Electronic Supplementary Information

Second-order asymmetric transformation; Application for practical synthesis of α-amino acids.

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CONTENTS

1. X-ray data of compound (S_C,R_N,R_C)-12a

Datos Físicos y Cristalográficos		Condiciones de Registro y Afinamiento	
Fórmula	$C_{35}H_{36}ClN_3NiO_3,CH_4O$ $C_{36}H_{40}ClN_3NiO_4$	Difractómetro	Agilent SuperNova Cu
M_r (g·mol^{-1})	672.85	Detector	CCD (Atlas)
Sistema cristalino	Orthorhombic	Temperatura (K)	100(1)°
Grupo espacial	$P2_12_12_1$ (No. 19)	λ (CuKα) (Å)	1.54184
a (Å)	6.2383(1)	Monocromador	Óptica multicapa
b (Å)	15.3670(2)	Colimador (mm)	0.2
c (Å)	32.9494(5)	Modo de barrido	Rotación ω
α (°)	90	Anchura de barrido (°)	1.0
β (°)	90	Tiempo por placa (s) (Total, h)	2;8 (8)
γ (°)	90	Intervalo de θ (°)	2.7-75.0
V (Å^3)	3158.66(8)	(hkl) mínimo	(–6 –19 –41)
Z	4 (Z'=1)	(hkl) máximo	(7 19 41)
F (000)	1416	Reflexiones medidas	28325
μ (CuKα) (mm^{-1})	2.026	Reflexiones independientes ($R_{int.}$)	6489(0.053)
D_x (g·cm^{-3})	1.415(1)	Reflexiones observadas [I>2σ(I)]	6227
Morfología	Aguja	Corrección de absorción	Analítica por caras
Color	Roja	Solución	OLEX2
Tamaño (mm)	0.46x 0.08x 0.05	Refinamiento	SHELXL97
		Número de parámetros	413
		Número de restricciones	0
		Δ/σ máximo	0.000
		Δ/σ media	0.000
		Δρ máximo (eÅ^{-3})	0.323
		Δρ mínimo (eÅ^{-3})	-0.331
		S (GOF)	1.043
Friedel coverage	**94%**	Coeficiente extinción secundaria[b]	0
Flack *x*	**-0.025(11)**	R(F) (I>2σ_I, todos los datos)	0.0288, 0.0308
Hooft *y*	**-0.024(8)**	$R_w(F^2)$[a] (I>2σ_I ,todos los datos)	0.0691, 0.0702
P2(wrong)	**$<10^{-99}$**		

[a] Esquema de pesado: $1/[\sigma^2(F_o^2)+(0.0343P)^2+0.2930P]$ donde $P = [Max(F_o^2,0)+2F_c^2]/3$.

[b] Expresión de extinción secundaria tipo SHELXL: $F_c^* = kF_c[1+0.001F_c^2\lambda^3 /sen(2\theta)]^{-1/4}$

[9] M;acrae, C. F., J. Appl. Cryst. 2008, 41, 466
[10] A. L. Spek (2010) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands; A. L. Spek, J. Appl. Cryst. 2003, 36, 7
[11] Farrugia, L. J., J. Appl. Cryst. 1999, 32, 837

Estructura molecular y cristalina de *SOLO1PHG*

En la unidad asimétrica de *SOLO1PHG* existe una molécula (Figura 1) coincidente con la molécula de interés. La configuración absoluta de átomos de carbono asimétricos presentes en la molécula N3, C2, C24 y C32 es *R*, *R*, *S* y *S*, respectivamente, ha sido asignada automáticamente por un programa, por favor, comprobarlo. Además del compuesto de interés existe una molécula de metanol de cristalización en la unidad asimétrica.

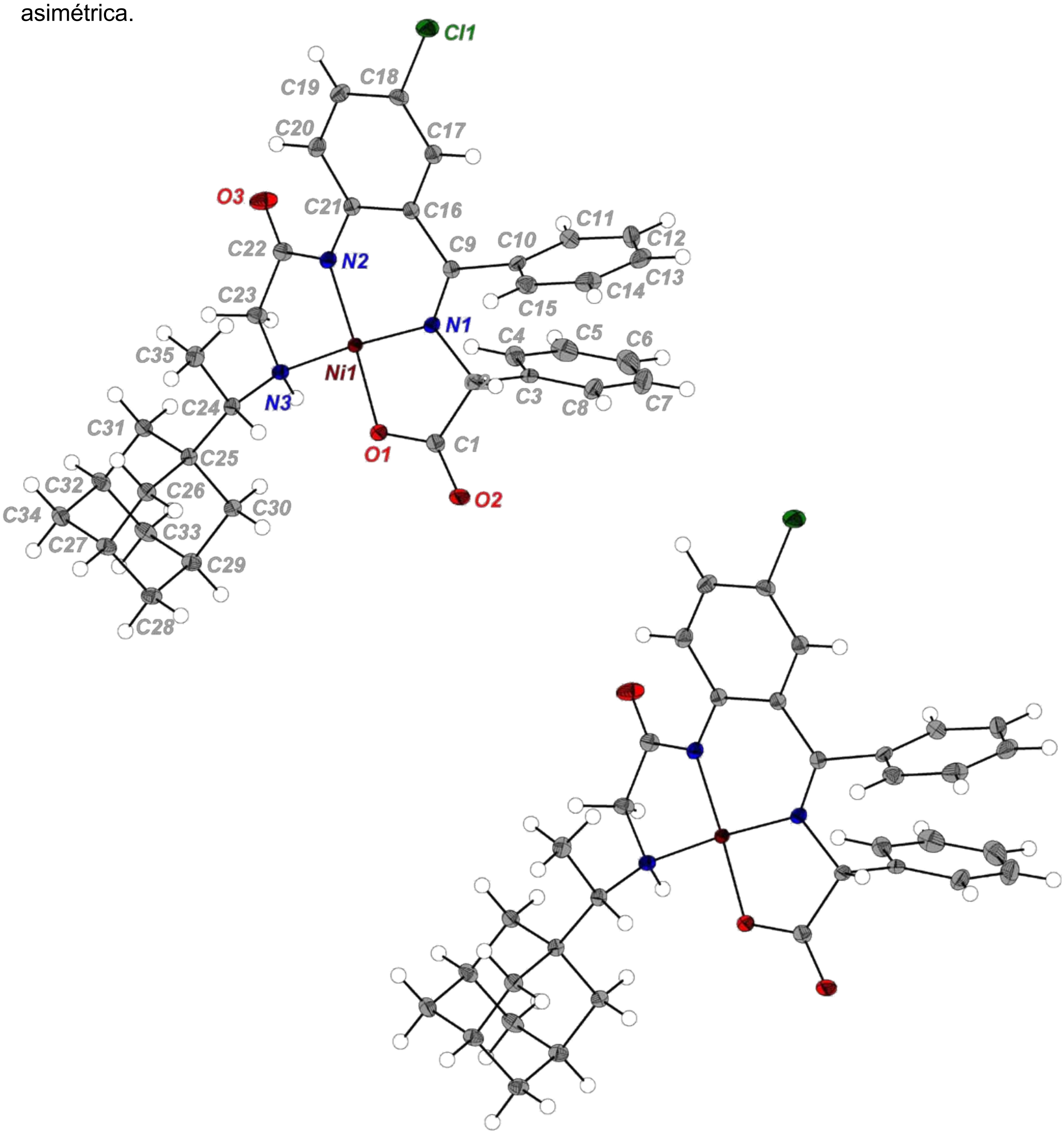


Figura 1. Diagrama ORTEP con los elipsoides térmicos al 50% de probabilidad de la molécula de interés de *SOLO1PHG* que está presente en la unidad asimétrica, con y sin nomenclatura de los átomos.

El empaquetamiento cristalino de la estructura a lo largo de los ejes cristalográficos a, b y c puede visualizarse en la figura 2. Se adjunta al informe un archivo con las tablas de los valores de las distancias de enlace, ángulos de enlace y ángulos de torsión de la molécula presentes en la estructura. También se incluyen los valores de las posibles interacciones de hidrogeno presentes en la estructura.

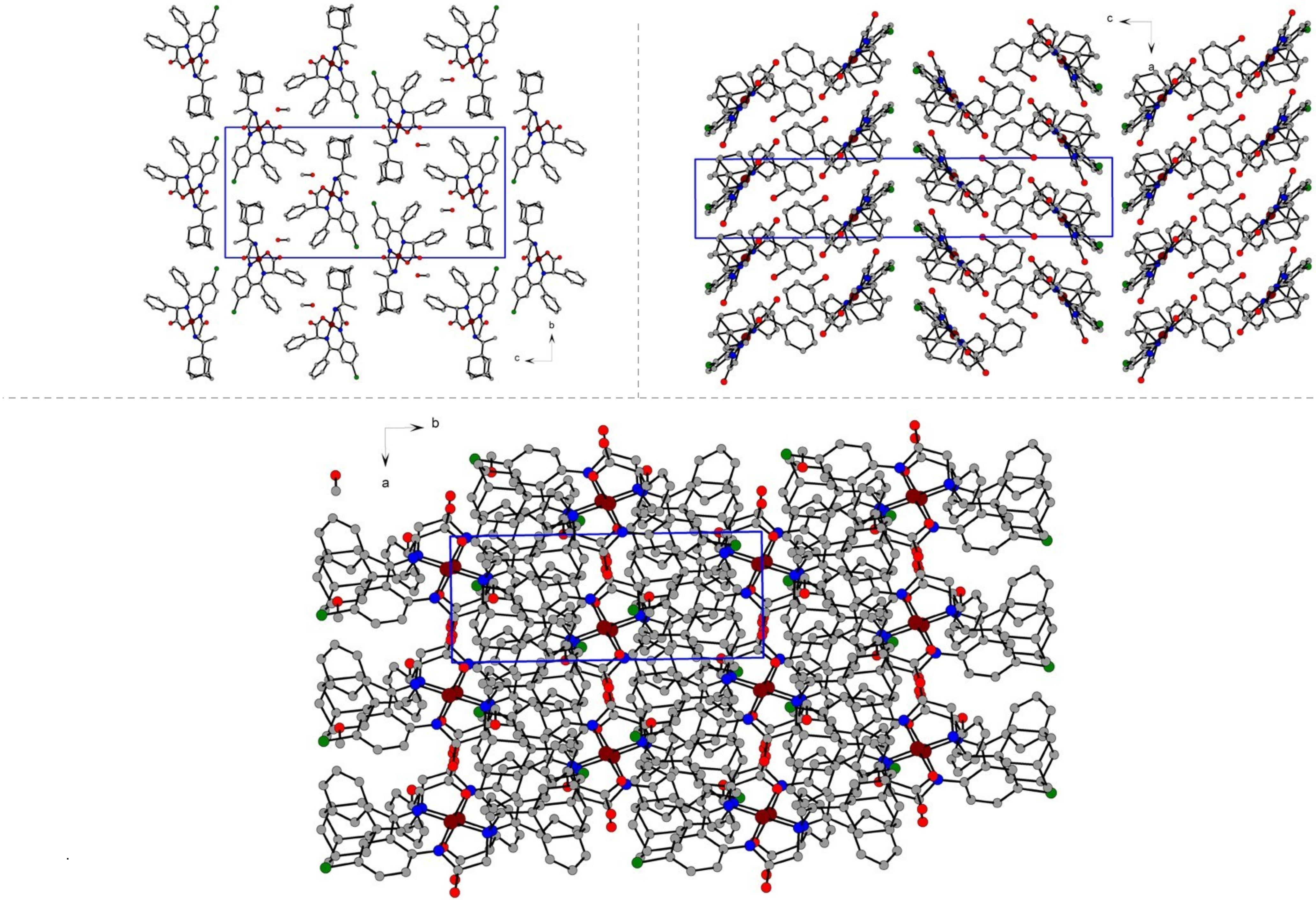


Figura 2. Vistas de la estructura cristalina de *SOLO1PHG* a lo largo de los ejes cristalográficos a, b y c, respectivamente. Los átomos de hidrógeno han sido eliminados por claridad

Table S1 - Crystal Data and Details of the Structure Determination
for: a2014151_solo1phg R = 0.03

Crystal Data

Formula	C35 H36 Cl N3 Ni O3, C H4 O
Formula Weight	672.85
Crystal System	Orthorhombic
Space group	P212121 (No. 19)
a, b, c [Angstrom]	6.2383(1) 15.3670(2) 32.9494(5)
V [Ang**3]	3158.66(8)
Z	4
D(calc) [g/cm**3]	1.415
Mu(CuKa) [/mm]	2.026
F(000)	1416
Crystal Size [mm]	0.46x 0.08x 0.05

Data Collection

Temperature (K)	100
Radiation [Angstrom] CuKa	1.54184
Theta Min-Max [Deg]	2.7, 75.0
Dataset	-6: 7 ; -19: 19 ; -41: 41
Tot., Uniq. Data, R(int)	28325, 6489, 0.053
Observed data [I > 2.0 sigma(I)]	6227

Refinement

Nref, Npar	6489, 413
R, wR2, S	0.0288, 0.0702, 1.04
w = 1/[\s^2^(Fo^2^)+(0.0343P)^2^+0.2930P] where P=(Fo^2^+2Fc^2^)/3	
Max. and Av. Shift/Error	0.00, 0.00
Flack x	-0.025(11)
Hooft y	-0.024(8)
Min. and Max. Resd. Dens. [e/Ang^3]	-0.33, 0.32

Table S5 - Bond Distances (Angstrom)
for: a2014151_solo1phg R = 0.03

Ni1-O1	1.8709(13)	C10-C15	1.394(3)
Ni1-N1	1.8523(14)	C11-C12	1.397(3)
Ni1-N2	1.8518(13)	C12-C13	1.385(3)
Ni1-N3	1.9142(14)	C13-C14	1.386(3)
Cl1-C18	1.7421(18)	C14-C15	1.392(3)
O1-C1	1.284(2)	C16-C17	1.416(2)
O2-C1	1.226(2)	C16-C21	1.430(2)
O3-C22	1.218(2)	C17-C18	1.371(2)
O1D-C1D	1.425(3)	C18-C19	1.390(3)
O1D-H1D	0.8400	C19-C20	1.379(3)
N1-C2	1.488(2)	C20-C21	1.417(2)
N1-C9	1.292(2)	C22-C23	1.517(2)
N2-C21	1.392(2)	C24-C35	1.527(2)
N2-C22	1.380(2)	C24-C25	1.552(2)
N3-C24	1.504(2)	C25-C30	1.546(2)
N3-C23	1.481(2)	C25-C26	1.544(3)
N3-H3	0.85(3)	C25-C31	1.536(3)
C1-C2	1.533(3)	C26-C27	1.536(3)
C2-C3	1.518(2)	C27-C34	1.529(3)
C3-C4	1.399(3)	C27-C28	1.531(2)
C3-C8	1.386(3)	C28-C29	1.527(3)
C4-C5	1.394(3)	C29-C30	1.543(2)
C5-C6	1.383(3)	C29-C33	1.535(3)
C6-C7	1.389(3)	C31-C32	1.550(2)
C7-C8	1.390(3)	C32-C33	1.530(3)
C9-C16	1.469(2)	C32-C34	1.535(3)
C9-C10	1.501(2)	C2-H2	1.0000
C10-C11	1.393(2)	C4-H4	0.9500
C5-H5	0.9500	C28-H28B	0.9900
C6-H6	0.9500	C28-H28A	0.9900
C7-H7	0.9500	C29-H29	1.0000
C8-H8	0.9500	C30-H30B	0.9900
C11-H11	0.9500	C30-H30A	0.9900
C12-H12	0.9500	C31-H31A	0.9900
C13-H13	0.9500	C31-H31B	0.9900
C14-H14	0.9500	C32-H32	1.0000
C15-H15	0.9500	C33-H33B	0.9900
C17-H17	0.9500	C33-H33A	0.9900
C19-H19	0.9500	C34-H34B	0.9900
C20-H20	0.9500	C34-H34A	0.9900
C23-H23B	0.9900	C35-H35C	0.9800

C23-H23A	0.9900	C35-H35A	0.9800
C24-H24	1.0000	C35-H35B	0.9800
C26-H26A	0.9900	C1D-H1DA	0.9800
C26-H26B	0.9900	C1D-H1DB	0.9800
C27-H27	1.0000	C1D-H1DC	0.9800

Table S6 - Bond Angles (Degrees)
for: a2014151_solo1phg R = 0.03

O1-Ni1-N1	87.77(6)	C4-C3-C8	119.46(16)
O1-Ni1-N2	176.21(6)	C3-C4-C5	120.02(18)
O1-Ni1-N3	88.02(6)	C4-C5-C6	120.0(2)
N1-Ni1-N2	95.75(6)	C5-C6-C7	120.2(2)
N1-Ni1-N3	174.58(6)	C6-C7-C8	119.94(19)
N2-Ni1-N3	88.38(6)	C3-C8-C7	120.38(18)
Ni1-O1-C1	115.23(11)	N1-C9-C16	122.13(14)
C1D-O1D-H1D	110.00	N1-C9-C10	119.80(14)
Ni1-N1-C2	110.75(10)	C10-C9-C16	118.07(14)
C2-N1-C9	120.22(13)	C9-C10-C15	119.46(15)
Ni1-N1-C9	128.83(11)	C9-C10-C11	120.62(16)
Ni1-N2-C22	113.84(12)	C11-C10-C15	119.89(16)
C21-N2-C22	120.70(14)	C10-C11-C12	119.82(18)
Ni1-N2-C21	125.39(12)	C11-C12-C13	120.15(19)
Ni1-N3-C23	107.75(10)	C12-C13-C14	119.98(18)
C23-N3-C24	117.43(13)	C13-C14-C15	120.37(18)
Ni1-N3-C24	111.54(9)	C10-C15-C14	119.79(17)
C23-N3-H3	105.0(17)	C9-C16-C21	124.02(15)
Ni1-N3-H3	103.7(16)	C17-C16-C21	118.88(16)
C24-N3-H3	110.4(16)	C9-C16-C17	117.10(15)
O1-C1-O2	125.50(17)	C16-C17-C18	121.02(16)
O2-C1-C2	119.15(16)	Cl1-C18-C19	118.40(14)
O1-C1-C2	115.33(15)	Cl1-C18-C17	120.73(13)
N1-C2-C3	110.75(14)	C17-C18-C19	120.87(16)
N1-C2-C1	108.33(13)	C18-C19-C20	119.49(17)
C1-C2-C3	109.20(14)	C19-C20-C21	122.02(17)
C2-C3-C8	120.11(16)	C16-C21-C20	117.63(15)
C2-C3-C4	120.43(16)	N2-C21-C16	121.34(15)
N2-C21-C20	121.00(15)	C27-C34-C32	109.13(15)
N2-C22-C23	113.22(15)	N1-C2-H2	109.00
O3-C22-N2	127.87(16)	C3-C2-H2	110.00
O3-C22-C23	118.88(16)	C1-C2-H2	109.00
N3-C23-C22	112.14(14)	C3-C4-H4	120.00
N3-C24-C35	109.38(13)	C5-C4-H4	120.00
N3-C24-C25	114.11(13)	C6-C5-H5	120.00
C25-C24-C35	115.49(14)	C4-C5-H5	120.00
C26-C25-C31	108.26(14)	C5-C6-H6	120.00
C24-C25-C31	115.13(14)	C7-C6-H6	120.00
C26-C25-C30	108.16(14)	C8-C7-H7	120.00
C24-C25-C26	107.63(13)	C6-C7-H7	120.00
C24-C25-C30	109.69(13)	C3-C8-H8	120.00

C30-C25-C31	107.77(14)	C7-C8-H8	120.00
C25-C26-C27	111.13(14)	C12-C11-H11	120.00
C26-C27-C34	108.60(15)	C10-C11-H11	120.00
C28-C27-C34	110.15(15)	C11-C12-H12	120.00
C26-C27-C28	110.03(14)	C13-C12-H12	120.00
C27-C28-C29	109.48(15)	C12-C13-H13	120.00
C28-C29-C30	108.98(14)	C14-C13-H13	120.00
C30-C29-C33	109.47(14)	C15-C14-H14	120.00
C28-C29-C33	109.41(14)	C13-C14-H14	120.00
C25-C30-C29	111.12(13)	C14-C15-H15	120.00
C25-C31-C32	110.49(15)	C10-C15-H15	120.00
C31-C32-C34	110.27(15)	C18-C17-H17	120.00
C31-C32-C33	109.00(14)	C16-C17-H17	119.00
C33-C32-C34	109.24(15)	C18-C19-H19	120.00
C29-C33-C32	109.65(15)	C20-C19-H19	120.00
C19-C20-H20	119.00	C29-C30-H30B	109.00
C21-C20-H20	119.00	H30A-C30-H30B	108.00
N3-C23-H23B	109.00	C25-C30-H30A	109.00
C22-C23-H23A	109.00	C25-C31-H31A	110.00
C22-C23-H23B	109.00	C25-C31-H31B	110.00
H23A-C23-H23B	108.00	C32-C31-H31B	110.00
N3-C23-H23A	109.00	H31A-C31-H31B	108.00
N3-C24-H24	106.00	C32-C31-H31A	110.00
C25-C24-H24	106.00	C31-C32-H32	110.00
C35-C24-H24	106.00	C34-C32-H32	109.00
C25-C26-H26B	109.00	C33-C32-H32	109.00
C27-C26-H26A	109.00	C29-C33-H33A	110.00
C27-C26-H26B	109.00	C32-C33-H33A	110.00
H26A-C26-H26B	108.00	C32-C33-H33B	110.00
C25-C26-H26A	109.00	H33A-C33-H33B	108.00
C26-C27-H27	109.00	C29-C33-H33B	110.00
C28-C27-H27	109.00	C27-C34-H34A	110.00
C34-C27-H27	109.00	C32-C34-H34A	110.00
C27-C28-H28B	110.00	C32-C34-H34B	110.00
C29-C28-H28A	110.00	C27-C34-H34B	110.00
C27-C28-H28A	110.00	H34A-C34-H34B	108.00
H28A-C28-H28B	108.00	C24-C35-H35B	109.00
C29-C28-H28B	110.00	C24-C35-H35C	109.00
C28-C29-H29	110.00	C24-C35-H35A	110.00
C33-C29-H29	110.00	H35A-C35-H35C	109.00
C30-C29-H29	110.00	H35B-C35-H35C	110.00
C25-C30-H30B	109.00	H35A-C35-H35B	109.00
C29-C30-H30A	109.00	O1D-C1D-H1DA	109.00
O1D-C1D-H1DB	109.00	H1DA-C1D-H1DC	109.00
O1D-C1D-H1DC	109.00	H1DB-C1D-H1DC	110.00
H1DA-C1D-H1DB	109.00		

Table S7 - Torsion Angles (Degrees)
for: a2014151_solo1phg R = 0.03

N1-Ni1-O1-C1	-5.17(13)
N3-Ni1-O1-C1	171.40(13)
O1-Ni1-N1-C2	12.90(11)
O1-Ni1-N1-C9	-172.33(14)
N2-Ni1-N1-C2	-165.69(11)
N2-Ni1-N1-C9	9.09(14)
N1-Ni1-N2-C21	-17.42(14)
N1-Ni1-N2-C22	159.38(11)
N3-Ni1-N2-C21	166.11(13)
N3-Ni1-N2-C22	-17.09(12)
O1-Ni1-N3-C23	-159.02(11)
O1-Ni1-N3-C24	70.72(10)
N2-Ni1-N3-C23	19.79(11)
N2-Ni1-N3-C24	-110.48(10)
Ni1-O1-C1-O2	177.66(14)
Ni1-O1-C1-C2	-4.13(19)
Ni1-N1-C2-C1	-17.07(16)
Ni1-N1-C2-C3	102.67(13)
C9-N1-C2-C1	167.64(14)
C9-N1-C2-C3	-72.62(18)
Ni1-N1-C9-C10	-177.38(11)
Ni1-N1-C9-C16	1.8(2)
C2-N1-C9-C10	-3.0(2)
C2-N1-C9-C16	176.13(14)
Ni1-N2-C21-C16	15.4(2)
Ni1-N2-C21-C20	-162.42(13)
C22-N2-C21-C16	-161.23(16)
C22-N2-C21-C20	21.0(2)
Ni1-N2-C22-O3	-168.71(16)
Ni1-N2-C22-C23	9.40(18)
C21-N2-C22-O3	8.3(3)
C21-N2-C22-C23	-173.63(15)
Ni1-N3-C23-C22	-18.89(17)
C24-N3-C23-C22	108.02(16)
Ni1-N3-C24-C25	-152.25(11)
Ni1-N3-C24-C35	76.68(13)
C23-N3-C24-C25	82.71(17)
C23-N3-C24-C35	-48.36(18)
O1-C1-C2-N1	13.9(2)
O1-C1-C2-C3	-106.78(17)
O2-C1-C2-N1	-167.73(15)
O2-C1-C2-C3	71.6(2)

N1-C2-C3-C4	-45.4(2)
N1-C2-C3-C8	133.84(17)
C1-C2-C3-C4	73.8(2)
C1-C2-C3-C8	-106.95(19)
C2-C3-C4-C5	179.70(17)
C8-C3-C4-C5	0.4(3)
C2-C3-C8-C7	-178.21(17)
C4-C3-C8-C7	1.1(3)
C3-C4-C5-C6	-1.3(3)
C4-C5-C6-C7	0.8(3)
C5-C6-C7-C8	0.7(3)
C6-C7-C8-C3	-1.7(3)
N1-C9-C10-C11	99.56(19)
N1-C9-C10-C15	-78.4(2)
C16-C9-C10-C11	-79.6(2)
C16-C9-C10-C15	102.45(19)
N1-C9-C16-C17	171.69(15)
N1-C9-C16-C21	-8.7(3)
C10-C9-C16-C17	-9.1(2)
C10-C9-C16-C21	170.51(16)
C9-C10-C11-C12	-176.96(16)
C15-C10-C11-C12	1.0(3)
C9-C10-C15-C14	177.48(17)
C11-C10-C15-C14	-0.5(3)
C10-C11-C12-C13	-0.6(3)
C11-C12-C13-C14	-0.2(3)
C12-C13-C14-C15	0.7(3)
C13-C14-C15-C10	-0.4(3)
C9-C16-C17-C18	-179.79(16)
C21-C16-C17-C18	0.6(3)
C9-C16-C21-N2	-0.3(3)
C9-C16-C21-C20	177.54(16)
C17-C16-C21-N2	179.32(16)
C17-C16-C21-C20	-2.8(3)
C16-C17-C18-Cl1	-178.99(14)
C16-C17-C18-C19	1.8(3)
Cl1-C18-C19-C20	179.08(14)
C17-C18-C19-C20	-1.6(3)
C18-C19-C20-C21	-0.8(3)
C19-C20-C21-N2	-179.13(17)
C19-C20-C21-C16	3.0(3)
O3-C22-C23-N3	-174.77(16)
N2-C22-C23-N3	6.9(2)
N3-C24-C25-C26	174.98(12)

N3-C24-C25-C30	57.52(18)
N3-C24-C25-C31	-64.21(18)
C35-C24-C25-C26	-57.01(17)
C35-C24-C25-C30	-174.46(14)
C35-C24-C25-C31	63.81(18)
C24-C25-C26-C27	-175.51(13)
C30-C25-C26-C27	-57.06(18)
C31-C25-C26-C27	59.46(18)
C24-C25-C30-C29	175.16(14)
C26-C25-C30-C29	58.03(19)
C31-C25-C30-C29	-58.80(19)
C24-C25-C31-C32	-177.58(14)
C26-C25-C31-C32	-57.11(17)
C30-C25-C31-C32	59.66(18)
C25-C26-C27-C28	58.98(19)
C25-C26-C27-C34	-61.66(18)
C26-C27-C28-C29	-59.98(19)
C34-C27-C28-C29	59.72(19)
C26-C27-C34-C32	60.70(18)
C28-C27-C34-C32	-59.86(19)
C27-C28-C29-C30	60.31(18)
C27-C28-C29-C33	-59.35(18)
C28-C29-C30-C25	-60.45(19)
C33-C29-C30-C25	59.17(19)
C28-C29-C33-C32	60.14(18)
C30-C29-C33-C32	-59.22(18)
C25-C31-C32-C33	-61.32(18)
C25-C31-C32-C34	58.59(19)
C31-C32-C33-C29	60.15(19)
C34-C32-C33-C29	-60.39(18)
C31-C32-C34-C27	-59.79(19)
C33-C32-C34-C27	59.98(18)

Table S9 - Hydrogen Bonds (Angstrom, Deg)

for: a2014151_solo1phg R = 0.03

O1D-H1D···O2	0.8400	1.9000	2.7217(18)	165.00	1_655
N3-H3···O1D	0.85(3)	2.11(3)	2.8660(19)	147(2)	.
C4-H4···O2	0.9500	2.5900	3.323(2)	134.00	1_655
C20-H20···O3	0.9500	2.1500	2.726(2)	118.00	.
C24-H24···O1	1.0000	2.5200	3.082(2)	115.00	.
C24-H24···O3	1.0000	2.5800	3.338(2)	132.00	1_455
C32-H32···Cl1	1.0000	2.7800	3.5422(18)	133.00	1_545

Translation of Symmetry Code to Equiv.Pos

a =[1455.00] = [1_455] =-1+x,y,z
b =[1565.00] = [1_565] =x,1+y,z
c =[3465.00] = [3_465] =-1/2+x,3/2-y,-z
e =[1655.00] = [1_655] =1+x,y,z
f =[4755.00] = [4_755] =2-x,1/2+y,1/2-z
g =[4655.00] = [4_655] =1-x,1/2+y,1/2-z
h =[3455.00] = [3_455] =-1/2+x,1/2-y,-z
i =[4645.00] = [4_645] =1-x,-1/2+y,1/2-z
j =[1545.00] = [1_545] =x,-1+y,z
k =[3555.00] = [3_555] =1/2+x,1/2-y,-z
l =[4755.00] = [4_755] =2-x,1/2+y,1/2-z
m =[4655.00] = [4_655] =1-x,1/2+y,1/2-z
n =[3565.00] = [3_565] =1/2+x,3/2-y,-z
o =[4745.00] = [4_745] =2-x,-1/2+y,1/2-z

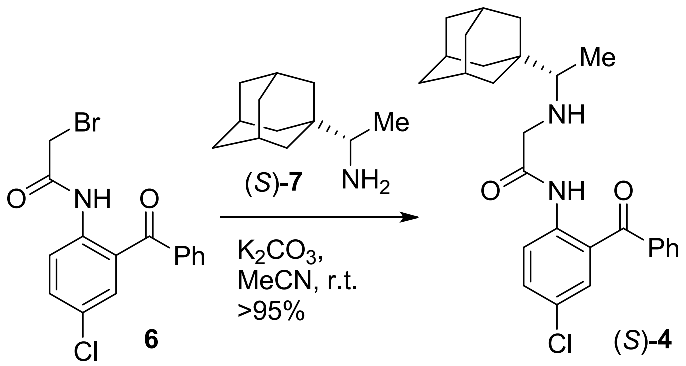
2. Experimental procedures and characterization data

General methods

All reagents and solvents were used as received. Reactions were magnetically stirred and monitored with the aid of thin-layer chromatography (TLC) on precoated silica gel plates, and visualization was carried out using UV light and ninhydrin. Flash chromatography was performed with the indicated solvents on silica gel (particle size 0.040-0.063 mm). Yields reported are for isolated, spectroscopically pure compounds. ^{1}H and ^{13}C spectra were recorded on a 300 MHz Brüker instrument. Chemical shifts are given in ppm (δ), referenced to the residual proton resonances of the solvents. Coupling constants (J) are given in hertz (Hz). The letters s, d, t, q, m, and br stand for singlet, doublet, triplet, quartet, multiplet, and broad, respectively. High-resolution mass spectra (HRMS) were recorded using an UPLC/Q-TOF MS system in the ESI mode.

(*S*)-*N*-(2-benzoyl-4-chlorophenyl)-2-(1-(1-adamantyl)ethylamino)acetamide (4)

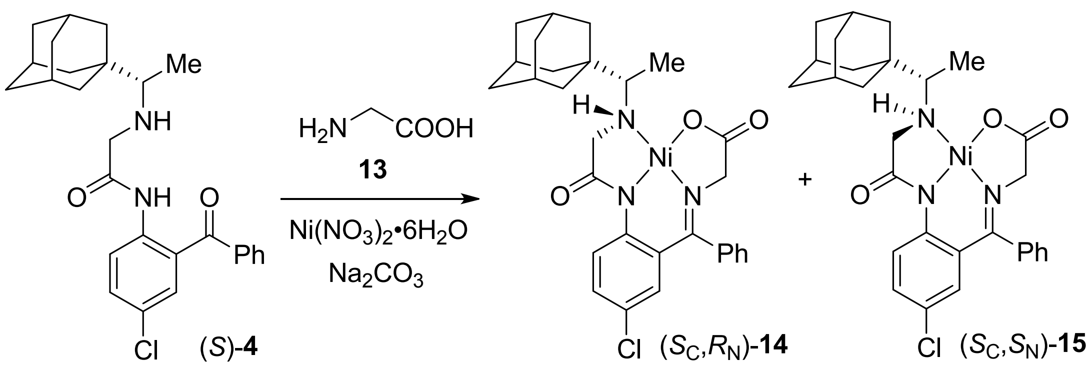
To a mixture of amide **6** (34.0 g, 96.4 mmol), (*S*)-rimantadine (20.7 g, 115.7 mmol) and acetonitrile (1020 mL) was added potassium carbonate (26.7 g, 192.9 mmol). The reaction mixture was stirred at room temperature for 15 hours (monitored by TLC). The insoluble salts were filtered off and washed with acetonitrile. The filtrate was concentrated under reduced pressure. Dichloromethane (100 mL) and water (100 mL) was added to the residue and separated. Aqueous layer was extracted with dichloromethane (100 mL), then combined organic layer was dried over sodium sulphate and evaporated. The obtained product was purified by column chromatography to afford ligand (*S*)-**4** as a corresponding acetamide.



Yield: 97.3%. $[\alpha]_D^{25}$ = +42 (c = 1.037, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (d, J = 6.6 Hz, 3H), 1.44 (d, J = 11.9 Hz, 3H), 1.53-1.62 (m, 9H), 1.84 (dr, 3H), 2.02 (q, J = 6.6 Hz, 1H), 3.24 (d, J = 17.4 Hz, 1H), 3.39 (d, J = 17.4 Hz, 1H), 7.37 (d, J = 17.4 Hz, 1H), 7.39-7.46 (m, 3H), 7.55 (tt, J = 1.3, 7.4 Hz, 1H), 7.66-7.73 (m, 2H), 8.52 (d, J = 8.8 Hz, 1H), 11.11 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ14.1, 28.9, 36.6, 37.6, 38.9, 53.3, 64.4, 123.6, 127.5, 127.9, 128.9, 130.6, 131.6, 133.2, 133.5, 137.6, 137.9, 172.6, 196.6. HRMS calcd for $C_{27}H_{32}ClN_2O_2$ $[M + H]^+$ 451.2152, found 451.2155.

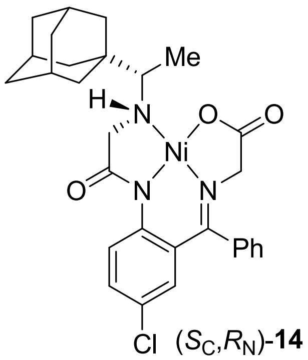
Procedure for preparation of Ni(II) complexes by reaction of ligand (*S*)-4 with glycine.

To a mixture of ligand (*S*)-**4** (3.0 g, 6.65 mmol), nickel(II) nitrate hexahydrate (2.1 g, 7.32 mmol), glycine (0.55 g, 7.32 mmol) and methanol (120 mL) was added sodium carbonate (7.1 g, 66.5 mmol) and the reaction mixture was stirred at reflux for 4 hours. After the ligand (*S*)-**4** was consumed, the reaction was quenched by pouring icy 5% aqueous acetic acid (450 mL) to give a precipitate. The precipitate was filtrated, washed with 5% aqueous acetic acid and dried *in vacuo* at 50 °C overnight to afford the diastereomixture of Ni(II) complex (S_C, R_N)-**14** and (S_C, S_N)-**15**.



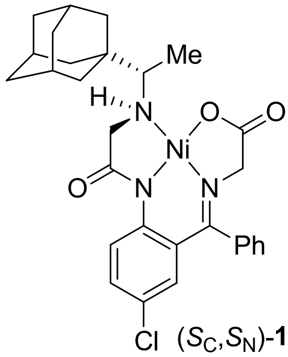
Yield: quantitative. A 85:15 mixture of two diastereomers was obtained, and pure fractions of (S_C, R_N)-**14** and (S_C, S_N)-**15** were isolated for characterization purposes.

(S_C, R_N)-14



$[\alpha]_D^{25}$ = –1901 (c = 0.055, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.45 (d, J = 10.8 Hz, 3H), 1.29-1.75 (m, 12H), 1.94 (s, 3H), 3.01 (q, J = 7.1 Hz, 1H), 3.26 (d, J = 17.1 Hz, 1H), 3.35 (d, J = 8.3 Hz, 1H), 3.57 (dd, J = 8.3, 17.1 Hz, 1H), 3.66 (s, 2H), 6.77 (d, J = 2.5 Hz, 1H), 6.86-6.93 (m, 1H), 7.01-7.09 (m, 1H), 7.21 (dd, J = 2.6, 10.1 Hz, 1H), 7.40-7.54 (m, 3H), 8.55 (d, J = 9.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.1, 28.0, 36.4, 36.5, 38.7, 50.6, 61.2, 63.5, 125.4, 125.5, 125.5, 126.0, 126.7, 129.5, 129.8, 132.0, 132.1, 133.9, 141.5, 170.6, 177.4, 180.5. HRMS calcd for $C_{29}H_{33}ClN_3NiO_3$ $[M + H]^+$ 564.1564, found 564.1566. m.p. 225 °C

(S_C, S_N)-15

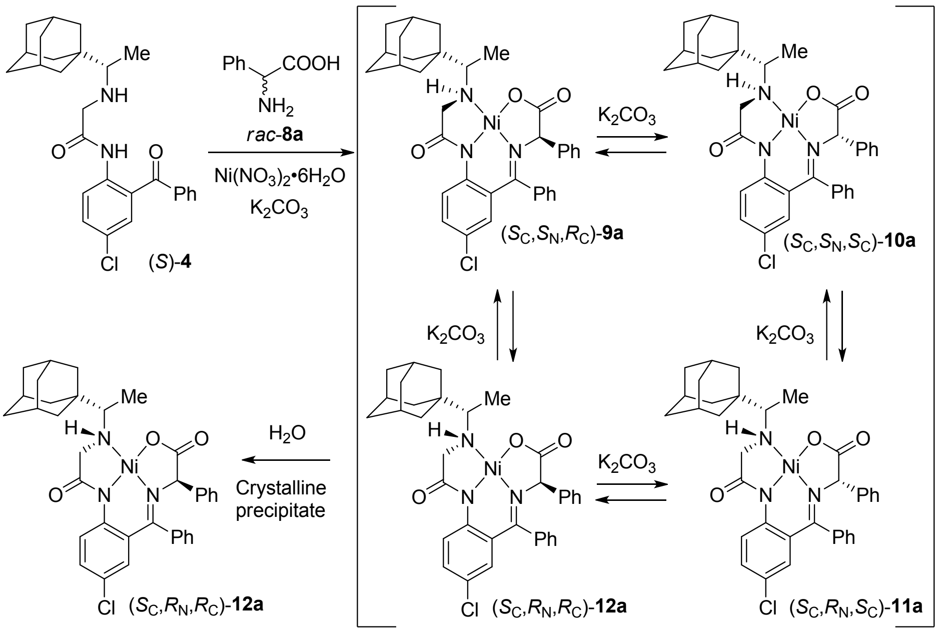


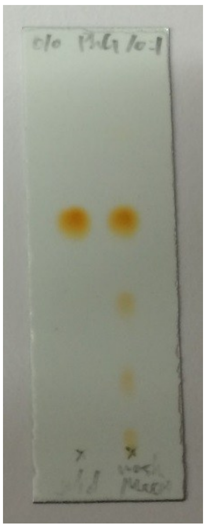
(S_C,S_N)-**15**

$[\alpha]_D^{25}$ = +2389 (c = 0.013, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.49-1.69 (m, 12H), 1.97 (s, 3H), 2.09 (q, J = 6.3 Hz, 1H), 2.28 (d, J = 6.8 Hz, 3H), 2.88-2.96 (m, 1H), 3.11 (d, J = 16.5 Hz, 1H), 3.61 (d, J = 1.2 Hz, 2H), 4.30 (dd, J = 7.1, 16.5 Hz, 1H), 6.77 (d, J = 2.5 Hz, 1H), 6.83-6.90 (m, 1H), 7.10-7.16 (m, 1H), 7.21 (dd, J = 2.6, 9.2 Hz, 1H), 7.41-7.4 (m, 3H), 8.36 (d, J = 9.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.9, 28.1, 36.6, 36.6, 38.3, 59.1, 60.8, 125.6, 71.3, 125.8, 126.1, 127.3, 129.6, 130.1, 130.1, 132.2, 132.4, 133.8, 141.1, 170.9, 177.2, 177.2. HRMS calcd for $C_{29}H_{33}ClN_3NiO_3$ $[M + H]^+$ 564.1564, found 564.1554. m.p. 220 ^{o}C

General procedure for preparation of Ni(II) complexes by reaction of ligand (*S*)-4 with amino acids

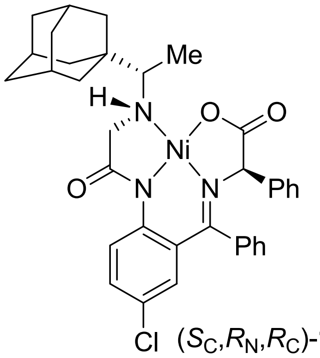
To a mixture of ligand (*S*)-**4** (100 mg, 0.22 mmol), nickel(II) nitrate hexahydrate (32 mg, 0.24 mmol), amino acid (0.24 mmol) and methanol (4 mL) was added potassium carbonate (123 mg, 0.89 mmol) and the reaction mixture was stirred at reflux for 2 hours. After the ligand (*S*)-**4** was consumed, several amount of water was dropped to the mixture to give a precipitate. The precipitate was filtrated, washed with aqueous methanol and dried *in vacuo* at 60 ^{o}C overnight to afford the corresponding Ni(II) complex.





TLC developing solvent: dichloromethane / acetone (10 : 1)

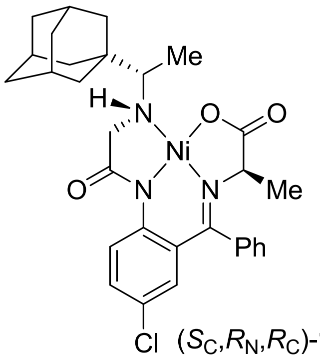
(S_C, R_N, R_C)-12a



(S_C,R_N,R_C)-**12a**

Yield: 90.8%. $[\alpha]_D^{25}$ = –2169 (c = 0.054, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.51 (d, J = 7.0 Hz, 3H), 1.36-1.62 (m, 12H), 1.90 (s, 3H), 3.00 (q, J = 7.1 Hz, 1H), 3.29 (d, J = 17.8 Hz, 1H), 3.45 (d, J = 8.2 Hz, 1H), 3.78 (dd, J = 8.4, 17.4 Hz, 1H), 4.73 (s, 1H), 5.96 (d, J = 7.6 Hz, 1H), 6.63 (d, J = 2.5 Hz, 1H), 6.94 (ddd, J = 0.7, 7.6, 7.6 Hz, 1H), 7.13 (d, J = 7.6 Hz, 1H), 7.16-7.24 (m, 4H), 7.31 (tt, J = 1.1, 7.6 Hz, 1H), 7.43 (ddd, J = 0.7, 7.6, 7.6 Hz, 1H), 7.59-7.64 (m, 2H), 8.58 (d, J = 9.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 9.8, 28.0, 36.4, 36.6, 38.7, 50.9, 63.8, 74.7, 125.0, 125.7, 126.0, 126.8, 127.1, 127.8, 128.0, 128.5, 128.5, 128.8, 129.6, 132.4, 132.6, 133.4, 138.0, 141.8, 171.6, 178.0, 180.3. HRMS calcd for $C_{35}H_{37}ClN_3NiO_3$ $[M + H]^+$ 640.1877, found 640.1883. m.p. 217 ^oC

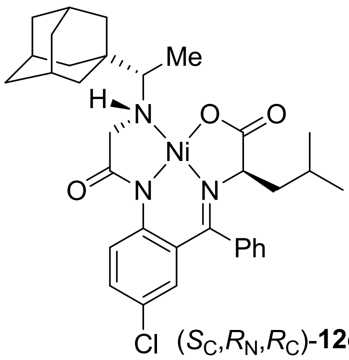
(S_C, R_N, R_C)-12b



(S_C,R_N,R_C)-**12b**

Yield: 74.0%. $[\alpha]_D^{25}$ = –2755 (c = 0.054, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.44 (d, J = 7.0 Hz, 3H), 1.45 (d, J = 7.2 Hz, 3H), 1.35-1.69 (m, 12H), 1.93 (s, 3H), 2.94 (q, J = 7.2 Hz, 1H), 3.27 (d, J = 17.3 Hz, 1H), 3.42 (d, J = 7.9 Hz, 1H), 3.72 (dd, J = 8.3, 17.5 Hz, 1H), 3.90 (q, J = 7.0 Hz, 1H), 6.62 (d, J = 2.6 Hz, 1H), 6.87-6.94 (m, 1H), 7.14-7.22 (m, 2H), 7.39-7.50 (m, 3H), 8.51 (d, J = 9.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 9.8, 21.2, 28.1, 36.5, 36.6, 38.8, 50.9, 63.7, 66.5, 124.7, 125.5, 126.9, 127.6, 128.0, 129.0, 129.3, 130.0, 132.3, 132.4, 132.4, 133.0, 141.5, 169.7, 179.7, 180.7. HRMS calcd for $C_{30}H_{35}ClN_3NiO_3$ $[M + H]^+$ 578.1720, found 578.1729. m.p. >250 ^oC

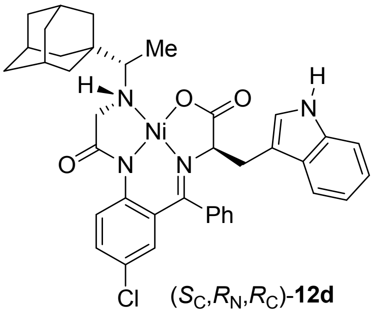
(S_C, R_N, R_C)-12c



(S_C,R_N,R_C)-**12c**

Yield: 87.9%. $[\alpha]_D^{25}$ = –2298 (c = 0.050, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.26 (d, J = 6.5 Hz, 3H), 0.79 (d, J = 6.7 Hz, 3H), 1.17 (ddd, J = 3.6, 10.6, 13.3 Hz, 1H), 1.45 (d, J = 7.1 Hz, 3H), 1.35-1.71 (m, 12H), 1.76-1.89 (m, 1H), 1.94 (s, 3H), 2.40 (ddd, J = 3.2, 11.1, 13.3 Hz, 1H), 2.93 (q, J = 7.1 Hz, 1H), 3.23-3.32 (m, 2H), 3.72 (dd, J = 8.4, 17.4 Hz, 1H), 3.81 (dd, J = 3.6, 11.1 Hz, 1H) , 6.63 (d, J = 2.5 Hz, 1H), 6.86-6.93 (m, 1H), 7.14-7.23 (m, 2H), 7.39-7.51 (m, 3H), 8.48 (d, J = 9.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 9.7, 20.4, 23.6, 24.2, 28.0, 36.4, 36.6, 38.8, 45.7, 51.0, 63.7, 69.0, 124.6, 125.5, 127.3, 127.8, 128.1, 129.0, 129.2, 130.1, 132.3, 132.9, 141.4, 168.8, 179.2, 179.3. HRMS calcd for $C_{33}H_{41}ClN_3NiO_3$ $[M + H]^+$ 620.2190, found 620.2194. m.p. >250 ^{o}C

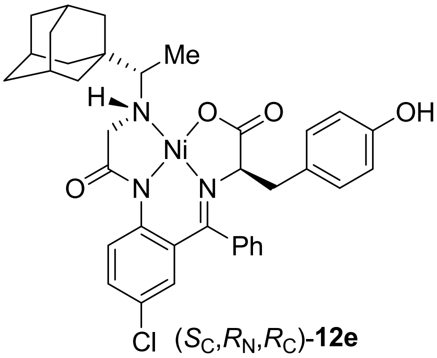
(S_C, R_N, R_C)-12d



(S_C,R_N,R_C)-**12d**

Yield: quant. $[\alpha]_D^{25}$ = –2541 (c = 0.038, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.12 (s, 3H), 1.23 (d, J = 7.0 Hz, 3H), 1.71-1.48 (m, 9H), 1.93 (s, 3H), 2.35 (q, J = 7.0 Hz, 1H), 2.45 (dd, J = 17.4, 8.6 Hz, 1H), 2.72 (d, J = 17.4 Hz, 1H), 2.84 (dd, J = 14.6, 6.7 Hz, 1H), 3.55-3.46 (m, 1H), 4.27 (dd, J = 6.6, 1.7 Hz, 1H), 6.74 (d, J = 2.5 Hz, 1H), 7.05 (d, J = 2.3 Hz, 1H), 7.13-7.07 (m, 1H), 7.30-7.18 (m, 4H), 7.35 (dd, J = 7.5, 7.5 Hz, 1H), 7.64-7.53 (m, 3H), 7.99 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 9.2 Hz, 1H), 8.64 (br, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 9.4, 28.0, 30.4, 36.2, 36.5, 38.4, 50.3, 62.6, 71.2, 111.0, 111.3, 120.2, 121.8, 122.6, 125.1, 125.6, 127.4, 127.4, 127.5, 129.3, 129.5, 130.4, 132.2, 133.0, 168.3, 179.2, 179.7. HRMS calcd for $C_{38}H_{40}ClN_4NiO_3$ $[M + H]^+$ 693.2142, found 693.2142. m.p. 237 ^{o}C

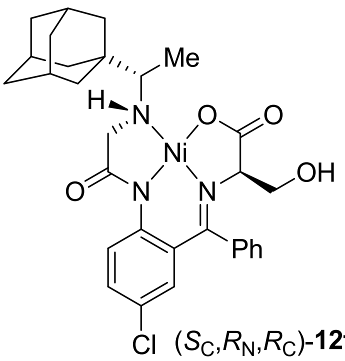
(S_C, R_N, R_C)-12e



(S_C,R_N,R_C)-**12e**

Yield: 65.9%. $[\alpha]_D^{25}$ = –2589 (*c* = 0.020, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 1.29 (d, *J* = 7.7 Hz, 3H), 1.22-1.38 (m, 3H), 1.45-1.69 (m, 9H), 1.92 (s, 3H), 2.38-2.52 (m, 2H), 2.58 (dd, *J* = 5.7, 13.6 Hz, 1H), 2.94-3.05 (m, 2H), 3.08 (ddd, *J* = 8.4, 17.7, 17.7 Hz, 1H), 4.20 (dd, *J* = 2.6, 5.6 Hz, 1H), 6.66 (d, *J* = 2.5 Hz, 1H), 7.00-7.06 (m, 3H), 7.18 (dd, *J* = 2.5, 9.2 Hz, 1H), 7.22-7.31 (m, 3H) , 7.46-7.54 (m, 3H), 8.30 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 9.9, 28.1, 36.3, 36.5, 38.8, 38.9, 50.5, 62.7, 72.7, 115.4, 125.3, 126.2, 127.4, 127.4, 127.6, 128.7, 129.3, 129.6, 130.5, 132.4, 132.4, 132.9, 133.0, 141.1, 156.7, 169.1, 178.2, 179.6. HRMS calcd for $C_{36}H_{39}ClN_3NiO_4$ $[M + H]^+$ 670.1983, found 670.1981. m.p. >250 °C

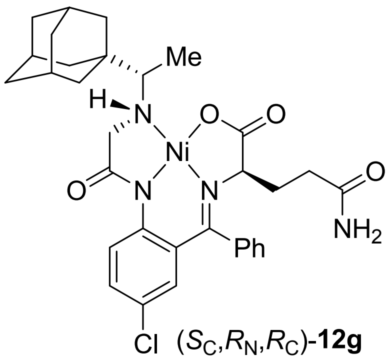
(S_C, R_N, R_C)-12f



(S_C,R_N,R_C)-**12f**

Yield: 55.4%. $[\alpha]_D^{25}$ = –1811 (*c* = 0.049, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 1.40 (d, *J* = 7.2 Hz, 3H), 1.31-1.65 (m, 12H), 1.91 (s, 3H), 2.62-2.72 (m, 2H), 3.20 (d, *J* = 17.5 Hz, 1H), 3.78 (dd, *J* = 8.4, 17.5 Hz, 1H), 3.94 (d, *J* = 8.4 Hz, 1H), 4.53 (t, *J* = 6.0 Hz, 1H), 6.57 (d, *J* = 2.5 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 7.13-7.26 (m, 3H), 7.26-7.41 (m, 2H), 8.58 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.1, 28.1, 36.5, 38.8, 51.2, 63.1, 68.0, 124.7, 125.4, 127.4, 127.7, 128.1, 128.7, 129.7, 130.4, 132.4, 132.5, 132.6, 142.3, 169.9, 177.9, 180.2. HRMS calcd for $C_{29}H_{33}ClN_3NiO_3$ $[M – CH_2O + H]^+$ 564.1564, found 564.1556. m.p. 211 °C

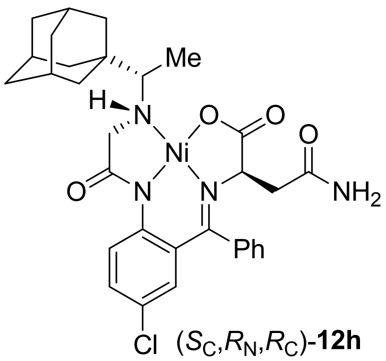
(S_C, R_N, R_C)-12g



(S_C,R_N,R_C)-**12g**

Yield: 92.2%. $[\alpha]_D^{25}$ = –3350 (c = 0.021, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.44 (d, J = 7.3 Hz, 3H), 1.34-1.73 (m, 12H), 1.73-1.88 (m, 1H), 1.95 (s, 3H), 2.23-2.38 (m, 1H), 2.39-2.63 (m, 2H), 2.90 (q, J = 7.2 Hz, 1H), 3.25 (d, J = 17.5 Hz, 1H), 3.42 (d, J = 8.2 Hz, 1H), 3.75 (dd, J = 8.2, 17.5 Hz, 1H), 3.83 (dd, J = 4.1, 9.6 Hz, 1H), 5.14 (br, 1H), 6.23 (br, 1H), 6.63 (d, J = 2.5 Hz, 1H), 7.02 (dd, J = 2.0, 4.4 Hz, 1H), 7.10-7.18 (m, 2H), 7.42-7.52 (m, 3H), 8.52 (d, J = 9.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.2, 28.5, 31.1, 32.0, 37.0, 37.1, 39.3, 51.4, 64.2, 69.9, 125.2, 126.2, 127.1, 128.2, 128.4, 129.6, 129.9, 130.8, 133.0, 133.1, 133.2, 142.1, 170.8, 174.1, 179.8, 179.9. HRMS calcd for $C_{32}H_{38}ClN_4NiO_4$ $[M + H]^+$ 635.1935, found 635.1946. m.p. 193 ^{o}C

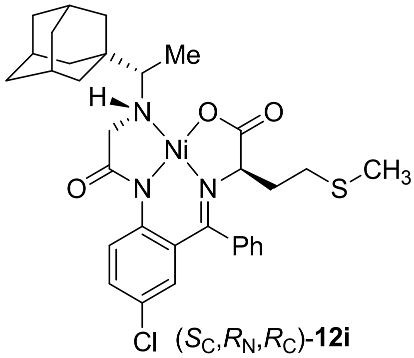
(S_C, R_N, R_C)-12h



(S_C,R_N,R_C)-**12h**

Yield: 75.4%. $[\alpha]_D^{25}$ = –2356 (c = 0.030, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.43 (d, J = 7.2 Hz, 3H), 1.35-1.68 (m, 12H), 1.92 (s, 3H), 2.45 (dd, J = 2.8, 15.7 Hz, 1H), 2.64 (dd, J = 7.8, 15.7 Hz, 1H), 2.87 (q, J = 7.1 Hz, 1H), 3.21 (d, J = 17.2 Hz, 1H), 3.67 (d, J = 8.2 Hz, 1H), 3.83 (dd, J = 8.2, 17.2 Hz, 1H), 4.10 (dd, J = 2.8, 7.8 Hz, 1H), 5.60 (br, 1H), 6.54 (br, 1H), 6.62 (d, J = 2.5 Hz, 1H), 6.92-6.99 (m, 1H), 7.14-7.22 (m, 2H), 7.42-7.52 (m, 3H), 8.51 (d, J = 9.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 9.9, 28.1, 36.5, 36.6, 38.6, 39.8, 51.1, 63.7, 66.6, 124.9, 125.2, 126.7, 127.7, 128.1, 129.3, 129.4, 130.2, 132.2, 132.4, 133.3, 142.1, 170.1, 171.1, 179.5, 180.2. HRMS calcd for $C_{31}H_{36}ClN_4NiO_4$ $[M + H]^+$ 621.1779, found 621.1776. m.p. 204 ^{o}C

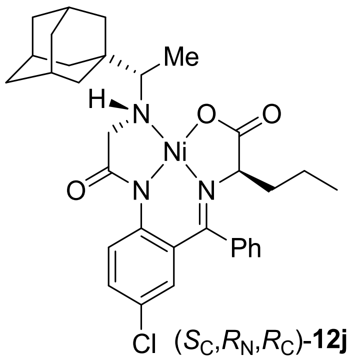
(S_C, R_N, R_C)-12i



(S_C,R_N,R_C)-**12i**

Yield: 61.4%. $[\alpha]_D^{25}$ = –2296 (c = 0.046, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 1.44 (d, J = 7.2 Hz, 3H), 1.36-1.70 (m, 12H), 1.72-1.87 (m, 1H), 1.96 (s, 6H), 2.09-2.25 (m, 1H), 2.44-2.61 (m, 1H), 2.86-3.04 (m, 2H), 3.22-3.33 (m, 2H), 3.71 (dd, J = 8.4, 17.3 Hz, 1H), 3.93 (dd, J = 3.6, 8.4 Hz, 1H), 6.63 (d, J = 2.5 Hz, 1H), 6.88-6.94 (m, 1H), 7.14-7.22 (m, 2H), 7.41-7.52 (m, 3H), 8.51 (d, J = 9.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.1, 15.9, 28.4, 30.2, 34.9, 36.9, 37.0, 39.2, 51.4, 64.1, 70.0, 125.1, 126.0, 127.4, 127.9, 128.5, 129.6, 129.8, 130.6, 132.8, 132.9, 133.5, 142.0, 170.2, 179.2, 179.8. HRMS calcd for $C_{32}H_{39}ClN_3NiO_3S$ $[M + H]^+$ 638.1754, found 638.1756. m.p. >250 ^oC

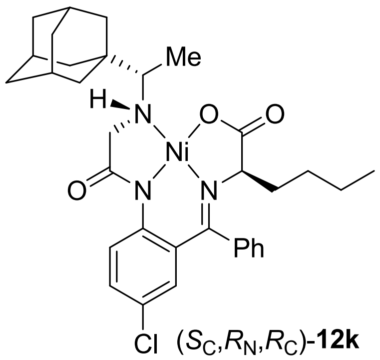
(S_C, R_N, R_C)-12j



(S_C,R_N,R_C)-**12j**

Yield: 84.0%. $[\alpha]_D^{25}$ = –2527 (c = 0.050, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 0.73 (t, J = 7.1 Hz, 3H), 1.44 (d, J = 7.0 Hz, 3H), 1.35-1.69 (m, 14H), 1.82-2.04 (m, 5H), 2.93 (q, J = 7.2 Hz, 1H), 3.22-3.33 (m, 2H), 3.72 (dd, J = 8.5, 17.5 Hz, 1H), 3.85 (dd, J = 3.5, 8.4 Hz, 1H), 6.63 (d, J = 2.5 Hz, 1H), 6.85-6.92 (m, 1H), 7.14-7.22 (m, 2H), 7.39-7.50 (m, 3H), 8.51 (d, J = 9.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 9.7, 13.6, 18.5, 28.0, 36.4, 36.5, 37.3, 38.7, 51.0, 63.7, 70.2, 124.6, 125.5, 127.0, 127.5, 128.1, 129.0, 129.2, 130.0, 132.3, 133.1, 141.4, 169.3, 179.4. HRMS calcd for $C_{32}H_{39}ClN_3NiO_3$ $[M + H]^+$ 606.2033, found 606.2035. m.p. >250 ^oC

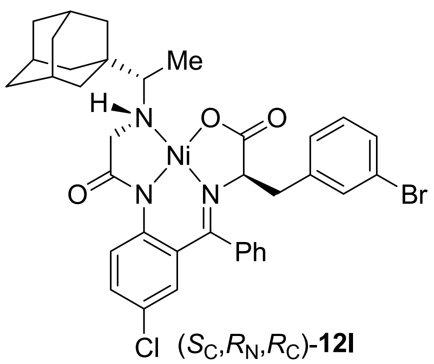
(S_C, R_N, R_C)-12k



(S_C,R_N,R_C)-**12k**

Yield: 86.5%. $[\alpha]_D^{25}$ = –2413 (c = 0.055, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 0.78 (t, J = 7.3 Hz, 3H), 1.03-1.24 (m, 2H), 1.44 (d, J = 7.2 Hz, 3H), 1.34-1.70 (m, 14H), 1.80-2.00 (m, 5H), 2.94 (q, J = 7.2 Hz, 1H), 3.22-3.32 (m, 2H), 3.72 (dd, J = 8.4, 17.4 Hz, 1H), 3.84 (dd, J = 3.4, 8.3 Hz, 1H), 6.63 (d, J = 2.5 Hz, 1H), 6.85-6.92 (m, 1H), 7.14-7.22 (m, 2H) , 7.39-7.50 (m, 3H), 8.51 (d, J = 9.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 9.7, 13.7, 22.2, 27.1, 28.0, 34.9, 36.4, 36.5, 38.7, 51.0, 63.7, 70.4, 124.6, 125.5, 127.0, 127.5, 128.1, 129.0, 129.2, 130.0, 132.3, 133.2, 141.5, 169.3, 179.4, 179.5. HRMS calcd for $C_{33}H_{41}ClN_3NiO_3$ $[M + H]^+$ 620.2190, found 620.2191. m.p. >250 °C

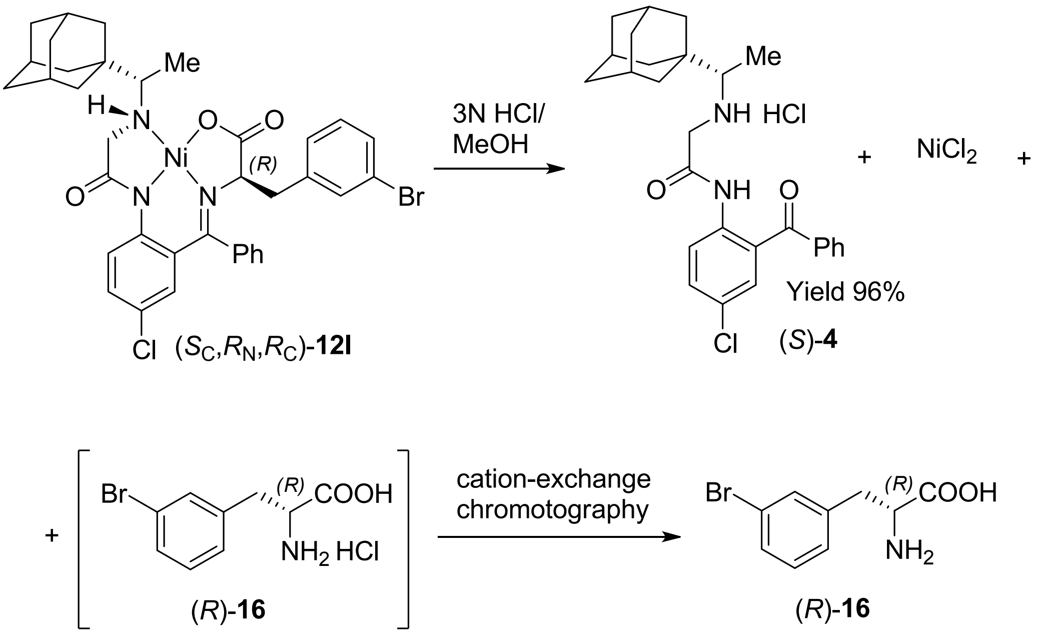
(S_C, R_N, R_C)-12l



(S_C,R_N,R_C)-**12l**

Yield: 92.4%. $[\alpha]_D^{25}$ = –1873 (c = 0.048, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 1.27 (d, J = 7.0 Hz, 3H), 1.22-1.42 (m, 6H), 1.46-1.68 (m, 6H), 1.93 (s, 3H) , 2.48-2.65 (m, 3H), 2.93-3.15 (m, 3H), 4.24 (dd, J = 2.6, 5.6 Hz, 1H), 6.66 (d, J = 2.4 Hz, 1H), 6.99-7.06 (m, 1H), 7.11-7.23 (m, 3H), 7.34 (dd, J = 7.8, 7.8 Hz, 1H), 7.46-7.55 (m, 3H), 7.67 (d, J = 7.8 Hz, 1H), 7.75 (s, 1H), 8.40 (d, J = 9.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 9.5, 28.0, 36.4, 36.5, 38.7, 39.0, 50.6, 63.0, 71.8, 122.7, 124.9, 125.6, 127.2, 127.3, 128.0, 129.3, 129.5, 130.2, 130.4, 130.7, 132.3, 132.5, 132.9, 134.2, 138.9, 141.8, 169.4, 177.9, 178.9. HRMS calcd for $C_{36}H_{38}BrClN_3NiO_3$ $[M + H]^+$ 732.1139, found 732.1134. m.p. >250 °C

Synthesis of (*R*)-*m*-bromo-phenylalanine, (*R*)-16.



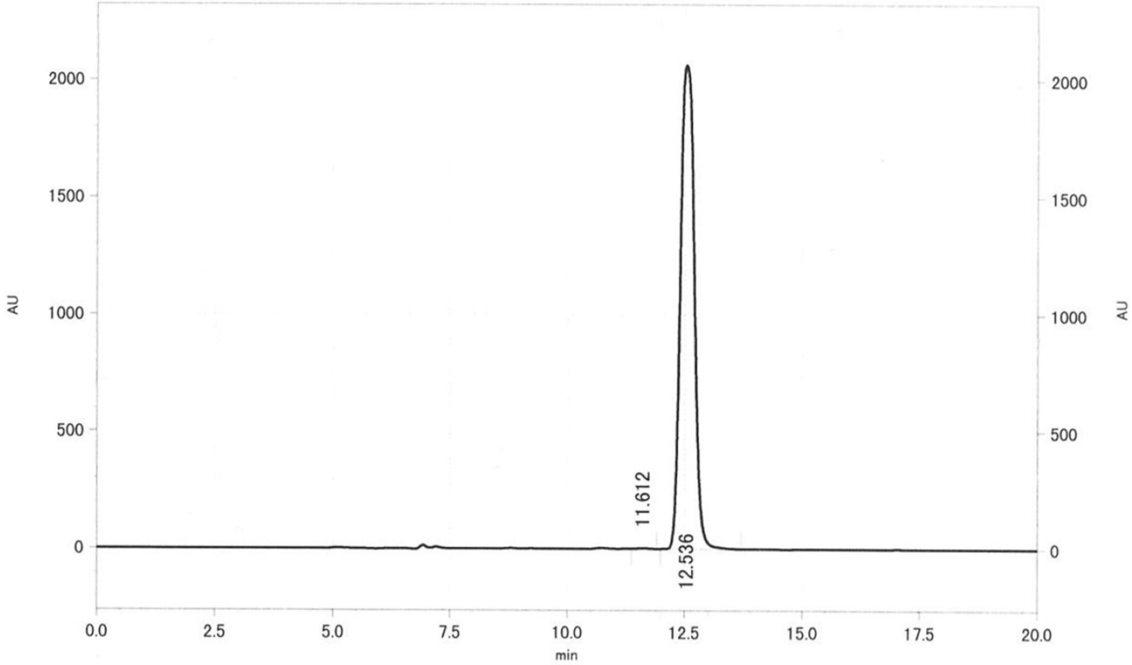
To a suspension of (S_C, R_N, R_C)-**12l** (1.88 g, 2.56 mmol) in methanol (10 mL) was added 3N HCl (4.3 mL, 12.8 mmol) and the whole was heated at 50 °C for 4 h. Upon disappearance of the red color of the starting complex, the reaction mixture was concentrated to dryness. To the residue were added dichloromethane (20 mL) and 2% ammonium hydroxide (10 mL). The organic phase was dried over sodium sulphate and evaporated under vacuum to afford the recycle ligand (*S*)-**4** (1.11 g, 96.0%). The aqueous phase was separated and concentrated to dryness. The residual solid was dissolved in 9% ammonium hydroxide (15 mL) and loaded onto a cation-exchange resin column using DIAION SK-1B (Mitsubishi Chemical Co., 120 mL). The column was first washed with de-ionized water until neutral and eluted with 2% ammonium hydroxide followed by 9% ammonium hydroxide to elute the desired amino acid. The aqueous solution obtained was evaporated to afford (*R*)-**16** (523 mg, 83.7%, 99.0% *ee*). The spectral data were found to be identical with commercial enantiopure sample.

^{1}H NMR (200 MHz, D_2O): δ 3.10 (dd, J = 7.9, 14.3 Hz, 1H), 3.27 (dd, J = 5.5, 14.3 Hz, 1H), 3.97 (dd, J = 5.5, 7.9 Hz, 1H), 7.24-7.39 (m, 2H), 7.49-7.58 (m, 2H).

<Chiral HPLC conditions for (*S*)-**4**>

Instrument: SHIMADZU LC-2010CHT chromatography system and a CLASS-VP™ analysis data system (SHIMADZU CORPORATION, Kyoto, Japan).
Column: DAICEL CHIRALPAK AD-H (particle size 5 μm, 250 x 4.6 mm i.d.)
Eluent: pH 2.0 $HClO_4$ aq.
Flow rate: 0.4 mL/min
Temp: 30 ºC
Detector: UV 254 nm

Chiral HPLC chart of recycle ligand (*S*)-**4**

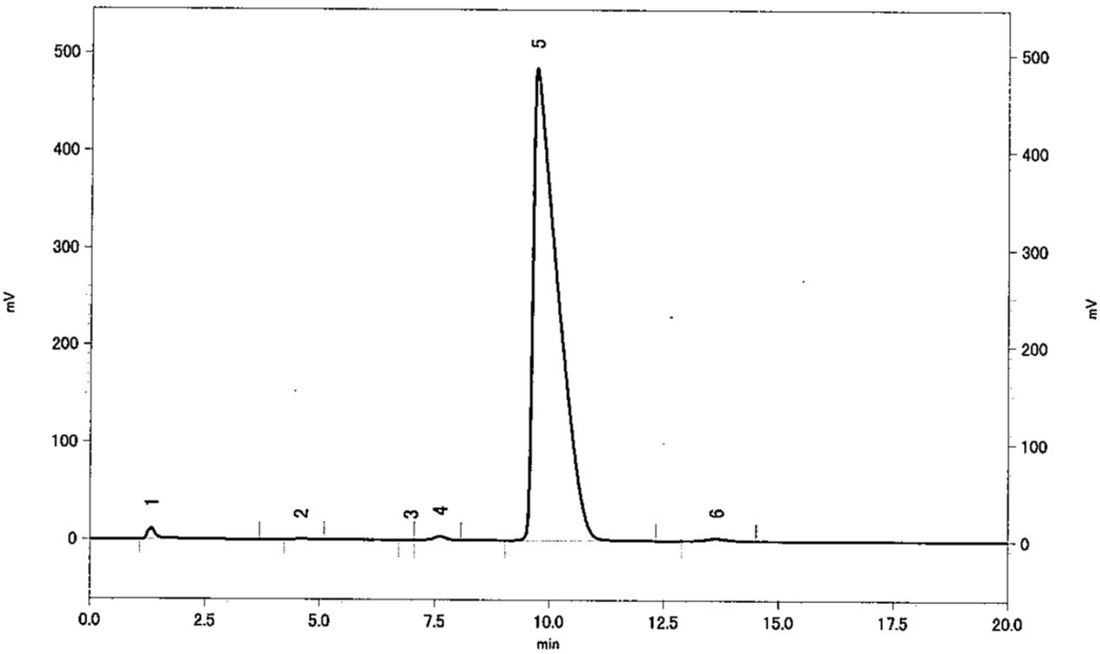


HPLC retention time (min)		Ratio ((*R*)-**4** : (*S*)-**4**)
(*R*)-**4**	(*S*)-**4**	
11.6	12.5	99.8% *ee* (99.9 : 0.1)

<Chiral HPLC conditions for (*R*)-**16**>

Instrument: SHIMADZU LC-2010CHT chromatography system and a CLASS-VP™ analysis data system (SHIMADZU CORPORATION, Kyoto, Japan).
Column: DAICEL CROWNPAK CR(+) (particle size 5 μm, 150 x 4.0 mm i.d.)
Eluent: A = pH 2.0 $HClO_4$ aq.
B = MeOH
A : B = 1 : 9
Flow rate: 1.0 mL/min
Temp: 40 ºC
Detector: UV 220 nm

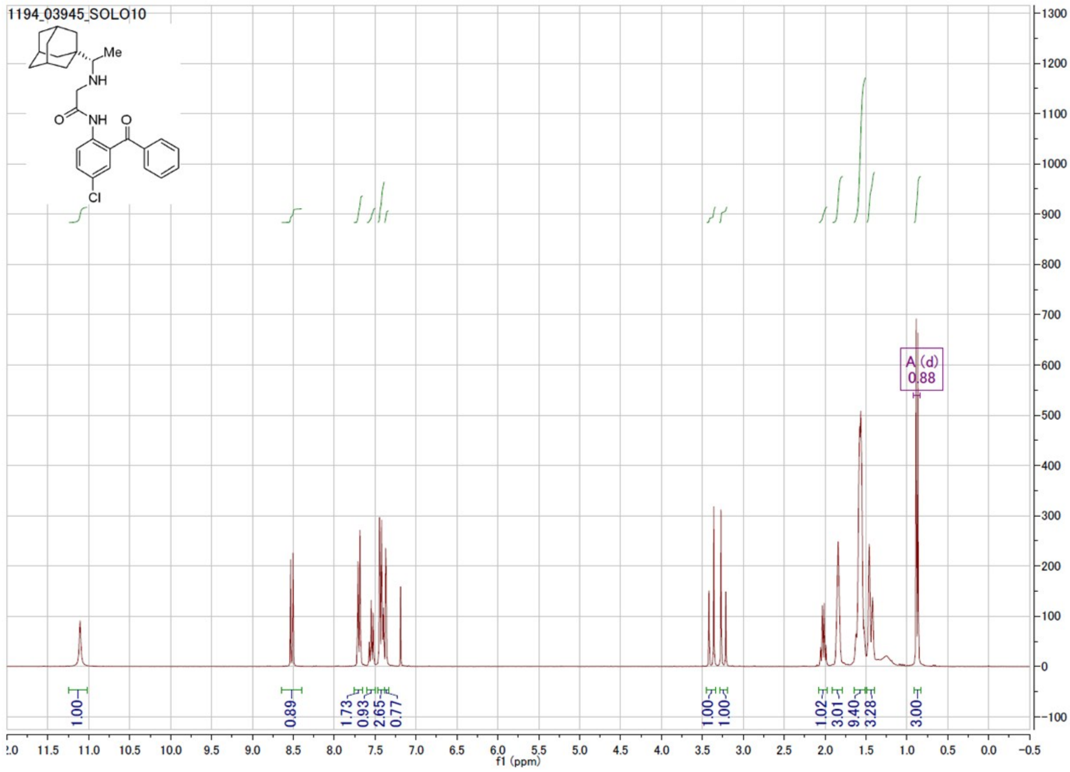
Chiral HPLC chart of (*R*)-**16**



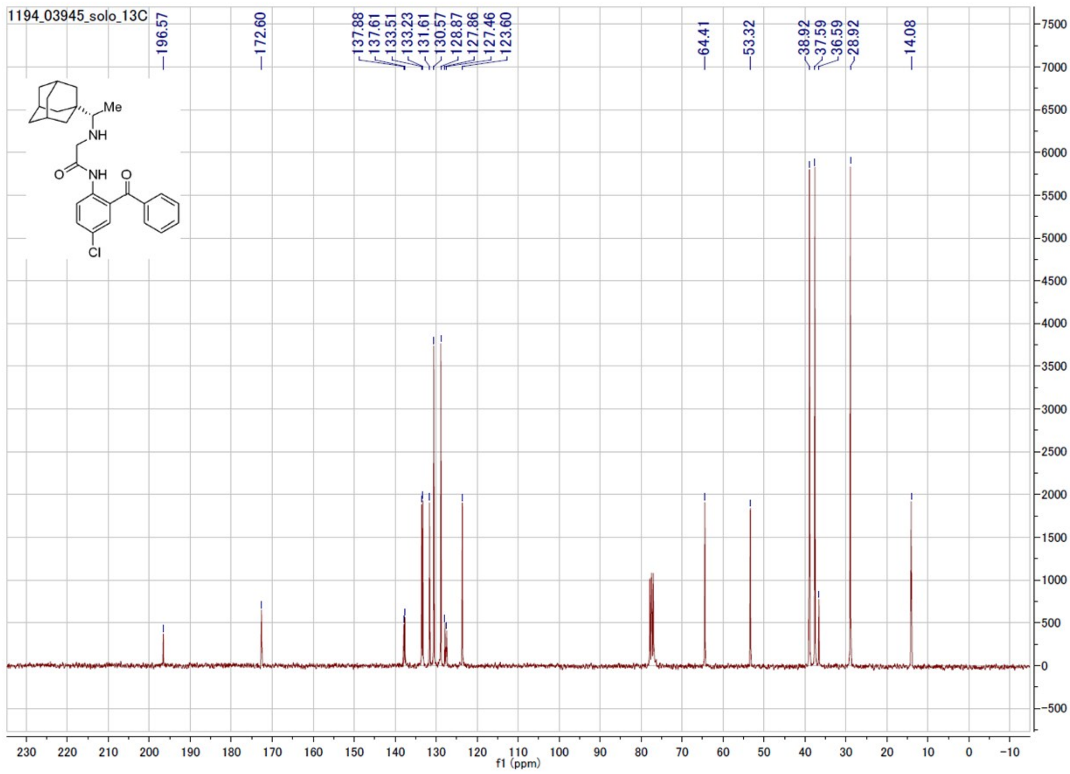
HPLC retention time (min)		Ratio ((*R*)-**16** : (*S*)-**16**)
(*R*)-**16**	(*S*)-**16**	
9.7	13.6	99.0% *ee* (99.5 : 0.5)

3. Copies of ^{1}H and ^{13}C-NMR spectra

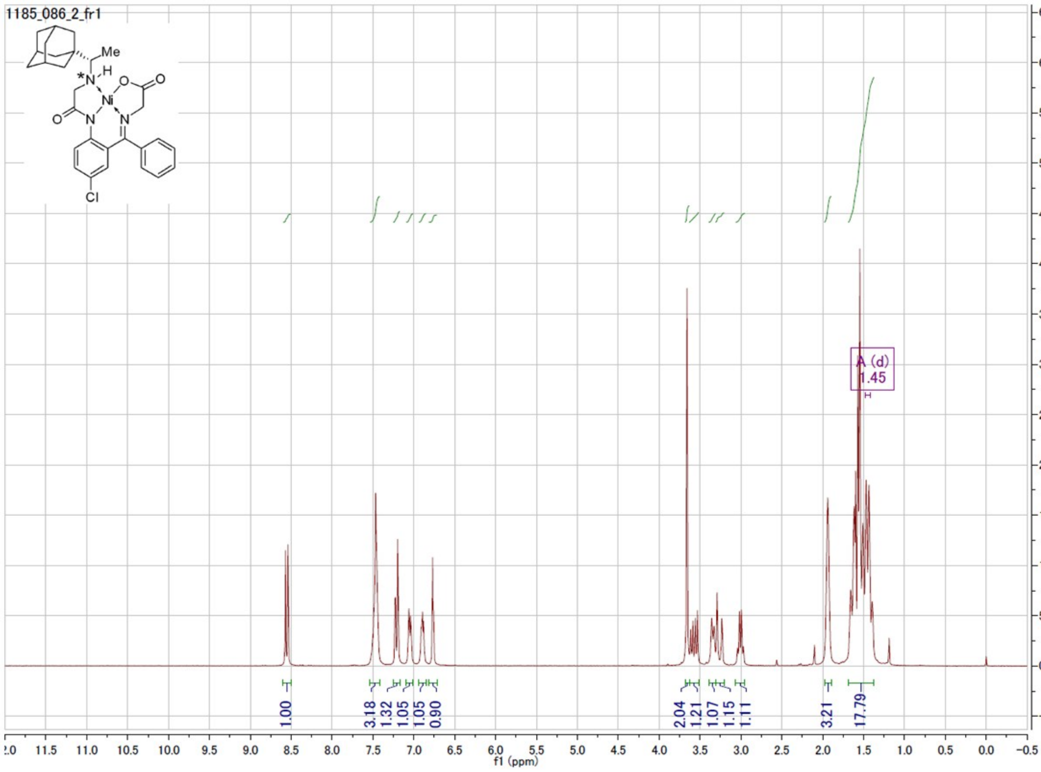
^{1}H-NMR (300 MHz, $CDCl_3$) of (*S*)-**4**



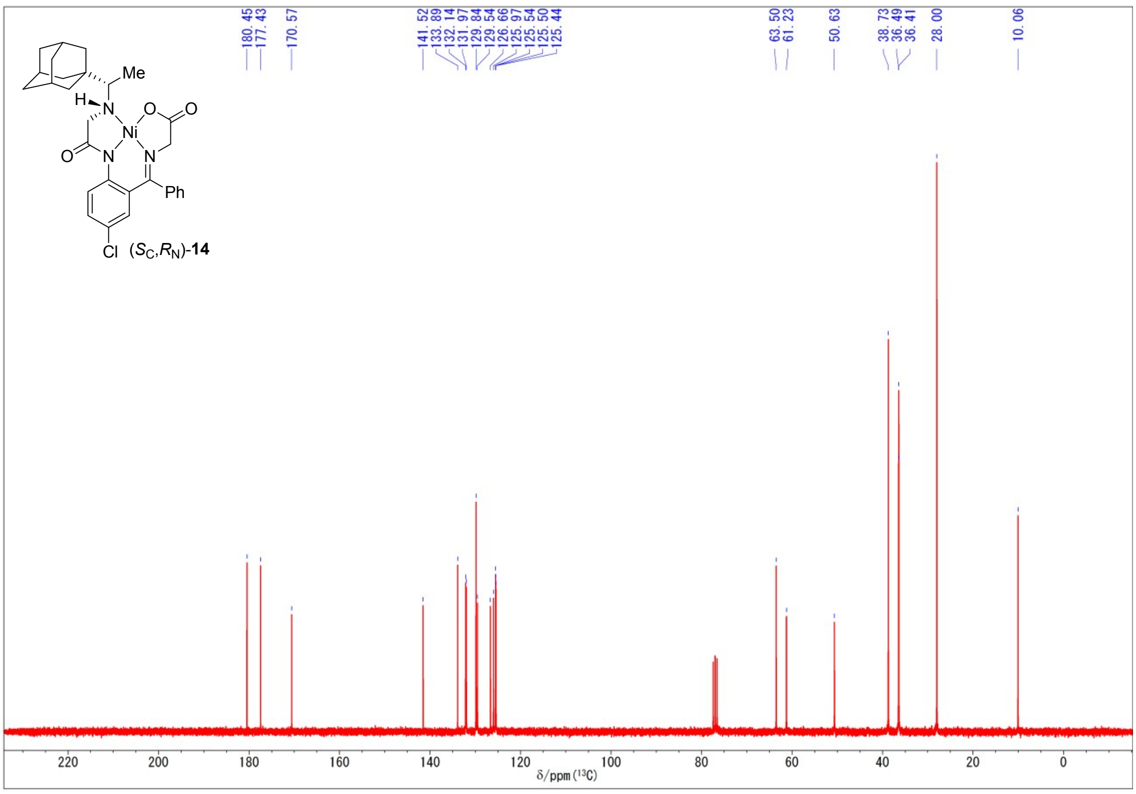
^{13}C-NMR (75 MHz, $CDCl_3$) of (*S*)-**4**



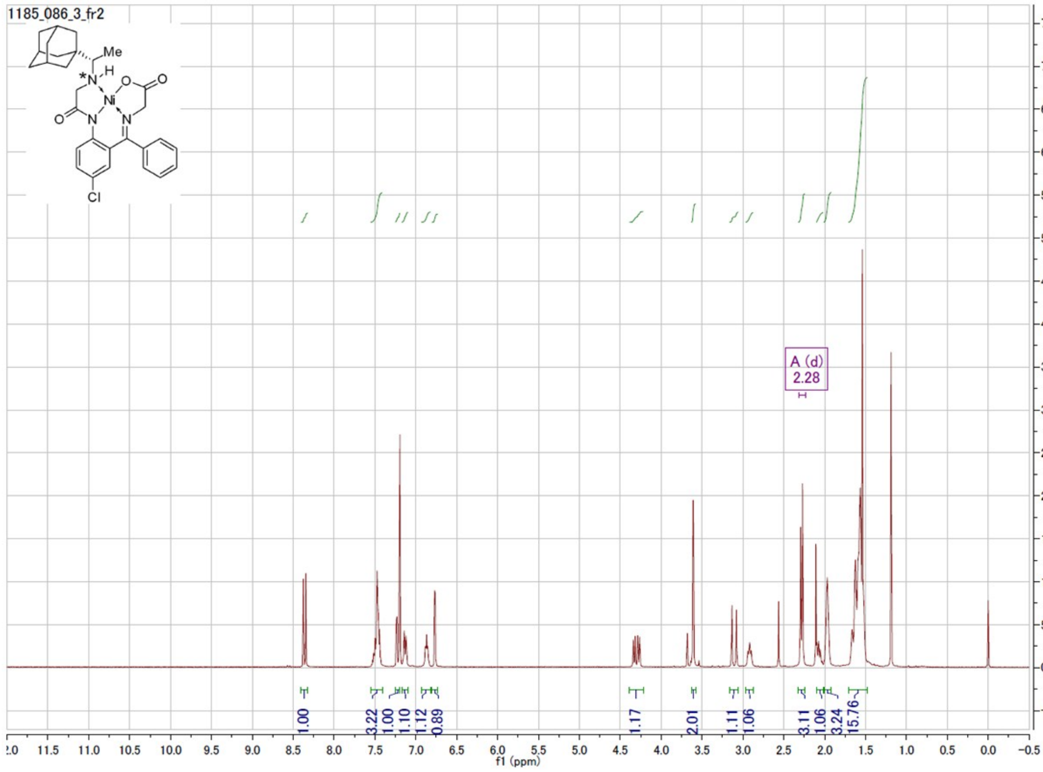
^{1}H-NMR (300 MHz, $CDCl_3$) of (S_C, R_N)-**14**



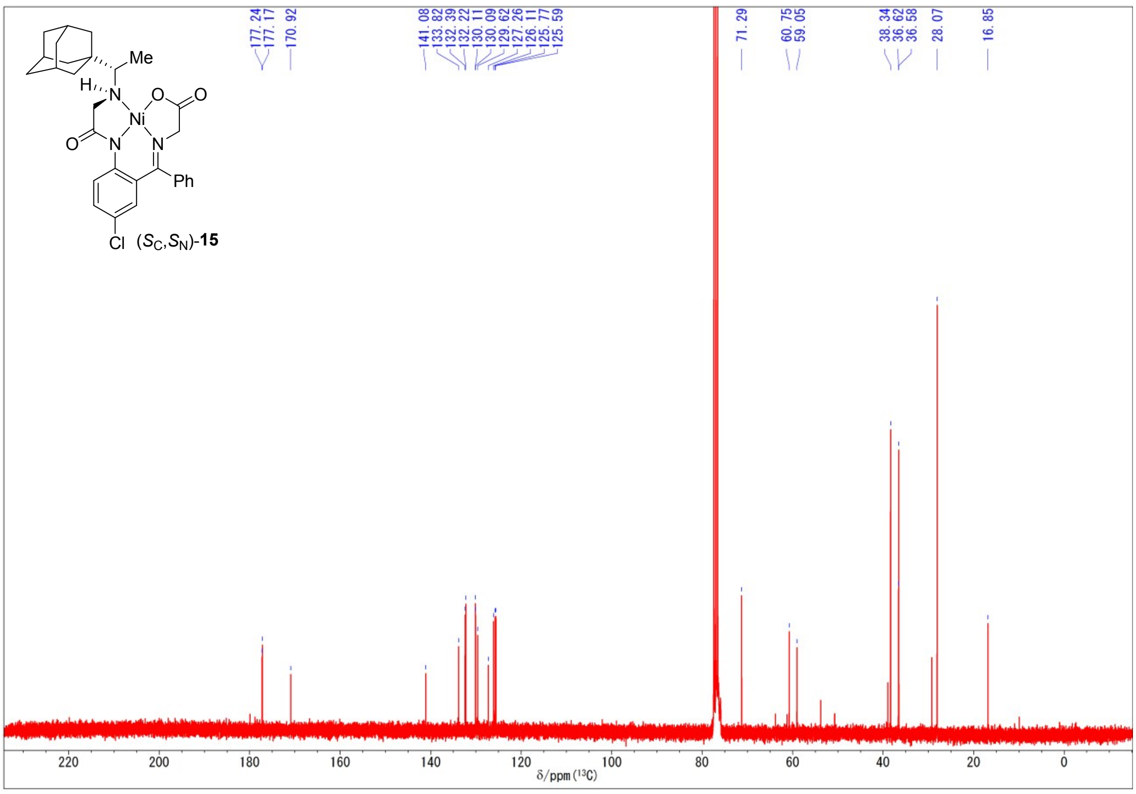
^{13}C-NMR (75 MHz, $CDCl_3$) of (S_C, R_N)-**14**



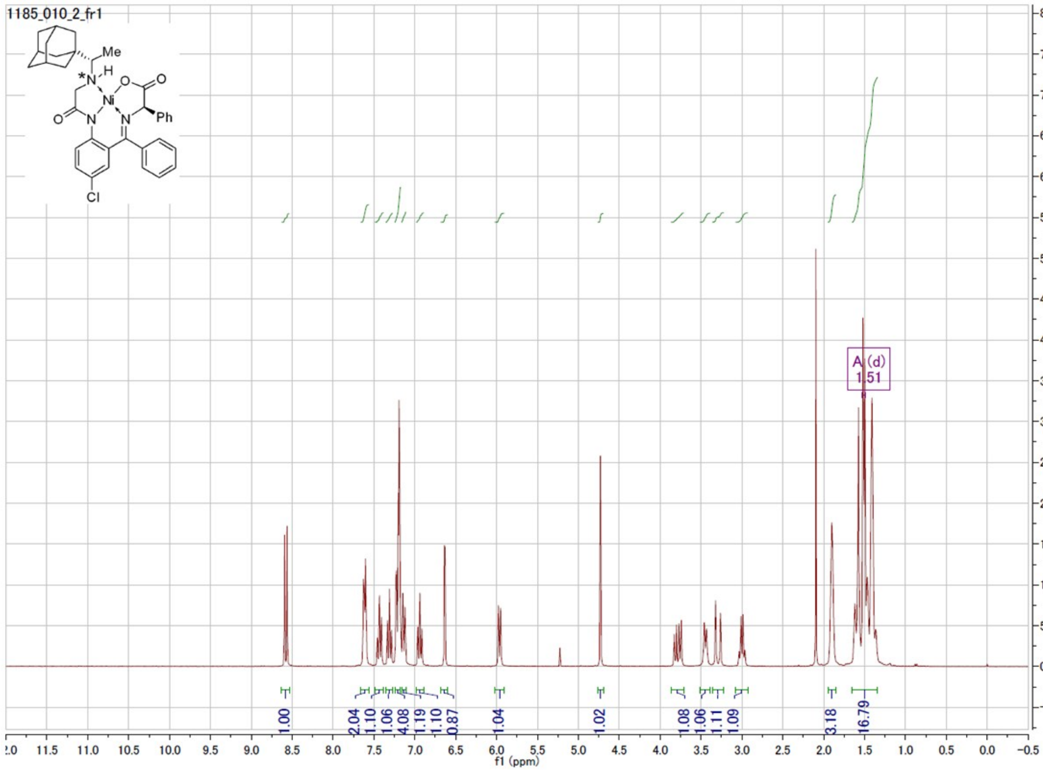
[1]H-NMR (300 MHz, $CDCl_3$) of (S_C, S_N)-**15**



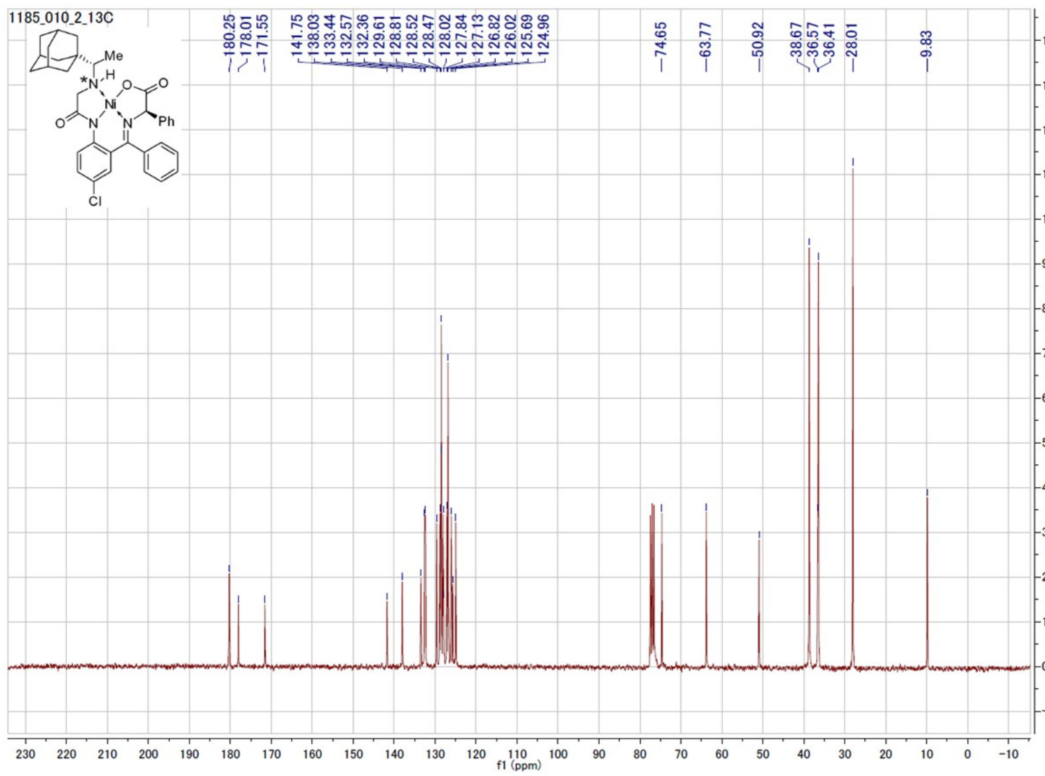
[13]C-NMR (75 MHz, $CDCl_3$) of (S_C, S_N)-**15**



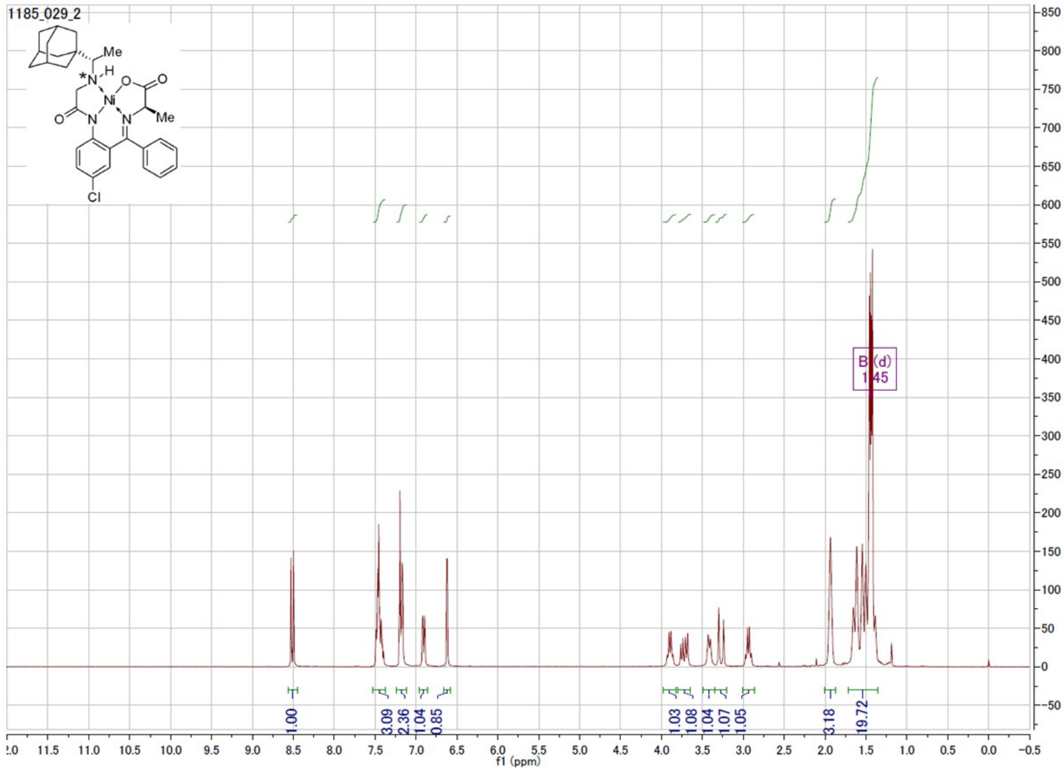
^{1}H-NMR (300 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12a**



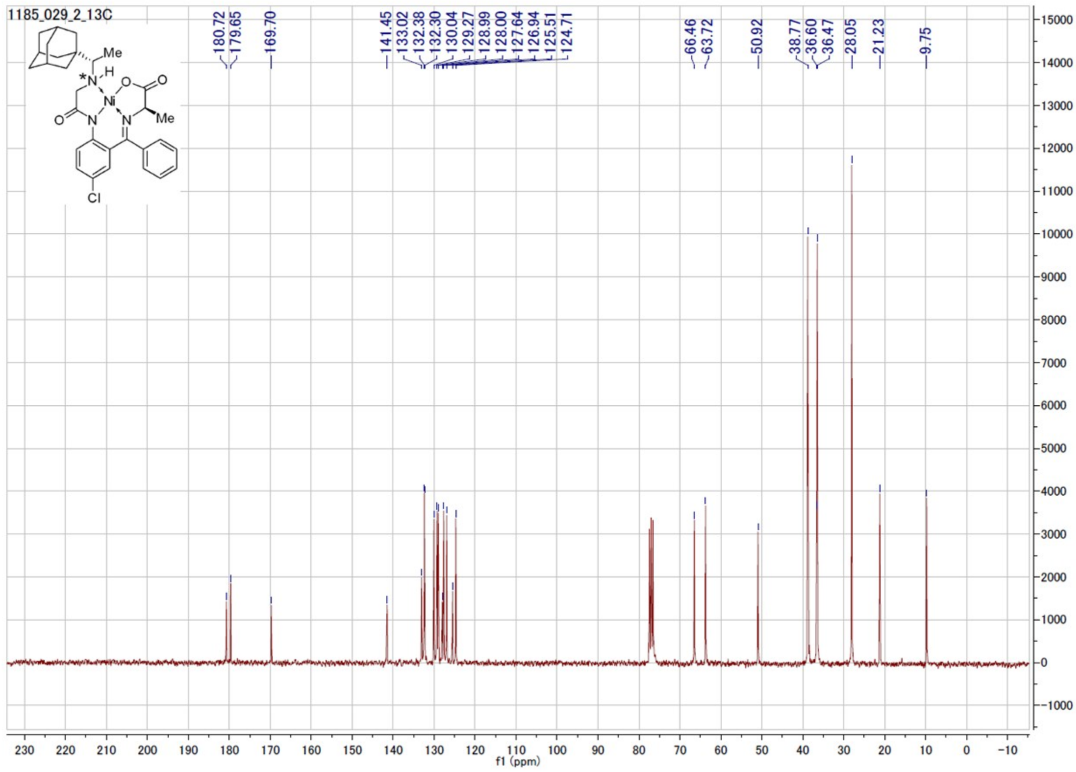
^{13}C-NMR (75 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12a**



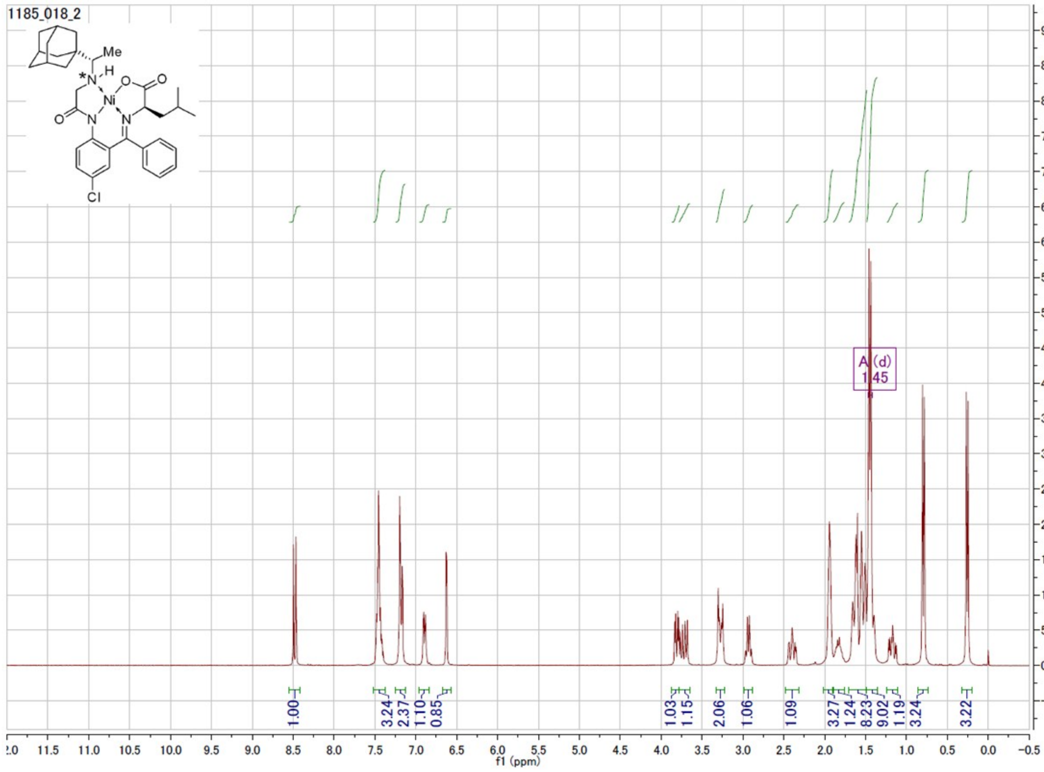
^{1}H-NMR (300 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12b**



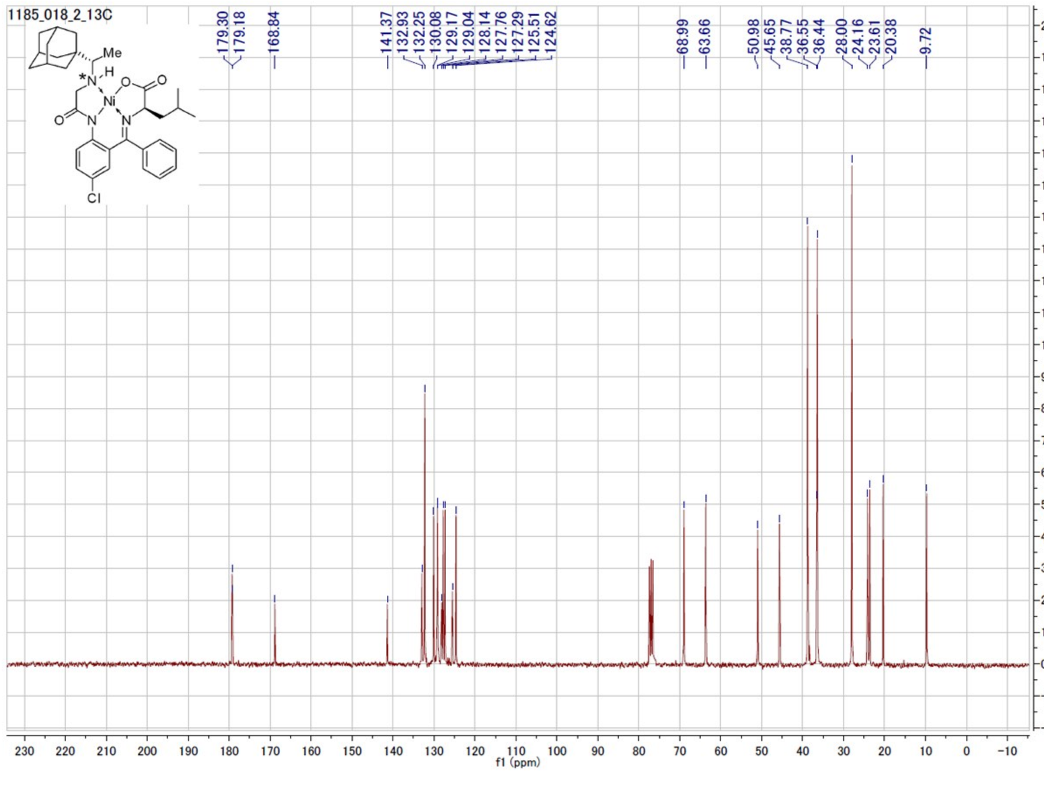
^{13}C-NMR (75 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12b**



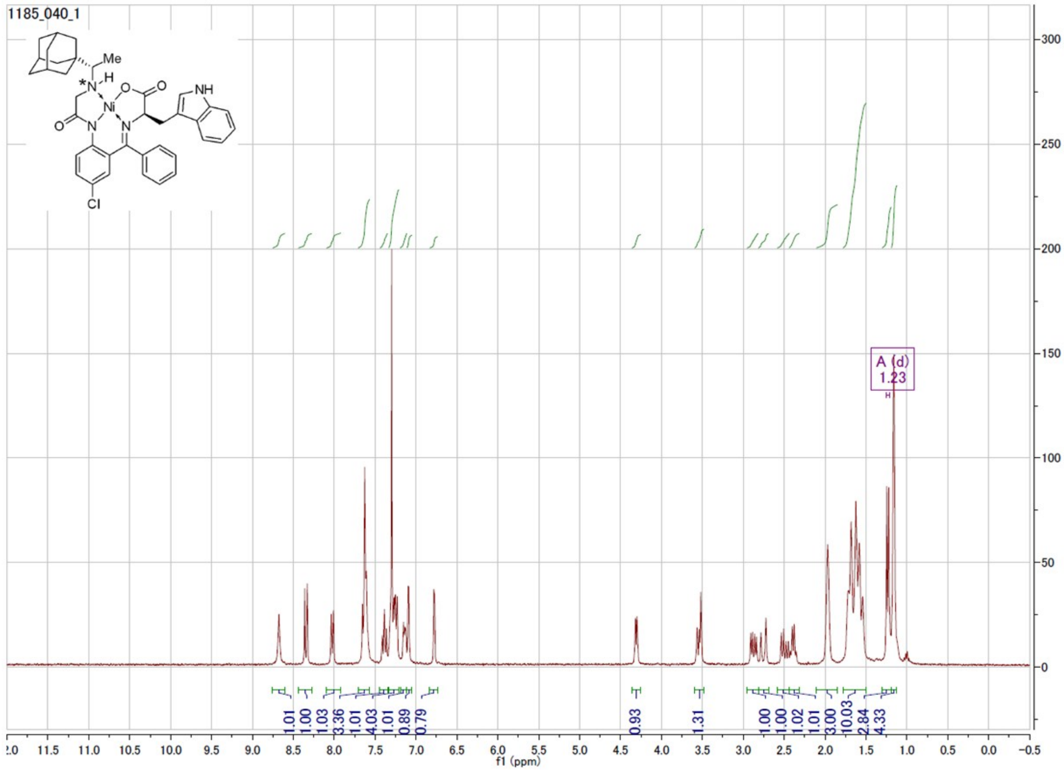
^{1}H-NMR (300 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12c**



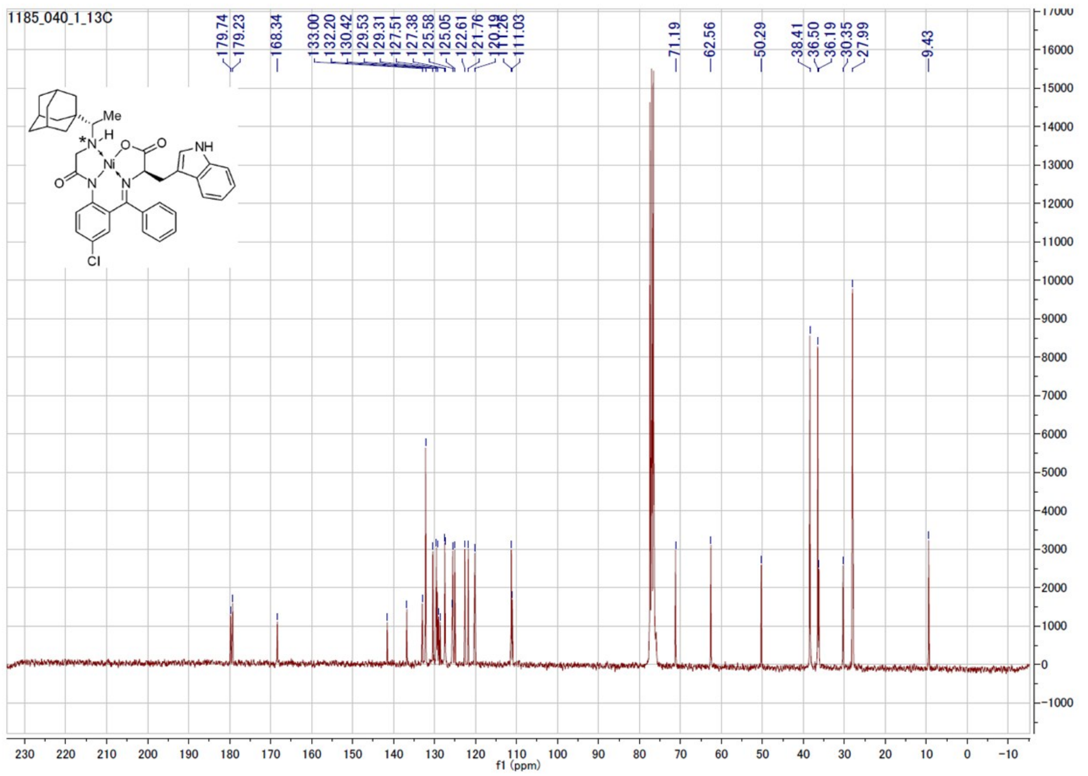
^{13}C-NMR (75 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12c**



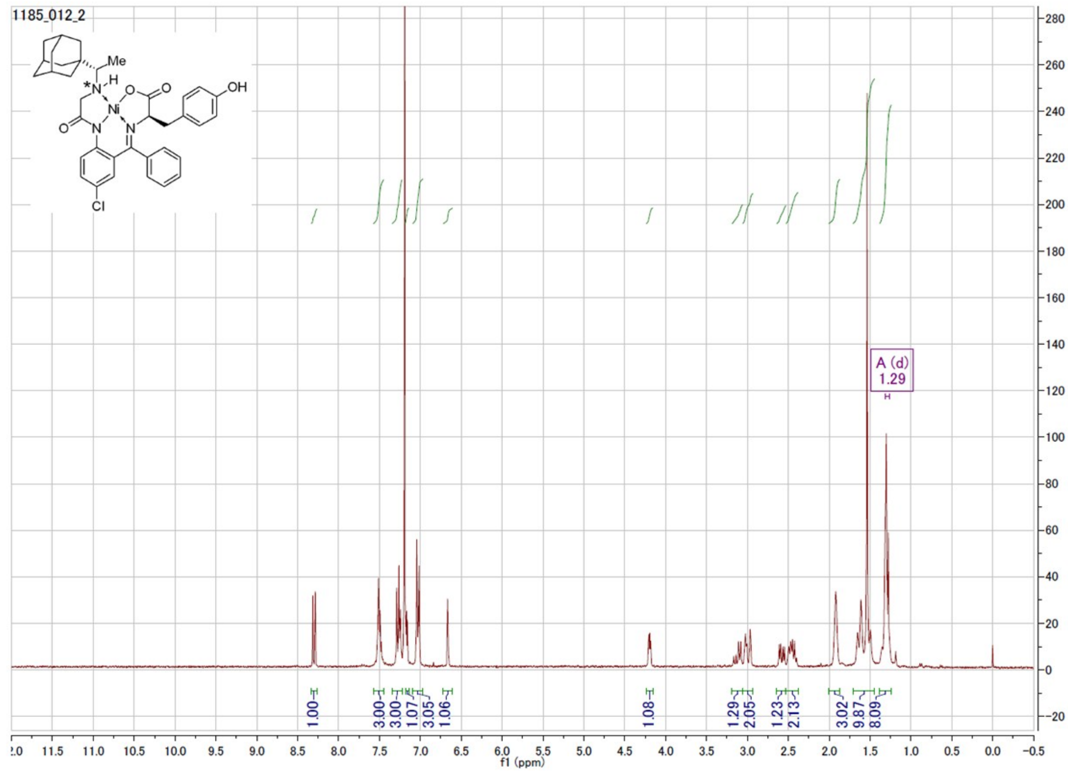
[1]H-NMR (300 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12d**



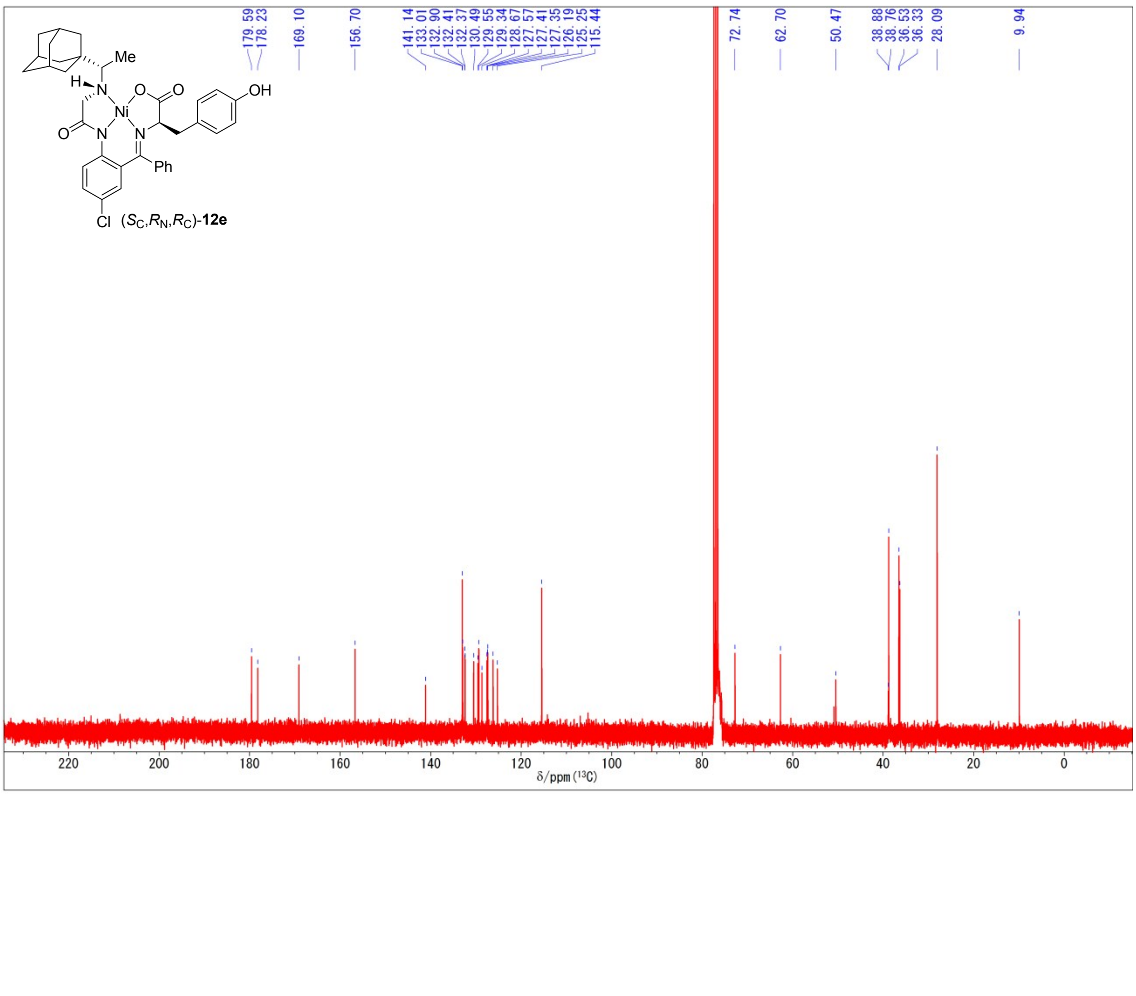
[13]C-NMR (75 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12d**



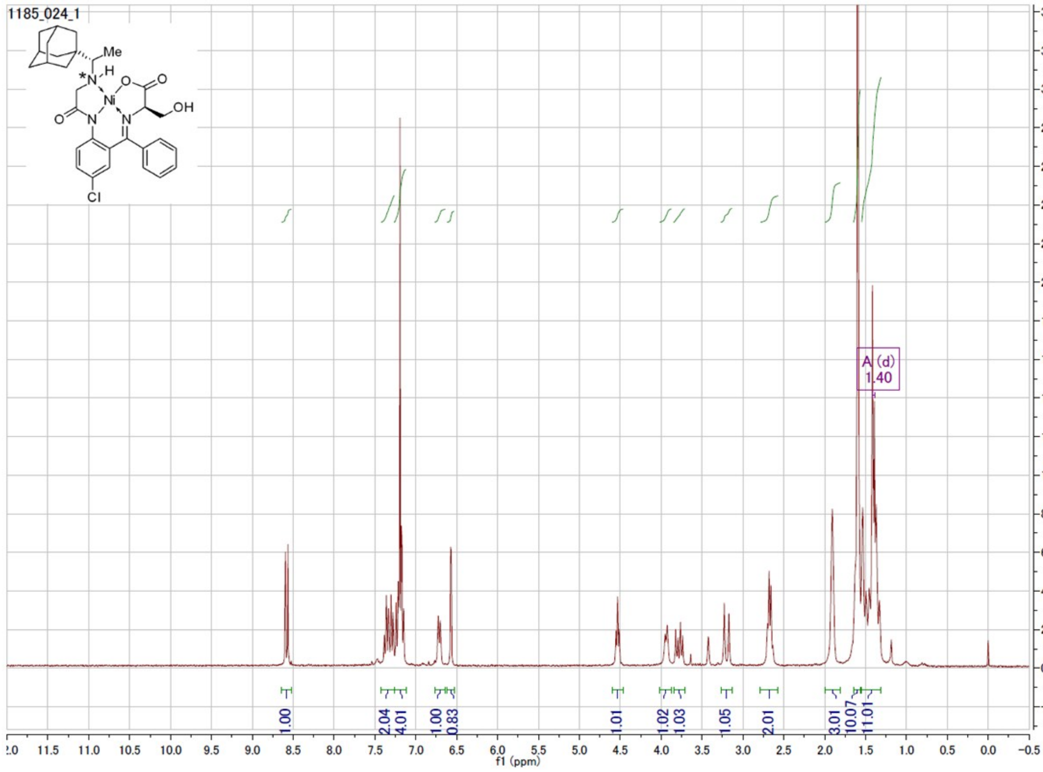
[1]H-NMR (300 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12e**



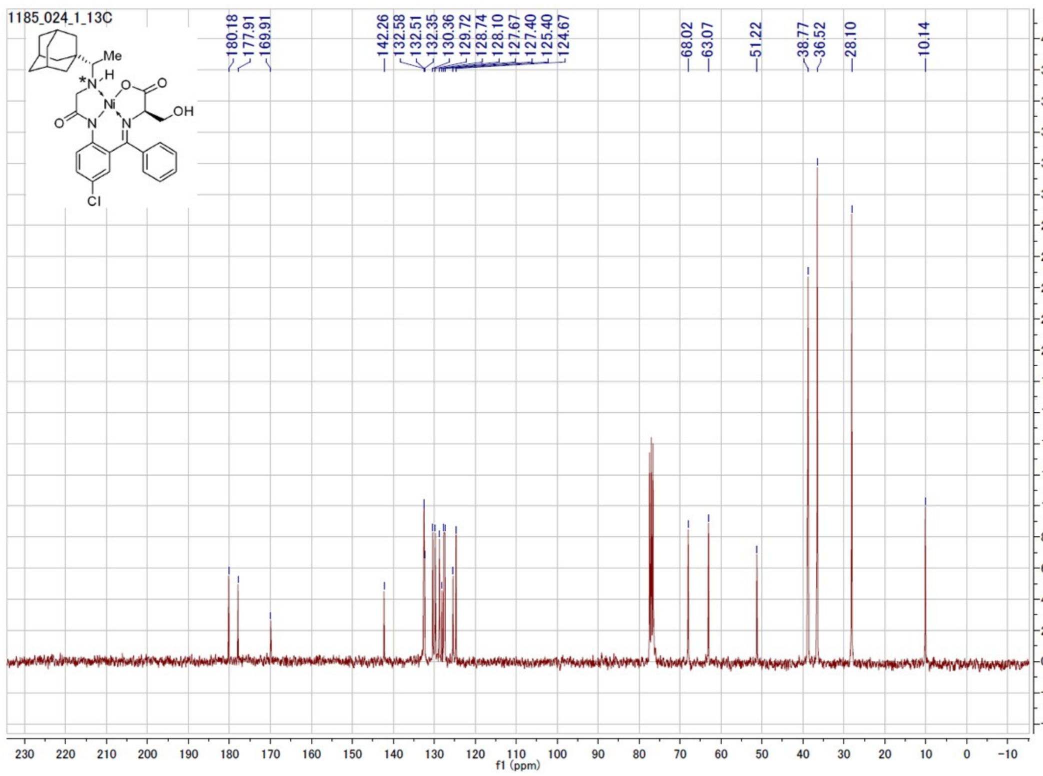
[13]C-NMR (75 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12e**



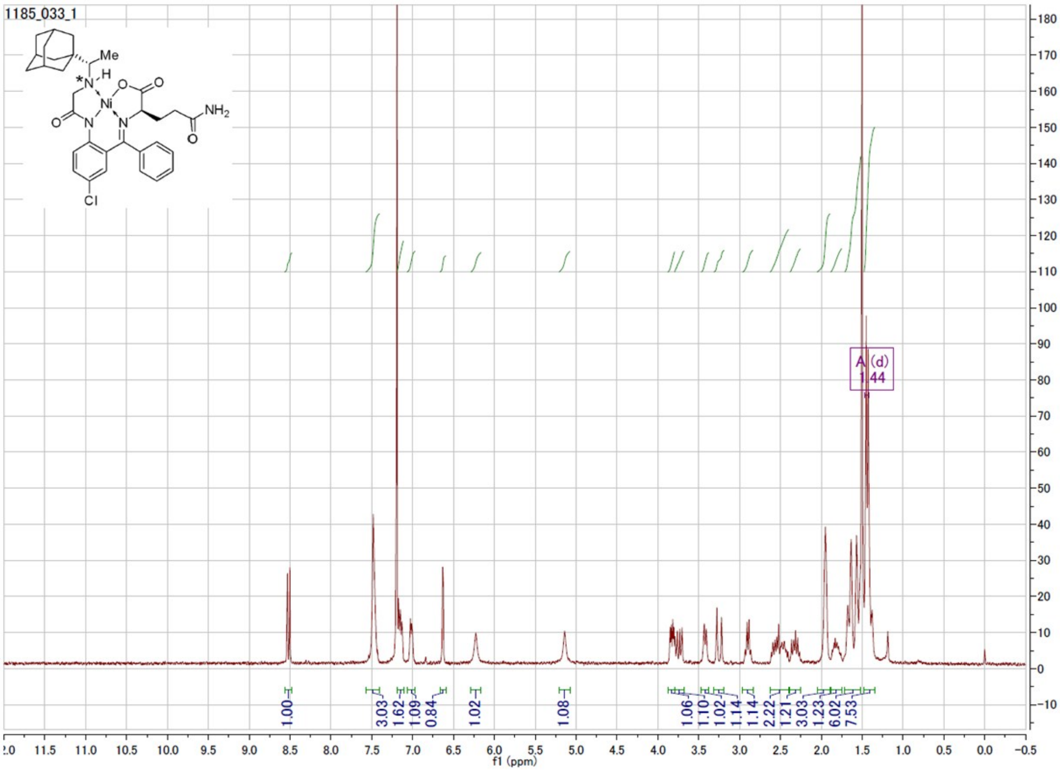
[1]H-NMR (300 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12f**



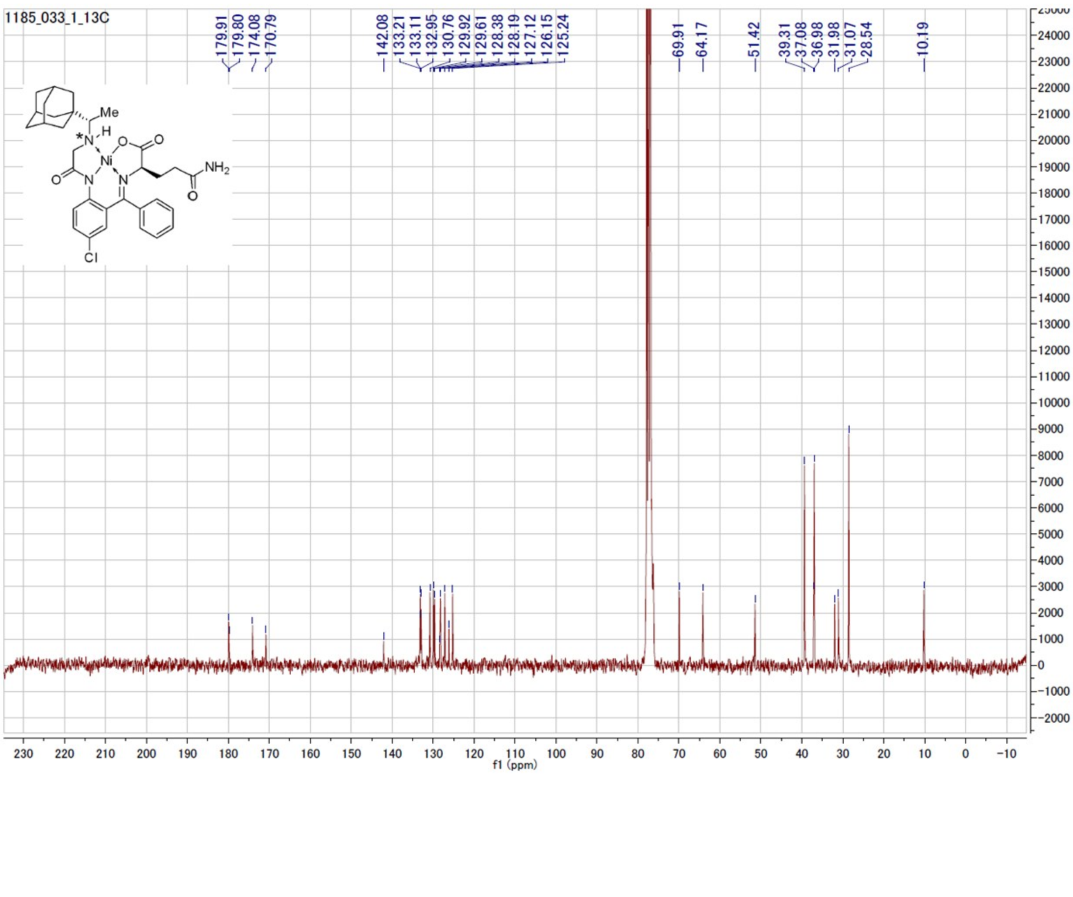
[13]C-NMR (75 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12f**



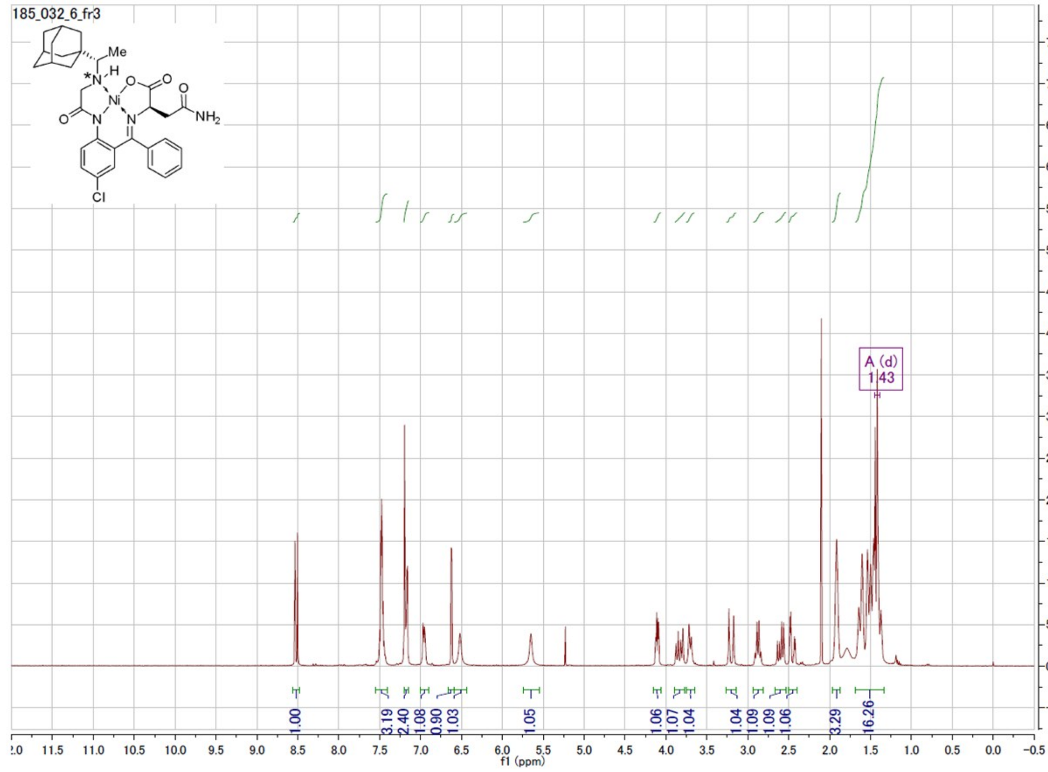
[1]H-NMR (300 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12g**



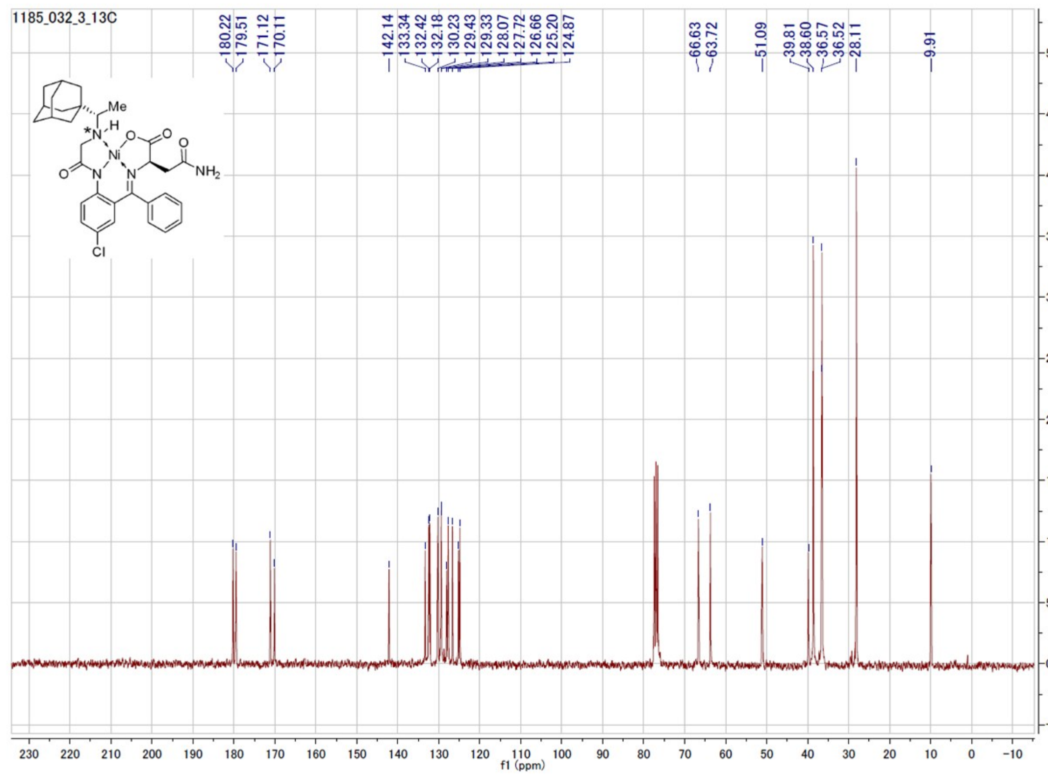
[13]C-NMR (75 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12g**



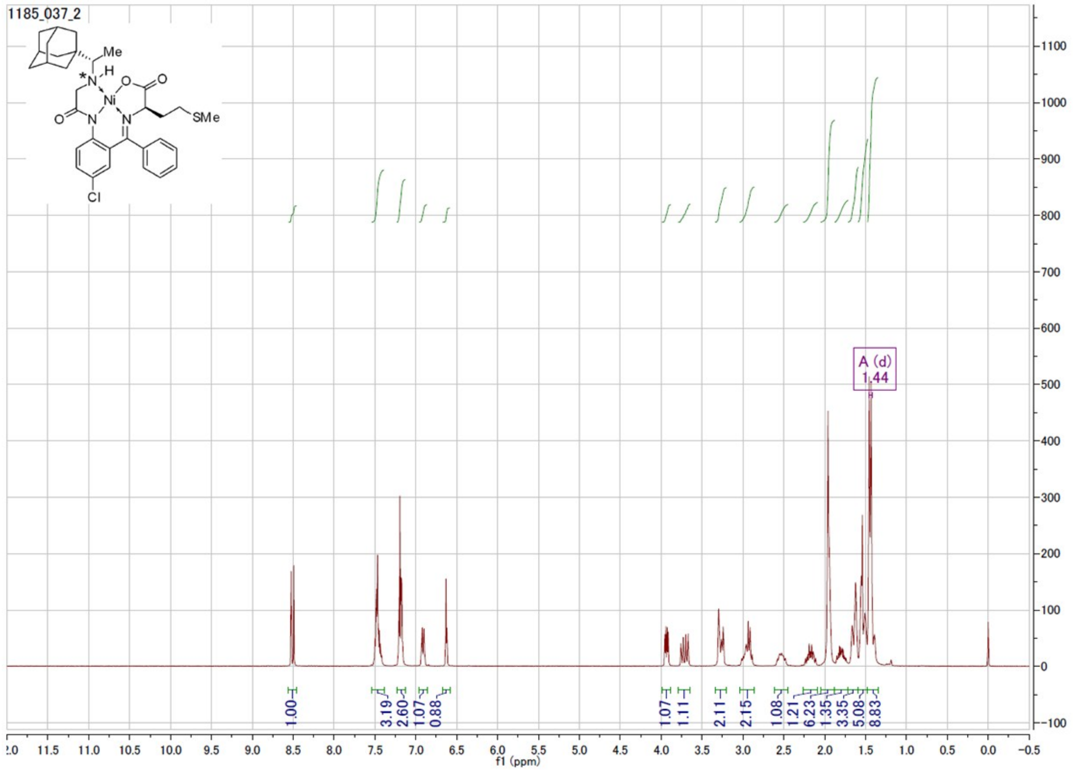
^{1}H-NMR (300 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12h**



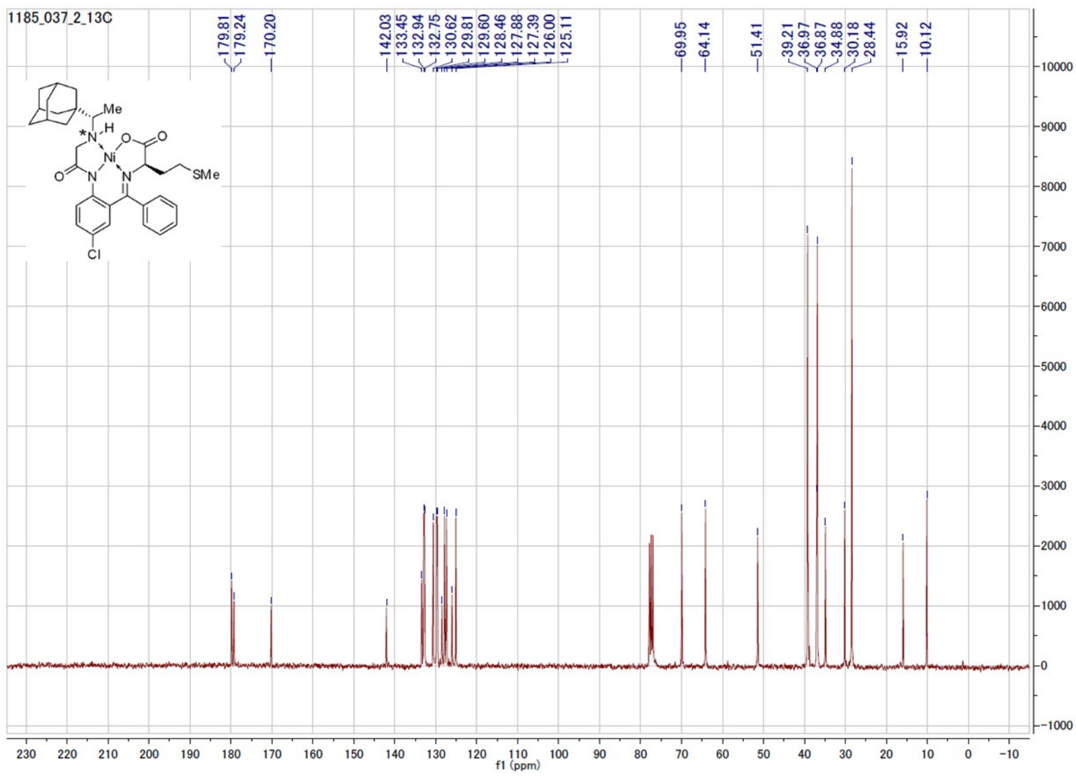
^{13}C-NMR (75 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12h**



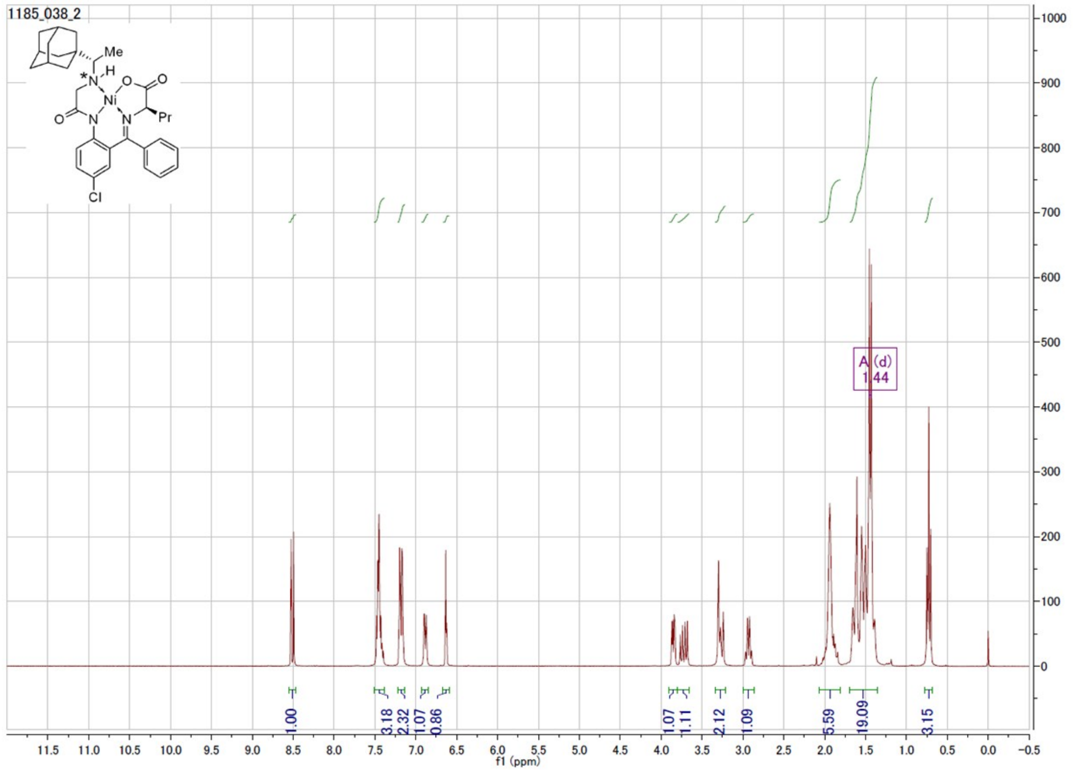
[1]H-NMR (300 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12i**



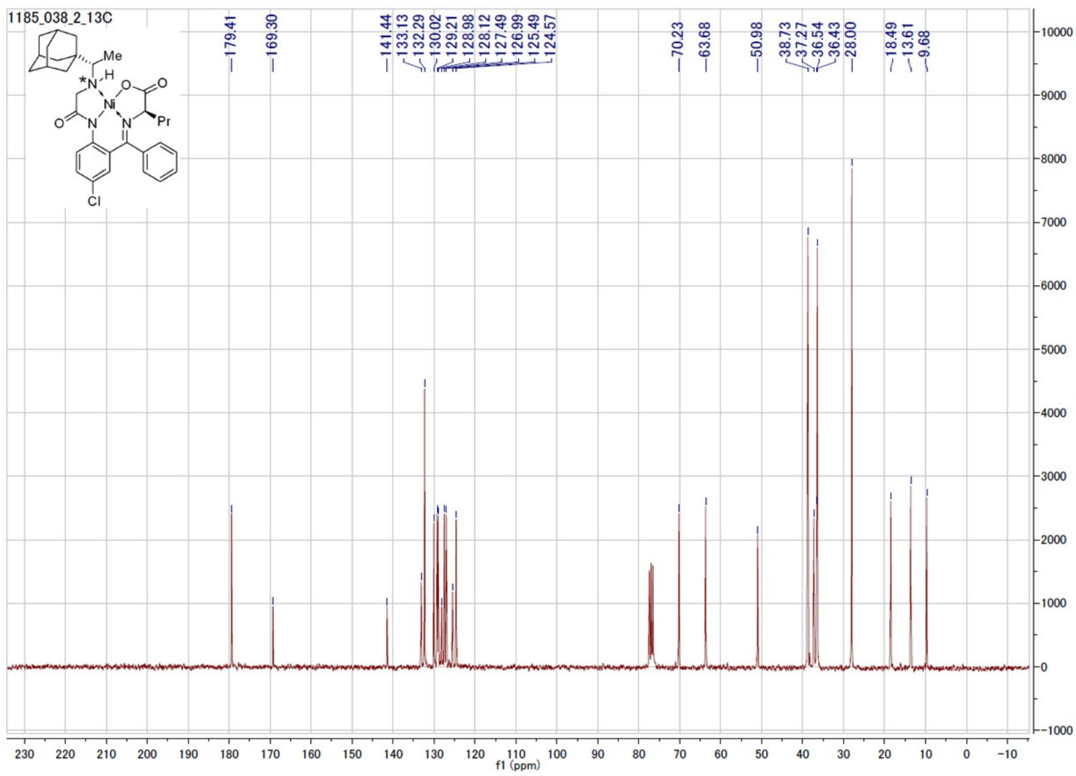
[13]C-NMR (75 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12i**



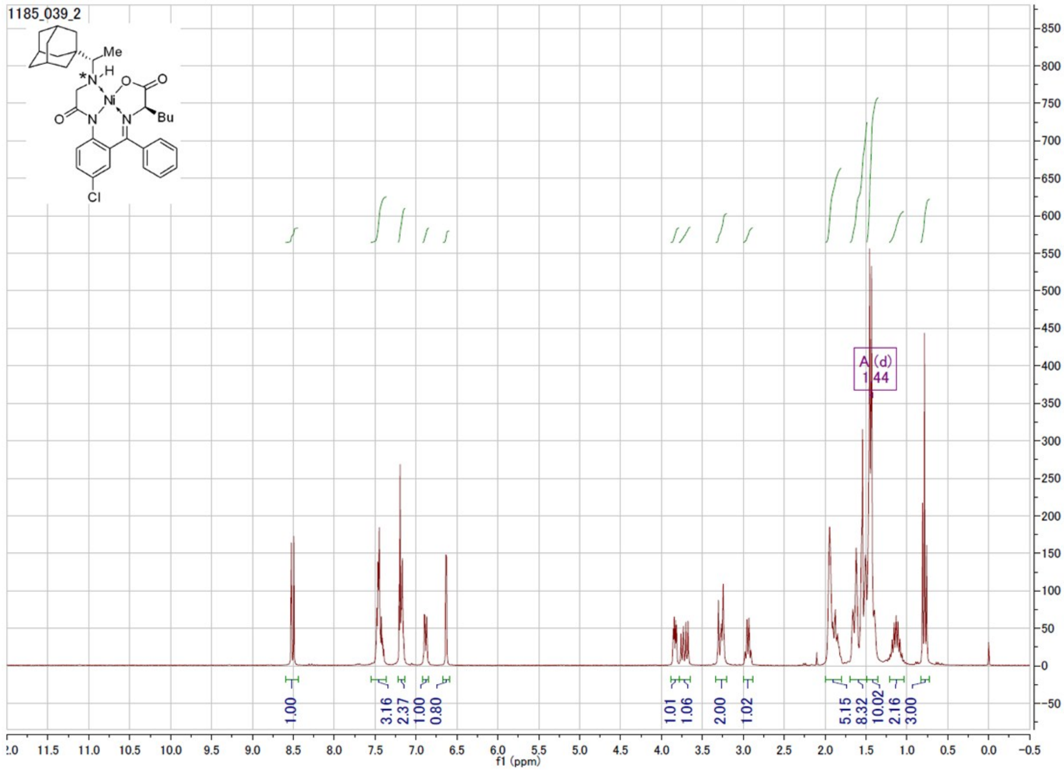
[1]H-NMR (300 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12j**



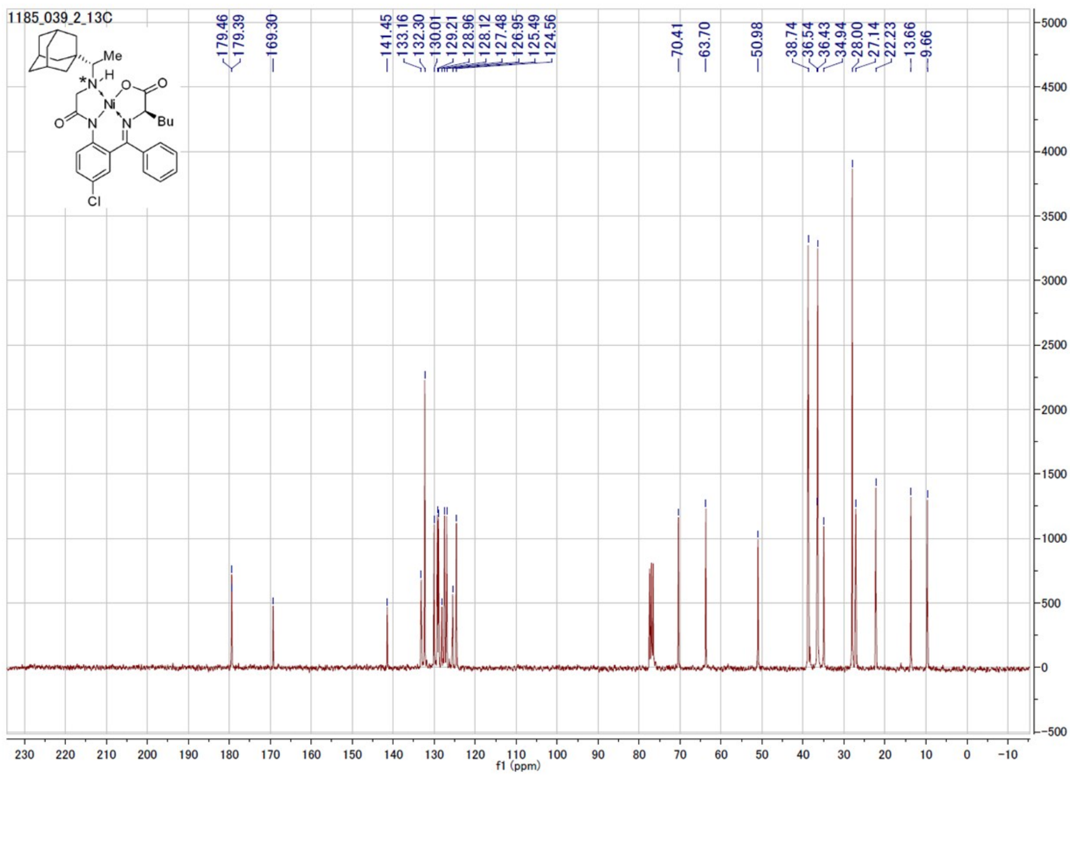
[13]C-NMR (75 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12j**



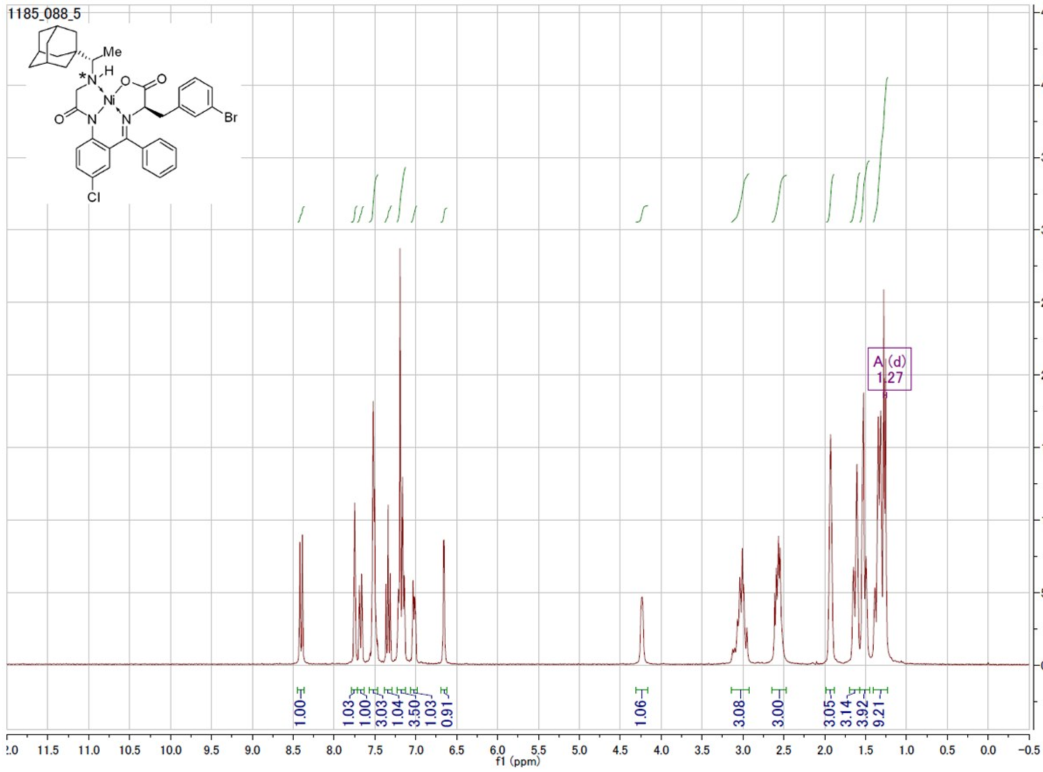
^{1}H-NMR (300 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12k**



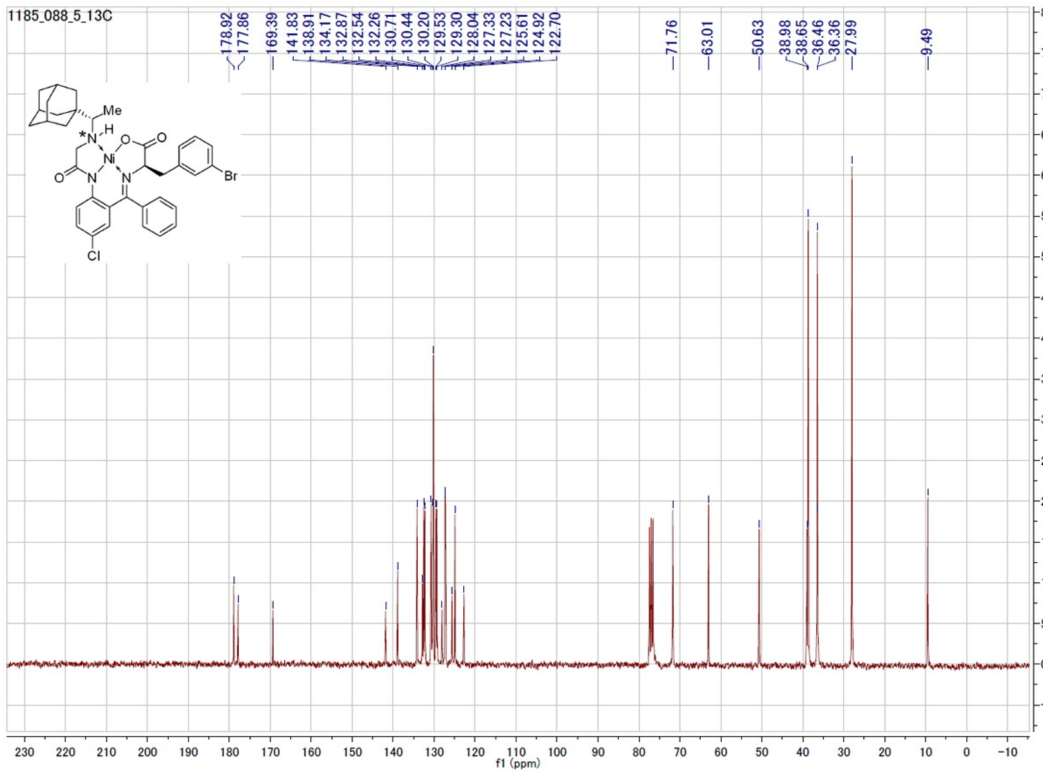
^{13}C-NMR (75 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12k**



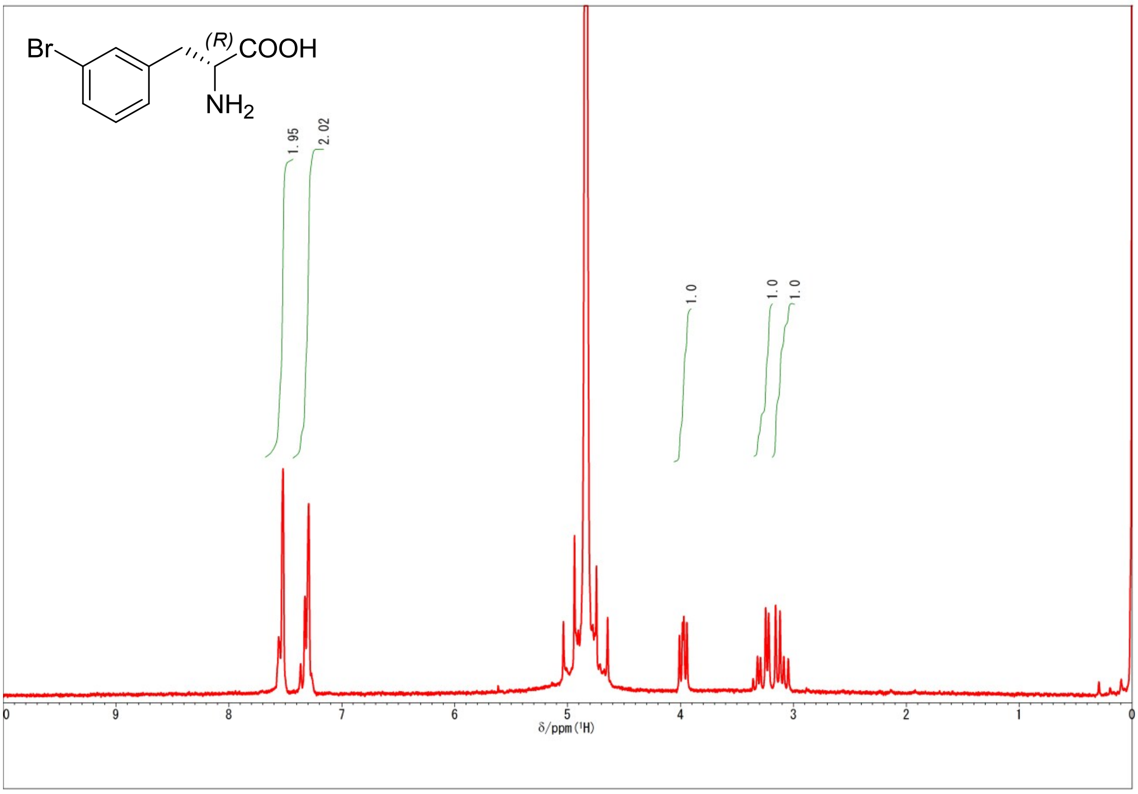
[1]H-NMR (300 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12l**



[13]C-NMR (75 MHz, $CDCl_3$) of (S_C, R_N, R_C)-**12l**



[1]H-NMR (200 MHz, D_2O) of (*R*)-**16**

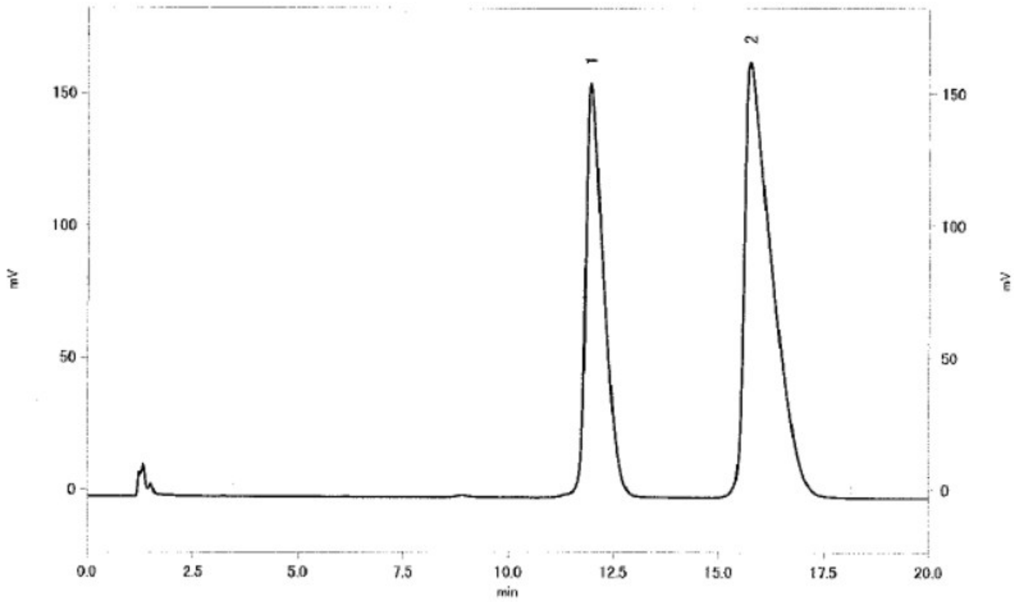


4. Additional data on enantiomeric purity of amino acid 16

<Chiral HPLC conditions for amino acid **16**>

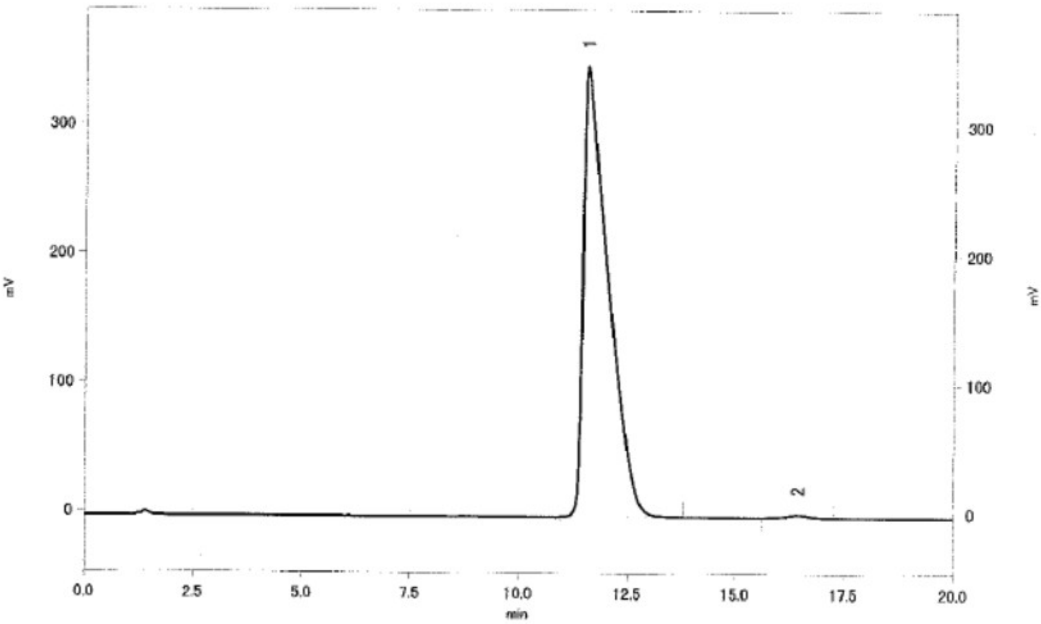
Instrument: SHIMADZU LC-2010CHT chromatography system and a CLASS-VP™ analysis data system (SHIMADZU CORPORATION, Kyoto, Japan).
Column: DAICEL CROWNPAK CR(+) (particle size 5 µm, 150 x 4.0 mm i.d.)
Eluent: A = pH 2.0 $HClO_4$ aq.
B = MeOH
A : B = 9 : 1
Flow rate: 1.0 mL/min
Temp: 40 ºC
Detector: UV 220 nm

Chiral HPLC chart of **16** enantiomixture



HPLC retention time (min)		Ratio ((*R*)-**16** : (*S*)-**16**)
(*R*)-**16**	(*S*)-**16**	
11.9	15.7	23.6% *ee* (38.2 : 61.8)

Chiral HPLC chart of (*R*)-**16**: additional data



HPLC retention time (min)		Ratio ((*R*)-**16** : (*S*)-**16**)
(*R*)-**16**	(*S*)-**16**	
11.5	16.4	99.0% *ee* (99.5 : 0.5)

<Chiral HPLC conditions for amino acid **16**: another instrument>

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

Column: DAICEL CROWNPAK CR(+) (particle size 5 μm, 150 x 4.0 mm i.d.)

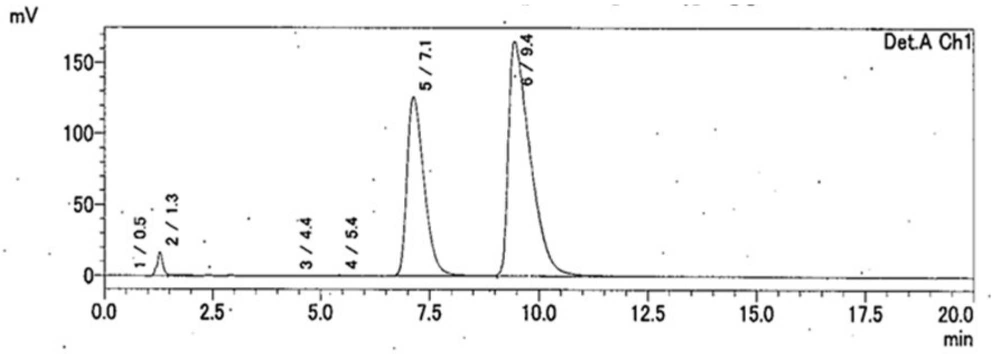
Eluent: A = pH 2.0 $HClO_4$ aq.
B = MeOH
A : B = 9 : 1

Flow rate: 1.0 mL/min

Temp: 40 ºC

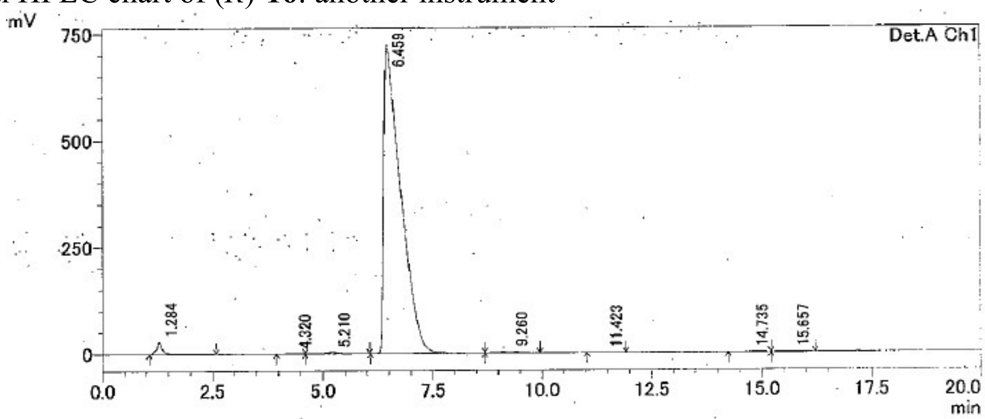
Detector: UV 220 nm

Chiral HPLC chart of **16** enantiomixture: another instrument



HPLC retention time (min)		Ratio ((*R*)-**16** : (*S*)-**16**)
(*R*)-**16**	(*S*)-**16**	
7.1	9.4	24.6% *ee* (37.7 : 62.3)

Chiral HPLC chart of (*R*)-**16**: another instrument



HPLC retention time (min)		Ratio ((*R*)-**16** : (*S*)-**16**)
(*R*)-**16**	(*S*)-**16**	
6.4	9.2	99.0% *ee* (99.5 : 0.5)