Tetrahedron 65 (2009) 6189–6195

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Fluorine-containing 1,10-phenanthrolines synthesis: an original and efficient approach by the pyridine-ring formation reaction of *N*-propargyl-5,7-bis-(trifluoroacetyl)-8-quinolylamine with various nucleophiles

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ARTICLE INFO

Article history:
Received 27 February 2009
Received in revised form 18 May 2009
Accepted 18 May 2009
Available online 23 May 2009

Keywords:
1,10-Phenanthrolines
Fluorine
Pyridine-ring formation
Propargylamines
8-Quinolylamines

ABSTRACT

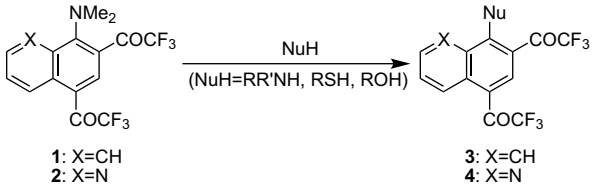
Novel fluorine-containing 1,10-phenanthrolines having a variety of substituents at the 3-position were easily synthesized in moderate yields by the pyridine-ring formation reaction of *N*-propargyl-5,7-bis-(trifluoroacetyl)-8-quinolylamine with various amines, thiols, and phenols. Unexpectedly, the reactive intermediates 1,4-dihydro-1,10-phenanthrolin-4-ols were isolated for the first time in the reactions with dialkylamines.

1. Introduction

In recent years considerable attention has been paid to the development of new methodologies for the synthesis of many kinds of fluorine-containing heterocycles, since these compounds are now widely recognized as important organic materials showing interesting biological activities for their potential use in medicinal and agricultural scientific fields.[1]

1,10-Phenanthroline and the related derivatives[2] have attracted much attention for their biological properties such as antibacterial,[3a,c] antifungal,[3a] and antitumor[3b,d] activities. They are also valuable classes of heterocyclic compounds because of being applicable as chelating ligands forming stable complexes with transition metals.[4] In particular, some of these complexes have been used as useful novel catalysts in phase-transfer[5] and asymmetric[6] reactions, and they are also potential DNA binding agents,[7] which can be expected to be developed as novel probes of nucleic acid structure and function.

We have previously reported that *N*,*N*-dimethyl-2,4-bis(trifluoroacetyl)-1-naphthylamine **1**[8] and *N*,*N*-dimethyl-5,7-bis(trifluoroacetyl)-8-quinolylamine **2**[9] react easily with various amines, thiols and alcohols under mild conditions to afford the corresponding N–N, N–S and N–O exchanged products **3** and **4** in excellent yields (Scheme 1). Moreover we succeeded in applying this type of aromatic nucleophilic substitution to the simple syntheses of various CF_3-containing heterocycles having naphthalene[10] and quinoline[11] skeletons.



Scheme 1.

In continuation of these studies, it was found that *N*-propargyl-2,4-bis(trifluoroacetyl)-1-naphthylamines **5**, prepared by N–N exchange reaction of **1** with propargylamine, undergoes novel pyridine-ring formation reaction with various nucleophiles to give the corresponding fluorine-containing benzo[*h*]quinolines **6** in excellent yields (Scheme 2).[12]

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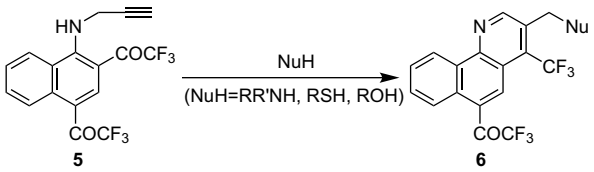
doi:10.1016/j.tet.2009.05.047



Scheme 2.

In connection to these syntheses, we have very recently reported that *N*-propargyl-5,7-bis(trifluoroacetyl)-8-quinolylamine **7** undergoes the pyridine-ring formation reaction with amines to afford the novel fluorine-containing 1,10-phenanthrolines **9** and the isolation of the reactive intermediates 1,4-dihydro-1,10-phenanthrolin-4-ols **8a**–**c**.[13] To the best of our knowledge, this was the first example of the isolation of 1,4-dihydro-1,10-phenanthrolin-4-ols as the precursor of 1,10-phenanthrolines.

Herein we report a full account of our systematic studies on this type of pyridine-ring formation reaction including an extension of the remarkable reactivity of **7** with various thiols and phenols, which are considerably less reactive than amines. This reaction afforded an easy and efficient way to introduce substitution diversity.

2. Results and discussion

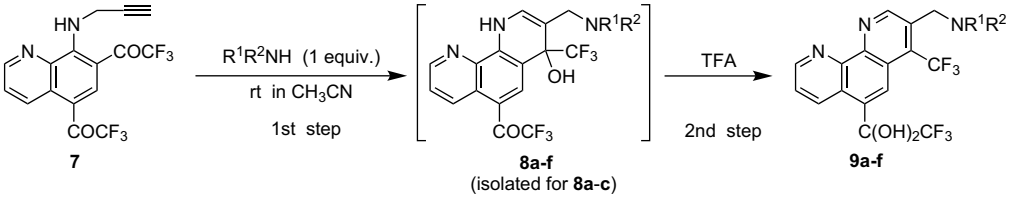
The requisite starting material **7** was quantitatively prepared by the aromatic nucleophilic N–N exchange reaction of **2** with propargylamine.[9]

We first examined the reaction of **7** with secondary amines (Scheme 3) and the results are summarized in Table 1. The cyclization of **7** with dimethylamine proceeded rapidly at room temperature in CH_3CN to give the unexpected intermediate, 1,4-dihydro-1,10-phenanthrolin-4-ols **8a**, in an almost quantitative yield without dehydration (entry 1; in the first step). Secondary amines such as diethylamine and piperidine also reacted cleanly to provide dihydrophenanthrolinols **8b** and **8c** quantitatively (entries 2 and 3).

Treatment of dihydrophenanthrolinols **8a**–**c** with trifluoroacetic acid (TFA) caused dehydration to furnish the corresponding phenanthrolines **9a**–**c** in 60–63% yields (entries 1–3; in the second step). The dehydration of piperidino derivative **8c** was carried out under mild conditions (with 1 equiv of TFA at room temperature in $CHCl_3$). However, forced reaction conditions (in refluxing TFA) were required for dimethyl- and diethylamino derivatives **8a** and **8b**. The reason is not clear at this stage. Interestingly, the 6-trifluoroacetyl group of prepared 1,10-phenanthrolines **9** was found to exist as hydrate form and this phenomenon was not observed in the case of benzo[*h*]quinolines **6**. It is speculated that the increase, which is caused by two pyridine rings (π-deficient system) fused to a central benzene ring, of the electron-withdrawing ability of 1,10-phenanthroline system makes the hydration of the trifluoroacetyl group easier than that of benzo[*h*]quinoline system.

In contrast, when the reaction with bulky primary amine such as *tert*-butylamine was performed under mild conditions (at room temperature for 4 h), a mixture of dihydrophenanthrolinol **8d** and phenanthroline **9d** was obtained but separation of the mixture was unsuccessful. Therefore, we performed the two-step reaction in a one-pot manner to obtain selectively the final target product **9d**. After stirring the solution of a mixture of **7** and *tert*-butylamine in CH_3CN for 4 h at room temperature, TFA (5 equiv) was added to the reaction mixture and then it was further stirred for 5 min at the same temperature to afford **9d** in 58% yield (entry 4). In a similar one-pot manner, aromatic primary amines, for example, *p*-anisidine and *p*-chloroaniline, reacted in the presence of triethylamine as a base to give the desired 1,10-phenanthrolines **9e** and **9f** in moderate yields (entries 5 and 6). In this pyridine-ring formation reaction, only 0.5 equiv of triethylamine was needed to force the reaction to completion. Unfortunately, the reactions with less bulky aliphatic primary amines such as methyl-, ethyl-, and *i*-propylamines furnished a complex mixture of the corresponding N–N exchanged 8-quinolylamine derivatives **4** (Nu: MeNH, EtNH, and *i*-PrNH) and decomposed products.

Next, we attempted to carry out the pyridine-ring formation reaction with various thiols (Scheme 4, Table 2). Reaction of **7** with aliphatic thiols such as benzyl mercaptan, ethanethiol, propanethiol, and *tert*-butanethiol in the presence of *t*-BuOK (0.1 equiv, entry 1; 0.5 equiv, entries 3–4 and 7–8; 1.0 equiv, entries 2 and 5–6) took place in CH_3CN at room temperature within 1 h to afford the desired 3-alkylthiomethyl-1,10-phenanthrolines **10a**–**d** in moderate yields (entries 1–4). In the case of low boiling ethanethiol, the reaction was performed with large amounts of reagent (5 equiv) to provide **10b**. Aromatic thiols such as *p*-substituted benzenethiols also underwent quickly the pyridine-ring formation reaction under



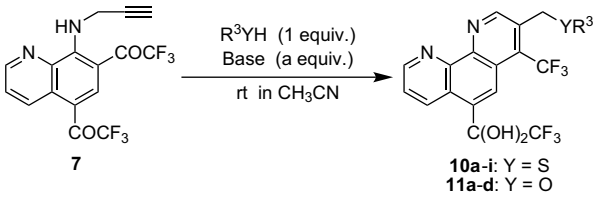
Scheme 3.

Table 1
Synthesis of 1,10-phenanthrolines **9** by the reaction of **7** with amines

Entry	First step				Second step					
	R^1R^2NH	Time (h)	Product	Yield (%)	TFA (equiv)	Temp.	Time (min)	Solvent	Product	Yield (%)
1	Me_2NH[a]	2	**8a**	98	54	Reflux	30	None	**9a**	62[b]
2	Et_2NH	2	**8b**	100	54	Reflux	30	None	**9b**	60[b]
3	Piperidine	1	**8c**	100	1	rt	30	$CHCl_3$	**9c**	63[b]
4	*t*-$BuNH_2$	4	—	—	5	rt	5	CH_3CN	**9d**	58[c]
5[d]	4-$MeOC_6H_4NH_2$	4	—	—	5	rt	5	CH_3CN	**9e**	51[c]
6[d]	4-$ClC_6H_4NH_2$	4	—	—	5	rt	5	CH_3CN	**9f**	58[c]

[a] Aqueous solution (50%) of dimethylamine was used.
[b] Isolated yields based on **8**.
[c] Isolated yields based on **7**.
[d] Triethylamine (0.5 equiv) was added.

similar conditions for aliphatic thiols, to give the corresponding arylthiomethylated 1,10-phenanthrolines **10e–i** (entries 5–9).



Scheme 4.

Table 2
Synthesis of 1,10-phenanthrolines **10** and **11** by the reaction of **7** with thiols and phenols

Entry	R^3YH	Base	*a* (equiv)	Time (h)	Product	Yield[a] (%)
1	$PhCH_2SH$	*t*-BuOK	0.1	1	**10a**	55
2	EtSH[b]	*t*-BuOK	1	1	**10b**	54
3	PrSH	*t*-BuOK	0.5	1	**10c**	46
4	*t*-BuSH	*t*-BuOK	0.5	1	**10d**	44
5	4-$MeOC_6H_4SH$	*t*-BuOK	1	1	**10e**	48
6	4-MeC_6H_4SH	*t*-BuOK	1	2	**10f**	45
7	PhSH	*t*-BuOK	0.5	1	**10g**	58
8	4-ClC_6H_4SH	*t*-BuOK	0.5	1	**10h**	58
9	4-$NO_2C_6H_4SH$	*t*-BuOK	1	1	**10i**	44
10	4-$MeOC_6H_4OH$	*i*-Pr_2NEt	0.5	8	**11a**	58
11	4-MeC_6H_4OH	Et_3N	0.5	2	**11b**	53
12	PhOH	*i*-Pr_2NEt	0.5	8	**11c**	46
13	4-ClC_6H_4OH	*i*-Pr_2NEt	0.5	8	**11d**	54

[a] Isolated yields.
[b] EtSH (5 equiv) was used.

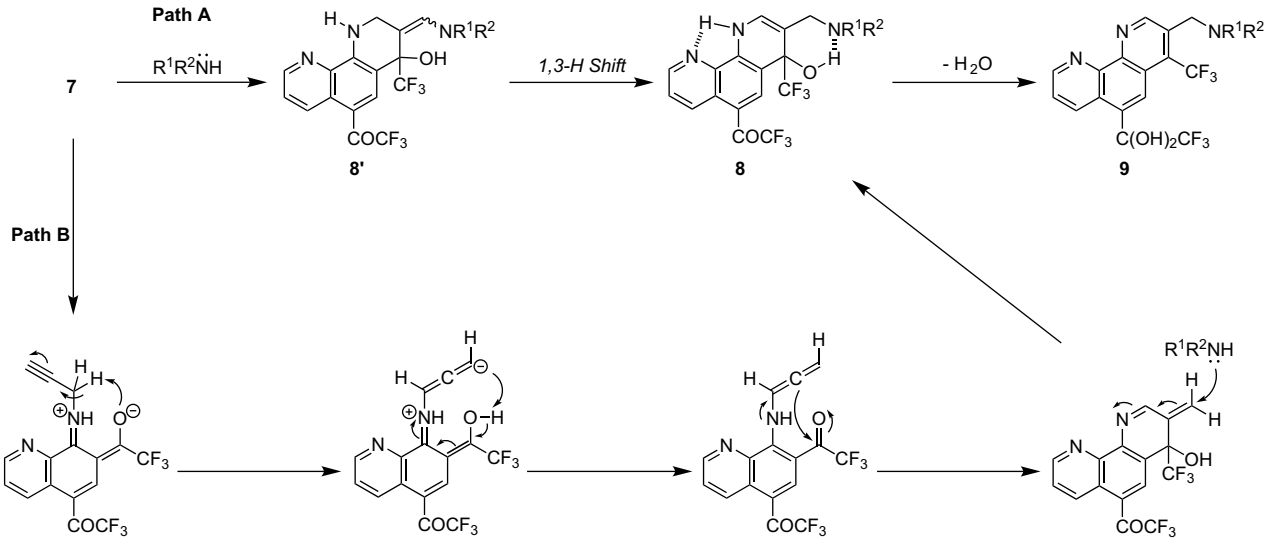
Furthermore, the present pyridine-ring formation reactions were applied to phenols (Scheme 4, Table 2) and alcohols. The cyclization formation of **7** with *p*-substituted phenols proceeded easily in the presence of *N*,*N*-diisopropylethylamine or triethylamine (0.5 equiv) as a base in CH_3CN to produce the corresponding 1,10-phenanthrolines **11a–d** having aryloxymethyl group at the 3-position, in moderate yields (entries 10–13). All the cyclization reactions with thiols and phenols did not proceed in the absence of base. However, in spite of our efforts, only decomposed products were formed in the reaction with any alcohols even under the more severe conditions.

In the reaction with thiols and phenols, the formation of the corresponding 1,4-dihydro-1,10-phenanthrolin-4-ols were also established from the ^1H NMR analysis of the crude mixtures. The isolation of intermediates is unsuccessful but the final target, 1,10-phenanthrolines were obtained after silica gel chromatography without dehydration using TFA.

Two possible mechanistic pathways (path A and B) for the formation of 1,10-phenanthrolines are presented in Scheme 5. In the path A, the addition of nucleophiles, e.g., amines, to the terminal acetylenic carbon and the attack of carbonyl carbon onto the internal acetylenic carbon occur concertedly to give the cyclization product **8′** having *exo*-methylene moiety. The subsequent 1,3-shift of allylic hydrogen in **8′** takes place to afford the intermediates, 1,4-dihydro-1,10-phenanthrolin-4-ols **8**, which undergoes dehydration to give 1,10-phenanthrolines **9**. In the path B, the tautomerization of keto to enol form causes the isomerization of propargyl to allenyl group and subsequent intramolecular cyclization gives the 3-methylene-1,10-phenanthroline derivative. Then, this product reacts with amines to give **8** leading to **9**. More studies are underway to elucidate clearly the mechanism.

The structures of all new compounds (**8**–**11**) were easily determined on the basis of their ^1H NMR and IR spectra, together with elemental analyses. For example, in ^1H NMR spectrum of **8a**, two adjacent protons (amine and olefin protons) at 1- and 2-positions appeared at 8.88 and 6.72 ppm as doublets with coupling constant J=4.0 Hz. When the H–D exchange of the amine proton (H-1) was carried out, the multiplicity of olefin proton (H-2) signal changed to singlet. The data clearly shows that the structure of the isolated intermediate is not **8′** but **8**.

It is noteworthy that we first succeeded in the isolation of the intermediates **8a–c**, which are the precursors of stable aromatized final products, 1,10-phenanthrolines **9a–c**, and which seem to be unstable. This is a great difference in reactivity between the 8-quinoline system **7** and the naphthalene one **5**, as in the naphthalene system this type of intermediate, for example, **12**, was not isolated and also not detected (Fig. 1).[12] Probably, it is reasonable to postulate that in **8a–c** the additional hydrogen bond between H-1 and N-10, which cannot exist in the naphthalene system **12**, has contributed to the stability of **8a–c**, namely, has interrupted the dehydration accompanied by aromatization. We attempted the NMR experiment, where **8a** was dissolved in DMSO-d_6 as a solvent to disfavor the hydrogen bond between H-1 and N-10, allowed to stand at 33 °C and the reaction progress was monitored by ^1H NMR.



Scheme 5.

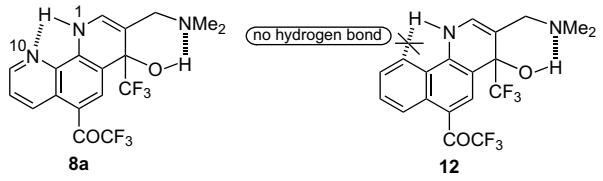


Figure 1.

It was found that **8a** is gradually converted to **9a** under the above-described conditions as follows: conversion/standing time; 38%/3 days; 100%/7 days. This result supports our speculation on stabilization of the intermediates **8a**–**c** by the intramolecular hydrogen bond.

3. Conclusion

In summary, we succeeded in extending the pyridine-ring formation reaction of *N*-propargyl-8-quinolylamine derivative **7** with amines to those with thiols and phenols and in providing an efficient synthetic method for CF_3-containing 1,10-phenanthrolines **9**, which are not easily obtained by other methods. The methodology presented is quite remarkable since no any kind of activation of the propargylamine system was needed to promote addition of the nucleophiles and subsequent ring formation. The mechanism of this reaction is not yet fully established although two reasonable mechanistic pathways have been presented.

4. Experimental

4.1. General

Mps were determined on an electrothermal digital melting point apparatus and are uncorrected. NMR spectra were obtained with a Bruker AVANCE 500 spectrometer (^{1}H at 500 MHz, ^{13}C at 126 MHz) using TMS as an internal standard and IR spectra were taken with a PerkinElmer ONE FT-IR spectrometer. Microanalyses were taken with a YANACO CHN-Coder MT-5 analyzer.

4.2. A typical procedure for the synthesis of 1,4-dihydro-1,10-phenanthrolin-4-ols (8a–c)

To a solution of **7**[9] (187 mg, 0.5 mmol) in CH_3CN (5 mL) was added aqueous solution (50%) of dimethylamine (51 mg, 0.56 mmol) and the mixture was stirred at room temperature for 2 h. Evaporation of the solvent in vacuo gave practically pure **8a** (205 mg, 98%).

*4.2.1. 3-Dimethylaminomethyl-6-trifluoroacetyl-4-trifluoromethyl-1,4-dihydro[1,10]phenanthrolin-4-ol (**8a**)*

Compound **8a**: 98%; mp 123–124 °C (dec) (*n*-hexane/AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.48 (dd, 1H, J=1.5, 8.5 Hz, H-7), 8.88 (br d, 1H, J=4.0 Hz, NH), 8.81 (dd, 1H, J=1.5, 4.0 Hz, H-9), 8.72 (s, 1H, H-5), 7.76–7.28 (br, 1H, OH), 7.62 (dd, 1H, J=4.0, 8.5 Hz, H-8), 6.72 (d, 1H, J=4.0 Hz, H-2), 3.99 (d, 1H, J_{gem}=13.0 Hz, CH_2), 2.82 (d, 1H, J_{gem}=13.0 Hz, CH_2), 2.31 (s, 6H, $N(CH_3)_2$); ^{13}C NMR (126 MHz, $CDCl_3$): δ 179.9 (q, J_{CF}=33.4 Hz), 148.9, 139.4, 136.8, 136.6, 134.9, 127.4, 127.3, 126.0 (q, J_{CF}=294.3 Hz), 124.9, 117.2, 117.0 (q, J_{CF}=293.0 Hz), 112.8, 104.4, 72.8 (q, J_{CF}=30.2 Hz), 61.5, 44.2; IR (KBr, cm^{-1}): 3402, 3094, 1697, 1676; Anal. Calcd for $C_{18}H_{15}F_6N_3O_2$: C, 51.56; H, 3.61; N, 10.02. Found: C, 51.63; H, 3.32; N, 9.89.

*4.2.2. 3-Diethylaminomethyl-6-trifluoroacetyl-4-trifluoromethyl-1,4-dihydro[1,10]phenanthrolin-4-ol (**8b**)*

Compound **8b**: 100%; mp 131–132 °C (dec) (*n*-hexane/AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.75–9.28 (br, 1H, OH), 9.47 (d, 1H, J=8.6 Hz, H-7), 8.96 (br d, 1H, J=3.9 Hz, H-9), 8.79 (d, 1H, J=4.6 Hz, NH), 8.71 (s, 1H, H-5), 7.60 (dd, 1H, J=3.9, 8.6 Hz, H-8), 6.73 (d, 1H, J=4.6 Hz, H-2), 4.06 (d, 1H, J_{gem}=13.2 Hz, CH_2), 3.00 (d, 1H, J_{gem}=13.2 Hz, CH_2), 2.85–2.78 (m, 2H, NCH_2CH_3), 2.47–2.37 (br m, 2H, NCH_2CH_3), 1.07 (t, 6H, J=6.6 Hz, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$): δ 179.8 (q, J_{CF}=33.5 Hz), 148.8, 139.6, 136.7, 136.6, 134.7, 127.4, 127.3, 126.1 (q, J_{CF}=290.9 Hz), 124.7, 117.0 (q, J_{CF}=292.6 Hz), 116.9, 112.8, 104.3, 72.8 (q, J_{CF}=30.2 Hz), 60.4, 45.5, 10.7; IR (KBr, cm^{-1}): 3409, 3089, 1698, 1676; Anal. Calcd for $C_{20}H_{19}F_6N_3O_2$: C, 53.69; H, 4.28; N, 9.39. Found: C, 53.77; H, 4.34; N, 9.26.

*4.2.3. 3-Piperidinomethyl-6-trifluoroacetyl-4-trifluoromethyl-1,4-dihydro[1,10]phenanthrolin-4-ol (**8c**)*

Compound **8c**: 100%; mp 172–173 °C (dec) (MeCN/H_2O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.75–9.41 (br, 1H, OH), 9.53 (dd, 1H, J=1.5, 8.5 Hz, H-7), 8.84 (dd, 1H, J=1.5, 4.0 Hz, H-9), 8.81 (br d, 1H, J=4.0 Hz, NH), 8.72 (br s, 1H, H-5), 7.65 (dd, 1H, J=4.0, 8.5 Hz, H-8), 6.68 (d, 1H, J=4.0 Hz, H-2), 3.93 (d, 1H, J_{gem}=13.0 Hz, CH_2), 3.05–2.19 (br, 4H, NCH_2CH_2), 2.90 (d, 1H, J_{gem}=13.0 Hz, CH_2), 1.60–1.57 (m, 6H, $NCH_2CH_2CH_2CH_2$); ^{13}C NMR (126 MHz, $CDCl_3$): δ 179.9 (q, J_{CF}=34.0 Hz), 148.9, 139.4, 136.8, 136.8, 134.9, 127.3, 127.2, 126.1 (q, J_{CF}=290.5 Hz), 124.9, 117.1, 117.0 (q, J_{CF}=293.0 Hz), 112.8, 104.0, 72.7 (q, J_{CF}=30.2 Hz), 61.0, 53.8, 25.8, 24.0; IR (KBr, cm^{-1}): 3394, 3085, 1692, 1676; Anal. Calcd for $C_{21}H_{19}F_6N_3O_2$: C, 54.90; H, 4.17; N, 9.15. Found: C, 55.00; H, 3.80; N, 9.43.

4.3. A typical procedure for the synthesis of 1,10-phenanthrolines (9a–c) from 1,4-dihydro-1,10-phenanthrolin-4-ols (8a–c)

A solution of **8a** (210 mg, 0.5 mmol) in CF_3CO_2H (2 mL) was stirred at reflux temperature for 30 min. The mixture was washed with saturated aqueous solution of Na_2CO_3, extracted with AcOEt, and dried over Na_2SO_4. The solvent was evaporated in vacuo and the crude product was purified by recrystallization from *n*-hexane and AcOEt to give **9a** (130 mg, 62%).

*4.3.1. 1-(8-Dimethylaminomethyl-7-trifluoromethyl[1,10]-phenanthrolin-5-yl)-2,2,2-trifluoroethane-1,1-diol (**9a**)*

Compound **9a**: 62%; mp 161–162 °C (*n*-hexane/AcOEt); ^{1}H NMR (500 MHz, CD_3CN/DMSO-d_6): δ 9.38 (d, 1H, J=8.5 Hz, H-4), 9.30 (s, 1H, H-9), 9.12 (d, 1H, J=4.0 Hz, H-2), 8.79 (s, 1H, H-6), 7.95 (br s, 2H, OH), 7.74 (dd, 1H, J=4.0, 8.5 Hz, H-3), 3.88 (s, 2H, CH_2), 2.28 (s, 6H, $N(CH_3)_2$); ^{13}C NMR (126 MHz, $CDCl_3$/DMSO-d_6): δ 153.9, 149.9, 146.3, 145.4, 136.4, 134.9, 132.1 (q, J_{CF}=30.7 Hz), 126.7, 124.5 (q, J_{CF}=283.0 Hz), 124.1, 124.1, 123.6 (q, J_{CF}=289.3 Hz), 123.0, 122.3, 94.3 (q, J_{CF}=31.4 Hz), 58.9, 45.2; IR (KBr, cm^{-1}): 3352, 3115; Anal. Calcd for $C_{18}H_{15}F_6N_3O_2$: C, 51.56; H, 3.61; N, 10.02. Found: C, 51.83; H, 3.85; N, 9.75.

*4.3.2. 1-(8-Diethylaminomethyl-7-trifluoromethyl[1,10]-phenanthrolin-5-yl)-2,2,2-trifluoroethane-1,1-diol (**9b**)*

Compound **9b**: 60%; mp 130–131 °C (AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$/DMSO-d_6): δ 9.60 (s, 1H, H-9), 9.45 (d, 1H, J=8.4 Hz, H-4), 9.16 (d, 1H, J=3.9 Hz, H-2), 8.87 (s, 1H, H-6), 7.87 (br s, 2H, OH), 7.68 (dd, 1H, J=3.9, 8.4 Hz, H-3), 4.05 (s, 2H, CH_2), 2.60 (q, 4H, J=7.0 Hz, NCH_2CH_3), 1.07 (t, 6H, J=7.0 Hz, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$/DMSO-d_6): δ 153.9, 149.9, 146.3, 145.8, 136.7, 134.6, 132.1 (q, J_{CF}=30.2 Hz), 126.8, 124.8, 124.7 (q, J_{CF}=279.2 Hz), 124.5, 123.6 (q, J_{CF}=293.0 Hz), 122.7, 122.4, 94.7 (q, J_{CF}=32.7 Hz), 53.7 (q, J_{CF}=3.8 Hz), 47.2, 12.0; IR (KBr, cm^{-1}): 3386, 3182; Anal. Calcd for $C_{20}H_{19}F_6N_3O_2$: C, 53.69; H, 4.28; N, 9.39. Found: C, 53.67; H, 4.37; N, 9.32.

*4.3.3. 2,2,2-Trifluoro-1-(8-piperidinomethyl-7-trifluoromethyl[1,10]phenanthrolin-5-yl)ethane-1,1-diol (**9c**)*

Compound **9c**: 63%; mp 140–141 °C (EtOH); ^{1}H NMR (500 MHz, $CDCl_3$/DMSO-d_6): δ 9.47 (s, 1H, H-9), 9.44 (d, 1H, J=8.4 Hz, H-4), 9.16

(d, 1H, J=3.8 Hz, H-2), 8.85 (s, 1H, H-6), 8.00 (br s, 2H, OH), 7.70 (dd, 1H, J=3.8, 8.4 Hz, H-3), 3.94 (s, 2H, CH_2), 2.48 (br s, 4H, NCH_2CH_2), 1.59 (br s, 4H, $NCH_2CH_2CH_2$), 1.47 (br s, 2H, $NCH_2CH_2CH_2$); ^{13}C NMR (126 MHz, $CDCl_3$/DMSO-d_6): δ 153.8, 149.8, 146.4, 145.7, 136.6, 134.8, 132.4 (q, J_{CF}=31.4 Hz), 126.8, 124.6 (q, J_{CF}=281.7 Hz), 124.4, 124.4, 123.6 (q, J_{CF}=288.0 Hz), 122.7, 122.5, 94.6 (q, J_{CF}=32.7 Hz), 58.4, 54.4, 25.8, 24.0; IR (KBr, cm^{-1}): 3341, 3121; Anal. Calcd for $C_{21}H_{19}F_6N_3O_2$: C, 54.90; H, 4.17; N, 9.15. Found: C, 55.19; H, 4.18; N, 8.85.

4.4. A typical procedure for the one-pot synthesis of 1,10-phenanthroline (9d–f) from *N*-propargyl-5,7-bis-(trifluoroacetyl)-8-quinolylamine (7)

To a solution of **7** (187 mg, 0.5 mmol) in CH_3CN (5 mL) were added *p*-anisidine (65 mg, 0.53 mmol) and triethylamine (25 mg, 0.25 mmol) and the mixture was stirred at room temperature for 4 h. Without work-up to the reaction mixture was added CF_3CO_2H (0.19 mL, 2.6 mmol) and then it was further stirred for 5 min at room temperature. The mixture was washed with saturated aqueous solution of Na_2CO_3, extracted with AcOEt, and dried over Na_2SO_4. Evaporation of the solvent gave a crude mixture, which was submitted to column chromatography on silica gel eluting with *n*-hexane/AcOEt (1:1) to give **9e** (127 mg, 51%).

*4.4.1. 1-(8-(tert-Butylaminomethyl)-7-trifluoromethyl[1,10]-phenanthrolin-5-yl)-2,2,2-trifluoroethane-1,1-diol (**9d**)*

Compound **9d**: 58%; mp 167–168 °C (*n*-hexane/AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$/DMSO-d_6): δ 9.41 (d, 1H, J=8.5 Hz, H-4), 9.39 (s, 1H, H-9), 9.16 (d, 1H, J=4.0 Hz, H-2), 8.85 (s, 1H, H-6), 7.65 (dd, 1H, J=4.0, 8.5 Hz, H-3), 7.51–7.25 (br, 1H, NH), 7.35 (s, 2H, OH), 4.17 (s, 2H, CH_2), 1.22 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (126 MHz, $CDCl_3$/DMSO-d_6): δ 154.9, 149.9, 146.3, 145.2, 136.4, 135.1, 131.5 (q, J_{CF}=29.3 Hz), 126.8, 124.7, 124.3 (q, J_{CF}=285.6 Hz), 124.0, 123.5 (q, J_{CF}=290.5 Hz), 123.1, 121.9, 94.3 (q, J_{CF}=31.2 Hz), 59.7, 41.7, 27.4; IR (KBr, cm^{-1}): 3473, 3352, 3148; Anal. Calcd for $C_{20}H_{19}F_6N_3O_2$: C, 53.69; H, 4.28; N, 9.39. Found: C, 53.94; H, 4.19; N, 9.23.

*4.4.2. 2,2,2-Trifluoro-1-(8-(4-methoxyphenylaminomethyl)-7-trifluoromethyl[1,10]phenanthrolin-5-yl)ethane-1,1-diol (**9e**)*

Compound **9e**: 51%; mp 136–137 °C (dec) (*n*-hexane/AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$/DMSO-d_6): δ 9.44 (d, 1H, J=9.0 Hz, H-4), 9.41 (s, 1H, H-9), 9.15 (d, 1H, J=4.0 Hz, H-2), 8.88 (s, 1H, H-6), 7.68 (br s, 2H, OH), 7.66 (dd, 1H, J=4.0, 9.0 Hz, H-3), 6.72 (d, 2H, J=8.5 Hz, H_{arom}), 6.60 (d, 2H, J=8.5 Hz, H_{arom}), 4.90–4.68 (br, 1H, NH), 4.81 (s, 2H, CH_2), 3.70 (s, 3H, OCH_3); ^{13}C NMR (126 MHz, $CDCl_3$/DMSO-d_6): δ 152.6, 152.1, 150.0, 149.9, 146.4, 145.6, 136.7, 135.0, 131.8 (q, J_{CF}=31.4 Hz), 126.8, 124.8 (q, J_{CF}=280.5 Hz), 124.2, 123.6 (q, J_{CF}=289.3 Hz), 123.0, 122.8, 122.4, 114.9, 114.0, 94.6 (q, J_{CF}=32.7 Hz), 55.6, 55.4; IR (KBr, cm^{-1}): 3415, 3363, 3115; Anal. Calcd for $C_{23}H_{17}F_6N_3O_3$: C, 55.54; H, 3.44; N, 8.45. Found: C, 55.75; H, 3.47; N, 8.23.

*4.4.3. 1-(8-(4-Chlorophenylaminomethyl)-7-trifluoromethyl-[1,10]phenanthrolin-5-yl)-2,2,2-trifluoroethane-1,1-diol (**9f**)*

Compound **9f**: 58%; mp 135–136 °C (AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$/DMSO-d_6): δ 9.46 (d, 1H, J=8.5 Hz, H-4), 9.40 (s, 1H, H-9), 9.13 (d, 1H, J=4.0 Hz, H-2), 8.85 (s, 1H, H-6), 8.03 (br s, 2H, OH), 7.70 (dd, 1H, J=4.0, 8.5 Hz, H-3), 6.69 (d, 2H, J=8.6 Hz, H_{arom}), 6.58 (d, 2H, J=8.6 Hz, H_{arom}), 4.79 (s, 2H, CH_2), 3.45–3.10 (br, 1H, NH); ^{13}C NMR (126 MHz, $CDCl_3$/DMSO-d_6): δ 152.6, 151.9, 149.7, 146.2, 145.4, 141.7, 136.8, 135.0, 133.4, 131.7 (q, J_{CF}=30.6 Hz), 126.8, 124.8 (q, J_{CF}=279.6 Hz), 124.2, 123.5 (q, J_{CF}=289.8 Hz), 122.8, 122.4, 114.8, 113.8, 94.5 (q, J_{CF}=31.4 Hz), 55.5; IR (KBr, cm^{-1}): 3485, 3291, 3117; Anal. Calcd for $C_{22}H_{14}ClF_6N_3O_2$: C, 52.66; H, 2.81; N, 8.37. Found: C, 52.82; H, 3.02; N, 8.00.

4.5. A typical procedure for the synthesis of 1,10-phenanthrolines (10a–i) by the pyridine-ring formation reaction of 7 with thiols

To a solution of benzyl mercaptan (0.06 mL, 0.5 mmol) and *t*-BuOK (6 mg, 0.05 mmol) in CH_3CN (5 mL) was added **7** (187 mg, 0.5 mmol) and the mixture was stirred at room temperature for 1 h. The mixture was washed with 1.0 N hydrochloric acid, extracted with AcOEt, and dried over Na_2SO_4. Evaporation of the solvent gave a crude mixture, which was submitted to column chromatography on silica gel eluting with *n*-hexane/AcOEt (1:2) to give **10a** (137 mg, 55%).

*4.5.1. 1-(8-Benzylthiomethyl-7-trifluoromethyl[1,10]-phenanthrolin-5-yl)-2,2,2-trifluoroethane-1,1-diol (**10a**)*

Compound **10a**: 55%; mp 137–138 °C (AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$/DMSO-d_6): δ 9.45 (d, 1H, J=8.3 Hz, H-4), 9.18 (br s, 1H, H-2), 9.04 (s, 1H, H-9), 8.85 (s, 1H, H-6), 7.68 (dd, 1H, J=4.0, 8.3 Hz, H-3), 7.62 (br s, 2H, OH), 7.39–7.27 (m, 4H, H_{arom}), 7.23 (t, 1H, J=7.1 Hz, H_{arom}), 4.05 (s, 2H, CH_2S), 3.76 (s, 2H, CH_2Ph); ^{13}C NMR (126 MHz, $CDCl_3$/DMSO-d_6): δ 153.8, 150.0, 146.4, 145.6, 137.1, 136.9, 135.2, 132.1, 131.9 (q, J_{CF}=30.2 Hz), 128.9, 128.5, 127.2, 127.0, 124.4 (q, J_{CF}=279.2 Hz), 124.4, 123.6 (q, J_{CF}=289.3 Hz), 123.0, 123.0, 94.7 (q, J_{CF}=32.7 Hz), 36.4, 31.7; IR (KBr, cm^{-1}): 3368, 3121; Anal. Calcd for $C_{23}H_{16}F_6N_2O_2S$: C, 55.42; H, 3.24; N, 5.62. Found: C, 55.64; H, 3.30; N, 5.34.

*4.5.2. 1-(8-Ethylthiomethyl-7-trifluoromethyl[1,10]phenanthrolin-5-yl)-2,2,2-trifluoroethane-1,1-diol (**10b**)*

Compound **10b**: 54%; mp 146–147 °C (AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$/DMSO-d_6): δ 9.44 (d, 1H, J=8.2 Hz, H-4), 9.19 (s, 1H, H-9), 9.16 (br s, 1H, H-2), 8.82 (s, 1H, H-6), 8.09 (br s, 2H, OH), 7.73 (dd, 1H, J=3.8, 8.2 Hz, H-3), 4.22 (s, 2H, CH_2S), 2.58 (q, 2H, J=7.3 Hz, CH_2CH_3), 1.27 (t, 3H, J=7.3 Hz, CH_3); ^{13}C NMR (126 MHz, DMSO-d_6): δ 154.3, 150.1, 145.3, 144.7, 136.3, 134.8, 133.5, 130.4 (q, J_{CF}=30.2 Hz), 126.3, 124.3 (q, J_{CF}=277.7 Hz), 123.7, 123.5 (q, J_{CF}=286.9 Hz), 123.4, 122.1, 94.0 (q, J_{CF}=33.0 Hz), 31.2, 25.4, 14.4; IR (KBr, cm^{-1}): 3368, 3126; Anal. Calcd for $C_{18}H_{14}F_6N_2O_2S$: C, 49.54; H, 3.23; N, 6.42. Found: C, 49.77; H, 3.29; N, 6.13.

*4.5.3. 2,2,2-Trifluoro-1-(8-propylthiomethyl-7-trifluoromethyl[1,10]phenanthrolin-5-yl)ethane-1,1-diol (**10c**)*

Compound **10c**: 46%; mp 151–152 °C (AcOEt); ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.36 (d, 1H, J=8.3 Hz, H-4), 9.28 (s, 1H, H-9), 9.17 (br s, 1H, H-2), 8.75 (s, 1H, H-6), 8.47 (br s, 2H, OH), 7.87 (dd, 1H, J=3.6, 8.3 Hz, H-3), 4.25 (s, 2H, CH_2S), 2.58–2.52 (m, 2H, SCH_2CH_2), 1.55 (sext, 2H, J=7.1 Hz, SCH_2CH_2), 0.91 (t, 3H, J=7.1 Hz, CH_3); ^{13}C NMR (126 MHz, DMSO-d_6): δ 154.3, 150.1, 145.8, 145.1, 135.9, 134.9, 133.3, 130.2 (q, J_{CF}=28.5 Hz), 126.3, 124.4 (q, J_{CF}=277.5 Hz), 123.7, 123.6 (q, J_{CF}=289.3 Hz), 123.2, 122.0, 94.1 (q, J_{CF}=32.7 Hz), 33.4, 31.5, 22.3, 13.0; IR (KBr, cm^{-1}): 3366, 3115; Anal. Calcd for $C_{19}H_{16}F_6N_2O_2S$: C, 50.67; H, 3.58; N, 6.22. Found: C, 50.69; H, 3.47; N, 6.03.

*4.5.4. 1-(8-(tert-Butylthiomethyl)-7-trifluoromethyl[1,10]-phenanthrolin-5-yl)-2,2,2-trifluoroethane-1,1-diol (**10d**)*

Compound **10d**: 44%; mp 168–169 °C (AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$/DMSO-d_6): δ 9.47 (d, 1H, J=8.5 Hz, H-4), 9.23 (s, 1H, H-9), 9.17 (d, 1H, J=4.0 Hz, H-2), 8.84 (s, 1H, H-6), 8.01 (br s, 2H, OH), 7.72 (dd, 1H, J=4.0, 8.5 Hz, H-3), 4.22 (s, 2H, CH_2), 1.44 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (126 MHz, $CDCl_3$/DMSO-d_6): δ 154.5, 149.6, 145.5, 144.9, 137.1, 135.2, 132.3, 131.5 (q, J_{CF}=30.7 Hz), 126.8, 124.2 (q, J_{CF}=279.2 Hz), 124.2, 123.5 (q, J_{CF}=291.8 Hz), 123.0, 122.5, 94.3 (q, J_{CF}=32.7 Hz), 43.9, 30.6, 29.0; IR (KBr, cm^{-1}): 3383, 3126; Anal. Calcd for $C_{20}H_{18}F_6N_2O_2S$: C, 51.72; H, 3.91; N, 6.03. Found: C, 51.78; H, 3.96; N, 5.92.

*4.5.5. 2,2,2-Trifluoro-1-(8-(4-methoxyphenylthiomethyl)-7-trifluoromethyl[1,10]phenanthrolin-5-yl)ethane-1,1-diol (**10e**)*

Compound **10e**: 48%; mp 185–186 °C (AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$/DMSO-d_6): δ 9.42 (d, 1H, J=8.5 Hz, H-4), 9.16 (d, 1H, J=4.0 Hz, H-2), 8.84 (s, 1H, H-9 or 6), 8.75 (s, 1H, H-6 or 9), 7.66 (dd, 1H, J=4.0, 8.5 Hz, H-3), 7.27 (br s, 2H, OH), 7.26 (d, 2H, J=8.5 Hz, H_{arom}), 6.77 (d, 2H, J=8.5 Hz, H_{arom}), 4.38 (br s, 2H, CH_2), 3.77 (s, 3H, OCH_3); ^{13}C NMR (126 MHz, DMSO-d_6): δ 160.0, 154.5, 150.6, 146.3, 145.7, 136.3, 135.7, 135.4, 132.8, 130.7 (q, J_{CF}=30.2 Hz), 126.8, 124.9 (q, J_{CF}=278.0 Hz), 124.2, 124.1 (q, J_{CF}=290.5 Hz), 123.7, 123.4, 122.4, 115.3, 94.6 (q, J_{CF}=32.7 Hz), 55.7, 36.7; IR (KBr, cm^{-1}): 3385, 3121; Anal. Calcd for $C_{23}H_{16}F_6N_2O_3S$: C, 53.70; H, 3.13; N, 5.45. Found: C, 53.42; H, 3.33; N, 5.54.

*4.5.6. 2,2,2-Trifluoro-1-(8-(p-tolylthiomethyl)-7-trifluoromethyl[1,10]phenanthrolin-5-yl)ethane-1,1-diol (**10f**)*

Compound **10f**: 45%; mp 159–160 °C (AcOEt); ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.33 (d, 1H, J=8.3 Hz, H-4), 9.13 (br s, 1H, H-2), 8.93 (s, 1H, H-9), 8.72 (s, 1H, H-6), 8.41 (br s, 2H, OH), 7.84 (dd, 1H, J=3.8, 8.3 Hz, H-3), 7.28 (d, 2H, J=7.5 Hz, H_{arom}), 7.12 (d, 2H, J=7.5 Hz, H_{arom}), 4.62 (s, 2H, CH_2), 2.27 (s, 3H, CH_3); ^{13}C NMR (126 MHz, DMSO-d_6): δ 154.4, 150.6, 146.4, 145.6, 138.0, 136.4, 135.4, 132.7, 132.6, 130.8 (q, J_{CF}=30.2 Hz), 130.3, 130.0, 126.9, 124.8 (q, J_{CF}=281.7 Hz), 124.2, 124.0 (q, J_{CF}=288.6 Hz), 123.7, 122.4, 94.6 (q, J_{CF}=32.7 Hz), 35.7, 21.1; IR (KBr, cm^{-1}): 3374, 3110; Anal. Calcd for $C_{23}H_{16}F_6N_2O_2S$: C, 55.43; H, 3.24; N, 5.62. Found: C, 55.37; H, 3.61; N, 5.29.

*4.5.7. 2,2,2-Trifluoro-1-(8-phenylthiomethyl-7-trifluoromethyl[1,10]phenanthrolin-5-yl)ethane-1,1-diol (**10g**)*

Compound **10g**: 58%; mp 145–146 °C (AcOEt); ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.34 (d, 1H, J=8.6 Hz, H-4), 9.13 (d, 1H, J=4.1 Hz, H-2), 9.02 (s, 1H, H-9), 8.72 (s, 1H, H-6), 8.42 (br s, 2H, OH), 7.85 (dd, 1H, J=4.1, 8.6 Hz, H-3), 7.41 (d, 2H, J=7.0 Hz, H_{arom}), 7.33–7.27 (m, 3H, H_{arom}), 4.69 (s, 2H, CH_2); ^{13}C NMR (126 MHz, DMSO-d_6): δ 154.5, 150.6, 146.3, 145.5, 136.5, 135.4, 133.9, 132.3, 131.9, 130.9 (q, J_{CF}=28.9 Hz), 129.7, 129.1, 126.9, 124.8 (q, J_{CF}=276.8 Hz), 124.1, 124.0 (q, J_{CF}=291.7 Hz), 123.7, 122.4, 94.6 (q, J_{CF}=32.7 Hz), 35.1; IR (KBr, cm^{-1}): 3335, 3121; Anal. Calcd for $C_{22}H_{14}F_6N_2O_2S$: C, 54.55; H, 2.91; N, 5.78. Found: C, 54.62; H, 3.07; N, 5.56.

*4.5.8. 1-(8-(4-Chlorophenylthiomethyl)-7-trifluoromethyl-[1,10]phenanthrolin-5-yl)-2,2,2-trifluoroethane-1,1-diol (**10h**)*

Compound **10h**: 58%; mp 144–145 °C (AcOEt); ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.34 (d, 1H, J=8.4 Hz, H-4), 9.14 (br d, 1H, J=3.9 Hz, H-2), 9.05 (s, 1H, H-9), 8.73 (s, 1H, H-6), 8.43 (br s, 2H, OH), 7.85 (dd, 1H, J=3.9, 8.4 Hz, H-3), 7.43 (d, 2H, J=8.0 Hz, H_{arom}), 7.38 (d, 2H, J=8.0 Hz, H_{arom}), 4.71 (s, 2H, CH_2); ^{13}C NMR (126 MHz, DMSO-d_6): δ 154.4, 150.6, 146.6, 145.6, 136.3, 135.5, 133.6, 133.0, 133.0, 132.0, 131.0 (q, J_{CF}=30.2 Hz), 129.6, 126.9, 124.8 (q, J_{CF}=278.3 Hz), 124.1, 124.0 (q, J_{CF}=290.5 Hz), 123.7, 122.4, 94.6 (q, J_{CF}=32.7 Hz), 35.1; IR (KBr, cm^{-1}): 3380, 3108; Anal. Calcd for $C_{22}H_{13}ClF_6N_2O_2S$: C, 50.93; H, 2.53; N, 5.40. Found: C, 51.00; H, 2.66; N, 5.20.

*4.5.9. 2,2,2-Trifluoro-1-(8-(4-nitrophenylthiomethyl)-7-trifluoromethyl[1,10]phenanthrolin-5-yl)ethane-1,1-diol (**10i**)*

Compound **10i**: 44%; mp 145–146 °C (AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$/DMSO-d_6): δ 9.37 (d, 1H, J=7.1 Hz, H-4), 9.33 (s, 1H, H-9), 9.16 (br s, 1H, H-2), 8.75 (s, 1H, H-6), 8.45 (br s, 2H, OH), 8.19 (d, 2H, J=7.9 Hz, H_{arom}), 7.86 (dd, 1H, J=2.7, 7.1 Hz, H-3), 7.72 (d, 2H, J=7.9 Hz, H_{arom}), 4.94 (s, 2H, CH_2); ^{13}C NMR (126 MHz, $CDCl_3$/DMSO-d_6): δ 153.8, 150.2, 146.3, 145.4, 145.0, 144.8, 136.0, 135.2, 131.2 (q, J_{CF}=30.2 Hz), 130.2, 128.3, 126.6, 124.2 (q, J_{CF}=278.0 Hz), 124.0, 123.6, 123.5 (q, J_{CF}=289.3 Hz), 123.3, 122.0, 94.1 (q, J_{CF}=32.7 Hz), 32.7; IR (KBr, cm^{-1}): 3379, 3116; Anal. Calcd for $C_{22}H_{13}F_6N_3O_4S$: C, 49.91; H, 2.48; N, 7.94. Found: C, 50.27; H, 2.41; N, 7.64.

4.6. A typical procedure for the synthesis of 1,10-phenanthrolines (11a–d) by the pyridine-ring formation reaction of 7 with phenols

To a solution of **7** (187 mg, 0.5 mmol) in CH_3CN (5 mL) were added *p*-methoxyphenol (62 mg, 0.5 mmol) and *N*,*N*-diisopropylethylamine (32 mg, 0.25 mmol) and the mixture was stirred at room temperature for 8 h. Evaporation of the solvent gave a crude mixture, which was submitted to column chromatography on silica gel eluting with *n*-hexane/AcOEt (1:1) to give **11a** (145 mg, 58%).

*4.6.1. 2,2,2-Trifluoro-1-(8-(4-methoxyphenoxymethyl)-7-trifluoromethyl[1,10]phenanthrolin-5-yl)ethane-1,1-diol (**11a**)*

Compound **11a**: 58%; mp 167–168 °C (AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$/DMSO-d_6): δ 9.49–9.48 (m, 2H, H-4, H-9), 9.18 (d, 1H, J=4.0 Hz, H-2), 8.88 (s, 1H, H-6), 8.00 (br s, 2H, OH), 7.73 (dd, 1H, J=4.0, 8.5 Hz, H-3), 6.97 (d, 2H, J=8.8 Hz, H_{arom}), 6.85 (d, 2H, J=8.8 Hz, H_{arom}), 5.51 (br s, 2H, CH_2), 3.76 (s, 3H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$/DMSO-d_6): δ 155.4, 152.0, 151.8, 149.9, 147.0, 145.4, 137.0, 135.4, 132.1 (q, J_{CF}=31.4 Hz), 129.9, 127.2, 124.4 (q, J_{CF}=279.2 Hz), 124.2, 123.5 (q, J_{CF}=290.5 Hz), 123.1, 122.4, 116.1, 114.7, 94.6 (q, J_{CF}=32.7 Hz), 66.8, 55.5; IR (KBr, cm^{-1}): 3352, 3121; Anal. Calcd for $C_{23}H_{16}F_6N_2O_4$: C, 55.43; H, 3.24; N, 5.62. Found: C, 55.41; H, 3.26; N, 5.62.

*4.6.2. 2,2,2-Trifluoro-1-(8-(p-tolyloxymethyl)-7-trifluoromethyl[1,10]phenanthrolin-5-yl)ethane-1,1-diol (**11b**)*

Compound **11b**: 53%; mp 171–172 °C (AcOEt); ^{1}H NMR (500 MHz, CD_3CN/DMSO-d_6): δ 9.46 (s, 1H, H-9), 9.38 (d, 1H, J=8.5 Hz, H-4), 9.14 (d, 1H, J=4.0 Hz, H-2), 8.79 (q, 1H, J_{HF}=2.0 Hz, H-6), 7.76 (dd, 1H, J=4.0, 8.5 Hz, H-3), 7.71–7.59 (br, 2H, OH), 7.15 (d, 2H, J=8.5 Hz, H_{arom}), 6.98 (d, 2H, J=8.5 Hz, H_{arom}), 5.54 (q, 2H, J_{HF}=1.5 Hz, CH_2), 2.28 (s, 3H, CH_3); ^{13}C NMR (126 MHz, DMSO-d_6): δ 155.8, 152.6, 150.2, 146.8, 145.1, 135.9, 135.1, 131.5 (q, J_{CF}=31.2 Hz), 130.1, 129.9, 129.9, 126.6, 124.2 (q, J_{CF}=278.6 Hz), 123.6, 123.5 (q, J_{CF}=287.8 Hz), 123.4, 121.7, 114.7, 94.1 (q, J_{CF}=32.7 Hz), 65.8, 20.0; IR (KBr, cm^{-1}): 3352, 3122; Anal. Calcd for $C_{23}H_{16}F_6N_2O_3$: C, 57.27; H, 3.34; N, 5.81. Found: C, 57.50; H, 3.40; N, 5.51.

*4.6.3. 2,2,2-Trifluoro-1-(8-phenoxymethyl-7-trifluoromethyl[1,10]phenanthrolin-5-yl)ethane-1,1-diol (**11c**)*

Compound **11c**: 46%; mp 158–159 °C (AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$/DMSO-d_6): δ 9.50 (s, 1H, H-9), 9.47 (d, 1H, J=8.5 Hz, H-4), 9.18 (br s, 1H, H-2), 8.87 (s, 1H, H-6), 8.03 (br s, 2H, OH), 7.73–7.72 (m, 1H, H-3), 7.33 (t, 2H, J=7.3 Hz, H_{arom}), 7.70–6.98 (m, 3H, H_{arom}), 5.58 (s, 2H, CH_2); ^{13}C NMR (126 MHz, DMSO-d_6): δ 157.8, 152.6, 150.1, 146.8, 145.1, 135.8, 135.1, 131.5 (q, J_{CF}=30.1 Hz), 129.6, 129.6, 126.5, 124.1 (q, J_{CF}=278.0 Hz), 123.5, 123.5 (q, J_{CF}=291.8 Hz), 123.3, 121.6, 121.3, 114.8, 94.0 (q, J_{CF}=32.7 Hz), 65.7; IR (KBr, cm^{-1}): 3313, 3128; Anal. Calcd for $C_{22}H_{14}F_6N_2O_3$: C, 56.42; H, 3.01; N, 5.98. Found: C, 56.46; H, 3.16; N, 5.79.

*4.6.4. 1-(8-(4-Chlorophenoxymethyl)-7-trifluoromethyl-[1,10]phenanthrolin-5-yl)-2,2,2-trifluoroethane-1,1-diol (**11d**)*

Compound **11d**: 54%; mp 173–174 °C (AcOEt); ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.51 (s, 1H, H-9), 9.38 (d, 1H, J=8.1 Hz, H-4), 9.19 (br d, 1H, J=3.8 Hz, H-2), 8.79 (s, 1H, H-6), 8.48 (br s, 2H, OH), 7.89 (dd, 1H, J=3.8, 8.1 Hz, H-3), 7.41 (d, 2H, J=7.9 Hz, H_{arom}), 7.16 (d, 2H, J=7.9 Hz, H_{arom}), 5.62 (s, 2H, CH_2); ^{13}C NMR (126 MHz, DMSO-d_6): δ 156.8, 152.6, 150.2, 147.0, 145.1, 135.9, 135.2, 131.6 (q, J_{CF}=31.1 Hz), 129.4, 129.3, 126.6, 125.2, 124.2 (q, J_{CF}=278.0 Hz), 123.6, 123.5 (q, J_{CF}=290.5 Hz), 123.4, 121.7, 116.7, 94.1 (q, J_{CF}=32.7 Hz), 66.2; IR (KBr, cm^{-1}): 3346, 3126; Anal. Calcd for

$C_{22}H_{13}ClF_6N_2O_3$: C, 52.55; H, 2.61; N, 5.57. Found: C, 52.46; H, 2.82; N, 5.45.

Acknowledgements

We would like to thank the Japan Society for the Promotion of Science (JSPS) and the Centre National de la Recherche Scientifique (CNRS) for support of this research, the Direction des Relations Internationales (DRI) of the CNRS for travel funds (M.M.) and JSPS for a research fellowship (M.M.).

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