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Palladium-Catalyzed Intramolecular *ipso*-Friedel–Crafts Allylic Alkylation of Phenols *via* Arylative Activation of Allenes

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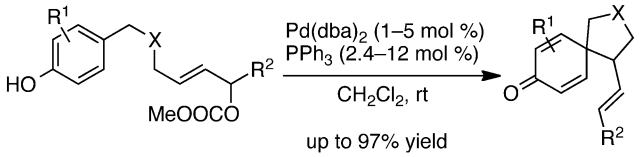
Abstract: A novel and efficient synthetic method for functionalized spiro[4.5]cyclohexadienones was developed based on the palladium-catalyzed sequential process: Heck insertion to an allene–intramolecular *ipso*-Friedel–Crafts allylic alkylation cascade. Using 5 mol% of palladium catalyst, a wide variety of spirocycles was obtained in good to excellent yields. The developed cascade process was also applicable to the synthesis of tetrahydronaphthalene derivatives.

Keywords: allylic substitution; cascade reactions; palladium; spiro compounds; synthetic methods

The efficient construction of spirocyclic frameworks is an important topic in synthetic organic chemistry due to their broad distribution in biologically active natural products and pharmaceuticals. Among the various spirocycles, spirocyclohexadienones are one of the most important classes of compounds in organic synthesis.[1] Functionalization of the cyclohexadienone unit provides an efficient and rapid access to multicyclic molecular frameworks,[2] indicating its potential utility in complex molecule syntheses. Extensive effort has therefore focused on the development of an efficient method for synthesizing this structural motif.[3]

As part of our ongoing studies aimed at developing novel synthetic methods based on intramolecular *ipso*-Friedel–Crafts-type reactions,[4] we recently reported a Pd-catalyzed intramolecular *ipso*-Friedel–Crafts allylic alkylation of phenols that provides spiro[4.5]cyclohexadienones in excellent yield with high diastereoselectivity under simple reaction conditions (Scheme 1).[4a,5] Substrate preparation for this Pd catalysis, however, requires a long multi-step process, making it difficult to divergently produce a wide variety of spiro[4.5]cyclohexadienones using this catalytic reaction system. We developed a reaction system to overcome this drawback. Herein we report a novel synthetic method for functionalized spiro[4.5]cyclohexadienones through a Pd-catalyzed sequential process: Heck insertion to an allene–intramolecular *ipso*-Friedel–Crafts allylic alkylation cascade.



Scheme 1. Pd-catalyzed intramolecular *ipso*-Friedel–Crafts allylic alkylation of phenols.

Aryl halides generally react with an allenyl substrate in the presence of a Pd(0) catalyst to give a 2-aryl *p*-allylpalladium(II) species through a Heck insertion process.[6] We envisioned that if this type of Heck insertion and an intramolecular *ipso*-Friedel–Crafts allylic alkylation of phenols proceeded sequentially in the presence of a Pd catalyst, various spiro[4.5]cyclohexadienones with a 1-arylvinyl substituent on the vicinal carbon to the spirocenter could be synthesized from a single allenyl substrate (Scheme 2).[7]

Based on this hypothesis, we optimized the reaction conditions using allenyl substrate **1** and iodobenzene as substrates (Table 1). We first examined the reaction using 5 mol% of $Pd(dba)_2$, 12 mol% of PPh_3, and 4 equiv. of K_2CO_3 at 70 °C in several solvent systems. The desired product **2a** was obtained in 53% yield when DMF was used as the solvent. Some by-products were detected in a ^1H NMR analysis of the crude sample and cyclic dimer **2a′**, formed by an intermolecular allylic etherification, was isolated as the major byproduct (8% yield: 16% of **1** was incorporated) (entry 4). The concentration of the reaction dramatically affected the yield of **2a**. When the reaction was

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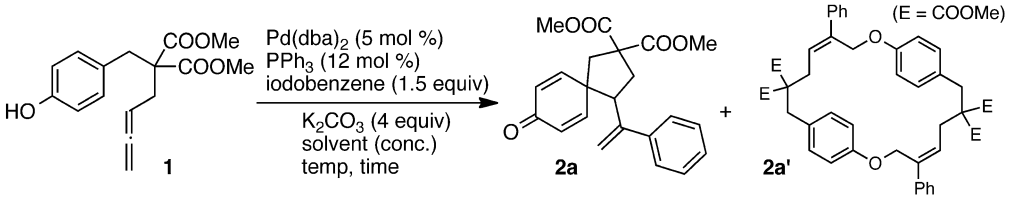
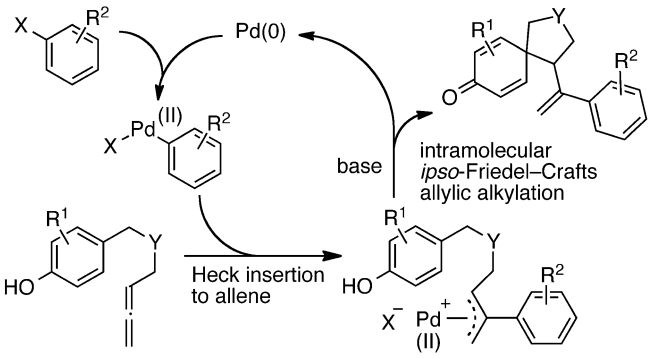
Table 1. Optimization of the reaction conditions using **1** and iodobenzene.



Entry	Solvent (conc.)	Temp. [°C]	Time [h]	Isolated yield [%]
1	THF (0.1 M)	reflux	8	no reaction
2	toluene (0.1 M)	70	8	no reaction
3	$(CH_2Cl)_2$ (0.1 M)	70	8	no reaction
4	DMF (0.1 M)	70	8	**2a** (53), **2a′** (8)
5	DMF (0.05 M)	70	8	**2a** (69), **2a′** (7)
6	DMF (0.02 M)	70	8	**2a** (78), **2a′** (4)
7	DMF (0.01 M)	70	8	**2a** (90), **2a′** (3)
8	DMF (0.01 M)	50	8	no reaction
9	DMF (0.01 M)	90	3	**2a** (94), **2a′** (2)



Scheme 2. Plan for the synthesis of spiro-[4.5]cyclohexadienones through the Heck insertion/intramolecular *ipso*-Friedel–Crafts allylic alkylation cascade.

performed at 0.01 M in DMF solution, **2a** was obtained in 90% yield, accompanied by the formation of small amount of **2a′** (3% yield: 6% of **1** was incorporated) (entry 7). Furthermore, the reactivity increased at a higher temperature and the desired spirocyclic adduct was obtained in 94% yield (entry 9).

Having established the optimized conditions (Table 1, entry 9), we next investigated the substrate scope of the developed spirocyclization process. We first examined reactions using substrate **1** and various aryl iodides in the presence of 5 mol% of the catalyst (Table 2). In addition to simple iodobenzene, *para*-substituted aryl iodides with an electron-withdrawing group as well as an electron-donating group were applicable to this reaction, affording the spirocyclic adducts **2b**–**2e** in a synthetically useful yield (70–87%). Both *meta*- and *ortho*-substituted aryl iodide derivatives were also suitable substrates for this process, affording the corresponding products **2f** and **2g** in 87% yield and 60% yield, respectively. Moreover, the reaction using 2-iodonaphthalene proceeded smoothly under the same reaction conditions to give the spirocyclic adduct **2h** in 83% yield. The generality of the allenyl substrates was investigated using iodobenzene as their partner (Table 3). *ortho*-Disubstituted phenol derivatives **3** and **5** reacted with iodobenzene under the optimized conditions and the corresponding products **4** and **6** were obtained in excellent yields. When *meta*-substituted phenol derivative **7** was utilized as a substrate, a spirocyclic adduct with contiguous chiral centers, **8**, was produced in 90% yield with good diastereoselectivity ($dr = 6.5:1$). The relative

Table 2. Substrate scope: aryl iodides.

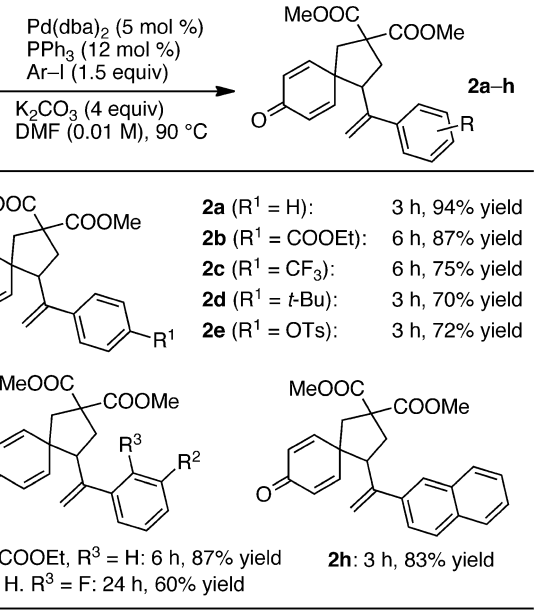


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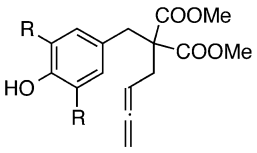
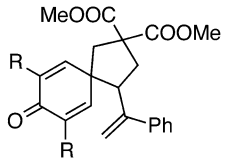
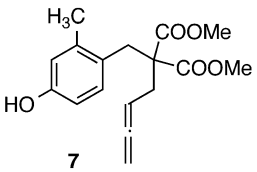
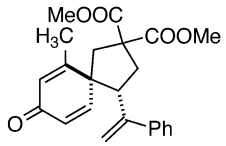
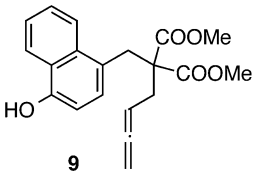
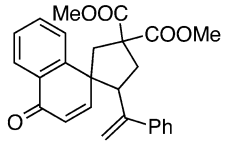
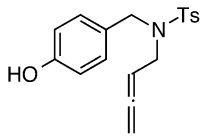
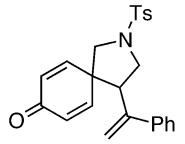
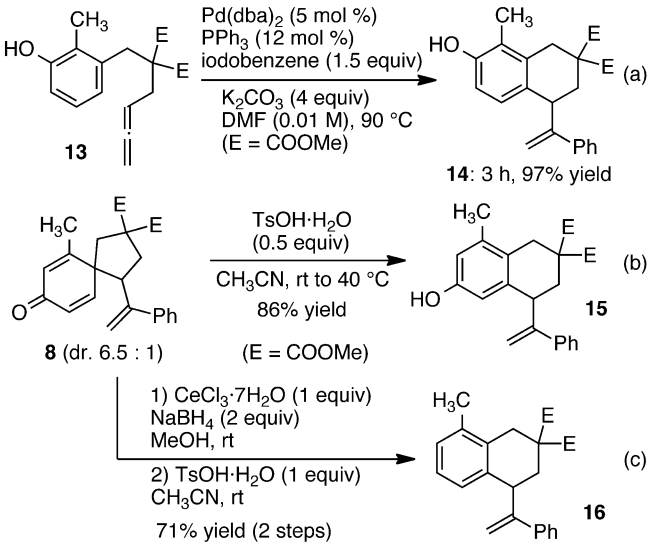
Table 3. Substrate scope: allenyl compounds.[a]

Substrate	Product
	
3 (R = Me) **5** (R = OMe)	**4** (R = Me): 5 h, 99% yield **6** (R = OMe): 5 h, 93% yield
	
7	**8**: 6 h, 90% yield (dr. 6.5:1)
	
9	**10**: 1 h, 85% yield (dr. 1.2:1)
	
11	**12**: 2 h, 70% yield

[a] *Reaction conditions:* $Pd(dba)_2$ (5 mol%), PPh_3 (12 mol%), iodobenzene (1.5 equiv.), K_2CO_3 (4 equiv.), DMF (0.01 M), 90 °C.

strereochemistry of the major isomer was determined by NOE experiments. Although the diastereoselectivity decreased, naphthol derivative **9** was also an applicable substrate and the corresponding naphthoquinone derivative **10** was obtained in 85% yield (dr = 1.2:1). In addition, when *N*-Ts-tethered allenyl substrate **11** was used as a substrate, spirocyclic adduct **12** was obtained in 70% yield.[8]

Furthermore, the present cascade process was applicable to the synthesis of tetrahydronaphthalene derivatives (Scheme 3). When *meta*-substituted phenol derivative **13** was treated under the same reaction conditions, Heck insertion to the allene, followed by an intramolecular Friedel–Crafts allylic alkylation of phenols,[9] proceeded sequentially to afford the product with a tetrahydronaphthalene skeleton **14** in 97% yield [Scheme 3(a)]. On the other hand, spirocyclic adduct **8** could be converted into tetrahydronaphthalene derivatives *via* acid-promoted skeletal rearrangements. Dienone-phenol rearrangement of spirocyclohexadienones is a useful method for synthesizing functionalized phenol derivatives. Treatment of **8** with 0.5 equiv. of *para*-toluenesulfonic acid (TsOH) in CH_3CN provided the rearranged phenol derivative **15**



Scheme 3. Synthesis of tetrahydronaphthalene derivatives.

in 86% yield [Scheme 3(b)]. Luche reduction of **8**, followed by treatment of the obtained alcohol intermediate with TsOH in CH_3CN, afforded the corresponding bicyclic adduct **16** in 71% yield over two steps [Scheme 3(c)]. The structures of **15** and **16** are complementary to that of **14**, demonstrating the synthetic utility of the developed process.

In conclusion, we have developed a novel method for synthesizing spiro[4.5]cyclohexadienone derivatives using a Pd-catalyzed sequential process: Heck insertion to an allene–intramolecular *ipso*-Friedel–Crafts allylic alkylation cascade. Structurally diverse spiro[4.5]cyclohexadienones were obtained in good to excellent yields under simple reaction conditions. Tetrahydronaphthalene derivatives were also accessible based on the developed process.

Experimental Section

General

IR spectra were recorded on a JASCO FT/IR 230 Fourier transform infrared spectrophotometer, equipped with ATR (Smiths Detection, DuraSample IR II). NMR spectra were recorded on a JEOL ecs 400 spectrometer, operating at 400 MHz for ^1H NMR, and 100 MHz for ^{13}C NMR. ESI-TOF mass spectra were measured on JEOL AccuTOF LC-plus JMS-T100 LP. Reactions were carried out in dry solvent under an argon atmosphere. Other reagents were purified by the usual methods.

Synthesis of Allenyl Substrates

Malonate-tethered allenyl substrates **1**, **3**, **5**, **7**, **9**, and **13** were prepared from dimethyl 2-(buta-2,3-dien-1-yl)malonate[10] and benzyl bromide derivatives according to the general procedure. *N*-Ts-tethered allenyl substrate **11** was pre-

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pared from *N*-(buta-2,3-dien-1-yl)-4-methylbenzenesulfonamide[11] and *p-tert*-butyldimethylsilyloxybenzyl bromide according to the general procedure.

General Procedure

To a stirred solution of dimethyl 2-(buta-2,3-dien-1-yl)malonate (386.8 mg, 2.10 mmol) in THF (4 mL) at 0 °C was added NaH (60% oil. 128.0 mg, 3.20 mmol), and the resulting mixture was kept stirring for 30 min. *p-tert*-Butyldimethylsilyloxybenzyl bromide (747.5 mg, 2.50 mmol in 3 mL of THF) was added to the reaction, and the reaction was stirred for 1 h at room temperature. The reaction was quenched with water, and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with brine, dried over Na_2SO_4, and then evaporated under vacuum. The obtained residue was purified by flash column chromatography (SiO_2, hexane/AcOEt = 50/1 to 30/1) to give the corresponding product; yield: 558.7 mg (66%).

To a stirred solution of the obtained product (558.7 mg, 1.38 mmol) and AcOH (0.16 mL, 2.80 mmol) in THF (7 mL) at 0 °C was added TBAF (1 M solution in THF, 2.8 mL, 2.80 mmol), and the resulting mixture was stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl, and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with brine, dried over Na_2SO_4, and then evaporated under vacuum. The obtained residue was purified by flash column chromatography (SiO_2, hexane/AcOEt = 10/1 to 4/1) to give *dimethyl 2-(buta-2,3-dien-1-yl)-2-(4-hydroxybenzyl)malonate* **1** as a colorless oil; yield: 315.5 mg (79%). IR (ATR): ν = 3440, 1722, 1517, 1440, 1202, 847 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.53 (dt, J = 7.6, 2.4 Hz, 2H), 3.20 (s, 2H), 3.72 (s, 6H), 4.73 (dt, J = 6.8, 2.4 Hz, 2H), 5.01 (tt, J = 6.8, 7.6 Hz, 1H), 5.42 (s, 1H), 6.68–6.71 (m, 2H), 6.93–6.96 (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 31.1, 37.1, 52.4 (2C), 59.2, 75.0, 84.4, 115.2 (2C), 127.5, 131.1 (2C), 154.8, 171.3 (2C), 210.1; HR-MS [(+)-ESI-TOF]: m/z = 313.1024, calcd. for $C_{16}H_{18}NaO_5^+$ ($M+Na^+$): 313.1046.

Dimethyl 2-(buta-2,3-dien-1-yl)-2-(4-hydroxy-3,5-dimethylbenzyl)malonate (3): White solid; mp 99–101 °C; IR (ATR): ν = 3522, 2951, 1728, 1490, 1435, 1201, 1153, 1075, 848 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.18 (s, 6H), 2.52 (dt, J = 8.0, 2.4 Hz, 2H), 3.14 (s, 2H), 3.72 (s, 6H), 4.55 (s, 1H), 4.73 (dt, J = 6.8, 2.4 Hz, 2H), 5.01 (tt, J = 6.8, 8.0 Hz, 1H), 6.69 (s, 2H); ^{13}C NMR ($CDCl_3$): δ = 15.9 (2C), 31.1, 37.1, 52.3 (2C), 59.2, 74.8, 84.6, 122.7 (2C), 127.1, 130.1 (2C), 151.2, 171.2 (2C), 210.2; HR-MS [(+)-ESI-TOF]: m/z = 341.1372, calcd. for $C_{18}H_{22}NaO_5^+$ ($M+Na^+$): 341.1359.

Dimethyl 2-(buta-2,3-dien-1-yl)-2-(4-hydroxy-3,5-dimethoxybenzyl)malonate (5): White solid; mp 79–81 °C; IR (ATR): ν = 3447, 2952, 1730, 1519, 1458, 1202, 1109, 1074, 844, 733 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.58 (dt, J = 8.0, 2.4 Hz, 2H), 3.20 (s, 2H), 3.73 (s, 3H), 3.84 (s, 3H), 4.76 (dt, J = 6.4, 2.4 Hz, 2H), 4.99 (tt, J = 6.4, 8.0 Hz, 1H), 5.48 (s, 1H), 6.35 (s, 2H); ^{13}C NMR ($CDCl_3$): δ = 31.0, 37.8, 52.3 (2C), 56.1 (2C), 59.1, 74.9, 84.6, 106.6 (2C), 126.5, 133.6, 146.7 (2C), 170.9 (2C), 210.2; HR-MS [(+)-ESI-TOF]: m/z = 373.1243, calcd. for $C_{18}H_{22}NaO_7^+$ ($M+Na^+$): 373.1258.

Dimethyl 2-(buta-2,3-dien-1-yl)-2-(4-hydroxy-2-methylbenzyl)malonate (7): White solid; mp 75–77 °C; IR (ATR): ν = 3444, 2952, 1720, 1506, 1436, 1203, 1113, 1071, 850 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.22 (s, 3H), 2.59 (dt, J = 7.6, 2.4 Hz, 2H), 3.27 (s, 2H), 3.70 (s, 6H), 4.67–4.70 (m, 2H), 5.05 (tt, J = 6.8, 7.6 Hz, 1H), 5.32 (s, 1H), 6.53 (dd, J = 2.4, 8.4 Hz, 1H), 6.61 (d, J = 2.4 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 19.9, 32.1, 33.8, 52.4 (2C), 59.2, 74.9, 84.7, 112.7, 117.2, 126.1, 131.3, 138.7, 154.3, 171.6 (2C), 209.9; HR-MS [(+)-ESI-TOF]: m/z = 327.1200, calcd. for $C_{17}H_{20}NaO_5^+$ ($M+Na^+$): 327.1203.

Dimethyl 2-(buta-2,3-dien-1-yl)-2-((4-hydroxynaphthalen-1-yl)methyl)malonate (9): Pale brown solid; mp 112–113 °C; IR (ATR): ν = 3369, 2952, 1711, 1585, 1434, 1374, 1290, 1202, 1057, 835, 762, 736 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.63 (dt, J = 7.2, 2.8 Hz, 2H), 3.59 (s, 6H), 3.72 (s, 2H), 4.71–4.74 (m, 2H), 5.09 (tt, J = 6.8, 7.2 Hz, 1H), 5.91 (br-s, 1H), 6.62 (d, J = 7.2 Hz, 1H), 7.16 (d, J = 7.6 Hz, 1H), 7.42–7.49 (m, 2H), 7.98 (d, J = 8.4 Hz, 1H), 8.19 (dd, J = 1.2, 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 32.1, 33.2, 52.4 (2C), 59.2, 75.0, 84.7, 107.9, 122.4, 123.6, 124.1, 124.6, 124.7, 126.2, 128.3, 133.7, 151.0, 171.6 (2C), 210.1; HR-MS [(+)-ESI-TOF]: m/z = 341.1372, calcd. for $C_{18}H_{22}NaO_5^+$ ($M+Na^+$): 341.1359.

***N*-(Buta-2,3-dien-1-yl)-*N*-(3-hydroxy-2-methylbenzyl)-4-methylbenzenesulfonamide (11):** White solid; mp 77–78 °C; IR (ATR): ν = 3435, 1515, 1330, 1152, 1091, 815, 758, 659 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.44 (s, 3H), 3.76 (dt, J = 7.2, 2.4 Hz, 2H), 4.30 (s, 2H), 4.62 (dt, J = 6.4, 2.4 Hz, 2H), 4.74 (tt, J = 6.4, 7.2 Hz, 1H), 5.74 (s, 1H), 6.78 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 21.5, 45.2, 49.5, 76.1, 85.0, 115.4 (2C), 127.2 (2C), 127.6, 129.7 (2C), 130.1 (2C), 137.5, 143.4, 155.4, 209.5; HR-MS [(+)-ESI-TOF]: m/z = 352.0979, calcd. for $C_{18}H_{20}NNaO_3S^+$ ($M+Na^+$): 352.0978.

Dimethyl 2-(buta-2,3-dien-1-yl)-2-(3-hydroxy-2-methylbenzyl)malonate (13): Pale yellow solid; mp 80–82 °C; IR (ATR): ν = 3445, 2952, 1718, 1586, 1435, 1200, 1072, 847, 779, 724 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.17 (s, 3H), 2.57 (dt, J = 7.6, 2.8 Hz, 2H), 3.37 (s, 2H), 3.70 (s, 6H), 4.68–4.71 (m, 2H), 4.70 (s, 1H), 5.06 (tt, J = 6.8, 7.6 Hz, 1H), 6.65 (d, J = 8.4 Hz, 1H), 6.70 (d, J = 7.6 Hz, 1H), 6.97 (dd, J = 7.6, 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 11.9, 31.9, 34.6, 52.4 (2C), 59.1, 74.9, 84.8, 113.5, 122.8, 123.8, 125.9, 135.8, 154.1, 171.4 (2C), 209.9; HR-MS [(+)-ESI-TOF]: m/z = 313.1020, calcd. for $C_{16}H_{18}NaO_5^+$ ($M+Na^+$): 313.1046.

Pd-Catalyzed Cascade Cyclization

Spirocyclic adducts **2a–h**, **4**, **6**, **8**, **10**, and **12**, and tetrahydronaphthol derivative **14** were prepared according to the general procedure.

General Procedure

A solution of **1** (52.2 mg, 0.18 mmol), $Pd(dba)_2$ (5.2 mg, 0.009 mmol), PPh_3 (5.8 mg, 0.022 mmol), K_2CO_3 (99.5 mg, 0.72 mmol), and iodobenzene (30 mL, 0.27 mmol) in DMF (18 mL) was heated at 90 °C for 3 h. The reaction mixture was cooled down to room temperature and the solvent was evaporated under reduced pressure. After dilution of the residue with Et_2O, the resulting solution was washed with water and brine, dried over Na_2SO_4, and then concentrated under vacuum. The crude residue was purified by flash column chromatography (SiO_2, hexane/AcOEt = 3/1) to give *dimethyl 8-oxo-4-(1-phenylvinyl)spiro[4.5]deca-6,9-diene-2,2-dicarboxylate* **2a** as colorless oil; yield: 58.4 mg (94%). IR

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(ATR): ν = 1729, 1662, 1252, 1200, 856, 733, 701 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.35 (d, *J* = 14.8 Hz, 1H), 2.70 (d, *J* = 14.8 Hz, 1H), 2.76 (dd, *J* = 6.4, 14.0 Hz, 1H), 2.90 (dd, *J* = 13.2, 14.0 Hz, 1H), 3.47 (dd, *J* = 6.0, 13.2 Hz, 1H), 3.79 (s, 3H), 3.83 (s, 3H), 5.10 (s, 1H), 5.11 (s, 1H), 5.59 (dd, *J* = 2.0, 10.0 Hz, 1H), 6.14 (dd, *J* = 2.0, 10.0 Hz, 1H), 6.44 (dd, *J* = 3.2, 10.0 Hz, 1H), 6.83 (dd, *J* = 3.2, 10.0 Hz, 1H), 7.02–7.05 (m, 2H), 7.17–7.20 (m, 3H); ^{13}C NMR ($CDCl_3$): δ = 37.5, 44.1, 50.5, 52.9, 53.2, 53.3, 57.5, 114.0, 126.9 (2C), 127.7, 127.7, 128.0 (2C), 128.5, 141.7, 146.5, 149.3, 153.2, 171.9, 172.4, 185.6; HR-MS [(+)-ESI-TOF]: *m/z* = 389.1385, calcd. for $C_{22}H_{22}NaO_5^+$ ($M+Na^+$): 389.1359.

Cyclic dimer (2a′): Pale yellow oil; IR (ATR): ν = 1730, 1510, 1205, 1175, 1016, 737, 699 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.74 (d, *J* = 7.6 Hz, 4H), 3.30 (s, 4H), 3.81 (s, 12H), 4.51 (s, 4H), 5.74 (t, *J* = 7.6 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 4H), 6.95 (d, *J* = 8.8 Hz, 4H), 7.27–7.36 (m, 6H), 7.42–7.45 (m, 4H); ^{13}C NMR ($CDCl_3$): δ = 30.7 (2C), 37.6 (2C), 52.8 (4C), 58.3 (2C), 65.3 (2C), 115.0 (4C), 126.4 (4C), 126.8 (2C), 127.4 (2C), 127.8 (2C), 128.3 (4C), 130.5 (4C), 138.5 (2C), 140.4 (2C), 157.9 (2C), 171.4 (4C); HR-MS [(+)-ESI-TOF]: *m/z* = 755.2821, calcd. for $C_{44}H_{44}NaO_{10}^+$ ($M+Na^+$): 755.2827.

Dimethyl 4-{1-[4-(ethoxycarbonyl)phenyl]vinyl}-8-oxospiro[4.5]deca-6,9-diene-2,2-dicarboxylate (2b): Pale yellow oil; IR (ATR): ν = 1722, 1712, 1662, 1252, 1174, 1101, 856, 715 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 1.39 (t, *J* = 7.2 Hz, 3H), 2.37 (d, *J* = 14.4 Hz, 1H), 2.71 (d, *J* = 14.4 Hz, 1H), 2.76 (dd, *J* = 6.4, 14.0 Hz, 1H), 2.90 (dd, *J* = 13.2, 14.0 Hz, 1H), 3.49 (dd, *J* = 6.4, 13.2 Hz, 1H), 3.80 (s, 3H), 3.84 (s, 3H), 4.35 (q, *J* = 7.2 Hz, 2H), 5.18 (s, 2H), 5.63 (dd, *J* = 2.0, 10.0 Hz, 1H), 6.16 (dd, *J* = 2.0, 10.0 Hz, 1H), 6.45 (dd, *J* = 2.8, 10.4 Hz, 1H), 6.84 (dd, *J* = 2.8, 10.4 Hz, 1H), 7.13 (dd, *J* = 1.6, 6.4 Hz, 2H), 7.88 (dd, *J* = 1.6, 6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 14.3, 37.5, 44.2, 50.6, 52.6, 53.3, 53.4, 57.4, 61.0, 115.5, 126.8 (2C), 128.3, 128.6, 129.4 (2C), 129.7, 145.7, 146.3, 149.2, 153.1, 166.2, 171.9, 172.4, 185.4; HR-MS [(+)-ESI-TOF]: *m/z* = 461.1595, calcd. for $C_{25}H_{26}NaO_7^+$ ($M+Na^+$): 461.1571.

Dimethyl 8-oxo-4-{1-[4-(trifluoromethyl)phenyl]vinyl}-spiro[4.5]deca-6,9-diene-2,2-dicarboxylate (2c): Pale yellow oil; IR (ATR): ν = 1731, 1663, 1323, 1254, 1162, 1110, 1064, 849 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.39 (d, *J* = 14.4 Hz, 1H), 2.71 (d, *J* = 14.4 Hz, 1H), 2.77 (dd, *J* = 6.4, 14.0 Hz, 1H), 2.90 (dd, *J* = 13.2, 14.0 Hz, 1H), 3.47 (dd, *J* = 6.0, 13.2 Hz, 1H), 3.80 (s, 3H), 3.84 (s, 3H), 5.18 (s, 1H), 5.20 (d, *J* = 1.2 Hz, 1H), 5.65 (dd, *J* = 2.0, 10.0 Hz, 1H), 6.17 (dd, *J* = 1.6, 10.4 Hz, 1H), 6.44 (dd, *J* = 3.2, 10.0 Hz, 1H), 6.84 (dd, *J* = 3.2, 10.4 Hz, 1H), 7.16–7.18 (m, 2H), 7.46–7.48 (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 37.5, 44.2, 50.6, 52.7, 53.3, 53.4, 57.4, 115.9, 123.9 (q, *J* = 270.8 Hz), 125.0 (q, *J* = 3.9 Hz) (2C), 125.3, 127.2 (2C), 128.3, 128.7, 129.8 (q, *J* = 32.5 Hz), 145.3, 145.4, 149.1, 153.0, 171.8, 172.4, 185.3; HR-MS [(+)-ESI-TOF]: *m/z* = 435.1387, calcd. for $C_{23}H_{22}F_3O_5^+$ ($M+H^+$): 435.1414.

Dimethyl 4-{1-[4-(*tert*-butyl)phenyl]vinyl}-8-oxospiro-[4.5]deca-6,9-diene-2,2-dicarboxylate (2d): Pale yellow oil; IR (ATR): ν = 2954, 1731, 1663, 1252, 1200, 1095, 857 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 1.28 (s, 9H), 2.34 (d, *J* = 14.8 Hz, 1H), 2.70 (d, *J* = 14.8 Hz, 1H), 2.75 (dd, *J* = 6.0, 14.0 Hz, 1H), 2.88 (dd, *J* = 13.2 Hz, 14.0 Hz, 1H), 3.46 (dd, *J* = 6.0, 13.2 Hz, 1H), 3.79 (s, 3H), 3.83 (s, 3H), 5.06 (s, 1H), 5.11 (s, 1H), 5.57 (dd, *J* = 2.0, 10.4 Hz, 1H), 6.13 (dd, *J* = 2.0, 10.4 Hz, 1H), 6.44 (dd, *J* = 2.8, 10.4 Hz, 1H), 6.82 (dd, *J* = 2.8, 10.4 Hz, 1H), 6.96–6.99 (m, 2H), 7.19–7.21 (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 31.3 (3C), 34.4, 37.6, 44.2, 50.6, 53.1, 53.2, 53.3, 57.5, 113.4, 124.9 (2C), 126.7 (2C), 127.5, 128.5, 138.8, 146.4, 149.3, 151.0, 153.3, 172.0, 172.5, 185.6; HR-MS [(+)-ESI-TOF]: *m/z* = 445.1984, calcd. for $C_{26}H_{30}NaO_5^+$ ($M+Na^+$): 445.1985.

Dimethyl 8-oxo-4-{1-[4-(tosyloxy)phenyl]vinyl}spiro-[4.5]deca-6,9-diene-2,2-dicarboxylate (2e): Pale yellow oil; IR (ATR): ν = 1731, 1664, 1257, 1199, 1176, 1155, 860 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.35 (d, *J* = 14.8 Hz, 1H), 2.47 (s, 3H), 2.70 (d, *J* = 14.8 Hz, 1H), 2.73 (dd, *J* = 6.4, 13.6 Hz, 1H), 2.87 (dd, *J* = 13.2, 13.6 Hz, 1H), 3.41 (dd, *J* = 6.4, 13.2 Hz, 1H), 3.79 (s, 3H), 3.83 (s, 3H), 5.08 (s, 1H), 5.11 (s, 1H), 5.60 (dd, *J* = 2.0, 10.0 Hz, 1H), 6.11 (dd, *J* = 2.0, 10.0 Hz, 1H), 6.43 (dd, *J* = 2.8, 10.0 Hz, 1H), 6.79 (dd, *J* = 2.8, 10.0 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 21.7, 37.4, 44.2, 50.4, 52.7, 53.3, 53.4, 57.4, 114.8, 122.1 (2C), 128.0, 128.0 (2C), 128.5, 128.5 (2C), 129.9 (2C), 132.2, 140.7, 145.3, 145.4, 149.1, 149.2, 153.2, 171.9, 172.4, 185.2; HR-MS [(+)-ESI-TOF]: *m/z* = 559.1427, calcd. for $C_{29}H_{28}NaO_8S^+$ ($M+Na^+$): 559.1397.

Dimethyl 4-{1-[3-(ethoxycarbonyl)phenyl]vinyl}-8-oxospiro[4.5]deca-6,9-diene-2,2-dicarboxylate (2f): Pale yellow oil; IR (ATR): ν = 1720, 1716, 1663, 1247, 857, 733 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 1.40 (t, *J* = 7.2 Hz, 3H), 2.35 (d, *J* = 15.2 Hz, 1H), 2.73 (d, *J* = 15.2 Hz, 1H), 2.78 (dd, *J* = 6.0, 13.6 Hz, 1H), 2.91 (dd, *J* = 13.2, 13.6 Hz, 1H), 3.50 (dd, *J* = 6.0, 13.2 Hz, 1H), 3.80 (s, 3H), 3.85 (s, 3H), 4.33–4.42 (m, 2H), 5.16 (s, 1H), 5.18 (d, *J* = 1.2 Hz, 1H), 5.60 (dd, *J* = 2.0, 10.0 Hz, 1H), 6.15 (dd, *J* = 2.0, 10.0 Hz, 1H), 6.46 (dd, *J* = 3.2, 10.4 Hz, 1H), 6.85 (dd, *J* = 3.2, 10.4 Hz, 1H), 7.19–7.26 (m, 2H), 7.76–7.77 (m, 1H), 7.87–7.90 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 14.3, 37.4, 44.2, 50.5, 52.6, 53.3, 53.4, 57.5, 61.1, 115.0, 127.7, 127.8, 128.3, 128.6, 128.8, 130.1, 131.6, 141.9, 145.7, 149.3, 153.2, 166.3, 171.9, 172.3, 185.4; HR-MS [(+)-ESI-TOF]: *m/z* = 439.1780, calcd. for $C_{25}H_{27}O_7^+$ ($M+H^+$): 439.1751.

Dimethyl 4-[1-(2-fluorophenyl)vinyl]-8-oxospiro[4.5]deca-6,9-diene-2,2-dicarboxylate (2g): Pale yellow oil; IR (ATR): ν = 1730, 1663, 1257, 1202, 858, 764 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.30 (d, *J* = 14.8 Hz, 1H), 2.74 (d, *J* = 14.8 Hz, 1H), 2.79 (dd, *J* = 6.4, 13.6 Hz, 1H), 2.91 (dd, *J* = 13.2, 13.6 Hz, 1H), 3.56 (dd, *J* = 6.4, 13.2 Hz, 1H), 3.79 (s, 3H), 3.83 (s, 3H), 5.13 (s, 1H), 5.26 (d, *J* = 1.2 Hz, 1H), 5.65 (dd, *J* = 2.0, 10.0 Hz, 1H), 6.16 (dd, *J* = 2.0, 10.0 Hz, 1H), 6.53 (dd, *J* = 2.8, 10.0 Hz, 1H), 6.83–6.95 (m, 4H), 7.16–7.22 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 37.1, 44.3, 50.6, 52.0 (d, *J* = 3.8 Hz), 53.2 53.3, 57.4, 115.1 (d, *J* = 21.9 Hz), 116.8, 124.0 (d, *J* = 2.8 Hz), 128.1, 128.7, 129.0 (d, *J* = 14.3 Hz), 129.5 (d, *J* = 8.6 Hz), 130.5 (d, *J* = 3.8 Hz), 142.4, 149.2, 153.0, 159.0 (d, *J* = 245.0 Hz), 172.0, 172.3, 185.6; HR-MS [(+)-ESI-TOF]: *m/z* = 407.1240, calcd. for $C_{22}H_{21}FNaO_5^+$ ($M+Na^+$): 407.1265.

Dimethyl 4-[1-(naphthalen-2-yl)vinyl]-8-oxospiro-[4.5]deca-6,9-diene-2,2-dicarboxylate (2h): Pale yellow oil; IR (ATR): ν = 1729, 1662, 1253, 1200, 856, 734 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.38 (d, *J* = 14.8 Hz, 1H), 2.72 (d, *J* = 14.8 Hz, 1H), 2.82 (dd, *J* = 6.0, 14.0 Hz, 1H), 2.95 (dd, *J* = 13.2, 14.0 Hz, 1H), 3.61 (dd, *J* = 6.0, 13.2 Hz, 1H), 3.80 (s, 3H), 3.85 (s, 3H), 5.20 (s, 1H), 5.23 (s, 1H), 5.46 (dd, *J* =

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2.0, 10.0 Hz, 1H), 6.18 (dd, J=2.0, 10.4 Hz, 1H), 6.44 (dd, J=3.2, 10.0 Hz, 1H), 6.89 (dd, J=3.2, 10.4 Hz, 1H), 7.18 (dd, J=1.6, 8.8 Hz, 1H), 7.43–7.51 (m, 3H), 7.73–7.78 (m, 3H); ^{13}C NMR ($CDCl_3$): δ=37.6, 44.3, 50.8, 53.2, 53.3, 53.4, 57.5, 114.7, 125.4, 125.5, 126.0, 126.3, 127.6, 127.8, 127.9, 128.0, 128.6, 132.7, 132.8, 139.2, 146.4, 149.4, 153.2, 172.0, 172.5, 185.5; HR-MS [(+)-ESI-TOF]: m/z=439.1535, calcd. for $C_{26}H_{24}NaO_5^+$ ($M+Na^+$): 439.1516.

Dimethyl 7,9-dimethyl-8-oxo-4-(1-phenylvinyl)spiro-[4.5]deca-6,9-diene-2,2-dicarboxylate (4): Yellow oil; IR (ATR): ν=1730, 1632, 1251, 1200, 901, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ=1.34 (s, 3H), 1.83 (s, 3H), 2.30 (d, J=14.4 Hz, 1H), 2.66 (d, J=14.4 Hz, 1H), 2.71 (dd, J=6.0, 14.0 Hz, 1H), 2.86 (dd, J=13.2, 14.0 Hz, 1H), 3.40 (dd, J=6.0, 13.2 Hz, 1H), 3.79 (s, 3H), 3.83 (s, 3H), 5.04 (s, 2H), 6.20 (d, J=1.2 Hz, 1H), 6.54 (d, J=1.2 Hz, 1H), 6.95–6.98 (m, 2H), 7.14–7.20 (m, 3H); ^{13}C NMR ($CDCl_3$): δ=15.4, 16.2, 37.4, 43.9, 49.7, 52.3, 53.1, 53.2, 57.6, 113.6, 126.9 (2C), 127.5, 127.9 (2C), 134.1, 134.3, 141.8, 144.5, 147.3, 149.3, 172.2, 172.7, 186.6; HR-MS [(+)-ESI-TOF]: m/z=417.1673, calcd. for $C_{24}H_{26}NaO_5^+$ ($M+Na^+$): 417.1672.

Dimethyl 7,9-dimethoxy-8-oxo-4-(1-phenylvinyl)spiro-[4.5]deca-6,9-diene-2,2-dicarboxylate (6): Yellow oil; IR (ATR): ν=1728, 1667, 1618, 1250, 1199, 1108, 777, 731, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ=2.33 (d, J=14.4 Hz, 1H), 2.74 (dd, J=6.4, 14.0 Hz, 1H), 2.80 (d, J=14.4 Hz, 1H), 2.99 (dd, J=13.2, 14.0 Hz, 1H), 3.18 (s, 3H), 3.48 (dd, J=6.4, 13.2 Hz, 1H), 3.61 (s, 3H), 3.80 (s, 3H), 3.84 (s, 3H), 5.08 (s, 1H), 5.09 (s, 1H), 5.31 (d, J=2.4 Hz, 1H), 5.79 (d, J=2.4 Hz, 1H), 6.99–7.02 (m, 2H), 7.16–7.28 (m, 3H); ^{13}C NMR ($CDCl_3$): δ=37.2, 46.0, 49.2, 53.2, 53.3, 54.1, 54.6, 55.1, 57.1, 114.1, 116.2, 121.3, 126.8 (2C), 127.5, 128.1 (2C), 142.3, 146.9, 149.9, 150.4, 172.5, 172.7, 176.0; HR-MS [(+)-ESI-TOF]: m/z=449.1588, calcd. for $C_{24}H_{26}NaO_7^+$ ($M+Na^+$): 449.1571.

Dimethyl 6-methyl-8-oxo-4-(1-phenylvinyl)spiro[4.5]deca-6,9-diene-2,2-dicarboxylate (8): Pale yellow oil; IR (ATR): ν=1734, 1665, 1457, 1364, 1204 cm^{-1}; ^{1}H NMR (major isomer, $CDCl_3$): δ=1.79 (s, 3H), 2.35 (d, J=14.8 Hz, 1H), 2.74 (dd, J=6.4, 14.0 Hz, 1H), 2.80 (d, J=14.8 Hz, 1H), 2.85 (dd, J=13.2, 14.0 Hz, 1H), 3.63 (dd, J=6.4, 13.2 Hz, 1H), 3.80 (s, 3H), 3.84 (s, 3H), 5.08 (s, 2H), 5.64 (d, J=2.0 Hz, 1H), 6.16 (dd, J=2.0, 10.4 Hz, 1H), 6.89 (d, J=10.4 Hz, 1H), 7.00–7.06 (m, 2H), 7.13–7.24 (m, 3H); ^{13}C NMR (major isomer, $CDCl_3$): δ=19.1, 37.7, 43.1, 50.4, 52.9, 53.3, 53.3, 57.5, 114.6, 126.8 (2C), 127.2, 127.7, 127.9 (2C), 129.6, 141.7, 146.5, 151.1, 159.2, 172.0, 172.6, 185.6; HR-MS [(+)-ESI-TOF]: m/z=403.1538, calcd. for $C_{23}H_{24}NaO_5^+$ ($M+Na^+$): 403.1516.

Dimethyl 4′-oxo-2-(1-phenylvinyl)-4′*H*-spiro[cyclopentane-1,1′-naphthalene]-4,4-dicarboxylate (10): Yellow oil; IR (ATR): ν=1728, 1662, 1255, 1203, 767, 734, 699 cm^{-1}; ^{1}H NMR (major isomer, $CDCl_3$): δ=2.80 (d, J=15.2 Hz, 1H), 2.84 (dd, J=6.0, 13.6 Hz, 1H), 3.07 (dd, J=1.2, 15.2 Hz, 1H), 3.08 (dd, J=13.2, 13.2 Hz, 1H), 3.70 (ddd, J=1.2, 6.0, 15.2 Hz, 1H), 3.83 (s, 3H), 3.91 (s, 3H), 4.83 (s, 1H), 4.91 (s, 1H), 5.84 (d, J=10.0 Hz, 1H), 6.50–6.52 (m, 2H), 6.86–7.01 (m, 4H), 7.33–7.64 (m, 3H), 7.93 (dd, J=1.2, 8.0 Hz, 1H); ^{13}C NMR (major isomer, $CDCl_3$): δ=39.6, 48.1, 50.1, 53.1, 53.2, 53.3, 59.1, 115.0, 126–146 (9C), 146.9, 155.4, 171.6, 172.6, 183.9; HR-MS [(+)-ESI-TOF]: m/z=439.1675, calcd. for $C_{26}H_{25}O_5^+$ ($M+H^+$): 417.1697.

4-(1-Phenylvinyl)-2-tosyl-2-azaspiro[4.5]deca-6,9-dien-8-one (12): Yellow oil; IR (ATR): ν=1664, 1344, 1162, 1091, 858, 703, 662 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ=2.49 (s, 3H), 3.40 (d, J=10.4 Hz, 1H), 3.44 (d, J=10.4 Hz, 1H), 3.50 (dd, J=8.0, 10.0 Hz, 1H), 3.71 (dd, J=10.0, 10.4 Hz, 1H), 3.90 (dd, J=8.0, 10.4 Hz, 1H), 4.99 (s, 1H), 5.18 (s, 1H), 5.72 (dd, J=2.0, 10.0 Hz, 1H), 6.09 (dd, J=2.0, 10.4 Hz, 1H), 6.28 (dd, J=3.2, 10.0 Hz, 1H), 6.41 (dd, J=3.2, 10.4 Hz, 1H), 6.97–7.00 (m, 2H), 7.16–7.22 (m, 3H), 7.41 (d, J=8.0 Hz, 2H), 7.78 (d, J=8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ=21.6, 49.8, 50.0, 51.7, 56.4, 115.1, 126.7 (2C), 127.5 (2C), 128.1, 129.6 (2C), 129.8, 130.0, 133.4 (2C), 141.1, 144.2, 144.3, 146.5, 148.8, 185.0; HR-MS [(+)-ESI-TOF]: m/z=406.1494, calcd. for $C_{24}H_{24}NO_3S^+$ ($M+H^+$): 406.1471.

Dimethyl 7-hydroxy-8-methyl-4-(1-phenylvinyl)-3,4-dihydronaphthalene-2,2(1*H*)-dicarboxylate (14): Yellow oil; IR (ATR): ν=3475, 1734, 1490, 1436, 1251, 1073, 703 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ=2.08 (dd, J=10.8, 13.2 Hz, 1H), 2.21 (s, 3H), 2.57 (dd, J=6.0, 13.2 Hz, 1H), 3.01 (d, J=16.8 Hz, 1H), 3.39 (d, J=16.8 Hz, 1H), 3.69 (s, 3H), 3.71 (s, 3H), 4.05 (dd, J=6.0, 10.8 Hz, 1H), 4.57 (s, 1H), 5.05 (s, 1H), 5.44 (s, 1H), 6.60 (d, J=8.4 Hz, 1H), 7.01 (d, J=8.4 Hz, 1H), 7.21–7.26 (m, 5H); ^{13}C NMR ($CDCl_3$): δ=11.3, 32.5, 34.0, 42.9, 52.8, 52.8, 53.8, 113.5, 116.3, 121.4, 126.8 (2C), 127.0, 127.4, 128.2 (2C), 129.0, 133.8, 140.9, 151.7, 151.7, 171.5, 172.2; HR-MS [(+)-ESI-TOF]: m/z=381.1679, calcd. for $C_{23}H_{25}O_5^+$ ($M+H^+$): 381.1697.

Dimethyl 6-Hydroxy-8-methyl-4-(1-phenylvinyl)-3,4-dihydronaphthalene-2,2(1*H*)-dicarboxylate (15)

To a solution of **8** (30.6 mg, 0.08 mmol) in CH_3CN (4 mL) at room temperature was added $TsOH{\cdot}H_2O$ (7.6 mg, 0.04 mmol) and the mixture was stirred at 40 °C for 12 h. The reaction was quenched with saturated aqueous $NaHCO_3$ and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with brine, dried over Na_2SO_4, and then concentrated under vacuum. The obtained residue was purified by flash column chromatography (SiO_2, hexane/acetone=3:1) to give **15** as a colorless oil; yield: 26.3 mg (86%). IR (ATR): ν=3445, 1732, 1435, 1238, 1080, 1030, 735, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ=2.09 (dd, J=11.2, 13.6 Hz, 1H), 2.26 (s, 3H), 2.58 (dd, J=2.0, 6.0 Hz, 13.6 Hz, 1H), 2.92 (d, J=16.0 Hz, 1H), 3.31 (dd, J=2.0, 16.0 Hz, 1H), 3.67 (s, 3H), 3.69 (s, 3H), 4.05 (dd, J=6.0, 11.2 Hz, 1H), 4.84 (s, 1H), 5.06 (s, 1H), 5.45 (d, J=0.8 Hz, 1H), 6.55 (d, J=2.4 Hz, 1H), 6.61 (d, J=2.4 Hz, 1H), 7.20–7.25 (m, 5H); ^{13}C NMR ($CDCl_3$): δ=19.9, 31.4, 34.1, 43.5, 52.7, 52.8, 53.8, 112.6, 115.6, 116.6, 124.5, 126.7 (2C), 127.5, 128.3 (2C), 137.8, 138.1, 140.7, 151.3, 153.5, 171.5, 172.2; HR-MS [(+)-ESI-TOF]: m/z=381.1673, calcd. for $C_{23}H_{25}O_5^+$ ($M+H^+$): 381.1697.

Dimethyl 8-Methyl-4-(1-phenylvinyl)-3,4-dihydronaphthalene-2,2(1*H*)-dicarboxylate (16)

To a stirred solution of **8** (32.4 mg, 0.085 mmol) in MeOH (1.7 mL) at room temperature was added $CeCl_3{\cdot}7H_2O$ (31.7 mg, 0.085 mmol), and the resulting suspension was stirred for 10 min. $NaBH_4$ (6.4 mg, 0.17 mmol) was added to the mixture and the reaction was stirred for 1 h at 0 °C, and then quenched with water. After a half of solvent had been

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evaporated under vacuum, the mixture was diluted with AcOEt, washed with brine, and then dried over Na_2SO_4. After concentration under vacuum, the obtained residue was directly utilized for the next reaction.

To a stirred solution of the crude product in CH_3CN (1.7 mL) at room temperature was added $TsOH{\cdot}H_2O$ (16.2 mg, 0.085 mmol). After 30 min, the reaction mixture was quenched with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with AcOEt, and the combined organic layers were washed with brine. After concentration under vacuum, the obtained residue was purified by flash column chromatography (SiO_2, hexane/acetone = 8:1) to give **16** as a colorless oil; yield: 21.7 mg (71%). IR (ATR): $\nu = 2952$, 1733, 1434, 1243, 1197, 1175, 779, 703 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.14$ (dd, $J = 10.8$, 13.6 Hz, 1H), 2.33 (s, 3H), 2.61 (ddd, $J = 1.6$, 6.0, 13.6 Hz, 1H), 3.04 (d, $J = 16.4$ Hz, 1H), 3.36 (dd, $J = 1.6$, 16.4 Hz, 1H), 3.68 (s, 3H), 3.71 (s, 3H), 4.13 (dd, $J = 6.0$, 10.8 Hz, 1H), 5.04 (s, 1H), 5.46 (d, $J = 0.8$ Hz, 1H), 7.03–7.16 (m, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 19.9$, 32.0, 34.1, 43.2, 52.7, 52.7, 53.7, 116.4, 125.9, 126.6, 126.7 (2C), 127.5, 128.0, 128.3 (2C), 132.4, 136.1, 136.7, 140.9, 151.6, 171.4, 172.1; HR-MS [(+)-ESI-TOF]: $m/z = 387.1575$, calcd. for $C_{23}H_{24}NaO_4^+$ ($M+Na^+$): 387.1567.

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