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Silver-Catalyzed Cascade 1,6-Addition/Cyclization of *para*-Quinone Methides with Propargyl Malonates: An Approach to Spiro[4.5]deca-6,9-dien-8-ones

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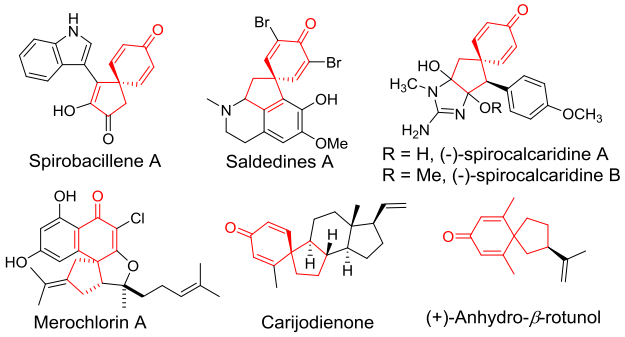
Abstract

An unprecedented silver-catalyzed cascade 1,6-addition/5-*exo*-*dig* cyclization reaction between *para*-quinone methides and propargyl malonates under mild reaction conditions has been described. This reaction provides an efficient method to construct versatile spiro[4.5]cyclohexadienones in moderate to excellent yields with high atom economy and scalability.

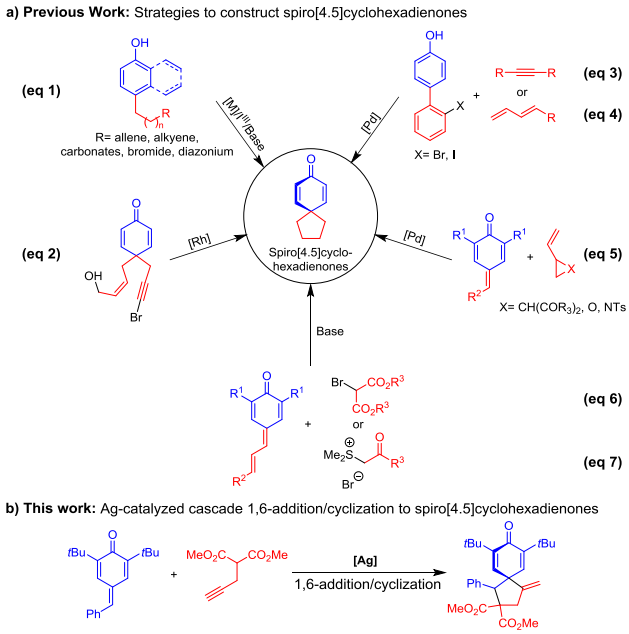
Spiro[4.5]cyclohexadienones are crucial skeletons for their abundant distribution in natural products and bioactive molecules[1] (Scheme 1), and employment as key intermediates in natural products syntheses.[2] As such, developing efficient methods to construct these frameworks is always a popular topic. Traditional methods included the intramolecular dearomatization reaction of phenol derivatives catalyzed or mediated by transition-metals,[3] hypervalent iodines[4] and strong bases[5] (Scheme 2a, eq 1). Rhodium-catalyzed enyne cycloisomerization reaction as an alternative method has been disclosed by Nicolaou and co-workers (Scheme 2a, eq 2).[6] Recently, palladium-catalyzed cross-coupling/dearomatization of phenol-based biaryls with internal alkynes (Scheme 2a, eq 3) or 1,3-dienes (Scheme 2a, eq 4) developed by Luan[7] have also been used to prepare such frameworks. These methods have been extensively explored in

synthesis despite the fact that well-designed substrates, heavy metal and harsh reaction conditions are needed.

Scheme 1. Natural products with spiro[4.5]cyclohexadienones



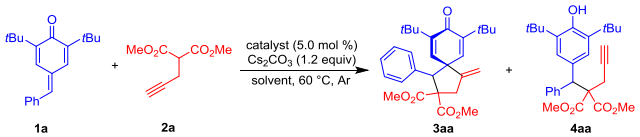
Scheme 2. Strategies to the construction of spiro[4.5]cyclohexadienones



Recently, *para*-quinone methides (*p*-QMs) have been proven as important reactive intermediates for their unique reactivities of 1,6-conjugated addition[8] and cycloaddition.[9] In 2016, our group[10a] and Zhao's group[10b] successively reported palladium-catalyzed [3+2] annulations of *p*-QMs with vinyl-cyclopropanes/aziridines/oxiranes to construct spiro[4.5]cyclohexadienones (Scheme 2a, eq 5). Very recently, our group[11a] and Fan's group[11b] independently reported the cascade 1,6-addition/VCP rearrangement reactions of vinyl *para*-quinone methides (*p*-

VQMs) with bromomalonates (Scheme 2a, eq 6) or sulfonium salts (Scheme 2a, eq 7) to synthesize spiro[4.5]deca-6,9-dien-8-ones, respectively. As part of our continuing interest in characterizing the reactivity of *p*-QMs[12] and preparing spirocyclic compounds[13], herein, we will describe an unprecedented silver-catalyzed cascade 1,6-addition/5-*exo*-*dig* cyclization of *p*-QMs with propargyl malonates to construct spiro[4.5]deca-6,9-dien-8-ones (Scheme 2b).

Table 1. Optimization of Reaction Conditions[a, b, c]



entry	cat.	solvent	**3aa** (%)	**4aa** (%)
1	CuI	DMF	63	N.D.
2	CuBr	DMF	22	N.D.
3	$CuOTf·(C_6H_6)_{1/2}$	DMF	< 5	N.D.
4	$Cu(OTf)_2$	DMF	37	N.D.
5	$PPh_3AuCl+AgNTf_2$	DMF	74	N.D.
6	PPh_3AuNTf_2	DMF	8	33
7	$AgNTf_2$	DMF	83	N.D.
8	AgOTf	DMF	79	N.D.
9	AgOMs	DMF	76	N.D.
10	$AgNO_3$	DMF	98 (93)	N.D.
11	$AgNO_3$	Toluene	N.D.	N.D.
12	$AgNO_3$	CH_2Cl_2	11	75
13	$AgNO_3$	EtOAc	14	41
14	$AgNO_3$	THF	6	32
15	-	DMF	N.D.	94

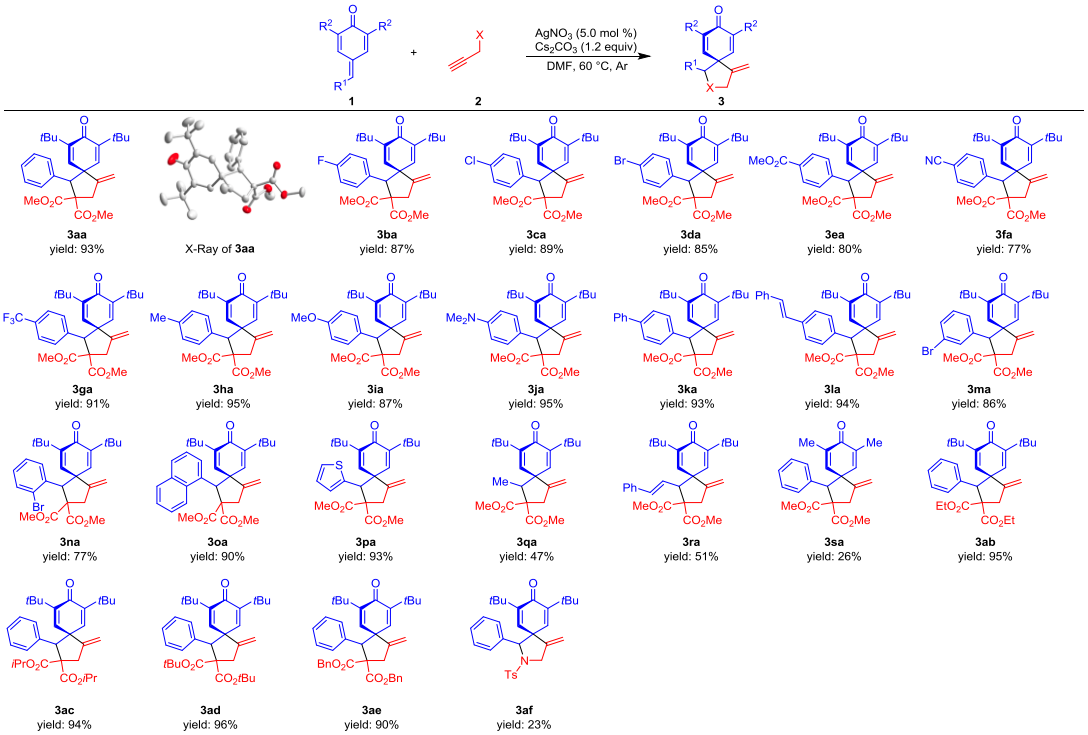
[a]All reactions were performed with **1a** (0.10 mmol), **2a** (0.15 mmol), catalyst (5.0 mol %) and Cs_2CO_3 (0.12 mmol) in solvent (1.0 mL) at 60 ºC for 48 h under argon. [b]The yields were determined by ^1H NMR analysis with dibromomethane as an internal standard. [c]Isolated yield was reported in parenthesis. N.D. = No detection.

We commenced our study by examining the reaction of *p*-QM **1a** and propargyl malonate **2a**. Initially, we tested various copper salts[14] as catalysts for that they are cheap and abundant on the earth. Encouragingly, the reaction was able to form the desired spirocyclic product **3aa**, although the yields were low to moderate (Table 1, entries 1–4). The structure of **3aa** was confirmed by ^{1}H, ^{13}C NMR spectra and X-ray crystallographic analysis.[15] To improve the yield, the combination of PPh_3AuCl and $AgNTf_2$ as catalyst was tested, which is a frequently-used catalyst system in functionalization of alkynes.[16] Delightfully, **3aa** could be achieved in 74% yield (Table 1, entry 5). However, when PPh_3AuNTf_2 was solely examined, only 8% yield of **3aa** was obtained with 1,6-addition product **4aa** in 33% yield, which suggested that the silver salt[17] might be the authentic catalyst (Table 1, entry 6). Subsequently, several silver salts were tested (Table 1, entries 7–10), and $AgNO_3$ performed as the most efficacious catalyst. DMF exhibited good results after the screening of solvents (Table 1, entries 11–14). In the absence of silver catalyst, only **4aa** could be detected (Table 1, entry 15).

With the optimized conditions in hand, we then examined the substrate scope[18] of this silver-catalyzed cascade 1,6-addition/5-*exo*-*dig* cyclization and the results are summarized in Scheme 3. Halogen groups (-F, -Cl, -Br), electron-withdrawing groups ($-CO_2Me$, -CN, $-CF_3$) or electron-donating groups (-Me, -OMe, $-NMe_2$) at the *para*-position of phenyl ring of *p*-QMs led to the corresponding products **3ba**–**ja** in 77–95% yields. Spiro[4.5]cyclohexadienones **3ka** and **3la** with phenyl or alkenyl groups were achieved in 93 and 94% yield, respectively. Substrates containing bromine group at either the *meta*- or *ortho*-position of the phenyl ring provided **3ma** and **3na** in 86 and 77% yields. These results indicated that the steric-hindrance played no obvious effect on the reaction. When the phenyl ring was replaced by 1-naphyl or 2-thiophenyl groups, the reaction could convert **1oa** and **1pa** into **3oa** and **3pa** in 90 and 93% yields. The transformation could also be extended to **1q** with an alkyl group, yielding **3qa** in 47% yield. Meanwhile, vinylogous *p*-QM **1r** could produce **3ra** in 51% yield. What is more, *p*-QM **1s** containing two methyl groups was also tolerated, giving **3sa** in 26% yield.

The substrate scope of propargyl malonates **2** was studied by the reactions with *p*-QM **1a**. Varying the dimethyl ester groups to diethyl, diisopropyl, di-*tert*-butyl and dibenzyl groups, **3ab**–**ae** were achieved in excellent yields. Additionally, this method was also compatible with propargyl *p*-toluenesulfonamide, delivering **3af** in a low yield. However, no desired products could be detected when the terminal hydrogen atom was replaced by methyl or phenyl group.

Scheme 3. Substrate Scope [a, b]

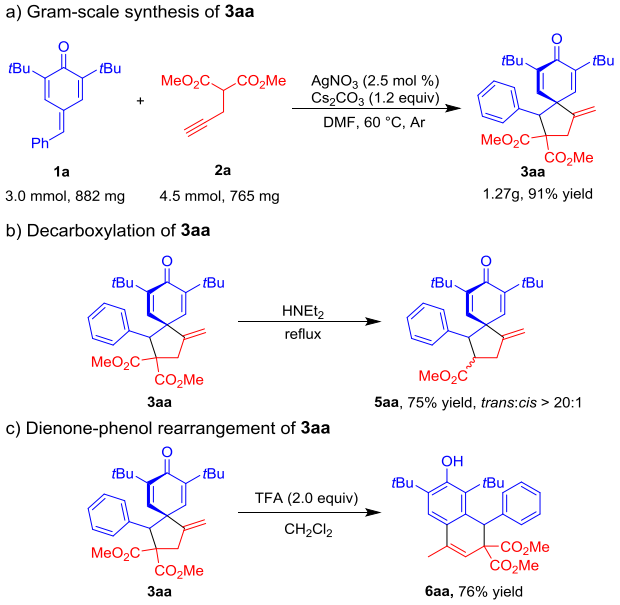


[a]All reactions were performed with **1** (0.10 mmol), **2** (0.15 mmol), $AgNO_3$ (5.0 mol %) and Cs_2CO_3 (0.12 mmol) in DMF (1.0 mL) at 60 °C for 48 h under argon. [b]Isolated yields.

To gain more insight into the utility of the reaction, the gram-scale experiment and further transformation of **3aa** were carried out. Reducing the amount of silver catalyst to 2.5 mol %, the reaction of **1a** (3.0 mmol, 882 mg) with **2a** (3.3 mmol, 765 mg) could still afford **3aa** (1.27 g) in 91% yield (Scheme 4a). Decarboxylation of diester groups was accomplished using diethylamine under refluxing conditions, furnishing **5aa** in 75% yield (Scheme 4b). Through 1,2-benzyl migration in dienone-phenol rearrangement,

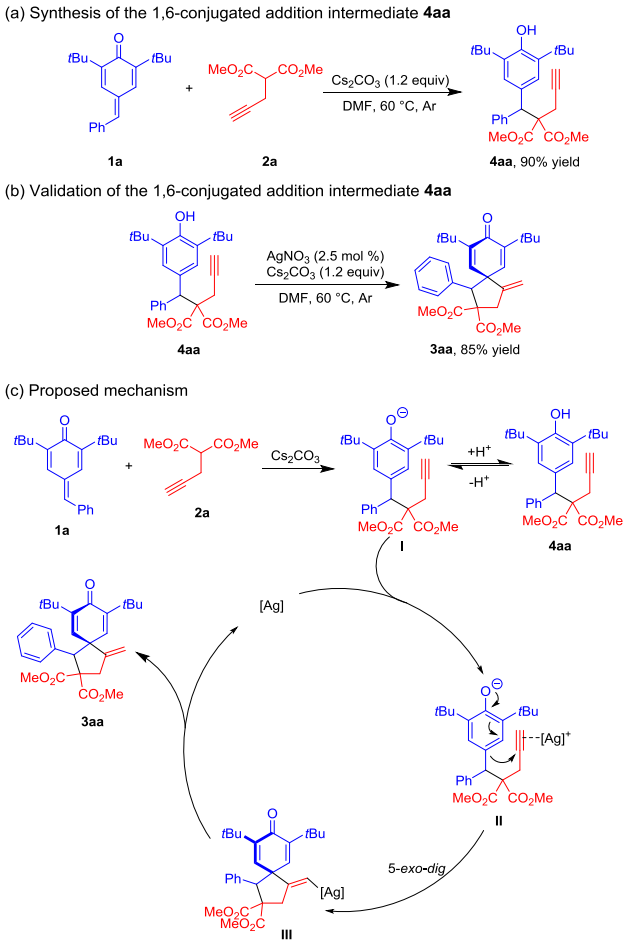
3aa could be transformed into 7,8-dihydronaphthalen-2-ol derivative **6aa** in 76% yield (Scheme 4c), which is also a crucial skeleton found in natural products.[19]

Scheme 4. Further Study on 3aa



Control experiments were then carried out to shed some light on the reaction pathway. As expected, the 1,6-conjugated addition intermediate **4aa** could be isolated in 90% yield under standard conditions without $AgNO_3$ (Scheme 5a). When **4aa** was utilized as the substrate, the 5-*exo-dig* cyclization reaction proceeded smoothly to deliver **3aa** in 85% yield (Scheme 5b). On the basis of the control experiments and previous works,[20] a proposed mechanism was shown in Scheme 5c. Firstly, in the presence of Cs_2CO_3, the nucleophilic 1,6-addition of *p*-QMs with propargyl malonates takes place to deliver intermediate **I**. **4aa** could be formed via protonation of **I**. Intermediate **I** coordinates to Ag catalyst, offering the intermediate **II**, followed by 5-*exo-dig* cyclization to give vinyl-silver intermediate **III**. Finally, protodemetallation of **III** delivers the spirocyclic product **3aa** and regenerates silver catalyst for a new catalytic cycle.

Scheme 5. Mechanistic Insights



In conclusion, we have described a novel cascade 1,6-addition/5-*exo-dig* cyclization reaction between *p*-QMs and propargyl malonates. The cheap and commercial available silver nitrate was employed as the catalyst. Spiro[4.5]deca-6,9-diene-8-ones were efficiently synthesized in high yields with good functional group tolerance and high atom economy. Through 1,2-benzyl migration in dienone-phenol rearrangement, spiro[4.5]deca-6,9-diene-8-one could be transformed into 7,8-dihydronaphthalen-2-ol derivative.

Experimental Section

General Information. NMR spectra were collected on a 300 MHz spectrometer using $CDCl_3$ as solvent. Infrared (IR) spectra were recorded using a thin film supported

on KBr disks. High Resolution Mass measurement was performed with electron spray ionization (ESI) method on a Q-TOF mass spectrometer operating in positive-ion mode. Melting point (m.p.) was measured on a microscopic melting point apparatus. Tetrahydrofuran (THF) was distilled from sodium/benzophenone, N, N-dimethyl formamide (DMF) from calcium hydride and dichloromethane (DCM) from phosphorus pentoxide. PE refers to petroleum ether (b.p. 60–90 °C) and EA refers to ethyl acetate. Flash column chromatography was carried out using commercially available 200–300 mesh under pressure unless otherwise indicated. Gradient flash chromatography was conducted eluting with PE/EA. All other starting materials and solvents were commercially available and were used without further purification unless otherwise stated.

General Procedure for the Preparation of *para*-Quinone Methides. Aldehydes (10 mmol) were added to a solution of phenols (10 mmol) in toluene (40 mL). The reaction mixture was heated in a Dean-Stark apparatus to reflux. Piperidine (20 mmol) was added drop wisely in 1 h, and the reaction mixture was continued to reflux for 3 h. After cooling just below the boiling point of toluene, acetic anhydride (20 mmol) was added and then the solution was stirred for 15 min. The residue was extracted with dichloromethane for 3 times. The combined organic layers were washed with water and brine sequentially, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography on silica gel (petroleum ether) to afford the corresponding product. **1a**–**1p** were synthesized by the general procedure.[21a] **1q**,[21b] **1r**[11a] and **1s**[21c], were prepared according to corresponding literatures.

General Procedure for the Preparation of Propargyl Malonates. A flame-dried round bottom flask was charged with NaH (60% in oil, 20 mmol) and THF (10 mL). The suspension was cooled to 0 °C and dimethyl malonate (15 mmol) in THF (10 mL) was added dropwise over 1 h. Then propargyl bromide (10 mmol) in THF (10 mL) was added dropwise over 1 h. The suspension was allowed to warm to room temperature and stirred overnight. The reaction mixture was added H_2O and extracted with EA. The combined organic layers were washed with H_2O, brine, dried over Na_2SO_4,

concentrated by rotary evaporation, and purified by column chromatography (EtOAc/petroleum ether = 1/200) to give corresponding product. **2a**–**2e**[22a] were synthesized by the general procedure. **2f**[22b] was prepared according to previous literature.

General Procedure for the Preparation of Spiro[2.5]octa-4,7-dien-6-ones. A sealed tube was charged with *para*-quinone methide (0.1 mmol, 1 equiv), propargyl malonates (0.15 mmol, 1.5 equiv), $AgNO_3$ (5 mol %), and Cs_2CO_3 (1.2 mmol, 1.2 equiv). The vial is thoroughly flushed with argon and dry dimethyl formamide (1.0 mL) was added under argon. Then the reaction mixture was stirred at 60 °C for 48 h. After the reaction vessel was cooled to room temperature, the solution was concentrated in *vacuo* and purified by careful chromatography on silica gel (EtOAc/petroleum ether = 1/200) to afford the desired product.

*Dimethyl 7,9-di-tert-butyl-4-methylene-8-oxo-1-phenylspiro[4.5]deca-6,9-diene-2,2-dicarboxylate (**3aa**)* 93% yield (43.3 mg). White solid, m.p. 96 – 97 °C. Rf = 0.5 (1/10 EA/PE). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 – 7.14 (m, 3H), 7.02 – 6.99 (m, 2H), 6.81 (d, *J* = 2.9 Hz, 1H), 6.47 (d, *J* = 2.9 Hz, 1H), 4.97 – 4.96 (m, 1H), 4.79 (dd, *J* = 1.8, 0.6 Hz, 1H), 4.27 (s, 1H), 3.99 (dt, *J* = 17.6, 2.6 Hz, 1H), 3.76 (s, 3H), 3.39 (s, 3H), 3.09 (d, *J* = 17.6 Hz, 1H), 1.12 (s, 9H), 1.11 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.9, 172.2, 171.2, 149.5, 147.7, 145.5, 142.5, 140.0, 135.8, 129.6, 127.5, 109.2, 63.0, 61.6, 55.9, 53.2, 52.5, 40.6, 34.9, 34.7, 29.4, 29.1 ppm. IR(KBr): 3000, 2956, 2868, 1727, 1658, 1639, 1458, 1433, 1366, 1250, 1217, 1195, 1172, 1094, 1043, 905, 751, 700, 671, 580, 491 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{37}O_5$ 465.2636; Found 465.2633.

*dimethyl 7,9-di-tert-butyl-1-(4-fluorophenyl)-4-methylene-8-oxospiro[4.5]deca-6,9-diene-2,2-dicarboxylate (**3ba**)* 87% yield (41.8 mg). White solid, m.p. 80 – 81 °C. Rf = 0.4 (1/10 EA/PE). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.03 – 6.98 (m, 2H), 6.88 – 6.82 (m, 3H), 6.43 (d, *J* = 3.0 Hz, 1H), 4.96 (dd, *J* = 2.5, 1.6 Hz, 1H), 4.80 (dd, *J* = 2.7, 1.6 Hz, 1H), 4.25 (s, 1H), 3.97 (dt, *J* = 17.6, 2.6 Hz, 1H), 3.76 (s, 3H), 3.43 (s, 3H), 3.07 (dt, *J* = 17.6, 1.6 Hz, 1H), 1.14 (s, 9H), 1.12 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.8,

172.1, 171.2, 162.0 (d, *J* = 246.7 Hz), 149.3, 148.2, 146.0, 142.2, 139.5, 131.6 (d, *J* = 3.5 Hz), 131.3 (d, *J* = 8.0 Hz), 114.3 (d, *J* = 21.3 Hz), 109.3, 62.9, 60.8, 55.9, 53.2, 52.6, 40.4, 34.9, 34.7, 29.4, 29.1 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -113.57 ppm. IR(KBr): 2998, 2958, 2869, 1730, 1658, 1638, 1511, 1459, 1436, 1367, 1269, 1253, 1228, 1174, 1164, 1091, 960, 910, 876, 843, 812, 580, 521 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{36}FO_5$ 483.2541; Found 483.2549.

*dimethyl 7,9-di-tert-butyl-1-(4-chlorophenyl)-4-methylene-8-oxospiro[4.5]deca-6,9-diene-2,2-dicarboxylate (**3ca**)* 89% yield (44.5 mg). White solid, m.p. 115 – 117 °C. Rf = 0.5 (1/10 EA/PE). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 2.9 Hz, 1H), 6.37 (d, *J* = 2.9 Hz, 1H), 4.92 – 4.90 (m, 1H), 4.74 (dd, *J* = 2.6, 1.6 Hz, 1H), 4.18 (s, 1H), 3.91 (dt, *J* = 17.6, 2.6 Hz, 1H), 3.71 (s, 3H), 3.38 (s, 3H), 3.02 (dt, *J* = 17.6, 1.6 Hz, 1H), 1.09 (s, 9H), 1.07 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.8, 172.1, 171.1, 149.1, 148.3, 145.9, 142.1, 139.4, 134.3, 133.4, 131.0, 127.6, 109.4, 62.8, 60.9, 55.8, 53.2, 52.7, 40.4, 35.0, 34.7, 29.4, 29.1 ppm. IR(KBr): 3000, 2956, 2865, 1728, 1656, 1637, 1493, 1435, 1367, 1270, 1254, 1210, 1173, 1092, 955, 910, 873, 808, 710, 580, 506 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{36}ClO_5$ 499.2246; Found 499.2248.

*dimethyl 1-(4-bromophenyl)-7,9-di-tert-butyl-4-methylene-8-oxospiro[4.5]deca-6,9-diene-2,2-dicarboxylate (**3da**)* 85% yield (46.0 mg). White solid, m.p. 122 – 123 °C. Rf = 0.5 (1/10 EA/PE). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 3.0 Hz, 1H), 6.42 (d, *J* = 2.9 Hz, 1H), 4.97 – 4.95 (m, 1H), 4.79 (dd, *J* = 2.7, 1.6 Hz, 1H), 4.21 (s, 1H), 3.95 (dt, *J* = 17.6, 2.6 Hz, 1H), 3.76 (s, 3H), 3.43 (s, 3H), 3.07 (d, *J* = 17.7 Hz, 1H), 1.14 (s, 9H), 1.12 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.8, 172.1, 171.1, 149.2, 148.3, 146.0, 142.1, 139.4, 135.0, 131.3, 130.6, 121.6, 109.4, 62.9, 61.0, 55.8, 53.2, 52.7, 40.5, 35.0, 34.8, 29.4, 29.2 ppm. IR(KBr): 2991, 2955, 2861, 1727, 1656, 1637, 1489, 1434, 1268, 1254, 1209, 1173, 1090, 907, 886, 810, 580, 503 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{36}BrO_5$ 543.1741; Found 543.1745.

dimethyl 7,9-di-tert-butyl-1-(4-(methoxycarbonyl)phenyl)-4-methylene-8-

*oxospiro[4.5]deca-6,9-diene-2,2-dicarboxylate (**3ea**)* 80% yield (42.0 mg). White solid, m.p. 136 – 137 °C. Rf = 0.3 (1/10 EA/PE). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.84 (s, 1H), 6.45 (s, 1H), 4.98 (s, 1H), 4.81 (s, 1H), 4.32 (s, 1H), 4.00 (d, *J* = 17.6 Hz, 1H), 3.88 (s, 3H), 3.77 (s, 3H), 3.40 (s, 3H), 3.10 (d, *J* = 17.7 Hz, 1H), 1.13 (s, 9H), 1.11 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.7, 172.0, 171.0, 166.6, 149.1, 148.2, 146.0, 142.0, 141.2, 139.3, 129.7, 129.2, 128.7, 109.5, 62.9, 61.3, 55.8, 53.3, 52.6, 52.0, 40.4, 34.9, 34.7, 29.4, 29.1 ppm. IR(KBr): 2997, 2955, 2861, 1729, 1658, 1639, 1612, 1436, 1368, 1282, 1252, 1214, 1189, 1172, 1110, 1039, 1016, 933, 874, 768, 709, 580, 491 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{39}O_7$ 523.2690; Found 523.2687.

*dimethyl 7,9-di-tert-butyl-1-(4-cyanophenyl)-4-methylene-8-oxospiro[4.5]deca-6,9-diene-2,2-dicarboxylate (**3fa**)* 77% yield (37.9 mg). Light yellow solid, m.p. 88 – 89 °C. Rf = 0.3 (1/10 EA/PE). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 3.0 Hz, 1H), 6.42 (d, *J* = 3.0 Hz, 1H), 5.00 – 4.99 (m, 1H), 4.82 (t, *J* = 2.1 Hz, 1H), 4.28 (s, 1H), 3.97 (dt, *J* = 17.7, 2.6 Hz, 1H), 3.77 (s, 3H), 3.43 (s, 3H), 3.09 (d, *J* = 17.6 Hz, 1H), 1.13 (s, 9H), 1.11 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.6, 171.8, 170.8, 148.8, 148.7, 146.4, 141.6, 141.5, 138.8, 131.1, 130.5, 118.4, 111.5, 109.8, 62.8, 61.3, 55.8, 53.3, 52.7, 40.4, 35.0, 34.8, 29.4, 29.1 ppm. IR(KBr): 3003, 2956, 2867, 2224, 1727, 1660, 1643, 1434, 1366, 1271, 1254, 1213, 1173, 1090, 1045, 954, 910, 874, 848, 813, 586, 550, 491 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{36}NO_5$ 490.2588; Found 490.2588.

*dimethyl 7,9-di-tert-butyl-4-methylene-8-oxo-1-(4-(trifluoromethyl)phenyl)spiro[4.5]deca-6,9-diene-2,2-dicarboxylate (**3ga**)* 91% yield (48.3 mg). White solid, m.p. 87 – 89 °C. Rf = 0.6 (1/10 EA/PE). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.81 (d, *J* = 2.9 Hz, 1H), 6.45 (d, *J* = 3.0 Hz, 1H), 4.99 – 4.98 (m, 1H), 4.81 (dd, *J* = 2.6, 1.6 Hz, 1H), 4.32 (s, 1H), 3.98 (dt, *J* = 17.6, 2.6 Hz, 1H), 3.77 (s, 3H), 3.41 (s, 3H), 3.10 (d, *J* = 17.6 Hz, 1H), 1.12 (s, 18H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.7, 172.0, 170.9, 149.0, 148.4, 146.1, 141.9, 140.2, 139.3, 130.0, 124.4 (q, *J* = 3.8 Hz), 109.6, 62.9, 61.1, 55.8, 53.3,

52.6, 40.5, 35.0, 34.8, 29.4, 29.1 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -36.62 ppm. IR(KBr): 2996, 2957, 2865, 1732, 1659, 1640, 1459, 1437, 1327, 1269, 1254, 1168, 1128, 1070, 902, 878, 845, 739, 673, 608, 494 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{36}F_3O_5$ 533.2509; Found 533.2504.

*dimethyl 7,9-di-tert-butyl-4-methylene-8-oxo-1-(p-tolyl)spiro[4.5]deca-6,9-diene-2,2-dicarboxylate (**3ha**)* 95% yield (45.7 mg). White solid, m.p. 60 – 61 °C. Rf = 0.6 (1/10 EA/PE). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.95 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 2.9 Hz, 1H), 6.45 (d, *J* = 2.9 Hz, 1H), 4.95 – 4.94 (m, 1H), 4.78 (dd, *J* = 2.7, 1.6 Hz, 1H), 4.22 (s, 1H), 3.96 (dt, *J* = 17.6, 2.5 Hz, 1H), 3.75 (s, 3H), 3.42 (s, 3H), 3.07 (dt, *J* = 17.6, 1.6 Hz, 1H), 2.23 (s, 3H), 1.12 (s, 9H), 1.12 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.1, 172.3, 171.3, 149.7, 147.7, 145.4, 142.7, 140.2, 137.0, 132.7, 129.5, 128.1, 109.1, 63.0, 61.4, 56.0, 53.1, 52.5, 40.7, 34.9, 34.7, 29.4, 29.1, 21.0 ppm. IR(KBr): 2997, 2955, 2868, 1731, 1658, 1638, 1514, 1484, 1458, 1435, 1367, 1312, 1263, 1255, 1213, 1171, 1093, 1044, 961, 887, 810, 577, 506 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{39}O_5$ 479.2792; Found 479.2788.

*dimethyl 7,9-di-tert-butyl-1-(4-methoxyphenyl)-4-methylene-8-oxospiro[4.5]deca-6,9-diene-2,2-dicarboxylate (**3ia**)* 87% yield (43.2 mg). White solid, m.p. 120 – 121 °C. Rf = 0.4 (1/10 EA/PE). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.94 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 2.9 Hz, 1H), 6.68 (d, *J* = 8.8 Hz, 2H), 6.44 (d, *J* = 2.9 Hz, 1H), 4.95 – 4.94 (m, 1H), 4.79 – 4.77 (m, 1H), 4.22 (s, 1H), 3.97 (dt, *J* = 17.6, 2.5 Hz, 1H), 3.75 (s, 3H), 3.72 (s, 3H), 3.43 (s, 3H), 3.06 (d, *J* = 17.5 Hz, 1H), 1.13 (s, 9H), 1.12 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.0, 172.3, 171.4, 158.8, 149.6, 147.9, 145.6, 142.7, 140.1, 130.8, 127.8, 112.8, 109.1, 63.0, 61.0, 56.1, 55.1, 53.1, 52.6, 40.6, 34.9, 34.7, 29.4, 29.1 ppm. IR(KBr): 2997, 2952, 2861, 1756, 1726, 1656, 1635, 1614, 1516, 1458, 1439, 1369, 1251, 1184, 1175, 1092, 1032, 912, 874, 821, 706, 577, 527, 488 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{39}O_6$ 495.2741; Found 495.2739.

*dimethyl 7,9-di-tert-butyl-1-(4-(dimethylamino)phenyl)-4-methylene-8-oxospiro[4.5]deca-6,9-diene-2,2-dicarboxylate (**3ja**)* 95% yield (48.2 mg). Brown solid, m.p. 59 – 61 °C. Rf = 0.4 (1/10 EA/PE).^{1}H NMR (300 MHz, $CDCl_3$) δ 6.90 – 6.84 (m,

3H), 6.51 – 6.45 (m, 3H), 4.93 (s, 1H), 4.77 (s, 1H), 4.19 (s, 1H), 3.96 (d, *J* = 17.6 Hz, 1H), 3.74 (s, 3H), 3.45 (s, 3H), 3.05 (d, *J* = 17.5 Hz, 1H), 2.85 (s, 6H), 1.14 (s, 9H), 1.13 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.1, 172.4, 171.5, 149.8, 149.7, 147.5, 145.1, 143.0, 140.5, 130.3, 123.2, 111.4, 108.8, 63.0, 61.2, 56.3, 53.0, 52.6, 40.6, 40.4, 34.8, 34.6, 29.4, 29.1 ppm. IR(KBr): 3000, 2954, 2867, 2802, 1729, 1658, 1637, 1615, 1524, 1457, 1435, 1367, 1357, 1255, 1169, 1090, 1039, 948, 883, 807, 580, 488 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{42}NO_5$ 508.3057; Found 508.3058.

*dimethyl 1-([1,1'-biphenyl]-4-yl)-7,9-di-tert-butyl-4-methylene-8-oxospiro[4.5]deca-6,9-diene-2,2-dicarboxylate (**3ka**)* 93% yield (50.2 mg). White solid, m.p. 129 – 131 °C. Rf = 0.5 (1/10 EA/PE). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 2H), 7.43 – 7.38 (m, 4H), 7.34 – 7.29 (m, 1H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.87 (d, *J* = 2.9 Hz, 1H), 6.49 (d, *J* = 2.9 Hz, 1H), 4.99 – 4.97 (m, 1H), 4.81 (dd, *J* = 2.7, 1.6 Hz, 1H), 4.32 (s, 1H), 4.01 (dt, *J* = 17.6, 2.6 Hz, 1H), 3.78 (s, 3H), 3.44 (s, 3H), 3.11 (d, *J* = 17.6 Hz, 1H), 1.13 (s, 18H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.9, 172.3, 171.3, 149.4, 147.9, 145.6, 142.5, 140.5, 140.1, 139.9, 134.9, 130.0, 128.7, 127.3, 126.9, 126.1, 109.3, 62.9, 61.3, 56.0, 53.2, 52.7, 40.6, 34.9, 34.7, 29.4, 29.1 ppm. IR(KBr): 2954, 2925, 2867 ,1730, 1656, 1638, 1617, 1523, 1484, 1458, 1434, 1367, 1315, 1268, 1249, 1214, 1170, 1039, 1007, 957, 901, 886, 848, 759, 695, 503, 488 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{41}O_5$ 541.2949; Found 541.2954.

*dimethyl (E)-7,9-di-tert-butyl-4-methylene-8-oxo-1-(4-styrylphenyl)spiro[4.5]deca-6,9-diene-2,2-dicarboxylate (**3la**)* 94% yield (53.2 mg). Light yellow solid, m.p. 77 – 79 °C. Rf = 0.5 (1/10 EA/PE). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.6 Hz, 2H), 7.33 – 7.23 (m, 5H), 7.02 (m, 4H), 6.87 (s, 1H), 6.48 (s, 1H), 4.97 (s, 1H), 4.80 (s, 1H), 4.29 (s, 1H), 4.00 (d, *J* = 17.6 Hz, 1H), 3.76 (s, 3H), 3.42 (s, 3H), 3.10 (d, *J* = 17.6 Hz, 1H), 1.14 (s, 18H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.8, 172.2, 171.2, 149.4, 147.8, 145.5, 142.4, 139.9, 137.1, 136.3, 135.2, 129.9, 128.6, 128.5, 128.0, 127.5, 126.4, 125.5, 109.2, 62.9, 61.3, 56.0, 53.2, 52.6, 40.5, 34.9, 34.7, 29.4, 29.1 ppm. IR(KBr): 3027, 2999, 2954, 2866, 1730, 1658, 1638, 1511, 1481, 1450, 1435, 1367, 1267, 1252, 1214,

1170, 1087, 1044, 963, 874, 807, 757, 692, 580, 533, 488 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{43}O_5$ 567.3105; Found 567.3107.

*dimethyl 1-(3-bromophenyl)-7,9-di-tert-butyl-4-methylene-8-oxospiro[4.5]deca-6,9-diene-2,2-dicarboxylate (**3ma**)* 86% yield (46.7 mg). White solid, m.p. 124 – 125 °C. Rf = 0.5 (1/10 EA/PE). ^1H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.7 Hz, 1H), 7.13 (s, 1H), 7.08 – 6.98 (m, 2H), 6.90 (d, *J* = 3.0 Hz, 1H), 6.42 (d, *J* = 3.0 Hz, 1H), 4.96 (s, 1H), 4.80 (s, 1H), 4.21 (s, 1H), 3.98 (d, *J* = 17.6 Hz, 1H), 3.76 (s, 3H), 3.50 (s, 3H), 3.05 (d, *J* = 17.6 Hz, 1H), 1.17 (s, 9H), 1.12 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.7, 172.0, 171.3, 149.0, 148.6, 146.1, 142.1, 139.0, 137.8, 132.3, 130.6, 129.0, 128.8, 121.2, 109.5, 62.6, 61.1, 55.9, 53.2, 52.7, 40.5, 35.0, 34.7, 29.4, 29.2 ppm. IR(KBr): 2997, 2955, 2868, 1731, 1658, 1639, 1568, 1458, 1434, 1366, 1269, 1248, 1214, 1172, 954, 884, 774, 701, 586, 491, 438 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{36}BrO_5$ 543.1741; Found 543.1734.

*dimethyl 1-(2-bromophenyl)-7,9-di-tert-butyl-4-methylene-8-oxospiro[4.5]deca-6,9-diene-2,2-dicarboxylate (**3na**)* 77% yield (41.8 mg). White solid, m.p. 157 – 159 °C. Rf = 0.5 (1/10 EA/PE). ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.9 Hz, 1H), 7.13 – 6.90 (m, 3H), 6.67 (s, 2H), 5.08 (s, 1H), 5.02 (s, 1H), 4.82 (s, 1H), 3.96 (d, *J* = 18.2 Hz, 1H), 3.77 (s, 3H), 3.45 (s, 3H), 3.19 (d, *J* = 17.7 Hz, 1H), 1.17 (s, 9H), 1.08 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.8, 171.9, 171.2, 149.1, 147.0, 146.0, 141.9, 139.3, 135.2, 133.2, 129.8, 128.8, 127.0, 125.8, 109.8, 63.2, 58.4, 56.2, 53.3, 52.6, 40.8, 34.8, 34.7, 29.2, 29.1 ppm. IR(KBr): 3000, 2955, 2923, 2868, 1735, 1658, 1639, 1459, 1434, 1367, 1266, 1245, 1169, 1024, 906, 882, 808, 755, 490 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{36}BrO_5$ 543.1741; Found 543.1737.

*dimethyl 7,9-di-tert-butyl-4-methylene-1-(naphthalen-1-yl)-8-oxospiro[4.5]deca-6,9-diene-2,2-dicarboxylate (**3oa**)* 90% yield (46.5 mg). White solid, m.p. 132 –133 °C. Rf = 0.6 (1/10 EA/PE). ^1H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.3 Hz, 1H), 7.77 – 7.74 (m, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.48 – 7.38 (m, 2H), 7.31 – 7.26 (m, 1H), 7.11 (d, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 3.0 Hz, 1H), 6.43 (d, *J* = 2.9 Hz, 1H), 5.44 (s, 1H), 5.05 (s, 1H), 4.80 (s, 1H), 4.10 (dt, *J* = 17.3, 2.6 Hz, 1H), 3.79 (s, 3H), 3.32 – 3.25 (m, 4H),

1.03 (s, 9H), 0.80 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.5, 172.4, 171.0, 149.5, 146.6, 145.1, 142.5, 140.3, 133.8, 133.0, 132.5, 128.7, 127.9, 126.2, 125.5, 125.3, 123.8, 123.5, 109.9, 63.8, 55.7, 53.4, 52.6, 41.2, 34.5, 34.5, 29.1, 28.8 ppm. IR(KBr): 3049, 2998, 2954, 2867, 1728, 1658, 1641, 1510, 1435, 1366, 1272, 1245, 1209, 1171, 1093, 1045, 963, 886, 800, 777, 731, 629, 576, 527, 494 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{33}H_{39}O_5$ 515.2792; Found 515.2795.

*dimethyl 7,9-di-tert-butyl-4-methylene-8-oxo-1-(thiophen-2-yl)spiro[4.5]deca-6,9-diene-2,2-dicarboxylate (**3pa**)* 93% yield (43.7 mg). White solid, m.p. 81 – 82 °C. Rf = 0.5 (1/10 EA/PE). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (dd, *J* = 4.8, 1.5 Hz, 1H), 6.99 (d, *J* = 3.0 Hz, 1H), 6.85 – 6.82 (m, 2H), 6.41 (d, *J* = 3.0 Hz, 1H), 4.93 – 4.92 (m, 1H), 4.79 – 4.78 (m, 1H), 4.62 (s, 1H), 3.92 (dt, *J* = 17.5, 2.6 Hz, 1H), 3.78 (s, 3H), 3.46 (s, 3H), 3.03 (d, *J* = 17.5 Hz, 1H), 1.20 (s, 9H), 1.15 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.9, 172.0, 171.0, 148.9, 148.7, 146.2, 142.2, 139.3, 137.4, 127.5, 125.9, 124.5, 109.2, 63.4, 56.1, 55.9, 53.2, 52.9, 40.3, 35.0, 34.8, 29.4, 28.9 ppm. IR(KBr): 2999, 2955, 2868, 1731, 1659, 1639, 1484, 1458, 1435, 1367, 1261, 1212, 1172, 1093, 1044, 903, 886, 854, 739, 699, 491 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{35}O_5S$ 471.2200; Found 471.2195.

*dimethyl 7,9-di-tert-butyl-1-methyl-4-methylene-8-oxospiro[4.5]deca-6,9-diene-2,2-dicarboxylate (**3qa**)* 47% yield (18.9 mg). Colorless oil. Rf = 0.5 (1/10 EA/PE). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.57 (d, *J* = 2.9 Hz, 1H), 6.33 (d, *J* = 2.9 Hz, 1H), 4.92 (s, 1H), 4.71 (s, 1H), 3.76 (s, 6H), 3.60 (d, *J* = 17.4 Hz, 1H), 3.00 (q, *J* = 7.2 Hz, 1H), 2.88 (d, *J* = 17.4 Hz, 1H), 1.23 (s, 9H), 1.19 (s, 9H), 0.80 (d, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.6, 172.0, 171.6, 149.7, 148.2, 146.1, 143.4, 139.9, 109.6, 61.8, 54.6, 52.9, 52.5, 50.2, 40.7, 35.0, 34.8, 29.6, 29.5, 11.6 ppm. IR(KBr): 2956, 2869, 1734, 1691, 1659, 1639, 1481, 1458, 1435, 1367, 1267, 1200, 1174, 1128, 1098, 1066, 1042, 1004, 960, 936, 880, 810, 777, 739, 494 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{35}O_5$ 403.2479; Found 403.2473.

*dimethyl (E)-7,9-di-tert-butyl-4-methylene-8-oxo-1-styrylspiro[4.5]deca-6,9-diene-2,2-dicarboxylate (**3ra**)* 51% yield (25.1 mg). White solid, m.p. 87 – 88 °C. Rf = 0.4

(1/10 EA/PE). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 – 7.17 (m, 5H), 6.67 (d, *J* = 2.9 Hz, 1H), 6.42 (d, *J* = 2.9 Hz, 1H), 6.33 (d, *J* = 15.5 Hz, 1H), 5.83 (dd, *J* = 15.6, 9.8 Hz, 1H), 5.00 (s, 1H), 4.79 (s, 1H), 3.77 – 3.63 (m, 8H), 3.02 (d, *J* = 17.1 Hz, 1H), 1.20 (s, 18H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.3, 171.6, 171.1, 149.4, 148.3, 146.5, 142.5, 139.2, 136.7, 134.3, 128.4, 127.5, 126.3, 123.1, 110.1, 62.2, 59.5, 55.5, 53.1, 52.7, 41.0, 34.9, 34.7, 29.6, 29.5 ppm. IR(KBr): 3121, 3015, 1729, 1655, 1635, 1400, 1260, 1166, 1072, 986, 945, 860, 748, 695, 547, 521 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{39}O_5$ 491.2792; Found 491.2796.

*dimethyl 7,9-dimethyl-4-methylene-8-oxo-1-phenylspiro[4.5]deca-6,9-diene-2,2-dicarboxylate(**3sa**)* 26% yield (10.0 mg). White solid, m.p. 83 – 84 °C. Rf = 0.3 (1/10 EA/PE). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 – 7.16 (m, 3H), 7.09 – 7.08 (m, 2H), 7.01 (s, 1H), 6.56 (s, 1H), 4.94 (s, 1H), 4.83 (s, 1H), 4.34 (s, 1H), 3.97 (dd, *J* = 17.5, 2.1 Hz, 1H), 3.75 (s, 3H), 3.33 (s, 3H), 3.04 (dd, *J* = 17.3, 1.8 Hz, 1H), 1.82 (s, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.0, 172.1, 171.2, 148.7, 146.5, 144.0, 136.0, 135.8, 133.8, 129.5, 127.7, 127.6, 109.3, 63.3, 60.9, 56.9, 53.1, 52.5, 40.6, 16.2, 16.1 ppm. IR(KBr): 2953, 2923, 2852, 1729, 1668, 1638, 1602, 1452, 1434, 1376, 1252, 1208, 1159, 1094, 1044, 904, 753, 702, 571, 524, 485, 459 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{25}O_5$ 381.1697; Found 381.1693.

*diethyl 7,9-di-tert-butyl-4-methylene-8-oxo-1-phenylspiro[4.5]deca-6,9-diene-2,2-dicarboxylate (**3ab**)* 95% yield (46.7 mg). White solid, m.p. 91 – 93 °C. Rf = 0.6 (1/10 EA/PE). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 – 7.13 (m, 3H), 7.05 – 7.02 (m, 2H), 6.73 (d, *J* = 2.9 Hz, 1H), 6.52 (d, *J* = 2.9 Hz, 1H), 4.96 (s, 1H), 4.78 (s, 1H), 4.28 – 4.18 (m, 3H), 4.02 – 3.92 (m, 2H), 3.77 – 3.67 (m, 1H), 3.09 (d, *J* = 17.5 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.14 (s, 9H), 1.08 (s, 9H), 0.81 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.9, 171.7, 170.5, 149.7, 147.2, 145.3, 142.6, 140.5, 136.3, 129.6, 127.4, 127.3, 109.1, 63.1, 61.9, 61.6, 61.2, 55.8, 40.6, 34.8, 34.6, 29.4, 29.0, 13.9, 13.3 ppm. IR(KBr): 2958, 2868, 1731, 1658, 1638, 1457, 1389, 1367, 1256, 1210, 1178, 1096, 1066, 1044, 1010, 883, 702, 580, 491 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{41}O_5$ 493.2949; Found 493.2956.

*diisopropyl 7,9-di-tert-butyl-4-methylene-8-oxo-1-phenylspiro[4.5]deca-6,9-diene-2,2-dicarboxylate (**3ac**)* 94% yield (48.9 mg). White solid, m.p. 96 – 97 °C. Rf = 0.7 (1/10 EA/PE). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 – 7.13 (m, 3H), 7.06 – 7.03 (m, 2H), 6.62 (d, *J* = 2.9 Hz, 1H), 6.57 (d, *J* = 2.9 Hz, 1H), 5.14 – 5.03 (m, 1H), 4.96 (s, 1H), 4.76 (s, 1H), 4.73 – 4.62 (m, 1H), 4.29 (s, 1H), 3.96 (dt, *J* = 17.4, 2.5 Hz, 1H), 3.07 (d, *J* = 17.3 Hz, 1H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.16 (s, 9H), 1.07 (d, *J* = 6.2 Hz, 3H), 1.04 (s, 9H), 0.50 (d, *J* = 6.3 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.0, 171.2, 169.7, 149.8, 146.6, 145.1, 142.7, 141.0, 136.8, 129.5, 127.5, 127.2, 109.0, 69.5, 69.4, 63.3, 60.8, 55.7, 40.9, 34.7, 34.6, 29.4, 29.0, 21.6, 21.4, 21.3, 20.4 ppm. IR(KBr): 2958, 2869, 1729, 1658, 1639, 1485, 1456, 1388, 1374, 1266, 1215, 1181, 1147, 1108, 1037, 934, 904, 882, 830, 702, 577, 491, 421 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{33}H_{45}O_5$ 521.3262; Found 521.3262.

*di-tert-butyl 7,9-di-tert-butyl-4-methylene-8-oxo-1-phenylspiro[4.5]deca-6,9-diene-2,2-dicarboxylate (**3ad**)* 96% yield (52.7 mg). White solid, m.p. 93 – 95 °C. Rf = 0.5 (1/20 EA/PE). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 – 7.16 (m, 3H), 7.09 – 7.06 (m, 2H), 6.62 (d, *J* = 2.9 Hz, 1H), 6.33 (d, *J* = 2.9 Hz, 1H), 4.97 (s, 1H), 4.72 (s, 1H), 4.19 (s, 1H), 3.89 (d, *J* = 17.7 Hz, 1H), 3.08 (d, *J* = 17.6 Hz, 1H), 1.49 (s, 9H), 1.19 (s, 9H), 1.03 (s, 9H), 0.98 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.2, 170.8, 168.5, 150.3, 145.2, 145.1, 142.9, 142.0, 137.9, 129.6, 127.7, 127.0, 108.9, 81.9, 81.8, 64.8, 60.4, 55.6, 40.6, 34.7, 34.6, 29.4, 29.0, 27.8, 27.1 ppm. IR(KBr): 3068, 2965, 2870, 1728, 1656, 1634, 1457, 1329, 1370, 1356, 1269, 1259, 1233, 1163, 1140, 1060, 1039, 930, 913, 883, 844, 737, 670, 653, 568, 506, 465 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{49}O_5$ 549.3575; Found 549.3576.

*dibenzyl 7,9-di-tert-butyl-4-methylene-8-oxo-1-phenylspiro[4.5]deca-6,9-diene-2,2-dicarboxylate(**3ae**)* 90% yield (55.5 mg). White solid, m.p. 114 – 115 °C. Rf = 0.4 (1/20 EA/PE). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 – 7.10 (m, 11H), 7.01 (d, *J* = 5.0 Hz, 2H), 6.79 – 6.75 (m, 3H), 6.50 (d, *J* = 2.9 Hz, 1H), 5.09 (q, *J* = 12.2 Hz, 2H), 4.94 – 4.78 (m, 3H), 4.58 (d, *J* = 12.2 Hz, 1H), 4.31 (s, 1H), 4.00 (d, *J* = 17.5 Hz, 1H), 3.10 (d, *J* = 17.5 Hz, 1H), 1.12 (s, 9H), 1.08 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.0, 171.4,

170.4, 149.4, 147.5, 145.4, 142.5, 140.3, 136.0, 135.0, 134.4, 129.6, 128.5, 128.4, 128.3, 128.1, 128.1, 128.0, 127.6, 127.5, 109.4, 67.8, 67.5, 63.2, 61.3, 55.9, 40.7, 34.8, 34.7, 29.4, 29.0 ppm. IR(KBr): 3032, 2957, 2867, 1728, 1658, 1638, 1496, 1481, 1456, 1368, 1254, 1167, 1087, 1031, 904, 880, 749, 698, 586, 497 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{41}H_{45}O_5$ 617.3262; Found 617.3262.

7,9-di-tert-butyl-4-methylene-1-phenyl-2-tosyl-2-azaspiro[4.5]deca-6,9-dien-8-one ***(3af)*** 23% yield (11.4 mg). brown solid, m.p. 157 – 158 ºC. Rf = 0.3 (1/10 EA/PE). ^1H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.23 (m, 5H), 7.07 (m, 2H), 6.14 (d, *J* = 2.9 Hz, 1H), 5.74 (d, *J* = 2.9 Hz, 1H), 5.04 (s, 1H), 4.74 (s, 1H), 4.64 (s, 1H), 4.49 (d, *J* = 14.1 Hz, 1H), 4.38 (d, *J* = 14.2 Hz, 1H), 2.43 (s, 3H), 1.08 (s, 9H), 0.97 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.9, 147.9, 146.3, 145.0, 143.9, 138.6, 138.4, 129.8, 128.0, 128.0, 127.5, 127.0, 110.1, 71.9, 54.6, 52.4, 34.9, 34.6, 29.1, 29.0, 21.5 ppm. IR(KBr): 2958, 2922, 2868, 2852, 1727, 1658, 1640, 1598, 1457, 1366, 1351, 1249, 1216, 1199, 1182, 1163, 1137, 1094, 1059, 1042, 995, 942, 883, 816, 780, 736, 697, 663, 612, 593, 580, 548, 512 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{38}NO_3S$ 504.2567; Found 504.2571.

General Procedure for the Preparation of Intermediate 4aa.

A sealed tube was charged with *para*-quinone methide (0.1 mmol, 1 equiv), propargyl malonates (0.15 mmol, 1.5 equiv) and Cs_2CO_3 (1.2 mmol, 1.2 equiv). The vial is thoroughly flushed with argon and dry dimethyl formamide (1.0 mL) was added under argon. Then the reaction mixture was stirred at 60 ºC. After the reaction vessel was cooled to room temperature, the solution was concentrated in *vacuo* and purified by careful chromatography on silica gel (EtOAc/petroleum ether = 1/50) to afford the desired product.

dimethyl 2-((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methyl)-2-(prop-2-yn-1-yl)malonate ***(4aa)*** 90% yield (41.9 mg). White solid, m.p. 115 – 117 ºC. Rf = 0.4 (1/10 EA/PE). ^1H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.1 Hz, 2H), 7.28 – 7.23 (m, 2H), 7.19 (m, 3H), 5.09 (s, 1H), 4.90 (s, 1H), 3.63 (s, 6H), 2.87 – 2.74 (m, 2H), 1.98 (t, *J* = 2.6 Hz, 1H), 1.40 (s, 18H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.4, 152.5,

140.6, 135.0, 129.9, 127.8, 126.7, 126.5, 79.6, 71.1, 62.1, 54.9, 52.5, 52.3, 34.3, 30.3, 26.2 ppm. IR(KBr): 3630, 2955, 2867, 1730, 1638, 1496, 1436, 1363, 1309, 1279, 1227, 1203, 1177, 1122, 1077, 1045, 978, 892, 871, 810, 771, 702, 645, 538 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{36}O_5Na$ 487.2455; Found 487.2459.

General Procedure for the Decarboxylation of 3aa with Diethylamine.

A sealed tube was charged with **3aa** (0.1 mmol, 1 equiv) and diethylamine (1.0 mL). The reaction mixture was stirred at 80 °C for 24 h. After the reaction vessel was cooled to room temperature, the solution was concentrated in *vacuo* and purified by careful chromatography on silica gel (EtOAc/petroleum ether = 1/200) to afford the desired product **5aa**.

*methyl 7,9-di-tert-butyl-4-methylene-8-oxo-1-phenylspiro[4.5]deca-6,9-diene-2-carboxylate (**5aa**)* 75% yield (30.5 mg), *trans*:cis > 20:1. White solid, m.p. 81 – 83 °C. Rf = 0.7 (1/10 EA/PE). ^{1}H NMR (300 MHz, CDCl3) δ 7.17 – 7.13 (m, 3H), 7.03 – 6.99 (m, 2H), 6.58 (d, J = 2.8 Hz, 1H), 6.28 (d, J = 2.8 Hz, 1H), 5.01 – 5.00 (m, 1H), 4.77 – 4.76 (m, 1H), 3.69 – 3.62 (m, 5H), 3.16 – 3.08 (m, 1H), 3.00 – 2.92 (m, 1H), 1.23 (s, 9H), 0.95 (s, 9H) ppm. ^{13}C NMR (75 MHz, CDCl3) δ 186.0, 174.3, 149.8, 147.7, 145.0, 143.1, 139.1, 135.7, 127.7, 127.3, 110.5, 59.4, 55.9, 52.1, 44.7, 36.3, 34.7, 34.4, 29.5, 28.9 ppm. IR(KBr): 3125, 3005, 2957, 2866, 1731, 1658, 1638, 1481, 1458, 1430, 1392, 1366, 1319, 1267, 1215, 1167, 1134, 1101, 1021, 924, 901, 885, 866, 827, 792, 745, 699, 671, 627, 568, 544, 524, 497, 488 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{35}O_3$ 407.2581; Found 407.2582.

General Procedure for the Further Transformation of 3aa with TFA

A sealed tube was charged with **3aa** (0.1 mmol, 1 equiv) and dichloromethane (1.0 mL). Trifluoroacetic acid was then added, and the reaction mixture was stirred at ambient temperature until the reaction was judged to be completed by TLC analysis. The mixture was extracted by dichloromethane, and the combined organic layers were washed with H_2O, brine, dried over Na_2SO_4. Then the solution was concentrated in *vacuo* and purified by chromatography on silica gel (EtOAc/petroleum ether = 1/50 – 1/20) to afford the desired product **6aa**.

*dimethyl 6,8-di-tert-butyl-7-hydroxy-4-methyl-1-phenylnaphthalene-2,2(1H)-dicarboxylate (**6aa**)* 76% yield (35.5 mg). White solid, m.p. 97 – 98 °C. Rf = 0.4 (1/10 EA/PE). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (s, 1H), 7.16 – 7.12 (m, 2H), 6.89 – 6.87 (m, 3H), 5.95 (s, 1H), 5.70 (s, 1H), 5.40 (s, 1H), 3.62 (s, 3H), 3.61 (s, 3H), 2.17 (s, 3H), 1.55 (s, 9H), 1.45 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 170.2, 155.3, 138.5, 135.8, 133.9, 133.4, 129.6, 127.8, 126.6, 121.3, 116.8, 61.3, 52.6, 52.4, 44.2, 37.7, 34.3, 32.9, 30.2, 20.7 ppm. IR(KBr): 3622, 2955, 2925, 2867, 1739, 1638, 1493, 1449, 1433, 1361, 1313, 1251, 1210, 1159, 1045, 883, 821, 774, 748, 701, 589 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{37}O_5$ 465.2636; Found 465.2638.

Associated content

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

^{1}H and ^{13}C NMR spectra for all new compounds (PDF)

X-ray crystallographic data for **3aa** (CIF)

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Notes

The authors declare no competing financial interest.

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