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SYNTHESIS AND PHYSICAL PROPERTIES OF π-EXTENDED MOLECULES HAVING *p*-METHYLENEQUINONE UNIT

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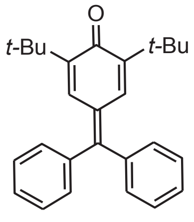
‡ This paper is dedicated to Professor Dr. Kaoru Fuji on celebration of his 80th birthday.

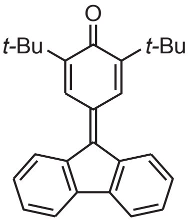
Abstract – In this paper, we reported the facile synthesis of the π-extended molecules having *p*-methylenequinone unit from the aromatic ketones, such as fluorenone, xanthone, thioxanthone, dibenzosuberenone, and acridone, in few steps and the results of their physical properties.

Redox active compounds, which exhibit strong absorption in the whole visible region, have been attracting a great deal of interest in view of the applications of organic materials, such as dye-sensitized solar cell.[1] Fuchsone having a *p*-methylenequinone structure has absorption in the visible region and exhibits a high molar extinction coefficient and the electrochemically activity.[2] Their derivatives have been utilized for dye and pigment.[3] In addition, fuchsone derivatives have been applicated to the inhibitors of the DNA binding of transcription factor NF-κB, the colorimetric arrays for detection of nerve gas, and the electrophotographic photoreceptors using novel charge-transporting agent.[4-6] However, there is a few reports on the synthesis of π-extended and π-condensed fuchsone derivatives. Compound **1** having a fluorene skeleton has been prepared by the reaction of *p*-benzoquinone derivative with phosphorus ylide under high temperature.[7] Compounds **2** and **3** have been also synthesized by the reaction of xanthone and thioxanthone with phenol derivative in the presence of oxalyl chloride, respectively.[8] However, in these methods, there are several drawbacks, such as high reaction temperature, handling of toxic agent, and limitation of the substrates.[9]

On the other hand, the overcrowded ethylenes, which have a similar structure to those of the π-extended and π-condensed fuchsone derivatives, are attractive compounds for the study of the homogeneous redox catalysis,[10] thermochromism,[11] and solvatochromism.[12] From these points of view, the π-extended molecules having *p*-methylenequinone unit would show the unique properties depending on their structures. In this paper, we report the convenient synthetic method of the π-extended molecules having *p*-methylenequinone unit **1-5** from the corresponding aromatic ketones and physical properties of them.



Fuchsone



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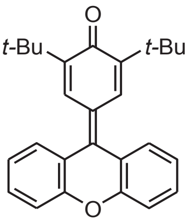

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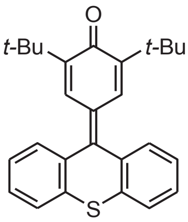

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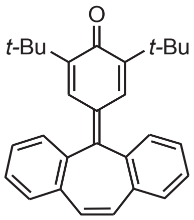

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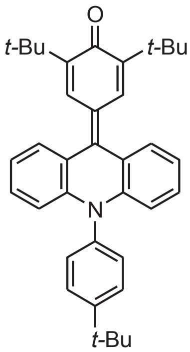
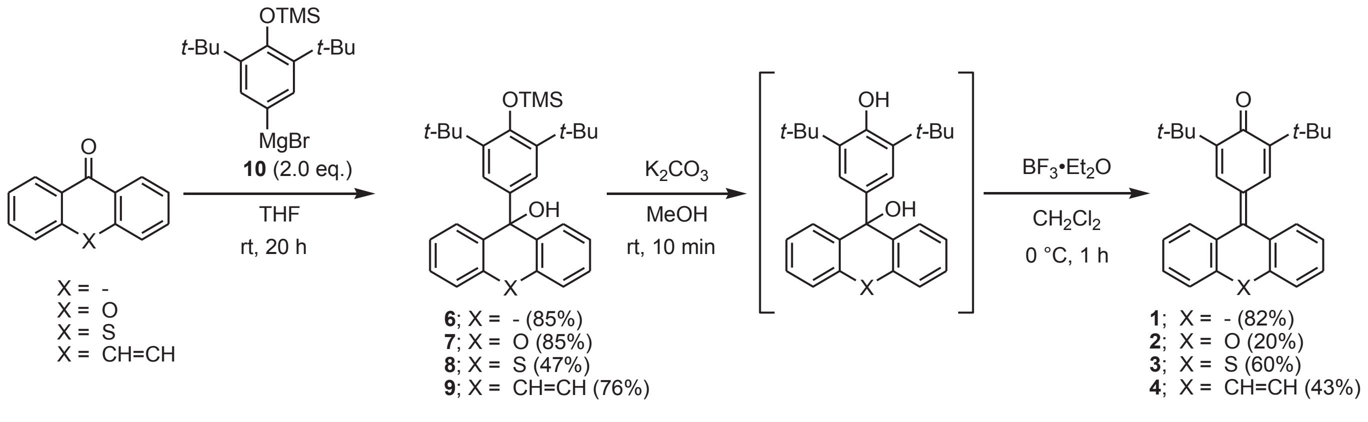


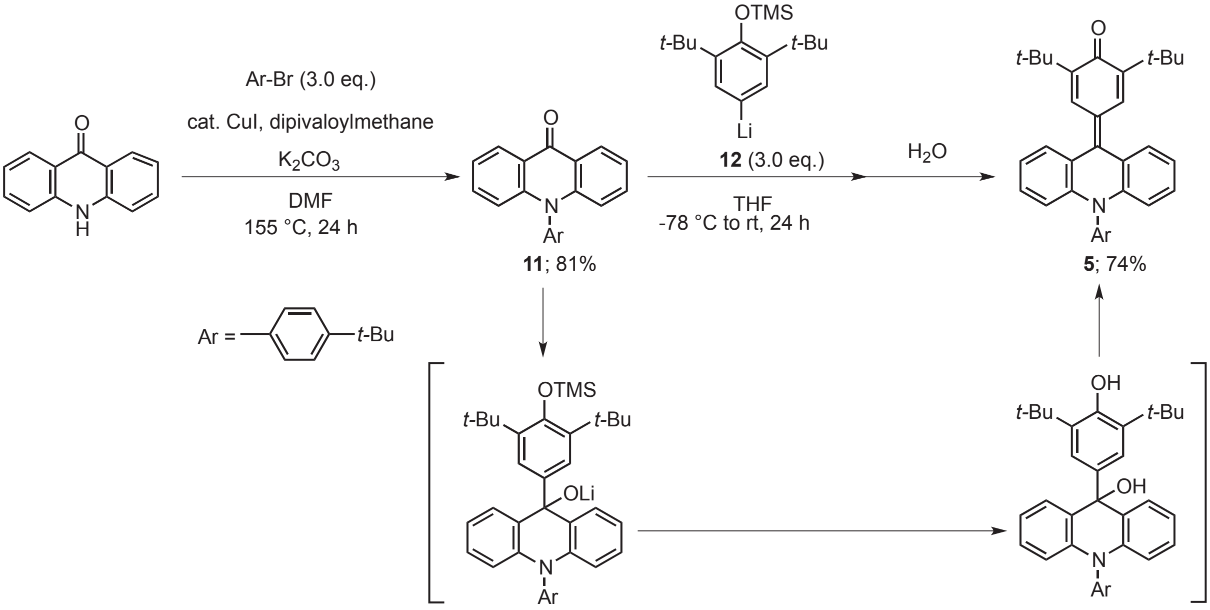
5

The synthesis of π-extended molecules **1-4** having *p*-methylenequinone unit are shown in Scheme 1. First, fluorenone as starting material was reacted with 2.0 equivalent of the Grignard reagent **10** to afford the addition product in 85% yield. Next, the desilylation of the addition product was carried out using potassium carbonate in methanol solvent followed by the treatment with boron trifluoride-diethyl ether complex at room temperature gave the *p*-methylenequinone derivative **1** together with the fluorene derivative, which was formed by the only dehydroxylation of five-membered ring, as by-product. Fortunately, when the reaction was carried out at low temperature (0 °C), the formation of this by-product could be suppressed, and the desired product **1** was obtained in 82% yield. Using same synthetic protocol, the *p*-methylenequinone derivatives **2-4** were also synthesized from the corresponding ketones as starting materials.[13]



Scheme 1. Synthesis of **1-4**

Next, we carried out the synthesis of the acridone derivative **5** (Scheme 2). The copper catalyzed *N*-arylation of acridone with 1-bromo-4-*tert*-butylbenzene afforded the *N*-arylacridone **11** in 81% yield.[14] Although the *N*-arylacridone **11** was reacted with the Grignard reagent **10**, no reaction took place. Interestingly, when **11** was reacted with the corresponding lithium reagent **12** and subjected to workup with water, the acridone derivative **5** was formed in 74% yield via the protonation, desilyation, and dehydration.



Scheme 2. Synthesis of **5**

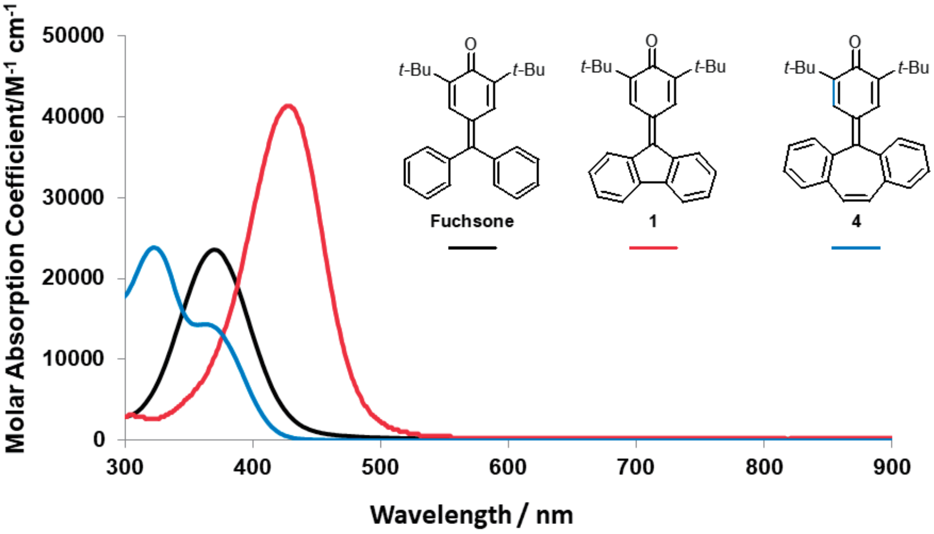


Figure 1. UV/vis Absorption Spectra of Fuchsone, **1**, and **4** in THF

First, the UV/vis absorption spectra of fuchsone, **1**, and **4** in THF solution are shown in Figure 1 and Table 1. The spectrum of **1** having the fluorene moiety showed a large absorption at 428 nm and was bathochromically shifted by 58 nm as compared with that of fuchsone. On the other hand, the spectrum of **4** showed the absorption at 323 and 363 nm. From the result of **4**, it seems that the seven-membered ring structure in **4** was not conjugated sufficiently.

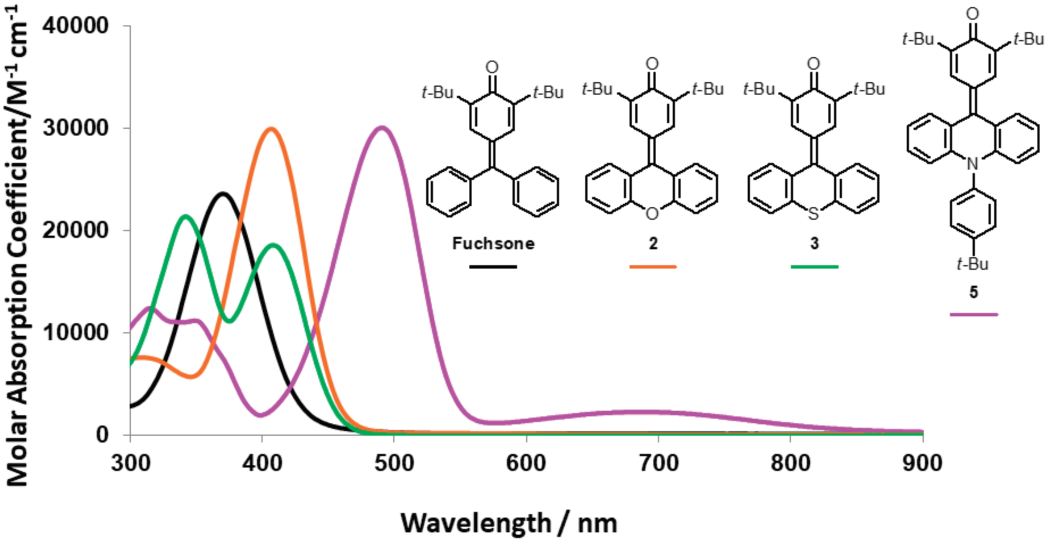


Figure 2. UV/vis Absorption Spectra of Fuchsone, **2**, **3**, and **5** in THF

Next, the results of UV/vis absorption spectra of fuchsone, **2**, **3**, and **5** in THF solution are shown in Figure 2 and Table 1. The spectra of **2** and **3** with xanthone and thioxanthone structures, respectively, showed the absorption around 400 nm and slightly shifted as compared with that of fuchsone. On the other hand, the spectrum of the acridone derivative **5** exhibited the large absorption at 491 nm and the weak absorption at 686 nm. In order to investigate the reason for the absorption at 686 nm of **5**, we measured the UV/vis absorption spectrum of **5** in various solvents (cyclohexane, toluene, THF, methylene chloride, acetonitrile, and DMSO) (see Figure S1 in SI). When cyclohexane as low polarity solvent was used, the absorption of **5** in the near infrared region was very weak. Interestingly, the absorption in the near infrared region increased upon the increasing polarity of the solvent. In the both cases of acetonitrile and DMSO, the same intensity of absorption in the near infrared region was observed.

Kubo and Hirao have already reported that the unsymmetrical bianthrone derivative, analogue of **5**, showed the polarity-dependent absorption change.[12] On their manuscript, they revealed that the absorption in the near infrared region is ascribed to the isomerization reaction between the folded and twisted isomers. The twisted isomer in polar solvents would be stabilized and increased the significant contribution of the zwitterionic character by the electron-donating acridane unit and the electron-withdrawing anthrone unit. From Kubo and Hirao's result, the longer absorption of **5** in polar solvents also indicated that the isomerization between the folded and twisted isomers leading to the contribution of the zwitterionic character, such as acridinium cation and phenoxy anion. The difference in the intensity of absorption of **5** in the near infrared region appears in the color of the solution. Namely, the solution in cyclohexane as low polarity solvent shows yellow color and the DMSO solution as high polarity solvent shows red color (see Figure S2 in SI).[15]

Table 1. Optical and Electrochemical Data for Fuchsone and **1-5**

Compd.	Absorption^a	CV^b		
	λ_{abs} /nm ε ($\times$ 10^3 $M^{-1}cm^{-1}$)	E_{ox} /eV	E_{red} /eV	E_{Gap} /eV
Fuchsone	370 (24.0)	-	-1.83	-
1	428 (41.3)	-	-1.74, -1.33	-
2	407 (30.0)	0.65	-1.57	2.22
3	408 (19.0), 342 (21.0)	0.69	-1.73	2.42
4	323 (23.7), 363 (14.0)	-	-1.96	-
5	491 (30.0), 686 (2.2)	0.04	-1.65	1.69

[a] $[c] = {\sim}10^{-5}$ M in THF.
[b] 1.0 mM, V versus (Ag/Ag^+) in 0.1 M with $n\mathrm{Bu_4NPF_6}$ in THF, scan rate: 100 mV/s, working electrode Pt, $Fc/Fc^+ = 0$ V.

The cyclic voltammetry (CV) of fuchsone and **1**-**5** were measured and their results are show in Table 1 (see Figure S3 and S4 in SI). In the case of fuchsone, although the reversible reduction wave of one electron was observed, no oxidation wave was observed. On the other hand, in the case of **1**, the two reversible reduction waves were observed. This result indicates that the dianion of **1** would be stabilized by both the formation of phenoxy anion and cyclopentadiene anion. The oxidation wave was not observed in compound **1** as well as that of fuchsone. The CV spectra of **2** and **3** showed the reversible reduction wave of one electron and the reduction potentials of them were lower than that of fuchsone. The CV of **2** and **3** detected the one-electron irreversible oxidation waves, which were derived from a six-membered heterocycle, xanthone and thioxanthone, respectively. As with fuchsone and **1**, the CV spectrum of **4** showed only the reversible reduction wave of one electron. We expected that the seven-membered ring of **4** would be oxidized to become tropylium cation and stabilized, but no oxidation wave was observed. As described above, the compound **4** could not have the efficient conjugation (see Figure 1) because of the deviation from planarity due to the steric hindrance between dibenzosuberenone and quinone moieties. Therefore, the oxidized **4** could not be stabilized. The reversible one-electron reduction and oxidation waves were observed in the CV spectrum of **5**. From these results, it was clearly that the oxidation and reduction abilities greatly depended on the initial ketone structure.

In conclusion, we developed the synthetic method of the π-extended molecules **1-5** having *p*-methylenequinone unit from the aromatic ketones, such as fluorenone, xanthone, thioxanthone, dibenzosuberenone, and acridone, in few steps. In addition, it was clearly found that the photophysical and electrochemical properties of **1-5** were significantly influenced by the π-extended and π-condensed structures.

EXPERIMENTAL

General: FT-IR spectra were recorded on a JASCO FT/IR-4100 instrument. ^{1}H-NMR spectra were recorded at 400 MHz and ^{13}C-NMR spectra at 100 MHz on a JEOL AL400 or ECS400. Chemical shifts were reported in ppm relative to tetramethylsilane or residual solvent as the internal standard. Mass spectral analyses were performed on a JEOL JMS-700 spectrometer for EI and FAB ionization. Preparative HPLC separation was undertaken with a JAI LC-908 chromatograph using 600 mm x 20 mm JAIGEL-1H and 2H GPC columns with $CHCl_3$ as an eluent. All reagents were obtained from commercial suppliers and used without purification.

General Synthesis of **6-9**: A solution of arylmagnesium bromide **10** (2.0 mmol), which was prepared from Mg turnings (486 mg, 20 mmol) and (4-bromo-2,6-di*tert*-butylphenoxy)trimethylsilane (2.0 mmol) in THF (10 mL), was added to a solution of the corresponding aromatic ketone (1.0 mmol) in THF (8.0 mL) at room temperature. After being stirred for 20 h at room temperature, to the reaction mixture was added water, then the resulting mixture was extracted several times with $CHCl_3$ and the organic fraction was washed with brine and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by chromatography on SiO_2 to give the compounds **6-9**. Further purification was carried out a recyclable preparative HPLC, if necessary.

6: mp 54-55 °C; IR (KBr) ν_{max} 3545, 3447, 3038, 2956, 1749, 1605, 1558, 1508, 1489, 1472, 1449, 1420, 1392, 1361, 1338, 1257, 1233, 1209, 1180, 1122, 1037, 987, 921, 889, 867, 845, 769, 757, 740 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 6.8 Hz, 2H), 7.46 (dd, *J* = 7.0, 0.4 Hz, 2H), 7.37 (td, *J* = 7.4, 1.2 Hz, 2H), 7.31 (s, 2H), 7.30-7.26 (m, 2H), 2.44 (s, 1H), 1.33 (s, 18H), 0.39 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.5, 150.2, 140.1, 139.5, 134.1, 128.8, 128.1, 124.9, 123.2, 119.9, 83.9, 35.2, 31.1, 3.9; MS (EI): *m/z* 458 (M$^+$); HRMS (EI): Calcd for $C_{30}H_{38}O_2Si$: 458.2641, Found 458.2616.

7: mp 121-122 °C; IR (KBr) ν_{max} 3544, 3030, 2958, 1600, 1572, 1473, 1446, 1418, 1391, 1362, 1308, 1237, 1205, 1178, 1151, 1124, 1094, 1050, 970, 944, 924, 882, 843, 751 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.29 (td, *J* = 8.0, 2.0 Hz, 2H), 7.19-7.17 (m, 4H), 7.10 (td, *J* = 7.6, 1.2 Hz, 2H), 2.60 (s, 1H), 1.30 (s, 18H), 0.37 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 151.8, 150.0, 140.0, 138.5, 128.7, 128.3, 127.9, 123.9, 123.3, 116.2, 70.9, 35.1, 3.8; MS (EI): *m/z* 474 (M$^+$); HRMS (EI): Calcd for $C_{30}H_{37}O_2Si$: 457.2563, Found 457.2568.

8: mp 205-206 °C; IR (KBr) ν_{max} 3586, 3059, 2954, 1457, 1441, 1421, 1391, 1362, 1257, 1205, 1178, 1124, 1032, 924, 886, 842, 754 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 7.8, 0.8 Hz, 2H), 7.38 (dd, *J* = 7.8, 0.8 Hz, 2H), 7.34 (td, *J* = 7.6, 1.6 Hz, 2H), 7.25-7.21 (m, 2H), 6.80 (s, 2H) 2.79 (br, 1H), 1.19 (s, 18H), 0.33 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.4, 140.4, 139.7, 133.9, 131.6, 127.0, 126.33, 126.29, 125.7, 124.9, 77.2, 35.0, 30.9, 3.9; MS (EI): *m/z* 490 (M$^+$). HRMS (EI): Calcd for $C_{30}H_{38}O_2SSi$: 490.2362, Found 490.2362.

9: mp 248-249 °C; IR (KBr) ν_{max} 3573, 3019, 2956, 1483, 1422, 1392, 1361, 1321, 1258, 1241, 1208, 1171, 1159, 1125, 1047, 1018, 970, 950, 921, 881, 842, 803, 773, 733 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.0 Hz, 2H), 7.49-7.45 (m, 2H), 7.31-7.26 (m, 4H), 6.60 (s, 2H), 6.46 (s, 2H), 2.27 (br, 1H), 1.14 (s, 18H), 0.31 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.1, 143.1, 139.4, 136.9, 133.4, 131.0, 128.3, 127.8, 126.4, 124.8, 124.4, 78.6, 34.9, 31.1, 3.5; MS (EI): *m/z* 484 (M$^+$); HRMS (EI): calcd For $C_{32}H_4O_2Si$: 484.2798, Found 484.2810.

General Synthesis of **1-4:** To a solution of **6-9** (0.3 mmol) in MeOH (5.0 mL) was slowly added to K_2CO_3 (1.2 mmol, 0.166 g) at room temperature for 10 min. After removal of the solvent, the residue was diluted with $CHCl_3$ and washed with NH_4Cl aq. and brine. The organic layer was dried over $MgSO_4$. The organic solution was concentrated under reduced pressure to afford the crude diol derivatives. The crude products were used without further purification in the next step. To the solution of crude diol in CH_2Cl_2 (10 mL) added $BF_3 \cdot Et_2O$ (0.3 mmol, 0.042 g) at 0 °C. After being stirred at 0 °C for 1 h, to the reaction mixture was added water, then the resulting mixture was extracted several times with $CHCl_3$ and the organic fraction was washed with brine and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by chromatography on SiO_2 to give the compounds **1-4**. Further purification was carried out a recyclable preparative HPLC, if necessary.

1: mp 225-229 °C; IR (KBr) ν_{max} 3170, 3053, 3012, 2979, 2952, 2915, 2861, 1639, 1591, 1518, 1479, 1467, 1445, 1388, 1354, 1337, 1303, 1281, 1251, 1198, 1169, 1158, 1102, 1085, 1022, 972, 946, 930, 911, 876, 852, 820, 783, 744, 729, cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 2H), 7.91 (d, *J* = 7.6 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.37 (td, *J* = 7.6, 1.2 Hz, 2H), 7.03 (td, *J* = 7.6, 1.2 Hz, 2H), 1.41 (s, 18H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 186.7, 149.0, 146.5, 141.9, 137.8, 132.9, 129.9, 129.4, 127.8, 127.6, 120.3, 35.8, 29.8; MS (EI): *m/z* 368 (M$^+$); HRMS (EI): Calcd for $C_{27}H_{28}O$: 368.2140, Found 368.2168.

2: mp 227-231 °C; IR (KBr) ν_{max} 3060, 2992, 2959, 2905, 2891, 1645, 1632, 1602, 1584, 1516, 1481, 1450, 1386, 1362, 1345, 1303, 1255, 1208, 1177, 1156, 1118, 1099, 1090, 1025, 966, 927, 916, 884, 858, 822, 804, 768, 759 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 2H), 7.66 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.18 (td, *J* = 8.4, 1.6 Hz, 2H), 7.36 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.29 (td, *J* = 7.6, 1.2 Hz, 2H), 1.32 (s, 18H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 186.7, 154.1, 148.0, 137.5, 130.0, 129.9, 129.1, 125.1, 123.8, 123.3, 116.9, 35.6, 29.6; MS (EI): *m/z* 384 (M$^+$); HRMS (EI): Calcd for $C_{27}H_{28}O_2$: 384.2089, Found 384.2080.

3: mp 238-239 °C; IR (KBr) ν_{max} 2957, 2859, 1631, 1608, 1579, 1565, 1515, 1455, 1431, 1386, 1361, 1340, 1257, 1088, 1072, 1024, 963, 927, 881, 821, 771, 755, 743 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.2, 1.2 Hz, 2H), 7.55-7.53 (m, 4H), 7.39 (td, *J* = 7.8, 1.6 Hz, 2H), 7.34 (td, *J* = 7.8, 1.6 Hz, 2H), 1.29 (s, 18H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 186.6, 148.4, 145.3, 135.1, 134.3, 130.14, 130.11, 127.9, 127.1, 126.9, 125.9, 35.6, 29.5; MS (EI): *m/z* 400 (M^+); HRMS (EI): Calcd for $C_{27}H_{28}OS$: 400.1861, Found 400.1860.

4: mp 218-220 °C; IR (KBr) ν_{max} 3057, 2998, 2949, 2923, 2858, 1737, 1645, 1610, 1561, 1534, 1482, 1455, 1431, 1408, 1387, 1362, 1338, 1306, 1254, 1219, 1198, 1178, 1160, 1102, 1083, 1040, 1024, 965, 927, 916, 878, 850, 821, 803, 767, 741 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.46-7.35 (m, 8H), 7.11 (s, 2H), 7.00 (s, 2H), 1.22 (s, 18H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 186.18, 151.7, 147.8, 136.5, 134.2, 131.0, 129.9, 129.1, 128.9, 128.4, 127.9, 127.6, 35.2, 29.4; MS (EI): *m/z* 394 (M^+); HRMS (EI): Calcd for $C_{29}H_{30}O$: 394.2297, Found 394.2316.

Synthesis of **11:** A solution of 9(10*H*)-acridone (0.50 mmol, 0.098 g), 1-bromo-4-*tert*-butylbenzene (0.50 mmol, 0.106 g), CuI (0.052 mmol, 0.010 g), dipivaloylmethane (0.11 mmol, 0.020 g), and K_2CO_3 (1.5 mmol, 0.103 g) in DMF (4.0 mL) was stirred at 155 °C under an argon atmosphere. After being stirred at 155 °C for 16 and 20 h, 1-bromo-4-*tert*-butylbenzene (0.50 mmol, 0.106 g) was added each time. After being stirred at 155 °C for 24 h, the reaction mixture was added with water and the resulting precipitate was collected by suction filtration and washed with MeOH to give **11** (81%, 0.41 mmol, 0.144 g).

11: mp >250 °C; IR (KBr) ν_{max} 3068, 2962, 1680, 1636, 1599, 1525, 1508, 1483, 1459, 1359, 1345, 1302, 1270, 1200, 1171, 1159, 1118, 1102, 1040, 1022, 935, 867, 840, 830, 757 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.29-7.26 (m, 4H), 6.79 (d, *J* = 8.8 Hz, 2H), 1.46 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 178.2, 152.8, 143.2, 136.0, 133.2, 129.3, 127.9, 127.2, 121.7, 121.4, 116.9, 35.0, 31.4; MS (EI): *m/z* 327 (M^+); HRMS (EI): Calcd for $C_{23}H_{21}NO$: 327.1623, Found 327.1633.

Synthesis of **5:** A solution of *N*-arylacridone **11** (0.5 mmol, 0.164 g) in THF (20 mL) was added to a solution of the lithium agent **12**, which was prepared from *n*-BuLi (1.6 mmol, 1.0 mL; 1.6 M in hexane solution) and (4-bromo-2,6-di*tert*-butylphenoxy)trimethylsilane (1.5 mmol, 0.536 g) in THF (4.0 mL) at -78 °C for 1 h. The reaction was conducted at -78 °C and gradually warmed to room temperature for 24 h, to the reaction mixture was added water, then the resulting mixture was extracted several times with $CHCl_3$. The organic fraction was washed with brine and dried over $MgSO_4$. After removal of the solvent, the residue was purified by chromatography on SiO_2 ($CHCl_3$/EtOAc/hexane = 1/1/2 as an eluent) to give the compound **5** (74%, 0.37 mmol, 0.178 g).

5: mp >250 °C; IR (KBr) ν_{max} 3081, 2954, 2905, 2876, 1595, 1573, 1576, 1505, 1481, 1451, 1424, 1383, 1356, 1283, 1252, 1207, 1170, 1139, 1107, 1093, 1052, 1018, 972, 923, 882, 845, 835, 814, 778, 752cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.78 (s, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.29-7.25 (m, 4H), 7.19 (t, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 8.0 Hz, 2H), 1.45 (s, 9H), 1.35 (s, 18H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 185.7, 152.4, 146.3, 143.2, 142.5, 136.3, 131.0, 129.81, 129.77, 129.56, 127.8, 123.5, 121.1, 121.0, 114.8, 35.6, 35.0, 31.4, 29.7; MS (EI): *m/z* 515 (M^+); HRMS (EI): Calcd for $C_{37}H_{41}NO$: 515.3188, Found 515.3171.

REFERENCES AND NOTES

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15. In order to investigate the structure of **5** in DMSO solution, the ^{1}H-NMR spectrum was measured in DMSO-d_6 at 100 °C due to low solubility in polar solvents. However, the ^{1}H-NMR spectrum of **5** in DMSO-d_6 was quite similar to that of **5** in $CDCl_3$.