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Asymmetric Synthesis and Photophysical Properties of Benzopyrano- or Naphthopyrano-Fused Helical Phosphafluorenes

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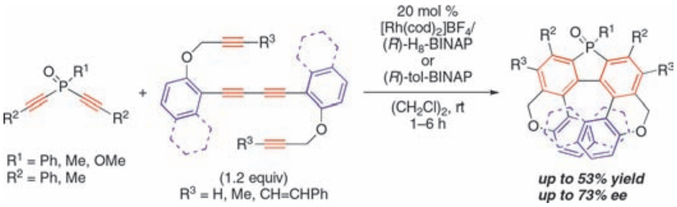
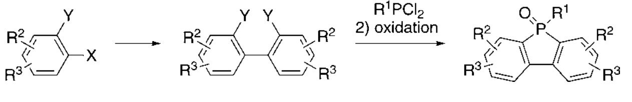
ABSTRACT



Enantioenriched benzopyrano- and naphthopyrano-fused helical phosphafluorenes have been synthesized by the rhodium-catalyzed enantioselective double [2 + 2 + 2] cycloaddition of dialkynyl phosphorus compounds with phenol- or naphthol-linked tetraynes. Photophysical properties of these phosphafluorenes are also disclosed.

Phosphafluorenes have attracted much attention as interesting candidates for organic semiconducting materials.[1] To synthesize a structurally diverse array of densely substituted phosphafluorenes, the synthetic methods that allow regioselective functionalization of the phosphafluorene core are highly attractive.[1,2] The most frequently employed method for their synthesis is biaryl coupling leading to 2,2′-dihalobiphenyls followed by the reaction with dichlorophosphines using a strong base and subsequent oxidation (Scheme 1).[1,2a−d] However, this method requires prior preparation of regioselectively substituted arenes and harsh reaction conditions.

Scheme 1



On the other hand, our research group demonstrated that cationic rhodium(I)/biaryl bisphosphine complexes are highly effective catalysts for the [2 + 2 + 2] cycloaddition to produce substituted arenes under mild reaction conditions.[3−5]

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(1) For selected recent examples, see: (a) Geramita, K.; McBee, J.; Tilley, T. D. *J. Org. Chem.* **2009**, *74*, 820. (b) Chen, R.-F.; Zhu, R.; Fan, Q.-L.; Huang, W. *Org. Lett.* **2008**, *10*, 2913. (c) Geramita, K.; McBee, J.; Tao, Y.; Segalman, R. A.; Tilley, T. D. *Chem. Commun.* **2008**, 5107.

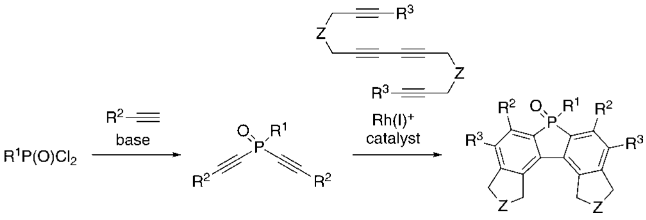
(2) For selected recent examples, see: (a) Widhalm, M.; Aichinger, C.; Mereiter, K. *Tetrahedron Lett.* **2009**, *50*, 2425. (b) Chen, R.-F.; Fan, Q.-L.; Zheng, C.; Huang, W. *Org. Lett.* **2006**, *8*, 203. (c) Dubrovina, N. V.; Jiao, H.; Tararov, V. I.; Spannenberg, A.; Kadyrov, R.; Monsees, A.; Christiansen, A.; Börner, A. *Eur. J. Org. Chem.* **2006**, 3412. (d) Leroux, F.; Mangano, G.; Schlosser, M. *Eur. J. Org. Chem.* **2005**, 5049. (e) Tsuji, H.; Komatsu, S.; Kanda, Y.; Umehara, T.; Saeki, T.; Tamao, K. *Chem. Lett.* **2006**, *35*, 758. (f) Fadhel, S.; Szieberth, D.; Deborde, V.; Lescop, C.; Nyulászi, L.; Hissler, M.; Réau, R. *Chem.—Eur. J.* **2009**, *15*, 4914.

(3) For our account, see: (a) Tanaka, K. *Synlett* **2007**, 1977. (b) Tanaka, K.; Nishida, G.; Suda, T. *J. Synth. Org. Chem. Jpn.* **2007**, *65*, 862.

10.1021/ol100227k

Furthermore our research group demonstrated that the rhodium-catalyzed double [2 + 2 + 2] cycloaddition is an effective method for the synthesis of symmetric biaryls,[6] spiranes,[7] and helicene-like molecules.[8] We anticipated that the rhodium-catalyzed double [2 + 2 + 2] cycloaddition between dialkynyl phosphine oxides[9,10] and tetraynes would be useful for the synthesis of symmetric and regioselectively substituted phosphafluorenes[11] because of the facile preparation of dialkynyl phosphine oxides from the corresponding terminal alkynes and dichlorophosphine oxides (Scheme 2).

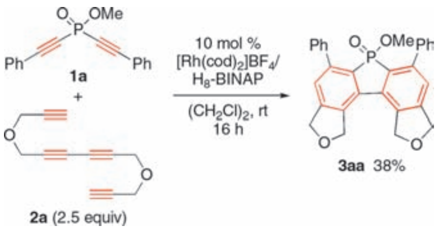
Scheme 2



In this paper, we disclose the synthesis of benzopyrano- and naphthopyrano-fused helical phosphafluorenes by the rhodium-catalyzed enantioselective double [2 + 2 + 2] cycloaddition. Photophysical properties of these phosphafluorenes are also disclosed.

We first examined the rhodium-catalyzed double [2 + 2 + 2] cycloaddition of dialkynyl phosphinate **1a** and terminal tetrayne **2a** leading to phosphafluorene **3aa** by using a cationic rhodium(I)/H_8-BINAP [2,2′-bis(diphenylphosphino)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl] complex as a catalyst. We were pleased to find that the desired reaction proceeded at room temperature to give **3aa** in 38% isolated yield, although excess **2a** (2.5 equiv) was required due to the rapid homo-[2 + 2 + 2] cycloaddition of **2a** (Scheme 3).

Scheme 3



We next examined the synthesis of helical phosphafluorenes by the rhodium-catalyzed enantioselective double [2 + 2 + 2] cycloaddition (Table 1).[12,13] After optimization of reaction conditions, the reaction of dialkynyl phosphinate **1a** and phenol-linked terminal tetrayne **2b** proceeded at room temperature for only 1 h to give benzopyrano-fused helical phosphafluorene **3ab** in 40% isolated yield with 73% ee by using a cationic rhodium(I)/(*R*)-tol-BINAP [2,2′-bis(di-*p*-tolylphosphino)-1,1′-binaphthyl] complex as a catalyst (entry 1). In this reaction, the homo-[2 + 2 + 2] cycloaddition of **2b** proceeded slowly, therefore a slight excess of **2b** (1.2 equiv) was sufficient. Thus the scope of helical phosphafluorene synthesis by the double [2 + 2 + 2] cycloaddition was examined. Dialkynyl phosphine oxides **1b**,**c** could react with

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(4) For a review of rhodium-catalyzed [2 + 2 + 2] cycloadditions, see: Fujiwara, M.; Ojima, I. In *Modern Rhodium-Catalyzed Organic Reactions*; Evans, P. A., Ed.; Wiley-VCH: Weinheim, Germany, 2005; Chapter 7, p 129.

(5) For recent reviews of transition metal-catalyzed [2 + 2 + 2] cycloadditions, see: (a) Galan, B. R.; Rovis, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 2830. (b) Tanaka, K. *Chem. Asian J.* **2009**, *4*, 508. (c) Varela, J. A.; Saá, C. *Synlett* **2008**, 2571. (d) Shibata, T.; Tsuchikama, K. *Org. Biomol. Chem.* **2008**, 1317. (e) Heller, B.; Hapke, M. *Chem. Soc. Rev.* **2007**, *36*, 1085. (f) Agenet, N.; Buisine, O.; Slowinski, F.; Gandon, V.; Aubert, C.; Malacria, M. *Organic Reactions*; RajanBabu, T. V., Ed.; John Wiley & Sons: Hoboken, NJ, 2007; Vol. 68, p 1. (g) Chopade, P. R.; Louie, J. *Adv. Synth. Catal.* **2006**, *348*, 2307. (h) Gandon, V.; Aubert, C.; Malacria, M. *Chem. Commun.* **2006**, 2209. (i) Kotha, S.; Brahmachary, E.; Lahiri, K. *Eur. J. Org. Chem.* **2005**, 4741. (j) Gandon, V.; Aubert, C.; Malacria, M. *Curr. Org. Chem.* **2005**, *9*, 1699. (k) Yamamoto, Y. *Curr. Org. Chem.* **2005**, *9*, 503.

(6) For examples by our research group, see: (a) Nishida, G.; Suzuki, N.; Noguchi, K.; Tanaka, K. *Org. Lett.* **2006**, *8*, 3489. (b) Nishida, G.; Ogaki, S.; Yusa, Y.; Yokozawa, T.; Noguchi, K.; Tanaka, K. *Org. Lett.* **2008**, *10*, 2849. For examples by other research groups, see: (c) Doherty, S.; Knight, J. G.; Smyth, C. H.; Harrington, R. W.; Clegg, W. *Org. Lett.* **2007**, *9*, 4925. (d) Doherty, S.; Smyth, C. H.; Harrington, R. W.; Clegg, W. *Organometallics* **2008**, *27*, 4837.

(7) Wada, A.; Noguchi, K.; Hirano, M.; Tanaka, K. *Org. Lett.* **2007**, *9*, 1295.

(8) For the rhodium-catalyzed enantioselective double [2 + 2 + 2] cycloaddition of dialkynylketones with phenol- or naphthol-linked tetraynes, see: Tanaka, K.; Fukawa, N.; Suda, T.; Noguchi, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 5470.

(9) Enantioselective synthesis of *P*-stereogenic alkynylphosphine oxides by the rhodium-catalyzed [2 + 2 + 2] cycloaddition of dialkynyl phosphine oxides with 1,6-diynes was reported;see: Nishida, G.; Noguchi, K.; Hirano, M.; Tanaka, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 3410.

(10) For transition metal-catalyzed [2 + 2 + 2] cycloadditions involving alkynyl phosphorus compounds, see: (a) Heller, B.; Gutnov, A.; Fischer, C.; Drexler, H.-J.; Spannenberg, A.; Redkin, D.; Sundermann, C.; Sundermann, B. *Chem.—Eur. J.* **2007**, *13*, 1117. (b) Nishida, G.; Noguchi, K.; Hirano, M.; Tanaka, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 3951. (c) Kondoh, A.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2007**, *129*, 6996. See also refs 6b,c, and d.

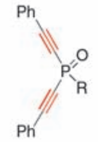
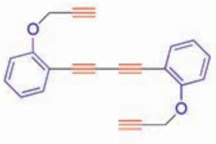
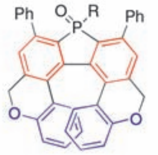
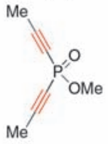
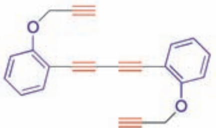
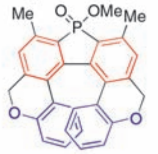
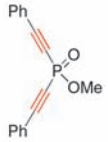
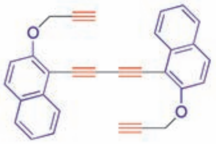
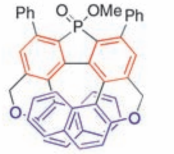
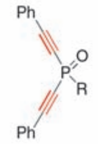
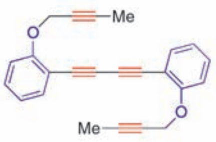
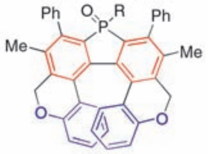
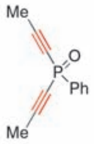
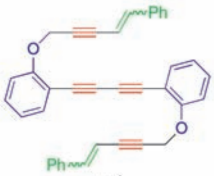
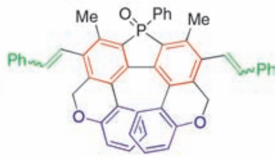
(11) Syntheses of heterofluorenes by transition metal-catalyzed [2 + 2 + 2] cycloadditions of heteroatom-bridged 1,6-diynes with monoynes have been reported. Carbazoles: (a) Witulski, B.; Alayrac, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 3281. (b) Alayrac, C.; Schollmeyer, D.; Witulski, B. *Chem. Commun* **2009**, 1464. Silafluorenes: (c) Matsuda, T.; Kadowaki, S.; Goya, T.; Murakami, M. *Org. Lett.* **2007**, *9*, 133. Dibenzofurans and azadibenzofurans: (d) Komine, Y.; Kamisawa, A.; Tanaka, K. *Org. Lett.* **2009**, *11*, 2361.

(12) For enantioselective syntheses of helicenes and helicene-like molecules by transition metal-mediated [2 + 2 + 2] cycloadditions, see: (a) Stará, I. G.; Starý, I.; Kollárovič, A.; Teplý, F.; Vyskočil, Š.; Šaman, D. *Tetrahedron Lett.* **1999**, *40*, 1993. (b) Teplý, F.; Stará, I. G.; Starý, I.; Kollárovič, A.; Šaman, D.; Vyskočil, Š.; Fiedler, P. *J. Org. Chem.* **2003**, *68*, 5193. (c) Caeiro, J.; Peña, D.; Cobas, A.; Pérez, D.; Guitián, E. *Adv. Synth. Catal.* **2006**, *348*, 2466. (d) Tanaka, K.; Kamisawa, A.; Suda, T.; Noguchi, K.; Hirano, M. *J. Am. Chem. Soc.* **2007**, *129*, 12078. See also ref 8.

(13) For a recent review of helicene synthesis, see: Urbano, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 3986.

(14) Nonphotochemical syntheses of higher order (≥[8]) helicenes or helicene-like molecules have been reported in a limited number; see: (a) Fox, J. M.; Katz, T. J. *J. Org. Chem.* **1999**, *64*, 302. (b) Norsten, T. B.; Peters, A.; McDonald, R.; Wang, M.; Branda, N. R. *J. Am. Chem. Soc.* **2001**, *123*, 7447. (c) Han, S.; Bond, A. D.; Disch, R. L.; Holmes, D.; Schulman, J. M.; Teat, S. J.; Vollhardt, K. P. C.; Whitener, G. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 3223. (d) Han, S.; Anderson, D. R.; Bond, A. D.; Chu, H. V.; Disch, R. L.; Holmes, D.; Schulman, J. M.; Teat, S. J.; Vollhardt, K. P. C.; Whitener, G. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 3227. (e) Miyasaka, M.; Rajca, A.; Pink, M.; Rajca, S. *J. Am. Chem. Soc.* **2005**, *127*, 13806. (f) Sehnal, P.; Stará, I. G.; Šaman, D.; Tichý, M.; Míšek, J.; Cvačka, J.; Rulíšek, L.; Chocholoušová, J.; Vacek, J.; Goryl, G.; Szymonski, M.; Císařová, I.; Starý, I. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 13169.

Table 1. Rh-Catalyzed Asymmetric Synthesis of Benzopyrano- or Naphthopyrano-Fused Helical Phosphafluorenes[a]

entry	1 (R)	2	3 % yield[b] (% ee)
			
1	**1a** (OMe)	**2b**	(−)-**3ab** 40 (73)
2	**1b** (Me)	**2b**	(−)-**3bb** 50 (34)
3	**1c** (Ph)	**2b**	(−)-**3cb** 53 (32)
			
4	**1d**	**2b**	(−)-**3db** 16 (57)
			
5	**1a**	**2c**	(+)-**3ac** 20 (23)
			
6	**1a** (OMe)	**2d**	(−)-**3ad** 23 (50)
7	**1b** (Me)	**2d**	(−)-**3bd** 46 (9)
8	**1c** (Ph)	**2d**	(−)-**3cd** 30 (47)
			
9[c]	**1e**	**2e**[d]	(+)-**3ee**[d] 16 (48[e])

[a] Reactions were conducted with $[Rh(cod)_2]BF_4$ (20 mol %), ligand (20 mol %), **1a**−**e** (1 equiv), and **2a**−**e** (1.2 equiv) in $(CH_2Cl)_2$ at rt for 1 h. Ligand: (*R*)-tol-BINAP (entries 1−4 and 9), (*R*)-H_8-BINAP (entries 5−8). [b] Isolated yield. [c] For 6 h. [d] A mixture of olefin geometric isomers. [e] ee value of the major olefin geometric isomer.

tetrayne **2b** to yield the corresponding phosphafluorenes in higher yields than that from dialkynyl phosphinate **1a**, although lower enantioselectivities were observed (entries 2 and 3). Not only phenyl-substituted dialkynyl phosphinate **1a** but also the methyl-substituted one **1d** could participate in this reaction albeit in low yield (entry 4). With respect to tetraynes, naphthol-linked terminal tetrayne **2c** could also react with **1a** to yield more overcrowded naphthopyrano-fused helical phosphafluorene **3ac**, possessing nine successive rings,[15] by using (*R*)-H_8-BINAP as a ligand (entry 5). Not only the phenol-linked terminal tetrayne **2b** but also the internal tetrayne **2d** could participate in this reaction by using (*R*)-H_8-BINAP as a ligand (entries 6−8). The introduction of the π-component at the 2- and 7-positions as well as the 4- and 5-positions of the phosphafluorene core is of interest for further extension of the conjugation. Therefore the reaction of dialkynyl phosphinate **1e** and styryl-substituted internal tetrayne **2e** leading to 2,7-styryl-substituted phosphafluorene **3ee** was investigated. Although the product yield was low, the desired reaction proceeded at room temperature by using the cationic rhodium(I)/(*R*)-tol-BINAP catalyst (entry 9).

In our previous report, gradual racemization of a benzopyrano-fused helical fluorenone proceeded in CH_2Cl_2 solution at room temperature.[8] On the contrary, the benzopyrano-fused helical phosphafluorenes of Table 1 possess stable helical chirality in CH_2Cl_2 solution at room temperature presumably due to the longer length of the C−P bond than the C−C bond. Indeed, the ORTEP diagram of benzopyrano-fused helical phosphafluorene (±)-**3bb** revealed that two 2-alkoxyphenyl rings of **3bb** largely overlapped each other (Figure 1).

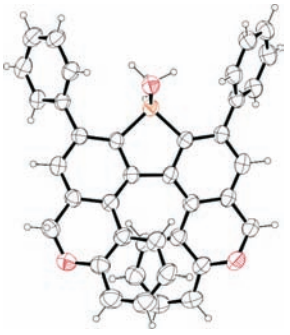


Figure 1. ORTEP diagram of helical phosphafluorene (±)-**3bb** (top view) with ellipsoids at 30% probability.

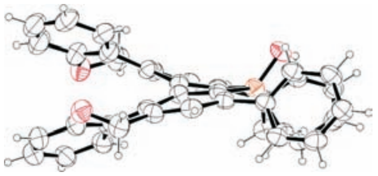


Figure 2. ORTEP diagram of helical phosphafluorene (±)-**3bb** (side view) with ellipsoids at 30% probability.

To compare the photophysical properties between 4,5- and 3,6-di(2-alkoxyphenyl)phosphafluorenes, the synthesis of 3,6-

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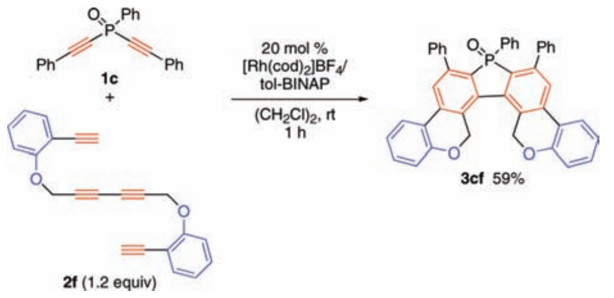
(15) For selected examples, see: (a) Adriaenssens, L.; Severa, L.; Šálová, T.; Císařová, I.; Pohl, R.; Šaman, D.; Rocha, S. V.; Finney, N. S.; Pospíšil, L.; Slavíček, P.; Teplý, F. *Chem.−Eur. J.* **2009**, *15*, 1072. (b) Graule, S.; Rudolph, M.; Vanthuyne, N.; Autschbach, J.; Roussel, C.; Crassous, J.; Reau, R. *J. Am. Chem. Soc.* **2009**, *131*, 3183. (c) Takenaka, N.; Sarangthem, R. S.; Captain, B. *Angew. Chem., Int. Ed.* **2008**, *47*, 9708. (d) Misek, J.; Teply, F.; Stara, I. G.; Tichy, M.; Saman, D.; Cisarova, I.; Vojtisek, P.; Stary, I. *Angew. Chem., Int. Ed.* **2008**, *47*, 3188. (e) Nakano, K.; Hidehira, Y.; Takahashi, K.; Hiyama, T.; Nozaki, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 7136. (f) Wigglesworth, T. J.; Sud, D.; Norsten, T. B.; Lekhi, V. S.; Branda, N. R. *J. Am. Chem. Soc.* **2005**, *127*, 7272. (g) Phillips, K. E. S.; Katz, T. J.; Jockusch, S.; Lovinger, A. J.; Turro, N. J. *J. Am. Chem. Soc.* **2001**, *123*, 11899, and references cited therein. See also refs 14a,b, and 14e.

Scheme 4



di(2-alkoxyphenyl)phosphafluorene **3cf** by the reaction of dialkynyl phosphine oxide **1c** and phenol-linked terminal tetrayne **2f** was investigated. The desired reaction proceeded at room temperature by using the cationic rhodium(I)/tol-BINAP catalyst to yield **3cf** in good yield (Scheme 4).

Table 2. Photophysical Properties of Representative Phosphafluorenes[a]

entry	3	UV absorption λ_{max} (nm)[b]	emission λ_{max} (nm)[b,c]	$[\alpha]^{25}_{D}$[d]
1	**3aa**	259, 341	375	
2	(−)-**3ab**	288, 341	477	699
3	(−)-**3bb**	288, 344	471	546
4	(−)-**3cb**	289, 337	474	636
5	(−)-**3db**	281, 338	469	584
6	(+)-**3ac**	308, 386	490	420
7	(−)-**3ad**	285, 343	464	586
8	(+)-**3ee**	281, 348[e]	482[e]	279[e]
9	**3cf**	275	406	

[a] Measured in $CHCl_3$. [b] Concentration: 1.0×10^{-5} M. [c] Excited at 280 nm. [d] Values are calculated as 100% ee. [e] Values were measured with use of a mixture of olefin geometric isomers.

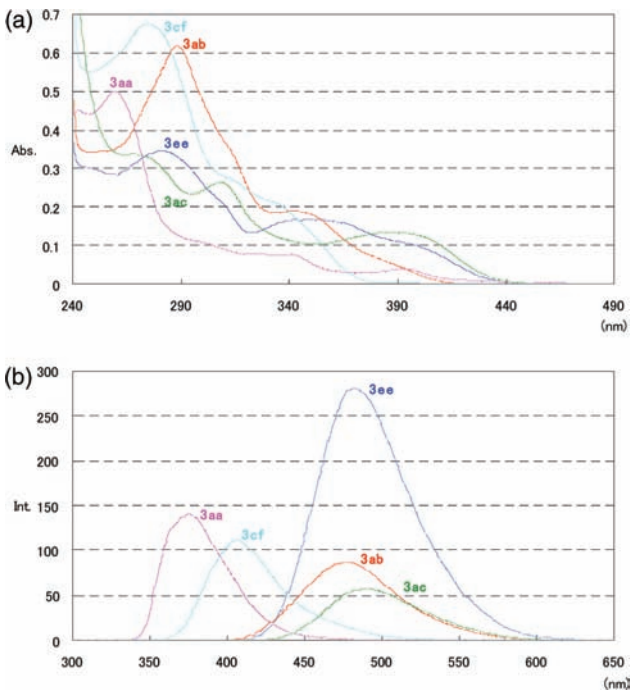


Figure 3. (a) UV−vis spectra and (b) emission spectra of **3aa**, **3ab**, **3ac**, **3ee**, and **3cf** in $CHCl_3$ (1.0×10^{-5} M).

Absorption and emission data of representative phosphafluorenes are shown in Table 2 and Figure 3. As expected, 4,5-di(2-alkoxynaphthyl)phosphafluorene **3ab** (entry 2) showed large red shifts of absorption and emission maxima compared with phosphafluorene **3aa**, which contained no 2-alkoxyphenyl group (entry 1). Further red shifts were observed in 4,5-di(2-alkoxynaphthyl)phosphafluorene **3ac** (entry 6). On the other hand, 3,6-di(2-alkoxyphenyl)phosphafluorene **3cf** showed smaller red shifts compared with **3aa** (entry 9). The substituents on the phosphorus appeared to have a small impact on absorption and emission maxima (entries 2−4). As shown in the ORTEP diagram of phosphafluorene (±)-**3bb** (Figure 2), two phenyl rings at the 1- and 8-positions and the phosphafluorene core are in the twisted conformation, which would inhibit the conjugation. Indeed, 1,8-diphenyl- (**3ab**, entry 2) and 1,8-dimethylphosphafluorenes (**3db**, entry 5) showed close absorption and emission maxima. With respect to the substituents at the 2- and 7-positions of the phosphafluorene core, 2,7-dimethyl (**3ad**, entry 7) and 2,7-distyryl substitution (**3ee**, entry 8) showed a small shift of emission maxima compared with **3ab** (entry 2) and **3db** (entry 5), respectively, while the emission intensity of **3ee** significantly increased (Figure 3). Optical rotation values of representative helical phosphafluorenes are also shown in Table 2. Interestingly, the more overcrowded naphthopyrano-fused phosphafluorene **3ac** (entry 6) exhibits a smaller optical rotation value than that of the less overcrowded benzopyrano-fused phosphafluorene **3ab** (entry 2).

In conclusion, we have successfully synthesized enantioenriched benzopyrano- or naphthopyrano-fused helical phosphafluorenes by the rhodium-catalyzed enantioselective double [2 + 2 + 2] cycloaddition of dialkynyl phosphorus compounds with phenol- or naphthol-linked tetraynes. We believe that the compounds synthesized in this paper are fascinating examples of helicene-like species containing heteroatoms in the helical backbone.[15] Future work will focus on application of this methodology to the synthesis of various heterofluorenes.

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Supporting Information Available: Experimental procedures, compound characterization data, and an X-ray crystallographic information file. This material is available free of charge via the Internet at http://pubs.acs.org.

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