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Asymmetric synthesis of *anti*-diastereoisomers of β-heterocycle substituted (*S*)-α-aminobutyric acids

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Abstract—A new efficient method for the asymmetric synthesis of β-heterocycle substituted (2*S*,3*S*)-α-aminobutyric acids through the diastereoselective addition of 5-thioxo-4-allyl-1,2,4-triazoles, containing various substituents at the 3-position, to the C=C double bond of (*E*)- and (*Z*)-dehydroaminobutyric acid in the Ni^{II} complexes of their Schiff base with chiral auxiliaries (*S*)-*N*-(2-benzoylphenyl)-1-benzylpyrrolidine-2-carboxamide [(*S*)-BPB], (*S*)-*N*-(2-benzoylphenyl)-1-(3,4-dichlorobenzyl)pyrrolidine-2-carboxamide [(*S*)-3,4-DCBPB], (*S*)-*N*-(2-benzoylphenyl)-1-(3,4-dimethylbenzyl)pyrrolidine-2-carboxamide [(*S*)-3,4-DMBPB], and (*S*)-*N*-(2-benzoylphenyl)-1-(2-chlorobenzyl)pyrrolidine-2-carboxamide [(*S*)-2-CBPB] has been elaborated upon. The nucleophilic addition proceeds with high diastereoselectivity with a preferential formation of (*S*,*S*,*S*)-diastereoisomers. After decomposition of a mixture of diastereomeric complexes, optically active β-heterocycle substituted (2*S*,3*S*)-α-aminobutyric acids with high diastereomeric purity (de >98%) were isolated.

1. Introduction

Optically active non-proteinogenic α-amino acids including β-substituted α-aminobutyric acids are important components of many physiologically active peptides, antibiotics, and other medicinal drugs.[1] Non-proteinogenic α-amino acids have also been successfully adapted in microbiology for the selection of highly active strains producing proteinogenic amino acids as their analogues.[2]

Heterocyclic α-amino acids that contain 1,2,4-triazole and thiodiazole substituents in the side chain have especially high activities, in particular, in the selection of active strains producing histidine, arginine, and other amino acids.[3,4] As a result, the optically active heterocycle derivatives of α-aminobutyric acid are also of interest.

Works devoted to the asymmetric synthesis of β-substituted α-amino acids based on the addition of nucleophiles to the C=C bond of the dehydroalanine moiety in the Ni^{II} complex of its Schiff's base with chiral auxiliary (*S*)-*N*-(2-benzoylphenyl)-1-benzylpyrrolidine-2-carboxamide [(*S*)-BPB] are widely known.[5,6] By using this complex, 1,2,4-triazole and 1,3,4-thiodiazole containing heterocyclic derivatives of (*S*)-alanine and (*R*)-cysteine were also synthesized.[7,8]

Recently, procedures for the asymmetric synthesis of *anti*-diastereoisomers of β-substituted L-α-aminobutyric acid through the addition of thioles and alcoholate ions to the C=C bond of (*E*)- and (*Z*)-dehydroaminobutyric acid moieties in the chiral Ni^{II} complexes of their Schiff bases with (*S*)-BPB[9] and (*S*)-*N*-(2-benzoylphenyl)-1-(3,4-dichlorobenzyl)pyrrolidine-2-carboxamide [(*S*)-3,4-DCBPB][10] have also been developed. Moreover, an increase in de and a reduction in duration of the asymmetric addition reaction were revealed in transition from complexes with (*S*)-BPB to complexes with (*S*)-3,4-DCBPB.

Herein, we report the asymmetric synthesis of *anti*-diastereoisomers of β-heterocycle substituted (*S*)-α-aminobutyric acids containing 4-allyl-5-thioxo-1,2,4-triazol moieties with various aliphatic and aromatic substituents at the

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3-position through the addition of the corresponding heterocyclic nucleophiles to the C=C bond of chiral Ni^{II} complexes of Schiff bases of (*E*)- and (*Z*)-dehydroaminobutyric acid with chiral auxiliaries (*S*)-BPB, (*S*)-3,4-DCBPB, (*S*)-*N*-(2-benzoylphenyl)-1-(2-chlorobenzyl)pyrrolidine-2-carboxamide [(*S*)-2-CBPB], and (*S*)-*N*-(2-benzoylphenyl)-1-(3,4-dimethylbenzyl)pyrrolidine-2-carboxamide [(*S*)-3,4-DMBPB].

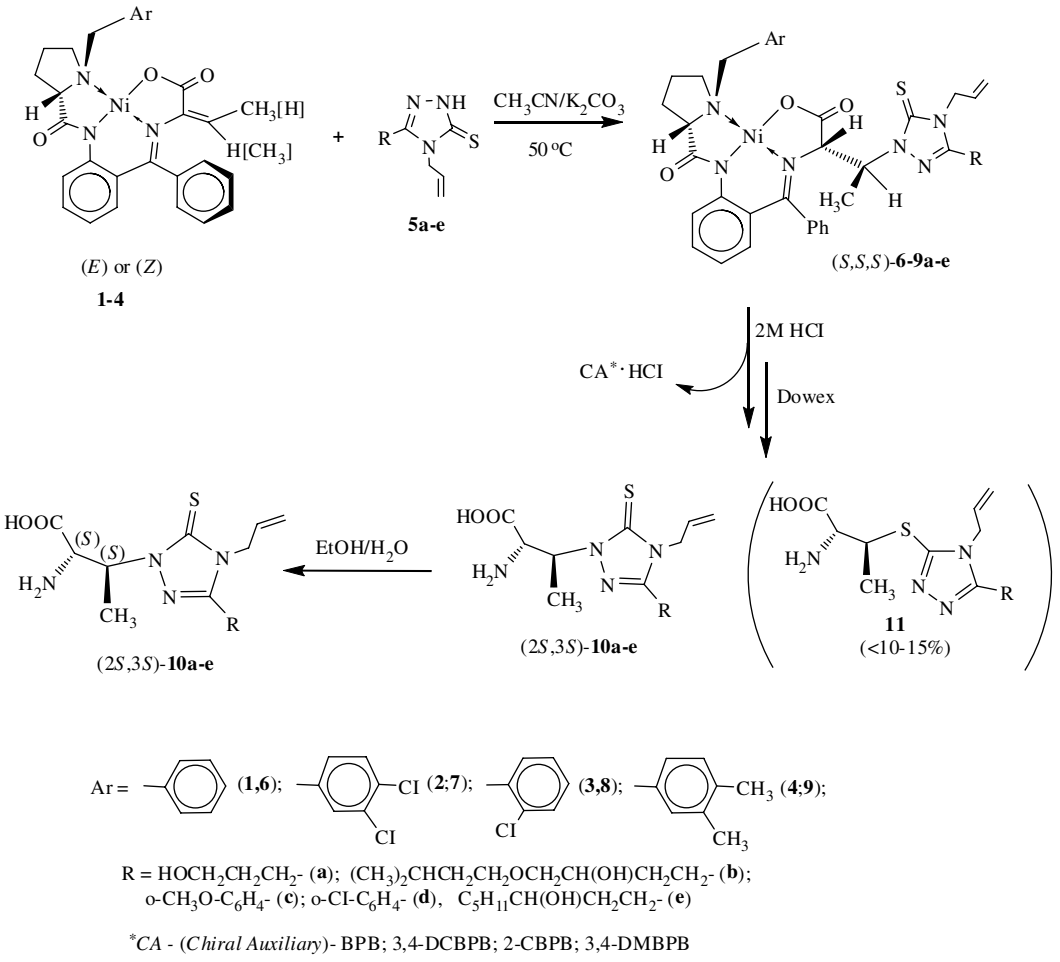
2. Results and discussion

The chiral Ni^{II} complexes of Schiff bases of (*E*)- and (*Z*)-dehydroaminobutyric acid with (*S*)-BPB **1**, (*S*)-3,4-DCBPB **2**, (*S*)-2-CBPB **3**, and (*S*)-3,4-DMBPB **4** were synthesized according to the methods previously elaborated by us.[9,11]

As heterocyclic nucleophiles 4-allyl-3-(3′-hydroxypropyl)-1*H*-1,2,4-triazole-5-thione **5a**, 4-allyl-3-(3′-hydroxy-4′-isoamyloxybutyl)-1*H*-1,2,4-triazole-5-thione **5b**, 4-allyl-3-(*o*-methoxyphenyl)-1*H*-1,2,4-triazole-5-thione **5c**, 4-allyl-3-(*o*-chlorophenyl)-1*H*-1,2,4-triazole-5-thione **5d**, and 4-allyl-3-(3′-hydroxyoctyl)-1*H*-1,2,4-triazole-5-thione **5e** were used.

The asymmetric addition of **5a**–**e** to the C=C bond of complexes **1**–**4** proceeded in CH_3CN in the presence of K_2CO_3 at 50–60 °C (Scheme 1). The reaction was monitored by TLC (SiO_2, $CHCl_3/CH_3COOC_2H_5$, 1:5) following the disappearance of traces of the initial complexes **1**–**4** and establishment of a thermodynamic equilibrium between the diastereoisomers formed of the addition products.

TLC and ^1H NMR analyses revealed that at the beginning of the addition reaction adding heterocyclic nucleophiles **2a**–**e** to the C=C bond of dehydroaminobutyric acid moiety complexes **1**–**4**, the excess of the basic diastereomer was ~85–90%, and after several hours it increased to give the results that are depicted in Table 1. In the case of the addition of **2a** to the unmodified complex of (*E*)-dehydroaminobutyric acid (*E*)-**1** before establishment of the thermodynamic equilibrium (after ~10 h, at approximately 30% conversion of the initial complex), we were successful in isolating the minor diastereomeric complex with an (*S*,*S*,*R*)-absolute configuration (in accordance with the polarimetric measurements and ^1H NMR) (II fraction on R_f value) by the TLC method. The ratio of this minor diastereomer to the basic diastereomer was 8%. The amount of this diastereomer decreased during establishment of the thermodynamic equilibrium and was ~2% after 120 h. Unfortunately, we failed to isolate the minor diastereomers of the modified complexes. Thus, by taking into account the above mentioned data, it is obvious that the addition of heterocyclic nucleophiles to the chiral Ni^{II} complex of the Schiff's base



Scheme 1.

Table 1. Results of asymmetric addition of **5(a–e)** to **1–4** (in CH_3CN/K_2CO_3 at 50 °C)

Run	Initial complex	Heterocyclic nucleophile	Time (h)	Main product	de[b] (%)	Yield[c] (%)
1	(*E*)-**1** [(*Z*)-**1**]	**2a**	120 (40 day)[a]	**6a**	96	72 (50)
2	(*E*)-**2**	**2a**	18	**7a**	97	86
3	(*E*)-**3** [(*Z*)-**3**]	**2a**	10	**8a**	98	88 (15)
4	(*E*)-**4**	**2a**	10	**9a**	94	84
5	(*E*)-**1** [(*Z*)-**1**]	**2b**	168 (50 day)	**6b**	94	74 (40)
6	(*E*)-**2**	**2b**	10	**7b**	96	90
7	(*E*)-**3**	**2b**	18	**8b**	96	90
8	(*E*)-**4**	**2b**	6	**9b**	90	81
9	(*E*)-**1** [(*Z*)-**1**]	**2c**	96 (32 day)	**6c**	97	83 (50)
10	(*E*)-**2**	**2c**	6	**7c**	>98	86
11	(*E*)-**3**	**2c**	13	**8c**	>98	89
12	(*E*)-**4**	**2c**	14	**9c**	97	70
13	(*E*)-**1** [(*Z*)-**1**]	**2d**	288 (80 day)	**6d**	97	85 (30)
14	(*E*)-**2**	**2d**	6	**7d**	>98	90
15	(*E*)-**3** [(*Z*)-**3**]	**2d**	42	**8d**	>98	92 (20)
16	(*E*)-**4**	**2d**	96	**9d**	97	92
17	(*E*)-**1** [(*Z*)-**1**]	**2e**	168 (60 day)	**6e**	86	75 (30)
18	(*E*)-**2**	**2e**	25	**7e**	89	78
19	(*E*)-**3**	**2e**	15	**8e**	91	80
20	(*E*)-**4**	**2e**	12	**9e**	88	72

[a] In brackets data of the nucleophilic addition to complexes (*Z*)-1–4 are given.
[b] de were determined by ^{1}H NMR analysis of the diastereomers mixture.
[c] Yield of a mixture of diastereomeric complexes.

of dehydroaminobutyric acid with chiral auxiliaries BPB, 3,4-DCBPB, 3,4-DMBPB, 2-CBPB was controlled by kinetic (at the beginning of the reaction) and thermodynamic factors. However, in our opinion, the contribution of the thermodynamic factor was more essential as shown previously in addition reactions of simple aliphatic nucleophiles to these complexes of dehydroaminobutyric acids.[9,11]

Nucleophilic addition resulted in the formation of a mixture of diastereomeric complexes with a high excess of the diastereoisomer with (*S*)-absolute configuration at the newly formed chiral centers at the 2- and 3-positions of the amino acid moiety. The major diastereomeric complexes of the addition products **6–9a–e** were separated by chromatography (20 × 30 cm, SiO_2, $CHCl_3/CH_3COOC_2H_5$, 1:3).

The configuration of the α-carbon atom of the amino acid moiety of the major diastereomers was determined by the sign of specific rotation at 589 nm (sodium D line), as was done earlier for complexes of the same amino acids with chiral auxiliaries (*S*)-BPB and (*S*)-3,4-DCBPB.[9,10] The configuration of the β-carbon atom of the aminobutyric acid moiety was determined by the values of the chemical shifts of ^{1}H NMR signals of the β-CH_3 protons. As was shown earlier for similar complexes of other β-substituted derivatives of α-aminobutyric acid, the ^{1}H NMR signals of the methyl groups of the *anti*-isomers [(*S*,*S*,*S*)-configuration of the complex] were located at stronger fields than those of the *syn*-isomers [(*S*,*S*,*R*)-configuration].[9,‡]

[‡] Such a difference in chemical shifts of signal of β-CH_3 protons is explained by the steric position of the CH_3 group of the aminobutyric fragment in the coordination plane of the metal ion. A shift of the signal in the methyl proton toward weak fields in ^{1}H NMR spectra is evidently the result of the magnetic anisotropy effect of the Ni^{2+} ion, positioned over the CH_3 group of the amino acid moiety in case of its (2*S*,3*R*)-*threo* absolute configuration.

Similar differences in chemical shifts of signals of the β-methyl protons of the amino acid moiety are also observed in ^{1}H NMR spectra of the synthesized diastereoisomeric complexes **6–9a–e**. It means that the major diastereoisomer of the addition products has (*S*,*S*,*S*)-absolute configuration containing the (*S*)-*anti* or (2*S*,3*S*)-*allo* β-substituted α-aminobutyric acid moiety.

Unfortunately, because of the small amounts concerned, we failed to chromatograph and establish the structure and absolute configuration of the concomitant diastereomeric complexes of the addition products.

We were unsuccessful in determining the de of the heterocyclic amino acids synthesized by the methods of chiral HPLC or GLC analyses. Therefore, by ^{1}H NMR spectroscopy, the diastereomeric ratio of complexes and isolated heterocyclic amino acids (in their mixtures, before chromatography or crystallization) was determined. For some products we managed to determine the diastereomeric excess proceeding from the ratio of signal integrals of aromatic protons in the region of 8–9 ppm or the ratio of signal integrals of methylene protons of the benzyl group of *N*-benzylproline moiety at 3.5–3.55 and 4.5–4.6 ppm (as it was earlier done for similarly designed complexes of aliphatic amino acids[9,10]). The most accurate results were recorded when determining the ratio of doublet signal integrals of the α-proton of the diastereomers of heterocycle substituted amino acids in the range of 4.2–4.4 ppm in ^{1}H NMR spectra of their mixture obtained after decomposition of the diastereomeric complexes mixture and ion-exchange isolation of the amino acid. The diastereomeric excess of the isolated amino acids **10a–e** based on ^{1}H NMR spectra data is given in Table 1.

The addition of triazoles **5a–e** to both the individually pure (*E*)- and (*Z*)-isomers of complexes **1–4** and their

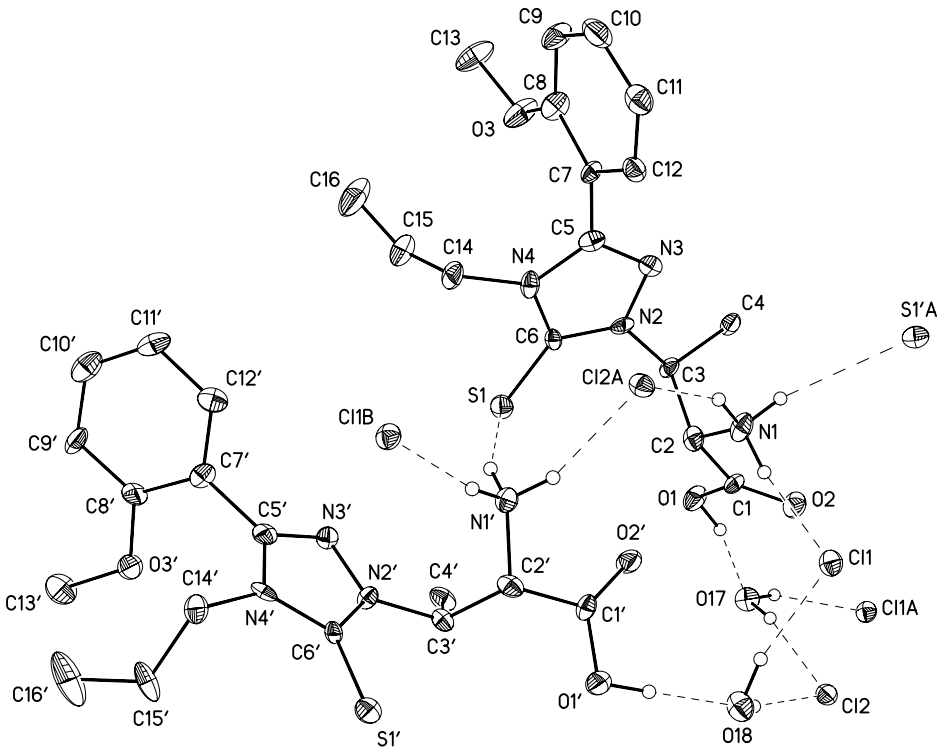


Figure 1. The structure of amino acid **10c** based on X-ray structural analysis data.

mixture was studied. It was shown that irrespective of the configuration of dehydroaminobutyric moiety of the initial complexes, the final main product appears as *anti*-diastereoisomers of β-heterocycle substituted (*S*)-α-aminobutyric acids, as shown earlier with alcoholate ion, thiols, etc. as a nucleophile.[9,10]

It follows from the data given in Table 1 that the maximum diastereoselectivity and minimum duration of the nucleophilic addition reaction are observed using initial dehydroaminobutyric acid complexes based on the modified chiral auxiliary (*S*)-2-CBPB **3**. An increase in diastereoselectivity and a reduction in the duration of the nucleophilic addition reaction in a series of complexes of chiral auxiliaries are given below (the average data):

BPB, (**1**), (86% de) → 3,4-DCBPB, (**2**), (90% de)
→ 3,4-DMBPB, (**4**), (91% de)
→ 2-CBPB, (**3**), (97% de)

The analogous regularity was also observed in the C-alkylation reactions of the similar complexes of glycine and alanine based on the same chiral auxiliaries.[12]

Besides, by analogy with the results obtained earlier[9,10] an increase in de and a sharp reduction in the duration of the nucleophilic addition reaction were observed in transition from the complex of (*Z*)-dehydroaminobutyric acid to the complexes of (*E*)-dehydroaminobutyric acid (see Table 1).

Decomposition of the diastereomeric complex mixtures and isolation of β-heterocyclic derivatives of (2*S*,3*S*)-α-aminobutyric acid **10a**–**e** were carried out by the standard procedures.[9] The initial chiral auxiliaries (*S*)-BPB, or (*S*)-3,4-DCBPB, or (*S*)-3,4-DMBPB, or (*S*)-2-CBPB were recovered in a yield of >90% without any loss of its initial enantiomeric excess.

The amino acid mixtures isolated before crystallization were analyzed by ^{1}H NMR and IR methods. According to the IR spectra the obtained β-heterocyclic substituted α-aminobutyric acids contained admixtures of the corresponding S-heterocyclic substituted cysteines **11**-products of addition of triazoles to the C=C bond of complexes **1**–**4** by sulfhydryl (SH) group.

This is proved by the presence of the absorption band in the region of 650–700 cm^{-1} in the IR spectra of the isolated amino acid mixtures, typical of the –S–C– bond. After recrystallization from a mixture of H_2O/C_2H_5OH[13] (1:1), individually pure β-heterocycle substituted α-aminobutyric acids **10a**–**e** of (*S*)-*anti* absolute configuration were obtained, which was confirmed by the X-ray structural analysis data.

The structures and absolute configurations of the synthesized heterocyclic amino acids were established by the spectral methods. Figure 1 depicts the molecular structure of (2*S*,3*S*)-*allo*-3-(4-allyl-5-(2-methoxyphenyl)-4*H*-1,2,4-triazol-3-ylthio)-2-aminobutyric acid **10c** based on the X-ray structural analysis data.

3. Conclusion

New β-heterocycle substituted (*S*)-α-aminobutyric acids: (2*S*,3*S*)-3-(4′-allyl-3′-hydroxypropyl-5′-thioxo-1,2,4-triazol-

1′-yl)-2-aminobutyric acid, (2*S*,3*S*)-3-(4′-allyl-3′-hydroxy-isoamyl-oxybutyl-5′-thioxo-1,2,4-triazol-1′-yl)-2-amino-butyric acid, (2*S*,3*S*)-3-(4′-allyl-3′-*o*-methoxyphenyl-5′-thioxo-1,2,4-triazol-1′-yl)-2-aminobutyric acid, (2*S*,3*S*)-3-(4′-allyl-3′-*o*-chlorophenyl-5′-thioxo-1,2,4-triazol-1′-yl)-2-aminobutyric acid, and (2*S*,3*S*)-3-(4′-allyl-3′-hydroxy-octyl-5′-thioxo-1,2,4-triazol-1′-yl)-2-aminobutyric acid, have been synthesized. The best results in de and reduction in the reaction duration were achieved by the use of a complex of dehydroaminobutyric acids based on the chiral auxiliary (*S*)-2-CBPB.

4. Experimental

The amino acids were purchased from 'Reanal' (Budapest); silica gel L-40/100 'Chemapol Praha' (Praque); $CHCl_3$, $(CH_3)_2CO$, *i*-PrOH, $CH_3COOC_2H_5$, CH_3COOH, CH_3CN, CH_3OH, K_2CO_3 from 'Reakhim' (Russia); 2-chlorobenzyl-chloride, 3,4-dichlorobenzylchloride, 3,4-dimethylbenzyl-chloride, benzylchloride, and 2-aminobenzophenone from 'Aldrich'. All solvents used were freshly distilled. The ^{1}H NMR spectra were recorded on a 'Mercury-300 Varian' (300 MHz) in DMSI-d_6/CCl_4: 1:3 (unless otherwise indicated). The optical rotations were measured on 'Perkin Elmer-341' polarimeter, in a 5 cm thermostated cell with an accuracy of 0.1%. IR spectra were recorded on a Nicolet/FT IR NEXUS spectrometer in the 4000–600 sm^{-1} region with 2 sm^{-1} resolution. The crystals were pressed in tablets with KBr in 1:200 under a pressure of 1.5 t/sm^2 for obtaining the spectra of amino acids. An absorption region at 600–700 sm^{-1}, which can be related to the –C–S– group, and an absorption region at 1280–1355 sm^{-1}, characteristic for valence fluctuations of the –C–N– group, were observed in the IR spectra of amino acids before crystallization.[13] Taking into account the intensity of the absorption ratio of pure **10 a–e** samples, the relative content of **11** was determined as much as 10–15% to weight in the mixture before crystallization.

4.1. General procedure for the asymmetric synthesis of 6–9a–e

To a solution of 5.3 mmol of complexes (*E*)- and (*Z*)-dehydroaminobutyric acid (2.77 g of **1**, 3.14 g of **2**, 2.95 g of **3** and 2.92 g of **4**) in 15 mL of MeCN were added with stirring 1.33 g (9.6 mmol) of K_2CO_3 and 8 mmol of nucleophile—1.6 g (**5a**), 2.4 g (**5b**), 1.97 g (**5c**), 2 g (**5d**), and 2.15 g (**5e**) at 50–60 °C. The reaction was monitored by TLC (SiO_2, $CHCl_3$/Me_2CO (3:1)) following the disappearance of the spot on the initial (*E*)-**1** complex. Upon completion of the reaction, the mixture was filtered, the K_2CO_3 precipitate washed with CH_3CN and the solution evaporated to dryness. A small part of the dry residue (~0.2 g) was chromatographed on SiO_2 ($CHCl_3$/Me_2CO, 3:1, 20 × 20 cm) to isolate individually pure diastereoisomeric complex—addition products.

4.1.1. Complex 6a. Anal. Calcd for $C_{37}H_{40}N_6NiO_4S$ (723.51): C, 61.42; H, 5.57; N, 11.62. Found: C, 61.47; H, 5.61; N, 11.64. Mp 120–122 °C. $[\alpha]_D^{20} = +1325.7$ (*c* 0.005, MeOH). ^{1}H NMR ($CDCl_3$): δ 1.19 (3H, d, >CH–CH(*Me*), $^3J = 7.2$ Hz); 1.86–2.10 (4H, m, –$CH_2CH_2CH_2OH$, β-H Pro, δ-H Pro); 2.40 (1H, m, γ-H Pro); 2.73 (1H, m, γ-H Pro); 2.79 (2H, t, –$CH_2CH_2CH_2OH$, $^3J = 7.0$ Hz); 2.95 (1H, m, β-H Pro); 3.38 (1H, m, δ-H Pro); 3.38 (1H, dd, α-H Pro, $^3J = 10.3$ Hz, $^3J = 6.3$ Hz); 3.60 (1H, d, NCH_2Ar, $^2J = 12.6$ Hz); 3.69 (2H, m, –$CH_2CH_2CH_2OH$); 4.16 (1H, d, >*CH*–CH(Me)–, $^3J = 4.0$ Hz); 4.39 (1H, d, NCH_2Ar, $^2J = 12.6$ Hz), 4.61 (1H, ddt, >N–CH_2–CH=CH_2, $^2J = 15.7$ Hz, $^3J = 5.5$ Hz, $^4J = 1.3$ Hz); 4.98 (1H, ddt, >N–CH_2–CH=CH_2, $^2J = 15.7$ Hz, $^3J = 5.5$ Hz, $^4J = 1.3$ Hz); 5.25 (1H, d, >N–CH_2–CH=CH_2, $^3J = 16.9$ Hz); 5.30 (1H, d, >N–CH_2–CH=CH_2, $^3J = 10.5$ Hz); 5.57 (1H, qd, >CH–*CH*(Me)–, $^3J = 7.2$ Hz, $^3J = 4.0$ Hz); 5.96 (1H, ddt, N–CH_2–*CH*=CH_2, $^3J = 16.9$ Hz, $^3J = 10.5$ Hz, $^3J = 5.5$ Hz); 6.64–6.73 (2H, m, Ar); 7.14–7.21 (2H, m, Ar); 7.27–7.35 (3H, m, Ar); 7.52–7.61 (4H, m, Ar); 7.96 (2H, m, Ar); 8.41 (1H, d, Ar, $^3J = 8.6$ Hz).

4.1.2. Complex 6b. Anal. Calcd for $C_{43}H_{52}N_6NiO_5S$ (823.67): C, 62.70; H, 6.36; N, 10.20. Found: C, 62.72; H, 6.39; N, 10.22. Mp 188–190 °C. $[\alpha]_D^{20} = +1418$ (*c* 0.05, MeOH). ^{1}H NMR ($CDCl_3$) δ 0.91 (6H, d, –CH_2–CH_2–CH(OH)–CH_2–O–CH_2–CH_2–CH(*Me*)$_2$, $^3J = 6.7$ Hz); 1.20 (3H, d, >CH–CH(*Me*), $^3J = 7.1$ Hz); 1.43 (2H, q, –CH_2–CH_2–CH(OH)–CH_2–O–CH_2–*CH_2*–CH(Me)$_2$, $^3J = 6.6$ Hz); 1.66 (1H, m, –CH_2–*CH_2*–CH(OH)–CH_2–O–CH_2–CH_2–CH(Me)$_2$); 1.70 (1H, m, –CH_2–CH_2–CH(OH)–CH_2–O–CH_2–CH_2–*CH*(Me)$_2$–); 1.82–2.01 (2H, m, γ-H Pro, –CH_2–*CH_2*–CH(OH)–CH_2–O–CH_2–CH_2–CH(Me)$_2$); 2.12 (1H, m, β-H Pro); 2.30–2.45 (2H, m, β-, γ-H Pro); 2.66–2.92 (2H, m, –*CH_2*–CH_2–CH(OH)–CH_2–O–CH_2–CH_2–CH(Me)$_2$); 3.17–3.38 (4H, m, δ-H Pro, –CH_2–CH_2–CH(OH)–*CH_2*–O–CH_2–CH_2–CH(Me)$_2$); 3.43 (2H, t, –CH_2–CH_2–CH(OH)–CH_2–O–*CH_2*–CH_2–CH(Me)$_2$, $^3J = 6.7$ Hz); 3.52 (1H, d, NCH_2Ar, $^2J = 12.2$ Hz); 3.56 (1H, m, –CH_2–CH_2–*CH*(OH)–CH_2–O–CH_2–CH_2–CH(Me)$_2$); 3.58–3.73 (1H, m, α-H Pro); 3.90 (1H, d, >*CH*–CH(Me)–, $^3J = 3.7$ Hz); 4.08 (1H, d, NCH_2Ar, $^2J = 12.2$ Hz); 4.29 (1H, m, OH); 4.70 (1H, dd, >N–CH_2–CH=CH_2, $^2J = 15.9$ Hz, $^3J = 5.6$ Hz); 4.85 (1H, dd, >N–CH_2–CH=CH_2, $^2J = 15.9$ Hz, $^3J = 5.6$ Hz); 5.23 (2H, m, >N–CH_2–CH=*CH_2*); 5.27 (1H, qd, >CH–*CH*(Me)–, $^3J = 7.1$ Hz, $^3J = 3.7$ Hz); 5.94 (1H, ddt, N–CH_2–*CH*=CH_2, $^3J = 17.3$ Hz, $^3J = 10.2$ Hz, $^3J = 5.6$ Hz); 6.56–6.65 (2H, m, Ar); 7.05 (1H, ddd, Ar, $^3J = 8.7$ Hz, $^3J = 6.3$ Hz, $^4J = 2.4$ Hz); 7.13 (1H, d, Ar, $^3J = 7.6$ Hz); 7.31 (2H, m, Ar); 7.42 (1H, d, Ar, $^3J = 8.7$ Hz); 7.54–7.60 (3H, m, Ar); 7.64 (1H, m, Ar); 8.17 (2H, d, Ar, $^3J = 7.6$ Hz); 8.28 (1H, d, Ar, $^3J = 8.7$ Hz).

4.1.3. Complex 6c. Anal. Calcd for $C_{41}H_{40}N_6NiO_4S$ (771.55): C, 63.82; H, 5.23; N, 10.89. Found: C, 63.86; H, 5.27; N, 10.91. Mp 136–138 °C. $[\alpha]_D^{20} = +1086$ (*c* 0.05, MeOH). ^{1}H NMR ($CDCl_3$): δ 1.28 (3H, d, >CH–CH(*Me*)–, $^3J = 7.0$ Hz); 1.92 (1H, m, β-H Pro); 2.10 (1H, m, γ-H Pro); 2.44 (1H, m, β-H Pro); 2.85 (1H, m, δ-H Pro); 2.94 (1H, m, δ-H Pro); 3.16 (1H, m, γ-H Pro); 3.43 (1H, dd, α-H Pro, $^3J = 10.3$ Hz, $^3J = 6.6$ Hz); 3.82 (1H, d, NCH_2Ar, $^2J = 12.8$ Hz); 3.86 (3H, s, OMe); 4.04 (1H, d, >*CH*–CH(Me)–, $^3J = 3.7$ Hz); 4.22 (1H, d, NCH_2Ar, $^2J = 12.8$ Hz); 4.53 (1H, ddt, >N–CH_2–CH=CH_2, $^2J = 15.4$ Hz, $^3J = 6.0$ Hz, $^4J = 1.5$ Hz); 4.78 (1H, ddt,

>N–*CH*$_2$–CH=CH$_2$, ^2J = 15.4 Hz, ^3J = 5.5 Hz, ^4J = 1.5 Hz); 4.91 (1H, dq, >N–CH$_2$–CH=*CH*$_2$, ^3J = 17.2 Hz, ^4J = 1.5 Hz); 5.06 (1H, dq, >N–CH$_2$–CH=*CH*$_2$, ^3J = 10.3 Hz, ^4J = 1.5 Hz); 5.34 (1H, qd, >CH–*CH*(Me)–, ^2J = 7.2 Hz, ^3J = 3.7 Hz); 5.78 (1H, dddd, N–CH$_2$–*CH*=CH$_2$, ^3J = 17.2 Hz, ^3J = 10.3 Hz, ^3J = 6.0 Hz, ^3J = 5.5 Hz); 6.58–6.66 (2H, m, Ar); 7.02–7.17 (4H, m, Ar); 7.28 (1H, dd, Ar, ^3J = 7.6 Hz, ^4J = 1.8 Hz); 7.25–7.37 (4H, m, Ar); 7.44 (1H, d, Ar, ^3J = 7.6 Hz); 7.50–7.68 (4H, m, Ar); 8.18 (1H, d, Ar, ^3J = 7.6 Hz); 8.29 (1H, d, Ar, ^3J = 8.7 Hz).

4.1.4. Complex 6d. Anal. Calcd for $C_{40}H_{37}ClN_6NiO_3S$ (775.97): C, 61.91; H, 4.81; N, 10.83. Found: C, 61.94; H, 4.85; N, 10.84. Mp 150–151 °C. $[\alpha]_D^{20}$ = +1130 (*c* 0.05, MeOH). ^{1}H NMR ($CDCl_3$): δ 1.26 (3H, d, >CH–CH(*Me*)–, ^3J = 6.8 Hz); 2.08 (1H, m, γ-H Pro); 2.14 (1H, m, β-H Pro); 2.42 (1H, m, β-H Pro); 2.62 (1H, m, γ-H Pro); 3.12 (1H, m, δ-H Pro); 3.48 (1H, m, δ-H Pro); 3.54 (1H, dd, α-H Pro, ^3J = 10.5 Hz, ^3J = 5.8 Hz); 3.82 (1H, d, N*CH*$_2$Ar, ^2J = 12.3 Hz); 4.43 (d, 1H, >*CH*–CH(Me)–, ^3J = 5.2 Hz); 4.38 (1H, d, N*CH*$_2$Ar, ^2J = 12.3 Hz); 4.48 (1H, dd, >N–*CH*$_2$–CH=CH$_2$, ^2J = 15.8 Hz, ^3J = 5.7 Hz); 4.65 (1H, dd, >N–*CH*$_2$–CH=CH$_2$, ^2J = 15.8 Hz, ^3J = 5.7 Hz); 4.91 (1H, d, >N–CH$_2$–CH=*CH*$_2$, ^3J = 17.3 Hz, ^3J = 10.4 Hz); 5.07 (1H, d, >N–CH$_2$–CH=*CH*$_2$, ^3J = 17.3 Hz, ^3J = 10.4 Hz); 5.67 (1H, m, >CH–*CH*(Me)–); 5.74 (1H, ddt, N–CH$_2$–*CH*=CH$_2$, ^3J = 17.3 Hz, ^3J = 10.4 Hz, ^3J = 5.7 Hz); 6.56 (1H, d, Ar, ^3J = 8.2 Hz); 6.66 (1H, dd, Ar, ^3J = 8.2 Hz, ^4J = 2.2 Hz); 7.05 (1H, ddd, Ar, ^3J = 8.7 Hz, ^3J = 6.0 Hz, ^4J = 2.5 Hz); 7.31 (1H, br d, ^3J = 7.0 Hz); 7.35 (1H, d, ^3J = 8.1 Hz); 7.48–7.67 (10H, m, Ar); 8.16 (1H, d, Ar, ^3J = 8.7 Hz); 8.24 (1H, dd, Ar, ^3J = 8.1 Hz, ^4J = 2.1 Hz); 8.67 (1H, d, Ar, ^4J = 2.1 Hz).

4.1.5. Complex 6e. Anal. Calcd for $C_{42}H_{50}N_6NiO_4S$ (793.64): C, 63.56; H, 6.35; N, 10.59. Found: C, 63.59; H, 6.38; N, 10.62. Mp 123–125 °C. $[\alpha]_D^{20}$ = +608 (*c* 0.05, MeOH). ^{1}H NMR ($CDCl_3$): δ 1.08 (3H, t, –(CH$_2$)$_2$–CH(OH)–(CH$_2$)$_4$–*Me*, ^3J = 6.8 Hz); 1.20 (3H, d, >CH–CH(*Me*)–, ^3J = 7.1 Hz); 1.24–1.45 (8H, m, –(CH$_2$)$_2$–CH(OH)–(CH$_2$)$_4$–Me); 1.65 (1H, m, –(CH$_2$)$_2$–CH(OH)–(CH$_2$)$_4$–Me); 1.81 (1H, m, –(CH$_2$)$_2$–CH(OH)–(CH$_2$)$_4$–Me); 1.96–2.15 (2H, m, β-, γ-H Pro); 2.47 (2H, m, β-, γ-H Pro); 2.65–2.96 (3H, m, –(CH$_2$)$_2$–CH(OH)–(CH$_2$)$_4$–CH$_3$); 3.11 (1H, m, δ-H Pro); 3.36–3.58 (2H, m, δ-, α-H Pro); 3.82 (1H, d, N*CH*$_2$Ar, ^2J = 12.7 Hz); 3.87 (1H, d, >*CH*–CH(Me)–, ^3J = 3.8 Hz); 4.23 (1H, d, N*CH*$_2$Ar, ^2J = 12.7 Hz); 4.71 (1H, dd, >N–*CH*$_2$–CH=CH$_2$, ^2J = 15.8 Hz, ^3J = 5.3 Hz); 4.88 (1H, dd, >N–*CH*$_2$–CH=CH$_2$, ^2J = 15.8 Hz, ^3J = 5.3 Hz); 5.25 (1H, qd, >CH–*CH*(Me)–, ^3J = 7.1 Hz, ^3J = 3.8 Hz); 5.28 (2H, m, >N–CH$_2$–CH=*CH*$_2$); 5.95 (1H, ddt, N–CH$_2$–*CH*=CH$_2$, ^3J = 17.3 Hz, ^3J = 10.0 Hz, ^3J = 5.3 Hz); 6.58–6.69 (2H, m, Ar); 7.10 (1H, ddd, ^3J = 8.6 Hz, ^3J = 6.1 Hz, ^4J = 2.4 Hz); 7.16 (1H, m, Ar); 7.30 (2H, m, Ar); 7.42 (1H, d, Ar, ^3J = 7.3 Hz); 7.55–7.61 (3H, m, Ar); 7.64 (2H, m, Ar); 8.14–8.31 (2H, m, Ar).

4.1.6. Complex 7a. Anal. Calcd for $C_{37}H_{38}Cl_2N_6NiO_4S$ (792.4): C, 56.08; H, 4.83; N, 10.61. Found: C, 56.06; H, 4.86; N, 10.67. Mp 144–146 °C. $[\alpha]_D^{20}$ = +1748 (*c* 0.025, $CHCl_3$). ^{1}H NMR: δ 1.20 (3H, d, >CH–CH(*Me*)–, ^3J = 7.1 Hz); 1.85 (2H, m, –CH$_2$*CH*$_2$CH$_2$OH); 2.02 (1H, m, β-H Pro); 2.12 (1H, m, γ-H Pro); 2.42 (2H, m, β-, γ-H Pro); 2.73 (1H, dt, –*CH*$_2$CH$_2$CH$_2$OH, ^2J = 16.3 Hz, ^3J = 7.8 Hz); 2.84 (1H, dt, –*CH*$_2$CH$_2$CH$_2$OH, ^2J = 16.3 Hz, ^3J = 7.8 Hz); 3.23 (1H, m, δ-H Pro); 3.42 (1H, d, N*CH*$_2$Ar, ^2J = 12.3 Hz); 3.49 (1H, m, δ-H Pro); 3.50 (2H, m, –CH$_2$CH$_2$*CH*$_2$OH); 3.51 (1H, dd, α-H Pro, ^3J = 9.5 Hz, ^3J = 5.2 Hz); 3.92 (1H, d, >*CH*–CH(Me)–, ^3J = 3.8 Hz); 4.05 (1H, d, N*CH*$_2$Ar, ^2J = 12.3 Hz), 4.23 (1H, t, OH, ^3J = 6.7 Hz); 4.70 (1H, ddt, >N–*CH*$_2$–CH=CH$_2$, ^2J = 15.7 Hz, ^3J = 5.5 Hz, ^4J = 1.5 Hz); 4.86 (1H, ddt, >N–*CH*$_2$–CH=CH$_2$, ^2J = 15.7 Hz, ^3J = 5.5 Hz, ^4J = 1.5 Hz); 5.26 (2H, m, >N–CH$_2$–CH=*CH*$_2$); 5.28 (1H, m, >CH–*CH*(Me)–); 5.93 (1H, ddt, N–CH$_2$–*CH*=CH$_2$, ^3J = 17.6 Hz, ^3J = 10.0 Hz, ^3J = 5.5 Hz); 6.58 (1H, d, Ar, ^3J = 8.2 Hz); 6.63 (1H, dd, Ar, ^3J = 8.2 Hz, ^4J = 2.5 Hz); 7.07 (1H, ddd, Ar, ^3J = 8.8 Hz, ^3J = 6.2 Hz, ^4J = 2.5 Hz); 7.37 (1H, d, Ar, ^3J = 8.2 Hz); 7.45 (1H, br d, Ar, ^3J = 7.4 Hz); 7.50–7.68 (4H, m, Ar); 8.18 (1H, d, Ar, ^3J = 8.8 Hz); 8.22 (1H, dd, Ar, ^3J = 8.2 Hz, ^4J = 2.1 Hz); 8.65 (1H, d, Ar, ^4J = 2.1 Hz).

4.1.7. Complex 7b. Anal. Calcd for $C_{43}H_{50}Cl_2N_6NiO_5S$ (892.56): C, 57.86; H, 5.65; N, 9.42. Found: C, 57.88; H, 5.70; N, 9.38. Mp 132–134 °C. $[\alpha]_D^{20}$ = +1426 (0.05, $CHCl_3$). ^{1}H NMR: δ 0.91 (6H, d, –CH$_2$–CH$_2$–CH(OH)–CH$_2$–O–CH$_2$–CH$_2$–CH(*Me*)$_2$, ^3J = 6.9 Hz); 1.22 (3H, d, >CH–CH(*Me*), ^3J = 7.1 Hz); 1.43 (2H, q, –CH$_2$–CH$_2$–CH(OH)–CH$_2$–O–CH$_2$–*CH*$_2$–CH(Me)$_2$, ^3J = 6.7 Hz); 1.64 (1H, m, –CH$_2$–*CH*$_2$–CH(OH)–CH$_2$–O–CH$_2$–CH$_2$–CH(Me)$_2$); 1.70 (1H, m, –CH$_2$–CH$_2$–CH(OH)–CH$_2$–O–CH$_2$–CH$_2$–*CH*(Me)$_2$); 1.88 (1H, m, –CH$_2$–*CH*$_2$–CH(OH)–CH$_2$–O–CH$_2$–CH$_2$–CH(Me)$_2$); 2.01 (1H, m, γ-H Pro); 2.12 (1H, m, β-H Pro); 2.37–2.46 (2H, m, β-, γ-H Pro); 2.66-2.96 (2H, m, –*CH*$_2$–CH$_2$–CH(OH)–CH$_2$–O–(CH$_2$)$_2$–CH(Me)$_2$); 3.16–3.34 (3H, m, δ-H Pro, –CH$_2$–CH$_2$–CH(OH)–*CH*$_2$–O–CH$_2$–CH$_2$–CH(Me)$_2$); 3.39 (1H, m, δ-H Pro); 3.43 (2H, t, –CH$_2$–CH$_2$–CH(OH)–CH$_2$–O–*CH*$_2$–CH$_2$–CH(Me)$_2$, ^3J = 6.7 Hz); 3.45 (1H, d, N*CH*$_2$Ar, ^2J = 12.3 Hz); 3.48 (1H, m, α-H Pro); 3.54–3.72 (1H, m, –CH$_2$–CH$_2$–*CH*(OH)–CH$_2$–O–CH$_2$–CH$_2$–CH(Me)$_2$); 3.93 (1H, d, >*CH*–CH(*Me*), ^3J = 4.0 Hz); 4.05 (1H, d, N*CH*$_2$Ar, ^2J = 12.3 Hz); 4.27 (1H, d, OH, ^3J = 5.5 Hz); 4.69 (1H, ddt, >N–*CH*$_2$–CH=CH$_2$, ^2J = 15.9 Hz, ^3J = 5.4 Hz, ^4J = 1.5 Hz); 4.84 (1H, ddt, >N–*CH*$_2$–CH=CH$_2$, ^2J = 15.9 Hz, ^3J = 5.4 Hz, ^4J = 1.5 Hz); 5.27 (2H, m, >N–CH$_2$–CH=*CH*$_2$); 5.28 (1H, m, >CH–*CH*(Me)–); 5.93 (1H, ddt, N–CH$_2$–*CH*=CH$_2$, ^3J = 17.3 Hz, ^3J = 10.0 Hz, ^3J = 5.5 Hz); 6.57 (1H, d, Ar, ^3J = 8.3 Hz); 6.62 (1H, dd, Ar, ^3J = 8.3 Hz, ^4J = 2.4 Hz); 7.07 (1H, ddd, Ar, ^3J = 8.8 Hz, ^3J = 6.2 Hz, ^4J = 2.4 Hz); 7.37 (1H, d, Ar, ^3J = 8.2 Hz); 7.46 (1H, br d, Ar, ^3J = 7.6 Hz); 7.48–7.66 (4H, m, Ar); 8.18 (1H, d, Ar, ^3J = 8.8 Hz); 8.23 (1H, dd, Ar, ^3J = 8.2 Hz, ^4J = 2.1 Hz); 8.65 (1H, d, Ar, ^4J = 2.1 Hz).

4.1.8. Complex 7c. Anal. Calcd for $C_{41}H_{38}Cl_2N_6NiO_4S$ (840.44): C, 58.59; H, 4.56; N, 10.00. Found: C, 58.62; H, 4.59; N, 10.06. Mp 101–103 °C. $[\alpha]_D^{20}$ = +1638 (*c* 0.05, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 1.28 (3H, d, >CH–CH(*Me*)–, ^3J = 7.0 Hz); 2.10 (1H, m, β-H Pro); 2.18 (1H, m, γ-H Pro); 2.40 (1H, m, β-H Pro); 2.87 (1H, m, δ-H

Pro); 3.08 (1H, m, δ-H Pro); 3.22 (1H, m, γ-H Pro); 3.40 (1H, dd, α-H Pro, $^3J = 10.5$ Hz, $^3J = 6.6$ Hz); 3.85 (1H, d, NCH_2Ar, $^2J = 12.6$ Hz); 3.86 (3H, s, OMe); 4.06 (1H, d, >CH–CH(Me)–, $^3J = 3.7$ Hz); 4.23 (1H, d, NCH_2Ar, $^2J = 12.6$ Hz); 4.59 (1H, ddt, >N–CH_2–CH=CH_2, $^2J = 15.2$ Hz, $^3J = 6.0$ Hz, $^4J = 1.4$ Hz); 4.76 (1H, ddt, >N–CH_2–CH=CH_2, $^2J = 15.2$ Hz, $^3J = 5.5$ Hz, $^4J = 1.4$ Hz); 4.94 (1H, dq, >N–CH_2–CH=CH_2, $^3J = 17.3$ Hz, $^4J = 1.5$ Hz); 5.00 (1H, dq, >N–CH_2–CH=CH_2, $^3J = 10.5$ Hz, $^4J = 1.5$ Hz); 5.33 (1H, qd, >CH–CH(Me)–, $^3J = 7.2$ Hz, $^3J = 3.7$ Hz); 5.78 (1H, dddd, N–CH_2–CH=CH_2, $^3J = 17.3$ Hz, $^3J = 10.5$ Hz, $^3J = 6.0$ Hz, $^3J = 5.5$ Hz); 6.62–6.68 (2H, m, Ar); 7.01–7.17 (4H, m, Ar); 7.26 (1H, dd, Ar, $^3J = 7.6$ Hz, $^4J = 1.8$ Hz); 7.30–7.38 (3H, m, Ar); 7.45 (1H, d, Ar, $^3J = 7.6$ Hz); 7.50–7.67 (3H, m, Ar); 8.26 (2H, m, Ar).

4.1.9. Complex 7d. Anal. Calcd for $C_{40}H_{35}Cl_3N_6NiO_3S$ (844.86): C, 56.86; H, 4.18; N, 9.95. Found: C, 56.90; H, 4.15; N, 10.01. Mp 96–98 °C. $[\alpha]_D^{20} = +1640$ (c 0.025, $CHCl_3$). ^{1}H NMR: δ 1.26 (3H, d, >CH–CH(Me)–, $^3J = 7.0$ Hz); 2.07 (1H, m, γ-H Pro); 2.16 (1H, m, β-H Pro); 2.47 (1H, m, β-H Pro); 2.62 (1H, m, γ-H Pro); 3.27 (1H, m, δ-H Pro); 3.40 (1H, m, δ-H Pro); 3.43 (1H, d, NCH_2Ar, $^2J = 12.3$ Hz); 3.54 (1H, dd, α-H Pro, $^3J = 10.5$ Hz, $^3J = 5.8$ Hz); 4.05 (1H, d, >CH–CH(Me)–, $^3J = 5.2$ Hz); 4.09 (1H, d, NCH_2Ar, $^2J = 12.3$ Hz); 4.59 (1H, dd, >N–CH_2–CH=CH_2, $^2J = 15.8$ Hz, $^3J = 5.7$ Hz); 4.63 (1H, dd, >N–CH_2–CH=CH_2, $^2J = 15.8$ Hz, $^3J = 5.7$ Hz); 4.90 (1H, d, >N–CH_2–CH=CH_2, $^3J = 17.3$ Hz, $^3J = 10.4$ Hz); 5.06 (1H, d, >N–CH_2–CH=CH_2, $^3J = 17.3$ Hz, $^3J = 10.4$ Hz); 5.69 (1H, m, >CH–CH(Me)–); 5.74 (1H, ddt, N–CH_2–CH=CH_2, $^3J = 17.3$ Hz, $^3J = 10.4$ Hz, $^3J = 5.7$ Hz); 6.59 (1H, d, Ar, $^3J = 8.2$ Hz); 6.64 (1H, dd, Ar, $^3J = 8.2$ Hz, $^4J = 2.2$ Hz); 7.09 (1H, ddd, Ar, $^3J = 8.7$ Hz, $^3J = 6.0$ Hz, $^4J = 2.5$ Hz); 7.27 (1H, br d, Ar, $^3J = 7.0$ Hz); 7.38 (1H, d, Ar, $^3J = 8.1$ Hz); 7.44–7.67 (8H, m, Ar); 8.19 (1H, d, Ar, $^3J = 8.7$ Hz); 8.26 (1H, dd, Ar, $^3J = 8.1$ Hz, $^4J = 2.1$ Hz); 8.68 (1H, d, Ar, $^4J = 2.1$ Hz).

4.1.10. Complex 7e. Anal. Calcd for $C_{42}H_{48}Cl_2N_6NiO_4S$ (862.53): C, 58.48; H, 5.61; N, 9.74. Found: C, 58.45; H, 5.58; N, 9.78. Mp 77–78 °C. $[\alpha]_D^{20} = +1968$ (c 0.025, $CHCl_3$). ^{1}H NMR: δ 0.91 (3H, t, –$(CH_2)_2$–CH(OH)–$(CH_2)_4$–Me, $^3J = 6.9$ Hz); 1.22 (3H, d, >CH–CH(Me)–, $^3J = 7.1$ Hz); 1.25–1.40 (8H, m, –$(CH_2)_2$–CH(OH)–$(CH_2)_4$–Me); 1.61 (1H, m, –$(CH_2)_2$–CH(OH)–$(CH_2)_4$–Me); 1.79 (1H, m, –$(CH_2)_2$–CH(OH)–$(CH_2)_4$–Me); 2.01 (1H, m, γ-H Pro); 2.13 (1H, m, β-H Pro); 2.42 (2H, m, β-, γ-H, Pro); 2.69 (1H, m, –$(CH_2)_2$–CH(OH)–$(CH_2)_4$–Me); 2.94 (2H, m, –$(CH_2)_2$–CH(OH)–$(CH_2)_4$–Me); 3.26 (1H, m, δ-H Pro); 3.41 (1H, d, NCH_2Ar, $^2J = 12.3$ Hz); 3.45 (1H, m, δ-H Pro); 3.48 (1H, dd, α-H Pro, $^3J = 10.5$ Hz, $^3J = 5.8$ Hz); 3.93 (1H, d, >CH–CH(Me)–, $^3J = 4.0$ Hz); 4.06 (1H, d, NCH_2Ar, $^2J = 12.3$ Hz); 4.11 (1H, d, OH, $^3J = 5.5$); 4.69 (1H, ddt, >N–CH_2–CH=CH_2, $^2J = 15.9$ Hz, $^3J = 5.4$ Hz, $^4J = 1.5$ Hz); 4.84 (1H, ddt, >N–CH_2–CH=CH_2, $^2J = 15.9$ Hz, $^3J = 5.4$ Hz, $^4J = 1.5$ Hz); 5.25 (2H, m, >N–CH$_2$–CH=CH_2); 5.32 (1H, qd, >CH–CH(Me)–, $^3J = 7.1$ Hz, $^3J = 4.0$ Hz); 5.93 (1H, m, N–CH$_2$–CH=CH_2); 6.58 (1H, d, Ar, $^3J = 8.3$ Hz); 6.62 (1H, dd, Ar, $^3J = 8.3$ Hz, $^4J = 2.4$ Hz); 7.07 (1H, ddd, Ar, $^3J = 8.8$ Hz, $^3J = 6.1$ Hz, $^4J = 2.4$ Hz); 7.37 (1H, d, Ar, $^3J = 8.2$ Hz); 7.46 (1H, br d, Ar, $^3J = 7.6$ Hz); 7.48–7.67 (4H, m, Ar); 8.18 (1H, d, Ar, $^3J = 8.8$ Hz); 8.23 (1H, dd, Ar, $^3J = 8.2$ Hz, $^4J = 2.1$ Hz); 8.65 (1H, d, Ar, $^4J = 2.1$ Hz).

4.1.11. Complex 8a. Anal. Calcd for $C_{37}H_{39}ClN_6NiO_4S$ (757.95): C, 58.63; H, 5.19; N, 11.09. Found: C, 58.67; H, 5.15; N, 11.13. Mp 89–91 °C. $[\alpha]_D^{20} = +1420$ (c 0.05, $CHCl_3$). ^{1}H NMR: δ 1.21 (3H, d, >CH–CH(Me), $^3J = 7.4$ Hz); 1.84–2.10 (4H, m, –$CH_2CH_2$$CH_2$OH, β-H Pro, γ-H Pro); 2.41 (1H, m, β-H Pro); 2.75 (1H, m, γ-H Pro); 2.76 (2H, t, –$CH_2CH_2CH_2$OH, $^3J = 7.2$ Hz); 2.95 (1H, m, δ-H Pro); 3.40 (1H, m, δ-H Pro); 3.42 (1H, dd, α-H Pro, $^3J = 10.2$ Hz, $^3J = 6.4$ Hz); 3.60 (1H, d, NCH_2Ar, $^2J = 12.7$ Hz); 3.69 (2H, m, –$CH_2CH_2CH_2$OH); 4.15 (1H, d, >CH–CH(Me)–, $^3J = 4.0$ Hz); 4.40 (1H, d, NCH_2Ar, $^2J = 12.7$ Hz), 4.61 (1H, ddt, >N–CH_2–CH=CH_2, $^2J = 15.6$ Hz, $^3J = 5.5$ Hz, $^4J = 1.1$ Hz); 4.97 (1H, ddt, >N–CH_2–CH=CH_2, $^2J = 15.6$ Hz, $^3J = 5.5$ Hz, $^4J = 1.1$ Hz); 5.25 (1H, d, >N–CH$_2$–CH=CH_2, $^3J = 16.8$ Hz); 5.31 (1H, d, >N–CH$_2$–CH=CH_2, $^3J = 10.2$ Hz); 5.57 (1H, qd, >CH–CH(Me)–, $^3J = 7.2$ Hz, $^3J = 4.0$ Hz); 5.94 (1H, ddt, N–CH$_2$–CH=CH_2, $^3J = 16.8$ Hz, $^3J = 10.2$ Hz, $^3J = 5.5$ Hz); 6.64–6.75 (2H, m, Ar); 7.15–7.23 (2H, m, Ar); 7.26–7.32 (2H, m, Ar); 7.52–7.66 (4H, m, Ar); 7.96 (2H, m, Ar); 8.42 (1H, d, Ar, $^3J = 8.6$ Hz).

4.1.12. Complex 8b. Anal. Calcd for $C_{43}H_{51}ClN_6NiO_5S$ (858.11): C, 60.19; H, 5.99; N, 9.79. Found: C, 60.21; H, 6.03; N, 9.83. Mp 75–77 °C. $[\alpha]_D^{20} = +1618$ (c 0.05, $CHCl_3$). ^{1}H NMR: δ 1.1 (6H, d, –CH$_2$–CH$_2$–CH(OH)–CH$_2$–O–CH$_2$–CH$_2$–CH(Me)$_2$, $^3J = 6.6$ Hz); 1.20 (3H, d, >CH–CH(Me), $^3J = 7.1$ Hz); 1.44 (2H, q, –CH$_2$–CH$_2$–CH(OH)–CH$_2$–O–CH$_2$–CH_2–CH(Me)$_2$, $^3J = 6.6$ Hz); 1.63 (1H, m, –CH$_2$–CH_2–CH(OH)–CH$_2$–O–CH$_2$–CH$_2$–CH(Me)$_2$); 1.75 (1H, m, –CH$_2$–CH$_2$–CH(OH)–CH$_2$–O–CH$_2$–CH$_2$–CH(Me)$_2$); 1.87 (1H, m, –CH$_2$–CH_2–CH(OH)–CH$_2$–O–CH$_2$–CH$_2$–CH(Me)$_2$); 2.00 (1H, m, γ-H Pro); 2.10 (1H, m, β-H Pro); 2.36-2.46 (2H, m, β-, γ-H Pro); 2.66–2.95 (2H, m, –CH_2–CH$_2$–CH(OH)–CH$_2$–O–(CH$_2$)$_2$–CH(Me)$_2$); 3.14–3.36 (3H, m, δ-H Pro, –CH$_2$–CH$_2$–CH(OH)–CH_2–O–CH$_2$–CH$_2$–CH(Me)$_2$); 3.41 (1H, m, δ-H Pro); 3.44 (2H, t, –CH$_2$–CH$_2$–CH(OH)–CH$_2$–O–CH_2–CH$_2$–CH(Me)$_2$, $^3J = 6.8$ Hz); 3.45 (1H, d, NCH_2Ar, $^2J = 12.3$ Hz); 3.49 (1H, m, α-H Pro); 3.52–3.71 (1H, m, –CH$_2$–CH$_2$–CH(OH)–CH$_2$–O–CH$_2$–CH$_2$–CH(Me)$_2$); 3.91 (1H, d, >CH–CH(Me)–, $^3J = 3.8$ Hz); 3.94 (1H, dd, α-H Pro, $^3J = 10.5$ Hz, $^3J = 4.0$ Hz); 4.04 (1H, d, NCH_2Ar, $^2J = 12.3$ Hz); 4.25 (1H, d, OH, $^3J = 5.5$ Hz); 4.71 (1H, ddt, >N–CH_2–CH=CH_2, $^2J = 15.9$ Hz, $^3J = 5.4$ Hz, $^4J = 1.5$ Hz); 4.85 (1H, ddt, >N–CH_2–CH=CH_2, $^2J = 15.9$ Hz, $^3J = 5.4$ Hz, $^4J = 1.5$ Hz); 5.26 (2H, m, >N–CH$_2$–CH=CH_2); 5.29 (1H, m, >CH–CH(Me)–); 5.99 (1H, ddt, N–CH$_2$–CH=CH_2, $^3J = 17.3$ Hz, $^3J = 10.0$ Hz, $^3J = 5.5$ Hz); 6.57 (1H, d, Ar, $^3J = 8.3$ Hz); 6.67 (1H, dd, Ar, $^3J = 8.3$ Hz, $^4J = 2.4$ Hz); 7.17 (1H, ddd, Ar, $^3J = 8.8$ Hz, $^3J = 6.2$ Hz, $^4J = 2.4$ Hz); 7.37 (1H, d, Ar, $^3J = 8.2$ Hz); 7.45 (1H, br d, Ar, $^3J = 7.6$ Hz); 7.48–7.66 (4H, m, Ar); 8.15 (1H, d, Ar, $^3J = 8.8$ Hz); 8.23 (1H, dd, Ar, $^3J = 8.2$ Hz, $^4J = 2.2$ Hz); 8.68 (1H, d, Ar, $^4J = 2.2$ Hz).

4.1.13. Complex 8c. Anal. Calcd for $C_{41}H_{39}ClN_6NiO_4S$ (806): C, 61.10; H, 4.88; N, 10.43. Found: C, 61.14; H, 4.90; N, 10.39. Mp 103–105 °C. $[\alpha]_D^{20} = +1836$ (*c* 0.025, $CHCl_3$). ^{1}H NMR: δ 1.34 (3H, d, >CH–CH(*Me*)–, $^3J = 7.2$ Hz); 1.93 (1H, m, β-H Pro); 2.08 (1H, m, γ-H Pro); 2.47 (1H, m, β-H Pro); 2.85 (1H, m, δ-H Pro); 2.98 (1H, m, δ-H Pro); 3.18 (1H, m, γ-H Pro); 3.43 (1H, dd, α-H Pro, $^3J = 10.3$ Hz, $^3J = 6.6$ Hz); 3.85 (1H, d, N*CH*$_2$Ar, $^2J = 12.8$ Hz); 3.86 (3H, s, OMe); 4.03 (1H, d, >*CH*–CH(Me)–, $^3J = 3.7$ Hz); 4.23 (1H, d, N*CH*$_2$Ar, $^2J = 12.8$ Hz); 4.53 (1H, ddt, >N–*CH*$_2$–CH=CH$_2$, $^2J = 15.4$ Hz, $^3J = 6.0$ Hz, $^4J = 1.5$ Hz); 4.76 (1H, ddt, >N–*CH*$_2$–CH=CH$_2$, $^2J = 15.4$ Hz, $^3J = 5.5$ Hz, $^4J = 1.5$ Hz); 4.91 (1H, dq, >N–CH$_2$–CH=*CH*$_2$, $^3J = 17.2$ Hz, $^4J = 1.5$ Hz); 5.06 (1H, dq, >N–CH$_2$–CH=*CH*$_2$, $^3J = 10.3$ Hz, $^4J = 1.5$ Hz); 5.33 (1H, qd, >CH–*CH*(Me)–, $^3J = 7.2$ Hz, $^3J = 3.7$ Hz); 5.76 (1H, dddd, N–CH$_2$–*CH*=CH$_2$, $^3J = 17.2$ Hz, $^3J = 10.3$ Hz, $^3J = 6.0$ Hz, $^3J = 5.5$ Hz); 6.59–6.67 (2H, m, Ar); 7.01–7.17 (4H, m, Ar); 7.26 (1H, dd, Ar, $^3J = 7.6$ Hz, $^4J = 1.8$ Hz); 7.28–7.38 (3H, m, Ar); 7.43 (1H, d, Ar, $^3J = 7.6$ Hz); 7.50–7.67 (4H, m, Ar); 8.22–8.27 (2H, m, Ar).

4.1.14. Complex 8d. Anal. Calcd for $C_{40}H_{36}CI_2N_6NiO_3S$ (810.42): C, 59.28; H, 4.48; N, 10.37. Found: C, 59.32; H, 4.50; N, 10.41. Mp 150–151 °C. $[\alpha]_D^{20} = +1660$ (*c* 0.025, $CHCl_3$). ^{1}H NMR: δ 1.24 (3H, d, >CH–CH(*Me*)–, $^3J = 7.2$ Hz); 1.97–2.17 (2H, m, β-, γ-H Pro); 2.49 (1H, m, γ-H Pro); 2.83 (1H, m, β-H Pro); 2.91 (1H, m, δ-H Pro); 3.09–3.27 (1H, m, δ-H Pro); 3.46 (1H, dd, α-H Pro, $^3J = 10.5$ Hz, $^3J = 6.7$ Hz); 3.86 (1H, d, N*CH*$_2$Ar, $^2J = 12.8$ Hz); 4.01 (1H, d, >*CH*–CH(Me)–, $^3J = 4.5$ Hz); 4.26 (1H, d, N*CH*$_2$Ar, $^2J = 12.8$ Hz); 4.58 (1H, ddt, >N–*CH*$_2$–CH=CH$_2$, $^2J = 15.8$ Hz, $^3J = 5.7$ Hz, $^4J = 1.5$ Hz); 4.68 (1H, ddt, >N–*CH*$_2$–CH=CH$_2$, $^2J = 15.8$ Hz, $^3J = 5.7$ Hz, $^4J = 1.5$ Hz); 4.91 (1H, dq, >N–CH$_2$–CH=*CH*$_2$, $^3J = 17.2$ Hz, $^4J = 1.5$ Hz); 5.07 (1H, dq, >N–CH$_2$–CH=*CH*$_2$, $^3J = 10.3$ Hz, $^4J = 1.5$ Hz); 5.55 (1H, qd, >CH–*CH*(Me)–, $^3J = 7.2$ Hz, $^3J = 4.5$ Hz); 5.76 (1H, ddt, N–CH$_2$–*CH*=CH$_2$, $^3J = 17.2$ Hz, $^3J = 10.3$ Hz, $^3J = 5.7$ Hz); 6.59–6.68 (2H, m, Ar); 7.07 (1H, ddd, Ar, $^3J = 8.7$ Hz, $^3J = 6.2$ Hz, $^4J = 2.4$ Hz); 7.15 (1H, ddd, Ar, $^3J = 8.7$ Hz, $^3J = 7.0$ Hz, $^4J = 1.7$ Hz); 7.28–7.36 (3H, m, Ar); 7.44–7.67 (8H, m, Ar); 8.21 (1H, d, Ar, $^3J = 8.7$ Hz); 8.27 (1H, d, Ar, $^3J = 7.7$ Hz).

4.1.15. Complex 8e. Anal. Calcd for $C_{42}H_{49}ClN_6NiO_4S$ (828.09): C, 60.92; H, 5.96; N, 10.15. Found: C, 60.98; H, 5.94; N, 10.19. Mp 80–82 °C. $[\alpha]_D^{20} = +1894$ (*c* 0.025, $CHCl_3$). ^{1}H NMR: δ 0.91 (3H, t, –(CH$_2$)$_2$–CH(OH)–(CH$_2$)$_4$–*Me*, $^3J = 6.8$ Hz); 1.19 (3H, d, >CH–CH(*Me*)–, $^3J = 7.1$ Hz); 1.22–1.44 (8H, m, –(CH$_2$)$_2$–CH(OH)–(CH$_2$)$_4$–CH$_3$); 1.62 (1H, m, –(CH$_2$)$_2$–CH(OH)–(CH$_2$)$_4$–CH$_3$); 1.78 (1H, m, –(CH$_2$)$_2$–CH(OH)–(CH$_2$)$_4$–CH$_3$); 1.94–2.15 (2H, m, β-, γ-H Pro); 2.46 (2H, m, β-, γ-H Pro); 2.61–2.93 (3H, m, –(CH$_2$)$_2$–CH(OH)–(CH$_2$)$_4$–CH$_3$); 3.11 (1H, m, δ-H Pro); 3.35–3.56 (2H, m, δ-, α-H Pro); 3.83 (d, 1H, N*CH*$_2$Ar, $^2J = 12.7$ Hz); 3.88 (1H, d, >*CH*–CH(Me)–, $^3J = 3.8$ Hz); 4.21 (1H, d, N*CH*$_2$Ar, $^2J = 12.7$ Hz); 4.69 (1H, dd, >N–*CH*$_2$–CH=CH$_2$, $^2J = 15.8$ Hz, $^3J = 5.3$ Hz); 4.87 (1H, dd, >N–*CH*$_2$–CH=CH$_2$, $^2J = 15.8$ Hz, $^3J = 5.3$ Hz); 5.23 (1H, qd, >CH–*CH*(Me)–, $^3J = 7.1$ Hz, $^3J = 3.8$ Hz); 5.26 (2H, m, >N–CH$_2$–CH=*CH*$_2$); 5.93 (1H, ddt, N–CH$_2$–*CH*=CH$_2$, $^3J = 17.3$ Hz, $^3J = 10.0$ Hz, $^3J = 5.3$ Hz); 6.57–6.66 (2H, m, Ar); 7.05 (1H, ddd, Ar, $^3J = 8.6$ Hz, $^3J = 6.1$ Hz, $^4J = 2.4$ Hz); 7.15 (1H, m, Ar); 7.28 (1H, m, Ar); 7.31 (1H, m, Ar); 7.41 (1H, d, Ar, $^3J = 7.3$ Hz); 7.53–7.59 (3H, m, Ar); 7.63 (1H, m, Ar); 8.14–8.30 (2H, m, Ar).

4.1.16. Complex 9a. Anal. Calcd for $C_{39}H_{44}N_6NiO_4S$ (751.56): C, 62.33; H, 5.90; N, 11.18. Found: C, 62.30; H, 5.85; N, 11.23. Mp 115–117 °C. $[\alpha]_D^{20} = +1766$ (*c* 0.05, $CHCl_3$). ^{1}H NMR: δ 1.20 (3H, d, >CH–CH(*Me*)–, $^3J = 7.1$ Hz); 1.86 (2H, m, –CH$_2$*CH*$_2$CH$_2$OH); 1.97 (1H, m, β-H Pro); 1.98 (3H, s, Me); 2.08 (1H, m, γ-H Pro); 2.09 (3H, s, Me); 2.32–2.45 (2H, m, β-, γ-H Pro); 2.68–2.89 (3H, m, δ-H Pro, –*CH*$_2$CH$_2$CH$_2$OH); 3.23 (1H, m, δ-H Pro); 3.34 (1H, m, α-H Pro); 3.51 (2H, m, –CH$_2$CH$_2$*CH*$_2$OH); 3.84 (d, 1H, N*CH*$_2$Ar, $^2J = 12.2$ Hz); 3.93 (1H, d, >*CH*–CH(Me)–, $^3J = 3.9$ Hz); 4.12 (1H, d, N*CH*$_2$Ar, $^2J = 12.2$ Hz); 4.18 (1H, t, OH, $^3J = 5.3$ Hz); 4.68 (1H, dd, >N–*CH*$_2$–CH=CH$_2$, $^2J = 15.8$ Hz, $^3J = 5.5$ Hz); 4.87 (1H, dd, >N–*CH*$_2$–CH=CH$_2$, $^2J = 15.8$ Hz, $^3J = 5.5$ Hz); 5.22–5.30 (3H, m, >CH–*CH*(Me)–, >N–CH$_2$–CH=*CH*$_2$); 5.93 (1H, ddt, N–CH$_2$–*CH*=CH$_2$, $^3J = 17.3$ Hz, $^3J = 10.0$ Hz, $^3J = 5.5$ Hz); 6.54 (1H, m, Ar); 6.60 (1H, m, Ar); 6.99 (1H, d, Ar, $^3J = 7.7$ Hz); 7.02 (1H, m, Ar); 7.41 (1H, dd, Ar, $^3J = 7.7$ Hz, $^4J = 2.1$ Hz); 7.50–7.66 (5H, m, Ar); 8.15 (1H, d, Ar, $^3J = 8.8$ Hz); 8.38 (1H, d, Ar, $^4J = 2.1$ Hz).

4.1.17. Complex 9b. Anal. Calcd for $C_{42}H_{56}N_6NiO_5S$ (851.72): C, 63.46; H, 6.63; N, 9.87. Found: C, 63.41; H, 6.69; N, 9.91. Mp 150–152 °C. $[\alpha]_D^{20} = +1789.4$ (*c* 0.05, $CHCl_3$). ^{1}H NMR: δ 0.91 (6H, d, –CH$_2$–CH$_2$–CH(OH)–CH$_2$–O–CH$_2$–CH$_2$–CH(*Me*)$_2$, $^3J = 6.6$ Hz); 1.22 (3H, d, >CH–CH(*Me*), $^3J = 7.1$ Hz); 1.43 (2H, q, –CH$_2$–CH$_2$–CH(OH)–CH$_2$–O–CH$_2$–*CH*$_2$–CH(Me)$_2$, $^3J = 6.6$ Hz); 1.65 (1H, m, –CH$_2$–*CH*$_2$–CH(OH)–CH$_2$–O–CH$_2$–CH$_2$–CH(Me)$_2$); 1.70 (1H, m, –CH$_2$–CH$_2$–CH(OH)–CH$_2$–O–CH$_2$–CH$_2$–*CH*(Me)$_2$); 1.88 (1H, m, –CH$_2$–*CH*$_2$–CH(OH)–CH$_2$–O–CH$_2$–CH$_2$–CH(Me)$_2$); 1.98 (3H, s, Me); 1.99 (1H, m, β-H Pro); 2.01 (3H, s, Me); 2.39 (2H, m, β-, γ-H Pro); 2.41 (1H, m, γ-H Pro); 2.67–2.91 (2H, m, –*CH*$_2$–CH$_2$–CH(OH)–CH$_2$–O–CH$_2$–CH$_2$–CH(Me)$_2$); 3.19–3.36 (4H, m, δ-H Pro, –CH$_2$–CH$_2$–CH(OH)–*CH*$_2$–O–CH$_2$–CH$_2$–CH(Me)$_2$); 3.31 (1H, d, N*CH*$_2$Ar, $^2J = 12.2$ Hz); 3.43 (2H, t, –CH$_2$–CH$_2$–CH(OH)–CH$_2$–O–*CH*$_2$–CH$_2$–CH(Me)$_2$, $^3J = 6.6$ Hz); 3.45 (1H, m, δ-H Pro); 3.55–3.71 (2H, m, α-H Pro, –CH$_2$–CH$_2$–*CH*(OH)–CH$_2$–O–CH$_2$–CH$_2$–CH(Me)$_2$); 3.93 (1H, d, >*CH*–CH(Me)–, $^3J = 4.0$ Hz); 4.12 (1H, d, N*CH*$_2$Ar, $^2J = 12.2$ Hz); 4.68 (1H, ddt, >N–*CH*$_2$–CH=CH$_2$, $^2J = 15.9$ Hz, $^3J = 5.7$ Hz, $^4J = 1.5$ Hz); 4.84 (1H, ddt, >N–*CH*$_2$–CH=CH$_2$, $^2J = 15.9$ Hz, $^3J = 5.7$ Hz, $^4J = 1.5$ Hz); 5.26 (2H, m, >N–CH$_2$–CH=*CH*$_2$); 5.31 (1H, qd, >CH–*CH*(Me)–, $^3J = 7.1$ Hz, $^3J = 4.0$ Hz); 5.93 (1H, ddt, N–CH$_2$–*CH*=CH$_2$, $^3J = 17.3$ Hz, $^3J = 10.1$ Hz, $^3J = 5.7$ Hz); 6.52–6.62 (2H, m, Ar); 6.98–7.05 (2H, m, Ar); 7.41 (1H, d, Ar, $^3J = 7.7$ Hz); 7.51–7.66 (5H, m, Ar); 8.15 (1H, d, Ar, $^3J = 8.6$ Hz); 8.37 (1H, d, Ar, $^4J = 1.8$ Hz).

4.1.18. Complex 9c. Anal. Calcd for $C_{43}H_{44}N_6NiO_4S$ (799.61): C, 64.59; H, 5.55; N, 10.51. Found: C, 64.63; H,

5.51; N, 10.55. Mp 132–134 °C. $[\alpha]_D^{20} = +1432$ (*c* 0.05, $CHCl_3$). ^1H NMR: δ 1.28 (3H, d, >CH–CH(*Me*)–, $^3J = 7.2$ Hz); 1.96 (1H, m, β-H Pro); 1.98 (s, 3H, Me); 2.08 (s, 3H, Me); 2.18 (1H, m, γ-H Pro); 2.40 (1H, m, β-H Pro); 2.83 (1H, m, δ-H Pro); 2.98 (1H, m, δ-H Pro); 3.18 (1H, m, γ-H Pro); 3.40 (1H, dd, α-H Pro, $^3J = 10.3$ Hz, $^3J = 6.7$ Hz); 3.82 (1H, d, N*CH*$_2$Ar, $^2J = 12.8$ Hz); 3.85 (3H, s, OMe); 4.05 (1H, d, >*CH*–CH(Me)–, $^3J = 3.7$ Hz); 4.20 (1H, d, N*CH*$_2$Ar, $^2J = 12.8$ Hz); 4.53 (1H, ddt, >N–*CH*$_2$–CH=CH$_2$, $^2J = 15.4$ Hz, $^3J = 6.0$ Hz, $^4J = 1.5$ Hz); 4.75 (1H, ddt, >N–*CH*$_2$–CH=CH$_2$, $^2J = 15.4$ Hz, $^3J = 5.5$ Hz, $^4J = 1.5$ Hz); 4.93 (1H, dq, >N–CH$_2$–CH=*CH*$_2$, $^3J = 17.2$ Hz, $^4J = 1.5$ Hz); 5.06 (1H, dq, >N–CH$_2$–CH=*CH*$_2$, $^3J = 10.3$ Hz, $^4J = 1.5$ Hz); 5.36 (1H, qd, >CH–*CH*(Me)–, $^3J = 7.2$ Hz, $^3J = 3.7$ Hz); 5.74 (1H, dddd, N–CH$_2$–*CH*=CH$_2$, $^3J = 17.2$ Hz, $^3J = 10.3$ Hz, $^3J = 6.0$ Hz, $^3J = 5.5$ Hz); 6.61–6.67 (2H, m, Ar); 7.01–7.18 (4H, m, Ar); 7.24 (1H, dd, Ar, $^3J = 7.6$ Hz, $^4J = 1.8$ Hz); 7.28–7.38 (3H, m, Ar); 7.42 (1H, d, Ar, $^3J = 7.6$ Hz); 7.49–7.66 (3H, m, Ar); 8.20–8.25 (2H, m, Ar).

4.1.19. Complex 9d. Anal. Calcd for $C_{42}H_{41}ClN_6NiO_3S$ (804.02): C, 62.74; H, 5.14; N, 10.45. Found: C, 62.78; H, 5.16; N, 10.50. Mp 102–104 °C. $[\alpha]_D^{20} = +1708$ (*c* 0.025, $CHCl_3$). ^1H NMR: δ 1.29 (3H, d, >CH–CH(*Me*)–, $^3J = 7.0$ Hz); 1.96 (s, 3H, Me); 2.07 (s, 3H, Me); 2.09 (1H, m, γ-H Pro); 2.16 (1H, m, β-H Pro); 2.44 (1H, m, β-H Pro); 2.65 (1H, m, γ-H Pro); 3.23 (1H, m, δ-H Pro); 3.41 (1H, m, δ-H Pro); 3.43 (1H, d, N*CH*$_2$Ar, $^2J = 12.3$ Hz); 3.55 (1H, dd, α-H Pro, $^3J = 10.5$ Hz, $^3J = 5.8$ Hz); 4.07 (1H, d, >*CH*–CH(Me)–, $^3J = 5.2$ Hz); 4.11 (1H, d, N*CH*$_2$Ar, $^2J = 12.3$ Hz); 4.62 (1H, dd, >N–*CH*$_2$–CH=CH$_2$, $^2J = 15.8$ Hz, $^3J = 5.7$ Hz); 4.65 (1H, dd, >N–*CH*$_2$–CH=CH$_2$, $^2J = 15.8$ Hz, $^3J = 5.7$ Hz); 4.88 (1H, d, >N–CH$_2$–CH=*CH*$_2$, $^3J = 17.3$ Hz, $^3J = 10.4$ Hz); 5.07 (1H, d, >N–CH$_2$–CH=*CH*$_2$, $^3J = 17.3$ Hz, $^3J = 10.4$ Hz); 5.68 (1H, m, >CH–*CH*(Me)–); 5.76 (1H, ddt, N–CH$_2$–*CH*=CH$_2$, $^3J = 17.3$ Hz, $^3J = 10.4$ Hz, $^3J = 5.7$ Hz); 6.57 (1H, d, Ar, $^3J = 8.2$ Hz); 6.64 (1H, dd, Ar, $^3J = 8.2$ Hz, $^4J = 2.2$ Hz); 7.09 (1H, ddd, Ar, $^3J = 8.7$ Hz, $^3J = 6.0$ Hz, $^4J = 2.5$ Hz); 7.24 (1H, br d, Ar, $^3J = 7.0$ Hz); 7.35 (1H, d, Ar, $^3J = 8.1$ Hz); 7.46–7.67 (8H, m, Ar); 8.19 (1H, d, Ar, $^3J = 8.7$ Hz); 8.25 (1H, dd, Ar, $^3J = 8.1$ Hz, $^4J = 2.1$ Hz); 8.58 (1H, d, Ar, $^4J = 2.1$ Hz).

4.1.20. Complex 9e. Anal. Calcd for $C_{44}H_{54}N_6NiO_4S$ (821.7): C, 64.31; H, 6.62; N, 10.23. Found: C, 64.28; H, 6.57; N, 10.28. Mp 115–117 °C. $[\alpha]_D^{20} = +2144$ (*c* 0.025, $CHCl_3$). ^1H NMR: δ 0.93 (3H, t, –(CH$_2$)$_2$–CH(OH)–(CH$_2$)$_4$–*Me*, $^3J = 6.7$ Hz); 1.17 (3H, d, >CH–CH(*Me*)–, $^3J = 7.1$ Hz); 1.21–1.45 (8H, m, –(CH$_2$)$_2$–CH(OH)–(CH$_2$)$_4$–CH$_3$); 1.63 (1H, m, –(CH$_2$)$_2$–CH(OH)–(CH$_2$)$_4$–CH$_3$); 1.78 (1H, m, –(CH$_2$)$_2$–CH(OH)–(CH$_2$)$_4$–CH$_3$); 1.94 (3H, s, Me); 1.95–2.14 (2H, m, β-, γ-H Pro); 2.07 (3H, s, Me); 2.45 (2H, m, β-, γ-H Pro); 2.63–2.98 (3H, m, –(CH$_2$)$_2$–CH(OH)–(CH$_2$)$_4$–CH$_3$); 3.15 (1H, m, δ-H Pro); 3.33–3.54 (2H, m, δ-, α-H Pro); 3.86 (d, 1H, N*CH*$_2$Ar, $^2J = 12.6$Hz); 3.86 (1H, d, >*CH*–CH(Me)–, $^3J = 3.8$ Hz); 4.23 (1H, d, N*CH*$_2$Ar, $^2J = 12.6$ Hz); 4.71 (1H, dd, >N–*CH*$_2$–CH=CH$_2$, $^2J = 15.8$ Hz, $^3J = 5.3$ Hz); 4.87 (1H, dd, >N–*CH*$_2$–CH=CH$_2$, $^2J = 15.8$ Hz, $^3J = 5.3$ Hz); 5.22 (1H, qd, >CH–*CH*(Me)–, $^3J = 7.1$ Hz, $^3J = 3.8$ Hz); 5.25 (2H, m, >N–CH$_2$–CH=*CH*$_2$); 5.92 (1H, ddt, N–CH$_2$–*CH*=CH$_2$, $^3J = 17.3$ Hz, $^3J = 10.0$ Hz, $^3J = 5.3$ Hz); 6.54–6.65 (2H, m, Ar); 7.06 (1H, ddd, $^3J = 8.6$ Hz, $^3J = 6.1$ Hz, $^4J = 2.4$ Hz); 7.14 (1H, m, Ar); 7.25 (1H, m, Ar); 7.31 (1H, m, Ar); 7.43 (1H, d, Ar, $^3J = 7.3$ Hz); 7.53–7.59 (3H, m, Ar); 7.61 (1H, m, Ar); 8.11–8.28 (2H, m, Ar).

4.1.21. The isolation of amino acids 10a–e. The isolation of amino acids **10a–e** was carried out in accordance with the previously described procedures.[5–11] The mixture of the diastereomeric complexes 8a–e was dissolved in 50 mL of CH_3OH and the solution was added slowly to 50 mL of aq 2 M HCl while being stirred. After disappearence of the red color of the solution, it was evaporated to dryness and 50 mL of water was added to it with the initial chiral auxiliary filtered. The water solution was extracted with $CHCl_3$ (2 × 20 mL) in order to secure complete recovery of the auxiliary. The final amino acids were isolated from the filtrates by ion-exchange techniques.[5–11] The amino acids were recrystallized from a water/EtOH mixture.

4.1.22. (2*S*,3*S*)-3-(4′-Allyl-3′-hydroxypropyl-5′-thioxo-1,2,4-triazol-1′-yl)-2-aminobutyric acid 10a. Yield: 0.68 g (2.28 mmol), 60%. Anal. Calcd for $C_{12}H_{20}N_4O_3S$ (300.38): C, 47.98; H, 6.71; N, 18.65. Found: C, 47.94; H, 6.76; N, 18.69. Mp 141–142 °C. $[\alpha]_D^{20} = -30$ (*c* 0.1, 6 M HCl). Diastereomeric excess by ^1H NMR analysis >99%. ^1H NMR (D_2O): δ 1.33 (3H, d, β-CH$_3$, $^3J = 7.2$ Hz); 1.81 (2H, q, –CH$_2$*CH*$_2$CH$_2$OH, $^3J = 7.0$ Hz); 2.66 (2H, dd, –*CH*$_2$CH$_2$CH$_2$OH, $^3J = 8.4$ Hz, $^3J = 6.6$ Hz); 3.47 (2H, t, –CH$_2$CH$_2$*CH*$_2$OH, $^3J = 6.0$ Hz); 3.70 (1H, d, α-H, $^3J = 3.9$ Hz); 4.66 (2H, d, >N–*CH*$_2$–CH=CH$_2$, $^3J = 5.1$); 5.09 (1H, d, >N–CH$_2$–CH=*CH*$_2$, $^3J = 17.1$ Hz); 5.21 (1H, d, >N–CH$_2$–CH=*CH*$_2$, $^3J = 10.5$ Hz); 5.40 (1H, dq, β-H, $^3J = 7.2$ Hz, $^3J = 7.0$ Hz); 5.88 (1H, ddt, >N–CH$_2$–*CH*=CH$_2$, $^3J = 17.1$ Hz, $^3J = 10.5$ Hz, $^3J = 5.1$ Hz).

4.1.23. (2*S*,3*S*)-3-(4′-Allyl-3′-hydroxyisoamyloxybutyl-5′-thioxo-1,2,4-triazol-1′-yl)-2-aminobutyric acid 10b. Yield: 0.7 g (1.76 mmol), 45%. Anal. Calcd for $C_{18}H_{32}N_4O_4S$ (400.54): C, 53.98; H, 8.05; N, 13.99. Found: C, 53.94; H, 8.10; N, 14.04. Mp 164–166 °C. $[\alpha]_D^{20} = -2.25$ (*c* 0.04, 4.9 M HCl). Diastereomeric excess by ^1H NMR analysis >99%. ^1H NMR (D_2O): δ 0.97 (6H, d, –CH$_2$–CH$_2$–CH(OH)–CH$_2$–O–CH$_2$–CH$_2$–CH(*Me*)$_2$, $^3J = 6.6$ Hz); 1.56 (1H, m, CH$_2$–CH$_2$–CH(OH)–CH$_2$–O–CH$_2$–CH$_2$–CH(Me)$_2$); 1.60 (3H, d, β-CH$_3$, $^3J = 7.1$); 1.73 (1H, m, CH$_2$–CH$_2$–CH(OH)–CH$_2$–O–CH$_2$–CH$_2$–CH(Me)$_2$); 1.93 (2H, m, CH$_2$–*CH*$_2$–CH(OH)–CH$_2$–O–CH$_2$–CH$_2$–CH(Me)$_2$); 2.06 (1H, m, CH$_2$–CH$_2$–CH(OH)–CH$_2$–O–CH$_2$–CH$_2$–CH(Me)$_2$); 2.85–3.04 (2H, m, CH$_2$–CH$_2$–CH(OH)–CH$_2$–O–CH$_2$–CH$_2$–CH(Me)$_2$); 3.50–3.69 (4H, m, CH$_2$–CH$_2$–CH(OH)–CH$_2$–O–CH$_2$–CH$_2$–CH(Me)$_2$); 3.97 (1H, m, CH$_2$–CH$_2$–CH(OH)–CH$_2$–O–CH$_2$–CH$_2$–CH(Me)$_2$); 4.23 (1H, d, α-H, $^3J = 3.7$ Hz); 4.52 (2H, d, >N–*CH*$_2$–CH=CH$_2$, $^3J = 4.9$ Hz); 5.11 (1H, dt, >N–CH$_2$–CH=*CH*$_2$, $^3J = 17.4$ Hz, $^4J_2 = 1.8$ Hz); 5.37 (1H, dt, >N–CH$_2$–CH=*CH*$_2$, $^3J = 10.6$ Hz, $^4J = 1.8$ Hz); 5.66 (1H, qd, β-H, $^3J = 7.1$, $^3J = 3.7$ Hz); 6.03 (1H, ddt, >N–CH$_2$–*CH*=CH$_2$, $^3J = 17.4$ Hz, $^3J = 10.6$ Hz, $^3J = 4.9$ Hz).

4.1.24. (2*S*,3*S*)-3-(4′-Allyl-3′-*o*-methoxyphenyl-5′-thioxo-1,2,4-triazol-1′-yl)-2-aminobutyric acid 10c. Yield: 1.14 g (3.3 mmol), 75%. Anal. Calcd for $C_{16}H_{20}N_4O_3S$ (348.42): C, 55.16; H, 5.79; N, 16.08. Found: C, 55.20; H 5.83; N 16.12. Mp 144–146 °C. $[\alpha]_D^{20} = -33.3$ (*c* 0.1, 4.9 M HCl). Diastereomeric excess by ^{1}H NMR analysis >99%. ^{1}H NMR (DMSI): δ 1.52 (3H, d, β-CH_3, $^3J = 7.0$ Hz); 3.82 (3H, s, OMe–); 4.38 (1H, d, α-H, $^3J = 7.1$ Hz); 4.43 (1H, ddt, >N–*CH_2*–CH=CH_2, $^2J = 16.3$ Hz, $^3J = 5.6$ Hz, $^4J = 1.7$ Hz); 4.57 (1H, ddt, >N–*CH_2*–CH=CH_2, $^2J = 16.3$ Hz, $^3J = 5.6$ Hz, $^4J = 1.7$ Hz); 4.85 (1H, dq, >N–CH_2–CH=*CH_2*, $^3J = 17.1$ Hz, $^4J = 1.4$ Hz); 5.01 (1H, dq, >N–CH_2–CH=*CH_2*, $^3J = 10.4$ Hz, $^4J = 1.4$ Hz); 5.44 (1H, dq, β-H, $^3J = 7.1$ Hz, $^3J = 7.0$ Hz); 5.66 (1H, ddt, >N–CH_2–*CH*=CH_2, $^3J = 17.1$ Hz, $^3J = 10.4$ Hz, $^3J = 5.3$ Hz); 7.10 (1H, br t, Ar, $^3J = 7.5$ Hz); 7.21 (1H, br d, Ar, $^3J = 8.3$ Hz); 7.42 (1H, dd, Ar, $^3J = 7.5$ Hz, $^4J = 1.8$ Hz); 7.60 (1H, ddd, Ar, $^3J = 8.3$ Hz, $^3J = 7.5$ Hz, $^4J = 1.8$ Hz).

4.1.25. (2*S*,3*S*)-3-(4′-Allyl-3′-*o*-chlorophenyl-5′-thioxo-1,2,4-triazol-1′-yl)-2-aminobutyric acid 10d. Yield: 0.52 g (1.48 mmol), 33%. Anal. Calcd for $C_{15}H_{17}N_4ClO_2S$ (352.84): C, 51.06; H, 4.86; N, 15.88. Found: C, 51.11; H, 4.89; N, 15.84. Mp 158–161 °C. $[\alpha]_D^{20} = -25.6$ (*c* 0.1, 4.9 M HCl). Diastereomeric excess by ^{1}H NMR analysis >99%. ^{1}H NMR (D_2O): δ 1.68 (3H, d, β-CH_3, $^3J = 7.1$ Hz); 4.34 (1H, d, α-H, $^3J = 4.0$ Hz); 4.71 (2H, dt, >N–*CH_2*–CH=CH_2, $^3J = 5.2$ Hz, $^4J = 1.7$ Hz); 4.98 (1H, dt, >N–CH_2–CH=*CH_2*, $^3J = 17.3$ Hz, $^4J = 1.7$ Hz); 5.21 (1H, dt, >N–CH_2–CH=*CH_2*, $^3J = 10.5$ Hz, $^4J = 1.7$ Hz); 5.77 (1H, qd, β-H, $^3J = 7.1$ Hz, $^3J = 4.0$ Hz); 5.83 (1H, ddt, >N–CH_2–*CH*=CH_2, $^3J = 17.3$ Hz, $^3J = 10.5$ Hz, $^3J = 5.2$ Hz); 7.58–7.69 (2H, m, Ar); 7.71–7.78 (2H, m, Ar).

4.1.26. (2*S*,3*S*)-3-(4′-Allyl-3′-hydroxyoctyl-5′-thioxo-1,2,4-triazol-1′-yl)-2-aminobutyric acid 10e. Yield: 0.41 g (1.113 mmol), 28%. Anal. Calcd for $C_{17}H_{30}N_4O_3S$ (370.51): C, 55.11; H, 8.16; N, 15.12. Found: C, 55.15; H, 8.20; N, 15.15. Mp 180–182 °C. $[\alpha]_D^{20} = -5.0$ (*c* 0.1, 4.9 M HCl). Diastereomeric excess by ^{1}H NMR analysis >98%. ^{1}H NMR (D_2O): δ 0.67 (3H, t, –$(CH_2)_2$–CH(OH)–$(CH_2)_4$–*Me*, $^3J = 6.6$ Hz); 1.03–1.33 (8H, m, –$(CH_2)_2$–CH(OH)–$(CH_2)_4$–Me); 1.44 (d, 3H, β-CH_3, $^3J = 7.0$ Hz); 1.63 (1H, m, –$(CH_2)_2$–CH(OH)–$(CH_2)_4$–Me); 1.74 (1H, m, –$(CH_2)_2$–CH(OH)–$(CH_2)_4$–Me); 2.54–2.71 (2H, m, –$(CH_2)_2$–CH(OH)–$(CH_2)_4$–Me); 3.51 (1H, br, –$(CH_2)_2$–CH(OH)–$(CH_2)_4$–Me); 4.33 (1H, d, α-H, $^3J = 5.2$ Hz); 4.52 (2H, d, >N–*CH_2*–CH=CH_2, $^3J = 5.0$ Hz); 4.82 (1H, d, >N–CH_2–CH=*CH_2*, $^3J = 17.2$ Hz); 5.09 (1H, d, >N–CH_2–CH=*CH_2*, $^3J = 10.6$ Hz); 5.42 (1H, dq, β-H, $^3J = 7.2$ Hz, $^3J = 7.0$ Hz) 5.74 (ddt, 1H, >N–CH_2–*CH*=CH_2, $^3J = 17.2$ Hz, $^3J = 10.6$ Hz, $^3J = 5.0$ Hz).

4.2. X-ray diffraction study of amino acid 10c

Crystal of **10c** ($C_{16}H_{23}N_4O_4SCl$, $M = 402.89$) was orthorhombic, space group $P2_12_12_1$; at $T = 120$ K: $a = 13.944(3)$, $b = 16.411(3)$, $c = 17.219(3)$ Å, $V = 3940.2(13)$ Å^3, $Z = 8$, $d_c = 1.358$ g/cm^3, $F(000) = 1696$, $\mu = 0.328$ mm^{-1}. Data were collected on a Bruker SMART 1000 CCD diffractometer (λ(Mo K$_\alpha$)-radiation, graphite monochromator, ω and φ scan mode, $\theta_{max} = 26°$) and corrected for Lorentz and polarization effects. The structure was determined by direct methods and by full-matrix least squares refinement with anisotropic thermal parameters for non-hydrogen atoms. The crystal contains two solvate water molecules. The absolute structure of compound **10c** was objectively determined by the refinement of Flack parameter, which has become equal to 0.00(13). The hydrogen atoms of the –OH and –NH_3 groups as well as the solvate water molecules were localized in the difference Fourier map and included in the refinement with fixed position and thermal parameters. The other hydrogen atoms were placed in calculated positions and refined in a riding model with fixed thermal parameters ($U_{iso}(H) = 1.5U_{eq}(C)$ for the CH_3-groups and $U_{iso}(H) = 1.2U_{eq}(C)$ for the other groups). The final *R*-factors are $R_1 = 0.0962$ for 4685 independent reflections with $I > 2\sigma(I)$ and $wR_2 = 0.1919$ for all 7597 independent reflections. All calculations were carried out by use of the SHELXTL (PC Version 5.10) program package.[14] Crystallographic data for **10c** have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 612972. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk). Empirical formula $C_{16}H_{23}ClN_4O_4S$; fw 402.89; *T* (K) 120(2); Crystal size (mm) 0.24 × 0.21 × 0.18; Crystal system Orthorhombic; Space group $P2_12_12_1$; *a* (Å) 13.944(3); *b* (Å) 16.411(3); *c* (Å) 17.219(3); *V* (Å^3) 3940.2(13); *Z* 8; d_c (g cm^{-3}) 1.358; *F*(000) 1696; μ (mm^{-1}) 0.328; $2\theta_{max}$ (deg) 52; Index range $-17 \leqslant h \leqslant 17$, $-20 \leqslant k \leqslant 20$, $-21 \leqslant l \leqslant 21$; No. of rflns collected 34,122; No. of unique rflns 7643; No. of rflns with $I > 2\sigma(I)$; 4731; Data/restraints/parameters 7643/0/469; *R*1; *wR*2 ($I > 2\sigma(I)$) 0.0953; 0.1875; *R*1; *wR*2 (all data) 0.1401; 0.2027; GOF on F^2 1.003; Absolute structure parameter 0.00(13); T_{min}; T_{max} 0.925; 0.943.

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