

Supporting Information

(S)- or (R)- α -(phenyl)ethylamine-derived NH-type ligands: Design, synthesis and applications for chemical resolution of α -amino acids

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X-Ray data of compound 14a

Physical and crystallographic data			Refinement conditions	
Formula	C ₃₄ H ₃₄ Cl N ₃ Ni O ₄		Diffractometer	Agilent SuperNova Cu
M _r (g·mol ⁻¹)	642.8		Detector	CCD (Atlas)
Crystal system	Tetragonal		Temperature (K)	100(1)°
Space group	P4 ₁ /n		λ (CuKα) (Å)	1.54184
a (Å)	9.76204(4)		Monochromator	Óptica multicapa
b (Å)	9.76204(4)		Collimator (mm)	0.2
c (Å)	31.9566(2)		Scan mode	Rotation ω
α (°)	90		Scan width (°)	1.0
β (°)	90		Time (s) (Total, h)	2;8 (4)
γ (°)	90		Interval θ (°)	4.53-71.44
V (Å ³)	3045.357(19)		(hkl) minimum	(-11 -12 -39)
Z	4 (Z'=1)		(hkl) maximum	(12 11 27)
F (000)	1344		Reflections collected	24338
μ (CuKα) (mm ⁻¹)	2.077		Independent reflections (R _{int})	5213(0.024)
D _x (g·cm ⁻³)	1.402 (1)		Observed reflections [I>2σ(I)]	5195
Morphology	Cubic prism		Absorption correction	Gaussian
Color	red		Solution	OLEX2
Crystal size (mm)	0.21x0.25x0.30		Refinement	SHELXL97
			Parameters	391
			Restraints	1
			Δ/σ maximum	0.002
			Δ/σ average	0.000
			Δρ maximum (eÅ ⁻³)	0.138
			Δρ minimum (eÅ ⁻³)	-0.147
			S (GOF)	1.115
			Secondary extinction coefficient ^[b]	0
			R(F) (I>2σ _i , all data)	0.0262, 0.0263
			R _w (F ²) ^[a] (I>2σ _i , all data)	0.0698, 0.0699
Friedel coverage	76%			
Flack x	0.006(12)			
Hooft y	0.000(3)			
P2(wrong)	<10 ⁻⁹⁹			

[a] Weighting: $1/[\sigma^2(F_o^2) + (0.0390P)^2]$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$.

[b] Secondary extinction expression SHELXL: $F_c^* = kF_c[1 + 0.001F_c^2\lambda^3/\sin(2\theta)]^{-1/4}$

Molecular and crystalline structure of 14a

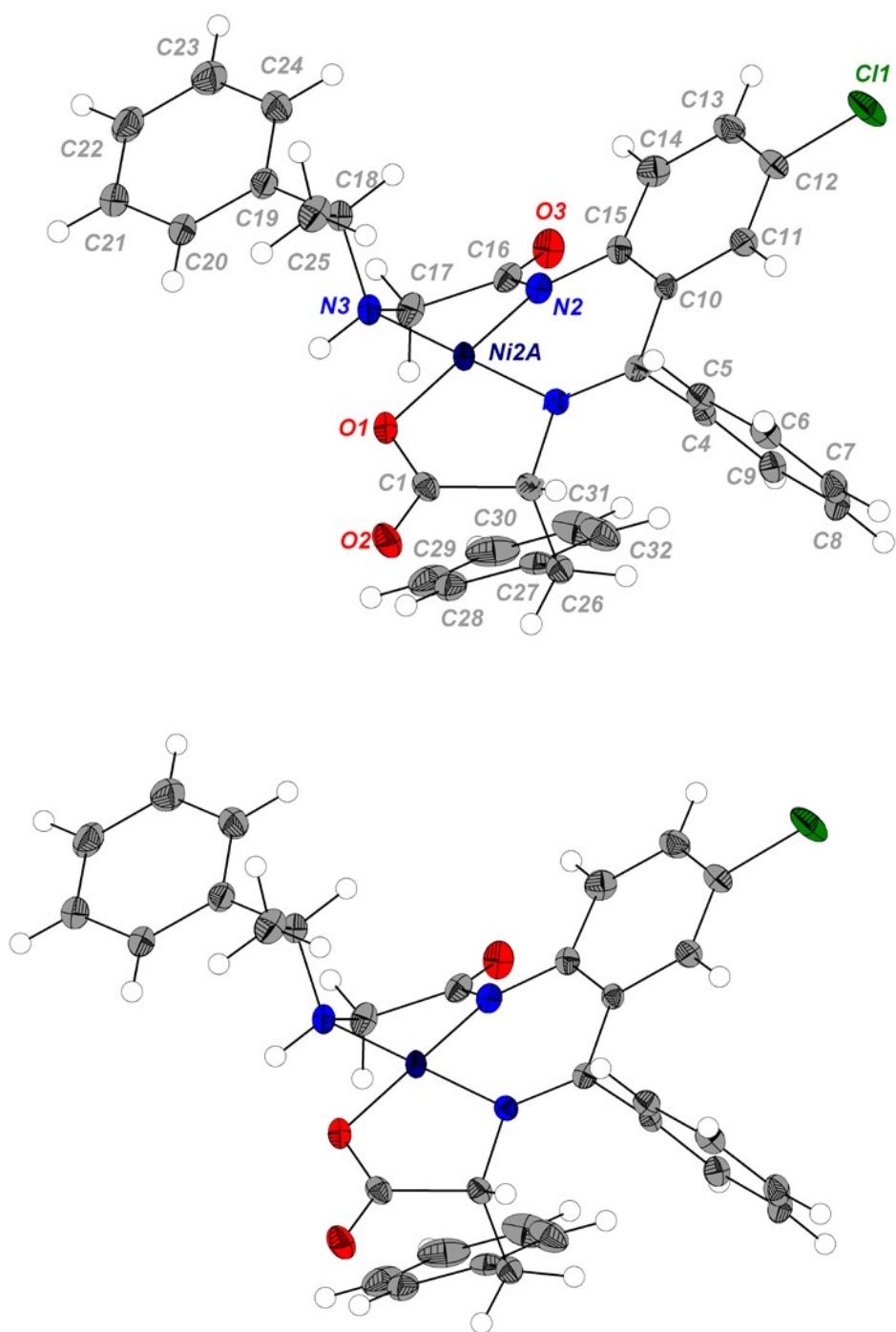


Figure S1. ORTEP diagram of **14a**. Ellipsoids displayed at 50% probability.

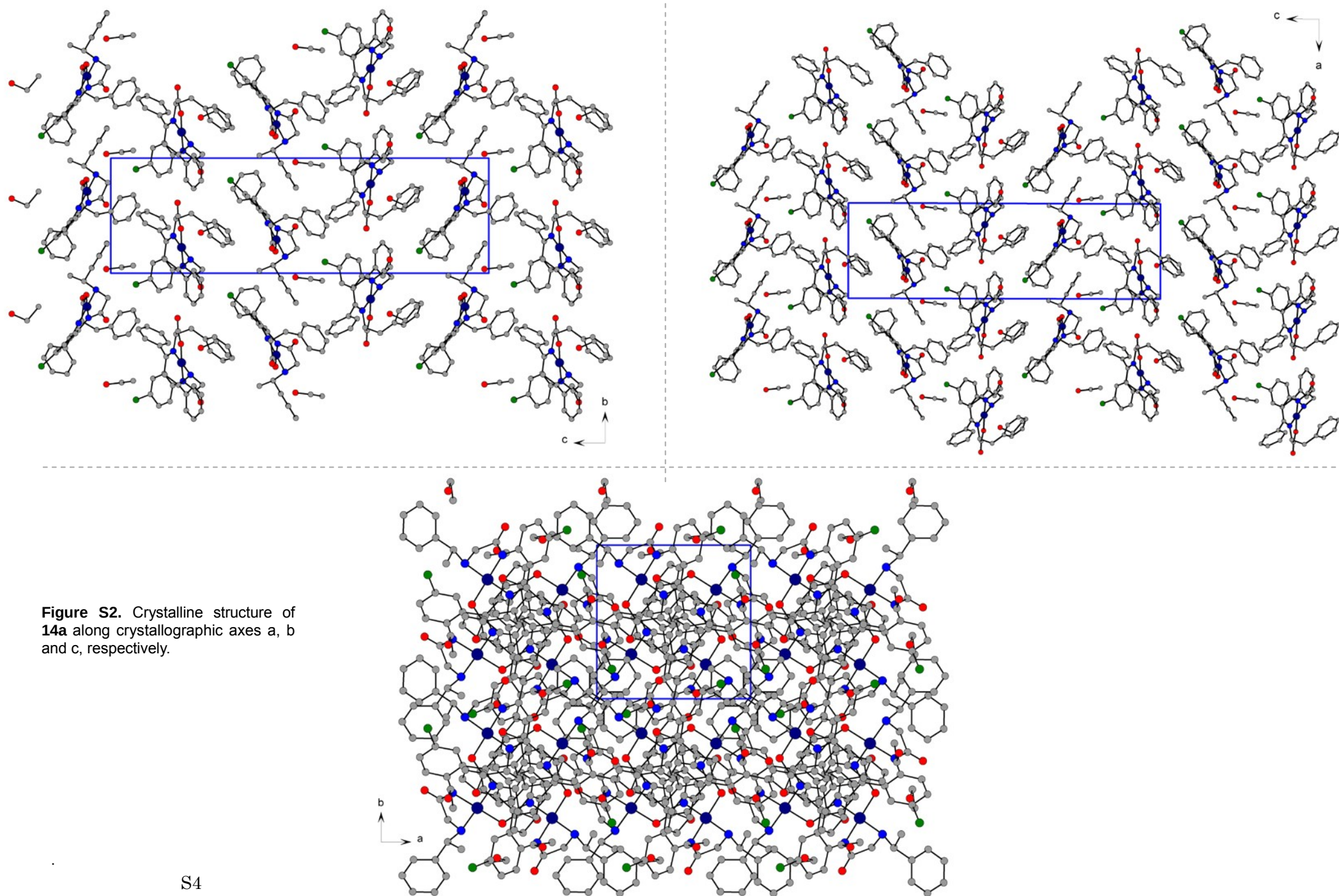


Figure S2. Crystalline structure of **14a** along crystallographic axes a, b and c, respectively.

Table S1. Bond lengths (Å) of **14a**

ATOMS	LENGTHS (Å)
Ni2A-O1	1.8692(14)
Ni2A-N1	1.8466(16)
Ni2A-N2	1.8404(17)
Ni2A-N3	1.9201(18)
C1-C12	1.737(2)
O1-C1	1.303(2)
O2-C1	1.213(2)
O3-C16	1.220(3)
N1-C3	1.302(3)
N1-C2	1.475(3)
N2-C16	1.374(3)
N2-C15	1.391(3)
N3-C18	1.510(3)
N3-C17	1.479(3)
C1-C2	1.531(3)
C2-C26	1.544(3)
C3-C10	1.466(3)
C3-C4	1.501(3)
C4-C9	1.388(3)
C4-C5	1.397(3)
C5-C6	1.388(3)
C6-C7	1.384(3)
C7-C8	1.384(3)
C8-C9	1.399(3)
C10-C15	1.423(3)
C10-C11	1.409(3)
C11-C12	1.376(3)
C12-C13	1.388(3)
C13-C14	1.378(3)
C14-C15	1.403(3)
C16-C17	1.518(3)
C18-C25	1.522(3)
C18-C19	1.517(3)
C19-C24	1.395(3)
C19-C20	1.390(3)
C20-C21	1.400(3)
C21-C22	1.388(4)
C22-C23	1.387(3)
C23-C24	1.385(3)
C26-C27	1.517(3)
C27-C32	1.384(4)
C27-C28	1.397(3)
C28-C29	1.391(3)
C29-C30	1.370(4)
C30-C31	1.377(4)
C31-C32	1.395(4)
solvent	
O1D-C1D	1.418(3)
C1D-C2D	1.541(6)

Table S2. Bond angles (°) of **14a**

ATOMS	ANGLES (°)
Ni2A-N1-C2	110.80(12)
Ni2A-N1-C3	127.44(14)
Ni2A-N2-C15	123.89(14)
Ni2A-N2-C16	113.53(14)
Ni2A-N3-C17	103.32(12)
Ni2A-N3-C18	113.49(13)
Ni2A-O1-C1	114.58(12)
O1-C1-C2	114.88(16)
O1-C1-O2	124.76(18)
O1-Ni2A-N1	86.89(7)
O1-Ni2A-N2	177.54(8)
O1-Ni2A-N3	94.05(7)
O2-C1-C2	120.31(18)
O3-C16-C17	121.24(19)
O3-C16-N2	127.86(19)
N1-C2-C1	107.29(15)
N1-C2-C26	111.51(16)
N1-C3-C10	121.58(17)
N1-C3-C4	120.77(17)
N1-Ni2A-N2	94.53(7)
N1-Ni2A-N3	178.61(8)
N2-C15-C10	120.39(17)
N2-C15-C14	120.86(18)
N2-C16-C17	110.89(17)
N2-Ni2A-N3	84.50(7)
N3-C17-C16	108.50(17)
N3-C18-C19	110.82(17)
N3-C18-C25	109.38(16)
Cl1-C12-C11	119.44(16)
Cl1-C12-C13	119.40(15)
C1-C2-C26	109.31(17)
C2-C26-C27	114.10(16)
C2-N1-C3	121.72(16)
C3-C10-C11	117.45(17)
C3-C10-C15	123.53(17)
C3-C4-C5	119.68(18)
C3-C4-C9	120.29(19)
C4-C3-C10	117.65(17)
C4-C5-C6	119.74(19)
C4-C9-C8	119.9(2)
C5-C4-C9	119.97(18)
C5-C6-C7	120.1(2)
C6-C7-C8	120.56(19)
C7-C8-C9	119.65(19)
C10-C11-C12	120.25(19)
C10-C15-C14	118.63(19)
C11-C10-C15	119.02(18)
C11-C12-C13	121.15(19)
C12-C13-C14	119.52(18)
C13-C14-C15	121.42(19)
C15-N2-C16	122.58(17)
C17-N3-C18	110.43(16)
C18-C19-C20	120.90(17)
C18-C19-C24	119.92(18)
C19-C18-C25	113.19(16)
C19-C20-C21	120.1(2)
C19-C24-C23	120.58(19)
C20-C19-C24	119.18(19)
C20-C21-C22	120.2(2)
C21-C22-C23	119.7(2)
C22-C23-C24	120.3(2)
C26-C27-C28	120.63(18)
C26-C27-C32	121.3(2)
C27-C28-C29	120.6(2)
C27-C32-C31	120.8(3)
C28-C27-C32	118.1(2)
C28-C29-C30	120.6(2)
C29-C30-C31	119.5(3)
C30-C31-C32	120.3(3)
solvent	
O1D-C1D-C2D	106.3(3)

Table S3. Torsion angles (°) of **14a**

ATOMS	ANGLES (°)		
N1-Ni2A-O1-C1	-11.42(15)	C10-C3-C4-C9	-79.7(2)
N3-Ni2A-O1-C1	167.56(15)	N1-C3-C10-C11	163.56(19)
O1-Ni2A-N1-C2	20.73(13)	N1-C3-C10-C15	-16.7(3)
N2-Ni2A-N1-C2	-157.26(14)	C9-C4-C5-C6	1.2(3)
O1-Ni2A-N1-C3	-161.51(17)	C3-C4-C9-C8	176.94(18)
N2-Ni2A-N1-C3	20.50(18)	C3-C4-C5-C6	-176.20(18)
N1-Ni2A-N2-C15	-31.42(17)	C5-C4-C9-C8	-0.4(3)
N3-Ni2A-N2-C15	149.57(17)	C4-C5-C6-C7	-0.6(3)
N1-Ni2A-N2-C16	149.34(15)	C5-C6-C7-C8	-0.8(3)
N3-Ni2A-N2-C16	-29.67(15)	C6-C7-C8-C9	1.5(3)
O1-Ni2A-N3-C17	-138.91(13)	C7-C8-C9-C4	-0.9(3)
N2-Ni2A-N3-C17	39.10(13)	C11-C10-C15-C14	0.5(3)
O1-Ni2A-N3-C18	101.48(13)	C3-C10-C11-C12	-179.81(19)
N2-Ni2A-N3-C18	-80.51(14)	C15-C10-C11-C12	0.5(3)
Ni2A-O1-C1-O2	-178.42(18)	C3-C10-C15-N2	4.7(3)
Ni2A-O1-C1-C2	-1	C3-C10-C15-C14	-179.26(19)
C3-N1-C2-C26	-82.9(2)	C11-C10-C15-N2	-175.55(19)
Ni2A-N1-C2-C1	-24.69(19)	C10-C11-C12-C11	177.33(16)
C3-N1-C2-C1	157.41(18)	C10-C11-C12-C13	-1.3(3)
Ni2A-N1-C3-C4	178.55(14)	C11-C12-C13-C14	-177.50(16)
C2-N1-C3-C10	176.72(18)	C11-C12-C13-C14	1.1(3)
C2-N1-C3-C4	-3	C12-C13-C14-C15	-0.1(3)
Ni2A-N1-C2-C26	94.98(16)	C13-C14-C15-N2	175.4(2)
Ni2A-N1-C3-C10	-0	C13-C14-C15-C10	-0.6(3)
Ni2A-N2-C16-O3	-167.53(18)	N2-C16-C17-N3	21.3(2)
C15-N2-C16-O3	13.2(3)	O3-C16-C17-N3	-159.98(19)
C16-N2-C15-C14	26.7(3)	N3-C18-C19-C20	60.1(3)
C16-N2-C15-C10	-157.43(19)	N3-C18-C19-C24	-119.1(2)
Ni2A-N2-C15-C10	23.4(3)	C25-C18-C19-C20	-63.2(3)
Ni2A-N2-C16-C17	11.1(2)	C25-C18-C19-C24	117.7(2)
Ni2A-N2-C15-C14	-152.52(17)	C18-C19-C20-C21	-178.5(2)
C15-N2-C16-C17	-168.18(18)	C24-C19-C20-C21	0.6(3)
Ni2A-N3-C18-C19	-179.25(12)	C18-C19-C24-C23	178.5(2)
C17-N3-C18-C25	-169.24(16)	C20-C19-C24-C23	-0.7(4)
C18-N3-C17-C16	80.43(19)	C19-C20-C21-C22	0.2(4)
Ni2A-N3-C17-C16	-41.26(17)	C20-C21-C22-C23	-1.0(4)
Ni2A-N3-C18-C25	-53.77(18)	C21-C22-C23-C24	1.0(4)
C17-N3-C18-C19	65.3(2)	C22-C23-C24-C19	-0.2(4)
O1-C1-C2-C26	-104.3(2)	C2-C26-C27-C28	-82.1(2)
O2-C1-C2-N1	-165.71(19)	C2-C26-C27-C32	97.3(2)
O2-C1-C2-C26	73.2(3)	C26-C27-C28-C29	-179.8(2)
O1-C1-C2-N1	16.7(3)	C32-C27-C28-C29	0.7(3)
C1-C2-C26-C27	69.8(2)	C26-C27-C32-C31	-179.6(2)
N1-C2-C26-C27	-48.7(2)	C28-C27-C32-C31	-0.1(4)
C4-C3-C10-C11	-15.8(3)	C27-C28-C29-C30	-1.1(4)
C4-C3-C10-C15	163.90(19)	C28-C29-C30-C31	0.8(4)
N1-C3-C4-C5	-81.7(3)	C29-C30-C31-C32	-0.2(4)
N1-C3-C4-C9	100.9(2)	C30-C31-C32-C27	-0.2(4)
C10-C3-C4-C5	97.7(2)		

Table S4. Possible hydrogen bonds (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O1D-H1D...O1 ⁱ	0.8400	2.0600	2.790(2)	144.00
N3-H3...O1D ⁱⁱ	0.9300	2.1100	3.000(3)	161.00
C6-H6...O3 ⁱⁱⁱ	0.9500	2.4800	3.196(3)	132.00
C14-H14...O3	0.9500	2.3100	2.851(3)	116.00
C17-H17A...Cl1 ^{iv}	0.9900	2.6300	3.432(2)	138.00
C24-H24...O2 ^v	0.9500	2.3800	3.283(3)	159.00

Symmetry options: (i)= 2-y,x,1/4+z z; (ii)= -y,2-x,-1/4+z; (iii)= -1-y,-1+x,1/4+z.. (iv)=1+y,2-x,-1/4+z z; (v)=-1+x,y,z

HPLC analysis data

General conditions for HPLC analysis of Ni(II) complexes 12-15:

Instrument: SHIMADZU LC-2010CHT chromatography system and a CLASS-VPTM analysis data system (SHIMADZU CORPORATION, Kyoto, Japan).

Column: InertsilTM ODS-3 (3 μ m, 150*4.6 mm i.d.)

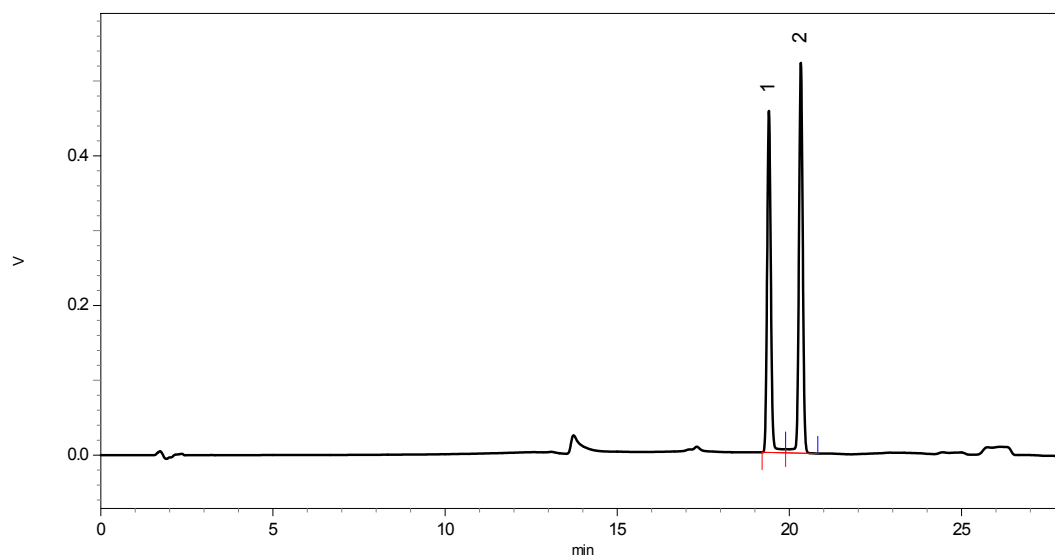
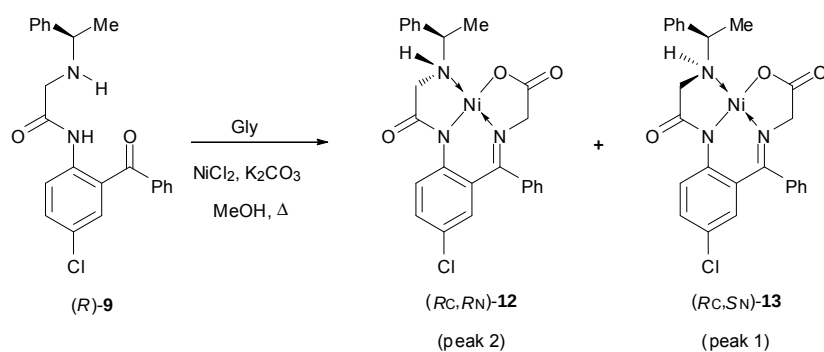
Eluent: A = 10mM ammonium formate 0.1% formic acid buffer
B = acetonitrile

Flow rate: 1.0 mL/min

Temp: 30 °C

Detector: UV 254 nm

Reaction of (R)-9 with glycine



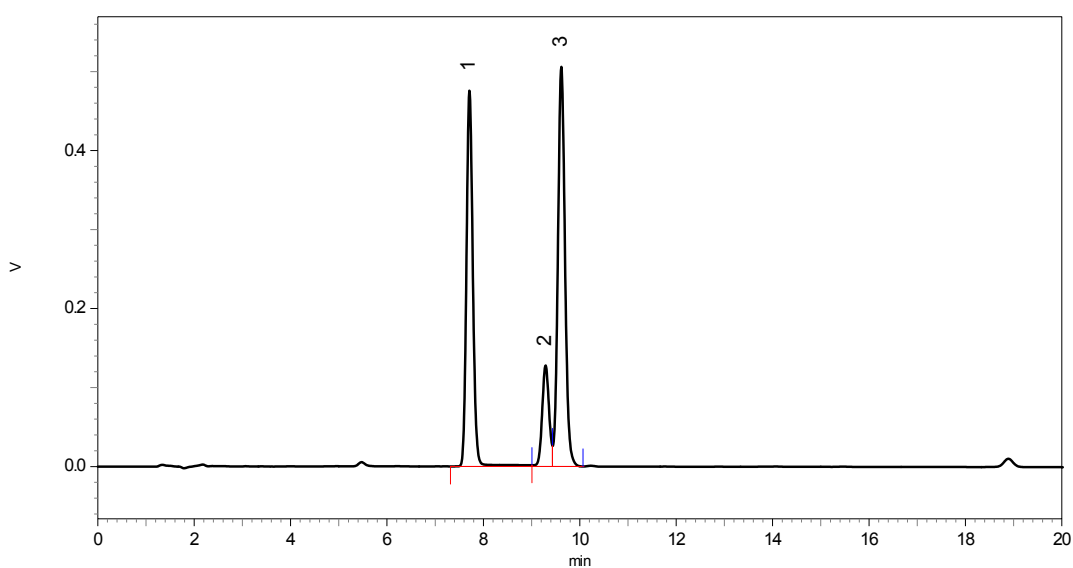
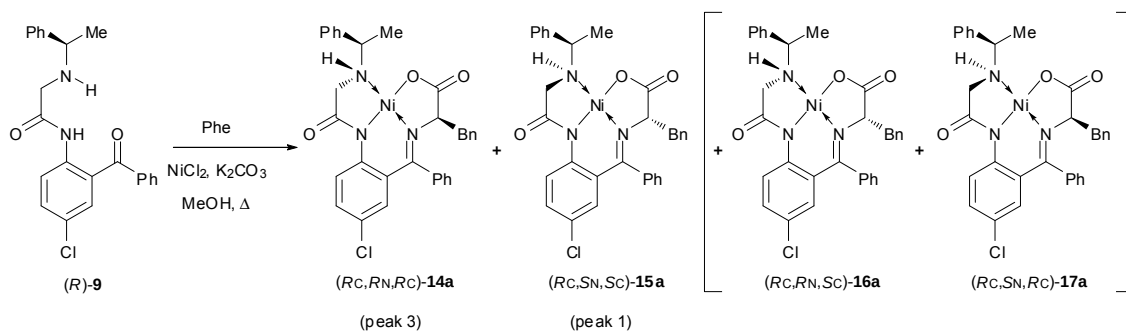
Detector A - 1 (254nm)

Peak Number	Retention Time	Area	Area%
1	19.402	3456701	46.22
2	20.330	4022287	53.78

Total		7478988	100.00
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Gradient A: B = 80:20 to 20:80 (0 to 25 min)

Reaction of (R)-9 with phenylalanine



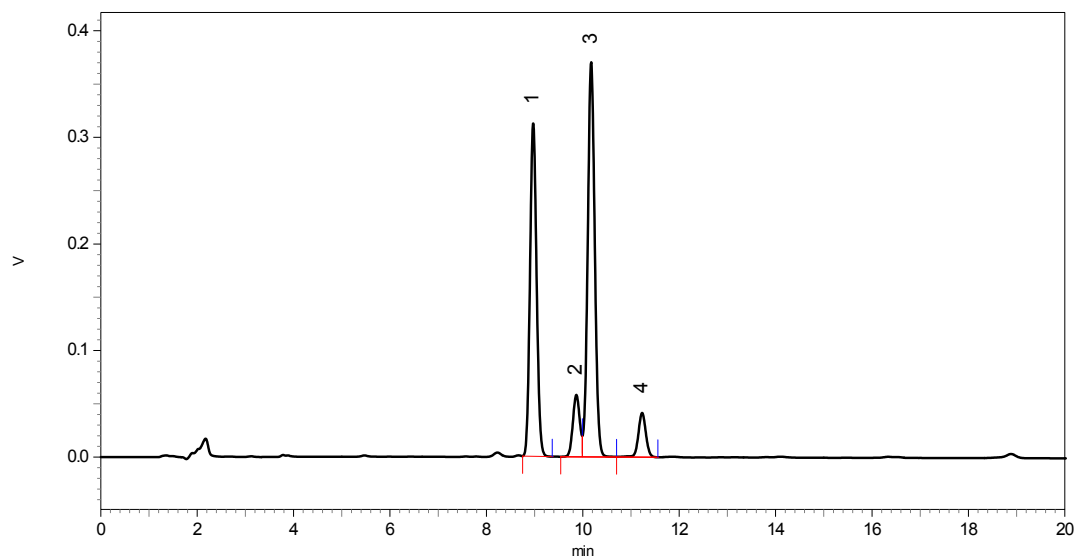
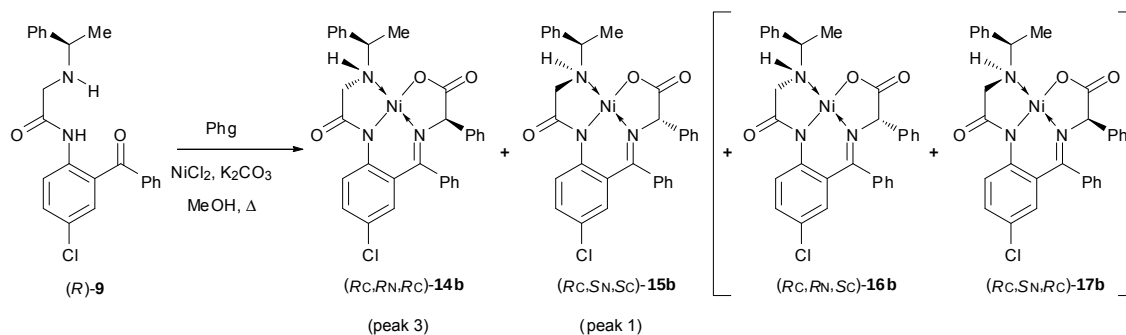
Detector A - 1 (254nm)

Peak Number	Retention Time	Area	Area%
1	7.707	4414629	40.70
2	9.286	1273188	11.74
3	9.613	5160205	47.57

Total		10848022	100.00
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Gradient A: B = 80:20 to 20:80 (0 to 25 min)

Reaction of (*R*)-9 with phenylglycine



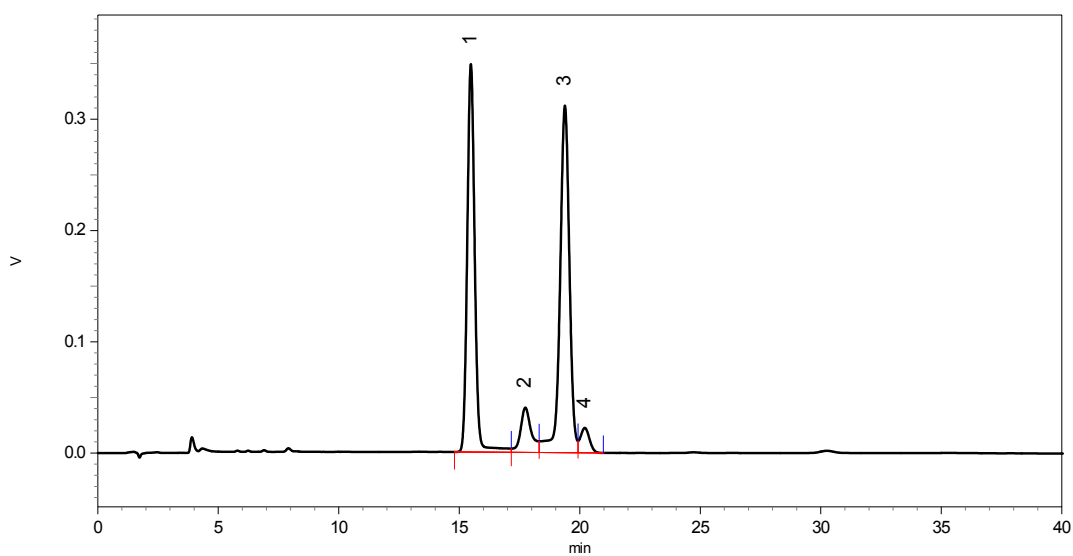
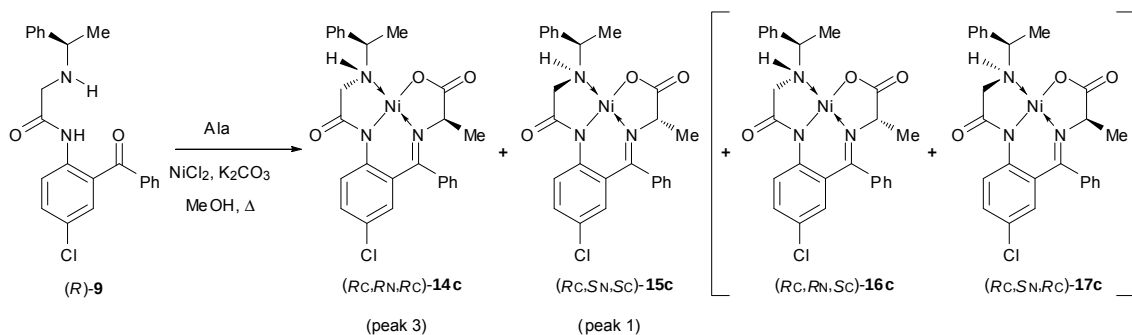
Detector A - 1 (254nm)

Peak Number	Retention Time	Area	Area%
1	8.967	2961579	38.22
2	9.862	584477	7.54
3	10.170	3753642	48.44
4	11.227	449027	5.79

Total		7748724	100.00
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Gradient A: B = 80:20 to 20:80 (0 to 25 min)

Reaction of (R)-9 with alanine



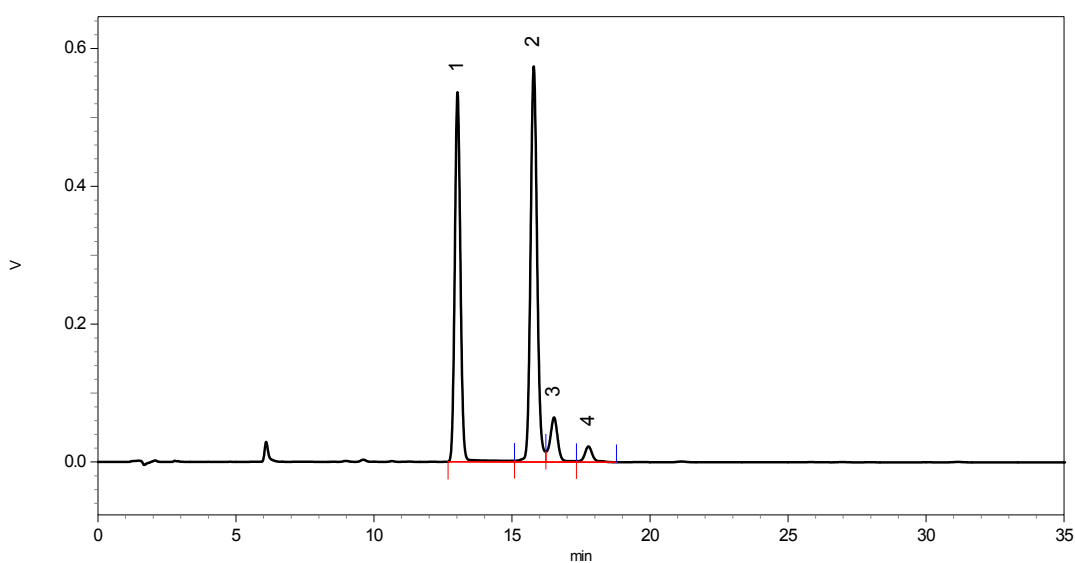
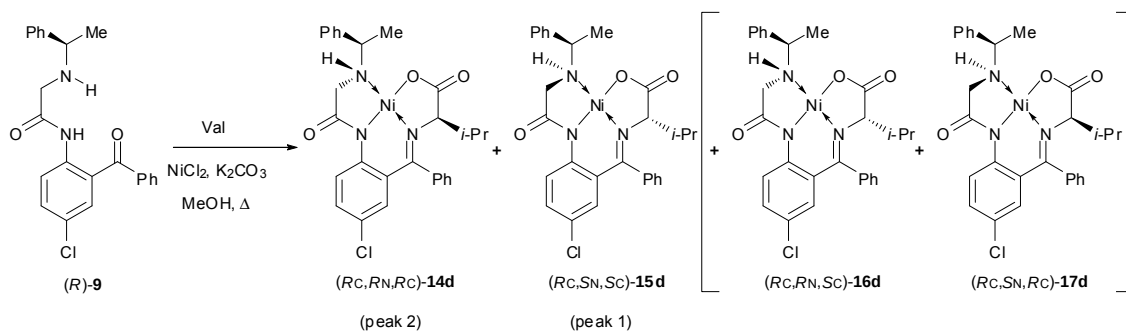
Detector A - 1 (254nm)

Peak Number	Retention Time	Area	Area%
1	15.476	7579592	42.25
2	17.737	1257630	7.01
3	19.379	8516962	47.47
4	20.205	587494	3.27

Total		17941678	100.00
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Gradient A: B = 55:45 (0 to 30 min)
55:45 to 10:90 (30 min to 50 min)

Reaction of (R)-9 with valine



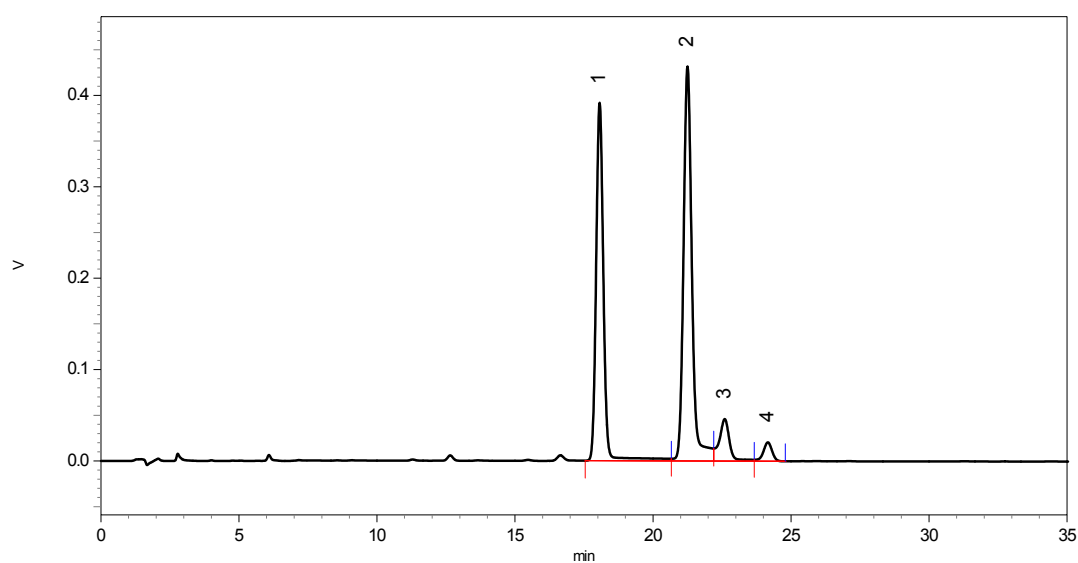
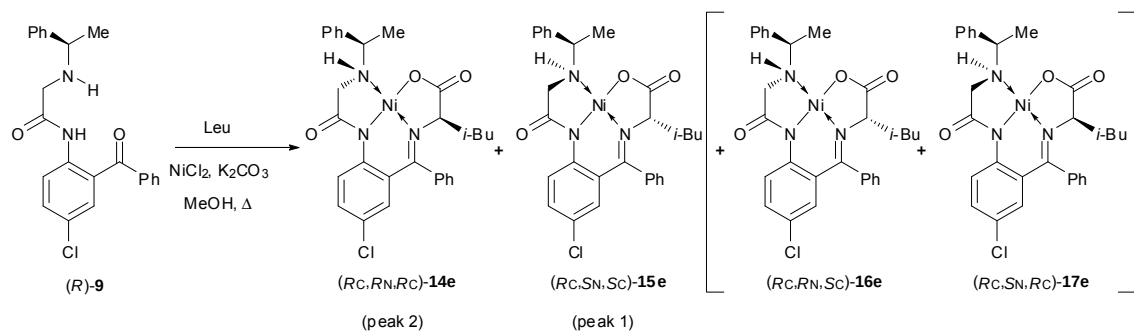
Detector A - 1 (254nm)

Peak Number	Retention Time	Area	Area%
1	13.022	7708983	40.71
2	15.784	9514754	50.25
3	16.519	1261960	6.66
4	17.765	448992	2.37

Total		18934689	100.00
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Gradient A: B = 50:50 to 40:60 (0 min to 30 min)
40:60 to 10:90 (30 min to 50 min)

Reaction of (*R*)-9 with leucine



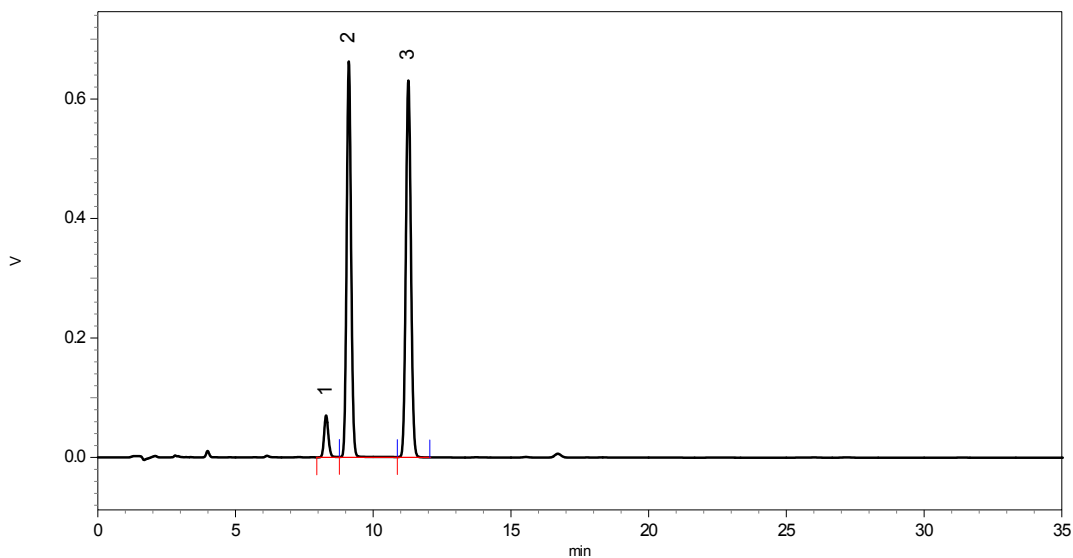
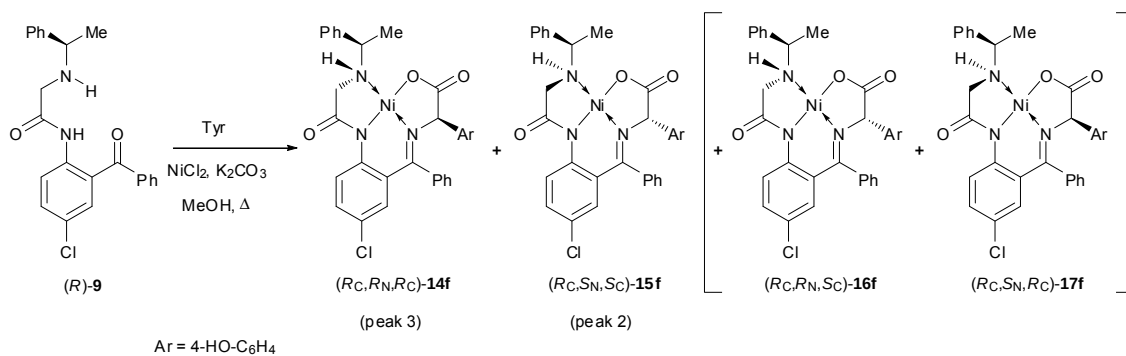
Detector A - 1 (254nm)

Peak Number	Retention Time	Area	Area%
1	18.062	7279518	40.12
2	21.245	9210736	50.76
3	22.594	1196224	6.59
4	24.158	457532	2.52

Total		18144009	100.00
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Gradient A: B = 50:50 to 40:60 (0 min to 30 min)
40:60 to 10:90 (30 min to 50 min)

Reaction of (*R*)-9 with tyrosine



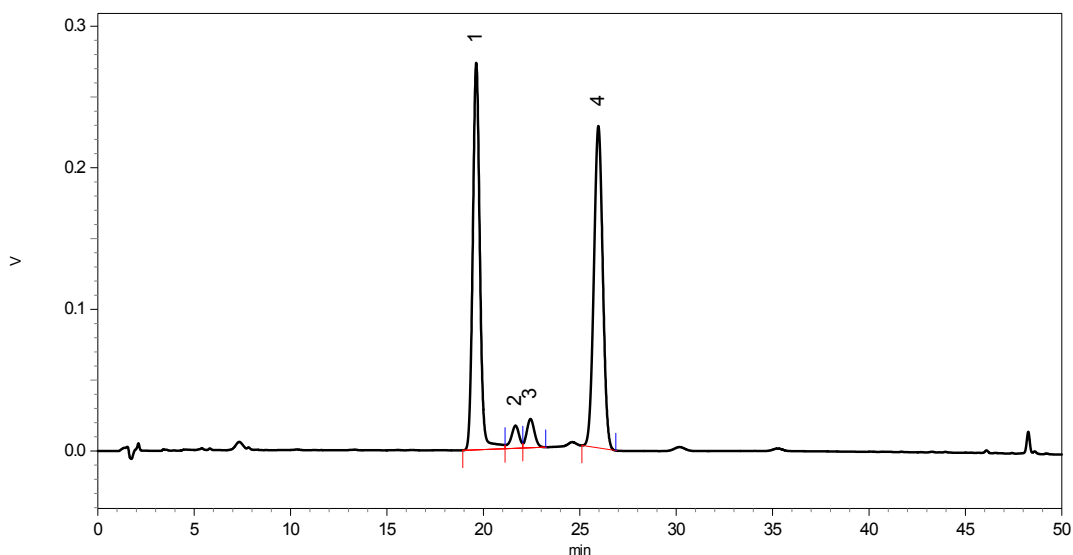
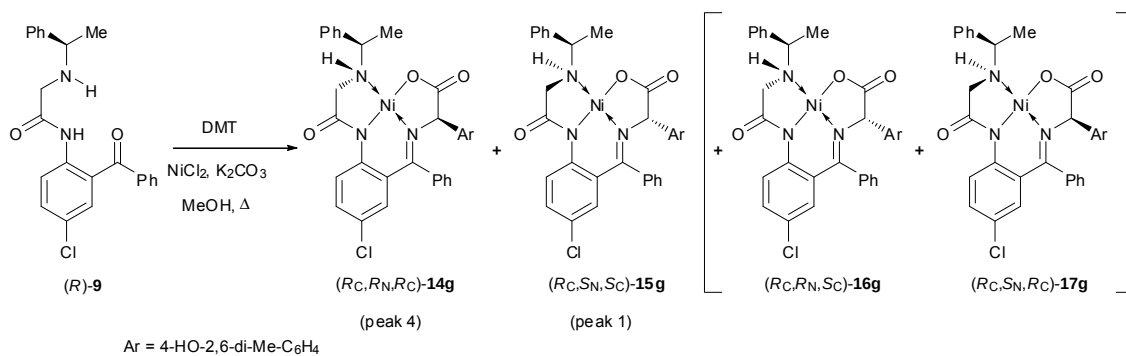
Detector A - 1 (254nm)

Peak Number	Retention Time	Area	Area%
1	8.286	766992	4.68
2	9.111	7519581	45.91
3	11.272	8091702	49.41

Total		16378275	100.00
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Gradient A: B = 50:50 to 40:60 (0 min to 30 min)
 40:60 to 10:90 (30 min to 50 min)

Reaction of (R)-9 with 2,6-dimethyltyrosine



Detector A - 1 (254nm)

Peak Number	Retention Time	Area	Area%
1	19.626	6977892	45.65
2	21.664	461378	3.02
3	22.437	570492	3.73
4	25.963	7277190	47.60

Total		15286952	100.00
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Gradient A: B = 55:45 (0 to 30 min)
55:45 to 10:90 (30 min to 50 min)

HPLC conditions for DMT complex samples

Instrument: SHIMADZU LC-2010CHT chromatography system and a CLASS-VPTM analysis data system (SHIMADZU CORPORATION, Kyoto, Japan).

Column: InertsilTM ODS-3 (3μm, 150*4.6 mm i.d.)

Eluent: A = 10mM ammonium formate 0.1% formic acid buffer
B = acetonitrile

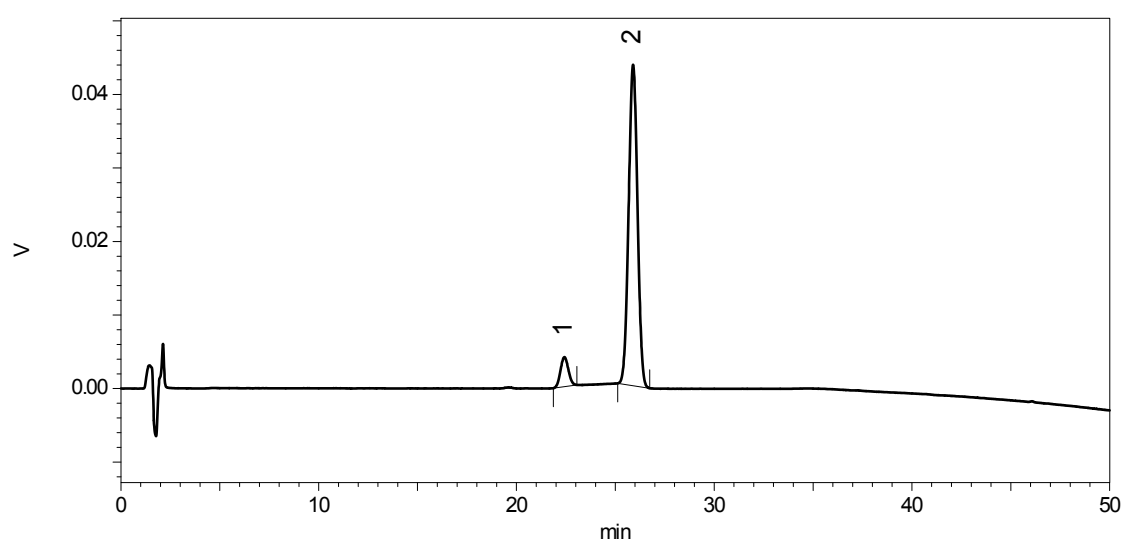
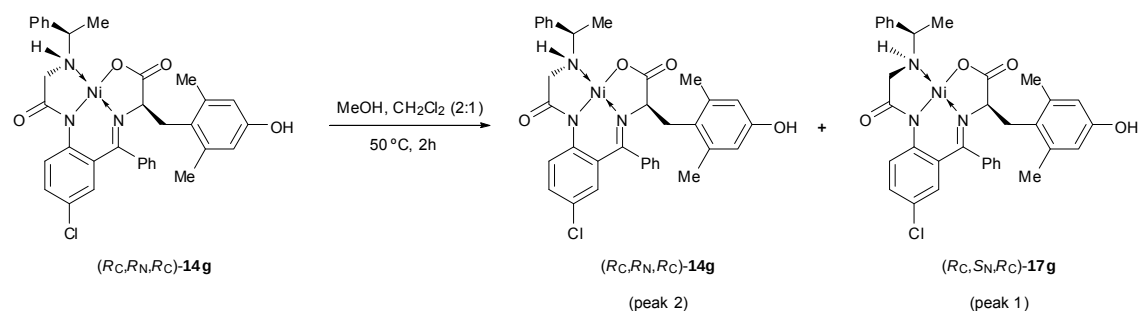
Gradient: A: B = 55:45 (0 to 30 min)
55:45 to 10:90 (30 min to 50 min)

Flow rate: 1.0 mL/min

Temp: 30 °C

Detector: UV 254 nm

Epimerization of 14g



Detector A - 1 (254nm)

Peak Number	Retention Time	Area	Area%
1	22.423	111960	7.60
2	25.896	1360937	92.40

Total		1472897	100.00
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HPLC conditions for chiral analysis of free DMT

Instrument: SHIMADZU chromatography system, consisting of a LC-10ADvp high-pressure gradient pump, a SPD-10Avp UV-VIS detector, and a CLASS-VPTM analysis data system (SHIMADZU CORPORATION, Kyoto, Japan)

Column: Astec CHIROBIOTICTM R

Eluent: H₂O/ MeOH = 8: 2

Flow rate: 0.5 mL/min

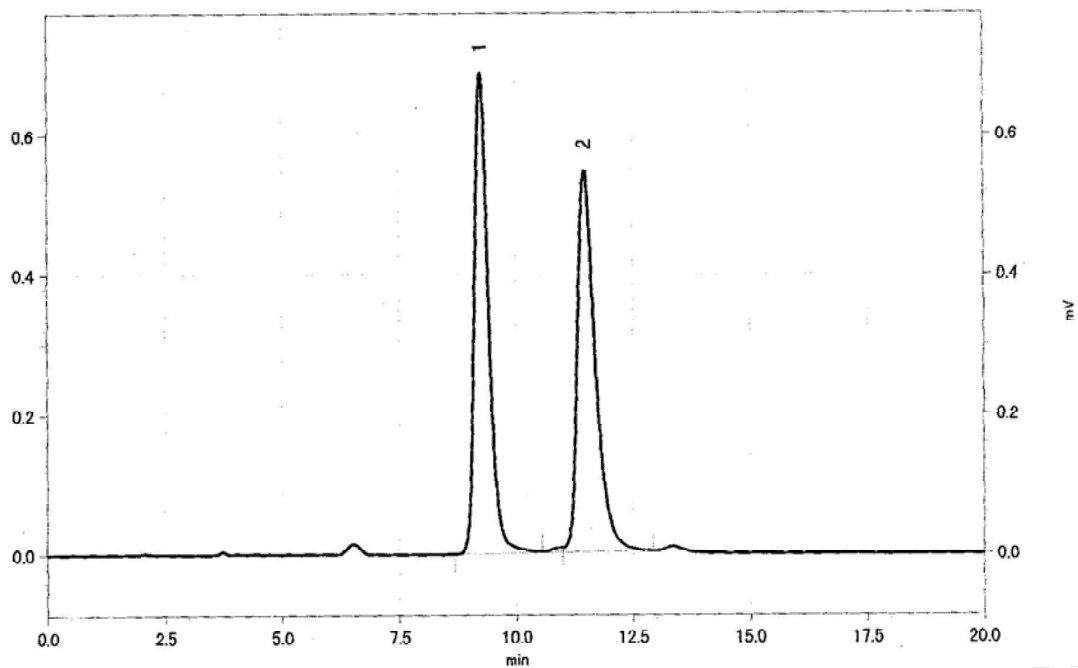
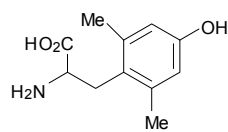
Temp: 25 °C

Detector: UV 205 nm

t_R: 9.2 min (*R*)-(-)-DMT

11.4 min (*S*)-(+)-DMT

HPLC of racemic DMT, (±)-18

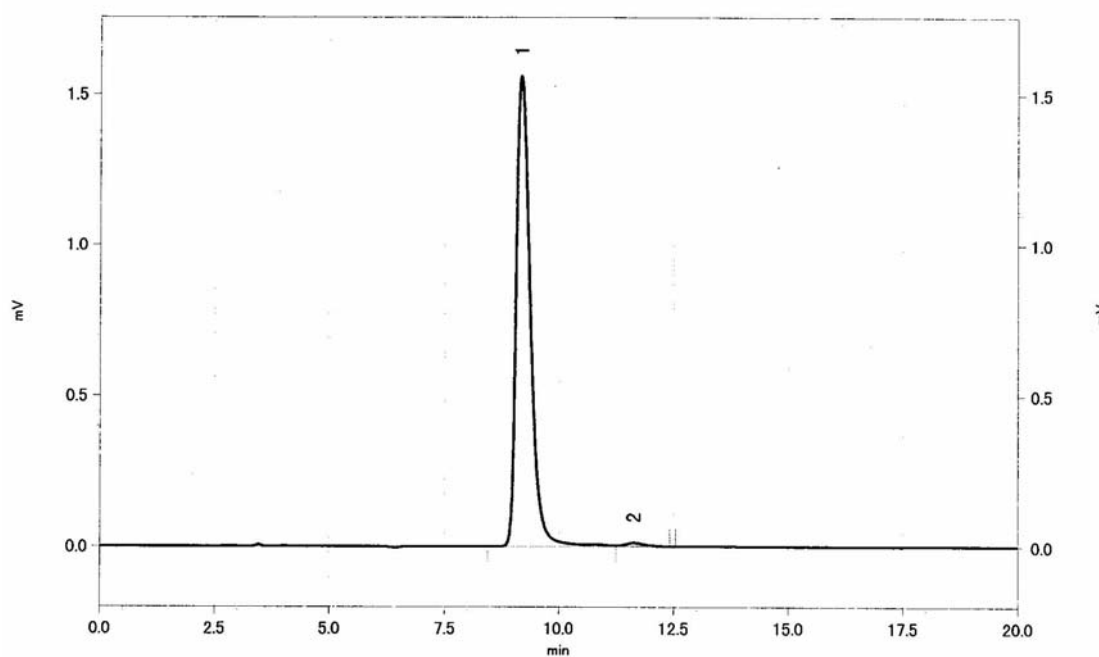
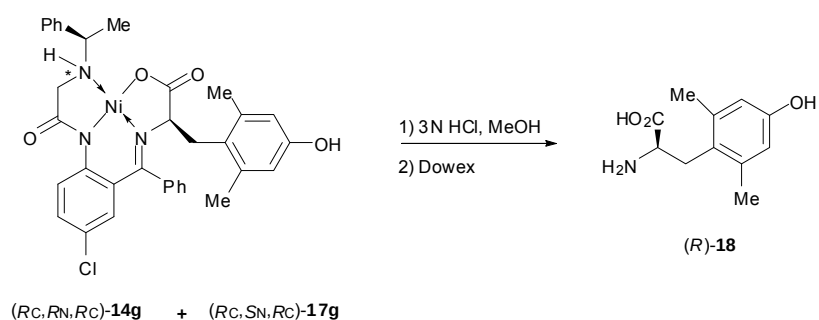


Detector A - 1 (205nm)

Peak Number	Retention Time	Area	Area%
1	9.243	14451749	49.72
2	11.465	14615997	50.28

Total		29067746	100.00
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Disassembly of 14 and 17

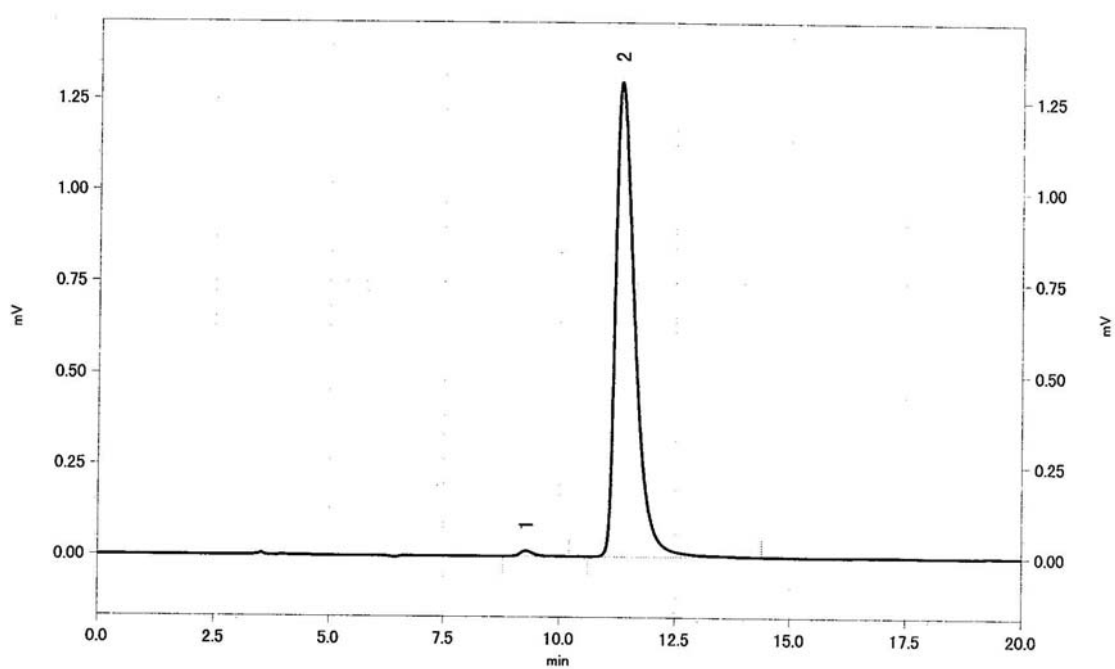
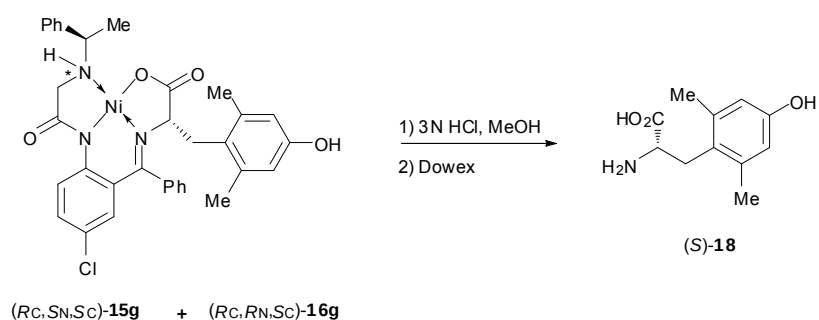


Detector A - 1 (205nm)

Peak Number	Retention Time	Area	Area%
1	9.173	34001570	99.24
2	11.631	34263359	0.76

Total		34263359	100.00
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Disassembly of 15 and 16

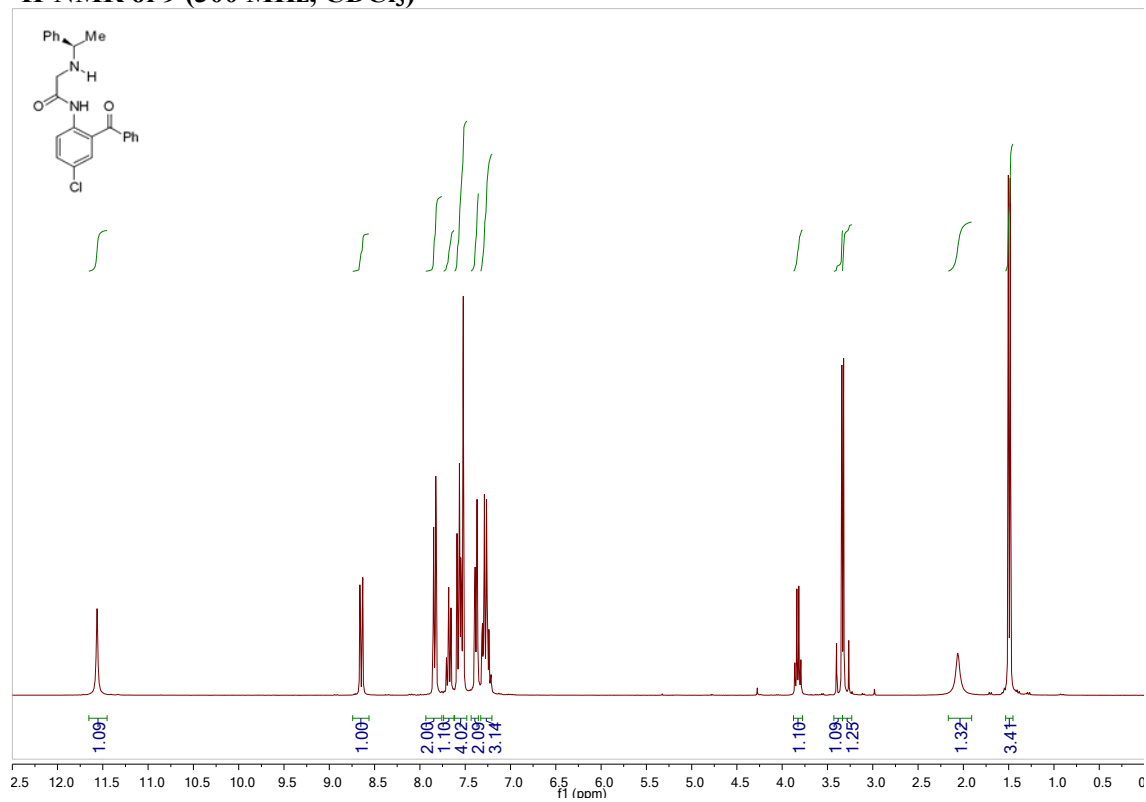


Detector A - 1 (205nm)

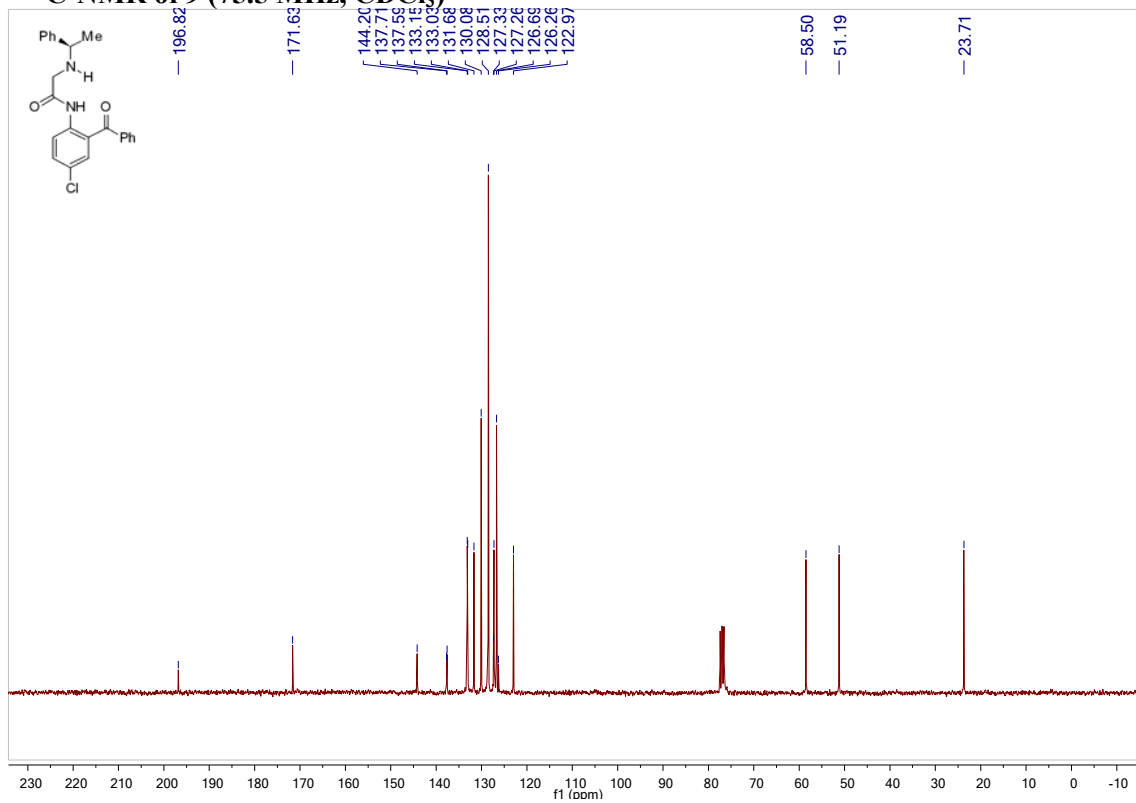
Peak Number	Retention Time	Area	Area%
1	9.276	302164	0.79
2	11.304	37923747	99.21

Total		38225911	100.00
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¹H-NMR of 9 (300 MHz, CDCl₃)



¹³C-NMR of 9 (75.5 MHz, CDCl₃)



[illegible][illegible]

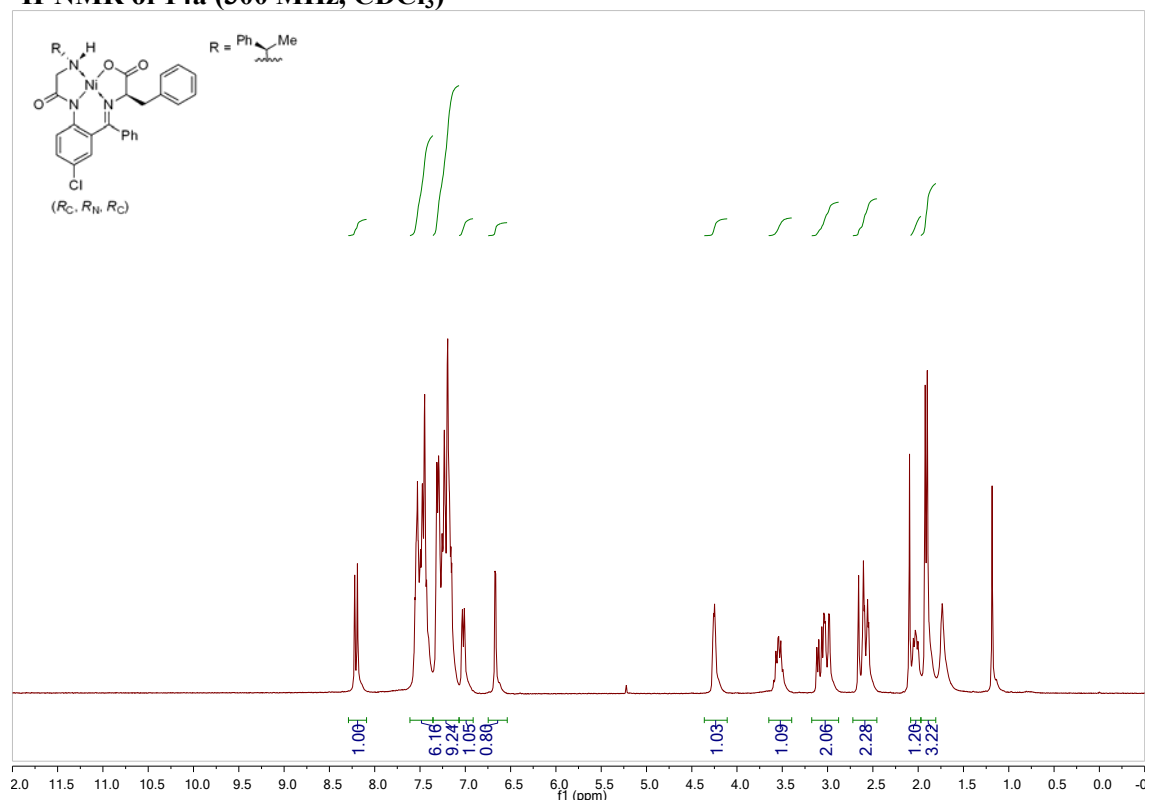
[illegible]

¹³C NMR of 15 (CDCl₃)

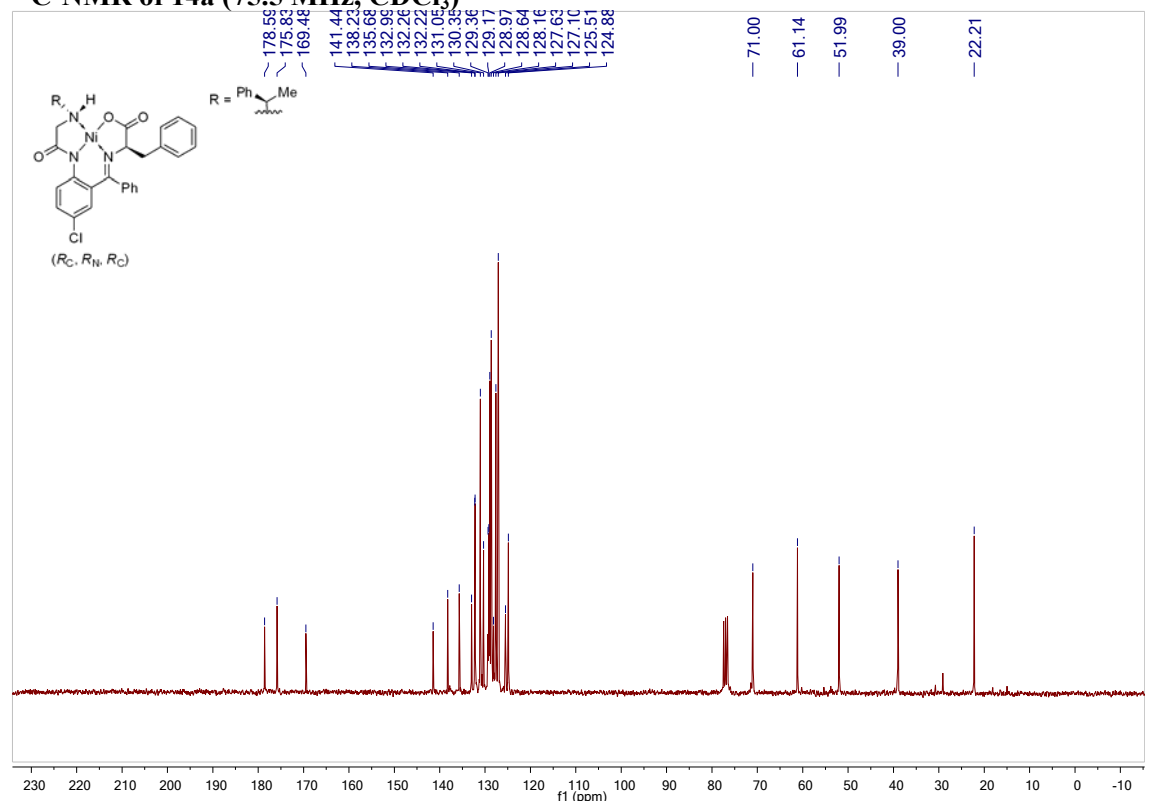
(R_C, S_N)

Chemical Shift (ppm)
178.86
177.86
170.86
141.36
137.84
133.95
132.20
131.97
130.08
130.03
129.65
129.65
128.88
128.81
128.29
126.73
126.10
125.68
125.60
60.90
59.76
51.02
17.98

¹H-NMR of 14a (300 MHz, CDCl₃)

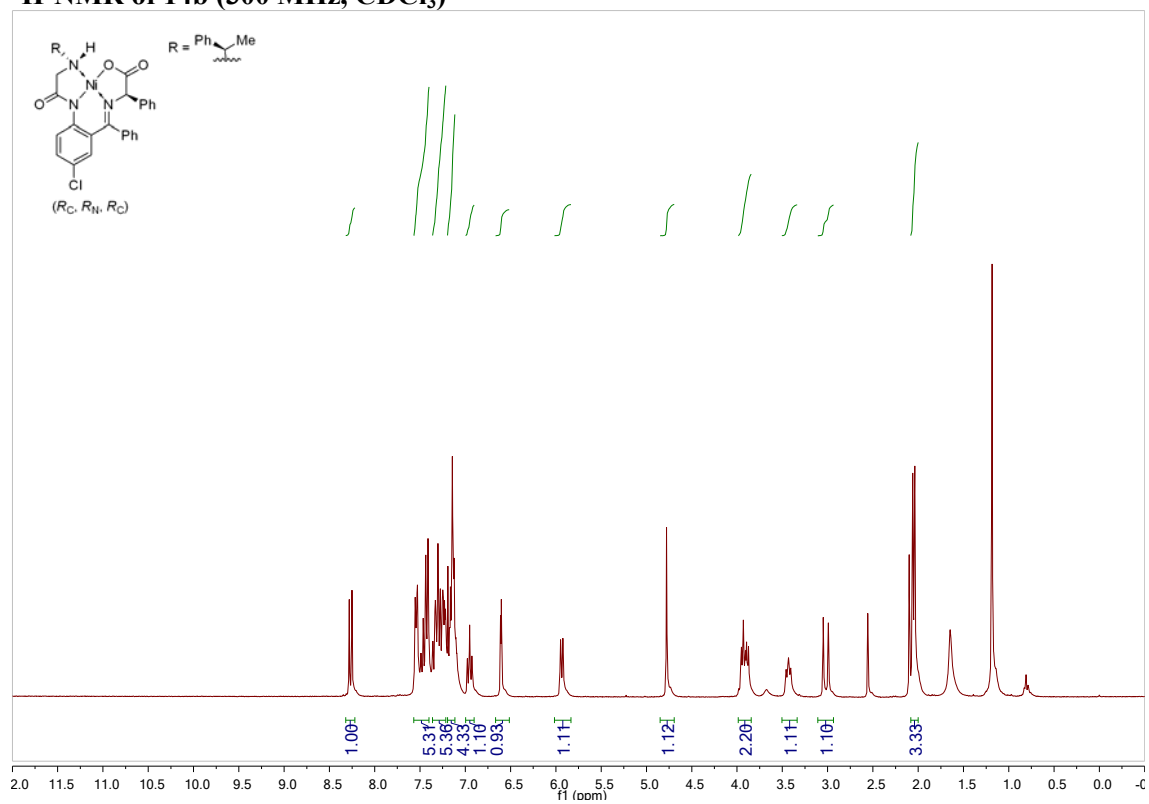


¹³C-NMR of 14a (75.5 MHz, CDCl₃)

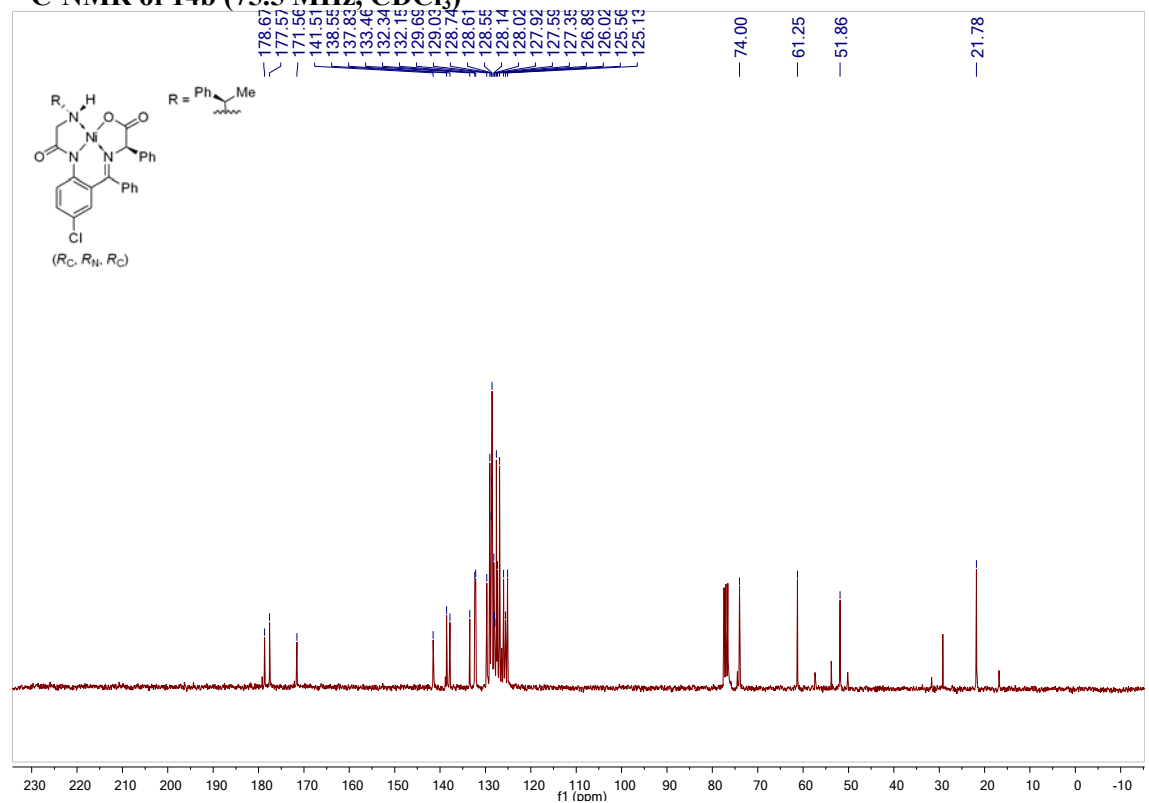


[illegible][illegible]

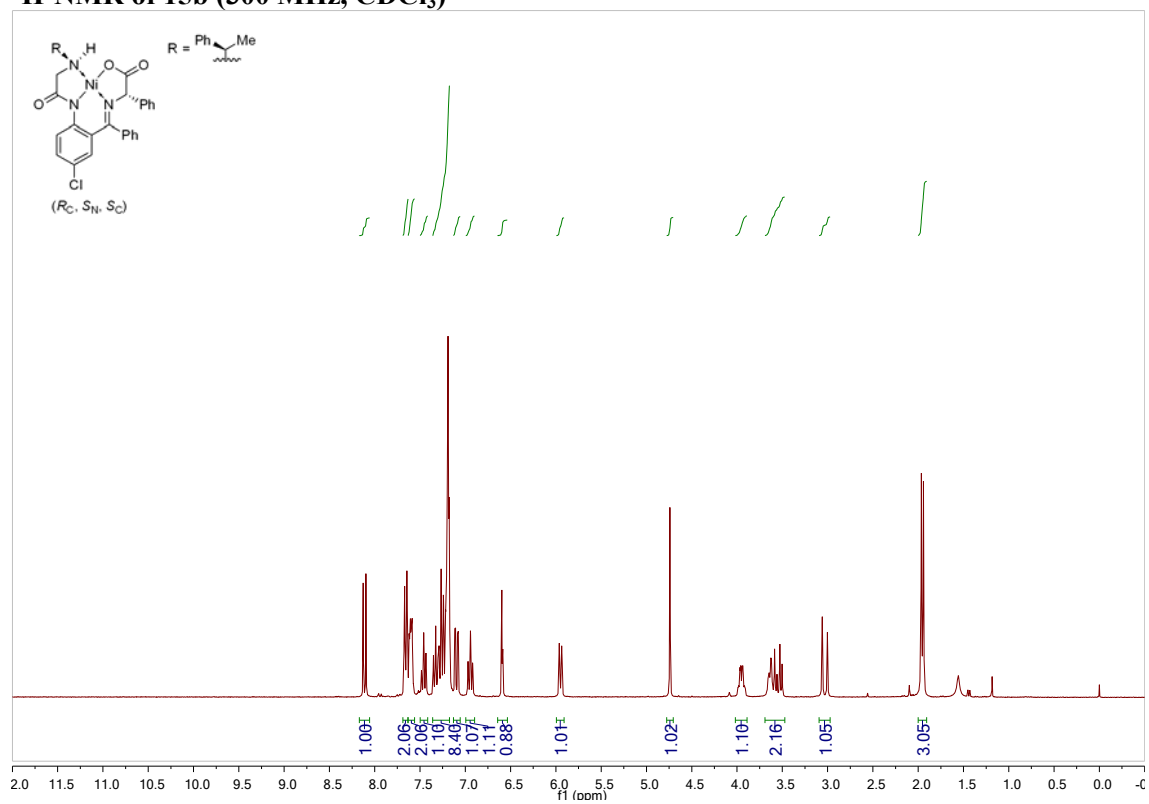
¹H-NMR of 14b (300 MHz, CDCl₃)



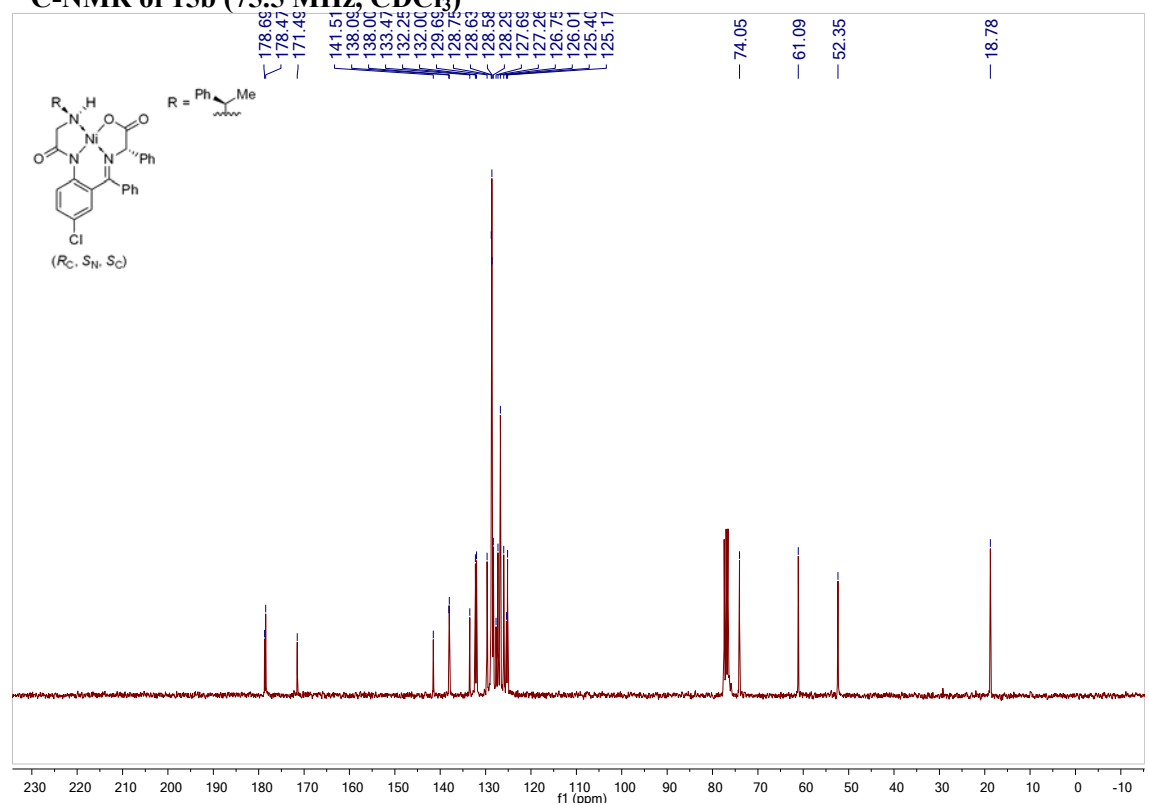
¹³C-NMR of 14b (75.5 MHz, CDCl₃)



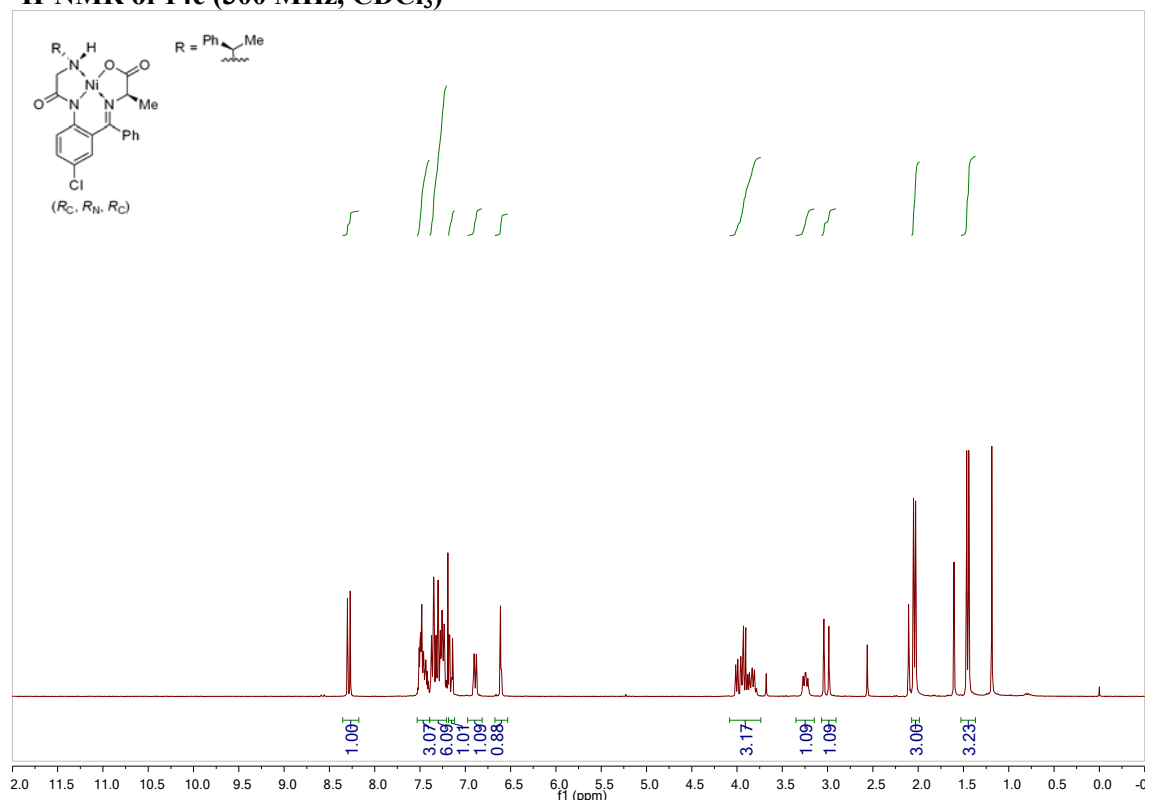
¹H-NMR of 15b (300 MHz, CDCl₃)



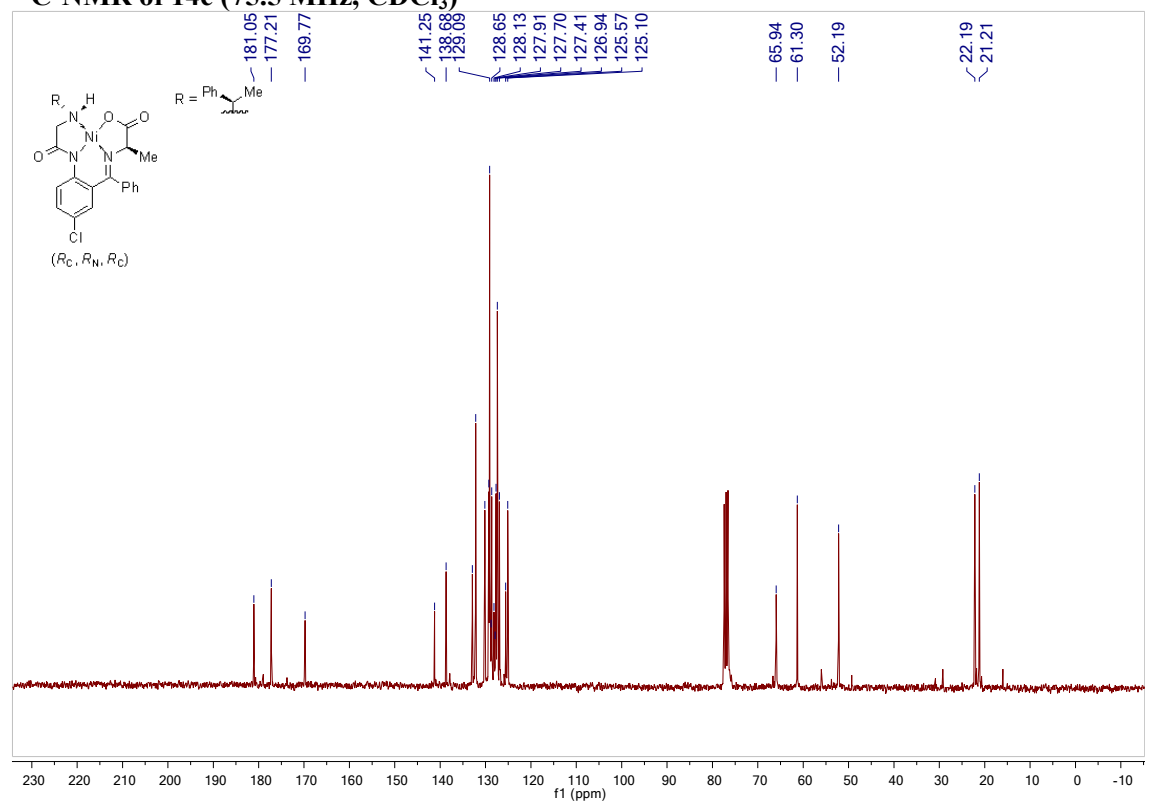
¹³C-NMR of 15b (75.5 MHz, CDCl₃)



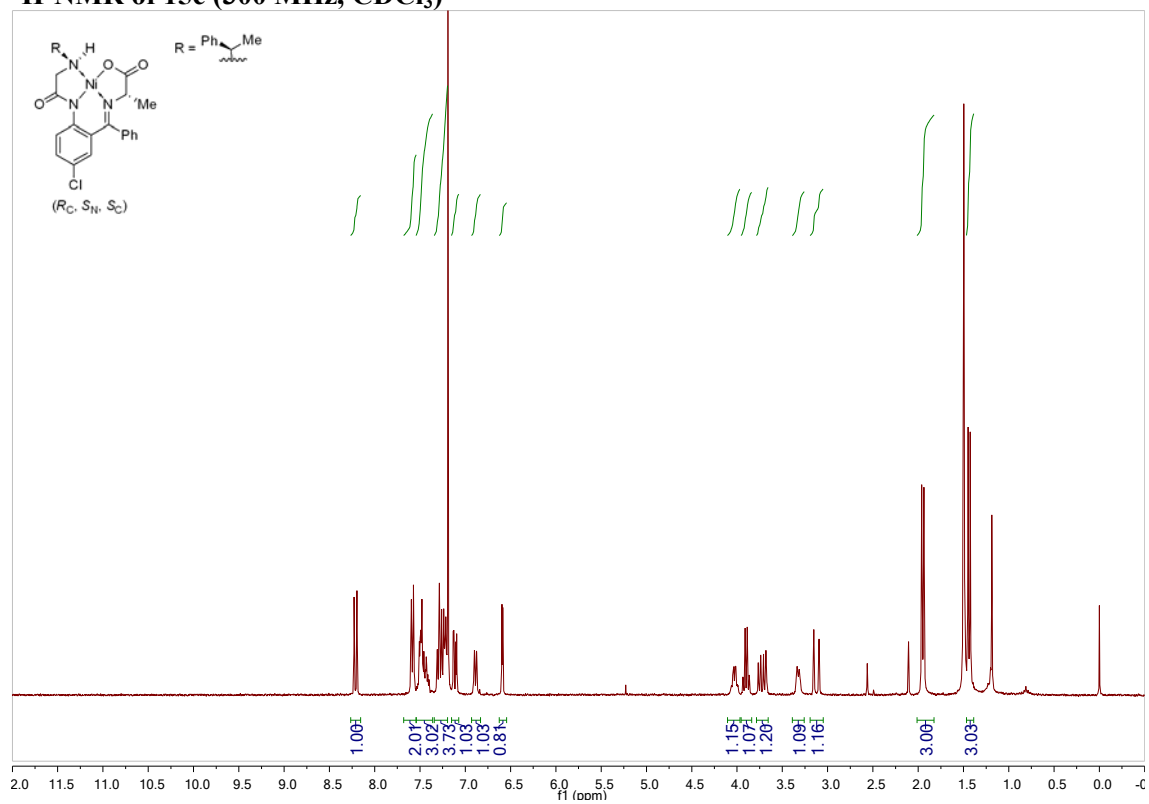
¹H-NMR of 14c (300 MHz, CDCl₃)



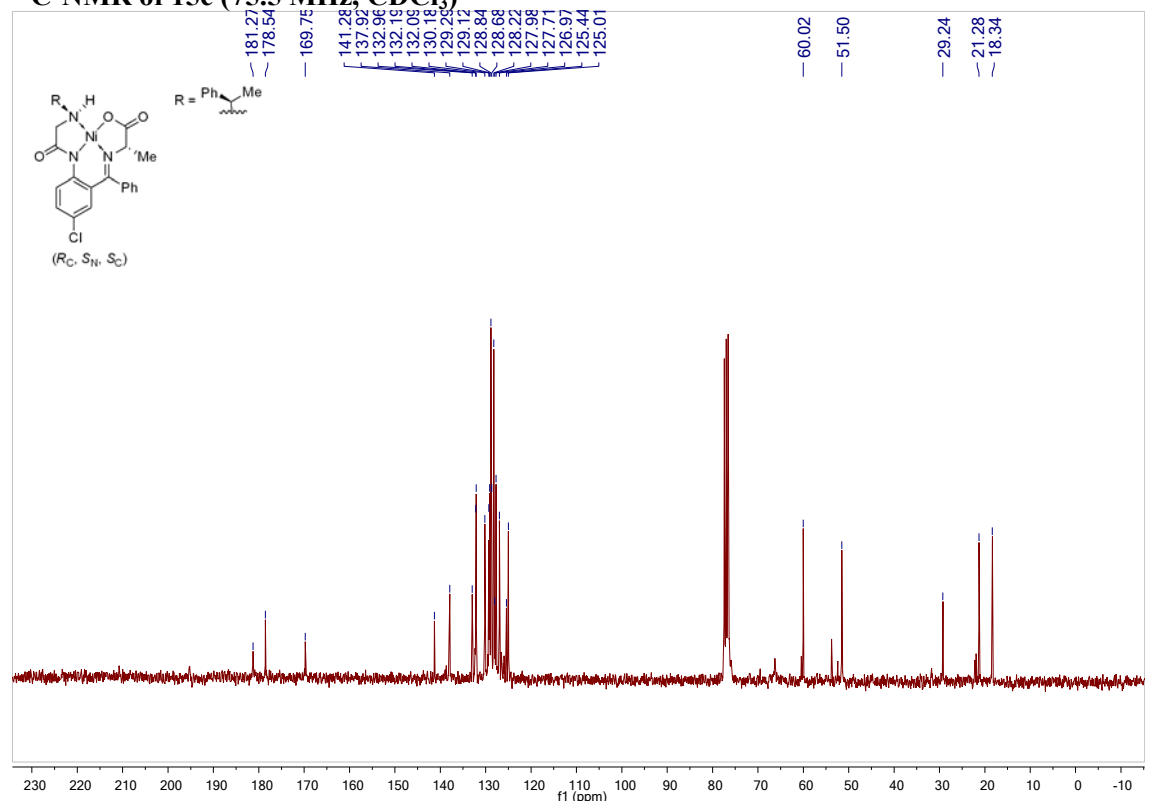
¹³C-NMR of 14c (75.5 MHz, CDCl₃)



¹H-NMR of 15c (300 MHz, CDCl₃)



¹³C-NMR of 15c (75.5 MHz, CDCl₃)



CC(C)C(=O)N1C(=O)N(C(=O)N1C(=O)c2ccc(Cl)cc2)C(=O)N(R)C

 (R_C, R_H, R_C)

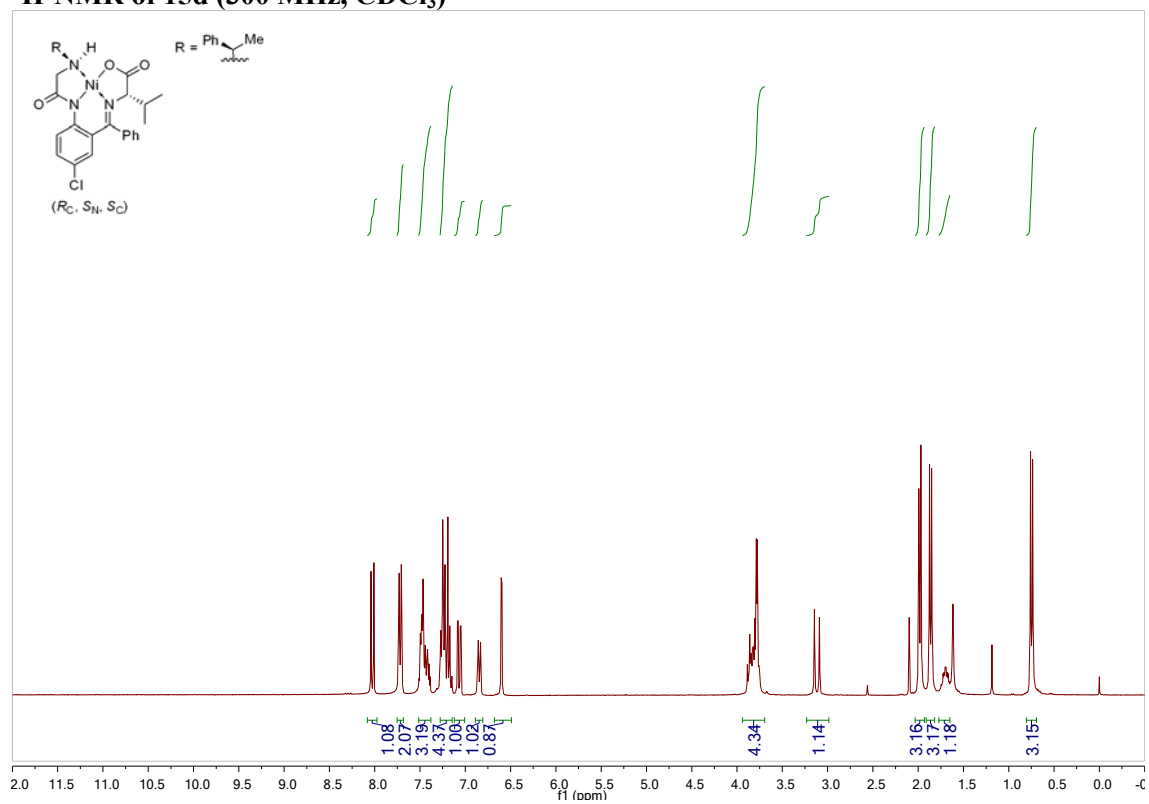
 $R = \text{Ph-CH(Me)-}$

$^1\text{H NMR}$ spectrum (CDCl₃) of compound **10**. The spectrum shows peaks corresponding to the structure, with integration values provided below the peaks.

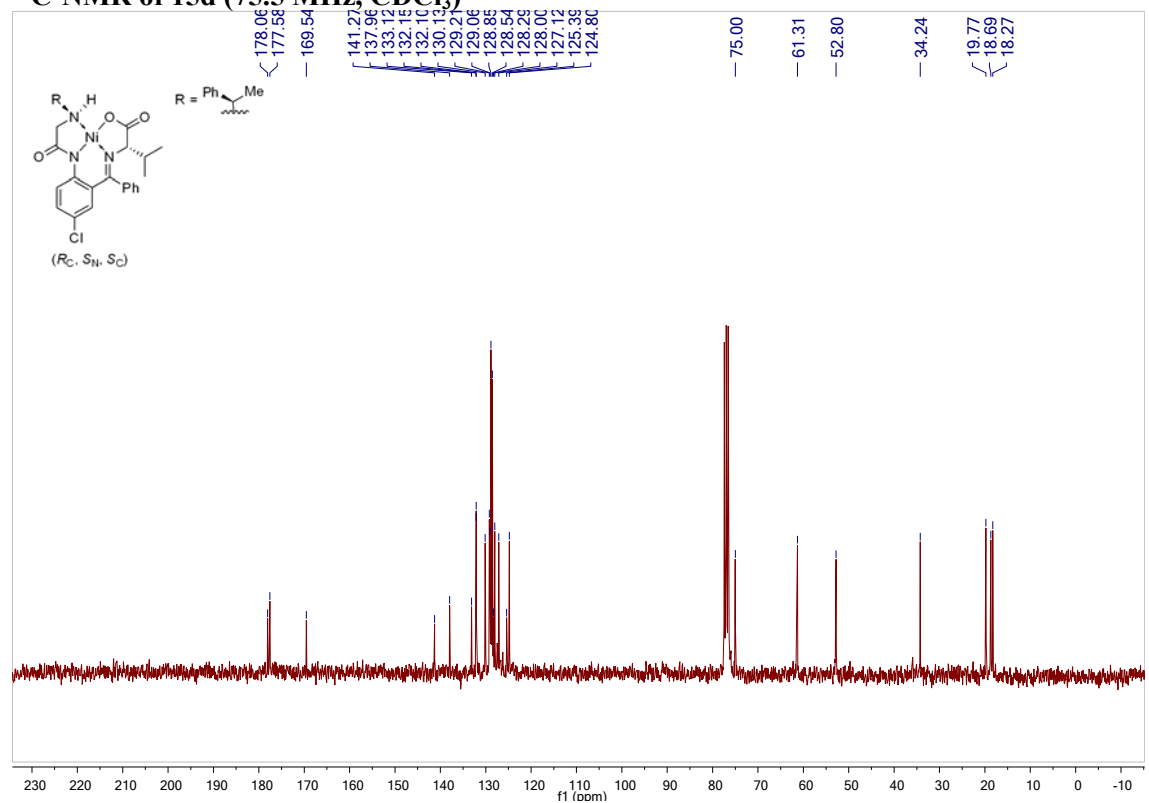
Chemical structure of the ligand **1** is shown, which is a nickel(II) complex of a 2-chlorophenyl-substituted 1,3-dioxane-5-carboxamide derivative. The structure is labeled with R_C , R_H , and R_G substituents. The structure of R is defined as $R = \text{Ph-CH(Me)-}$.

The ^1H NMR spectrum (400 MHz, CDCl_3) shows peaks at δ 7.85, 7.74, 7.60, 7.56, 7.48, 7.44, 7.32, 7.20, 7.14, 7.08, 6.96, 6.84, 6.72, 6.56, 6.44, 6.32, 6.24, 6.12, 6.04, 5.92, 5.84, 5.72, 5.60, 5.48, 5.36, 5.24, 5.12, 5.04, 4.92, 4.84, 4.72, 4.60, 4.48, 4.36, 4.24, 4.12, 4.04, 3.92, 3.84, 3.72, 3.60, 3.48, 3.36, 3.24, 3.12, 3.04, 2.92, 2.84, 2.72, 2.60, 2.48, 2.36, 2.24, 2.12, 2.04, 1.92, 1.84, 1.72, 1.60, 1.48, 1.36, 1.24, 1.12, 1.04, 0.92, 0.84, 0.72, 0.60, 0.48, 0.36, 0.24, 0.12, 0.04, -0.08, -0.16, -0.24, -0.32, -0.40, -0.48, -0.56, -0.64, -0.72, -0.80, -0.88, -0.96, -1.04, -1.12, -1.20, -1.28, -1.36, -1.44, -1.52, -1.60, -1.68, -1.76, -1.84, -1.92, -2.00, -2.08, -2.16, -2.24, -2.32, -2.40, -2.48, -2.56, -2.64, -2.72, -2.80, -2.88, -2.96, -3.04, -3.12, -3.20, -3.28, -3.36, -3.44, -3.52, -3.60, -3.68, -3.76, -3.84, -3.92, -4.00, -4.08, -4.16, -4.24, -4.32, -4.40, -4.48, -4.56, -4.64, -4.72, -4.80, -4.88, -4.96, -5.04, -5.12, -5.20, -5.28, -5.36, -5.44, -5.52, -5.60, -5.68, -5.76, -5.84, -5.92, -6.00, -6.08, -6.16, -6.24, -6.32, -6.40, -6.48, -6.56, -6.64, -6.72, -6.80, -6.88, -6.96, -7.04, -7.12, -7.20, -7.28, -7.36, -7.44, -7.52, -7.60, -7.68, -7.76, -7.84, -7.92, -8.00, -8.08, -8.16, -8.24, -8.32, -8.40, -8.48, -8.56, -8.64, -8.72, -8.80, -8.88, -8.96, -9.04, -9.12, -9.20, -9.28, -9.36, -9.44, -9.52, -9.60, -9.68, -9.76, -9.84, -9.92, -10.00, -10.08, -10.16, -10.24, -10.32, -10.40, -10.48, -10.56, -10.64, -10.72, -10.80, -10.88, -10.96, -11.04, -11.12, -11.20, -11.28, -11.36, -11.44, -11.52, -11.60, -11.68, -11.76, -11.84, -11.92, -12.00, -12.08, -12.16, -12.24, -12.32, -12.40, -12.48, -12.56, -12.64, -12.72, -12.80, -12.88, -12.96, -13.04, -13.12, -13.20, -13.28, -13.36, -13.44, -13.52, -13.60, -13.68, -13.76, -13.84, -13.92, -14.00, -14.08, -14.16, -14.24, -14.32, -14.40, -14.48, -14.56, -14.64, -14.72, -14.80, -14.88, -14.96, -15.04, -15.12, -15.20, -15.28, -15.36, -15.44, -15.52, -15.60, -15.68, -15.76, -15.84, -15.92, -16.00, -16.08, -16.16, -16.24, -16.32, -16.40, -16.48, -16.56, -16.64, -16.72, -16.80, -16.88, -16.96, -17.04, -17.12, -17.20, -17.28, -17.36, -17.44, -17.52, -17.60, -17.68, -17.76, -17.84, -17.92, -18.00, -18.08, -18.16, -18.24, -18.32, -18.40, -18.48, -18.56, -18.64, -18.72, -18.80, -18.88, -18.96, -19.04, -19.12, -19.20, -19.28, -19.36, -19.44, -19.52, -19.60, -19.68, -19.76, -19.84, -19.92, -20.00, -20.08, -20.16, -20.24, -20.32, -20.40, -20.48, -20.56, -20.64, -20.72, -20.80, -20.88, -20.96, -21.04, -21.12, -21.20, -21.28, -21.36, -21.44, -21.52, -21.60, -21.68, -21.76, -21.84, -21.92, -22.00, -22.08, -22.16, -22.24, -22.32, -22.40, -22.48, -22.56, -22.64, -22.72, -22.80, -22.88, -22.96, -23.04, -23.12, -23.20, -23.28, -23.36, -23.44, -23.52, -23.60, -23.68, -23.76, -23.84, -23.92, -24.00, -24.08, -24.16, -24.24, -24.32, -24.40, -24.48, -24.56, -24.64, -24.72, -24.80, -24.88, -24.96, -25.04, -25.12, -25.20, -25.28, -25.36, -25.44, -25.52, -25.60, -25.68, -25.76, -25.84, -25.92, -26.00, -26.08, -26.16, -26.24, -26.32, -26.40, -26.48, -26.56, -26.64, -26.72, -26.80, -26.88, -26.96, -27.04, -27.12, -27.20, -27.28, -27.36, -27.44, -27.52, -27.60, -27.68, -27.76, -27.84, -27.92, -28.00, -28.08, -28.16, -28.24, -28.32, -28.40, -28.48, -28.56, -28.64, -28.72, -28.80, -28.88, -28.96, -29.04, -29.12, -29.20, -29.28, -29.36, -29.44, -29.52, -29.60, -29.68, -29.76, -29.84, -29.92, -30.00, -30.08, -30.16, -30.24, -30.32, -30.40, -30.48, -30.56, -30.64, -30.72, -30.80, -30.88, -30.96, -31.04, -31.12, -31.20, -31.28, -31.36, -31.44, -31.52, -31.60, -31.68, -31.76, -31.84, -31.92, -32.00, -32.08, -32.16, -32.24, -32.32, -32.40, -32.48, -32.56, -32.64, -32.72, -32.80, -32.88, -32.96, -33.04, -33.12, -33.20, -33.28, -33.36, -33.44, -33.52, -33.60, -33.68, -33.76, -33.84, -33.92, -34.00, -34.08, -34.16, -34.24, -34.32, -34.40, -34.48, -34.56, -34.64, -34.72, -34.80, -34.88, -34.96, -35.04, -35.12, -35.20, -35.28, -35.36, -35.44, -35.52, -35.60, -35.68, -35.76, -35.84, -35.92, -36.00, -36.08, -36.16, -36.24, -36.32, -36.40, -36.48, -36.56, -36.64, -36.72, -36.80, -36.88, -36.96, -37.04, -37.12, -37.20, -37.28, -37.36, -37.44, -37.52, -37.60, -37.68, -37.76, -37.84, -37.92, -38.00, -38.08, -38.16, -38.24, -38.32, -38.40, -38.48, -38.56, -38.64, -38.72, -38.80, -38.88, -38.96, -39.04, -39.12, -39.20, -39.28, -39.36, -39.44, -39.52, -39.60, -39.68, -39.76, -39.84, -39.92, -40.00, -40.08, -40.16, -40.24, -40.32, -40.40, -40.48, -40.56, -40.64, -40.72, -40.80, -40.88, -40.96, -41.04, -41.12, -41.20, -41.28, -41.36, -41.44

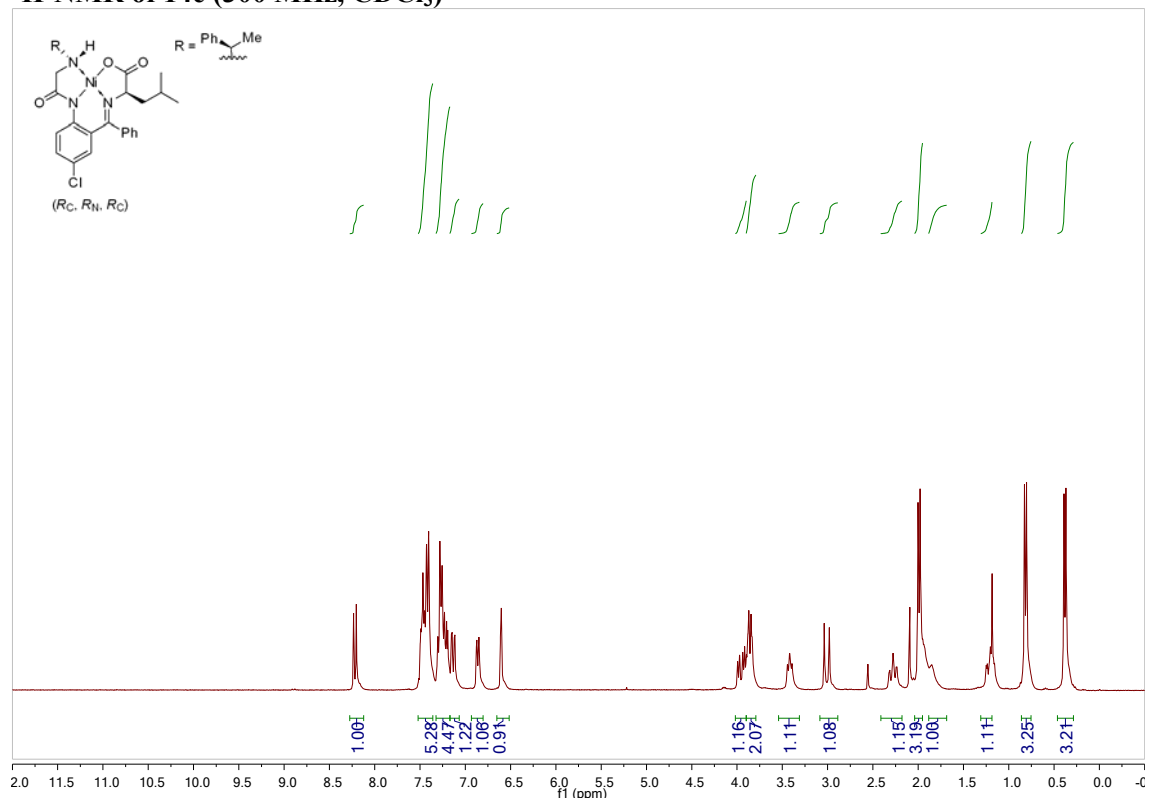
¹H-NMR of 15d (300 MHz, CDCl₃)



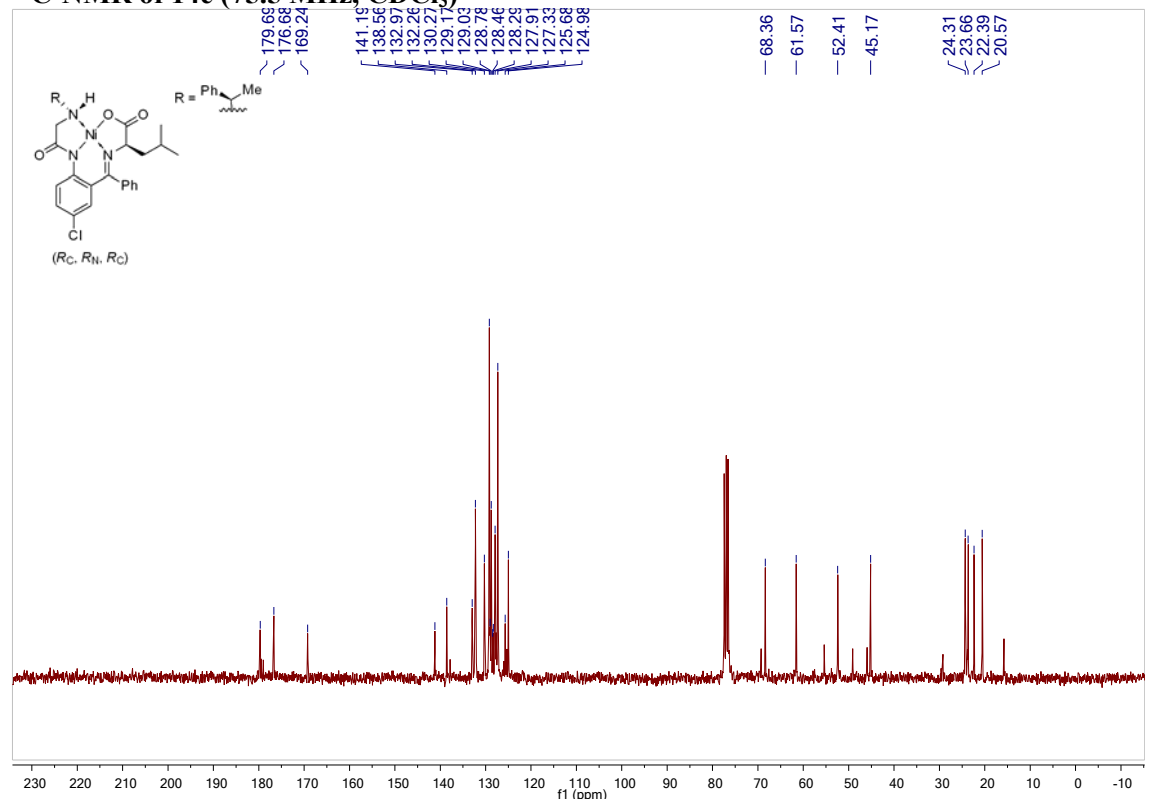
¹³C-NMR of 15d (75.5 MHz, CDCl₃)



¹H-NMR of 14e (300 MHz, CDCl₃)



¹³C-NMR of 14e (75.5 MHz, CDCl₃)



CC(C)[C@@H](C(=O)N1C(=O)N(C(=O)N1C2=CC=C(C=C2)Cl)C(=O)N(C)C)C(=O)N(C)C

 $R = \text{Ph-CH(Me)-}$

 (R_C, S_H, S_C)

^1H NMR spectrum (CDCl₃) of compound 10. The x-axis is labeled f1 (ppm) and ranges from 2.0 to -0.5. Integration values are shown below the peaks: 0.93, 2.05, 3.21, 4.34, 1.02, 1.01, 0.75, 4.13, 0.95, 0.93, 3.09, 1.08, 1.32, 3.09, 3.05.

¹³C NMR of 1b

(R_C, S_N, S_C)

Chemical structure of 1b: A macrocyclic complex with a central Ni atom coordinated by two N atoms of a 1,2-bis(phenyl)-4-chlorophenyl-1,2-dihydro-1H-imidazole-4-carboxamide derivative. The Ni atom is also coordinated by a hydrogen atom and a carbonyl oxygen of a 2-isobutyl-2-oxo-1,3-dioxolane-5-carboxamide derivative. The R group is defined as a 1-phenyl-2-methylpropyl chain.

¹³C NMR spectrum (CDCl₃):

Chemical shift (ppm): 179.88, 178.00, 169.04, 141.20, 137.92, 132.98, 132.06, 130.22, 129.20, 129.16, 128.86, 128.78, 128.38, 128.12, 127.88, 127.33, 125.42, 124.92, 68.67, 60.81, 52.11, 45.34, 24.36, 23.80, 20.58, 18.45.

Assignment: The spectrum shows peaks corresponding to the carbonyl carbons (179.88, 178.00, 169.04 ppm), aromatic carbons (141.20, 137.92, 132.98, 132.06, 130.22, 129.20, 129.16, 128.86, 128.78, 128.38, 128.12, 127.88, 127.33, 125.42, 124.92 ppm), the CDCl₃ solvent triplet (77.0 ppm), and aliphatic carbons (68.67, 60.81, 52.11, 45.34, 24.36, 23.80, 20.58, 18.45 ppm).

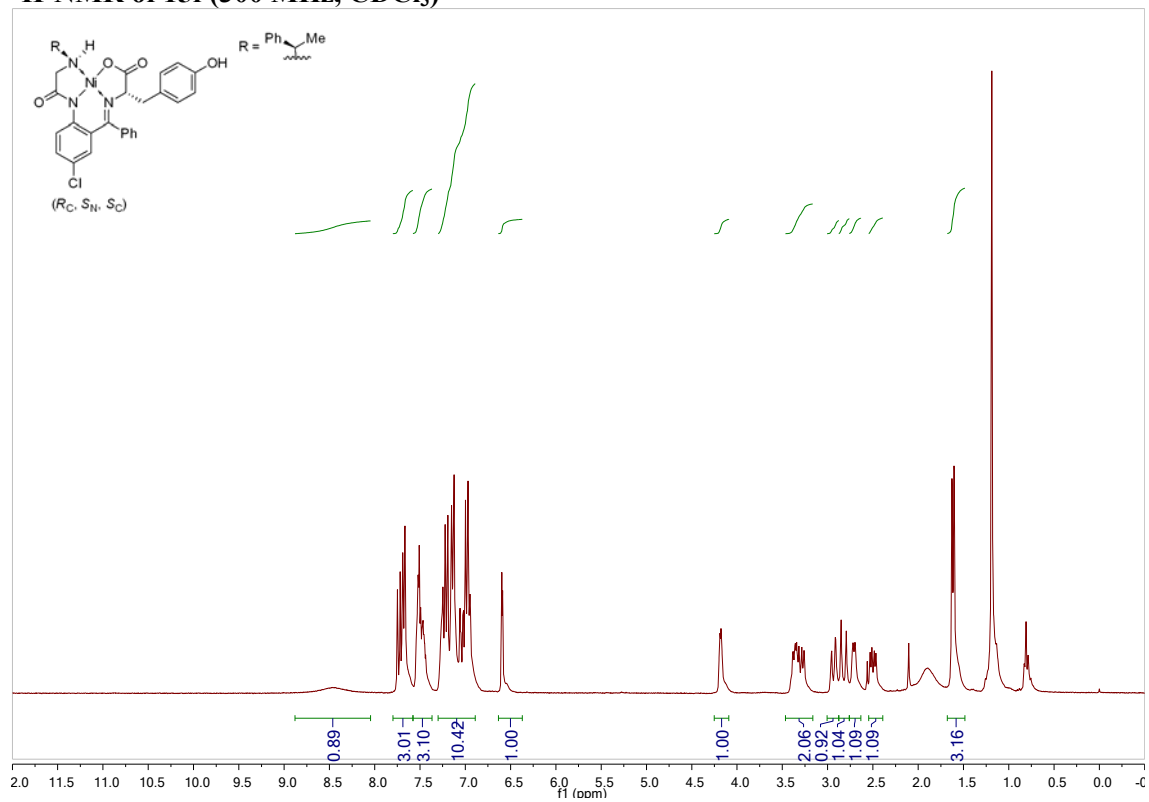
CC(C)C1=CC=C(C=C1)C2=CC=CC=C2C3=C(C(=O)N3C(=O)N(C(=O)N2C(=O)c4ccc(O)cc4)C5=CC=CC=C5)C6=CC=C(C=C6)Cl (R_C, R_H, R_D)

$R = \text{Ph} \text{---} \text{CH}(\text{Me}) \text{---}$

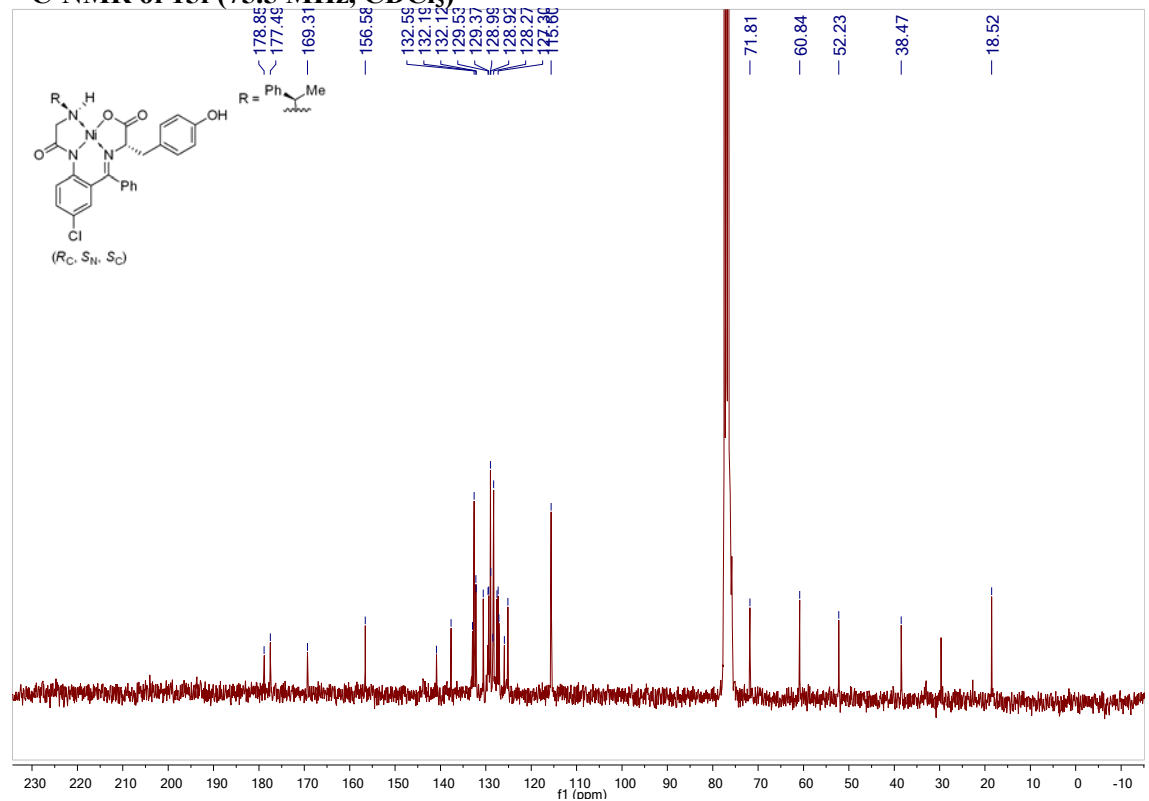
1H NMR spectrum (CDCl₃) of compound 10. The spectrum shows peaks from 0 to 8 ppm. Integration values are provided below the peaks: 0.81, 1.04, 3.22, 9.78, 1.15, 2.15, 0.89, 1.08, 1.12, 1.08, 1.13, 1.24, 2.81, and 3.13. A red vertical line marks the solvent peak at approximately 7.26 ppm.

[illegible]

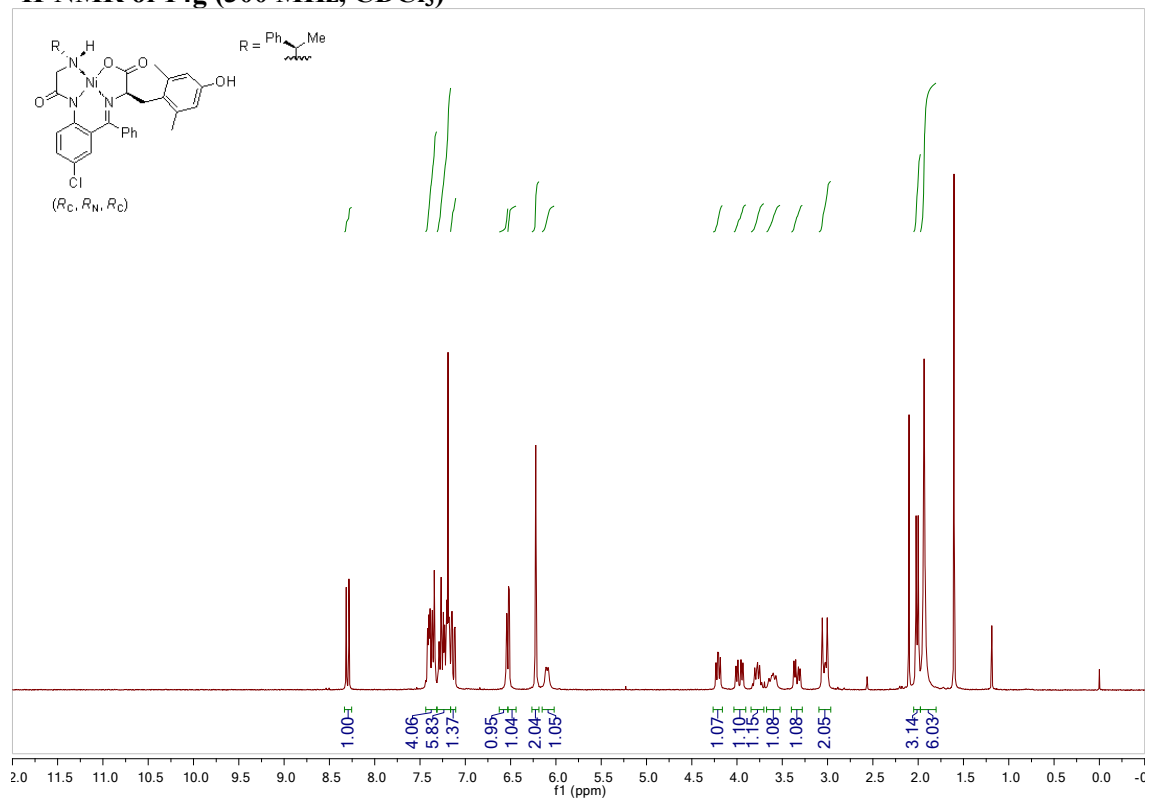
¹H-NMR of 15f (300 MHz, CDCl₃)



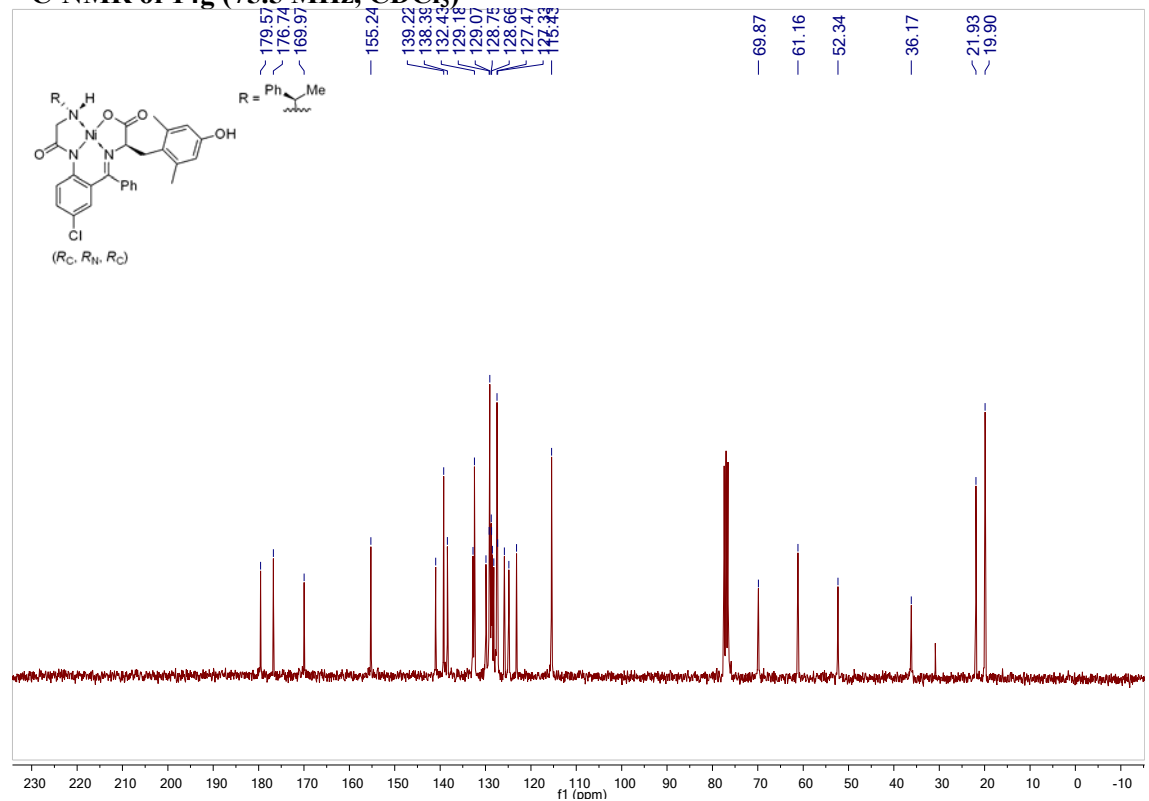
¹³C-NMR of 15f (75.5 MHz, CDCl₃)



¹H-NMR of 14g (300 MHz, CDCl₃)



¹³C-NMR of 14g (75.5 MHz, CDCl₃)



CC(C)C1=CC=C(C=C1)C2=CC=CC=C2C3=C(C=C2)OC4C(C=C3)OC(=O)N5C(=O)N(C(=O)N5C6=CC=C(C=C6)Cl)C7=CC=C(C=C7)C8=CC=C(C=C8)C=C9C(=C(C=C9)O)C

 $R = \text{Ph-CH(Me)-}$

 (R_C, S_N, S_C)

^1H NMR spectrum (CDCl_3) of compound **10**. The spectrum shows peaks corresponding to the structure, with integration values indicated below the peaks.

Chemical structure of compound 10

Chemical structure of compound 10 is shown, featuring a central metal complex (likely a macrocyclic ligand) coordinated to a metal center (M). The structure includes a phenyl group (Ph) and a methyl group (Me) attached to the metal center. The structure is labeled with (R_C, S_N, S_C) .

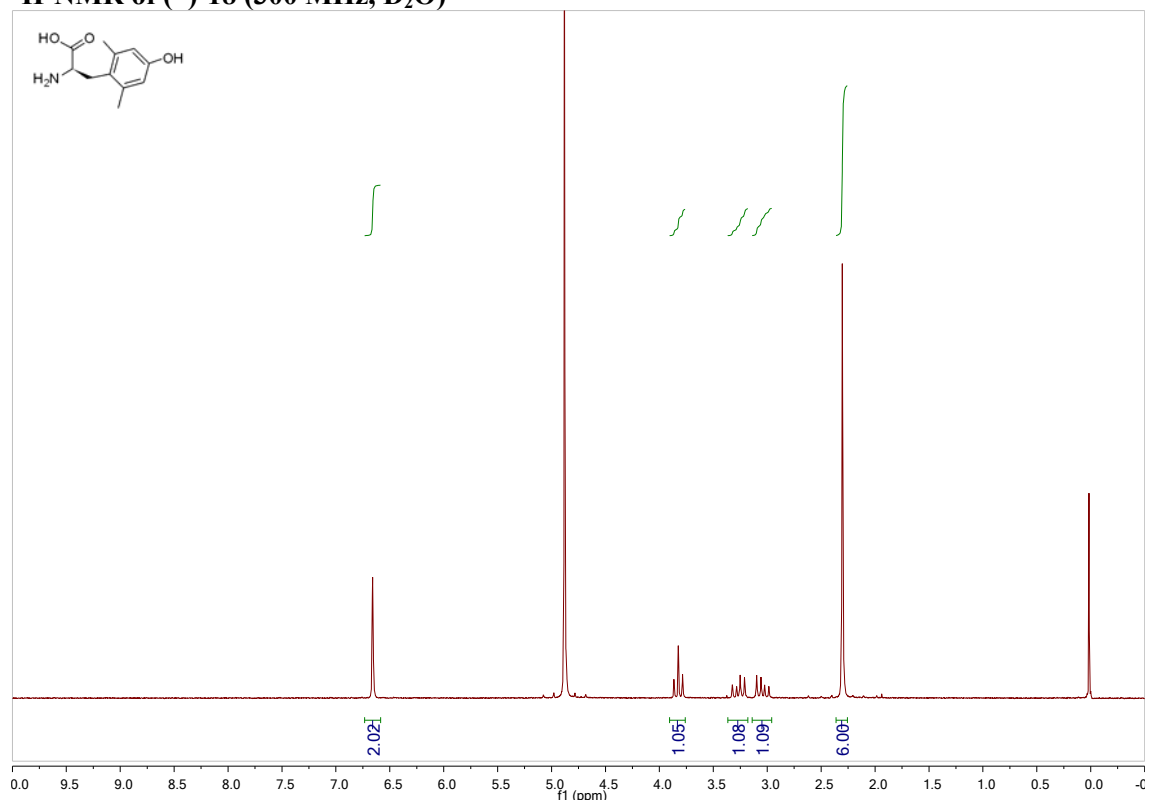
¹³C NMR spectrum of compound 10

The ¹³C NMR spectrum of compound 10 is displayed, showing peaks corresponding to the carbon atoms in the molecule. The x-axis represents the chemical shift in ppm (f1 (ppm)), ranging from -10 to 230. The spectrum shows several sharp peaks, with the most prominent ones around 170-180 ppm and 120-130 ppm.

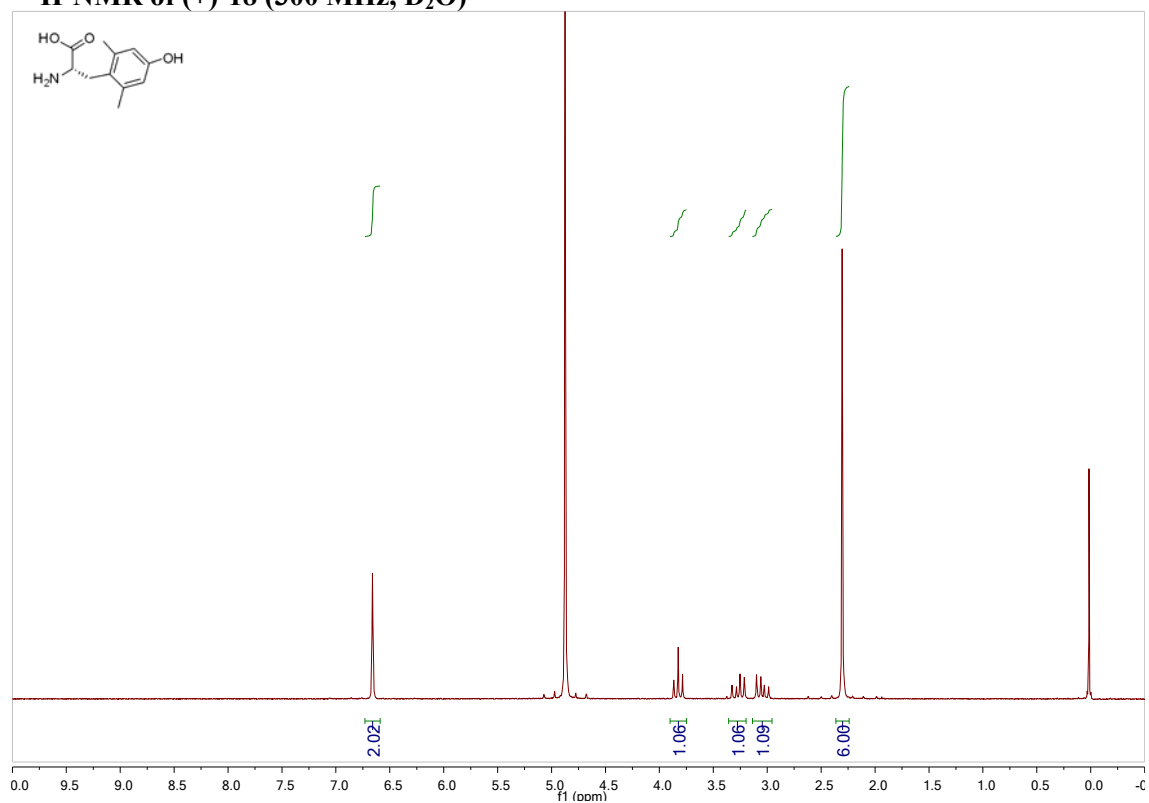
Peak list (ppm):

- 179.77
- 177.81
- 169.77
- 155.29
- 139.50
- 132.54
- 132.46
- 129.21
- 129.22
- 128.80
- 128.72
- 128.48
- 70.12
- 61.19
- 52.97
- 35.87
- 20.03
- 18.71

¹H-NMR of (–)-18 (300 MHz, D₂O)



¹H-NMR of (+)-18 (300 MHz, D₂O)



¹H-NMR of recovered (R)-9 (300 MHz, CDCl₃)

