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# Catalytic amide base system generated *in situ* for 1,3-diene formation from allylbenzenes and carbonyls

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**General methods.** All reactions were carried out under N<sub>2</sub> or Ar atmosphere. Flash column chromatography was performed with Kanto silica gel 60 N (spherical, neutral, 70-230  $\mu$ m). Preparative thin-layer chromatography was performed with silica gel (Wakogel<sup>®</sup> B-5F). Melting points (Mp) were determined with a Yazawa micro melting point apparatus without correction. Infrared (IR) data were recorded on SensIR ATR (Attenuated Total Reflectance) FT-IR, and absorbance frequencies are reported in reciprocal centimeters (cm<sup>-1</sup>). NMR data were recorded on a JEOL AL400 spectrometer (395.75 MHz for <sup>1</sup>H, 99.50 MHz for <sup>13</sup>C) or a JEOL ECA600 spectrometer (150.907 MHz for 13C). Chemical shifts are expressed in  $\delta$  (parts per million, ppm) values, and coupling constants are expressed in herts (Hz). <sup>1</sup>H NMR spectra were referenced to tetramethylsilane as an internal standard or to a solvent signal (CDCl<sub>3</sub>: 7.26 ppm). <sup>13</sup>C NMR spectra were referenced to a solvent signal (CDCl<sub>3</sub>: 7.0 ppm; CD<sub>3</sub>OD: 49.0 ppm). Low and high resolution mass spectra (LRMS and HRMS) were obtained from Mass Spectrometry Resource, Graduate School of Pharmaceutical Sciences, Tohoku University, on a JEOL JMS-DX 303 and JMS-700/JMS-T 100 GC spectrometer, respectively.

**Materials.** Unless otherwise noted, materials were purchased from Tokyo Kasei Co., Aldrich Inc. and other commercial suppliers and were used as received. Tetramethylammonium fluoride (TMAF) and N(TMS)<sub>3</sub> were purchased from Aldrich Inc. and Acros Co., respectively, and were used as received. DMF was distilled over CaH<sub>2</sub> under a reduced pressure. DMI was distilled over 4Å molecular sieves under a reduced pressure. **1b**<sup>1</sup>, **1c**<sup>1</sup>, **1d**<sup>2</sup>, **1f**<sup>1</sup>, **1g**<sup>1</sup>, **1h**<sup>3</sup>, **1j**<sup>4</sup>, **1I**<sup>5</sup>, **1m**<sup>6</sup>, **1n**,<sup>3</sup> and **1o**<sup>7</sup> were prepared according to the literature procedures. **1e** was prepared according to the following Schemes S3. Flash column chromatography was performed with Kanto silica gel 60 N (spherical, neutral, 70–230 mesh).

Scheme S1. Reactions of 1a and 2a in the presence of KHMDS or NaHMDS.<sup>*a, b*</sup>



<sup>a</sup>Reactions were conducted on a 0.2 mmol scale. <sup>b</sup>Yields were determined by <sup>1</sup>H-NMR analysis.





<sup>a</sup>Reactions were conducted on a 0.2 mmol scale. <sup>b</sup>Yields were determined by <sup>1</sup>H-NMR analysis.

7

0%

16%

8

0%

0%

3be

20%

5%

KHMDS:

NaHMDS:

Scheme S3. Preparation of 1e



**1-AllyI-3-chlorobenzene** (**1e**). To a solution of 1-bromo-3-chlorobenzene (**S1**, 1.53 g, 8.00 mmol) in Et<sub>2</sub>O (18 mL) were added dropwise *i*-PrMgCl·LiCl in THF (1.30 M, 2.2 mL, 2.9 mmol) and *n*-BuLi in hexane (1.56 M, 3.6 mL, 5.6 mmol) at -10 °C. After stirring for 2 h at -10 °C, allyl bromide (0.76 mL, 8.8 mmol) was added to the reaction mixture at the temperature. After stirring at room temperature for 15 h, the reaction mixture was quenched with saturated NH<sub>4</sub>Cl aqueous solution and extracted with Et<sub>2</sub>O. The combined organic layer was washed with brine, dried over MgSO<sub>4</sub>, and concentrated. The residue was purified by column chromatography on silica gel (hexane) to give **1b** (0.32 g, 2.08 mmol, 51%) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  3.36 (d, 2H, *J* = 6.8 Hz), 5.04-5.14 (m, 2H), 5.86-6.00 (m, 1H), 7.06 (d, 1H, *J* = 6.8 Hz), 7.15-7.27 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  39.78, 116.5, 126.3, 126.8, 128.7, 129.6, 136.5, 142.1. LRMS (EI) *m/z*: 152 (M<sup>+</sup>). HRMS Calcd. for C<sub>9</sub>H<sub>9</sub>Cl: 152.0392, found: 152.0379. IR (neat): 3080, 2980, 2908, 1597, 1574, 1476, 1430, 1079, 992, 916, 777, 710 cm<sup>-1</sup>.

General procedure of amide-base generated *in situ* catalyzed 1,3-diene formations (Table 1, Figures 2 and 3, and Scheme 1)



(*E*)-Buta-1,3-diene-1,1,4-triyltribenzene (3aa). In a glove box under an Ar atmosphere, to a mixture of 1a (25.1 mg, 0.212 mmol), 2a (73.3 mg, 0.402 mmol), and N(TMS)<sub>3</sub> (142.4 mg, 0.610 mmol) in DMF (1 mL) was added TMAF (3.7 mg, 0.040 mmol) in a vial equipped with a stirrer bar. The vial was sealed with a cap containing an inner Teflon film. After stirring at room temperature for 5 h, H<sub>2</sub>O (1 mL) was added to the reaction mixture at room temperature. The mixture was stirred at room temperature for 1 h, and H<sub>2</sub>O (10 mL) was added. The mixture was extracted with AcOEt (10 mL x 3), washed with H<sub>2</sub>O (10 mL) and brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The crude material was purified by column chromatography on silica gel (hexane:toluene = 10:1) to afford **3aa** (53.7 mg, 0.190 mmol, 90%) as a white crystal: Mp 99-100 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane) (lit. 100-102°C<sup>8a</sup>). <sup>1</sup>H NMR

(400 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  6.69-6.78 (m, 1H), 6.84-6.94 (m, 2H), 7.17 (t, 1H, *J* = 7.1 Hz), 7.22-7.33 (m, 11H), 7.34-7.45 (m, 3H). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  126.2, 126.4, 127.1, 127.7, 127.77, 127.81, 127.9, 128.5, 128.6, 128.9, 130.1, 134.1, 137.0, 139.2, 141.4, 142.5. LRMS (EI) *m/z*: 282 (M<sup>+</sup>). HRMS: Calcd. for C<sub>23</sub>H<sub>20</sub>: 282.1408. Found: 282.1416. IR (neat): 3056, 3027, 2306, 1487, 1442, 965, 752, 701 cm<sup>-1</sup>. The spectra data matched those reported in the literature.<sup>8b</sup>



(*E*)-(4-(4-Fluorophenyl)buta-1,3-diene-1,1-diyl)dibenzene (3ba). According to the general procedure analogous to that described for 3aa, 3ba (55.4 mg, 0.184 mmol, 89%) was obtained from 1b (28.2 mg, 0.207 mmol) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  6.68 (d, 1H, *J* = 14.8 Hz), 6.75-6.89 (m, 2H), 6.95 (t, 2H, *J* = 8.8 Hz), 7.20-7.32 (m, 9H), 7.34-7.46 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  115.5 (d, *J* = 22.9 Hz), 126.8, 127.48, 127.51, 127.56, 127.9, 128.0 (d, *J* = 14.3 Hz), 128.22, 128.25, 130.6, 132.5, 133.7 (d, *J* = 4.3 Hz), 139.7, 142.2, 143.2, 162.2 (d, *J* = 247.8 Hz). LRMS (EI) *m/z*: 300 (M<sup>+</sup>). HRMS Calcd. for C<sub>22</sub>H<sub>17</sub>F: 300.1314, found: 300.1339. IR (neat): 3029,1599, 1505, 1232, 1156, 965, 815, 760 cm<sup>-1</sup>.



(*E*)-(4-(4-Chlorophenyl)buta-1,3-diene-1,1-diyl)dibenzene (3ca). According to the general procedure analogous to that described for 3aa, 3ca (54.0 mg, 0.170 mmol, 87%) was obtained from 1c (30.0 mg, 0.197 mmol) as a white solid: Mp 124-126 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  6.58-6.68 (m, 1H), 6.79-6.88 (m, 2H), 7.14-7.20 (m, 4H), 7.22-7.31 (m, 7H), 7.34-7.43 (m, 3H). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  127.2, 127.7, 127.80, 127.84, 127.9, 128.5, 128.6, 128.9, 130.1, 132.0, 132.8, 135.9, 139.0, 141.4, 143.0. LRMS (EI) *m/z*: 316 (M<sup>+</sup>). HRMS Calcd. for C<sub>22</sub>H<sub>17</sub>Cl: 316.1018, found: 316.1015. IR (neat): 3021, 2367, 1487, 1089, 976, 768, 703 cm<sup>-1</sup>.



(*E*)-(4-(4-Bromophenyl)buta-1,3-diene-1,1-diyl)dibenzene (3da). According to the general procedure analogous to that described for 3aa, 3da (67.4 mg, 0.187 mmol, 83%) was obtained from 1d (44.1 mg, 0.224 mmol) as a white solid: Mp 134-136 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  6.62-6.69 (m, 1H), 6.82-6.91 (m, 2H), 7.15 (d, 2H, *J* = 8.3 Hz), 7.24-7.32 (m, 7H),

7.35-7.40 (m, 3H), 7.40-7.45 (m, 2H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  121.1, 127.6, 127.76, 127.81, 127.84, 127.9, 128.3, 130.56, 130.60, 131.6, 131.7, 132.4, 136.4, 139.6, 142.1, 143.8. LRMS (EI) *m/z*: 360 (M<sup>+</sup>). HRMS Calcd. for C<sub>22</sub>H<sub>17</sub>Br: 360.0513, found: 360.0499. IR (neat): 3028, 1594, 1483, 1443, 1069, 976, 810, 768, 702 cm<sup>-1</sup>.



(*E*)-(4-(3-Chlorophenyl)buta-1,3-diene-1,1-diyl)dibenzene (3ea). According to the general procedure analogous to that described for 3aa, 3ea (54.7 mg, 0.173 mmol, 84%) was obtained from 1e (31.5 mg, 0.206 mmol) as a white solid: Mp 92 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  6.60-6.69 (m, 1H), 6.82-6.91 (m, 2H), 7.11-7.19 (m, 3H), 7.23-7.32 (m, 8H), 7.36-7.40 (m, 1H), 7.40-7.45 (m, 2H). <sup>13</sup>C NMR (150 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  124.3, 127.0, 127.5, 127.9, 128.0, 128.1, 128.3, 128.57, 128.59, 128.62, 130.0, 130.9, 132.8, 134.9, 139.8, 140.1, 142.7, 144.6. LRMS (EI) *m/z*: 316 (M<sup>+</sup>). HRMS Calcd. for C<sub>22</sub>H<sub>17</sub>Cl: 316.1018, found: 316.1037. IR (neat): 3026, 2366,1584, 1557, 1476, 1441, 1074, 975, 962, 767 cm<sup>-1</sup>.



(*E*)-(4-(*o*-Tolyl)buta-1,3-diene-1,1-diyl)dibenzene (3fa). According to the general procedure analogous to that described for 3aa, 3fa (49.4 mg, 0.167 mmol, 81%) was obtained from 1f (27.1 mg, 0.205 mmol) as a colorless oil: Mp 92 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  2.37 (s, 3H), 6.81 (dd, 1H, *J* = 11.0 Hz, 15.4 Hz), 6.94 (dd, 2H, *J* = 12.9 Hz, 15.9 Hz), 7.05-7.15 (m, 3H), 7.21-7.35 (m, 8H), 7.35-7.44 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  19.8, 125.2, 126.0, 127.38, 127.41, 127.44, 127.6, 128.17, 128.19, 128.22, 128.6, 130.4, 130.6, 131.4, 135.5, 136.3, 139.8, 142.3, 143.0. LRMS (EI) *m/z*: 296 (M<sup>+</sup>). HRMS Calcd. for C<sub>22</sub>H<sub>18</sub>: 296.1565, found: 296.1546. IR (neat): 3021, 2926, 1598, 1443, 965, 748, 700 cm<sup>-1</sup>.



(*E*)-(4-(*p*-Tolyl)buta-1,3-diene-1,1-diyl)dibenzene (3ga). According to the general procedure analogous to that described for 3aa, except that the reaction was conducted with 2a (41.2 mg, 0.226 mmol), 3ga (37.5 mg, 0.127 mmol, 62%) was obtained from 1g (29.5 mg, 0.223 mmol) as a white

solid: Mp 117-119 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane) (lit. 116-117 °C (EtOH)<sup>9</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  2.30 (s, 3H), 6.65-6.75 (m, 1H), 6.80-6.89 (m, 2H), 7.05 (d, 2H, J = 7.8 Hz), 7.19 (d, 2H, J = 8.3 Hz), 7.22-7.32 (m, 7H), 7.32-7.44 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 21.2, 126.2, 126.4, 127.3, 127.4, 127.6, 128.19, 128.21, 128.5, 129.3, 130.7, 133.9, 134.7, 137.4, 139.9, 142.4, 142.5. LRMS (EI) *m/z*: 296 (M<sup>+</sup>). HRMS Calcd. for C<sub>23</sub>H<sub>20</sub>: 196.1565, found: 296.1551. IR (neat): 3028, 2917, 1442, 979, 766, 700 cm<sup>-1</sup>.

(*E*)-4-(4,4-Diphenylbuta-1,3-dien-1-yl)-1,1'-biphenyl (3ha). According to the general procedure analogous to that described for 3aa, 3ha (60.0 mg, 0.167 mmol, 85%) was obtained from 1h (38.3 mg, 0.197 mmol) as a white solid: Mp 143 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane). <sup>1</sup>H NMR (600MHz, CDCl<sub>3</sub>/TMS)  $\delta$ 6.71-6.81 (m, 1H), 6.87-6.98 (m, 2H), 7.23-7.27 (m, 1H), 7.27-7.34 (m, 7H), 7.34-7.46 (m, 7H), 7.50 (d, 2H, *J* = 7.6 Hz), 7.56 (d, 2H, *J* = 7.6 Hz). <sup>13</sup>C NMR (150 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  127.2, 127.3, 127.4, 127.5, 127.6, 127.76, 127.80, 128.1, 128.57, 128.61, 128.9, 129.0, 131.1, 134.2, 137.0, 140.4, 140.6, 141.1, 142.9, 143.6. LRMS (EI) *m/z*: 358 (M<sup>+</sup>). HRMS Calcd. for C<sub>28</sub>H<sub>22</sub>: 358.1721, found: 358.1713. IR (neat): 3030, 1598, 1484, 1445, 976, 820 cm<sup>-1</sup>.



(*E*)-(4-(4-Methoxyphenyl)buta-1,3-diene-1,1-diyl)dibenzene (3ia). According to the general procedure analogous to that described for 3aa, except that the crude material was purified by preparative thin-layer chromatography of silica gel (hexane:toluene = 6:1), 3ia (54.3 mg, 0.174 mmol, 87%) was obtained from 1i (29.7 mg, 0.200 mmol) as a white solid: Mp 96-97 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane) (lit. 87-89 °C<sup>10</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  3.78 (s, 3H), 6.65-6.92 (m, 5H), 7.21-7.32 (m, 9H), 7.34-7.44 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  55.1, 114.0, 125.0, 127.2, 127.3, 127.4, 127.6, 128.1, 128.2, 128.5, 130.3, 130.6, 133.5, 139.9, 141.8, 142.3, 159.2. LRMS (EI) *m/z*: 312 (M<sup>+</sup>). HRMS Calcd. for C<sub>23</sub>H<sub>20</sub>O: 312.1514, found: 312.1498. IR (neat): 3022, 1603, 1507,1248, 1174, 1032, 976, 821, 760, 702 cm<sup>-1</sup>.



(E)-4-(4,4-Diphenylbuta-1,3-dien-1-yl)-N,N-dimethylaniline (3ja). In a glove box under an Ar atmosphere, to a mixture of 1j (31.9 mg, 0.198 mmol), 2a (74.9 mg, 0.411 mmol), and N(TMS)<sub>3</sub> (139.9 mg, 0.599 mmol) in DMF (1 mL) was added TMAF (4.1 mg, 0.044 mmol) in a vial equipped with a stirrer bar. The vial was sealed with a cap containing an inner Teflon film. After stirring at room temperature for 5 h, H<sub>2</sub>O (1 mL) was added to the reaction mixture at room temperature. The mixture was stirred at room temperature for 1 h, and H<sub>2</sub>O (10 mL) was added. The mixture was extracted with AcOEt (10 mL x 3), washed with H<sub>2</sub>O (10 mL) and brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. A solution of the residue in conc. HCl (1 mL) and DMF (1 mL) was heated at 60 °C for 2 h, and saturated NaHCO<sub>3</sub> aqueous solution (5 mL) was added. The mixture was extracted with AcOEt (10 mL x 3), washed with H<sub>2</sub>O (10 mL) and brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The crude material was filtered through a pad of silica gel (CH<sub>2</sub>Cl<sub>2</sub>) and concentrated, and that the residue was purified by GPC (CHCl<sub>3</sub>) to afford **3ja** (55.3 mg, 0.170 mmol, 86%) as a yellow solid: Mp 175-178 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane) (lit. 179-180 °C<sup>11</sup>). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>/TMS) δ 2.94 (s, 6H), 6.62 (d, 2H, J = 8.9 Hz), 6.65-6.75 (m, 2H), 6.86 (d, 1H, J = 9.7 Hz), 7.19-7.24 (m, 3H), 7.26-7.31 (m, 6H), 7.33-7.37 (m, 1H), 7.39-7.43 (m, 2H). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) δ 39.9, 112.3, 121.9, 124.9, 126.9, 127.2, 127.4, 127.5, 128.4, 128.6, 128.7, 130.2, 134.8, 139.5, 139.6, 141.8, 150.1. LRMS (EI) m/z: 325 (M<sup>+</sup>). HRMS Calcd. for C<sub>24</sub>H<sub>23</sub>N: 325.1830, found: 325.1833. IR (neat): 3022, 1584, 1517, 1441, 1354, 1189, 976, 814, 767 cm<sup>-1</sup>.



(*E*)-5-(4,4-Diphenylbuta-1,3-dien-1-yl)benzo[*d*][1,3]dioxole (3ka). According to the general procedure analogous to that described for 3aa, except that the crude material was purified by preparative thin-layer chromatography of silica gel (hexane:AcOEt = 10:1) and GPC (CHCl<sub>3</sub>), 3ka (66.8 mg, 0.205 mmol, 96%) was obtained from 1k (34.5 mg, 0.213 mmol) as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  5.92 (s, 2H), 6.61-6.87 (m, 6H), 7.21-7.33 (m, 8H), 7.34-7.46 (m, 3H). <sup>13</sup>C NMR (150 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  101.0, 106.2, 108.6, 121.6, 125.8, 127.6, 127.7, 128.0, 128.5, 128.6, 129.0, 131.0, 132.5, 134.4, 140.4, 142.7, 143.0, 147.8, 148.6. LRMS (EI) *m/z*: 326 (M<sup>+</sup>). HRMS Calcd. for C<sub>23</sub>H<sub>18</sub>O<sub>2</sub>: 326.1306, found: 326.1300. IR (neat): 3029, 2894, 1487, 1445, 1039, 964, 934, 754 cm<sup>-1</sup>.



Ethyl (*E*)-4-(4,4-Diphenylbuta-1,3-dien-1-yl)benzoate (3la). According to the general procedure analogous to that described for 3aa, except that the crude material was filtered through a pad of silica gel (hexane:AcOEt = 10:1) and concentrated, and that the residue was purified by GPC (CHCl<sub>3</sub>), **3la** 

(59.1 mg, 0.176 mmol, 82%) was obtained from **11** (38.7 mg, 0.203 mmol) as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  1.38 (t, 3H, J = 7.1 Hz), 4.35 (q, 2H, J = 7.2 Hz), 6.75 (d, 1H, J = 15.1 Hz), 6.89 (d, 1H, J = 11.2 Hz), 6.99 (dd, 1H, J = 15.1, 11.2 Hz), 7.20-7.53 (m, 12H), 7.93 (d, 2H, J = 8.3 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  14.3, 60.8, 126.2, 127.71, 127.73, 127.76, 127.81, 128.27, 128.29, 129.0, 129.5, 129.9, 130.6, 132.6, 139.5, 141.9, 142.0, 144.8, 166.3. LRMS (EI) *m/z*: 354 (M<sup>+</sup>). HRMS Calcd. for C<sub>25</sub>H<sub>22</sub>O<sub>2</sub>: 354.1619, found: 354.1604. IR (neat): 2981, 1710, 1602, 1269, 1176, 1106, 761 cm<sup>-1</sup>.



(*E*)-4-(4,4-Diphenylbuta-1,3-dien-1-yl)-*N*,*N*-diethylbenzamide (3ma). According to the general procedure analogous to that described for **3aa**, except that the crude material was purified by preparative thin-layer chromatography of silica gel (hexane:AcOEt = 10:1), **3ma** (68.4 mg, 0.179 mmol, 87%) was obtained from **1m** (45.0 mg, 0.207 mmol) as a yellow oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  1.15 (br, 6H), 3.38 (br, 4H), 6.71 (d, 1H, *J* = 15.1 Hz), 6.84-6.94 (m, 2H), 7.22-7.33 (m, 11H), 7.34-7.39 (m, 1H), 7.39-7.44 (m, 2H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  12.9, 14.1, 39.3, 43.2, 126.3, 126.7, 127.6, 127.9, 128.0, 128.18, 128.21, 130.5, 132.9, 135.9, 138.3, 139.6, 142.1, 143.9, 171.0. LRMS (EI) *m/z*: 381 (M<sup>+</sup>). HRMS Calcd. for C<sub>27</sub>H<sub>27</sub>NO: 381.2092, found: 381.2056. IR (neat): 2975, 2240, 1623, 1429, 1288, 1096, 909, 729 cm<sup>-1</sup>.



(*E*)-2-(4,4-Diphenylbuta-1,3-dien-1-yl)benzo[*b*]thiophene (3na). According to the general procedure analogous to that described for 3aa, 3na (63.4 mg, 0.187 mmol, 94%) was obtained from 1n (34.8 mg, 0.200 mmol) as an orange solid: Mp 140-144 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  6.77 (dd, 1H, *J* = 14.9, 11.0 Hz), 6.85 (d, 1H, *J* = 11.2 Hz), 6.94 (d, 1H, *J* = 14.6 Hz), 7.14 (s, 1H), 7.20-7.34 (m, 9H), 7.37-7.48 (m, 3H), 7.66 (dd, 2H, *J* = 11.7, 7.8 Hz). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  122.4, 123.7, 123.8, 124.9, 125.1, 127.1, 127.2, 127.5, 127.9, 128.0, 128.55, 128.63, 128.8, 130.1, 138.1, 138.9, 140.0, 141.1, 142.4, 143.5. LRMS (EI) *m/z*: 338 (M<sup>+</sup>). HRMS Calcd. for C<sub>24</sub>H<sub>18</sub>S: 338.1129, found: 338.1105. IR (neat): 3058, 3013, 1489, 1445, 966, 752 cm<sup>-1</sup>.



(*E*)-2-(4,4-Diphenylbuta-1,3-dien-1-yl)-1-methyl-1*H*-indole (3oa). According to the general procedure analogous to that described for **3aa**, except that the reaction was conducted with TMAF (5.4 mg, 0.058 mmol) in DMI (1 mL), **3oa** (62.3 mg, 0.186 mmol, 88%) was obtained from **1o** (36.1 mg, 0.211 mmol) as a yellow solid: Mp 169-172 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  3.74 (s, 3H), 6.57 (s, 1H), 6.72-6.86 (m, 1H), 6.87-7.01 (m, 2H), 7.01-7.10 (m, 1H), 7.12-7.20 (m, 1H), 7.20-7.36 (m, 8H), 7.36-7.46 (m, 3H), 7.48 (d, 1H, *J* = 8.0 Hz). <sup>13</sup>C NMR (150 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  29.1, 100.5, 109.4, 120.3, 120.9, 122.2, 122.6, 127.8, 127.9, 128.1, 128.60, 128.64, 128.77, 128.83, 128.9, 131.0, 138.3, 138.8, 140.3, 142.8, 143.5. LRMS (EI) *m/z*: 335 (M<sup>+</sup>). HRMS Calcd. for C<sub>25</sub>H<sub>21</sub>N: 335.1674, found: 335.1680. IR (neat): 3044, 1456, 1446, 1321, 972, 789, 766, 728 cm<sup>-1</sup>.



(*E*)-4,4'-(4-Phenylbuta-1,3-diene-1,1-diyl)bis(fluorobenzene) (3ab). According to the general procedure analogous to that described for 3aa, except that the crude material was purified by column chromatography on silica gel (hexane:toluene = 20:1), 3ab (49.8 mg, 0.156 mmol, 79%) was obtained from 1a (23.4 mg, 0.198 mmol) as a white solid: Mp 123-125 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  6.68-6.87 (m, 3H), 6.99 (t, 2H, *J* = 8.8 Hz), 7.12 (t, 2H, *J* = 8.5 Hz), 7.17-7.34 (m, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  115.2 (d, *J* = 21.4 Hz), 115.4 (d, *J* = 21.4 Hz), 126.5, 126.6, 127.7, 128.4, 128.6, 129.1 (d, *J* = 7.4 Hz), 132.2 (d, *J* = 8.2 Hz), 134.3, 135.5 (d, *J* = 3.3 Hz), 137.3, 138.3 (d, *J* = 3.3 Hz), 140.9, 162.3 (d, *J* = 249.4 Hz), 162.4 (d, *J* = 248.6 Hz). LRMS (EI) *m/z*: 318 (M<sup>+</sup>). HRMS Calcd. for C<sub>22</sub>H<sub>16</sub>F<sub>2</sub>: 318.1220, found: 318.1216. IR (neat): 3030, 2363, 1899, 1599, 1503, 1222, 1158, 970, 842, 831, 752 cm<sup>-1</sup>.



(*E*)-4,4'-(4-Phenylbuta-1,3-diene-1,1-diyl)bis(chlorobenzene) (3ac). According to the general procedure analogous to that described for 3aa, 3ac (50.1 mg, 0.143 mmol, 71%) was obtained from 1a (23.9 mg, 0.202 mmol) as a white solid: Mp 132-134 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  6.70-6.87 (m, 3H), 7.14-7.23 (m, 5H), 7.23-7.34 (m, 6H), 7.40 (d, 2H, *J* = 7.8 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 126.3, 126.5, 127.9, 128.5, 128.6, 128.67, 128.73, 129.1, 131.9, 133.5, 133.7, 135.0, 137.1, 137.8, 140.36, 140.45. LRMS (EI) *m/z*: 350 (M<sup>+</sup>). HRMS Calcd. for C<sub>22</sub>H<sub>16</sub>Cl<sub>2</sub>: 350.0629, found: 350.0622. IR (neat): 3049, 1487, 1085, 1013, 824, 750 cm<sup>-1</sup>.



(*E*)-4,4'-(4-Phenylbuta-1,3-diene-1,1-diyl)bis(methoxybenzene) (3ad). According to the general procedure analogous to that described for 3aa, except that the crude material was purified by column chromatography on silica gel (hexane:AcOEt = 10:1), 3ad (65.3 mg, 0.191 mmol, 92%) was obtained from 1a (24.6 mg, 0.208 mmol) as a white solid: Mp 126 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  3.80 (s, 3H), 3.86 (s, 3H), 6.68 (d, 1H, *J* = 15.6 Hz), 6.74 (d, 1H *J* = 10.8 Hz), 6.83 (d, 2H, *J* = 8.8 Hz), 6.86-6.97 (m, 3H), 7.12-7.33 (m, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  55.2, 55.3, 113.56, 113.58, 126.3, 126.4, 127.2, 127.5, 128.5, 128.9, 131.8, 132.3, 132.5, 135.3, 137.7, 142.5, 159.0, 159.2. LRMS (EI) *m/z*: 342 (M<sup>+</sup>). HRMS Calcd. for C<sub>24</sub>H<sub>22</sub>O<sub>2</sub>: 342.1619, found: 342.1632. IR (neat): 3028, 3006, 2943, 2832, 1601, 1507, 1246, 1174, 1033, 969, 753 cm<sup>-1</sup>. The spectra data matched those reported in the literature.<sup>12</sup>



(*E*)-9-(3-Phenylallylidene)-9*H*-xanthene (3ae). According to the general procedure analogous to that described for 3ae, except that the crude material was purified by preparative thin-layer chromatography of silica gel (hexane:toluene = 10:1), 3ae (46.3 mg, 0.156 mmol, 81%) was obtained from 1a (22.8 mg, 0.193 mmol) as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  6.65 (d, 1H, *J* = 11.2 Hz), 6.76 (d, 1H, *J* = 15.6 Hz), 7.05-7.25 (m, 6H), 7.25-7.33 (m, 3H), 7.40 (d, 2H, *J* = 7.8 Hz), 7.49 (t, 1H, *J* = 13.4 Hz), 7.60 (d, 1H, *J* = 7.8 Hz), 7.68 (d, 1H, *J* = 7.8 Hz). <sup>13</sup>C NMR (150 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$ 117.0, 117.2, 123.3, 123.4, 123.5, 124.1, 124.5, 125.9, 126.3, 126.8, 127.6, 127.8, 128.6, 128.7, 129.0, 129.2, 135.2, 138.1, 152.1, 153.4. LRMS (EI) *m/z*: 296 (M<sup>+</sup>). HRMS Calcd. for C<sub>22</sub>H<sub>16</sub>O: 296.1201, found: 296.1234. IR (neat): 3034,1594,1450, 1261, 746 cm<sup>-1</sup>.



(*E*)-9-(3-Phenylallylidene)-9*H*-thioxanthene (3af). According to the general procedure analogous to that described for 3aa, except that the crude material was purified by preparative thin-layer chromatography of silica gel (hexane:toluene = 10:1) and GPC (CHCl<sub>3</sub>), 3af (60.8 mg, 0.195 mmol, 97%) was obtained from 1a (23.8 mg, 0.201 mmol) as a yellow solid: Mp 163-166 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane) (lit. 165-166 °C<sup>13</sup>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  6.70 (d, 1H, *J* = 11.7 Hz), 6.82 (d, 1H, *J* = 15.6 Hz), 7.18-7.42 (m, 11H), 7.48 (d, 1H, *J* = 7.8 Hz), 7.58 (t, 2H, *J* = 8.1 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  125.2, 125.88, 125.90, 126.1, 126.6, 126.8, 126.9, 127.0, 127.3, 127.7, 128.6, 129.5, 130.0, 131.9, 133.6, 133.7, 135.5, 136.1, 137.3, 137.8. LRMS (EI) *m/z*: 312 (M<sup>+</sup>). HRMS Calcd. for C<sub>22</sub>H<sub>16</sub>S: 312.0972, found: 312.0963. IR (neat): 3060, 1460, 1436, 969, 765 cm<sup>-1</sup>.



(E)-9-(3-Phenylallylidene)-9H-fluorene (3ag). According to the procedure analogous to that

described for **3ja**, except that the reaction was conducted with TMAF (5.4 mg, 0.058 mmol) in DMI (1 mL) at 40 °C and that the crude material was purified by preparative thin-layer chromatography of silica gel (hexane:toluene = 10:1), **3ag** (34.9 mg, 0.124 mmol, 60%) was obtained from **1a** (24.5 mg, 0.207 mmol) as a yellow solid: Mp 163-164 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  7.01 (d, 1H, J = 15.2 Hz), 7.25-7.44 (m, 8H), 7.59 (d, 2H, J = 7.6 Hz), 7.65-7.78 (m, 3H), 7.97 (dd, 1H, J = 15.2, 12.4 Hz), 8.02-8.09 (m, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  119.6, 120.0, 120.1, 124.8, 125.0, 126.88, 126.95, 127.06, 127.14, 127.78, 127.89, 128.5, 128.8, 135.1, 137.0, 137.2, 138.7, 138.9, 139.6, 140.9. LRMS (EI) *m/z*: 280 (M<sup>+</sup>). HRMS Calcd. for C<sub>22</sub>H<sub>16</sub>: 280.1252, found: 280.1247. IR (neat): 3050, 2997, 1618, 1446, 1439, 957, 779, 722 cm<sup>-1</sup>.



(*E*)-5-(3-Phenylallylidene)-5*H*-dibenzo[*a*,*d*][7]annulene (3ah). According to the procedure analogous to that described for 3ja, except that the crude material was purified by column chromatography on silica gel (hexane:toluene = 10:1), 3ah (49.2 mg, 0.161 mmol, 77%) was obtained from 1a (24.8 mg, 0.210 mmol) as a white solid: Mp 148 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  6.37 (d, 1H, *J* = 11.2 Hz), 6.65 (d, 1H, *J* = 15.6 Hz), 6.81-6.93 (m, 3H), 7.12-7.42 (m, 13H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  125.9, 126.4, 127.1, 127.3, 127.4, 127.5, 128.0, 128.50, 128.52, 128.85, 128.87, 129.9, 131.3, 131.4, 133.0, 134.20, 134.22, 135.0, 137.3, 137.4, 142.3, 142.8. LRMS (EI) *m/z*: 306 (M<sup>+</sup>). HRMS Calcd. for C<sub>24</sub>H<sub>18</sub>: 306.1408, found: 306.1387. IR (neat): 3052, 3022, 1488, 1430, 968, 777 cm<sup>-1</sup>.



((1*E*,3*Z*)-5,5-Dimethylhexa-1,3-diene-1,4-diyl)dibenzene (3ai). According to the general procedure analogous to that described for 3aa, except that the crude material was purified by column chromatography on silica gel (hexane:toluene = 10:1) and GPC (CHCl<sub>3</sub>), 3ai (36.6 mg, 0.139 mmol, 67%) was obtained from 1a (24.6 mg, 0.208 mmol) as a colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  1.14 (s, 1H), 6.26 (dd, 1H, *J* = 15.3, 10.5 Hz), 6.38 (d, 1H, *J* = 10.2 Hz), 6.51 (d, 1H, *J* = 15.0 Hz), 7.06-7.22 (m, 7H), 7.28-7.38 (m, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$ 29.7, 36.3, 124.6, 126.2, 126.5, 127.0, 127.56, 127.62, 128.4, 130.0, 131.0, 137.7, 140.1, 153.9. LRMS (EI) *m/z*: 262 (M<sup>+</sup>). HRMS Calcd. for C<sub>20</sub>H<sub>22</sub>: 262.1721, found: 262.1695. IR (neat): 2965, 2952, 1490, 1479, 1358, 1233, 965, 746, 713 cm<sup>-1</sup>.



((1*E*,3*E*)-5,5-Dimethylhexa-1,3-dien-1-yl)benzene (3aj). According to the procedure analogous to that described for 3aa, except that the reaction was conducted with TMAF (5.2 mg, 0.056 mmol) in DMI (1 mL) at 60 °C and that the crude material was purified by column chromatography on silica gel (hexane:toluene = 10:1), 3aj (27.3 mg, 0.147 mmol, 67%) was obtained from 1a (25.7 mg, 0.218 mmol) as a colorless oil. <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN)  $\delta$  1.07 (s, 9H), 5.91 (d, 1H, *J* = 15.8 Hz), 6.20 (dd, 1H, *J* = 15.8, 10.3 Hz), 6.51 (d, 1H, *J* = 15.8 Hz), 6.83 (dd, 1H, *J* = 15.8, 10.3 Hz), 7.21 (t, 1H, *J* = 7.5 Hz), 7.31 (t, 2H, *J* = 7.9 Hz), 7.42 (d, 2H, *J* = 7.6 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 29.6, 33.4, 125.4, 126.1, 127.0, 128.5, 129.9, 130.2, 137.7, 146.8. LRMS (EI) *m/z*: 186 (M<sup>+</sup>). HRMS Calcd. for C<sub>14</sub>H<sub>18</sub>: 186.1408, found: 186.1403. IR (neat): 2959, 1595, 1248, 989, 747, 702 cm<sup>-1</sup>. The spectra data matched those reported in the literature.<sup>14</sup>



((1*E*,3*Z*)-5-methylhexa-1,3-diene-1,4-diyl)dibenzene (3ak). According to the general procedure analogous to that described for 3aa, except that the reaction was conducted in DMI (1 mL) at 60 °C and that the crude material was purified by column chromatography on silica gel (hexane:toluene = 10:1), 3ak (35.7 mg, 0.144 mmol, 73%) was obtained from 1a (23.2 mg, 0.196 mmol) as a colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  1.09 (d, 6H, *J* = 6.8 Hz), 2.66-2.78 (m, 1H), 6.26 (d, 1H, *J* = 11.0 Hz), 6.54 (d, 1H, *J* = 15.8 Hz), 6.64 (dd, 1H, *J* = 15.8, 11.0 Hz), 7.11-7.15 (m, 1H), 7.18 (d, 2H, *J* = 6.9 Hz), 7.20-7.23 (m, 3H), 7.28-7.34 (m, 2H), 7.37 (t, 2H, *J* = 7.5 Hz). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  22.0, 36.1, 124.6, 126.3, 126.9, 127.12, 127.15, 128.1, 128.6, 129.2, 131.4, 137.9, 141.1, 151.1. LRMS (EI) *m/z*: 248 (M<sup>+</sup>). HRMS Calcd. for C<sub>19</sub>H<sub>20</sub>: 248.1565, found: 248.1559.



(*E*)-9-(3-(4-Methoxyphenyl)allylidene)-9*H*-xanthene (3be). According to the general procedure analogous to that described for 3aa, except that the reaction was conducted with TMAF (5.9 mg, 0.063 mmol) in DMI (1 mL) at room temperature, 3be (72.6 mg, 0.222 mmol, 98%) was obtained from 4b (33.6 mg, 0.227 mmol) as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS)  $\delta$  3.81 (s, 3H), 6.68 (d, 1H,

J = 11.2 Hz), 6.76 (d, 1H, J = 15.1 Hz), 6.87 (d, 2H, J = 8.8 Hz), 7.07-7.46 (m, 10H), 7.63 (d, 1H, J = 7.8 Hz), 7.72 (d, 1H, J = 6.8 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  55.3, 114.2, 116.6, 116.8, 122.97, 123.04, 123.1, 123.8, 123.9, 124.3, 125.6, 126.1, 127.7, 128.1, 128.3, 128.8, 130.5, 134.5, 151.5, 152.9, 159.3. LRMS (EI) m/z: 326 (M<sup>+</sup>). HRMS Calcd. C<sub>23</sub>H<sub>18</sub>O<sub>2</sub>: 326.1306, found: 326.1280. IR (neat): 3036, 2930, 2835, 1597, 1508, 1450, 1248, 1172, 1031, 750 cm<sup>-1</sup>.

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<sup>1</sup>H NMR spectra of **3aa** 



<sup>1</sup>H NMR spectra of **3ba** 



S18

<sup>1</sup>H NMR spectra of **3ca** 



<sup>1</sup>H NMR spectra of **3da** 



<sup>1</sup>H NMR spectra of **3ea** 





DEPT 45 spectra of 3ea





DEPT 135 spectra of 3ea







<sup>13</sup>C NMR spectra of **3ga** 



<sup>13</sup>C NMR spectra of **3ha** 



#### DEPT 90 NMR spectra of 3ha





#### <sup>1</sup>H NMR spectra of **3ia**



## <sup>1</sup>H NMR spectra of **3ja**





## S30

## DEPT 135 spectra of 3ja



<sup>13</sup>C NMR spectra of **3ka** 





## <sup>1</sup>H NMR spectra of **3la**



## <sup>1</sup>H NMR spectra of **3ma**



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<sup>1</sup>H NMR spectra of **3na** 



<sup>1</sup>H NMR spectra of **30a** 









## <sup>13</sup>C NMR spectra of **3ab**



<sup>13</sup>C NMR spectra of **3ac** 





<sup>13</sup>C NMR spectra of **3ae** 



DEPT 90 spectra of 3ae



<sup>1</sup>H NMR spectra of **3af** 



<sup>1</sup>H NMR spectra of **3ag** 



#### <sup>1</sup>H NMR spectra of **3ah**



## <sup>1</sup>H NMR spectra of 3ai



Expansion of H-H NOESY spectra of 3ai (CDCl<sub>3</sub>, 600 MHz)



<sup>1</sup>H NMR spectra of 3aj



<sup>1</sup>H NMR spectra of **3ak** 



Expansion of H-H NOESY spectra of 3ak (CDCl<sub>3</sub>, 600 MHz)



 $^{13}\mathrm{C}$  NMR spectra of 3ak



#### <sup>1</sup>H NMR spectra of **3be**

