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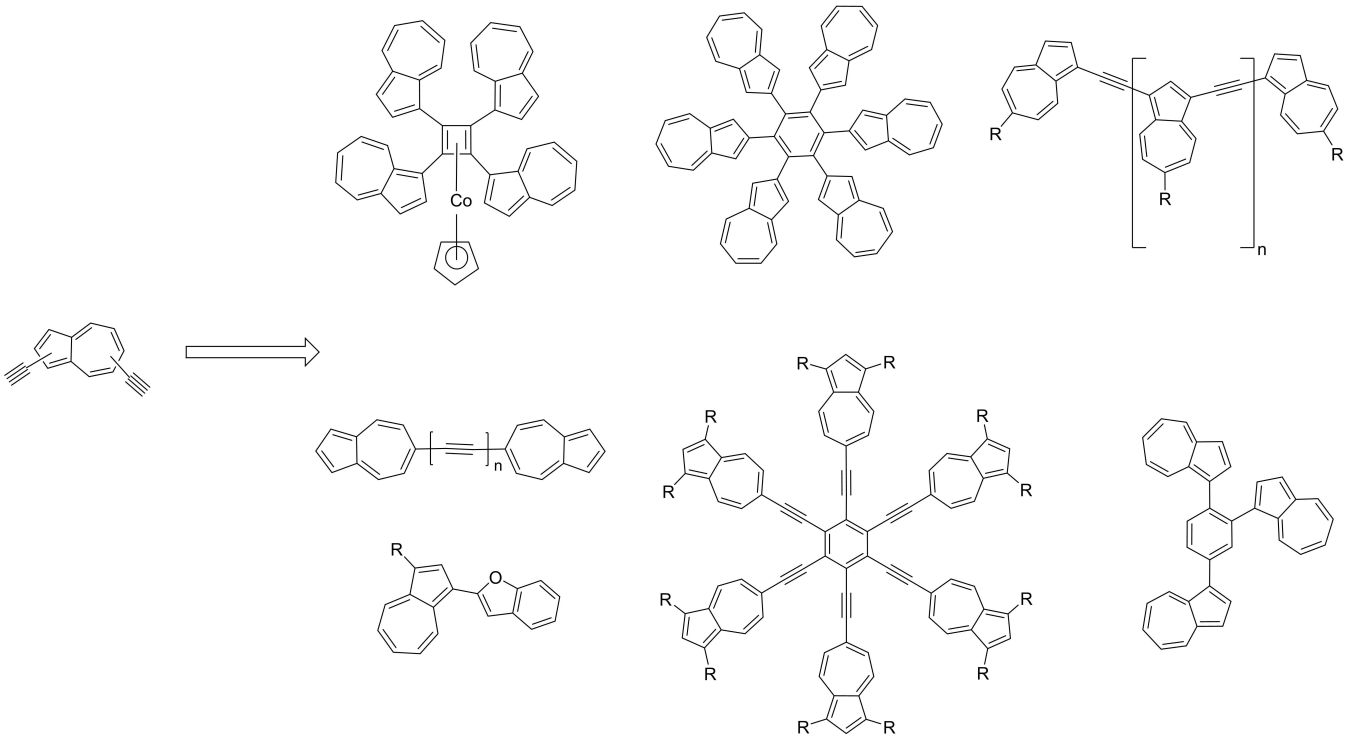
Review

Special Collection

Alkynylazulenes as Building Blocks for Highly Unsaturated Scaffolds

Ahmed H. M. Elwahy*[a] and Klaus Hafner[b]

In memory of *Klaus Hafner*.



Abstract: Recently developed routes to the synthesis of mono- and polyethynylated azulenes and their transformations into linear oligoazulenes with ethynyl and butadiynyl bridges as well as azulenyl-substituted benzenes, cyclobutadiene complexes, and azulene-substituted tetracyanobutadienes are reviewed. The utility of ethynylazulene derivatives for the synthesis of azulene-substituted heterocycles has also been reviewed.

1. Introduction

Among the non-benzenoid aromatic compounds, azulene has attracted the interest of many research groups because of its remarkable polarizability and tendency to form stabilized cations and anions as well as radical cations and anions.[1–3] Azulene derivatives were also found in numerous natural products with a variety of biological activities.[4] Owing to its unusual properties, the functionalization of such compounds aiming at modifying their structures has extensively been studied.

Moreover, acetylenes, and their highly conjugated homologues, have been found to promote strong electronic communication between terminal subunits and to favor rigid, rodlike structures that have found application in the design of molecular wires.[5] Today, progress in acetylene based molecular structure is greatly fueled by the advent of powerful novel metal-catalyzed acetylenic homo- and cross coupling protocols.[5–8]

Interest in the synthesis of polyethynylated substituted benzenoid and heteroaromatic compounds has increased over the last decade due to the importance of these compounds in the preparation of materials with special properties for molecular devices.[9] Recently attention has focused on incorporating azulenes into polyethynylated π-systems. The successful attachment of ethynyl groups at different positions of the azulene system make them suitable candidates for this purpose. In this respect, Ito *et al.*[10a] recently reviewed advances made in the preparation of aryl- and heteroarylazulenes using transition-metal-catalyzed electrophilic heteroarylation reactions of azulene. Ito and Morita[10b] demonstrated also the broad applicability of organic molecules containing azulene chromophores as terminal groups for the preparation of stabilized electrochromic as well as polyelectrochromic materials. Emphasis on both reviews was given to study the redox properties of the synthesized molecules.

The aim of this review is to cover the developed approaches to the synthesis of mono- and polyethynylated azulenes and their transformations into linear oligoazulenes with ethynyl and butadiynyl bridges as well as azulenyl-substituted benzenes, heteroarenes and cyclobutadiene complexes. Yields of the target molecules reported in this review are those given in the last step in the reaction except in some few cases in which overall yield was not given.

2. General and specific synthesis of ethynylazulenes

The most commonly used methods for the synthesis of terminal alkyne derivatives are Corey-Fuchs reaction,[11] Colvin rearrangement,[12] Bestmann-Ohira reagent[13] and Gilbert-Seyferth reagent.[14] Recent development with transition metal-catalyzed carbon-carbon coupling reactions such as Sonogashira coupling,[15] has evolved into a valuable synthetic methodology for the preparation of alkynes.

Efficient ethynylation of azulene at the five or seven-membered ring are mainly performed by one of three methods:

i) Pd-catalyzed cross-coupling under Sonogashira-Hagihara conditions.
ii) Corey-Fuchs reaction for the conversion of aldehydes into acetylenes.
iii) Ethynylation of chloroazulenes with lithium acetylide in liquid ammonia.

2.1. Ethynylation of the five membered ring

2.1.1. Synthesis of 1-ethynylazulenes

The first attempt to synthesize 1-ethynylazulene (**4**) was performed by Wentrup and Winter through condensation of 3-methyl-5(4*H*)-isooxazolone (**1**) with 1-formylazulene (**2**) in ethanol-morpholine at room temperature to give the corresponding 4-[1-azulen-1-yl-methylidene]-3-methyl-4*H*-isoxazol-5-one (**3**). Subsequent pyrolysis of **3** at 700 °C afforded **4** in 93% yield (Scheme 1).[16]

Hafner *et al.*[17,18] described efficient routes to mono-, di- and triethynylazulenes based on Sonogashira coupling of iodoazulenes. Thus, the iodoazulenes **5a**,**b**, which are readily available by electrophilic substitution of azulene with *N*-iodosuccinimide in positions 1,[19] undergo alkynylation with trimethylsilylacetylene (TMSA) under Sonogashira conditions to furnish the protected monoethynylazulenes **6a**,**b**, which afforded the 1-ethynylazulenes **4a**,**b** as blue crystals in 38 and 42% yields, upon treatment with potassium hydroxide in methanol (Scheme 2).

[a] *Prof. Dr. A. H. M. Elwahy*
Chemistry Department, Faculty of Science
Cairo University, Giza (Egypt)
E-mail: aelwahy@hotmail.com
[b] *Prof. Dr. K. Hafner*
Clemens Schöpf-Institut für Organische Chemie und Biochemie
Technische Universität, Darmstadt
Petersenstraβe 22, D-64287 Darmstadt (Germany)
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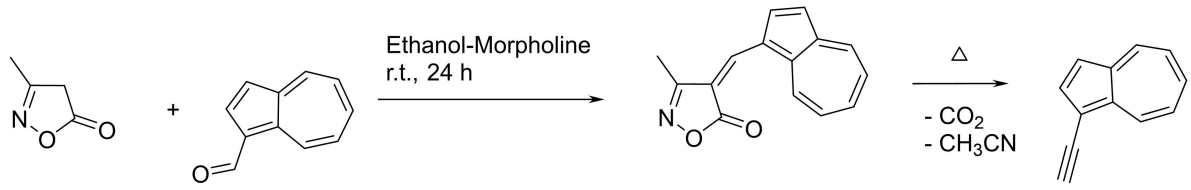


Scheme 1. Synthesis of 1-ethynylazulene *via* pyrolysis of the corresponding isoxazol-5-one.

Ahmed H. M. Elwahy was born in 1963 in Giza, Egypt. He graduated from Cairo University, Egypt in 1984 then he got his M.Sc. and Ph.D. degrees in 1988 and 1991, respectively, at Cairo University in the field of organic synthesis. He was awarded the Alexander von Humboldt research fellowship in 1998–2000 with Prof. Klaus Hafner, at TU Darmstadt, Germany and reinvited in 2003, 2005, 2009, 2010 and 2012. In 2002 he was appointed as a full Professor of Organic chemistry at Cairo University. In 2001 he received the State-Award in Chemistry and in 2016, he also received Cairo University Appreciation-Award in Basic Science. He published around 150 scientific papers in distinguished international journals.

Klaus Hafner was born in Potsdam, the capital city of the German Federal State of Brandenburg in the year 1927. In Marburg, from 1946 to 1950, he studied chemistry and medicine. He was appointed as a research associate from 1951 to 1955, with Prof. Dr. H.c. Mult. Karl Ziegler, Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr (Germany). He worked at Philipps-University Marburg/Lahn as a Chemistry lecturer from 1956 to 1961. (Germany). He served at the Technical University Darmstadt (Germany) as a Full Professor of Organic Chemistry and Chairman of the Institute of Organic Chemistry from 1965 to 1996 (following Prof. Dr. H.c. Clemens Schöpf). He served as Editor-in-Chief of Liebigs Annalen from 1981 to 1997, Senior Editor of European Journal of Organic Chemistry from 1998 to 2000, Co-Editor of Chemische Berichte from 1995 to 1997, and Co-Editor of Topics in Current Chemistry from 1966 to 1995. He served as Chairman of the German Chemical Society's Court of Honour from 1998 to 2020. He has over 200 research papers published in prestigious international journals. In 1980, he was awarded the Carus and Adolf von-Baeyer Gold Medals. He passed away on the 25th of January, 2021.

This approach could be exploited to synthesize functionalized mono- as well as poly- ethynylazulenes. Thus ethynylazulenes **7** and **8a** were prepared in 72 and 45% yields, respectively, by Pd-catalysed cross-coupling of the corresponding iodoazulenes with trimethylsilylacetylene and subsequent desilylation (Figure 1). Condensation of **8a** with hydroxylamine hydrochloride and subsequent dehydration with acetic anhydride/pyridine led to the formation of the corresponding 3-ethynyl-1-cyanoazulene **8b** as brown crystals in 70% yield.[20,21]

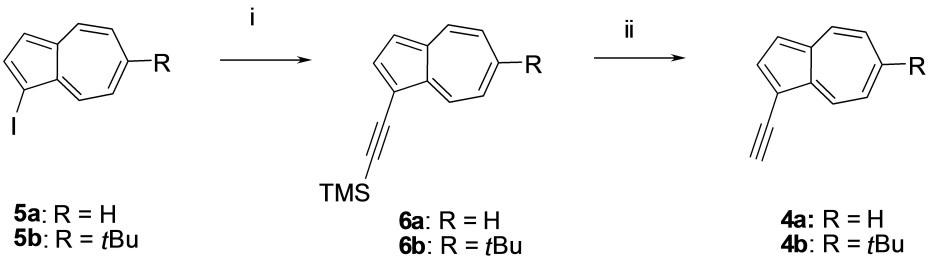
Mono- azulene **11** could be obtained in 97% yield from diiodoazulenes **9b** by cross-coupling with one equivalent of TMSA under Sonogashira conditions to give the corresponding trimethylsilyl-protected ethynylazulene **10**, followed by deprotection with potassium hydroxide in methanol (Figure 2).[17]

Ito *et al.* and others have also synthesized some substituted ethynylazulenes **12**–**17** from the corresponding iodo- or bromoazulenes by employing the Sonogashira coupling methodology and subsequent desilylation (Figure 3).[22–27] In many cases, they carried out the iodination procedure using *N*-chlorosuccinimide (NCS) and NaI in acetic acid at room temperature, rather than the expensive NIS reagent.

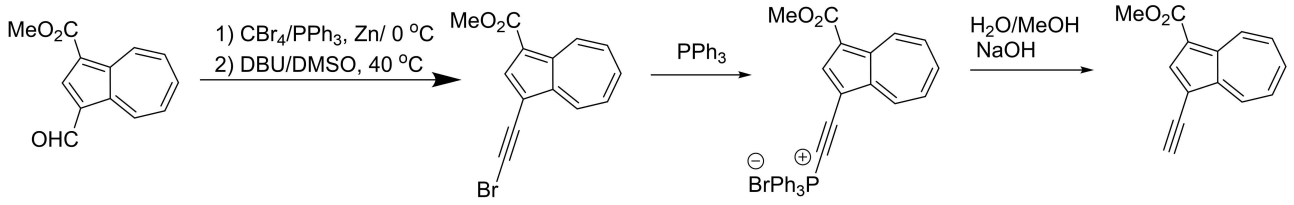
The synthesis of methyl 3-ethynylazulene-1-carboxylate **21** was accomplished firstly by the reaction of methyl 3-formylazulene-1-carboxylate **18** with tetrabromomethane in the presence of triphenylphosphine followed by dehydrobromination upon treatment with DBU to give the corresponding bromoethynylazulene derivative **19**. Compound **19** reacted then with triphenylphosphine in ether at reflux to give 2-(3-methoxycarbonylazulen-1-yl)ethynyltriphenylphosphonium bromide **20** in 85% yield. Subsequent hydrolysis of the latter compound in aqueous sodium hydroxide afforded **21** in excellent yield (Scheme 3).[28]

Shoji *et al.* reported also the synthesis of some functionalized ethynylazulenes namely, *N*-(3-(azulen-1-yl)prop-2-yn-1-yl)-4-methylbenzenesulfonamides **22a**–**h**, *tert*-butyl (3-(azulen-1-yl) prop-2-yn-1-yl)carbamate **23a**–**j** and 3-(azulen-1-yl)prop-2-yn-1-ol **24a**–**j** by coupling of the appropriate 1-iodoazulenes with each of *N*-tosyl propargylamine, *N*-*tert*-butoxycarbonylpropargylamine and 2-propyn-1-ol, respectively (Figures 4–6).[29,30]

Very recently, Szèkely *et al.* reported a gold catalyzed synthesis of alkynylazulenes **27a**–**r** using hypervalent iodonium reagent (TIPS-EBX) **26** under mild reaction conditions. This method was found suitable for the alkynylation of azulenes **25** equipped with aldehyde, chloroacetyl, or ketoester motifs, which are also excellent functional groups for further chemical transformations (Scheme 4).[31]



Scheme 2. Synthesis of 1-ethynylazulene *via* Sonogashira-Hagihara conditions. i) 0.04 mol% $PdCl_2(PPh_3)_2$, 0.08 mol% CuI, NEt_3, 1 eq. TMSA, r.t.; ii) 1 M KOH in H_2O, MeOH, r.t.



Scheme 3. Synthesis of methyl 3-ethynylazulene-1-carboxylate **21**.

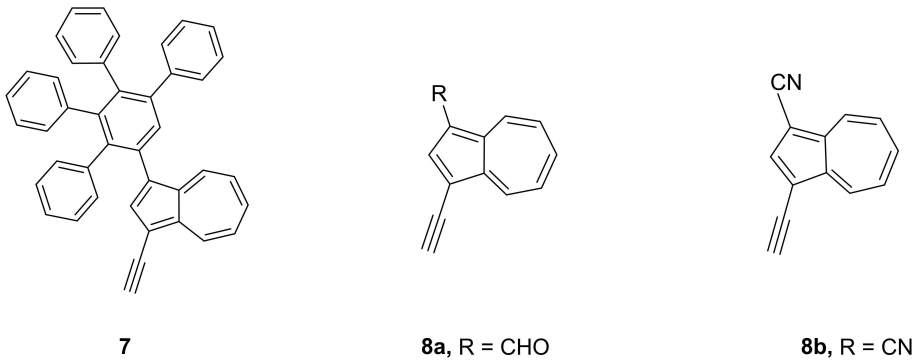


Figure 1. Structures of some functionalized 1-ethynylazulenes.

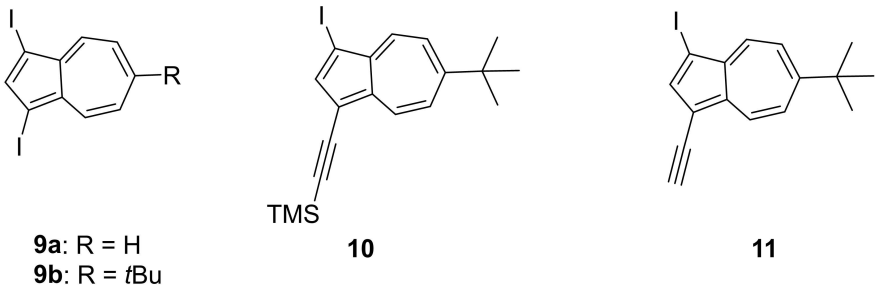
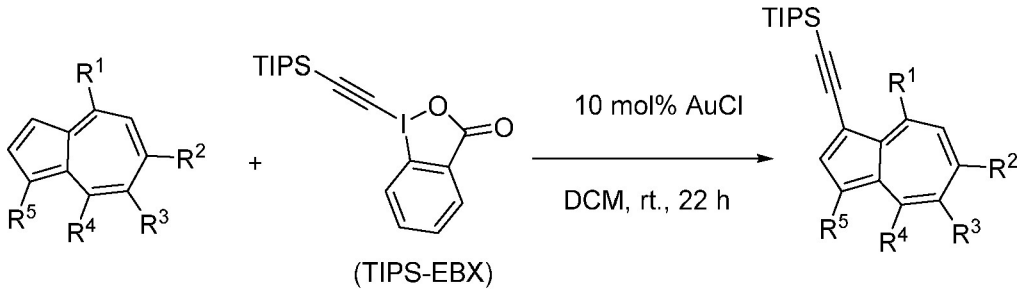


Figure 2. Structures of some functionalized iodoazulenes.

2.1.2. Synthesis of 2-ethynylazulenes

In a similar reaction sequence, 2-ethynylazulene (**29**) could be prepared in 99% yield from 2-iodoazulene **28a**[32] *via* the trimethylsilyl-protected derivative **28b**. Functionalized 2-ethynylazulenes **30**–**32** were also obtained in 68–100% yields, respectively, from the corresponding iodoazulenes *via* trimethylsilylethynylation and subsequent desilylation (Figure 7).[33–36]

On the other hand, Morita *et al.*[37] reported the synthesis of 2-ethynylazulene (**29**) starting from 2-formylazulene (**33**)[38] by firstly reaction with CBr_4 in the presence of triphenylphosphine to give 2-(2,2-dibromovinyl)azulene (**34**) in 87% yield followed by treatment with DBU to afford 2-bromoethynylazulene (**35**) in

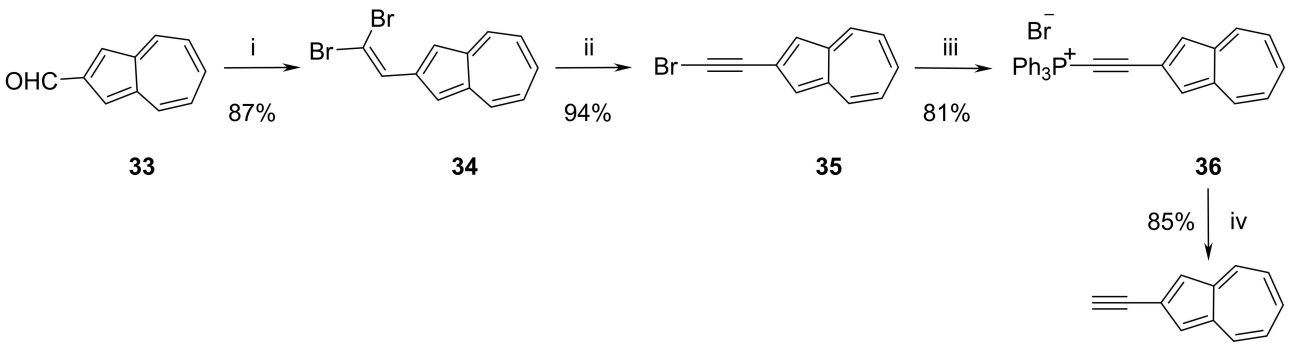


25 (TIPS-EBX) **26** **27a-r**

(TIPS-EBX) = (triisopropylsilylethynyl-1,2-benziodoxol-3(1 *H*)-one

Entry	R^1	R^2	R^3	R^4	R^5	Yield [%]
a	Me	H	*i*Pr	H	Me	73
b	H	Me	H	H	I	35
c	H	H	H	H	CHO	44
d	H	Me	H	H	CHO	69
e	Me	Me	H	Me	CHO	32
f	H	*t*Bu	H	H	CHO	57
g	H	Ph	H	H	CHO	79
h	H	CH_2CO_2Et	H	H	CHO	50
i	H	H	H	H	$COCH_2Cl$	71
j	H	Me	H	H	$COCH_2Cl$	57
k	H	*t*Bu	H	H	$COCH_2Cl$	67
l	H	Ph	H	H	$COCH_2Cl$	69
m	H	H	H	H	$COCO_2Me$	39
n	H	Me	H	H	$COCO_2Me$	59
o	H	*t*Bu	H	H	$COCO_2Me$	67
p	H	Ph	H	H	$COCO_2Me$	53
q	H	CH_2CO_2Et	H	H	$COCO_2Me$	42
r	Me	Me	H	Me	$COCO_2Me$	53

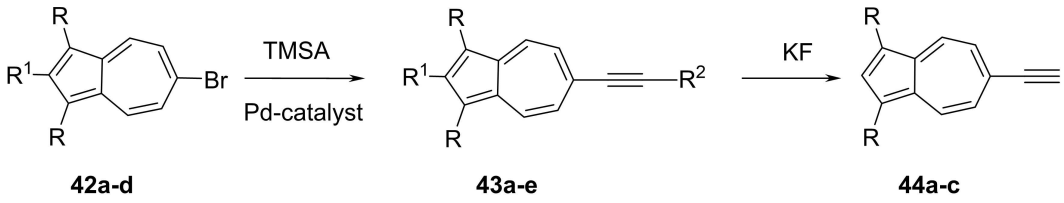
Scheme 4. Synthesis of alkynylazulenes **27a–r**.



33 **34** **35** **36** **29**

i) CBr_4/Ph_3P ii) DBU iii) Ph_3P/Diethylether iv) H_2O

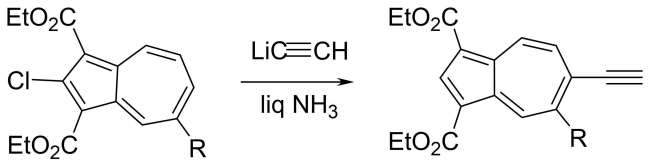
Scheme 5. Synthesis of 2-ethynylazulene (**29**).



42a-d **43a-e** **44a-c**

42a, R = H; **42b**, R = CO_2Et; **42c**, R = $CO_2C_6H_{13}$, **42a-c**, R^1 = H
42d, R = CO_2Et; R^1 = OMe
43a, R = H; **40b,** R = CO_2Et; **43c**, R = $CO_2C_6H_{13}$, **43a-c**, R^1 = H, R^2 = TMS
43d, R = CO_2Et; R^1 = OMe, R^2 = C_6H_9
43e, R = CO_2Et; R^1 = OMe, R^2 = $C_{10}H_{17}$
44a, R = H; **44b,** R = CO_2Et**; 44c,** R = $CO_2C_6H_{13}$

Scheme 6. Synthesis of 6-ethynylazulene derivatives **43a–e** and **44a–c**.



45a,b **46a,b**

a: R = Me
b: R = *iso*-Pr

Scheme 7. Synthesis of 6-ethynylazulene-1,3-dicarboxylates **46a,b**.

94% yield. Conversion of the latter compound to 2-(2-azulenyl) ethynyltriphenylphosphonium bromide (**36**) was accomplished upon treatment with triphenylphosphane in dry ether. Reaction of **36** with water afforded **29** in 85% yield (Scheme 5).

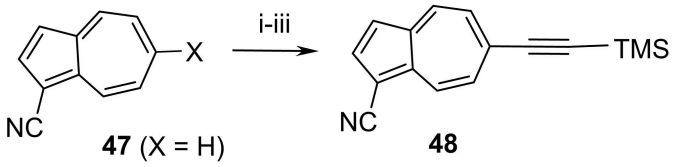
2.1.3. Synthesis of 1,3-diethynylazulenes

1,3-Diethynylazulenes **37c** and **37d** could be obtained in 90 and 42% yields, respectively, from diiodoazulenes **9a** and **9b** by cross-coupling with two equivalents of TMSA under Sonogashira conditions to give the corresponding trimethylsilyl-protected ethynylazulenes **37a** and **37b**, followed by deprotection with potassium hydroxide in methanol (Figure 8).[17]

Shoji *et al.* reported also the synthesis of *N,N'*-((6-(*tert*-butyl) azulene-1,3-diyl)bis(prop-2-yne-3,1-diyl))bis(4-methylbenzenesulfonamide) **38** and di-*tert*-butyl ((6-(*tert*-butyl) azulene-1,3-diyl)bis(prop-2-yne-3,1-diyl))dicarbamate **39** in 40 and 80% yields by coupling of 6-(*tert*-butyl)-1,3-diiodoazulene with each of *N*-tosyl propargylamine and *N*-*tert*-buthoxycarbonylpropargylamine, respectively (Figure 9).[29,30]

2.1.4. Synthesis of 1,2-diethynylazulenes2.1.5. Synthesis of 1,2,3-triethynylazulenes

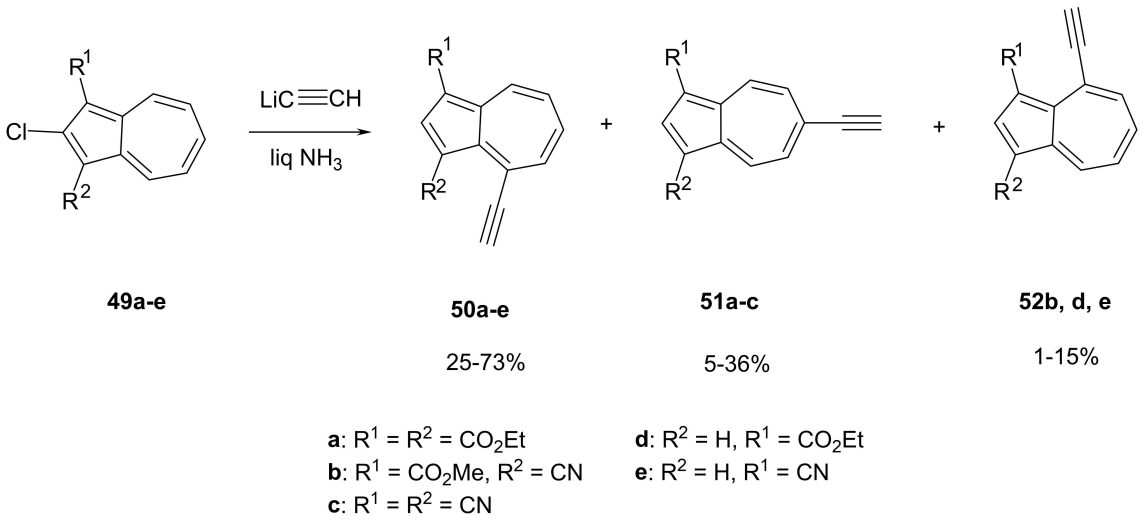
The reaction of **28** with one or two equivalents of *N*-iodosuccinimide followed by coupling with TMSA under Sonogashira conditions and subsequent desilylation afforded the 1,2-di- and 1,2,3-triethynylazulenes **40** and **41** as greenish blue crystals in 98% and 96% yields, respectively (Figure 10).[17,18]



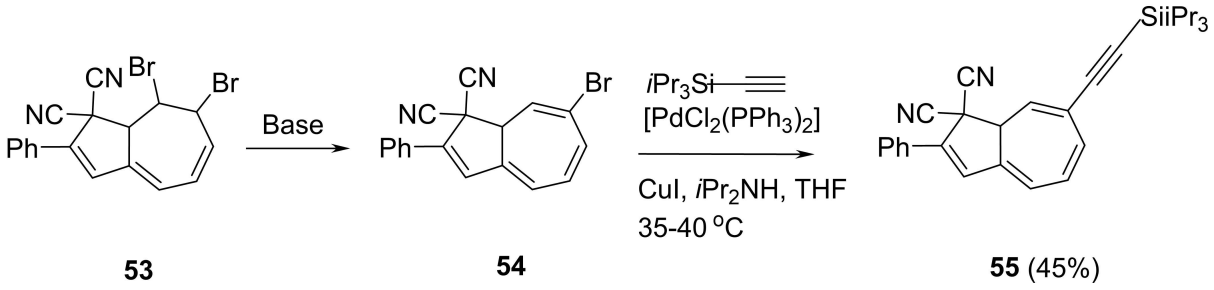
47 (X = H) **48**

i) *t*-BuOOH, *t*-BuOK/NH_3(liq)-THF, -30 °C → X = OH
ii) Tf_2O, NEt_3, CH_2Cl_2, -78 °C → X = OTf
iii) TMSA, $Pd(PPh_3)_2Cl_2$/ PPh_3 → **48**

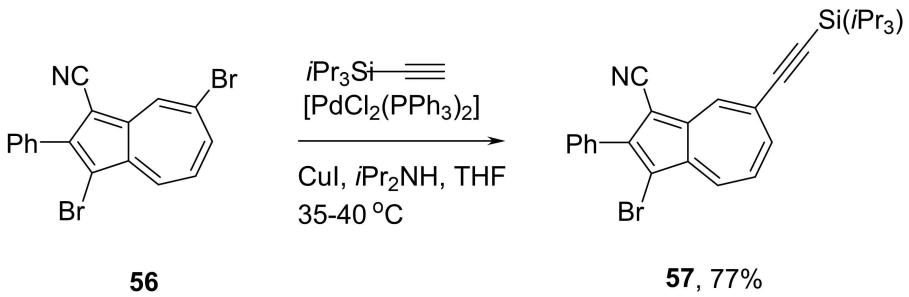
Scheme 8. Synthesis of 1-cyano-6-trimethylsilylethynylazulene (**48**).



Scheme 9. Reaction of diethyl 2-chloroazulene-1,3-dicarboxylate (**49a–e**) with lithium acetylide in liquid ammonia.



Scheme 10. Synthesis of 1,8a-dihydro-7-ethynylazulene **55**.



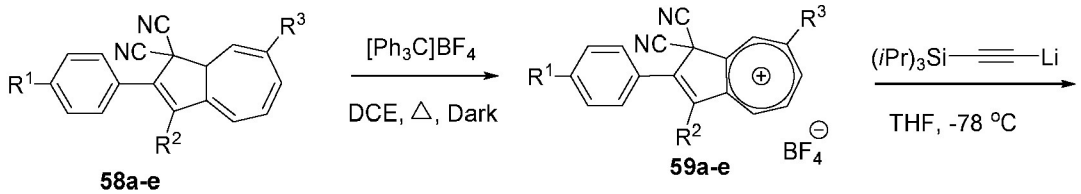
Scheme 11. Synthesis of 7-alkynylazulene **57**.

2.2. Ethynylation of the seven membered ring

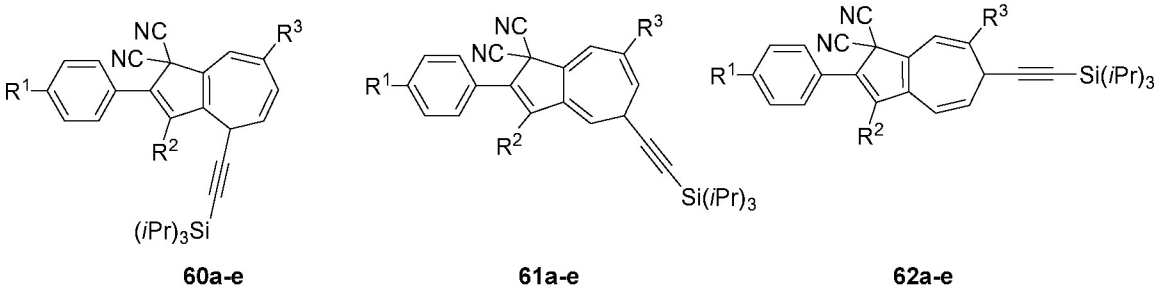
2.2.1. Synthesis of 6-ethynylazulenes

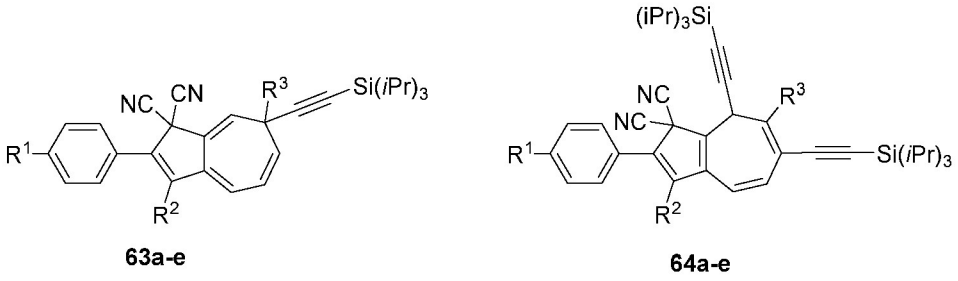
Ito *et al.* reported also that Pd-catalyzed cross-coupling reactions is an an efficient method for ethynylation of azulene in a seven-membered ring. Thus, reaction of 6-bromoazulenes **42a–c**[39] with trimethylsilylacetylene (TMSA) at room temperature under Pd catalysis afforded the 6-(trimethylsilylethynyl)azulenes **43a–c** in 86, 84 and 100% yields, respectively. Treatment of **43a–c** with potassium fluoride in DMF or DMF/THF furnished 6-ethynylazulenes **44a–c** in 79, 92 and 96% yields, respectively (Scheme 6).[40–42] Moreover, Pd-catalyzed cross-coupling reaction of **42d** with 1-hexyne and 1-decyne under Sonogashira-Hagihara conditions afforded diethyl 6-hexynyl- and 6-decynyl-2-methoxyazulene-1,3-dicarboxylates (**43d** and **43e**) in 85% and 87% yields.[43]

Furthermore, Takase *et al.*[44] reported the synthesis of diethyl 6-ethynylazulene-1,3-dicarboxylates **46a,b** by the reaction of diethyl 5-alkyl-2-chloroazulene-1,3-dicarboxylate **45a,b**[45] with lithium acetylide in liquid ammonia by an abnormal substitution reaction (Scheme 7). A mechanism for this unusual substitution reaction seems to involve initial attack of the acetylide at the 6-position of the azulene nucleus to give an anionic intermediate with a cyclopentadienide structure which could be facilitated by the electron withdrawing groups



	R^1	R^2	R^3	Yield
a	H	H	H	93%
b	OMe	H	H	85%
c	CN	H	H	71%
d	H	Ph	H	69%
e	H	Ph	Ph	78%





No.	Overall yield [%]	% of isomers **a**	**b**	**c**	**d**	**e**
60	73	29	47	9	10	5
61	57	28	28	27	12	5
62	40	19	30	39	9	3
63	44	6	51	20	16	7
64	25	25	21	54	-	-

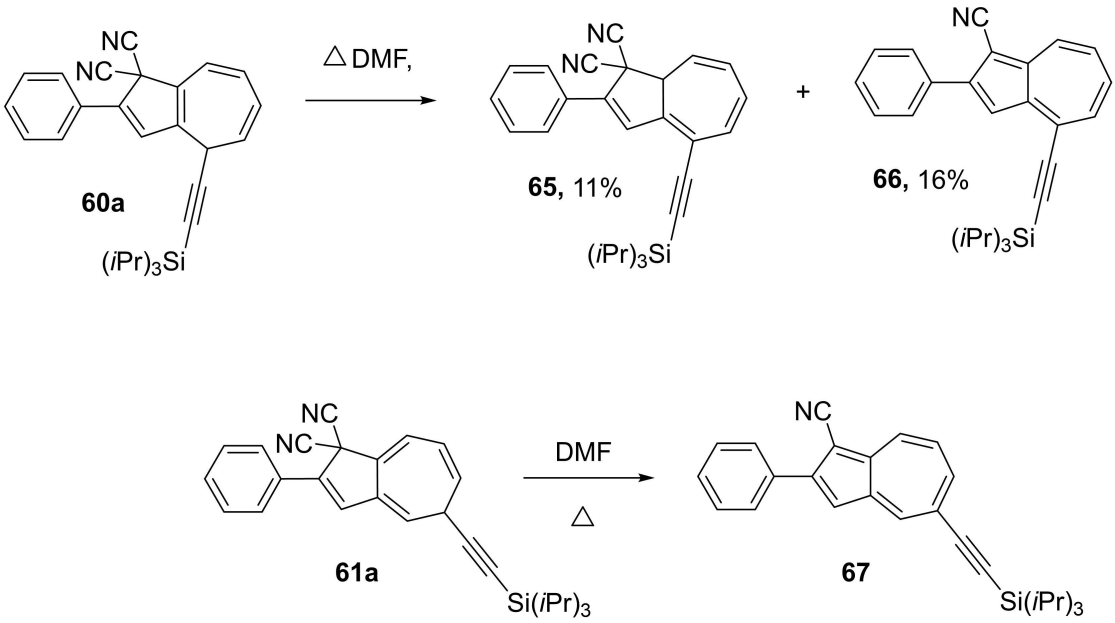
Scheme 12. Synthesis of some 1,8a-dihydroethynylazulenes **60**–**64**.

at the 1- and 3-positions. Subsequent protonation at the 2-position and dehydrochlorination afforded the target ethynylazulene derivatives.

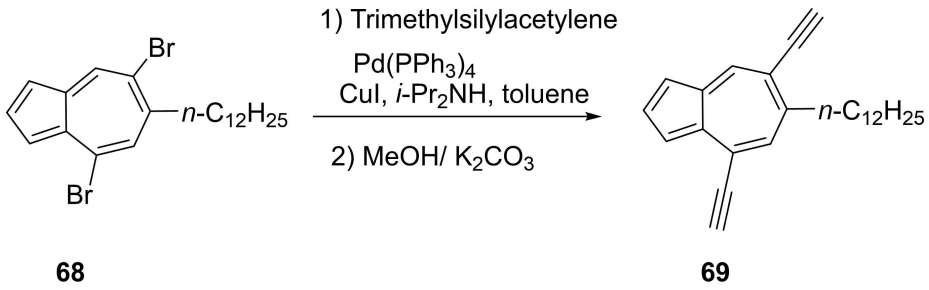
Makosza *et al.* reported the synthesis of 1-cyano-6-trimethylsilylethynylazulene (**48**) in 97% yield from 1-cyanoazulene (**47**) by firstly vicarious nucleophilic substitution (VNS) hydroxylation at 6-position to give 6-hydroxyazulene-1-carbonitrile followed by 6-*O*-sulphonylation to afford the corresponding trifluoromethanesulfonate derivative and subsequent reaction with TMSA under Sonogashira conditions (Scheme 8).[46]

2.2.2. Synthesis of 4(8)- and 6-ethynylazulenes

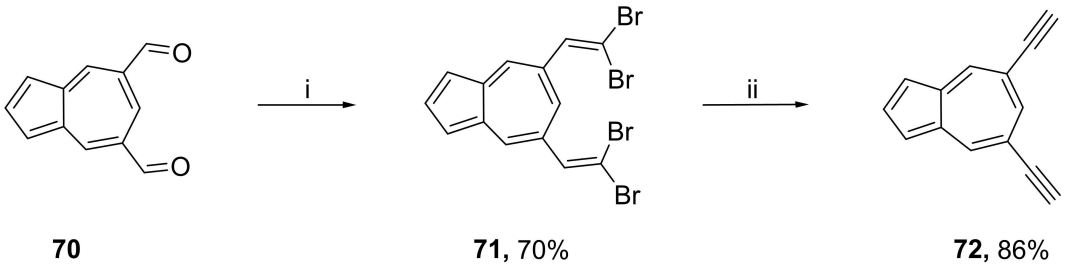
The reaction of diethyl 2-chloroazulene-1,3-dicarboxylate (**49a**) with lithium acetylide in liquid ammonia gave a mixture of diethyl 4- and 6-ethynylazulene-1,3-dicarboxylates **50a** and **51a**



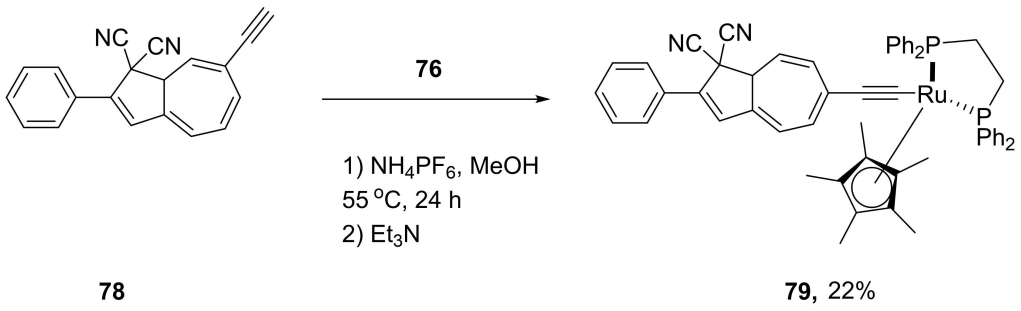
Scheme 13. Conversion of **60a** and **61a** to azulene isomers **65**–**67**.



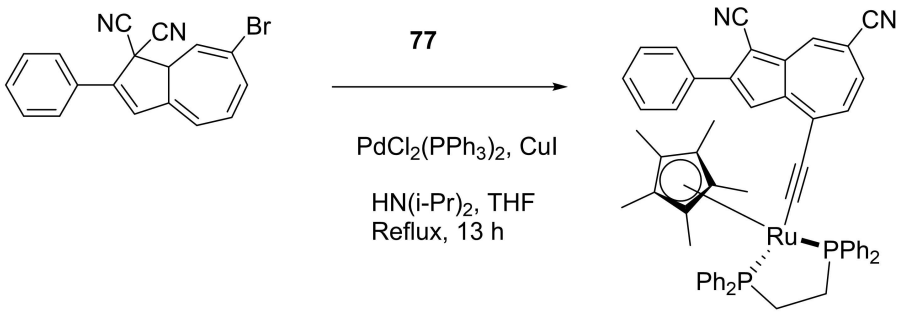
Scheme 14. Synthesis of 4,7-diethynyl-6-dodecylazulene **69**.



Scheme 15. Synthesis of 5,7-diethynylazulene **72**. i) PPh_3, CBr_4, CH_2Cl_2, room temp.; ii) 6 equiv. LDA, THF, −90 °C – room temp.

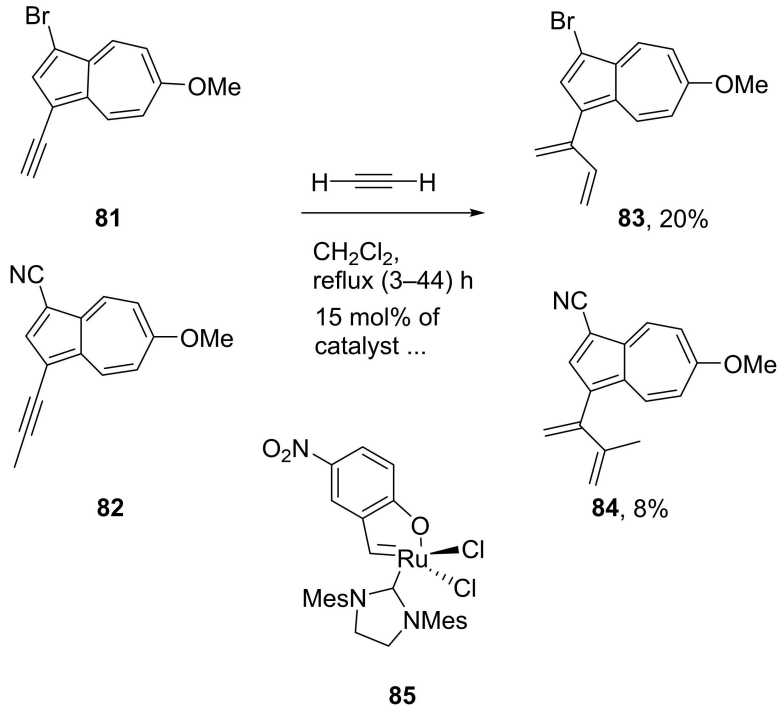


Scheme 16. Synthesis of ruthenium complex **79**.

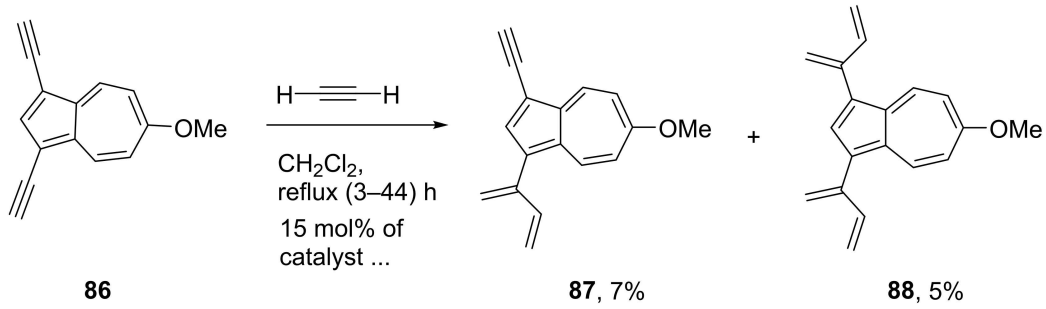


54 **80**

Scheme 17. Synthesis of the azulene complex **80**.

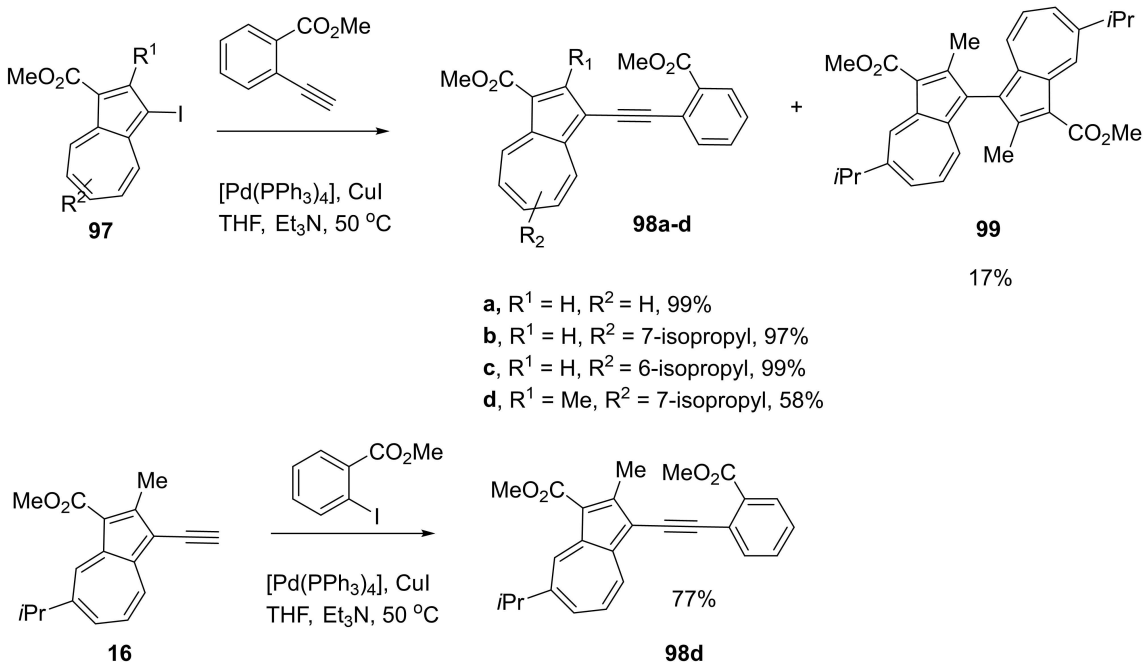


Scheme 18. Synthesis of dienes **83** and **84**.

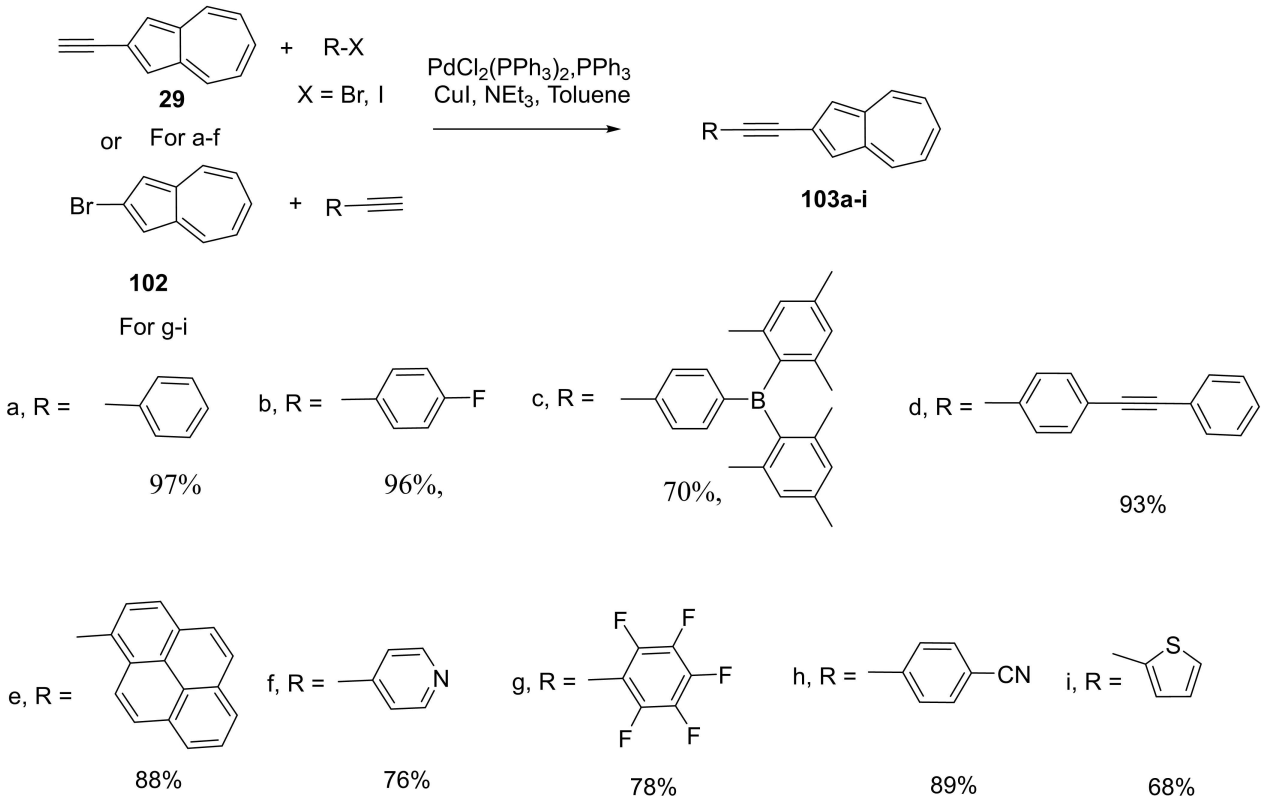


Scheme 19. Synthesis of mono-diene **87** and di-diene **88**.

by an unusual substitution reaction. In a similar manner, some 2-chloroazulenes **49b–e**, possessing alkoxycarbonyl and/or cyano substituents at the 1- and 3-position of azulene nucleus, gave a mixture of the corresponding 4 (or 8)- and 6-ethynylazulenes **50**–**52** (Scheme 9).[44,47]



Scheme 20. Synthesis of azulene derivatives bearing a methyl *o*-ethynylbenzoate **98a–d**.

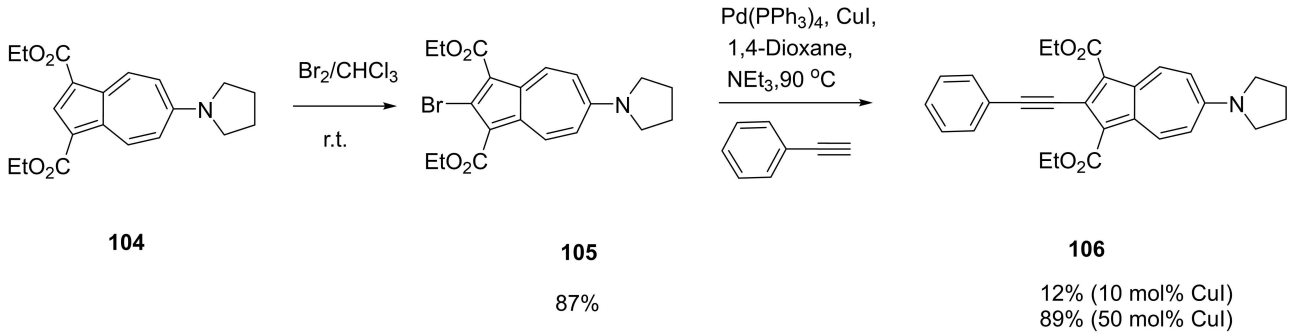


Scheme 21. Synthesis of aryl-substituted 2-ethynylazulenes **103a–i**.

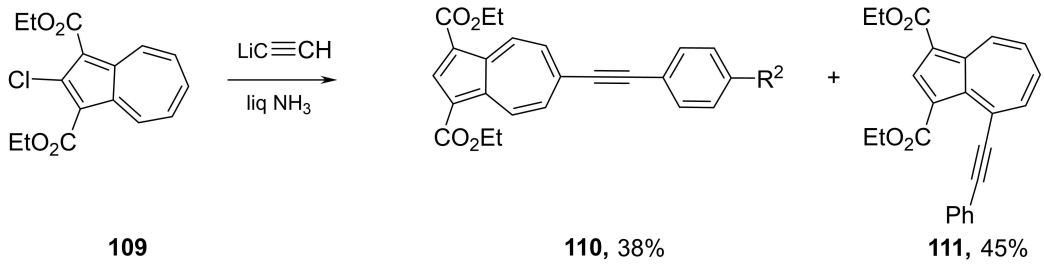
It is worthy to mention that Müller *et al.* reported earlier the synthesis of 4-alkynylazulene by the photochemical dimerization of *o*-diethynylbenzenes.[48,49]

2.2.3. Synthesis of 7-ethynylazulenes

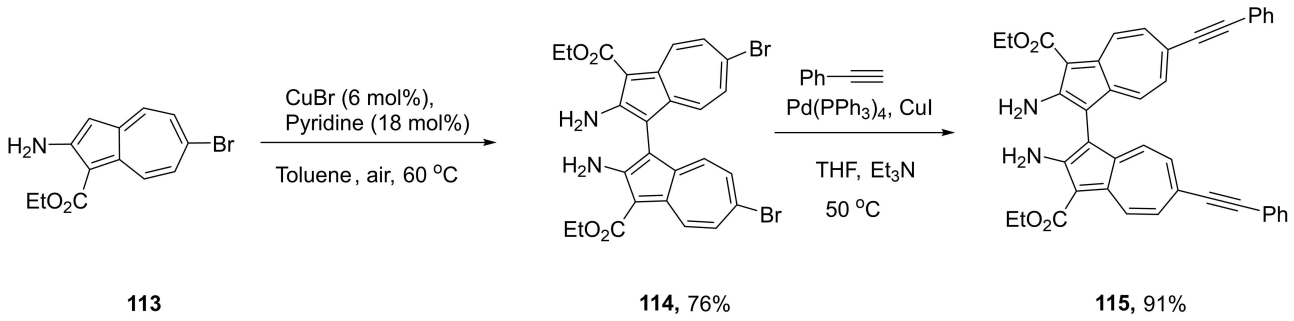
Nielsen *et al.* reported a protocol for the synthesis of 1,8a-dihydro-7-ethynylazulene **55** based on a regioselective bromi-



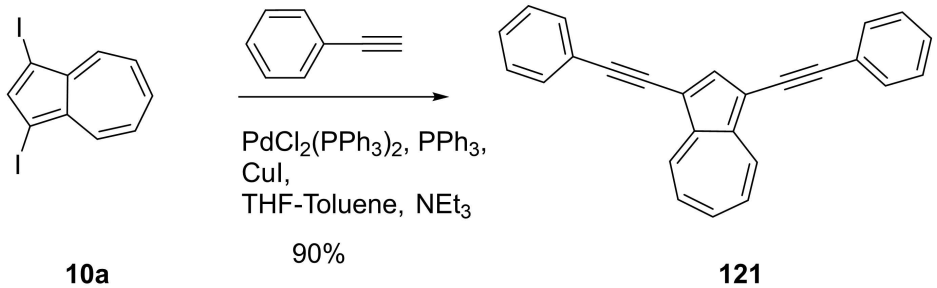
Scheme 22. Synthesis of diethyl 2-(phenylethynyl)-6-(pyrrolidin-1-yl)azulene-1,3-dicarboxylate **106**.



Scheme 23. Synthesis of 6-arylethynylazulene **110** and 4-(phenylethynyl)azulene **111**.

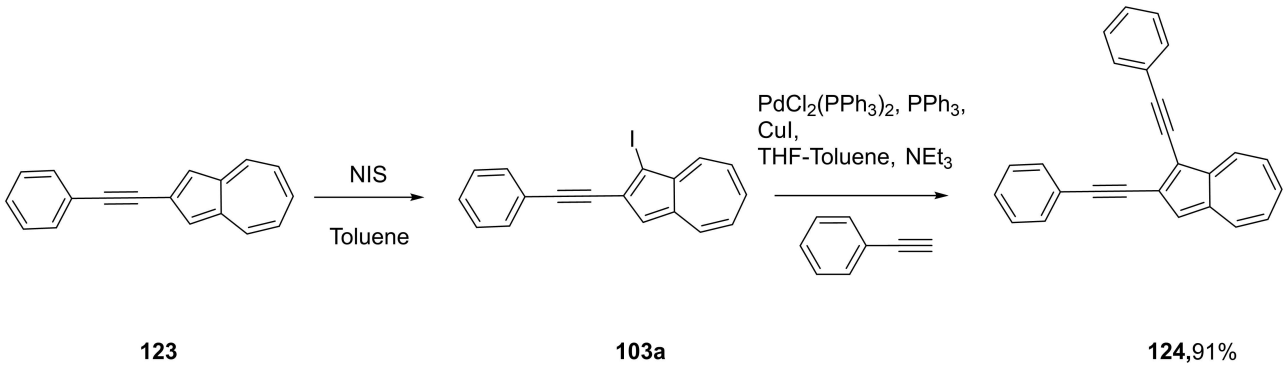


Scheme 24. Synthesis of diethyl 2,2′-diamino-6,6′-dibromo-[1,1′-biazulene]-3,3′-dicarboxylate **114**.



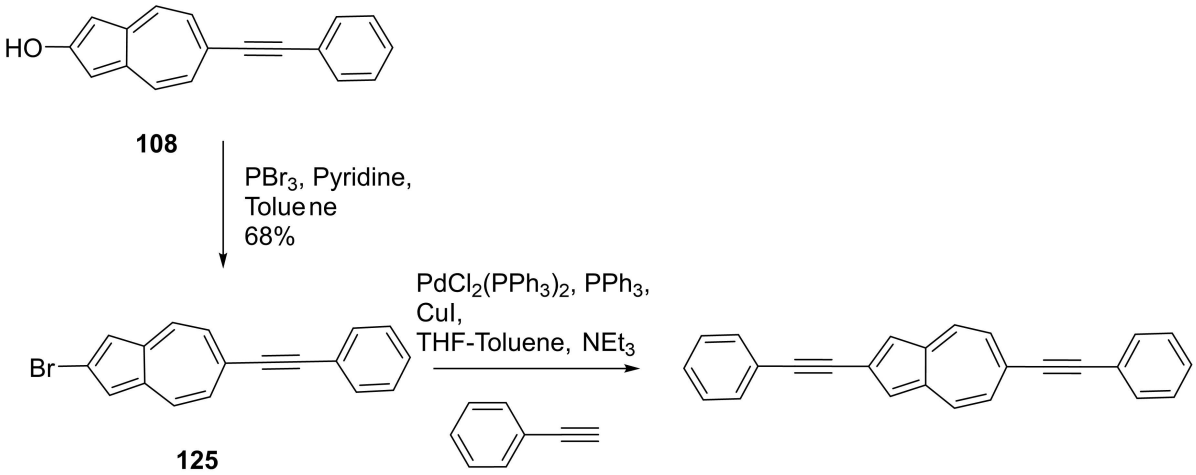
Scheme 25. Synthesis of 1,3-bis(phenylethynyl)azulene **121**.

nation, followed by a regioselective elimination of HBr, and finally a palladium-catalyzed cross-coupling reaction with a terminal alkyne. Thus, treatment of the dibromide **53** with 1 molar equivalent of $LiN(SiMe_3)_2$ in THF gave 7-bromo-2-phenylazulene-1,1(8*aH*)-dicarbonitrile **(54)** in an 90% yield. Subsequent cross-coupling reaction of **54** with triisopropylsilylacetylene afforded the acetylenic 1,8a-dihydroazulene (DHA) **55** as yellow green solid (Scheme 10). The overall yield of the conversion of **53** to **55** was 45%. The dibromo compound **53** was obtained in quantitative yield by selective bromination of the corresponding dihydroazulene at the 7,8-positions (Scheme 10).[50]



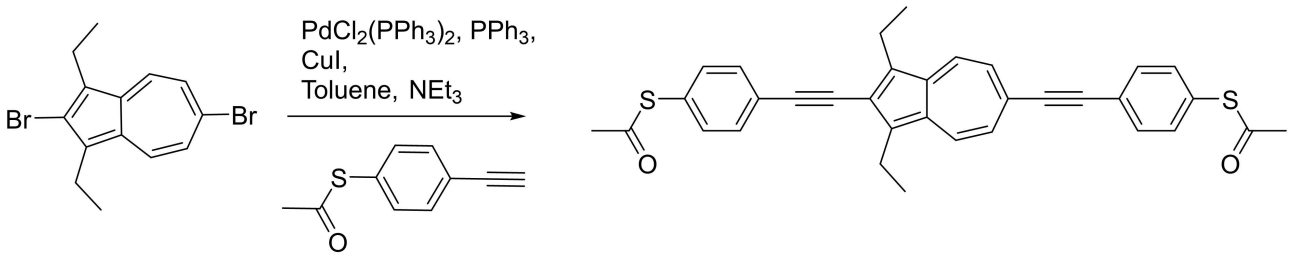
123 **103a** **124**,91%

Scheme 26. Synthesis of 1,2-bis(phenylethynyl)azulene **95**.



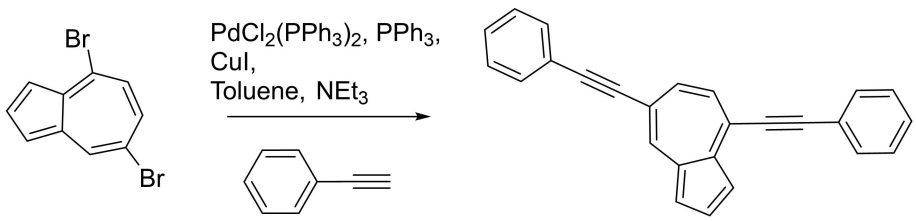
126, 96%

Scheme 27. Synthesis of 2,6-bis(phenylethynyl)azulene **126**.



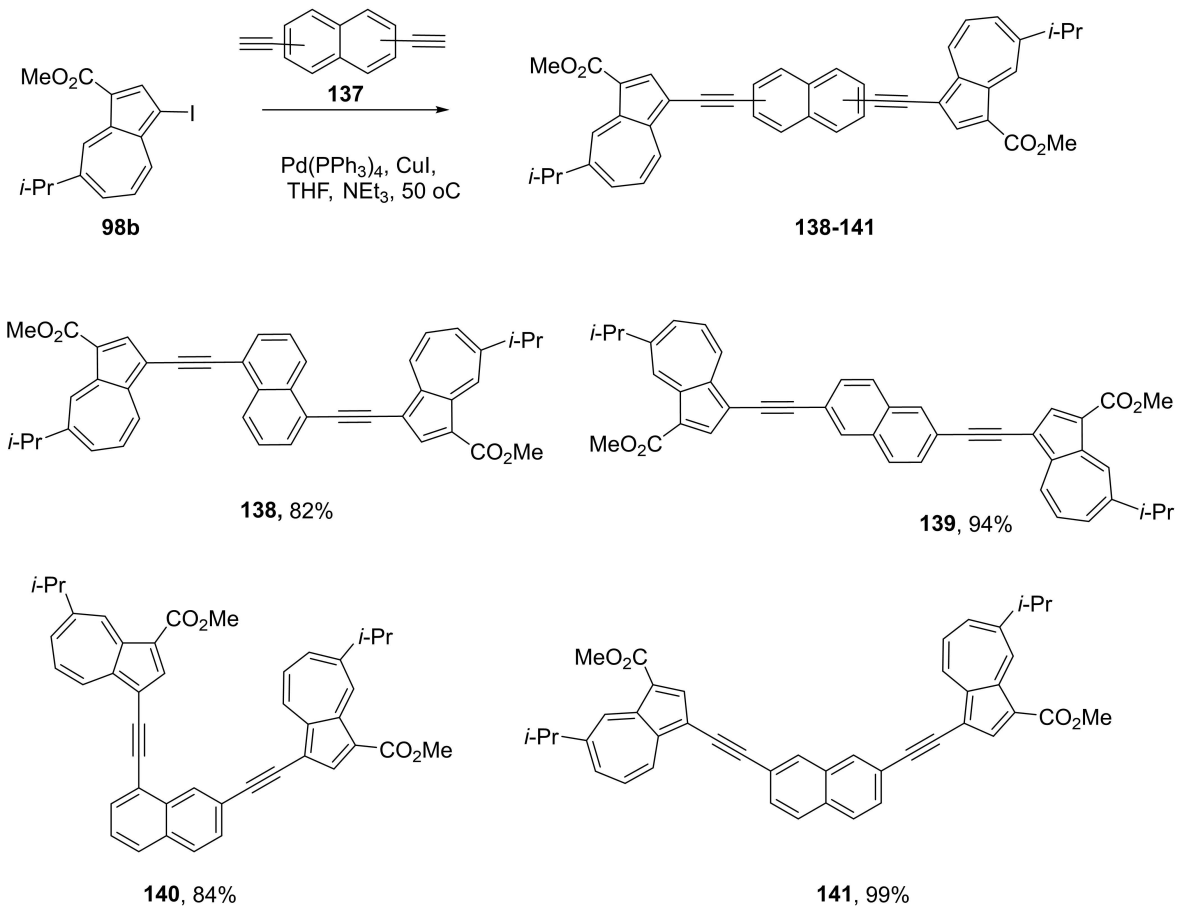
127 **128** **129**, 92%

Scheme 28. Synthesis of 2,6-bis(arylethynyl)azulene **129**.

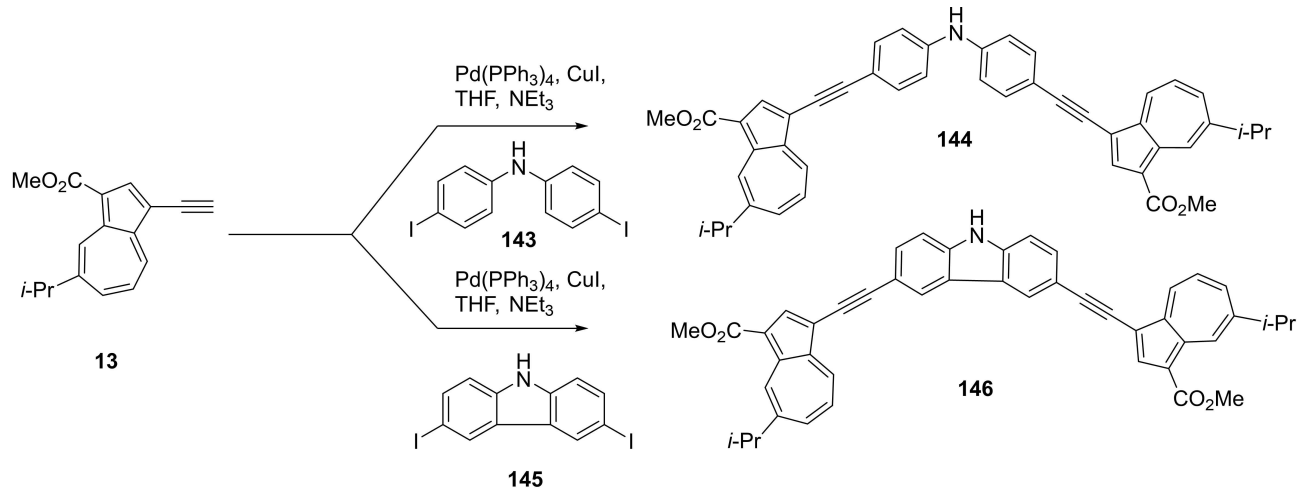


130 **131,** 93%

Scheme 29. Synthesis of 4,7-bis(arylethynyl)azulene **131**.



Scheme 30. Synthesis of bis(1-azulenyl)naphthalene derivatives **138**–**141**.

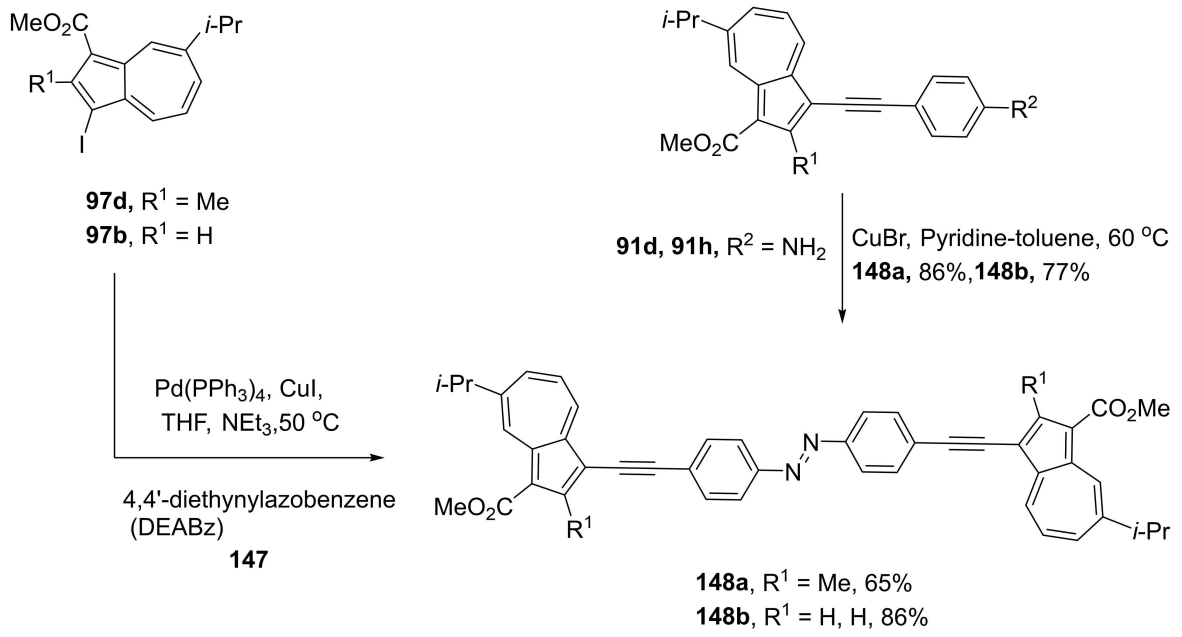


Scheme 31. Synthesis of 1-ethynylazulenes connected to arylamine **144** or carbazole **146** cores.

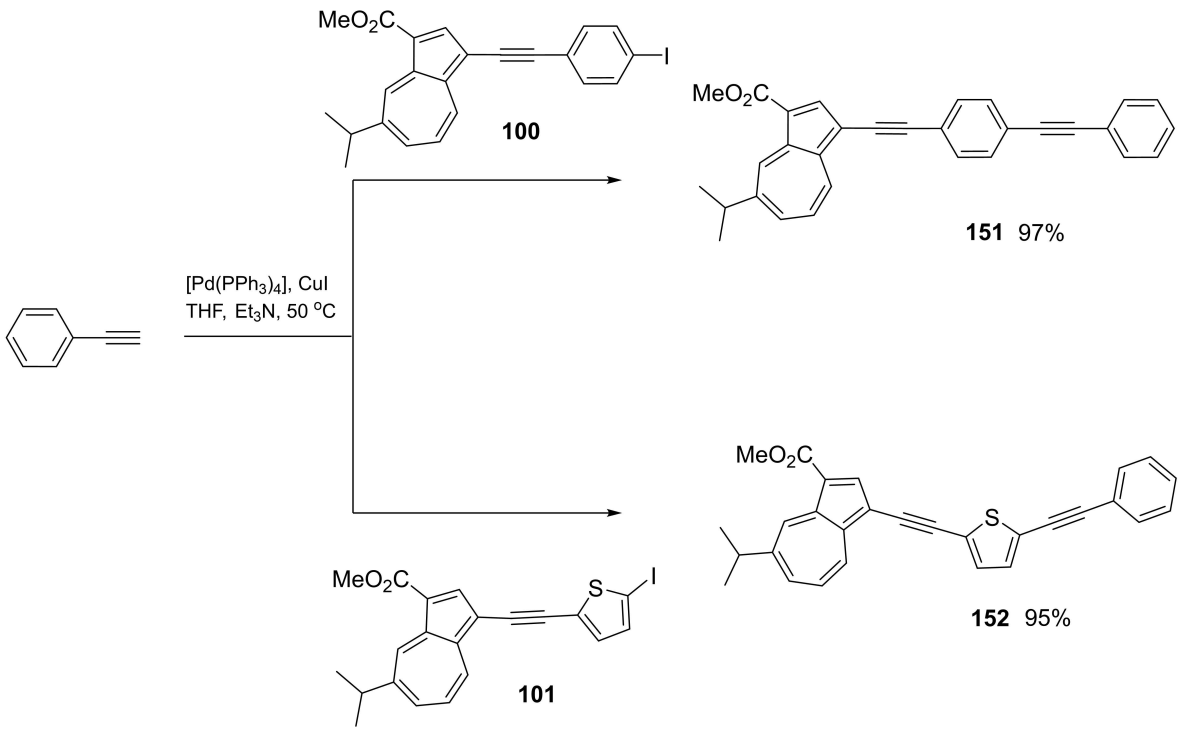
Mazzanti *et al.* reported that subjecting of 3,7-dibromo-2-phenylazulene-1-carbonitrile **56** to a Sonogashira coupling with triisopropylsilylacetylene using the $Pd(PPh_3)_2Cl_2$/CuI catalyst system gave only the mono coupled product **57** in 77% yield (Scheme 11).[51]

2.2.4. Synthesis of 4-, 5-, 6-, 7- and 8-ethynylazulenes

Nielsen *et al.* reported the synthesis of some 1,8a-dihydroethynylazulenes **60**–**64** by the reaction of the electrophilic tropylium cation **59**, obtained from 1,8a-dihydroazulenes (1,8*a*-DHAs) **58** incorporating two cyano groups at C-1 upon treatment with



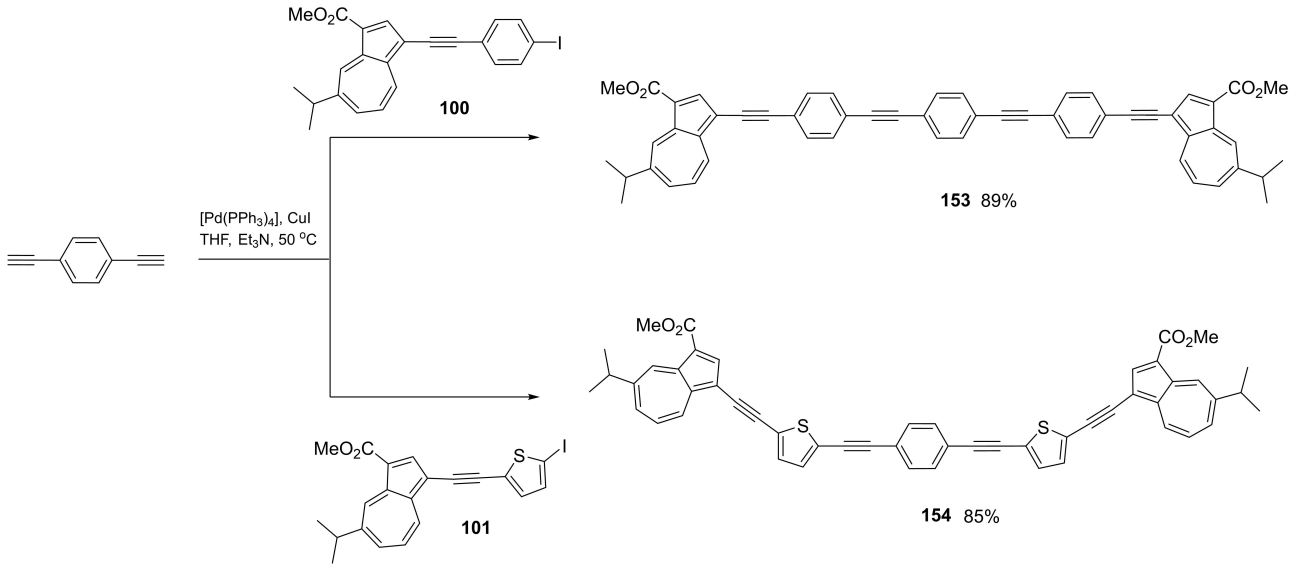
Scheme 32. Synthesis of azobenzene having two azulen-1-yl groups derivatives **148a** and **148b**.



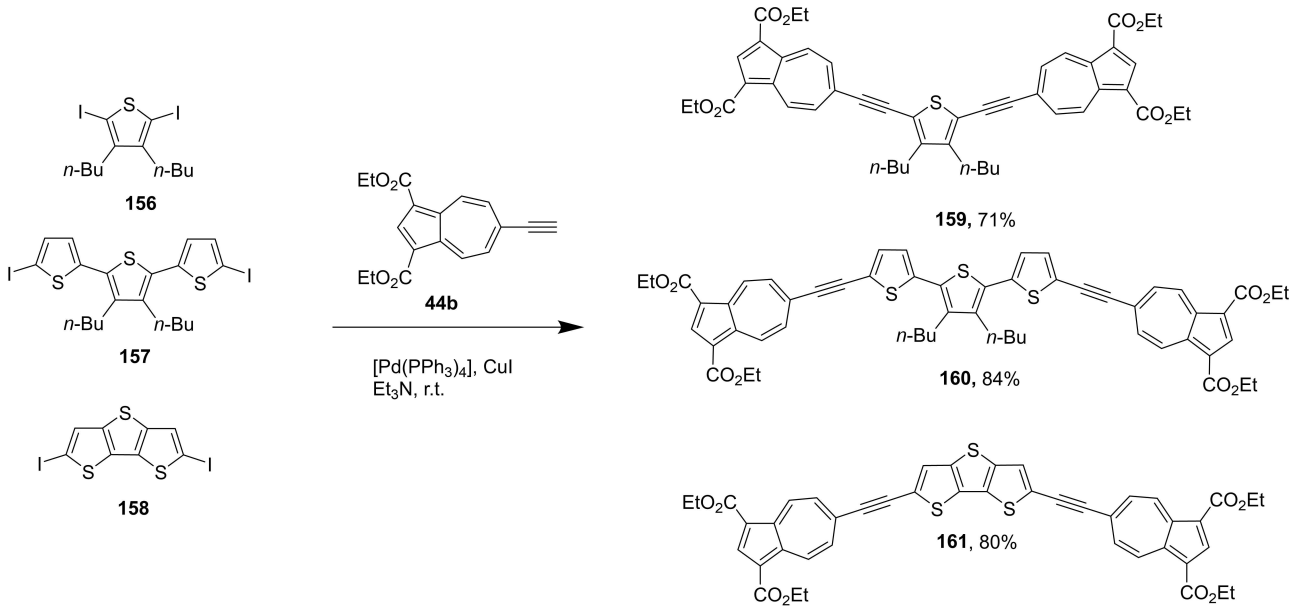
Scheme 33. Synthesis of azulene-substituted ethyne derivatives **151** and **152**.

$[Ph_3C]BF_4$ in refluxing 1,2-dichloroethane, with lithium triisopropylsilylacetylide (Scheme 12).[52] Noteworthily, generation of the azulenium ion required a long reaction time in the presence of the electron-withdrawing cyano substituent (R^1). The position of attack of the acetylide anion was in general found to occur preferentially at positions C-4, C-5, and C-6, and to a minor extent at positions C-7 and C-8. The outcome was a mixture of non-photochromic, regioisomeric DHAs **60**–**64**.[52]

The 4-isomer **60a** was partly tautomerized upon heating to the photoactive compound **65** (in 11%) and the corresponding azulene **66** (in 16%), arising from the loss of hydrogen cyanide. On the other hand, thermolysis of the 5-substituted isomer **61a** in DMF did not yield any photoswitching products, instead significant conversion to the azulene **67** was achieved. The structure of **67** was confirmed by X-ray crystallography (Scheme 13).



Scheme 34. Synthesis of azulene-substituted ethyne derivatives **153** and **154**.



Scheme 35. Synthesis of bis(6-azulenylethynyl)thiophene **159**, terthiophene **160**, and dithienothiophene **161**.

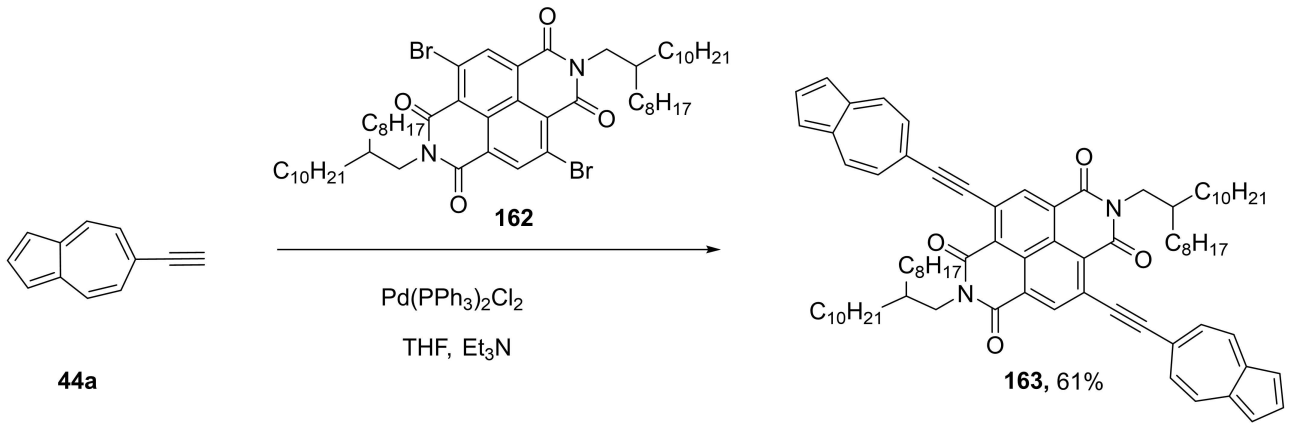
2.2.5. Synthesis of 4,7-diethynylazulenes

Murai *et al.* synthesized 4,7-diethynyl-6-dodecylazulene **69** in quantitative yield from the corresponding 4,7-dibromoazulene **68** *via* trimethylsilylethynylation and subsequent desilylation (Scheme 14).[53]

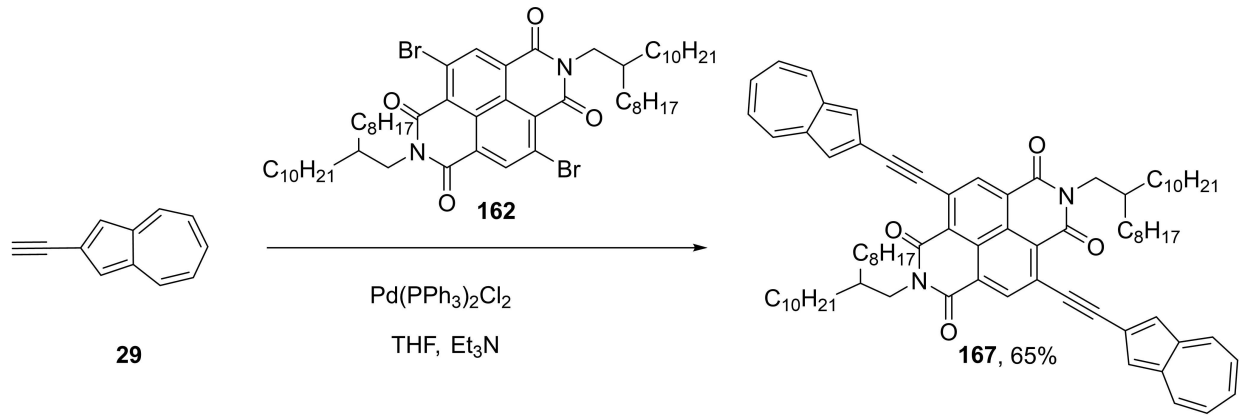
2.2.6. Synthesis of 5,7-diethynylazulenes

Hafner *et al.* also achieved an ethynylation of the 5- and 7-position of azulene by using the Corey-Fuchs[11] method for the conversion of aldehydes into acetylenes. Thus, treatment of the corresponding 5,7-diformylazulene (**70**)[54] with triphenylphosphane and tetrabromomethane in dichloromethane furnished the tetrabromo diolefin **71** as greenish-blue crystals in 70% yield. The latter could be converted into the 5,7-diethynylazulene (**72**; 86%) upon treatment with six equivalents of LDA (Scheme 15).[17]

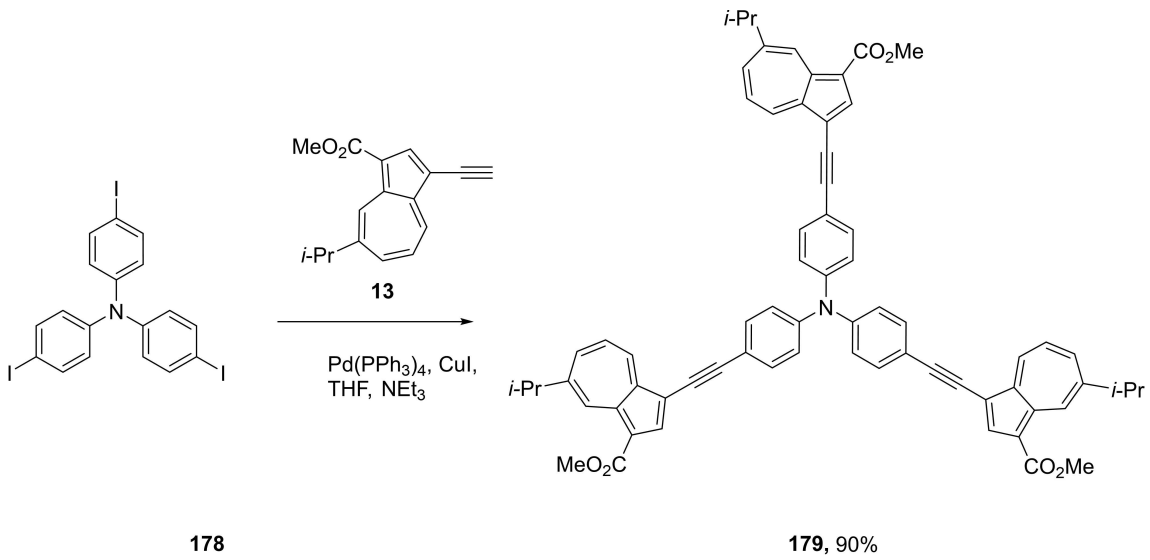
Thus with the described methods, azulene can be successfully ethynylated at nearly all positions of its 5- and 7-membered rings. The ethynylazulenes so far prepared are slightly stable and can be easily manipulated under ambient conditions, especially as long as the alkyne groups are protected by trimethylsilyl groups. Most of the deprotected ethynylazulenes are only slightly stable at room temperature



Scheme 36. Synthesis of bis(2-octyldodecyl)benzo[*lmn*][3,8]phenanthrolinetetraone **162**.

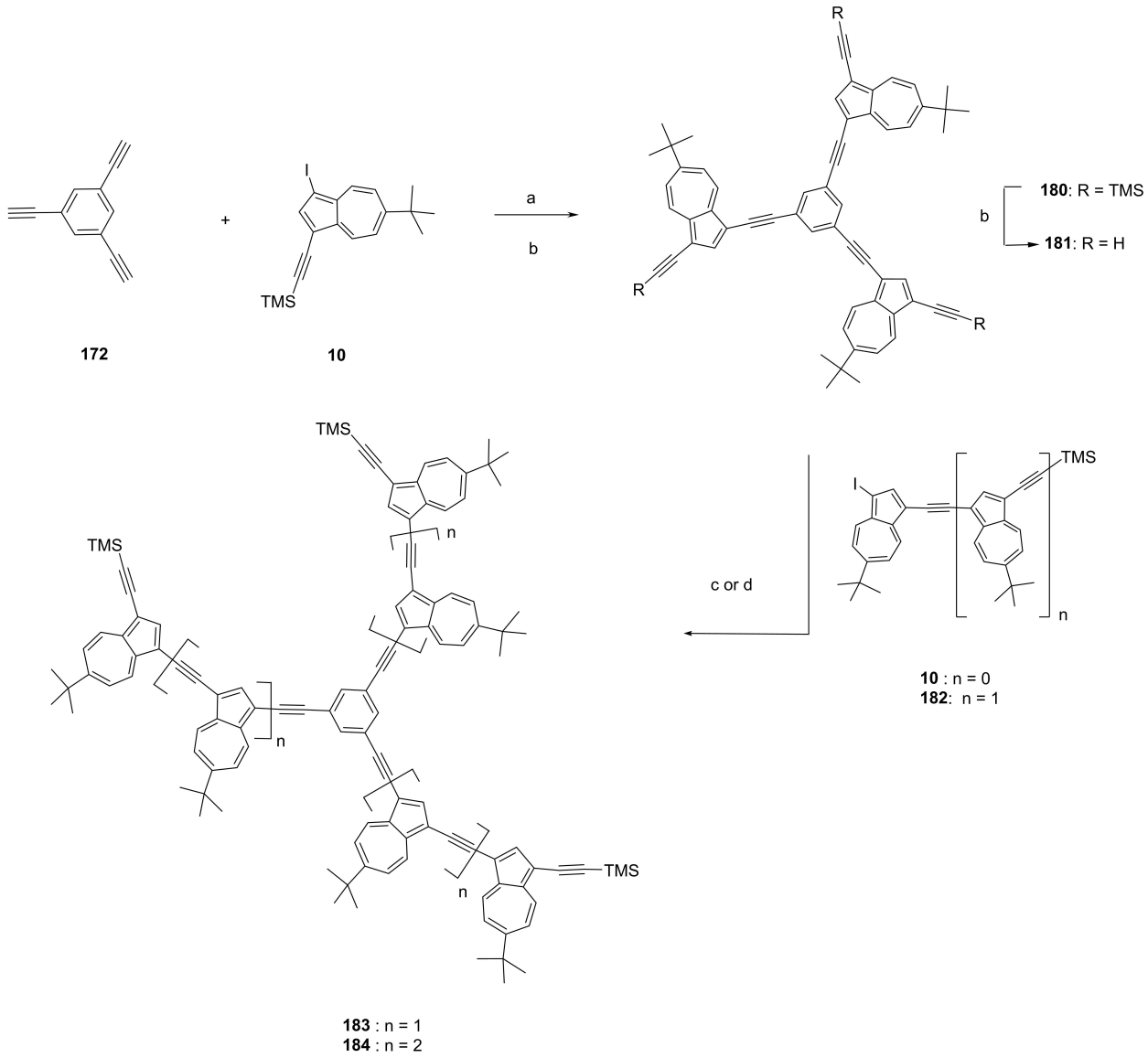


Scheme 37. Synthesis of naphthalenediimide (NDI) end-capped with 2-ethynylazulene units **167**.



Scheme 38. Synthesis of 1-ethynylazulenes connected to triphenylamine core **179**.

and form black solids with metallic luster after a few hours which could not be characterized so far due to their insolubility. The ethynyl substituents effect in all positions of the bicyclic system a bathochromic shift of the light absorption of azulene due to both inductive and mesomeric effects, respectively. Depending on the number and position of the ethynyl groups



Scheme 39. Synthesis of tripodal polyynes **180**, **181**, **183** and **184**. a) 0.04 mol% $PdCl_2(PPh_3)_2$, 0.08 mol % CuI, NEt_3, rt; b) 1.1 equiv. 1 M KOH in H_2O, MeOH, rt; c) 0.04 mol% $PdCl_2(PPh_3)_2$, 0.08 mol% CuI, NEt_3, 3 equiv. **10**, rt; d) 0.04 mol% $PdCl_2(PPh_3)_2$, 0.08 mol % CuI, NEt_3, 3 equiv. **182**, rt.

in the azulene-system the bathochromic shift ranged from 3–48 nm.

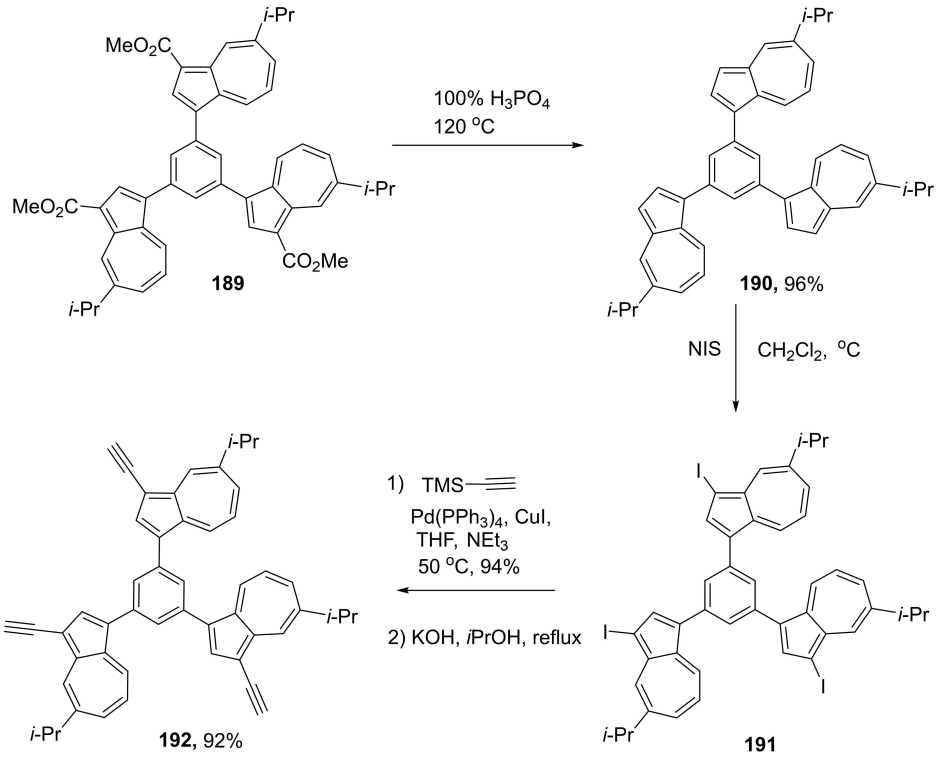
3. Reactions of ethynylazulenes

3.1. Synthesis of *bis*(stannaylvinyl)-, *bis*(silylvinyl)- and *bis*(borylvinyl)azulenes

Jung *et al.* reported a facile hydrostannation of 1,3-diethynylazulene **37 c** to the corresponding *bis*- stannylvinyl derivative **73** upon treatment with tributyltin hydride under thermal reaction (Figure 11).[55] Moreover, Lee *et al.* reported the hydrosilylation of **37 c** to 1,3-bis(chlorosilylvinyl)azulene **74** with dimethylsilyl chlorid in the presence of platinum catalyst (Figure 11). Among the platinum catalysts tested, the Karstedt catalyst exhibited the highest activity, completing the hydrosilylation under mild condition.[56] Lee *et al.* synthesized also 1,3-*bis*(borylvinyl) azulene products **75** by the Rh(I)-catalyzed hydroboration of **37 c** (Figure 11).[57] The hydrostannation, the hydrosilylation and the hydroboration products could then be used as precursors for interesting fluorescent dyes *via* the Stille cross-coupling reaction, substitution reactions or Suzuki cross-coupling reactions interesting fluorescent dyes.

3.2. Synthesis of ruthenium-alkynylazulene comlplexes

Vlasceanu *et al.* reported on functionalization of DHA system with ruthenium-based Cp*(dppe)Ru ([Ru*]) metal complexes **76** and **77** (Figure 12).[58]



Scheme 40. Synthesis of 1,3,5-tris(3-ethynyl-5-isopropylazulen-1-yl)benzene **192**.

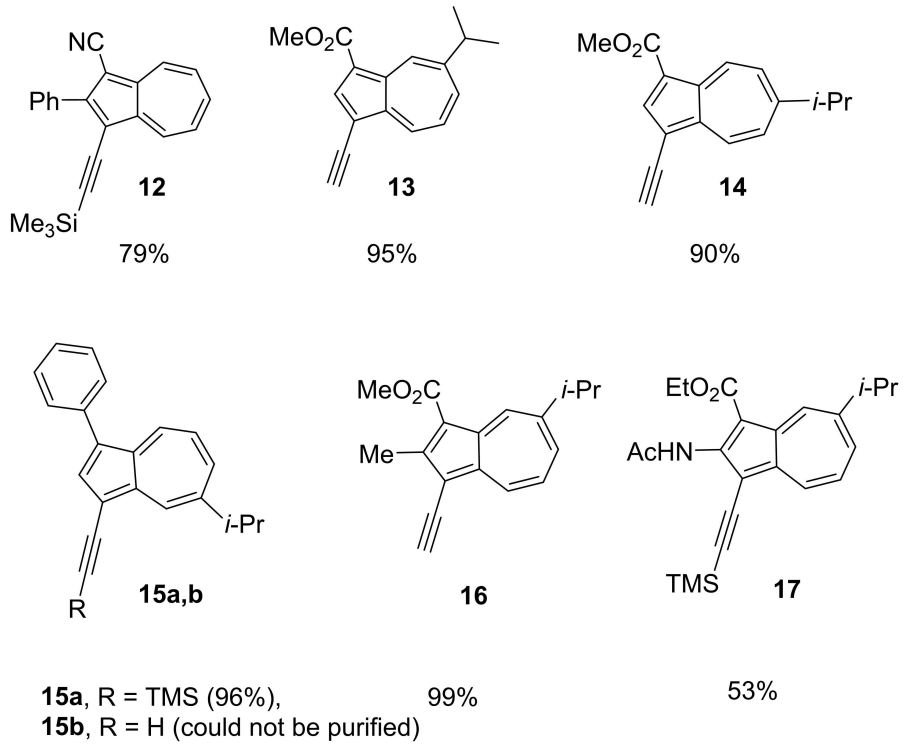
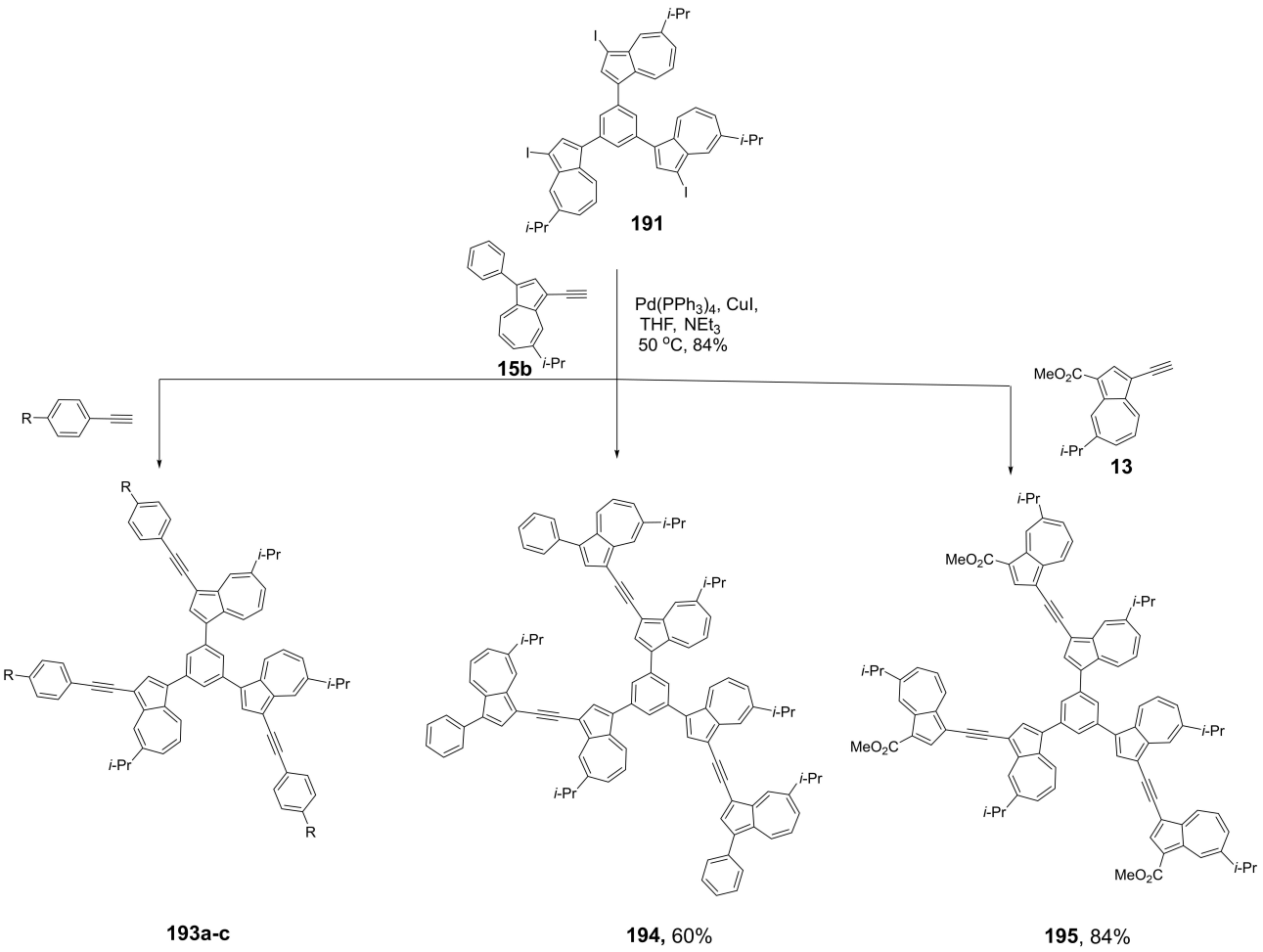


Figure 3. Structures of some substituted ethynylazulenes **12**–**17**.

The syntheses of ruthenium complex **79** was accomplished *via* the metalation strategy by combining **76** with 7-ethynyl-substituted DHA **78** (Scheme 16). The reaction proceeded through an isomerization by which the ruthenium-alkynyl substituent shifted from position 7 to position 6 on the DHA core.



Scheme 41. Synthesis of tris(1-arylacetylene) **193** and tris(1-azulenylacetylene) chromophores **194** and **195**.

On the other hand, a Sonogashira reaction between **77** and 7-bromo-substituted DHA **54** afforded minute quantities of the azulene complex **80** in which the alkyne substituent has moved to position 4 and a cyano group has been incorporated at position 7 *via* a more complex reactions (Scheme 17).

3.3. Synthesis of diene-substituted azulene

Mikus *et al.* developed a selective synthesis of azulenes with an extended π-electron system by enyne cross-metathesis. Thus, when azulenes **81** and **82** bearing an acetylenic function on the five membered rings was subjected to enyne metathesis with ethylene in the presence of ruthenium catalyst **85**, the corresponding dienes **83** and **84** were afforded in 20 and 8%, respectively (Scheme 18).[59]

In the case of 1,3-diacetylenic substrate **86** a mixture of mono-diene **87** and di-diene **88** was produced in 7% and 5% yields, respectively (Scheme 19).[59]

On the other hand, the metathesis of the appropriate acetylene-substituted azulenes in seven-membered ring proceeds satisfactorily giving azulene-diene building blocks **89** and **90**, respectively (Figure 13).[59]

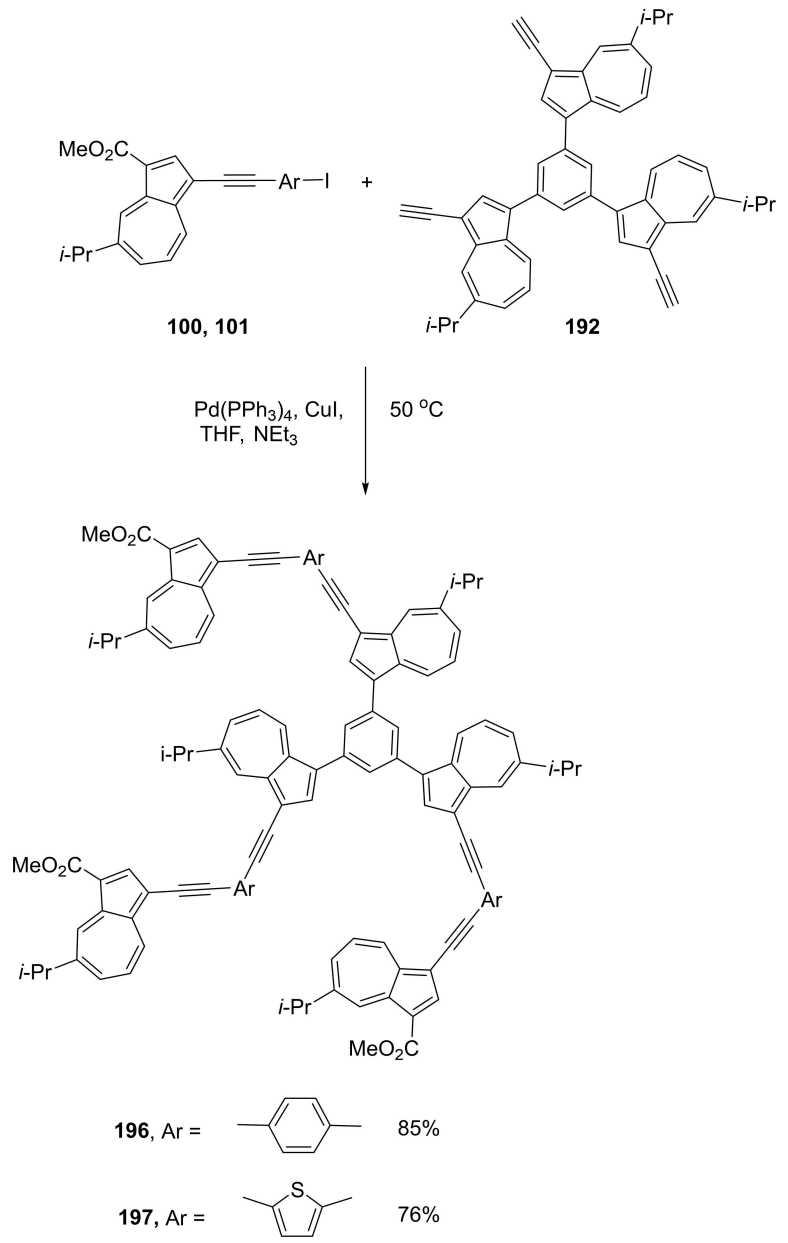
3.4. Synthesis of azulenylethynylarenes and azulenylethynylheteroarenes

3.4.1. Synthesis of mono- azulenylethynylarenes or heteroarenes

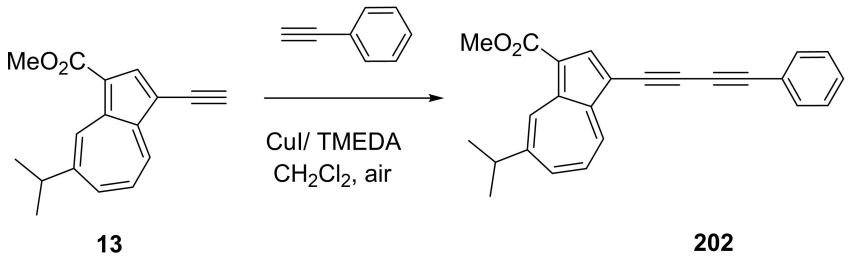
3.4.1.1. From 1-ethynyl(halo)azulene

Ito *et al.* and other research groups reported the synthesis of arylethynylazulenes **91**–**96** in 37–99% yield by Pd-catalyzed cross coupling of the appropriate ethynylazulene with haloarenes or the inverse cross coupling reaction of the appropriate haloazulene with the corresponding ethynylbenzenes (Figure 14).[23,25,26,60–66]

Shoji *et al.* prepared azulene derivatives bearing a methyl *o*-ethynylbenzoate moiety **98a**–**c** in excellent yields (97–99%) by the Sonogashira-Hagihara reaction of 1-iodoazulenes **97a**–**c**

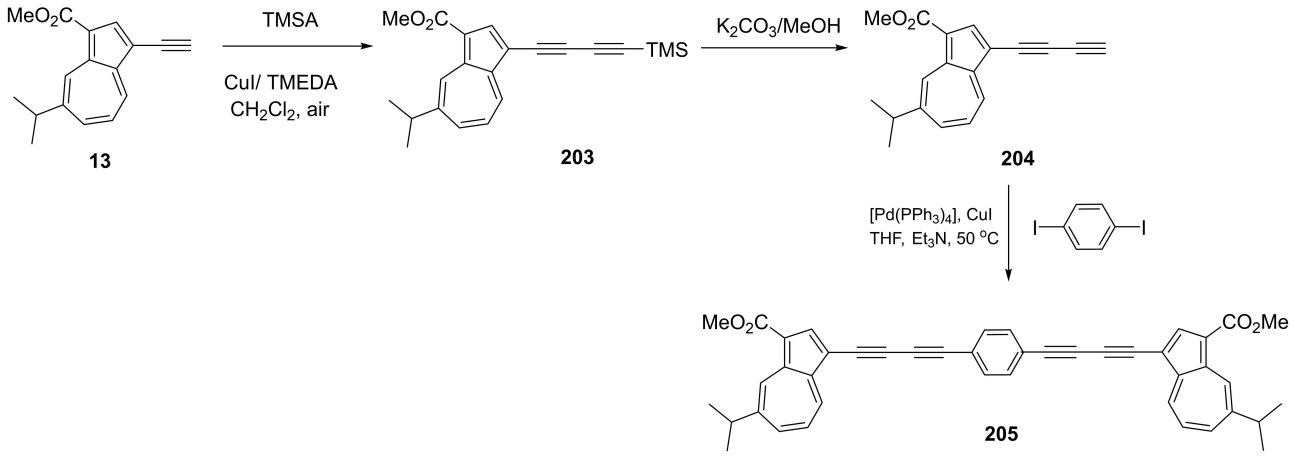


Scheme 42. Synthesis of tris(1-azulenylethynylarylacetylene) chromophores **196** and **197**.

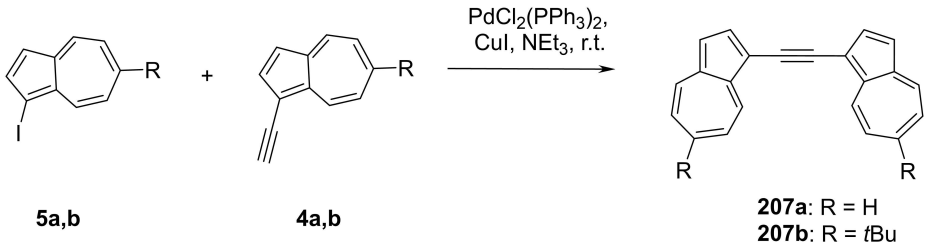


Scheme 43. Synthesis of azulene-substituted butadiene **202**.

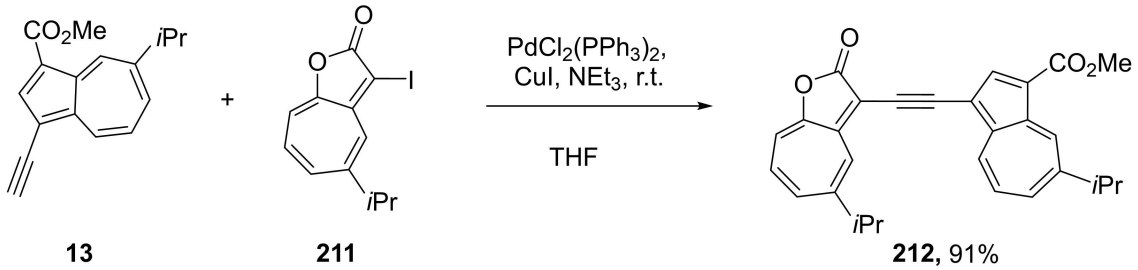
with methyl o-ethynylbenzoate. A similar reaction was used to make compound **98d** from **97d**, however the yield was relatively low (58%) owing to the formation of 1,1′-biazulene **99** (17%) as a by-product. The generation of 1,1′-biazulene **99** might indicate that the transmetalation process of copper acetylide is a rate-determining step in the reaction of **97d**.



Scheme 44. Synthesis of (1,4-phenylene*bis*(buta-1,3-diyne-4,1-diyl))*bis*(azulene) **205**.



Scheme 45. Synthesis of bis(azulen-1-yl)ethynes **207 a** and **207 b**.



Scheme 46. Synthesis of methyl 7-isopropyl-3-((5-isopropyl-2-oxo-2H-cyclohepta[*b*]furan-3-yl)ethynyl)azulene-1-carboxylate **212**.

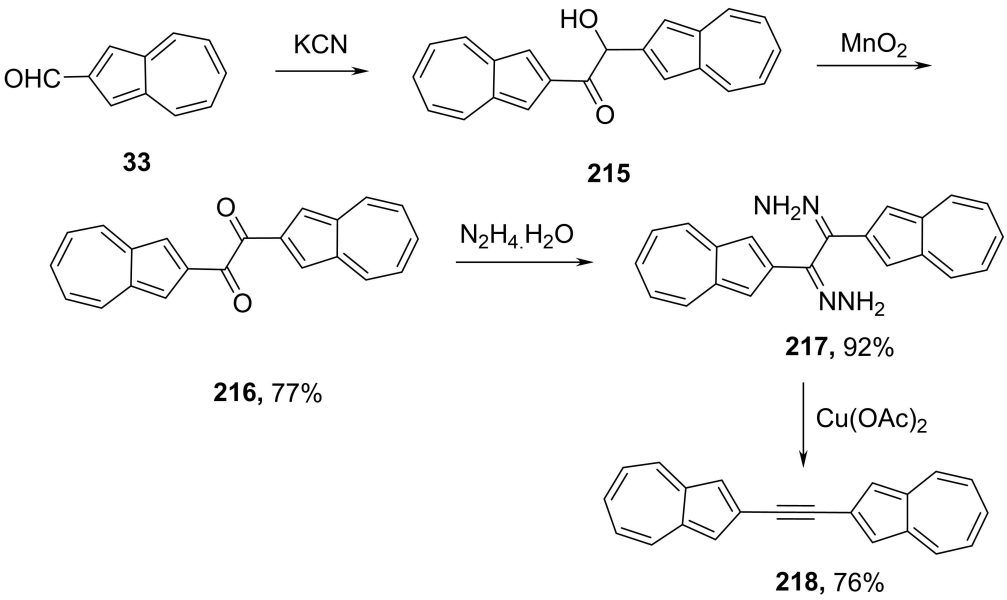
However, alkyne **98 d** was prepared in good yield (77%) by the reaction of **16** with methyl *o*-iodobenzoate, without the formation of **99**, as shown in Scheme 20.[24]

The Sonogashira Hagihara cross-coupling reaction of 1-ethynylazulene with excess of 1,4-diiodobenzene and 2,5-diiodothiophene at room temperature afforded methyl 3-[(4-iodophenyl)ethynyl]-7-isopropylazulene-1-carboxylate (**100**) and methyl 3-[(5-iodo-2-thienyl)ethynyl]-7-isopropylazulene-1-carboxylate (**101**) both in 74% yield (Figure 15).[61]

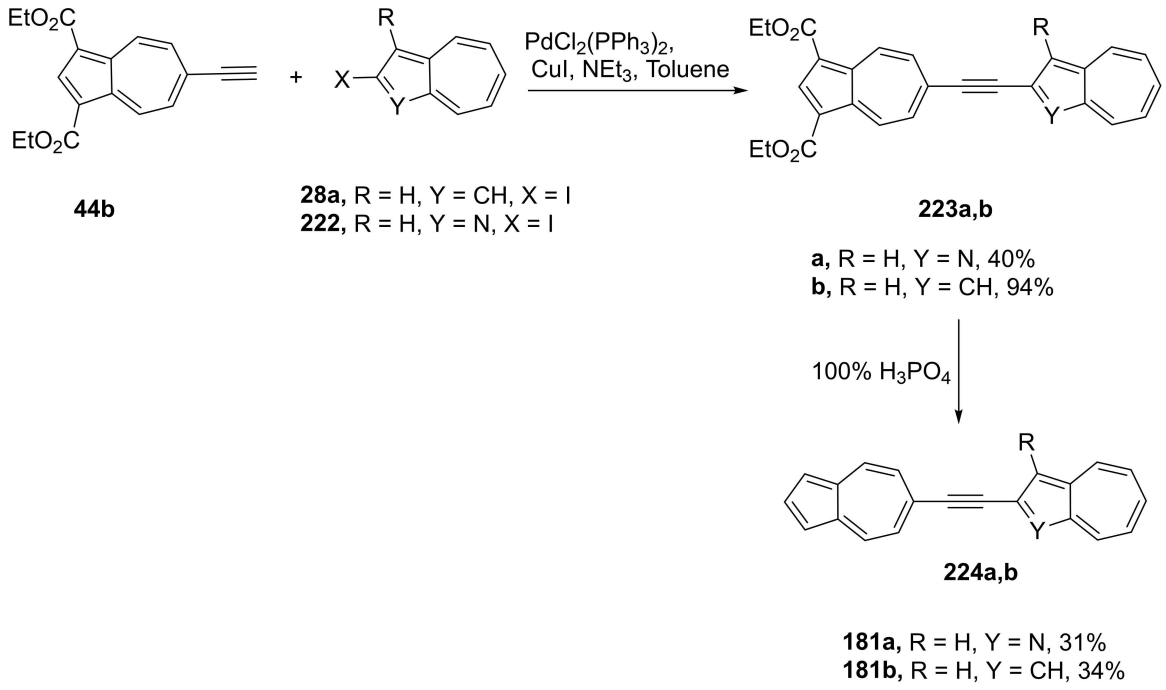
3.4.1.2. From 2-ethynyl(halo)azulene

Various aryl-substituted 2-ethynylazulenes **103 a**–**i** have been synthesized starting from 2-bromoazulene **102** by coupling with the corresponding ethynylarenes under Sonogashira coupling conditions using a catalytic amounts of CuI and $Pd(PPh_3)_2Cl_2$ in the presence of an excess amount of Et_3N. 2-Ethynylazulene **29** was also utilized as the key starting material to prepare the corresponding aryl-substituted 2-ethynylazulenes **103** by reacting with the appropriate aryl halides under Sonogashira coupling conditions (Scheme 21).[67]

Although Sonogashira-Hagihara cross-coupling of **105**, obtained upon treatment of diethyl 6-(pyrrolidin-1-yl)azulene-1,3-dicarboxylate **104**, with ethynylbenzene in the presence of 3 mol% Pd-catalyst and 10 mol% CuI produced the cross-coupling product **106** in low yield (12%) along with the recovery of **105** (85%), the use of excess CuI (50 mol%) has shown a significant improvement of the yield of **106** (89%) (Scheme 22). These results suggest the coordination of CuI to the pyrrolidine moiety in **105** that leads to a decrease in the activity of the Cu-catalyst because 2-haloazulenes without the 6-amino substituent give the products in good-to-excellent yields in the presence of catalytic amount of CuI.[68]



Scheme 47. Synthesis of di-2-azulenylacetylene **218**.



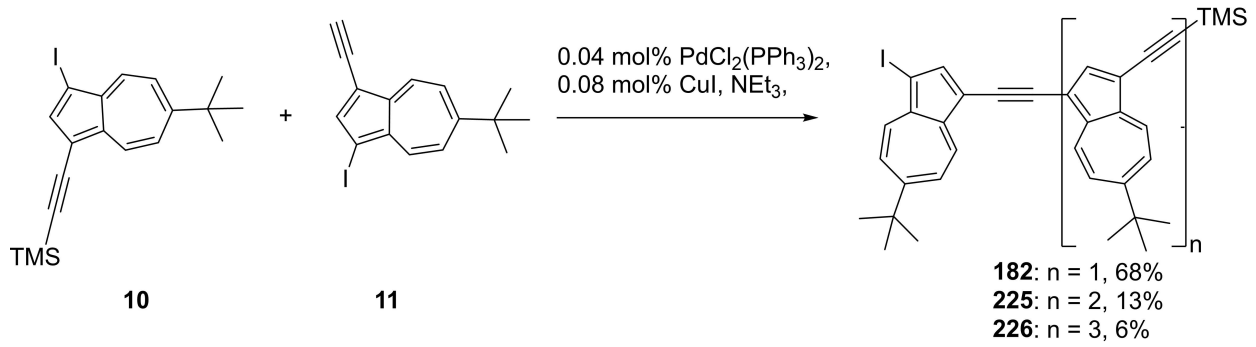
Scheme 48. Synthesis of 6-(1-azaazulen-2-yl)ethynylazulene (**224 a**) and 6-(2-azulenyl)ethynylazulene (**224 b**).

3.4.1.3. From 6-ethynyl(halo)azulene

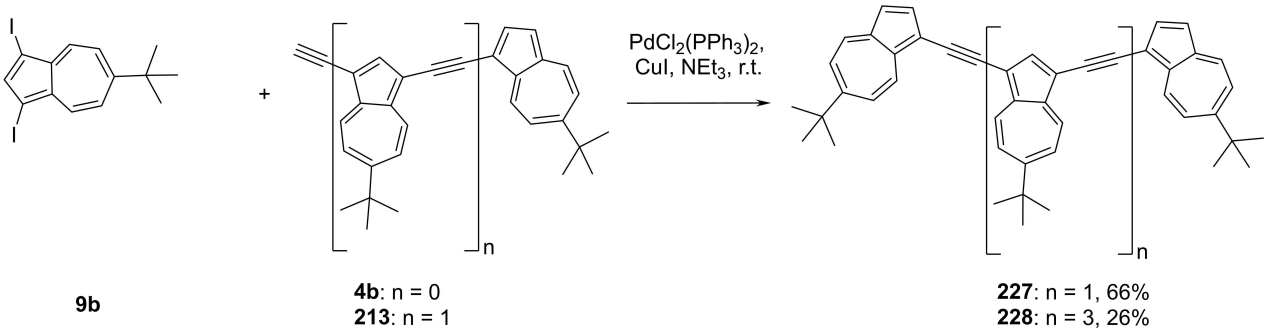
Ito *et al.* and other research groups reported the synthesis of arylethynylazulene **107 a**–**e** in 37–95% yield by Pd-catalyzed cross coupling of the appropriate ethynylazulene with haloarenes or the inverse cross coupling reaction of the appropriate halooazulene with the corresponding ethynylbenzenes (Figure 16). Compound **107 e** was subsequently thermally dealkoxycarboxylated with LiCl to give 2-hydroxy-6-phenylethynylazulene **108** in 56% yield.[69]

6-Arylethynylazulene **110** could be alternatively obtained in 38% yield together with 4-(phenylethynyl)azulene **111** (45%) by an unusual substitution reaction of 2-chloro-1,3-azulene dicarboxylic acid diethylester (**109**) with lithium phenylacetylide in liq. ammonia (Scheme 23).[44]

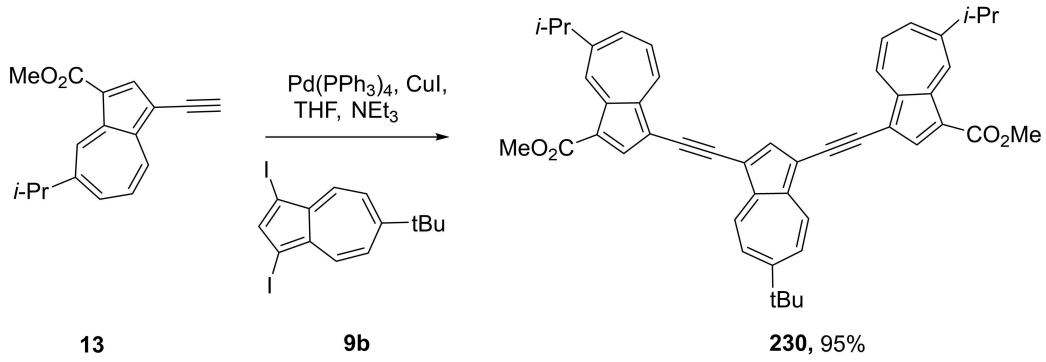
Förster *et al.* synthesized diethyl 2-amino-6-[(thiophen-3-yl) ethynyl]azulene-1,3-dicarboxylate **112**[37] starting from the diethyl 2-amino-6-bromoazulene-1,3-dicarboxylate upon treatment with 3-ethynylthiophene in a mixture of diisopropylamine and tetrahydrofuran (Figure 17).[70]



Scheme 49. Synthesis of poly(azulen-1-ylethynes) **182**, **225** and **226**.



Scheme 50. Synthesis of poly(azulen-1-ylethynes) **227** and **228**.

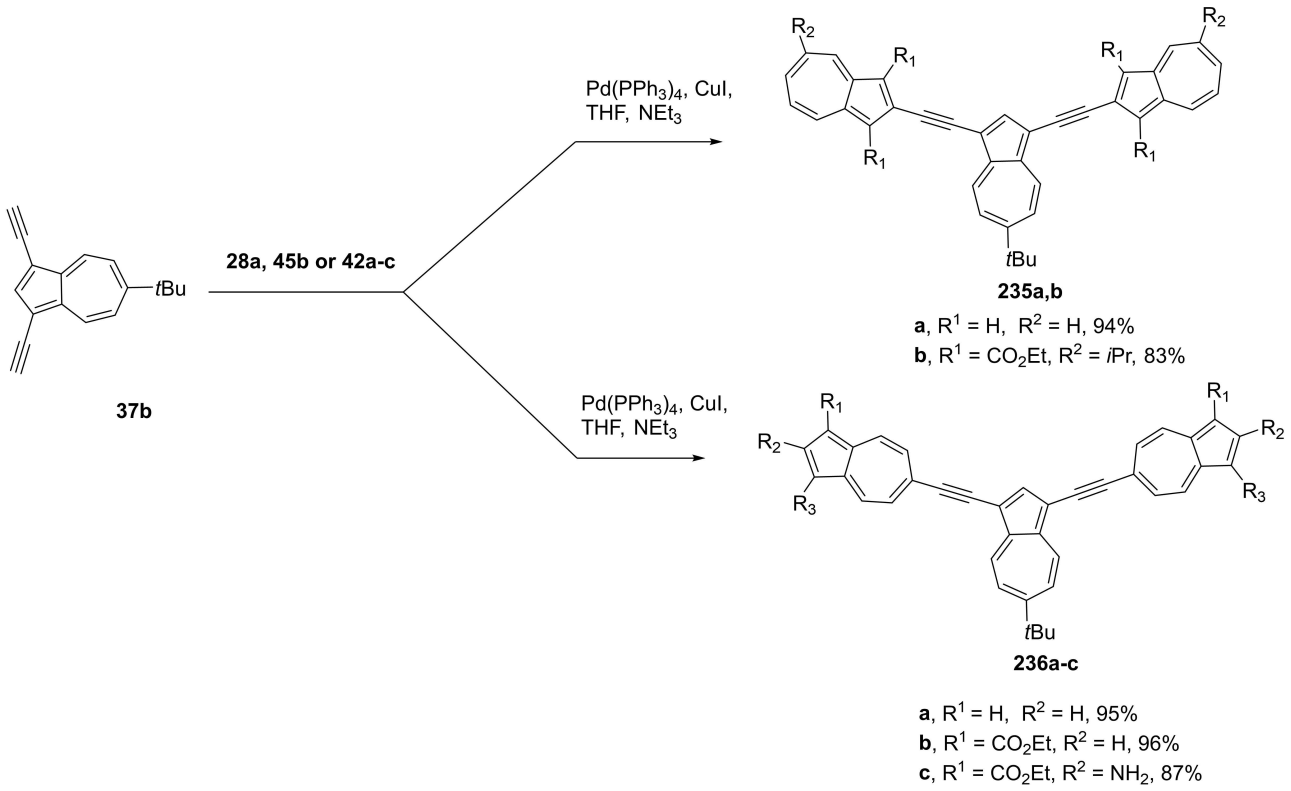


Scheme 51. Synthesis of 1,3-bis(1-azulenylethynyl)azulene **230**.

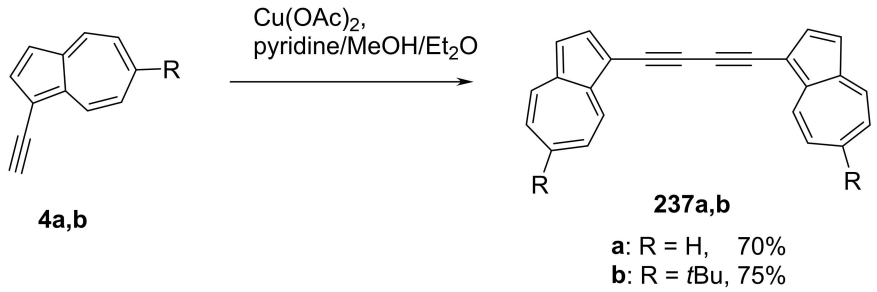
The Sonogashira Hagihara reaction of diethyl 2,2′-diamino-6,6′-dibromo-[1,1′-biazulene]-3,3′-dicarboxylate **114** with ethynylbenzene, using [Pd(PPh$_3$)$_4$] as a catalyst, afforded the cross-coupled product **115** in 91% yield. Compound **114** was obtained in 76% yield by homocoupling reaction of the corresponding 2-aminoazulene **113** using 6 mol% CuBr and 18 mol% pyridine in toluene at 60 °C under aerobic conditions (Scheme 24).[71]

3.4.1.4. From 7-bromoazulene

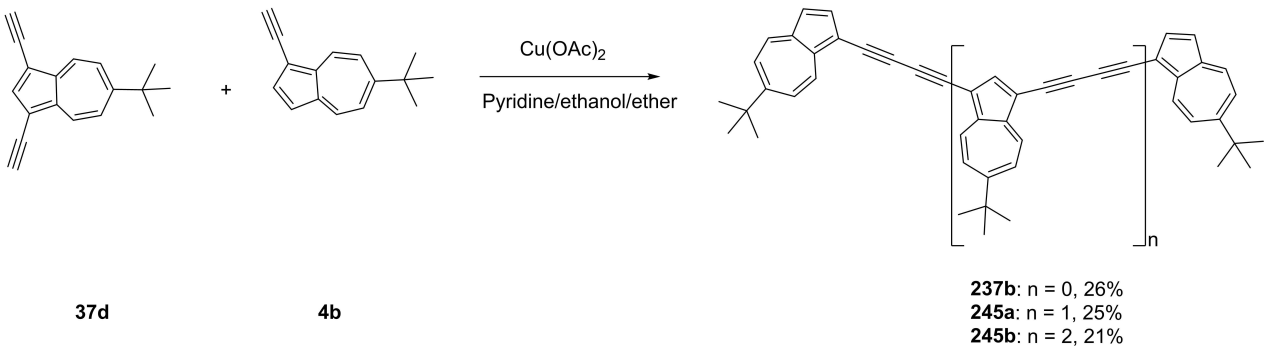
7-Arylethynyldihydroazulenes **116a–c** were prepared by a similar palladium-catalyzed Sonogashira cross-coupling reactions employing a suitable bromo-functionalized dihydroazulene **54**. The dihydroazulenes **116a–c** underwent a light-induced ring-opening to vinylheptafulvenes (VHFs) which were thermally converted to a mixture of two DHA regioisomers, one of which the original dihydroazulenes **116** and the other was 6-arylethynyldihydroazulenes **117a–c**, in a ratio that depends on the wavelength of irradiation and solvent polarity (Figure 18). The influence of the aryl groups on the DHA and VHF interconversion was investigated and rates of the switching events were finely tuned by the donor or acceptor strength of the aryl group.[72]



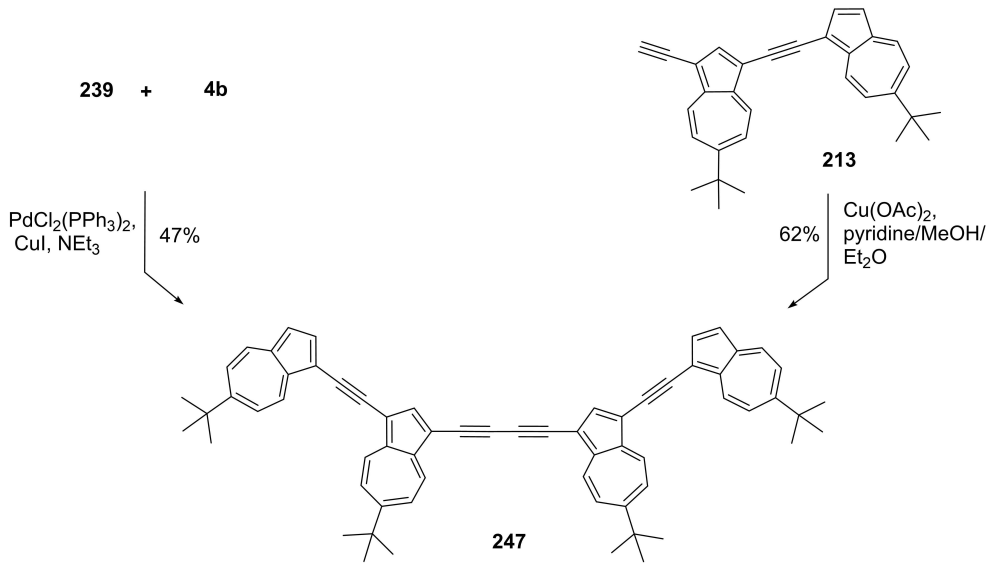
Scheme 52. Synthesis of bis(azulen-2-ylethynyl)azulenes **235a** and **235b** and bis(azulen-6-ylethynyl)-1,3-azulenes **236a–c**.



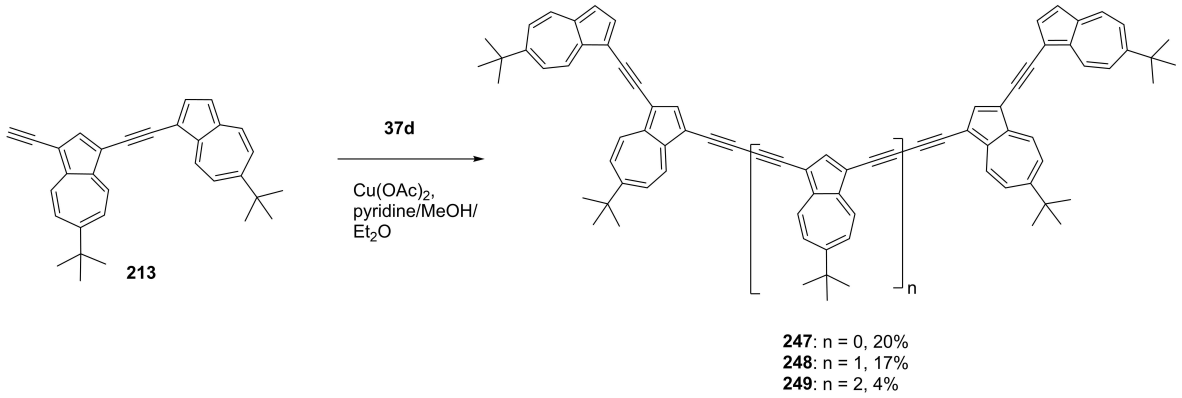
Scheme 53. Synthesis of 1,4-di(azulen-1-yl)buta-1,3-diynes **237a** and **237b**.



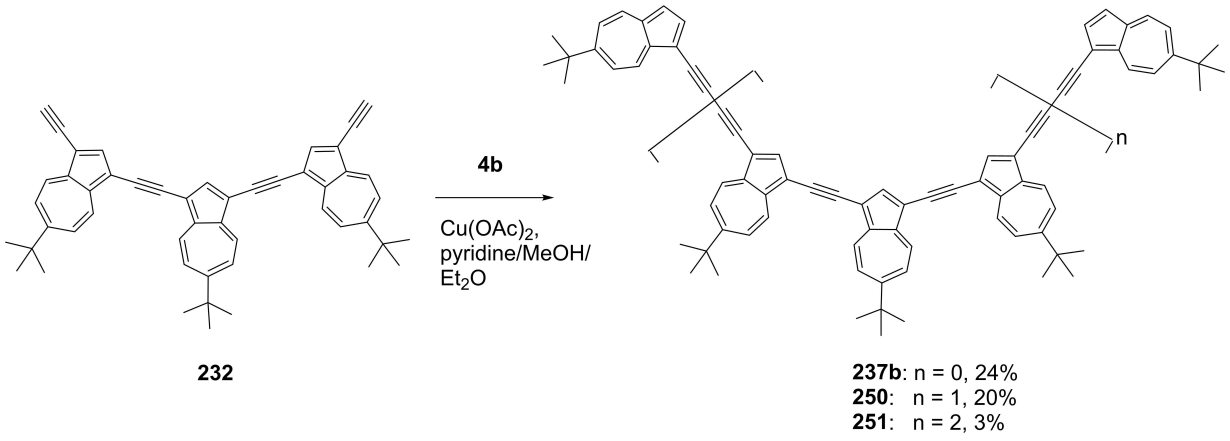
Scheme 54. Synthesis of butadiynylene-bridged trimer **245a** and tetramer **245b**.



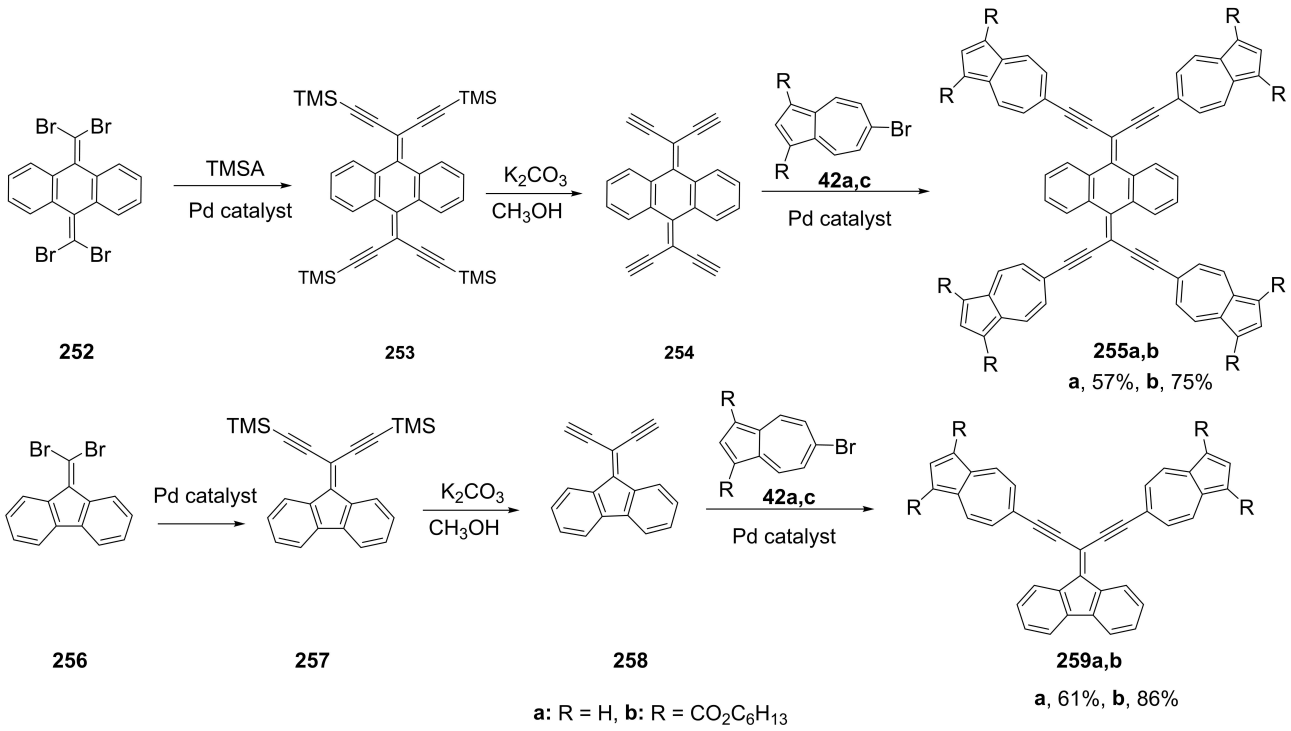
Scheme 55. Synthesis of oligoazulene with mixed ethynyl and butadienyl bridges **247**.



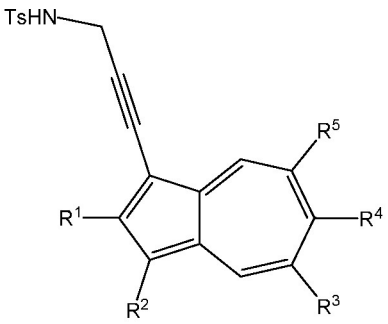
Scheme 56. Synthesis of oligoazulene with mixed ethynyl and butadienyl bridges **247**–**249**.



Scheme 57. Synthesis of oligoazulene with mixed ethynyl and butadienyl bridges **237 b**, **250** and **251**.



Scheme 58. Synthesis of mono- and bis(enediyne)s attached to anthracene and fluorene **255a,b** and **259a,b**.



22a-h

Entry	R^1	R^2	R^3	R^4	R^5	Yield [%]
a	H	CO_2Me	H	H	H	79
b	H	CO_2Me	*i*-Pr	H	H	87
c	H	CO_2Me	H	*i*-Pr	H	97
d	Me	CO_2Me	*i*-Pr	H	H	62
e	H	CHO	H	*t*Bu	H	87
f	H	$COCF_3$	H	*t*Bu	H	94
g	H	COMe	H	H	*i*-Pr	83
h	H	Ph	H	H	*i*-Pr	17

Figure 4. Structures of some *N*-(3-(azulen-1-yl)prop-2-yn-1-yl)-4-methylbenzenesulfonamides **22a–h**.

3.4.2. Synthesis of azulenylethynyl-ferrocene

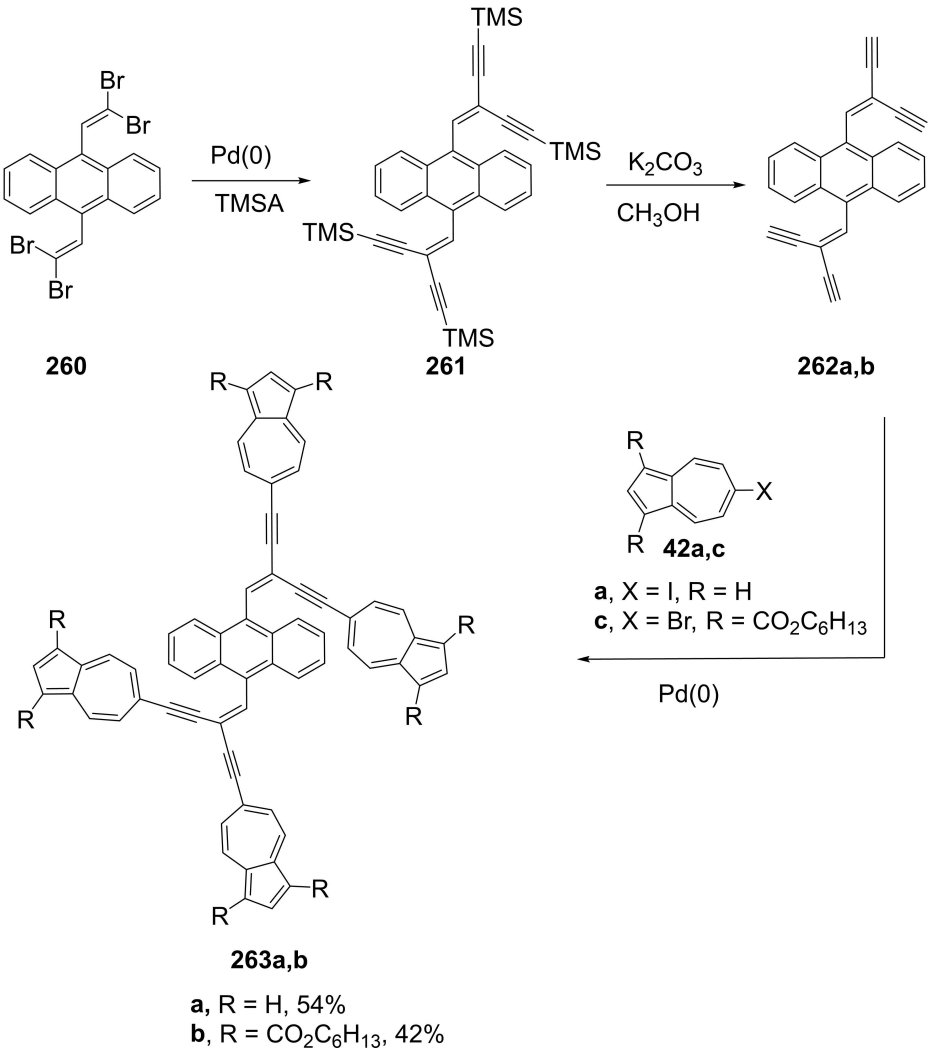
(Ferrocenylethynyl)azulenes **118–120** were prepared in excellent yields by palladium-catalyzed alkynylation of ethynylferrocene with the corresponding haloazulenes under the Sonogashira-Hagihara conditions (Figure 19).[73]

3.4.3. Synthesis of bis(arylethynyl)azulene

3.4.3.1. 1,3-Bis(arylethynyl)azulene

Application of Sonogashira coupling conditions on the reaction of 1,3-diiodoazulene **10a** with an excess amount of phenyl acetylene at elevated temperature gave 1,3-bis(phenylethynyl) azulene **121** in very good yield (Scheme 25).[69]

Using a similar approach, Förster *et al.* and Thanh *et al.* reported the synthesis of some 1,3-bis(arylethynyl)azulenes **122a–f** in moderate to good yields by the reaction of 1,3-diiodoazulene with the corresponding arylacetylenes. However, the synthesis of 1,3-bis[(4-acetylthiophenyl)ethynyl]azulene **122g** was adopted in 15% yield by the reaction of 1,3-diethynylazulene with 4-(acetylthio)iodobenzene (Figure 20).[74–76] Schwarz *et al.* reported the synthesis of **122** in 93% yield by the reaction of 1,3-diiodoazulene with *S*-(4-ethynylphenyl) ethanethioate.[77] Nöll *et al.* also reported the synthesis of 1,3-bis[4-{*N*,*N*-di(4-methoxyphenyl)amino}phenyl-ethynyl] azulene **122h** by the reaction of *N*,*N*-di(4-methoxyphenyl)-*N*-(4-ethynylphenyl)amine with 1,3-dibromoazulene.[78] Chen *et al.* employed a sealed oxygen-free two-chamber reaction system



Scheme 59. Synthesis of azulene-substituted bis(enediyne) systems **263a** and **263b**.

for the synthesis of **122i** *via* Sonogashira coupling reaction of dihaloazulene with 2-ethynyl-6-methoxynaphthalene to overcome the presence of homocoupling side reactions.[79] Filichev *et al.* also reported the synthesis of 2-(4-{3-[4-(2-hydroxyethoxymethyl)phenylethynyl]azulen-1-ylethynyl}benzyloxy)ethanol **122** by Sonogashira coupling reaction of 1,3-diiodoazulene with 2-(4-ethynylbenzyloxy)ethanol (Figure 20). Compound **122j** was prepared to act as a precursor for intercalating linker to connect two 8-mer sequences with inverted polarity to generate a Hoogsteen-type triplex, with a considerable increase in the thermal stability.[80]

3.4.3.2. 1,2-Bis(arylethynyl)azulene

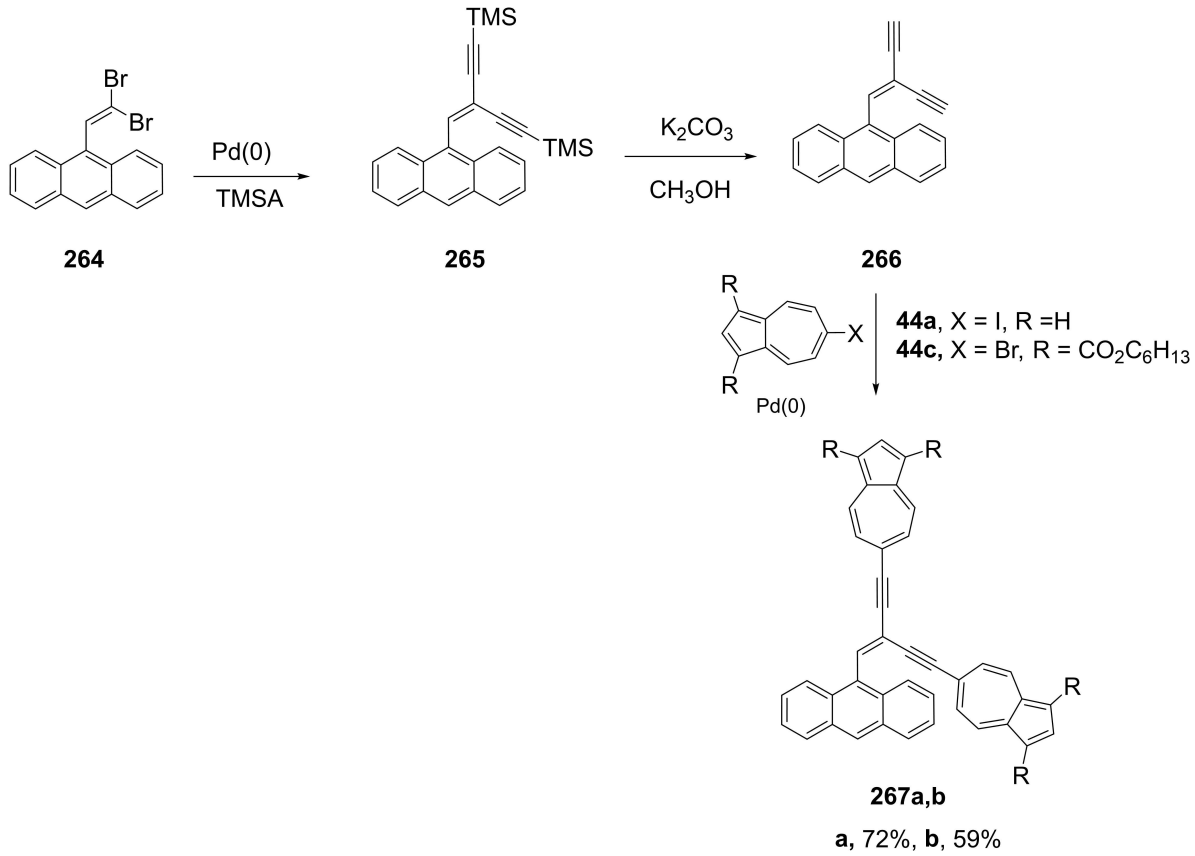
1,2-Bis(phenylethynyl)azulene **124** was prepared in 91% yield from 2-(phenylethynyl)azulene **103a** by firstly iodination with 1 eq. of NIS to give 1-iodo-2-(phenylethynyl)azulene **123** followed by Sonogashira coupling with phenylacetylene (Scheme 26).[69]

3.4.3.3. 2,6-Bis(arylethynyl)azulene

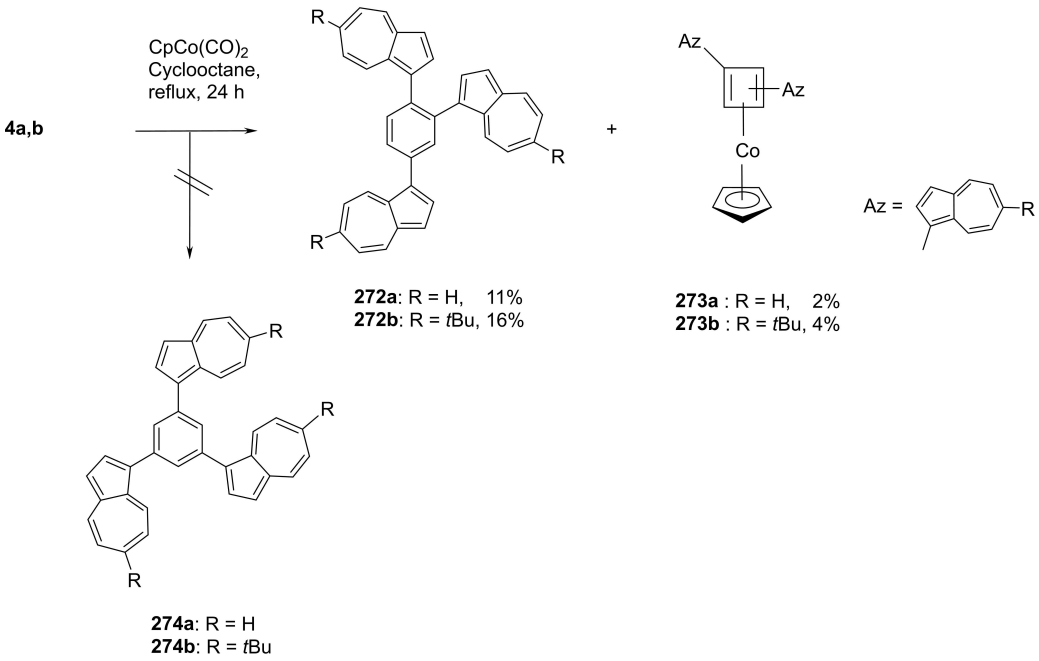
2,6-Bis(phenylethynyl)azulene **126** was obtained in 96% yield starting from 6-(phenylethynyl)azulen-2-ol **108** by firstly conversion to the corresponding bromo derivative **125** (68%) upon treatment with PBr_3 followed by Sonogashira coupling with phenylacetylene (Scheme 27).[69]

2,6-Bis(arylethynyl)azulene **129** was obtained in 92% yield starting from 2,6-*bis*(bromo)azulene **127** by Sonogashira coupling with *S*-(4-ethynylphenyl) ethanethioate **128** (Scheme 28).[77]

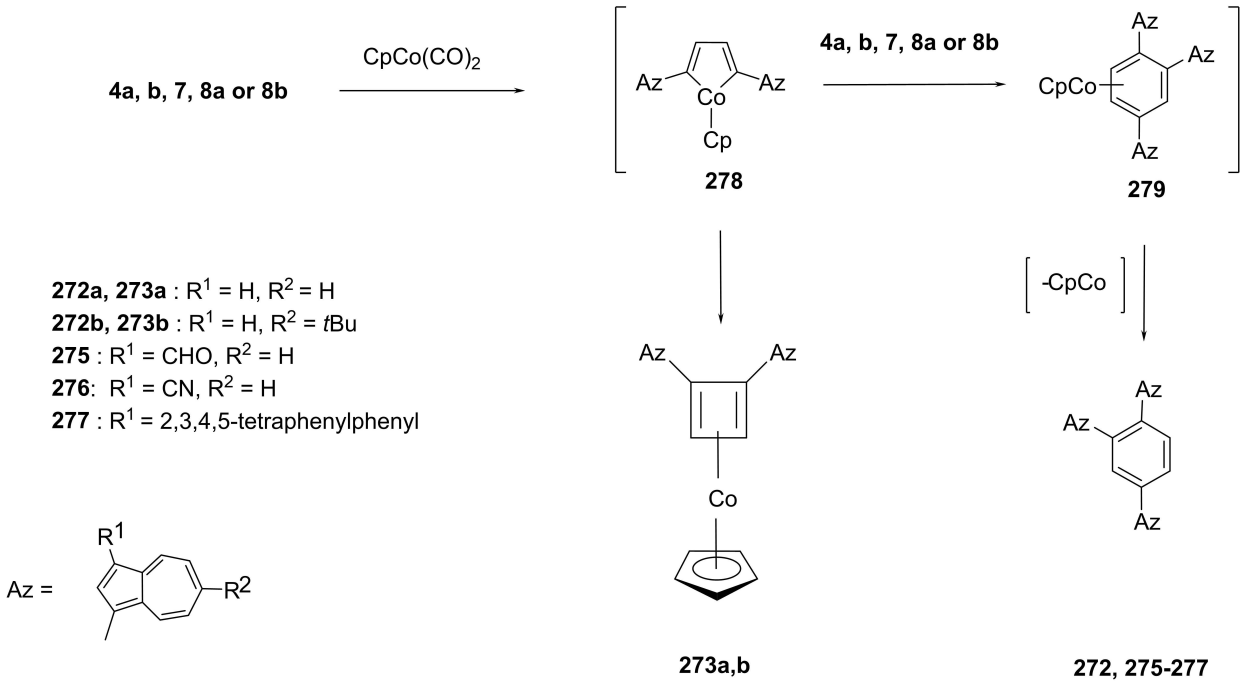
Azulene derivative **129** could be highly interesting building blocks for memory applications or neuromorphicdevices in next-generation nanoelectronic applications.



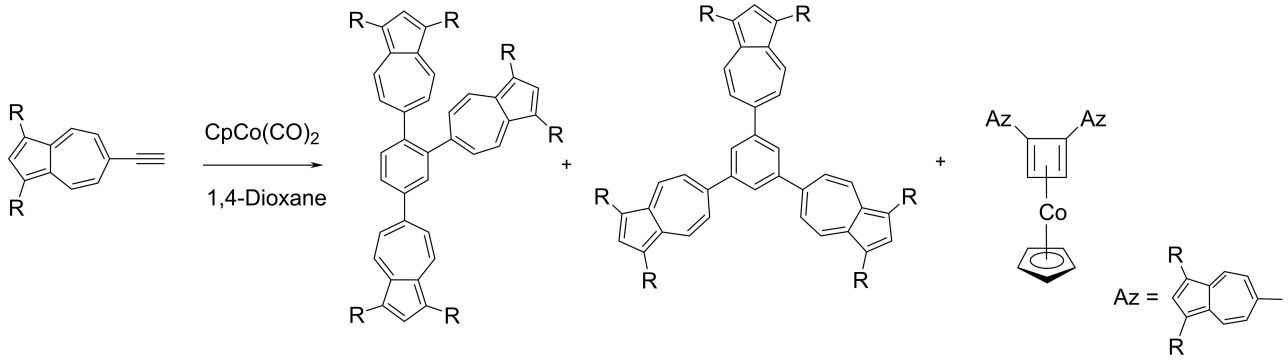
Scheme 60. Synthesis of mono(enediyne) derivatives **267 a** and **267 b**.



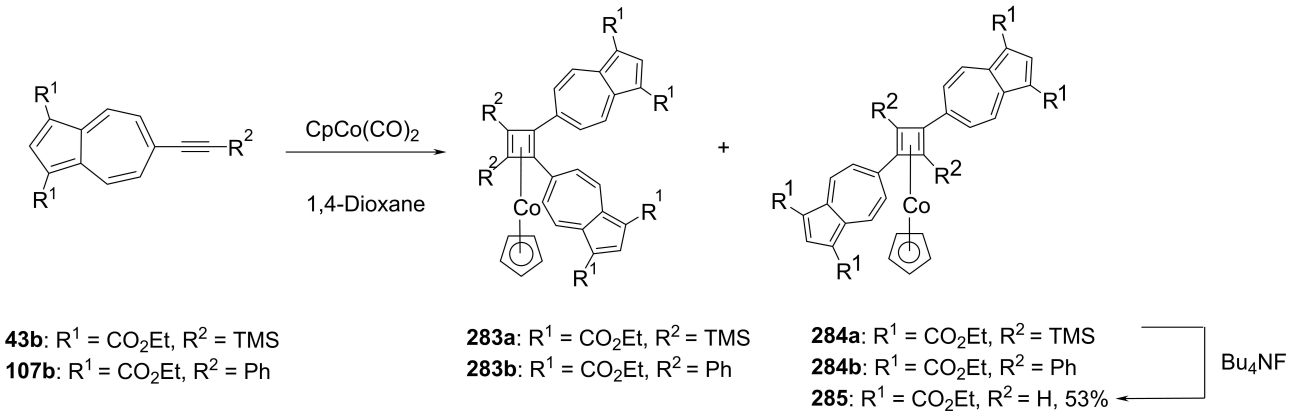
Scheme 61. Synthesis of 1,2,4-tris(azulen-1-yl)benzene derivatives **272 a** and **272 b**.



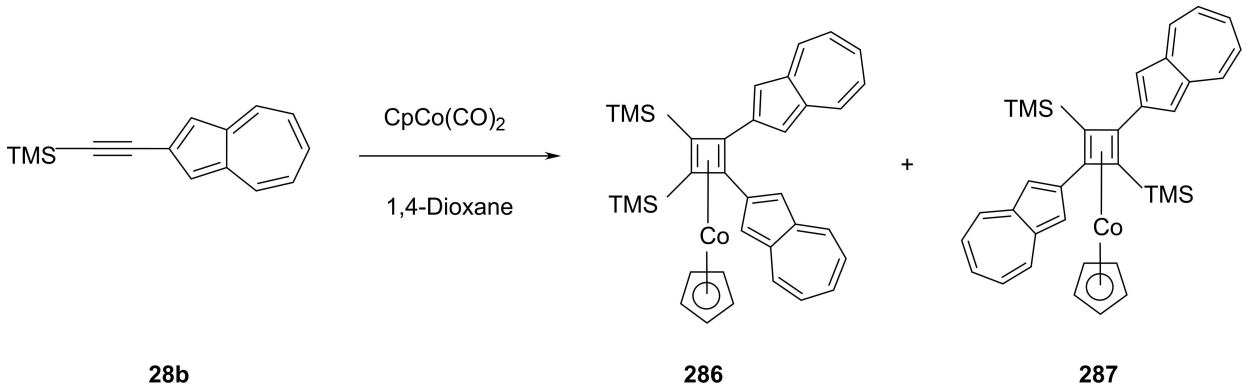
Scheme 62. A plausible mechanism for the formation of 1,2,4-tris(azulen-1-yl)benzenes **272** and **275**–**277**.



Scheme 63. Synthesis of tris(azulen-6-yl)benzenes **280** and **281**.

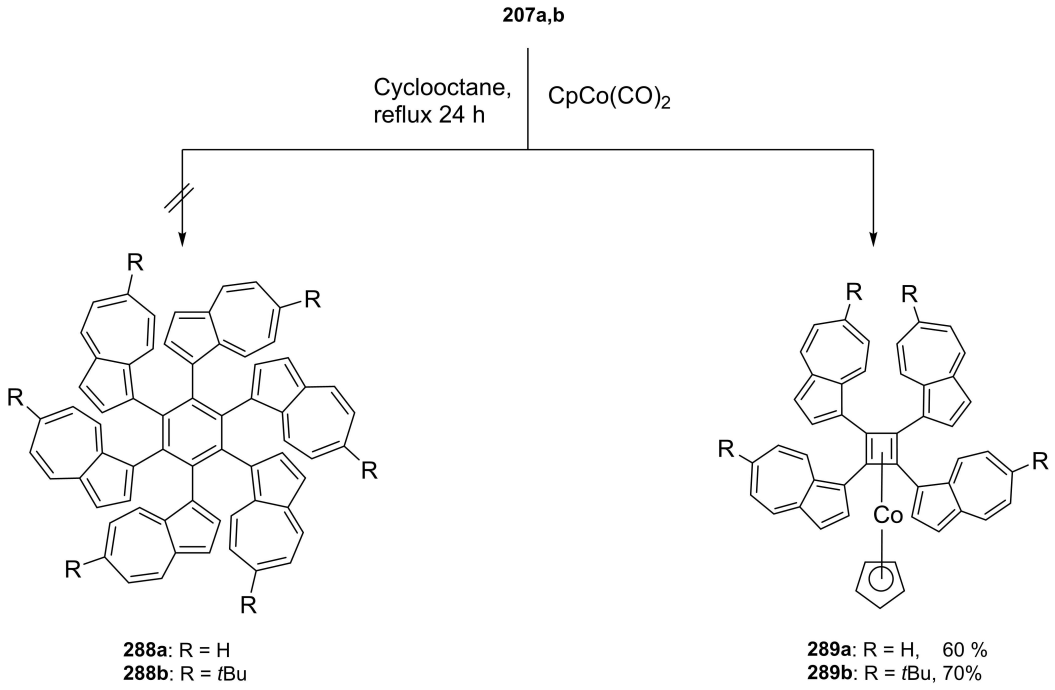


Scheme 64. Synthesis of (cyclobutadiene)cobalt complexes **283** and **284**.



28b **286** **287**

Scheme 65. Synthesis of bis(trimethylsilyl)-cyclobutadiene]cobalt complexes **286** and **287**.



288a: R = H
288b: R = *t*Bu

289a: R = H, 60 %
289b: R = *t*Bu, 70%

Scheme 66. Synthesis of tetrakis(azulen-1-yl)cyclobutadiene cobalt complexes **289a,b**.

3.4.3.4. 4,7-Bis(arylethynyl)azulene

4,7-Bis(phenylethynyl)azulene **131** was synthesized in 93% yield starting from 4,7-dibromoazulene **130**[81,82] upon treatment with phenylacetylene under Sonogashira conditions (Scheme 29).[69]

Using a similar approach, Schwarz *et al.* synthesized 4,7-bis (arylethynyl)azulene **132** in 84% yield starting from the corresponding 4,7-dibromoazulene (Figure 21).[77]

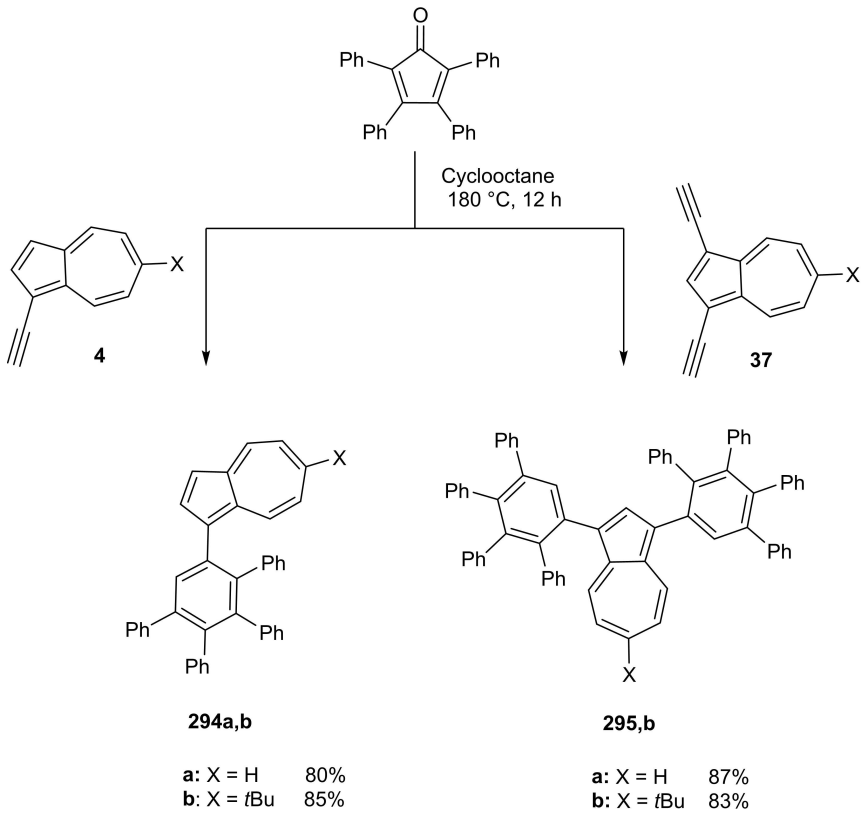
3.4.4. Synthesis of bis(azulenylethynyl)arenes or heteroarenes

3.4.4.1. From 1-ethynyl(halo)azulene

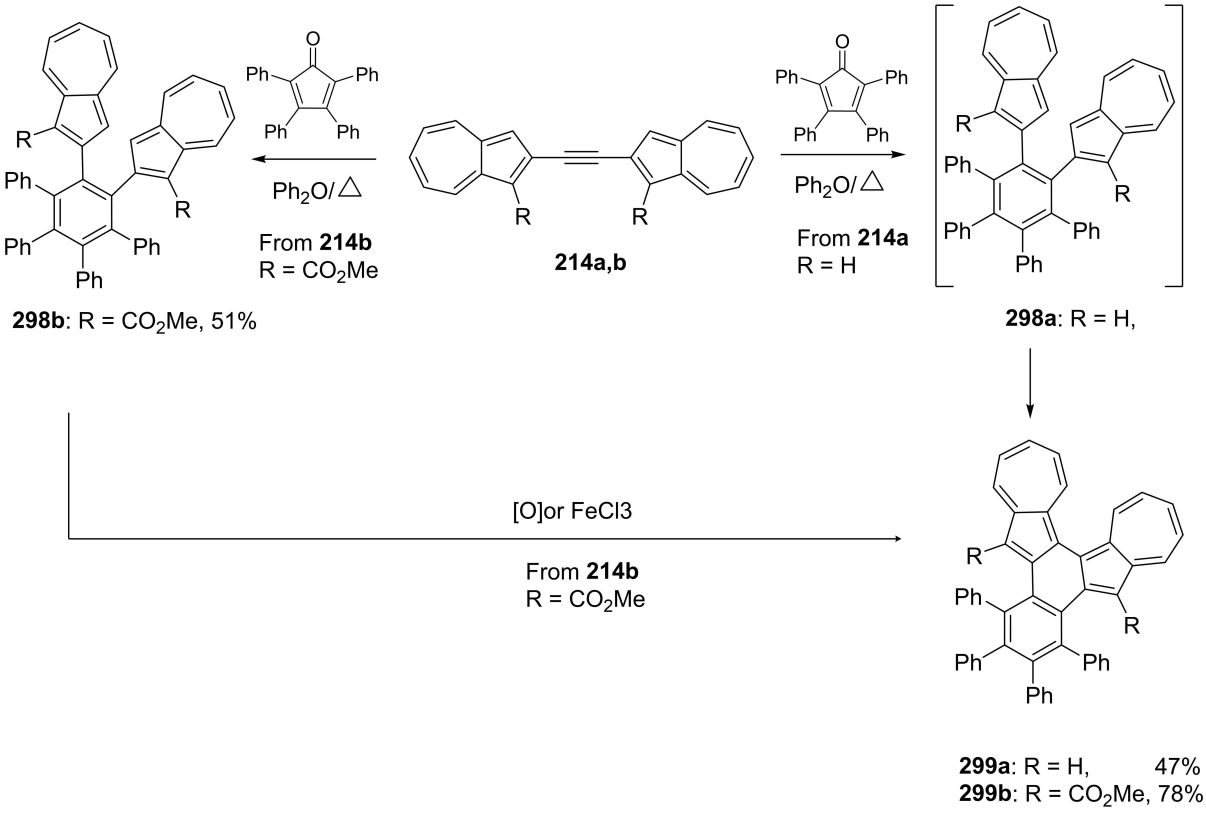
Hafner *et al.*[83] reported the synthesis of 1,4-bis(azulen-1-ylethynyl)benzene **133** as well as 2,5-bis(azulen-1-ylethynyl) thiophene **134** from 1,4-diiodobenzene and 2,5-diiodothiophene,[84] respectively, *via* a Sonogashira coupling with the appropriate ethynylazulene in good yield (Figure 22).

Likewise, the reaction of methyl 3-iodo-7-isopropylazulene-1-carboxylate with 1,4-diethynylbenzene afforded 1,4-bis[(5-isopropyl-3-methoxycarbonyl-1-azulenyl)ethynyl]benzene (**135**) in 91% yield. 2,5-Bis[(5-isopropyl-3-methoxycarbonyl-1-azulenyl) ethynyl]thiophene **136** was also obtained by the reaction of 1-ethynylazulene derivative **13** with 2,5-diiodothiophene in the presence of [Pd (PPh_3)$_4$] in 72% yield (Figure 23).[23]

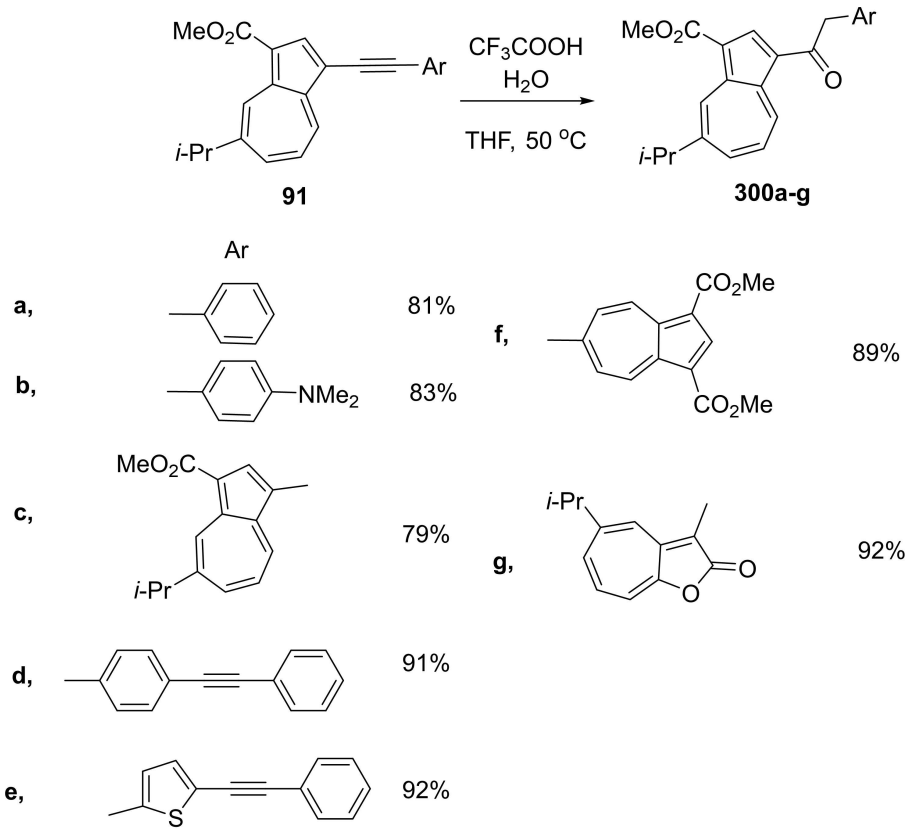
Bis(1-azulenyl)naphthalene derivatives **138**–**141**[65] were also synthesized by Pd-catalyzed alkynylation of iodoazulene **98b** with the corresponding diethynylnaphthalenes **137** (Scheme 30).[85]



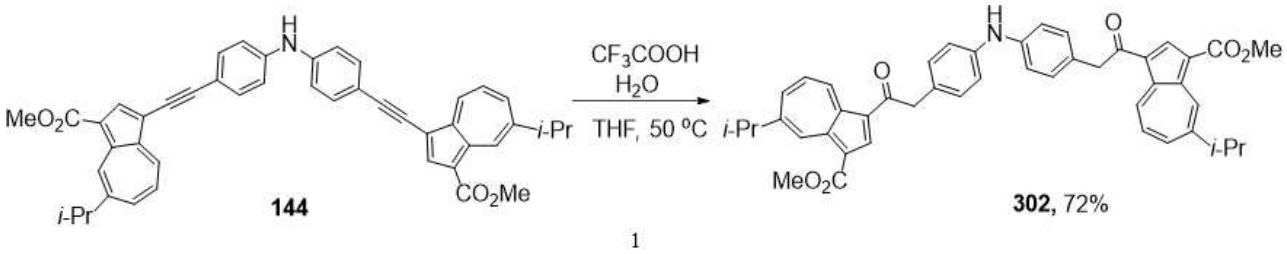
Scheme 67. Synthesis of 1-(3′,6′-diphenyl-[terphenyl]-4′-yl)azulene **294** and 1,3-bis(3′,6′-diphenyl-[terphenyl]-4′-yl)azulene **295 a,b**.



Scheme 68. Synthesis of 1,2-bis(2-azulenyl)tetraphenylbenzene **298** and diazuleno[2,1-*a*:1,2-*c*]naphthalene (**299**).



Scheme 69. Synthesis of 1-azulenylketones **300a–g**.



Scheme 70. Synthesis of diketone **302**.

Shoji *et al.* synthesized dihexyl 3,3′-(pyrene-1,6-diylbis (ethyne-2,1-diyl))bis(7-isopropylazulene-1-carboxylate) **142** using a similar approach (Figure 24).[66]

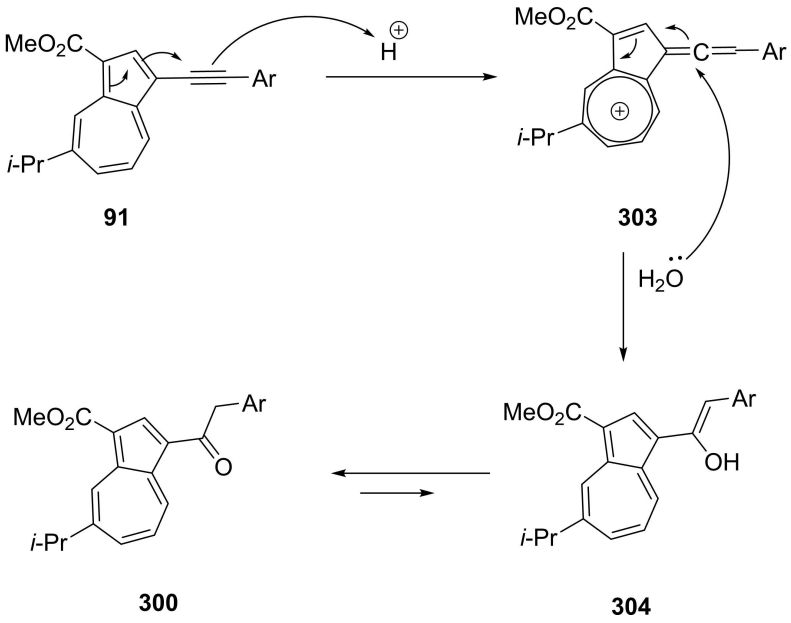
1-Ethynylazulenes connected to arylamine **144** or carbazole **146** cores have been prepared in 94% and 85% yields, respectively, *via* cross-coupling of 3,6-diiodo-9*H*-carbazole **143** and bis(4-iodophenyl)amine **145**, respectively, with methyl 3-ethynyl-7-isopropylazulene-1-carboxylate **13** using $Pd(PPh_3)_4$ as a catalyst (Scheme 31).[62]

The azobenzene derivatives **148a** and **148b** having two azulen-1-yl groups were prepared in 65% and 86% yields, respectively, by a similar cross-coupling reaction of 4,4-diethynylazobenzene **147** (DEABz) **147** with iodoazulenes **98d** and **98b**.[64] Compounds **148a** and **148b** could also be synthesized by copper-mediated oxidative homocoupling reaction of **91d** and **91h** in 86% and 77% yields, respectively (Scheme 32).[86]

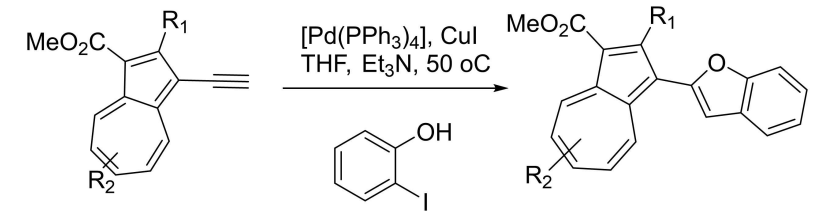
Kim *et al.* reported the synthesis of 5,15-bis(azulenylethynyl) substituted zinc(II) porphyrin **150** in 43% yield by Sonogashira coupling reactions of 5,15-diethynyl zinc(II) porphyrin **149** with 1-iodo-3-hexyloxycarbonylazulene (Figure 25).[87]

Insertion of additional phenylalkyne groups to the skeleton of **91** and **92** was employed by Sonogashira coupling of phenylacetylene with the appropriate iodo derivatives **100** and **101** to give azulene-substituted ethyne derivatives **151** and **152**, respectively (Scheme 33).[61]

Using the same methodology, azulene-substituted ethyne derivatives **153** and **154** could be obtained by Sonogashira coupling of iodo derivatives **100** and **101** with diethynylbenzene (Scheme 34).[61]



Scheme 71. A plausible mechanism for the formation of ketone **300**.

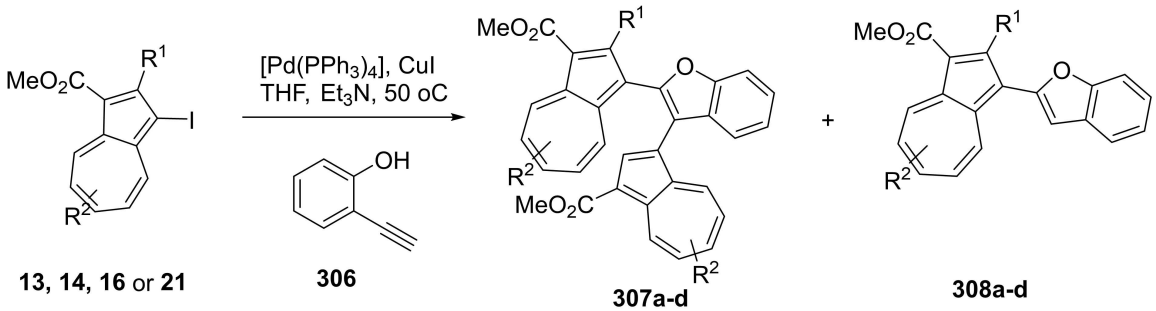


13, 14, 16 or **21**

305a-d

a, R^1 = H, R^2 = H, 65%
b, R^1 = H, R^2 = 7-isopropyl, 55%
c, R^1 = H, R^2 = 6-isopropyl, 72%
d, R^1 = Me, R^2 = 7-isopropyl,31%

Scheme 72. Synthesis of azulene-substituted benzofurans **305a–d**.



13, 14, 16 or **21**

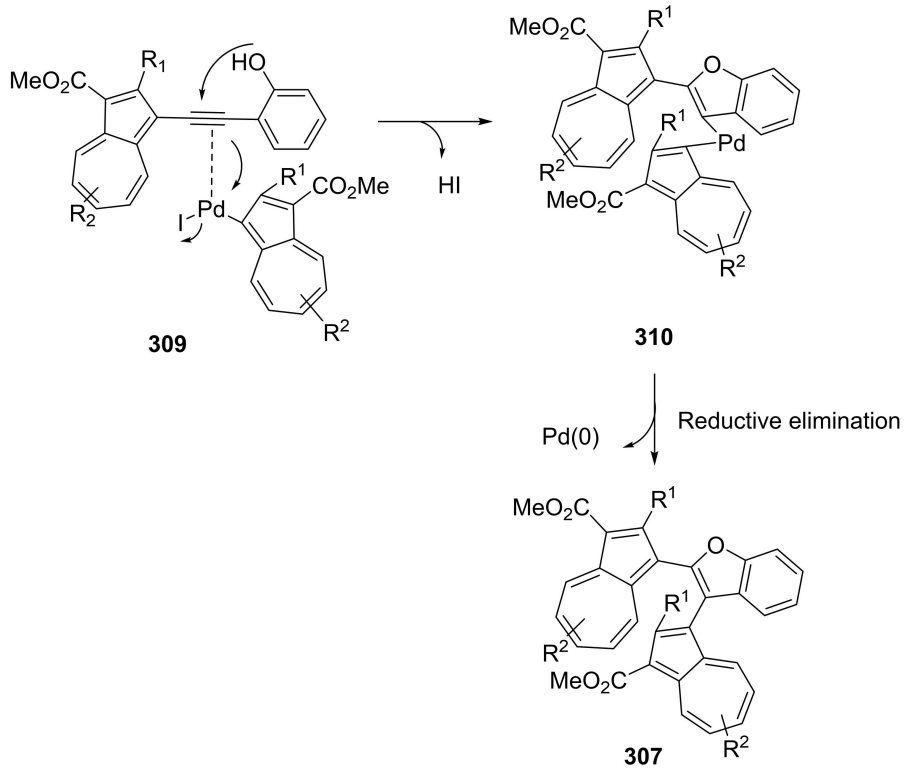
306

307a-d

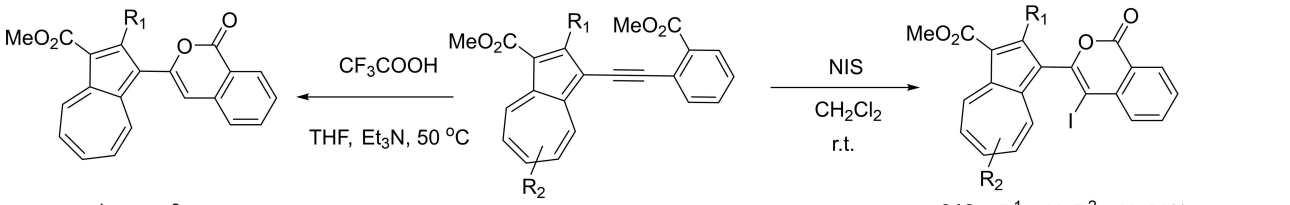
308a-d

a, R^1 = H, R^2 = H,	19%	10%
b, R^1 = H, R^2 = 7-isopropyl,	30%	30%
c, R^1 = H, R^2 = 6-isopropyl,	27%	13%
d, R^1 = Me, R^2 = 7-isopropyl,	33%	23%

Scheme 73. Synthesis of 2-(1-azulenyl)benzofurans **307a–d** and **308a–d**.



Scheme 74. A plausible mechanism for the formation of 2,3-*bis*(1-azulenyl)benzofuran derivatives **307**.



311a, R^1 = H, R^2 = H, 80%
311b, R^1 = H, R^2 = 7-isopropyl, 68%
311c, R^1 = H, R^2 = 6-isopropyl,79%
311d, R^1 = Me, R^2 = 7-isopropyl, 95%

312a, R^1 = H, R^2 = H, 36%
312b, R^1 = H, R^2 = 7-isopropyl, 46%
312c, R^1 = H, R^2 = 6-isopropyl, 57%
312d, R^1 = Me, R^2 = 7-isopropyl,42%

Scheme 75. Synthesis of 1-azulenylisocoumarin derivatives **311a–d** and **312a–d**.

3.4.4.2. From 6-ethynylazulene

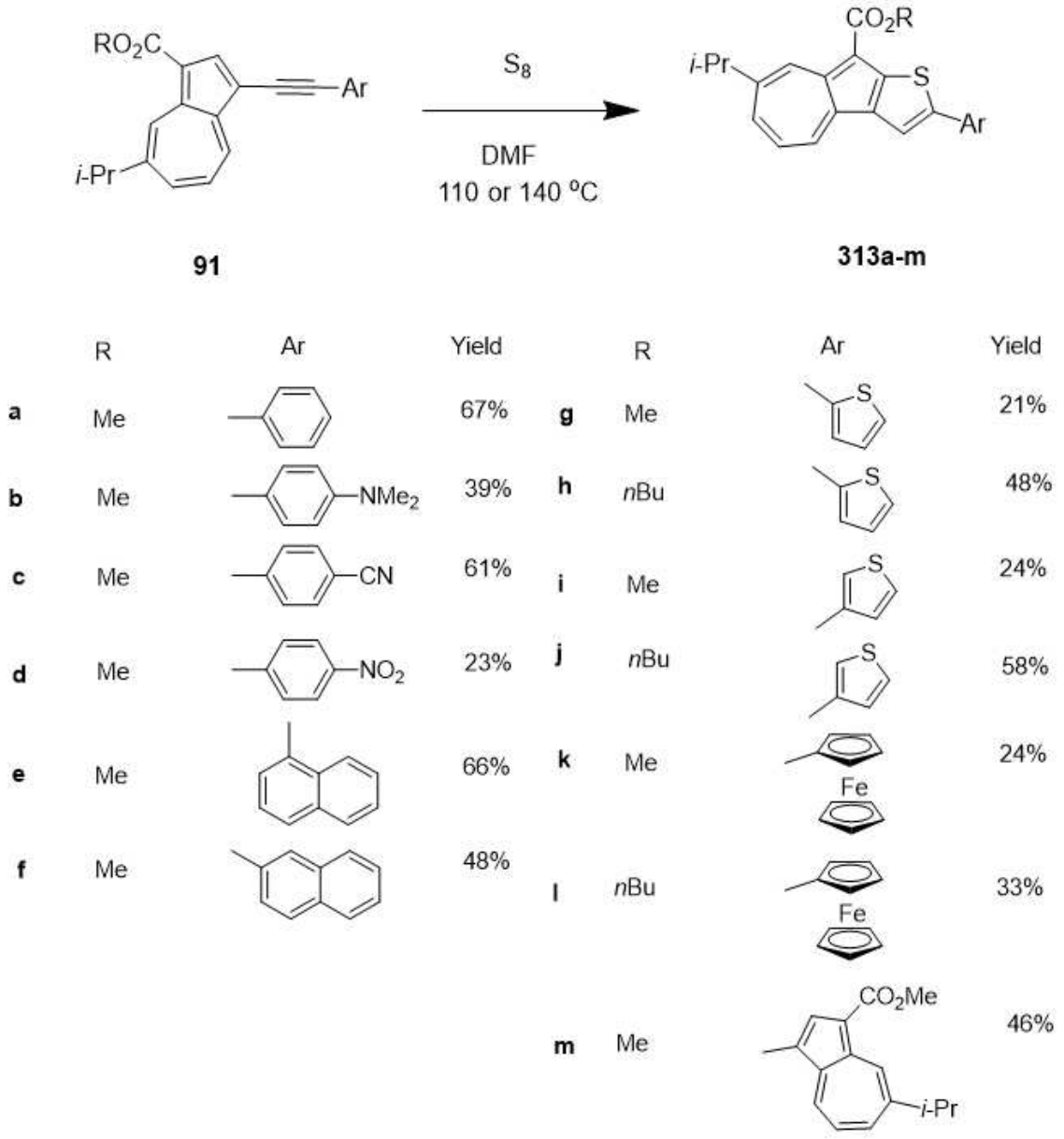
Likewise, diazulen-6-ylethynylbenzenes **155a,b** can also be prepared in 25 and 43% yields, respectively, by the Pd catalyzed cross coupling reaction of of the appropriate 6-ethynylazulene with 1,4-diiodobenzene (Figure 26).[40]

Similarly, preparation of bis(6-azulenylethynyl)thiophene **159**, terthiophene **160**, and dithienothiophene **161** was accomplished by the palladium-catalyzed cross-coupling reaction of 6-ethynylazulene **44** with the corresponding diiodides **156**–**158**, respectively, under Sonogashira-Hagihara conditions (Scheme 35).[38] The absorption band of these compounds in their UV/Vis spectra spreads into the near-infrared region due to the decrement of HOMO-LUMO energy gap basis on the expansion of the π-conjugated system.[88]

Furthermore, Xin *et al.* reported the synthesis of 1,4,5,8-naphthalenediimide (NDI) end capped with 6-ethynylazulene units **163** by the palladium-catalyzed cross-coupling reaction of 6-ethynylazulene **44b** with 4,9-dibromo-2,7-bis(2-octyldodecyl) benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone **162**, under Sonogashira-Hagihara conditions (Scheme 36).[89]

5,15-Bis(azulenylethynyl) substituted zinc(II) porphyrin **164** was obtained in 87% yield by Sonogashira coupling reactions of 5,15-diethynyl zinc(II) porphyrin **149** with 6-bromo-1,3-dihexyloxycarbonylazulene (Figure 27).[87]

Porphyrin **166** was prepared in overall 87% yield from the partially silylated intermediate **165**, which was prepared from **149** upon treatment with triisopropylsilyl chloride (TIPSCl) in the presence of lithium bis(trimethylsilyl)amide and pyridine. Thus, Sonogashira coupling reaction of **165** with 1-iodo-3-hexyloxycarbonylazulene followed by desilylation and subse-



Scheme 76. Synthesis of azuleno[2,1-b]thiophenes **313a–m**.

quent coupling with 6-bromo-1,3-dihexyloxycarbonylazulene afforded **166** in overa 87% yield (Figure 28).[87] Intramolecular charge transfer in 5,15-bis(azulenylethynyl) substituted zinc(II) porphyrin leads to a significant enhancement of two-photon absorption at near-IR region, which has been investigated by femtosecond *Z*-scan method.

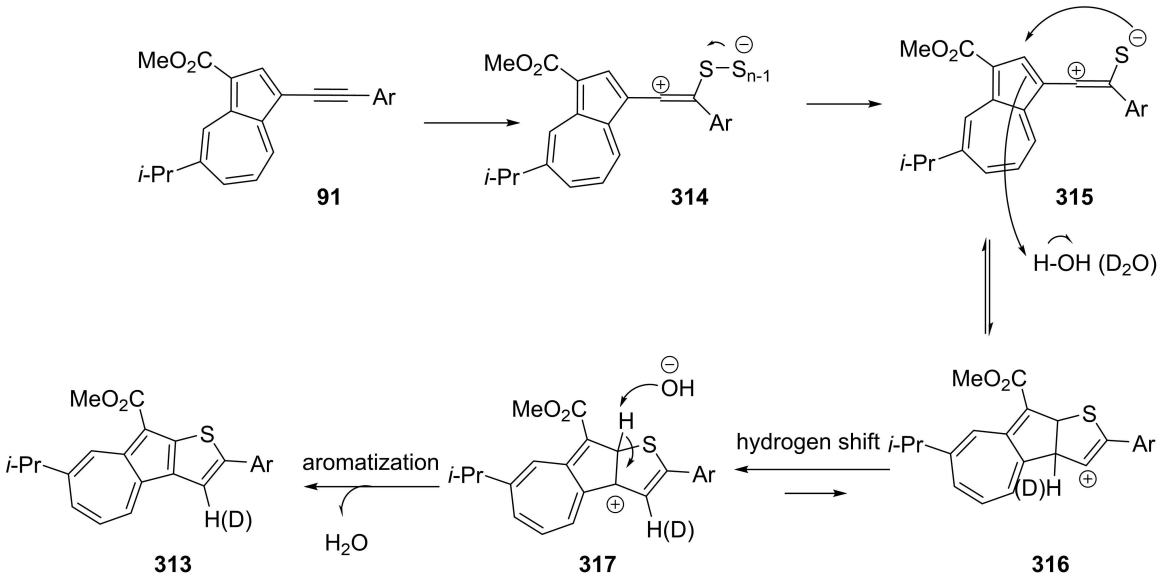
3.4.4.3. From 2-ethynylazulene

Using a similar approach, the same group reported the synthesis of 1,4,5,8-naphthalenediimide (NDI) end-capped with 2-ethynylazulene units **167** in 65% yield by the palladium-catalyzed cross-coupling reaction of 2-ethynylazulene **29** with **162** (Scheme 37). It is interesting that these two compounds show remarkably different physicochemical properties, thermal stabilities and organic field-effect transistors (OFET) performance resulting from the different connections of an electron-rich five-membered ring and an electron-poor seven-membered ring.[89]

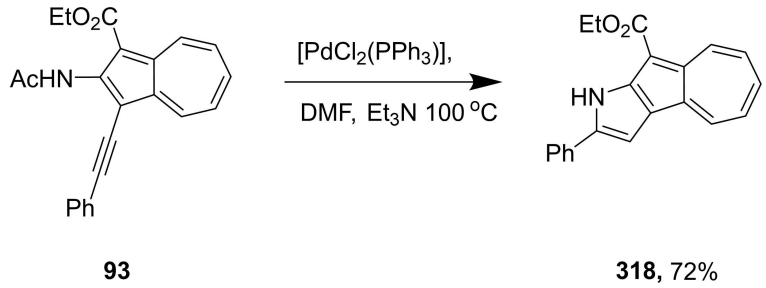
3.4.5. Synthesis of star-shaped azulenylethynylbenzene and azulenylethynylthiophene

3.4.5.1. From 1-ethynyl(halo)azulene

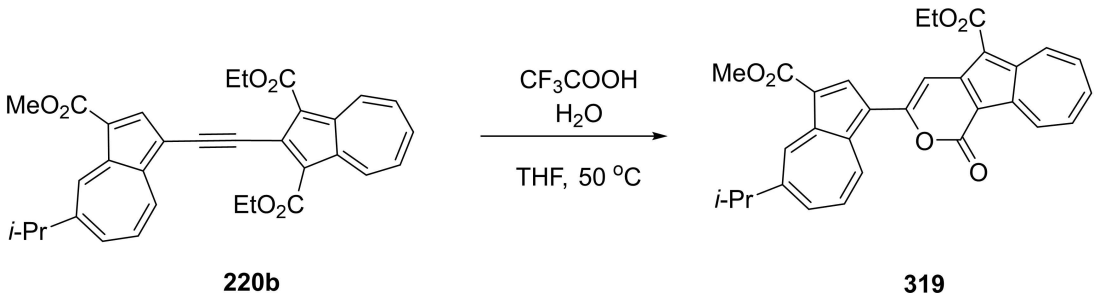
Elwahy and Hafner used Sonogashira coupling method in the synthesis of benzene- and thiophene-bridged polyalkynylazulenes. The synthesis of poly(azulen-1-ylethynyl) benzene deriva-



Scheme 77. A plausible mechanism for the formation of azuleno [2,1-*b*]thiophene derivatives **313**.



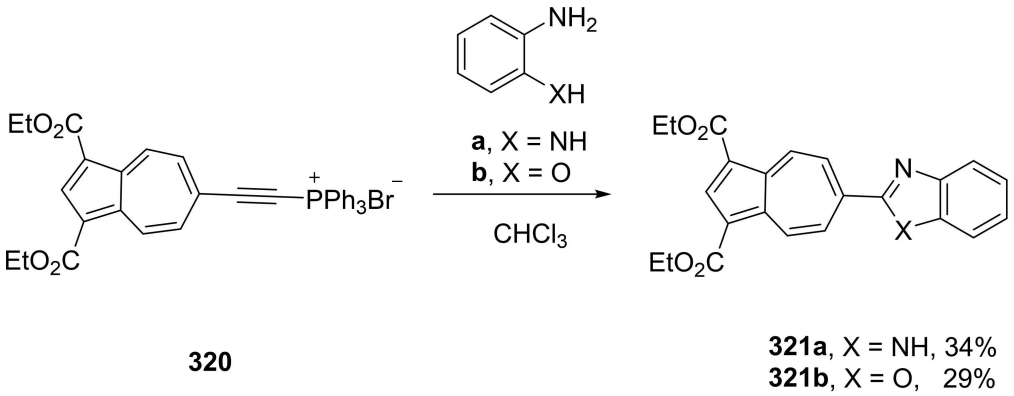
Scheme 78. Synthesis of pyrrole-fused azulene derivative **318**.



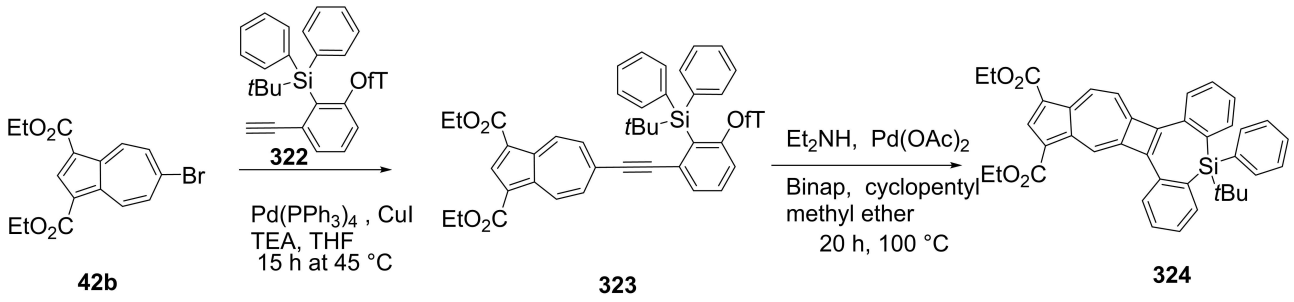
Scheme 79. Synthesis of ethyl 3-(5-isopropyl-3-(methoxycarbonyl)azulen-1-yl)-1-oxo-1*H*-azuleno[1,2-c]pyran-5-carboxylate **319**.

tives **168**–**170** was performed in 22–44% yields by coupling of the appropriate polyhalobenzene with the corresponding equivalents of 1-ethynylazulene **4b** in the presence of bis (triphenylphosphine)palladium chloride and CuI in triethylamine (TEA).[90] The isolation of the pentakis(azulen-1-ylethynyl)-benzene **170** from the coupling reaction of **4b** with hexaiodobenzene[91] instead of the expected hexakis analogue may be as a result of a competitive reductive deiodonation of one iodosubstituent of hexaiodobenzene.[92] Similarly, tetrakis(1-azulenylethynyl)thiophene **171** can be prepared in 75% yield by Pd-catalyzed alkynylation of tetraiodothiophene[93] with ethynylazulene **4b** (Figure 29).[83] 6-*tert*-Butyl-1-ethynylazulene (**4b**) was chosen as a starting material to secure the solubility of the products.

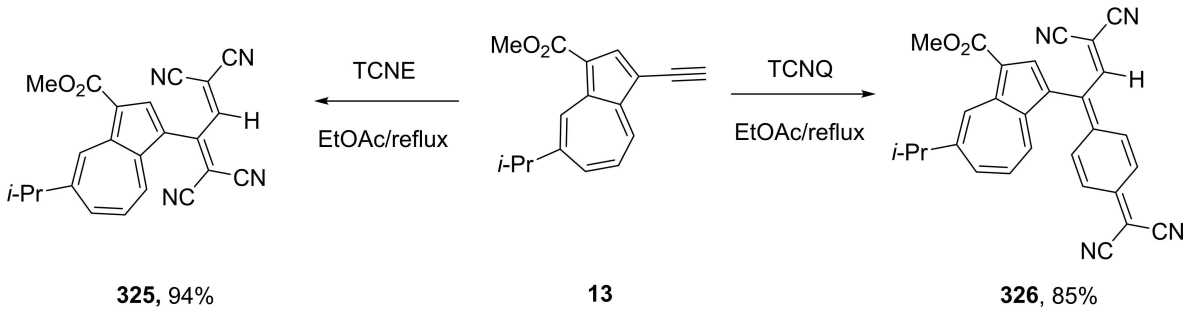
This procedure has been utilized by Ito *et al* to synthesize poly(azulenylethynyl)arene derivatives **173** and **174**. Tris (azulenylethynyl)benzene was obtained by the reaction of 1-iodoazulene with the corresponding tris(ethynyl)benzene **172**. On the other hand, tetrakis(azulenylethynyl)benzene **174** was obtained by the inverse cross-coupling Pd-catalyzed alkynylation of tetraiodobenzene with ethynylazulene (Figure 30).[23]



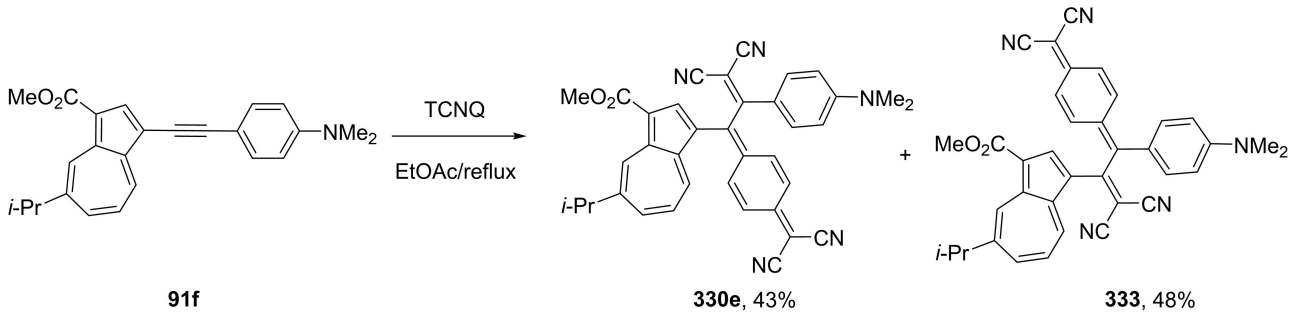
Scheme 80. Synthesis of 2-[1,3-bis(ethoxycarbonyl)azulen-6-yl]benzoazoles **321 a** and **321 b**.



Scheme 81. Synthesis of 5*H*-azuleno[5′,6′:3,4]cyclobuta[1,2-*d*]dibenzo[*b*,*f*]silepine **324**.

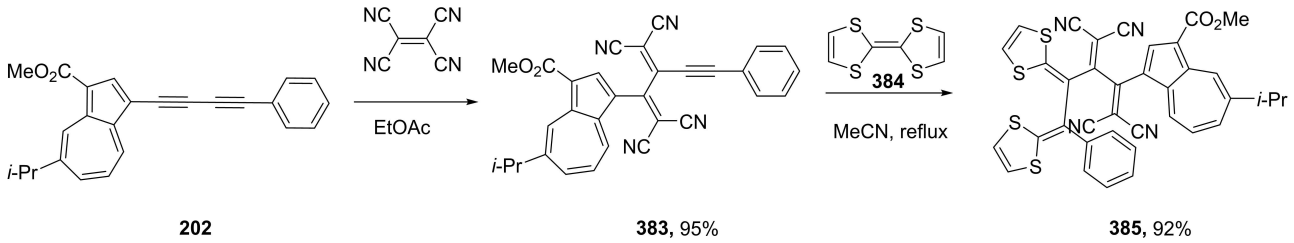


Scheme 82. Reaction of ethynylazulene **13** with (TCNE) and (TCNQ).



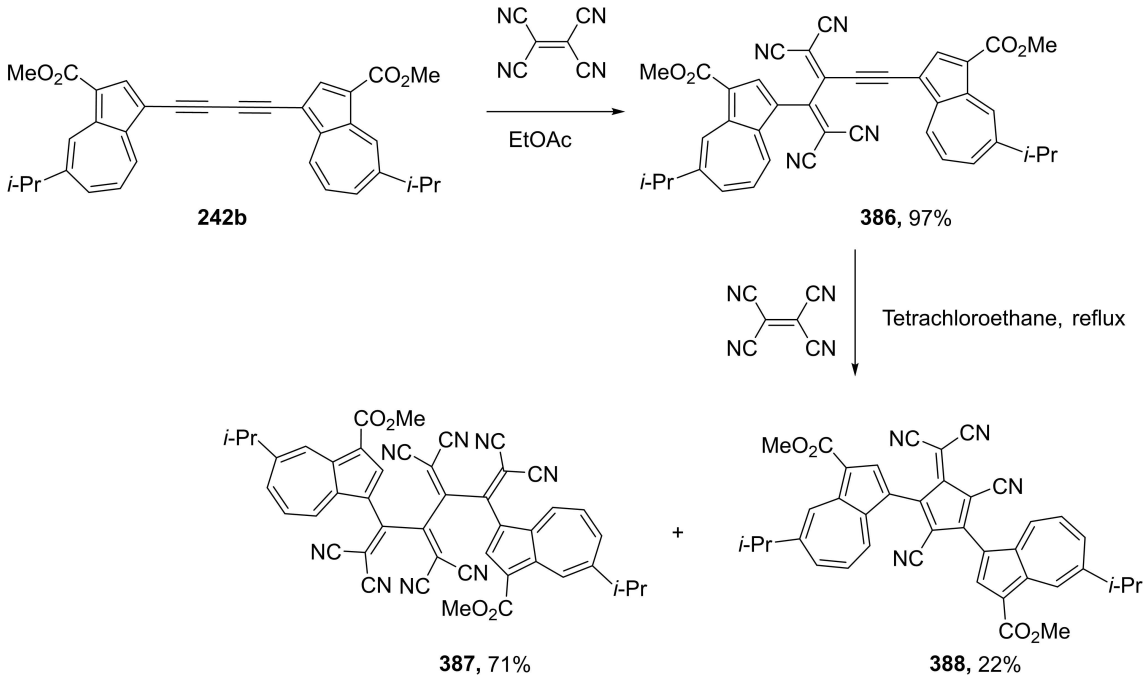
Scheme 83. Synthesis of compounds **330 e** and **333** from the reaction of **91 f** with TCNQ.

Following a similar methodology, Shoji *et al.* reported also the synthesis of 1-ethynylazulenes connected to pyrene **175**, hexaphenylbenzene **176**, hexabenzocoronene **177** cores (Figure 31).[72,94]



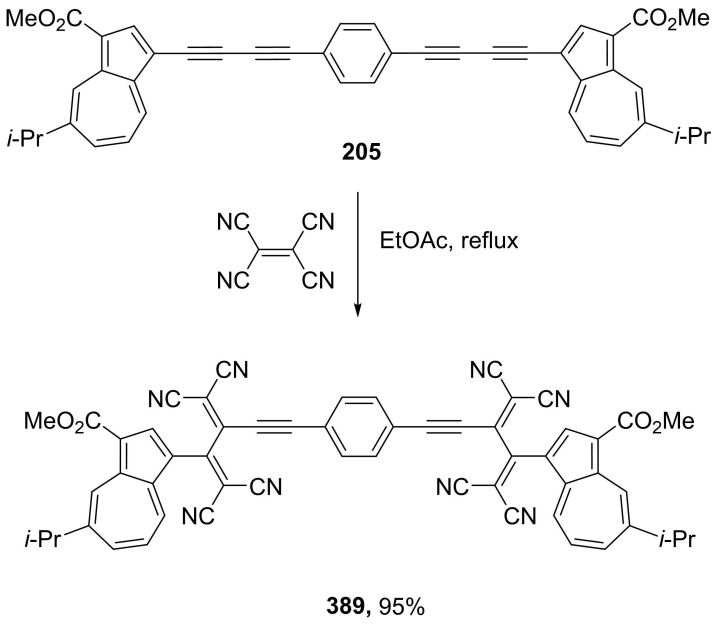
202 **383,** 95% **385,** 92%

Scheme 84. Synthesis of compound **385** by the subsequent reaction of **202** with TCNE and TTF.



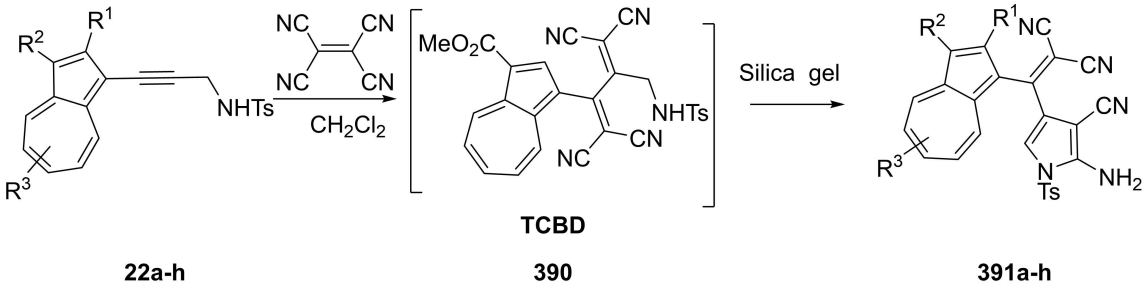
242b **386,** 97% **387,** 71% **388,** 22%

Scheme 85. Reaction of butadiyne **242 b** with TCNE.



205 **389,** 95%

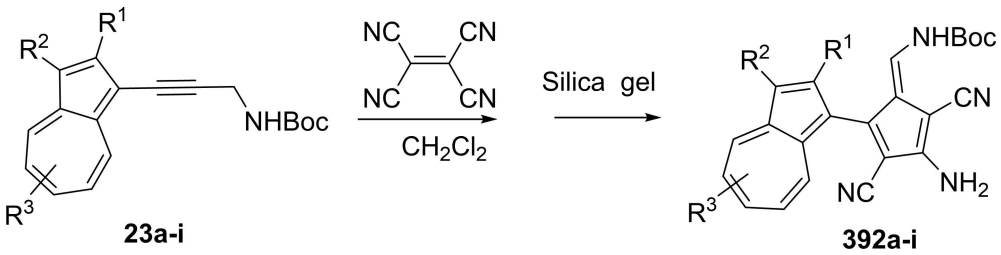
Scheme 86. Reaction of 1,4-bis(azulen-1-ylbuta-1,3-diyn-1-yl)benzene **205** with TCNE.



22a-h **390** **TCBD** **391a-h**

a, R^1 = H, R^2 = CO_2Me, R^3 = H, 76%
b, R^1 = H, R^2 = CO_2Me, R^3 = 7-*iso*propyl, 83%
c, R^1 = H, R^2 = CO_2Me, R^3 = 6-*iso*propyl, 79%
d, R^1 = Me, R^2 = CO_2Me, R^3 = 7-*iso*propyl, 80%
e, R^1 = H, R^2 = CHO, R^3 = 6-*t*Bu, 82%
f, R^1 = $COCF_3$, R^2 = H, R^3 = 6-*t*Bu, 85%
g, R^1 = COMe, R^2 = H, R^3 = 5-*iso*propyl, 86%
h, R^1 = Ph, R^2 = H, R^3 = 5-*iso*propyl, 98%

Scheme 87. Synthesis of 2-((1*H*-pyrrol-3-yl)(azulen-1-yl)methylene)malononitrile **391**.



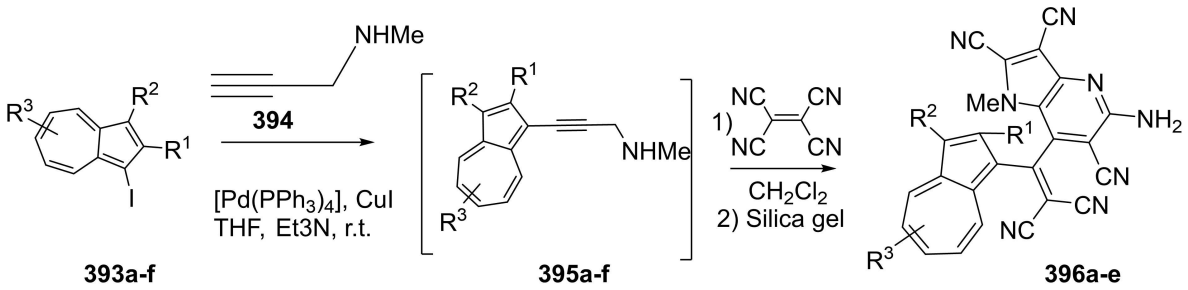
23a-i **392a-i**

a, R^1 = H, R^2 = CO_2Me, R^3 = H, 86%
b, R^1 = H, R^2 = CO_2Me, R^3 = 7-*iso*propyl, 83%
c, R^1 = H, R^2 = CO_2Me, R^3 = 6-*iso*propyl, 83%
d, R^1 = Me, R^2 = CO_2Me, R^3 = 7-*iso*propyl, 61%
e, R^1 = H, R^2 = CHO, R^3 = H, 82%
f, R^1 = H, R^2 = $COCF_3$, R^3 = 6-*t*Bu, 87%
g, R^1 = H, R^2 = COMe, R^3 = 5-*iso*propyl, 81%
h, R^1 = H, R^2 = Et, R^3 = 5-*iso*propyl, 64%
i, R^1 = H, R^2 = Ph, R^3 = 5-*iso*propyl, 50%

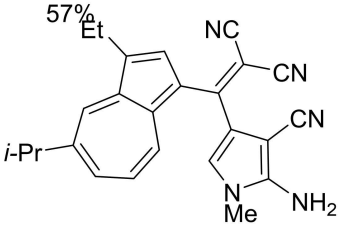
Scheme 88. Synthesis of ((5-(azulen-1-yl)-2,4-dicyanocyclopenta-2,4-dien-1-ylidene)methyl)carbamates **392a–i**.

1-Ethynylazulenes connected to triphenylamine core have also been reported. Thus, Shoji *et al.* reported the synthesis of trimethyl 3,3′,3″-((nitrilotris(benzene-4,1-diyl))tris(ethyne-2,1-diyl))tris(7-isopropylazulene-1-carboxylate) **179** in 90% yield[62] by the cross-coupling reaction of tris(4-iodophenyl)amine **178**[95] with methyl 3-ethynyl-7-isopropylazulene-1-carboxylate **13** in the presence of catalytic palladium (Scheme 38).

Moreover, Hafner and Elwahy[90] reported on the peripheral extention of the skeleton of **168** by insertion of additional azulenylalkyne groups. Thus, the new tripodal polyynes **180**, **181**, **183** and **184** were synthesized as shown in scheme 28. 1,3,5-Triethynylbenzene (**172**)[96] underwent Pd/Cu-catalyzed cross coupling reaction with 6-*tert*-butyl-1-iodo-3-trimethylsilylethynylazulene (**10**) in TEA at room temperature to afford a 53% yield of **180** as green crystals. Desilylation of the latter compound with KOH in methanol furnished the core molecule **181** in almost quantitative yield. Subsequent catalytic cross coupling reaction of **181** with **10** as well as with 1-(6-*tert*-butyl-3-iodoazulene-1-yl)-2-(6-*tert*-butyl-3-trimethylsilylethynylazulen-1-yl)ethyne (**182**) led to the formation of the corresponding tripodal polyynes **183** (36%) and **184** (29%), respectively (Scheme 39). The electronic absorption spectra of the polyynes **180**, **184**, and **184** exhibit an increase in the absorption maxima from 602 nm for **180** to 625 nm for **183** and 631 nm for **184**.



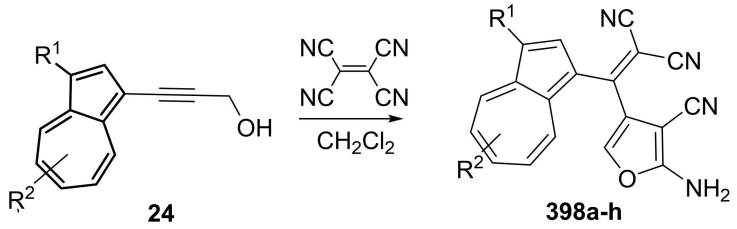
a, R^1 = H, R^2 = CO_2Me, R^3 = H, 53%
b, R^1 = H, R^2 = CO_2Me, R^3 = 7-*iso*propyl, 56%
c, R^1 = H, R^2 = CO_2Me, R^3 = 6-*iso*propyl, 46%
d, R^1 = Me, R^2 = CO_2Me, R^3 = 7-*iso*propyl,28%
e, R^1 = H, R^2 = COMe, R^3 = 5-*iso*propyl, 57%



397, 48%

From **393f**, R^1 = Me, R^2 = CO_2Me, R^3 = 7-*iso*propyl

Scheme 89. Synthesis of 7-(1-(azulen-1-yl)-2,2-dicyanovinyl)-1*H*-pyrrolo[3,2-*b*]pyridines **396a–e**.

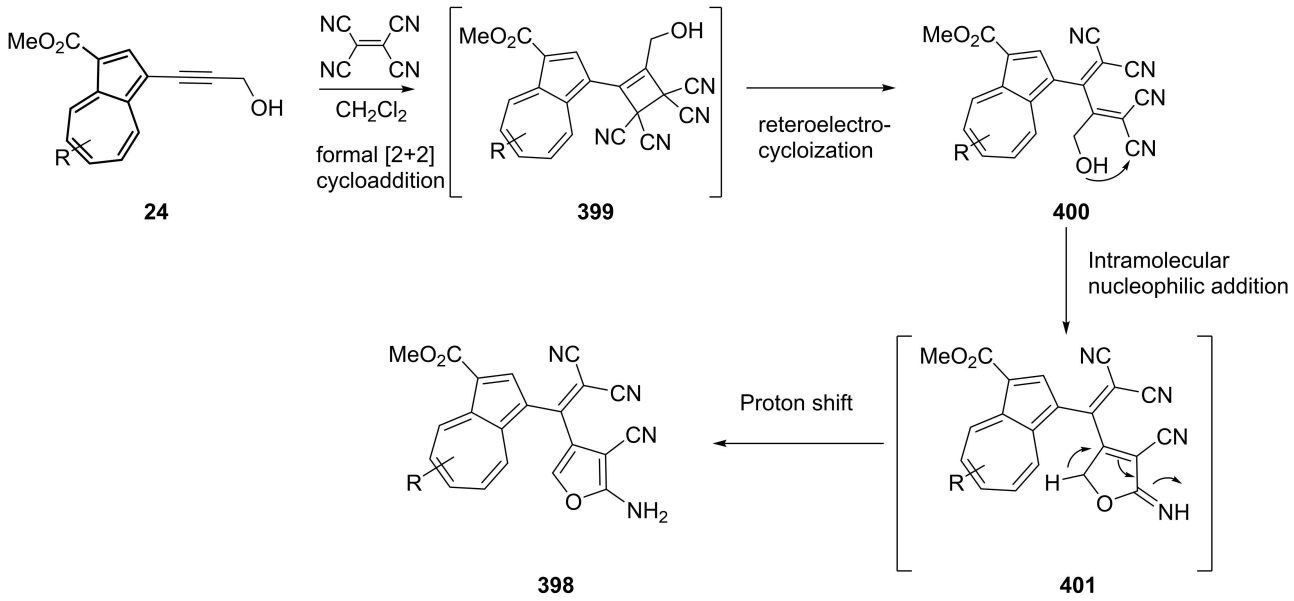


a, R^1 = CO_2Me, R^2 = 7-*iso*propyl, 77%
b, R^1 = CO_2Me, R^2 = 6-*iso*propyl, 79%
c, R^1 = COMe, R^2 = H, 60%
d, R^1 = CN, R^2 = H, 70%
e, R^1 = Cl, R^2, H, 99%
f, R^1 = Ph, R^2 = 5-*iso*propyl, 71%
g, R^1 = Me, R^2, 5-*iso*propyl, 61%
h, R^1 = Et, R^2, 5-*iso*propyl, 77%

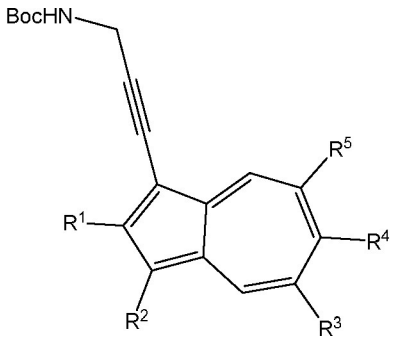
Scheme 90. Synthesis of 2-((furan-3-yl)(azulen-1-yl)methylene)malononitrile **398a–h**.

Ito *et al.* has also synthesized tris- and tetrakis[(1-azulenylethynyl)phenylethynyl- and (1-azulenylethynyl)-2-thienylethynyl] benzenes **185**–**188** in 74–85% yield from the appropriate iodo derivatives *via* Sonogashira coupling with the corresonding polyalkynylbenzenes (Figure 32).[61]

1,3,5-Tris(3-ethynyl-5-isopropylazulen-1-yl)benzene **192** was prepared as outlined in scheme 2. Thus, 1,3,5-tris(5-isopropyl-3-methoxycarbonyl-1-azulenyl)benzene (**189**), obtained in 56% yield by trimerization of methyl 3-acetyl-7-isopropylazulene-1-carboxylate with excess thionyl chloride ($SOCl_2$) in ethanol at



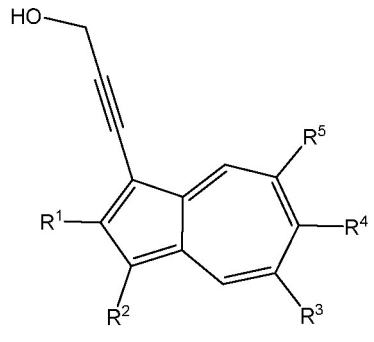
Scheme 91. Presumed reaction mechanism for the reaction of 3-(1-azulenyl)-2-propyn-1-ols **24** with TCNE.



23a-i

Entry	R^1	R^2	R^3	R^4	R^5	Yield [%]
a	H	CO_2Me	H	H	H	93
b	H	CO_2Me	*i*-Pr	H	H	95
c	H	CO_2Me	H	*i*-Pr	H	97
d	Me	CO_2Me	*i*-Pr	H	H	80
e	H	CHO	H	H	H	84
f	H	$COCF_3$	H	*t*Bu	H	87
g	H	COMe	H	H	*i*-Pr	95
h	H	Et	H	H	*i*-Pr	52
i	H	Ph	H	H	*i*-Pr	74

Figure 5. Structures of some *tert*-butyl (3-(azulen-1-yl)prop-2-yn-1-yl) carbamate derivatives **23a–j**.



24a-j

Entry	R^1	R^2	R^3	R^4	R^5	Yield [%]
a	H	CO_2Me	H	H	H	92
b	H	CO_2Me	*i*-Pr	H	H	95
c	H	CO_2Me	H	*i*-Pr	H	88
d	Me	CO_2Me	*i*-Pr	H	H	83
e	H	COMe	H	H	H	99
f	H	CN	H	H	H	53
g	H	Cl	H	H	H	62
h	H	Ph	H	H	*i*-Pr	53
i	H	Me	H	H	*i*-Pr	39
j	H	Et	H	H	*i*-Pr	61

Figure 6. Structures of some 3-(azulen-1-yl)prop-2-yn-1-ol derivatives **24a–j**.

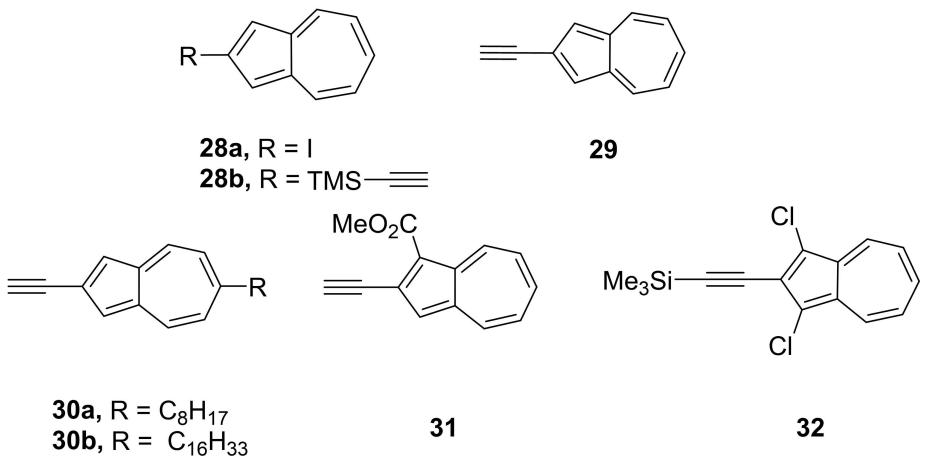


Figure 7. Structures of some 2-ethynylazulene derivatives **28**–**32**.

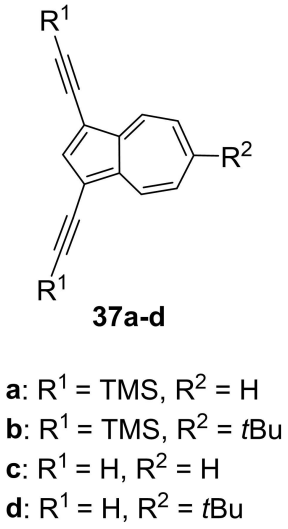


Figure 8. Structures of some 1,3-diethynylazulenes **37a**–**d**.

room temperature, underwent removal of the three ester functions by heating in 100% H_3PO_4 to give **190**. Subsequent iodination of **190** with *N*-iodosuccinimide (NIS) at 0 °C in excellent yield afforded **191** in 90% yield. The reaction of **191** with trimethylsilylacetylene in the presence of $[Pd(PPh_3)_4]$ as a catalyst at 50 °C gave the protected alkyne derivative in 94% yield followed by desilylation upon treatment with KOH in *i*PrOH at reflux to afford **192** in 92% yield (Scheme 40).[97]

The tris(3-iodo-1-azulenyl)benzene **191** was succefully utilized as a precursor for tris(1-arylacetylene) **193** and tris(1-azulenylacetylene) chromophores **194** and **195** each connected to a 1,3,5-tri(1-azulenyl)benzene core. Thus, compounds **193**–**195** were prepared by the Sonogashira-Hagihara reaction of tris (3-iodo-1-azulenyl)benzene derivative **191** with the corresponding alkyne precursors in the presence of $[Pd(PPh_3)_4]$ as a catalyst in THF/triethylamine at 50 °C (Scheme 41).[25,97]

Tris(1-azulenylethynylarylacetylene) chromophores **196** and **197** connected to a 1,3,5-tri(1-azulenyl)benzene core were also prepared by simple Pd-catalyzed alkynylation of alkyne **192** with the appropriate iodo derivatives **100** and **101** under Sonogashira-Hagihara cross-coupling conditions. (Scheme 42).[97]

3.4.5.2. From 6-ethynyl(halo)azulene

Ito *et al.* synthesized poly(azulen-6-ylethynyl)arene derivatives **198**–**200**[40] *via* cross-coupling reactions of 6-bromoaloazulene

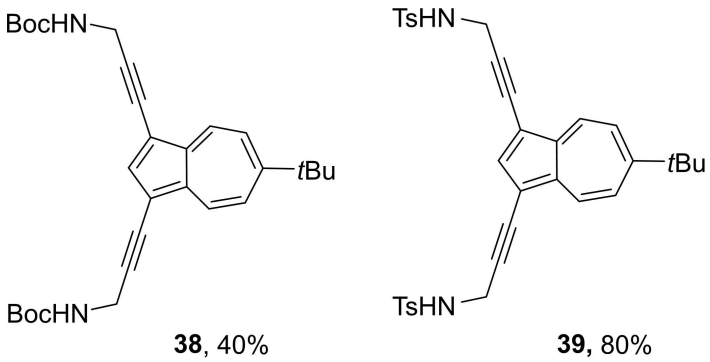
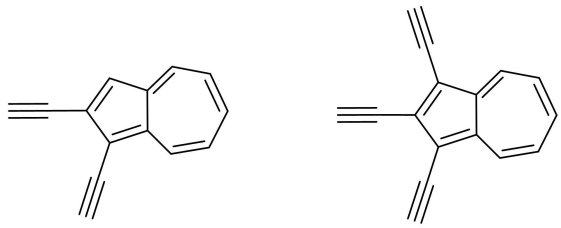


Figure 9. Structures of some 1,3-diethynylazulene derivatives **38** and **39**.



40 **41**

Figure 10. Structures of 1,2-di- and 1,2,3-triethynylazulenes **40** and **41**.

with the corresponding polyethynylbenzene (Figure 33). These compounds exemplify a principle for multielectron redox behavior and at the same time display liquid crystalline properties.[98]

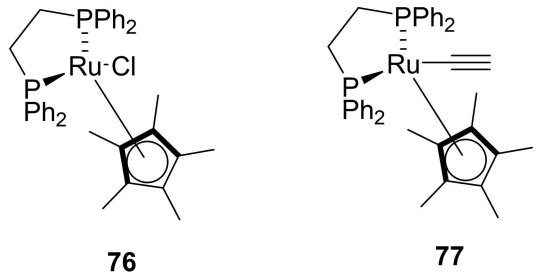
3.4.5.3. From 2-ethynyl(halo)azulene

Ito *et al* reported also the synthesis of hexakis(azulen-2-ylethynyl)benzene **201**[10b] *via* Pd-catalyzed alkynylation of hexa (iodo)benzene with the 2-ethynylazulene (Figure 34).

3.4.6. Synthesis of azulenyl-butadiinylbenzene

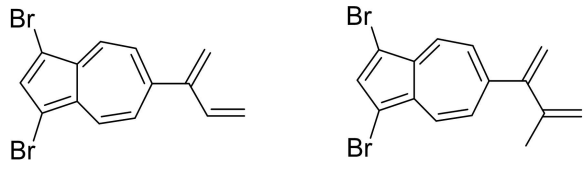
Azulene-substituted butadiene **202** was obtained by Cu-mediated Hay cross- and Glaser homo-coupling conditions.[99] Thus, cross-coupling reaction of methyl 7-isopropyl-3-ethynylazulene-1-carboxylate **13** with excess of ethynylbenzene, using CuI/tetramethylethylenediamine (TMEDA) as a catalyst, afforded **202** in 74% yield (Scheme 43).[100]

Butadiyne **203** was obtained in 76% yield by the reaction of **13** with 5 equiv. trimethylsilylacetylene. Deprotection of **203** with potassium carbonate solution generate the corresponding butadiyne **204**. The cross-coupling reaction of **204** with 1,4-diiodobenzene using $Pd(PPh_3)_4$ as a catalyst, afforded (1,4-



76 **77**

Figure 12. Structures of ruthenium-based Cp*(dppe)Ru ([Ru*]) metal complexes **76** and **77**.

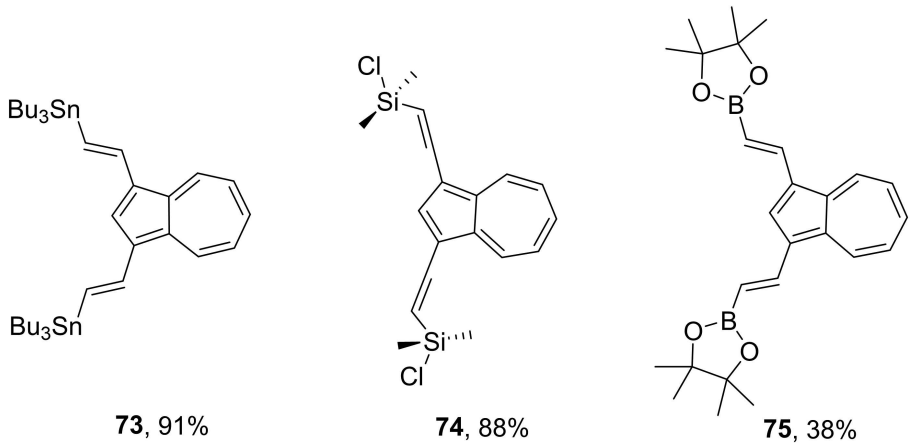


89, 46% **90**, 49%

Figure 13. Structures of azulene-dienes **89** and **90**.

phenylenebis(buta-1,3-diyne-4,1-diyl))*bis*(azulene) **205** in 87% yield (Scheme 44).[54]

Furthermore, the Eglinton[101] coupling of 1,3-diethynylazulene **37b** in the presence of phenylacetylene as end-capping reagent afforded butadiynylene-bridged compound **206a** in 58% yield. In addition to **206a**, higher oligomers **206b** and **206c** could also be isolated in 7 and 2% yields, respectively (Figure 35).[102]



73, 91% **74**, 88% **75**, 38%

Figure 11. Structures of *bis*(stannaylvinyl)-, *bis*(silylvinyl)- and *bis*(borylvinyl)azulenes.

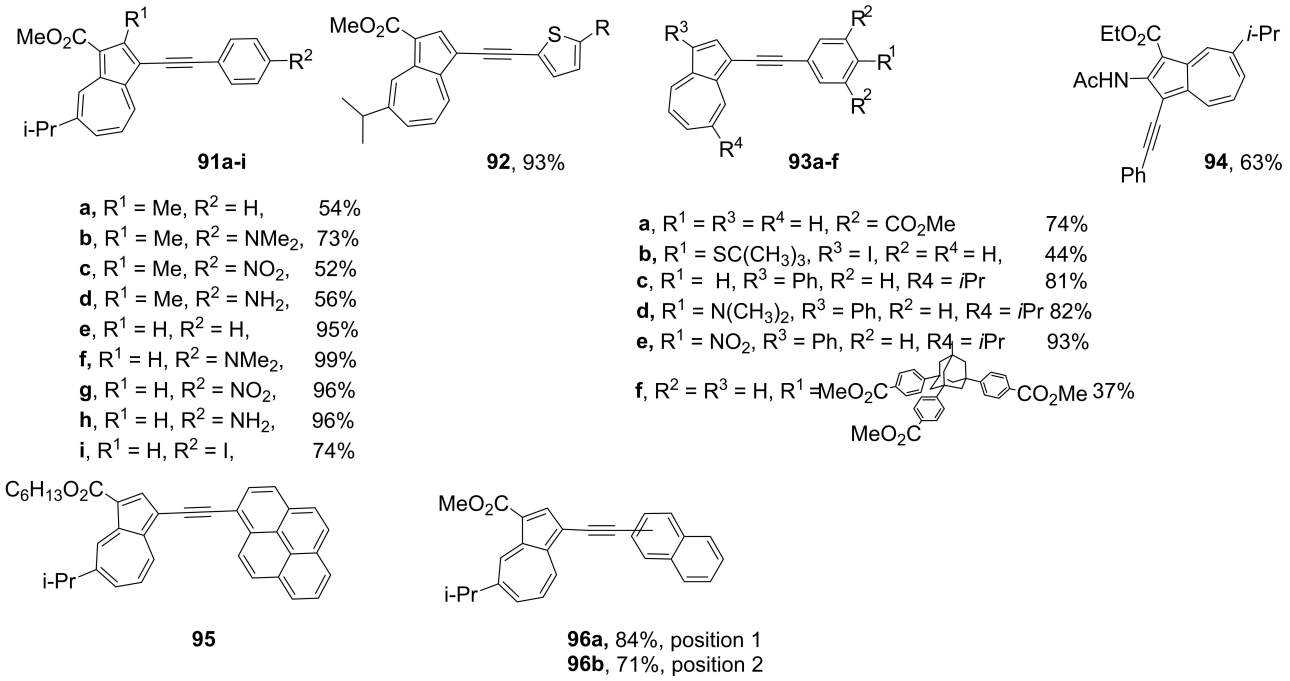


Figure 14. Structures of some arylethynylazulenes **91**–**96**.

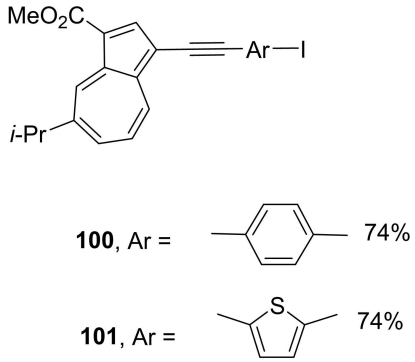


Figure 15. Structures of iodophenylethynylazulene **100** and (5-iodo-2-thienyl)ethynyl]azulene **101**.

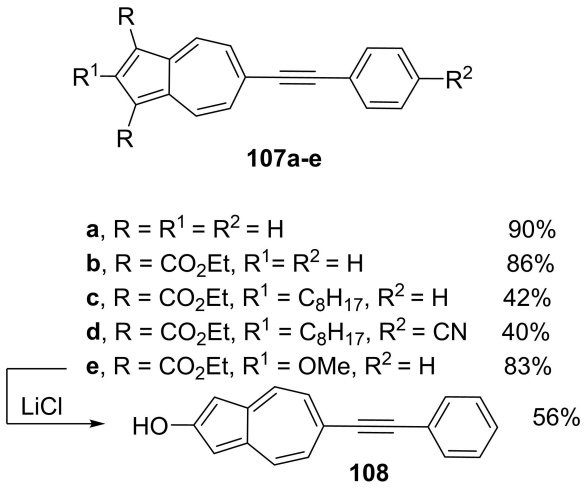


Figure 16. Structures of some arylethynylazulene **107a**–**e** and **108**.

3.5. Synthesis of oligoazulenes

3.5.1. Bis-azulenes with ethynyl bridges

3.5.1.1. Bis(azulen-1-yl)ethynes

After the successful synthesis of arylethynylazulenes by Sonogashira coupling reaction, the same methodology has been applied to the synthesis of oligoazulenes with ethynyl bridges. Thus, Hafner *et al.* reported the synthesis of the bis(azulen-1-yl) ethynes **207a** and **207b** in 40% and 32% yields, respectively, by Sonogashira coupling of the deprotected 1-ethynylazulenes **4a** and **4b** with 1-iodoazulenes **5a** and **5b** (Scheme 45).[17]

Similarly, *bis*(azulenyl)acetylenes **208**–**210** could be obtained by Pd-catalyzed coupling of the appropriate ethynylazulene with the corresponding iodoazulenes (Figure 36).[17,20,23–25,64]

3.5.1.2. (Cyclohepta[b]*furan-3-yl)ethynylazulene*

The Sonogashira-Hagihara reaction of methyl 3-ethynyl-7-isopropylazulene-1-carboxylate **13** with 3-iodo-5-isopropyl-2*H*-

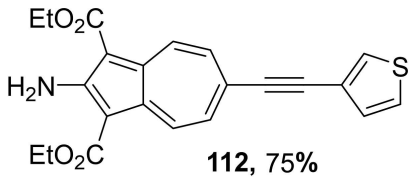
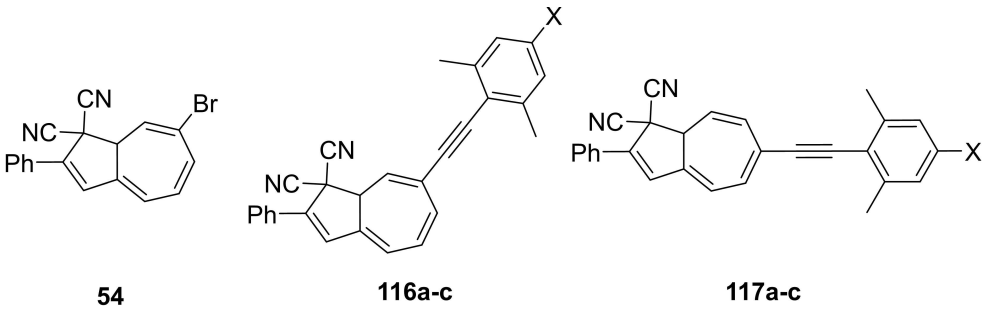
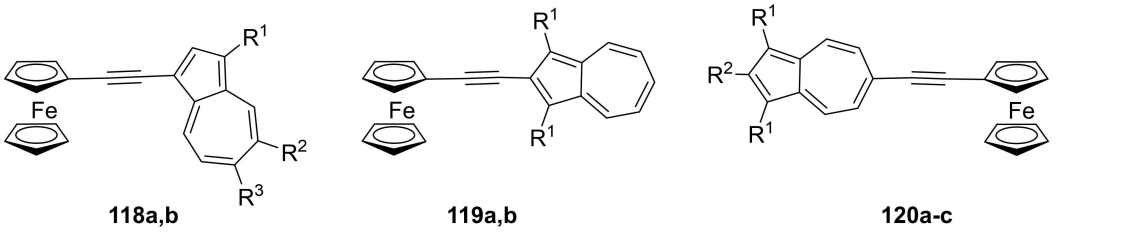


Figure 17. Structure of diethyl 2-amino-6-[(thiophen-3-yl)ethynyl]azulene-1,3-dicarboxylate **112**.



a, X = H 36%
b, X = NH_2 50%
c, X = NO_2 20%

Figure 18. Structures of 7-arylethynyldihydroazulenes **116a–c** and 6-arylethynyldihydroazulenes **117a–c**.



a, R^1 = H, R^2 = H, 99%
b, R^1 = CO_2Et, R^2 = H, 97%
c, R^1 = CO_2Et, R^2 = NH_2, 95%

a, R^1 = H, X = I, 96%
b, R^1 = CO_2Et, X = Cl, 92%

a, R^1 = R^3 = *t*Bu, R^2 = H, 92%
b, R^1 = CO_2Me, R^2 = *i*Pr, R^3 = H, 96%

Figure 19. Structures of some (ferrocenylethynyl)azulenes **118**–**120**.

cyclohepta[*b*]furan-2-one **211** gave methyl 7-isopropyl-3-((5-isopropyl-2-oxo-2H-cyclohepta[*b*]furan-3-yl)ethynyl)azulene-1-carboxylate **212** in 91% yield (Scheme 46).[103]

6-(*tert*-Butyl)-1-((6-(*tert*-butyl)azulen-1-yl)ethynyl)-3-ethynylazulene **213** was prepared by a Pd/Cu-catalyzed cross-coupling reaction of 6-*tert*-butyl-1-trimethylsilylethynyl-3-iodoazulene **10** with 6-*tert*-butyl-1-ethynylazulene **4b** and subsequent desilylation with methanolic potassium hydroxide (Figure 37).[17]

3.5.1.3. Bis(azulen-2-yl)ethynes

Di-2-azulenylacetylenes **214a–d** were obtained by the Pd-catalyzed cross-coupling reaction of the appropriate 2-iodoazulenes with the corresponding 2-ethynylazulenes (Figure 38).[33–35]

Di-2-azulenylacetylene **218** was alternatively prepared starting from azulene-2-carbaldehyde (**33**).[29] Thus, benzoin condensation reaction of **33** in the presence of potassium cyanide afforded **215** which underwent subsequent oxidation with activated manganese-(IV) oxide to give the di-2-azulenylethanedione (**216**) in 77% overall yield. The reaction of **216** with hydrazine monohydrate in ethanol at reflux afforded the dihydrazone **217** in 92% yield. Treatment of **217** with copper(II) acetate in a mixture of methanol and dichloromethane afforded the desired **218** in 76% yield (Scheme 47).[35,38]

3.5.1.4. Bis(azulen-6-yl)ethynes

The cross coupling reaction of the 6-bromoazulenes with the corresponding 6-ethynylazulenes utilizing $Pd(PPh_3)_4$ as a catalyst exclusively gave the desired *bis*(azulen-6-yl)ethynes **219a** and **219b** in 98 and 96% yields, respectively (Scheme 39).[42]

3.5.1.5. (1-Azulenyl)(2-azulenyl)acetylene

(1-Azulenyl)(2-azulenyl)acetylene **220a** was obtained in 99% yield by the cross coupling reaction[104] of **13** with 2-iodoazulene **97b**[35] in the presence of $Pd(PPh_3)_4$ as a catalyst in THF/Et_3N at 50 °C. The reaction of diethyl 2-chloroazulene-1,3-dicarboxylate (**109**)[32] with 1-ethynylazulene **13** under similar reaction conditions afforded **220b**[104] in 92% yield (Figure 39). Although azulenyl chlorides are usually less reactive toward the palladium catalyzed cross-coupling reaction than azulenyl iodides and bromides,[105] high yield of the product **220b** was attributable to both the high reactivity of 1-ethynylazulene and the electro-

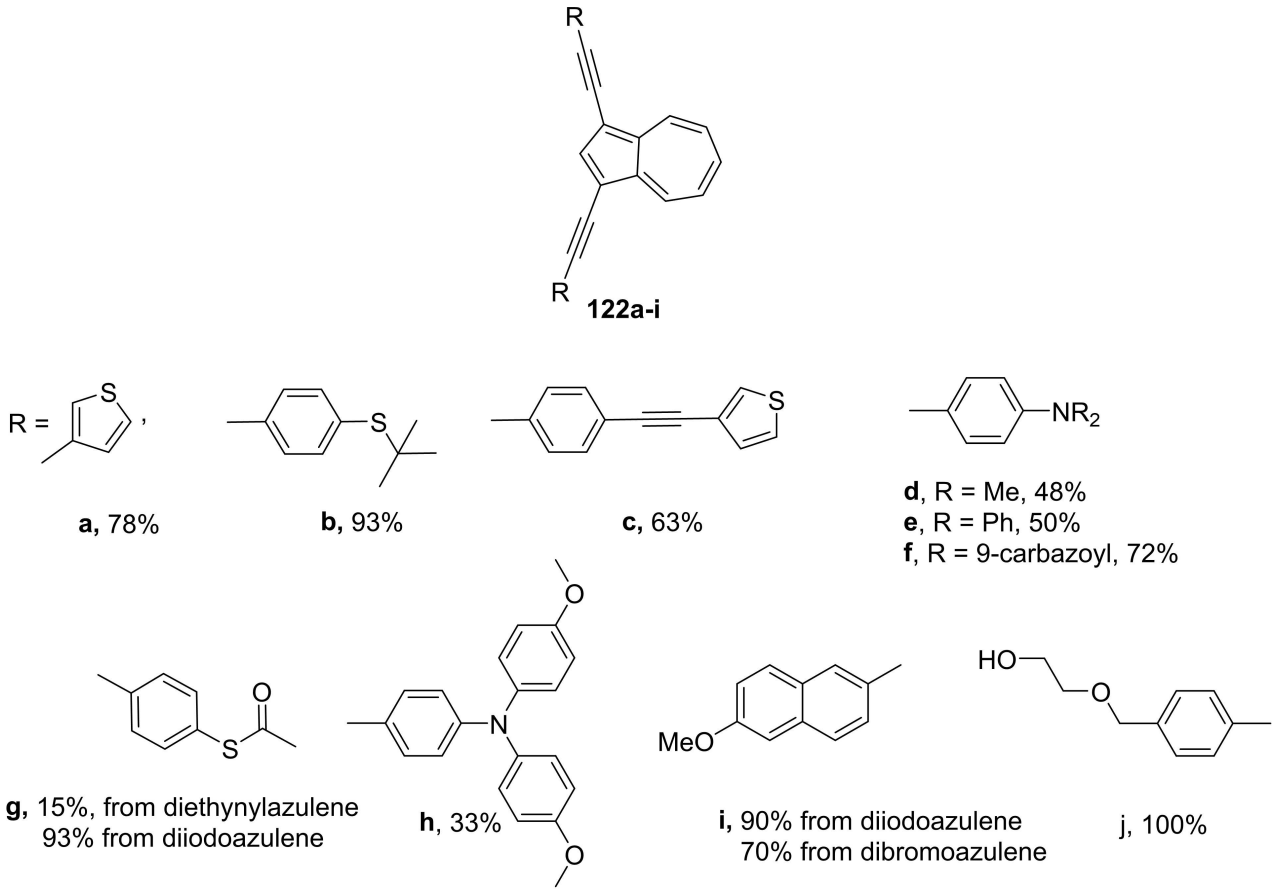


Figure 20. Structures of some 1,3-bis(arylethynyl)azulenes **122a–i**.

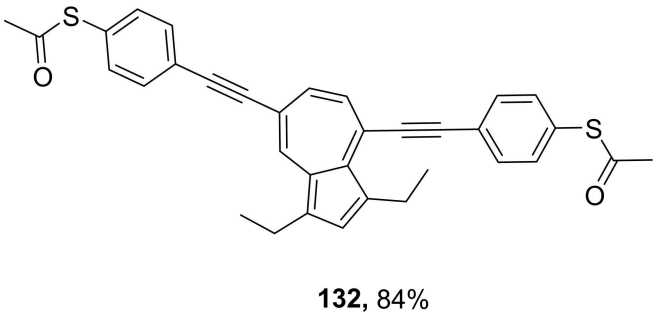


Figure 21. Structures of 4,7-bis(arylethynyl)azulene **132**.

nwithdrawing nature of the 1,3-*bis*-ethoxycarbonyl groups on the azulene ring, which should increase the reactivity toward the oxidative addition of the palladium catalyst.

3.5.1.6. (1-Azulenyl)(6-azulenyl)acetylene

The cross-coupling reaction of the appropriate 6-bromoazulenes[39,106] with the corresponding 1-ethynylazulene in the presence of the palladium catalyst afforded (1-azulenyl)(6-azulenyl)acetylenes **221a–c** in 92–99% yields (Figure 40).[105]

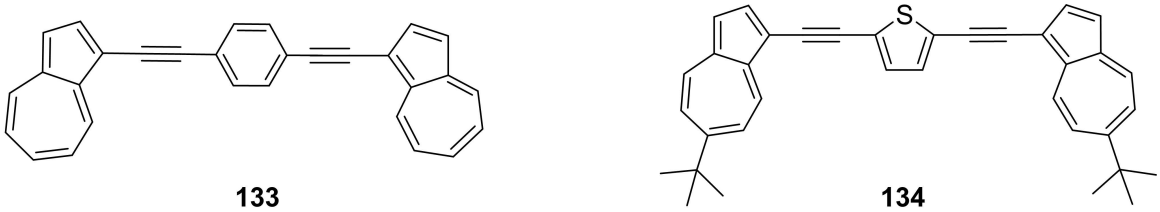
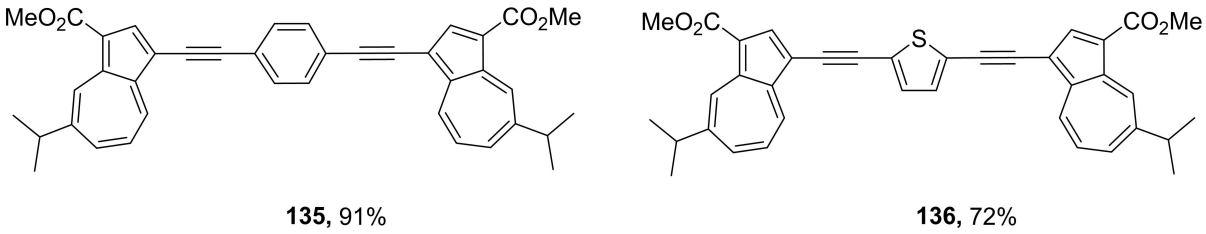
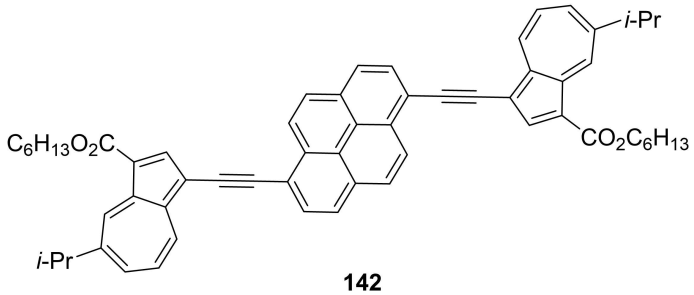


Figure 22. Structures of 1,4-bis(azulen-1-ylethynyl)benzene **133** and 2,5-bis(azulen-1-ylethynyl)thiophene **134**.



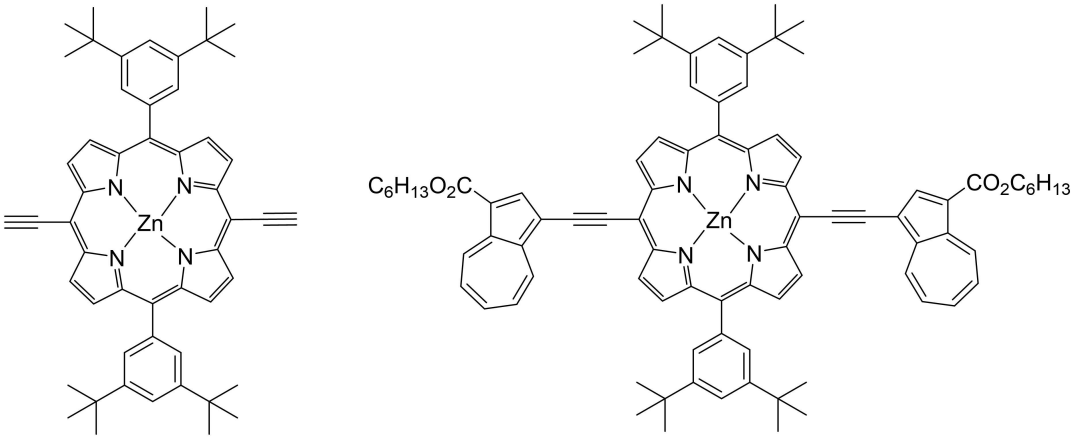
135, 91% **136**, 72%

Figure 23. Structures of 1,4-bis[(3-methoxycarbonyl-1-azulenyl)ethynyl]benzene (**135**) and 2,5-bis[(3-methoxycarbonyl-1-azulenyl)ethynyl]thiophene **136**.



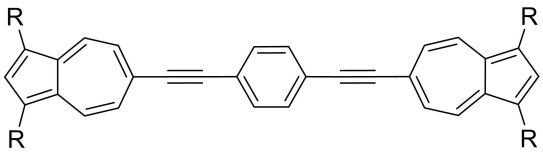
142

Figure 24. Structure of 3,3′-(pyrene-1,6-diylbis(ethyne-2,1-diyl))bis(7-isopropylazulene-1-carboxylate) **142**.



149 **150**, 43%

Figure 25. Structure of 5,15-diethynyl zinc(II) porphyrin **149** and 5,15-bis(azulenylethynyl) substituted zinc(II) porphyrin **150**.



155a: R = CO_2Et
155b: R = $COOC_6H_{13}$

Figure 26. Structures of diazulen-6-ylethynylbenzenes **155a,b**.

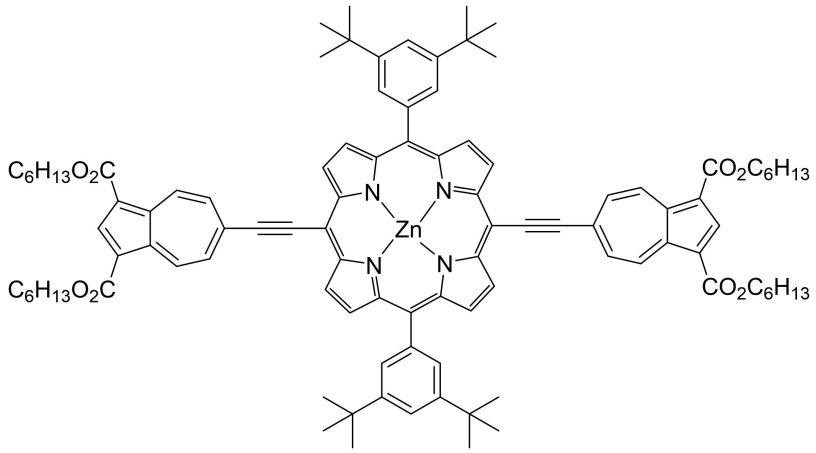
3.5.1.7. 6-(2-Azulenyl)ethynylazulene

6-(1-Azaazulen-2-yl)ethynylazulene (**224a**) and 6-(2-azulenyl) ethynylazulene (**224b**), were synthesized using the Sonogashira-Hagihara cross-coupling reaction of 6-ethynylazulene **44b** with 2-iodoazaazulenes **222** and **28a**, respectively, to give the corresponding diazulenylethyne **223** followed by decarboxylation with concentrated phosphoric acid (Scheme 48).[107]

3.5.2. Poly(azulenylethynes)

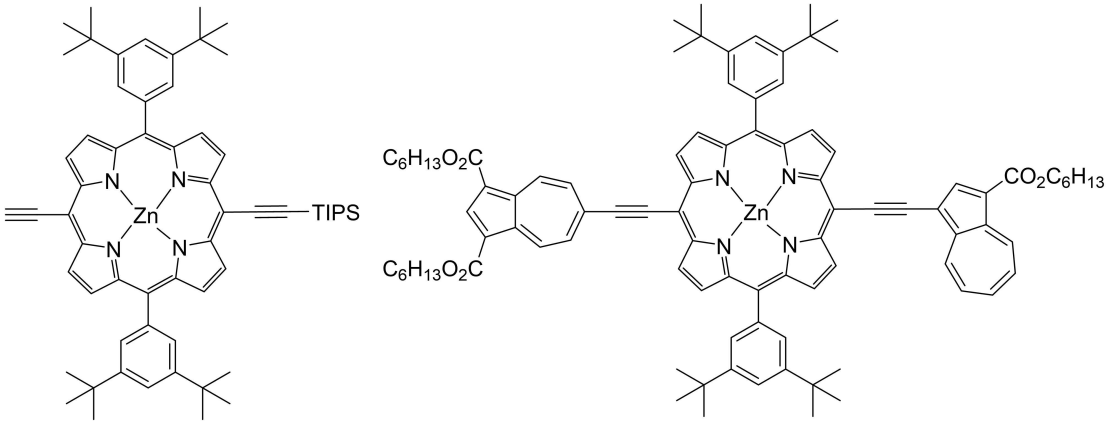
3.5.2.1. Poly(azulen-1-ylethynes)

Moreover, Hafner *et al.* reported on the extension of the skeleton of **207** by substitution with additional azulenylethyne groups utilizing 6-*tert*-butylazulene derivatives to ensure sufficient solubility of the higher oligomers in organic solvents and thus to enable easier isolation and purification. The trimeth-



164

Figure 27. Structure of 1,5-bis(azulenylethynyl) substituted zinc(II) porphyrin **164**.



165 166

Figure 28. Structure of 5,15-bis(azulenylethynyl) substituted zinc(II) porphyrin **166**.

ylsilyl-protected iodoethynylazulene **182** was synthesized in 68% yield together with 13% of the trimer **225** and 6% of the tetramer **226** by cross-coupling of 6-*tert*-butyl-1-ethynyl-3-iodoazulene (**11**) with **10** (Scheme 49).[17]

The trimer **227** and the pentamer **228** could be obtained in 66 and 26%, respectively, by coupling two equivalents of the ethynylazulenes **4b** as well as **213** with 6-*tert*-butyl-1,3-diiodoazulene (**9b**) at room temperature under Sonogashira conditions (Scheme 50).[17]

Under similar conditions, Elwahy reported the synthesis of 3,3′-((6-(*tert*-butyl)azulene-1,3-diyl)*bis*(ethyne-2,1-diyl))*bis*(1-(3′,6′-diphenyl-[1,1′:2′,1″-terphenyl]-4′-yl)azulene) **229** in 41% yield by coupling two equivalents of the ethynylazulene **7** with 6-*tert*-butyl-1,3-diiodoazulene (**9b**) (Figure 41).[20]

Shoji *et al.* used a similar approach for the synthesis of 1,3-bis(1-azulenylethynyl)azulene **230** in 95% yield by the reaction of 6-*tert*-butyl-1,3-diiodoazulene **9b** with the 1-ethynylazulene **13** in the presence of [Pd(PPh_3)$_4$] (Scheme 51).[108]

Furthermore, a cross-coupling reaction of 6-*tert*-butyl-1,3-diethynylazulene (**37b**) with 6-*tert*-butyl-3-iodo-1-(trimethylsilylethynyl)azulene (**10**) under similar conditions furnished the corresponding trimethylsilyl-protected trimer **231**, which was easily deprotected upon treatment with methanolic potassium hydroxide to give the 3,3′-(6-*tert*-butylazulene-1,3-diyl)bis(ethyne-2,1-diyl)bis(6-*tert*-butyl-1-ethynylazulene) **232**. Sonogashira coupling of the latter with **10** or its dimer **182** led to the formation of 31% of the pentamer **233** and 19% of the heptamer **234** as green and brownish-black high melting crystals, respectively (Figure 42).[17]

The UV/Vis spectra of the ethynyl-bridged oligomers **231**, **233** and **234** as well as the monomer 6-*tert*-butyl-1,3-bis(trimethylsilylethynyl)azulene **37b** showed that the longest wavelength absorption maximum (λmax) shifts bathochromically with increasing chain length. However, the shift differences diminish with enhancing length of the oligomers and tend towards a limiting value. This value can be determined by plotting the longest wavelength absorption (λmax) vs. reciprocal chain length 1/*n*, which gives a linear relationship.[109,110] This allows an estimation of the band gap (*Eg*) of poly(1,3-azulenylethynylene)s lower than 2 eV. For comparison, the

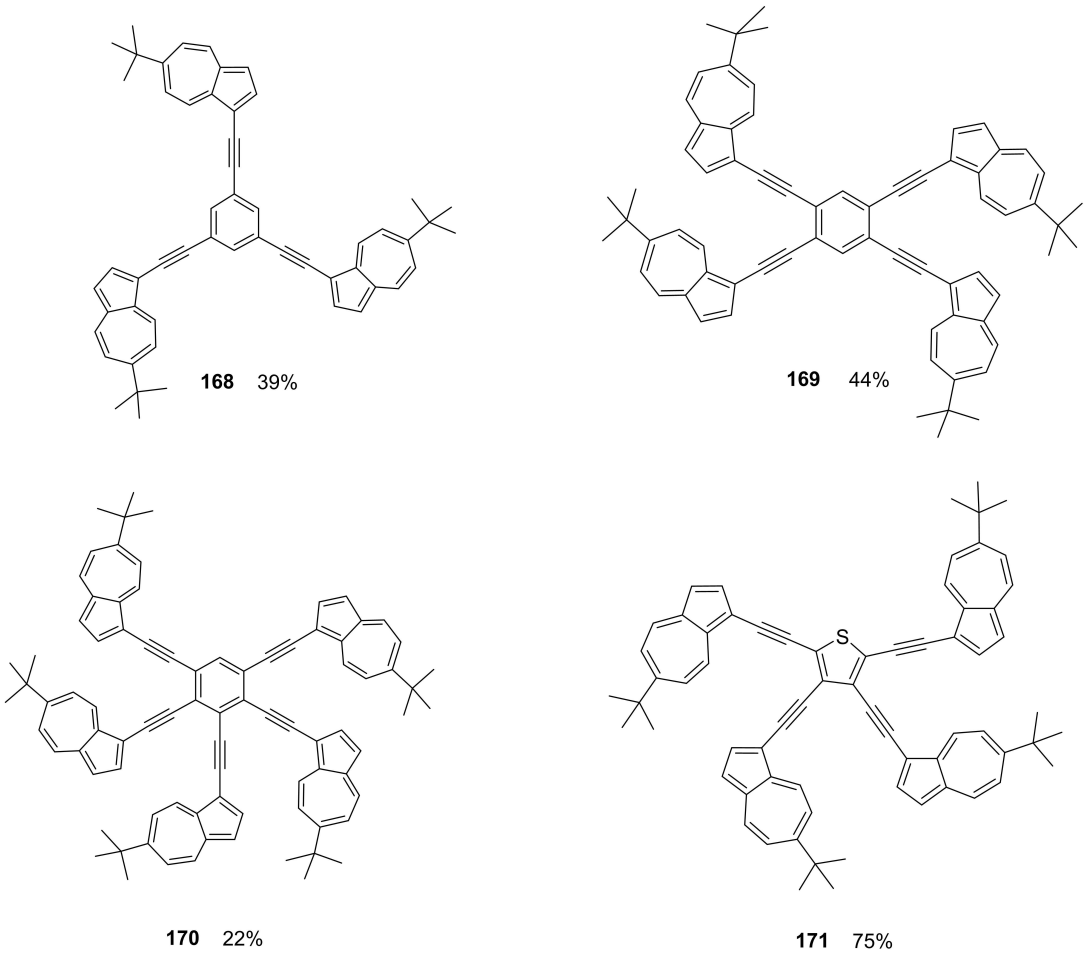
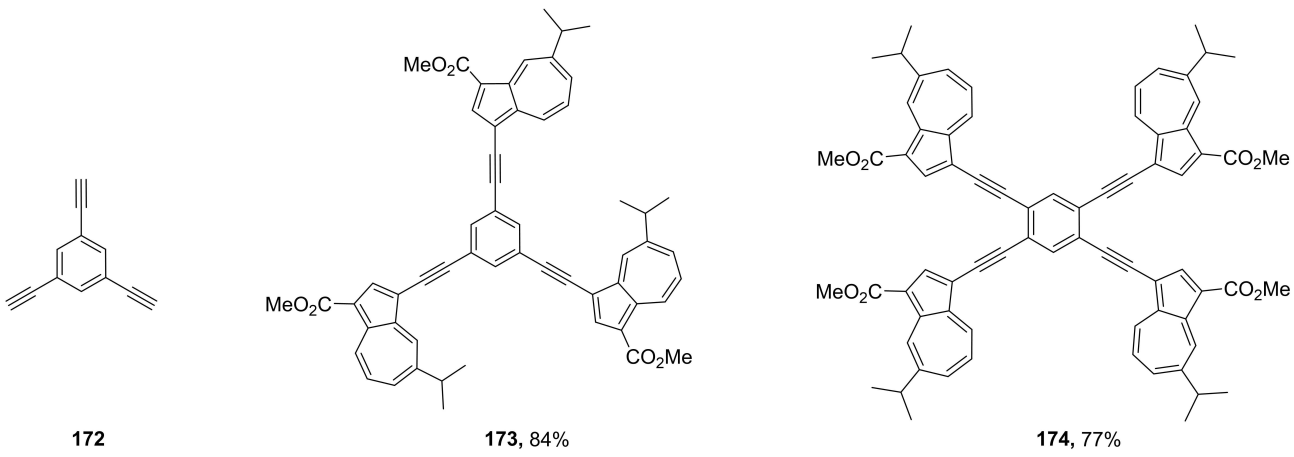


Figure 29. Structures of poly(azulen-1-ylethynyl)benzene derivatives **168**–**170** and tetrakis(1-azulenylethynyl)thiophene **171**.



172 **173**, 84% **174**, 77%

Figure 30. Structures of poly(azulenylethynyl)arene derivatives **173** and **174**.

corresponding value for polyacetylene was determined to be 1.4 eV, while the corresponding value for poly(*p*-phenyleneethynylene)s was determined to be about 3.25 eV.[17]

3.5.2.2. Bis(azulen-2-ylethynyl)-1,3-azulene

Bis(azulen-2-ylethynyl)azulenes **235a** and **235b** have been prepared by palladium-catalyzed alkynylation of 1,3-diethynylazulene **37b** with 2-iodoazulene **28a** or 2-chloroazulene **45b** under Sonogashira-Hagihara conditions (Scheme 52).[108]

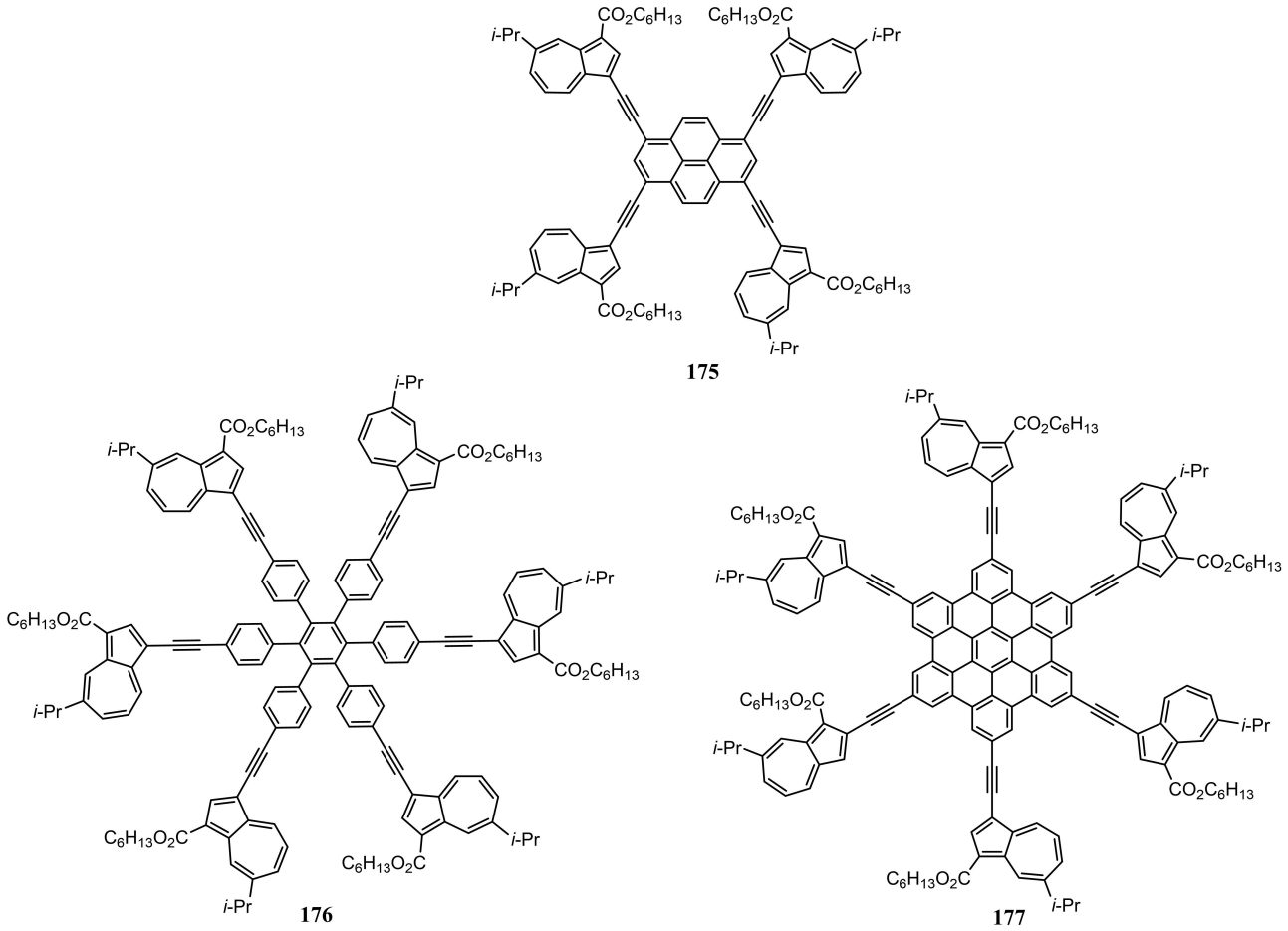


Figure 31. Structures of 1-ethynylazulenes connected to pyrene **175**, hexaphenylbenzene **176**, hexabenzocoronene **177** cores.

3.5.2.3. Bis(azulen-6-ylethynyl)-1,3-azulene

The synthesis of bis(azulen-2-ylethynyl)azulenes **236 a** and **236 b** have been accomplished by palladium-catalyzed alkynylation of 1,3-diethynylazulene **37 b** with 6-bromoazulenes **42 a**–**c**, under Sonogashira-Hagihara conditions (Scheme 52).[108]

3.5.3. Oligoazulenes with butadienyl bridges

3.5.3.1. Bis(azulen-1-yl)buta-1,3-diyne

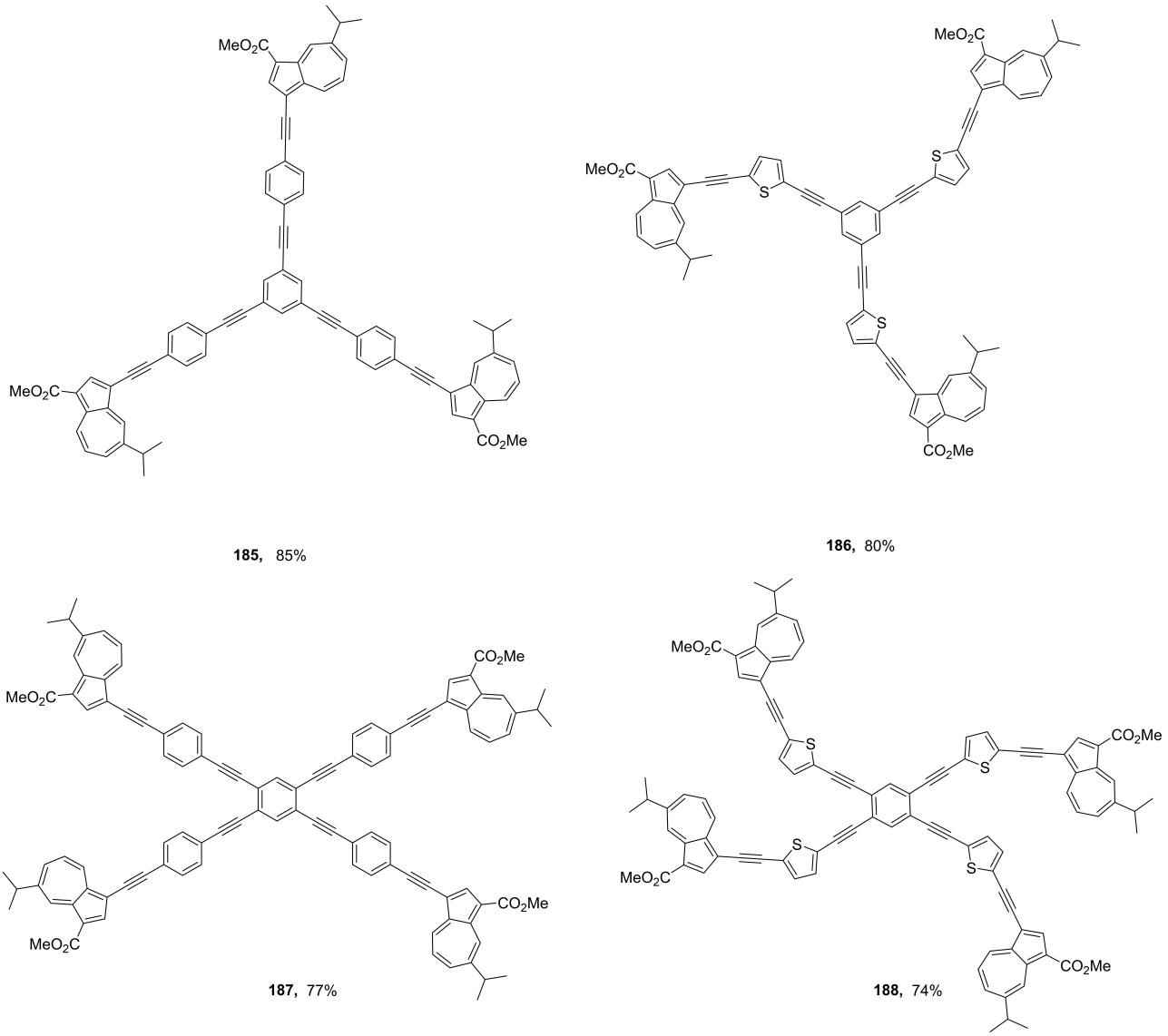
Hafner *et al.* reported also the synthesis of 1,4-di(azulen-1-yl) buta-1,3-diynes **237 a** and **237 b** in 70 and 75% yields, respectively, by oxidative Eglinton coupling[101] of 1-ethynylazulenes **4 a**,**b** (Scheme 53).[17]

Under similar conditions, Elwahy reported the synthesis of the butadiynyl-bridged azulene system **238** in 35% yield by the copper mediated *Eglinton* coupling of ethynylazulene **7**.[17] The conventional Eglinton coupling has also proved to be an effective methodology for the synthesis of mono- and diiodo derivative of butadiynyl-bridged oligoazulenes. Thus, oxidative Eglinton coupling of 6-*tert*-butyl-1-ethynyl-3-iodoazulene (**11**) with $Cu(OAc)_2$ in a boiling pyridine/ methanol/diethyl ether mixture furnished 1,4-bis(6-*tert*-butyl-3-iodoazulen-1-yl)-1,3-butadiyne (**239**) as brown crystals in good yield (84%).[111] Similar to **239**, also 1-(6-*tert*-butyl-3-iodoazulen-1-yl)-4-(6- *tert*-butylazulen-1-yl)-1,3-butadiyne (**240**) could be prepared in 40% yield by oxidative coupling of a mixture of ethynylazulenes **4 b** and **11** (Figure 43).

Furthermore, Nielsen *et al.*[22] and Ito *et al.*[64,100] reported the synthesis of the azulene dimers **241** and **242 a** and **242 b** in 27, 91, and 97% yields, respectively, by the Glaser homo-coupling[99] reaction of the corresponding alkynylazulene using CuI/ tetramethylethylenediamine (TMEDA) as the catalysts (Figure 44).

3.5.3.2. Bis(azulen-2-yl)buta-1,3-diyne

Ito *et al.* reported also the synthesis of di(azulen-2-yl)buta-1,3-diynes **243 a,b** by the Pd-catalyzed ($PdCl_2(PPh_3)_2$) oxidative coupling of the appropriate 2-ethynylazulenes in the presence of CuI and triethylamine as a base (Figure 45).[35,42]



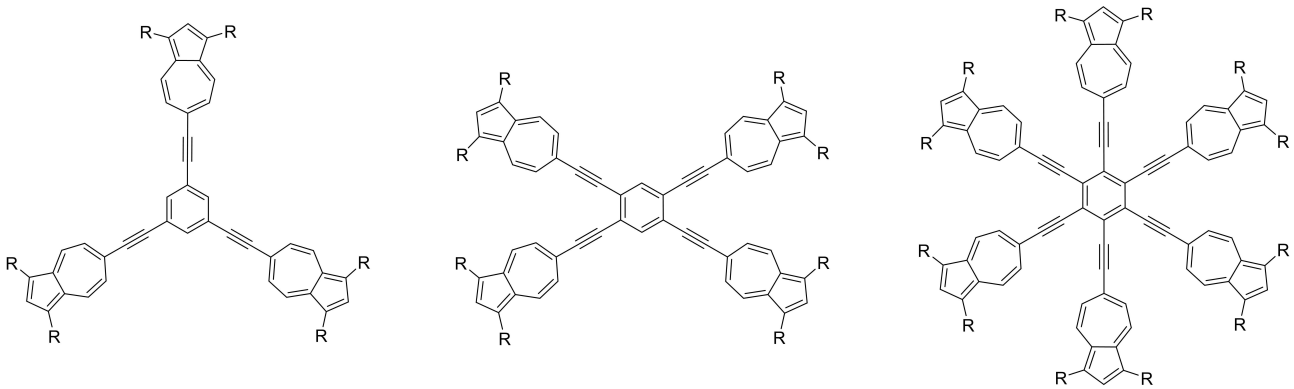
185, 85%

186, 80%

187, 77%

188, 74%

Figure 32. Structures of tris- and tetrakis[(1-azulenylethynyl)phenylethynyl- and (1-azulenylethynyl)-2-thienylethynyl]benzenes **185**–**188**.



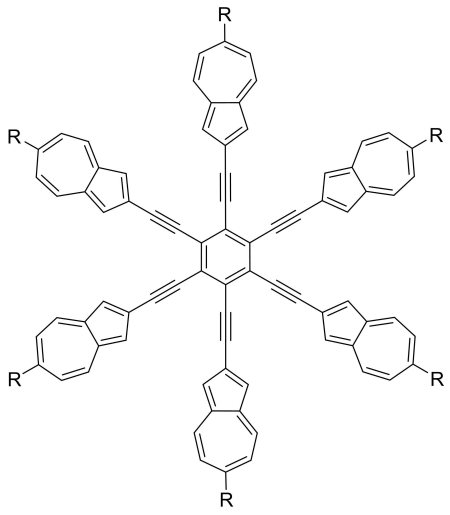
198, 96%

199, 66%

200, 55%

R = $COOC_6H_{13}$

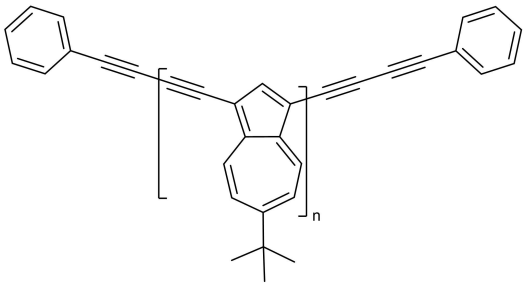
Figure 33. Structures of poly(azulen-6-ylethynyl)arene derivatives **198**–**200**.



201

$R = C_{16}H_{33}$

Figure 34. Structure of hexakis(azulen-2-ylethynyl)benzene **201**.



206a-c
a, n = 1, 58%
b, n = 2, 7%
c, n = 3, 2%

Figure 35. Structures of 1,3-bis(phenylbuta-1,3-diyn-1-yl)azulene and higher oligomers **206a–c**.

3.5.3.3. Bis(azulen-6-yl)buta-1,3-diyne

Similarly, di(azulen-6-yl)buta-1,3-diynes **244a,b** were obtained in good yields by the Pd-catalyzed ($PdCl_2(PPh_3)_2$) oxidative coupling of the appropriate 6-ethynylazulenes (Figure 45).[35,42]

3.5.3.4. Poly(azulen-1-ylbuta-1,3-diyne)

Higher oligomers with extended π-electron systems are accessible by the Eglinton coupling of 1,3-diethynylazulene **37d** in the presence of 1-ethynylazulene **4b** as end-capping reagent. As expected, butadiynylene-bridged trimer **245a** and tetramer **245b** were obtained as black crystals in 25% and 21% yields, respectively. As a result of homo-coupling (oxidative acetylene dimerization) of **4b**, the dimer **237b** could also be isolated from the reaction mixture in 26% yield (Scheme 54).[17] The UV/Vis spectra of these butadiynyl-bridged oligomers **237b, 245a** and **245b** show no significant bathochromic shift of the longest wavelength absorption in their electronic spectra with increasing length of the oligomers, presumably due to a reduced conjugation.

Similarly, oxidative coupling of 6-*tert*-butyl-1,3-diethynylazulene (**37d**) in the presence of **11** as end-capping reagent led to the formation of 6-*tert*-butyl-1,3-bis[(6-*tert*-butyl-3-iodoazulen-1-yl)butadiynyl] azulene (**246**) in 22% yield. In addition to the trimer **246**, also the dimer **239** could be isolated in 24% yield (Figure 46).[111]

3.5.4. Oligoazulenes with mixed ethynyl and butadienyl bridges

Oligoazulenes with mixed ethynyl and butadiynyl bridges could also be prepared by oxidative Eglinton coupling from the readily accessible ethynylazulenes as well as by Pd/Cu-catalyzed cross coupling reactions with the appropriate iodoazulenes. Thus, coupling of **239** with 2 equiv. of 6-*tert*-butyl-1-ethynylazulene (**4b**) resulted in the formation of the tetramer **247** with 47% yield as green crystals. The same compound can be obtained in 62% yield by Eglinton coupling of 1-(6-*tert*-butyl-3-ethynylazulen-1-yl)-2-(6-*tert*-butylazulene-1-yl)ethyne (**213**)[17] using $Cu(OAc)_2$ in a boiling pyridine/methanol/diethyl ether mixture (Scheme 55).[111]

Likewise, also the pentamer **248** with outer ethynyl and inner butadiynyl bridges can be synthesized in 37% yield by the Pd/Cu-catalyzed cross-coupling reaction of the trimer **246** with 2 equiv. of **4b**. The latter was alternatively obtained in 17% yield by oxidative coupling of a mixture of **213** and **37b** using the common copper(II)-mediated coupling conditions [$Cu(OAc)_2$, pyridine/methanol/diethyl ether]. In addition to **248**, also the hexamer **249** as well as the tetramer **247** could be isolated as black and green crystals in 4% and 20% yields, respectively (Scheme 56).[111]

Moreover, the pentamer **250** with outer butadiynyl and inner ethynyl bridges could be obtained by Pd/Cu-catalyzed cross-coupling reaction of **240** with 2 equiv. of **37b** in 33% yield as black crystals. Compound **250** resulted also in 20% yield from the oxidative coupling of 6-*tert*-butyl 1,3-bis-{[(6-*tert*-butyl-3-ethynyl)azulen-1-yl]ethynyl}azulene (**232**)[17] in the presence of **4b** as end-capping reagent. In addition, 3% of the octamer **251** and 24% of the dimer **237b** could be isolated (Scheme 57).[111]

The UV/Vis spectra of the oligoazulenes **247**–**251** surprisingly show only a small hypsochromic shift of the longest wavelength absorption maximum from 615 nm for the tetramer **247** to 610 nm for the octamer **251**, presumably due to a reduced conjugation which may be as a result of a less planar conjugated backbone.

3.6. Synthesis of enediyne scaffolds

The enediyne unit is a unique class of π-conjugated building blocks designed for construction of molecular architectures that contain one- and two-dimensional carbon networks.[57] Interest

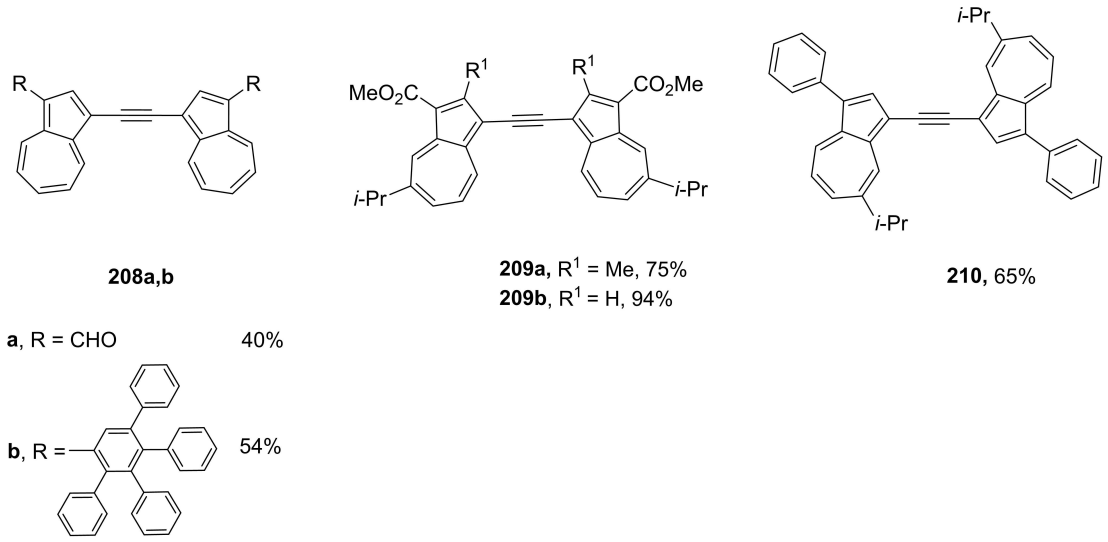


Figure 36. Structures of some *bis*(azulenyl)acetylenes **208**–**210**.

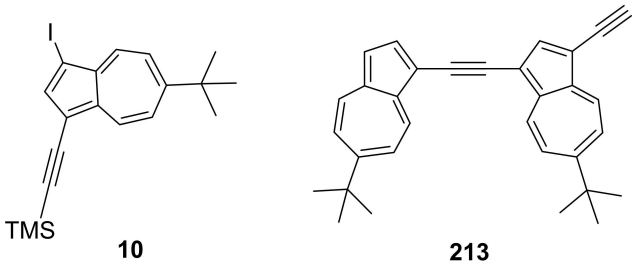


Figure 37. Structure of functionalized *bis*(azuleny)ethynes **213**.

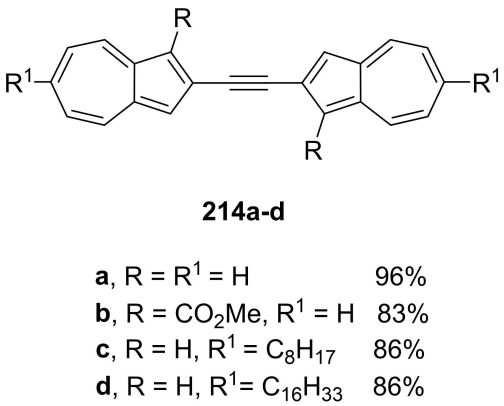


Figure 38. Structures of di-2-azulenylacetylenes **214a**–**d**.

in conjugated enediynes has grown because of their wide range of applications, for example in molecular wires, non-linear optics (NLO), and molecular switches.[112]

3.6.1. Ene-diyne systems possessing 6-azulenyl groups

In this respect, Ito *et al.* reported the synthesis of mono- and bis (enediyne) scaffolds connected by a 9*H*-fluorene or 9,10-

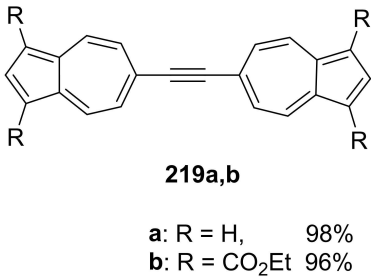


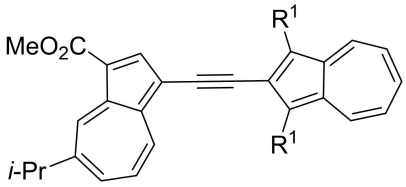
Figure 39. Structures of *bis*(azulen-6-yl)ethynes **219a** and **219b**.

anthracenediyl spacer as a redox-active substructures with 6-azulenyl moieties as π-electron-accepting groups in their periphery by a one-pot reaction involving repeated Pd-catalyzed alkynylation of the appropriate 6-bromoazulenes with the correponding bis(enediyne) derivative.[113,114]

Compounds **255a** and **255b** were prepared by a simple one pot reaction involving repeated Pd-catalyzed alkynylation of 6-bromoazulenes **42a** and **42b** with the enediyne scaffold **254**, prepared by desilylation of 9,10-bis[3-trimethylsilyl-1-(trimethylsilylethynyl)-2-propynylidene]-9,10-dihydroanthracene (**253**),[115] under Sonogashira-Hagihara conditions (Scheme 46). Compound **253** was obtained by a Pd-catalyzed alkynylation of 9,10-bis(dibromomethylene)-9,10-dihydroanthracene **252** upon treatment with TMSA (Scheme 46).[113]

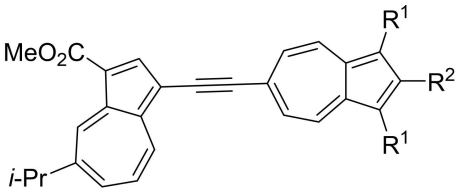
Similarly, the reaction of 9-bis(ethynyl)methylene-9*H*-fluorene (**258**), prepared by the desilylation of 9-[bis (trimethylsilylethynyl)methylene]-9*H*fluorene (**257**), with 6-bromoazulenes **42a** and **42c** afforded the desired mono(enediyne) s attached to fluorene **259a** (61%) and **259b** (86%). Compound **257** was obtained by Pd-catalyzed alkynylation of 9-(dibromomethylene)-9*H*-fluorene[116] **256** with TMSA (Scheme 58).[113]

Azulene-substituted bis(enediyne) systems **263a** and **263b** were prepared in 54 and 42% yields, respectively, by a simple



220a,b

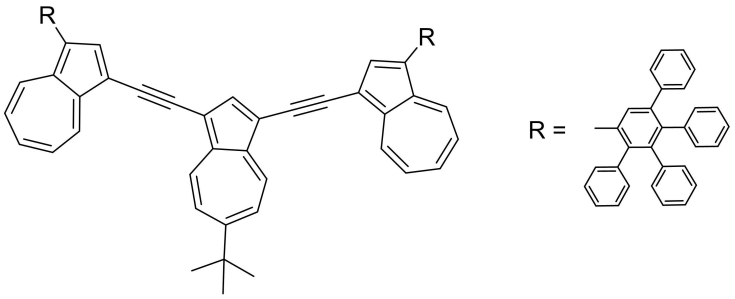
a, R^1 = H, 99%
b, R^1 = CO_2Et, 92%



221a-c

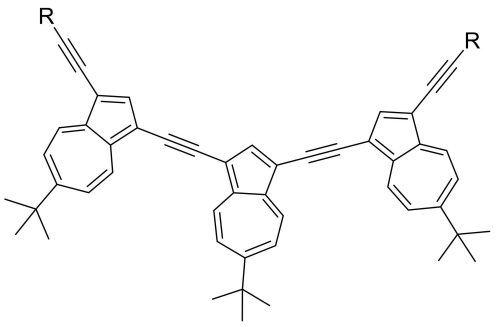
178a, R^1 = R^2 = H, 99%
178b, R^1 = CO_2Et, R^2 = H, 99%
178c, R^1 = CO_2Et, R^2 = NH_2, 92%

Figure 40. Structures of (1-azulenyl)(2-azulenyl)acetylene **220** and (1-azulenyl)(6-azulenyl)acetylenes **221**.

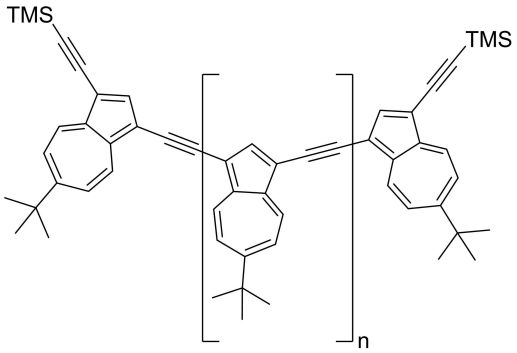


229, 41%

Figure 41. Structure of 3,3′-((6-(*tert*-butyl)azulene-1,3-diyl)*bis*(ethyne-2,1-diyl))*bis*(1-(3′,6′-diphenyl-[1,1′:2′,1″-terphenyl]-4′-yl)azulene) **229**.



231: R = TMS, 43%
232: R = H, 67%

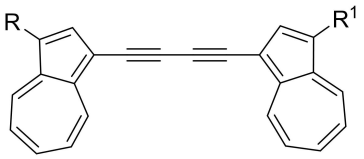


233: n = 3, 31%
234: n = 5, 19%

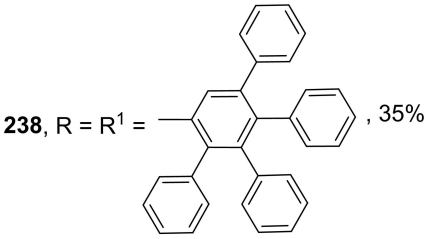
Figure 42. Structures of trimethylsilyl-protected trimer **231**, pentamer **232** and heptamer **234**.

one-pot reaction involving repeated Pd-catalyzed alkynylation of the bis(enediyne) scaffold **262** with 6-bromoazulenes **42 b** or **42 c** under Sonogashira-Hagihara conditions (Scheme 1). The anthracene derivative **262** was prepared by the Pd-catalyzed alkynylation of 9,10-bis(2,2-dibromovinyl) anthracene (**260**)[117] with (trimethylsilyl)acetylene to give **261** followed by desilylation (Scheme 59).[114]

The mono(enediyne) derivatives **267 a** and **267 b** were also prepared in 72 and 59% yields, respectively, by a Pd-catalyzed cross-coupling reaction of 1-(9-anthryl)-2-ethynylbut-1-en-3-yne (**266**), obtained by the desilylation of 1-(9-anthryl)-4-(trimethylsilyl)-2-[2-(trimethylsilyl)ethynyl]-but-1-en-3-yne (**265**) upon treatment with potassium carbonate in methanolic THF, with 6-haloazulenes **42 b** and **42 c**. Compound **265** was obtained by the Pd-catalyzed alkynylation of 9-(2,2-dibromovinyl)anthracene **264**[118] with (trimethylsilyl)acetylene under Sonogashira-Hagihara conditions (Scheme 60).[114]



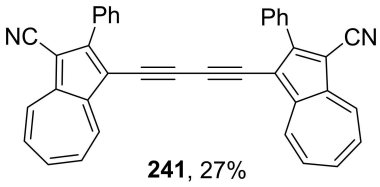
238-240



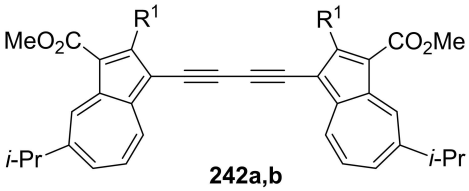
238, R = R^1 = , 35%

239, R = R^1 = I, 84% **240**, R = H, R^1 = I, 40%

Figure 43. Structures of butadiynyl-bridged azulene systems **238**–**240**.



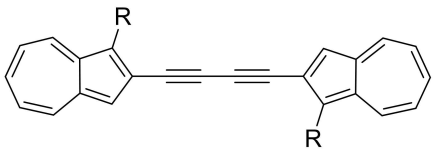
241, 27%



242a,b

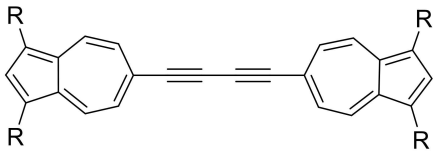
a, R^1 = H, 91%
b, R^1 = Me, 97%

Figure 44. Structures of butadiynyl-bridged azulene systems **241** and **242**.



243a,b

a: R = H 69%
b: R = CO_2Me 76%



244a,b

a: R = H 86%
b: R = CO_2Et 58%

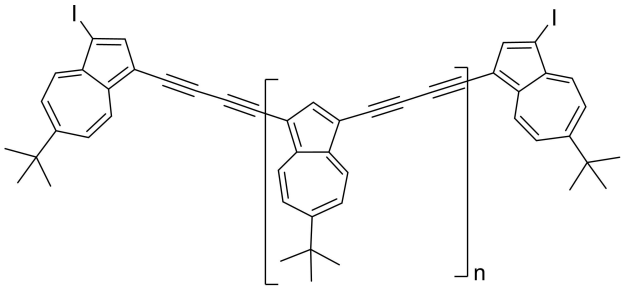
Figure 45. Structures of di(azulen-2-yl)buta-1,3-diynes **243 a,b** and di(azulen-6-yl)buta-1,3-diynes **244 a,b**.

3.6.2. Ene-diyne systems possessing 1-azulenyl groups

Ene-diyne systems possessing 1-azulenyl groups at the periphery **268** and **269** were prepared in 89 and 74% yields by palladium-catalyzed crosscoupling reaction of 1-ethynylazulenes with 9-dibromomethylene-9*H*-fluorene and 9,10-bis (dibromomethylene)-9,10-dihydroanthracene, respectively, under Sonogashira-Hagihara conditions (Figure 46).[119]

3.6.3. Ene-diyne systems possessing 2-azulenyl groups

Similarly, ene-diyne systems possessing 2-azulenyl groups **270** and **2271** at the periphery were prepared in 80% yield and very small amount, by palladium-catalyzed crosscoupling reaction of 2-ethynylazulenes with 9-dibromomethylene-9*H*-fluorene and 9,10-bis(dibromomethylene)-9,10-dihydroanthracene. On the other hand, reaction of 2-iodoazulene with 9,10-bis (diethynylmethylene)-9,10-dihydroanthracene under Sonogashira-Hagihara conditions afforded **271** in 57% yield (Figure 47).[119]



239: n = 0, 24%
246: n = 1, 22%

Figure 46. Structure of 6-*tert*-butyl-1,3-bis[(6-*tert*-butyl-3-iodoazulen-1-yl) butadiynyl] azulene (**246**).

3.7. Co- catalyzed cyclooligomerization of ethynylazulenes

3.7.1. Synthesis of azulenyl-substituted benzenes as well as cyclobutadiene complexes

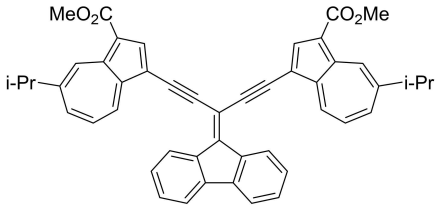
Since Reppe *et al.*[120] discovered the transition metal-catalyzed [2+2+2] cyclotrimerization of alkynes, this synthetic method was applied for the construction of highly functionalized carbo- and heterocycles.[121] Although an extensive number of different metal complexes derived from the whole range of transition metals[122] can be used for this catalytic reactions, cobalt is still the most effective.[123]

In general, cobalt complexes react with alkynes to undergo cyclotrimerization reactions via a formal [2+2+2] cycloaddition yielding either free arene or arene complexes. Alternatively, also cyclodimerization sometimes results in Co-cyclobutadiene complexes.[124] This is possible due to the slow insertion of the third π system into the organocobalt intermediate formed in the course of the reaction. It was shown that, as the substituents on the alkyne get larger, the cyclodimerization reaction becomes easier.[125]

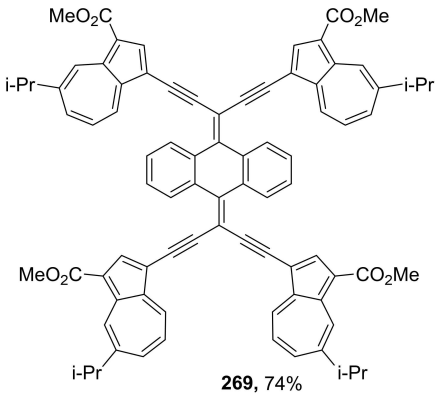
Hafner *et al.* and Ito *et al.* reported that the cyclooligomerization of ethynylazulenes in the presence of Co-catalyst proved to be a useful protocol for the synthesis of azulenyl-substituted benzenes as well as cyclobutadiene complexes. The mode of the reaction and the product spectrum obtained was found to depend largely on the position of alkyne substituent on the azulene ring as well as on the ligand structure of the used catalyst.

3.7.1.1. Synthesis of tris(azulen-1-yl)benzene

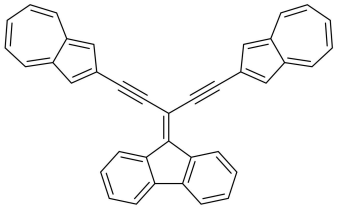
Treatment of 1-ethynylazulenes **4a**,**b** with catalytic amounts of $CpCo(CO)_2$ in refluxing cyclooctane for 24 h furnished 1,2,4-tris (azulen-1-yl)benzenes **272a** and **272b** in 11% and 16% yields, respectively (Scheme 17). In both cases, the 1,3,5-tris(azulen-1-yl)benzene derivatives **274a** and **274b** could not be obtained even in traces.[21] In addition to the major products **272a** and **272b**, the [η^4-bis(azulen-1-yl)cyclobutadiene](η^5-cyclopentadienyl)cobalt complexes **273a** and **273b** could also be isolated



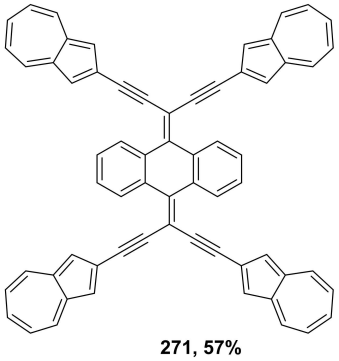
268, 89%



269, 74%

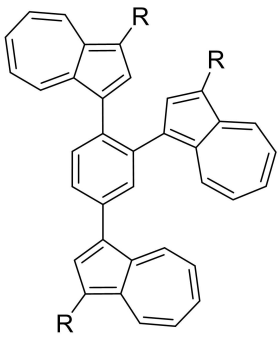


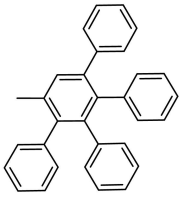
270, 80%



271, 57%

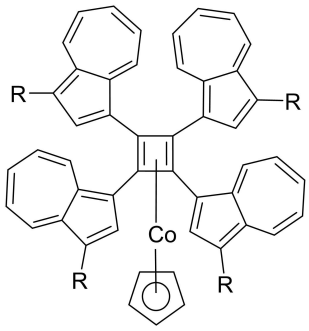
Figure 47. Structures of ene-diyne systems possessing 1-azulenyl and 2-azulenyl groups at the periphery **268**–**271**.



275, R =  10% **276**, R = CHO 14%
277, R = CN 12%

275-277

Figure 48. Structures of functionalized 1,2,4-tris(azulen-1-yl)benzenes **275**–**277**.



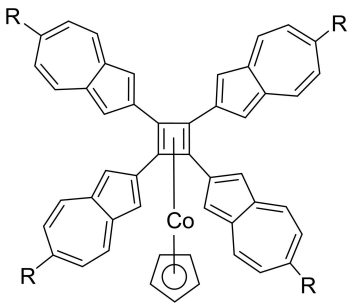
290a, R = CHO, 60%
290b, R = CN, 30%

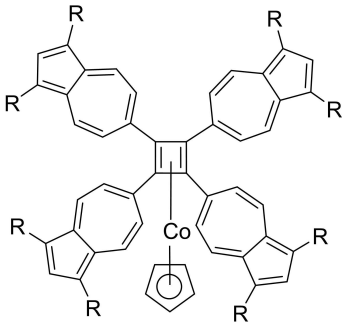
Figure 49. Structures of tetrakis(azulen-1-yl)cyclobutadiene cobalt complexes **290 a,b**.

in 2% and 4%, yields, respectively (Scheme 61). The NMR spectroscopic data of **273 a** and **273 b** did not allow a decision between the two expected regioisomeric 1,2- and 1,3-bis (azulen-1-yl)cyclobutadiene complexes and crystals suitable for an X-ray structure analysis could not be obtained.[21]

Similarly, functionalized 1,2,4-tris(azulen-1-yl)benzenes **275**–**277** could be obtained in 10–14% yield upon treatment of the appropriate ethynylazulenes with catalytic amounts of CpCo $(CO)_2$ in refluxing cyclooctane. In all cases, the corresponding 1,3,5-triazulenylbenzenes as well as cyclobutadiene cobalt complexes were not detected in the reaction products. Compound **276** could also be alternatively obtained in 45% yield by condensation of **276** with hydroxylamine hydrochloride and subsequent dehydration with acetic anhydride/pyridine (Figure 48).[20,21]

The formation of **272 a** and **272 b** and **275**–**277** is in accordance with results obtained by Vollhardt and others[126] for the cyclotrimerization of alkynes, and let assume the formation of the cobaltacycle **278** as an intermediate which reacts with a further molecule of **4 a** and **4 b**, or **7** and **8** *via* a metal-mediated [4 + 2]-cycloaddition to generate the η^4-benzene complex **279**. A subsequent displacement of the ligand in **279** by the appropriate ethynylazulenes should result in the formation of **272 a** and **272 b** and **275**–**277**. Therefore, it can be expected that **273 a** and **273 b** are formed *via* a reductive cycloelimination of the cobaltacycle **278** and hence should be the 1,2-bis

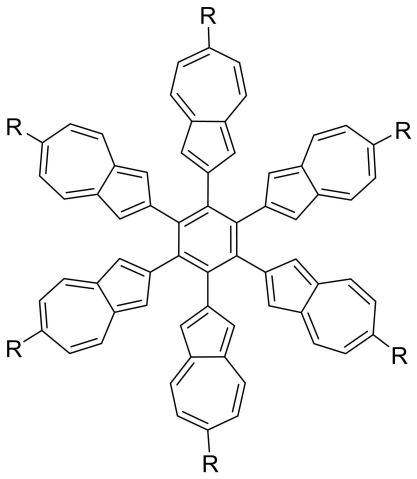




291a: R = H 79%
291b: R = C_8H_{17} 52%

292a: R = H 43%
292b: R = CO_2Et 81%

Figure 50. Structures of tetrakis(azulenyl)cyclobutadiene cobalt complexes **291 a,b** and **292 a,b**.



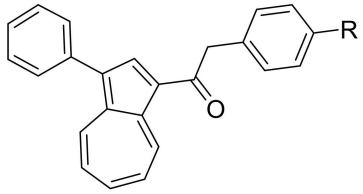
293a: R = H, 91%
293b: R = C_8H_{17}, 78%

Figure 51. Structures of hexakis(azulen-2-yl)benzenes **293 a,b**.

(azulenyl)cyclobutadiene complexes (Scheme 62). The absence of cyclobutadiene cobalt complexes in the cyclooligomerization of **7** or **8** let assume a relatively high reactivity of the cobaltacycle **278** towards **7**–**9** to give **275**–**277**, respectively, compared with that of the reductive cycloelimination.[21]

3.7.1.2. Synthesis of tris(azulen-6-yl)benzene

On the other hand, Ito *et al.* reported that the cyclooligomerization of 6-ethynylazulenes **44 a** and **44 b** in the presence of $CpCo(CO)_2$ in refluxing 1,4-dioxane afforded as major products the [η^4-bis(azulen-6-yl)cyclobutadiene](η^5-cyclopentadienyl)cobalt complexes **282 a** and **282 b** in 19% and 47% yields, respectively, besides the 1,2,4- and 1,3,5-tris(azulen-6-yl)benzene derivatives **280 a** and **280 b** and **281 a** and **281 b** in minor yields (Scheme 63).[42,127] The regiochemistry of the cobalt complex **281** could be confirmed by the ^{13}C satellite signals in the ^1H NMR spectrum,[128] which were definitely identified by the 2D HMQC spectrum measured under non-decoupling conditions. The negligibly small coupling constant (<1 Hz) between the



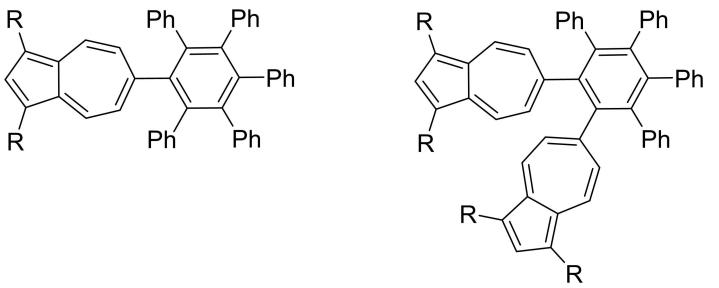
301a, R = H, 71%
301b, R = NMe_2, 82%
301c, R = NO_2, 97%

Figure 53. Structures of 2-aryl-1-(3-phenylazulen-1-yl)ethan-1-ones **301 a**–**c**.

cyclobutadiene protons clearly shows the presence of the 1,2-disubstitution pattern in the cyclobutadiene ring.[129]

3.7.1.3. Synthesis of bis(azulen-6-yl)cyclobutadiene cobalt complexes

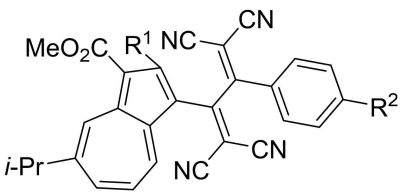
Reaction of 6-trimethylsilylethynylazulene **43 b** with $CpCo(CO)_2$ afforded a mixture (1 : 4.1) of the *cis*- and *trans*-(η^5-cyclopentadienyl)[bis(1,3-diethoxycarbonyl-6-azulenyl)bis (trimethylsilyl)cyclo-butadiene]cobalt complexes (**283 a** and **284 a**) in 82% yields, which were separable by gel permeation chromatography (GPC) with chloroform (Scheme 64). The regiochemistry of **283 a** and **284 a** could not be determined by NMR spectroscopy. Thus, the relative stereochemistry of the major isomer **284 a** was established by X-ray crystallography as a trans-cobalt complex. The reaction of 6-phenylethynylazulene **107 b** with $CpCo(CO)_2$ also afforded a mixture (1 : 1.1) of the *cis*- and *trans*-(η^5-cyclopentadienyl)-[bis(1,3-diethoxycarbonyl-6-azulenyl)di(phenyl)cyclobutadiene] cobalt complexes (**283 b** and **284 b**) in 94% yields (Scheme 64).[42] The regiochemistries of **283 b** and **284 b** were tentatively assigned by the comparison of the chemical shifts of their azulene and benzene ring protons in ^1H NMR spectra.[130] The exclusive formation of the (cyclobutadiene)cobalt complexes **283 a,b** and **284 a,b** may be attributable to the steric effect among the aromatic rings and/or the trimethylsilyl groups.[42] The deprotection of the trimeth-



296a: R = H 32%
296b: R = CO_2Et 93%

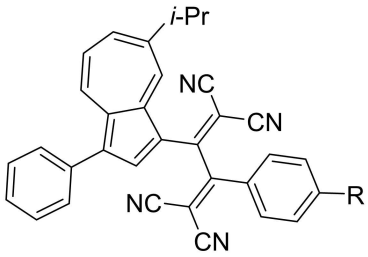
297a: R = H 13%
297b: R = CO_2Et 90%

Figure 52. Structures of (6-azulenyl)tetraphenylbenzenes **296 a,b** and 1,2-bis(6-azulenyl)tetraphenylbenzenes **297 a,b**.



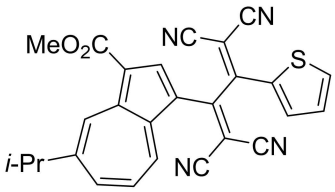
327a-f

a, R^1 = Me, R^2 = H, 87%
b, R^1 = Me, R^2 = NMe_2, 90%
c, R^1 = Me, R^2 = NO_2, 90%
d, R^1 = H, R^2 = H, 96%
e, R^1 = H, R^2 = NMe_2, 97%
f, R^1 = H, R^2 = NO_2, 91%

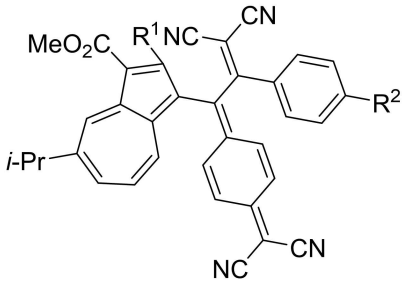


328a-c

a, R = H, 79%
b, R = NMe_2, 66%
c, R = NO_2, 93%

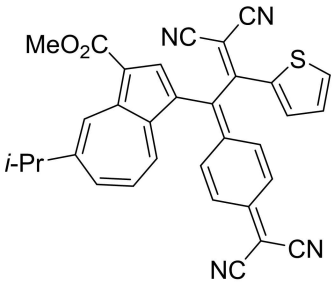


329, 86%

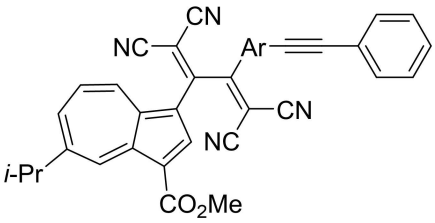


330a-f

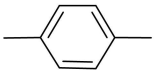
a, R^1 = Me, R^2 = H, 98%
b, R^1 = Me, R^2 = NMe_2, 89%
c, R^1 = Me, R^2 = NO_2, 97%
d, R^1 = H, R^2 = H, 96%
e, R^1 = H, R^2 = NMe_2, 43%
f, R^1 = H, R^2 = NO_2, 94%



331, 93%



332a,b

a, Ar =  97%

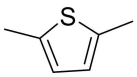
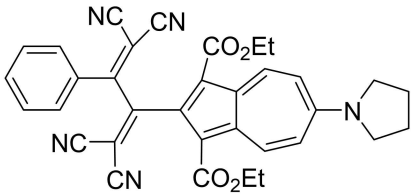
b,  96%

Figure 54. Structures of tetracyanobutadienes (TCBDs) and dicyanoquinodimethanes (DCNQs), **327**–**332** from aryl/heteroaryl-substituted -ethynylazules.



334, 94%

Figure 55. Structure of TCBD derivative **334**.

ylsilyl groups of **284a** upon treatment with tetrabutylammonium fluoride in tetrahydrofuran furnished **285** in 53% yield.[42]

3.7.1.4. Synthesis of bis(2-azulen-2-yl)cyclobutadiene cobalt complex

Reaction of 2-(trimethylsilylethynyl)azulene (**28b**) with CpCo$(CO)_2$ produced a mixture (16:84) of the *cis*- and *trans*-(η^5-cyclopentadienyl)[bis(1,3-diethoxycarbonyl-6-azulenyl)bis (trimethylsilyl)-cyclobutadiene]cobalt complexes (**286** and **287**) in 50% yields. The major isomer **287** could be separated by recrystallization and its regiochemistry was determined to be a *trans*-cobalt complex by X-ray structure determination (Scheme 65).[33]

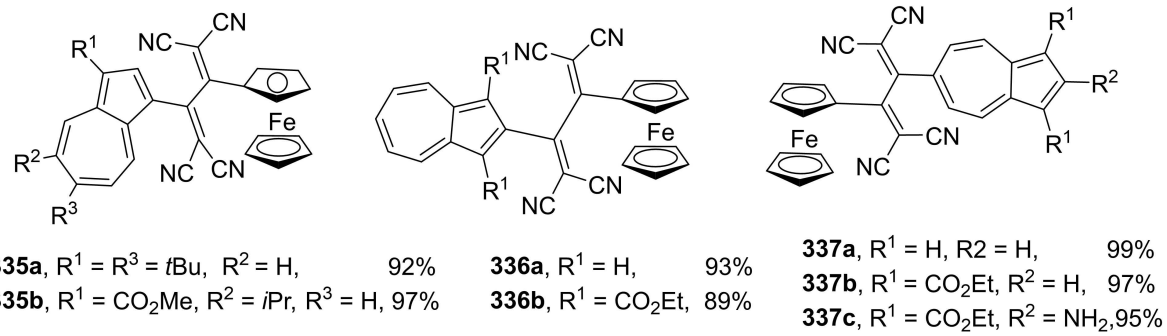


Figure 56. Structures of AzTCBDs **335**–**337** from Ferrocenyl-substituted -ethynylazules.

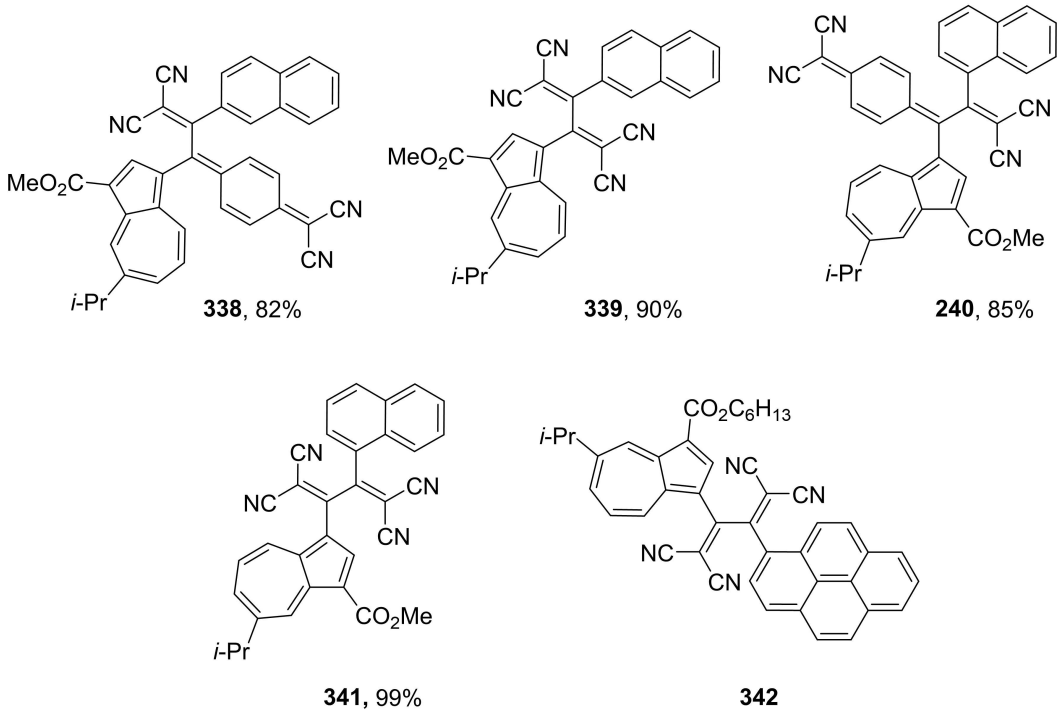


Figure 57. Structures of AzTCBDs and AzDCNQs **338**–**342** from naphthalene/pyrene-substituted -ethynylazules.

3.7.1.5. Synthesis of tetrakis(azulen-1-yl)cyclobutadiene cobalt complex

The reaction of the bis(azulen-1-yl)ethynes **207 a**,**b** with $CpCo(CO)_2$ (20 mole %) in refluxing cyclooctane did not yield the expected hexakis(azulen-1-yl)benzenes **288 a**,**b** obviously due to steric hindrance. Instead, the interesting black crystalline tetrakis(azulen-1-yl)cyclobutadiene cobalt complexes **289 a**,**b** were obtained with 20–25% yield which could be raised to 60–70% by increasing the amount of $CpCo(CO)_2$ to 60 mole % (Scheme 66). Repeated attempts to cyclotrimerize **207 a**,**b** in the presence of bis(benzonitrile)palladium chloride or cobaltoctacarbonyl[131] were also unsuccessful and the starting materials were recovered almost completely.[21]

Similarly, the tetrakis(azulen-1-yl)cyclobutadiene cobalt complex **290 a** could be obtained in 60% yield upon treatment of the bis(azulen-1-yl)ethyne **208 a** with $CpCo(CO)_2$ (60 mole%) in refluxing cyclooctane. Condensation of **290 a** with hydroxylamine hydrochloride and subsequent dehydration with acetic anhydride/pyridine led to the formation of the tetrakis(azulen-1-yl)cyclobutadiene cobalt complexe **290 b** in 30% yield (Figure 49).[21]

3.7.1.6. Synthesis of tetrakis(azulen-2-yl)cyclobutadiene cobalt complex

Ito *et al.* reported also the exclusive formation of the tetrakis (azulen-2-yl)cyclobutadiene cobalt complexes **291 a**,**b** by the cyclodimerization of the corresponding bis(azulenyl)ethynes **214 a**,**c** in the presence of $CpCo(CO)_2$ in refluxing 1,4-dioxane (Figure 49).[33,34,42,127]

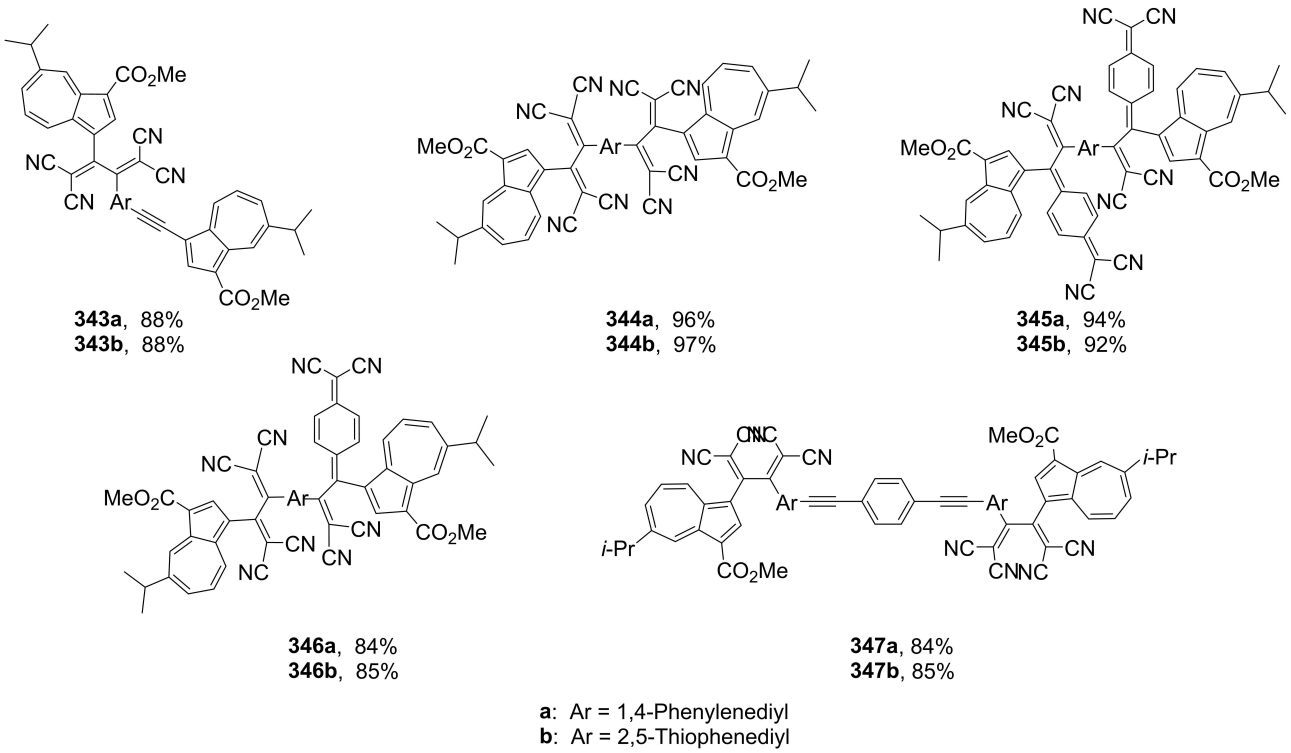


Figure 58. Structures of AzTCBDs and AzDCNQs **343**–**347** from bis(azulenylethynyl)arenes or heteroarenes.

3.7.1.7. Synthesis of tetrakis(azulen-6-yl)cyclobutadiene cobalt complex

Likewise, cyclodimerization of the appropriate bis(azulenyl) ethynes **219 a,b**, in the presence of $CpCo(CO)_2$ in refluxing 1,4-dioxane afforded exclusively the corresponding tetrakis (azulenyl)cyclobutadiene cobalt complexes **292 a,b** by the (Figure 50).[33,34,42,127]

3.7.1.8. Synthesis of hexakis(azulen-2-yl)benzene

Contrary to this, the cyclooligomerization of bis(6-octylazulen-2-yl)ethynes **214 a,c** with $Co_2(CO)_8$ as a catalyst in refluxing dioxane led to the formation of the hexakis(azulen-2-yl)benzene **293 a,b** in 91 and 78% yields, respectively. The latter compounds seem to be less sterically hindered in comparison to the corresponding hexakis(azulen-1-yl)benzenes **288 a,b** or hexakis (azulen-6-yl)benzenes (Figure 51).[33,34]

3.8. Synthesis of azulenyl-substituted benzenes by Diels-Alder cycloaddition reactions

[4 + 2] Cycloaddition reactions of tetraphenylcyclopentadienone with suitable aryl acetylene derivatives are an effective route to branched oligophenylenes.[132] In analogy, Diels-Alder reaction[133] of azulenyl-substituted acetylene with tetraphenylcyclopentadienone offer another interesting route to azulenyl- and polyazulenylbenzene derivatives.

3.8.1. Synthesis of (1-azulenyl)tetraphenylbenzene

Diels-Alder cycloaddition of tetraphenylcyclopentadienone to 1-ethynylazulenes **4 a,b** and 1,3-diethynylazulenes **37 a,b** furnished the the corresponding 1-(3′,6′-diphenyl-[1,1′:2′,1″-terphenyl]-4′-yl)azulene **294** and 1,3-bis(3′,6′-diphenyl-[1,1′:2′,1″-terphenyl]-4′-yl)azulene **295 a,b**, respectively (Scheme 67).[20]

3.8.2. Synthesis of (6-azulenyl)tetraphenylbenzene

Likewise, cycloaddition of tetraphenylcyclopentadienone with 6-ethynylazulenes **107 a,b** furnished the the corresponding (6-azulenyl)tetraphenylbenzenes **296 a,b**.[41,42] Under similar conditions, Diels-Alder reaction of 1,2-di(6-azulenyl)benzene derivative **219 a,b** with tetraphenylcyclopentadienone afforded 1,2-bis (6-azulenyl)tetraphenylbenzenes **297 a,b** in 13 and 90% yields, respectively (Figure 52).[41,42]

3.8.3. Synthesis of (2-azulenyl)tetraphenylbenzene

Azulene-fused naphthalene derivative (**299 a**), were obtained in 47% yield by the Diels-Alder reaction of di(2-azulenyl)acetylene (**214 a**) with tetraphenylcyclopentadienone in one pot.[35] Direct formation of **299 a** is ascribed to the autoxidation of the presumed cycloaddition product, 1,2-bis(2-azulenyl) tetraphenylbenzene derivative (**298 a**), under the reaction conditions. A similar reaction of bis(1-methoxycarbonyl-2-azulenyl)acetylene (**214 b**) gives the presumed 1,2-bis(2-azulen-

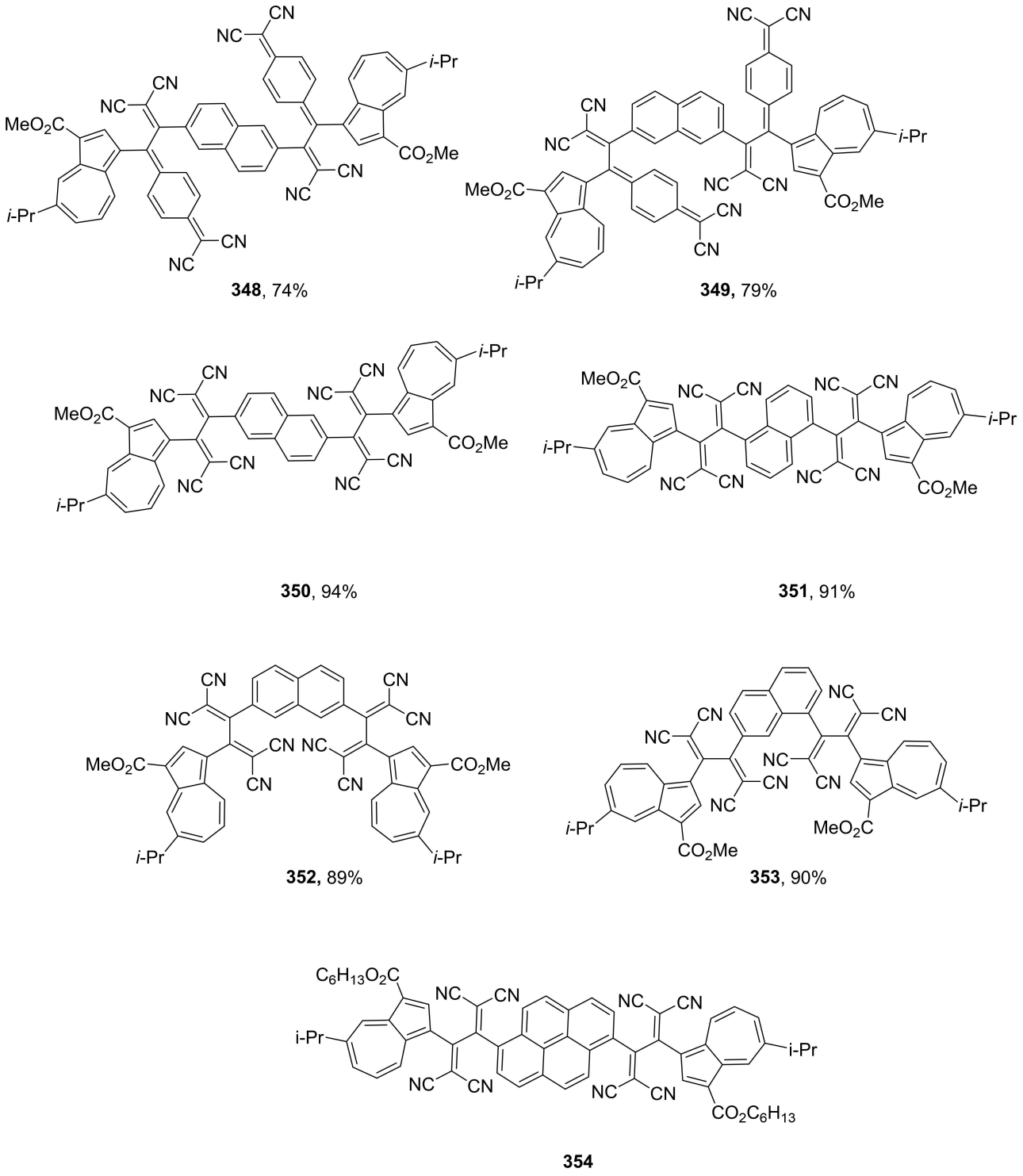


Figure 59. Structures of AzTCBDs and AzDCNQs **348**–**354** from bis-azulenylethynylnaphthalenes or pyrenes.

yl)benzene derivative (**298 b**), which is transformed into diazuleno[2,1-*a*:1,2-*c*]naphthalene (**299 b**, 78%) by the cyclodehydrogenation with iron(III) chloride (Scheme 68).[35]

3.9. Synthesis of azulen-1-ylyl ketones from 1-azulenylketones

1-Azulenylketones **300 a**–**g** were successfully synthesized in good to excellent yields by metal-free hydration of methyl 7-isopropyl-3-(arylethynyl)azulene-1-carboxylate **91** using trifluoroacetic acid as a Brønsted acid. The reaction was accom-

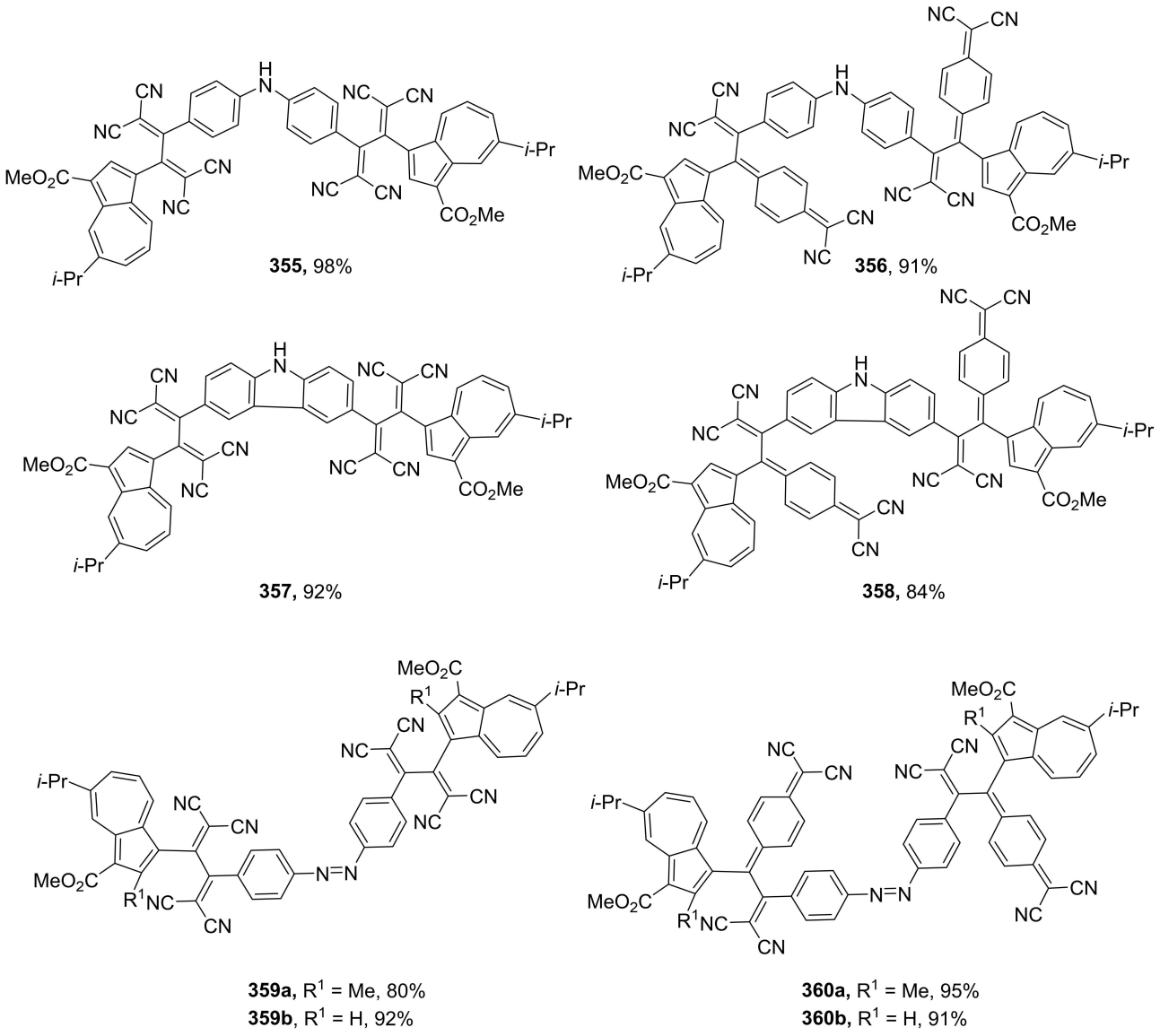


Figure 60. Structures of AzTCBDs and AzDCNQs **355**–**360** from bisazulenylethynyl linked to diphenylamine, carbazole and azobenzene.

plished at a relatively low temperature with complete regioselectivity and compatibility of several functional groups (Scheme 69).[134]

Under similar conditions, 2-aryl-1-(3-phenylazulen-1-yl) ethan-1-ones **301 a**–**c** were also obtained in 71%, 82% and 97% yields, respectively, from the corresponding 1-phenylazulenylalkynes (Figure 53).[134]

Likewise, hydration of bis-alkyne **144** afforded the desired diketone product **302** in 72% yield (Scheme 70).[134]

The presumed reaction mechanism is illustrated in scheme 59. At the first, alkyne **91** is protonated with Brønsted acid to give the azulenium allene intermediate **303** due to the electrondonating nature of the azulene ring at the 1-position. Addition of water to the azulenium allene intermediate **303** should afford the enol **304**, which then tautomerized to form ketone **300** (Scheme 71).[134]

3.10. Synthesis of heterocycles-substituted azulenes

3.10.1. Synthesis of 2-(azulen-1-yl)benzofuran

Shoji *et al.* established an efficient method for the preparation of azulene-substituted benzofurans **305 a**–**d** *via* the intramolecular cyclization of the appropriate 1-ethynylazulenes with 2-iodophenol under Sonogashira-Hagihara conditions (Scheme 72).

On the other hand, the reaction of 1-iodoazulenes with 2-ethynylphenol **306** gave 2,3-bis(1-azulenyl)benzofurans **307 a**–**d**, unexpectedly, along with the 2-(1-azulenyl)benzofurans **308 a**–**d** under the Sonogashira-Hagihara conditions (Scheme 73).[24]

The formation of 2,3-bis(1-azulenyl)benzofurans **307 a**–**d** by the reaction of 1-iodoazulenes with 2-ethynylphenol should be in accordance with the reaction mechanism proposed by Arcadi

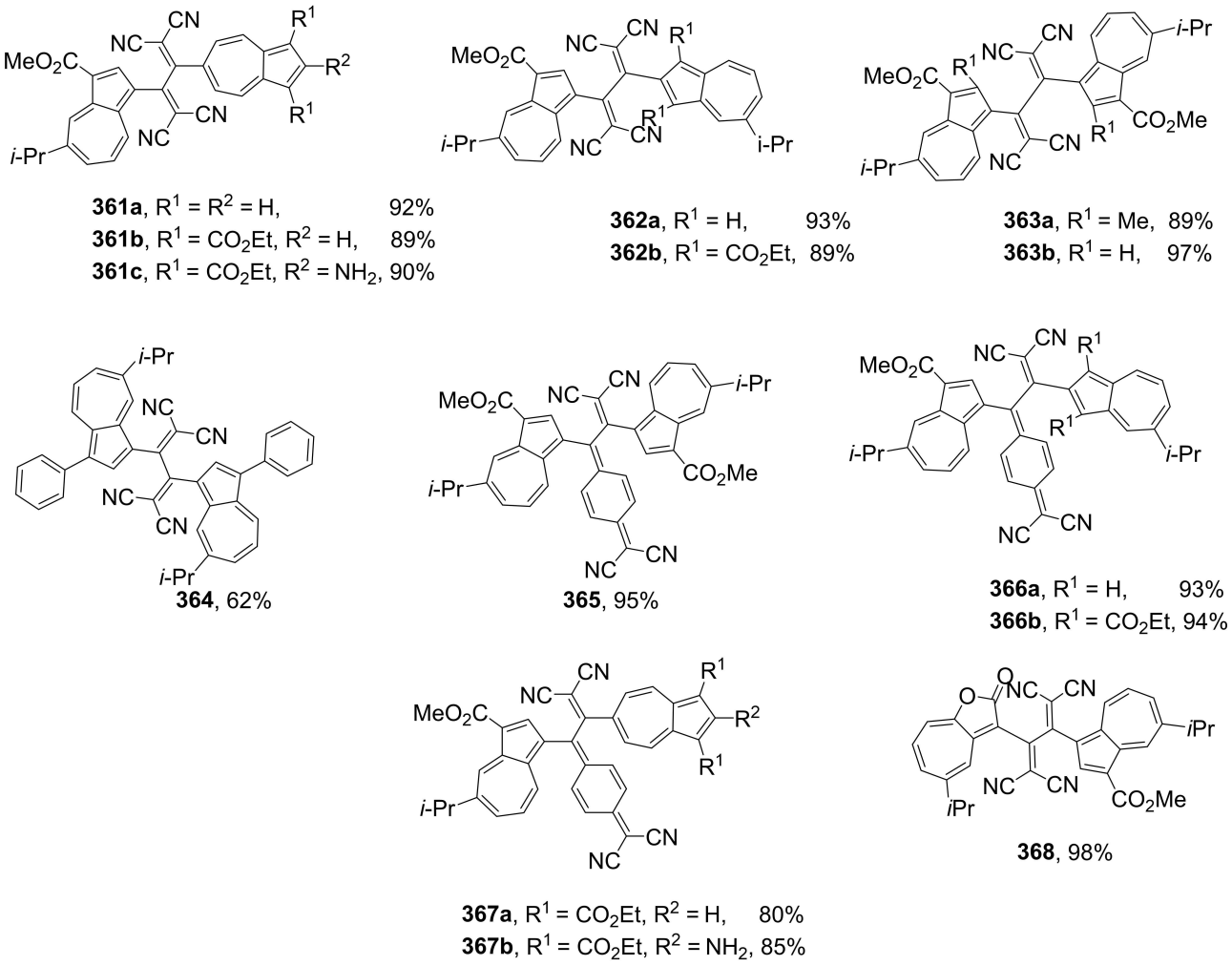


Figure 61. Structures of AzTCBDs and AzDCNQs **361**–**368** from bis-azulenyl ethynes.

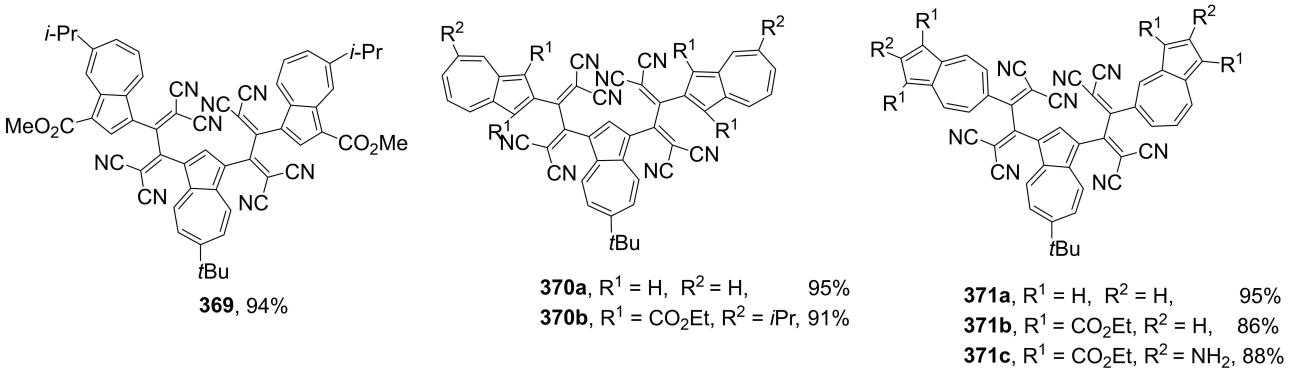


Figure 62. Structures of AzTCBDs **369**–**371** from *bis*-azulenylethynylazulenes.

et al.;[135] initially, the usual cross-coupling reaction of 1-iodoazulenes with 2-ethynylphenol proceeds to form 1-ethynylazulene intermediates with a phenol substituent at the alkyne terminus, which gave the arylpalladium species **309** by the coordination to their alkyne moiety, and then the intramolecular nucleophilic addition of the oxygen nucleophile occurred to afford **310** followed by reductive elimination to give the 2,3-bis(1-azulenyl)benzofuran derivatives **307** (Scheme 74).

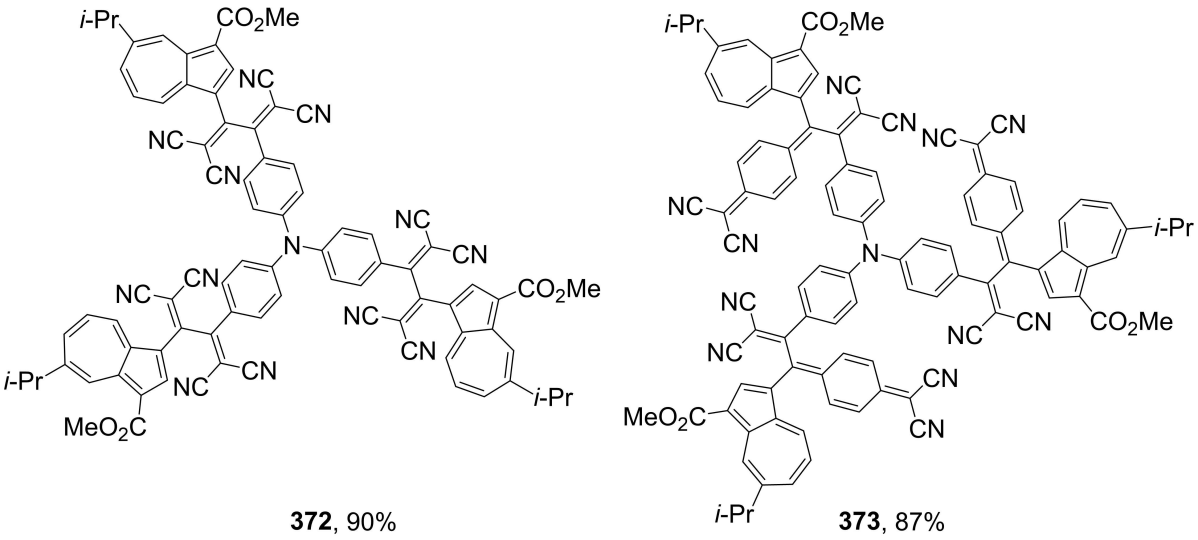


Figure 63. Structures of AzTCBDs and AzDCNQs **372** and **373** from polyazulenylethynyl linked to triphenylamine.

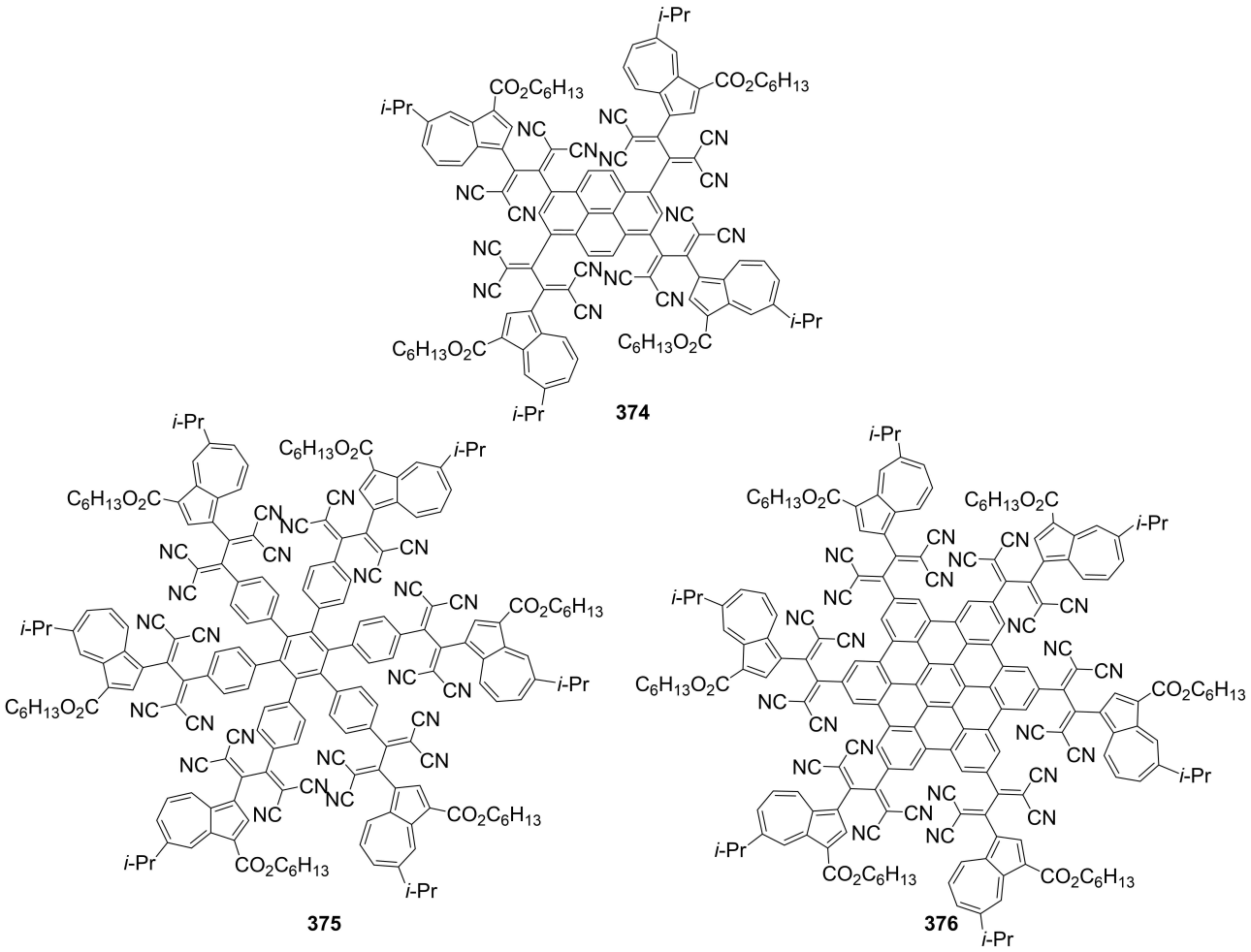
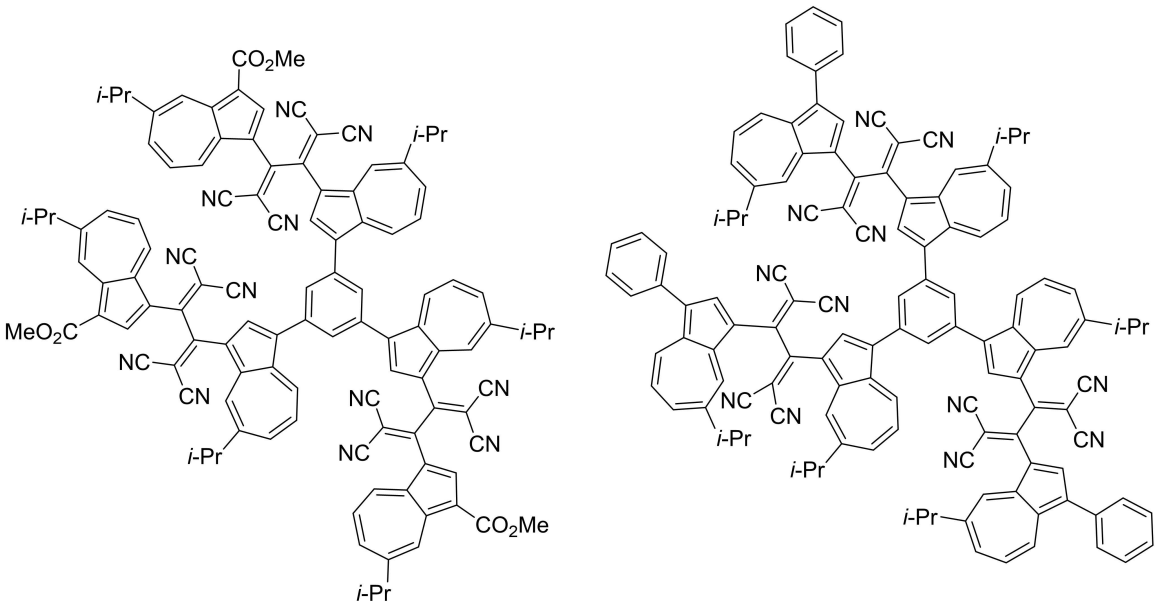


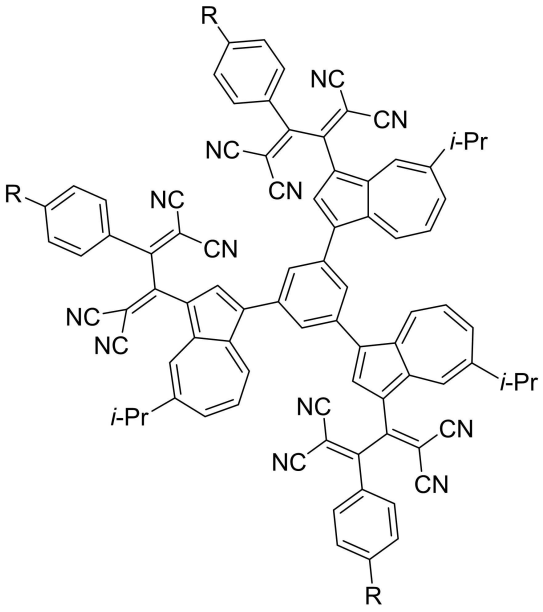
Figure 64. Structures of AzTCBDs **374**–**376** from polyazulenylethynyl linked to polyaromatic compounds.



377, 85%

378, 93%

Figure 65. Structures of AzTCBDs **377** and **378** from polyazulenylethynyl linked to triazulenylbenzene.



379a, R = H, 100%
79b, R = NMe_2, 88%
379c, R = NO_2, 97%

Figure 66. Structures of AzTCBDs **379a–c** from polyarylethynyl linked to triazulenylbenzene.

3.10.2. Synthesis of 3-(azulen-1-yl)isochromene

The intramolecular cyclization of alkynes **99a–d** in the presence of trifluoroacetic acid produced the corresponding 1-azulenylisocoumarin derivatives **311a–d** in good to excellent yields (Scheme 3). The synthesis of azulene-substituted 4-iodoisocoumarin derivatives **312a–d** was investigated by the iodocyclization reaction of **99a–d** with *N*-iodosuccinimide (NIS) (Scheme 75).[24]

3.10.3. Synthesis of azuleno[2,1-b]thiophenes

The reaction of several azulenylalkynes having an aryl substituent with elemental sulfur in DMF at 110 or 140 °C afforded the corresponding azuleno[2,1-*b*]thiophenes **313a–m** in moderate to good yields (Scheme 76). The structural features of the azuleno[2,1-*b*]thiophene derivatives were revealed by X-ray single-crystal analysis. The optical and electrochemical properties of the azuleno[2,1-*b*]thiophene derivatives were investigated by UV/Vis spectroscopy, voltammetry experiments and theoretical calculations.[136]

The more plausible reaction route for the formation of azuleno[2,1-*b*]thiophenes from azulenylalkyne derivatives could be represented as shown in scheme 65. Initially, the reaction is started by the electrophilic reaction of the alkyne moiety with (S8) to produce intermediate **314**, in which the cation at the vinyl moiety is stabilized by the conjugation with the azulene ring. Then, **314** is transformed into thiolate ion **315** by the elimination of extra sulfur atoms. The nucleophilic reaction of the thiolate ion **315** to the 2-position of the azulene ring followed by the protonation by residual water in DMF affords the dihydrothiophene intermediate **316**, which isomerizes to the more stable tertiary cation **317** by a 1,2-hydride shift. Eventually, the azuleno[2,1-*b*]thiophene derivative **313** is generated from **317** by the deprotonative aromatization (Scheme 77).[136]

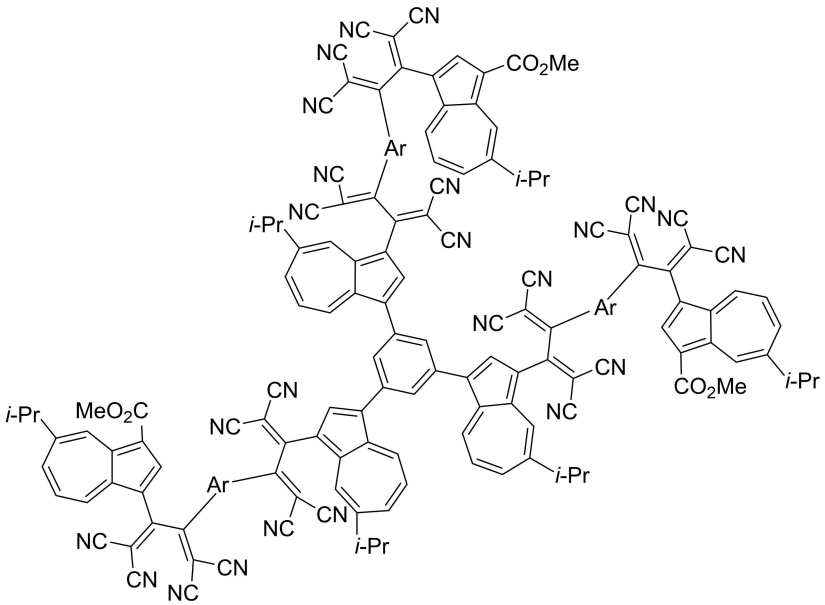


Figure 67. Structures of AzTCBDs **380 a** and **380 b** from polyazulenylethynylarylethynyl linked to triazulenylbenzene.

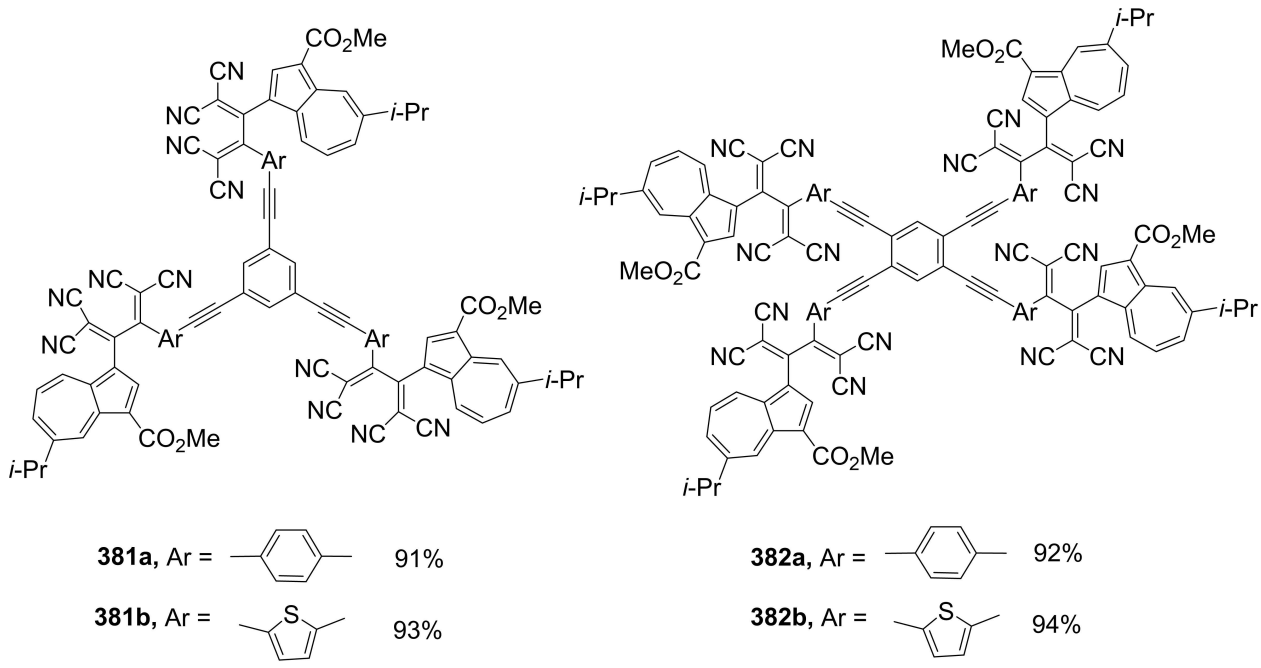


Figure 68. Structures of AzTCBDs **381** and **382** from polyazulenylethynylaryl linked to tris- and tetrakis-ethynylbenzene.

3.10.4. Synthesis of azuleno[2,1-b]pyrrole

Abe *et al.* have achieved two-step synthesis of pyrrole-fused azulene derivative **318** in 72% yield by cyclization of **93** in the presence of $PdCl_2(PPh_3)_2$ and Et_3N as a base in DMF *via* the elimination of the acetyl group on the nitrogen atom (Scheme 78).[26]

3.10.5. Synthesis of 3-(azulen-1-yl)-1H-azuleno[1,2-c]pyran

Metal-free hydration of diethyl 2-((5-isopropyl-3-(methoxycarbonyl)azulen-1-yl)ethynyl)azulene-1,3-dicarboxylate **220b** using trifluoroacetic acid as a Brønsted acid afforded the ethyl 3-(5-isopropyl-3-(methoxycarbonyl)azulen-1-yl)-1-oxo-1*H*-azuleno[1,2-c]pyran-5-carboxylate **319** in 90% yield (Scheme 79).[134]

3.10.6. Synthesis of 2-[1,3-bis(ethoxycarbonyl)azulen-6-yl] benzoazoles

Morita *et al.* reported the synthesis of 2-[1,3-bis(ethoxycarbonyl) azulen-6-yl]benzoazoles **321a** and **321b** by the reaction of 2-[3-(methoxycarbonyl)azulen-1-yl]ethynyltriphenyl- phosphonium bromide **320** with the appropriate *o*-substituted anilines in $CHCl_3$. Compound **320** was obtained from diethyl 6-ethynyl-1,3-azulenedicarboxylate firstly by the reaction with NBS to give diethyl 6-(bromoethynyl)azulene-1,3-dicarboxylate followed by treatment with PPh_3 (Scheme 80).[137]

3.10.7. Synthesis of azuleno[5′,6′:3,4]cyclobuta[1,2-d]dibenzo[b,f]silepine

Very recently, Tsuda *et al.* developed a palladium-catalyzed synthesis of 5*H*-azuleno[5′,6′:3,4]cyclobuta[1,2-*d*]dibenzo[*b,f*] silepine **324** as a class of potentially useful silicon-bridged π-conjugated compounds. The reaction proceeds *via* Pd-catalyzed cyclization of 3-((1,3-bis(ethoxycarbonyl)azulen-6-yl)ethynyl)-2-(*tert*-butyldiphenylsilyl) trifluoromethanesulfonate **323**. The reaction sequence is composed of 1,*n*-palladium migrations and unusual *anti*-carbopalladation of alkynes.[138] Compound **323** was obtained by Pd-catalyzed reaction of 6-bromoazulene **42b** with 2-(*tert*-butyldi(phenyl)silyl)-3-(ethynyl)phenyl trifluoromethanesulfonate **322** (Scheme 81).

3.11. Synthesis of azulene-substituted redox-active chromophores

Thermal [2 + 2] cycloadditions of tetracyanoethylene (TCNE) with electron-rich alkynes yield cyclobutenes, which have been shown to undergo retro-electrocyclization to form 1,1,4,4-tetracyanobuta-1,3-dienes (TCBDs). This class of chromophores features intense intramolecular charge transfer (CT) interactions with absorption maxima in the visible spectral range as well as promising third-order optical nonlinearities.[139] The 1-position of the azulene ring possesses electron-donating properties with high reactivity toward electrophilic substitution reactions. Thus, 1-ethynylazulene derivatives should be expected to afford [2 + 2] cycloaddition products with TCNE. The optical and electrochemical properties of the AzTCBDs were clarified by UV/Vis and voltammetry. The AzTCBD derivatives exhibited electrochromism, showing a multi-step color change under electrochemical redox conditions. The multistage redox properties of AzTCBDs could be useful for the development of novel organic electronic materials.

In this section, we collected all the reported azulene-substituted redox-active chromophores, prepared by the [2 + 2] cycloaddition/cycloreversion reactions of the appropriate azulene-substituted ethynes with tetracyanoethylene (TCNE) or 7,7,8,8-tetracyanoquinodimethane (TCNQ).[23,74,100,140] The TCNE/TCNQ double adducts could also be prepared both by stepwise and also by one pot cascade reactions with TCNE and TCNQ.

3.11.1. Synthesis of AZTCBDS and AZDCNQS

3.11.1.1. From 1-ethynylazulenes

Reaction of 1-ethynylazulene **13** with tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) in a formal [2 + 2] cycloaddition-retroelectrocyclization reaction in ethylacetate at reflux afforded the corresponding new tetracyanobutadienes (TCBDs) **325** and dicyanoquinodimethanes (DCNQs) **326**, respectively, in excellent yields (Scheme 82).[105]

3.11.1.2. From aryl/heteroaryl-substituted -ethynylazules

Similarly, [2 + 2] cycloaddition-retroelectrocyclization reaction of aryl/heteroaryl-substituted-ethynylazules with tetracyanoethylene and 7,7,8,8-tetracyanoquinodimethane afforded the corresponding tetracyanobutadienes (TCBDs) and dicyanoquinodimethanes (DCNQs), **327**–**332**, in excellent yields. The results imply that the steric hindrance of the 2-methyl moiety on the azulene ring have a little effect on the [2 + 2] CA-RE reaction (Figure 54).[25,61,64]

Although, the reaction of **91f** with TCNE in refluxing EtOAc yielded **327e** in 97% yield as the sole product, reaction of **91f** with TCNQ led to the formation of compounds **330e** and **333** in 43% and 48% yields, respectively (Scheme 5).[62] Recently, Diederich *et al.* have reported that the regioselectivity of [2 + 2] cycloadditions of C≡C triple bonds with TCNQ correlates to the electrondonating property of the substituent on the ethynyl group.[141] Thus, the reduced selectivity for generation of **330e** and **333** suggests that the 1-azulenyl group in **91f** possesses almost the same electron-donating character as that of the *N,N*-dimethylanilino (DMA) group (Scheme 83).

Although the reaction of 2-ethynyl- and 2-phenylethynylazulenes with TCNE did not afford the corresponding TCBD derivative, since the 2-azulenyl moiety is an unfavorable activating group toward the [2 + 2] CA-RE reaction. Contrary to these results, compound **106** reacted with TCNE at room temperature to afford the corresponding TCBD derivative **334** in 94% yield, despite the deactivation of the alkyne moiety by the adjacent two electron-withdrawing groups.[68] Generation of **334** in high yield under the mild condition should be attributed to the strong electron-donating property of the pyrrolidinyl group at the 6-position that enhances the reactivity of the alkyne moiety of **106** (Figure 55).[139]

Shoji *et al.* used a similar approach to synthesize a variety of AzTCBDs and AzDCNQs.

3.11.1.3. From Ferrocenyl-substituted -ethynylazules

See Figure 56.[73]

3.11.1.4. From naphthalene/pyrene-substituted -ethynylazules

See Figure 57.[65,66]

3.11.1.5. From bis(azulenylethynyl) linked to arenes or heteroarenes

See Figure 58.[23,61,100,140]

3.11.1.6. From bis(azulenylethynyl) linked to naphthalenes or pyrenes

See Figure 59.[53,66]

3.11.1.7. From bis(azulenylethynyl) linked to diphenylamine, carbazole and azobenzene

See Figure 60.[62,64]

3.11.1.8. From bis(azulenyl)ethynes

See Figure 61.[64,103,105]

3.11.1.9. From bis(azulenylethynyl)azulenes

See Figure 62.[108]

3.11.1.10. Synthesis of star-shaped AzTCBDs and AzDCNQs

3.11.1.10.1. From poly(azulenylethynyl) linked to triphenylamine

See Figure 63.[62]

3.11.1.10.2. From poly(azulenylethynyl) linked to polyaromatic compounds

See Figure 64.[66]

3.11.1.10.3. From poly(azulenylethynyl) linked to triazulenylbenzene

See Figure 65.[25,97]

3.11.1.10.4. From poly(arylethynyl) linked to triazulenylbenzene

See Figure 66.[25]

3.11.1.10.5. From poly(azulenylethynylarylethynyl) linked to triazulenylbenzene

See Figure 67.[97]

3.11.1.10.6. From poly(azulenylethynylaryl) linked to tris- and tetrakis-ethynylbenzene

See Figure 68.[61]

3.11.1.11. From 1-(phenylbuta-1,3-diyn-1-yl)azulene[100]

The reaction of **202** with TCNE in ethyl acetate at room temperature yielded **383** in 95% yield. Subsequent [2+2] cycloaddition reaction of the remaining ethynyl moiety of **383**, contiguous to the phenyl group, with excess TCNE did not proceed even under reflux conditions in DMF. These results indicate the low reactivity of the C≡C triple bond attached to the highly electron-withdrawing TCBD moiety. The synthesis of the TCNE/TTF (tetrathiafulvalene) double adduct **385** was achieved in 92% yield by the [2+2] cycloaddition reaction of **383** with TTF **384** (Scheme 84). The one-pot cascade reaction of **202** with TCNE and TTF also gave **385** in 70% yield, which corresponds to an 84% yield in each step. However, the cascade reaction requires a tedious separation process.[100]

3.11.1.12. From 1,4-di(azulen-1-yl)buta-1,3-diyne

Likewise, the reaction of butadiyne **242b** with TCNE at room temperature afforded TCBD **386** in 97% yield. The subsequent [2+2] cycloaddition of **386** with TCNE under reflux conditions in 1,1,2,2-tetrachloroethane afforded the double TCNE-adduct **387** in 71% yield, along with the novel 6,6-dicyanofulvene derivative **388** in 22% yield (Scheme 85).[66]

3.11.1.13. From 1,4-bis(azulen-1-ylbuta-1,3-diyn-1-yl)benzene

The reaction of **205** with TCNE afforded the bis-adduct **389** in 95% yield. The reaction of **389** with TTF did not afford the TCNE/TTF double adduct but led instead to the formation of an insoluble complex mixture (Scheme 86). It should be attributed to instability of the compound under the reaction conditions.[100]

3.12. Reaction of functionalized ethynylazulene with TCNE

3.12.1. Synthesis of 2-((1H-pyrrol-3-yl)(azulen-1-yl)methylene) malononitrile

Shoji *et al.* described an efficient and atom economical synthesis of highly functionalized pyrroles **391** in 76–98% yield, by [2 + 2] cycloaddition-retroelectrocyclization of propargylamines **22a–h** having *N*-tosyl substituent with tetracyanoethylene, followed by the treatment of the intermediately obtained tetracyanobutadiene derivatives **390** with silica gel. In this reaction, silica gel plays an important role to promote the intramolecular cyclization to afford the heterocyclic products from the tetracyanobutadiene intermediates (Scheme 87).[30]

3.12.2. Synthesis of ((5-(azulen-1-yl)-2,4-dicyanocyclopenta-2,4-dien-1-ylidene) methyl)carbamate

The reaction of *tert*-butyl (3-(azulen-1-yl)prop-2-yn-1-yl) carbamate **23a–i** with TCNE, afforded pentafulvene derivatives **392a–i** in good to excellent yields. The corresponding pentafulvenes were obtained in high yields with azulenes possessing an electron-withdrawing group, but the reaction of azulenes having an electron-donating group resulted in lower product yields due to the decomposition of the products during the treatment with silica gel (Scheme 88).[30]

3.12.3. Synthesis of 7-(1-(azulen-1-yl)-2,2-dicyanovinyl)-1H-pyrrolo[3,2-b]pyridine

The reaction of iodoazulene **393a–e** with propargylamines **394** led to the formation of 3-(azulen-1-yl)-*N*-methylprop-2-yn-1-amine **395a–f** which then underwent reaction with TCNE and subsequent treatment with silica gel gave pyrrolopyridine derivatives **396a–e**, unexpectedly, in moderate yields. The products indicate that the propargylamines having *N*-Me substituent reacted with two TCNE molecules, except for the reaction of **393f** which produced the pyrrole derivative **397** under the same reaction condition in 48% yield (Scheme 89).[30]

3.12.4. Synthesis of 2-((Furan-3-yl)(azulen-1-yl)methylene) malononitrile

Shoji *et al.* reported that the [2 + 2] cycloaddition-retroelectrocyclization of 3-(1-azulenyl)-2-propyn-1-ols **24** with TCNE, followed by intramolecular nucleophilic addition of the hydroxyl group to the initially formed tetracyanobutadiene TCBD moiety led to the formation of 2-((furan-3-yl)(azulen-1-yl) methylene)malononitrile **398a–h**. The reaction proceeds under milder conditions with a short reaction time without metal catalyst (Scheme 90).[29]

Presumed reaction mechanism for the formation of **398** is illustrated in Scheme 91. The reaction commences with the formal [2 + 2] cycloaddition of the alkyne **24** with TCNE to form strained cyclobutene derivative **399**, followed by ring-opening by retroelectrocyclization of the cyclobutene ring to give the TCBD derivative **400**. Intramolecular nucleophilic addition of the hydroxyl group to the cyano moiety in TCBD **400** results in the dihydrofuran **401**, which then tautomerize to form **398**. Since the TCBD **400** is not obtained in the reaction, intramolecular nucleophilic addition to form **401** should be a faster process than that of the formal [2 + 2] CA-RE to form TCBD **401** (Scheme 91).[29]

4. Conclusions

This review provides an overview of the so far known approaches to the synthesis of mono- and polyethynylazulenes and the diversity of their chemical transformations. Efficient ethynylation of azulene at the five-membered or the seven-membered ring are performed by Pd-catalyzed cross-coupling under Sonogashira conditions, Cory-Fuchs reaction for the conversion of aldehydes into acetylenes or by the reaction of chloroazulenes with lithium acetylide in liquid ammonia.

The reactions discussed in this report demonstrate that ethynylazulenes are interesting building blocks for the synthesis of ethynylazulene-substituted benzenes as well as oligoazulenes with ethynyl and/or butadiynyl bridges by Pd-catalyzed cross-coupling reaction and by Cu-mediated Eglinton, Hay cross- and Glaser homo-coupling conditions.

Moreover, cyclooligomerization of ethynylazulenes in the presence of Co-catalyst proved to be a useful protocol for the synthesis of azulenyl-substituted benzenes as well as cyclobutadiene complexes. Diels-Alder reaction of azulenyl-substituted acetylene with tetraphenylcyclopentadienone offer another interesting route to azulenyl- and polyazulenylbenzene derivatives.

Furthermore, the reactivity of mono- and poly[(azulenyl) ethynyl]benzene derivatives towards the [2 + 2] cycloaddition/cycloreversion reactions with TCNE as well as TCNQ to give the corresponding buta-1,3-dienes as new class of charge-transfer chromophores have also been dicussed. Ethynylazulene derivatives have also been utilized for the synthesis of azulene-substituted heterocycles for applications in materials science by taking advantage of their unique properties.

It seems likely that ethynylazulenes could be interesting building blocks for new materials with unprecedented properties and useful different applications.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Ethynylazulenes · Synthesis · Cross-coupling · Cycloaddition · Cyclooligomerization · Palladium Catalyst · Cobalt Catalyst

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