The Ti-BINOLate-Catalyzed, Enantioselective Ring-Opening of *meso*-Aziridines with Amines

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Supplementary Material

Detailed Information about ESI-MS analysis of the formed BINOL/Ti complexes

High resolution ESI mass spectra for the analysis of BINOL/Ti complexes were recorded on a Brucker APEX II FT-ICR, the low resolution ESI-MS/MS spectra were recorded on an ESQUIRE 3000 Plus (Bruker Daltonics). Because of the special isotopic pattern of such complexes with often more than 100 carbon atoms and some titanium atoms, the calculated exact mass often differs from the observed maximum of the signal with $\Delta m = 1$. This is in agreement with the calculated isotopic pattern.

BINOL as ligand

ESI-MS-experiments were carried out with a mixture of $Ti(O\mathit{t}Bu)_4$, (*R*)-BINOL and aniline (1:2.2:10) in CH_2Cl_2, which had been prepared according to the general synthetic protocol.

Table 1 Results with CH_2Cl_2 as solvent

Species	Molecular formular	*m/z* (calcd.)	*m/z* (found)	Δppm
$[5\ BINOL + 3\ Ti + O + H]^+$	$C_{100}H_{61}O_{11}Ti_3$	1581.26523	1581.27209	4
$[6\ BINOL + 4\ Ti + 2\ O + 2\ H_2O + H]^+$	$C_{120}H_{77}O_{16}Ti_4$	1965.31240	1965.31907	3

Table 2 Additional Species with CH_2Cl_2/MeCN as solvent

Species	Molecular formular	*m/z* (calcd.)	*m/z* (found)	Δppm
$[6\ BINOL + 3\ Ti + H]^+$	$C_{120}H_{73}O_{12}Ti_3$	1849.35350	1849.36931	8

Table 3 Results after addition of 10 eq. aziridine 1a in CH_2Cl_2

Species	Molecular formular	*m/z* (calcd.)	*m/z* (found)	Δppm
$[6\ BINOL + 4\ Ti + 4\ H_2O + 3$ aziridine + 3 aniline$]^+$	$C_{174}H_{143}N_6O_{16}Ti_4$	2764.84730	2764.81534	11

Bridged bis-BINOL 11 as ligand

ESI-MS-experiments were carried out with a mixture of Ti(O*t*Bu)$_4$, the linked bis-BINOL ligand **11** and aniline (1:1.1:10) in CH_2Cl_2 which had been prepared according to the general synthetic protocol.

Table 4 Results with CH_2Cl_2 as solvent

Species	Molecular formular	*m/z* (calcd.)	*m/z* (found)	Δppm
[2 **11** + 2 Ti + H_2O - H]$^-$	$C_{84}H_3O_{11}Ti_2$	1333.25523	1333.25118	3

Table 5 Additional Species with CH_2Cl_2/MeCN as solvent

Species	Molecular formular	*m/z* (calcd.)	*m/z* (found)	Δppm
[**11** + Ti + H]$^+$	$C_{42}H_{27}O_5Ti$	659.1338	659.13666	4
[2 **11** + 2 Ti + H]$^+$	$C_{84}H_{53}O_{10}Ti_2$	1317.25977	1317.26233	2
[2 **11** + 2 Ti + H_2O + H]$^+$	$C_{84}H_{55}O_{11}Ti_2$	1335.2703	1335.27083	0,4
[3 **11** + 3 Ti + H_2O + H]$^+$	$C_{126}H_{81}O_{16}Ti_3$	1994.3963	1994.43480	19[a]

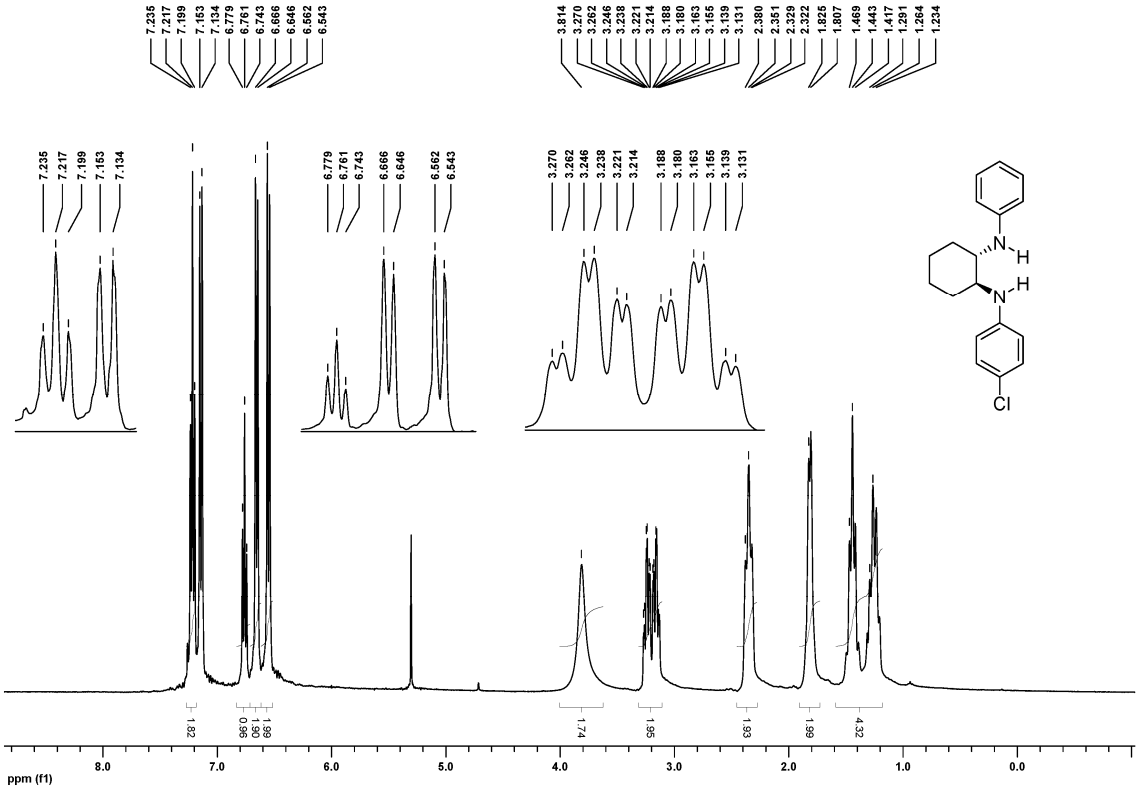
[a] higher aberration between calculated und found *m/z* because of measuring at the detection limit.

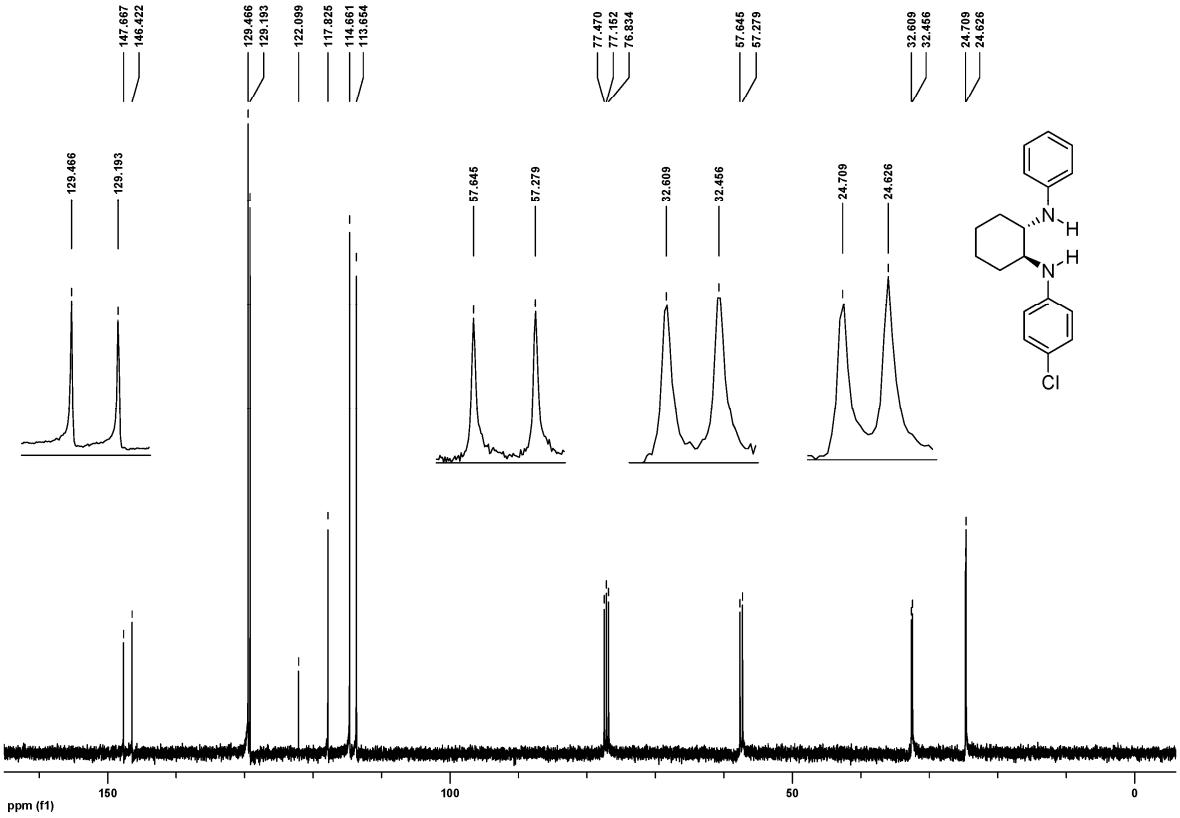
Table 6 Results after addition of 10 eq. aziridine 1a in CH_2Cl_2

Species	Molecular formular	*m/z* (calcd.)	*m/z* (found)	Δppm
[2 **11** + 2 Ti + aziridine + aniline + H]$^+$	$C_{102}H_{75}N_2O_{10}Ti_2$	1583.4381	1583.43296	3

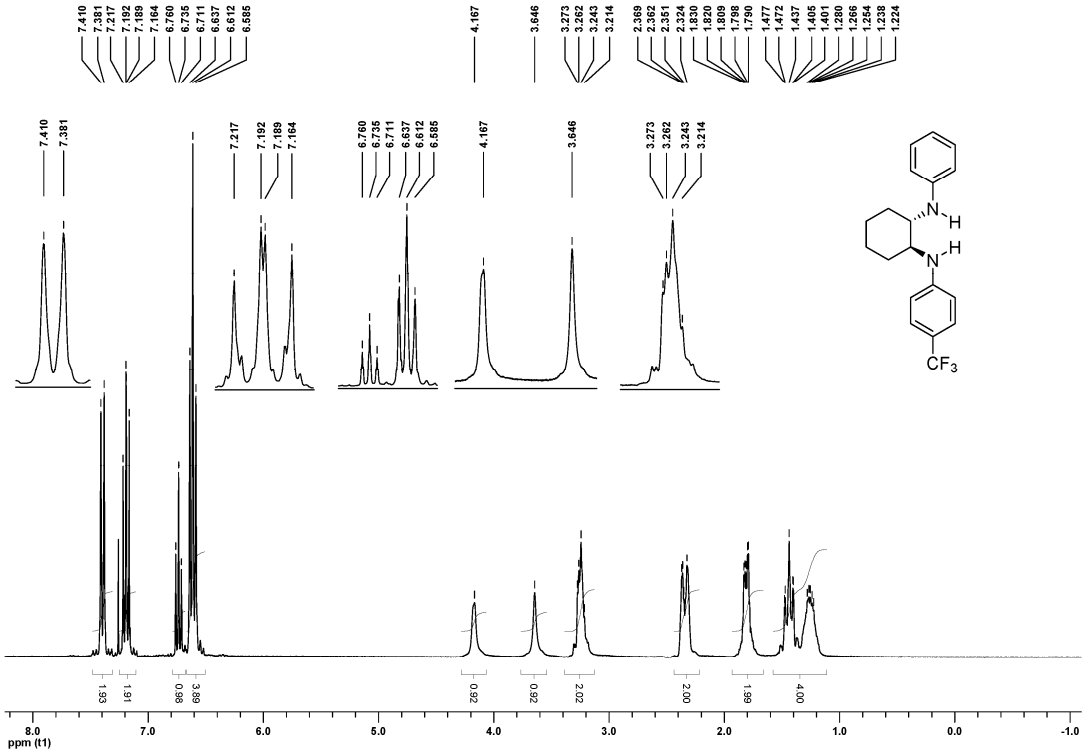
Experimental Data of new compounds/Compounds synthesized by a new method

(1*S*,2*S*)-*N*-(4-Chlorophenyl)-*N'*-phenylcyclohexane-1,2-diamine (3e)

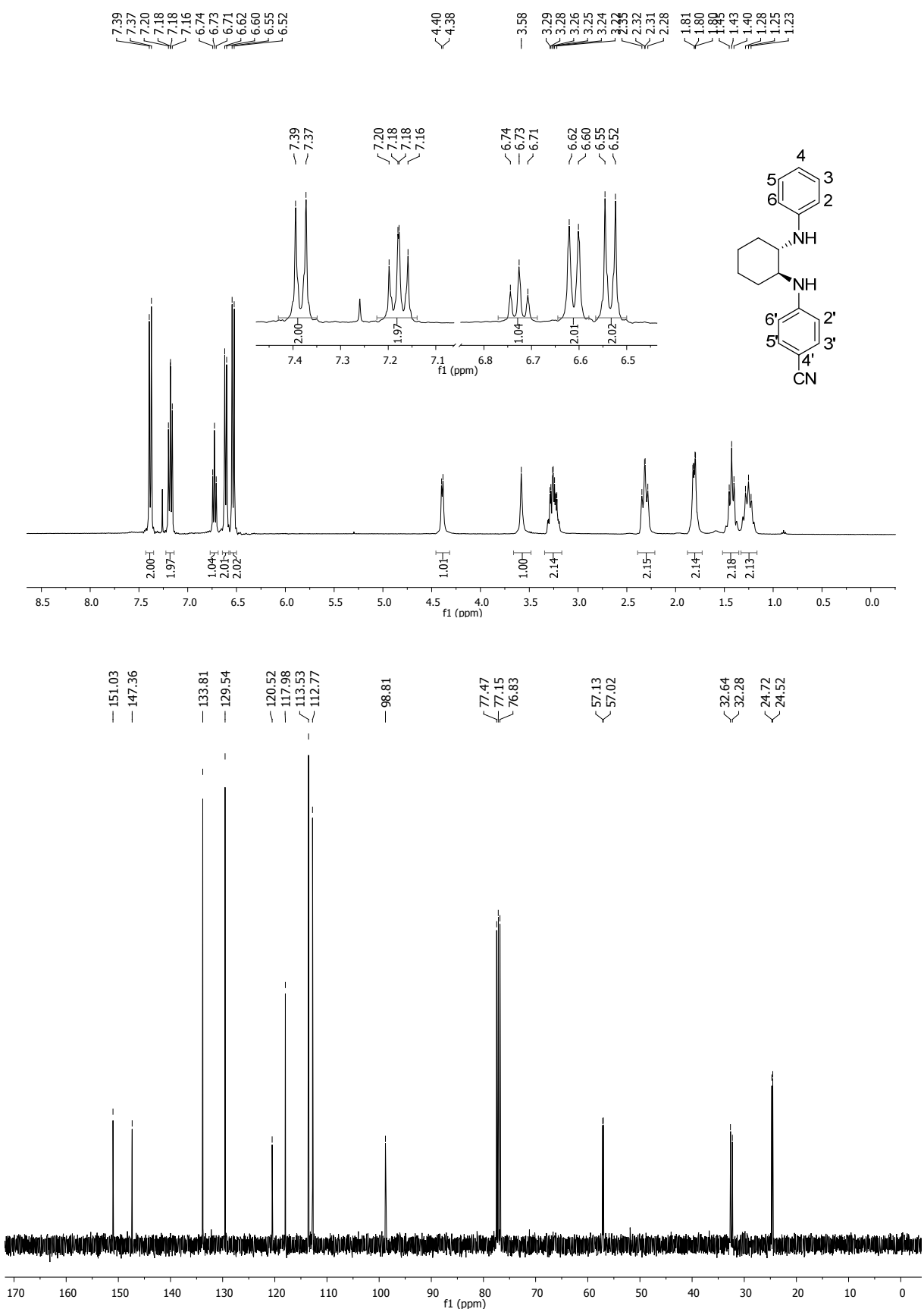




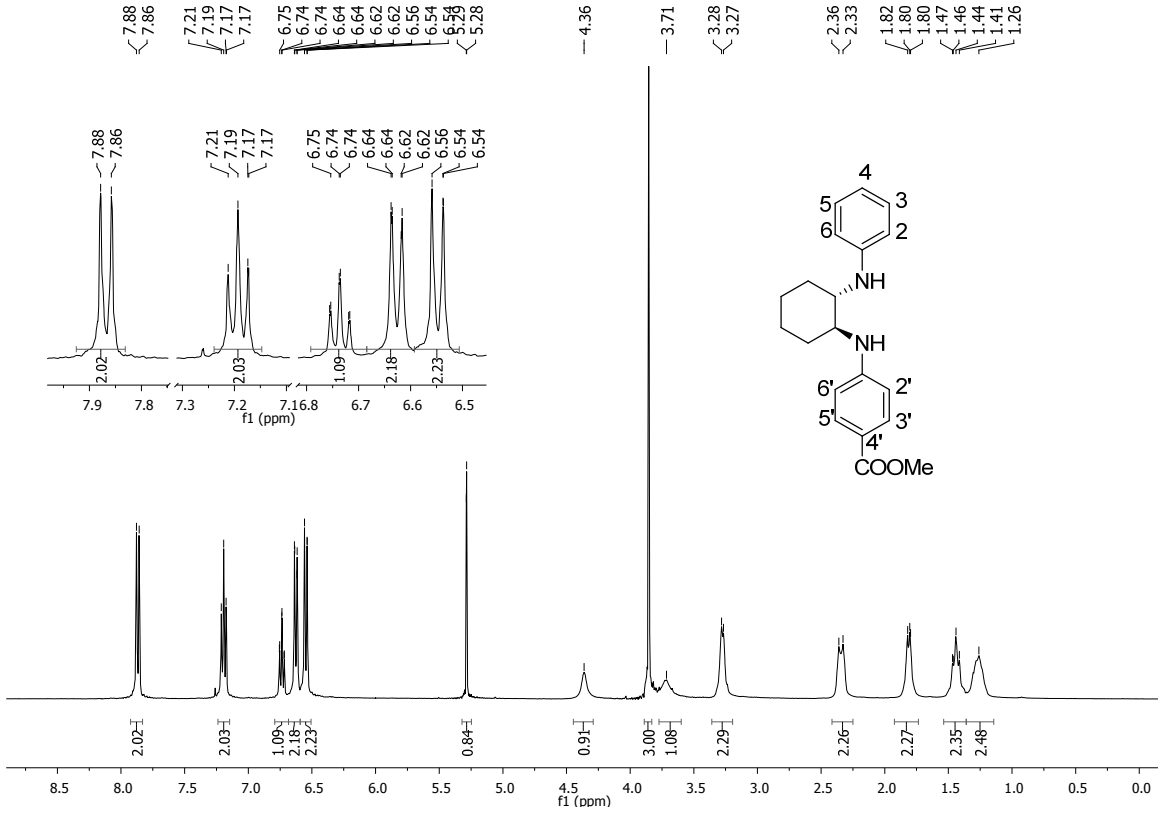
(1*S*,2*S*)-*N*-(Phenyl)-*N'*-(4-trifluoromethylphenyl)-cyclohexane-1,2-diamine (3g)

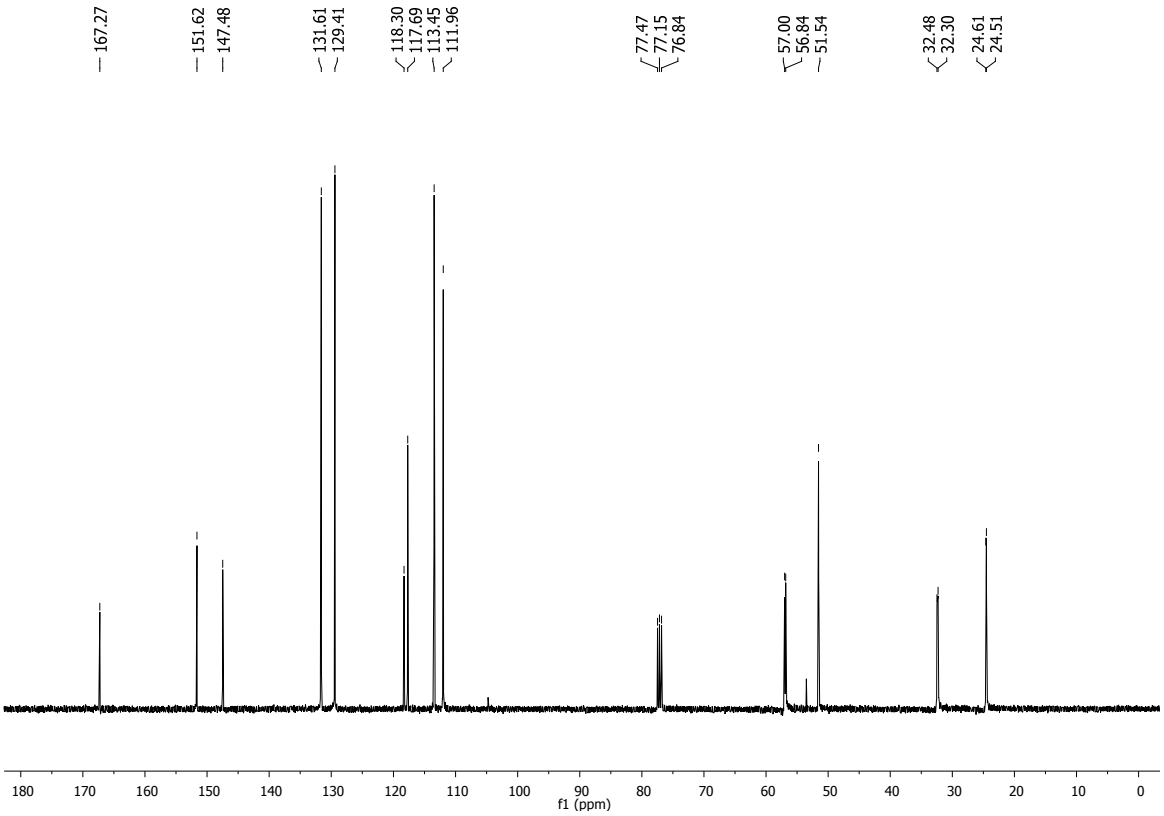


(1*S*,2*S*)-*N*-(4-Cyanophenyl)-*N'*-phenylcyclohexane-1,2-diamine (3h)

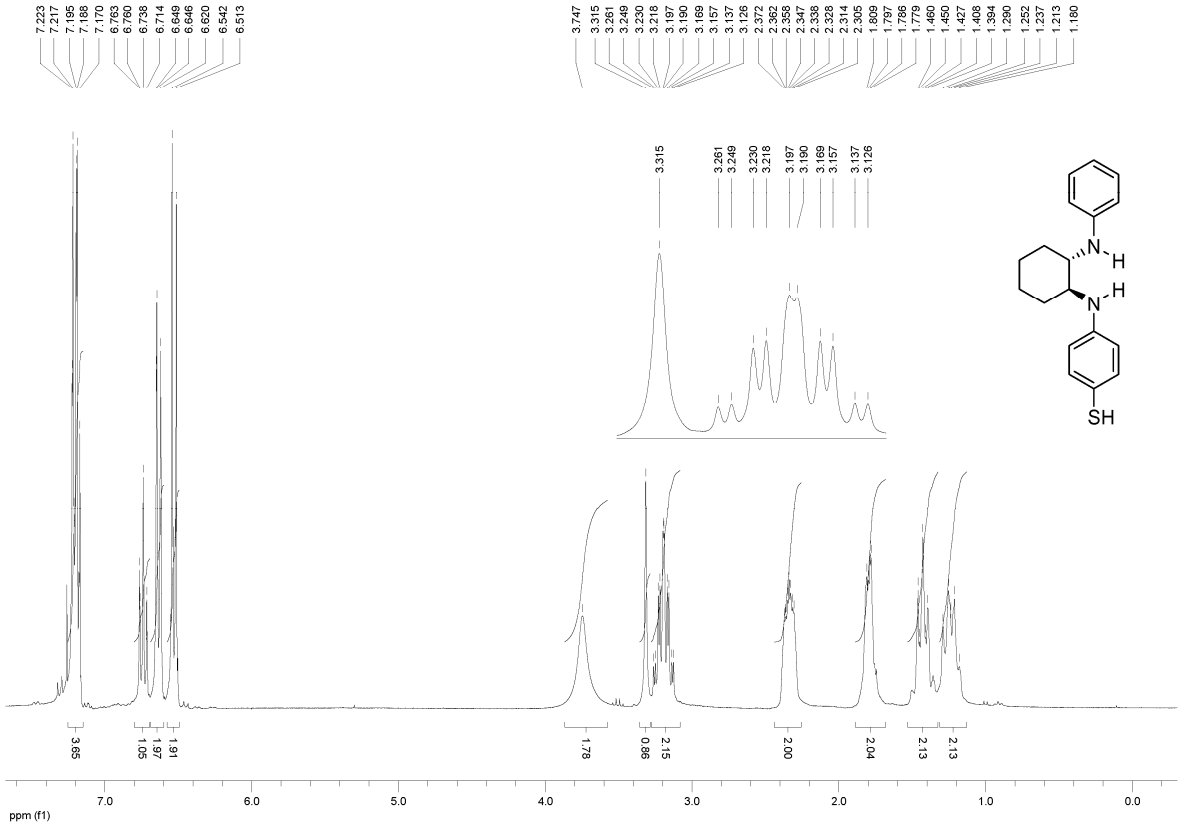


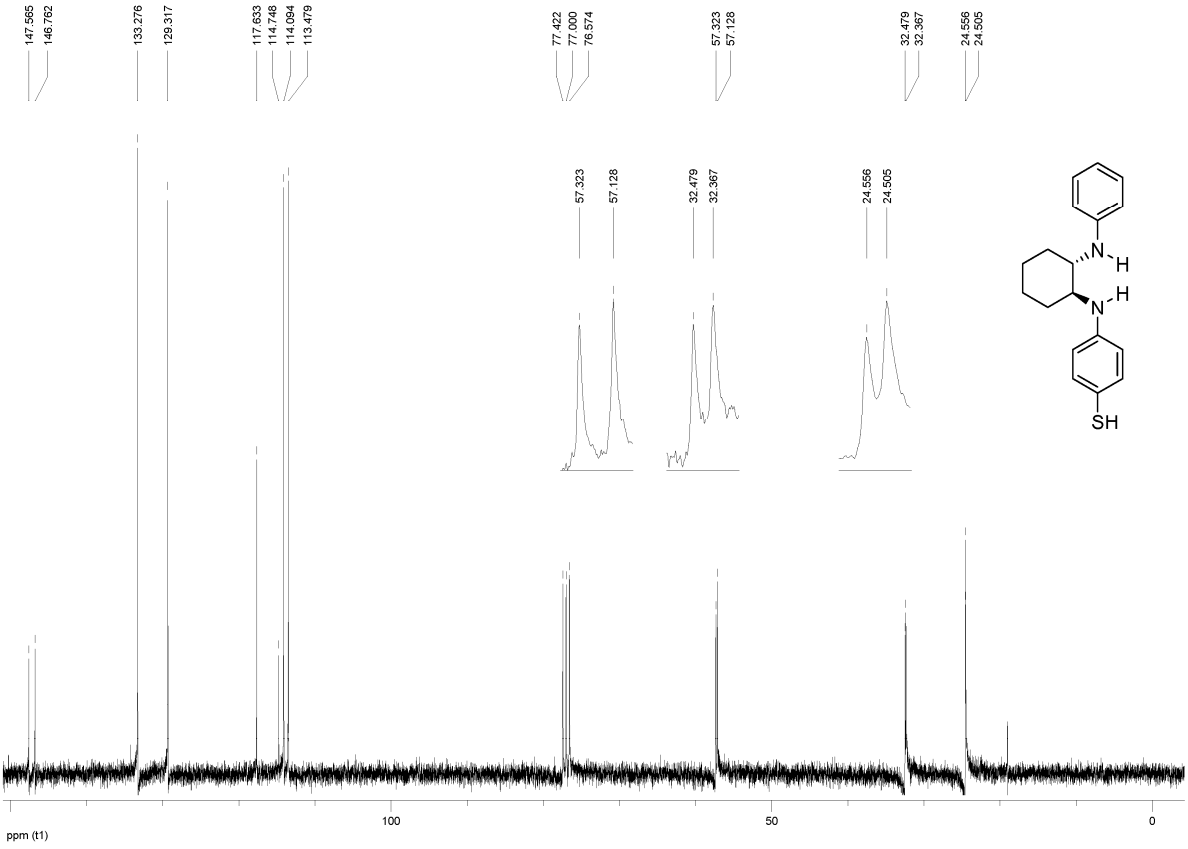
(1*S*,2*S*)-*N*-(4-Carbomethoxyphenyl)-*N'*-phenylcyclohexane-1,2-diamine (3i)



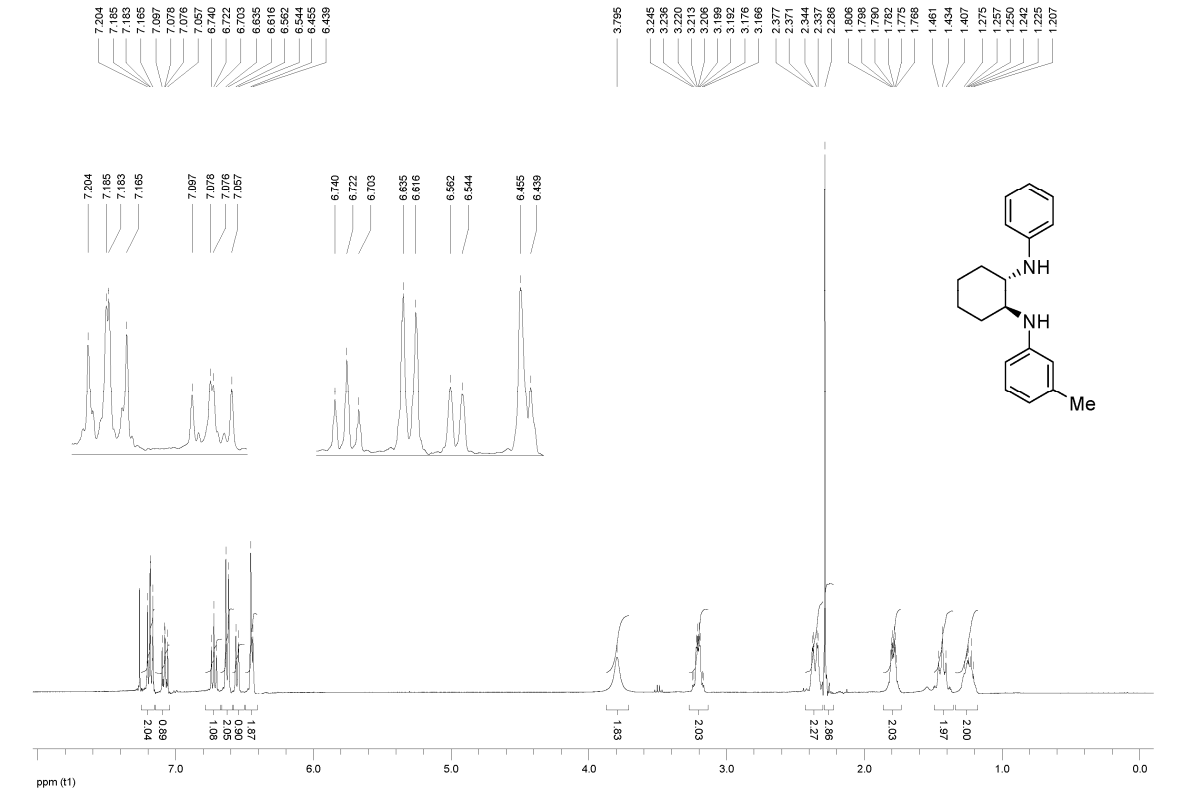


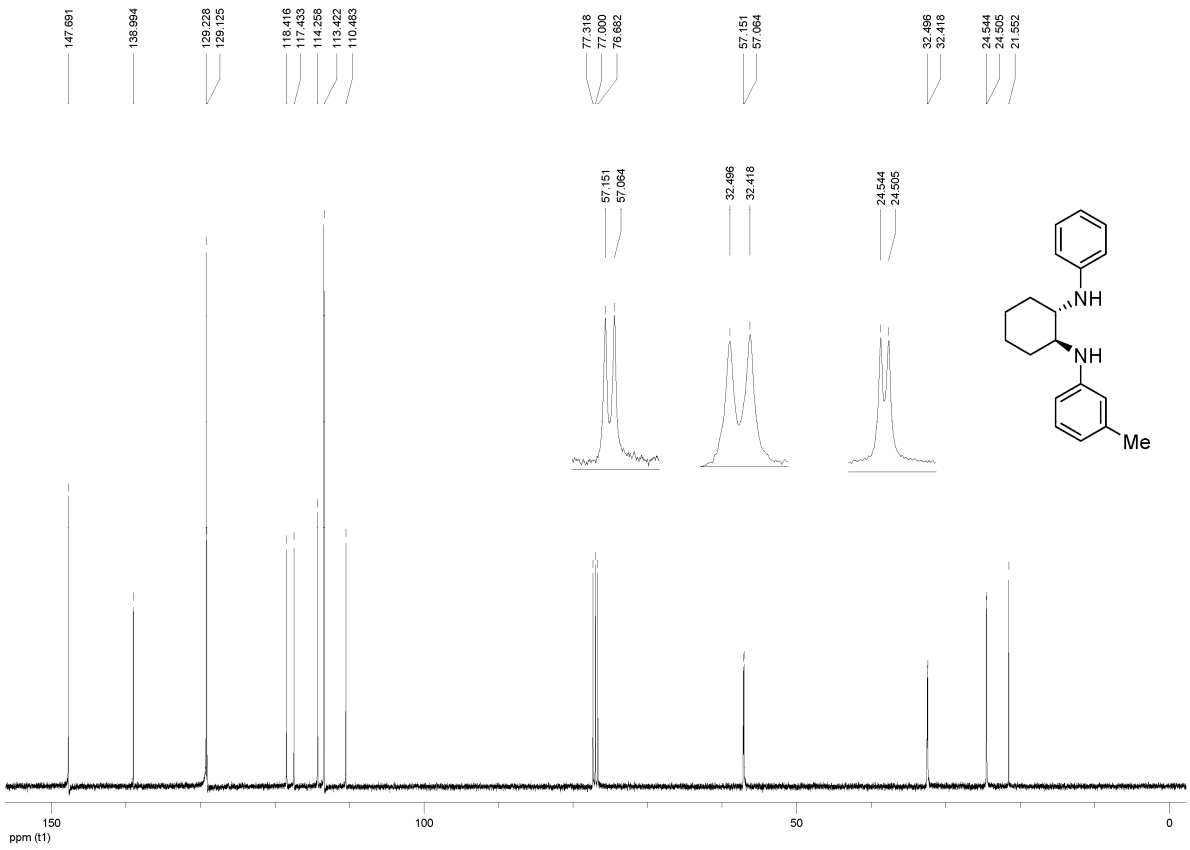
4-((1*S*,2*S*)-2-(Phenylamino)cyclohexylamino)benzenethiol (3k)



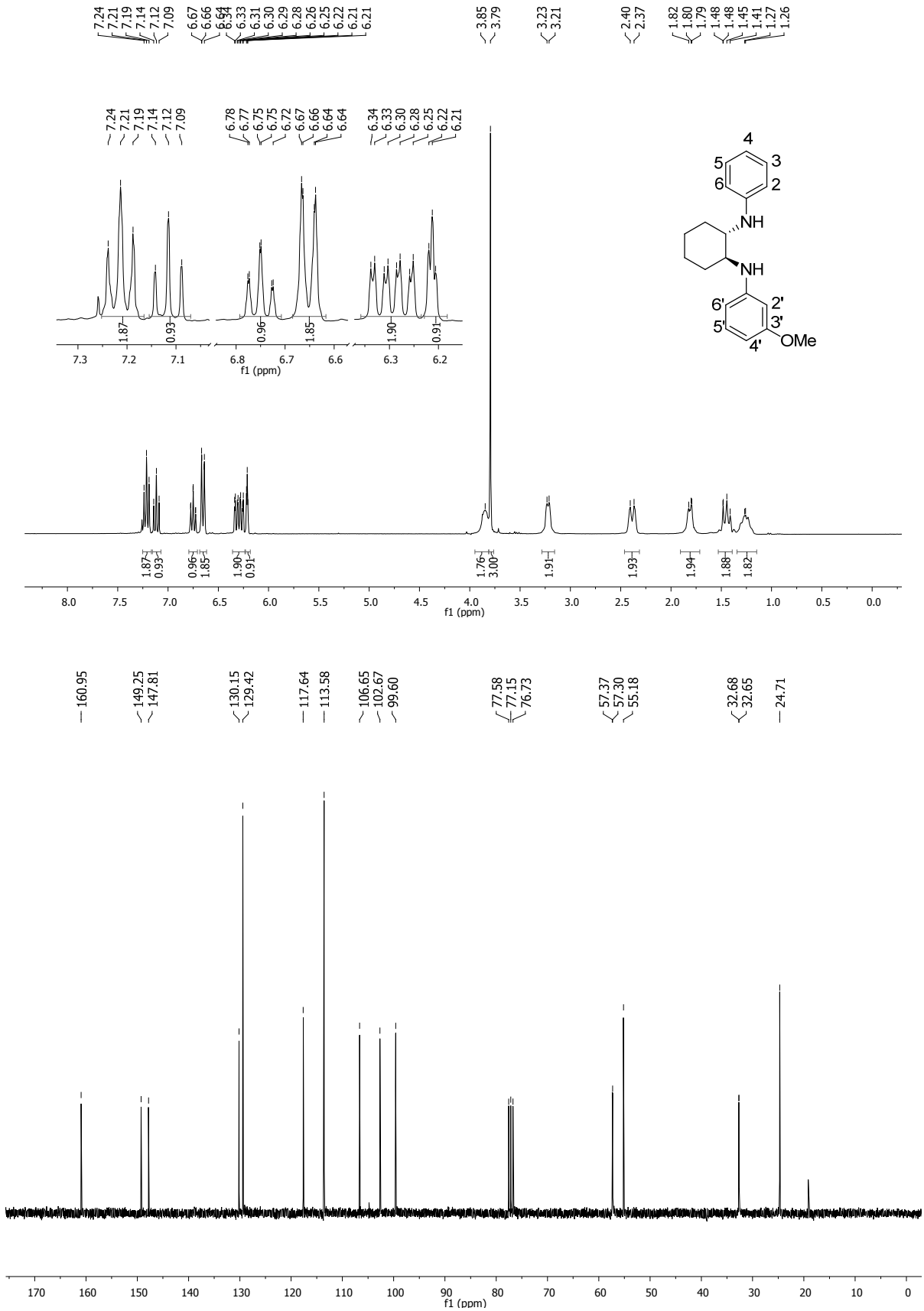


(1*S*,2*S*)-*N*-Phenyl-*N'*-*m*-tolylcyclohexane-1,2-diamine (3l)

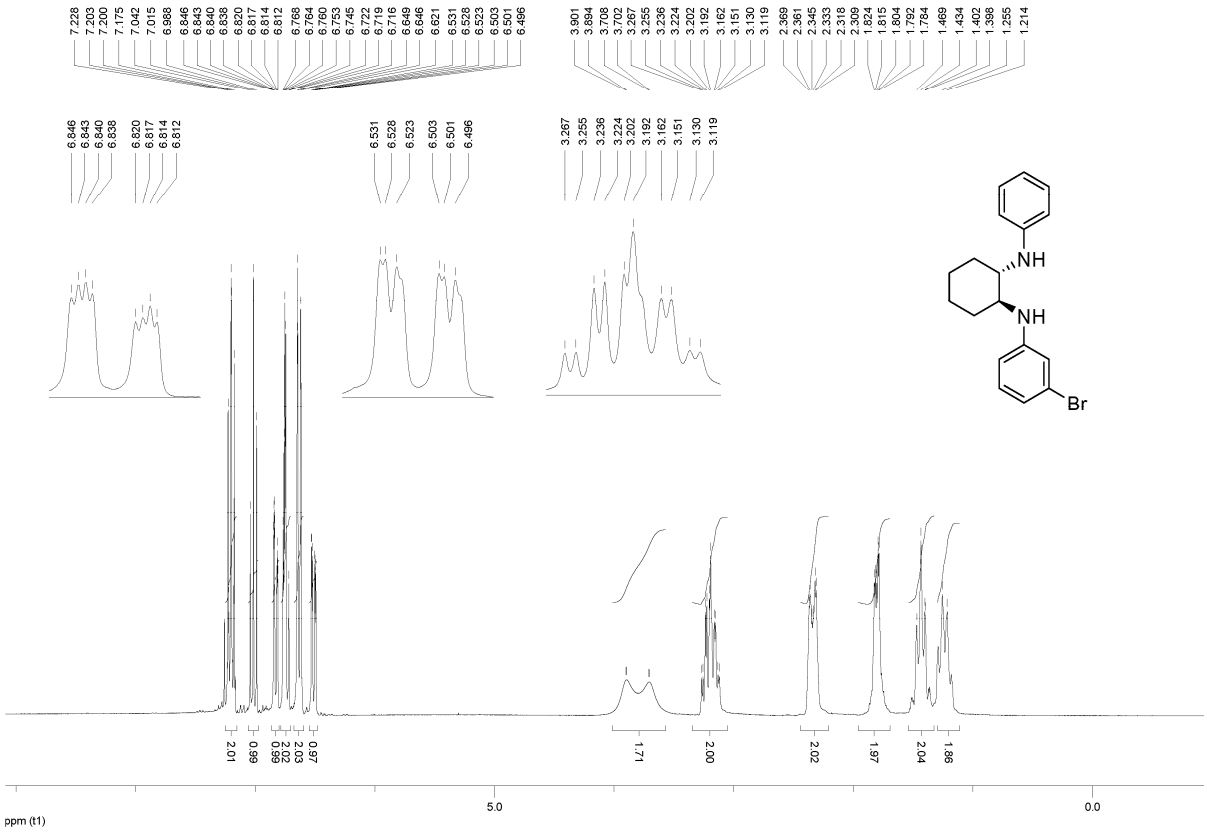




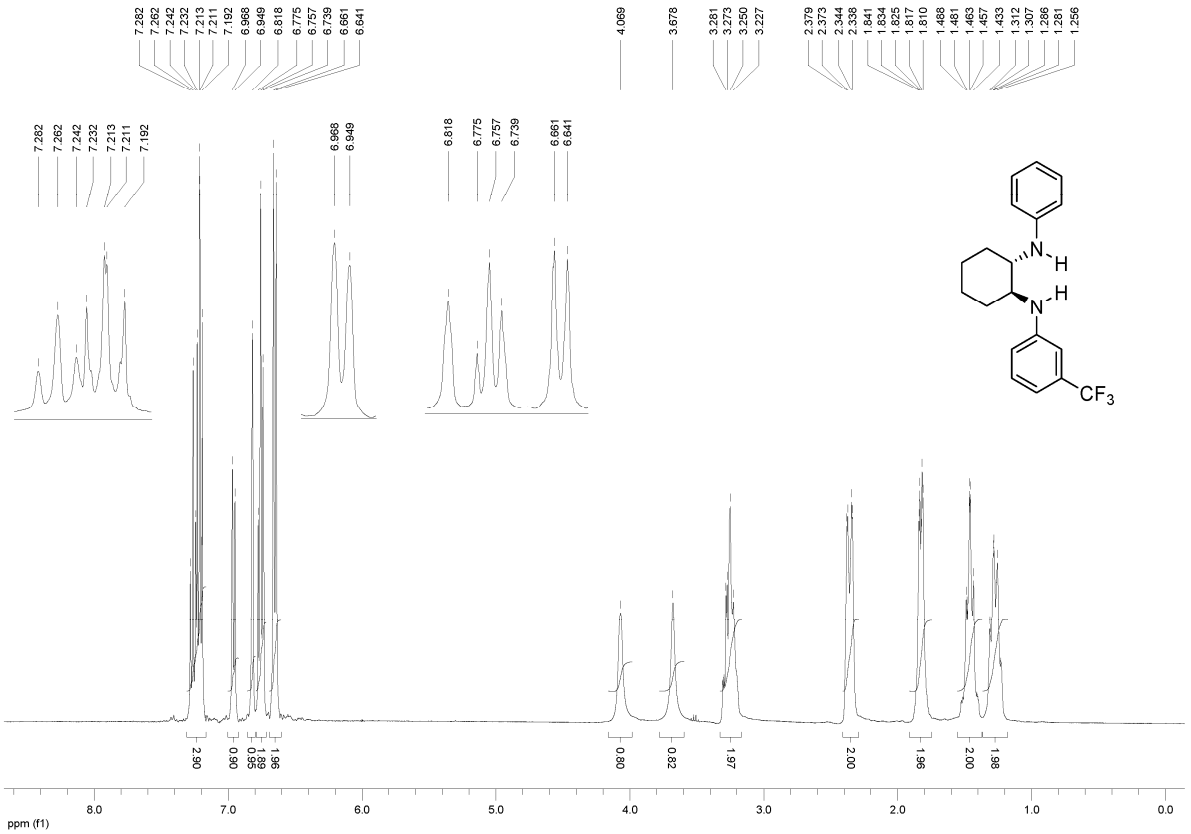
(1*S*,2*S*)-*N*-(3-Methoxyphenyl)-*N'*-phenylcyclohexane-1,2-diamine (3m)

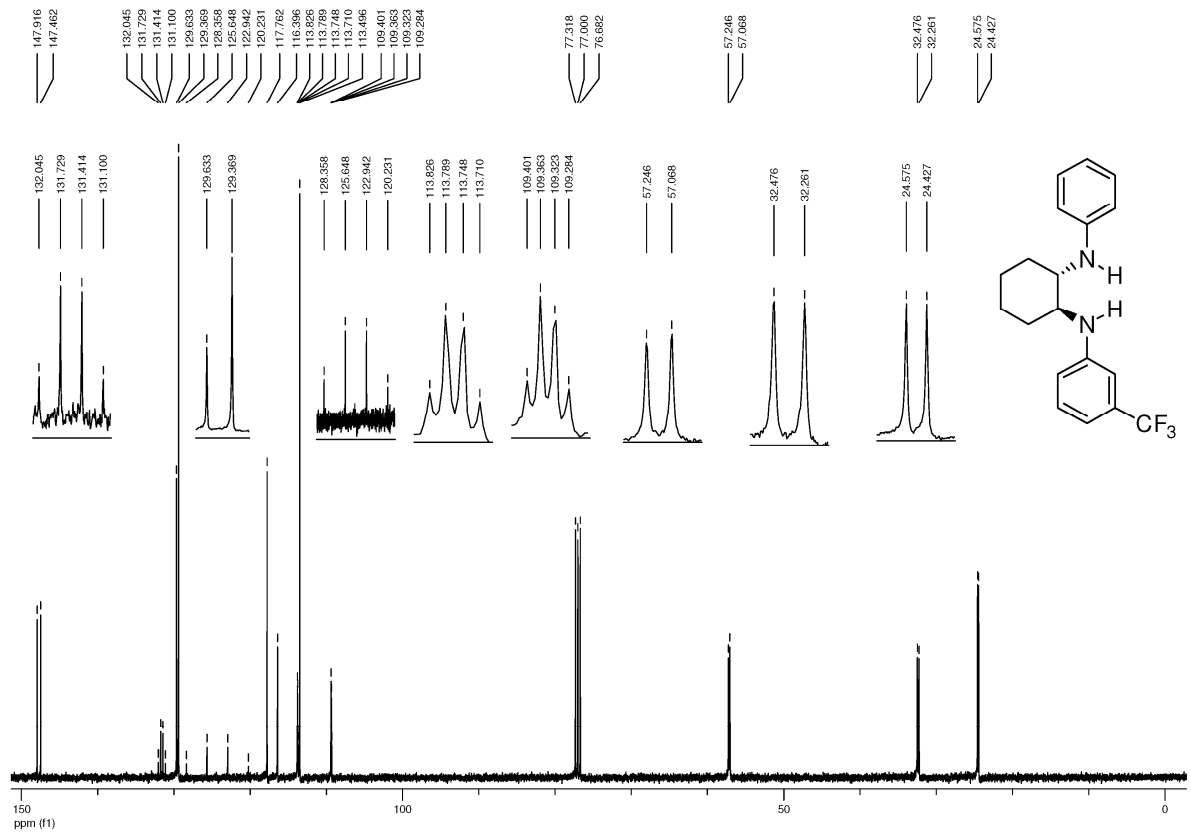


(1*S*,2*S*)-*N*-(3-Bromophenyl)-*N'*-phenylcyclohexane-1,2-diamine (3n)

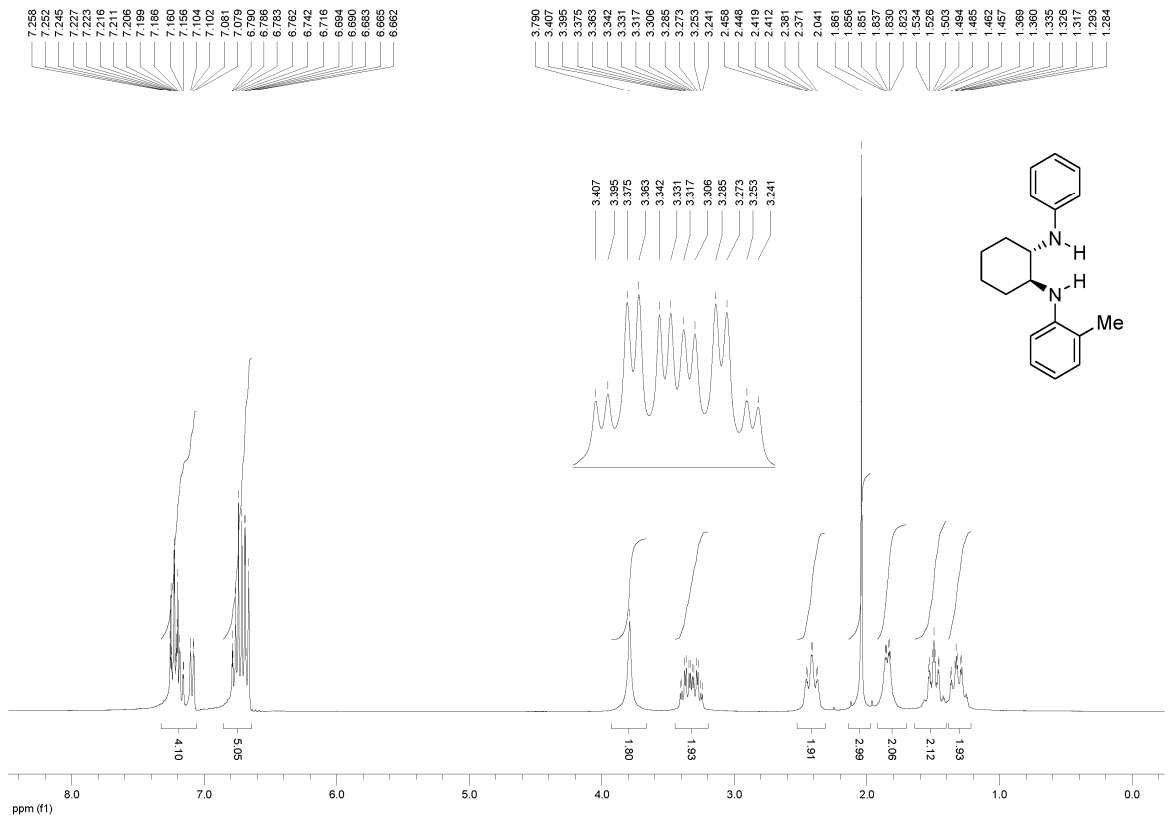


(1*S*,2*S*)-*N*-Phenyl-*N'*-(3-trifluoromethylphenyl)cyclohexane-1,2-diamine (3o)

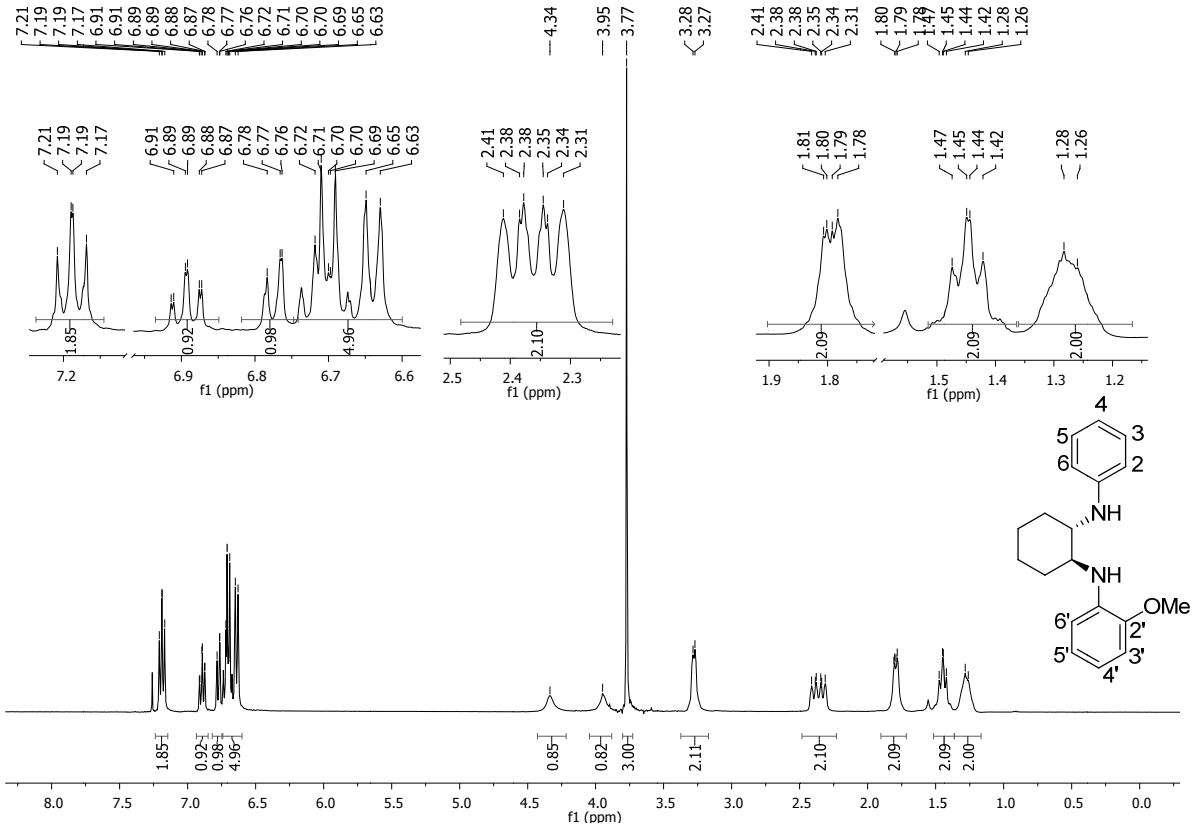




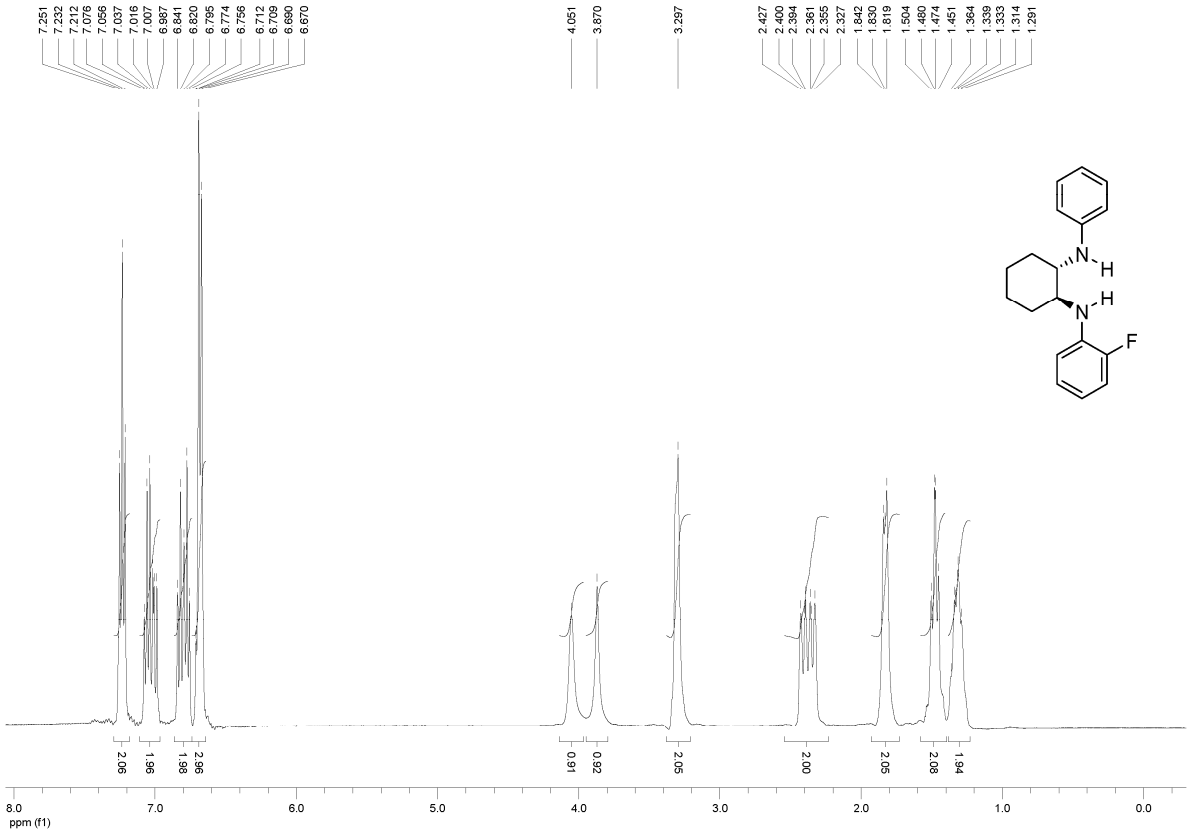
(1*S*,2*S*)-*N*-Phenyl-*N'*-*o*-tolylcyclohexane-1,2-diamine (3p)

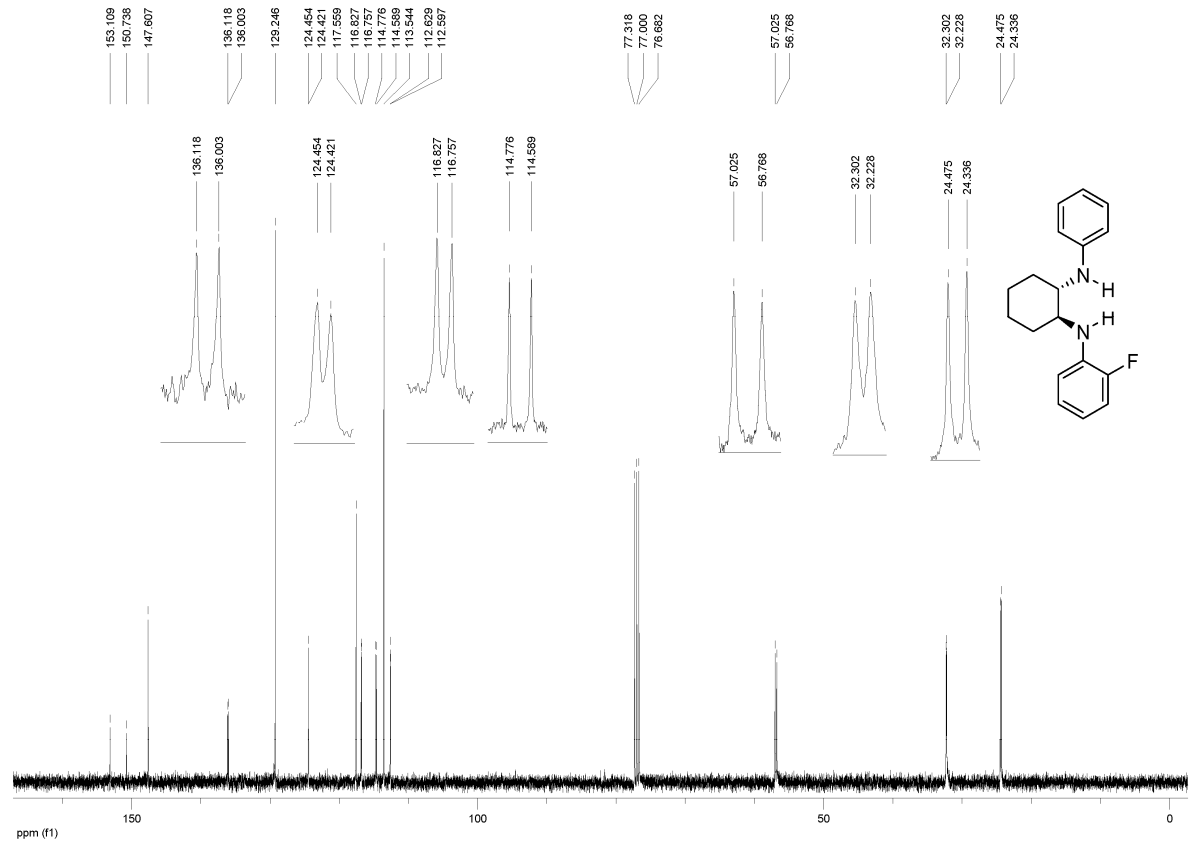


(1*S*,2*S*)-*N*-(2-Methoxyphenyl)-*N'*-phenylcyclohexane-1,2-diamine (3q)

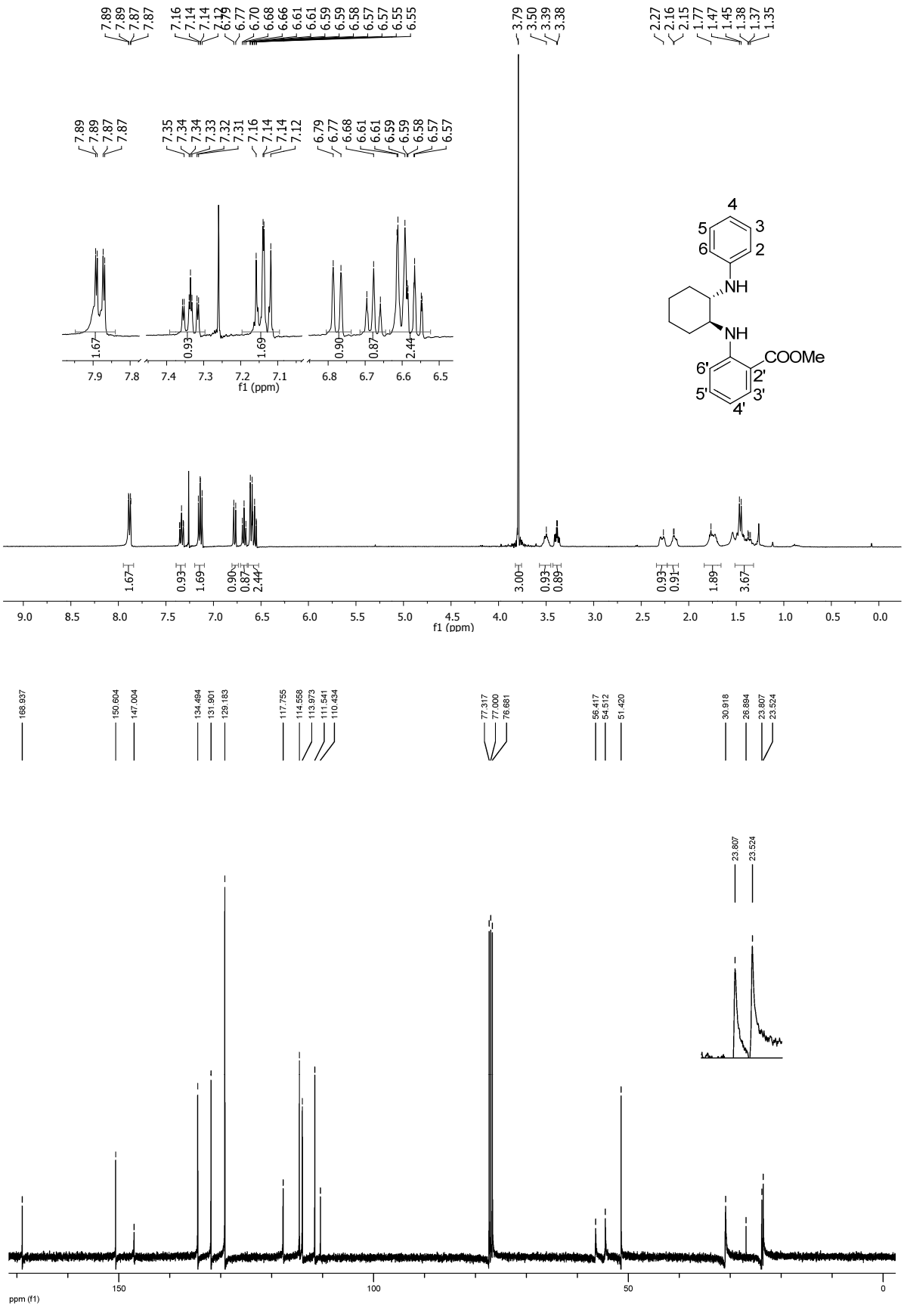


(1*S*,2*S*)-*N*-(2-Flurophenyl)-*N*'-phenylcyclohexane-1,2-diamine (3r)

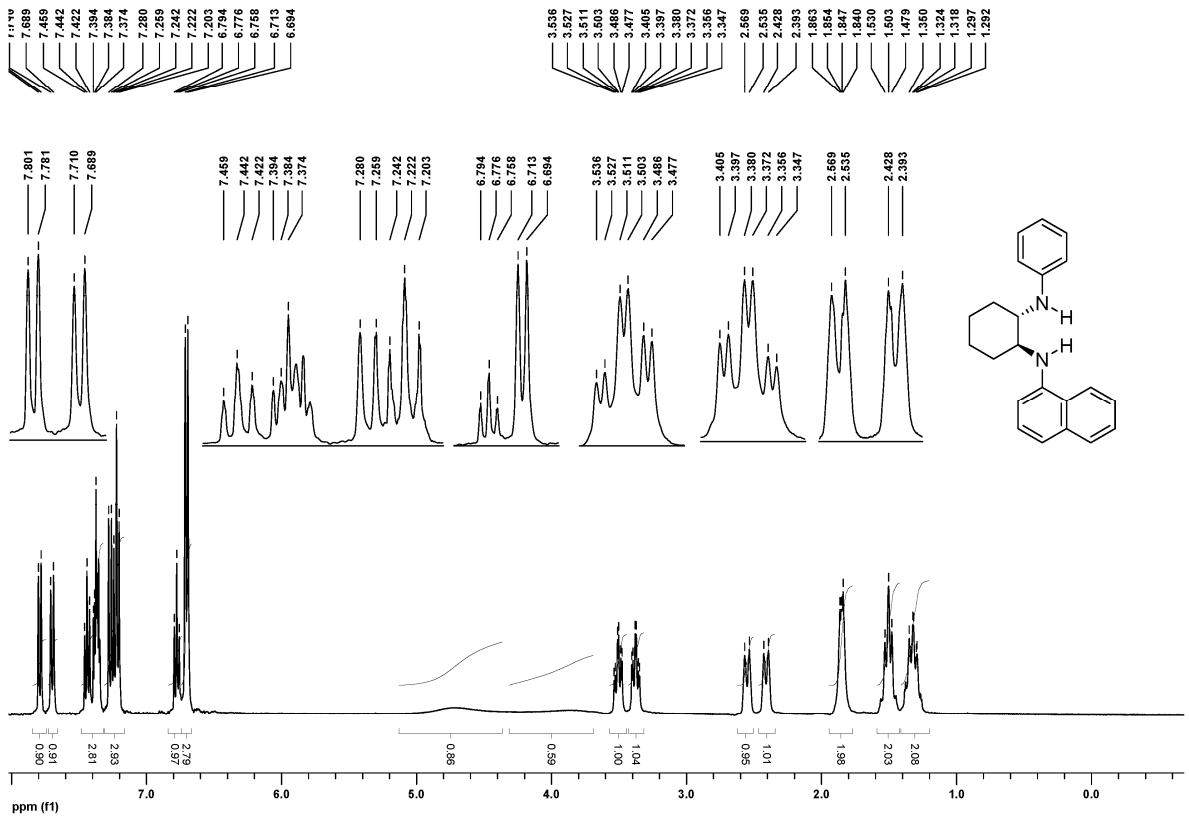


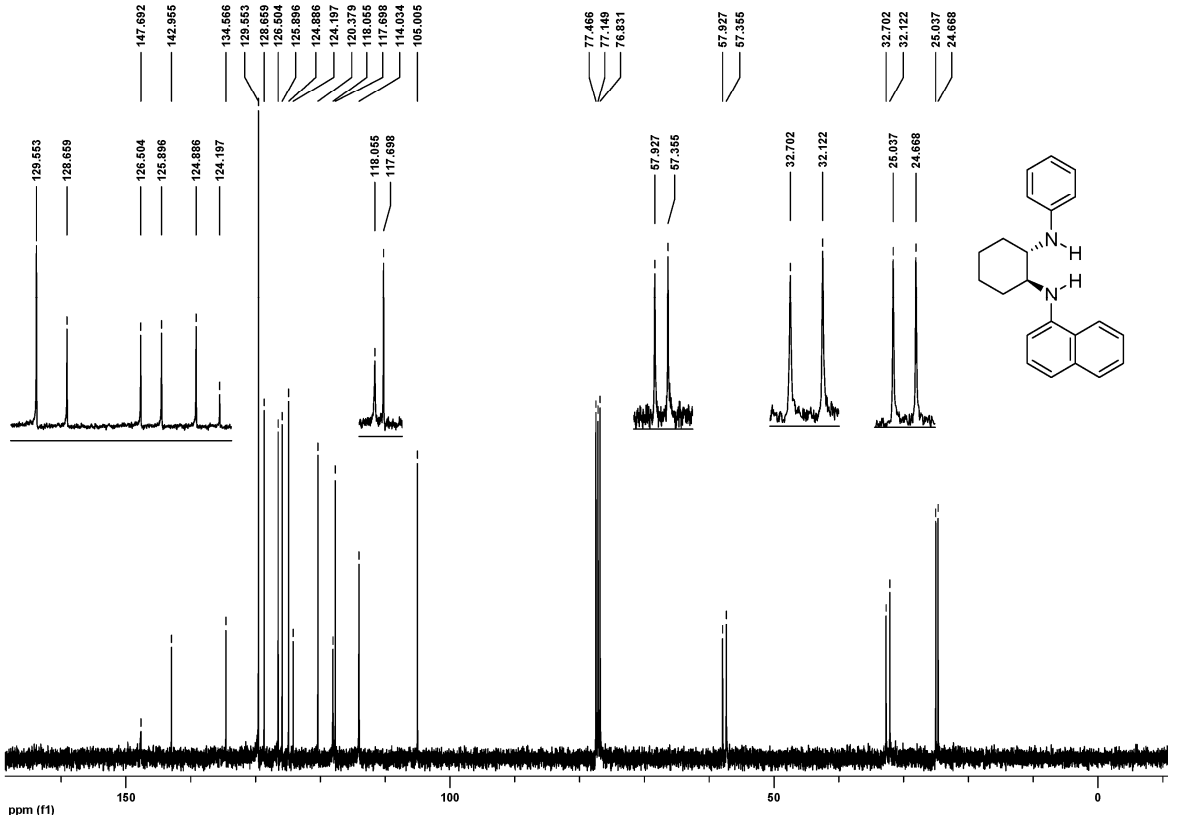


(1*S*,2*S*)-*N*-(2-Carbomethoxyphenyl)-*N'*-phenylcyclohexane-1,2-diamine (3s)

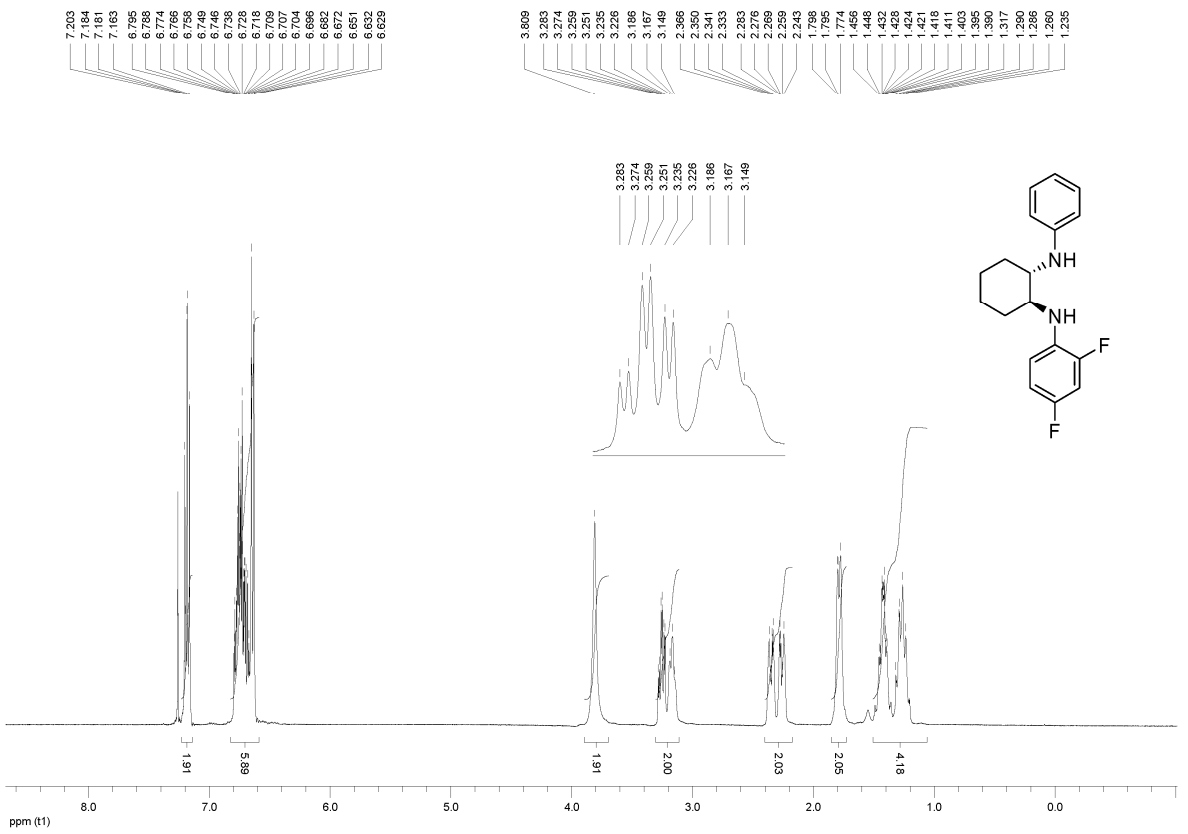


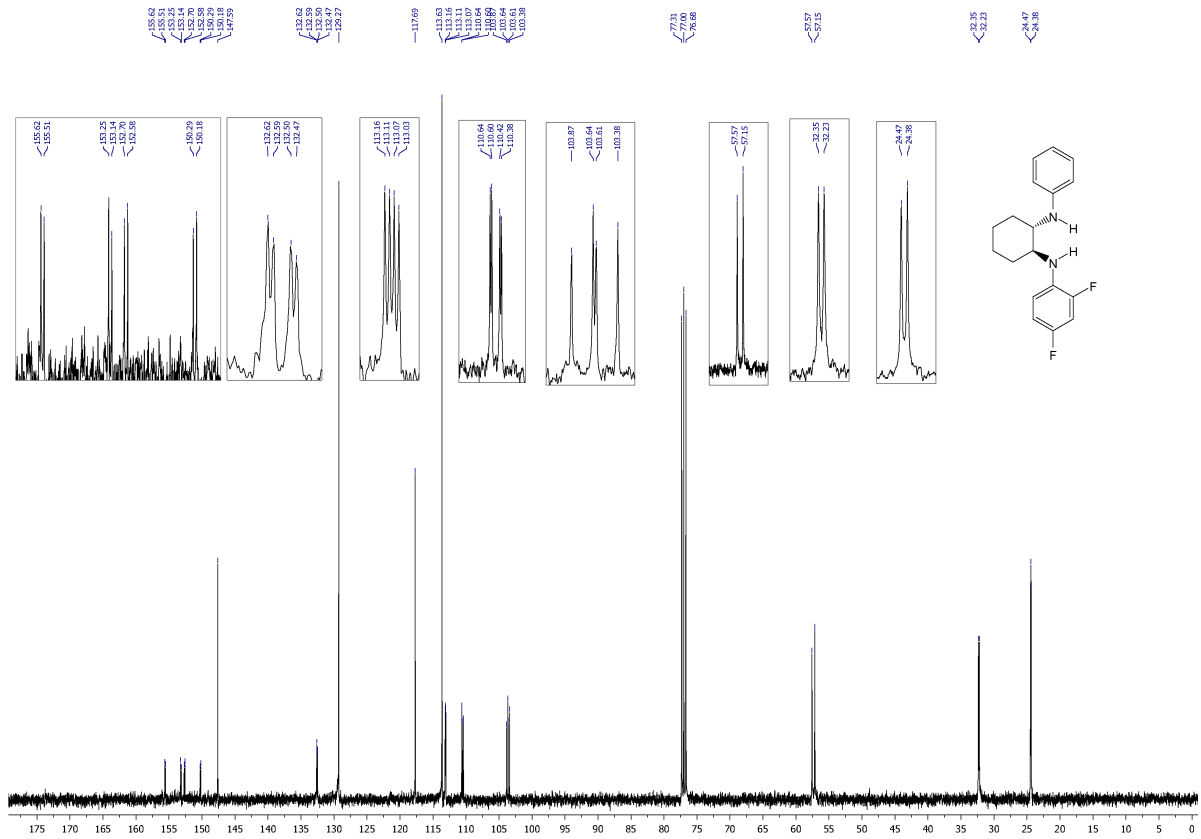
(1*S*,2*S*)-*N*-(1-Naphthyl)-*N*′-phenylcyclohexane-1,2-diamine (3t)



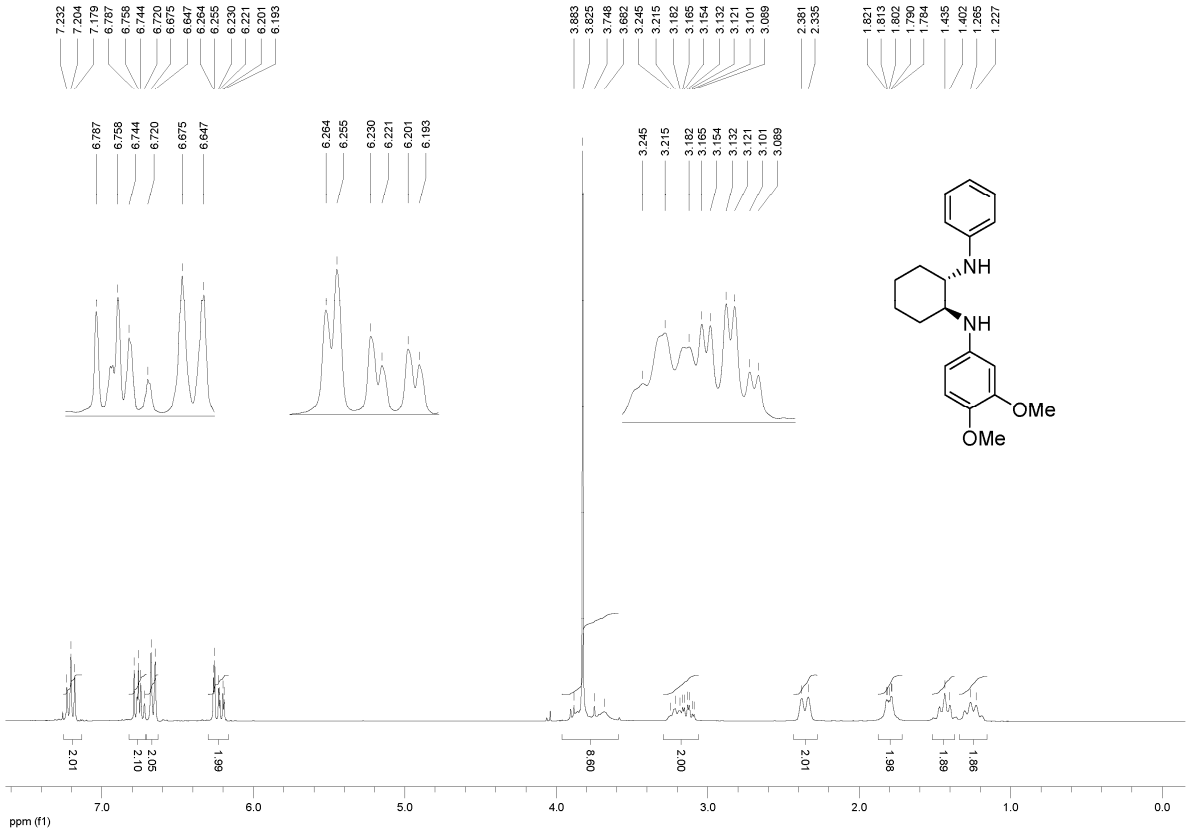


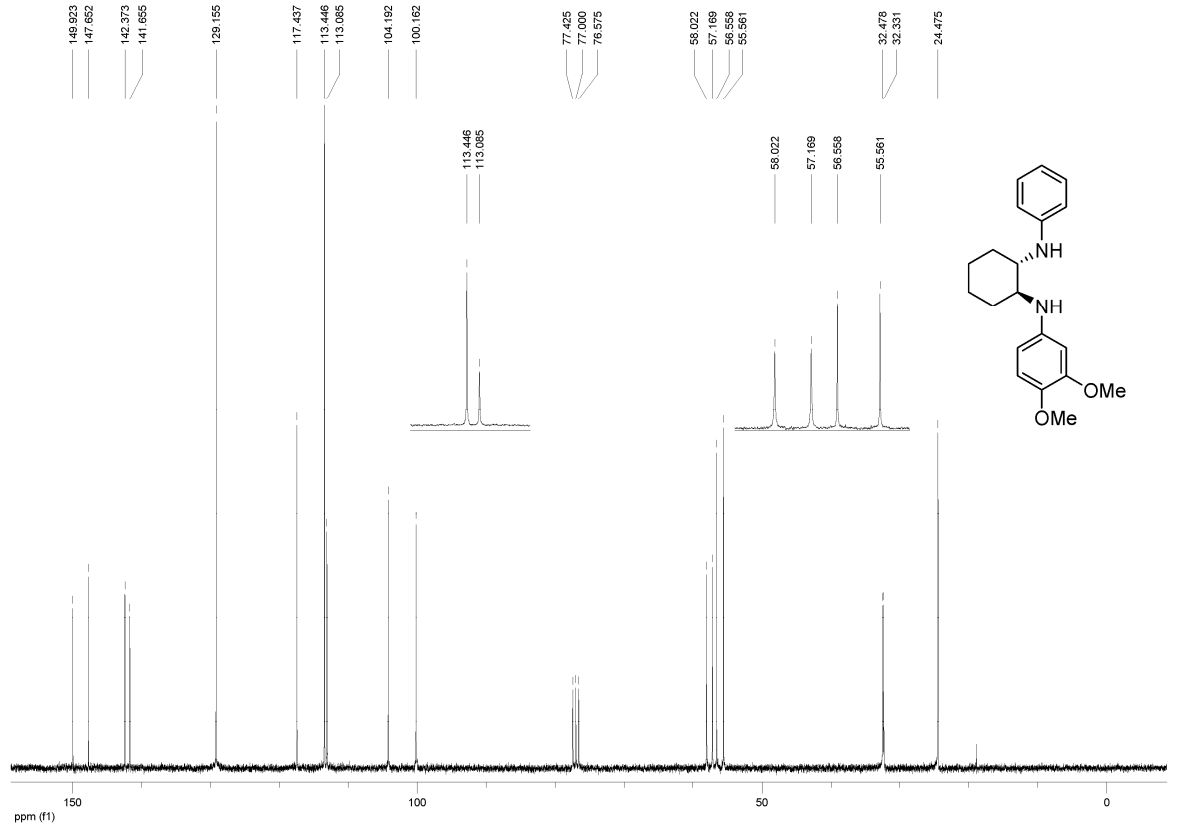
(1*S*,2*S*)-*N*-(2,4-Diflurophenyl)-*N'*-phenylcyclohexane-1,2-diamine (3u)



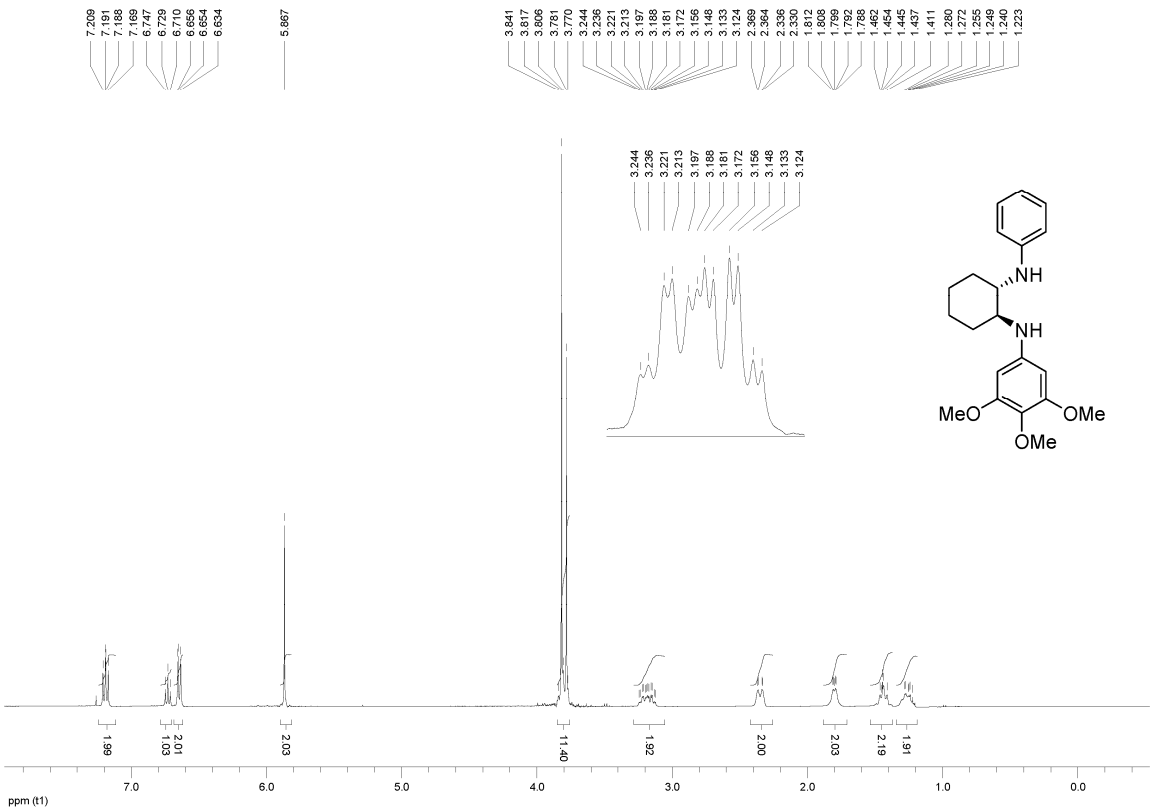


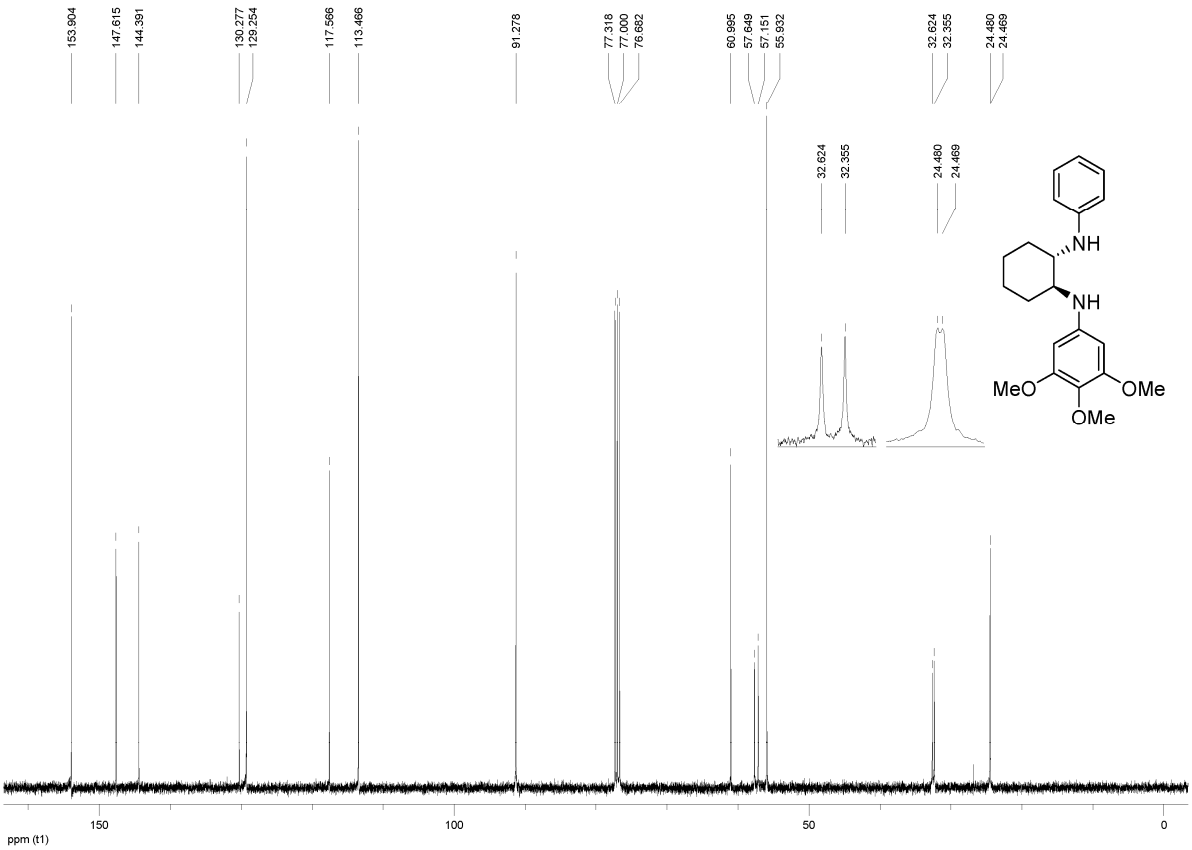
(1*S*,2*S*)-*N*-(3,4-Dimethoxyphenyl)-*N'*-phenylcyclohexane-1,2-diamine (3v)



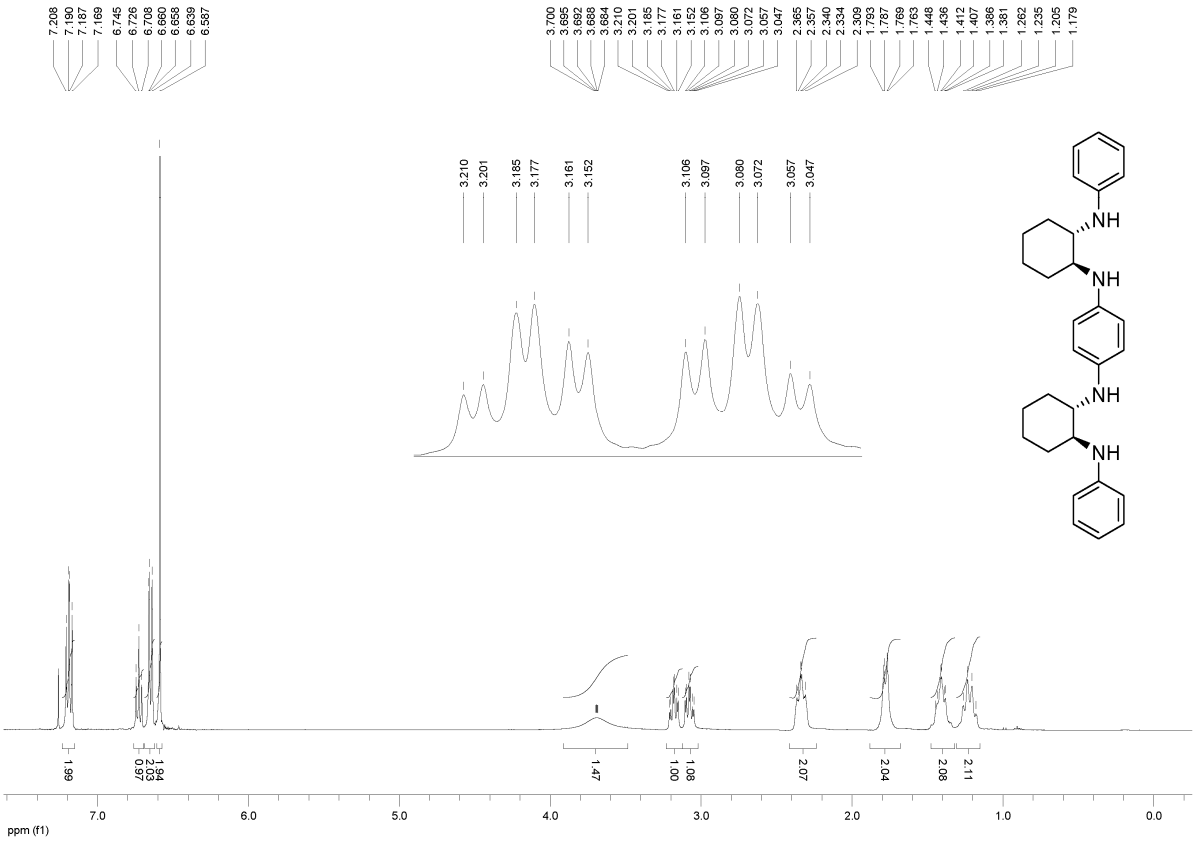


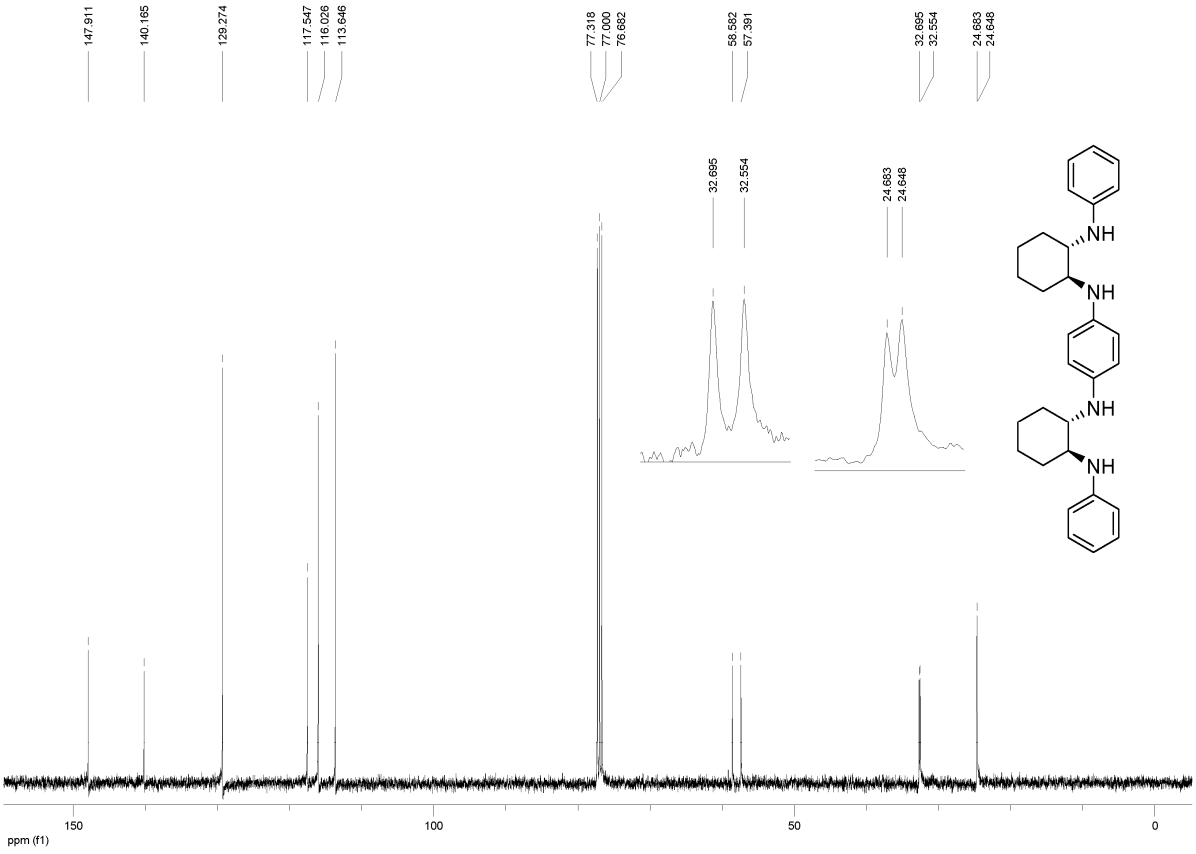
(1*S*,2*S*)-*N*-Phenyl-*N'*-(3,4,5-trimethoxyphenyl)cyclohexane-1,2-diamine (3w)



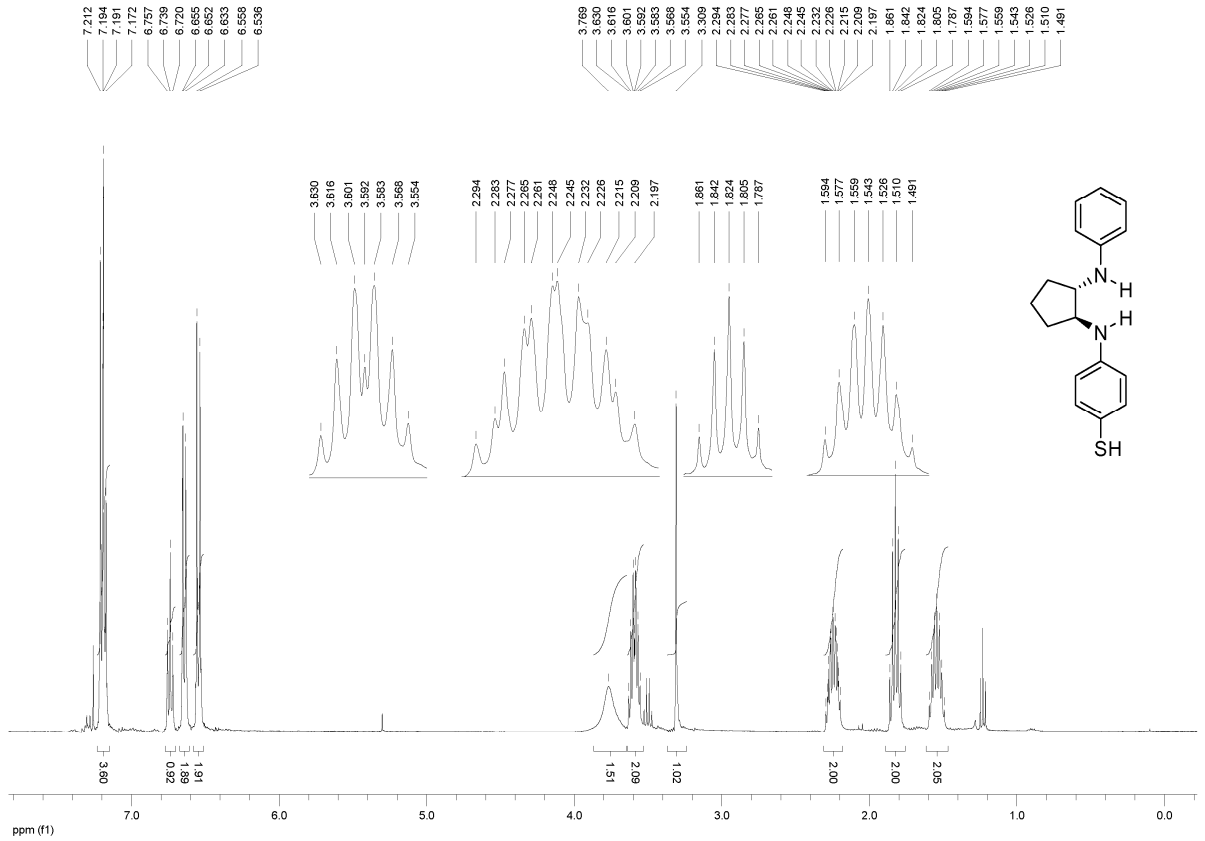


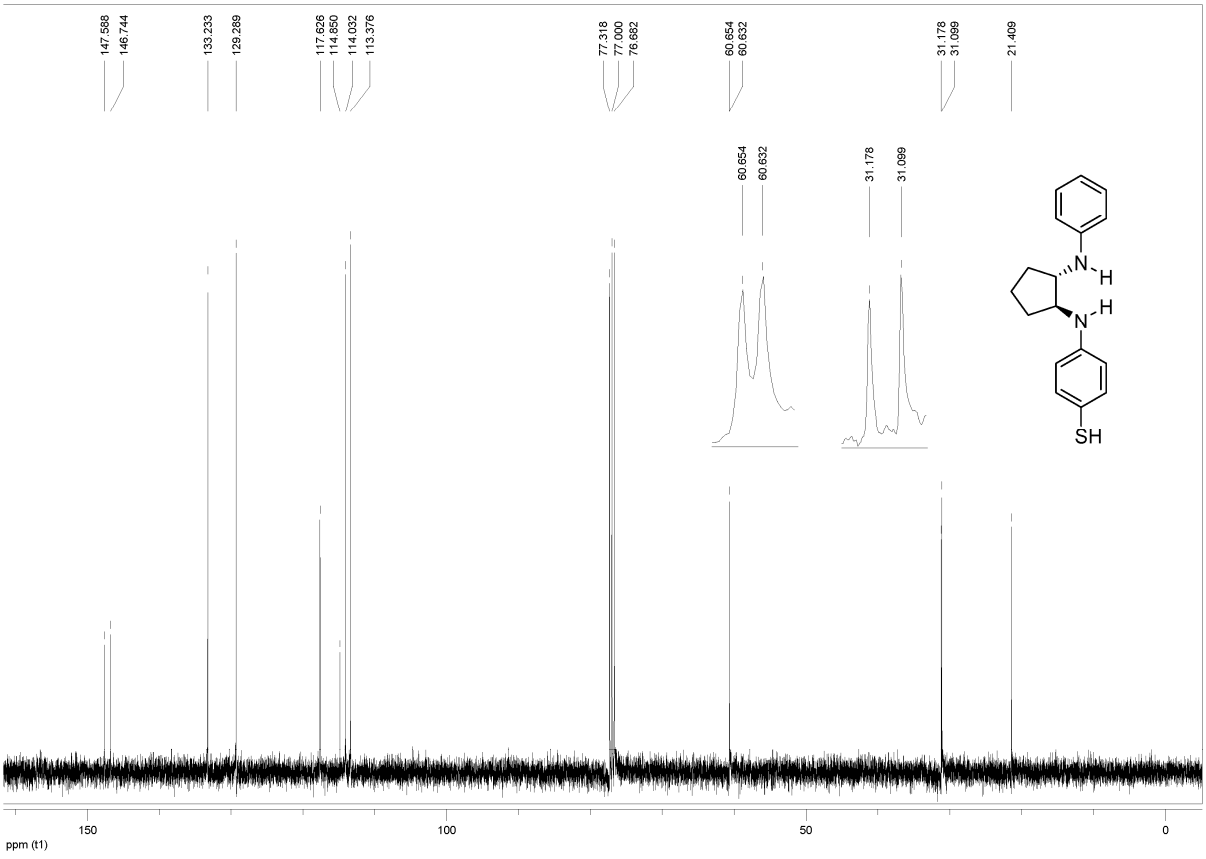
(1*S*,1'*S*,2*S*,2'*S*)-N^1,N^1'-(1,4-Phenylene)bis(N^2-phenylcyclohexane-1,2-diamine) (3x)



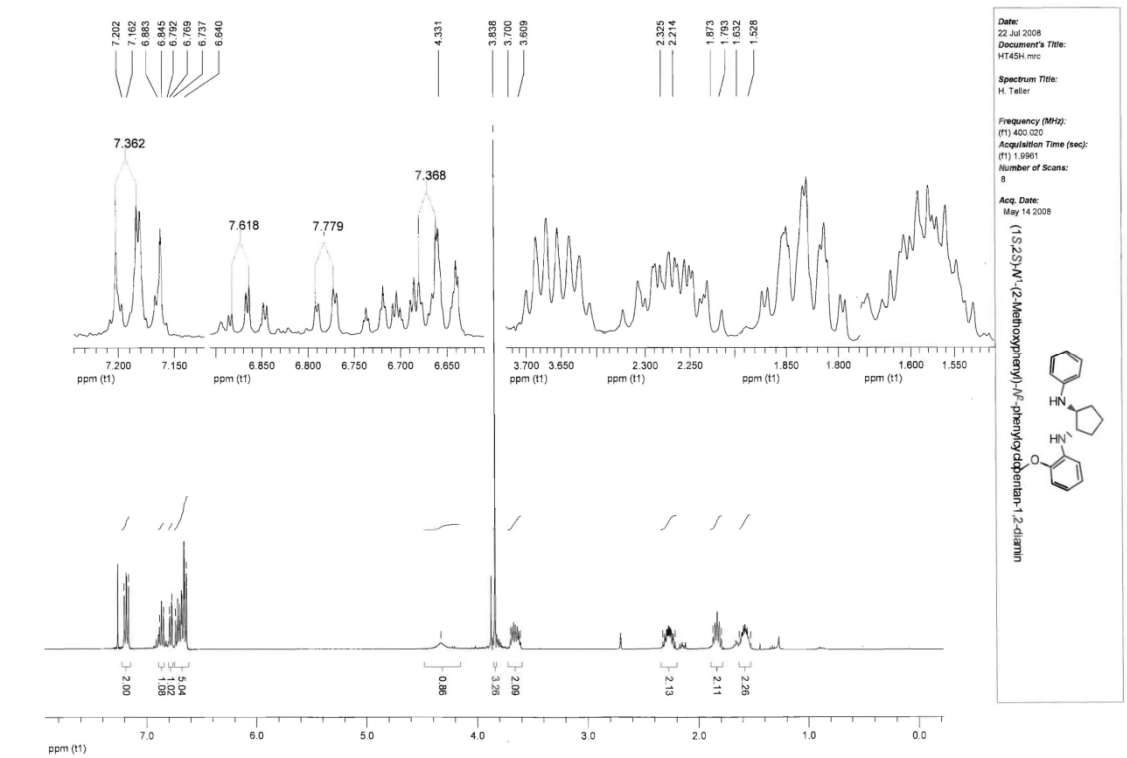


4-((1*S*,2*S*)-2-(Phenylamino)cyclopentylamino)benzenethiol (4e)

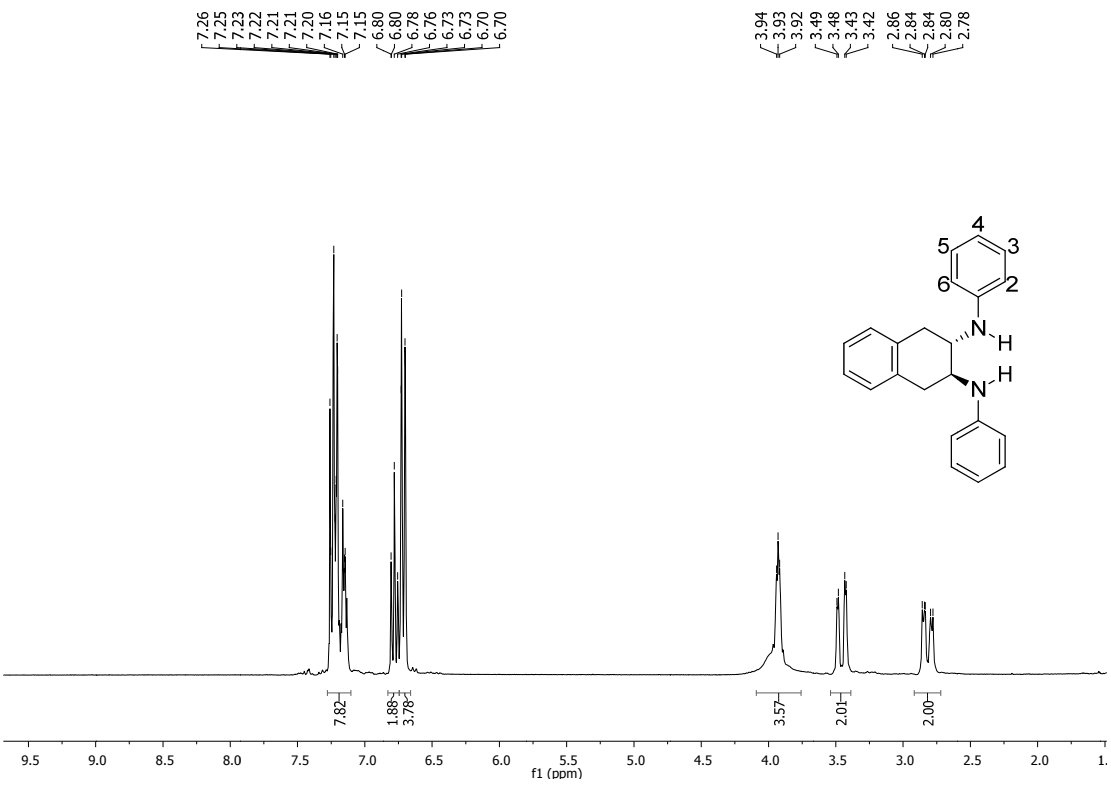




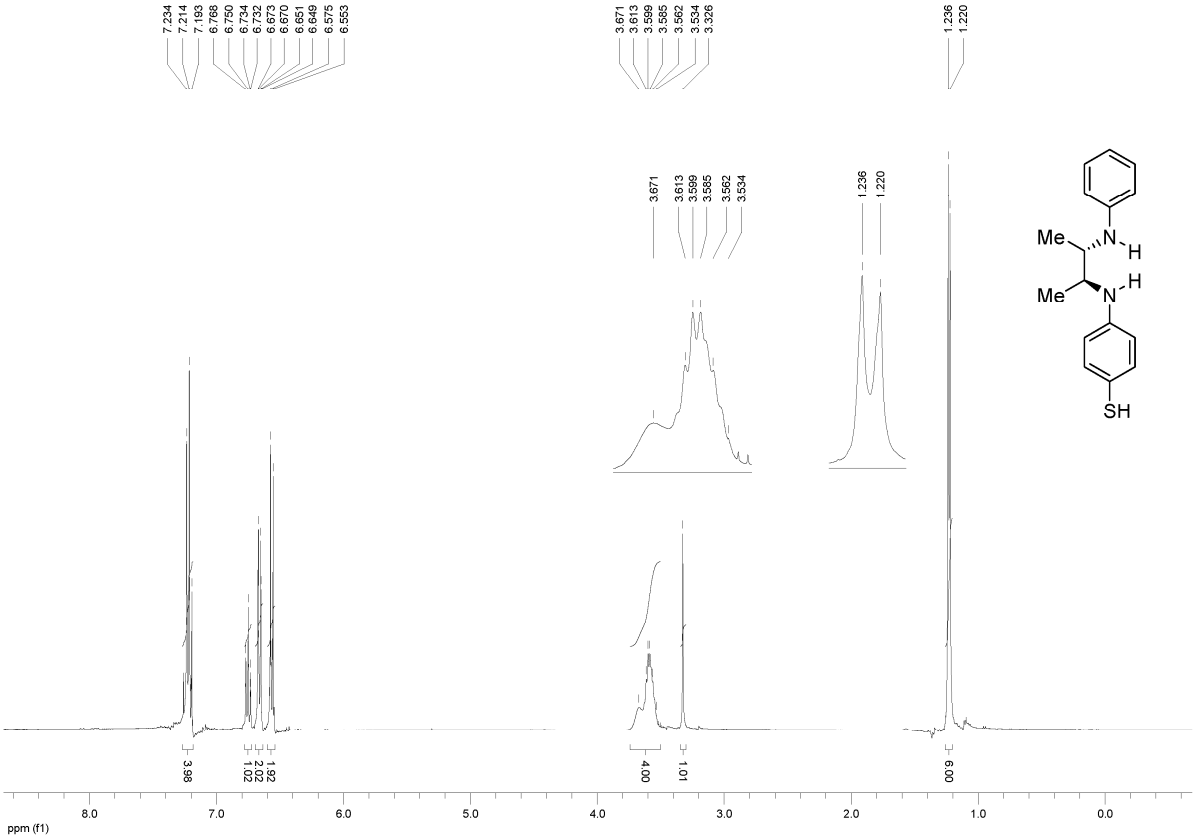
(1*S*,2*S*)-*N*-(2-Methoxyphenyl)-*N*'-phenylcyclopentan-1,2-diamine (4f)

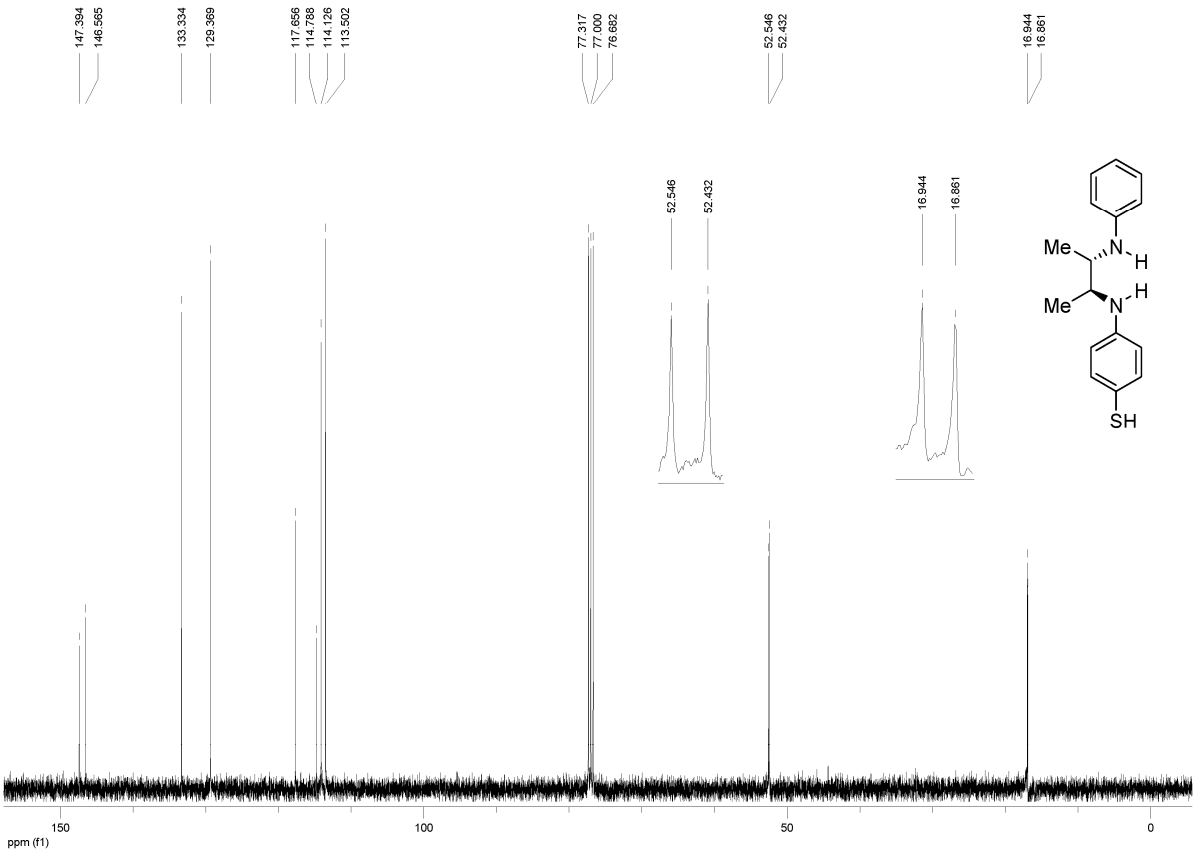


(2*S*,3*S*)-N^2,N^3-Diphenyl-1,2,3,4-tetrahydronaphthalen-2,3-diamine (6a)

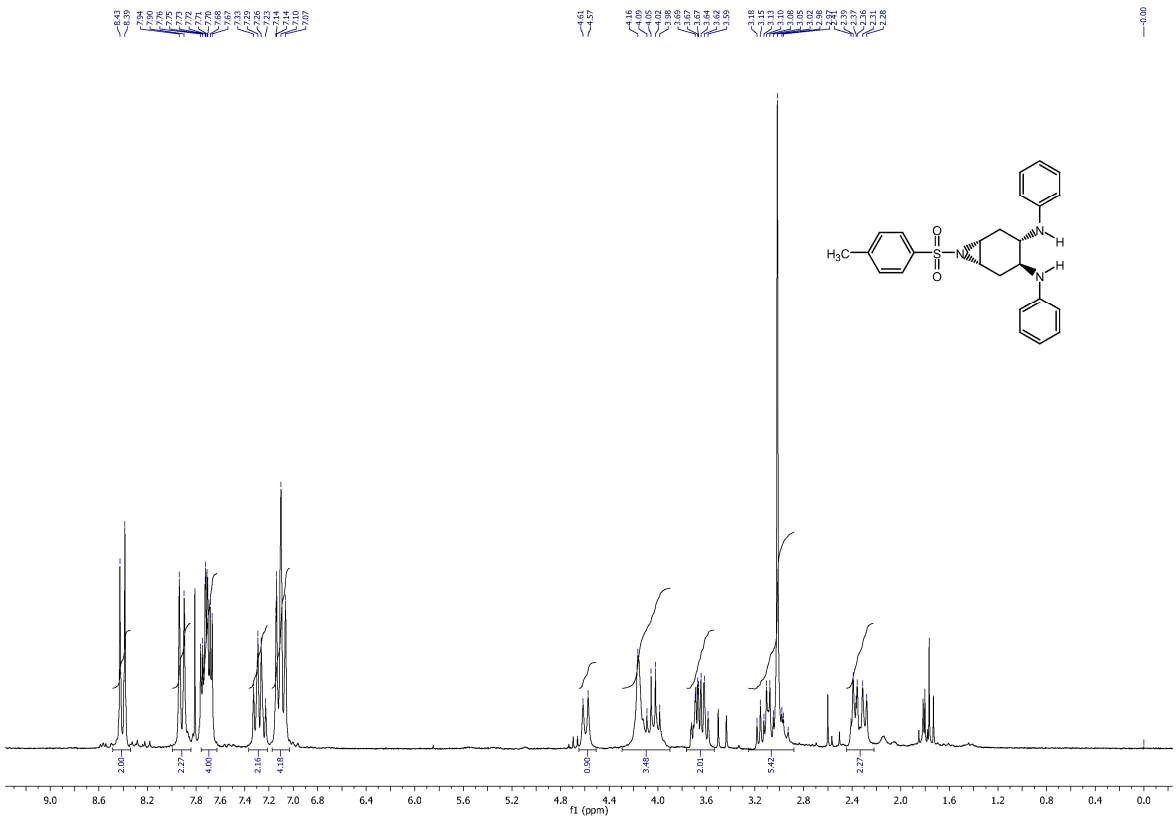


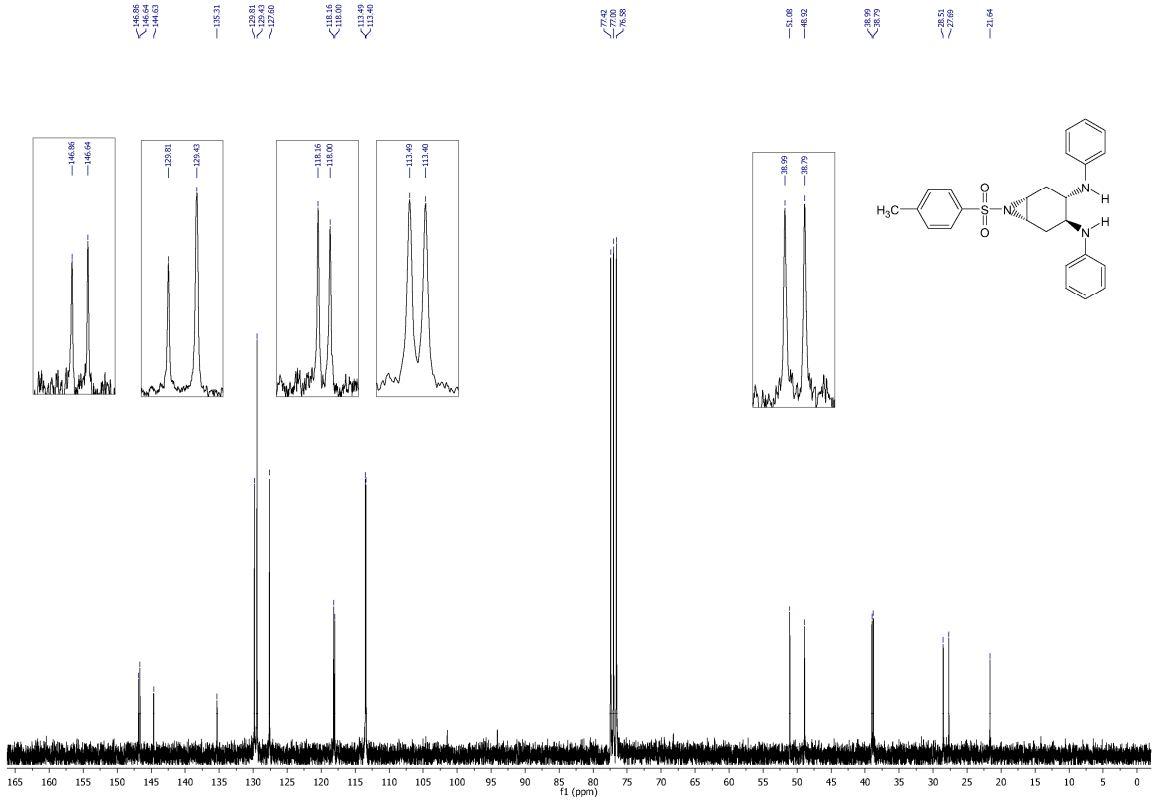
4-[(2S,3S)-3-(phenylamino)butan-2-ylamino]benzenethiol (7b)



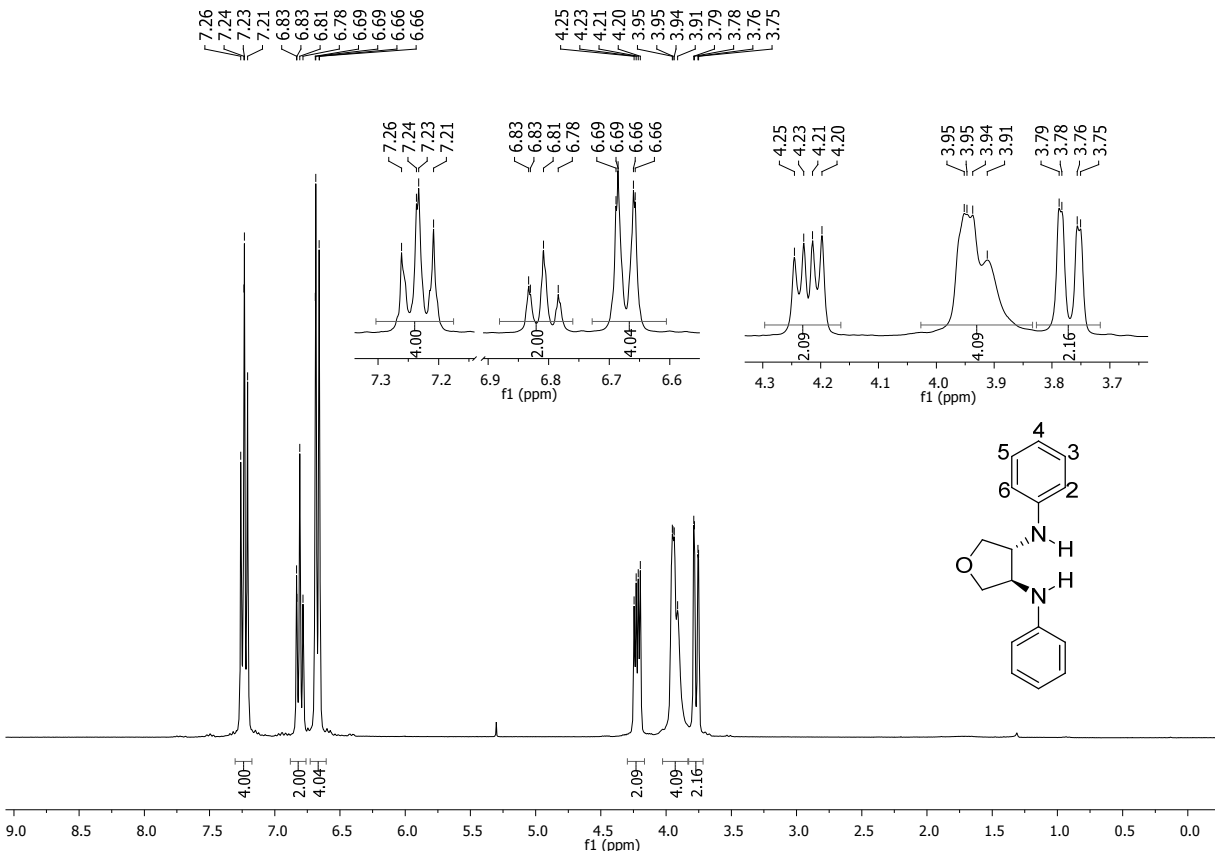


(1*R*,3*S*,4*S*,6*S*)-*N*,*N*'-Diphenyl-7-tosyl-7-azabicyclo[4.1.0]-heptane-3,4-diamine (8a)

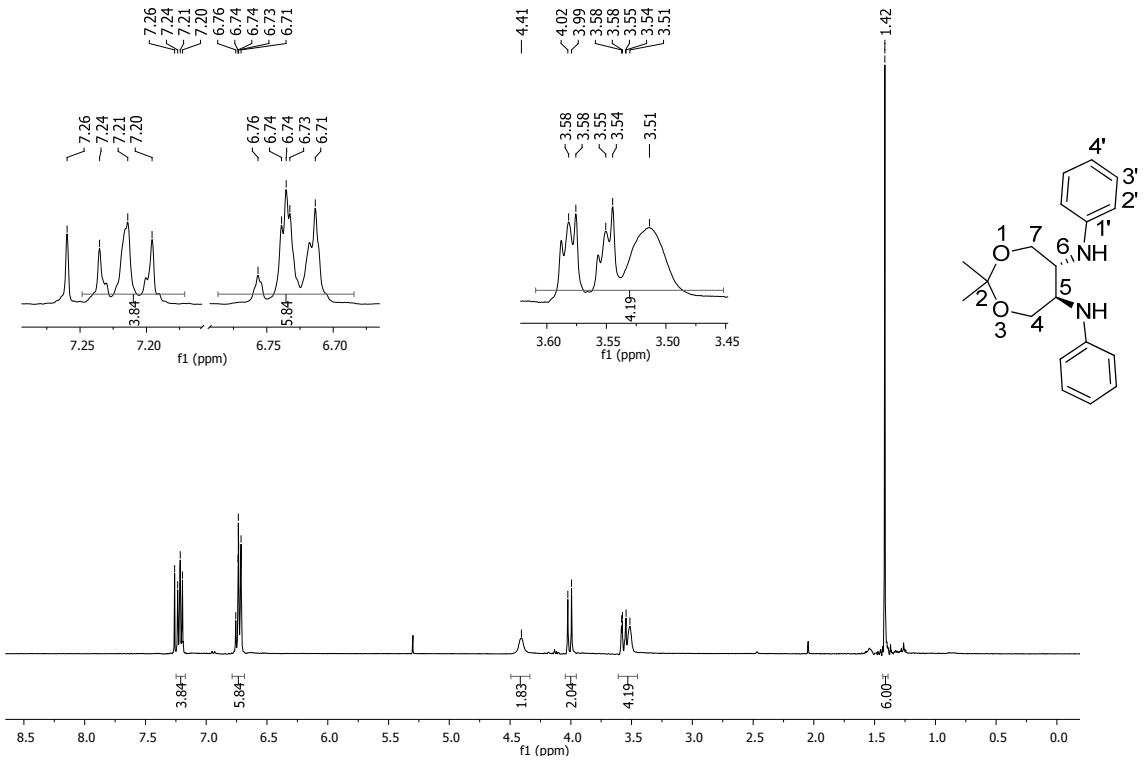




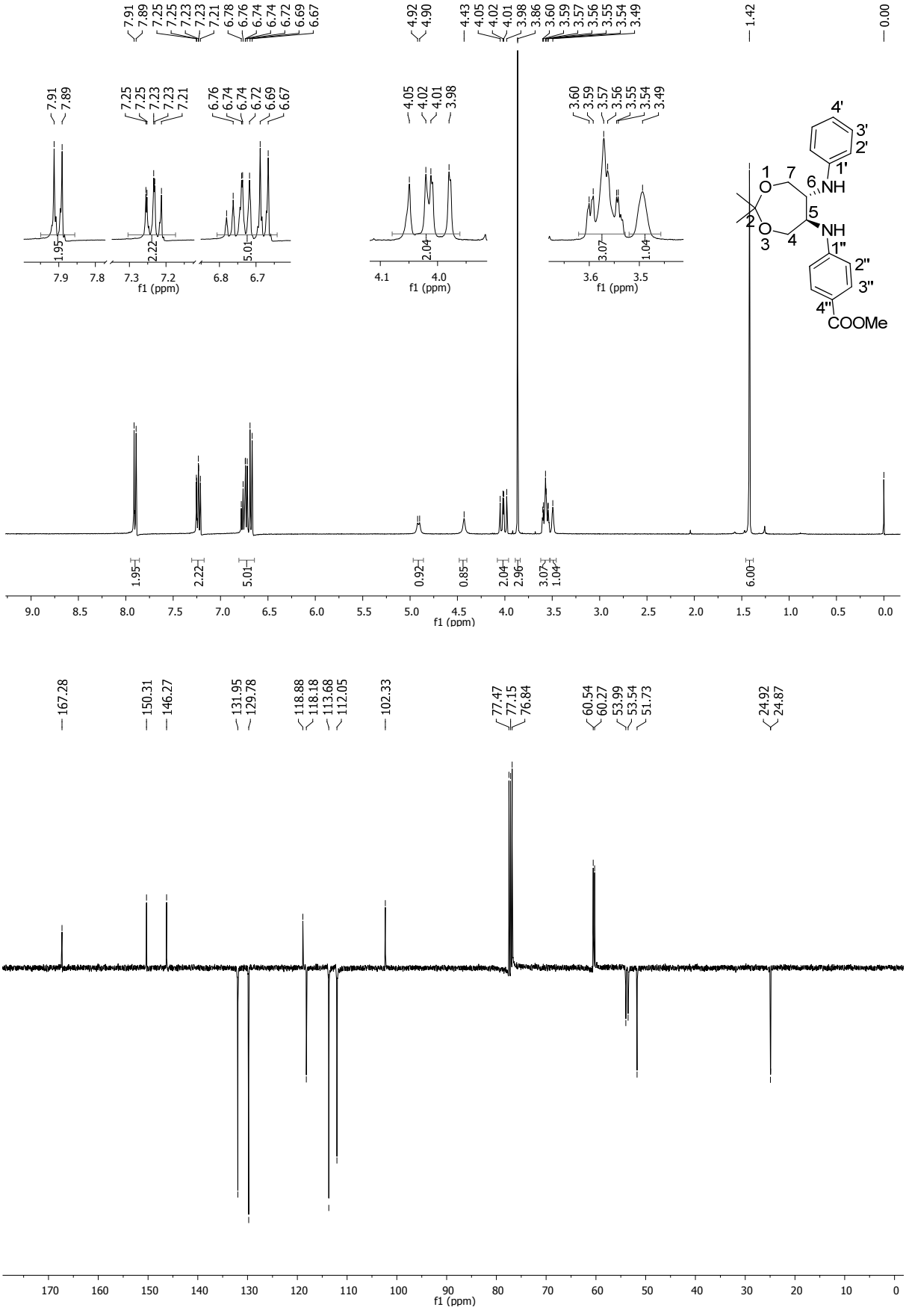
(3*S*,4*S*)-*N*,*N*'-Diphenyltetrahydrofuran-3,4-diamine (9a)



(5*S*,6*S*)-2,2-Dimethyl-*N*,*N*'-diphenyl-1,3-dioxepan-5,6-diamine (10a)



(5*S*,6*S*)-Methyl-4-((-2,2-dimethyl-6-(phenylamino)-1,3-dioxepan-5-yl)amino)benzoate (10b)



(5*S*,6*S*)-4-(2,2-Dimethyl-6-(phenylamino)-1,3-dioxepan-5-yl)a**mino)benzonitrile (10c)**