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Enantioselective intramolecular [2+2+2] cycloaddition of triynes for the synthesis of atropisomeric chiral *ortho*-diarylbenzene derivatives

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Dedicated to Professor Jack Halpern on the occasion of his 80th birthday

Abstract—An iridium-chiral diphosphine complex was used to catalyze an enantioselective [2+2+2] cycloaddition of oxygen- and nitrogen-bridged triynes with *ortho*-substituted aryl groups on their termini. *ortho*-Diarylbenzenes with atropisomeric chiralities were obtained in high yield and enantiomeric excess.

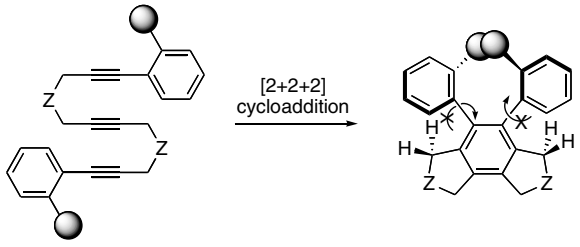
1. Introduction

Cyclotrimerization of alkynes is an atom-economical and straightforward method for the construction of substituted benzene derivatives.[1] In 1948, Reppe et al. reported the Ni-catalyzed cyclization of acetylene and identified benzene amongst the cycloadducts.[2] Yamazaki reported the pioneering work of cobalt complex-mediated cycloaddition of phenylacetylene, and opened the way of transition metal-mediated or catalyzed [2+2+2] cycloaddition of alkynes in organic synthesis.[3] Furthermore, due to the synthesis of various types of polycyclic compounds, including the application to natural product synthesis, by Vollhardt, it has been recognized as a powerful synthetic protocol.[4]

The [2+2+2] cycloaddition is classified into three types: an intermolecular reaction of three alkynes, a semi-intramolecular one of a diyne and a monoalkyne, and an intramolecular one of a triyne. Compared with the first two types, the examples of the third type are not common: Rh,[5] Ni,[6] Pd,[7] Ru,[8] Co,[9] Mo,[10] and Fe[11] complexes have been reported as catalysts. Among them, however, the enantioselective reaction is limited to the cobalt-catalyzed reaction, which gave helically chiral helicene derivatives with moderate ee and yield.[12]

Recently, we[13] and other groups[14,15] independently reported an enantioselective semi-intramolecular and intermolecular [2+2+2] cycloaddition for the synthesis of axially chiral compounds with high to excellent ee.[16,17] We herein report the first example of an enantioselective intramolecular [2+2+2] cycloaddition of triynes for the construction of atropisomeric biaryl skeletons with axial chiralities.

When the cyclotrimerization of a triyne with *ortho*-substituted aryl groups on its alkyne termini proceeds and the free rotation of two single bonds of biaryls is restricted, two enantiomers and a *meso* isomer can be obtained. In 1,2-di(naphthalen-1-yl)benzene, they were freely rotating at room temperature,[18] however, two five-membered systems, which are fused to benzene ring, would probably deter the free rotation (Scheme 1).



Scheme 1. Construction of atropisomeric chiral *o*-diarylbenzene derivatives.

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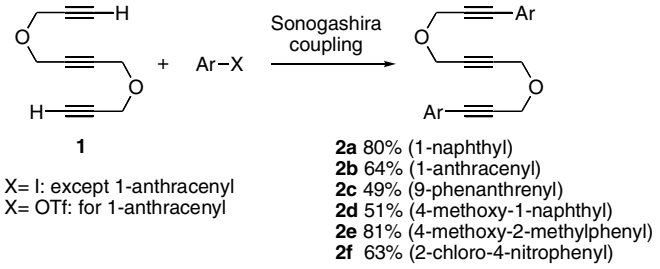
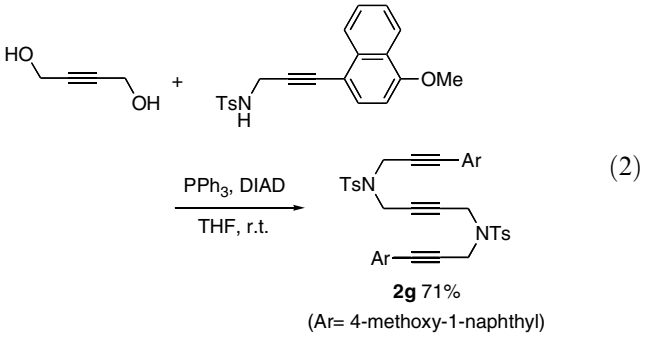
2. Results and discussion

Heteroatom-bridged symmetrical triynes **2a**–**g** were readily prepared: oxygen-bridged triynes **2a**–**f** were synthesized by double Sonogashira coupling of unsubstituted triyne **1**[5a] with aryl iodides or an aryl triflate (Eq. 1). Nitrogen-bridged triyne **2g** was prepared by the reaction of propargyl amine with but-2-yne-1,4-diol under Mitsunobu reaction conditions (Eq. 2).[19]



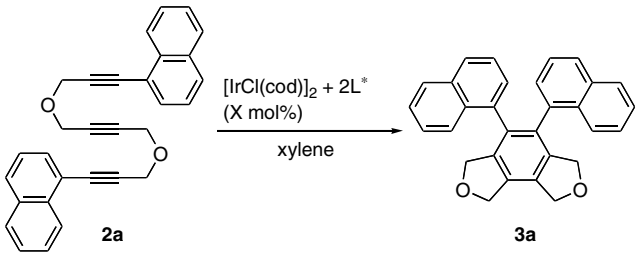
(1)



(2)

We chose oxygen-bridged triyne **2a**, with naphthyl groups on its alkyne termini, as a model substrate and examined an enantioselective intramolecular [2+2+2] cycloaddition using a chiral iridium catalyst, prepared in situ from $[IrCl(cod)]_2$ and a chiral diphosphine ligand (Table 1). When (*S*,*S*)-MeDUPHOS was used as a chiral ligand, which was the best for semi-intramolecular reaction of diynes and monoalkynes,[13] the cycloaddition proceeded even at room temperature and the cycloadduct **3a** was obtained in good yield and high ee; however, it required a long reaction time (entry 1). At 60 °C,[20,21] triyne **2a** was completely consumed within 30 min with almost the same yield and enantioselectivity being achieved (entry 2).[22] In 1,2-dimethoxyethane (DME), the yield lowered but the ee was improved (entry 3). (*R*,*R*)-MeDUPHOS certainly induced the opposite enantioselectivity (entry 4). A decrease in yield, ee and the ratio of *dl*/*meso* isomers was observed with a somewhat bulkier ligand, EtDUPHOS (entry 5). Chiral diphosphine, BINAP, elevated the catalytic activity and triyne **2a** was completely consumed within 30 min even at room temperature to give **3a** in high yield; however, ee was very low (entry 6). A bulkier ligand, 3,5-xylylBINAP, gave almost the same results (entry 7). The reaction efficiently proceeded even with 2 mol % of Ir-MeDUPHOS catalyst (entry 8). It required a longer reaction time; although, only 0.5 mol % catalyst was sufficient for good yield with high enantioselectivity (entry 9).

Table 1. Investigation of reaction conditions for the enantioselective [2+2+2] cycloaddition of triyne **2a**



Entry[a]	*X*	L*[b]	Temp/°C	Time/h	Yield/%	ee/%	*dl*:*meso*
1	10	A	rt	168	81	90	6:1
2	10	A	60	0.5	82	90	5:1
3[c]	10	A	60	0.5	69	94	7:1
4	10	B	60	0.5	80	−90	5:1
5	10	C	60	3	67	69	3:1
6	10	D	rt	0.5	94	23	4:1
7	10	E	rt	0.5	94	22	6:1
8	2	A	60	0.5	79	91	5:1
9	0.5	A	60	4	78	88	6:1

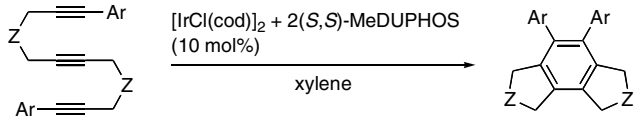
[a] Concentration of catalyst: 2.5×10^{-3} M for entries 1–7. 5×10^{-4} M for entries 8 and 9.
[b] A = (*S*,*S*)-MeDUPHOS, B = (*R*,*R*)-MeDUPHOS, C = (*S*,*S*)-EtDUPHOS, D = (*S*)-BINAP, E = (*S*)-3,5-xylylBINAP.
[c] The reaction was examined in DME.

Next, we examined various triynes **2b**–**g**, which have *ortho*-substituted aryl groups on their alkyne termini, using the Ir-MeDUPHOUS catalyst (Table 2). When an anthracenyl substituent was used in place of a naphthyl one, the reaction proceeded at room temperature and high ee was also achieved. The *meso* isomer could not be detected by 400 MHz NMR analysis (entry 1). It is noteworthy that cycloadduct **3b** has an extraordinary large [α] value of 604°. It required a higher reaction temperature, but phenanthrenyl-substituted triyne **2c** was also transformed into cycloadduct **3c** with high ee (entries 2 and 3). A methoxy substituent on the naphthalene ring was tolerable, and high ee and a higher *dl*/*meso* ratio were attained (entry 4). 4-Methoxy-2-methylphenyl and 2-chloro-4-nitrophenyl substituents also realized the highly enantioselective cycloaddition, and *ortho*-diarylbenzene derivatives **3e**,**f** were obtained in high yield and ee (entries 6–8) with the absolute configuration of **3f** determined to be (*S*,*S*)-form by X-ray measurement (Fig. 1). Nitrogen-bridged triyne **2g** was also an appropriate substrate and the corresponding multicyclic adduct **3g** obtained in high ee (entry 9). In general, higher yields were achieved in xylene rather than DME (entries 3, 5, and 7).

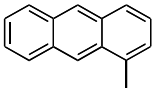
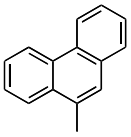
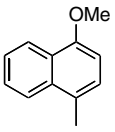
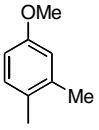
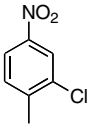
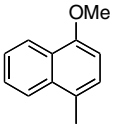
3. Conclusion

In conclusion, we have developed an enantioselective intramolecular [2+2+2] cycloaddition of various triynes, having *ortho*-substituted aryl groups on their alkyne termini, using the chiral iridium catalyst. The present

Table 2. Iridium-catalyzed enantioselective intramolecular [2+2+2] cycloaddition of triynes **2b–g**



2b-g **3b-g**

Entry	Z	Ar	Triyne	Temp/°C	Time/h	Yield/%	ee/%	*dl*:*meso*
1	O		**2b**	rt	18	68 (**3b**)	87	>20:1
2	O		**2c**	60	0.3	92 (**3c**)	87	5:1
3[a]			**2c**	60	6	71 (**3c**)	87	7:1
4	O		**2d**	60	0.3	86 (**3d**)	90	14:1
5[a]			**2d**	60	0.3	81 (**3d**)	90	5:1
6	O		**2e**	60	0.3	>99 (**3e**)	95	2:1
7[a]			**2e**	60	0.3	74 (**3e**)	90	3:1
8	O		**2f**	60	0.5	95 (**3f**)	90	12:1
9	NTs		**2g**	60	0.5	89 (**3g**)	ca. 95[b]	2:1

[a] The reaction was examined in DME.
[b] *d*- and *l*-Isomers were not completely divided by HPLC using various chiral columns, which we examined.

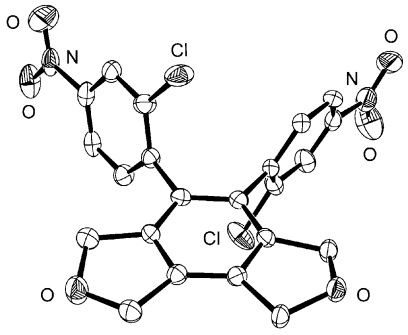


Figure 1. ORTEP diagram of (*S*,*S*)-**3f**.

reaction provides a new and efficient protocol for the enantioselective synthesis of atropisomeric 1,2-diarylbenzene derivatives with axial chiralities.

4. Experimental

4.1. General

Optical rotations were measured with Jasco DIP-1000 polarimeter. IR spectra were recorded with Horiba FT730 spectrophotometer. NMR spectra were measured with JEOL AL-400 and Lambda500 spectrometers using tetramethylsilane as an internal standard and $CDCl_3$ was used as a solvent. Mass spectra were measured with JEOL JMS-SX102A and elemental analyses with Perkin Elmer PE2400II. Dehydrated DMF, toluene, and xylene are commercially available and they were dried over molecular sieves 4 Å (MS 4 Å) and degassed by argon bubbling before use. All reactions were examined under an argon atmosphere.

4.2. Experimental procedures for Sonogashira coupling (Eq. 1)

The preparation of triyne **2b**: $PdCl_2(PPh_3)_2$ (19.2 mg, 0.027 mmol), CuI (9.6 mg, 0.050 mmol), and **1** (46.4 mg, 0.29 mmol) were stirred in degassed Et_3N/DMF (1/1, 1.5 mL) and a Et_3N/DMF (1/1) solution (1.5 mL) of 1-anthracenyl trifluoromethanesulfonate (199.1 mg, 0.61 mmol) was added. After stirring at 50 °C for 4.5 h, the solvent was removed under reduced pressure. The residue was dissolved in AcOEt (50 mL) and washed with 1 M HCl (30 mL), H_2O (20 mL × 2), and brine (30 mL), and dried over $MgSO_4$. Purification of the crude products by thin layer chromatography (benzene/AcOEt = 40/1) gave pure **2b** (94.0 mg, 64% yield).

The preparation of triyne **2c**: $Pd(PPh_3)_4$ (96.3 mg, 0.083 mmol), CuI (31.1 mg, 0.16 mmol), and **1** (134.8 mg, 0.83 mmol) were stirred in degassed toluene (3.0 mL) and a toluene solution (3.0 mL) of 9-iodophenanthrene (559.0 mg, 1.84 mmol) was added. After the addition of *i*-Pr_2NH (0.70 mL, 4.98 mmol), the resulting mixture was stirred at room temperature for 4.5 h. After removing the solvent under reduced pressure, the residue was dissolved in benzene (30 mL), filtered, and evaporated in vacuo. Purification of the crude products by column chromatography (hexane/AcOEt = 7/1) gave pure **2c** (207.8 mg, 49% yield).

4.2.1. 1,12-Di(naphthalen-1-yl)-4,9-dioxadodeca-1,6,11-triyne 2a. Yellow oil. IR (neat) 1068, 773 cm^{-1}; ^1H NMR $\delta = 4.49$ (s, 4H), 4.66 (s, 4H), 7.39–7.84 (m, 12H), 8.32 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR $\delta = 57.0$, 57.6, 82.4, 85.0, 88.9, 119.9, 125.0, 125.9, 126.3, 126.8, 128.2, 129.0, 130.7, 133.0, 133.2; HRMS (FAB) for M found *m*/*e* 414.1665, calcd for $C_{30}H_{22}O_2$: 414.1620.

4.2.2. 1,12-Di(anthracen-1-yl)-4,9-dioxadodeca-1,6,11-triyne 2b. Brown solid. Mp 127–128 °C; IR (KBr disk) 1066, 731 cm^{-1}; ^1H NMR $\delta = 4.57$ (s, 4H), 4.75 (s, 4H), 7.36–7.49 (m, 6H), 7.70 (d, $J = 6.8$ Hz, 2H), 7.98–8.09 (m, 6H), 8.42 (s, 2H), 8.87 (s, 2H). ^{13}C NMR $\delta = 57.0$, 57.8, 82.5, 85.2, 89.3, 120.0, 124.4, 124.8, 125.8, 125.8, 126.8, 127.9, 128.5, 129.4, 130.7, 130.8, 131.0, 131.8, 132.0; HRMS (FAB) for M found *m*/*e* 514.1920, calcd for $C_{38}H_{26}O_2$: 514.1933.

4.2.3. 1,12-Di(phenanthren-9-yl)-4,9-dioxadodeca-1,6,11-triyne 2c. Brown oil. IR (CH_2Cl_2) 1066, 725 cm^{-1}; ^1H NMR $\delta = 4.53$ (s, 4H), 4.70 (s, 4H), 7.57–7.69 (m, 8H), 7.83 (d, $J = 7.8$ Hz, 2H), 8.01 (s, 2H), 8.41–8.43 (m, 2H), 8.64–8.69 (m, 4H). ^{13}C NMR $\delta = 57.0$, 57.6, 82.5, 85.2, 88.6, 118.8, 122.6, 122.7, 126.8, 127.0, 127.1, 127.6, 128.6, 130.0, 130.2, 130.4, 131.0, 132.4, 135.2; HRMS (FAB) for M+1 found *m*/*e* 515.2015, calcd for $C_{38}H_{27}O_2$: 515.2011.

4.2.4. 1,12-Bis(4-methoxynaphthalen-1-yl)-4,9-dioxadodeca-1,6,11-triyne 2d. Yellow solid. Mp 66–67 °C; IR (KBr disk) 1099, 766 cm^{-1}; ^1H NMR $\delta = 4.00$ (s, 6H), 4.48 (s, 4H), 4.64 (s, 4H), 6.75 (d, $J = 8.0$ Hz, 2H), 7.27–7.59 (m, 4H), 7.63 (d, $J = 8.0$ Hz, 2H), 8.25–8.27 (m, 4H). ^{13}C NMR $\delta = 55.6$, 56.8, 57.7, 82.4, 85.3, 87.3, 103.4, 112.1, 122.2, 125.3, 125.7, 125.8, 127.4, 131.6, 134.3, 156.2; HRMS (FAB) for M found *m*/*e* 474.1855, calcd for $C_{32}H_{26}O_4$: 474.1831.

4.2.5. 1,12-Bis(4-methoxy-2-methylphenyl)-4,9-dioxadodeca-1,6,11-triyne 2e. Dark yellow oil. IR (neat) 1070, 814 cm^{-1}; ^1H NMR $\delta = 2.41$ (s, 6H), 3.79 (s, 6H), 4.39 (s, 4H), 4.51 (s, 4H), 6.67 (dd, $J = 2.6$, 8.4 Hz, 2H), 6.73 (d, $J = 2.6$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR $\delta = 21.0$, 55.2, 56.6, 57.5, 82.2, 85.8, 86.4, 111.2, 114.5, 115.0, 133.5, 142.2, 159.7; HRMS (FAB) for M+1 found *m*/*e* 403.1920, calcd for $C_{26}H_{27}O_4$: 403.1909.

4.2.6. 1,12-Bis(2-chloro-4-nitrophenyl)-4,9-dioxadodeca-1,6,11-triyne 2f. Yellow solid. Mp 101 °C; IR (KBr disk) 1516, 1352, 1054, 731 cm^{-1}; ^1H NMR $\delta = 4.44$ (s, 4H), 4.58 (s, 4H), 7.64 (d, $J = 8.5$ Hz, 2H), 8.09 (dd, $J = 2.3$, 8.5 Hz, 2H), 8.29 (d, $J = 2.3$ Hz, 2H). ^{13}C NMR $\delta = 57.1$, 57.2, 82.2, 82.3, 94.9, 121.4, 124.4, 128.8, 133.7, 136.9, 147.3. Anal. Calcd for $C_{22}H_{14}Cl_2N_2O_6$: C, 55.66; H, 2.94; N, 5.66. Found: C, 55.83; H, 2.98; N, 5.92.

4.2.7. 1,12-Bis(4-methoxynaphthalen-1-yl)-4,9-bis(*p*-toluenesulfonyl)-4,9-diazadodeca-1,6,11-triyne 2g. Yellow solid. Mp 67–68 °C; IR (CH_2Cl_2) 1350, 1163, 1095, 768 cm^{-1}; ^1H NMR $\delta = 2.21$ (s, 6H), 3.98 (s, 6H), 4.17 (s, 4H), 4.41 (s, 4H), 6.60 (d, $J = 8.1$ Hz, 2H), 7.17 (d, $J = 8.1$ Hz, 4H), 7.26–7.50 (m, 6H), 7.71 (d, $J = 8.1$ Hz, 4H), 7.85–8.24 (m, 4H). ^{13}C NMR $\delta = 21.4$, 36.7, 37.6, 55.6, 78.6, 84.2, 84.4, 103.2, 111.6, 122.2, 125.1, 125.4, 125.6, 127.3, 127.7, 129.5, 131.4, 133.9, 134.9, 143.9, 156.0; HRMS (FAB) for M+1 found *m*/*e* 781.2398, calcd for $C_{46}H_{41}N_2O_6S_2$: 781.2406.

4.3. Typical experimental procedure (Table 1, entry 2)

(*S*,*S*)-MeDUPHOS (6.1 mg, 0.02 mmol) and $[IrCl(cod)]_2$ (6.7 mg, 0.01 mmol) were stirred in degassed xylene (1.0 mL) at room temperature to give a reddish yellow solution. After the addition of a xylene solution (3.0 mL) of triyne **2a** (41.5 mg, 0.10 mmol), the resulting mixture was further stirred at 60 °C for 30 min. The solvent was removed under reduced pressure, and purification of the crude products by thin layer chromatography (benzene/AcOEt = 20/1) gave pure **3a** (33.9 mg, 82% yield). The ee was determined by HPLC analysis using a chiral column.

4.3.1. 4,5-Di(naphthalen-1-yl)-1,3,6,8-tetrahydro-2,7-dioxa*as*-indacene 3a. White solid. Mp >230 °C (decomposed); IR (KBr disk) 1055, 773 cm^{-1}; ^1H NMR $\delta = 4.67$ (d, $J = 12.4$ Hz, 2H), 4.73 (d, $J = 12.4$ Hz, 2H), 5.22 (d, $J = 12.6$ Hz, 2H), 5.26 (d, $J = 12.6$ Hz, 2H), 6.84–7.77 (m, 14H). ^{13}C NMR $\delta = 72.9$, 73.6, 124.9, 125.4, 125.6, 125.9, 126.2, 127.4, 128.3, 131.1, 131.4, 133.1, 133.3, 135.7, 139.7. Anal. Calcd for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35. Found: C, 86.75; H, 5.49. $[\alpha]_D^{29} = -347.9$ (*c* 1.7, $CHCl_3$, 90% ee). Ee was determined by HPLC analysis using Daicel Chiralpak AD-H × 2 (eluent: 5% 2-propanol in hexane, flow

rate: 1.0 mL/min, retention time: 14 min for major isomer and 15 min for minor isomer).

4.3.2. 4,5-Di(anthracen-1-yl)-1,3,6,8-tetrahydro-2,7-dioxa*as*-indacene 3b. Pale yellow solid. Mp >200 °C (decomposed); IR (KBr disk) 1045, 733 cm^{-1}; ^1H NMR $\delta = 4.74$ (d, $J = 12.4$ Hz, 2H), 4.78 (d, $J = 12.4$ Hz, 2H), 5.31 (d, $J = 12.4$ Hz, 2H), 5.35 (d, $J = 12.4$ Hz, 2H), 6.83–6.92 (m, 4H), 7.48–7.50 (m, 4H), 7.64–7.72 (m, 2H), 7.99–8.07 (m, 4H), 8.26 (s, 2H), 8.36 (s, 2H). ^{13}C NMR $\delta = 73.0$, 73.7, 124.2, 124.5, 125.4, 125.5, 125.6, 126.9, 127.9, 128.0, 128.5, 130.2, 131.5, 131.5, 131.6, 131.9, 133.6, 135.9, 140.1; HRMS (FAB) for M found *m/e* 514.1931, calcd for $C_{38}H_{26}O_2$: 514.1933. $[\alpha]_D^{23} = -604.3$ (*c* 0.19, $CHCl_3$, 87% ee). Ee was determined by HPLC analysis using Daicel Chiralpak IA (eluent: 10% 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 8 min for major isomer and 9 min for minor isomer).

4.3.3. 4,5-Di(phenanthren-9-yl)-1,3,6,8-tetrahydro-2,7-dioxa*as*-indacene 3c. Pale yellow solid. Mp >220 °C (decomposed); IR (KBr disk) 1043, 746 cm^{-1}; ^1H NMR $\delta = 4.70$–4.84 (m, 4H), 5.22–5.29 (m, 4H), 7.25–7.47 (m, 8H), 7.59–7.74 (m, 4H), 7.82–7.84 (m, 2H), 8.39–8.45 (m, 2H), 8.54–8.56 (m, 2H). ^{13}C NMR $\delta = 72.9$, 73.6, 122.2, 123.0, 126.3, 126.4, 126.4, 126.4, 126.5, 126.7, 128.4, 129.9, 130.2, 130.8, 130.9, 131.4, 133.4, 134.4, 140.1; HRMS (FAB) for M found *m/e* 514.1956, calcd for $C_{38}H_{26}O_2$: 514.1933. $[\alpha]_D^{23} = -120.6$ (*c* 0.79, $CHCl_3$, 87% ee). Ee was determined by HPLC analysis using Daicel Chiralpak AD-H and AS-H (eluent: 5% 2-propanol in hexane, flow rate: 0.7 mL/min, retention time: 28 min for minor isomer and 31 min for major isomer).

4.3.4. 4,5-Bis(4-methoxynaphthalen-1-yl)-1,3,6,8-tetrahydro-2,7-dioxa*as*-indacene 3d. Colorless oil. IR (CH_2Cl_2) 1092, 769 cm^{-1}; ^1H NMR $\delta = 3.80$ (s, 6H), 4.66 (d, $J = 12.2$ Hz, 2H), 4.70 (d, $J = 12.2$ Hz, 2H), 5.20 (d, $J = 12.4$ Hz, 2H), 5.24 (d, $J = 12.4$ Hz, 2H), 6.32 (d, $J = 7.8$ Hz, 2H), 6.76 (d, $J = 7.8$ Hz, 2H), 7.43–7.49 (m, 4H), 7.61–7.63 (m, 2H), 8.19–8.21 (m, 2H). ^{13}C NMR $\delta = 55.2$, 72.9, 73.7, 103.2, 122.2, 124.9, 125.2, 125.3, 126.0, 126.6, 128.3, 130.9, 132.4, 133.8, 140.2, 154.5; HRMS (FAB) for M found *m/e* 474.1831, calcd for $C_{32}H_{26}O_4$: 474.1831. $[\alpha]_D^{24} = -282.8$ (*c* 1.8, $CHCl_3$, 90% ee). Ee was determined by HPLC analysis using Daicel Chiralpak AD-H (eluent: 3% 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 14 min for minor isomer and 15 min for major isomer).

4.3.5. 4,5-Bis(4-methoxy-2-methylphenyl)-1,3,6,8-tetrahydro-2,7-dioxa*as*-indacene 3e. Colorless oil. IR (neat) 1047, 681 cm^{-1}; ^1H NMR $\delta = 2.04$ (s, 6H), 3.73 (s, 6H), 4.71 (d, $J = 10.5$ Hz, 2H), 4.77 (d, $J = 10.5$ Hz, 2H), 5.11–5.18 (m, 4H), 6.53–6.61 (m, 4H), 6.82 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR $\delta = 20.2$, 55.0, 72.9, 73.8, 110.9, 114.9, 129.2, 130.5, 130.6, 134.1, 136.7, 139.2, 158.5. HRMS (FAB) for M found *m/e* 402.1820, calcd for $C_{26}H_{26}O_4$: 402.1831. $[\alpha]_D^{21} = -31.6$ (*c* 0.61, $CHCl_3$, 95% ee). Ee was determined by HPLC analysis using Daicel Chiralpak AD-H (eluent: 2% 2-propanol in hexane, flow rate: 0.5 mL/min, retention time: 27 min for major isomer and 37 min for minor isomer).

4.3.6. 4,5-Bis(2-chloro-4-nitrophenyl)-1,3,6,8-tetrahydro-2,7-dioxa*as*-indacene 3f. Yellow solid. Mp >250 °C; IR (KBr disk) 1516, 1340, 1070, 742 cm^{-1}; ^1H NMR $\delta = 4.76$ (d, $J = 12.5$ Hz, 2H), 4.94 (d, $J = 12.5$ Hz, 2H), 5.16–5.23 (m, 4H), 7.35 (d, $J = 8.4$ Hz, 2H), 7.99 (dd, $J = 2.1$, 8.4 Hz, 2H), 8.23 (d, $J = 2.1$ Hz, 2H). ^{13}C NMR $\delta = 72.7$, 72.9, 121.9, 124.7, 129.1, 130.1, 133.4, 134.0, 139.0, 143.0, 148.0; HRMS (FAB) for M−1 found *m/e* 471.0152, calcd for $C_{22}H_{13}Cl_2N_2O_6$: 470.9951. $[\alpha]_D^{21} = -116.9$ (*c* 1.8, $CHCl_3$, 90% ee). Ee was determined by HPLC analysis using Daicel Chiralpak AD-H (eluent: 50% 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 6 min for major isomer and 8 min for minor isomer). Crystal data: $C_{22}H_{14}Cl_2N_2O_6$, $M = 473.27$, monoclinic, space group $P2_1$ (#4), $a = 10.107(4)$ Å, $b = 21.555(7)$ Å, $c = 10.608(5)$ Å, $\beta = 115.66(14)°$, $V = 2083(13)$ Å^3, $T = 123$ K, $Z = 4$, μ(Mo Kα) = 35.50 cm^{-1}, number of reflections measured: total 19,691, unique: 8692 ($R_{int} = 0.047$), $R1 = 0.049$, $wR2 = 0.121$, Flack parameter (Friedel Pairs = 3947) − 0.03(5).

4.3.7. 4,5-Bis(4-methoxynaphthalen-1-yl)-2,7-bis(*p*-toluenesulfonyl)-1,3,6,8-tetrahydro-2,7-diaza*as*-indacene 3g. Dark yellow solid. Mp 169–171 °C; IR (CH_2Cl_2) 1348, 1165, 1095, 769 cm^{-1}; ^1H NMR $\delta = 2.44$ (s, 6H), 3.78 (s, 6H), 4.09 (d, $J = 13.8$ Hz, 2H), 4.13 (d, $J = 13.8$ Hz, 2H), 4.62 (s, 4H), 6.26 (d, $J = 8.1$ Hz, 2H), 6.59 (d, $J = 7.8$ Hz, 2H), 7.26–7.46 (m, 10H), 7.62 (d, $J = 8.3$ Hz, 4H), 8.19 (d, $J = 8.1$ Hz, 2H). ^{13}C NMR $\delta = 21.6$, 52.8, 53.7, 55.3, 103.1, 122.4, 124.6, 124.9, 125.2, 125.7, 126.6, 127.0, 127.5, 128.2, 129.2, 129.8, 132.0, 135.7, 137.5, 143.6, 154.6; HRMS (FAB) for M+1 found *m/e* 781.2408, calcd for $C_{46}H_{41}N_2O_6S_2$: 781.2406. $[\alpha]_D^{21} = -258.8$ (*c* 0.54, $CHCl_3$, ca. 95% ee). Ee was determined by HPLC analysis using Daicel Chiralpak IA (eluent: 30% 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 15 min for major isomer and 18 min for minor isomer).

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22. When $[RhCl(cod)]_2$ was used in place of $[IrCl(cod)]_2$, cycloadduct **3a** was obtained in 89% yield yet with 57% ee (*dl*:*meso* = 1:1).