The Diels–Alder Approach for the Synthesis of Tetralin-Based α-Amino Acid Derivatives and their Modification by the Suzuki–Miyaura Cross-Coupling Reaction

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Abstract: Tetralin-based α-amino acid (AAA) is a constrained analogue of phenylalanine (Phe) and is used extensively in the design and synthesis of a variety of bioactive peptides. Due to the nonavailability of simple synthetic methods to deliver complex cyclic AAAs, only simplest members of this class have been used in the peptide area. In this regard, we have developed a new method to prepare various highly functionalized tetralin-based unusual AAA derivatives **22**, **37**–**43** by trapping *o*-xylylene (or *o*-quinodimethane) intermediate with methyl 2-acetamidoacrylate (**12**). In addition, we have also modified the diidotetralin derivative **40** by the Suzuki–Miyaura cross-coupling reaction.

Key words: amino acids, coupling, Diels–Alder reaction, palladium, peptides

Traditional peptide structure-activity studies employing proteinogenic amino acids have a limited potential. Many exciting possibilities are opened up when such studies involve the incorporation of non-proteinogenic amino acids with sterically demanding side-chains. For example, a large variety of structural variations are feasible even with tri- or tetrapeptide by single amino acid replacement with unusual AAA derivatives.[1] The realization of these goals are aided by the development of new and general synthetic methods[2] that can deliver nonproteinogenic (or unusual) AAAs with varying degree of topographical,[3] steric and electronic properties. On several occasions, when phenylalanine (Phe) (**1**) is replaced with 2-indanylglycine **2** in peptide modifications, the resulting peptidomemitics have shown enhanced desirable properties.[4] In this regard, we had demonstrated several methodologies for various derivatives of **2**.[5a–f] At this juncture, we were also interested in developing new methodology for the synthesis of various tetralin-based AAA derivatives (e.g. **3**).

Conformationally constrained 2-aminotetralin-2-carboxylic acid (Atc) is a constrained Phe analog, which has been incorporated in place of Phe[3] into μ and δ-selective opioid peptides.[6–9] Also, another unusual AAA derivative Hat (6-hydroxy-2-aminotetralin-2-carboxylic acid) has been incorporated for Try[1] in leucine enkephalin and related peptides.[10–12]

Narcotic analgesics such as morphine has been used as a potential drug in the treatment of severe pain therapy.[13,14] A dynorphin analog, E-2078 has been studied as a potential analgesic and also another application in κ-selective compounds as potential neuroprotective and anticovulsant agents.[15–17] Recently, Aldrich et al. have synthesized the heptadecapeptide dynorphin A (Dyn A) analogs by solid-phase synthesis using F-moc protected AAA and modified by incorporating S-Act and R-Act at Phe[4] position of Dyn A.[18,19]

In addition to the above-mentioned applications of tetralin-based AAAs, tetralin nucleus is an important structural element, which can fix the relative position of functional groups to impart a greater specificity for biological activity. Daunomycin (**4**), adriamycine (**5**) are two important antitumor antibiotics. In this regard, Ishizumi and coworkers have reported (+)-9-amino-9-deoxydaunomycin (**6**)[20] (Figure 2) and its related compounds. In this sequence, the key precursor tetralin-based AAA **7** has been synthesized by Bucherer–Berg method.[21,22]

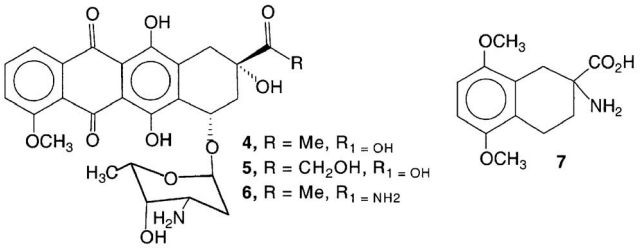

Figure 2 Compounds **4**–**7**

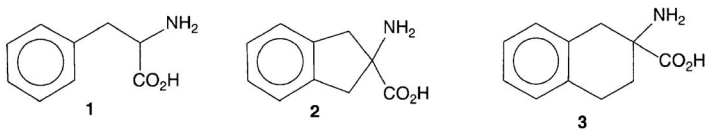

Figure 1 Compounds **1**–**3**

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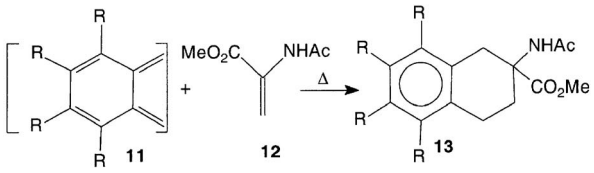
Synthesis of cyclic AAAs via Bucherer–Berg[23] method begins with the corresponding carbonyl derivative as the starting material. Thus, treatment of the ketone **8** with potassium cyanide and ammonium carbonate generates spirohydantoin **9**, which upon hydrolysis gives AAA **10** (Scheme 1).

Denyer et al. have synthesized various amino alkyl substituted tetralin based AAA derivatives via hydantoin intermediate of the corresponding tetralone in a step-wise manner.[24] Along similar lines, Markquez et al. have reported several amino alkyl substituted tetralin-based AAA derivatives.[25] Recently, Undheim et al. have prepared[26] rigid indacene-bridged bis AAA derivative via a [2+2+2] cycloaddition reaction using Grubbs catalyst and Solladie-Cavallo et al. have reported the synthesis of (+)-(*R*)-methyl 2-aminotetralin-2-carboxylate[27] via Schollköpf's bislactim method.[28–31]

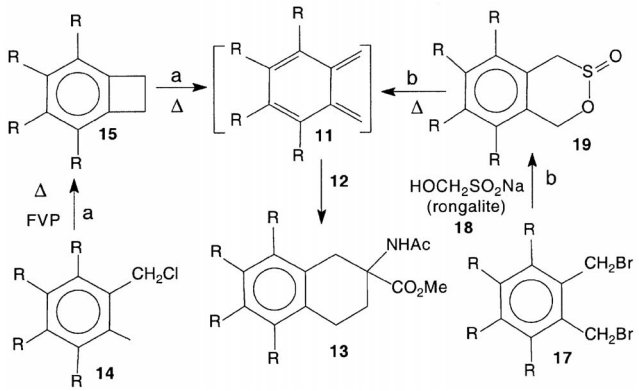
As part of our major program directed towards the synthesis of constrained AAA derivatives via 'Building Block Approach',[32] we conceived a new strategy[33] for the preparation of 2-aminotetralin-2-carboxylic acid derivatives **13** using the Diels–Alder reaction as a key step.

Generally, synthetic approach to **3** involves (BB) the method starting from the commercially available 2-tetralone. Hydrolysis of the intermediate spirohydantoin requires drastic reaction conditions and consequently sensitive substrates are not suitable for this purpose.[34] Here, we would like to report our results towards the synthesis of tetralin-based AAA derivatives by trapping various transient *o*-xylylene intermediates[35] (e.g. **11**) with methyl 2-acetamidoacrylate (**12**)[36] in a Diels–Alder fashion (Equation 1). The detailed retrosynthetic strategy for tetralin-based AAA derivative **13** is shown in Scheme 2. Path a involves the thermal isomerization of the benzocyclobutene (BCB) **15** to *o*-xylylene **11** followed by the Diels–Alder reaction with **12**. The second route (path b) rely on chelotropic elimination of sulfur dioxide from sultine **19** leading to the formation of transient intermediate **11** which in turn reacts with **12** to generate AAA derivative **13**. Although both these routes involve the same intermediate, the method of generation of the intermediate **11** is crucial in present context. Several other reductive elimination methods for the generation of **11** that are incompatible with **12** are not considered here.[35]

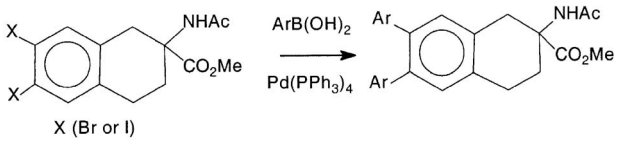
Towards this goal, a general methodology based on 'Building Block Approach'[32] was pursued. 'Building Block Approach' involves generation of several target molecules of diverse structures starting from a common precursor. By adopting this strategy one can deliver a series of tetralin-based ααAAs with varying shape, size and redox properties within a very short period of time. Also, we report the extension of the 'Building Block Approach' by using the Suzuki–Miyaura cross-coupling reaction[37] as a key step (Scheme 3) for the synthesis of various aryl functionalized tetralin-based ααAAA derivatives.



Equation 1

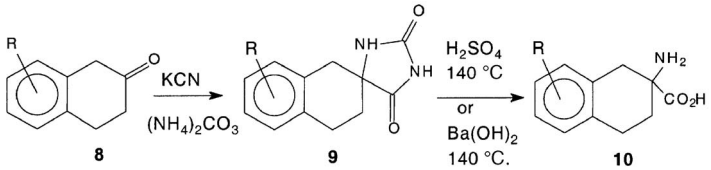


Scheme 2



Scheme 3

Towards the synthesis of compounds of type **13**, initially benzocyclobutene (BCB) was reacted with **12** at different temperatures (80–120 °C) and it was found that no Diels–Alder product was formed. Since the parent BCB undergoes cyclobutene ring opening at 200 °C,[38] BCB **15** (R = H) and **12** was reacted in xylene in a sealed tube at 180–200 °C, which gave several products as indicated by TLC analysis. At this juncture it occurred to us that a milder method for the generation of *o*-xylylene **11** is desirable. Moreover, generation of **11** in the absence of dienophile is known to give dimerization and/or

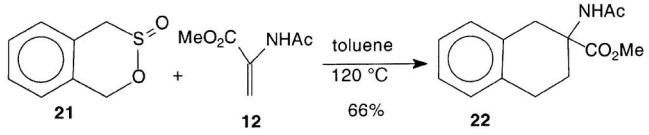


Scheme 1

polymerization to generate unwanted products. A perusal of literature indicated that generation of *o*-xylylene[39–44] such as **11** by thermal elimination of sulfur dioxide from the sultine, 1,4-dihydro-2,3-benzoxathiin-3-oxide requires lower temperature.

In this regard, the parent sultine **21**[45] was prepared according to the literature procedure by treating of *o*-xylene dibromide **20** with sodium hydroxymethane sulfinate (rongalite, **18**)[46] in presence of tetrabutylammonium bromide (TBAB) in DMF at 0 °C (Scheme 4). Having the sultine derivative **21**[47] in hand, it was reacted with methyl 2-acetamidoacrylate (**12**) at benzene reflux temperature to give the required product **22** in 66% isolated yield. The structure of **22** was fully in agreement with its spectral data (Scheme 5).

Scheme 4



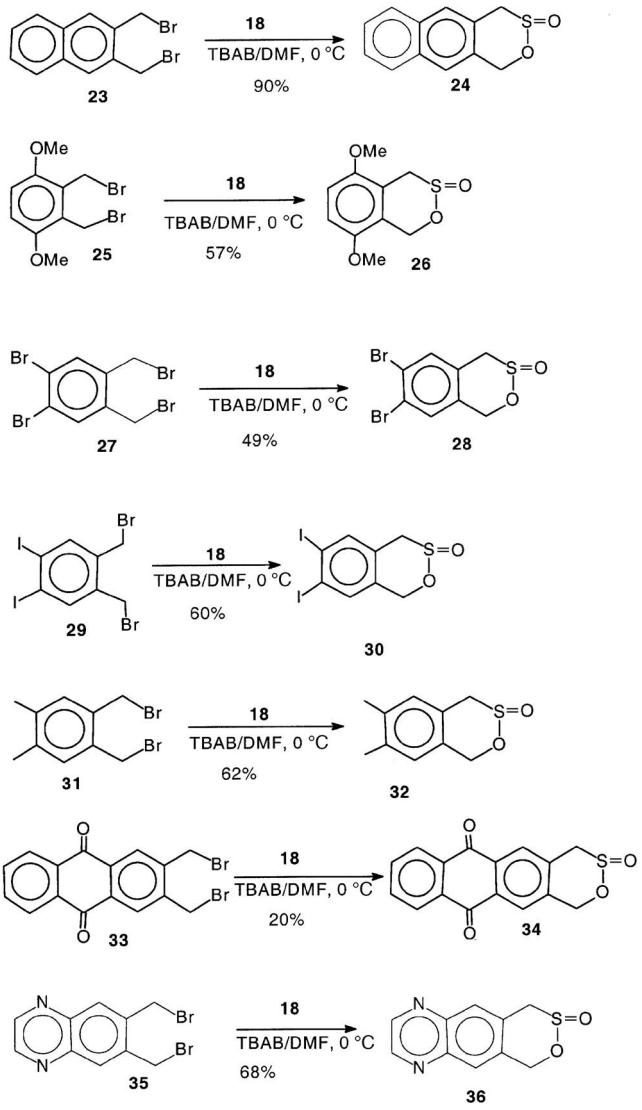
Scheme 5

Having established the conditions for trapping *o*-xylylene in the presence of **12**, the attention was turned next to expand this strategy to other related substrates. The synthetic routes adopted for the preparation of various sultine derivatives are shown in Scheme 6. Various tetralin-based AAA prepared in this regard are included in Table 1.

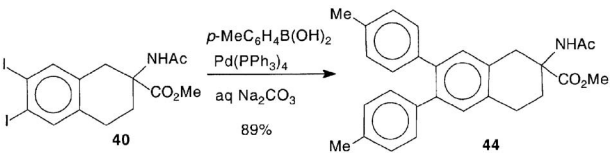
Having prepared the diiodo compound **40** in good yield, it was treated with *p*-methylphenylboronic acid in the presence of Pd(0) catalyst, $[Pd(PPh_3)_4]$, aqueous Na_2CO_3 and THF–toluene to deliver the disubstituted tetralin-based AAA derivative **44** in 89% yield (Scheme 7). Although there are several methods for aryl–aryl cross-coupling reaction, the Suzuki–Miyaura cross-coupling reaction seems to tolerate various functional groups compared to the other methods.[48]

Then, the Suzuki–Miyaura coupling reaction was attempted with several boronic acids (4-methoxyphenylboronic acid, 4-fomylphenylboronic acid, 4-acetylphenylboronic acid, etc.) using $[Pd(PPh_3)_4]$ catalyst and the results of the reactions are outlined in Table 2. Typically, 65–91% yields of the coupling product were observed. All the coupling products **44**–**49** were characterized by appropriate spectral data (IR, UV, ^1H NMR, ^{13}C NMR, HRMS).

We have shown that various *o*-xylylene derivatives derived from sultines have been trapped with methyl 2-acetamidoacrylate (**12**) in a Diels–Alder fashion to generate various tetralin-based constrained AAA derivatives. It is worth mentioning that compounds of type **42** are inaccessible by the currently available methods such as BB method due the presence of keto functionality. Moreover, the synthesis of starting keto precursor required for BB method is not trivial exercise. We also modified the diiodotetralin derivative **40** by Suzuki–Miyaura coupling reaction with various functionalized aryl boronic acids under Pd(0) catalyst and the insertion of various aryl functionalities into tetralin-based AAA is much easily accessible than other classical methods. Since constrained AAA derivatives play an important role in the design of biologically active peptides, our results may be of interest to medicinal and bioorganic chemists working in these areas.

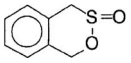
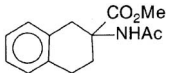
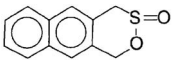
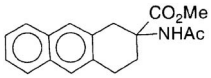
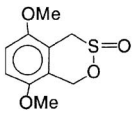
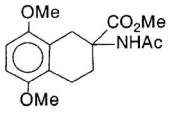
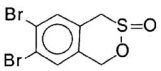
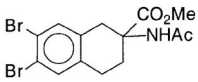
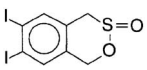
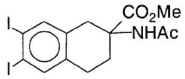
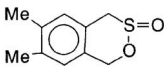
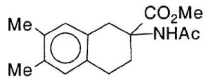
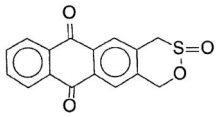
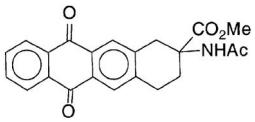
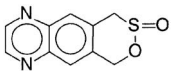
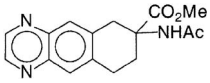


Scheme 6



Scheme 7

Table 1 Various Tetralin-Based AAA Derivatives Prepared by the Diels–Alder Strategy

Entry	Sultine	Yield (%)	Diels–Alder Product	Yield (%)
1	 **21**[45]	83	 **22**	66
2	 **24**	90[a]	 **37**	65
3	 **26**	57	 **38**	64
4	 **28**	49[a]	 **39**	67[a]
5	 **30**	60	 **40**	92
6	 **32**	62	 **41**	36
7	 **34**	20	 **42**	53[a]
8	 **36**[42]	68	 **43**	60

[a] Improved yields were obtained as compared to previously reported results.[33]

Analytical TLC was performed on (10 × 5 cm) glass plates coated with Acme's silica gel G or GF 254 (containing 13% $CaSO_4$ as a binder). Visualization of the spots on TLC plate was achieved either by exposure to I_2 vapor, or UV light. Flash chromatography was performed using Acme's silica gel (100–200 mesh) and the column was usually eluted with EtOAc and petroleum ether (bp 60–80 °C) mixture. Melting points are uncorrected. FT-IR spectra were recorded as KBr pellets unless otherwise mentioned. UV spectra were taken in $CHCl_3$ solvent. MeCN and CCl_4 were distilled over P_2O_5. Anhyd THF and Et_2O were obtained by distillation over sodium-benzophenone ketyl. For all the reactions, anhyd $MgSO_4$ was used as the drying agent after workup. Palladium catalyst, $[Pd(PPh_3)_4]$ was prepared according to the literature procedure.[49] 4-Methylphenylboronic acid, 2-furylboronic acid, 2-thienylboronic acid were prepared according to the literature[50] procedure and other remaining boronic acids were purchased from Lancaster Chemical Co (UK) and Aldrich Chemical Co (USA). ^1H and ^{13}C NMR samples were prepared in $CDCl_3$ solvent and the chemical shifts were reported in δ scale using tetramethylsilane as the internal standard. 300 MHz ^1H and 75.4 MHz ^{13}C NMR spectra were recorded on a Bruker spectrometer. Coupling constants (*J*) are reported in Hertz.

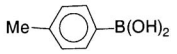
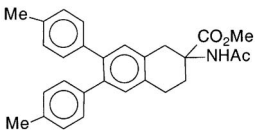
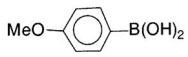
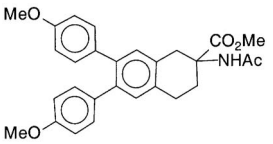
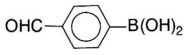
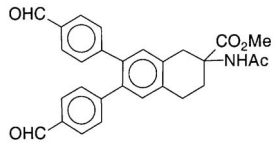
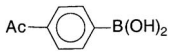
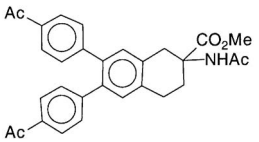
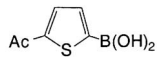
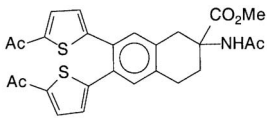
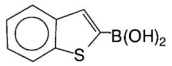
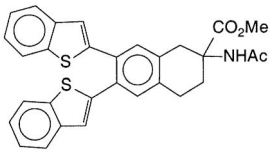
Sultine Derivatives from the Corresponding *o*-Xylene Dibromides; General Procedure (Scheme 6)

A mixture of *o*-xylene dibromide (1 equiv), sodium hydroxy methanesulfinate (**18**; rongalite, 5–6 equiv), and tetrabutylammonium bromide (TBAB, ca. 10 mol%) in anhyd DMF was stirred at 0 °C. Typically the reaction required stirring for 3–4 h at 0 °C and for 2–3 h at r.t. At the conclusion of the reaction (TLC monitoring), the mixture was diluted with H_2O and extracted with Et_2O. The combined organic layers were washed with H_2O, brine and dried ($MgSO_4$). The solvent was evaporated and the crude product was charged on a silica gel column. Elution of the column with EtOAc–petroleum ether gave the desired sultine derivative.

1,4-Dihydronaphth[2,3-*d*][1,2]oxathiin-3-oxide (24)

A suspension of rongalite (**18**; 460 mg, 3 mmol) in DMF (4 mL) was added to 2,3-bis(bromomethyl)naphthalene (**23**;[51] 96 mg, 0.3 mmol) and TBAB (30 mg, 0.1 mmol) at 0 °C and the resulting suspension was stirred at 0 °C for 6 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with 5% EtOAc–petroleum ether gave the compound **24** (60 mg, 90%) as a white solid; mp 175–176 °C.

Table 2 Various Tetralin-Based AAA Derivatives Modified by the Suzuki–Miyaura Cross-Coupling Reaction

Entry	Boronic Acid	Coupling Product	Yield (%)
1		 **44**	89
2		 **45**	91
3		 **46**	87
4		 **47**	65
5		 **48**	78
6		 **49**	79

IR (neat): 1639, 1440, 1116 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.75 (d, *J* = 15.1 Hz, 1 H), 4.67 (d, *J* = 15.1 Hz, 1 H), 5.13 (d, *J* = 13.1 Hz, 1 H), 5.50 (d, *J* = 13.1 Hz, 1 H), 7.50–7.55 (m, 2 H), 7.76–7.87 (m, 4 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 58.7, 64.3, 124.8, 125.3, 127.0, 127.08, 127.8, 128.0, 128.9, 131.9, 132.7, 133.4.

HRMS: *m*/*z* calcd for $C_{12}H_{10}SO_2$ [M + H]: 219.0479; found: 219.0480.

UV ($CHCl_3$): λ_{max} (ε) = 248 (3041), 278 nm (4591).

1,4-Dihydro-5,8-dimethoxy-2,3-benzoxathiin-3-oxide (26)

A suspension of rongalite (**18**; 332 mg, 2.16 mmol) in DMF (2.5 mL) was added to 1,4-dimethoxy-2,3-dibromoxylylene (**25**;[52] 70 mg, 0.21 mmol), TBAB (60 mg, 0.18 mmol) at 0 °C under N_2. The resulting suspension was stirred at 0 °C for 4 h and then the mixture was stirred at r.t. for 3 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with 5% EtOAc–petroleum ether gave the compound **26** (28 mg, 57%) as a white solid; mp 118–119 °C.

IR (KBr): 1480, 1436, 1261, 1108 cm^{-1}.

^1H NMR (300 MHZ, $CDCl_3$): δ = 3.62 (d, *J* = 16.4 Hz, 1 H), 3.78 (s, 6 H), 4.11 (d, *J* = 16.4 Hz, 1 H), 5.09 (d, *J* = 15.1 Hz, 1 H), 5.15 (d, *J* = 15.1 Hz, 1 H), 6.77 (s, 2 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 48.2, 55.9, 56.0, 56.8, 109.1, 109.3, 114.6, 122.0, 149.3, 151.4.

HRMS: *m*/*z* calcd for $C_{10}H_{12}SO_4$ [M + H]: 229.0534; found: 229.0534.

UV ($CHCl_3$): λ_{max} (ε) = 246 (1674), 296 nm (4190).

6,7-Dibromo-1,4-dihydro-2,3-benzoxathiin-3-oxide (28)

A suspension of rongalite (**18**; 3.5 g, 23 mmol) in DMF (3 mL) was added to 1,2-bis(bromomethyl)-4,5-dibromobenzene (**27**;[53] 1 g, 2.3 mmol) and (TBAB) (200 mg, 0.7 mmol) at 0 °C and the resulting suspension was stirred at 0 °C for 3 h and then at r.t. for 3 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with 5% EtOAc–petroleum ether gave the compound **28** (356 mg 48%) as a white solid; mp 110 °C.

IR (neat): 1485, 1406, 1374, 1321, 1196, 1117 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.51 (d, *J* = 15.5 Hz, 1 H), 4.26 (d, *J* = 15.5 Hz, 1 H), 4.89 (d, *J* = 14.4 Hz, 1 H), 5.22 (d, *J* = 14.4 Hz, 1 H), 7.49 (s, 1 H), 7.51 (s, 1 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 55.3, 61.3, 124.4, 124.8, 126.8, 130.7, 133.8, 134.8.

HRMS: *m*/*z* Calcd for $C_8H_6Br_2SO_2$ [M + H]: 327.8414; found: 327.8435.

UV ($CHCl_3$): λ_{max} (ε) = 246 nm (3035).

1,4-Dihydro-6,7-diiodo-2,3-benzoxathiin-3-oxide (30)

A suspension of rongalite (**18**; 298 mg, 1.9 mmol) in DMF (3 mL) was added to 1,2-bis(bromomethyl)-4,5-diidobenzene (**29**;[54,5g] 100 mg, 0.19 mmol) and (TBAB) (61 mg, 2 mmol) at 0 °C and the resulting suspension was stirred at 0 °C for 3 h and then at r.t.for 3 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with 5% EtOAc–petroleum ether gave the compound **30** (45 mg, 60%) as a white solid; mp 90–91 °C.

IR (neat): 1654, 1455, 1321, 1105 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.47 (d, *J* = 15.5 Hz, 1 H), 4.21 (d, *J* = 15.5 Hz, 1 H), 4.85 (d, *J* = 14.4 Hz, 1 H), 5.17 (d, *J* = 14.4 Hz, 1 H), 7.71 (s, 1 H), 7.73 (s, 1 H).

HRMS: *m*/*z* Calcd for $C_8H_6I_2SO_2$ [M + H]: 420.8256; found: 420.8249.

UV ($CHCl_3$): λ_{max} (ε) = 252 nm (19507).

1,4-Dihydro-6,7-dimethyl-2,3-benzoxathiin-3-oxide (32)[55]

A suspension of rongalite (**18**; 210 mg, 1.37 mmol) in DMF (7 mL) was added to the dibromo compound **31**[56] (165 mg, 0.57 mmol) and TBAB (522 mg, 3.39 mmol) at 0 °C and the resulting suspension was stirred at 0 °C for 2.5 h and then at r.t. for 3 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with 5% EtOAc–petroleum ether gave the compound **32** (64 mg, 62%) as a white solid; mp 51–52 °C.

IR (neat): 1500, 1453, 1112, 1025 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.26 (s, 6 H), 3.51 (d, *J* = 15.3 Hz, 1 H), 4.29 (d, *J* = 15.3 Hz, 1 H), 4.89 (d, *J* = 13.5 Hz, 1 H), 5.24 (d, *J* = 13.5 Hz, 1 H), 6.98 (s, 1 H), 7.01 (s, 1 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 19.52, 19.7, 56.6, 63.2, 123.1, 126.8, 130.8, 130.9, 136.5, 137.2.

FAB-MS: *m*/*z* = 197 [M + H].

UV ($CHCl_3$): λ_{max} (ε) = 246 (911), 268 nm (912).

1,4-Dihydroanthra[2,3-*d*][1,2]oxathiin-5,11-dione-3-oxide (34)
A suspension of rongalite (**18**; 278 mg, 1.8 mmol) in DMF (2 mL) was added to dibromo compound **33**[57,5f] (71 mg, 0.18 mmol) and TBAB (100 mg, 0.3 mmol) at 0 °C and the resulting suspension was stirred at 0 °C for 4 h and then at r.t. for 3 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with 5% EtOAc–petroleum ether gave the compound **34** (11 mg, 20%) as a white solid; mp 183–184 °C.

IR (KBr): 1678, 1592, 1402, 1342, 1293, 1120, 1093 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.79 (d, *J* = 15.7 Hz, 1 H), 4.48 (d, *J* = 15.7 Hz, 1 H), 5.7 (d, *J* = 14.8 Hz, 1 H), 5.46 (d, *J* = 14.8 Hz, 1 H), 7.81–7.85 (m, 2 H), 8.18 (s, 2 H), 8.31–8.36 (m, 2 H).

MS-ES$^+$: *m*/*z* calcd for $C_{25}H_{16}O_2S$: 298.0299; found: 298.0231.

Tetralin-Based AAA Derivatives by the Diels–Alder Reaction with Various Sultine Derivatives and Methyl 2-Acetamidoacrylate (12) General Procedure (Table 1)
A solution of sultine (1 equiv) and methyl 2-acetamidoacrylate (**12**; 1.5–2 equiv) in benzene or toluene was refluxed until the starting materials had disappeared. At the conclusion of the reaction (TLC monitoring), the solvent was removed at reduced pressure and the crude product was purified by silica gel column chromatography. Elution of the column with EtOAc–petroleum ether mixture gave the required tetralin-based AAA derivative (Table 1).

2-(Acetylamino)-1,2,3,4-tetrahydro-2-naphthalenecarboxylic Acid Methyl Ester (22)
A solution of the sultine **21** (24 mg, 0.18 mmol), methyl 2-acetamidoacrylate (**12**; 26 mg, 0.14 mmol) and distilled benzene (1.5 mL) was stirred at 85 °C for 20 h. At the conclusion of reaction (TLC monitoring), the mixture was worked up according to the general procedure and the crude product was purified by a silica gel column chromatography. Elution of the column with 30% EtOAc–petroleum ether gave the compound **22** (20 mg, 66%) as a white solid; mp 127–128 °C.

IR (KBr): 3296 (NH), 1731 (ester C=O), 1650 (NC=O) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.92 (s, 3 H), 2.09–2.18 (m, 1 H), 2.55–2.6 (m, 1 H), 2.78–2.84 (m, 2 H), 2.98 (d, *J* = 16.5 Hz, 1 H), 3.27 (d, *J* = 16.5 Hz, 1 H), 3.76 (s, 3 H), 5.75 (s, 1 H), 7.06–7.26 (m, 4 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 23.0, 25.1, 27.7, 37.8, 52.5, 57.7, 126.1, 126.5, 128.8, 129.5, 131.9, 134.9, 170.1, 173.9.

HRMS: *m*/*z* calcd for $C_{14}H_{17}NO_3$ [M + H]: 248.1286; found: 248.1284.

UV ($CHCl_3$): λ_{max} (ε) = 274 (460), 266 nm (546).

2-(Acetylamino)-1,2,3,4-tetrahydro-2-anthracenecarboxylic Acid Methyl Ester (37)
A solution of the sultine **24** (60 mg, 0.27 mmol), methyl 2-acetamidoacrylate (**12**; 75 mg, 0.54 mmol) and toluene (2.5 mL) was stirred at 130 °C for 40 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure and the crude product was purified by a silica gel column chromatography. Elution of the column with 30% EtOAc–petroleum ether gave the compound **37** (53 mg, 65%) as a white solid; mp 220–221 °C.

IR (KBr): 3276 (NH), 1739 (ester C=O), 1654 (NC=O) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.90 (s, 3 H), 2.22–2.32 (m, 1 H), 2.56–2.61 (m, 1 H), 2.91–3.11 (m, 2 H), 3.21 (d, *J* = 16.2 Hz, 1 H), 3.42 (d, *J* = 16.2 Hz, 1 H), 3.78 (s, 3 H), 5.71 (s, 1 H), 7.39–7.40 (m, 2 H), 7.57 (s, 1 H), 7.61 (s, 1 H), 7.72–7.75 (m, 2 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 23.0, 25.4, 28.6, 38.3, 52.6, 58.1, 125.4, 125.7, 126.8, 127.0, 127.7, 130.9, 132.1, 132.5, 133.4, 170.1, 173.9.

HRMS: *m*/*z* calcd for $C_{18}H_{19}NO_3$: 297.1240; found: 297.1235.

UV ($CHCl_3$): λ_{max} (ε) = 323 (434), 285 nm (3828).

2-(Acetylamino)-1,2,3,4-tetrahydro-5,8-dimethoxy-2-naphthalenecarboxylic Acid Methyl Ester (38)
A solution of the sultine **26** (25 mg, 0.11 mmol), methyl 2-acetamidoacrylate (**12**; 35.5 mg, 0.23 mmol) and toluene (1 mL) was stirred in a sealed tube at 130 °C for 48 h. At the conclusion of reaction (TLC monitoring), the mixture was worked up according to the general procedure and the crude product was purified by a silica gel column chromatography. Elution of the column with 30% EtOAc–petroleum ether gave the compound **38** (21.5 mg, 64%) as a white solid; mp 168–170 °C.

IR (KBr): 3285 (NH), 1742 (ester C=O), 1661 (NC=O) cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.92 (s, 3 H), 1.98–2.04 (m, 1 H), 2.40–2.67 (m, 2 H), 2.89 (d, *J* = 17.2 Hz, 2 H), 3.08 (d, *J* = 17.2 Hz, 1 H), 3.76 (s, 6 H), 3.79 (s, 3 H), 5.60 (s, 1 H), 6.65 (s, 2 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 19.6, 23.0, 26.2, 32.6, 52.5, 55.5, 56.9, 107.0, 107.3, 122.0, 125.5, 151.0, 151.5, 169.9, 174.2.

HRMS: *m*/*z* calcd for $C_{16}H_{21}NO_3$: 307.1419; found: 307.1416.

UV ($CHCl_3$): λ_{max} (ε) = 289 (5228), 243 nm (3742).

2-(Acetylamino)-6,7-dibromo-1,2,3,4-tetrahydro-2-naphthalenecarboxylic Acid Methyl Ester (39)
A solution of the sultine **28** (50 mg, 0.12 mmol), methyl 2-acetamidoacrylate (**12**; 36 mg, 0.24 mmol) and toluene (1.5 mL) was stirred in a sealed tube at 120 °C for 48 h. At the conclusion of reaction (TLC monitoring), the mixture was worked up according to the general procedure and the crude product was purified by a silica gel column chromatography. Elution of the column with 35% EtOAc–petroleum ether gave the compound **39** (41 mg, 67%) as a white solid; mp 267–268 °C.

IR (KBr): 3344 (NH), 1721 (ester C=O), 1670 (NC=O) cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.77 (s, 3 H), 1.75–1.89 (m, 1 H), 2.21–2.25 (m, 1 H), 2.55–2.68 (m, 2 H), 2.89 (d, *J* = 17.0 Hz, 1 H), 3.13 (d, *J* = 17.0 Hz, 1 H), 3.57 (s, 3 H), 5.75 (s, 1 H), 7.81 (s, 2 H), 8.1 (s, 1 H).

^{13}C NMR (75.4 MHz, DMSO-d_6): δ = 22.2, 24.0, 27.8, 35.7, 52.0, 56.3, 120.4, 120.5, 133.1, 133.8, 135.6, 136.7, 169.6, 173.5.

HRMS: *m*/*z* calcd for $C_{14}H_{15}Br_2NO_3$: 402.9418; found: 402.9419.

UV ($CHCl_3$): λ_{max} (ε) = 242 (3272), 280 (1579) 288 nm (1573).

2-(Acetylamino)-1,2,3,4-tetrahydro)-6,7-diiodo-2-naphthalenecarboxylic Acid Methyl Ester (40)
A solution of the sultine **30** (90 mg, 0.21 mmol), methyl 2-acetamidoacrylate (**12**; 61 mg, 0.42 mmol) and toluene (3.5 mL) was stirred in a sealed tube at 130 °C for 72 h. At the conclusion of reaction (TLC monitoring), the mixture was worked up according to the general procedure and the crude product was purified by a silica gel column chromatography. Elution of the column with 35% EtOAc–

petroleum ether gave the compound **40** (98 mg, 92%) as a white solid; mp 272–273 °C.

IR (KBr): 3305 (NH), 1735 (ester C=O), 1651 (NC=O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.95 (s, 3 H), 2.03–2.13 (m, 1 H), 2.46–2.51 (m, 1 H), 2.68–2.76 (m, 2 H), 2.91 (d, *J* = 17.0 Hz, 1 H), 3.21 (d, *J* = 17.0 Hz, 1 H), 3.75 (s, 3 H), 5.56 (s, 1 H), 7.57 (s, 1 H), 7.63 (s, 1 H).

^{13}C NMR (75.4 MHz, DMSO-d_6): δ = 22.2, 23.8, 27.7, 35.6, 51.9, 56.3, 104.6, 104.8, 135.9, 137.1, 138.6, 139.3, 169.6, 173.5.

MS: *m*/*z* = 499 (M^+).

UV ($CHCl_3$): λ_{max} (ε) = 293 nm (1245).

Anal. Calcd for $C_{14}H_{15}I_2NO_3$: C, 33.67; H, 3.03; N, 2.80. Found: C, 33.71; H, 3.04; N, 2.62.

2-(Acetylamino)-1,2,3,4-tetrahydro)-6,7-dimethyl-2-naphthalenecarboxylic Acid Methyl Ester (41)

A solution of the sultine **32** (16 mg, 0.08 mmol), methyl 2-acetamidoacrylate (**12**; 17 mg, 0.12 mmol) and toluene (1 mL) was stirred in a sealed tube at 130 °C for 6 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure and the crude product was purified by a silica gel column chromatography. Elution of the column with 35% EtOAc–petroleum ether gave the compound **41** (8 mg, 36%) as a pale yellow solid; mp 188–190 °C.

IR (neat): 3354 (NH), 1722 (ester C=O), 1663 (NC=O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.92 (s, 3 H), 2.03–2.14 (m, 1 H), 2.21 (s, 6 H), 2.56–2.82 (m, 3 H), 2.88 (d, *J* = 16.8 Hz, 1 H), 3.17 (d, *J* = 16.8 Hz, 1 H), 3.76 (s, 3 H), 5.62 (s, 1 H), 6.84 (s, 1 H), 6.91 (s, 1 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 19.2, 23.0, 24.5, 27.5, 29.6, 37.7, 52.5, 57.8, 128.9, 129.9, 130.5, 132.2, 134.5, 135.0, 170.0, 174.0.

HRMS: *m*/*z* calcd for $C_{16}H_{21}NO_3$: 275.1521; found: 275.1521.

UV ($CHCl_3$): λ_{max} (ε) = 280 (1116), 272 nm (1102).

2-(Acetylamino)-1,2,3,4,6,11-hexahydro-6,11-dioxo-2-naphthacenecarboxylic Acid Methyl Ester (42)

A solution of the sultine **34** (24 mg, 0.08 mmol), methyl 2-acetamidoacrylate (**12**; 17 mg, 0.12 mmol) and toluene (1 mL) was stirred at 110 °C for 9 h. At the conclusion of reaction (TLC monitoring), the mixture was worked up according to the general procedure and the crude product was purified by a silica gel column chromatography. Elution of the column with 50% EtOAc–petroleum ether gave the compound **42** (16 mg, 53%) as a yellow solid; mp 230–232 °C.

IR (neat): 3358 (NH), 1731 (ester C=O), 1674 (NC=O), 1589 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.01 (s, 3 H), 2.15–2.25 (m, 1 H), 2.58–2.63 (m, 1 H), 2.96–3.01 (m, 2 H), 3.21 (d, *J* = 17.1 Hz, 1 H), 3.46 (d, *J* = 17.1 Hz, 1 H), 3.78 (s, 3 H), 6.03 (s, 1 H), 7.80 (d, *J* = 3.8 Hz, 2 H), 7.91 (s, 1 H), 7.93 (s, 1 H), 8.24 (d, *J* = 3.6 Hz, 2 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 23.11, 25.8, 28.0, 37.9, 52.8, 57.5, 127.1,127.6, 128.2, 131.5, 131.6, 133.4, 134.1, 139.9, 142.1, 170.4, 173.4, 182.7, 182.9.

FAB-MS: *m*/*z* = 400 [M + Na].

HRMS: *m*/*z* calcd for $C_{22}H_{19}NO_5$ [M + Na]: 400.1160; found: 400.1156.

UV ($CHCl_3$): λ_{max} (ε) = 331 (5660), 263 nm (54764).

2-(Acetylamino)-1,2,3,4-tetrahydro)-2-benzo[*g*]quinoxalinecarboxylic Acid Methyl Ester (43)

A solution of the sultine **36** (50 mg, 0.23 mmol), methyl 2-acetamidoacrylate (**12**; 66.8 mg, 0.47 mmol) and toluene (2 mL) was stirred in sealed tube at 120 °C for 24 h. At the conclusion of reaction (TLC monitoring), the mixture was worked up according to the general procedure and the crude product was purified by a silica gel column chromatography. Elution of the column with 50% EtOAc–petroleum ether gave the compound **43** (41 mg, 60%) as a white solid; mp 168–170 °C.

IR (KBr): 3305 (NH), 1735 (ester C=O), 1651 (NC=O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.97 (s, 3 H), 2.32 (br s, 1 H), 2.57 (br s, 1 H), 3.13 (s, 2 H), 3.33 (d, *J* = 16.5 Hz, 1 H), 3.56 (d, *J* = 16.5 Hz, 1 H), 3.78 (s, 3 H), 6.03 (s, 1 H), 7.78 (s, 1 H), 7.84 (s, 1 H), 8.76 (s, 2 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 23.1, 25.7, 28.7, 38.0, 52.8, 57.8, 127.9, 128.7, 136.5, 138.5, 141.5, 141.7, 144.5, 144.6, 170.3, 173.6.

HRMS: *m*/*z* calcd for $C_{16}H_{17}N_3O_3$: 299.1269; found: 299.1266.

UV ($CHCl_3$): λ_{max} (ε) = 324 (9880), 245 nm (18952).

SM Cross-Coupling of Arylboronic Acids with 2-(Acetylamino)-1,2,3,4-tetrahydro-6,7-diido-2-naphthalenecarboxylic Acid Methyl Ester (40); General Procedure (Table 2)

A mixture of the diiodocompound **40** (1 equiv), arylboronic acid (3–4 equiv), $(PPh_3)_4Pd$ (ca. 5–10 mol%), Na_2CO_3 (4 equiv) in H_2O, THF, and toluene was heated at 80 °C under N_2. At the conclusion of the reaction, (TLC monitoring) the mixture was diluted with H_2O (5 mL) and extracted with CH_2Cl_2. The combined organic layers were washed with H_2O, brine and dried ($MgSO_4$). The solvent was evaporated and the crude product left was charged on a silica gel column. Elution of the column with EtOAc–petroleum ether gave the desired cross-coupling product (Table 2).

2-(Acetylamino)-1,2,3,4-tetrahydro-6,7-bis(4′-methylphenyl)-2-naphthalenecarboxylic Acid Methyl Ester (44)

A mixture of **40** (25 mg, 0.05 mmol), 4-methylphenylboronic acid (41 mg, 0.3 mmol), $(PPh_3)_4Pd$ (12 mg, 0.01 mmol), Na_2CO_3 (32 mg, 0.3 mmol), H_2O (1 mL), THF (2 mL), and toluene (2 mL) was refluxed at 80 °C for 7 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with 25% EtOAc–petroleum ether gave the compound **44 (**19 mg, 89%) as a white crystalline solid; mp 232–234 °C.

IR (KBr): 3329 (NH), 1739 (ester C=O), 1675 (NC=O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.98 (s, 3 H), 2.14–2.22 (m, 1 H), 2.31 (s, 6 H), 2.62–2.68 (m, 1 H), 2.83–2.89 (m, 2 H), 3.02 (d, *J* = 17.2 Hz, 1 H), 3.32 (d, *J* = 17.2 Hz, 1 H), 3.78 (s, 3 H), 5.71 (s, 1 H), 7.01 (s, 8 H), 7.11 (s, 1 H), 7.16 (s, 1 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 21.3, 23.3, 25.0, 27.8, 37.9, 52.8, 58.0, 128.8, 128.9, 129.7, 131.1, 131.8, 134.2, 136.3, 138.3, 138.7, 170.4, 174.1.

MS: *m*/*z* = 427 (M^+).

HRMS: *m*/*z* calcd for $C_{28}H_{29}NO_5$ [M + H]: 428.2225; found: 428.2222.

UV ($CHCl_3$): λ_{max} (ε) = 252 nm (19507).

2-(Acetylamino)-1,2,3,4-tetrahydro-6,7-bis(4′-methoxyphenyl)-2-naphthalenecarboxylic Acid Methyl Ester (45)

A mixture of **40** (15 mg, 0.03 mmol), 4-methoxyphenylboronic acid (27 mg, 0.18 mmol), $(PPh_3)_4Pd$ (12 mg, 0.01 mmol), Na_2CO_3 (19 mg, 0.18 mmol), H_2O (1 mL), THF (2 mL), and toluene (2 mL) was refluxed 80 °C for 9 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with 25% EtOAc–petro-

leum ether gave the compound **45 (**12.5 mg, 91%) as a yellow crystalline solid; mp 178–179 °C.

IR (KBr): 3341 (NH), 1733 (ester C=O), 1674 (NC=O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.98 (s, 3 H), 2.04–2.22 (m, 1 H), 2.63–2.68 (m, 1 H), 2.83–2.89 (m, 2 H), 3.02 (d, *J* = 17.0 Hz, 1 H), 3.32 (d, *J* = 17.0 Hz, 1 H), 3.78 (s, 9 H), 5.7 (s, 1 H), 6.76 (d, *J* = 8.7 Hz, 4 H), 7.01–7.06 (m, 4 H), 7.09 (s, 1 H), 7.15 (s, 1 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 23.4, 25.0, 27.9, 37.9, 52.9, 55.4, 58.1, 113.5, 113.6, 130.9, 131.2, 131.7, 133.7, 134.0, 138.4, 138.7, 158.4, 170.4, 174.1.

MS: *m*/*z* = 459 (M^+).

HRMS: *m*/*z* calcd for $C_{28}H_{29}NO_5$ [M + H]: 460.2123; found: 460.2116.

UV ($CHCl_3$): λ_{max} (ε) = 252 nm (18502).

2-(Acetylamino)-1,2,3,4-tetrahydro-6,7-bis(4′-formylphenyl)-2-naphthalenecarboxylic Acid Methyl Ester (46)

A mixture of **40** (30 mg, 0.06 mmol), 4-formylphenylboronic acid (23 mg, 0.15 mmol), $(PPh_3)_4Pd$ (7 mg, 0.006 mmol), Na_2CO_3 (16 mg, 0.15 mmol), H_2O (1 mL), THF (2.5 mL), and toluene (2.5 mL) was refluxed 80 °C at for 8 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with 25% EtOAc–petroleum ether gave the compound **46 (**24 mg, 87%) as a yellow crystalline solid; mp 218–220 °C.

IR (KBr): 3342 (NH), 1730 (ester C=O), 1702 (CHO), 1665 (NC=O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.0 (s, 3 H), 2.04–2.26 (m, 1 H), 2.58–2.63 (m, 1 H), 2.90–2.97 (m, 2 H), 3.12 (d, *J* = 17.2 Hz, 1 H), 3.45 (d, *J* = 17.2 Hz, 1 H), 3.79 (s, 3 H), 5.73 (s, 1 H), 7.19–7.28 (m, 6 H), 7.73 (d, *J* = 8.4 Hz, 4 H), 9.96 (s, 2 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 23.4, 25.2, 28.4, 37.6, 52.9, 57.9, 129.7, 130.5, 131.2, 131.7, 133.7, 134.9, 135.6, 147.0, 147.1, 170.5, 173.9, 192.0.

HRMS: *m*/*z* calcd for $C_{28}H_{27}NO_5$ [M + H]: 457.1888; found: 457.1883.

UV ($CHCl_3$): λ_{max} (ε) = 274 nm (21113).

2-(Acetylamino)-1,2,3,4-tetrahydro-6,7-bis(4′-acetylphenyl)-2-naphthalenecarboxylic Acid Methyl Ester (47)

A mixture of **40** (30 mg, 0.06 mmol), 4-acetylphenylboronic acid (60 mg, 0.36 mmol), $(PPh_3)_4Pd$ (14 mg, 0.01 mmol), Na_2CO_3 (39 mg, 0.36 mmol), H_2O (1 mL), THF (2.5 mL), and toluene (2.5 mL) was refluxed 80 °C at for 8 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with 25% EtOAc–petroleum ether gave the compound **47** (19 mg, 65%) as a white crystalline solid; mp 188–190 °C.

IR (KBr): 3348 (NH), 1738 (ester C=O), 1677 (NC=O), 1604, 1551 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.99 (s, 3 H), 2.15–2.35 (m, 1 H), 2.57 (s, 6 H), 2.54–2.64 (m, 1 H), 2.89–2.94 (m, 2 H), 3.10 (d, *J* = 16.8 Hz, 1 H), 3.42 (d, *J* = 16.8 Hz, 1 H), 3.79 (s, 3 H), 5.75 (s, 1 H), 7.16–7.23 (m, 6 H), 7.8 (m, 4 H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 23.4, 25.2, 26.7, 28.3, 37.6, 52.9, 58.0, 128.4, 130.1, 131.2, 131.7, 132.9, 135.3, 135.6, 137.7, 138.0, 145.8, 145.9, 170.4, 173.9, 177.9.

HRMS: *m*/*z* calcd for $C_{30}H_{31}NO_5$ [M + H]: 485.2280; found: 485.2252.

UV ($CHCl_3$): λ_{max} (ε) = 270 nm (22197).

2-(Acetylamino)-1,2,3,4-tetrahydro-6,7-bis(5′-acetylthienylphenyl)-2-naphthalenecarboxylic Acid Methyl Ester (48)

A mixture of **40** (30 mg, 0.06 mmol), 5′-acetylthienylboronic acid (35 mg, 0.2 mmol), $(PPh_3)_4Pd$ (7 mg, 0.006 mmol), Na_2CO_3 (16 mg, 0.36 mmol), H_2O (1 mL), THF (2.5 mL), and toluene (2.5 mL) was refluxed at 80 °C for 12 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with 30% EtOAc–petroleum ether gave the compound **48 (**23.5 mg, 78%) as a semi-solid.

IR (KBr): 3348 (NH), 1738 (ester C=O), 1677 (NC=O), 1604, 1551 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.99 (s, 3 H), 2.15–2.20 (m, 1 H), 2.25–2.35 (m, 1 H), 2.52 (s, 6 H), 2.71–2.75 (m, 1 H), 2.88–2.91 (m, 1 H), 3.06 (d, *J* = 17.4 Hz, 1 H), 3.39 (d, *J* = 17.4 Hz, 1 H), 3.77 (s, 3 H), 5.76 (s, 1 H), 6.79 (d, *J* = 3.6 Hz, 2 H), 7.20 (s, 2 H), 7.49 (d, *J* = 3.6 Hz, 2 H).

HRMS: *m*/*z* calcd for $C_{26}H_{25}NO_5S_2$ [M + H]: 496.1252; found: 496.1249.

UV ($CHCl_3$): λ_{max} (ε) = 242 (5164), 306 nm (7168).

2-(Acetylamino)-1,2,3,4-tetrahydro-6,7-bis(2′-benzothienylphenyl)-2-naphthalenecarboxylic Acid Methyl Ester (49)

A mixture of **40** (30 mg, 0.07 mmol), 2-benzothienylphenylboronic acid (32 mg, 0.18 mmol), $(PPh_3)_4Pd$ (8 mg, 0.006 mmol), Na_2CO_3 (16 mg, 0.36 mmol), H_2O (1 mL) THF (2.5 mL), and toluene (2.5 mL) was refluxed at 80 °C for 12 h. At the conclusion of the reaction (TLC monitoring), the mixture was worked up according to the general procedure. The crude product was purified by a silica gel column chromatography. Elution of the column with 30% EtOAc–petroleum ether gave the compound **49 (**28.5 mg, 79%) as a white solid; mp 173–174 °C.

IR (KBr): 3334 (NH), 1731 (ester C=O), 1657 (NC=O) cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.00 (s, 3 H), 2.14–2.34 (m, 2 H), 2.61–2.65 (m, 1 H), 2.86–2.92 (m, 1 H), 3.08 (d, *J* = 16.9 Hz, 1 H), 3.38 (d, *J* = 16.9 Hz, 1 H), 3.79 (s, 3 H), 5.76 (s, 1 H), 7.15–7.74 (m, 12 H).

HRMS: *m*/*z* calcd for $C_{30}H_{25}NO_3S_2$ [M + H]: 512.1353; found: 512.1344.

UV ($CHCl_3$): λ_{max} (ε) = 248 (28045), 300 (19281), 314 nm (20799).

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