Supporting Information

Syngas as a synergistic reducing agent for the selective reductive amination – a mild route to bioactive amines

Evgeniya Podyacheva,[a,b] Alexandra I. Balalaeva, [a] Oleg I. Afanasyev,[a,c] Sofiya A. Runikhina,[a] Olga Chusova,[a,d] Andrey S. Kozlov,[a] Saihu Liao,[e] Denis Chusov*[a,b]

[a] A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Russia, 119334, Moscow, Vavilova St. 28, bld. 1, INEOS.
[b] National Research University Higher School of Economics, Miasnitskaya Str. 20, Moscow 101000, Russian Federation.
[c] Plekhanov Russian University of Economics, Stremyanny per. 36, 117997 Moscow, Russian Federation
[d] Faculty of Science, RUDN University, 6 Miklukho-Maklaya St., Moscow, 117198, Russia.
[e] State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, China

E-mail: chusov@ineos.ac.ru

Table of contents

1. General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification, THF was used from MBRAUN Solvent Purification System MB-SPS-7, without stabilizer.

Isolation of products was performed using column chromatography (Macherey-Nagel, silica gel 0.04–0.063 mm) or using preparative flash chromatograph InterChim PuriFlash; hexane-ethyl acetate and hexane-ethyl acetate-triethylamine systems were used as an eluent. All details about particular chromatographic parameters are provided with the description of each compound.

^{1}H, ^{13}C, and ^{19}F spectra were recorded in $CDCl_3$ on Bruker Avance 300, Bruker Avance 400, or Varian Inova 400 spectrometers. Chemical shifts are reported in parts per million relative to $CHCl_3$ (7.26 and 77.16 ppm for ^{1}H and ^{13}C respectively). The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, dd = doublet of dublets, t = triplet, tt = triplet of triplets, q = quartet, quint. = quintet, m = multiplet, br = broad, sept = septet; coupling constants are given in Hertz (Hz).

Analytical gas chromatography (GC) was performed using a Chromatec Crystal 5000.2 gas chromatograph fitted with a flame ionization detector and a MS detector. Chromatec CR-5MS (30 meters) capillary column were used.

GC settings for the yield determination using FID detector and CR5ms column:

The injector temperature was 250°C, split ratio of 30:1 at the moment of injection, the FID temperature was 250°C. Column compartment temperature program: 100°C for 2 min, 100°C → 280°C at 30°C/min, 280°C for 3 min. Flow rate 1 mL/min, column CR-5ms.

GC settings for the qualitative analysis using MS detector and CR5-ms column:

The injector temperature was 250°C, split ratio of 40:1 at the moment of injection. Column compartment temperature program: 60°C for 4 min, 60°C → 250°C at 30°C/min, 250°C for 12 min. Flow rate 1 mL/min. MSD parameters: ion source temperature 200°C, transfer line temperature 290°C. Retention times (t_R) and integrated ratios were obtained using Chromatec Analytic Software.

Analysis of the gas mixtures was performed using Chromatec Crystal 5000.2 gas chromatograph fitted with the thermal conductivity detector. Argon was used as a career gas (15 ml/min flow rate). Column zeolite CaX, 0.25-0.5 mm, 2 m x 3 mm. Isotermic mode, t = 60°C. H_2 retention time is 1.42 min, CO retention time is 4.84 min. A gas mixture to be analyzed (from the gas tank or an autoclave) was diluted in argon to achieve a concentration in the range 1-5 % v/v, and this diluted gas mixture was injected into GC. Quantities of the gases were determined using external calibration.

Reactions with pressure were carried out in autoclaves made from stainless steel.

Syngas preparation: to a gas tank with ca. 25 bar of carbon monoxide ca. 25 bar of hydrogen were added (to achieve a total pressure of 50 bar). The tank was equilibrated at room temperature for 24 hours, and the resulting gas mixture was analyzed by GC. The gas was used if H_2:CO ratio was 1-1.3:1. The analysis was repeated periodically, if the ratio was outside the above-mentioned range, it was adjusted by addition of the corresponding gas followed by equilibration and GC analysis.

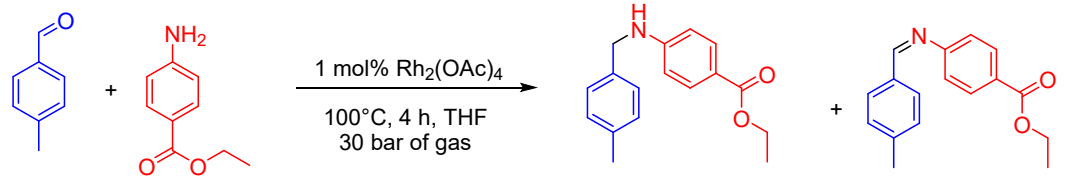
2. Reductive amination using syngas as a reducing agent

2.1. Optimization of reaction conditions

Procedure

$Rh_2(OAc)_4$ (0.49-2.78 μmol, 0.005-1 mol%), carbonyl compound (0.24-12.22 mmol, 100 mol%), amine (0.25-12.83 mmol, 105 mol%), were charged into a glass vial in a 10 mL stainless steel autoclave. THF was added and the autoclave was sealed, flushed three times with 5 atm of syngas, and then charged with indicated pressure of the gas. The reactor was placed into a preheated oil bath. After the indicated time of heating, the reactor was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH_2Cl_2 or EtOAc in order to get rid of catalyst reaction mixture was passed through a small pad of silica gel; combined solvents were removed on a rotary evaporator. The yield of the product was determined by ^{1}H NMR.

Table S1. Reductive amination using CO, Syngas, H_2 (30 bar)

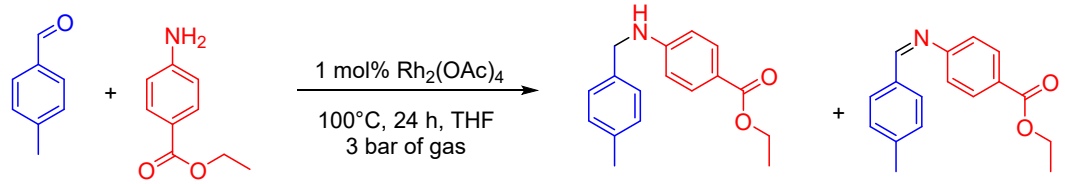


1 equiv. 1.05 equiv. 1 2

Gas	Yield of **1**, %	Yield of **2**, %
CO	24	71
Syngas	99	0
H_2	8	50

2.1-2.4 μmol $Rh_2(OAc)_4$, 0.21-0.24 mmol of 4-methylbenzaldehyde, 0.22-0.25 mmol of ethyl 4-aminobenzoate, 100°C, 30 bar of gas, THF, 4 h. Yields were determined by ^{1}H NMR.

Table S2. Reductive amination using CO, Syngas, H_2 (3 bar)

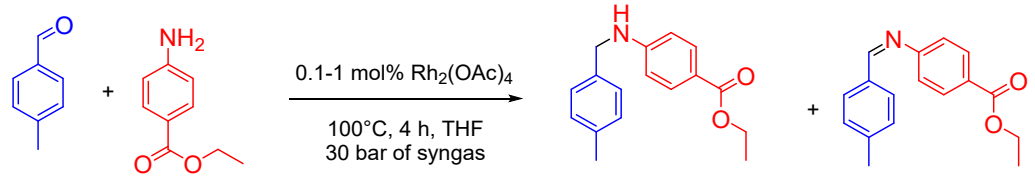


1 equiv. 1.05 equiv. 1 2

Gas	Yield of **1**, %	Yield of **2**, %
CO	1	99
Syngas	81	<1
H_2	7	40

2.1-2.8 μmol $Rh_2(OAc)_4$, 0.21-0.28 mmol of 4-methylbenzaldehyde, 0.22-0.29 mmol of ethyl 4-aminobenzoate, 100°C, 3 bar of gas, THF, 24 h. Yields were determined by ^{1}H NMR.

Table S3. Effect of catalyst loading

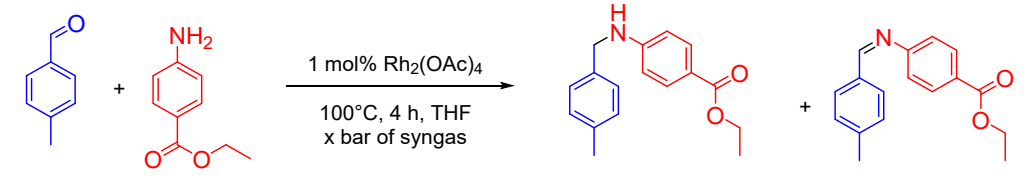


1 equiv. 1.05 equiv. 1 2

Catalyst loading, %	Yield of **1**, %	Yield of **2**, %
1.0	99	0
0.5	86	3
0.1	24	64

1.0-2.4 μmol $Rh_2(OAc)_4$, 0.24-1.04 mmol of 4-methylbenzaldehyde, 0.25-1.1 mmol of ethyl 4-aminobenzoate, 100°C, 30 bar of syngas, THF, 4 h. Yields were determined by ^1H NMR.

Table S4. Influence of syngas pressure

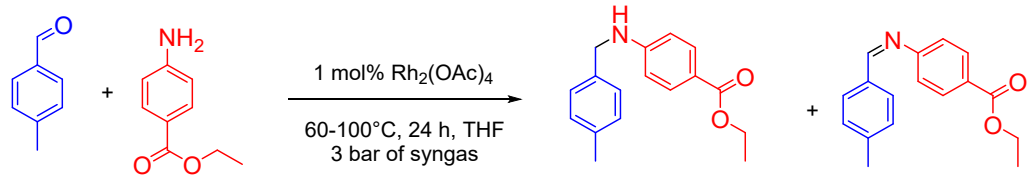


1 equiv. 1.05 equiv. 1 2

Pressure of syngas, bar	Reaction time, h	Yield of **1**, %	Yield of **2**, %
30	4	99	0
20	4	94	0
10	4	95	0
5	4	60	26
5	24	84	0
3	24	81	<1
1	24	7	30

1.56-2.0 μmol $Rh_2(OAc)_4$, 0.156-0.2 mmol of 4-methylbenzaldehyde, 0.164-0.21 mmol of ethyl 4-aminobenzoate, 100°C, 1-30 bar of syngas, THF, 4-24 h. Yields were determined by ^1H NMR.

Table S5. Influence of temperature

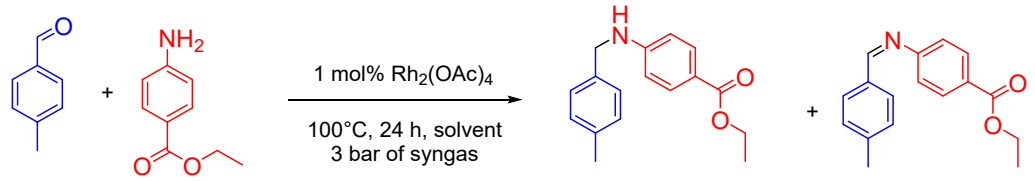


1 equiv. 1.05 equiv. 1 2

T, °C	Yield of **1**, %	Yield of **2**, %
100	81	<1
80	53	14
60	3	72

2.7-2.9 μmol $Rh_2(OAc)_4$, 0.27-0.29 mmol of 4-methylbenzaldehyde, 0.29-0.31 mmol of ethyl 4-aminobenzoate, 3 bar of syngas, THF, 24 h. Yields were determined by ^{1}H NMR.

Table S6. Influence of solvents



1 equiv. 1.05 equiv. 1 2

Solvent	Yield of **1**, %	Yield of **2**, %
neat	72	20
^{t}BuOH	100	0
CH_3CN	93	<1
dioxane	93	<1
toluene	86	<1
THF	81	<1

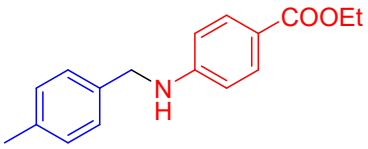
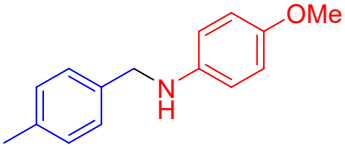
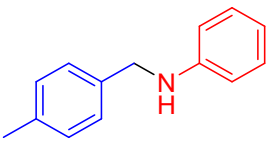
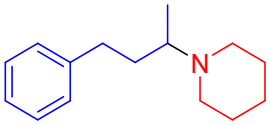
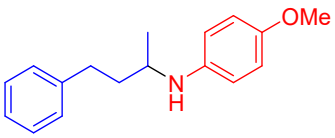
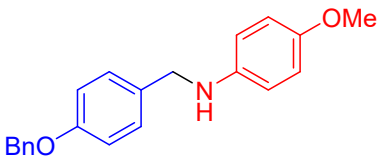
2.9-3.7 μmol $Rh_2(OAc)_4$, 0.29-0.37 mmol of 4-methylbenzaldehyde, 0.31-0.38 mmol of ethyl 4-aminobenzoate, 100°C, 3 bar of syngas, 24 h. Yields were determined by ^{1}H NMR.

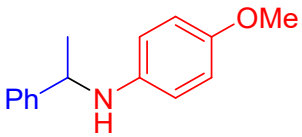
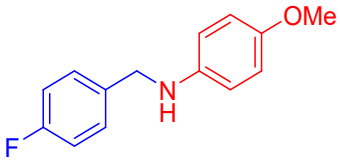
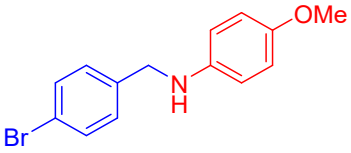
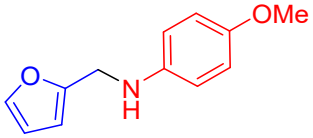
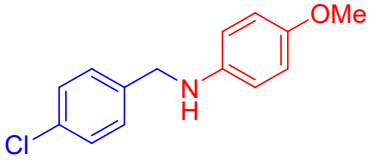
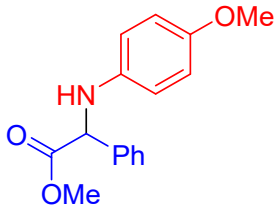
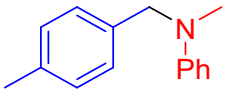
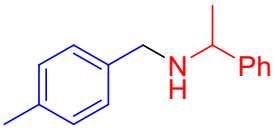
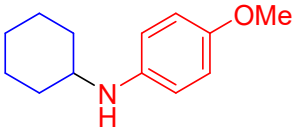
2.2. Bioassays of fungicidal activities

Study of biological activities of new compounds is important for drug development and agricultural chemistry. Herein, we investigated the activity of synthesized compounds *in vitro* against six phytopathogenic fungi: *Rhizoctonia solani* (*R.s.*), *Venturia inaequalis* (*V.i.*), *Sclerotinia sclerotiorum (S.s.), Phoma eupyrena* (*P.e.*), *Fusarium oxysporum* (*F.o.*), and *Fusarium nivale (F.m.n.)* (Table 2). The activity of each tested substance was compared with negative and positive controls treated with a reference fungicide (Triadimefon). Effect of the chemicals on mycelial radial growth was determined by dissolving concentration 3 mg/mL in acetone and suspending aliquots in potato-saccharose agar at 50℃ to give the concentration 30 μg/mL. The final solvent concentration was 10 mL/L. Petri dishes containing 15 mL of the agar medium were inoculated by placing 2-mm mycelial agar discs on the agar surface. Plates were incubated at 25℃ and radial growth was measured after 72 h. The agar medium without sample was used as the blank control. Three replicates of each test were carried out. The mycelium elongation diameter (mm) of fungi settlements was measured after 72 h of culture. The growth inhibition rates (***I***) were calculated using the following equation:

$$I = \frac{Control\ settlement\ diameter\ (mm)\ -\ Test\ settlement\ diameter\ (mm)}{Control\ settlement\ diameter\ (mm)} * 100\%$$

The results are summarized in the table below.

Amine	Compound	Mycelium growth inhibition, %					
		R.s.	***V.i.***	***P.e.***	***S.s.***	***F.o.***	***F.m.n.***
3aa		11	10	38	11	20	11
3ba		48	68	61	25	34	52
3ca		60	61	76	38	65	59
3db		13	36	20	21	15	19
3bb		39	49	50	17	25	48
3be		5	48	52	17	20	14

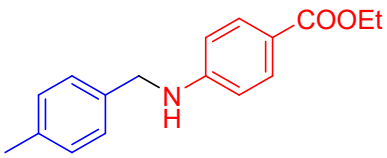
Amine	Compound	Mycelium growth inhibition, %					
		R.s.	***V.i.***	***P.e.***	***S.s.***	***F.o.***	***F.m.n.***
3bf		19	51	59	14	29	42
3bg		54	56	62	33	38	54
3bh		68	45	60	40	49	51
3bi		13	37	48	2	9	13
3bj		80	61	61	42	41	52
3bk		8	29	22	5	21	31
3ea		37	29	65	19	21	30
3fa		7	26	3	7	16	22
3bl		16	24	33	5	14	22
	Triadimefon	43	65	56	64	70	60

2.3. Compounds characterization, spectroscopic and analytical data for reductive amination

General procedure of reductive amination

$Rh_2(OAc)_4$ (1 mol%), carbonyl compound (100 mol%), amine (105 mol%), were charged into a glass vial in a 10 mL stainless steel autoclave. THF was added and the autoclave was sealed, flushed three times with 5 bar of syngas, and then charged with identified pressure of syngas. The reactor was placed into an oil bath preheated to 100°C. After 24 h of heating, the reactor was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH_2Cl_2 or EtOAc; in order to get rid of catalyst reaction mixture was passed through a small pad of silica gel; combined solvents were removed on a rotary evaporator. The yield of the product was determined by ^{1}H NMR. The residue was purified using preparative flash chromatograph InterChim PuriFlash or using column chromatography.

Ethyl-4-[(4-methylbenzyl)amino]benzoate (3aa)



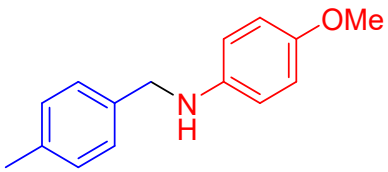
$Rh_2(OAc)_4$ (0.8 mg, 1.8 μmol, 1 mol%), *p*-tolylaldehyde (21.3 μL, 0.18 mmol, 100 mol%) and ethyl 4-aminobenzoate (31.4 mg, 0.19 mmol, 105 mol%) were charged into a glass vial in a 10 mL stainless steel autoclave. 47 μL of THF was added and the autoclave was sealed, flushed three times with 5 bar of syngas, and then charged with 3 bar of syngas. The reactor was placed into an oil bath preheated to 100°C. After 24 h of heating, the reactor was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH_2Cl_2; in order to get rid of catalyst reaction mixture was passed through a small pad of silica gel; combined solvents were removed on a rotary evaporator. NMR yield of ethyl 4-((4-methylbenzyl)amino)benzoate was 81%. Target product was purified by flash chromatograph InterChim PuriFlash, gradient elution was applied (hexane/CH_2Cl_2; 1:0 (pure hexane) → 0:1 (pure CH_2Cl_2)); R_f=0.4 in CH_2Cl_2. White solid. M.p.: 111-113°C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.58 (d, *J* = 8.5 Hz, 2H), 4.46 (br. s, 1H), 4.35-4.27 (m, 4H), 2.35 (s, 3H), 1.35 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.0, 151.8, 137.3, 135.4, 131.6, 129.6, 127.5, 119.0, 111.7, 60.3, 47.6, 21.2, 14.6.

NMR spectra are in agreement with the literature data[1].

4-Methoxy-N-(4-methylbenzyl)aniline (3ba)



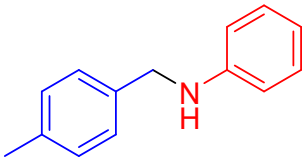
$Rh_2(OAc)_4$ (1.29 mg, 2.9 μmol, 1 mol%), 4-methylbenzaldehyde (34.4 μL, 0.29 mmol, 100 mol%) and 4-methoxyaniline (37.7 mg, 0.31 mmol, 105 mol%) were charged into a glass vial in a 10 mL stainless steel autoclave. 110 μL of THF was added and the autoclave was sealed, flushed three times with 5 bar of syngas, and then charged with 3 bar of syngas. The reactor was placed into an oil bath preheated to 100°C. After 24 h of heating, the reactor was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH_2Cl_2; in order to get rid of catalyst reaction mixture was passed through a small pad of silica gel; combined solvents were removed on a rotary evaporator. NMR yield of 4-methoxy-N-(4-methylbenzyl)aniline was 92%. Target product was purified by flash chromatograph InterChim PuriFlash, dry loading, gradient elution was applied (hexane/ethyl acetate/triethylamine; 15:1:0.1 → 0:1:0 (pure ethyl acetate)); R_f=0.13. Beige solid. M. p.: 68–70°C (lit. 69–70°C)[2].

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 6.78 (d, *J* = 9.0 Hz, 2H), 6.26 – 6.18 (m, 1H), 4.24 (s, 2H), 3.74 (s, 4H), 2.35 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 152.2, 142.6, 136.9, 136.7, 129.4, 127.7, 115.0, 114.2, 55.9, 49.1, 21.2.

NMR spectra are in agreement with the literature data[3].

N-(4-methylbenzyl)aniline (3ca)



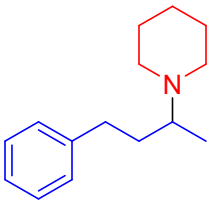
$Rh_2(OAc)_4$ (1.37 mg, 3.1 μmol, 1 mol%), 4-methylbenzaldehyde (36.6 μL, 0.31 mmol, 100 mol%) and aniline (39.2 μL, 0.33 mmol, 105 mol%) were charged into a glass vial in a 10 mL stainless steel autoclave. 116 μL of THF was added and the autoclave was sealed, flushed three times with 5 bar of syngas, and then charged with 3 bar of syngas. The reactor was placed into an oil bath preheated to 100°C. After 24 h of heating, the reactor was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH_2Cl_2; in order to get rid of catalyst reaction mixture was passed through a small pad of silica gel; combined solvents were removed on a rotary evaporator. NMR yield of N-(4-methylbenzyl)aniline was 87%. Target product was purified by column chromatography, hexane/ethyl acetate; 5:1; R_f=0.78. Light-yellow solid. M. p.: 45–47°C (lit. 46–47°C)[4].

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29 (d, *J* = 7.9 Hz, 2H), 7.25 – 7.15 (m, 4H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 2H), 4.31 (s, 2H), 4.00 (br. s, 1H), 2.38 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 148.3, 137.0, 136.4, 129.4, 129.3, 127.6, 117.6, 112.9, 48.1, 21.2.

NMR spectra are in agreement with the literature data[5].

1-(4-phenylbutan-2-yl)piperidine (3db)



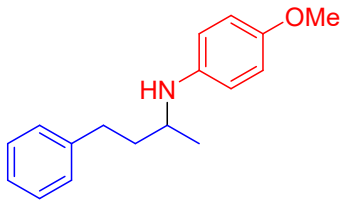
$Rh_2(OAc)_4$ (1.05 mg, 2.4 μmol, 1 mol%), benzylacetone (35.6 μL, 0.24 mmol, 100 mol%) and piperidine (24.7 μL, 0.25 mmol, 105 mol%) were charged into a glass vial in a 10 mL stainless steel autoclave. 54 μL of THF was added and the autoclave was sealed, flushed three times with 5 bar of syngas, and then charged with 10 bar of syngas. The reactor was placed into an oil bath preheated to 100°C. After 24 h of heating, the reactor was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH_2Cl_2; in order to get rid of catalyst reaction mixture was passed through a small pad of silica gel; combined solvents were removed on a rotary evaporator. NMR yield of 1-(4-phenylbutan-2-yl)piperidine was 81%. Target product was purified by flash chromatograph InterChim PuriFlash, gradient elution was applied (CH_2Cl_2/ethylacetate; 1:0 (pure CH_2Cl_2) → 0:1 (pure ethylacetate)); R_f=0.34 in 5/1 CH_2Cl_2-ethylacetate. Beige oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (m, 2H), 7.21-7.16 (m, 3H), 2.71-2.47 (m, 5H), 2.41-2.39 (m, 2H), 1.91-1.83 (m, 1H), 1.60-1.51 (m, 5H), 1.45-1.41 (m, 2H), 1.00 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 143.1, 128.6, 128.4, 125.7, 59.0, 49.4, 35.7, 33.4, 26.7, 25.2, 13.9.

NMR spectra are in agreement with the literature data[6].

4-methoxy-N-(4-phenylbutan-2-yl)aniline (3bb)



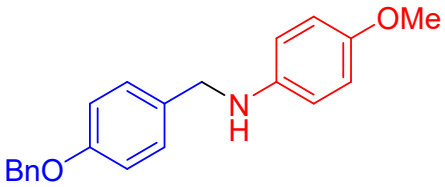
$Rh_2(OAc)_4$ (1.03 mg, 2.3 μmol, 1 mol%), benzylacetone (34.9 μL, 0.23 mmol, 100 mol%) and *p*-anisidine (30.1 mg, 0.24 mmol, 105 mol%) were charged into a glass vial in a 10 mL stainless steel autoclave. 53 μL of THF was added and the autoclave was sealed, flushed three times with 5 bar of syngas, and then charged with 10 bar of syngas. The reactor was placed into an oil bath preheated to 100°C. After 24 h of heating, the reactor was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH_2Cl_2; in order to get rid of catalyst reaction mixture was passed through a small pad of silica gel; combined solvents were removed on a rotary evaporator. NMR yield of 4-methoxy-N-(4-phenylbutan-2-yl)aniline was 99%. Target product was purified by flash chromatograph InterChim PuriFlash, gradient elution was applied (hexane/CH_2Cl_2; 5:1 (hexane/CH_2Cl_2) → 0:1 (pure CH_2Cl_2)); R_f=0.67 in 10/1 CH_2Cl_2-ethylacetate. Brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.27 (m, 2H), 7.21-7.17 (m, 3H), 6.76 (d, *J* = 8.9 Hz, 2H), 6.53 (d, *J* = 8.9 Hz, 2H), 3.75 (s, 3H), 3.40 (sext, *J* = 6.7 Hz, 1H), 2.73 (t, *J* = 7.9 Hz, 2H), 1.92-1.83 (m, 1H), 1.79-1.70 (m, 1H), 1.20 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 152.0, 142.2, 141.7, 128.6, 128.5, 125.9, 115.0, 115.0, 55.9, 49.1, 38.9, 32.6, 20.9.

NMR spectra are in agreement with the literature data[7].

N-(4-(benzyloxy)benzyl)-4-methoxyaniline (3be)



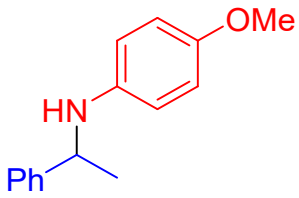
$Rh_2(OAc)_4$ (1.67 mg, 3.8 μmol, 1 mol%), 4-(benzyloxy)benzaldehyde (80.6 mg, 0.38 mmol, 100 mol%) and 4-methoxyaniline (48.8 mg, 0.40 mmol, 105 mol%) were charged into a glass vial in a 10 mL stainless steel autoclave. 142 μL of THF was added and the autoclave was sealed, flushed three times with 5 bar of syngas, and then charged with 10 bar of syngas. The reactor was placed into an oil bath preheated to 100°C. After 24 h of heating, the reactor was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH_2Cl_2; in order to get rid of catalyst reaction mixture was passed through a small pad of silica gel; combined solvents were removed on a rotary evaporator. NMR yield of N-(4-(benzyloxy)benzyl)-4-methoxyaniline was 84%. Target product was purified by flash chromatograph InterChim PuriFlash, dry loading, gradient elution was applied (hexane/ethyl acetate/triethylamine; 10:1:0.1 → 0:1:0 (pure ethyl acetate)); R_f=0.3. White solid. M. p.: 102–104°C (lit. 100–102°C)[3].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.28 (m, 7H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.9 Hz, 2H), 6.62 (d, *J* = 8.9 Hz, 2H), 5.07 (s, 2H), 4.22 (s, 2H), 3.76 (s, 4H, C**H**$_3$O + N**H**).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.1, 152.2, 142.6, 137.1, 132.1, 129.0, 128.7, 128.1, 127.6, 115.0, 114.9, 114.2, 70.1, 55.9, 48.8.

NMR spectra are in agreement with the literature data[3].

4-Methoxy-N-(1-phenylethyl)aniline (3bf)



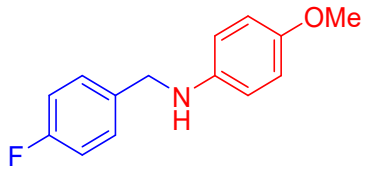
$Rh_2(OAc)_4$ (1.46 mg, 3.3 μmol, 1 mol%), acetophenone (38.5 μL, 0.33 mmol, 100 mol%) and 4-methoxyaniline (42.7 mg, 0.35 mmol, 105 mol%) were charged into a glass vial in a 10 mL stainless steel autoclave. 124 μL of THF was added and the autoclave was sealed, flushed three times with 5 bar of syngas, and then charged with 10 bar of syngas. The reactor was placed into an oil bath preheated to 100°C. After 24 h of heating, the reactor was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH_2Cl_2; in order to get rid of catalyst reaction mixture was passed through a small pad of silica gel; combined solvents were removed on a rotary evaporator. NMR yield of 4-methoxy-N-(1-phenylethyl)aniline was 96%. Target product was purified by flash chromatograph InterChim PuriFlash, dry loading, gradient elution was applied (hexane/ethyl acetate; 30:1 → 0:1 (pure ethyl acetate)); R_f=0.2. Yellow solid. M. p.: 64–66°C (lit. 64–65°C)[8].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.27 (m, 4H), 7.26 – 7.18 (m, 1H), 6.70 (d, *J* = 8.8 Hz, 2H), 6.48 (d, *J* = 8.8 Hz, 2H), 4.42 (q, *J* = 6.6 Hz, 1H), 3.69 (s, 4H, C**H**$_3$O + N**H**), 1.50 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 152.1, 145.6, 141.7, 128.7, 126.9, 126.02, 114.9, 114.7, 55.9, 54.4, 25.2.

NMR spectra are in agreement with the literature data[9].

N-(4-fluorobenzyl)-4-methoxyaniline (3bg)



$Rh_2(OAc)_4$ (0.89 mg, 2.0 μmol, 1 mol%), *p*-fluorobenzaldehyde (21.6 μL, 0.20 mmol, 100 mol%) and *p*-anisidine (26.0 mg, 0.21 mmol, 105 mol%) were charged into a glass vial in a 10 mL stainless steel autoclave. 54 μL of THF was added and the autoclave was sealed, flushed three times with 5 bar of syngas, and then charged with 10 bar of syngas. The reactor was placed into an oil bath preheated to 100°C. After 24 h of heating, the reactor was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH_2Cl_2; in order to get rid of catalyst reaction mixture was passed through a small pad of silica gel; combined solvents were removed on a rotary evaporator. NMR yield of N-(4-fluorobenzyl)-4-methoxyaniline was 87%. Target product was purified by flash chromatograph InterChim PuriFlash, gradient elution was applied (hexane/CH_2Cl_2; 9:1 (hexane/CH_2Cl_2) → 0:1 (pure CH_2Cl_2)); R_f=0.33 in 5/1 hexane-ethylacetate. Brown solid. M. p.: 29-30°C (lit. 25-26°C)[10].

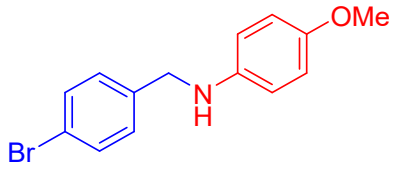
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.32 (m, 2H), 7.05-7.00 (m, 2H), 6.78 (d, *J* = 8.9 Hz, 2H), 6.59 (d, *J* = 8.9 Hz, 2H), 4.25, (s, 2H), 3.74 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.1 (d, $^2J_{C\text{-}F}$ = 245.0 Hz), 152.4, 142.3, 135.5, 129.2 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 115.5 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 115.0, 114.3, 55.9, 48.7.

^{19}F NMR (282 MHz, $CDCl_3$): δ -115.69.

NMR spectra are in agreement with the literature data[11,12].

N-(4-bromobenzyl)-4-methoxyaniline (3bh)



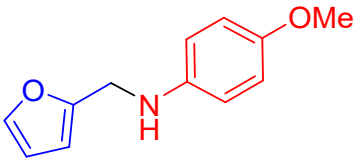
$Rh_2(OAc)_4$ (0.96 mg, 2.2 μmol, 1 mol%), *p*-bromobenzaldehyde (40.2 mg, 0.22 mmol, 100 mol%) and *p*-anisidine (28.1 mg, 0.23 mmol, 105 mol%) were charged into a glass vial in a 10 mL stainless steel autoclave. 82 μL of THF was added and the autoclave was sealed, flushed three times with 5 bar of syngas, and then charged with 10 bar of syngas. The reactor was placed into an oil bath preheated to 100°C. After 24 h of heating, the reactor was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH_2Cl_2; in order to get rid of catalyst reaction mixture was passed through a small pad of silica gel; combined solvents were removed on a rotary evaporator. NMR yield of N-(4-bromobenzyl)-4-methoxyaniline was 81%. Target product was purified by flash chromatograph InterChim PuriFlash, gradient elution was applied (hexane/CH_2Cl_2; 9:1 (hexane/CH_2Cl_2) → 0:1 (pure CH_2Cl_2)); R_f=0.42 in 1/2 hexane/CH_2Cl_2. Yellow solid. M.p.: 68-69°C (lit. 73-75°C)[11].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 8.9 Hz, 2H), 6.57 (d, *J* = 8.9 Hz, 2H), 4.25, (s, 2H), 3.74 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 152.4, 142.1, 138.9, 131.7, 129.2, 120.9, 115.0, 114.2, 55.9, 48.6.

NMR spectra are in agreement with the literature data[11].

N-(furan-2-ylmethyl)-4-methoxyaniline (3bi)



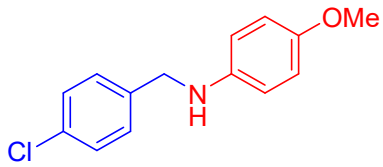
$Rh_2(OAc)_4$ (1.79 mg, 4.0 μmol, 1 mol%), furfural (33.5 μL, 0.40 mmol, 100 mol%) and 4-methoxyaniline (52.3 mg, 0.42 mmol, 105 mol%) were charged into a glass vial in a 10 mL stainless steel autoclave. 1.012 mL (0.4 M) of THF was added and the autoclave was sealed, flushed three times with 5 bar of syngas, and then charged with 10 bar of syngas. The reactor was placed into an oil bath preheated to 100°C. After 24 h of heating, the reactor was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH_2Cl_2; in order to get rid of catalyst reaction mixture was passed through a small pad of silica gel; combined solvents were removed on a rotary evaporator. NMR yield of N-(furan-2-ylmethyl)-4-methoxyaniline was 92%. Target product was purified by flash chromatograph InterChim PuriFlash, dry loading, gradient elution was applied (hexane/ethyl acetate; 15:1 → 0:1 (pure ethyl acetate)); R_f=0.18. Yellow solid. M. p.: 44–46°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.32 (m, appears as s, δ 7.37, 1H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 8.9 Hz, 2H), 6.38 – 6.29 (m, appears as s, δ 6.33, 1H), 6.27 – 6.19 (m, 1H), 4.28 (s, 2H), 3.76 (s, 4H, C**H**$_3$O + N**H**).

^{13}C NMR (101 MHz, $CDCl_3$): δ 153.2, 152.7, 142.0 (2C), 115.0, 114.8, 110.4, 107.0, 55.9, 42.6.

NMR spectra are in agreement with the literature data[10].

N-(4-chlorobenzyl)-4-methoxyaniline (3bj)



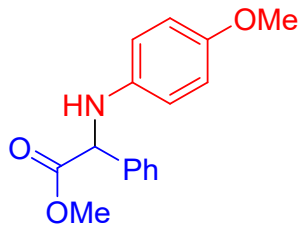
$Rh_2(OAc)_4$ (0.92 mg, 2.1 μmol, 1 mol%), *p*-chlorobenzaldehyde (29.3 mg, 0.21 mmol, 100 mol%) and *p*-anisidine (26.9 mg, 0.22 mmol, 105 mol%) were charged into a glass vial in a 10 mL stainless steel autoclave. 78 μL of THF was added and the autoclave was sealed, flushed three times with 5 bar of syngas, and then charged with 10 bar of syngas. The reactor was placed into an oil bath preheated to 100°C. After 24 h of heating, the reactor was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH_2Cl_2; in order to get rid of catalyst reaction mixture was passed through a small pad of silica gel; combined solvents were removed on a rotary evaporator. NMR yield of N-(4-chlorobenzyl)-4-methoxyaniline was 89%. Target product was purified by flash chromatograph InterChim PuriFlash, gradient elution was applied (hexane/CH_2Cl_2; 9:1 (hexane/CH_2Cl_2) → 0:1 (pure CH_2Cl_2)); R_f=0.35 in 5/1 hexane-ethylacetate. Brown solid. M. p.: 69–70°C (lit. 70–72°C)[13].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (m, 4H, appears as s), 6.77 (d, *J* = 8.9 Hz, 2H), 6.58 (d, *J* = 8.9 Hz, 2H), 4.26 (s, 2H), 3.82-3.78 (br. s, 1H), 3.74 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 152.4, 142.2, 138.4, 132.9, 128.9, 128.8, 115.0, 114.3, 55.9, 48.6.

NMR spectra are in agreement with the literature data[14].

Methyl 2-((4-methoxyphenyl)amino)-2-phenylacetate (3bk)



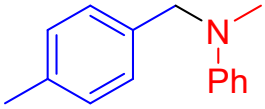
$Rh_2(OAc)_4$ (1.65 mg, 3.7 μmol, 1 mol%), methyl 2-oxo-2-phenylacetate (53.0 μL, 0.37 mmol, 100 mol%) and 4-methoxyaniline (48.1 mg, 0.39 mmol, 105 mol%) were charged into a glass vial in a 10 mL stainless steel autoclave. 140 μL of THF was added and the autoclave was sealed, flushed three times with 5 bar of syngas, and then charged with 10 bar of syngas. The reactor was placed into an oil bath preheated to 100°C. After 24 h of heating, the reactor was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH_2Cl_2; in order to get rid of catalyst reaction mixture was passed through a small pad of silica gel; combined solvents were removed on a rotary evaporator. NMR yield of methyl 2-((4-methoxyphenyl)amino)-2-phenylacetate was 76%. Target product was purified by flash chromatograph InterChim PuriFlash, dry loading, gradient elution was applied (hexane/ethyl acetate/triethylamine; 12:1:0.1 → 0:1:0 (pure ethyl acetate)); R_f=0.28. Yellow solid. M. p.: 106–108°C (lit. 107–108°C)[15].

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.0 Hz, 2H), 7.42 – 7.29 (m, 3H), 6.74 (d, *J* = 8.9 Hz, 2H), 6.55 (d, *J* = 8.9 Hz, 2H), 5.04 (d, *J* = 5.8 Hz, 1H), 4.71 (d, *J* = 5.6 Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.6, 152.6, 140.2, 137.9, 129.0, 128.4, 127.4, 114.9, 114.8, 61.7, 55.7, 52.8.

NMR spectra are in agreement with the literature data[16].

N-methyl-N-(4-methylbenzyl)aniline (3ea)



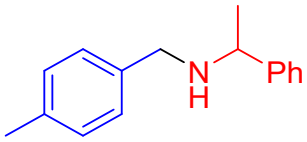
$Rh_2(OAc)_4$ (0.84 mg, 1.9 μmol, 1 mol%), *p*-tolylaldehyde (22.4 μL, 0.19 mmol, 100 mol%) and N-methylaniline (21.6 μL, 0.20 mmol, 105 mol%) were charged into a glass vial in a 10 mL stainless steel autoclave. 49 μL of THF was added and the autoclave was sealed, flushed three times with 5 bar of syngas, and then charged with 10 bar of syngas. The reactor was placed into an oil bath preheated to 100°C. After 24 h of heating, the reactor was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH_2Cl_2; in order to get rid of catalyst reaction mixture was passed through a small pad of silica gel; combined solvents were removed on a rotary evaporator. NMR yield of N-methyl-N-(4-methylbenzyl)aniline was 92%. Target product was purified by flash chromatograph InterChim PuriFlash, gradient elution was applied (hexane/CH_2Cl_2; 1:0 (pure hexane) → 1:1 (hexane/ CH_2Cl_2)); R_f=0.8 in 1/1 hexane/CH_2Cl_2. Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (m, 2H), 7.19 (m, 4H, appears as s), 6.82 (d, *J* = 8.1 Hz, 2H), 6.79-6.75 (m, 1H), 4.56 (s, 2H), 3.06 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 149.9, 136.5, 136.0, 129.4, 129.3, 126.8, 116.5, 112.5, 56.5, 38.5, 21.2.

NMR spectra are in agreement with the literature data[17].

N-(4-methylbenzyl)-1-phenylethan-1-amine (3fa)



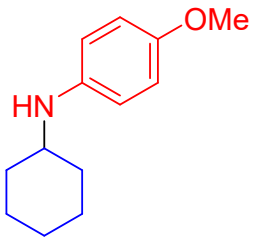
$Rh_2(OAc)_4$ (1.33 mg, 3.0 μmol, 1 mol%), 4-methylbenzaldehyde (35.5 μL, 0.30 mmol, 100 mol%) and 1-phenylethylamine (40.7 μL, 0.32 mmol, 105 mol%) were charged into a glass vial in a 10 mL stainless steel autoclave. 113 μL of THF was added and the autoclave was sealed, flushed three times with 5 bar of syngas, and then charged with 10 bar of syngas. The reactor was placed into an oil bath preheated to 100°C. After 24 h of heating, the reactor was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH_2Cl_2; in order to get rid of catalyst reaction mixture was passed through a small pad of silica gel; combined solvents were removed on a rotary evaporator. NMR yield of N-(4-methylbenzyl)-1-phenylethan-1-amine was 94%. Target product was purified by flash chromatograph InterChim PuriFlash, dry loading, gradient elution was applied (hexane/ethyl acetate/triethylamine; 10:1:0.1 → 0:1:0 (pure ethyl acetate)); R_f=0.3. Yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 – 7.34 (m, 4H), 7.34 – 7.27 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 3.84 (q, *J* = 6.5 Hz, 1H), 3.67 (d, *J* = 13.0 Hz, 1H), 3.59 (d, *J* = 13.0 Hz, 1H), 2.37 (s, 3H), 1.77 (br. s, 1H), 1.40 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 145.6, 137.6, 136.5, 129.2, 128.6, 128.2, 127.0, 126.8, 57.5, 51.4, 24.6, 21.2.

NMR spectra are in agreement with the literature data[18].

N-cyclohexyl-4-methoxyaniline (3bl)



$Rh_2(OAc)_4$ (1.50 mg, 3.4 μmol, 1 mol%), cyclohexanone (35.1 μL, 0.34 mmol, 100 mol%) and 4-methoxyaniline (43.8 mg, 0.36 mmol, 105 mol%) were charged into a glass vial in a 10 mL stainless steel autoclave. 128 μL of THF was added and the autoclave was sealed, flushed three times with 5 bar of syngas, and then charged with 10 bar of syngas. The reactor was placed into an oil bath preheated to 100°C. After 24 h of heating, the reactor was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH_2Cl_2; in order to get rid of catalyst reaction mixture was passed through a small pad of silica gel; combined solvents were removed on a rotary evaporator. NMR yield of N-cyclohexyl-4-methoxyaniline was 98%. Target product was purified by column chromatography, hexane/ethyl acetate; 5:1; R_f=0.55. Yellow solid. M. p.: 42–44°C (lit. 43–44°C)[19].

$Rh_2(OAc)_4$ (1.0 mg, 2.3 μmol, 1 mol%), cyclohexanone (23.7 μL, 0.23 mmol, 100 mol%) and 4-methoxyaniline (29.6 mg, 0.24 mmol, 105 mol%) were charged into a glass vial in a 10 mL stainless steel autoclave. 62 μL of THF was added and the autoclave was sealed, flushed three times with 5 bar of syngas, and then charged with 3 bar of syngas. The reactor was placed into an oil bath preheated to 100°C. After 24 h of heating, the reactor was cooled to the room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH_2Cl_2; in order to get rid of catalyst reaction mixture was passed through a small pad of silica gel; combined solvents were removed on a rotary evaporator. NMR yield of N-cyclohexyl-4-methoxyaniline was 55%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (d, *J* = 8.9 Hz, 2H), 6.58 (d, *J* = 8.9 Hz, 2H), 3.75 (s, 3H), 3.17 (tt, *J* = 10.1, 3.6 Hz, 2H, C**H** + N**H**), 2.13 – 2.01 (m, 2H), 1.81 – 1.72 (m, 2H), 1.70 – 1.61 (m, 1H), 1.46 – 1.07 (m, 5H).

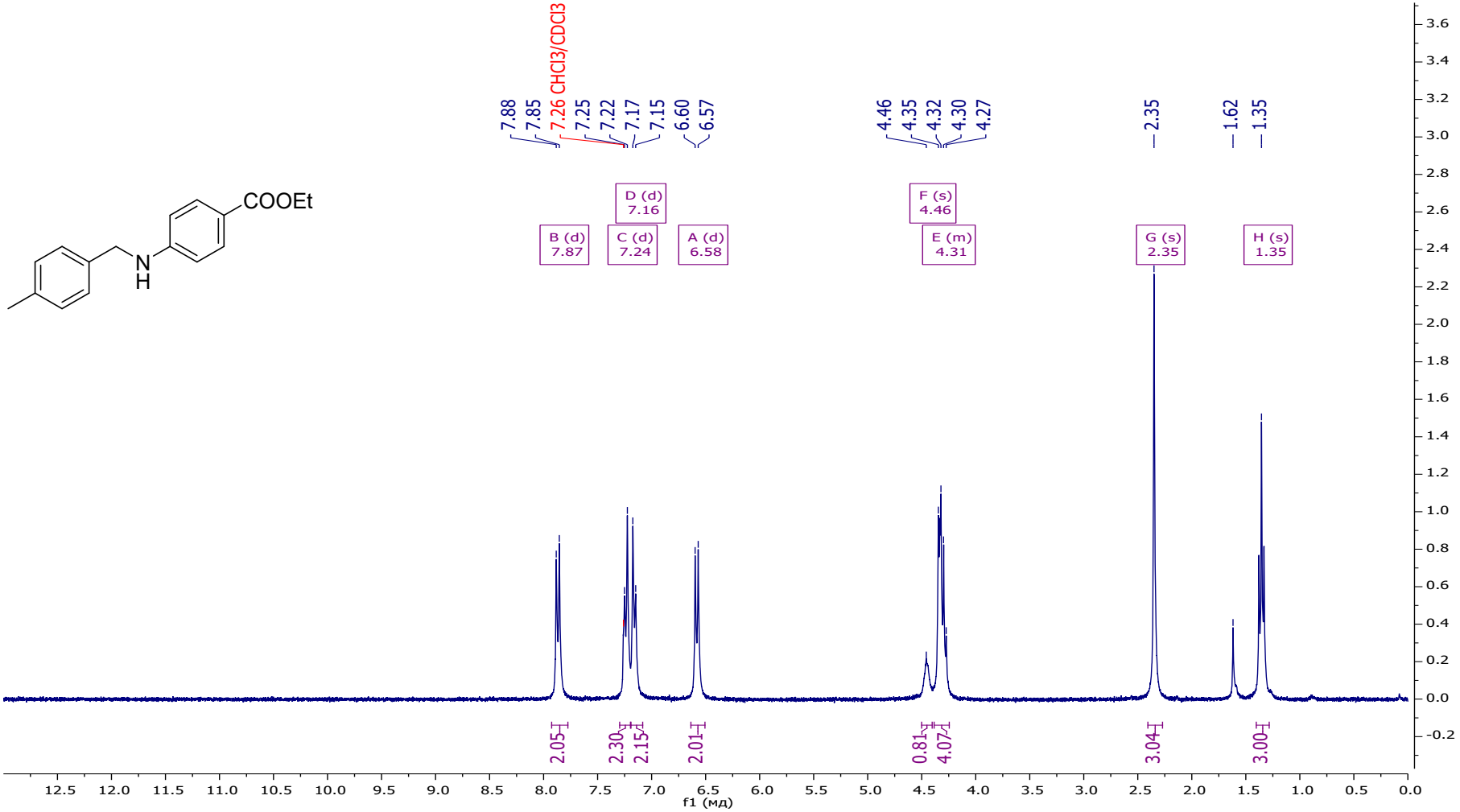
^{13}C NMR (101 MHz, $CDCl_3$): δ 151.3, 141.7, 115.0, 114.9, 55.9, 52.9, 33.7, 26.1, 25.2.

NMR spectra are in agreement with the literature data[19].

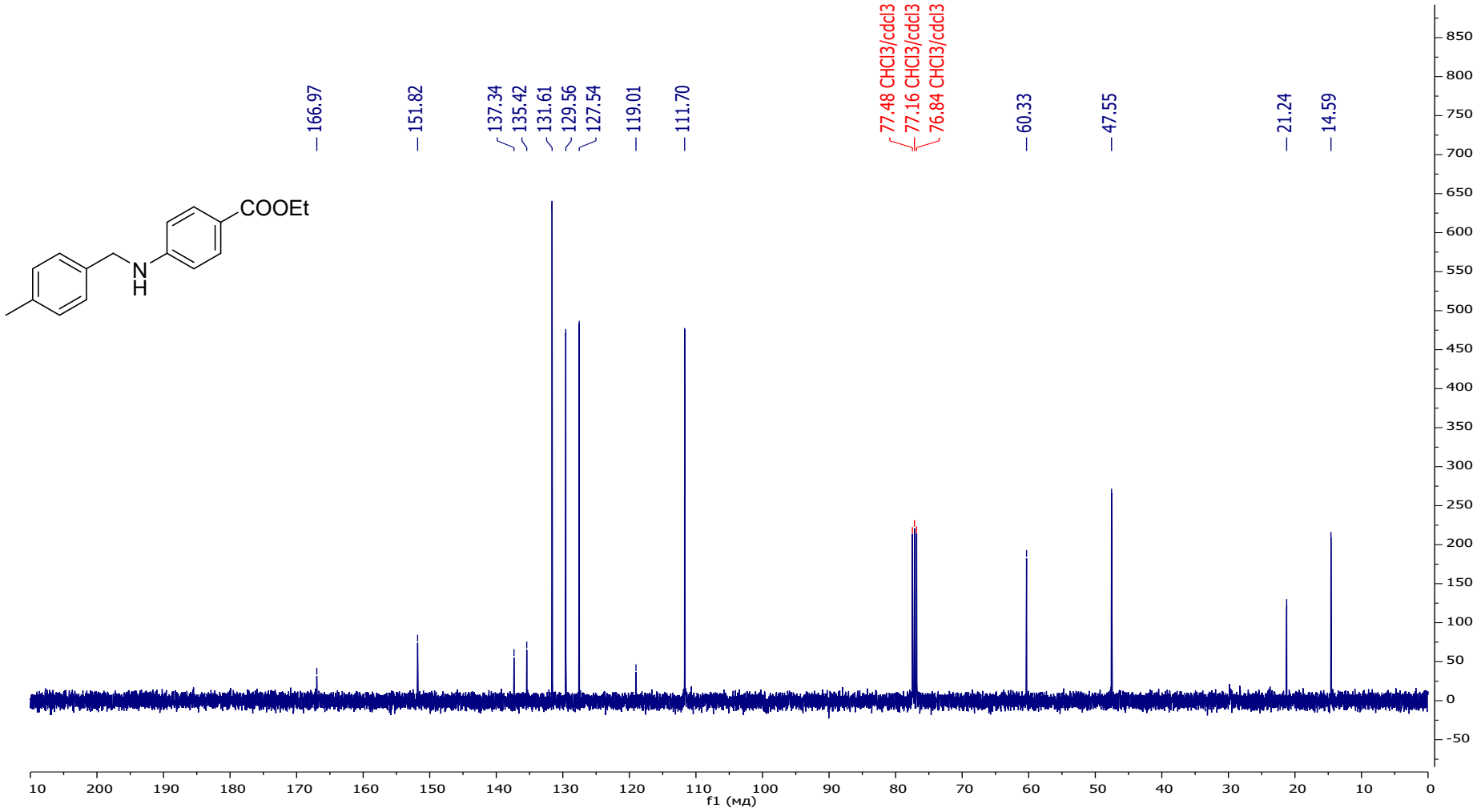
3. ^{1}H, ^{13}C, ^{19}F NMR spectra of obtained compounds

3.1. NMR spectra of amines

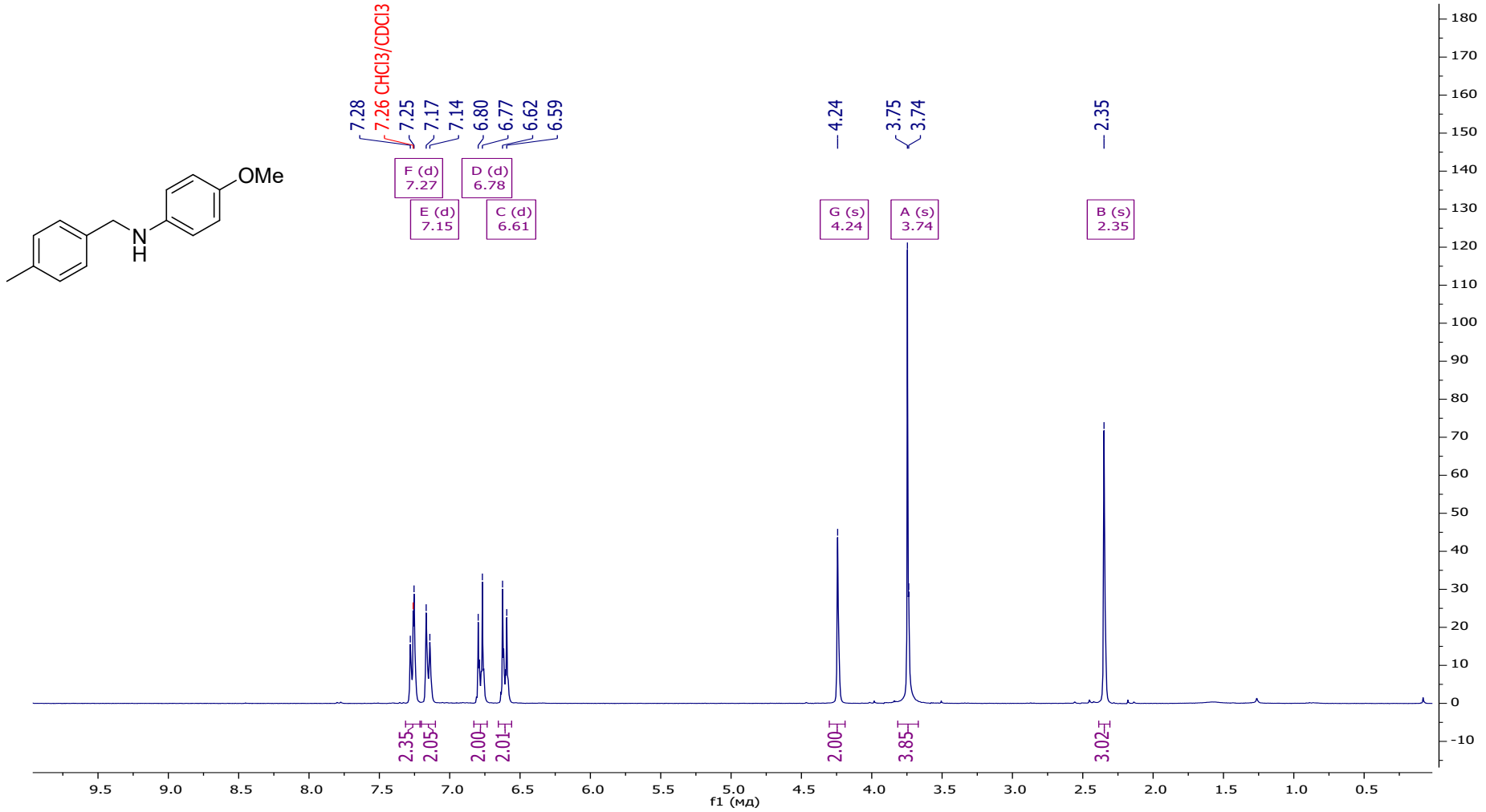
Ethyl-4-[(4-methylbenzyl)amino]benzoate (^{1}H NMR, $CDCl_3$, 300 MHz), (3aa)



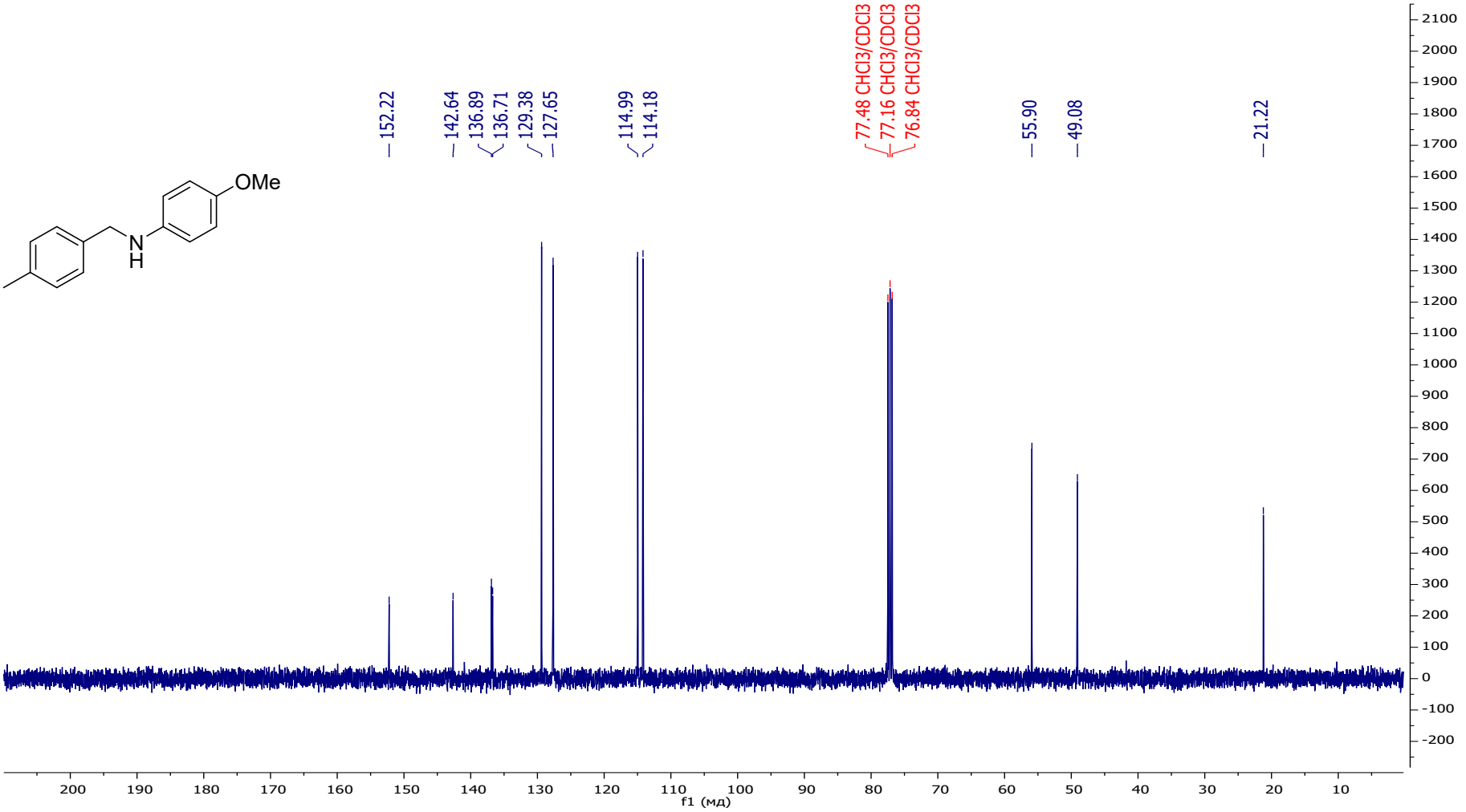
Ethyl-4-[(4-methylbenzyl)amino]benzoate (^{13}C NMR, $CDCl_3$, 75 MHz), (3aa)



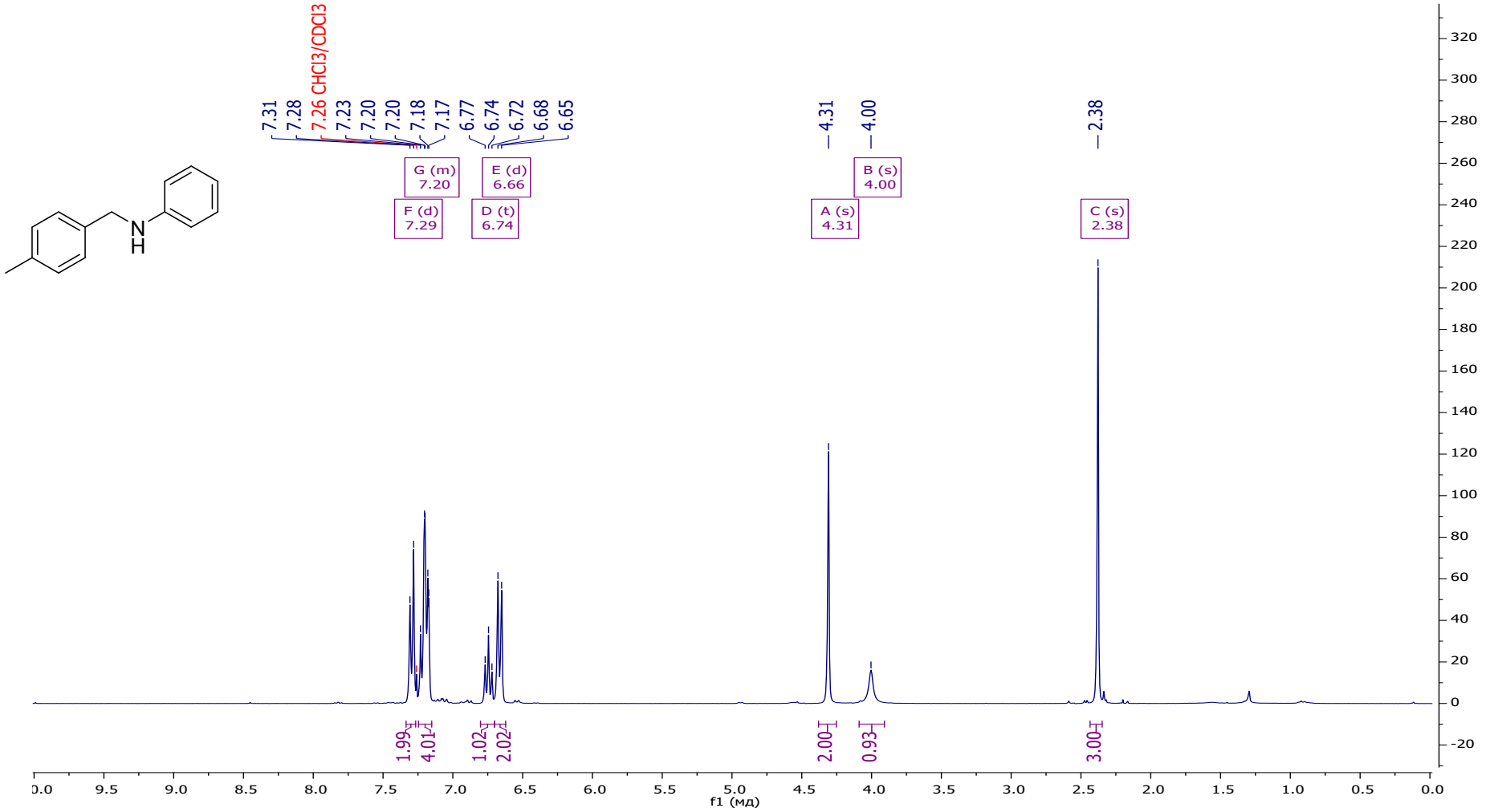
4-Methoxy-N-(4-methylbenzyl)aniline (^{1}H NMR, $CDCl_3$, 300 MHz), (3ba)



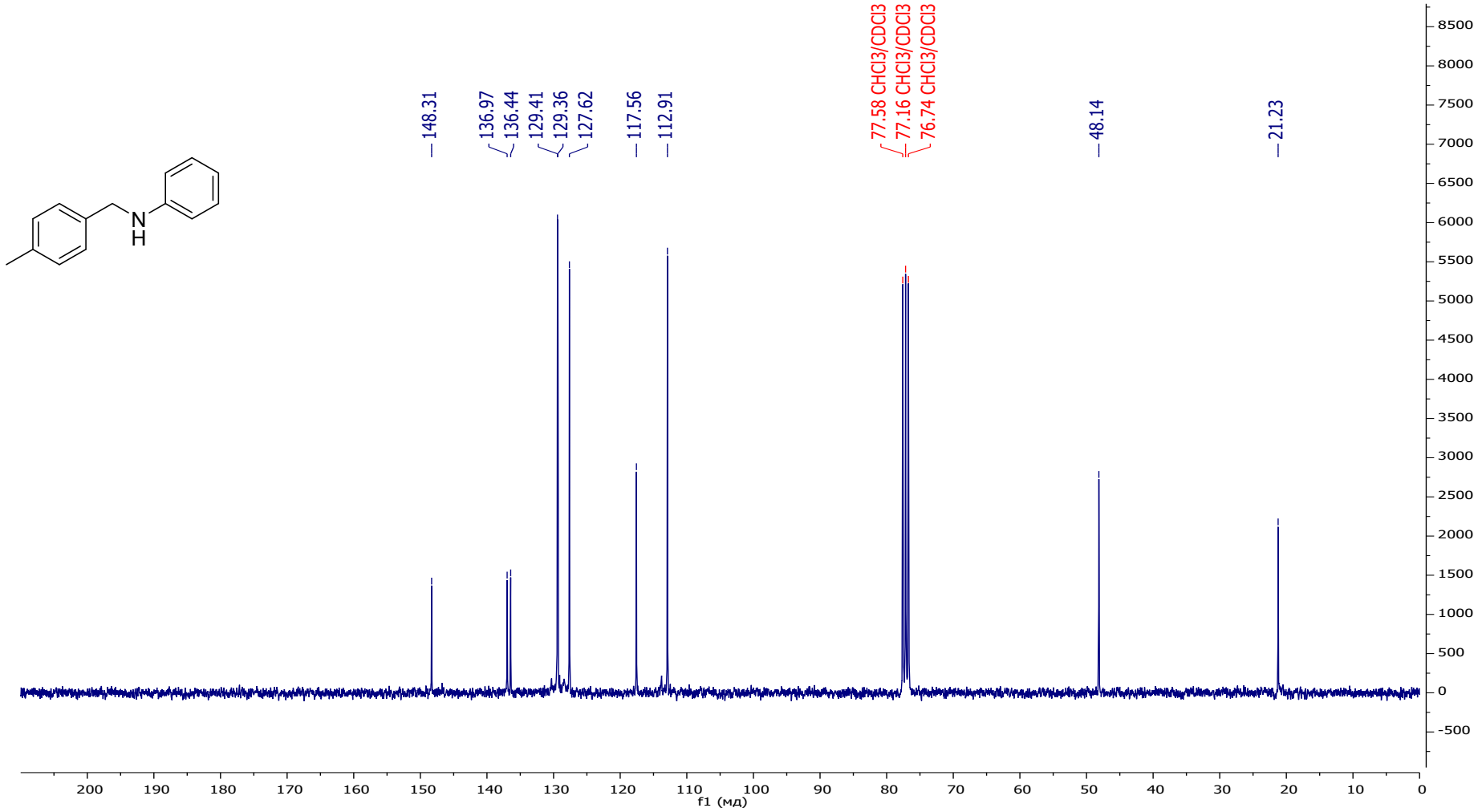
4-Methoxy-N-(4-methylbenzyl)aniline (^{13}C NMR, $CDCl_3$, 75 MHz), (3ba)



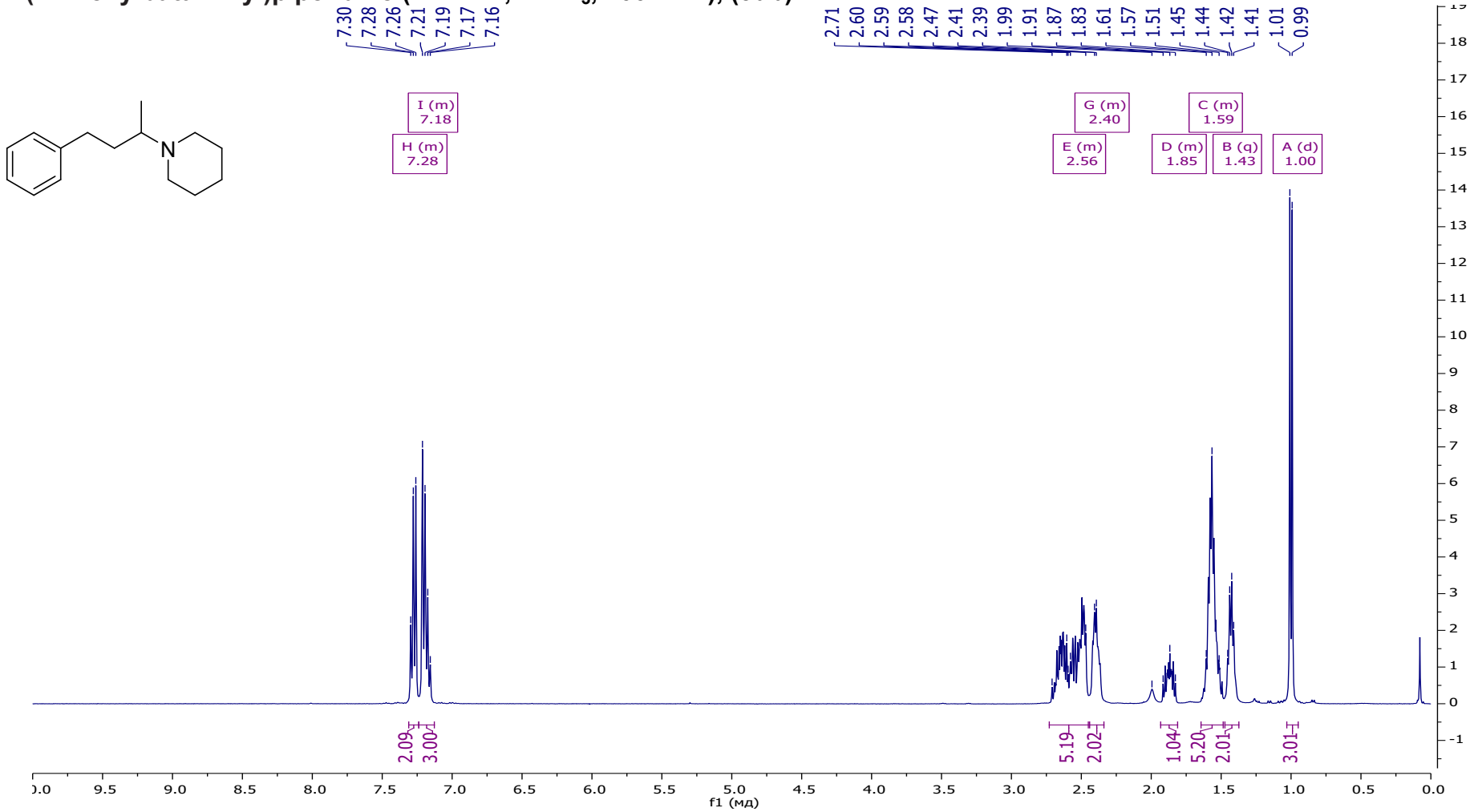
N-(4-methylbenzyl)aniline (^{1}H NMR, $CDCl_3$, 300 MHz), (3ca)



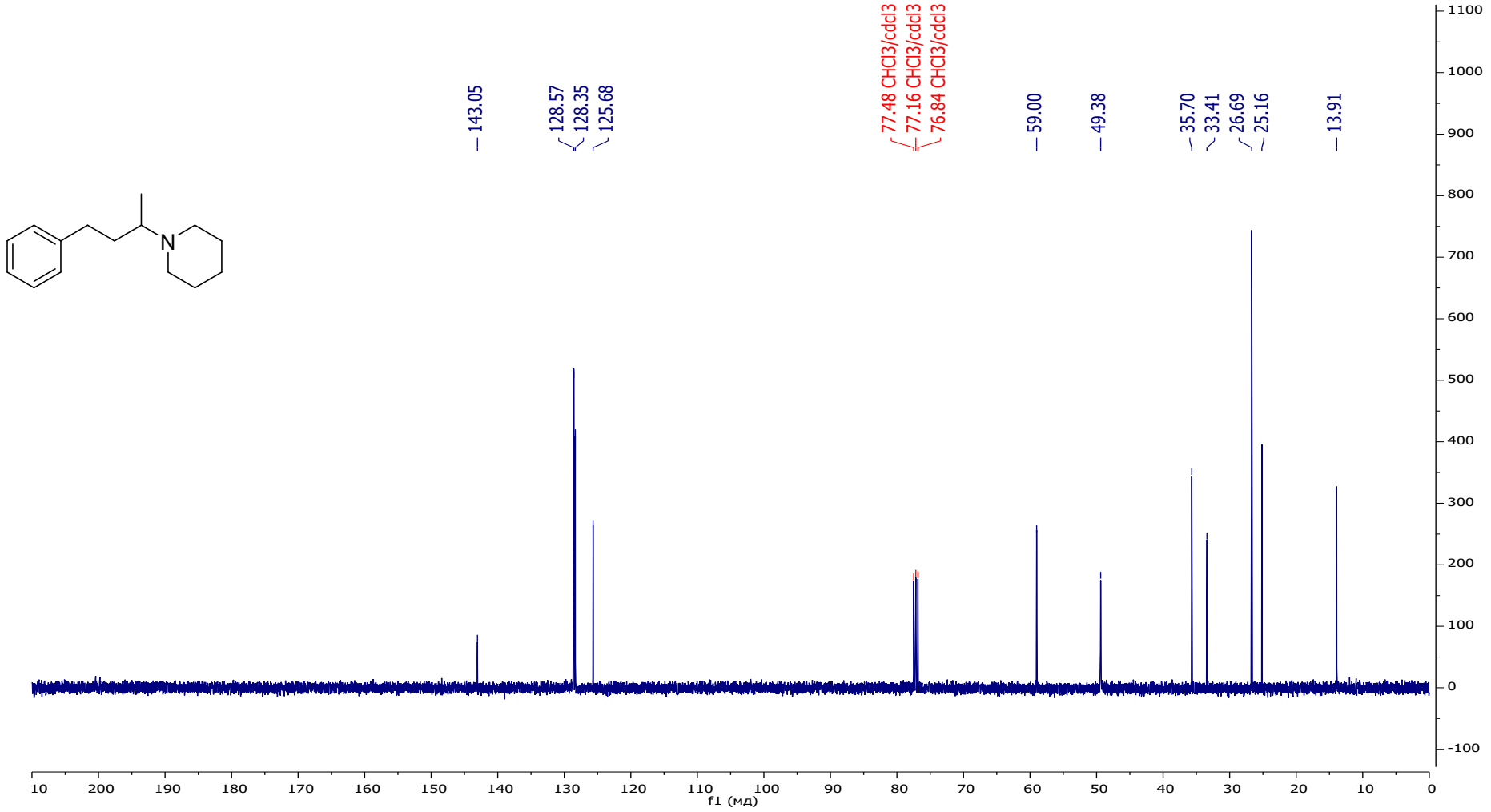
N-(4-methylbenzyl)aniline (^{13}C NMR, $CDCl_3$, 75 MHz), (3ca)



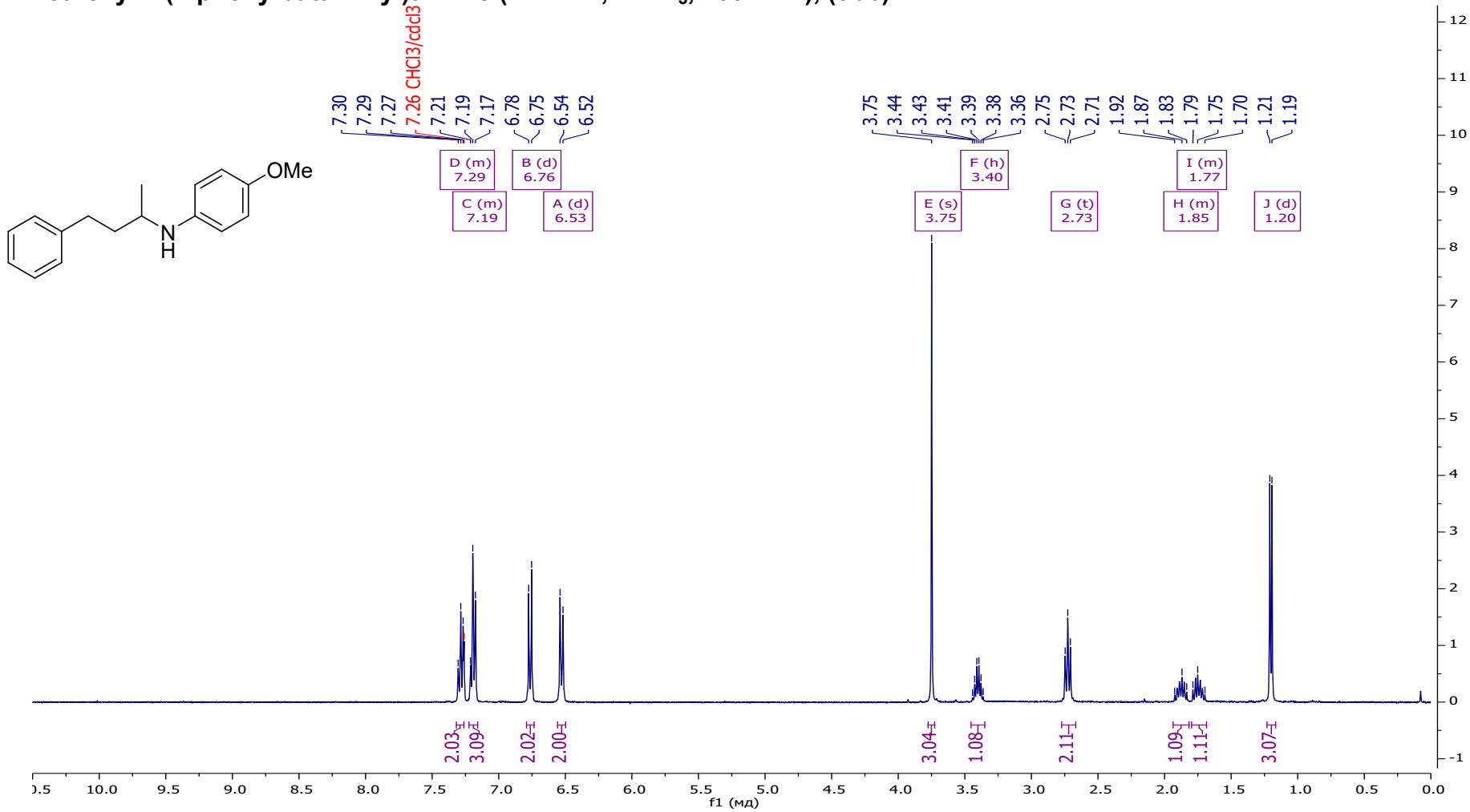
1-(4-Phenylbutan-2-yl)piperidine (^{1}H NMR, $CDCl_3$, 400 MHz), (3db)



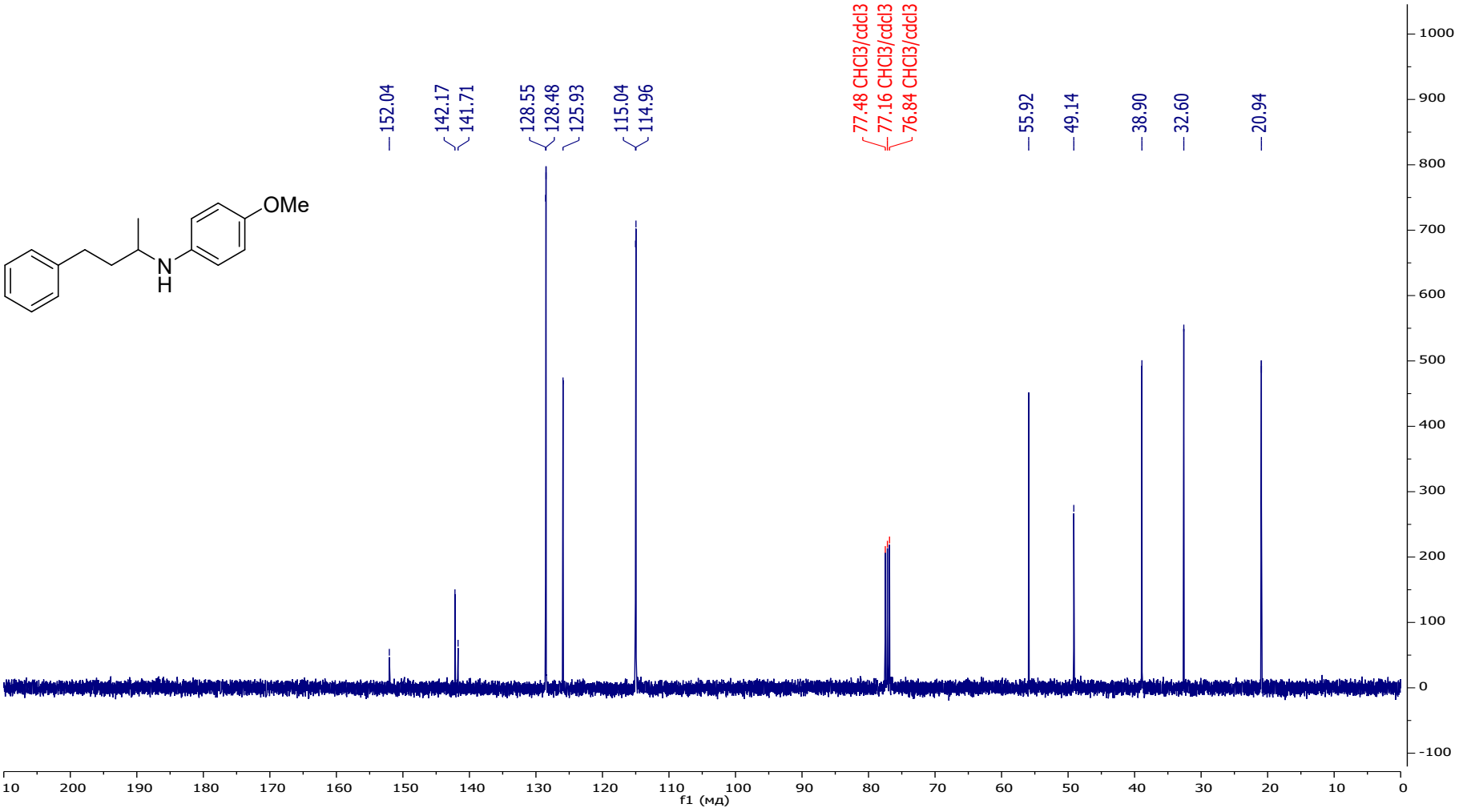
1-(4-Phenylbutan-2-yl)piperidine (^{13}C NMR, $CDCl_3$, 101 MHz), (3db)



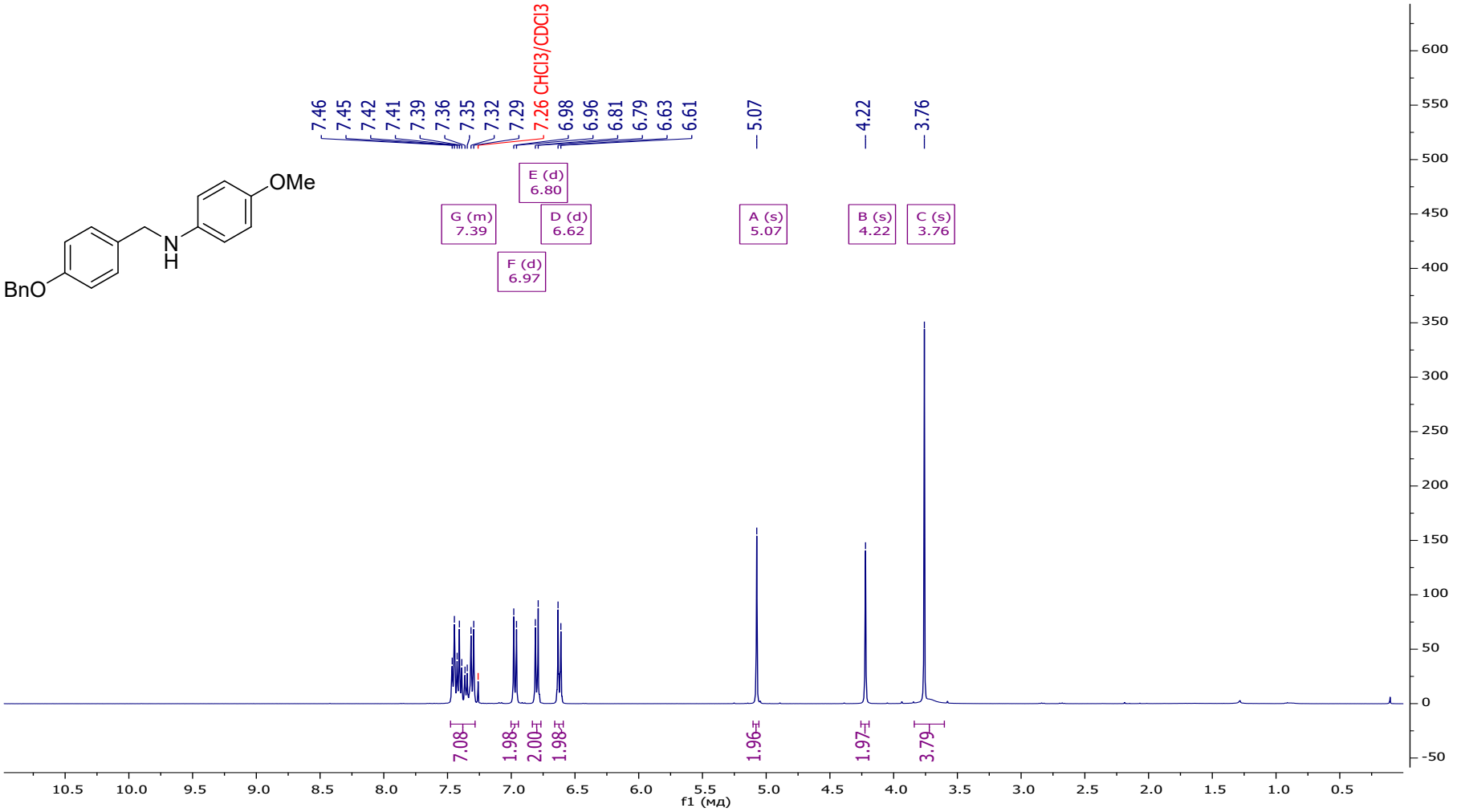
4-Methoxy-N-(4-phenylbutan-2-yl)aniline (^{1}H NMR, $CDCl_3$, 400 MHz), (3bb)



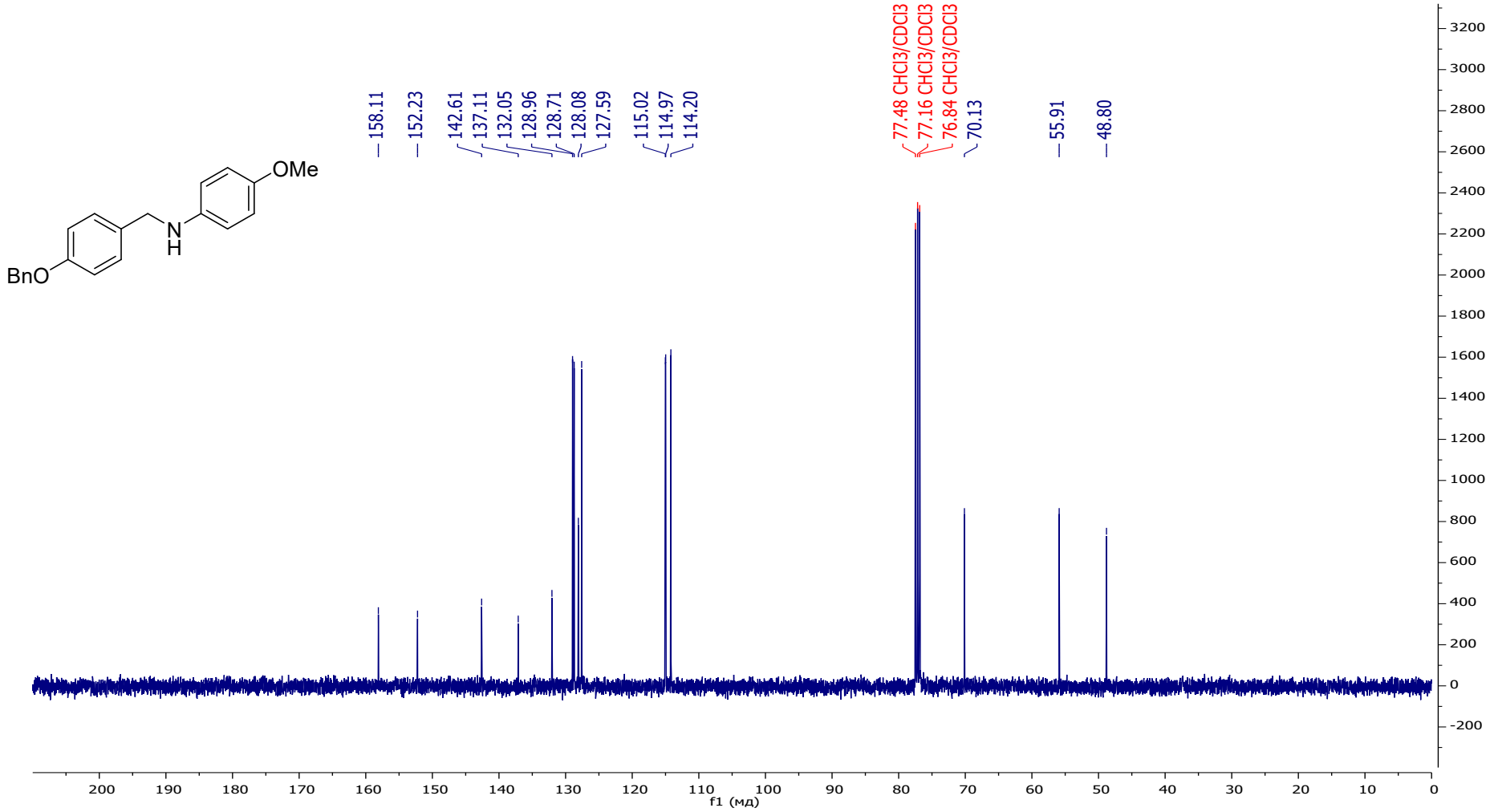
4-Methoxy-N-(4-phenylbutan-2-yl)aniline (^{13}C NMR, $CDCl_3$, 101 MHz), (3bb)



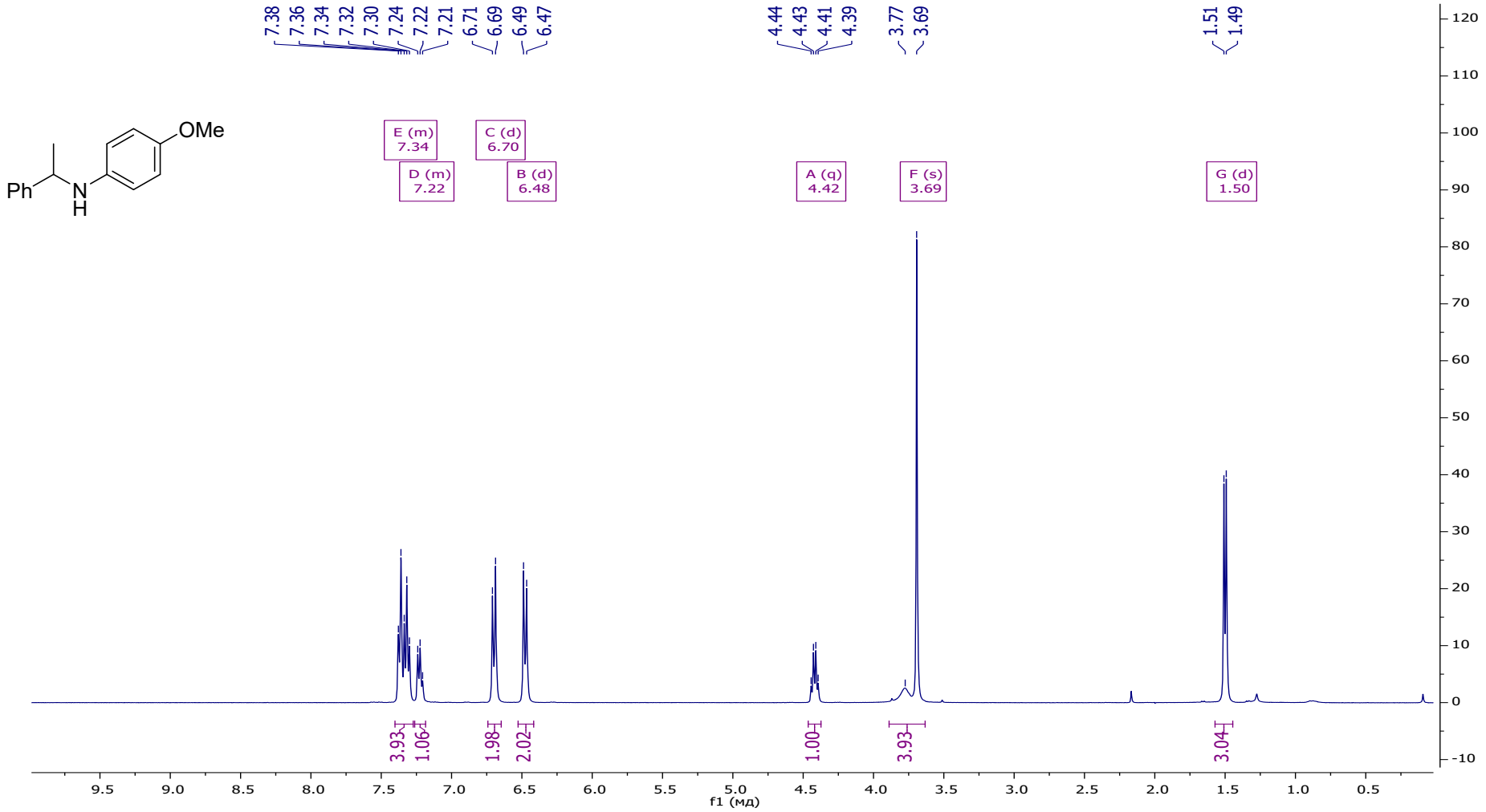
N-(4-(benzyloxy)benzyl)-4-methoxyaniline (^{1}H NMR, $CDCl_3$, 400 MHz), (3be)



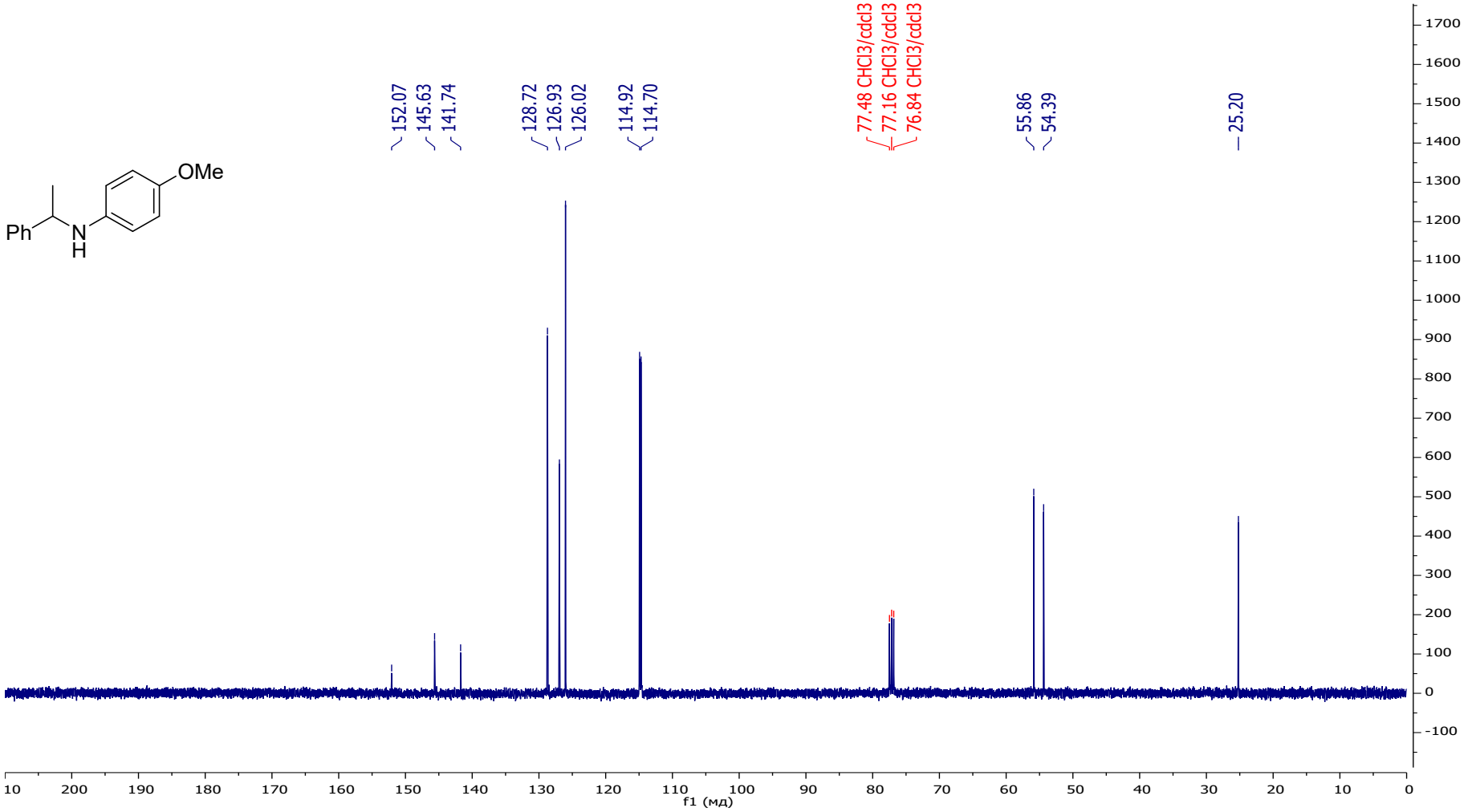
N-(4-(benzyloxy)benzyl)-4-methoxyaniline (^{13}C NMR, $CDCl_3$, 101 MHz), (3be)



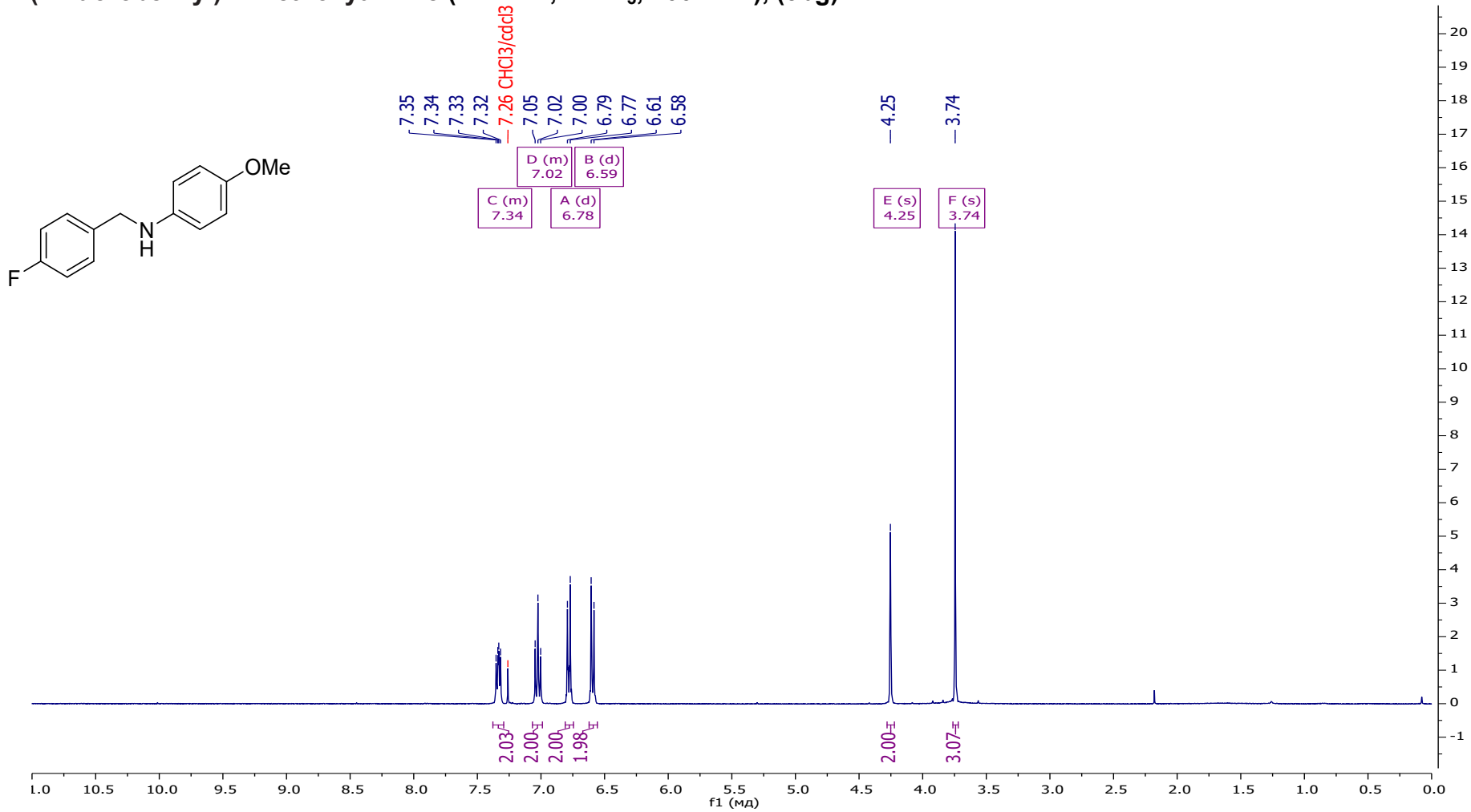
4-Methoxy-N-(1-phenylethyl)aniline (^{1}H NMR, $CDCl_3$, 400 MHz), (3bf)



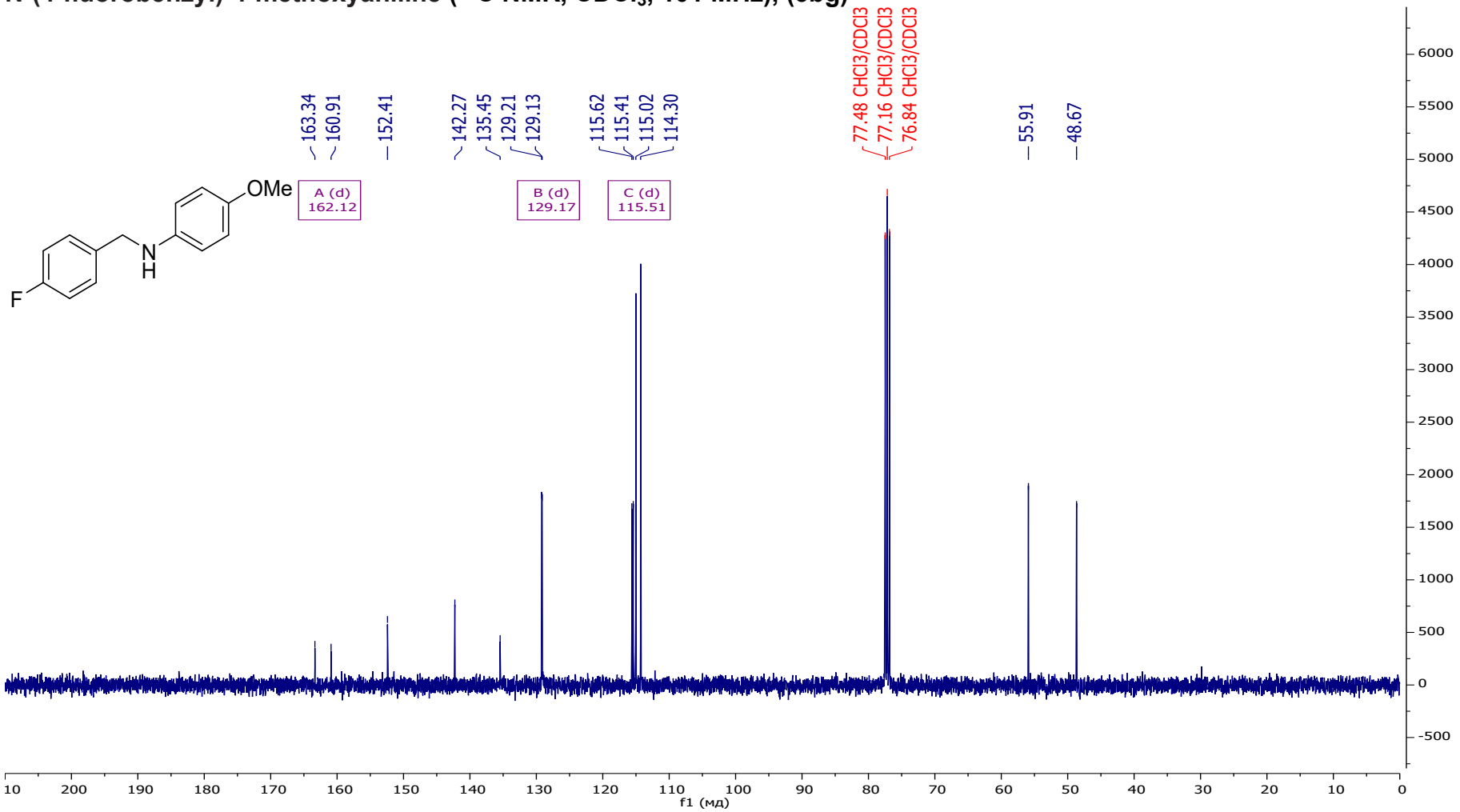
4-Methoxy-N-(1-phenylethyl)aniline (^{13}C NMR, $CDCl_3$, 101 MHz), (3bf)



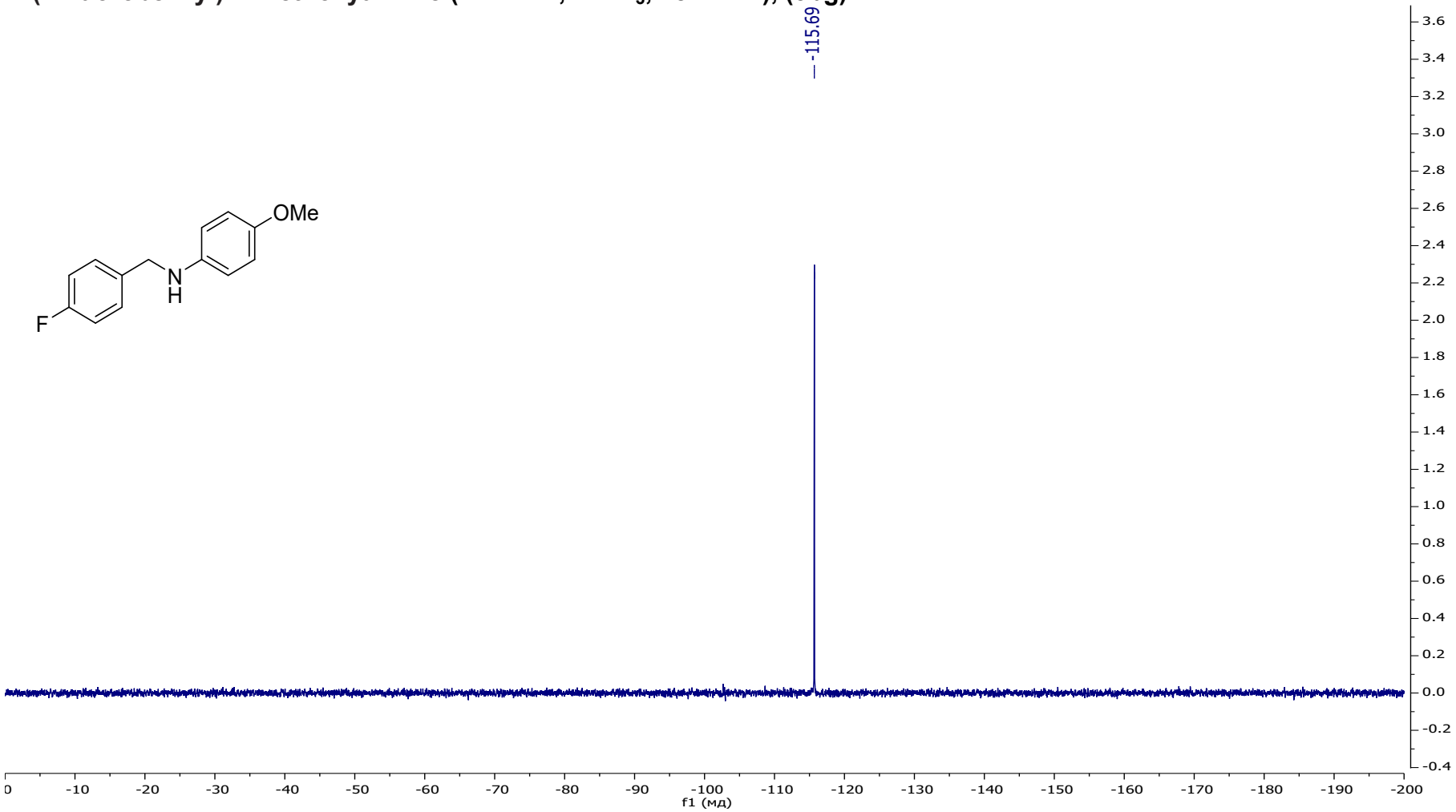
N-(4-fluorobenzyl)-4-methoxyaniline (^{1}H NMR, $CDCl_3$, 400 MHz), (3bg)



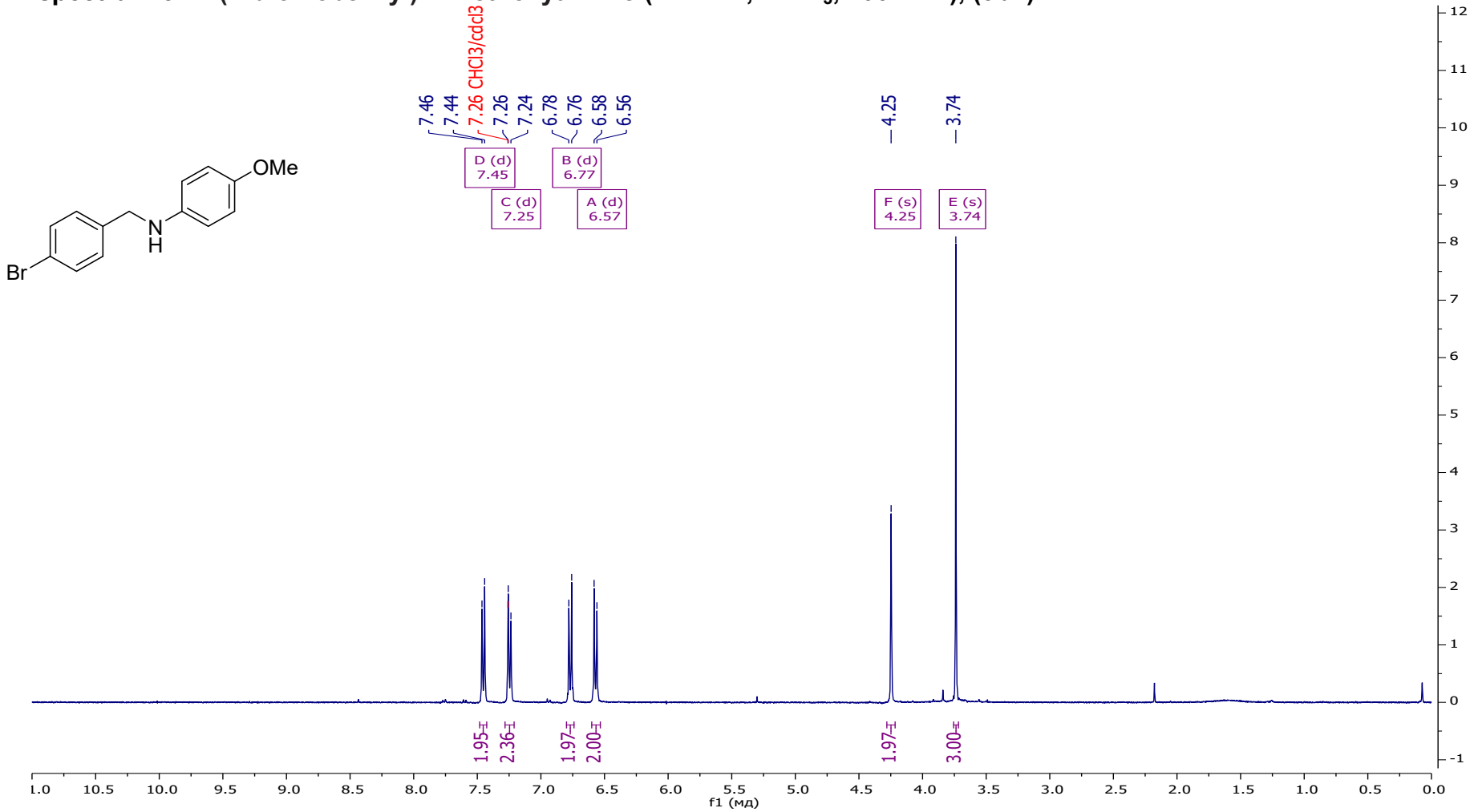
N-(4-fluorobenzyl)-4-methoxyaniline (^{13}C NMR, $CDCl_3$, 101 MHz), (3bg)



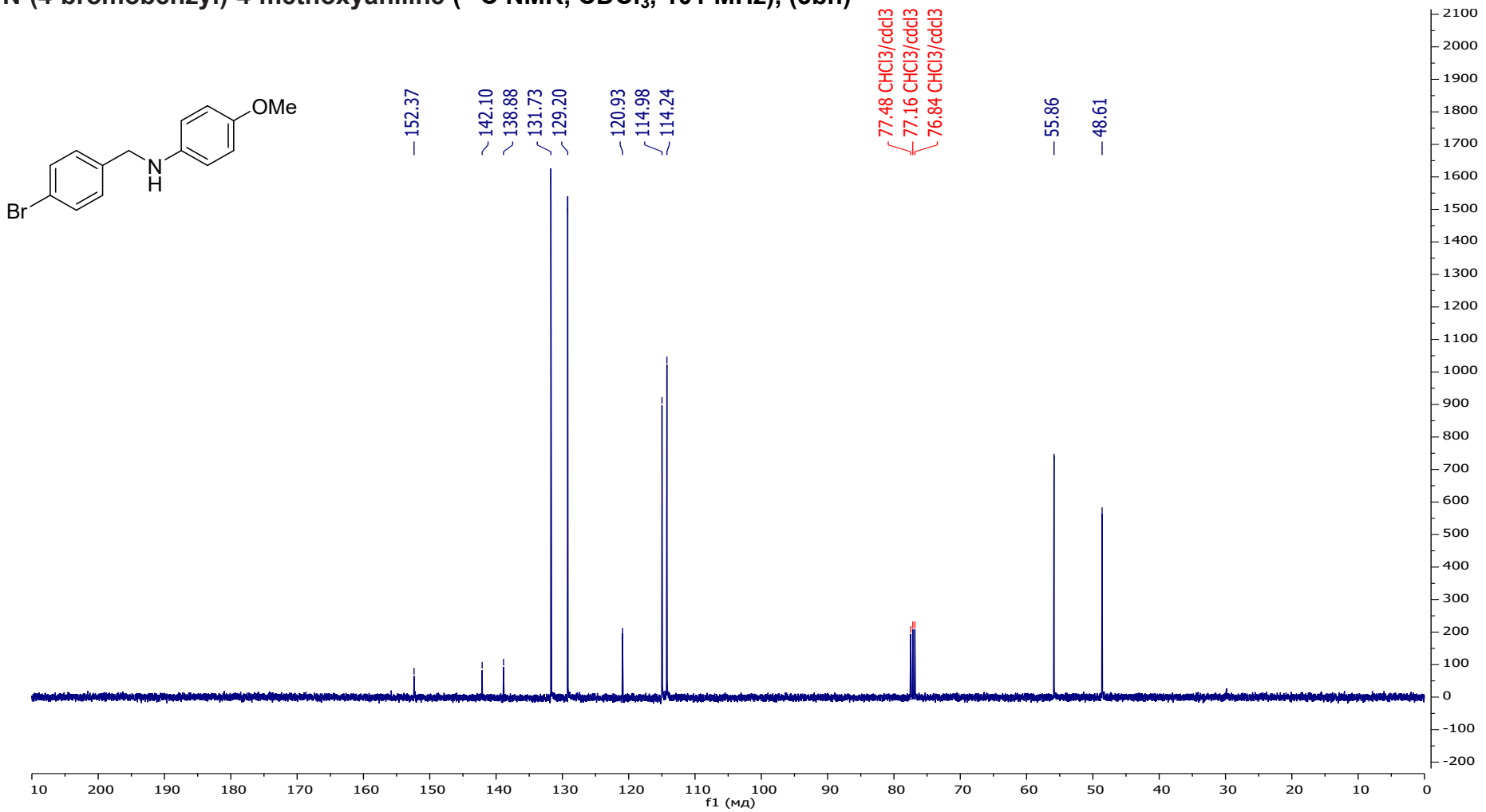
N-(4-fluorobenzyl)-4-methoxyaniline (^{19}F NMR, $CDCl_3$, 282 MHz), (3bg)



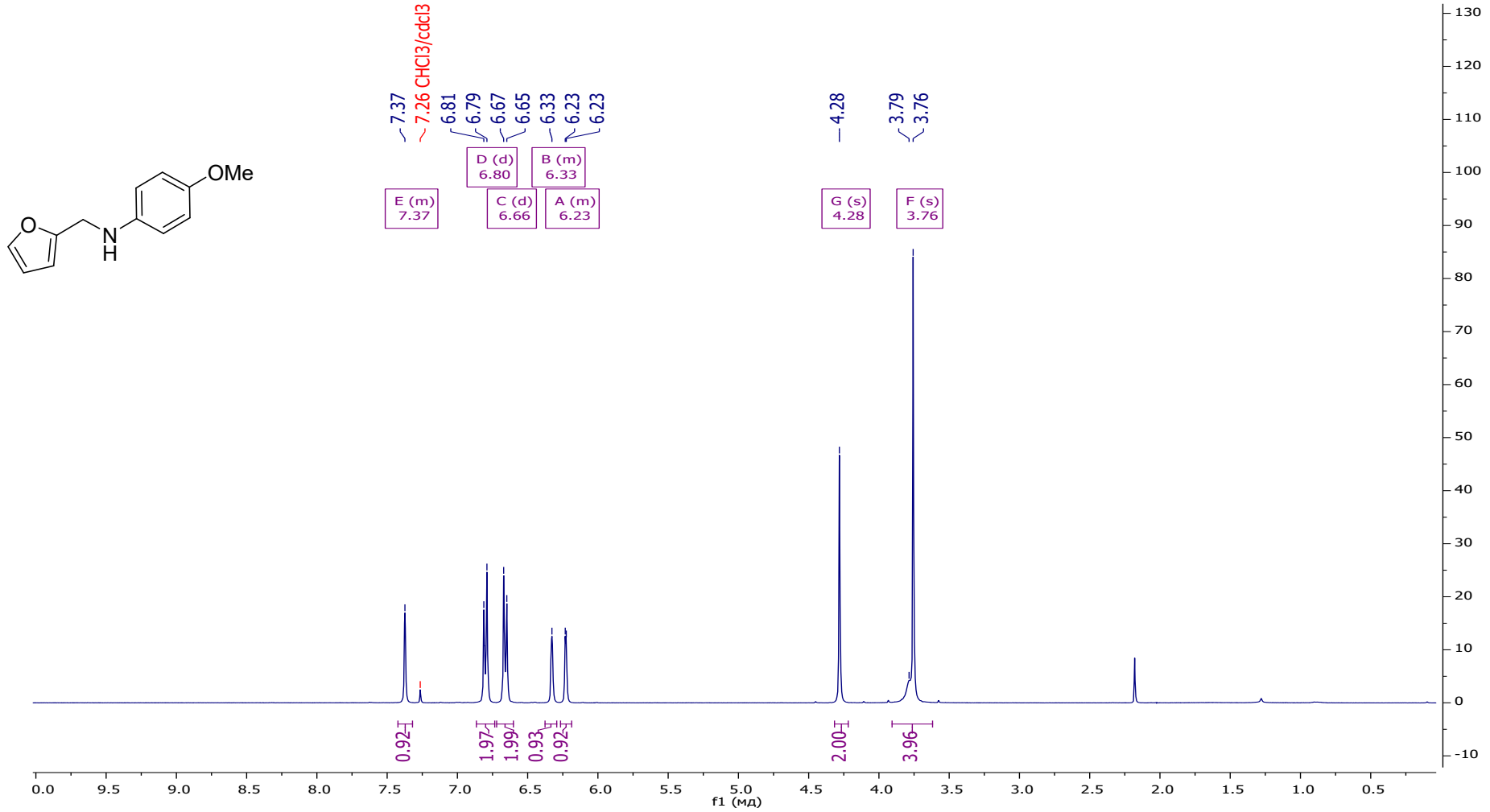
^{1}H spectrum of N-(4-bromobenzyl)-4-methoxyaniline (^{1}H NMR, $CDCl_3$, 400 MHz), (3bh)



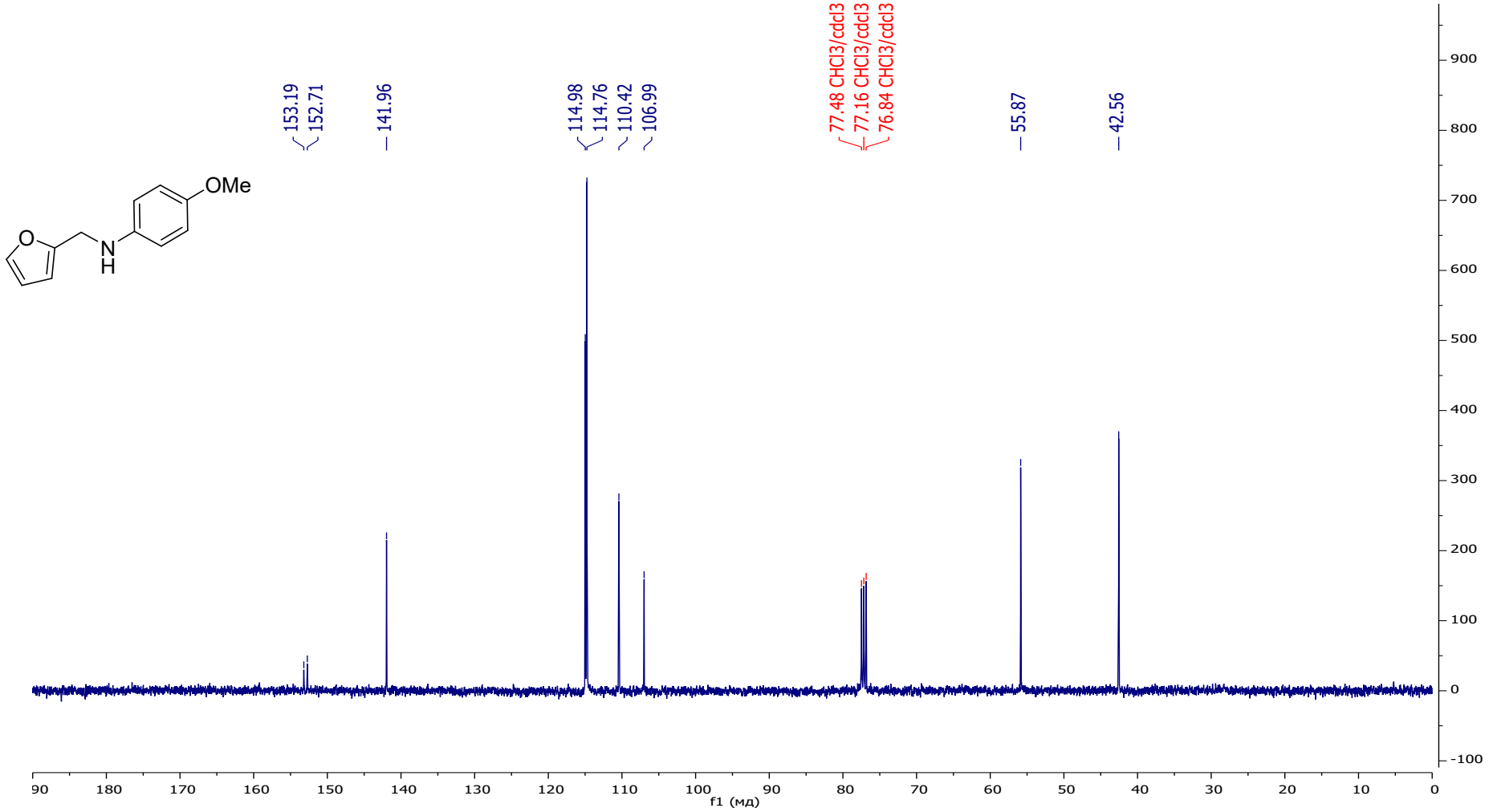
N-(4-bromobenzyl)-4-methoxyaniline (^{13}C NMR, $CDCl_3$, 101 MHz), (3bh)



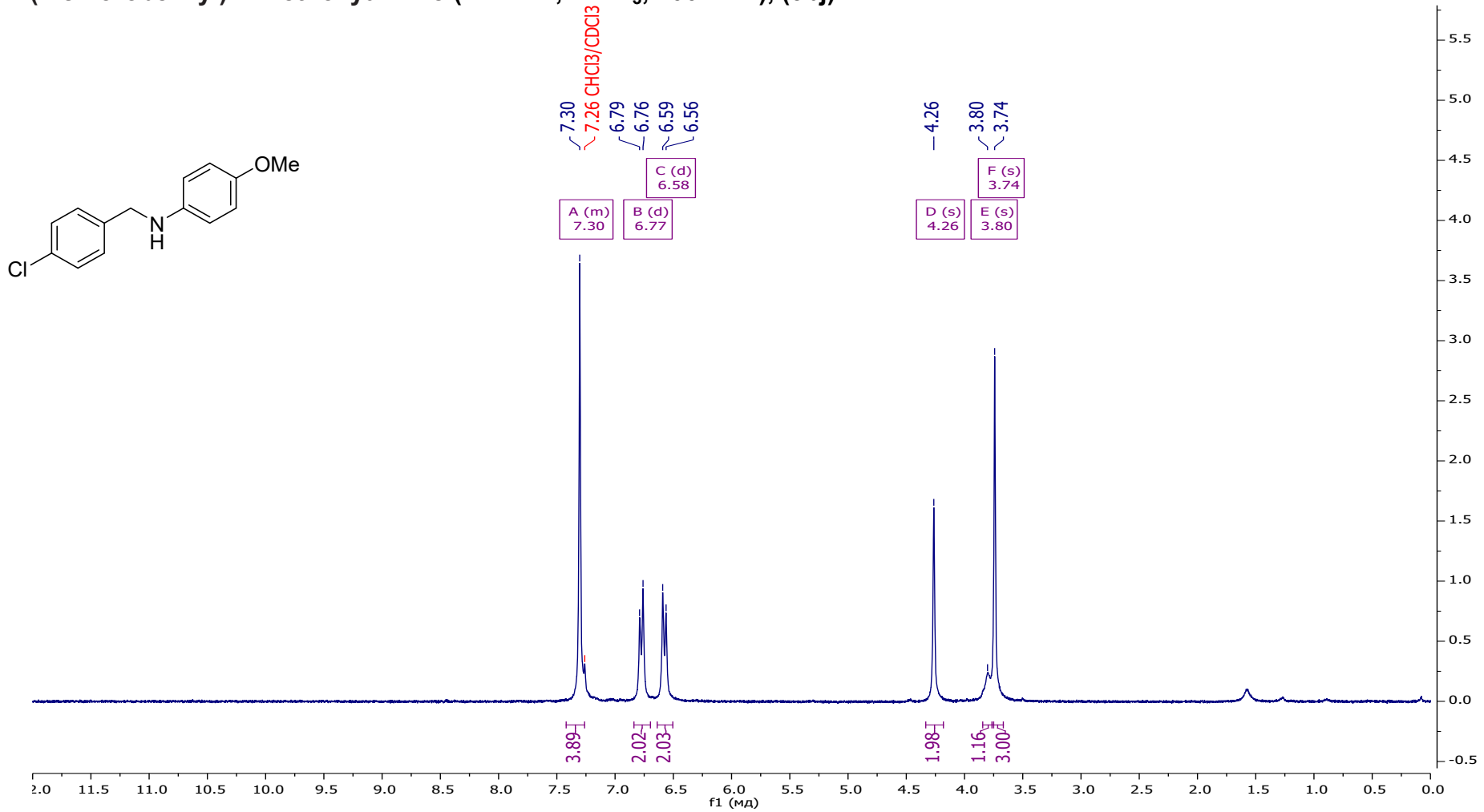
N-(furan-2-ylmethyl)-4-methoxyaniline (^{1}H NMR, $CDCl_3$, 400 MHz), (3bi)



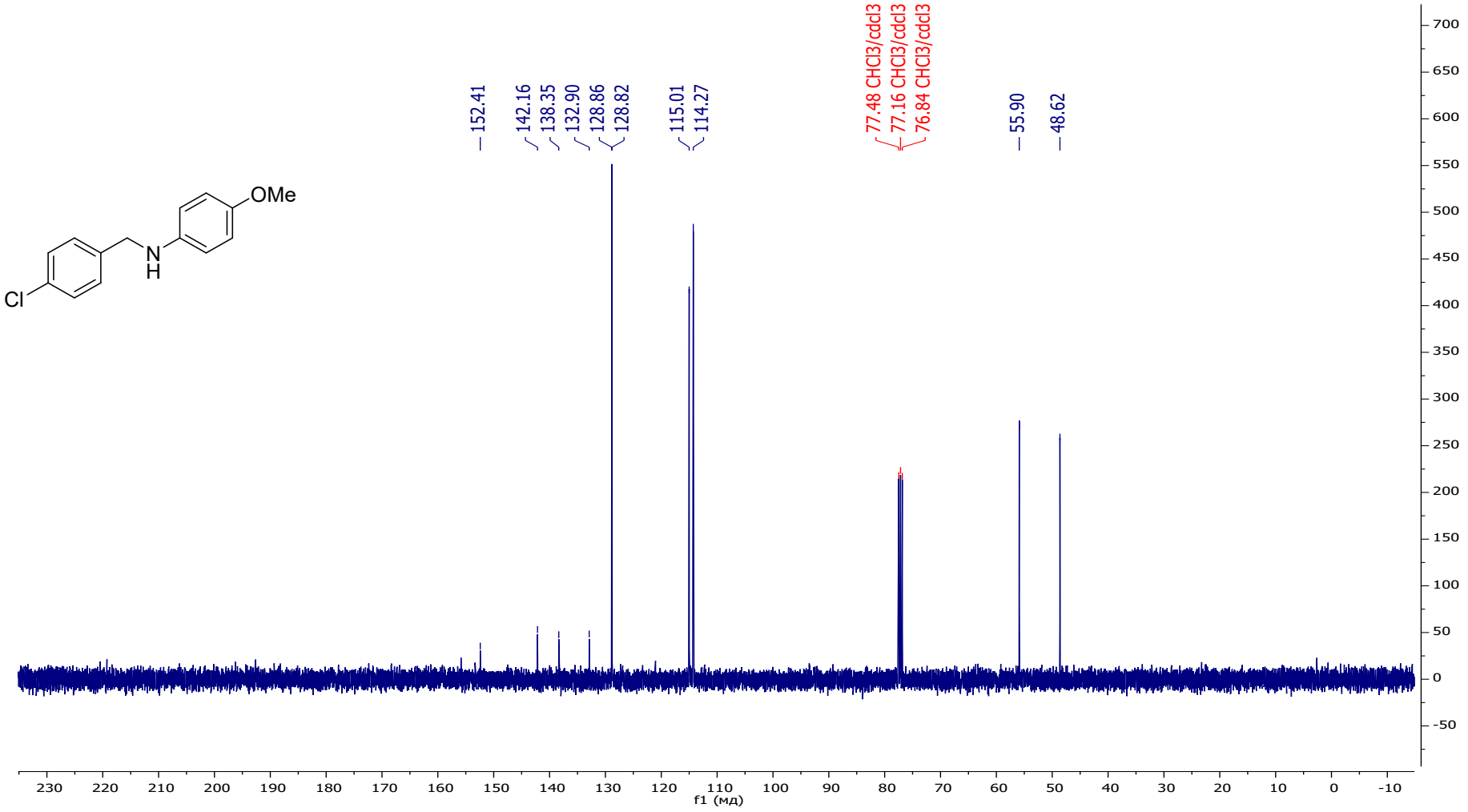
N-(furan-2-ylmethyl)-4-methoxyaniline (^{13}C NMR, $CDCl_3$, 101 MHz), (3bi)



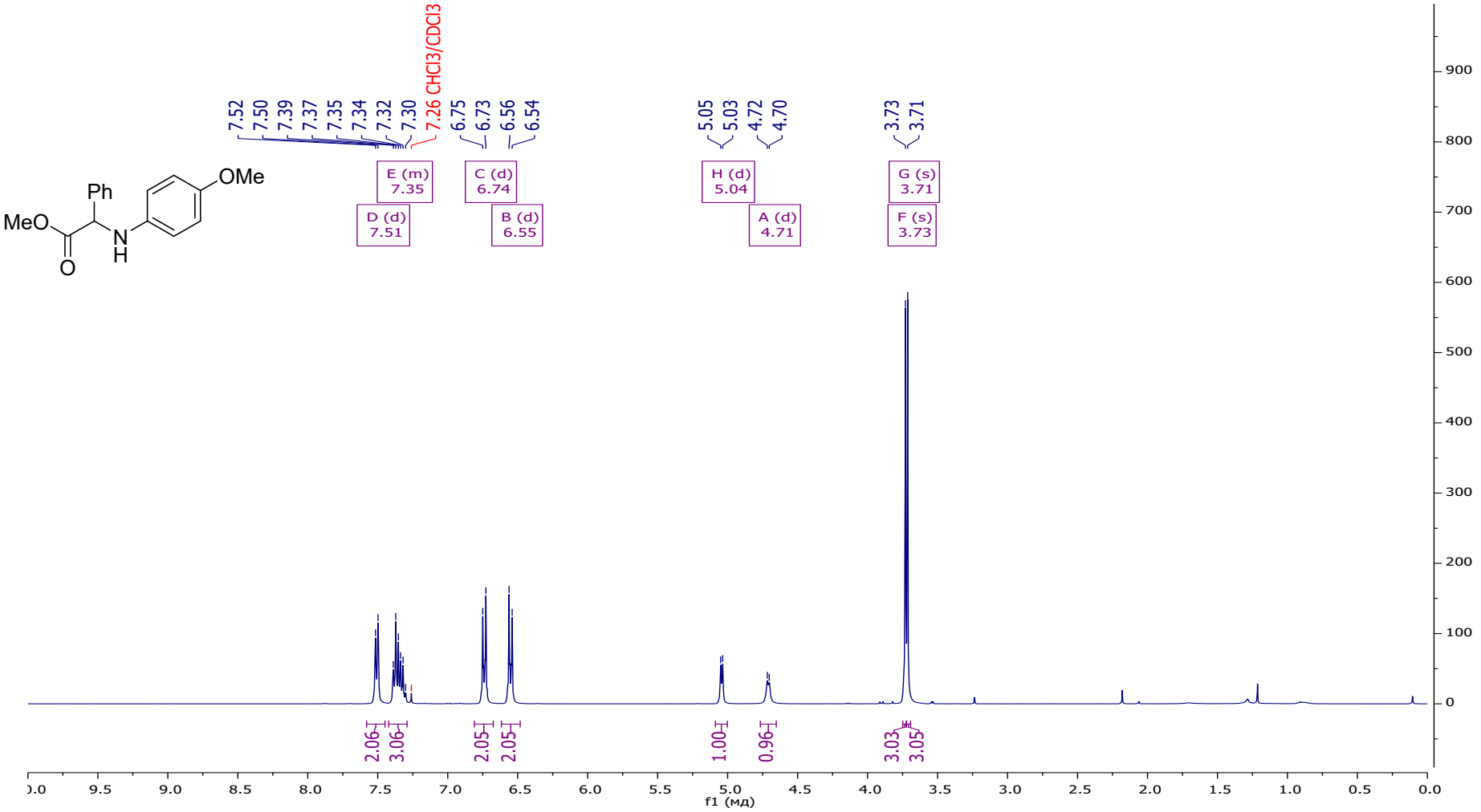
N-(4-chlorobenzyl)-4-methoxyaniline (^{1}H NMR, $CDCl_3$, 400 MHz), (3bj)



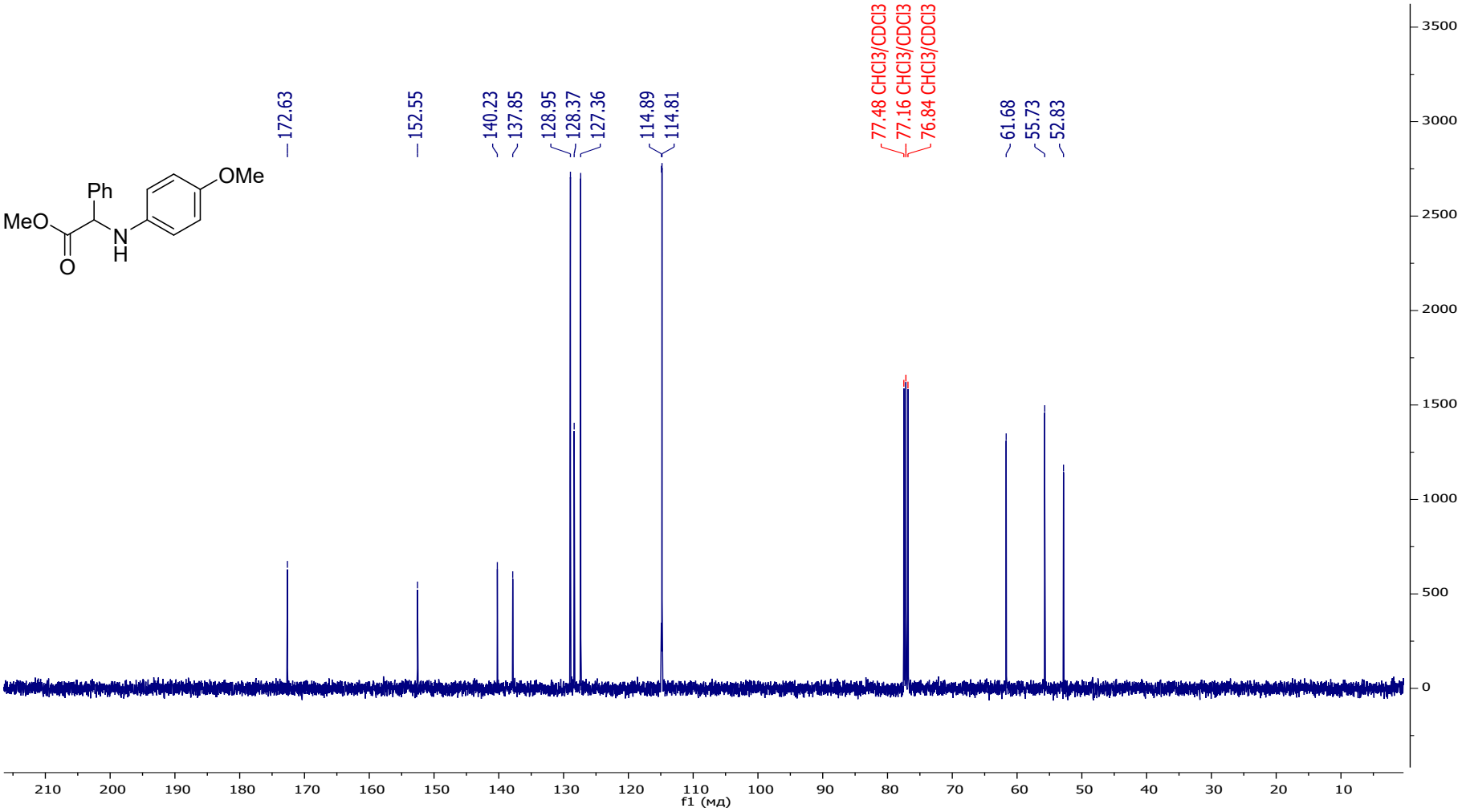
N-(4-chlorobenzyl)-4-methoxyaniline (^{13}C NMR, $CDCl_3$, 101 MHz), (3bj)



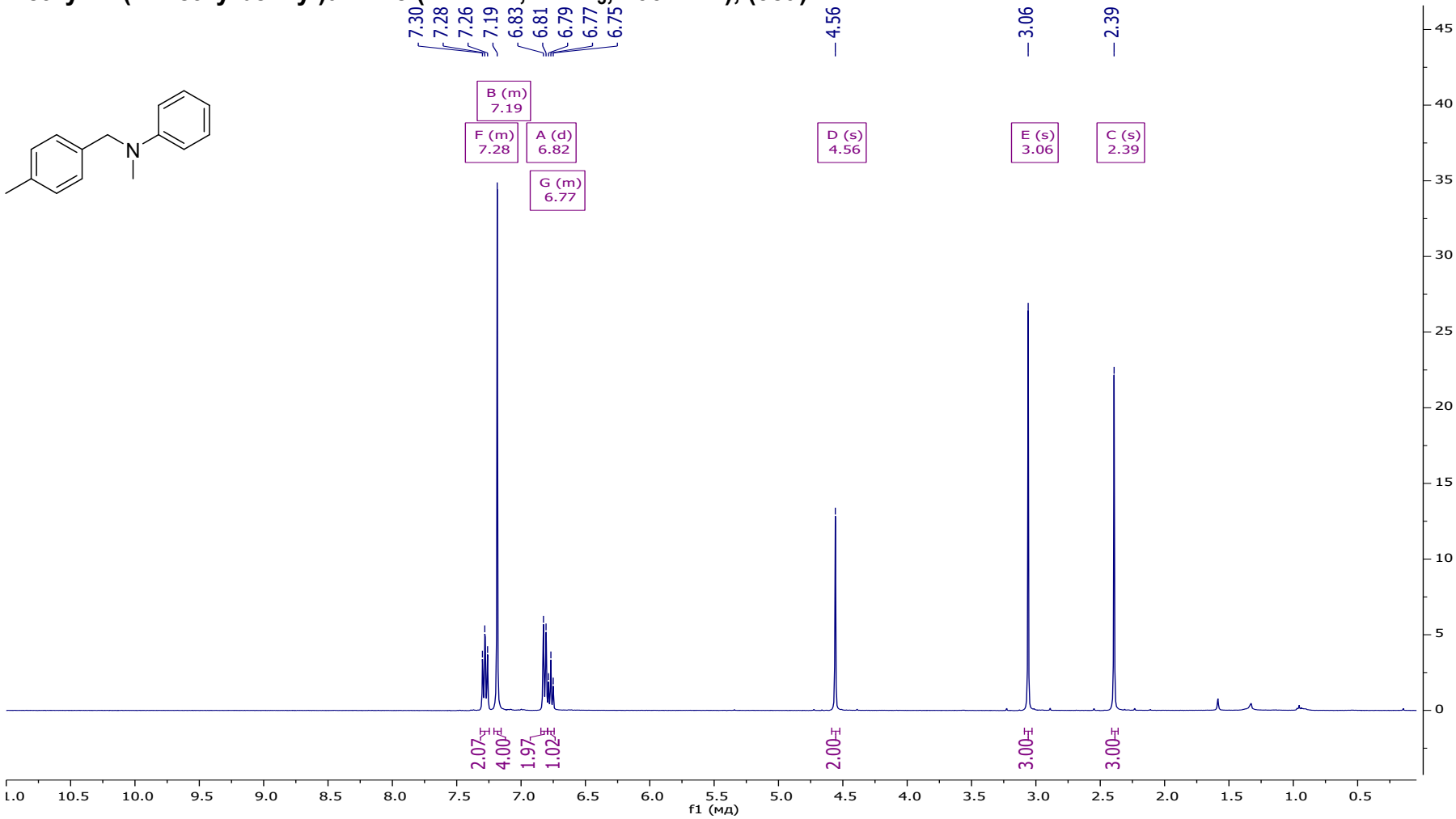
Methyl 2-((4-methoxyphenyl)amino)-2-phenylacetate (^{1}H NMR, $CDCl_3$, 400 MHz), (3bk)



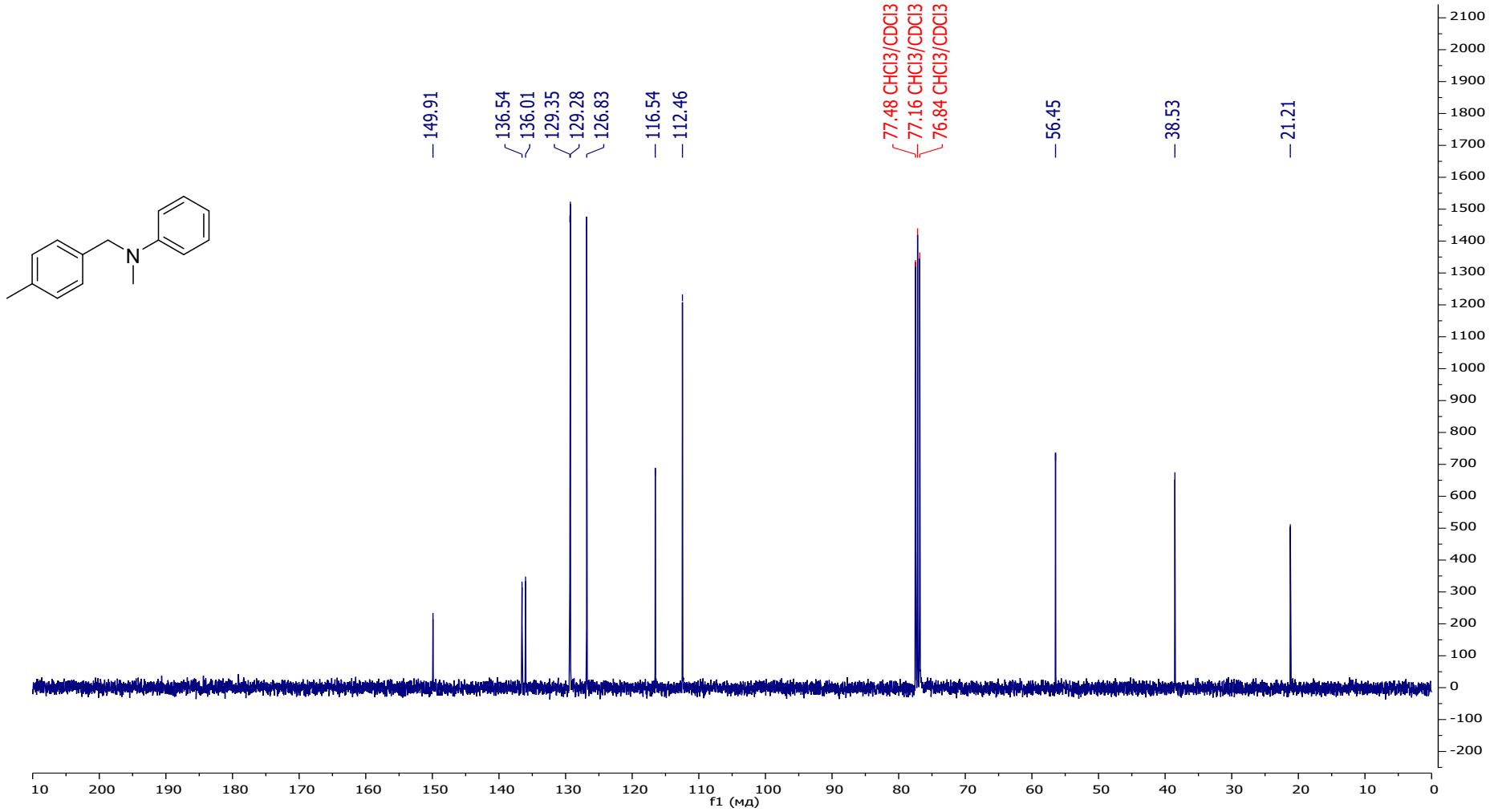
Methyl 2-((4-methoxyphenyl)amino)-2-phenylacetate (^{13}C NMR, $CDCl_3$, 101 MHz), (3bk)



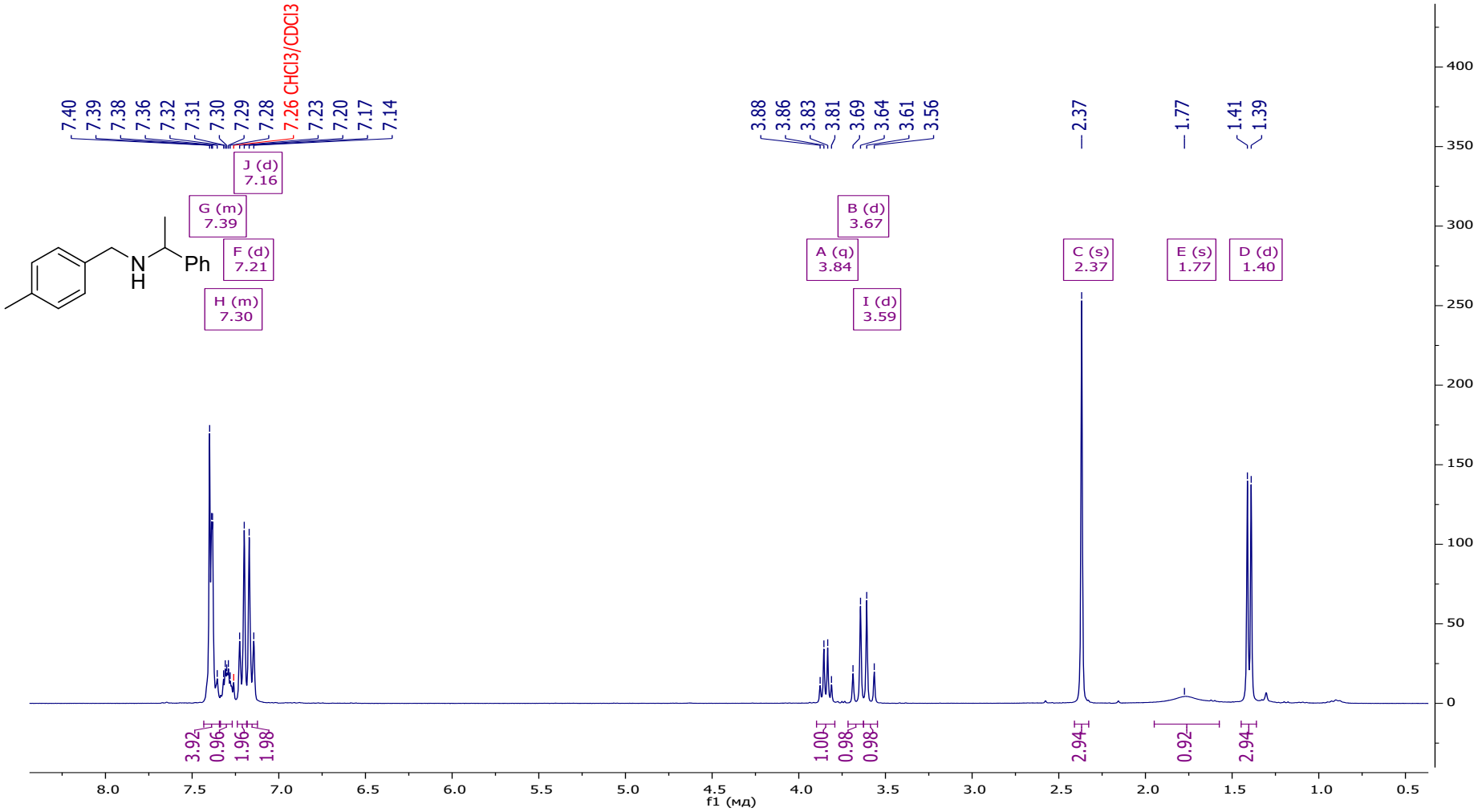
N-methyl-N-(4-methylbenzyl)aniline (^{1}H NMR, $CDCl_3$, 400 MHz), (3ea)



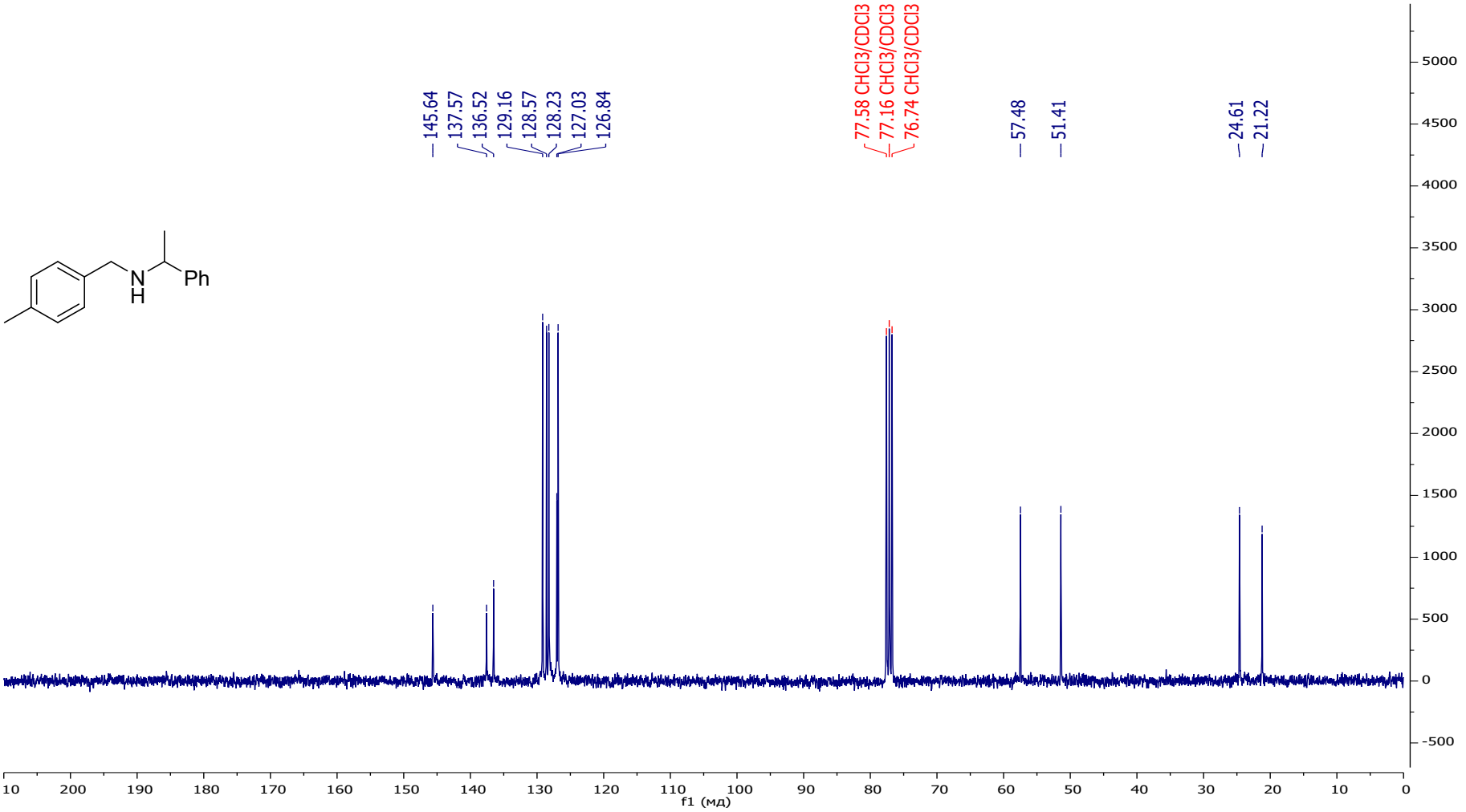
N-methyl-N-(4-methylbenzyl)aniline (^{13}C NMR, $CDCl_3$, 101 MHz), (3ea)



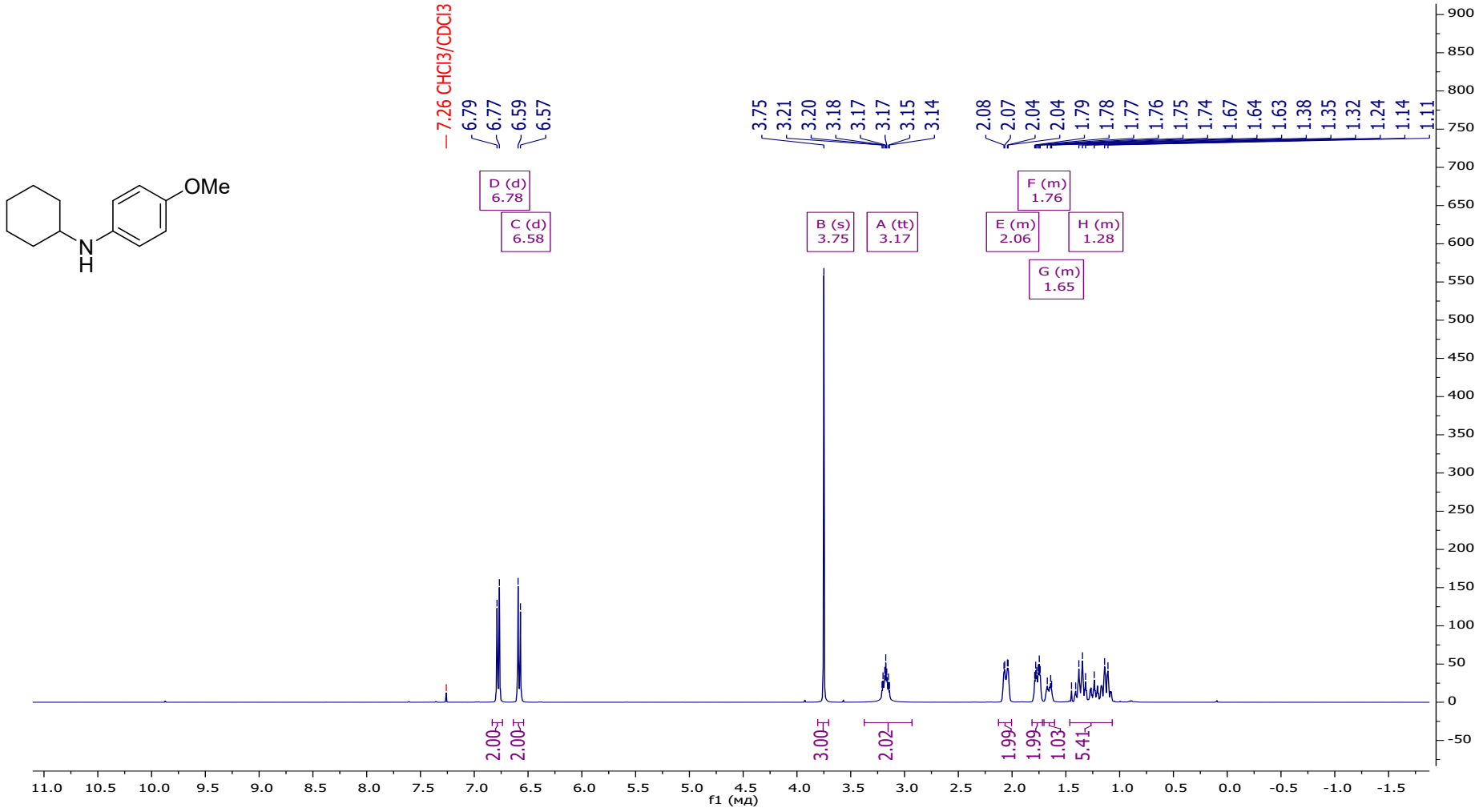
N-(4-methylbenzyl)-1-phenylethan-1-amine (^{1}H NMR, $CDCl_3$, 300 MHz), (3fa)



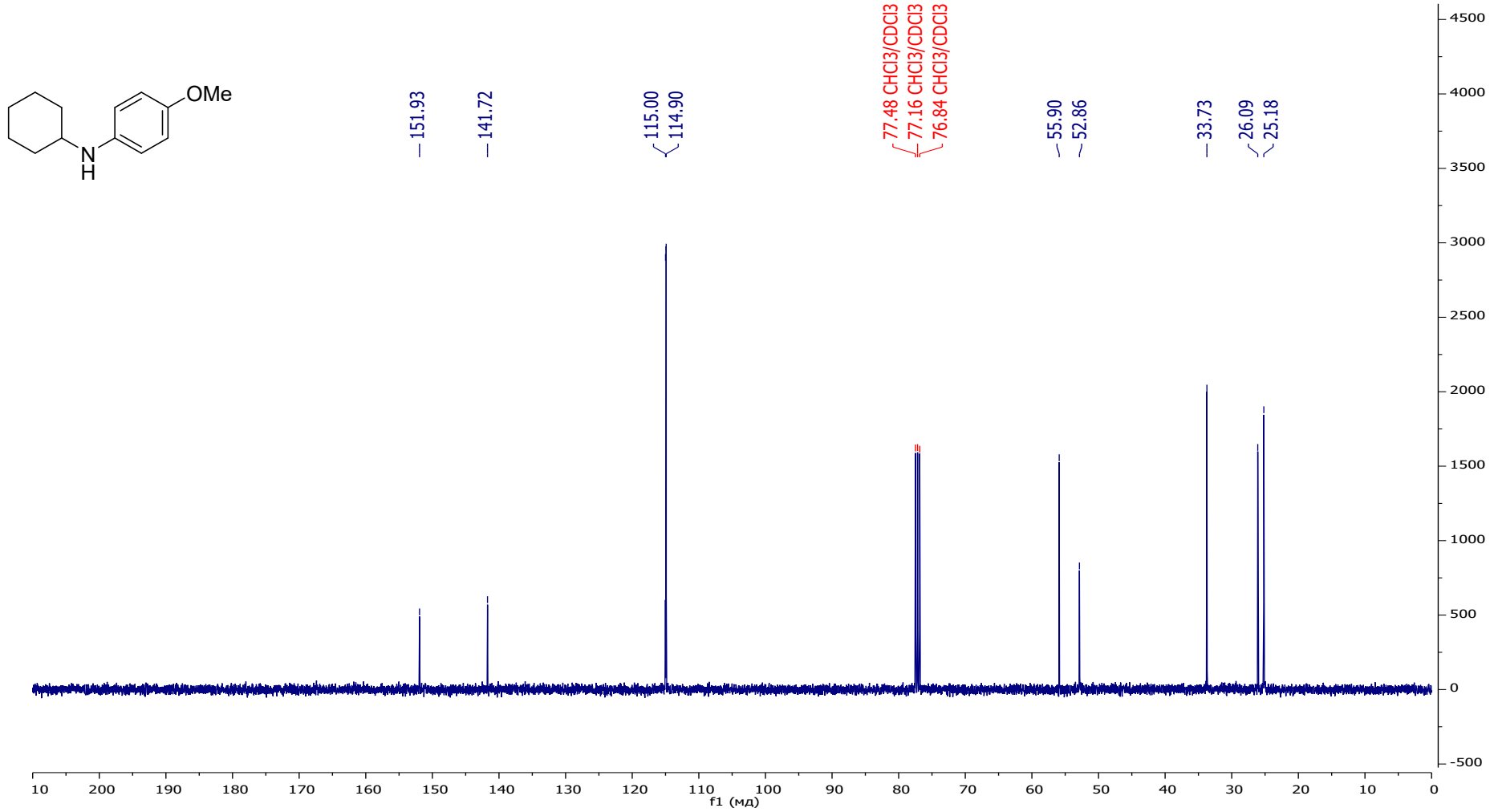
N-(4-methylbenzyl)-1-phenylethan-1-amine (^{13}C NMR, $CDCl_3$, 75 MHz), (3fa)



N-cyclohexyl-4-methoxyaniline (^{1}H NMR, $CDCl_3$, 400 MHz), (3bl)



N-cyclohexyl-4-methoxyaniline (^{13}C NMR, $CDCl_3$, 101 MHz), (3bl)



4. References

1 S. D. Nielsen, G. Smith, M. Begtrup and J. L. Kristensen, *European J. Org. Chem.*, 2010, **2010**, 3704–3710.

2 V. B. Kharitonov, M. Makarova, M. A. Arsenov, Y. V. Nelyubina, O. Chusova, A. S. Peregudov, S. S. Zlotskii, D. Chusov and D. A. Loginov, *Organometallics*, 2018, **37**, 2553–2562.

3 P. N. Kolesnikov, N. Z. Yagafarov, D. L. Usanov, V. I. Maleev and D. Chusov, *Org. Lett.*, 2015, **17**, 173–175.

4 G. Wang, C. Chen, T. Du and W. Zhong, *Adv. Synth. Catal.*, 2014, **356**, 1747–1752.

5 J. Chen, Z. Zhang, Z. Bao, Y. Su, H. Xing, Q. Yang and Q. Ren, *ACS Appl. Mater. Interfaces*, 2017, **9**, 9772–9777.

6 V. B. Kharitonov, E. Podyacheva, Y. V Nelyubina, D. V Muratov, A. S. Peregudov, G. Denisov, D. Chusov and D. A. Loginov, *Organometallics*, 2019, **38**, 3151–3158.

7 T. J. Barker and E. R. Jarvo, *Angew. Chemie Int. Ed.*, 2011, **50**, 8325–8328.

8 C. J. A. Warner, S. S. Berry and S. Jones, *Tetrahedron*, 2019, **75**, 130733.

9 D. Gülcemal, S. Gülcemal, C. M. Robertson and J. Xiao, *Organometallics*, 2015, **34**, 4394–4400.

10 F. I. López, F. N. de la Cruz, J. López, J. M. Martínez, Y. Alcaraz, F. Delgado, A. Sánchez-Recillas, S. Estrada-Soto and M. A. Vázquez, *Med. Chem. Res.*, 2017, **26**, 1325–1335.

11 Q. Lei, Y. Wei, D. Talwar, C. Wang, D. Xue and J. Xiao, *Chem. – A Eur. J.*, 2013, **19**, 4021–4029.

12 S. Coufourier, D. Ndiaye, Q. G. Gaillard, L. Bettoni, N. Joly, M. D. Mbaye, A. Poater, S. Gaillard and J.-L. Renaud, *Tetrahedron*, 2021, **90**, 132187.

13 Z.-P. Xiao, W.-K. Shi, P.-F. Wang, W. Wei, X.-T. Zeng, J.-R. Zhang, N. Zhu, M. Peng, B. Peng, X.-Y. Lin, H. Ouyang, X.-C. Peng, G.-C. Wang and H.-L. Zhu, *Bioorg. Med. Chem.*, 2015, **23**, 4508–4513.

14 E. Kuchuk, K. Muratov, D. S. Perekalin and D. Chusov, *Org. Biomol. Chem.*, 2019, **17**, 83–87.

15 N. Kise and S. Morimoto, *Tetrahedron*, 2008, **64**, 1765–1771.

16 G. Shang, Q. Yang and X. Zhang, *Angew. Chemie Int. Ed.*, 2006, **45**, 6360–6362.

17 Y. Pan, Z. Luo, J. Han, X. Xu, C. Chen, H. Zhao, L. Xu, Q. Fan and J. Xiao, *Adv. Synth. Catal.*, 2019, **361**, 2301–2308.

18 S. Shirai, H. Nara, Y. Kayaki and T. Ikariya, *Organometallics*, 2009, **28**, 802–809.

19 J. W. Park and Y. K. Chung, *ACS Catal.*, 2015, **5**, 4846–4850.