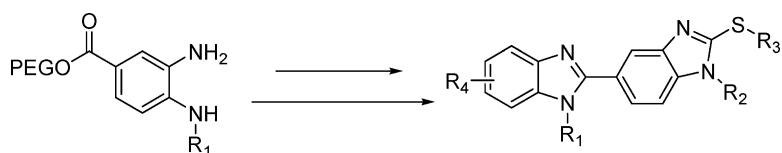Article

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Parallel Synthesis of 2-Sulphanylated Bis-benzimidazoles on Soluble Polymer Support

Chia-Mao Chang,[†] Manohar V. Kulkarni,[†] Chih-Hau Chen,[†] Chi-Hsiang Wang,[‡] and
Chung-Ming Sun*,[†]

*Department of Applied Chemistry, National Chiao Tung University, Hsinchu 300-10, Taiwan, ROC, and
Department of Applied Science, National Taitung University, Taitung 950, Taiwan, ROC*

A well-sustained multistep synthetic protocol has been designed for the PEG-functionalized aromatic acid amide to generate a molecular library of 2-alkylthio bis-benzimidazoles. An attempted synthesis of benzimidazole-2-thiol in dichloromethane has led to *S*-chloromethyl methyl sulfides, mimicking bacterial enzymatic systems. Regioselective S-alkylation was brought about under controlled conditions using a mild base at room temperature. The polymer-free compounds, 2-sulfanylated bisbenzimidazoles, were obtained in high yields and high purities. Chemical shift changes in proton and carbon NMR have been employed to monitor the progress of the reaction steps and to prove the site of S-alkylation, respectively.

Introduction

Nitrogen-containing heterocyclic derivatives possess immense pharmaceutical significance, and the development of novel strategy for their synthesis is an important field of organic chemistry.[1] Combinatorial synthesis of heterocycles provides enormous structural diversity, which has greatly helped in the design and choice of lead structures in the drug discovery process.[2] The two established techniques in this field are solid-[3] and liquid-phase synthetic strategies,[4] employing a polymer support. Polyethylene glycol (PEG) is usually employed as the soluble polymer support in liquid-phase synthesis. The PEG−monomer conjugates obtained are easily soluble in organic solvents, and the reactions can be monitored by traditional analytical techniques. Our group has been exploring this method to generate molecular libraries of diazepinones, fused hydantoins, piperazinones, pyrimidinethiones, quinoxalinones, and tricyclic carbolines.[5–10]

The benzimidazole ring, classed as a privileged structure, is present in clinically approved anthelmintics, antiulcers, antivirals, antifungals, and antihistamines.[11] Recently, there were reports on benzimidazole derivatives exhibiting antitumor and antimicrobial properties and acting as thrombopoietin receptor agonists.[12] It is quite obvious that a large number of benzimidazoles have been synthetic targets for combinatorial approaches with the hope of delivering structures with improved pharmacological activity and lesser side effects.[13,14]

In recent years, two newer aspects connected with their biological properties have emerged. The first one is their ability to bind with the DNA minor groove found in bis-benzimidazoles, and the second is enzyme activity observed in 2-mercaptobenzimidazoles and their corresponding sulfides (Figure 1).[15] The sequence-selective ability of bis-benzimidazoles to bind to the DNA minor groove has been enhanced by the bispyridyl derivatives and has also been subjected to computational analysis (Figure 1A).[16] The origin of this effect lies in the optimum distance between the two nitrogens located in the two rings, and it has been linked with their antitumor activities through topoisomerase-I inhibition (Figure 1B).[17,18] The pyridyl methyl sulfinyl benzimidazoles are well-known as in vivo and in vitro inhibitors of gastric (H^+-K^+)-ATP by covalent modification of the thiol group.[19] The cyclic thioureide structure is also recognized for its thyroid peroxide inhibiting activity, which makes such compounds potential candidates for treatment of hyperthyroidism.[20] Hepatic monooxygenases metabolize benzimidazolin-2-thione to benzimidazole, which is of immense significance in the design of thiocarbanilides with reduced toxicity.[21] The 2-mercapto-1-(4-pyridylethyl) benzimidazole (MPB) is known to inhibit rRNA synthesis, which is responsible for its antiviral activity (Figure 1C).[22] This compound has also been reported to induce melanogenesis in murine melanoma cells; this is useful in the differentiation of solid tumors.[23] Recently, the crystal structure of the iodine adduct formed with benzimidazolin-2-thione was investigated for its mechanism of antithyroid action.[24]

Earlier we reported a microwave-assisted liquid-phase synthesis of the *S*-alkyl benzimidazole moiety.[14a–d] The design concept for the presently synthesized molecular library originated from the recognition of the biological role of the *S*-alkyl benzimidazole moiety. The generation of a combined bis-benzimidazole skeleton that resembles druglike molecules has a substantial intellectual appeal. Therefore, the biological

* To whom correspondence should be addressed. E-mail: cmsun@
mail.nctu.edu.tw.
    [†] National Chiao Tung University.
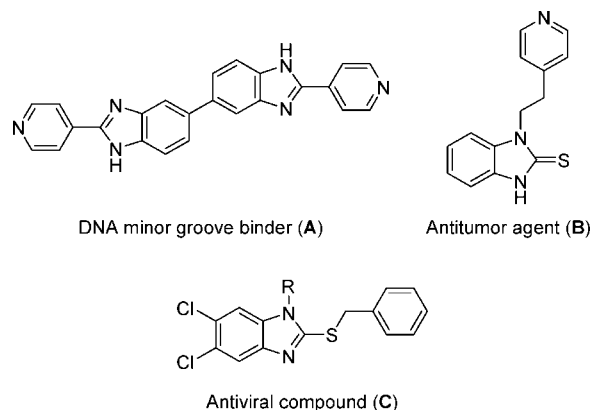   [‡] National Taitung University.

Figure 1. Biologically active benzimidazoles and sulfides.

potential of these two pharmacophores have been assembled into a single molecular library with three points of structural diversity.

Results and Discussions

The steps involved in the synthesis of bisbenzimidazolin-2-thiones are outlined in Scheme 1. PEG (MW ≈ 6000) was employed during this work, and the polymer conjugates **1** were obtained from a four-step synthetic protocol reported by our group.[14e,25] These substrates possess a built-in structural diversity (R1), from which a six-step sequence has been initiated by an intramolecular nucleophilic attack of the amino group on the amide carbonyl group. This ring closure reaction, followed by dehydration, was achieved using TFA (5%) in 1,2-dichloroethane under refluxing conditions to lead the benzimidazole conjugates **2**. The addition of anhydrous magnesium sulfate in this transformation reduced the reaction time from 20 to 12 h by facilitation of the elimination of water during this step.

Magnesium sulfate was filtered off, and the polymer conjugate **2** precipitated and washed with excess of cold ether. The purity of this intermediate was excellent (^{1}H NMR), and it was used directly for further steps in the present sequence. The reactivity of the *ortho*-fluoro nitro groups of **2** was explored in a cascaded manner with the introduction of second point of structural diversity (R2). The *ipso*-fluoro displacement with primary amines at room temperature in a typical S_NAr reaction resulted in the polymer bound *o*-nitroanilines **3**. Generally, the transformation of the nitro group to an amino function requires either a mineral acid or an alkali. Both these conditions may induce a premature cleavage from the polymer support. For the selective reduction, without the cleavage from the support, neutral conditions using excess of zinc dust and ammonium formate in methanol were employed. The reaction was found to be complete in 30 min at room temperature, leading to the diamine **4**, which is the precursor for the cyclic thioureide moiety. The progress of this reaction was monitored periodically by checking the proton NMR spectra of the crude reaction mixtures. Earlier we found that both thiophosgene and thiocarbonyl imidazole (TCI) can complete this cyclization.[14e,25] During the present investigation, we employed thiocarbonyl imidazole and triethylamine for one-pot cyclization in 1,2-

dichloroethane, and the results were identical to those obtained by the use of thiophosgene. The reaction was found to occur at room temperature in 15 h. To decrease the reaction time, refluxing conditions were applied in dichloromethane, which reduced the reaction time but gave rise to an unexpected byproduct in the form of the chloromethyl sulfide **5**, which was confirmed when the polymer support was released to give the monomers **6**. It is important to note that further alkylation occurring after the formation of the cyclic thiourea would necessarily give rise to either a bis-N−N′-substitution or an N−S-substitution, resulting from the nucleophilic attacks of the ring nitrogen or that of the exocyclic sulfur. The ^{1}H NMR of this product was characterized by a singlet belonging to methylene protons at 5.46 ppm. The predicted carbon NMR chemical shift (43.2 ppm) for the respective carbon also agreed with this observation. Compounds **6** did not exhibit any signal in the range of 60 ppm, indicating the absence of the N−CH$_2$Cl group (Table 1). These predicted values support the S-chloromethylation very well. It is interesting to note that similar chloromethylation is observed in the enzymatic reaction of rat liver glutathione-S-transferases. The present reaction can be a nonenzymatic model for the biochemical process.[26] Compounds isolated in considerable yields and purity are presented in Table 1.

However, the reaction of diamines **4** with TCI at room temperature gave the desired polymer-bound bis-benzimidazolyl-2-thiones **7** when the solvent was changed from dichloromethane to 1,2-dichloroethane. This resulted in our first molecular library of benzimidazolyl benzimidazolin-2-thiolnes **8**, after cleavage, with two points of structural diversity (Table 2). To the best of our knowledge, it is the first report on this skeleton.

The third point of chemical diversity was introduced by the N-alkylation of benzimidazolin-2-thione polymer conjugates **7**. A survey in reactivity profile of benzimidazolin-2-thiones with carbon electrophiles indicates that use of formaldehyde and the corresponding Mannich reactions will lead to N−N′-bis-alkylation.[28,29] Under mild alkaline conditions, S-alkylation has been reported to occur and was employed to synthesize a number of biologically active sulfides, as well as to be kinetically investigated.[30] The use of 1,3-dialkyl halides leads to tricyclic thiazinobenzimidazoles via S−N-bis-alkylation.[31] In accordance with these reports, alkylation of **7** in principle can result in N- or S-alkylation. Under the room-temperature conditions employed, the reactions with various alkyl halides in presence of triethylamine led to S-alkylated conjugates **9**. Similar cleavage of the polymer, under identical conditions was also marked by the disappearance of the strong signal around 4.2 ppm caused by the O−CH$_2$−PEG with the appearance of a singlet around 3.9−4.0 ppm, which is caused by the OCH$_3$ protons of the methyl ester. This resulted in the final 2-sulfanylated bis-benzimidazoles **10** (Table 3 and Scheme 2). In the proton NMR, the predicted chemical shifts for th N−CH$_3$ and S−CH$_3$ protons are 3.70 and 2.57 ppm, respectively. The chemical shift values in case of the compounds **10a**−**c** are in the

Scheme 1. Synthetic Route for Bis-benzimidazolyl-2-thiones **8**
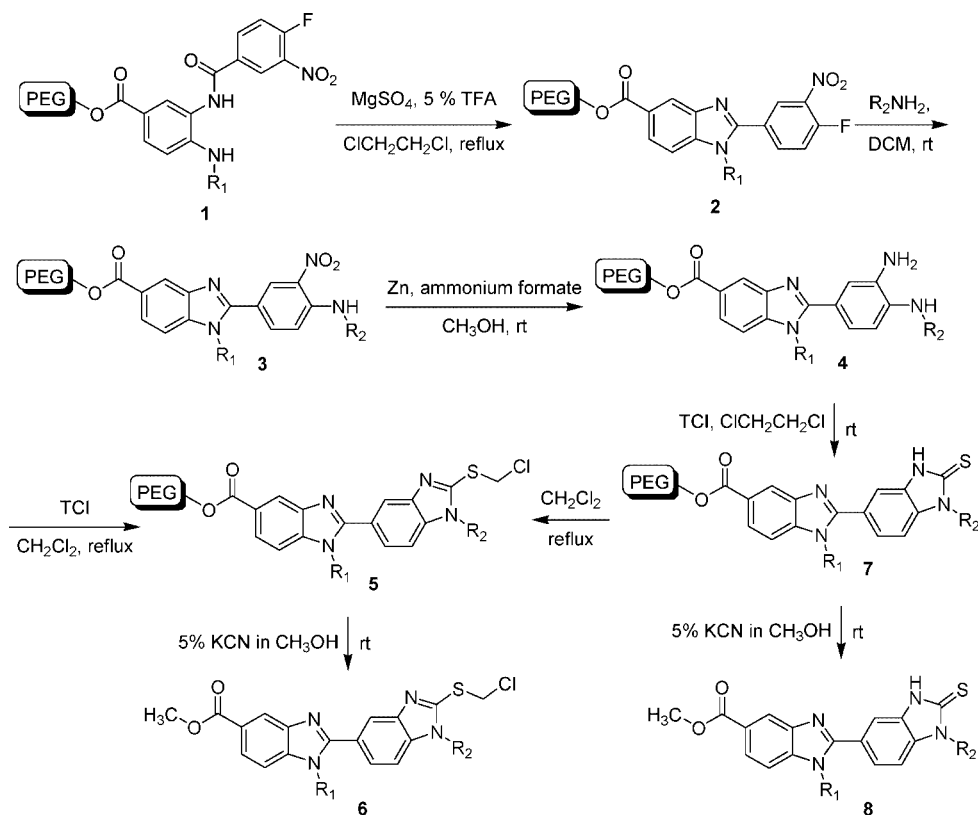
Table 1. Bis-benzimidazolyl Chloromethyl Sulphides **6**

Entry	R₁NH₂	R₂NH₂	LRMS[a]	isolated yield (%)[b]
6a	∿NH₂	⟩–NH₂	470	66
6b	⟩–NH₂	∿O∿NH₂	486	68
6c	∿O∿NH₂	⟩–NH₂	500	72
6d	⟩–NH₂	∿∿NH₂	470	76
6e	∿O∿NH₂	∿NH₂	514 (M+1)	69
6f	∿∿NH₂	⟩–NH₂	471 (M+1)	70

[a] LRMS were detected with EI ionization source. [b] Yields were based on loading of soluble support.

range of 2.81−2.83 ppm, which also supports the observed regioselectivity. This twenty-member molecular library (Table 3) was obtained after seven steps, and all the final compounds have a high degree of purity (HPLC), so that they can be used directly in biological assays without any purification.

Conclusions

The hitherto described multistep sequence of reactions has led to the generation of molecular libraries with two core skeletons suitable for DNA minor groove recognition and enzyme susceptibility. This investigation also caused a model reaction that can mimic the bacterial enzymatic pathway. The site of alkylation has been proven by ^{1}H and ^{13}C NMR spectra. The introduction of the alkyl groups was carried out in an unambiguous manner without formation of any mixtures, and
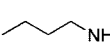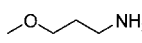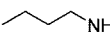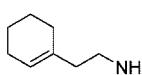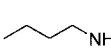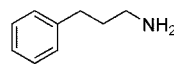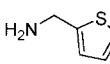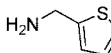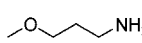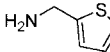
Scheme 2. Liquid-Phase Synthesis of 2-Sulphanylated Bisbenzimidazoles
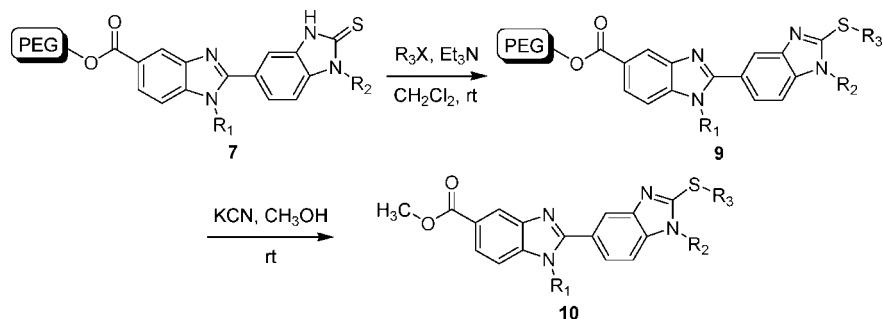
Table 2. Synthesis of Bis-benzimidazolyl-2-thiones **8**

Entry	R₁NH₂	R₂NH₂	LRMS[a]	isolated yield (%)[b]
8a			422	66
8b			422	64
8c			448	73
8d			452	62
8e			474	73
8f			499 (M+1)	66
8g			491 (M+1)	79
8h			462	81
8i			476	86

[a] LRMS were detected with EI ionization source. [b] Yields were based on loading of soluble support.

all the final products have been obtained in high yields and purities by simple ether precipitation and washing.

Experimental Section

General Procedures for the Synthesis of Benzimidazolyl Benzimidazolones (8 and 10). To the solution of polymer immobilized conjugate **1** (0.33 mmol, 1.0 equiv) in 1,2-dichloroethane, trifluoroacetic acid (0.5 mL) and magnesium sulfate (0.5 g) were added. The mixture was refluxed for 12 h, and the progress of the reaction was monitored by ¹H NMR. After completion of the reaction, MgSO₄ was removed by filtration through a layer of Celite. Then the solvent was evaporated, and the product was precipitated by slow addition of an excess of cold ether. The precipitated benzimidazole conjugate **2** was filtered through a fritted funnel and washed with ether. The resulting conjugate **2** was treated with various amines (2.31 mmol, 7.0 equiv) in dichloromethane at ambient temperature for 12 h. When the reaction was finished, the solvent was changed from dichloromethane to methanol because most of the excess amine that would hinder the zinc reduction can be removed by precipitation from methanol and because a small amount of conjugate **3** may be lost during ether washing. Conjugate **3** in methanol was completely reduced by zinc (3.3 mmol, 30.0 equiv) and ammonium formate (3.75 mmol, 15.0 equiv) for 30 min at ambient temperature. Zinc was removed by centrifugation and filtration, and dichloromethane was added to precipitate ammonium formate. After filtration through Celite, polymer-immobilized diamine **4** was obtained. Polymer conjugate **4** (0.33 mmol, 1.0 equiv), triethylamine (0.78 mmol, 2.6 equiv), and thiocarbonyldiimidazole (0.78 mmol, 2.6 equiv) were mixed in 1,2-dichloroethane, and the reaction mixtures

were refluxed for 12 h. The cyclyzed conjugated **7** was isolated by a similar ether precipitation and washing procedure. To the conjugated **7** (0.33 mmol, 1.0 equiv) in dichloromethane was added triethylamine (1.0 mmol, 3.3 equiv) and various alkyl halides (1.0 mmol, 3.3 equiv) at room temperature, and the reaction mixture was reacted for 14 h under ambient temperature. Conjugated **9** was purified by precipitation and washing with ether. The target compound was obtained by treating conjugate **9** with potassium cyanide in methanol for 3 days. The crude products **8** and **10** were obtained and subsequently checked by HPLC after precipitation. The crude products were then purified by column chromatography (CH₂Cl₂/MeOH = 30:1 for **8**; CH₂Cl₂/MeOH = 50:1 for **10**), and the final products were obtained in high overall yield.
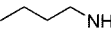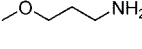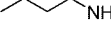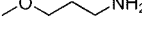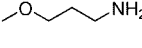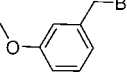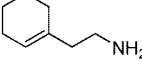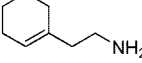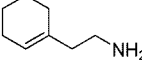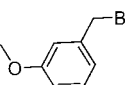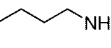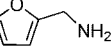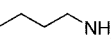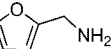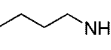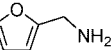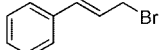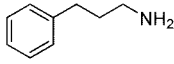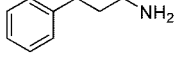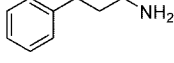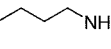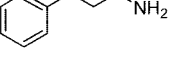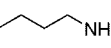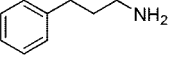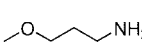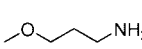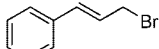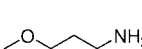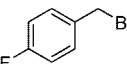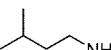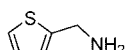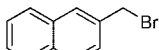
General procedures for the Synthesis of Benzimidazolyl Benzimidazolones (6). Polymer conjugate **4** (0.33 mmol, 1.0 equiv), triethylamine (0.78 mmol, 2.6 equiv), and thiocarbonyldiimidazole (0.78 mmol, 2.6 equiv) were mixed in dichloromethane, and the reaction mixture was refluxed for 12 h. The cyclyzed conjugated **5** was isolated by a similar ether precipitation and washing procedure. Target compound **6** was obtained by treatment of conjugate **5** with potassium cyanide in methanol for 3 h. Spectroscopic data are enclosed in the Supporting Information.

1′-Isobutyl-1-isopropyl-2′-methylsulfanyl-1*H*,1′*H*-[2,5′]bibenzoimidazolyl-5-carboxylic Acid Methyl Ester (10a). ¹H NMR (300 MHz, CDCl₃): δ 8.52 (d, *J* = 1.1 Hz, 1H), 8.00 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.85 (d, *J* = 1.1 Hz, 1H), 7.68 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 1H), 5.02−4.9 (m, 1H), 3.95 (s, 3H), 3.97∼3.91 (m, 2H), 2.83 (s, 3H), 2.25 (septet, *J* = 7.0 Hz, 1H), 1.65 (d, *J* = 6.9 Hz, 6H), 1.00 (d, *J* = 6.6 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 167.7, 156.0, 155.4, 143.2, 143.1, 138.0, 136.8, 124.2, 123.9, 123.7, 122.2, 118.7, 111.9, 109.7, 52.1, 51.8, 50.6, 49.1, 29.0, 21.5, 20.3, 14.8. IR (KBr): 2960, 1715, 1434, 1303 cm⁻¹. EI-MS *m/z* 436 (M⁺). HRMS *m/z* calcd for C₂₄H₂₈N₄O₂S: 436.1929. Found: 436.1933.

1′-Butyl-1-isobutyl-2′-methylsulfanyl-1*H*,1′*H*-[2,5′]bibenzoimidazolyl-5-carboxylic acid methyl ester (10b). ¹H NMR (300 MHz, CDCl₃): δ 8.50 (d, *J* = 1.1 Hz, 1H), 8.01 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.89 (d, *J* = 1.2 Hz, 1H), 7.58 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.41−7.32 (m, 2H), 4.16 (d, *J* = 7.6 Hz, 2H), 4.10 (t, *J* = 7.1 Hz, 2H), 3.93 (s, 3H), 2.81 (s, 3H), 2.18−2.00 (m, 1H), 1.86−1.77 (m, 2H), 1.45−1.34 (m 2H), 0.94 (t, *J* = 7.1 Hz, 3H), 0.67 (d, *J* = 6.6 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 167.7, 156.7, 154.7, 143.4, 142.7, 139.2, 137.5, 124.3, 123.9, 123.7, 122.1, 118.8, 111.2, 109.2, 52.1, 52.0, 44.1, 31.3, 28.7, 20.1, 19.9, 14.6, 13.7. IR (KBr): 2958, 1714, 1435, 1301 cm⁻¹. EI-MS *m/z*: 450 (M⁺) HRMS *m/z* calcd for C₂₅H₃₀N₄O₂S: 450.2089. Found: 450.2092.

1′-Butyl-1-(3-methoxy-propyl)-2′-methylsulfanyl-1*H*,1′*H*-[2,5′]bibenzo-imidazolyl-5-carboxylic Acid Methyl Ester (10c). ¹H NMR (300 MHz, CDCl₃): δ 8.52 (d, *J* = 1.2 Hz, 1H), 8.04 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.96 (d, *J* = 1.1 Hz, 1H), 7.65 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 4.46 (t, *J* = 7.0 Hz, 2H), 4.41 (d, *J* = 7.2 Hz, 2H), 3.96 (s, 3H), 3.22 (t, *J* = 5.6 Hz, 2H), 3.18 (s, 3H), 2.83 (s, 3H), 2.05−1.92 (m, 2H), 1.90−1.78 (m, 2H), 1.55−1.30 (m, 2H), 0.98 (t, *J* = 7.2

Table 3. 2-Sulphanylated Bis-benzimidazoles **10**

Entry	R₁NH₂	R₂NH₂	R₃	LRMS[a]	isolated yield (%)[b]	HPLC purity[c]
10a			CH₃I	436	76	78
10b			CH₃I	450	78	85
10c			CH₃I	466	80	76
10d				508	55	68
10e				572	78	97
10f			CH₃I	488	81	94
10g				502	73	97
10h				594	76	89
10i				500	80	88
10j				528	71	97
10k				576	74	82
10l				512	66	68
10m				524	78	92
10n				526	57	58
10o				538	76	80
10p				526	71	94
10q				534	81	94
10r				582	80	90
10s				574	78	93
10t				630	68	82

[a] LRMS were detected with EI ionization source. [b] Yields were based on loading of soluble support. [c] Crude products were analyzed by normal-phase HPLC and monitored with a UV detector at a 254 nm wavelength (column silica, 250 × 4.6 mm, 5μm; eluent 5% MeOH in CH₂Cl₂).

Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 167.7, 155.4, 142.9, 142.1, 141.8, 140.7, 138.9, 137.1, 134.7, 130.2, 129.2, 129.1, 129.0, 128.6, 128.5, 127.9, 127.7, 127.5, 127.1, 126.9, 126.8, 126.0, 124.0, 123.5, 122.2, 120.7, 119.1, 112.7, 111.9, 80.5, 59.0, 56.1, 53.3, 52.0, 44.9, 34.7, 33.7, 31.6, 30.0, 27.6, 27.5, 25.9, 25.8. IR (KBr): 2955, 1714, 1434, 1301 cm⁻¹. EI-MS

m/z: 466 (M⁺). HRMS *m/z* calcd for C₂₅H₃₀N₄O₃S: 466.2039. Found: 466.2030.

2′-Butylsulfanyl-1′-isobutyl-1-(3-methoxy-propyl)-1H,1′H-[2,5′]bibenzo-imidazolyl-5-carboxylic Acid Methyl Ester (10d). ¹H NMR (300 MHz, CDCl₃): δ 8.50 (d, *J* = 1.2 Hz, 1H), 8.02 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.93 (d, *J* = 1.2 Hz,

1H), 7.62 (dd, J = 8.3, 1.5 Hz, 1H), 7.47 (d, J = 8.6 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H), 4.45 (t, J = 7.1 Hz, 2H), 3.94 (s, 3H), 3.91 (d, J = 7.7 Hz, 2H), 3.42 (t, J = 7.3 Hz, 2H), 3.20 (t, J = 5.6 Hz, 2H), 3.16 (s, 3H), 2.40−2.20 (m, 2H), 2.03−1.94 (m, 2H), 1.85−1.72 (m, 2H), 1.55−1.46 (m, 2H), 0.97 (d, J = 6.7 Hz, 6H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 167.7, 149.3, 149.0, 142.2, 138.4, 135.0, 129.3, 127.0, 124.9, 123.3, 118.7, 114.6, 68.3, 52.0, 49.6, 44.0, 21.9, 20.0, 20.0. IR (KBr): 2957, 1715, 1433, 1301 cm^{-1}. EI-MS *m/z*: 508 (M$^+$). HRMS *m/z* calcd for C$_{28}$H$_{36}$N$_4$O$_3$S: 508.2508. Found: 508.2500.

1′-Isobutyl-2′-(4-methoxy-benzylsulfanyl)-1-(3-methoxy-propyl)-1*H*,1′*H*-[2,5′]bibenzoimidazolyl-5-carboxylic Acid Methyl Ester (10e). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.52 (d, J = 1.3 Hz, 1H), 8.02 (dd, J = 8.5, 1.5 Hz, 1H), 7.98 (d, J = 1.3 Hz, 1H), 7.64 (dd, J = 8.3, 1.5 Hz, 1H), 7.48 (d, J = 8.6 Hz, 1H), 7.37 (d, J = 8.3 Hz, 1H), 7.22 (t, J = 7.9 Hz, 1H), 7.05−6.96 (m, 2H), 6.80 (dd, J = 8.8, 1.8 Hz, 1H), 4.61 (s, 2H), 4.46 (t, J = 6.9 Hz, 2H), 3.94 (s, 3H), 3.87 (d, J = 7.6 Hz, 2H), 3.75 (s, 3H), 3.21 (t, J = 5.6 Hz, 2H), 3.17 (s, 3H), 2.30−2.15 (m, 1H), 2.06−1.95 (m, 2H), 0.93 (d, J = 6.7 Hz, 6H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 202.6, 166.9, 148.0, 147.8, 135.2, 131.8, 130.2, 129.0, 128.7, 128.5, 128.1, 123.7, 123.4, 122.0, 121.1, 120.4, 117.9, 117.7, 111.0, 58.0, 53.4, 51.7, 51.3, 28.0, 20.5. IR (KBr): 2957, 1714, 1434, 1301 cm^{-1}. EI-MS *m/z*: 572 (M$^+$). HRMS *m/z* calcd for C$_{32}$H$_{36}$N$_4$O$_4$S: 572.2457. Found: 572.2465.

1-(2-Cyclohex-1-enyl-ethyl)-1′-isopropyl-2′-methylsulfanyl-1*H*,1′*H*-[2,5′]bibenzoimidazolyl-5-carboxylic Acid Methyl Ester (10f). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.48 (s, 1H), 7.97 (d, J = 8.5 Hz, 2H), 7.92 (s, 1H), 7.54 (q, J = 8.5 Hz, 2H) 5.12 (s, 1H), 4.66 (septet, J = 6.9 Hz, 1H), 3.90 (s, 3H), 2.77 (s, 3H), 2.29 (t, J = 6.8 Hz, 2H), 1.84∼1.62 (m, 4H), 1.61 (d, J = 6.9 Hz, 6H), 1.42−1.30 (m, 4H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 167.8, 156.1, 142.8, 142.7, 142.3, 142.2, 138.9, 133.2, 129.1, 128.5, 128.5, 128.4, 127.9, 127.7, 127.2, 125.8, 124.7, 124.4, 124.1, 122.1, 120.8, 117.4, 114.6, 109.9, 72.6, 52.1, 48.5, 43.8, 38.0, 33.5, 29.7, 28.2, 25.2, 22.7, 22.0. IR (KBr): 2929, 1714, 1435, 1294 cm^{-1}. EI-MS *m/z*: 488 (M$^+$). HRMS *m/z* calcd for C$_{28}$H$_{32}$N$_4$O$_2$S: 488.2246. Found: 488.2251.

1-(2-Cyclohex-1-enyl-ethyl)-2′-ethylsulfanyl-1′-isopropyl-1*H*,1′*H*-[2,5′]bibenzoimidazolyl-5-carboxylic Acid Methyl Ester (10g). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.50 (d, J = 1.3 Hz, 1H), 8.01 (dd, J = 8.5, 1.5 Hz, 1H), 7.93 (s, 1H), 7.64−7.56 (m, 2H), 7.41 (d, J = 8.5 Hz, 1H), 5.16 (s, 1H), 4.73 (septet, J = 6.9 Hz, 1H), 4.39 (t, J = 7.1 Hz, 2H), 3.93 (s, 3H), 3.39 (q, J = 7.4 Hz, 2H), 2.33 (t, J = 7.1 Hz, 2H), 1.84−1.66 (m, 4H), 1.63 (d, J = 6.9 Hz, 6H), 1.46 (t, J = 7.4 Hz, 3H), 1.42−1.35 (m, 4H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 156.1, 145.1, 144.6, 143.3, 142.7, 138.9, 136.6, 134.2, 133.2, 130.8, 129.2, 128.9, 128.7, 128.5, 128.45, 127.9, 127.7, 126.2, 126.1, 126.05, 125.8, 125.0, 124.9, 124.7, 124.6, 124.4, 122.1, 120.3, 117.4, 109.9, 52.1, 50.0, 48.5, 48.1, 43.9, 42.4, 38.0, 33.8, 31.6, 29.8, 28.2, 25.1, 22.7. IR (KBr): 2930, 1715, 1434, 1293 cm^{-1}. EI-MS *m/z*: 502 (M$^+$). HRMS *m/z* calcd for C$_{29}$H$_{34}$N$_4$O$_2$S: 502.2402. Found: 502.2404.

1-(2-Cyclohex-1-enyl-ethyl)-1′-isopropyl-2′-(4-methoxy-benzylsulfanyl)-1*H*,1′*H*-[2,5′]bibenzoimidazolyl-5-carboxylic Acid Methyl Ester (10h). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.52 (d, J = 1.3 Hz, 1H), 8.03 (dd, J = 8.5, 1.5 Hz, 1H), 7.98 (d, J = 1.1 Hz, 1H), 7.61 (dd, J = 8.5, 1.5 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.42 (d, J = 8.5 Hz, 1H), 7.21 (t, J = 7.8 Hz, 1H), 6.99 (d, J = 9.6 Hz, 2H), 6.80 (d, J = 8.1 Hz, 1H), 5.19 (s, 1H), 4.71 (septet, J = 6.9 Hz, 1H), 4.60 (s, 2H), 4.41 (d, J = 6.9 Hz, 2H), 3.95 (s, 3H), 3.75 (s, 3H), 2.36 (t, J = 7.0 Hz, 2H), 1.84−1.70 (m, 4H), 1.59 (d, J = 6.9 Hz, 6H), 1.48−1.30 (m, 4H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 167.7, 161.9, 158.6, 155.9, 143.0, 142.6, 138.9, 138.5 129.8, 129.7, 129.2, 129.2, 129.0, 128.5, 128.3 127.9, 127.7, 127.3, 124.4, 124.2, 123.9, 123,8, 122.1, 120.3, 117.7, 116.0, 115.7, 114.5, 114.4, 109.8, 96.0, 88.1, 70.0, 67.0, 57.0, 52.1, 47.7, 44.8, 31.9, 29.7, 20.0, 15.6, 13.6. IR (KBr): 2932, 1714, 1434, 1294 cm^{-1}. ESI-MS *m/z*: 595 (M + 1). HRMS *m/z* calcd for C$_{35}$H$_{38}$N$_4$O$_3$S: 594.2665. Found: 594.2659.

2′-Allylsulfanyl-1-butyl-1′-furan-2-ylmethyl-1*H*,1′*H*-[2,5′]bibenzoimid-azolyl-5-carboxylic Acid Methyl Ester (10i). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.52 (d, J = 1.1 Hz, 1H), 8.04 (dd, J = 8.5, 1.5 Hz, 1H), 7.93 (d, J = 1.1 Hz, 1H), 7.64 (dd, J = 8.5, 1.5 Hz, 1H), 7.52 (d, J = 8.5 Hz, 1H), 7.43 (d, J = 8.5 Hz, 1H), 7.36 (s, 1H), 6.40∼6.28 (m, 2H), 6.12−5.96 (m, 1H), 5.35 (d, J = 18.3 Hz, 1H), 5.32 (s, 2H), 5.12 (d, J = 9.9 Hz, 1H), 4.29 (t, J = 7.5 Hz, 2H), 4.07 (d, J = 7.0 Hz, 2H), 3.95 (s, 3H), 1.89−1.76 (m, 2H), 1.27−1.21 (m, 2H), 0.83 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 167.7, 156.0, 142.9, 142.6, 140.8 139.0, 138.6, 133.5, 129.5, 129.3, 128.8, 128.3, 128.0, 127.3, 127.1, 124.4, 124.2, 123.5, 122.1, 120.0, 117.6, 114.2, 109.8, 73.2, 57.0, 52.1, 45.6, 44.7, 31.8, 22.7, 19.9, 13.6. IR (KBr): 2956, 1713, 1435, 1302 cm^{-1}. ESI-MS *m/z*: 501 (M + 1). HRMS *m/z* calcd for C$_{28}$H$_{28}$N$_4$O$_3$S: 500.1882. Found: 500.1888.

1-Butyl-1′-furan-2-ylmethyl-2′-(3-methyl-but-2-enylsulfanyl)-1*H*,1′*H*-[2,5′]bibenzoimidazolyl-5-carboxylic Acid Methyl Ester (10j). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.52 (d, J = 1.1 Hz, 1H), 8.04 (dd, J = 8.5, 1.5 Hz, 1H), 7.93 (d, J = 1.1 Hz, 1H), 7.64 (dd, J = 8.5, 1.5 Hz, 1H), 7.52 (d, J = 8.5 Hz, 1H), 7.43 (d, J = 8.5 Hz, 1H), 7.36 (s, 1H), 6.38−6.32 (m, 2H), 5.43 (t, J = 7.9 Hz, 1H), 5.30 (s, 2H), 4.29 (t, J = 7.5 Hz, 2H), 4.07 (d, J = 7.9 Hz, 2H), 3.95 (s, 3H), 1.84−1.70 (m, 8H), 1.28−1.21 (m, 2H), 0.83 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 167.8, 161.5, 158.2, 156.1, 143.6, 142.6, 138.9, 130.6, 130.4, 129.4, 129.3, 129.0, 1288, 128.7, 126.9, 124.3, 124.0, 123.7, 123.6, 122.1, 121.7, 117.2, 115.9, 115.6, 114.0, 109.8, 64.1, 59.1, 52.1, 44.6, 43.7, 31.8, 31.7, 31.6, 30.7, 29.7, 26.3, 25.7, 22.7, 19.9, 14.2. IR (KBr): 2955, 1713, 1435, 1302 cm^{-1}. EI-MS *m/z*: 528 (M$^+$). HRMS *m/z* calcd for C$_{30}$H$_{32}$N$_4$O$_3$S: 528.2195. Found: 528.2200.

Butyl-1′-furan-2-ylmethyl-2′-(3-phenyl-allylsulfanyl)-1*H*,1′*H*-[2,5′]bibenzoimidazolyl-5-carboxylic Acid Methyl Ester (10k). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.53 (d, J = 1.1 Hz, 1H), 8.04 (dd, J = 8.5, 1.5 Hz, 1H), 7.96 (d, J = 1.1 Hz, 1H), 7.64 (dd, J = 8.5, 1.5 Hz, 1H), 7.52 (d, J = 8.5 Hz, 1H), 7.44 (d, J = 8.5 Hz, 1H), 7.36−7.22 (m, 6H), 6.67 (d, J = 15.6 Hz, 1H), 6.48−6.28 (m, 3H), 5.30 (s, 2H),

4.30 (t, *J* = 7.5 Hz, 2H), 4.25 (dd, *J* = 7.4, 1.0 Hz, 2H), 3.94 (s, 3H), 1.86−1.72 (m, 2H), 1.32−1.20 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 167.7, 156.1, 143.6, 142.7, 141.7, 138.9, 133.5, 129.2, 129.0, 127.1, 124.4, 124.1, 122.8, 122.2, 122.1, 117.2, 114.0, 109.8, 60.4, 53.5, 52.1, 44.6, 43.0, 31.8, 31.6, 31.1, 26.2, 26.0, 25.9, 19.9, 13.5. IR (KBr): 2955, 1713, 1435, 1301 cm^{-1}. ESI-MS *m/z*: 577 (M + 1). HRMS *m/z* calcd for C$_{34}$H$_{32}$N$_4$O$_3$S: 576.2195. Found: 576.2200.

2′-Ethylsulfanyl-1′-isopropyl-1-(3-phenyl-propyl)-1*H*,1′*H*-[2,5′]bibenzo-imidazolyl-5-carboxylic Acid Methyl Ester (10l). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.55 (d, *J* = 1.1 Hz, 1H), 8.02 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.94 (s, 1H), 7.54 (s, 2H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.26−7.12 (m, 3H), 7.04 (d, *J* = 6.5 Hz, 2H), 4.77 (septet, *J* = 6.9 Hz, 1H), 4.33 (t, *J* = 7.5 Hz, 2H), 3.96 (s, 3H), 3.44 (q, *J* = 7.4 Hz, 2H), 2.56 (t, *J* = 7.4 Hz, 2H), 2.18∼2.08 (m, 2H), 1.68 (d, *J* = 6.9 Hz, 6H), 1.51 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 167.8, 156.1, 149.3, 143.7, 142.7, 138.9, 136.7, 129.0, 126.7, 124.3, 124.0, 123.0, 122.5, 122.0, 121.7, 117.7, 115.2, 109.8, 71.2, 59.0, 52.1, 44.7, 44.6, 31.8, 31.2, 26.0, 25.8, 19.9, 13.6. IR (KBr): 2978, 1714, 1434, 1294 cm^{-1}. ESI-MS *m/z*: 513 (M + 1). HRMS *m/z* calcd for C$_{30}$H$_{32}$N$_4$O$_2$S: 512.2246. Found: 512.2201.

2′-Allylsulfanyl-1′-isopropyl-1-(3-phenyl-propyl)-1*H*,1′*H*-[2,5′]bibenzo-imidazolyl-5-carboxylic Acid Methyl Ester (10m). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.53 (d, *J* = 1.1 Hz, 1H), 8.01 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.93 (s, 1H), 7.53 (s, 2H), 7.27 (d, *J* = 8.6 Hz, 1H), 7.25−7.13 (m, 3H), 7.03 (d, *J* = 6.5 Hz, 2H), 6.14−6.09 (m, 1H), 5.37 (dd, *J* = 16.8, 1.3 Hz, 1H), 5.19 (dd, *J* = 10.0, 1.3 Hz, 1H), 4.80 (septet, *J* = 6.9 Hz, 1H), 4.32 (t, *J* = 7.5 Hz, 2H), 4.07 (d, *J* = 6.1 Hz, 2H), 3.95 (s, 3H), 2.56 (t, *J* = 7.4 Hz, 2H), 2.20−2.09 (m, 2H), 1.67 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 202.6, 166.9, 148.0, 147.8, 135.2, 131.8, 130.2, 129.0, 128.7, 128.5, 128.1, 123.7, 123.4, 122.0, 121.1, 120.4, 117.9, 117.7, 111.0, 58.0, 53.4, 51.7, 51.3, 28.0, 20.5. IR (KBr): 2946, 1714, 1434, 1294 cm^{-1}. ESI-MS *m/z*: 525 (M + 1). HRMS *m/z* calcd for C$_{31}$H$_{32}$N$_4$O$_2$S: 524.2246. Found: 524.2238.

1′-Isopropyl-1-(3-phenyl-propyl)-2′-propylsulfanyl-1*H*,1′*H*-[2,5′]bibenzo-imidazolyl-5-carboxylic Acid Methyl Ester (10n). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.55 (d, *J* = 1.1 Hz, 1H), 8.02 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.94 (s, 1H), 7.55 (s, 2H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.26−7.12 (m, 3H), 7.05 (d, *J* = 6.5 Hz, 2H), 4.80 (septet, *J* = 6.9 Hz, 1H)), 4.34 (t, *J* = 7.5 Hz, 2H), 3.97 (s, 3H), 3.43 (t, *J* = 7.2 Hz, 2H), 2.57 (t, *J* = 7.4 Hz, 2H), 2.19∼2.10 (m, 2H), 1.94−1.82 (m, 2H), 1.69 (d, *J* = 6.9 Hz, 6H), 1.12 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 167.7, 159.3, 156.6, 145.0, 144.8, 143.4, 143.0, 136.6, 133.9, 129,4, 128.5, 128.4, 127.9, 127.8, 127.8, 127.5, 126.2, 126.1, 124.1, 123.5, 122.4, 121.0, 117.7, 114.7, 113.8, 111.4, 73.0, 57.6, 55.3, 52.0, 50.1, 49.1, 48.5, 45.2, 45.1, 33.9, 30.4, 25.3. IR (KBr): 2948, 1714, 1434, 1293 cm^{-1}. ESI-MS *m/z*: 527 (M + 1). HRMS *m/z* calcd for C$_{31}$H$_{34}$N$_4$O$_2$S: 526.2402. Found: 526.2422.

2′-Allylsulfanyl-1-butyl-1′-(3-phenyl-propyl)-1*H*,1′*H*-[2,5′]bibenzo-imidazolyl-5-carboxylic Acid Methyl Ester (10o). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.54 (d, *J* = 1.2 Hz, 1H), 8.05 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.95 (d, *J* = 1.2

Hz, 1H), 7.62 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.44 (d, *J* = 8.6 Hz, 1H), 7.38−7.16 (m, 6H), 6.14−5.94 (m, 1H), 5.38 (dd, *J* = 16.9, 1.0 Hz, 1H), 5.20 (dd, *J* = 9.9, 1.0 Hz, 1H), 4.32 (t, *J* = 7.5 Hz, 2H), 4.18 (t, *J* = 7.4 Hz, 2H), 4.09 (d, *J* = 7.0 Hz, 2H), 3.97 (s, 3H), 2.74 (t, *J* = 7.5 Hz, 2H), 2.27−2.16 (m, 2H), 1.91−1.79 (m, 2H), 1.30−1.21 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 167.7, 156.0, 143.4, 143.0, 142.5, 136.9, 129.3, 128.4, 127.8, 127.6, 127.3, 124.0, 123.6, 122.3, 121.3, 117.5, 114.6, 111.8, 73.2, 60.7, 52.0, 49.0, 48.9, 26.6, 21.5, 20.8, 20.8. IR (KBr): 2956, 1715, 1434, 1301 cm^{-1}. ESI-MS *m/z*: 539 (M + 1). HRMS *m/z* calcd for C$_{32}$H$_{34}$N$_4$O$_2$S: 538.2402. Found: 538.2439.

1-Butyl-2′-ethylsulfanyl-1′-(3-phenyl-propyl)-1*H*,1′*H*-[2,5′]bibenzo-imidazolyl-5-carboxylic Acid Methyl Ester (10p). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.52 (d, *J* = 1.2 Hz, 1H), 8.04 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.92 (d, *J* = 1.1 Hz, 1H), 7.60 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.34−7.16 (m, 6H), 4.31 (t, *J* = 7.5 Hz, 2H), 4.16 (t, *J* = 7.4 Hz, 2H), 3.96 (s, 3H), 3.43 (q, *J* = 7.4 Hz, 2H), 2.73 (t, *J* = 7.9 Hz, 2H), 2.27−2.16 (m, 2H), 1.83−1.74 (m, 2H), 1.49 (t, *J* = 7.4 Hz, 3H), 1.30−1.21 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 167.7, 159.1, 156.0, 143.4, 143.0, 142.5, 136.9, 129.3, 128.4, 127.8, 127.6, 127.3, 124.0, 123.6, 122.3, 121.3, 117.5, 114.6, 111.8, 73.2, 60.7, 52.0, 49.0, 48.9, 26.6, 21.5, 20.8, 20.8; IR (KBr): 2954, 1714, 1434, 1301 cm^{-1}. ESI-MS *m/z*: 527 (M + 1). HRMS *m/z* calcd for C$_{31}$H$_{34}$N$_4$O$_2$S: 526.2402. Found: 526.2384.

1-(3-Methoxy-propyl)-2′-(3-methyl-but-2-enylsulfanyl)-1′-(3-methyl-butyl)-1*H*,1′*H*-[2,5′]bibenzoimidazolyl-5-carboxylic Acid Methyl Ester (10q). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.51 (d, *J* = 1.1 Hz, 1H), 8.02 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.94 (d, *J* = 1.1 Hz, 1H), 7.63 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 5.42 (t, *J* = 8.0 Hz, 1H), 4.44 (t, *J* = 7.2 Hz, 2H), 4.11 (t, *J* = 7.5 Hz, 2H), 4.06 (d, *J* = 8.0 Hz, 2H), 4.00 (s, 3H), 3.21 (t, *J* = 5.7 Hz, 2H), 3.17 (s, 3H), 2.04−1.95 (m, 2H), 1.74 (s, 6H), 1.66−1.60 (m, 3H), 1.00 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 167.7, 159.1, 156.0, 143.4, 143.0, 142.5, 136.9, 129.3, 128.4, 127.8, 127.6, 127.3, 124.0, 123.6, 122.3, 121.3, 117.5, 114.6, 111.8, 73.2, 60.7, 52.0, 49.0, 48.9, 26.6, 21.5, 20.8, 20.8. IR(KBr): 2954, 1715, 1433, 1301 cm^{-1}. ESI-MS *m/z*: 535 (M + 1). HRMS *m/z* calcd for C$_{30}$H$_{38}$N$_4$O$_3$S: 534.2665. Found: 534.2665.

1-(3-Methoxy-propyl)-1′-(3-methyl-butyl)-2′-(3-phenyl-allylsulfanyl)-1*H*,1′*H*-[2,5′]bibenzoimidazolyl-5-carboxylic Acid Methyl Ester (10r). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.53 (d, *J* = 1.2 Hz, 1H), 8.04 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.00 (d, *J* = 1.1 Hz, 1H), 7.65 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.42−7.18 (m, 6H), 6.68 (d, *J* = 15.7 Hz, 1H), 6.50−6.34 (m, 1H), 4.63 (t, *J* = 7.0 Hz, 1H), 4.25 (d, *J* = 7.4 Hz, 2H), 4.13 (t, *J* = 7.3 Hz, 2H), 3.96 (s, 3H), 3.23 (t, *J* = 5.6 Hz, 2H), 3.18 (s, 3H), 2.04−1.94 (m, 3H), 1.74−1.62 (m, 3H), 1.00 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 167.7, 156.1, 153.0, 143.4, 142.6, 139.3, 137.2, 136.4, 134.0, 128.5, 127.8, 126.4, 124.3, 124.1, 123.7, 123.6, 123.5,

122.0, 118.8, 109.8, 109.2, 68.7, 58.5, 52.0, 42.8, 41.8, 38.1, 35.2, 30.0, 29.6, 25.8, 22.4. IR (KBr): 2953, 1713, 1433, 1301 cm^{-1}. ESI-MS *m/z*: 583 (M + 1). HRMS *m/z* calcd for $C_{34}H_{38}N_4O_3S$: 582.2665. Found: 582.2690.

2′-(4-Fluoro-benzylsulfanyl)-1-(3-methoxy-propyl)-1′-(3-methyl-butyl)-1*H*,1′*H*-[2,5′]bibenzoimidazolyl-5-carboxylic Acid Methyl Ester (10s). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.53 (d, *J* = 1.3 Hz, 1H), 8.05 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.02 (d, *J* = 1.2 Hz, 1H), 7.65 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.35−7.44 (m, 3H), 7.05−6.95 (m, 2H), 4.62 (s, 2H), 4.47 (t, *J* = 6.7 Hz, 2H), 4.08 (t, *J* = 7.1 Hz, 2H), 3.96 (s, 3H), 3.24 (t, *J* = 5.6 Hz, 2H) 3.19 (s, 3H), 2.07−1.95 (m, 2H), 1.80−1.51 (m, 3H), 0.98 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 167.5, 163.7, 160.4, 155.9, 152.7, 144.2, 143.2, 139.0, 136.9, 132.5, 130.7, 130.6, 124.2, 123.9, 123.4, 123.3, 121.8, 118.8, 115.5, 115.2, 109.7, 109.1, 68.6, 58.4, 51.9, 42.6, 41.7, 37.8, 36.0, 29.8, 25.6, 22.2. IR (KBr): 2955, 1714, 1433, 1301 cm^{-1}. ESI-MS *m/z*: 575 (M + 1). HRMS *m/z* calcd for $C_{32}H_{35}N_4O_3S$: 574.2414. Found: 574.2366.

1-(3-Methyl-butyl)-2′-(naphthalen-2-ylmethylsulfanyl)-1′-thiophen-2-ylmethyl-1*H*,1′*H*-[2,5′]bibenzoimidazolyl-5-carboxylic Acid Methyl Ester (10t). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.55 (d, *J* = 1.2 Hz, 1H), 8.12−8.00 (m, 2H), 7.88 (s, 1H), 7.84−7.76 (m, 3H), 7.65 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.56 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.53−7.43 (m, 4H), 7.21 (dd, *J* = 5.0, 1.2 Hz, 1H), 6.96 (d, *J* = 3.0 Hz, 1H), 6.89 (dd, *J* = 8.5, 1.5 Hz, 1H), 5.43 (s, 2H), 4.85 (s, 2H), 4.33 (t, *J* = 7.8 Hz, 2H), 3.98 (s, 3H), 1.74 (q, *J* = 7.0 Hz, 2H), 1.65−1.50 (m, 1H), 0.88 (d, *J* = 6.5 Hz, 6H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 168.1, 156.4, 153.4, 143.9, 143.2, 139.3, 137.9, 137.2, 134.3, 133.7, 133.2, 129.0, 128.4, 128.2, 128.1, 127.4, 127.3, 127.2, 126.7, 126.6, 126.4, 124.8, 124.5, 122.6, 119.6, 110.1, 52.5, 43.9, 43.2, 38.9, 38.3, 26.4, 22.7. IR (cm^{-1}, neat): 2953, 1711, 1433, 1301. ESI-MS *m/z*: 631 (M + 1). HRMS *m/z* calcd for $C_{37}H_{34}N_4O_2S_2$: 630.2123. Found: 630.2133.

Supporting Information Available. Proton and carbon NMR spectra of compounds **6a−f**, **8a−i**, and **10a−i**. This information is available free of charge via the Internet at http://pubs.acs.org.

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