Enantioselective Synthesis of 2-Substituted-Tetrahydroisoquinolin-1-yl Glycine Derivatives via Oxidative Cross-Dehydrogenative Coupling of Tertiary Amines and Chiral Nickel(II) Glycinate

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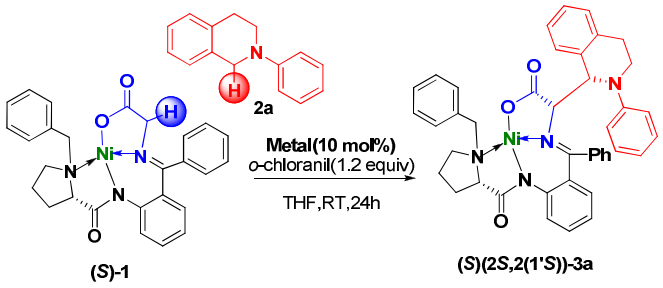
(A) Metal screening, equivalent, and temperature optimization

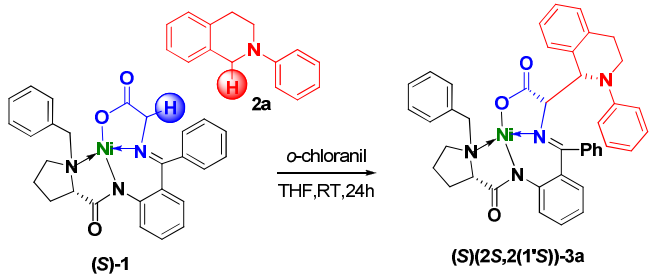
Table S1: Metal screening for the *o*-chloranil mediated CDC reaction.[a]



Entry	Metal	*t* [h]	Yield [%][b]	*syn/anti*[c]
1	CuBr	24	17	1.3:1
2	CuI	24	13	1.2:1
3	Cu(OTf)	24	15	1.1:1
4	$CuBr_2$	24	20	1:1.2
5	$Cu(OAc)_2$	24	25	1:2

[a] Reaction conditions: (*S*)-**1** (0.1 mmol), **2a** (0.12 mmol), *o*-chloranil (0.12 mmol), metal (0.01 mmol) and THF (1.0 mL). [b] Isolated yield of combined **3a** (*syn* and *anti*). [c] The diastereomeric ratios of **3a** determined by ^{1}H NMR.

Table S2: Equivalent screening for the *o*-chloranil mediated CDC reaction.[a]

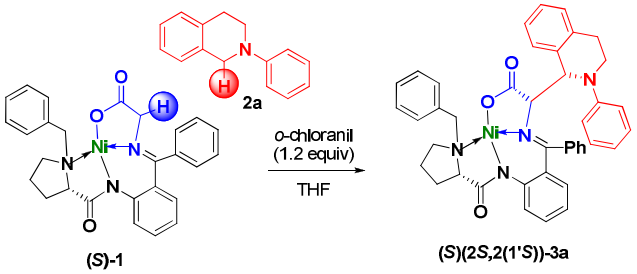


Entry	**1**/**2a**/*o*-chloranil	*t* [h]	Yield [%][b]	*syn/anti*[c]

1	1/1.2/1.2	24	64	4.6:1
2	1/1.2/1.5	24	50	3:1
3	1/1.5/1.2	24	65	2.5:1
4	1.2/1/1	24	55	2.8:1

[a] Reaction conditions: (*S*)-**1** (0.1 mmol), **2a** (0.12 mmol), *o*-chloranil (0.12 mmol), and THF(1.0 mL). [b] Isolated yield of combined **3a** (*syn* and *anti*). [c] The diastereomeric ratios of **3a** determined by ^{1}H NMR.

Table S3: Temperature screening for the *o*-chloranil mediated CDC reaction.[a]

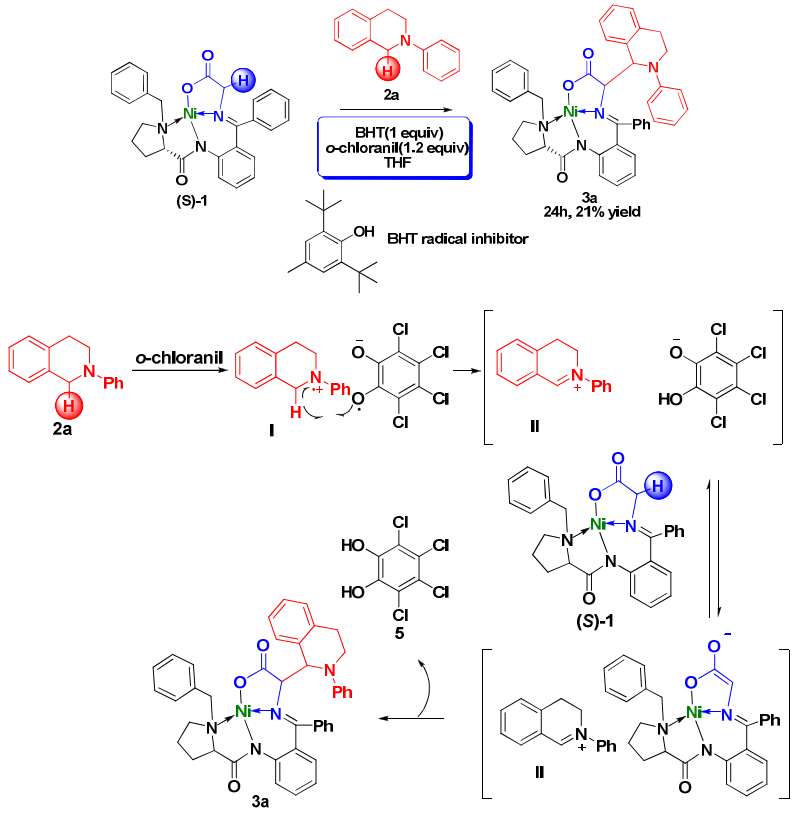


Entry	T (^{o}C)	*t* [h]	Yield [%][b]	*syn/anti* [c]
1	60	8	70	2.3:1
2	40	16	65	2.5:1
3	20	24	64	4.6:1
4	0	36	<10	n.d.
5	-20	36	0	n.d.

[a] Reaction conditions: (*S*)-**1** (0.1 mmol), **2a** (0.12 mmol), *o*-chloranil (0.12 mmol), and THF (1.0 mL). [b] Isolated yield of combined **3a** (*syn* and *anti*). [c] The diastereomeric ratios of **3a** determined by ^{1}H NMR. n.d. = not determined.

(B) Mechanistic experiments and proposed reaction pathways

The plausible reaction pathway for the coupling is postulated to involve a single-electron transfer (SET) radical mechanism[1] in Scheme S1. A single electron transfer from the tertiary amine **2a** to *o*-chloranil generates a radical cation **I** and a *o*-chloranil radical anion. The radical oxygen of the *o*-chloranil radical anion then abstracts α-H-atom from the radical cation **I** generates the key intermediate iminium cation **II**. With one equivalent of 2,6-di-*tert*-butyl-4-methylphenol (BHT), a radical inhibitor, the yield of the coupling product decreased dramatically from 64% to 21%. These results were interpreted as the generation of radicals as key intermediate, and are in consistence with the observations by Wang *et al*[2] and Chi *et al*[3]. Then the anionic oxygen of *o*-chloranil radical anion then abstracts an α-hydrogen from the glycinate to generate an enolate. Finally, the nucleophilic attack of the enolate on the iminium cation **II** generates the CDC product **3a** and the 3,4,5,6-tetrachlorobenzene-1,2-diol **5**.



Scheme S1. Mechanistic experiments and proposed reaction pathways

(C) Stereochemical Transition of CDC

Considering the stereochemical outcome of the reaction under study, we could propose two transition (TS) **A** and **B** (Figure S1), leading to diastereomers (*S*)(2*S*,2(1'*S*))-**3**/(*S*)(2*S*,2(1'*R*))-**3** (**3**-*syn*/**3**-*anti*), respectively. In TS **A**, the *N*-phenyl group occupies a position of the larger substituent, thus avoiding unfavorable non-bonding interactions with the phenyl ring at the imine bond of the Ni(II) complex, which render **A** more favorable than **B**. Under optimized oxidative conditions, iminiums were attacked highly selectively from the *si*-face of Ni(II) glycinate[4,5,6] generating excellent diastereoselectivity. Therefore, the CDC reaction didn't generate the diastereomers (*S*)(2*R*,2(1'*R*))-**3**/(*S*)(2*R*,2(1'*S*))-**3**. The relative and absolute configuration of major coupling compound **3a-*syn*** was determined to be (*S*)(2*S*,2(1'*S*)) and the minor one **3k-*anti*** was determined to be (*S*)(2*S*,2(1'*R*)) by X-ray crystallography (Figure S3).

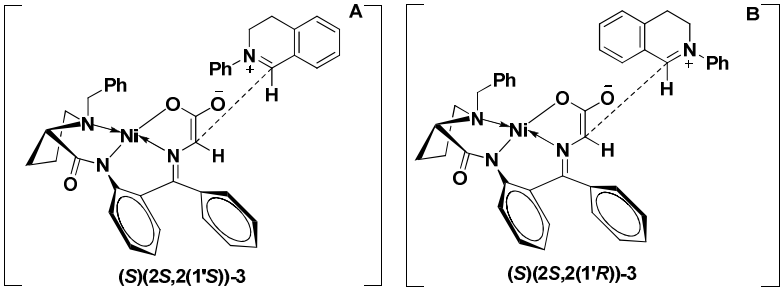


Figure S1. Stereochemical Transition of CDC

(D) The Absolute Configuration of 3a-*syn* and 3k-*anti*

X-ray Single Crystal Stucture Analysis of (*S*)(2*S*,2(1'*S*))-**3a**:

X-ray crystallographic data of (*S*)(2*S*,2(1'*S*))-**3a** were solutions at T = 293(2) K: $C_{42}H_{38}N_4NiO_3$, M_r = 705.47, monoclinic. Space group *P2* (1), a = 15.670 (3) Å, b = 10.967 (3) Å, c = 21.785 (6) Å, α = 90°, β = 107.289 (8)°, γ = 90°, V = 3574.7 (16) Å^3, Z = 4.

(*S*)(2*S*,2(1'*S*))-**3a:**

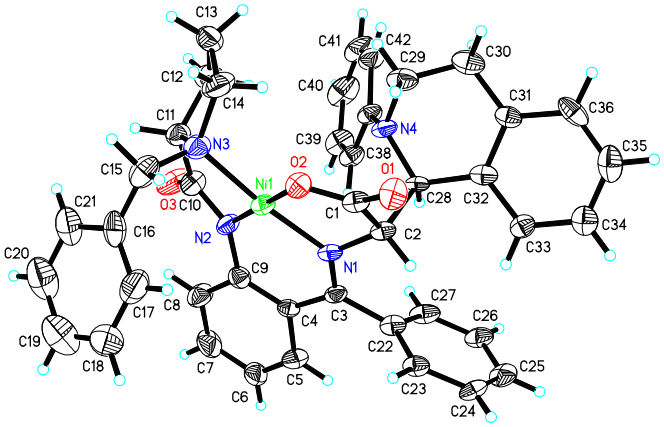


Figure S2. The crystal structure of (*S*)(2*S*,2(1'*S*))-**3a** by X-ray analysis.

(*S*)(2*S*,2(1'*R*))-**3k:**

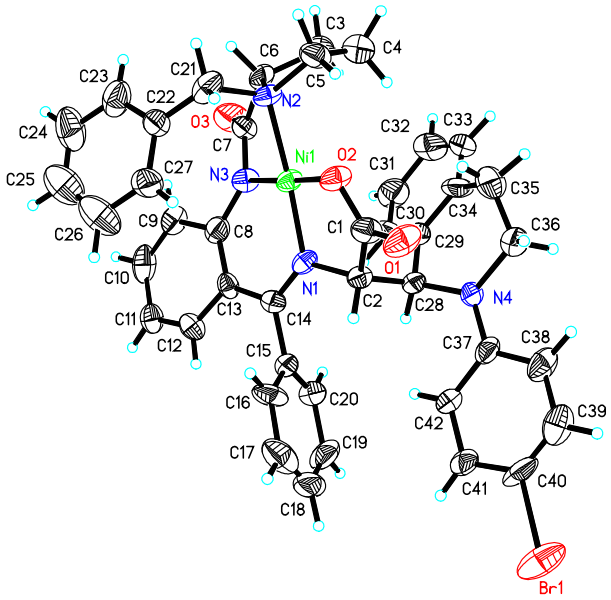
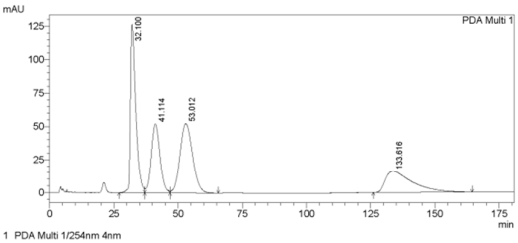


Figure S3. The crystal structure of (*S*)(2*S*,2(1'*R*))-**3k** by X-ray analysis.

These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif, the CCDC numbers are 927172 for (*S*)(2*S*,2(1'*S*))-**3a**, and 962699 for (*S*)(2*S*,2(1'*R*))-**3k**.

(E) HPLC spectra for *de* determination

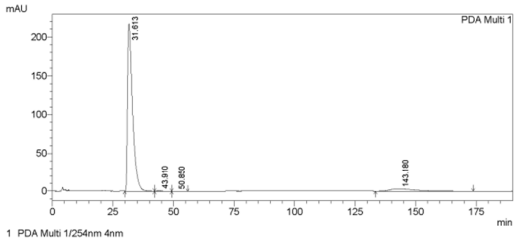
3a



PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.100	18384018	126550	30.339	51.134
2	41.114	12442867	52225	20.534	21.102
3	53.012	18012468	52617	29.726	21.260
4	133.616	11756042	16096	19.401	6.504
Total		60595396	247487	100.000	100.000



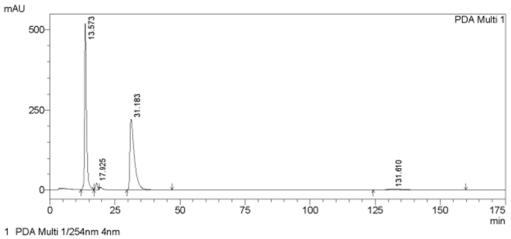
PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.613	31325254	217081	93.340	98.158
2	43.910	127514	883	0.380	0.399
3	50.850	15399	166	0.046	0.075
4	143.180	2092382	3026	6.235	1.368
Total		33560549	221156	100.000	100.000

The *de* was determined by HPLC with a Chiralpak AD-H column (^{n}-hexane/^{i}-PrOH = 75/25, λ = 254 nm, 0.8 mL/min). For the *syn*-isomer: t_R (major enantiomer) = 31.61 min, t_R (minor enantiomer) = 50.85 min, > 99% *de*; for the *anti*-isomer: t_R (major enantiomer) = 143.18 min, t_R (minor enantiomer) = 43.91 min, 88% *de*.

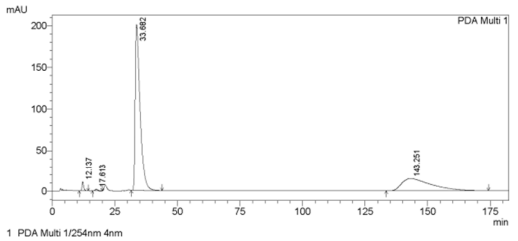
3b



PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.573	26486453	518222	48.194	67.947
2	17.925	1231113	20473	2.240	2.684
3	31.183	26167060	221474	47.613	29.039
4	131.610	1072845	2517	1.952	0.330
Total		54957471	762687	100.000	100.000



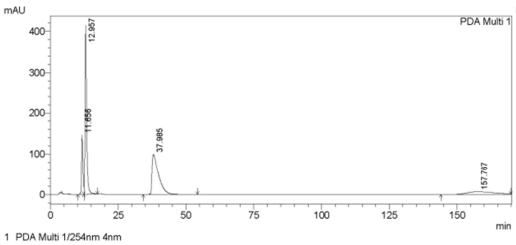
PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.137	476078	10793	1.189	4.732
2	17.613	148197	1893	0.370	0.830
3	33.682	27369635	200546	68.349	87.934
4	143.251	12049743	14833	30.092	6.504
Total		40043653	228064	100.000	100.000

The *de* was determined by HPLC with a Chiralpak IA column (^{n}-hexane/^{i}-PrOH = 60/40, λ = 254 nm, 1.0 mL/min). For the *syn*-isomer: t_R (major enantiomer) = 33.68 min, t_R (minor enantiomer) = 12.14 min, 96% *de*; for the *anti*-isomer: t_R (major enantiomer) = 143.25 min, t_R (minor enantiomer) = 17.61 min, 97% *de*.

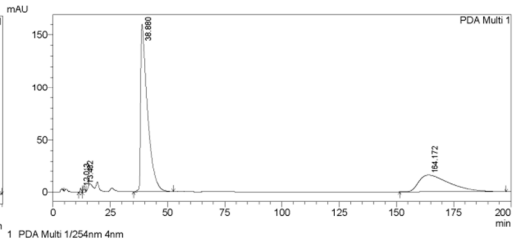
3c



PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.656	4917087	146695	11.301	22.020
2	12.957	17325363	413635	39.818	62.090
3	37.985	16643927	99313	38.252	14.908
4	157.767	462458	6537	10.628	0.981
Total		43510935	666180	100.000	100.000



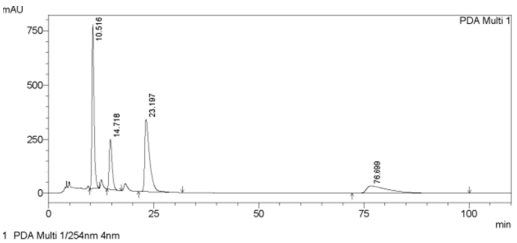
PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.013	138237	3649	0.285	1.971
2	13.482	297779	5977	0.613	3.228
3	38.880	33392350	159769	68.784	86.281
4	164.172	14718336	15777	30.318	8.520
Total		48546701	185173	100.000	100.000

The *de* was determined by HPLC with a Chiralpak IA column (^{n}-hexane/^{i}-PrOH = 60/40, λ = 254 nm, 1.0 mL/min). For the *syn*-isomer: t_R (major enantiomer) = 38.88 min, t_R (minor enantiomer) = 13.48 min, 98% *de*; for the *anti*-isomer: t_R (major enantiomer) = 164.17 min, t_R (minor enantiomer) = 12.01 min, 98% *de*.

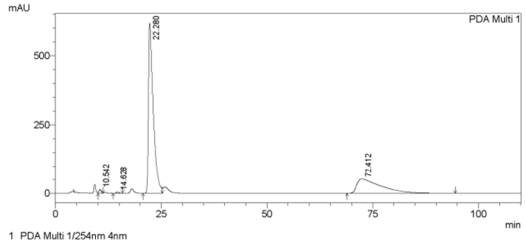
3f



PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.516	26135392	756343	34.505	55.697
2	14.718	11068888	233388	14.614	17.187
3	23.197	26791385	335632	35.371	24.716
4	76.699	11747497	32587	15.510	2.400
Total		75743163	1357951	100.000	100.000



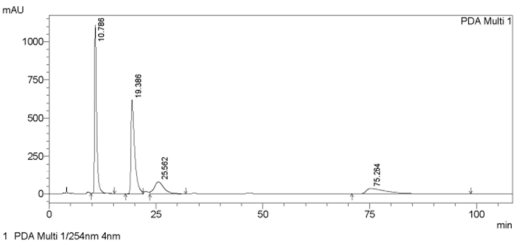
PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.542	503255	14016	0.718	2.040
2	14.628	179939	4041	0.257	0.588
3	22.280	48759248	616922	69.598	89.795
4	72.412	20615675	52058	29.427	7.577
Total		70058117	687037	100.000	100.000

The *de* was determined by HPLC with a Chiralpak IA column (^{n}-hexane/^{i}-PrOH = 60/40, λ = 254 nm, 1.0 mL/min). For the *syn*-isomer: t_R (major enantiomer) = 22.28 min, t_R (minor enantiomer) = 10.54 min, 98% *de*; for the *anti*-isomer: t_R (major enantiomer) = 72.41 min, t_R (minor enantiomer) = 14.63 min, 98% *de*.

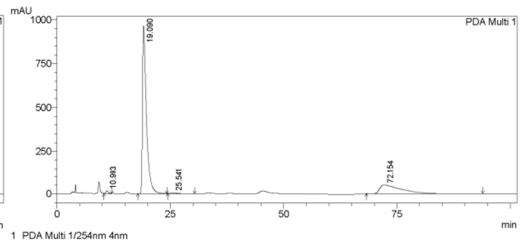
3g



PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.786	36732206	1105629	37.277	60.104
2	19.386	37670964	619732	38.230	33.690
3	25.562	13004350	79578	13.197	4.326
4	75.264	11131028	34579	11.296	1.880
Total		98538549	1839518	100.000	100.000



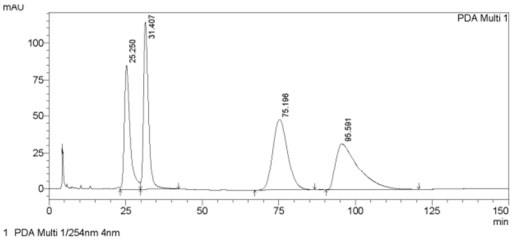
PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.993	722511	17483	0.938	1.683
2	19.090	58819132	965707	76.388	92.965
3	25.541	5868845	5215	0.762	0.502
4	72.154	16872069	50383	21.912	4.850
Total		77000556	1038788	100.000	100.000

The *de* was determined by HPLC with a Chiralpak IA column (^{n}-hexane/^{i}-PrOH = 75/25, λ = 254 nm, 1.0 mL/min). For the *syn*-isomer: t_R (major enantiomer) = 19.09 min, t_R (minor enantiomer) = 10.99 min, 97% *de*; for the *anti*-isomer: t_R (major enantiomer) = 72.15 min, t_R (minor enantiomer) = 25.54 min, 98% *de*.

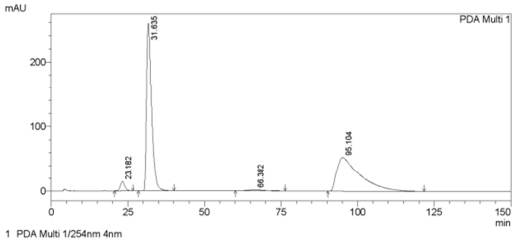
3h



PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.250	10997775	85281	19.528	30.501
2	31.407	12802066	114332	22.732	40.891
3	75.196	16282910	48304	28.913	17.276
4	95.591	16234680	31686	28.827	11.332
Total		56317432	279602	100.000	100.000



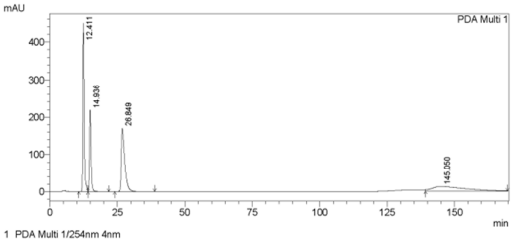
PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.182	1469715	14369	2.479	4.398
2	31.635	29529082	258094	49.811	79.007
3	66.382	492108	1350	0.830	0.413
4	95.104	27791027	52858	46.879	16.181
Total		59281932	326670	100.000	100.000

The *de* was determined by HPLC with a Chiralpak AD-H column (^{n}-hexane/^{i}-PrOH = 80/20, λ = 254 nm, 0.8 mL/min). For the *syn*-isomer: t_R (major enantiomer) = 31.64 min, t_R (minor enantiomer) = 23.18 min, 90% *de*; for the *anti*-isomer: t_R (major enantiomer) = 95.10 min, t_R (minor enantiomer) = 66.38 min, 96% *de*.

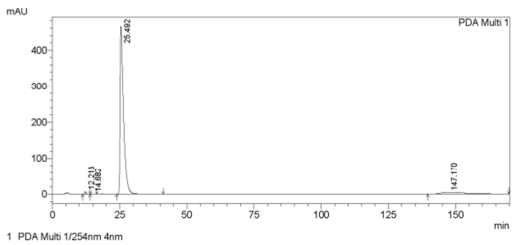
3i



PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.411	15600754	48933	31.227	52.815
2	14.936	8662321	218360	17.339	25.689
3	26.849	15340329	170296	30.706	20.034
4	145.050	10355874	12424	20.729	1.462
Total		49959279	850013	100.000	100.000



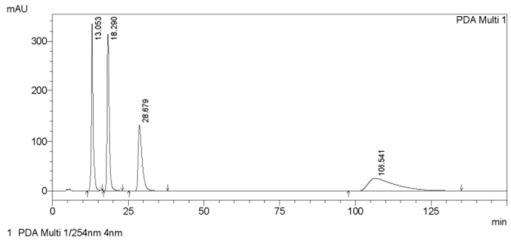
PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.213	243554	6728	0.550	1.412
2	14.682	34398	973	0.078	0.204
3	25.492	40866751	464091	92.306	97.412
4	147.170	3128307	4628	7.066	0.971
Total		44273010	476420	100.000	100.000

The *de* was determined by HPLC with a Chiralpak IA column (^{n}-hexane/^{i}-PrOH = 60/40, λ = 254 nm, 1.0 mL/min). For the *syn*-isomer: t_R (major enantiomer) = 25.49 min, t_R (minor enantiomer) = 12.21 min, 99% *de*; for the *anti*-isomer: t_R (major enantiomer) = 147.17 min, t_R (minor enantiomer) = 14.68 min, > 98% *de*.

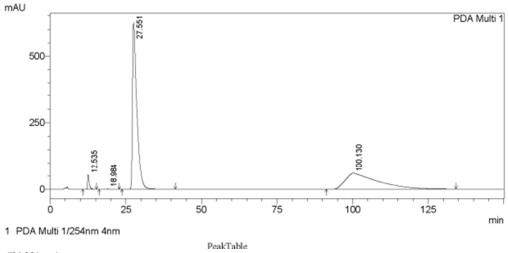
3j



PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.053	13579806	334192	24.338	41.541
2	18.290	15269572	313518	27.366	38.971
3	28.679	11924992	132023	21.372	16.411
4	106.541	15022305	24760	26.923	3.078
Total		55796674	804493	100.000	100.000



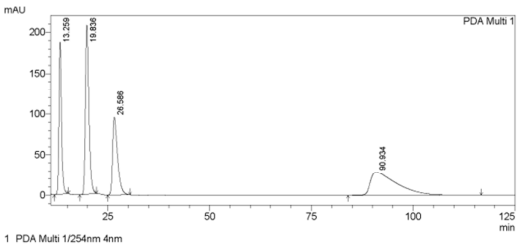
PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.535	2110570	53748	1.943	7.269
2	18.984	89517	1040	0.082	0.141
3	27.551	62063804	625092	57.130	84.542
4	100.130	44372593	59508	40.845	8.048
Total		108636483	739389	100.000	100.000

The *de* was determined by HPLC with a Chiralpak IA column (^{n}-hexane/^{i}-PrOH = 60/40, λ = 254 nm, 1.0 mL/min). For the *syn*-isomer: t_R (major enantiomer) = 27.55 min, t_R (minor enantiomer) = 12.54 min, 93% *de*; for the *anti*-isomer: t_R (major enantiomer) = 100.13 min, t_R (minor enantiomer) = 18.98 min, > 99% *de*.

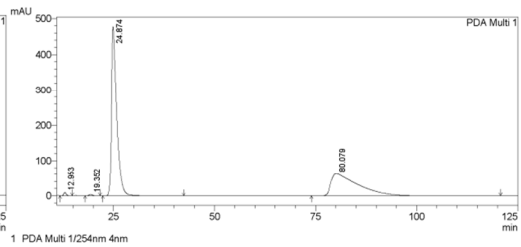
3k



PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.259	8115677	187252	19.561	36.084
2	19.836	12483078	207206	30.088	39.929
3	26.586	8105000	95766	19.536	18.455
4	90.934	12784399	28707	30.815	5.532
Total		41488154	518932	100.000	100.000



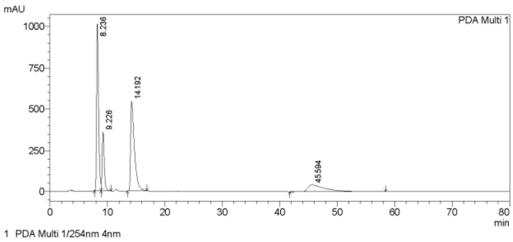
PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.953	379985	9041	0.528	1.638
2	19.352	223926	3660	0.311	0.663
3	24.874	42770442	477355	59.415	86.475
4	80.079	28611853	61956	39.746	11.224
Total		71986206	552013	100.000	100.000

The *de* was determined by HPLC with a Chiralpak IA column (^{n}-hexane/^{i}-PrOH = 60/40, λ = 254 nm, 1.0 mL/min). For the *syn*-isomer: t_R (major enantiomer) = 24.87 min, t_R (minor enantiomer) = 12.95 min, 98% *de*; for the *anti*-isomer: t_R (major enantiomer) = 80.08 min, t_R (minor enantiomer) = 19.35 min, 98% *de*.

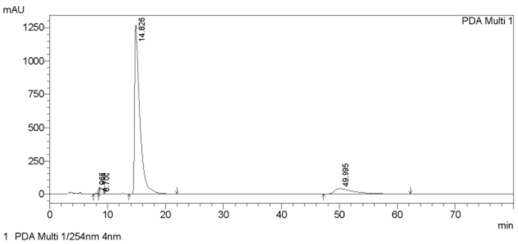
3l



PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.236	23673464	1009273	35.920	51.702
2	9.226	8860812	359867	13.444	18.435
3	14.192	24770513	542730	37.584	27.802
4	45.594	8602131	40233	13.052	2.061
Total		65906920	1952104	100.000	100.000



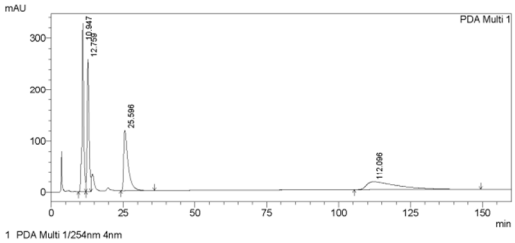
PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.968	67403	2957	0.076	0.226
2	8.700	15219	543	0.017	0.041
3	14.826	79619960	1268083	89.931	96.777
4	49.995	8831596	38727	9.975	2.956
Total		88534179	1310310	100.000	100.000

The *de* was determined by HPLC with a Chiralpak IA column (^{n}-hexane/^{i}-PrOH = 60/40, λ = 254 nm, 1.0 mL/min). For the *syn*-isomer: t_R (major enantiomer) = 14.83 min, t_R (minor enantiomer) = 7.97 min, > 99% *de*; for the *anti*-isomer: t_R (major enantiomer) = 49.99 min, t_R (minor enantiomer) = 8.70 min, > 99% *de*.

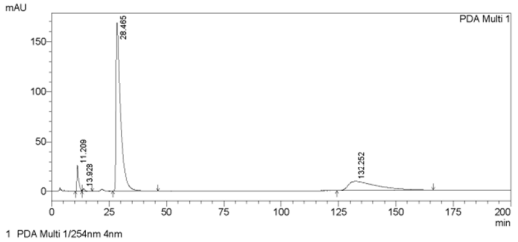
3m



PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.947	13335907	327017	27.219	45.537
2	12.759	11817785	258213	24.121	35.956
3	25.596	12538645	118050	25.592	16.438
4	112.096	11302062	14854	23.068	2.068
Total		48994399	718134	100.000	100.000



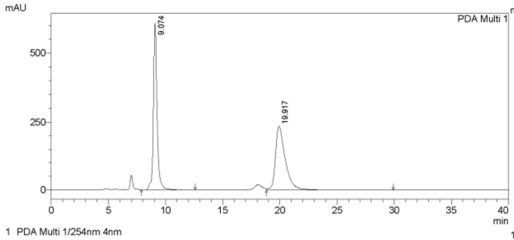
PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.209	1331576	26544	4.118	12.910
2	13.928	157930	2222	0.488	1.080
3	28.465	23015174	167912	71.168	81.666
4	132.252	7834556	8929	24.226	4.343
Total		32339235	205608	100.000	100.000

The *de* was determined by HPLC with a Chiralpak IA column (^{n}-hexane/^{i}-PrOH = 60/40, λ = 254 nm, 1.0 mL/min). For the *syn*-isomer: t_R (major enantiomer) = 28.47 min, t_R (minor enantiomer) = 11.21 min, 89% *de*; for the *anti*-isomer: t_R (major enantiomer) = 132.25 min, t_R (minor enantiomer) = 13.93 min, 96% *de*.

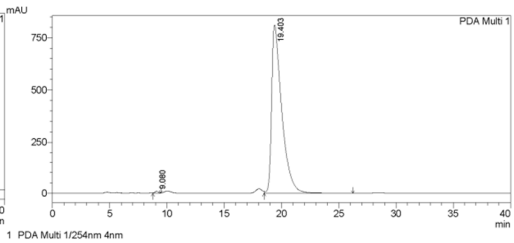
3n-*Syn*



PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.074	13705255	608850	48.988	72.103
2	19.917	14271671	235561	51.012	27.897
Total		27976927	844411	100.000	100.000



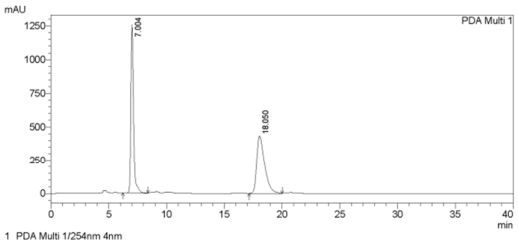
PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.080	223444	9768	0.445	1.192
2	19.403	50035883	809915	99.555	98.808
Total		50259326	819683	100.000	100.000

The *de* was determined by HPLC with a Chiralpak IA column (^{n}-hexane/^{i}-PrOH = 60/40, λ = 254 nm, 1.0 mL/min). For the *syn*-isomer: t_R (major enantiomer) = 19.40 min, t_R (minor enantiomer) = 9.08 min, 99% *de*.

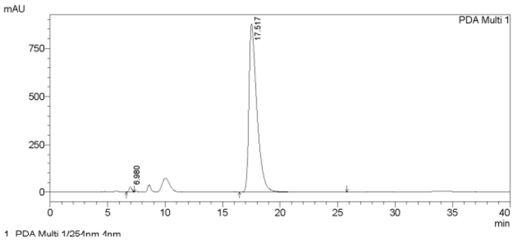
3n-*anti*



PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.004	20542794	1254932	49.653	74.359
2	18.050	20829636	432736	50.347	25.641
Total		41372430	1687667	100.000	100.000



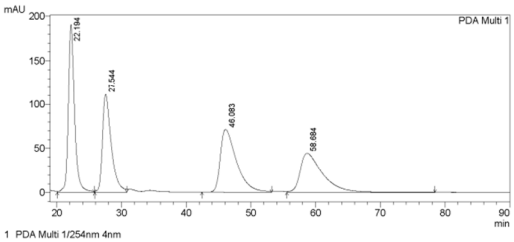
PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.980	458052	26733	1.081	2.963
2	17.517	41923011	875581	98.919	97.037
Total		42381063	902314	100.000	100.000

The *de* was determined by HPLC with a Chiralpak IA column (^{n}-hexane/^{i}-PrOH = 60/40, λ = 254 nm, 1.0 mL/min). For the *anti*-isomer: t_R (major enantiomer) = 17.52 min, t_R (minor enantiomer) = 6.98 min, 98% *de*.

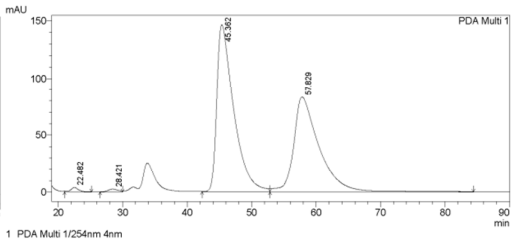
3o



PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.194	12768526	190315	27.464	45.631
2	27.544	10585030	111042	22.768	26.624
3	46.083	12449366	71330	26.778	17.103
4	58.684	10688299	44383	22.990	10.642
Total		46491222	417070	100.000	100.000



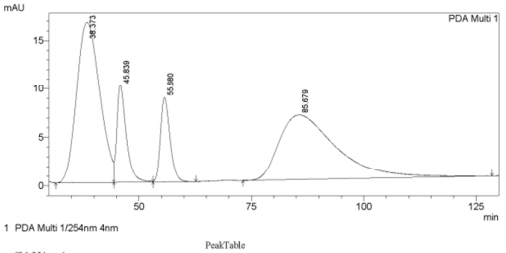
PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.482	357421	4037	0.706	1.712
2	28.421	286658	2530	0.567	1.073
3	45.362	26699030	146062	52.768	61.960
4	57.829	23253871	83109	45.959	35.255
Total		50596980	235737	100.000	100.000

The *de* was determined by HPLC with a Chiralpak IA column (^{n}-hexane/^{i}-PrOH = 60/40, λ = 254 nm, 1.0 mL/min). For the *syn*-isomer: t_R (major enantiomer) = 45.36 min, t_R (minor enantiomer) = 22.48 min, 97% *de*; for the *anti*-isomer: t_R (major enantiomer) = 57.83 min, t_R (minor enantiomer) = 28.42 min, 97% *de*.

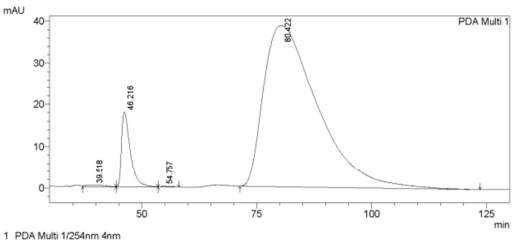
3p



PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	38.373	5901898	16540	40.510	39.472
2	45.839	1468661	10021	10.081	23.914
3	55.680	1283873	8685	8.812	20.726
4	85.679	5914392	6658	40.596	15.888
Total		14568823	41905	100.000	100.000



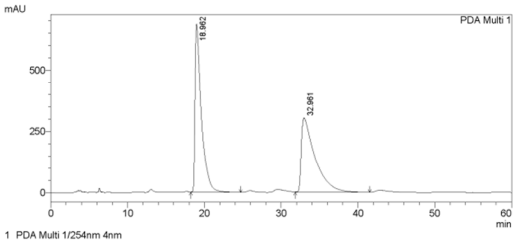
PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	39.518	111782	382	0.328	0.670
2	46.216	2361448	17883	6.927	31.329
3	54.757	18613	131	0.055	0.230
4	80.422	31600622	38685	92.691	67.771
Total		34092466	57082	100.000	100.000

The *de* was determined by HPLC with a Chiralpak AD-H column (^{n}-hexane/^{i}-PrOH = 75/25, λ = 254 nm, 1.0 mL/min). For the *syn*-isomer: t_R (major enantiomer) = 80.42 min, t_R (minor enantiomer) = 39.52 min, 99% *de*; for the *anti*-isomer: t_R (major enantiomer) = 46.22 min, t_R (minor enantiomer) = 54.76 min, 98% *de*.

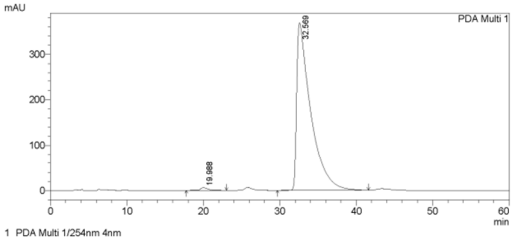
3q



PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.962	39388715	684035	51.074	69.328
2	32.961	37732821	302624	48.926	30.672
Total		77121537	986658	100.000	100.000



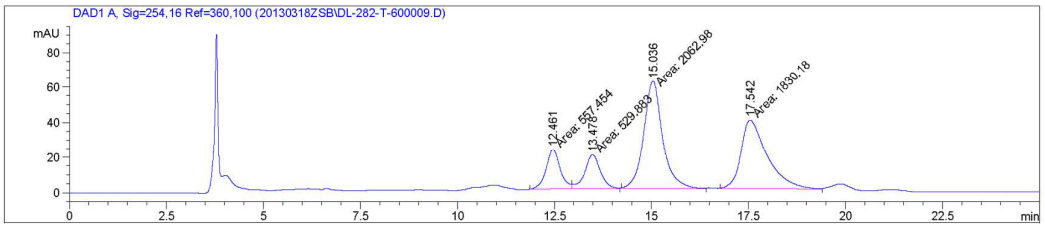
PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.988	416780	5751	0.879	1.539
2	32.569	47009327	367940	99.121	98.461
Total		47426107	373690	100.000	100.000

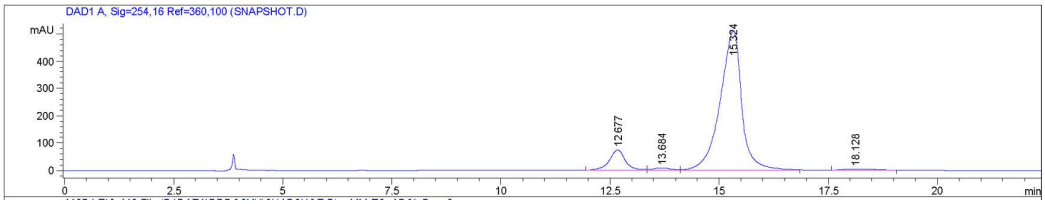
The *de* was determined by HPLC with a Chiralpak IA column (^{n}-hexane/^{i}-PrOH = 80/20, λ = 254 nm, 1.0 mL/min). For the *anti*-isomer: t_R (major enantiomer) = 32.57 min, t_R (minor enantiomer) = 19.99 min, 98% *de*.

(2*S*,2(1*S'*))-4a



Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.461	MF	0.4159	557.45447	22.34072	11.1928
2	13.478	FM	0.4615	529.88281	19.13818	10.6392
3	15.036	MM	0.5635	2062.97656	61.01554	41.4211
4	17.542	MM	0.7822	1830.18140	38.99652	36.7470
Totals :				4980.49524	141.49096	

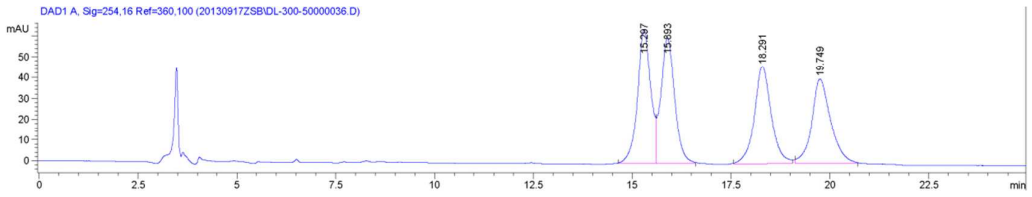


Signal 1: DAD1 A, Sig=254,16 Ref=360,100

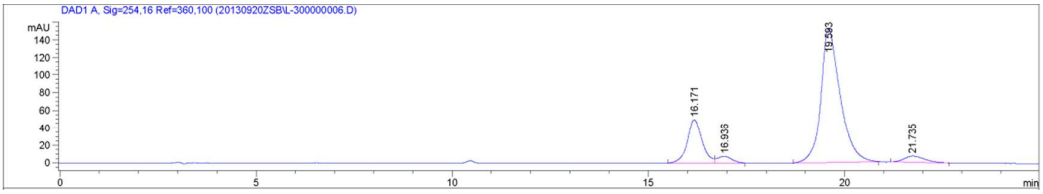
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.677	BB	0.3721	1808.59814	72.24689	9.2849
2	13.684	BV	0.3805	201.42226	7.92663	1.0341
3	15.324	VB	0.5067	1.73064e4	508.96738	88.8472
4	18.128	BB	0.6001	162.42070	3.93069	0.8338
Totals :				1.94788e4	593.07159	

The enantiomeric excess was determined by HPLC with a Chirobiotic T column (25 cm × 4.6 mm, 5 μm) (H_2O/MeOH = 60/40, λ = 254 nm, 0.5 mL/min). For the *syn*-isomer: t_R (major enantiomer) = 15.32 min, t_R (minor enantiomer) = 18.13 min, 98% *ee*; for the anti-isomer: t_R (major enantiomer) = 12.68 min, t_R (minor enantiomer) = 13.68 min, 80% *ee*.

(2*S*,2(1*S'*))-4i



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.297	BV	0.3447	1505.48865	64.41623	26.3383
2	15.893	VB	0.3588	1455.15503	60.46096	25.4577
3	18.291	BB	0.4429	1396.65552	46.70523	24.4343
4	19.749	BB	0.4914	1358.67346	40.49881	23.7698
Totals :				5715.97266	212.08124	

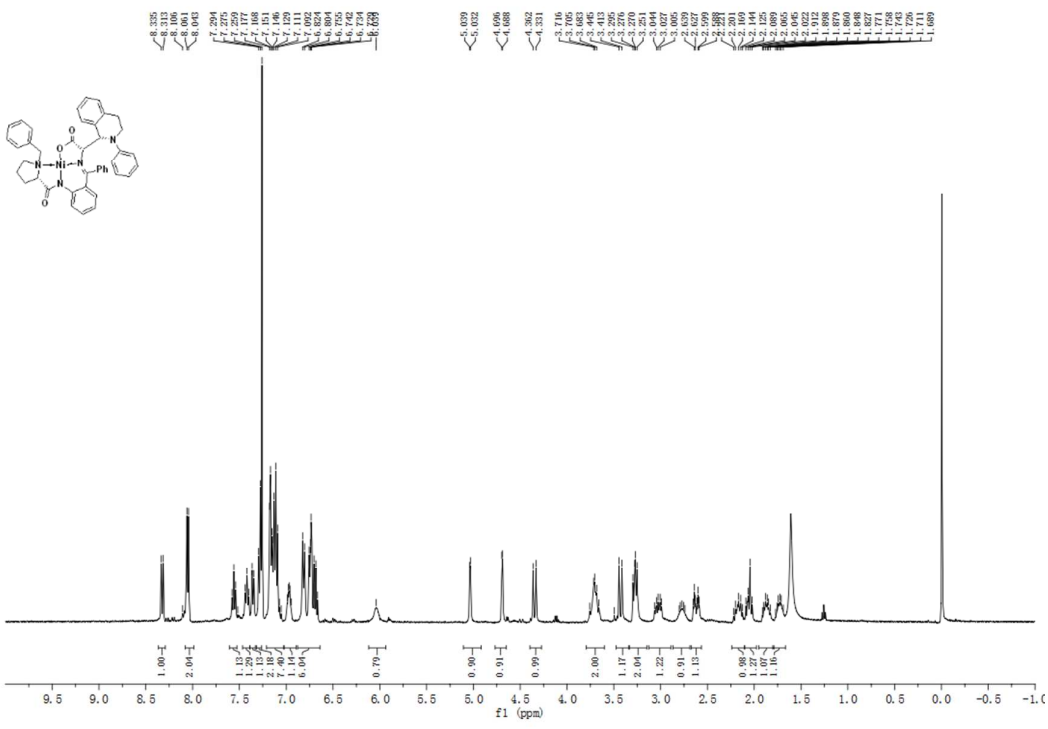


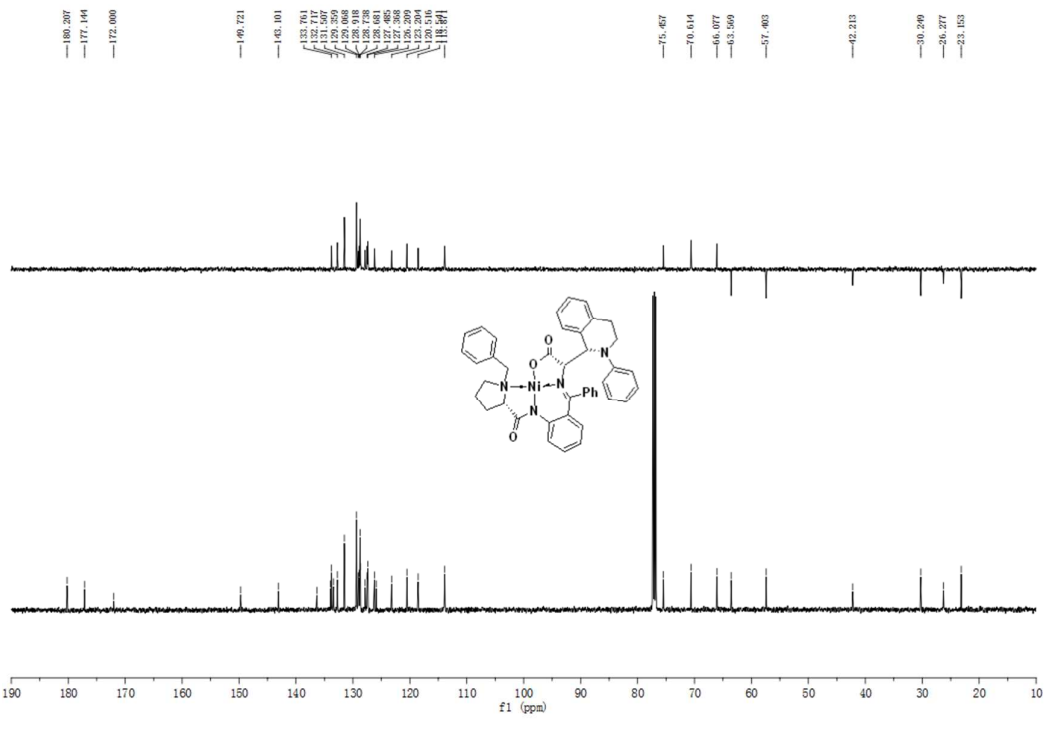
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.171	BV	0.3871	1303.66101	49.85438	18.6289
2	16.936	VB	0.3822	203.83260	7.81762	2.9127
3	19.593	BB	0.5022	5231.63574	152.51328	74.7585
4	21.735	BB	0.4958	258.91888	6.99586	3.6999
Totals :				6998.04823	217.18114	

The enantiomeric excess was determined by HPLC with a Chirobiotic T column (25 cm × 4.6 mm, 5 μm) (H_2O/MeOH = 50/50, λ = 254 nm, 0.5 mL/min). For the *syn*-isomer: t_R (major enantiomer) = 19.59 min, t_R (minor enantiomer) = 21.73 min, 90% *ee*; for the anti-isomer: t_R (major enantiomer) = 16.17 min, t_R (minor enantiomer) = 16.94 min, 73% *ee*.

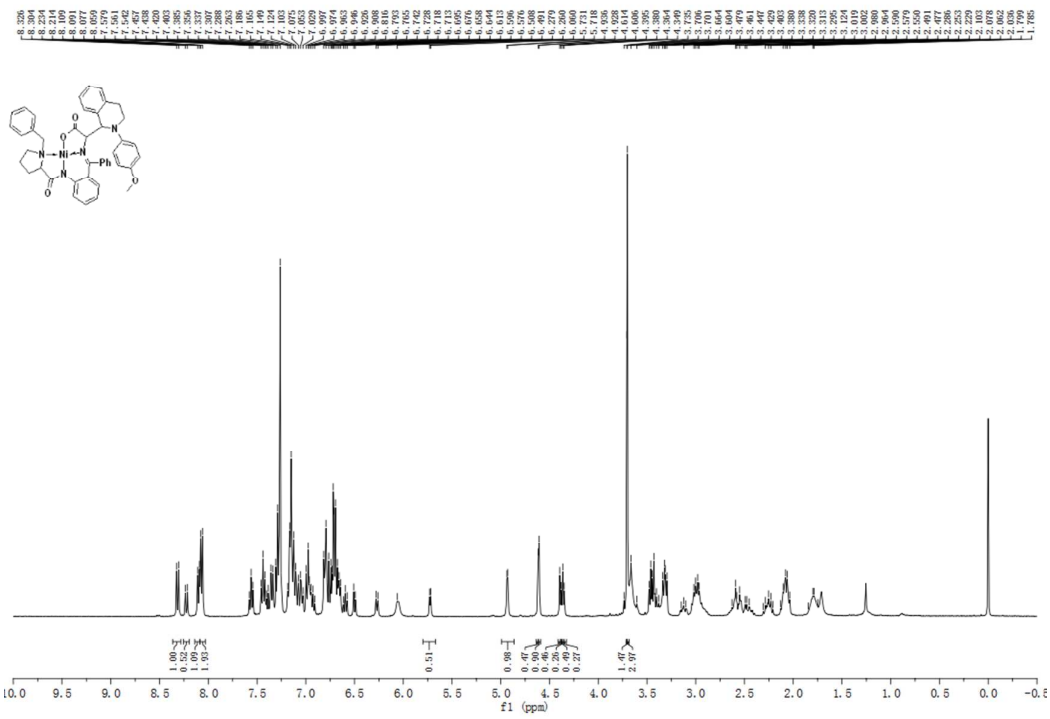
(F) Copies of ^{1}H NMR and ^{13}C NMR Spectra for the Products

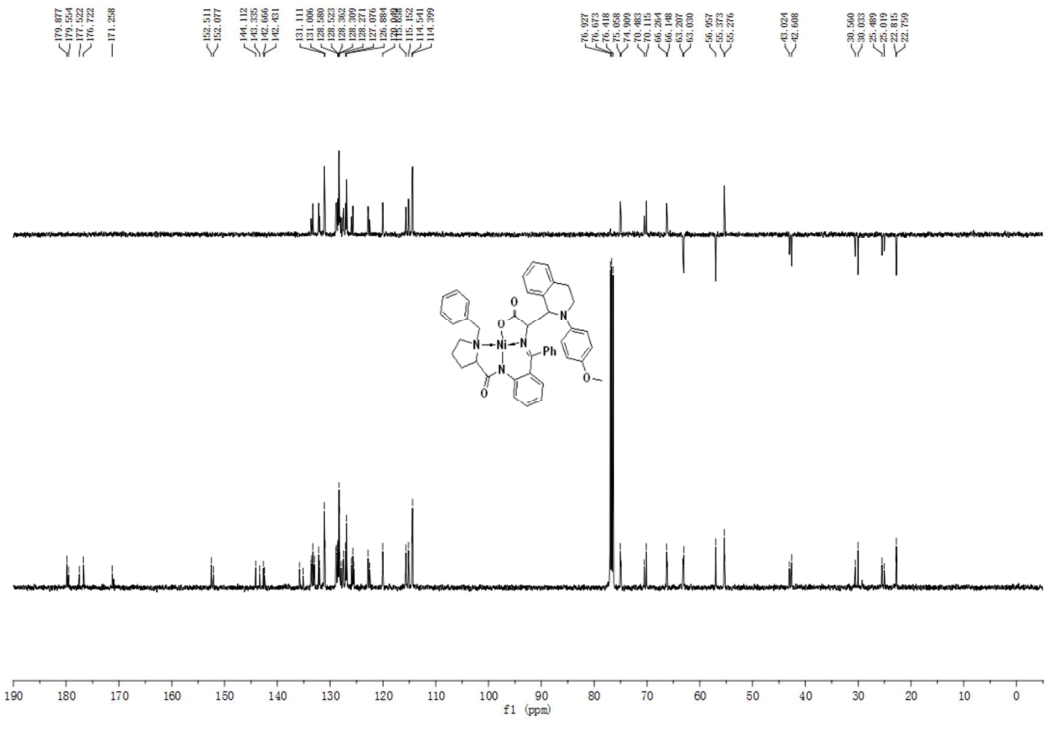
Nickel(II)-(*S*)-BPB/2-Amino-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl) acetic acid Schiff Base Complex 3a



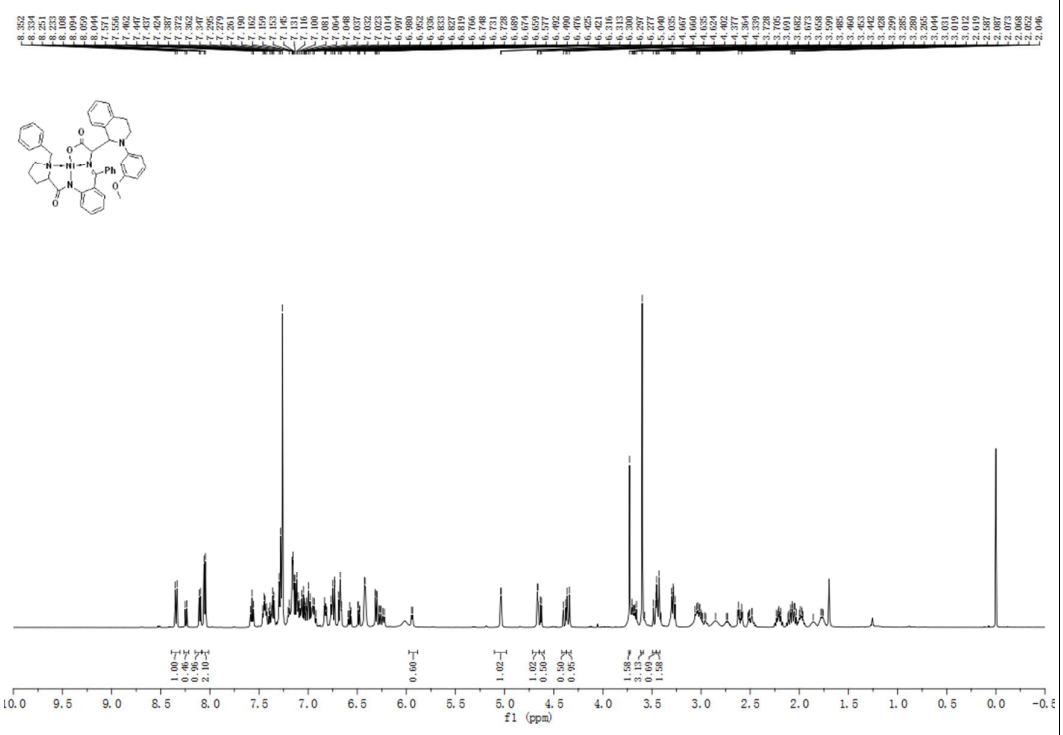


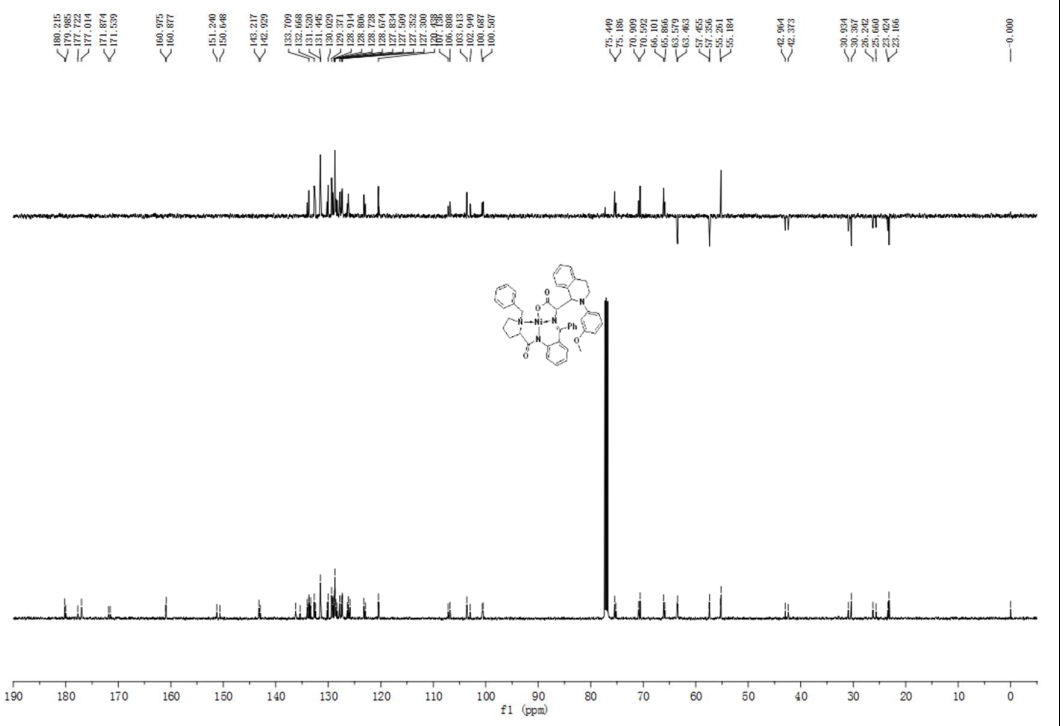
Nickel(II)-(*S*)-BPB/2-amino-2-(2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl) acetic acid Schiff Base Complex 3b



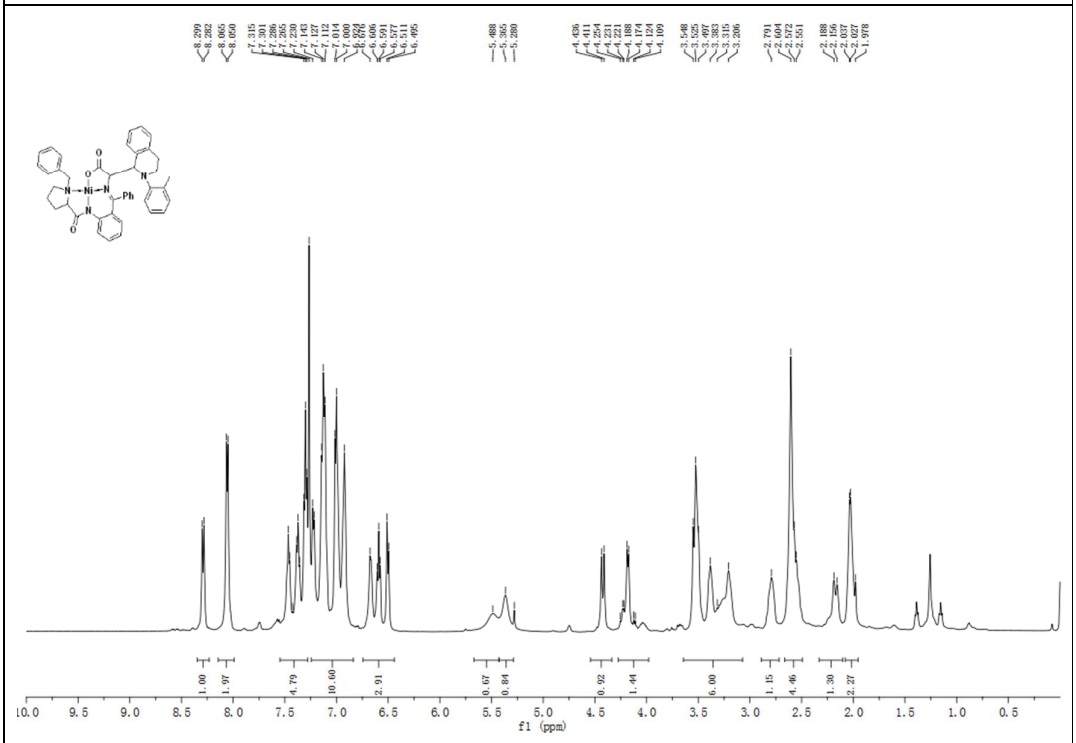


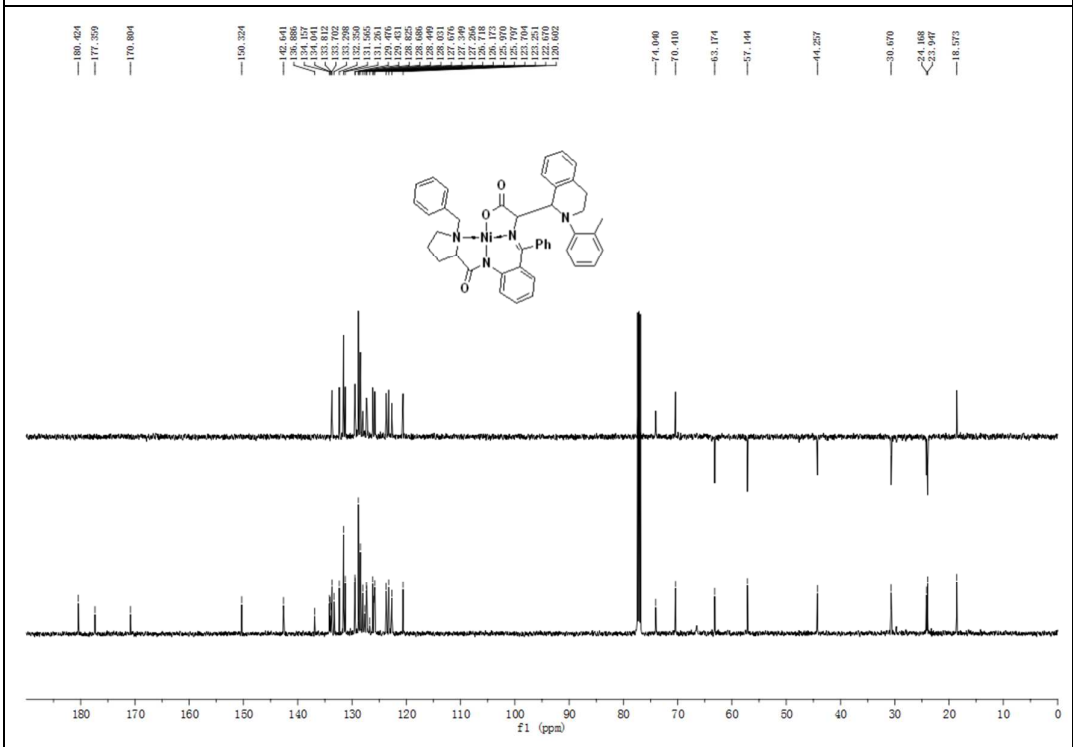
Nickel(II)-(*S*)-BPB/2-amino-2-(2-(3-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl) acetic acid Schiff Base Complex 3c



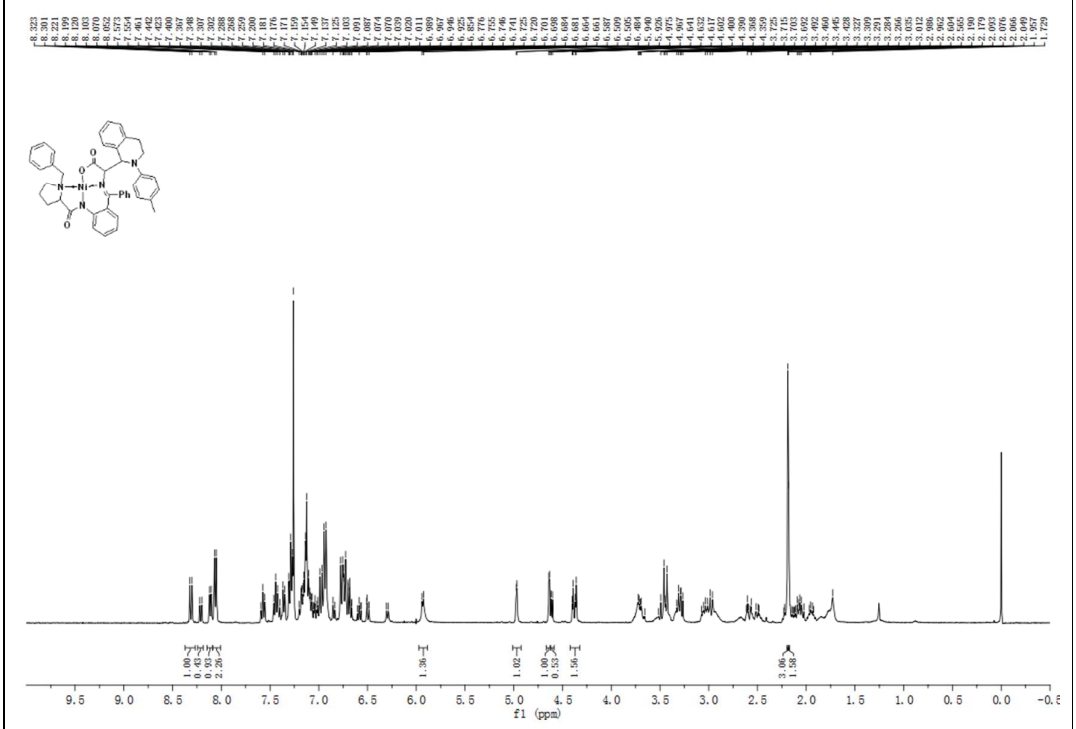


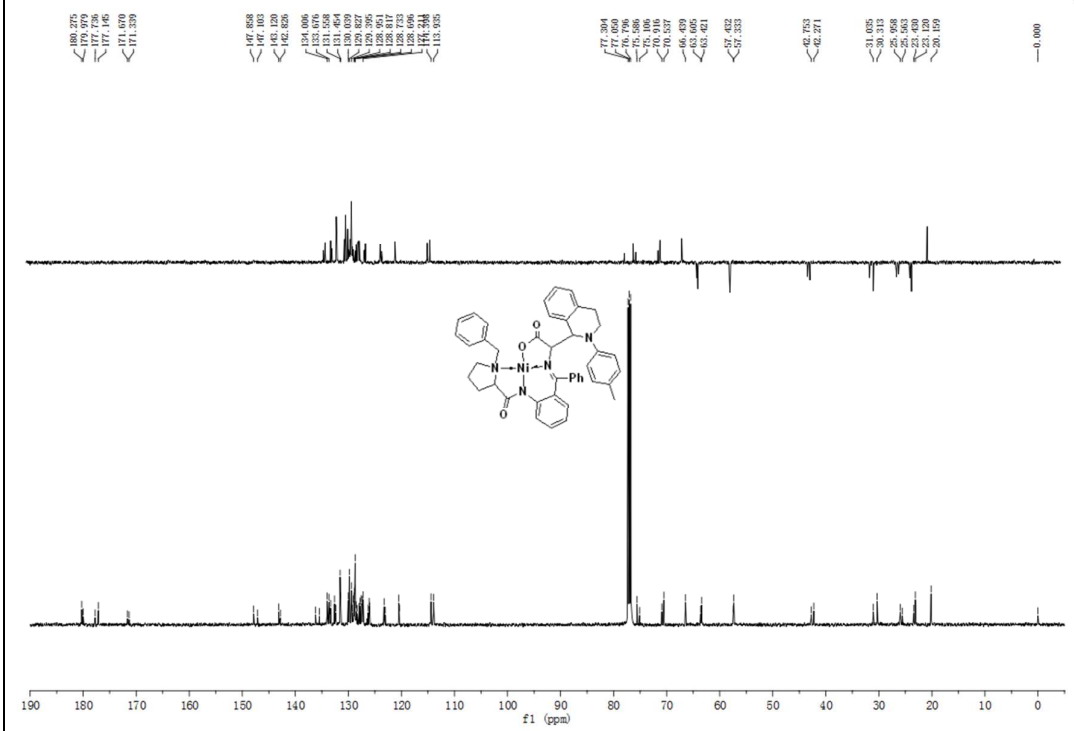
Nickel(II)-(*S*)-BPB/2-Amino-2-(2-(2-methylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl) acetic acid Schiff Base Complex 3e



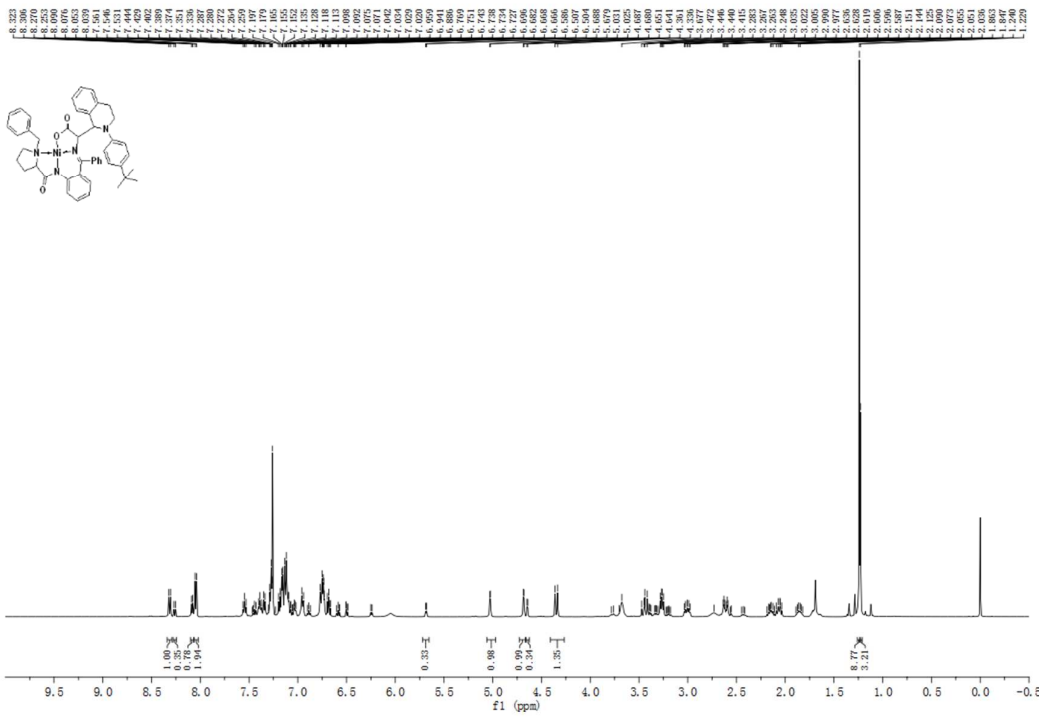


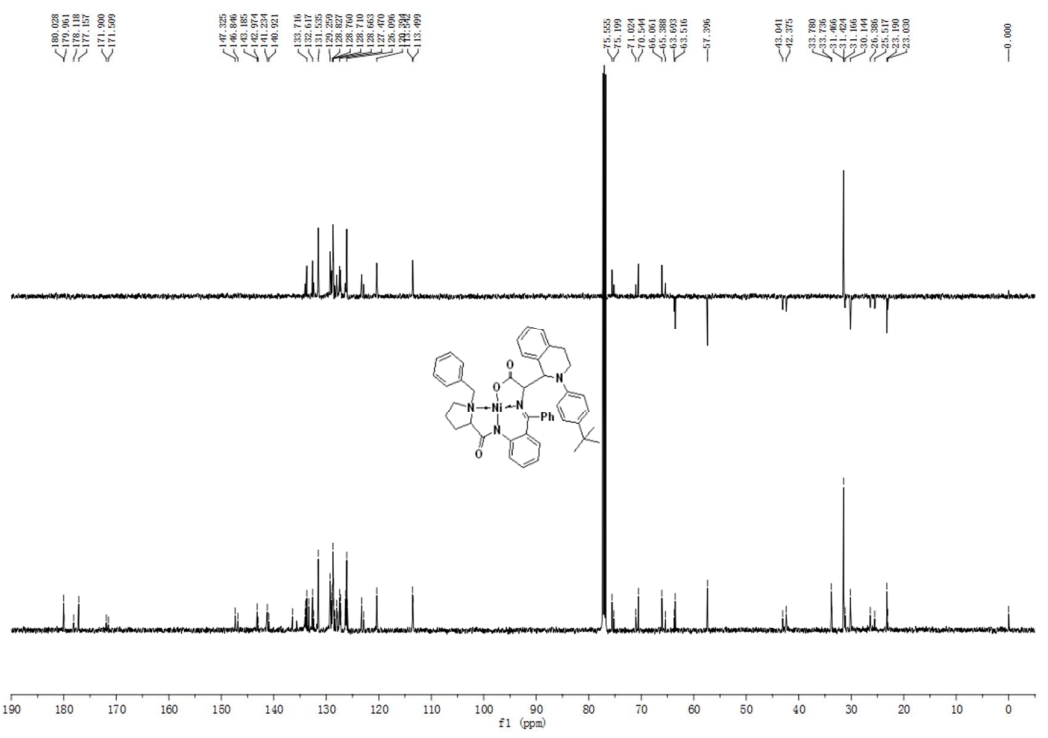
Nickel(II)-(*S*)-BPB/2-Amino-2-(2-(4-methylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl) acetic acid Schiff Base Complex 3f



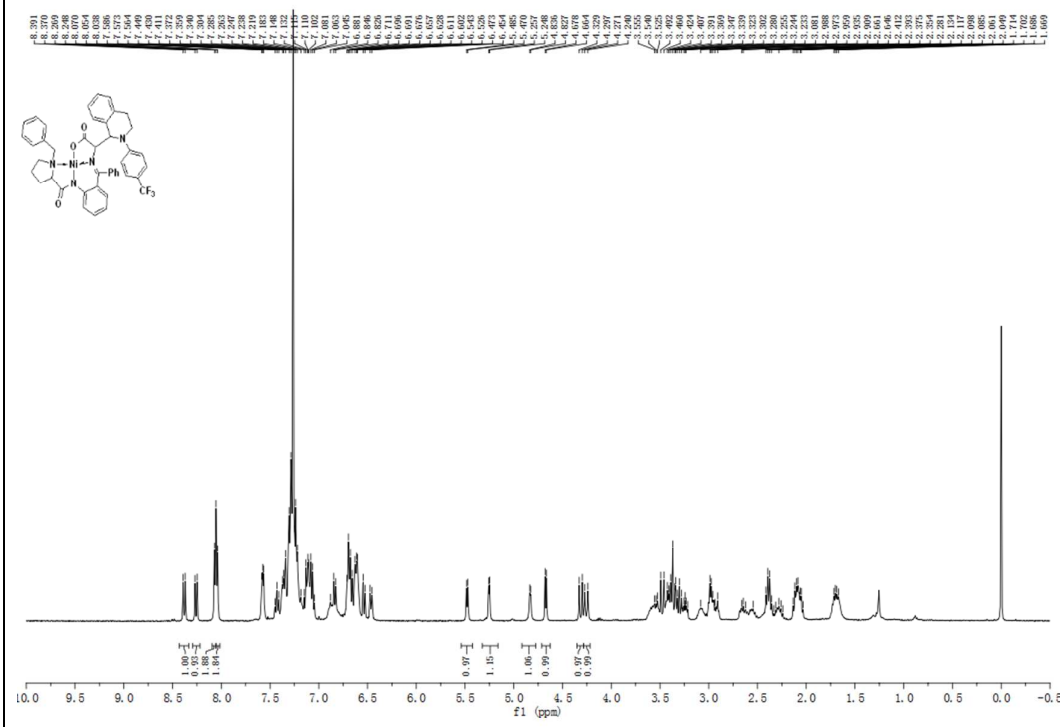


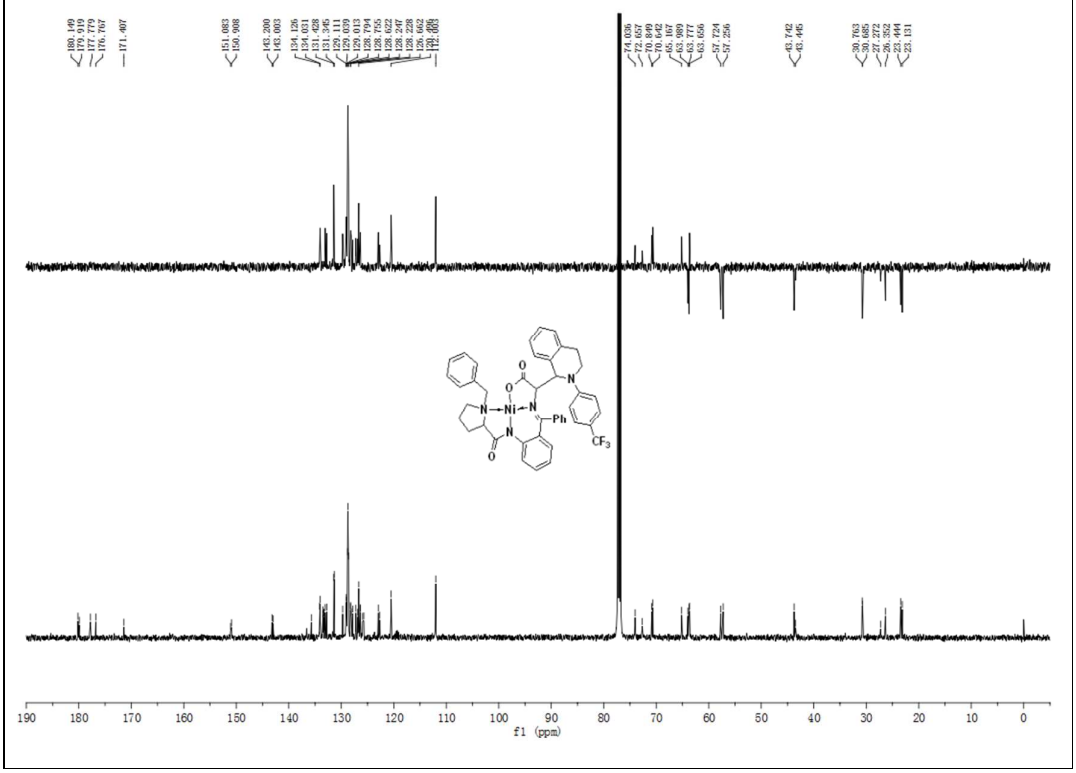
Nickel(II)-(*S*)-BPB/2-Amino-2-(2-(4-tert-butylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl) acetic acid Schiff Base Complex 3g



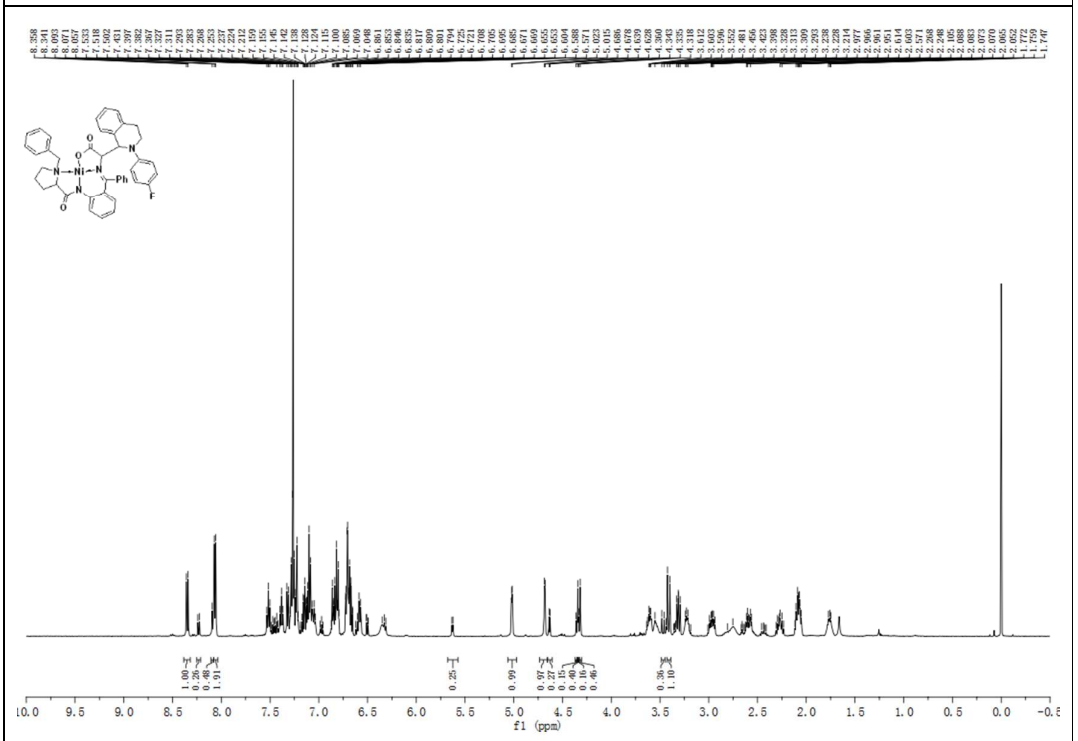


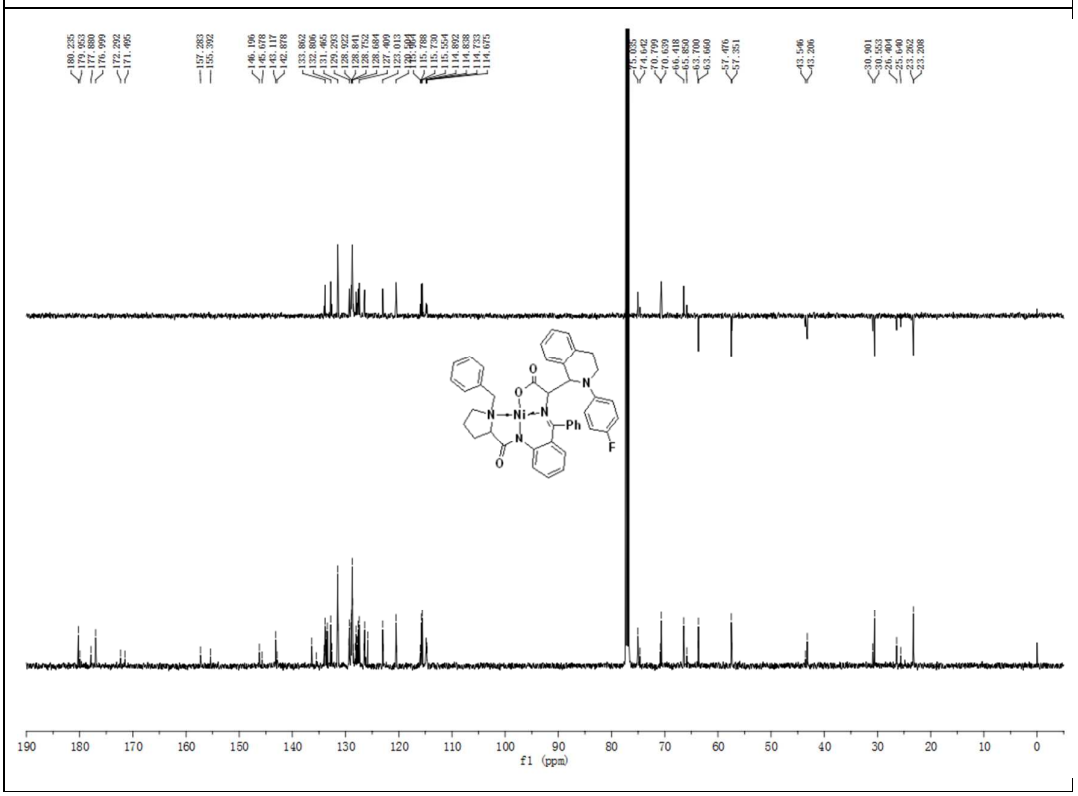
Nickel(II)-(*S*)-BPB/2-Amino-2-(2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl) acetic acid Schiff Base Complex 3h



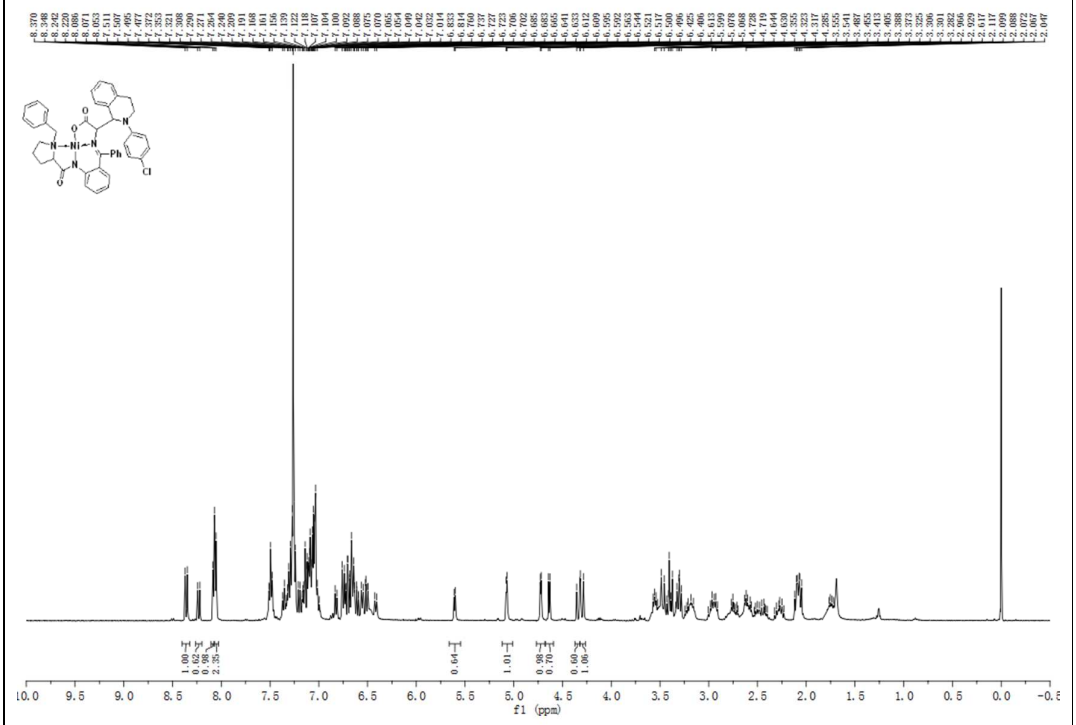


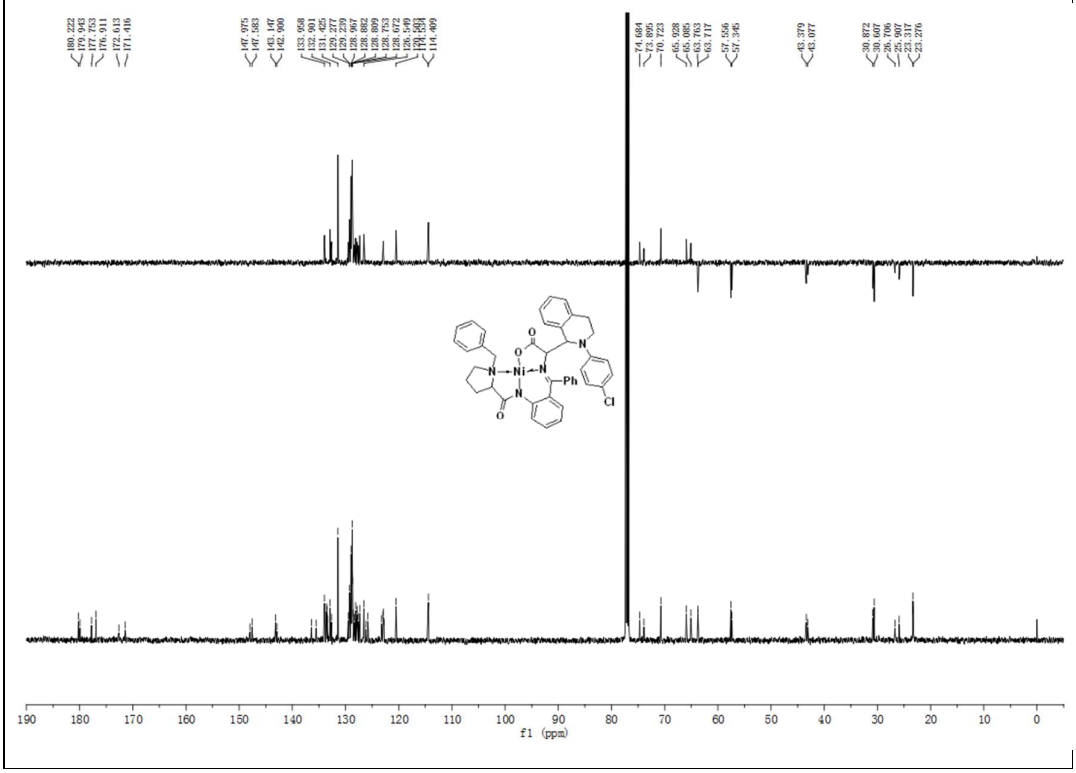
Nickel(II)-(*S*)-BPB/2-Amino-2-(2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl) acetic acid Schiff Base Complex 3i



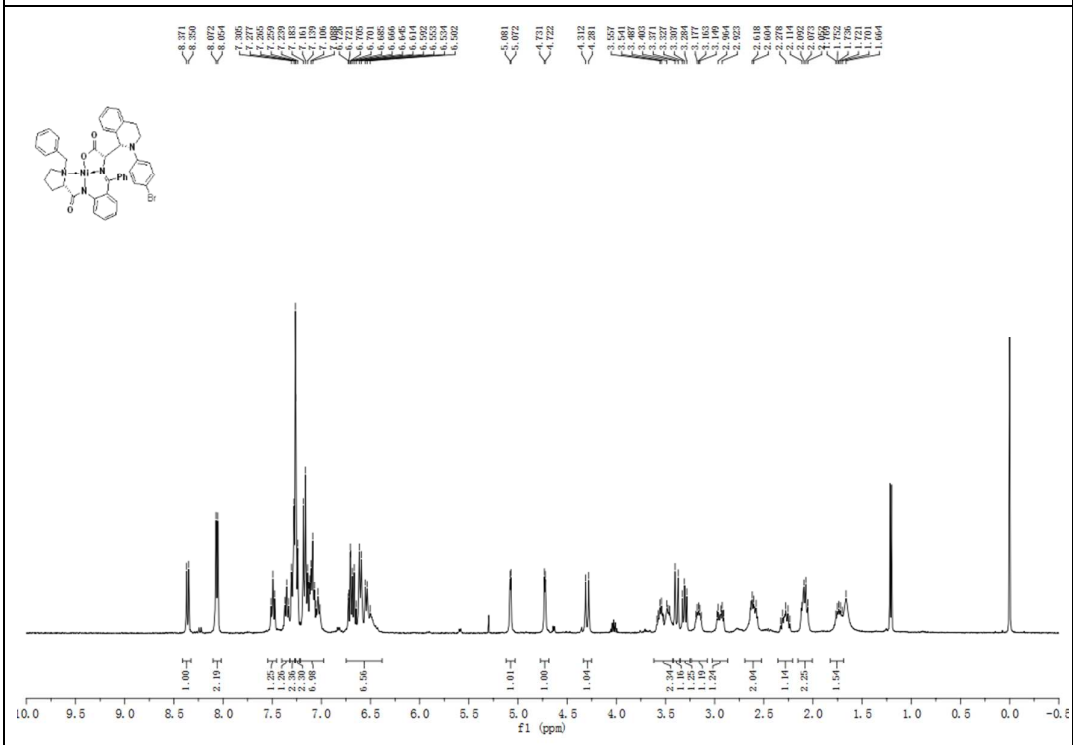


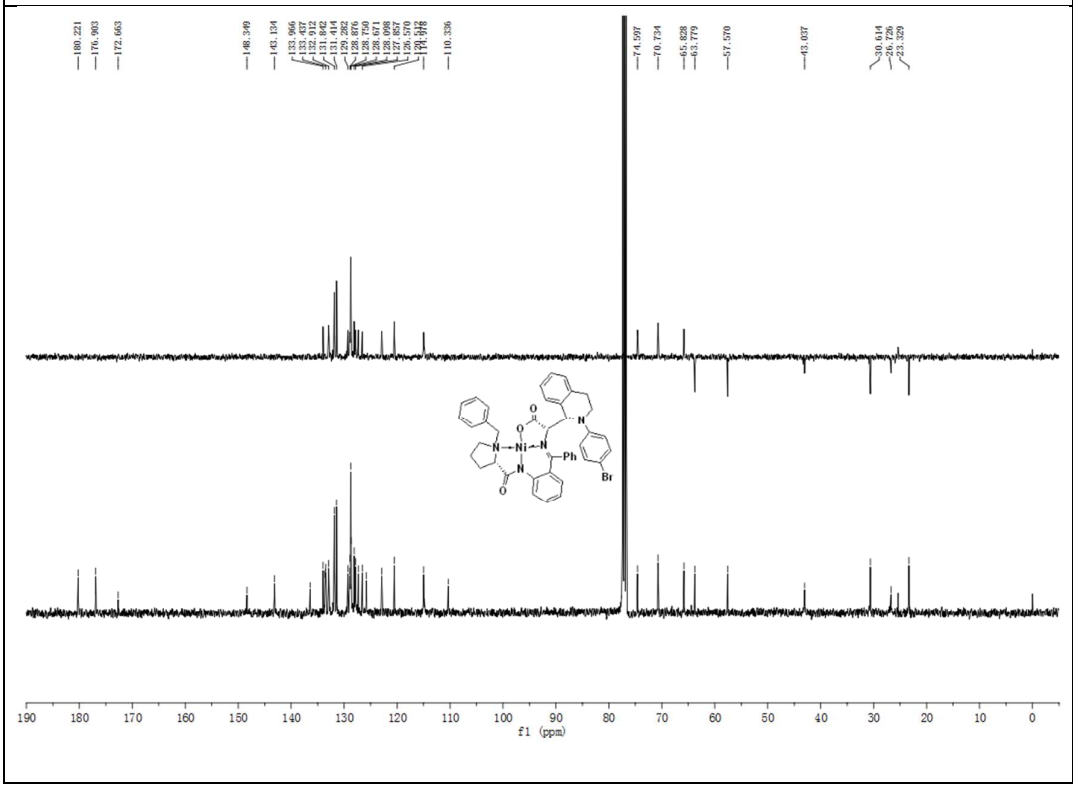
Nickel(II)-(*S*)-BPB/2-Amino-2-(2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl) acetic acid Schiff Base Complex 3j



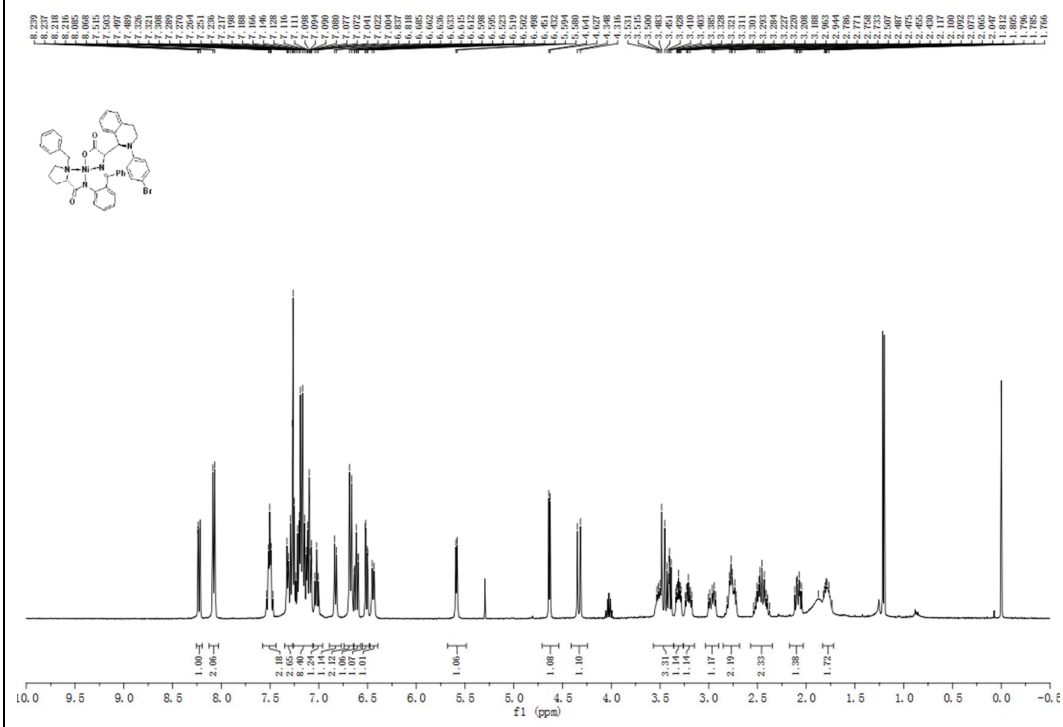


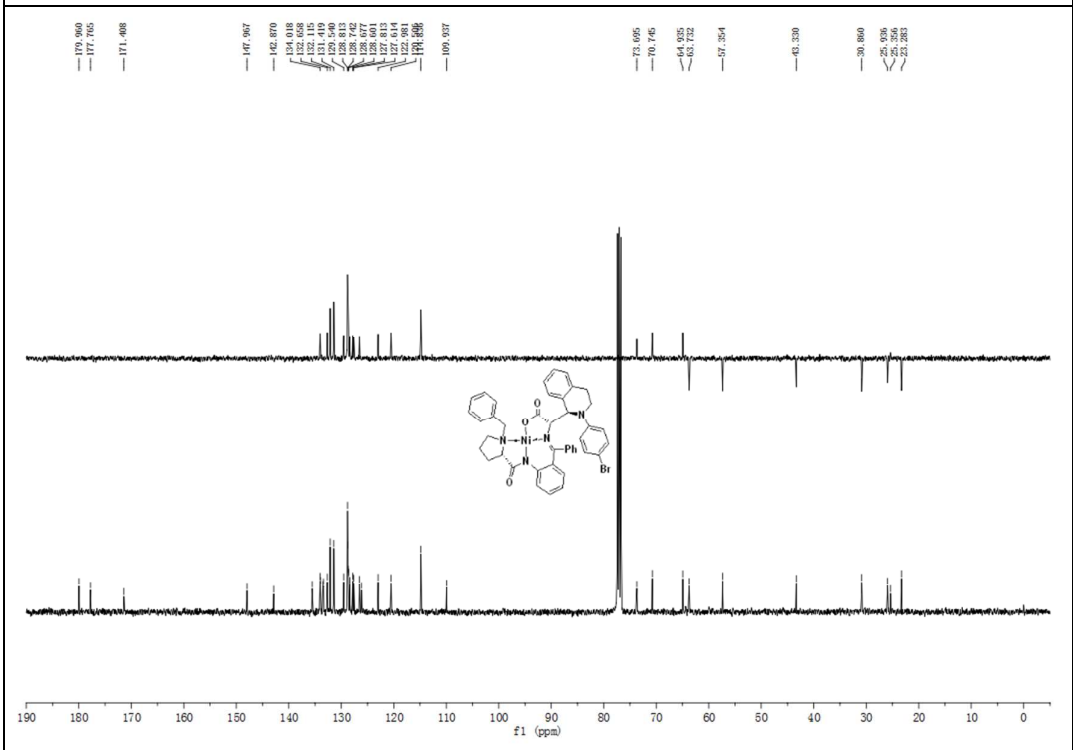
Nickel(II)-(*S*)-BPB/(*S*)2-Amino-2-((*S*)-2-(4-bromophenyl))-1,2,3,4-tetrahydroisoquinolin-1-yl) acetic acid Schiff Base Complex 3k-*syn*



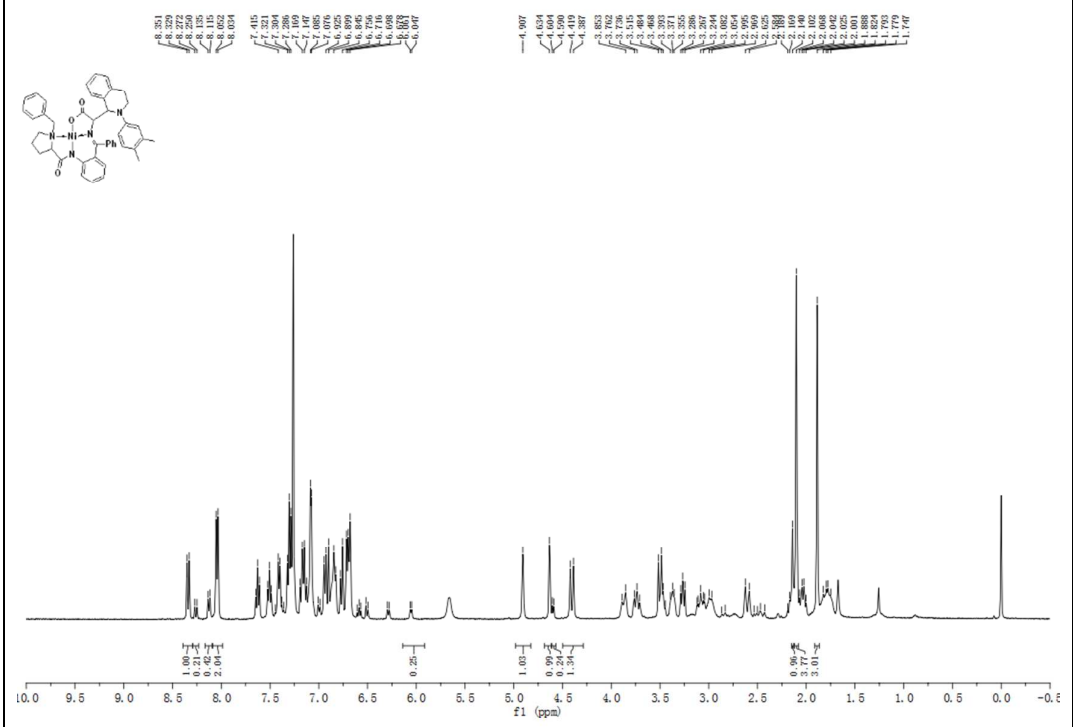


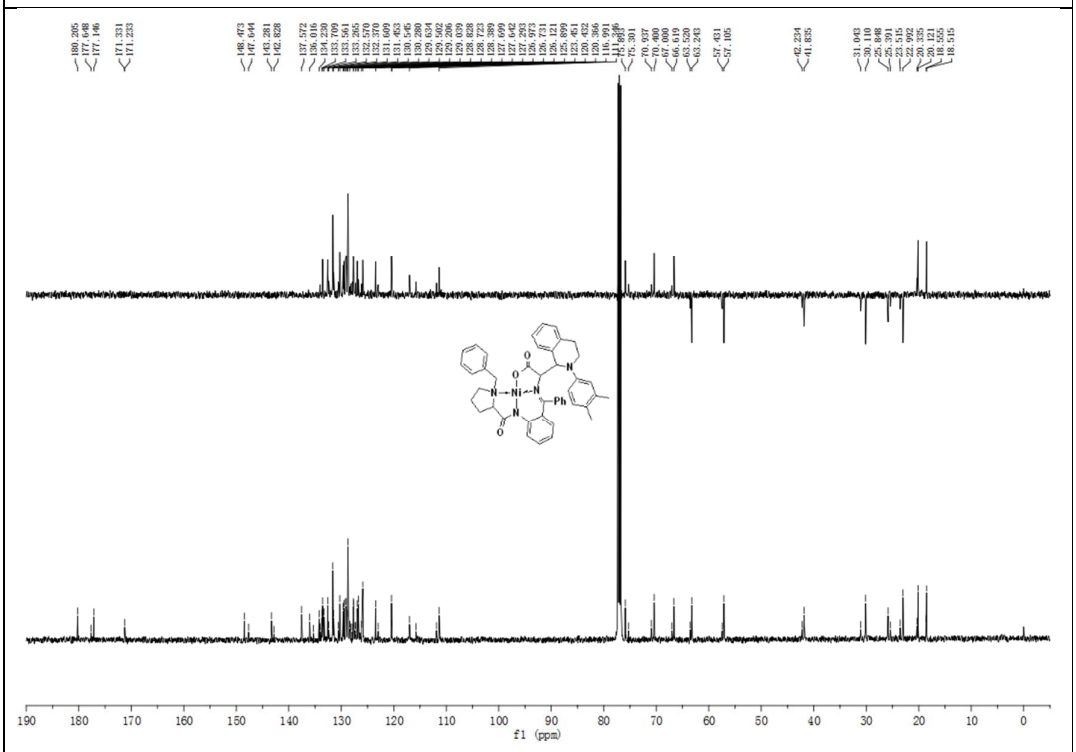
Nickel(II)-(*S*)-BPB/(*S*)2-Amino-2-((*R*)-2-(4-bromophenyl))-1,2,3,4-tetrahydroisoquinolin-1-yl) acetic acid Schiff Base Complex 3k-*anti*



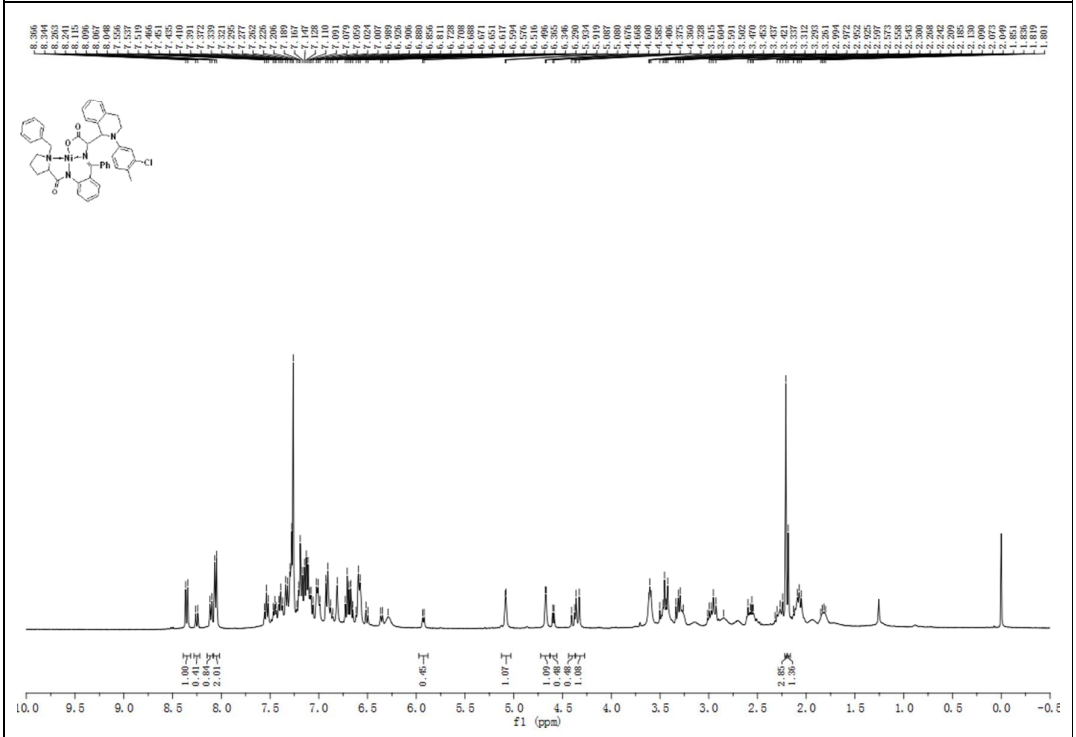


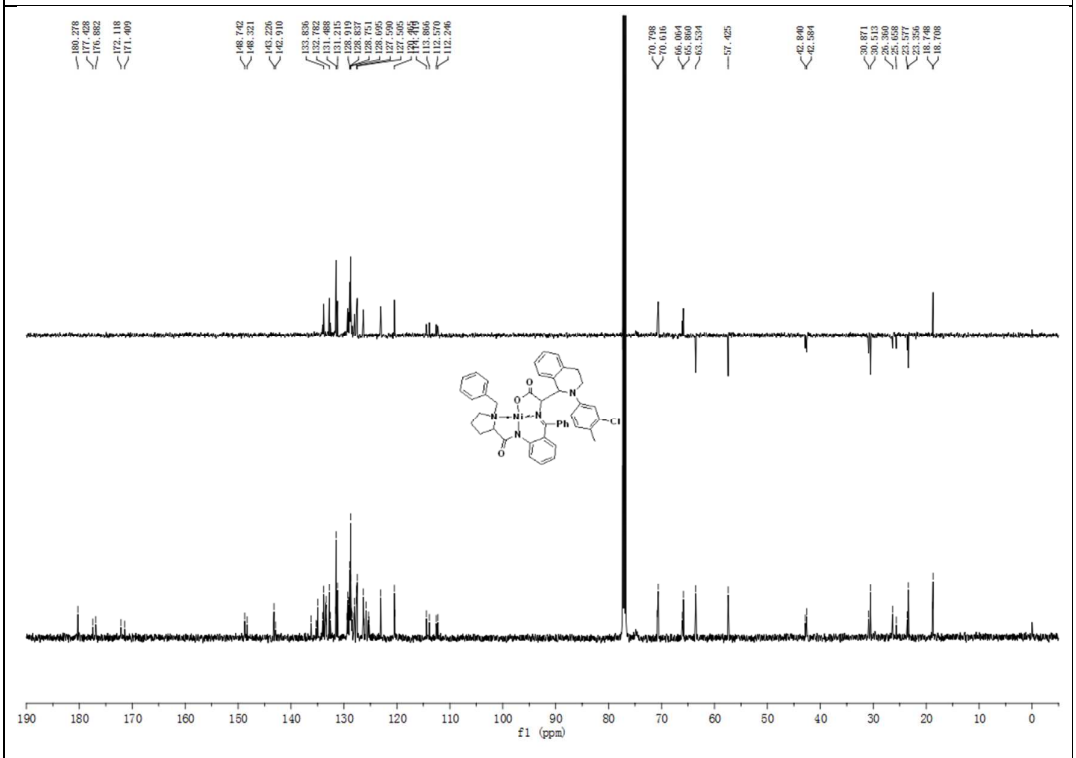
Nickel(II)-(*S*)-BPB/2-Amino-2-(2-(3,4-dimethylphenyl))-1,2,3,4-tetrahydroisoquinolin-1-yl) acetic acid Schiff Base Complex 3l



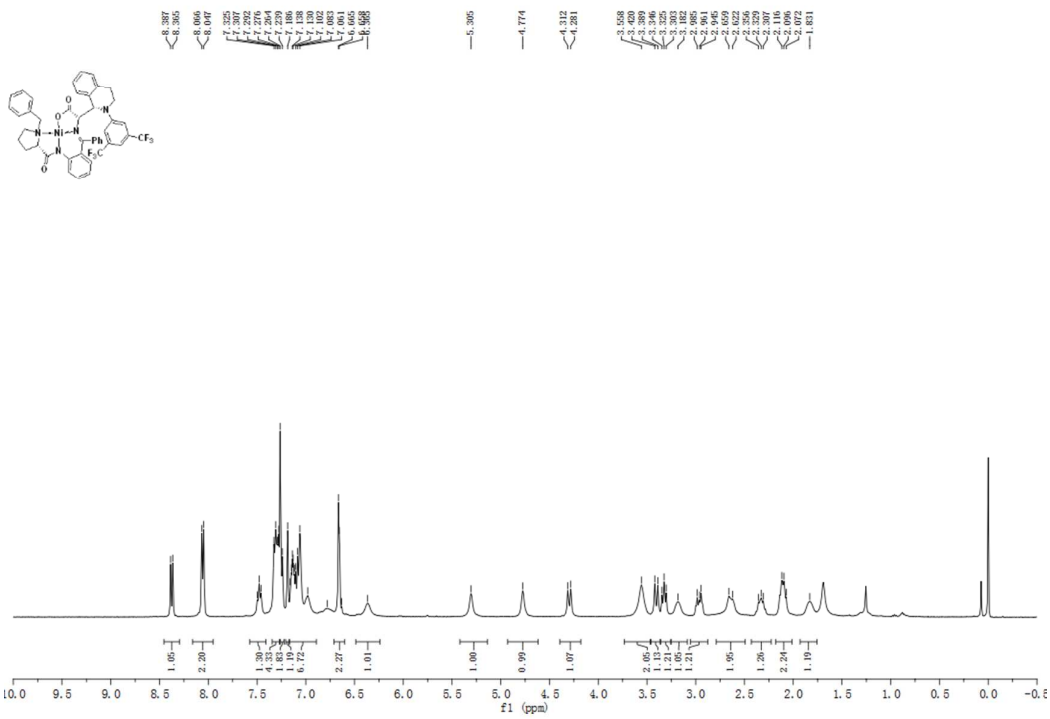


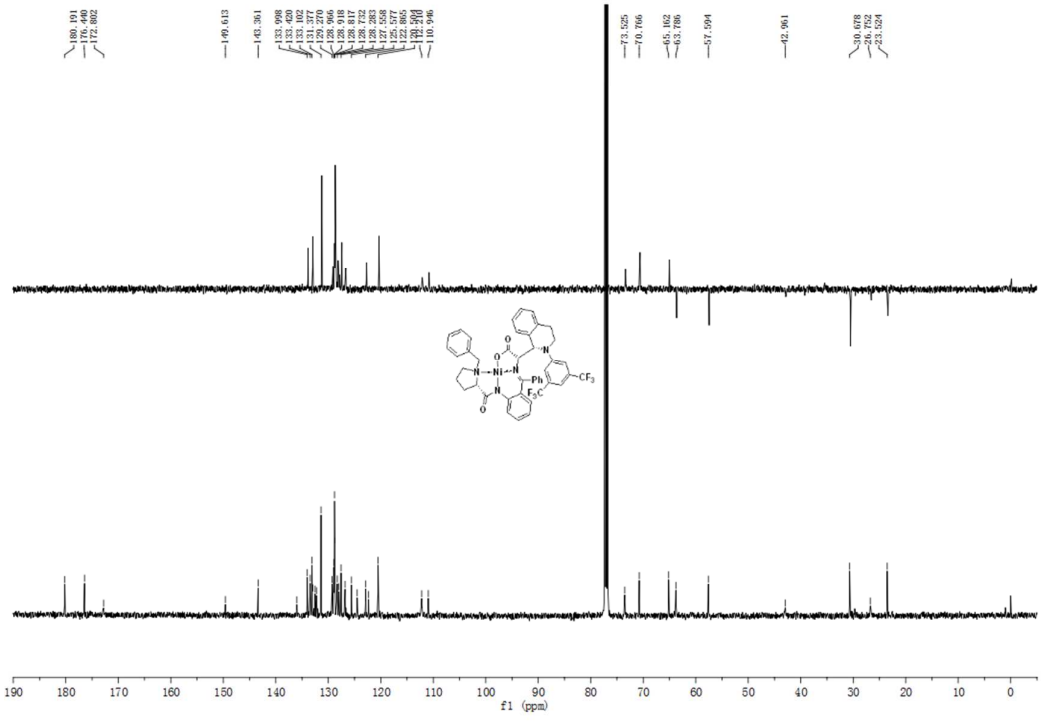
Nickel(II)-(*S*)-BPB/2-Amino-2-(2-(3-chloro-4-methylphenyl))-1,2,3,4-tetrahydroisoquinolin-1-yl) acetic acid Schiff Base Complex 3m



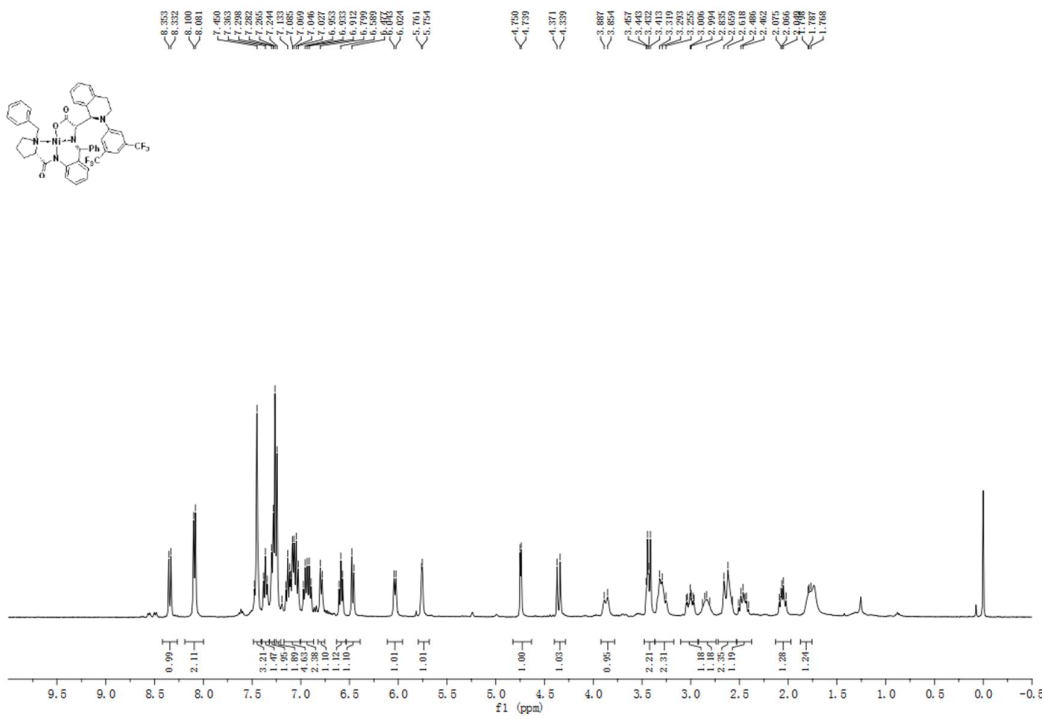


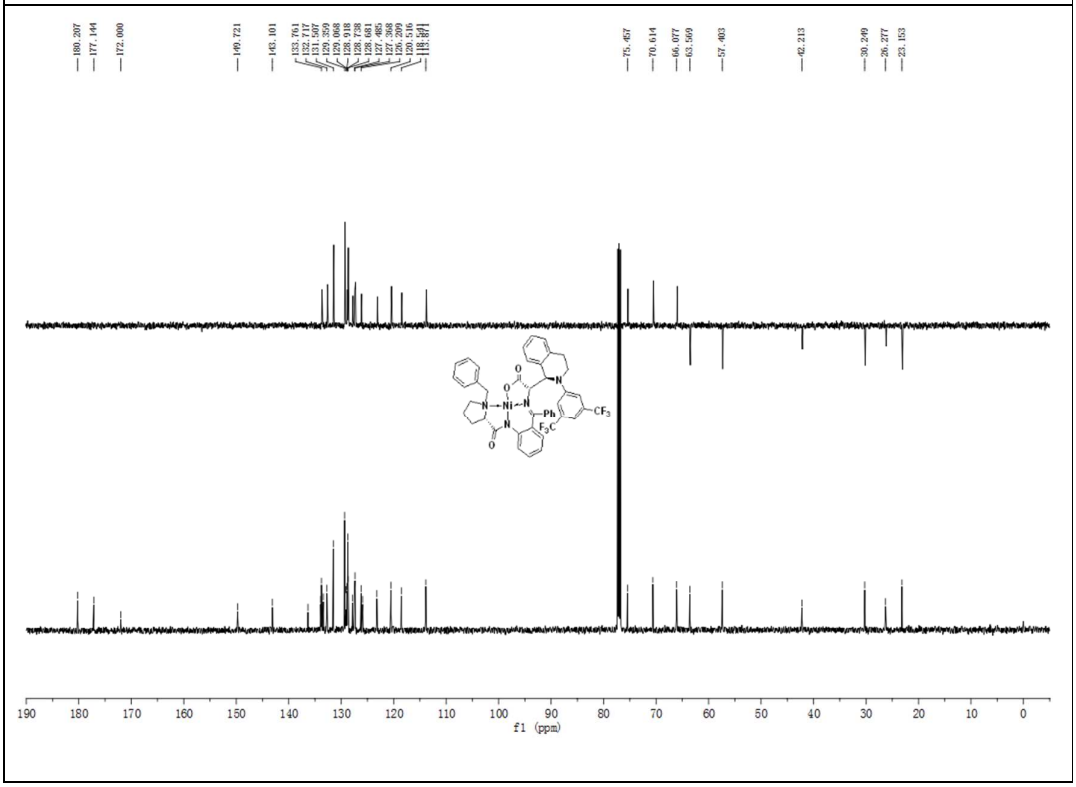
Nickel(II)-(*S*)-BPB/(*S*)-2-Amino-2-((*S*)-2-(3,5-bis(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl) acetic acid Schiff Base Complex 3n-*syn*



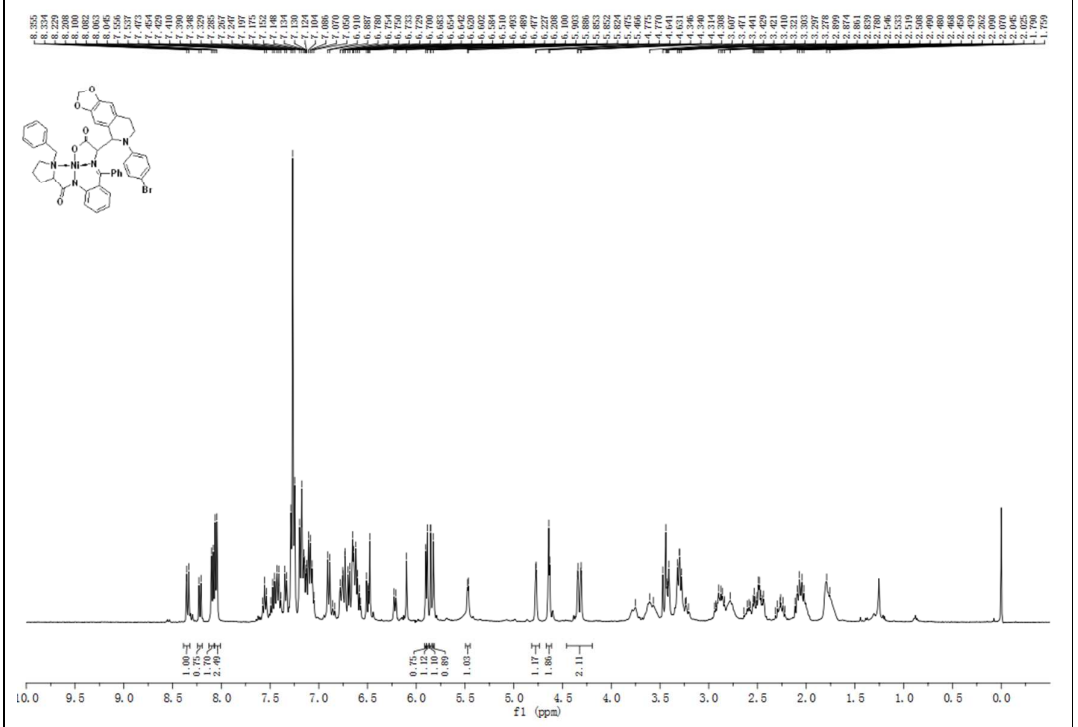


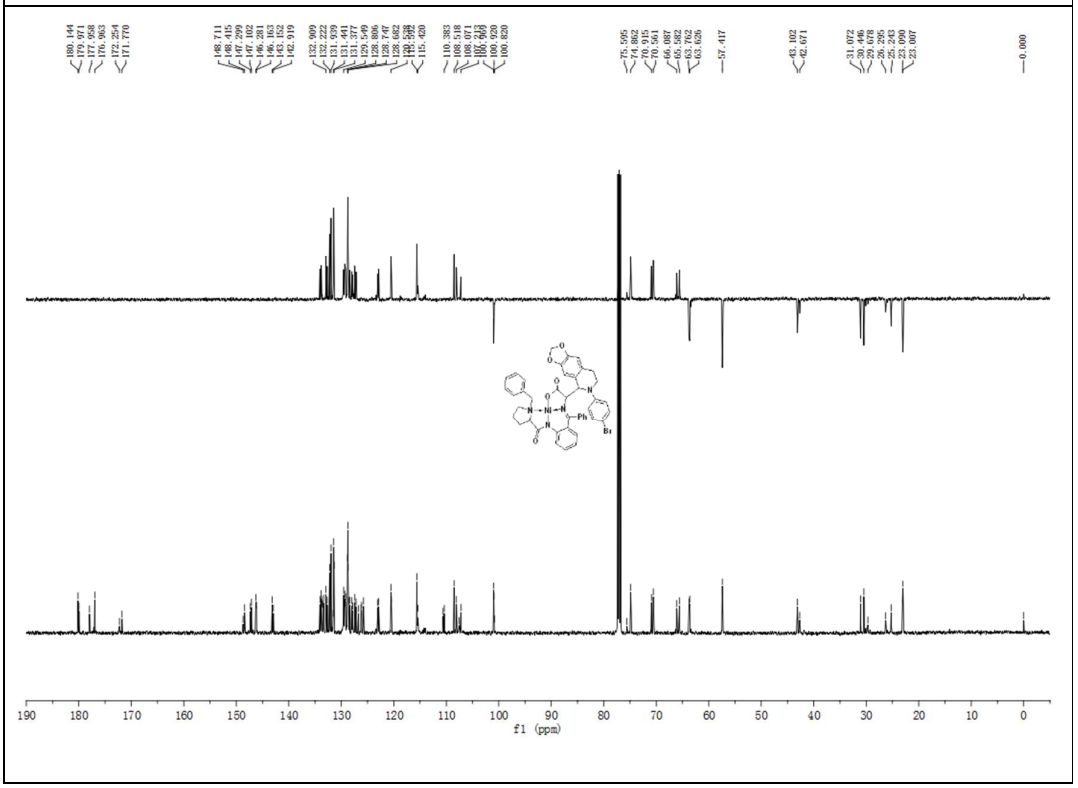
Nickel(II)-(*S*)-BPB/(*S*)-2-Amino-2-((*R*)-2-(3,5-bis(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl) acetic acid Schiff Base Complex 3n-*anti*



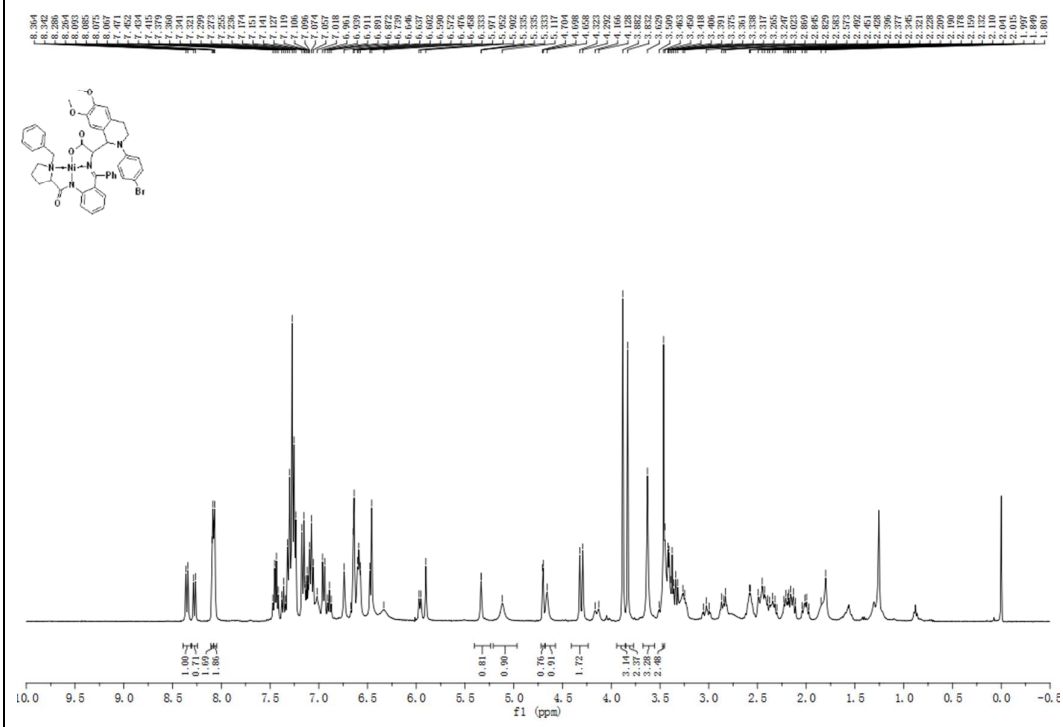


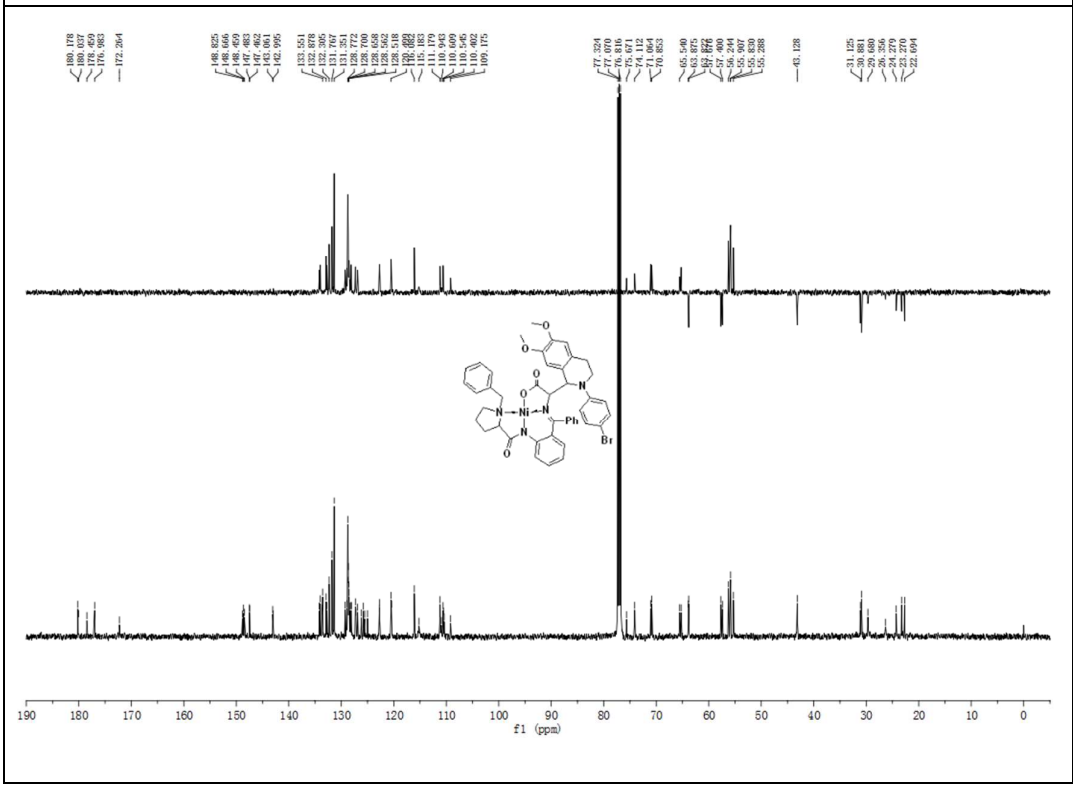
Nickel(II)-(*S*)-BPB/2-amino-2-((6-(4-bromophenyl)-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-g]isoquinolin-5-yl) acetic acid Schiff Base Complex 3o



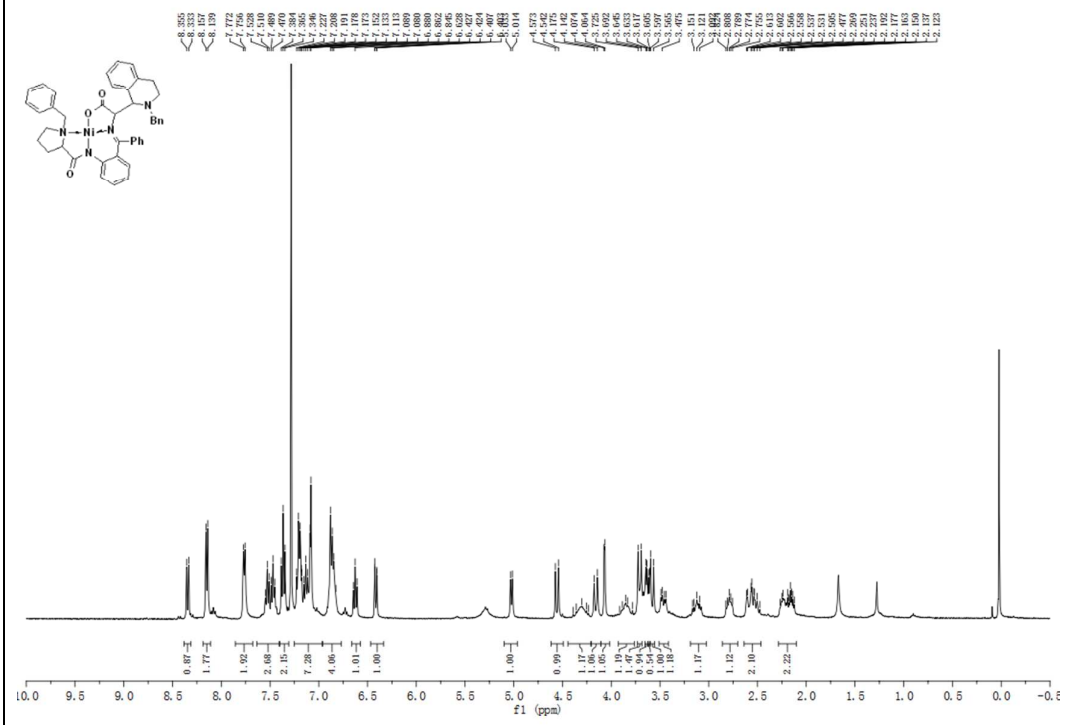


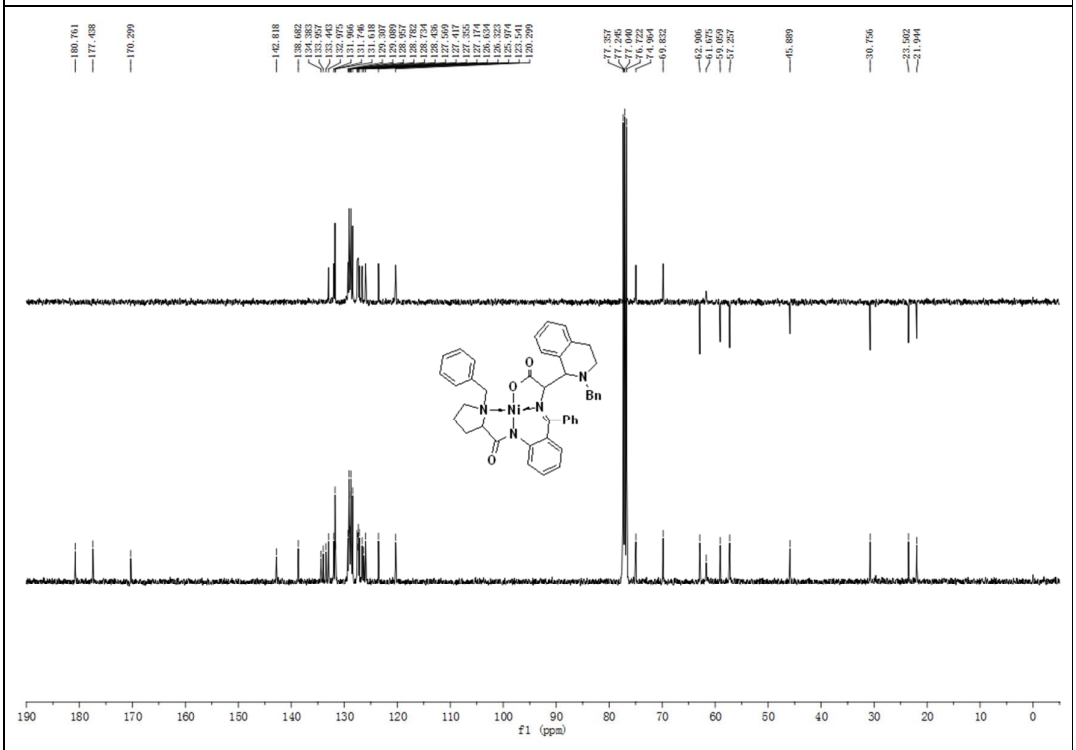
Nickel(II)-(*S*)-BPB/2-amino-2-(2-(4-bromophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolin-1-yl) acetic acid Schiff Base Complex 3p



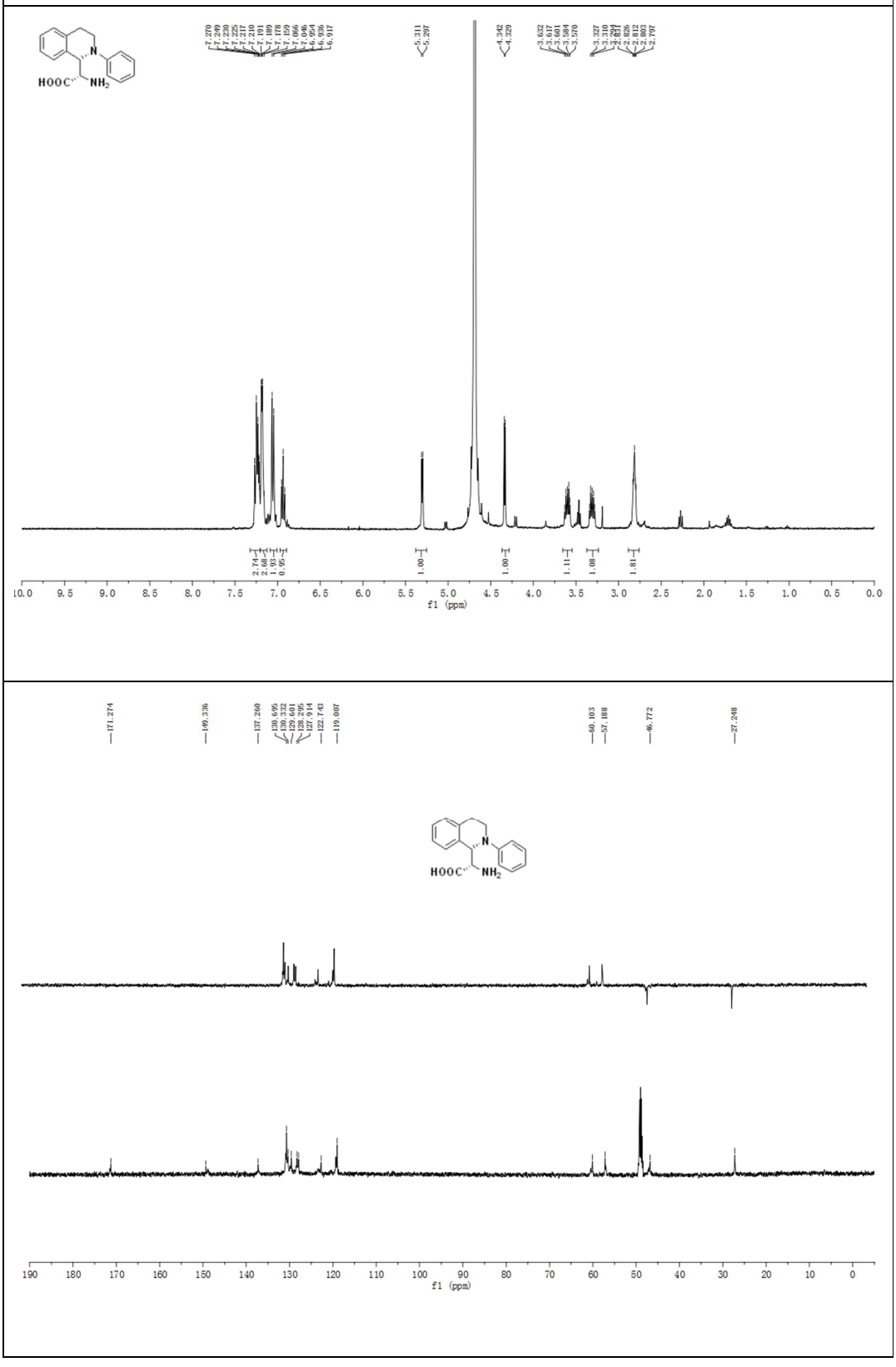


Nickel(II)-(*S*)-BPB/2-amino-2-(2-benzyl-1,2,3,4-tetrahydroisoquinolin-1-yl) acetic acid Schiff Base Complex 3q

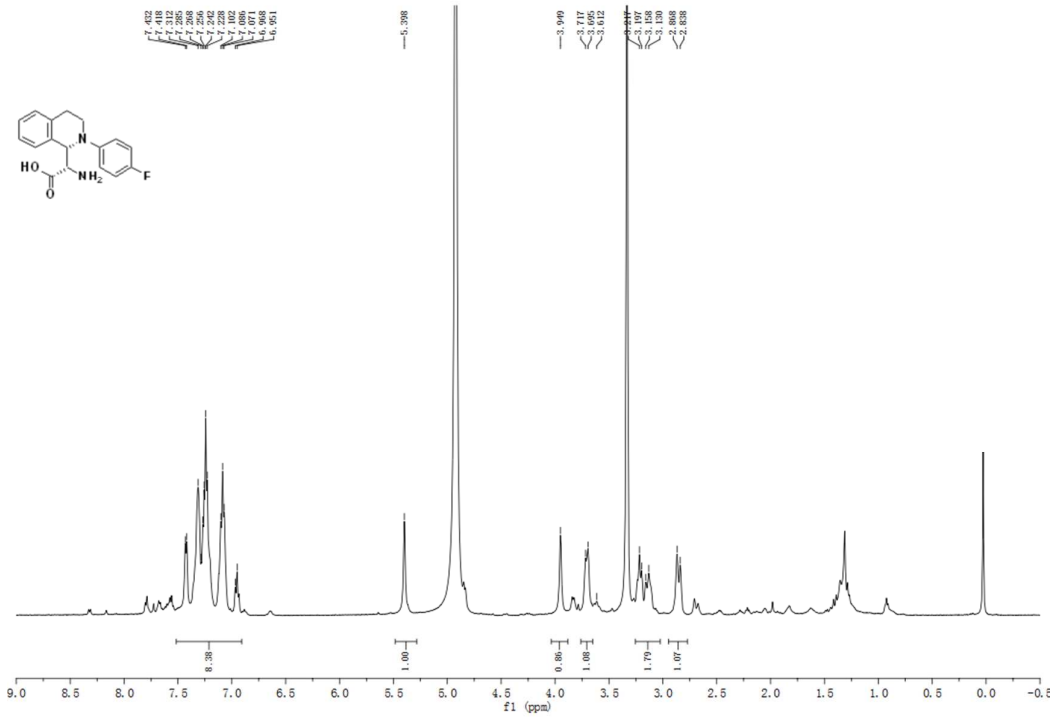


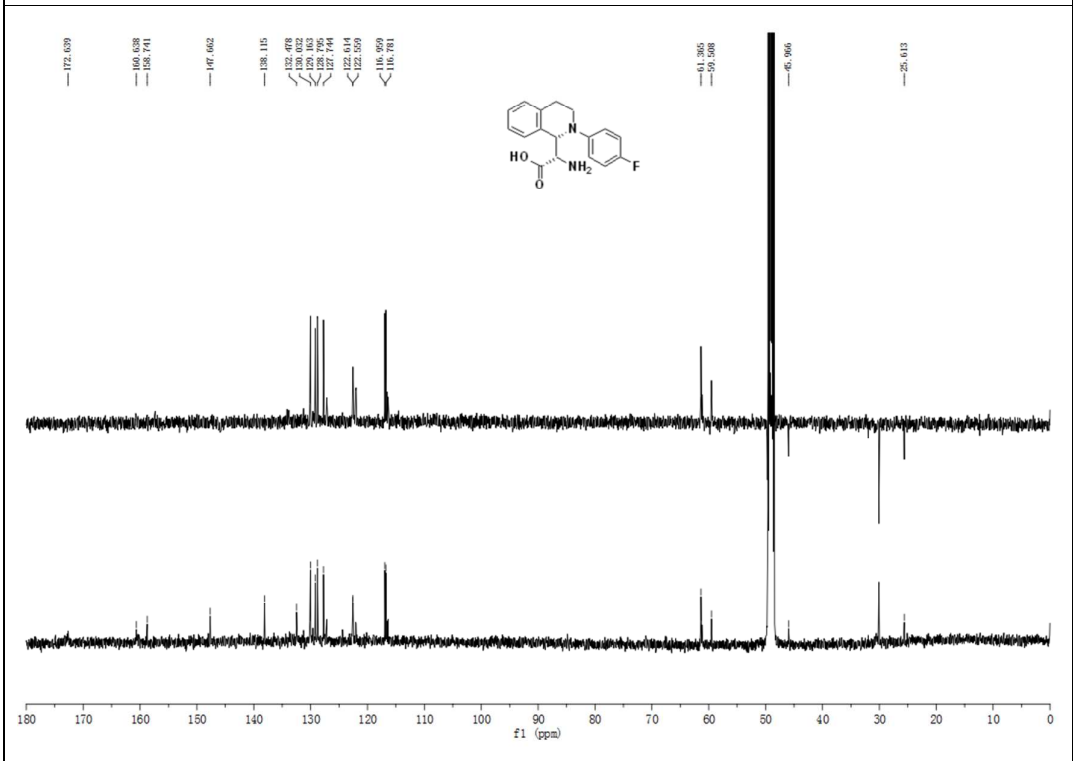


(*S*)-2-amino-2-((*S*)-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)acetic acid 4a



(*S*)-2-amino-2-((*S*)- 2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)acetic acid 4i





(G) References

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(3) Zhang, J.; Tiwari, B.; Xing, C.; Chen, X.; Chi, Y. R. *Angew. Chem. Int. Ed.* **2012**, *51*, 3649-3652.

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(6) Lin, D. Z.; Wang, J.; Zhang, X.; Zhou, S. B.; Lian, J.; Jiang, H. L.; Liu, H. *Chem. Commun.* **2013**, *49*, 2575-2577.