Supporting Information

Cobalt-Rhodium Heterobimetallic Nanoparticle-Catalyzed N-Alkylation of Amines with Alcohols to Secondary and Tertiary Amines

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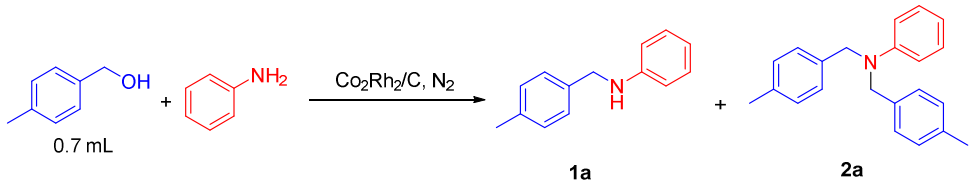
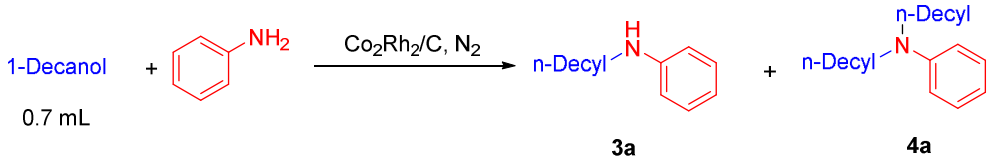
Contents

1. Optimization data



Entry	Time (h)	Temp (^{o}C)	Co_2Rh_2 (mol%)	Yield (%)[a]	
				1a	**2a**
1	24	90	5	83	0
2	24	100	5	99	0
3	18	100	5	74	0
4	24	110	5	99	0
5	24	120	5	87	12
6	24	120	10	54	43
7	24	140	10	7	92
8	24	150	10	10	89

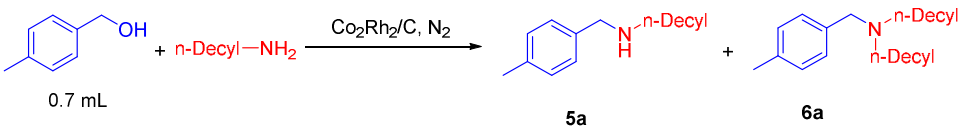
Reaction conditions: Aniline 0.5 mmol, 4-Methylbenzyl alcohol 0.7 ml [a)]Yields are of isolated yield.



Entry	Time (h)	Temp (^{o}C)	Co_2Rh_2 (mol%)	Yield (%)[b]	
				3a	**4a**
1[a)]	24	100	5	N.R	N.R
2[a)]	24	130	5	28	0
3[a)]	24	150	5	81	0
4	24	120	5	30	0
5	18	130	5	71	0
6	24	130	5	90	trace
7	24	140	5	91	6

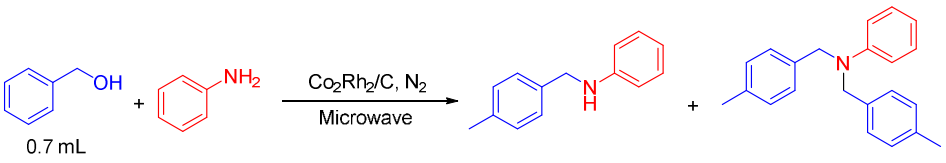
8	24	160	10	9	90
9	24	165	10	6	94
10	24	170	10	4	95

Reaction conditions: Aniline 0.5 mmol, 4-Methylbenzyl alcohol 0.7 ml. [a] Aniline 0.5 mmol, Alcohol 0.5 mmol, Mesitylene 0.7 ml. [b]Yields are of isolated yield.



Entry	Time	Temp	Co_2Rh_2	Yield (%)[b]	
	(h)	(°C)	(mol%)	**5a**	**6a**
1	24	70	5	77	0
2	24	80	5	92	0
3	18	80	5	82	0
4	24	100	5	47	43
5	24	120	5	0	88[a]
6	18	120	5	0	71[a]
7	24	130	5	0	89[a]

Reaction conditions: Aniline 0.5 mmol, 4-Methylbenzyl alcohol 0.7 ml. [a] N-(4-methylbenzyl)-N,N-didecyl-1-amine was also formed. [b]Yields are of isolated yield.



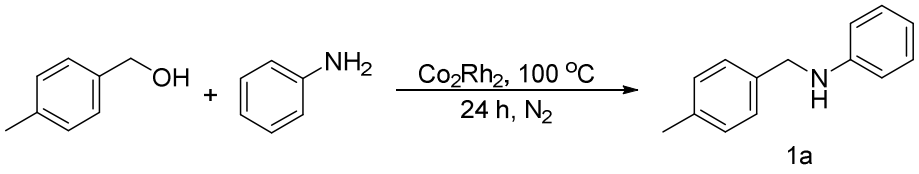
Entry	Time	Temp	Co_2Rh_2	Yield (%)[a]	
	(h)	(°C)	(mol%)	**5a**	**6a**
1	0.5	25	5	0	0
2	0.5	50	5	0	0
3	0.5	100	5	5	0

4	4	100	5	48	0
5	12	100	5	99	0

Reaction conditions: Aniline 0.5 mmol, Benzyl alcohol 0.7 ml. [a)] Yields are of isolated yield.

2. Recycle test

After each reaction, the catalyst was separated from the reaction mixture by centrifuge, dried in vacuum, and then reused for the further catalytic reactions. The catalytic system exhibited a great capability of reuse and significant air stability under the set reaction conditions. The catalyst maintained a high level of activity even after being reused for ten times. For ten runs, 97~99 % yields were observed. The conversion rate for each cycle was almost 100%. The catalyst is quite stable under our established reaction conditions. Although the maximum reusability was not tested, we expect the catalyst to be semi-permanent.



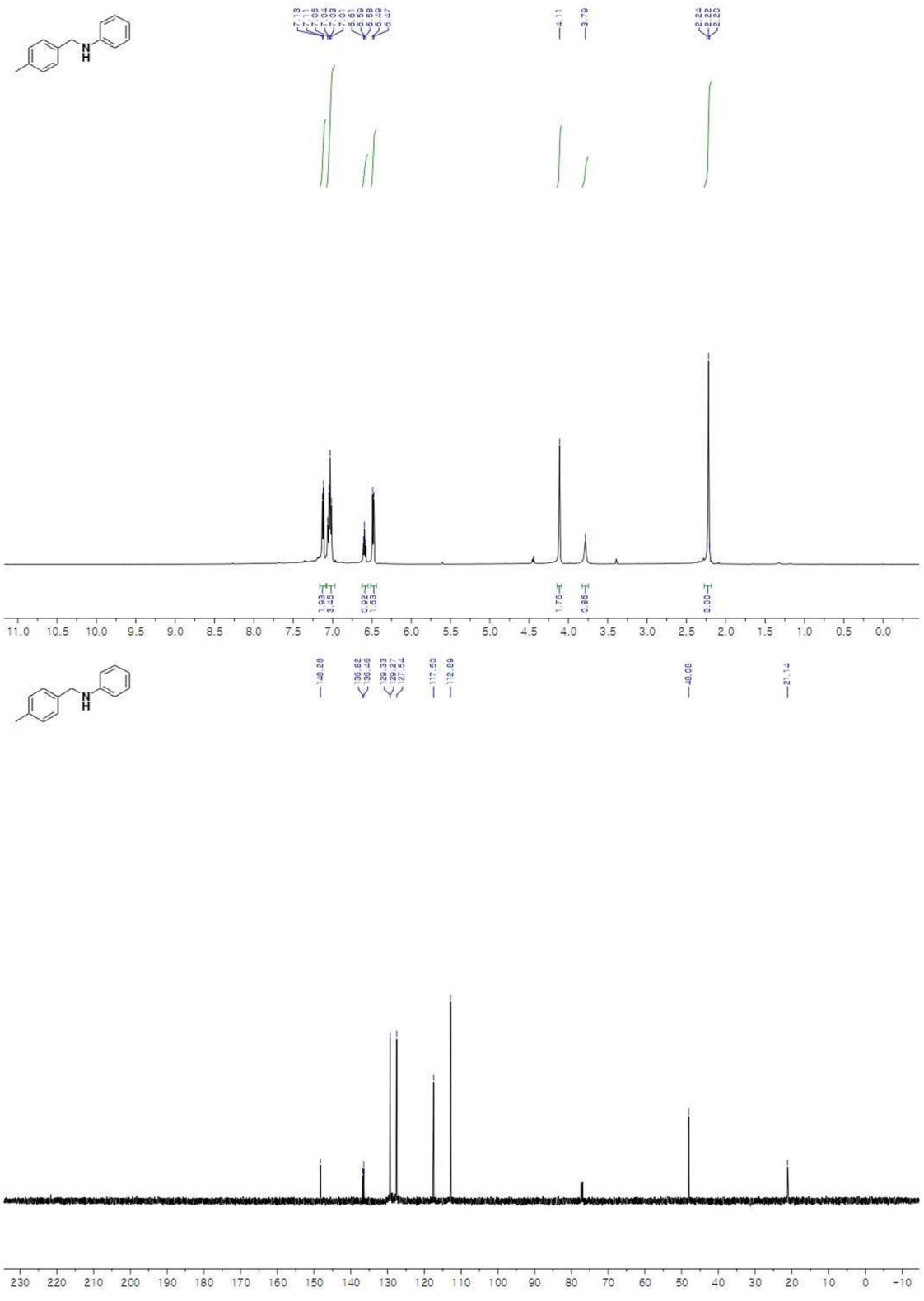
1a

run	yield (%)
	1a
1	99
2	99
3	98
4	99
5	97
6	98
7	98
8	99
9	97
10	99

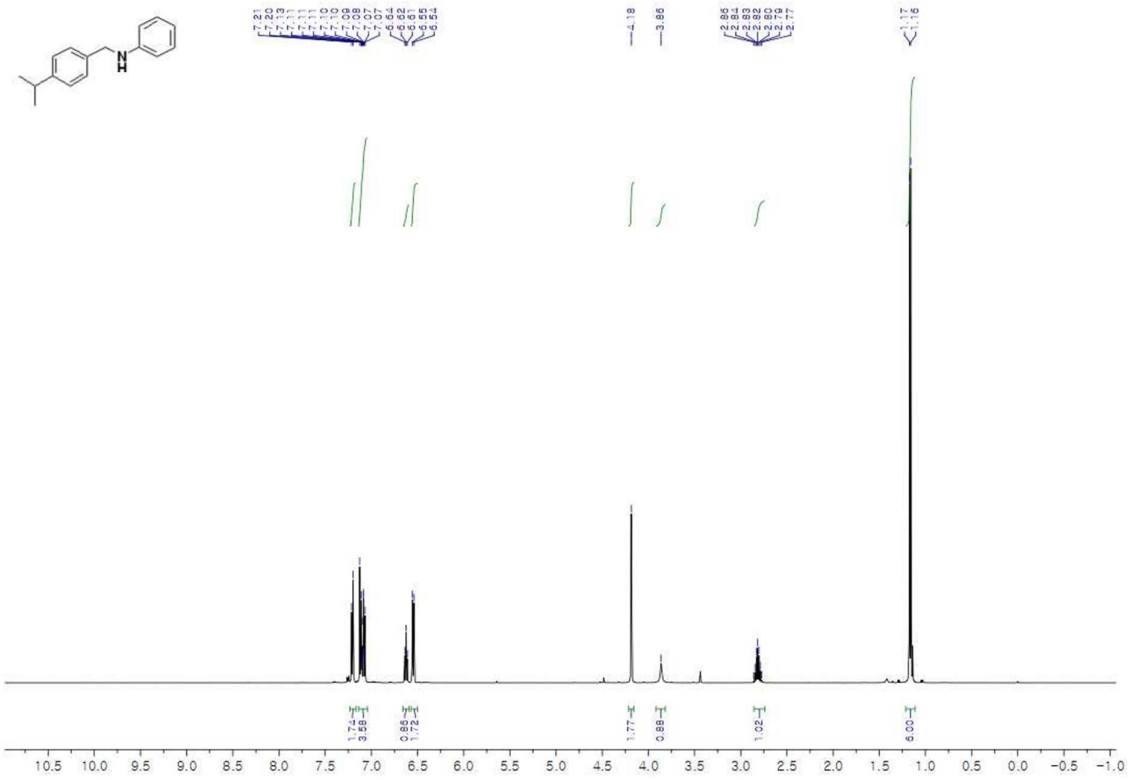
Yields are of isolated yield. Reaction conditions: Aniline 0.5 mmol, 4-methylbenzyl alcohol 0.7 ml, Co_2Rh_2 5 mol%, 100 ^{o}C, 24h, N_2.

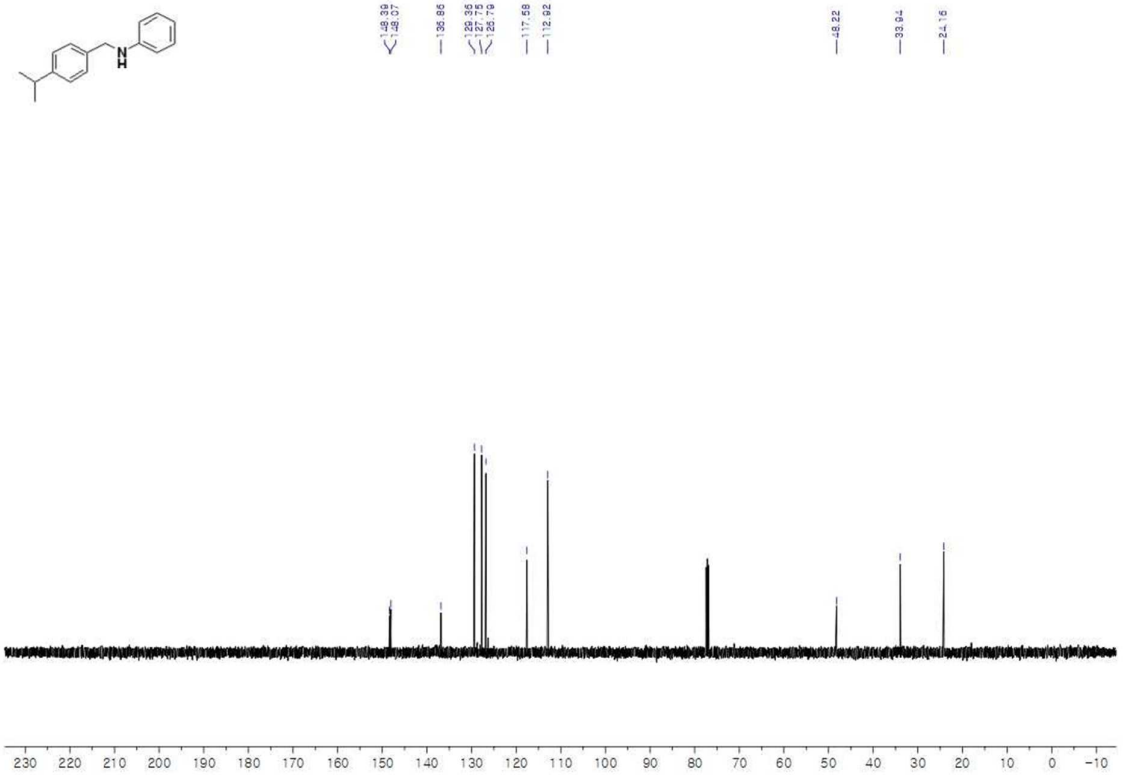
3. NMR Spectra

N-(4-methylbenzyl)aniline – (Table 2, 1a)

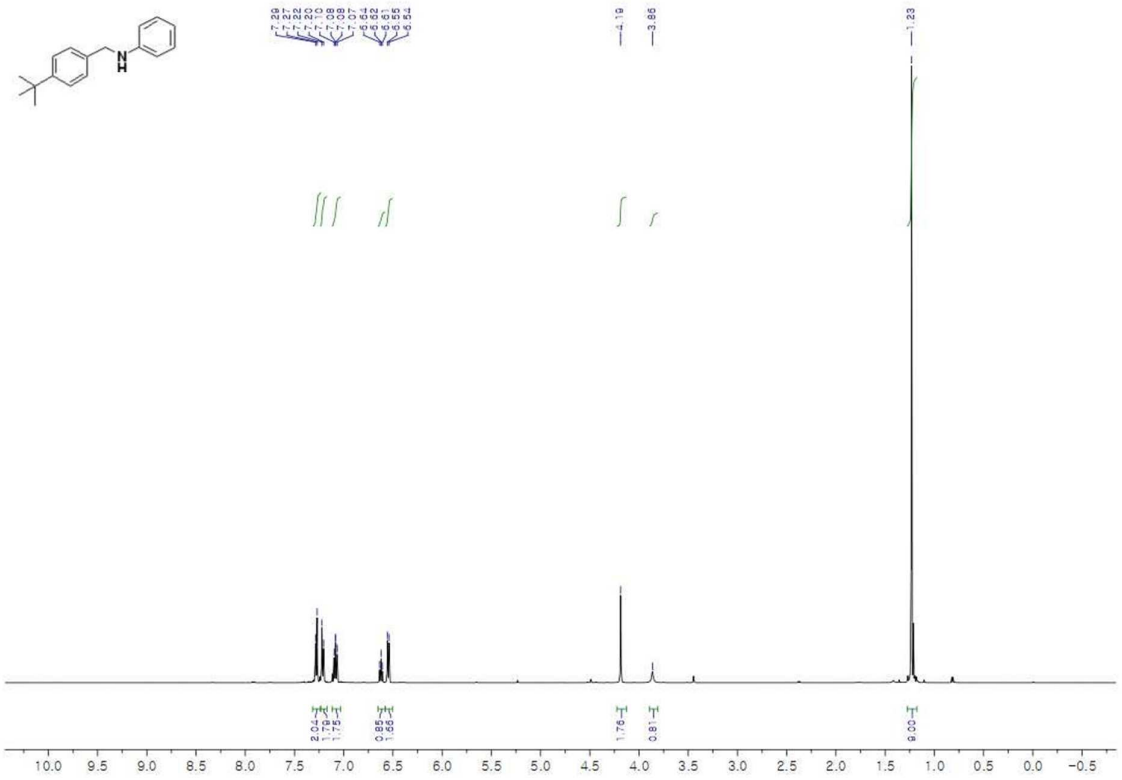


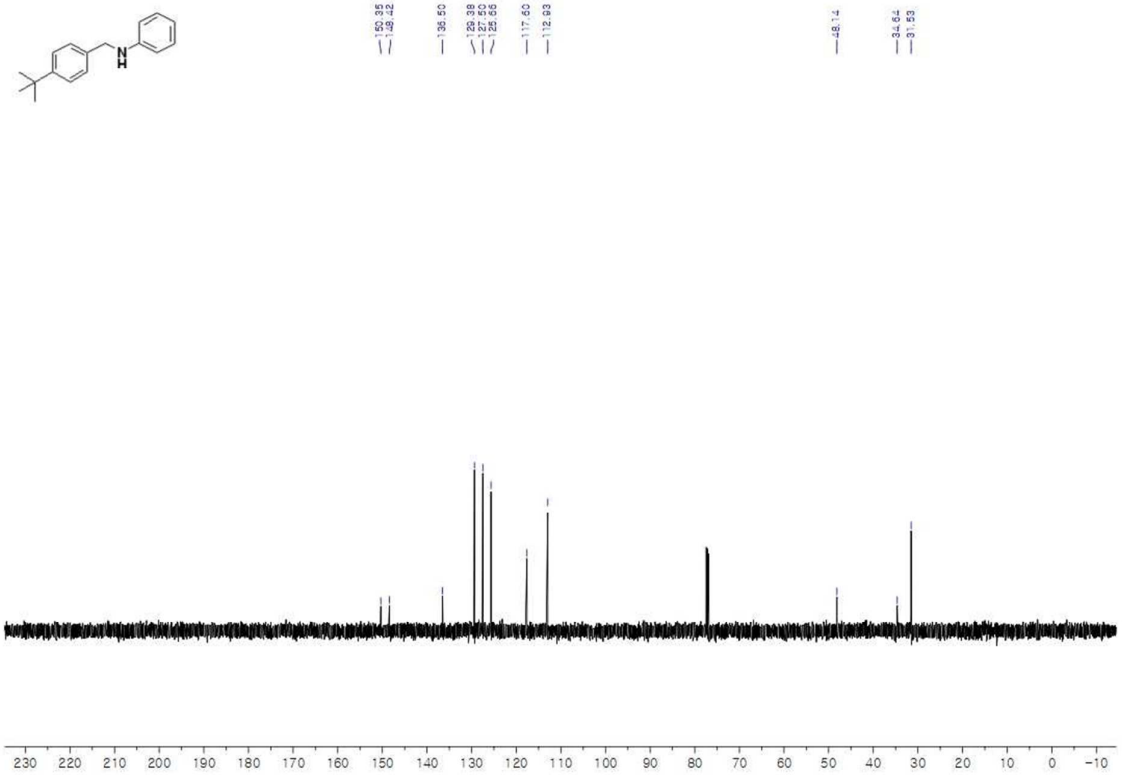
***N*-(4-isopropylbenzyl)aniline – (Table 2, 1c)**



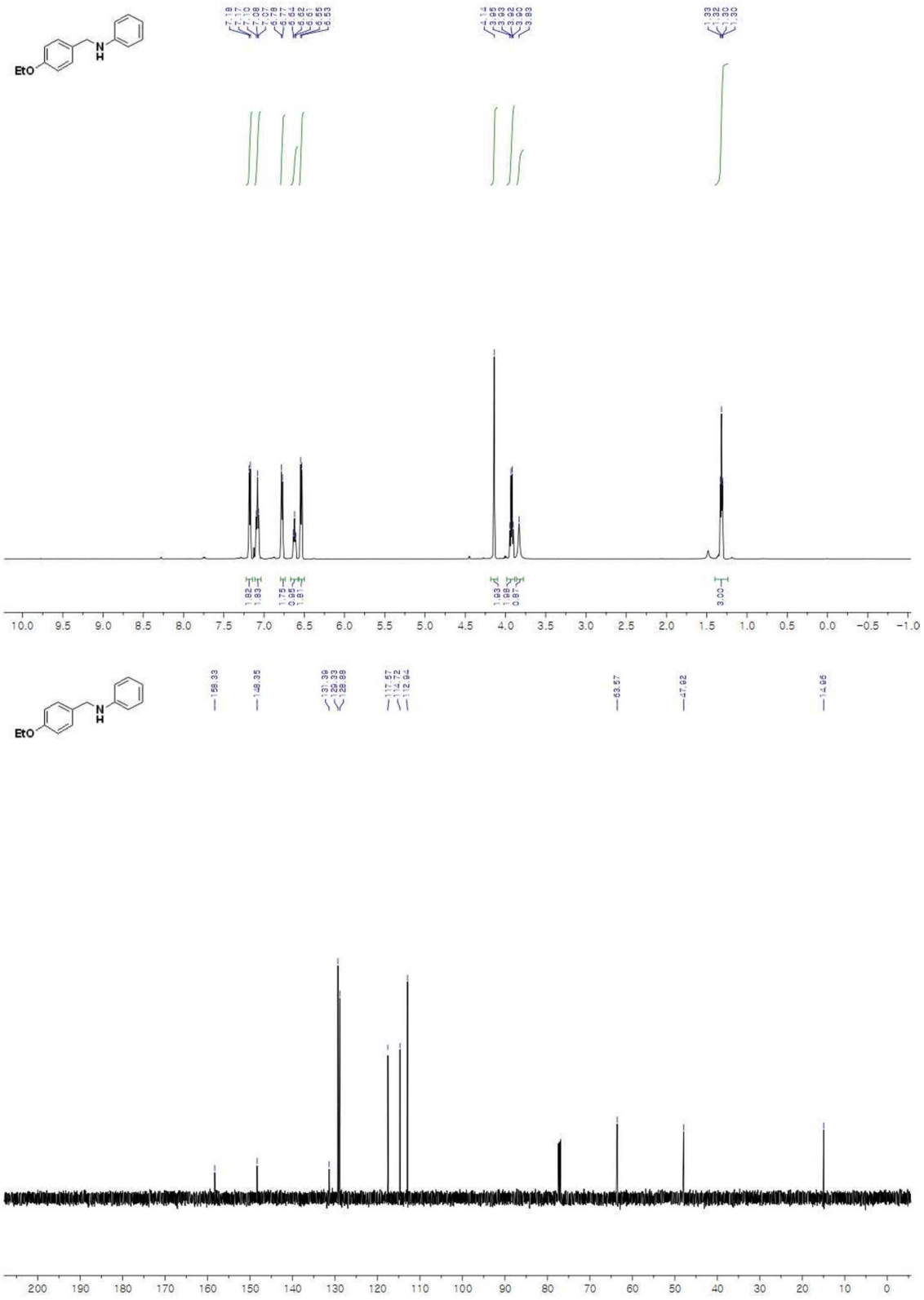


***N*-(4-(tert-butyl)benzyl)aniline – (Table 2, 1d)**

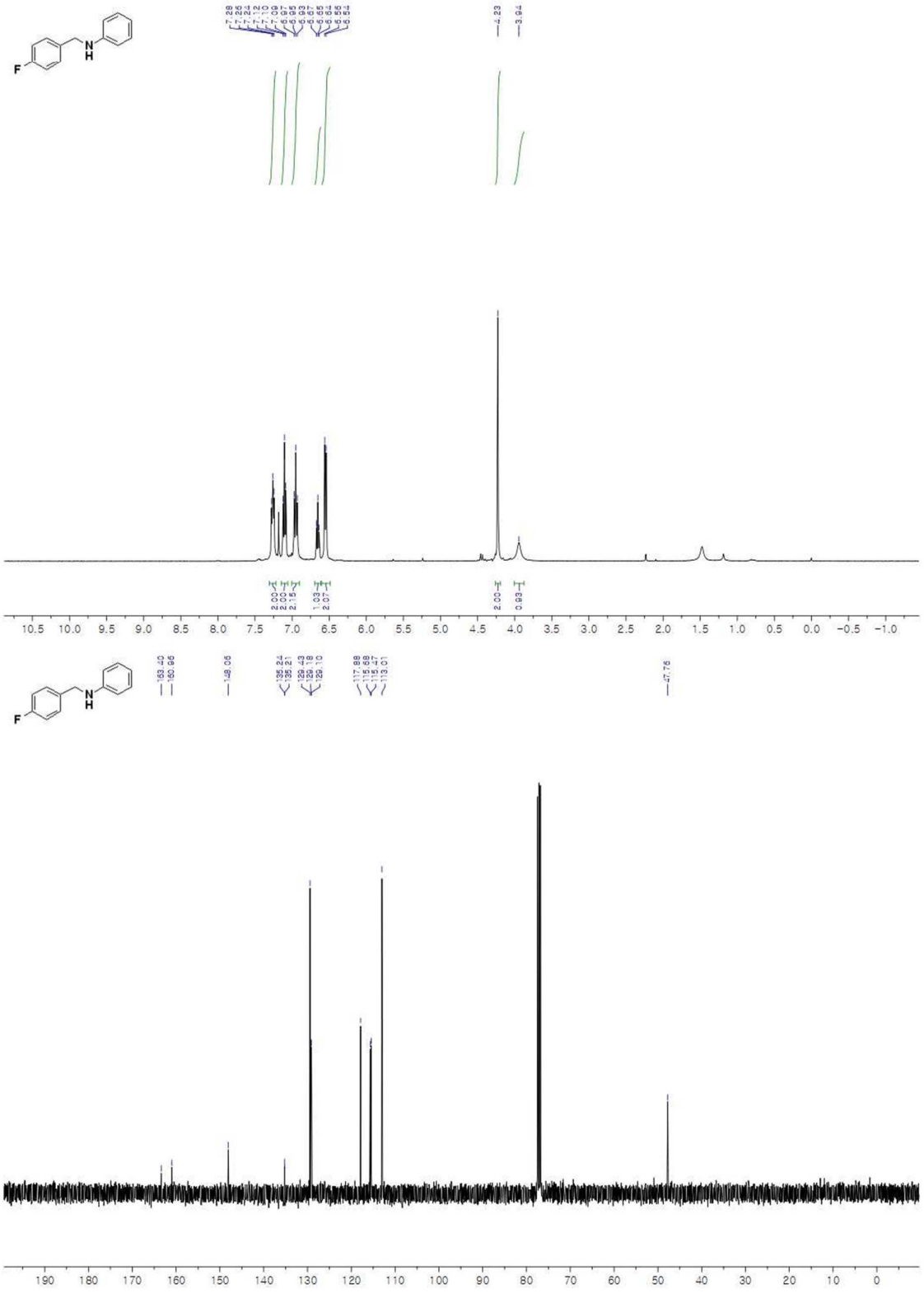




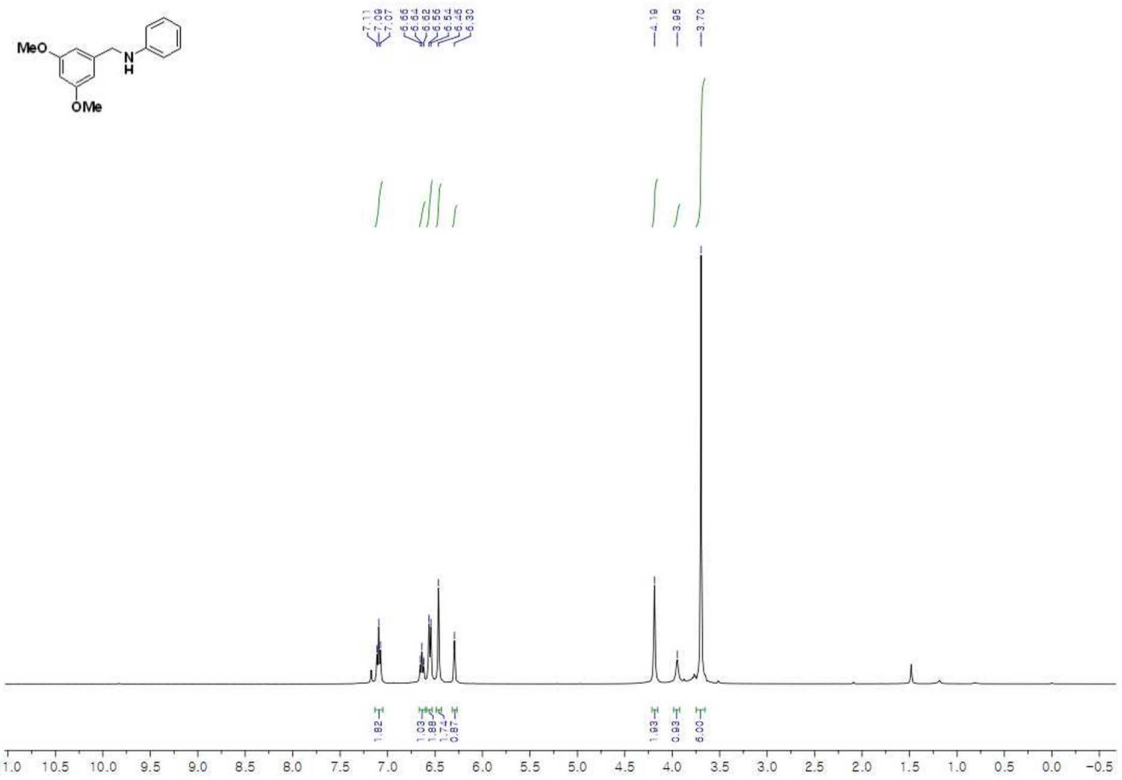
***N*-(4-ethoxybenzyl)aniline – (Table 2, 1e)**

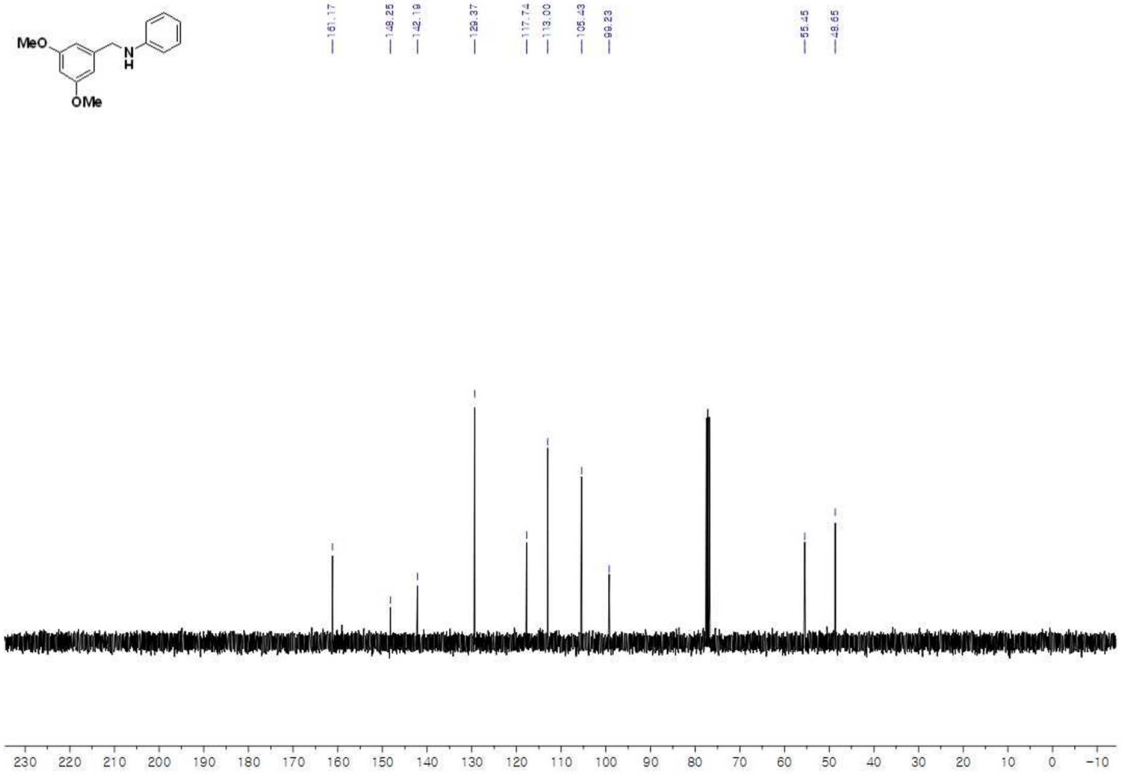


***N*-(4-fluorobenzyl)aniline – (Table 2, 1f)**

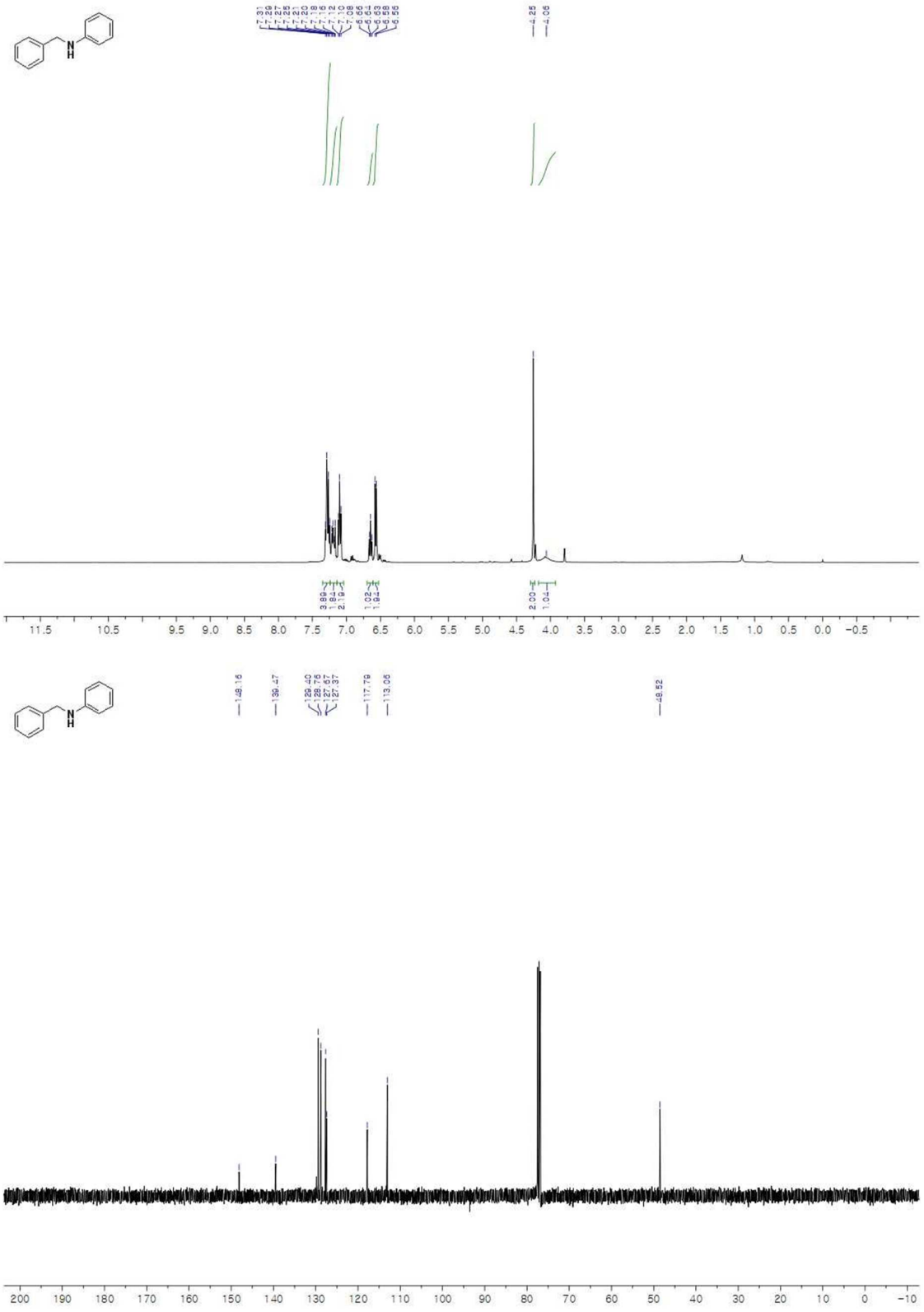


***N*-(3,5-dimethoxybenzyl)aniline – (Table 2, 1g)**

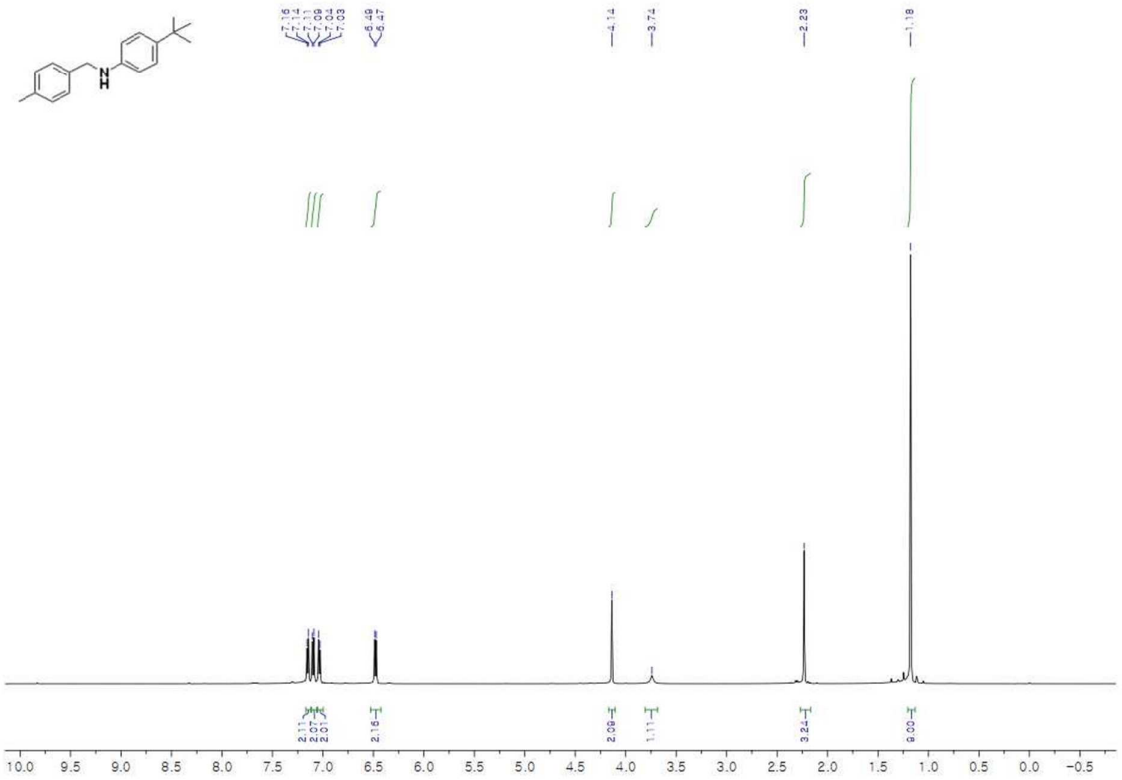


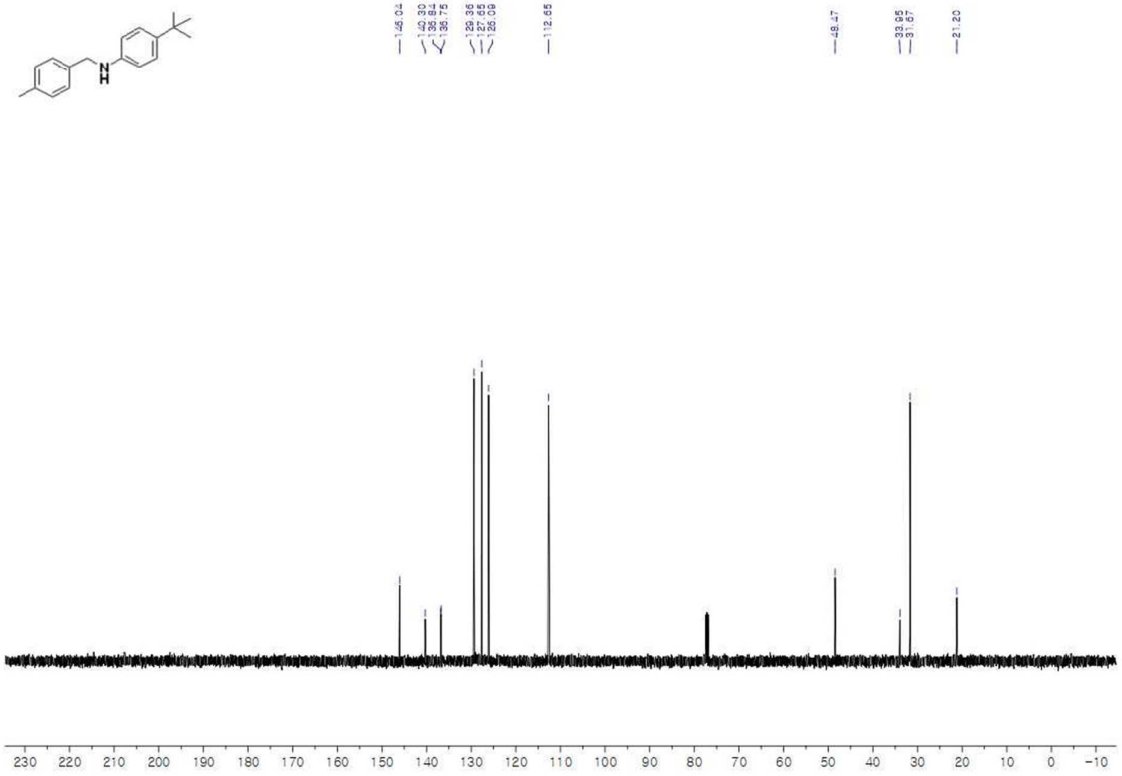


***N*-benzylaniline – (Table 2, 1b)**

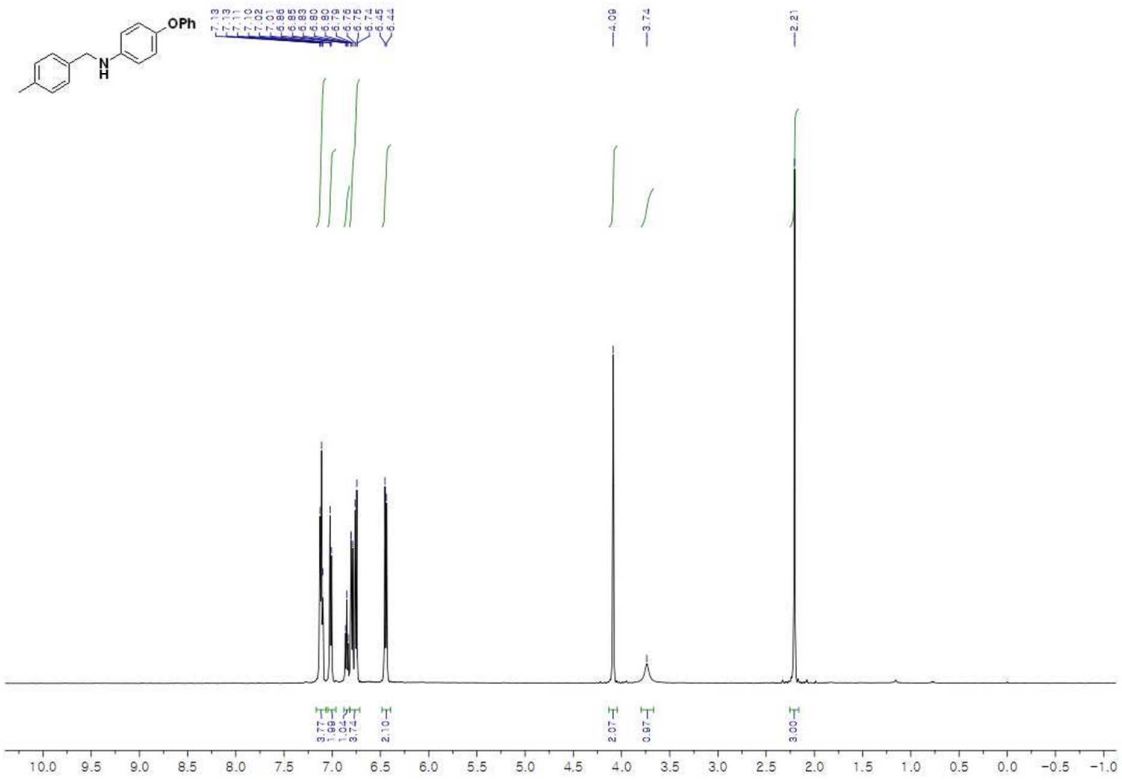


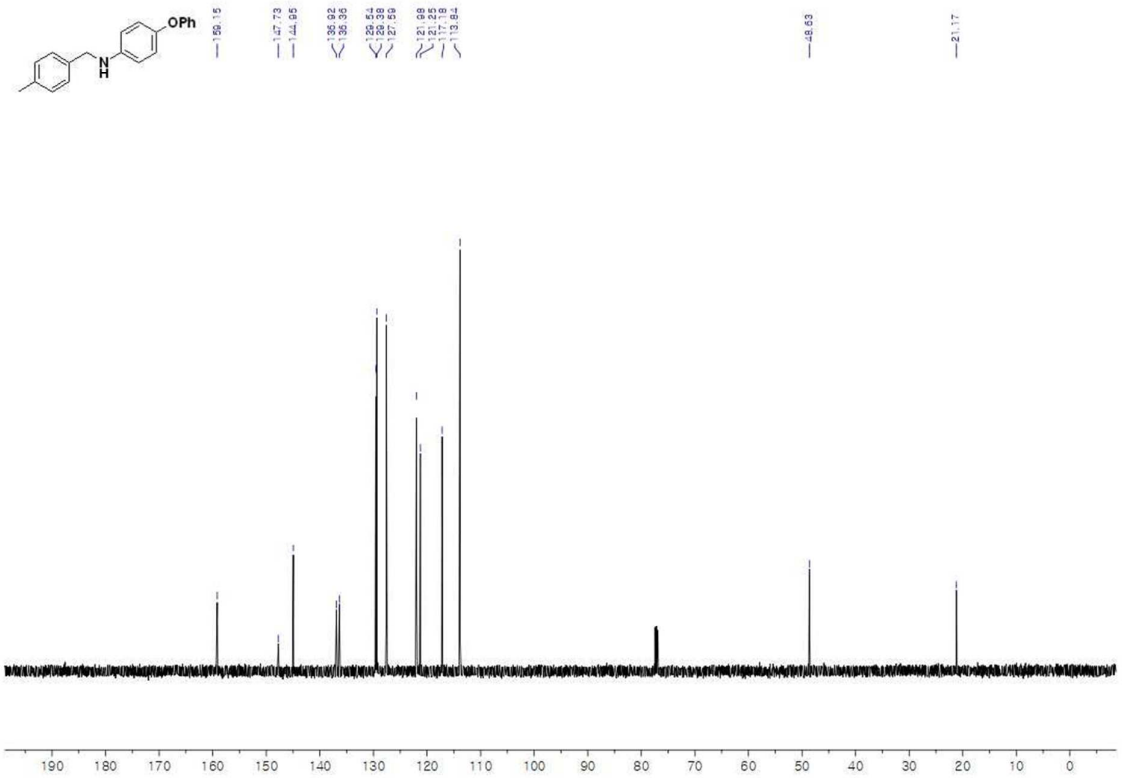
4-(*tert*-butyl)-*N*-(4-methylbenzyl)aniline – (Table 2, 1h)



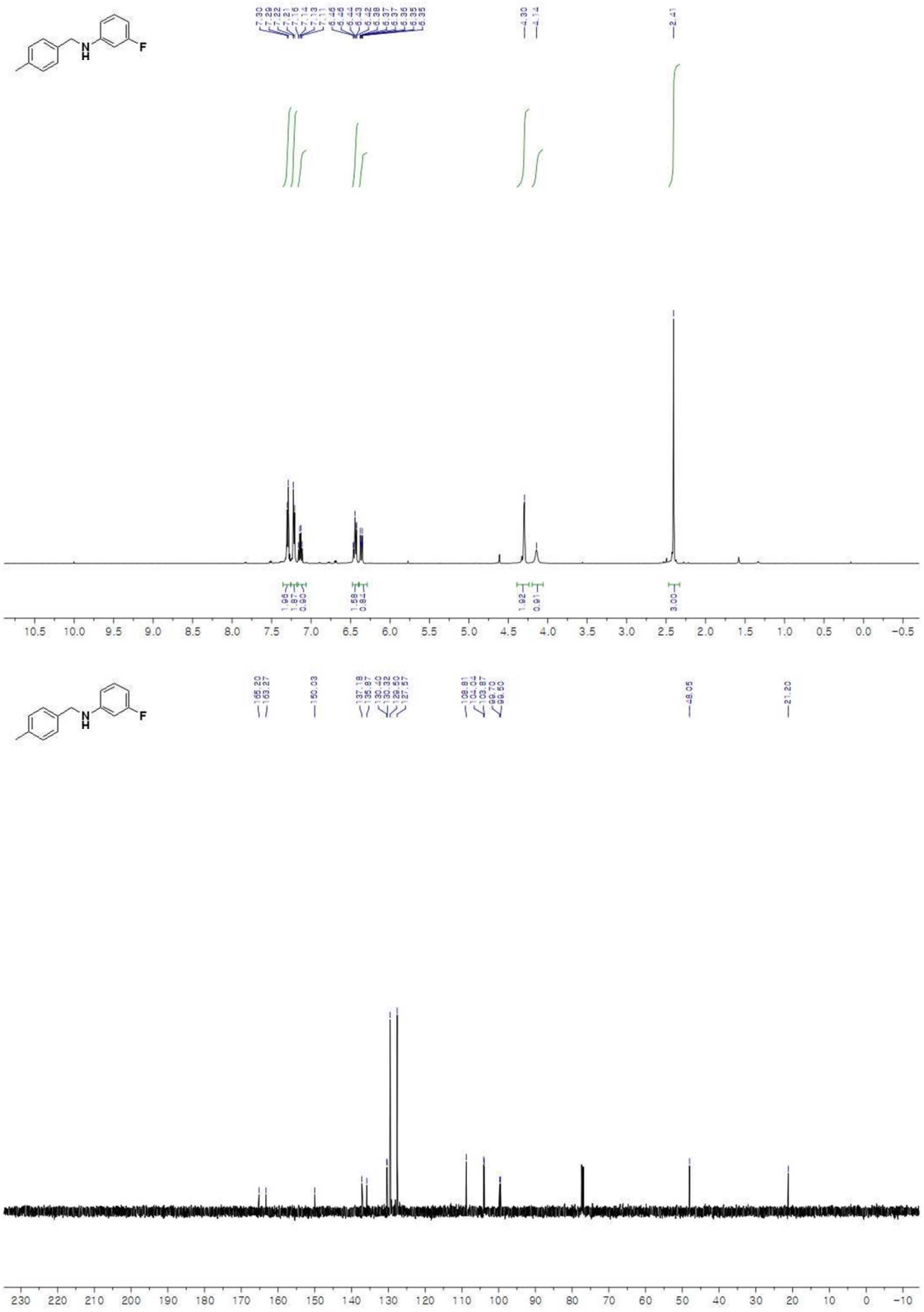


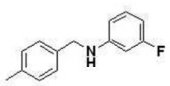
***N*-(4-methylbenzyl)-4-phenoxyaniline – (Table 2, 1i)**

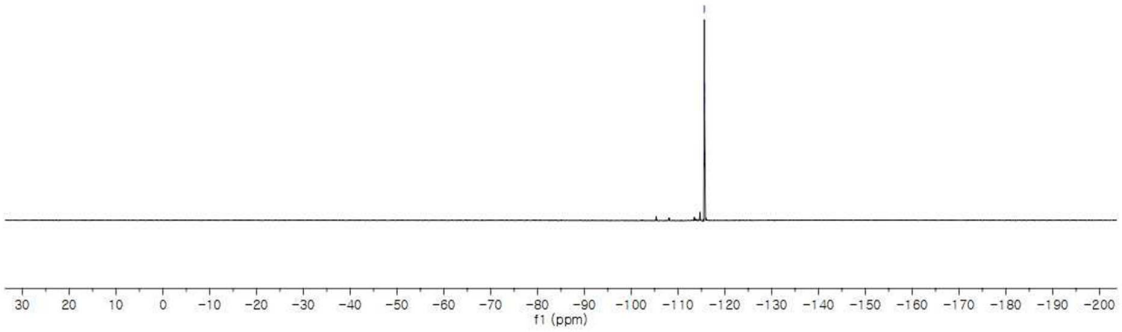




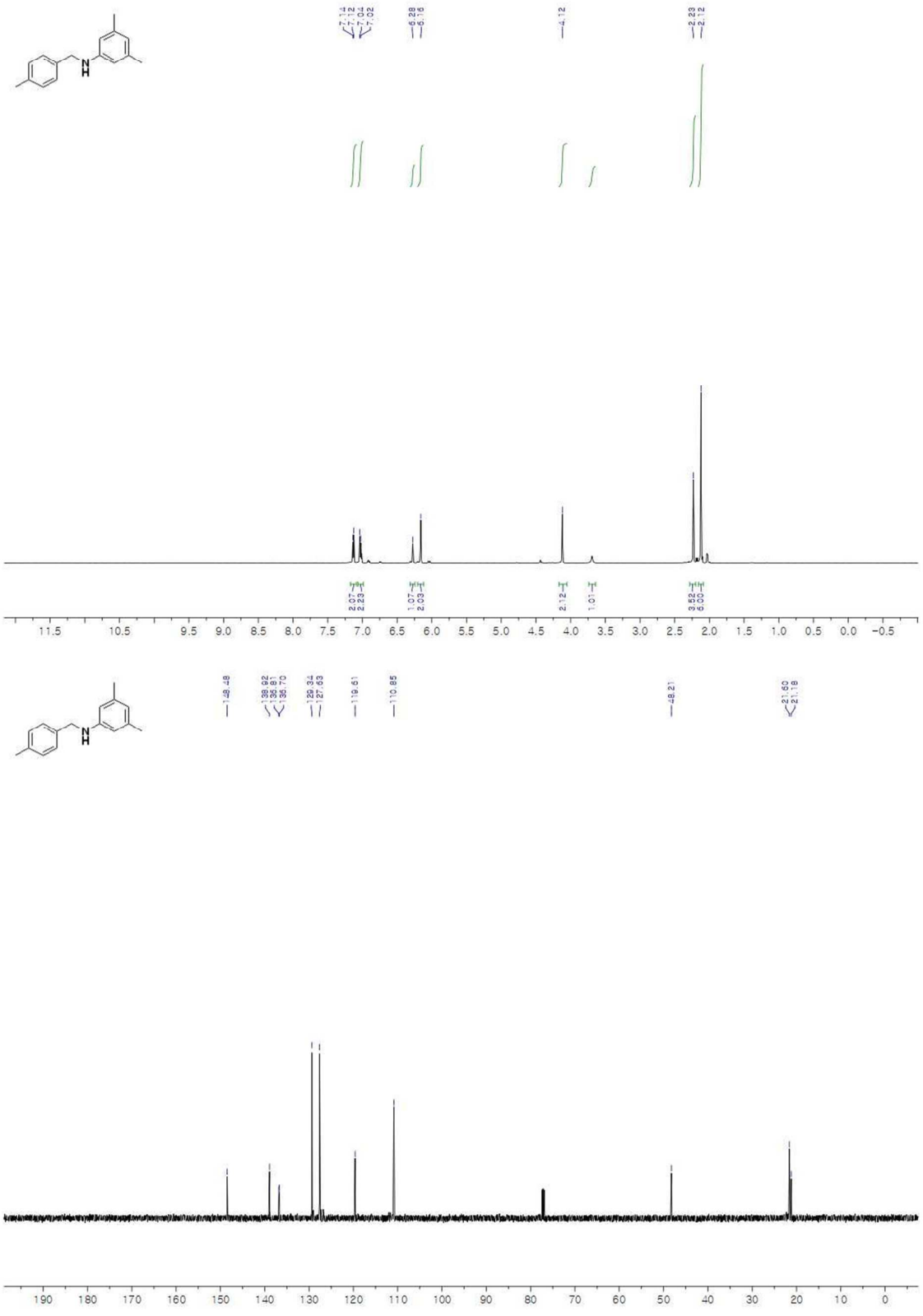
3-fluoro-*N*-(4-methylbenzyl)aniline – (Table 2, 1j)



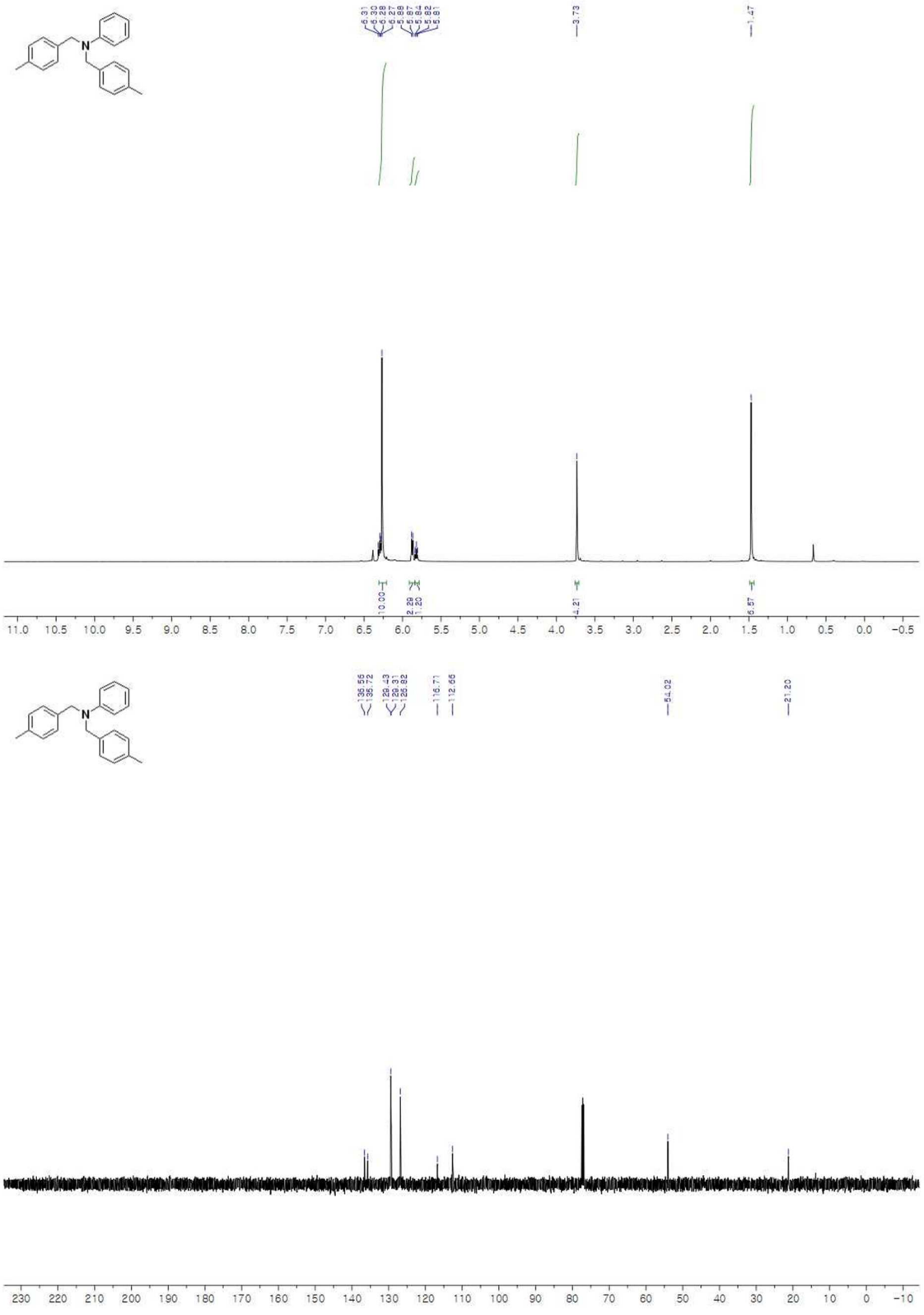

N
H
F


30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

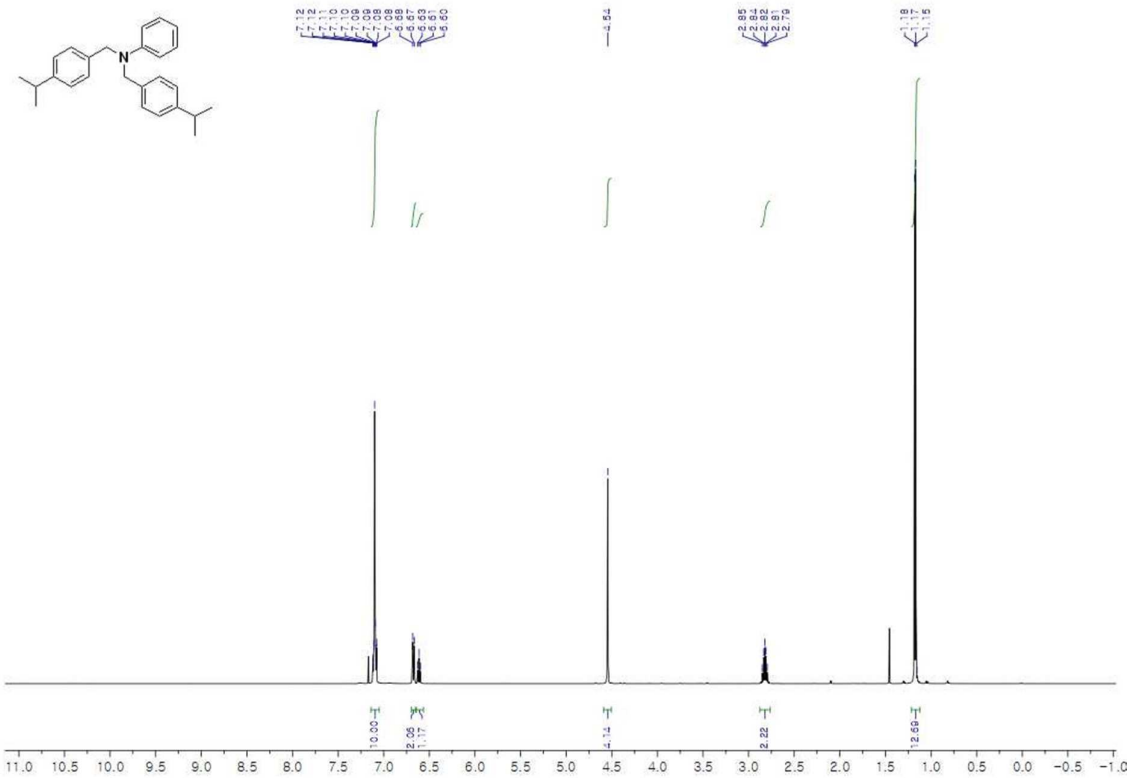
3,5-dimethyl-*N*-(4-methylbenzyl)aniline – (Table 2, 1k)

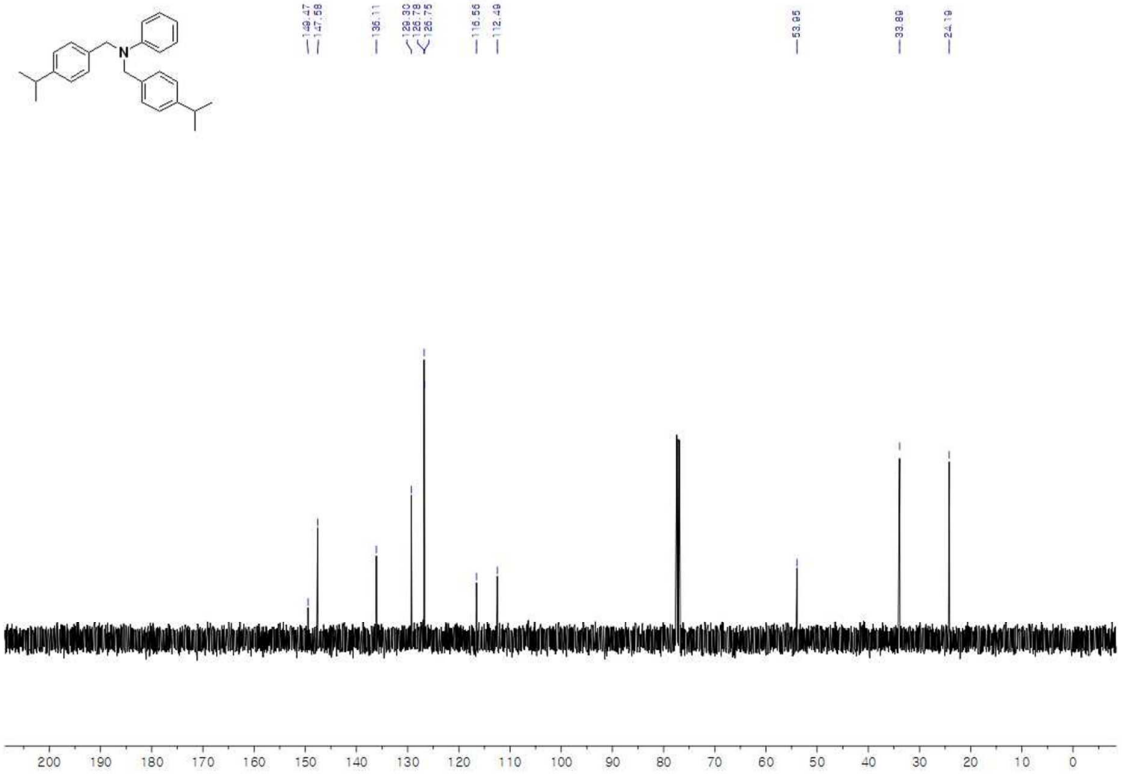


***N*,*N*-bis(4-methylbenzyl)aniline – (Table 2, 1aa)**

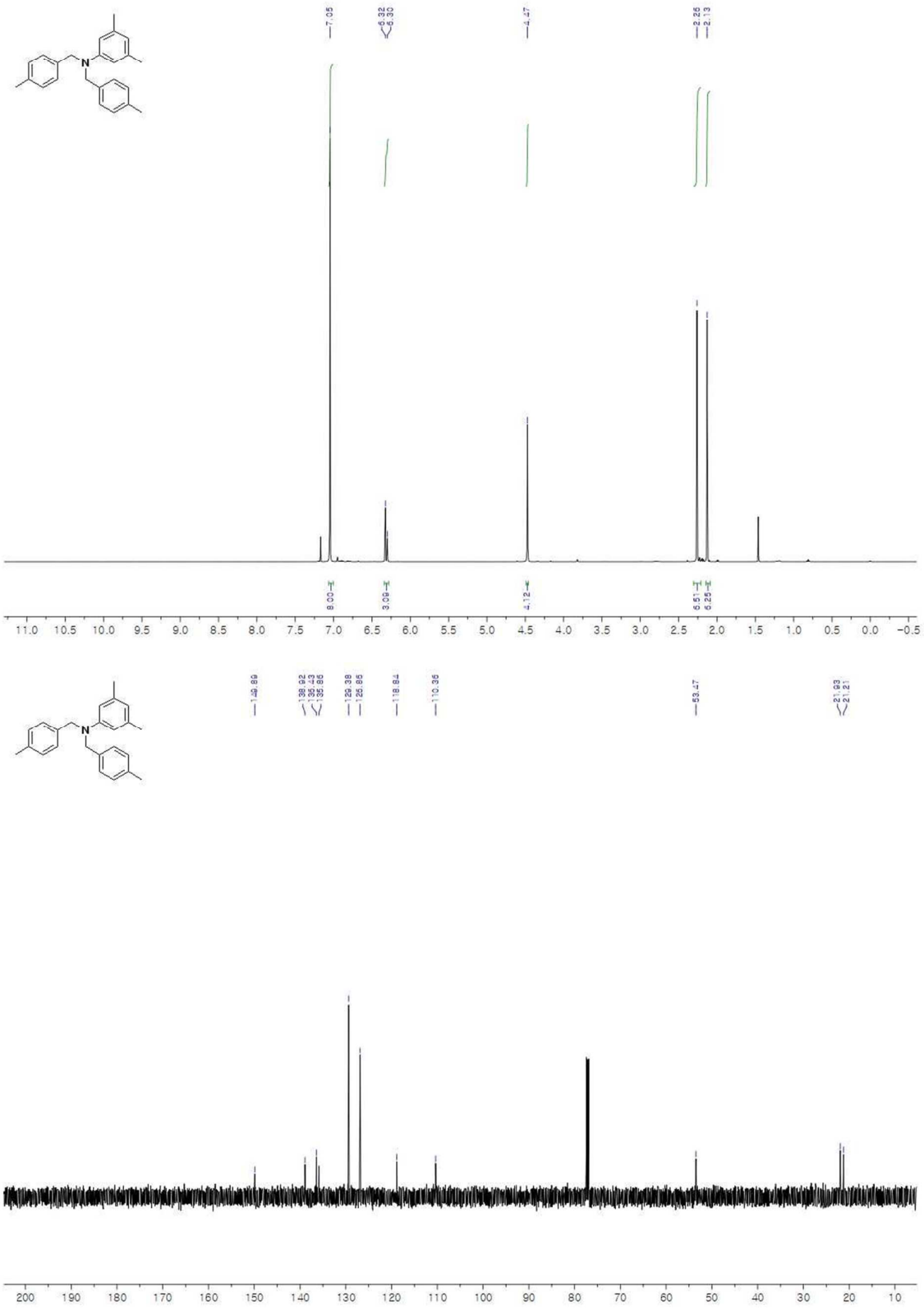


***N,N*-bis(4-isopropylbenzyl)aniline – (Table 2, 1bb)**

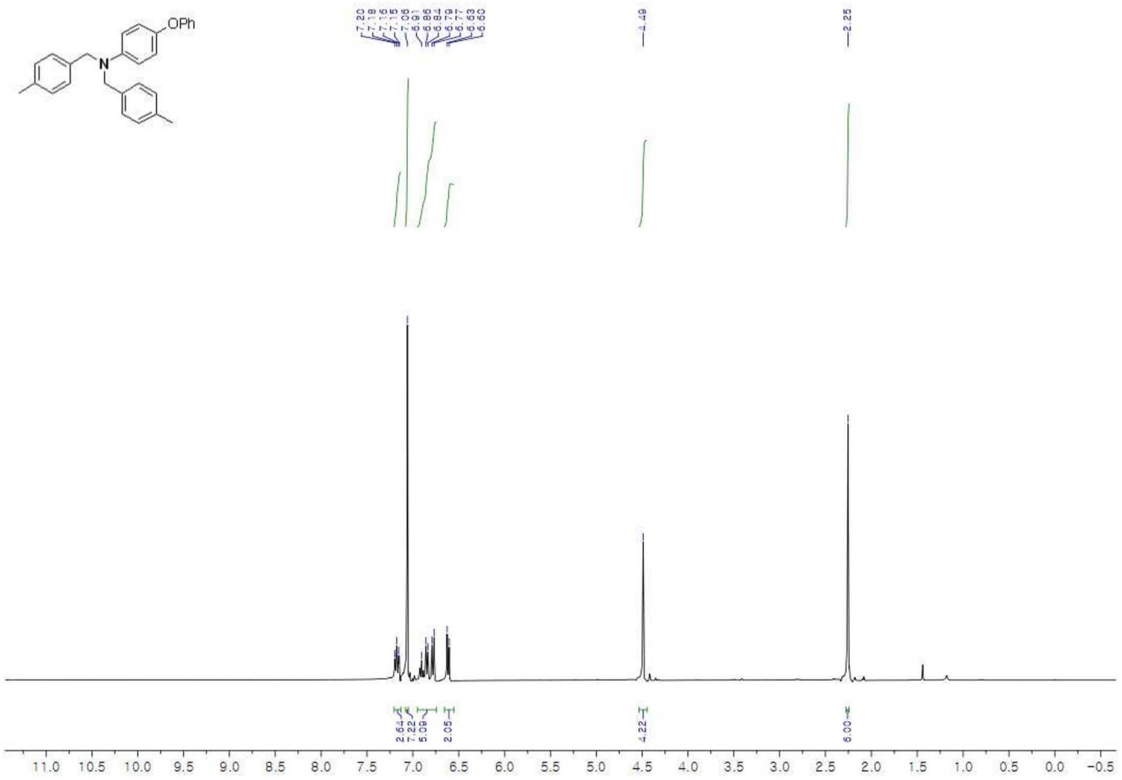


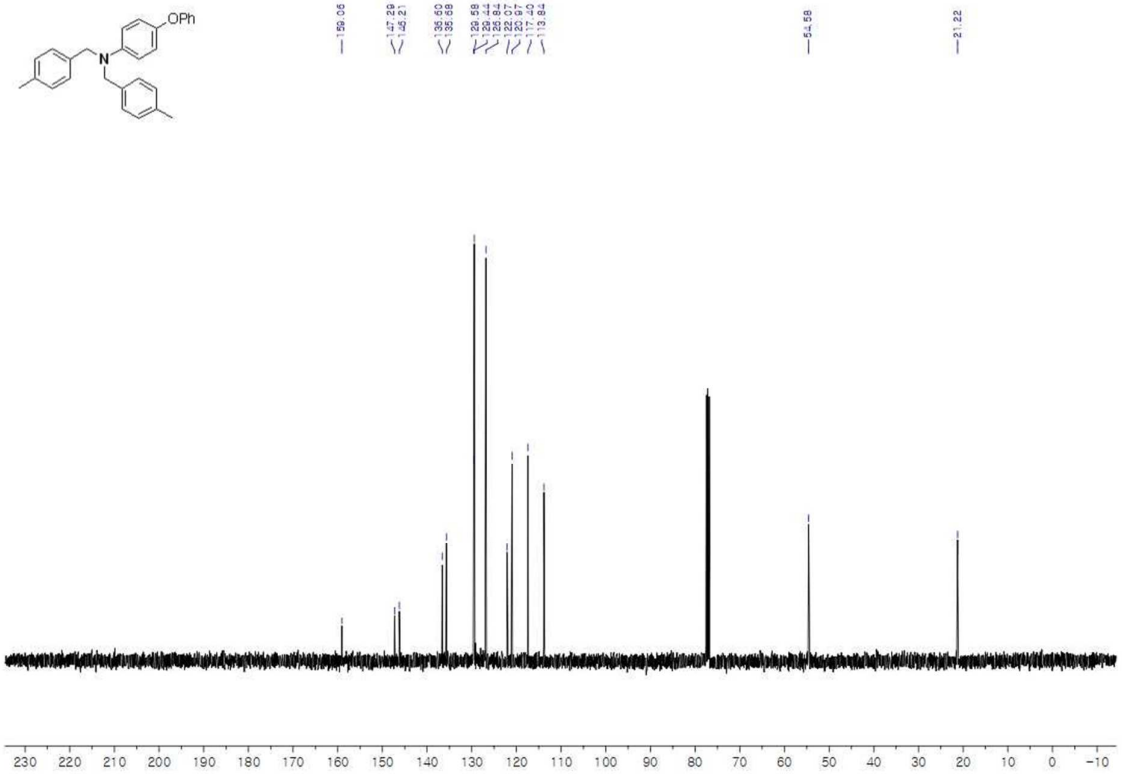


3,5-dimethyl-*N*,*N*-bis(4-methylbenzyl)aniline – (Table 2, 1cc)

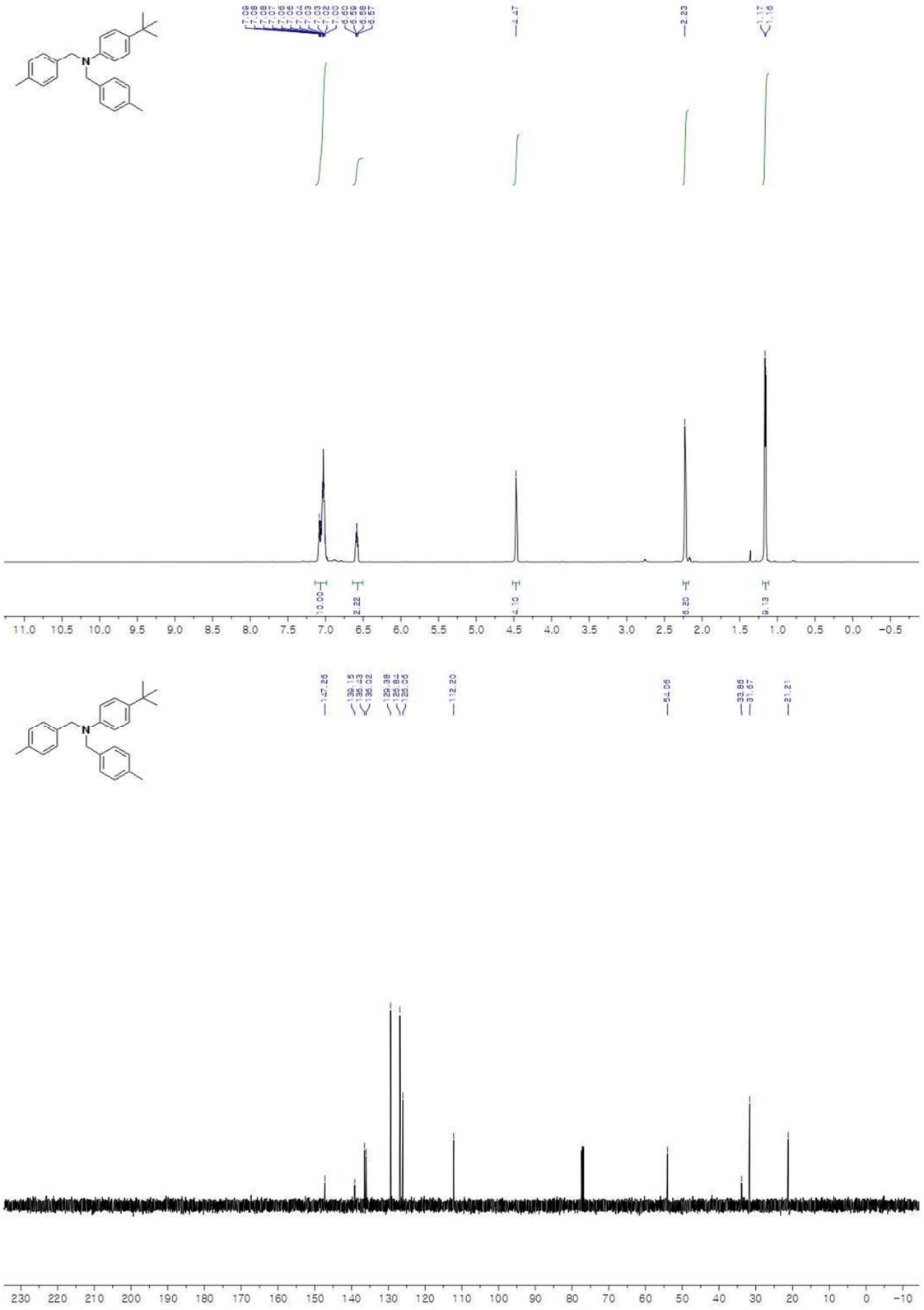


***N,N*-bis(4-methylbenzyl)-4-phenoxyaniline – (Table 2, 1dd)**

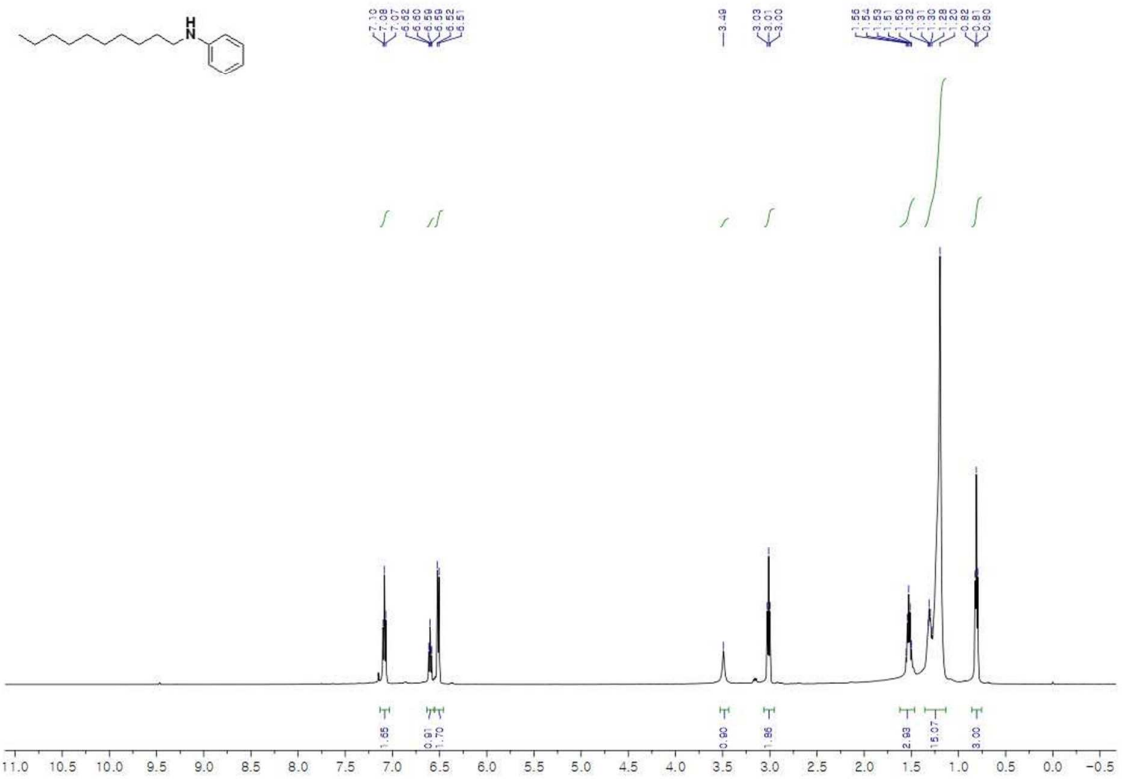


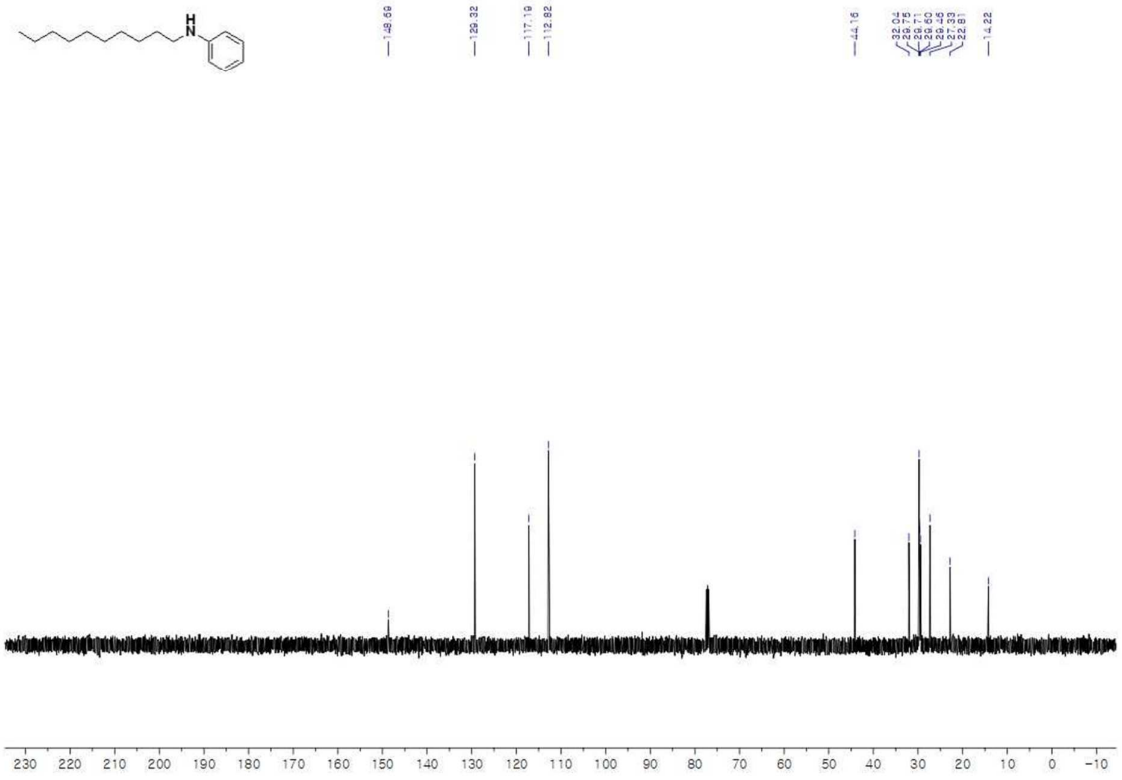


4-(*tert*-butyl)-*N*,*N*-bis(4-methylbenzyl)aniline – (Table 2, 1ee)

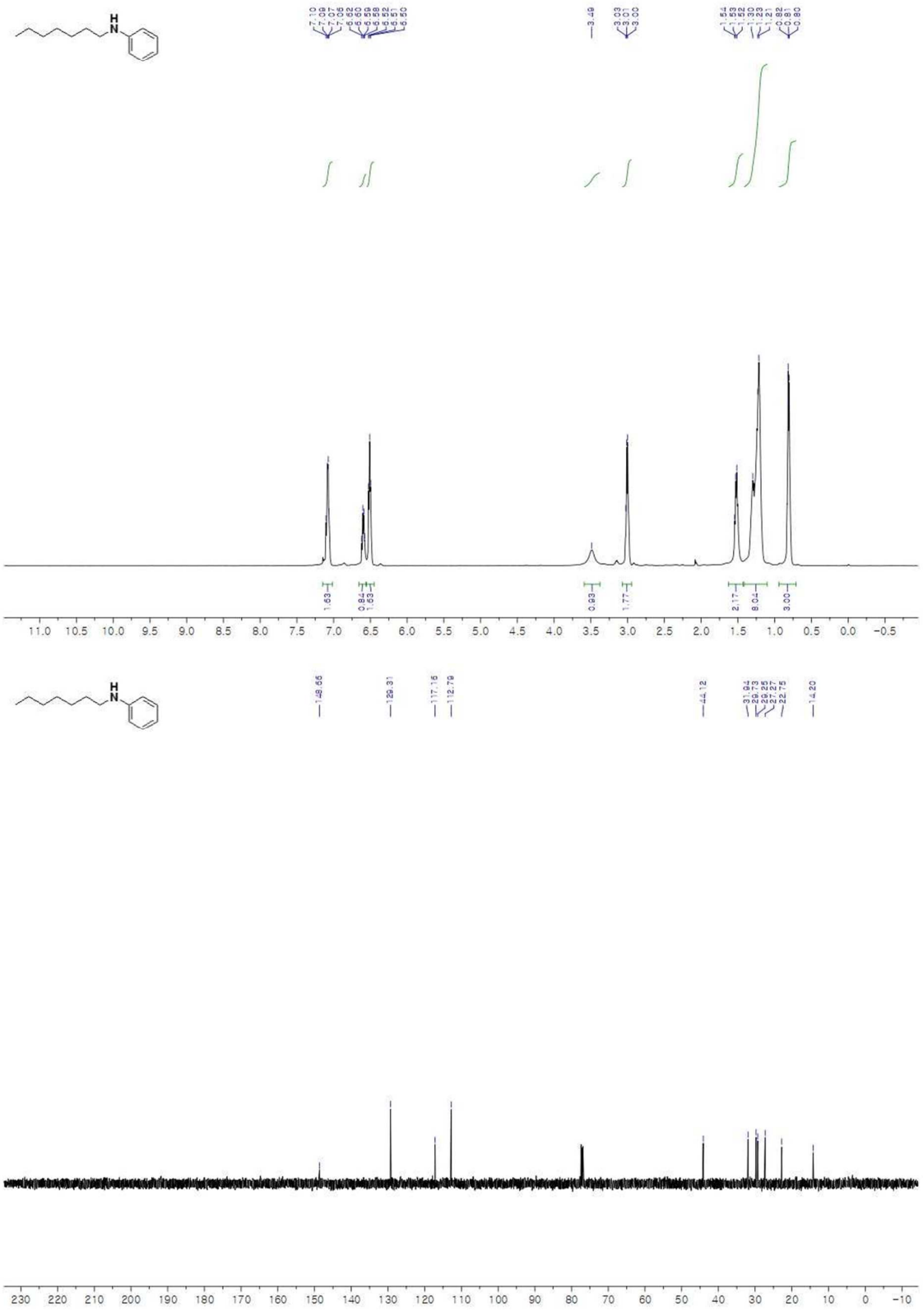


***N*-decylaniline – (Table 3, 2b)**

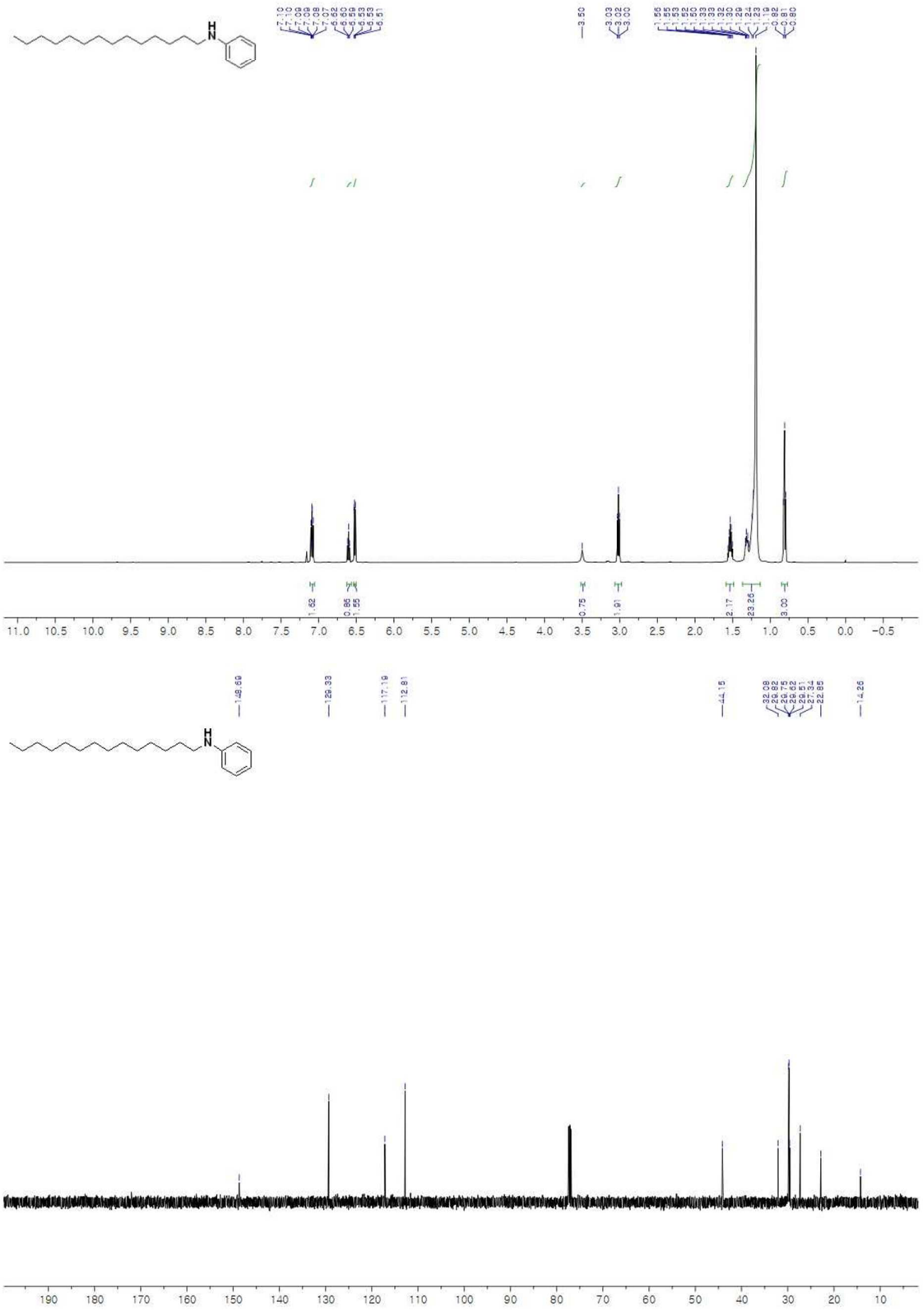




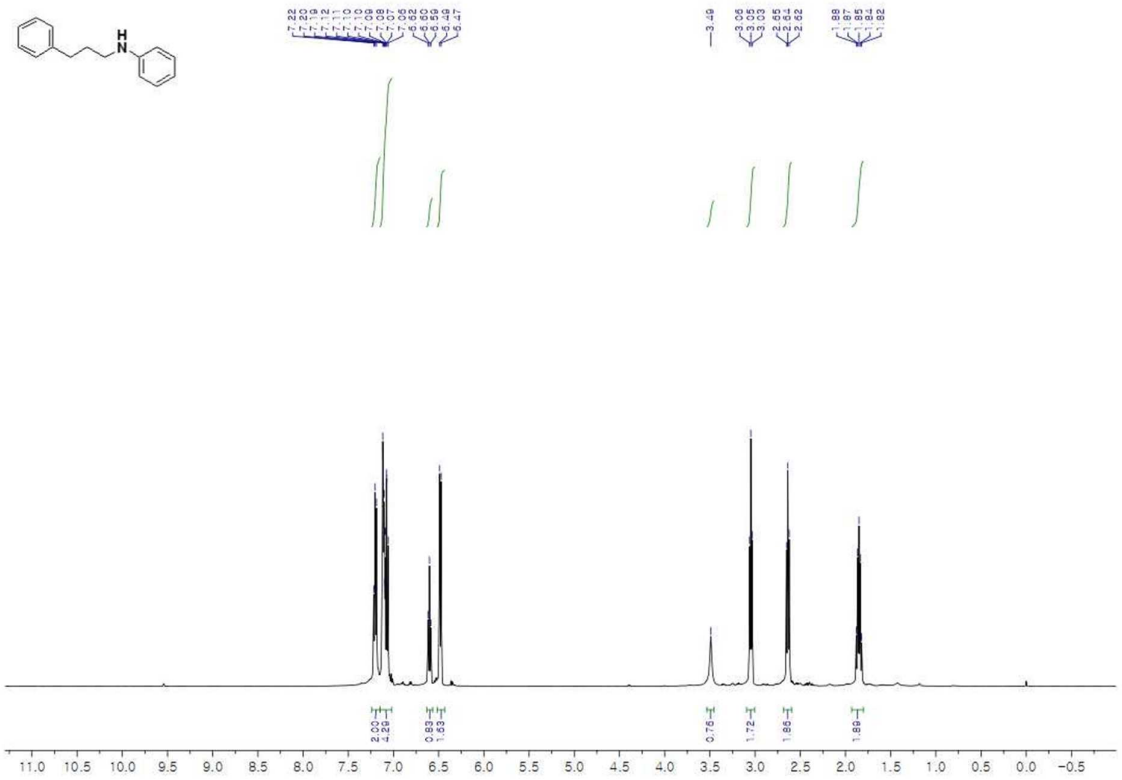
***N*-heptylaniline – (Table 3, 2a)**

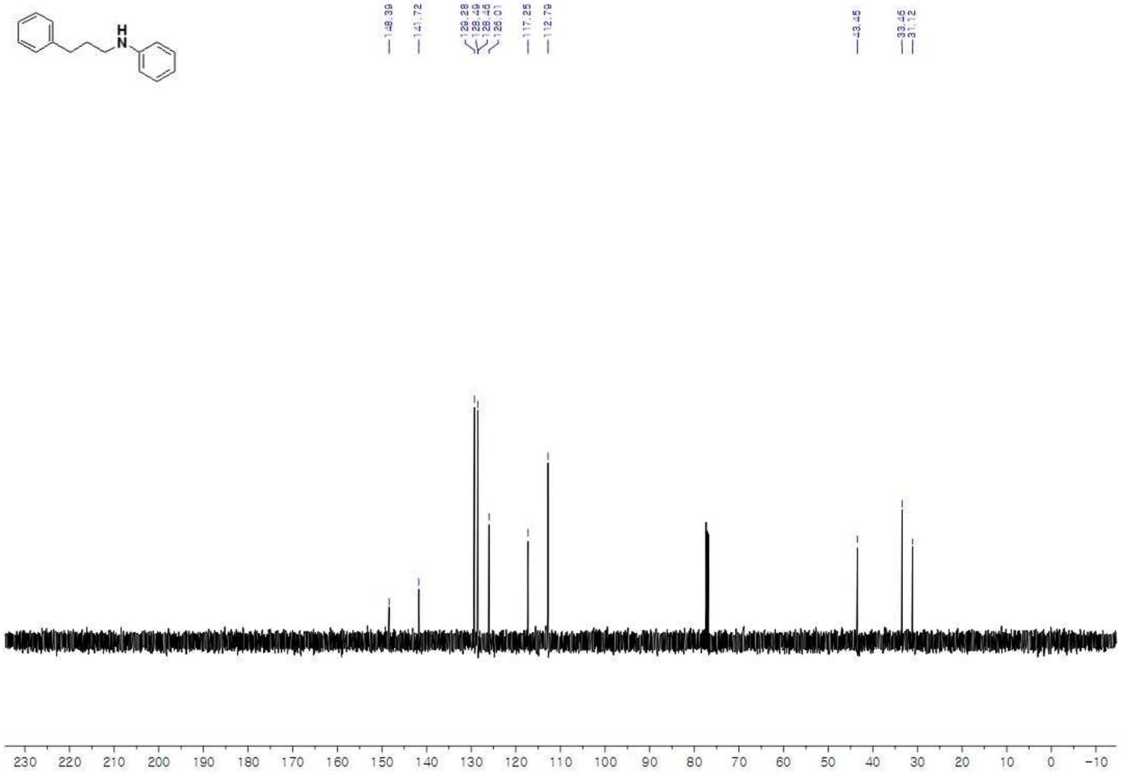


***N*-tetradecylaniline – (Table 3, 2c)**

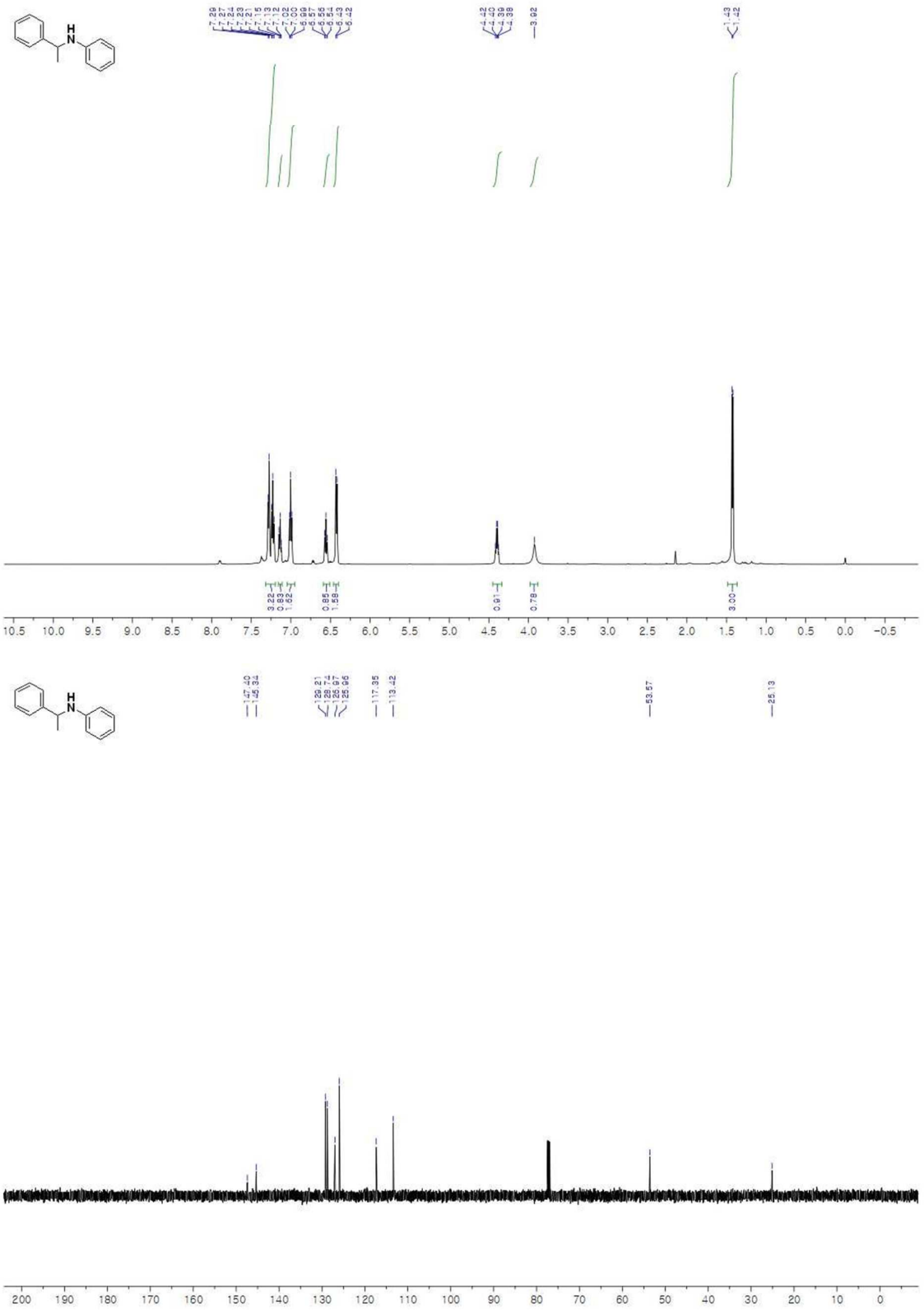


***N*-(3-phenylpropyl)aniline – (Table 3, 2d)**

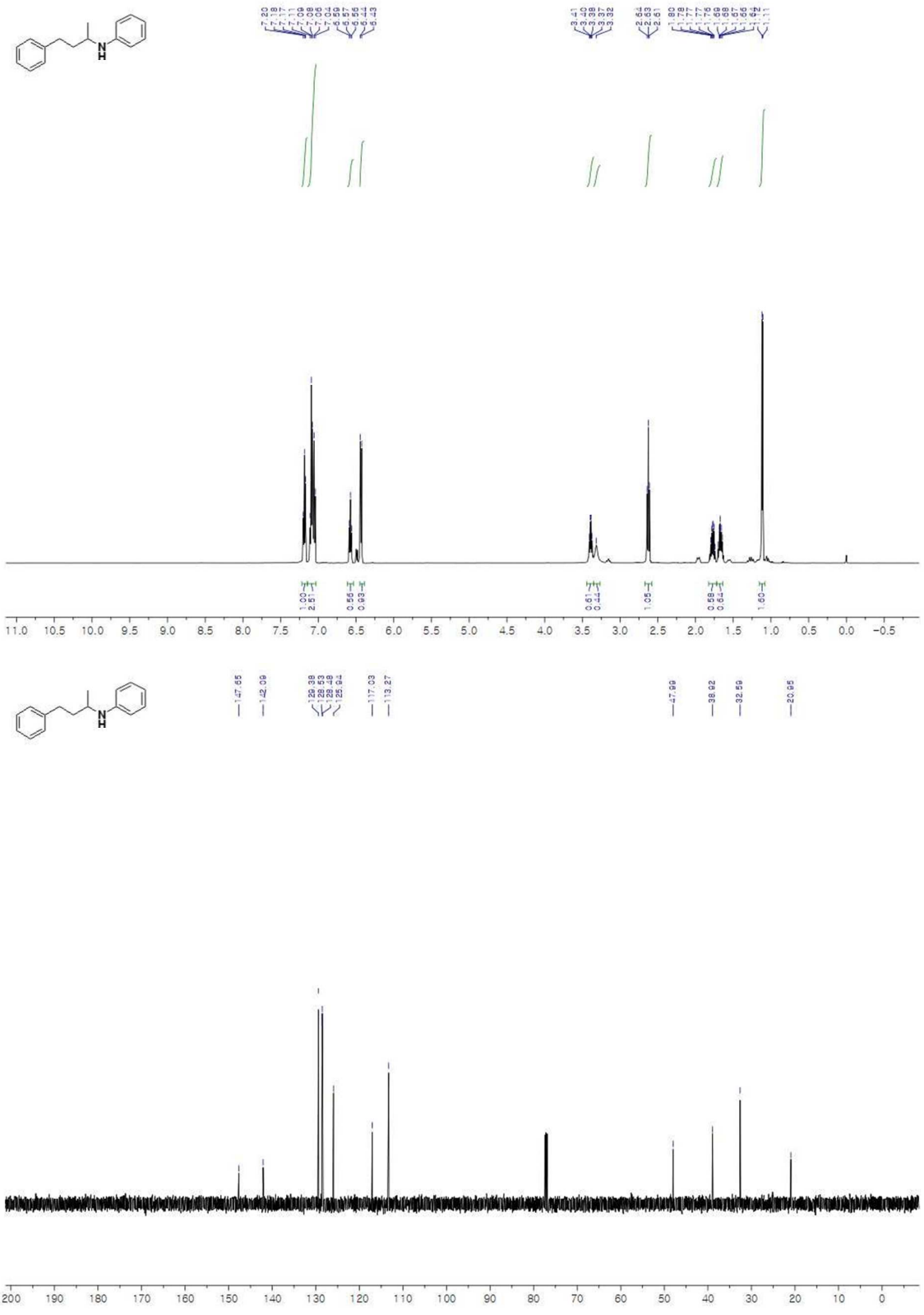




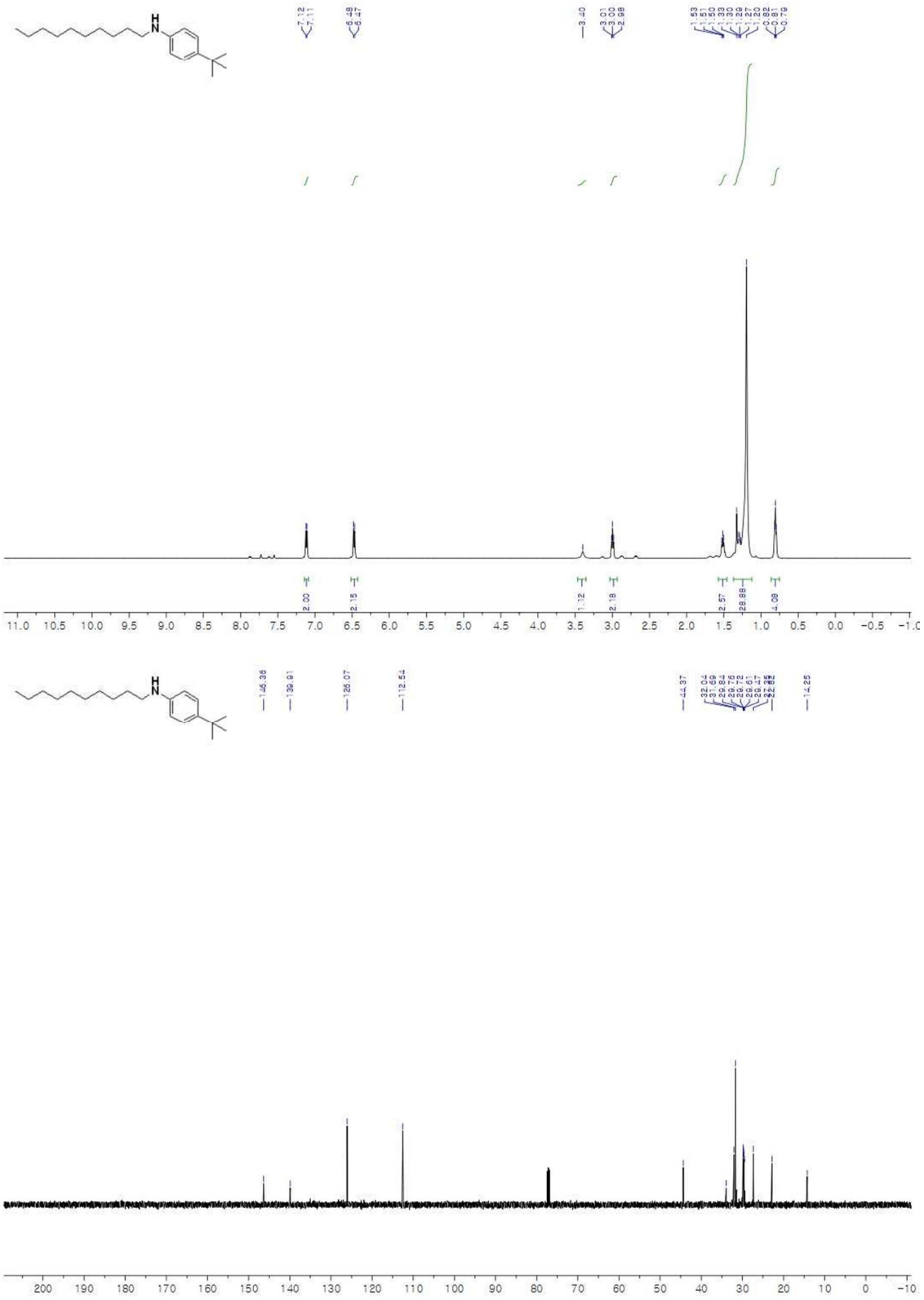
***N*-(1-phenylethyl)aniline – (Table 3, 2e)**



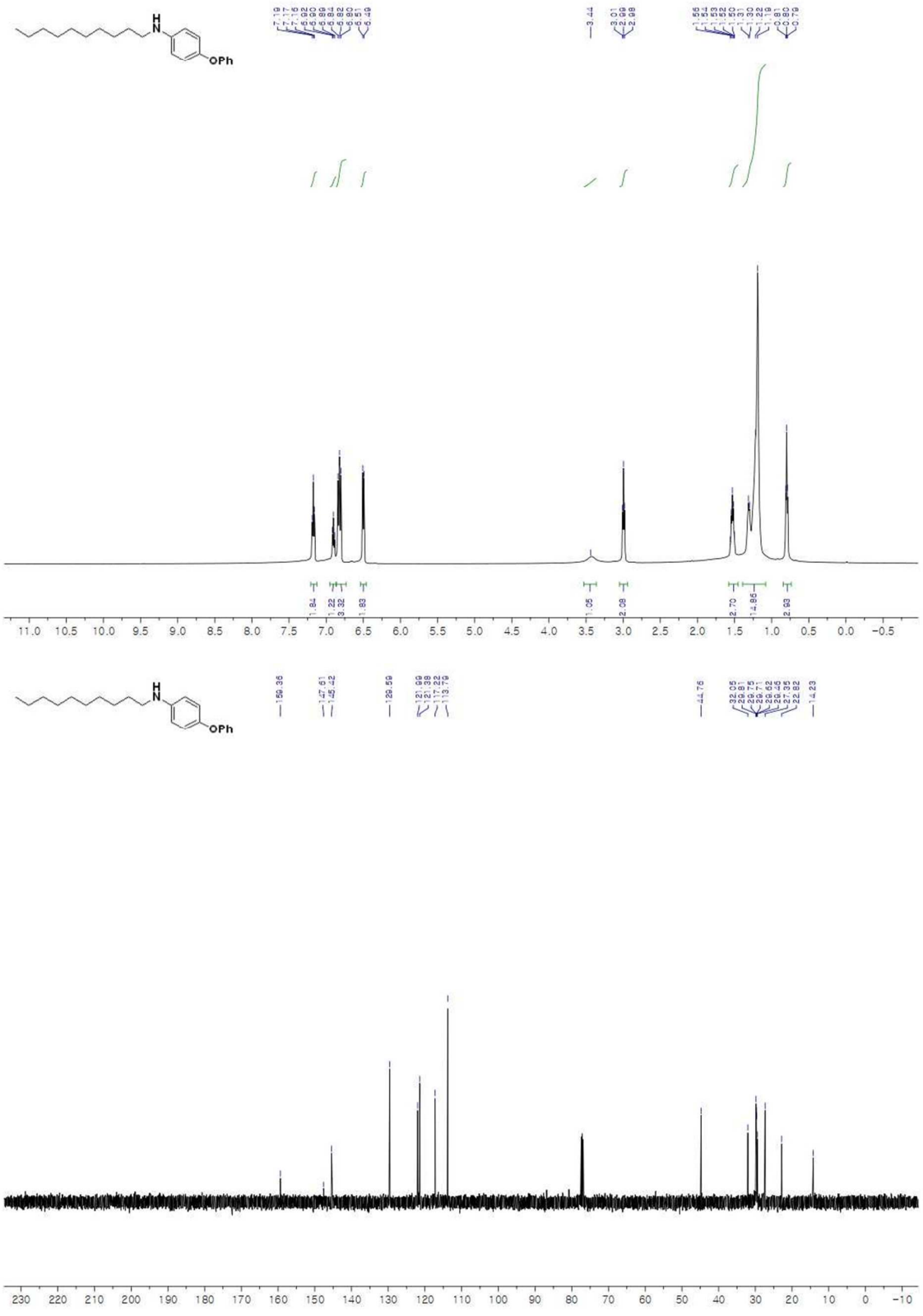
***N*-(4-phenylbutan-2-yl)aniline – (Table 3, 2f)**



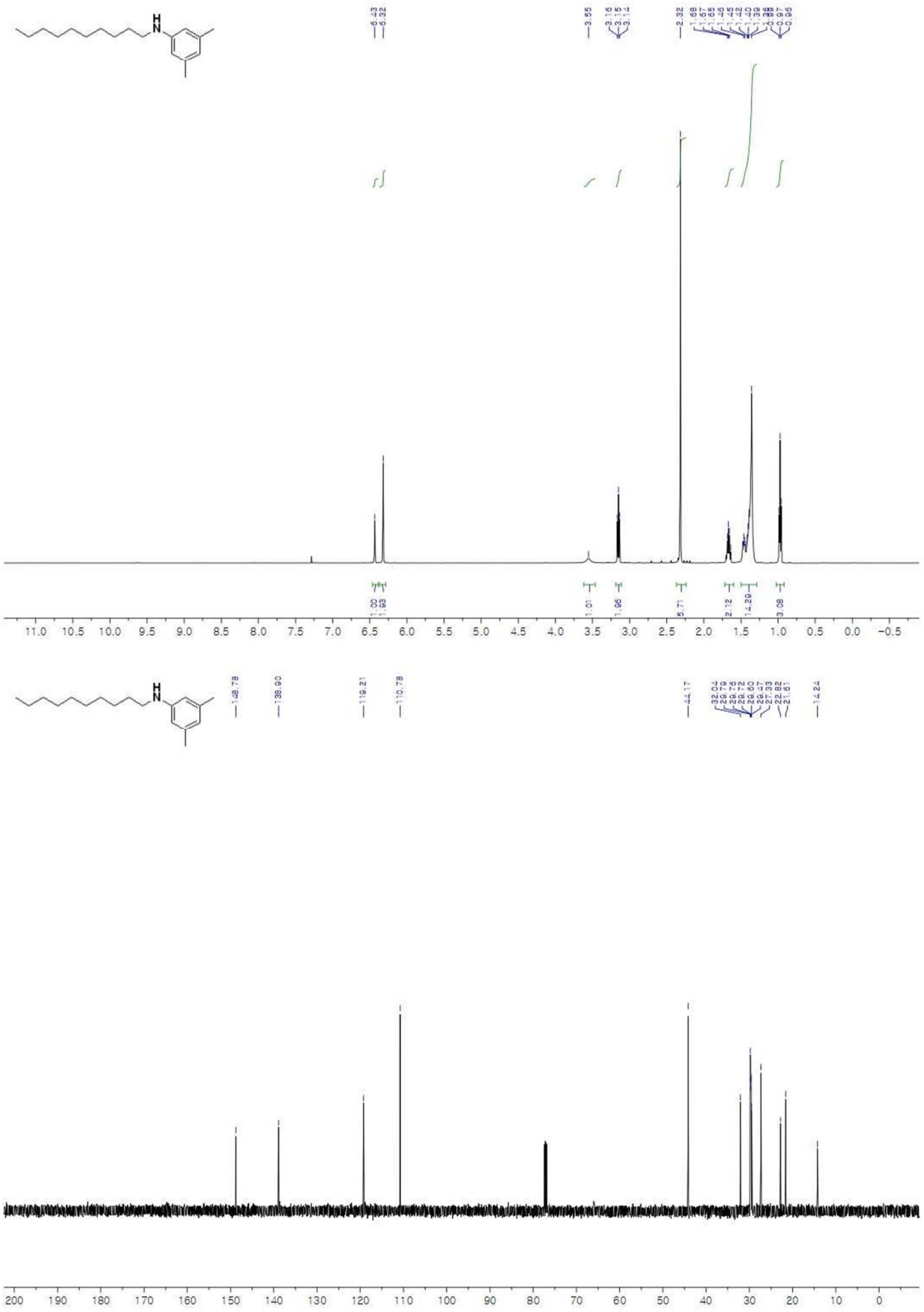
4-(*tert*-butyl)-*N*-decylaniline – (Table 3, 2i)



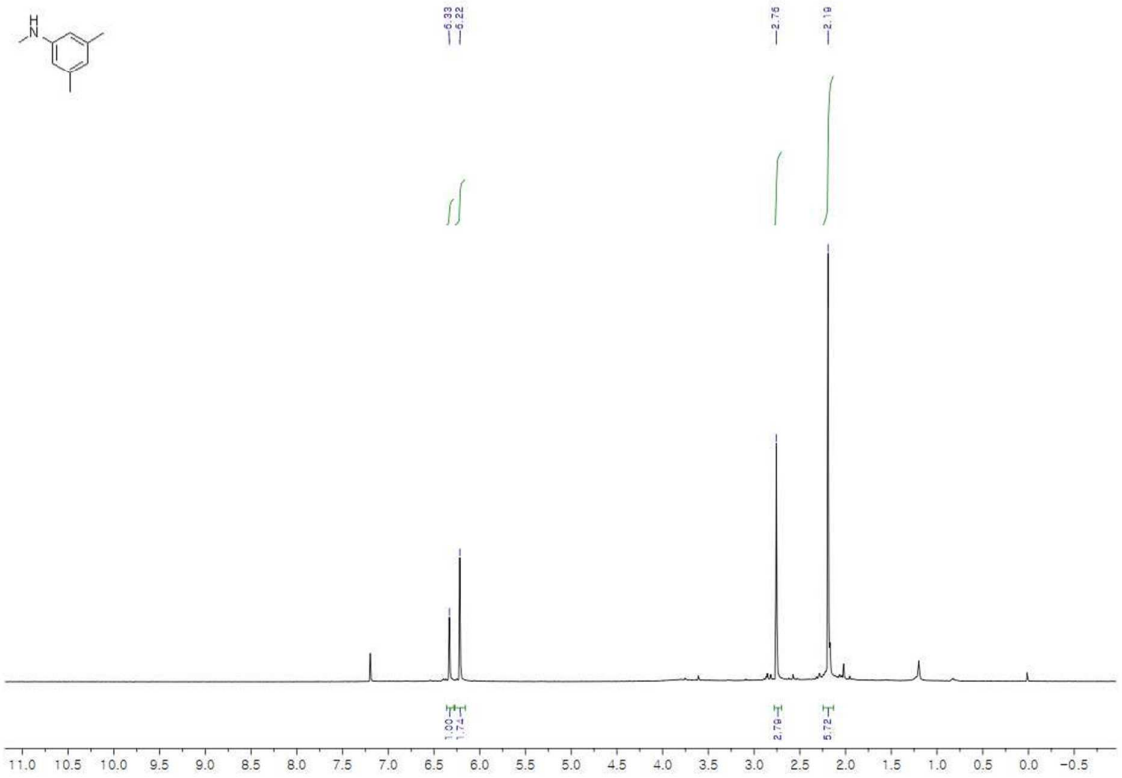
***N*-decyl-4-phenoxyaniline – (Table 3, 2j)**

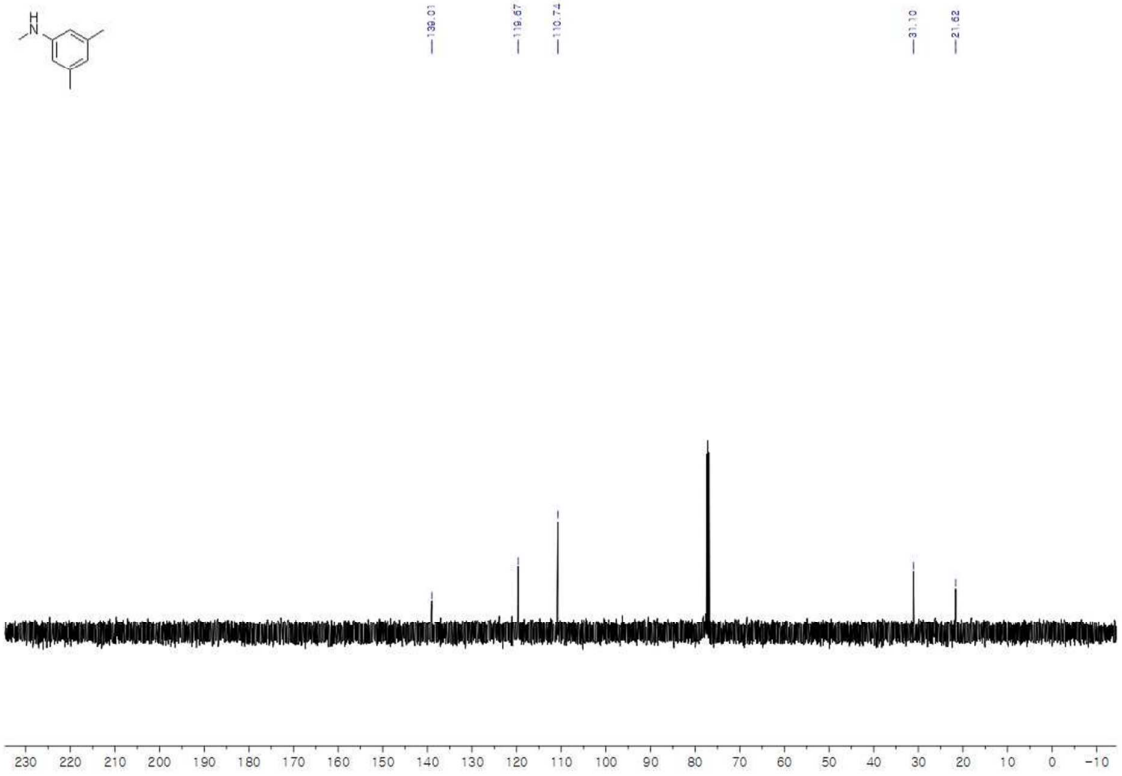


***N*-decyl-3,5-dimethylaniline – (Table 3, 2k)**

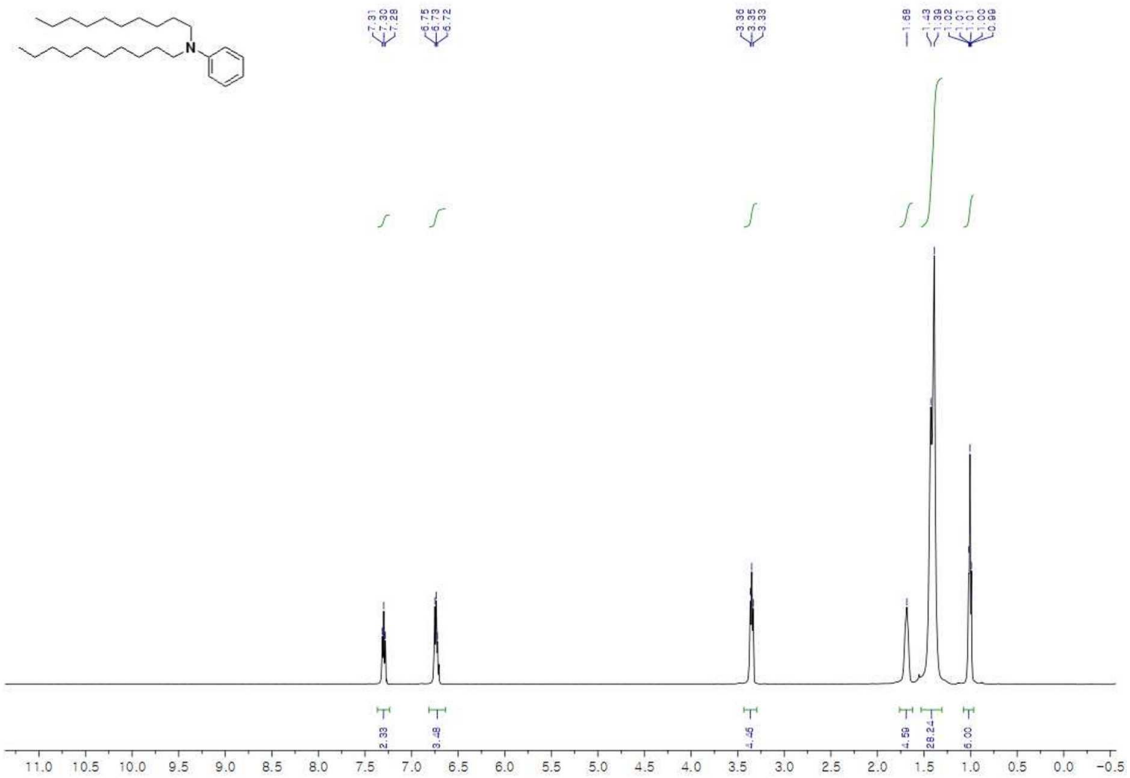


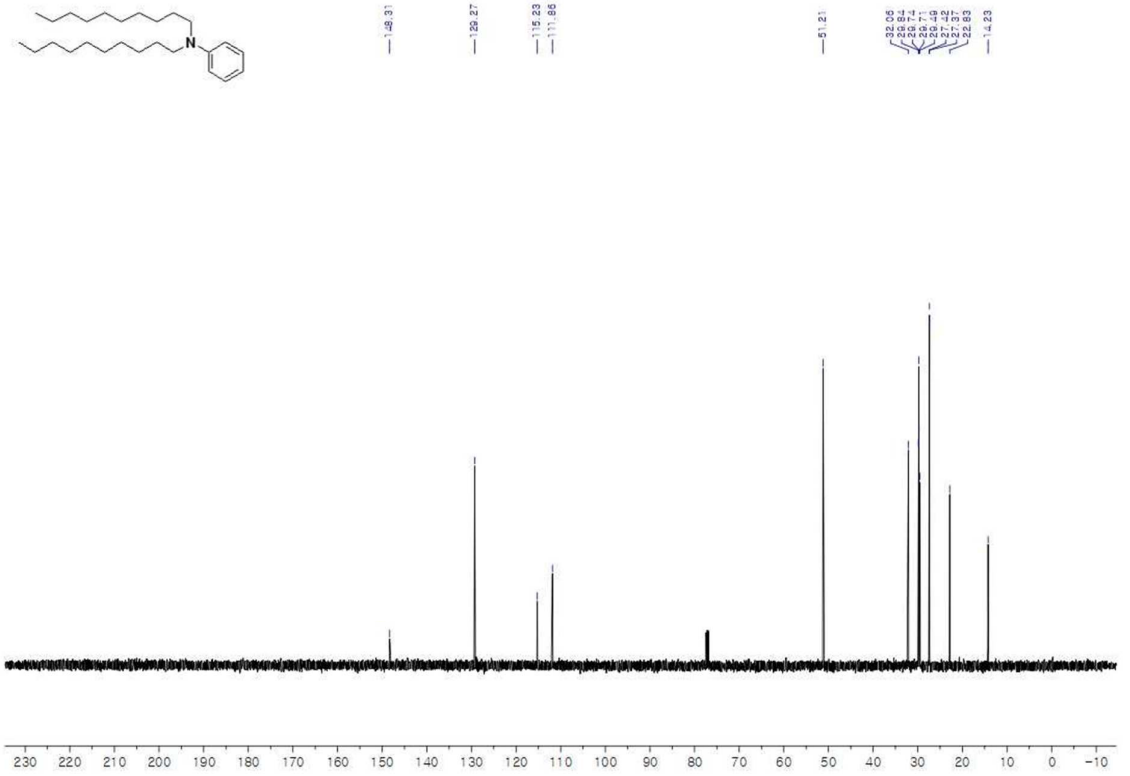
***N*-3,5-trimethylaniline – (Table 3, 2h)**



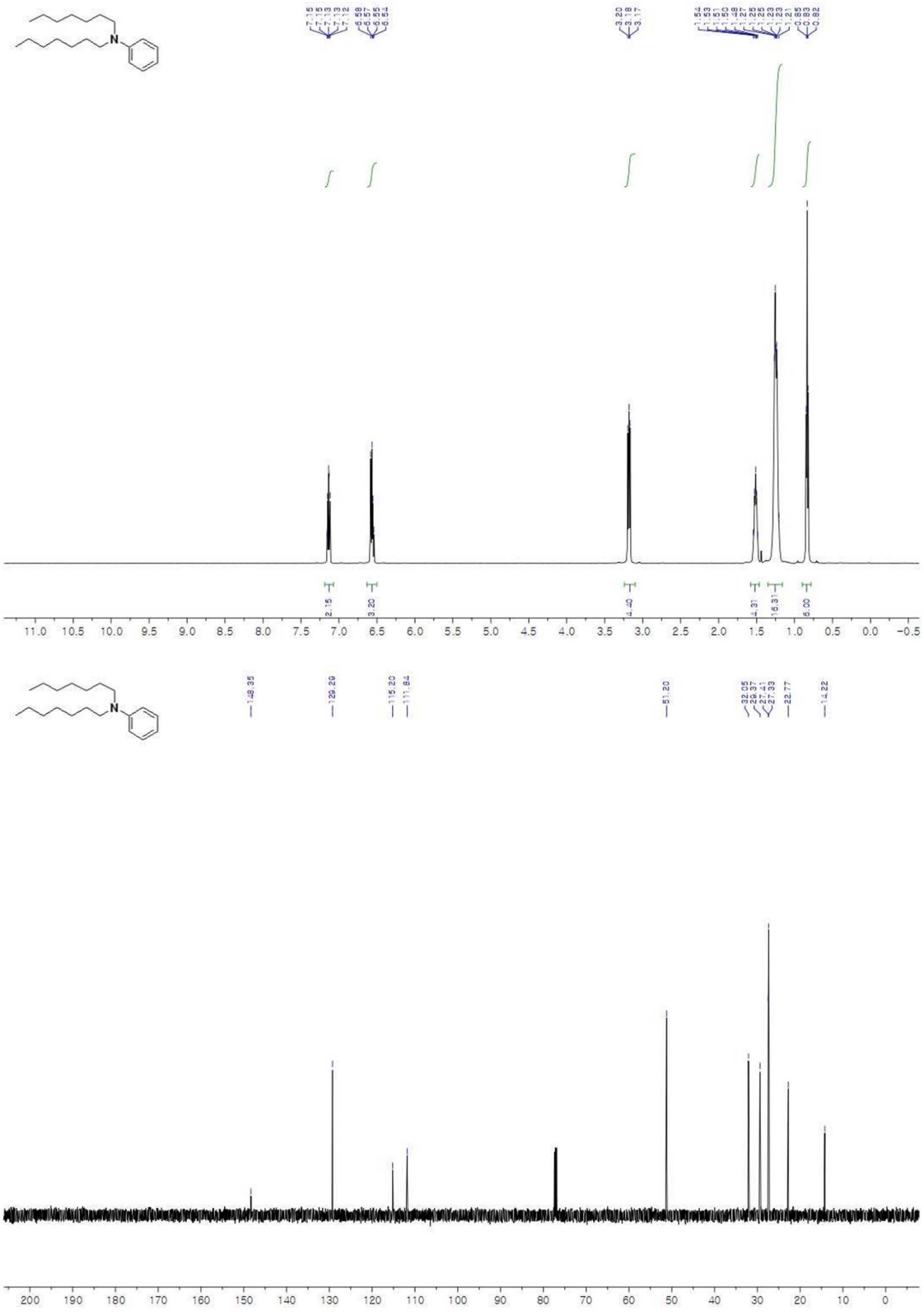


***N,N*-didecylaniline – (Table 3, 2bb)**

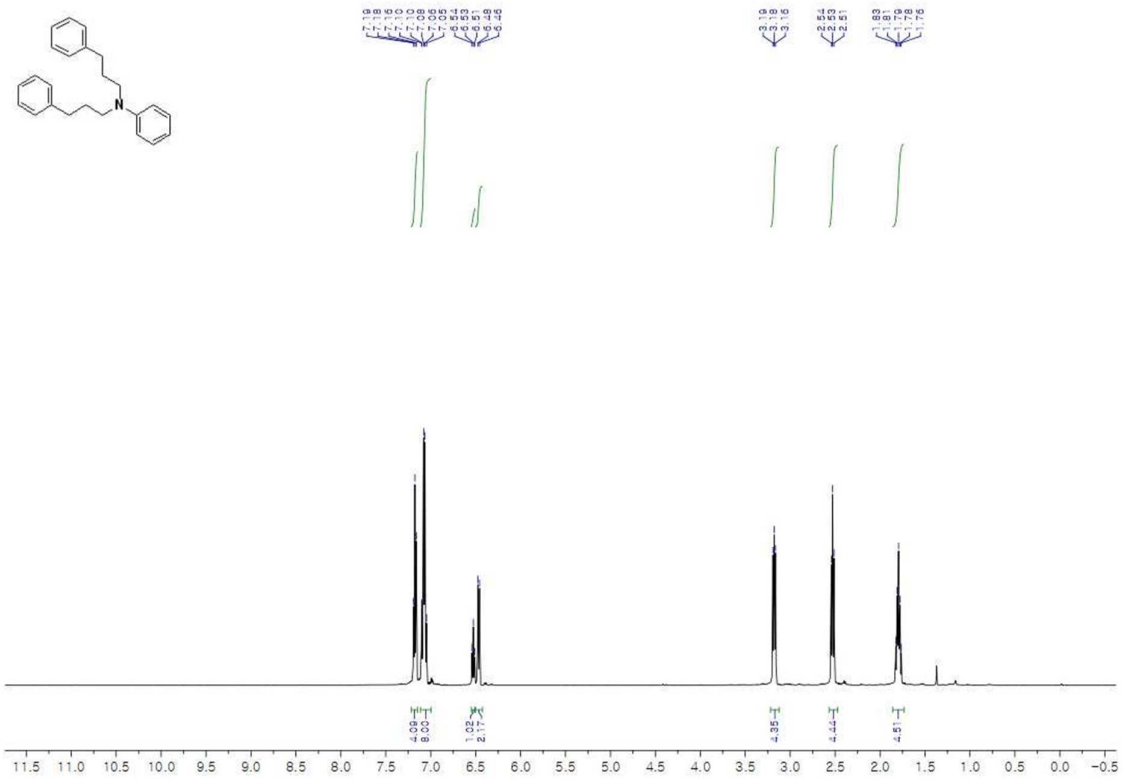


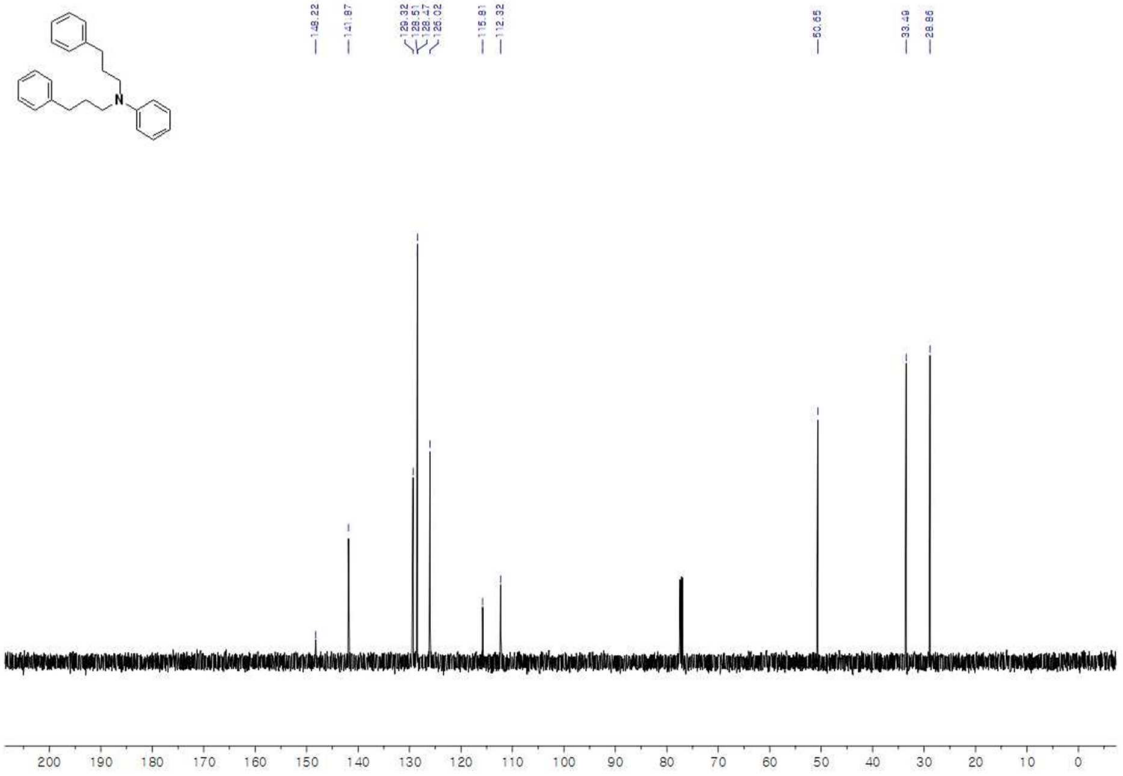


***N,N*-diheptylaniline – (Table 3, 2aa)**

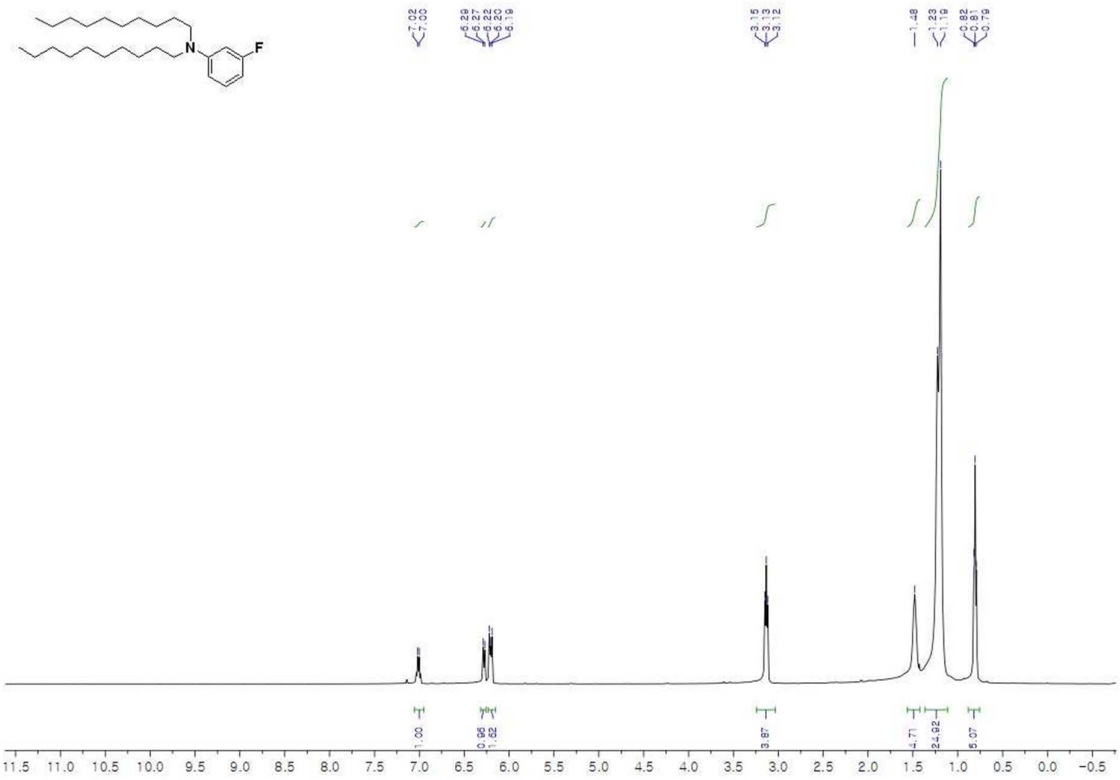


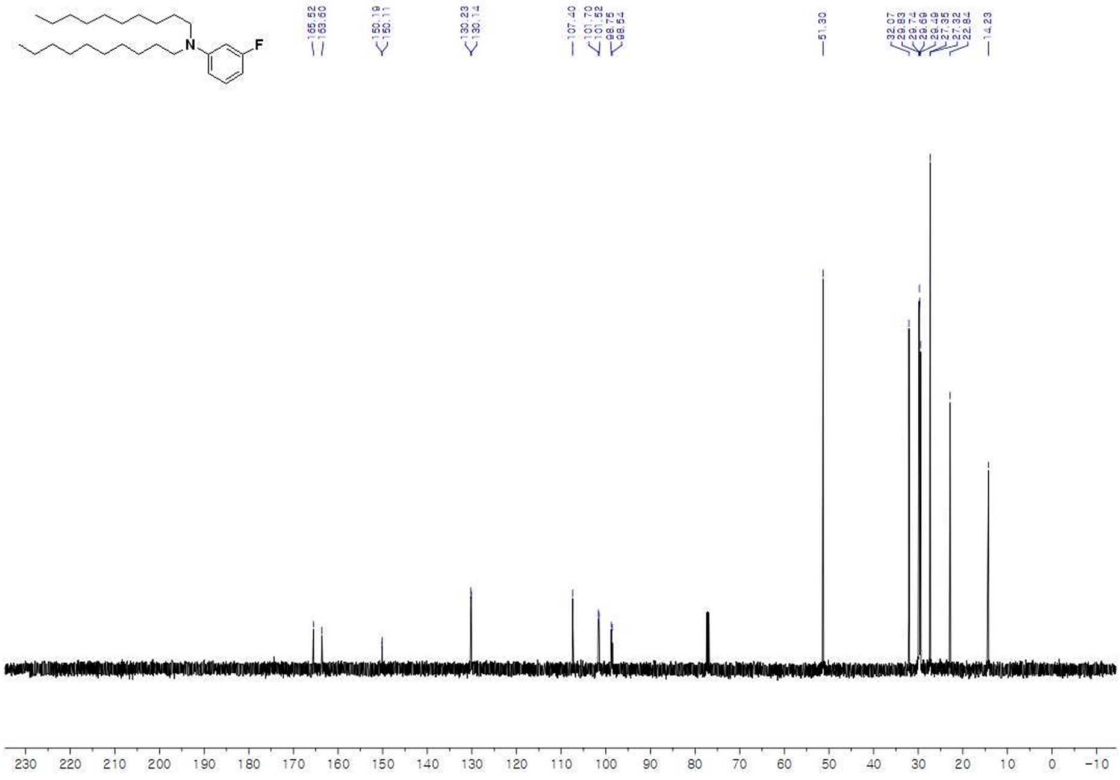
***N,N*-bis(3-phenylpropyl)aniline – (Table 3, 2cc)**

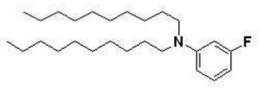




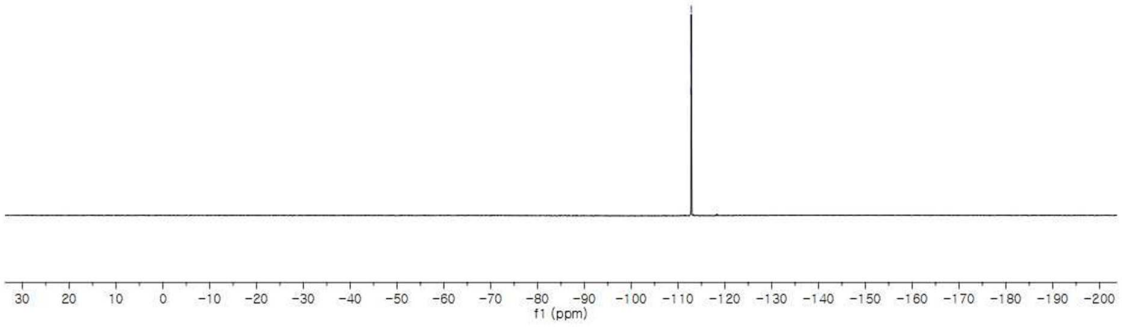
***N,N*-didecyl-3-fluoroaniline – (Table 3, 2dd)**



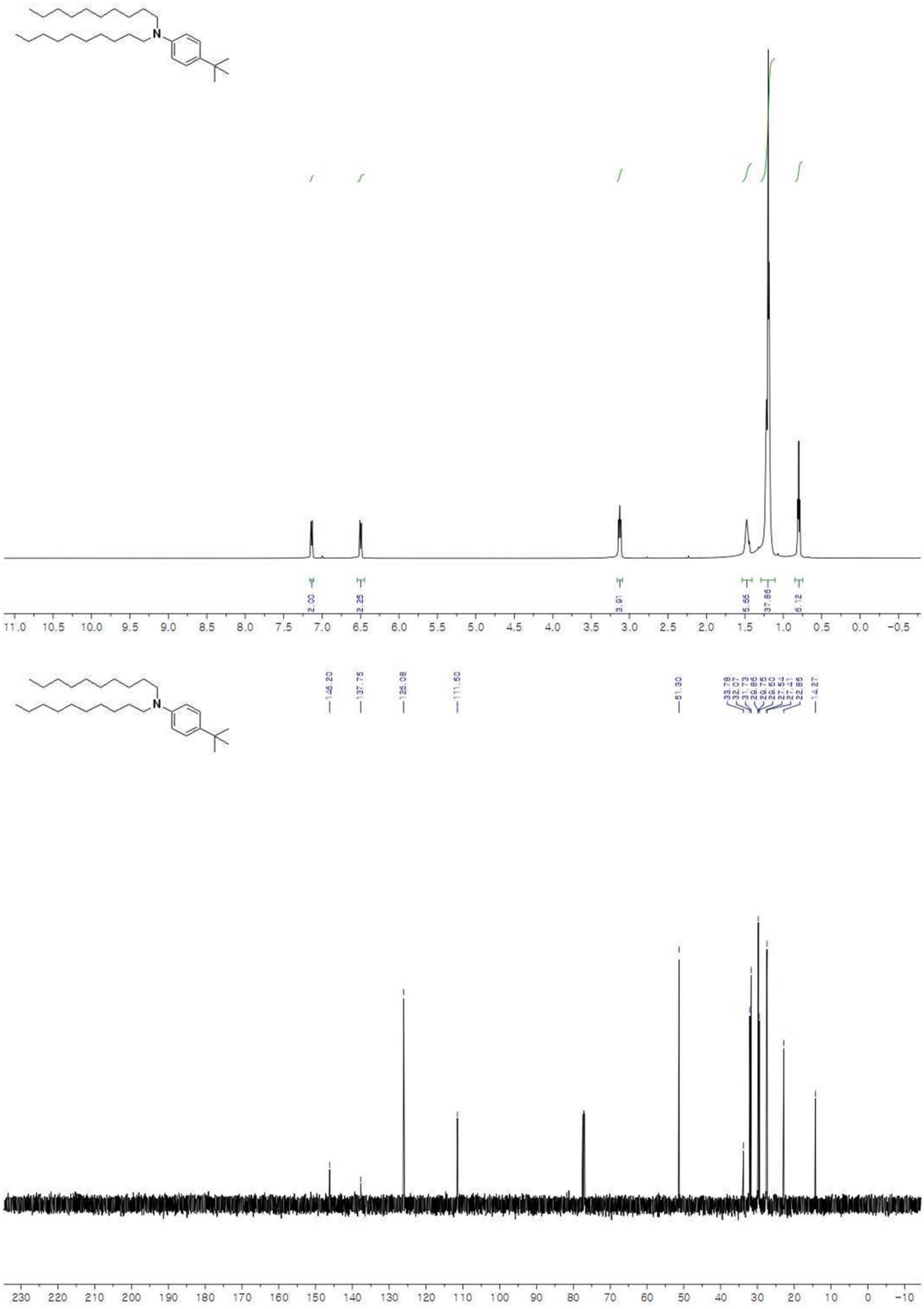



N
F

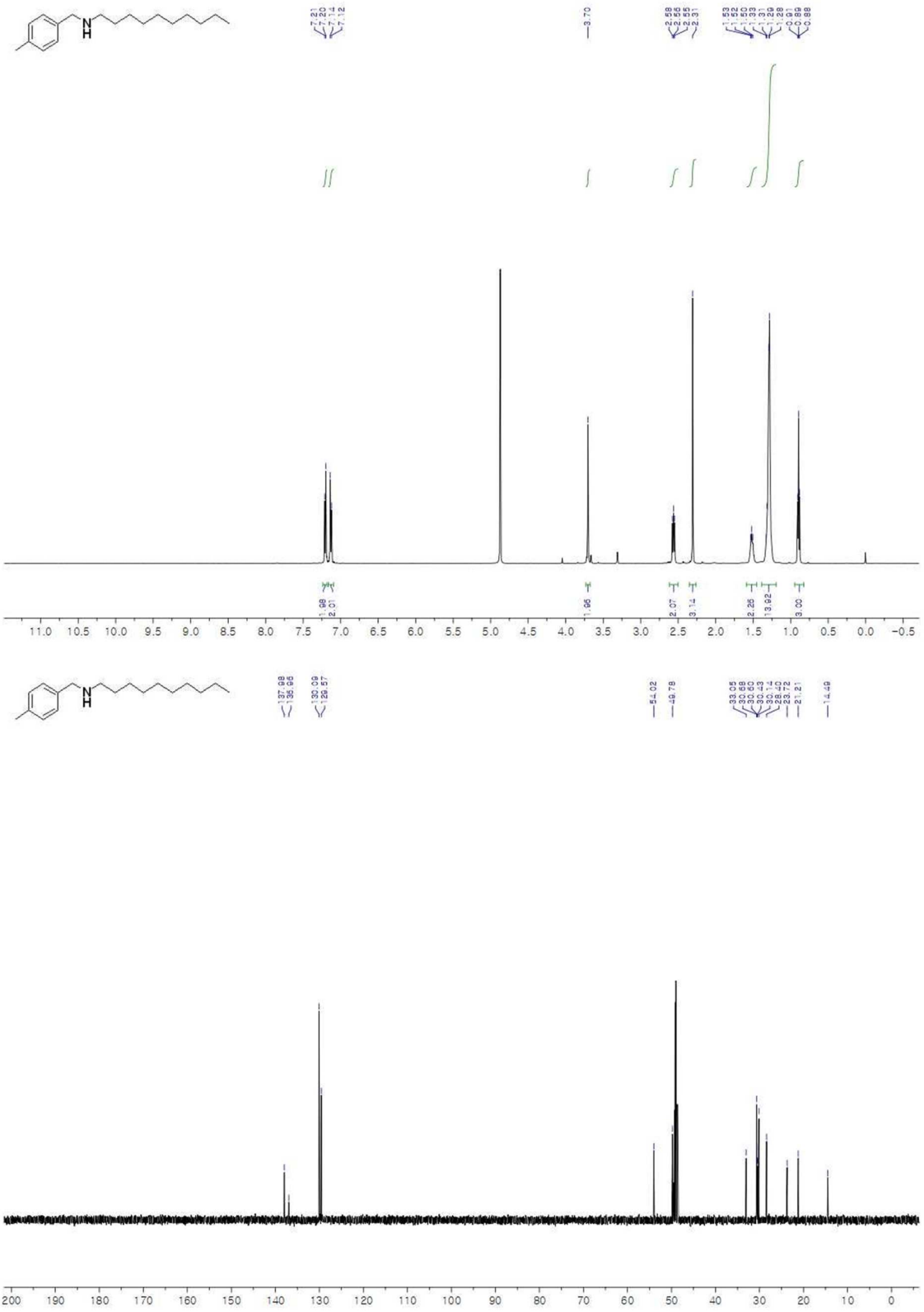

-112.80
-112.82
-112.83
-112.84
-112.85
-112.87


30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

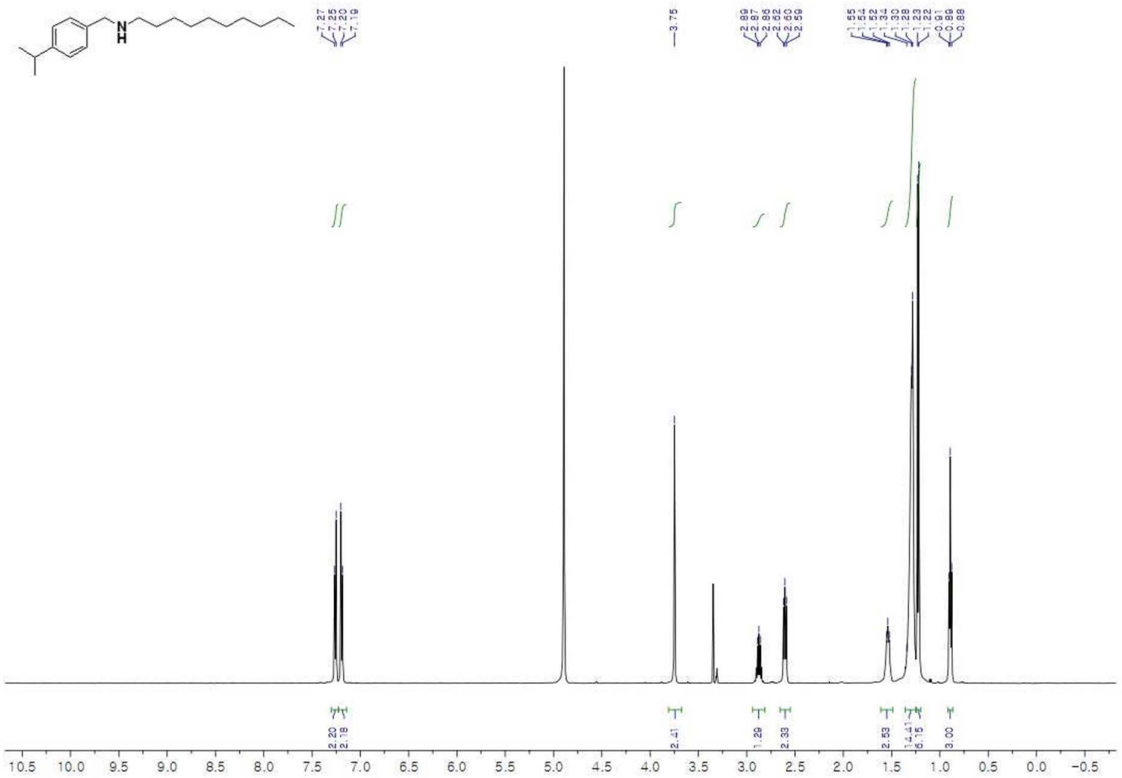
4-(*tert*-butyl)-*N,N*-didecylaniline – (Table 3, 2ee)

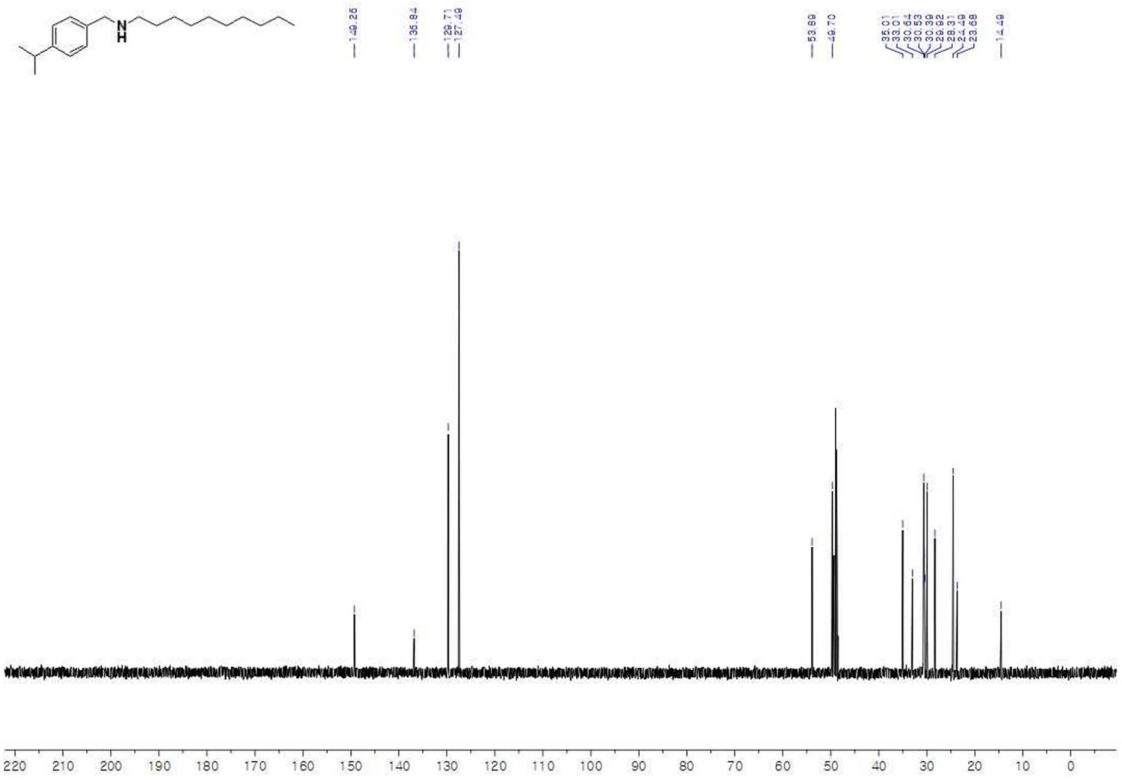


***N*-(4-methylbenzyl)decan-1-amine – (Table 4, 3a)**

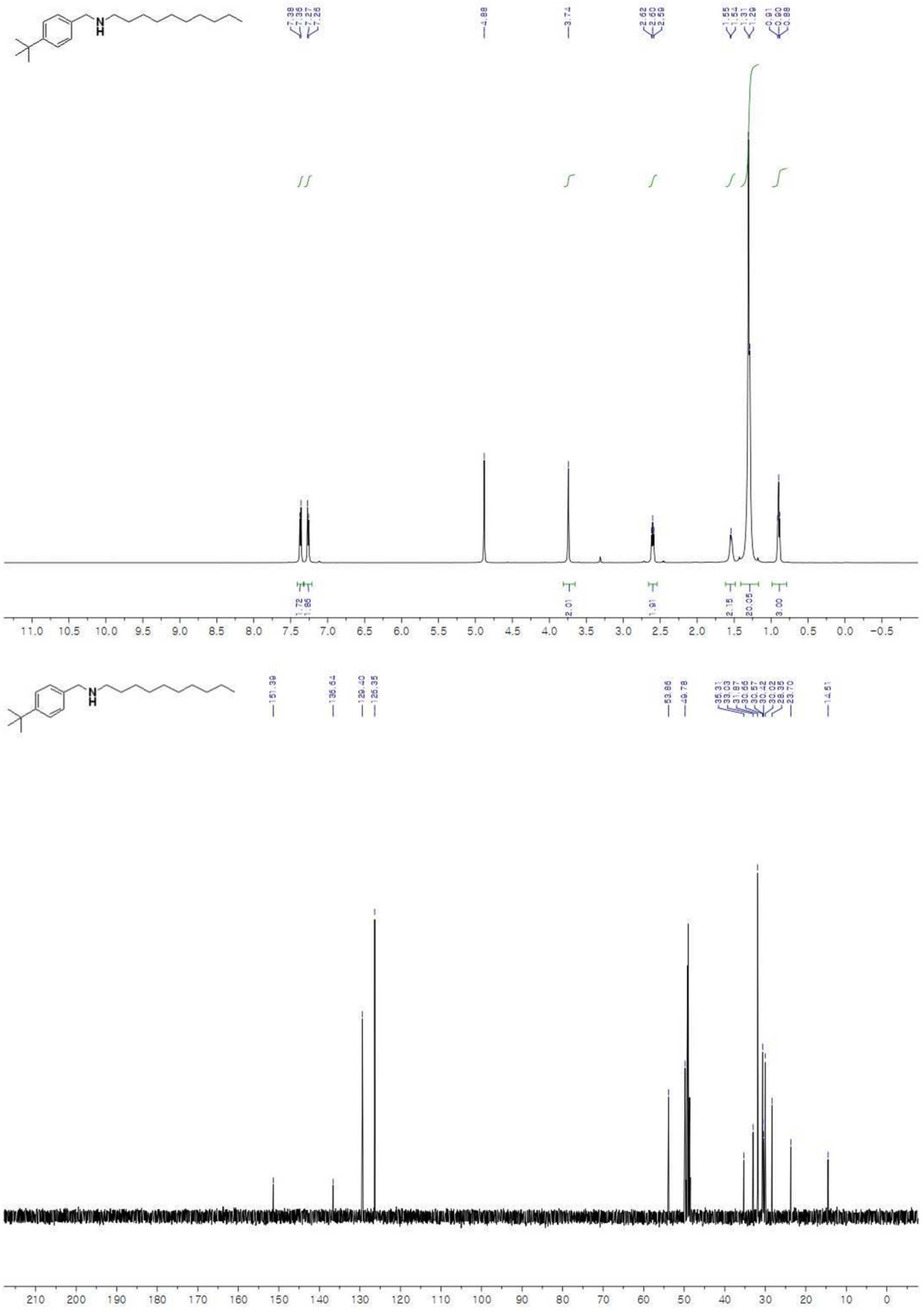


***N*-(4-isopropylbenzyl)decan-1-amine – (Table 4, 3b)**

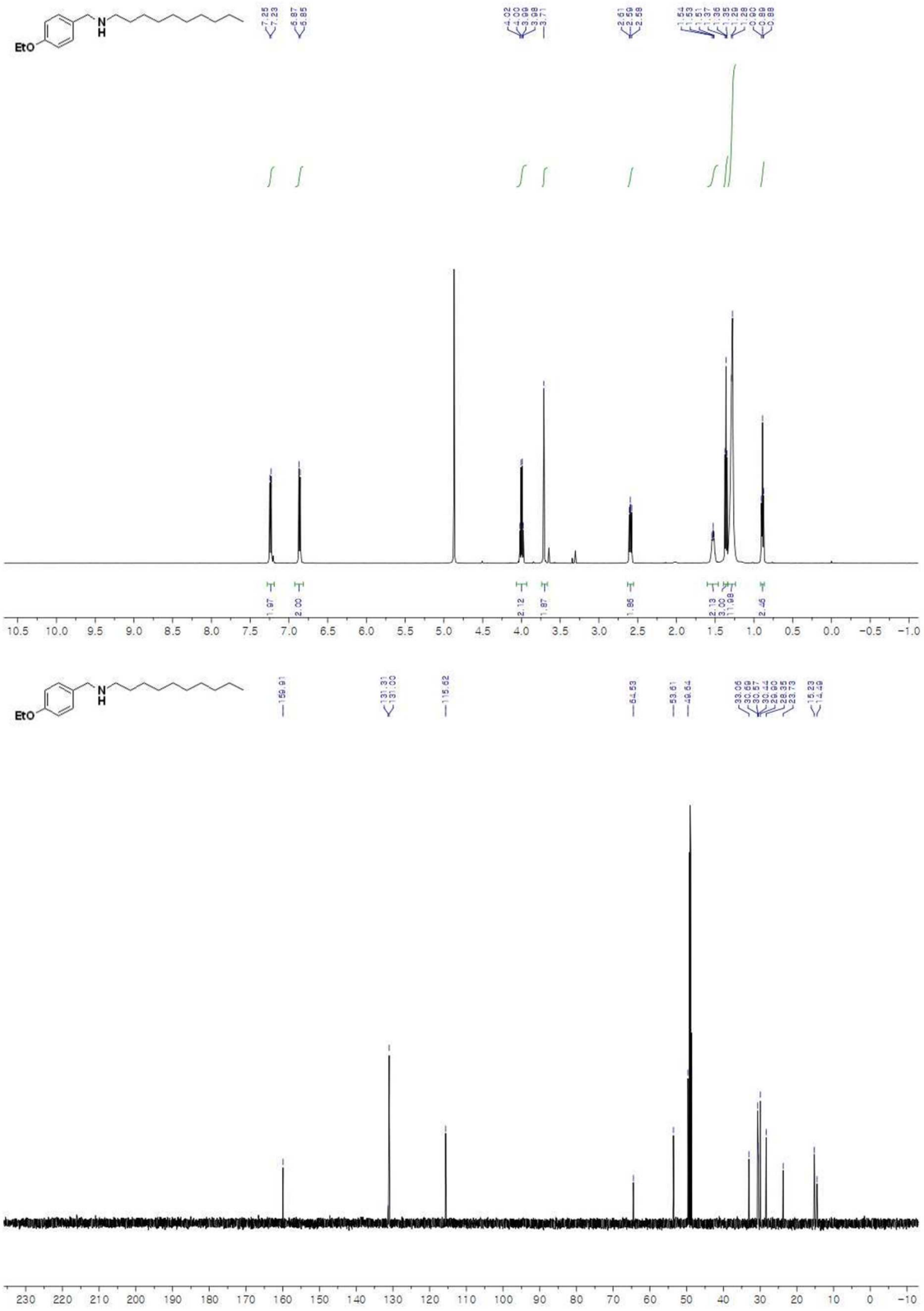




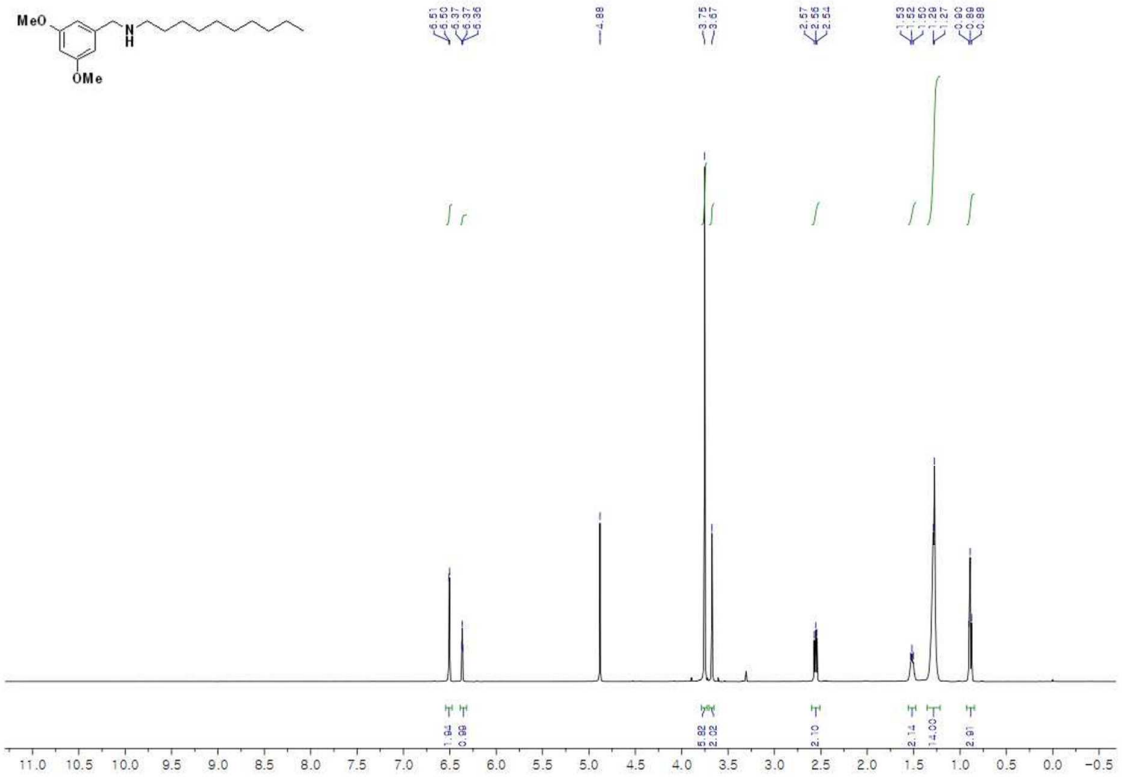
***N*-(4-(tert-butyl)benzyl)decan-1-amine – (Table 4, 3c)**

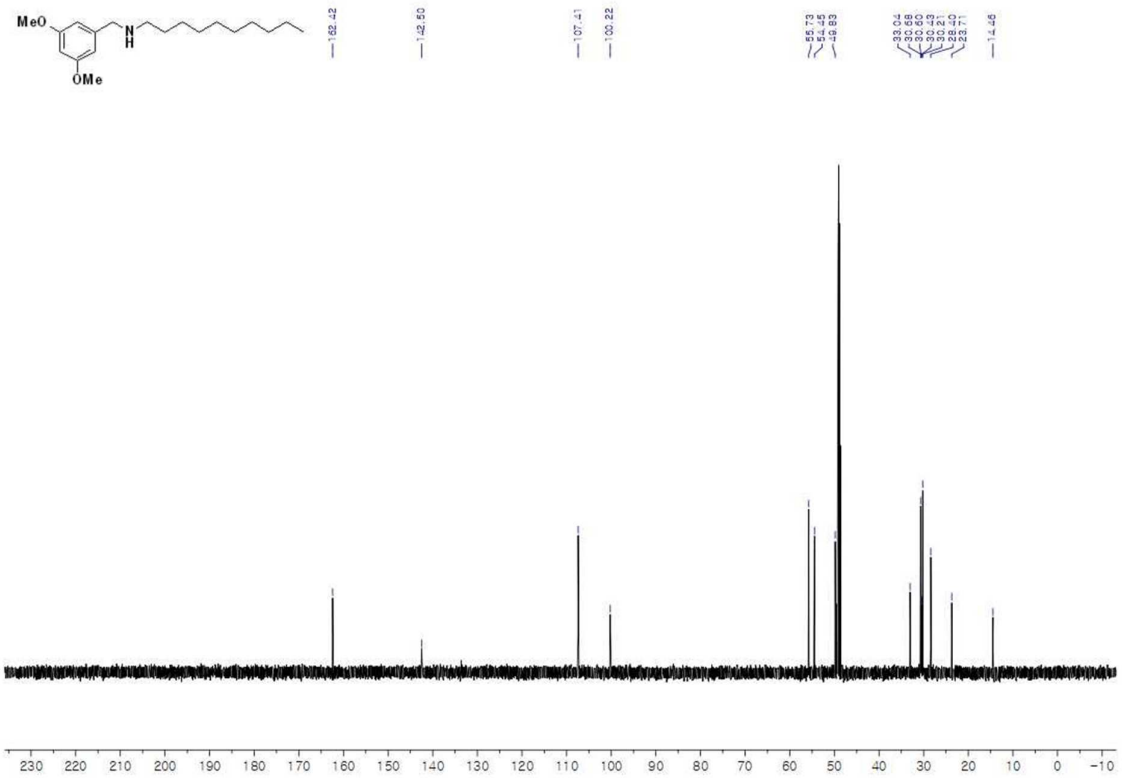


***N*-(4-ethoxybenzyl)decan-1-amine – (Table 4, 3d)**

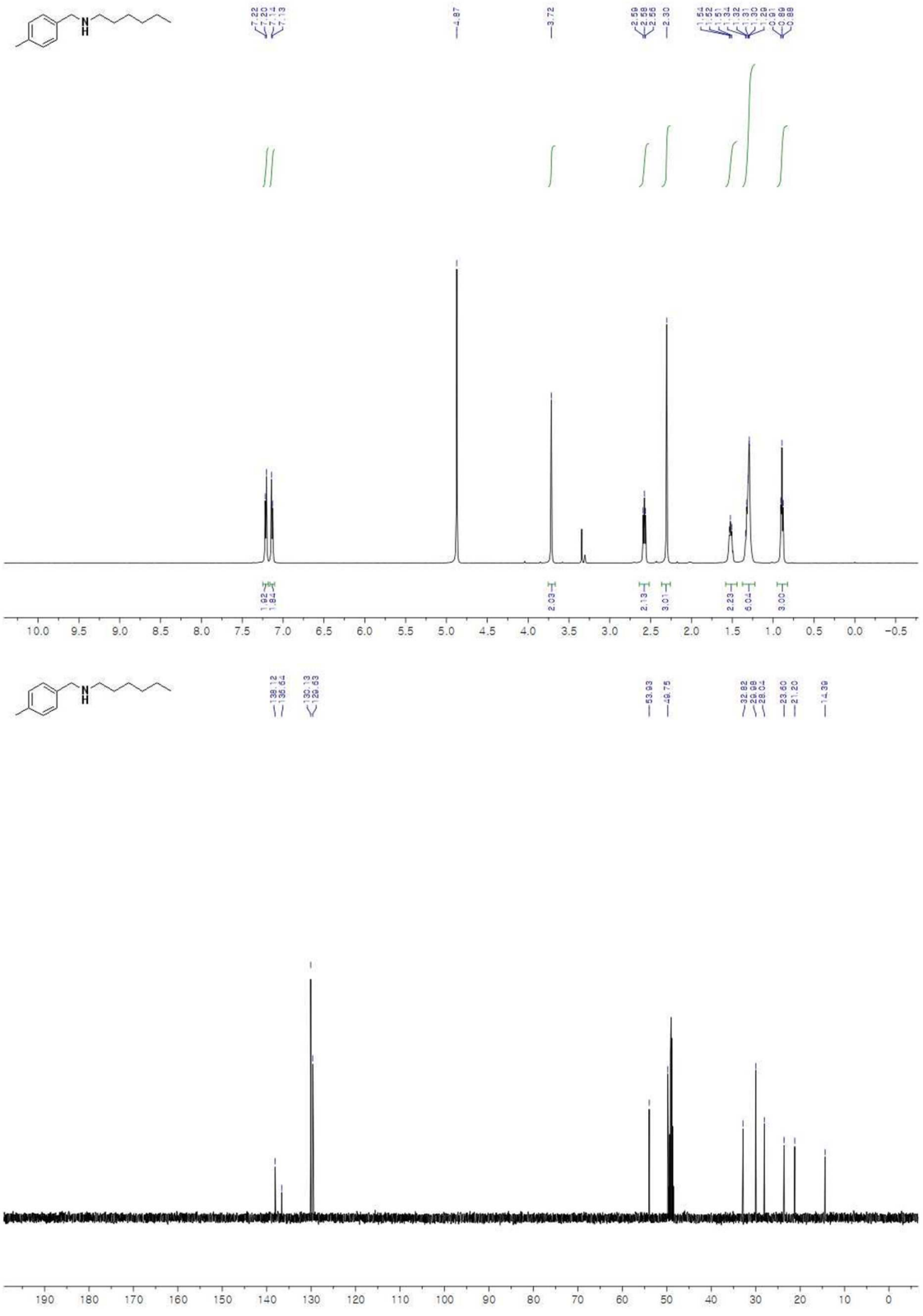


***N*-(3,5-dimethoxybenzyl)decan-1-amine – (Table 4, 3e)**

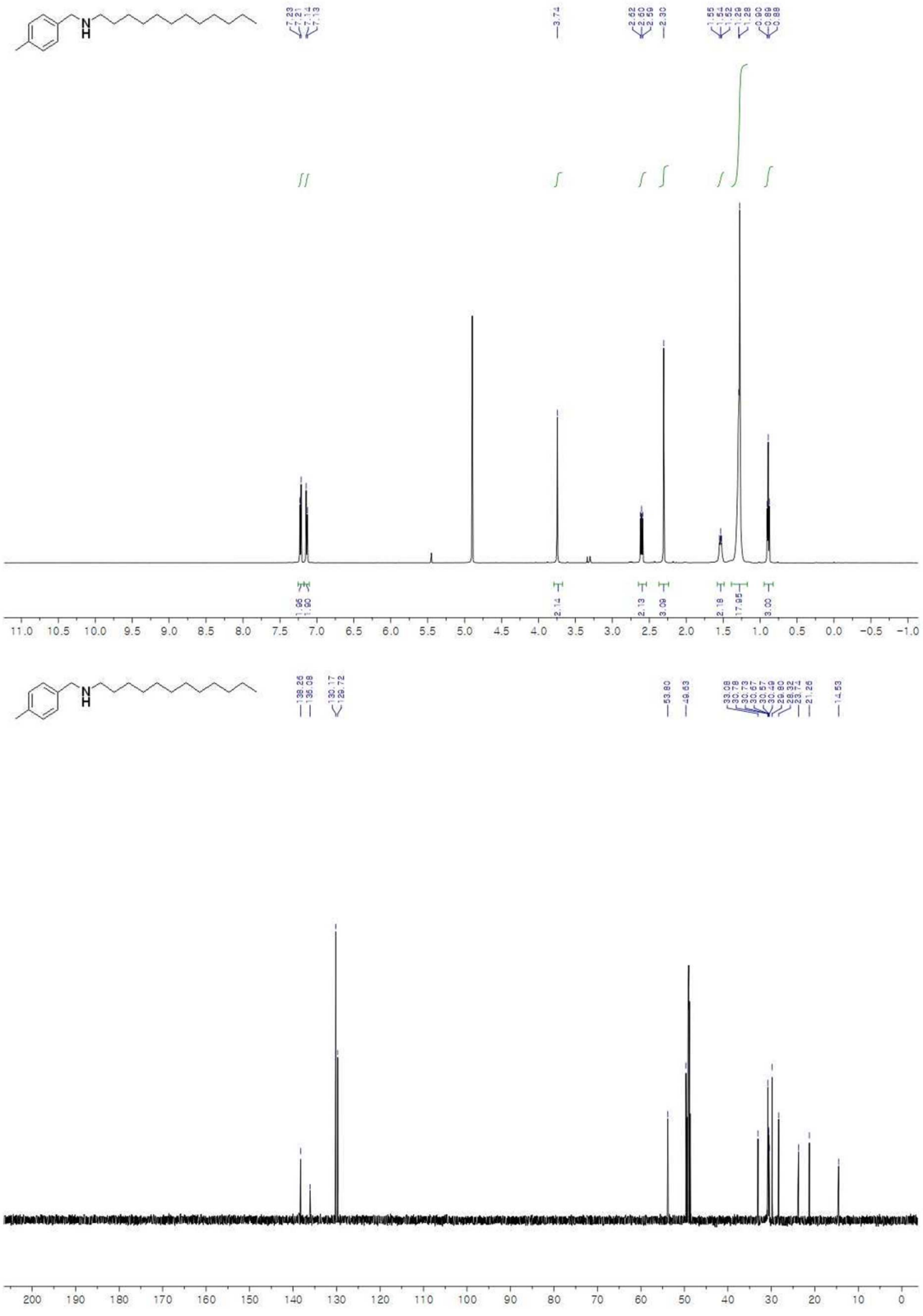




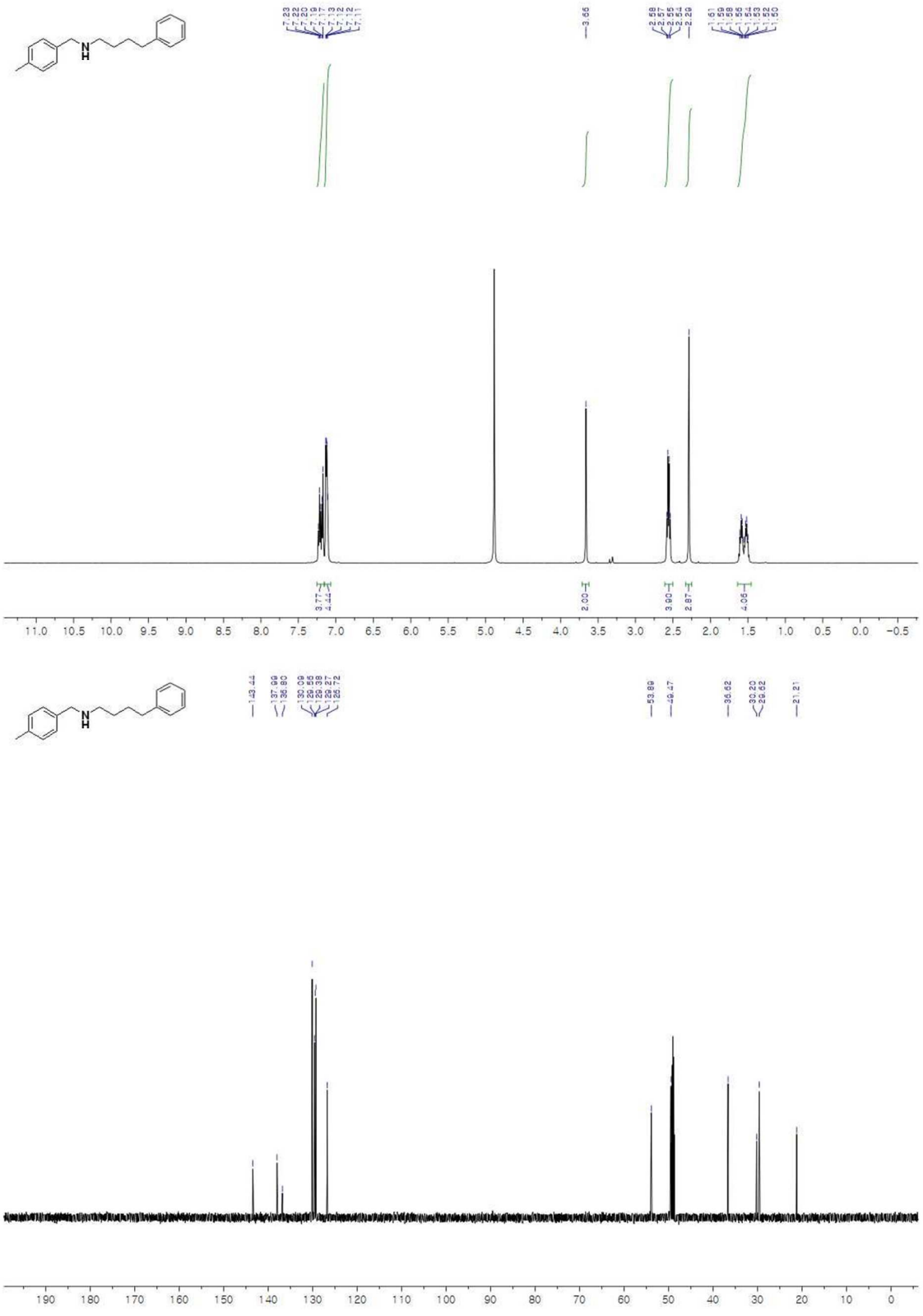
***N*-(4-methylbenzyl)hexan-1-amine – (Table 4, 3f)**



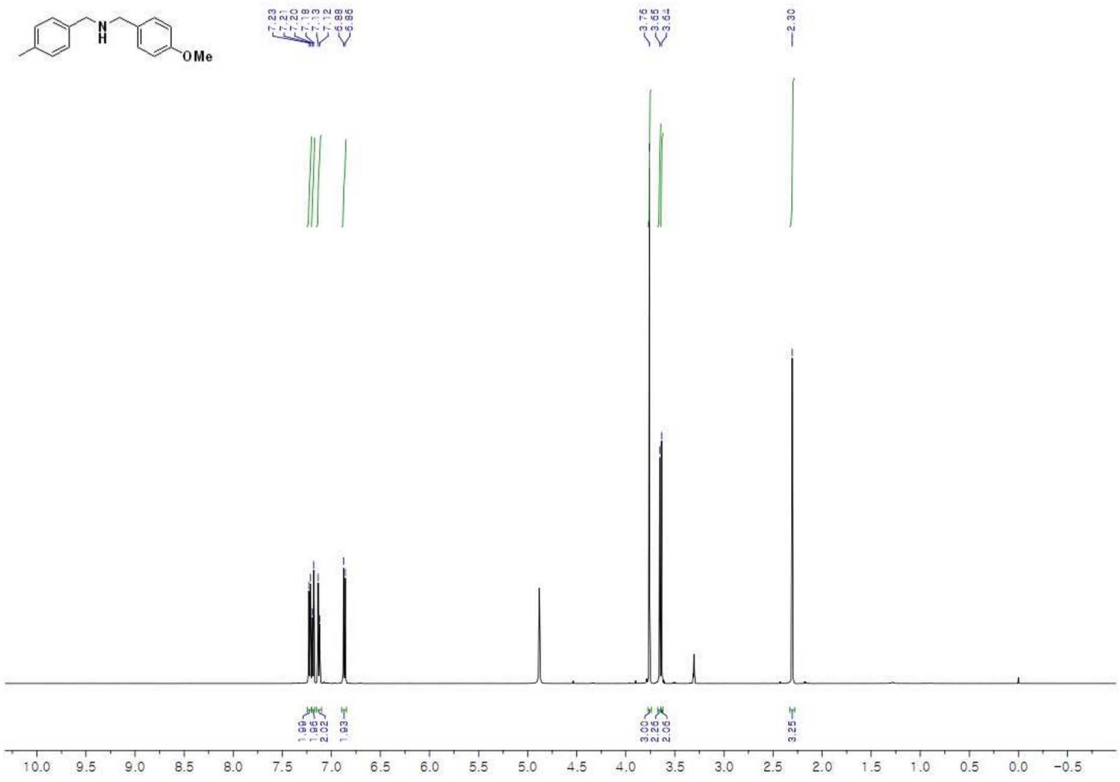
***N*-(4-methylbenzyl)dodecan-1-amine – (Table 4, 3g)**

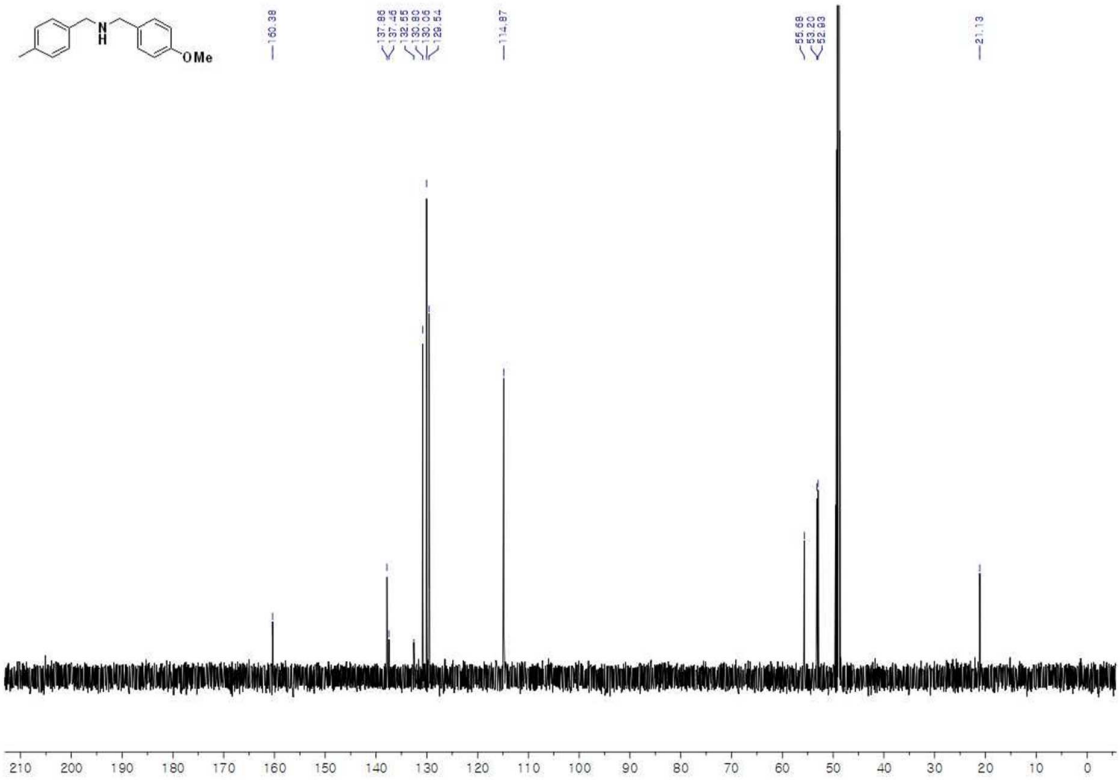


***N*-(4-methylbenzyl)-4-phenylbutan-1-amine – (Table 4, 3h)**

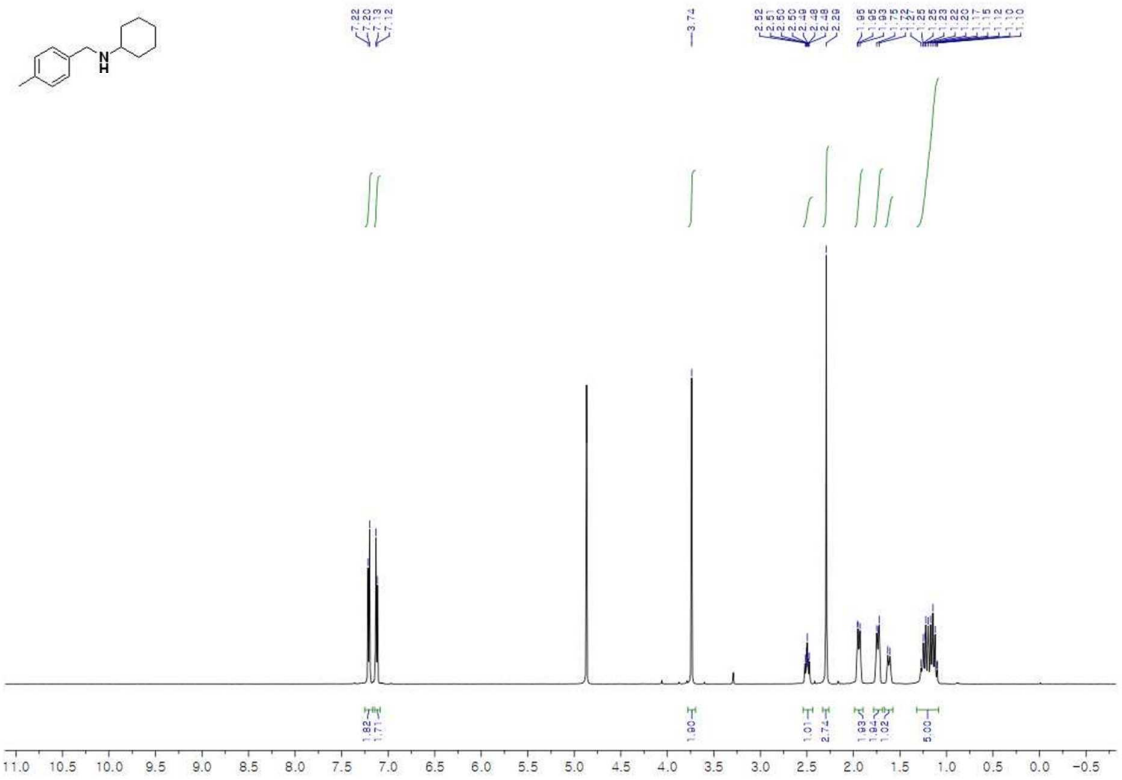


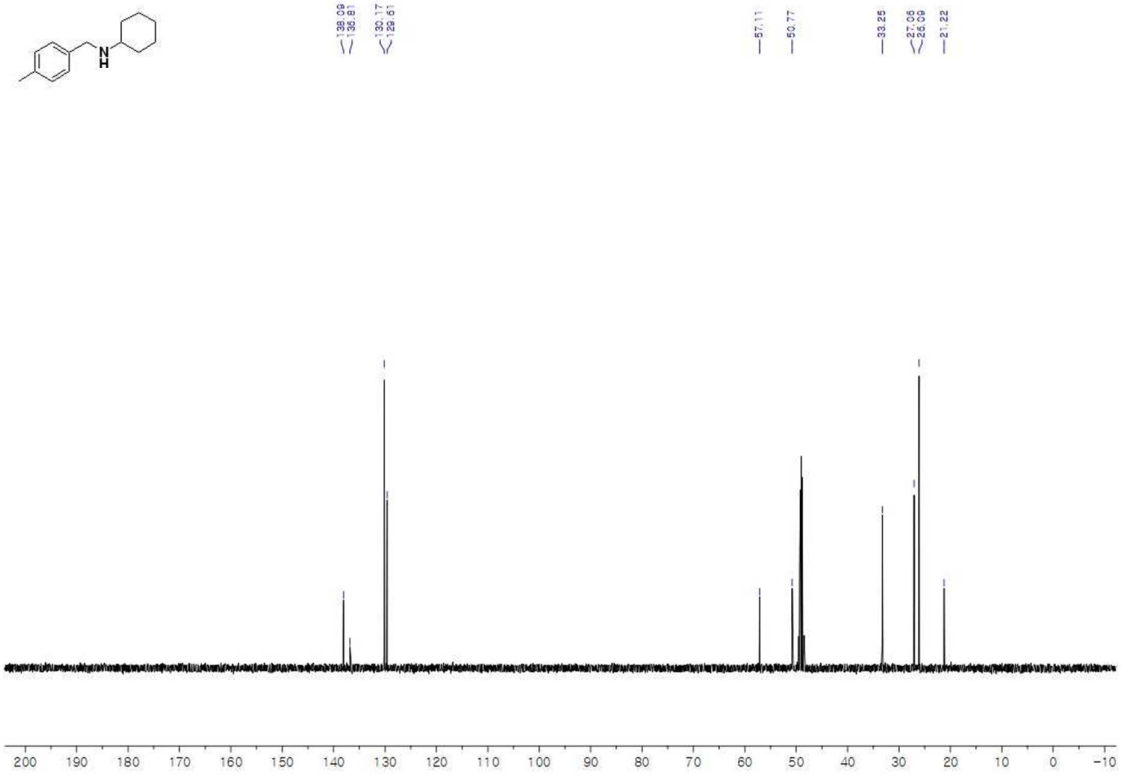
***N*-(4-methoxybenzyl)-1-(*p*-tolyl)methanamine – (Table 4, 3i)**



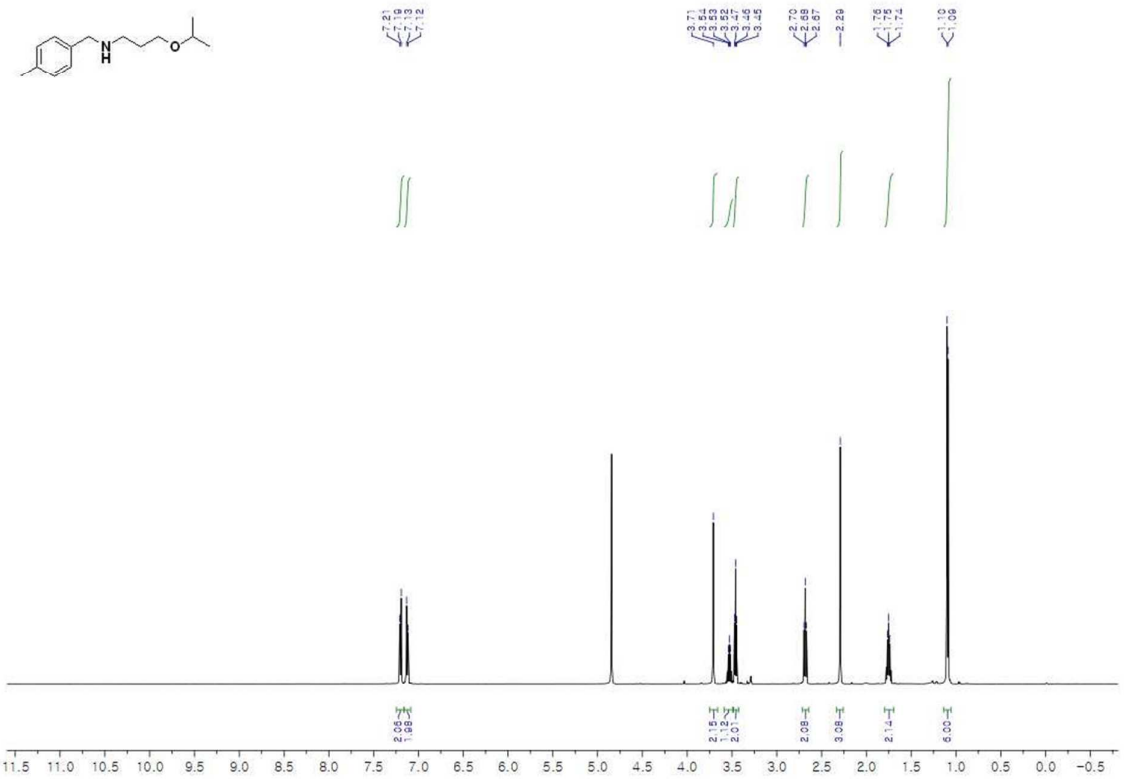


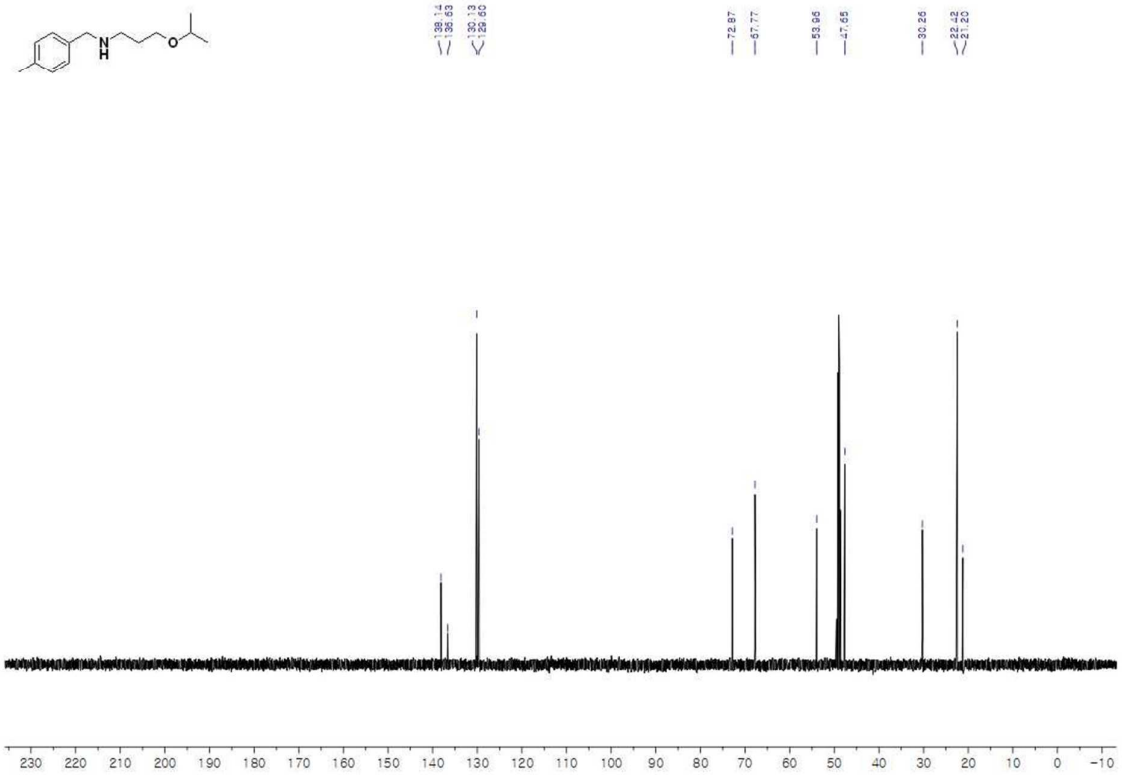
***N*-(4-methylbenzyl)cyclohexanamine – (Table 4, 3j)**



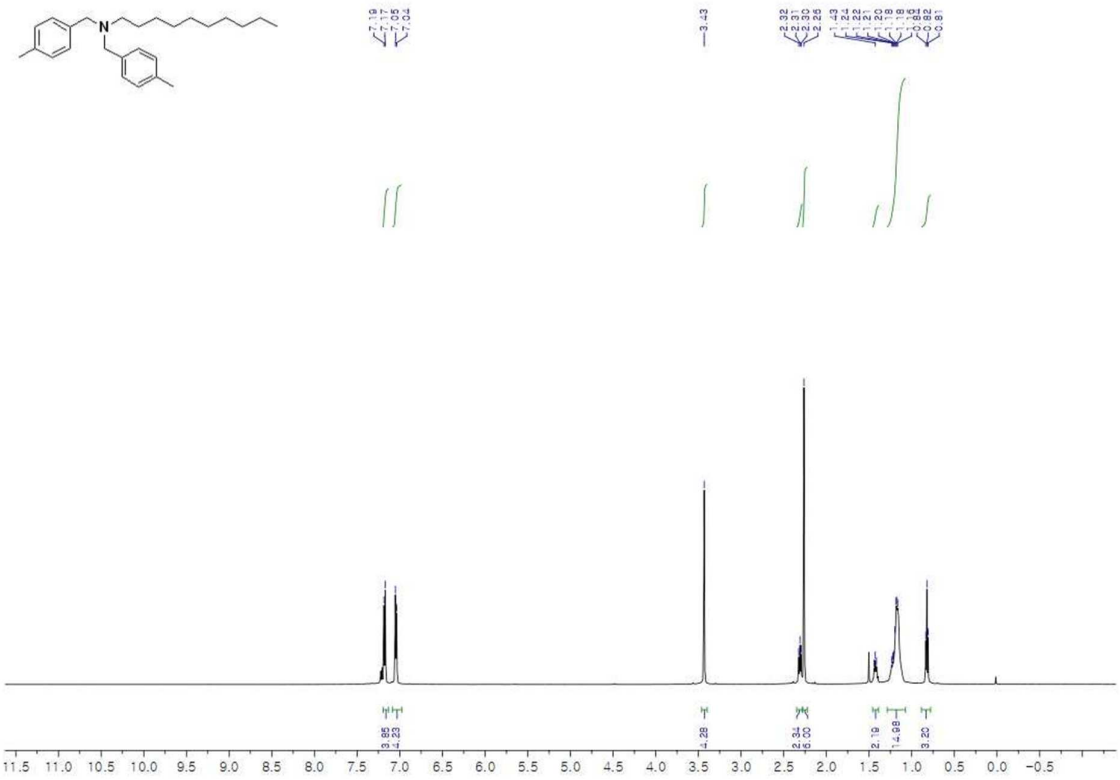


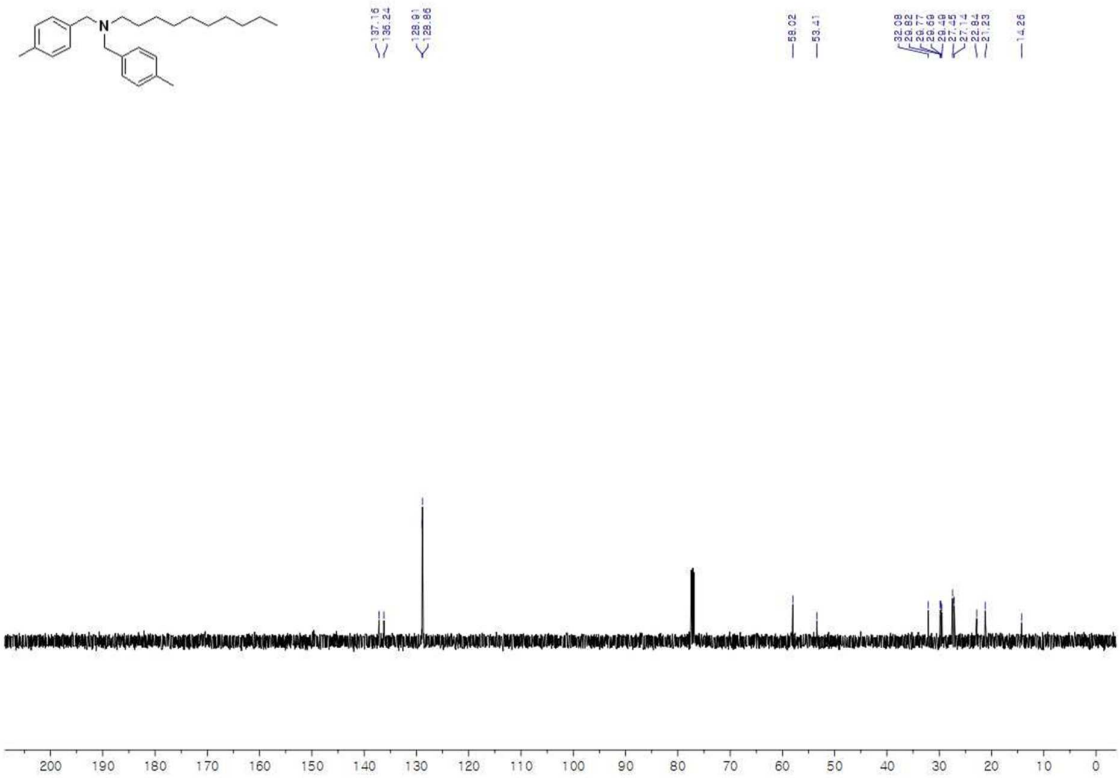
3-isopropoxy-*N*-(4-methylbenzyl)propan-1-amine – (Table 4, 3k)



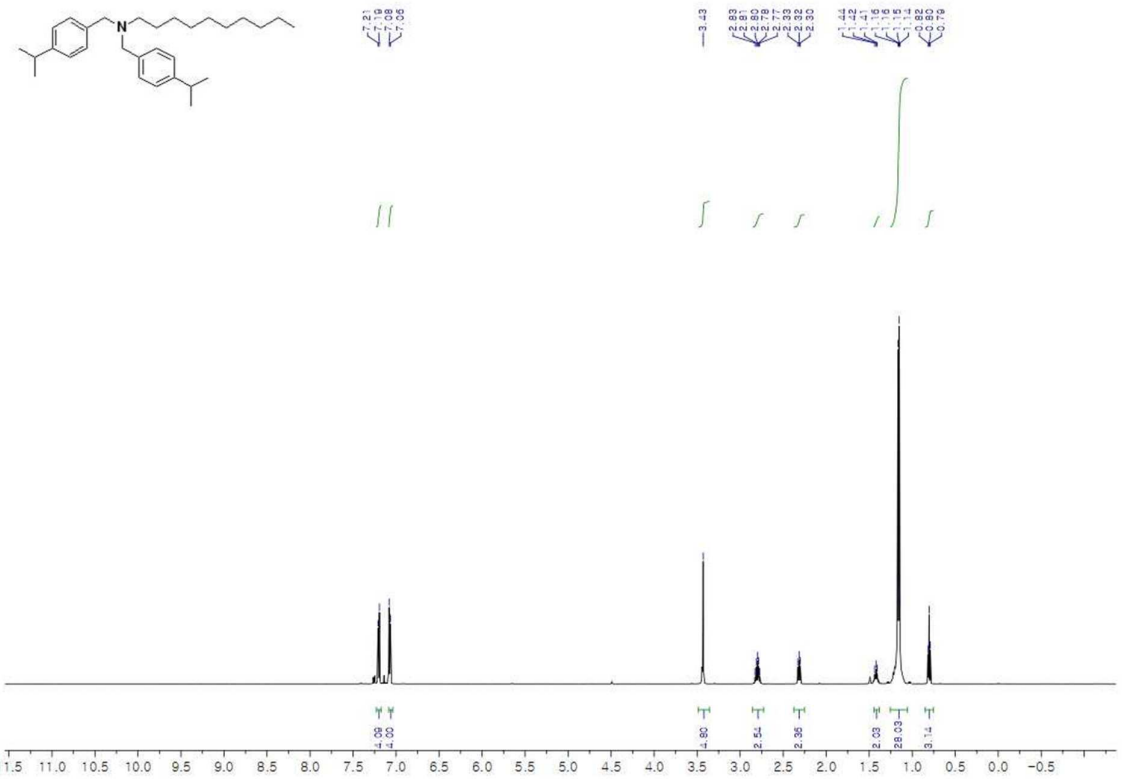


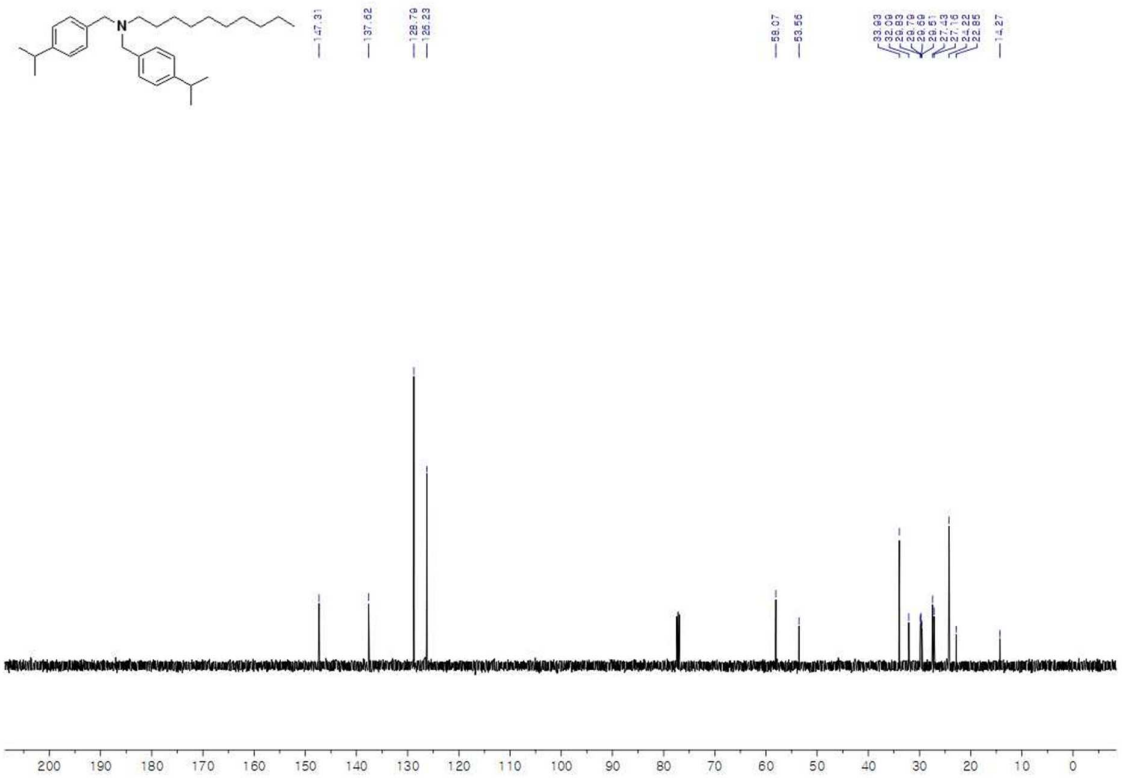
***N*,*N*-bis(4-methylbenzyl)decan-1-amine – (Table 4, 3aa)**



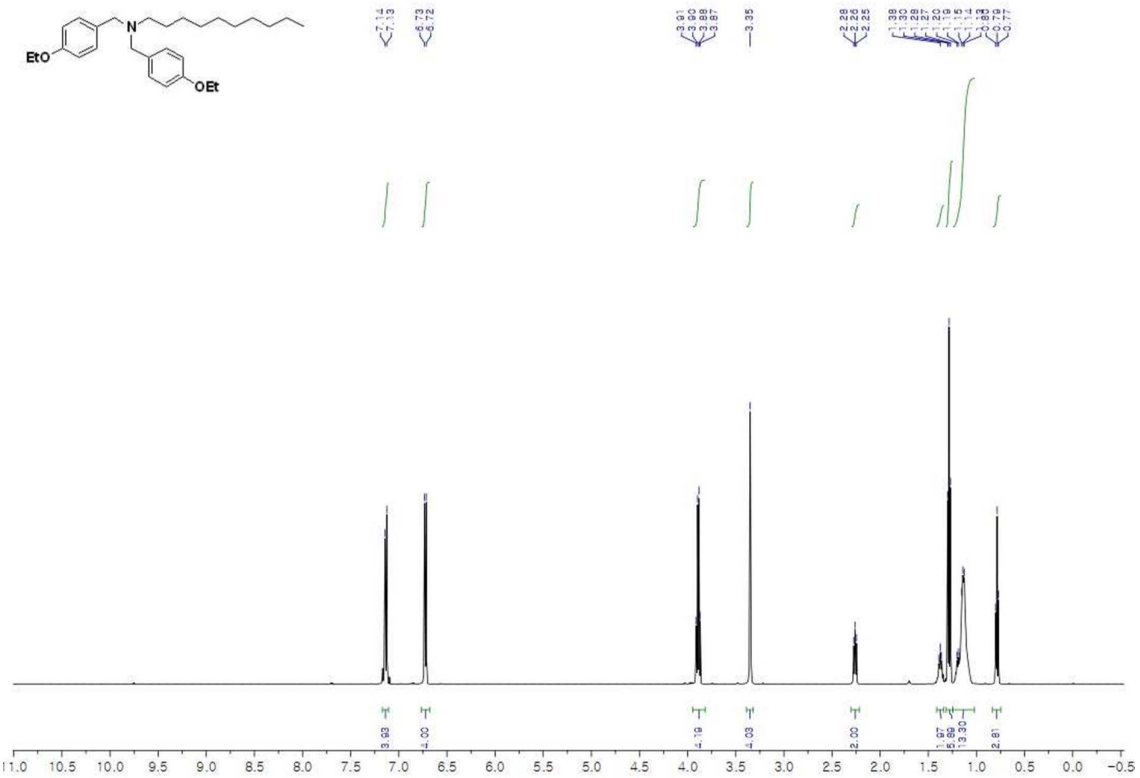


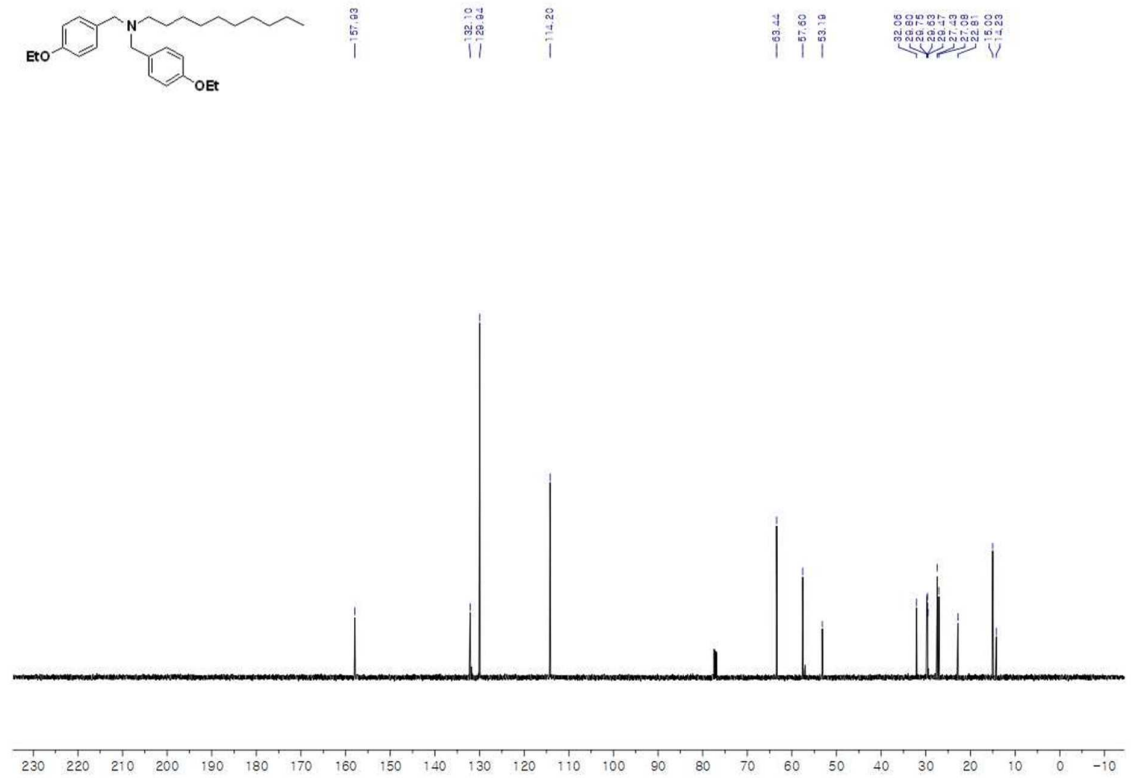
***N,N*-bis(4-isopropylbenzyl)decan-1-amine – (Table 4, 3bb)**



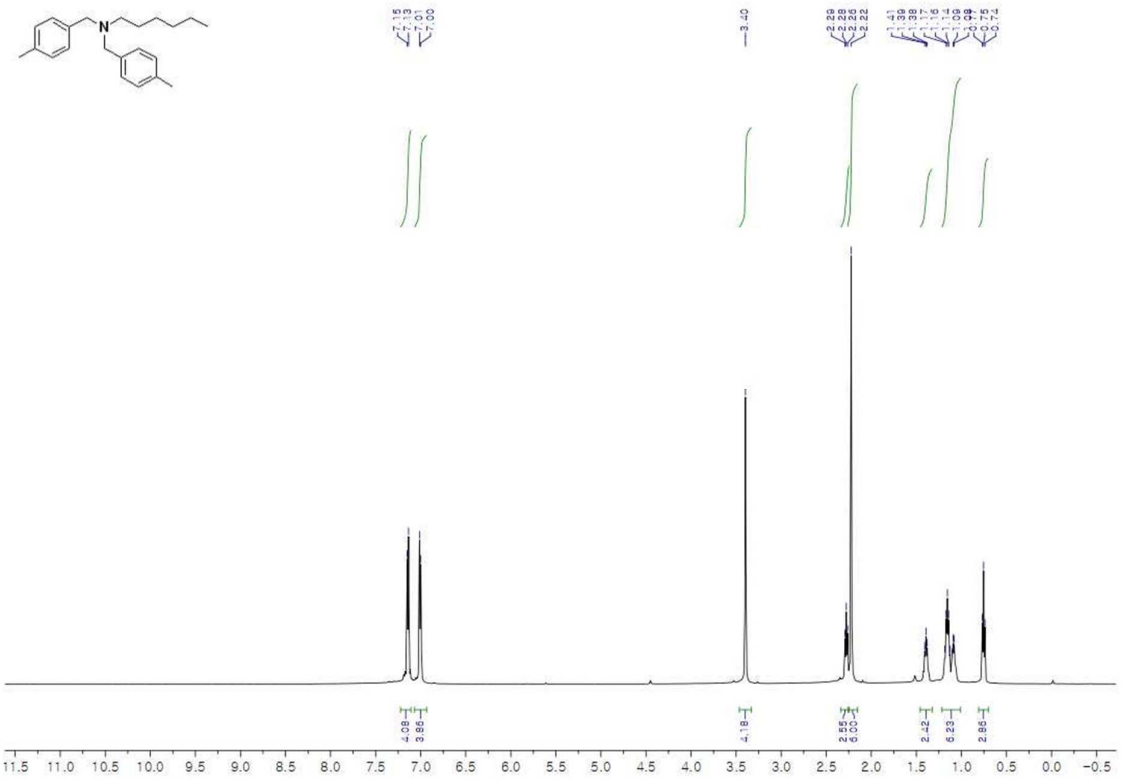


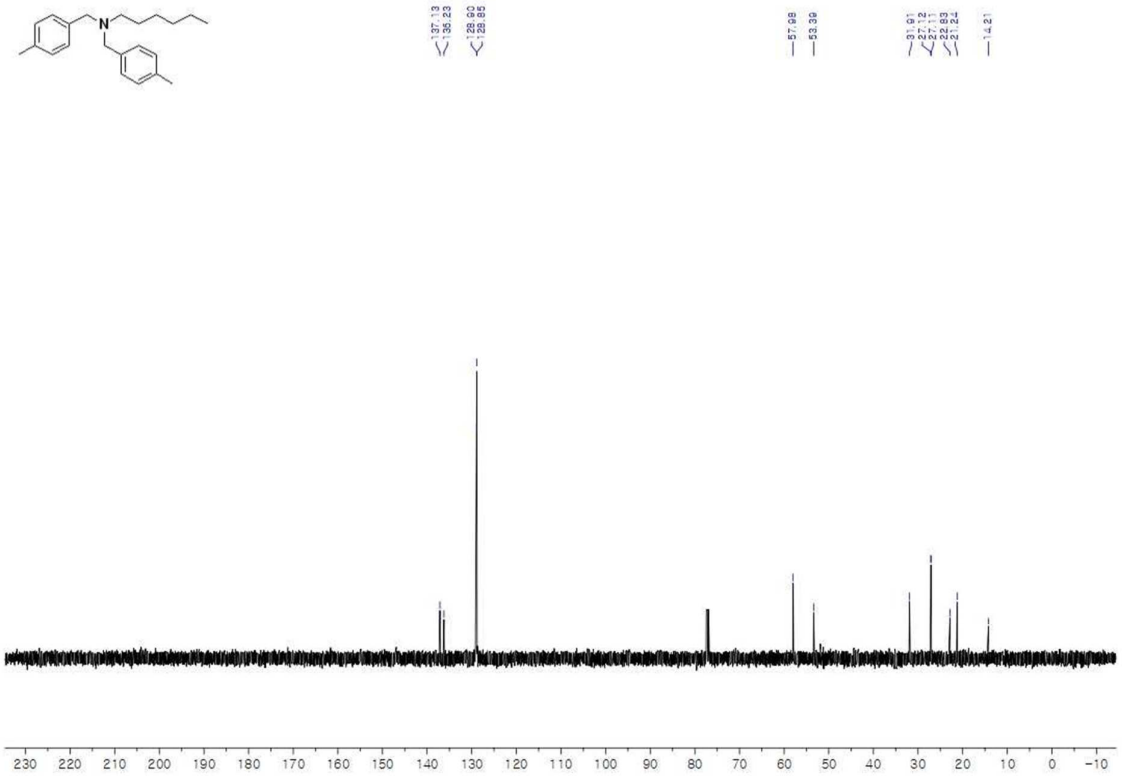
***N,N*-bis(4-ethoxybenzyl)decan-1-amine – (Table 4, 3cc)**



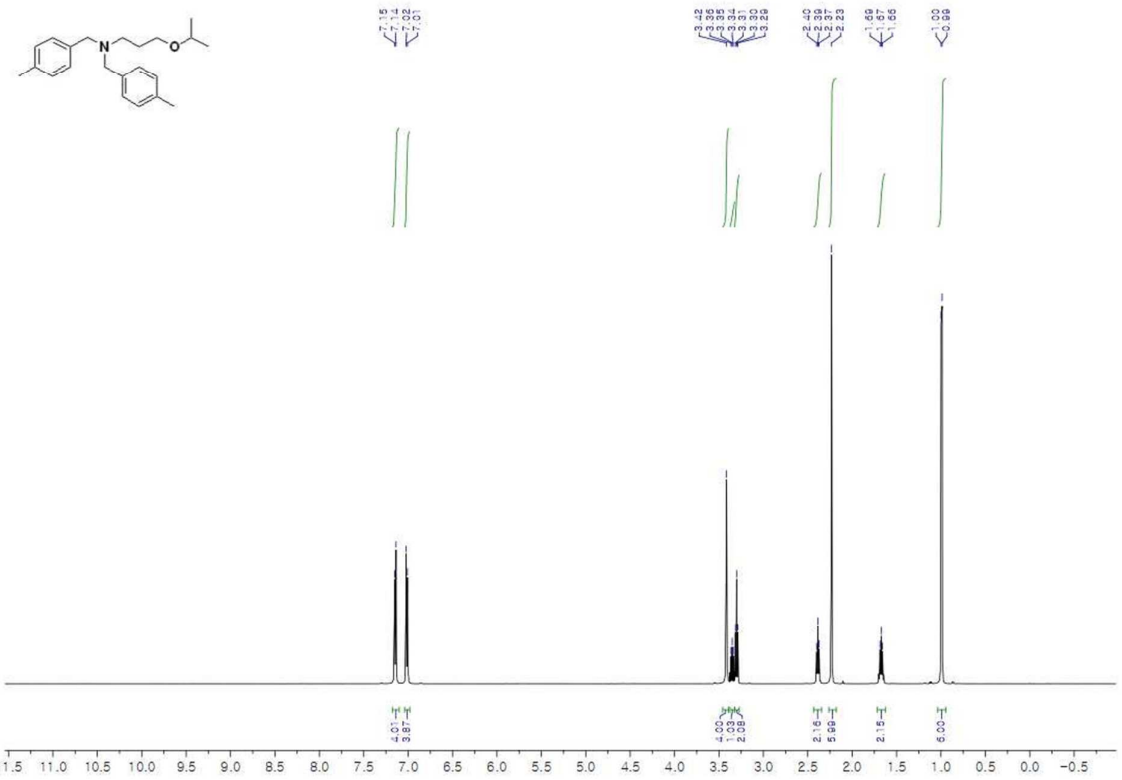


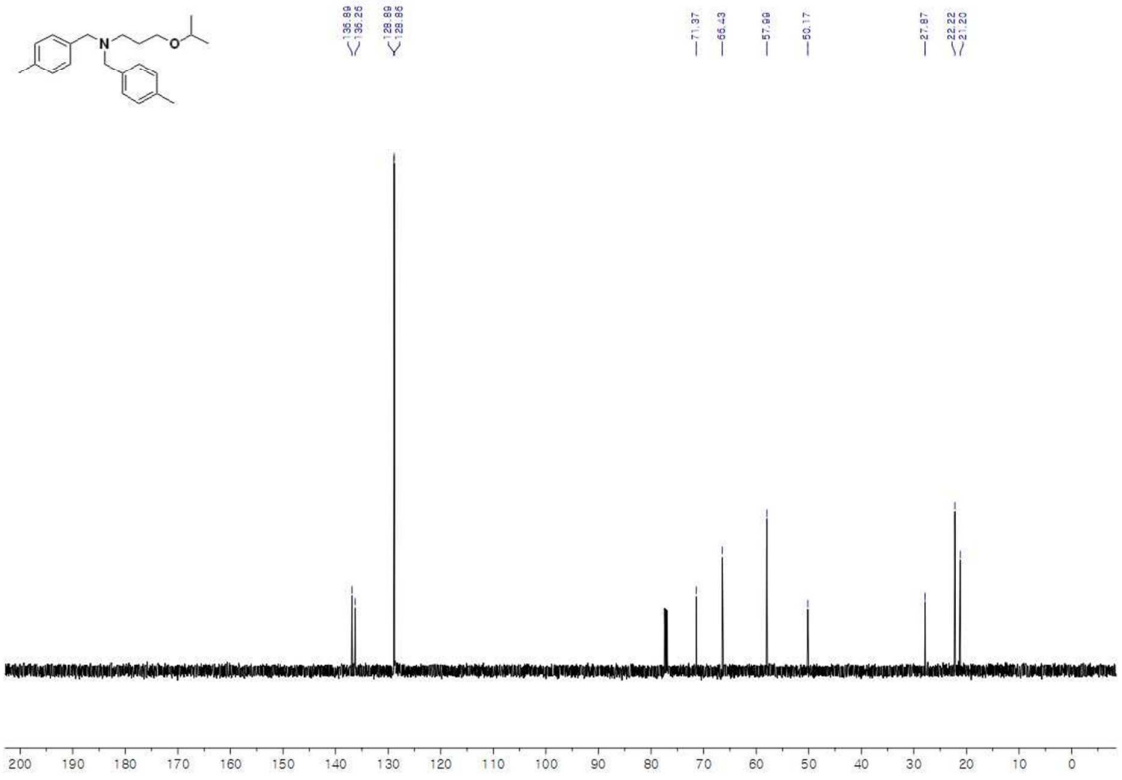
***N,N*-bis(4-methylbenzyl)hexan-1-amine – (Table 4, 3dd)**



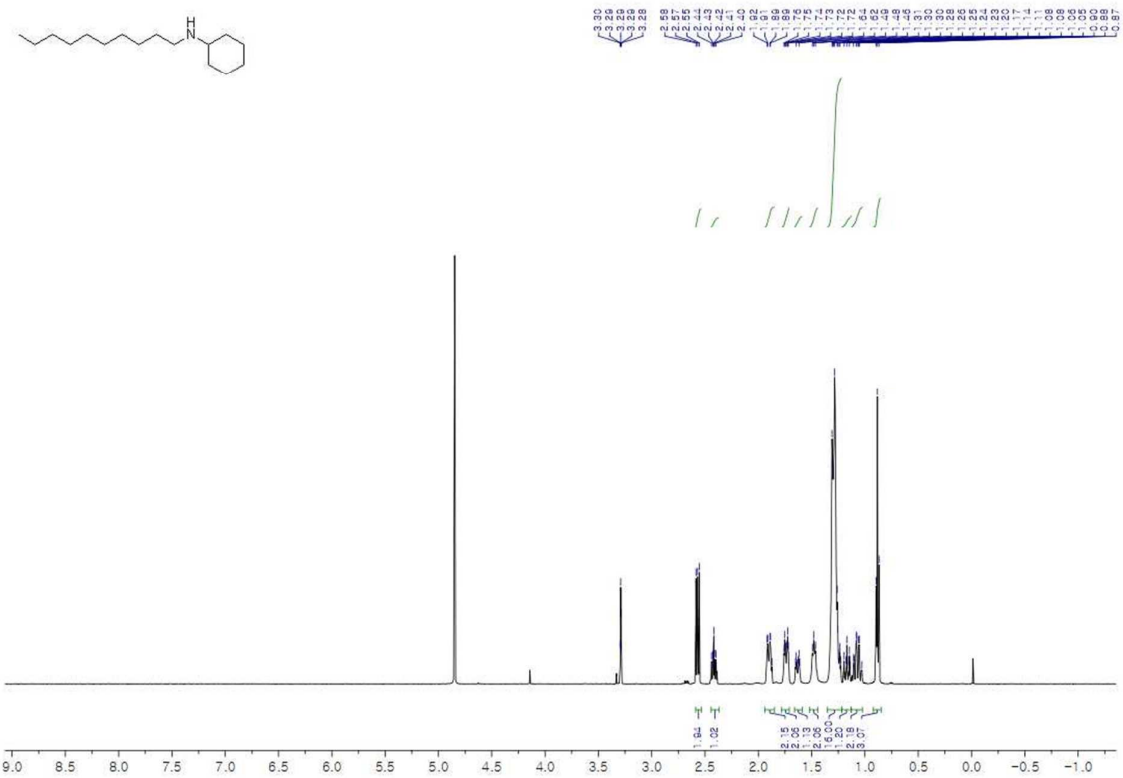


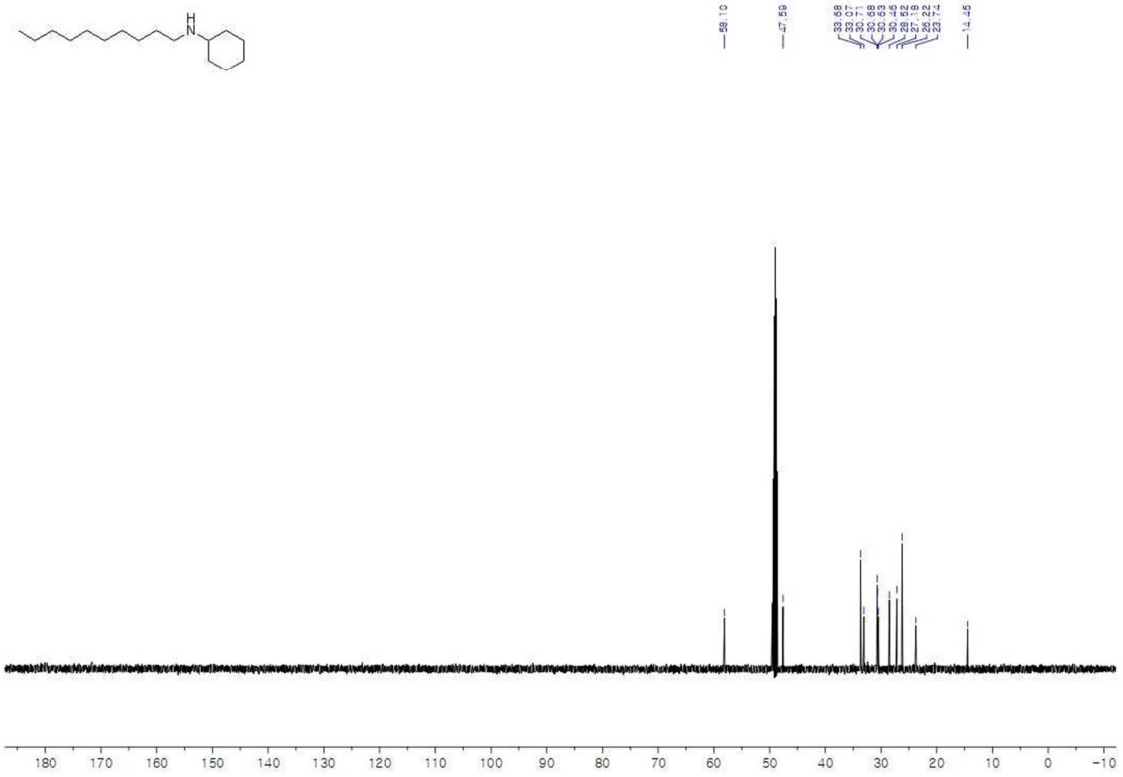
3-isopropoxy-*N*,*N*-bis(4-methylbenzyl)propan-1-amine – (Table 4, 3ee)



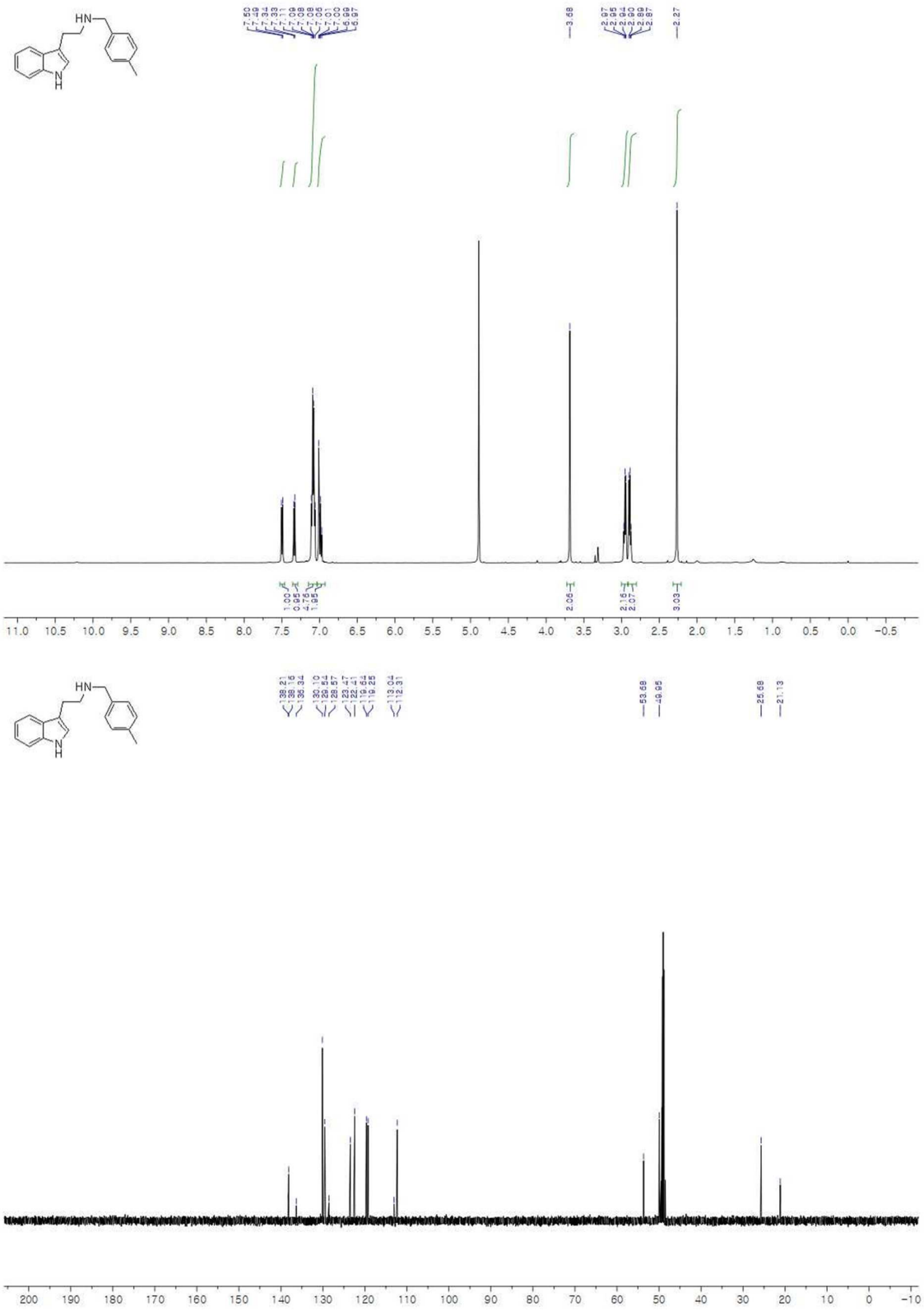


***N*-decylcyclohexanamine – (Table 4, 3l)**

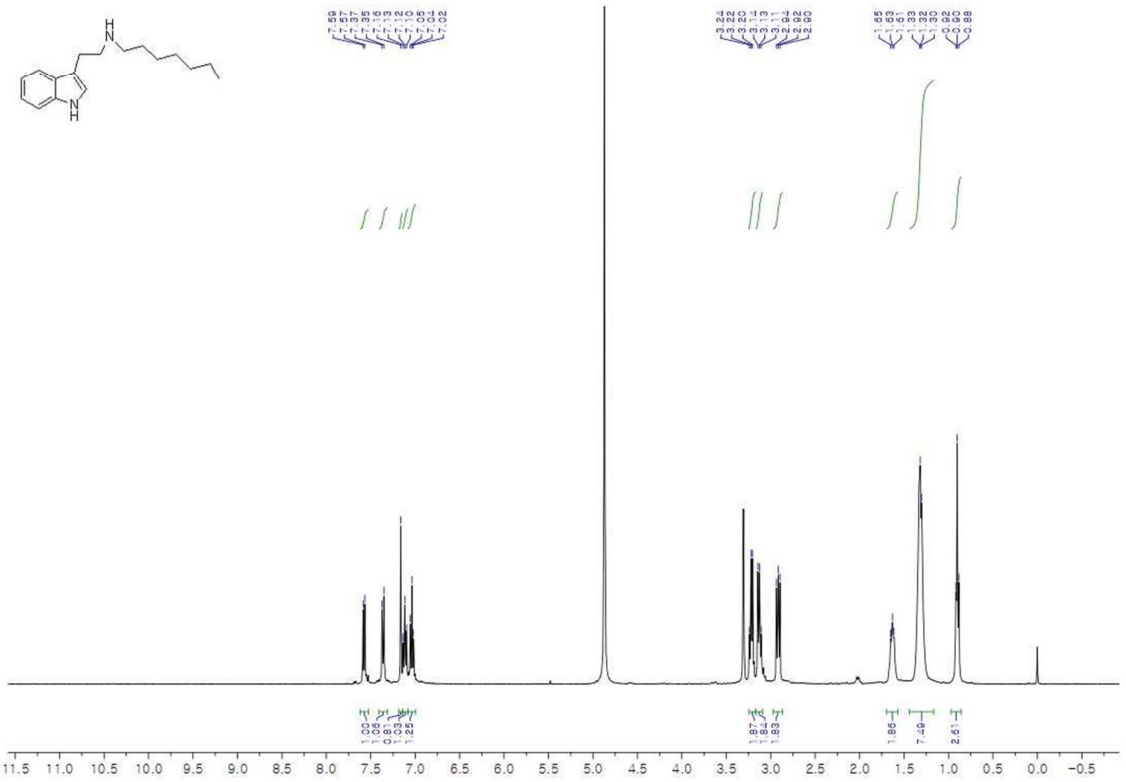


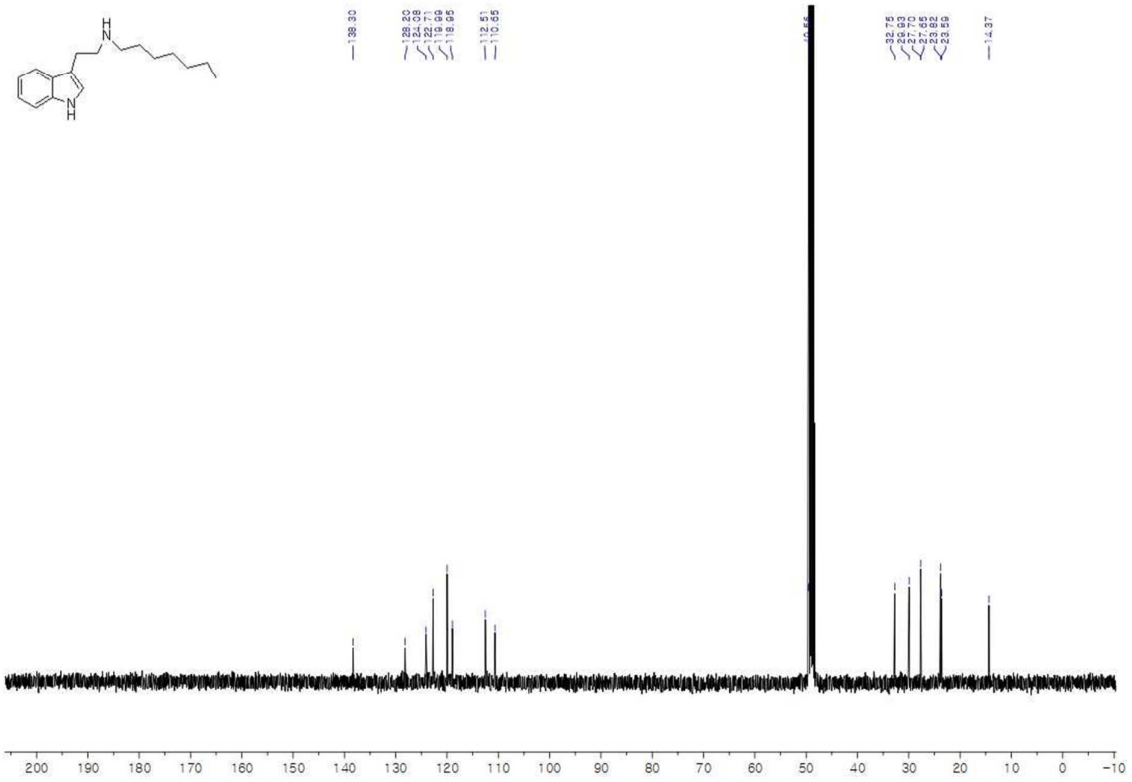


2-(1*H*-indol-3-yl)-*N*-(4-methylbenzyl)ethan-1-amine – (Scheme 1, 4a)

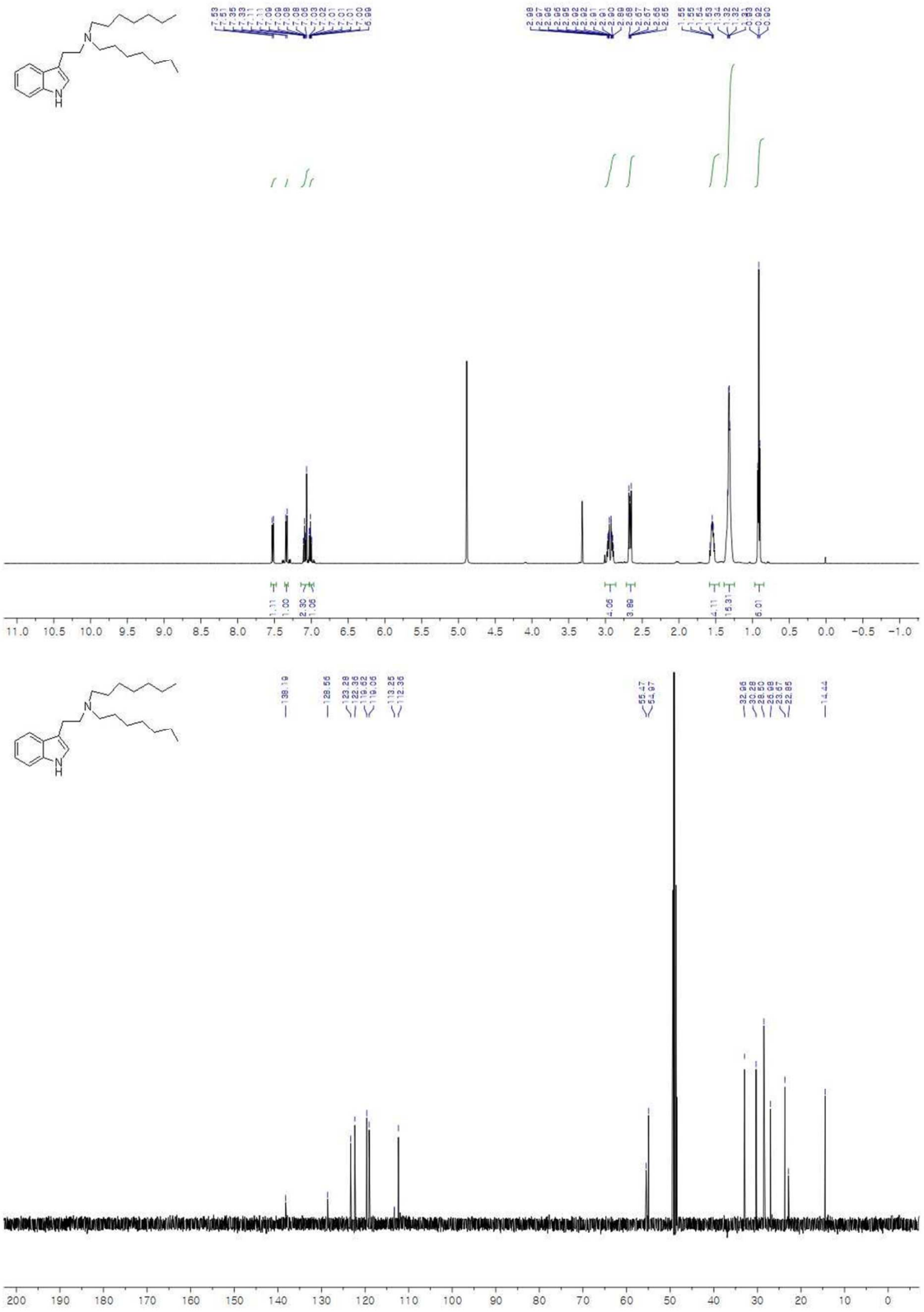


***N*-(2-(1*H*-indol-3-yl)ethyl)heptan-1-amine – (Scheme 1, 4b)**

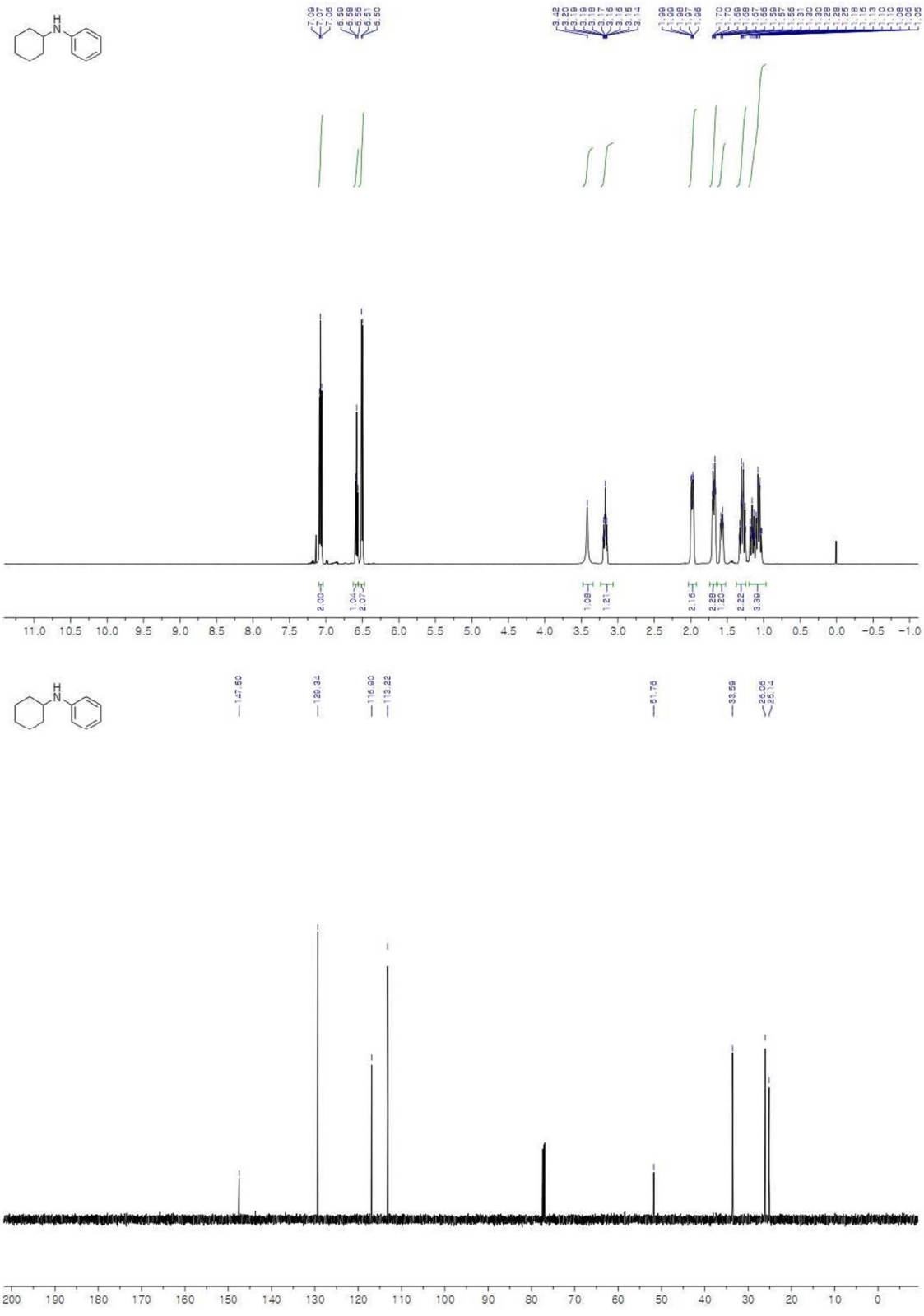




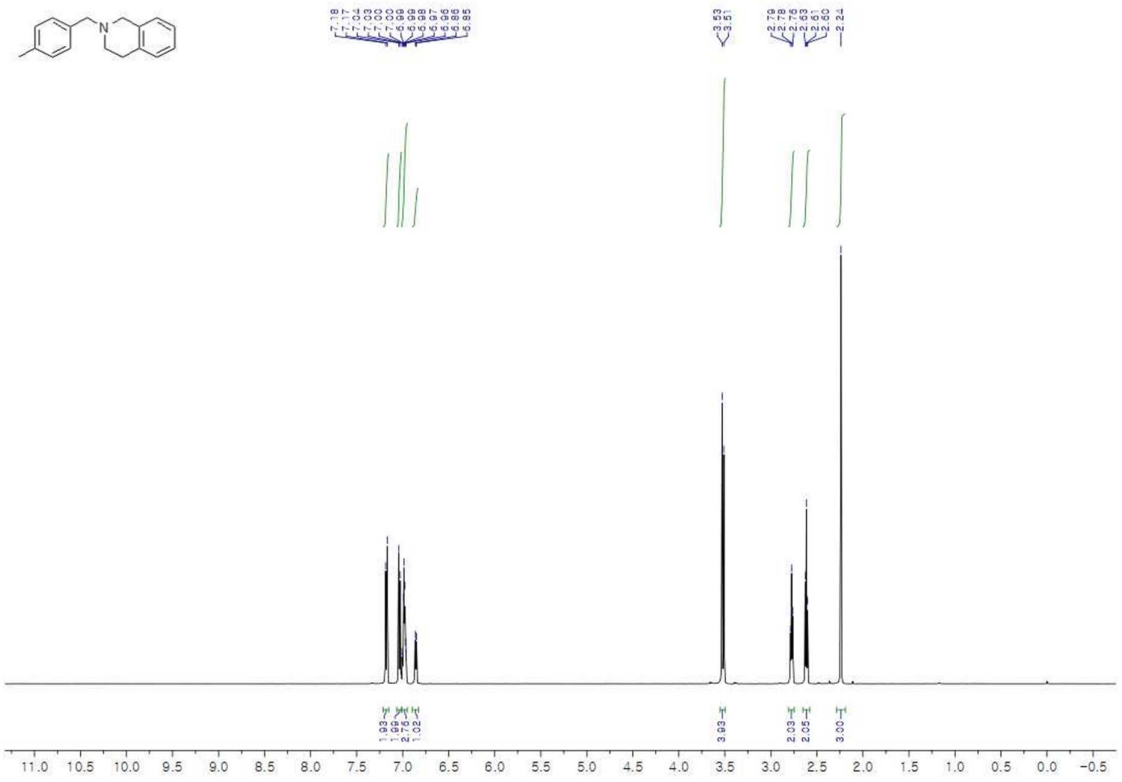
***N*-(2-(*1H*-indol-3-yl)ethyl)-*N*-heptylheptan-1-amine – (Scheme 1, 4c)**

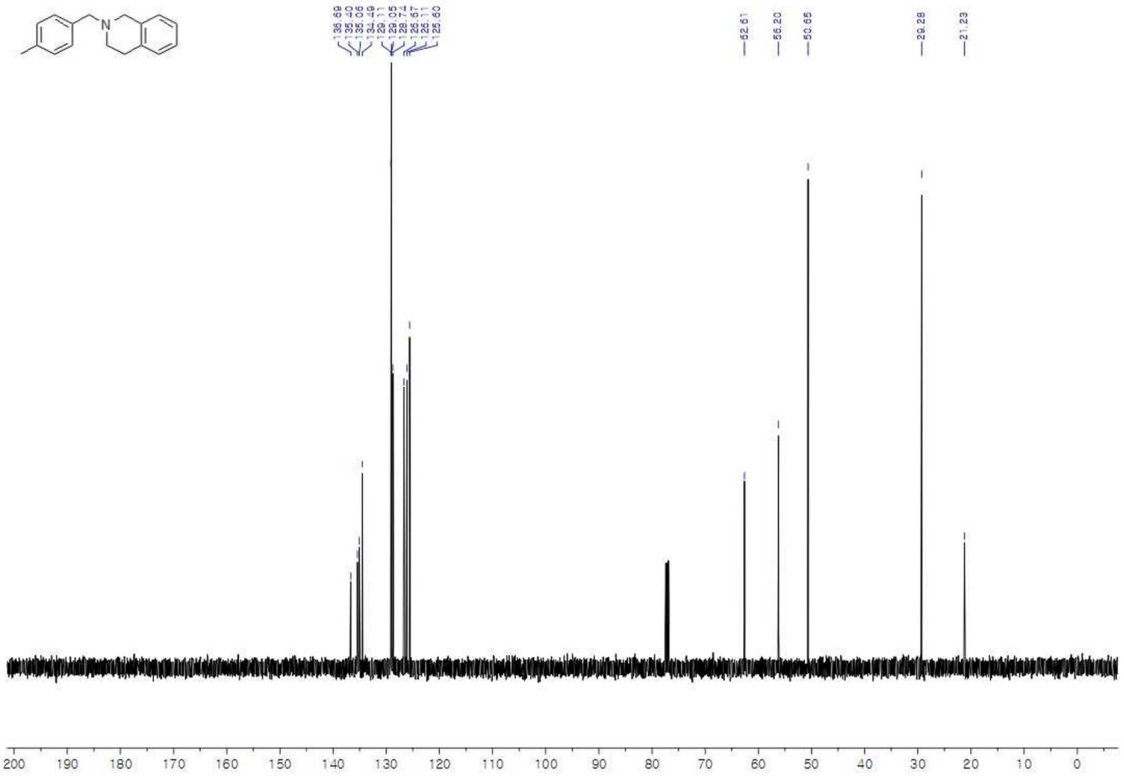


***N*-cyclohexylaniline – (Table 3, 2l)**

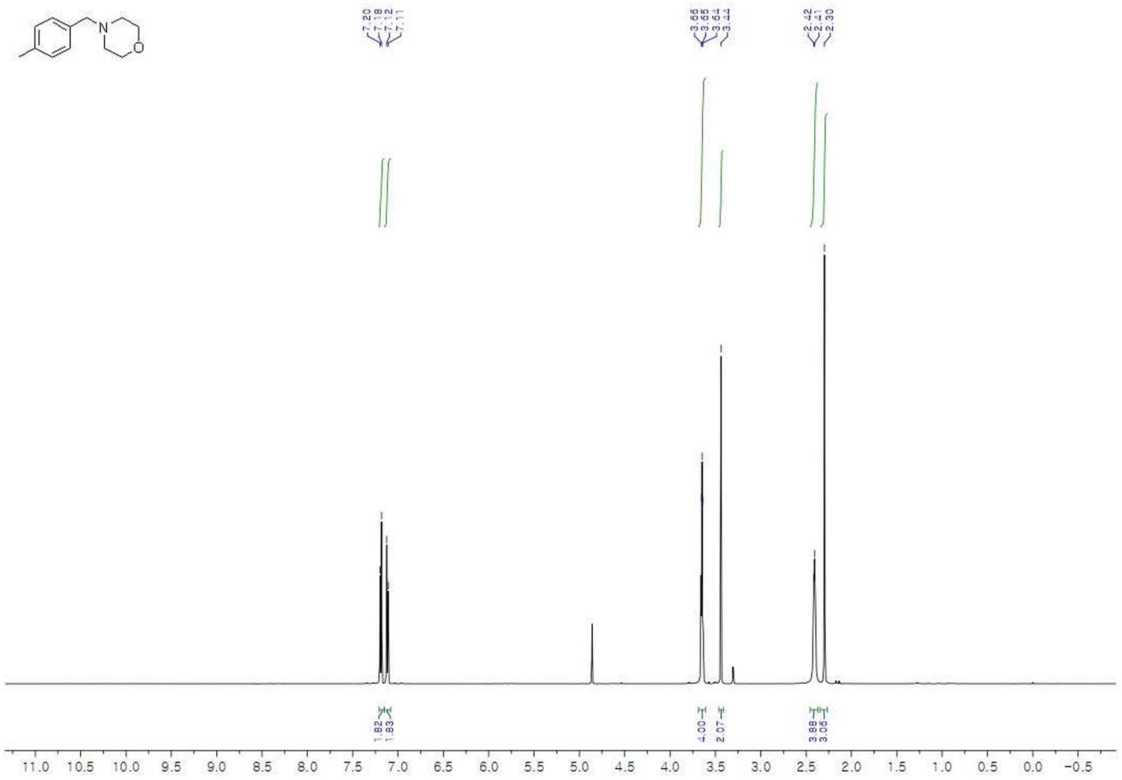


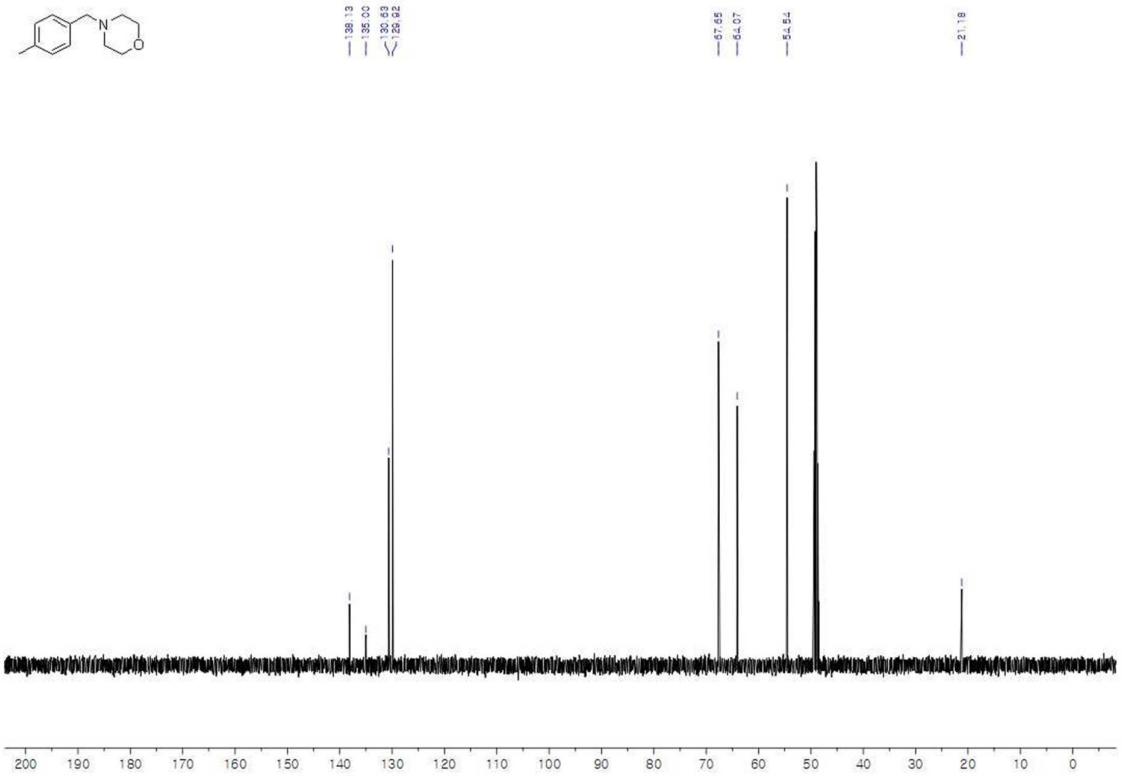
2-(4-methylbenzyl)-1,2,3,4-tetrahydroisoquinoline – (Scheme 2, 5b)



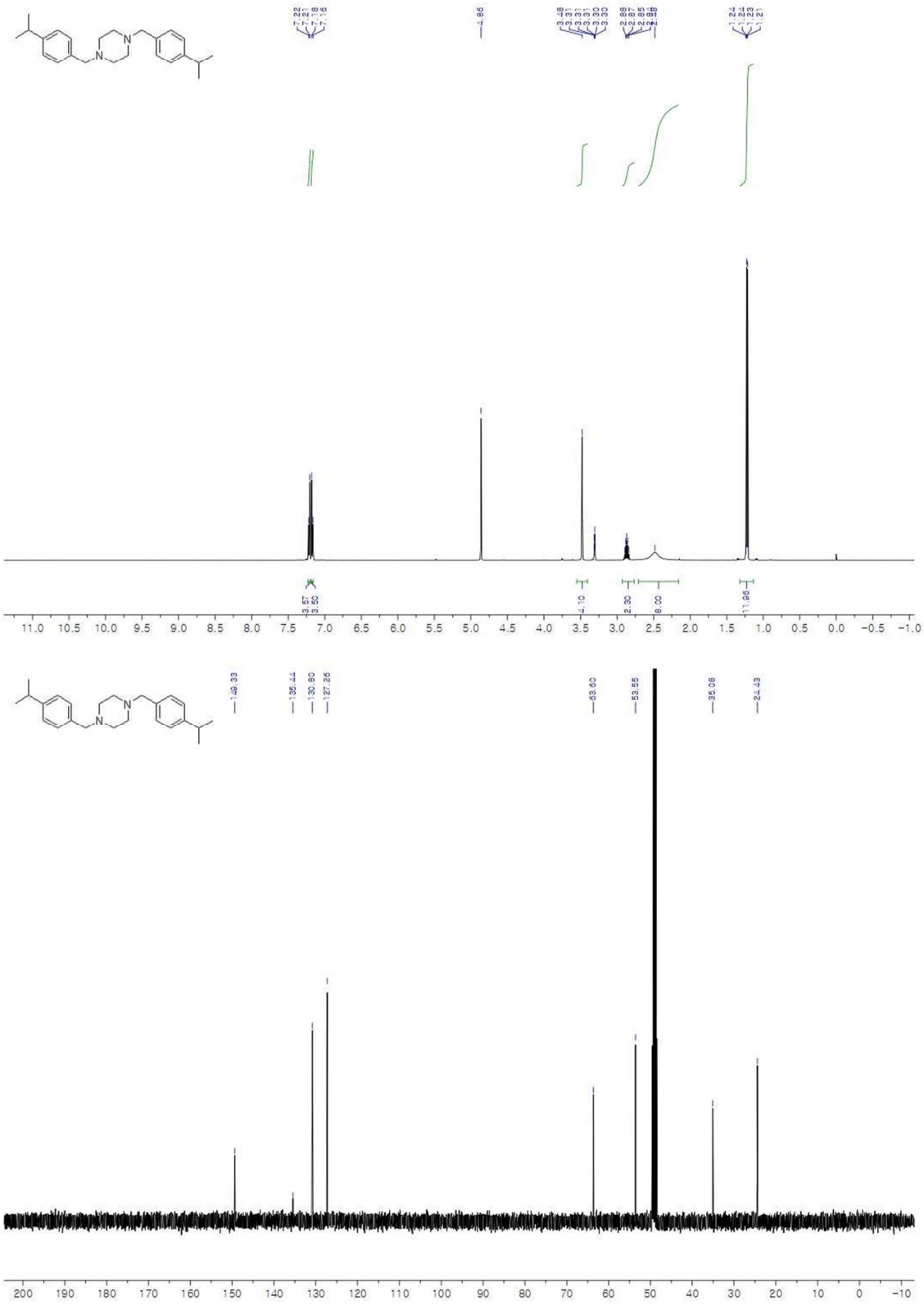


4-(4-methylbenzyl)morpholine – (Scheme 2, 5a)

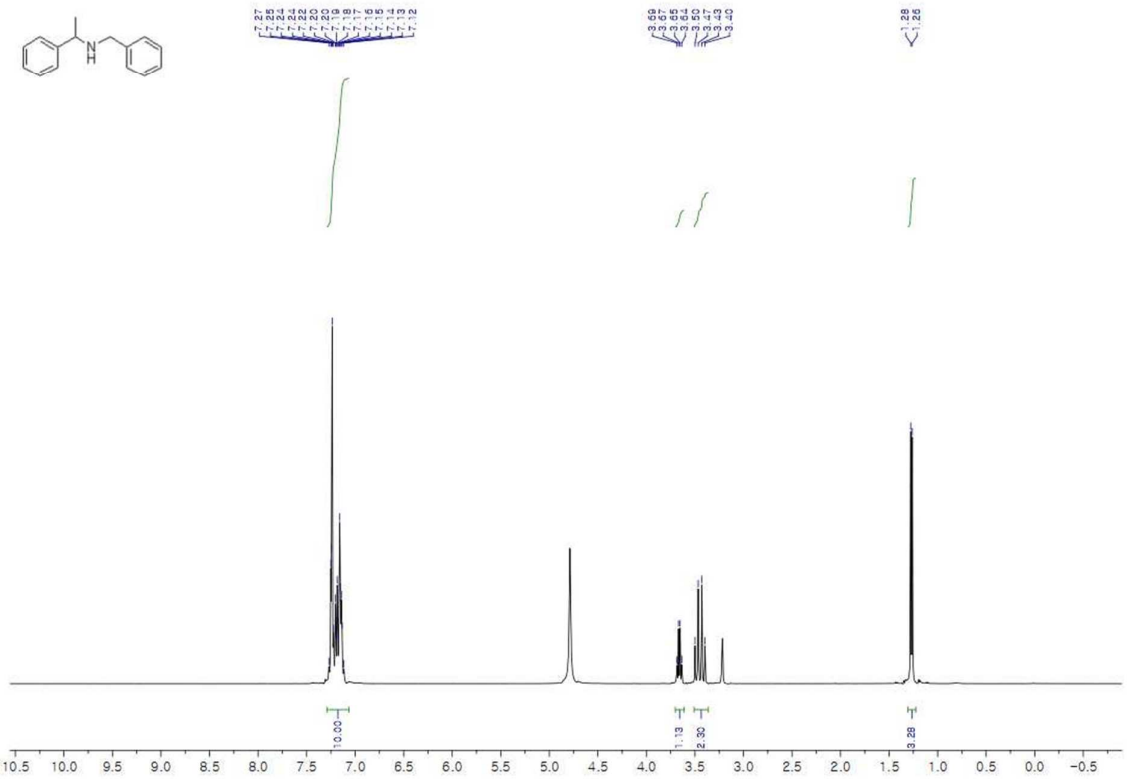


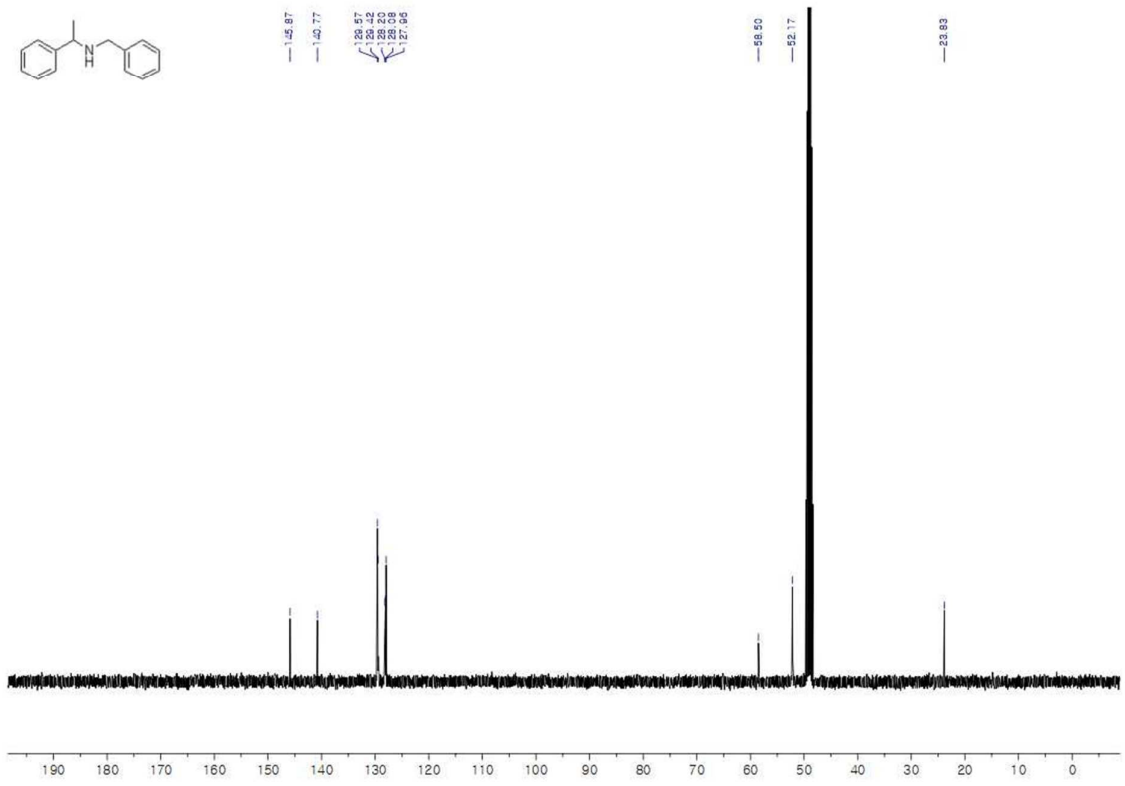


1,4-bis(4-isopropylbenzyl)piperazine – (Scheme 2, 5c)

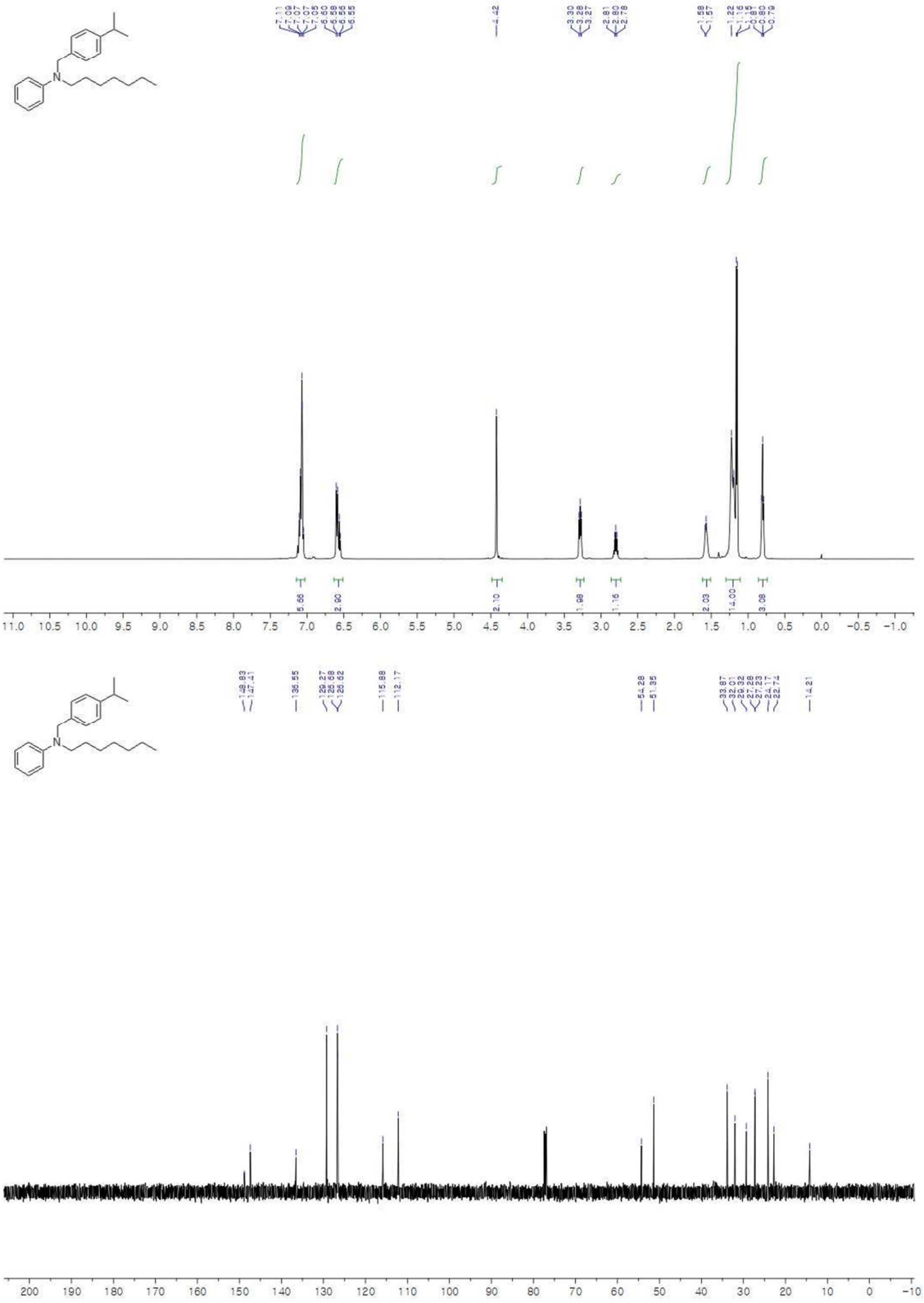


***N*-benzyl-1-pehnylethan-1-amine (eq2)**

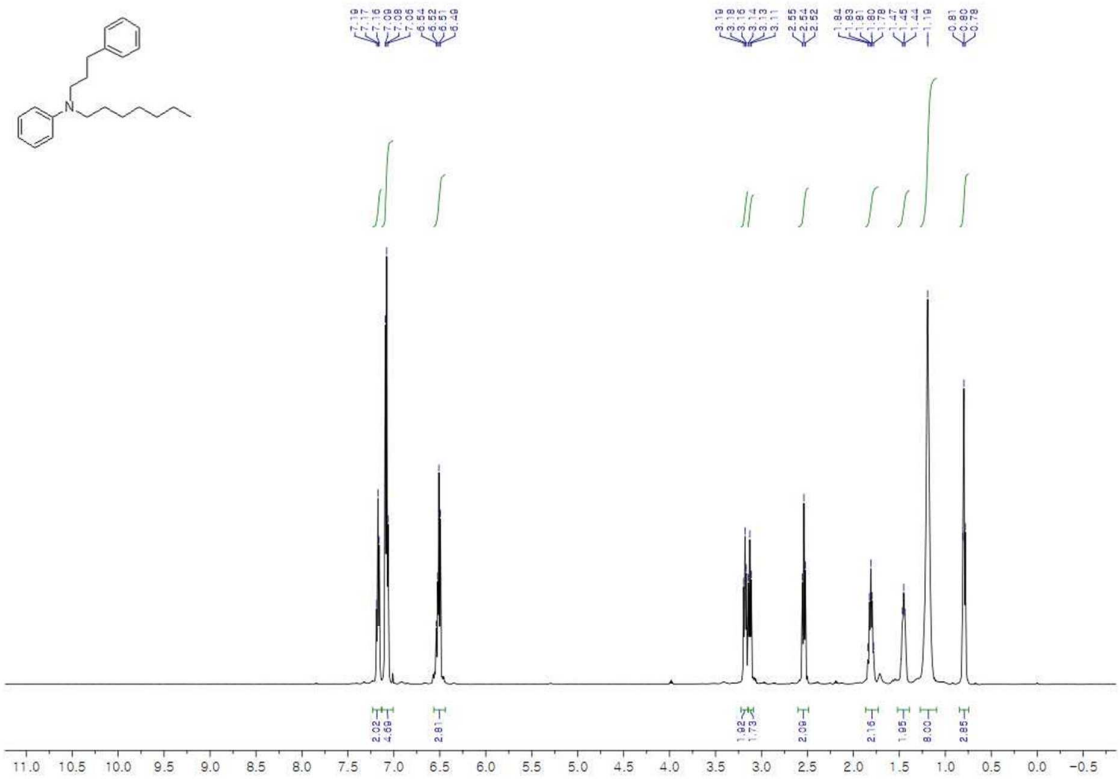


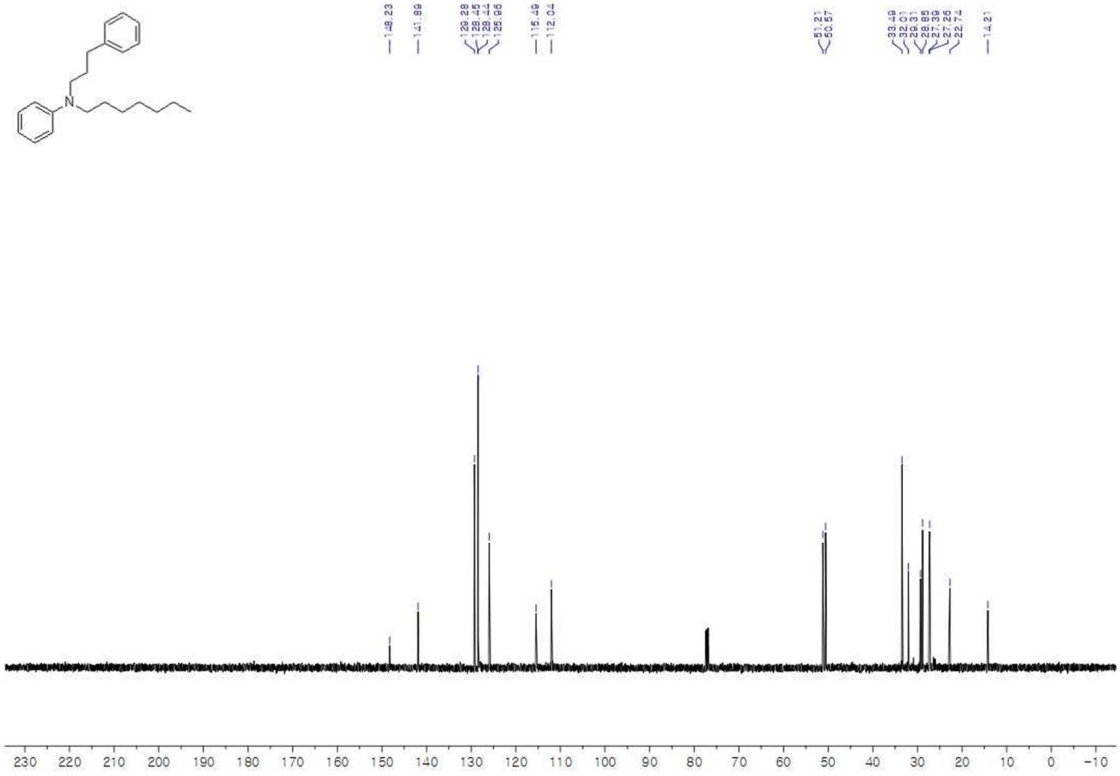


***N*-heptyl-*N*-(4-isopropylbenzyl)aniline – (eq 5, 6a)**

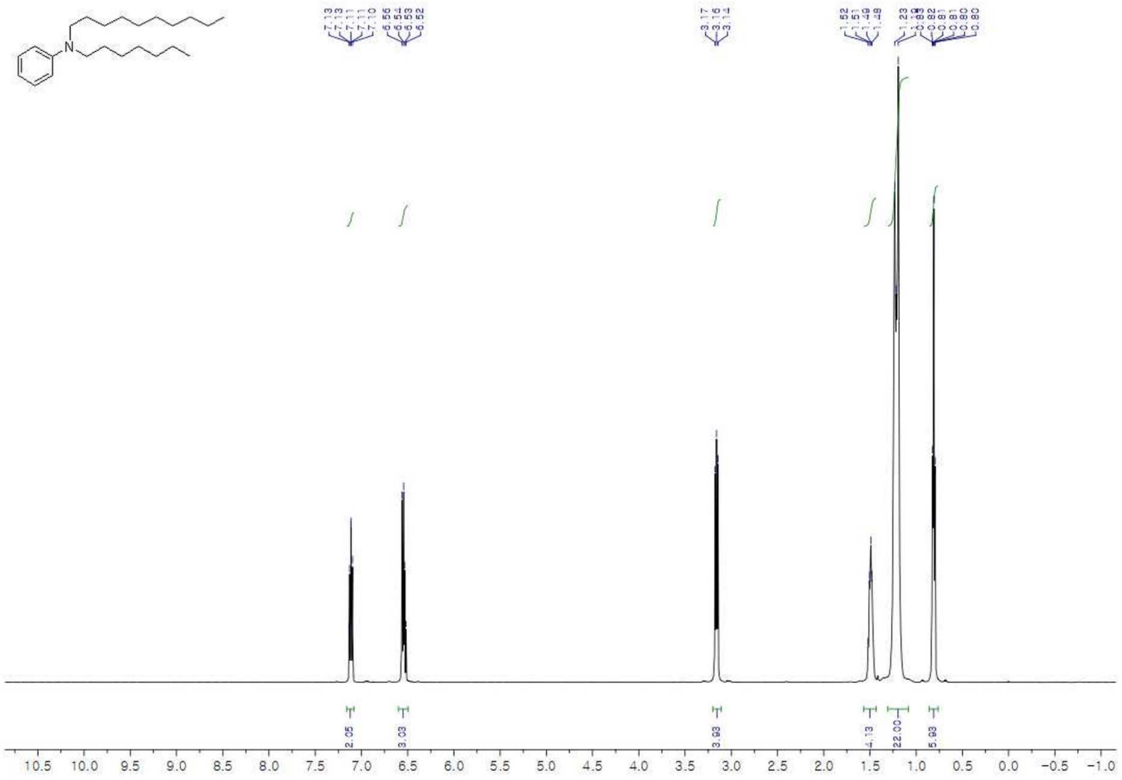


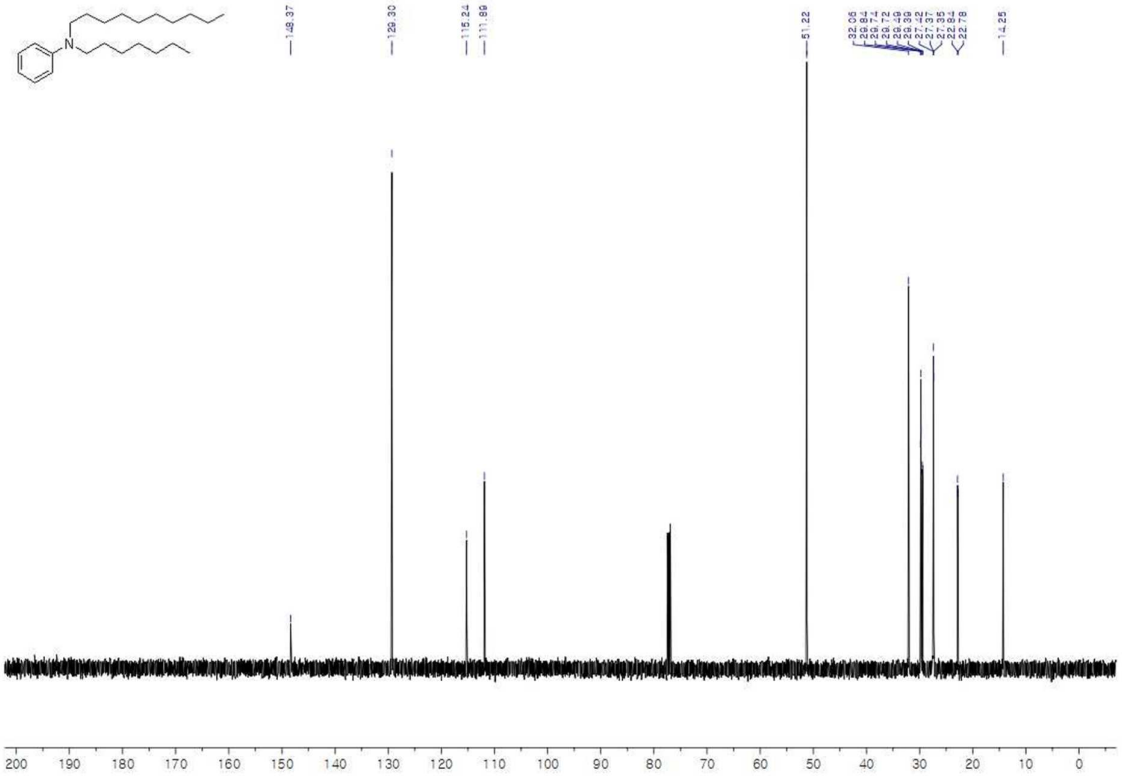
***N*-heptyl-*N*-(3-phenylpropyl)aniline – (eq 5, 6b)**



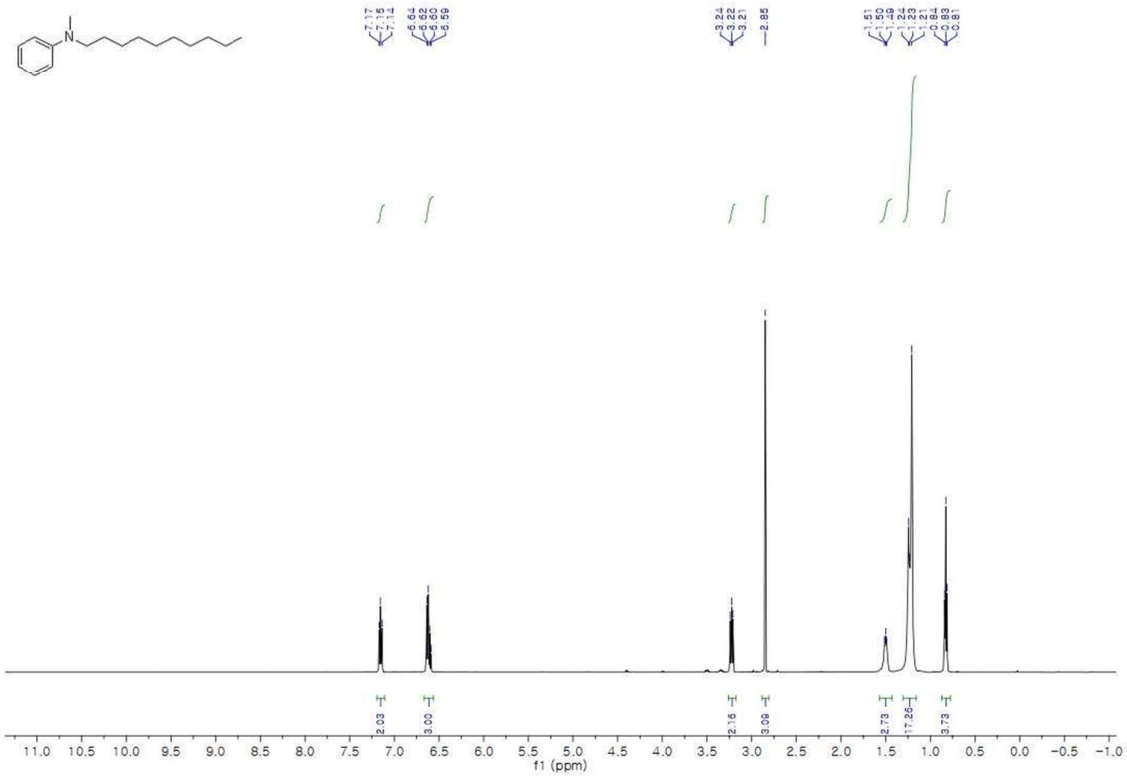


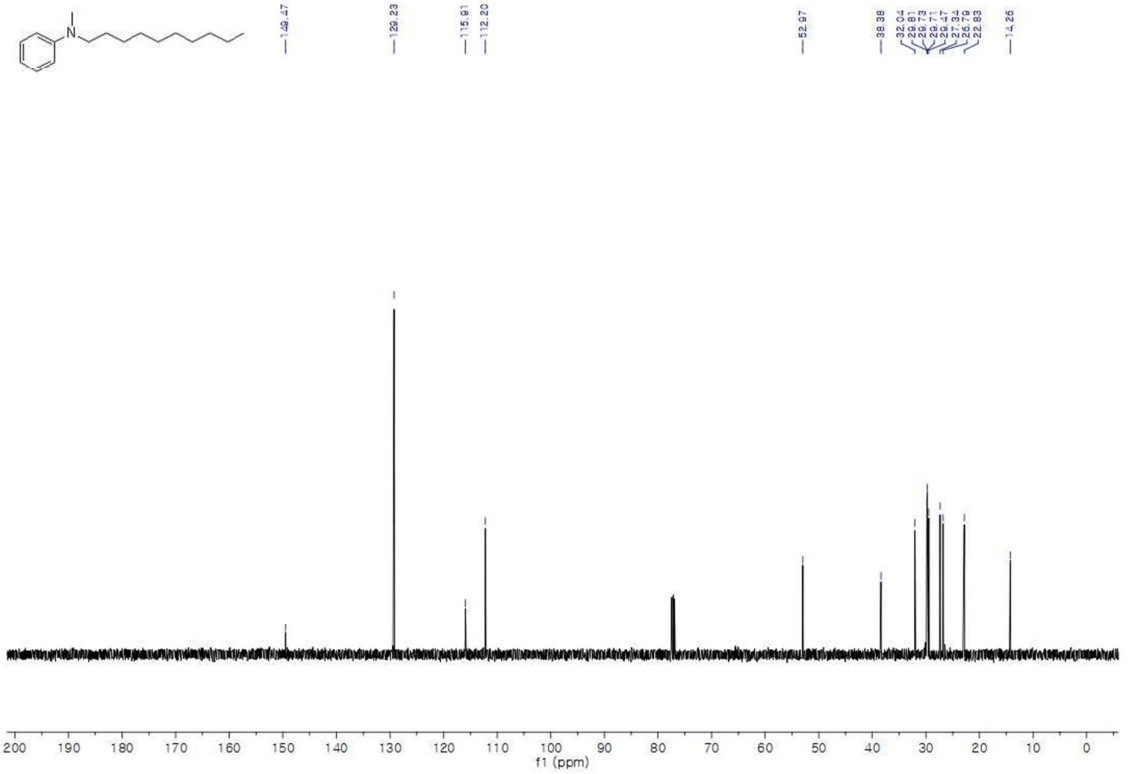
***N*-decyl-*N*-heptylaniline – (eq 5, 6c)**



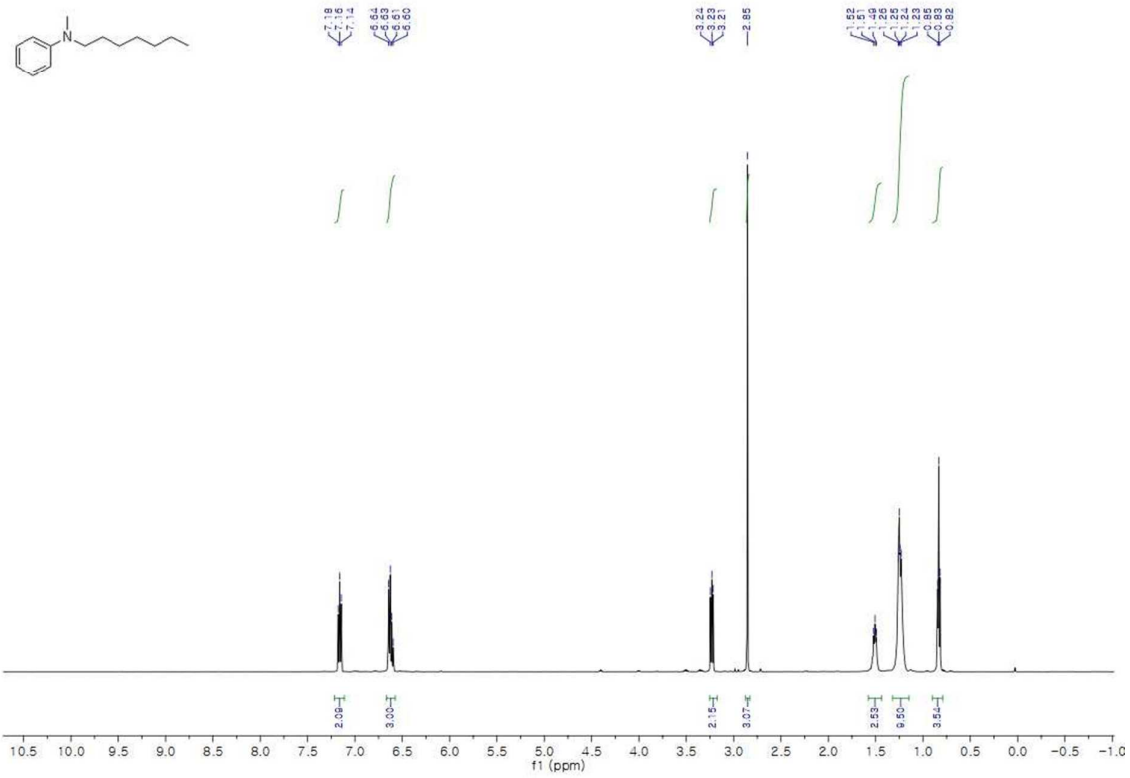


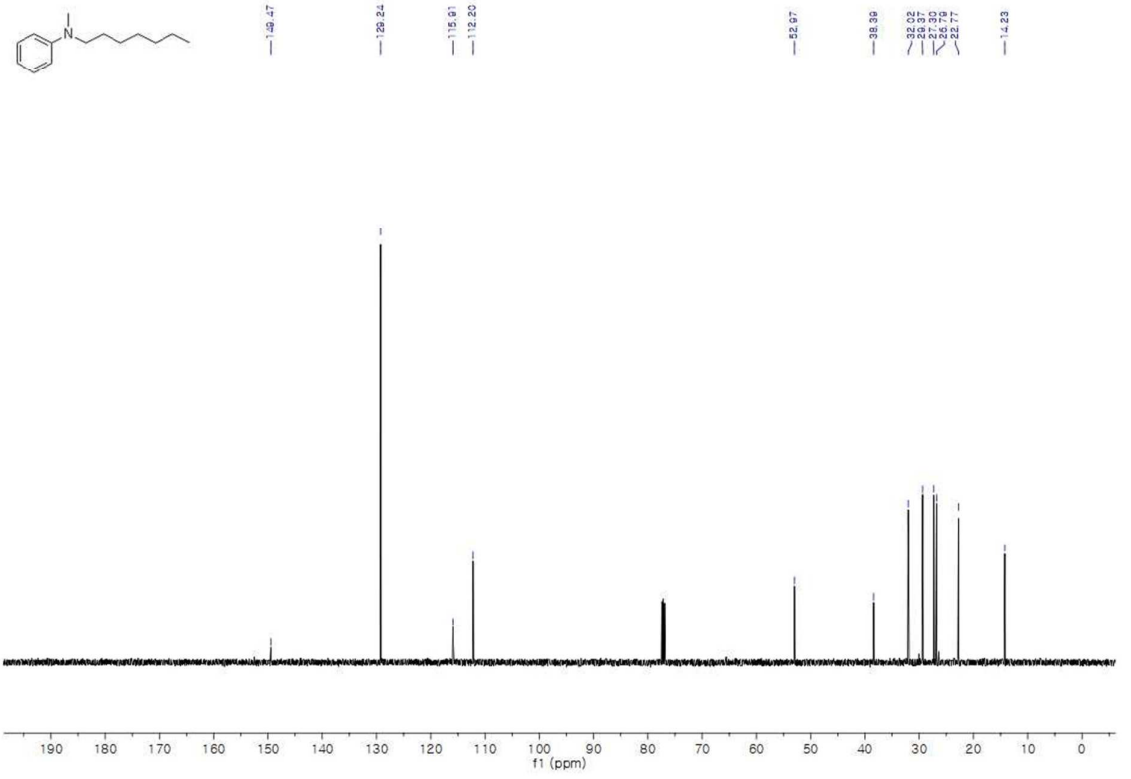
***N*-decyl-*N*-methylaniline – (eq 5, 6d)**





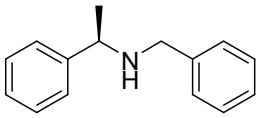
***N*-heptyl-*N*-methylaniline – (eq 5, 6e)**

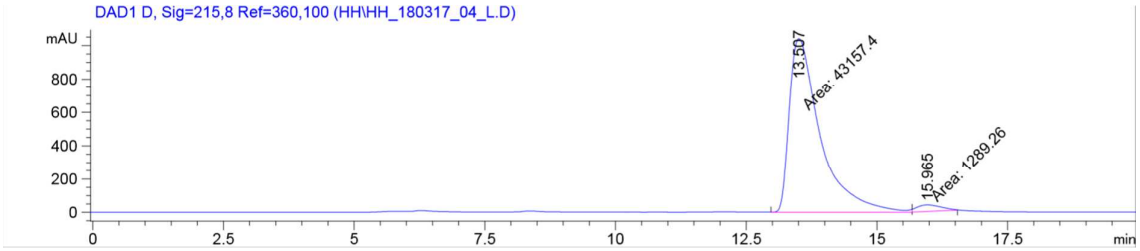




4. HPLC Chromatogram

D-form

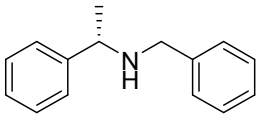


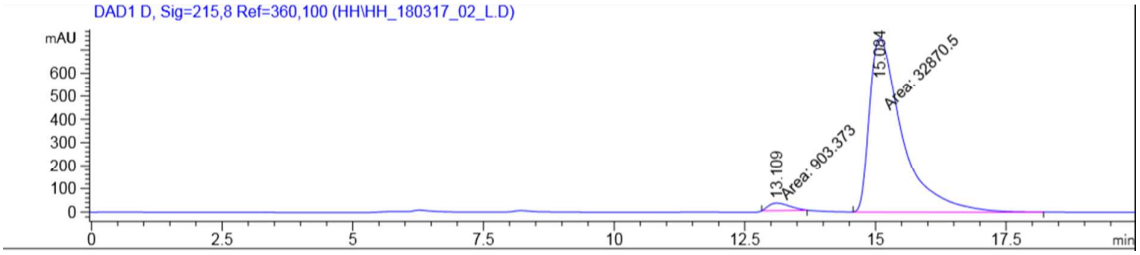


Signal 4: DAD1 D, Sig=215,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.507	MM	0.6900	4.31574e4	1042.52161	97.0993
2	15.965	MM	0.5432	1289.25708	39.55890	2.9007
Totals :				4.44466e4	1082.08051	

L-form





Signal 4: DAD1 D, Sig=215,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.109	MM	0.4686	903.37305	32.13210	2.6748
2	15.084	MM	0.7306	3.28705e4	749.89319	97.3252
Totals :				3.37739e4	782.02529	