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Rhodium-catalyzed convenient synthesis of functionalized tetrahydronaphthalenes

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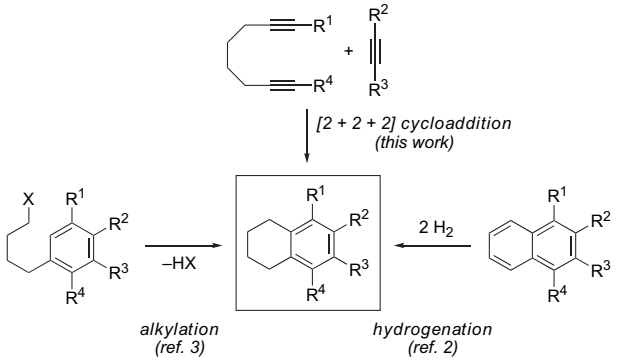
ABSTRACT

Convenient as well as convergent synthesis of functionalized tetrahydronaphthalenes has been accomplished under mild reaction conditions by the cationic rhodium(I)/H_8-BINAP complex-catalyzed [2+2+2] cycloaddition of 1,7-octadiyne derivatives with functionalized monoynes. The effect of the diyne tether lengths was investigated, which revealed that 1,6-heptadiyne and 1,7-octadiyne exhibit higher reactivity than 1,8-nonadiyne. Mechanistic studies indicated that the present rhodium-catalyzed [2+2+2] cycloaddition proceeds through the rhodacyclopentadiene intermediate generated by oxidative coupling of a diyne with rhodium. On the other hand, in the reactions of diynes and dimethyl acetylenedicarboxylate, the rhodacyclopentadiene intermediate generated by oxidative coupling of a diyne and a monoyne with rhodium would also be involved.

1. Introduction

Tetrahydronaphthalene derivatives are found in several pharmaceutical ingredients,[1] therefore their convenient as well as convergent synthesis is highly desirable.[2,3] Representatively, tetrahydronaphthalenes can be synthesized through the hydrogenation of the corresponding naphthalenes[2] or the intramolecular alkylation of the corresponding benzenes[3] (Scheme 1). However, these methods require prior preparation of substituted naphthalene or benzene precursors. On the other hand, the [2+2+2] cycloaddition between 1,7-octadiyne derivatives, that can be obtained from commercial sources or prepared in one-step from commercially available reagents, with monoynes would be attractive, because various substituents can be introduced to the benzene ring in one-step by changing the substituents of two alkyne components (Scheme 1).[4,5]

Despite the potential utility of the [2+2+2] cycloaddition between 1,7-octadiyne derivatives with monoynes for the synthesis of tetrahydronaphthalene derivatives, successful examples have been limited in number.[6–13] In general, the metal-mediated oxidative cyclization efficiency of 1,7-diynes is lower than that of 1,6-diynes.[14] Especially, the cyclization of 1,7-octadiyne derivatives is rather difficult due to the lack of the Thorpe–Ingold effect induced by the tertiary center[15] and the heteroatom coordination to the metals.[14a] Therefore, a majority of previously reported examples require the prior formation of metallacyclopentadienes from 1,7-octadiyne derivatives using a stoichiometric amount of metal complexes, such as Ta,[6] Mo,[7] Mg/Mn,[8] Co,[9] and Ni[10] complexes. In the case of using a catalytic amount of a metal complex, rapid formation of the metallacyclopentadiene from the 1,7-octadiyne derivative is necessary. Although several nickel-catalyzed reactions have been reported, diyne substrates are strictly limited to electron-deficient 1,7-octadiyne derivatives bearing ester or amide groups at the terminal positions.[11,12] Furthermore, elevated temperature[11a] or under microwave[11b] heating are necessary.



Scheme 1. Synthetic routes for the preparation of tetrahydronaphthalene derivatives.

In 2003, our research group discovered that cationic rhodium(I)/biaryl bisphosphine complexes are highly effective catalysts for

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the [2+2+2] cycloaddition of alkynes, leading to substituted benzenes.[16–18] This new catalyst system could be applicable to the [2+2+2] cycloaddition of not only 1,6-diynes[17] but also 1,9-decadiyne or longer tethered-terminal 1,*n*-diynes (*n*=10–15) with monoalkynes, leading to bicyclic benzene derivatives.[16] These results prompted our investigation into the synthesis of functionalized tetrahydronaphthalenes by the [2+2+2] cycloadditions of 1,7-octadiyne derivatives with monoynes. Recently, the successful [2+2+2] cycloadditions of 1,7-octadiyne with alkynylphosphine sulfides[19] and oxides[20] using a cationic rhodium(I)/BINAP complex as a catalyst have been reported by Oshima, Yorimitsu, and co-workers,[19] and Doherty and co-workers,[20] respectively, for the synthesis of phosphine ligands. However, detailed studies concerning further catalyst tuning and the substrate scope have not been reported. In this paper, we describe the cationic rhodium(I)/H_8-BINAP complex-catalyzed [2+2+2] cycloaddition of 1,7-octadiyne derivatives with monoynes for the synthesis of functionalized tetrahydronaphthalenes. Mechanistic insight of this reaction is also discussed.

2. Results and discussion

2.1. Screening of rhodium(I) catalysts for [2+2+2] cycloaddition of 1,7-octadiyne with ethyl 2-butynoate

We first examined the reaction of commercially available 1,7-octadiyne (**1a**) with ethyl 2-butynoate (**2a**) at room temperature in the presence of a cationic rhodium(I) complex (5 mol %) with various bisphosphine ligands (Fig. 1) (Table 1, entries 1–7). In our previous reports of cationic rhodium(I) complex-catalyzed [2+2+2] cycloadditions of alkynes, cationic rhodium(I) complexes of biaryl bisphosphine ligands showed significantly higher catalytic activity than those of conventional mono- and bisphosphine ligands (Ph_3P, *n*-Bu_3P, dppe, dppb, and dppf), although precise mechanism is not clear.[16,17] Especially, a cationic rhodium(I)/H_8-BINAP complex showed the highest catalytic activity.[16] Consistent with our previous reports, biaryl bisphosphines were found to be suitable ligands (entries 4–7) and the use of H_8-BINAP furnished the desired tetrahydronaphthalene **3aa** in the highest yield (entry 7). Importantly, a cationic character of the catalyst is essential to promote the desired cycloaddition (entry 8). Not only an isolated cationic rhodium(I) complex, $[Rh(cod)_2]BF_4$, but also a cationic rhodium(I) complex generated in situ by mixing $[Rh(cod)Cl]_2$ and $AgBF_4$ could be employed (entry 9).

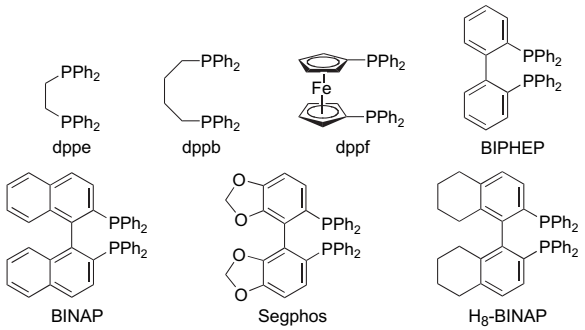
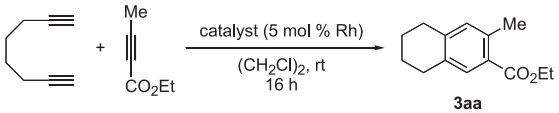


Figure 1. Structures of bisphosphine ligands.

2.2. Rhodium-catalyzed [2+2+2] cycloadditions of 1,7-octadiyne derivatives with monoynes

Thus, the scope of monoynes in the [2+2+2] cycloaddition with 1,7-octadiyne (**1a**) was investigated at room temperature by using 5 mol % of the cationic rhodium(I)/H_8-BINAP complex as shown in Table 2. Not only ethyl 2-butynoate (**2a**) but also ethyl phenylpropiolate (**2b**) reacted with **1a** to give the corresponding tetrahydronaphthalenes in high yields (entries 1 and 2), while the cycloadditions of *tert*-butyl propiolate (**2c**) and dimethyl acetylenedicarboxylate (**2d**) with **1a** proceeded in moderate yields due to the formation of homo-[2+2+2] cycloaddition products from **2c** and **2d** (entries 3 and 4).[21] Not only electron-deficient monoynes **2a–d** but also electron-rich monoynes (propargylic alcohols) **2e–h** could also participate in this reaction to give the corresponding tetrahydronaphthalenes in high yields (entries 5–8).[22]

Table 1
Screening of rhodium catalysts for [2+2+2] cycloaddition of 1,7-octadiyne (**1a**) with ethyl 2-butynoate (**2a**)[a]

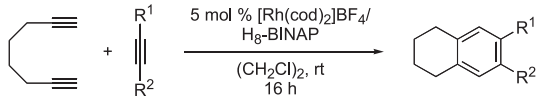


1a (0.05 M) **2a** (1.1 equiv) **3aa**

Entry	Catalyst	Yield[b] (%)
1	$[Rh(nbd)_2]BF_4$/dppe	5
2	$[Rh(cod)_2]BF_4$/dppb	9
3	$[Rh(cod)_2]BF_4$/dppf	6
4	$[Rh(cod)_2]BF_4$/BIPHEP	42
5	$[Rh(cod)_2]BF_4$/BINAP	45
6	$[Rh(cod)_2]BF_4$/Segphos	57
7	$[Rh(cod)_2]BF_4$/H_8-BINAP	69
8	$[Rh(cod)Cl]_2$/2BINAP	0
9	$[Rh(cod)Cl]_2$/2$AgBF_4$/2H_8-BINAP	70

[a] A $(CH_2Cl)_2$ solution of **1a** and **2a** was added dropwise over 10 min to a $(CH_2Cl)_2$ solution of a rhodium catalyst.
[b] Isolated yield.

Table 2
Rhodium-catalyzed [2+2+2] cycloadditions of 1,7-octadiyne (**1a**) with monoynes **2a–h**[a]



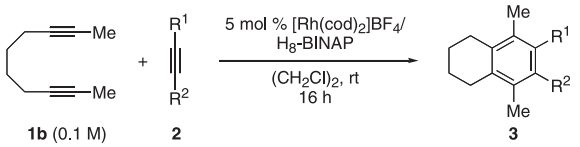
1a (0.1 M) **2** **3**

Entry	**2**	R^1	R^2	**2** (equiv)	**3**	Yield[b] (%)
1	**2a**	Me	CO_2Et	1.1	**3aa**	77
2[c]	**2b**	Ph	CO_2Et	1.1	**3ab**	92
3[d]	**2c**	H	CO_2t-Bu	2.0	**3ac**	52
4[d,e]	**2d**	CO_2Me	CO_2Me	2.0	**3ad**	53
5	**2e**	Me	CH_2OH	1.1	**3ae**	80
6	**2f**	Ph	CH_2OH	1.1	**3af**	90
7[d]	**2g**	H	CH_2OH	2.0	**3ag**	94
8[f]	**2h**	CH_2OH	CH_2OH	1.1	**3ah**	94

[a] A $(CH_2Cl)_2$ solution of **1a** was added dropwise over 10 min to a $(CH_2Cl)_2$ solution of **2** and Rh catalyst.
[b] Isolated yield.
[c] Concentration of **1a**: 0.05 M.
[d] A $(CH_2Cl)_2$ solution of **1a** and **2** was added dropwise over 10 min to a $(CH_2Cl)_2$ solution of Rh catalyst.
[e] Ligand: BINAP.
[f] Solvent: THF. For 1 h.

The scope of monoynes in the reactions with commercially available 2,8-decadiyne (**1b**) was also investigated as shown in Table 3. The cycloadditions of electron-deficient internal monoynes **2a**, **2b**, and **2d** with **1b** proceeded in moderate to high yields (entries 1, 2, and 4), while that of electron-deficient terminal monoyne **2c** with **1b** did not proceed due to the rapid homo-[2+2+2] cycloaddition of **2c** (entry 3). Interestingly, although electron-rich monoynes **2e–g** could react with **1b** in fare to good yields (entries 5–7), 2-butyne-1,4-diol (**2h**) failed to react with **1b** and no conversions of both **1b** and **2h** were observed (entry 8).

Table 3
Rhodium-catalyzed [2+2+2] cycloadditions of 2,8-decadiyne (**1b**) with monoynes **2a–h**[a]

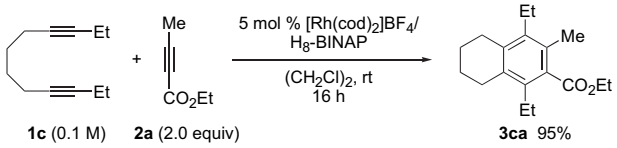


1b (0.1 M) **2** **3**

Entry	**2**	R^1	R^2	**2** (equiv)	**3**	Yield[b] (%)
1	**2a**	Me	CO_2Et	2.0	**3ba**	89
2	**2b**	Ph	CO_2Et	2.0	**3bb**	84
3[c]	**2c**	H	CO_2t-Bu	2.0	**3bc**	0
4[c,d,e]	**2d**	CO_2Me	CO_2Me	2.0	**3bd**	46
5[e]	**2e**	Me	CH_2OH	2.0	**3be**	43
6[f]	**2f**	Ph	CH_2OH	2.0	**3bf**	76
7[c,f]	**2g**	H	CH_2OH	5.0	**3bg**	30
8[g]	**2h**	CH_2OH	CH_2OH	2.0	**3bh**	0

[a] A $(CH_2Cl)_2$ solution of **1b** was added dropwise over 10 min to a $(CH_2Cl)_2$ solution of **2** and Rh catalyst.
[b] Isolated yield.
[c] A $(CH_2Cl)_2$ solution of **1b** and **2** was added dropwise over 10 min to a $(CH_2Cl)_2$ solution of Rh catalyst.
[d] Ligand: BINAP.
[e] At 80 °C.
[f] At 50 °C.
[g] Solvent: THF.

Not only 2,8-decadiyne (**1b**) but also commercially available 3,9-dodecadiyne (**1c**) could be equally employed for this reaction (Scheme 2).



1c (0.1 M) **2a** (2.0 equiv) **3ca** 95%

Scheme 2. Rhodium-catalyzed [2+2+2] cycloaddition of internal 3,9-dodecadiyne (**1c**) with monoyne **2a**.

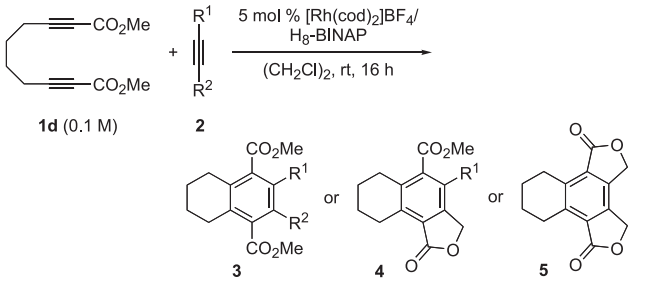
Other than electron-rich 1,7-octadiyne derivatives, methoxy carbonyl-substituted electron-deficient 1,7-octadiyne **1d**, that can be readily prepared in one-step from commercially available **1a**,[23] was employed for this reaction as shown in Table 4. Electron-deficient internal monoynes **2a**, **2b**, and **2d** were able to react with **1d** (entries 1, 2, and 4), while electron-deficient terminal monoyne **2c** failed to react with **1d** due to the rapid homo-[2+2+2] cycloadditions of both **1d** and **2c** (entry 3). In the reactions of **1d** and propargylic alcohols **2e–g**, sequential [2+2+2] cycloaddition-lactonization[24] proceeded to yield the corresponding lactones in excellent yields (entries 5–7). However, 2-butyne-1,4-diol (**2h**) failed to react with **1d** and no conversions of both **1d** and **2h** were observed (entry 8).

Not only propargylic alcohol (**2g**) but also protected propargyl amine **2i** was able to react with 1,7-diynes **1a**, **1b**, and **1d** to yield the corresponding protected 2-tetrahydronaphthalenemethylamine derivatives (Scheme 3), while non-protected propargyl amine could not participate in this reaction.[25]

2.3. Comparison of reactivity of 1,6-heptadiyne, 1,7-octadiyne, and 1,8-nonadiyne

The effect of the diyne tether lengths on the reactivity toward the cationic rhodium(I)/H_8-BINAP complex-catalyzed [2+2+2] cycloaddition was systematically investigated as shown in Table 5. Electron-rich (**2e**) and moderately electron-deficient monoynes (**2a**) reacted with 1,6-heptadiyne (**1e**) and 1,7-octadiyne (**1a**) to give the corresponding 5–6 and 6–6 fused bicyclic benzenes in high yields (entries 1, 2, 4, and 5). Monoynes **2e** and **2a** were also able to

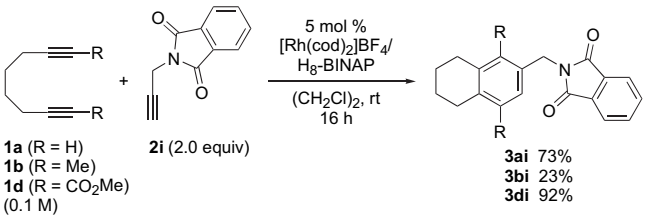
Table 4
Rhodium-catalyzed [2+2+2] cycloadditions of electron-deficient 1,7-octadiyne derivative **1d** with monoynes **2a–h**[a]



1d (0.1 M) **2** **3** **4** **5**

Entry	**2**	R^1	R^2	**2** (equiv)	**3**	Yield[b] (%)
1[c]	**2a**	Me	CO_2Et	2.0	**3da**	86
2[c]	**2b**	Ph	CO_2Et	2.0	**3db**	96
3[d]	**2c**	H	CO_2t-Bu	2.0	**3dc**	0
4[d,e]	**2d**	CO_2Me	CO_2Me	2.0	**3dd**	21
5	**2e**	Me	CH_2OH	2.0	**4de**	98
6[f]	**2f**	Ph	CH_2OH	2.0	**4df**	96
7[d]	**2g**	H	CH_2OH	5.0	**4dg**	97
8[g]	**2h**	CH_2OH	CH_2OH	2.0	**5**	0

[a] A $(CH_2Cl)_2$ solution of **1d** was added dropwise over 10 min to a $(CH_2Cl)_2$ solution of **2** and Rh catalyst.
[b] Isolated yield.
[c] Concentration of **1d**: 0.05 M.
[d] A $(CH_2Cl)_2$ solution of **1d** and **2** was added dropwise over 10 min to a $(CH_2Cl)_2$ solution of Rh catalyst.
[e] Ligand: BINAP.
[f] At 40 °C.
[g] Solvent: THF.



1a (R = H)
1b (R = Me)
1d (R = CO_2Me)
(0.1 M)
2i (2.0 equiv)
3ai 73%
3bi 23%
3di 92%

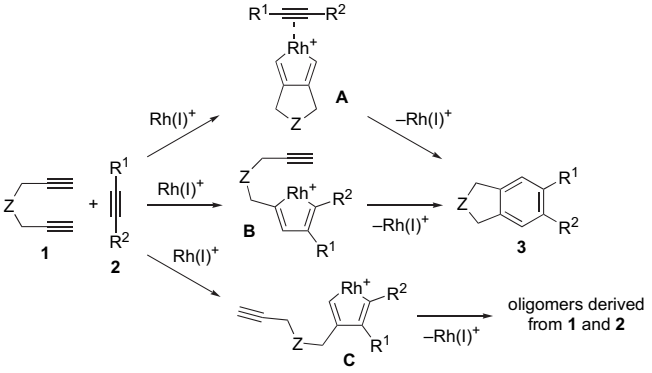
Scheme 3. Rhodium-catalyzed [2+2+2] cycloadditions of 1,7-octadiyne derivatives **1** with protected propargyl amine **2i**.

react with 1,8-nonadiyne (**1f**) to give the corresponding 6–7 fused bicyclic benzenes in moderate yields (entries 3 and 6). As the transition-metal-mediated [2+2+2] cycloaddition of 1,8-nonadiyne derivatives with monoynes was scarcely reported, these successful reactions are worthy of note.[13,26,27] However, highly electron-deficient monoyne **2d** reacted with 1,7-diyne **1a** in very low yield (entry 7). The use of BINAP as a ligand instead of H_8-BINAP was found to be effective, and the corresponding 5–6 and 6–6 fused phthalates were obtained in fair yields (entries 8 and 9), although less reactive 1,8-diyne **1f** failed to react with **2d** (entry 10).

2.4. Mechanistic consideration

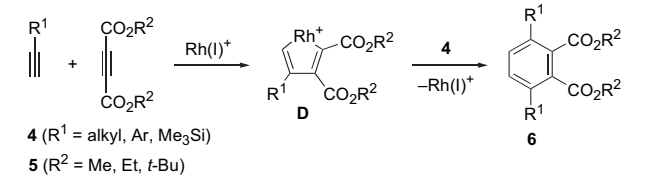
A plausible mechanism for the rhodium-catalyzed [2+2+2] cycloaddition of terminal diynes **1** with monoynes **2** is shown in Scheme 4. Bicyclic benzene **3** can be obtained through rhodacyclopentadiene intermediate **A** or **B**, generated by oxidative coupling of diyne **1** with rhodium or diyne **1** and monoyne **2** with rhodium, respectively. In the reactions of terminal diynes **1e**, **1a**, and **1f** with electron-rich (**2e**) and moderately electron-deficient monoynes (**2a**), homo-[2+2+2] cycloaddition products of diynes were generated as major by-products. Therefore rhodacyclopentadiene **A** would be a major intermediate. Similarly, homo-[2+2+2]

cycloaddition products of diynes were generated as major by-products in the reactions of internal diynes **1b–d** with monoynes **2a–g**, and so the rhodacyclopentadiene generated by oxidative coupling of diynes **1b–d** with rhodium would be a major intermediate.



Scheme 4. Plausible mechanism for rhodium-catalyzed [2+2+2] cycloaddition of diynes **1** with monoynes **2**.

On the other hand, we previously reported that dialkyl acetylenedicarboxylate **5** is an excellent partner for the cationic rhodium(I)/H_8-BINAP complex-catalyzed chemo- and regioselective cross-[2+2+2] cycloaddition with two terminal monoynes **4** leading to the corresponding 3,6-disubstituted phthalate **6** (Scheme 5).[16] The mechanistic study indicated that this reaction proceeds through the chemo- and regioselective formation of rhodacyclopentadiene intermediate **D**.[16b]



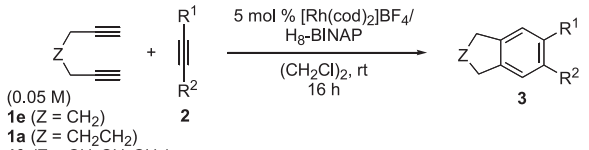
Scheme 5. Cationic rhodium(I)/H_8-BINAP complex-catalyzed cross-[2+2+2] cycloaddition of two terminal monoynes **4** with one dialkyl acetylenedicarboxylate **5**.[16b]

Therefore the reactions of diynes **1** with monoyne **2d** might proceed through not only intermediate **A** but also intermediate **B**. Indeed, the use of H_8-BINAP as a ligand furnished phthalate **3ad** in low yield along with a large amount of oligomers derived from **1a** and **2d** presumably through the predominant formation of intermediate **C** (Table 5, entry 7). On the other hand, the rhodium-catalyzed reaction of 1-dodecyne (**4a**) with diethyl acetylenedicarboxylate (**5a**) by using BINAP as a ligand furnishes 4,5-disubstituted phthalate **8a** in significantly higher yield than that using H_8-BINAP as a ligand (Scheme 6).[16b] In accordance with this previous observation, the use of BINAP significantly increased the yield of 4,5-disubstituted phthalate **3ad** presumably due to increased formation of intermediate **B** (Table 5, entry 8).

3. Conclusions

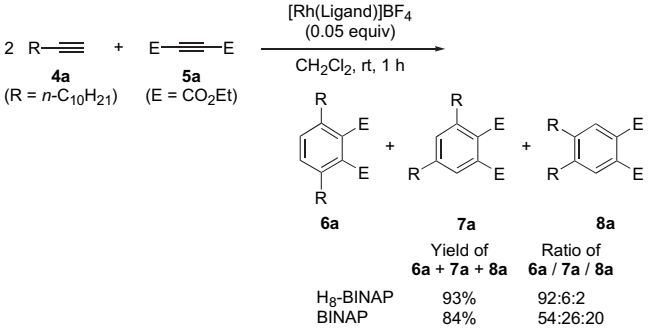
In conclusion, convenient as well as convergent synthesis of functionalized tetrahydronaphthalenes has been accomplished under mild reaction conditions by the cationic rhodium(I)/H_8-BINAP complex-catalyzed [2+2+2] cycloaddition of 1,7-octadiyne derivatives with functionalized monoynes. Among the bisphosphine ligands examined, H_8-BINAP was the best ligand, which is consistent with our previously reported cationic rhodium(I) complex-catalyzed [2+2+2] cycloadditions of alkynes.[16,17] As the previously

Table 5
Rhodium-catalyzed [2+2+2] cycloadditions of 1,6-heptadiyne (**1e**), 1,7-octadiyne (**1a**), and 1,8-nonadiyne (**1f**) with monoynes **2**[a]



Entry	1	2	R^1	R^2	2 (equiv)	3	Yield (%)[b]
1[c]	**1e**	**2e**	Me	CH_2OH	1.1	**3ee**	79
2[c,d]	**1a**	**2e**	Me	CH_2OH	1.1	**3ae**	80
3[e]	**1f**	**2e**	Me	CH_2OH	2.0	**3fe**	39
4[c]	**1e**	**2a**	Me	CO_2Et	1.1	**3ea**	91
5[c,d]	**1a**	**2a**	Me	CO_2Et	1.1	**3aa**	77
6[e]	**1f**	**2a**	Me	CO_2Et	2.0	**3fa**	45
7	**1a**	**2d**	CO_2Me	CO_2Me	2.0	**3ad**	11
8[d,f]	**1a**	**2d**	CO_2Me	CO_2Me	2.0	**3ad**	53
9[f]	**1e**	**2d**	CO_2Me	CO_2Me	2.0	**3ed**	29[g]
10[f]	**1f**	**2d**	CO_2Me	CO_2Me	2.0	**3fd**	—[h]

[a] A $(CH_2Cl)_2$ solution of **1** and **2** was added dropwise over 10 min to a $(CH_2Cl)_2$ solution of Rh catalyst.
[b] Isolated yield.
[c] A $(CH_2Cl)_2$ solution of **1** was added dropwise over 10 min to a $(CH_2Cl)_2$ solution of **2** and Rh catalyst.
[d] Concentration of **1**:0.1 M.
[e] At 40 °C.
[f] Ligand: BINAP.
[g] Determined by ^1H NMR using 1,4-dimethoxybenzene as an internal standard.
[h] A trace amount of **3fd** was generated, while that could not be isolated in a pure form.



Scheme 6. Effect of ligands on regioselectivity of cross-[2+2+2] cycloaddition of monoynes **4** with one dialkyl acetylenedicarboxylate (**5**).[16b]

reported nickel-catalyzed reactions are limited to the use of electron-deficient 1,7-octadiyne derivatives at elevated temperature[11a] or under microwave heating,[11b] allowing use of both electron-rich and electron-deficient 1,7-octadiyne derivatives under mild reaction conditions in the present cationic rhodium(I)/H_8-BINAP complex-catalyzed reactions is advantageous than the nickel catalyses. Furthermore, a variety of electron-rich and deficient monoynes can also be employed as a cycloaddition partner, although some limitations exist. Both diynes and monoynes can be obtained from commercial sources or prepared in one-step from commercially available reagents, and thus this method enables a convenient synthesis of new functionalized tetrahydronaphthalenes. The effect of the diyne tether lengths on the reactivity was investigated, which revealed that 1,6-heptadiyne and 1,7-octadiyne exhibited higher reactivity than 1,8-nonadiyne. A mechanism of the rhodium-catalyzed [2+2+2] cycloaddition is proposed that the reactions proceeds through the rhodacyclopentadiene generated by oxidative coupling of a diyne with rhodium. In the reactions of diynes and dimethyl acetylenedicarboxylate, the rhodacyclopentadiene generated by oxidative coupling of a diyne and a monoyne with rhodium would also be involved.

4. Experimental

4.1. General

^{1}H NMR spectra were recorded on 300 MHz (JEOL AL 300). ^{13}C NMR spectra were obtained with complete proton decoupling on 75 MHz (JEOL AL 300). Infrared spectra were obtained on a JASCO FT/IR-4100. HRMS data were obtained on a Bruker micrOTOF Focus II. All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring.

4.2. Materials

Anhydrous $(CH_2Cl)_2$ (No. 28450-5) and THF (No. 18656-2) were obtained from Aldrich and used as received. 1,7-Diyne **1d** was prepared according to the literature.[21] All other reagents were obtained from commercial sources and used as received.

4.3. Representative procedures for the rhodium-catalyzed [2+2+2] cycloadditions of diynes 1 with monoynes 2

Method A: Table 2, entry 1. H_8-BINAP (9.5 mg, 0.015 mmol) and $[Rh(cod)_2]BF_4$ (6.1 mg, 0.015 mmol) were dissolved in CH_2Cl_2 (3.0 mL), and the reaction mixture was stirred at room temperature for 5 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 1 h, the resulting solution was concentrated to dryness and the residue was redissolved in $(CH_2Cl)_2$ (0.5 mL) and a $(CH_2Cl)_2$ (0.5 mL) solution of **2a** (37.0 mg, 0.330 mmol) was added. A $(CH_2Cl)_2$ (2.0 mL) solution of **1a** (31.8 mg, 0.300 mmol) was added dropwise to this solution over 10 min at room temperature (concentration of **1a**: 0.1 M). The reaction mixture was stirred at room temperature for 16 h. The resulting solution was concentrated and purified by a preparative TLC (*n*-hexane/ethyl acetate=20:1), which furnished **3aa** (50.4 mg, 0.231 mmol, 77% yield) as a colorless oil.

Method B: Table 2, entry 3. H_8-BINAP (9.5 mg, 0.015 mmol) and $[Rh(cod)_2]BF_4$ (6.1 mg, 0.015 mmol) were dissolved in CH_2Cl_2 (3.0 mL), and the reaction mixture was stirred at room temperature for 5 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 1 h, the resulting solution was concentrated to dryness and the residue was redissolved in $(CH_2Cl)_2$ (1.0 mL). To this solution was added a $(CH_2Cl)_2$ (2.0 mL) solution of **1a** (31.8 mg, 0.300 mmol) and **2c** (75.7 mg, 0.600 mmol) at room temperature (concentration of **1a**: 0.1 M). The reaction mixture was stirred at room temperature for 16 h. The resulting solution was concentrated and purified by a preparative TLC (*n*-hexane/ethyl acetate=20:1), which furnished **3ac** (35.9 mg, 0.155 mmol, 52% yield) as a colorless oil.

*4.3.1. 3-Methyl-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid ethyl ester (**3aa**).* Method A; colorless oil; IR (neat) 2931, 1715, 1447, 1264, 1141, 1056 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.64 (s, 1H), 6.93 (s, 1H), 4.33 (q, J=7.2 Hz, 2H), 2.85–2.64 (m, 4H), 2.52 (s, 3H), 1.81–1.76 (m, 4H), 1.38 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 167.7, 141.5, 136.7, 134.4, 132.2, 131.3, 126.9, 60.3, 29.2, 28.7, 23.1, 22.9, 21.2, 14.3; HRMS (ESI) calcd for $C_{14}H_{18}O_2Na$ $[M+Na]^+$ 241.1199, found 241.1225.

*4.3.2. 3-Phenyl-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid ethyl ester (**3ab**)[28].* Method A (concentration of **1a**: 0.05 M); pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.57 (s, 1H), 7.43–7.20 (m, 5H), 7.05 (s, 1H), 4.05 (q, J=7.2 Hz, 2H), 2.90–2.72 (m, 4H), 1.85–1.81 (m, 4H), 0.97 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 168.8, 141.8, 140.8, 139.7, 136.3, 131.3, 130.6, 128.4, 128.2, 127.8, 126.7, 60.6, 29.4, 28.9, 23.0, 22.9, 13.6.

*4.3.3. 5,6,7,8-Tetrahydronaphthalene-2-carboxylic acid tert-butyl ester (**3ac**)[29,30].* Method B; colorless oil; ^{1}H NMR ($CDCl_3$) δ 7.75–7.65 (m, 2H), 7.14–7.04 (m, 1H), 2.87–2.69 (m, 4H), 1.83–1.78 (m, 4H), 1.59 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 166.1, 142.2, 137.0, 130.2, 129.1, 128.9, 126.3, 80.5, 29.5, 29.3, 28.2, 23.0, 22.9.

*4.3.4. 5,6,7,8-Tetrahydronaphthalene-2,3-dicarboxylic acid dimethyl ester (**3ad**)[30,31].* Method B (ligand: BINAP); colorless oil; ^{1}H NMR ($CDCl_3$) δ 7.42 (s, 2H), 3.88 (s, 6H), 2.87–2.70 (m, 4H), 1.82–1.78 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 168.3, 140.8, 129.7, 128.9, 52.4, 29.2, 22.6.

*4.3.5. (3-Methyl-5,6,7,8-tetrahydronaphthalen-2-yl)methanol (**3ae**).* Method A; colorless solid; mp 66.6–67.9 °C; IR (KBr) 3306, 2914, 1435, 1006 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.04 (s, 1H), 6.90 (s, 1H), 4.64 (s, 2H), 2.81–2.63 (m, 4H), 2.31 (s, 3H), 1.81–1.77 (m, 4H), 1.51 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 136.6, 135.9, 134.6, 133.1, 131.0, 128.6, 63.4, 29.0, 28.9, 23.3, 23.2, 18.1; HRMS (ESI) calcd for $C_{12}H_{16}ONa$ $[M+Na]^+$ 199.1093, found 199.1089.

*4.3.6. (3-Phenyl-5,6,7,8-tetrahydronaphthalen-2-yl)methanol (**3af**).* Method A; pale yellow solid; Mp 61.4–62.5 °C; IR (KBr) 3277, 2932, 1442, 1036, 703 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.45–7.26 (m, 5H), 7.22 (s, 1H), 7.00 (s, 1H), 4.54 (s, 2H), 2.92–2.66 (m, 4H), 1.93–1.69 (m, 4H), 1.78–1.56 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 140.8, 138.7, 136.70, 136.67, 135.2, 130.8, 129.3, 129.2, 128.2, 127.0, 63.1, 29.09, 29.07, 23.2; HRMS (ESI) calcd for $C_{17}H_{18}ONa$ $[M+Na]^+$ 261.1250, found 261.1259.

*4.3.7. (5,6,7,8-Tetrahydronaphthalen-2-yl)methanol (**3ag**)[31].* Method B; pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.14–7.01 (m, 3H), 4.62 (d, J=4.2 Hz, 2H), 2.87–2.66 (m, 4H), 1.82–1.78 (m, 4H), 1.67–1.55 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 138.0, 137.3, 136.6, 129.3, 127.8, 124.3, 65.2, 29.3, 29.1, 23.2, 23.1.

*4.3.8. (3-Hydroxymethyl-5,6,7,8-tetrahydronaphthalen-2-yl)methanol (**3ah**).* Method A (solvent: THF); colorless solid; mp 105.0–106.3 °C; IR (KBr) 3420, 2922, 1087, 1001 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.06 (s, 2H), 4.68 (s, 4H), 2.85–2.64 (m, 4H), 1.81–1.77 (m, 4H), 1.59 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 137.3, 136.4, 130.6, 63.9, 29.0, 23.0; HRMS (ESI) calcd for $C_{12}H_{16}O_2Na$ $[M+Na]^+$ 215.1043, found 215.1073.

*4.3.9. 1,3,4-Trimethyl-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid ethyl ester (**3ba**).* Method A; colorless solid; mp 70.8–71.6 °C; IR (KBr) 2926, 1725, 1433, 1267, 1190 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.40 (q, J=7.2 Hz, 2H), 2.74–2.52 (m, 4H), 2.20 (s, 3H), 2.13 (s, 6H), 1.80–1.76 (m, 4H), 1.39 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 171.3, 136.5, 133.4, 132.9, 132.7, 129.1, 128.6, 60.7, 28.1, 27.4, 22.9, 22.7, 17.1, 16.1, 14.7, 14.2; HRMS (ESI) calcd for $C_{16}H_{22}O_2Na$ $[M+Na]^+$ 269.1512, found 269.1505.

*4.3.10. 1,4-Dimethyl-3-phenyl-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid ethyl ester (**3bb**).* Method A; colorless solid; mp 72.9–74.5 °C; IR (KBr) 2930, 1725, 1286, 1187, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.42–7.11 (m, 5H), 3.89 (q, J=7.2 Hz, 2H), 2.76–2.55 (m, 4H), 2.19 (s, 3H), 1.94 (s, 3H), 1.84–1.80 (m, 4H), 0.88 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 170.2, 140.1, 137.1, 136.0, 135.2, 132.6, 132.1, 129.8, 129.4, 127.7, 126.8, 60.4, 28.1, 27.5, 22.8, 22.7, 16.3, 16.1, 13.6; HRMS (ESI) calcd for $C_{21}H_{24}O_2Na$ $[M+Na]^+$ 331.1660, found 331.1512.

*4.3.11. 1,4-Dimethyl-5,6,7,8-tetrahydronaphthalene-2,3-dicarboxylic acid dimethyl ester (**3bd**).* Method B (ligand: BINAP, temperature: 80 °C); colorless solid; mp 63.6–64.9 °C; IR (KBr) 2929, 1725, 1438, 1265, 1213, 1031 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.85 (s, 6H), 2.73–2.53 (m, 4H), 2.21 (s, 6H), 1.88–1.67 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 169.6, 138.7, 132.2, 129.4, 52.2, 27.8, 22.5, 16.1; HRMS (ESI) calcd for $C_{16}H_{20}O_4Na$ $[M+Na]^+$ 299.1254, found 299.1254.

*4.3.12. (1,3,4-Trimethyl-5,6,7,8-tetrahydronaphthalen-2-yl)methanol (**3be**).* Method A (temperature: 80 °C); colorless solid; mp 101.5–

102.8 °C; IR (KBr) 3335, 2924, 1432, 988 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.80 (s, 2H), 2.78–2.53 (m, 4H), 2.37 (s, 3H), 2.30 (s, 3H), 2.18 (s, 3H), 1.89–1.66 (m, 4H), 1.25 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 135.8, 133.9, 133.6, 133.1, 132.9, 132.7, 59.9, 28.4, 28.1, 23.1, 15.9, 15.3, 14.8; HRMS (ESI) calcd for $C_{14}H_{20}ONa$ $[M+Na]^+$ 227.1406, found 227.1408.

*4.3.13. (1,4-Dimethyl-3-phenyl-5,6,7,8-tetrahydronaphthalen-2-yl)-methanol (**3bf**).* Method A (temperature: 50 °C); pale yellow solid; mp 68.0–69.5 °C; IR (KBr) 3313, 2925, 1429, 984, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.50–7.32 (m, 3H), 7.22–7.14 (m, 2H), 4.40 (s, 2H), 2.85–2.60 (m, 4H), 2.37 (s, 3H), 1.88 (s, 3H), 1.95–1.76 (m, 4H), 1.22 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 141.4, 139.8, 135.8, 135.6, 133.7, 133.4, 132.1, 129.4, 128.2, 126.7, 60.6, 28.2, 28.1, 23.0, 22.9, 16.8, 14.8; HRMS (ESI) calcd for $C_{19}H_{22}O$ $[M+H]^+$ 289.1563, found 289.1572.

*4.3.14. (1,4-Dimethyl-5,6,7,8-tetrahydronaphthalen-2-yl)methanol (**3bg**).* Method B (temperature: 50 °C); colorless solid; mp 75.9–77.4 °C; IR (KBr) 3379, 2925, 1442, 1031, 876 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.00 (s, 1H), 4.67 (s, 2H), 2.76–2.54 (m, 4H), 2.22 (s, 6H), 1.83–1.78 (m, 4H), 1.46 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 136.2, 135.6, 135.4, 133.8, 132.4, 127.2, 64.3, 27.7, 27.4, 23.1, 22.7, 19.3, 14.0; HRMS (ESI) calcd for $C_{13}H_{18}ONa$ $[M+Na]^+$ 213.1250, found 213.1260.

*4.3.15. 1,4-Diethyl-3-methyl-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid ethyl ester (**3ca**).* Method A; colorless oil; IR (neat) 2933, 1725, 1451, 1259, 1181, 1056 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.40 (q, J=7.2 Hz, 2H), 2.84–2.65 (m, 4H), 2.64 (q, J=7.5 Hz, 2H), 2.54 (q, J=7.5 Hz, 2H), 2.23 (s, 3H), 1.81–1.76 (m, 4H), 1.39 (t, J=7.2 Hz, 3H), 1.61 (t, J=7.5 Hz, 3H), 1.10 (t, J=7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 171.4, 138.7, 136.3, 135.3, 133.12, 133.05, 128.4, 60.7, 27.0, 26.3, 23.7, 23.1, 22.8, 21.8, 16.1, 14.6, 14.2, 13.2; HRMS (ESI) calcd for $C_{18}H_{26}O_2Na$ $[M+Na]^+$ 297.1825, found 297.1843.

*4.3.16. 3-Methyl-5,6,7,8-tetrahydronaphthalene-1,2,4-tricarboxylic acid 2-ethyl ester 1,4-dimethyl ester (**3da**).* Method A (concentration of **1d**: 0.05 M); colorless solid; mp 55.4–57.0 °C; IR (KBr) 2944, 1727, 1439, 1231, 1066 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.30 (q, J=7.2 Hz, 2H), 3.90 (s, 3H), 3.84 (s, 3H), 2.85–2.65 (m, 2H), 2.75–2.60 (m, 2H), 2.27 (s, 3H), 1.77–1.73 (m, 4H), 1.33 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 169.6, 168.5, 167.6, 137.2, 136.5, 133.4, 133.3, 130.2, 129.7, 61.5, 52.21, 52.19, 27.2, 26.9, 22.2, 21.9, 17.0, 14.0; HRMS (ESI) calcd for $C_{18}H_{22}O_6Na$ $[M+Na]^+$ 357.1309, found 357.1312.

*4.3.17. 3-Phenyl-5,6,7,8-tetrahydronaphthalene-1,2,4-tricarboxylic acid 2-ethyl ester 1,4-dimethyl ester (**3db**).* Method A (concentration of **1d**: 0.05 M); colorless solid; mp 85.0–86.8 °C; IR (KBr) 2929, 1728, 1434, 1208, 1020, 708 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.37–7.26 (m, 3H), 7.26–7.16 (m, 2H), 3.90 (q, J=7.2 Hz, 2H), 3.86 (s, 3H), 3.46 (s, 3H), 2.91–2.77 (m, 2H), 2.83–2.68 (m, 2H), 1.83–1.78 (m, 4H), 0.85 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 168.7, 168.4, 167.5, 137.8, 136.62, 136.56, 135.6, 134.9, 133.4, 130.0, 128.8, 127.7, 127.6, 61.2, 52.4, 51.8, 27.3, 27.1, 22.1, 21.9, 13.4; HRMS (ESI) calcd for $C_{23}H_{24}O_6Na$ $[M+Na]^+$ 419.1465, found 419.1465.

*4.3.18. 5,6,7,8-Tetrahydronaphthalene-1,2,3,4-tetracarboxylic acid tetramethyl ester (**3dd**)[32].* Method B (ligand: BINAP); colorless solid; mp 147.8–149.3 °C; ^1H NMR ($CDCl_3$) δ 3.88 (s, 6H), 3.83 (s, 6H), 2.88–2.70 (m, 4H), 1.80–1.76 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 167.7, 166.6, 138.8, 134.7, 128.3, 52.9, 52.6, 27.5, 21.7.

*4.3.19. 4-Methyl-1-oxo-1,3,6,7,8,9-hexahydronaphtho[1,2-c]furan-5-carboxylic acid methyl ester (**4de**).* Method A; colorless solid; mp >280.0 °C; IR (KBr) 2952, 1761, 1722, 1213, 1016 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.16 (s, 2H), 3.95 (s, 3H), 3.28–3.12 (m, 2H), 2.80–2.63 (m, 2H), 2.19 (s, 3H), 1.83–1.79 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 171.1, 169.4, 144.0, 139.3, 136.8, 135.2, 125.5, 123.1, 68.1, 52.3, 26.9, 24.8, 22.2, 21.6, 14.7; HRMS (ESI) calcd for $C_{15}H_{16}O_4Na$ $[M+Na]^+$ 283.0941, found 283.0944.

*4.3.20. 1-Oxo-4-phenyl-1,3,6,7,8,9-hexahydronaphtho[1,2-c]furan-5-carboxylic acid methyl ester (**4df**).* Method A (temperature: 40 °C); colorless solid; mp 129.1–131.0 °C; IR (KBr) 2949, 1753, 1452, 1205, 1111, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.50–7.33 (m, 3H), 7.20–7.34 (m, 2H), 5.07 (s, 2H), 3.58 (s, 3H), 3.42–3.18 (m, 2H), 2.92–2.69 (m, 2H), 2.10–1.72 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.8, 168.8, 143.5, 138.8, 138.6, 135.7, 131.4, 128.8, 128.4, 128.1, 123.5, 68.3, 52.1, 27.0, 25.1, 22.2, 21.5; HRMS (ESI) calcd for $C_{20}H_{18}O_4Na$ $[M+Na]^+$ 345.1097, found 345.1101.

*4.3.21. 1-Oxo-1,3,6,7,8,9-hexahydronaphtho[1,2-c]furan-5-carboxylic acid methyl ester (**4dg**)[10b].* Method B; colorless solid; mp 129.4–130.9 °C; ^1H NMR ($CDCl_3$) δ 7.60 (s, 1H), 5.20 (s, 2H), 3.89 (s, 3H), 3.30–3.13 (m, 2H), 3.07–2.89 (m, 2H), 1.80–1.76 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 170.5, 167.9, 143.9, 140.2, 138.9, 136.2, 125.0, 120.2, 68.4, 52.4, 27.8, 25.5, 22.3, 21.3.

*4.3.22. 2-(5,6,7,8-Tetrahydronaphthalen-2-ylmethyl)isoindole-1,3-dione (**3ai**).* Method B; colorless solid; mp 121.6–122.4 °C; IR (neat) 2935, 1713, 1391, 951, 713 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.90–7.75 (m, 2H), 7.77–7.62 (m, 2H), 7.22–7.08 (m, 2H), 7.00 (d, J=7.8 Hz, 1H), 4.77 (s, 2H), 2.84–2.61 (m, 4H), 1.85–1.66 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 168.0, 137.4, 136.8, 133.8, 133.4, 132.1, 129.34, 129.29, 125.8, 123.2, 41.3, 29.3, 29.1, 23.1, 23.0; HRMS (ESI) calcd for $C_{19}H_{17}NO_2Na$ $[M+Na]^+$ 314.1151, found 314.1172.

*4.3.23. 2-(1,4-Dimethyl-5,6,7,8-tetrahydronaphthalen-2-ylmethyl)-isoindole-1,3-dione (**3bi**).* Method B; colorless solid; mp 153.8–155.6 °C; IR (KBr) 2924, 1712, 1391, 1109, 952, 714 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.92–7.79 (m, 2H), 7.78–7.65 (m, 2H), 7.00 (s, 1H), 4.87 (s, 2H), 2.73–2.51 (m, 4H), 2.31 (s, 3H), 2.15 (s, 3H), 1.85–1.79 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 168.3, 136.0, 135.4, 133.9, 133.8, 132.2, 132.0, 130.7, 127.4, 123.3, 39.8, 27.9, 27.3, 23.1, 22.6, 19.5, 14.4; HRMS (ESI) calcd for $C_{21}H_{21}NO_2Na$ $[M+Na]^+$ 342.1465, found 342.1450.

*4.3.24. 2-(1,3-Dioxo-1,3-dihydroisoindol-2-ylmethyl)-5,6,7,8-tetrahydronaphthalene-1,4-dicarboxylic acid dimethyl ester (**3di**)[10b].* Method B; colorless solid; mp 162.3–164.1 °C; ^1H NMR ($CDCl_3$) δ 7.92–7.74 (m, 2H), 7.78–7.60 (m, 2H), 7.77 (s, 1H), 4.84 (s, 2H), 3.96 (s, 3H), 3.85 (s, 3H), 3.14–2.85 (m, 2H), 2.85–2.55 (m, 2H), 1.85–1.59 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 169.0, 167.74, 167.69, 138.7, 136.8, 135.5, 134.0, 131.9, 131.6, 129.7, 129.1, 123.3, 52.5, 52.0, 39.0, 27.8, 27.5, 22.2, 22.0.

*4.3.25. (6-Methylindan-5-yl)-methanol (**3ee**).* Method A (concentration of **1e**: 0.05 M); colorless solid; mp 65.9–67.0 °C; IR (KBr) 3348, 2913, 2841, 1454, 1063 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.22 (s, 1H), 7.08 (s, 1H), 4.66 (s, 2H), 2.89 (t, J=7.5 Hz, 4H), 2.12 (s, 3H), 2.07 (quint, J=7.5 Hz, 2H), 1.61 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 144.0, 141.9, 136.5, 133.9, 126.3, 123.9, 63.7, 32.6, 32.4, 25.5, 18.6; HRMS (ESI) calcd for $C_{11}H_{14}ONa$ $[M+Na]^+$ 185.0937, found 185.0948.

*4.3.26. (3-Methyl-6,7,8,9-tetrahydro-5H-benzocyclohepten-2-yl)-methanol (**3fe**).* Method A (temperature: 40 °C, concentration of **1f**: 0.05 M); colorless solid; mp 107.0–108.8 °C; IR (KBr) 3330, 2909, 1442, 1075, 1033 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.08 (s, 1H), 6.94 (s, 1H), 4.64 (s, 2H), 2.85–2.69 (m, 4H), 2.31 (s, 3H), 1.92–1.75 (m, 2H), 1.74–1.50 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 143.0, 141.0, 135.9, 133.4, 131.3, 128.8, 63.3, 36.24, 36.18, 32.7, 28.44, 28.35, 18.0; HRMS (ESI) calcd for $C_{13}H_{18}ONa$ $[M+Na]^+$ 213.1250, found 213.1258.

*4.3.27. 6-Methylindan-5-carboxylic ethyl ester (**3ea**).* Method A; colorless oil; IR (neat) 2956, 2360, 1716, 1251, 1112 cm^{-1}; ^1H NMR

($CDCl_3$) δ 7.78 (s, 1H), 7.10 (s, 1H), 4.34 (q, J=7.2 Hz, 2H), 2.90 (t, J=7.5 Hz, 4H), 2.57 (s, 3H), 2.08 (quint, J=7.5 Hz, 2H), 1.39 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 168.0, 148.8, 141.6, 138.1, 127.7, 127.5, 126.2, 60.4, 32.8, 32.2, 25.4, 21.7, 14.3; HRMS (ESI) calcd for $C_{13}H_{16}O_2Na$ $[M+Na]^+$ 227.1043, found 227.1048.

*4.3.28. 3-Methyl-6,7,8,9-tetrahydro-5H-benzocycloheptene-2-carboxylic acid ethyl ester (**3fa**).* Method B (temperature: 40 °C, concentration of **1f**: 0.05 M); colorless oil; IR (neat) 2924, 1716, 1448, 1269, 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.66 (s, 1H), 6.97 (s, 1H), 4.33 (q, J=7.2 Hz, 2H), 2.79 (t, J=5.4 Hz, 2H), 2.77 (t, J=5.4 Hz, 2H), 2.53 (s, 3H), 1.90–1.75 (m, 2H), 1.71–1.52 (m, 4H), 1.38 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 167.8, 147.8, 140.7, 137.8, 132.6, 131.0, 127.0, 60.4, 36.5, 36.0, 32.6, 28.3, 28.1, 21.2, 14.4; HRMS (ESI) calcd for $C_{15}H_{20}O_2Na$ $[M+Na]^+$ 255.1356, found 255.1382.

*4.3.29. Indan-5,8-dicarboxylic acid dimethyl ester (**3ed**)[33].* Method B (concentration of **1e**: 0.05 M, ligand: BINAP); ^{1}H NMR ($CDCl_3$) δ 7.55 (s, 2H), 3.88 (s, 6H), 2.94 (t, J=7.5 Hz, 4H), 2.12 (quint, J=7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 168.6, 147.9, 130.2, 124.8, 52.5, 32.7, 25.2.

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