

Supporting Information

Efficient nickel-catalysed *N*-alkylation of amines with alcohols

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1. General methods and procedures

All reactions were carried out under an argon atmosphere using oven (140 °C) dried glassware and using standard Schlenk techniques. Bis(1,5-cyclooctadiene)nickel(0) and nickel(II) trifluoromethanesulfonate were purchased from Strem Chemicals; Nickel(II) chloride ethylene glycol dimethyl ether complex and nickel (II) bromide were purchased from Sigma-Aldrich; Cyclopentyl methyl ether (CPME, 99.9%, anhydrous) was purchased from Sigma-Aldrich and used without further purification. All other reagents were purchased from Sigma-Aldrich, Acros and TCI in reagent or higher grade and were used as received without further purification.

Chromatography and spectroscopy

Column chromatography was performed using Merck silica gel type 9385 230-400 mesh and typically pentane and ethyl acetate as eluent.

TLC: Merck silica gel 60, 0.25 mm. The components were visualized by UV or KMnO₄ staining.

Gas Chromatography with flame ionization detector (GC-FID): Conversions and product selectivities were determined using GC-FID (Agilent Technologies 6890) with an HP-5MS column (30 m x 0.25 mm x 0.25 µm) using nitrogen as carrier gas. The temperature program started at 50 °C and held for 5 min followed by a 10°C/minute temperature ramp to 300 °C and the final temperature was held for 5 min.

Gas Chromatography mass spectrometry (GC-MS): Product identification was performed using a GC-MS (Shimadzu QP2010 Ultra) with an HP-1MS column (30 m x 0.25 mm x 0.25 µm), and helium as carrier gas. The temperature program started at 40 °C, followed by a 10°C/minute temperature ramp to 250 °C and the final temperature was held for 5 min.

Mass spectrometry: Mass spectra were recorded on an AEI-MS-902 mass spectrometer (EI⁺) or a LTQ Orbitrap XL (ESI⁺).

NMR spectroscopy: ¹H and ¹³C NMR spectra were recorded on a Varian Mercury Plus 400, Agilent MR 400 (400 and 100.59 MHz, respectively) using CDCl₃ as a solvent. ¹H and ¹³C NMR spectra were recorded at room temperature. Chemical shift values are reported in ppm with the solvent resonance as the internal standard (CDCl₃: 7.26 for ¹H, 77.00 for ¹³C). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br. = broad, m = multiplet), coupling constants (Hz), and integration.

Representative procedures

Representative procedure for catalytic *N*-alkylation of amines with alcohols

General procedure: An oven-dried 20 mL Schlenk tube, equipped with a stirring bar, was charged with the specified amount of alcohol, amine, base, catalyst precursor and solvent. Typically, amine (0.5 mmol, 1 equiv.), alcohol (0.75 mmol, 1.5 equiv.), Ni(COD)₂ (0.015 mmol, 3 mol%), KOH (0.15 mmol, 0.3 equiv., 30 mol%) and cyclopentyl methyl ether (solvent, 2 mL) were used. The solid materials were weighed into the Schlenk tube under air, Ni(COD)₂ was weighed in the glovebox; then the Schlenk tube was removed from the glovebox, subsequently connected to an argon line and vacuum-argon exchange was performed three times. Liquid starting materials and solvent were charged under an argon stream. The Schlenk tube was capped and the mixture was rapidly stirred at room temperature for 1 min, then was placed into a pre-heated oil bath at the appropriate temperature (typically 140 °C) and stirred for a given time (typically 18 hours). The reaction mixture was cooled down to room temperature. After taking a sample (app. 0.5 mL) for GC analysis, the crude mixture was filtered through silica gel, eluted with ethyl-acetate, and concentrated *in vacuo*. The residue was purified by flash column chromatography to provide the pure amine product.

TEM and STEM/EDX measurements

At the RUG: TEM and STEM/EDX measurements were performed on a FEI Tecnai T20 electron microscope operating at 200 keV. EDX spectra were recorded with an Oxford Instruments X-max 80T SDD detector. Samples were prepared by applying 5 μ l of stock solution on a plain carbon coated copper grid. After one minute the excess of the sample was blotted with filter paper.

At CNR-ITAE in Messina, TEM images were acquired and elaborated by a Philips CM12 instrument at 120 kV accelerating voltage, equipped with a high-resolution camera and able to achieve a 0.19 nm point-to-point resolution and a 0.14 nm line resolution. After solvent evaporation, the stock solutions were dispersed in toluene under ultrasound irradiation, put drop-wise on a holey carbon-coated 300 mesh, 3.05 mm Cu grid (TAAB Laboratories Equipment Ltd, UK) and then dried at room temperature for 1h prior to the measurement. An amount of 200 Ni particles was counted to obtain a particle size distribution histogram for the NiNPs samples.

2. Experimental section

Scheme S1: Amination of benzyl alcohol (1a) with aniline (2a')

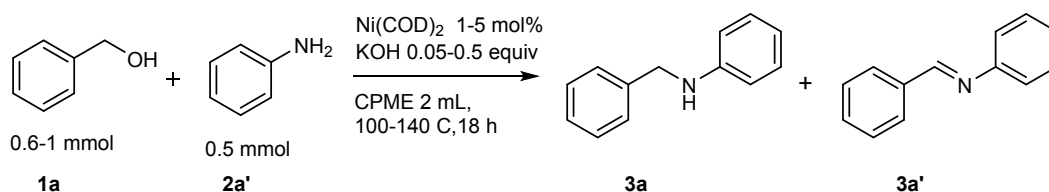


Table S1: Screening of different Ni precursors

Entry	Alcohol (equiv.)	Base (equiv.)	"Ni" precursor (mol%)	Conv. of 2a' [%]	Sel. of 3a [%]	Sel. of 3a' [%]
1	2	KOH (0.5)	Ni(COD)_2 (5)	>99	99	1
2	2	KOH (0.5)	$\text{NiCl}_2(\text{dme})$ (5)	86	79	7
3	2	KOH (0.5)	Ni(OTf)_2 (5)	73	63	10
4	2	KOH (0.5)	NiBr_2 (5)	78	70	5

General reaction conditions: General Procedure, 1 mmol of 1a, 0.5 mmol of 2a', 0.025 mmol of Ni precursor, 0.25 mmol KOH, 140 °C, 2 mL CPME, 18 h. Conversion and selectivity were determined by GC-FID using decane as an internal standard.

Table S2: The effect of various bases

Entry	Alcohol (equiv.)	Base (equiv.)	"Ni" precursor (mol%)	Conv. of 2a' [%]	Sel. of 3a [%]	Sel. of 3a' [%]
1	2	KOH (0.5)	Ni(COD)_2 (5)	>99	>99	<1
2	2	LiOH (0.5)	Ni(COD)_2 (5)	>99	7	74
3	2	NaOH (0.5)	Ni(COD)_2 (5)	>99	10	90
4	2	KO ^t Bu (0.5)	Ni(COD)_2 (5)	90	87	3
5	2	K_2CO_3 (0.5)	Ni(COD)_2 (5)	10	0	7

General reaction conditions: General Procedure, 1 mmol of 1a, 0.5 mmol of 2a', 0.025 mmol Ni(COD)_2 , 0.25 mmol of base, 140 °C, 2 mL CPME, 18 h. Conversion and selectivity were determined by GC-FID using decane as an internal standard.

Table S3: Screening of the effect of various "Ni precursor" / base / and alcohol amounts

Entry	Alcohol (equiv.)	Base (equiv.)	"Ni" precursor (mol%)	Conv. of 2a' [%]	Sel. of 3a [%]	Sel. of 3a' [%]
1	2	KOH (0.3)	Ni(COD)_2 (5)	>99	>99	<1
2	2	KOH (0.1)	Ni(COD)_2 (5)	>99	88	12
3	2	KOH (0.5)	Ni(COD)_2 (3)	>99	>99	<1
4	2	KOH (0.5)	Ni(COD)_2 (1)	>99	>99	<1
5	2	KOH (0.05)	Ni(COD)_2 (1)	61	28	33
6	2	KOH (0.075)	Ni(COD)_2 (1)	85	31	49
7	2	KOH (0.3)	Ni(COD)_2 (3)	>99	>99	<1
8	2	KOH (0.1)	Ni(COD)_2 (3)	67	30	30
9	1.5	KOH (0.3)	Ni(COD)_2 (3)	>99	>99	<1
10	1.2	KOH (0.3)	Ni(COD)_2 (3)	94	92	2

General reaction conditions: General Procedure, 0.6-1 mmol of 1a, 0.5 mmol of 2a', 0.005-0.025 mmol Ni(COD)_2 , 0.025-0.25 mmol KOH, 140 °C, 2 mL CPME, 18 h. Conversion and selectivity were determined by GC-FID using decane as an internal standard.

Table S4: Reaction temperature screening

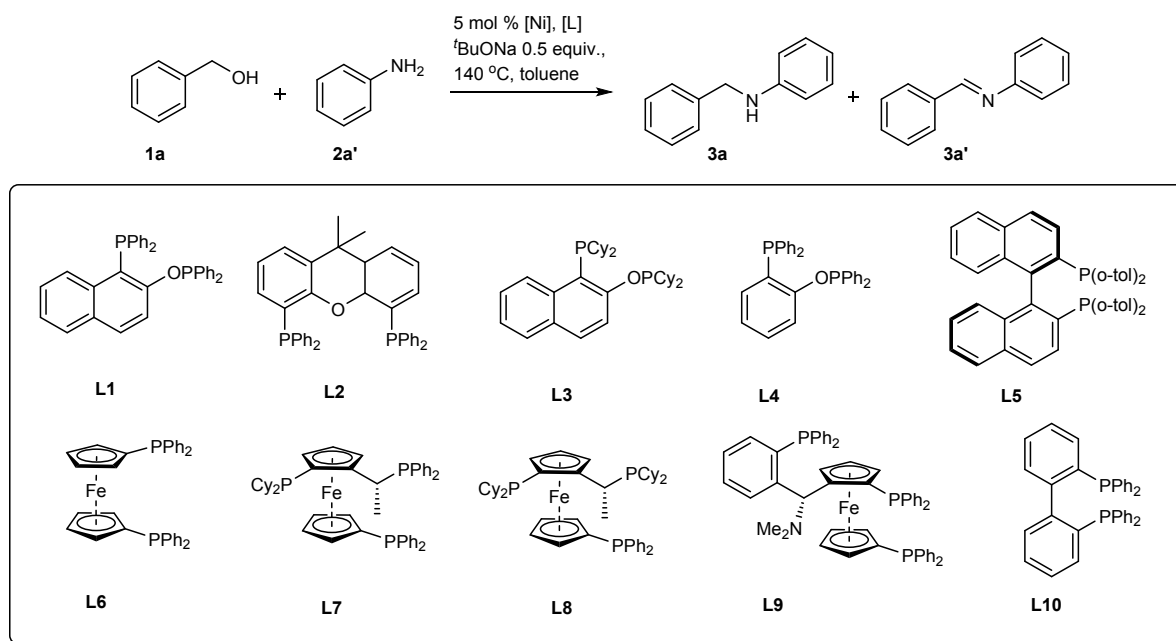
Entry	Alcohol (equiv.)	Base (equiv.)	"Ni" precursor (mol%)	Temp. [°C]	Solv.	Conv. of 2a' [%]	Sel. of 3a [%]	Sel. of 3a' [%]
1	2	KOH (0.5)	Ni(COD)_2 (5)	100	CPME	23	16	7
2	2	KOH (0.5)	Ni(COD)_2 (5)	120	CPME	31	19	9
3	2	KOH (0.5)	Ni(COD)_2 (5)	140	neat	26	18	2
4	2	KOH (0.5)	Ni(COD)_2 (5)	140	CPME	>99	>99	<1

General reaction conditions: General Procedure, 1 mmol of 1a, 0.5 mmol of 2a', 0.025 mmol Ni(COD)_2 , 0.25 mmol KOH, temperature as specified, 2 mL CPME, 18 h. Conversion and selectivity were determined by GC-FID using decane as an internal standard.

Table S5: Reaction time screening

Entry	Alcohol (equiv.)	Base (equiv.)	"Ni" precursor (mol%)	Time [h]	Conv. of 2a' [%]	Sel. of 3a [%]	Sel. of 3a' [%]
1	2	KOH (0.5)	Ni(COD) ₂ (5)	1	17	15	2
2	2	KOH (0.5)	Ni(COD) ₂ (5)	2	43	27	12
3	2	KOH (0.5)	Ni(COD) ₂ (5)	4	70	56	14
4	2	KOH (0.5)	Ni(COD) ₂ (5)	6	86	65	21

General reaction conditions: General Procedure, 1 mmol of **1a**, 0.5 mmol of **2a'**, 0.025 mmol Ni(COD)₂, 0.25 mmol KOH, 140 °C, 2 mL CPME, time as specified. Conversion and selectivity were determined by GC-FID using decane as an internal standard.

Scheme S2: Optimization of the reaction conditions - ligand screening**Table S6: Ligand screening**

Entry	Alcohol (equiv.)	Base (equiv.)	Ligand (mol%)	"Ni" precursor (mol%)	Temp. [°C]	Time [h]	Conv. [%]	Select. 3a [%]	Select. 3a' [%]
1	4	NaO ^t Bu (0.5)	L1 (5)	Ni(COD) ₂ (5)	140	18	>99	30	16
2	4	NaO ^t Bu (0.5)	L2 (5)	Ni(COD) ₂ (5)	130	18	93	8	85
3	4	NaO ^t Bu (0.5)	L3 (5)	Ni(COD) ₂ (5)	130	18	97	24	73
4	4	NaO ^t Bu (0.5)	L4 (5)	Ni(COD) ₂ (5)	130	18	44	19	25
5	4	NaO ^t Bu (0.5)	L5 (5)	Ni(COD) ₂ (5)	130	18	99	5	95
6	4	NaO ^t Bu (0.5)	L6 (5)	Ni(COD) ₂ (5)	130	18	99	7	93
7	4	NaO ^t Bu (0.5)	L7 (5)	Ni(COD) ₂ (5)	130	18	86	10	76
8	4	NaO ^t Bu (0.5)	L8 (5)	Ni(COD) ₂ (5)	130	18	98	24	72
9	4	NaO ^t Bu (0.5)	L9 (5)	Ni(COD) ₂ (5)	130	18	68	26	42
10	4	NaO ^t Bu (0.5)	L10 (5)	Ni(COD) ₂ (5)	130	18	95	3	83

General reaction conditions: General Procedure, 2 mmol of **1a**, 0.5 mmol of **2a'**, 0.025 mmol Ni(COD)₂, 0.025 mmol of ligand (**L1-L10**), 0.25 mmol NaO^tBu, 140 °C, 2 mL toluene, 18 h. Conversions and selectivity were determined by GC-FID using decane as an internal standard.

Table S7: Poisoning experiments

Entry	Alcohol (equiv.)	Base (equiv.)	"Ni"precursor (mol%)	Poisoning agent (equiv.)	Conv. [%]	Select. 3a [%]	Select. 3a' [%]
1	1.5	KOH (0.3)	Ni(COD) ₂ (3)	Hg (30)	25	20	5
2	1.5	KOH (0.3)	Ni(COD) ₂ (3)	-	26	18	8
3	1.5	KOH (0.3)	Ni(COD) ₂ (3)	Hg (30)	27	19	8

General reaction conditions: General Procedure, 1.5 mmol of **1a**, 1 mmol of **2a'**, 0.03 mmol Ni(COD)₂, 0.3 mmol KOH, 140 °C, 2 mL CPME, 20 h. Conversion and selectivity were determined by GC-FID.

Note 1: Experiments with the use of Hg to investigate the heterogeneity of the system were carried out in two different ways. The results shown in Entry 1 were obtained as follows:

An oven-dried 20 mL Schlenk tube, equipped with a stirring bar, was charged with aniline (1 mmol, 1 equiv.), benzyl alcohol (1.5 mmol, 1.5 equiv.), Ni(COD)₂ (0.03 mmol, 3 mol%), KOH (0.3 mmol, 0.3 equiv., 30 mol%) and cyclopentyl methyl ether (solvent, 2 mL). The solid materials were weighed into the Schlenk tube under air, Ni(COD)₂ was weighed in the glovebox; then the Schlenk tube was removed from the glovebox, subsequently connected to an argon line and vacuum-argon exchange was performed three times. Liquid starting materials, solvent and Hg (30 mmol, 30 equiv.) were charged under an argon stream. The Schlenk tube was capped and the mixture was rapidly stirred at room temperature for 1 min, then was placed into a pre-heated oil bath at 140 °C and stirred for 18 hours. The reaction mixture was cooled down to room temperature. The crude mixture was filtered through silica gel, eluted with ethyl-acetate, then a sample (app. 0.5 mL) for GC analysis was prepared.

The results shown in Entry 2 and Entry 3 were obtained as follows:

An oven-dried 20 mL Schlenk tube, equipped with a stirring bar, was charged with aniline (1 mmol, 1 equiv.), benzyl alcohol (1.5 mmol, 1.5 equiv.), Ni(COD)₂ (0.03 mmol, 3 mol%), KOH (0.3 mmol, 0.3 equiv., 30 mol%) and cyclopentyl methyl ether (solvent, 2 mL). The solid materials were weighed into the Schlenk tube under air, Ni(COD)₂ was weighed in the glovebox; then the Schlenk tube was removed from the glovebox, subsequently connected to an argon line and vacuum-argon exchange was performed three times. Liquid starting materials and solvent were charged under an argon stream. The Schlenk tube was capped and the mixture was rapidly stirred at room temperature for 1 min, then was placed into a pre-heated oil bath at 140 °C and stirred for 20 min. Then the reaction mixture was cooled down to room temperature, connected to the argon line and Hg (30 mmol, 30 equiv.) was added under an argon stream. The Schlenk tube was capped and the mixture was placed into a pre-heated oil bath at 140 °C and stirred for 1 hours. The crude mixture was filtered through silica gel, eluted with ethyl-acetate, then a sample (app. 0.5 mL) for GC analysis was prepared.

Table S8: Recycling test

Entry	Time [h]	Conv. [%]	Select. 3a [%]	Select. 3a' [%]
	14	>99	90	5
1 st reuse	14	70	58	8
2 nd reuse	14	50	39	8
3 rd reuse	18	36	25	8

General reaction conditions: General Procedure, 1.5 mmol of **1a**, 1 mmol of **2a'**, 0.03 mmol Ni(COD)₂, 0.3 mmol KOH, 140 °C, 2 mL CPME. Conversion and selectivity were determined by GC-FID.

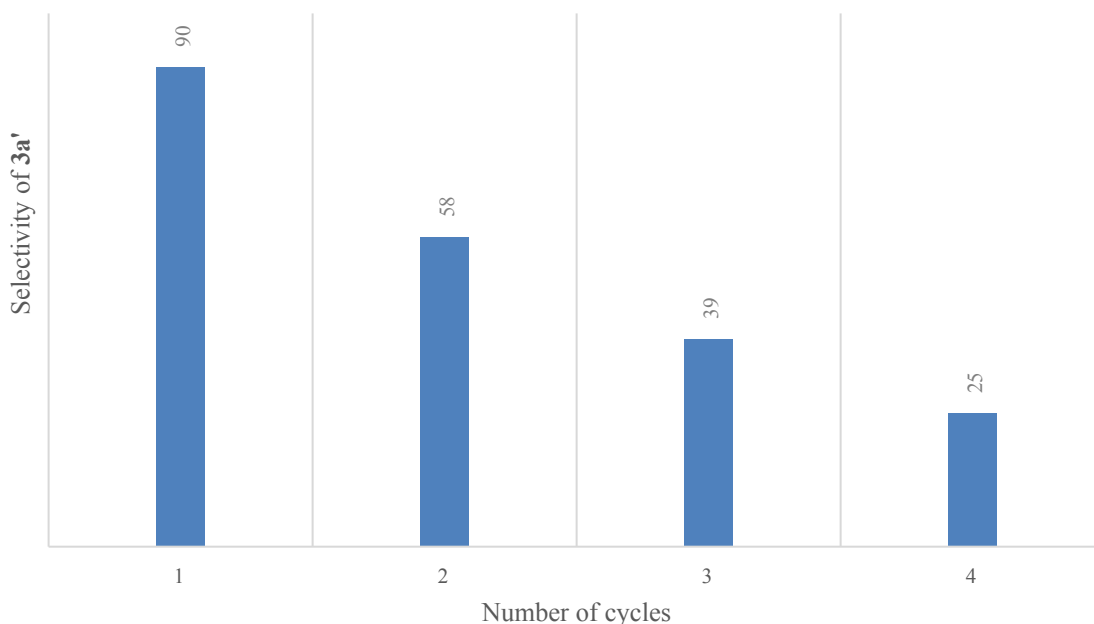


Figure S1. Recycling test of the *in situ* generated NiNP.

Note 2: Recycling test was carried out in the following way:

An oven-dried 20 mL Schlenk tube, equipped with a stirring bar, was charged with aniline (1 mmol, 1 equiv.), benzyl alcohol (1.5 mmol, 1.5 equiv.), Ni(COD)₂ (0.03 mmol, 3 mol%), KOH (0.3 mmol, 0.3 equiv., 30 mol%) and cyclopentyl methyl ether (solvent, 2 mL). The solid materials were weighed into the Schlenk tube under air, Ni(COD)₂ was weighed in the glovebox; then the Schlenk tube was removed from the glovebox, subsequently connected to an argon line and vacuum-argon exchange was performed three times. Liquid starting materials and solvent were charged under an argon stream. The Schlenk tube was capped and the mixture was rapidly stirred at room temperature for 1 min, then was placed into a pre-heated oil bath at 140 °C and stirred for 14 hours. Then the reaction mixture was cooled down to room temperature and connected to an argon line. Under an argon stream, 0.5 mL of the crude mixture was taken and filtered through silica gel, eluted with ethyl-acetate and analyzed by GC-FID. Then for the next cycle to the reaction mixture CPME (0.5 mL), benzyl alcohol (1.5 mmol, 1.5 equiv.) and aniline (1 mmol, 1 equiv.) were added. The Schlenk tube was capped and the mixture was placed into a pre-heated oil bath at 140 °C and stirred for 14 hours. The procedure was repeated as before for four consecutive runs.

The drop of the selectivity in each run might be due to dilution of total volume. There may also be a catalyst deactivation effect due to the formation of water in our reaction. To prove the effect of water in our system, the reaction was carried out in the presence of water (0.1 mL) under optimized condition [benzyl alcohol (0.75 mmol), aniline (0.5 mmol), Ni(COD)₂ (3 mol%), KOH (30 mol%), 140 °C, 2 mL CPME, 18 h] which gave 20% conversion, 17% corresponding imine **3a'** and 3% product **3a**. In another experiment, Ni(COD)₂ (3 mol%), KOH (30 mol%) in CPME were heated to 140 °C, after 1 h the reaction mixture was cooled to RT and water (0.1 mL), Benzyl alcohol (0.75 mmol), aniline (0.5 mmol), were added. Then, the reaction performed at 140 °C for 18 h gave 9% conversion, 0% amine **3a** and 9% imine **3a'**. In these reactions the substantial amount of water which was added in the beginning of the reaction significantly affected the catalysis.

Note 3: Experiment using distilled alcohol substrate in order to exclude possible catalytic activity of aldehyde (or other) impurities.

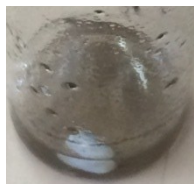
An oven-dried 20 mL Schlenk tube, equipped with a stirring bar, was charged with aniline (1 mmol, 1 equiv.), freshly distilled benzyl alcohol (1.5 mmol, 1.5 equiv.), Ni(COD)₂ (0.03 mmol, 3 mol%), KOH (0.3 mmol, 0.3 equiv., 30 mol%) and cyclopentyl methyl ether (solvent, 2 mL). The solid materials were weighed into the Schlenk tube under air, Ni(COD)₂ was weighed in the glovebox; then the Schlenk tube

was removed from the glovebox, subsequently connected to an argon line and vacuum-argon exchange was performed three times. Liquid starting materials and solvent were charged under an argon stream. The Schlenk tube was capped and the mixture was rapidly stirred at room temperature for 1 min, then was placed into a pre-heated oil bath at 140 °C and stirred for 18 hours. The reaction mixture was cooled down to room temperature. After taking a sample (app. 0.5 mL) for GC analysis, the crude mixture was filtered through silica gel, eluted with ethyl-acetate, and concentrated *in vacuo*. GC-FID yield: 95% - desired amine product. The reaction was repeated 2 more times with the following results: 2nd experiment: 99% conversion, 97% yield of product amine **3a** and 2% imine **3a'**; 3rd experiment: 99% conversion, 98% amine selectivity, and traces of imine.

Note 4: Experiment under non-inert conditions

In order to demonstrate that the reaction methodology in principle does not require the use of Glove-box, we have conducted a reaction under normal conditions. In such an experiment an oven-dried 20 mL Schlenk tube, equipped with a stirring bar, was charged with aniline (1 mmol, 1 equiv.), freshly distilled benzyl alcohol (1.5 mmol, 1.5 equiv.), Ni(COD)₂ (0.03 mmol, 3 mol%), KOH (0.3 mmol, 0.3 equiv., 30 mol%) and cyclopentyl methyl ether (solvent, 2 mL). All solid and liquid materials as well as solvent were charged under air. Ni(COD)₂ was weighed in the glovebox; then the Schlenk tube was removed from the glovebox and opened under air for 1 h. Then, the Schlenk tube was capped and the mixture was rapidly stirred at room temperature for 1 min, placed into a pre-heated oil bath at 140 °C and stirred for 18 hours. The reaction mixture was cooled down to room temperature. After taking a sample (app. 0.5 mL) for GC analysis, the crude mixture was filtered through silica gel, eluted with ethyl-acetate, and concentrated *in vacuo*. GC-FID yield: 93% - desired amine product.

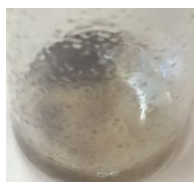
3. Characterization of samples prepared under different conditions



Sample 1.

The corresponding TEM image displayed on Figure 2a.

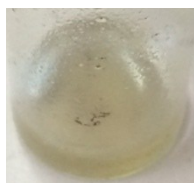
Sample containing $\text{Ni}(\text{COD})_2$ (0.015 mmol) and 1 mL CPME as a solvent at 140 °C, after 20 minutes of stirring.



Sample 2.

The corresponding TEM image displayed on Figure 2b.

Sample containing $\text{Ni}(\text{COD})_2$ (0.015 mmol), KOH (0.15 mmol) and 1 mL CPME as a solvent at 140 °C, after 20 minutes of stirring.



Sample 3.

The corresponding TEM image displayed on Figure 2c.

Sample containing $\text{Ni}(\text{COD})_2$ (0.015 mmol), K_2CO_3 (0.15 mmol) and 1 mL CPME as a solvent at 140 °C, after 20 minutes of stirring.



Sample 4.

The corresponding TEM image displayed on Figure 2d.

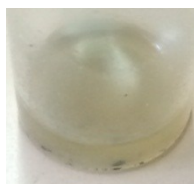
Sample containing $\text{Ni}(\text{COD})_2$ (0.015 mmol), benzyl alcohol (0.75 mmol) and 1 mL CPME as a solvent at 140 °C, after 20 minutes of stirring.



Sample 5.

The corresponding TEM image displayed on Figure 2e.

Sample containing $\text{Ni}(\text{COD})_2$ (0.015 mmol), KOH (0.15 mmol), benzyl alcohol (0.75 mmol) and 1 mL CPME as a solvent at 140 °C, after 20 minutes of stirring.



Sample 6.

The corresponding TEM image displayed on Figure S3a.

Reaction mixture containing $\text{Ni}(\text{COD})_2$ (0.015 mmol), KOH (0.15 mmol), benzyl alcohol (0.75 mmol), aniline (0.5 mmol) and 1 mL CPME as a solvent at 140 °C, after 20 minutes of stirring.



Sample 7.

The corresponding TEM image displayed on Figure 2f.

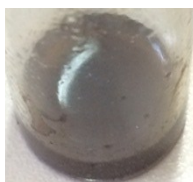
Reaction mixture containing $\text{Ni}(\text{COD})_2$ (0.015 mmol), KOH (0.15 mmol), benzyl alcohol (0.75 mmol), aniline (0.5 mmol) and 1 mL CPME as a solvent at 140 °C, after 18 hours of stirring.



Sample 8.

The corresponding TEM image displayed on Figure S3b.

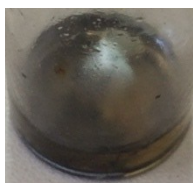
Sample containing $\text{Ni}(\text{COD})_2$ (0.015 mmol), aniline (0.5 mmol) and 1 mL CPME as a solvent at 140 °C, after 18 hours of stirring.



Sample 9.

The corresponding TEM image displayed on Figure S3c.

Sample containing $\text{Ni}(\text{COD})_2$ (0.015 mmol), pentyl amine (0.5 mmol) and 1 mL CPME as a solvent at 140 °C, after 18 hours of stirring.

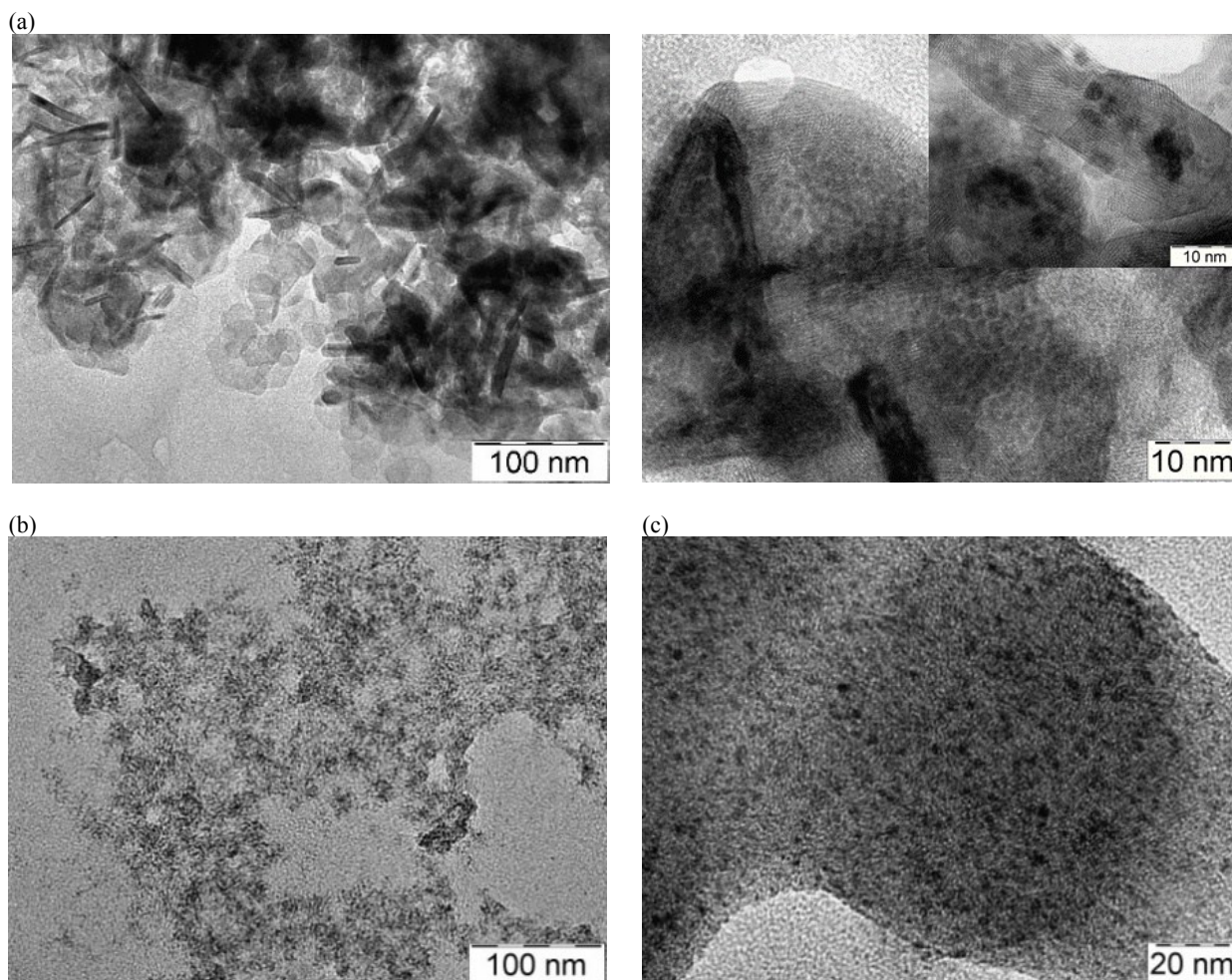


Sample 10.

The corresponding TEM image displayed on Figure S3d.

Reaction mixture containing $\text{Ni}(\text{COD})_2$ (0.015 mmol), KOH (0.15 mmol), benzyl alcohol (0.75 mmol), pentyl amine (0.5 mmol) and 1 mL CPME as a solvent at 140 °C, after 18 hours of stirring.

Figure S2. Photographs of samples generated for TEM measurement.



(d)

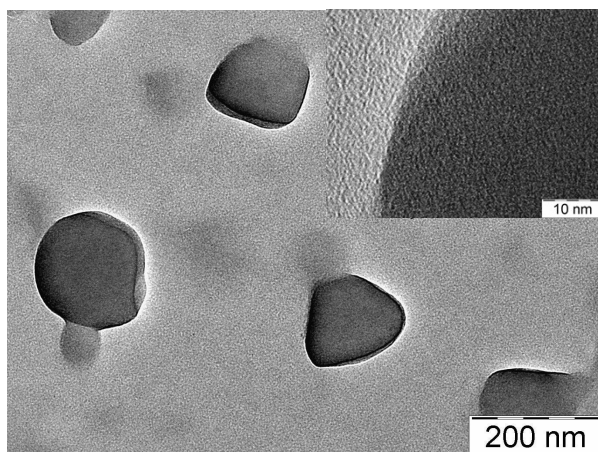
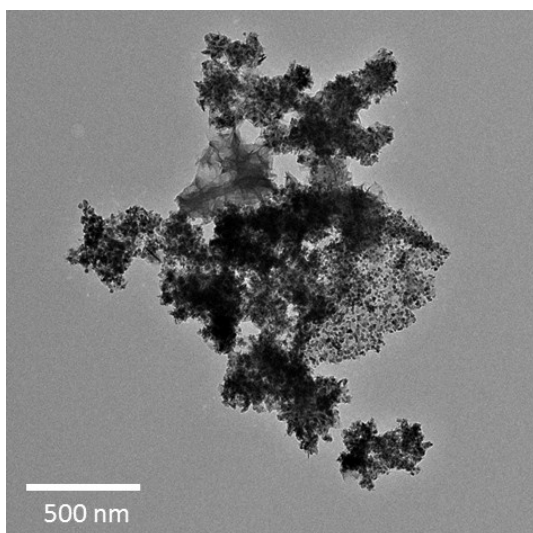
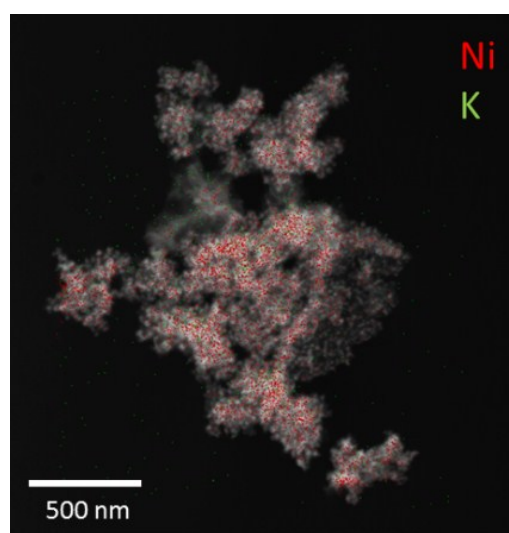


Figure S3. TEM micrographs of Ni-NPs corresponding to (a): Sample 6, (b): Sample 8, (c): Sample 9, (d): Sample 10 displayed on Figure S2.

(a)



(b)



(c)

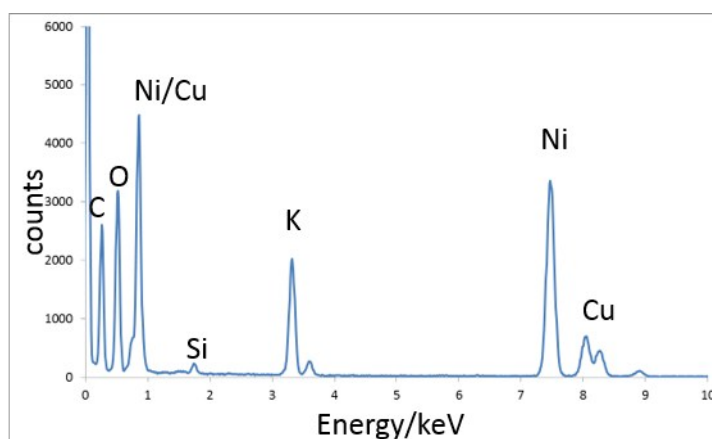


Figure S4. Bright-field TEM image of the *in situ* generated NiNPs from Ni(COD)₂ (3 mol%), KOH (30 mol%), benzyl alcohol (0.75 mmol) in 1 mL CPME at 140 °C after 20 min (a), HAADF-STEM image of the NiNPs with overlay EDX map for Ni and K (b), X-ray EDS of the NiNPs from the area in Figure S4b (c).

4. Scope of the reaction

Scheme S3: Direct amination of various primary alcohols (1a-z) with aniline (2a')

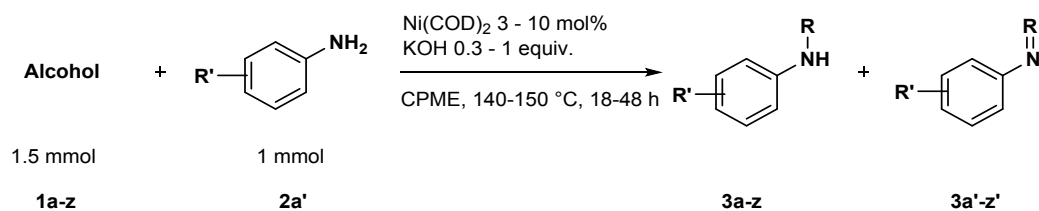
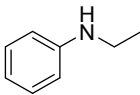
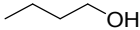
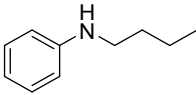
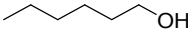
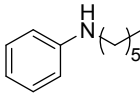
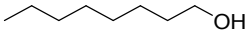
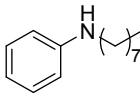
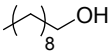
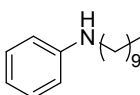
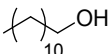
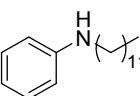
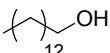
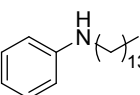
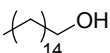
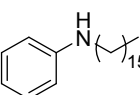
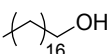
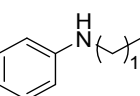
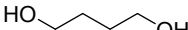
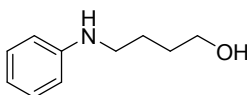
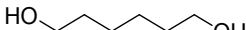
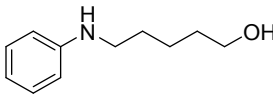
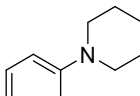
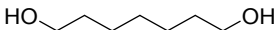
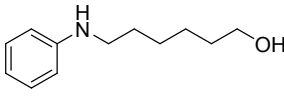
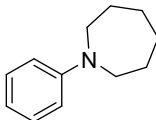
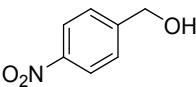
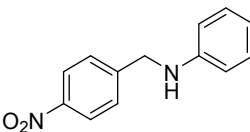
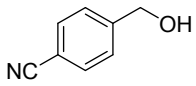
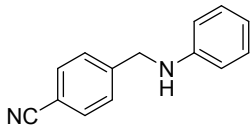
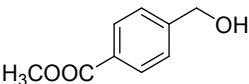
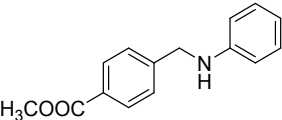
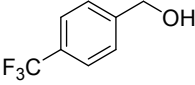
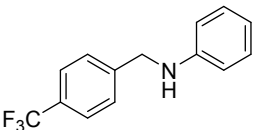


Table S9: Amination of various alcohols (1a-z) with aniline (2a')

Entry	Alcohol (1)	Product (3 or/and 3')	Conversion [%]	Yield [%]
1	1a 	3a 	>99	99(90)
2	1b 	3b 	>99	97(85)
3	1c 	3c 	91	91(84)
4	1d 	3d 	>99	99(98)
5	1e 	3e 	>99	99(92)
6	1f 	3f 	86	75(72)
7	1g 	3g 	86	67(62)
8	1h 	3h 	73	67(51)
9	1i 	3i 	89	77(69)
10 ^a	1j MeOH	3j 	38	38

11 ^a	1k	EtOH	3k		82	82(69)
12	1l		3l		>99	99(90)
13	1m		3m		>99	99(89)
14	1n		3n		>99	99(87)
15	1o		3o		>99	99(89)
16	1p		3p		>99	99(89)
17	1q		3q		>99	99(88)
18	1r		3r		>99	99(85)
19	1s		3s		>99	99(90)
20	1t		3t		35	14(12)
21	1u		3ua		91	71(63)
			3ub			16
22	1v		3va		99	71(67)
			3vb			28(28)
23	1w		3w		41	41(3w')
24	1x		3x		14	6+8(3x')

25	1y		3y		32	32(3y')
26	1z		3z		26	13+13(3z')

General reaction conditions: General Procedure, 1.5 mmol **1a-z**, 1 mmol of aniline (**2a'**), 0.03 mmol Ni(COD)₂, 0.3 mmol KOH, 140 °C, 2 mL CPME, 18 h. Conversion and selectivity were calculated based on GC-FID; isolated yields are in parenthesis. ^a 1 mmol of aniline, 0.1 mmol Ni(COD)₂, 1 mmol KOH, 150 °C, 1 mL of methanol or ethanol, 2 mL CPME, 48 h.

Scheme S4: Direct amination of 1-butanol with various amines (**2a-E**)

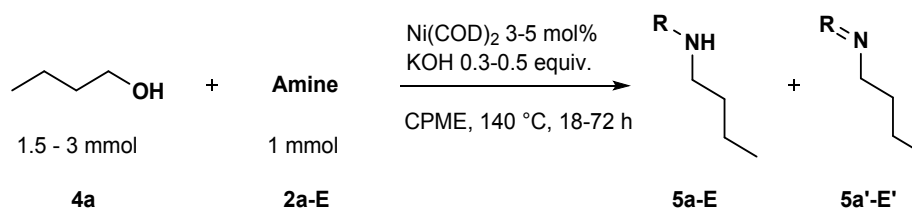
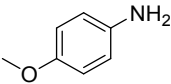
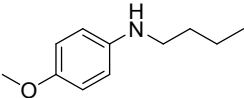
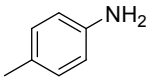
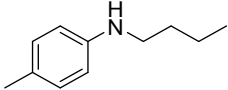
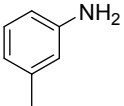
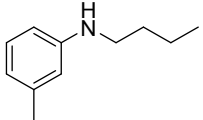
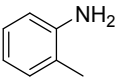
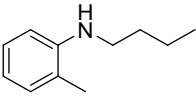
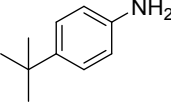
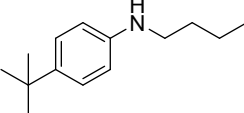
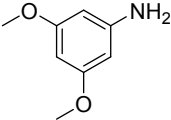
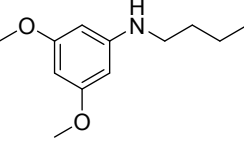
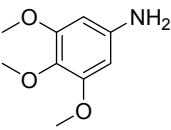
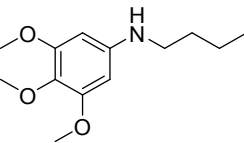
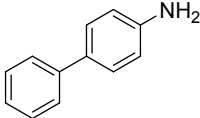
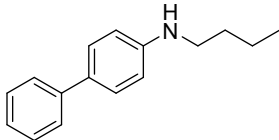
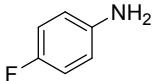
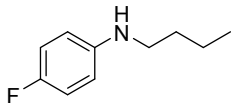
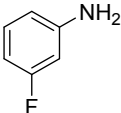
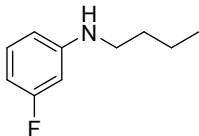
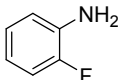
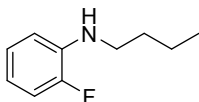
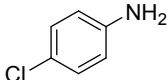
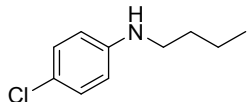
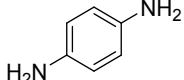
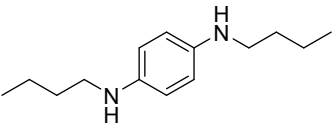
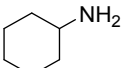
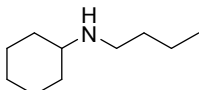
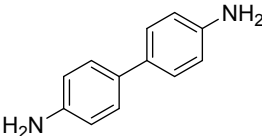
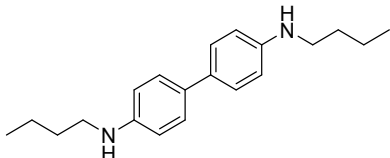
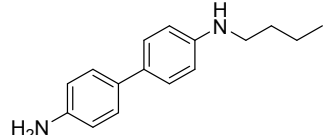
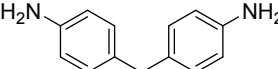
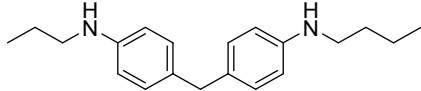
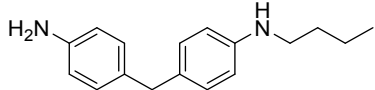
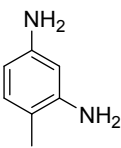
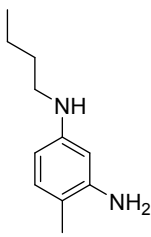
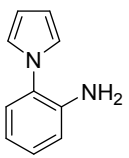
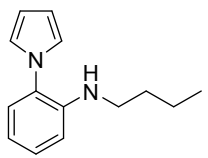
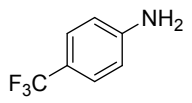
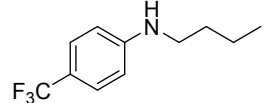
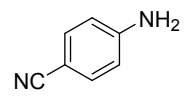
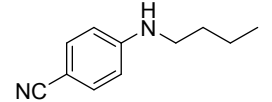
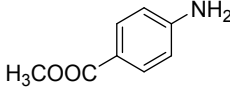
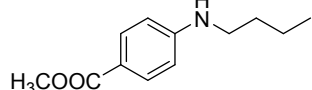
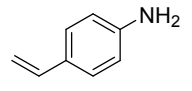
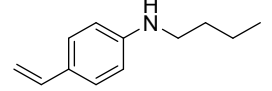
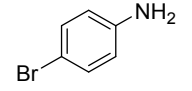
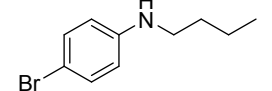
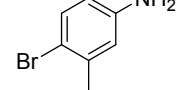
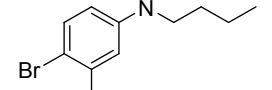
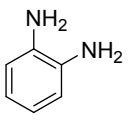
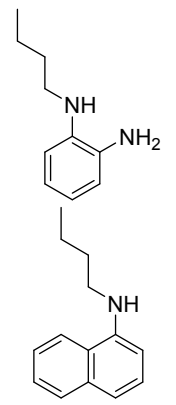
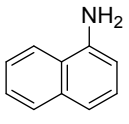
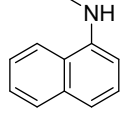
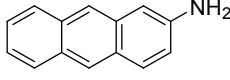
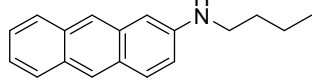
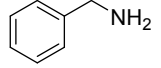
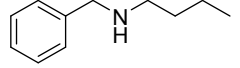
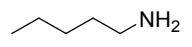
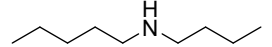
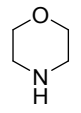
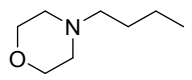
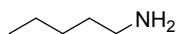
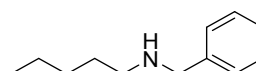


Table S10: Amination of 1-butanol with various amines (2a-E**)**

Entry		Amine (2)		Product (5 or/and 5')	Conversion [%]	Yield [%]
1	2a		5a		>99	94(78)
2	2b		5b		98	98(77)
3	2c		5c		75	75(53)
4	2d		5d		43	43(32)
5	2e		5e		86	86(70)
6	2f		5f		98	98(86)
7	2g		5g		88	88(65)

8 ^a	2h		5h		50	50(42)
9	2i		5i		88	88(72)
10	2j		5j		78	78(62)
11	2k		5k		78	78(36)
12	2l		5l		75	72(64)
13 ^a	2m		5m		>99	92(72)
14	2n		5n		>99	32+67(5n')
15 ^a	2o		5oa		88	41(25)
			5ob			47(39)
16 ^a	2p		5pa		91	47(32)
			5pb			44(43)
17 ^a	2q		5q		68	68(32)

18 ^b	2r		5r		60	60(57)
19	2s		5s		5	5
20	2t		5t		5	5
21	2u		5u		14	14
22	2v		5v		29	29
23	2w		5w		9	9
24	2x		5x		11	11
25 ^a	2y		5y		17	17
26	2z		5z		18	18
27	2A		5A		25	25
28	2B		5B		0	0
29	2C		5C		0	0
30	2D		5D		0	0

31^c**2E****5E**

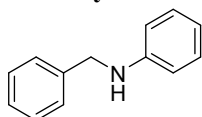
16

16(**5E'**)

General reaction conditions: General Procedure, 1 mmol **2a-E**, 1.5 mmol of *n*-butanol, 0.03 mmol Ni(COD)₂, 0.3 mmol KOH, 140 °C, 2 mL CPME, 18 h. Conversion and selectivity were calculated based on GC-FID; isolated yields are in parenthesis. ^a 3 mmol of *n*-butanol, 1 mmol of corresponding amine, 0.03 mmol Ni(COD)₂, 0.3 mmol KOH, 140 °C, 2 mL CPME, 48 h. ^b 3 mmol of *n*-butanol, 1 mmol of corresponding amine, 0.05 mmol Ni(COD)₂, 0.5 mmol KOH, 140 °C, 2 mL CPME, 72 h. ^c Used 1.5 mmol of benzyl alcohol instead of *n*-butanol.

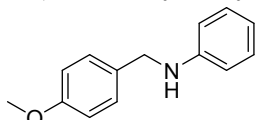
5. Spectral data of isolated compounds

N-benzylaniline (**3a**)



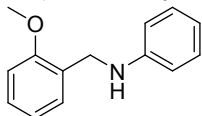
The compound was synthesized according to the **General procedure** using aniline (46.5 mg, 0.5 mmol) and benzyl alcohol (81 mg, 0.75 mmol) to afford **3a** (82 mg, 90% yield). Yellow solid was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 90:10). **¹H NMR** (400 MHz, CDCl₃): δ 7.46-7.33 (m, 5H), 7.28-7.23 (m, 2H), 6.82-6.78 (m, 1H), 6.71 (d, *J* = 7.6 Hz, 2H), 4.39 (s, 2H), 4.05 (*br s*, 1H, NH). **¹³C NMR** (101 MHz, CDCl₃): δ 150.88, 142.18, 132.00, 131.36, 130.23, 129.95, 120.29, 115.58, 51.03. **HRMS** (APCI⁺, *m/z*) calculated for C₁₃H₁₄N[M+H]⁺: 184.11262; found: 184.11320. The spectral data are identical to the previously reported.¹

N-(4-methoxybenzyl)aniline (**3b**)



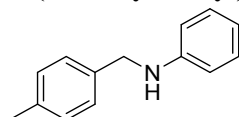
The compound was synthesized according to the **General procedure** using aniline (93 mg, 1 mmol) and 4-methoxybenzyl alcohol (207 mg, 1.5 mmol) to afford **3b** (181 mg, 85% yield). Yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 90:10). **¹H NMR** (400 MHz, CDCl₃): δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.81 (t, *J* = 7.2 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 2H), 4.32 (s, 2H), 4.01 (*br s*, 1H, NH), 3.87 (s, 3H, OCH₃). **¹³C NMR** (101 MHz, CDCl₃): δ 161.59, 150.97, 134.18, 131.99, 131.53, 120.21, 116.77, 115.59, 58.01, 50.49. **HRMS** (APCI⁺, *m/z*) calculated for C₁₄H₁₆NO [M+H]⁺: 214.12319; found: 214.12420. The spectral data are identical to the previously reported.¹

N-(2-methoxybenzyl)aniline (**3c**)



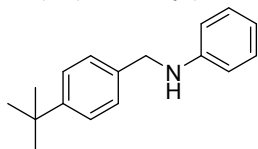
The compound was synthesized according to the **General procedure** using aniline (93 mg, 1 mmol) and 2-methoxybenzyl alcohol (207 mg, 1.5 mmol) to afford **3c** (179 mg, 84% yield). Yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 90:10). **¹H NMR** (400 MHz, CDCl₃): δ 7.35-7.26 (m, 2H), 7.19 (t, *J* = 7.6 Hz, 2H), 6.96-6.91 (m, 2H), 6.72 (t, *J* = 7.2 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 2H), 4.36 (s, 2H), 4.14 (*br s*, 1H, NH), 3.88 (s, 3H, OCH₃). **¹³C NMR** (101 MHz, CDCl₃): δ 160.06, 151.10, 131.84, 131.56, 130.96, 130.02, 123.20, 120.00, 115.73, 112.92, 57.98, 46.13. **HRMS** (APCI⁺, *m/z*) calculated for C₁₄H₁₆NO[M+H]⁺: 214.12319; found: 214.12437. The spectral data are identical to the previously reported.²

N-(4-methylbenzyl)aniline (**3d**)



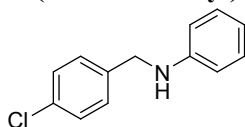
The compound was synthesized according to the **General procedure** using aniline (93 mg, 1 mmol) and 4-methylbenzyl alcohol (183 mg, 1.5 mmol) to afford **3d** (194 mg, 98% yield). White solid was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 95:5). **¹H NMR** (400 MHz, CDCl₃): δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.40-7.35 (m, 4H), 6.93 (t, *J* = 7.2 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 2H), 4.44 (s, 2H), 4.10 (*br s*, 1H, NH), 2.57 (s, 3H, CH₃). **¹³C NMR** (101 MHz, CDCl₃): δ 151.11, 139.64, 139.30, 132.18, 132.12, 130.37, 120.32, 115.72, 50.87, 24.00. **HRMS** (APCI⁺, *m/z*) calculated for C₁₄H₁₆N [M+H]⁺: 198.12827; found: 198.12912. The spectral data are identical to the previously reported.³

N-(4-(*tert*-butyl)benzyl)aniline (**3e**)



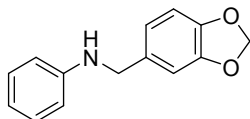
The compound was synthesized according to the **General procedure** using aniline (93 mg, 1 mmol) and 4-*tert*-butylbenzyl alcohol (246 mg, 1.5 mmol) to afford **3e** (220 mg, 92% yield). White solid was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 95:5). **¹H NMR** (400 MHz, CDCl₃): δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 6.90 (t, *J* = 7.2 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 2H), 4.44 (s, 2H), 4.10 (*br s*, 1H, NH), 1.53 (s, 9H, *t*Bu). **¹³C NMR** (101 MHz, CDCl₃): δ 152.98, 151.12, 139.25, 132.09, 130.22, 128.36, 120.28, 115.65, 50.80, 37.34, 34.27. **HRMS** (APCI⁺, *m/z*) calculated for C₁₇H₂₂N[M+H]⁺: 240.17522; found: 240.17665. The spectral data are identical to the previously reported.⁴

N-(4-chlorobenzyl)aniline (**3f**)



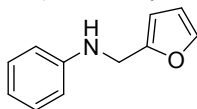
The compound was synthesized according to the **General procedure** using aniline (93 mg, 1 mmol) and 4-chlorobenzyl alcohol (214 mg, 1.5 mmol) to afford **3f** (157 mg, 72% yield). Yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 90:10). **¹H NMR** (400 MHz, CDCl₃): δ 7.34-7.30 (m, 4H), 7.22-7.18 (m, 2H), 6.78-6.73 (m, 1H), 6.64-6.62 (m, 2H), 4.32 (s, 2H), 4.08 (*br s*, 1H, NH). **¹³C NMR** (101 MHz, CDCl₃): δ 150.47, 140.66, 135.53, 131.97, 131.41, 131.37, 120.50, 115.59, 50.29. **HRMS** (APCI⁺, *m/z*) calculated for C₁₃H₁₃ClN [M+H]⁺: 218.07365; found: 218.07472. The spectral data are identical to the previously reported.¹

N-(benzo[d][1,3]dioxol-5-ylmethyl)aniline (**3g**)



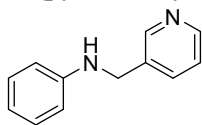
The compound was synthesized according to the **General procedure** using aniline (93 mg, 1 mmol) and piperonyl alcohol (228 mg, 1.5 mmol) to afford **3g** (141 mg, 62% yield). White solid was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 95:5). **¹H NMR** (400 MHz, CDCl₃): δ 7.22-7.17 (m, 2H), 6.89-6.72 (m, 4H), 6.66-6.64 (m, 2H), 5.95 (s, 2H), 4.25 (s, 2H), 4.01 (*br s*, 1H, NH). **¹³C NMR** (101 MHz, CDCl₃): δ 150.73, 150.57, 149.40, 136.02, 131.93, 123.26, 120.27, 115.55, 110.97, 110.72, 103.66, 50.80. **HRMS** (APCI⁺, *m/z*) calculated for C₁₄H₁₄NO₂ [M+H]⁺: 228.10245; found: 228.10380. The spectral data are identical to the previously reported.⁵

N-(furan-2-ylmethyl)aniline (**3h**)



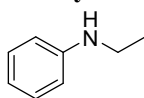
The compound was synthesized according to the **General procedure** using aniline (93 mg, 1 mmol) and furfuryl alcohol (147 mg, 1.5 mmol) to afford **3h** (87 mg, 52% yield). Yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 95:5). **¹H NMR** (400 MHz, CDCl₃): δ 7.39-7.38 (m, 1H), 7.21 (t, *J* = 7.6 Hz, 2H), 6.76 (td, *J* = 7.2 Hz, *J* = 0.8 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 2H), 6.34 (dd, *J* = 2.8 Hz, *J* = 2.0 Hz, 1H), 6.26 (dd, *J* = 2.8 Hz, *J* = 0.8 Hz, 1H), 4.33 (s, 2H), 4.03 (*br s*, 1H, NH). **¹³C NMR** (101 MHz, CDCl₃): δ 155.42, 150.30, 144.57, 131.90, 120.69, 115.82, 113.01, 109.64, 44.11. **HRMS** (APCI⁺, *m/z*) calculated for C₁₁H₁₂NO[M+H]⁺: 174.09189; found: 174.09240. The spectral data are identical to the previously reported.¹

N-(pyridin-3-ylmethyl)aniline (**3i**)



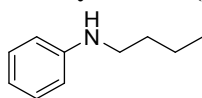
The compound was synthesized according to the **General procedure** using aniline (93 mg, 1 mmol) and 2-pyridinemethanol (164 mg, 1.5 mmol) to afford **3i** (127 mg, 69% yield). White solid was obtained after column chromatography (SiO₂, Pentane/EtOAc 70:30 to 50:50). **¹H NMR** (400 MHz, CDCl₃): δ 8.60 (s, 1H), 8.51 (d, *J* = 3.6 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.24-7.16 (m, 3H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 2H), 4.32 (s, 2H), 4.23 (*br s*, 1H, NH). **¹³C NMR** (101 MHz, CDCl₃): δ 151.77, 151.26, 150.41, 137.77, 137.71, 132.00, 126.22, 120.56, 115.60, 48.35. **HRMS** (APCI⁺, *m/z*) calculated for C₁₂H₁₃N₂ [M+H]⁺: 185.10787; found: 185.10875. The spectral data are identical to the previously reported.⁵

N-ethylaniline (**3k**)



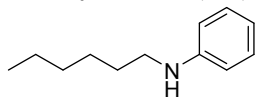
The compound was synthesized according to the **General procedure** using aniline (93 mg, 1 mmol) and ethanol (1 mL, 17 mmol) to afford **3k** (74 mg, 69% yield). Yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 95:5). **¹H NMR** (400 MHz, CDCl₃): δ 7.17 (t, *J* = 7.2 Hz, 2H), 6.69 (t, *J* = 7.2 Hz, 1H), 6.61 (d, *J* = 7.6 Hz, 2H), 3.54 (*br s*, 1H, NH), 3.16 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 6.8 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 151.16, 131.92, 119.89, 115.45, 41.15, 17.58. **HRMS** (APCI⁺, *m/z*) calculated for C₈H₁₂N [M+H]⁺: 122.09697; found: 122.09643. The spectral data are identical to the previously reported.⁶

N-butylaniline (**3l**)



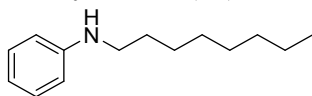
The compound was synthesized according to the **General procedure** using aniline (93 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **3l** (134 mg, 90% yield). Yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 90:10). **¹H NMR** (400 MHz, CDCl₃): δ 7.28-7.23 (m, 2H), 6.79-6.75 (m, 1H), 6.69-6.66 (m, 2H), 3.60 (*br s*, 1H, NH), 3.18 (td, *J* = 6.8 Hz, *J* = 2.8 Hz, 2H), 1.71-1.63 (m, 2H), 1.56-1.46 (m, 2H), 1.07-1.02 (m, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 151.28, 131.92, 119.76, 115.40, 46.39, 34.42, 23.05, 16.66. **HRMS** (APCI⁺, *m/z*) calculated for C₁₀H₁₆N [M+H]⁺: 150.12827; found: 150.12869. The spectral data are identical to the previously reported.⁷

N-hexylaniline (**3m**)



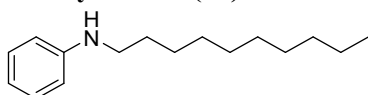
The compound was synthesized according to the **General procedure** using aniline (93 mg, 1 mmol) and 1-hexanol (153 mg, 1.5 mmol) to afford **3m** (157 mg, 89% yield). Yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 90:10). **¹H NMR** (400 MHz, CDCl₃): δ 7.26 (t, *J* = 7.6 Hz, 2H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 2H), 3.60 (*br s*, 1H, NH), 3.17 (t, *J* = 7.2 Hz, 2H), 1.69 (p, *J* = 7.6 Hz, 2H), 1.52-1.39 (m, 6H), 1.01 (t, *J* = 6.8 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 151.29, 131.93, 119.76, 115.41, 46.73, 34.42, 32.30, 29.62, 25.40, 16.80. **HRMS** (APCI⁺, *m/z*) calculated for C₁₂H₂₀N [M+H]⁺: 178.15957; found: 178.16039. The spectral data are identical to the previously reported.⁸

***N*-octylaniline (3n)**



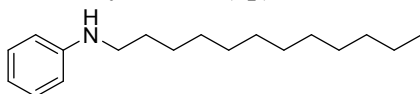
The compound was synthesized according to the **General procedure** using aniline (93 mg, 1 mmol) and 1-octanol (195 mg, 1.5 mmol) to afford **3n** (179 mg, 87% yield). Yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 95:5). **¹H NMR** (400 MHz, CDCl₃): δ 7.30 (t, *J* = 7.6 Hz, 2H), 6.83 (t, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 7.6 Hz, 2H), 3.64 (*br s*, 1H, NH), 3.21 (t, *J* = 7.2 Hz, 2H), 1.73 (p, *J* = 6.8 Hz, 2H), 1.52-1.45 (m, 10H), 1.06-1.05 (m, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 151.34, 131.96, 119.79, 115.45, 46.77, 34.68, 32.40, 32.27, 32.12, 30.02, 25.51, 16.92. **HRMS** (APCI⁺, *m/z*) calculated for C₁₄H₂₄N[M+H]⁺: 206.19087; found: 206.19195. The spectral data are identical to the previously reported.²

***N*-decylaniline (3o)**



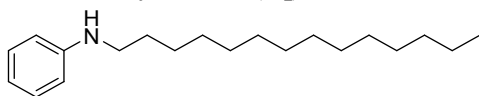
The compound was synthesized according to the **General procedure** using aniline (93 mg, 1 mmol) and 1-decanol (237 mg, 1.5 mmol) to afford **3o** (207 mg, 89% yield). Yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0). **¹H NMR** (400 MHz, CDCl₃): δ 7.20 (t, *J* = 7.2 Hz, 2H), 6.71 (t, *J* = 7.2 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 2H), 3.56 (*br s*, 1H, NH), 3.12 (t, *J* = 7.2 Hz, 2H), 1.64 (p, *J* = 7.6 Hz, 2H), 1.44-1.31 (m, 14H), 0.92 (t, *J* = 6.8 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 151.21, 131.87, 119.73, 115.35, 46.68, 34.59, 32.30, 32.28, 32.26, 32.15, 32.02, 29.88, 25.37, 16.80. **HRMS** (APCI⁺, *m/z*) calculated for C₁₆H₂₈N[M+H]⁺: 234.22217; found: 234.22348. The spectral data are identical to the previously reported.²

***N*-dodecylaniline (3p)**



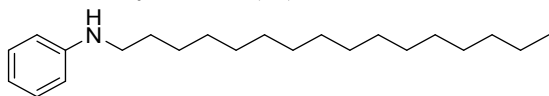
The compound was synthesized according to the **General procedure** using aniline (93 mg, 1 mmol) and 1-dodecanol (279 mg, 1.5 mmol) to afford **3p** (232 mg, 89% yield). Yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 90:10). **¹H NMR** (400 MHz, CDCl₃): δ 7.26 (t, *J* = 8.0 Hz, 2H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 2H), 3.43 (*br s*, 1H, NH), 3.18 (t, *J* = 7.2 Hz, 2H), 1.70 (p, *J* = 7.6 Hz, 2H), 1.51-1.40 (m, 18H), 1.01 (t, *J* = 6.8 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 151.28, 131.91, 119.78, 115.41, 46.75, 34.73, 32.49, 32.46, 32.44, 32.43, 32.37, 32.28, 32.17, 29.99, 25.50, 16.90. **HRMS** (APCI⁺, *m/z*) calculated for C₁₈H₃₂N[M+H]⁺: 262.25348; found: 262.25487. The spectral data are identical to the previously reported.⁹

***N*-tetradecylaniline (3q)**



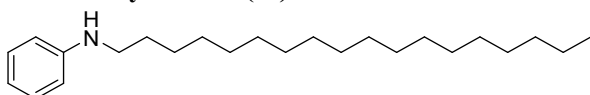
The compound was synthesized according to the **General procedure** using aniline (93 mg, 1 mmol) and 1-tetradecanol (321 mg, 1.5 mmol) to afford **3q** (247 mg, 85% yield). White solid was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 95:5). **¹H NMR** (400 MHz, CDCl₃): δ 7.20 (t, *J* = 7.6 Hz, 2H), 6.72 (t, *J* = 7.2 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 2H), 3.60 (*br s*, 1H, NH), 3.13 (t, *J* = 7.2 Hz, 2H), 1.65 (p, *J* = 7.6 Hz, 2H), 1.45-1.31 (m, 22H), 0.93 (t, *J* = 6.8 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 151.22, 131.87, 119.72, 115.34, 46.68, 34.64, 32.41, 32.39, 32.38, 32.37, 32.33, 32.32, 32.29, 32.17, 32.08, 29.89, 25.40, 16.82. **HRMS** (APCI⁺, *m/z*) calculated for C₂₀H₃₆N[M+H]⁺: 290.28478; found: 290.28669.

***N*-hexadecylaniline (3r)**



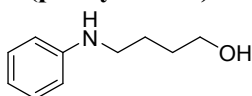
The compound was synthesized according to the **General procedure** using aniline (93 mg, 1 mmol) and 1-hexadecanol (364 mg, 1.5 mmol) to afford **3r** (280 mg, 88% yield). White solid was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 95:5). **¹H NMR** (400 MHz, CDCl₃): δ 7.22 (t, *J* = 7.6 Hz, 2H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 7.6 Hz, 2H), 3.60 (*br s*, 1H, NH), 3.14 (t, *J* = 7.2 Hz, 2H), 1.65 (p, *J* = 7.2 Hz, 2H), 1.46-1.32 (m, 26H), 0.94 (t, *J* = 6.8 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 151.22, 131.88, 119.73, 115.36, 46.70, 34.65, 32.43, 32.41, 32.39, 32.34, 32.33, 32.30, 32.19, 32.10, 29.91, 25.42, 16.83. **HRMS** (APCI⁺, *m/z*) calculated for C₂₂H₄₀N[M+H]⁺: 318.31608; found: 318.31829. The spectral data are identical to the previously reported.¹⁰

***N*-octadecylaniline (3s)**



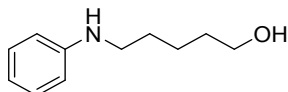
The compound was synthesized according to the **General procedure** using aniline (93 mg, 1 mmol) and 1-octadecanol (406 mg, 1.5 mmol) to afford **3s** (311 mg, 90% yield). White solid was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 95:5). **¹H NMR** (400 MHz, CDCl₃): δ 7.23 (t, *J* = 7.6 Hz, 2H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 2H), 3.55 (*br s*, 1H, NH), 3.15 (t, *J* = 6.8 Hz, 2H), 1.67 (p, *J* = 7.2 Hz, 2H), 1.47-1.34 (m, 30H), 0.96 (t, *J* = 6.8 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 151.23, 131.88, 119.75, 115.37, 46.71, 34.69, 32.47, 32.45, 32.43, 32.38, 32.37, 32.33, 32.23, 32.13, 29.94, 25.45, 16.85. **HRMS** (APCI⁺, *m/z*) calculated for C₂₄H₄₄N[M+H]⁺: 346.34738; found: 346.34949. The spectral data are identical to the previously reported.¹¹

4-(phenylamino)butan-1-ol (3t)



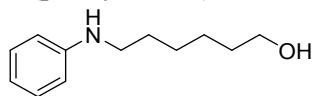
The compound was synthesized according to the **General procedure** using aniline (93 mg, 1 mmol) and 1,4-butanediol (135 mg, 1.5 mmol) to afford **3t** (20 mg, 12% yield). Yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 40:60). **¹H NMR** (400 MHz, CDCl₃): δ 7.18 (t, *J* = 7.6 Hz, 2H), 6.71 (t, *J* = 7.2 Hz, 1H), 6.62 (d, *J* = 7.6 Hz, 2H), 3.68 (t, *J* = 6.0 Hz, 2H), 3.15 (t, *J* = 6.4 Hz, 2H), 2.53 (*br s*, 2H), 1.71-1.69 (m, 4H). **¹³C NMR** (101 MHz, CDCl₃): δ 150.95, 131.90, 120.11, 115.61, 65.26, 46.56, 33.02, 28.75. **HRMS** (APCI⁺, *m/z*) calculated for C₁₀H₁₆NO[M+H]⁺: 166.12319; found: 166.12374. The spectral data are identical to the previously reported.¹²

5-(phenylamino)pentan-1-ol (3ua)



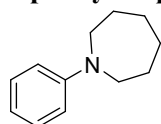
The compound was synthesized according to the **General procedure** using aniline (93 mg, 1 mmol) and 1,5-pentanediol (156 mg, 1.5 mmol) to afford **3ua** (101 mg, 63% yield). Colorless oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 40:60). **¹H NMR** (400 MHz, CDCl₃): δ 7.19 (t, *J* = 7.2 Hz, 2H), 6.71 (t, *J* = 7.2 Hz, 1H), 6.62 (d, *J* = 7.6 Hz, 2H), 3.64 (t, *J* = 6.4 Hz, 2H), 3.12 (t, *J* = 7.2 Hz, 2H), 2.70 (*br s*, 2H), 1.69-1.58 (m, 4H), 1.51-1.44 (m, 2H). **¹³C NMR** (101 MHz, CDCl₃): δ 151.10, 131.90, 119.88, 115.43, 65.33, 46.57, 35.10, 31.97, 26.04. **HRMS** (APCI⁺, *m/z*) calculated for C₁₁H₁₈NO[M+H]⁺: 180.13884; found: 180.13961. The spectral data are identical to the previously reported.¹³

5-(phenylamino)hexan-1-ol (3va)



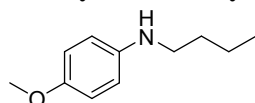
The compound was synthesized according to the **General procedure** using aniline (93 mg, 1 mmol) and 1,6-hexanediol (177 mg, 1.5 mmol) to afford **3va** (130 mg, 67% yield). Yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 60:40). **¹H NMR** (400 MHz, CDCl₃): δ 7.19 (t, *J* = 7.2 Hz, 2H), 6.71 (t, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 2H), 3.63 (t, *J* = 6.8 Hz, 2H), 3.11 (t, *J* = 7.2 Hz, 2H), 2.73 (*br s*, 2H), 1.67-1.38 (m, 8H). **¹³C NMR** (101 MHz, CDCl₃): δ 151.14, 131.89, 119.85, 115.45, 65.38, 46.60, 35.30, 32.18, 29.64, 28.27. **HRMS** (APCI⁺, *m/z*) calculated for C₁₂H₂₀NO[M+H]⁺: 194.15449; found: 194.15532.

1-phenylazepane (3vb)



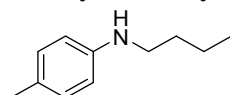
The compound was synthesized according to the **General procedure** using aniline (93 mg, 1 mmol) and 1,6-hexanediol (177 mg, 1.5 mmol) to afford **3vb** (49 mg, 28% yield). Yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 90:10). **¹H NMR** (400 MHz, CDCl₃): δ 7.19 (t, *J* = 7.6 Hz, 2H), 6.71 (t, *J* = 7.2 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 2H), 3.13 (t, *J* = 7.2 Hz, 2H), 1.67-1.28 (m, 10H). **¹³C NMR** (101 MHz, CDCl₃): δ 151.11, 131.89, 119.81, 115.36, 46.54, 32.21, 29.67. **HRMS** (APCI⁺, *m/z*) calculated for C₁₂H₁₈N[M+H]⁺: 176.14392; found: 176.14445. The spectral data are identical to the previously reported.¹⁴

N-butyl-4-methoxyaniline (5a)



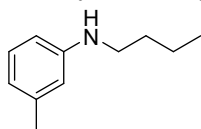
The compound was synthesized according to the **General procedure** using 4-methoxyaniline (123 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5a** (139 mg, 78% yield). Yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 95:5). **¹H NMR** (400 MHz, CDCl₃): δ 6.82 (d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H, OCH₃), 3.28 (*br s*, 1H, NH), 3.09 (t, *J* = 7.2 Hz, 2H), 1.62 (p, *J* = 7.2 Hz, 2H), 1.46 (sext, *J* = 7.6 Hz, 2H), 1.00 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 154.61, 145.61, 117.57, 116.67, 58.46, 47.37, 34.50, 23.04, 16.64. **HRMS** (APCI⁺, *m/z*) calculated for C₁₁H₁₈NO[M+H]⁺: 180.13884; found: 180.13965. The spectral data are identical to the previously reported.⁷

N-butyl-4-methylaniline (5b)



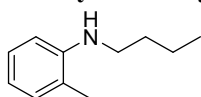
The compound was synthesized according to the **General procedure** using 4-methylaniline (107 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5b** (125 mg, 77% yield). Yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 95:5). **¹H NMR** (400 MHz, CDCl₃): δ 7.08 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 2H), 3.43 (*br s*, 1H, NH), 3.17 (t, *J* = 7.2 Hz, 2H), 2.34 (s, 3H, CH₃), 1.68 (p, *J* = 7.2 Hz, 2H), 1.51 (sext, *J* = 7.6 Hz, 2H), 1.05 (t, *J* = 7.6 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 149.07, 132.43, 128.93, 115.63, 46.79, 34.49, 23.11, 23.08, 16.68. **HRMS** (APCI⁺, *m/z*) calculated for C₁₁H₁₈N [M+H]⁺: 164.14392; found: 164.14446. The spectral data are identical to the previously reported.⁷

***N*-butyl-3-methylaniline (5c)**



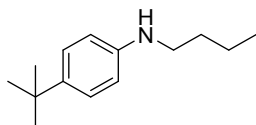
The compound was synthesized according to the **General procedure** using 4-methylaniline (107 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5c** (87 mg, 53% yield). Yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 95:5). **¹H NMR** (400 MHz, CDCl₃): δ 7.14 (t, *J* = 7.2 Hz, 1H), 6.59 (d, *J* = 7.6 Hz, 1H), 6.50–6.48 (m, 2H), 3.54 (*br s*, 1H, NH), 3.16 (t, *J* = 6.8 Hz, 2H), 2.35 (s, 3H, CH₃), 1.66 (p, *J* = 7.2 Hz, 2H), 1.51 (sext, *J* = 7.6 Hz, 2H), 1.03 (t, *J* = 7.6 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 151.32, 141.63, 131.79, 120.72, 116.18, 112.58, 46.42, 34.45, 24.35, 23.04, 16.65. **HRMS** (APCI⁺, *m/z*) calculated for C₁₁H₁₈N [M+H]⁺: 164.14392; found: 164.14479. The spectral data are identical to the previously reported.⁷

***N*-butyl-2-methylaniline (5d)**



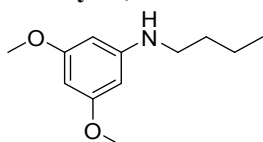
The compound was synthesized according to the **General procedure** using 4-methylaniline (107 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5d** (51 mg, 32% yield). Yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 95:5). **¹H NMR** (400 MHz, CDCl₃): δ 7.18 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.70–6.64 (m, 2H), 3.47 (*br s*, 1H, NH), 3.19 (t, *J* = 6.8 Hz, 2H), 2.17 (s, 3H, CH₃), 1.69 (p, *J* = 7.6 Hz, 2H), 1.49 (sext, *J* = 8.0 Hz, 2H), 1.01 (t, *J* = 7.6 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 149.09, 132.67, 129.80, 124.33, 119.28, 112.27, 46.32, 34.42, 23.08, 20.12, 16.64. **HRMS** (APCI⁺, *m/z*) calculated for C₁₁H₁₈N [M+H]⁺: 164.14392; found: 164.14467. The spectral data are identical to the previously reported.⁷

4-(*tert*-butyl)-*N*-butylaniline (5e)



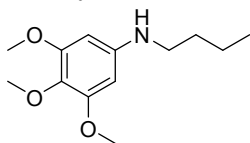
The compound was synthesized according to the **General procedure** using 4-(*tert*-butyl)aniline (149 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5e** (144 mg, 70% yield). Yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 95:5). **¹H NMR** (400 MHz, CDCl₃): δ 7.31 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 3.52 (*br s*, 1H, NH), 3.19 (t, *J* = 6.8 Hz, 2H), 1.69 (p, *J* = 7.6 Hz, 2H), 1.52 (sext, *J* = 7.6 Hz, 2H), 1.39 (s, 9H, ^{*t*}Bu), 1.06 (t, *J* = 7.6 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 148.97, 142.50, 128.69, 115.15, 46.64, 36.55, 34.55, 34.32, 23.08, 16.68. **HRMS** (APCI⁺, *m/z*) calculated for C₁₄H₂₄N [M+H]⁺: 206.19087; found: 206.19198. The spectral data are identical to the previously reported.¹⁵

***N*-butyl-3,5-dimethoxyaniline (5f)**



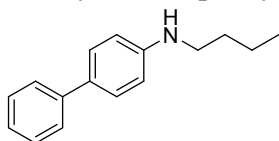
The compound was synthesized according to the **General procedure** using 3,5-dimethoxyaniline (153 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5f** (180 mg, 86% yield). Colorless oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 90:10 to 80:20). **¹H NMR** (400 MHz, CDCl₃): δ 5.90 (t, *J* = 2.0 Hz, 1H), 5.82 (d, *J* = 2.4 Hz, 2H), 3.76 (s, 6H, OCH₃), 3.09 (t, *J* = 6.8 Hz, 2H), 1.60 (p, *J* = 7.2 Hz, 2H), 1.44 (sext, *J* = 7.6 Hz, 2H), 0.98 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 164.40, 153.19, 94.14, 92.07, 57.72, 46.32, 34.28, 22.99, 16.58. **HRMS** (APCI⁺, *m/z*) calculated for C₁₂H₂₀NO₂ [M+H]⁺: 210.14940; found: 210.15056.

N-butyl-3,4,5-trimethoxyaniline (**5g**)



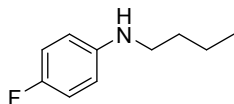
The compound was synthesized according to the **General procedure** using 3,4,5-trimethoxyaniline (183 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5g** (156 mg, 65% yield). Yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 90:10 to 70:30). **¹H NMR** (400 MHz, CDCl₃): δ 5.82 (s, 2H), 3.80 (s, 6H, OCH₃), 3.74 (s, 3H, OCH₃), 3.06 (t, *J* = 7.2 Hz, 2H), 1.58 (p, *J* = 7.2 Hz, 2H), 1.41 (sext, *J* = 7.6 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 156.57, 148.05, 132.48, 92.84, 63.69, 58.53, 46.72, 34.34, 22.95, 16.55. **HRMS** (APCI⁺, *m/z*) calculated for C₁₃H₂₂NO₃ [M+H]⁺: 240.15997; found: 240.16133. The spectral data are identical to the previously reported.¹⁶

N-butyl-[1,1'-biphenyl]-4-amine (**5h**)



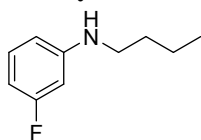
The compound was synthesized according to the **General procedure** using [1,1'-biphenyl]-4-amine (169 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5h** (95 mg, 42% yield). Yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 95:5). **¹H NMR** (400 MHz, CDCl₃): δ 7.55-7.52 (m, 2H), 7.45-7.43 (m, 2H), 7.40-7.37 (m, 2H), 7.27-7.25 (m, 1H), 6.71-6.69 (m, 2H), 3.16 (t, *J* = 7.2 Hz, 2H), 1.64 (p, *J* = 7.6 Hz, 2H), 1.45 (sext, *J* = 7.6 Hz, 2H), 0.97 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 150.65, 144.03, 132.62, 131.32, 130.59, 128.93, 128.65, 115.61, 46.39, 34.37, 23.02, 16.63. **HRMS** (APCI⁺, *m/z*) calculated for C₁₆H₂₀N[M+H]⁺: 226.15957; found: 226.16054.

N-butyl-4-fluoroaniline (**5i**)



The compound was synthesized according to the **General procedure** using 4-fluoroaniline (111 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5i** (120 mg, 72% yield). Yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 95:5). **¹H NMR** (400 MHz, CDCl₃): δ 6.91 (t, *J* = 8.8 Hz, 2H), 6.55 (dd, *J* = 8.8 Hz, *J* = 4.4 Hz, 2H), 3.42 (*br s*, 1H, NH), 3.08 (t, *J* = 7.2 Hz, 2H), 1.62 (p, *J* = 7.2 Hz, 2H), 1.46 (sext, *J* = 7.6 Hz, 2H), 1.00 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 158.32 (d, *J*_{C-F} = 235.3 Hz), 147.65, 118.23 (d, *J*_{C-F} = 22.3 Hz), 116.10 (d, *J*_{C-F} = 7.4 Hz), 47.04, 34.33, 22.98, 16.57. **HRMS** (APCI⁺, *m/z*) calculated for C₁₀H₁₅FN[M+H]⁺: 168.11885; found: 168.11975.

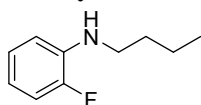
N-butyl-3-fluoroaniline (**5j**)



The compound was synthesized according to the **General procedure** using 3-fluoroaniline (111 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5j** (104 mg, 62% yield). Yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 100:0 to 95:5). **¹H NMR** (400 MHz, CDCl₃): δ 7.13-7.08 (m, 1H), 6.41-6.36 (m, 2H), 6.33-6.29 (m, 1H), 3.72 (*br s*, 1H, NH), 3.10 (t, *J* = 7.2 Hz, 2H), 1.62 (p, *J* = 7.6 Hz, 2H), 1.45 (sext, *J* = 7.6 Hz, 2H), 0.99 (t, *J* = 7.6 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 166.98 (d, *J*_{C-F} = 243.4 Hz), 153.01 (d, *J*_{C-F} = 11.1 Hz), 132.84 (d, *J*_{C-F} = 10.1 Hz), 111.23 (d, *J*_{C-F} = 2.0 Hz),

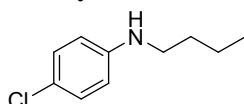
105.96 (d, $J_{\text{C-F}} = 22.2$ Hz), 101.78 (d, $J_{\text{C-F}} = 25.3$ Hz), 46.22, 34.15, 22.93, 16.53. **HRMS** (APCI⁺, m/z) calculated for $\text{C}_{10}\text{H}_{15}\text{FN}[\text{M}+\text{H}]^+$: 168.11885; found: 168.11952.

N-butyl-4-2-fluoroaniline (**5k**)



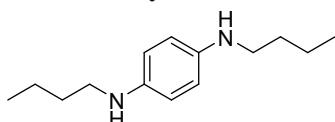
The compound was synthesized according to the **General procedure** using 2-fluoroaniline (111 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5k** (60 mg, 36% yield). Yellow oil was obtained after column chromatography (SiO_2 , Pentane/EtOAc 100:0 to 95:5). **¹H NMR** (400 MHz, CDCl_3): δ 7.04-6.96 (m, 2H), 6.72 (t, $J = 8.0$ Hz, 1H), 6.65-6.60 (m, 1H), 3.88 (*br s*, 1H, NH), 3.17 (t, $J = 7.2$ Hz, 2H), 1.66 (p, $J = 7.6$ Hz, 2H), 1.47 (sext, $J = 7.6$ Hz, 2H), 1.00 (t, $J = 7.2$ Hz, 3H). **¹³C NMR** (101 MHz, CDCl_3): δ 154.19 (d, $J_{\text{C-F}} = 238.9$ Hz), 139.69 (d, $J_{\text{C-F}} = 11.1$ Hz), 127.22 (d, $J_{\text{C-F}} = 2.0$ Hz), 118.81 (d, $J_{\text{C-F}} = 7.1$ Hz), 116.93 (d, $J_{\text{C-F}} = 19.2$ Hz), 114.60 (d, $J_{\text{C-F}} = 3.0$ Hz), 45.94, 34.24, 22.92, 16.55. **HRMS** (APCI⁺, m/z) calculated for $\text{C}_{10}\text{H}_{15}\text{FN} [\text{M}+\text{H}]^+$: 168.11885; found: 168.11956. The spectral data are identical to the previously reported.⁷

N-butyl-4-chloroaniline (**5l**)



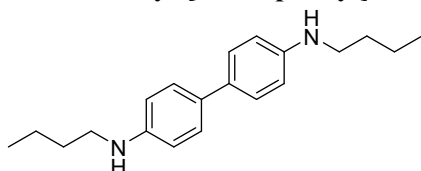
The compound was synthesized according to the **General procedure** using 4-chloroaniline (128 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5l** (117 mg, 64% yield). Yellow oil was obtained after column chromatography (SiO_2 , Pentane/EtOAc 100:0 to 95:5). **¹H NMR** (400 MHz, CDCl_3): δ 7.10 (d, $J = 8.8$ Hz, 2H), 6.51 (d, $J = 8.8$ Hz, 2H), 3.60 (*br s*, 1H, NH), 3.07 (t, $J = 6.8$ Hz, 2H), 1.59 (p, $J = 7.6$ Hz, 2H), 1.42 (sext, $J = 7.6$ Hz, 2H), 0.96 (t, $J = 7.2$ Hz, 3H). **¹³C NMR** (101 MHz, CDCl_3): δ 149.72, 131.64, 124.19, 116.33, 46.43, 34.18, 22.91, 16.53. **HRMS** (APCI⁺, m/z) calculated for $\text{C}_{10}\text{H}_{15}\text{ClN}[\text{M}+\text{H}]^+$: 184.08930; found: 184.09024. The spectral data are identical to the previously reported.¹⁶

N,N'-dibutylbenzene-1,4-diamine (**5m**)



The compound was synthesized according to the **General procedure** using benzene-1,4-diamine (108 mg, 1 mmol) and 1-butanol (222 mg, 3 mmol) to afford **5m** (159 mg, 72% yield). Light orange solid was obtained after column chromatography (SiO_2 , Pentane/EtOAc 95:5 to 60:40). **¹H NMR** (400 MHz, CDCl_3): δ 6.59 (s, 4H), 3.18-3.09 (m, 4H), 1.62 (p, $J = 7.6$ Hz, 4H), 1.46 (sext, $J = 7.6$ Hz, 4H), 1.00 (t, $J = 7.6$ Hz, 6H). **¹³C NMR** (101 MHz, CDCl_3): δ 143.63, 117.41, 47.79, 34.66, 23.08, 16.68. **HRMS** (APCI⁺, m/z) calculated for $\text{C}_{14}\text{H}_{25}\text{N}_2 [\text{M}+\text{H}]^+$: 221.20177; found: 221.20297. The spectral data are identical to the previously reported.¹⁷

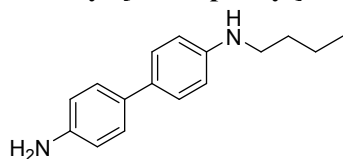
N,N'-dibutyl-[1,1'-biphenyl]-4,4'-diamine (**5oa**)



The compound was synthesized according to the **General procedure** using benzidine (184 mg, 1 mmol) and 1-butanol (222 mg, 3 mmol) to afford **5oa** (73 mg, 25% yield). Yellow solid was obtained after column chromatography (SiO_2 , Pentane/EtOAc 90:10). **¹H NMR** (400 MHz, CDCl_3): δ 7.42 (d, $J = 8.4$ Hz, 4H), 6.69 (d, $J = 8.4$ Hz, 4H), 3.61 (*br s*, 2H, NH), 3.18 (t, $J = 7.2$ Hz, 4H), 1.66 (p, $J = 7.2$ Hz, 4H), 1.48 (sext, $J = 7.2$ Hz, 4H), 1.01 (t, $J = 7.2$ Hz, 6H). **¹³C NMR** (101 MHz, CDCl_3): δ 149.74, 133.20,

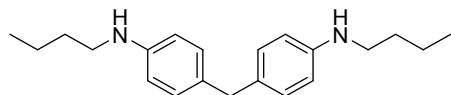
129.78, 115.71, 46.55, 34.44, 23.03, 16.65. **HRMS** (APCI⁺, m/z) calculated for C₂₀H₂₉N₂ [M+H]⁺: 297.23306; found: 297.23498.

*N*⁴-butyl-[1,1'-biphenyl]-4,4'-diamine (**5ob**)



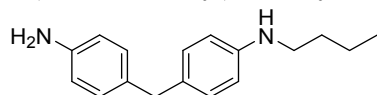
The compound was synthesized according to the **General procedure** using benzidine (184 mg, 1 mmol) and 1-butanol (222 mg, 3 mmol) to afford **5ob** (93 mg, 39% yield). Orange solid was obtained after column chromatography (SiO₂, Pentane/EtOAc 70:30). **¹H NMR** (400 MHz, CDCl₃): δ 7.42-7.38 (m, 4H), 6.75 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 8.0 Hz, 2H), 3.61 (*brs*, 3H, NH), 3.17 (t, *J* = 7.2 Hz, 2H), 1.65 (p, *J* = 7.6 Hz, 2H), 1.48 (sext, *J* = 7.6 Hz, 2H), 1.01 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 149.90, 147.45, 134.70, 132.96, 129.90, 129.83, 118.18, 115.71, 46.53, 34.40, 23.02, 16.65. **HRMS** (APCI⁺, m/z) calculated for C₁₆H₂₁N₂M+H]⁺: 241.17046; found: 241.17178.

4,4'-methylenebis(*N*-butylaniline) (**5pa**)



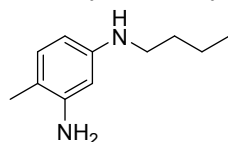
The compound was synthesized according to the **General procedure** using 4,4'-methylenedianiline (198 mg, 1 mmol) and 1-butanol (222 mg, 3 mmol) to afford **5pa** (101 mg, 32% yield). Light yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 90:10). **¹H NMR** (400 MHz, CDCl₃): δ 7.06 (d, *J* = 8.0 Hz, 4H), 6.60 (d, *J* = 8.4 Hz, 4H), 3.84 (s, 2H), 3.44 (*br s*, 2H, NH), 3.15 (t, *J* = 6.8 Hz, 4H), 1.65 (p, *J* = 7.2 Hz, 4H), 1.49 (sext, *J* = 7.6 Hz, 4H), 1.03 (t, *J* = 7.2 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃): δ 149.38, 133.41, 132.28, 115.55, 46.68, 42.85, 34.48, 23.06, 16.68. **HRMS** (APCI⁺, m/z) calculated for C₂₁H₃₁N₂[M+H]⁺: 311.24871; found: 311.25059.

4-(4-aminobenzyl)-*N*-butylaniline (**5pb**)



The compound was synthesized according to the **General procedure** using 4,4'-methylenedianiline (198 mg, 1 mmol) and 1-butanol (222 mg, 3 mmol) to afford **5pb** (108 mg, 43% yield). Light yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 70:30). **¹H NMR** (400 MHz, CDCl₃): δ 7.07-7.03 (m, 4H), 6.65 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 8.4 Hz, 2H), 3.85 (s, 2H), 3.53 (*br s*, 3H, NH), 3.15 (t, *J* = 7.2 Hz, 2H), 1.66 (p, *J* = 7.6 Hz, 2H), 1.50 (sext, *J* = 7.6 Hz, 2H), 1.04 (t, *J* = 7.6 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 149.42, 147.02, 134.89, 133.23, 132.33, 132.30, 117.99, 115.59, 46.69, 42.91, 34.46, 23.07, 16.71. **HRMS** (APCI⁺, m/z) calculated for C₁₇H₂₃N₂[M+H]⁺: 255.18611; found: 255.18753.

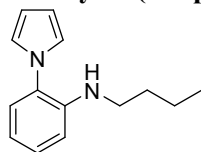
*N*⁴-butyl-4-methylbenzene-1,3-diamine (**5q**)



The compound was synthesized according to the **General procedure** using 4-methylbenzene-1,3-diamine (122 mg, 1 mmol) and 1-butanol (222 mg, 3 mmol) to afford **5q** (57 mg, 32% yield). Orange oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 95:5 to 70:30). **¹H NMR** (400 MHz, CDCl₃): δ 6.86 (d, *J* = 8.0 Hz, 1H), 6.05 (d, *J* = 8.0 Hz, 1H), 6.00 (d, *J* = 2 Hz, 1H), 3.43 (*br s*, 3H, NH), 3.09 (t, *J* = 7.2 Hz, 2H), 2.09 (s, 3H, CH₃), 1.60 (p, *J* = 7.2 Hz, 2H), 1.44 (sext, *J* = 7.6 Hz, 2H), 0.98 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 150.72, 147.95, 133.68, 114.21, 106.66, 102.46,

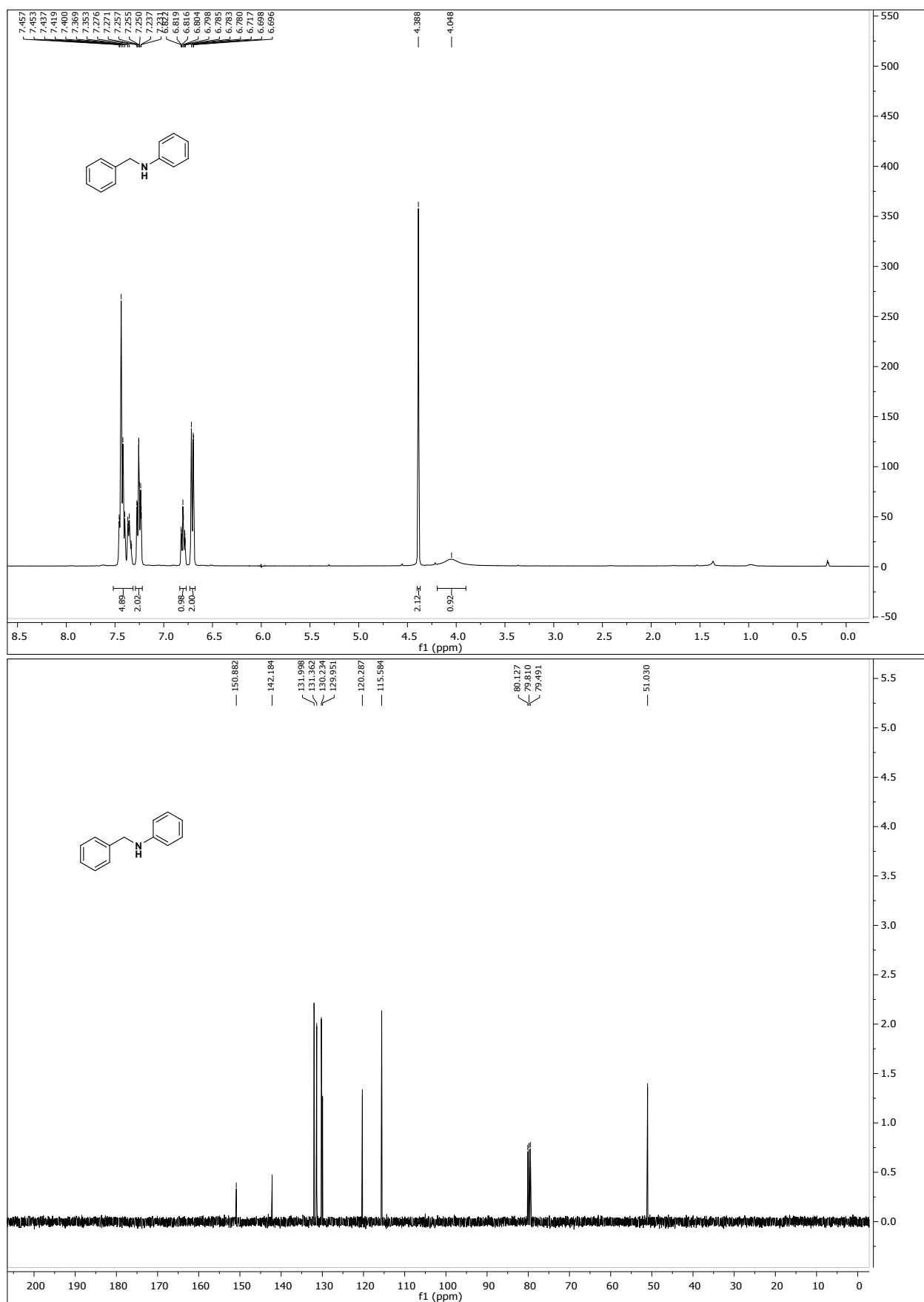
46.70, 34.46, 23.02, 19.08, 16.63. **HRMS** (APCI⁺, m/z) calculated for C₁₁H₁₉N₂ [M+H]⁺: 179.15482; found: 179.15570.

***N*-butyl-2-(1H-pyrrol-1-yl)aniline (5r)**

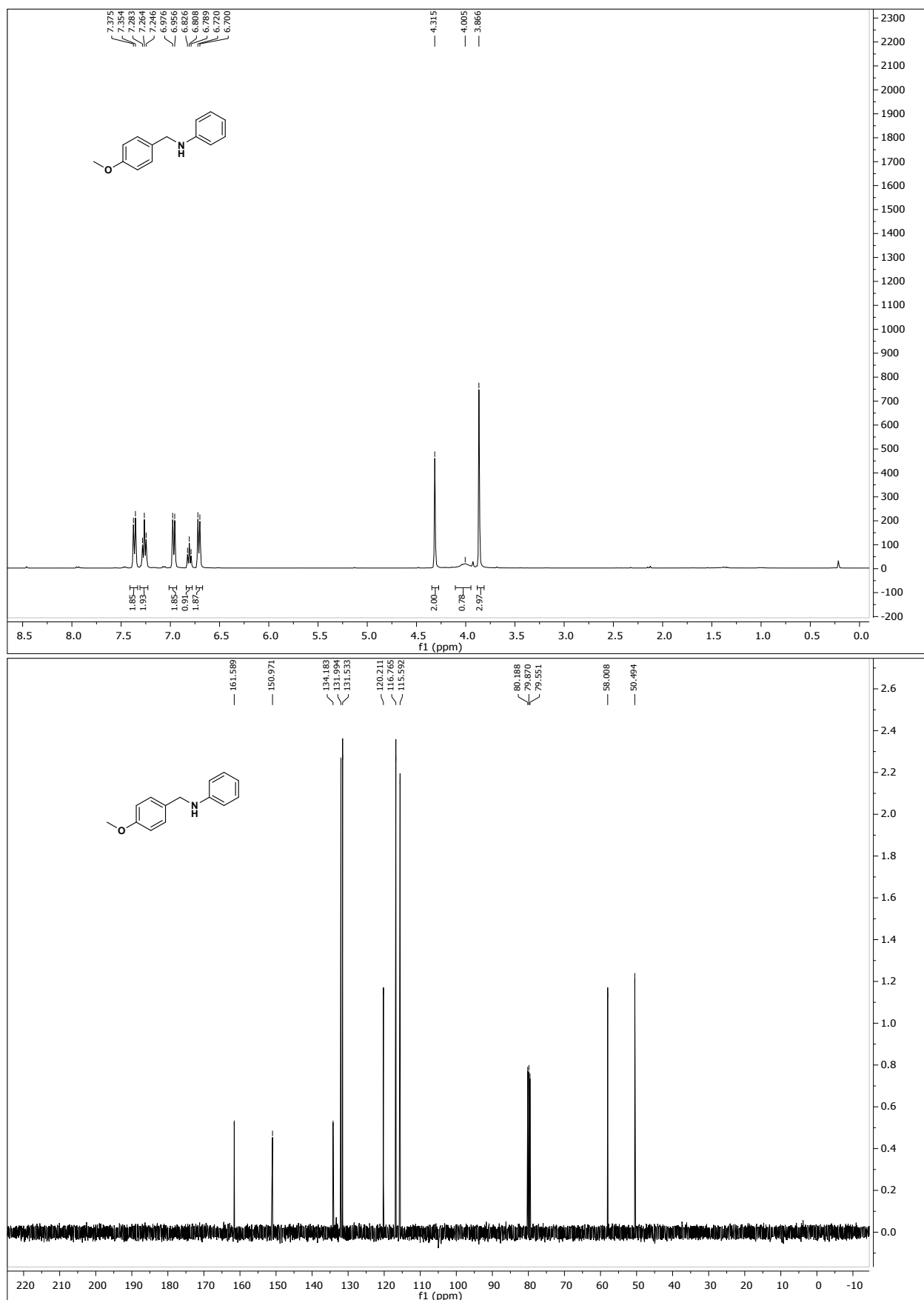


The compound was synthesized according to the **General procedure** using 2-(1H-pyrrol-1-yl)aniline (158 mg, 1 mmol) and 1-butanol (222 mg, 3 mmol) to afford **5r** (121 mg, 57% yield). Yellow oil was obtained after column chromatography (SiO₂, Pentane/EtOAc 95:5 to 70:30). **¹H NMR** (400 MHz, CDCl₃): δ 7.33-7.29 (m, 1H), 7.21-7.19 (m, 1H), 6.87 (t, *J* = 2.0 Hz, 2H), 6.81-6.77 (m, 2H), 6.42 (t, *J* = 2.0 Hz, 2H), 3.83 (*br s*, 1H, NH), 3.16 (t, *J* = 7.2 Hz, 2H), 1.60 (p, *J* = 7.2 Hz, 2H), 1.42 (sext, *J* = 7.6 Hz, 2H), 1.00 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃): δ 146.75, 131.61, 129.76, 124.57, 118.78, 113.71, 112.09, 112.08, 45.93, 34.05, 22.93, 16.57. **HRMS** (APCI⁺, m/z) calculated for C₁₄H₁₉N₂[M+H]⁺: 215.15482; found: 215.15568.

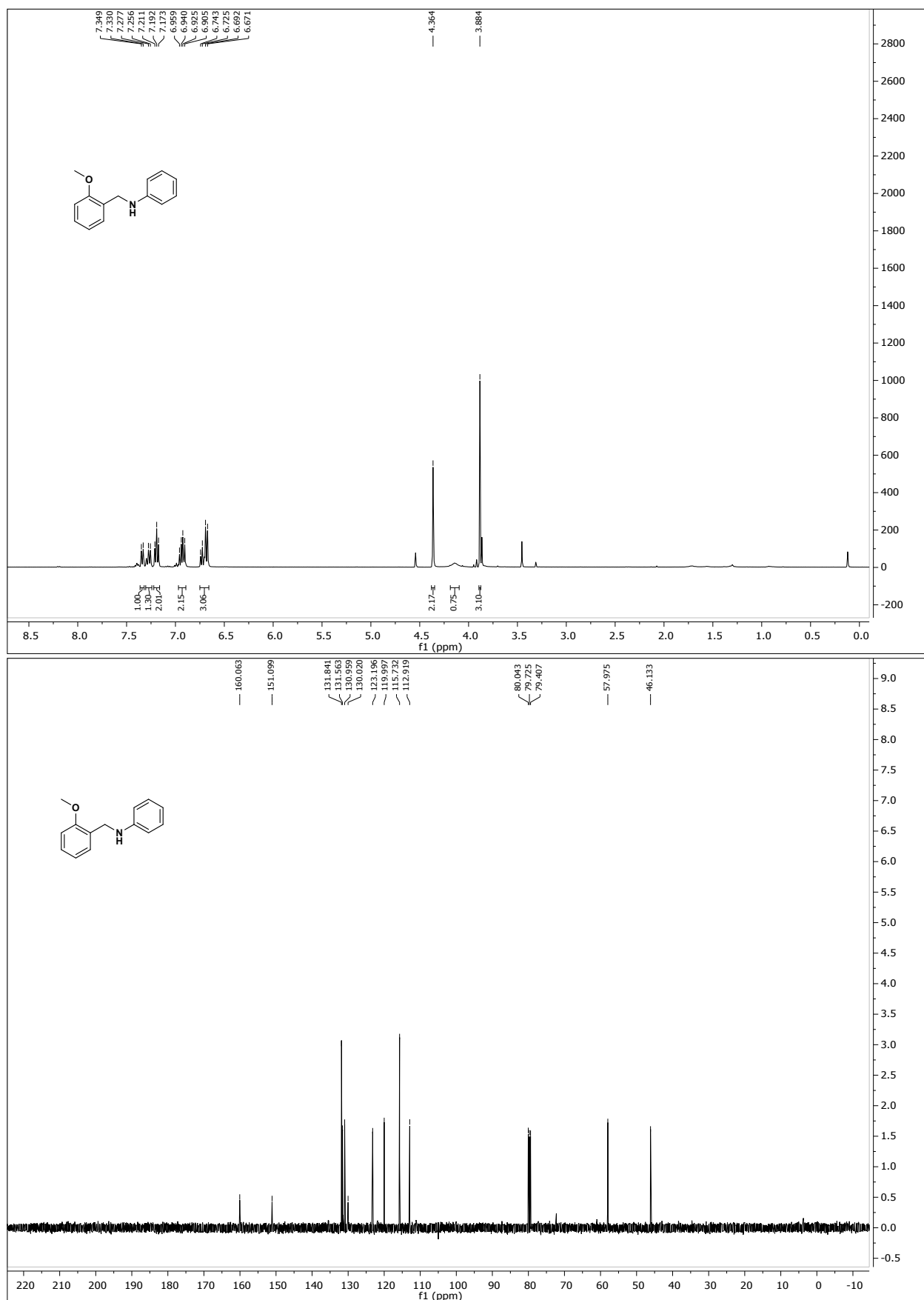
6. ^1H and ^{13}C NMR spectra



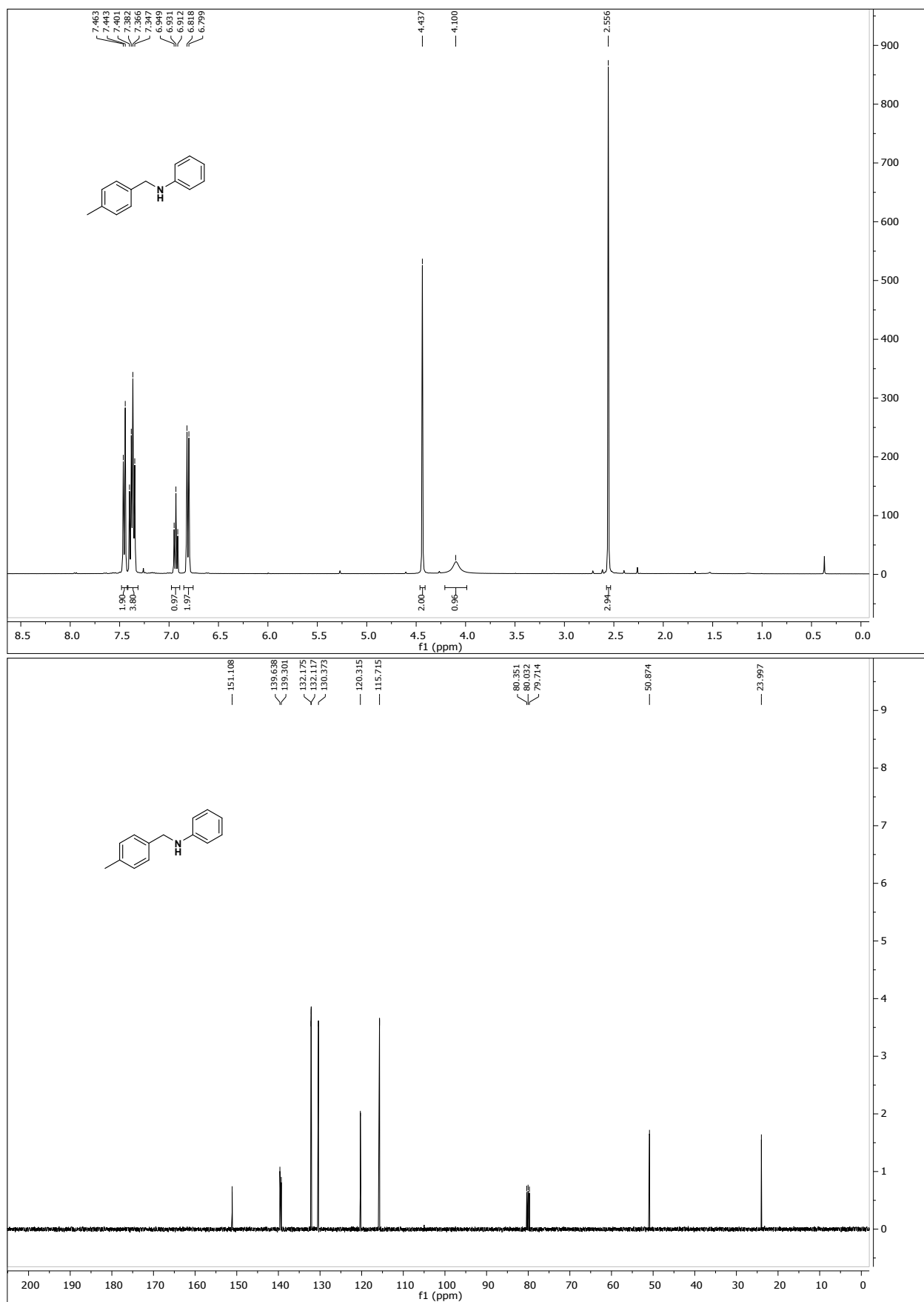
Supplementary Figure 1. ^1H and ^{13}C NMR of compound **3a**.



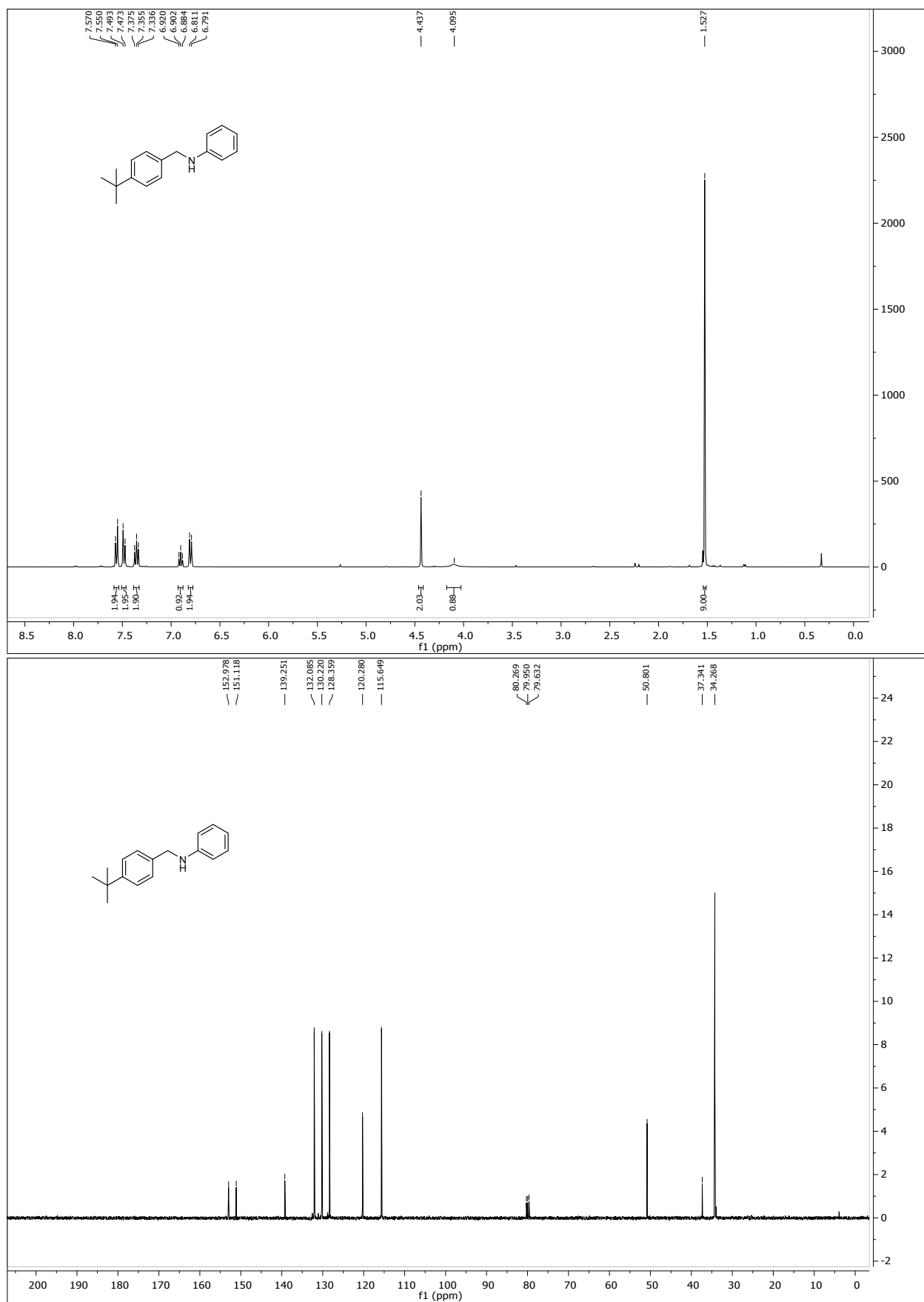
Supplementary Figure 2. ¹H and ¹³C NMR of compound **3b**.



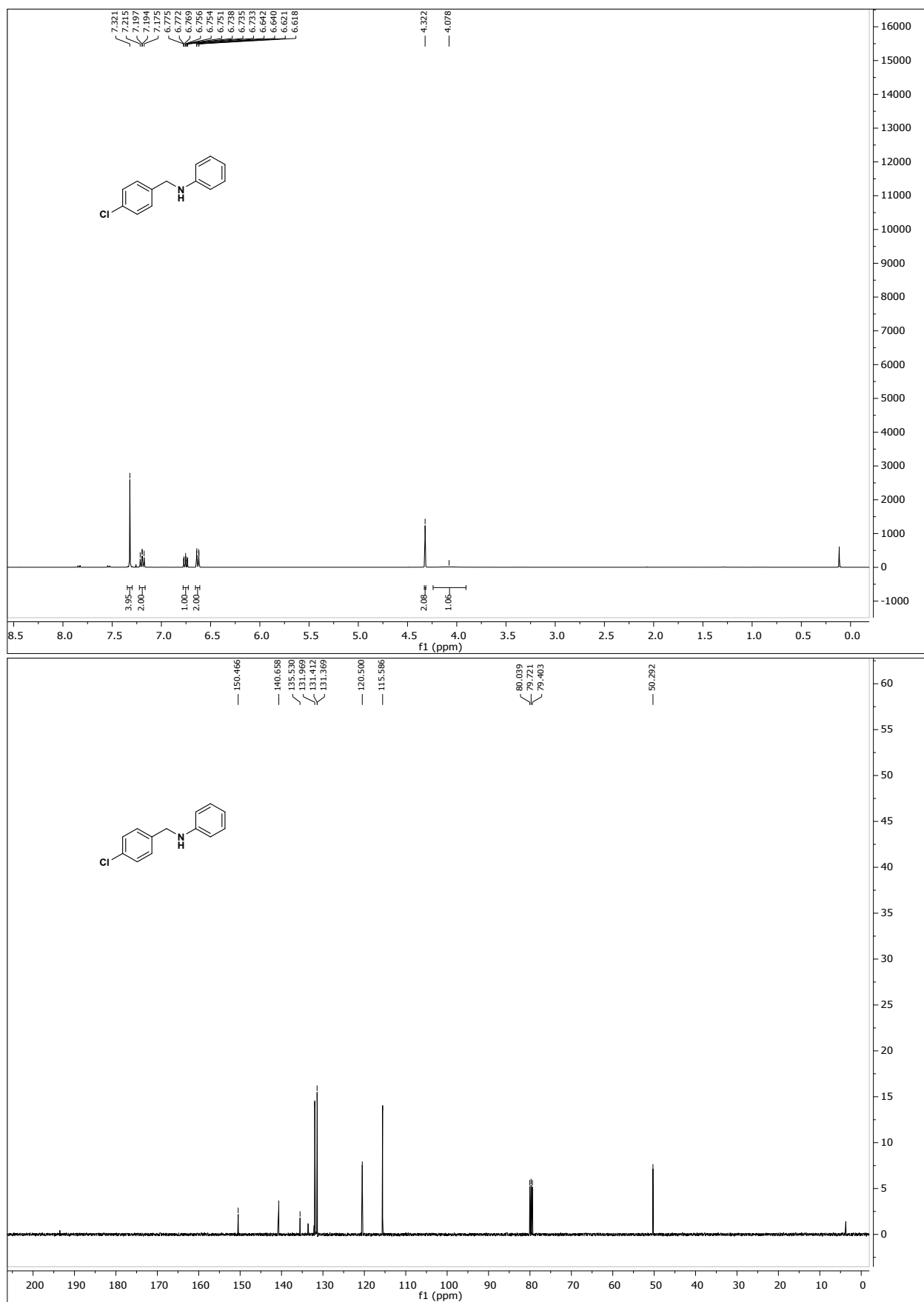
Supplementary Figure 3. ^1H and ^{13}C NMR of compound **3c**.



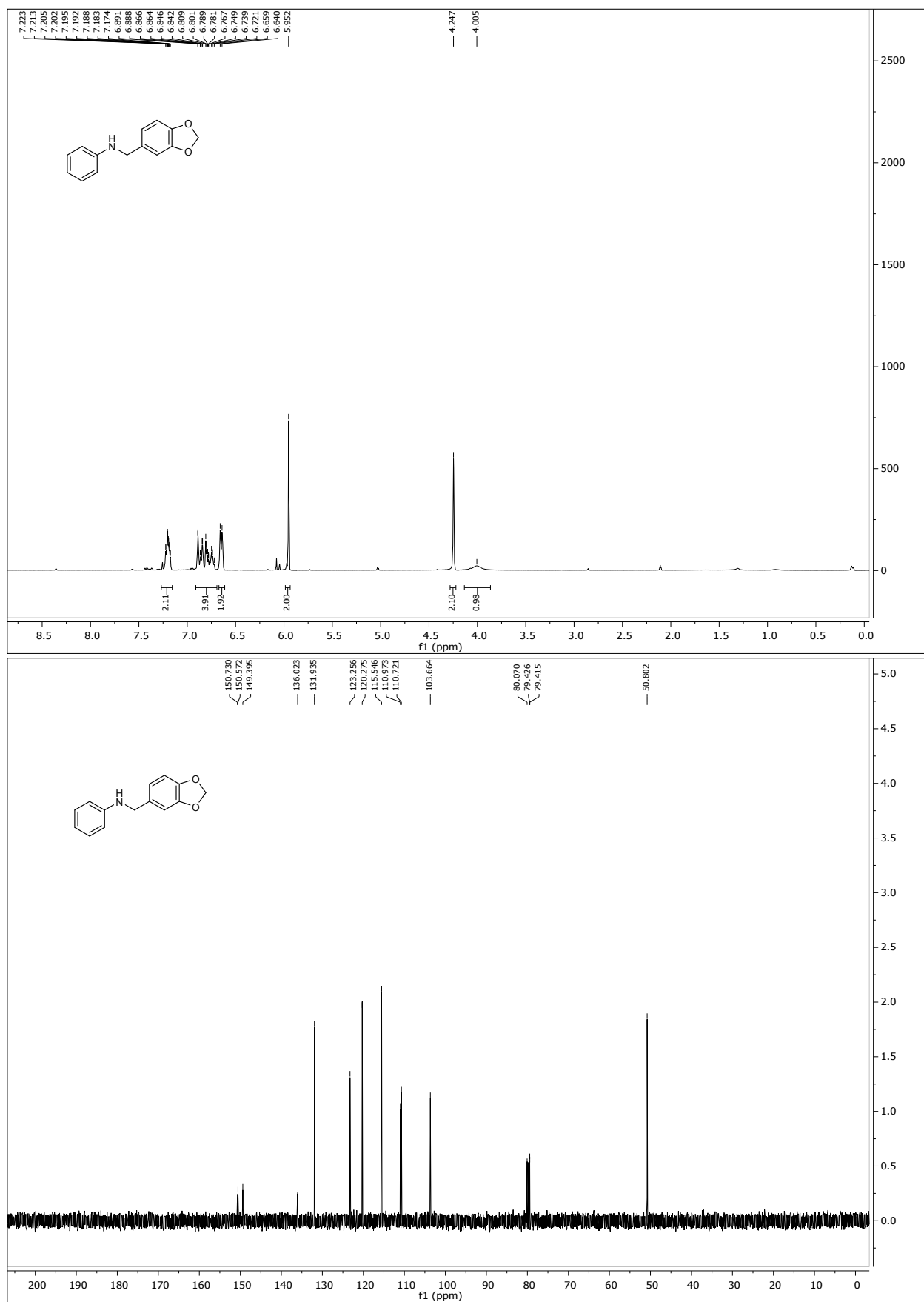
Supplementary Figure 4. ¹H and ¹³C NMR of compound **3d**.



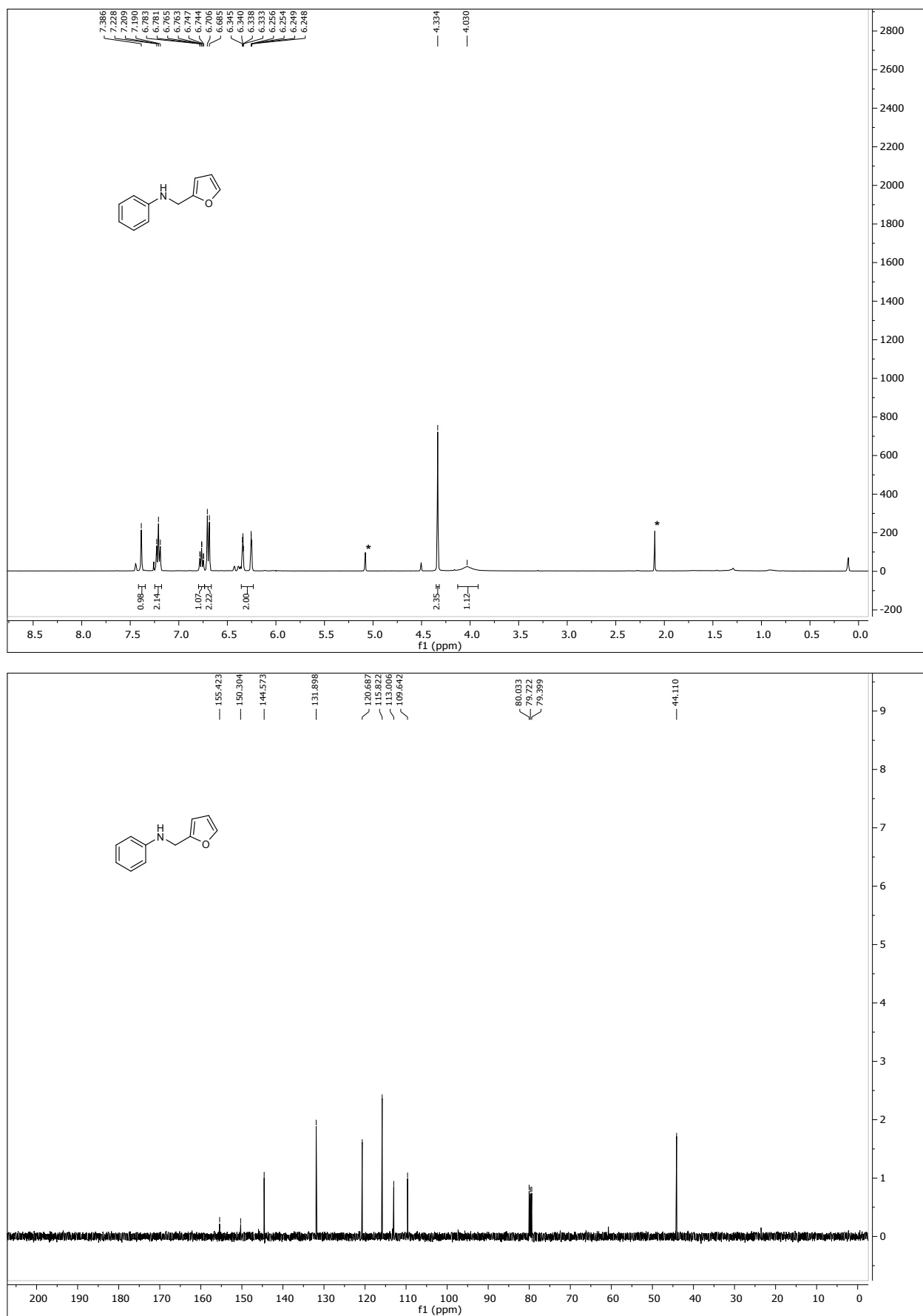
Supplementary Figure 5. ¹H and ¹³C NMR of compound **3e**.



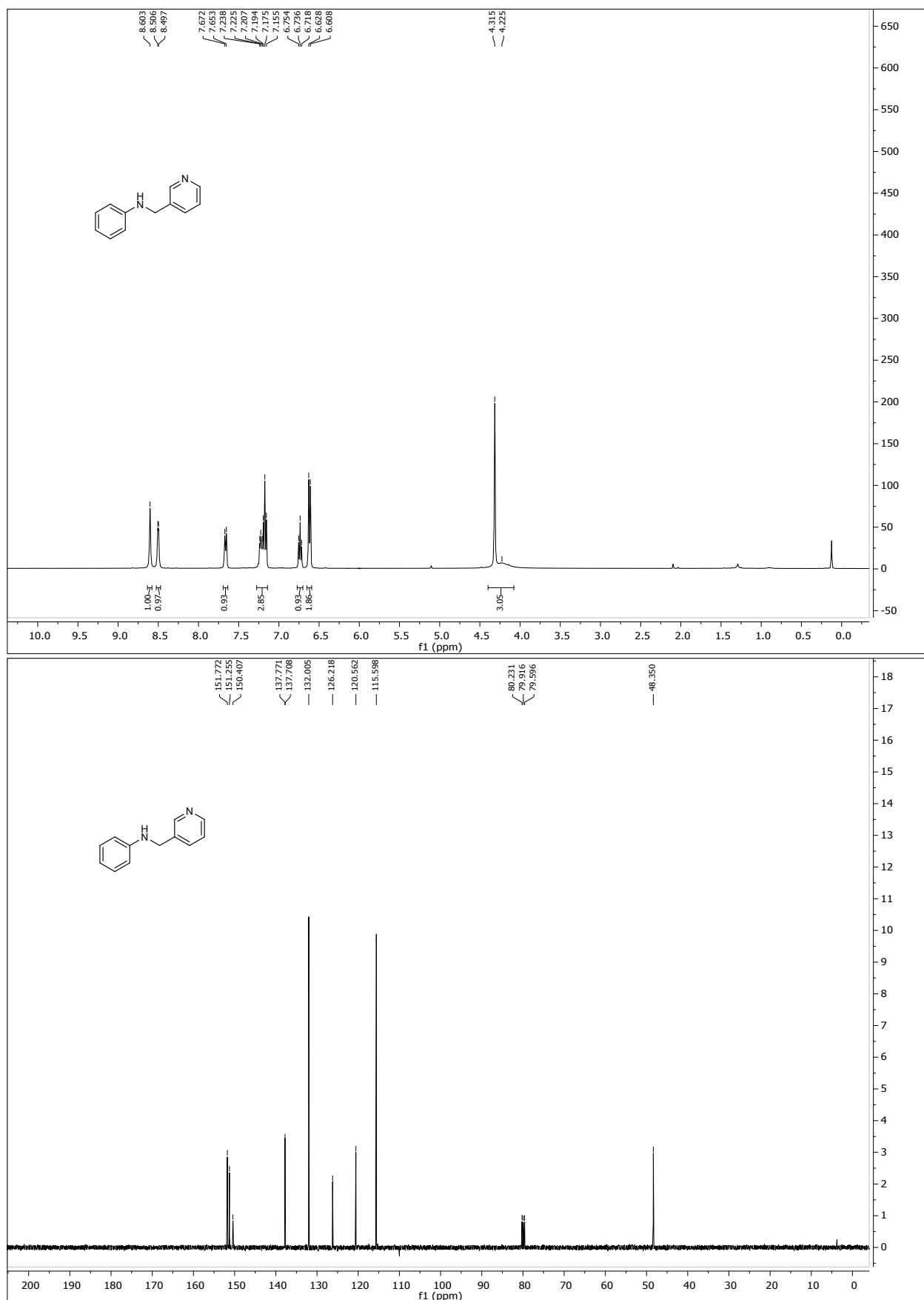
Supplementary Figure 6. ¹H and ¹³C NMR of compound **3f**.



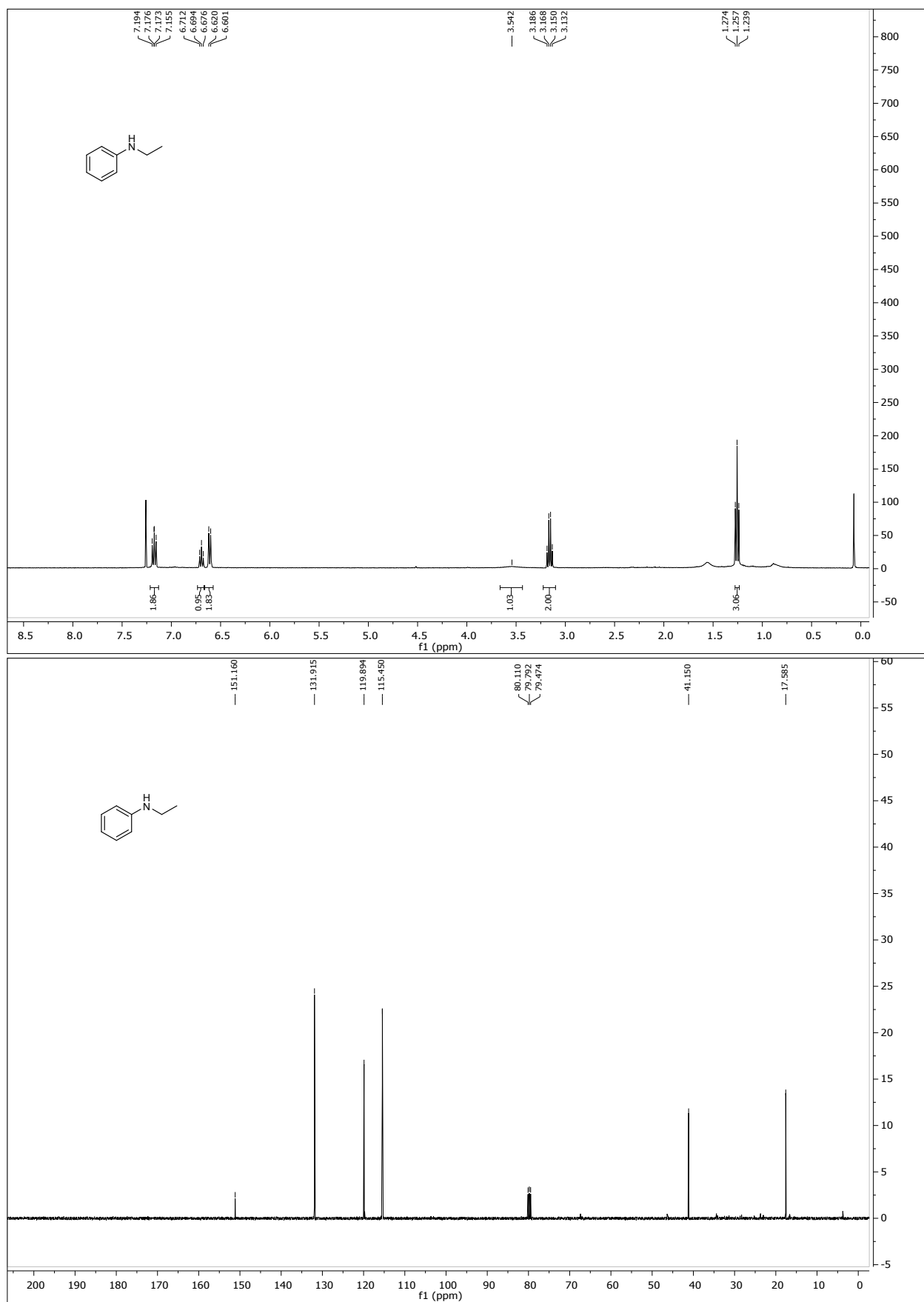
Supplementary Figure 7. ¹H and ¹³C NMR of compound **3g**.



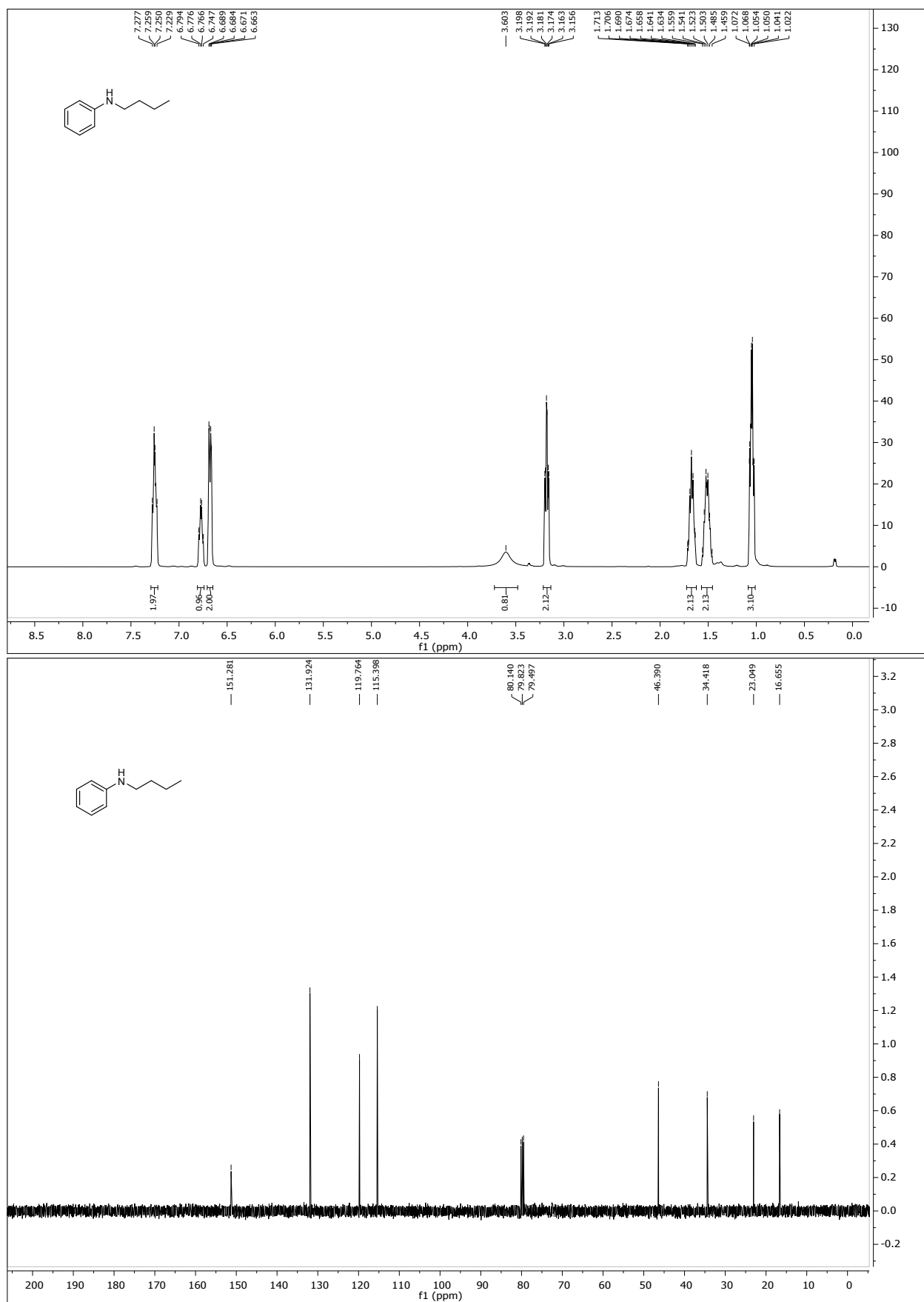
Supplementary Figure 8. ¹H and ¹³C NMR of compound **3h**.



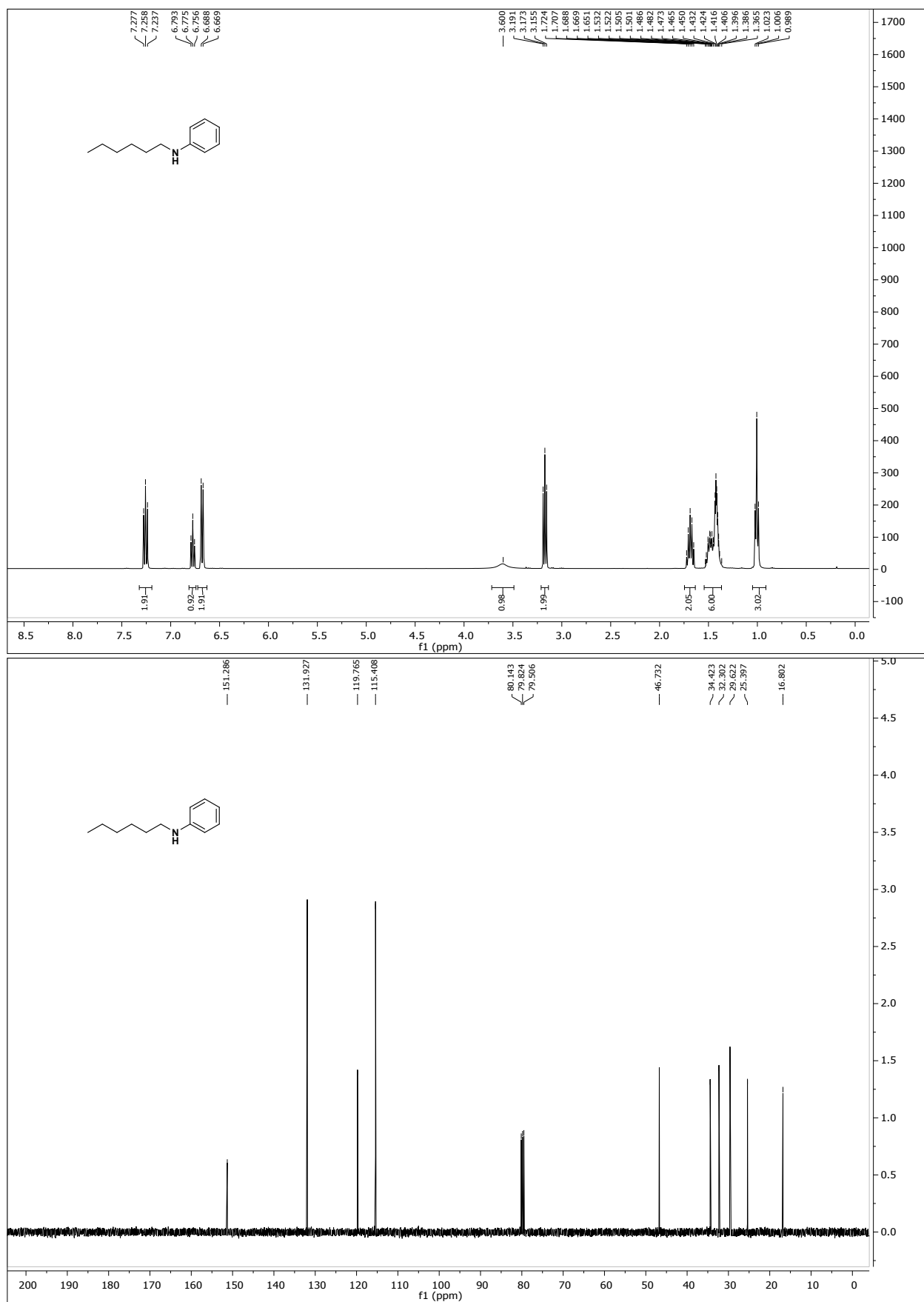
Supplementary Figure 9. ¹H and ¹³C NMR of compound 3i.



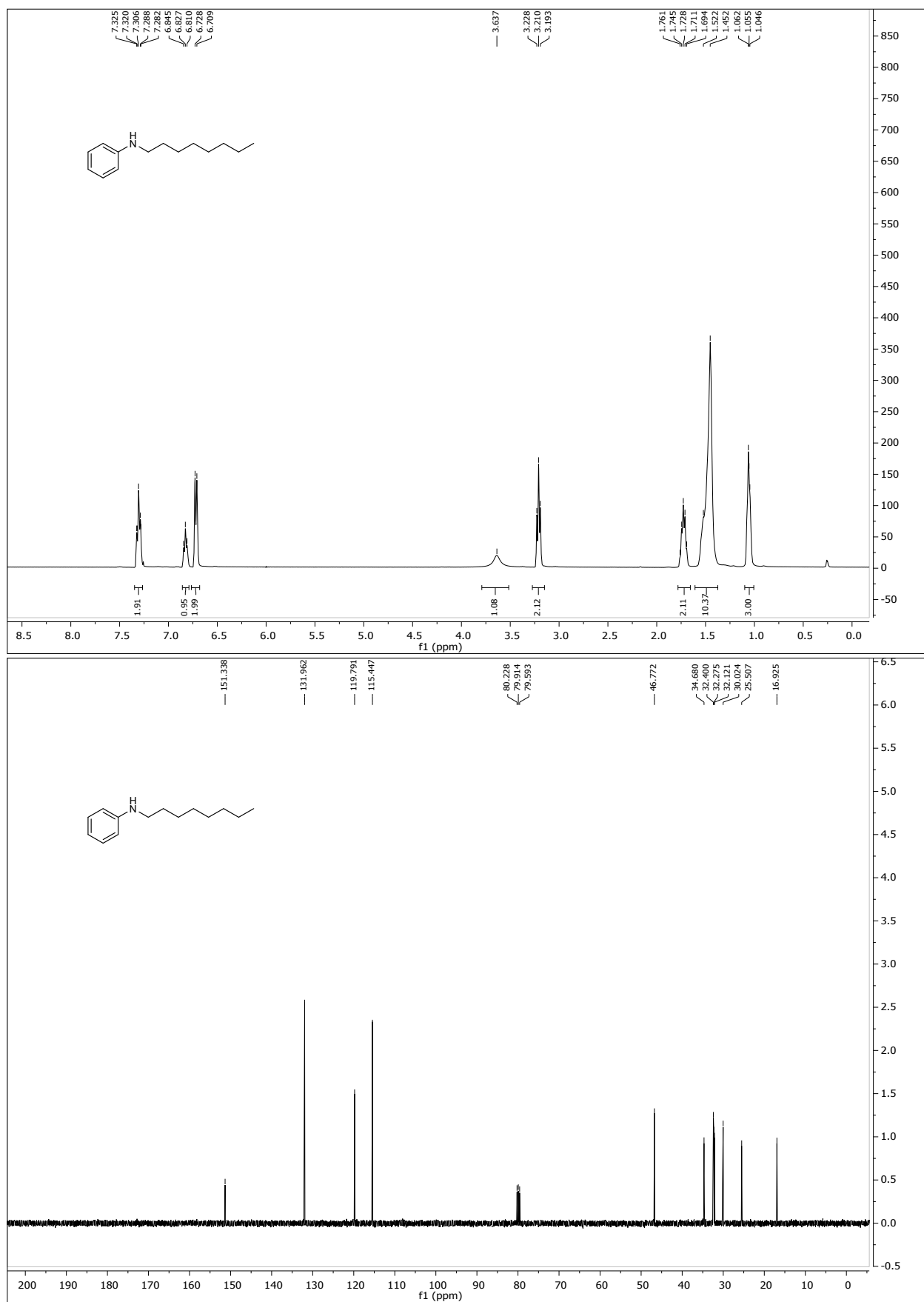
Supplementary Figure 10. ¹H and ¹³C NMR of compound 3k.



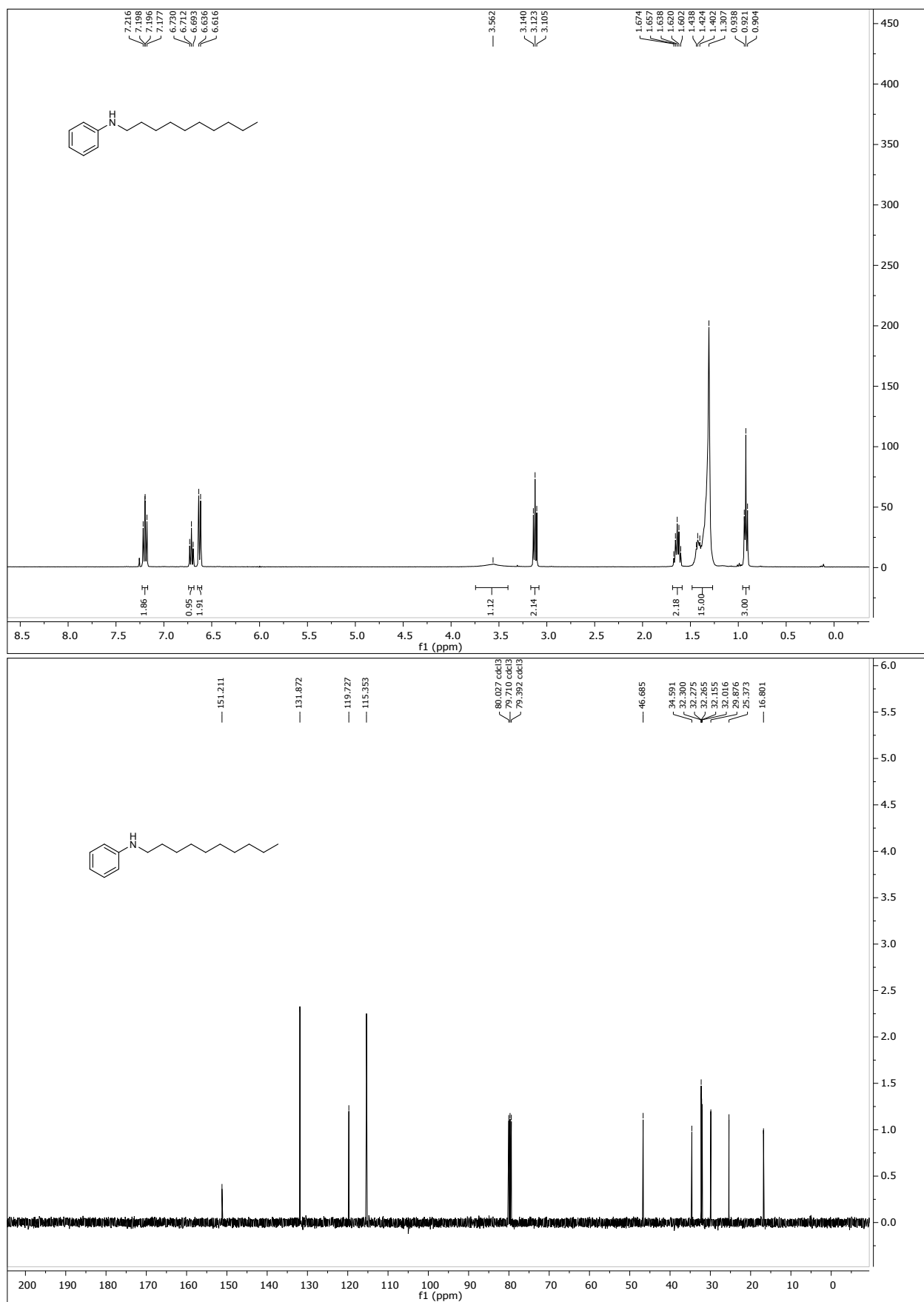
Supplementary Figure 11. ¹H and ¹³C NMR of compound 31.



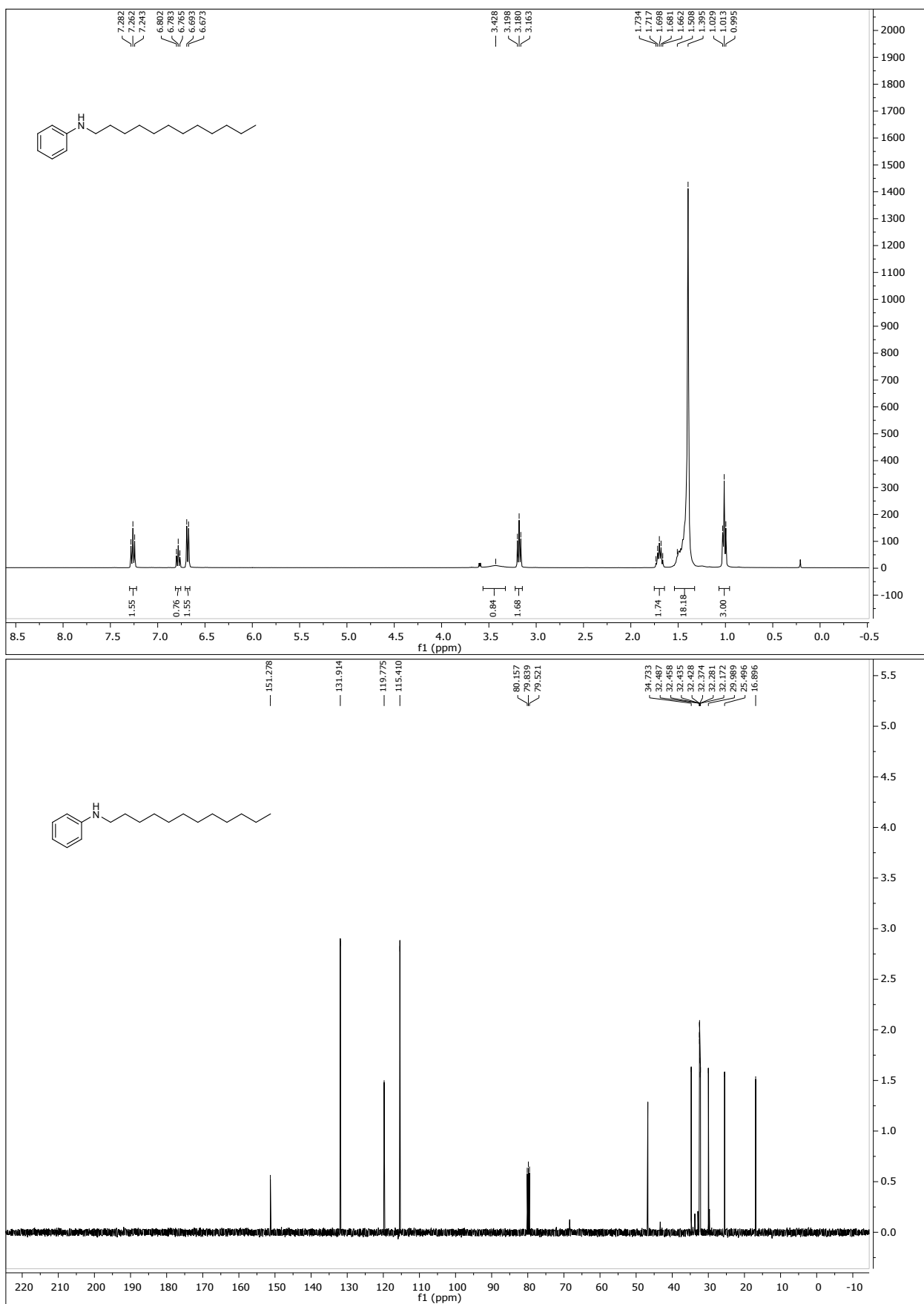
Supplementary Figure 12. ¹H and ¹³C NMR of compound **3m**.



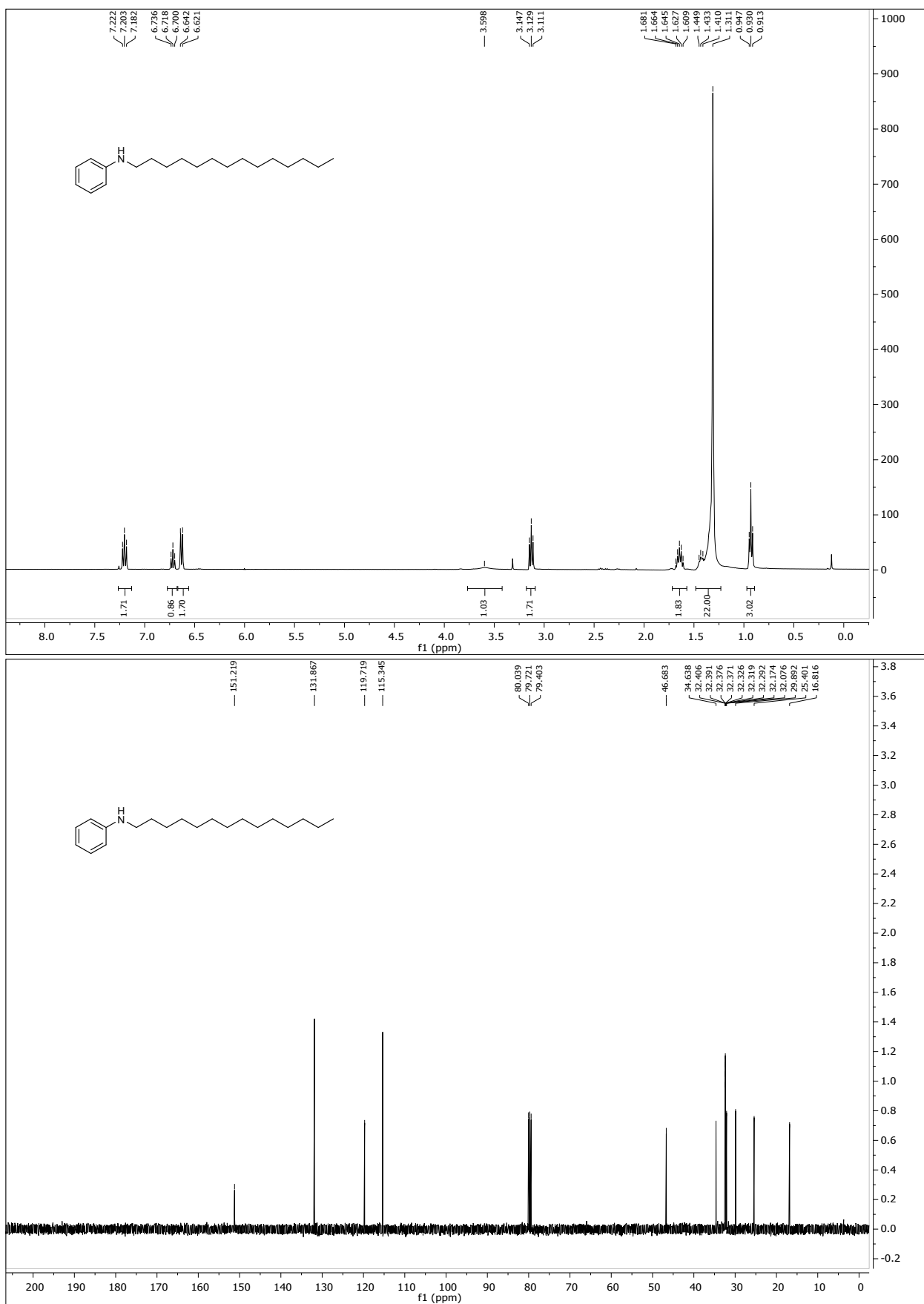
Supplementary Figure 13. ¹H and ¹³C NMR of compound **3n**.



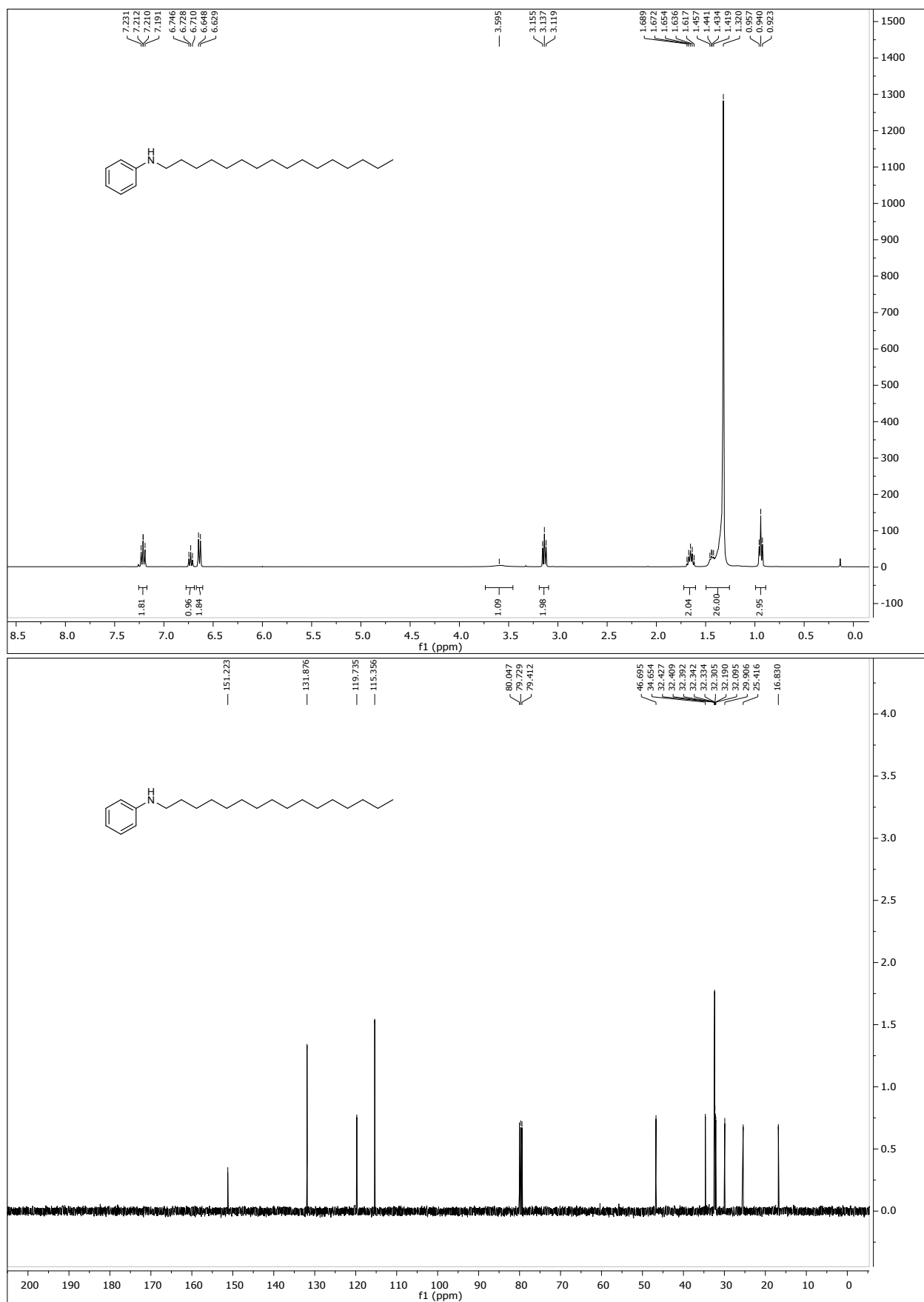
Supplementary Figure 14. ¹H and ¹³C NMR of compound **3o**.



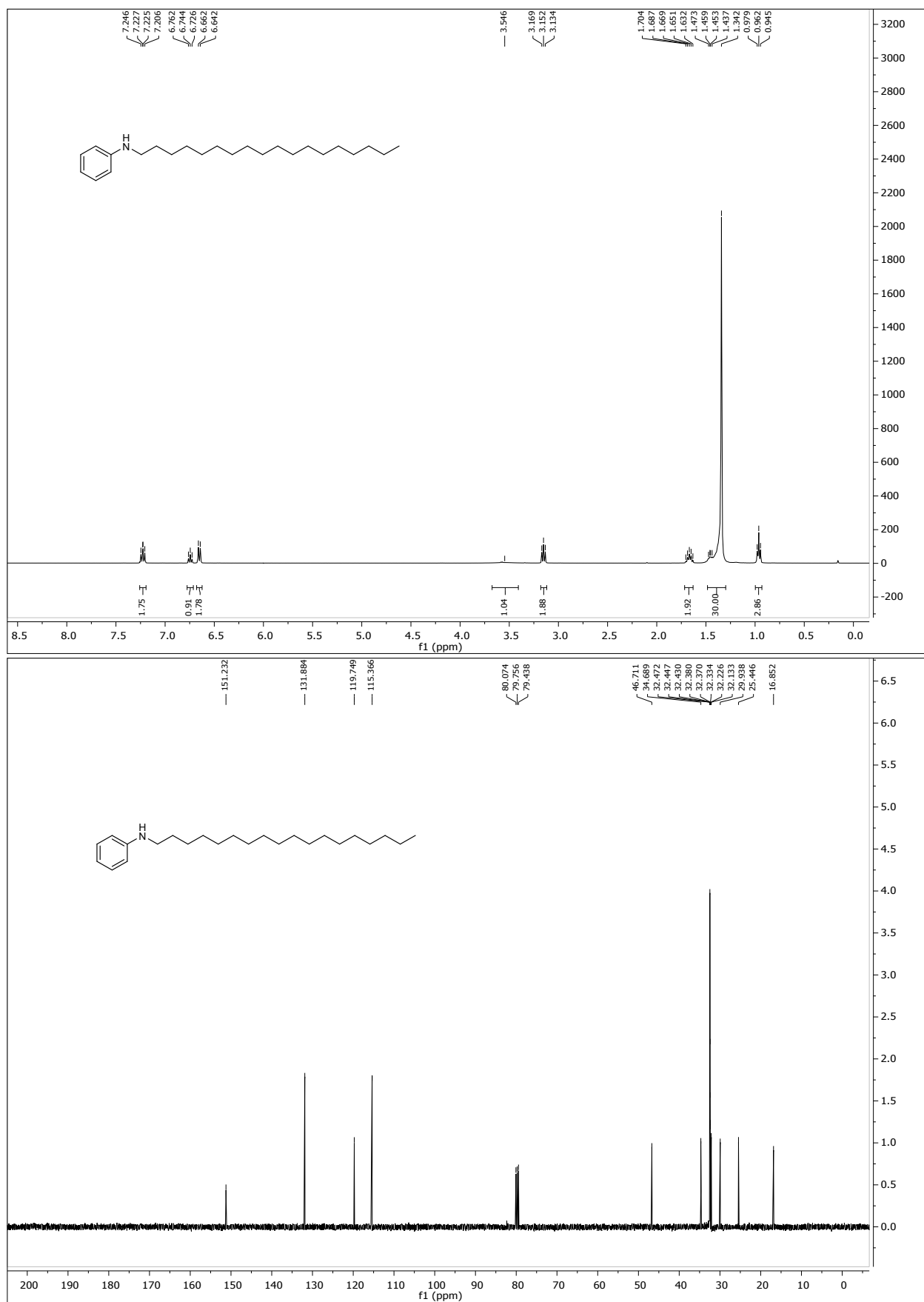
Supplementary Figure 15. ¹H and ¹³C NMR of compound 3p.



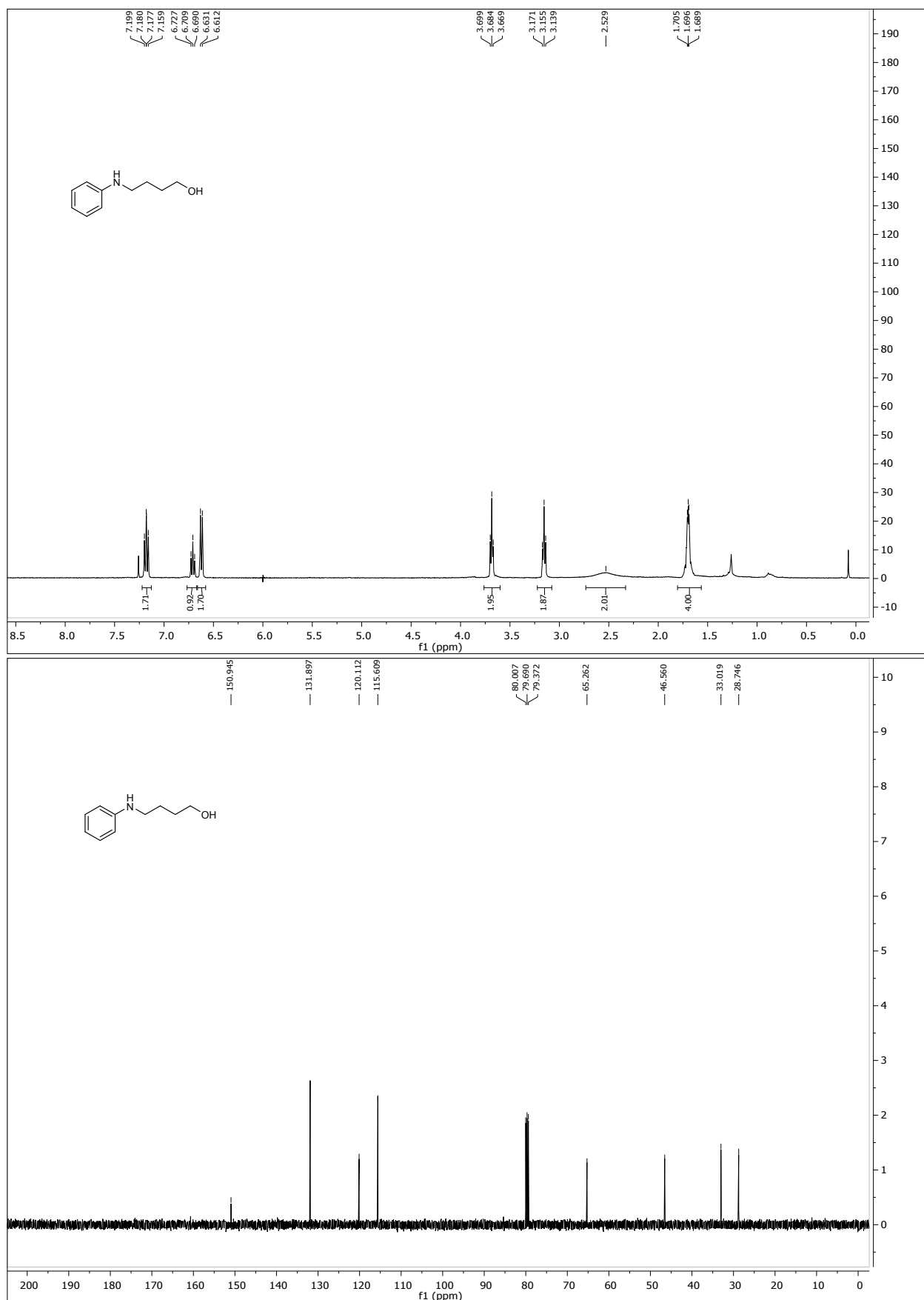
Supplementary Figure 16. ¹H and ¹³C NMR of compound 3q.



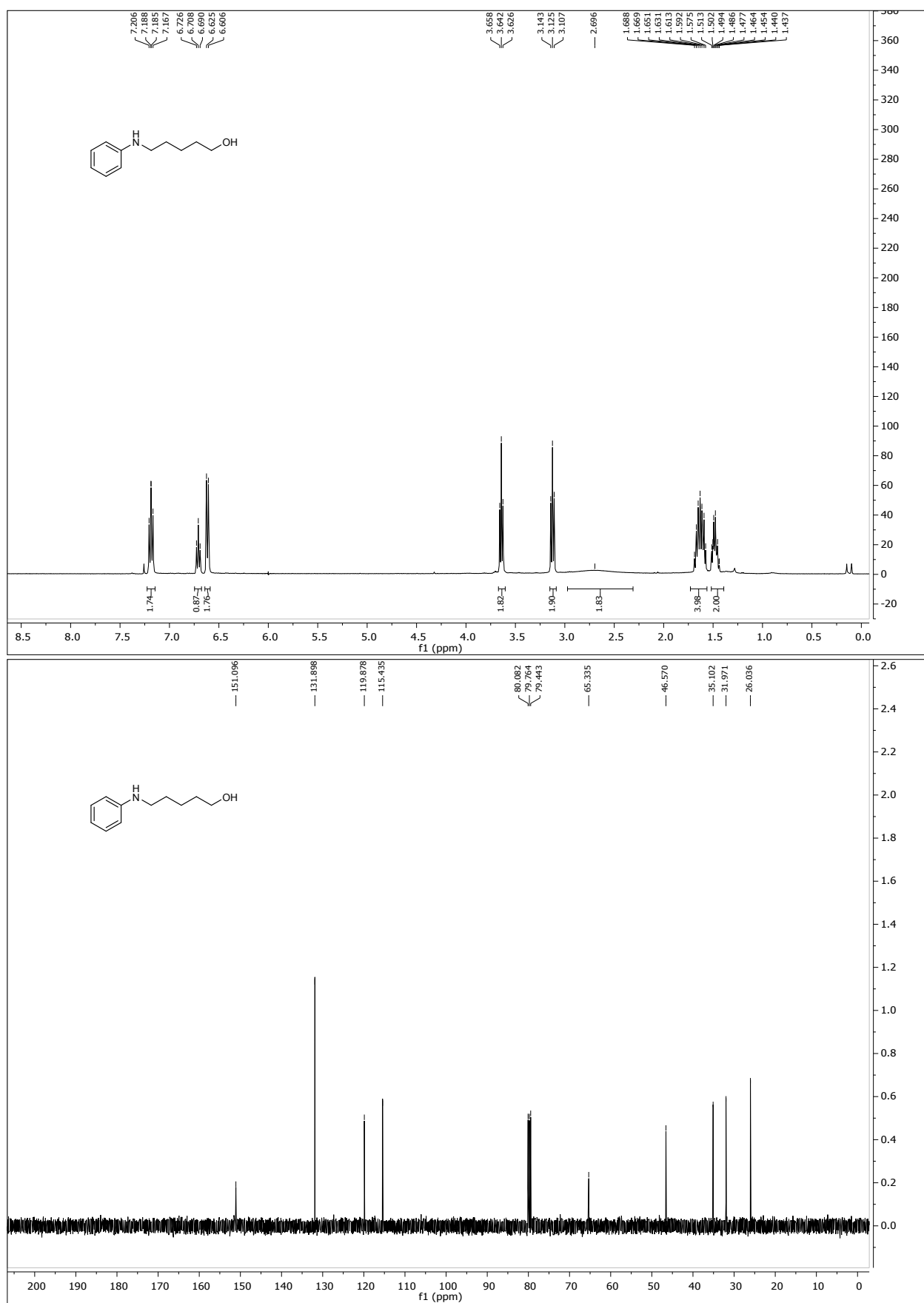
Supplementary Figure 17. ¹H and ¹³C NMR of compound **3r**.



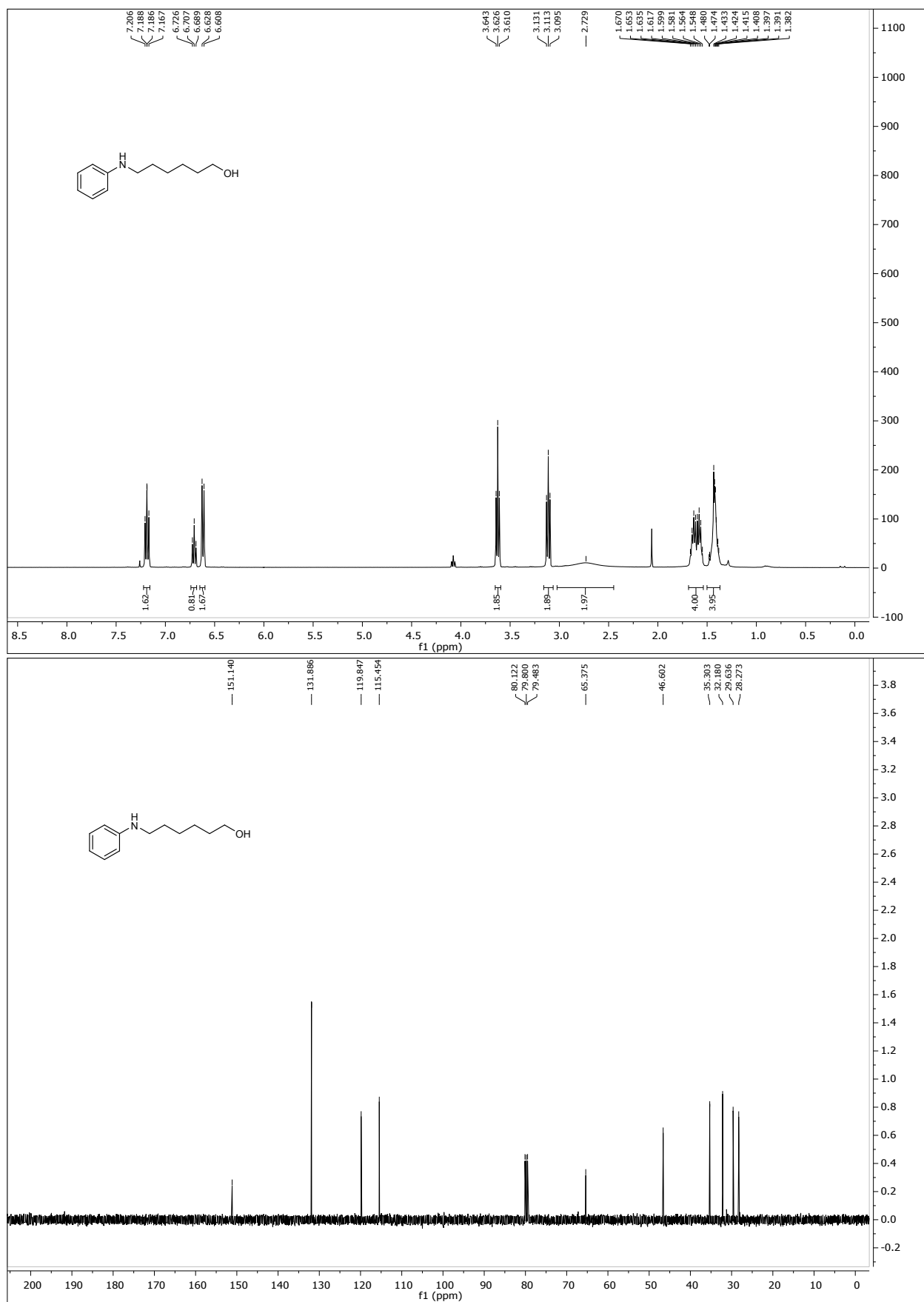
Supplementary Figure 18. ¹H and ¹³C NMR of compound **3s**.



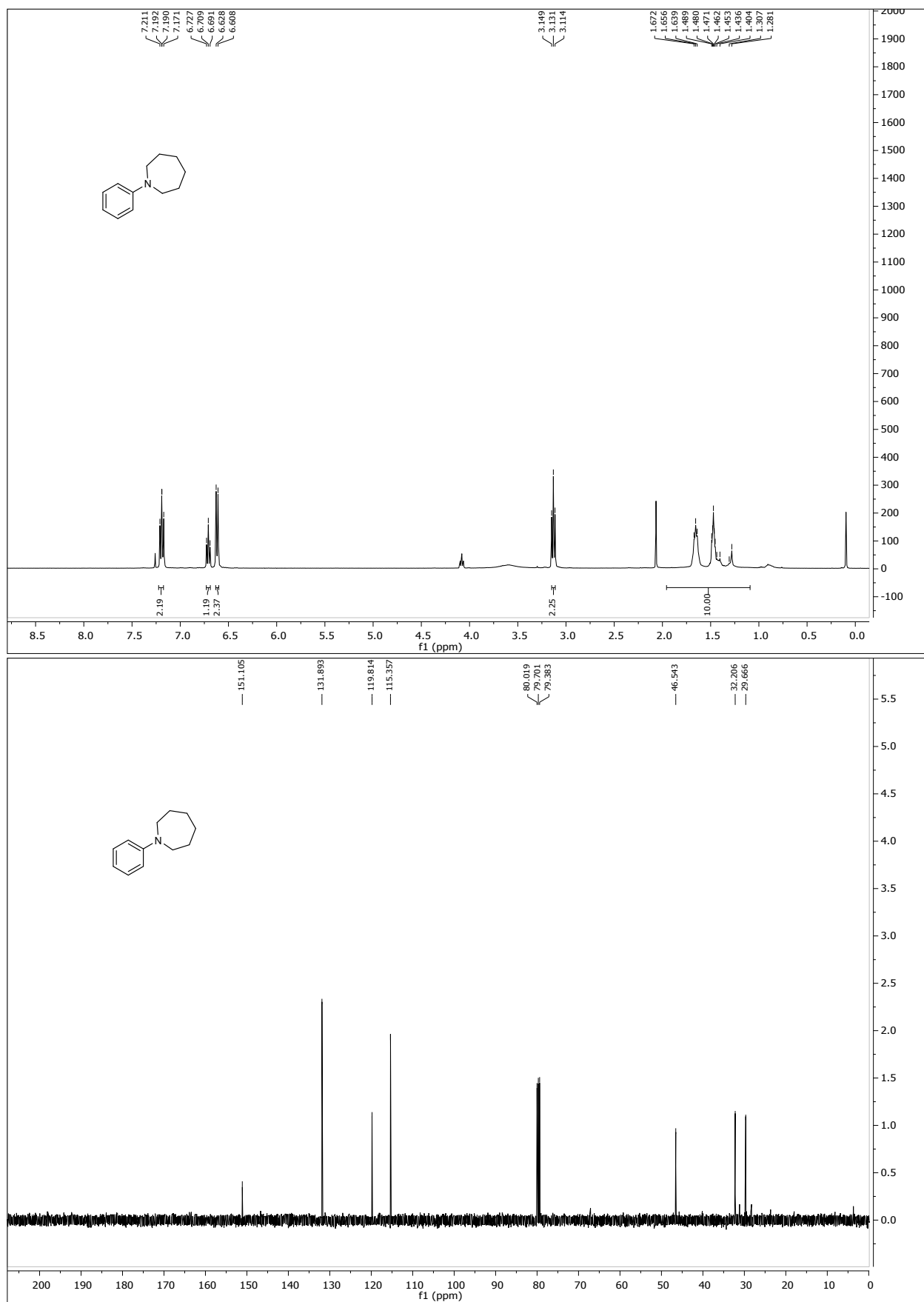
Supplementary Figure 19. ¹H and ¹³C NMR of compound **3t**.



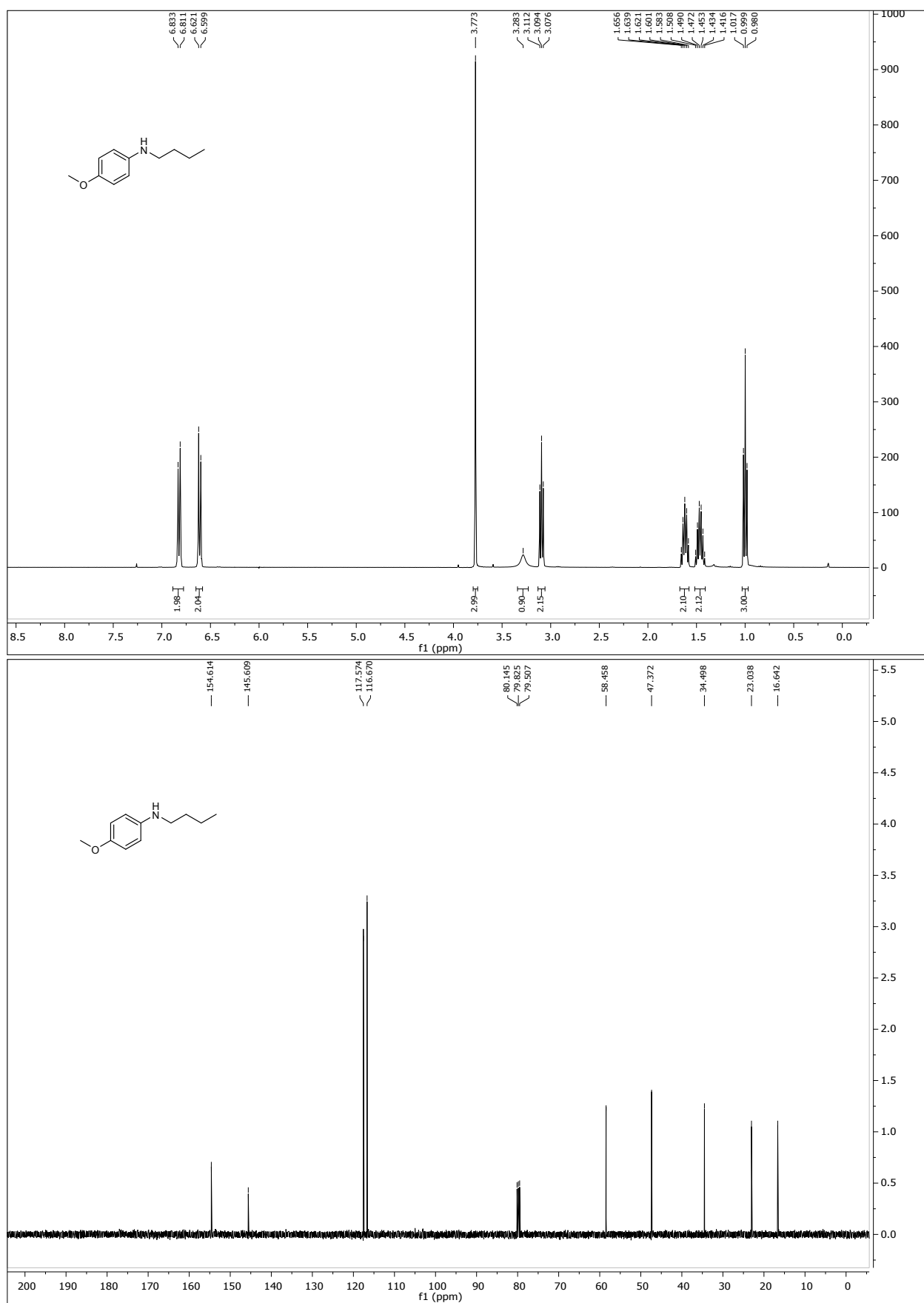
Supplementary Figure 20. ¹H and ¹³C NMR of compound **3ua**.



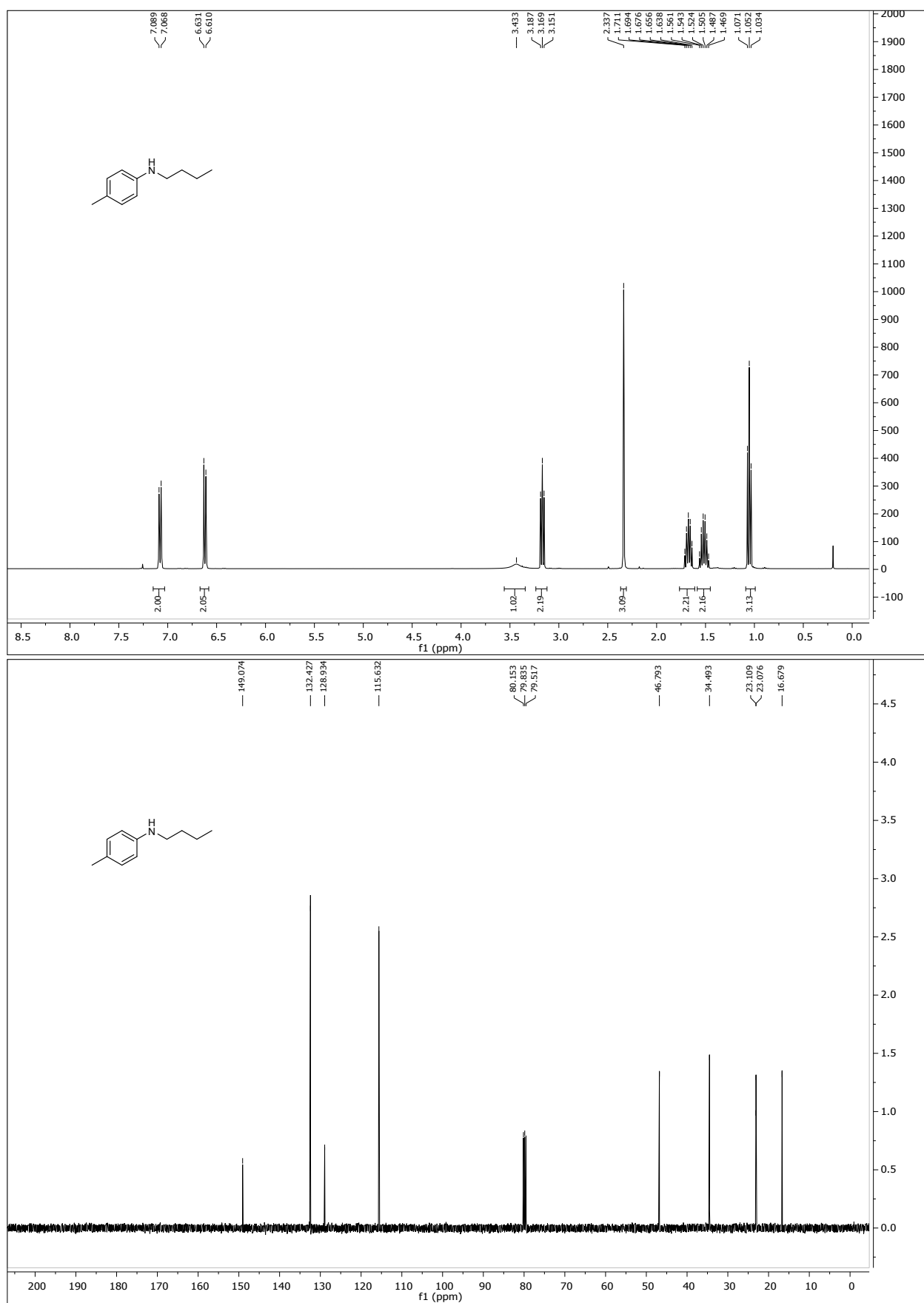
Supplementary Figure 21. ¹H and ¹³C NMR of compound **3va**.



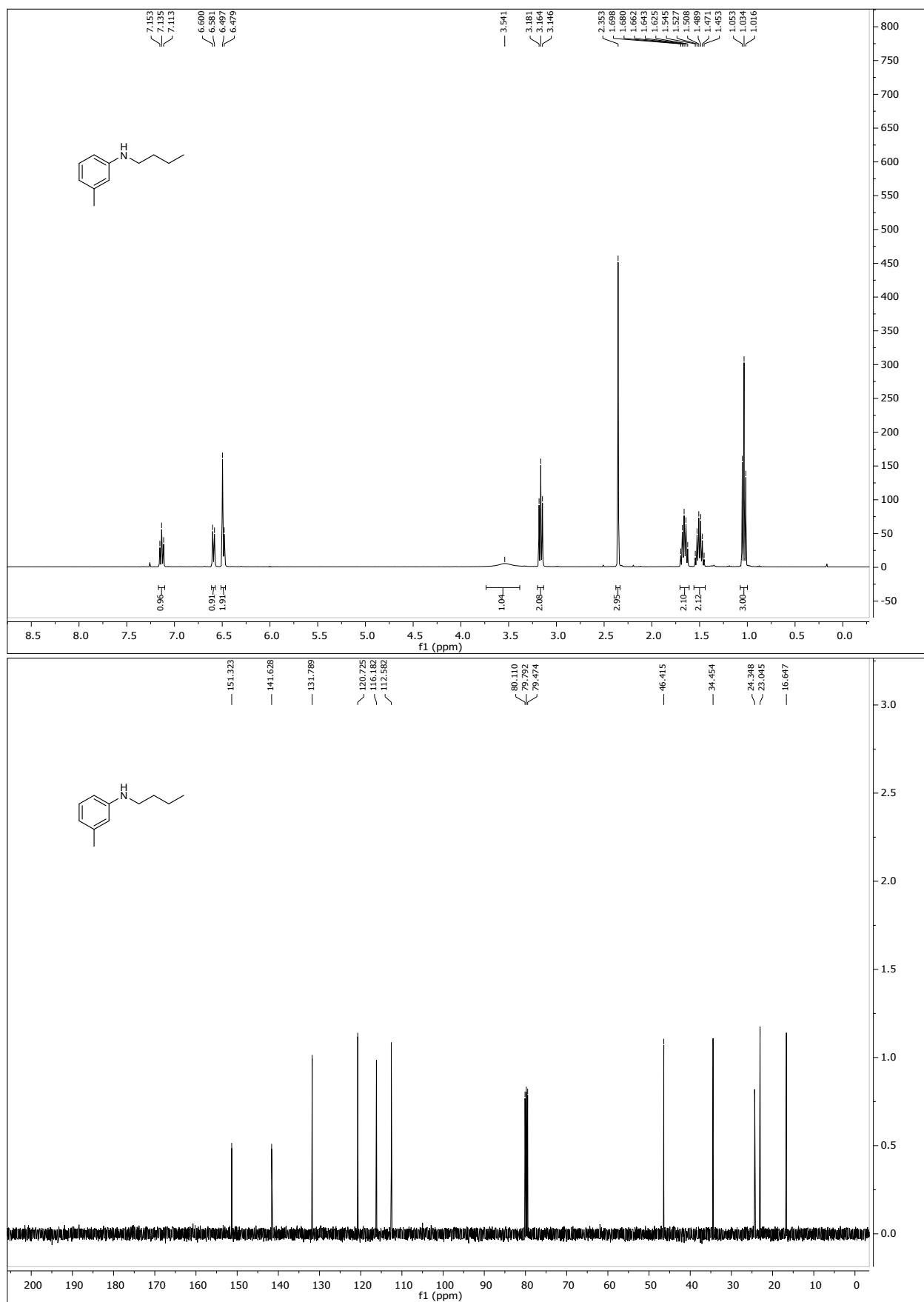
Supplementary Figure 22. ¹H and ¹³C NMR of compound 3vb.



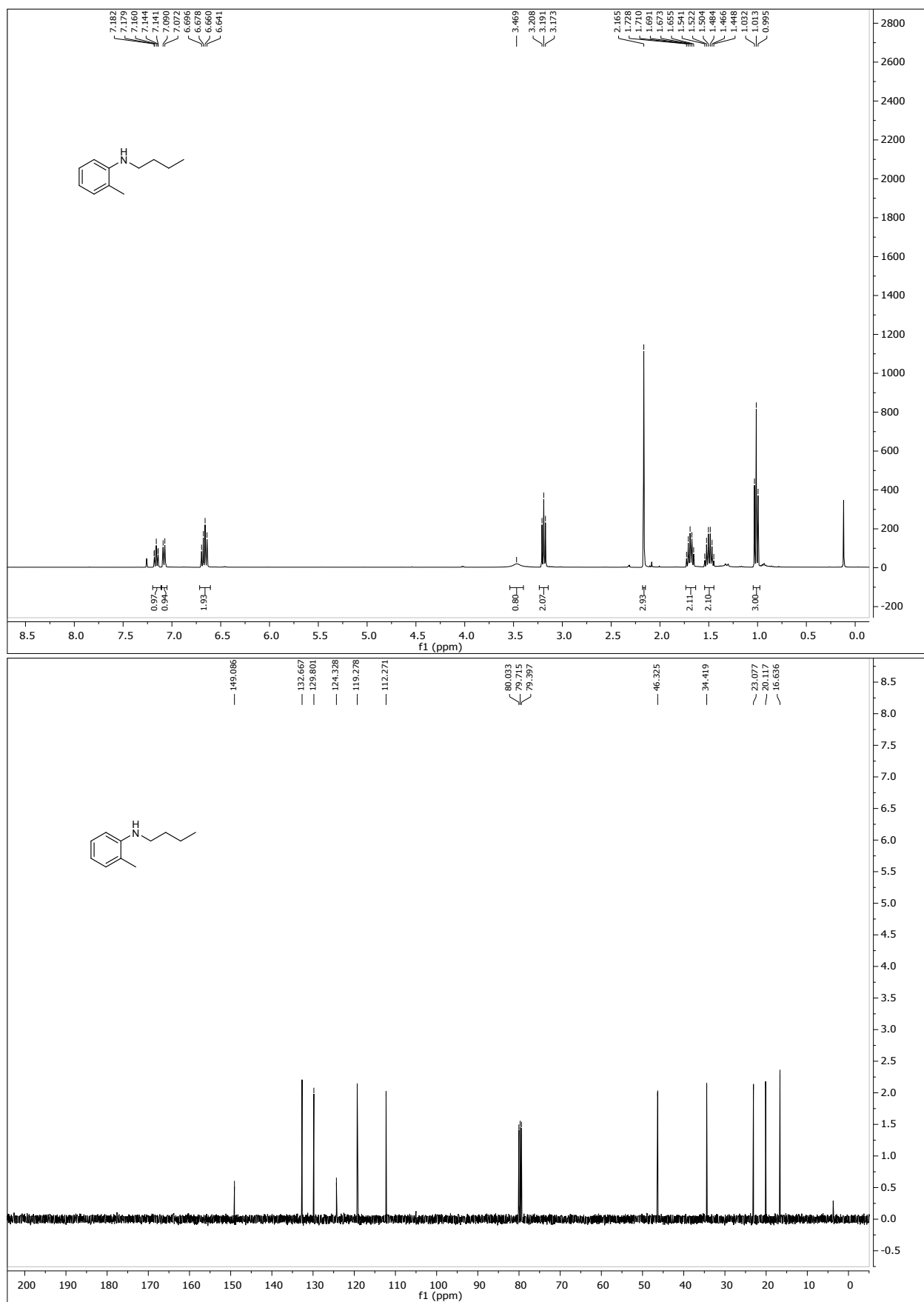
Supplementary Figure 23. ¹H and ¹³C NMR of compound 5a.



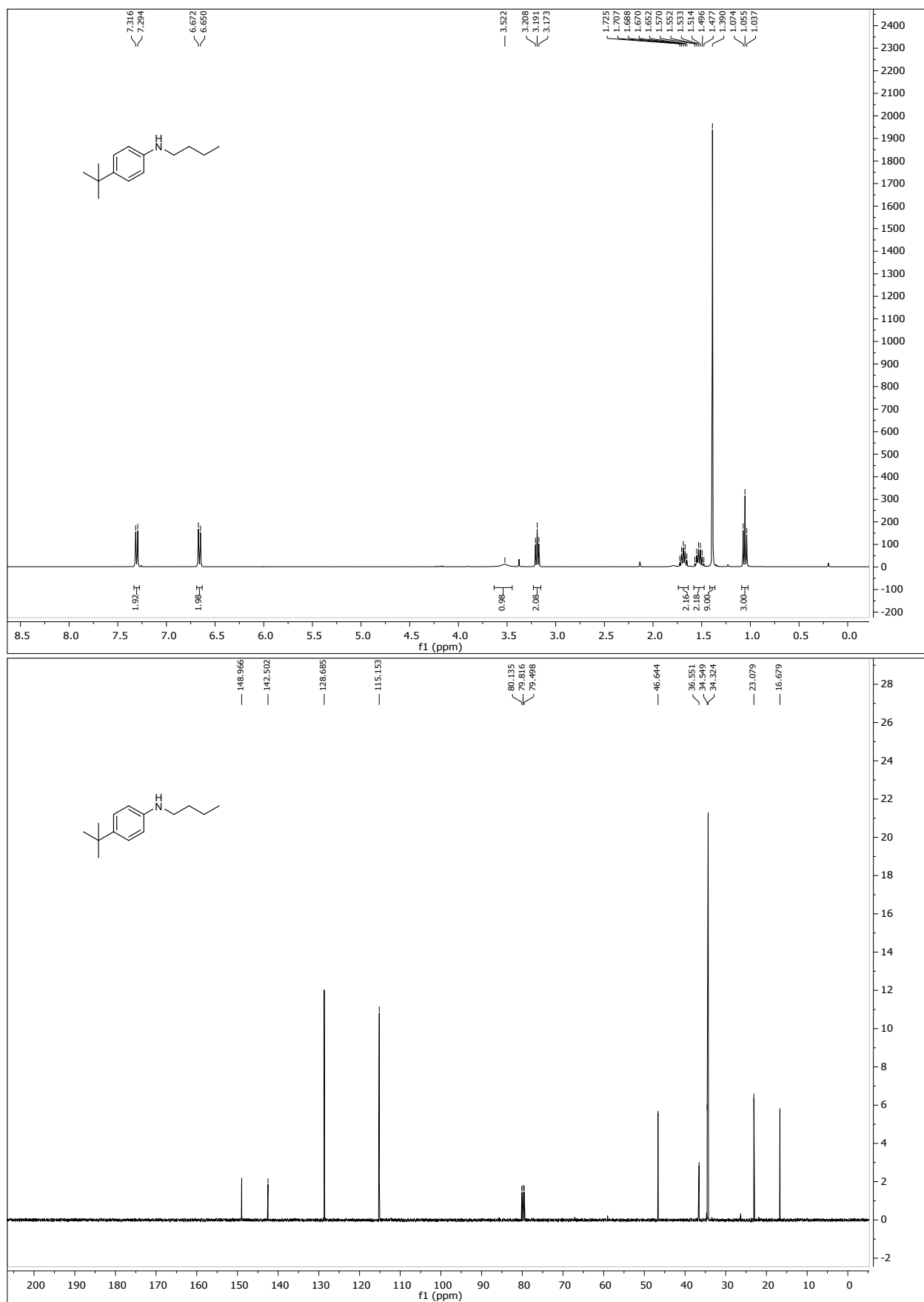
Supplementary Figure 24. ¹H and ¹³C NMR of compound 5b.



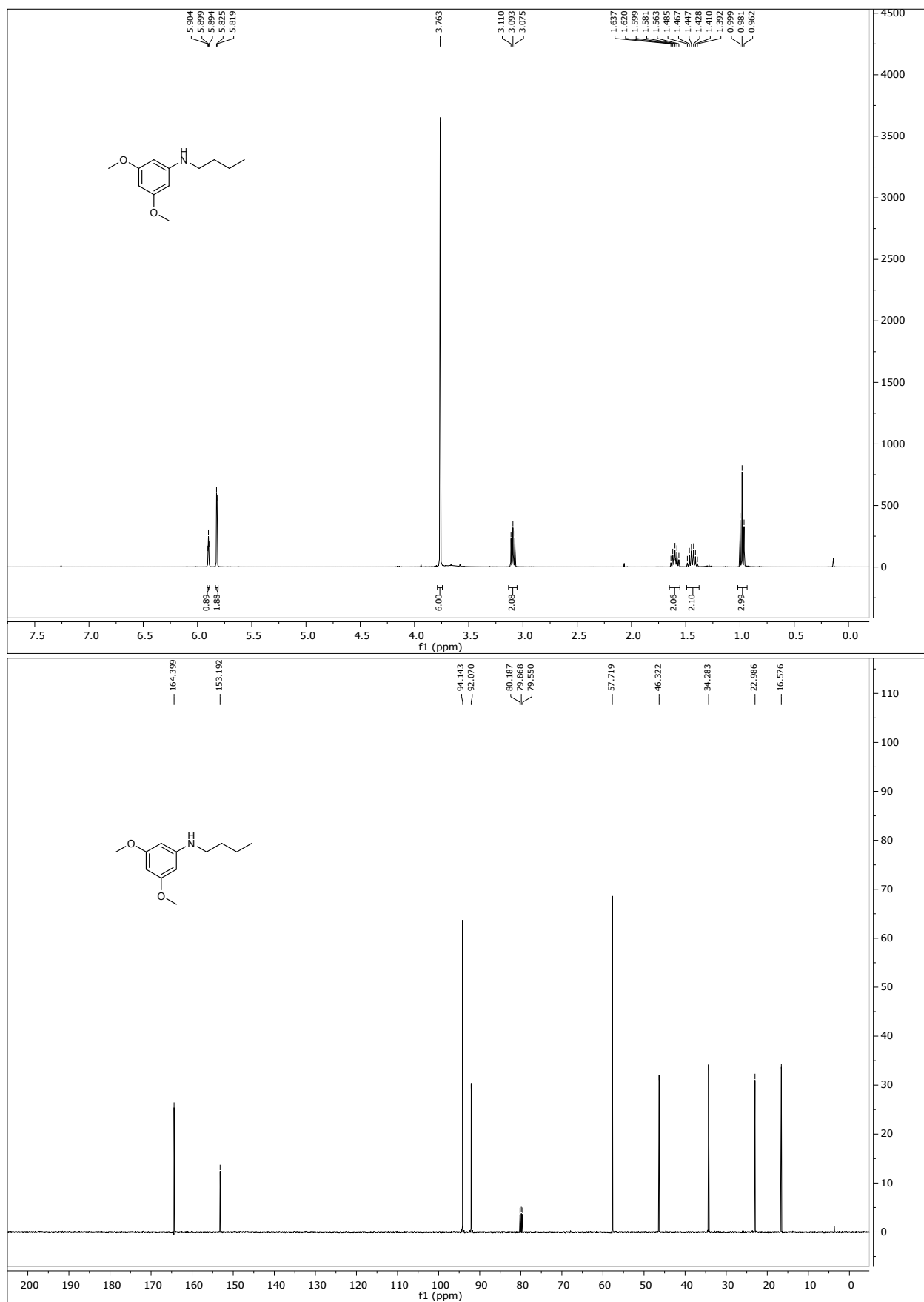
Supplementary Figure 25. ¹H and ¹³C NMR of compound 5c.



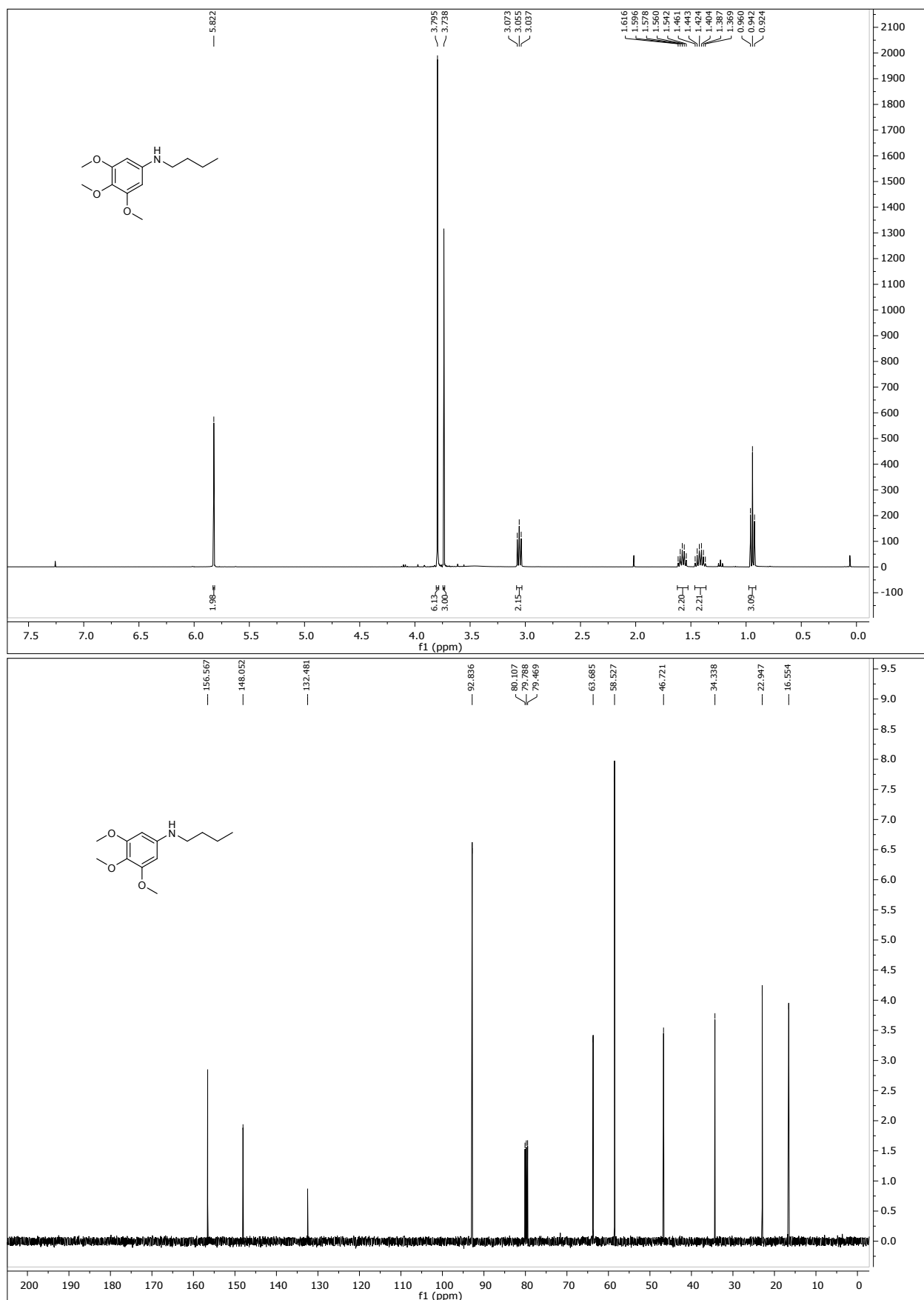
Supplementary Figure 26. ¹H and ¹³C NMR of compound **5d**.



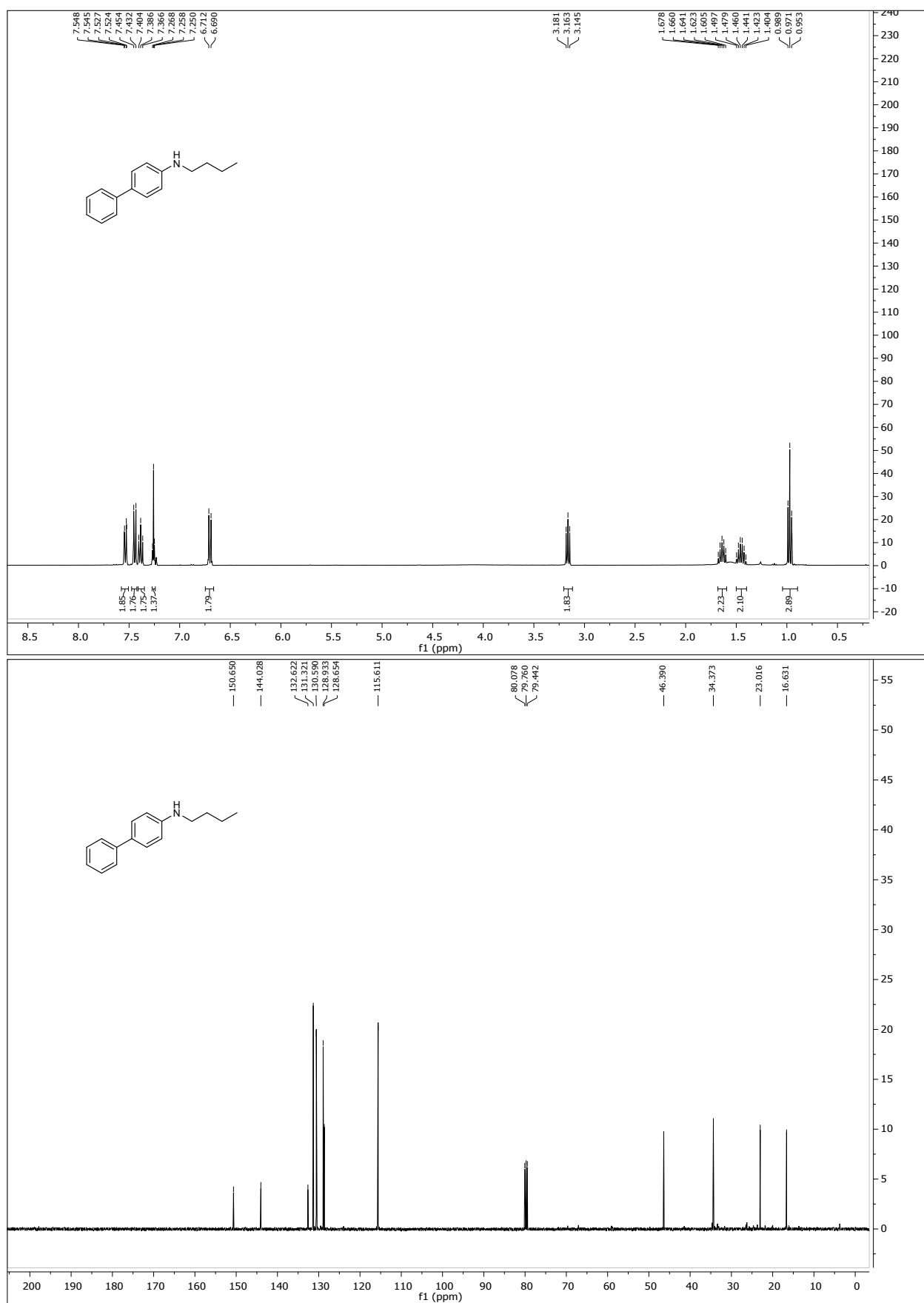
Supplementary Figure 27. ¹H and ¹³C NMR of compound 5e.



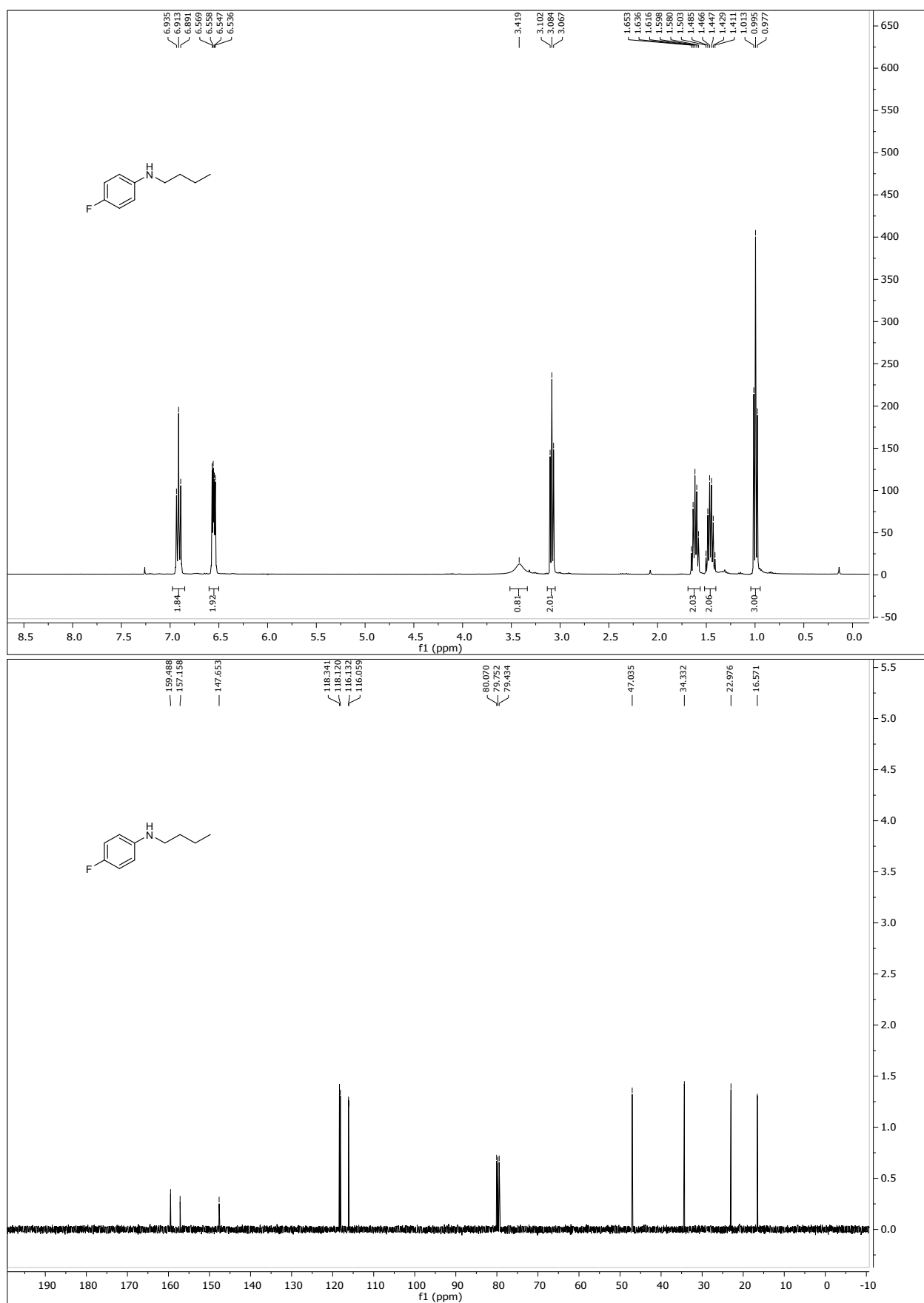
Supplementary Figure 28. ¹H and ¹³C NMR of compound **5f**.



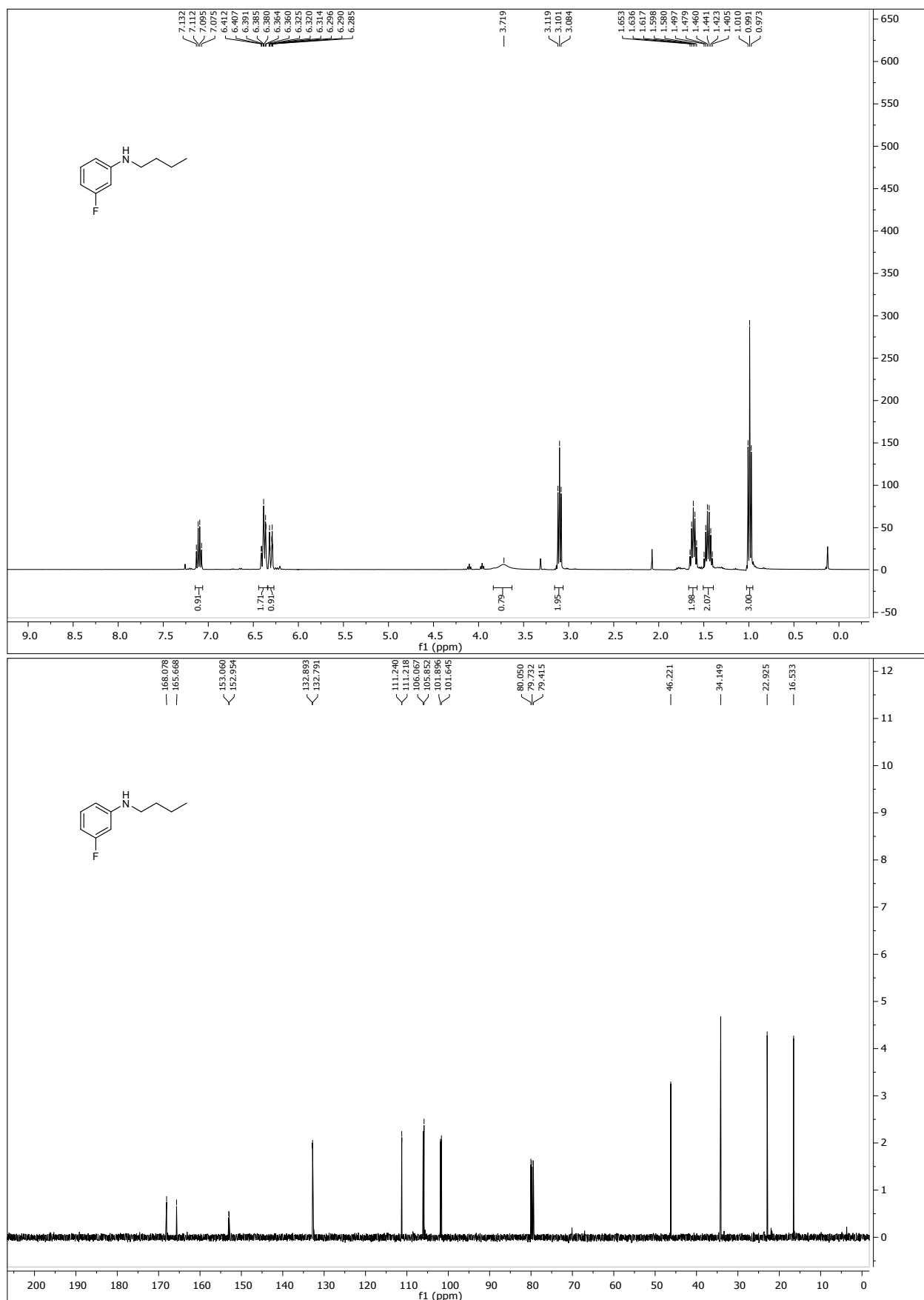
Supplementary Figure 29. ¹H and ¹³C NMR of compound 5g.



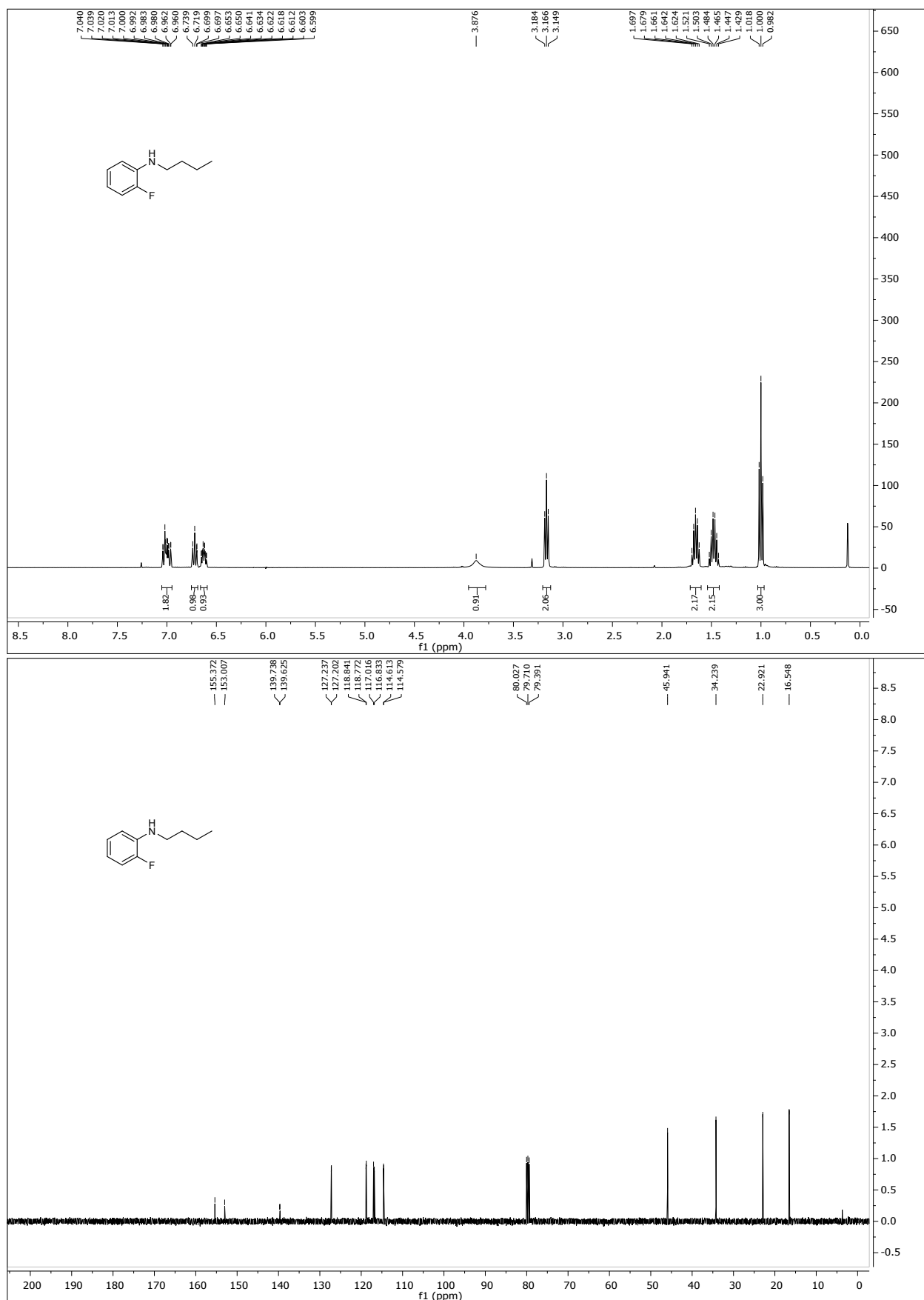
Supplementary Figure 30. ¹H and ¹³C NMR of compound 5h.



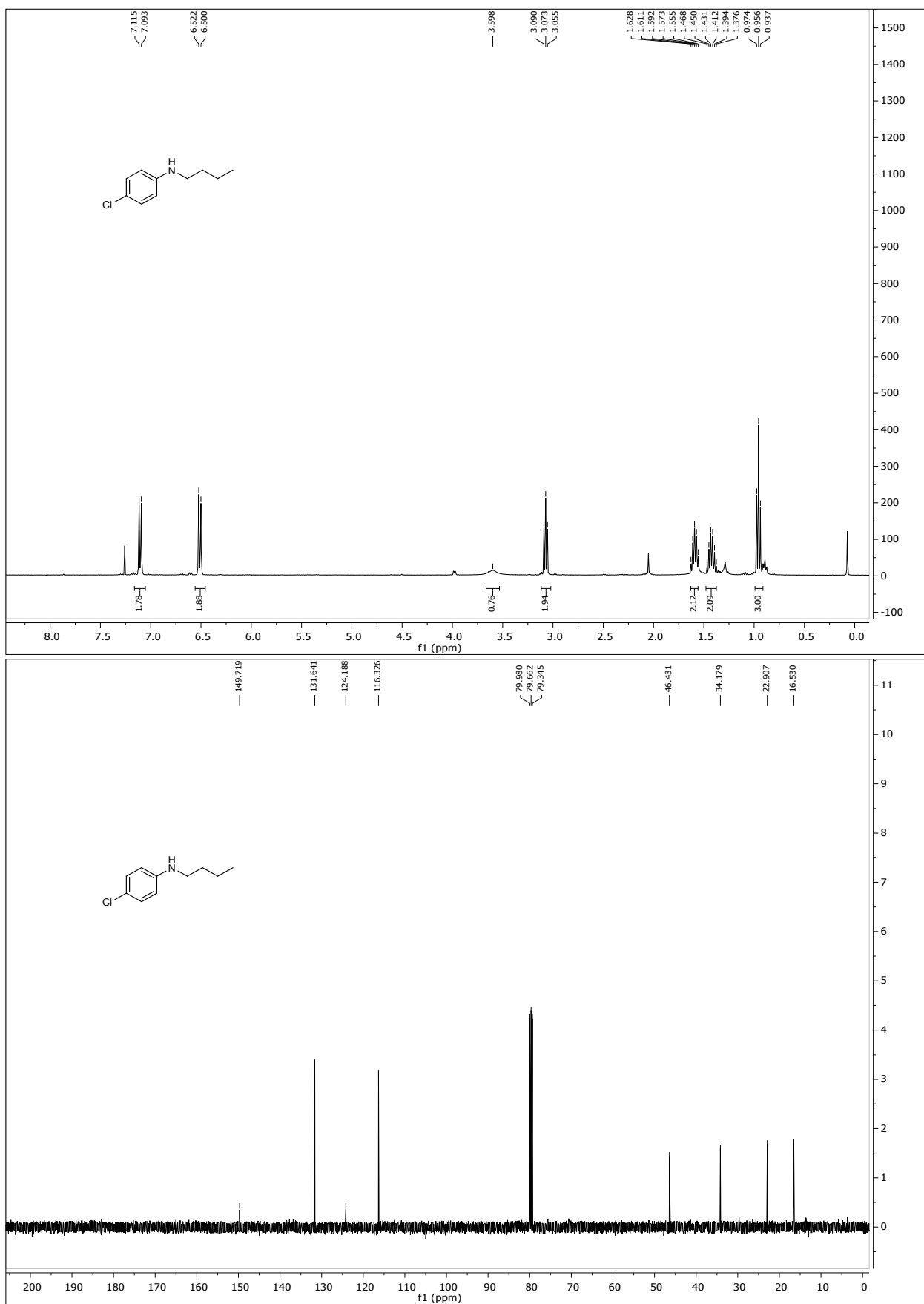
Supplementary Figure 31. ¹H and ¹³C NMR of compound **5i**.



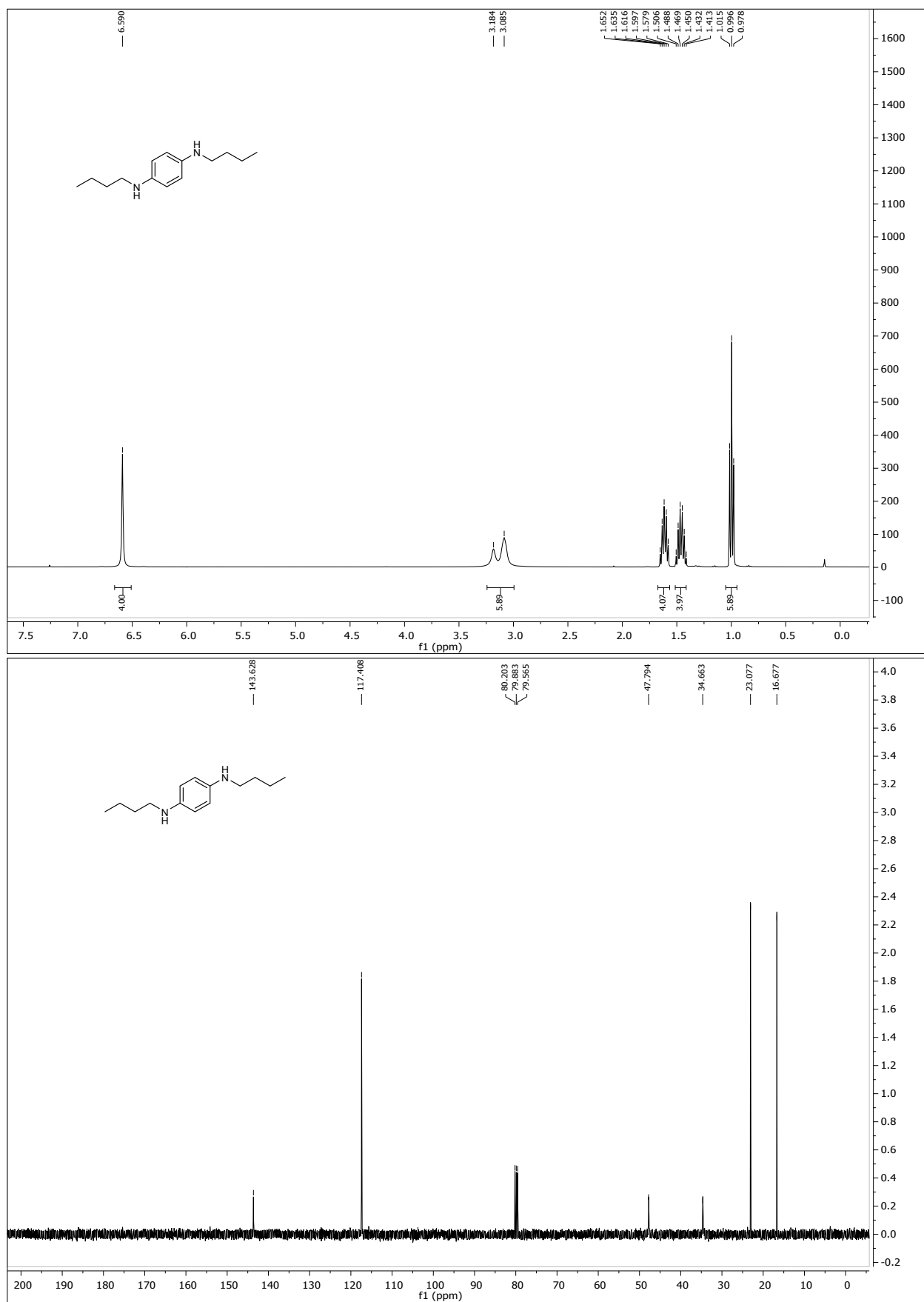
Supplementary Figure 32. ¹H and ¹³C NMR of compound 5j.



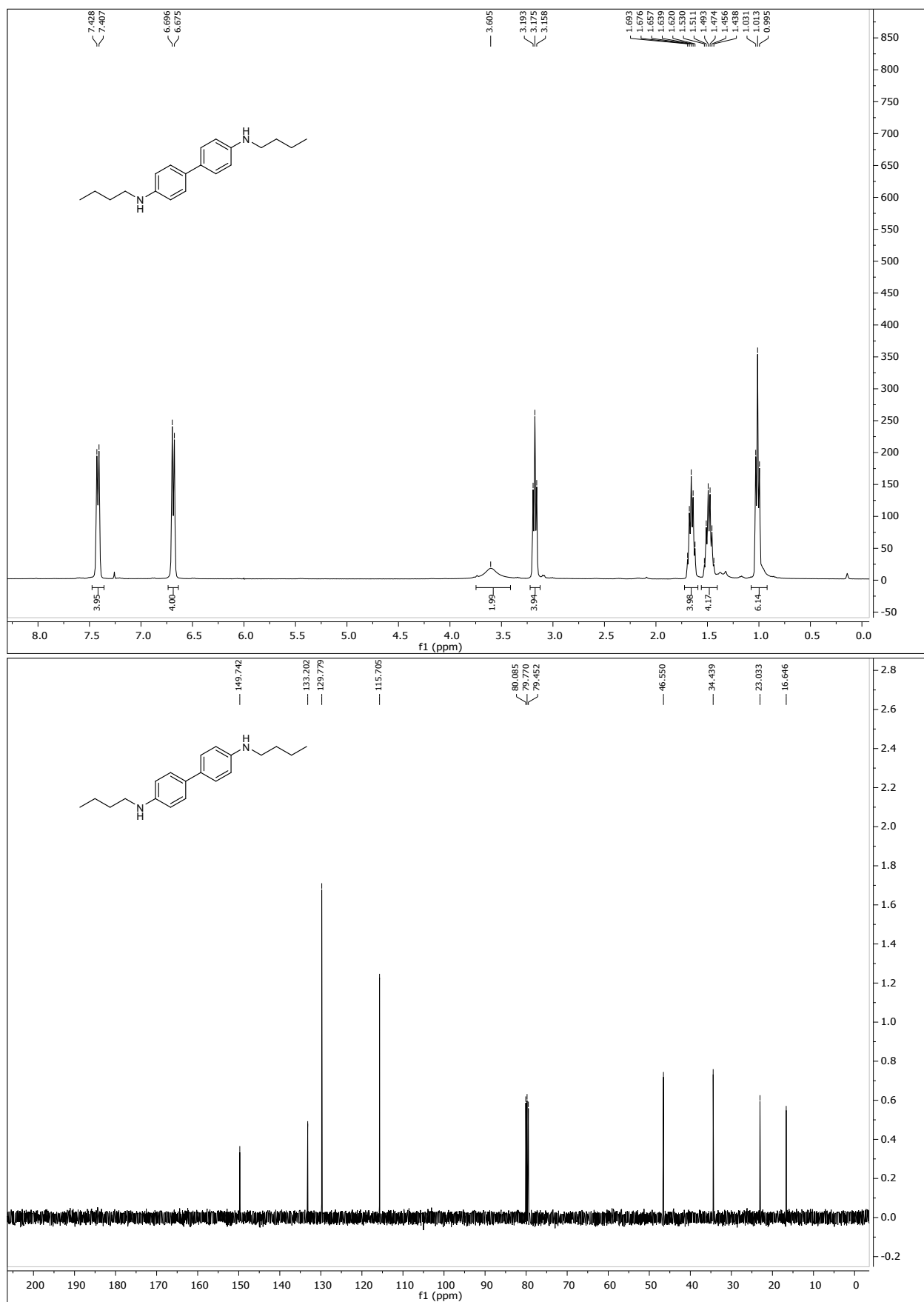
Supplementary Figure 33. ¹H and ¹³C NMR of compound 5k.



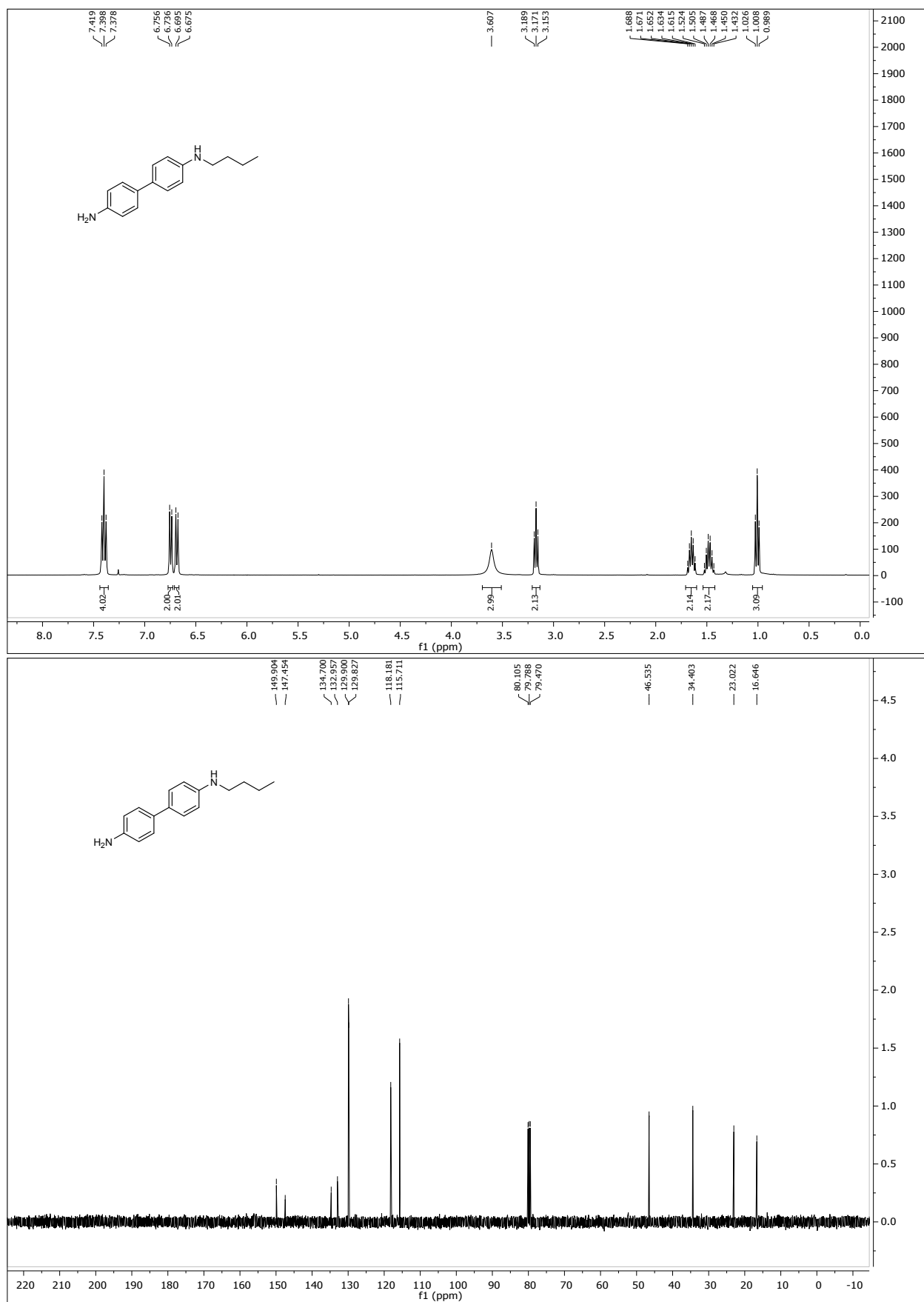
Supplementary Figure 34. ¹H and ¹³C NMR of compound 5I.



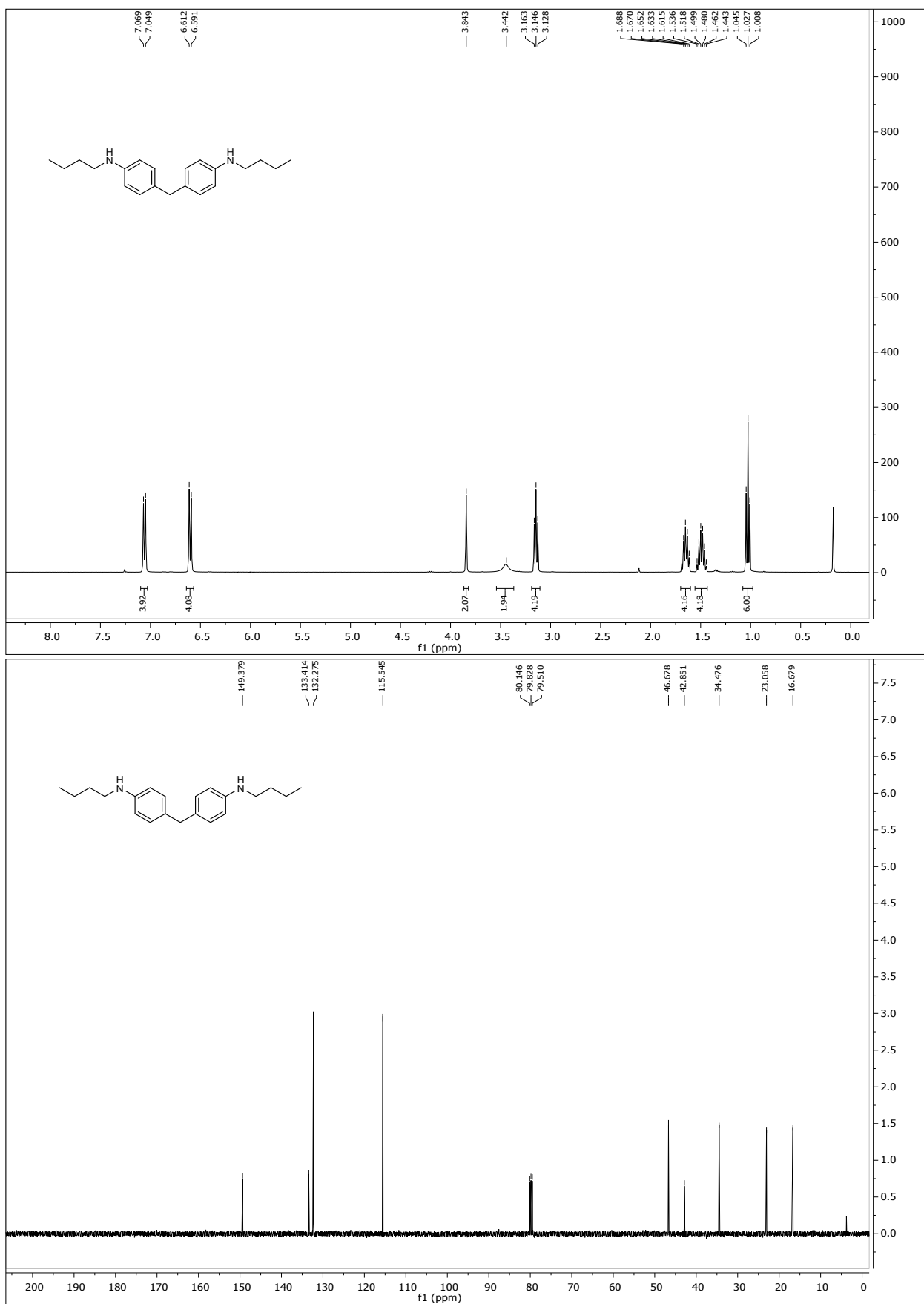
Supplementary Figure 35. ¹H and ¹³C NMR of compound 5m.



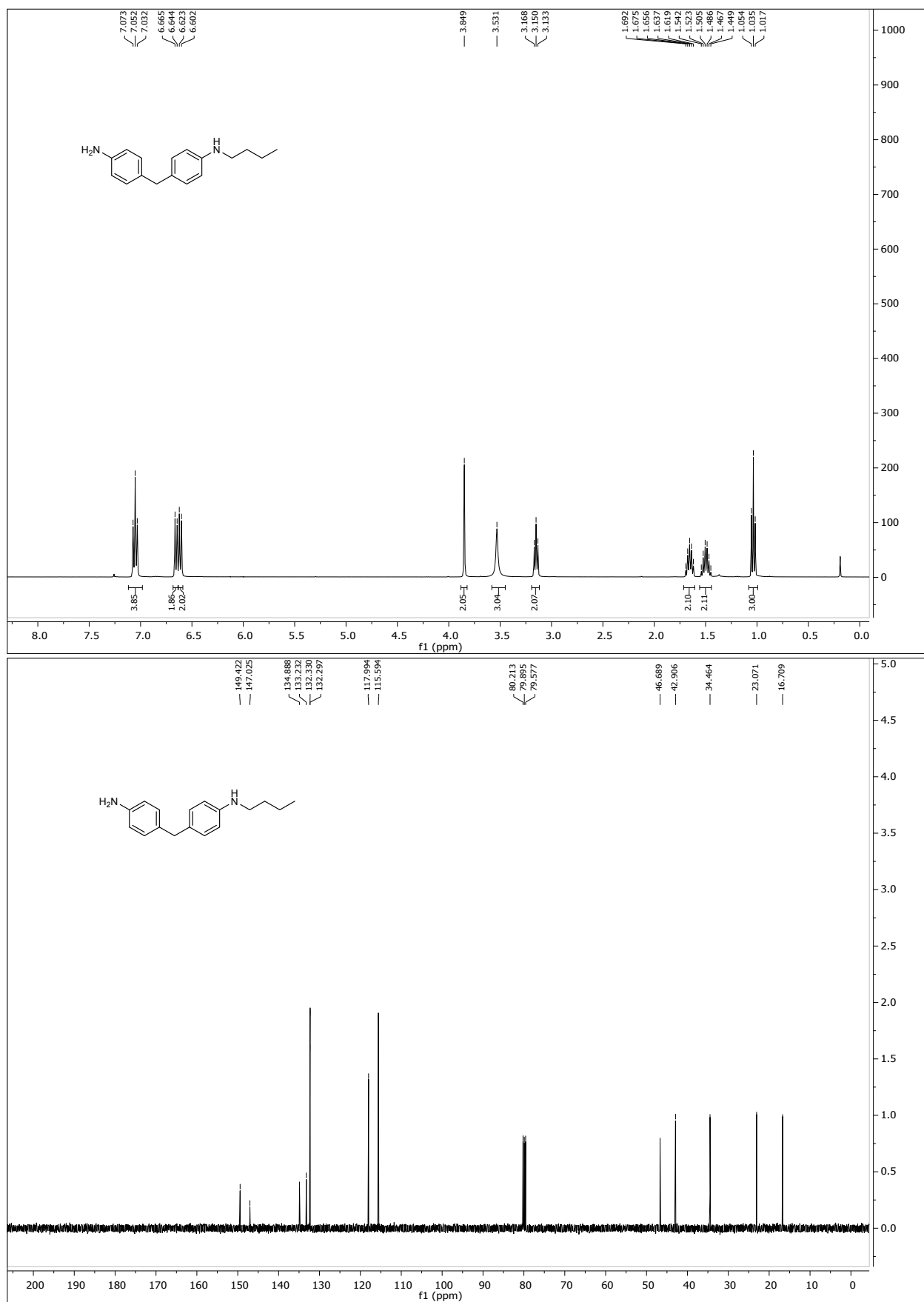
Supplementary Figure 36. ^1H and ^{13}C NMR of compound 50a.



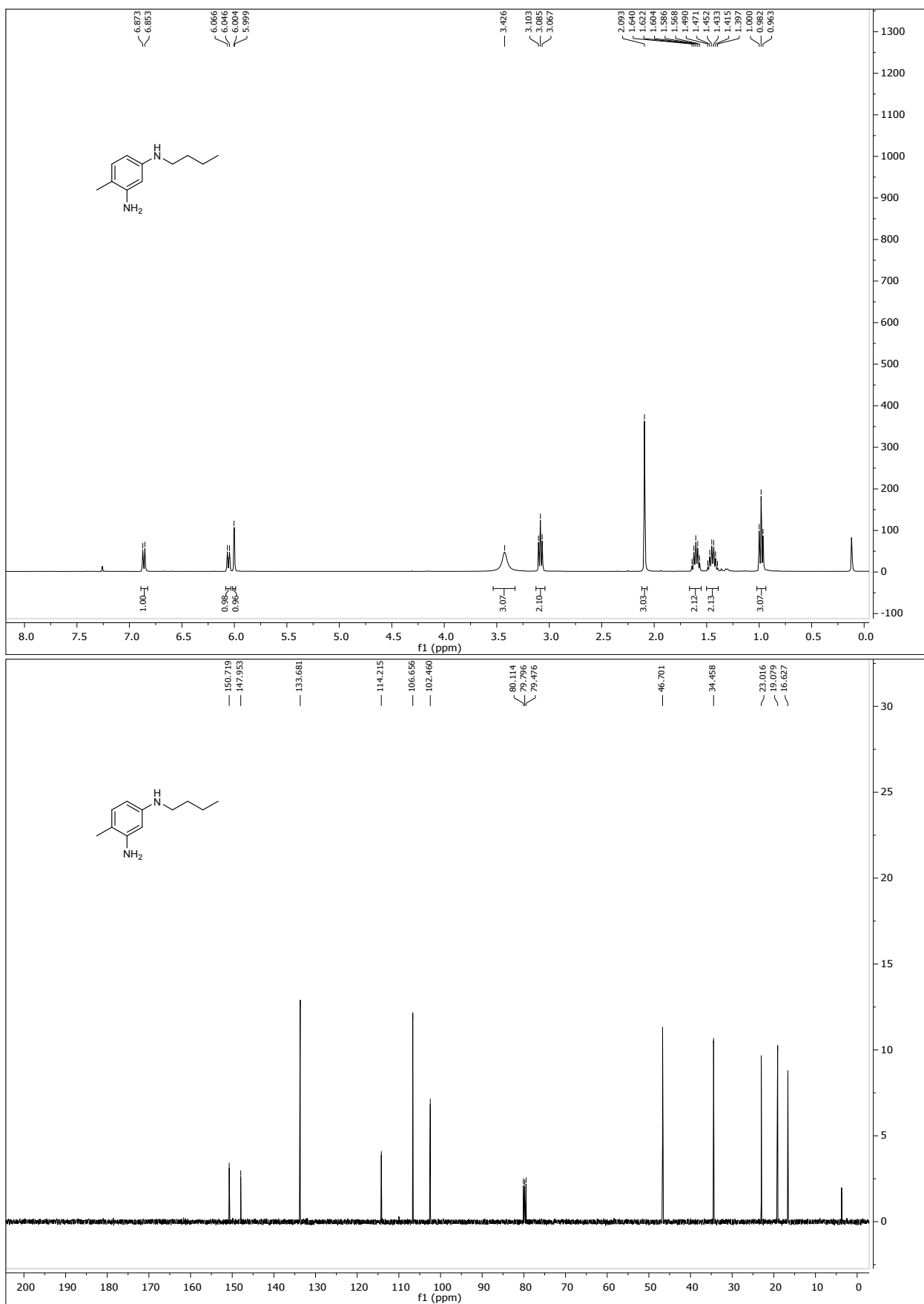
Supplementary Figure 37. ^1H and ^{13}C NMR of compound **5ob**.



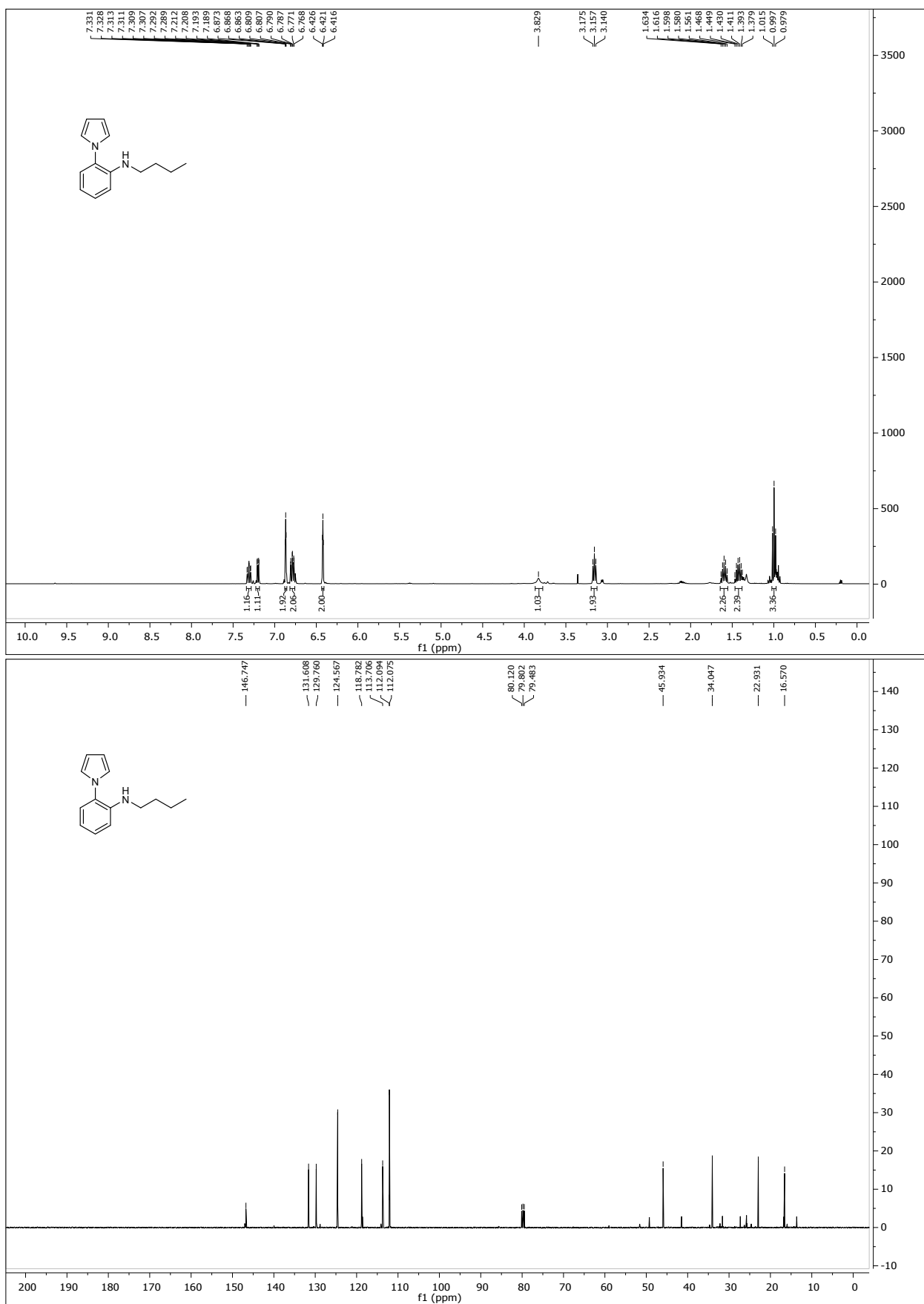
Supplementary Figure 38. ¹H and ¹³C NMR of compound 5pa.



Supplementary Figure 39. ¹H and ¹³C NMR of compound **5pb**.



Supplementary Figure 40. ¹H and ¹³C NMR of compound 5q.



Supplementary Figure 41. ¹H and ¹³C NMR of compound **5r**.

7. References

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