Supporting Information

for

Hypervalent iodine(III)-mediated decarboxylative acetoxylation at tertiary and benzylic carbon centers

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Experimental procedures, characterization data, copies of the ^{1}H, ^{13}C, and ^{19}F NMR spectra

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1. General

New compounds were characterized by ^{1}H, ^{13}C, ^{19}F, IR, and HRMS. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a JEOL JMTC-400/54/SS spectrometer (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz; ^{19}F NMR, 377 MHz). ^{1}H NMR chemical shifts were determined relative to Me_4Si (0.0 ppm) as an internal standard. ^{13}C NMR chemical shifts were determined relative to $CDCl_3$ (77.0 ppm). ^{19}F NMR chemical shifts were determined relative to C_6F_6 (−164.9 ppm) as an external standard. Infrared spectra were recorded on a SHIMADZU IRAffinity-1 FT-IR Spectrometer. High-resolution mass spectra were obtained on a JMS-700 mass spectrometer. Melting points were determined on a Stanford Research Systems MPA100 OptiMelt Automated Melting Point System. All reactions were carried out under nitrogen. Otherwise noted, reactions were performed on the benchtop with a fluorescent light on the ceiling. Products were purified by chromatography on silica gel BW-300 (Fuji Silysia Chemical Ltd.). Analytical thin-layer chromatography (TLC) was performed on pre-coated silica gel glass plates (Merck silica gel 60 F_{254} and Fuji Silysia Chromatorex NH, 0.25 mm thickness). Compounds were visualized with UV lamp or treatment with an ethanolic solution of phosphomolybdic acid followed by heating.

2. Materials

Starting materials **1a–j** were prepared according to literature procedures.[1] Alkyl iodide **5** was prepared according to a literature procedure.[1] All other starting materials, solvents, and reagents were purchased and used as obtained.

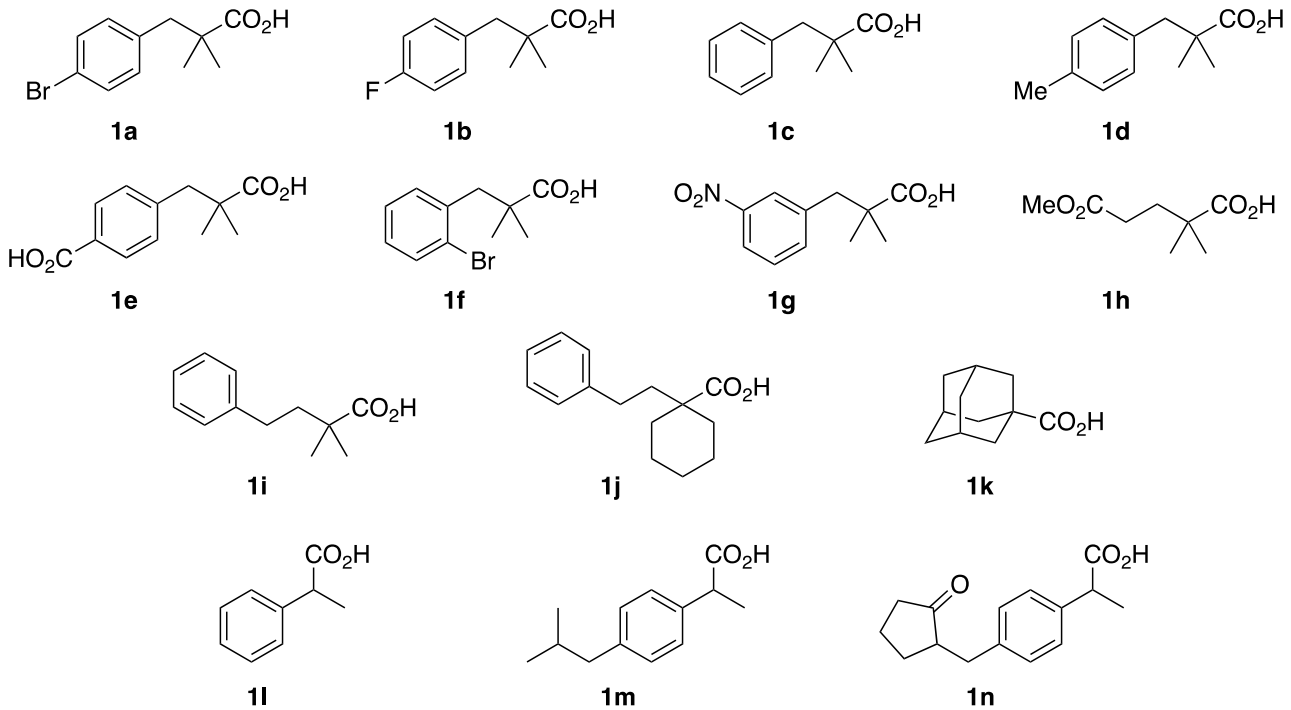


Figure S1: List of substrates.

3. ^{1}H NMR monitoring of the reaction mixture of PhI(OAc)$_2$ and 1a

The mixture of PhI(OAc)$_2$ (64.4 mg, 0.20 mmol) and 3-(4-bromophenyl)-2,2-dimethylpropanoic acid (**1a**, 25.8 mg, 0.10 mmol) in CD_2Cl_2/CD_3CO_2D (v/v = 1:1, 0.50 mL) was prepared. After mixing for 5 min at room temperature, the mixture was transferred into an NMR tube. The resulting ^{1}H NMR spectra are shown in Figure S2. The reaction provided a mixture of PhI(OAc)$_2$ and **4a** in a ratio of 11:1.

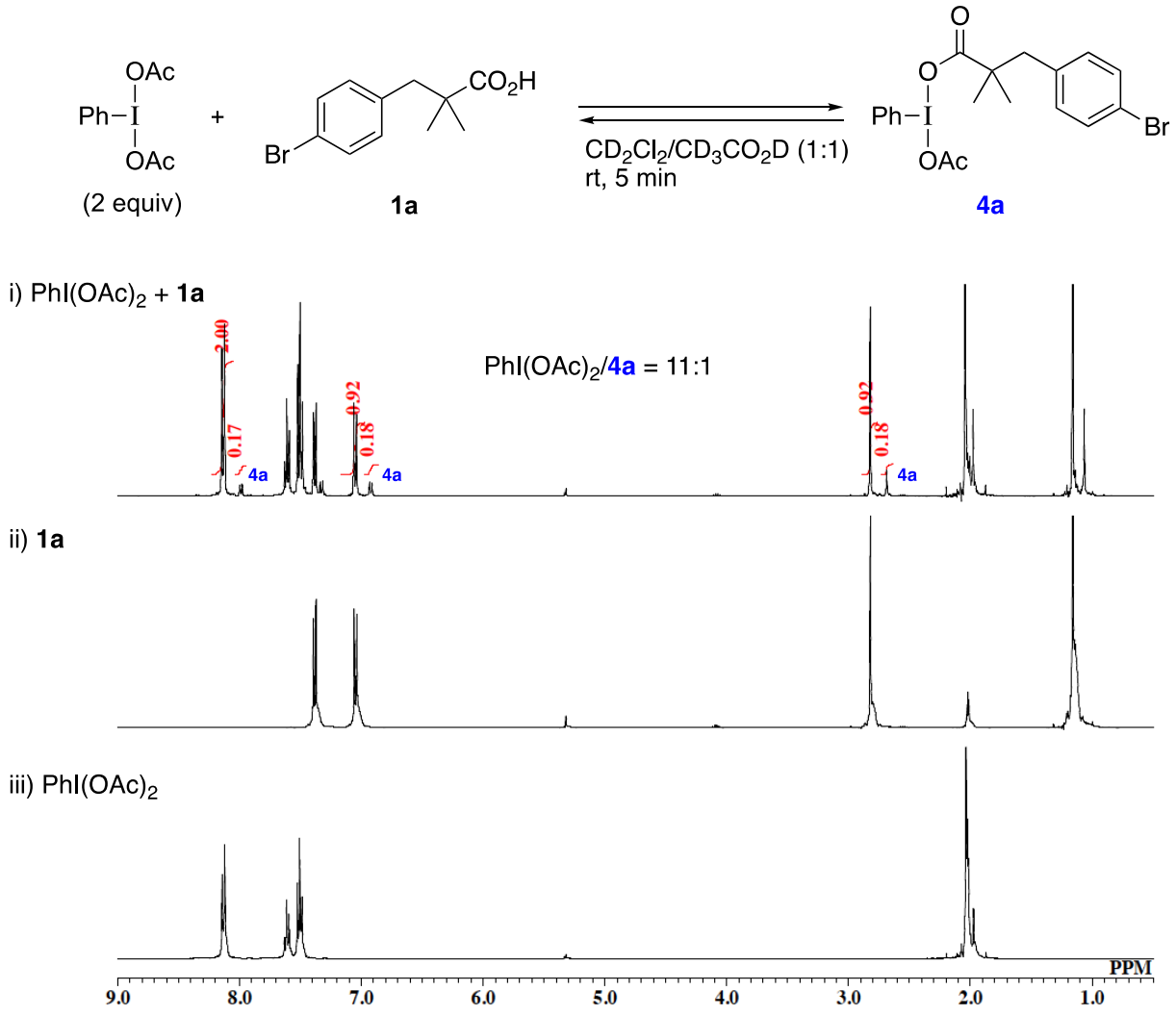
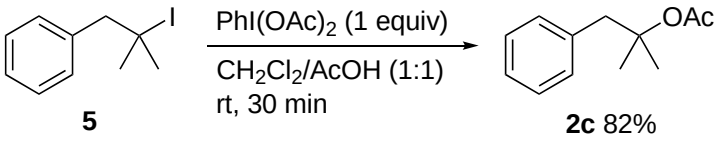


Figure S2: ^{1}H NMR spectra in CD_2Cl_2/CD_3CO_2D (v/v = 1:1). i) A mixture of **1a** and 2 equivalents of PhI(OAc)$_2$. ii) **1a**. iii) PhI(OAc)$_2$.

4. Acetoxylation of alkyl iodide 5

A heat-gun-dried two-necked reaction flask containing a magnetic stirring bar was charged with (2-iodo-2-methylpropyl)benzene (**5**) (53.9 mg, 0.21 mmol), PhI(OAc)$_2$ (64.5 mg, 0.20 mmol), and CH_2Cl_2/AcOH (v/v = 1:1, 1 mL). The reaction mixture was stirred for 30 min at room temperature. The reaction was quenched by $Na_2S_2O_3$ aq. (1 M, 5 mL) and sat. $NaHCO_3$ aq. (5 mL). The mixture

was extracted with Et_2O (3 x 10 mL)and the collected organic layers were dried over Na_2SO_4. The solution was concentrated under reduced pressure to give the crude product, which was analyzed by ^1H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard.



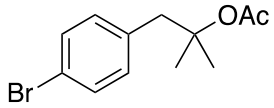
5 **2c** 82%

5. Decarboxylative acetoxylation: typical procedure and product data

Typical procedure: A heat-gun-dried two-necked reaction flask containing a magnetic stirring bar was charged with carboxylic acid **1** (0.5 mmol), $PhI(OAc)_2$ (1.00 or 1.50 mmol), and CH_2Cl_2/AcOH (v/v = 1:1, 1.25 or 2.5 mL). To the mixture, I_2 (0.25 or 0.38 mmol) was added, and the reaction mixture was stirred at room temperature for 6 h. The reaction was quenched by $Na_2S_2O_3$ aq. (1 M, 10 mL) and sat. $NaHCO_3$ aq. (10 mL). The mixture was extracted with Et_2O (3 × 20 mL). The collected organic layers were dried over Na_2SO_4. The solution was concentrated under reduced pressure to give the crude product, which was analyzed by ^1H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. Purification by flash column chromatography on silica gel (hexane/EtOAc) gave the pure product.

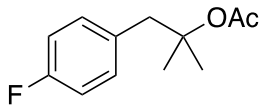
Product data

1-(4-Bromophenyl)-2-methylpropan-2-yl acetate (2a)



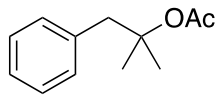
According to the typical procedure, the reaction using 3-(4-bromophenyl)-2,2-dimethylpropanoic acid (**1a**, 128.6 mg, 0.50 mmol), $PhI(OAc)_2$ (321.8 mg, 1.00 mmol), AcOH (0.63 mL), CH_2Cl_2 (0.63 mL), and I_2 (63.7 mg, 0.25 mmol) was conducted at room temperature for 6 h. Purification by flash column chromatography on silica gel (hexane/ethyl acetate = 95:5) gave the product as a colorless liquid (96.3 mg, 71% yield). ^1H NMR: (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 3.00 (s, 2H), 1.97 (s, 3H), 1.43 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 136.2, 132.1, 131.0, 120.4, 81.5, 45.7, 25.8, 22.5; IR: (ATR) 2976, 2930, 1732 cm^{-1}; HRMS: (FAB) calcd for ($C_{12}H_{14}BrO_2$) 269.0177 ($[M-H]^-$), found *m*/*z* 269.0170

1-(4-Fluorophenyl)-2-methylpropan-2-yl acetate (2b)



According to the typical procedure, the reaction using 3-(4-fluorophenyl)-2,2-dimethylpropanoic acid (**1b**, 98.3 mg, 0.50 mmol), $PhI(OAc)_2$ (320.2 mg, 1.00 mmol), AcOH (0.63 mL), CH_2Cl_2 (0.63 mL), and I_2 (63.3 mg, 0.25 mmol) was conducted at room temperature for 6 h. Purification by flash column chromatography on silica gel (hexane/ethyl acetate = 95:5) gave the product as a colorless liquid (74.1 mg, 70% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.18–7.11 (m, 2H), 7.02–6.94 (m, 2H), 3.02 (s, 2H), 1.97 (s, 3H), 1.43 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 161.7 (d, J_{CF} = 242.9 Hz), 132.9 (d, J_{CF} = 3.3 Hz), 131.8 (d, J_{CF} = 7.4 Hz), 114.7 (d, J_{CF} = 21.4 Hz), 81.8, 45.5, 25.9, 22.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ –119.5; IR: (ATR) 2978, 2936, 1732 cm^{-1}; HRMS: (FAB) calcd for ($C_{12}H_{14}FO_2$) 209.0978 ([M−H]$^-$), found *m*/*z* 209.0975

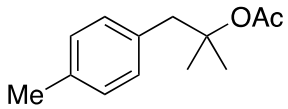
2-Methyl-1-phenylpropan-2-yl acetate (2c)



According to the typical procedure, the reaction using 2,2-dimethyl-3-phenylpropanoic acid (**1c**, 89.2 mg, 0.50 mmol), $PhI(OAc)_2$ (483.8 mg, 1.50 mmol), AcOH (1.25 mL), CH_2Cl_2 (1.25 mL), and I_2 (64.1 mg, 0.25 mmol) was conducted at room temperature for 6 h. Purification by flash column chromatography on silica gel (hexane/ethyl acetate = 95:5) gave the product as a colorless liquid (63.2 mg, 65% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.33–7.12 (m, 5H), 3.05 (s, 2H), 1.97 (s, 3H), 1.44 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 137.2, 130.5, 127.9, 126.4, 82.0, 46.3, 25.9, 22.5

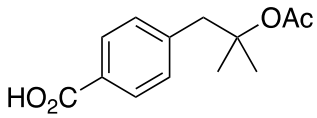
The analytical data for this compound were in excellent agreement with the reported data.[2]

2-Methyl-1-(4-tolyl)propan-2-yl acetate (2d)



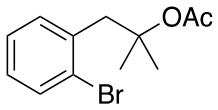
According to the typical procedure, the reaction using 2,2-dimethyl-3-(4-tolyl)propanoic acid (**1d**, 95.7 mg, 0.50 mmol), $PhI(OAc)_2$ (322.2 mg, 1.00 mmol), AcOH (0.63 mL), CH_2Cl_2 (0.63 mL), and I_2 (63.4 mg, 0.25 mmol) was conducted at room temperature for 6 h. Purification by flash column chromatography on silica gel (hexane/ethyl acetate = 95:5) gave the product as a colorless liquid (68.2 mg, 66% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.14–7.04 (m, 4H), 3.01 (s, 2H), 2.33 (s, 3H) 1.97 (s, 3H), 1.43 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 135.9, 134.2, 130.4, 128.7, 82.1, 45.9, 25.9, 22.6, 21.0; IR: (ATR) 2978, 2924, 1732 cm^{-1}; HRMS: (FAB) calcd for ($C_{13}H_{17}O_2$) 205.1229 ([M−H]$^-$), found *m*/*z* 205.1232

1-(4-Carboxyphenyl)-2-methylpropan-2-yl acetate (2e)



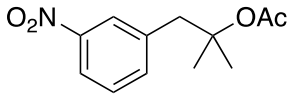
According to the typical procedure, the reaction using 3-(4-carboxyphenyl)-2,2-dimethylpropanoic acid (**1e**, 111.4 mg, 0.50 mmol), $PhI(OAc)_2$ (483.1 mg, 1.50 mmol), AcOH (1.25 mL), CH_2Cl_2 (1.25 mL), and I_2 (127.3 mg, 0.50 mmol) was conducted at room temperature for 6 h. Purification by flash column chromatography on silica gel (hexane/ethyl acetate = 90:10) gave the product as a white solid (88.8 mg, 75% yield). mp: 159.8–161.1 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.14 (s, 2H), 1.99 (s, 3H), 1.47 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 170.7, 143.8, 130.7, 129.9, 127.5, 81.7, 46.4, 26.1, 22.5; IR: (ATR) 2976, 2553, 1730, 1672 cm^{-1}; HRMS: (FAB) calcd for ($C_{13}H_{15}O_4$) 235.0970 ([M−H]$^-$), found *m*/*z* 235.0972

1-(2-Bromophenyl)-2-methylpropan-2-yl acetate (2f)



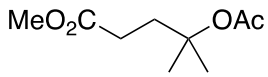
According to the typical procedure, the reaction using 3-(2-bromophenyl)-2,2-dimethylpropanoic acid (**1f**, 128.4 mg, 0.50 mmol), $PhI(OAc)_2$ (484.1 mg, 1.50 mmol), AcOH (1.25 mL), CH_2Cl_2 (1.25 mL), and I_2 (95.7 mg, 0.38 mmol) was conducted at room temperature for 6 h. Purification by flash column chromatography on silica gel (hexane/ethyl acetate = 95:5) gave the product as a colorless liquid (90.7 mg, 67% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.33–7.21 (m, 2H), 7.09 (ddd, *J* = 8.0, 8.0, 2.0 Hz, 1H), 3.27 (s, 2H), 2.01 (s, 3H), 1.51 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 137.1, 133.0, 132.3, 128.1, 126.9, 126.1, 82.7, 45.2, 25.8, 22.6; IR: (ATR) 3062, 2980, 2935, 1732 cm^{-1}; HRMS: (FAB) calcd for ($C_{12}H_{14}BrO_2$) 269.0177 ([M−H]$^-$), found *m*/*z* 269.0172

2-Methyl-1-(3-nitrophenyl)propan-2-yl acetate (2g)



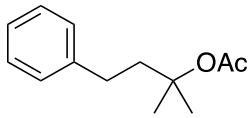
According to the typical procedure, the reaction using 2,2-dimethyl-3-(3-nitrophenyl)propanoic acid (**1g**, 111.2 mg, 0.50 mmol), $PhI(OAc)_2$ (320.2 mg, 0.99 mmol), AcOH (0.63 mL), CH_2Cl_2 (0.63 mL), and I_2 (63.6 mg, 0.25 mmol) was conducted at room temperature for 6 h. Purification by flash column chromatography on silica gel (hexane/ethyl acetate = 90:10) gave the product as a pale yellow solid (80.4 mg, 68% yield). mp: 76.9–78.1 °C; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.16–8.07 (m, 2H), 7.57–7.45 (m, 2H), 3.15 (s, 2H), 2.00 (s, 3H), 1.47 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 148.0, 139.2, 136.7, 128.8, 125.2, 121.7, 81.2, 46.0, 25.9, 22.4; IR: (ATR) 2974, 2928, 1719 cm^{-1}; HRMS: (FAB) calcd for ($C_{12}H_{15}NO_4$) 237.1001 (M$^-$), found *m*/*z* 237.1006

4-Methoxycarbonyl-2-methylbutan-2-yl acetate (2h)



According to the typical procedure, the reaction using 2,2-dimethyl-4-methoxycarbonylbutanoic acid (**1h**, 82.8 mg, 0.48 mmol), $PhI(OAc)_2$ (484.7 mg, 1.50 mmol), AcOH (1.25 mL), CH_2Cl_2 (1.25 mL), and I_2 (63.3 mg, 0.25 mmol) was conducted at room temperature for 6 h. Purification by flash column chromatography on silica gel (hexane/ethyl acetate = 90:10) gave the product as a colorless liquid (37.6 mg, 42% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 3.68 (s, 3H), 2.43–2.35 (m, 2H), 2.11–2.03 (m, 2H), 1.97 (s, 3H), 1.46 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 170.3, 81.1, 51.7, 36.1, 29.0, 25.6, 22.3; IR: (ATR) 2980, 2953, 1732 cm^{-1}; HRMS: (FAB) calcd for ($C_9H_{15}O_4$) 187.0970 ($[M-H]^-$), found *m*/*z* 187.0966

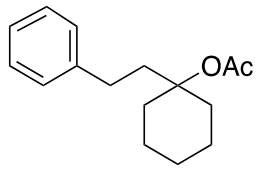
2-Methyl-4-phenylbutan-2-yl acetate (2i)



According to the typical procedure, the reaction using 2,2-dimethyl-4-phenylbutanoic acid (**1i**, 96.3 mg, 0.50 mmol), $PhI(OAc)_2$ (322.0 mg, 1.00 mmol), AcOH (0.63 mL), CH_2Cl_2 (0.63 mL), and I_2 (63.2 mg, 0.25 mmol) was conducted at room temperature for 6 h. Purification by flash column chromatography on silica gel (hexane/ethyl acetate = 95:5) gave the product as a colorless liquid (79.7 mg, 77% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.32–7.22 (m, 2H), 7.22–7.13 (m, 3H), 2.67–2.59 (m, 2H), 2.10–2.01 (m, 2H), 1.97 (s, 3H), 1.49 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 142.0, 128.3, 125.7, 81.8, 42.6, 30.3, 26.0, 22.3

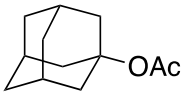
The analytical data for this compound were in excellent agreement with the reported data.[3]

1-Phenethylcyclohexyl acetate (2j)



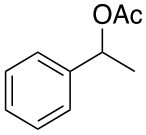
According to the typical procedure, the reaction using 1-phenethylcyclohexanecarboxylic acid (**1j**, 117.9 mg, 0.51 mmol), $PhI(OAc)_2$ (488.5 mg, 1.52 mmol), AcOH (1.25 mL), CH_2Cl_2 (1.25 mL), and I_2 (63.4 mg, 0.25 mmol) was conducted at room temperature for 6 h. Purification by flash column chromatography on silica gel (hexane/ethyl acetate = 95:5) gave the product as a colorless liquid (40.5 mg, 33% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.31–7.22 (m, 2H), 7.22–7.10 (m, 3H), 2.63–2.54 (m, 2H), 2.30–2.17 (m, 4H), 2.02 (s, 3H), 1.70–1.49 (m, 4H), 1.49–1.35 (m, 2H), 1.35–1.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 142.2, 128.4, 128.3, 125.7, 83.7, 39.4, 34.6, 29.6, 25.6, 22.2, 21.9; IR: (ATR) 2932, 2860, 1730 cm^{-1}; HRMS: (FAB) calcd for ($C_{16}H_{21}O_2$) 245.1452 ($[M-H]^-$), found *m*/*z* 245.1539

Adamantan-1-yl acetate (2k)



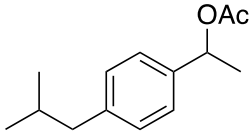
According to the typical procedure, the reaction using 1-adamantancarboxylic acid (**1k**, 90.6 mg, 0.50 mmol), $PhI(OAc)_2$ (322.2 mg, 1.00 mmol), AcOH (0.63 mL), CH_2Cl_2 (0.63 mL) and I_2 (63.8 mg, 0.25 mmol) was conducted at room temperature for 6 h. Purification by flash column chromatography on silica gel (hexane/ethyl acetate = 95:5) gave the product as a white solid (78.9 mg, 81% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 2.20–2.13 (m, 3H), 2.13–2.10 (m, 6H), 1.97 (s, 3H), 1.72–1.58 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 80.2, 41.3, 36.2, 30.7, 22.7
The analytical data for this compound were in excellent agreement with the reported data.[4]

1-Phenylethyl acetate (2l)



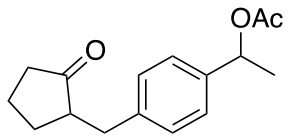
According to the typical procedure, the reaction using 2-phenylpropanoic acid (**1l**, 77.0 mg, 0.51 mmol), $PhI(OAc)_2$ (321.5 mg, 1.00 mmol), AcOH (1.25 mL), CH_2Cl_2 (1.25 mL), and I_2 (63.7 mg, 0.25 mmol) was conducted at room temperature for 6 h. Purification by flash column chromatography on silica gel (hexane/ethyl acetate = 95:5) gave the product as a colorless liquid (85.2 mg, 93% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.41–7.23 (m, 5H), 5.88 (q, *J* = 6.8 Hz, 1H), 2.06 (s, 3H), 1.53 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 141.6, 128.5, 127.8, 126.1, 72.3, 22.2, 21.3
The analytical data for this compound were in excellent agreement with the reported data.[5]

1-(4-Isobutylphenyl)ethyl acetate (2m)



According to the typical procedure, the reaction using 2-(4-isobutylphenyl)propionic acid (**1m**, 103.0 mg, 0.50 mmol), $PhI(OAc)_2$ (322.1 mg, 1.00 mmol), AcOH (1.25 mL), CH_2Cl_2 (1.25 mL), and I_2 (63.7 mg, 0.25 mmol) was conducted at room temperature for 6 h. Purification by flash column chromatography on silica gel (hexane/ethyl acetate = 95:5) gave the product as a colorless liquid (102.6 mg, 93% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.87 (q, *J* = 6.4 Hz, 1H), 2.46 (d, *J* = 7.2 Hz, 2H), 2.06 (s, 3H), 1.92–1.78 (m, 1H), 1.53 (d, *J* = 6.4 Hz, 2H), 0.90 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 141.4, 138.8, 129.1, 125.9, 72.2, 45.1, 30.1, 22.3, 22.0, 21.4; IR: (ATR) 2955, 2930, 2868, 1736, 1238 cm^{-1};HRMS: (FAB) calcd for ($C_{14}H_{20}O_2$) 220.1463 (M^+), found *m*/*z* 220.1464

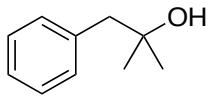
1-[4-((2-Oxocyclopentyl)methyl)phenyl]ethyl acetate (2n)



According to the typical procedure, the reaction using loxoprofen (**1n**, 125.1 mg, 0.50 mmol), $PhI(OAc)_2$ (323.0 mg, 1.00 mmol), AcOH (1.25 mL), CH_2Cl_2 (1.25 mL), and I_2 (64.0 mg, 0.25 mmol) was conducted at room temperature for 6 h. Purification by flash column chromatography on silica gel (hexane/ethyl acetate = 90:10) gave the product as a colorless liquid (124.2 mg, 94% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.86 (q, *J* = 6.4 Hz, 1H), 3.14 (dd, *J* = 14.0, 4.0 Hz, 1H), 2.52 (dd, *J* = 14.0, 9.6 Hz, 1H), 2.41–2.29 (m, 2H), 2.19–2.05 (m, 2H), 2.07 (s, 3H), 2.01–1.92 (m, 1H), 1.81–1.64 (m, 1H), 1.61–1.49 (m, 1H), 1.52 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.1, 170.3, 139.7, 139.5, 129.0, 126.2, 72.1, 51.0, 38.1, 35.2, 29.2, 22.1, 21.4, 20.5; IR: (ATR) 2963, 2934, 2874, 1732 cm^{-1}; HRMS: (FAB) calcd for ($C_{16}H_{19}O_3$) 259.1334 ($[M-H]^-$), found *m*/*z* 259.1328

6. Hydrolysis of acetates

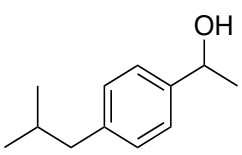
2-Methyl-1-phenylpropan-2-ol (3c)



A two-necked reaction flask containing a magnetic stirring bar was charged with 1,1-dimethyl-2-phenylethyl acetate (**2c**, 95.0 mg, 0.49 mmol), NaOH (62.7 mg, 1.57 mmol), and MeOH (3 mL). The reaction mixture was stirred at room temperature for 24 h. The reaction was neutralized with HCl aq. (2 M), and the mixture was extracted with EtOAc (3 × 20 mL). The collected organic layers were dried over Na_2SO_4. The solution was concentrated under reduced pressure to give the crude product, which was analyzed by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. Purification by flash column chromatography on silica gel (hexane/ethyl acetate = 85:15) gave the product as a colorless liquid (70.5 mg, 95% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.46–7.17 (m, 5H), 2.77 (s, 2H), 1.23 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 130.4, 128.2, 126.5, 70.7, 49.7, 29.1

The analytical data for this compound were in excellent agreement with the reported data.[6]

1-(4-Isobutylphenyl)ethan-1-ol (3m)



Two-necked reaction flask containing a magnetic stirring bar was charged with 1-(4-isobutylphenyl)ethyl acetate (**2m**, 116.3 mg, 0.53 mmol), NaOH (60.3 mg, 1.50 mmol), and MeOH (3 mL). The reaction mixture was stirred at room temperature for 24 h. The reaction was neutralized with HCl aq. (2 M), and the mixture was extracted with EtOAc (3 × 20 mL). The collected organic layers were dried over Na_2SO_4. The solution was concentrated under reduced pressure to give the crude product, which was analyzed by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. Purification by flash column chromatography on silica gel (hexane/ethyl acetate = 85:15) gave the product as a colorless liquid (89.4 mg, 95% yield). ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 4.91–4.85 (m, 1H), 2.46 (d, *J* = 6.8 Hz, 2H), 1.90–1.80 (m, 1H), 1.77 (brs, 1H), 1.49 (d, *J* = 6.4 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 141.0, 129.2, 125.2, 70.3, 45.1, 30.2, 25.0, 22.4

The analytical data for this compound were in excellent agreement with the reported data.[7]

7. References

(1) Kiyokawa, K.; Watanabe, T.; Fra, L.; Kojima, T.; Minakata, S. *J. Org. Chem.* **2017**, *82*, 11711.

(2) Chakraborti, A. K.; Shivani *J. Org. Chem.* **2006**, *71*, 5785.

(3) Nishimoto, Y.; Okita, A.; Yasuda, M.; Baba, A. *Org. Lett.* **2012**, *14*, 1846.

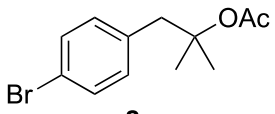
(4) Liu, Z.; Ma, Q.; Liu, Y.; Wang, Q. *Org. Lett.* **2014**, *16*, 236.

(5) Yu, W.; Zhou, M.; Wang, T.; He, Z.; Shi, B.; Xu, Y.; Huang, K. *Org. Lett.* **2017**, *19*, 5776.

(6) Liu, Z.; Zhang, Y.; Cai, Z.; Sun, H.; Cheng, X. *Adv. Synth. Catal.* **2015**, *357*. 589.

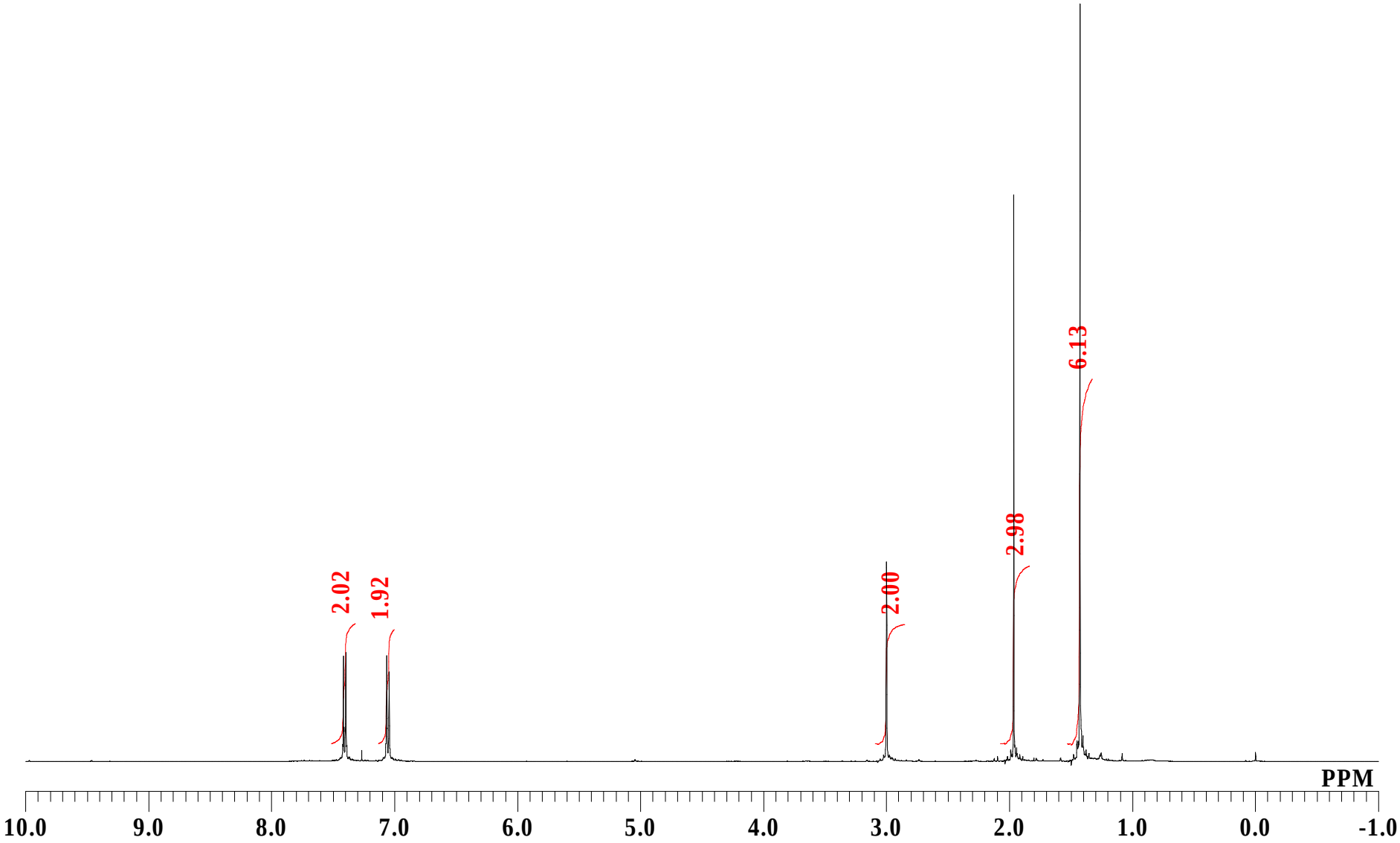
(7) Song, H.-T.; Ding, W.; Zhou, Q.-Q.; Liu, J.; Lu, L.-Q.; Xiao, W.-J. *J. Org. Chem.* **2016**, *81*, 7250.

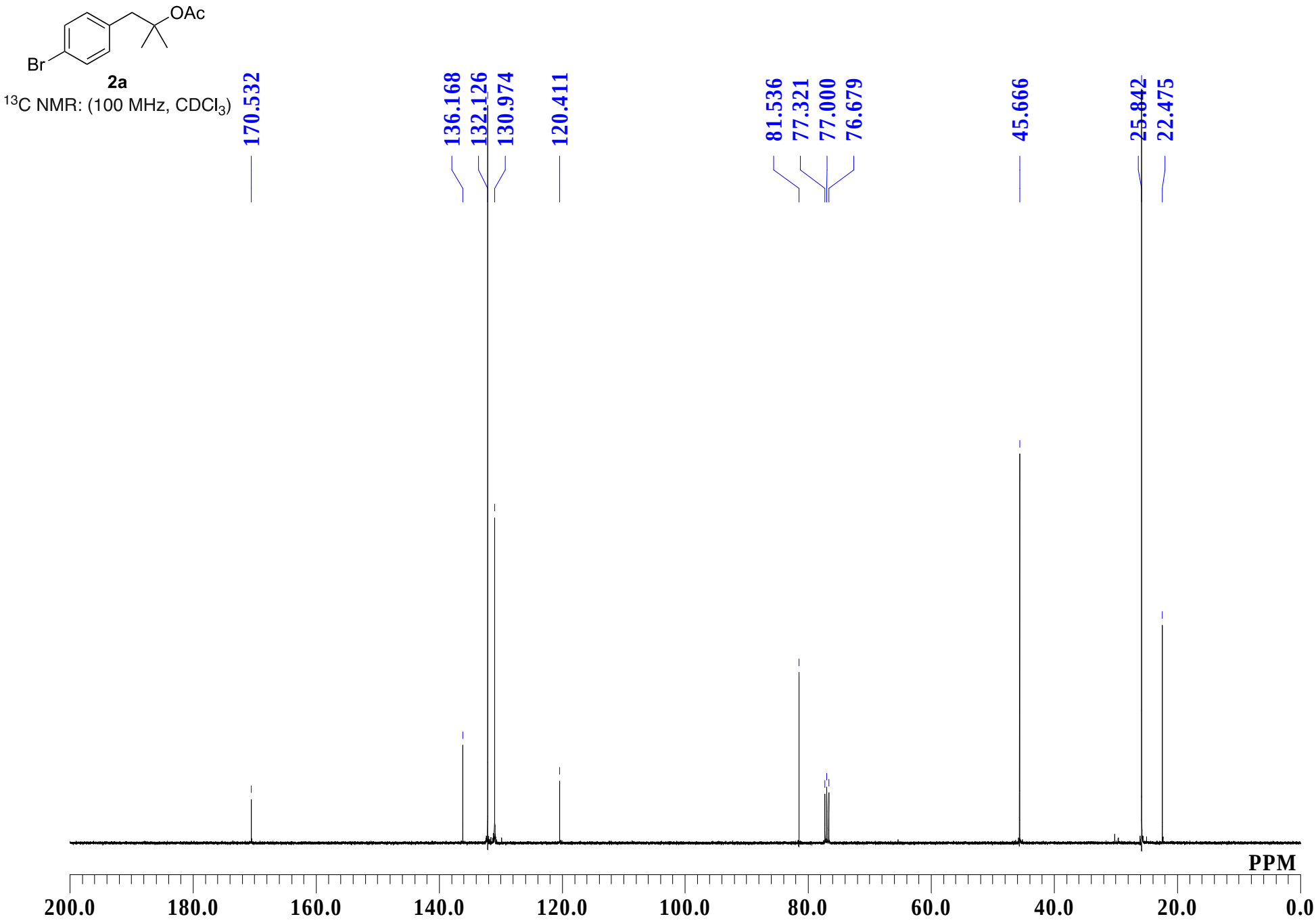
8. NMR spectra

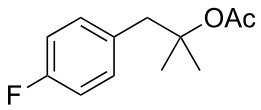


2a

^{1}H NMR: (400 MHz, $CDCl_3$)

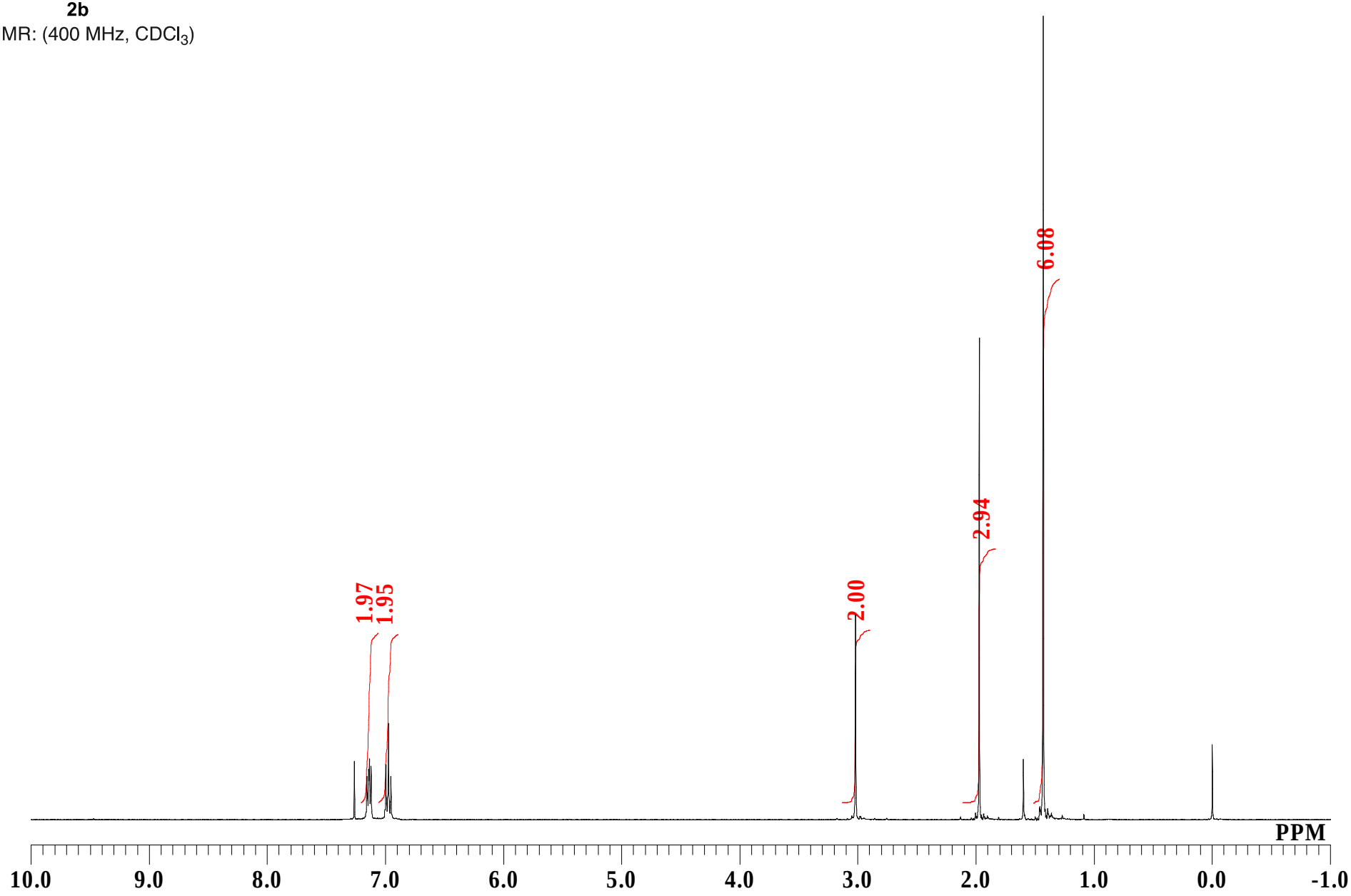


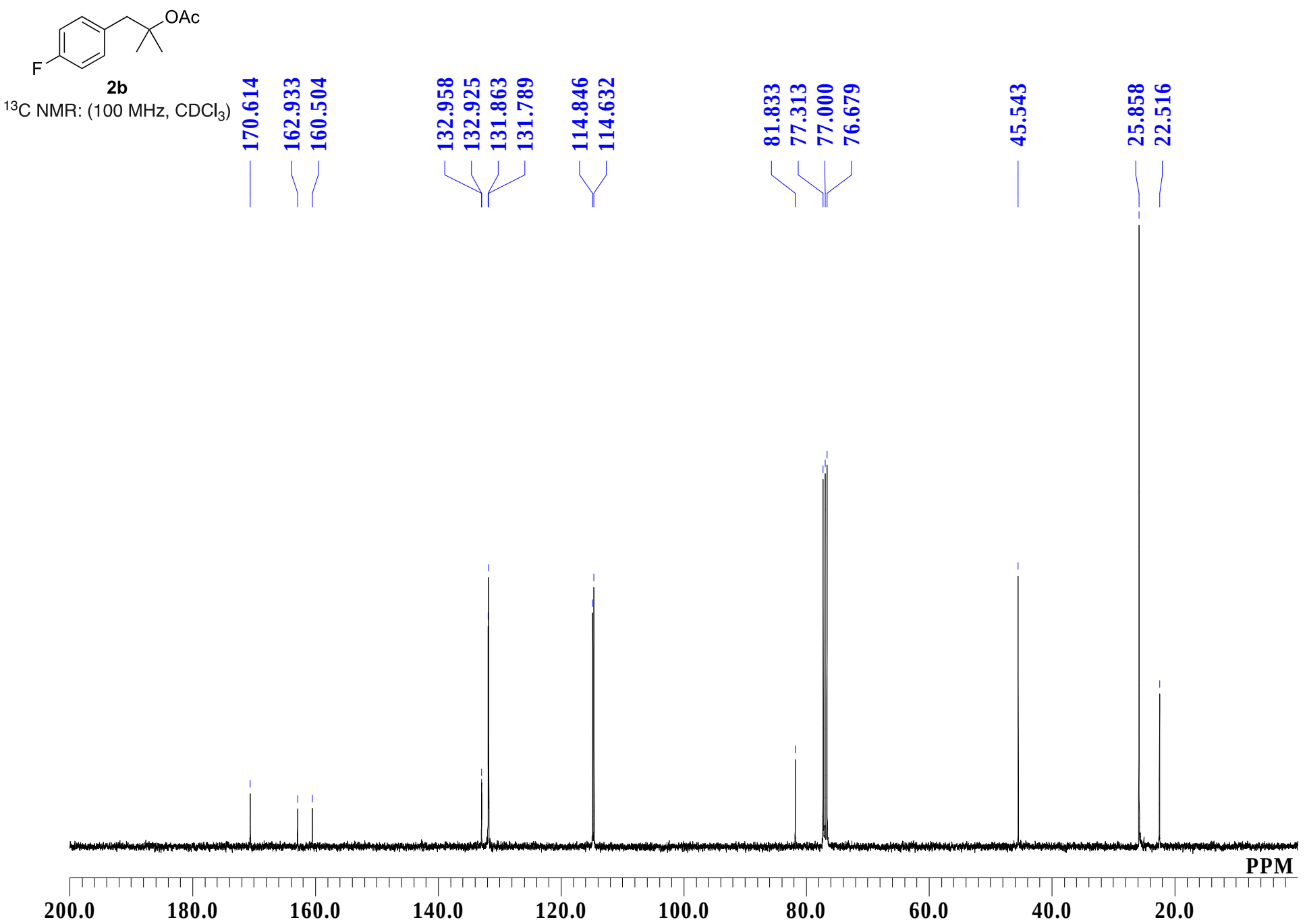

OAc
Br
2a
13C NMR: (100 MHz, CDCl3)
170.532
136.168
132.126
130.974
120.411
81.536
77.321
77.000
76.679
45.666
25.842
22.475
PPM
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0

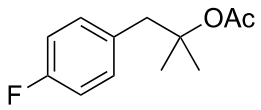


2b

^{1}H NMR: (400 MHz, $CDCl_3$)

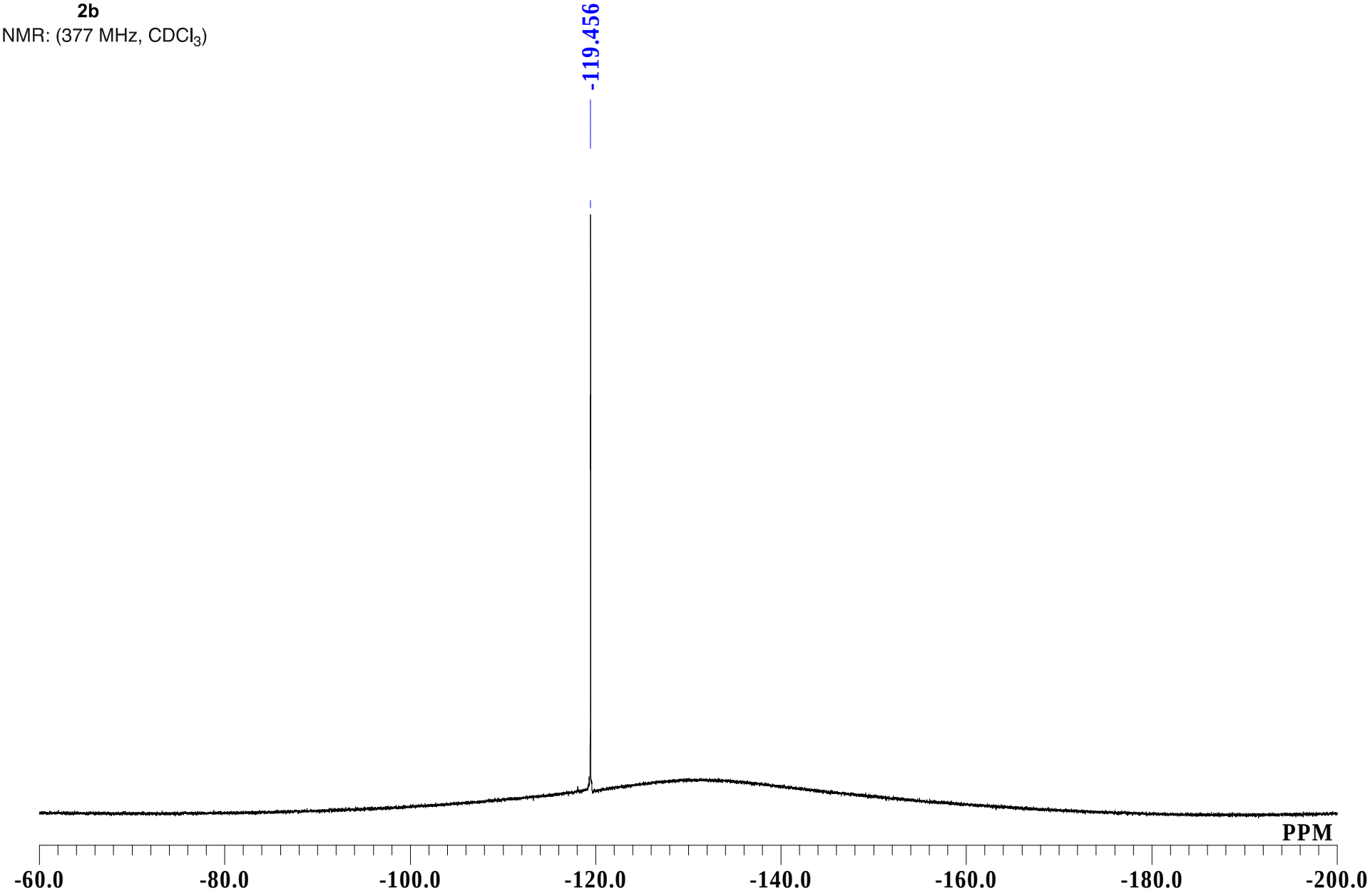


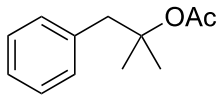

OAc
F
2b
^{13}C NMR: (100 MHz, $CDCl_3$)
170.614
162.933
160.504
132.958
132.925
131.863
131.789
114.846
114.632
81.833
77.313
77.000
76.679
45.543
25.858
22.516
PPM
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0



2b

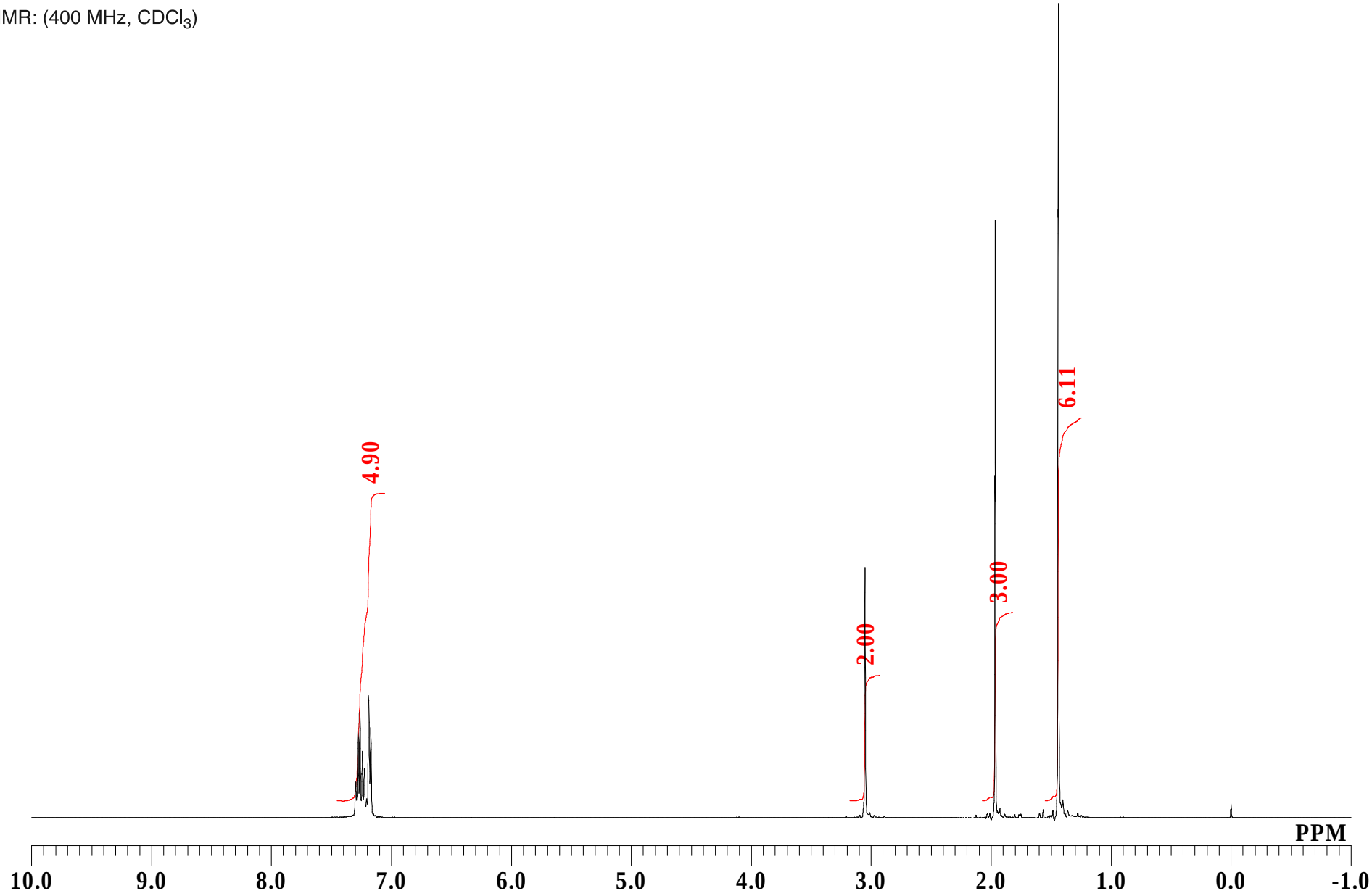
^{19}F NMR: (377 MHz, $CDCl_3$)

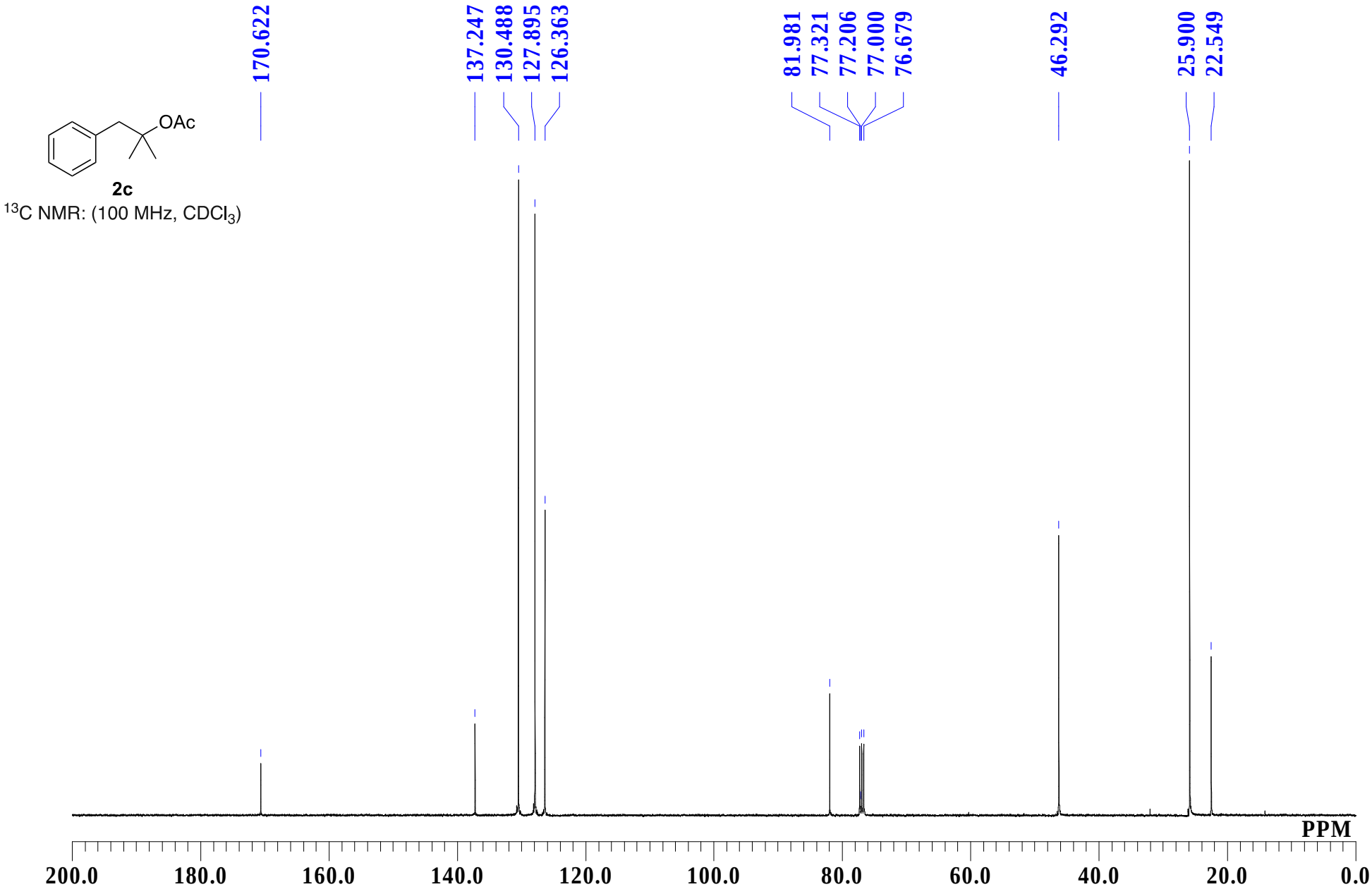


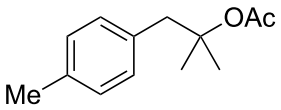


2c

^{1}H NMR: (400 MHz, $CDCl_3$)

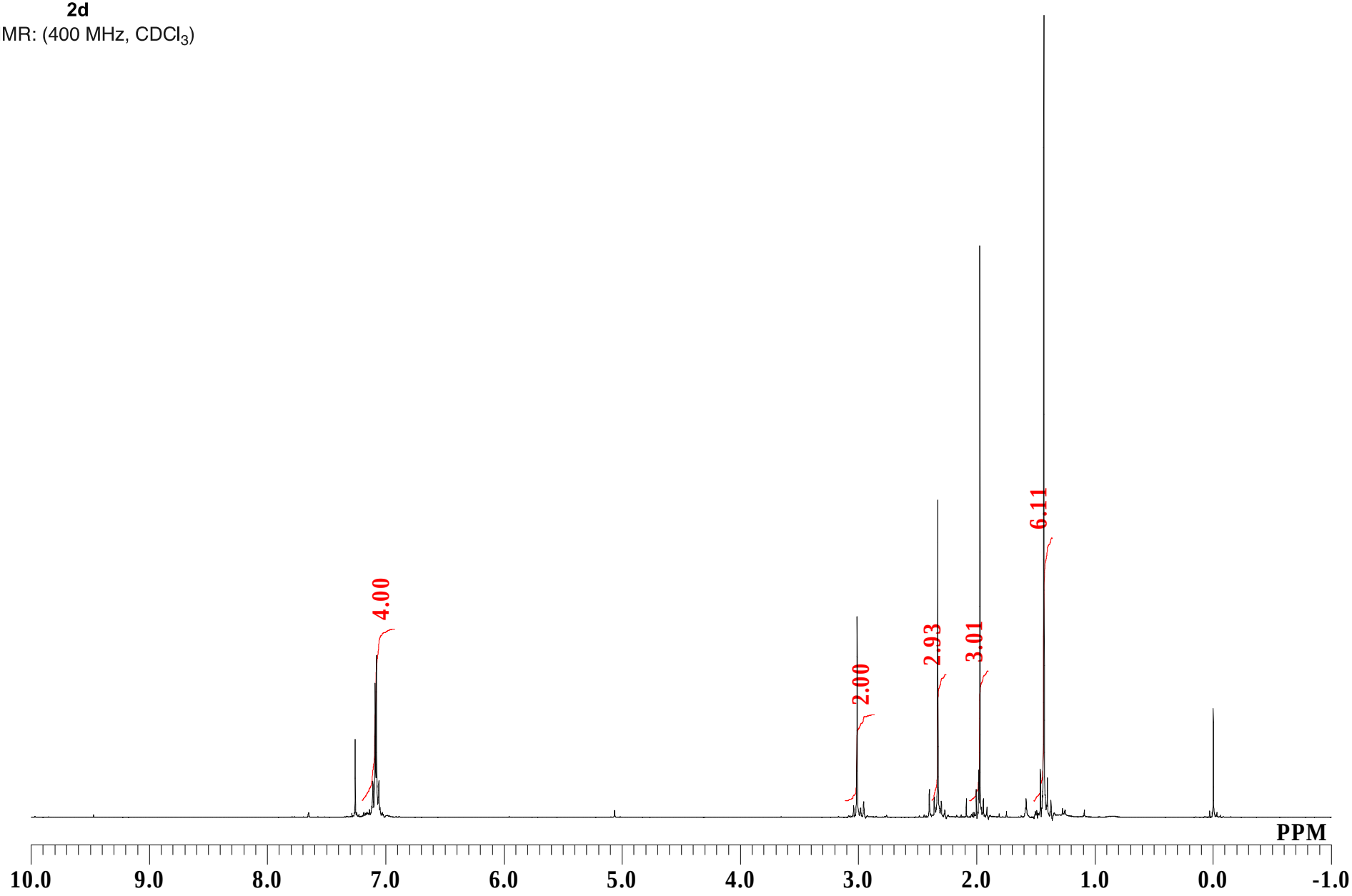


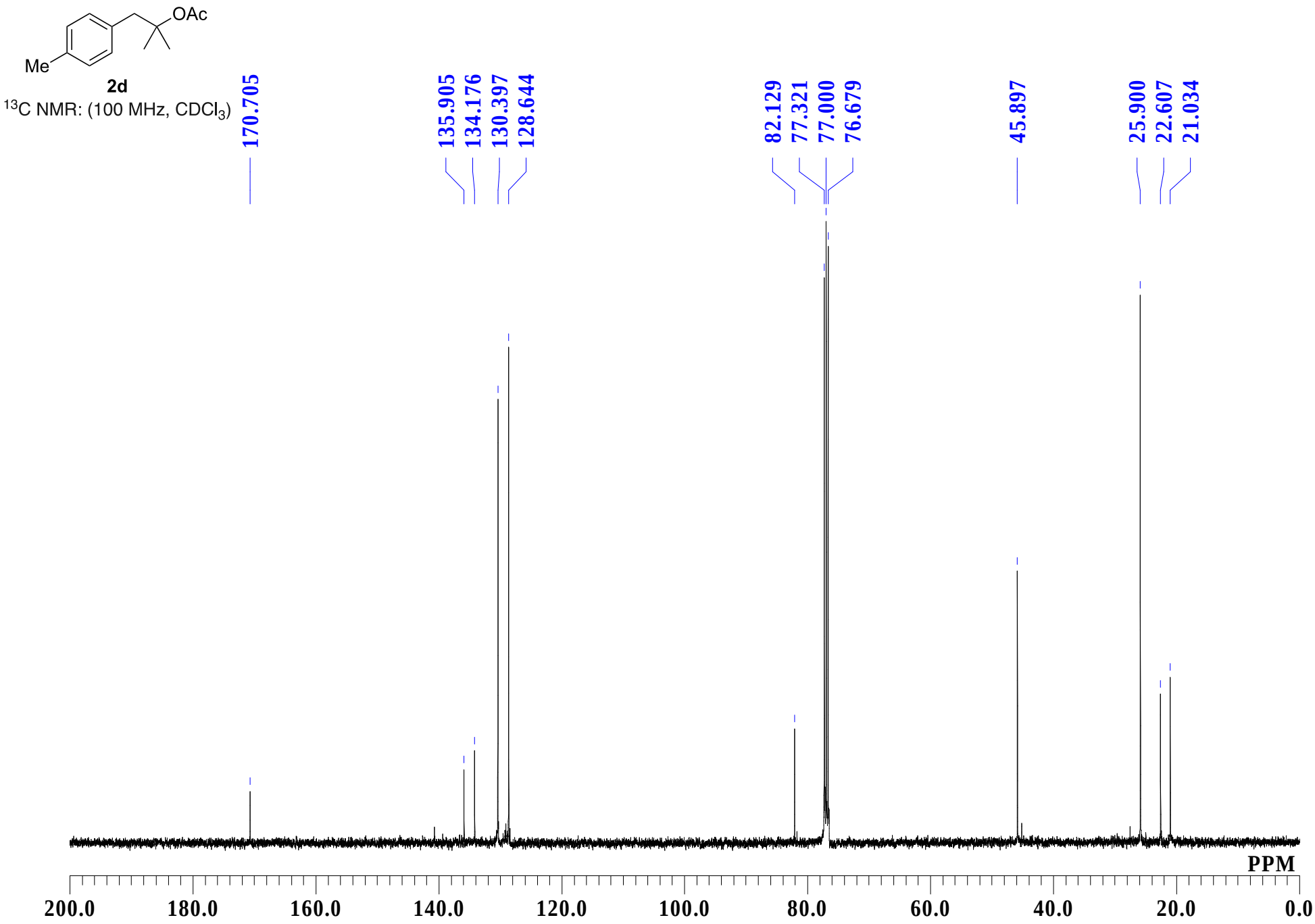

170.622
137.247
130.488
127.895
126.363
81.981
77.321
77.206
77.000
76.679
46.292
25.900
22.549
OAc
2c
13C NMR: (100 MHz, CDCl3)
PPM
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0

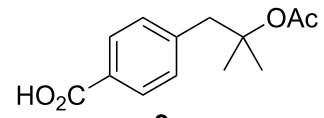


2d

^{1}H NMR: (400 MHz, $CDCl_3$)

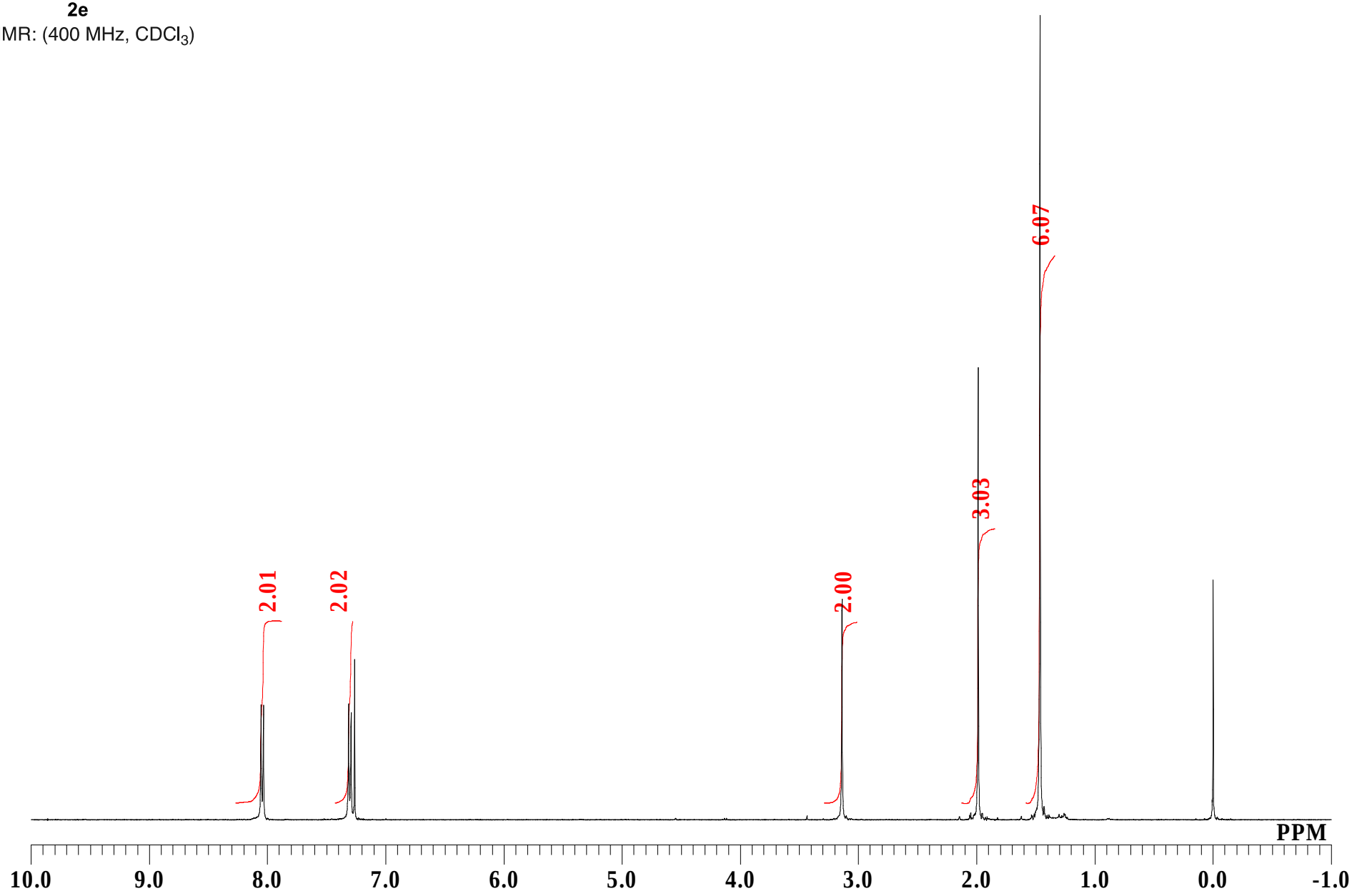


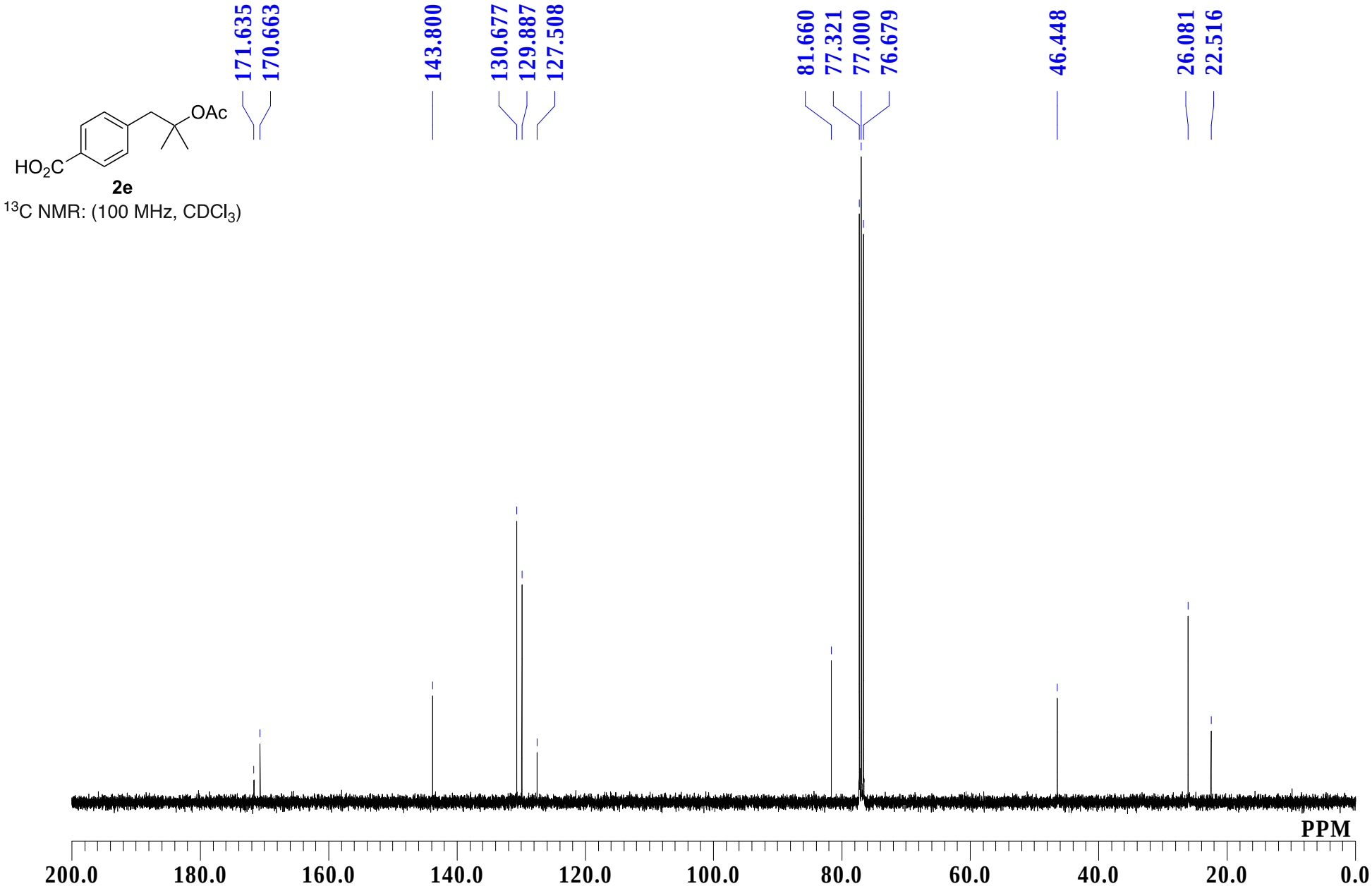

OAc
Me
2d
^{13}C NMR: (100 MHz, $CDCl_3$)
170.705
135.905
134.176
130.397
128.644
82.129
77.321
77.000
76.679
45.897
25.900
22.607
21.034
PPM
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0

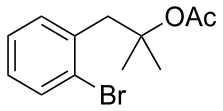


2e

^{1}H NMR: (400 MHz, $CDCl_3$)

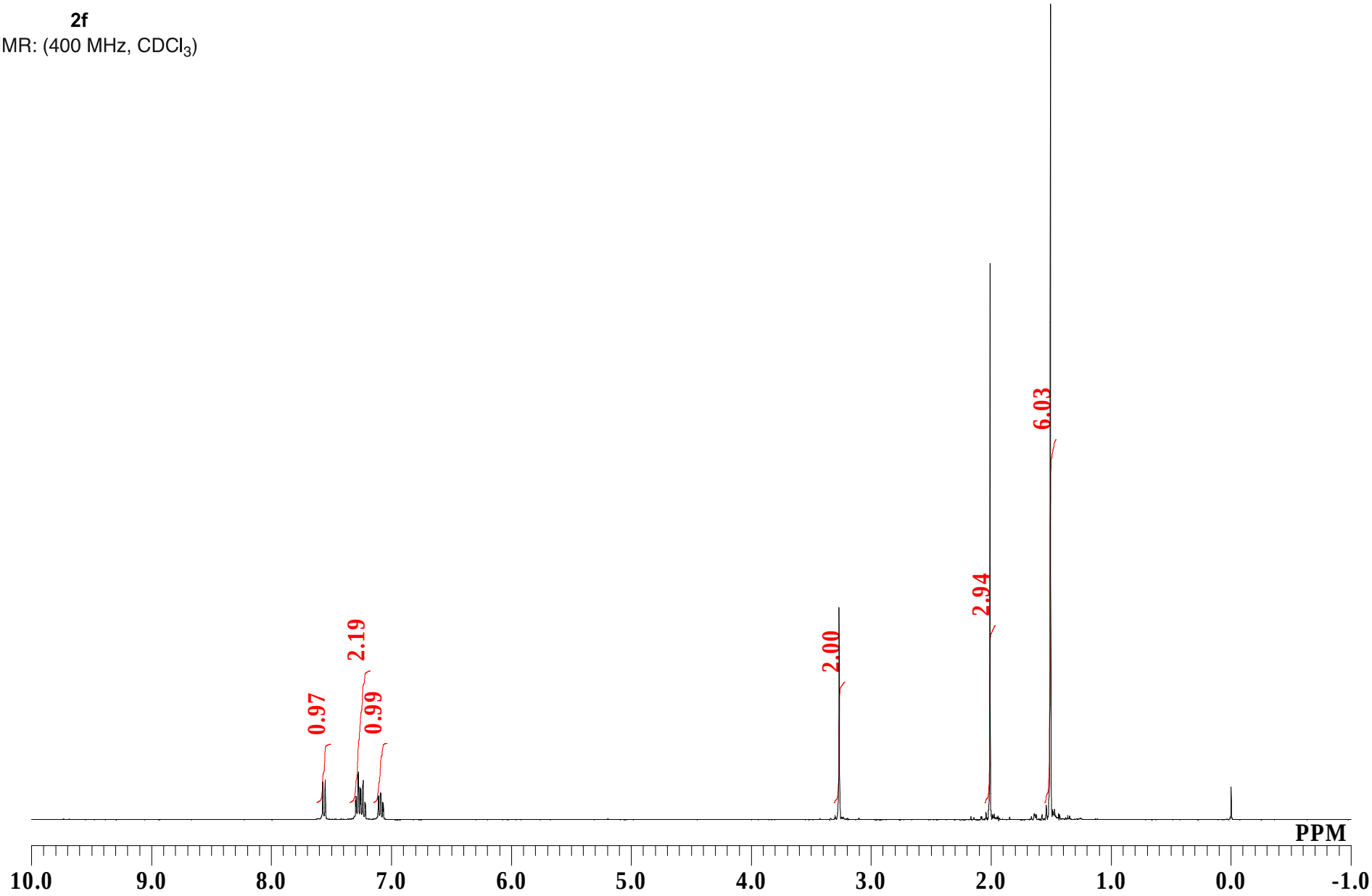


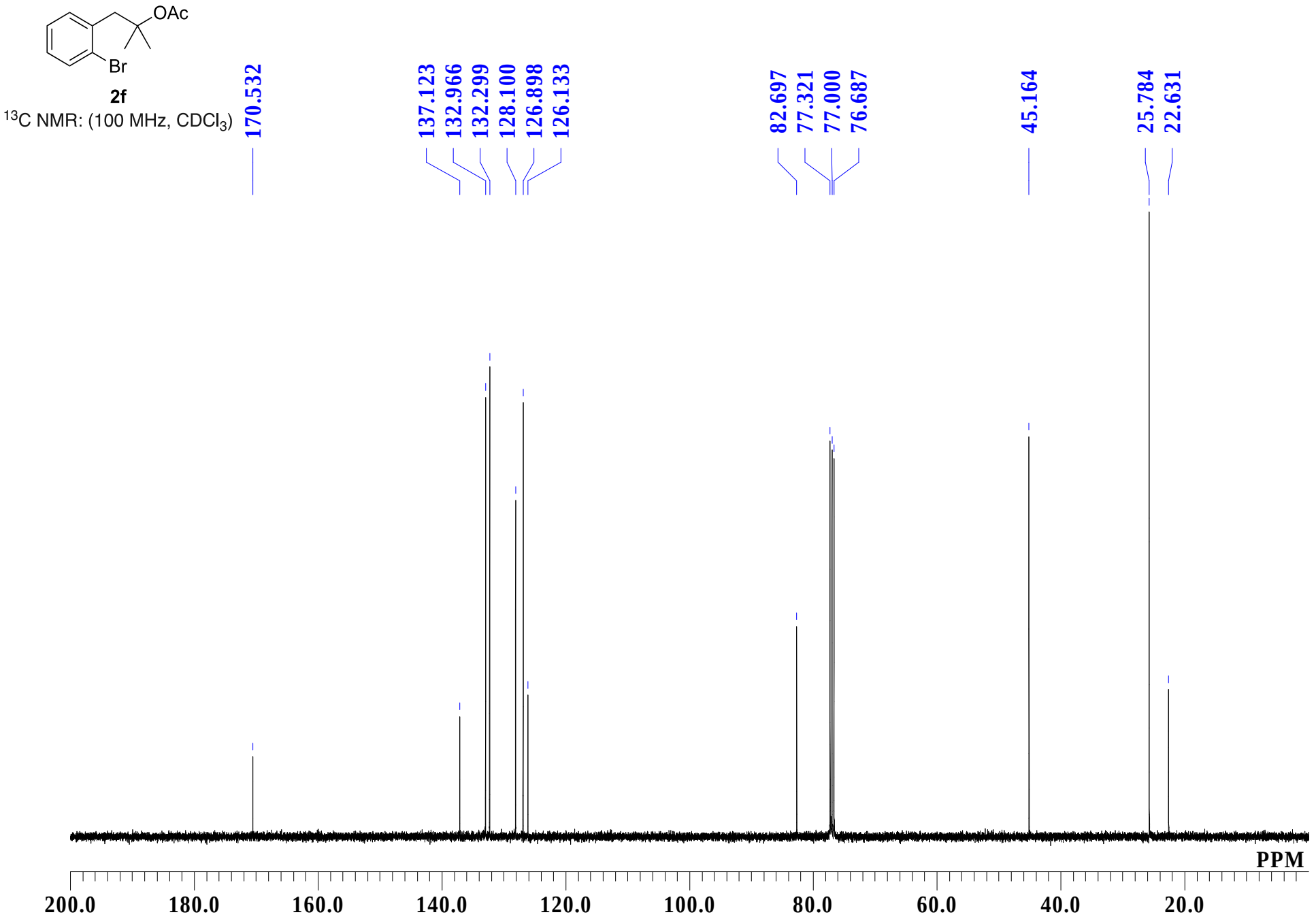

171.635
170.663
143.800
130.677
129.887
127.508
81.660
77.321
77.000
76.679
46.448
26.081
22.516
OAc
HO2C
2e
13C NMR: (100 MHz, CDCl3)
PPM
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0

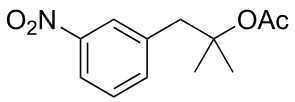


2f

^{1}H NMR: (400 MHz, $CDCl_3$)

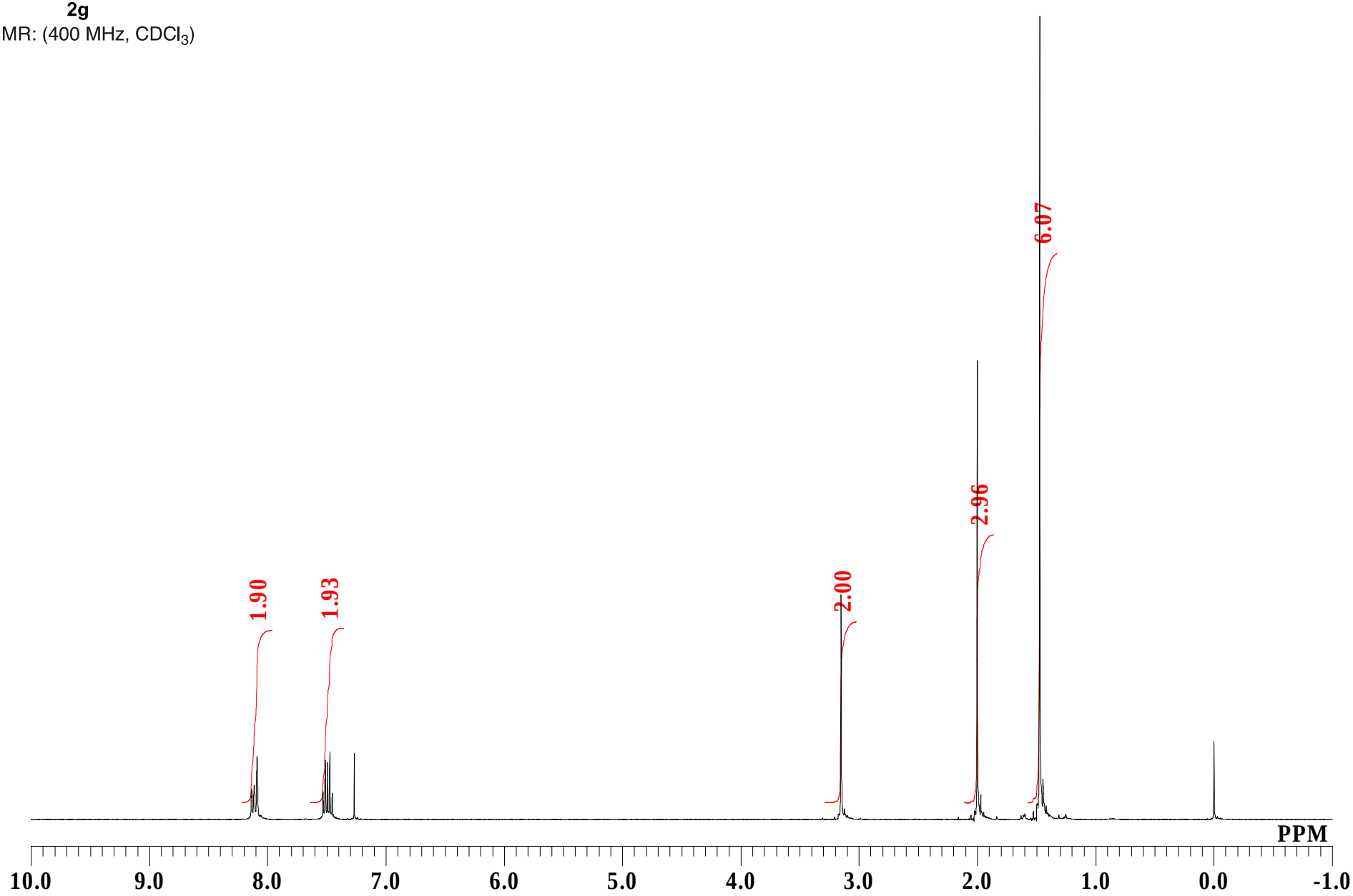


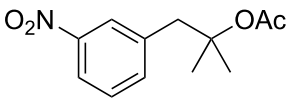

OAc
Br
2f
13C NMR: (100 MHz, CDCl3)
170.532
137.123
132.966
132.299
128.100
126.898
126.133
82.697
77.321
77.000
76.687
45.164
25.784
22.631
PPM
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0



2g

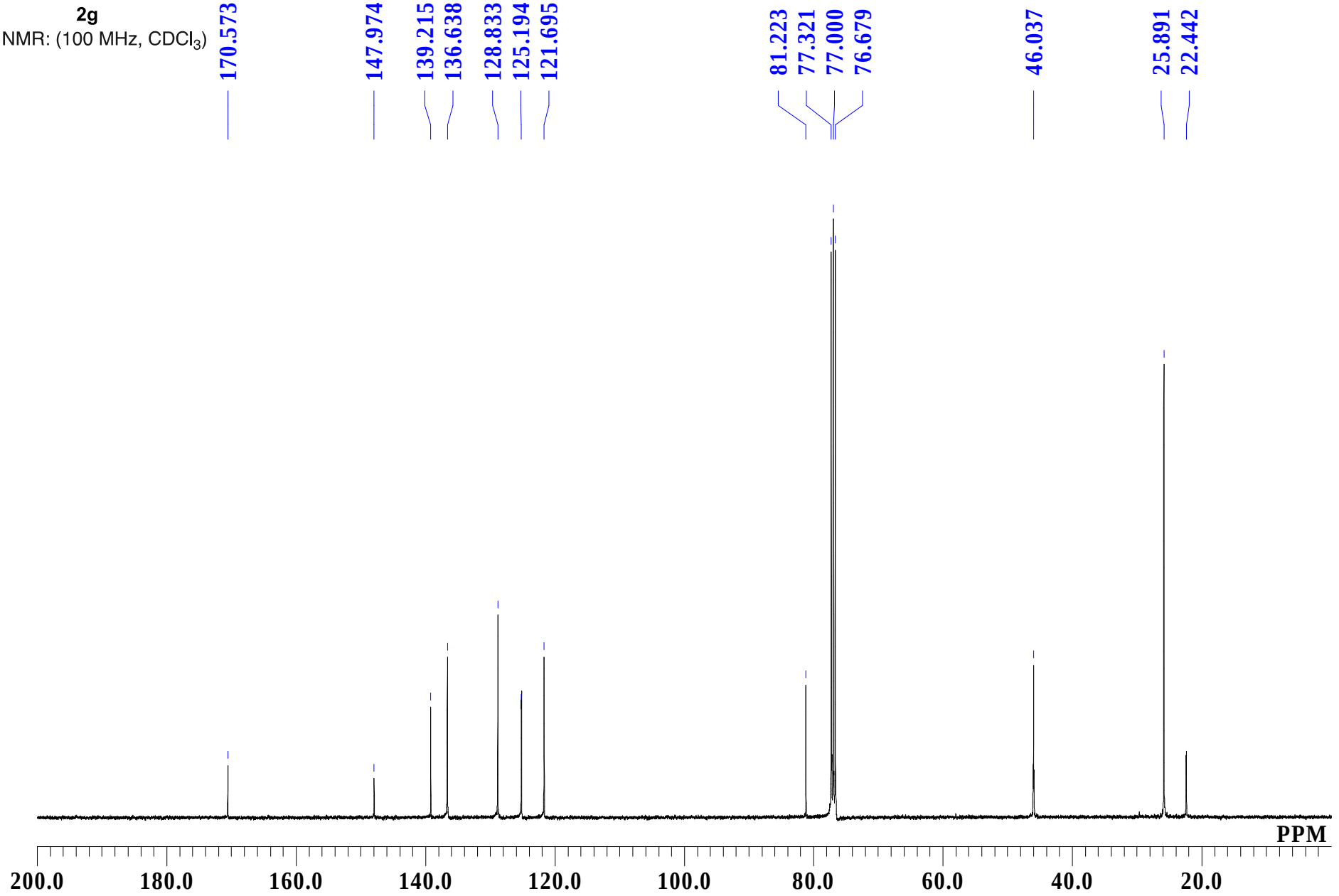
^{1}H NMR: (400 MHz, $CDCl_3$)

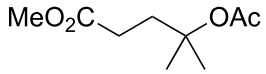




2g

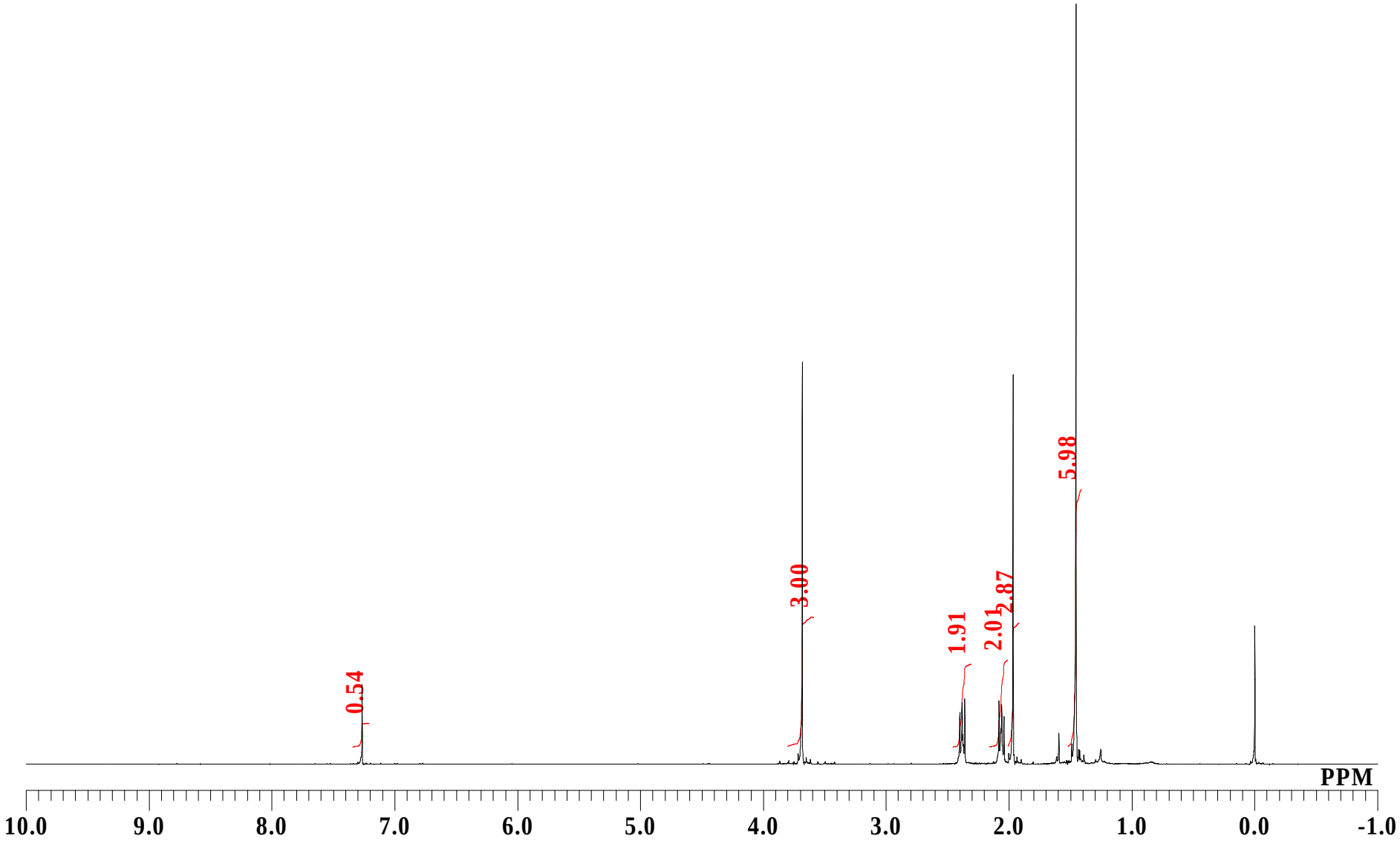
^{13}C NMR: (100 MHz, $CDCl_3$)

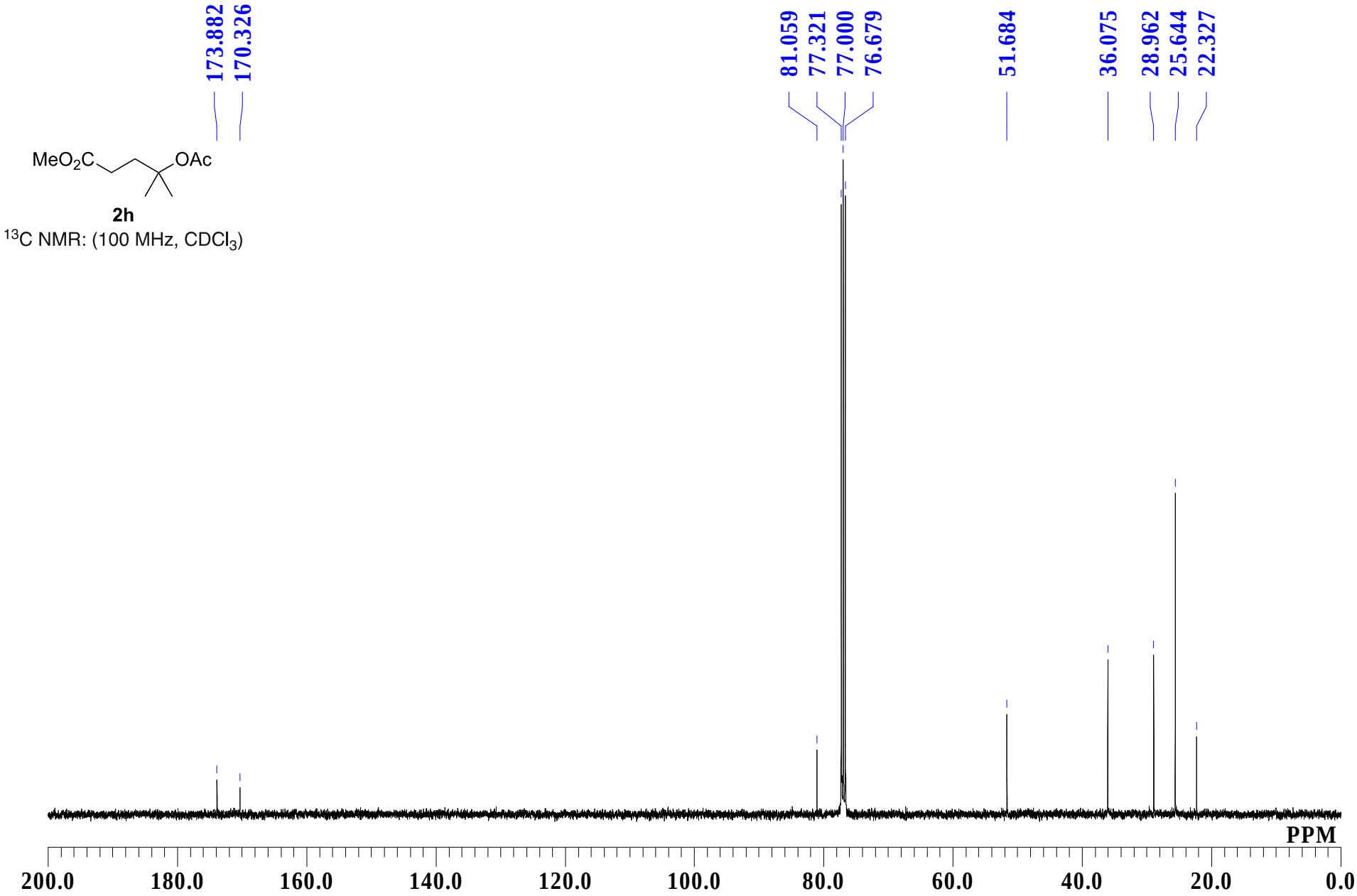


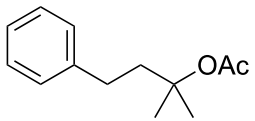


2h

^{1}H NMR: (400 MHz, $CDCl_3$)

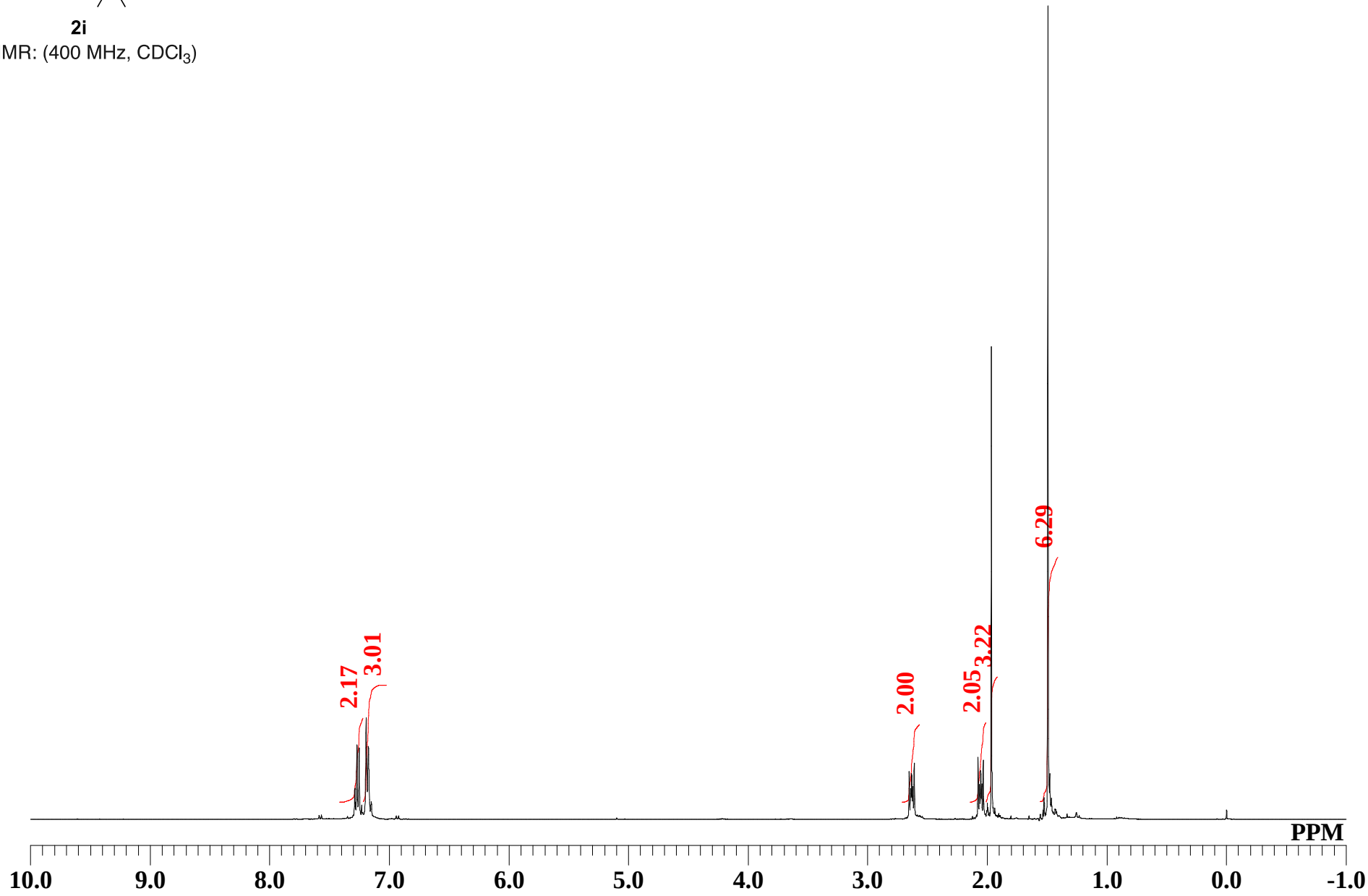


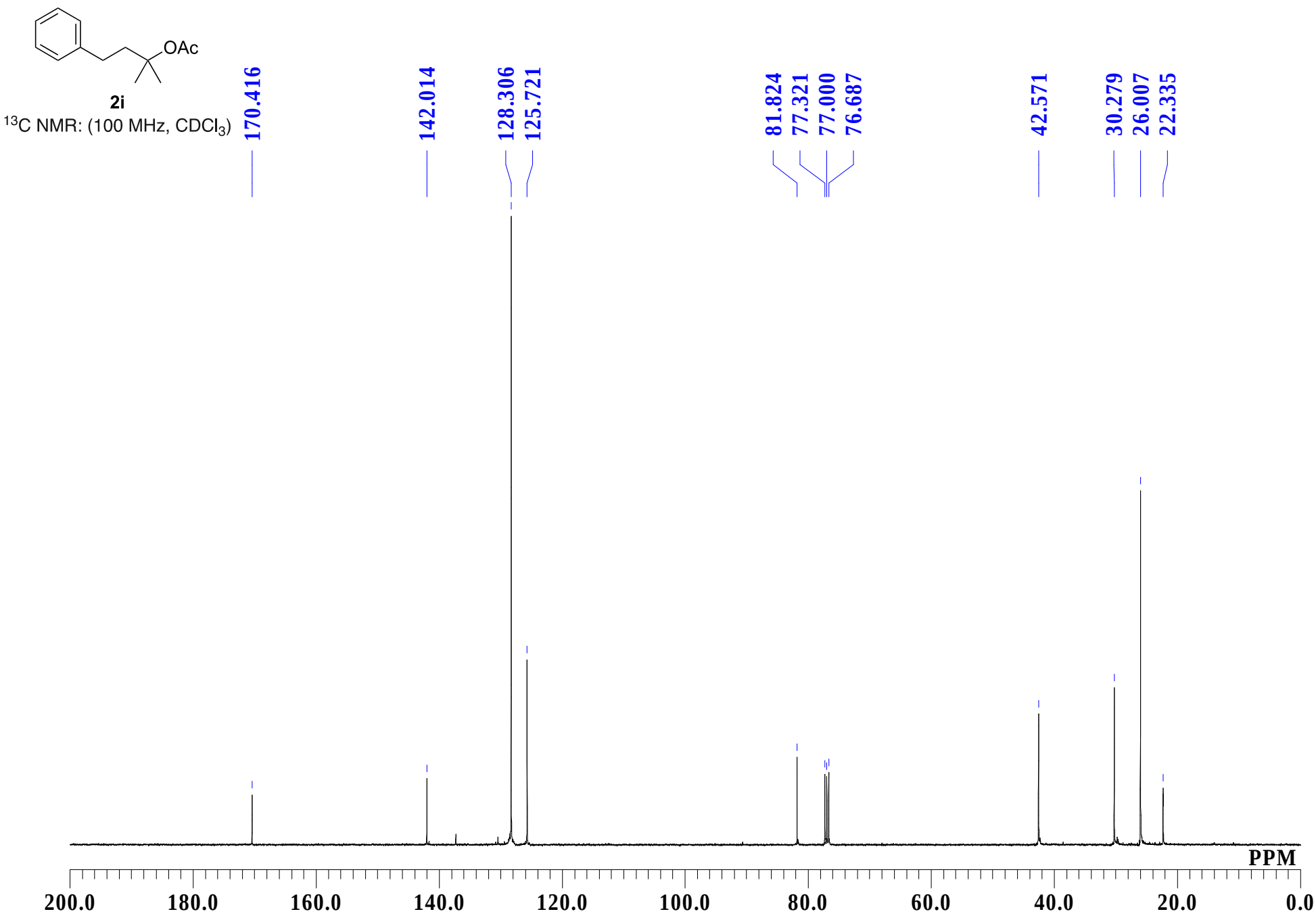

173.882
170.326
81.059
77.321
77.000
76.679
51.684
36.075
28.962
25.644
22.327
MeO2C
OAc
2h
13C NMR: (100 MHz, CDCl3)
PPM
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0

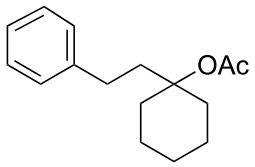


2i

^{1}H NMR: (400 MHz, $CDCl_3$)

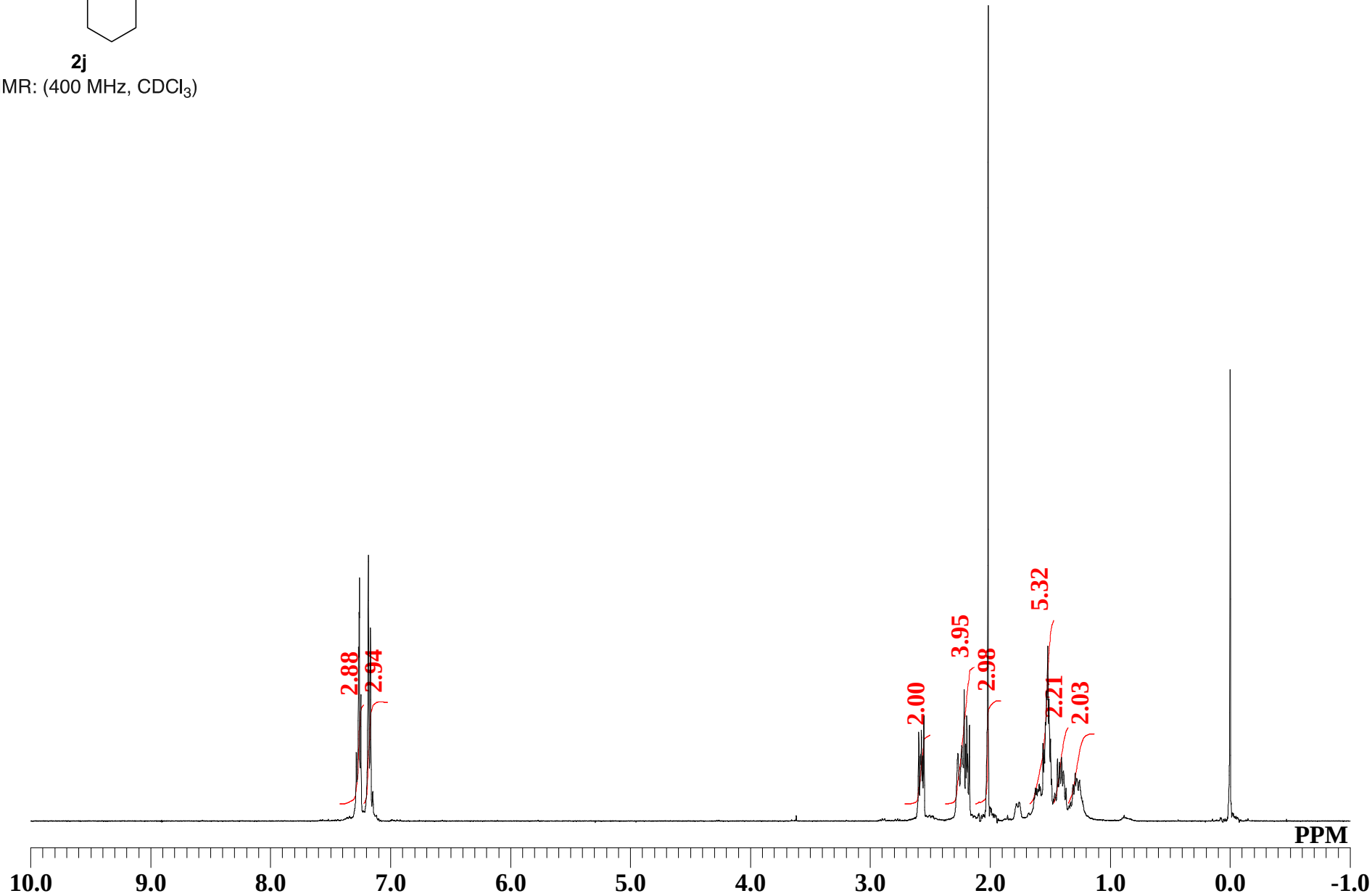


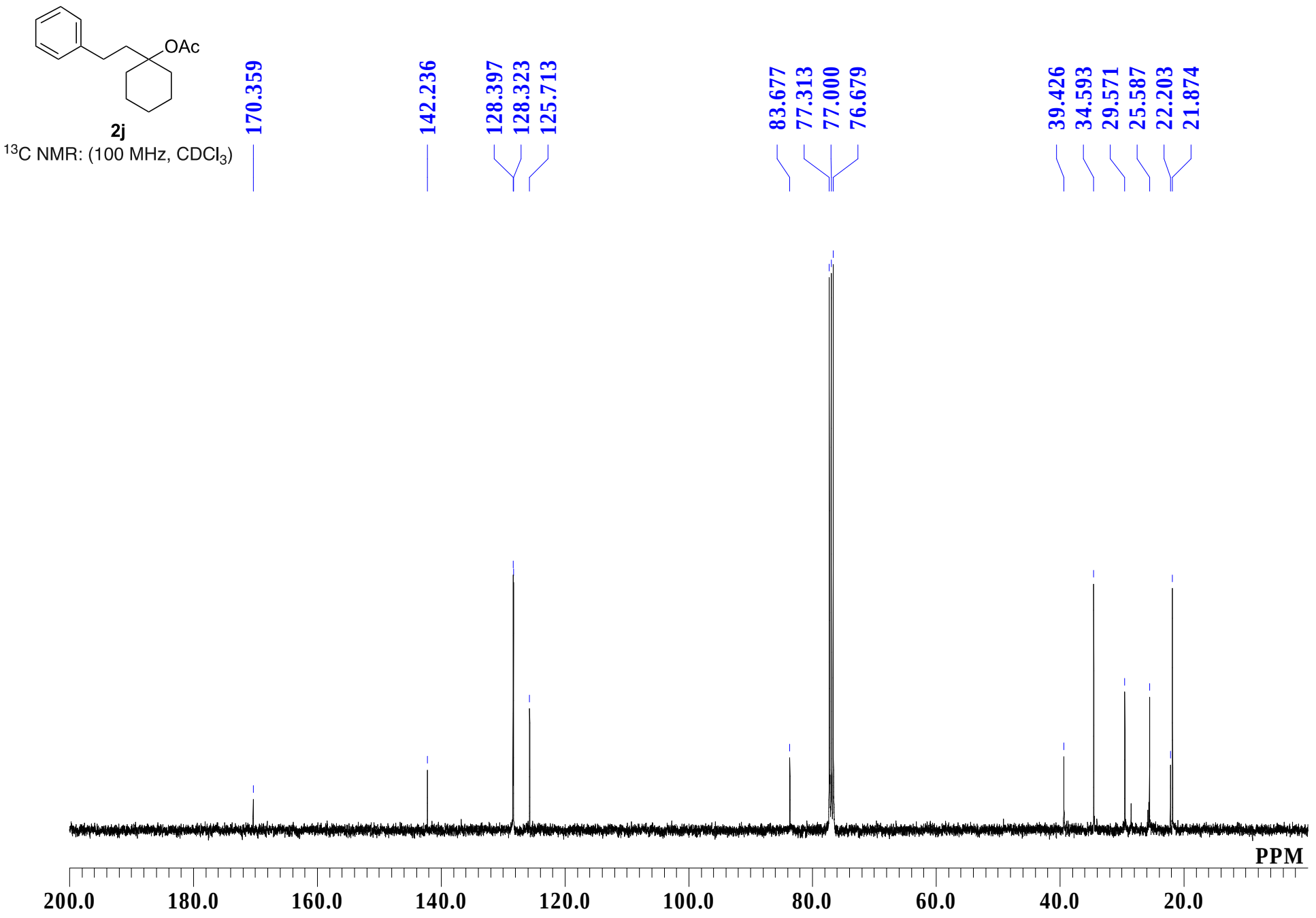

OAc
2i
^{13}C NMR: (100 MHz, $CDCl_3$)
170.416
142.014
128.306
125.721
81.824
77.321
77.000
76.687
42.571
30.279
26.007
22.335
PPM
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0

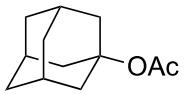


2j

^{1}H NMR: (400 MHz, $CDCl_3$)

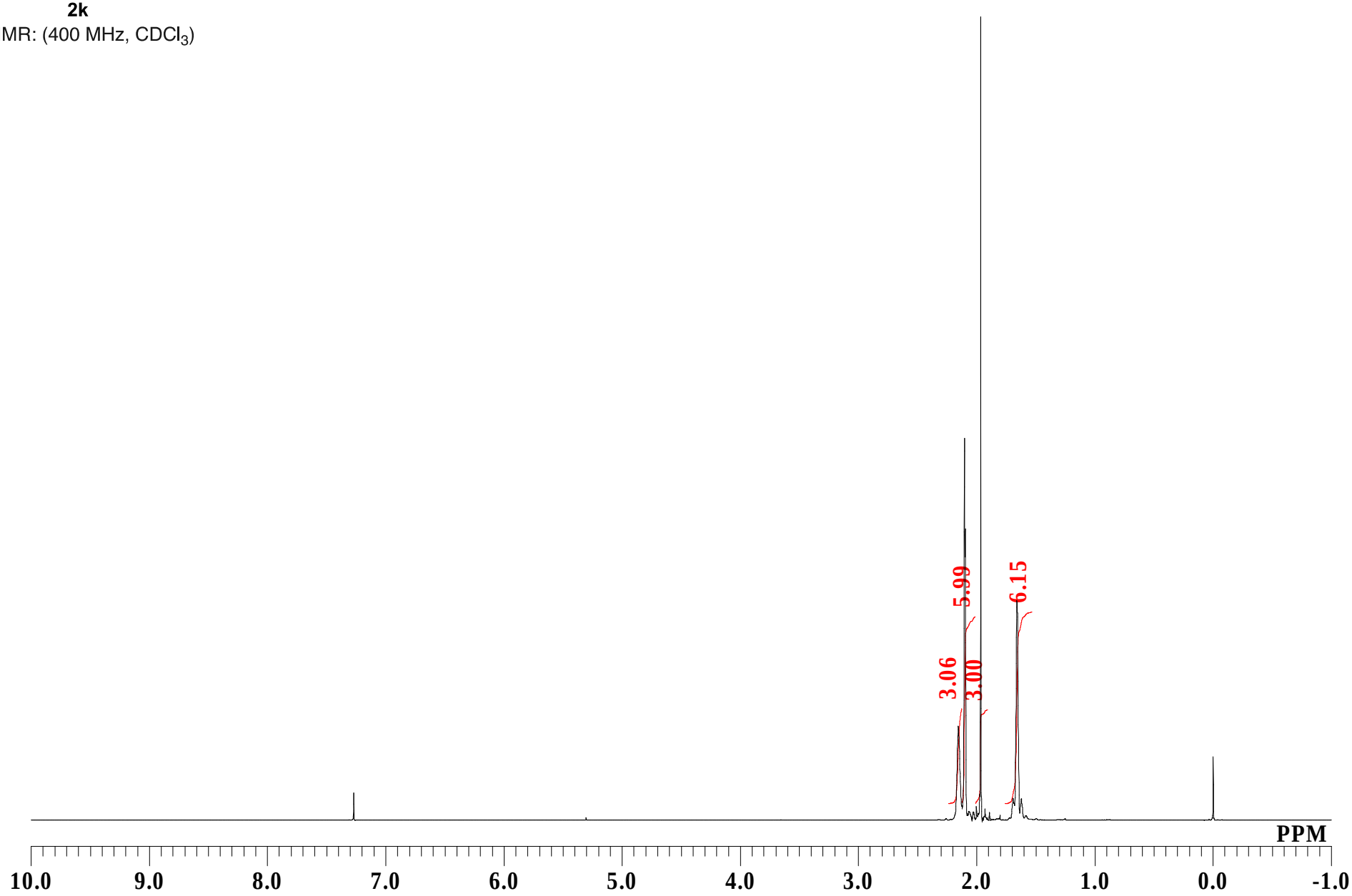


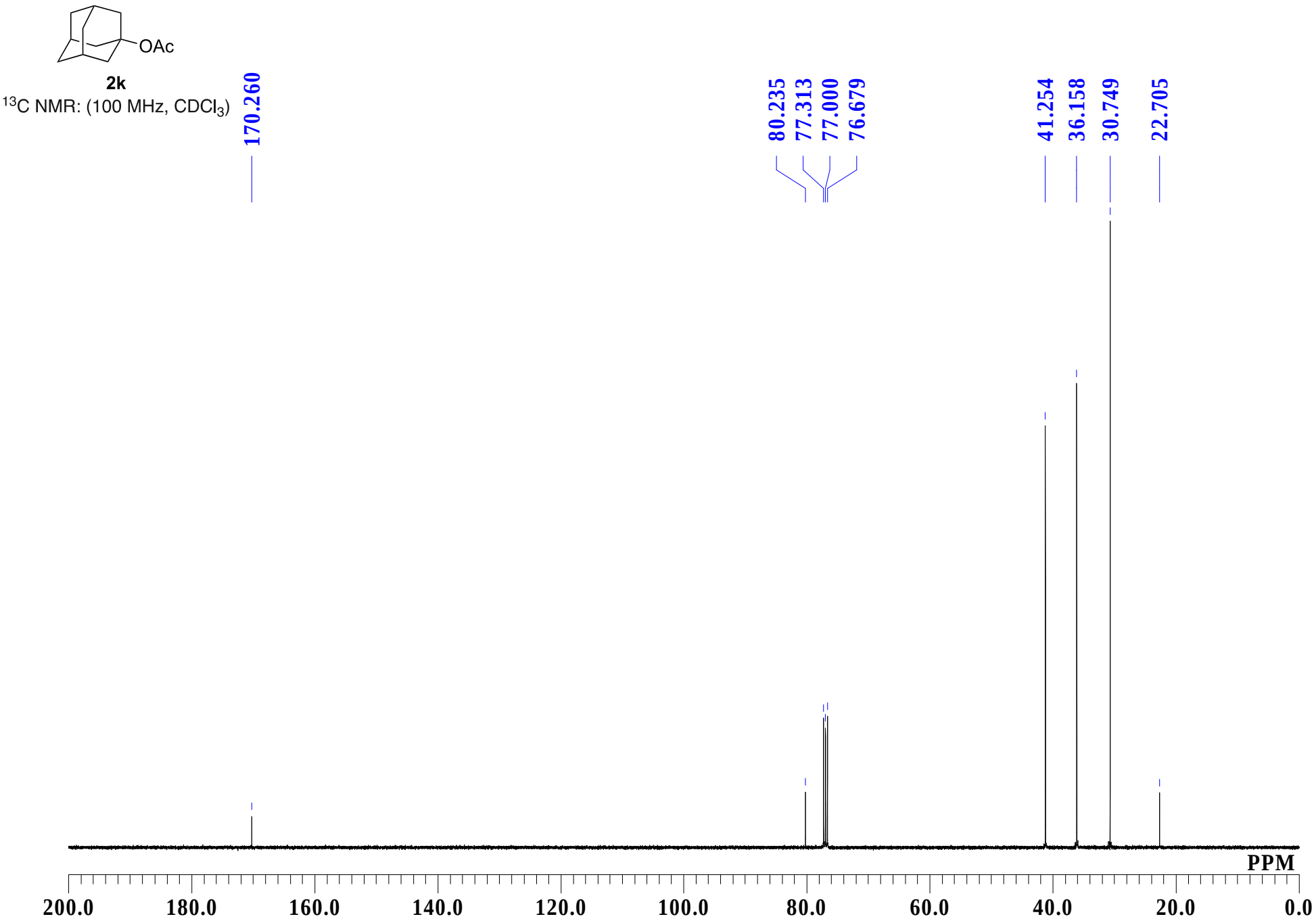

OAc
2j
^{13}C NMR: (100 MHz, $CDCl_3$)
170.359
142.236
128.397
128.323
125.713
83.677
77.313
77.000
76.679
39.426
34.593
29.571
25.587
22.203
21.874
PPM
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0

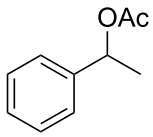


2k

^{1}H NMR: (400 MHz, $CDCl_3$)

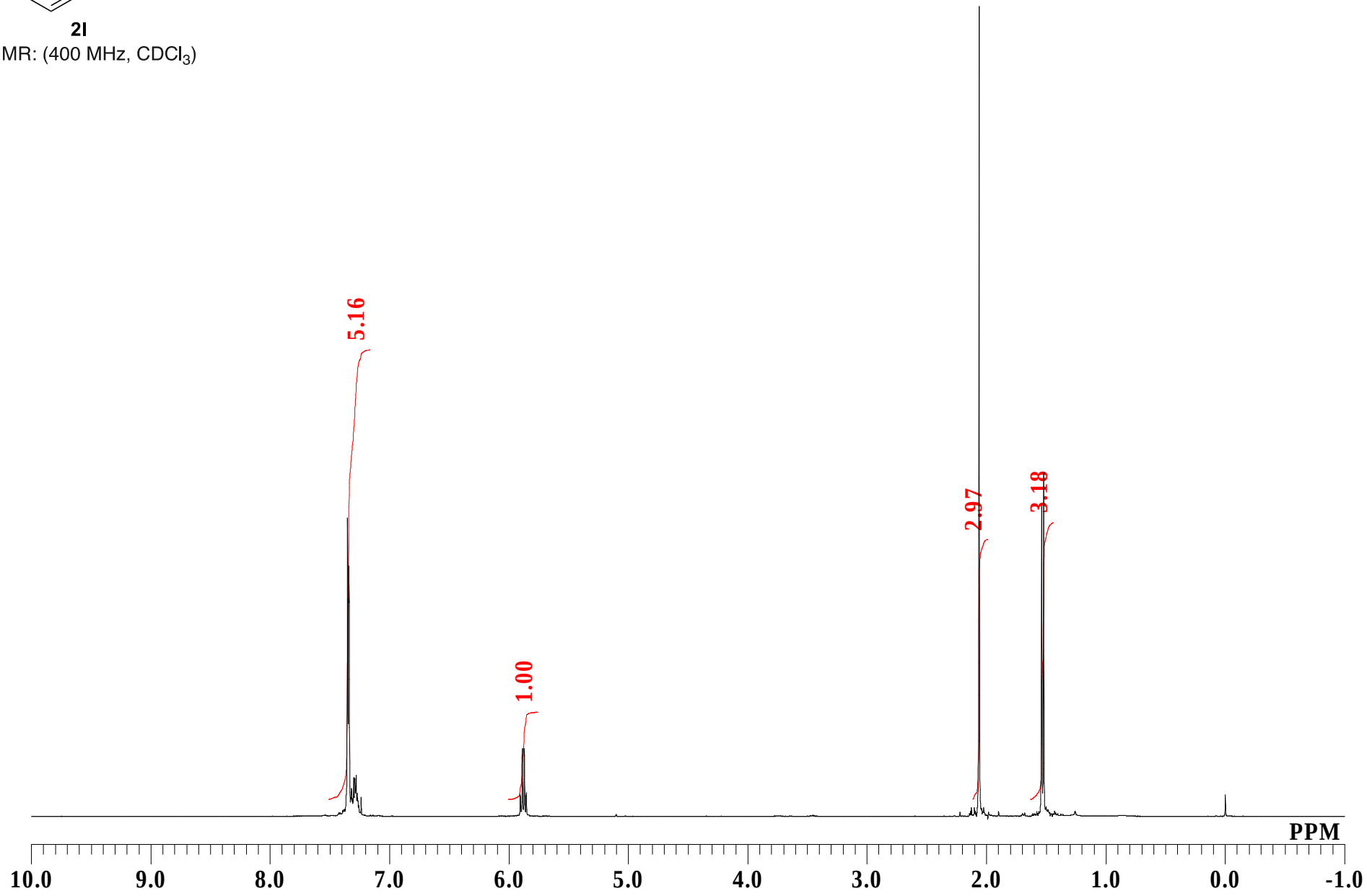


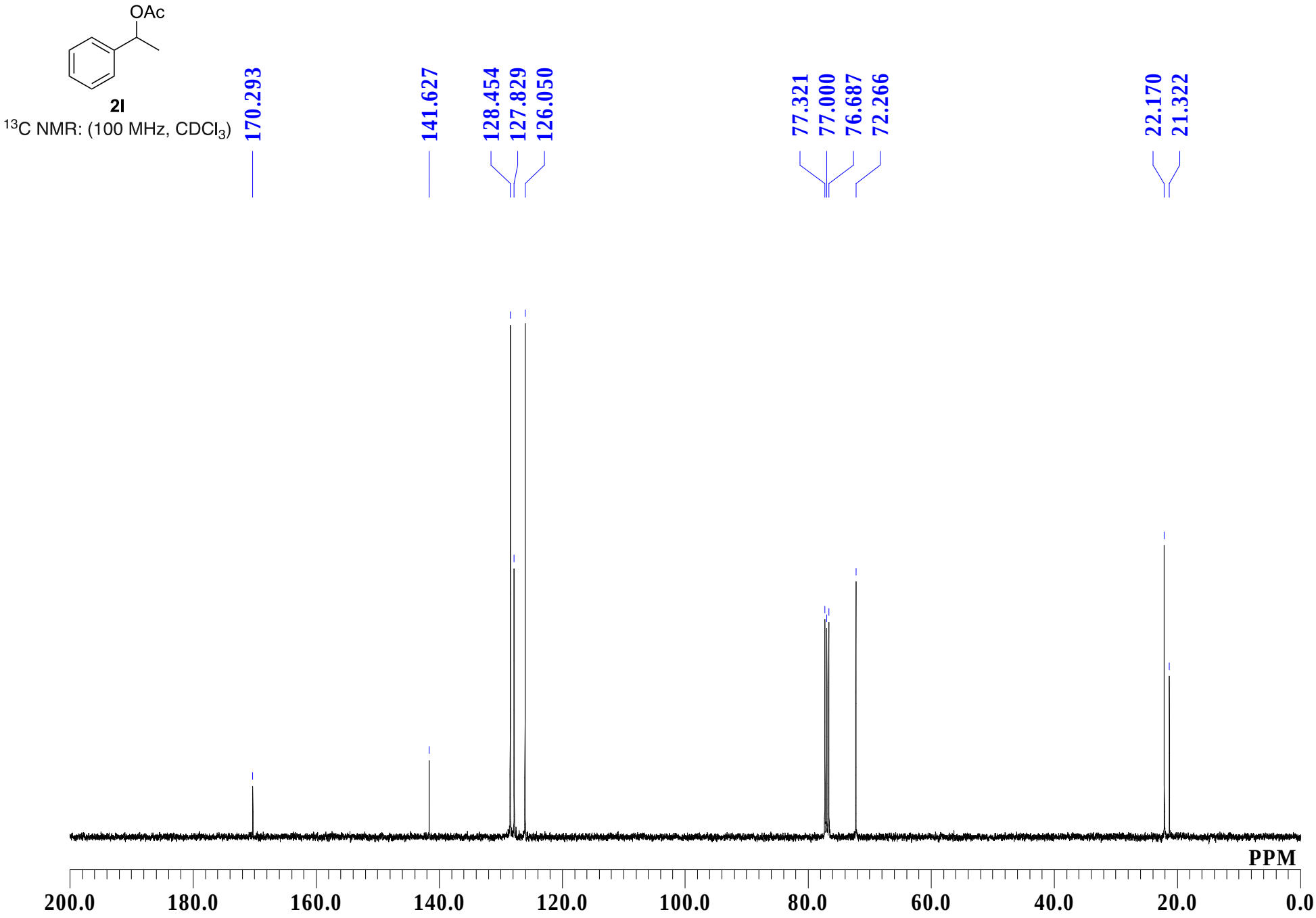

OAc
2k
13C NMR: (100 MHz, CDCl3)
170.260
80.235
77.313
77.000
76.679
41.254
36.158
30.749
22.705
PPM
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0

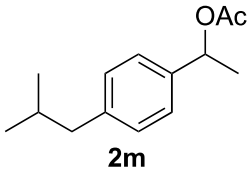


2l

^{1}H NMR: (400 MHz, $CDCl_3$)

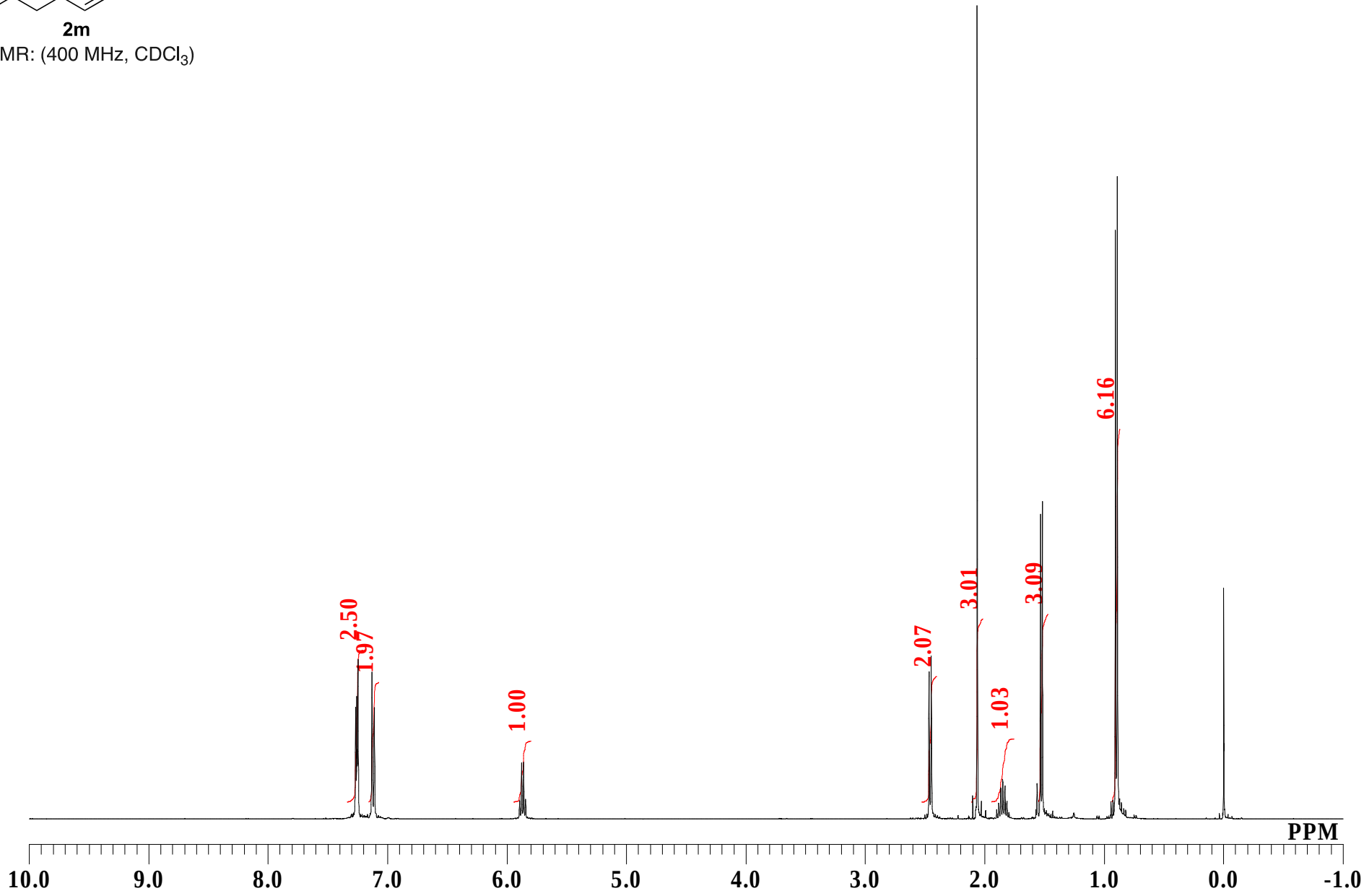


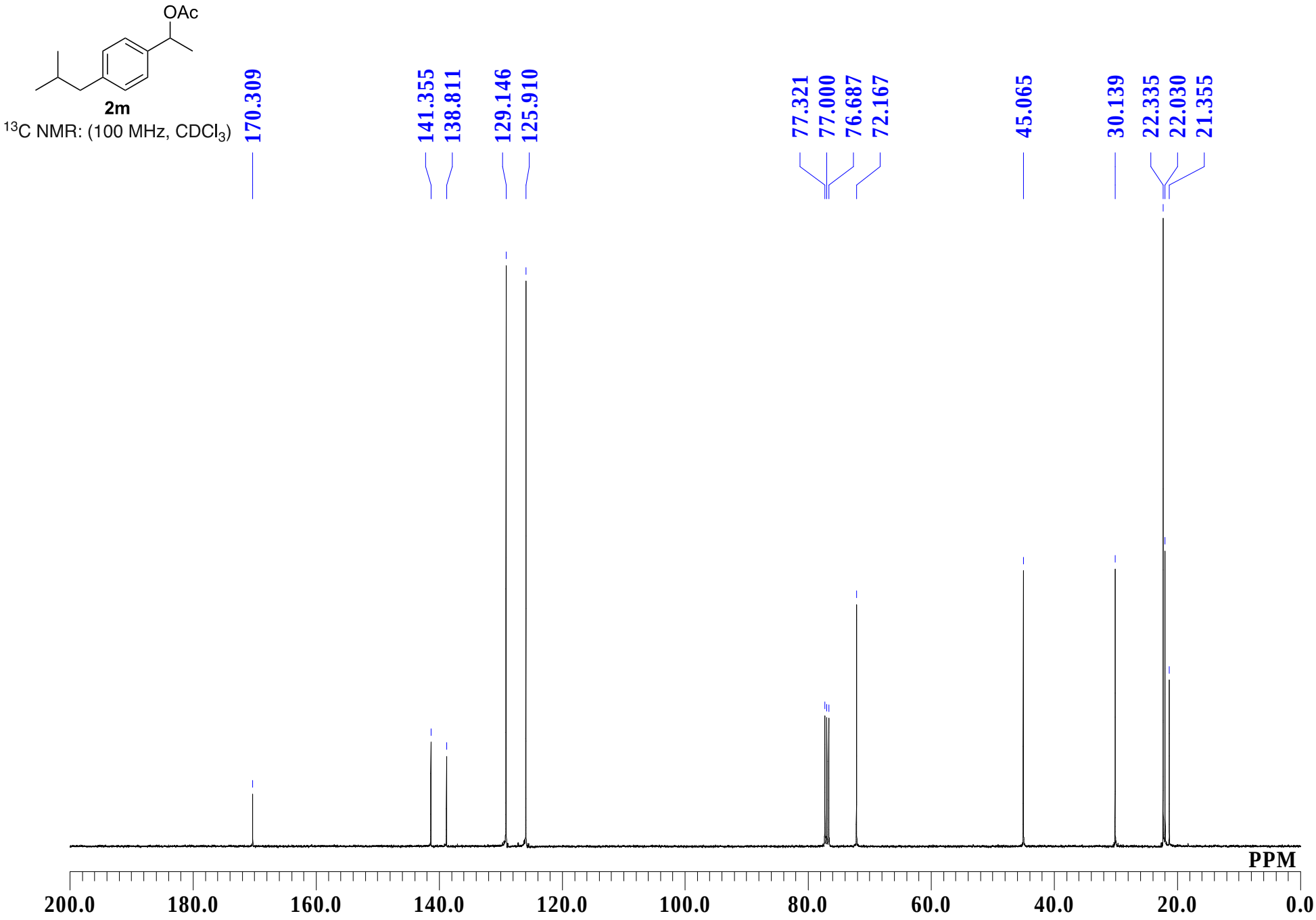

OAc
2l
^{13}C NMR: (100 MHz, $CDCl_3$)
170.293
141.627
128.454
127.829
126.050
77.321
77.000
76.687
72.266
22.170
21.322
PPM
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0

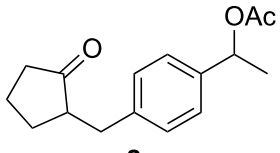


2m

^{1}H NMR: (400 MHz, $CDCl_3$)

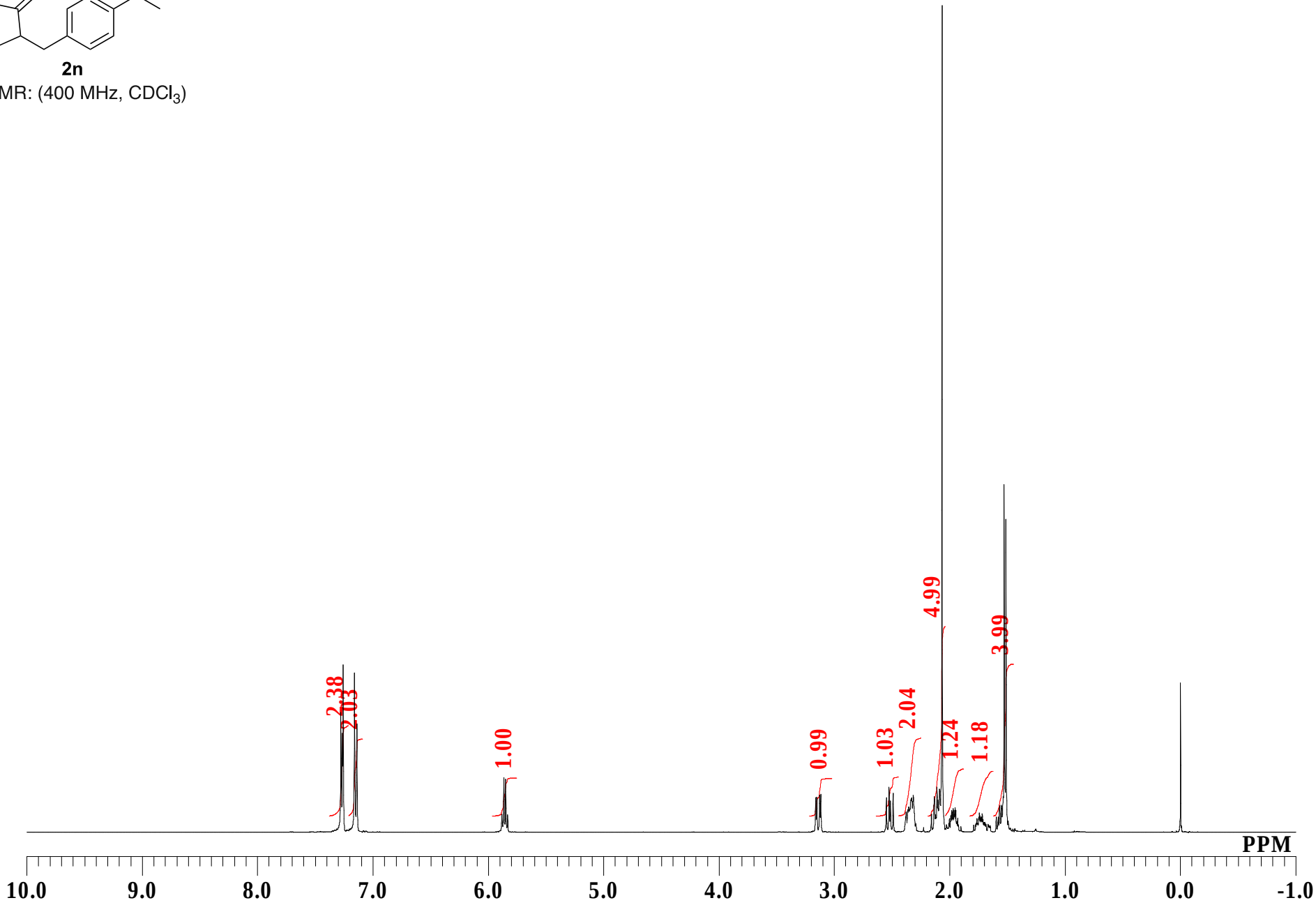


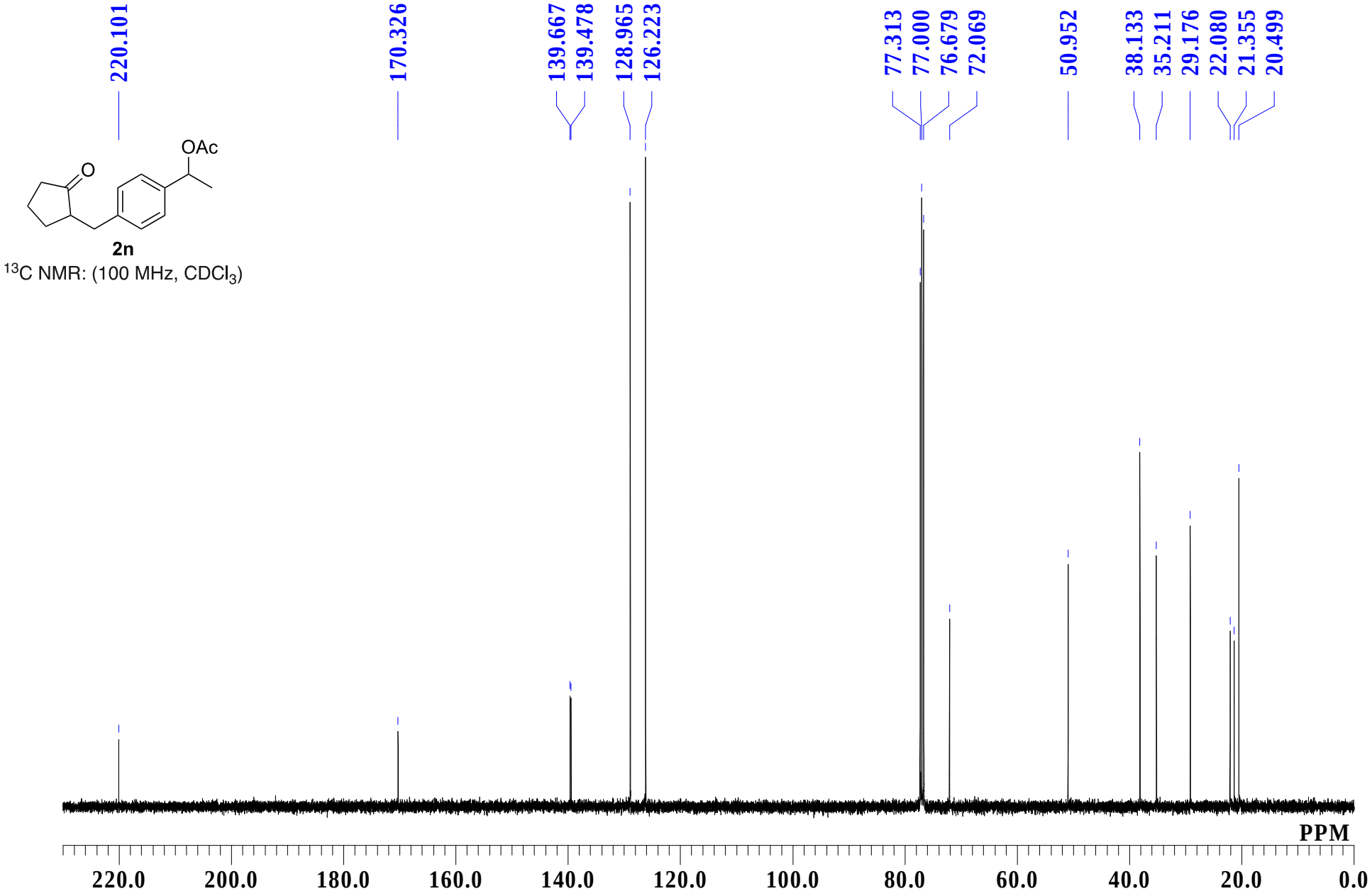

OAc
2m
^{13}C NMR: (100 MHz, $CDCl_3$)
170.309
141.355
138.811
129.146
125.910
77.321
77.000
76.687
72.167
45.065
30.139
22.335
22.030
21.355
PPM
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0



2n

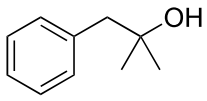
^{1}H NMR: (400 MHz, $CDCl_3$)





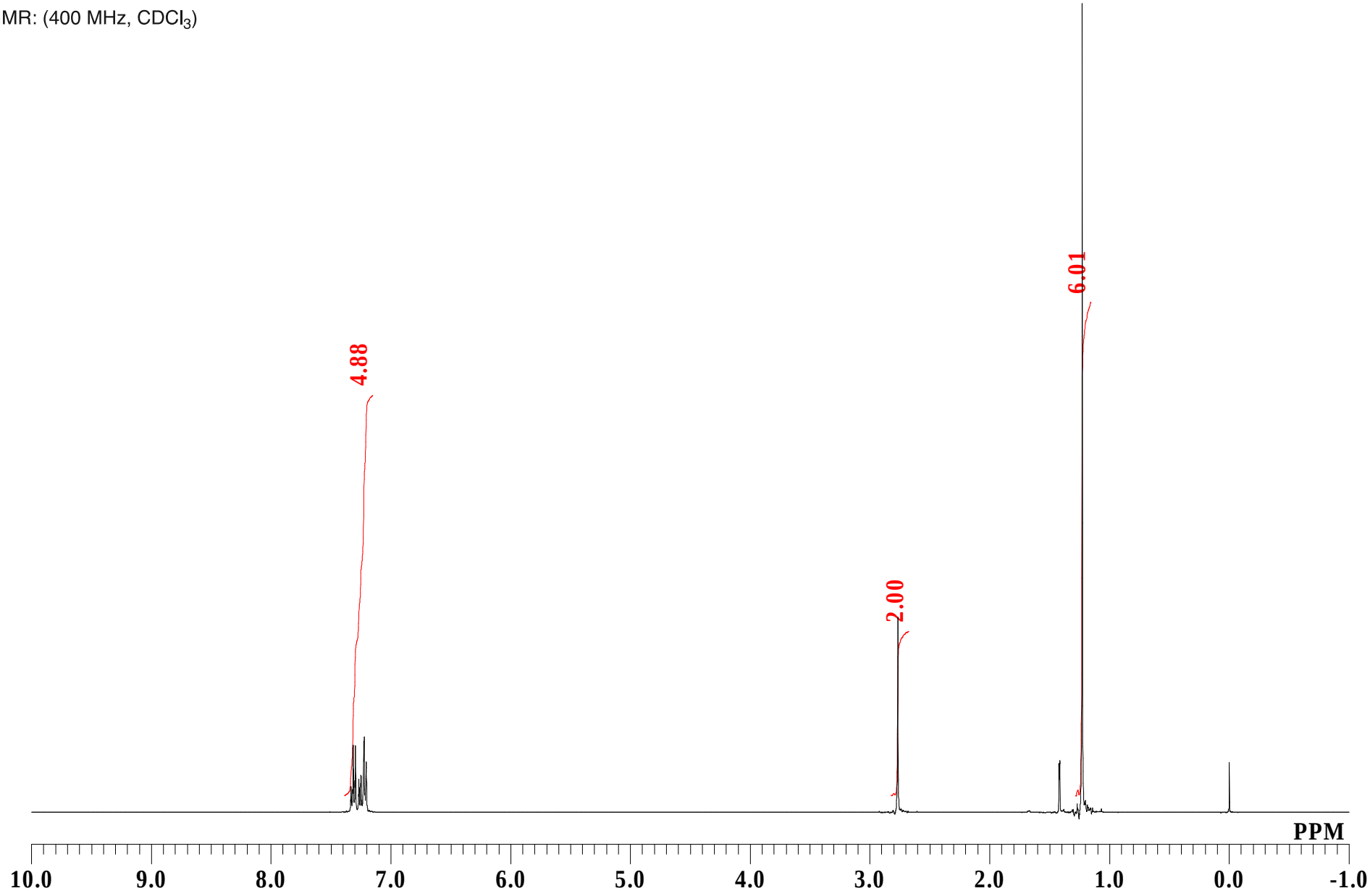
2n

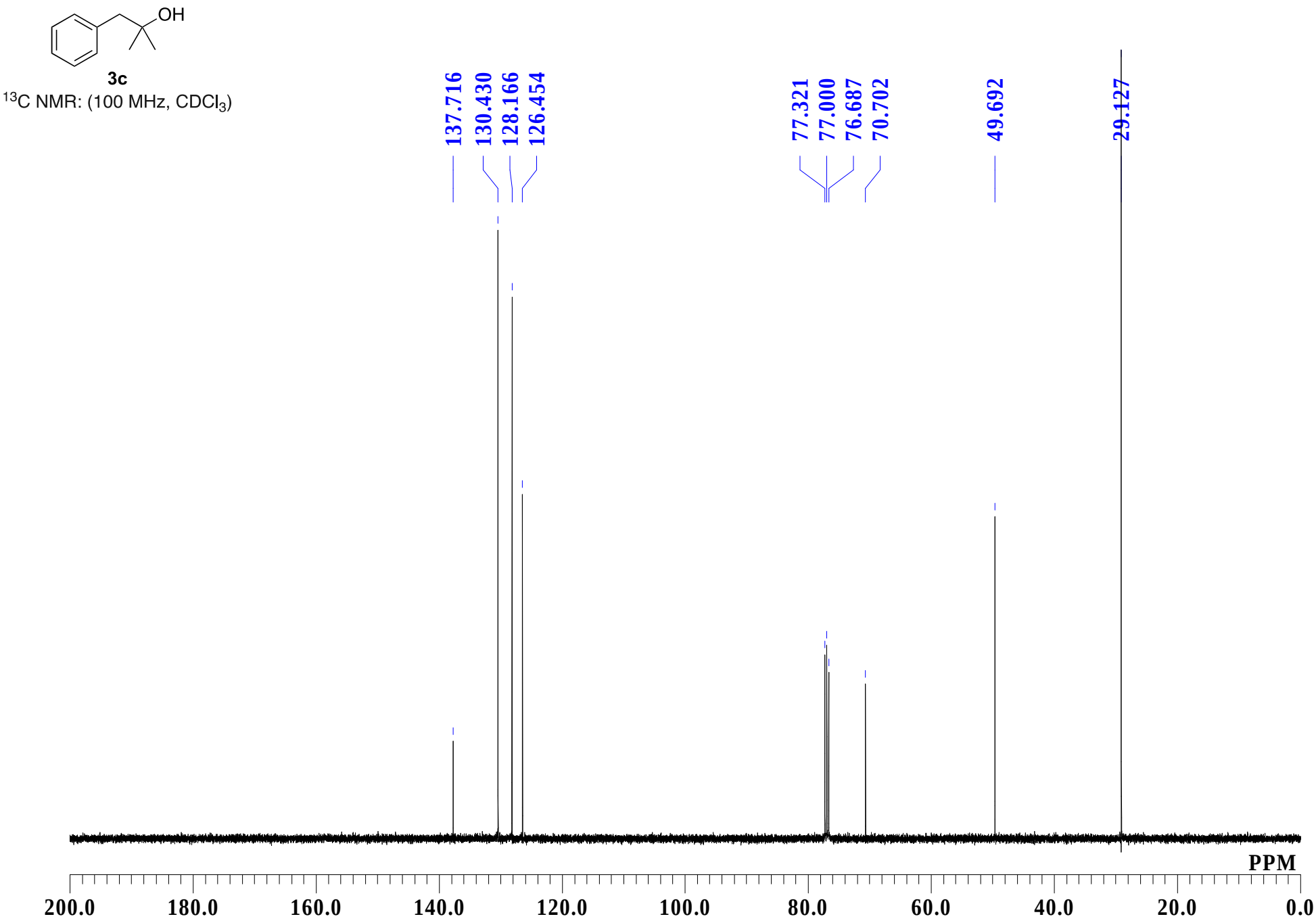
^{13}C NMR: (100 MHz, $CDCl_3$)

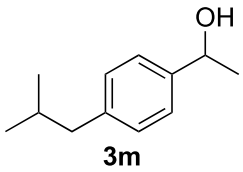


3c

^{1}H NMR: (400 MHz, $CDCl_3$)

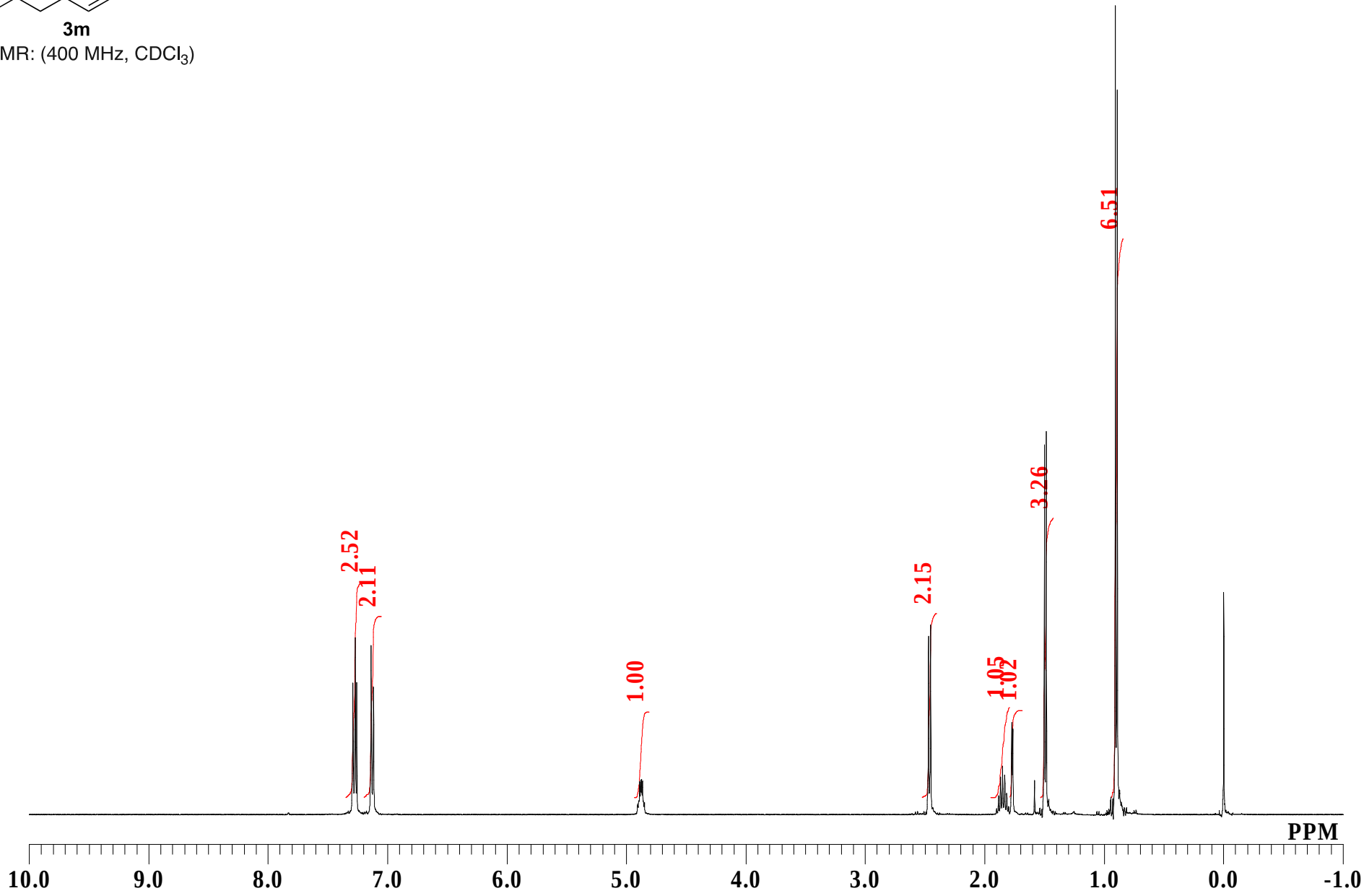


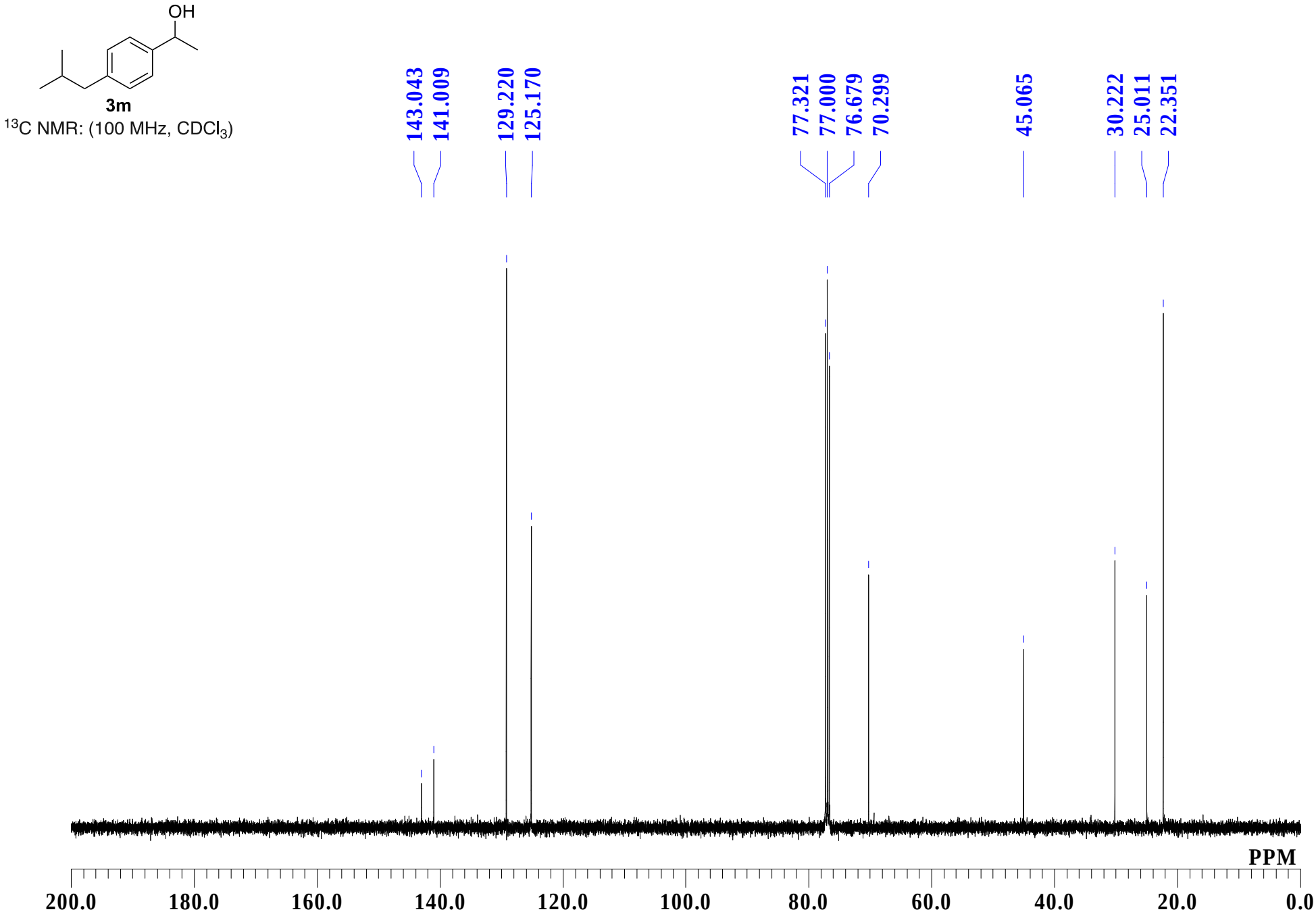

OH
3c
13C NMR: (100 MHz, CDCl3)
137.716
130.430
128.166
126.454
77.321
77.000
76.687
70.702
49.692
29.127
PPM
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0



3m

^{1}H NMR: (400 MHz, $CDCl_3$)




OH
3m
^{13}C NMR: (100 MHz, $CDCl_3$)
143.043
141.009
129.220
125.170
77.321
77.000
76.679
70.299
45.065
30.222
25.011
22.351
PPM
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0