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Reduction of substituted 1,10-phenanthrolines as a route to rigid chiral benzimidazolylidenes

Costa Metallinos,[a,*] Fred B. Barrett,[a] Yao Wang,[a] Shufen Xu[a] and Nicholas J. Taylor[b]

[a]*Department of Chemistry, Brock University, 500 Glenridge Avenue, St. Catharines, Ontario L2S 3A1, Canada*
[b]*Department of Chemistry, University of Waterloo, 200 University Avenue West, Waterloo, Ontario N2L 3G1, Canada*

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Abstract—Variously substituted 1,10-phenanthrolines are reduced to octahydrophenanthrolines in moderate to good yields with $NaBH_3CN$ in acetic acid/methanol. The exact solvent composition is important to avoid the formation of tetrahydrophenanthrolines and *N*-alkylated by-products, and to optimize the formation of octahydrophenanthrolines. Resolution of a racemic reduction product gives an enantiomerically pure C_2-symmetric diamine from which the corresponding rigid benzimidazolylidene is prepared, whereas reduction of chiral phenanthrolines derived from bicyclic ketones affords diastereomerically pure diamines, which may also be converted to benzimidazolylidenes.
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1. Introduction

N-Heterocyclic carbenes (NHCs) with an imidazolidine framework can be classified into one of three general structural types: (a) saturated imidazolinylidenes (e.g., **1**, Fig. 1), (b) unsaturated imidazolylidenes (**2**), and (c) benzimidazolylidenes (**3**).[1] Imidazolylidenes and imidazolinylidenes are being extensively examined as reagents for asymmetric synthesis, although benzimidazolylidenes (**3**) have not been scrutinized to the same degree.[2] This may be because current synthetic approaches used to prepare benzimidazole-based NHCs are more limited, making the preparation of chiral analogs a challenging endeavor. Examples of chiral benzimidazolium salts that have been reported include α-methylbenzyl derivatives by Diver et al.[3,4] (**3a**,**b**, Fig. 2), acetonides **4** and **5** by Marshall et al.,[5] and Benaglia et al.,[6] and binaphthyl **6** by Duan et al.[7]

The preceding chiral NHCs are typically prepared by the introduction of one or two chiral substituents α to nitrogen by aryl amination,[3] or by quaternization[8,9] of the imidazole nitrogen. While analogous methods have been used to prepare chiral imidazolinylidene (**1**) and imidazolylidene NHCs (**2**),[10] existing methodology is less applicable for the preparation of chiral benzimidazolylidenes.[2] For example, chirality in the backbone of benzimidazolylidenes (**3**), such as in Grubbs' imidazolinylidene[11] **1**, is precluded by the presence of a fused aromatic ring. In addition, condensation of chiral amines with glyoxal, as in the preparation imidazolylidene **2**,[12,13] is not possible for benzimidazolylidenes. As a result, the current state-of-the-art for the synthesis of chiral benzimidazolylidenes such as **3** involves double Pd-catalyzed aryl amination of 1,2-dibromobenzene, followed by formylative ring closure.[3,4] The use of 2-nitrophenyl isocyanide, which holds promise for the synthesis of non-chiral benzimidazolylidenes, may not be adaptable to chiral derivatives.[14]

The main limitation of established routes to chiral benzimidazolylidenes is that chirality often occurs in freely-rotating acyclic pendant groups (**3a**,**b**), or in remote positions (**4**) that may not give well-defined chiral environments in catalytic processes (Fig. 2).[15] Consequently, chiral benzimidazolylidenes remain underrepresented as potential reagents for asymmetric synthesis, even though their electronic characteristics are intermediate between imidazolylidenes (**2**) and

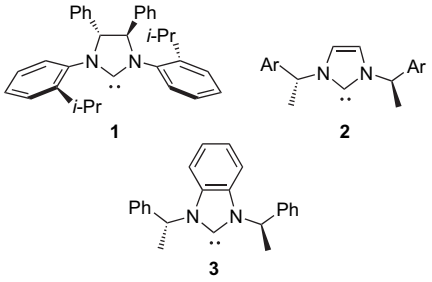

Figure 1. Examples of imidazolinylidenes (**1**), imidazolylidenes (**2**), and benzimidazolylidenes (**3**).

Keywords: Phenanthrolines; *N*-Heterocyclic carbenes; Benzimidazolylidenes; Reduction; Diastereoselective.
* Corresponding author. Tel.: +1 905 688 5550; fax: +1 905 682 9020; e-mail: metallic@brocku.ca

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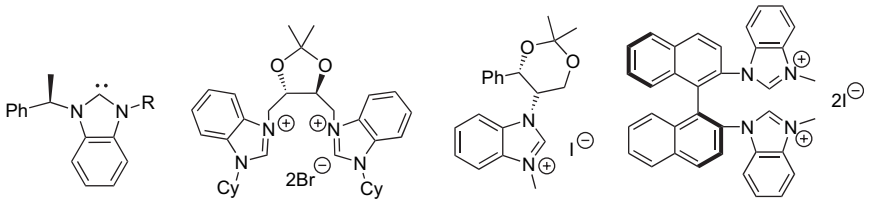


3a, R = CH(Me)Ph
3b, R = Ph
4 **5** **6**

Figure 2. Examples of chiral benzimidazolylidenes.

imidazolinylidenes (**1**).[3] In fact, benzimidazolylidenes have the advantage of being electronically tuneable by the introduction of substituents *para* to nitrogen on the aromatic ring.[16]

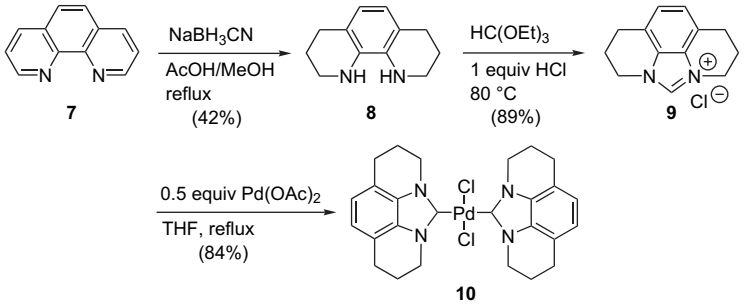
Given that free NHCs are often prepared by deprotonation of azolium salts,[8,9] new approaches toward the preparation of chiral benzimidazolium salts may lead to their structural diversification and increase their utility. The structural diversification of chiral benzimidazolylidenes is warranted considering that they have shown promise recently as organocatalysts[17,1c] and in Rh-catalyzed reductions,[7] and because they are vastly outnumbered[2] in comparison to imidazol(in)ylidenes for which desirable structural trends are emerging.[1]

Substituted 1,10-phenanthrolines have a rich history as ligands for transition-metal catalysis, but the majority of reported compounds retain the aromaticity of the entire tricyclic core.[18] Less attention has been directed toward the use of reduced phenanthrolines as precursors for new ligands.[19] It is known that nitrogen containing π-deficient heteroaromatics (pyridines, quinolines) undergo reduction to piperidines or tetrahydroquinolines under a wide range of conditions,[20,21] including the use of borohydrides in acid.[22] The use of borohydride reagents for the reduction of variously substituted 1,10-phenanthrolines to octahydrophenanthrolines has not been investigated, but is attractive in that the diamine products may serve as precursors to rigid benzimidazolium salts after treatment with orthoesters.

Previously, we have demonstrated the feasibility of this approach by synthesizing a catalytically active bis(benzimidazolylidene)palladium complex (**10**) in three steps from fully aromatic 1,10-phenanthroline (Scheme 1).[23,1a] The key step in the preparation of this ligand involved a convenient reduction of the pyridyl rings in 1,10-phenanthroline with sodium cyanoborohydride in refluxing AcOH/MeOH to provide octahydro-1,2,3,4,7,8,9,10-phenanthroline **8** in useful yield. This method precluded the need for high-pressure hydrogenation to prepare diamine **8**.[24] It was envisioned that the tetracyclic framework exemplified by **9** may serve as a prototype for the preparation of rigid chiral benzimidazolylidenes containing stereogenic centers α to nitrogen, but without freely-rotating pendant groups. In order to realize this potential, two questions first required an answer regarding the methodology: (a) could sterically encumbered phenanthrolines bearing substituents at the 2-, 2,9- and 2,3-positions (Scheme 4) be reduced with equal facility to the corresponding octahydrophenanthrolines using $NaBH_3CN$ in AcOH, and (b) could substituted phenanthrolines bearing chiral moieties be diastereoselectively reduced to provide stereochemically pure diamines for the preparation of structurally rigid benzimidazolylidenes. Herein we report the results of these studies.

2. Results and discussion

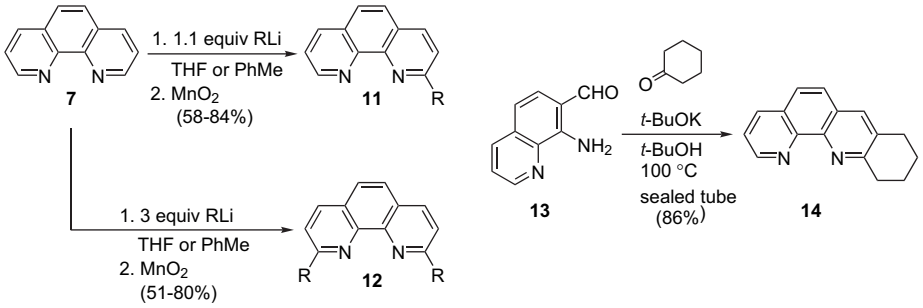
To answer the first question regarding the scope of the reduction conditions on substrates with greater steric demand than **7**, a series of 2-, 2,9- and 2,3-substituted 1,10-phenanthrolines were prepared by established methods such as nucleophilic aromatic substitution–oxidation for 2- and 2,9-derivatives, or de novo synthesis for 2,3-derivatives. Thus, treatment of **7** with 1.1 equiv of MeLi, BuLi, *i*-PrLi, PhLi or *t*-BuLi, in THF or toluene, followed by MnO_2 oxidation of the intermediate dihydro adducts, provided the required 2-substituted phenanthrolines **11** (Scheme 2).[25,26] Similarly, the 2,9-disubstituted phenanthrolines **12** were prepared by treatment of **7** with 3 equiv of MeLi, BuLi, *i*-PrLi or PhLi.[27] The 2,3-disubstituted derivatives were prepared via the Friedländer[28,29] reaction, as in the condensation of quinoline **13** with cyclohexanone.[30,31]



7 **8** **9**

10

Scheme 1. A benzimidazolylidene derived from octahydrophenanthroline.



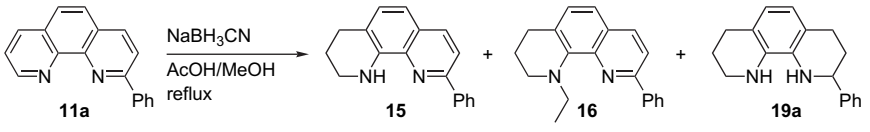
Scheme 2. Preparation of 2-, 2,9- and 2,3-substituted phenanthrolines.

2.1. Reduction of achiral 2-, 2,9- and 2,3-substituted phenanthrolines

Early investigations into the reduction of substituted compounds focused on optimizing the conditions required to reduce 2-phenyl-1,10-phenanthroline (**11a**, R=Ph) to the corresponding octahydrophenanthroline. Reduction of **11a** with $NaBH_3CN$ in 50:50 AcOH/MeOH gave tetrahydrophenanthroline **15** in 60% yield in which only the unsubstituted pyridyl ring was reduced (Scheme 3). In an attempt to force the reduction of the substituted ring, the reaction was repeated in neat AcOH. Under these conditions, only *N*-ethyltetrahydrophenanthroline **16** was isolated in 57% yield. These results mirror similar observations made by Gribble and Heald[22] in the $NaBH_4$/AcOH mediated reductive alkylation of tetrahydroquinoline **17** (Scheme 3), which afforded *N*-ethyltetrahydroquinoline (**18**). At first, the exclusive formation of **16** in neat AcOH implied that it would not be possible to reduce the phenyl-substituted ring under any conditions using $NaBH_3CN$. However, a series of experiments in which the solvent composition was varied by 10% increments from 50:50 AcOH/MeOH to neat AcOH revealed an interesting trend. Whereas products **15** and **16** were isolated exclusively using 50:50 AcOH/MeOH or neat AcOH, respectively, a mixture of **15** (43%) and the desired 2-phenyloctahydrophenanthroline **19a** (21%) was isolated using 60:40 AcOH/MeOH as the solvent medium. Using 70:30 AcOH/MeOH gave **15** and **19a** in 21 and 30% yields, respectively, while 80:20 AcOH/MeOH afforded predominantly the desired **19a** in 57% yield. Raising the acetic acid concentration to 90:10 resulted in a significant decrease in the yield of **19a** (18%), along with concomitant formation of **16** (17%).

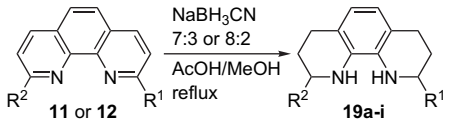
The preceding results indicate that the formation of tetrahydrophenanthroline **15** is relatively facile, but that two competing reactions occur on the initially formed intermediate depending on the proportion of acid present. In neat acetic acid, ethylation of the newly formed piperidyl nitrogen appears to proceed faster than reduction of the phenyl-substituted pyridyl ring, whereas utilizing proportionately less acetic acid (80%) allows reduction of the substituted pyridyl ring to predominate. The fact that *N*-ethylation inhibits further reduction of **16** may be tentatively attributed to the greater basicity of the *N*-ethyl piperidyl nitrogen compared to the remaining pyridyl nitrogen.

Based on the experiments performed on **11a**, the remaining 2- and 2,9-substituted phenanthrolines were subjected to reduction using a solvent mixture of either 70:30 or 80:20 AcOH/MeOH. Yields of racemic 2-substituted octahydrophenanthrolines ranged from 57% for 2-Me to 70% for 2-*i*-Pr (**19a–d**, Scheme 4). The 2-*tert*-Butyl-octahydrophenanthroline (**19e**) was produced in lower 23% yield, indicating a steric limitation in the reduction of these systems with $NaBH_3CN$.[22] When 2,9-disubstituted derivatives were subjected to the same reduction conditions, octahydrophenanthrolines **19f–i** were produced in yields of 62–73% as mixtures of *meso* and *rac* isomers. Reduction of 8,9,10,11-tetrahydro-benzo[*b*][1,10]phenanthroline (**14**) afforded the corresponding octahydrophenanthroline **20** as a mixture of *syn* and *anti* isomers in 54% yield. Thus, with the exception of **19e**, useful yields of octahydrophenanthrolines may be obtained by treatment of achiral 2-, 2,9- and 2,3-substituted phenanthrolines with $NaBH_3CN$ in AcOH/MeOH.

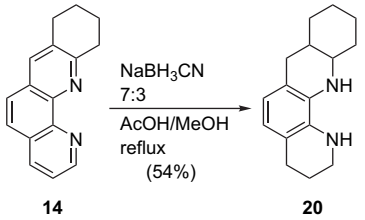


AcOH:MeOH	yld, % **15**	yld, % **16**	yld, % **19a**
50:50	60	0	0
60:40	43	0	21
70:30	21	0	30
80:20	<5	0	57
90:10	0	17	18
100:0	0	57	0

Scheme 3. Effect of solvent in the reduction of 2-phenyl-1,10-phenanthroline to 2-phenyl-1,2,3,4,7,8,9,10-octahydro-1,10-phenanthroline (**19a**).



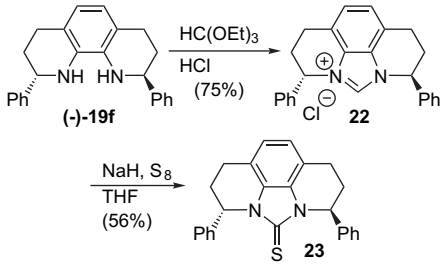
Compound	R^1	R^2	Prod.	yld, % **19**
11a	Ph	H	**19a**	57
11b	Me	H	**19b**	57
11c	*n*-Bu	H	**19c**	63
11d	*i*-Pr	H	**19d**	70
11e	*t*-Bu	H	**19e**	23
12a	Ph	Ph	**19f**	63
12b	Me	Me	**19g**	73
12c	*n*-Bu	*n*-Bu	**19h**	65
12d	*i*-Pr	*i*-Pr	**19i**	62



Scheme 4. Reduction of variously 2-, 2,9- and 2,3-substituted phenanthrolines.

2.2. Resolution of 2,9-diphenyloctahydrophenanthroline and NHC synthesis

Recently, Herrmann et al. have reported an expedient resolution of *rac*-2,2′-bipiperidine as a cyclic chiral phosphorus(V) adduct, prepared in one pot from PCl_3, (−)-menthol, and elemental sulfur.[32] This procedure is potentially applicable for the resolution of C_2-symmetric 2,9-substituted octahydrophenanthrolines (**19f–i**). As a test case, *meso*/*rac*-2,9-diphenyloctahydrophenanthroline (**19f**) was treated with PCl_3 which, following addition of (−)-menthol and S_8, afforded the analogous cyclic adducts **21a–c** (Scheme 5) as a mixture of three diastereomers in approximately equal amounts, as determined by ^{31}P NMR spectroscopy. Recrystallization of the crude mixture of adducts **21a–c** allowed for the purification of two of these diastereomers (**21a**,**b**), which were individually converted back to the free diamines **19f** with $LiAlH_4$ in refluxing THF. Of the separated diamines, the product derived from **21a** had a large negative optical



Scheme 6. A C_2-symmetric benzimidazolylidene derived from (−)-**19f** trapped as a thiourea (**23**).

rotation,[33] while the product derived from **21b** was optically inactive, indicating that it was *meso*-**19f**. Treatment of (−)-**19f** with triethyl orthoformate and HCl furnished the rigid C_2-symmetric benzimidazolium salt **22**, which was deprotonated and trapped with elemental sulfur to give thiourea **23**, thus indicating the generation of the putative free NHC (Scheme 6). The stereochemistry of **21a** was determined by X-ray crystallographic analysis (Fig. 3).

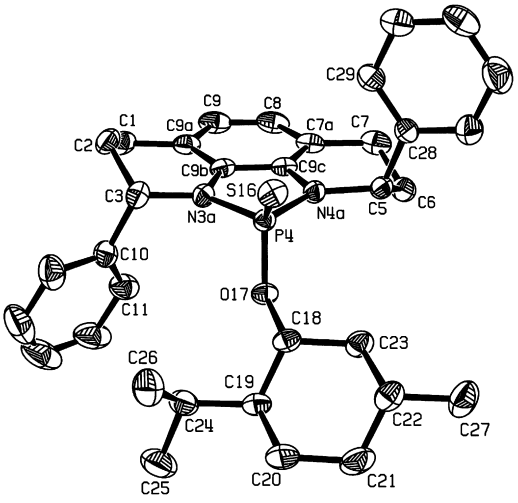
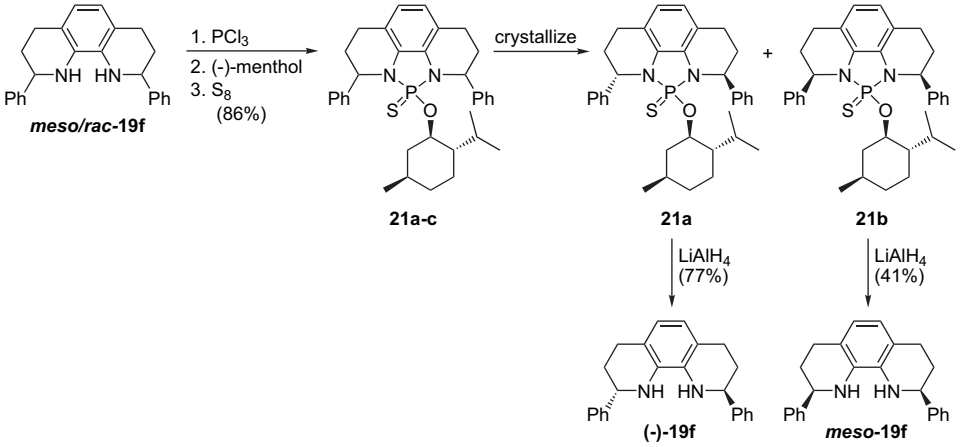


Figure 3. ORTEP® plot of **21a** at 30% probability. Hydrogen atoms are omitted for clarity.



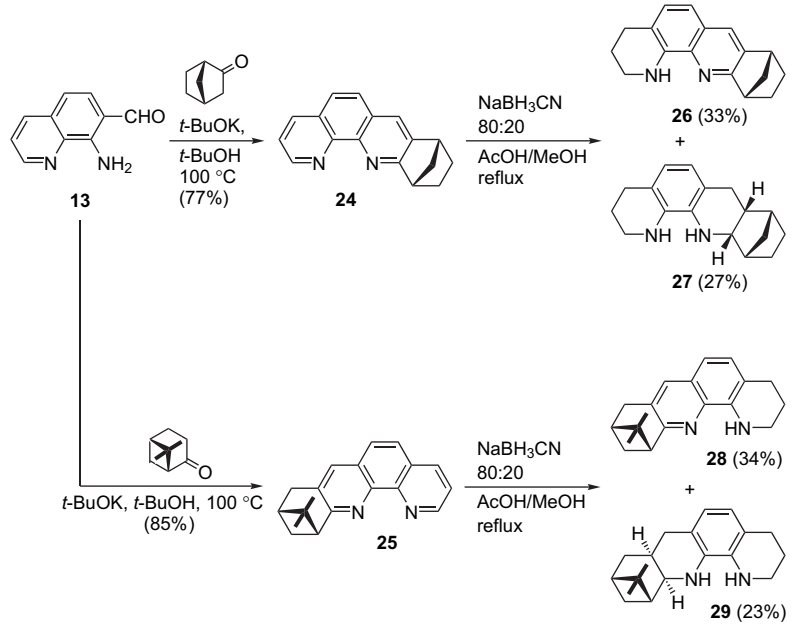
Scheme 5. Separation of (−)-**19f** and *meso*-**19f** via covalent diastereomers.

2.3. Benzimidazolylidenes derived from chiral 2,3-substituted phenanthrolines

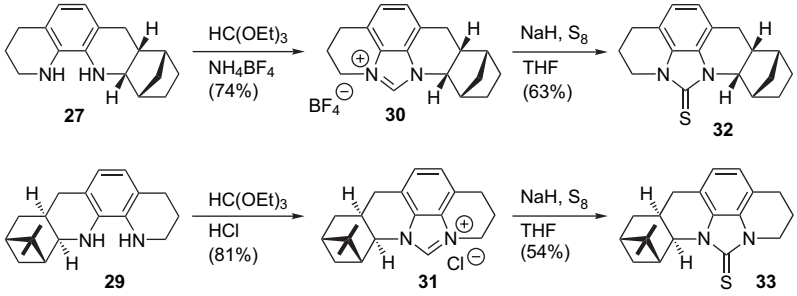
The introduction of chiral moieties into otherwise flat phenanthrolines normally involves de novo construction of the phenanthroline from chiral ketones,[34] analogous to the preparation of achiral cyclohexanone adduct **14**. Judicious selection of chiral bicyclic ketones with *endo* and *exo* faces would be expected to provide a degree of stereoselectivity during subsequent reduction to the octahydrophenanthrolines. This would avert the potentially tedious task of separating *syn* and *anti* diastereomers, as was the case in the reduction of **14**. For example, the bicyclic adduct derived by the Friedländer condensation of **13** with (+)-norcamphor (**24**, Scheme 7) would be expected to undergo hydride attack and protonation primarily from the *exo* face to afford the *syn* diastereomer. Similarly, reduction of the (+)-nopinone adduct[35] **25** ought to occur mainly from the '*endo*' face because of the presence of *exo* geminal methyl groups, also resulting in the selective formation of a *syn* diastereomer.

These predictions were borne out experimentally. Treatment of the norcamphor-derived phenanthroline **24** with $NaBH_3CN$ in 80:20 AcOH/MeOH provided the tetrahydrophenanthroline **26** (33%), along with the desired octahydrophenanthroline **27** (27%) *as a single diastereomer*, as determined by ^1H and ^{13}C NMR analyses. Reduction of the (+)-nopinone adduct **25** under the same conditions afforded the analogous products **28** and **29**. Examination of the ^1H and ^{13}C NMR spectra established that the reduction had been completely stereoselective, with only one product being discernible. All attempts to increase the yield[36] of **27** and **29** by performing the reduction in neat acetic acid resulted only in the formation of the corresponding *N*-ethylated tetrahydrophenanthrolines, as observed previously for **11a**.

Nevertheless, diamines **27** and **29** readily cyclized upon treatment with triethyl orthoformate and 1 equiv of acid (NH_4BF_4 or HCl) to the rigid chiral benzimidazolium salts **30** and **31** (Scheme 8). Deprotonation of these salts with NaH in the presence of elemental sulfur afforded thioureas **32** and **33** via the putative free NHCs. Spectroscopic analysis confirmed that the stereochemical integrity of the benzimidazolium salts was retained in the corresponding thioureas. Moreover, COSY and NOESY[37] experiments established the *syn* relative stereochemistry of **32** and **33**, as depicted



Scheme 7. Preparation and reduction of chiral 2,3-substituted phenanthrolines.



Scheme 8. Preparation of rigid chiral benzimidazolium salts and sulfur trapping experiments of their derived NHCs.

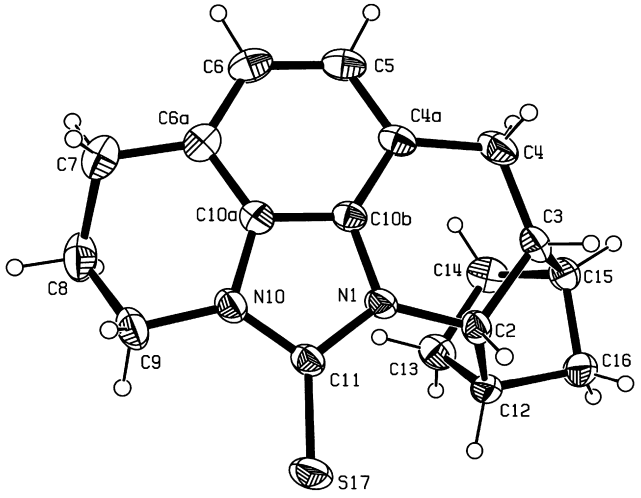


Figure 4. ORTEP® plot of **32** at 30% probability.

in Scheme 8, indicating that reduction of phenanthrolines **24** and **25** had occurred from the *exo* and *endo* faces, respectively. Crystals of **32** suitable for X-ray crystallographic analysis were grown and the molecular structure (Fig. 4) was obtained to verify the stereochemical assignment made by the COSY and NOESY experiments.[38]

3. Conclusions

It has been demonstrated that variously 2-, 2,9- and 2,3-substituted phenanthrolines may be reduced to octahydrophenanthrolines in useful yields with $NaBH_3CN$ in refluxing 7:3 or 8:2 AcOH/MeOH. Resolution of 2,9-diphenyloctahydrophenanthroline (**19f**) as a chiral phosphorus(V) adduct[33] gives access to a rigid C_2-symmetric benzimidazolylidene by deprotonation of the benzimidazolium salt (**22**). The reduction methodology may be extended to chiral phenanthrolines bearing bicyclic moieties, resulting in a high degree of diastereoselectivity by virtue of predominant *exo* (**24**) or *endo* (**25**) approach of the reagents (albeit in lower yields). The resulting optically active diamines may be cyclized to provide rigid chiral benzimidazolium salts, from which it is possible to generate the putative free NHCs with NaH, as indicated by trapping experiments with sulfur. The relative stereochemistry of thioureas **32** and **33** was established by COSY and NOESY NMR experiments, and for **32** it was further confirmed by X-ray analysis.[37]

We are currently exploring the resolution of C_2-symmetric amines **19h–i**, as well as the preparation of structurally more diverse 2- and 2,9-substituted octahydrophenanthrolines for the synthesis of additional NHCs in this series. Carbene precursors **22**, **30**, and **31**, and others derived by this approach, are under investigation as organocatalysts, and as ligands for transition-metal catalysis. A preliminary experiment has shown that ligand **22** and $Pd(dba)_2$ catalyze the formation of 1,3-dimethyl-3-phenyloxindole in an unoptimized 48% ee via the putative NHC–Pd complex. Previous chiral NHC-mediated syntheses of this compound have given 57 and 67% ee.[39] The outcome of this, and other studies, will be reported in due course.

4. Experimental

4.1. General

All reagents were purchased from Aldrich, Fisher Scientific, Acros or Strem and used as received unless otherwise indicated. Tetrahydrofuran (THF) was freshly dried and distilled over sodium/benzophenone ketyl under an atmosphere of nitrogen. Toluene was distilled over sodium under a nitrogen atmosphere. Dichloromethane was distilled over CaH_2 under an atmosphere of nitrogen. Organolithium reagents were titrated against *N*-benzylbenzamide[40] to a blue endpoint. All reactions were performed under argon in flame- or oven-dried glassware using syringe–septum cap techniques unless otherwise indicated. Column chromatography was performed on Silicycle silica gel 60 (70–230 mesh). NMR spectra were obtained on a Bruker Avance 300 or Avance 600 instrument and are referenced to TMS or to the residual proton signal of the deuterated solvent for ^1H spectra, and to the carbon multiplet of the deuterated solvent for ^{13}C spectra according to values given in *Spectrometric Identification of Organic Compounds, Seventh Edition*, pp 200 and 240. FTIR spectra were recorded on an ATI Mattson Research Series spectrometer. Low- and high-resolution mass spectral data were obtained on a Kratos Concept 1S Double Focusing spectrometer. Optical rotations were measured on a Rudolph Research Autopol III automatic polarimeter. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA, USA. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected.

4.1.1. 2-Isopropyl-1,10-phenanthroline (11d). A stirred solution of anhyd 1,10-phenanthroline (1.00 g, 5.55 mmol) in PhMe (40 mL) at ambient temperature under argon was treated with a solution of isopropyllithium[41] (3.61 mL, 1.69 M in THF, 6.10 mmol). The resulting dark red solution was stirred for 16 h, cooled to 0 °C, and worked-up by addition of water (20 mL). The organic layer was separated and the remaining aqueous layer was extracted with CH_2Cl_2 (3×10 mL). The combined organic layer was treated with MnO_2[42] (4 g, 46 mmol) and stirred for 30 min, after which anhyd $MgSO_4$ was added, and stirring continued for an additional 30 min. The resulting mixture was filtered and concentrated in vacuo. Column chromatography (neutral alumina, 69:30:1 hexanes/EtOAc/Et_3N, R_f=0.33) afforded **11d** (745 mg, 60%) as a pale yellow oil; IR (KBr, neat): ν_{max} 3045, 2963, 2928, 2869 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.22 (dd, 1H, J=4.3, 1.6 Hz), 8.22–8.16 (m, 2H), 7.74 (d, 1H, J=8.9 Hz), 7.69 (d, 1H, J=8.8 Hz), 7.61–7.56 (m, 2H), 3.68 (septet, 1H, J=7.0 Hz), 1.46 (d, 6H, J=7.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 168.4, 150.1, 146.0, 145.2, 136.4, 135.9, 128.6, 127.0, 126.3, 125.4, 122.4, 119.9, 37.5, 23.0; EIMS [m/z (%)]: 222 (M^+, 44), 207 (100); HRMS (EI) calcd for $C_{15}H_{14}N_2$: 222.1157, found: 222.1161.

4.1.2. 2,9-Diisopropyl-1,10-phenanthroline (12d). A stirred solution of anhyd 1,10-phenanthroline (1.00 g, 5.55 mmol) in PhMe (40 mL) at ambient temperature under argon was treated with a solution of isopropyllithium (9.9 mL, 1.69 M in THF, 16.6 mmol). The resulting dark red solution was stirred for 16 h, cooled to 0 °C, and worked-up by addition of water (20 mL). The organic layer was

separated and the remaining aqueous layer was extracted with CH_2Cl_2 (3×10 mL). The combined organic layer was treated with MnO_2 (4 g, 46 mmol) and stirred for 30 min, after which anhyd $MgSO_4$ was added, and stirring continued for an additional 30 min. The resulting mixture was filtered and concentrated in vacuo. Column chromatography (silica gel, 85:15 hexanes/EtOAc, R_f=0.22) afforded **12d** (753 mg, 51%) as a pale yellow oil; IR (KBr): ν_{max} 3041, 2963, 2928, 2869 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.13 (d, 2H, J=8.3 Hz), 7.67 (s, 2H), 7.54 (d, 2H, J=8.4 Hz), 3.57 (septet, 2H, J=6.9 Hz), 1.48 (d, 12H, J=7.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 167.7, 145.1, 136.3, 127.2, 125.3, 120.0, 37.2, 22.8; EIMS [m/z (%)]: 264 (M^+, 44), 249 (49); HRMS (EI) calcd for $C_{18}H_{20}N_2$: 264.1626, found: 264.1619.

4.1.3. (+)-2,3-(Bicyclo[2.2.1]heptanyl)-1,10-phenanthroline (24). A solution of aminoaldehyde **13** (600 mg, 3.49 mmol) and (+)-norcamphor[43] (386 mg, 3.50 mmol) in saturated *t*-BuOK/*t*-BuOH (6 mL) was heated to 100 °C in a sealed tube for 5 h. After cooling to room temperature, the solvent was removed in vacuo, and the residue was taken up in CH_2Cl_2 (20 mL). The organic phase was washed with water (3×5 mL), brine, dried over anhyd Na_2SO_4, and concentrated in vacuo. Column chromatography (neutral alumina, 98:2 EtOAc/Et_3N, R_f=0.43) gave phenanthroline **24** (658 mg, 77%) as a pale yellow solid; mp>200 °C (sublimes); $[\alpha]_D^{18}$ +78.4 (c 1.0, $CHCl_3$); IR (KBr): ν_{max} 2973, 2869, 1499, 1383 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.21–9.19 (m, 1H), 8.25 (dd, 1H, J=8.1, 1.0 Hz), 7.88 (s, 1H), 7.75 (ABq, 2H), 7.59 (dd, 1H, J=8.1, 4.5 Hz), 3.89 (s, 1H), 3.62 (s, 1H), 2.17–2.09 (m, 2H), 2.02–1.98 (m, 1H), 1.79–1.76 (m, 1H), 1.54 (t, 1H, J=7.2 Hz), 1.36 (t, 1H, J=6.9 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 170.7, 149.8, 145.8, 143.6, 142.1, 136.0, 128.0, 127.7, 126.0, 126.2, 124.8, 122.1, 47.5, 45.6, 42.4, 27.1, 25.5; EIMS [m/z (%)]: 246 (M^+, 93), 218 (100); HRMS (EI) calcd for $C_{17}H_{14}N_2$: 246.1157, found: 246.1158; Anal. Calcd for $C_{17}H_{14}N_2$: C, 82.91; H, 5.73. Found: C, 82.67; H, 5.78.

4.1.4. (1*R*,5*S*)-(2,3-*b*)-Pineno-1,10-phenanthroline (25). Prepared by a modification of the procedure of Thummel et al.[30] A solution of aminoaldehyde **13** (1.00 g, 5.81 mmol) and (+)-nopinone (803 mg, 5.81 mmol) in saturated *t*-BuOK/*t*-BuOH (10 mL) was heated to 100 °C in a sealed tube for 5 h. After cooling to room temperature, the solvent was removed in vacuo and the residue was taken up in CH_2Cl_2 (20 mL). The organic phase was washed with water (3×10 mL), brine, dried over anhyd Na_2SO_4, and concentrated in vacuo. Column chromatography (neutral alumina, 60:40 hexanes/EtOAc, R_f=0.18) gave phenanthroline **25** (1.35 g, 85%) as a pale yellow solid; mp 167–169 °C (lit.[30] 168–170 °C); ^1H NMR (300 MHz, $CDCl_3$): δ 9.18–9.16 (m, 1H), 8.24–8.21 (m, 1H), 7.95 (s, 1H), 7.73 (ABq, 2H), 7.57 (dd, 1H, J=8.1, 4.5 Hz), 3.62 (t, 1H, J=5.4 Hz), 3.20 (s, 2H), 2.85–2.82 (m, 1H), 2.43–2.41 (m, 1H), 1.48 (s, 3H), 1.41 (d, 1H, J=9.9 Hz), 0.73 (s, 3H).

4.1.5. *rac*-2-Methyl-1,2,3,4,7,8,9,10-octahydro-1,10-phenanthroline (19b). *Typical procedure*: a round-bottomed flask containing a rapidly stirred solution of **11b** (550 mg, 2.83 mmol) in glacial acetic acid (18 mL) and methanol (7 mL) was treated with an equal mass of $NaBH_3CN$ (550 mg, 8.8 mmol) in portions over 5 min. A reflux condenser was attached and the resulting deep red mixture heated to reflux. After 2 h, an additional 550 mg portion of $NaBH_3CN$ was added, a process that was repeated every 2 h for 4 more hours (2.2 g of $NaBH_3CN$ was added in total). Two hours after the last addition of $NaBH_3CN$, a color change from deep red to orange was observed, indicating completion of the reduction. The solution was cooled to room temperature and the majority of the methanol was removed on a rotary evaporator in vacuo. The resulting mixture was treated with 6 M aq NaOH (50 mL) and the whole was extracted with CH_2Cl_2 (4×10 mL). The combined organic extract was washed with water, brine, dried over anhyd Na_2SO_4, filtered, and concentrated in vacuo. Column chromatography (silica gel, 85:15 hexanes/EtOAc, R_f=0.24) gave diamine **19b** (315 mg, 57%) as a clear oil; IR (KBr, neat): ν_{max} 3342, 2924, 2843, 1581, 1485, 1331, 1255 cm^{-1}; ^1H NMR (600 MHz, acetone-d_6): δ 6.25 (d, 1H, J=7.2 Hz), 6.23 (d, 1H, J=9.0 Hz), 3.65 (br, 1H), 3.56 (br, 1H), 3.29–3.23 (m, 3H), 2.82–2.71 (m, 1H), 2.65–2.57 (m, 3H), 1.89–1.84 (m, 1H), 1.80 (quintet, 2H, J=6.0 Hz), 1.48–1.41 (m, 1H), 1.20 (d, 3H, J=6.3 Hz); ^{13}C NMR (150.9 MHz, acetone-d_6): δ 133.6, 133.0, 119.9, 119.4, 119.0, 118.8, 48.4, 43.1, 31.3, 27.9, 27.6, 23.3, 22.8; EIMS [m/z (%)]: 202 (M^+, 100); HRMS (EI) calcd for $C_{13}H_{18}N_2$: 202.1470, found: 202.1466.

4.1.6. *rac*-2-Phenyl-1,2,3,4,7,8,9,10-octahydro-1,10-phenanthroline (19a). According to the *typical procedure*, a solution of **11a** (256 mg, 1.00 mmol) in glacial acetic acid (8 mL) and MeOH (2 mL) was treated with $NaBH_3CN$ (256 mg, 4.07 mmol), and the reaction mixture was heated to reflux. Three subsequent additions of $NaBH_3CN$ (256 mg each) were made every 2 h for over 6 h total. Standard workup and column chromatography (silica gel, 90:10 hexanes/EtOAc, R_f=0.15) gave diamine **19a** (150 mg, 57%) as a colorless solid; mp 90–91 °C; IR (KBr): ν_{max} 3347, 3283, 3023, 2935, 2922, 2839, 1614, 1581, 1492, 1439, 1331, 1252 cm^{-1}; ^1H NMR (300 MHz, acetone-d_6): δ 7.41 (d, 2H, J=7.6 Hz), 7.32 (t, 2H, J=8.7 Hz), 7.25 (t, 1H, J=7.2 Hz), 6.31–6.28 (ABq, 2H), 4.39 (d, 1H, J=8.9 Hz), 3.95 (br, 1H), 3.92 (br, 1H), 3.31–3.22 (m, 2H), 2.85–2.80 (m, 2H), 2.70–2.65 (m, 2H), 2.58 (dt, 1H, J=15.6, 5.6 Hz), 2.03–2.01 (m, 1H), 1.91–1.85 (m, 1H), 1.81 (quintet, 2H, J=6.0 Hz); ^{13}C NMR (75.5 MHz, acetone-d_6): δ 146.4, 133.5, 132.9, 129.1, 127.8, 127.4, 120.3, 119.3, 119.2, 118.8, 57.1, 43.1, 31.8, 28.0, 27.2, 23.3; EIMS [m/z (%)]: 264 (M^+, 100), 187 (15); HRMS (EI) calcd for $C_{18}H_{20}N_2$: 264.1626, found: 264.1627.

4.1.7. *rac*-2-*n*-Butyl-1,2,3,4,7,8,9,10-octahydro-1,10-phenanthroline (19c). According to the *typical procedure*, a solution of **11c** (365 mg, 1.54 mmol) in glacial acetic acid (7 mL) and MeOH (3 mL) was treated with $NaBH_3CN$ (365 mg, 5.8 mmol), and the reaction mixture was heated to reflux. Three subsequent additions of $NaBH_3CN$ (365 mg each) were made every 2 h for over 6 h total. Standard workup and column chromatography (silica gel, 90:8:2 hexanes/EtOAc/Et_3N, R_f=0.67) gave diamine **19c** (236 mg, 63%) as a pale yellow oil; IR (KBr, neat): ν_{max} 3337, 2926, 2853, 1583, 1486, 1348, 1252 cm^{-1}; ^1H NMR (300 MHz, acetone-d_6): δ 6.27–6.22 (ABq, 2H), 3.77 (br, 1H), 3.50 (br, 1H), 3.27–3.24 (m, 2H), 3.14–3.12 (m, 1H), 2.77–2.55

(m, 4H), 1.93–1.86 (m, 1H), 1.81 (quintet, 2H, J=6.0 Hz), 1.58–1.30 (m, 7H), 0.92 (t, 3H, J=7.2 Hz); ^{13}C NMR (75.5 MHz, acetone-d_6): δ 133.5, 133.1, 120.0, 119.7, 119.0, 118.8, 52.8, 43.1, 37.2, 29.2, 28.7, 27.9, 27.4, 23.6, 23.3, 14.4; EIMS [m/z (%)]: 244 (M^+, 55), 187 (100); HRMS (EI) calcd for $C_{16}H_{24}N_2$: 244.1939, found: 244.1935.

4.1.8. *rac*-2-Isopropyl-1,2,3,4,7,8,9,10-octahydro-1,10-phenanthroline (19d). According to the *typical procedure*, a solution of **11d** (105 mg, 0.47 mmol) in glacial acetic acid (7 mL) and MeOH (3 mL) was treated with $NaBH_3CN$ (105 mg, 1.67 mmol), and the reaction mixture was heated to reflux. Three subsequent additions of $NaBH_3CN$ (105 mg each) were made every 2 h for over 6 h total. Standard workup and column chromatography (silica gel, 88:10:2 hexanes/EtOAc/Et_3N, R_f=0.22) gave diamine **19d** (76 mg, 70%) as a pale yellow oil; IR (KBr, neat): ν_{max} 3339, 3037, 2954, 2927, 2870, 2841, 1583, 1485, 1437, 1347, 1256 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6): δ 6.26 (d, 1H, J=7.8 Hz), 6.23 (d, 1H, J=8.1 Hz), 3.81 (br, 1H), 3.48 (br, 1H), 3.31–3.18 (m, 2H), 2.98–2.92 (m, 1H), 2.72–2.62 (m, 4H), 1.90–1.69 (m, 4H), 1.55–1.50 (m, 1H), 1.00 (d, 3H, J=6.9 Hz), 0.98 (d, 3H, J=6.9 Hz); ^{13}C NMR (75.5 MHz, acetone-d_6): δ 133.8, 133.1, 120.1, 119.8, 119.0, 118.8, 58.5, 43.1, 33.3, 27.9, 27.6, 25.5, 23.3, 19.0, 18.6; EIMS [m/z (%)]: 230 (M^+, 28), 187 (100); HRMS (EI) calcd for $C_{15}H_{22}N_2$: 230.1783, found: 230.1795.

4.1.9. *rac*-2-*tert*-Butyl-1,2,3,4,7,8,9,10-octahydro-1,10-phenanthroline (19e). According to the *typical procedure*, a solution of **11e** (171 mg, 0.75 mmol) in glacial acetic acid (8 mL) and MeOH (2 mL) was treated with $NaBH_3CN$ (177 mg, 2.82 mmol), and the reaction mixture was heated to reflux. Three subsequent additions of $NaBH_3CN$ (177 mg each) were made every 2 h for over 6 h total. Standard workup and column chromatography (silica gel, 90:10 hexanes/EtOAc, R_f=0.32) gave diamine **19e** (42 mg, 23%) as a colorless solid; mp 71–72 °C; IR (KBr): ν_{max} 3346, 3300, 2955, 2933, 2851, 1614, 1582, 1475, 1429, 1335 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6): δ 6.27 (d, 1H, J=7.2 Hz), 6.24 (d, 1H, J=7.8 Hz), 3.82 (br, 1H), 3.44 (br, 1H), 3.28–3.21 (m, 2H), 2.86 (dt, 1H, J=10.8, 2.4 Hz), 2.79–2.56 (m, 4H), 1.99–1.93 (m, 1H), 1.83–1.74 (m, 2H), 1.53–1.41 (m, 1H), 0.99 (s, 9H); ^{13}C NMR (75.5 MHz, acetone-d_6): δ 134.3, 133.2, 120.3, 120.0, 119.0, 118.7, 62.2, 43.1, 34.1, 28.3, 27.9, 26.3, 24.2, 23.3; EIMS [m/z (%)]: 244 (M^+, 18), 187 (100); HRMS (EI) calcd for $C_{16}H_{24}N_2$: 244.1939, found: 244.1942.

4.1.10. *meso*/*rac*-2,9-Diphenyl-1,2,3,4,7,8,9,10-octahydro-1,10-phenanthroline (19f). According to the *typical procedure*, a solution of **12a** (250 mg, 0.75 mmol) in glacial acetic acid (8 mL) and MeOH (2 mL) was treated with $NaBH_3CN$ (250 mg, 3.98 mmol), and the reaction mixture was heated to reflux. Three subsequent additions of $NaBH_3CN$ (250 mg each) were made every 2 h for over 6 h total. Standard workup and column chromatography (silica gel, 96:4 hexanes/EtOAc, R_f=0.38) gave diamine **19f** (161 mg, 63%), a pale yellow solid, as a mixture of stereoisomers; mp 107–110 °C; IR (KBr): ν_{max} 3339, 3030, 2944, 2919, 2835, 1580, 1473, 1420, 1335, 1252 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6): δ 7.39 (d, 4H, J=7.0 Hz), 7.30 (t, 4H, J=7.0 Hz), 7.22 (d, 2H, J=7.2 Hz), 6.35 (s, 2H), 4.43–4.40 (m, 2H), 4.25 (br, 2H), 2.91–2.75 (m, 4H), 2.61 (dt, 2H, J=15.9, 5.2 Hz), 1.97–1.88 (m, 2H); ^{13}C NMR (75.5 MHz, acetone-d_6): δ 146.3, 132.8, 129.0, 127.7, 127.4, 119.6, 118.9, 57.0, 31.4, 26.9; EIMS [m/z (%)]: 340 (M^+, 54); HRMS (EI) calcd for $C_{24}H_{24}N_2$: 340.1939, found: 340.1942; Anal. Calcd for $C_{24}H_{24}N_2$: C, 84.67; H, 7.11. Found: C, 84.35; H, 7.10.

4.1.11. *meso*/*rac*-2,9-Dimethyl-1,2,3,4,7,8,9,10-octahydro-1,10-phenanthroline (19g). According to the *typical procedure*, a solution of neocuproine **12b** (217 mg, 1.00 mmol) in glacial acetic acid (3.5 mL) and MeOH (1.5 mL) was treated with $NaBH_3CN$ (217 mg, 3.45 mmol), and the reaction mixture was heated to reflux. Three subsequent additions of $NaBH_3CN$ (217 mg each) were made every 2 h for over 6 h total. Standard workup and column chromatography (silica gel, 92:8 PhMe/Et_3N, R_f=0.22) gave **19g** (158 mg, 73%), a colorless solid, as a 1:1 mixture of *meso* and *rac* stereoisomers; mp 63–65 °C; IR (KBr): ν_{max} 3324, 3036, 2959, 2918, 2839, 1582, 1480, 1446, 1334, 1255 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6): δ 6.23 (s, 2H), 3.64 (br, 1H), 3.55 (br, 1H), 3.31–3.23 (m, 2H), 2.78–2.54 (m, 4H), 1.87–1.82 (m, 2H), 1.48–1.38 (m, 2H), 1.18 (d, 3H, J=6.3 Hz), 1.17 (d, 3H, J=6.3 Hz); ^{13}C NMR (75.5 MHz, acetone-d_6): δ 133.1, 133.0, 119.4, 119.3, 118.8, 118.7, 48.4, 48.3, 31.2, 27.5, 27.5, 22.9, 22.7; FABMS [m/z (%)]: 216 (M^+, 100); HRMS (FAB) calcd for $C_{14}H_{20}N_2$: 216.1626, found: 216.1619.

4.1.12. *meso*/*rac*-2,9-Di-*n*-butyl-1,2,3,4,7,8,9,10-octahydro-1,10-phenanthroline (19h). According to the *typical procedure*, a solution of **12c** (236 mg, 0.81 mmol) in glacial acetic acid (7 mL) and MeOH (3 mL) was treated with $NaBH_3CN$ (236 mg, 3.76 mmol), and the reaction mixture was heated to reflux. Three subsequent additions of $NaBH_3CN$ (236 mg each) were made every 2 h for over 6 h total. Standard workup and column chromatography (silica gel, 94:5:1 hexanes/EtOAc/Et_3N, R_f=0.14) gave **19h** (156 mg, 65%), a colorless oil, as a 1:1 mixture of *meso* and *rac* stereoisomers; IR (KBr, neat): ν_{max} 3339, 3038, 2953, 2926, 2869, 2855, 1584, 1482, 1438, 1347, 1258 cm^{-1}; ^{1}H NMR (600 MHz, acetone-d_6): δ 6.26 (s, 1H), 6.25 (s, 1H), 3.57 (br, 1H), 3.48 (br, 1H), 3.16–3.11 (m, 2H), 2.79–2.67 (m, 2H), 2.63–2.59 (m, 2H), 1.92–1.89 (m, 2H), 1.57–1.34 (m, 12H), 0.92 (t, 6H, J=6.9 Hz); ^{13}C NMR (75.5 MHz, acetone-d_6): δ 133.2, 133.2, 120.0, 119.9, 119.0, 118.8, 52.9, 52.8, 37.2, 37.1, 29.1, 29.0, 28.9, 28.7, 23.6, 23.6, 14.4; EIMS [m/z (%)]: 300 (M^+, 72), 243 (89), 239 (100); HRMS (EI) calcd for $C_{20}H_{32}N_2$: 300.2565, found: 300.2561.

4.1.13. *meso*/*rac*-2,9-Diisopropyl-1,2,3,4,7,8,9,10-octahydro-1,10-phenanthroline (19i). According to the *typical procedure*, a solution of **12d** (233 mg, 0.88 mmol) in glacial acetic acid (8 mL) and MeOH (2 mL) was treated with $NaBH_3CN$ (233 mg, 3.71 mmol), and the reaction mixture was heated to reflux. Three subsequent additions of $NaBH_3CN$ (233 mg each) were made every 2 h for over 6 h total. Standard workup and column chromatography (silica gel, 94:5:1 hexanes/EtOAc/Et_3N, R_f=0.22) gave a diamine **19i** (149 mg, 62%), a colorless solid, as an unequal mixture of *meso* and *rac* stereoisomers; mp 49–50 °C; IR (KBr): ν_{max} 3352, 3041, 2959, 2915, 2873, 2836, 1586, 1483, 1432, 1336, 1261 cm^{-1}; ^{1}H NMR (300 MHz,

acetone-d_6): δ 6.27 (s, 2H), 3.45 (br, 2H), 2.92 (br, 2H), 2.70–2.63 (m, 4H), 1.90–1.80 (m, 2H), 1.78–1.69 (m, 2H), 1.60–1.44 (m, 2H), 1.02 (d, 6H, J=6.9 Hz), 0.98 (d, 6H, J=6.6 Hz); ^{13}C NMR (75.5 MHz, acetone-d_6): δ 133.6, 133.5, 120.2, 118.9, 118.8, 58.6, 58.5, 33.3, 33.1, 27.5, 27.4, 25.4, 25.3, 19.3, 19.0, 18.7, 18.4; EIMS [m/z (%)]: 272 (M^+, 33), 229 (79), 126 (100), 98 (90); HRMS (FAB) calcd for $C_{18}H_{28}N_2$: 272.2252, found: 272.2242.

4.1.14. *syn/anti*-1,2,3,4,7,7a,8,9,10,11,11a,12-Dodecahydro-benzo[*b*][1,10]phenanthroline (20). According to the *typical procedure*, a solution of **14** (117 mg, 0.50 mmol) in glacial acetic acid (3.5 mL) and MeOH (1.5 mL) was treated with $NaBH_3CN$ (117 mg, 1.86 mmol), and the reaction mixture was heated to reflux. Three subsequent additions of $NaBH_3CN$ (117 mg each) were made every 2 h for over 6 h total. Standard workup and column chromatography (silica gel, 90:10 hexanes/EtOAc, R_f=0.33) gave diamine **20** (66 mg, 54%), a pale yellow solid, as a mixture of *syn* and *anti* isomers; mp 95–105 °C; IR (KBr): ν_{max} 3345, 3033, 2921, 2851, 1581, 1487, 1433 cm^{-1}; ^{1}H NMR (600 MHz, acetone-d_6, major diastereomer as determined by HSQC): δ 6.26 (s, 2H), 3.73 (br, 1H), 3.49 (br, 1H), 3.26–3.22 (m, 2H), 2.84–2.80 (m, 1H), 2.73 (td, 1H, J=10.8, 3.6 Hz), 2.63 (t, 2H, J=6.6 Hz), 2.52 (dd, 1H, J=15.6, 5.4 Hz), 2.36 (dd, 1H, J=16.2, 11.4 Hz), 1.99–1.96 (m, 1H), 1.81–1.70 (m, 5H), 1.40–1.31 (m, 4H); ^{13}C NMR (150.9 MHz, acetone-d_6, major diastereomer as determined by HSQC and DEPT): δ 133.2, 132.8, 119.9, 119.8, 119.0, 118.7, 57.2, 43.0, 38.6, 35.6, 34.3, 32.9, 27.9, 26.8, 25.6, 23.3; EIMS [m/z (%)]: 242 (M^+, 100); HRMS (EI) calcd for $C_{16}H_{22}N_2$: 242.1783, found: 242.1777.

4.2. 4-[(1*R*,2*S*,5*R*)-Menthyloxy)]-3,5-diphenyl-1,2,3,5,6,7-hexahydro-3a,4a-diaza-4-phosphacyclopenta[*def*]phenanthrene 4-sulfide (21a–c)

A solution of **19f** (1.25 g, 3.67 mmol) and dimethylaniline (2.6 mL, 20.2 mmol) in CH_2Cl_2 (13 mL) under argon was treated with PCl_3 (0.32 mL, 3.7 mmol), added dropwise by syringe. The resulting yellow solution darkened and evolved heat for 15 min, at which point a reflux condenser was attached and the mixture heated to reflux under argon. After 1 h, (−)-menthol (573 mg, 3.67 mmol) was added in one portion from the top of the condenser and reflux was continued. After 1 h, S_8 (1.18 g, 36.7 mmol) was added in one portion and the mixture was refluxed for an additional 25 min. The solvent was removed in vacuo and the residue was suspended in 8 M aq HCl (25 mL). The aqueous phase was extracted with Et_2O (3×25 mL), and the combined organic extract was dried over anhyd Na_2SO_4, filtered, and concentrated in vacuo. Column chromatography (silica gel, first with hexanes to remove S_8, then 96:4 hexanes/EtOAc) gave **21a–c** (1.76 g, 86%), a pale yellow solid, as an approximately 1:1:1 mixture of three stereoisomers as determined by ^{31}P NMR [δ 69.7 (**21a**), 64.4 (**21b**), 66.4 (**21c**)]. The mixture of stereoisomers was suspended in abs MeOH (115 mL) and heated to reflux for 4 h. Hot filtration of the mixture afforded enriched **21a** (404 mg). Recrystallization from pentane/CH_2Cl_2 gave the pure **21a** diastereomer (353 mg). The filtrate was concentrated to approximately half the original volume in vacuo and standing at room temperature afforded crystals of **21b** (100 mg), which were collected by filtration. Concentration of the remaining mother liquor gave a residue that was enriched in **21c**; attempts to recrystallize **21c** from several solvents did not afford **21c** completely free of **21a** and **21b**.

4.2.1. Compound 21a. Pale yellow solid; mp 225–227 °C (pentane/CH_2Cl_2); $[\alpha]_D^{18}$ −249 (c 1.0, $CHCl_3$); X-ray analysis (CCDC 612643) was performed on a colorless plate fragment (0.40×0.21×0.10 mm), which was obtained by recrystallization from pentane/CH_2Cl_2. $C_{34}H_{41}N_2OPS$: M=556.74 g/mol, orthorhombic, $P2_12_12_1$, a=6.5541(4) Å, b=21.0909(13) Å, c=21.9930(14) Å, V=3040.1(3) Å^3, Z=4, D_c=1.216 g/cm^3, $F(000)$=1192, T=295(2) K. Data were collected on a Bruker APEX CCD system with graphite monochromated Mo Kα radiation (λ=0.71073 Å), 25,619 data were collected. The structure was solved by Patterson and Fourier (SHELXTL) and refined by full-matrix least squares on F^2 resulting in final R, R_w, and GOF [for 6612 data with $F>2\sigma(F)$] of 0.0583, 0.0733, and 1.621, respectively, for solution using the 3*S*,5*S* model, Flack parameter=0.00(6); IR (KBr): ν_{max} 3054, 3029, 2948, 2919, 2865, 1471, 1289, 1152, 1110 cm^{-1}; ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 69.7; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31–7.11 (m, 10H), 6.57 (s, 2H), 5.34–5.28 (m, 1H), 5.18–5.13 (m, 1H), 4.20 (qd, 1H, J=10.5, 4.2 Hz), 2.62–2.57 (m, 1H), 2.52–2.39 (m, 2H), 2.34–2.06 (m, 5H), 1.60–1.58 (m, 2H), 1.47–1.35 (m, 2H), 1.18–1.07 (m, 1H), 1.02–0.98 (m, 1H), 0.94 (d, 3H, J=6.9 Hz), 0.88–0.67 (m, 3H), 0.30 (d, 3H, J=6.9 Hz), 0.25 (d, 3H, J=6.9 Hz); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 142.9, 141.3, 128.5, 128.4, 128.1, 127.1, 127.0, 126.4, 126.3, 117.85, 117.82, 117.25, 117.21, 116.8, 116.7, 80.9 (d, $^2J_{^{13}C-^{31}P}$ = 8.8 Hz), 52.69, 52.66, 47.31, 47.25, 44.2, 33.9, 31.5, 30.3, 30.2, 29.91, 29.87, 24.4, 22.3, 22.2, 20.9, 19.52, 19.48, 15.2; EIMS [m/z (%)]: 556 (M^+, 12), 418 (100); HRMS (EI) calcd for $C_{34}H_{41}N_2OPS$: 556.2677, found: 556.2674.

4.2.2. Compound 21b. Pale yellow solid; mp 230–231 °C (MeOH/$CHCl_3$); $[\alpha]_D^{18}$ −17 (c 0.23, $CHCl_3$); IR (KBr): ν_{max} 3050, 3026, 2927, 2867, 2857, 1470, 1291, 1168, 1110 cm^{-1}; ^{31}P NMR (243 MHz, $CDCl_3$): δ 64.4; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32–7.28 (m, 4H), 7.25–7.21 (m, 4H), 7.19 (d, 2H, J=7.8 Hz), 6.59 (s, 2H), 5.11–5.10 (m, 1H), 5.06–5.05 (m, 1H), 4.29 (qd, 1H, J=10.8, 4.8 Hz), 2.61–2.57 (m, 2H), 2.49–2.42 (m, 2H), 2.32–2.26 (m, 2H), 2.19–2.10 (m, 4H), 1.67–1.65 (m, 2H), 1.46–1.42 (m, 1H), 1.35–1.31 (m, 1H), 1.09–0.96 (m, 2H), 0.94 (d, 3H, J=7.2 Hz), 0.93 (d, 3H, J=6.6 Hz), 0.90 (d, 3H, J=7.2 Hz), 0.87–0.80 (m, 1H); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 141.5, 141.2, 128.5, 128.4, 128.33, 128.26, 128.2, 127.0, 126.9, 126.4, 126.1, 118.2, 117.2 117.1, 117.04, 117.00, 80.0 (d, $^2J_{^{13}C-^{31}P}$ = 9.1 Hz), 52.53, 52.50, 52.47, 52.44, 48.0, 47.9, 31.5, 30.52, 30.48, 29.90, 29.87, 25.7, 22.7, 22.1, 21.0, 20.3, 20.0, 16.1; EIMS [m/z (%)]: 556 (M^+, 15), 418 (100); HRMS (EI) calcd for $C_{34}H_{41}N_2OPS$: 556.2677, found: 556.2672.

4.2.3. (−)-(2*S*,9*S*)-19f. A stirred solution of **21a** (181 mg, 0.32 mmol) in THF (4 mL) under Ar was treated with $LiAlH_4$ (143 mg, 3.58 mmol) and heated at reflux for 100 min. The mixture was cooled in an ice bath and Et_2O (10 mL) was added. The mixture was treated sequentially with water (0.14 mL), 10% aq NaOH solution (0.14 mL),

and water (0.43 mL). The precipitated aluminum salts were removed by filtration through a pad of Celite in a sintered funnel and washed thoroughly with small aliquots of Et_2O. The filtrate was dried over anhyd Na_2SO_4, filtered, and concentrated in vacuo. Column chromatography (silica gel, 96:4 hexanes/EtOAc, R_f=0.40) gave (−)-**19f** (85 mg, 77%) as a pale yellow solid; mp 147–149 °C; $[\alpha]_D^{18}$ −287 (*c* 1.38, acetone); ^{1}H NMR (300 MHz, acetone-d_6): δ 7.41 (d, 4H, *J*=7.2 Hz), 7.29 (t, 4H, *J*=6.9 Hz), 7.21 (d, 2H, *J*=8.4 Hz), 6.35 (s, 2H), 4.46–4.42 (m, 2H), 4.24 (br, 2H), 2.94–2.75 (m, 4H), 2.62 (td, 2H, *J*=15.9, 4.8 Hz), 1.97–1.88 (m, 2H); ^{13}C NMR (75.5 MHz, acetone-d_6): δ 146.4, 133.2, 129.0, 127.7, 127.5, 119.7, 119.0, 57.2, 32.1, 27.3.

4.2.4. *meso*-19f. A stirred solution of **21b** (32 mg, 0.057 mmol) in THF (1 mL) under Ar was treated with $LiAlH_4$ (25 mg, 0.63 mmol) and heated at reflux for 45 min. The mixture was cooled in an ice bath and treated sequentially with water (0.03 mL), 10% aq NaOH solution (0.03 mL), and water (0.08 mL). The precipitated aluminum salts were removed by filtration through a pad of Celite in a sintered funnel and washed thoroughly with small aliquots of Et_2O. The filtrate was dried over anhyd Na_2SO_4, filtered, and concentrated in vacuo. Column chromatography (silica gel, 97:3 hexanes/EtOAc, R_f=0.40) gave *meso*-**19f** (8 mg, 41%) as a pale yellow solid; mp 97–99 °C; $[\alpha]_D^{18}$ 0; ^{1}H NMR (300 MHz, acetone-d_6): δ 7.37 (d, 4H, *J*=7.2 Hz), 7.29 (t, 4H, *J*=6.9 Hz), 7.22 (d, 2H, *J*=7.2 Hz), 6.34 (s, 2H), 4.46–4.42 (m, 2H), 4.25 (br, 2H), 2.86–2.75 (m, 4H), 2.61 (td, 2H, *J*=15.9, 5.1 Hz), 2.00–1.92 (m, 2H); ^{13}C NMR (75.5 MHz, acetone-d_6): δ 146.4, 132.9, 129.1, 127.8, 127.4, 119.6, 119.0, 57.0, 31.4, 27.0.

4.2.5. (−)-(3*S*,5*S*)-Diphenyl-1,2,3,5,6,7-hexahydro-3a-aza-cyclopenta[*def*]phenanthren-4a-azonium chloride (22). A stirred solution of diamine (−)-**19f** (48 mg, 0.14 mmol) in $(EtO)_3CH$ (4 mL) was treated with concentrated HCl solution (12 μL, 0.14 mmol) under argon and heated to 80 °C. After 1 h, the septum was removed and the mixture heated at 80 °C for an additional 2 h, then cooled to ambient temperature. Et_2O (6 mL) was added to induce precipitation of the product, which was collected on a Hirsch funnel, washed with cold ether, and dried under high vacuum to give **22** (41 mg, 75%) as a beige powder; mp 244–245 °C; $[\alpha]_D^{18}$ −205 (*c* 1.0, $CHCl_3$); IR (KBr): ν_{max} 3155, 3035, 2926, 2854, 1629, 1499, 1454, 1175 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.46 (s, 1H), 7.48–7.23 (m, 12H), 6.28 (br, 2H), 3.20–3.18 (m, 2H), 3.08–3.05 (m, 2H), 2.66 (br, 2H), 2.52 (br, 2H); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 138.7, 136.8, 129.5, 129.3, 128.3, 127.0, 124.6, 123.0, 60.0, 31.9, 21.7; FABMS [*m*/*z* (%)]: 351 (M−Cl$^-$, 100), HRMS (FAB) calcd for $C_{25}H_{23}N_2$: 351.1861, found: 351.1807.

4.2.6. (−)-(3*S*,5*S*)-Diphenyl-1,2,3,5,6,7-hexahydro-3a,4a-diazacyclopenta[*def*]phenanthrene-4-thione (23). A stirred suspension of **22** (34 mg, 0.09 mmol) and S_8 (3 mg, 0.1 mmol) in THF (3 mL) under argon was treated with NaH (6 mg, 0.14 mmol, 60% dispersion in mineral oil) and stirred for 50 min. The reaction mixture was worked-up with water (3 mL) and the product was extracted with Et_2O (4×1.5 mL). The combined organic extract was dried over anhyd Na_2SO_4, filtered, and concentrated in vacuo. Gradient column chromatography (silica gel, 90:10 hexanes/EtOAc, then 80:20 hexanes/EtOAc, R_f=0.12) gave **23** (19 mg, 56%) as a colorless solid; mp>255 °C; $[\alpha]_D^{18}$ −285 (*c* 0.59, $CHCl_3$); IR (KBr): ν_{max} 3034, 2952, 2922, 2892, 2857, 1480, 1382, 1360, 1328 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31–7.20 (m, 6H), 6.98–6.94 (m, 6H), 5.89 (t, 2H, *J*=3.0 Hz), 2.85–2.77 (dt, 2H, *J*=16.2, 3.6 Hz), 2.73–2.62 (m, 2H), 2.49–2.43 (m, 4H); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 166.8, 139.5, 128.7, 128.3, 127.4, 125.8, 120.2, 118.4, 54.9, 30.7, 19.6; EIMS [*m*/*z* (%)]: 382 (M$^+$, 100), HRMS (EI) calcd for $C_{25}H_{22}N_2S$: 382.1504, found: 382.1499.

4.3. Reduction of norcamphor adduct 24

According to the *typical procedure*, a solution of **24** (96 mg, 0.39 mmol) in glacial acetic acid (4 mL) and MeOH (1 mL) was initially treated with $NaBH_3CN$ (96 mg, 1.53 mmol), and the reaction mixture was heated to reflux. Three subsequent additions of $NaBH_3CN$ (96 mg each) were made every 2 h for over 6 h total. Standard workup and column chromatography (silica gel, 9:1 hexanes/EtOAc) gave, sequentially, tetrahydrophenanthroline **26** (32 mg, 33%, R_f=0.30) and octahydrophenanthroline **27** (27 mg, 27%, R_f=0.16).

4.3.1. Compound 26. Pale yellow solid; mp 95–96 °C; $[\alpha]_D^{18}$ +79 (*c* 1.0, acetone); IR (KBr): ν_{max} 3404, 3048, 2936, 2923, 2868, 2812, 1517, 1490, 1335 cm^{-1}; ^{1}H NMR (600 MHz, acetone-d_6): δ 7.64 (s, 1H), 6.99 (d, 1H, *J*=8.4 Hz), 6.85 (d, 1H, *J*=8.4 Hz), 6.02 (br, 1H), 3.50–3.47 (m, 3H), 3.35 (br, 1H), 2.84 (t, 2H, *J*=6.6 Hz), 2.05–2.02 (m, 2H), 1.98 (quin, 2H, *J*=6.0 Hz), 1.83–1.81 (m, 1H), 1.70 (d, 1H, *J*=9.0 Hz), 1.32–1.27 (m, 2H); ^{13}C NMR (150.9 MHz, acetone-d_6): δ 167.6, 141.7, 139.9, 136.1, 128.2, 127.4, 126.2, 116.1, 113.9, 47.3, 46.0, 42.9, 41.9, 28.2, 27.7, 26.5, 22.9; EIMS [*m*/*z* (%)]: 250 (M$^+$, 100), 221 (21); HRMS (EI) calcd for $C_{17}H_{18}N_2$: 250.1470, found: 250.1475.

4.3.2. Compound 27. Colorless glass; $[\alpha]_D^{18}$ −37.9 (*c* 0.71, acetone); IR (KBr): ν_{max} 3423, 3033, 2941, 2870, 1093 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6): δ 6.34 (d, 1H, *J*=7.8 Hz), 6.27 (d, 1H, *J*=7.8 Hz), 4.03 (br, 1H), 3.31 (dd, 1H, *J*=10.3, 3.0 Hz), 3.28–3.22 (m, 2H), 2.84 (br, 1H), 2.68 (t, 2H, *J*=6.5 Hz), 2.41 (dd, 1H, *J*=13.4, 6.4 Hz), 2.29–2.22 (m, 2H), 2.15–2.10 (m, 2H), 1.92–1.86 (m, 1H), 1.80 (quin, 2H, *J*=5.2 Hz), 1.68–1.64 (m, 1H), 1.48–1.47 (m, 1H), 1.39–1.37 (m, 1H), 1.33–1.28 (m, 1H), 1.25–1.18 (m, 1H); ^{13}C NMR (150.9 MHz, acetone-d_6): δ 136.0, 132.5, 125.2, 120.9, 119.4, 117.8, 57.4, 43.20, 43.18, 41.8, 41.3, 38.8, 28.4, 28.1, 23.6, 23.4, 21.0; EIMS [*m*/*z* (%)]: 254 (M$^+$, 100), 185 (44), 84 (80); HRMS (EI) calcd for $C_{17}H_{22}N_2$: 254.1783, found: 254.1781.

4.4. Reduction of nopinone adduct 25

According to the *typical procedure*, a solution of **25** (100 mg, 0.36 mmol) in glacial acetic acid (4 mL) and MeOH (1 mL) was initially treated with $NaBH_3CN$ (100 mg, 1.59 mmol), and the reaction mixture was heated to reflux. Three subsequent additions of $NaBH_3CN$ (100 mg each) were made every 2 h for over 6 h total. Standard workup and column chromatography (silica gel, 95:5 hexanes/EtOAc) gave, sequentially, tetrahydrophenanthroline **28** (35 mg, 34%,

R_f=0.21) and octahydrophenanthroline **29** (24 mg, 23%, R_f=0.07).

4.4.1. Compound 28. Off-white solid; mp 155–157 °C; $[\alpha]_D^{18}$ +23.0 (*c* 1.0, $CHCl_3$); IR (KBr): ν_{max} 3407, 2968, 2951, 2927, 2833, 1568, 1514, 1489, 1381, 1348, 1325 cm^{-1}; ^1H NMR (300 MHz, acetone-d_6): δ 7.73 (s, 1H), 6.99 (d, 1H, *J*=8.1 Hz), 6.84 (d, 1H, *J*=8.1 Hz), 6.03 (br, 1H), 3.49–3.45 (m, 2H), 3.09–3.08 (m, 2H), 3.02 (t, 1H, *J*=5.4 Hz), 2.86–2.75 (m, 2H), 2.39–2.33 (m, 1H), 2.02–1.94 (m, 2H), 1.44 (s, 3H), 1.30 (d, 2H, *J*=9.6 Hz), 0.65 (s, 3H); ^{13}C NMR (75.5 MHz, acetone-d_6): δ 164.1, 141.4, 135.2, 134.5, 128.7, 128.4, 127.6, 116.0, 113.1, 51.9, 41.8, 41.0, 40.1, 31.6, 31.3, 27.7, 26.4, 22.8, 21.7; EIMS [*m*/*z* (%)]: 278 (M^+, 100); HRMS (EI) calcd for $C_{19}H_{22}N_2$: 278.1783, found: 278.1787.

4.4.2. Compound 29. Off-white solid; mp 103–105 °C; $[\alpha]_D^{18}$ −73.0 (*c* 1.0, acetone); IR (KBr): ν_{max} 3421, 3298, 2933, 2856, 1473 cm^{-1}; ^1H NMR (300 MHz, acetone-d_6): δ 6.36 (d, 1H, *J*=7.5 Hz), 6.27 (d, 1H, *J*=7.5 Hz), 4.00–3.50 (br, 2H), 3.51 (dd, 1H, *J*=9.6, 4.4 Hz), 3.23 (m, 2H), 2.75 (dd, 1H, *J*=13.7, 7.0 Hz), 2.67 (t, 2H, *J*=6.6 Hz), 2.60–2.20 (m, 5H), 1.94 (m, 1H), 1.79 (quin, 2H, *J*=5.5 Hz), 1.66 (dd, 1H, *J*=13.8, 8.4 Hz), 1.32 (d 1H, *J*=8.6 Hz), 1.21 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (150.9 MHz, acetone-d_6): δ 136.8, 132.4, 124.2, 120.7, 119.6, 117.7, 59.5, 47.3, 43.1, 42.5, 39.2, 34.7, 34.4, 30.6, 28.5 (2C), 28.1, 23.4, 23.3; EIMS [*m*/*z* (%)]: 282 (M^+, 100), 278 (49), 211 (39); HRMS (EI) calcd for $C_{19}H_{26}N_2$: 282.2096, found: 282.2093.

4.4.3. Benzimidazolium tetrafluoroborate 30. A solution of diamine **27** (77 mg, 0.30 mmol) in $(EtO)_3CH$ (10 mL) was treated with NH_4BF_4 (32 mg, 0.30 mmol). A reflux condenser was attached and the mixture was stirred at 80 °C under argon for 13 h. After cooling to room temperature, ether (10 mL) was added to induce precipitation of the product, which was collected by Büchner filtration on medium porosity (slow-flow) filter paper. After washing with ether, the product was dried thoroughly under high vacuum to give **30** (78 mg, 74%) as a colorless solid; mp 62–63 °C; $[\alpha]_D^{18}$ +22.4 (*c* 0.58, $CHCl_3$); IR (KBr): ν_{max} 3134, 2995, 2922, 2870, 1510, 1084 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 9.33 (s, 1H), 7.28 (d, 1H, *J*=7.4 Hz), 7.26 (d, 1H, *J*=8.0 Hz), 4.91 (dd, 1H, *J*=10.5, 5.4 Hz), 4.68–4.60 (m, 2H), 3.21 (dd, 1H, *J*=18.9, 9.7 Hz), 3.09–3.05 (m, 3H), 2.99–2.95 (m, 2H), 2.44–2.42 (m, 1H), 2.42–2.35 (m, 2H), 1.84 (d, 1H, *J*=9.9 Hz), 1.65 (d, 1H, *J*=10.3 Hz), 1.42–1.31 (m, 2H), 1.14–1.09 (m, 1H), 0.34–0.29 (m, 1H); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 138.3, 127.4, 127.2, 124.4, 123.9, 122.3, 121.2, 55.5, 45.0, 43.4, 43.3, 38.7, 36.8, 22.7 (2C), 22.2, 21.8, 21.7; FABMS [*m*/*z* (%)]: 265 ($M-BF_4^-$, 100); HRMS (FAB) calcd for $C_{18}H_{21}N_2$: 265.1705, found: 265.1691.

4.4.4. Benzimidazolium chloride 31. A solution of diamine **29** (40 mg, 0.14 mmol) in $(EtO)_3CH$ (3 mL) was treated with concentrated HCl solution (12 μL, 0.14 mmol). A reflux condenser was attached and the mixture was stirred at 80 °C under argon for 15 h, after which the condenser was removed and heating was continued in air for an additional 2 h. After cooling to room temperature, the solvent was carefully decanted and the precipitated residue washed repeatedly with Et_2O and dried thoroughly under high vacuum to give **31** (39 mg, 81%) as a hygroscopic amorphous solid foam; mp>250 °C; $[\alpha]_D^{19}$ <+1 (*c* 0.5, acetone); IR (KBr): ν_{max} 3088, 2994, 2917, 2866, 1634, 1509, 1470, 1329 cm^{-1}; ^1H NMR (600 MHz, acetone-d_6): δ 11.59 (br, 1H), 7.40 (d, 1H, *J*=7.0 Hz), 7.35 (d, 1H, *J*=7.1 Hz), 5.25 (br, 1H), 4.86 (br, 1H), 4.63 (br, 1H), 3.42–3.36 (m, 3H), 3.10 (m, 2H), 2.93 (d, 1H, *J*=15.9 Hz), 2.42–2.39 (m, 2H), 2.32 (br, 1H), 2.19 (quin, 1H, *J*=7.6 Hz), 1.97 (br, 1H), 1.91 (d, 1H, *J*=10.5 Hz), 1.68 (t, 1H, *J*=13.1 Hz), 1.27 (s, 3H), −0.05 (s, 3H); ^{13}C NMR (150.9 MHz, acetone-d_6): δ 128.8, 128.4, 125.4, 124.8, 124.1, 122.2, 58.3, 46.0, 45.7, 41.9, 40.4, 32.4, 27.9, 27.7, 27.6, 26.0, 24.1, 23.6, 19.1; FABMS [*m*/*z* (%)]: 293 ($M-Cl^-$, 100); HRMS (FAB) calcd for $C_{20}H_{25}N_2$: 293.2018, found: 293.2075.

4.4.5. Thiourea 32. A flame-dried 25 mL round-bottom flask under argon was charged with tetrafluoroborate **30** (20 mg, 0.057 mmol), sodium hydride (3.7 mg, 60% dispersion in mineral oil, 0.091 mmol), and S_8 (1.8 mg, 0.057 mmol). Dry THF (2 mL) was added and the resulting suspension was stirred at ambient temperature for 45 min. The reaction mixture was worked-up with water (2 mL) and the product extracted with Et_2O (3×2 mL). The combined organic layer was washed with water (2 mL), brine (2 mL), dried over anhyd Na_2SO_4, filtered, and concentrated in vacuo. Column chromatography (silica gel, 5:1 hexanes/EtOAc, R_f=0.34) gave **32** (10.5 mg, 63%) as a colorless powder; mp 156–158 °C; $[\alpha]_D^{20}$ +130.7 (*c* 0.82, $CHCl_3$); X-ray analysis (CCDC 617690) was performed on a pale yellow prism fragment (0.30×0.27×0.19 mm), which was obtained by crystallization from MeOH. $C_{18}H_{20}N_2S$: *M*=296.42 g/mol, triclinic, $P\bar{1}$, *a*=9.067(5) Å, *b*=9.5590(6) Å, *c*=10.3151(6) Å, α=63.723(1)°, β=65.662(1)°, γ=76.558(1)°, *V*=729.03(7) $Å^3$, *Z*=2, D_c=1.350 g/cm^3, *F*(000)=316, *T*=295(2) K. Data were collected on a Bruker APEX CCD system with graphite monochromated Mo Kα radiation (λ=0.71073 Å), 6057 data were collected. The structure was solved by Patterson and Fourier (SHELXTL) and refined by full-matrix least squares on F^2 resulting in final *R*, R_w, and GOF [for 3294 data with $F>2\sigma(F)$] of 0.0648, 0.1083, and 1.934, respectively; IR (KBr): ν_{max} 2951, 2875, 1493, 1406, 1365 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 6.89 (d, 1H, *J*=7.8 Hz), 6.85 (d, 1H, *J*=7.5 Hz), 4.50 (dd, 1H, *J*=10.5, 3.9 Hz), 4.15–4.02 (m, 2H), 3.60 (s, 1H), 3.05–2.77 (m, 5H), 2.32 (s, 1H), 2.26–2.16 (m, 2H), 1.72 (d, 1H, *J*=10.2 Hz), 1.54 (d, 1H, *J*=10.2 Hz), 1.32–1.21 (m, 3H), 0.63–0.55 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 166.6, 128.2, 128.0, 120.1, 119.5, 117.5, 117.3, 53.6, 44.0, 41.6, 40.1, 38.4, 37.4, 23.3, 23.0, 22.8, 22.2, 21.7; EIMS [*m*/*z* (%)]: 296 (M^+, 100); HRMS (EI) calcd for $C_{18}H_{20}N_2S$: 296.1347, found: 296.1355.

4.4.6. Thiourea 33. A flame-dried 25 mL round-bottom flask under argon was charged with vacuum-dried salt **31** (72 mg, 0.22 mmol), sodium hydride (13.8 mg, 60% dispersion in mineral oil, 0.35 mmol), and S_8 (7.1 mg, 0.22 mmol). Dry THF (7 mL) was added and the resulting suspension was stirred at ambient temperature for 2.5 h. The reaction mixture was worked-up with water (3 mL) and the product extracted with Et_2O (3×3 mL). The combined organic layer was washed with water (2 mL), brine (2 mL), dried over anhyd Na_2SO_4, filtered, and concentrated in vacuo. Column

chromatography (silica gel, 5:1 hexanes/EtOAc, R_f=0.35) gave **33** (38.3 mg, 54%) as a clear colorless glass; $[\alpha]_D^{19}$ +125 (*c* 0.5, $CHCl_3$); IR (NaCl, thin film): ν_{max} 2997, 2937, 1493, 1373, 1352 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 6.88 (ABq, 2H), 4.81 (dd, 1H, *J*=7.2, 5.4 Hz), 4.30 (q, 1H, *J*=5.7 Hz), 4.05 (t, 2H, *J*=5.7 Hz), 3.24–3.12 (m, 1H), 3.06–2.98 (m, 1H), 2.93–2.80 (m, 2H), 2.68 (d, 1H, *J*=16.2 Hz), 2.33–2.26 (m, 1H), 2.22–2.03 (m, 3H), 1.97–1.91 (m, 1H), 1.80–1.68 (m, 2H), 1.25 (s, 3H), 0.17 (s, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 166.3, 129.1, 128.0, 120.3, 120.0, 117.7, 117.1, 57.0, 41.8, 41.5, 40.6, 39.0, 32.6, 28.1, 27.6 (2C), 25.2, 23.3, 22.9, 18.8; EIMS [*m*/*z* (%)]: 324 (M^+, 95), 291 (75), 203 (100); HRMS (EI) calcd for $C_{20}H_{24}N_2S$: 324.1660, found: 324.1653.

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Supplementary data

^{13}C NMR data for all new compounds, ^{31}P NMR spectra for **21a** and **21b**, and COSY/NOESY experiments for **32** and **33**. This material is available via the Internet at http://www.sciencedirect.com. CCDC 612643 and 617690 contain the supplementary crystallographic data for compounds **21a** and **32**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.09.023.

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