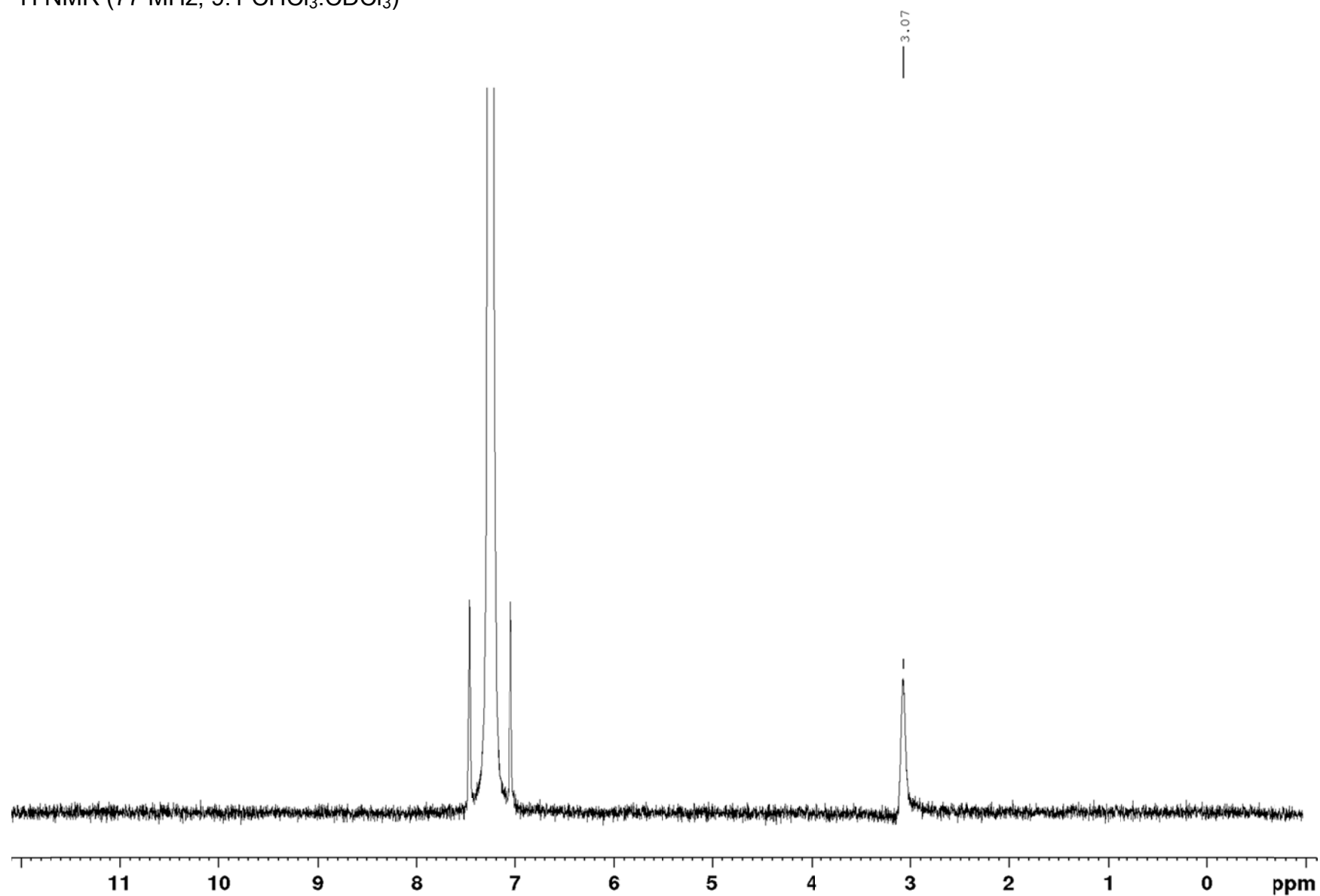
^2H NMR (77 MHz, 9:1 $\text{CHCl}_3:\text{CDCl}_3$)

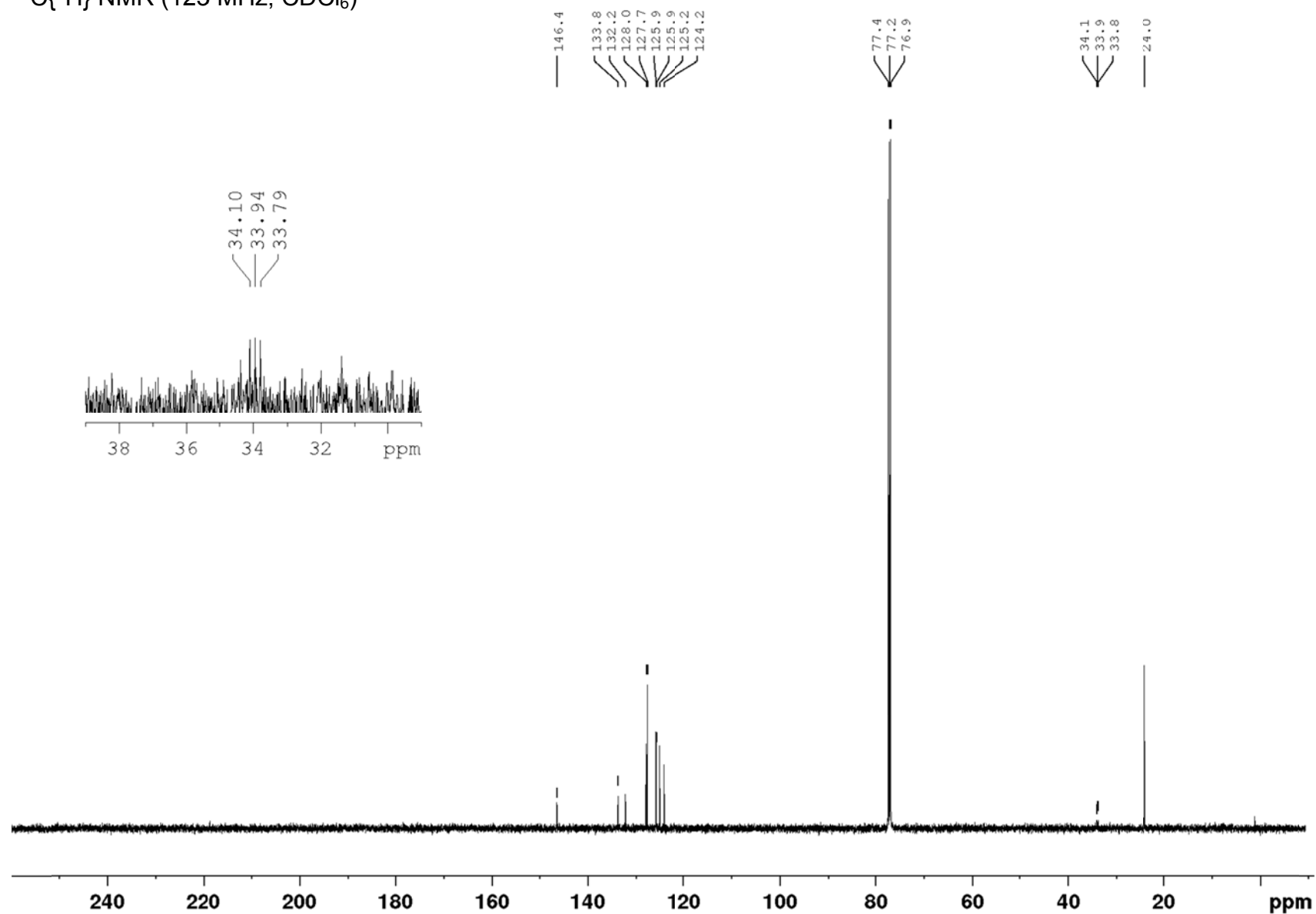


$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

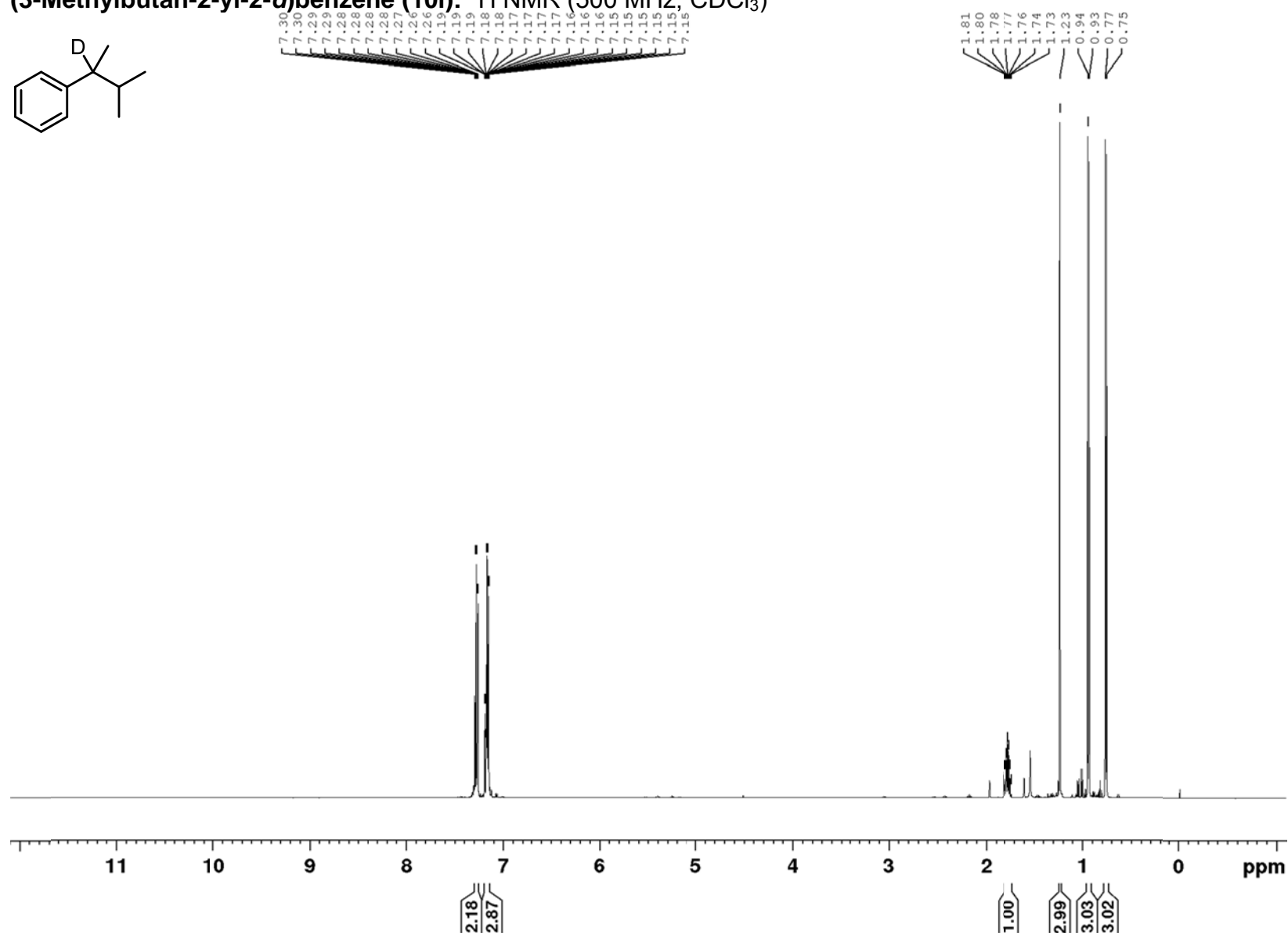
2-(Propan-2-yl-2-*d*)naphthalene (10k): ^1H NMR (500 MHz, CDCl_3)

^2H NMR (77 MHz, 9:1 $\text{CHCl}_3:\text{CDCl}_3$)

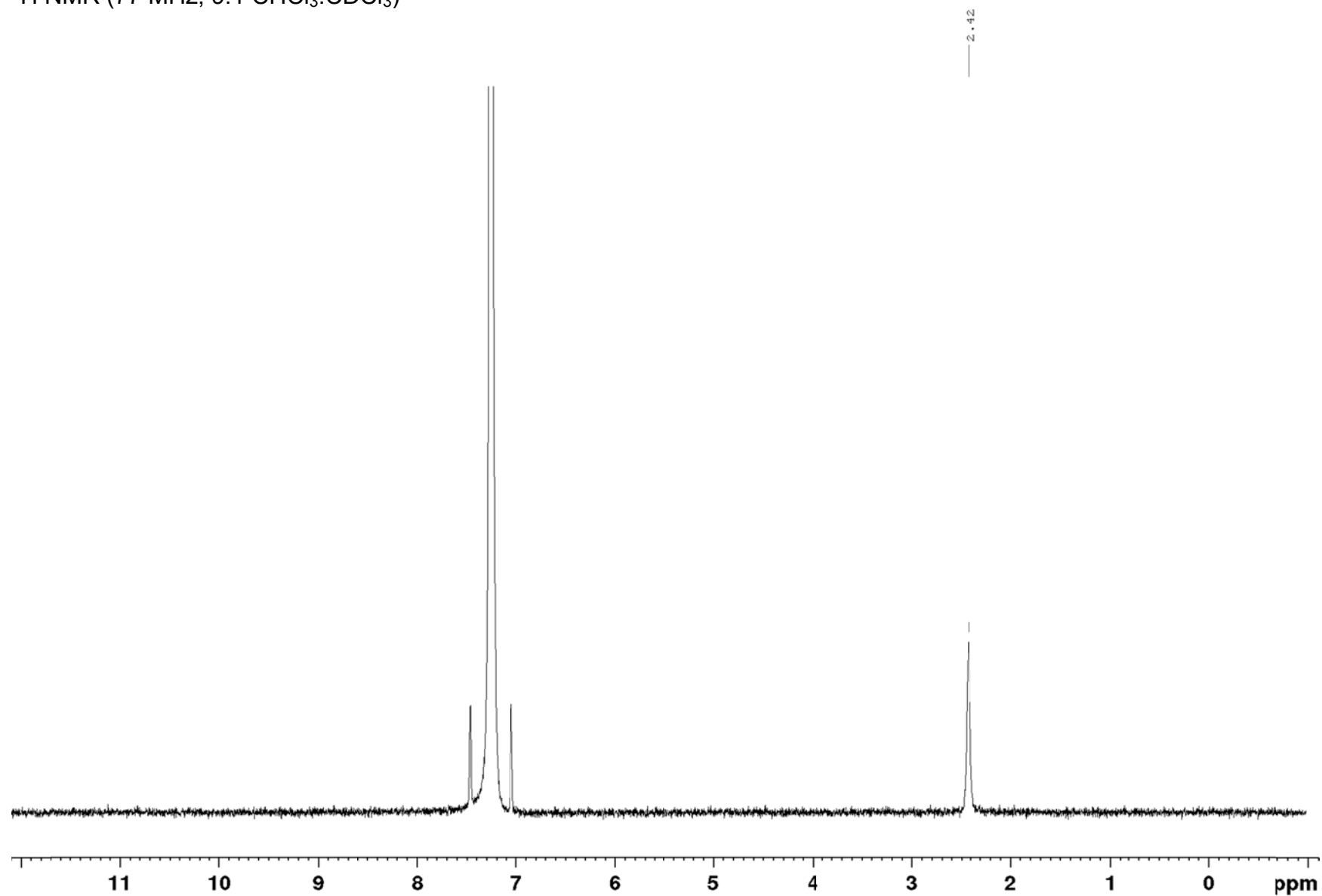


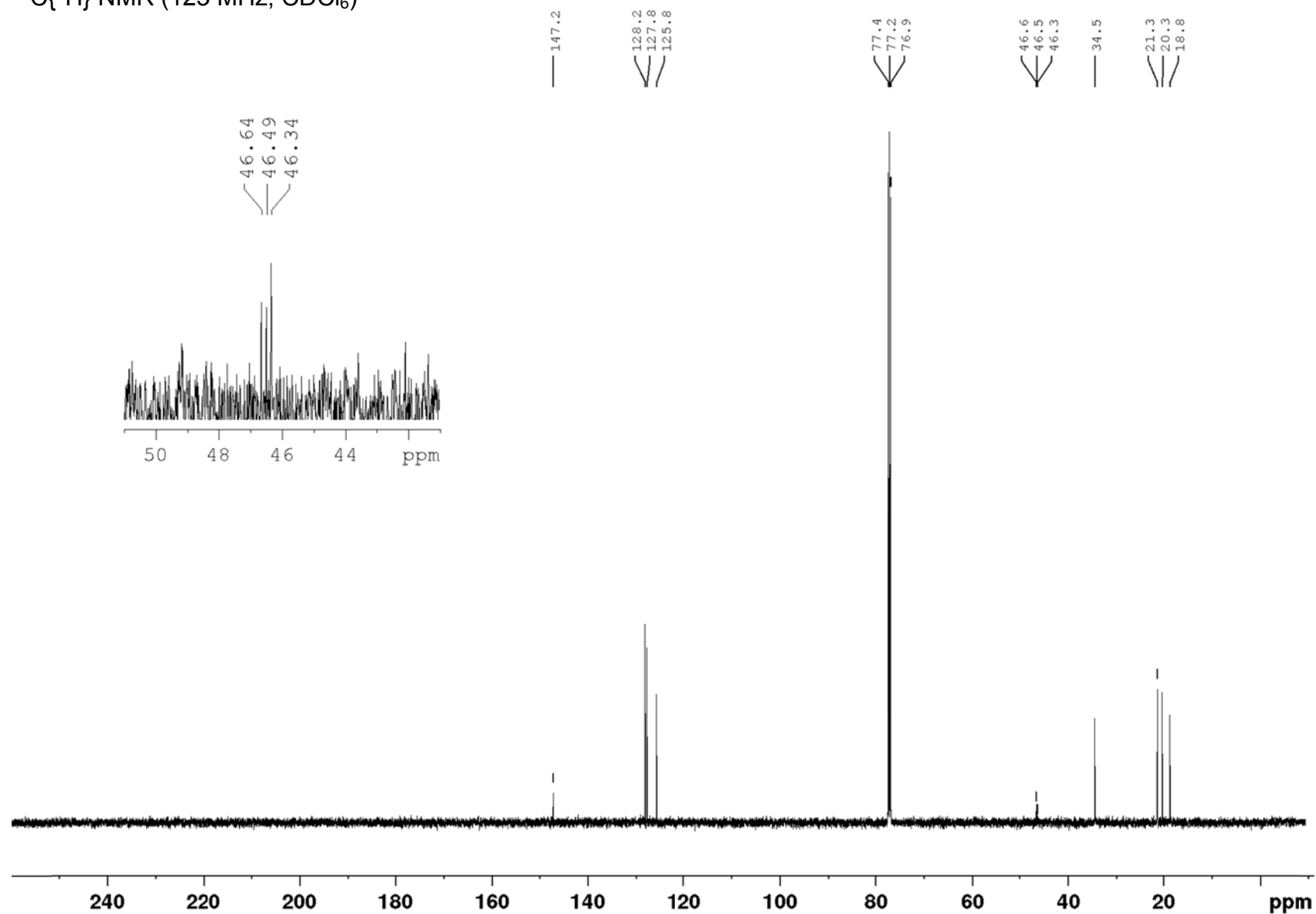
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

(3-Methylbutan-2-yl-2-*d*)benzene (10I): ^1H NMR (500 MHz, CDCl_3)

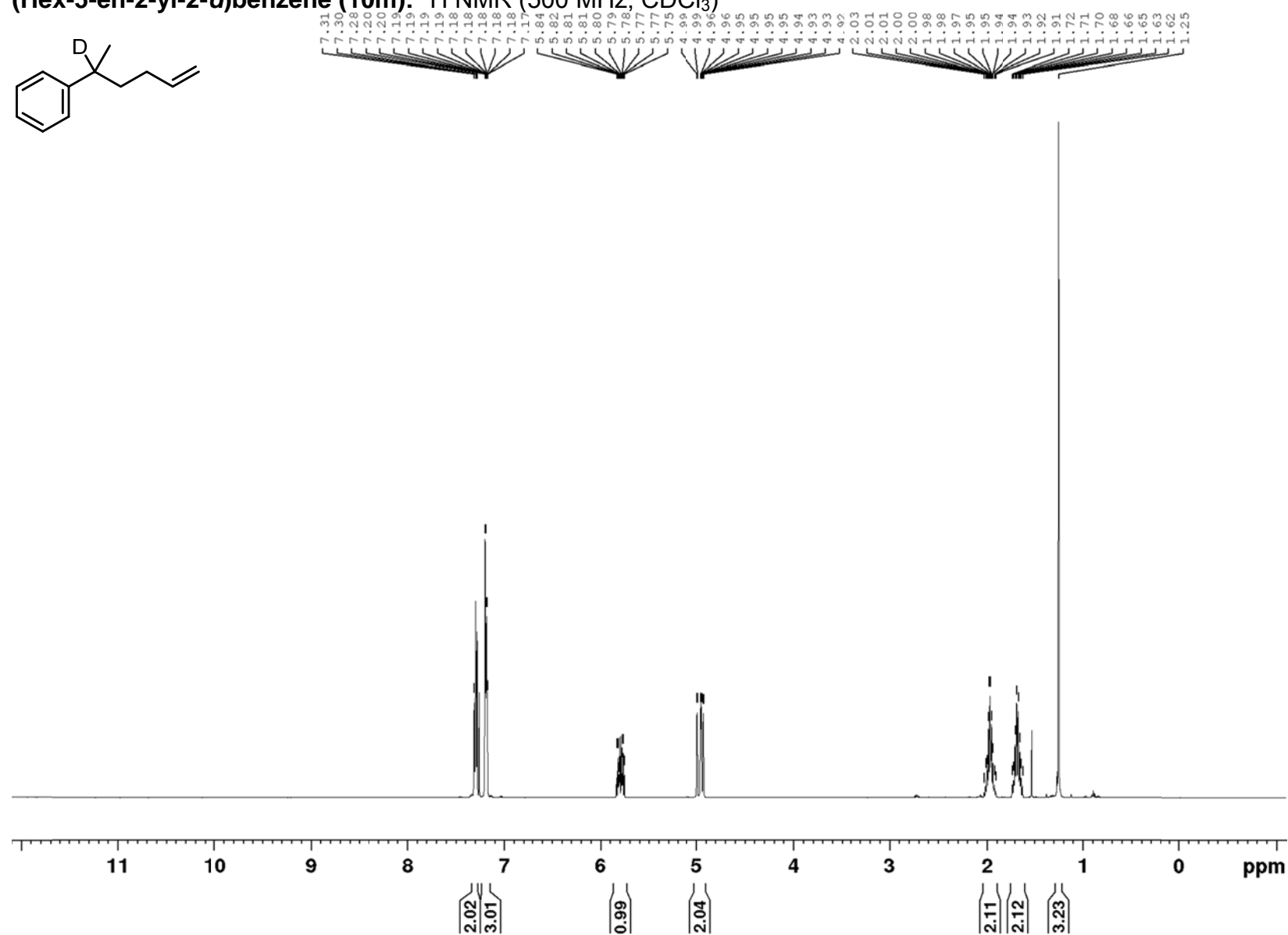
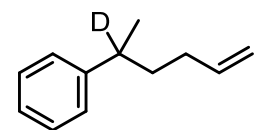


^2H NMR (77 MHz, 9:1 $\text{CHCl}_3:\text{CDCl}_3$)

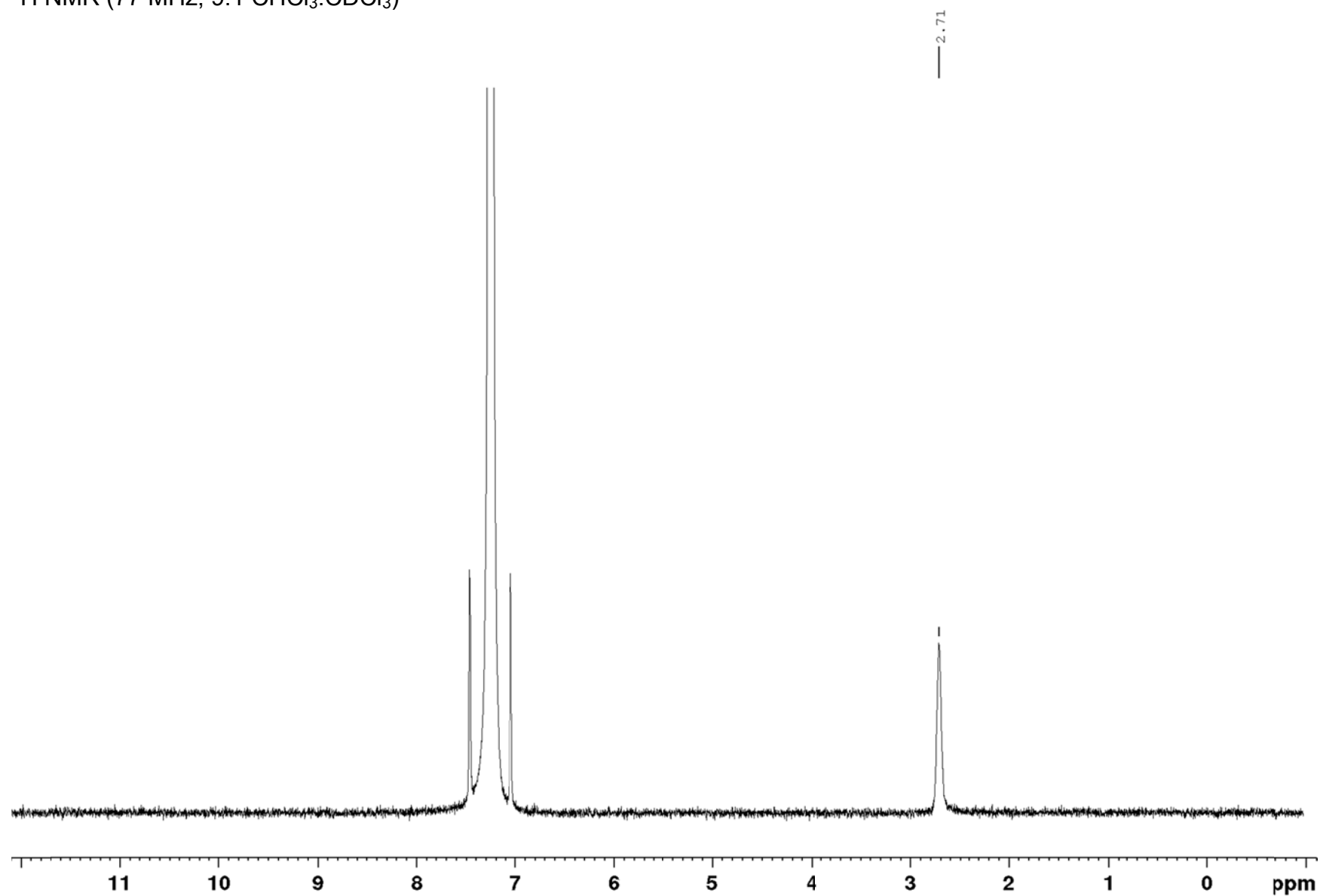


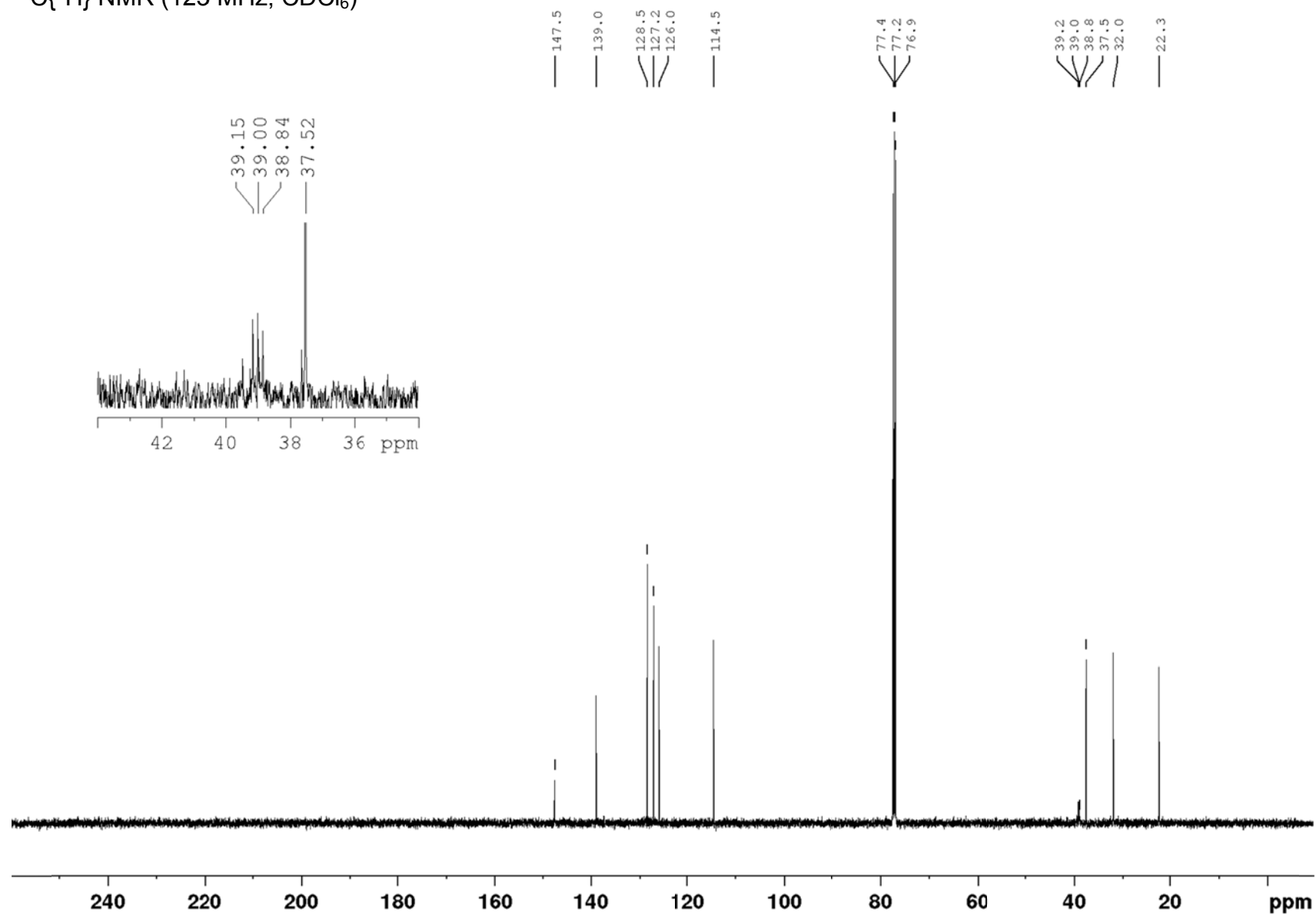
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

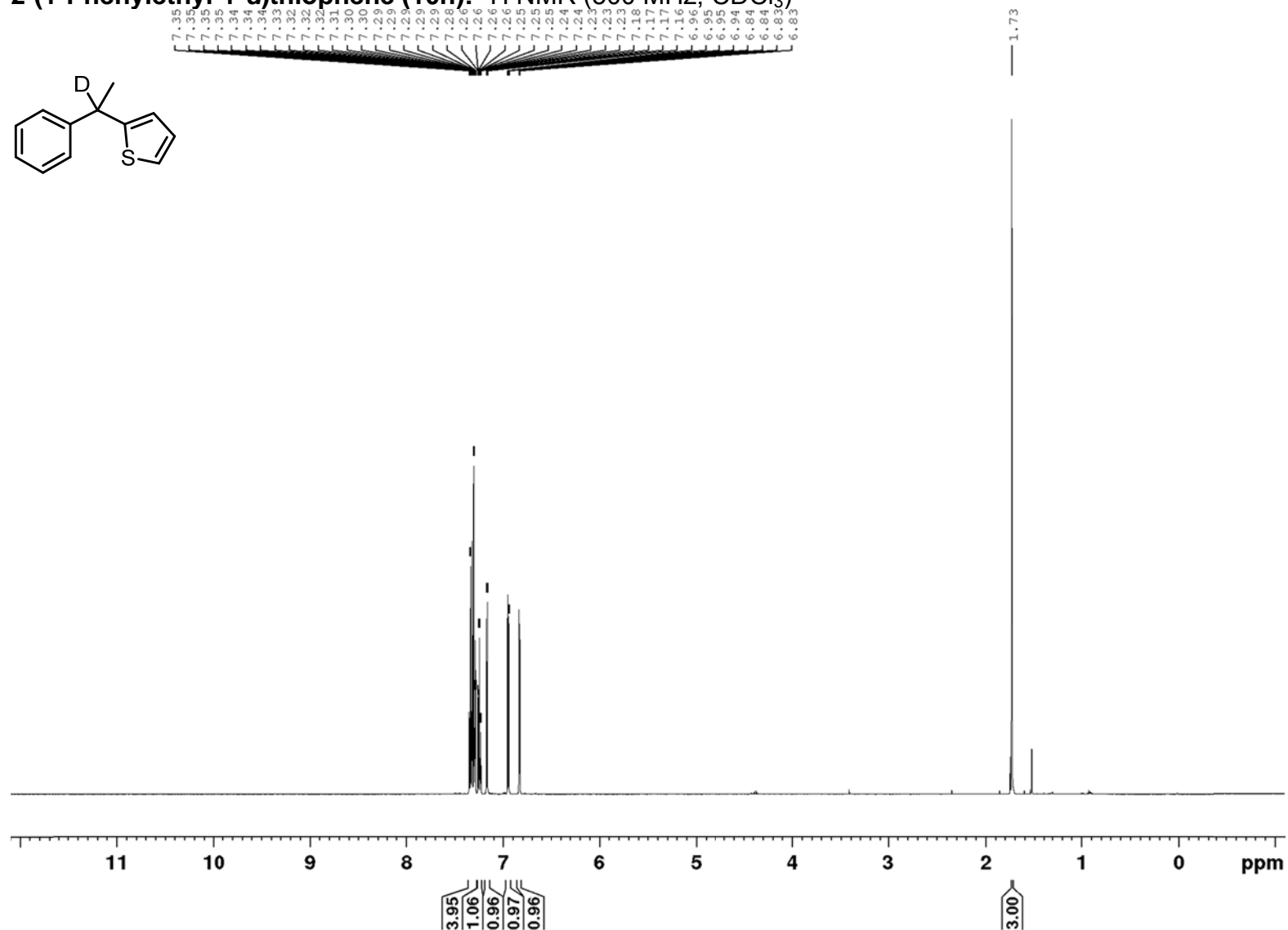
(Hex-5-en-2-yl-2-*d*)benzene (10m): ^1H NMR (500 MHz, CDCl_3)



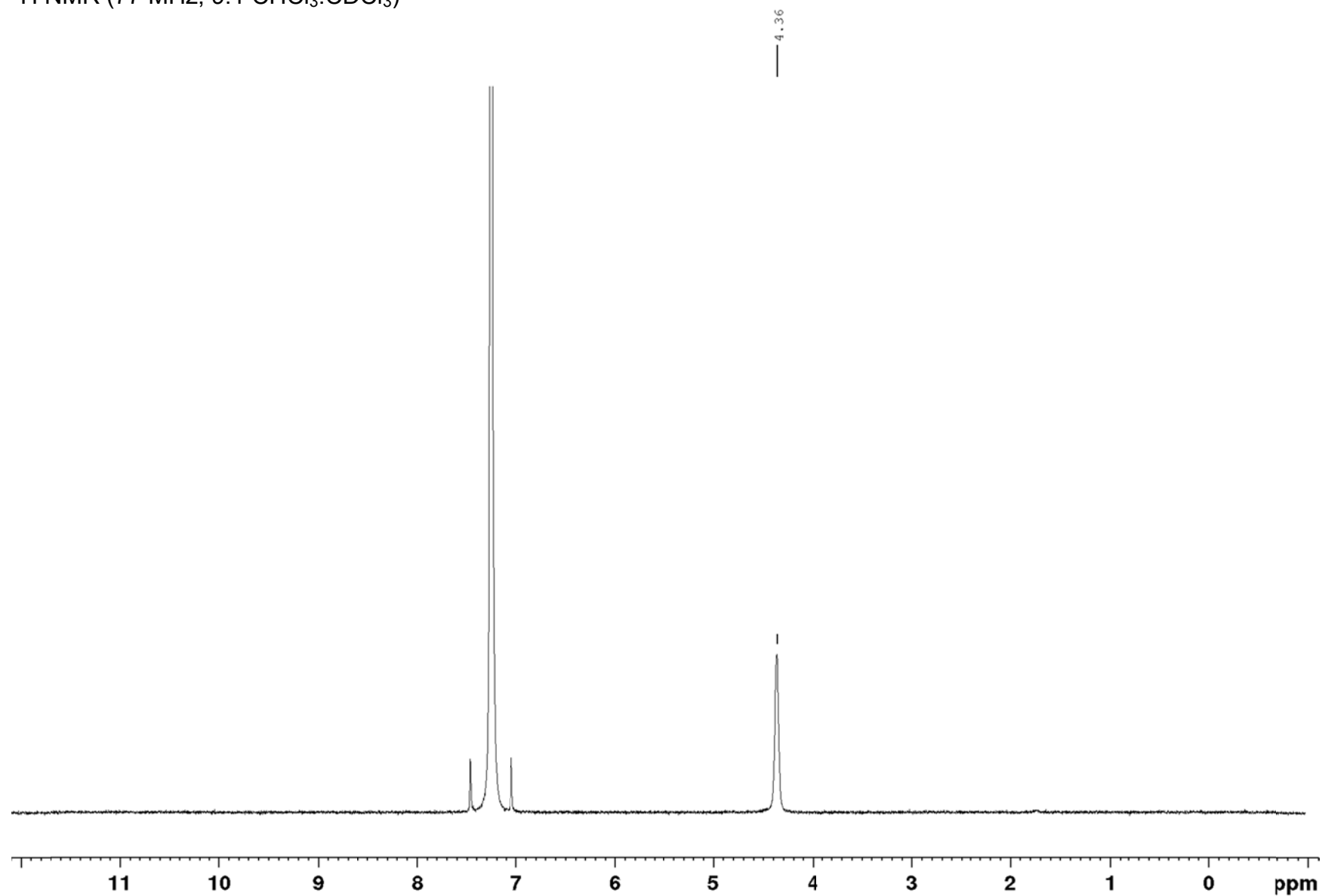
^2H NMR (77 MHz, 9:1 $\text{CHCl}_3:\text{CDCl}_3$)

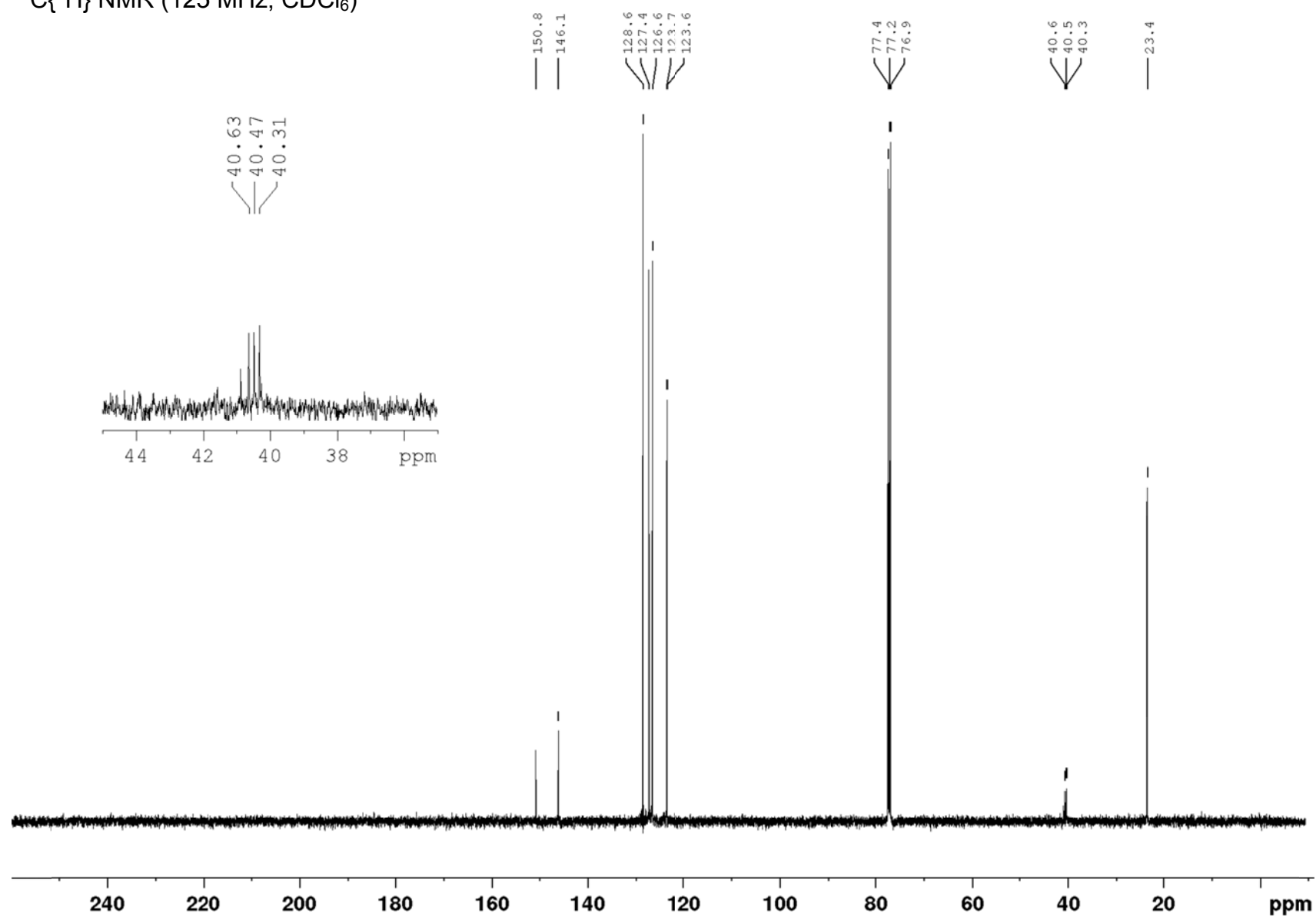


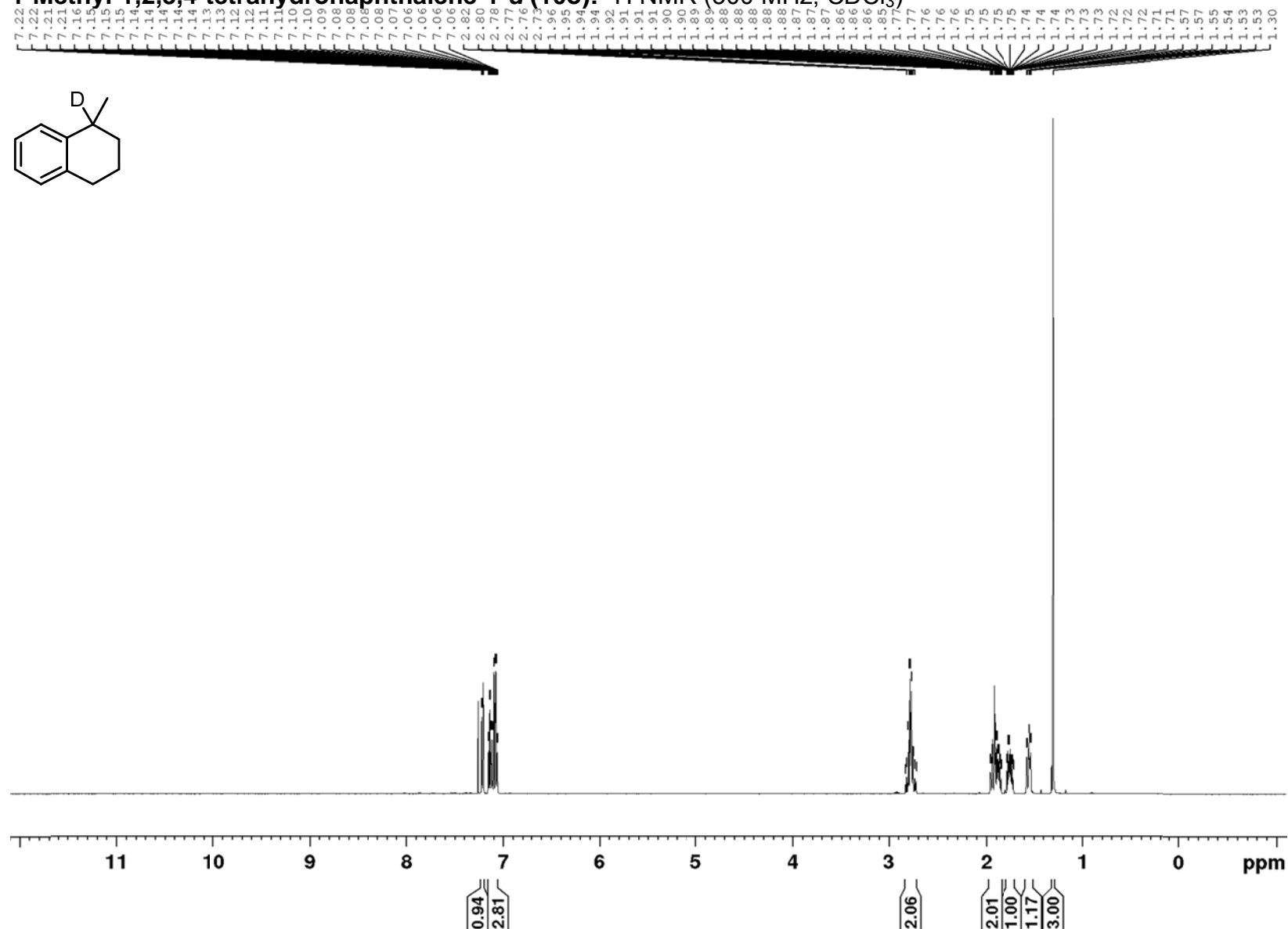
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

2-(1-Phenylethyl-1-*d*)thiophene (10n): ^1H NMR (500 MHz, CDCl_3)

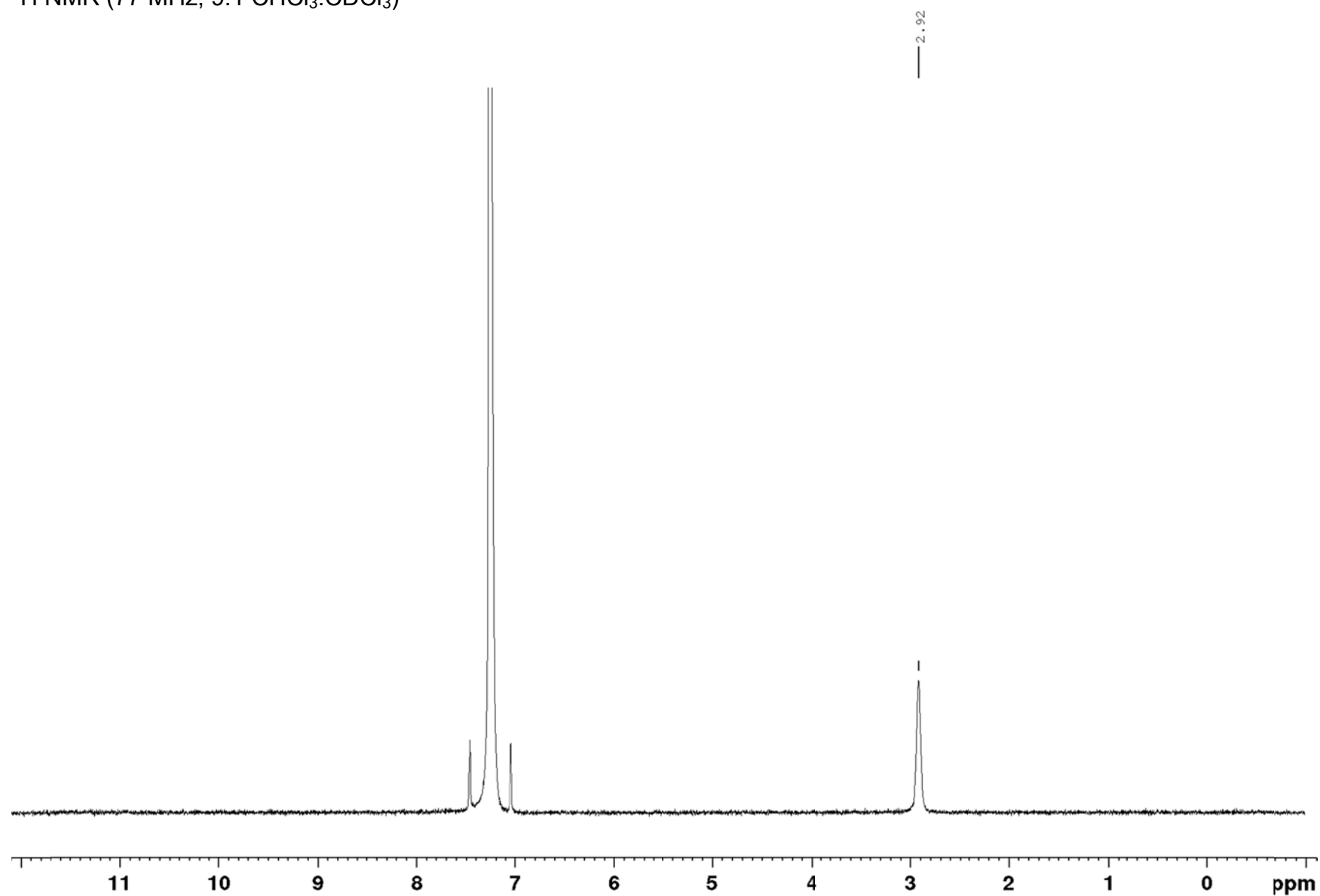
^2H NMR (77 MHz, 9:1 $\text{CHCl}_3:\text{CDCl}_3$)

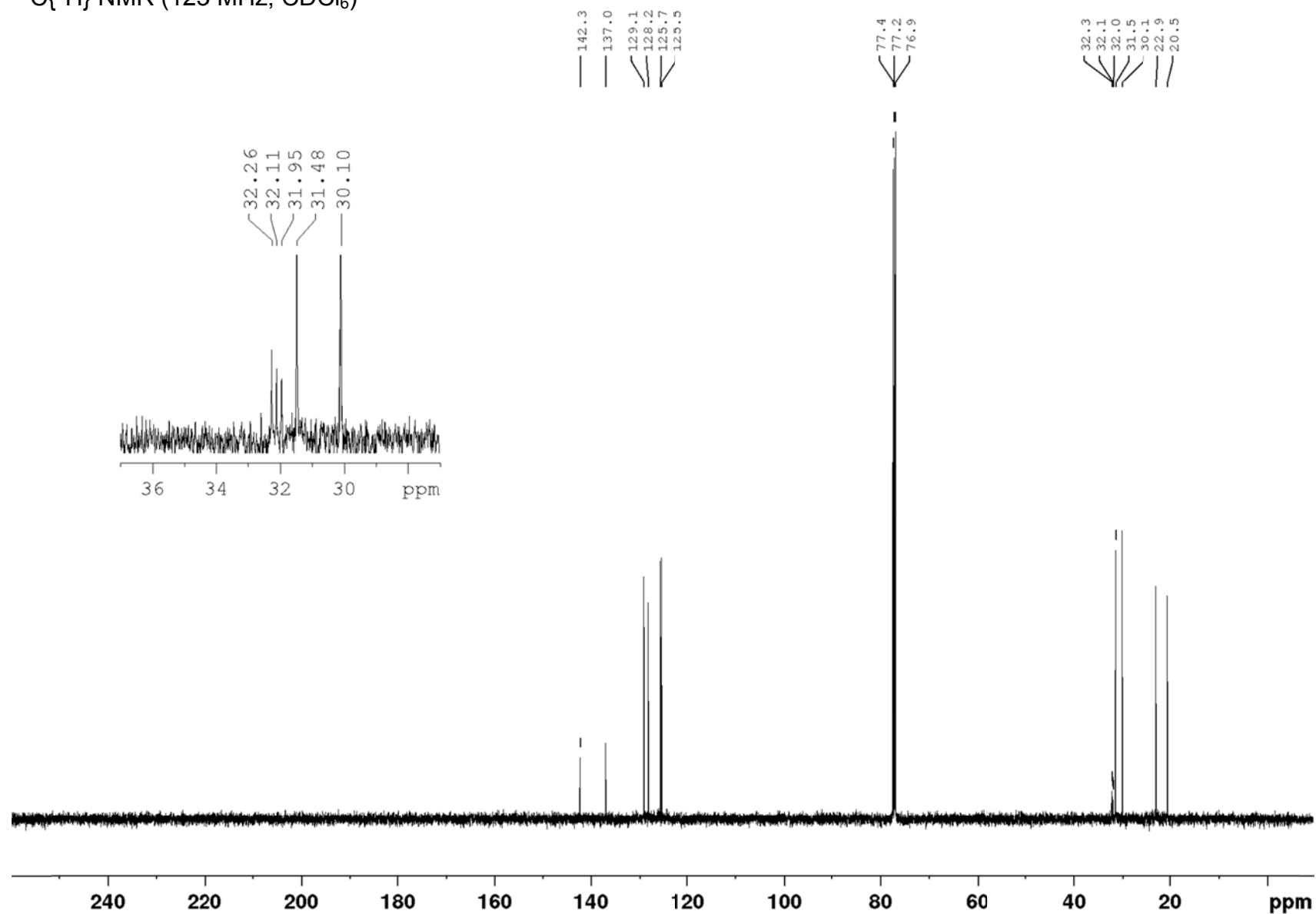


$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

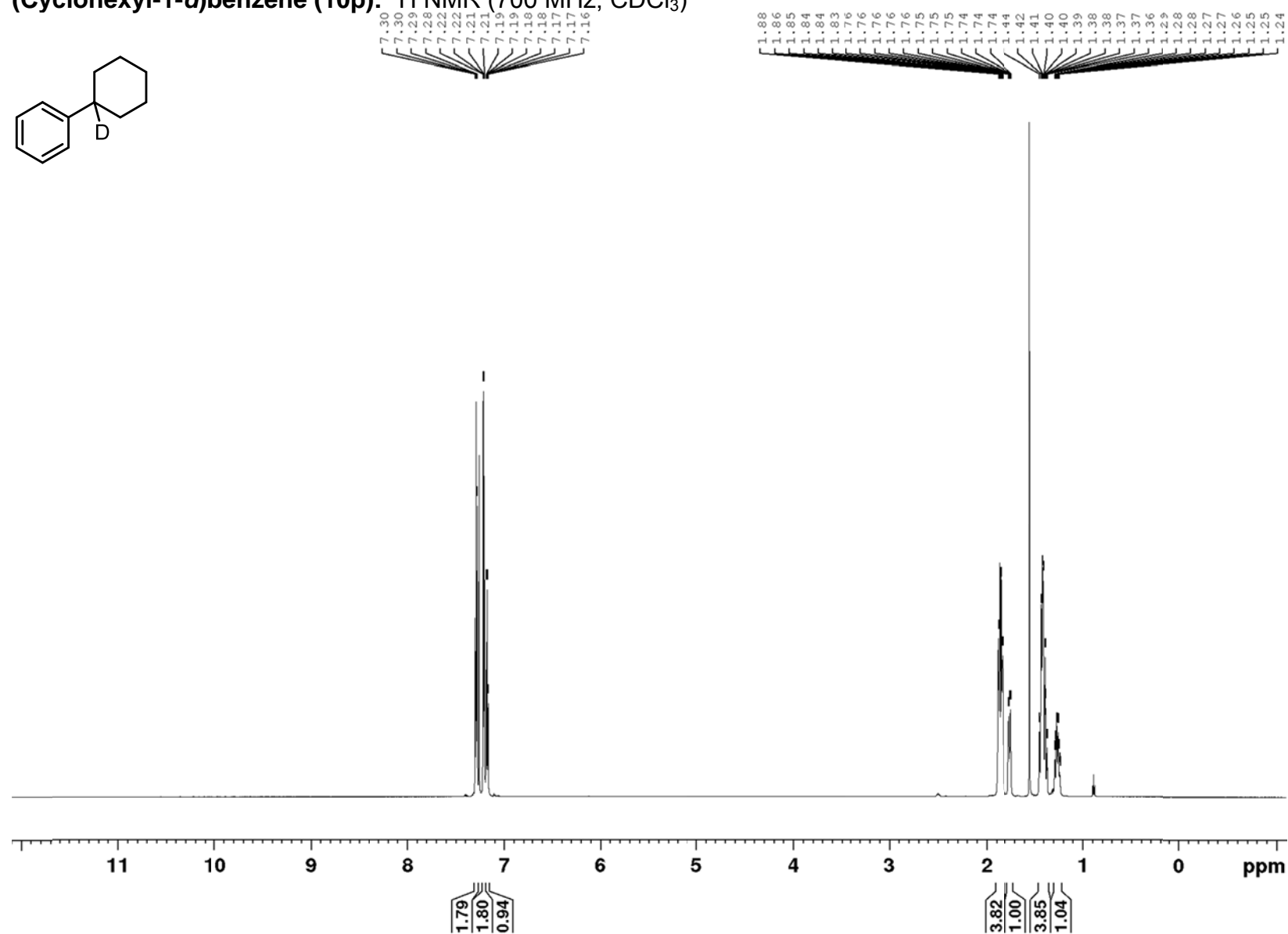
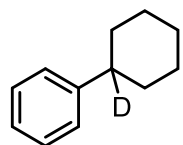
1-Methyl-1,2,3,4-tetrahydronaphthalene-1-*d* (10o): ^1H NMR (500 MHz, CDCl_3)

^2H NMR (77 MHz, 9:1 $\text{CHCl}_3:\text{CDCl}_3$)

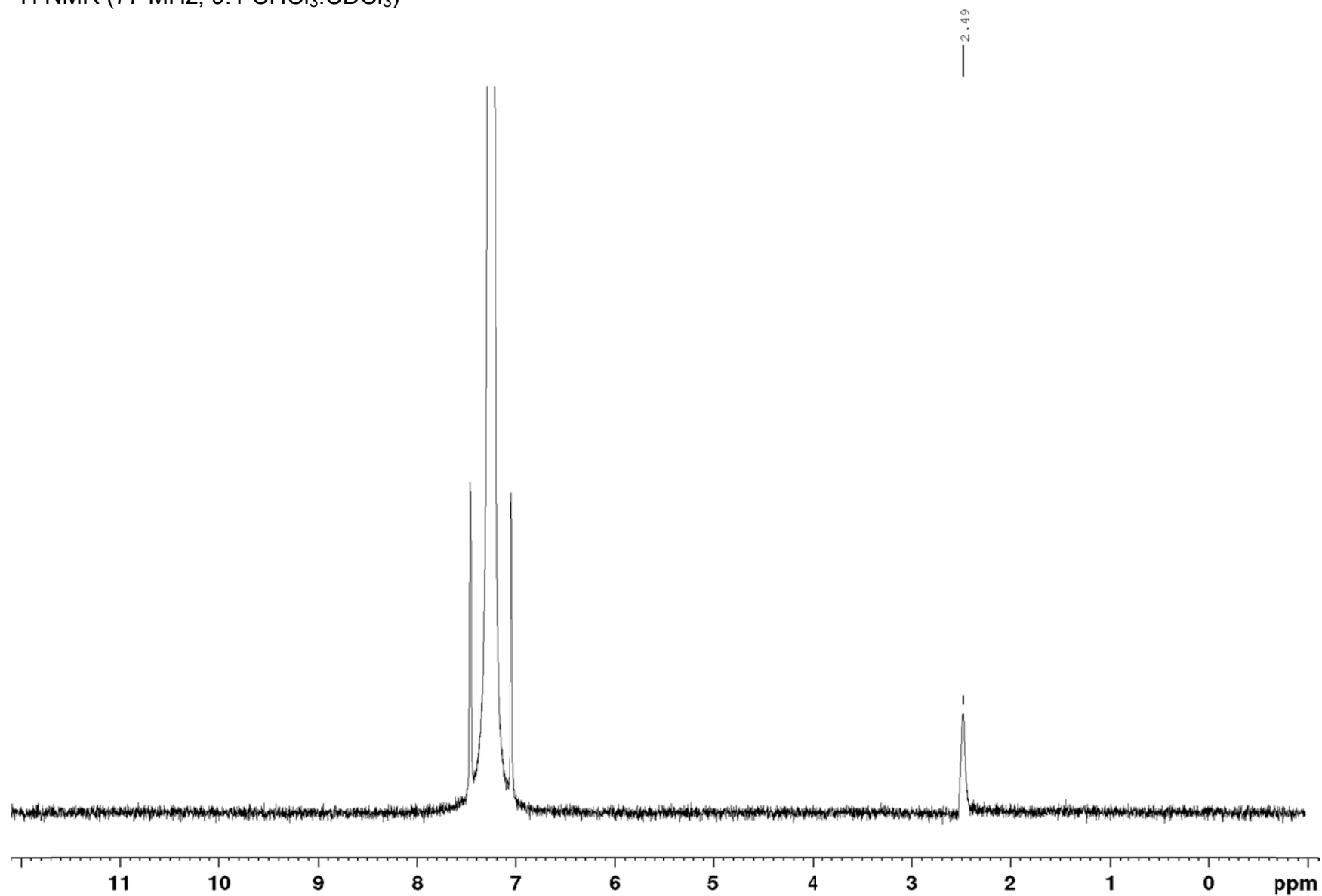


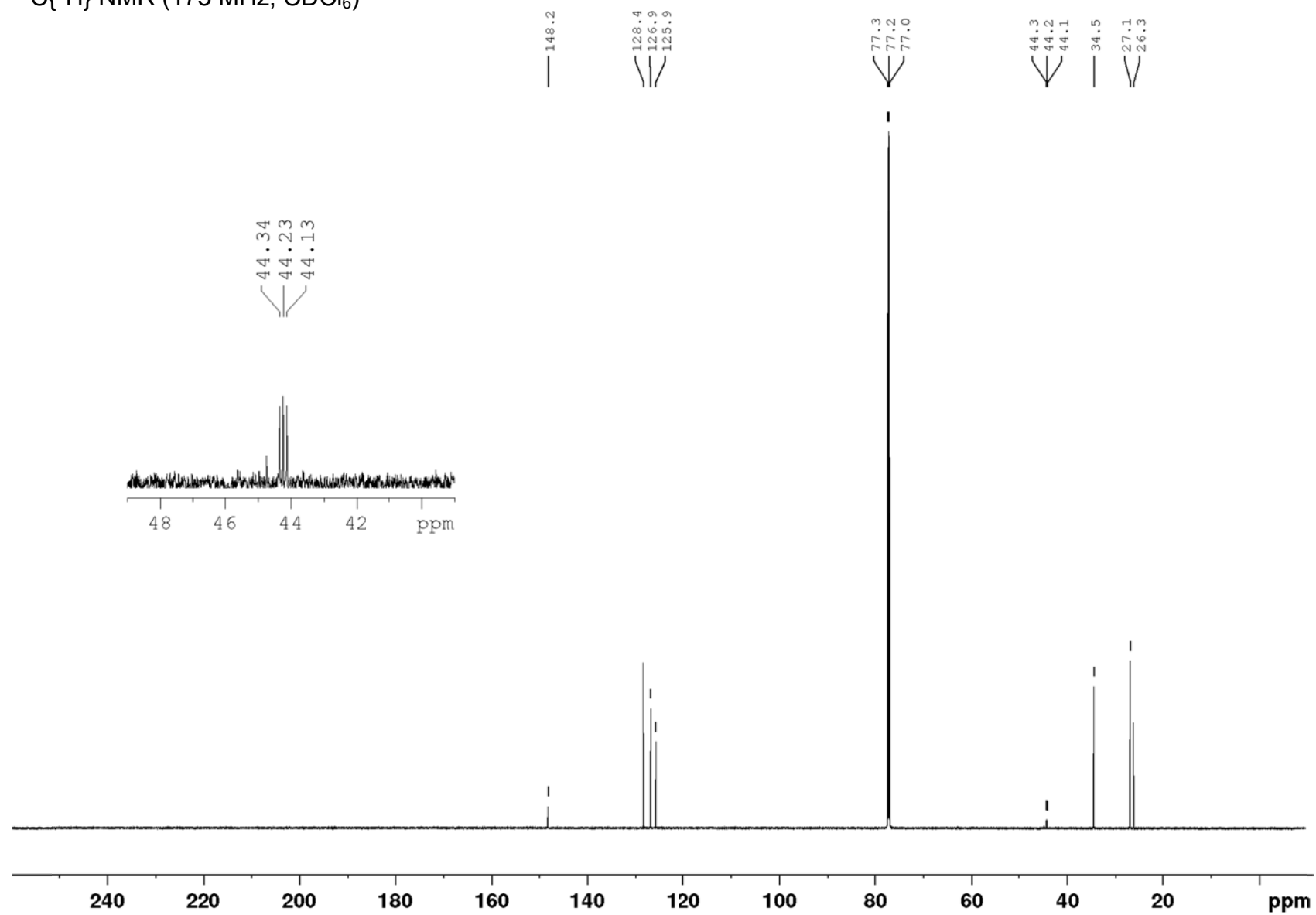
$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3)

(Cyclohexyl-1-*d*)benzene (10p): ^1H NMR (700 MHz, CDCl_3)



^2H NMR (77 MHz, 9:1 $\text{CHCl}_3:\text{CDCl}_3$)



$^{13}\text{C}\{^1\text{H}\}$ NMR (175 MHz, CDCl_3)

8. References

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