Brønsted Acid-Catalyzed Transfer Hydrogenation of Imines and Alkenes Using Cyclohexa-1,4-dienes as Dihydrogen Surrogates

Indranil Chatterjee and Martin Oestreich*

Institut für Chemie, Technische Universität Berlin,
Straße des 17. Juni 115, 10623 Berlin, Germany
martin.oestreich@tu-berlin.de

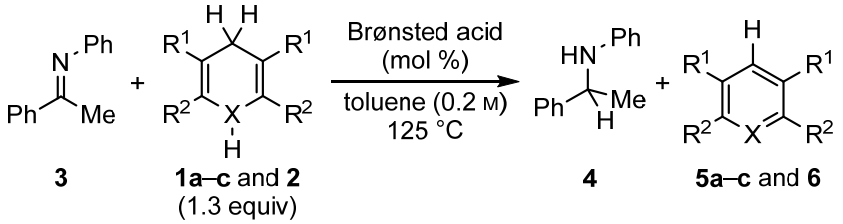
Supporting Information

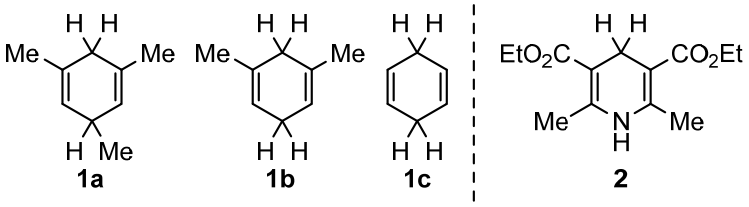
Table of Contents

1 General Information

Reactions were performed in flame-dried glassware using an *MBraun* glove box or conventional Schlenk techniques under a static pressure of nitrogen unless otherwise stated. Liquids and solutions were transferred with syringes. Solvents were dried and purified following standard procedures. Technical grade solvents for extraction or chromatography (cyclohexane, ethyl acetate, and CH_2Cl_2) were distilled prior to use. $CDCl_3$ was stored over 4 Å molecular sieves. Toluene (HPLC grade), ethene-1,1-diyldibenzene, prop-1-en-2-ylbenzene, 2-methylnon-1-ene, cyclohexa-1,4-diene and 1,3,5-trimethylcyclohexa-1,4-diene were purchased from commercial suppliers and used without further purification. Imines[S1-S3] and alkenes[S4-S6] were prepared according to reported procedures. 1,5-Dimethylcyclohexa-1,4-diene was synthesized according to literature procedures.[S7] Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F254 glass plates by *Merck*. Flash column chromato-graphy was performed on silica gel 60 (40–63 µm, 230–400 mesh, ASTM) by *Merck* using the indicated solvents. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$ on *Bruker* AV500 or *Bruker* AV400 instruments. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CHCl_3$: δ = 7.26 ppm for ^1H NMR and $CDCl_3$: δ = 77.16 ppm for ^{13}C NMR). Data are reported as follows: chemical shift, multiplicity (br s = broad singlet, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, sept = septet, m = multiplet), coupling constants (Hz), and integration. Gas-liquid chromatography (GLC) was performed on an *Agilent Technologies* 7820A gas chromatograph equipped with a FS-SE-54 capillary column (30 m × 0.32 mm, 0.25 µm film thickness) by *CS-Chromatographie Service* using the following program: N_2 carrier gas, injection temperature 240 °C, detector temperature 300 °C, flow rate: 1.74 mL/min; temperature program: start temperature 40 °C, heating rate 10 °C/min, end temperature 280 °C for 10 min. Mass spectra (MS) were obtained from the Analytical Facility at the Institut für Chemie, Technische Universität Berlin.

2 Optimization of the Brønsted Acid-Catalyzed Transfer Hydrogenation of Imines





entry	surrogate	Brønsted acid	mol %	time (h)	conv[a] (%)
1	**1a**	$C_6F_5CO_2H$	10	12	—
2	**1a**	$Ph_2P(O)OH$	10	12	—
3	**1a**	CSA	10	12	—
4	**1a**	nicotinic acid	10	12	—
5	**1a**	TsOH	10	12	—
6	**1a**	TfOH	10	12	30
7	**1a**	Tf_2NH	10	12	50
8	**1b**	Tf_2NH	10	12	18
9	**1c**	Tf_2NH	10	12	—
10	**2**	Tf_2NH	10	12	quant.
11	**1a**	Tf_2NH	10	48	82
12	**1a**	Tf_2NH	15	48	98 (86)[b]
13	**1a**	Tf_2NH	20	48	quant.

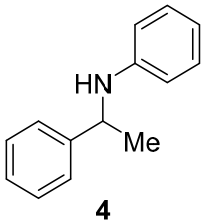
[a]Determined by GLC analysis with reference to starting material. [b]Isolated yield after flash chromatography on silica gel in parentheses.

3 General Procedure I for the Brønsted Acid-Catalyzed Transfer Hydrogenation of imines

An oven-dried Schlenk tube is charged with the imine (0.10 mmol) and diene **1a** (16.0 mg, 0.13 mmol, 1.30 equiv). Toluene (0.5 mL) is added to the mixture. A solution of Tf_2NH (0.1M in toluene, 150µL, 15.0 µmol, 15.0 mol %) is added to the mixture, and the Schlenk tube is sealed properly and transferred to a pre-heated oil bath at 125 °C (oil-bath temperature). After 48 h, the reaction mixture is cooled to room temperature and passed through a pad of Celite. The Schlenk tube is rinsed twice with dichloromethane, and the collected organic solvents are evaporated under reduced pressure, and the crude mixture is used to measure the conversion (w.r.t. starting material imine) by GLC analysis. The analytically pure amine is obtained by column chromatography on silica gel using *n*-pentane/diethyl ether mixtures as eluent.

4 Experimental Details for the Brønsted Acid-Catalyzed Transfer Hydrogenation of imines

4.1 *N*-(1-Phenylethyl)aniline (4)



4

$C_{14}H_{15}N$

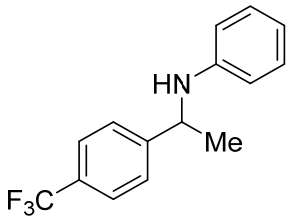
M = 197.28 g/mol

Prepared from (*E*)-*N*,1-diphenylethan-1-imine (**3**, 19.5 mg, 0.10 mmol, 1.0 equiv), **1a** (16.0 mg, 0.13 mmol, 1.3 equiv), and Tf_2NH (150µL, 15.0 µmol, 15.0 mol %) according to the General Procedure **I**. The reaction mixture was stirred for 48 h at 125 °C. The amine **4** (17.0 mg, 86%) was obtained as colorless oil.

GLC (SE-54): t_R = 17.00 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.55 (d, *J* = 6.7 Hz, 3H), 4.50 (q, *J* = 6.75 Hz, 1H), 6.55–6.57 (m, 2H), 6.66–6.70 (m, 1H), 7.08–7.12 (m, 2H), 7.21–7.25 (m, 1H), 7.30–7.34 (m, 2H), 7.36–7.39 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 24.7, 54.1, 114.0, 117.9, 126.0, 127.0, 128.7, 129.1, 144.6, 146.5 ppm.

4.2 *N*-(1-(4-(Trifluoromethyl)phenyl)ethyl)aniline (12)



12

$C_{15}H_{14}F_3N$

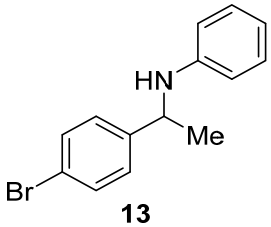
M = 265.28 g/mol

Prepared from (*E*)-*N*-phenyl-1-(4-(trifluoromethyl)phenyl)ethan-1-imine (**7**, 26.3 mg, 0.10 mmol, 1.0 equiv), **1a** (16.0 mg, 0.13 mmol, 1.3 equiv), and Tf_2NH (150µL, 15.0 µmol, 15.0 mol %) according to the General Procedure **I**. The reaction mixture was stirred for 48 h at 125 °C. The amine **12** (20.5 mg, 77%) was obtained as light yellow oil.

GLC (SE-54): t_R = 16.96 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.56 (d, *J* = 6.74 Hz, 3H), 4.98 (br s, 1H), 4.54 (q, *J* = 6.74 Hz, 1H), 6.53–6.55 (m, 2H), 6.70–6.74 (m, 1H), 7.10–7.14 (m, 2H), 7.50 (d, *J* = 8.12 Hz, 2H), 7.58 (d, *J* = 8.12 Hz, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 24.7, 54.0, 114.1, 118.5, 124.5 (q, *J* = 272 Hz), 125.7 (q, *J* = 3.8 Hz), 126.4, 129.2 (q, *J* = 32 Hz), 129.2, 146.0, 148.8 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ = –62.4 ppm.

4.3 *N*-(1-(4-Bromophenyl)ethyl)aniline (13)



13

$C_{14}H_{14}BrN$

M = 276.18 g/mol

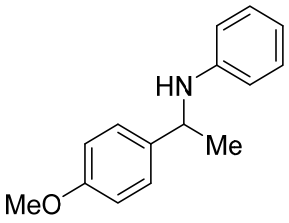
Prepared from (*E*)-1-(4-bromophenyl)-*N*-phenylethan-1-imine (**8**, 27.3 mg, 0.10 mmol, 1.0 equiv), **1a** (16.0 mg, 0.13 mmol, 1.3 equiv), and Tf_2NH (150µL, 15.0 µmol, 15.0 mol %) according to the General Procedure **I**. The reaction mixture was stirred for 48 h at 125 °C. The amine **13** (23.0 mg, 84%) was obtained as colorless oil.

GLC (SE-54): t_R = 20.54 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.52 (d, *J* = 6.8 Hz, 3H), 4.44 (q, *J* = 6.8 Hz, 1H), 6.53–6.55 (m, 2H), 6.70–6.73 (m, 1H), 7.09–7.13 (m, 2H), 7.24–7.27 (m, 2H), 7.41–7.45 (m, 2H) ppm. **^{13}C**

NMR (101 MHz, $CDCl_3$): δ = 24.6, 53.9, 114.2, 118.5, 120.8, 127.9, 129.2, 131.8, 143.6, 145.9 ppm.

4.4 *N*-(1-(4-methoxyphenyl)ethyl)aniline (14)



14

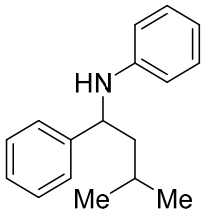
$C_{15}H_{17}NO$

M = 227.31 g/mol

Prepared from (*E*)-1-(4-methoxyphenyl)-N-phenylethan-1-imine (**9**, 22.5 mg, 0.10 mmol, 1.0 equiv), **1a** (16.0 mg, 0.13 mmol, 1.3 equiv), and Tf_2NH (150µL, 15.0 µmol, 15.0 mol %) according to the General Procedure **I**. The reaction mixture was stirred for 48 h at 125 °C. The NMR yield of amine **14** was (30%).

GLC (SE-54): t_R = 20.51 min.

4.5 *N*-(3-Methyl-1-phenylbutyl)aniline (15)



15

$C_{17}H_{21}N$

M = 239.36 g/mol

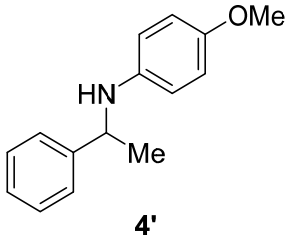
Prepared from (*E*)-3-methyl-N,1-diphenylbutan-1-imine (**10**, 23.7 mg, 0.10 mmol, 1.0 equiv), **1a** (16.0 mg, 0.13 mmol, 1.3 equiv), and Tf_2NH (150µL, 15.0 µmol, 15.0 mol %) according to the General Procedure **I**. The reaction mixture was stirred for 48 h at 125 °C. The amine **15** (19.0 mg, 81%) was obtained as colorless oil.

GLC (SE-54): t_R = 19.13 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (d, *J* = 6.25 Hz, 3H), 0.97 (d, *J* = 6.27 Hz, 3H), 1.62–1.66 (m, 2H); 1.73–1.79 (m, 1H); 4.37 (t, *J* = 7.0 Hz, 1H), 6.59 (d, *J* = 7.30 Hz, 2H), 6.68 (t, *J* = 7.28 Hz, 1H), 7.07–7.11 (m, 2H), 7.20–7.23 (m, 1H), 7.28–7.35 (m, 4H) ppm. **^{13}C NMR** (101 MHz,

$CDCl_3$): δ = 22.5, 22.8, 25.0, 47.9, 57.4, 114.1, 117.6, 126.6, 127.1, 128.6, 129.1, 138.4, 140.8 ppm.

4.6 4-Methoxy-*N*-(1-phenylethyl)aniline (4')



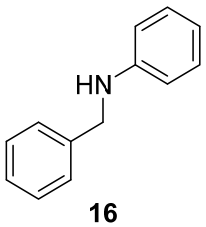
4'
$C_{15}H_{17}NO$
M = 227.31 g/mol

Prepared from (*E*)-*N*-(4-methoxyphenyl)-1-phenylethan-1-imine (**3'**, 22.5 mg, 0.10 mmol, 1.0 equiv), **1a** (16.0 mg, 0.13 mmol, 1.3 equiv), and Tf_2NH (150µL, 15.0 µmol, 15.0 mol %) according to the General Procedure **I**. The reaction mixture was stirred for 48 h at 125 °C. The amine **4'** (14.0 mg, 62%) was obtained as light orange oil.

GLC (SE-54): t_R = 19.75 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.56 (d, *J* = 6.74 Hz, 3H), 3.70 (s, 3H), 4.42 (q, *J* = 6.74 Hz, 1H), 6.57–6.59 (m, 2H), 6.67–6.70 (m, 2H), 7.21–7.25 (m, 1H), 7.29–7.32 (m, 2H), 7.36–7.38 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 24.2, 55.4, 55.7, 114.7, 116.4, 126.4, 127.2, 128.7, 139.4, 143.9, 153.1 ppm.

4.7 *N*-benzylaniline (16)



16
$C_{13}H_{13}N$
M = 183.25 g/mol

Prepared from (*E*)-*N*,1-diphenylmethanimine (**11**, 18.0 mg, 0.10 mmol, 1.0 equiv), **1a** (16.0 mg, 0.13 mmol, 1.3 equiv), and Tf_2NH (100µL, 10.0 µmol, 10.0 mol %) according to the General Procedure **I**. The reaction mixture was stirred for 12 h at 125 °C. The amine **16** (16.0 mg, 87%) was obtained as colorless oil.

GLC (SE-54): t_R = 17.21 min.

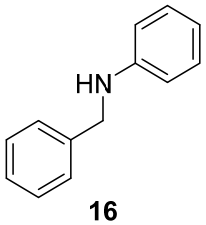
^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.34 (s, 2H), 6.67–6.69 (m, 2H), 6.74–6.78 (m, 1H), 7.17–7.21 (m, 2H), 7.29–7.40 (m, 5H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 48.7, 113.4, 118.1, 127.4, 127.7, 128.7, 129.3, 139.0, 147.6 ppm.

5 General Procedure II for the Brønsted Acid-Catalyzed Reductive Amination

An oven-dried Schlenk tube is charged with the aldehyde (0.10 mmol), the aniline (0.10 mmol), and diene **1a** (16.0 mg, 0.13 mmol, 1.30 equiv). Toluene (0.5 mL) is added to the mixture. A solution of Tf_2NH (0.1M in toluene, 100µL, 10.0 µmol, 10.0 mol %) is added to the mixture, and the Schlenk tube is sealed properly and transferred to a pre-heated oil bath at 125 °C (oil-bath temperature). After 12 h, the reaction mixture is cooled to room temperature and passed through a pad of Celite. The Schlenk tube is rinsed twice with dichloromethane, and the collected organic solvents are evaporated under reduced pressure, and the crude mixture is used to measure the conversion (w.r.t. starting material imine) by GLC analysis. The analytically pure amine is obtained by column chromatography on silica gel using *n*-pentane/diethyl ether mixtures as eluent.

6 Experimental Details for the Brønsted Acid-Catalyzed Reductive Amination

6.1 *N*-benzylaniline (16)



16

$C_{13}H_{13}N$

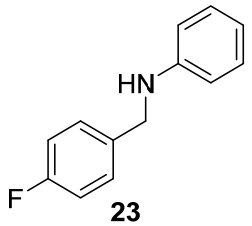
M = 183.25 g/mol

Prepared from benzaldehyde (**17**, 10.6 mg, 0.10 mmol, 1.0 equiv), aniline (**20**, 9.3 mg, 0.10 mmol, 1.0 equiv), **1a** (16.0 mg, 0.13 mmol, 1.3 equiv), and Tf_2NH (100µL, 10.0 µmol, 10.0 mol %) according to the General Procedure **II**. The reaction mixture was stirred for 12 h at 125 °C. The amine **16** (16.0 mg, 86%) was obtained as colorless oil.

GLC (SE-54): t_R = 17.21 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.34 (s, 2H), 6.67–6.69 (m, 2H), 6.74–6.78 (m, 1H), 7.17–7.21 (m, 2H), 7.29–7.40 (m, 5H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 48.7, 113.4, 118.1, 127.4, 127.7, 128.7, 129.3, 139.0, 147.6 ppm.

6.2 *N*-(4-fluorobenzyl)aniline (23)



23

$C_{13}H_{12}N$

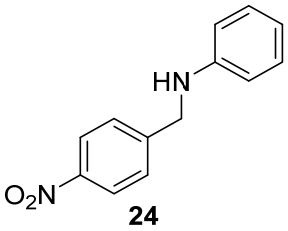
M = 201.24 g/mol

Prepared from 4-fluorobenzaldehyde (**18**, 12.4 mg, 0.10 mmol, 1.0 equiv), aniline (**20**, 9.3 mg, 0.10 mmol, 1.0 equiv), **1a** (16.0 mg, 0.13 mmol, 1.3 equiv), and Tf_2NH (100µL, 10.0 µmol, 10.0 mol %) according to the General Procedure **II**. The reaction mixture was stirred for 12 h at 125 °C. The amine **23** (17.0 mg, 84%) was obtained as colorless oil.

GLC (SE-54): t_R = 17.26 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.31 (s, 2H), 6.74–6.76 (m, 2H), 6.82–6.86 (m, 1H), 6.98–7.03 (m, 2H), 7.18–7.23 (m, 2H), 7.32–7.36 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 49.0, 114.8, 115.5 (d, *J* = 21.7 Hz), 119.8, 129.4, 129.7 (d, *J* = 7.97 Hz), 133.4 (d, *J* = 3.1 Hz), 145.6, 162.3 (d, *J* = 244.1 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ = -117.2

6.3 *N*-(4-nitrobenzyl)aniline (24)



24

$C_{13}H_{12}N_2O_2$

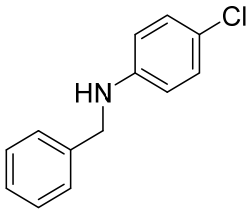
M = 228.25 g/mol

Prepared from 4-nitrobenzaldehyde (**19**, 15.1 mg, 0.10 mmol, 1.0 equiv), aniline (**20**, 9.3 mg, 0.10 mmol, 1.0 equiv), **1a** (16.0 mg, 0.13 mmol, 1.3 equiv), and Tf_2NH (100µL, 10.0 µmol, 10.0 mol %) according to the General Procedure **II**. The reaction mixture was stirred for 12 h at 125 °C. The amine **24** (21.0 mg, 92%) was obtained as colorless oil.

GLC (SE-54): t_R = 22.72 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.48 (s, 2H), 5.35 (bs, 1H), 6.65 (d, *J* = 7.80 Hz, 2H), 6.80 (t, *J* = 7.35 Hz, 1H), 7.19 (t, *J* = 7.93 Hz, 2H), 7.54 (d, *J* = 8.60 Hz, 2H), 8.18 (d, *J* = 8.60 Hz, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 48.2, 113.8, 119.2, 123.9, 128.1, 129.5, 146.3, 146.6, 147.3 ppm.

6.4 *N*-benzyl-4-chloroaniline (25)



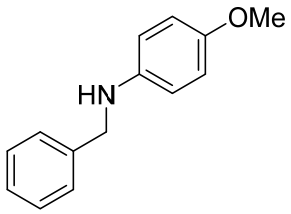
25
$C_{13}H_{12}ClN$
M = 217.70 g/mol

Prepared from benzaldehyde (**17**, 10.6 mg, 0.10 mmol, 1.0 equiv), 4-chloroaniline (**21**, 12.8 mg, 0.10 mmol, 1.0 equiv), **1a** (16.0 mg, 0.13 mmol, 1.3 equiv), and Tf_2NH (100µL, 10.0 µmol, 10.0 mol %) according to the General Procedure **II**. The reaction mixture was stirred for 12 h at 125 °C. The amine **25** (19.0 mg, 88%) was obtained as colorless oil.

GLC (SE-54): t_R = 19.94 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.31 (s, 2H), 4.64 (bs, 1H), 6.56-6.60 (m, 2H), 7.10-7.12 (m, 2H), 7.28-7.36 (m, 5H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 48.7, 114.4, 122.6, 127.5, 127.6, 128.7, 129.1, 138.6, 146.2 ppm.

6.5 *N*-benzyl-4-methoxyaniline (26)



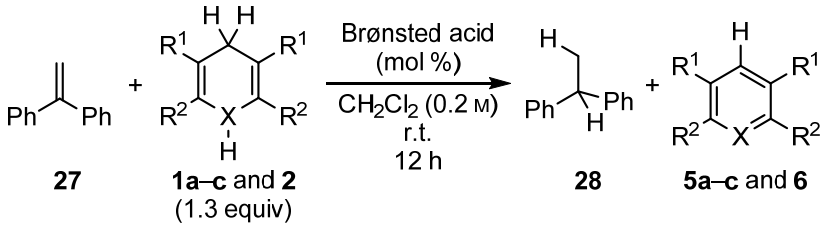
26
$C_{13}H_{15}NO$
M = 213.28 g/mol

Prepared from benzaldehyde (**17**, 10.6 mg, 0.10 mmol, 1.0 equiv), 4-methoxyaniline (**22**, 12.3 mg, 0.10 mmol, 1.0 equiv), **1a** (16.0 mg, 0.13 mmol, 1.3 equiv), and Tf_2NH (100µL, 10.0 µmol, 10.0 mol %) according to the General Procedure **II**. The reaction mixture was stirred for 12 h at 125 °C. The amine **26** (18.0 mg, 85%) was obtained as colorless oil.

GLC (SE-54): t_R = 20.00 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.75 (s, 3H), 4.29 (s, 2H), 6.63-6.67 (m, 2H), 6.77-6.81 (m, 2H), 7.25-7.30 (m, 1H), 7.33-7.39 (m, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 49.6, 55.8, 114.7, 114.9, 127.3, 127.8, 128.6, 139.2, 141.6, 152.6 ppm.

7 Optimization of the Brønsted Acid-Catalyzed Transfer Hydrogenation of Alkenes



27 **1a–c** and **2** (1.3 equiv) **28** **5a–c** and **6**

entry	surrogate	Brønsted acid	mol %	conv[a] (%)
1	**1a**	$C_6F_5CO_2H$	10	—
2	**1a**	$Ph_2P(O)OH$	10	—
3	**1a**	CSA	10	—
4	**1a**	nicotinic acid	10	—
5	**1a**	TsOH	10	93
6	**1a**	TfOH	10	92
7	**1a**	Tf_2NH	10	quant.
8	**1b**	Tf_2NH	10	97
9	**1c**	Tf_2NH	10	quant.
10	**2**	Tf_2NH	10	—
11	**1a**	Tf_2NH	5.0	quant. (99)[b]

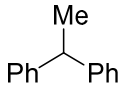
[a]Determined by GLC analysis with reference to starting material. [b]Isolated yield after flash chromatography on silica gel in parentheses.

8 General Procedure III for the Brønsted Acid-Catalyzed Transfer Hydrogenation of Alkenes

An oven-dried Schlenk tube is charged with the alkene (0.10 mmol) and diene **1a** (16.0 mg, 0.13 mmol, 1.30 equiv). Dichloromethane (0.5 mL) is added to the mixture. A solution of Tf_2NH (0.1M in dichloromethane, 50µL, 5.0 µmol, 5.0 mol %) is added to the mixture, and the Schlenk tube is sealed properly and stirred at room temperature. After 12 h, the reaction mixture is passed through a pad of silica. The Schlenk tube is rinsed twice with dichloromethane, and the collected organic solvents are evaporated under reduced pressure, and the crude mixture is used to measure the conversion (w.r.t. starting material imine) by GLC analysis. The analytically pure amine is obtained by column chromatography on silica gel using *n*-pentane as eluent.

9 Experimental Details for the Brønsted Acid-Catalyzed Transfer Hydrogenation of alkenes

9.1 Ethane-1,1-diyldibenzene (28)



28

$C_{14}H_{14}$

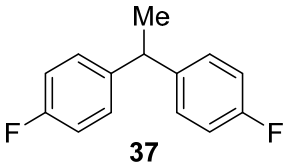
M = 182.27 g/mol

Prepared from ethene-1,1-diyldibenzene (**27**, 18.0 mg, 0.10 mmol, 1.0 equiv), **1a** (16.0 mg, 0.13 mmol, 1.3 equiv), and Tf_2NH (50µL, 5.0 µmol, 5.0 mol %) according to the General Procedure **III**. The reaction mixture was stirred at room temperature. Alkane **28** (18.0 mg, 99%) was obtained as a colorless oil.

GLC (SE-54): t_R = 14.34 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.65 (d, *J* = 7.24 Hz, 3H), 4.17 (q, *J* = 7.23 Hz, 1H), 7.17–7.25 (m, 6H); 7.27–7.231 (m, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 21.9, 44.8, 126.0, 127.7, 128.4, 146.4 ppm.

9.2 4,4'-(Ethane-1,1-diyl)bis(fluorobenzene) (37)



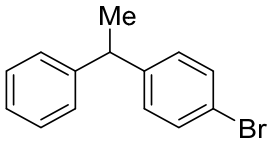
37

$C_{14}H_{12}F_2$
M = 218.25 g/mol

Prepared from 4,4'-(ethene-1,1-diyl)bis(fluorobenzene) (**29**, 21.6 mg, 0.10 mmol, 1.0 equiv), **1a** (16 mg, 0.13 mmol, 1.3 equiv), and Tf_2NH (50µL, 5.0 µmol, 5.0 mol %) according to the General Procedure **III**. The reaction mixture was stirred at room temperature. Alkane **37** (21.0 mg, 96%) was obtained as a colorless oil.

GLC (SE-54): t_R = 14.50 min.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.61 (d, *J* = 7.3 Hz, 3H), 4.13 (q, *J* = 7.3 Hz, 1H), 6.95–7.01 (m, 4H), 7.13–7.18 (m, 4H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 21.1, 42.3, 114.1 (d, *J* = 21.1 Hz), 127.9 (d, *J* = 7.55 Hz), 140.9 (d, *J* = 3.1 Hz), 160.3 (d, *J* = 244.1 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ = -117.2

9.3 1-Bromo-4-(1-phenylethyl)benzene (38)



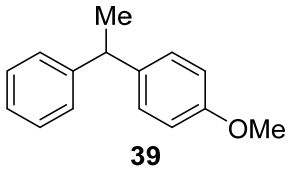
38

$C_{14}H_{13}Br$
M = 261.16 g/mol

Prepared from 1-bromo-4-(1-phenylvinyl)benzene (**30**, 26.0 mg, 0.10 mmol, 1.0 equiv), **1a** (16 mg, 0.13 mmol, 1.3 equiv), and Tf_2NH (50µL, 5.0 µmol, 5.0 mol %) according to the General Procedure **III**. The reaction mixture was stirred at room temperature. Alkane **38** (26.0 mg, 99%) was obtained as a colorless oil.

GLC (SE-54): t_R = 18.18 min.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.63 (d, *J* = 7.2 Hz, 3H), 4.12 (q, *J* = 7.2 Hz, 1H), 7.09–7.12 (m, 2H), 7.19–7.23 (m, 3H), 7.28–7.33 (m, 2H), 7.40–7.43 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 21.8, 44.3, 119.9, 126.3, 127.6, 128.5, 129.5, 131.5, 145.4, 145.7 ppm.

9.4 1-Methoxy-4-(1-phenylethyl)benzene (39)



39

$C_{15}H_{16}O$

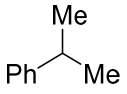
M = 212.29 g/mol

Prepared from 1-methoxy-4-(1-phenylvinyl)benzene (**31**, 21.0 mg, 0.10 mmol, 1.0 equiv), **1a** (16 mg, 0.13 mmol, 1.3 equiv), and Tf_2NH (50µL, 5.0 µmol, 5.0 mol %) according to the General Procedure **III**. The reaction mixture was stirred at room temperature. Alkane **39** (15.0 mg, 71%) was obtained as a colorless oil.

GLC (SE-54): t_R = 17.63 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.64 (d, *J* = 7.3 Hz, 3H), 3.80 (s, 3H), 4.13 (q, *J* = 7.3 Hz, 1H), 6.84–6.87 (m, 2H), 7.15–7.24 (m, 5H) 7.28–7.32 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 22.1, 44.0, 55.3, 113.8, 126.0, 127.6, 128.4, 128.6, 138.6, 146.8, 157.9 ppm.

9.5 Cumene (40)



40

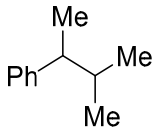
C_9H_{12}

M = 120.20 g/mol

Prepared from prop-1-en-2-ylbenzene (**32**, 11.8 mg, 0.10 mmol, 1.0 equiv), **1a** (16.0 mg, 0.13 mmol, 1.3 equiv), and Tf_2NH (50µL, 5.0 µmol, 5.0 mol %) according to the General Procedure **III**. The reaction mixture was stirred at room temperature. The NMR yield of alkane **40** was (41%). The crude NMR was compared with the reported one.[S8]

GLC (SE-54): t_R = 5.67 min.

9.6 (3-Methylbutan-2-yl)benzene (41)



41

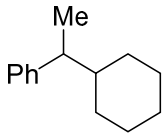
$C_{11}H_{16}$

M = 148.25 g/mol

Prepared from (3-methylbut-1-en-2-yl)benzene (**33**, 14.6 mg, 0.10 mmol, 1.0 equiv), **1a** (16.0 mg, 0.13 mmol, 1.3 equiv), and Tf_2NH (50µL, 5.0 µmol, 5.0 mol %) according to the General Procedure **III**. The reaction mixture was stirred at room temperature. The NMR yield of alkane **41** was (99%). The crude NMR was compared with the reported one.[S9]

GLC (SE-54): t_R = 8.26 min.

9.7 (1-Cyclohexylethyl)benzene (42)



42

$C_{14}H_{20}$

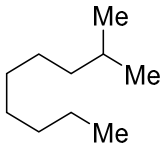
M = 188.31 g/mol

Prepared from (1-cyclohexylvinyl)benzene (**34**, 18.5 mg, 0.15 mmol, 1.0 equiv), **1a** (16.0 mg, 0.13 mmol, 1.3 equiv), and Tf_2NH (50µL, 5.0 µmol, 5.0 mol %) according to the General Procedure **III**. The reaction mixture was stirred at room temperature. Alkane **42** (18.5 mg, 99%) was obtained as a colorless oil.

GLC (SE-54): t_R = 14.01 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.77–0.85 (m, 2H), 0.91–0.94 (m, 1H), 1.06–1.11 (m, 2H), 1.21 (d, *J* = 7.26 Hz, 3H), 1.34–1.44 (m, 2H), 1.59–1.61 (m, 2H), 1.71–1.75 (m, 1H), 1.85–1.88 (m, 1H), 2.42 (quin, *J* = 7.26 Hz, 1H), 7.11–7.17 (m, 3H), 7.24–7.28 (m, 2H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 18.9, 26.6, 26.6, 30.7, 31.5, 44.2, 46.0, 125.7, 127.7, 128.0, 147.2 ppm.

9.8 2-Methylnonane (43)



43

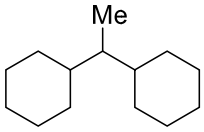
$C_{10}H_{22}$

M = 142.29 g/mol

Prepared from 2-methylnon-1-ene (**35**, 14.0 mg, 0.10 mmol, 1.0 equiv), **1a** (16.0 mg, 0.13 mmol, 1.3 equiv), and Tf_2NH (50µL, 5.0 µmol, 5.0 mol %) according to the General Procedure **III**. The reaction mixture was stirred at room temperature. The NMR yield of alkane **43** was (57%). The crude NMR was compared with the reported one.[S10]

GLC (SE-54): t_R = 6.26 min.

9.9 Ethane-1,1-diyldicyclohexane (44)



44

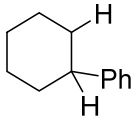
$C_{14}H_{26}$

M = 194.36 g/mol

Prepared from ethene-1,1-diyldicyclohexane (**36**, 19.0 mg, 0.10 mmol, 1.0 equiv), **1a** (16.0 mg, 0.13 mmol, 1.3 equiv), and Tf_2NH (50µL, 5.0 µmol, 5.0 mol %) according to the General Procedure **III**. The reaction mixture was stirred at room temperature. The NMR yield of alkane **44** was (96%). The crude NMR was compared with the reported one.[S11]

GLC (SE-54): t_R = 14.34 min.

9.10 Cyclohexylbenzene (46)



46

$C_{12}H_{16}$

M = 160.26 g/mol

Prepared from 2,3,4,5-tetrahydro-1,1'-biphenyl (**45**, 15.8 mg, 0.10 mmol, 1.0 equiv), **1a** (16.0 mg, 0.13 mmol, 1.3 equiv), and Tf_2NH (50µL, 5.0 µmol, 5.0 mol %) according to the General Procedure **II**. The reaction mixture was stirred at room temperature. The NMR yield of alkane **46** was (96%). The crude NMR was compared with the reported one.[S11]

GLC (SE-54): t_R = 11.92 min.

10 References

[S1] D. J. Vyas, R. Fröhlich, M. Oestreich, *Org. Lett.* **2011**, *13*, 2094–2097.

[S2] J. Hermeke, M. Mewald, M. Oestreich, *J. Am. Chem. Soc.* **2013**, *135*, 17537–17546.

[S3] J. Hermeke, H. F. T. Klare, M. Oestreich, *Chem. Eur. J.* **2014**, *20*, 9250–9254 and references cited therein.

[S4] W.-B. Zhang, B. Sun, H. Li, X. Ren, J. Janosk, S. Sahoo, D. E. Dabney, C. Wesdemiotis, R. P. Quirk, S. Z. D. Cheng, *Macromolecules* **2009**, *42*, 7258–7262.

[S5] S. Monfette, Z. R. Turner, S. P. Semproni, P. J. Chirik, *J. Am. Chem. Soc.* **2012**, *134*, 4561–4564.

[S6] T. W. Liwosz, S. R. Chemler, *Chem. Eur. J.* **2013**, *19*, 12771–12777.

[S7] I. Gbara-Haj-Yahia, G. Zvilichovsky, N. Seri, *J. Org. Chem.* **2004**, *69*, 4135–4139.

[S8] M. Pérez, C. B. Caputo, R. Dobrovetsky, D. W. Stephan, *Proc. Natl. Acad. Sci. USA* **2014**, *111*, 10917–10921.

[S9] V. Jurčík, S. P. Nolan, C. S.J. Cazin, *Chem. Eur. J.* **2009**, *15*, 2509–2511.

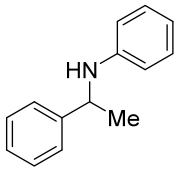
[S10] A.G. Martíneza, J.O. Barcinaa, B.R. Díeza, L.R. Subramanian, *Tetrahedron* **1994**, *50*, 13231-13238.

[S11] H.-S. Dang, B. P. Roberts, *J. Chem. Soc., Perkin Trans. 1* **2002**, 1161-1170.

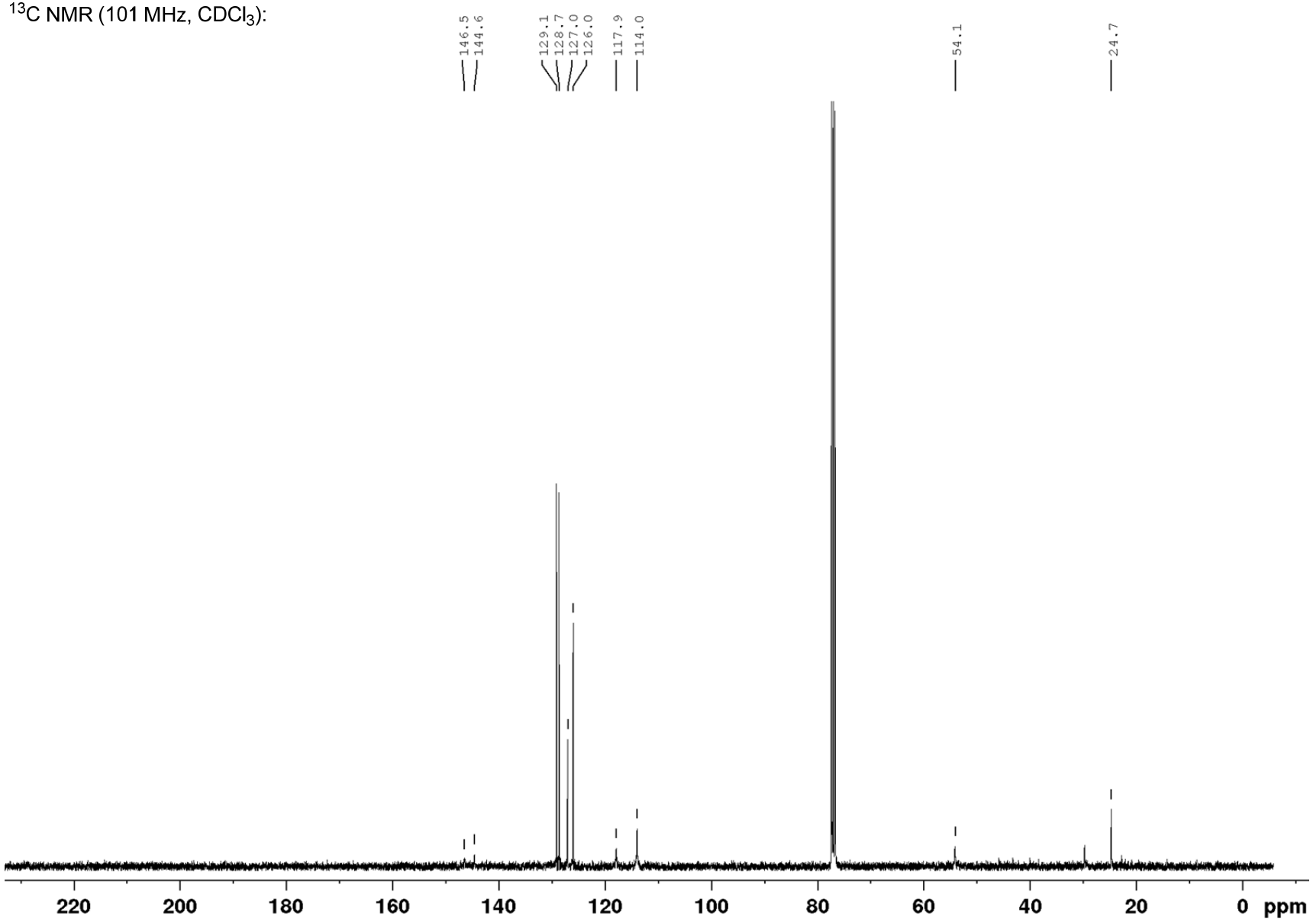
11 NMR Spectra

***N*-(1-Phenylethyl)aniline (4)**

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

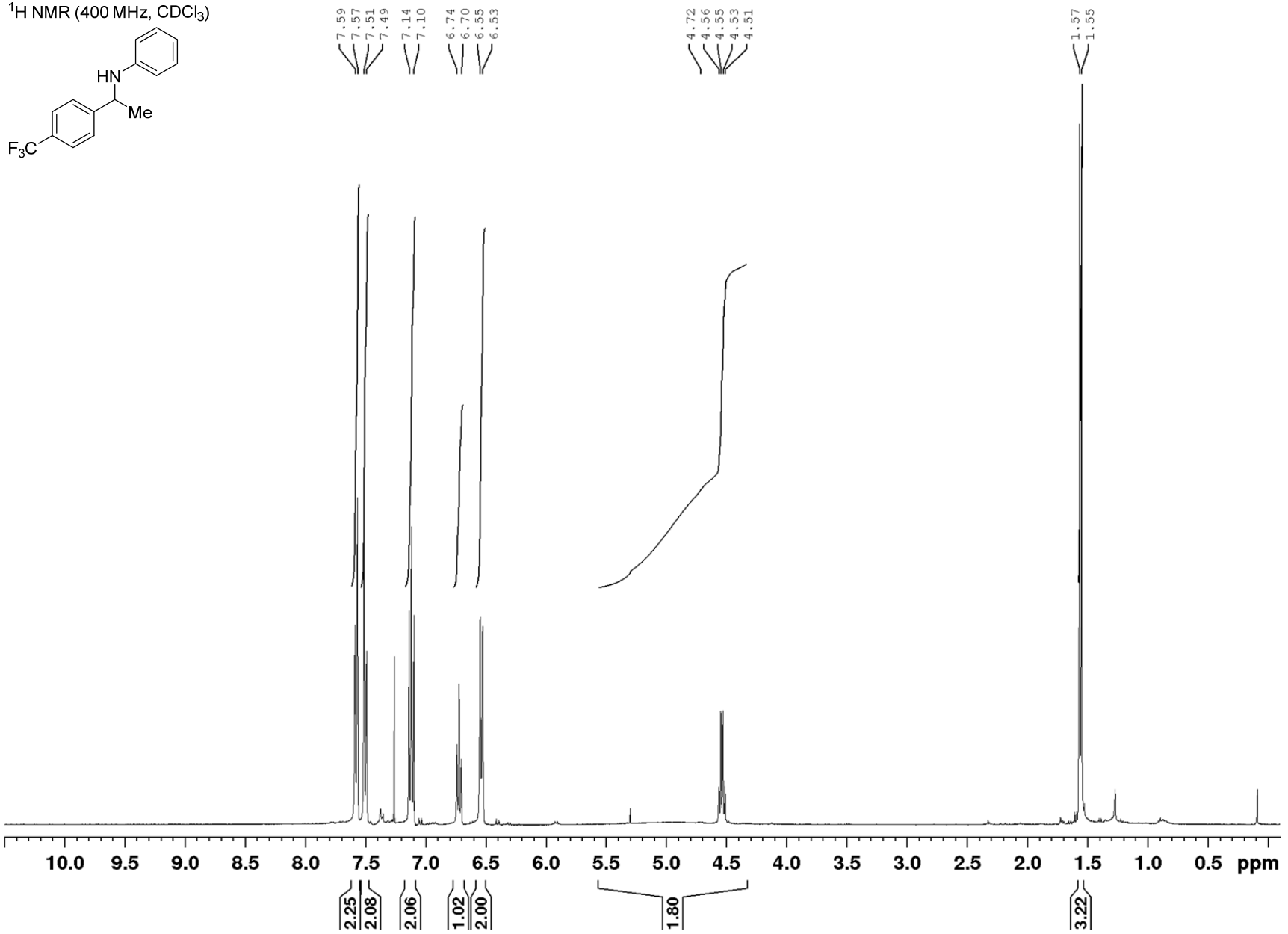


^{13}C NMR (101 MHz, $CDCl_3$):

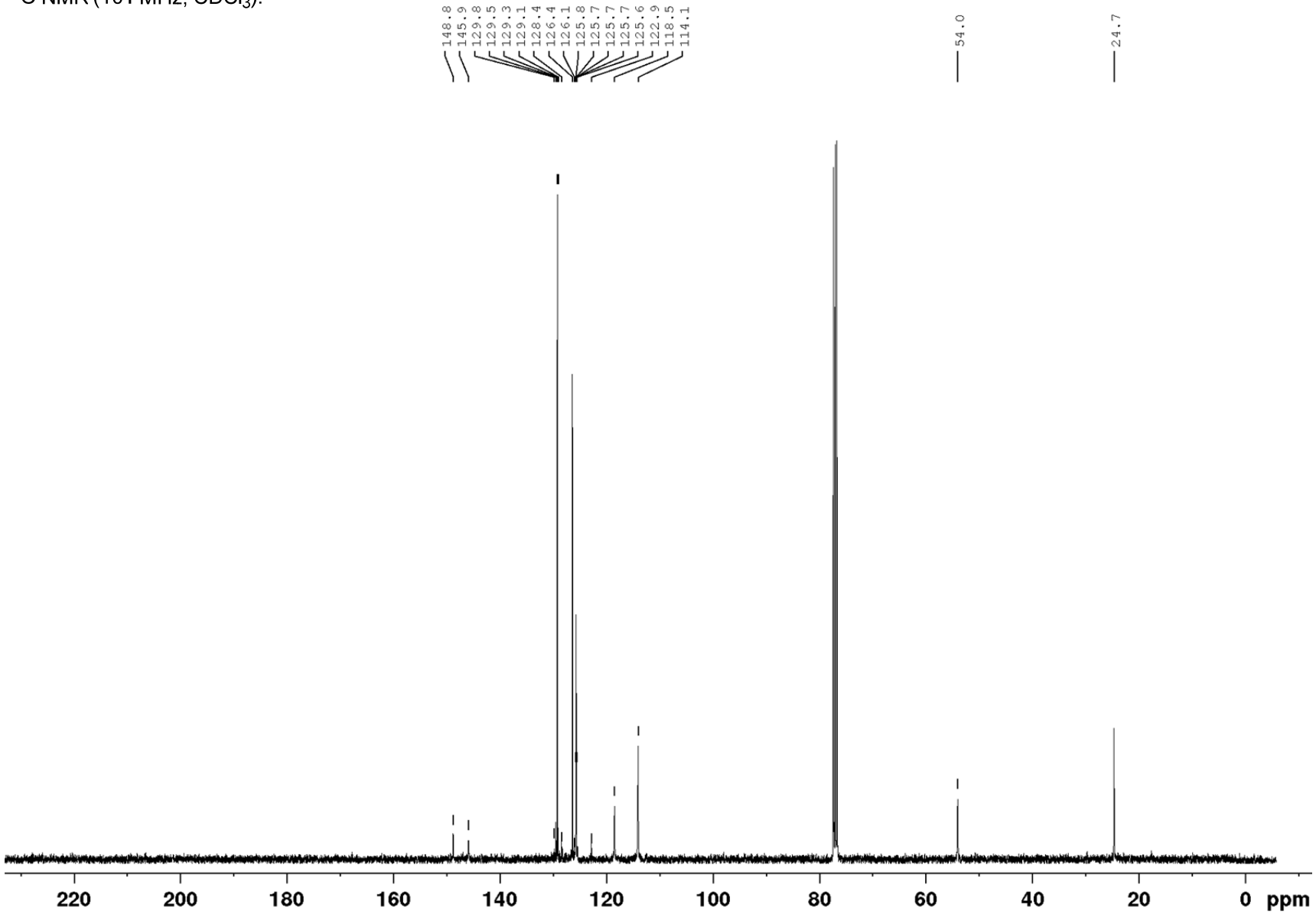


***N*-(1-(4-(Trifluoromethyl)phenyl)ethyl)aniline (12)**

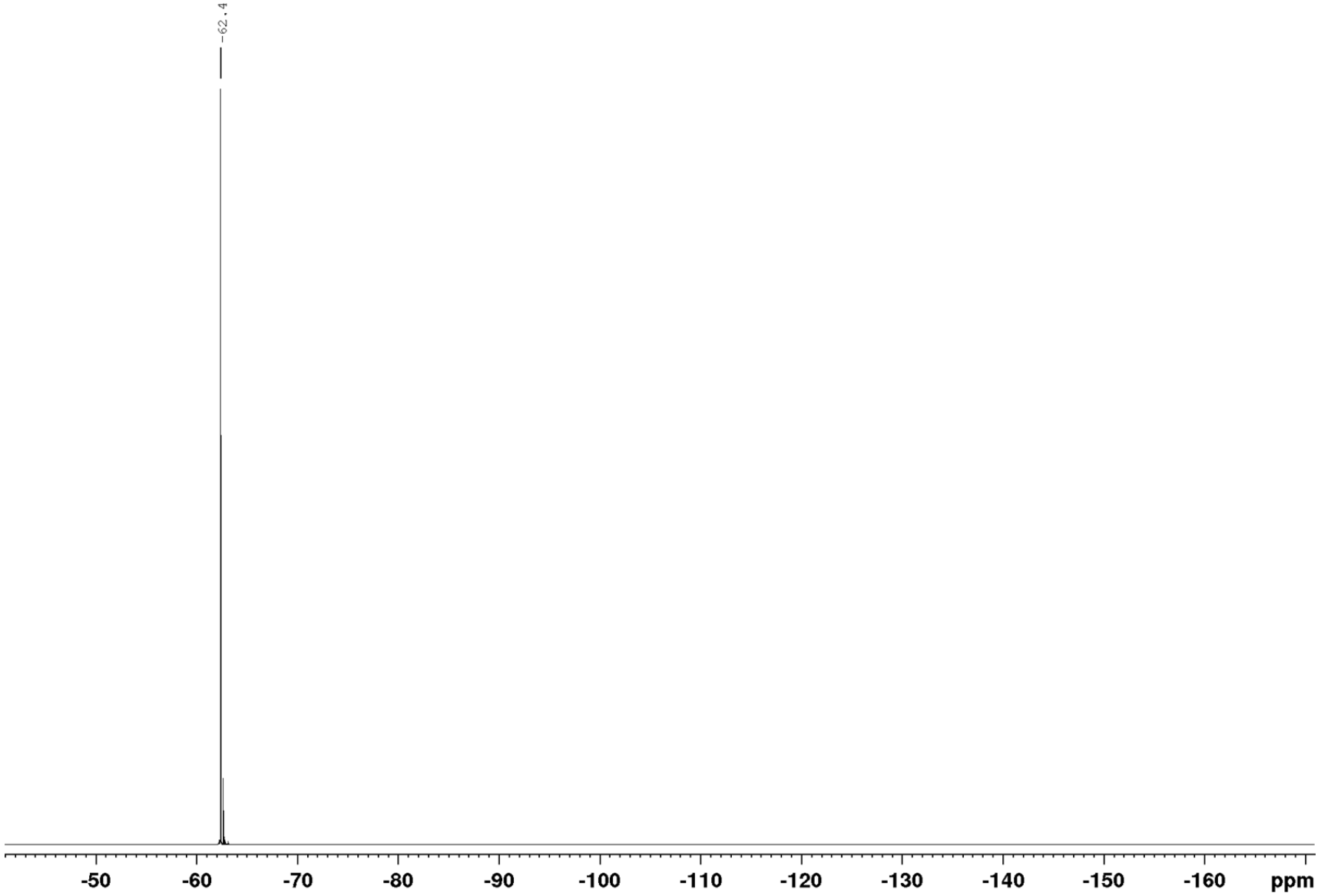
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$):

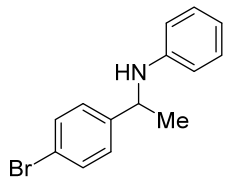


^{19}F NMR (471 MHz, $CDCl_3$):

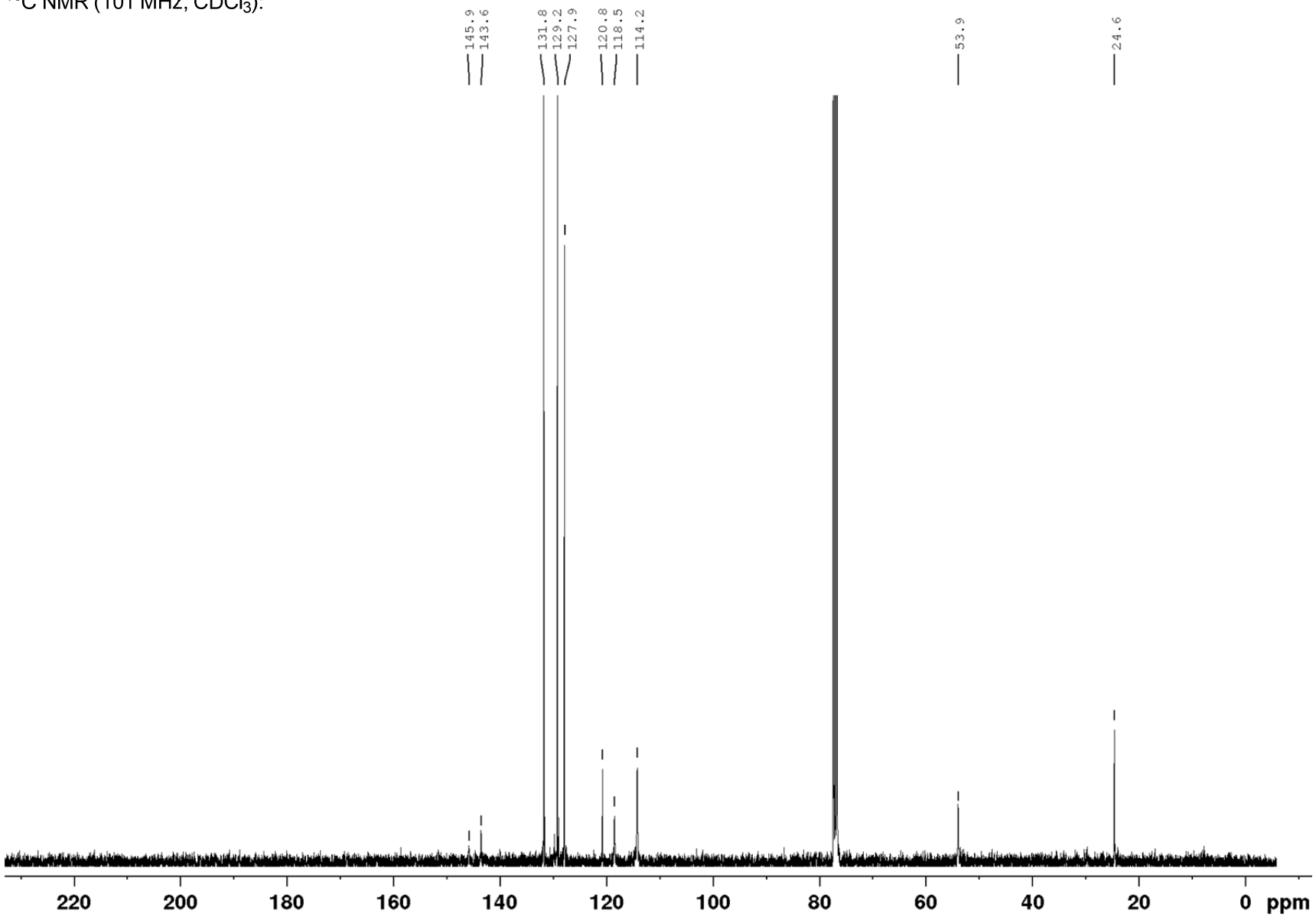


***N*-(1-(4-Bromophenyl)ethyl)aniline (13)**

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

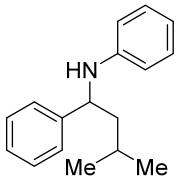


^{13}C NMR (101 MHz, $CDCl_3$):

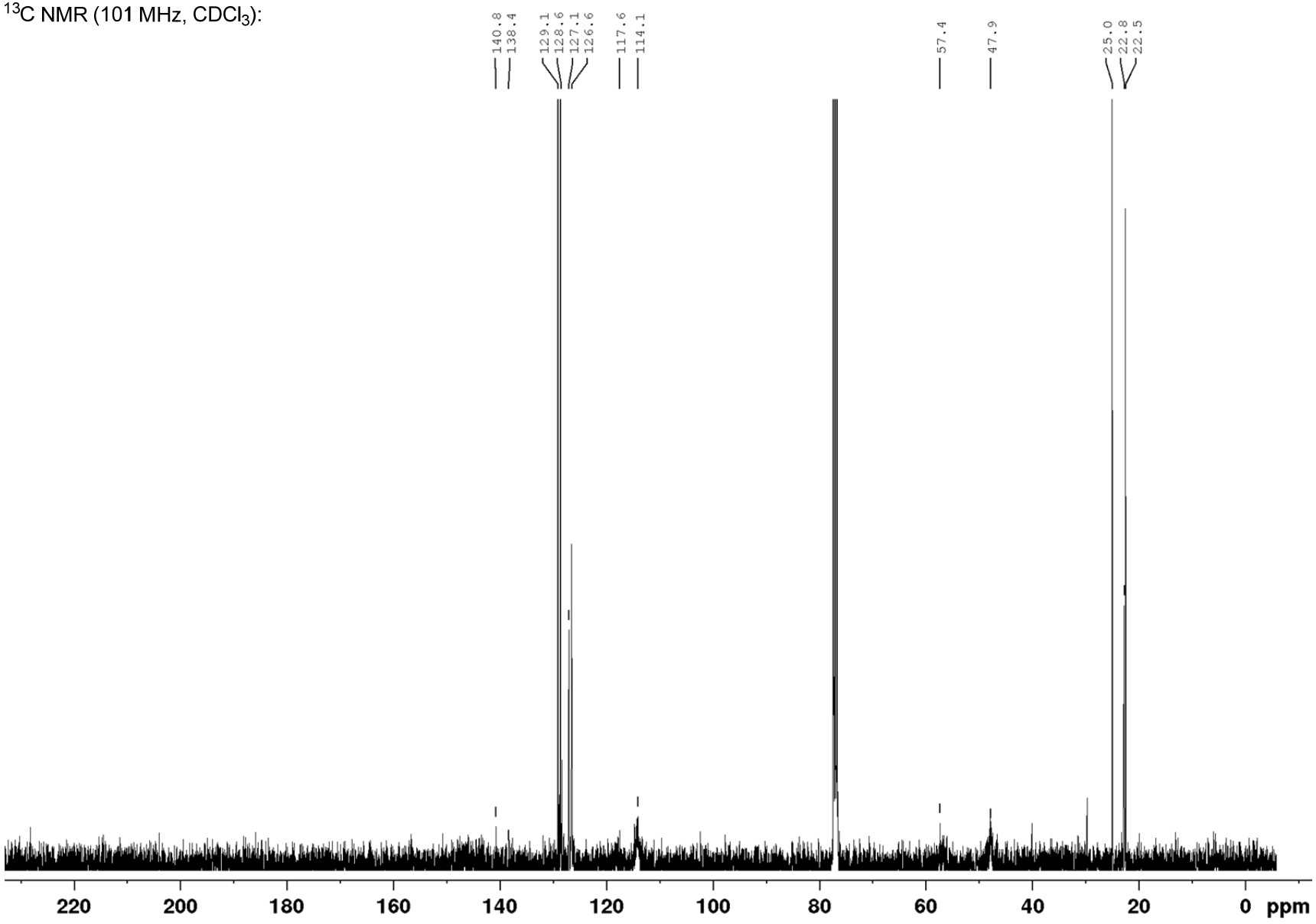


***N*-(3-Methyl-1-phenylbutyl)aniline (15)**

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

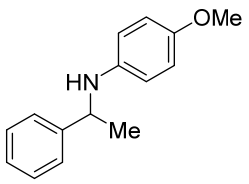


^{13}C NMR (101 MHz, $CDCl_3$):

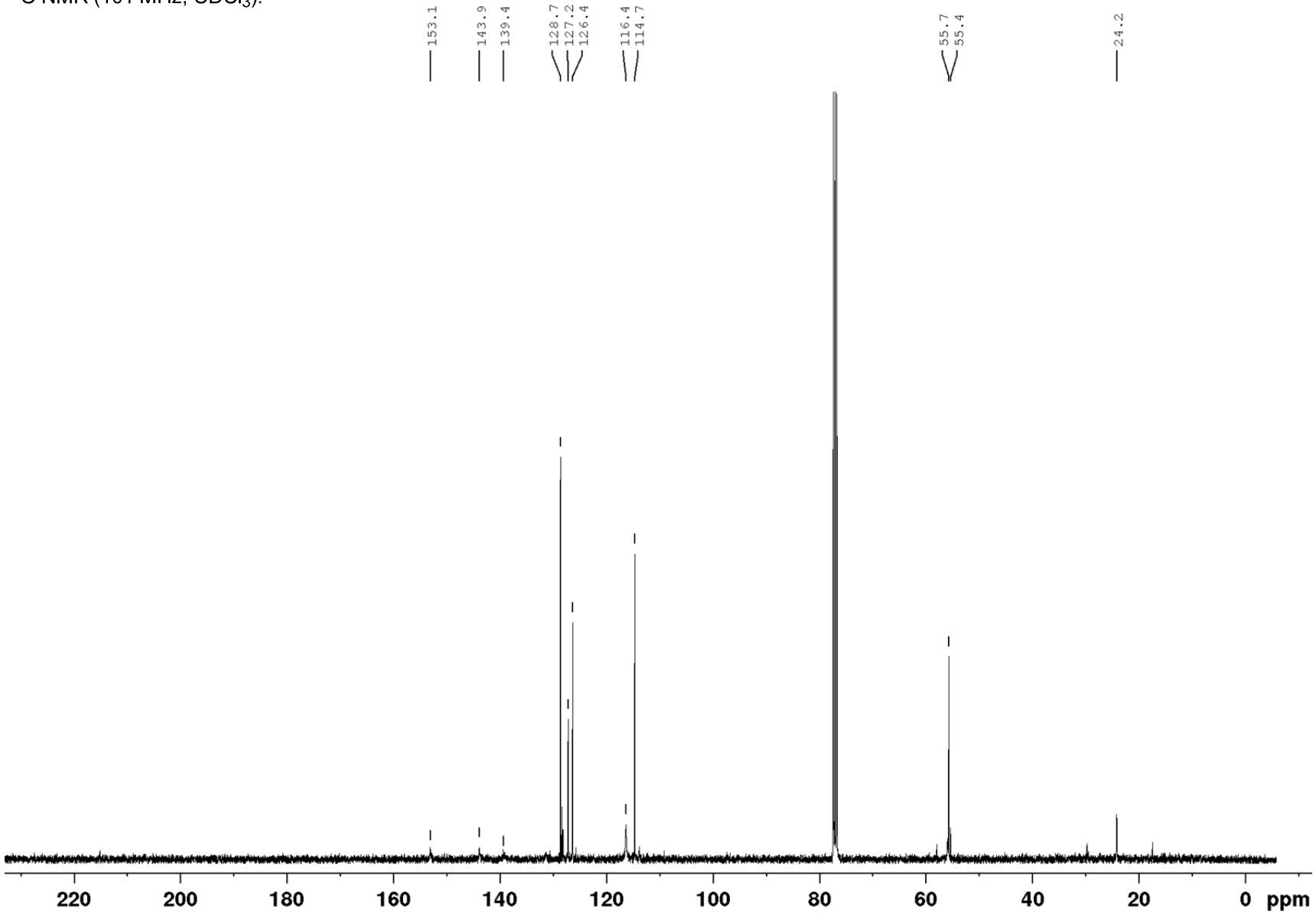


4-Methoxy-*N*-(1-phenylethyl)aniline (4')

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

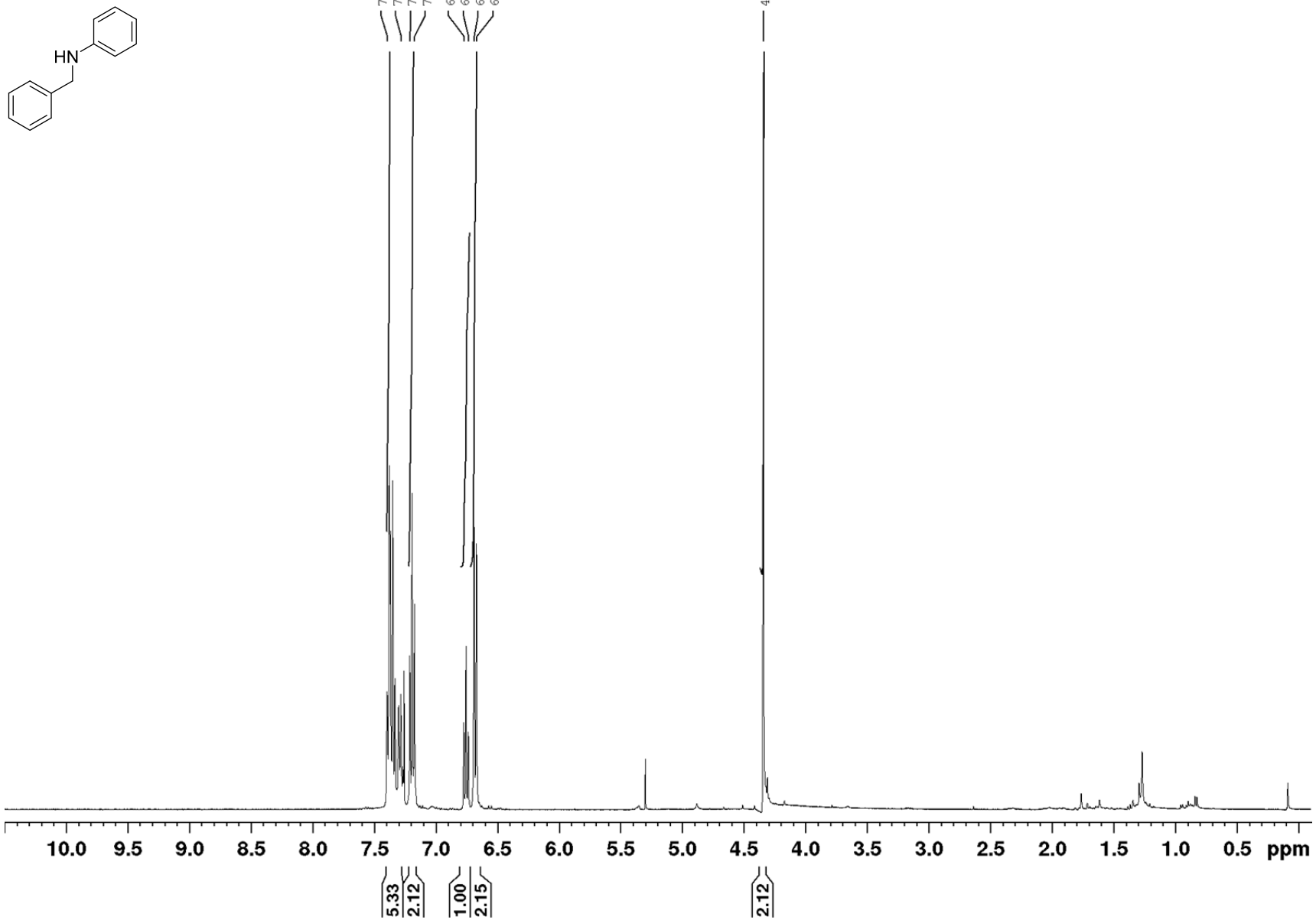


^{13}C NMR (101 MHz, $CDCl_3$):

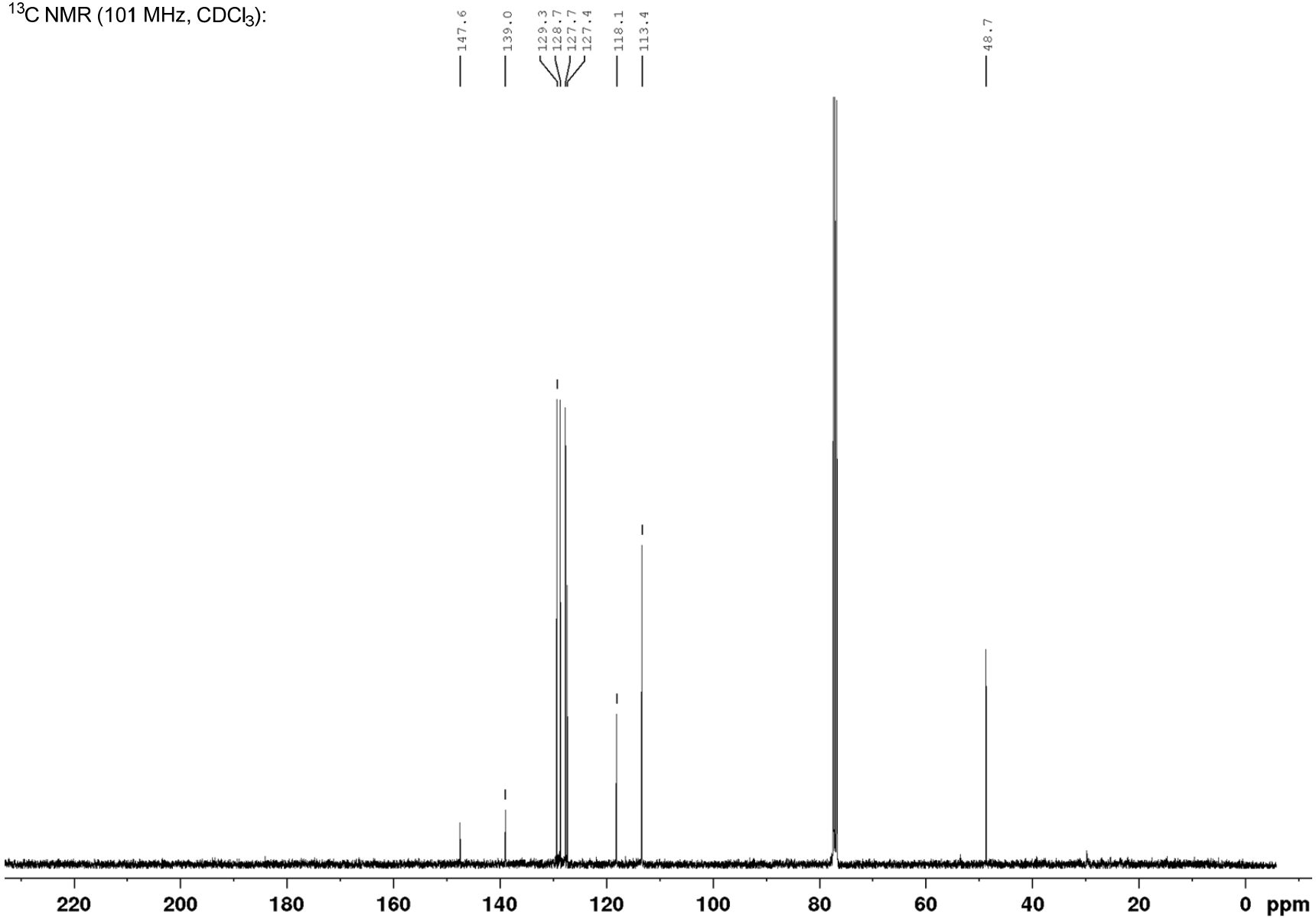


N-benzylaniline (16)

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

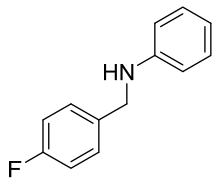


^{13}C NMR (101 MHz, $CDCl_3$):

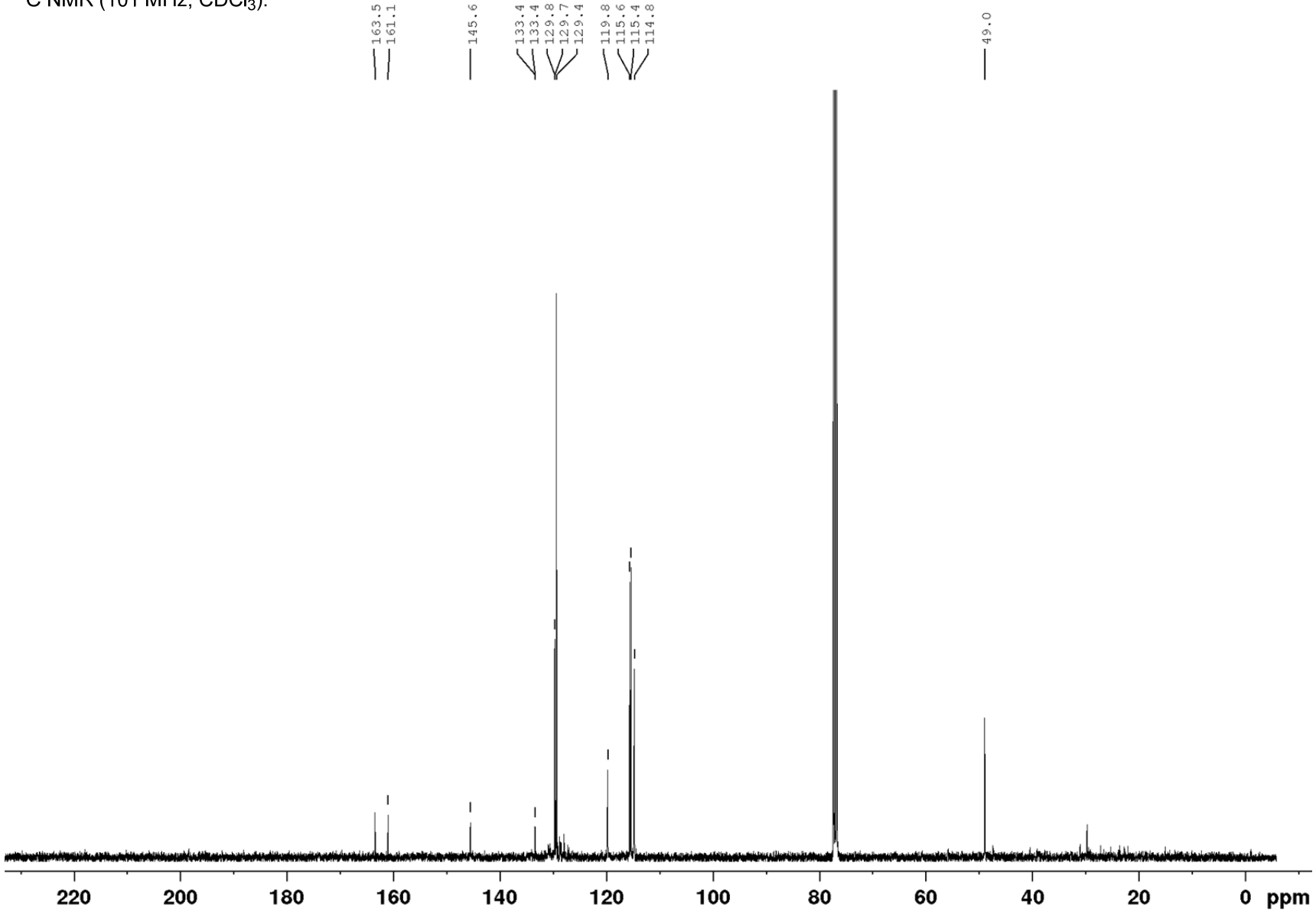


***N*-(4-fluorobenzyl)aniline (23)**

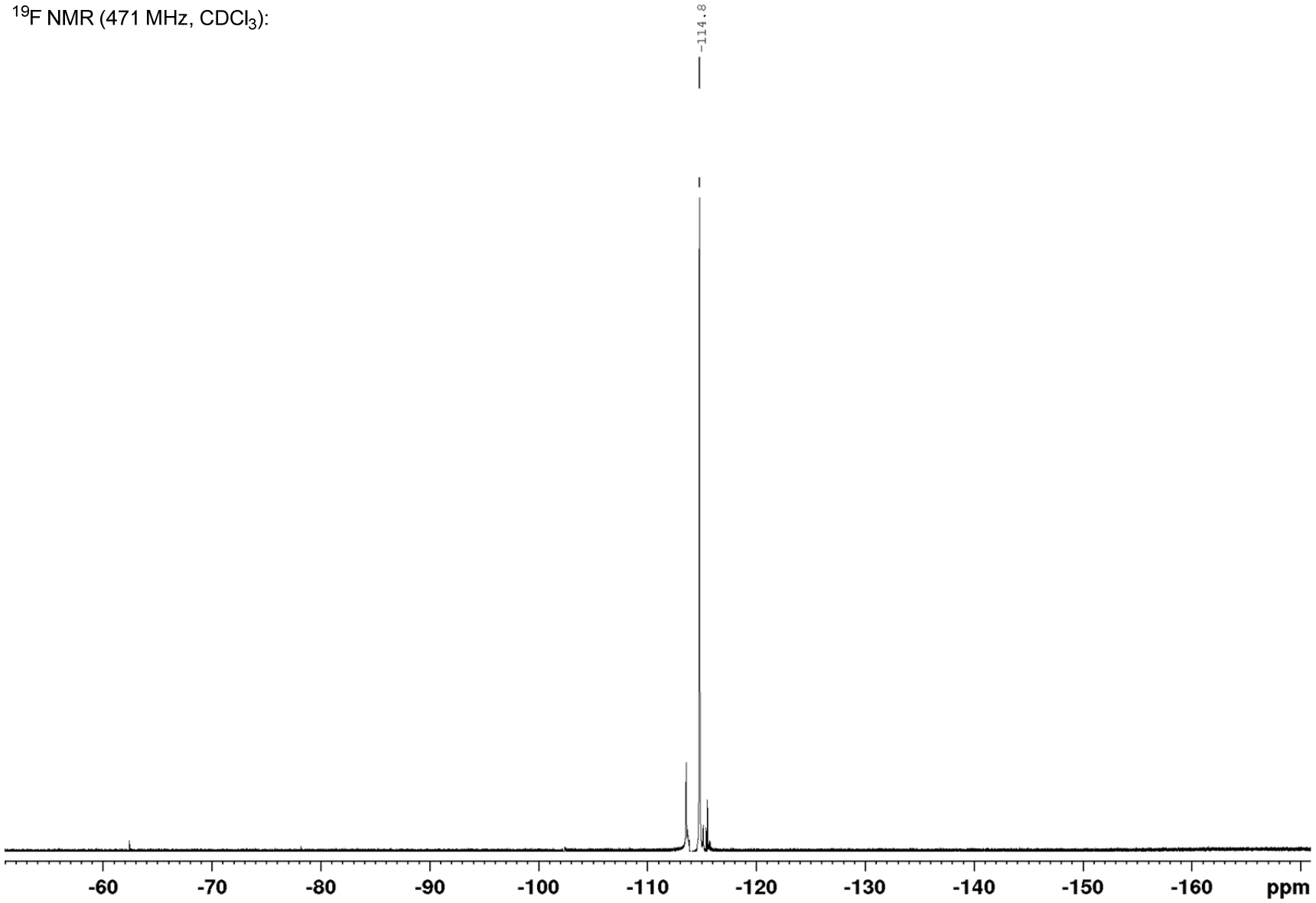
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$):

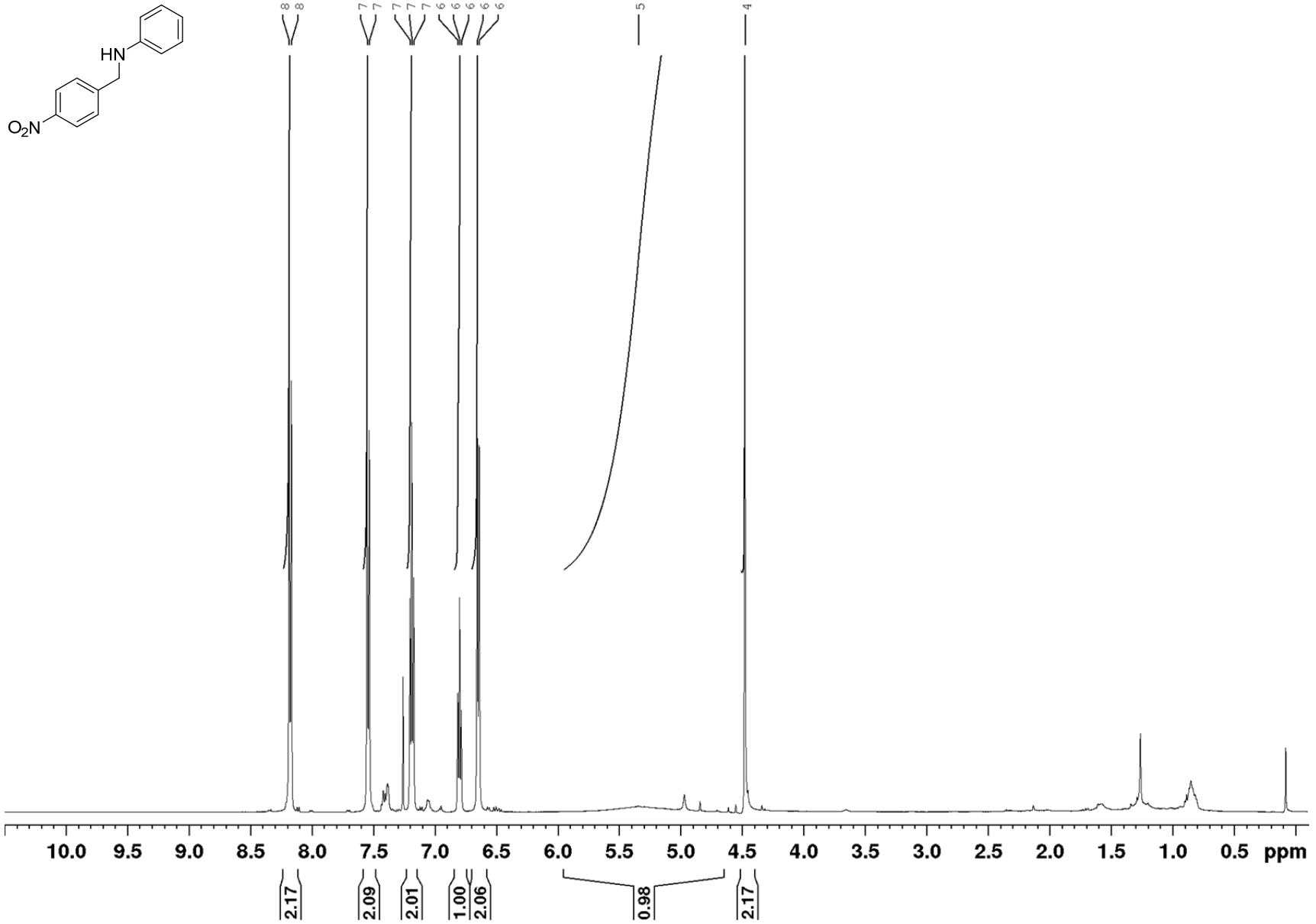


^{19}F NMR (471 MHz, $CDCl_3$):

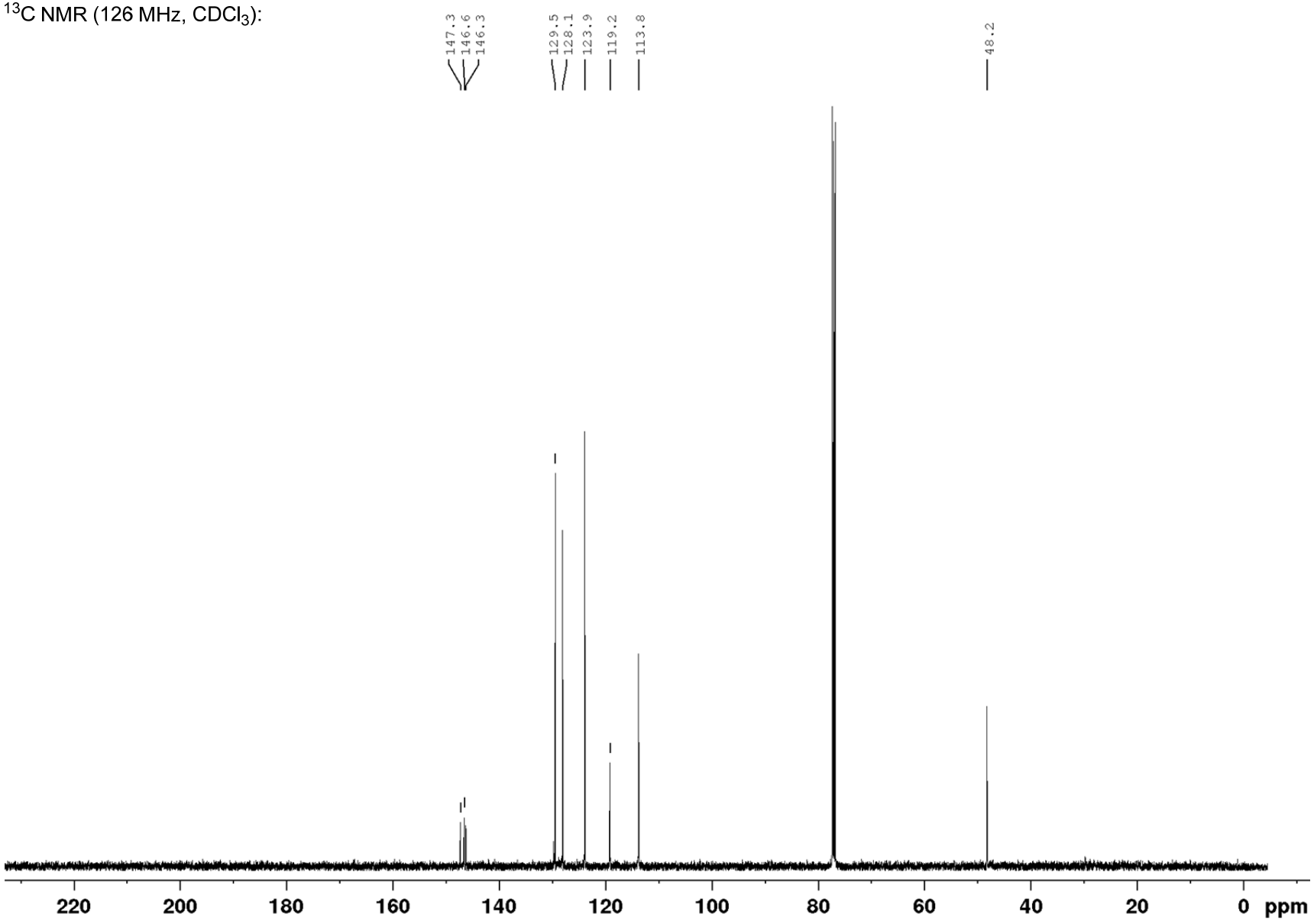


***N*-(4-nitrobenzyl)aniline (24)**

^{1}H NMR (500 MHz, $CDCl_3$)

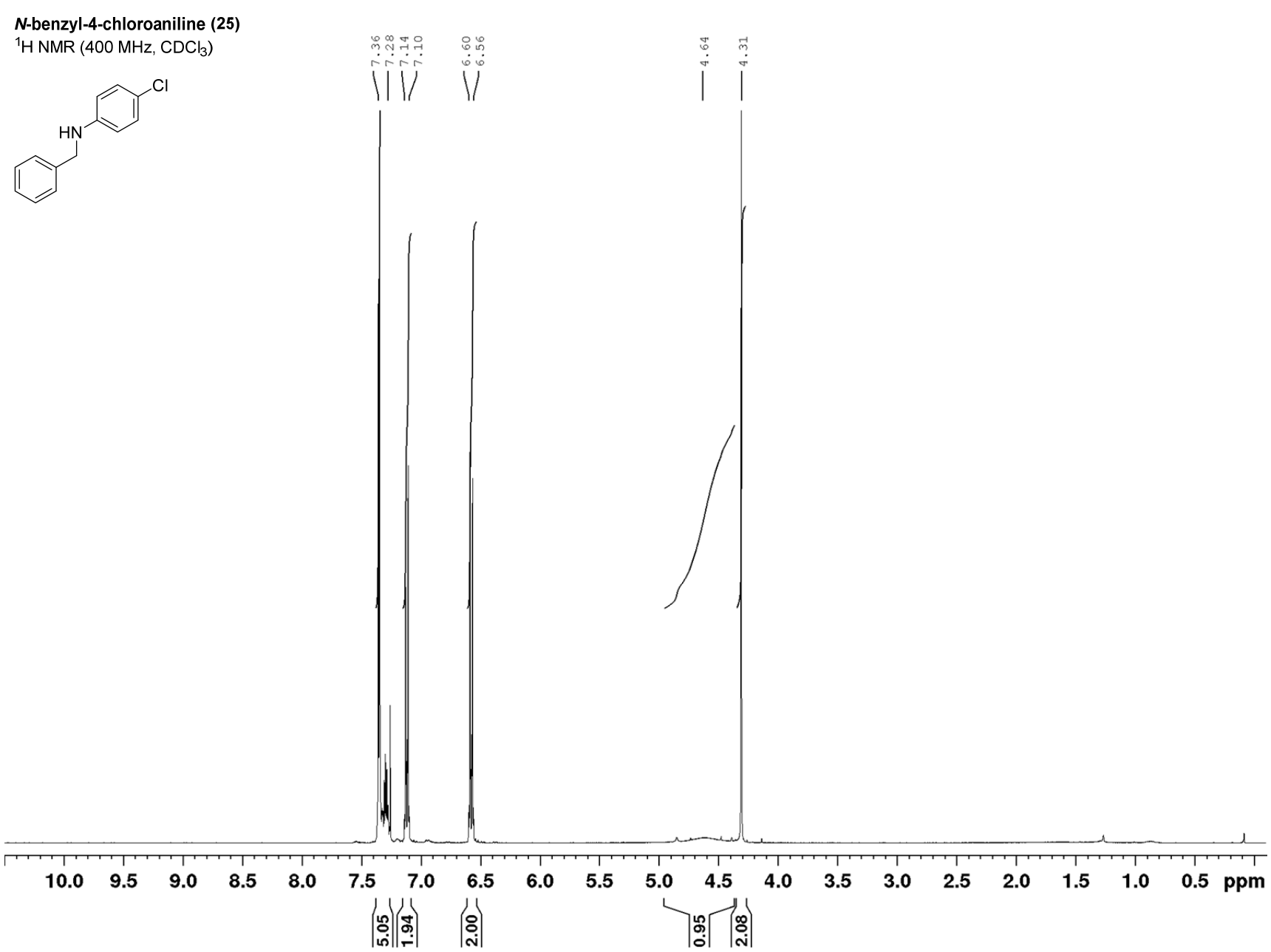


^{13}C NMR (126 MHz, $CDCl_3$):

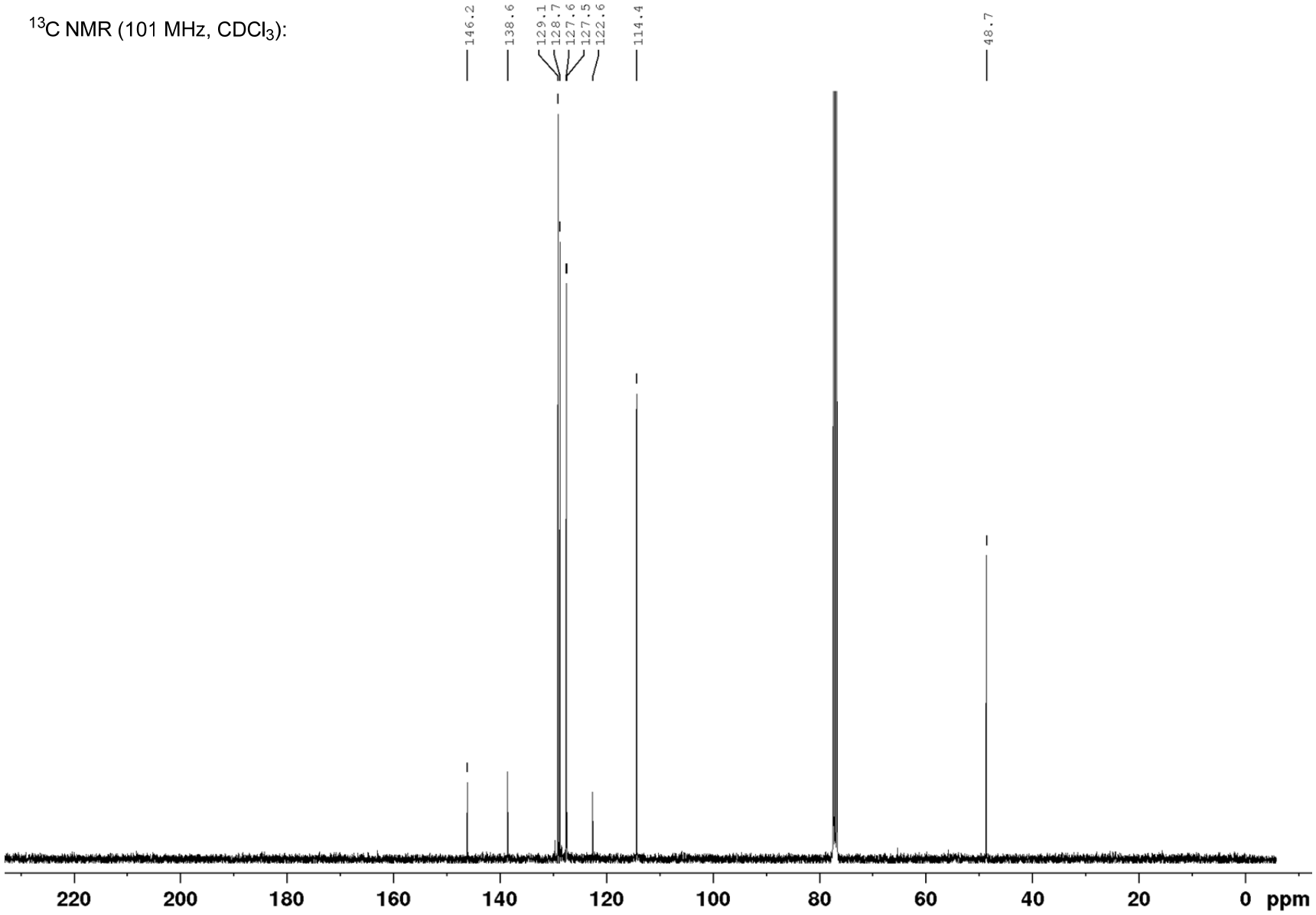


_N_-benzyl-4-chloroaniline (25)

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

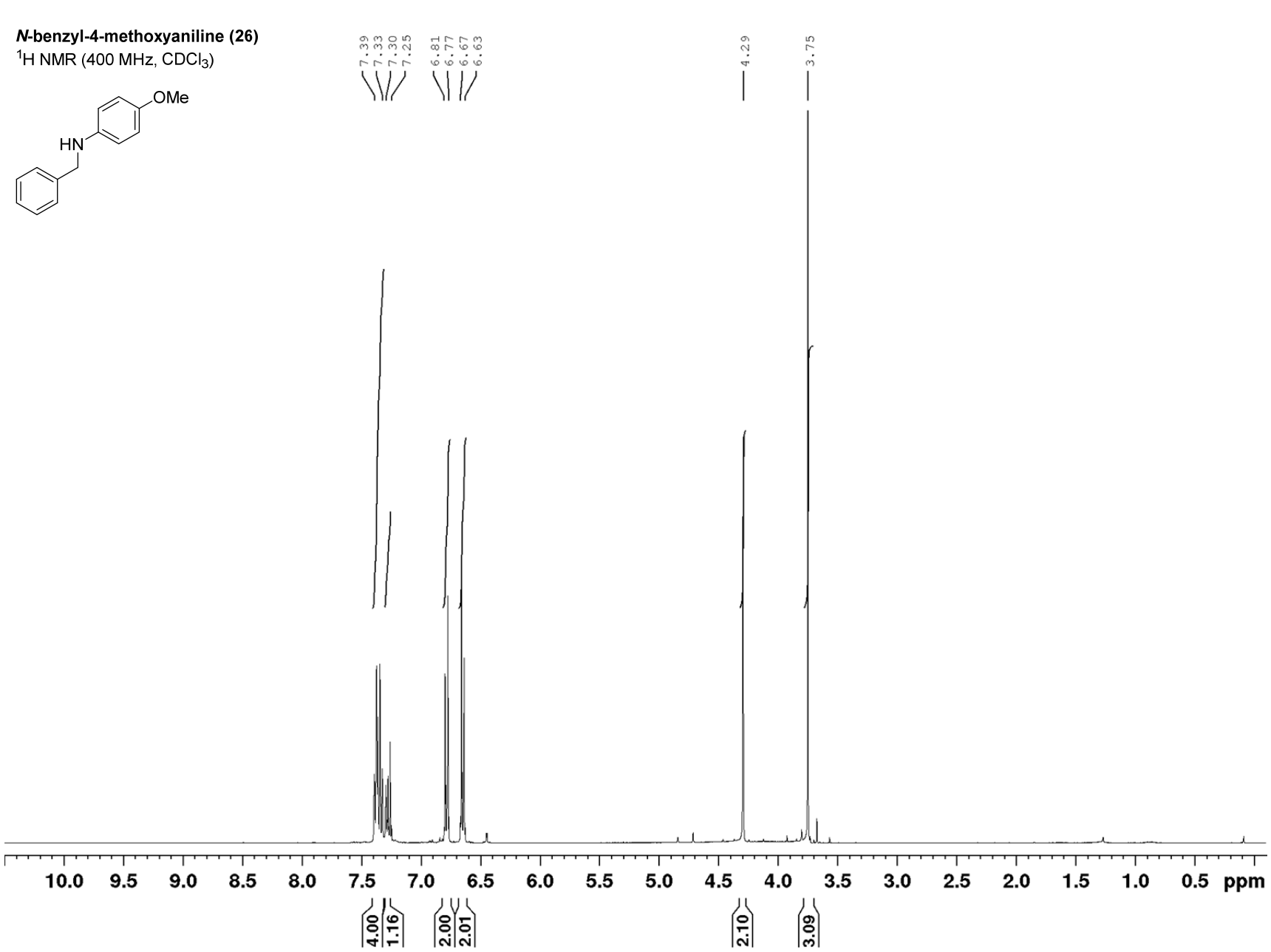


^{13}C NMR (101 MHz, $CDCl_3$):

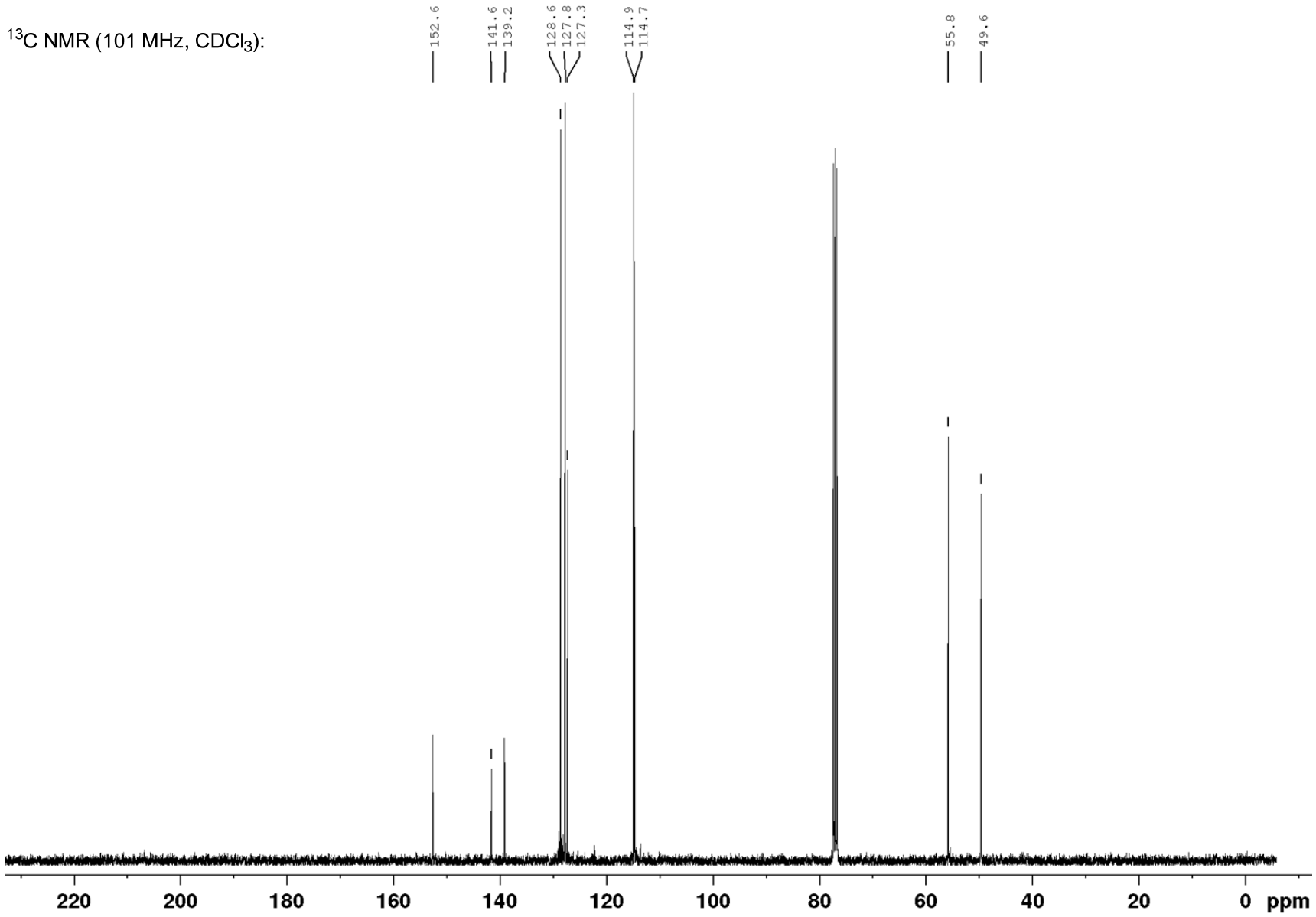


***N*-benzyl-4-methoxyaniline (26)**

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

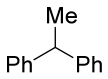


^{13}C NMR (101 MHz, $CDCl_3$):

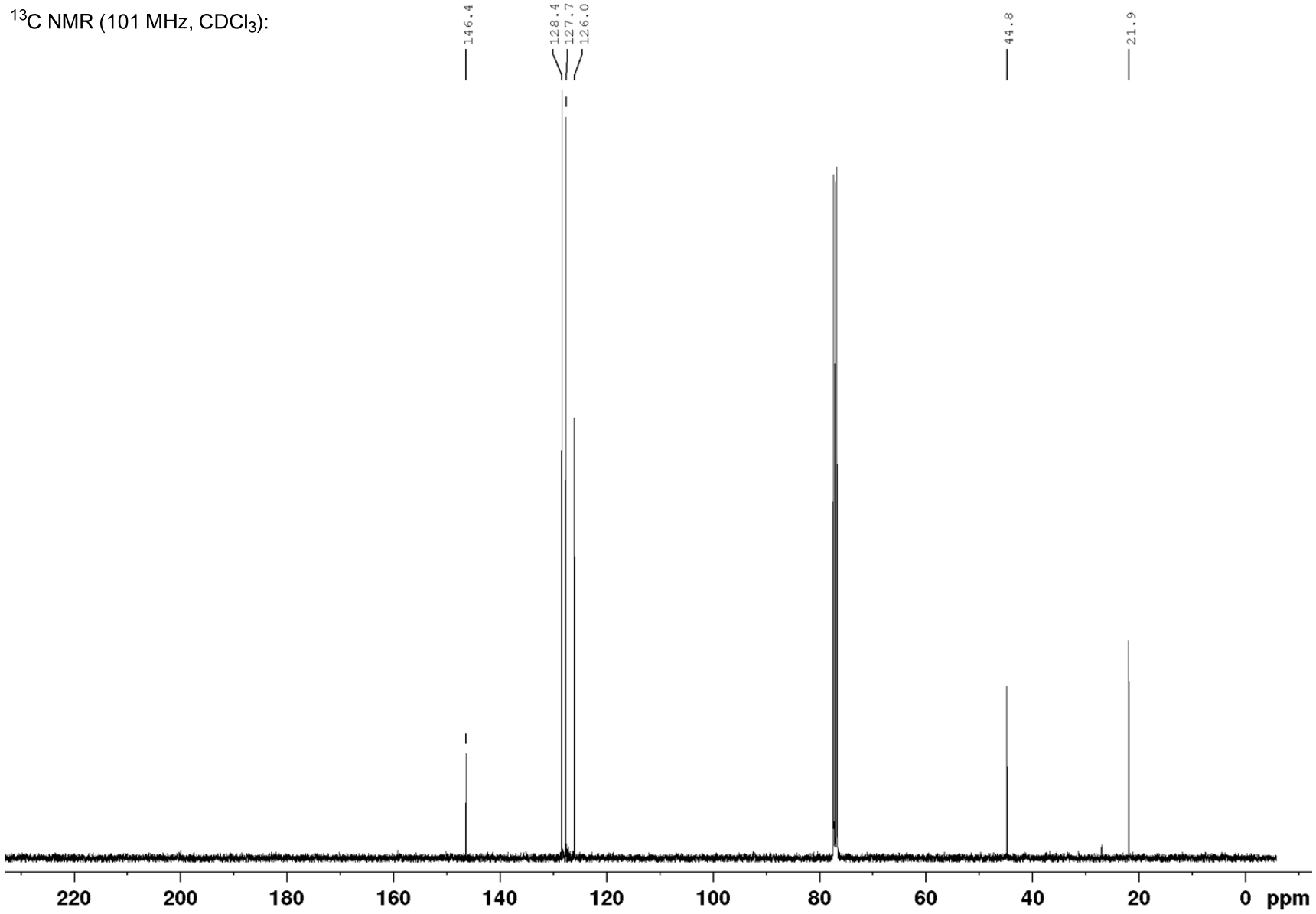


Ethane-1,1-diyldibenzene (28)

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

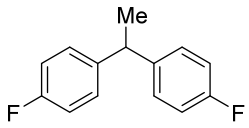


^{13}C NMR (101 MHz, $CDCl_3$):

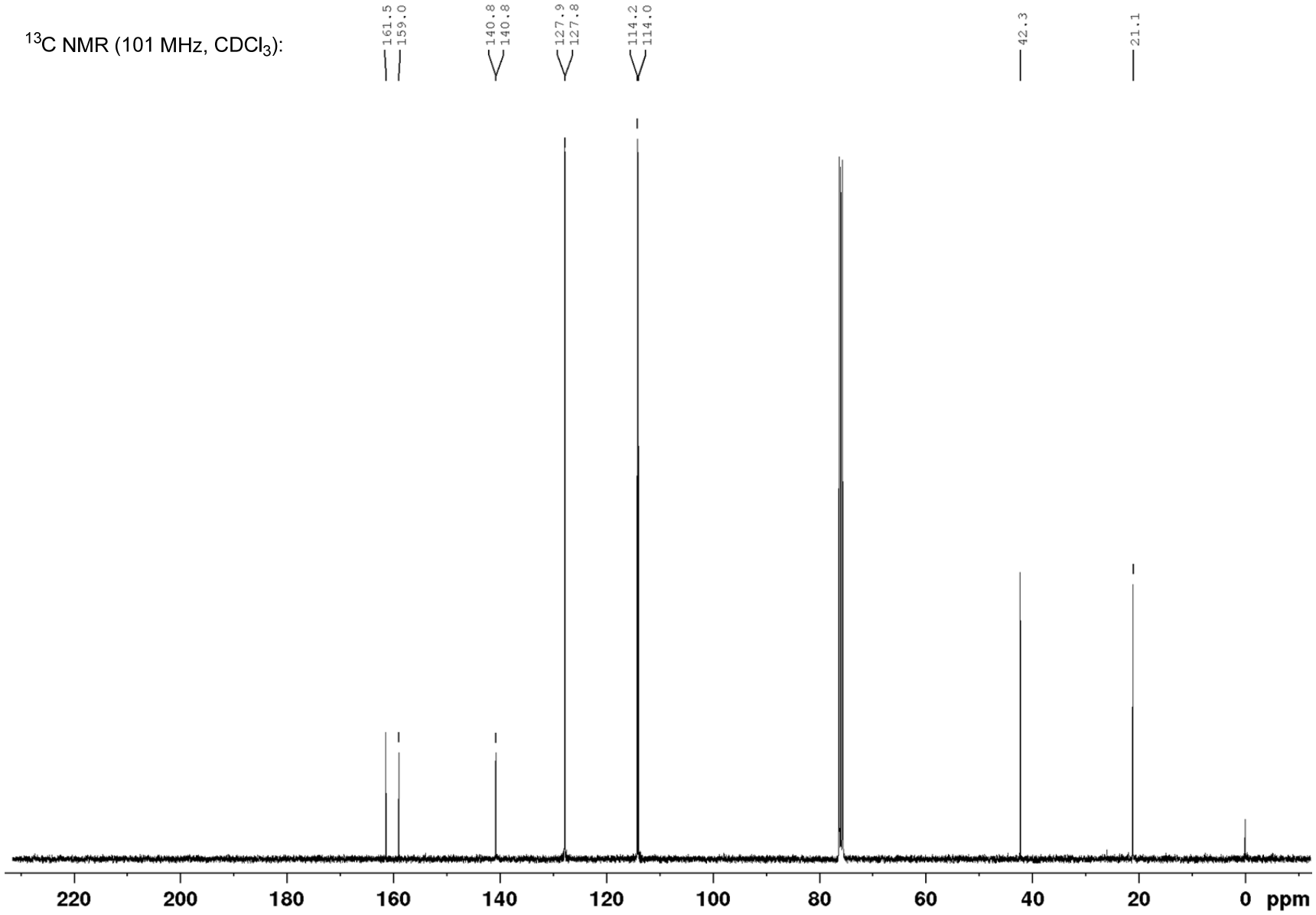


4,4'-(Ethane-1,1-diyl)bis(fluorobenzene) (37)

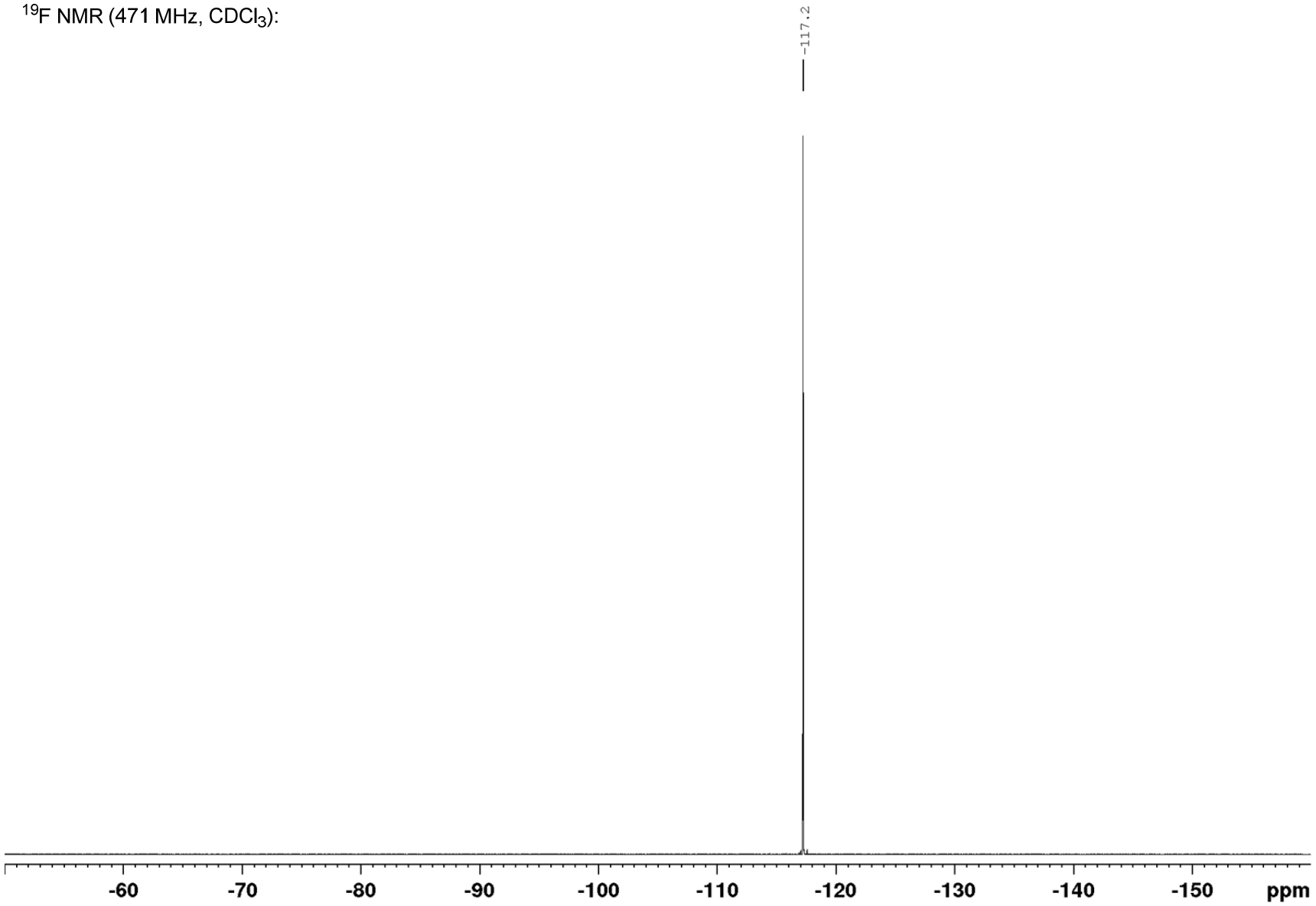
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$):

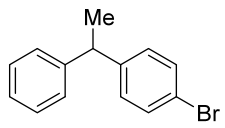


^{19}F NMR (471 MHz, $CDCl_3$):

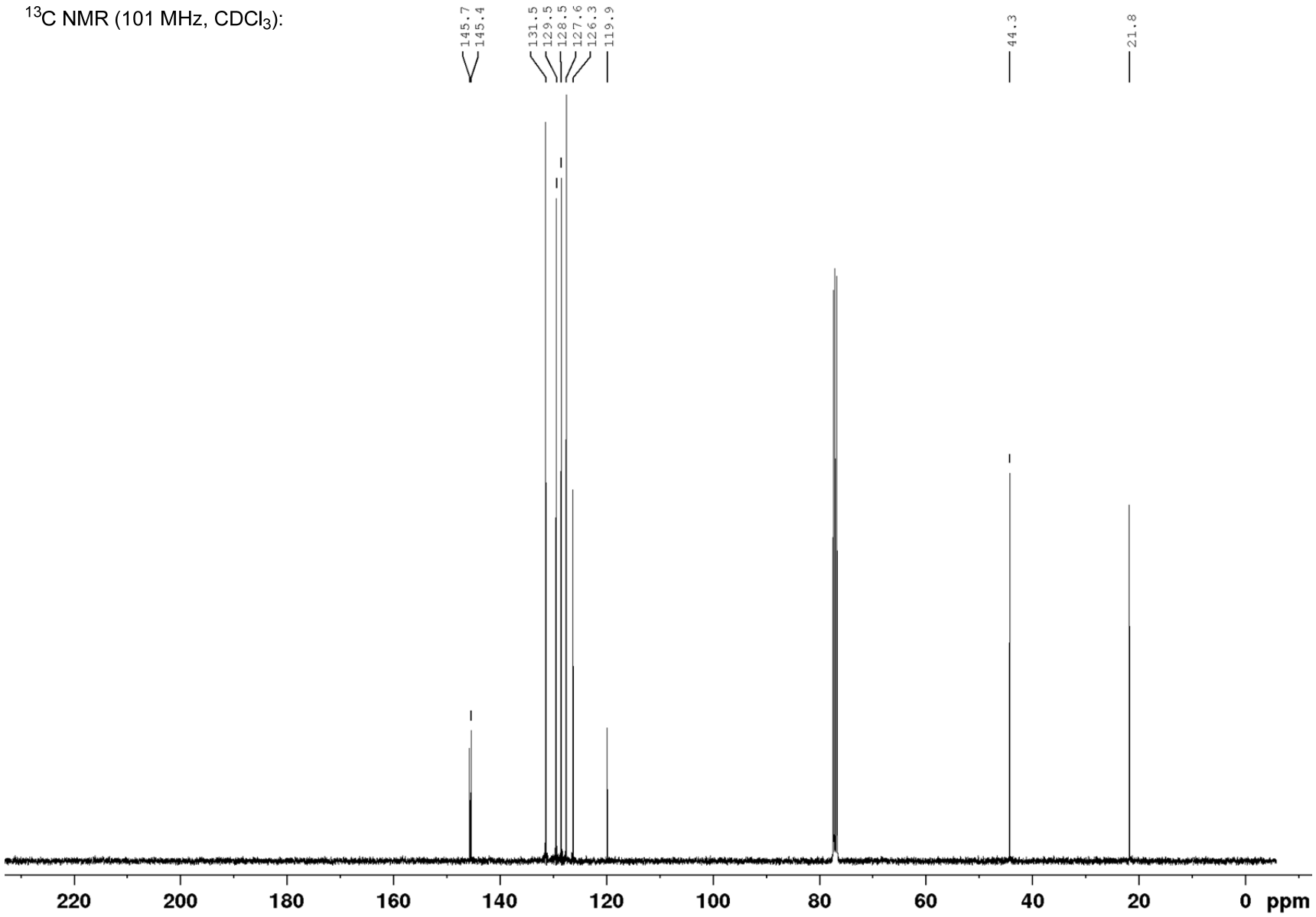


1-Bromo-4-(1-phenylethyl)benzene (38)

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

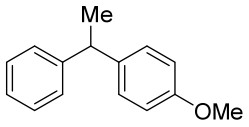


^{13}C NMR (101 MHz, $CDCl_3$):

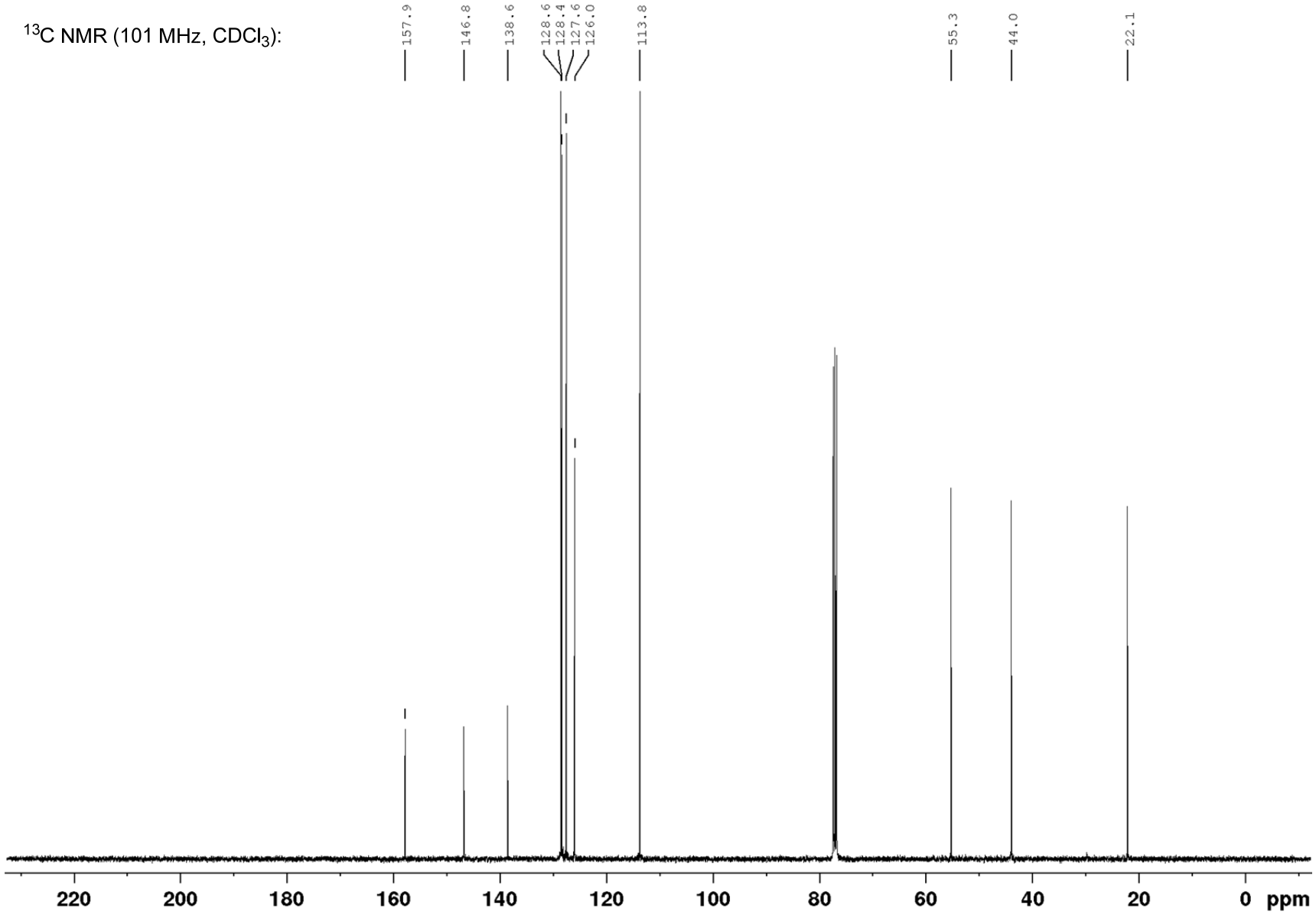


1-Methoxy-4-(1-phenylethyl)benzene (39)

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

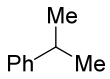


^{13}C NMR (101 MHz, $CDCl_3$):



Cumene (40)

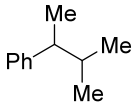
^{1}H NMR (400 MHz, CD_2Cl_2)



* mesitylene

(3-Methylbutan-2-yl)benzene (41)

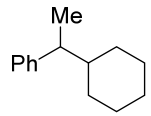
^{1}H NMR (400 MHz, CD_2Cl_2)



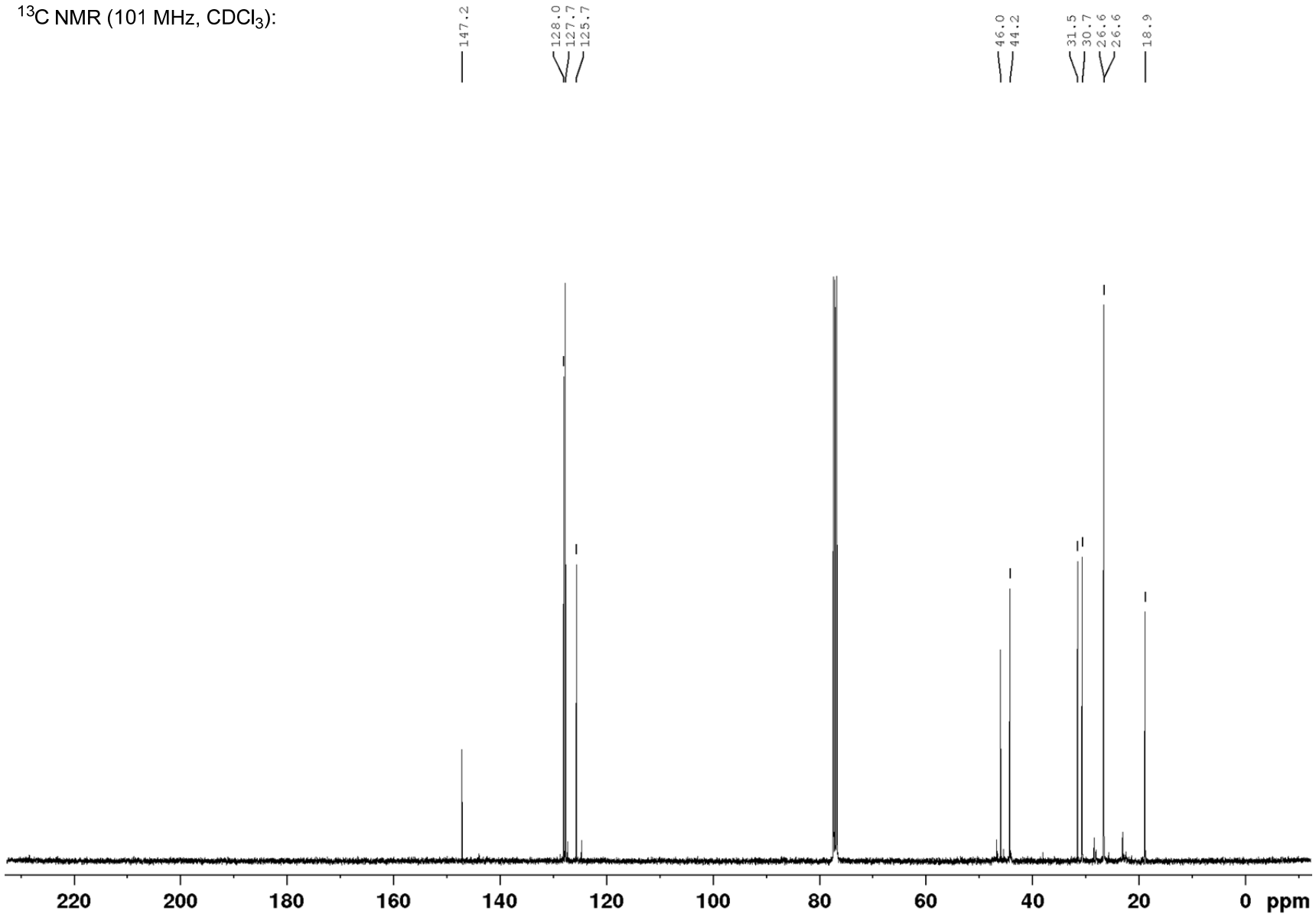
* mesitylene

(1-Cyclohexylethyl)benzene (42)

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

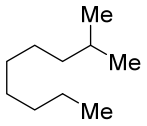


^{13}C NMR (101 MHz, $CDCl_3$):



2-Methylnonane (43)

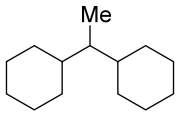
^{1}H NMR (400 MHz, CD_2Cl_2)



* mesitylene

Ethane-1,1-diyldicyclohexane (44)

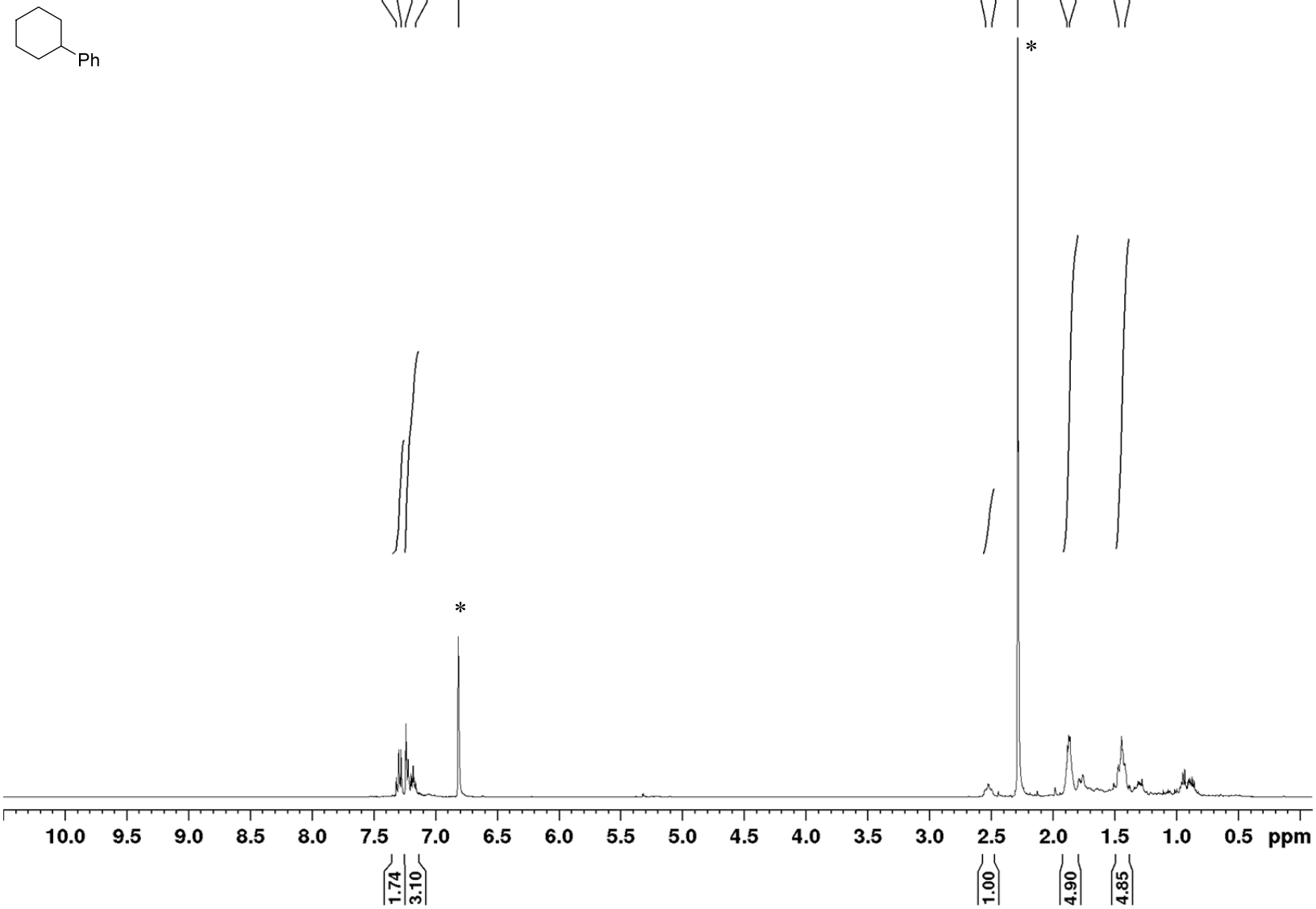
^{1}H NMR (400 MHz, CD_2Cl_2)



* mesitylene

cyclohexylbenzene (46)

^{1}H NMR (400 MHz, CD_2Cl_2)



* mesitylene