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SUPPORTING INFORMATION

A Waste-Minimized Protocol for Copper-Catalyzed Ullmann-Type Reaction in a Biomass Derived Furfuryl Alcohol/Water Azeotrope

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General Information

Unless otherwise stated, all solvents and reagents were used as obtained from commercial sources, without further purification. Furfuryl alcohol was distilled prior to use to ensure purity. GC analyses were performed by using a Hewlett-Packard HP 5890A equipped with a capillary column DB-35MS (30 m, 0.53 mm) and a FID detector. GC-EIMS analyses were carried out using a Hewlett-Packard HP 6890N Network GC system/5975 MassSelective Detector equipped with an electron impact ionizer at 70 eV. NMR spectra were recorded on a Bruker DRX-ADVANCE 400 MHz (^{1}H at 400 MHz, ^{13}C at 100.6 MHz and ^{19}F at 376 MHz), using $CDCl_3$ as solvent, and calibrated using residual solvent peaks. Elemental analyses were conducted on a Fisons EA1108CHN. Melting points were measured on a Büchi 510.

Calculation of E-factors for Representative Literature Procedures

1) X. Li, D. Yang, Y. Jiang and H. Fu,*Green Chem.***2010**, *12*, 1097-1105
E-factor for the preparation of 1-(*p*-tolyl)-1*H*-imidazole (1 mmol scale) = [0.068(imidazole) + 0.262 (4-iodotoluene) + 0.005 (CuCl) + 0.080 (NaOH) + 0.009 ((1*E*,2*E*)-oxalaldehyde dioxime) + 0.033 (TBAB) + 1.5 (water) + 8.07 (EtOAc) – 0.139 (product)] / 0.139(product) = **71.1**

2) J. Engel-Andreasen, B. Shimpukade and T. Ulven, *Green Chem.***2013**, *15*, 336-340
E-factor for the preparation of 1-phenyl-1*H*-imidazole (0.6 mmol scale) = [0.041(imidazole) + 0.102 (iodobenzene) + 0.004 (CuBr) + 1.05 (aq. KOH) + 0.016 (DPPhen) + 0.04(PEG) + 8.07(EtOAc) – 0.070(product)] / 0.070(product) = **132.2**

3) R. A. Altman and S. L. Buchwald, *Org. Lett.***2006**, *8*, 2779-2782
E-factor for the preparation of 1-phenyl-1*H*-imidazole (1 mmol scale) = [0.082(imidazole) + 0.204 (iodobenzene) + 0.004(Cu_2O) + 0.450(Cs_2CO_3) + 0.018(ligand) + 0.200(PEG) + 0.514(NMP) + 79.8(DCM) – 0.131(product)] / 0.131(product) = **619.4**

General Procedures

General procedure A (imidazole arylation; no column chromatography):
In a screw capped vial equipped with a magnetic stirring bar imidazole (3 mmol, 204 mg), K_3PO_4 (1.27 g, 6 mmol), CuI (1 mol %, 0.03mmol, 5.7 mg), furfuryl alcohol/water azeotrope (3 mL) and the aryl halide (3 mmol) were consecutively added. The resulting mixture was left under stirring at 150 °C. After reaction completion, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere, allowing the recovery of ca. 2.6 mL. The residue was then dissolved in 2.4 mL of ethyl acetate, filtered and evaporated to give the pure product.

General procedure B (imidazole arylation; purification by column chromatography):
In a screw capped vial equipped with a magnetic stirring bar imidazole (3 mmol, 204 mg), K_3PO_4 (1.27 g, 6 mmol), CuI (1 mol %, 0.03mmol, 5.7 mg), furfuryl alcohol/water azeotrope (3 mL) and the aryl halide (3 mmol) were consecutively added. The resulting mixture was left under stirring at 150 °C. After reaction completionthe mixture was cooled down to room temperature, diluted with ethyl acetate (10 ml), washed with water (10 mL x 3), dried over Na_2SO_4, filtered and concentrated to remove solvent. The solid obtained was purified through flash column chromatography on silica gel (petroleum ether/ethyl acetate 1:1).

General procedure C (carbazole arylation; no column chromatography):
In a screw capped vial equipped with a magnetic stirring bar carbazole (1 mmol, 167 mg), K_3PO_4 (424 mg, 3 mmol), CuI (5 mol %, 0.05 mmol, 9.5 mg), furfuryl alcohol/water azeotrope (2 mL) and the aryl halide (1 mmol) were consecutively added. The resulting mixture was left under stirring at 150 °C. After reaction completion, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere, allowing the recovery of ca. 1.7 mL. The residue was then dissolved in 0.8 mL of ethyl acetate, filtered and evaporated to give the pure product.

General procedure D (imidazole arylation on large scale; no column chromatography):
In a screw capped vial equipped with a magnetic stirring bar imidazole (30 mmol, 2.04 g), K_3PO_4 (12.7 g, 60 mmol), CuI (1 mol %, 0.3mmol, 57 mg), furfuryl alcohol/water azeotrope (30 mL) and the aryl halide (30 mmol) were consecutively added. The resulting mixture was left under stirring at 150 °C. After reaction completion, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere, allowing the recovery of ca. 28 mL. The residue was then dissolved in 20 mL of ethyl acetate, filtered and evaporated to give the pure product.

Calculation of *E*-factors for Our Procedures

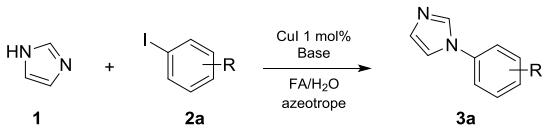
E-factor for the preparation of 1-(*p*-tolyl)-1*H*-imidazole (1 mmol scale) = [0.068 (imidazole) + 0.218 (4-iodotoluene) + 0.423(K_3PO_4) + 0.002 (CuI) + 1.027 (FA/H_2O) + 0.714 (EtOAc) –0.145 (product) – 0.890(recovered FA/H_2O)]/ 0.145 (product) = **9.8**

E-factor for the preparation of 1-phenyl-1*H*-imidazole (3 mmol scale) = [0.204 (imidazole) + 0.612 (iodobenzene) + 1.27 (K_3PO_4) + 0.0057 (CuI) + 3.08 (FA/H_2O) + 2.14 (EtOAc) – 0.380 (product) – 2.67 (recovered FA/H_2O)]/ 0.380 (product) = **11.2**

E-factor for the preparation of 1-phenyl-1*H*-carbazole (1 mmol scale) = [0.167 (carbazole) + 0.204 (iodobenzene) + 0.424 (K_3PO_4) + 0.009 (CuI) + 2.05 (FA/H_2O) + 0.714 (EtOAc) – 0.155(product) – 1.74 (recovered FA/H_2O)]/ 0.155 (product) = **10.8**

E-factor for the preparation of 1-phenyl-1*H*-imidazole (30 mmol scale) = [2.04 (imidazole) + 6.12 (iodobenzene) + 12.70(K_3PO_4) + 0.057 (CuI) + 30.81 (FA/H_2O) + 17.80 (EtOAc) – 3.8 (product) – 28.75(recovered FA/H_2O)]/ 3.8 (product) = **9.7**

Table S1. Effect of the base on the Formation of 1-phenyl-1*H*-imidazole 3a.



1 **2a** **3a**

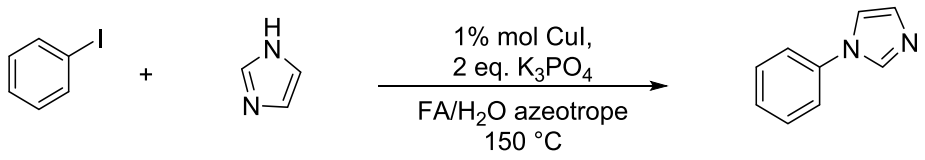
Entry	Base	T (°C)	time (h)	C (%)
1	-	120	24	20[a]
2	Cs_2CO_3	120	24	83[a]
3	K_3PO_4	120	24	86[b]
4	K_3PO_4	150	24	100[a]
5	Na_2CO_3	150	24	95[a]

Reaction condition: imidazole 1 eq, Aryl iodide 1 eq, CuI 1 mol% Base 2 eq, FA/H_2O azeotrope 1mL [1M] a) determined by GC analysis. b) isolated yield

Table S2. Effect of the Amount of FA on the Formation of 1-phenyl-1*H*-imidazole 3a.

entry	w/w ratio	weight	Yield
1	100% water (1mL)	1g	42%
2	95% water -5% FA	(1mL) 1.0067 g	50% 73mg
3	90% water-10% FA	(1mL) 1.0135g	84% 122mg
4	85% water-15 % FA	(1mL) 1.02025g	86% 125mg
5	**80% water-20 %FA**	**(1mL) 1.027g**	**87% 127mg**
6	75% water-25 % FA	(1mL) 1.03375g	85% 124 mg
7	70% water-30% FA	(1mL) 1.0405g	82% 119mg
8	65% water- 35% FA	(1mL) 1.04725g	62% 90mg
9	60% water-45% FA	(1mL) 1.054g	40% 58mg
10	55% water- 40% FA	(1mL) 1,06075g	20% 30mg
11	50% water-50% FA	(1mL) 1,0675g	14% 20mg
12	45% water-55% FA	(1mL) 1,07425g	10% 14mg
13	40% water-60% FA	(1mL) 1,081g	8% 11mg
14	30% water-70% FA	(1mL) 1,0945g	5% 7mg
15	20% water-80%FA	(1mL) 1,108g	2% 3mg
16	10% water-90% FA	(1mL) 1,1215g	0%
17	100% FA (1mL)	1.135g	0%

Chem. Name	1-phenyl-1*H*-imidazole (3a)
Lit. Ref.	*Tetrahedron,* **2013**, *69*, 8974-8977



METHOD:
In a screw capped vial equipped with a magnetic stirring bar imidazole (3 mmol, 204 mg), K_3PO_4 (1.27 g, 6 mmol), CuI (1 mol %, 0.03 mmol, 5.7 mg), furfuryl alcohol/water azeotrope (3 mL) and iodobenzene (3 mmol, 336 µL) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 24h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 2.4 mL of ethyl acetate, filtered and evaporated to give the pure product as a pale yellow oil (380 mg, 87% yield).

Mol Formula	$C_9H_8N_2$	**m.p.**	

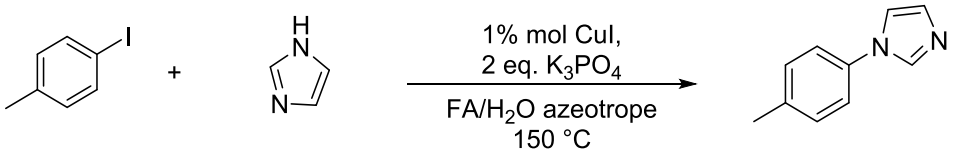
Elemental Analysis: Calc.: C: 74.98; H: 5.59; N: 19.43. Found: C: 74.95; H: 5.57; N: 19.46.

^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	7.77	1	*s*	
	7.44-7.32	2	*m*	
	7.31-7.22	3	*m*	
	7.20	1	*s*	
	7.12	1	*s*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 118.2, 121.5, 127.5, 129.9, 130.4, 135.6, 137.4

GC-EIMS (m/z, %): 144 (100), 117 (52), 90 (34), 77 (20)

Chem. Name	**1-(*p*-tolyl)-1*H*-imidazole (3b)**
Lit. Ref.	*Green Chem*., **2012**, *14*, 1268-1271



METHOD:
In a screw capped vial equipped with a magnetic stirring bar imidazole (1 mmol, 68 mg), K_3PO_4 (424 mg, 2 mmol), CuI (1 mol %, 0.01 mmol, 1.9 mg), furfuryl alcohol/water azeotrope (1 mL) and 4-iodotoluene (1 mmol, 218 mg) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 24h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 0.8 mL of ethyl acetate, filtered and evaporated to give the pure product as a pale yellow solid (145 mg, 90% yield).

Mol Formula	$C_{10}H_{10}N_2$	**m.p.**	63-65 °C

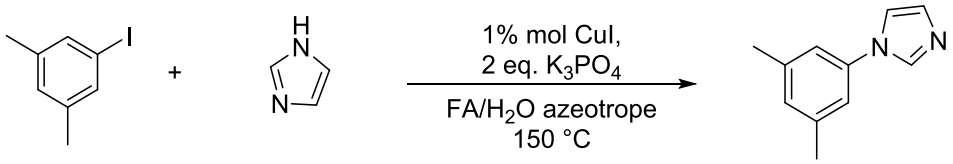
Elemental Analysis: Calc.: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.89; H, 6.40; N, 17.72.

^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	7.83	1	*s*	
	7.35-7.25	5	*m*	
	7.20	1	*s*	
	2.41	3	*s*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 21.0, 118.4, 121.5, 130.2, 130.4, 135.0, 135.6, 137.5

GC-EIMS (m/z, %): 158 (100), 131 (53), 130 (50), 104 (33), 91 (21), 65 (21)

Chem. Name	1-(3,5-dimethylphenyl)-1*H*-imidazole (3c)
Lit. Ref.	*Green Chem.,* **2010**, *12*, 1097-1105



METHOD:
In a screw capped vial equipped with a magnetic stirring bar imidazole (1 mmol, 68 mg), K_3PO_4 (424 mg, 2 mmol), CuI (1 mol %, 0.01 mmol, 1.9 mg), furfuryl alcohol/water azeotrope (1 mL) and 1-iodo-3,5-dimethylbenzene (1 mmol, 144 µL) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 24h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 0.8 mL of ethyl acetate, filtered and evaporated to give the pure product as a yellow oil (185 mg, 80% yield).

Mol Formula	$C_{11}H_{12}N_2$	**m.p.**	

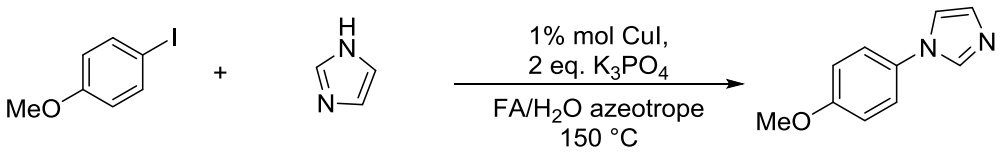
Elemental Analysis: Calc.: C, 76.71; H, 7.02; N, 16.27. Found: C, 76.74; H, 7.01; N, 16.23.

^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	7.86	1	*s*	
	7.35-7.20	2	*m*	
	7.02	3	*s*	
	2.40	6	*s*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 21.2, 118.4, 119.1, 128.9, 130.2, 135.7, 137.2, 139.7

GC-EIMS (m/z, %): 172 (100), 145 (53), 144 (45), 130 (58), 117 (26), 77 (29)

Chem. Name	1-(4-methoxyphenyl)-1*H*-imidazole (3d)
Lit. Ref.	*Green Chem*., **2012**, *14*, 1268-1271



METHOD:
In a screw capped vial equipped with a magnetic stirring bar imidazole (1 mmol, 68 mg), K_3PO_4 (424 mg, 2 mmol), CuI (1 mol %, 0.01 mmol, 1.9 mg), furfuryl alcohol/water azeotrope (1 mL) and 4-iodoanisole (1 mmol, 234 mg) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 24h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 0.8 mL of ethyl acetate, filtered and evaporated to give the pure product as a brown solid (150 mg, 86% yield).

Mol Formula	$C_{10}H_{10}N_2O$	**m.p.**	66-68 °C

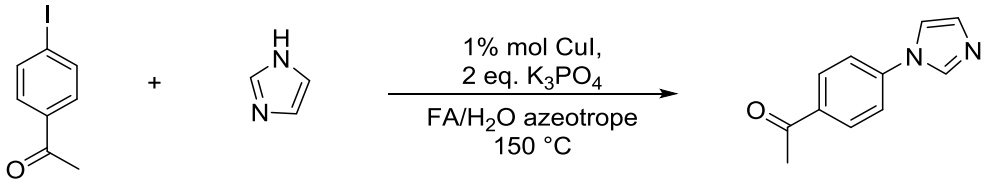
Elemental Analysis: Calc.: C, 68.95; H, 5.79; N, 16.08. Found: C, 68.98; H, 5.76; N, 16.10.

^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	7.75	1	*s*	
	7.33-7.28	2	*m*	
	7.20-7.16	2	*m*	
	7.05-6.90	2	*m*	
	3.84	3	*s*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 55.6, 114.9, 118.8, 123.2, 130.1, 130.7, 135.9, 158.9

GC-EIMS (m/z, %): 174 (100), 159 (45), 147 (34), 134 (30), 132 (65), 131 (24), 120 (49), 104 (43), 92 (20), 91 (24), 77 (57), 64 (24), 63 (29), 51 (21)

Chem. Name	1-(4-(1*H*-imidazol-1-yl)phenyl)ethan-1-one (3e)
Lit. Ref.	*Green Chem*., **2012**, *14*, 1268-1271



METHOD:
In a screw capped vial equipped with a magnetic stirring bar imidazole (1 mmol, 68 mg), K_3PO_4 (424 mg, 2 mmol), CuI (1 mol %, 0.01 mmol, 1.9 mg), furfuryl alcohol/water azeotrope (1 mL) and 1-(4-iodophenyl)ethanone (1 mmol, 246 mg) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 21h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 0.8 mL of ethyl acetate, filtered and evaporated to give the pure product as a dark yellow solid (130 mg, 70% yield).

Mol Formula	$C_{11}H_{10}N_2O$	**m.p.**	63-65 °C

Elemental Analysis: Calc.: C, 70.95; H, 5.41; N, 15.04. Found: C, 70.96; H, 5.39; N, 15.00.

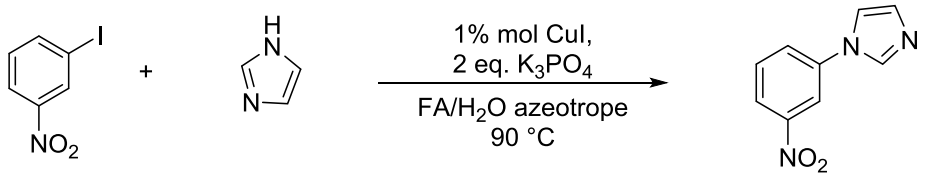
^{1}H NMR 400 MHz $CDCl_3$

δ value	No. H	Mult.	j value/Hz
8.12-8.07	2	*m*	
7.95	1	*s*	
7.52-7.47	2	*m*	
7.35	1	*s*	
7.28-7.22	2	*m*	
2.64	3	*s*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 26.6, 117.7, 120.7, 130.3, 131.2, 135.4, 135.8, 140.7, 196.5

GC-EIMS (m/z, %): 186 (87), 171 (100), 143 (55), 116 (48), 89 (33), 63 (20)

Chem. Name	1-(3-nitrophenyl)-1*H*-imidazole (3f)
Lit. Ref.	*Green Chem.,* **2013**, *15*, 336-340



METHOD:
In a screw capped vial equipped with a magnetic stirring bar imidazole (1 mmol, 68 mg), K_3PO_4 (424 mg, 2 mmol), CuI (1 mol %, 0.01 mmol, 1.9 mg), furfuryl alcohol/water azeotrope (1 mL) and 1-iodo-3-nitrobenzene (1 mmol, 249 mg) were consecutively added. The resulting mixture was left under stirring at 90 °C. After 40h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 0.8 mL of ethyl acetate, filtered and evaporated. The obtained solid was purified through flash column chromatography on silica gel (petroleum ether/ethyl acetate 7:3) to give the pure product as a white solid (115 mg, 60% yield).

Mol Formula	$C_9H_7N_3O_2$	**m.p.**	62-64 °C

Elemental Analysis: Calc.: C, 57.14; H, 3.73; N, 22.21. Found: C, 57.18; H, 3.70; N, 22.19.

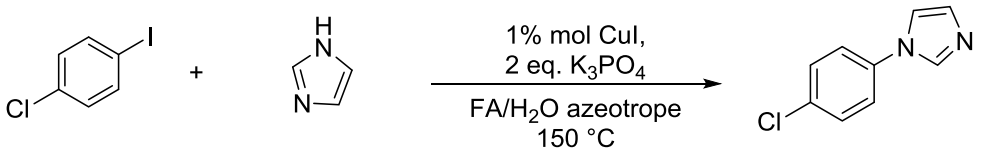
^{1}H NMR 400 MHz $CDCl_3$

δ value	No. H	Mult.	j value/Hz
8.28	1	*s*	
8.24	1	*d*	8.0
7.95	1	*s*	
7.80-7.65	2	*m*	
7.37	1	*s*	
7.27	1	*s*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 116.3, 118.0, 122.1, 126.8, 131.1, 131.5, 135.5, 138.3, 149.1

GC-EIMS (m/z, %): 189 (100), 116 (55), 89 (29)

Chem. Name	1-(4-chlorophenyl)-1*H*-imidazole (3g)
Lit. Ref.	*Catal. Commun.*, **2015**, *60*, 92-95



METHOD:
In a screw capped vial equipped with a magnetic stirring bar imidazole (1 mmol, 68 mg), K_3PO_4 (424 mg, 2 mmol), CuI (1 mol %, 0.01 mmol, 1.9 mg), furfuryl alcohol/water azeotrope (1 mL) and 1-chloro-4-iodobenzene (1 mmol, 238 mg) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 24h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 0.8 mL of ethyl acetate, filtered and evaporated to give the pure product as a white solid (146 mg, 80% yield).

Mol Formula	$C_9H_7ClN_2$	**m.p.**	86-88 °C

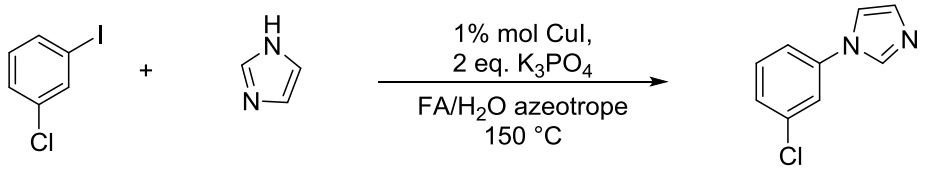
Elemental Analysis: Calc.: C, 60.52; H, 3.95; N, 15.68. Found: C, 60.47; H, 3.93; N, 15.70.

^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	7.87	1	*s*	
	7.50-7.45	2	*m*	
	7.40-7.33	2	*m*	
	7.33-7.20	2	*m*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 117.5, 122.0, 122.8, 130.1, 132.0, 133.3, 136.0

GC-EIMS (m/z, %): 180 (33), 178 (100), 153 (24), 151 (72), 124 (30), 116 (21), 111 (26), 89 (25), 75 (38)

Chem. Name	1-(3-chlorophenyl)-1*H*-imidazole (3h)
Lit. Ref.	-



METHOD:
In a screw capped vial equipped with a magnetic stirring bar imidazole (1 mmol, 68 mg), K_3PO_4 (424 mg, 2 mmol), CuI (1 mol %, 0.01 mmol, 1.9 mg), furfuryl alcohol/water azeotrope (1 mL) and 1-chloro-3-iodobenzene (1 mmol, 124 µL) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 12h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 0.8 mL of ethyl acetate, filtered and evaporated to give the pure product as a yellow oil (135 mg, 75% yield).

Mol Formula	$C_9H_7ClN_2$	m.p.	

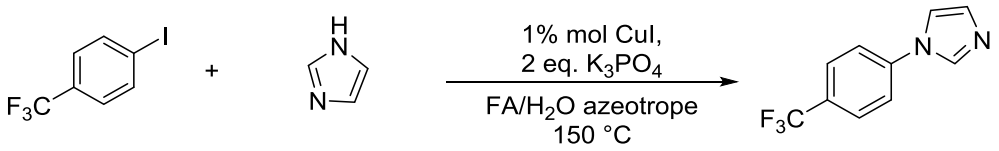
Elemental Analysis: Calc.: C, 60.52; H, 3.95; N, 15.68. Found: C, 60.56; H, 3.93; N, 15.63.

^{1}H NMR 400 MHz $CDCl_3$	δ value	No. H	Mult.	j value/Hz
	8.28	1	*m*	
	8.24	1	*d*	8.0
	7.96	1	*s*	
	7.80-7.67	2	*m*	
	7.37	1	*s*	
	7.28	1	*s*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 117.9, 119.3, 121.4, 127.4, 130.6, 130.9, 135.3, 135.4, 138.2

GC-EIMS (m/z, %): 180 (33), 178 (100), 153 (24), 151 (72), 124 (30), 116 (21), 111 (26), 89 (25), 75 (38)

Chem. Name	1-(4-(trifluoromethyl)phenyl)-1*H*-imidazole (3i)
Lit. Ref.	*Chem. Eur. J.,* **2004**, *10*, 5607-5622



METHOD:
In a screw capped vial equipped with a magnetic stirring bar imidazole (1 mmol, 68 mg), K_3PO_4 (424 mg, 2 mmol), CuI (1 mol %, 0.01 mmol, 1.9 mg), furfuryl alcohol/water azeotrope (1 mL) and 1-iodo-4-(trifluoromethyl)benzene (1 mmol, 144. µL) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 12h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 0.8 mL of ethyl acetate, filtered and evaporated to give the pure product as a white solid (176 mg, 83% yield).

Mol Formula	$C_{10}H_7F_3N_2$	**m.p.**	69-70 °C

Elemental Analysis: Calc.: C: 56.61; H: 3.33; N: 13.20. Found: C: 56.57; H: 3.30; N: 13.24.

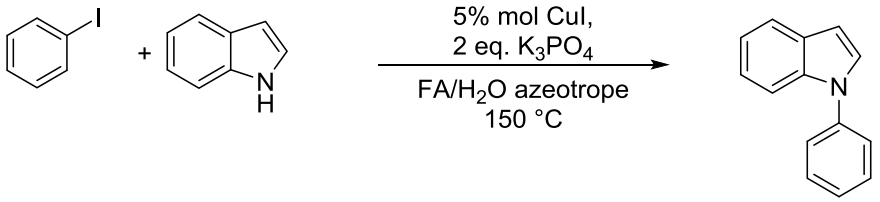
^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	7.92	1	*s*	
	7.80-7.72	2	*m*	
	7.58-7.50	2	*m*	
	7.33	1	*s*	
	7.25	1	*s*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 117.9, 121.3, 123.6 (q, J_{FC} 272 Hz), 127.3, 129.6 (q, J_{FC} 33 Hz) 131.1, 135.4, 140.0

^{19}F NMR (376.3 MHz, $CDCl_3$) δ: -62.5

GC-EIMS (m/z, %): 212 (100), 185 (69), 158 (38), 145 (41)

Chem. Name	**1-phenyl-1*H*-indole (5a)**
Lit. Ref.	*Chem. Eur. J.,* **2014**, *20*, 14619-14623



METHOD:
In a screw capped vial equipped with a magnetic stirring bar indole (1 mmol, 117 mg), K_3PO_4 (424 mg, 2 mmol), CuI (5 mol %, 0.05 mmol, 9.5 mg), furfuryl alcohol/water azeotrope (1 mL) and iodobenzene (1 mmol, 112 µL) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 30h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 0.8 mL of ethyl acetate, filtered and evaporated. The obtained crude mixture was purified through flash column chromatography on silica gel (petroleum ether/ethyl acetate 9:1) to give the pure product as a colorless oil (163 mg, 84% yield).

Mol Formula	$C_{14}H_{11}N$	**m.p.**	

Elemental Analysis: Calc.: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.98; H, 5.72; N, 7.27.

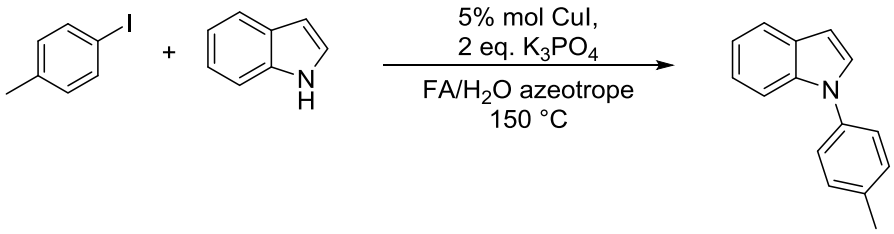
^{1}H NMR 400 MHz $CDCl_3$

δ value	**No. H**	**Mult.**	**j value/Hz**
6.74	1	*d*	3.2
7.35-7.20	2	*m*	
7.45-7.35	2	*m*	
7.63-7.52	4	*m*	
7.63	1	*d*	8.0
7.76	1	*d*	7.6

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 103.7, 110.6, 120.5, 121.3, 122.5,124.5, 126.5, 128.0, 129.4, 130.0, 135.9, 139.9

GC-EIMS (m/z, %): 193 (100), 192 (82), 191 (38), 166 (22), 165 (98), 90 (30), 89 (45), 51 (28)

Chem. Name	**1-(*p*-tolyl)-1*H*-indole (5b)**
Lit. Ref.	*Angew. Chem. Int. Ed.*, **2017**, *56*, 3961-3965



METHOD:
In a screw capped vial equipped with a magnetic stirring bar indole (1 mmol, 117 mg), K_3PO_4 (424 mg, 2 mmol), CuI (5 mol %, 0.05 mmol, 9.5 mg), furfuryl alcohol/water azeotrope (1 mL) and 4-iodotoluene (1 mmol, 218 mg) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 30h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 0.8 mL of ethyl acetate, filtered and evaporated. The obtained crude mixture was purified through flash column chromatography on silica gel (hexane/ethyl acetate 9:1) to give the pure product as a yellow oil (165 mg, 80% yield).

Mol Formula	$C_{15}H_{13}N$	**m.p.**	

Elemental Analysis: Calc.: C, 86.92; H, 6.32; N, 6.76. Found: C, 86.96; H, 6.29; N, 6.77.

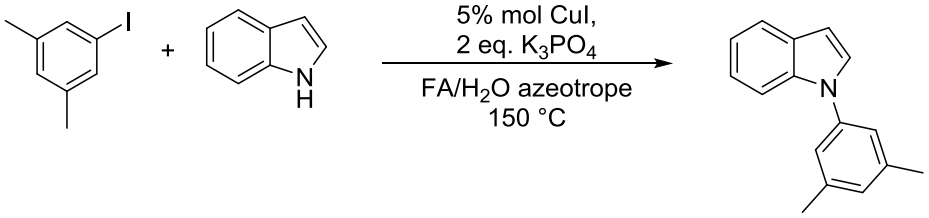
^{1}H NMR 400 MHz $CDCl_3$

δ value	**No. H**	**Mult.**	**j value/Hz**
2.49	3	*s*	
6.71	1	*d*	3.2
7.30-7.18	2	*m*	
7.40-7.32	3	*m*	
7.48-7.41	2	*m*	
7.56	1	*d*	7.6
7.73	1	*d*	7.6

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 20.9, 103.2, 110.5, 120.2, 121.0, 122.2, 124.4, 128.0, 129.3, 130.1, 136.2, 136.3, 137.4

GC-EIMS (m/z, %): 207 (100), 206 (100), 204 (40), 192 (36), 191 (35), 178 (36), 165 (47), 102 (40), 89 (54)

Chem. Name	1-(3,5-dimethylphenyl)-1*H*-indole (5c)
Lit. Ref.	*J. Am. Chem. Soc.*, **2001**, *123*, 7727-7729



METHOD:
In a screw capped vial equipped with a magnetic stirring bar indole (1 mmol, 117 mg), K_3PO_4 (424 mg, 2 mmol), CuI (5 mol %, 0.05 mmol, 9.5 mg), furfuryl alcohol/water azeotrope (1 mL) and 1-iodo-3,5-dimethylbenzene (1 mmol, 144µL) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 48h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 0.8 mL of ethyl acetate, filtered and evaporated. The obtained crude mixture was purified through flash column chromatography on silica gel (hexane/ethyl acetate 19:1) to give the pure product as a colorless oil (190 mg, 85% yield).

Mol Formula	$C_{16}H_{15}N$	**m.p.**	

Elemental Analysis: Calc.: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.80; H, 6.88; N, 6.31.

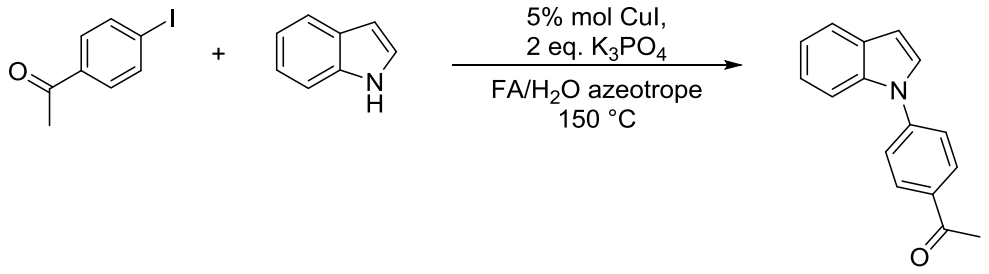
^{1}H NMR 400 MHz $CDCl_3$

δ value	No. H	Mult.	j value/Hz
2.46	6	*s*	
6.72	1	*d*	3.2
7.05	1	*s*	
7.30-7.10	4	*m*	
7.38	1	*d*	3.2
7.63	1	*d*	8.0
7.74	1	*d*	7.6

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 21.4, 103.2, 110.7, 120.2, 121.0, 122.1, 122.1, 129.2, 135.9, 139.4, 139.7

GC-EIMS (m/z, %): 221 (100), 220 (41), 206 (32), 205 (21), 204 (28)

Chem. Name	1-(4-(1*H*-indol-1-yl)phenyl)ethanone (5d)
Lit. Ref.	*Tetrahedron*, **2013**, *69*, 5444-5450



METHOD:
In a screw capped vial equipped with a magnetic stirring bar indole (1 mmol, 117 mg), K_3PO_4 (424 mg, 2 mmol), CuI (5 mol %, 0.05 mmol, 9.5 mg), furfuryl alcohol/water azeotrope (1 mL) and 1-(4-iodophenyl)ethanone (1 mmol, 246 mg) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 30h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 0.8 mL of ethyl acetate, filtered and evaporated. The obtained crude mixture was purified through flash column chromatography on silica gel (hexane/ethyl acetate 4:6) to give the pure product as a dark yellow oil (207 mg, 88% yield).

Mol Formula	$C_{16}H_{13}NO$	**m.p.**	

Elemental Analysis: Calc.: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.73; H, 5.55; N, 5.92.

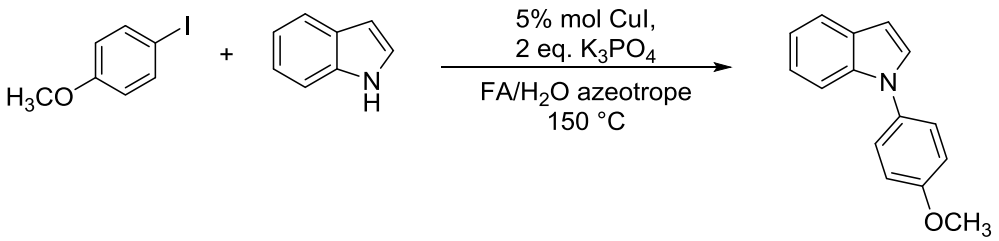
^{1}H NMR 400 MHz $CDCl_3$

δ value	No. H	Mult.	j value/Hz
2.66	3	s	
6.75	1	*d*	3.2
7.32-7.18	2	*m*	
7.39	1	*d*	3.2
7.73-7.58	4	*m*	
8.15-8.10	2	*m*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 26.6, 105.1, 110.6, 121.1, 121.5, 123.0, 123.3, 127.4, 129.9, 130.4, 134.6, 135.4, 143.8, 196.9

GC-EIMS (m/z, %): 235 (100), 221 (31), 220 (86), 193 (21), 192 (71), 191 (70), 190 (25), 95 (23)

Chem. Name	1-(4-methoxyphenyl)-1*H*-indole (5e)
Lit. Ref.	*Organometallics*, **2017**, *36*, 679-686



METHOD:
In a screw capped vial equipped with a magnetic stirring bar indole (1 mmol, 117 mg), K_3PO_4 (424 mg, 2 mmol), CuI (5 mol %, 0.05 mmol, 9.5 mg), furfuryl alcohol/water azeotrope (1 mL) and 4-iodoanisole (1 mmol, 234 mg) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 30h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 0.8 mL of ethyl acetate, filtered and evaporated. The obtained crude mixture was purified through flash column chromatography on silica gel (hexane/ethyl acetate 7:3) to give the pure product as a yellow oil (190 mg, 85% yield).

Mol Formula	$C_{15}H_{13}NO$	m.p.	

Elemental Analysis: Calc.: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.63; H, 5.90; N, 6.31.

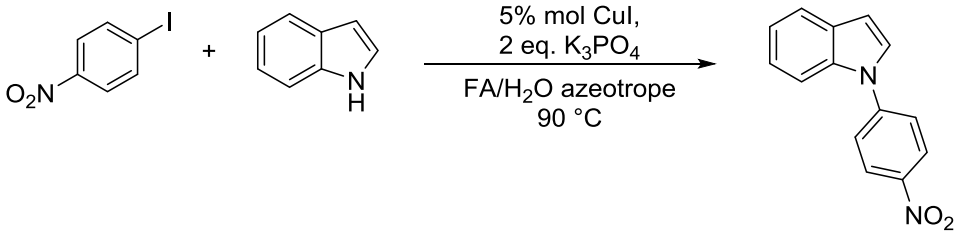
^{1}H NMR 400 MHz $CDCl_3$

δ value	No. H	Mult.	j value/Hz
3.89	3	*s*	
6.67	1	*d*	2.8
7.08-7.00	2	*m*	
7.24-7.13	2	*m*	
7.30-7.25	1	*m*	
7.45-7.38	2	*m*	
7.47	1	*d*	8.0
7.69	1	*d*	7.6

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 55.6, 102.9, 110.4, 114.7, 120.1, 121.0, 122.1, 126.0, 128.3, 128.9, 132.8, 136.3, 158.2

GC-EIMS (m/z, %): 223 (100), 222 (49), 208 (28), 207 (30)

Chem. Name	1-(4-nitrophenyl)-1*H*-indole (5f)
Lit. Ref.	*Org. Biomol. Chem.*, **2016**, *14*, 10861-10865



METHOD:
In a screw capped vial equipped with a magnetic stirring bar indole (1 mmol, 117 mg), K_3PO_4 (424 mg, 2 mmol), CuI (5 mol %, 0.05 mmol, 9.5 mg), furfuryl alcohol/water azeotrope (1 mL) and 1-iodo-4-nitrobenzene (1 mmol, 249 mg) were consecutively added. The resulting mixture was left under stirring at 90 °C. After 48h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 0.8 mL of ethyl acetate, filtered and evaporated. The obtained crude mixture was purified through flash column chromatography on silica gel (hexane/ethyl acetate 1:1) to give the pure product as a yellow oil (155 mg, 65% yield).

Mol Formula	$C_{14}H_{10}N_2O_2$	**m.p.**	138-140 °C

Elemental Analysis: C, 70.58; H, 4.23; N, 11.76. Found: C, 70.64; H, 4.19; N, 11.73.

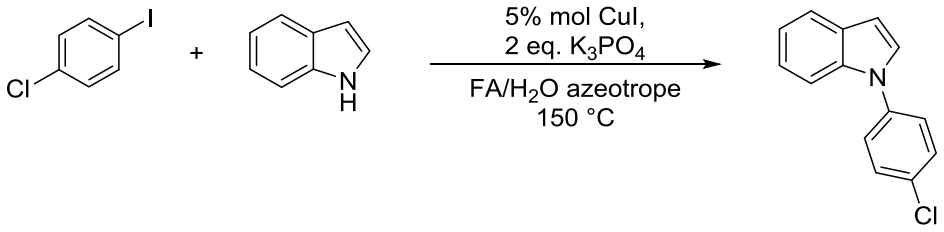
^{1}H NMR 400 MHz $CDCl_3$

δ value	No. H	Mult.	j value/Hz
8.44-8.37	2	*m*	
7.77-7.62	4	*m*	
7.39	1	*d*	3.6
7.35-7.21	2	*m*	
6.79	1	*d*	3.6

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 106.3, 110.6, 121.7, 121.8, 123.4, 123.5, 125.6, 127.2, 130.2, 135.3, 145.1, 145.4

GC-EIMS (m/z, %): 238 (100), 192 (61), 191 (77)

Chem. Name	1-(4-chlorophenyl)-1*H*-indole (5g)
Lit. Ref.	*Tetrahedron*, **2009**, *65*, 10459-10462



METHOD:
In a screw capped vial equipped with a magnetic stirring bar indole (1 mmol, 117 mg), K_3PO_4 (424 mg, 2 mmol), CuI (5 mol %, 0.05 mmol, 9.5 mg), furfuryl alcohol/water azeotrope (1 mL) and 1-chloro-4-iodobenzene (1 mmol, 238 mg) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 30h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 0.8 mL of ethyl acetate, filtered and evaporated. The obtained crude mixture was purified through flash column chromatography on silica gel (hexane/ethyl acetate 4:1) to give the pure product as a white oil (170 mg, 75% yield).

Mol Formula	$C_{14}H_{10}ClN$	m.p.	

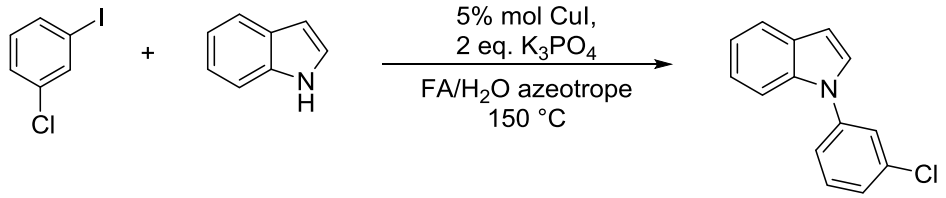
Elemental Analysis: Calc.: C, 73.85; H, 4.43; N, 6.15. Found: C, 73.80; H, 4.47; N, 6.13.

^{1}H NMR 400 MHz $CDCl_3$	δ value	No. H	Mult.	j value/Hz
	6.71	1	*d*	3.2
	7.28-7.16	2	*m*	
	7.30	1	*d*	3.6
	7.55-7.42	5	*m*	
	7.70	1	*d*	7.6

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 104.1, 110.3, 120.6, 121.3, 122.6, 125.5, 127.7, 129.4, 129.8, 132.0, 135.8, 138.4

GC-EIMS (m/z, %): 229 (55), 228 (37), 227 (100), 192 (27), 191 (34), 190 (20), 165 (41), 95 (25), 89 (23)

Chem. Name	1-(3-chlorophenyl)-1*H*-indole (5h)
Lit. Ref.	*Tetrahedron*, **2009**, *65*, 10459-10462



METHOD:
In a screw capped vial equipped with a magnetic stirring bar indole (1 mmol, 117 mg), K_3PO_4 (424 mg, 2 mmol), CuI (5 mol %, 0.05 mmol, 9.5 mg), furfuryl alcohol/water azeotrope (1 mL) and 1-chloro-3-iodobenzene (1 mmol, 238 mg) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 48h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 0.8 mL of ethyl acetate, filtered and evaporated. The obtained crude mixture was purified through flash column chromatography on silica gel (hexane/ethyl acetate 4:1) to give the pure product as a pale yellow oil (165 mg, 73% yield).

Mol Formula	$C_{14}H_{10}ClN$	**m.p.**	

Elemental Analysis: Calc.: C, 73.85; H, 4.43; N, 6.15. Found: C, 73.80; H, 4.48; N, 6.12.

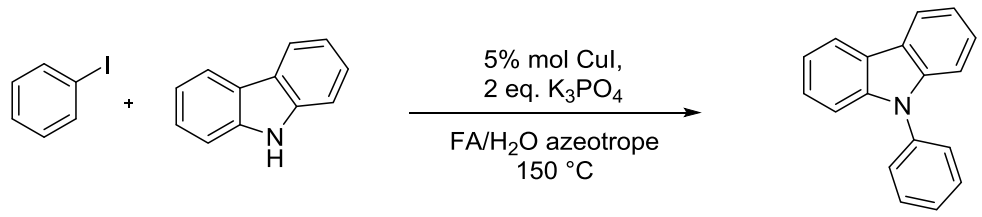
^{1}H NMR 400 MHz $CDCl_3$

δ value	No. H	Mult.	j value/Hz
6.71	1	*d*	3.2
7.28-7.17	2	*m*	
7.38-7.30	2	*m*	
7.50-7.40	2	*m*	
7.55-7.54	1	*m*	
7.58	1	*d*	8.0
7.70	1	*d*	7.6

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 104.3, 110.4, 120.7, 121.3, 122.3, 122.7, 124.4, 126.5, 127.6, 129.5, 130.6, 135.2, 135.6, 141.0

GC-EIMS (m/z, %): 229 (33), 228 (18), 227 (100), 191 (19), 165 (29), 89 (22), 75 (18)

Chem. Name	9-phenyl-9*H*-carbazole (5i)
Lit. Ref.	*Org. Lett.*, **2015**, *17*, 3640-3642



METHOD:
In a screw capped vial equipped with a magnetic stirring bar carbazole (1 mmol, 167 mg), K_3PO_4 (424 mg, 2 mmol), CuI (5 mol %, 0.05 mmol, 9.5 mg), furfuryl alcohol/water azeotrope (1 mL) and iodobenzene (1 mmol, 112 µL) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 12h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 0.8 mL of ethyl acetate, filtered and evaporated. The obtained solid was crystallized using 2 mL of methanol and dried under vacuum to give the pure product as a dark yellow solid (145 mg, 60% yield).

Mol Formula	$C_{18}H_{13}N$	**m.p.**	88-90 °C

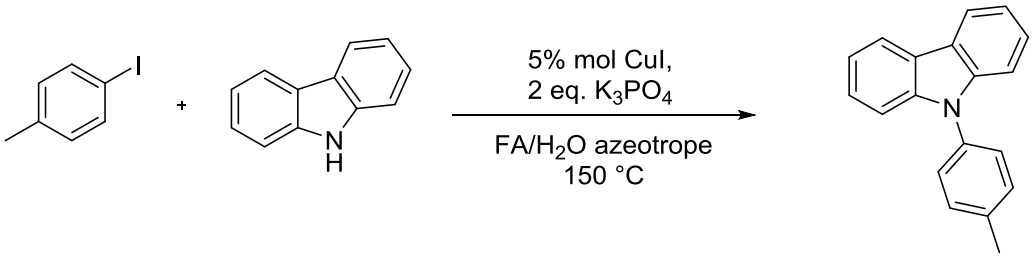
Elemental Analysis: C, 88.86; H, 5.39; N, 5.76. Found: C, 88.92; H, 5.41; N, 5.72.

^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	7.35-7.28	2	*m*	
	7.53-7.38	5	*m*	
	7.68-7.54	4	*m*	
	8.17	2	*d*	7.6

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 109.7, 119.9, 120.3, 123.3, 125.9, 127.1, 127.4, 129.8, 137.7, 140.9

GC-EIMS (m/z, %): 243 (100), 242 (75), 241 (73), 240 (18), 166 (12), 140 (15), 121 (19), 120 (30)

Chem. Name	9-(p-tolyl)-9*H*-carbazole (5j)
Lit. Ref.	*Org. Lett.*, **2015**, *17*, 3640-3642



METHOD:
In a screw capped vial equipped with a magnetic stirring bar carbazole (1 mmol, 167 mg), K_3PO_4 (424 mg, 2 mmol), CuI (5 mol %, 0.05 mmol, 9.5 mg), furfuryl alcohol/water azeotrope (1 mL) and 4-iodotoluene (1 mmol, 218 mg) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 72h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 0.8 mL of ethyl acetate, filtered and evaporated. The obtained solid was crystallized using 2 mL of methanol and dried under vacuum to give the pure product as a dark yellow solid (102 mg, 40% yield).

Mol Formula	$C_{19}H_{15}N$	**m.p.**	112-114 °C

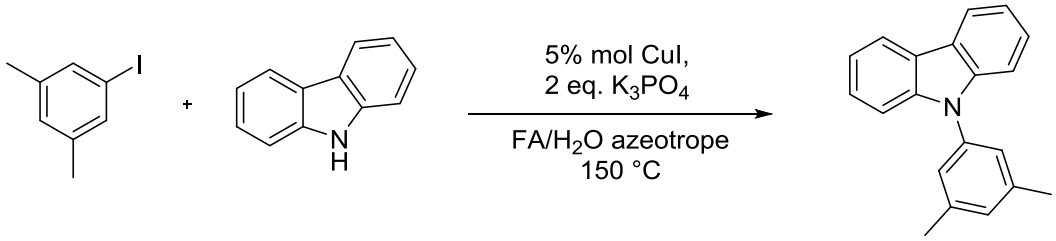
Elemental Analysis: C, 88.68; H, 5.88; N, 5.44. Found: C, 88.62; H, 5.91; N, 5.42.

^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	8.16	2	*d*	8.0
	7.48-7.37	8	*m*	
	7.35-7.25	2	*m*	
	2.50	3	*s*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 21.3, 109.8, 119.7, 120.3, 123.2, 125.9, 127.0, 130.4, 135.0, 137.4, 141.1

GC-EIMS (m/z, %): 257 (100), 254 (20), 241 (13)

Chem. Name	9-(3,5-dimethylphenyl)-9*H*-carbazole (5k)
Lit. Ref.	*Adv. Synth. Catal.*, **2017**, *359*, 1631-1636



METHOD:
In a screw capped vial equipped with a magnetic stirring bar carbazole (1 mmol, 167 mg), K_3PO_4 (424 mg, 2 mmol), CuI (5 mol %, 0.05 mmol, 9.5 mg), furfuryl alcohol/water azeotrope (1 mL) and 1-iodo-3,5-dimethylbenzene (1 mmol, 144 µL) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 48h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 0.8 mL of ethyl acetate, filtered and evaporated. The obtained solid was crystallized using methanol and dried under vacuum to give the pure product as a pale yellow solid (148 mg, 55% yield).

Mol Formula	$C_{20}H_{17}N$	**m.p.**	103-105 °C

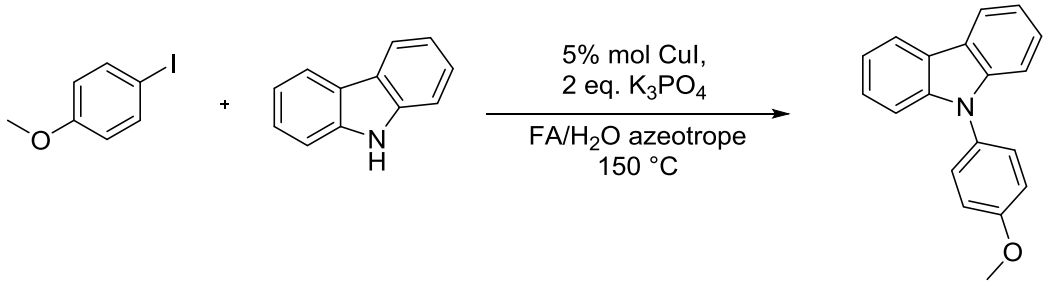
Elemental Analysis: C, 88.82; H, 6.31; N, 5.16. Found: C, 88.85; H, 6.27; N, 5.10.

^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	8.15	2	*d*	7.6
	7.45-7.36	4	*m*	
	7.34-7.22	2	*m*	
	7.18	2	*s*	
	7.11	1	*s*	
	2.44	6	*s*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 20.9, 109.4, 119.2, 119.7, 122.7, 124.2, 125.3, 128.7, 137.0, 139.1, 140.5

GC-EIMS (m/z, %): 271 (100), 254 (15), 241 (12)

Chem. Name	9-(4-methoxyphenyl)-9*H*-carbazole (5l)
Lit. Ref.	*Org. Lett.*, **2015**, *17*, 3640-3642



METHOD:
In a screw capped vial equipped with a magnetic stirring bar carbazole (1 mmol, 167 mg), K_3PO_4 (424 mg, 2 mmol), CuI (5 mol %, 0.05 mmol, 9.5 mg), furfuryl alcohol/water azeotrope (1 mL) and 4-iodoanisole (1 mmol, 234 mg) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 72h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 0.8 mL of ethyl acetate, filtered and evaporated. The obtained solid was crystallized using 2 mL of methanol and dried under vacuum to give the pure product as a white solid (177 mg, 65% yield).

Mol Formula	$C_{19}H_{15}NO$	**m.p.**	158-160 °C

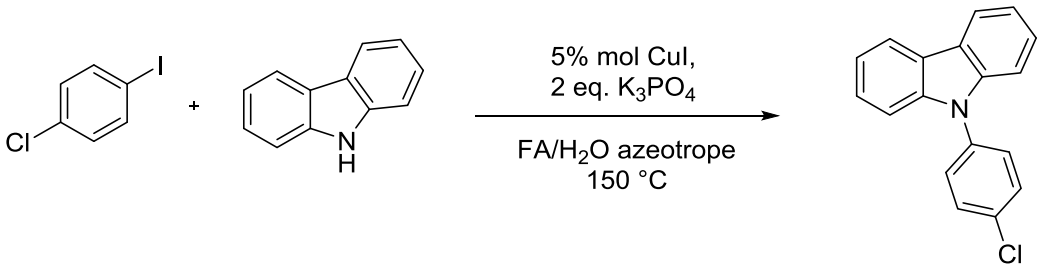
Elemental Analysis: C, 83.49; H, 5.53; N, 5.12. Found: C, 83.56; H, 5.58; N, 5.07.

^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	8.14	2	*d*	7.6
	7.50-7.18	8	*m*	
	7.15-7.07	2	*m*	
	3.92	3	*s*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 55.6, 109.7, 115.1, 119.6, 120.2, 123.1, 125.8, 128.6, 130.3, 141.4, 158.8

GC-EIMS (m/z, %): 273 (100), 258 (20), 257 (21), 228 (22)

Chem. Name	9-(4-chlorophenyl)-9*H*-carbazole (5m)
Lit. Ref.	*Org. Lett.*, **2015**, *17*, 3640-3642



METHOD:
In a screw capped vial equipped with a magnetic stirring bar carbazole (1 mmol, 167 mg), K_3PO_4 (424 mg, 2 mmol), CuI (5 mol %, 0.05 mmol, 9.5 mg), furfuryl alcohol/water azeotrope (1 mL) and 1-chloro-4-iodobenzene (1 mmol, 238 mg) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 48h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 0.8 mL of ethyl acetate, filtered and evaporated. The obtained solid was crystallized using 2 mL of methanol and dried under vacuum to give the pure product as a light yellow solid (138 mg, 50% yield).

Mol Formula	$C_{18}H_{12}ClN$	**m.p.**	137-139 °C

Elemental Analysis: C, 77.84; H, 4.35; N, 5.04. Found: C, 77.76; H, 4.38; N, 5.10.

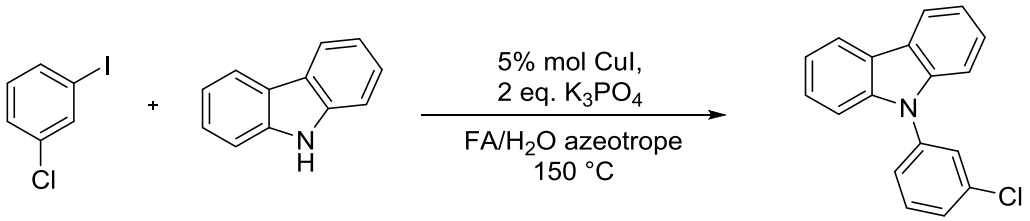
^{1}H NMR 400 MHz $CDCl_3$

δ value	No. H	Mult.	j value/Hz
8.16	2	*d*	7.6
7.65-7.55	2	*m*	
7.55-7.48	2	*m*	
7.47-7.36	4	*m*	
7.32	2	*t*	7.6

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 109.6, 120.2, 120.4, 123.5, 126.1, 128.4, 130.1, 133.0, 136.3, 140.7

GC-EIMS (m/z, %): 279 (36), 277 (100), 242 (14), 241 (36), 240 (10), 140 (10), 120 (10)

Chem. Name	9-(3-chlorophenyl)-9*H*-carbazole (5n)
Lit. Ref.	*Adv. Synth. Catal.*, **2010**, *352*, 616-620



METHOD:
In a screw capped vial equipped with a magnetic stirring bar carbazole (1 mmol, 167 mg), K_3PO_4 (424 mg, 2 mmol), CuI (5 mol %, 0.05 mmol, 9.5 mg), furfuryl alcohol/water azeotrope (1 mL) and 1-chloro-3-iodobenzene (1 mmol, 238 mg) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 72h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 0.8 mL of ethyl acetate, filtered and evaporated. The obtained solid was crystallized using 2 mL of methanol and dried under vacuum to give the pure product as a dark yellow solid (152 mg, 55% yield).

Mol Formula	$C_{18}H_{12}ClN$	**m.p.**	140-142 °C

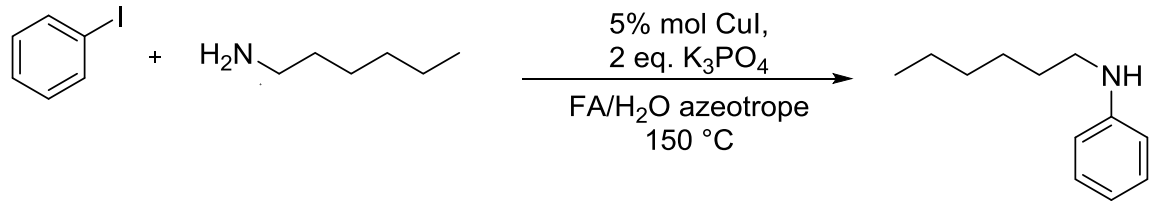
Elemental Analysis: C, 77.84; H, 4.35; N, 5.04. Found: C, 77.79; H, 4.38; N, 5.11.

^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	8.15	2	*d*	8.0
	7.62-7.58	1	*m*	
	7.57-7.40	7	*m*	
	7.35-7.28	2	*m*	

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 109.6, 120.3, 120.4, 123.5, 125.3, 126.1, 127.3, 127.6, 130.9, 135.4, 139.0,140.6

GC-EIMS (m/z, %): 279 (31), 278 (23), 277 (100), 242 (15), 241 (40), 240 (13), 140 (14), 139 (12), 121 (14)

Chem. Name	***N*-hexylaniline (7a)**
Lit. Ref.	*Adv. Synth. Catal.*, **2013**, *355*, 1117-1125



METHOD:
In a screw capped vial equipped with a magnetic stirring bar hexylamine (1 mmol, 132 µL), K_3PO_4 (424 mg, 2 mmol), CuI (5 mol %, 0.05 mmol, 9.5 mg), furfuryl alcohol/water azeotrope (1 mL) and iodobenzene (2 mmol, 224 µL) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 48h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The obtained crude mixture was purified through flash column chromatography on silica gel (petroleum ether as eluent) to give the pure product as a yellow oil (132 mg, 75% yield).

Mol Formula	$C_{12}H_{19}N$	**m.p.**	

Elemental Analysis: Calc.: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.24; H, 10.85; N, 7.87.

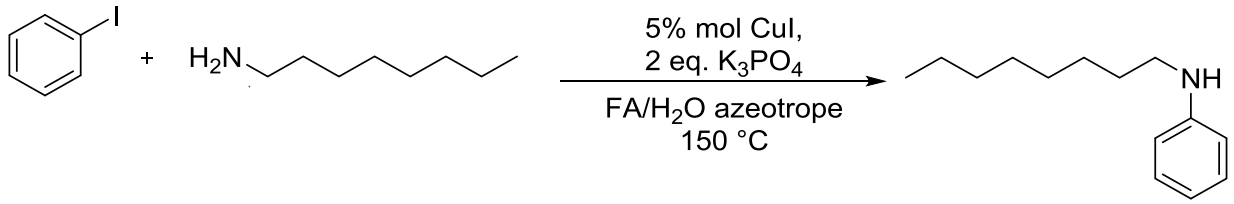
^{1}H NMR 400 MHz $CDCl_3$

δ value	**No. H**	**Mult.**	**j value/Hz**
7.18	2	*t*	8.4
6.69	1	*t*	7.2
6.61	2	*d*	8.0
3.60	1	*bs*	
3.11	2	*t*	7.2
1.69-1.58	2	*m*	
1.47-1.26	6	*m*	
0.91	3	*t*	6.8

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 14.1, 22.6, 26.9, 29.5, 31.6, 44.1, 112.8, 117.2, 129.2, 148.5

GC-EIMS (m/z, %): 177 (79), 107 (32), 106 (100), 77 (43)

Chem. Name	***N*-octylaniline (7b)**
Lit. Ref.	*J. Org. Chem.*, **2017**, *82*, 1943-1950



METHOD:
In a screw capped vial equipped with a magnetic stirring bar octylamine (1 mmol, 165 µL), K_3PO_4 (424 mg, 2 mmol), CuI (5 mol %, 0.05 mmol, 9.5 mg), furfuryl alcohol/water azeotrope (1 mL) and iodobenzene (1 mmol, 112 µL) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 48h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 1.5 mL of ethyl acetate, filtered and evaporated. The obtained crude mixture was purified through flash column chromatography on silica gel (petroleum ether as eluent) to give the pure product as a yellow oil (120 mg, 58% yield).

Mol Formula	$C_{14}H_{23}N$	**m.p.**	

Elemental Analysis: Calc.: C, 81.89; H, 11.29; N, 6.82. Found: C, 81.95; H, 11.33; N, 6.78.

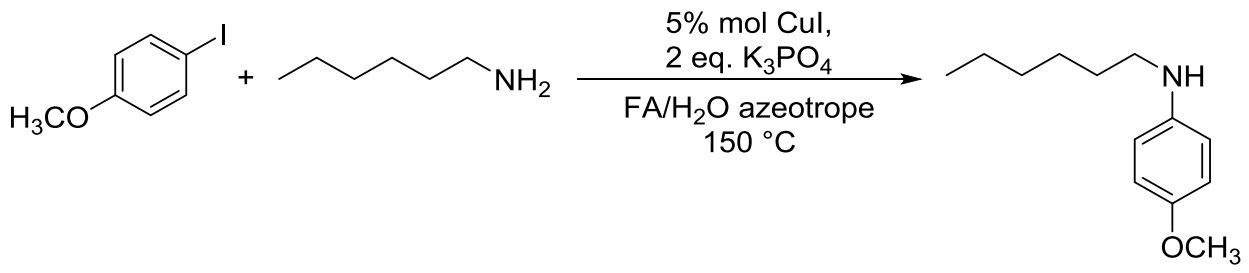
^{1}H NMR 400 MHz $CDCl_3$

δ value	No. H	Mult.	j value/Hz
7.18	2	*t*	8.0
6.70	1	*t*	7.2
6.62	2	*d*	7.6
3.52	1	*bs*	
3.11	2	*t*	7.2
1.69-1.58	2	*m*	
1.45-1.20	10	*m*	
0.91	3	*t*	7.2

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 14.1, 22.7, 27.2, 29.3, 29.4, 29.6, 31.9, 44.1, 112.7, 117.1, 129.2, 148.5

GC-EIMS (m/z, %): 205 (51), 107 (24), 106 (100), 77 (25)

Chem. Name	***N*-hexyl-4-methoxyaniline (7c)**
Lit. Ref.	*Adv. Synth. Catal.*, **2010**, *352*, 201-211



METHOD:
In a screw capped vial equipped with a magnetic stirring bar hexylamine (1 mmol, 132 µL), K_3PO_4 (424 mg, 2 mmol), CuI (5 mol %, 0.05 mmol, 9.5 mg), furfuryl alcohol/water azeotrope (1 mL) and 4-iodoanisole (1 mmol, 234 mg) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 48h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 1.5 mL of ethyl acetate, filtered and evaporated. The obtained crude mixture was purified through flash column chromatography on silica gel (hexane/ethyl acetate 20:1) to give the pure product as a dark yellow oil (165 mg, 80% yield).

Mol Formula	$C_{13}H_{21}NO$	**m.p.**	

Elemental Analysis: Calc.: C: 75.32; H:10.21; N: 6.76. Found: C: 75.36; H:10.17; N: 6.71.

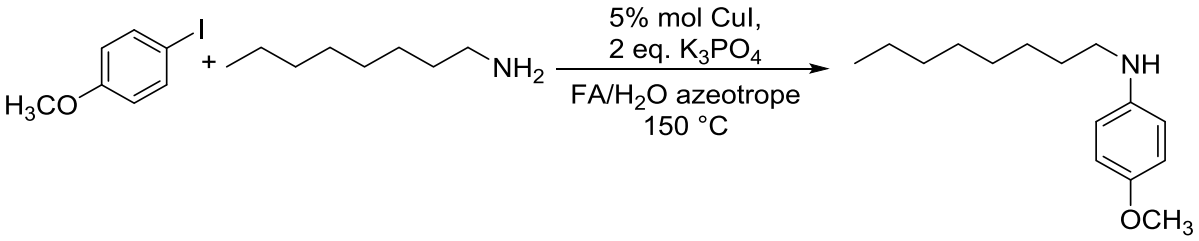
^{1}H NMR 400 MHz $CDCl_3$

δ value	No. H	Mult.	j value/Hz
6.81-6.75	2	*m*	
6.61-6.55	2	*m*	
3.75	3	*s*	
3.39	1	*bs*	
3.06	2	*t*	7.2
1.66-1.54	2	*m*	
1.44-1.21	6	*m*	
0.90	3	*t*	6.8

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 14.1, 22.6, 26.9, 29.7, 31.7, 45.1, 55.9, 114.0, 114.9, 142.9, 152.0

GC-EIMS (m/z, %): 207 (40), 136 (100)

Chem. Name	***N*-octyl-4-methoxyaniline (7d)**
Lit. Ref.	



METHOD:
In a screw capped vial equipped with a magnetic stirring bar octylamine (1 mmol, 165 µL), K_3PO_4 (424 mg, 2 mmol), CuI (5 mol %, 0.05 mmol, 9.5 mg), furfuryl alcohol/water azeotrope (1 mL) and 4-iodoanisole (1 mmol, 234 mg) were consecutively added. The resulting mixture was left under stirring at 150 °C. After 48h, the furfuryl alcohol/water azeotrope was distilled at 100 °C under a nitrogen atmosphere. The residue was then dissolved in 1.5 mL of ethyl acetate, filtered and evaporated. The obtained crude mixture was purified through flash column chromatography on silica gel (hexane/ethyl acetate 20:1) to give the pure product as a dark yellow oil (178 mg, 75% yield).

Mol Formula	$C_{15}H_{25}NO$	**m.p.**	

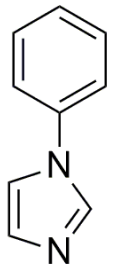
Elemental Analysis: Calc.: C: 76.55; H:10.71; N: 5.95. Found: C: 76.49; H:10.73; N: 5.91.

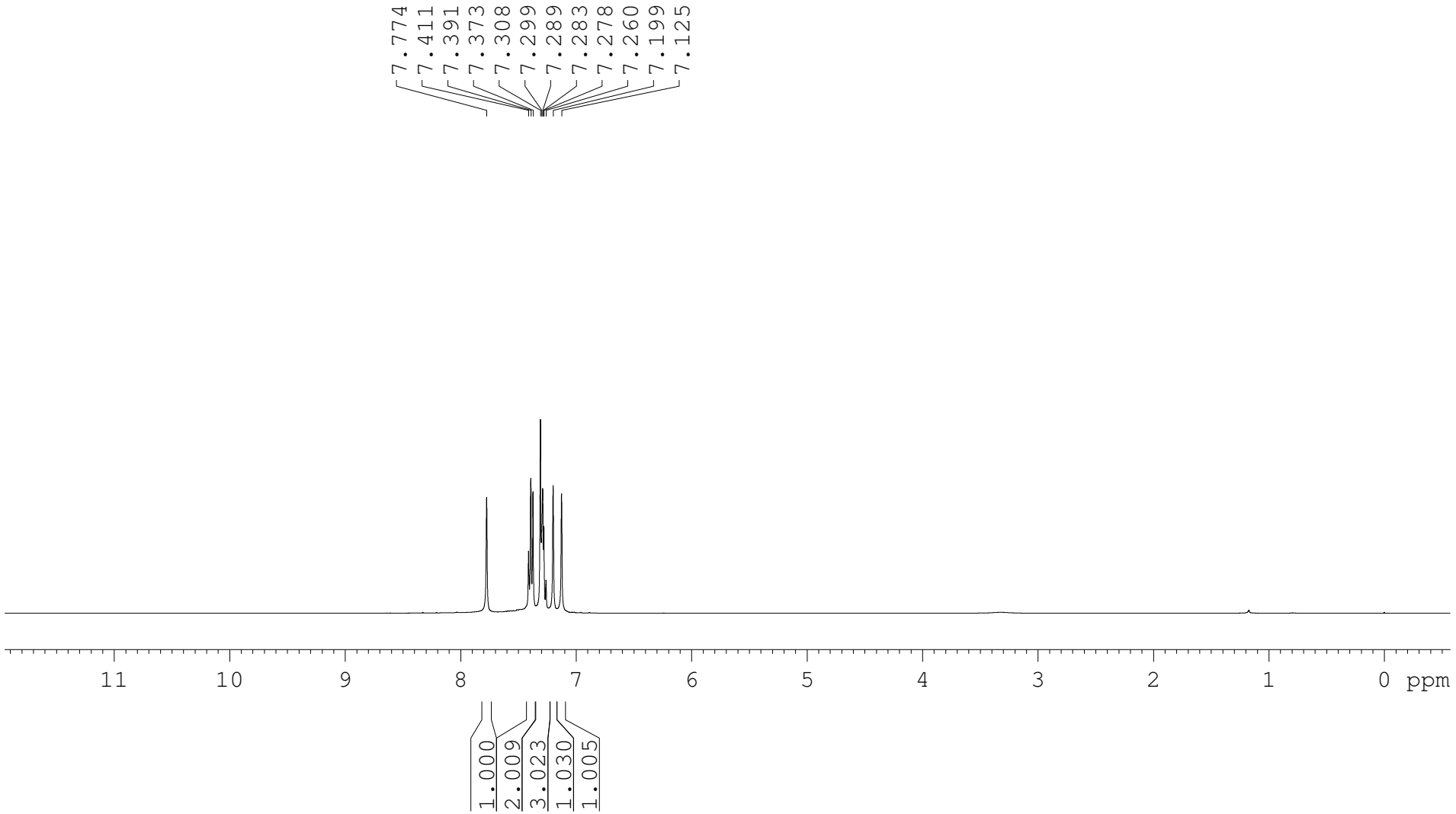
^{1}H NMR 400 MHz $CDCl_3$	**δ value**	**No. H**	**Mult.**	**j value/Hz**
	6.82-6.76	2	*m*	
	6.60-6.55	2	*m*	
	3.75	3	*s*	
	3.28	1	*bs*	
	3.06	2	*t*	7.2
	1.67-1.55	2	*m*	
	1.43-1.18	10	*m*	
	0.89	3	*t*	7.2

^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 14.1, 22.7, 27.2, 29.3, 29.5, 29.7, 31.8, 45.0, 55.8, 114.0, 114.9, 142.9, 152.0

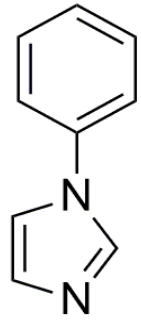
GC-EIMS (m/z, %): 235 (100), 137 (49), 136 (100), 121 (22)

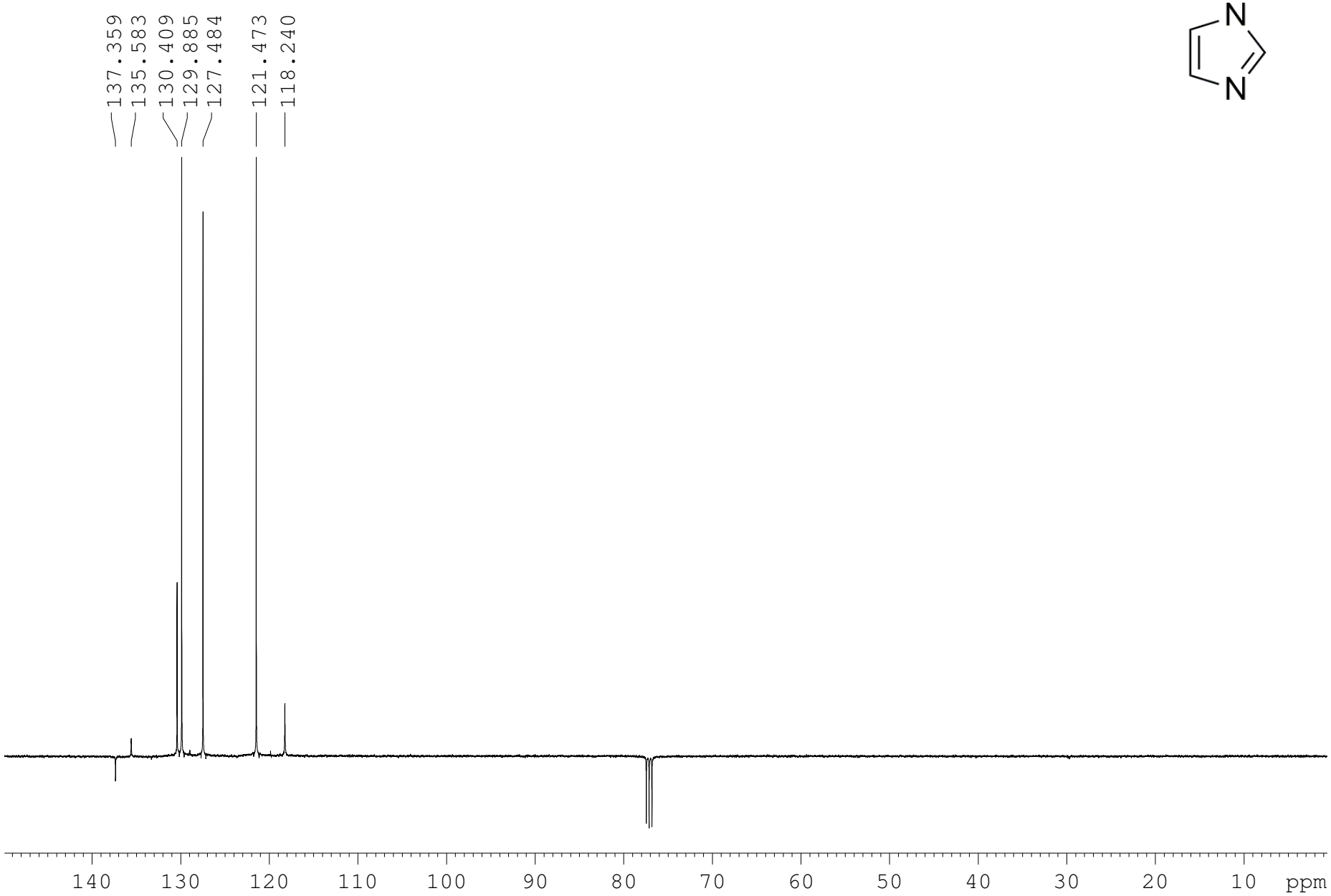
1-phenyl-1H-imidazole (3a)



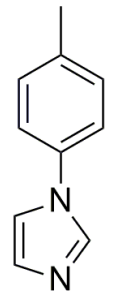


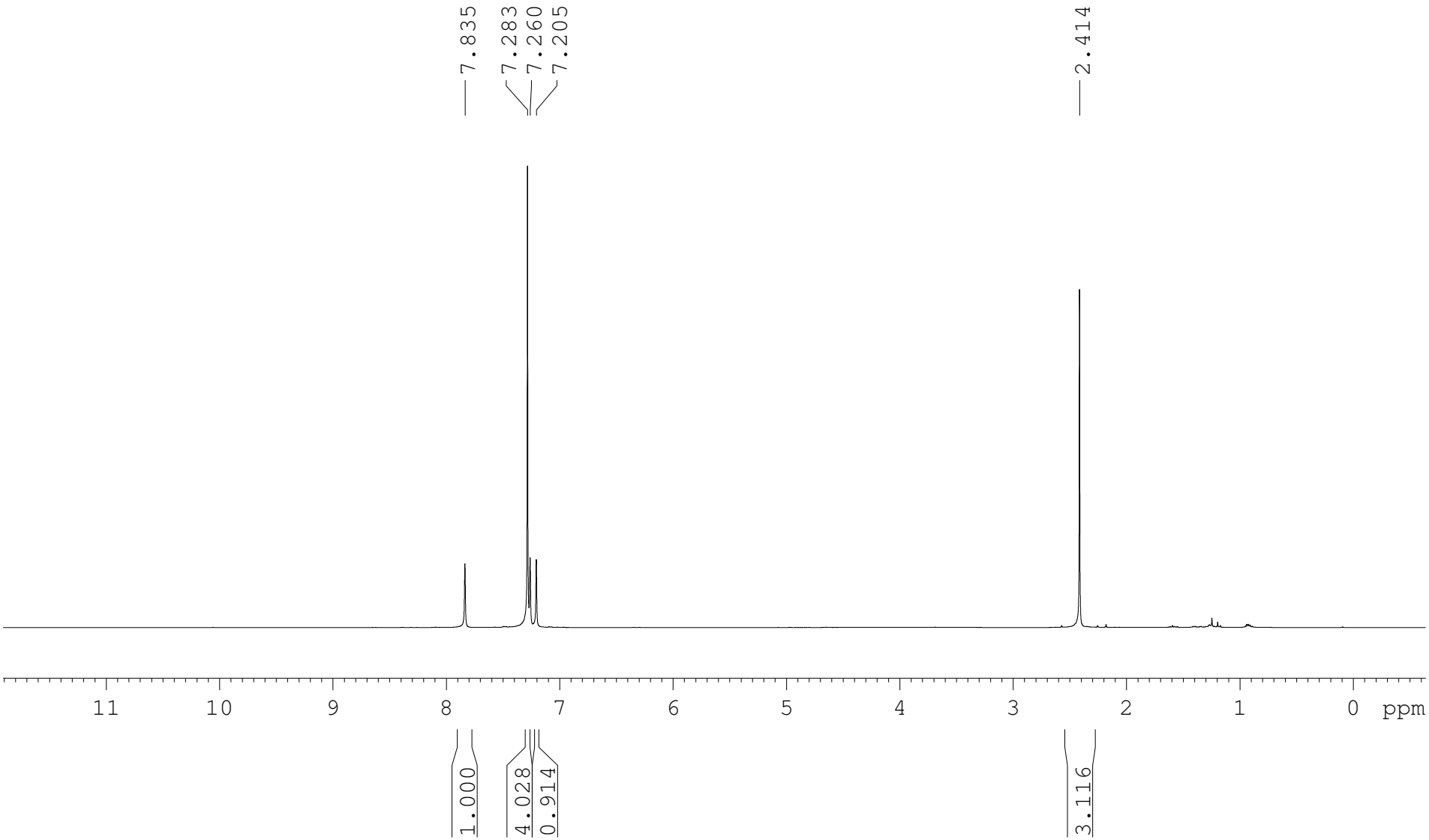
1-phenyl-1H-imidazole (3a)



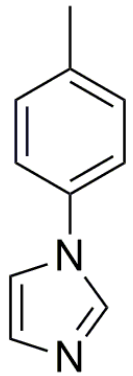


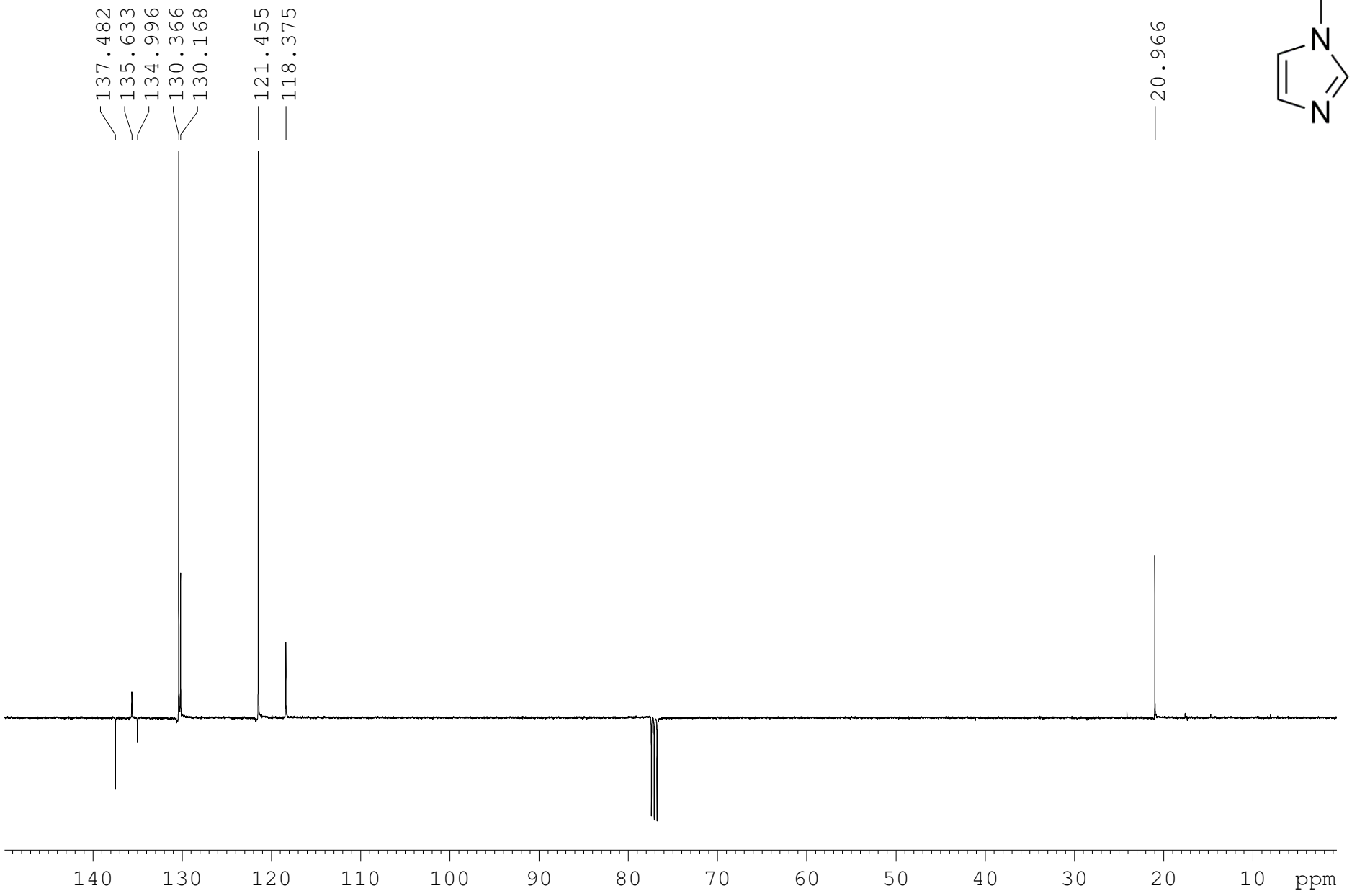
1-(p-tolyl)-1H-imidazole (3b)



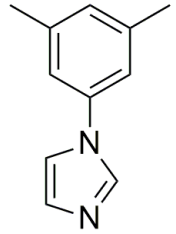


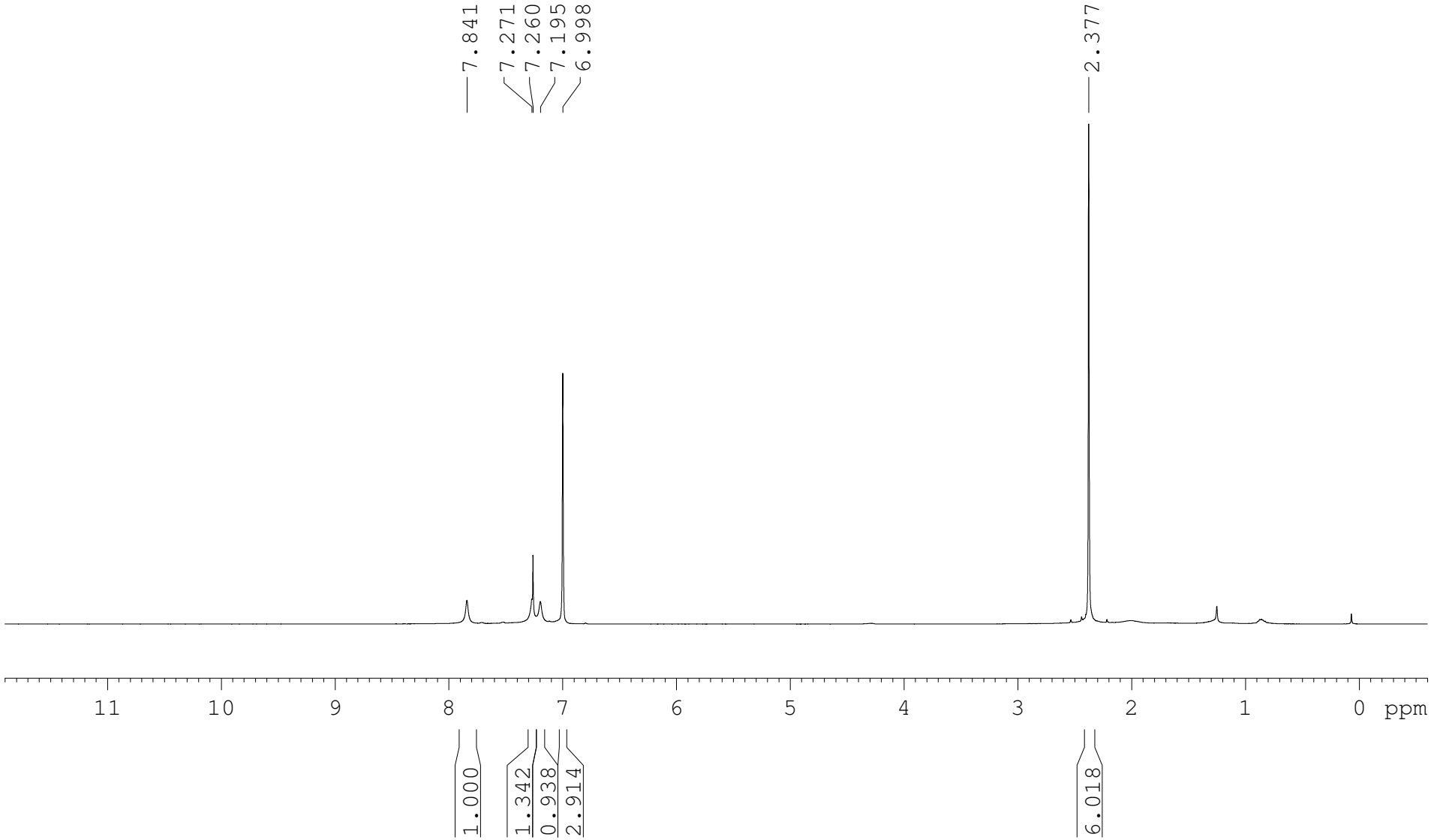
1-(p-tolyl)-1H-imidazole (3b)



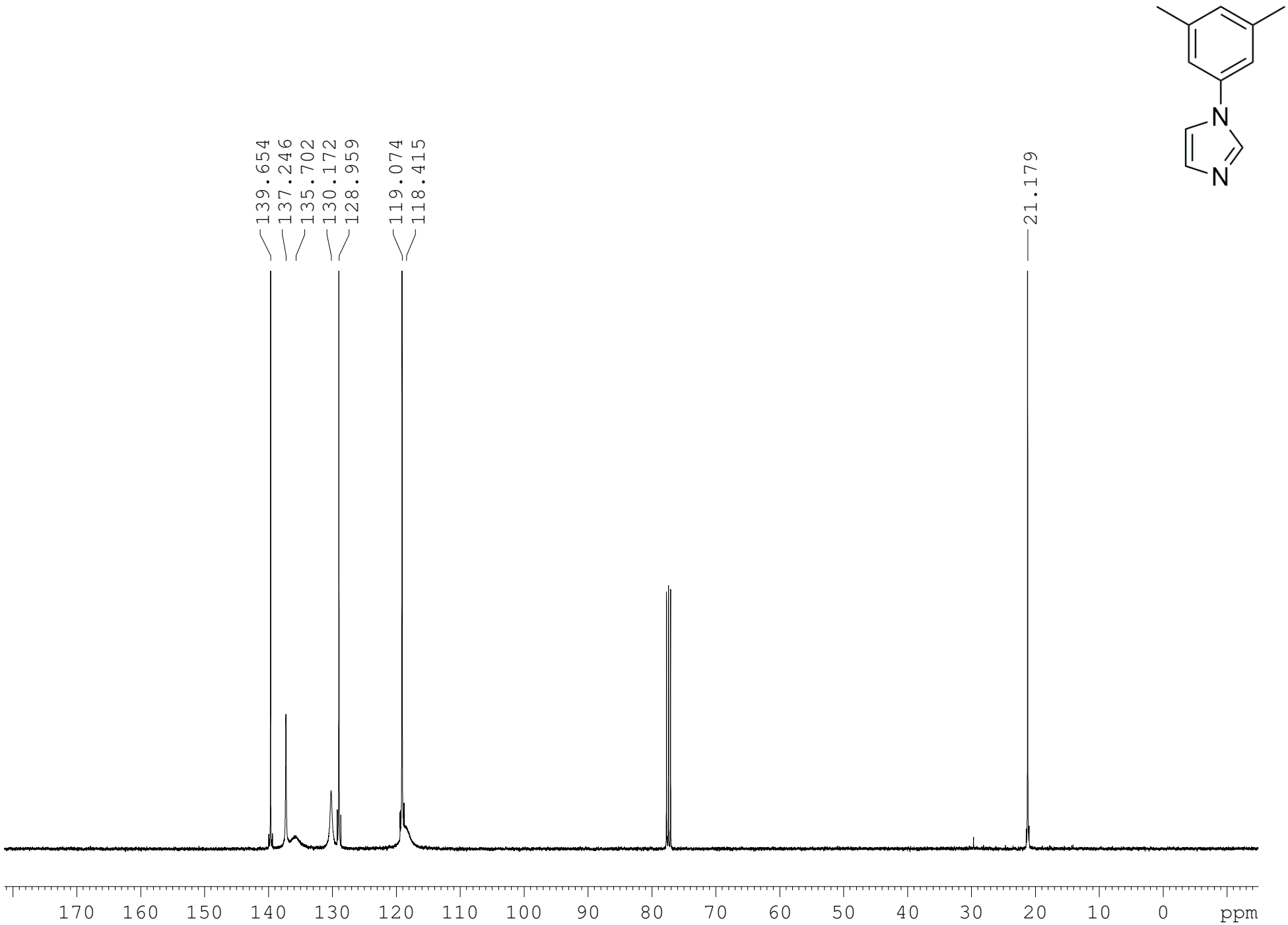


1-(3,5-dimethylphenyl)-1H-imidazole (3c)

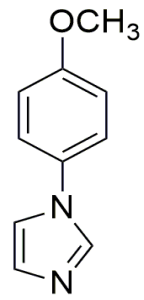


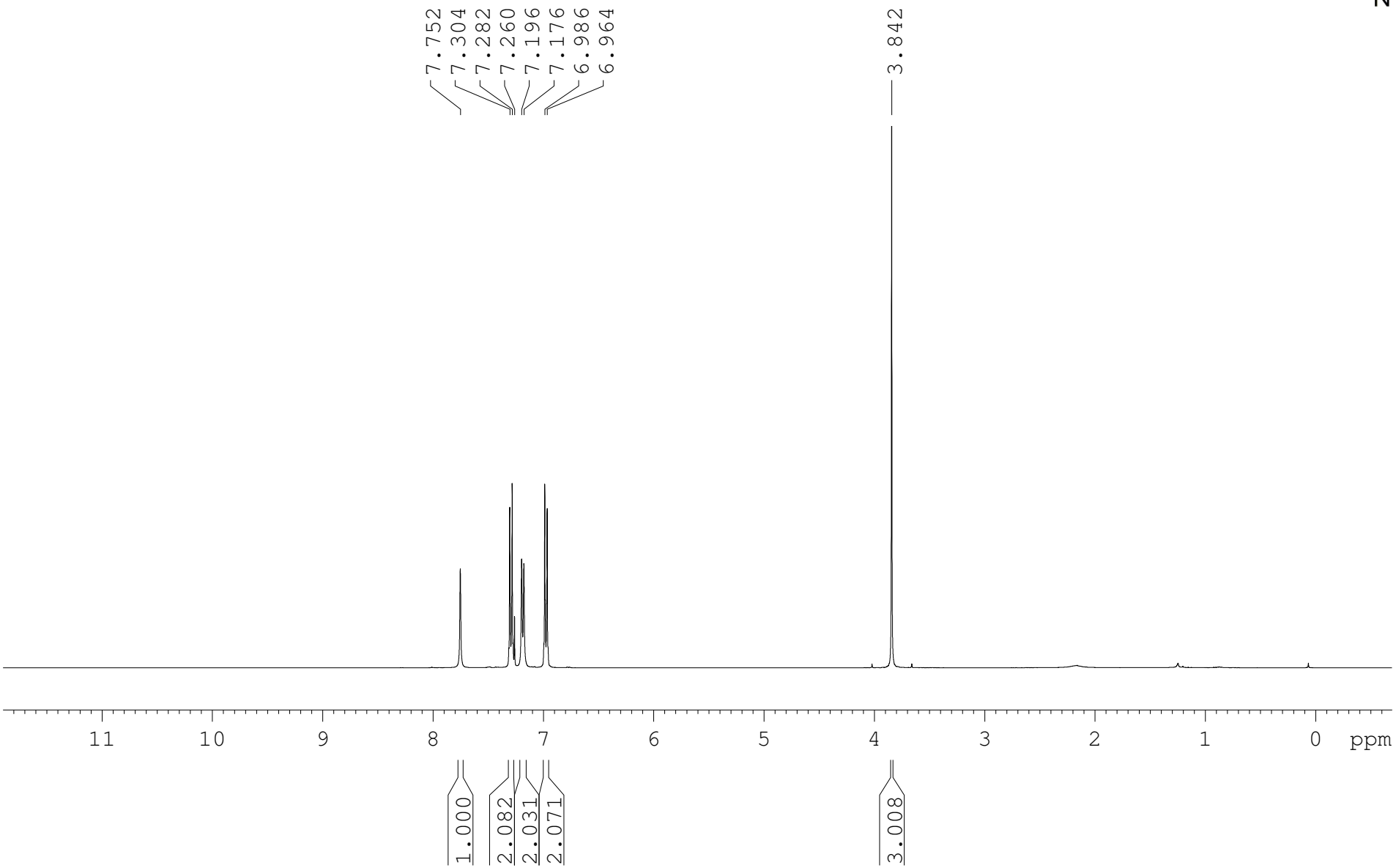


1-(3,5-dimethylphenyl)-1H-imidazole (3c)

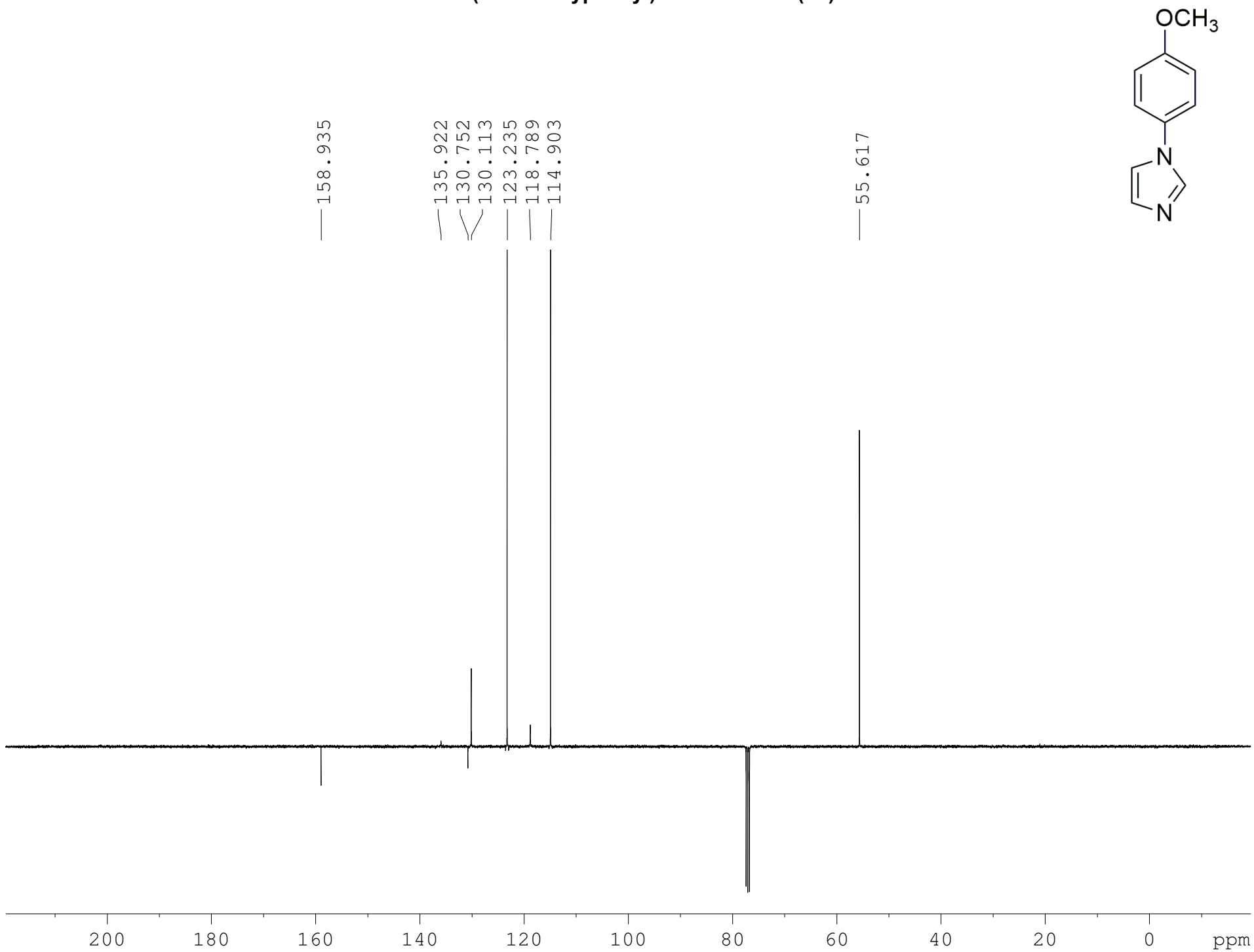


1-(4-methoxyphenyl)-1H-imidazole (3d)

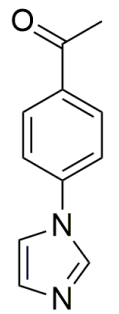


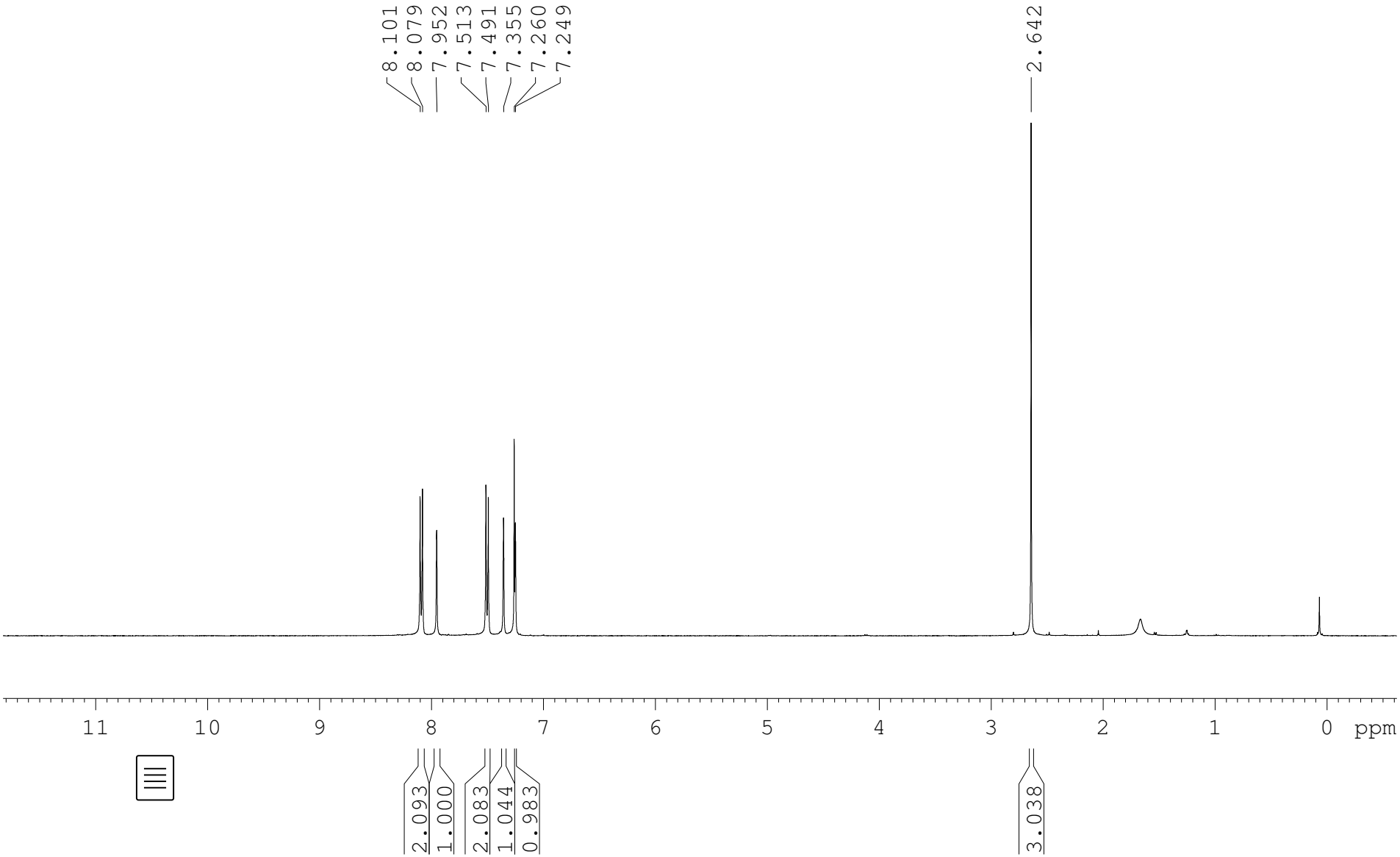


1-(4-methoxyphenyl)-1H-imidazole (3d)

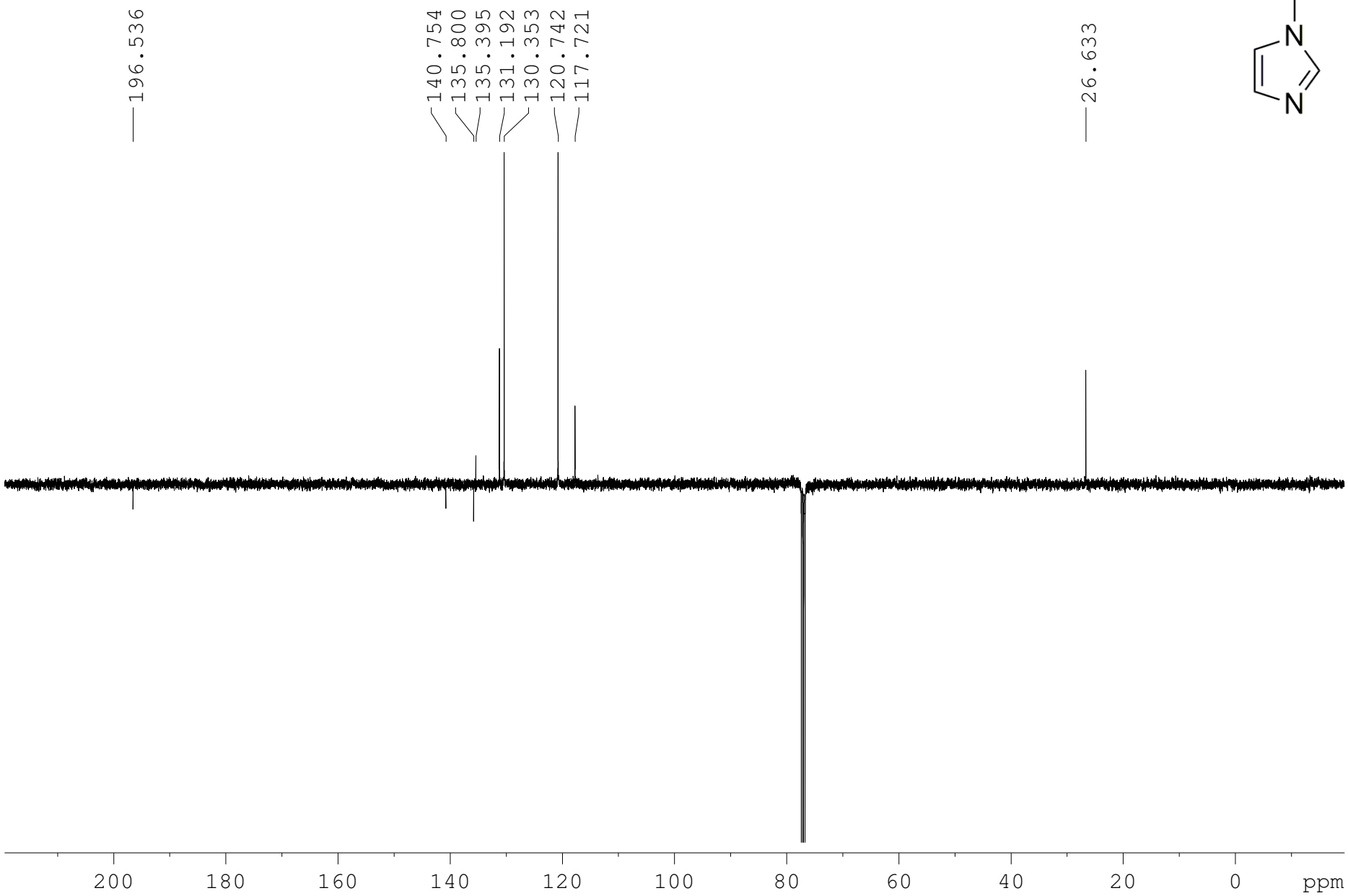


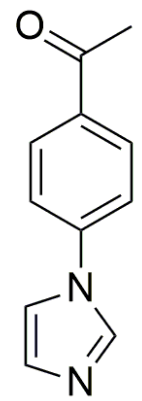
1-(4-(1H-imidazol-1-yl)phenyl)ethanone (3e)



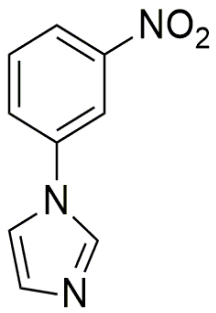


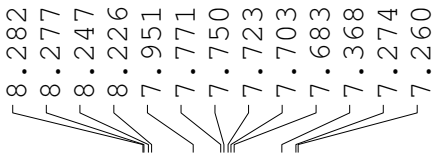
1-(4-(1H-imidazol-1-yl)phenyl)ethanone (3e)

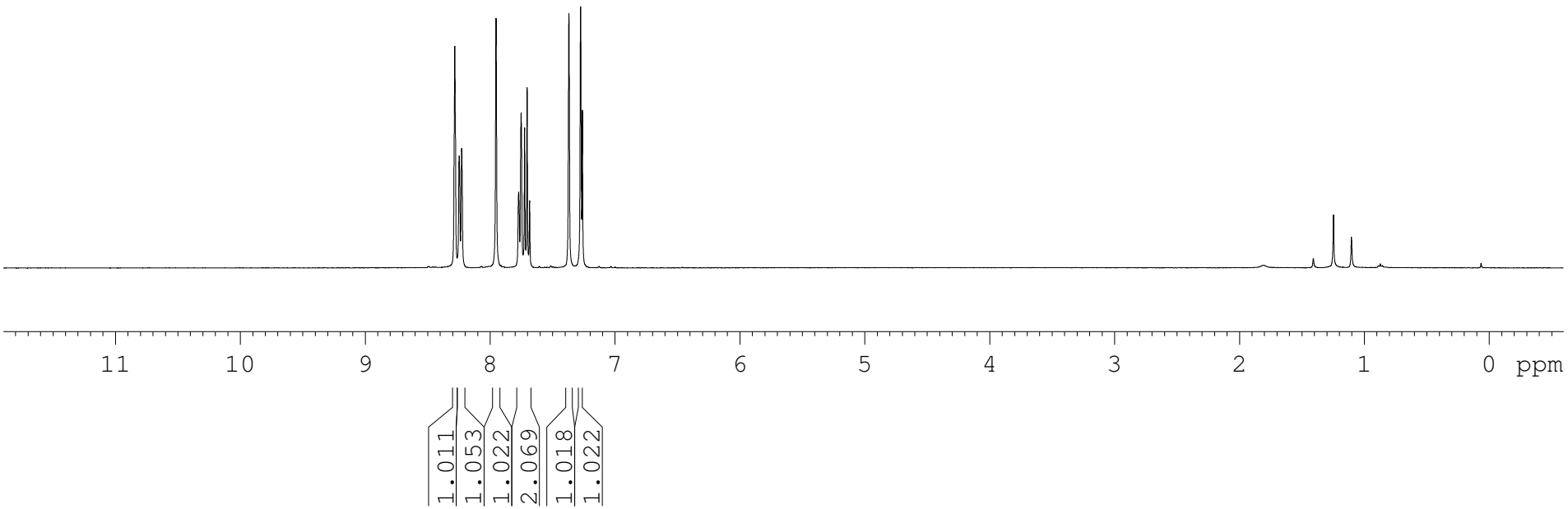




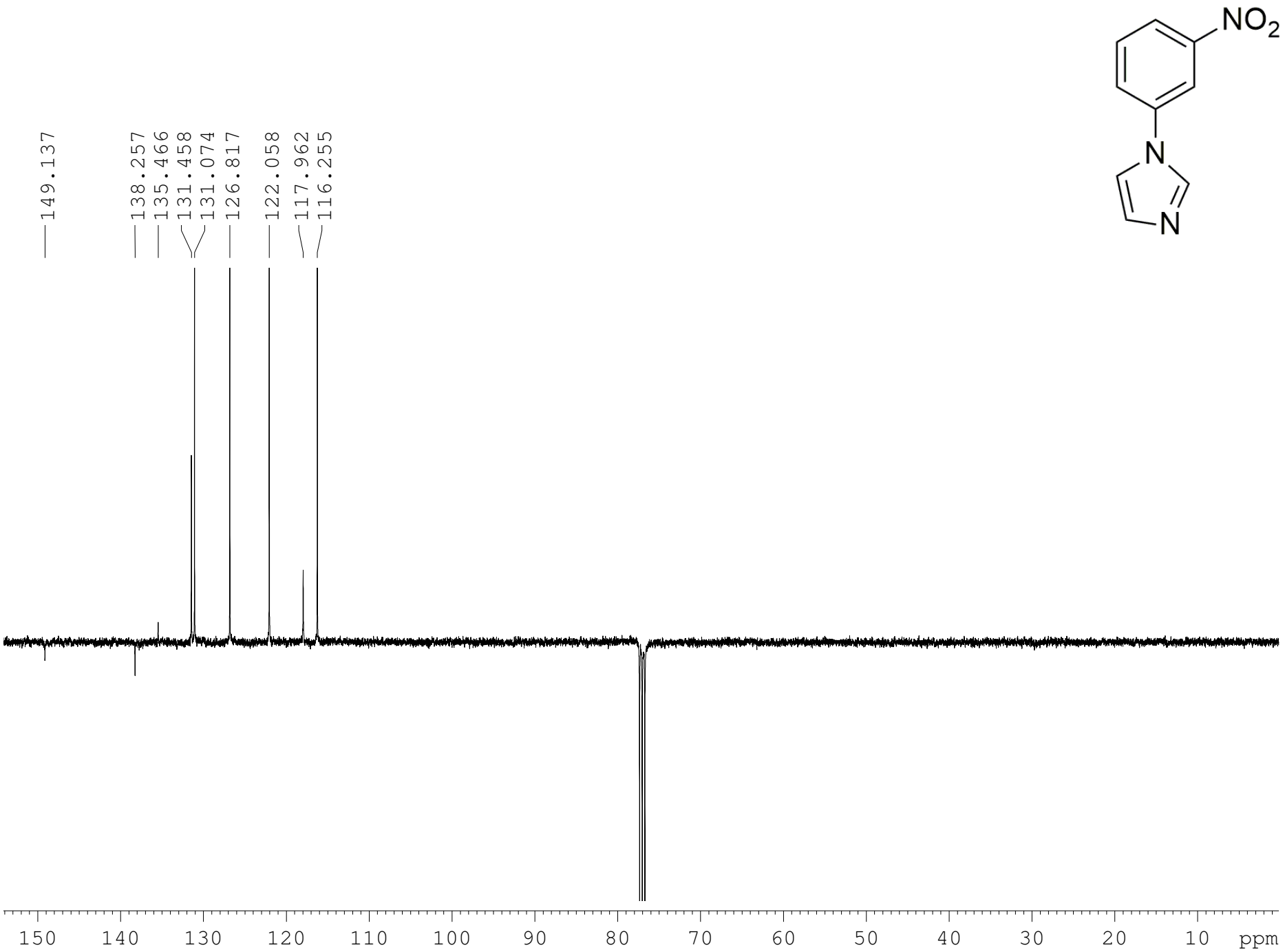
1-(3-nitrophenyl)-1H-imidazole (3f)



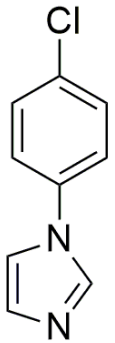


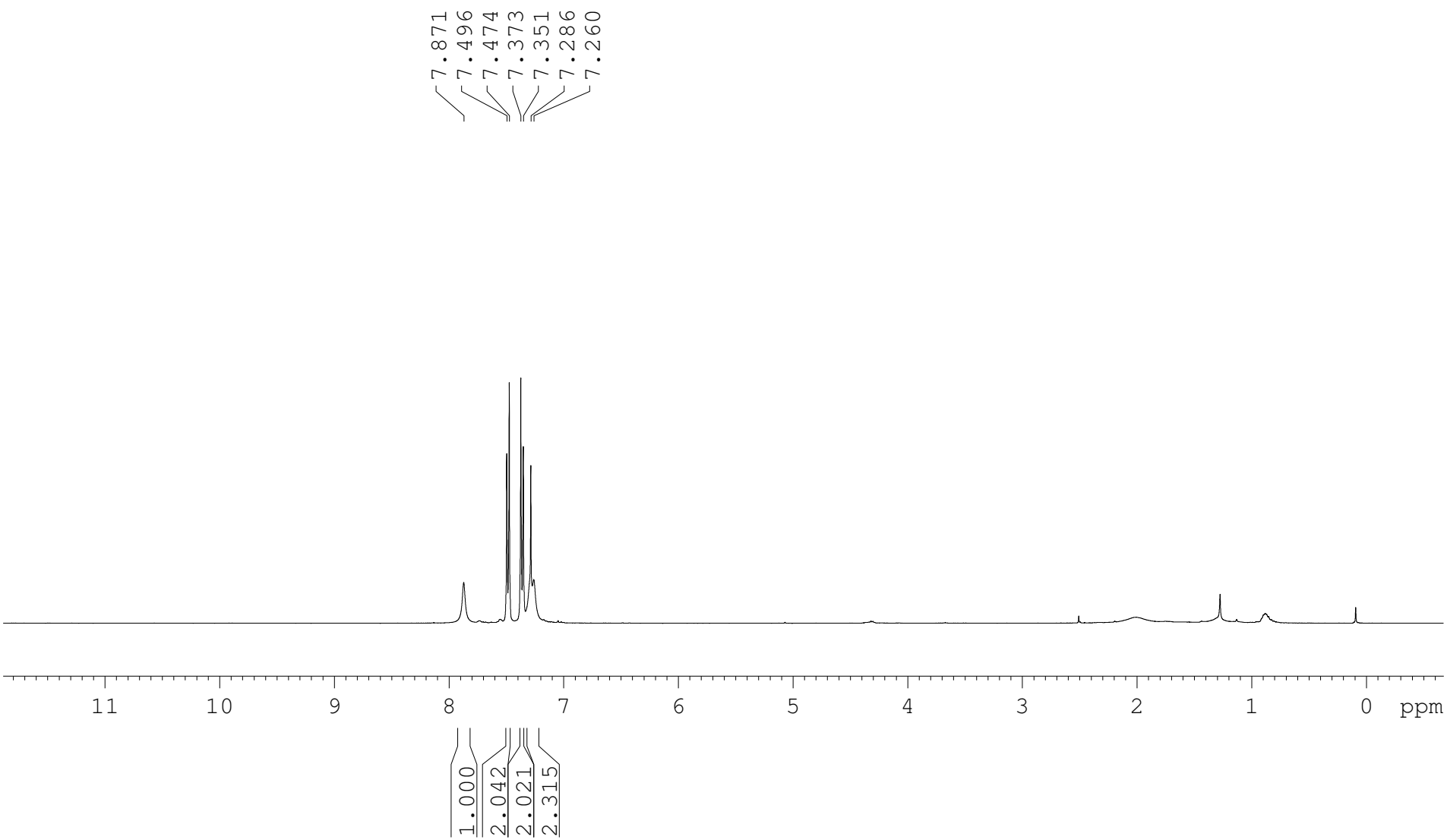


1-(3-nitrophenyl)-1H-imidazole (3f)

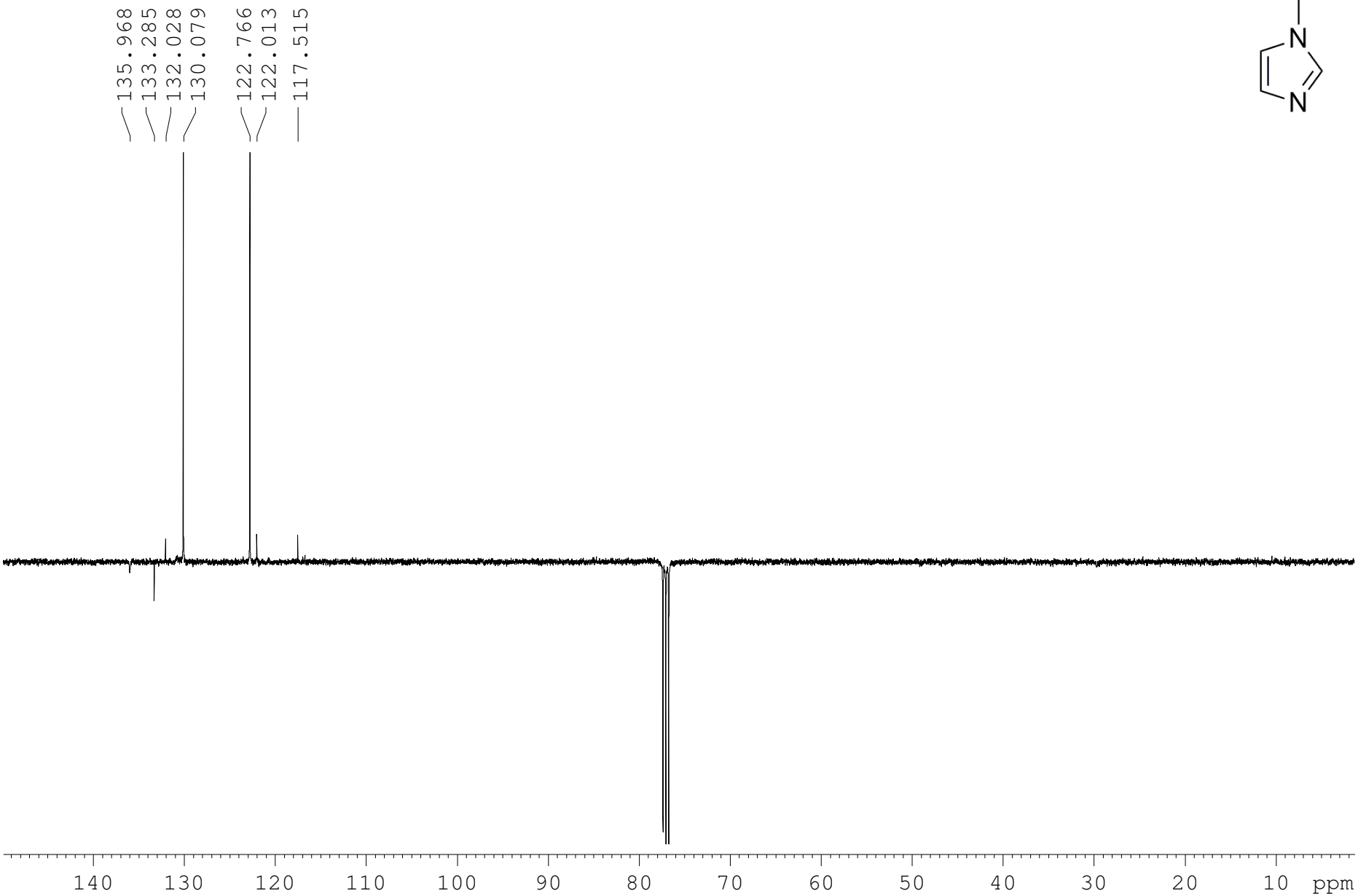


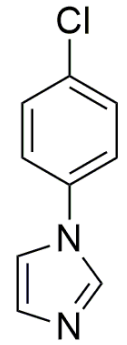
1-(4-chlorophenyl)-1H-imidazole (3g)



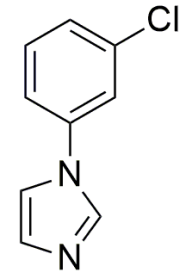


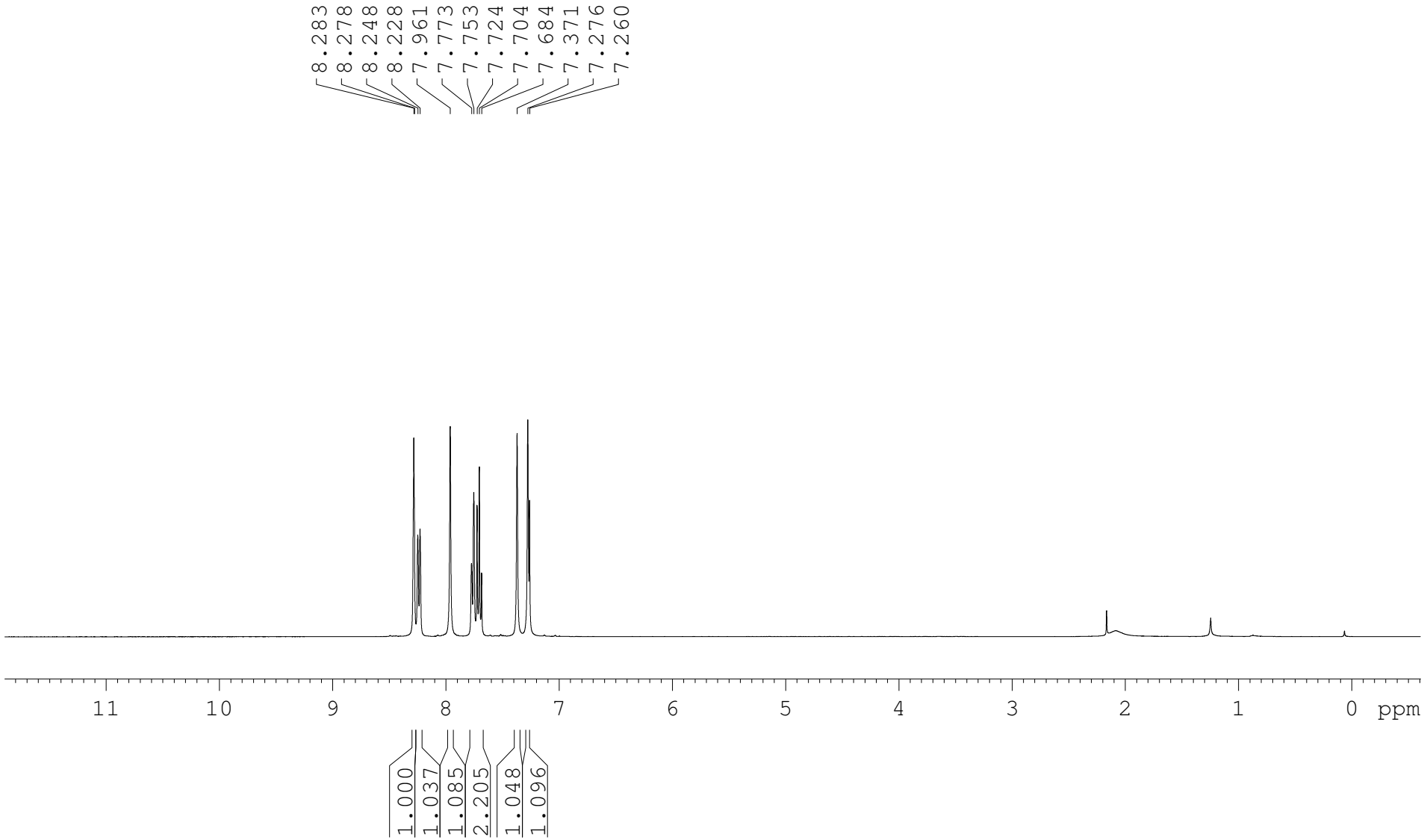
1-(4-chlorophenyl)-1H-imidazole (3g)



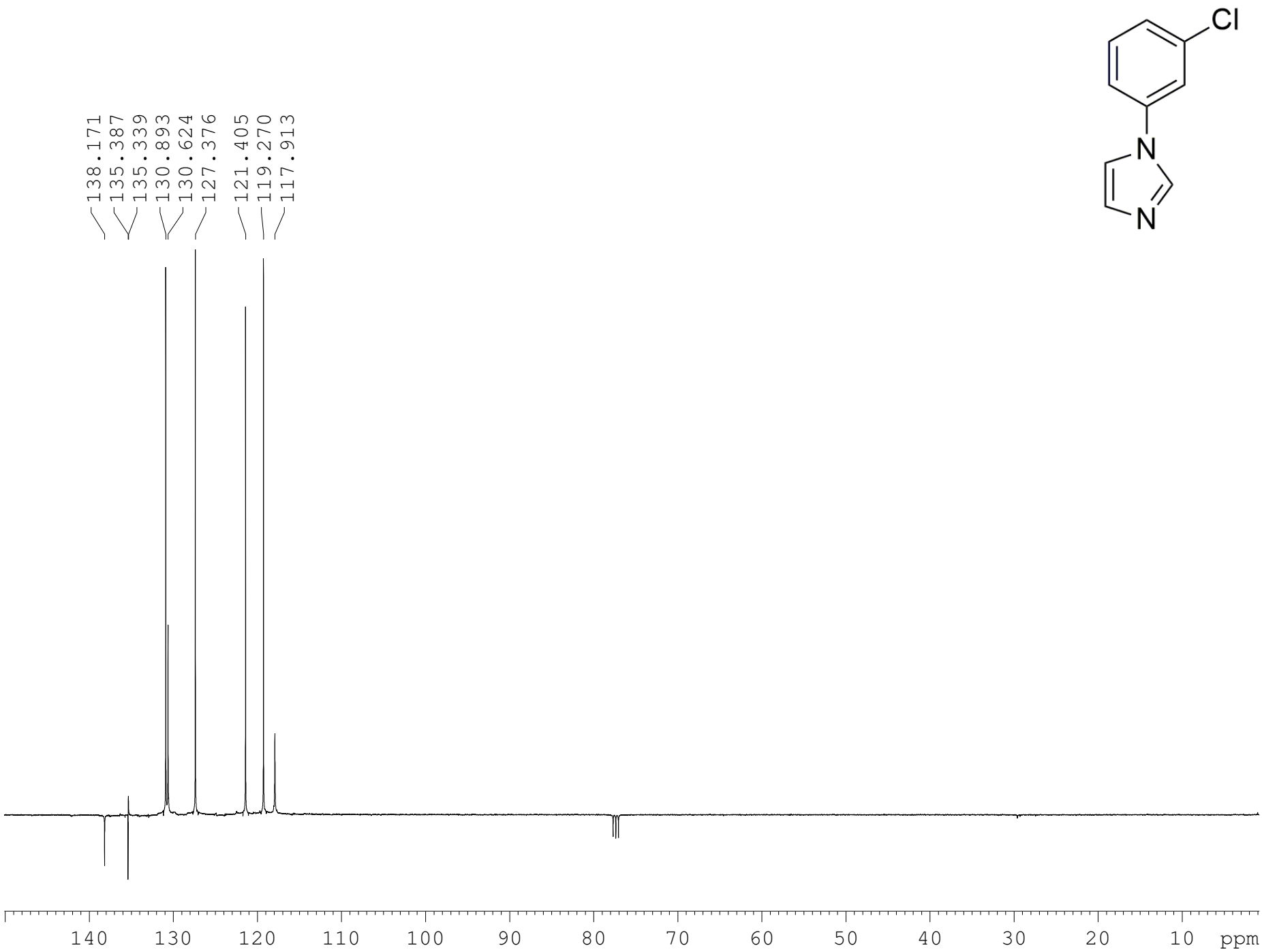


1-(3-chlorophenyl)-1H-imidazole (3h)

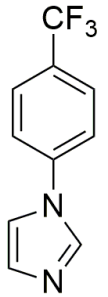


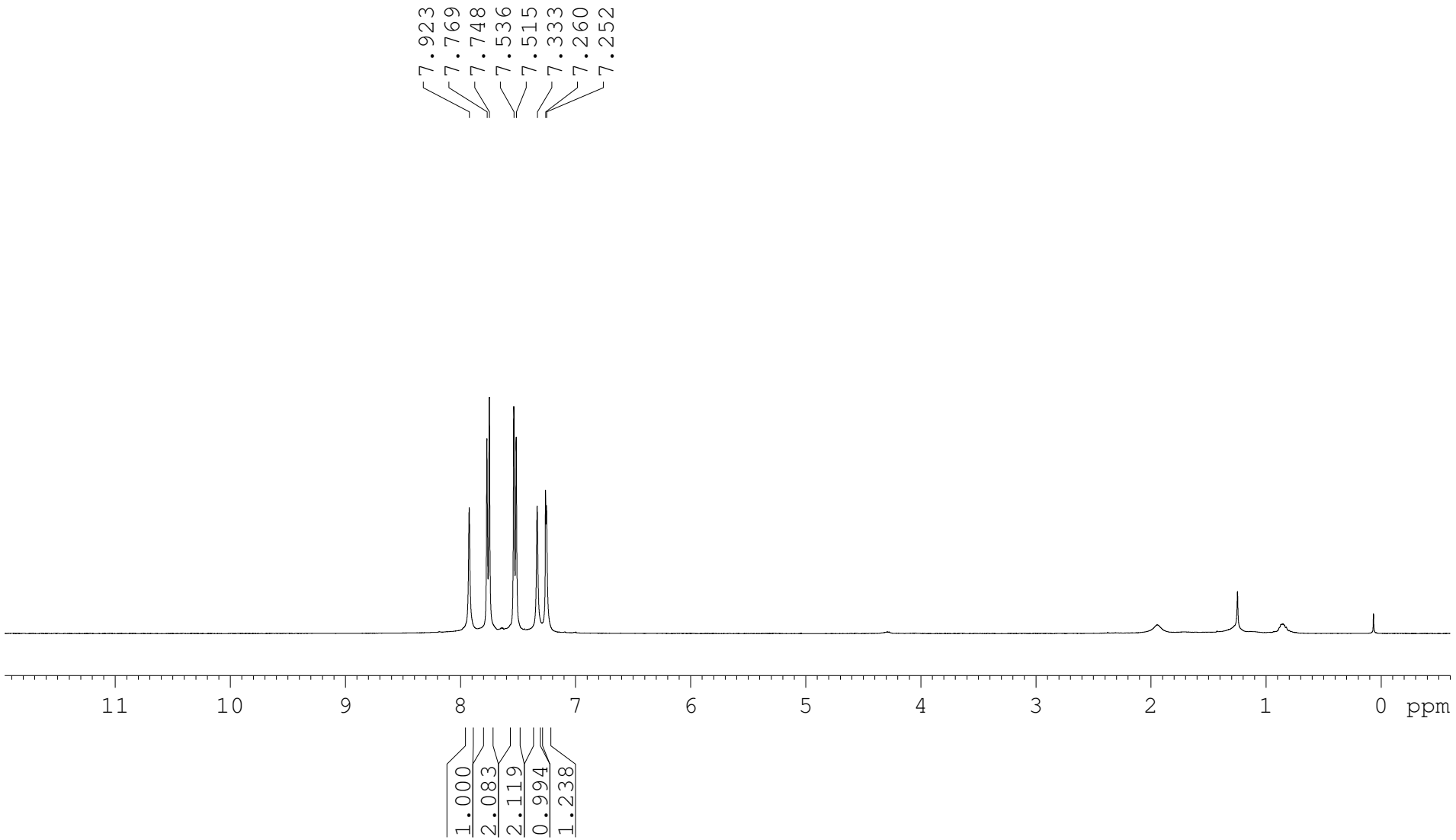


1-(3-chlorophenyl)-1H-imidazole (3h)

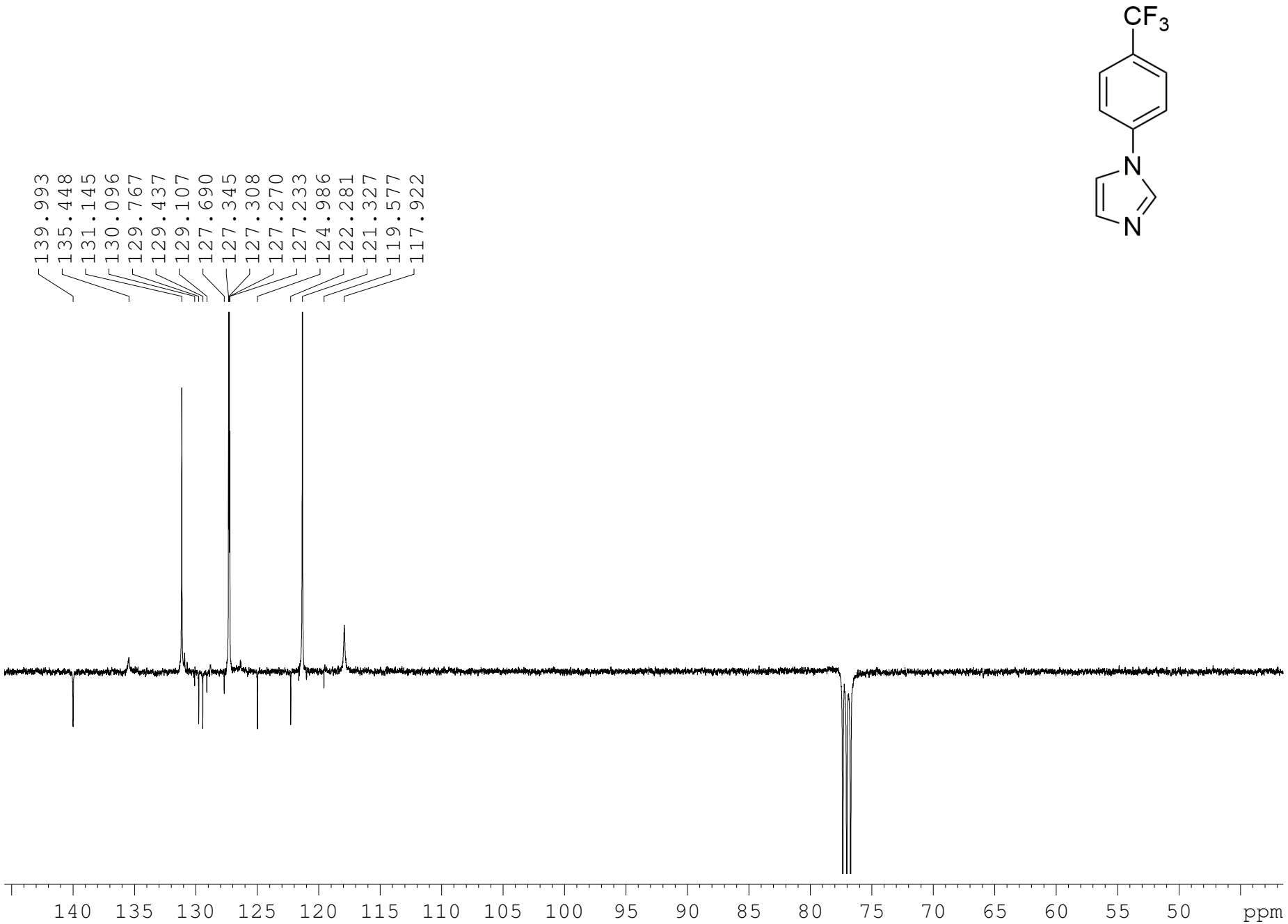


1-(4-(trifluoromethyl)phenyl)-1H-imidazole (3i)

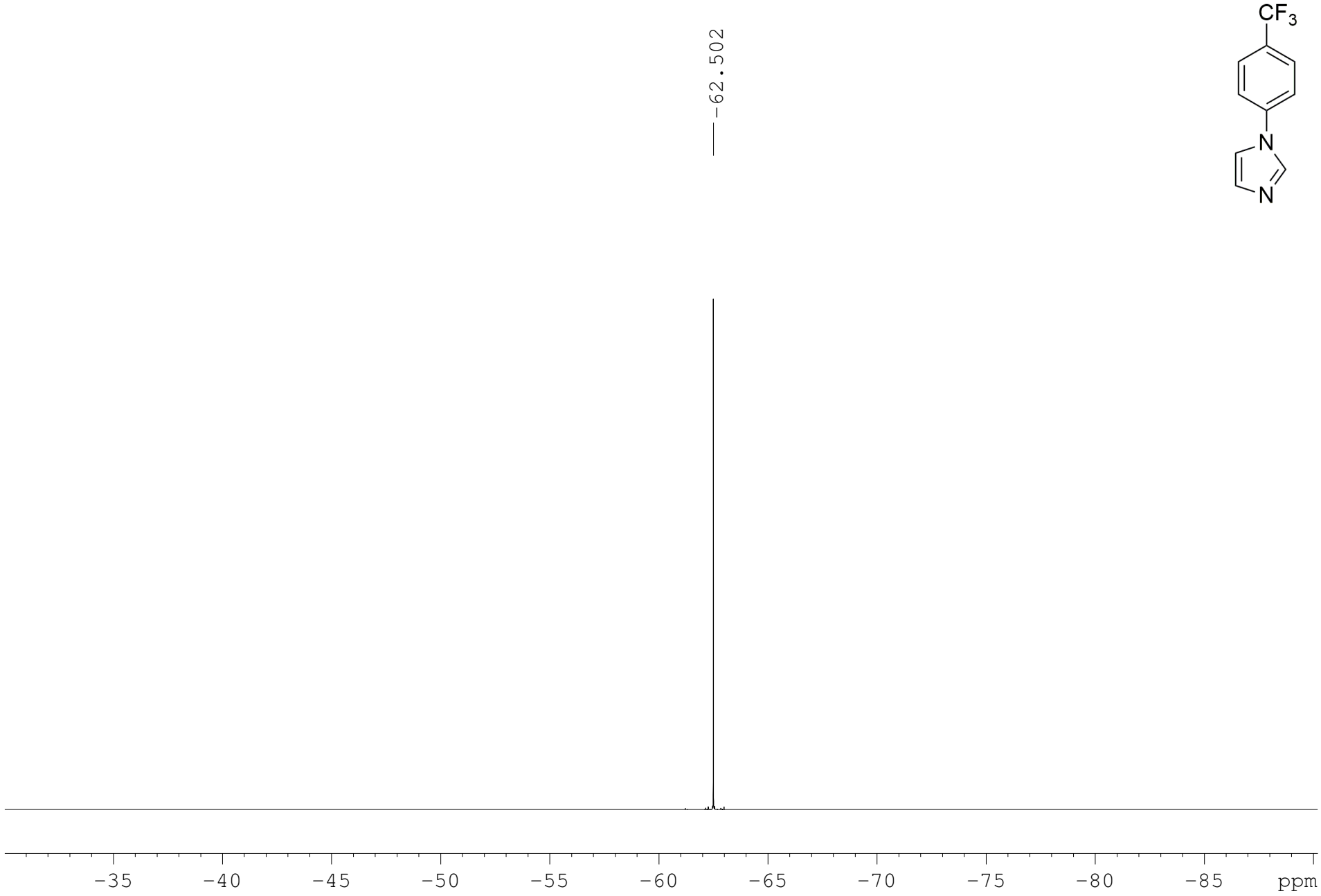




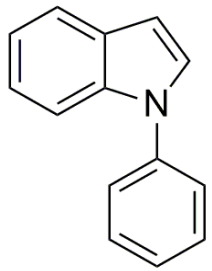
1-(4-(trifluoromethyl)phenyl)-1H-imidazole (3i)

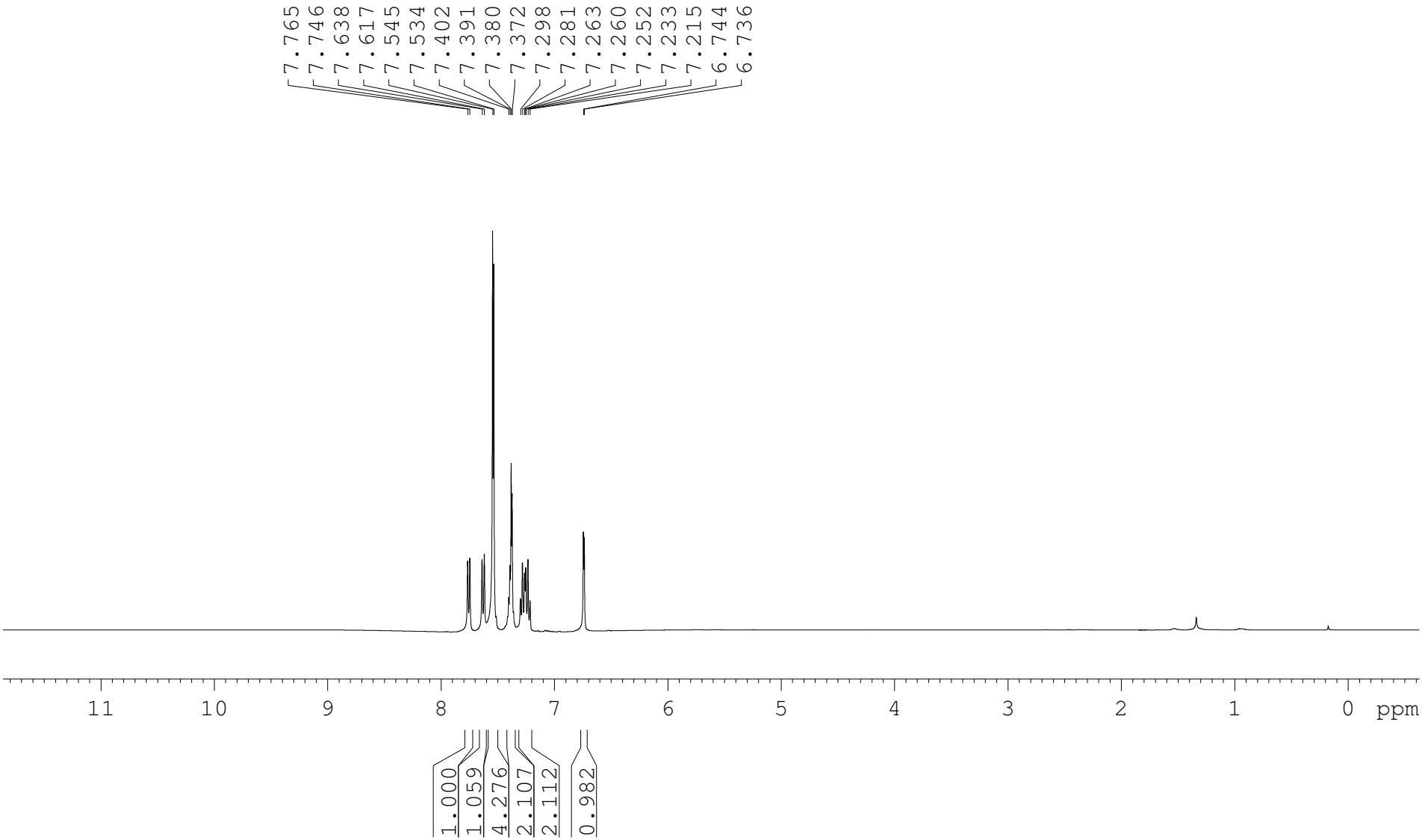


1-(4-(trifluoromethyl)phenyl)-1H-imidazole (3i)

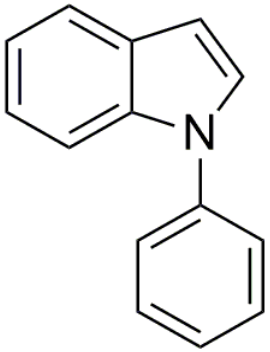


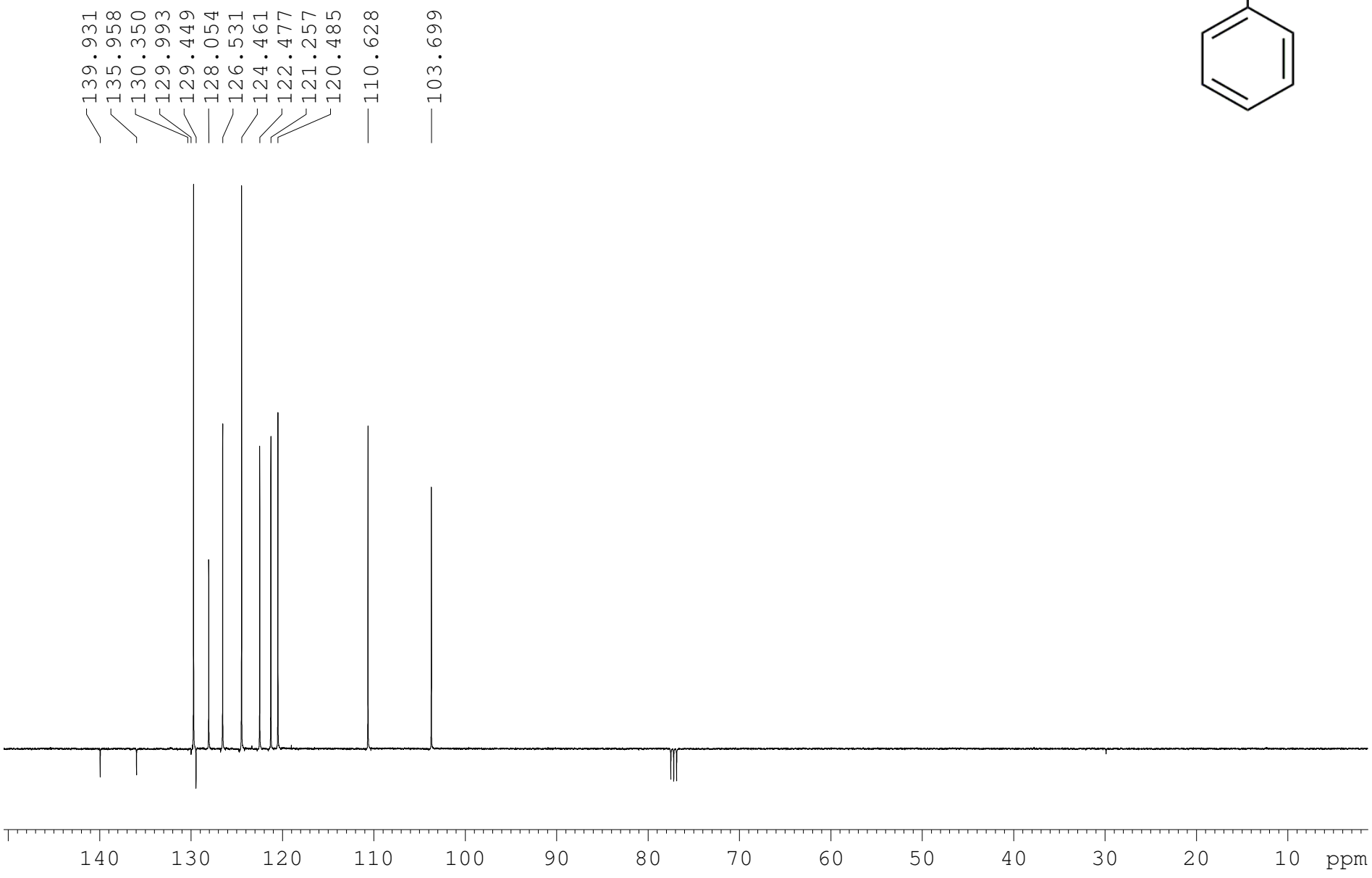
1-phenyl-1H-indole (5a)



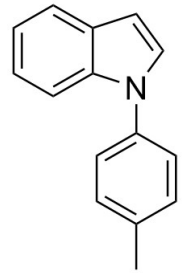


1-phenyl-1H-indole (5a)

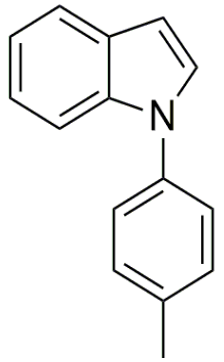


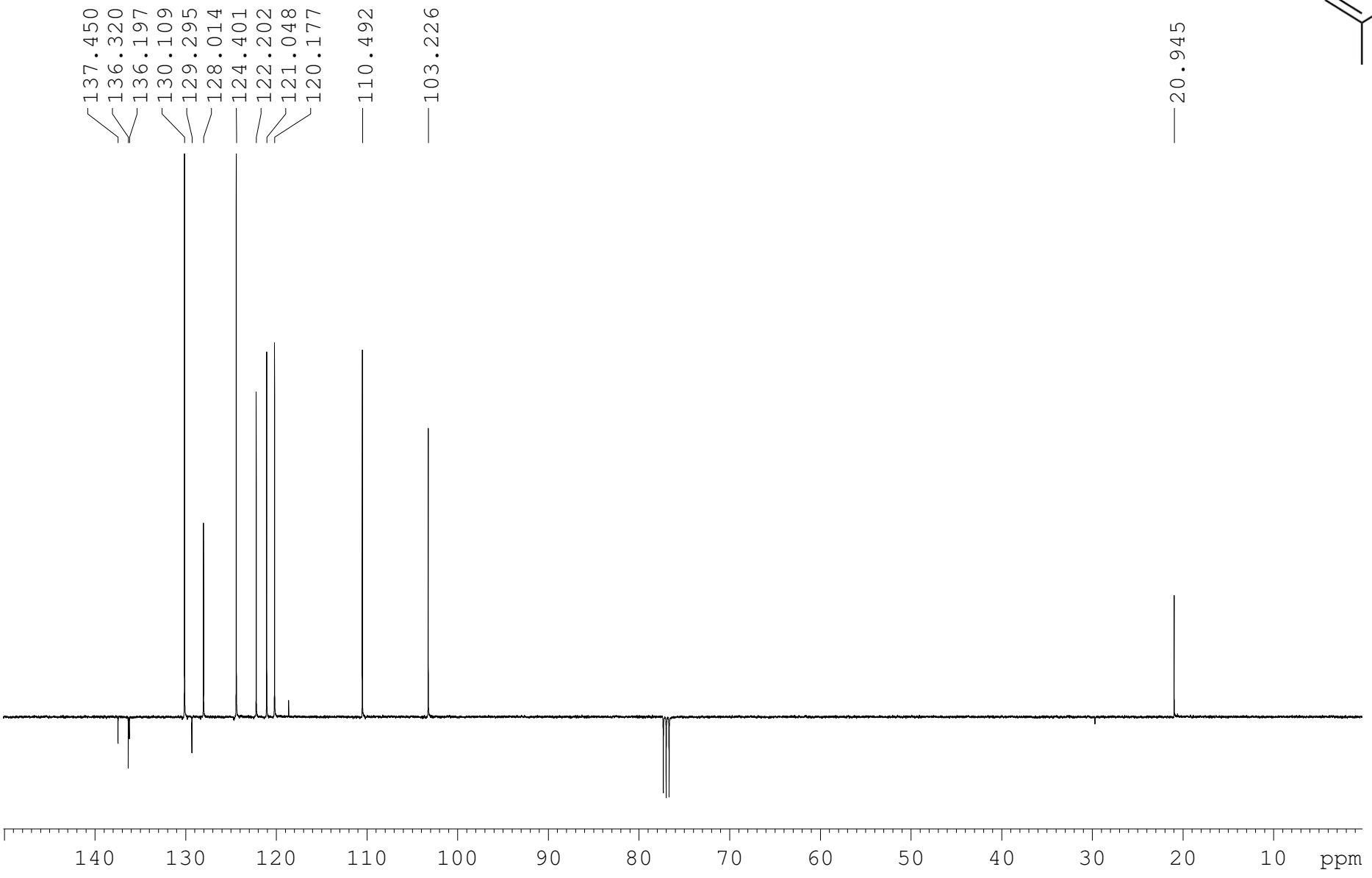


1-(p-tolyl)-1H-indole (5b)

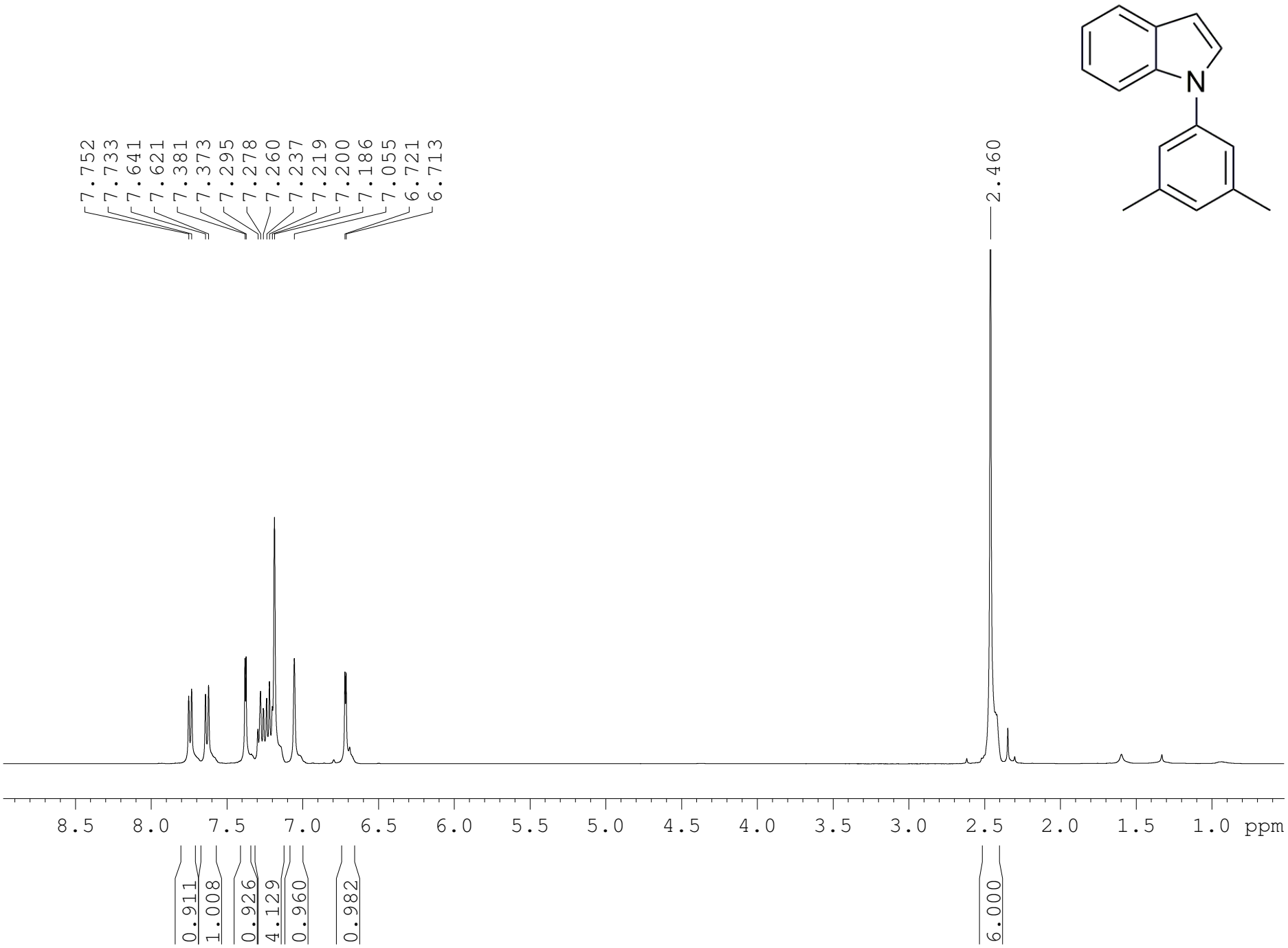


1-(p-tolyl)-1H-indole (5b)

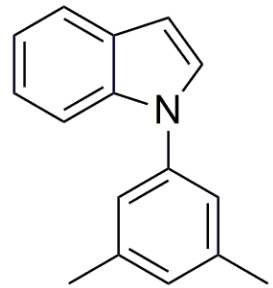


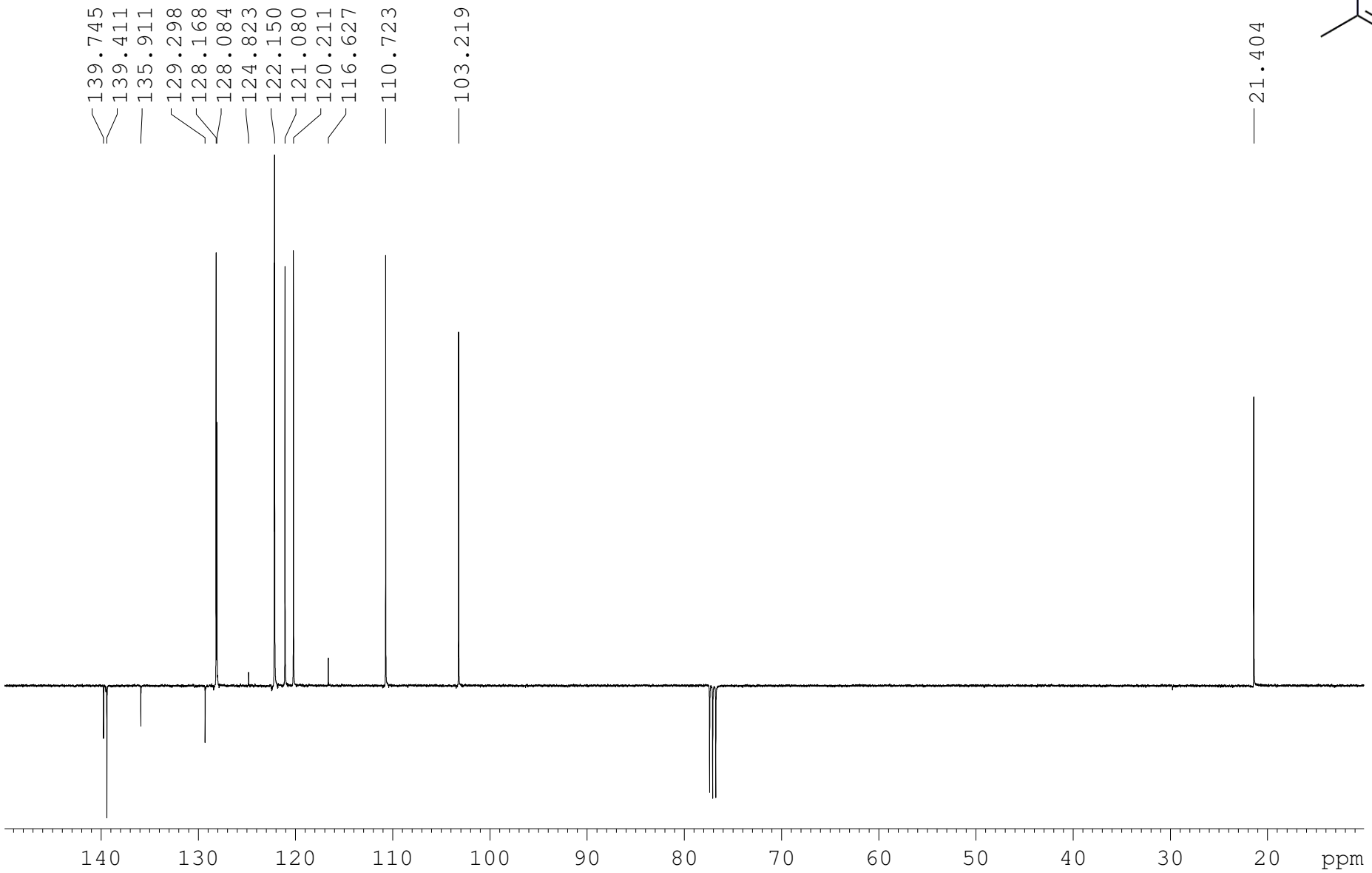


1-(3,5-dimethylphenyl)-1H-indole (5c)

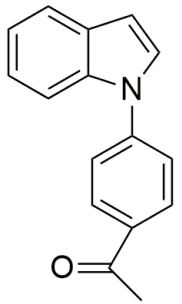


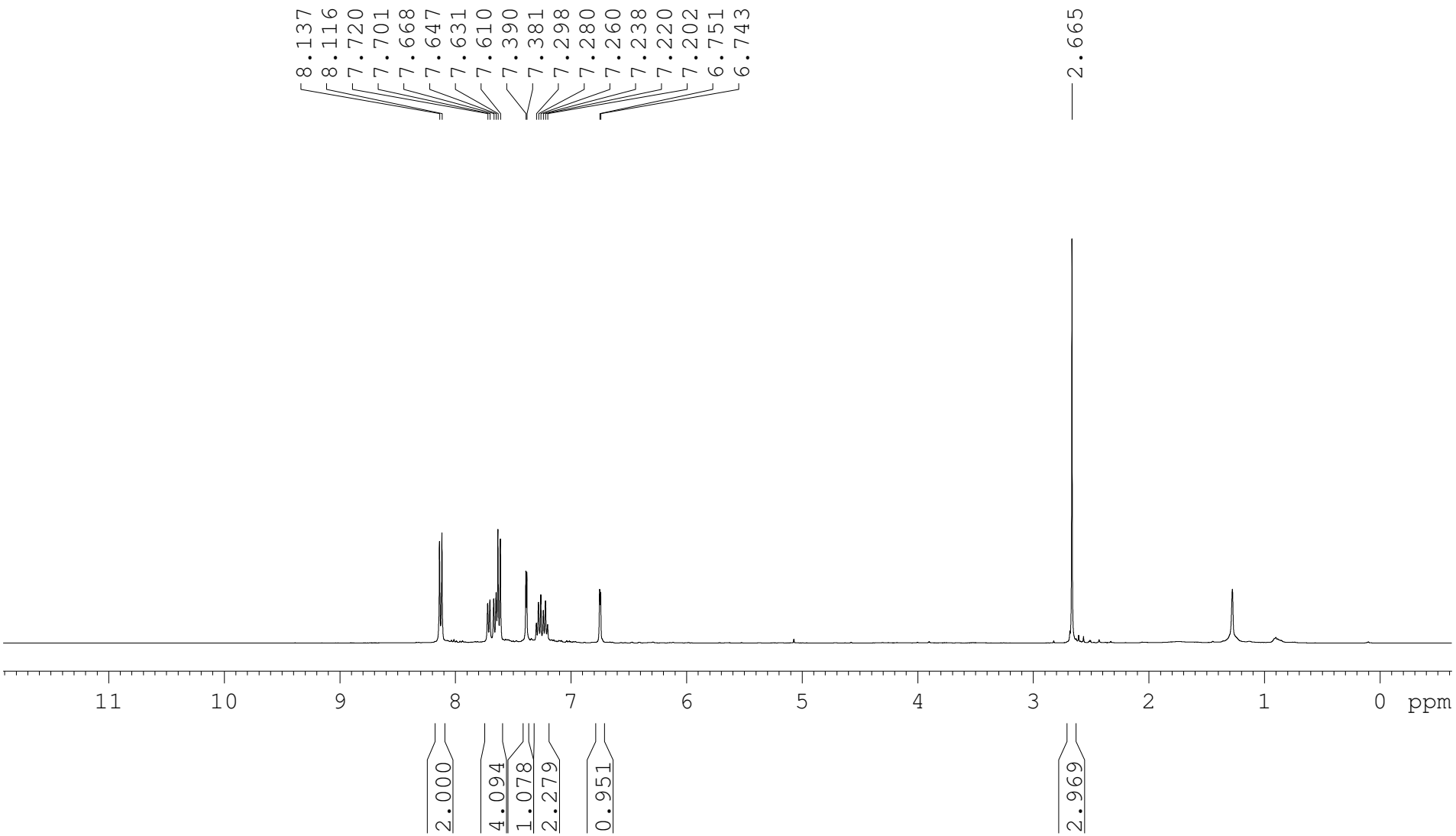
1-(3,5-dimethylphenyl)-1H-indole (5c)



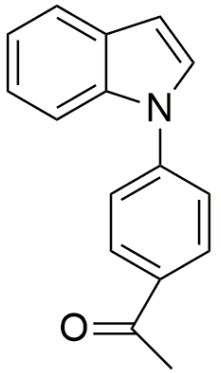


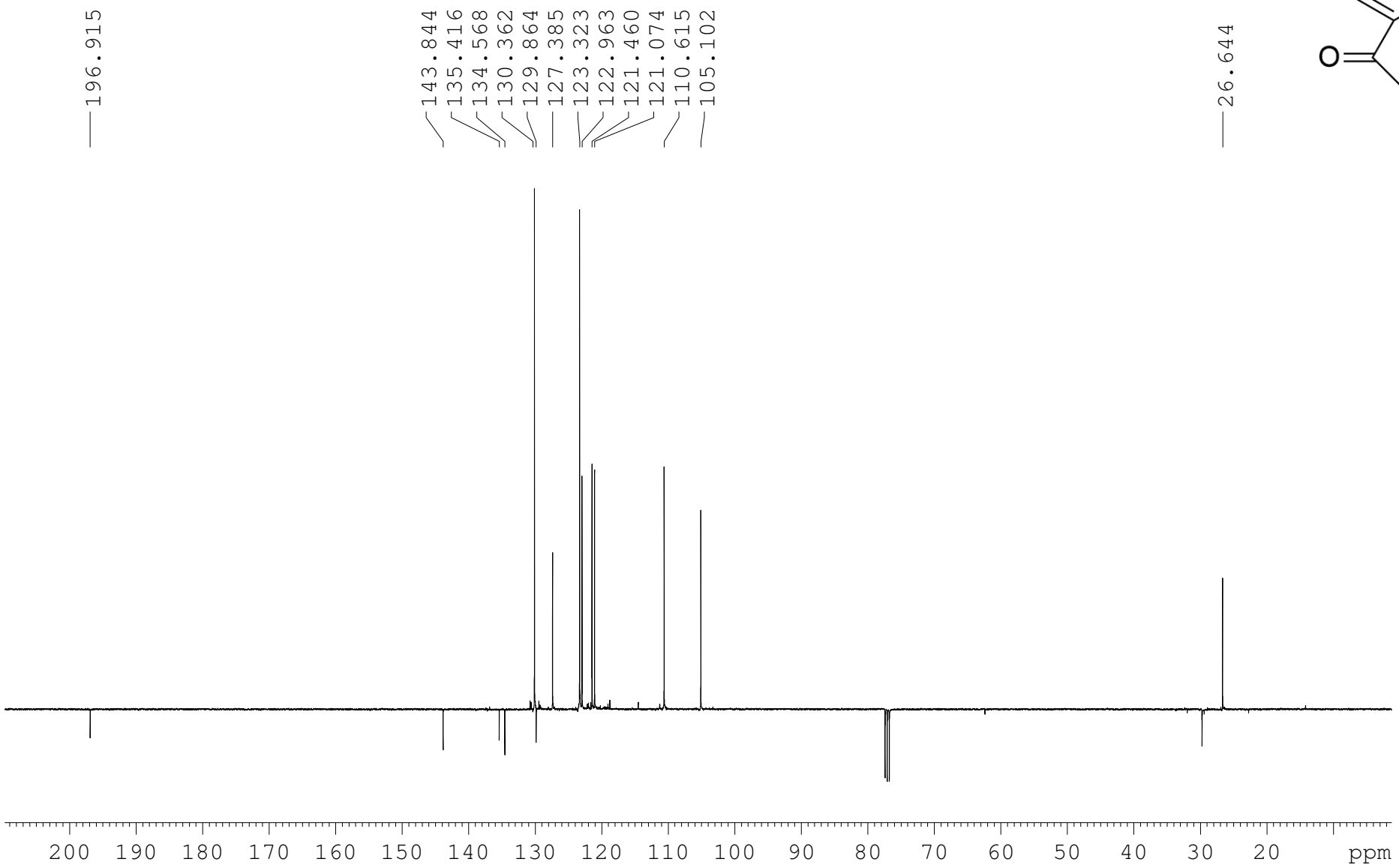
1-(4-(1H-indol-1-yl)phenyl)ethanone (5d)



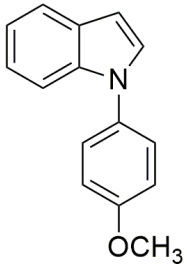


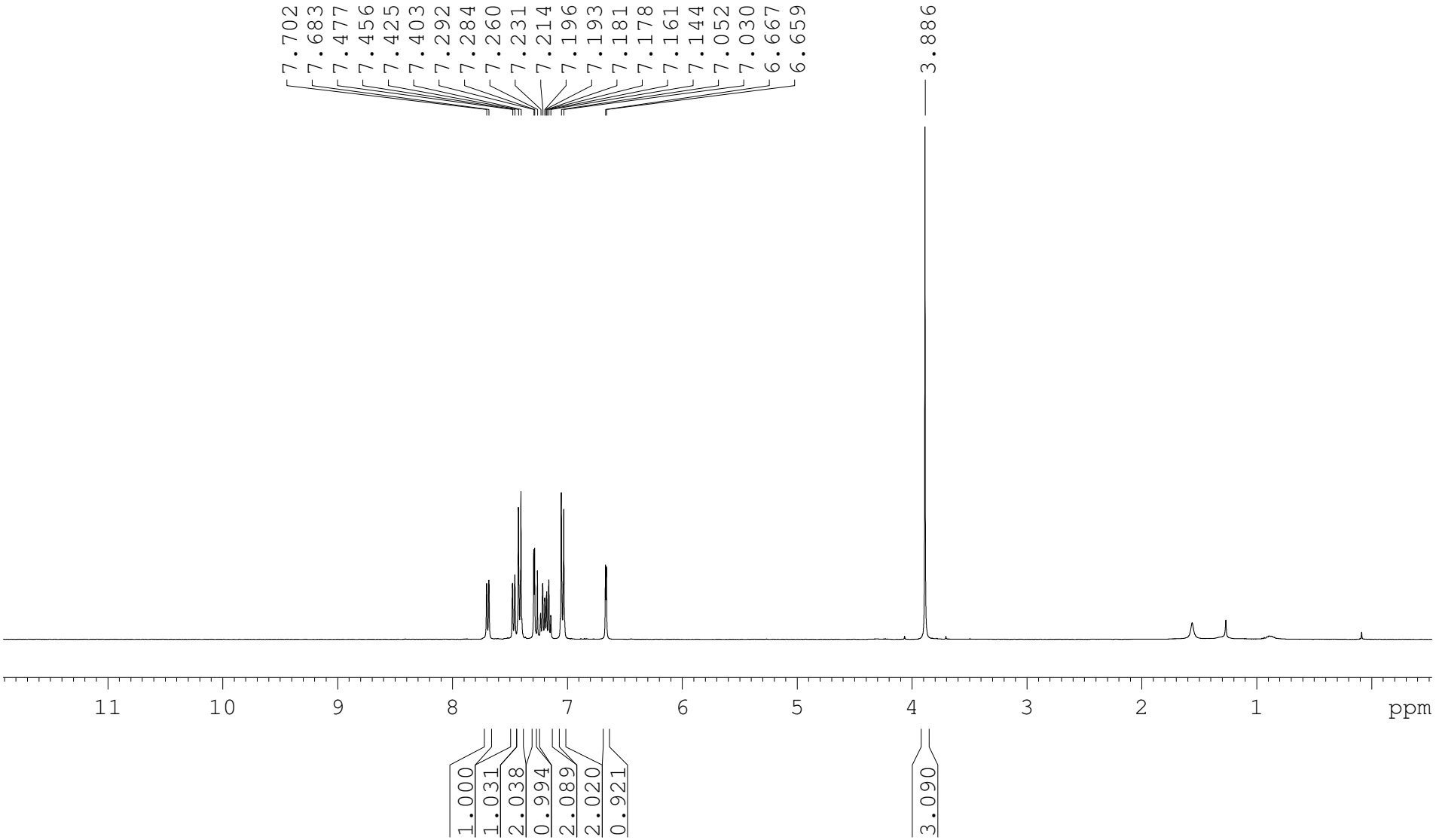
1-(4-(1H-indol-1-yl)phenyl)ethanone (5d)



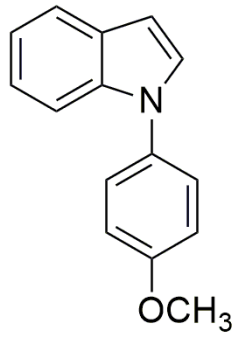


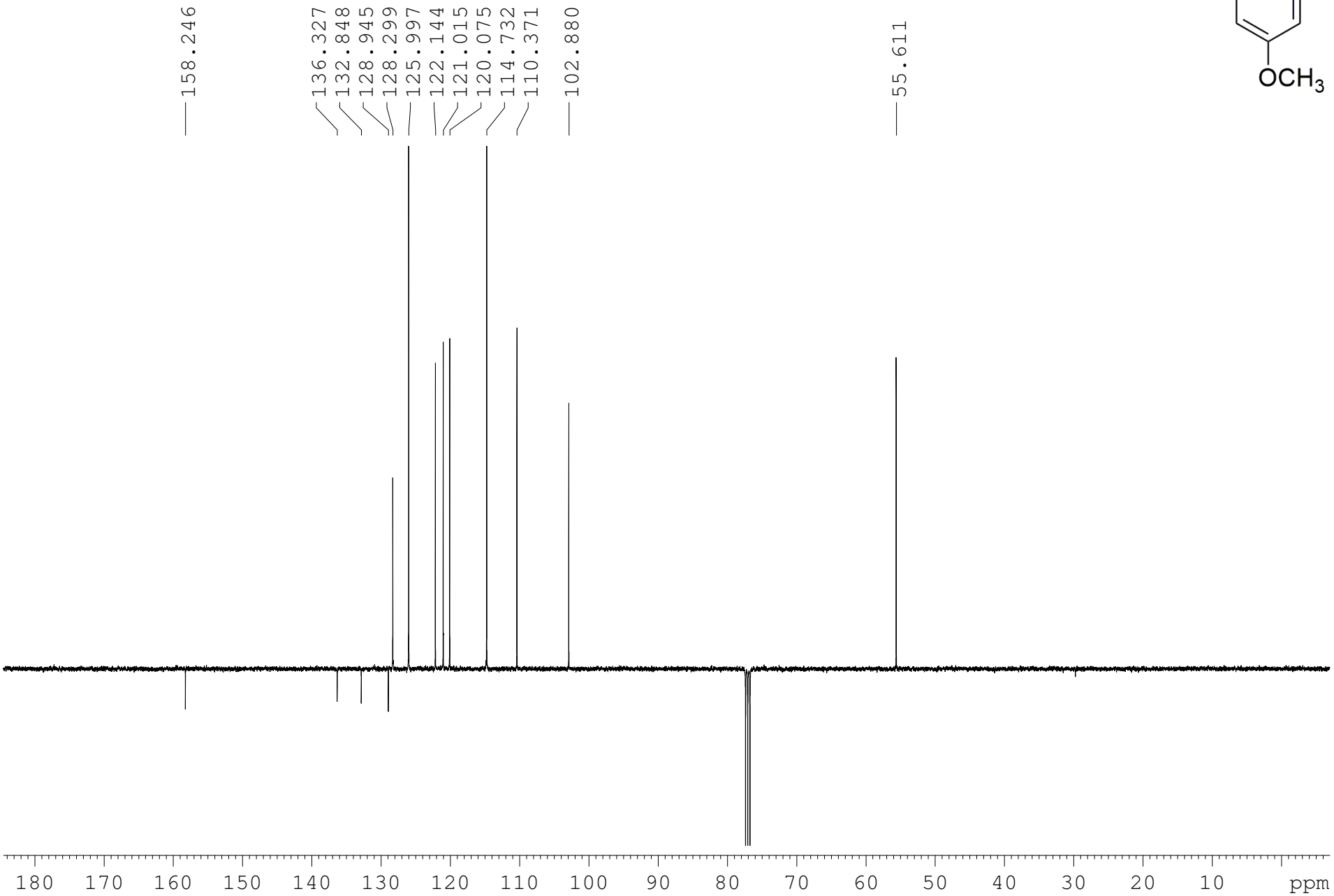
1-(4-methoxyphenyl)-1H-indole (5e)



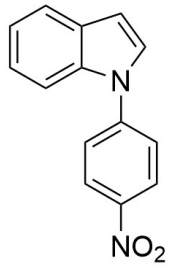


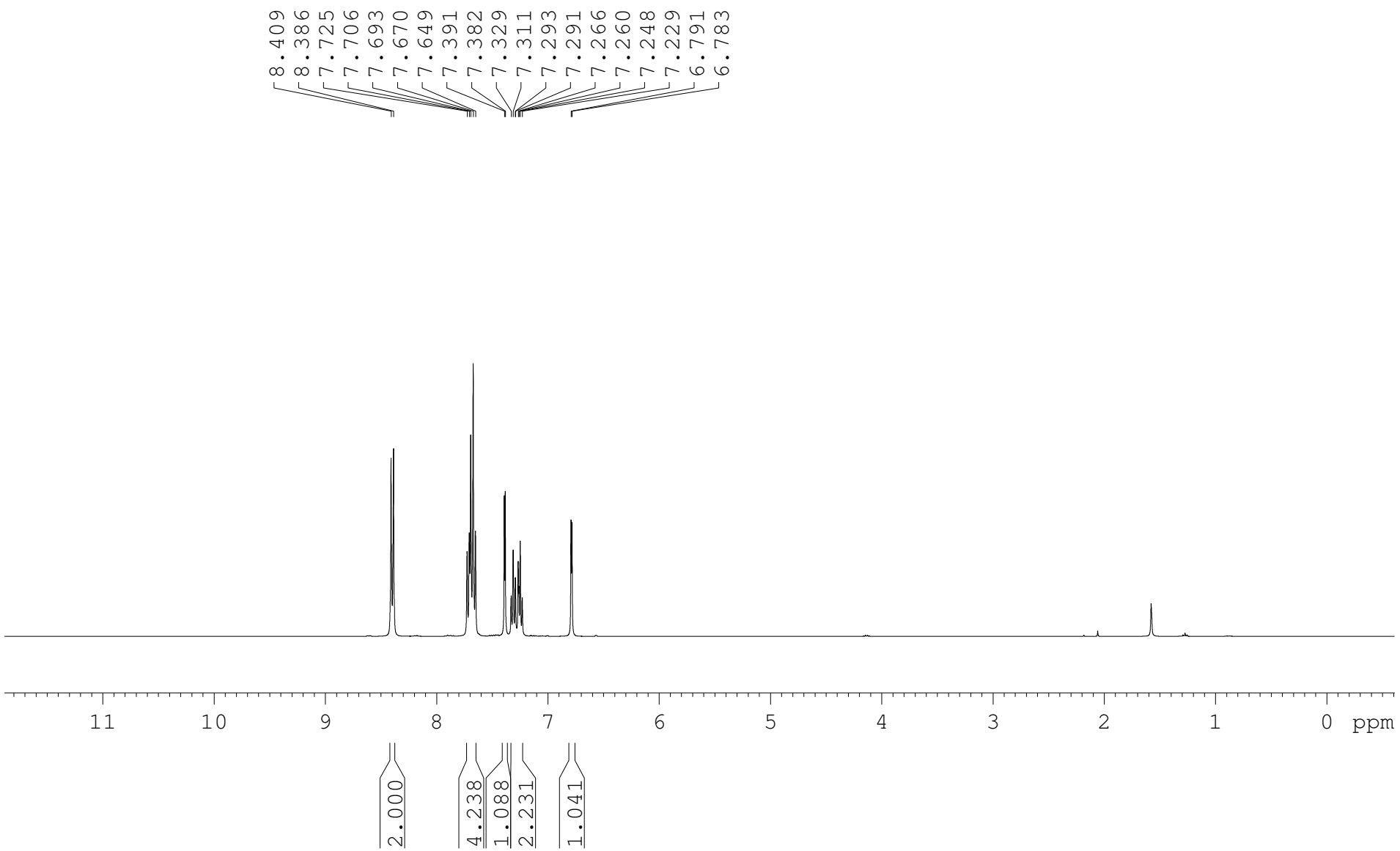
1-(4-methoxyphenyl)-1H-indole (5e)



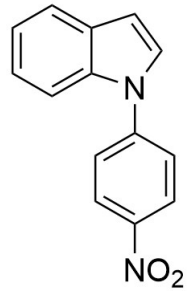


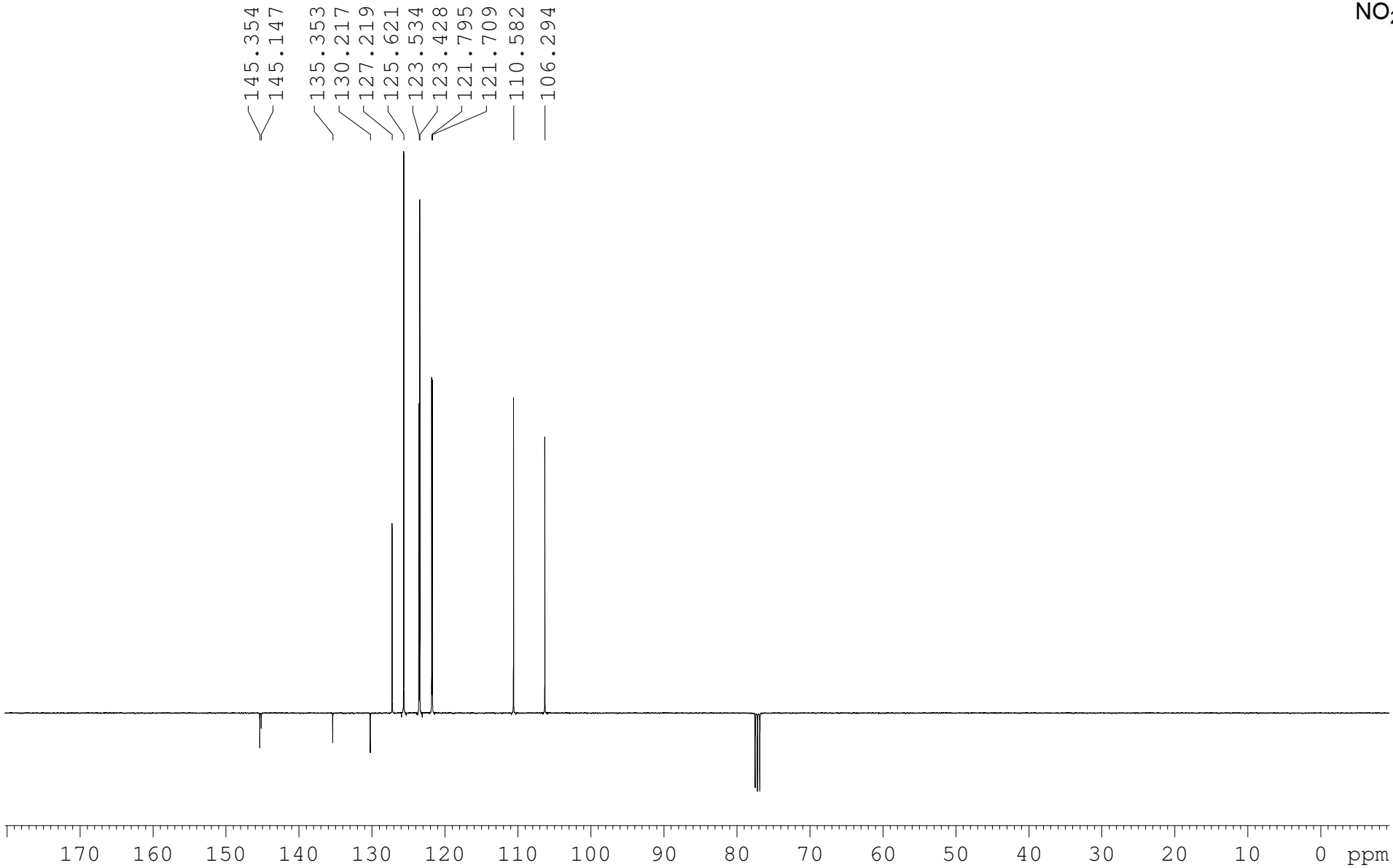
1-(4-nitrophenyl)-1H-indole (5f)



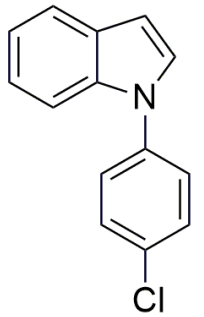


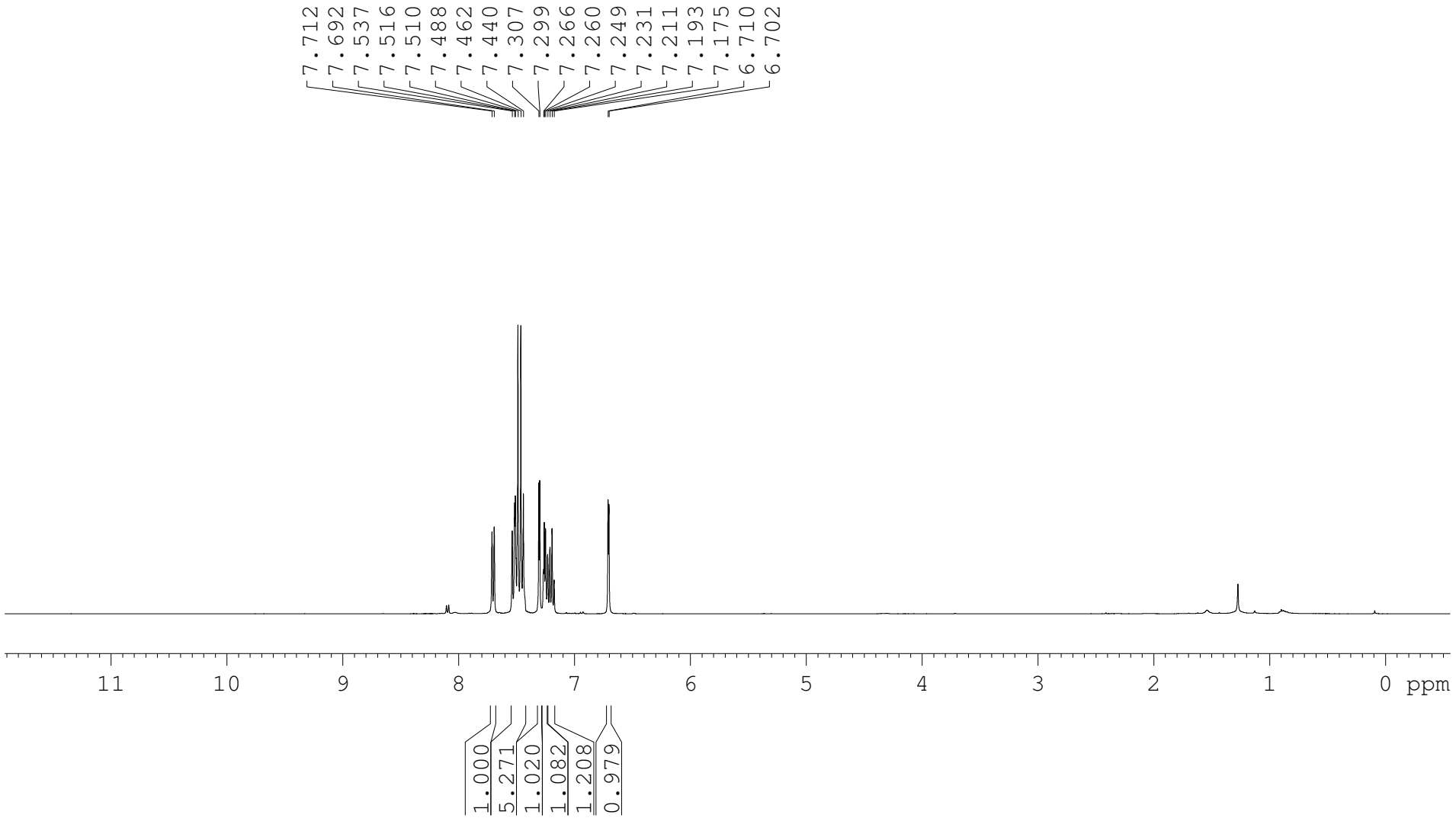
1-(4-nitrophenyl)-1H-indole (5f)



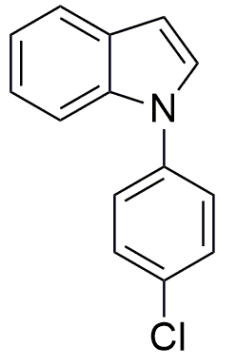


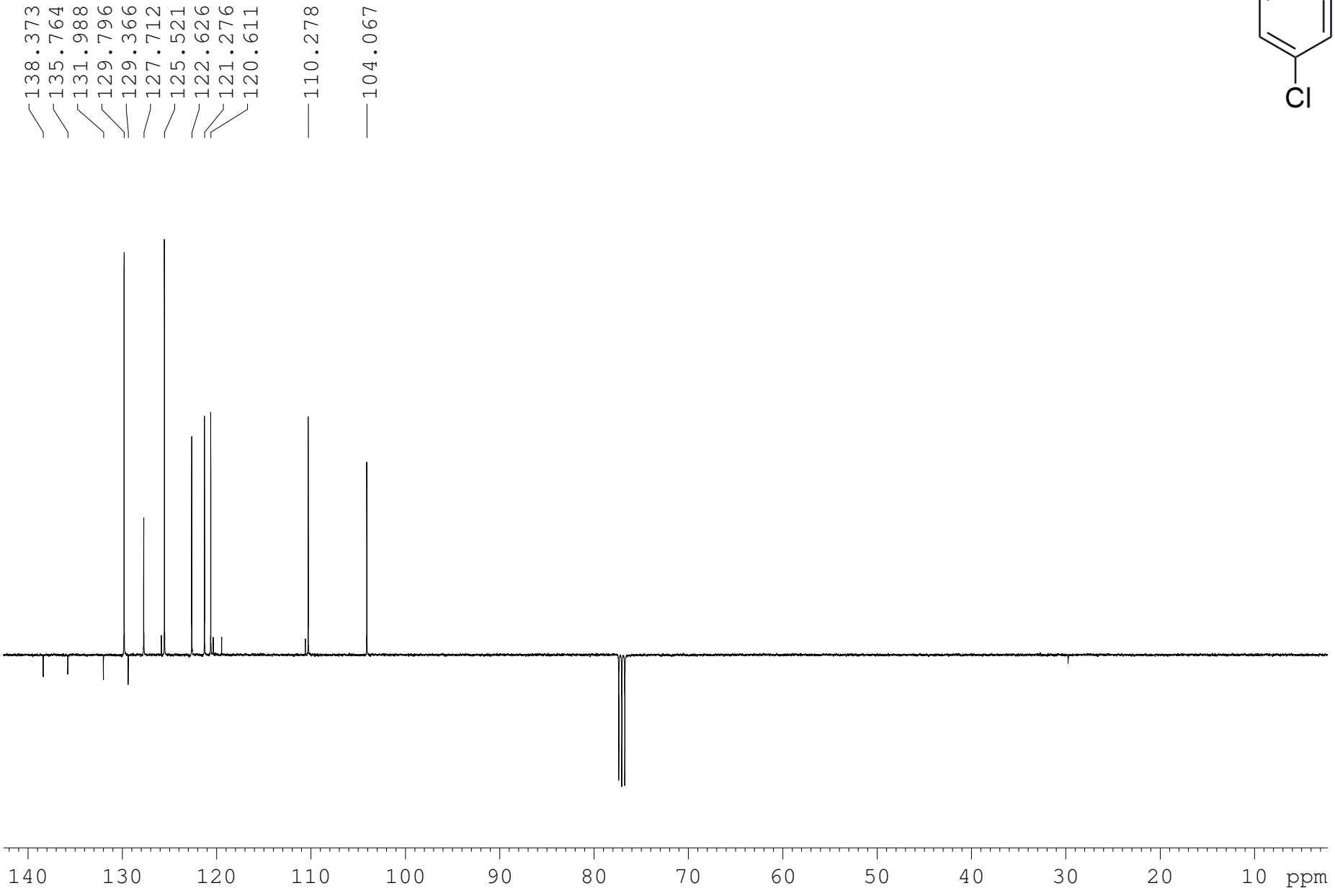
1-(4-chlorophenyl)-1H-indole (5g)



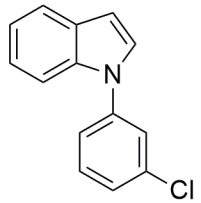


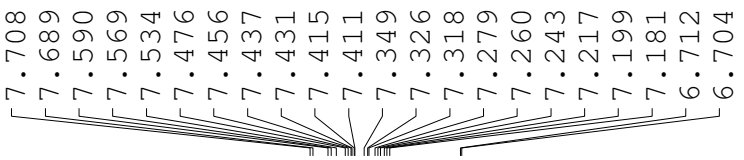
1-(4-chlorophenyl)-1H-indole (5g)

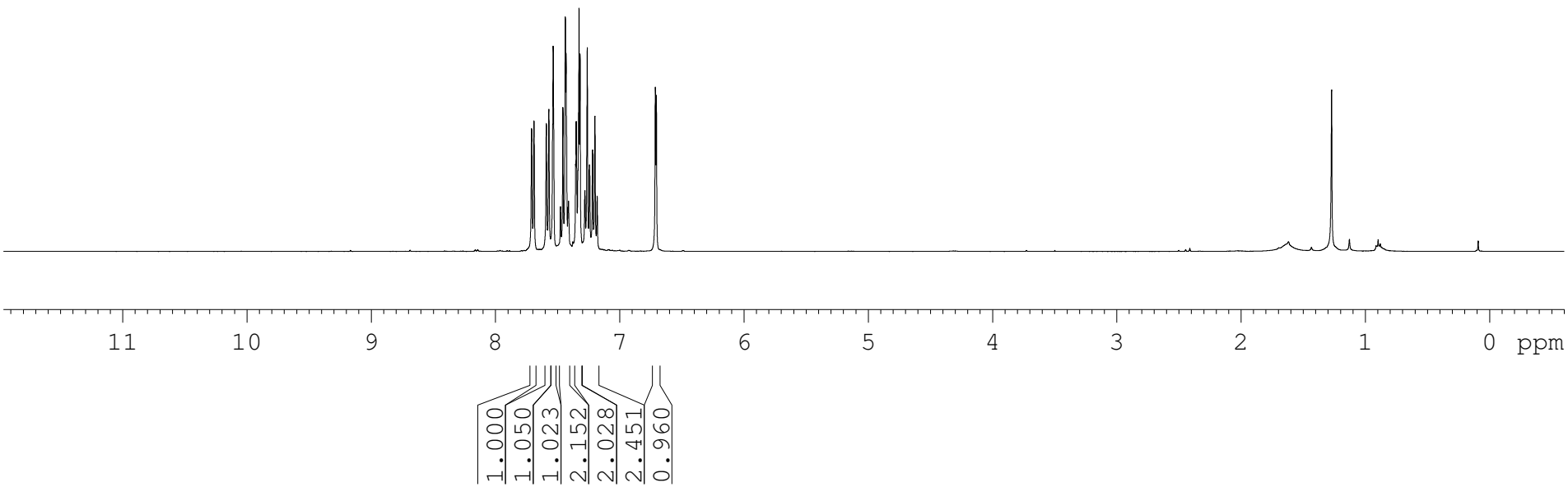




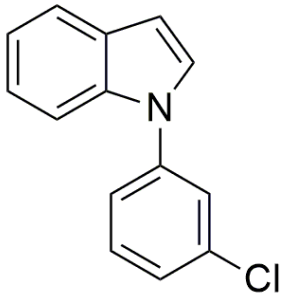
1-(3-chlorophenyl)-1H-indole (5h)

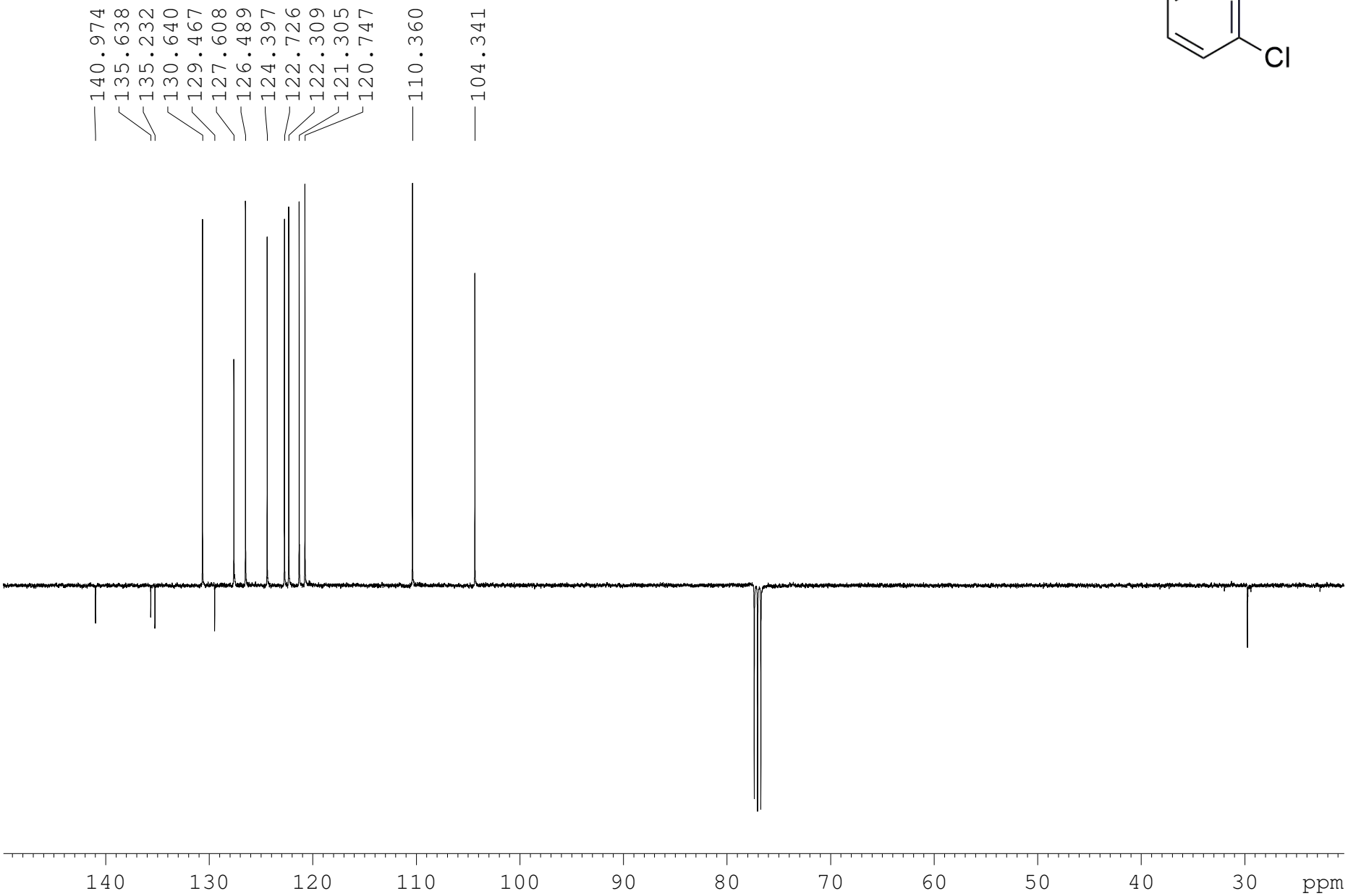




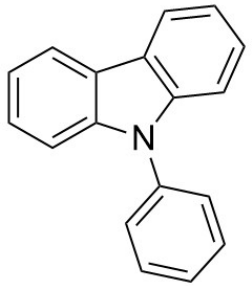


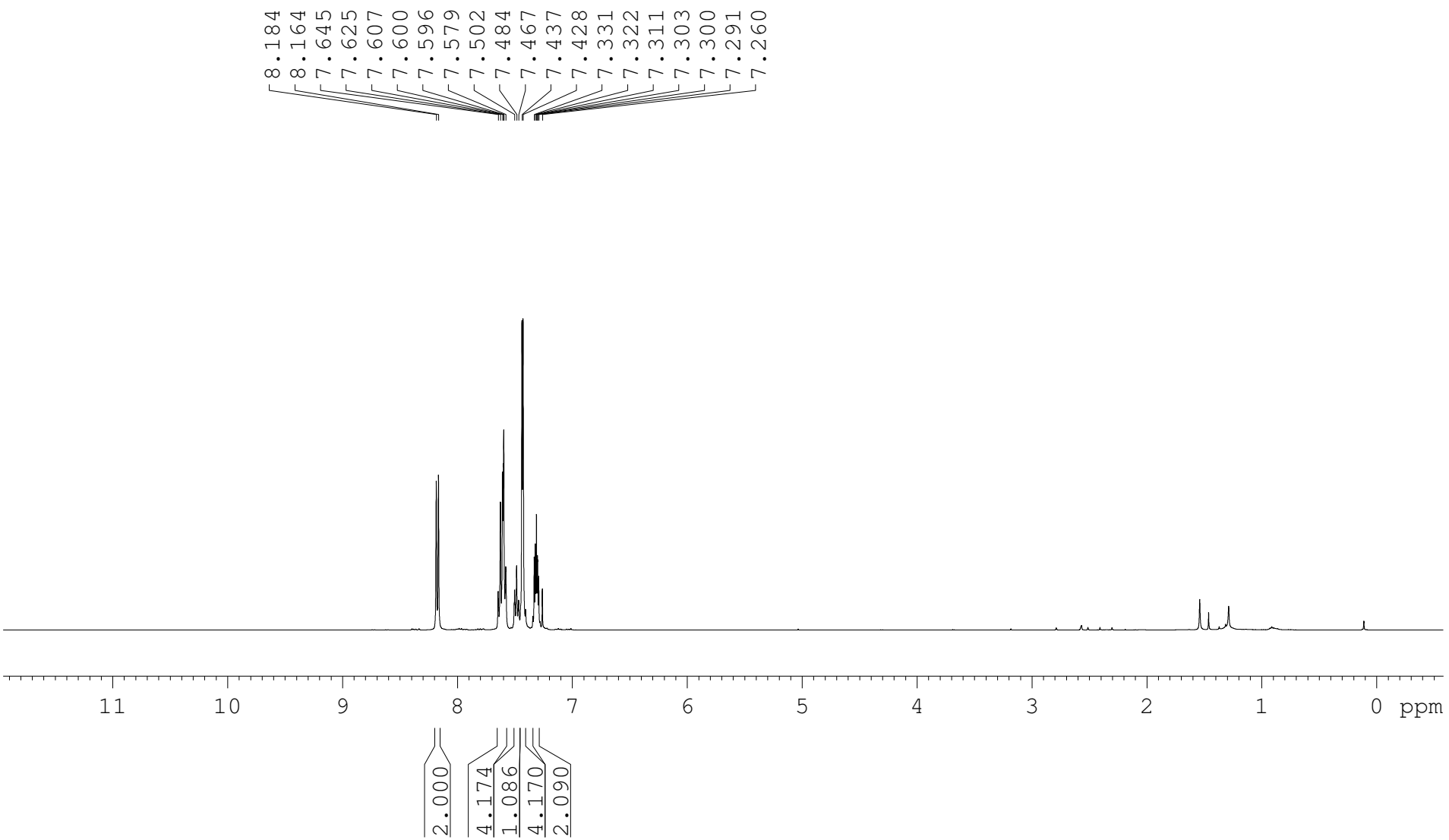
1-(3-chlorophenyl)-1H-indole (5h)



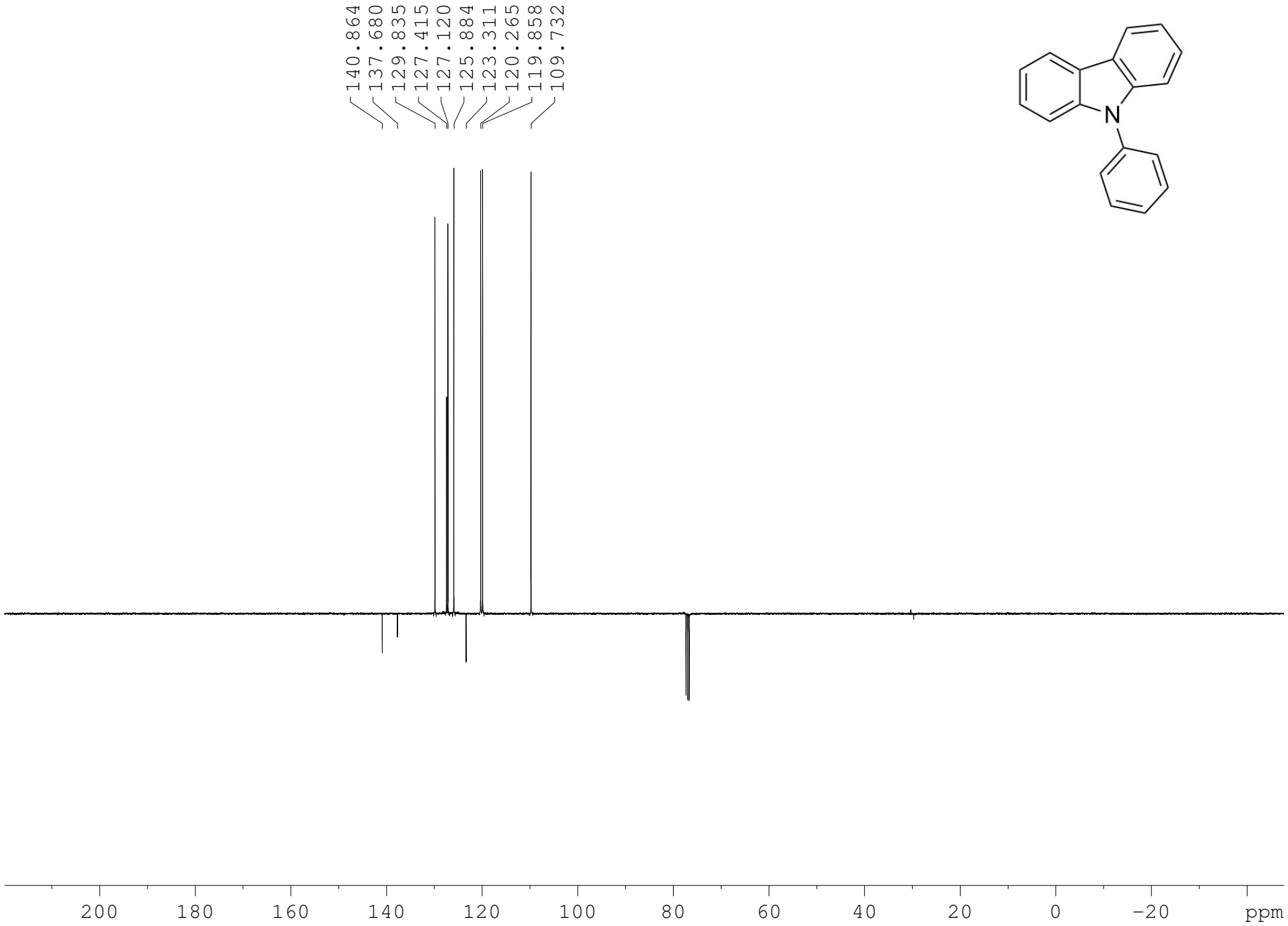


9-phenyl-9H-carbazole (5i)

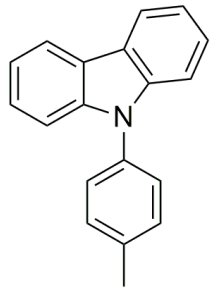


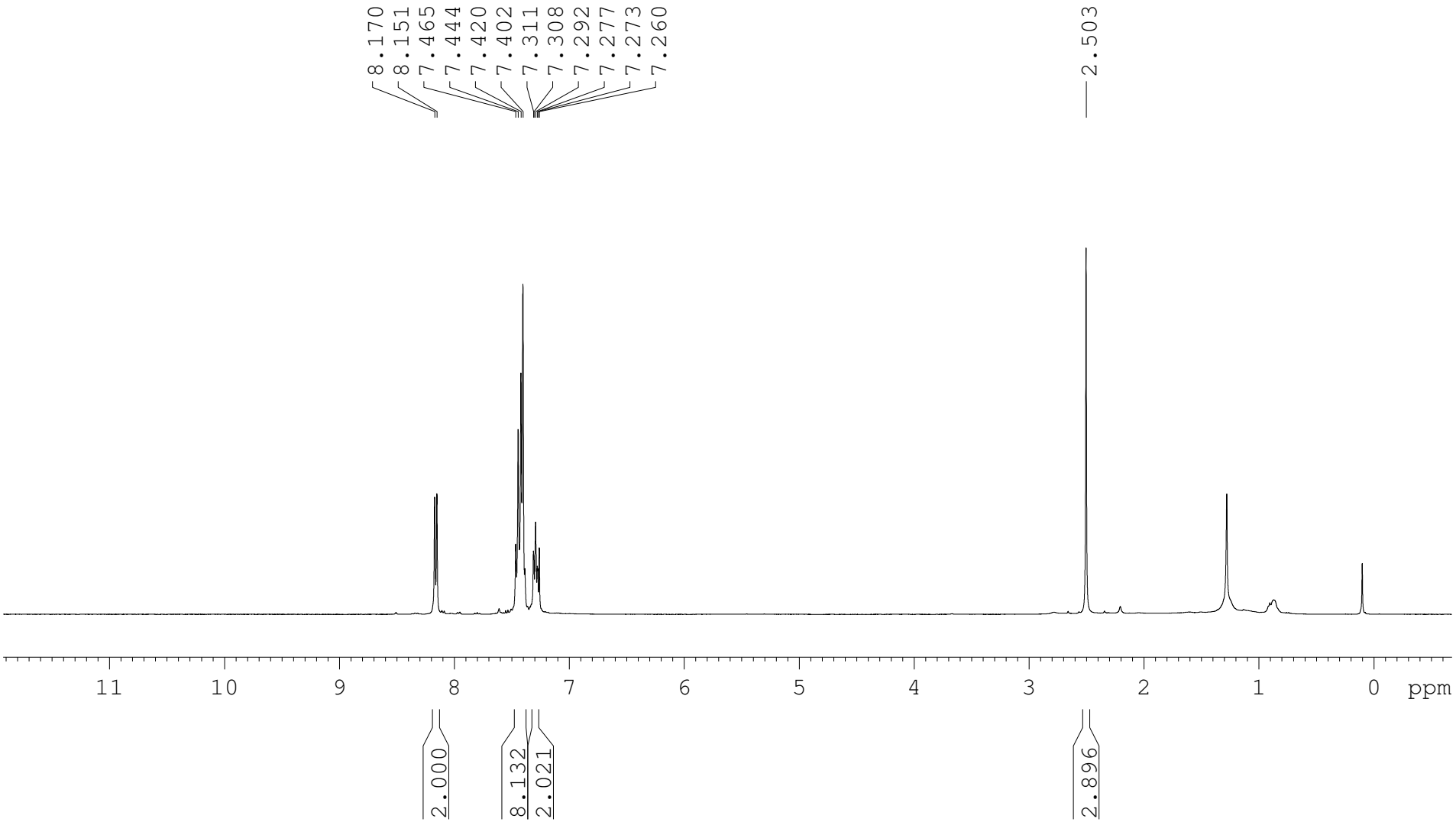


9-phenyl-9H-carbazole (5i)

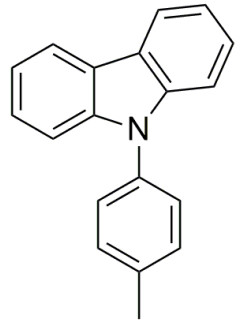


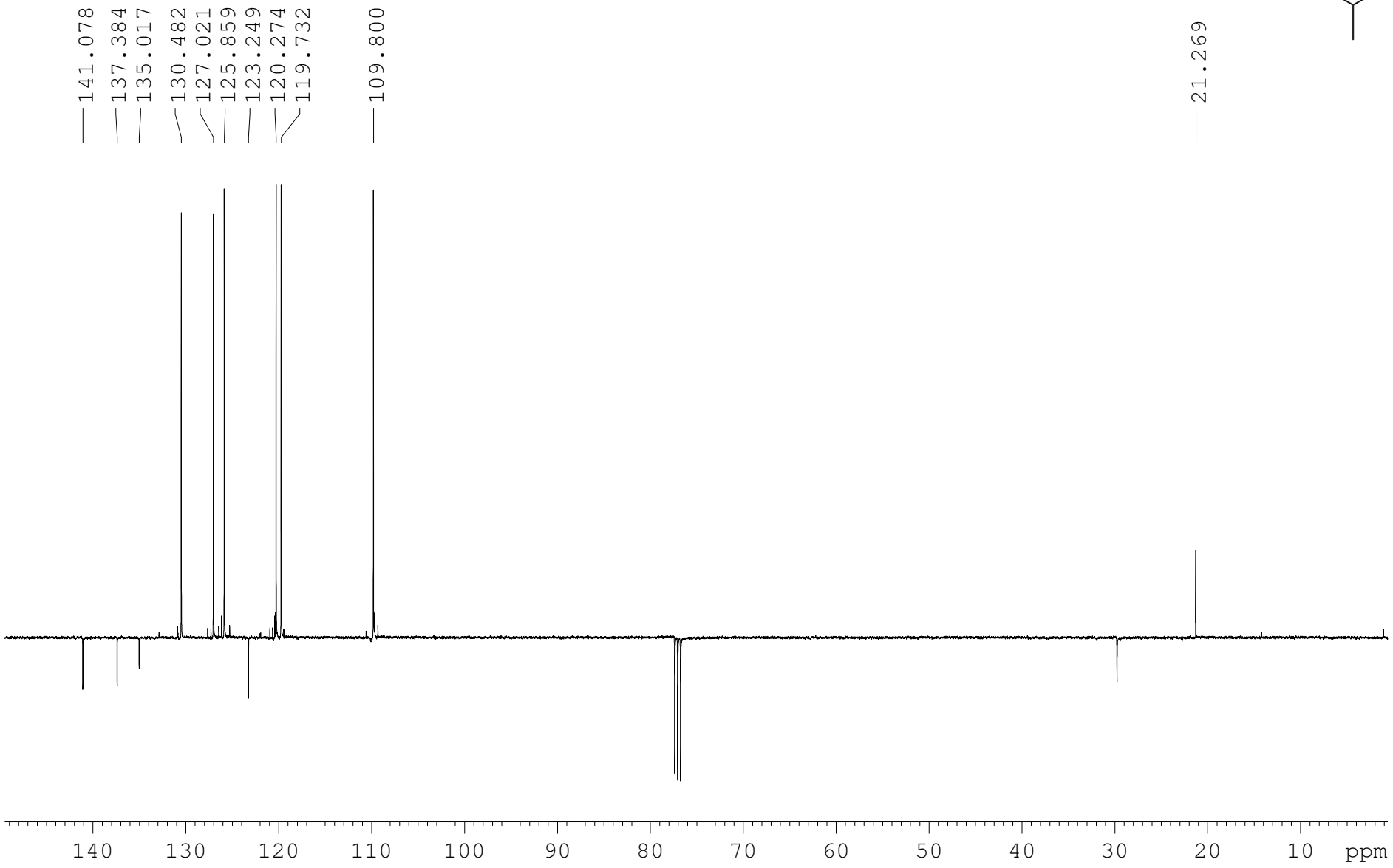
9-(p-tolyl)-9H-carbazole(5j)



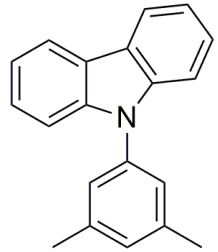


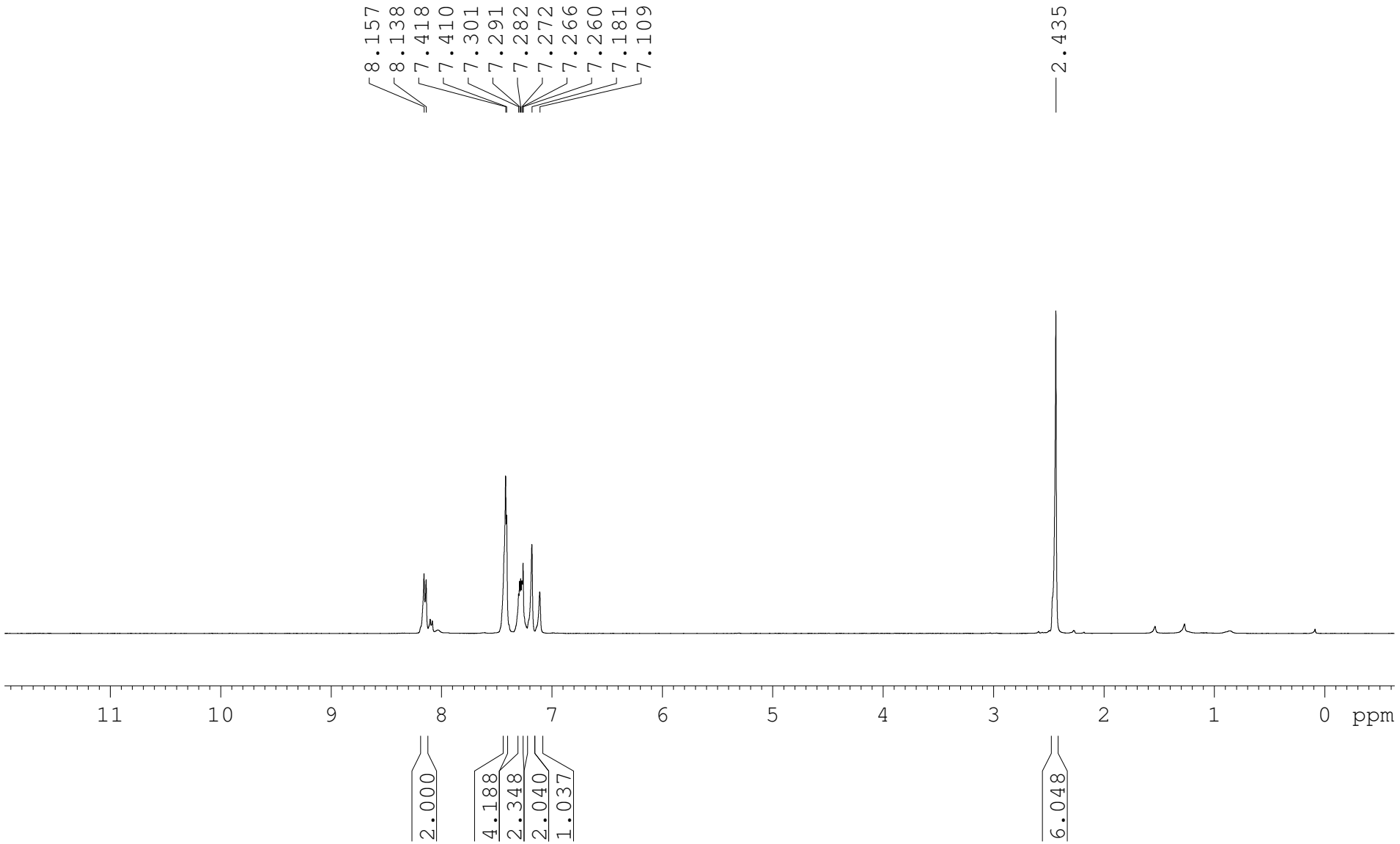
9-(p-tolyl)-9H-carbazole(5j)



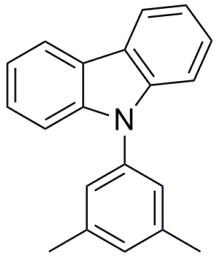


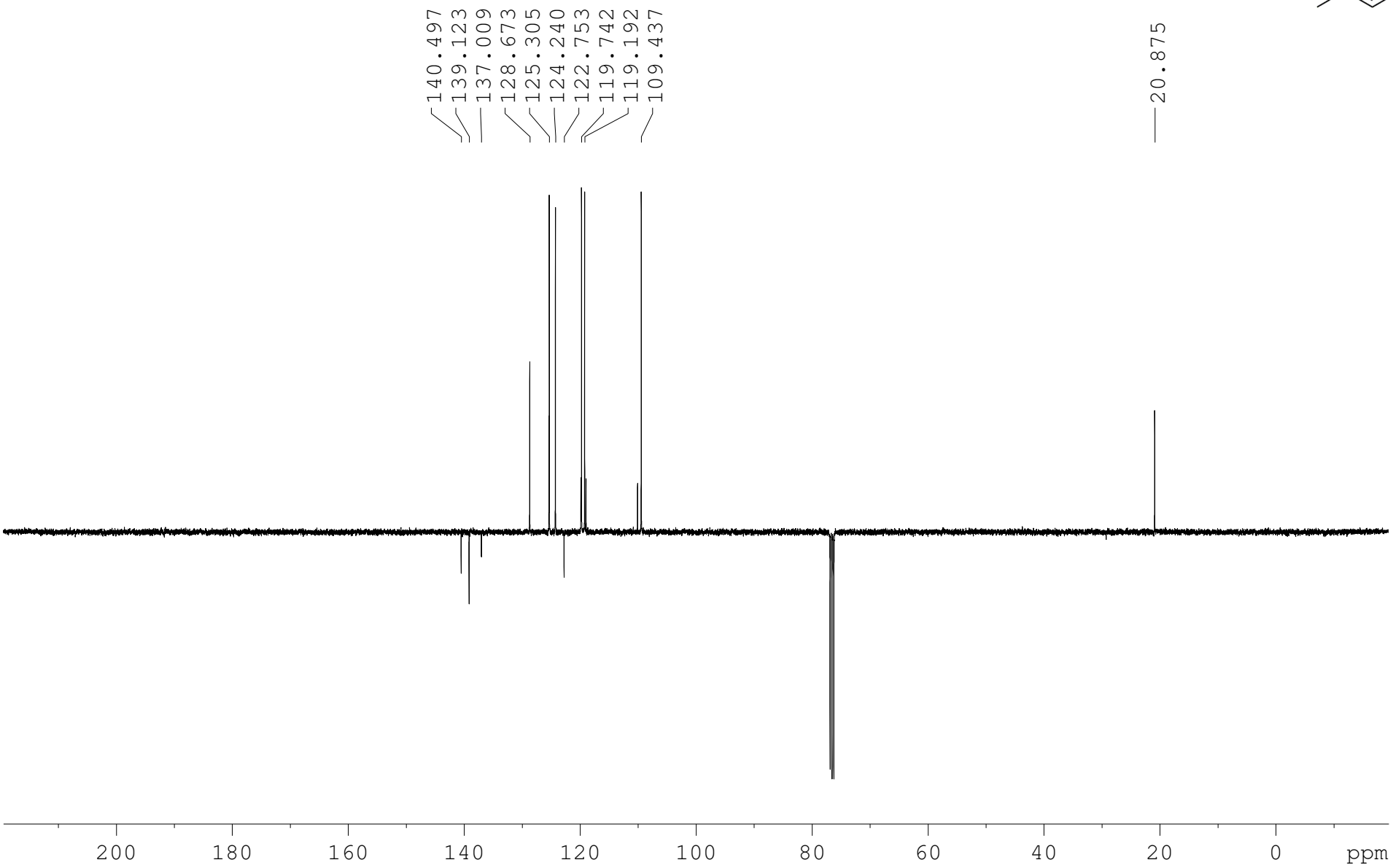
9-(3,5-dimethylphenyl)-9H-carbazole (5k)



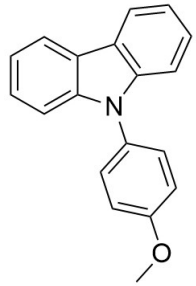


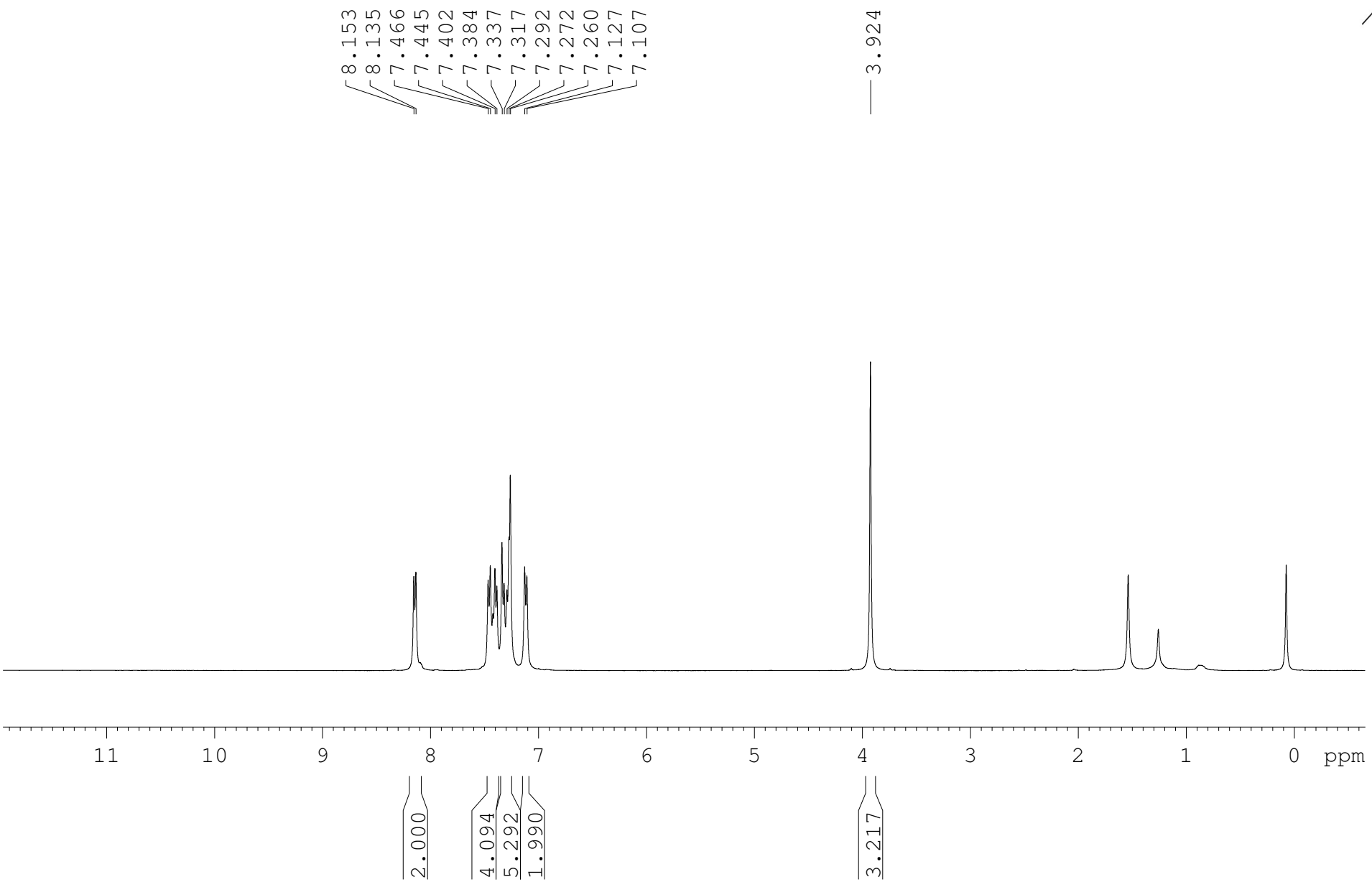
9-(3,5-dimethylphenyl)-9H-carbazole (5k)



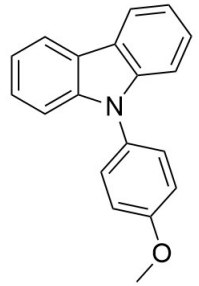


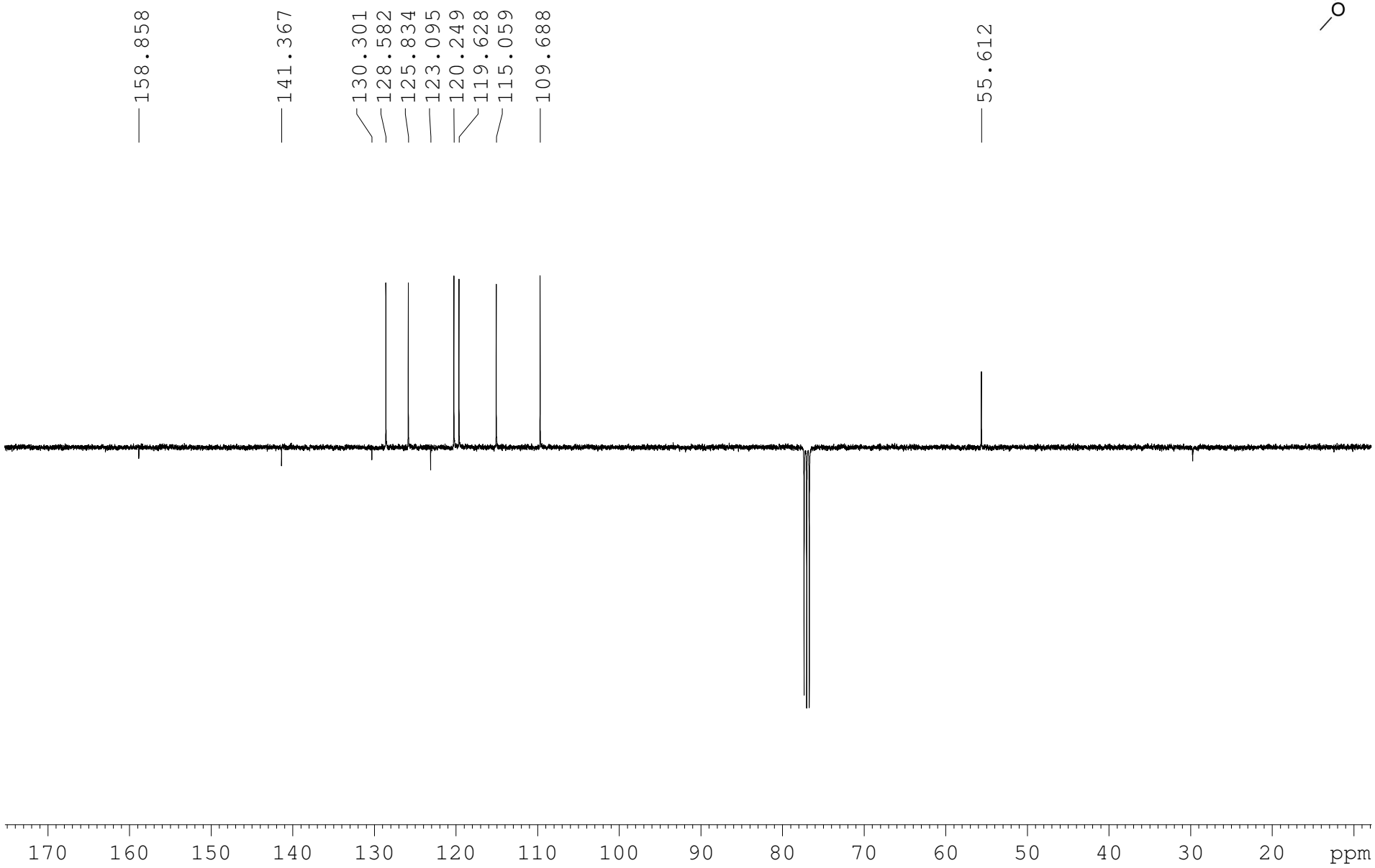
9-(4-methoxyphenyl)-9H-carbazole (5l)



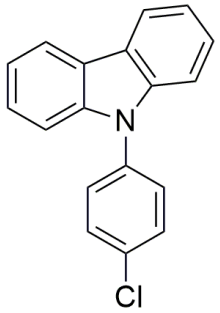


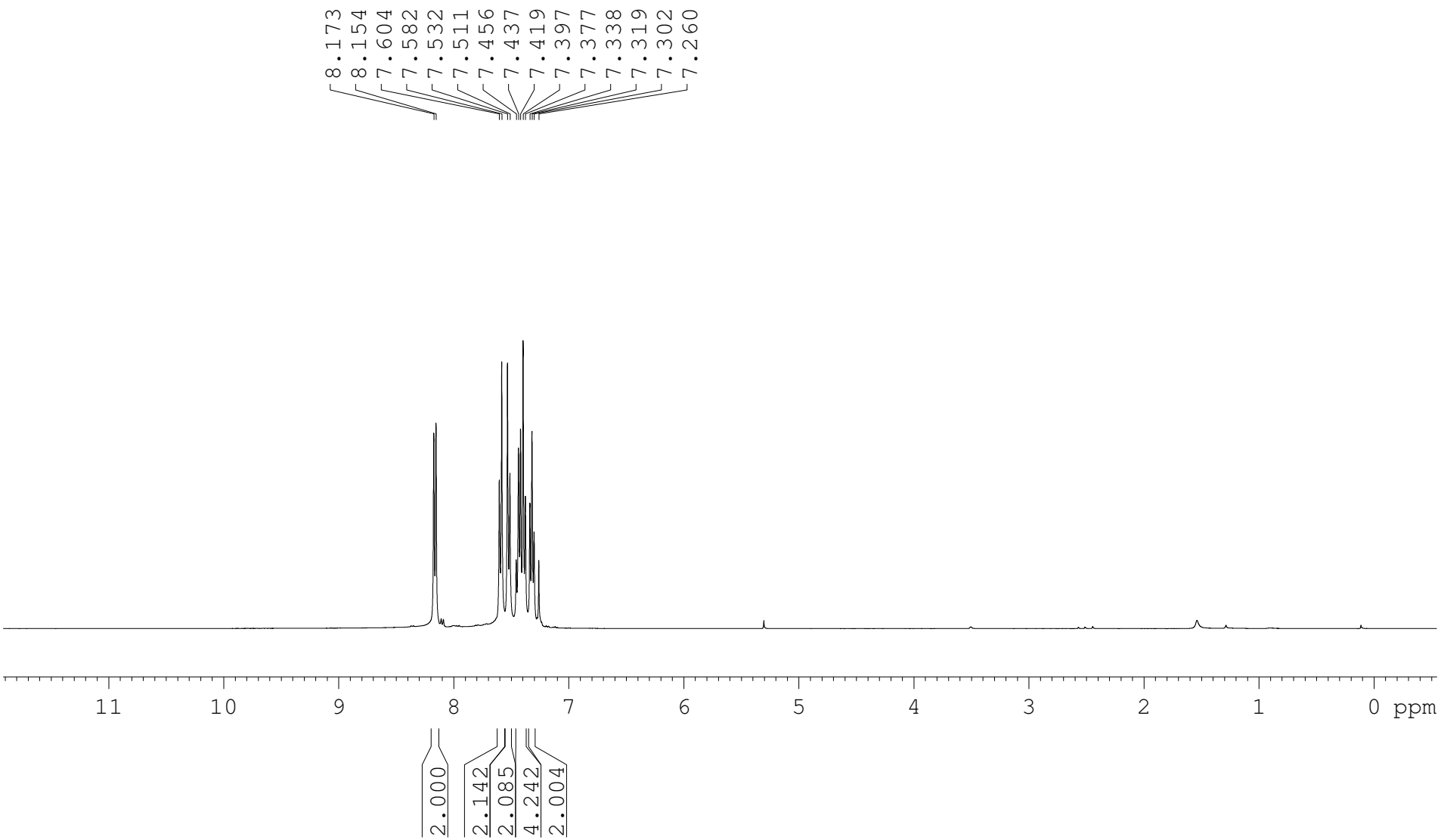
9-(4-methoxyphenyl)-9H-carbazole (5l)



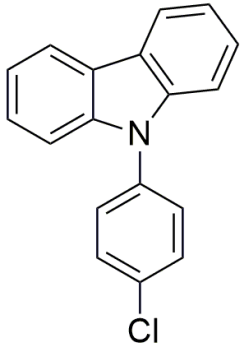


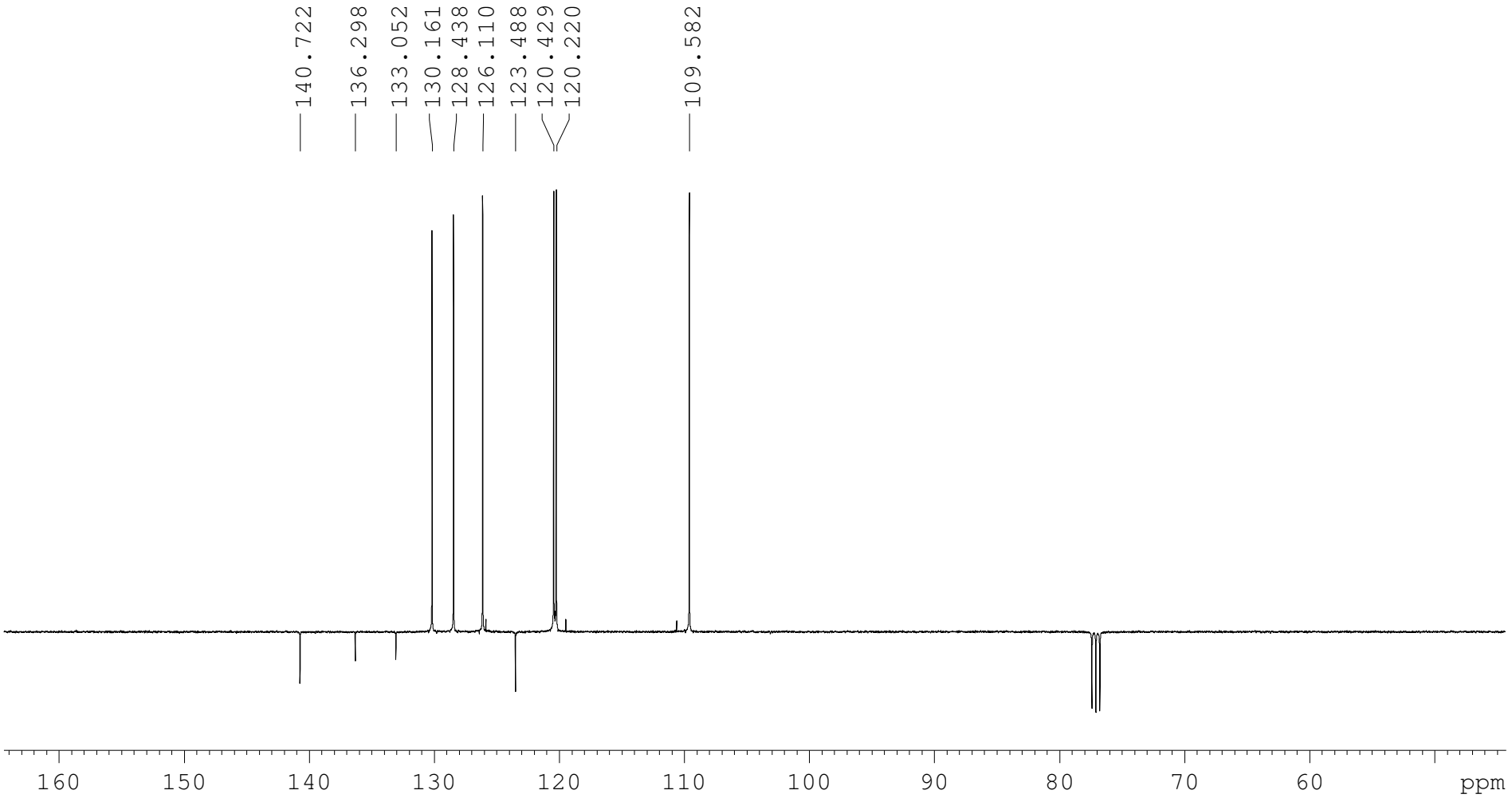
9-(4-chlorophenyl)-9H-carbazole (5m)





9-(4-chlorophenyl)-9H-carbazole (5m)





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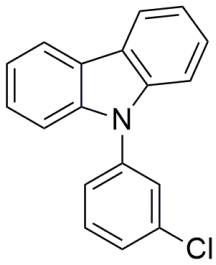
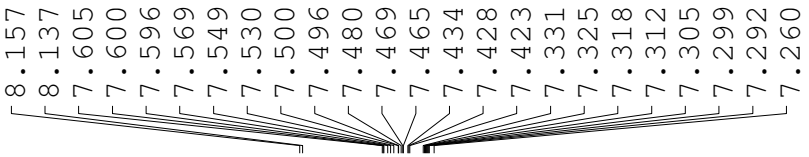
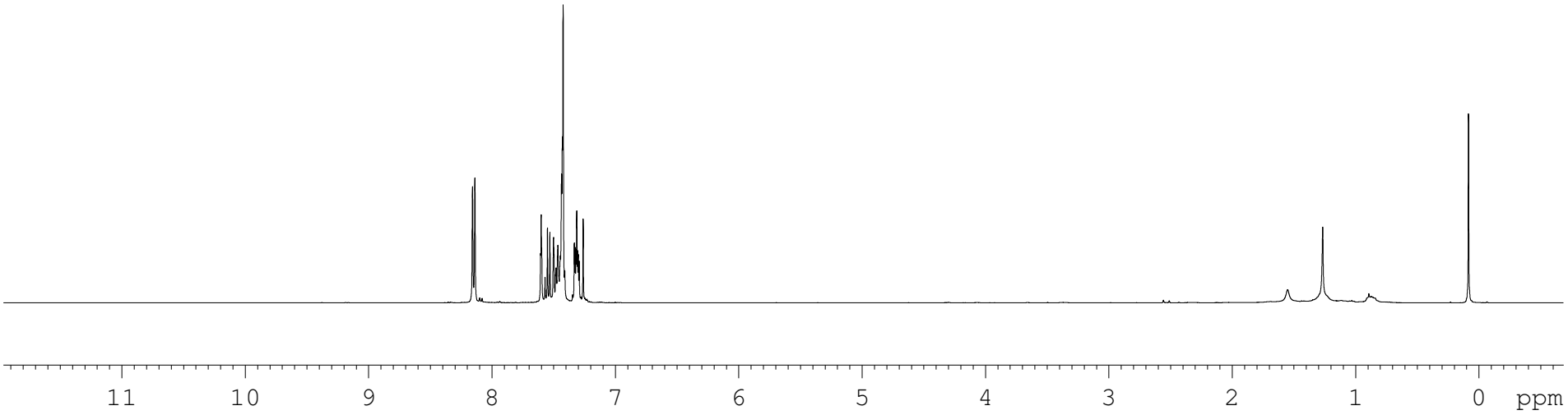
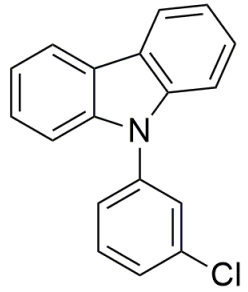
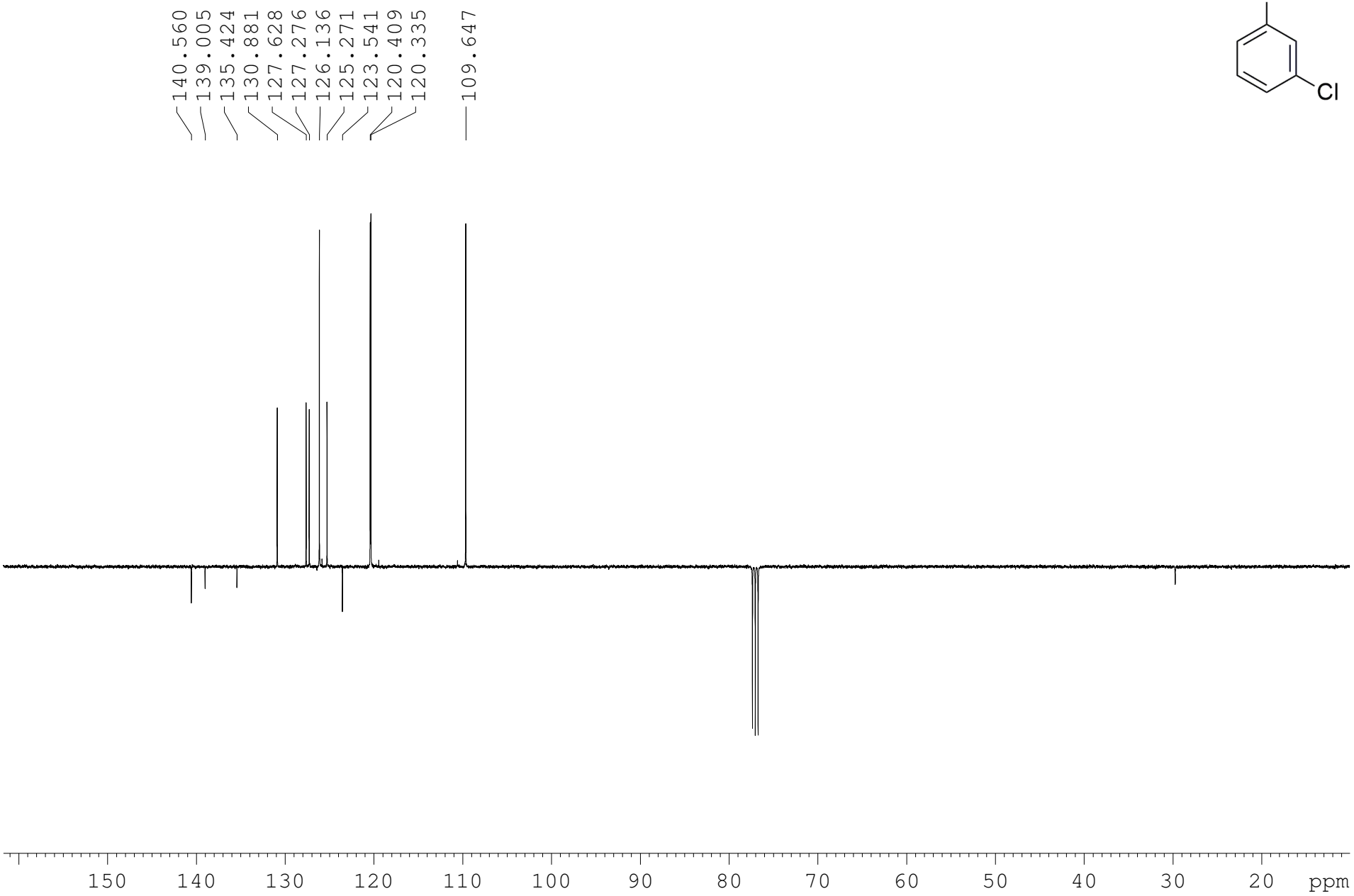




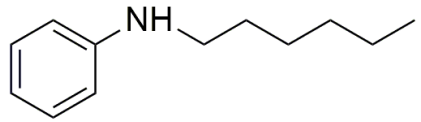


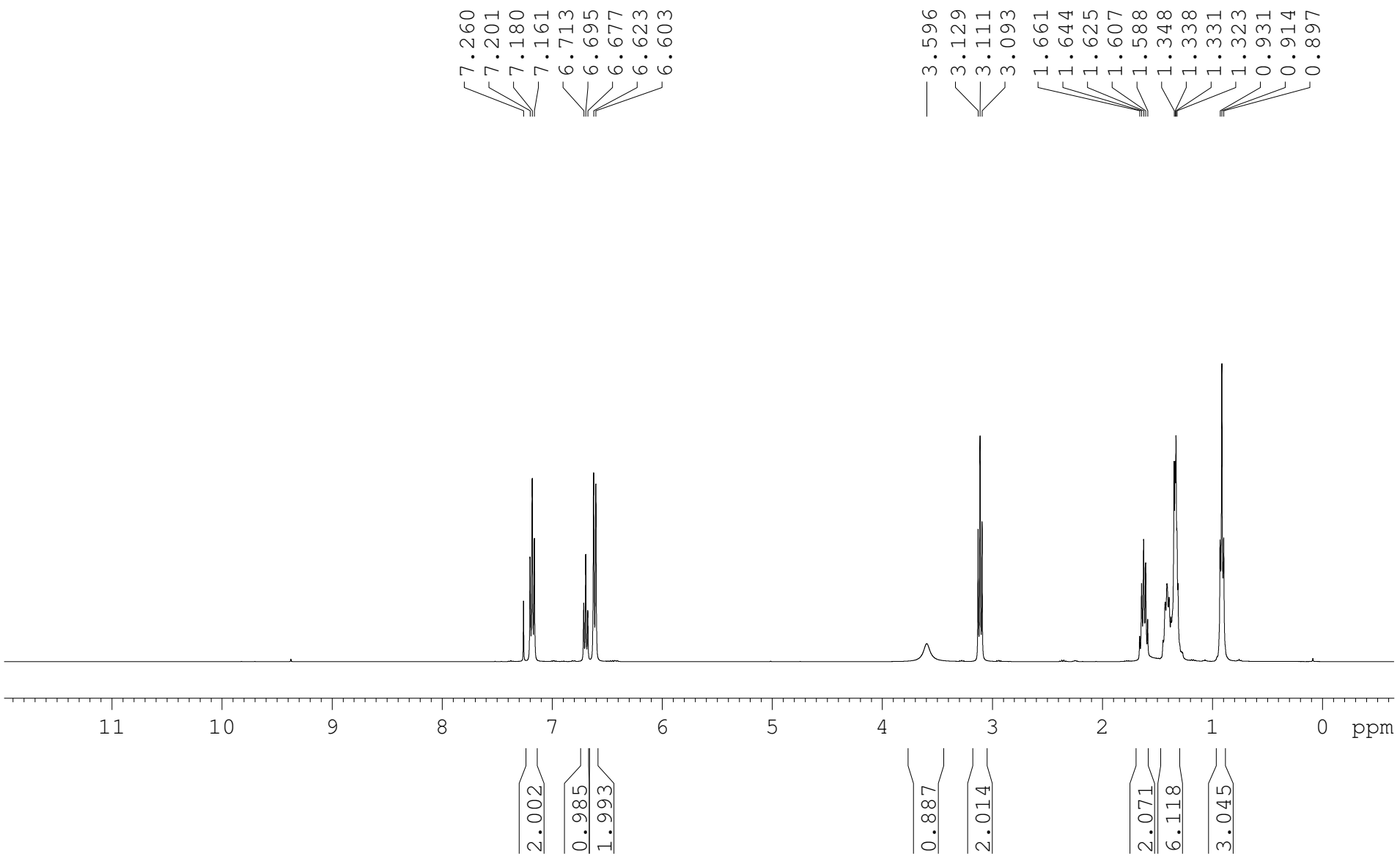
9-(3-chlorophenyl)-9H-carbazole (5n)



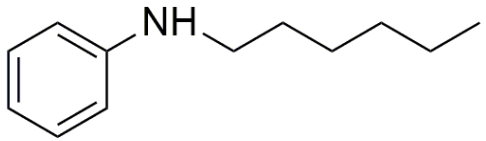


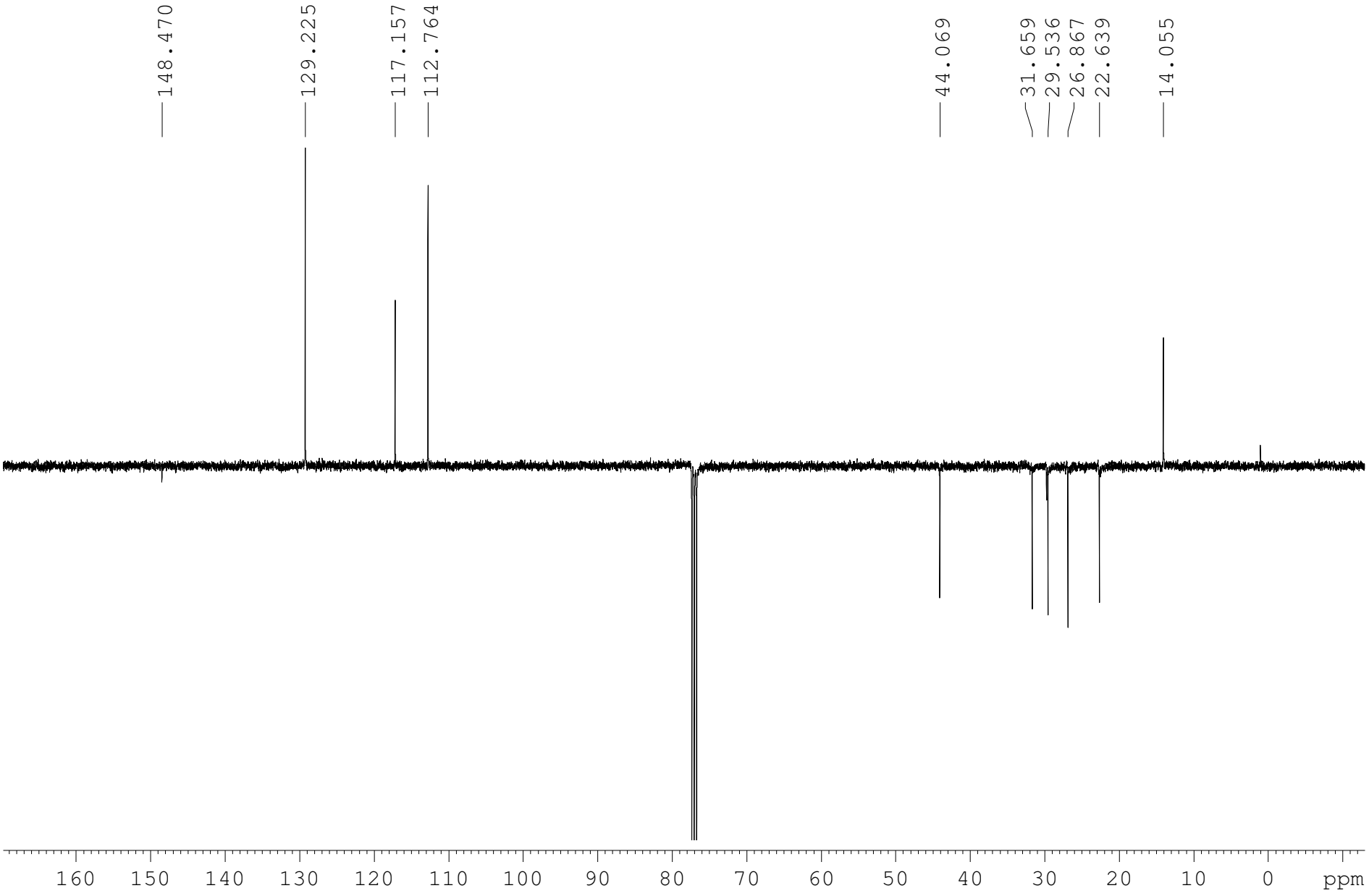
N-hexylaniline (7a)



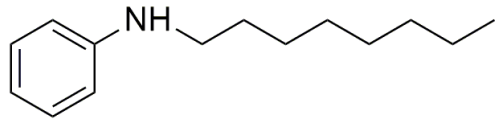


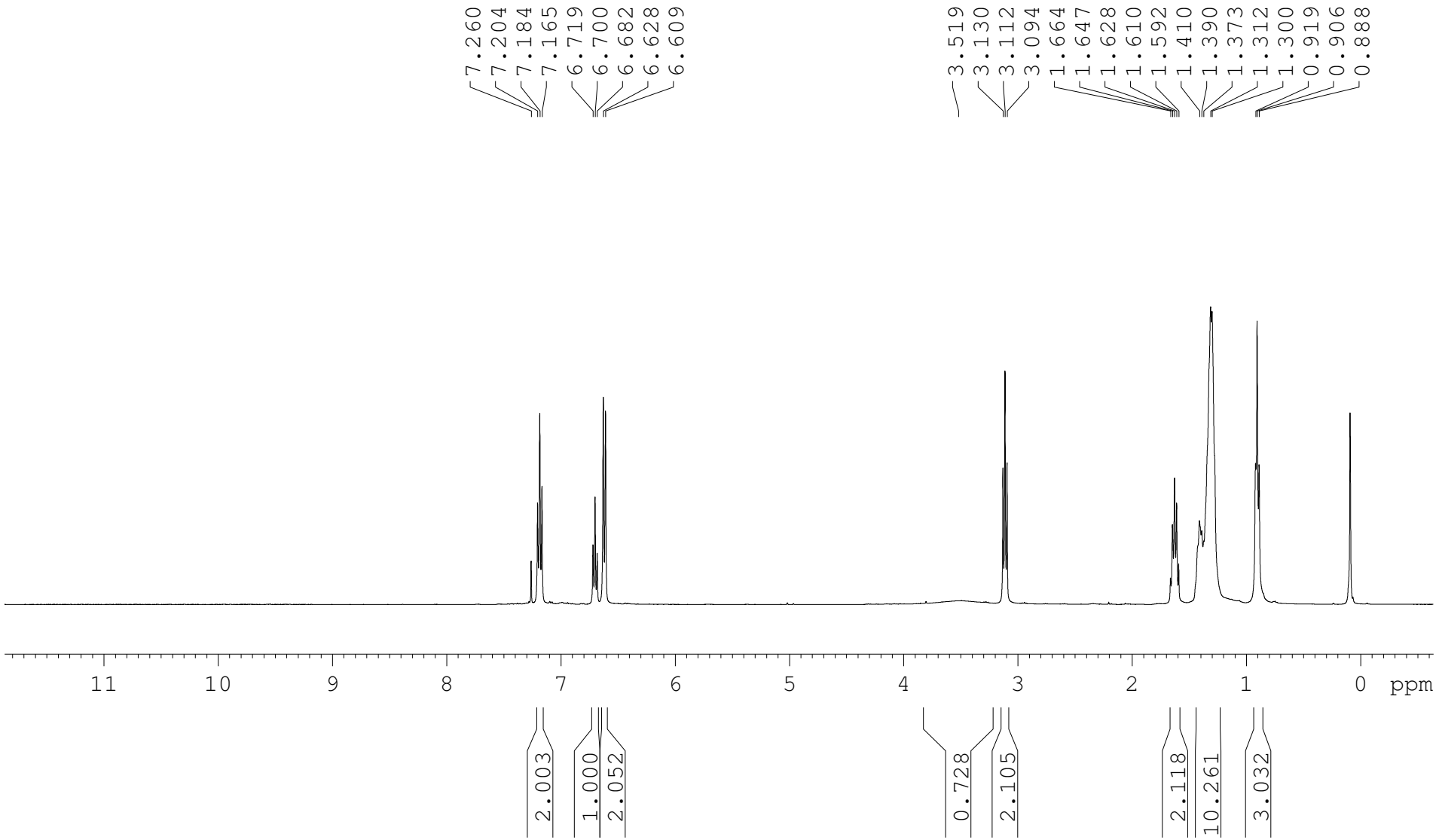
N-hexylaniline (7a)



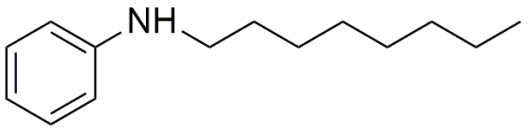


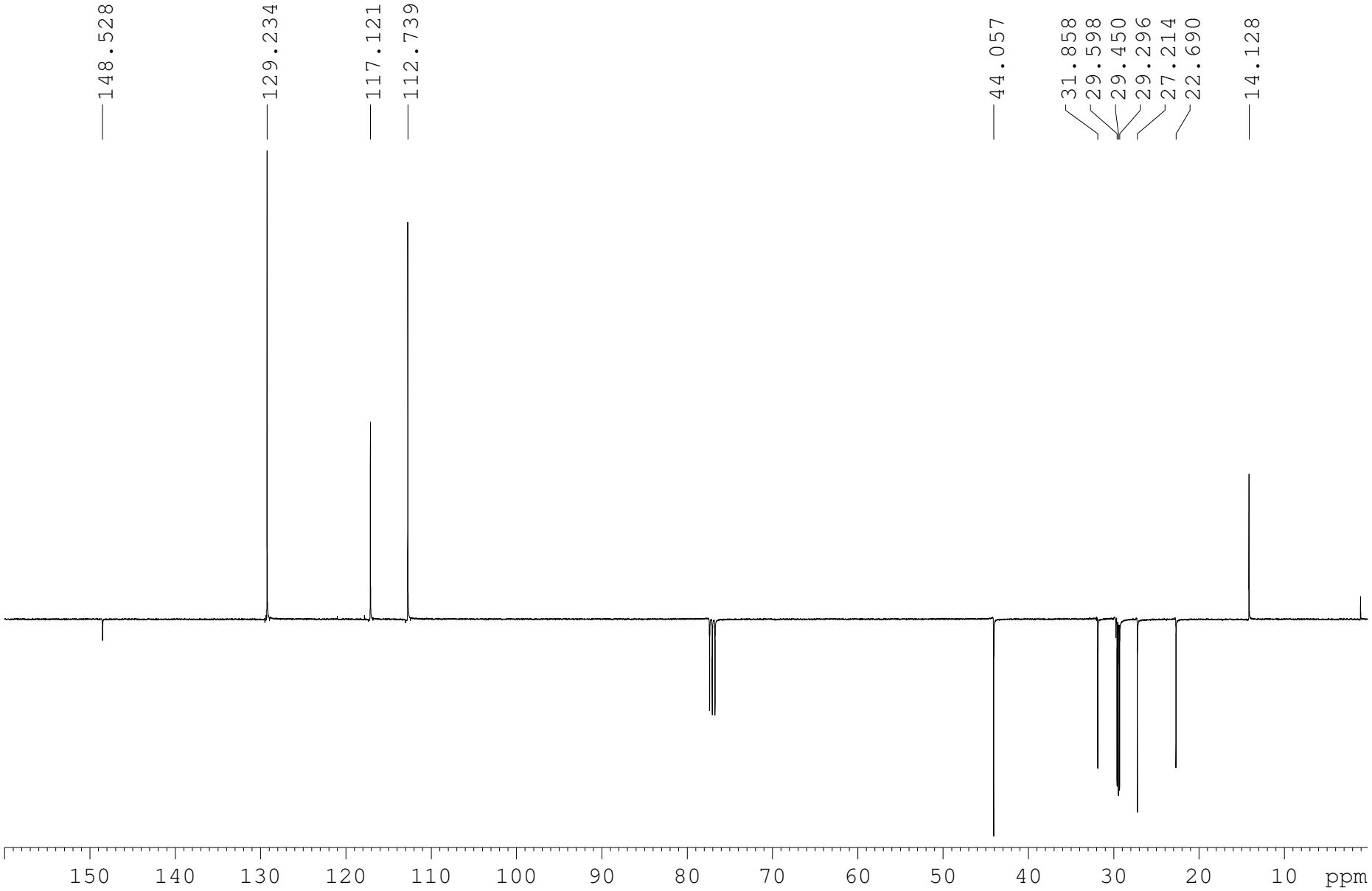
N-octylaniline (7b)



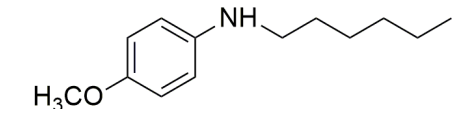


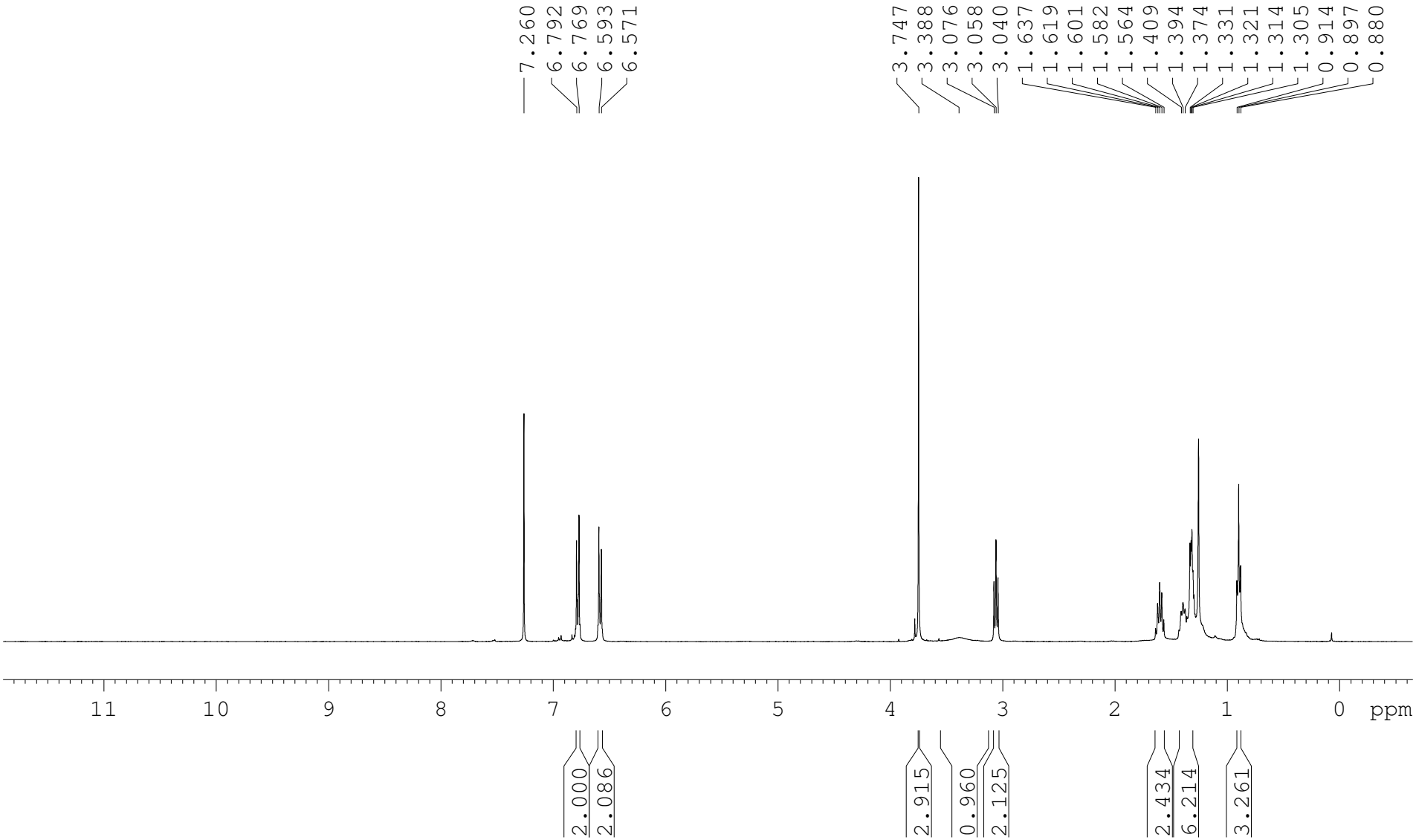
N-octylaniline (7b)



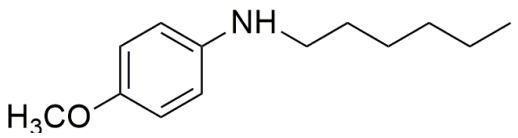


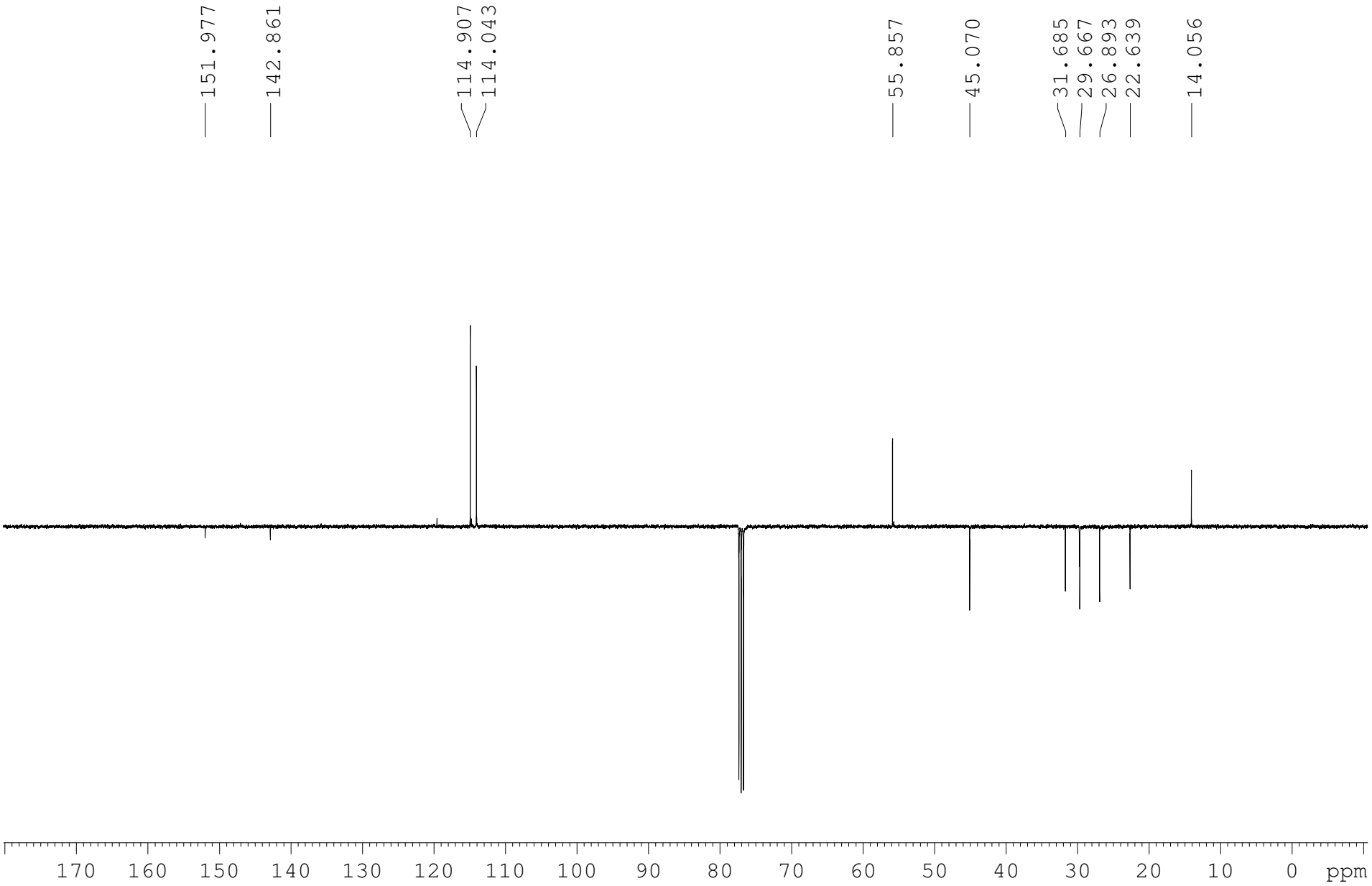
N-hexyl-4-methoxyaniline (7c)



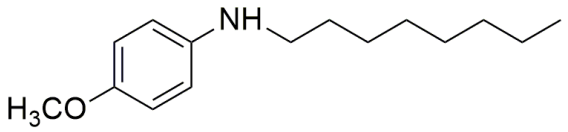


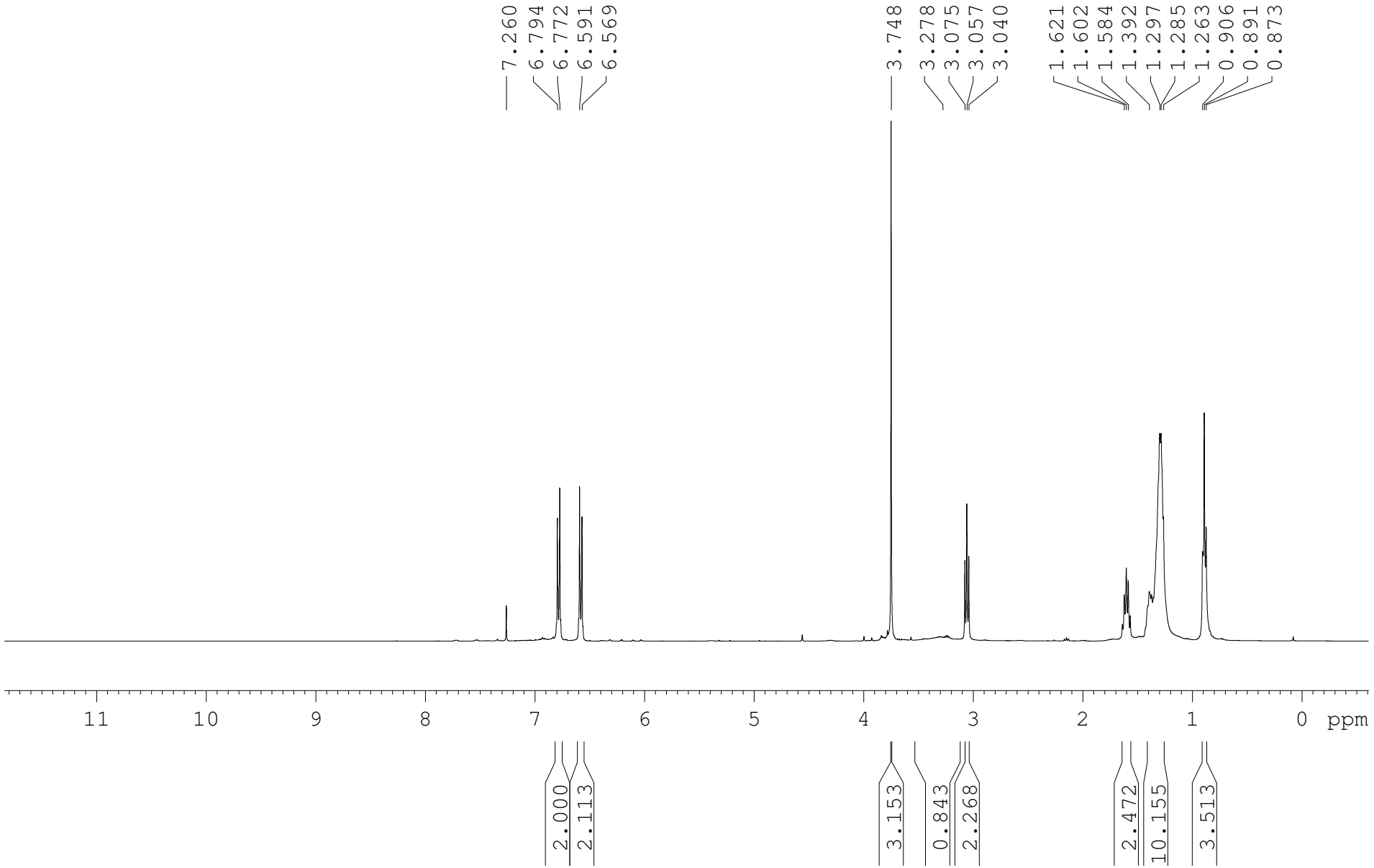
N-hexyl-4-methoxyaniline (7c)





N-octyl-4-methoxyaniline (7d)





N-octyl-4-methoxyaniline (7d)