ChemComm

Cite this: *Chem. Commun.*, 2012, **48**, 1311–1313

www.rsc.org/chemcomm

COMMUNICATION

Highly enantioselective synthesis of silahelicenes using Ir-catalyzed [2 + 2 + 2] cycloaddition†

Takanori Shibata,*[a] Toshifumi Uchiyama,[a] Yusuke Yoshinami,[a] Satoshi Takayasu,[a] Kyoji Tsuchikama[a] and Kohei Endo[b]

Received 1st November 2011, Accepted 17th November 2011
DOI: 10.1039/c1cc16762f

Silahelicenes, which contain two silole moieties in a helically chiral structure, were synthesized by a chiral Ir-catalyzed intermolecular [2 + 2 + 2] cycloaddition of tetraynes with diynes along with a Ni-mediated intramolecular [2 + 2 + 2] cycloaddition. The photophysical properties of the obtained highly enantiomerically enriched silahelicenes (up to 93% ee) were also measured.

Helicenes are *ortho*-fused poly-aromatic compounds with helical chirality. In helicene-like compounds, a poly-aromatic skeleton contains non-aromatic motif(s). Due to their structurally unique helical chirality, helicenes and helicene-like compounds have attracted great attention as a source of chirality in asymmetric synthesis, a chiral material, and a chiral discriminator of biomolecules.[1] Regarding the construction of a helicene structure, the oxidative cyclization of stilbene derivatives under photo-irradiation was accepted as a general protocol until around 1990. Since then, other approaches have been reported, including the Diels–Alder reaction,[2] carbenoid coupling,[3] transition metal-catalyzed [2 + 2 + 2] cycloaddition of alkynes,[4] radical cyclization,[5] olefin metathesis,[6] the Friedel–Crafts reaction,[7] cycloisomerization,[8] and electrophilic aromatic cyclization.[9] For the preparation of chiral helicenes, resolution of racemic compounds was generally used until 1999, when Stará and Starý reported their pioneering work on the enantioselective intramolecular [2 + 2 + 2] cycloaddition of triynes using a chiral Ni catalyst (up to 48% ee).[10] Recently, Tanaka *et al.* enhanced this strategy using a chiral Rh catalyst for the preparation of [7]helicene-like compounds containing two 2*H*-pyran moieties (up to 85% ee).[11a] They further reported consecutive [2 + 2 + 2] cycloadditions of tetraynes possessing a 1,3-diyne moiety and diynes for the synthesis of higher-order [9]helicene-like compounds, which also contained two 2*H*-pyran moieties (up to 60% ee).[11b,c]

In contrast, silacyclopentadiene (silole) also has a unique structure, where the σ* orbital of two exocyclic σ-bonds of the silicon atom and the π* orbital of the 1,3-butadiene moiety interact to provide a σ*–π* conjugated system. The resulting low LUMO level leads to various characteristic optoelectronic features.[12] For example, high fluorescence quantum yield was achieved with a ladder-type dibenzosilole.[13] Moreover, the high electron transport ability of siloles has been used as a key component in organic light-emitting diodes (OLED).

Against these backgrounds, we focused on the enantioselective synthesis of silahelicenes as a new class of chiral compounds, where two unique π-conjugated systems of helicene and silole merge, and we expected that it would show new optoelectronic properties.[14] In recent years, organic molecules, which emit circularly polarized light (CPL), have attracted much attention,[15] because they have tremendous potential in optical devices.[16] Actually, helicity is a promising structure of CPL emission.[17] We report here the first synthesis of chiral silahelicenes using the Ir-catalyzed enantioselective [2 + 2 + 2] cycloaddition.[18]

We planned a consecutive inter- and intramolecular [2 + 2 + 2] cycloaddition for construction of the silahelicene skeleton (Scheme 1). The intermolecular reaction of a silicon-tethered tetrayne having a conjugated diyne moiety with an *ortho*-phenylene-bridged diyne will give regioisomeric cycloadducts **A** and **B**. The obtained triyne **A** will undergo an intramolecular reaction to give a desired silahelicene. Therefore, regio- and stereocontrol were required for the efficient synthesis of chiral silahelicenes.

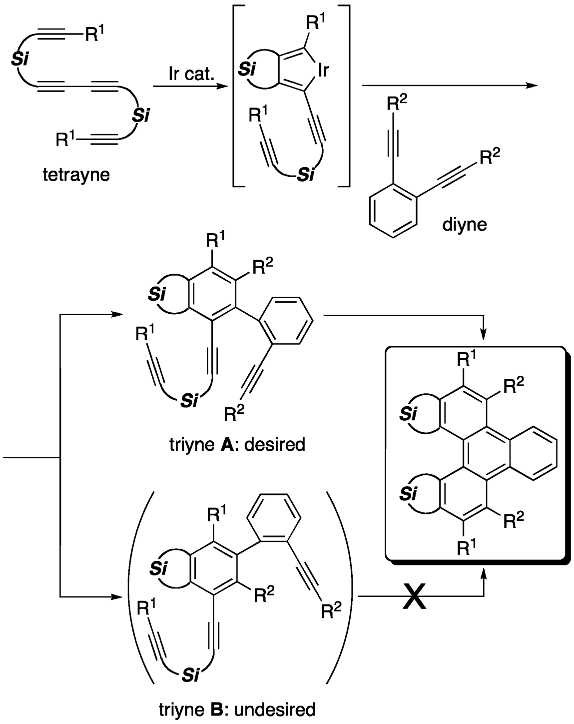
We chose silicon-tethered tetrayne **1a** as a model substrate and subjected it to an intermolecular [2 + 2 + 2] cycloaddition with an *ortho*-phenylene-tethered diyne using an achiral Ir–DPPBenz catalyst (DPPBenz: 1,2-bis(diphenylphosphino)benzene) (Scheme 2).[19] The reaction with **2a** possessing an ethoxycarbonyl group on its alkyne termini proceeded regioselectively to give the desired cycloadduct **3aa** (triyne **A** in Scheme 1), but in moderate yield,[20] and the generation of axial chirality was ascertained by HPLC analysis using a chiral column. In contrast, the reaction with **2b** possessing a methoxymethyl group gave almost a 1 : 1 regioisomeric mixture of cycloadducts **3ab** and **4ab**. These results imply that the substituent on the alkyne termini plays a key role in the regioselectivity in the cycloaddition.

We next screened several chiral phosphorus ligands in the intermolecular reaction of **1a** with **2a** (Table 1).

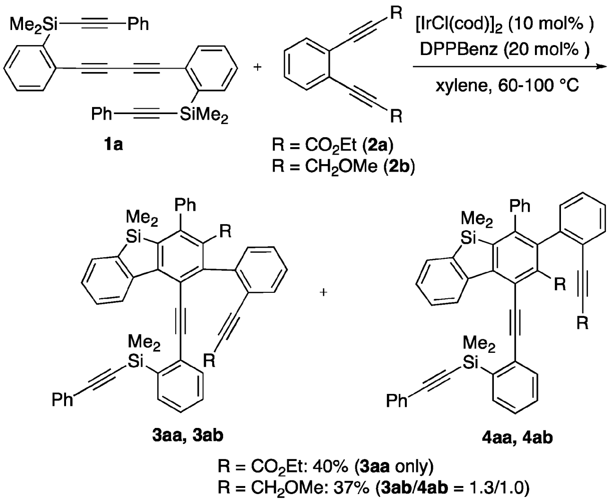
---

[a] *Department of Chemistry and Biochemistry, School of Advanced Science and Engineering, Waseda University, Shinjuku, Tokyo, 169-8555, Japan. E-mail: tshibata@waseda.jp; Fax: +81-3-5286-8098; Tel: +81-3-5286-8098*
[b] *Waseda Institute for Advanced Study, Shinjuku, Tokyo, 169-8050, Japan*

† Electronic supplementary information (ESI) available: CCDC reference number 844257. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc16762f



Scheme 1 Possible reaction scheme.



Scheme 2 Effect of substituents on the regioselectivity.

When MeDUPHOS was used, which gave an excellent asymmetric induction of axial chirality in several alkyne-trimerizations,[18] the reaction proceeded efficiently within 1 h at 100 °C, and cycloadduct **3aa** was obtained in good yield and ee (entry 1).[21] For MeBPE and CHIRAPHOS, the results were worse in terms of both yield and ee (entries 2 and 3). BINAP was an ineffective ligand in this reaction (entry 4). After further screening of several ligands, we finally found that EtFerroTANE gave the best results, and the enantiomeric excess exceeded 90% (entry 5). To convert the triyne **3aa** into silahelicene by subsequent intramolecular [2 + 2 + 2] cycloaddition in a single pot, the reaction mixture obtained in entry 5 was further stirred at a higher reaction temperature (150 °C), but we could not detect the formation of silahelicene **5aa**.

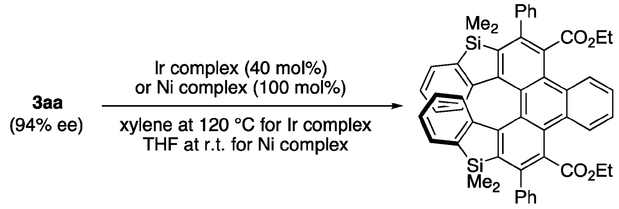
Table 1 Screening of chiral ligands in the Ir-catalyzed cycloaddition

$$\mathbf{1a} + \mathbf{2a} \xrightarrow[\text{xylene, 100 °C}]{\substack{[\text{IrCl(cod)}]_2\ (10\ \text{mol\%}) \\ \text{ligand (20 mol\%)}}} \mathbf{3aa}$$

Entry	Ligand[a]	Time/h	Yield (%)	ee (%)
1	(*S*,*S*)-MeDUPHOS	1	85	71
2	(*S*,*S*)-MeBPE	5	35	−38
3	(*S*,*S*)-CHIRAPHOS	5	39	−35
4	(*S*)-BINAP	5	< 5	ND[b]
5	(*S*,*S*)-EtFerroTANE	4	74	−94

[a] MeDUPHOS: 1,2-bis(2,5-dimethylphospholano)benzene, MeBPE: 1,2-bis(2,5-dimethylphospholano)ethane, CHIRAPHOS: 2,3-bis(diphenylphosphino)butane, EtFerroTANE: 1,1′-bis(2,4-diethylphospholano)ferrocene. [b] Not determined.

Table 2 Transformation into helically chiral silahelicene **5aa**



5aa

Entry	Ir or Ni complex	Time/h	Yield (%)	ee (%)
1	$[\text{IrCl(cod)}]_2$ + 2DPPBenz	3	24	76
2	$[\text{IrCl(cod)}]_2$ + 2*rac*-BINAP	2	Trace	—
3	$[\text{IrCl(cod)}]_2$ + 2BIPHEP[a]	2	Trace	—
4	$[\text{Ni(cod)}_2]$ + 2PPh$_3$	4	94	93

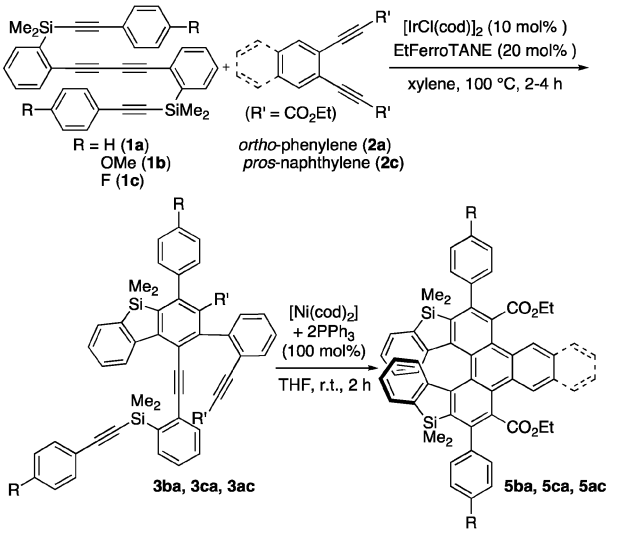
[a] BIPHEP: 2,2′-bis(diphenylphosphino)-1,1′-biphenyl.

We next focused on the stereospecific transformation of axially chiral triyne **3aa** into helically chiral silahelicene **5aa** by an intramolecular [2 + 2 + 2] cycloaddition (Table 2). We examined a few Ir–diphosphine complexes (entries 1–3) and obtained the desired silahelicene **5aa** by using DPPBenz. However, the yield was low, and the decrease in enantiomeric excess was observed in the cycloadduct (entry 1). In the presence of a stoichiometric amount of $[\text{Ni(cod)}_2]$ with triphenylphosphine, the reaction proceeded at room temperature in excellent yield, and an almost perfect transfer from axial to helical chirality was achieved (entry 4).[22–24] The enantiomeric excess (93%) is highest, which is derived from the [2 + 2 + 2] cycloaddition approach.[25]

We examined the scope of tetrayne and diyne substrates under the optimal reaction conditions (Table 3). Electron-donating and -withdrawing groups could be installed to the benzene rings of tetrayne termini, and high enantioselectivity was achieved in the Ir-catalyzed intermolecular reaction (entries 1 and 2). Naphthalene-tethered diyne **2c** also reacted to give axially chiral triyne **3ac**. In each case, the yield was moderate because the starting materials were not completely consumed. The Ni-mediated transformation of triynes **3ba**, **3ca**, **3ac** proceeded with almost no loss of enantiomeric excess, and the corresponding silahelicenes were obtained.

We measured the photophysical properties of the obtained silahelicenes **5aa**, **5ba**, **5ca**, and **5ac** (Table 4). In UV-vis spectra of **5aa**, **5ba**, and **5ca**, $\lambda_{\max}$ were observed at 293–296 nm.

Table 3 Enantioselective synthesis of chiral silahelicenes



	Triyne **3**		Silahelicene **5**	
Entry	Yield (%)	ee (%)	Yield (%)	ee (%)
1	39 (**3ba**)	94	84 (**5ba**)	92
2	51 (**3ca**)	92	97 (**5ca**)	90
3	50 (**3ac**)	93	75 (**5ac**)	92

Table 4 Photophysical properties of silahelicenes **5aa**, **5ba**, **5ca**, **5ac**

Entry	Helicene	UV-vis λ (log ε)	Emission λ^a (Φ_F)
1	**5aa**	296 nm (4.60)	464 nm (0.030)
2	**5ba**	293 nm (4.51)	466 nm (0.033)
3	**5ca**	295 nm (4.57)	465 nm (0.029)
4	**5ac**	320 nm (4.74)	457 nm (0.084)

[a] Quantum yield was determined by using quinine sulfate as a standard.

In contrast, a red shift was observed in the UV-vis spectra of **5ac**. With regard to fluorescence spectra, silahelicene **5ca** has a slightly shorter absorption wavelength, and its fluorescence quantum yield was the highest among the four helicenes.

In conclusion, we realized the first synthesis of silahelicenes, which have helical chirality including silole moieties. Intermolecular Ir-catalyzed enantioselective [2 + 2 + 2] cycloaddition and the subsequent Ni-mediated intramolecular stereospecific [2 + 2 + 2] cycloaddition provided highly enantiomerically enriched silahelicenes. The extreme stability of silahelicene **5aa**[26] is noteworthy for the application in optical devices. We expect that these structurally unique silahelicenes will exhibit electron transport ability and will use them as emitting layer in an OLED.[27]

We thank Prof. Yukio Furukawa and Heisuke Sakai (Waseda University, Japan) for their helpful discussion. This work was supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan (No. 22350046) and Rohm Foundation.

Notes and references

1 (*a*) C. Schmuck, *Angew. Chem., Int. Ed.*, 2003, **42**, 2448–2452; (*b*) A. Urbano, *Angew. Chem., Int. Ed.*, 2003, **42**, 3986–3989.
2 L. Liu and T. J. Katz, *Tetrahedron Lett.*, 1990, **31**, 3983–3986.
3 F. Dubois and M. Gingras, *Tetrahedron Lett.*, 1998, **39**, 5039–5040.
4 Co: (*a*) I. G. Stará, I. Starý, A. Kollárovič, F. Teplý, D. Šaman and M. Tichý, *J. Org. Chem.*, 1998, **63**, 4046–4050; Ni: (*b*) I. G. Stará, I. Starý, A. Kollárovič, F. Teplý, Š. Vyskočil and D. Šaman, *Tetrahedron Lett.*, 1999, **40**, 1993–1996; Pd: (*c*) D. Peña, A. Cobas, D. Pérez, E. Guitián and L. Castedo, *Org. Lett.*, 2003, **5**, 1863–1866; Rh: (*d*) L. Severa, L. Adriaenssens, J. Vávra, D. Šaman, I. Císařová, P. Fiedler and F. Teplý, *Tetrahedron*, 2010, **66**, 3537–3552.
5 D. C. Harrowven, M. I. T. Nunn and D. R. Fenwick, *Tetrahedron Lett.*, 2002, **43**, 3189–3191.
6 S. K. Collins, A. Grandbois, M. P. Vachon and J. Côté, *Angew. Chem., Int. Ed.*, 2006, **45**, 2923–2926.
7 J. Ichikawa, M. Yokota, T. Kudo and S. Umezaki, *Angew. Chem., Int. Ed.*, 2008, **47**, 4870–4873.
8 J. Storch, J. Sýkora, J. Čermák, J. Karban, I. Císařová and A. Růžička, *J. Org. Chem.*, 2009, **74**, 3090–3093.
9 G. Pieters, A. Gaucher, D. Prim and J. Marrot, *Chem. Commun.*, 2009, 4827–4828.
10 F. Teplý, I. G. Stará, I. Starý, A. Kollárovič, D. Šaman, Š. Vyskočil and P. Fiedler, *J. Org. Chem.*, 2003, **68**, 5193–5197.
11 (*a*) K. Tanaka, A. Kamisawa, T. Suda, K. Noguchi and M. Hirano, *J. Am. Chem. Soc.*, 2007, **129**, 12078–12079; (*b*) K. Tanaka, N. Fukawa, T. Suda and K. Noguchi, *Angew. Chem., Int. Ed.*, 2009, **48**, 5470–5473; (*c*) N. Fukawa, T. Osaka, K. Noguchi and K. Tanaka, *Org. Lett.*, 2010, **12**, 1324–1327.
12 Reviews: (*a*) J. Dubac, A. Laporterie and G. Manuel, *Chem. Rev.*, 1990, **90**, 215–263; (*b*) E. Colomer, R. J. P. Corriu and M. Lheureux, *Chem. Rev.*, 1990, **90**, 265–282; (*c*) B. Wrackmeyer, *Coord. Chem. Rev.*, 1995, **145**, 125–156; (*d*) S. Yamaguchi and K. Tamao, *J. Chem. Soc., Dalton Trans.*, 1998, 3693–3702.
13 S. Yamaguchi, C. Xu and K. Tamao, *J. Am. Chem. Soc.*, 2003, **125**, 13662–13663.
14 Recently, a helicene was used as emission layer in OLED: S. Sahasithiwat, T. Mophuang, L. Menbangpung, S. Kamtonwong and T. Sooksimuang, *Synth. Met.*, 2010, **160**, 1148–1152.
15 H. Maeda, Y. Bando, K. Shimomura, I. Yamada, M. Naito, K. Nobusawa, H. Tsumatori and T. Kawai, *J. Am. Chem. Soc.*, 2011, **133**, 9266–9269, and references therein.
16 Selected examples: (*a*) P. Dyreklev, M. Berggren, O. Inganäs, M. R. Andersson, O. Wennerström and T. Hjertberg, *Adv. Mater.*, 1995, **7**, 43–45; (*b*) S. H. Chen, D. Katsis, A. W. Schmid, J. C. Mastrangelo, T. Tsutsui and T. N. Blanton, *Nature*, 1999, **397**, 506–508.
17 (*a*) J. E. Field, G. Muller, J. P. Riehl and D. Venkataraman, *J. Am. Chem. Soc.*, 2003, **125**, 11808–11809; (*b*) T. Kaseyama, S. Furumi, X. Zhang, K. Tanaka and M. Takeuchi, *Angew. Chem., Int. Ed.*, 2011, **50**, 3684–3687.
18 (*a*) T. Shibata, T. Fujimoto, K. Yokota and K. Takagi, *J. Am. Chem. Soc.*, 2004, **126**, 8382–8383; (*b*) T. Shibata and K. Tsuchikama, *Chem. Commun.*, 2005, 6017–6019; (*c*) T. Shibata, K. Tsuchikama and M. Otsuka, *Tetrahedron: Asymmetry*, 2006, **17**, 614–619; (*d*) T. Shibata, Y. Arai, K. Takami, K. Tsuchikama, T. Fujimoto, S. Takebayashi and K. Takagi, *Adv. Synth. Catal.*, 2006, **348**, 2475–2483; (*e*) T. Shibata, T. Chiba, H. Hirashima, Y. Ueno and K. Endo, *Heteroat. Chem.*, 2011, **22**, 363–370.
19 Ir-catalyzed [2 + 2 + 2] cycloaddition for the synthesis of non-chiral multiaromatic siloles: T. Matsuda, S. Kadowaki, T. Goya and M. Murakami, *Org. Lett.*, 2007, **9**, 133–136.
20 Undesired cycloadduct **4aa** (triyne **B** in Scheme 1) could not be detected in the reaction mixture.
21 Cycloadduct **4aa** was obtained in 9% yield.
22 Stereospecific transformation from axial chirality to helical chirality for the synthesis of chiral helicenes; (*a*) M. Miyasaka, A. Rajca, M. Pink and S. Rajca, *J. Am. Chem. Soc.*, 2005, **127**, 13806–13807; (*b*) K. Nakano, Y. Hidehira, K. Takahashi, T. Hiyama and K. Nozaki, *Angew. Chem., Int. Ed.*, 2005, **44**, 7136–7138.
23 A catalytic amount of the Ni complex (20 mol%) gave only a trace amount of silahelicene **5aa**.
24 We ascertained the structural details of silahelicene **5aa** by X-ray crystallographic analysis (see ESI†).
25 [Ni(cod)$_2$]-mediated reaction of **1a** and **2a** did not proceed at all.
26 Silahelicene **5aa** remained intact in air for almost 2 years.
27 As a preliminary experiment, **5aa** was used as an emission layer in OLED, and the emission of blue fluorescence was observed. The detailed results will be disclosed in the near future.