▮ Gold Catalysis

Gold-Catalyzed Regiospecific Annulation of Unsymmetrically Substituted 1,5-Diynes for the Precise Synthesis of Bispentalenes

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Abstract: Precise control of the selectivity in organic synthesis is important to access the desired molecules. We demonstrate a regiospecific annulation of unsymmetrically substituted 1,2-di(arylethynyl)benzene derivatives for a geometry-controlled synthesis of linear bispentalenes, which is one of the promising structures for material science. A gold-catalyzed annulation of unsymmetrically substituted 1,2-di(aryl-ethynyl)benzene could produce two isomeric pentalenes, but both electronic and steric effects on the aromatics at the terminal position of the alkyne prove to be crucial for the selectivity; especially a regiospecific annulation was achieved with sterically blocked substituents; namely, 2,4,6-trimethyl benzene or 2,4-dimethyl benzene. This approach enables the geometrically controlled synthesis of linear bispentalenes from 1,2,4,5-tetraethynylbenzene or 2,3,6,7-tetraethynylnaphthalene. Moreover, the annulation of a series of tetraynes with a different substitution pattern regioselectively provided the bispentalene scaffolds. A computational study revealed that this is the result of a kinetic control induced by the bulky NHC ligands.

Introduction

Antiaromatic molecules have received much attention due to unique optoelectronic properties. Pentalene as well as the structurally similar indenofluorene[1] is one of the important core structures for material science. Due to the low stability of the pure pentalene core,[2] various syntheses of dibenzo[a,e]-

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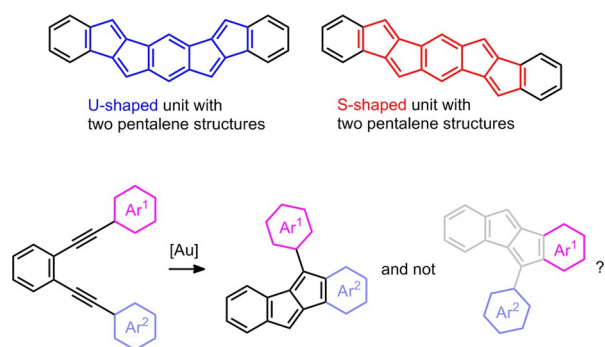69120 Heidelberg (Germany)
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pentalenes, which are stabilized by the fused aromatic moieties, have been developed.[3] The properties of pentalene are of high interest for organic semiconductors. Especially, π-extended pentalenes prove to act as p- or n-type organic transistors, although tuning optoelectronic properties by the introduction of functional groups are still desirable for higher performance.[4] Therefore, the development of modular synthetic methods to access polycyclic π-extended pentalenes is a promising research topic.

Homogeneous gold catalysis has received much attention, and due to the mild carbophilic π Lewis acidity of the gold catalyst, the field majorly contributed to the intensive development of nucleophilic addition reactions to unsaturated carbon–carbon multiple bonds.[5] For instance, the gold-catalyzed annulation of diyne compounds enabled the synthesis of extended π-conjugated compounds, such as azahelicene, polycyclic indole and benzothiophen derivatives.[6] Our recent work also contributed to the gold-catalyzed synthesis of dibenzo[a,e]pentalene and quinoxaline/phenazine-fused pentalene derivatives from 1,5-diynes.[3n,t] Moreover, the gold catalyst led to both U-shaped and S-shaped bispentalenes from the readily available tetra(arylethynyl)benzenes and -naphthalenes, albeit fortunately those mixtures could be separated (Scheme 1, top).[4e] During that study, the naphthalene-based linear bispentalene (S-shaped) was found to be a highly suitable scaffold for transistor applications. In these symmetric tetraynes, however, the chemoselectivity towards U-shaped and S-shaped bispentalenes is not controlled. Unsymmetrically substituted diynes or tetraynes as substrates could be a method to selectively synthesize specific isomers, still it is unknown whether the selectivity will be pronounced enough to deliver only one

Scheme 1. Possible selectivity control by different aryl groups in the gold-catalyzed annulation of unsymmetrically substituted 1,5-diynes.

isomer (Scheme 1, bottom). From the synthetic point of view, it would be interesting to see if the reaction of unsymmetrical-ly substituted 1,5-diynes can be controlled by electronic or steric effects, which would allow to control the precise regio-chemistry and thus the geometry in the synthesis of pentalene derivatives. Herein, we report a study of selectivity control in the gold-catalyzed annulation of unsymmetrically substituted 1,5-diynes, and the use of these principles in the regiospecific synthesis of S-shaped benzene- and naphthalene-based bis-pentalenes by an "inside-out" bidirectional approach. In addition, we investigated an "outside-in" mode of cyclization, tet-raynes with different substitution patterns successfully provid-ed bispentalenes, which with respect to the overall synthetic route represents a much more convergent and thus flexible approach. The opto-electronic properties of the obtained bis-pentalene derivatives are also reported.

Results and Discussion

During the annulation of a symmetric 1,5-diyne, one alkyne acts as a nucleophile and the other alkyne as the electrophile. If electron-rich and electron-deficient alkynes are arranged in an unsymmetrical substrate, the annulation could proceed re-giospecifically. We first prepared the unsymmetrically substitut-ed diynes 1 with methoxy (1a), fluoro (1b), and trifluoromethyl substituents (1c), and attempted the gold-catalyzed reactions with them (Table 1). The annulation of methoxy-substituted

Table 1. Electronic effect on the selectivity.

Entry[a]	R		Time [h]	Yield [%][b]	2:3[c]
1	OMe	1a	1	40	96:4
2	F	1b	1	62	42:58
3	CF$_3$	1c	16	29	6:94

[a] 1 (0.05 mmol), catalysts (0.005 mmol) in solvent (1 mL). [b] Combined yield of 2 and 3. [c] Determined by ^{1}H NMR of the crude mixture.

diyne gave a mixture of isomers 2a and 3a in 40% yield with a ratio of 96:4 (entry 1). Fluoro-substituted diyne 1b afforded isomers 2b and 3b in 62% yield in a ratio of 42:58 (entry 2). When a trifluoromethyl group (1c), which is a strong electron-withdrawing group, was attached to the aromatic ring, the ratio of 2c and 3c was 6:94 (entry 3). Overall, the results dem-onstrated that the selectivity can be controlled by the elec-tronic properties with the electron-rich alkyne acting as nucle-ophile, while the electron-deficient alkyne serves as the elec-trophile, even though the yield lower and the isomers are in-separable.

To explore another mode of substituent control of the selec-tivity, two o-positions of the aryl group on the alkyne were blocked by methyl groups, which probably inhibits the ap-proach of the gold catalysts to the sterically more hindered alkyne, even though a cyclization of the vinyl cation and mesi-tylene followed by a 1,2-methyl shift might still be possible. The gold catalysts promoted the reaction of the diyne 1d and afforded the desired pentalene 2d in 94% yield (Table 2,

Table 2. Reaction of mesitylene-substituted diynes.

Entry[a]	Ar	R		Time [h]	Yield [%][b]
1	mesityl	H	1d	1	94
2	mesityl	OMe	1e	3	63
3[c]	mesityl	CF$_3$	1f	20	41
4	mesityl	Br	1g	20	60
5	2,4-dimethylbenzene	H	1h	1	91

[a] 1 (0.05 mmol), catalysts (0.005 mmol) in solvent (2 mL). [b] Isolated yield. [c] 40 °C.

entry 1). Methoxy- or trifluoromethyl-substituted diynes 1e and 1f were also converted to pentalenes 2e and 2f in 63 and 41% yield, respectively (entries 2 and 3). The annulation of bromo-substituted diyne 1g gave pentalene 2g in 60% yield, which could be useful for further transformations by common coupling reactions (entry 4). The mesityl group indeed enables a control of the pentalene synthesis. It is interesting to note that the reaction of the 2,4-dimethylbenzene-substituted diyne 1h resulted in the clean formation of the corresponding penta-lene 2h in 91% yield and no generation of the pentalene 3h (entry 5). As shown in Scheme 2, the gold-catalyzed reaction of diyne 1h possibly leads to two intermediates Ia and Ib. Vinyl cation intermediate Ib might be unfavorable because the cycli-zation of Ib, which should proceed through a planar configu-ration is probably prohibited by the steric hindrance between the gold catalyst and the o-methyl substituent of the aromatic moiety. This results in the selective formation of 2h. This step could be crucial for controlling the reaction of the mesitylene-substituted diyne 1d. Overall, those results indicated that re-giospecific annulation was achieved by the introduction of a mesityl group or 2,4-dimethylbenzene.
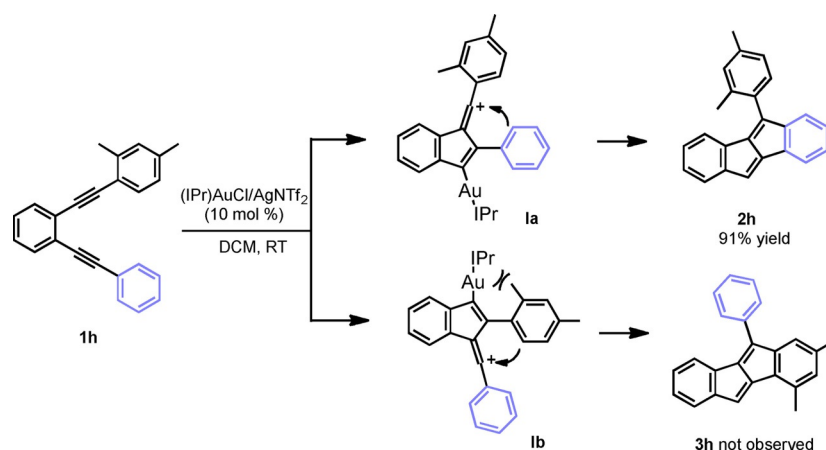
Scheme 2. Gold-catalyzed reaction to form pentalene **2 h**.
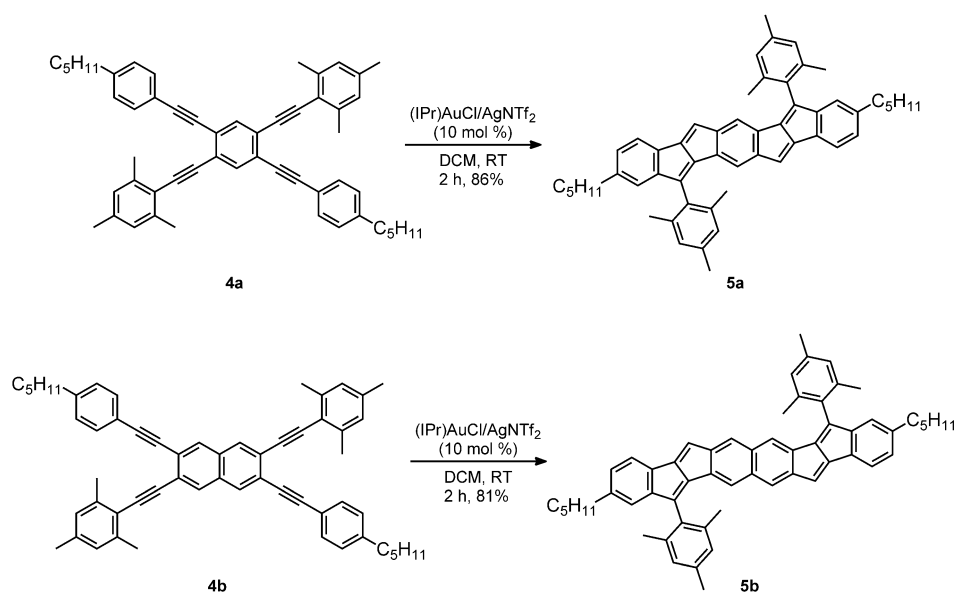
Scheme 3. Top) Gold-catalyzed annulation of 1,2,4,5-tetra(ethynyl)benzene (**4 a**), and bottom) 2,3,6,7-tetra(ethynyl)naphthalene (**4 b**) .

Based on the results with the diynes being blocked at the *o*-positions, the selective synthesis of S-shape bispentalenes should be feasible. We then designed and synthesized the benzene- and naphthalene-based tetraynes **4 a** and **4 b** with mesitylene (Scheme 3). The tetraynes **4 a** and **4 b** were conveniently prepared by sequential Sonogashira-coupling reactions of 1,4-dibromo-2,5-diiodobenzene or 3,7-dibromonaphthalene-2,6-diyl-bis(trifluoromethanesulfonate). Using (IPr)AuCl/AgNTf$_2$, the benzene-based tetrayne **4 a** was completely consumed within 2 h, the corresponding linear bispentalene **5 a** was obtained in 81% yield as a reddish-brown solid. In addition, the annulation of naphthalene-based tetrayne **4 b** with (IPr)AuCl/AgNTf$_2$ proceeded at room temperature and gave the linear bispentalene **5 b** in 86% yield as a red solid.

The connectivity of **5 b** in the solid state was confirmed by X-ray crystallography (Figure 1). Due to the mesityl group, the
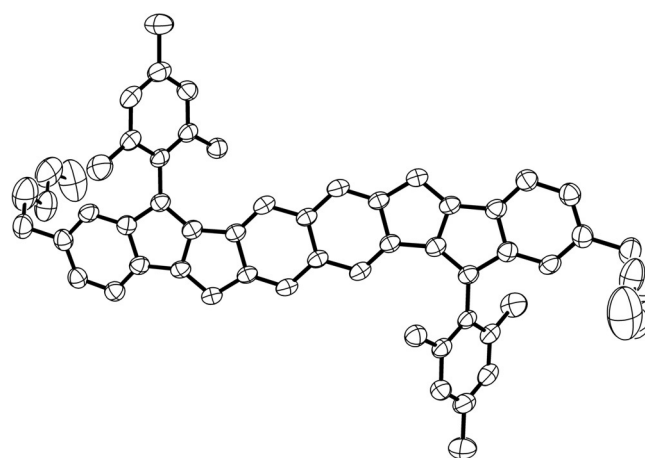

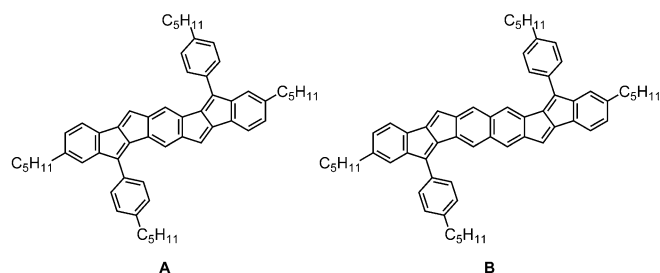**Figure 1.** Solid-state molecular structure of **5 b**.

Figure 2. Previously reported bispentalenes **A** and **B**.

Figure 3. Solid-state molecular structure of **8 a**.

previously reported *n*-pentyl substituted S-shape bispentalene **B** (Figure 2)[4e] shows significantly smaller torsion angles (34.2–37.9°) between the pentalene core and the peripheral aryl group than pentalene **5 b** (63.5–69.3°).

We considered tetrayne **6 a**, having a different substitution pattern, as another approach to access the bispentalene scaffold. It could potentially afford two isomers, **7 a** and **8 a**, because the second annulation could occur on both carbon atoms of the intermediate **II a** (Scheme 4). Indeed, the intramolecular annulation with 5 mol% of gold catalysts in dichloroethane afforded pentalenes **7 a** and **8 a** in 20 and 72% yield, respectively. The structure of **8 a** was unambiguously confirmed by single-crystal X-ray crystallography (Figure 3). Interestingly, the pentalene core and the peripheral mesityl group are nearly vertical and the two mesityl groups are parallel.

When the cyclization of **6 a** was performed using (IPr)AuCl/AgNTf2, isomers **7 a** and **8 a** were produced in a 22:78 ratio. In our previous report,[4e] the bulkiness of the ligand had a significant effect on the ratio of the resulting bispentalene isomers. Therefore, a set of differently sized ligands on the catalysts was investigated to prove this effect on the selectivity of isomeric bispentalenes **7 a** and **8 a.** Pre-activated [(IPr)Au(NCMe)]SbF6 and [(IPr)Au]NTf2 catalysts[7] gave the same results as (IPr)AuCl/AgNTf2 (Table 3, entries 2 and 6). On the other hand, the PPh3 ligand only gave poor yields of the products **7 a** and **8 a** (entry 3). No reaction took place with a nitrogen acyclic carbene (NAC) complex (entry 4). As expected, no reaction occurred in the complete absence of a gold catalyst, using only
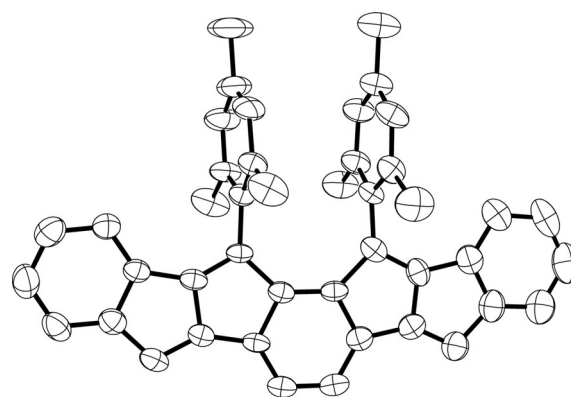
Table 3. Examination of different ligands on the gold catalysts with substrate **6 a**.

Entry[a]	Catalyst	Time [h]	Yield [%][b] **7 a:8 a**	Ratio **7 a:8 a**
1	(IPr)AuCl/AgNTf2	2	20:72	22:78
2	[(IPr)Au(NCMe)]SbF6	1.5	21:72	23:77
3	Ph3PAuNTf2	3	15:55	21:79
4	NACAuCl/AgSbF6	4	ND	ND
5	(IPr)*AuCl/AgNTf2	3.5	62[c]	4:96[d]
6	[(IPr)Au]NTf2	2.5	18:71	20:80
7	AgNTf2	4.5	ND	ND

[a] Reaction performed in a vial in DCE (1 mL), **6 a** (0.02 mmol) and catalyst (0.005 mmol). [b] Isolated yield. [c] Combined yield of **7 a** and **8 a**. [d] Determined by 1H NMR.
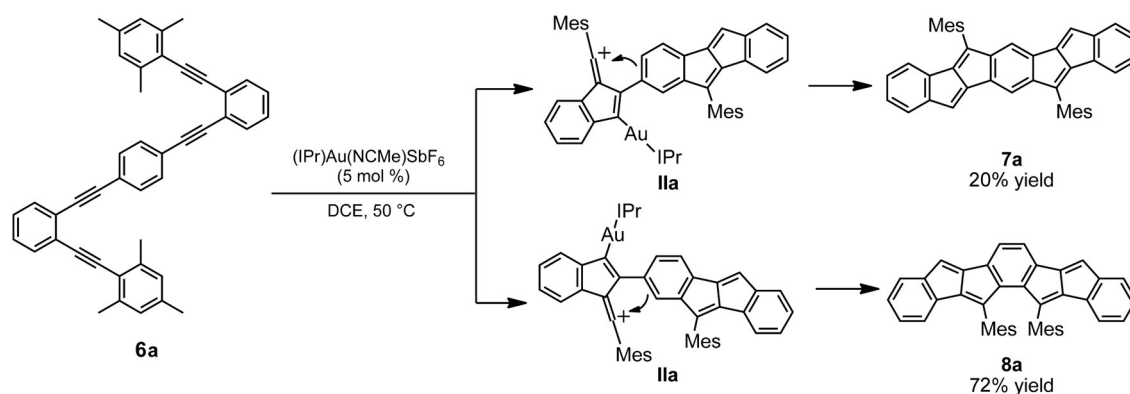
Scheme 4. Gold-catalyzed reaction to form bispentalenes **7 a** and **8 a**.

AgNTf₂ (entry 7). The short ligand screening finally revealed that the sterically bulky IPr* ligand[8] increases the ratio of pentalen **8a** (entry 5). This can be rationalized by the steric hindrance between the mesitylene substituent and the gold complex on the intermediate **IIa**, which ultimately leads to the formation of product **8a**.

The selective formation of **8a** was investigated by using M06-2X-CPCM/BS2//B3LYP-CPCM/BS1 calculations. It was found that the selectivity is mainly controlled by a steric repulsion between the mesityl substituent and the IPr ligand in **TS-1b** (Figure 4). This destabilizing interaction is absent in **TS-1a**, causing this transition structure to be 0.3 kcal mol⁻¹ lower in energy than in **TS-1b**. To support this assertion, the IPr carbene ligand was replaced by the IMe carbene ligand, in which the bulky N-substituents of IPr are replaced by methyl groups. The results starting from this new model system are shown in Figure 5. In contrast to the real system in which **TS-1a** is calculated to be slightly lower in energy than **TS-1b**, for the less bulky model system, the energy order of the transition structures becomes reversed. In this case, **TS-1b-M** is calculated to be 2.0 kcal mol⁻¹ lower in energy than **TS-1a-M** (Figure 5). The energy order of transition structures **TS-1b-M** and **TS-1a-M** is most likely set by the thermodynamic aspects of the transformation. Indeed, **7a** is about 6 kcal mol⁻¹ more stable than **8a**, resulting in **TS-1b-M** lying lower in energy than **TS-1a-M**. Thus, although the formation of **7a** is thermodynamically fa-

vored over **8a**, the steric interaction between the IPr ligand and the Mes substituent in **TS1-b** leads to less **7a** than **8a** being formed.

Figure 4 shows quite similar energy values of **TS-1a** and **TS-1b** with **TS-1a** being lower in energy by 0.3 kcal mol⁻¹. This is consistent with the experimental 22:78 ratio of the two products. Figure 5 shows a higher difference in energy for **TS-1a-M** and **TS-1b-M** with a reversed order, now with **TS-1b-M** being lower. Since the repulsive interactions of the two aryl substituents in **TS-1a** and **TS-1a-M** are almost identical, this clearly indicates that the ligand–aryl steric interaction in **TS-1b** is stronger than that in **TS-1b-M**.

Next, several electron-withdrawing and electron-donating substituents on the aromatic moieties were investigated using [(IPr)Au(NCMe)]SbF₆ as the catalyst. In the case of tetrayne **6a**, the gold-catalyzed reaction afforded bispentalenes **7a** and **8a** in a ratio of 22:78 (Table 4, entry 1). Fluoro-substituted substrate **6b** led to the separable bispentalene isomers **7b** and **8b** with a ratio of 35:65 in 25 and 55% yield, respectively (entry 2). Tetrayne **6c** with dimethyl substituents on the outer aromatic moieties exhibit higher selectivity towards the formation of **8c** over **7c** (entry 3, 91:9 ratio, 36 and 3% yield, respectively), although the overall yield significantly dropped. These results indicate that the substituents on outer aromatics influence the selectivity of the transformation.
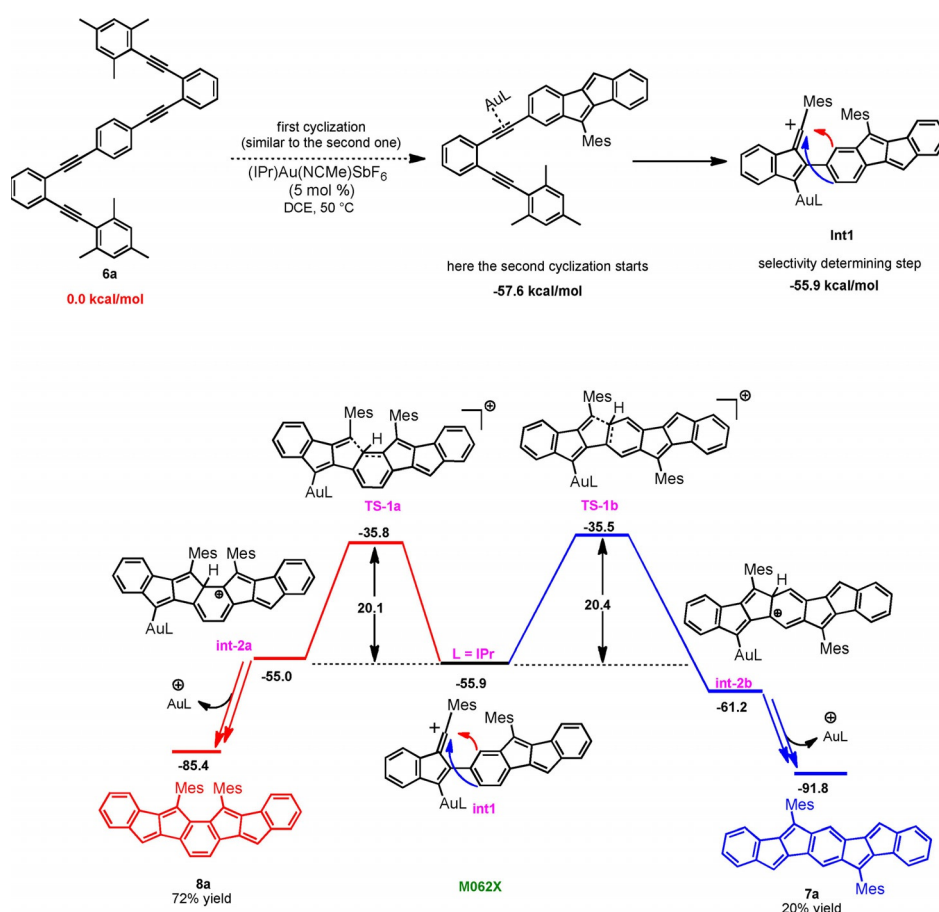

Figure 4. The selectivity-determining step with the IPr carbene ligand (energies in kcal mol⁻¹).
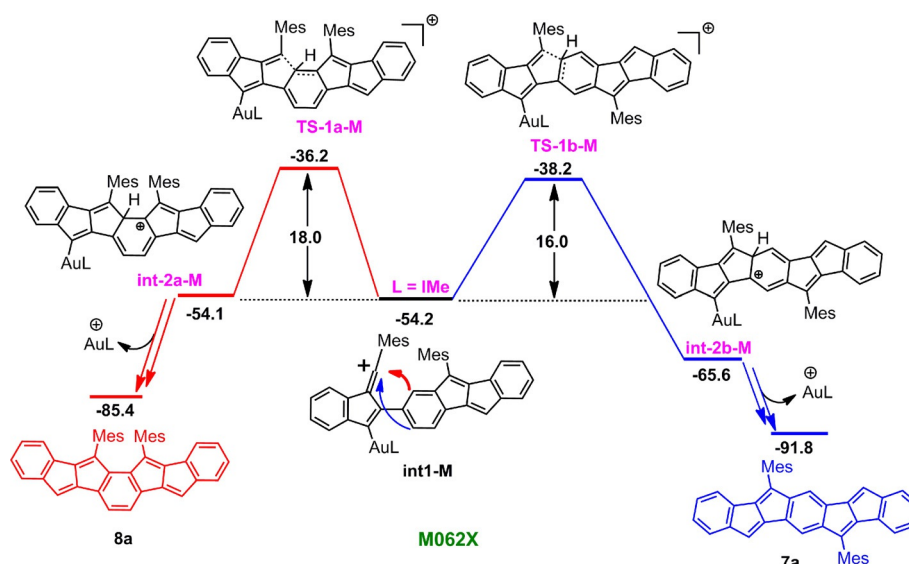
Figure 5. The selectivity-determining step with the smaller IMe carbene ligand (energies in kcal mol^{-1}).

Table 4. Bispentalene derivatives.[a]

Entry	Compound	R^1	R^2	Time [h]	Yield [%][b] 7:8
1	**6a**	H	H	2	20:72
2	**6b**	F	H	2	25:55
3	**6c**	Me	Me	3	3:36

[a] Reaction performed in a vial in DCE (1 mL), **6** (0.05 mmol) and catalyst (0.005 mmol). [b] Yield of isolated product.
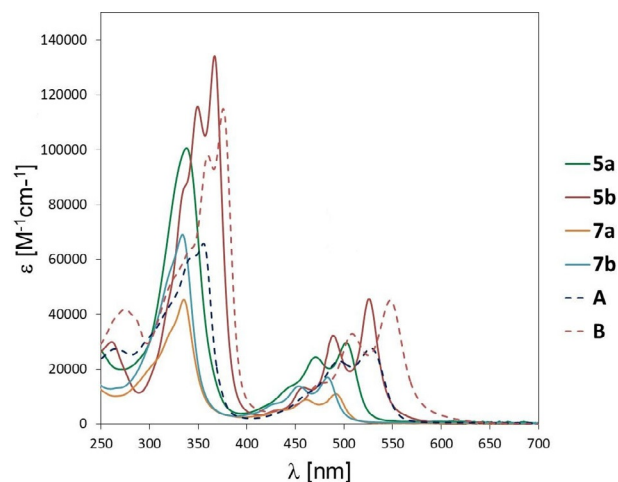

Figure 6. UV–Vis absorption of **5a**, **5b**, **7a**, and **7b**.

The optical properties of bispentalenes **5a**, **5b**, **7a** and **7b** were examined by UV–Vis absorption spectroscopy in dichloromethane (Figure 6). Based on previous work,[4e] the two characteristic absorptions ($\lambda = 450$–550 nm) of **5a**, **7a**, and **7b** might be assigned to HOMO→LUMO+1 and HOMO−1→LUMO transitions. The introduction of mesityl groups has a significant effect on the absorption. Thus, the absorption peaks ($\lambda_{max} = 474$ and 502 nm) of mesitylene-substituted **5a** were red-shifted (30 nm) compared to the S-shaped benzene-based bispentalene **A** ($\lambda_{max} = 496$ and 532 nm). A similar tendency was observed between naphthalene-based bispentalenes **5b** ($\lambda_{max} = 490$ and 525 nm) and **B** ($\lambda_{max} = 510$ and 550 nm). In addition, from the comparison of **5a** ($\lambda_{max} = 474$ and 502 nm) and **7a** ($\lambda_{max} = 460$ and 490 nm), differences on the substitution position of mesityl groups caused significant blue-shift.

The HOMO and LUMO levels of the series of bispentalenes **5a**, **5b**, **7a**, and **7b** in CH$_2$Cl$_2$ were estimated by cyclic voltam-metry (Table 5). Compared to the previously synthesized benzene-based bispentalene **A** and naphthalene-based bispenta-lene **B** (Figure 2), the HOMO levels of **5a** (-5.24 eV) and **5b** (-5.50 eV) are lower than the HOMO levels of the corresponding compounds **A** (-5.20 eV) and **B** (-5.38 eV). The LUMO levels of **5a** (-3.11 eV) and **5b** (-2.93 eV) are significantly higher than the LUMO level of the corresponding compounds **A** (-3.23 eV) and **B** (-3.09 eV), which resulted in the larger HOMO–LUMO energy gap of **5a** and **5b**. Based on the solid-state structure of **5b** (Figure 1), the peripheral mesitylene might contribute less to the core π-system, which could have an effect on the HOMO and LUMO energy levels. The HOMO and LUMO levels of the S-shaped bispentalenes **7a** (HOMO = -5.30 eV, LUMO = -3.18 eV) and **7b** (HOMO = -5.40 eV, LUMO = -3.25 eV) are lower compared to **5a**. The HOMO–LUMO gaps for **7a** and **7b** ($E_{gap} = 2.15$ eV) are not significantly different from that of **5a** ($E_{gap} = 2.13$ eV).

	E_{ox1} [V]	E_{red1} [V]	E_{HOMO}[c] [eV]	E_{LUMO}[c] [eV]	E_{gap} [eV]
A[a]	0.40	−1.57	−5.20	−3.23	1.98
5 a[a]	0.44	−1.69	−5.24	−3.11	2.13
B[a]	0.58	−1.71	−5.38	−3.09	2.29
5 b[a]	0.70	−1.87	−5.50	−2.93	2.57
7 a[b]	0.51	−1.65	−5.30	−3.15	2.15
7 b[b]	0.60	−1.55	−5.40	−3.25	2.15

[a] Cyclic voltammetry in CH_2Cl_2 containing 0.1 M nBu$_4$NPF$_6$ with ferrocene on a Pt working electrode, a Pt/Ti counter electrode, and a Ag reference electrode at a scan rate of 0.2 V s^{-1}. All potentials are given versus the Fc$^+$/Fc couple used as an internal standard. [b] Electrochemical data obtained at a scan rate of 0.2 V s^{-1} in CH_2Cl_2 containing 0.1 M nBu$_4$NPF$_6$ on a glassy carbon working electrode, a Pt/Ti counter electrode, and Ag reference electrode. [c] HOMO and LUMO energy levels in eV were approximated using the equation $HOMO = -(4.80 + E_{ox})$, $LUMO = -(4.80 + E_{red})$, $E_{gap} = LUMO - HOMO$.

Conclusions

We report the regiospecific annulation of unsymmetrically substituted 1,2-di(arylethynyl)benzene derivatives. Both electronic and steric effects on the aromatic moieties of the substrates are crucial for the selectivity. Especially, the introduction of sterically blocked substituents, such as 2,4,6-trimetylbenzene or 2,4-dimethylbenzene, enabled the regiospecific annulation. This method provided the geometrically-controlled synthesis of S-shaped bispentalenes from 1,2,4,5-tetraethynlbenzene or 2,3,6,7-tetraethynlnaphthalene. Moreover, the annulation of a series of tetraynes with a different substitution pattern regioselectively provided bispentalenes. Our computational studies showed that **7 a** is the thermodynamic product of the reaction, whereas **8 a** is the kinetic product, preferentially formed with bulky NHC ligands (like IPr, but better IPr*).

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

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