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Ru(II)-Catalyzed Oxidative Spiroannulation of 2-Arylphenols with Alkynes via a C−H Activation/Dearomatization Strategy

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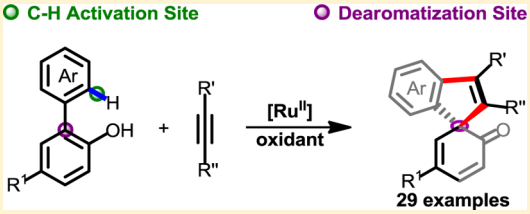
Supporting Information

ABSTRACT: An intermolecular spiroannulation reaction of appropriately substituted 2-arylphenols with internal alkynes has been developed by using a Ru(II) catalyst and an oxidant. This transformation was realized by a phenol-directed C−H activation, migratory insertion of the alkyne, and subsequent dearomatization of the phenolic ring, providing a broad range of highly functionalized spirocyclic compounds in moderate yields with high regioselectivity.



Phenols are a class of readily available and cheap chemical feedstock.[1] The functionalization of phenolic compounds has received considerable attention due to its extensive applications for the preparation of pharmaceuticals, functional materials, and natural products. Recently, transition-metal-catalyzed C−H activation[2−5] has proven to be a versatile and efficient tool to render shorter synthetic routes for a diverse range of important heterocycles from simple phenol derivatives.[6] Meanwhile, transition-metal-catalyzed C−C bond forming dearomatization of phenols has emerged as a magical tool for the construction of three-dimensional spirocyclohexadienones bearing all-carbon quaternary stereocenters.[7] Despite significant progress has been gained for the functionalization of phenols by using the C−H activation or dearomatization approach respectively, the employment of these two valuable tools in a single synthetic process, which has the potential to enable unconventional syntheses with high levels of atom- and step-economy, still represents a formidable challenge.

In 2013, we launched a dual activation research program focusing on the simultaneous activation of C−H bond and dearomatization of those easily accessible aromatic substances by using transition-metal catalysis. After numerous attempts, we have finally realized the first example within this category, which is a Ru(II)-catalyzed oxidative annulation reaction of 1-aryl-2-naphthols with alkynes (Scheme 1, top).[8] This reaction proceeded via sequential cleavage of C−H bond, migratory insertion of the alkyne and dearomatization of the naphthol ring to generate a new class of spirocyclic compounds bearing the spiro[indene-1,1′-naphthalen] skeleton. In that study, the phenolic fragment was restricted on 2-naphthols, and the reactions with 2-phenylphenol could not produce the desired spirocyclic molecule in a synthetically useful yield (<5%) under the reported reaction conditions. Accordingly, the energy barrier for breaking the aromaticity of phenols is significantly higher than that of naphthol compounds.[7h,9] Given the fact that phenols are the more useful building blocks in the organic synthesis, the expansion of substrate scope to phenols is still highly desirable.[10] Herein, we present our efforts on the development of an oxidative spiroannulation of 2-arylphenols with alkynes via C−H activation/dearomatization strategy (Scheme 1, bottom).

The investigation was started by reacting different kinds of phenol substrates with 1,2-diphenylethyne (**2a**) under the standard reaction conditions developed in our previous research work (2.5 mol % $[RuCl_2(p\text{-cymene})_2]$, 2.1 equiv of $Cu(OAc)_2$, 2.0 equiv of K_2CO_3, 1,4-dioxane at 90 °C, 48 h).[8] The catalytic results for four representative phenol substrates (**1a−d**) are shown in Table 1. For the runs with **1a−c** as the coupling partner, no desired products **3a−c** were observed by NMR analysis of the unpurified reaction mixtures. Stimulated by an encouraging observation in our recent Pd(0)-catalyzed process,[11] we endeavored to study a 2-phenylphenol substrate containing an additional *tert*-butyl group at the 4-position for this title transformation. To our delight, the desired spirocyclic product **3d** could be obtained in 19% yield.

Based on this initial observation, we decided to use **1d** as the standard substrate for further optimization (Table 2). First, complexes $Pd(OAc)_2$, $[RhCp^*Cl_2]_2$ and PEPPSI-IPr were introduced to replace $[RuCl_2(p\text{-cymene})_2]$ (entries 2−4). The experimental results indicated that these precatalysts were ineffective for the desired transformation. Next, several organic solvents including ^{t}AmOH, DME and toluene were examined (entries 5−7). As a result, ^{t}AmOH was found to be the beneficial solvent, and the anticipated product **3d** could be produced in 33% yield. Furthermore, the reaction performance was significantly enhanced by elevating the temperature (entries 8−9). Finally, increasing catalyst loading to 5.0 mol % led to the formation of compound **3d** in 70% yield (entry 10). It should be noted that adapting those rhodium catalysis conditions[10] for the analogous 2-arylphenol **1d** to produce the envisioned spiroannulation product **3d** were found to be

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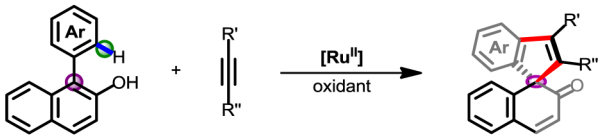
Scheme 1. Transition-Metal-Catalyzed Oxidative Dearomatization of Phenolic Derivatives

Our previous work (2013):



This work:

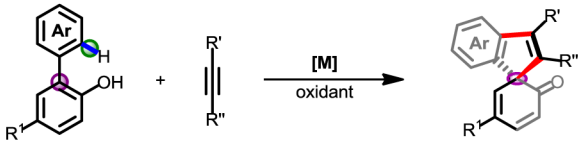
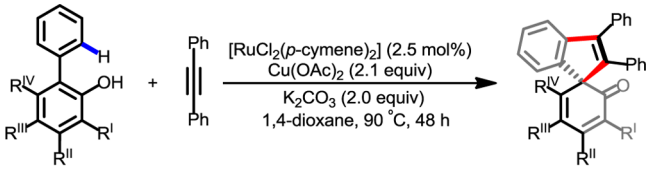


Table 1. Studies on the Substituents of the Phenolic Ring



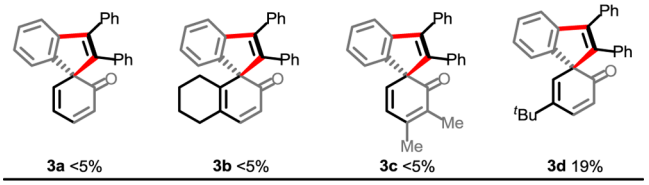
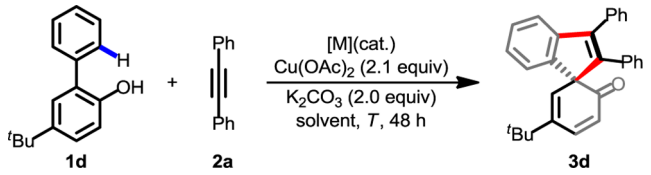


Table 2. Optimization of the Reaction Conditions[a]



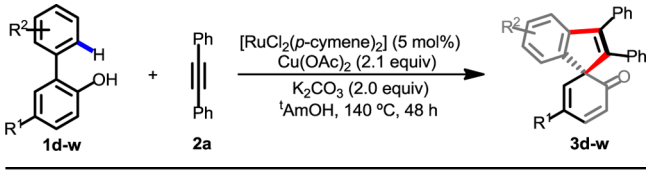
entry	[M], amount (mol %)	solvent	T (°C)	yield (%)[b]
1	$[RuCl_2(p\text{-cymene})_2]$, 2.5	1,4-dioxane	90	19
2	$Pd(OAc)_2$, 5.0	1,4-dioxane	90	<5
3	$[RhCp^*Cl_2]_2$, 2.5	1,4-dioxane	90	<5
4	PEPPSI-IPr, 5.0	1,4-dioxane	90	<5
5	$[RuCl_2(p\text{-cymene})_2]$, 2.5	^{t}AmOH	90	33
6	$[RuCl_2(p\text{-cymene})_2]$, 2.5	DME	90	13
7	$[RuCl_2(p\text{-cymene})_2]$, 2.5	toluene	90	9
8	$[RuCl_2(p\text{-cymene})_2]$, 2.5	^{t}AmOH	120	47
9	$[RuCl_2(p\text{-cymene})_2]$, 2.5	^{t}AmOH	140	61
10	$[RuCl_2(p\text{-cymene})_2]$, 5.0	^{t}AmOH	140	70

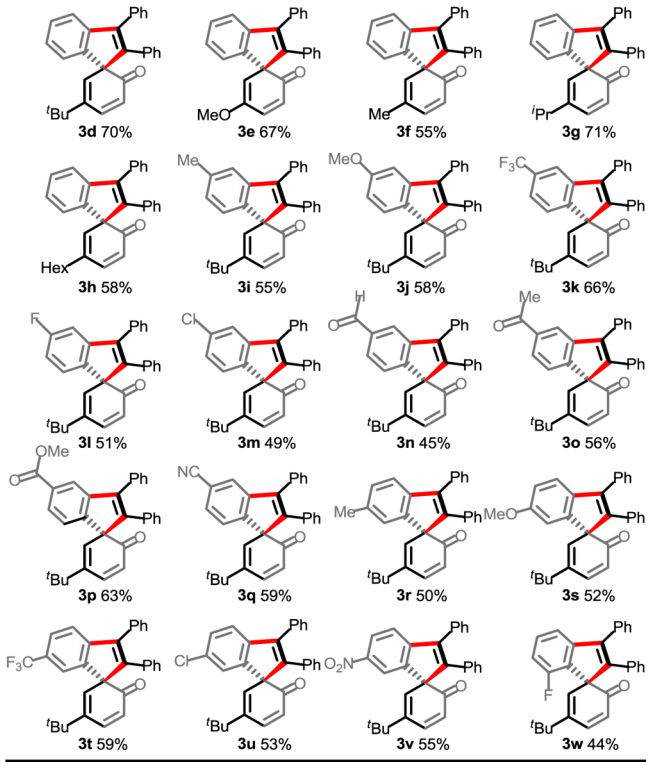
[a]0.20 mmol of **1a**, 0.40 mmol of **2a**, 0.42 mmol of $Cu(OAc)_2$, 0.40 mmol of K_2CO_3, 2.0 mL solvent. [b]Isolated yield.

inapplicable. Thereby, the optimal conditions for the title transformation are 5.0 mol % of $[RuCl_2(p\text{-cymene})_2]$, 2.1 equiv of $Cu(OAc)_2$ and 2.0 equiv of K_2CO_3, 2.0 equiv of alkyne **2a** in ^{t}AmOH at 140 °C for 48 h.

Having identified optimal reaction conditions for Ru(II)-catalyzed dearomatizing oxidative spiroannulation of 2-arylphenols with alkynes, we first examined the substrate scope of this transformation with respect to the 2-arylphenol coupling partner. The catalytic results are summarized in Table 3. With substrates **1d–h**, which contain electron-rich groups such as *tert*-butyl, methoxy, methyl, isopropyl, and cyclohexyl at the 4-position of the phenolic ring, the envisioned spirocyclic enones **3d–h** were obtained in 55–71% yields. However, substrates with an electron-withdrawing group *para* to the hydroxyl group were not tolerated, generally leading to decomposition. Regarding the upper phenyl group, the *para*-

Table 3. Survey the Scope of 2-Arlyphenols





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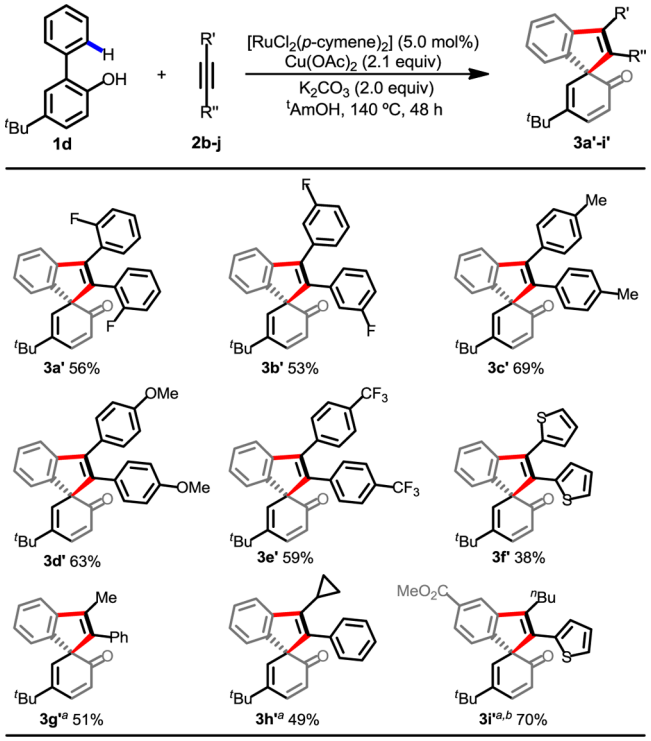
and *meta*-positions are compatible with electron-neutral or electron-donating groups such as methyl (**3i**,**r**), methoxy (**3j**,**s**), and electron-withdrawing groups such as trifluoromethyl (**3k**,**t**), fluoro (**3l**), chloro (**3m**,**u**), formyl (**3n**), acetyl (**3o**), ester (**3p**), cyano (**3q**), and nitro (**3v**) groups. With *meta*-substituted phenyl groups, C−H functionalization occurred exclusively at the less sterically hindered position (**3r**−**v**), whereas the other regioisomer was not observed. Noteworthy, the substrate with an *ortho*- substituent (fluoro) (**1w**), which was totally inactive in the previous studies,[8,12] could undergo the desired spiroannulation to give compound **3w** in 44% yield.

As shown in Table 4, the success of the reaction is not restricted to 1,2-diphenylethyne **2a**, but also works with other

Table 4. Survey the Scope of Alkynes

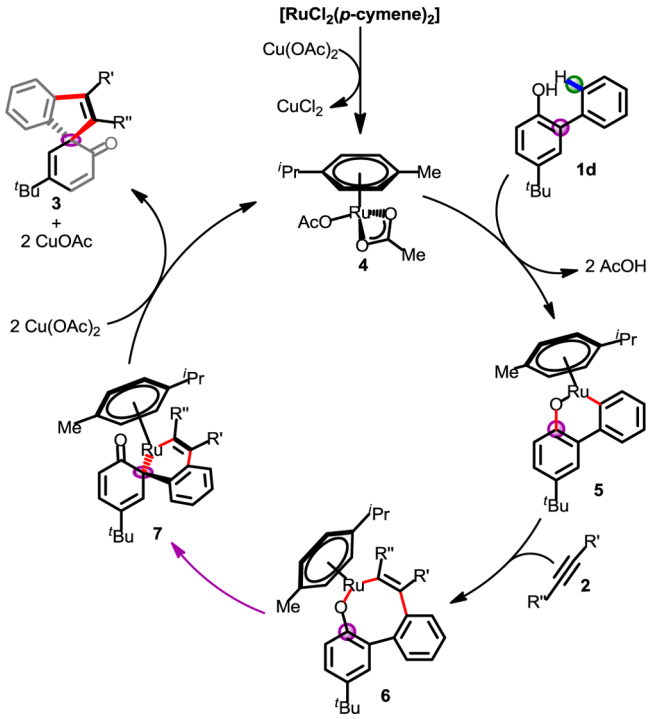


[a]>19:1 regioselectivity in all cases. [b]Phenol **1k** was used to replace **1d**.

symmetrical and unsymmetrical alkynes. Symmetrical diaryl alkynes bearing electron-deficient groups such as fluoro (**2b**−**c**) and trifluoromethyl (**2f**) and electron-rich group such as methoxy (**2e**) at the *ortho*- (**2b**), *meta*- (**2c**), or *para*-position (**2d**-**f**) of the aromatic motifs were tolerated. With 1,2-di(thiophen-2-yl)ethyne (**2g**) containing two heterocyclic groups, the corresponding reaction proceeded smoothly to generate the desired spirocyclic product **3f′**. However, dialkyl or terminal alkynes were not tolerated under the examined reaction conditions. Finally, unsymmetrical alkynes **2h**−**j** were employed to study the regioselectivity for this transformation. Gratifyingly, the reactions were highly regioselective for the preparation of **3g′**−**i′**, with initial C−C bond formation occurring exclusively at the alkyl-substituted carbon atom of the alkyne.

A possible reaction mechanism for this oxidative spiroannulation is illustrated in Scheme 2. Reaction of $[RuCl_2(p\text{-cymene})_2]$ with $Cu(OAc)_2$ generates an active catalyst **4**. The catalytic cycle is then initiated by a phenol-directed C−H activation of the substrate **1d** with **4** to form a six-membered

Scheme 2. Proposed Mechanism



ruthenacycle **5**. Next, a strained eight-membered intermediate **6** is obtained through the coordination and migratory insertion of alkyne **2**. The key step should be the unique enol-keto tautomerization of phenolic ring in **6** to provide a dearomatized intermediate **7**, which is the less strained tautomer. Finally, a C−C bond-forming reductive elimination of the ring contracted ruthenacycle **7** delivers the spirocyclic product **3** and Ru^0, which can be reoxidized by $Cu(OAc)_2$ to regenerate Ru(II) for the next catalytic cycle.

In summary, we have developed a ruthenium-catalyzed dearomatizing spiroannulation reaction of 2-arylphenols with alkynes via a C−H activation approach. This current process allows transferring the more challenging phenol substrates into a class of highly functionalized spirocyclic compounds, and the substrate limitation remaining in the previous reports[8,10] have been significantly overcome. Moreover, we expect this novel C−H activation/dearomatization strategy could gain broad applications in the field of chemical synthesis.

EXPERIMENTAL SECTION

General Information. All reactions were carried out under an argon atmosphere using standard Schlenk-Lines or a glovebox. All solvents were distilled and dried before used. Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F_{254}); visualization of the developed chromatogram was performed by fluorescence. Flash chromatography was performed with silica gel (300−400 mesh). Proton nuclear magnetic resonance (^{1}H NMR) data and Carbon-13 nuclear magnetic resonance (^{13}C NMR) data were acquired at 400, 100 MHz, respectively, in $CDCl_3$ with TMS as internal standard. Infrared (IR) data were recorded as films on potassium bromide plates on FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeter (cm^{-1}). Mass spectra were acquired on a MicroTof-Q II mass spectrometer. Compounds **1d**,[13a] **1e**,[13b] **1f**,[13c] and **2a**−**j**[13d] were prepared according to literature methods.

General Procedure for the Preparation of Phenol Substrates.[14] A 50 mL round-bottom flask with a stir bar is fitted with a rubber septum and flame-dried under high vacuum. The flask is purged

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with argon and charged with $Pd(PPh_3)_4$ (115.6 mg, 0.1 mmol), Na_2CO_3 (445.2 mg, 4.2 mmol), aryl bromide (2.0 mmol, 1.0 equiv), arylboronic acid (4.0 mmol, 2.0 equiv), 10.0 mL of toluene, 2.0 mL of ethanol, and 2.2 mL of deoxygenated water. The reaction mixture was then heated at 80 °C for 20 h. After the reaction was cooled down to room temperature, the organic layer was separated, and the aqueous layer was extracted with ethyl acetate (10 mL × 3), and the combined organic layer was dried over $MgSO_4$ and concentrated. The crude products were purified by flash chromatography on silica gel to afford desired product.

*5-Isopropyl-[1,1′-biphenyl]-2-ol (**1g**).* Colorless oil (0.31 g, 72% yield). PE/EA = 20:1, R_f = 0.21. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55−7.53 (m, 5H), 7.44 (s, 1H), 7.18 (s, 1H), 6.98 (d, J = 7.9 Hz, 1H), 5.24 (s, 1H), 2.96 (dt, J = 13.7, 6.8 Hz, 1H), 1.33 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 141.5, 137.8, 129.5, 129.4, 128.4, 128.1, 128.0, 127.3, 115.9, 33.7, 24.6. IR: 3442, 3029, 2959, 1487, 1383, 1124, 851. HRMS (ESI) m/z calcd for $C_{15}H_{16}ONa$ $[M + Na]^+$ 235.1099, found 235.1095.

*5-Cyclohexyl-[1,1′-biphenyl]-2-ol (**1h**).* Colorless oil (0.40 g, 79% yield). PE/EA = 20:1, R_f = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54−7.41 (m, 4H), 7.37 (dq, J = 8.8, 4.2 Hz, 1H), 7.14−7.04 (m, 2H), 6.89 (d, J = 8.1 Hz, 1H), 5.10 (s, 1H), 2.56−2.37 (m, 1H), 1.95−1.78 (m, 4H), 1.73 (d, J = 12.6 Hz, 1H), 1.50−1.34 (m, 4H), 1.30−1.15 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.7, 140.9, 137.9, 129.4, 128.9, 128.1, 128.0, 127.7, 116.0, 44.1, 35.1, 27.3, 26.5. IR: 3444, 3028, 2923, 2850, 1503, 1487, 1447, 1333, 1137, 880. HRMS (ESI) m/z calcd for $C_{18}H_{20}ONa$ $[M + Na]^+$ 275.1412, found 275.1420.

*5-(tert-Butyl)-4′-methyl-[1,1′-biphenyl]-2-ol (**1i**).* White solid (0.33 g, 69% yield). PE/EA = 20:1, R_f = 0.34. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 7.5 Hz, 2H), 7.44−7.34 (m, 4H), 7.02 (d, J = 8.2 Hz, 1H), 5.28 (s, 1H), 2.51 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 143.8, 137.8, 135.0, 130.2, 129.3, 127.7, 127.5, 126.1, 115.6, 34.5, 31.9, 21.5. IR: 3456, 3026, 2962, 1493, 1394, 1363, 1134, 818. HRMS (ESI) m/z calcd for $C_{17}H_{20}ONa$ $[M + Na]^+$ 263.1412, found 263.1418.

*5-(tert-Butyl)-4′-methoxy-[1,1′-biphenyl]-2-ol (**1j**).* Yellow oil (0.39 g, 76% yield). PE/EA = 20:1, R_f = 0.32. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.3 Hz, 2H), 7.37 (s, 2H), 7.12 (d, J = 8.3 Hz, 2H), 7.02 (d, J = 9.0 Hz, 1H), 5.55 (s, 1H), 3.93 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 150.6, 143.8, 130.7, 130.4, 127.6, 127.5, 126.0, 115.7, 114.9, 55.6, 34.5, 31.9. IR: 3438, 3034, 2961, 1464, 1396, 1135, 821. HRMS (ESI) m/z calcd for $C_{17}H_{20}O_2Na$ $[M + Na]^+$ 279.1361, found 279.1363.

*5-(tert-Butyl)-4′-(trifluoromethyl)-[1,1′-biphenyl]-2-ol (**1k**).* White solid (0.50 g, 85% yield). PE/EA = 20:1, R_f = 0.24. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (s, 2H), 7.65 (d, J = 7.7 Hz, 2H), 7.32 (s, 1H), 7.26 (d, J = 8.0 Hz, 1H), 6.91 (s, 1H), 4.86 (s, 1H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 144.3, 141.9, 129.8, 128.9 (q, J = 10.0 Hz). 127.5, 127.0, 126.4, 126.1 (q, J = 4.0 Hz), 121.8 (q, J = 272.4 Hz), 116.0, 34.4, 31.7. IR: 3416, 3033, 2964, 1465, 1396, 1364, 878, 846. HRMS (ESI) m/z calcd for $C_{17}H_{17}OF_3Na$ $[M + Na]^+$ 317.1129, found 317.1130.

*5-(tert-Butyl)-4′-fluoro-[1,1′-biphenyl]-2-ol (**1l**).* Pale gray solid (0.40 g, 81% yield). PE/EA = 20:1, R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49−7.43 (m, 2H), 7.28 (dd, J = 8.5, 2.5 Hz, 1H), 7.21 (d, J = 2.4 Hz, 1H), 7.20−7.14 (m, 2H), 6.90 (d, J = 8.5 Hz, 1H), 4.98−4.86 (s, 1H), 1.32 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6 (d, J = 247.0 Hz), 150.3, 144.1, 134.1, 131.3 (d, J = 7.9 Hz), 131.2, 127.6, 127.0, 126.4, 116.3 (d, J = 19.6 Hz), 116.1 (d, J = 17.8 Hz), 115.9, 34.5, 31.9. IR: 3431, 3023, 2963, 2869, 1421, 1393, 1364, 1136, 878. HRMS (ESI) m/z calcd for $C_{16}H_{17}OFNa$ $[M + Na]^+$ 267.1161, found 267.1167.

*5-(tert-Butyl)-4′-chloro-[1,1′-biphenyl]-2-ol (**1m**).* Brown solid (0.44 g, 84% yield). PE/EA = 20:1, R_f = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 5.8 Hz, 4H), 7.28 (dd, J = 8.5, 2.5 Hz, 1H), 7.21 (d, J = 2.5 Hz, 1H), 6.89 (d, J = 8.5 Hz, 1H), 4.88 (s, 1H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 144.1, 136.5, 133.8, 130.8, 129.4, 127.4, 126.6, 115.9, 115.0, 34.4, 31.8. IR: 3417, 3032, 2963, 1487, 1390, 1137, 819. HRMS (ESI) m/z calcd for $C_{16}H_{17}OClNa$ $[M + Na]^+$ 283.0866, found 283.0863.

*5′-(tert-Butyl)-2′-hydroxy-[1,1′-biphenyl]-4-carbaldehyde (**1n**).* White solid (0.33 g, 65% yield). PE/EA = 10:1, R_f = 0.26. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.06 (s, 1H), 7.99 (d, J = 7.8 Hz, 2H), 7.73 (d, J = 7.4 Hz, 2H), 7.31−7.25 (m, 2H), 6.93 (d, J = 8.2 Hz, 1H), 5.31 (s, 1H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.3, 150.4, 144.9, 144.3, 135.3, 130.5, 130.1, 127.5, 127.1, 126.5, 116.2, 110.0, 34.4, 31.8. IR: 3409, 3036, 2962, 2866, 1699, 1603, 1499, 1389, 1139, 818. HRMS (ESI) m/z calcd for $C_{17}H_{18}O_2Na$ $[M + Na]^+$ 277.1204, found 277.1205.

*1-(5′-(tert-Butyl)-2′-hydroxy-[1,1′-biphenyl]-4-yl)ethanone (**1o**).* White solid (0.37 g, 69% yield). PE/EA = 10:1, R_f = 0.19. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 7.9 Hz, 1H), 7.68 (d, J = 7.9 Hz, 2H), 7.32 (d, J = 7.2 Hz, 1H), 6.96 (d, J = 8.1 Hz, 1H), 6.07 (s, 1H), 2.65 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.7, 150.8, 144.6, 143.9, 135.8, 129.7, 129.3, 129.1, 127.7, 127.5, 126.9, 126.7, 116.1, 34.4, 31.8, 27.0. IR: 3410, 3023, 2963, 1680, 1421, 1395, 1139, 821. HRMS (ESI) m/z calcd for $C_{18}H_{20}O_2Na$ $[M + Na]^+$ 291.1361, found 291.1366.

*Methyl 5′-(tert-butyl)-2′-hydroxy-[1,1′-biphenyl]-4-carboxylate (**1p**).* White solid (0.42 g, 74% yield). PE/EA = 20:1, R_f = 0.27. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 7.9 Hz, 2H), 7.35−7.28 (m, 2H), 6.94 (d, J = 8.4 Hz, 1H), 5.39 (s, 1H), 3.96 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 150.4, 144.1, 143.2, 130.4, 129.5, 127.4, 126.9, 116.0, 52.5, 34.4, 31.8. IR: 3421, 3035, 2956, 1731, 1437, 1395, 1364, 1181, 821. HRMS (ESI) m/z calcd for $C_{18}H_{20}O_3Na$ $[M + Na]^+$ 307.1310, found 307.1306.

*5′-(tert-Butyl)-2′-hydroxy-[1,1′-biphenyl]-4-carbonitrile (**1q**).* White solid (0.39 g, 78% yield). PE/EA = 10:1, R_f = 0.24. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 7.0 Hz, 1H), 7.27 (s, 1H), 6.90 (d, J = 8.4 Hz, 1H), 4.99 (s, 1H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 144.4, 143.6, 132.6, 130.3, 127.5, 127.3, 126.1, 119.2, 116.3, 110.8, 34.5, 31.7. IR: 3445, 3022, 2959, 2229, 1497, 1384, 1138, 842. HRMS (ESI) m/z calcd for $C_{17}H_{17}ONNa$ $[M + Na]^+$ 274.1208, found 274.1210.

*5-(tert-Butyl)-3′-methyl-[1,1′-biphenyl]-2-ol (**1r**).* Yellow oil (0.38 g, 79% yield). PE/EA = 20:1, R_f = 0.39. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (t, J = 7.4 Hz, 1H), 7.26 (s, 3H), 7.22 (d, J = 7.8 Hz, 2H), 6.93 (d, J = 8.4 Hz, 1H), 5.12 (s, 1H), 2.43 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 143.7, 139.3, 137.8, 130.1, 129.4, 128.8, 127.7, 127.3, 126.4, 126.2, 115.5, 34.4, 31.8, 21.8. IR: 3446, 3035, 2964, 2896, 1485, 1395, 1365, 822. HRMS (ESI) m/z calcd for $C_{17}H_{20}ONa$ $[M + Na]^+$ 263.1412, found 263.1420.

*5-(tert-Butyl)-3′-methoxy-[1,1′-biphenyl]-2-ol (**1s**).* White solid (0.36 g, 71% yield). PE/EA = 20:1, R_f = 0.29. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 7.4 Hz, 1H), 7.33 (d, J = 8.2 Hz, 1H), 7.29 (s, 1H), 7.10 (d, J = 6.6 Hz, 1H), 7.05 (s, 1H), 7.00−6.93 (m, 2H), 5.26 (s, 1H), 3.88 (s, 3H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 150.4, 143.8, 139.4, 130.6, 127.2, 126.7, 126.4, 121.7, 115.7, 115.0, 113.6, 55.6, 34.5, 31.9. IR: 3440, 3057, 3961, 1486, 1364, 821. HRMS (ESI) m/z calcd for $C_{17}H_{20}O_2Na$ $[M + Na]^+$ 279.1361, found 279.1366.

*5-(tert-Butyl)-3′-(trifluoromethyl)-[1,1′-biphenyl]-2-ol (**1t**).* White solid (0.46 g, 78% yield). PE/EA = 20:1, R_f = 0.37. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (s, 1H), 7.71 (d, J = 5.9 Hz, 1H), 7.66−7.58 (m, 2H), 7.32 (d, J = 8.5 Hz, 1H), 7.25 (s, 1H), 6.91 (d, J = 8.4 Hz, 1H), 4.84 (s, 1H). 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 144.5, 139.3, 133.0 (q, J = 32.1 Hz), 131.6, 131.3, 129.5, 127.7, 126.9, 126.7, 126.5 (q, J = 4.0 Hz), 125.9, 124.4 (q, J = 3.5 Hz), 123.1 (q, J = 267.0 Hz), 116.1, 34.5, 31.8. IR: 3406, 3061, 2964, 1486, 1396, 1364, 1128, 823. HRMS (ESI) m/z calcd for $C_{17}H_{17}OF_3Na$ $[M + Na]^+$ 317.1129, found 317.1133.

*5-(tert-Butyl)-3′-chloro-[1,1′-biphenyl]-2-ol (**1u**).* Yellow oil (0.33 g, 64% yield). PE/EA = 20:1, R_f = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.49 (d, J = 4.3 Hz, 1H), 7.47−7.39 (m, 3H), 7.37 (s, 1H), 6.97 (d, J = 8.0 Hz, 1H), 5.63 (s, 1H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 144.2, 140.2, 135.0, 130.4, 129.7, 127.9, 127.7, 127.5, 126.8, 126.7, 116.1, 34.5, 31.9. IR: 3417, 3060, 2963,

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1467, 1394, 1136, 887. HRMS (ESI) m/z calcd for $C_{16}H_{17}OClNa$ [M + Na]$^+$ 283.0866, found 283.0863.

*5-(tert-Butyl)-3′-nitro-[1,1′-biphenyl]-2-ol (**1v**).* Yellow solid (0.37 g, 69% yield). PE/EA = 20:1, R_f = 0.18. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 1H), 8.22 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 7.6 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.39−7.26 (m, 2H), 6.88 (d, J = 8.2 Hz, 1H), 4.87 (s, 1H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 148.5, 144.5, 140.3, 135.8, 129.6, 127.6, 127.2, 125.6, 124.6, 122.3, 116.2, 34.5, 31.8. IR: 3457, 3032, 2963, 2866, 1479, 1271, 1139, 890, 821. HRMS (ESI) m/z calcd for $C_{16}H_{17}O_3NNa$ [M + Na]$^+$ 294.1106, found 294.1109.

*5-(tert-Butyl)-2′-fluoro-[1,1′-biphenyl]-2-ol (**1w**).* Colorless solid (0.33 g, 67% yield). PE/EA = 20:1, R_f = 0.36. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 6.7 Hz, 2H), 7.35 (d, J = 6.5 Hz, 1H), 7.29−7.21 (m, 3H), 6.96 (d, J = 8.5 Hz, 1H), 4.82 (s, 1H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.7, 143.8, 132.3, 130.1 (d, J = 8.0 Hz), 128.2, 127.0, 124.9 (d, J = 3.8 Hz), 122.3, 116.6, 115.9, 110.0, 34.4, 31.8. IR: 3446, 3022, 2963, 2868, 1487, 1364, 1136, 823. HRMS (ESI) m/z calcd for $C_{16}H_{17}OFNa$ [M + Na]$^+$ 267.1161, found 267.1163.

General Procedure for Ru(II)-Catalyzed Oxidative Spiroannulation of 2-Arylphenols with Alkynes. In a glovebox, a 5.0 mL vial equipped with a stir bar was charged with $[RuCl_2(p\text{-cymene})_2]$ (6.1 mg, 0.01 mmol), $Cu(OAc)_2$ (76.0 mg, 0.42 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), 1-aryl-2-phenol (0.20 mmol), and alkyne (0.40 mmol), followed by sequential addition of ^{t}AmOH (2.0 mL). The vial was sealed with a Teflon screw cap, and then the reaction mixture was heated at 140 °C for 48 h. The crude reaction mixture was then subjected to a silica gel column to afford the desired product.

*3-(tert-Butyl)-2′,3′-diphenylspiro[cyclohexa[2,4]diene-1,1′-inden]-6-one (**3d**).* Yellow solid (56.3 mg, 70% yield). PE/EA = 10:1, R_f = 0.27. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50−7.44 (m, 4H), 7.43−7.37 (m, 1H), 7.31 (d, J = 3.5 Hz, 2H), 7.21−7.15 (m, 3H), 7.13 (d, J = 2.2 Hz, 3H), 7.07−7.05 (m, 2H), 6.35 (d, J = 10.1 Hz, 1H), 6.01 (s, 1H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.1, 146.8, 144.5, 144.4, 144.1, 143.7, 142.4, 135.3, 135.0, 133.7, 129.7, 129.0, 128.9, 128.3, 128.2, 128.0, 127.8, 127.5, 126.5, 122.0, 121.9, 70.5, 34.7, 29.1. IR: 3054, 2958, 2925, 1665, 1635, 1480, 1221, 785. HRMS (ESI) m/z calcd for $C_{30}H_{26}ONa$ [M + Na]$^+$ 425.1881, found 425.1875.

*3-Methoxy-2′,3′-diphenylspiro[cyclohexa[2,4]diene-1,1′-inden]-6-one (**3e**).* Yellow solid (50.4 mg, 67% yield). PE/EA = 10:1, R_f = 0.23. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44−7.39 (m, 3H), 7.36 (d, J = 7.1 Hz, 2H), 7.27 (d, J = 6.1 Hz, 2H), 7.20−7.18 (m, 2H), 7.11−7.09 (m, 4H), 7.05−7.03 (m, 2H), 6.29 (d, J = 10.1 Hz, 1H), 5.12 (s, 1H), 3.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 151.7, 146.1, 145.3, 144.8, 143.8, 143.3, 135.2, 134.9, 129.7, 129.0, 128.9, 128.3, 128.0, 127.5, 126.6, 122.1, 121.9, 110.0, 107.3, 69.1, 55.5. IR: 3053, 2956, 2924, 1664, 1639, 1461, 1234, 800, 758, 699. HRMS (ESI) m/z calcd for $C_{27}H_{20}O_2Na$ [M + Na]$^+$ 399.1361, found 399.1354.

*3-Methyl-2′,3′-diphenylspiro[cyclohexa[2,4]diene-1,1′-inden]-6-one (**3f**).* Yellow solid (39.6 mg, 55% yield). PE/EA = 10:1, R_f = 0.37. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46−7.44 (m, 5H), 7.40−7.36 (m, 2H), 7.27−7.16 (m, 3H), 7.16−7.09 (m, 3H), 7.09−7.03 (m, 2H), 6.30 (d, J = 9.8 Hz, 1H), 5.96 (s, 1H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 147.5, 146.7, 144.2, 144.0, 143.5, 137.2, 135.2, 135.0, 130.1, 129.7, 129.0, 128.9, 128.3, 128.0, 127.7, 127.4, 126.5, 122.0, 121.9, 110.0, 70.9, 21.5. IR: 3060, 2922, 1670, 1643, 1488, 1384, 1125, 831. HRMS (ESI) m/z calcd for $C_{27}H_{20}ONa$ [M + Na]$^+$ 383.1412, found 383.1421.

*3-Isopropyl-2′,3′-diphenylspiro[cyclohexa[2,4]diene-1,1′-inden]-6-one (**3g**).* Yellow solid (55.1 mg, 71% yield). PE/EA = 10:1, R_f = 0.31. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50−7.41 (m, 3H), 7.39 (d, J = 6.9 Hz, 1H), 7.31−7.24 (m, 3H), 7.17 (t, J = 7.9 Hz, 3H), 7.12 (d, J = 3.1 Hz, 3H), 7.08−7.05 (m, 2H), 6.34 (d, J = 9.9 Hz, 1H), 5.96 (s, 1H), 2.60 (dt, J = 13.5, 6.7 Hz, 1H), 1.16 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 146.8, 145.5, 144.3, 144.1, 143.7, 140.2, 135.3, 135.0, 134.7, 129.7, 129.0, 128.9, 128.2, 128.2, 128.0, 127.4, 126.5, 122.0, 121.9, 70.7, 33.5, 21.9, 21.8. IR: 3063, 2957, 2922, 1662, 1638, 1462, 1262, 751. HRMS (ESI) m/z calcd for $C_{29}H_{24}ONa$ [M + Na]$^+$ 411.1725, found 411.1731.

*4-Cyclohexyl-2′,3′-diphenylspiro[cyclohexa[3,5]diene-2,1′-inden]-1-one (**3h**).* Yellow solid (49.7 mg, 58% yield). PE/EA = 10:1, R_f = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47−7.40 (m, 3H), 7.40−7.33 (m, 2H), 7.28−7.22 (m, 3H), 7.17−7.12 (m, 2H), 7.11−7.06 (m, 3H), 7.06−7.00 (m, 2H), 6.29 (d, J = 10.0 Hz, 1H), 5.91 (s, 1H), 2.16 (t, J = 11.3 Hz, 1H), 1.80 (d, J = 9.9 Hz, 4H), 1.71 (d, J = 12.9 Hz, 1H), 1.39−1.13 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.4, 146.8, 146.2, 143.6, 139.5, 135.4, 129.7, 129.0, 128.9, 128.2, 128.0, 127.8, 127.4, 126.5, 122.0, 121.9, 70.7, 43.6, 32.3, 32.1, 26.6, 26.2. IR: 3061, 2956, 2924, 2852, 1663, 1636, 1463, 1337, 1086. HRMS (ESI) m/z calcd for $C_{32}H_{28}ONa$ [M + Na]$^+$ 451.2038, found 451.2041.

*3-(tert-Butyl)-5′-methyl-2′,3′-diphenylspiro[cyclohexa[2,4]diene-1,1′-inden]-6-one (**3i**).* Yellow solid (45.8 mg, 55% yield). PE/EA = 10:1, R_f = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53−7.38 (m, 6H), 7.09 (d, J = 3.9 Hz, 4H), 7.02 (d, J = 7.4 Hz, 4H), 6.31 (d, J = 10.1 Hz, 1H), 5.97 (s, 1H), 2.34 (s, 3H), 1.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.4, 147.0, 144.5, 144.1, 142.2, 140.8, 138.2, 135.4, 135.0, 133.9, 129.7, 129.0, 128.9, 128.2, 128.0, 127.7, 127.4, 127.3, 122.6, 121.7, 70.1, 34.6, 29.1, 21.9. IR: 3060, 2980, 1668, 1634, 1480, 1361, 697. HRMS (ESI) m/z calcd for $C_{31}H_{28}ONa$ [M + Na]$^+$ 439.2038, found 439.2044.

*3-(tert-Butyl)-5′-methoxy-2′,3′-diphenylspiro[cyclohexa[2,4]-diene-1,1′-inden]-6-one (**3j**).* Yellow solid (50.1 mg, 58% yield). PE/EA = 10:1, R_f = 0.45. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51−7.35 (m, 6H), 7.09 (s, 3H), 7.00 (d, J = 6.0 Hz, 3H), 6.80 (s, 1H), 6.71 (d, J = 7.6 Hz, 1H), 6.29 (d, J = 10.1 Hz, 1H), 5.92 (s, 1H), 3.76 (s, 3H), 1.17 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.3, 160.3, 148.3, 145.5, 144.4, 143.9, 142.1, 135.7, 135.2, 135.0, 133.9, 129.6, 129.0, 128.9, 128.1, 128.0, 127.6, 127.5, 122.6, 112.3, 107.6, 69.7, 55.8, 34.6, 29.1. IR: 3061, 2956, 1667, 1634, 1464, 1219, 698. HRMS (ESI) m/z calcd for $C_{31}H_{28}O_2Na$ [M + Na]$^+$ 455.1987, found 455.1986.

*3-(tert-Butyl)-2′,3′-diphenyl-5′-(trifluoromethyl)spiro[cyclohexa-[2,4]diene-1,1′-inden]-6-one (**3k**).* White solid (62.0 mg, 66% yield). PE/EA = 10:1, R_f = 0.27. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56−7.42 (m, 8H), 7.22 (s, 1H), 7.13 (d, J = 6.8 Hz, 3H), 7.03 (d, J = 6.7 Hz, 2H), 6.35 (d, J = 10.1 Hz, 1H), 5.94 (s, 1H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 147.5, 147.3, 146.2, 144.7, 143.3, 143.2, 134.4, 132.3, 130.9 (q, J = 8.4 Hz), 130.6, 129.5, 129.3, 128.9, 128.4, 128.3, 127.9, 127.8, 123.6 (q, J = 272.4 Hz), 122.3, 118.5 (q, J = 4.0 Hz), 70.3, 34.8, 29.1. IR: 3056, 2960, 2850, 1668, 1635, 1432, 1350, 1165, 894, 700. HRMS (ESI) m/z calcd for $C_{31}H_{25}F_3ONa$ [M + Na]$^+$ 493.1755, found 493.1761.

*3-(tert-Butyl)-5′-fluoro-2′,3′-diphenylspiro[cyclohexa[2,4]diene-1,1′-inden]-6-one (**3l**).* White solid (42.9 mg, 51% yield). PE/EA = 10:1, R_f = 0.37. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44−7.42 (m, 7H), 7.13−7.07 (m, 3H), 7.04−7.01 (m, 2H), 6.98 (d, J = 9.1 Hz, 1H), 6.86 (t, J = 8.5 Hz, 1H), 6.32 (d, J = 10.1 Hz, 1H), 5.95 (s, 1H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8, 164.6 (d, J = 244.0 Hz), 149.0 (d, J = 8.9 Hz), 146.3, 144.5, 142.6, 139.1, 134.6, 133.1, 129.5, 129.1, 128.9, 128.3 (d, J = 4.0 Hz), 128.2, 127.8, 127.7, 123.1 (d, J = 9.0 Hz), 122.9, 113.3, 113.1, 109.2, 109.0, 69.7, 34.7, 29.1. IR: 3061, 2957, 2923, 1667, 1635, 1465, 1071, 736. HRMS (ESI) m/z calcd for $C_{30}H_{25}FONa$ [M + Na]$^+$ 443.1787, found 443.1781.

*3-(tert-Butyl)-5′-chloro-2′,3′-diphenylspiro[cyclohexa[2,4]diene-1,1′-inden]-6-one (**3m**).* Brown solid (42.7 mg, 49% yield). PE/EA = 10:1, R_f = 0.41. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44−7.40 (m, 6H), 7.26 (d, J = 12.0 Hz, 2H), 7.12−7.10 (m, 3H), 7.04 (d, J = 3.2 Hz, 3H), 6.32 (d, J = 10.3 Hz, 1H), 5.94 (s, 1H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5, 148.6, 145.9, 144.5, 143.2, 142.8, 141.9, 134.5, 134.3, 132.8, 129.5, 129.1, 128.9, 128.2, 127.7, 126.4, 123.0, 122.0, 69.9, 34.7, 29.1. IR: 3059, 2959, 1664, 1634, 1456, 1263, 748, 699. HRMS (ESI) m/z calcd for $C_{30}H_{25}ClONa$ [M + Na]$^+$ 459.1492, found 459.1503.

*3-(tert-Butyl)-6-oxo-2′,3′-diphenylspiro[cyclohexa[2,4]diene-1,1′-indene]-5′-carbaldehyde (**3n**).* White solid (38.7 mg, 45% yield). PE/EA = 10:1, R_f = 0.15. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.95 (s, 1H), 7.77 (s, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.46−7.43 (m, 6H), 7.26 (d, J = 5.7 Hz, 2H), 7.12 (d, J = 6.9 Hz, 2H), 7.03 (d, J = 6.3 Hz, 2H), 6.35 (d, J = 10.2 Hz, 1H), 5.94 (s, 1H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9, 192.3, 150.2, 149.7, 148.3, 147.8, 145.9, 144.6, 136.8,

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134.4, 132.1, 129.5, 129.2, 128.9, 128.3, 127.9, 122.6, 122.4, 70.5, 34.8, 29.0. IR: 3055, 2961, 2925, 1697, 1668, 1636, 1488, 1395, 1384, 1141, 849. HRMS (ESI) m/z calcd for $C_{31}H_{26}O_2Na$ $[M + Na]^+$ 453.1830, found 453.1839.

*5′-Acetyl-3-(tert-butyl)-2′,3′-diphenylspiro[cyclohexa[2,4]diene-1,1′-inden]-6-one (**3o**).* Yellow solid (49.7 mg, 56% yield). PE/EA = 10:1, R_f = 0.19. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86−7.79 (m, 2H), 7.46−7.44 (m, 6H), 7.20 (d, J = 6.3 Hz, 2H), 7.12 (d, J = 6.1 Hz, 2H), 7.03 (d, J = 5.8 Hz, 2H), 6.34 (d, J = 10.1 Hz, 1H), 5.90 (s, 1H), 2.57 (s, 3H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.1, 197.2, 148.8, 147.3, 144.6, 143.2, 137.6, 134.6, 132.4, 129.6, 129.2, 128.9, 128.2, 127.9, 127.2, 122.1, 121.4, 70.6, 34.7, 29.1, 27.1. IR: 3056, 2967, 2845, 1680, 1665, 1634, 1489, 1387, 1123, 823. HRMS (ESI) m/z calcd for $C_{32}H_{28}O_2Na$ $[M + Na]^+$ 467.1987, found 467.1980.

*Methyl-3-(tert-butyl)-6-oxo-2′,3′-diphenylspiro[cyclohexa[2,4]-diene-1,1′-indene]-5′-carboxylate (**3p**).* Yellow solid (58.0 mg, 63% yield). PE/EA = 10:1, R_f = 0.45. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 13.2 Hz, 2H), 7.46−7.44 (m, 6H), 7.17 (d, J = 7.6 Hz, 1H), 7.12−7.10 (m, 3H), 7.03−7.01 (m, 2H), 6.33 (d, J = 10.1 Hz, 1H), 5.94 (s, 1H), 3.89 (s, 3H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 167.2, 148.6, 147.1, 145.5, 144.6, 143.5, 143.1, 134.6, 132.5, 130.4, 129.6, 129.2, 128.9, 128.2, 127.9, 127.8, 122.7, 121.9, 70.4, 52.4, 34.7, 29.1. IR: 3060, 2954, 2923, 1721, 1668, 1630, 1463, 1286, 1098. HRMS (ESI) m/z calcd for $C_{32}H_{28}O_3Na$ $[M + Na]^+$ 483.1936, found 483.1940.

*3-(tert-Butyl)-6-oxo-2′,3′-diphenylspiro[cyclohexa[2,4]diene-1,1′-indene]-5′-carbonitrile (**3q**).* Yellow solid (50.4 mg, 59% yield). PE/EA = 10:1, R_f = 0.29. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 0.9 Hz, 1H), 7.43−7.38 (m, 6H), 7.18 (d, J = 7.8 Hz, 2H), 7.12 (td, J = 8.7, 4.7 Hz, 3H), 7.01 (dd, J = 8.1, 1.5 Hz, 2H), 6.34 (d, J = 10.1 Hz, 1H), 5.90 (s, 1H), 1.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 148.5, 147.8, 146.7, 144.7, 143.7, 142.6, 133.9, 131.5, 130.4, 129.4, 129.3, 128.9, 128.6, 128.3, 128.2, 127.9, 125.0, 122.8, 119.3, 112.2, 70.6, 34.8, 29.0. IR: 3058, 2962, 2856, 2230, 1683, 1636, 1466, 1384, 1131, 849. HRMS (ESI) m/z calcd for $C_{31}H_{25}ONNa$ $[M + Na]^+$ 450.1834, found 450.1841.

*3-(tert-Butyl)-6′-methyl-2′,3′-diphenylspiro[cyclohexa[2,4]diene-1,1′-inden]-6-one (**3r**).* Yellow solid (41.6 mg, 50% yield). PE/EA = 10:1, R_f = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48−7.36 (m, 6H), 7.27 (s, 1H), 7.18 (d, J = 7.6 Hz, 1H), 7.10−7.08 (m, 3H), 7.03−6.99 (m, 2H), 6.92 (s, 1H), 6.32 (d, J = 10.1 Hz, 1H), 5.98 (s, 1H), 2.35 (s, 3H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.4, 144.5, 144.2, 144.0, 143.9, 143.4, 142.2, 136.5, 135.4, 135.1, 133.9, 129.6, 129.0, 128.9, 128.9, 128.1, 127.9, 127.8, 127.3, 122.8, 121.6, 70.3, 34.7, 29.1, 21.8. IR: 3055, 2963, 1667, 1636, 1479, 1384, 1139, 821. HRMS (ESI) m/z calcd for $C_{31}H_{28}ONa$ $[M + Na]^+$ 439.2038, found 439.2043.

*3-(tert-Butyl)-6′-methoxy-2′,3′-diphenylspiro[cyclohexa[2,4]-diene-1,1′-inden]-6-one (**3s**).* Yellow solid (44.9 mg, 52% yield). PE/EA = 10:1, R_f = 0.44. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47−7.38 (m, 6H), 7.19 (d, J = 8.3 Hz, 1H), 7.08 (d, J = 3.1 Hz, 2H), 7.01 (d, J = 3.5 Hz, 3H), 6.83 (d, J = 8.4 Hz, 1H), 6.70 (s, 1H), 6.32 (d, J = 10.2 Hz, 1H), 5.99 (s, 1H), 3.73 (s, 3H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 158.9, 145.4, 144.4, 143.7, 142.3, 139.7, 135.5, 135.2, 133.9, 129.6, 128.9, 128.7, 128.1, 127.9, 127.7, 127.1, 122.4, 113.1, 109.4, 70.2, 55.8, 34.6, 29.1. IR: 3064, 2958, 2925, 1665, 1635, 1480, 1279, 1082, 785, 699. HRMS (ESI) m/z calcd for $C_{31}H_{28}O_2Na$ $[M + Na]^+$ 455.1987, found 455.1995.

*3-(tert-Butyl)-2′,3′-diphenyl-6′-(trifluoromethyl)spiro[cyclohexa-[2,4]diene-1,1′-inden]-6-one (**3t**).* White solid (55.5 mg, 59% yield). PE/EA = 10:1, R_f = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 7.9 Hz, 1H), 7.43 (d, J = 8.6 Hz, 6H), 7.38 (d, J = 6.7 Hz, 1H), 7.32 (s, 1H), 7.14 (d, J = 6.8 Hz, 3H), 7.05 (d, J = 6.8 Hz, 2H), 6.36 (d, J = 10.1 Hz, 1H), 5.95 (s, 1H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1, 150.2, 147.2, 144.7, 144.2, 143.4, 143.2, 134.5, 134.3 (q, J = 14.0 Hz), 132.1, 129.5, 129.1, 128.9, 128.6, 128.3, 128.2, 128.0, 127.9 (q, J = 12.6 Hz), 125.7 (q, J = 267.0 Hz), 121.8, 118.9, 70.3, 34.8, 29.0. IR: 3058, 2960, 1665, 1635, 1324, 1262, 1125, 748. HRMS (ESI) m/z calcd for $C_{31}H_{25}F_3ONa$ $[M + Na]^+$ 493.1755, found 493.1748.

*3-(tert-Butyl)-6′-chloro-2′,3′-diphenylspiro[cyclohexa[2,4]diene-1,1′-inden]-6-one (**3u**).* Yellow solid (46.2 mg, 53% yield). PE/EA = 10:1, R_f = 0.23. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44−7.35 (m, 6H), 7.25 (dd, J = 4.7, 3.4 Hz, 2H), 7.18 (d, J = 8.2 Hz, 1H), 7.11−7.06 (m, 3H), 7.02−6.96 (m, 2H), 6.31 (d, J = 10.2 Hz, 1H), 5.92 (s, 1H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.8, 144.7, 144.7, 144.2, 144.0, 142.6, 142.4, 134.1, 133.9, 131.9, 131.5, 128.9, 128.5, 128.2, 127.8, 127.6, 127.2, 127.1, 122.0, 121.9, 69.5, 34.1, 28.5. IR: 3059, 2963, 1663, 1637, 1461, 1228, 846, 751. HRMS (ESI) m/z calcd for $C_{30}H_{25}ClONa$ $[M + Na]^+$ 459.1492, found 459.1496.

*3-(tert-Butyl)-6′-nitro-2′,3′-diphenylspiro[cyclohexa[2,4]diene-1,1′-inden]-6-one (**3v**).* Yellow solid (49.2 mg, 55% yield). PE/EA = 10:1, R_f = 0.31. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 7.2 Hz, 1H), 7.94 (s, 1H), 7.53−7.37 (m, 7H), 7.15−7.12 (m, 3H), 7.03 (d, J = 7.1 Hz, 2H), 6.37 (d, J = 10.1 Hz, 1H), 5.92 (s, 1H), 1.20 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4, 153.3, 150.1, 146.3, 144.9, 143.0, 133.9, 130.9, 129.5, 129.3, 128.9, 128.6, 128.5, 128.4, 127.9, 124.6, 121.7, 117.6, 70.1, 34.9, 29.0. IR: 3060, 2964, 2927, 1670, 1637, 1478, 1386, 1340, 1227, 1134, 850. HRMS (ESI) m/z calcd for $C_{30}H_{25}NO_3Na$ $[M + Na]^+$ 470.1732, found 470.1739.

*3-(tert-Butyl)-7′-fluoro-2′,3′-diphenylspiro[cyclohexa[2,4]diene-1,1′-inden]-6-one (**3w**).* White solid (37.0 mg, 44% yield). PE/EA = 10:1, R_f = 0.38. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47−7.34 (m, 7H), 7.17−7.10 (m, 4H), 7.06 (t, J = 11.0 Hz, 2H), 6.90 (t, J = 8.6 Hz, 1H), 6.35 (d, J = 11.2 Hz, 1H), 5.86 (s, 1H), 1.17 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1, 156.6 (d, J = 252.0 Hz), 149.8, 145.9, 144.3, 143.6, 134.6 (d, J = 10.3 Hz), 134.5, 130.9, 130.2, 130.1 (d, J = 7.0 Hz), 129.9, 129.7, 129.0, 128.9, 128.3, 128.1, 127.8, 117.5, 114.1 (d, J = 20.1 Hz), 113.9, 68.1, 34.7, 29.0. IR: 3061, 2960, 2924, 1664, 1636, 1468, 1275, 749. HRMS (ESI) m/z calcd for $C_{30}H_{25}FONa$ $[M + Na]^+$ 443.1787, found 443.1795.

*3-(tert-Butyl)-2′,3′-bis(2-fluorophenyl)spiro[cyclohexa[2,4]diene-1,1′-inden]-6-one (**3a′**).* Yellow solid (49.1 mg, 56% yield). PE/EA = 10:1, R_f = 0.29. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.30 (m, 3H), 7.24−7.20 (m, 2H), 7.14 (d, J = 6.4 Hz, 3H), 7.09 (t, J = 7.2 Hz, 3H), 6.93 (d, J = 7.6 Hz, 1H), 6.88 (t, J = 8.7 Hz, 1H), 6.20 (d, J = 10.0 Hz, 1H), 5.98 (s, 1H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.1, 161.2 (d, J = 237.0 Hz), 158.9 (d, J = 248.0 Hz), 145.4, 144.9, 144.3, 142.8, 141.0, 131.5 (d, J = 3.0 Hz), 131.4, 130.1 (d, J = 7.9 Hz), 130.0 (d, J = 8.0 Hz), 129.8, 129.7, 128.2, 127.5, 126.8, 124.2 (d, J = 4.0 Hz), 123.7 (d, J = 3.9 Hz), 122.7, 121.9, 116.1 (d, J = 21.1 Hz), 115.9 (d, J = 23.2 Hz), 115.6, 115.4, 110.4, 71.5, 34.6, 29.0. IR: 3056, 2985, 1676, 1632, 1478, 1389, 1362, 1134, 790. HRMS (ESI) m/z calcd for $C_{30}H_{24}OF_2Na$ $[M + Na]^+$ 461.1693, found 461.1699.

*3-(tert-Butyl)-2′,3′-bis(3-fluorophenyl)spiro[cyclohexa[2,4]diene-1,1′-inden]-6-one (**3b′**).* White solid (46.4 mg, 53% yield). PE/EA = 10:1, R_f = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51−7.38 (m, 2H), 7.33−7.18 (m, 4H), 7.17−7.05 (m, 4H), 6.87−6.75 (m, 3H), 6.32 (J = 10.1 Hz, 1H), 5.95 (s, 1H). 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 163.9, 163.2 (d, J = 246.0 Hz), 161.4 (d, J = 243.0 Hz), 160.8, 145.3, 144.0, 143.2, 143.1, 142.9, 142.3, 136.2 (d, J = 4.2 Hz), 132.2, 130.2 (d, J = 8.4 Hz), 130.1 (d, J = 9.0 Hz), 129.2, 129.1, 127.9, 127.2, 126.5, 124.8, 124.1, 121.6, 121.3, 115.9 (d, J = 20.4 Hz), 115.7, 115.0 (d, J = 6.5 Hz), 114.8, 114.7, 114.6 (d, J = 21.3 Hz), 114.1, 113.9, 69.8, 34.1, 28.5. IR: 3057, 2958, 1660, 1634, 1463, 1377, 1263, 744. HRMS (ESI) m/z calcd for $C_{30}H_{24}OF_2Na$ $[M + Na]^+$ 461.1693, found 461.1688.

*3-(tert-Butyl)-2′,3′-di-p-tolylspiro[cyclohexa[2,4]diene-1,1′-inden]-6-one (**3c′**).* Yellow solid (59.3 mg, 69% yield). PE/EA = 10:1, R_f = 0.38. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 10.1 Hz, 1H), 7.36 (d, J = 7.7 Hz, 2H), 7.26 (d, J = 6.2 Hz, 4H), 7.09 (s, 1H), 6.96−6.90 (m, 5H), 6.32 (d, J = 10.1 Hz, 1H), 5.98 (s, 1H), 2.42 (s, 3H), 2.24 (s, 3H), 1.20 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.3, 147.1, 144.4, 143.5, 142.1, 137.6, 137.1, 134.2, 132.4, 132.2, 129.7, 129.5, 128.9, 128.7, 128.2, 127.8, 126.3, 121.9, 121.7, 70.4, 34.6, 29.1, 21.7, 21.4. IR: 3056, 2956, 2845, 1667, 1632, 1478, 1387, 1153, 879. HRMS (ESI) m/z calcd for $C_{32}H_{30}ONa$ $[M + Na]^+$ 453.2194, found 453.2188.

*3-(tert-Butyl)-2′,3′-bis(4-methoxyphenyl)spiro[cyclohexa[2,4]-diene-1,1′-inden]-6-one (**3d′**).* White solid (58.2 mg, 63% yield). PE/

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EA = 10:1, R_f = 0.42. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (dd, J = 10.2, 2.6 Hz, 2H), 7.31 (d, J = 8.7 Hz, 2H), 7.21−7.17 (m, 3H), 7.05 (s, 1H), 7.01 (s, 1H), 6.92−6.86 (m, 4H), 6.56 (d, J = 8.9 Hz, 2H), 6.24 (d, J = 10.2 Hz, 1H), 5.88 (s, 1H), 3.79 (s, 3H), 3.65 (s, 3H), 1.11 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$): δ 198.4, 159.3, 158.7, 147.2, 144.4, 143.4, 142.2, 134.2, 130.9, 130.1, 128.2, 127.7, 126.1, 121.9, 121.5, 114.4, 113.6, 70.6, 55.5, 55.3, 34.6, 29.1. IR: 3056, 2958, 1665, 1635, 1459, 1260, 1009, 798. HRMS (ESI) m/z calcd for $C_{32}H_{30}O_3Na$ $[M + Na]^+$ 485.2093, found 485.2099.

*3-(tert-Butyl)-2′,3′-bis(4-(trifluoromethyl)phenyl)spiro[cyclohexa-[2,4]diene-1,1′-inden]-6-one (**3e′**).* White solid (63.5 mg, 59% yield). PE/EA = 10:1, R_f = 0.47. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 7.9 Hz, 2H), 7.58 (d, J = 7.9 Hz, 2H), 7.48 (d, J = 8.1 Hz, 1H), 7.39 (d, J = 7.6 Hz, 2H), 7.33 (d, J = 5.2 Hz, 1H), 7.24 (s, 1H), 7.22 (s, 1H), 7.16 (d, J = 6.4 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H), 6.34 (d, J = 10.2 Hz, 1H), 5.97 (s, 1H), 1.20 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 145.6, 144.7 (q, J = 10.2 Hz), 143.7 (q, J = 6.0 Hz), 143.2, 138.5, 132.4, 129.9, 129.0, 128.6, 127.8, 127.4, 126.2 (q, J = 272.2 Hz), 125.3 (q, J = 272.2 Hz), 122.2, 122.0, 70.9, 34.8, 29.1. IR: 3029, 2957, 1487, 1384, 1166, 889. HRMS (ESI) m/z calcd for $C_{32}H_{24}F_6ONa$ $[M + Na]^+$ 561.1629, found 561.1634.

*3-(tert-Butyl)-2′,3′-di(thiophen-2-yl)spiro[cyclohexa[2,4]diene-1,1′-inden]-6-one (**3f′**).* Yellow solid (31.5 mg, 38% yield). PE/EA = 10:1, R_f = 0.36. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57−7.50 (m, 2H), 7.27 (d, J = 7.2 Hz, 2H), 7.22 (d, J = 7.7 Hz, 2H), 7.16−7.14 (m, 2H), 7.08 (d, J = 7.3 Hz, 1H), 6.87−6.82 (m, 1H), 6.70 (d, J = 3.1 Hz, 1H), 6.35 (d, J = 10.2 Hz, 1H), 5.98 (s, 1H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.4, 146.8, 144.5, 142.5, 142.1, 141.2, 137.3, 134.5, 133.9, 128.9, 128.6, 128.1, 127.6, 127.5, 127.2, 126.9, 126.7, 121.8, 121.6, 70.1, 34.7, 29.0. IR: 3066, 2964, 2925, 1669, 1637, 1463, 1386, 1263, 1123, 850. HRMS (ESI) m/z calcd for $C_{26}H_{22}OS_2Na$ $[M + Na]^+$ 437.1010, found 437.1013.

*3-(tert-Butyl)-3′-methyl-2′-phenylspiro[cyclohexa[2,4]diene-1,1′-inden]-6-one (**3g′**).* White solid (34.7 mg, 51% yield). PE/EA = 10:1, R_f = 0.37. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41−7.32 (m, 3H), 7.30−7.27 (m, 2H), 7.24 (s, 3H), 7.17 (d, J = 7.1 Hz, 1H), 7.06 (d, J = 7.3 Hz, 1H), 6.23 (d, J = 10.0 Hz, 1H), 5.85 (s, 1H), 2.30 (s, 3H), 1.15 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.0, 147.6, 144.5, 144.0, 143.6, 142.2, 139.6, 135.6, 133.5, 128.7, 128.3, 128.2, 127.7, 127.4, 126.4, 121.9, 120.6, 70.6, 34.6, 29.1, 12.5. IR: 3056, 2962, 1667, 1636, 1467, 1384, 1264, 843. HRMS (ESI) m/z calcd for $C_{25}H_{24}ONa$ $[M + Na]^+$ 363.1725, found 363.1732.

*3-(tert-Butyl)-3′-cyclopropyl-2′-phenylspiro[cyclohexa[2,4]diene-1,1′-inden]-6-one (**3h′**).* Yellow solid (35.9 mg, 49% yield). PE/EA = 10:1, R_f = 0.33. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 7.5 Hz, 1H), 7.34 (t, J = 6.8 Hz, 4H), 7.30−7.22 (m, 3H), 7.14 (t, J = 7.4 Hz, 1H), 7.03 (d, J = 7.4 Hz, 1H), 6.21 (d, J = 10.1 Hz, 1H), 5.81 (s, 1H), 1.93 (s, 1H), 1.14 (s, 9H), 1.00−0.83 (m, 2H), 0.61−0.59 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.7, 147.3, 144.7, 144.4, 144.1, 143.9, 142.1, 135.4, 133.7, 128.9, 128.1, 127.9, 127.7, 127.4, 126.1, 121.9, 121.4, 70.4, 34.6, 29.1, 9.1, 7.3, 7.2. IR: 3056, 2961, 2925, 1667, 1636, 1465, 1384, 1366, 1120, 843. HRMS (ESI) m/z calcd for $C_{27}H_{26}ONa$ $[M + Na]^+$ 389.1881, found 389.1884.

*Methyl-3-(tert-butyl)-3′-butyl-6-oxo-2′-(thiophen-2-yl)spiro-[cyclohexa[2,4]diene-1,1′-indene]-5′-carboxylate (**3i′**).* White solid (62.4 mg, 70% yield). PE/EA = 10:1, R_f = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.83 (d, J = 7.8 Hz, 1H), 7.52−7.50 (m, 1H), 7.29 (d, J = 4.8 Hz, 1H), 7.09 (d, J = 7.8 Hz, 1H), 7.00−6.94 (m, 1H), 6.76 (d, J = 3.2 Hz, 1H), 6.35 (d, J = 10.2 Hz, 1H), 5.81 (s, 1H), 3.94 (s, 3H), 3.01−2.95 (m, 2H), 1.74−1.72 (m, 2H), 1.61−1.55 (m, 2H), 1.19 (s, 9H), 1.02 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.8, 166.7, 147.1, 146.4, 143.9, 142.41, 142.1, 137.2, 136.8, 133.1, 129.8, 127.4, 127.1, 126.7, 125.5, 125.4, 121.0, 120.8, 69.6, 51.9, 34.1, 29.9, 28.4, 26.3, 22.8, 13.7. IR: 3067, 2959, 1723, 1668, 1636, 1259, 696. HRMS (ESI) m/z calcd for $C_{28}H_{30}O_3SNa$ $[M + Na]^+$ 469.1813, found 469.1821.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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