CHEMISTRY
A European Journal

A Journal of
ChemPubSoc Europe

Accepted Article

Title: Gold-catalyzed Regiospecific Annulation of Asymmetric 1,5-Diyne for Precise Synthesis of Bispentalenes

Authors: Sara Tavakkolifard, Kohei Sekine, Lisa Reichert, Mina Ebrahimi, Ketevan Museridz, Elena Michel, Frank Rominger, Rasool Babaahmadi, Alireza Ariafard, Brian Yates, Matthias Rudolph, and A. Stephen K. Hashmi

To be cited as: *Chem. Eur. J.* 10.1002/chem.201902381

Link to VoR: http://dx.doi.org/10.1002/chem.201902381

Supported by
ACES

WILEY-VCH

Gold-catalyzed Regiospecific Annulation of Unsymmetrically Substituted 1,5-Diyne for Precise Synthesis of Bispentalenes

Sara Tavakkolifard,[a],+ Kohei Sekine,[a],+ Lisa Reichert,[a] Mina Ebrahimi,[a] Ketevan Museridz,[a] Elena Michel,[a] Frank Rominger,[a] Rasool Babaahmadi,[b] Alireza Ariafard,*,[b] Brian Yates,*,[b] Matthias Rudolph,[a] and A. Stephen K. Hashmi*,[a,c]

[a] M.Sc. S. Tavakkolifard, Dr. K. Sekine, B.Sc. L. Reichert, B.Sc. M. Ebrahimi, B.Sc. K. Museridz, B.Sc. E. Michel, Dr. F. Rominger, Dr. M. Rudolph, and Prof. Dr. A. S. K. Hashmi
Organisch-Chemisches Institut, Heidelberg University, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
[b] R. Babaahmadi, Prof. A. Ariafard, Prof. B. Yates
School of Physical Sciences (Chemistry)
University of Tasmania
Private Bag 75, Hobart TAS 7001 (Australia)
[c] Prof. Dr. A. S. K. Hashmi
Chemistry Department, Faculty of Science
King Abdulaziz University, Jeddah 21589, Saudi Arabia
+ Equal contribution

Keywords: gold catalysis, pentalene, polycyclic aromatic hydrocarbons, regiospecific

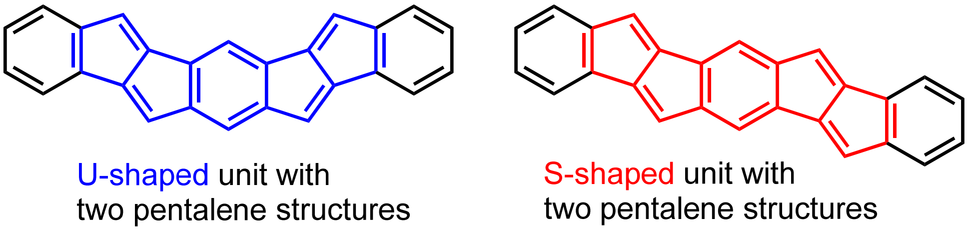
Abstract

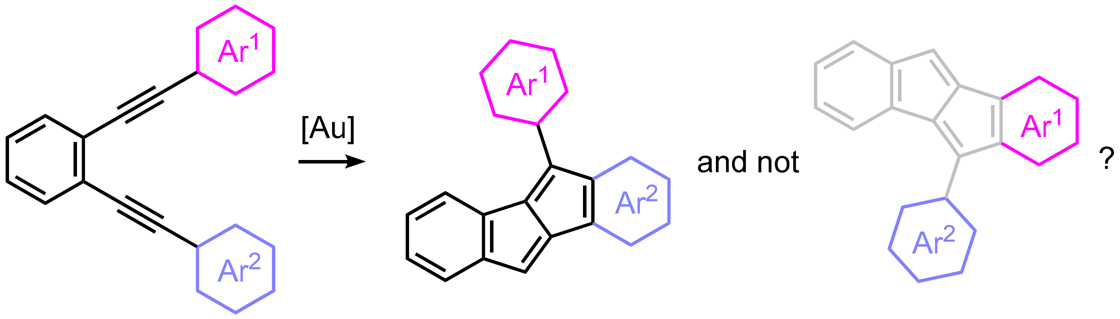
Precise control of the selectivity in organic synthesis is important to access the desired molecules. We demonstrate a regiospecific annulation of unsymmetrically substituted 1,2-di(arylethynyl)benzene derivatives for a geometry controlled synthesis of a linear bispentalene which is one of the promising structures for material science. A gold-catalyzed annulation of unsymmetrically substituted 1,2-di(arylethynyl)benzene possibly produces two isomers of pentalenes, but both electronic and steric effects on the aromatics at a terminal position of alkyne prove to be crucial for the selectivity; especially a regiospecific annulation was achieved with sterically blocked substituents, 2,4,6-trimetyl 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 bispentalene scaffolds. A computational study revealed that this is the result of a kinetic control induced by 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*]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 π- or n-type organic transistors, though 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-fuzed pentalene derivatives from 1,5-diynes.[3n,t] Moreover, the gold catalyst leads to both U-shaped and S-shaped bispentalenes from the readily available tetra(arylethynyl)benzenes and -naphthalenes, but lucky enough could be separated (Scheme 1, top).[4e] During that study, the naphthalene-based linear bispentalene (S-shaped) turned out 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 isomer (Scheme 1, bottom). From the synthetic point of view, it would be interesting to see if the reaction of unsymmetrically substituted 1,5-diynes can be controlled by electronic or steric effects, which would allow to control the precise regiochemistry and thus 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 bispentalenes by an *inside-out* bidirectional approach. In addition, we investigated an *outside-in* mode of cyclization, tetraynes with different substitution patterns successfully provided bispentalenes, which with respect to the total synthetic rout represents a much more convergent and thus flexible approach. The opto-electronic properties of the obtained bispentalene derivatives are also reported.





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

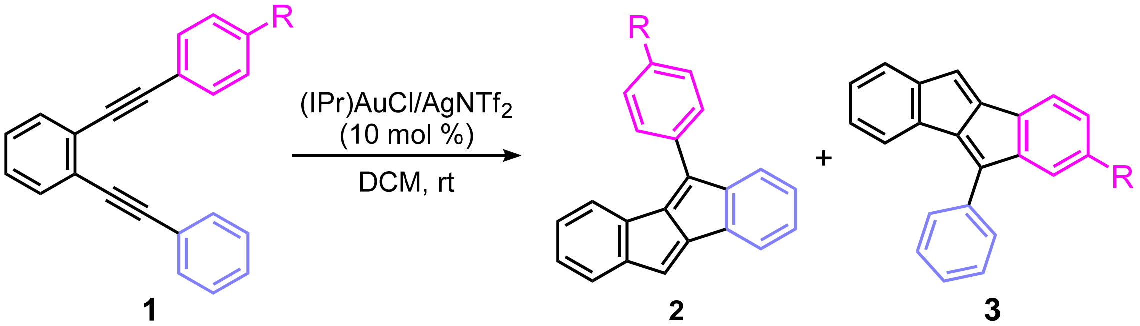
Results and Discussion

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 regiospecifically. We first prepared the unsymmetrically substituted 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 diyne gave a mixture of isomers **2a** and **3a** in 40% yield with a ratio of 4:96 (Entry 1). The fluoro-substituted diyne **1b** afforded the isomers **2b** and **3b** in 62% yield in a ratio of 58:42 (Entry 2). When a trifluoromethyl group

10.1002/chem.201902381

(**1c**), which is a strong electron-withdrawing group, was attached to aromatic ring, the ratio of **2c** and **3c** was 6:94 (Entry 3). Overall, the results demonstrated the selectivity can be controlled by the electronic properties and that an electron-rich alkyne as nucleophile and electron deficient alkyne as electrophile, even though the yield lower and the isomers are inseparable.

Table 1. Electronic effect on the selectivity.



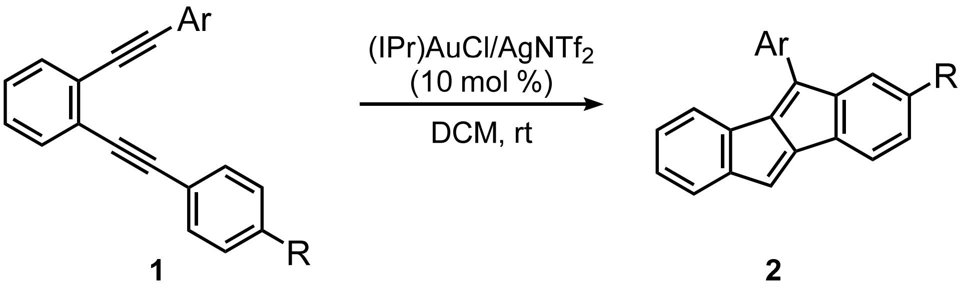
1 **2** **3**

Entry[a]	R		Time	Yield[b]/%	**2** : **3**[c]
1	OMe	**1a**	1 h	40	96:4
2	F	**1b**	1 h	62	42:58
3	CF_3	**1c**	16 h	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.

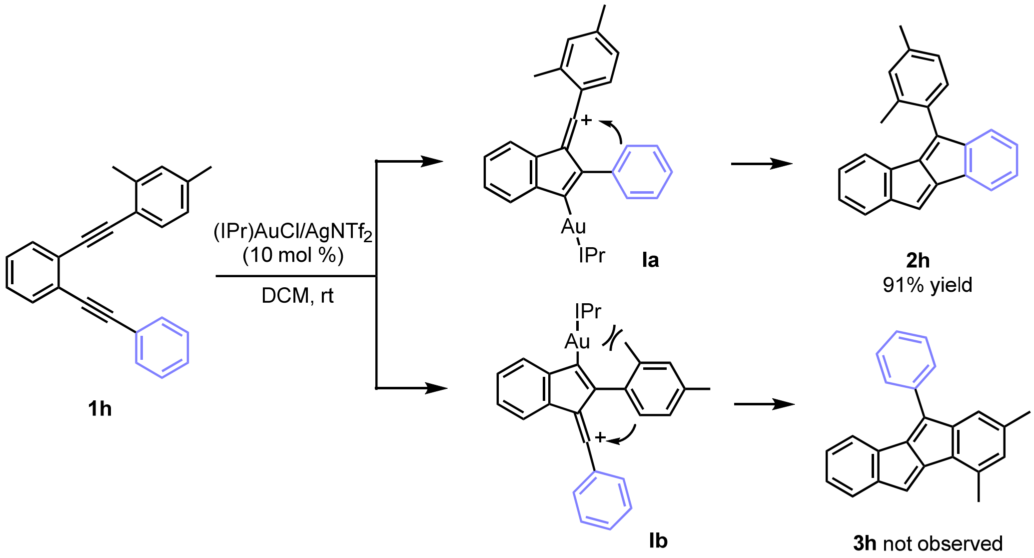
To explore another mode of substituent control of the selectivity, two *o*-positions of the aryl group on the alkyne were blocked by methyl groups, which probably inhibits the approach of gold catalysts to one of the two alkynes, even though the cyclization of vinyl cation and mesitylene, and 1,2-methyl transfer possibly proceed to give a pentalene derivative. The gold catalysts promoted the reaction of the diyne **1d** and afforded the desired pentalene **2d** in excellent yield, 94% were obtained (Entry 1, Table 2). Methoxy- or trifluoromethyl-substituted diynes **1e** and **1f** were also converted to the pentalenes **2e** and **2f** in 63% and 41% yields, respectively (Entries 2 and 3). The annulation of the bromo-substituted diyne **1g** gave the 60% yield of the pentalene **2g**, which is 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 pentalene **2h** in 91% yield and no generation of the pentalene **3h** (Entry 5). As shown in Scheme 3, the gold-catalysed reaction of diyne **1h** possibly leads to two intermediates **Ia** and **Ib**. Vinylcation intermediate **Ib** might be unfavorable because the cyclization of **Ib**, which should proceed via planar configuration is probably prohibited by the steric hindrance between the gold catalyst and *o*-methyl substituent of 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 regiospecific annulation was achieved by the introduction of a mesityl group or 2,4-dimethylbenzene.

Table 2. Reaction of mesitylene-substituted diynes.



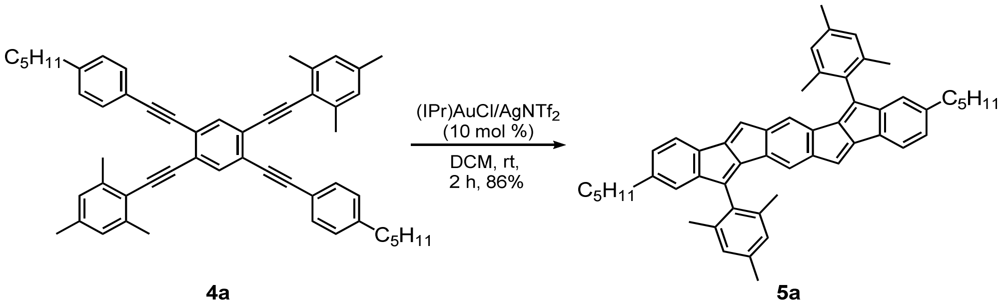
Entry[a]	Ar	R		Time	Yield[b]/%
1	Mesityl	H	**1d**	1 h	94
2	Mesityl	OMe	**1e**	3 h	63
3[c]	Mesityl	CF_3	**1f**	20 h	41
4	Mesityl	Br	**1g**	20 h	60
5	2,4-Dimethylbenzene	H	**1h**	1 h	91

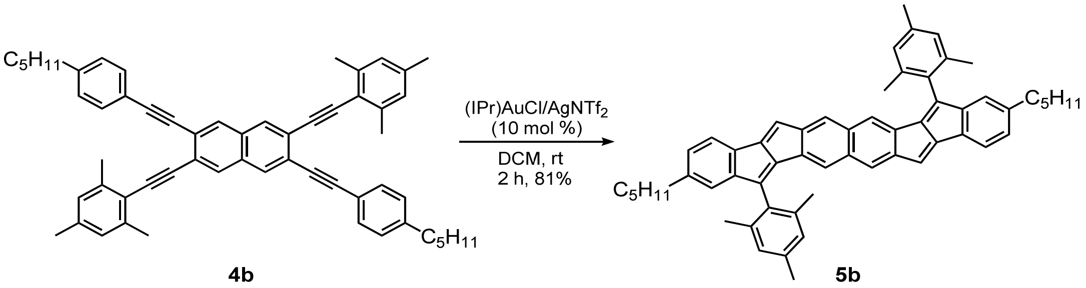
a) **1** (0.05 mmol), catalysts (0.005 mmol) in solvent (2 mL).
b) Isolated yield. c) 40 °C.



Scheme 2. Gold-catalyzed reaction to form pentalene **2h**

Based on the results with the diynes being blocked at *o*-positions, the selective synthesis of S-shape bispentalenes should be feasible. We then designed and synthesized the benzene- and naphthalene-based tetraynes **4a** and **4b** with mesitylene (Scheme 2). The tetraynes **4a** and **4b** 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 **4a** was completely consumed within 2 h, the corresponding linear bispentalene **5a** was obtained in 86% yield as a reddish brown solid. In addition, the annulation of naphthalene-based tetrayne **4b** with (IPr)AuCl/AgNTf$_2$ proceeded at room temperature and gave the 86% yield of the linear bispentalene **5b** as a red solid.





Scheme 3. Gold-catalyzed annulation of 1,2,4,5-tetra(ethynyl)benzene **4a** (top) and 2,3,6,7-tetra(ethynyl)naphthalene **4b** (bottom).

The connectivity of **5b** at a solid state was confirmed by X-ray crystallography (Figure 1). Due to the mesityl group, the 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 **5b** (63.5°–69.3°).

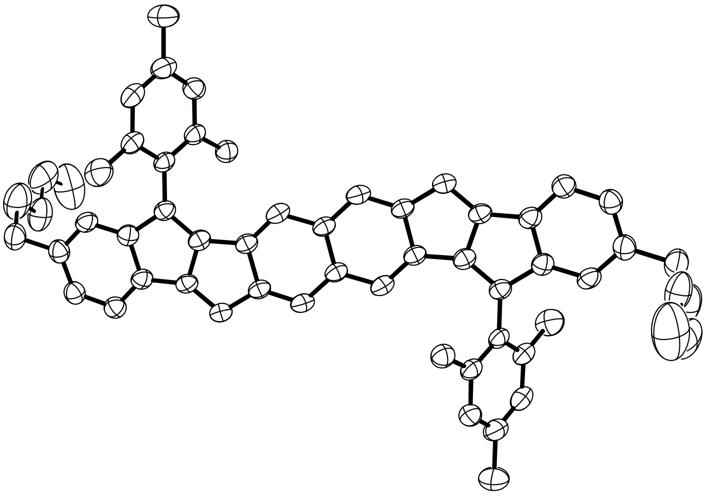
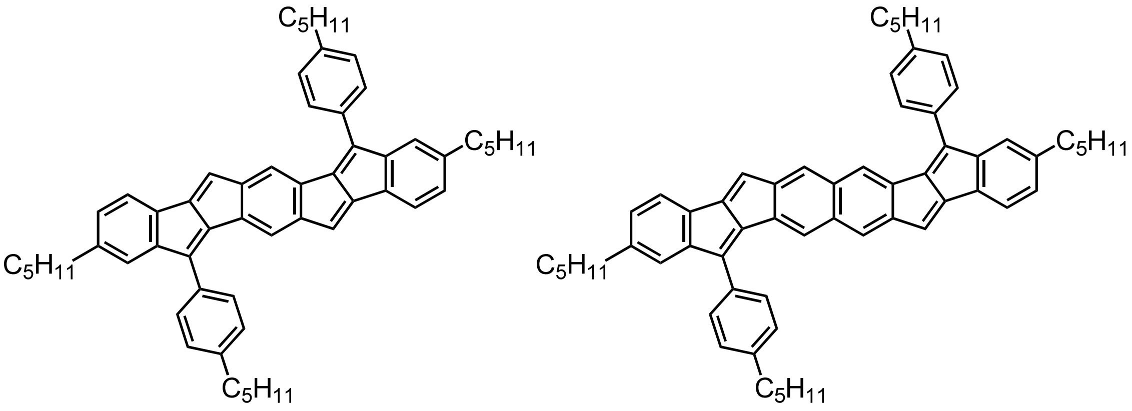


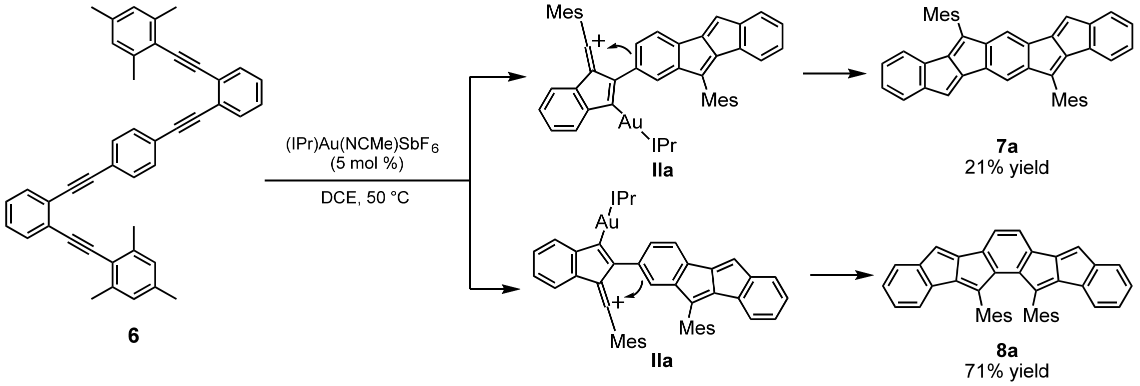
Figure 1. Solid state molecular structure of **5b**.



A **B**

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

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



Scheme 4. Gold-catalyzed reaction to form bispentalenes **7a** and **8a**.

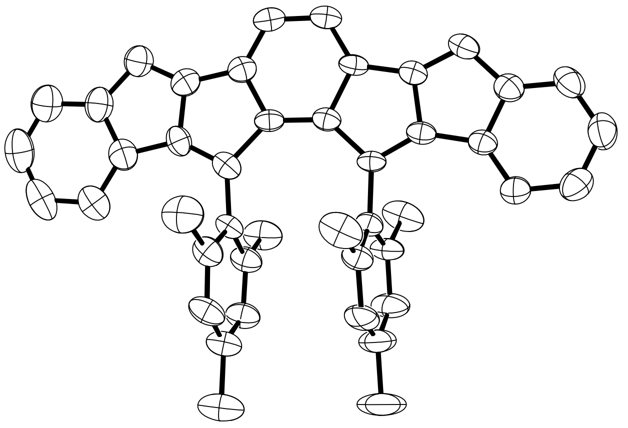
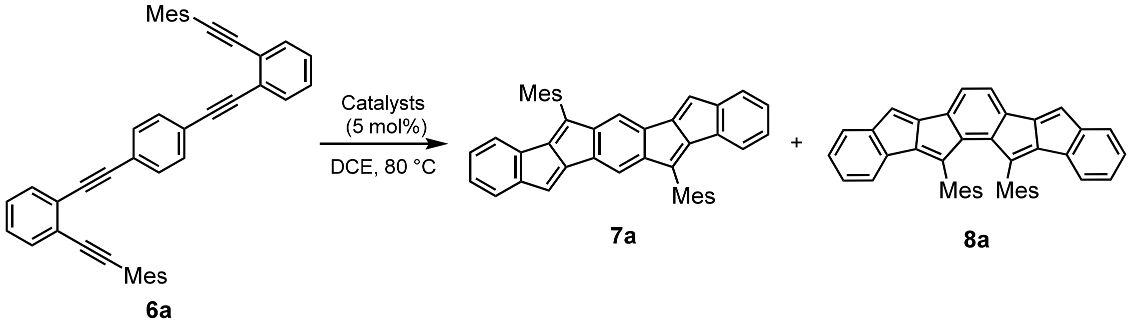


Figure 3. Solid-state molecular structure of **8a.**

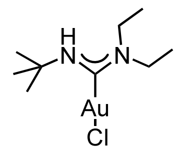
At the above experiment with (IPr)AuCl/AgNTf$_2$, isomers **7a** and **8a** produced in the ratio of 22:78. In the previous report,[4e] the bulkiness of the ligand had a significant effect on the ratio of the bispentalene isomers. Therefore, we now explored a set of differently sized ligands on the catalysts in order to prove this effect on the selectivity of isomeric bispentalenes **7a** and **8a.** We applied pre-activated [IPrAu(NCMe)]SbF$_6$ and [IPrAu]NTf$_2$ catalysts,[7] which gave the same results as (IPr)AuCl/AgNTf$_2$ (entries 2 and 6). On the other hand, the PPh$_3$ ligand only gave poor yields of the products **7a** and **8a** (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 $AgNTf_2$ (entry 7). The short ligand screening finally revealed that the sterically bulky IPr* ligand[8] increases the ratio of pentalen **8a** (entry 5) (Table 3). This can be rationalized by the steric hindrance between the mesitylen substituent and the gold complex on the intermediate **IIa,** which ultimately leads to the formation of the products **8a**.

Table 3. Examination of different ligands on the gold catalysts with substrate **6a**.

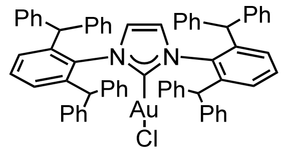


Entry^a	Catalysts	Time (h)	Yield(%) **7a**/**8a**^{b}	Ratio **7a**/**8a**
1	$(IPr)AuCl/AgNTf_2$	2	20/72	22/78
2	$(IPr)Au(NCMe)/SbF_6$	1.5	21/72	23/77
3	$Ph_3PAuNTf_2$	3	15/55	21/79
4	$NACAuCl/AgSbF_6$	4	ND	ND
5	$(IPr)^*AuCl/AgNTf_2$	3.5	62^c	4/96^d
6	$(IPr)AuCl/NTf_2$	2.5	18/71	20/80
7	$AgNTf_2$	4.5	ND	ND

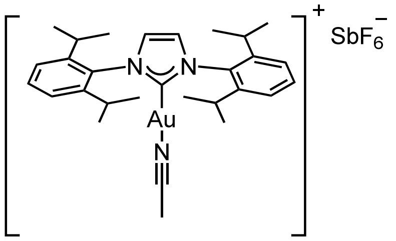
a) Reaction run in a vial in DCE (1 mL), **6a** (0.02 mmol) and catalysts (0.005 mmol), b) Isolated yield. c) Combined yield of **7a** and **8a**. d) Determined by ^1H NMR.



(NAC)AuCl



(IPr*)AuCl



$[(IPr)Au(NCMe)]SbF_6$

We investigated the selective formation of **8a** by using M06-2X-CPCM/BS2//B3LYP-CPCM/BS1 calculations and found that the selectivity is mainly controlled by a steric repulsion between the mesityl substituent and the IPr ligand in **TS-1b** (Figure 3). This destabilizing interaction is absent in **TS-1a**, causing this transition structure to be 0.3 kcal/mol lower in energy than in **TS-1b**. To support this assertion, we replaced the IPr carbene ligand by the IMe carbene ligand, in which the bulky *N*-substituents of IPr are replaced by methyl groups.

10.1002/chem.201902381

The calculation results starting from this new model system is shown in Figure 4. 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 lower in energy than **TS-1a-M** (Figure 4). The energy order of transition structures **TS-1b-M** and **TS-1a-M** is most likely set by the thermodynamic aspects of the transformations. Indeed, **7a** is about 6 kcal/mol more stable than **8a**, resulting in **TS-1b-M** lying lower in energy than **TS-1a-M**. It follows that although formation of **7a** is thermodynamically favoured over **8a**, the steric interaction between IPr ligand and the Mes substituent in **TS1-b** leads to less **7a** than **8a** being formed.

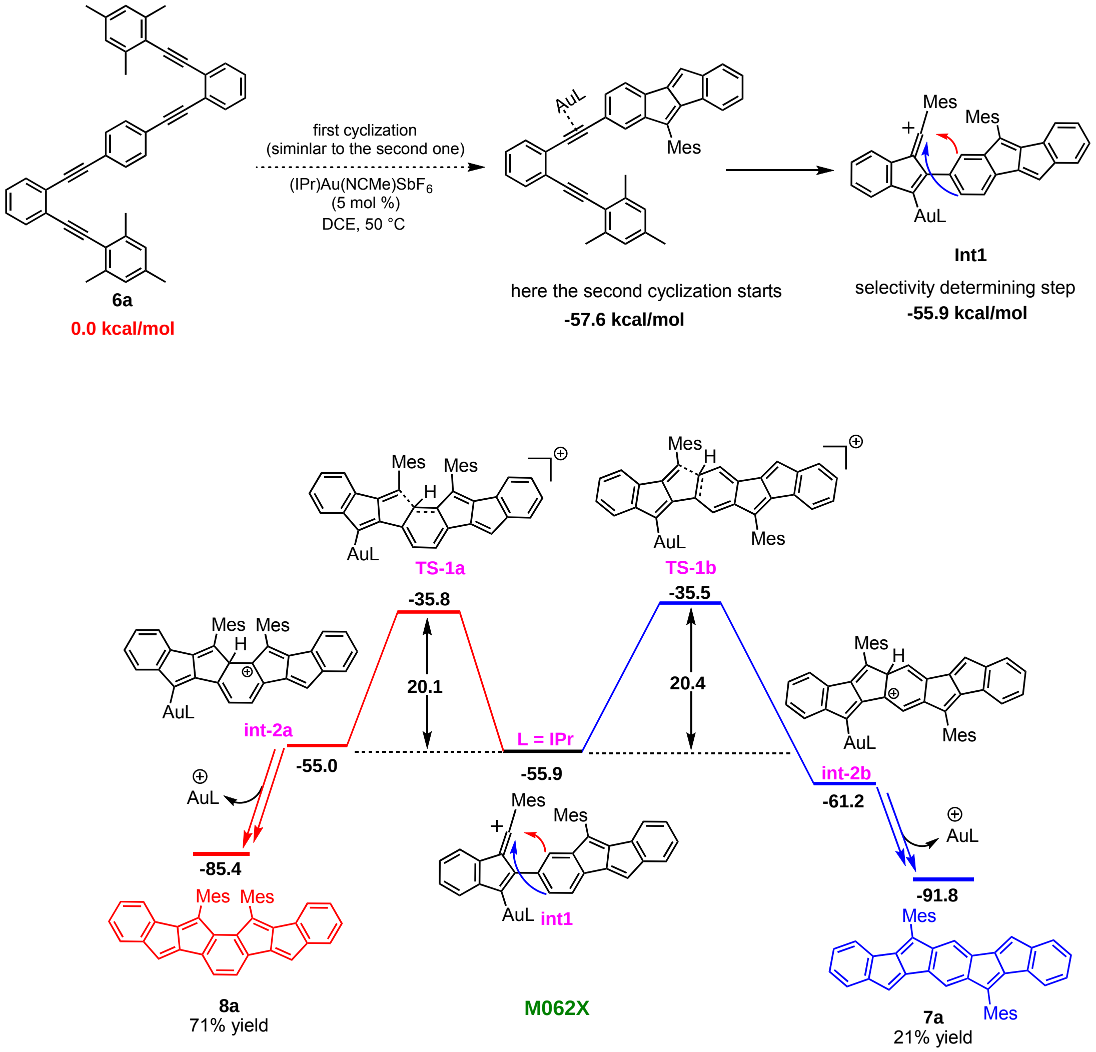


Figure 3. The selectivity-determining step with the IPr carbene ligand (energies in kcal/mol).

Figure 3 shows quite similar energy values of **TS-1a** and **TS-1b** with former being lower in energy by 0.3 kcal/mol. This is consistent with the experimental 22:78

ratio of the two products. Figure 4 shows a higher difference in energy for **TS-1a-M** and **TS-1b-M** with a reverse oder, now with **TS-1b-M** being lower. Since the repulsive interaction of the two aryl substituents in **TS-1a** and **TS-1a-M** is almost identical, *this clearly indicates that the ligand-aryl steric interaction in **TS-1b** is stronger than that in **TS-1b-M***.

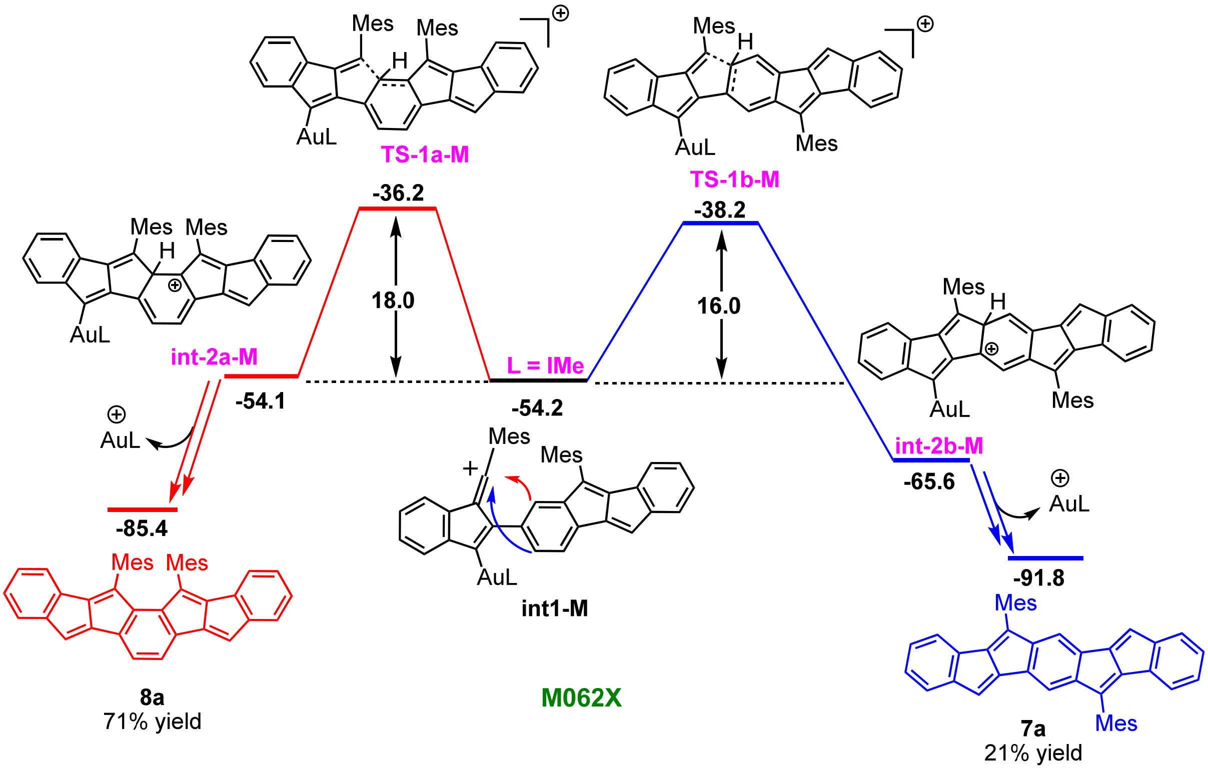
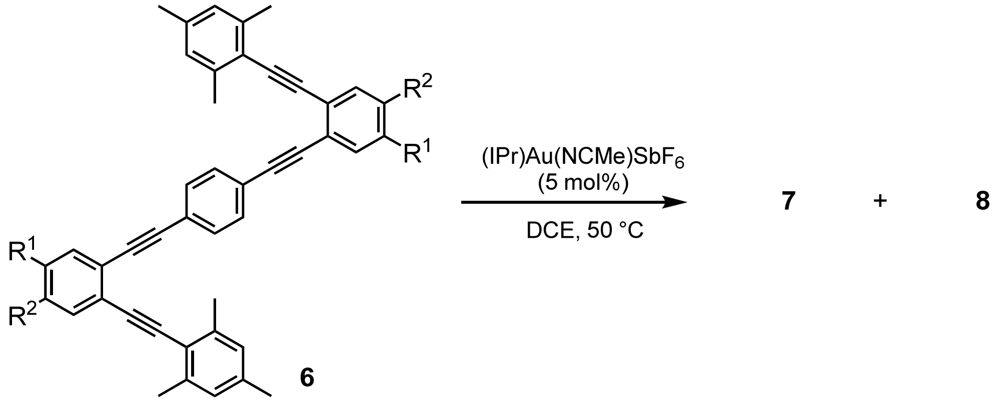


Figure 4. The selectivity-determining step with the smaller IMe carbene ligand (energies in kcal/mol).

Next, we investigated the several electron-withdrawing and electron-donating substituents on the aromatic moieties with (IPr)Au(NCMe)SbF_6. In the case of tetrayne **6a**, the gold-catalyzed reaction afforded the bispentalenes **7a** and **8a** in a ratio of 22:78 (Entry 1). The fluoro-substituted substrate **6b** led to separable bispentalene isomers **7b** and **8b** with a ratio of 35:65 in 25% and 55% yield, respectively (entry2). Tetrayne **6c** with dimethyl substituents on outer aromatic moieties gave rise in the high selectivity toward **8c** (91:9) in 36% yield and **7c** in 3% (Entry 3), though the combined yield significantly dropped. These results indicate that the substituents on outer aromatics have an effect on the selectivity of two isomers.

Table 4. Bispentalene derivatives



Entry[a]	compound, $R^{1,}$ R^2	Time (h)	Yield(%) **7**/**8**[b]
1	**6a** H, H	2	20/72
2	**6b** F, H	2	25/55
3	**6c** Me, Me	3	3/36

(a) Isolated yields.

The optical properties of bispentalenes **5a**, **5b**, **7a** and **7b** were examined by UV/Vis absorption spectroscopy in dichlromethane (Figure 6). Based on the previous work,[4e] the two characterisitic absorptions (λ = 450-550 nm) of **5a**, **7a**, and **7b** might be assigned to HOMO → LUMO+1 and HOMO-1 → LUMO transitions. Introduction of mesityl groups has significant effect on the absorption; the absorption peaks (λ_{max}= 474 and 502 nm) of mesithylene-substituted **5a** were red-shifted (30 nm) compared to S-shaped benzene-based bispentalenes **A** (λ_{max}= 496 and 532 nm). Similar tendency was observed between naphthalene-based bispentalenes **5b** (λ_{max} = 490 and 525 nm) and **B** (λ_{max}= 510 and 550 nm). In addition, from the comparison of **5a** (λ_{max}= 474 and 502 nm) and **7a** (λ_{max} = 460 and 490 nm), different substitution position of mesityl groups caused significant blue-shift.

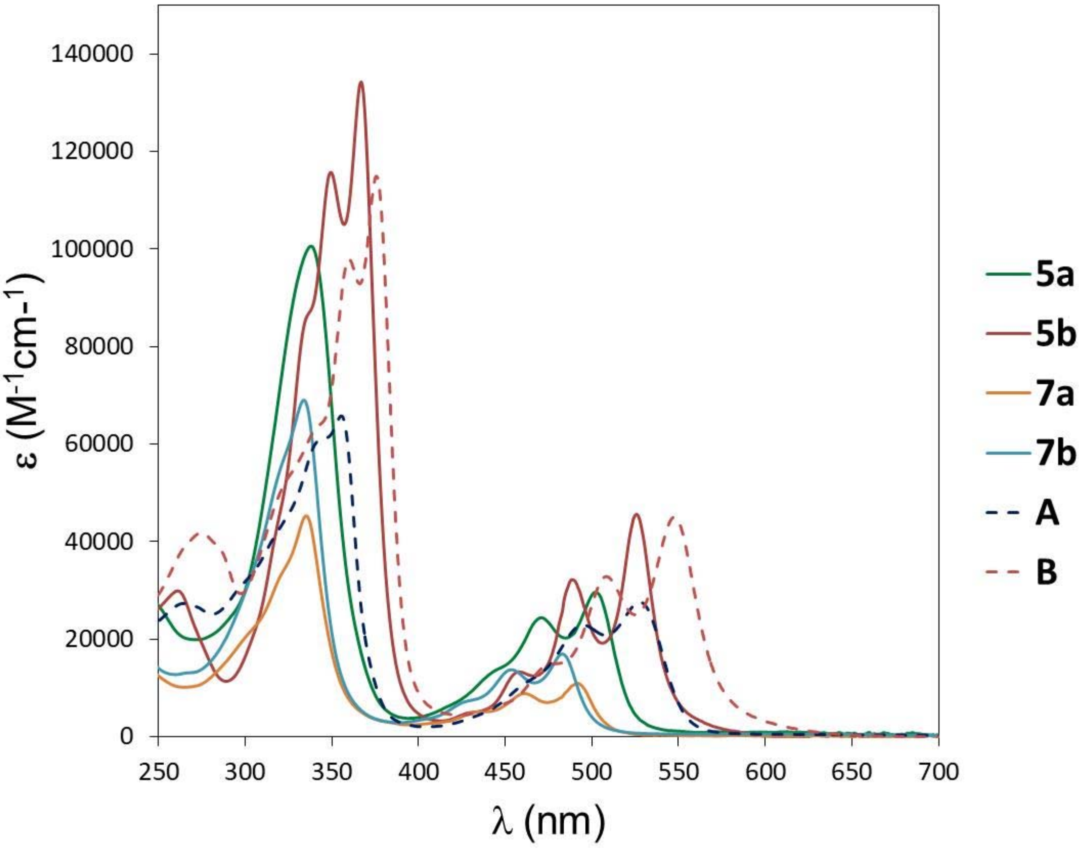


Figure 6. UV absorption of **5a**, **5b**, **7a**, and **7b**.

The HOMO and LUMO levels of the series of bispentalenes **5a**, **5b**, **7a**, and **7b** in CH_2Cl_2 solution were estimated by cyclic voltammetry (Table 5). Compared to the previously synthesized benzen-based bispentalene **A** and naphthalene-based bispentalene **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 less contribute to the core π-system, which could have an effect on 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).

Table 5. Cyclic voltammetry data and estimated HOMO and LUMO energies

	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
5a^{a}	0.44	-1.69	-5.24	-3.11	2.13
B^{a}	0.58	-1.71	-5.38	-3.09	2.29
5b^{a}	0.70	-1.87	-5.50	-2.93	2.57
7a^{b}	0.51	-1.65	-5.30	-3.15	2.15
7b^{b}	0.60	-1.55	-5.40	-3.25	2.15

[a] Cyclic voltammetry in CH_2Cl_2 containing 0.1 M $^{n}Bu_4NPF_6$ with ferrocene on a Pt working electrode, a Pt/Ti counter electrode, and a Ag reference electrode at a scan rate of 0.2 Vs^{-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 Vs^{-1} in CH_2Cl_2 containing 0.1 M $n$$Bu_4NPF_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.

Conclusion

We demonstrated the regiospecific annulation of unsymmetrically substituted 1,2-di(arylethynyl)benzene derivatives. Both electronic and steric effects on the aromatics of substrates are crucial for the selectivity; especially introduction of sterically blocked substituents, 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, annulation of a series of tetraynes with a different substitution pattern regioselectively provided bispentalenes. The computational study showed that **7a** is the thermodynamic product of the reaction, **8a** is the kinetic product formed with bulky NHC ligands (like IPr, but better IPr*).

References

[1] C. K. Frederickson, B. D. Rose, M. M. Haley, *Acc. Chem. Res.* **2017**, *50, 977*.

[2] T. Bally, S. Chai, M. Neuenschwander, Z. Zhu, J. Am. *Chem. Soc*. **1997**, *119, 1869*.

[3] Review for the synthesis and optoelectronic properties of pentalenes, please see a) M. Saito, *Symmetry* **2010,** *2, 950*. For recent publications about

monobenzopentalene, see b) P. Rivera-Fuentes, M. von Wantoch Rekowski, W. B. Schweizer, J- P. Gisselbrecht, C. Boudon, F. Diederich, *Org. Lett.* **2012**, *14, 4066*; c) G. London, M. von Wantoch Rekowski, O. Dumele, W. B. Schweizer, J.-P. Gisselbrecht, C. Boudon, F. Diederich, *Chem. Sci*. **2014**, *5, 965*; d) S. Kato, S. Kuwako, N. Takahashi, T. Kijima, Y. Nakamura, *J. Org. Chem*. **2016**, *81, 7700*. For dibenzopentalene, see e) K. Katsumoto, C. Kitamura, T. Kawase, Eur. *J. Org. Chem*. **2011**, *4885*; f) M. Saito, Y. Hashimoto, T. Tajima, K. Ishimura, S. Nagase, M. Minoura, *Chem. Asian J*. **2012**, *7, 480*; g) A. S. K. Hashmi, M. Wieteck, I. Braun, P. Nosel, L. Jongbloed, M. Rudolph, F. Rominger, *Adv. Synth. Catal*. **2012**, *354, 555*; h) C. Chen, M. Harhausen, R. Liedtke, K. Bussmann, A. Fukazawa, S. Yamaguchi, J. L. Petersen, C. G. Daniliuc, R. Frçhlich, G. Kehr, G. Erker, *Angew*. *Chem*. *Int. Ed*. **2013**, *52, 5992*; *Angew. Chem*. **2013**, *125, 6108*; i) T. Maekawa, Y. Segawa, K. Itami, *Chem. Sci*. **2013**, *4, 2369*; j) J. Zhao, K. Oniwa, N. Asao, Y. Yamamoto, T. Jin, *J. Am. Chem. Soc*. **2013**, *135,* 10222; k) J. Shen, D. Yuan, Y. Qiao, X. Shen, Z. Zhang, Y. Zhong, Y. Yi, X. Zhu, *Org. Lett*. **2014**, *16, 4924*; l) C. Chen, M. Harhausen, A. Fukazawa, S. Yamaguchi, R. Frçhlich, C. G. Daniliuc, J. L. Petersen, G. Kehr, G. Erker, *Chem. Asian J*. **2014,** *9, 1671*; m) B. Wei, H. Li, W.-X. Zhang, Z. Xi, *Organometallics* **2016**, *35, 1458*; n) T. Wurm, J. Bucher, S. B. Duckworth, M. Rudolph, F. Rominger, A. S. K. Hashmi, *Angew. Chem. Int. Ed*. **2017**, *56, 3364*; *Angew. Chem*. **2017**, *129, 3413*; o) K. Takahashi, S. Ito, R. Shintani, K. Nozaki, *Chem. Sci*. **2017**, *8, 101*; p) H. Oshima, A. Fukazawa, S. Yamaguchi, *Angew. Chem*. *Int. Ed*. **2017**, *56, 3270*; *Angew. Chem*. **2017**, *129, 3318*; q) A. Konishi, Y. Okada, M. Nakano, K. Sugisaki, K. Sato, T. Takui, M. Yasuda, *J. Am. Chem. Soc*. **2017**, *139, 15284*; r) D. C. Grenz, M. Schmidt, D. Kratzert, B. Esser, *J. Org. Chem*. **2018**, *83, 656*; s) T. Wurm, E. C. Rediger, J. Schulmeister, S. Koser, M. Rudolph, F. Rominger, U. H. F. Bunz, A. S. K. Hashmi, *Chem. Eur. J.* **2018**, *24, 2735*; t) K. Sekine, F. Stuck, J. Schulmeister, T. Wurm, D. Zetschok, F. Rominger, M. Rudolph, A. S. K. Hashmi, *Chem. Eur. J.* **2018,** *24, 12515*.

[4] 4p-type: (a) T. Kawase, T. Fujiwara, C. Kitamura, A. Konishi, Y. Hirano, K. Matsumoto, H. Kurata, t. Kubo, S. Shinamura, H. Mori, E. Miyazaki K. Takimiya, *Angew. Chem. Int. Ed*. **2010**, *49, 7728*; (b) C. Liu, X. Xu, W. Zhu, X. Zhu, W. Hu, Z. Li Z. Wang, *Chem. Eur. J*. **2015**, *21, 17016*; (c) G. Dai, J. Chang, W. Zhang, S. Bai, K.-W. Huang, J. Xu, C. Chi, *Chem. Commun*. **2015**, *51, 503*; (d) C. Li, C. Liu, Y. Li, X. Zhu, A. Wang, *Chem. Commun*. **2015**, *51, 693*. (e) K. Sekine, J. Schulmeister, F. Paulus, K. P. Goetz, F. Rominger, M. Rudolph, J. Zaumseil, A. S. K. Hashmi, *Chem. Eur. J*. **2019**, *25, 216*; n-type: f) M. Nakano, I. Osaka, K. Takimiya, T. Koganezawa, *J. Mater. Chem. C* **2014**, *2, 64*; g) M. Nakano, I. Osaka, K. Takimiya, *J. Mater. Chem. C* **2015**, *3, 283*; h) G. Dai, J. Chang, L. Jing, C. Chi, *J. Mater. Chem. C*. **2016**, *4, 8758*; i) D. C. Grenz, M. Schmidt, D. Kratzert, B. Esser, *J. Org. Chem.* **2018**, *83, 656*.

[5] a) D. Pflästerer, A. S. K. Hashmi, *Chem. Soc. Rev*. **2016**, *45, 1331*; b) R. Dorel, A. M. Echavarren, *Chem. Rev.* **2015**, *115, 9028*; c) L. Zhang, *Acc. Chem. Res*. **2014**, *47*, *877*; d) L. P. Liu, G. B. Hammond, *Chem. Soc. Rev*. **2012**, *41, 3129*; e) H. Ohno, *Isr. J. Chem*. **2013**, *53, 869*; f) A. Ferstner, *Chem. Soc. Rev*. **2009**, *38, 3208*; g) N. Bongers, N. Krause, *Angew. Chem. Int. Ed*. **2008**, *47, 2178*; *Angew. Chem*. **2008**, *120, 2208*; h) A. Ferstner, P. W. Davies, *Angew. Chem. Int. Ed*. **2007**, *46, 3410*; *Angew. Chem*. **2007**, *119, 3478*; i) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem*. *Int. Ed*. **2006**, *45, 7896*; *Angew. Chem*. **2006**, *118, 8064*; j) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107, 3180*; k) D. J. Gorin, F. D. Toste, *Nature* **2007**, *446, 395*; l) for early results, see: A. S. K. Hashmi, L. Schwarz, J.-H. Choi, Ta. M. Frost, *Angew. Chem*. Int. Ed. **2000**, *39, 2285*; *Angew. Chem*. **2000**, *112, 2382*; m) A. S. K. Hashmi, T. M. Frost, J. W. Bats, *J. Am. Chem. Soc.* **2000**, *122, 11553*.

[6] a) A. M. Asiri, A. S. K. Hashmi, *Chem. Soc. Rev*. **2016**, *45, 4471*; b) A. S. K. Hashmi, *Acc. Chem. Res.* **2014**, *47, 864*; c) I. Braun, A. M. Asiri, A. S. K. Hashmi, *ACS Catal*. **2013**, *3, 1902*.

[7] P. de Frémont, N. Marion, S. P. Nolan, *J. Organomet. Chem*. **2009**, *694, 551*.

[8] A. Collado, A. Gómez-Suárez, A. R. Martin, A. M. Z. Slawin, S. P. Nolan, *Chem. Commun*. **2013**, 49, 5541.

10.1002/chem.201902381

TOC