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Electronic Supplementary Information

Primary Amine Synthesis by Hydrogen-involving Reactions over Heterogeneous Co Catalysts

Kahoko Kato,[a] Dian Deng,[a] Yusuke Kita,[a] Keigo Kamata,[a] Michikazu Hara[a,b]*

[a] Laboratory for Materials and Structures, Institute of Innovative Research, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8503 (Japan)

[b] Advanced Low Carbon Technology Research and Development Program (ALCA), Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi 332-0012 (Japan)

email: hara.m.ae@m.titech.ac.jp

Experimental details

Materials

Unless noted otherwise, all chemicals were purchased from commercial sources with purity with over 95 % and used without further purification.

Basic manipulations were performed under inert gas atmosphere using glovebox (Ar) or high-vacuum techniques (10^{-5} mbar).

Catalyst preparation

Commercially available metal oxide supports were obtained from various sources, including: MgO from Ube Material Industries and SiO_2 (CARiACT Q-10) from Fuji Silysia Chemicals were provided by the Catalysis Society of Japan, Nb_2O_5 was obtained by calcination of Niobic acid (Companhia Brasileira de Metalurgia e Mineraçáo) at 400 °C for 2 h.

All cobalt catalysts were prepared via a wet impregnation method. Typically, a certain amount of cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, Kanto, 3N5) was dissolved in 50 mL deionized water, and approximately 1 g of support was then impregnated with the aqueous solution. After the mixture was continuously stirred at room temperature for 1 h, water was removed by rotary evaporation and the powders were then dried under vacuum (ca. 0.25 kPa, 100 °C) for 1 h to give a purple solid. The dried powder was gently ground in an agate mortar, transferred to a ceramic crucible, and then pyrolyzed under N_2 flow for 2 h at 400 °C with a heating rate of 3.3 °C/min.

The resultant powder was then reduced in a 30 mL/min H_2 flow with heating from room temperature to 600 °C at a ramp rate of ca. 3.3 °C/min and held at 600 °C for 2 h. After cooling down to room temperature in a continuous H_2 flow, the reduced Co/SiO_2 catalysts were obtained and transferred to an Ar glovebox for storage and further use.

20 wt % Pd/SiO_2 was prepared according to previous literature.[S1] Palladium(II) nitrate ($Pd(NO_3)_2$, Wako), 1 g of SiO_2 were added to a flask. The suspension was stirred at room temperature, evaporated to remove the water, and dried at 110 °C overnight. The dried precursor was reduced at 260 °C for 6 h with H_2 flow (30 mL/min) to obtain Pd/SiO_2.

20 wt% Ru/SiO_2 was prepared according to previous report.[S2] Aqueous nitrosyl ruthenium(III) nitrate solution ($Ru(NO)(NO_3)_3$, Aldrich), 1 g of SiO_2 and water (50 mL) were added to a flask. The suspension was stirred for 1 h at room temperature, followed by evaporation and vacuum drying (50 °C, 2 h). The resulting precursor was reduced at 300 °C for 2 h with 5% H_2/Ar flow (50 mL/min) to give Ru/SiO_2.

20 wt% Pt/SiO_2 was prepared according to the previous literature.[S3] Hexachloroplatinum(IV) acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, Wako) and SiO_2 were stirred

with 50 mL water for 1 h at room temperature, then evaporated to remove the water and dried at 110 °C overnight. The dried precursor powder was reduced at 500 °C for 2 h with H_2 flow (30 mL/min) to obtain Pt/SiO_2.

Characterizations

Nitrogen adsorption–desorption isotherms were measured at -196 °C by using automated gas sorption analyzer (NOVA 4200e Quantachrome). Samples were degassed at 150 °C for 1 h under vacuum prior to analysis. The Brunauer-Emmett-Teller (BET) surface area was calculated from nitrogen adsorption data in a relative pressure range from 0.05–0.3.

X-ray diffraction (XRD) measurements was conducted in a Rigaku Ultima-IV system equipped with a D/teX Ultra detector using CuKα radiation (40 kV, 40 mA). Prior to the XRD analysis, sample was loaded on an air-sensitive sample holder (Rigaku) inside the Ar-filled glove box to prevent exposure to atmospheric conditions during the measurements. The data was collected in a 2θ range from 20° to 90°, with a scanning step of 0.01°/s. The diffraction patterns were compared to reference patterns of the Powder Diffraction File of the International Centre for Diffraction Data (PDF-2 Release 2008)

The morphologies and sizes of the fresh and used catalysts were observed by transmission electron microscope (TEM, JEOL 2100F). Prior to TEM characterization, the samples were ultrasonically dispersed in ethanol and then dropped onto a carbon-supported copper grid. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analyses were performed with a Shimadzu ICPS-8100 spectrometer. Thermogravimetry-Differential thermal analysis (TG-DTA) was performed with Rigaku TG-DTA8122 equipped with Rigaku smart loader auto sampler. Approximately 10 mg sample was pressed in the Platina sample holder. The thermal profiles were measured from room temperature to 600 °C.

Hydrogen temperature programmed reduction (H_2-TPR) was carried out in a quartz tubular reactor with a mixture of 5% H_2/Ar as the reductive gas. The calcined catalysts (0.1 g) were reduced in a flow of 30 mL/min and the temperature was raised from 60 °C to 800 °C at the ramp rate of 3.3 °C/min. The consumption of hydrogen was monitored by a TCD after passing through a 3 A molecular sieve trap to remove the produced water. In part of the measurements the effluent gas was also analyzed by a mass spectrometer (BELMass, BEL Japan).

NMR spectra were recorded on a Bruker Avance III-400 MHz NMR spectrometer (^{1}H-NMR 400 MHz; ^{13}C-NMR 100MHz). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), and integration.

Typical procedure for the hydrogenation of benzonitrile

In an Ar-filled glovebox, a magnetic stirring bar, 0.5 mmol of benzonitrile, 20 mg of catalyst, and 5 mL of solvent (cyclohexane/DMF = 4) were placed into a Teflon-lined stainless steels autoclave (inner cylinder volume is 18 mL). The reactor was sealed, removed from the glovebox and then charged with the required H_2 pressure. The autoclave was placed into an aluminum block, heated to the desired temperature with thorough stirring (600 rpm). After completion of the reaction, the autoclave was cooled to room temperature, and excess gas was vented in a fume hood.

Yields and conversion rates were determined by quantitative gas chromatography (GC) analysis (Shimadzu GC-17A, equipped with an InertCap 17MS capillary column (internal diameter = 0.25 mm, length = 30 m) and a flame ionization detector (FID), the temperature was raised from 70 °C to 260 °C at the ramp rate of 10 °C/min and kept for 11 min.), with chlorobenzene as an internal standard.

Typical procedure for the reductive amination

In an Ar-filled glovebox, a magnetic stirring bar, 0.5 mmol of aldehyde, 20 mg of catalyst, and 5 mL of solvent were placed into a Teflon-lined stainless steels autoclave (inner cylinder volume is 18 mL). The reactor was sealed, removed from the glovebox and purged with 0.1 MPa NH_3, and then charged with the required H_2 pressure. The autoclave was placed into an aluminum block, heated to the desired temperature with thorough stirring (600 rpm). After completion of the reaction, the autoclave was cooled to room temperature, and excess gas was vented in a fume hood.

Yields and conversion rates were determined by quantitative gas chromatography (GC) analysis (Shimadzu GC-17A, equipped with an InertCap 17MS capillary column (internal diameter = 0.25 mm, length = 30 m) and a flame ionization detector (FID), the temperature was raised from 70 °C to 260 °C at the ramp rate of 10 °C/min and kept for 11 min.), with chlorobenzene as the internal standard.

General procedure for the hydrogenation of nitriles

In an Ar filled glove box, a magnetic stir bar, 0.5 mmol nitrile, 20 mg of 20 wt% Co/SiO_2, and 5 mL of solvent were added into a Teflon-lined stainless steels autoclave. The reactor was sealed, removed from glovebox and subsequently completed up to 1 MPa with H_2. Reactions were also carried out in the glass vessel-fitted autoclaves wherever required. After completion of the reaction, the autoclave was cooled to room temperature, and excess gas was vented in fuming hood.

The combined organic fractions were concentrated in vacuo with the aid of a rotary evaporator. The crude product residue was purified by automated flash chromatography system (Smart Flash EPCLC AI-580S, Yamazen) with amino gel using a solvent mixture (ethyl acetate and methanol) as an eluent to afford the purified amine products.

Competitive Adsorption of 3a and 4a on metal nanoparticle

Co or Pt nanoparticle (400 mg) was added in a 20 mL Schlenk flask. After cooling to –15 °C, primary amine **3a** (0.2 mmol), secondary imine **4a** (0.2 mmol) in toluene (2 mL) was added dropwise. The concentration of **3a** and **4a** in the reaction mixture was determined by sampling a small amount of the reaction solution after a predetermined time and measuring by GC.

Leaching studies

Hot filtration was conducted to determine the effect of leached Co. 0.5 mmol **1a**, 20 mg of Co/SiO_2 and 5 mL of solvent (cyclohexane/DMF = 4) were added into an autoclave. The autoclave was pressurized with H_2 (0.5 MPa). After the reaction at 100 °C for 2 h, the reaction mixture was filtered in a glove box. The filtrate was added to an autoclave and pressurized with H_2 (0.5 MPa). The autoclave was heated at 100 °C for 4 h with stirring. The yield of **3a** was determined by GC analysis using chlorobenzene as an internal standard.

The catalyst was separated by suction filtration after the reaction under typical conditions. The filtrate was evaporated and dried under reduced pressure. After the addition of 5 mL of concentrated nitric acid (HNO_3 1.38, Kanto), the nitric acid concentration was adjusted to 6% with H_2O. The resulting solution was used for ICP-AES measurement.

The catalyst after reaction was dissolved in 5 mL of concentrated nitric acid and then the nitric acid concentration was adjusted to 6% by adding H_2O. The resulting solution was used for ICP-AES measurement. The Co content of the catalyst after reaction was determined to be 20.3 wt%.

Reusability

Co/SiO_2 can be easily separated by a remote magnetic field due to the intrinsic magnetic nature of metallic Co. An autoclave with a glass inner cylinder was used to facilitate easy removal with a magnet (inner cylinder volume is 32 mL). The reactions were set up according to the model hydrogenation of nitrile procedure with 0.5 mmol **1a** as substrate in 5 mL of solvent (cyclohexane/DMF = 4). After reaction, the autoclave was introduced into the glovebox and the glass tube put on top of a neodymium magnet for 5 min. The

supernatant was carefully removed using a glass Pasteur pipette, and the catalysts were washed three times with total 10 mL cyclohexane. Thereafter, fresh substrate and solvent were added, the tube was put back into the autoclave, subsequently purged with hydrogen. Conversion and yield were determined by GC analysis using chlorobenzene as an internal standard.

Table S1 Comparison of the reported non-noble metal based catalytic systems for hydrogenation of nitriles with present protocols

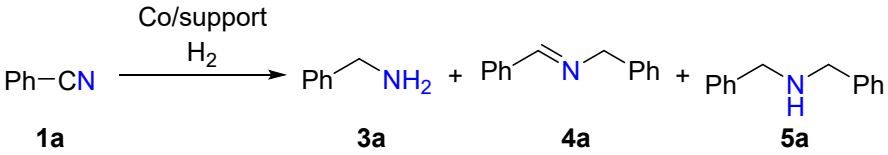
catalyst	Substrate	Ammonia	Solvent	pH_2 (MPa)	Temp. (°C)	Time (h)	Yield (%)	TON	Ref
Co/SiO_2	benzonitrile	none	cyclohexane	0.5	50	20	78	5.8	This work
Co/SiO_2	benzonitrile	none	cyclohexane/DMF	1	100	6	89	6.6	This work
Co_2P NR/HT	valeronitrile	none	2-propanol	4	150	2	90	9	S4
$CoBr_2$ + $NaBHEt_3$	benzonitrile	none	THF	2	110	4	83	48	S5
Zr_{12}-TPDC-Co	benzonitrile	none	toluene	4	110	42	100	200	S6
Co_2P/HT	valeronitrile	NH_3 aq. (31.7 equiv.)	2-propanol	4	150	1	99	5000	S7
$Co(OAc)_2$ + Zn	benzonitrile	NH_3 aq. (1 equiv.)	methanol	4	120	15	94	19	S8
Co-B_{12}@CeO_2	benzonitrile	NH_3 aq. (10 equiv.)	2-propanol	3	120	15	96	60	S9
Co-MOF@C-800	benzonitrile	pNH_3 (0.5 MPa)	toluene	2.5	120	16	97	25	S10
$Co(OAc)_2$/Phen @Al_2O_3	heptanenitrile	NH_3 aq. (8 equiv.)	2-propanol	4	85	24	98	25	S11
Co-N-C@MgO-700	benzonitrile	NH_3 aq. (2.5 equiv.)	2-propanol	2	80	24	91	91	S12

Table S2 Specific surface area and crystallite diameter of the metal catalysts

Catalyst	Crystallite diameter (nm)	Specific surface area (m^2 g^{-1})	Pore size (nm)	Pore volume (mL/g)
Co/SiO_2	12	242	5.6	1.1
Co/MgO	16	71	6.4	0.4
Co/ZrO_2	18	110	1.3	0.1
Co/Nb_2O_5	16	29	-	-
Ru/SiO_2	-[a]	226	5.6	0.8
Pd/SiO_2	21	281	3.9	1.1
Pt/SiO_2	8	219	5.3	0.9
Co	<50[b]	16	-	-
Pt	<50[b]	11	-	-

[a] The value could not be determined because the peaks are too small. [b] Particle size determined by TEM.

Table S3 Support effect on hydrogenation of **1a** over supported Co catalysts[a]

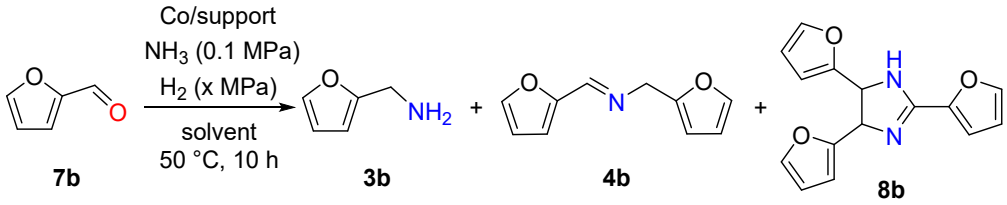


1a **3a** **4a** **5a**

Entry	Support	pH_2 (MPa)	Temp. (°C)	Time (h)	Conv. (%)	Yield (%)		
						3a	**4a**	**5a**
1	SiO_2	0.5	50	20	>99	68	1	25
2	MgO	0.5	50	20	36	14	11	-
3	ZrO_2	0.5	50	20	21	3	8	-
4	Nb_2O_5	0.5	50	20	19	2	8	-
5	SiO_2	2	80	20	>99	58	-	36
6	MgO	2	80	95	>99	88	-	19
7	ZrO_2	2	80	95	>99	79	-	31
8	Nb_2O_5	2	80	95	>99	79	22	8

[a] Reaction conditions: Co/support (20 mg), **1a** (0.5 mmol), cyclohexane (5 mL), pH_2 (x MPa). Yields were determined by GC analysis with chlorobenzene as internal standard.

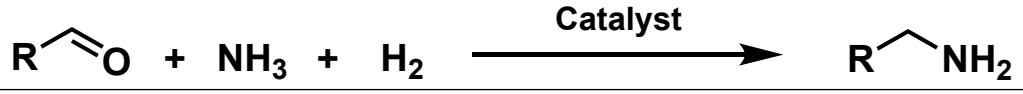
Table S4 Reductive amination of furfural using Co/SiO_2[a]



Entry	Support	Solvent	Substrate (mmol)	Catalyst loading (mol%)	Conv. (%)	Yield (%)		
						3b	**4b**	**8b**
1	SiO_2	MeOH	0.5	6.8	>99	97	1	2
2	SiO_2	EtOH	0.5	6.8	>99	85	11	-
3	SiO_2	2-PrOH	0.5	6.8	>99	26	47	-
4	SiO_2	THF	0.5	6.8	>99	37	49	-
5	SiO_2	MeCN	0.5	6.8	>99	-	52	-
6	SiO_2	Toluene	0.5	6.8	>99	53	37	-
7	SiO_2	cyclohexane	0.5	6.8	>99	71	11	1
8[b]	SiO_2	Toluene	0.5	13.6	>99	97	-	-
9	SiO_2	Toluene	1	3.4	>99	43	45	4
10[c]	SiO_2	Toluene	1	3.4	>99	94	-	6
11[d]	SiO_2	Toluene	0.5	13.6	>99	74	19	1
12[d]	MgO	Toluene	0.5	13.6	60	-	1	18
13[d]	ZrO_2	Toluene	0.5	13.6	80	-	56	15
14[d]	Nb_2O_5	Toluene	0.5	13.6	88	-	39	9

[a] Reaction conditions: Co/support (20 g), **7b** (x mmol), toluene (5 mL), NH_3 (0.1 MPa), pH_2 (y MPa) at 50 °C for 10 h. Yields were determined by GC analysis with chlorobenzene as an internal standard. [b] Run for 24 h. [c] Run for 36 h using 60 mL autoclave. [d] Run at 90 °C for 2 h with pH_2 (4 MPa).

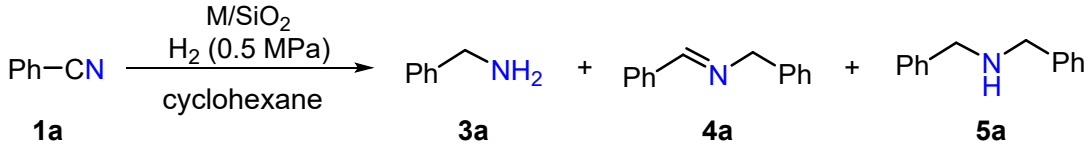
Table S5 Comparison of the reported non-noble metal based catalytic systems for reductive amination of carbonyls with present protocols.



Catalyst	Substrate	NH_3 (equiv.)	pH_2 (MPa)	Temp. (°C)	Time (h)	Yield (%)[a]	Ref.
Co/SiO_2 (13.6 mol%)	furfural 0.5 mmol	0.1 (MPa)	0.5	50	10	97(83)	***This work***
Co-DABCO-TPA@C-800 (3.5 mol%)	furfural 0.5 mmol	0.5-0.7 (MPa)	4.0	120	15	87	S13
Co@NC-800 (0.68 mol%)	furfural 0.5 mmol	28	1.0	130	12	96.9	S14
Raney Co (33 mol%)	furfural 0.5 mmol	0.1 (MPa)	1.0	120	2	98	S15
in situ Co-NPs (6 mol%)	furfural 0.5 mmol	0.5 (MPa)	4.5	120	24	(89)	S16
Co/N-SiC (1.5 mol%)	acetophenone 0.5 mmol	118	0.1	50	20	99	S17
Ni/Al_2O_3 (1.2 mol%)	furfural 0.5 mmol	13.4	1.0	80	20	99	S18
Ni-TA@SiO_2-800 (6 mol%)	furfural 0.5 mmol	0.5-0.7 (MPa)	2.0	120	24	88	S19
Fe_3O_4@SiO_2-Ni (5 mol%)	furfural 0.5 mmol	10	2.0	115	2	>99[c]	S20
Ni/NiO@C-700 (7 mol%)	benzaldehyde 0.5 mmol	20	1.0	90	4	99	S21
Fe/(N)SiC (8.6 mol%)	benzaldehyde 0.5 mmol	93.8	6.5	130	20	89	S22
Fe-P_{900}-PCC (0.019 mol%)	1-formylbenzoic acid 47 mmol	2.1	6	75	20	97	S23

[a]The value in the parenthesis is isolated yield. [b]Reactions performed under MW irradiation. [c]Conversion (determined by GC/MS).

Table S6 Hydrogenation of **1a** over SiO_2-supported metal catalysts[a]

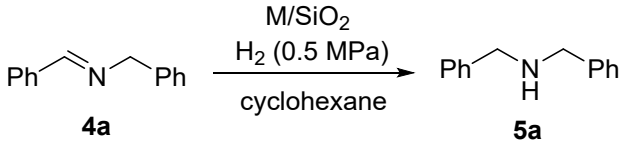


1a **3a** **4a** **5a**

M	Metal loading (mol%)	Time (h)	Conv. (%)	Yield (%)		
				3a	**4a**	**5a**
Co	13.6	5	54	2	43	-
		10	>99	39	56	3
		20	>99	77	3	19
		25	>99	79	-	21
Pd	7.5	10	82	12	60	2
		20	>99	52	29	6
		30	>99	65	-	30
Ru	7.9	20	93	9	74	2
		80	>99	57	-	40
Pt	4.1	1	56	-	-	34
		5	94	-	-	63
		20	98	-	-	45
		20[b]	59	-	9	23

[a] Reaction conditions: M/SiO_2 (20 mg), **1a** (0.5 mmol), cyclohexane (5 mL), pH_2 (0.5 MPa) at 50 °C for 20 h. Yields were determined by GC analysis with chlorobenzene as internal standard. [b] Run with pH_2 (0.1 MPa).

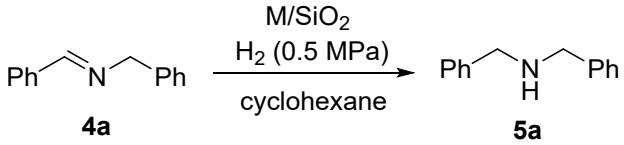
Table S7 Hydrogenation of **4a** over Co/SiO_2 and Pt/SiO_2[a]



Entry	Metal	Substrate (mmol)	Time (h)	Conv. (%)	yield (%)
1	Co	0.25	2	>99	78
2	Pt	0.25	2	>99	74
3	Co	0.5	3	>99	>99
4	Pt	0.5	3	>99	>99
5	Co	5	2	19	8
6	Pt	5	2	22	9

[a] Reaction conditions: **4a** (0.5 mmol), M/SiO_2 (0.02 g), cyclohexane (5 mL), pH_2 (0.5 MPa), 50 °C.

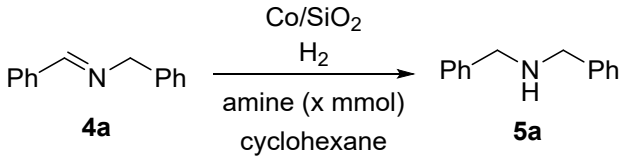
Table S8 Support effects on the hydrogenation of **4a** over supported Co catalysts[a]

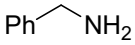
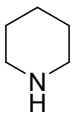
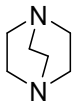


Entry	support	**3a** (mmol)	pH_2 (MPa)	Temp. (°C)	Conv. (%)	yield (%)
1	SiO_2	0	0.5	50	>99	>99
2		0.5	0.5	50	17	14
3	MgO	0	0.5	50	71	68
4		0.5	0.5	50	38	29
5	ZrO_2	0	0.5	50	26	10
6		0.5	0.5	50	24	12
7		0	2	50	56	48
8		0.5	2	50	31	22
9	Nb_2O_5	0	0.5	50	<1	-
10		0.5	0.5	50	<1	-
11		0	3	100	19	2
12		0.5	3	100	<1	-

[a] Reaction conditions: **4a** (0.5 mmol), Co/support (0.02 g), cyclohexane (5 mL), pH_2 (x MPa), for 2 h.

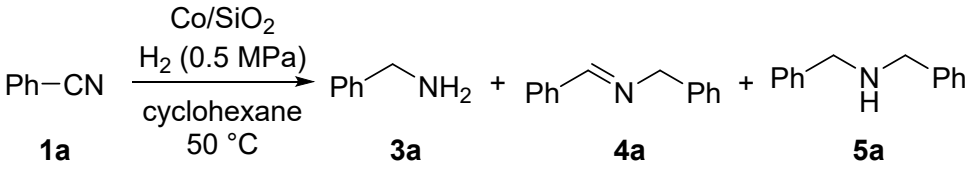
Table S9 Additive effects of *N*-containing compounds on the hydrogenation of **4a**[a]



Entry	Amine	x (mmol)	Conv. (%)	Yield (%)
1	none	0	>99	>99
2		0.5	17	14
3		0.1	66	44
4		0.5	19	6
5	Et_3N	0.5	31	20
6		0.5	19	12
7	DMF	0.5	30	38

[a] Reaction conditions: **4a** (0.5 mmol), amine (x mmol), Co/SiO_2 (0.02 g), cyclohexane (5 mL), pH_2 (0.5 MPa), 50 °C, 2 h.

Table S10 Time-course for the hydrogenation of **1a** over Co/SiO_2[a]



Entry	Additive	Time (h)	Conv. (%)	Yield (%)		
				3a	**4a**	**5a**
1	None	5	54	2	43	2
2		10	>99	39	56	3
3		20	>99	77	3	19
4		25	>99	79	-	21
5	DMF (0.5 mmol)	20	>99	66	31	3
6		24	>99	71	26	3
7		40	>99	82	16	5

[a] Reaction conditions: **1a** (0.5 mmol), DMF (0 or 0.5 mmol), Co/SiO_2 (0.02 g), cyclohexane (5 mL), pH_2 (0.5 MPa), 50 °C.

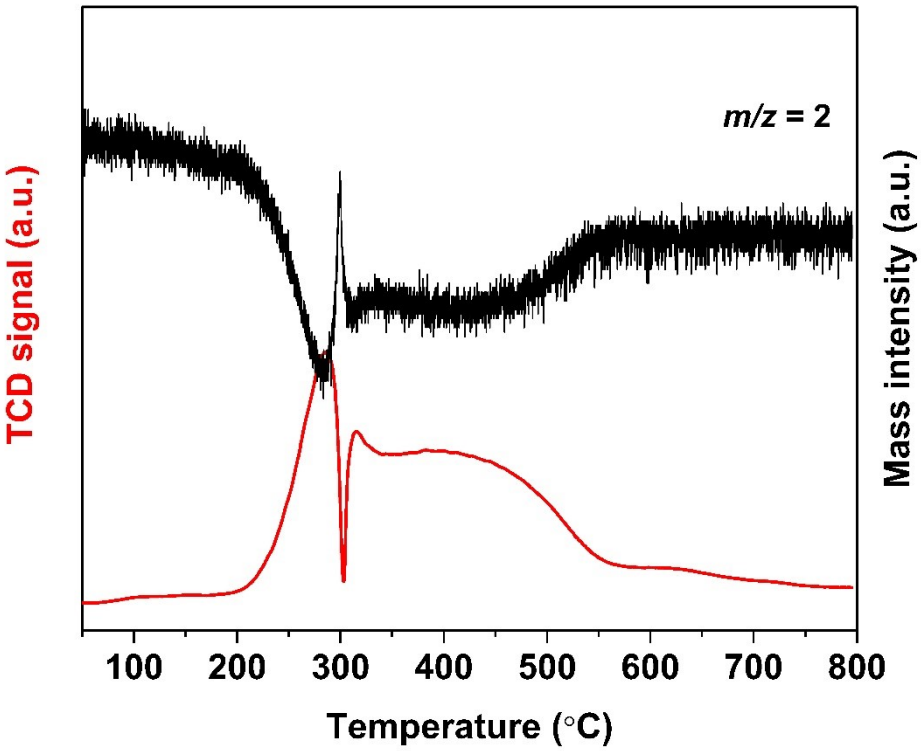


Fig. S1 TPR profile of unreduced 20 wt% Co/SiO_2

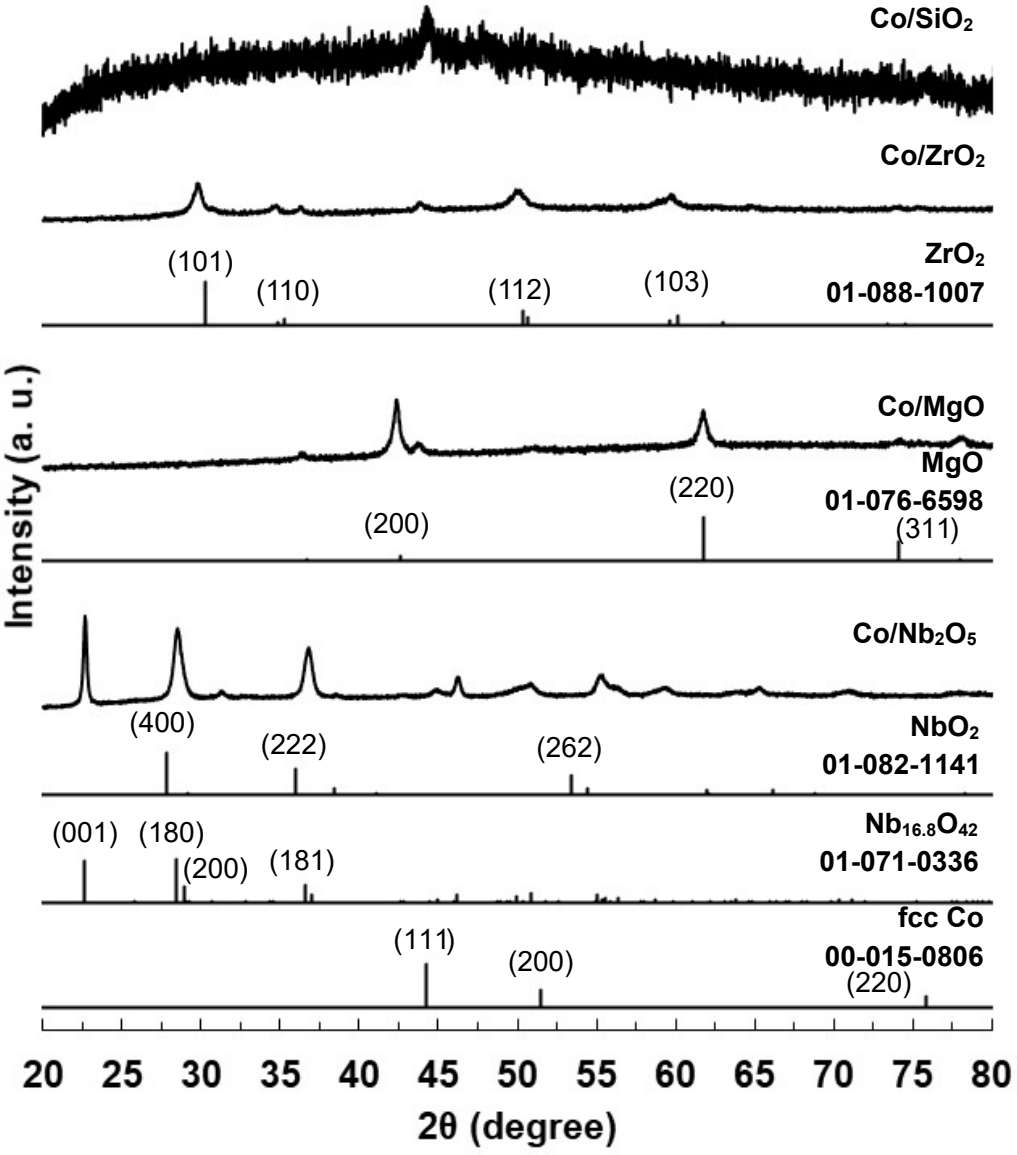


Fig. S2 XRD patterns of various cobalt-based catalysts on various supports.

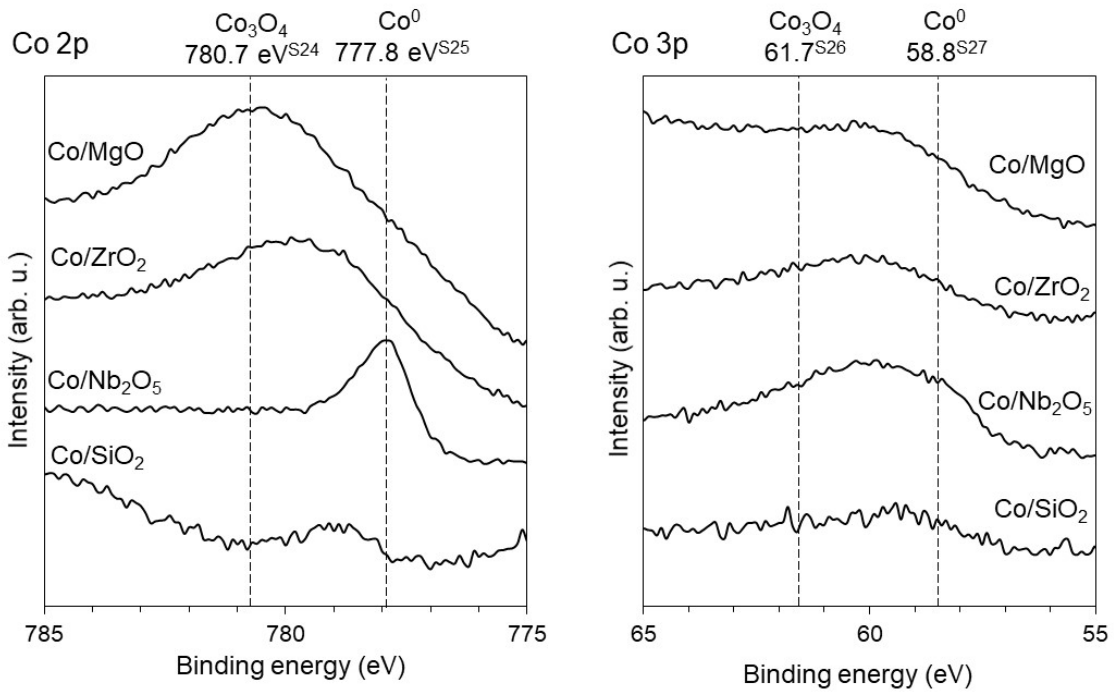


Fig. S3 XPS spectra for supported Co catalysts.

The adsorption experiments were carried out without H_2 at low temperature because of the facile hydrogenation of **4a** even at low hydrogen pressure and the formation of benzonitrile through dehydrogenation of **3a**.

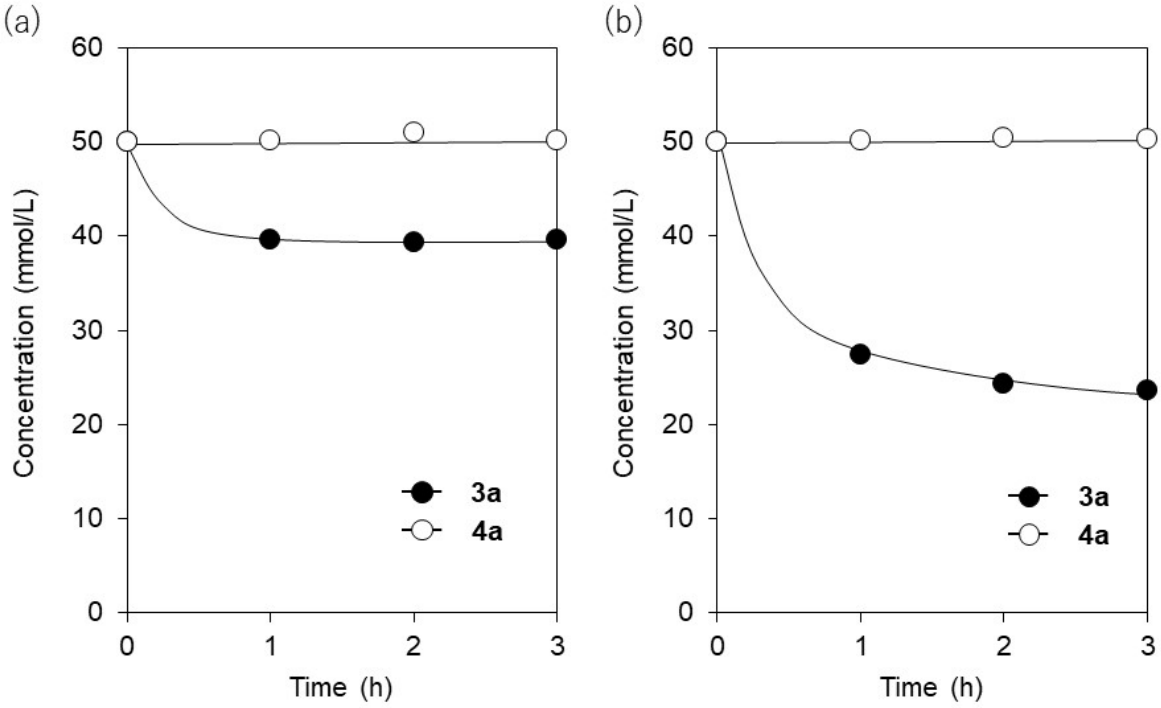


Fig. S4 Time course of **3a** and **4a** concentration in the mixture of (a) Co, (b) Pt nanoparticles, **3a** and **4a** solution. Reaction conditions: metal nanoparticle, 0.4 g; **3a**, 0.1 mmol; **4a**, 0.1 mmol; toluene, 2 mL; –15 °C

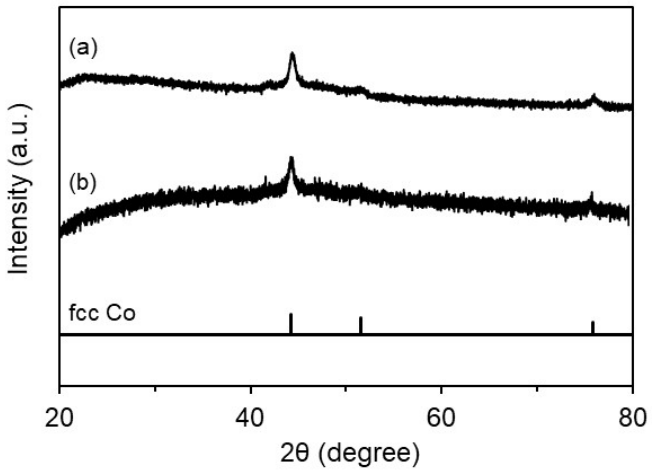


Fig. S5 XRD patterns of (a) fresh Co/SiO_2, (b) recovered Co/SiO_2 after hydrogenation of benzonitrile and fcc Co (JCPDS 00-015-0806).

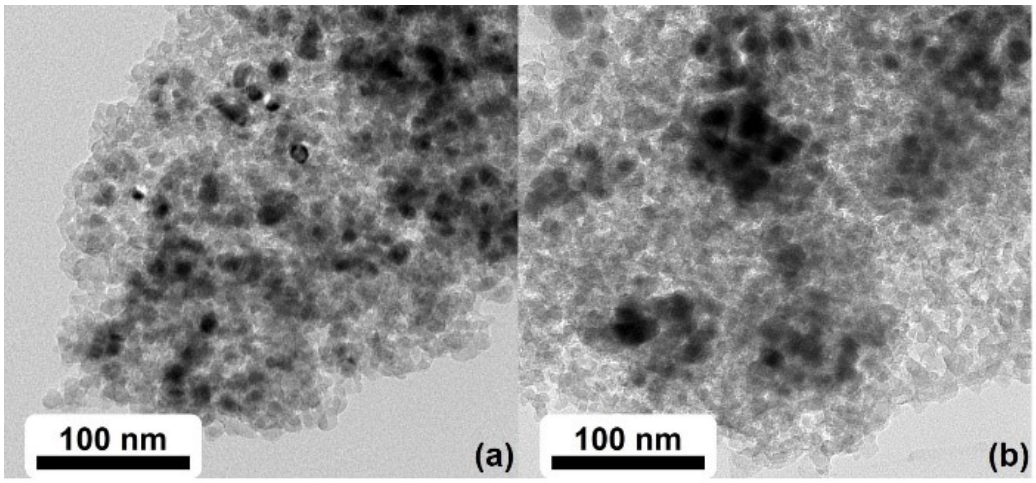


Fig. S6 TEM images of (a) fresh Co/SiO_2 and (b) recovered Co/SiO_2 after reductive amination of furfural.

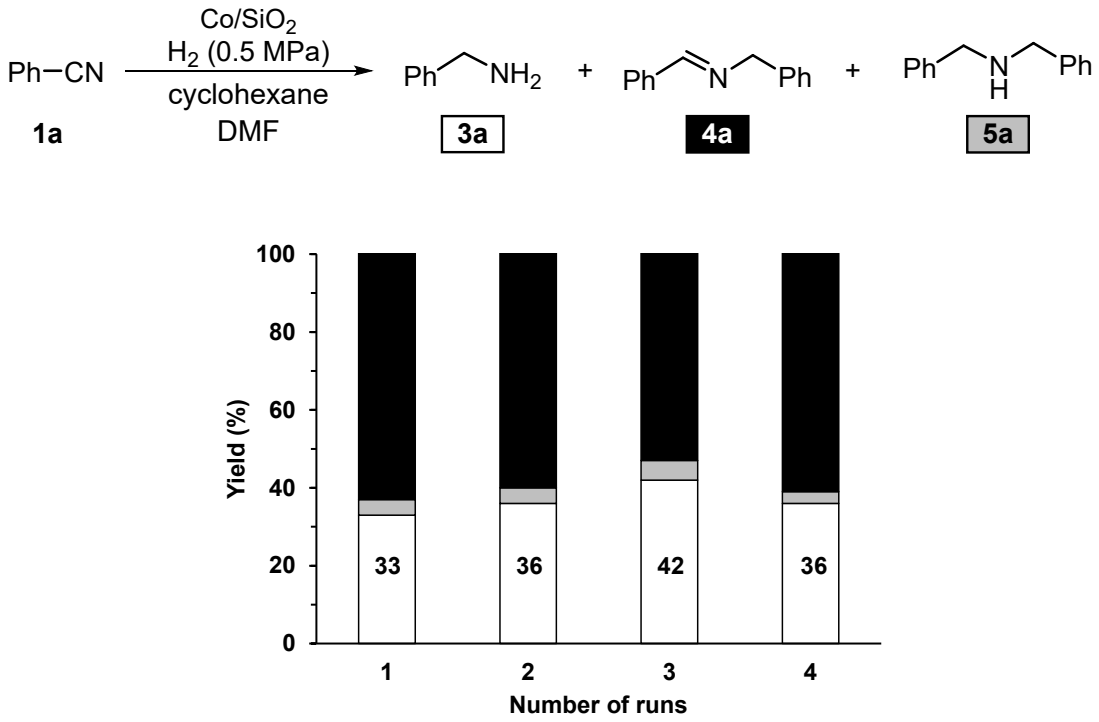


Fig. S7 Reuse experiments with the Co/SiO_2 catalyst for the hydrogenation of **1a**. Reaction conditions: Co/SiO_2 (20 mg), **1a** (0.5 mmol), DMF (1 mL), cyclohexane (4 mL), pH_2 (0.5 MPa) at 100 °C for 2 h. Yields were determined by GC analysis with chlorobenzene as an internal standard.

Since the reuse experiments was performed in a large-capacity autoclave for ease of recovery, the yield of **3a** was lower than that obtained using a small-capacity autoclave.

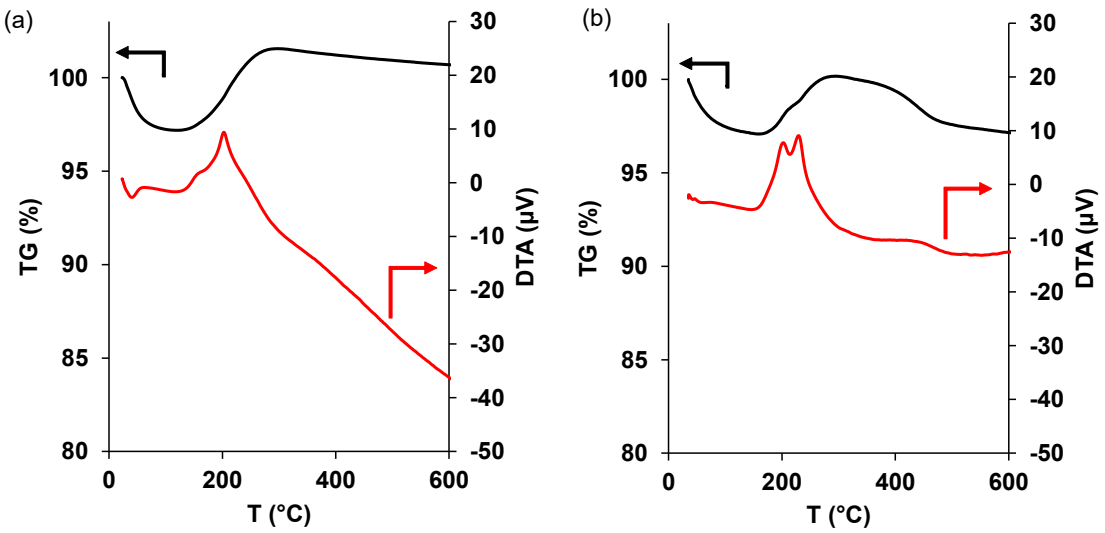
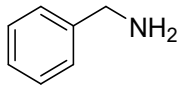


Fig. S8 TG-DTA chart of (a) fresh Co/SiO_2 and (b) used Co/SiO_2 after hydrogenation of **1a**.

Spectral Data

Benzylamine (**3a**)[S28]

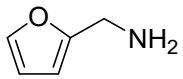


After the reaction was completed, the crude product was purified by flash column chromatography (EtOAc:MeOH = 10:0 to 6:4) to give the pure title compound (86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21–7.35 (m, 5H), 3.85 (s, 2H), 1.60 (br s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.3, 128.5, 127.1, 126.8, 46.5.

Furfurylamine (**3b**) [S15]

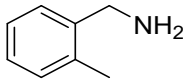


After the reaction was completed, the catalyst was separated by filtration and the obtained solution was evaporated to give the analytically pure title compound (83%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (s, 1H), 6.30–6.31 (q, 1H), 6.13 (d, *J* = 3.2 Hz, 1H), 3.82 (s, 2H), 1.64 (br s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.6, 141.6, 110.2, 105.0, 39.3.

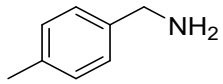
2-Methylbenzyl amine (**3c**)[S29]



After the reaction was completed, the catalyst was separated by filtration. The crude product was purified by flash column chromatography (EtOAc:MeOH = 10:0 to 6:4) to give the mixture of the title compound with side products. The yield was calculated based on 3.84 ppm peak assigned to the benzylic position (69%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.15 (m 4H), 3.84 (s 2H), 2.33 (s 3H), 1.48 (brs 2H).

4-Methylbenzyl amine (**3d**)[S30]

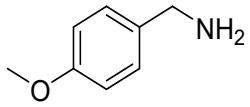


After the reaction was completed, the catalyst was separated by filtration. The crude product was purified by flash column chromatography (EtOAc:MeOH = 10:0 to 6:4) to give the mixture of the title compound with side products. The yield was calculated based on 3.81 peak assigned to the benzylic position (64%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 3.81

(s, 2H), 2.33 (s, 3H), 1.52 (s, 2H).

4-Methoxybenzyl amine (**3e**) [S31]

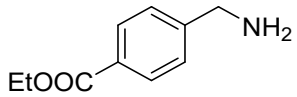


After the reaction was completed, the catalyst was separated by filtration. The crude product was purified by flash column chromatography (EtOAc:MeOH = 10:0 to 6:4) to give the pure title compound (83%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 3.78 (s, 5H), 1.60 (br s, 2H).

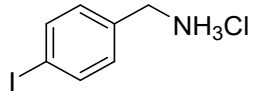
^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5, 135.6, 128.3, 113.9, 55.3, 45.9.

4-Ethoxycarbonylbenzylamine (**3f**) [S32]



After the reaction was completed, the catalyst was separated by filtration. The crude product was purified by flash column chromatography (EtOAc:MeOH = 10:0 to 6:4) to give the mixture of the title compound with side products. The yield was calculated based on the peak at 3.87 ppm assigned to the benzylic position (53%). *N,N,N*-Tris(4-ethoxycarbonylbenyl)amine was also observed in 14% yield (3.79 ppm).

4-Iodobenzyl amine hydrochloric acid (**3g**•HCl)[S33]

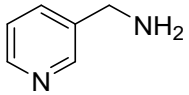


After the reaction was completed, the catalyst was separated by filtration and Hydrogen chloride ethyl ether solution was added dropwise to the resulting solution to obtain the hydrochloride salt. (79%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.68 (s, 3H), 7.77 (d, *J* = 4.1 Hz, 2H), 7.34 (d, *J* = 4.2 Hz, 2H), 3.97 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.7, 134.3, 131.8, 95.3, 42.0.

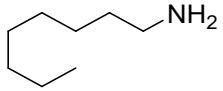
pyridin-3-ylmethanamine (**3h**)



Yield was determined by GC analysis with chlorobenzene as the internal standard. The

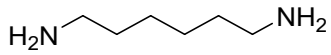
retention time of the title compound is 13.2 minutes (62%).

octan-1-amine (**3i**)



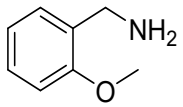
Yield was determined by GC analysis with chlorobenzene as the internal standard. The retention time of the title compound is 11.8 minutes (78%).

1,6-hexanediamine (**3j**)



Yield was determined by GC analysis with phenanthrene as the internal standard. The retention time of the title compound is 12.6 minutes (73%).

2-Methoxybenzylamine (**3k**)[S31]

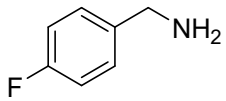


After the reaction was completed, the catalyst was separated by filtration. The crude product was purified by flash column chromatography (EtOAc:MeOH = 10:0 to 6:4) to give the pure title compound (95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.189–7.24 (m, 2H), 6.84−6.92 (m, 2H), 3.82 (s, 3H), 3.80 (s, 2H), 2.22 (br s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4, 131.5, 128.6, 128.1, 120.6, 110.3, 55.2, 42.5.

4-Fluorobenzylamine (**3l**)[S31]

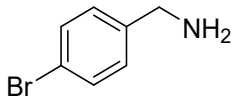


After the reaction was completed, the crude product was purified by flash column chromatography (EtOAc:MeOH = 10:0 to 6:4) to give the pure title compound (81%).

^{1}H NMR (100 MHz, $CDCl_3$): δ = 7.25–7.28 (q, 2 H), 6.98–7.03 (t, 2H), 3.83 (s, 2 H), 1.76 (br s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.8 (d, J = 242.8 Hz), 138.8, 128.6 (d, J = 7.8 Hz), 115.2 (d, J = 21.1), 45.7.

4-Bromobenzylamine (**3m**)[S18]

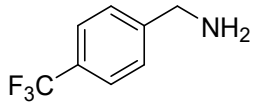


After the reaction was completed, the catalyst was separated by filtration. The crude product was purified by flash column chromatography (EtOAc:MeOH = 10:0 to 6:4) to give the pure title compound (86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 3.82 (s, 2H), 1.59 (br s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.1, 131.5, 128.8, 120.5, 45.8.

4-(Trifluoromethyl)benzylamine (**3n**)[S18]

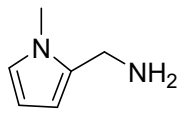


After the reaction was completed, the crude product was purified by flash column chromatography (EtOAc:MeOH = 10:0 to 6:4) to give the pure title compound (88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2 H), 3.93 (s, 2H), 1.85 (br s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.9, 129.1 (q, *J* = 32.0 Hz), 127.3, 125.4 (q, *J* = 3.5 Hz), 124.2 (q, *J* = 270.1 Hz), 45.9.

2-Aminomethylpyrrole (**3o**)[S19]

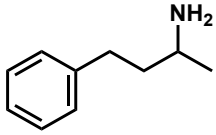


After the reaction was completed, the catalyst was separated by filtration and the obtained solution was evaporated to give the analytically pure title compound (87%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.56 (s, 1H) , 6.00−6.05 (m, 2H), 3.79 (s, 2H), 3.59 (s, 3H), 2.14 (s, 2H).

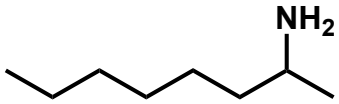
^{13}C NMR (100 MHz, $CDCl_3$): δ =133.7, 122.3, 106.7, 106.5, 37.8, 33.6.

4-Phenylbutan-2-amine (**3p**)[S34]



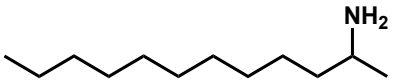
After the reaction was completed, the catalyst was separated by filtration and the obtained solution was evaporated to give the analytically pure title compound (76%).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.23 (m, 2H), 7.18-7.14 (m, 3H), 2.94–2.89 (m, 1H), 2.69–2.59 (m, 2H), 1.69–1.63 (m, 2H), 1.11 (d, *J* = 6.4 Hz, 3H)
^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.2, 128.4, 128.3, 125.8, 46.6, 41.2, 32.7, 23.4

Octan-2-amine (**3q**) [S35]



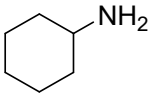
After the reaction was completed, the catalyst was separated by filtration. The obtained solution was evaporated to dryness. Yield of the title compound was determined ^{1}H NMR analysis based on phenanthrene as an internal standard.

Dodecan-2-amine (**3r**) [S36]



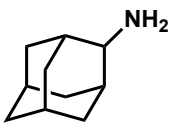
After the reaction was completed, the catalyst was separated by filtration. The obtained solution was evaporated to dryness. Yield of the title compound was determined by ^{1}H NMR analysis based on phenanthrene as an internal standard.

Cyclohexylmethylamine (**3s**)[S37]



After the reaction was completed, the catalyst was separated by filtration and the obtained solution was evaporated to give the analytically pure title compound (74%).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.59−2.66 (m, 1H), 1.57−1.86 (m, 5H), 1.00−1.32 (m, 5H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 50.4, 36.8, 25.6, 25.1.

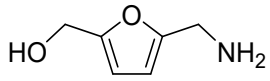
2-Adamanylamine (**3t**)[S38]



After the reaction was completed, the catalyst was separated by filtration. The obtained

solution was evaporated to dryness. Yield of the title compound was determined based on phenanthrene as an internal standard.

(5-(Aminomethyl)furan-2-yl)methanol (**3u**)[S39]

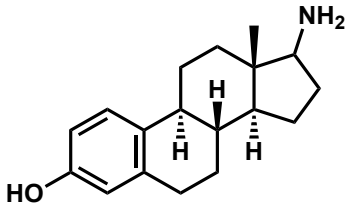


After the reaction was completed, the catalyst was separated by filtration and the obtained solution was evaporated to give the analytically pure title compound (93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.18 (d, *J* = 3.2 Hz, 1H), 6.07 (d, *J* = 3.2 Hz, 1H), 4.53 (d, *J* = 6.8 Hz, 1H), 3.79 (s, 2H), 2.10 (br s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.3, 153.3, 108.3, 106.0, 57.3, 39.2.

17β-amino-1,3,5(10)-estratrien-3-ol (**3v**) [S9]



After the reaction was completed, the catalyst was separated by filtration and the obtained solution was evaporated to give the analytically pure title compound (83%).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.99 (s, 2H), 7.05–7.03 (d, *J* = 8.4 Hz, 1H), 6.53–6.50 (m, 1H), 6.46–6.45 (m, 1H), 2.77–2.73 (m, 2H), 2.41–2.39 (m, 1H), 2.32–2.22 (m, 1H), 2.13–1.29 (m, 12H), 0.82 (s, 3H)

^{13}C NMR (100 MHz, DMSO-d_6): δ = 155.5, 137.6, 130.4, 126.5, 115.4, 113.3, 50.1, 47.8, 43.9, 38.5, 35.8, 31.9, 29.5, 26.6, 26.0, 21.6, 14.0.

References

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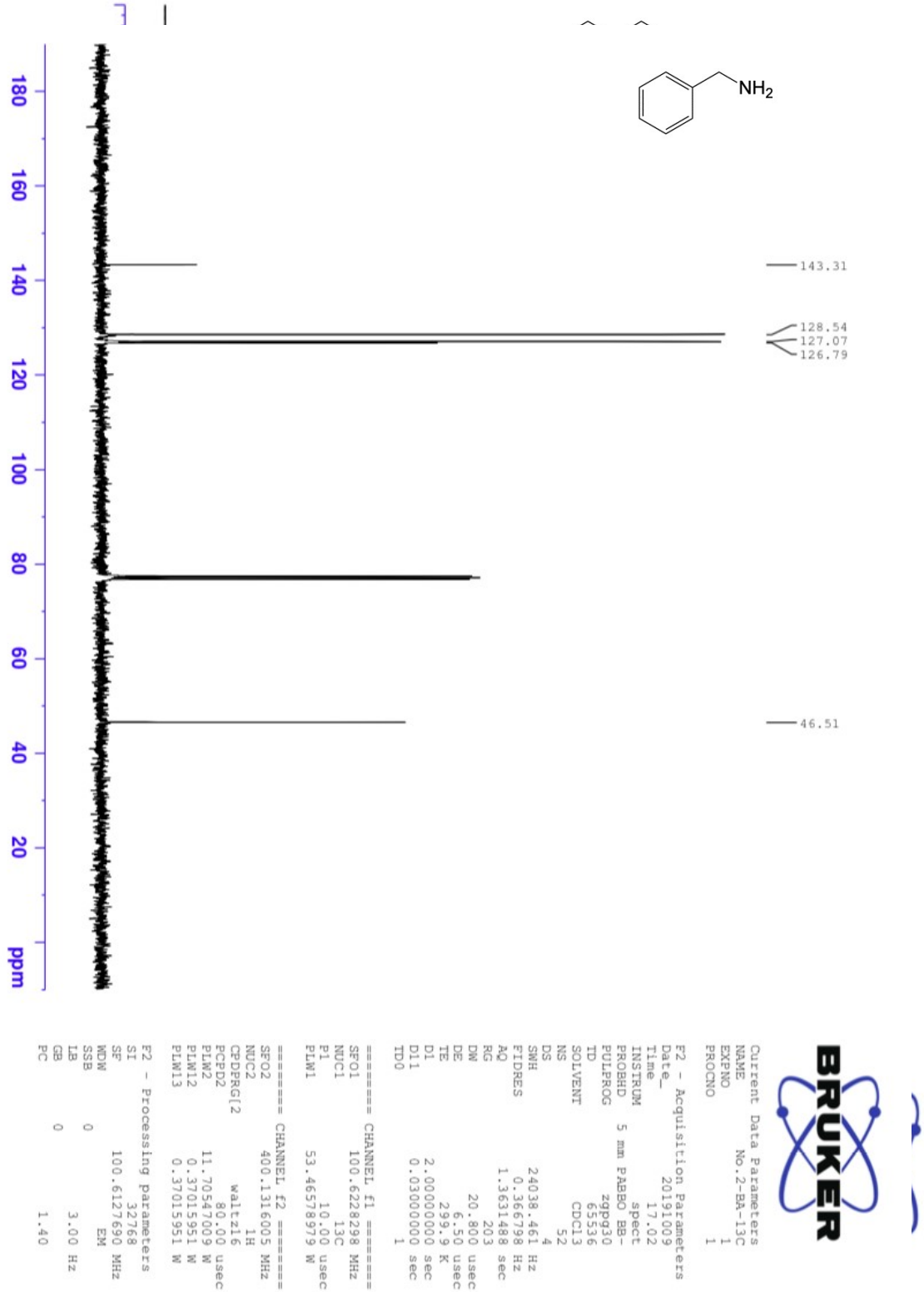
NMR spectra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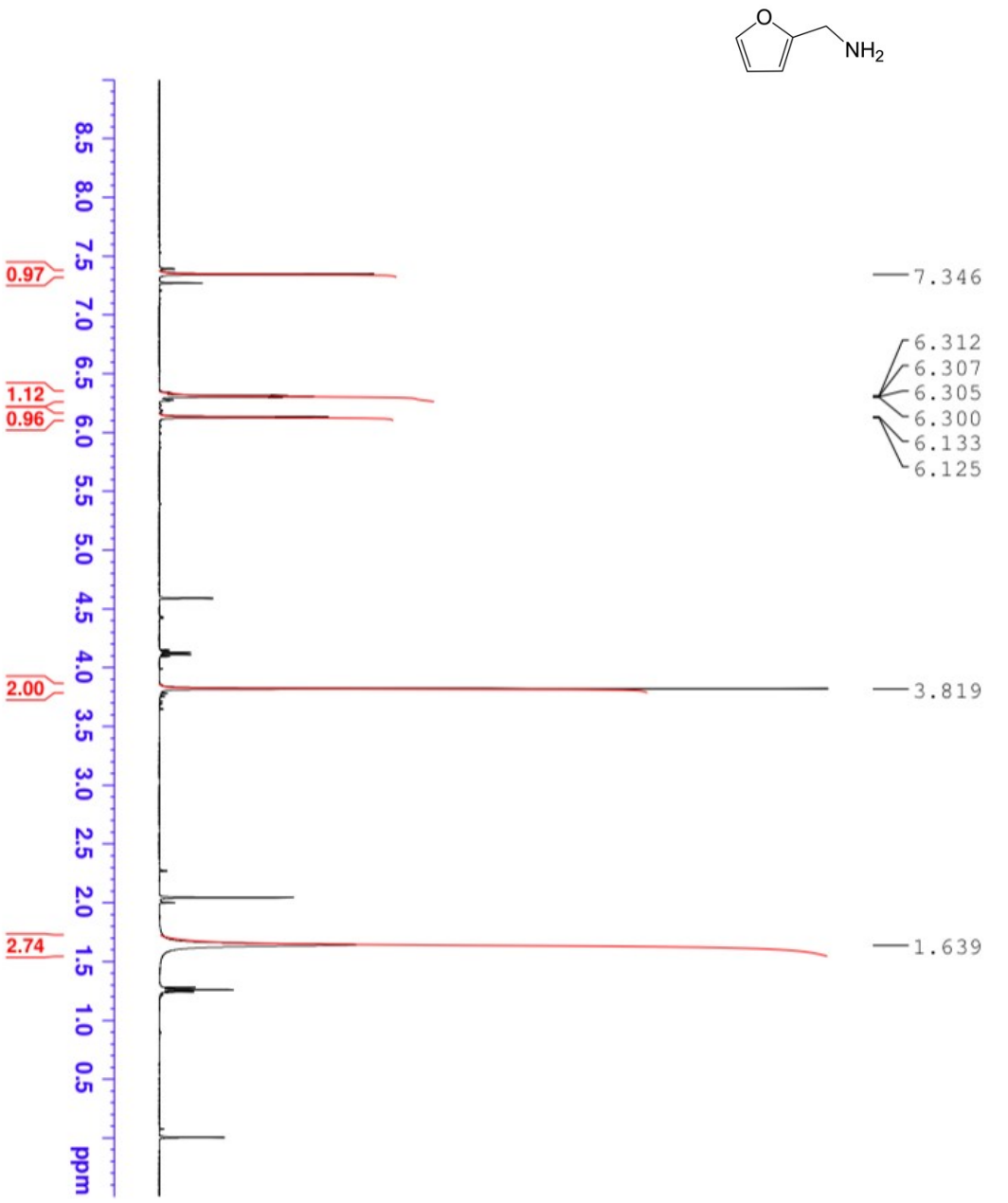


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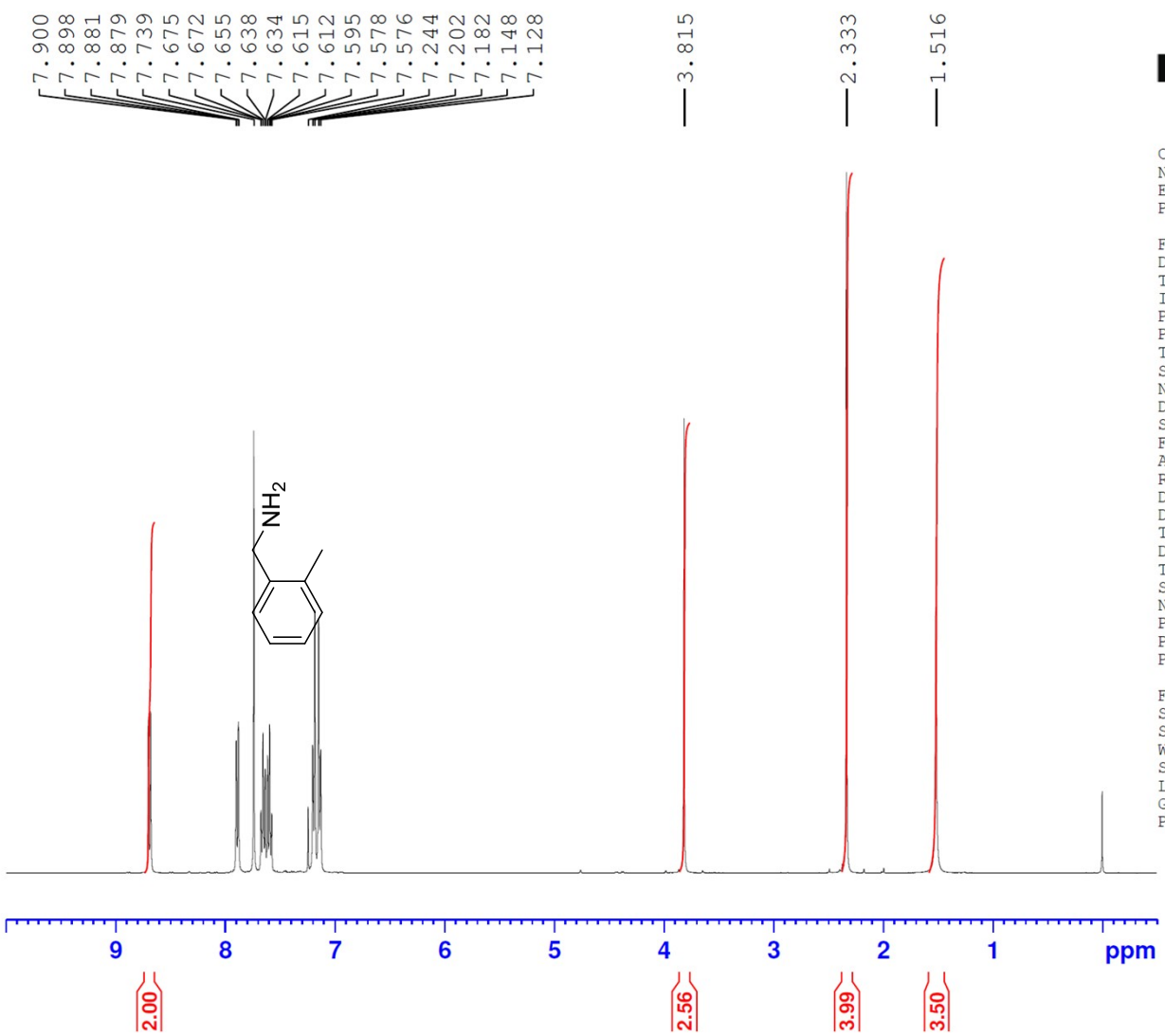

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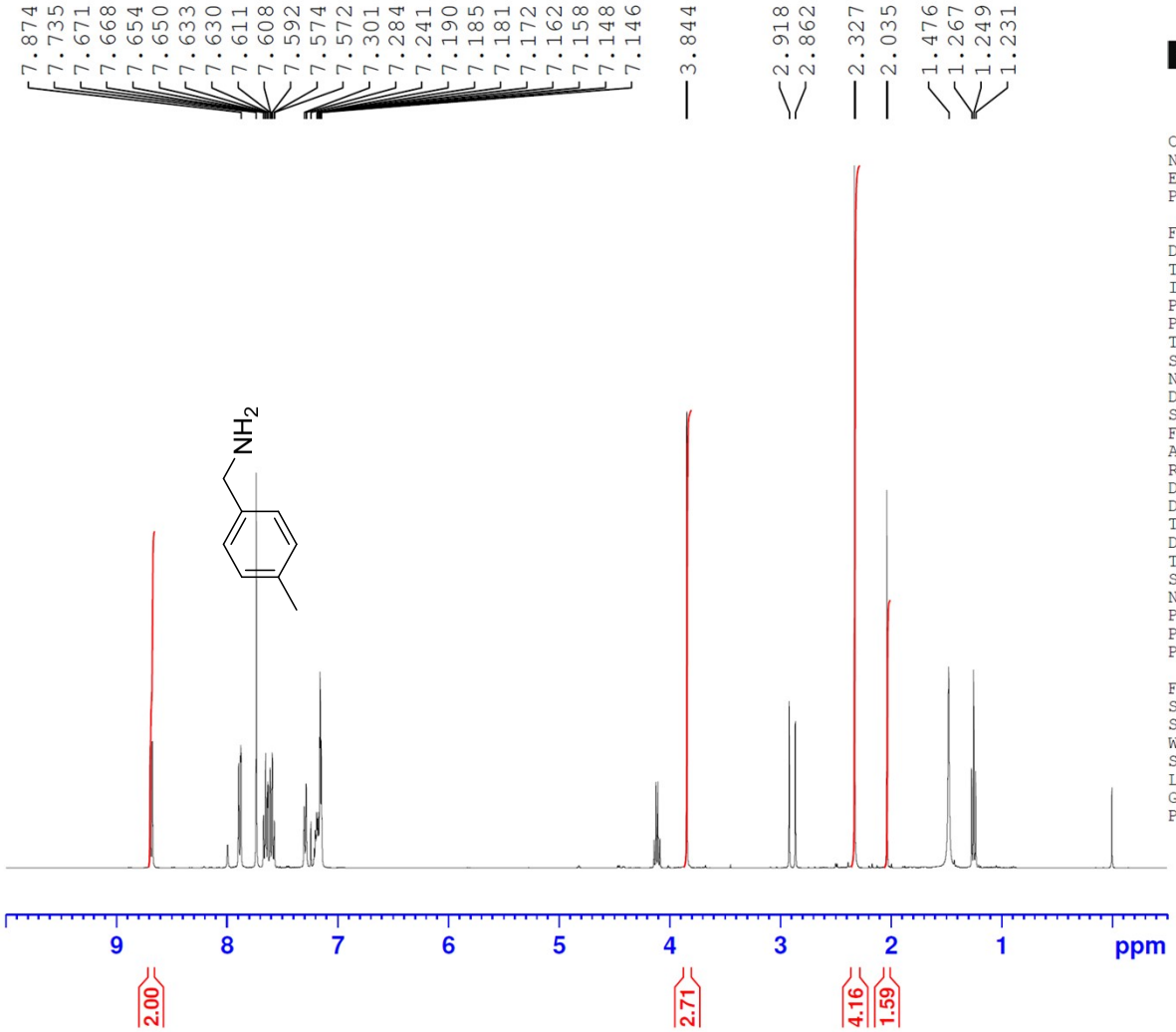

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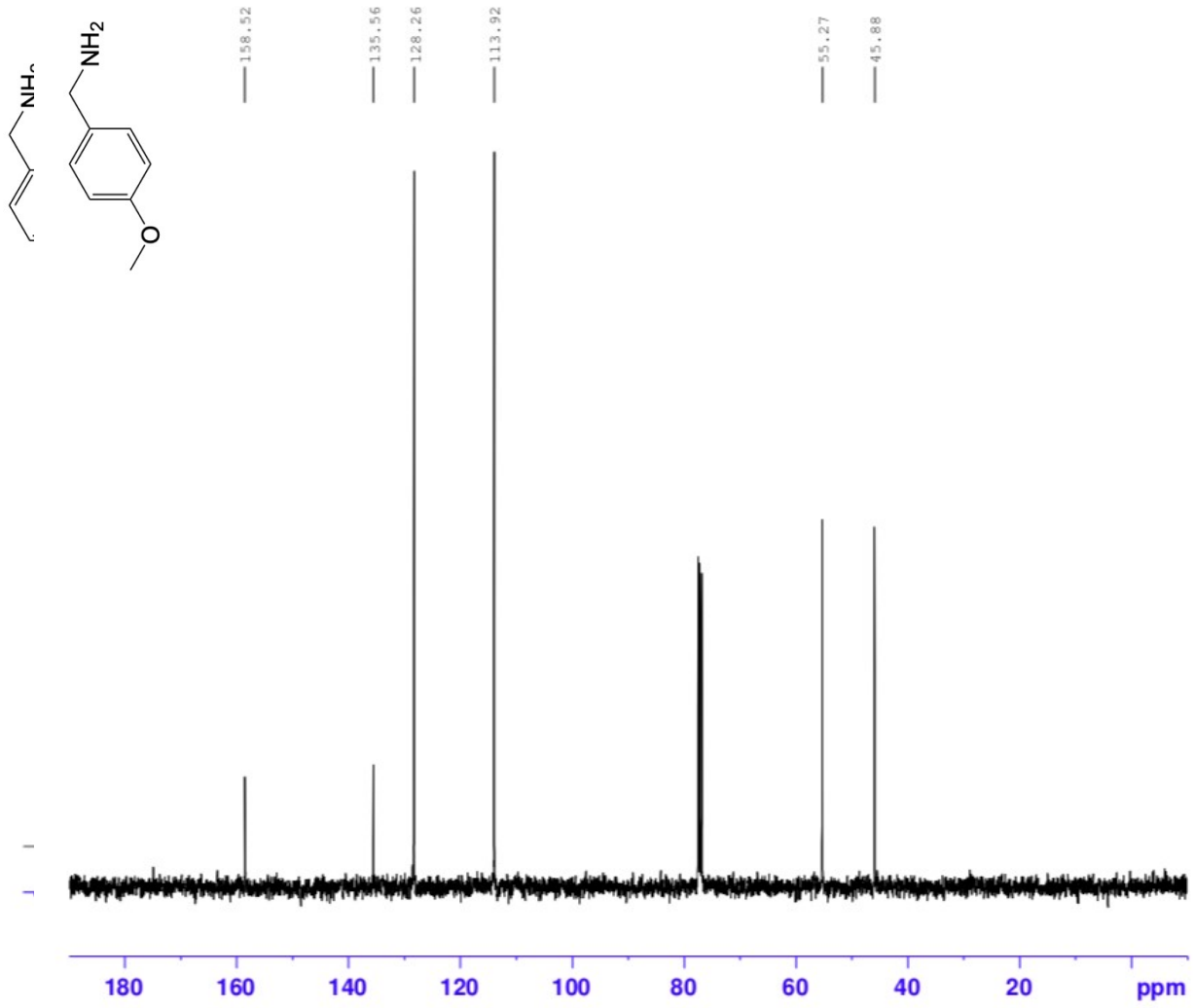


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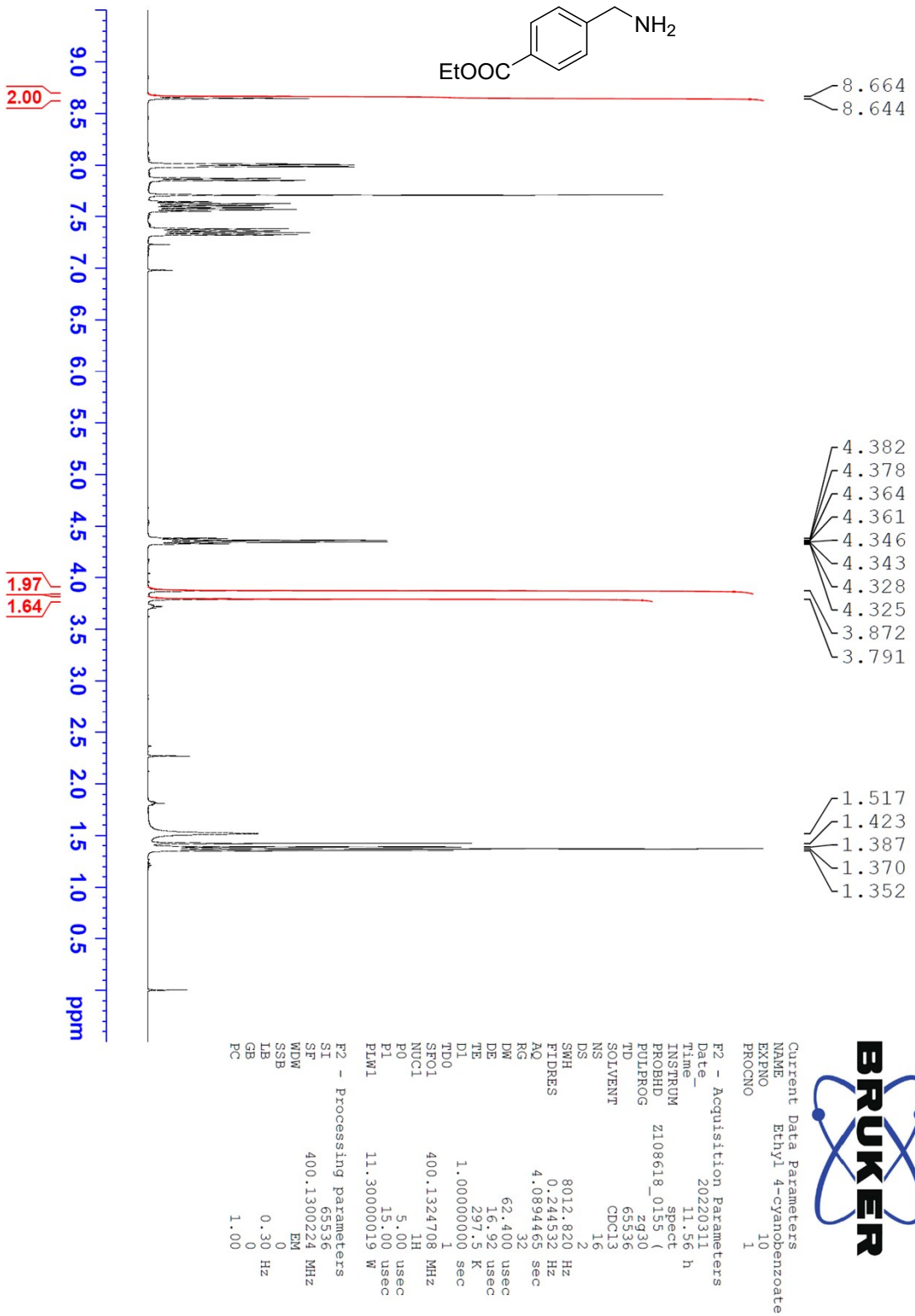
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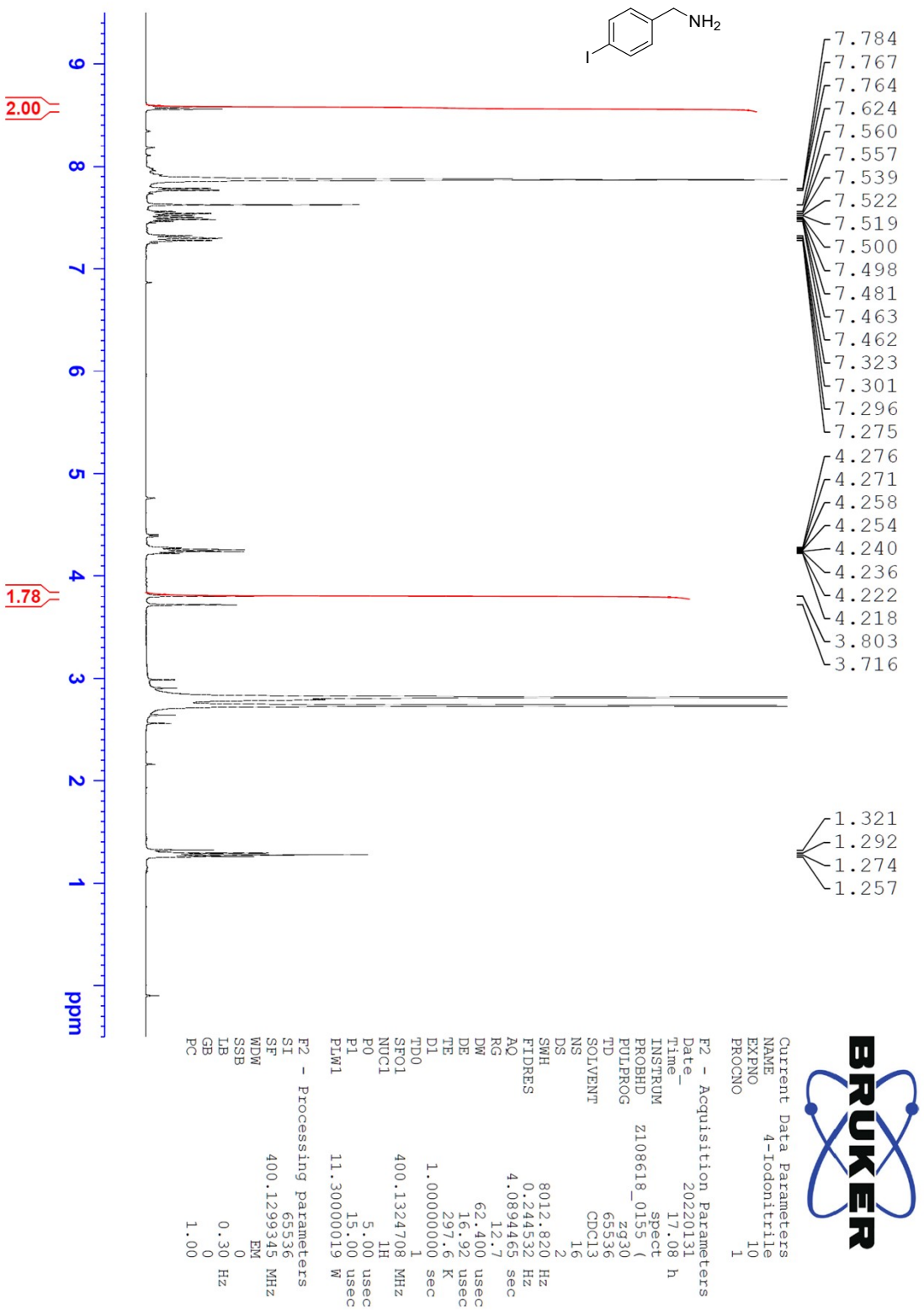
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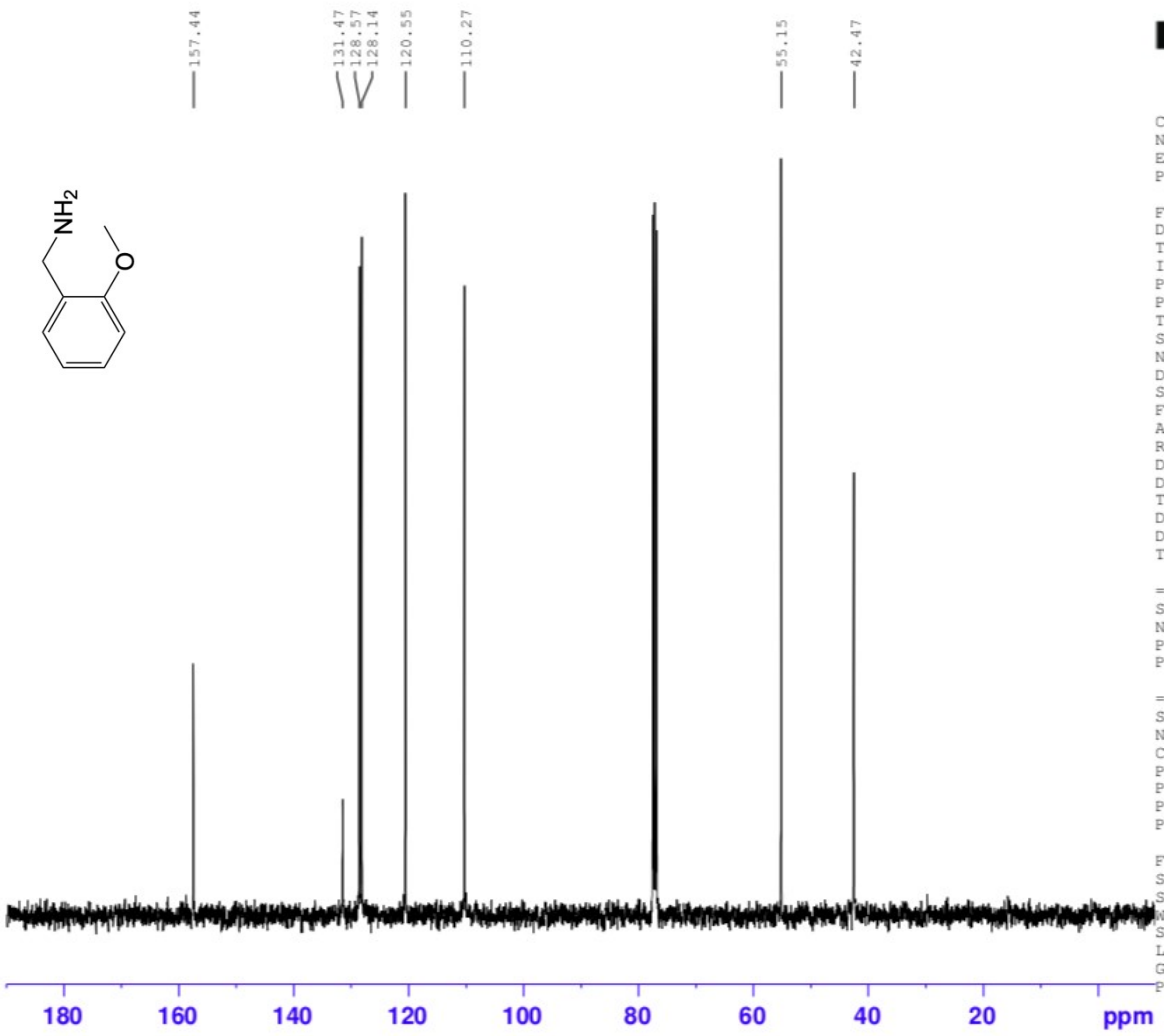

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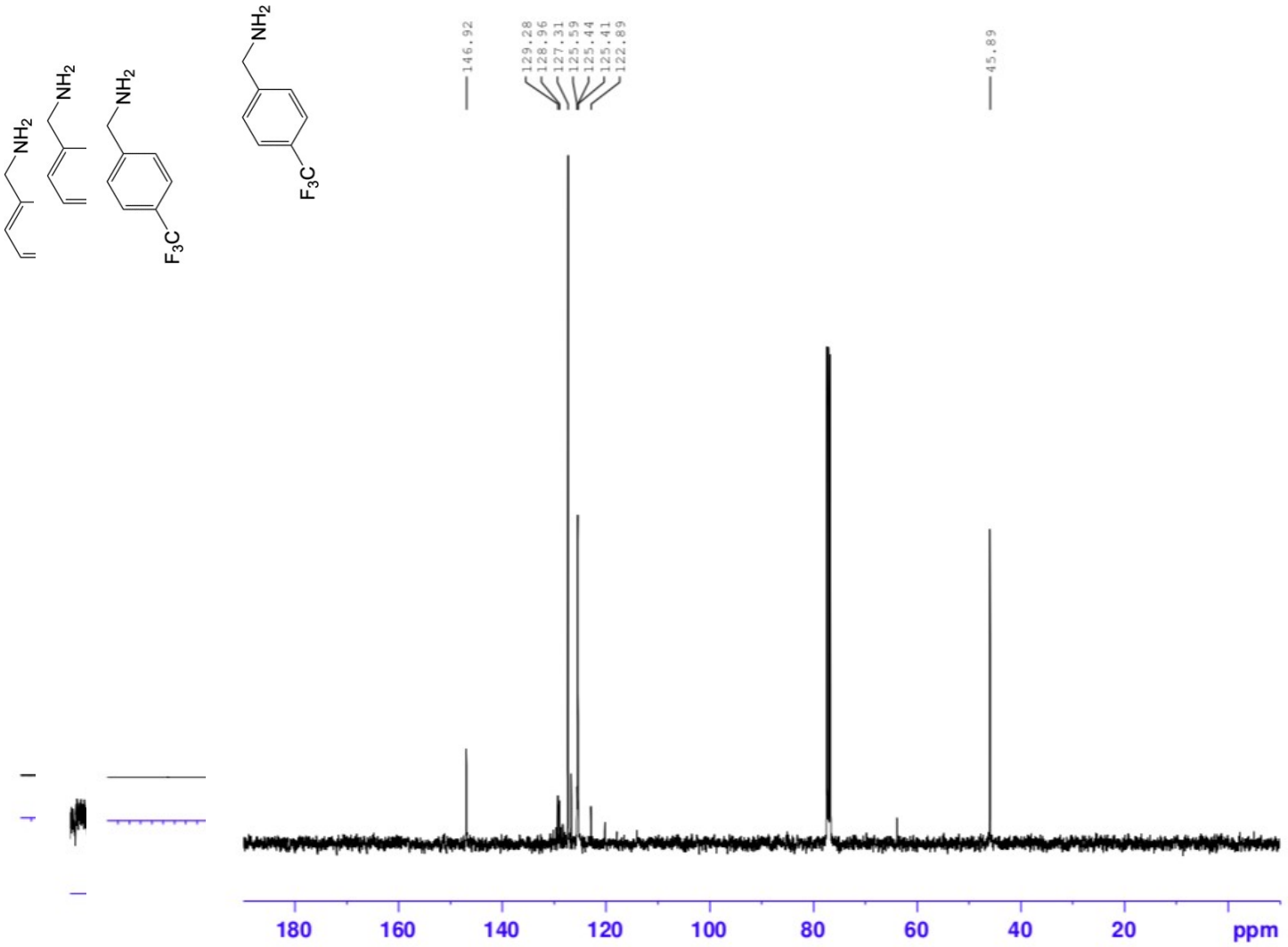

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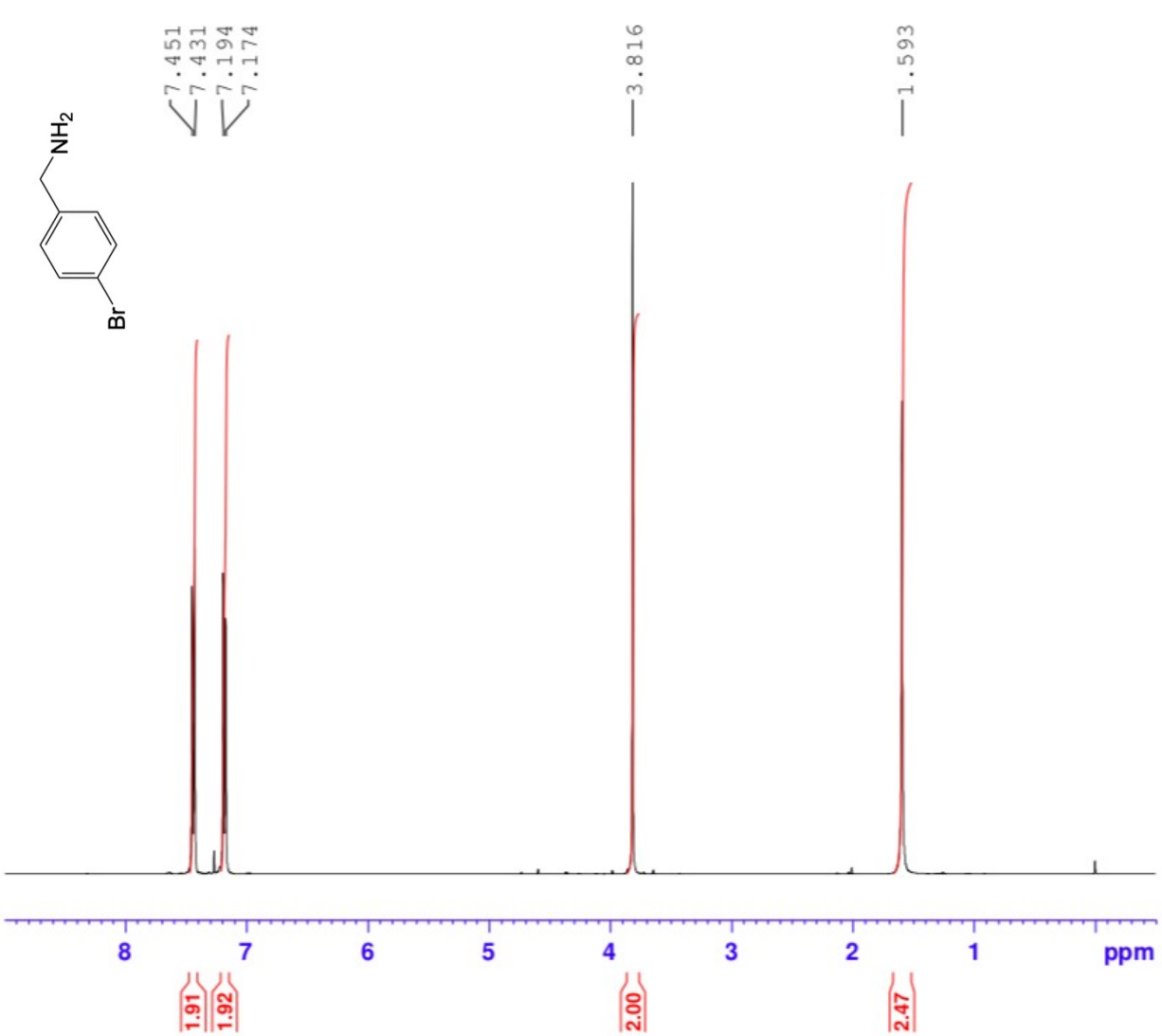


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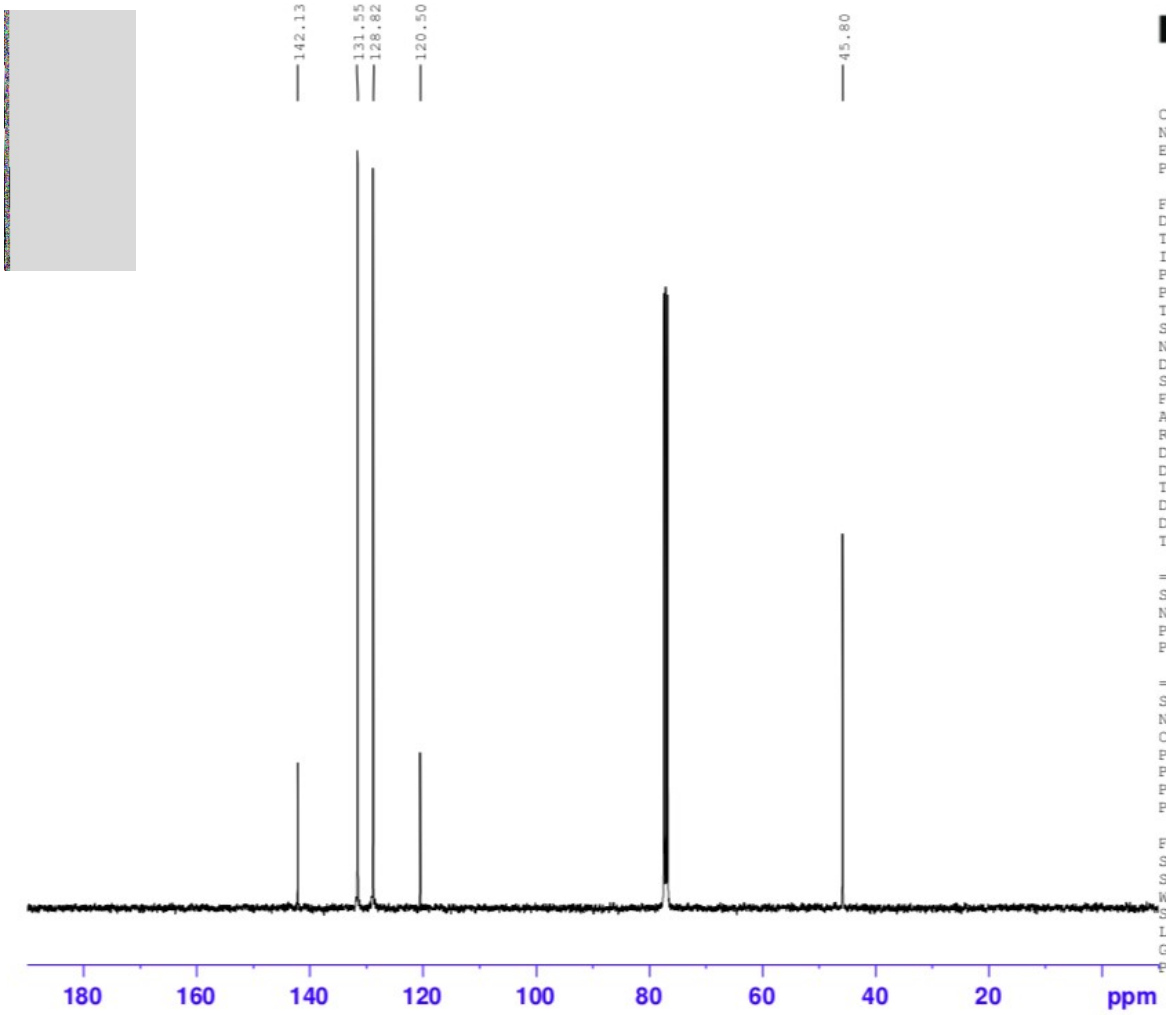
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     9
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894465 sec
RG                  80.6
DW                62.400 usec
DE                 6.50 usec
TE                301.2 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                 15.00 usec
PLW1         11.89999962 W

F2 - Processing parameters
SI                 65536
SF           400.1300053 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



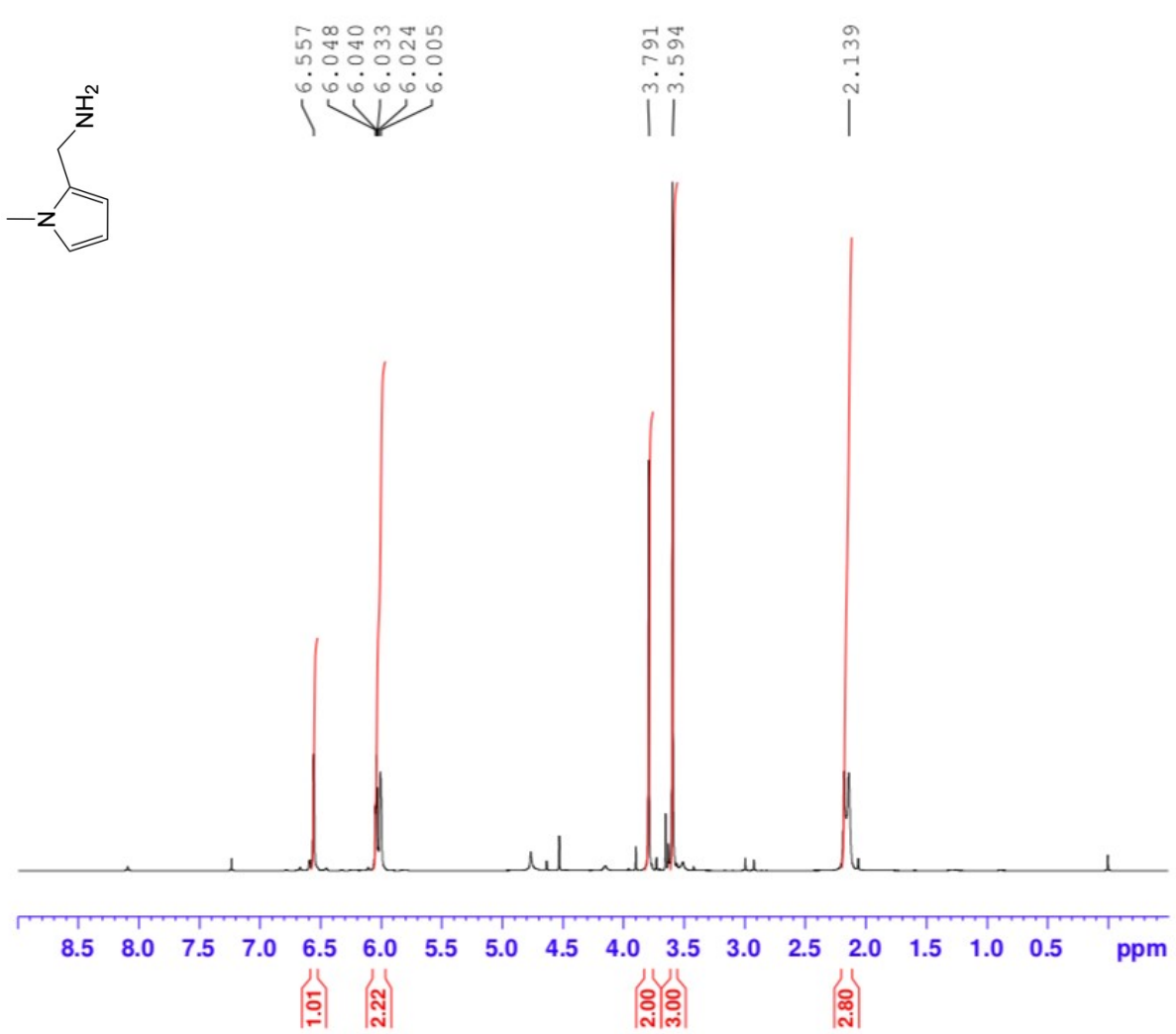

```
Current Data Parameters
NAME       No.1-4BBA-13C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190719
Time               17.56
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                  292
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                  114
DW               20.800 usec
DE                6.50 usec
TE                303.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6228298 MHz
NUC1                13C
P1                10.00 usec
PLW1        53.46578979 W

======== CHANNEL f2 ========
SFO2        400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        11.70547009 W
PLW12        0.37015951 W
PLW13        0.37015951 W

F2 - Processing parameters
SI                 32768
SF          100.6127690 MHz
WDW                   EM
SSB       0
LB                 3.00 Hz
GB        0
PC                 1.40
```

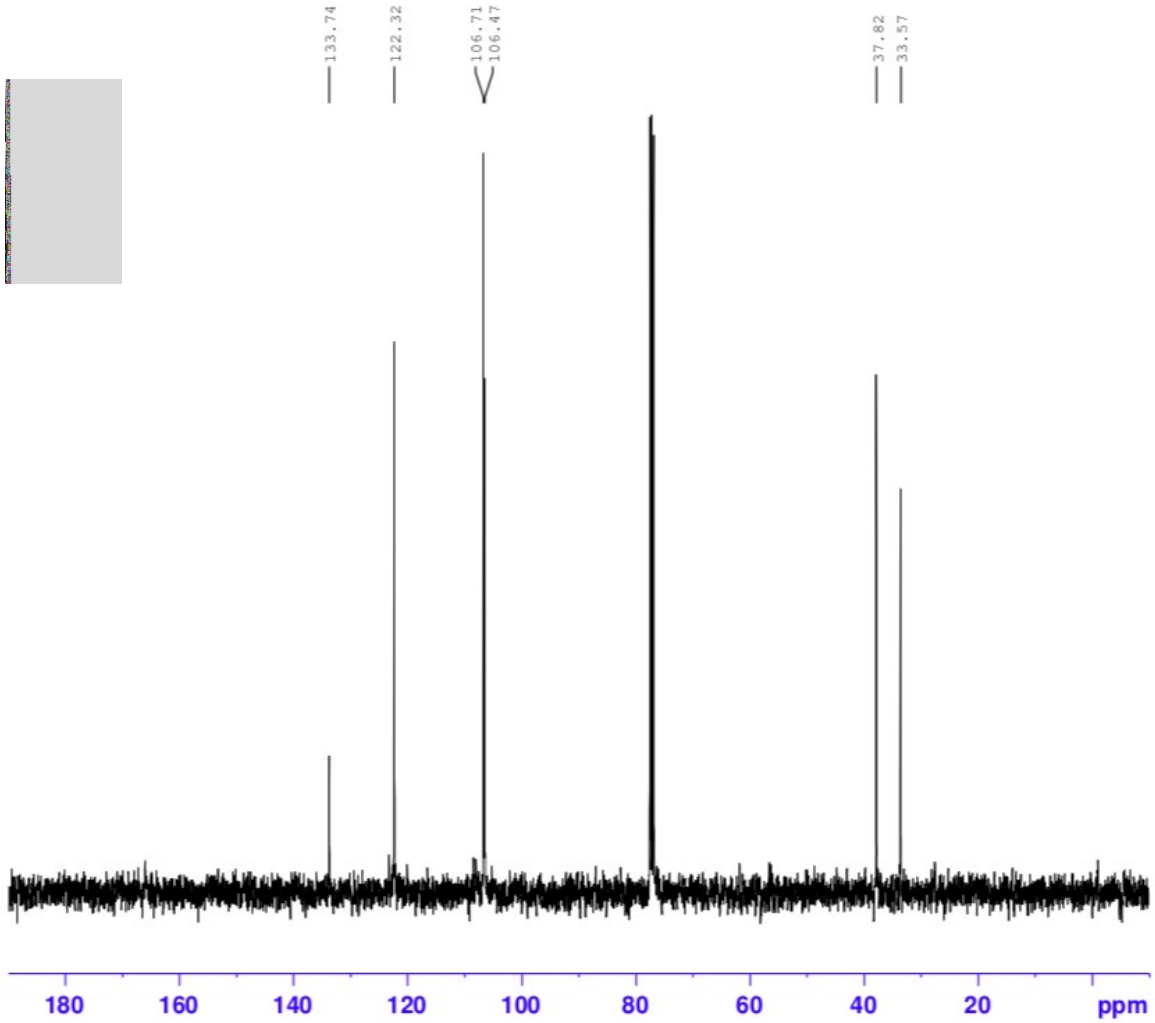



```
Current Data Parameters
NAME      No.2-M2PCA-25h-1H
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20191029
Time              17.05
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDC13
NS                    9
DS                    2
SWH            8012.820 Hz
FIDRES        0.122266 Hz
AQ            4.0894465 sec
RG                   32
DW              62.400 usec
DE               6.50 usec
TE              298.3 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1                  1H
P1              15.00 usec
PLW1        11.89999962 W

F2 - Processing parameters
SI                65536
SF          400.1300195 MHz
WDW                  EM
SSB       0
LB              0.30 Hz
GB        0
PC              1.00
```



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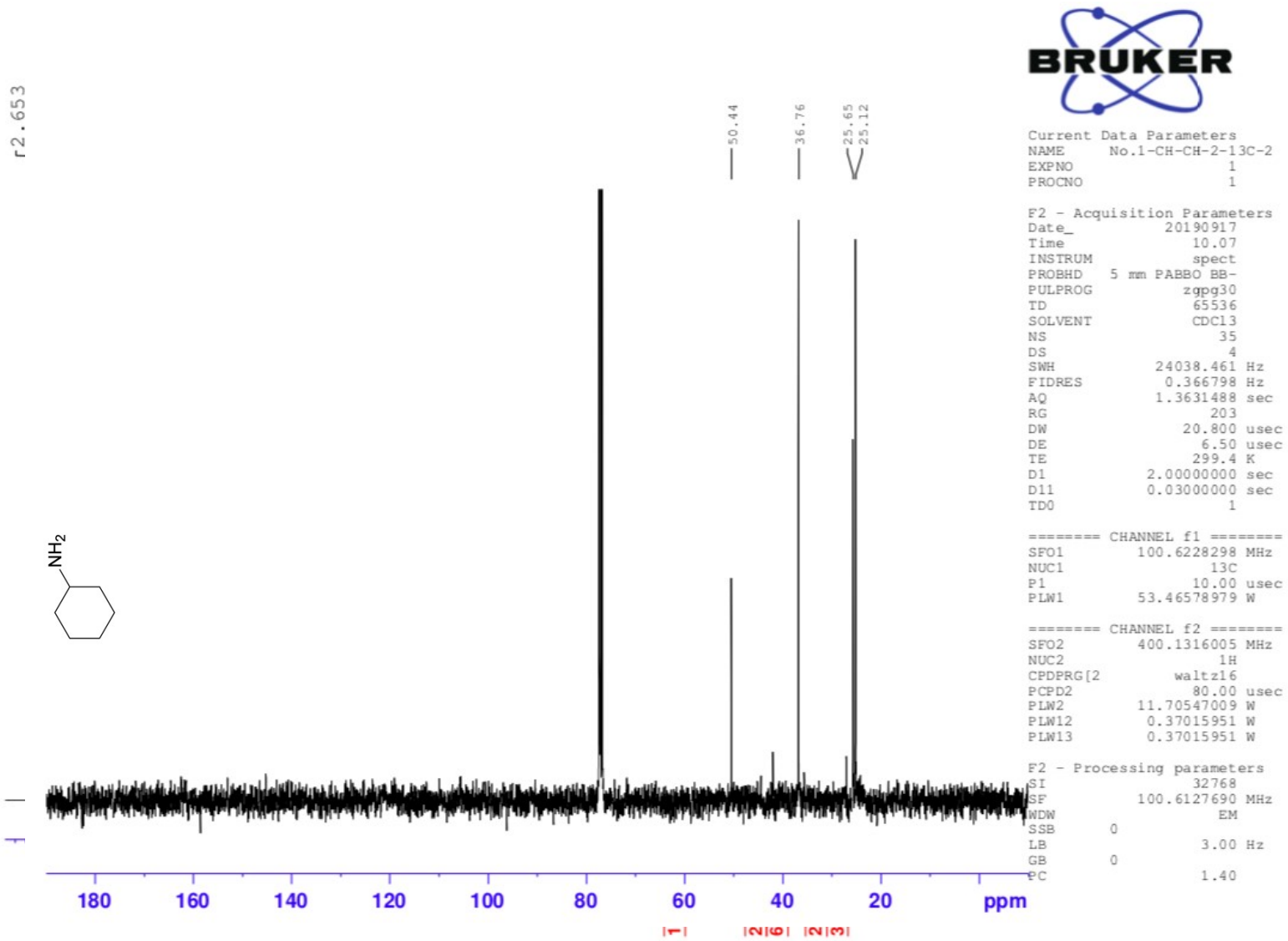
```
Current Data Parameters
NAME      No.2-M2PCA-25h-13C
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20191029
Time                  17.10
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3631488 sec
RG                      203
DW                   20.800 usec
DE                    6.50 usec
TE                   298.7 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            100.6228298 MHz
NUC1                    13C
P1                    10.00 usec
PLW1           53.46578979 W

======== CHANNEL f2 ========
SFO2            400.1316005 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                 80.00 usec
PLW2           11.70547009 W
PLW12           0.37015951 W
PLW13           0.37015951 W

F2 - Processing parameters
SI                    32768
SF              100.6127690 MHz
WDW                     EM
SSB       0
LB                     3.00 Hz
GB        0
PC                     1.40
```



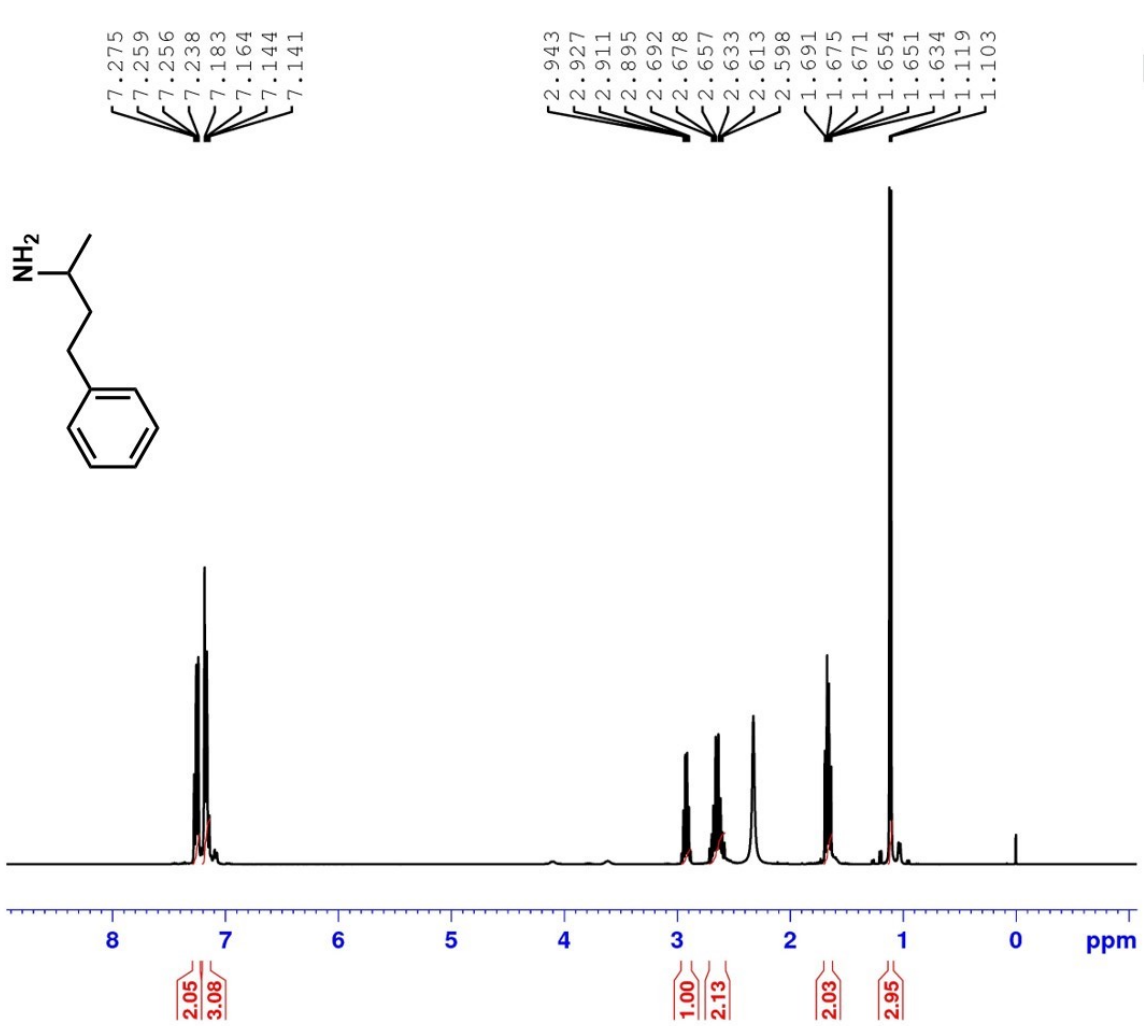

```
Current Data Parameters
NAME      No.1-CH-CH-2-13C-2
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20190917
Time                 10.07
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     35
DS                      4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631488 sec
RG                    203
DW                 20.800 usec
DE                  6.50 usec
TE                 299.4 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1           100.6228298 MHz
NUC1                   13C
P1                  10.00 usec
PLW1           53.46578979 W

======== CHANNEL f2 ========
SFO2           400.1316005 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2               80.00 usec
PLW2           11.70547009 W
PLW12           0.37015951 W
PLW13           0.37015951 W

F2 - Processing parameters
SI                    32768
SF             100.6127690 MHz
WDW                    EM
SSB       0
LB                   3.00 Hz
GB        0
PC                   1.40
```



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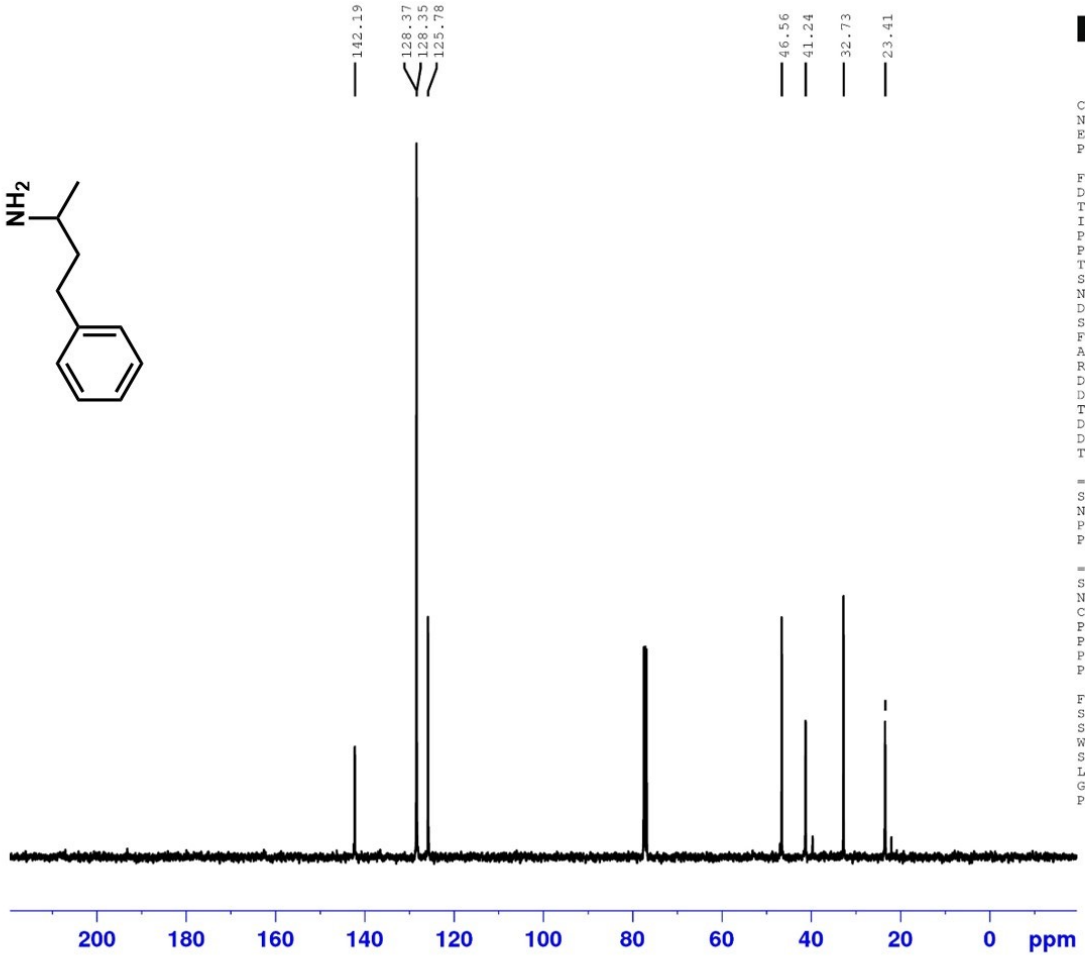
```
Current Data Parameters
NAME      4-phenyl-2-butanone-210402
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210402
Time              16.34
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894465 sec
RG                   32
DW                62.400 usec
DE                 6.50 usec
TE                299.4 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                 1H
P1                15.00 usec
PLW1         11.89999962 W

F2 - Processing parameters
SI                65536
SF           400.1300153 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```



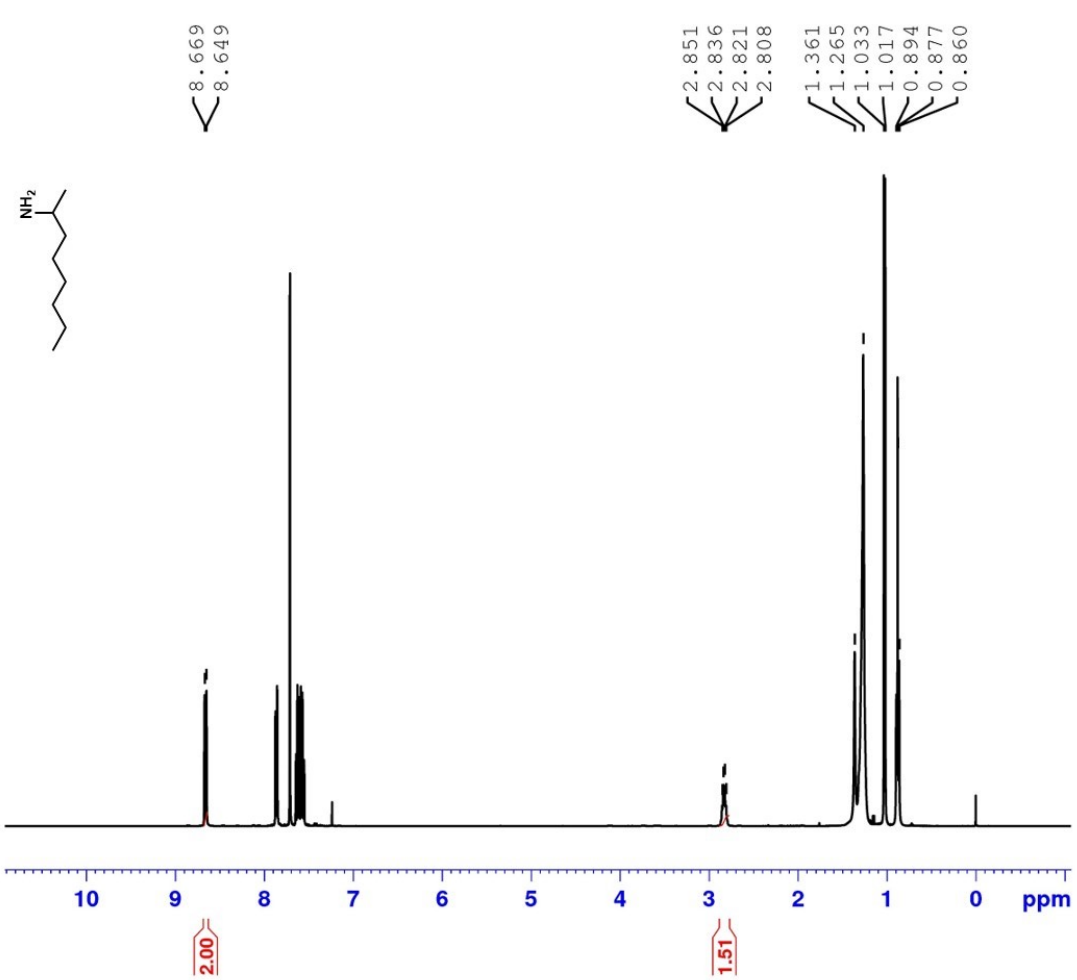

```
Current Data Parameters
NAME      4-phenyl-2-butanone-210416-13C
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210416
Time               9.04
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   50
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631488 sec
RG                  203
DW               20.800 usec
DE                6.50 usec
TE               300.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                13C
P1                10.00 usec
PLW1         54.50000000 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2         11.89999962 W
PLW12         0.33056000 W
PLW13         0.26774999 W

F2 - Processing parameters
SI                 32768
SF           100.6127685 MHz
WDW                   EM
SSB       0
LB                 3.00 Hz
GB        0
PC                 1.40
```

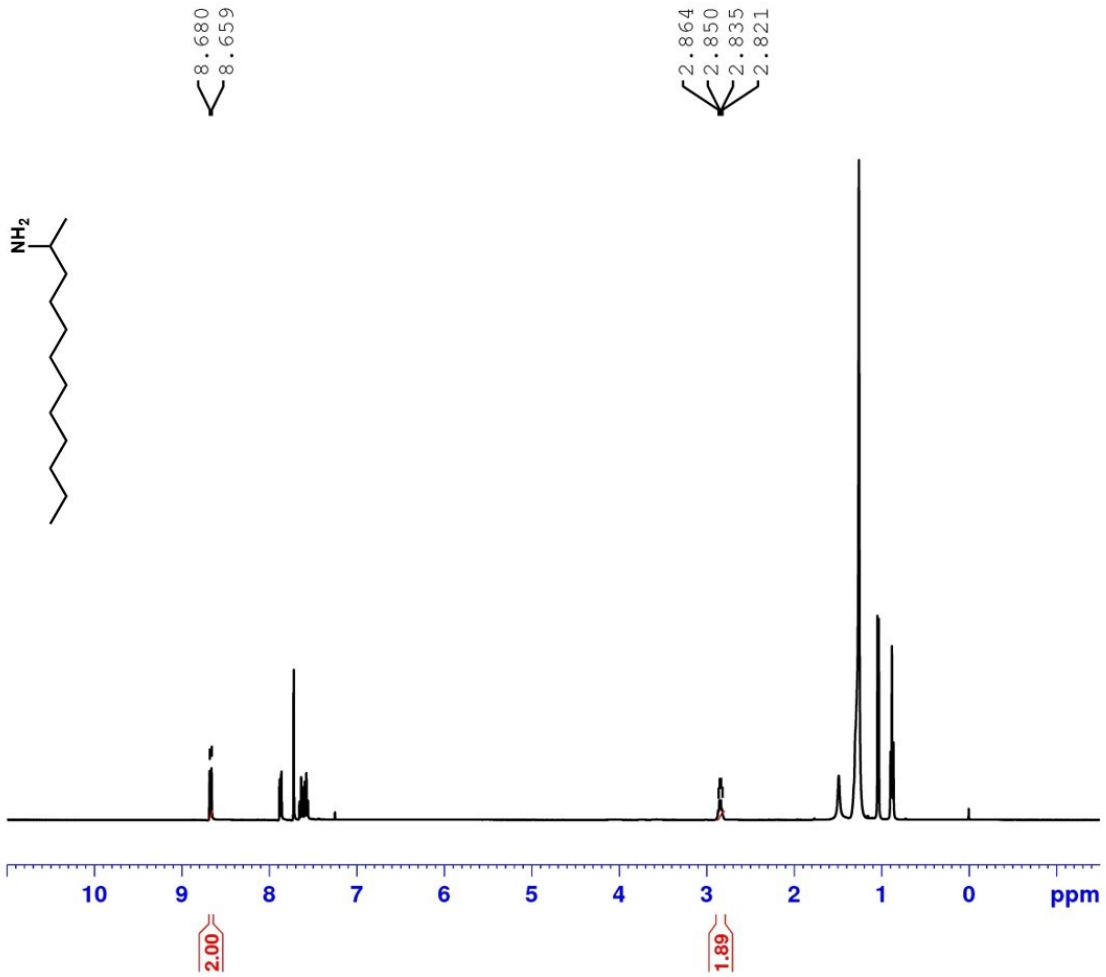


Current Data Parameters
NAME 2-octanone-210422
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210422
Time 10.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 32
DW 62.400 usec
DE 6.50 usec
TE 299.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 15.00 usec
PLW1 11.89999962 W

F2 - Processing parameters
SI 65536
SF 400.1300189 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

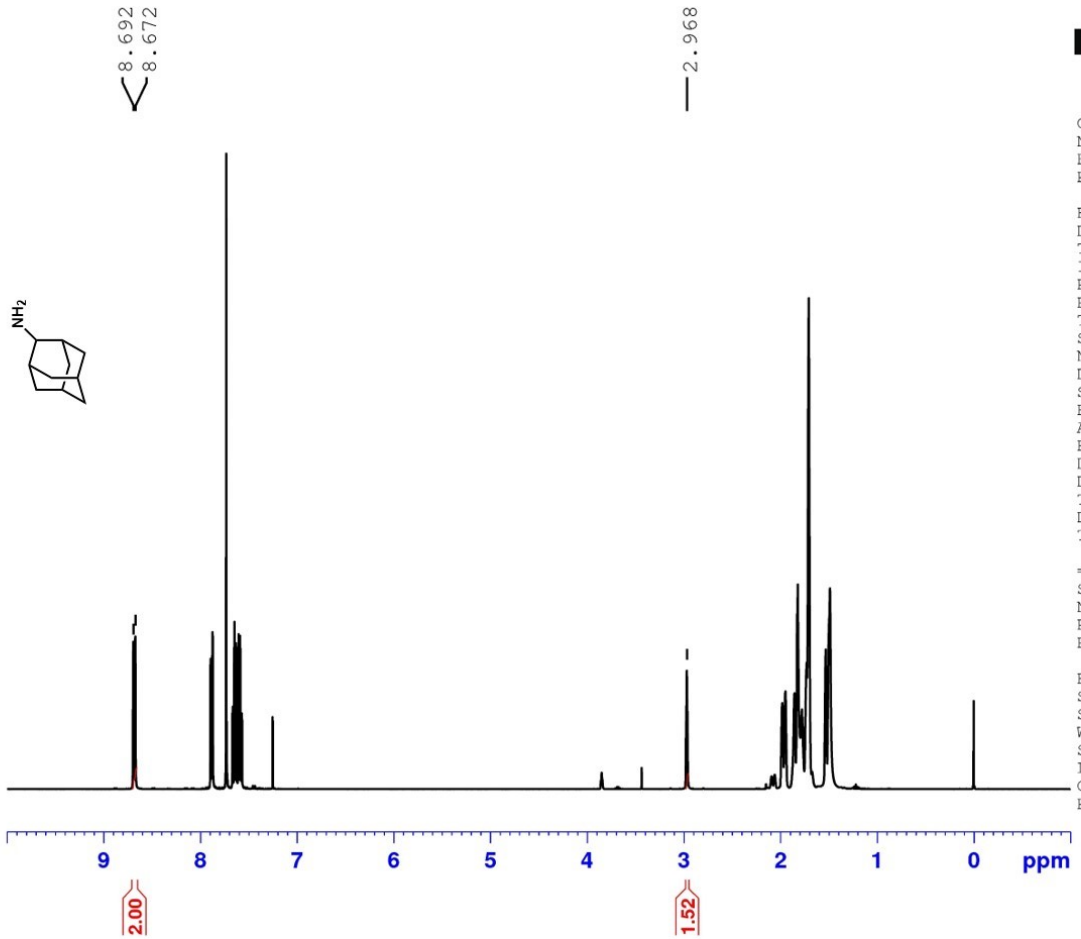



```
Current Data Parameters
NAME      2-dodecanone-210422
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20210422
Time                 10.11
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8012.820 Hz
FIDRES               0.122266 Hz
AQ                4.0894465 sec
RG                      32
DW                   62.400 usec
DE                    6.50 usec
TE                   299.2 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                    1H
P1                   15.00 usec
PLW1          11.89999962 W

F2 - Processing parameters
SI                   65536
SF            400.1300145 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```

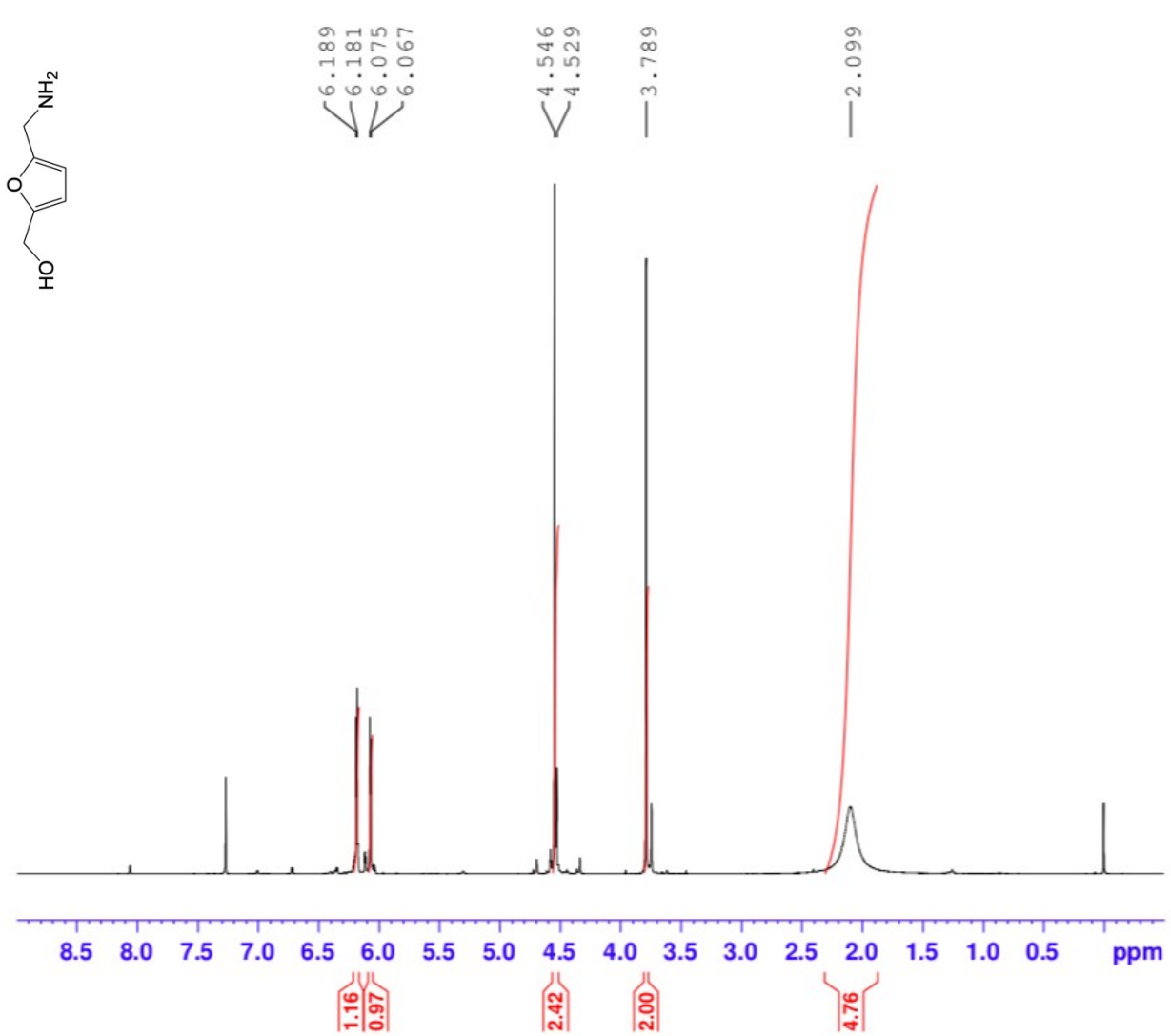


Current Data Parameters
NAME 2-adamantone
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210419
Time 19.43
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 64
DW 62.400 usec
DE 6.50 usec
TE 299.9 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 15.00 usec
PLW1 11.89999962 W

F2 - Processing parameters
SI 65536
SF 400.1300141 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

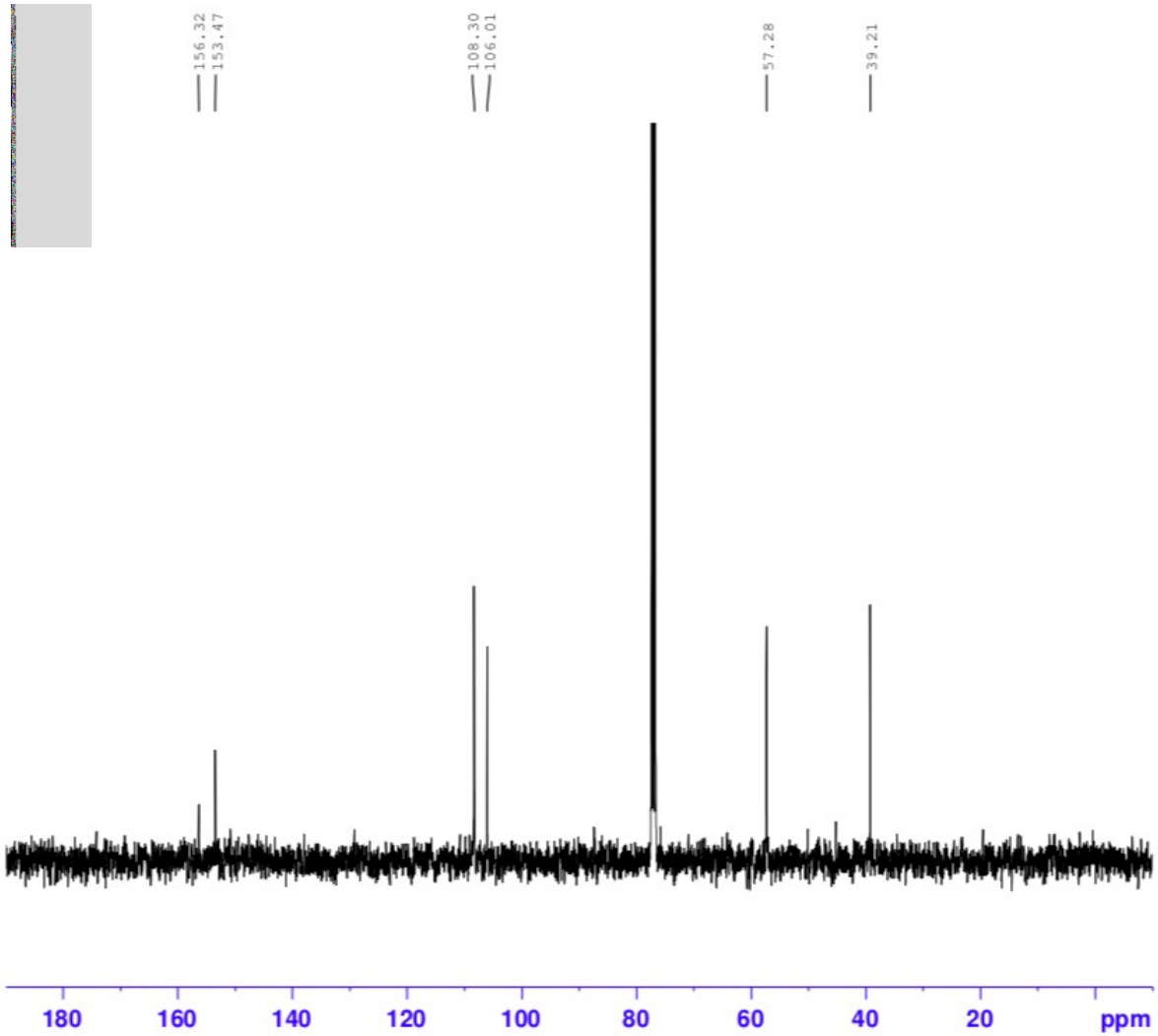



```
Current Data Parameters
NAME      No.1-5HMF-2-1H
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190830
Time               15.35
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     9
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894465 sec
RG                   181
DW                62.400 usec
DE                 6.50 usec
TE                302.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                 15.00 usec
PLW1         11.89999962 W

F2 - Processing parameters
SI                 65536
SF           400.1300058 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



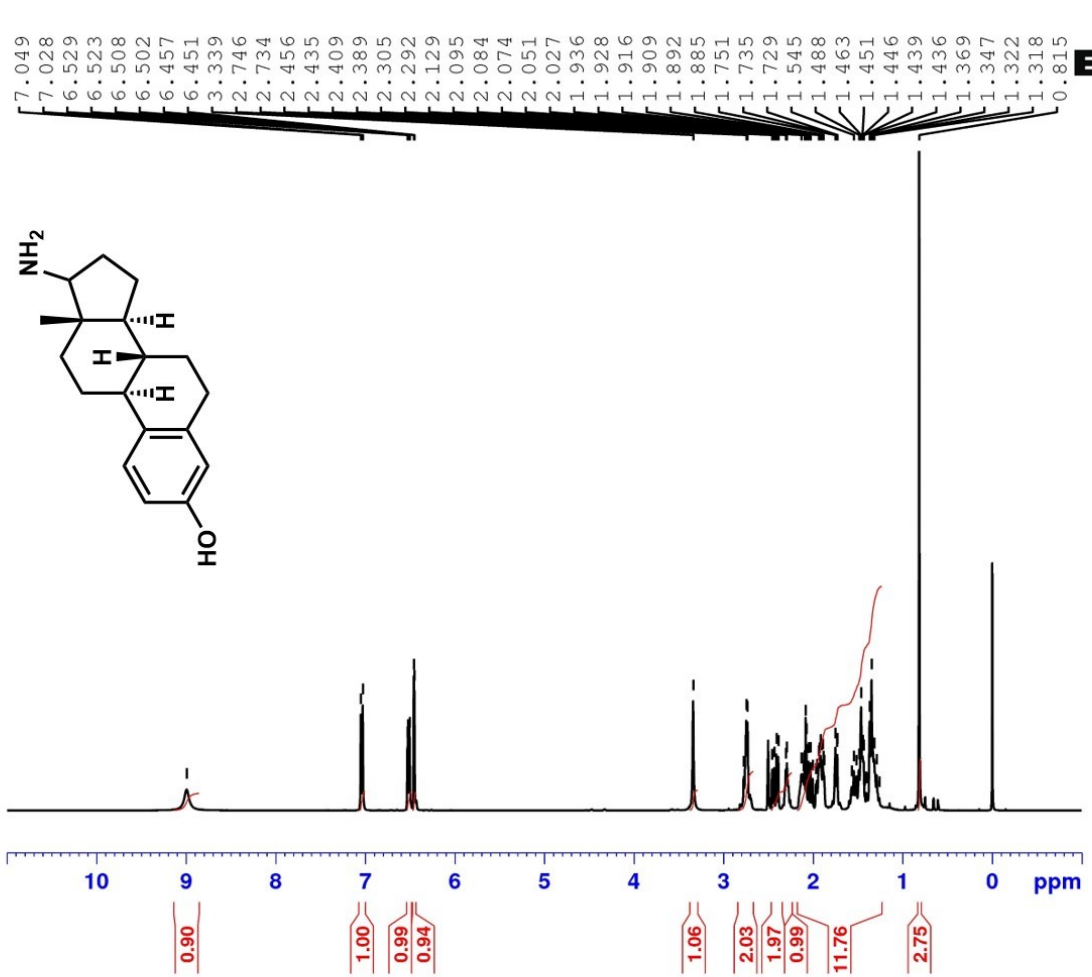

```
Current Data Parameters
NAME      No.1-5HMF-2-13C
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20190830
Time               15.43
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   80
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                  114
DW                20.800 usec
DE                 6.50 usec
TE                303.3 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         100.6228298 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         53.46578979 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2         11.70547009 W
PLW12         0.37015951 W
PLW13         0.37015951 W

F2 - Processing parameters
SI                  32768
SF           100.6127690 MHz
WDW                  EM
SSB       0
LB                 3.00 Hz
GB        0
PC                 1.40
```



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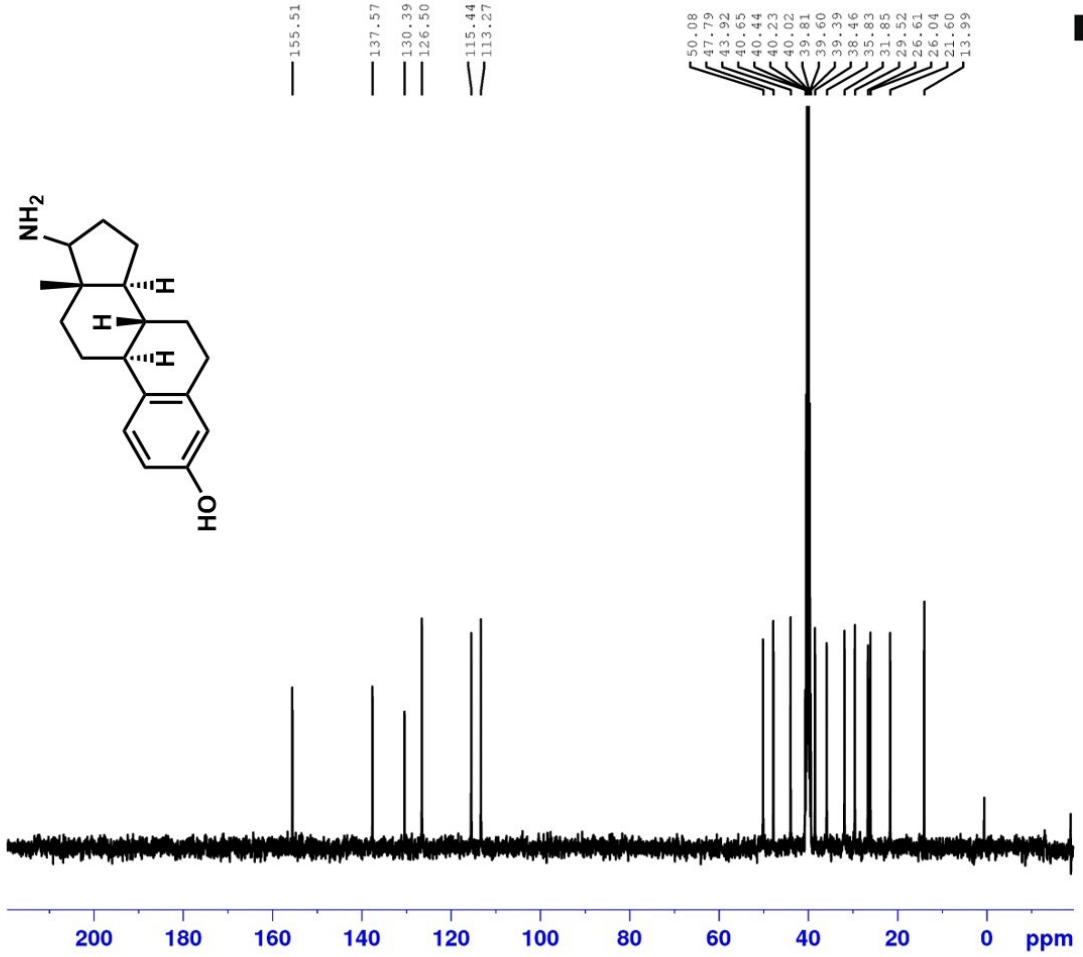
```
Current Data Parameters
NAME      estrone-210426-1H
EXPNO                   20
PROCNO                   1

F2 - Acquisition Parameters
Date_           20210426
Time              10.57
INSTRUM           spect
PROBHD    5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT             DMSO
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894465 sec
RG                    57
DW                62.400 usec
DE                 6.50 usec
TE                299.4 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                 1H
P1                15.00 usec
PLW1         11.89999962 W

F2 - Processing parameters
SI                65536
SF           400.1300025 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```



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```
Current Data Parameters
NAME      estrone-210426-13C
EXPNO                     20
PROCNO                     1

F2 - Acquisition Parameters
Date_           20210426
Time              11.03
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD                65536
SOLVENT             DMSO
NS                   50
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631488 sec
RG                  203
DW               20.800 usec
DE                6.50 usec
TE                300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6228293 MHz
NUC1               13C
P1               10.00 usec
PLW1        54.50000000 W

======== CHANNEL f2 ========
SFO2        400.1316005 MHz
NUC2               1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2        11.89999962 W
PLW12        0.33056000 W
PLW13        0.26774999 W

F2 - Processing parameters
SI                32768
SF          100.6127685 MHz
WDW                EM
SSB       0
LB               3.00 Hz
GB        0
PC               1.40
```