# Supplementary data

Facile Synthesis of multisubstituted buta-1,3-dienes *via*Suzuki-Miyaura and Kumada Cross-Coupling Strategy of
2,4-Diiodo-buta-1-enes with Arylboronic Acids and Grignard
Reagents

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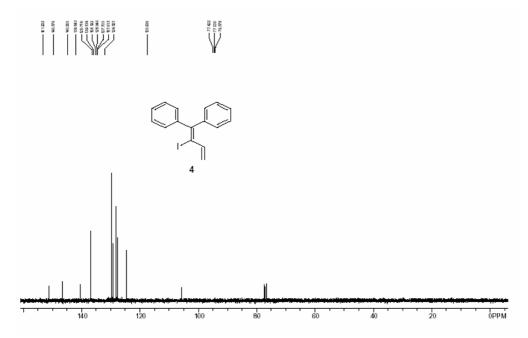
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General remarks. <sup>1</sup>H-NMR spectra were recorded on a 300 MHz spectrometer in CDCl<sub>3</sub> using tetramethylsilane as the internal standard. Infrared spectra were measured on a PERKIN-ELMER 983 spectrometer. Mass spectra were recorded with a HP-5989 instrument and HRMS was measured by a Finnigan MA<sup>+</sup> mass spectrometer. Satisfactory CHN microanalyses were obtained with a Carlo-Erba 1106 analyzer. Melting points are uncorrected. All reactions were monitored by TLC with Huanghai GF<sub>254</sub> silica gel coated plates. Flash Column Chromatography was carried out using 300-400 mesh silica gel.

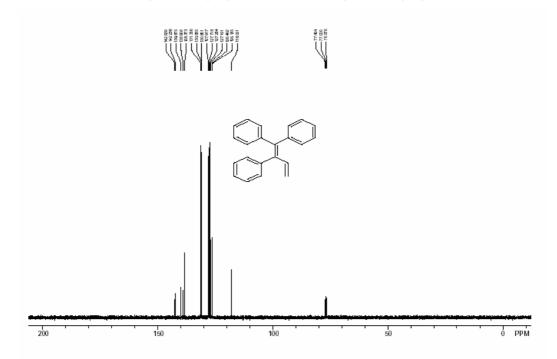
General Reaction Procedure for the Suzuki-Miyaura-type Reaction. Under an argon atmosphere, **1** (0.25 mmol), **2** (0.30 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.025 mmol), tetrabutylammonium chloride (TBAC) (0.25 mmol) and KOH (1.2 mmol) were added into a Schlenk tube with degassed THF/H<sub>2</sub>O (1.0 mL/0.3 mL). The reaction mixture was stirred under reflux temperature for about 48 hrs, then diluted with dichloromethane, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and purified by a flash column chromatography.

Product 4. A colorless liquid,  ${}^{1}H$  NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta = 5.33$  (dd, 1H, J = 0.9, 10.2 Hz), 5.65 (dd, 1H, J = 0.9, 15.6 Hz), 6.13 (dd, 1H, J = 10.2, 15.6 Hz), 7.16-7.37 (m, 10H, Ar).  ${}^{13}C$  NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta = 105.91$ , 124.52, 127.61, 127.70, 128.05, 128.19, 129.11, 129.72, 136.84, 140.56, 146.58, 151.20. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu = 3075$ , 3055, 3011, 2918, 1697, 1596, 1489, 1265, 740 cm<sup>-1</sup>. MS (%): m/e = 332 (M<sup>+</sup>, 12.47), 205 (100). HRMS Calcd. for C<sub>16</sub>H<sub>13</sub>I: 332.0062, Found: 332.0049.

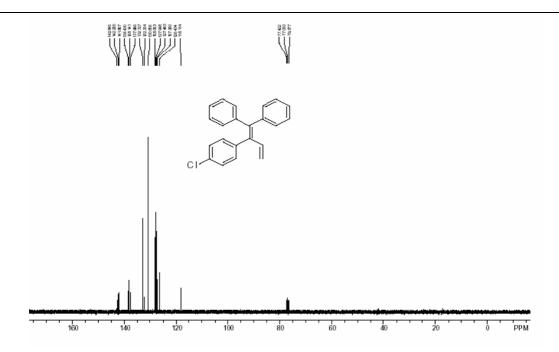


Product **3a**. A white solid, Mp: 110-111 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta$  = 4.93 (dd, 1H, J = 2.1, 17.4 Hz,), 5.15 (dd, 1H, J = 2.1, 10.5 Hz), 6.76 (dd, 1H, J = 10.5, 17.4 Hz), 6.86-6.89 (m, 2H, Ar), 6.90-7.01 (m, 3H, Ar), 7.13-7.35 (m, 10H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 118.06, 126.19, 126.49, 127.16, 127.28, 127.72, 127.92, 130.86, 130.89, 131.37, 138.37, 138.97, 139.88, 142.24, 142.59. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  = 3078, 3054, 3021, 2935, 2855, 1949, 1884, 1598, 1576, 1492, 1443 cm<sup>-1</sup>. MS (%): m/e = 282 (M<sup>+</sup>, 100), 191 (97.13).

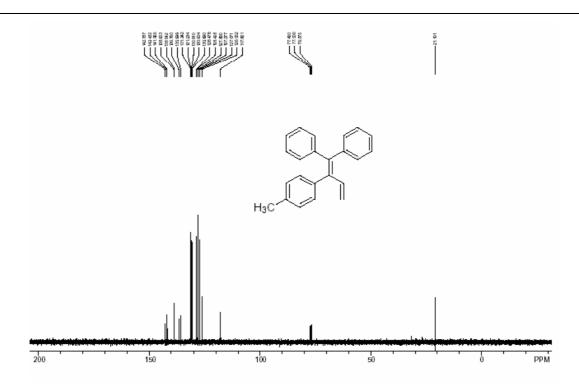
Anal. Calcd. for C<sub>22</sub>H<sub>18</sub>: C, 93.58%; H, 6.42%. Found: C, 93.46%; H, 6.33%.



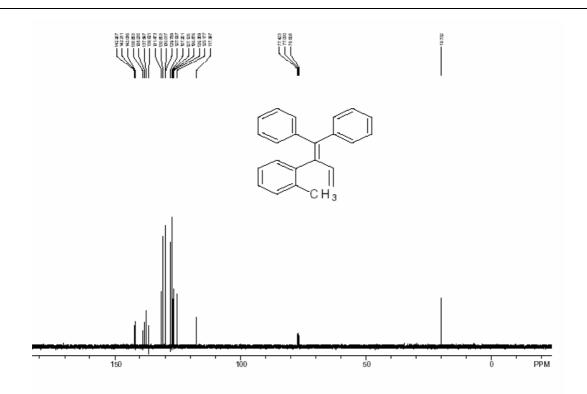
Product **3b**. A white solid, Mp: 124-127 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta$  = 4.91 (dd, 1H, J = 1.8, 17.4 Hz), 5.16 (dd, 1H, J = 1.8, 11.1 Hz), 6.73 (dd, 1H, J = 11.1, 17.4 Hz), 6.78-6.88 (m, 2H, Ar), 7.02-7.17 (m, 5H, Ar), 7.23-7.26 (m, 2H, Ar), 7.30-7.34 (m, 5H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 118.11, 126.43, 127.33, 127.49, 127.95, 128.02, 130.81, 132.30, 132.73, 137.70, 138.14, 138.42, 141.93, 142.24, 142.80. IR (CH<sub>2</sub>Cl<sub>2</sub>): v = 3080, 3054, 2290, 1905, 1827, 1606, 1491, 1442, 1265, 741 cm<sup>-1</sup>. MS (%): m/e = 316 (M<sup>+</sup>, 100), 191 (89.73). Anal. Calcd. for C<sub>22</sub>H<sub>17</sub>Cl: C, 83.40%; H, 5.41%. Found: C, 83.35%; H, 5.26%.



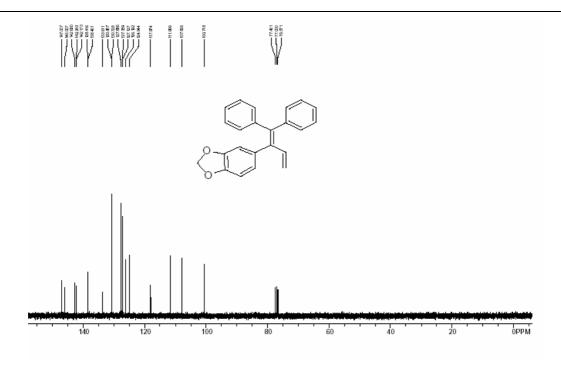
Product **3c**. A white solid, Mp: 108-110 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta$  = 2.27 (s, 3H, CH<sub>3</sub>), 4.95 (dd, 1H, J = 1.8, 17.1 Hz), 5.14 (dd, 1H, J = 1.8, 10.5 Hz), 6.74 (dd, 1H, J = 10.5, 17.1 Hz), 6.87-6.90 (m, 2H, Ar), 7.00-7.04 (m, 7H, Ar), 7.23-7.34 (m, 5H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 21.19, 117.92, 126.06, 127.07, 127.28, 127.89, 128.47, 128.48, 130.89, 130.90, 130.91, 131.23, 131.24, 136.00, 136.76, 138.54, 138.90, 141.96, 142.43, 142.79. IR (CH<sub>2</sub>Cl<sub>2</sub>): v = 3087, 3043, 3014, 2920, 2870, 1819, 1735, 1590, 1509, 1491, 1442 cm<sup>-1</sup>. MS (%): m/e = 296 (M<sup>+</sup>, 100). HRMS Calcd. for C<sub>23</sub>H<sub>20</sub>: 296.1565, Found: 296.1546.



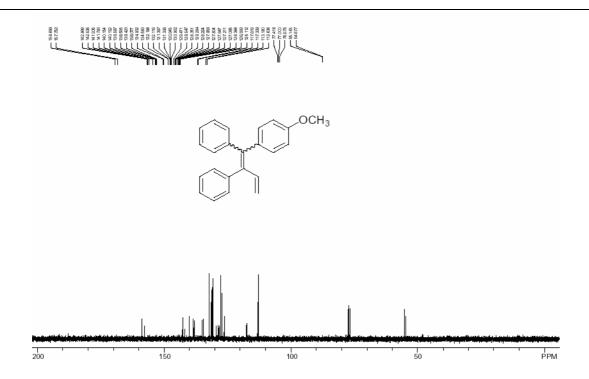
Product **3d**. A white solid, Mp: 69-70 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta$  = 2.15 (s, 3H, CH<sub>3</sub>), 4.70 (dd, 1H, J = 1.8, 17.4 Hz), 5.08 (dd, 1H, J = 1.8, 10.5 Hz), 6.74 (dd, 1H, J = 10.5, 17.4 Hz), 6.87-6.90 (m, 2H, Ar), 6.97-7.00 (m, 3H, Ar), 7.06-7.10 (m, 4H, Ar), 7.28-7.36 (m, 5H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 19.73, 117.40, 125.18, 126.36, 126.88, 127.13, 127.20, 127.97, 130.02, 130.80, 131.47, 136.62, 137.60, 138.24, 138.88, 142.09, 142.21, 142.27. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  = 3059, 2958, 2927, 2860, 2319, 1938, 1600, 1491, 1460, 1379, 1265 cm<sup>-1</sup>. MS (%): m/e = 296 (M<sup>+</sup>, 100). HRMS Calcd. for C<sub>23</sub>H<sub>20</sub> (Maldi): 297.1638, Found: 297.1609 ± 0.005 (M+H<sup>+</sup>).



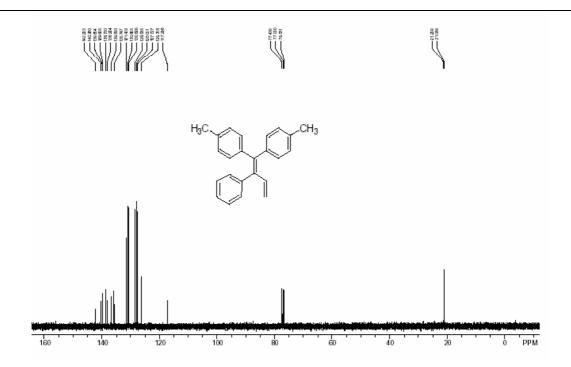
Product **3e**. A white solid, Mp: 146-148 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta$  = 4.99 (dd, 1H, J = 1.8, 17.4 Hz), 5.15 (dd, 1H, J = 1.8, 10.8 Hz), 5.89 (s, 2H), 6.56-6.75 (m, 4H, Ar + CH=CH<sub>2</sub>), 6.89-6.92 (m, 2H, Ar), 7.01-7.05 (m, 3H, Ar), 7.22-7.34 (m, 5H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 100.72, 107.87, 111.70, 117.97, 124.94, 126.19, 127.13, 127.39, 127.89, 130.73, 130.86, 133.61, 138.40, 138.42, 142.17, 142.24, 142.68, 146.07, 147.01. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  = 3087, 3054, 3017, 2893, 2761, 1956, 1666, 1604, 1501, 1486, 1246, 123 cm<sup>-1</sup>. MS (%): m/e = 326 (M<sup>+</sup>, 100). HRMS Calcd. for C<sub>23</sub>H<sub>18</sub>O<sub>2</sub>: 326.1307, Found: 326.1295.



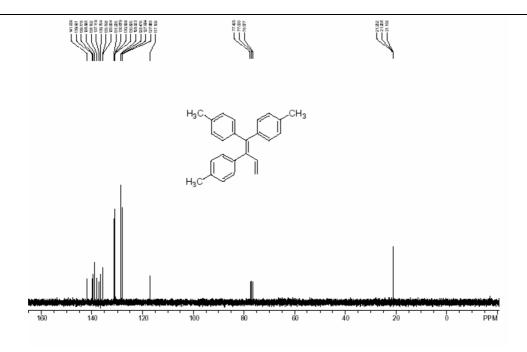
Product **3f**. A yellow solid, Mp: 40-48 °C, (*Z*, trans-isomer) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta = 3.74$  (s, 3H, CH<sub>3</sub>O), 5.01 (dd, 1H, J = 1.8, 17.4 Hz), 5.21 (dd, 1H, J = 1.8, 11.1 Hz), 6.64 (d, 2H, J = 9.3 Hz, Ar), 6.83 (dd, 1H, J = 11.1, 17.4 Hz), 6.88-7.11 (m, 5H, Ar), 7.21-7.46 (m, 7H, Ar). (*E*, trans-isomer) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta = 3.90$  (s, 3H, CH<sub>3</sub>O), 5.04 (dd, 1H, J = 1.8, 15.3 Hz), 5.26 (dd, 1H, J = 1.8, 10.8 Hz), 6.64 (d, 2H, J = 9.3 Hz, Ar), 6.79-7.11 (m, 6H, Ar + CH=CH<sub>2</sub>), 7.21-7.46 (m, 7H, Ar). (*Z*, trans-isomer) <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta = 54.88, 112.64, 117.34, 126.11, 126.37, 127.21, 127.80, 128.22, 128.35, 129.47, 130.94, 131.40, 132.20, 134.93, 138.42, 138.60, 140.15, 142.54, 157.75. ($ *E* $, trans-isomer) <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS): <math>\delta = 55.14, 113.18, 117.62, 126.34, 127.09, 127.65, 127.86, 128.28, 128.55, 130.90, 131.34, 132.12, 134.58, 138.08, 138.54, 140.13, 141.78, 142.87, 158.70. IR (CH<sub>2</sub>Cl<sub>2</sub>): <math>v = 3054, 3037, 2896, 2837, 2319, 1956, 1885, 1804, 1734, 1649, 1605, 1509, 1442, 1247, 1034, 739 cm<sup>-1</sup>. MS (%): m/e = 312 (M<sup>+</sup>, 100), 281 (24.44), 235 (48.06), 221 (82.12). HRMS Calcd. for C<sub>25</sub>H<sub>24</sub>: 312.1500, Found: 312.1509.$ 



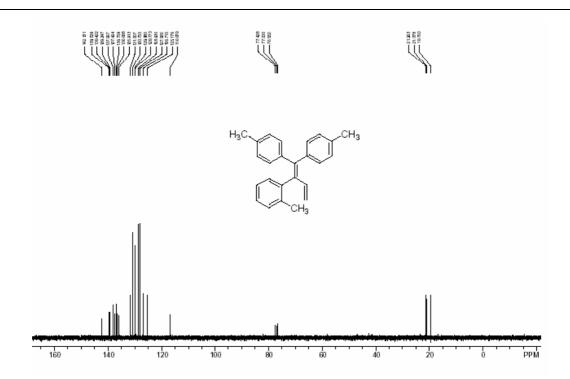
Product **3g**. A white solid, Mp: 99-102 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta$  = 2.17 (s, 3H, CH<sub>3</sub>), 2.37 (s, 3H, CH<sub>3</sub>), 4.89 (dd, 1H, J = 1.8, 17.4 Hz), 5.11 (dd, 1H, J = 1.8, 10.5 Hz), 6.71-6.82 (m, 5H, Ar + CH=CH<sub>2</sub>), 7.13-7.19 (m, 10H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 21.09, 21.26, 117.30, 126.32, 127.73, 128.00, 128.59, 130.83, 130.86, 131.40, 135.75, 136.82, 138.26, 138.75, 139.61, 139.80, 140.28, 142.22. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  = 3054, 2987, 2924, 2686, 2306, 1509, 1422, 1265 cm<sup>-1</sup>. MS (%): m/e = 310 (M<sup>+</sup>, 100), 295 (65.34), 219 (60.28). HRMS Calcd. for C<sub>24</sub>H<sub>22</sub>: 310.1721, Found: 310.1732.



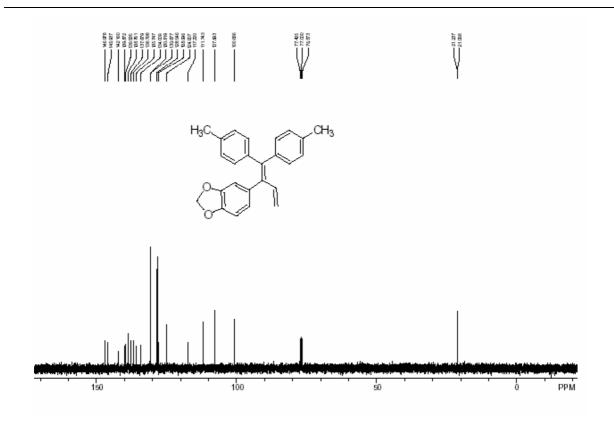
Product **3h**. A white solid, Mp: 143-146 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta$  = 2.21 (s, 3H, CH<sub>3</sub>), 2.31 (s, 3H, CH<sub>3</sub>), 2.39 (s, 3H, CH<sub>3</sub>), 4.93 (dd, 1H, J = 1.8, 17.4 Hz), 5.12 (dd, 1H, J = 1.8, 10.8 Hz), 6.71-6.85 (m, 5H, Ar + CH=CH<sub>2</sub>), 7.00-7.07 (m, 4H, Ar), 7.16 (s, 4H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 21.11, 21.21, 21.25, 117.17, 127.985, 127.994, 128.47, 128.48, 128.55, 130.83, 130.87, 130.88, 131.23, 135.60, 135.80, 136.70, 137.12, 138.16, 138.90, 139.78, 139.96, 141.91. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  = 3050, 3020, 2958, 2924, 2854, 1910, 1705, 1509, 1459, 1096, 816 cm<sup>-1</sup>. MS (%): m/e = 324 (M<sup>+</sup>, 100), 309 (61.58), 219 (99.76). HRMS Calcd. for C<sub>25</sub>H<sub>24</sub>: 324.1878, Found: 324.1915.



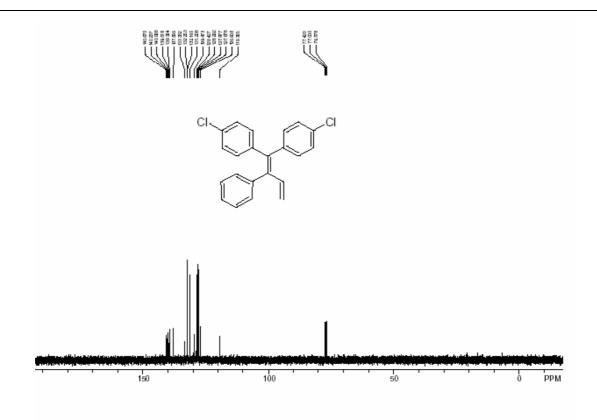
Product **3i**. A white solid, Mp: 89-90 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta$  = 2.13 (s, 3H, CH<sub>3</sub>), 2.15 (s, 3H, CH<sub>3</sub>), 2.37 (s, 3H, CH<sub>3</sub>), 4.65 (dd, 1H, J = 2.1, 17.1 Hz), 5.03 (dd, 1H, J = 2.1, 10.5 Hz), 6.69-6.78 (m, 5H, Ar + CH=CH<sub>2</sub>), 7.07-7.10 (m, 4H, Ar), 7.16 (s, 4H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 19.75, 21.08, 21.26, 116.68, 125.18, 126.72, 127.94, 128.64, 129.77, 129.99, 130.76, 131.51, 135.91, 136.69, 136.76, 137.46, 137.97, 139.25, 139.42, 139.53, 142.18. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  = 3050, 3022, 2987, 2922, 2865, 2305, 1908, 1806, 1605, 1509, 1265 cm<sup>-1</sup>. MS (%): m/e = 324 (M<sup>+</sup>, 100), 309 (70.92), 219 (96.79). Anal. Calcd. for C<sub>25</sub>H<sub>24</sub>: C, 92.48%; H, 7.46%. Found: C, 92.48%; H, 7.79%.



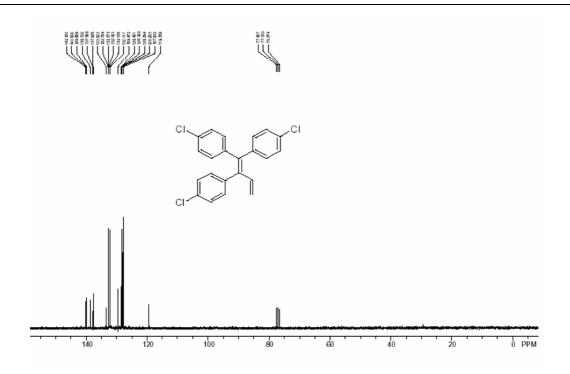
Product **3j**. A yellow solid, Mp: 100-101 °C, ¹H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta$  = 2.22 (s, 3H, CH<sub>3</sub>), 2.38 (s, 3H, CH<sub>3</sub>), 4.95 (d, 1H, J = 17.4 Hz), 5.12 (d, 1H, J = 11.1 Hz), 5.92 (s, 2H), 6.56-6.71 (m, 4H, Ar + CH=CH<sub>2</sub>), 6.74-6.87 (m, 4H, Ar), 7.10-7.17 (m, 4H, Ar). ¹³C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 21.10, 21.24, 100.69, 107.89, 111.74, 117.22, 124.91, 128.10, 128.55, 130.68, 130.82, 134.01, 135.75, 136.80, 137.68, 138.76, 139.59, 139.87, 142.16, 145.94, 146.98. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  = 3051, 3021, 2921, 2768, 2304, 1902, 1744, 1605, 1506, 1484, 1433, 1265 cm<sup>-1</sup>. MS (%): m/e = 354 (M<sup>+</sup>, 100). HRMS calcd. for C<sub>25</sub>H<sub>22</sub>O<sub>2</sub>: 354.1620, Found: 354.1630.



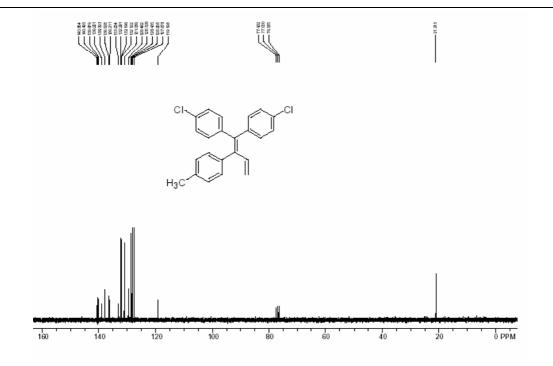
Product **3k**. A yellow solid, Mp: 124-127 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta$  = 4.96 (dd, 1H, J = 1.2, 17.1 Hz), 5.21 (dd, 1H, J = 1.2, 10.8 Hz), 6.69 (dd, 1H, J = 10.8, 17.1 Hz), 6.77 (d, 2H, J = 8.4 Hz, Ar), 6.98 (d, 2H, J = 8.4 Hz, Ar), 7.09-7.23 (m, 7H, Ar), 7.33 (d, 2H, J = 8.4 Hz, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 119.33, 126.91, 127.68, 127.98, 128.29, 128.43, 129.47, 131.21, 132.16, 132.25, 133.33, 137.87, 139.32, 139.50, 140.03, 140.24, 140.67. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  = 3054, 2987, 2686, 2306, 1589, 1491, 1422, 1265 cm<sup>-1</sup>. MS (%): m/e = 350 (M<sup>+</sup>, 80.52), 315 (100). HRMS Calcd. for C<sub>22</sub>H<sub>16</sub>Cl<sub>2</sub>: 350.0629, Found: 350.0596.



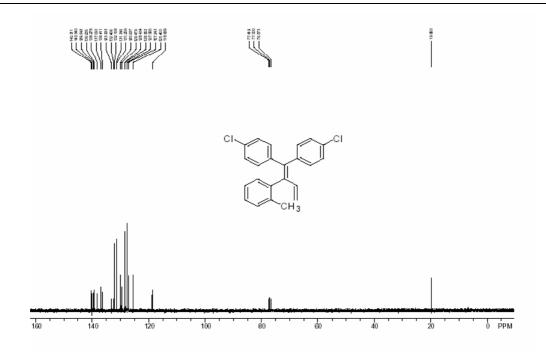
Product **31**. A yellow solid, Mp: 83-85 °C,  $^{1}$ H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta$  = 4.94 (dd, 1H, J = 1.2, 17.4 Hz), 5.22 (dd, 1H, J = 1.2, 10.2 Hz), 6.67 (dd, 1H, J = 10.2, 17.4 Hz), 6.77 (d, 2H, J = 8.1 Hz, Ar), 7.00-7.06 (m, 4H, Ar), 7.14-7.24 (m, 4H, Ar), 7.33 (d, 2H, J = 8.1 Hz, Ar).  $^{13}$ C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 119.39, 127.91, 128.12, 128.30, 128.34, 128.43, 129.48, 129.87, 132.12, 132.19, 132.58, 132.79, 133.59, 137.64, 137.85, 138.77, 139.93, 140.05, 140.39. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  = 3051, 2993, 2312, 1902, 1728, 1659, 1591, 1491, 1265, 739 cm<sup>-1</sup>. MS (%): m/e = 384 (M<sup>+</sup>, 68.55), 349 (100), 314 (82.40). HRMS calcd. for C<sub>22</sub>H<sub>15</sub>Cl<sub>3</sub>: 384.0239, Found: 384.0191.



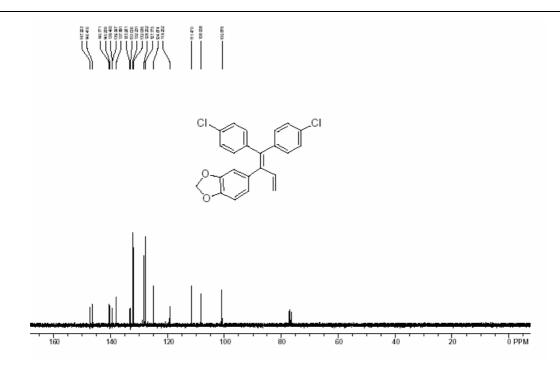
Product **3m**. A white solid, Mp: 114-116 °C, ¹H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta$  = 2.29 (s, 3H, CH<sub>3</sub>), 4.98 (dd, 1H, J = 1.5, 17.1 Hz), 5.19 (dd, 1H, J = 1.5, 10.5 Hz), 6.67 (dd, 1H, J = 10.5, 17.1 Hz), 6.76-6.79 (m, 2H, Ar), 6.97-7.00 (m, 5H, Ar), 7.14-7.23 (m, 3H, Ar), 7.30-7.33 (m, 2H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 21.22, 119.20, 127.68, 128.13, 128.27, 128.44, 128.73, 129.48, 131.09, 132.12, 132.20, 132.29, 133.23, 136.21, 136.54, 138.02, 139.20, 139.98, 140.43, 140.86. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  = 3087, 3047, 3025, 2921, 2866, 2290, 1905, 1673, 1589, 1509, 1489, 1265 cm<sup>-1</sup>. MS (%): m/e = 364 (M<sup>+</sup>, 85.29), 329 (75.03), 138 (100). HRMS Calcd. for C<sub>23</sub>H<sub>18</sub>Cl<sub>2</sub>: 364.0786, Found: 364.0804.



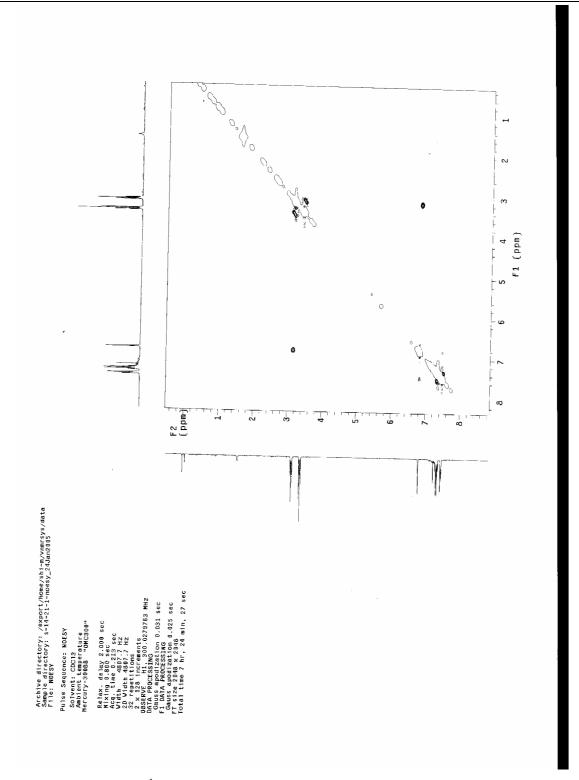
Product **3n**. A yellow liquid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta$  = 2.11 (s, 3H, CH<sub>3</sub>), 4.74 (dd, 1H, J = 1.8, 17.7 Hz), 5.13 (dd, 1H, J = 1.8, 10.8 Hz), 6.67 (dd, 1H, J = 10.8, 17.7 Hz), 6.77 (d, 2H, J = 8.4 Hz, Ar), 6.97 (d, 2H, J = 8.4 Hz, Ar), 7.07-7.24 (m, 6H, Ar), 7.34 (d, 2H, J = 8.4 Hz, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 19.71, 118.69, 125.40, 127.24, 127.60, 128.35, 128.43, 129.48, 130.04, 131.26, 131.35, 132.16, 132.40, 133.31, 136.41, 137.06, 138.28, 139.24, 139.55, 140.04, 140.31. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  = 3059, 3016, 2923, 2841, 1903, 1727, 1673, 1589, 1409 cm<sup>-1</sup>. MS (%): m/e = 364 (M<sup>+</sup>, 57.83), 329 (61.29), 248 (67.37), 138 (100). HRMS Calcd. for C<sub>23</sub>H<sub>18</sub>Cl<sub>2</sub>: 364.0786, Found: 364.0797.



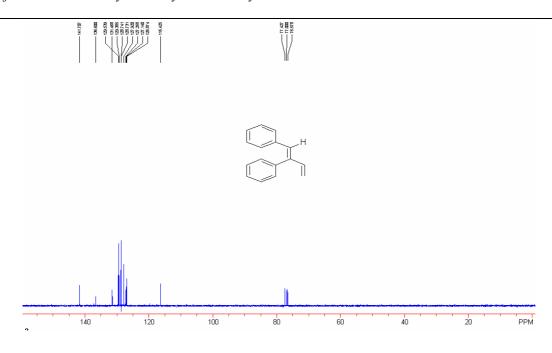
Product **30**. A yellow liquid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta = 5.04$  (dd, 1H, J = 1.8, 17.4 Hz), 5.22 (dd, 1H, J = 1.8, 10.2 Hz), 5.93 (s, 2H), 6.54-6.68 (m, 4H, Ar + CH=CH<sub>2</sub>), 6.82 (d, 2H, J = 8.4 Hz, Ar), 7.04 (d, 2H, J = 8.4 Hz, Ar), 7.15 (d, 2H, J = 8.4 Hz, Ar), 7.32 (d, 2H, J = 8.4 Hz, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta = 100.88$ , 108.07, 111.47, 119.25, 124.87, 126.83, 127.78, 128.25, 132.04, 132.23, 133.01, 133.28, 137.89, 139.40, 139.46, 140.23, 140.77, 146.42, 147.20. IR (CH<sub>2</sub>Cl<sub>2</sub>): v = 3053, 2987, 2891, 2297, 1608, 1586, 1504, 1489, 1265 cm<sup>-1</sup>. MS (%): m/e = 394 (M<sup>+</sup>, 100). HRMS Calcd. for C<sub>23</sub>H<sub>16</sub>Cl<sub>2</sub>O<sub>2</sub>: 394.0527, Found: 394.0539.



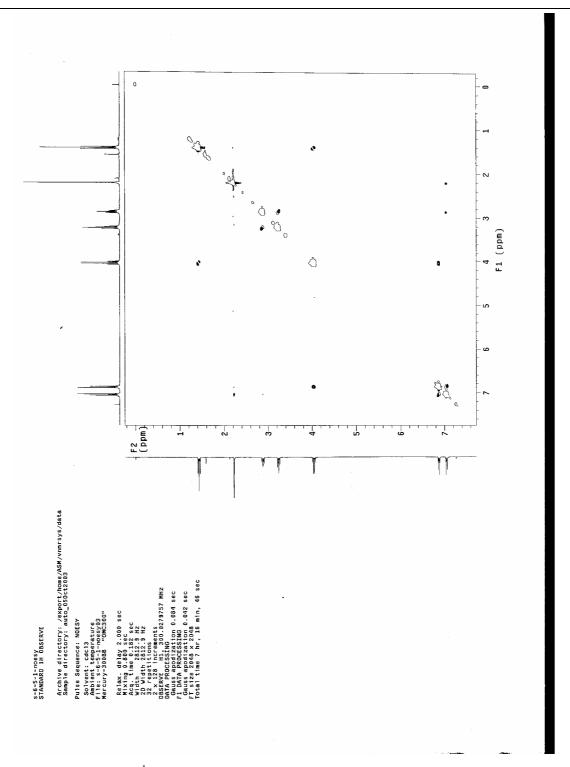
Product **3p**. A colorless liquid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta$  = 4.83 (d, 1H, J = 16.5 Hz), 5.15 (d, 1H, J = 10.5 Hz), 6.60 (s, 1H), 6.74 (dd, 1H, J = 10.5, 16.5 Hz), 6.87-6.91 (m, 2H, Ar), 7.07-7.08 (m, 2H, Ar), 7.15-7.18 (m, 2H, Ar), 7.33-7.41 (m, 4H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 116.43, 126.87, 127.14, 127.27, 127.92, 128.73, 128.74, 129.39, 129.54, 131.47, 136.60, 141.71. IR (CH<sub>2</sub>Cl<sub>2</sub>): v = 3080, 3056, 3022, 2965, 1948, 1812, 1599, 1493, 1444, 1074, 987, 907, 779, 757, 701 cm<sup>-1</sup>. MS (%): m/e = 206 (M<sup>+</sup>, 100), 205 (54), 191 (24), 128 (31), 91 (63). HRMS Calcd. for C<sub>16</sub>H<sub>14</sub> (Maldi): 229.0988, Found: 229.0998 ± 0.003 (M+Na<sup>+</sup>).



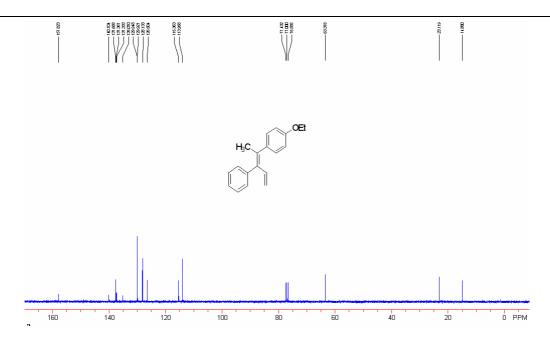
<sup>1</sup>H NMR NOESY spectrum of compound **1e**.



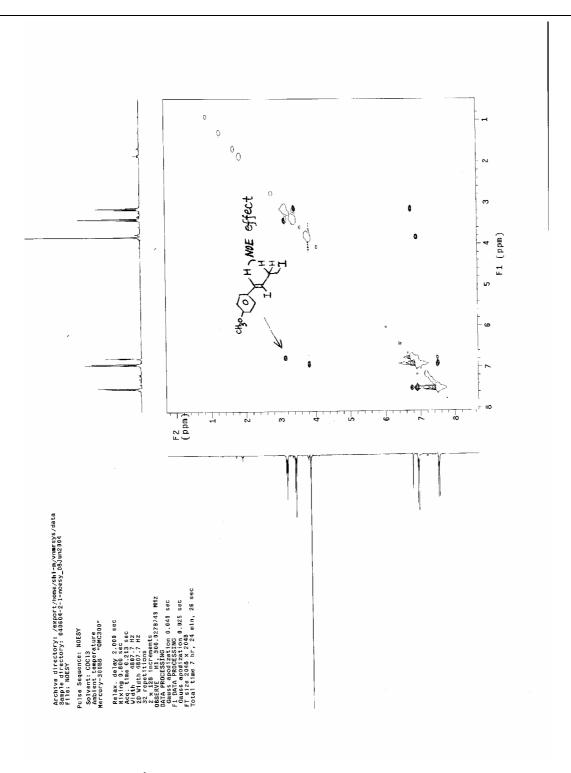
Product **3q**. A white solid, Mp: 48-50 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta$  = 1.43 (t, 3H, J = 6.9 Hz), 1.86 (s, 3H), 4.06 (q, 2H, J = 6.9 Hz), 4.55 (dd, 1H, J = 1.2, 17.4 Hz,), 4.91 (dd, 1H, J = 1.2, 10.8 Hz), 6.67 (dd, 1H, J = 10.8, 17.4 Hz), 6.91 (d, 2H, J = 8.7 Hz, Ar), 7.19-7.42 (m, 7H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 14.88, 23.12, 63.38, 113.96, 115.36, 126.50, 128.13, 129.92, 129.95, 135.07, 137.33, 137.37, 137.67, 140.10, 157.82. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  = 3081, 3032, 3030, 2980, 2927, 1606, 1507, 1477, 1441, 1392, 1281, 1243, 1177, 1117, 1048, 835, 702 cm<sup>-1</sup>. MS (%): m/e = 250 (M<sup>+</sup>, 18), 249 (100), 221 (76). HRMS Calcd. for C<sub>18</sub>H<sub>18</sub>O (Maldi): 251.1430, Found: 251.1445 ± 0.003 (M+H<sup>+</sup>).



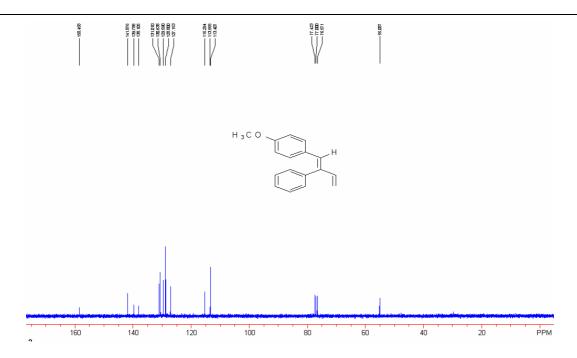
<sup>1</sup>H NMR NOESY spectrum of compound **1f**.



Product **3r**. A colorless liquid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta$  = 3.71 (s, 3H, CH<sub>3</sub>O), 4.77 (d, 1H, J = 17.4 Hz,), 5.09 (d, 1H, J = 10.2 Hz), 6.54 (s, 1H), 6.63 (d, 2H, J = 9.0 Hz, Ar), 6.72 (dd, 1H, J = 10.2, 17.4 Hz), 6.82 (d, 2H, J = 9.0 Hz, Ar), 7.16-7.19 (m, 2H, Ar), 7.34-7.42 (m, 3H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 55.09, 113.41, 113.56, 115.29, 127.15, 128.80, 129.59, 130.64, 131.01, 138.11, 139.79, 141.88, 158.46. IR (CH<sub>2</sub>Cl<sub>2</sub>): v = 3082, 3068, 3002, 2954, 2930, 2835, 1604, 1595, 1509, 1441, 1302, 1254, 1177, 1035, 889, 827, 702 cm<sup>-1</sup>. MS (%): m/e = 236 (M<sup>+</sup>, 100), 235 (37), 205 (46), 178 (34), 165 (35), 145 (35). HRMS Calcd. for C<sub>17</sub>H<sub>16</sub>O (Maldi): 237.1274, Found: 237.1288 ± 0.003 (M+H<sup>+</sup>).



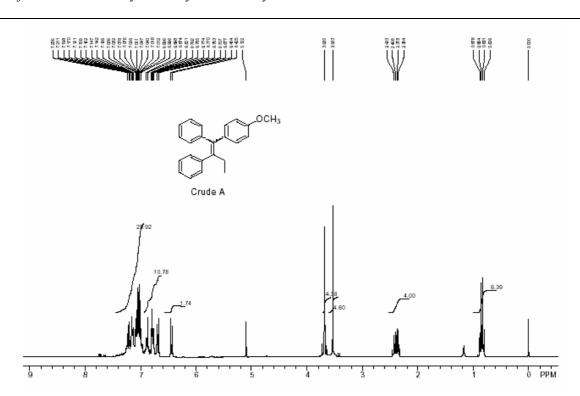
<sup>1</sup>H NMR NOESY spectrum of compound **1g**.



## **Scheme 1** Synthesis of (E, Z)-Tamoxifen from (E, Z)-3f.

### A. The Reduction Step.

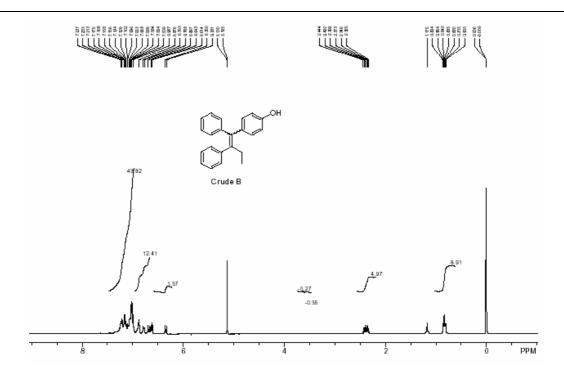
35% H<sub>2</sub>O<sub>2</sub> (2.6 mmol) was added during 10 minutes to a solution of **3f** (0.44 mmol) in 99% EtOH (0.5 mL), CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL) and 85% N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (3.6 mmol) below –60 °C with stirring (acetone-solid carbon dioxide cooled). After addition, the reaction mixture was allowed to warm to room temperature naturally and stirred at room temperature for about 24 hrs. The reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with saturated aq. Na<sub>2</sub>SO<sub>3</sub> and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were washed with saturated brine, then dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue **A** was <sup>1</sup>H NMR determined and was used for the next step without further purification.



#### B. The Demethylation Step.

A solution of **A** in dry CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was cooled to –60 °C under argon, BBr<sub>3</sub> (2.0 mmol) was added. After 1 hr, the reaction mixture was allowed to warm to room temperature and stirred at room temperature for 4 hrs. MeOH (2.0 mL) was added under cooling at 0 °C, diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with saturated brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue **B** was <sup>1</sup>H NMR determined and was used for the next step without further purification.

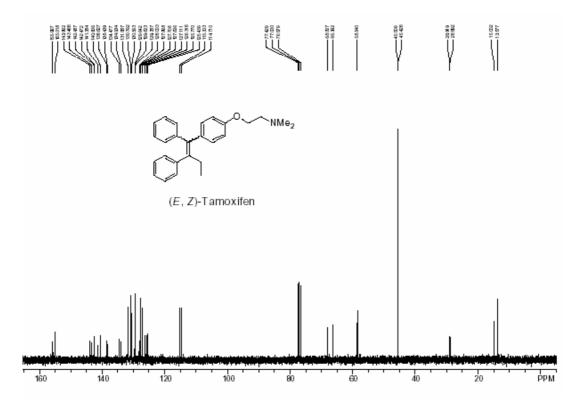
25



#### C. The Synthesis of (E,Z)-Tamoxifen.

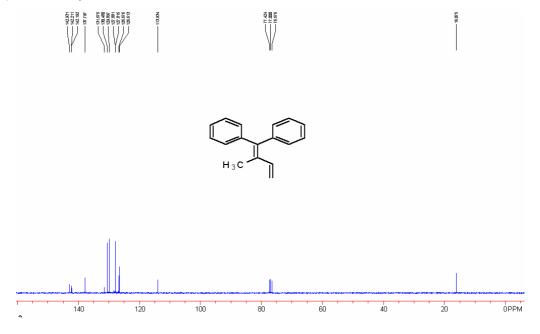
To a solution of sodium ethoxide in absolute ethanol [prepared by adding sodium metal (35) mg, 1.5 mmol) to absolute ethanol (5 mL)] was added the obtained crude product **B** in absolute ethanol (5 mL). To this mixture was then added in one portion a solution of 2-(dimethylamino)ethyl chloride hydrochloride (144 mg, 1 mmol) in warm absolute ethanol (5 mL). The resultant mixture was refluxed for 24 hrs, cooled to room temperature, poured into water and extracted with ether. The combined organic layers were washed with 5% sodium hydroxide solution and saturated brine and dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of solvent under reduced pressure gave 125 mg of crude (E, Z)-Tamoxifen as a yellow oil which resisted attempts at crystallization. This crude material was dissolved in anhydrous ether (12 mL), and hydrogen chloride gas was passed through the solution for 3 minutes. Evaporation of the solvent gave a residue which was recrystallized from ethyl acetate-petroleum ether to give (E, Z)-Tamoxifen hydrochloride as a pale yellow solid. This material was treated with an aqueous solution of 0.5 N sodium hydroxide (20 mL), and the product was extracted with ether. The combined organic layers were washed with saturated brine and dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent gave 105 mg (64% overall yield from 3f) of (E, Z)-Tamoxifen as a white solid. (*E*-isomer)  $^{1}$ H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta = 0.86-0.98$  (m, 3H), 2.37 (s,

6H), 2.42-2.54 (m, 2H), 2.78 (t, 2H, J = 5.7 Hz), 4.10 (t, 2H, J = 5.7 Hz), 6.70-6.98 (m, 4H, Ar), 7.08-7.37 (m, 10H, Ar). (*Z*-isomer) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta = 0.86$ -0.98 (m, 3H), 2.31 (s, 6H), 2.42-2.54 (m, 2H), 2.68 (t, 2H, J = 5.7 Hz), 3.94 (t, 2H, J = 5.7 Hz), 6.54 (d, 2H, J = 8.7 Hz, Ar), 6.70-6.98 (m, 2H, Ar), 7.08-7.37 (m, 10H, Ar). (*E*-isomer) <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta = 13.58$ , 28.89, 45.43, 58.54, 66.39, 114.71, 125.44, 126.32, 127.63, 127.93, 129.39, 129.64, 130.79, 134.03, 138.44, 140.61, 142.47, 143.49, 155.02. (*Z*-isomer) <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta = 15.00$ , 28.92, 45.51, 58.54, 68.03, 115.30, 125.77, 127.11, 128.00, 129.62, 130.56, 131.89, 134.48, 138.63, 141.38, 142.49, 143.92, 155.93.

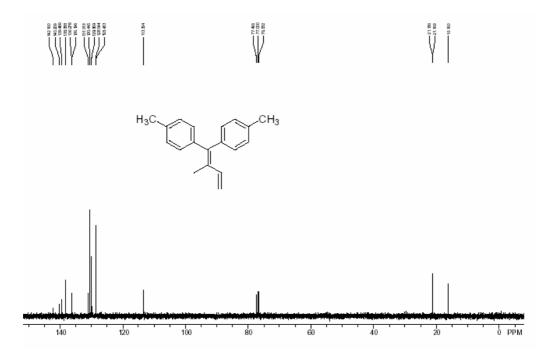


General Reaction Procedure for the Kumada-type Reaction. Under an argon atmosphere, 1 (0.25 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.25 mmol) and THF (1.0 ml) were added into a Schlenk tube. The reaction mixture was stirred at room temperature for about 8 hrs, then NiCl<sub>2</sub>(dppp) (0.025 mmol) and Grignard reagent (1.0 mmol) were added successively. And the obtained mixture was stirred for a further 8 hrs at room temperature. Then the reactions was quenched by addition of water, washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and purified by a flash column chromatography.

Product **5a**. A yellow liquid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta = 1.97$  (s, 3H), 5.11 (dd, 1H, J = 0.9, 10.5 Hz), 5.36 (dd, 1H, J = 0.9, 17.1 Hz), 6.67 (dd, 1H, J = 10.5, 17.1 Hz), 7.16-7.19 (m, 4H, Ar), 7.25-7.36 (m, 6H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta = 16.08$ , 113.93, 126.61, 126.68, 127.82, 127.88, 129.90, 130.48, 131.58, 137.80, 142.19, 142.20, 142.93. IR (CH<sub>2</sub>Cl<sub>2</sub>): v = 3078, 3055, 3019, 2921, 2857, 2726, 1937, 1878, 1812, 1668, 1599, 1576, 1490, 1442, 1405, 1376, 902, 763, 700 cm<sup>-1</sup>; MS (%): m/e = 220 (M<sup>+</sup>, 64.75), 205 (100); HRMS Calcd. for C<sub>17</sub>H<sub>16</sub>: 220.1252, Found: 220.1275.

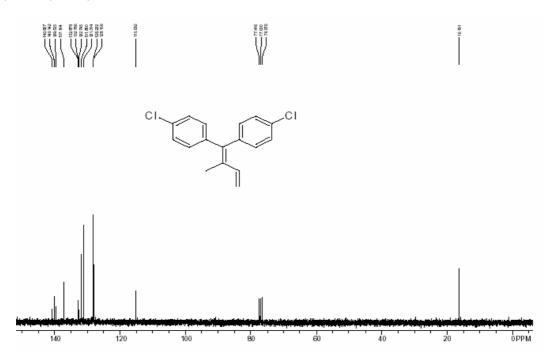


Product **5b**. A white semi-solid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta = 1.98$  (s, 3H), 2.37 (s, 6H), 5.09 (dd, 1H, J = 1.2, 10.8 Hz), 5.34 (dd, 1H, J = 1.2, 17.1 Hz), 6.70 (dd, 1H, J = 10.8, 17.1 Hz), 7.06 (d, 2H, J = 8.4 Hz, Ar), 7.07 (d, 2H, J = 8.4 Hz, Ar), 7.137 (d, 2H, J = 8.4 Hz, Ar), 7.144 (d, 2H, J = 8.4 Hz, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta = 16.16$ , 21.17, 21.19, 113.36, 128.48, 128.54, 129.86, 130.45, 131.02, 136.20, 136.28, 138.09, 139.49, 140.21, 142.16. IR (neat): v = 3086, 3046, 3020, 2920, 2862, 2741, 1904, 1797, 1616, 1509, 1453 cm<sup>-1</sup>; MS (%): m/e = 248 (M<sup>+</sup>, 56.31), 233 (100), 218 (52.04); HRMS Calcd. for C<sub>19</sub>H<sub>20</sub>: 248.1565, Found: 248.1557.

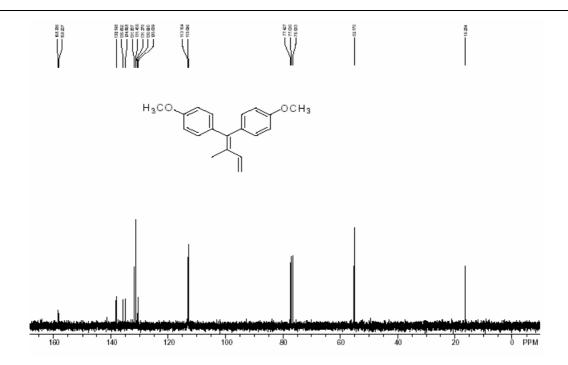


Product **5c**. A colorless liquid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta = 1.85$  (s, 3H), 5.06 (dd, 1H, J = 1.2, 10.8 Hz), 5.30 (dd, 1H, J = 1.2, 17.4 Hz), 6.50 (dd, 1H, J = 10.8, 17.4 Hz), 6.97 (d, 2H, J = 8.7 Hz, Ar), 6.98 (d, 2H, J = 8.7 Hz, Ar), 7.20 (d, 2H, J = 8.7 Hz, Ar), 7.21 (d, 2H, J = 8.7 Hz, Ar), 7.20 (d, 2H, J = 8.7 Hz, Ar), 7.21 (d, 2H, J = 8.7 Hz, Ar), 7.20 (d, 2H, J = 8.7 Hz, Ar), 7.21 (d, 2H, J = 8.7 Hz, Ar), 7.20 (d, 2H, J = 8.7 Hz, Ar), 7.21 (d, 2H, J = 8.7 Hz, Ar), 7.20 (d, 2H, J = 8.7 Hz, Ar), 7.21 (d, 2H, J = 8.7 Hz,

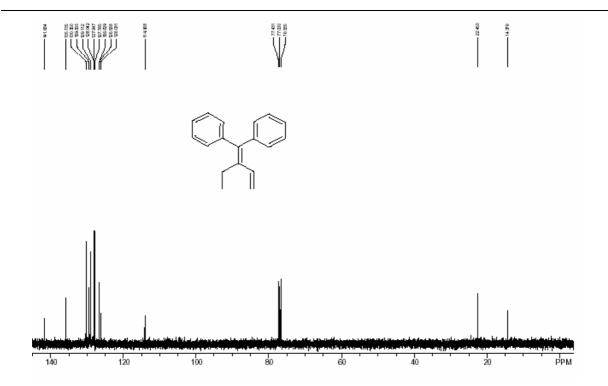
8.7 Hz, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 16.19, 115.09, 128.16, 128.23, 131.31, 131.86, 132.75, 132.79, 132.88, 137.16, 139.53, 140.14, 140.87. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  = 3089, 3021, 2922, 2855, 2741, 1904, 1808, 1589, 1454, 1397 cm<sup>-1</sup>; MS (%): m/e = 288 (M<sup>+</sup>, 27.78), 253 (100), 218 (85.19); HRMS Calcd. for C<sub>17</sub>H<sub>14</sub>Cl<sub>2</sub>: 288.0473, Found: 288.0508.



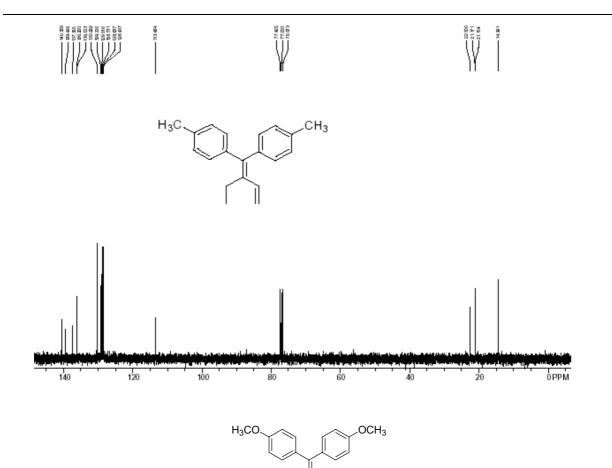
Product **5d**. A yellow liquid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta = 1.94$  (s, 3H), 3.80 (s, 6H), 5.05 (dd, 1H, J = 0.9, 10.5 Hz), 5.29 (dd, 1H, J = 0.9, 17.4 Hz), 6.66 (dd, 1H, J = 10.5, 17.4 Hz), 6.825 (d, 2H, J = 8.4 Hz, Ar), 6.834 (d, 2H, J = 8.4 Hz, Ar), 7.04 (d, 2H, J = 8.4 Hz, Ar), 7.05 (d, 2H, J = 8.4 Hz, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta = 16.28$ , 55.17, 113.10, 113.15, 130.63, 130.92, 131.27, 131.46, 131.81, 134.93, 135.66, 138.20, 158.21, 158.34. IR (neat):  $\nu = 3032$ , 2999, 2950, 2933, 2835, 2548, 2052, 1882, 1717, 1657, 1604, 1580, 1509 cm<sup>-1</sup>; MS (%): m/e = 280 (M<sup>+</sup>, 89.67), 265 (100); HRMS Calcd. for C<sub>19</sub>H<sub>20</sub>O<sub>2</sub>: 280.1463, Found: 280.1453.



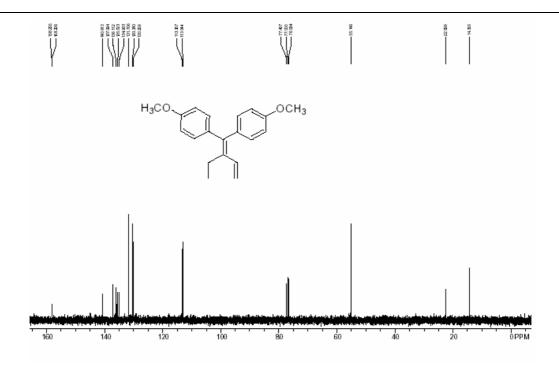
Product **5e**. A colorless liquid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta$  = 1.11 (t, 3H, J = 7.2 Hz), 2.36 (q, 2H, J = 7.2 Hz), 5.12 (dd, 1H, J = 1.5, 11.1 Hz), 5.35 (dd, 1H, J = 1.5, 17.7 Hz), 6.49 (dd, 1H, J = 11.1, 17.7 Hz), 7.13-7.32 (m, 10H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 14.38, 22.45, 114.06, 126.03, 126.59, 126.63, 127.79, 127.95, 128.04, 129.11, 129.51, 130.35, 135.74, 141.68. IR (CH<sub>2</sub>Cl<sub>2</sub>): v = 3078, 3055, 3019, 2921, 2857, 2726, 1937, 1878, 1812, 1668, 1599, 1576, 1490, 1442, 1405, 1376 cm<sup>-1</sup>; MS (%): m/e = 234 (M<sup>+</sup>, 12.44), 205 (100); HRMS Calcd. for C<sub>18</sub>H<sub>18</sub> (Maldi): 235.1481, Found: 235.1486 ± 0.003 (M+H<sup>+</sup>).



Product **5f**. A colorless liquid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta = 1.13$  (t, 3H, J = 7.2 Hz), 2.34-2.42 (m, 8H), 5.11 (dd, 1H, J = 1.5, 11.1 Hz), 5.34 (dd, 1H, J = 1.5, 17.7 Hz), 6.53 (dd, 1H, J = 11.1, 17.7 Hz), 7.03-7.15 (m, 8H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta = 14.39$ , 21.15, 21.17, 22.50, 113.48, 128.44, 128.69, 128.73, 129.02, 129.31, 130.29, 136.00, 136.20, 137.36, 139.47, 140.39. IR (neat): v = 3085, 3019, 2965, 2933, 2872, 1908, 1712, 1610, 1509 cm<sup>-1</sup>; MS (%): m/e = 262 (M<sup>+</sup>, 23.40), 233 (100); HRMS Calcd. for C<sub>20</sub>H<sub>22</sub> (Maldi): 263.1794, Found: 263.1804 ± 0.003 (M+H<sup>+</sup>).

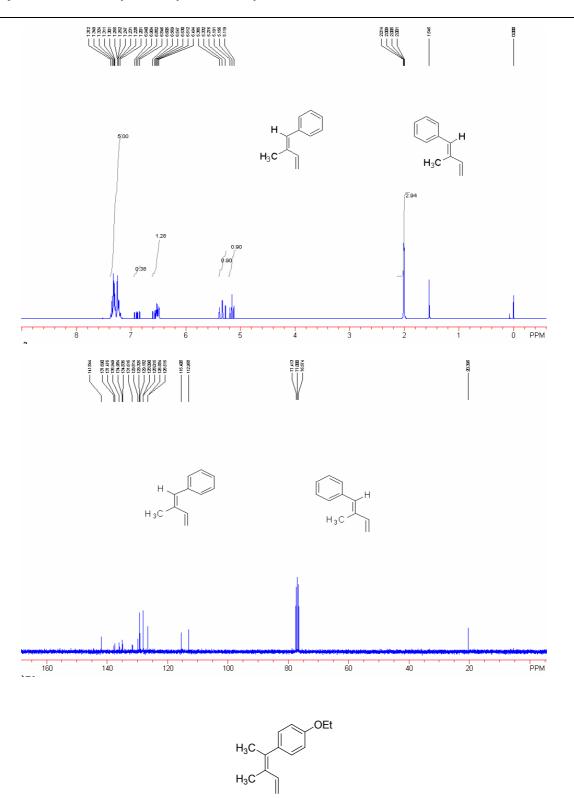


Product **5g**. A colorless liquid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta = 1.13$  (t, 3H, J = 8.1 Hz), 2.39 (q, 2H, J = 8.1 Hz), 3.81 (s, 3H, CH<sub>3</sub>O), 3.82 (s, 3H, CH<sub>3</sub>O), 5.11 (dd, 1H, J = 1.5, 11.1 Hz), 5.33 (dd, 1H, J = 1.5, 17.4 Hz), 6.52 (dd, 1H, J = 11.1, 17.4 Hz), 6.83 (d, 2H, J = 8.7 Hz, Ar), 6.86 (d, 2H, J = 8.7 Hz, Ar), 7.04-7.12 (m, 4H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta = 14.37$ , 22.60, 55.15, 113.04, 113.36, 130.26, 130.38, 131.71, 134.93, 135.52, 136.11, 137.09, 140.91, 158.21, 158.26. IR (neat): v = 3031, 2999, 2962, 2935, 2875, 2837, 2533, 2074, 1878, 1713, 1656, 1607, 1582, 1509 cm<sup>-1</sup>; MS (%): m/e = 294 (M<sup>+</sup>, 1.13), 227 (58.83), 49 (100); HRMS Calcd. for C<sub>20</sub>H<sub>22</sub>O<sub>2</sub> (Maldi): 295.1693, Found: 295.1692 ± 0.003 (M+H<sup>+</sup>).



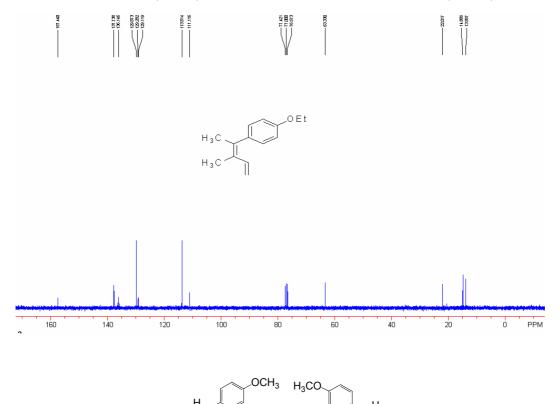
$$H_3C$$
  $H_3C$ 

Product **5h**. A colorless liquid, (*E*- or *Z*-isomer)  $^{1}$ H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta$  = 2.00 (d, 3H, J = 1.2 Hz), 5.14 (d, 1H, J = 11.1 Hz), 5.30 (d, 1H, J = 16.8 Hz), 6.49 (s, 1H), 6.56 (dd, J = 11.1, 16.8 Hz), 7.20-7.37 (m, 5H, Ar). (*Z*- or *E*-isomer)  $^{1}$ H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta$  = 2.01 (d, 3H, J = 1.5 Hz), 5.17 (d, 1H, J = 10.5 Hz), 5.36 (d, 1H, J = 15.9 Hz), 6.53 (s, 1H), 6.89 (dd, J = 10.5, 15.9 Hz), 7.20-7.37 (m, 5H, Ar). (*E*- or *Z*-isomer)  $^{13}$ C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 20.40, 112.96, 126.52, 128.02, 129.18, 129.81, 134.84, 135.95, 137.69. (*Z*- or *E*-isomer)  $^{13}$ C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 20.40, 115.41, 126.58, 128.09, 129.33, 131.62, 134.98, 137.48, 141.84. IR (neat):  $\nu$  = 3082, 3059, 3025, 2958, 2924, 2851, 2214, 1940, 1723, 1673, 1601, 1493, 1450, 1376, 1262, 1072, 1009, 756, 699 cm<sup>-1</sup>; MS (%): m/e = 144 (M<sup>+</sup>, 46.43), 143 (41.29), 129 (100), 128 (84.86); HRMS Calcd. for C<sub>11</sub>H<sub>12</sub>: 144.0939, Found: 144.0925.

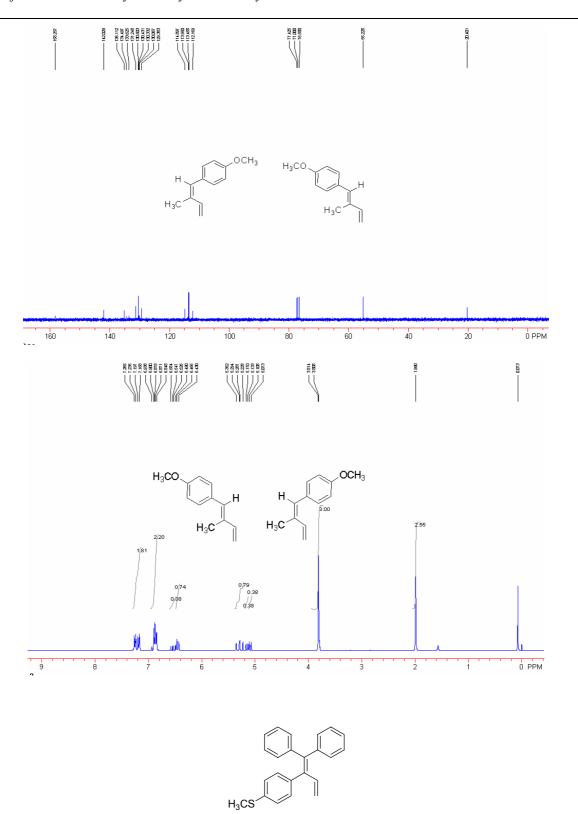


Product **5i**. A colorless liquid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta$  = 1.42 (t, 3H, J = 6.9 Hz), 1.91 (s, 3H), 2.08 (s, 3H), 4.03 (q, 2H, J = 6.9 Hz), 4.86 (d, 1H, J = 11.1 Hz), 5.11 (d, 1H, J = 17.7 Hz), 6.48 (dd, 1H, J = 11.1, 17.7 Hz), 6.85 (d, 2H, J = 8.7 Hz, Ar), 7.06 (d, 2H, J = 8.7 Hz, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 13.86, 14.89, 22.02, 63.33, 111.12, 113.81, 129.12,

129.28, 129.87, 136.15, 137.74, 157.44. IR (neat): v = 2978, 2925, 1606, 1509, 1478, 1392, 1243, 1175, 1116, 1048, 892 cm<sup>-1</sup>; MS (%): m/e = 202 (M<sup>+</sup>, 58.16), 187 (100), 159 (83.30); HRMS Calcd. for  $C_{14}H_{18}O$  (Maldi): 203.1430, Found: 203.1440 ± 0.003 (M+H<sup>+</sup>).

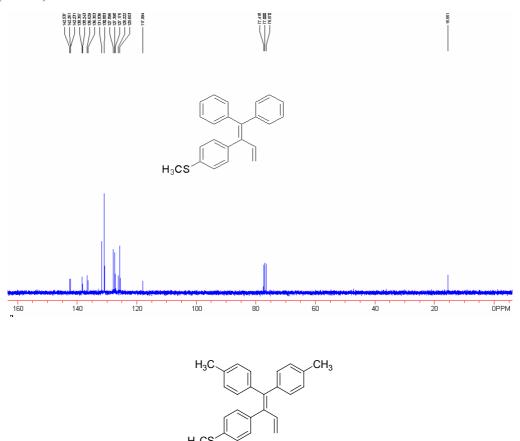


Product **5j**. A colorless liquid, (*E*- or *Z*-isomer) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta = 1.99$  (s, 3H), 3.808 (s, 3H, CH<sub>3</sub>O), 5.09 (d, 1H, J = 10.5 Hz), 5.23 (d, 1H, J = 17.7 Hz), 6.43 (s, 1H), 6.54 (dd, J = 10.5, 17.7 Hz), 6.86 (d, 2H, J = 9.0 Hz), 7.25 (d, 2H, J = 9.0 Hz). (*E*- or *Z*-isomer) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta = 1.99$  (s, 3H), 3.814 (s, 3H, CH<sub>3</sub>O), 5.15 (d, 1H, J = 11.1 Hz), 5.32 (d, 1H, J = 17.4 Hz), 6.47 (s, 1H), 6.899 (d, 2H, J = 8.7 Hz), 6.990 (dd, J = 11.1, 17.4 Hz), 7.18 (d, 2H, J = 8.7 Hz). (*E*- or *Z*-isomer) <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta = 20.40$ , 55.23, 112.17, 113.56, 129.38, 130.33, 130.50, 133.63, 135.11, 158.26. (*Z*- or *E*-isomer) <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta = 20.40$ , 55.23, 113.46, 114.90, 130.07, 130.43, 131.25, 134.50, 142.03, 158.26. IR (neat): v = 3089, 3001, 2956, 2932, 2835, 1572, 1509, 1464, 1300, 1251, 1176, 1036, 899, 829 cm<sup>-1</sup>; MS (%): m/e = 174 (M<sup>+</sup>, 79.88), 159 (100), 144 (52.39); HRMS Calcd. for C<sub>12</sub>H<sub>14</sub>O (Maldi): 175.1117, Found: 175.1124 ± 0.003 (M+H<sup>+</sup>).

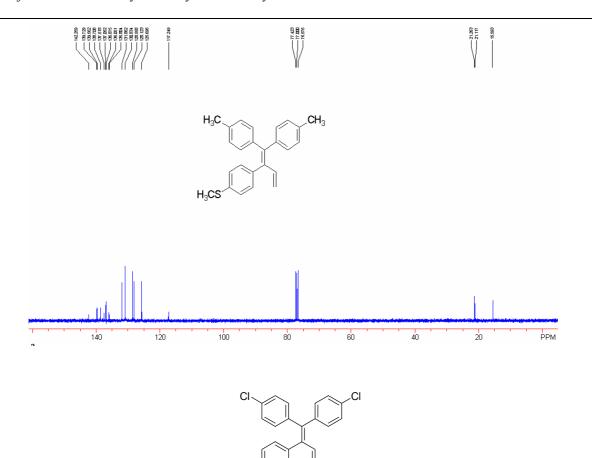


Product **5k**. A pale yellow solid, Mp: 153-154 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta$  = 2.44 (s, 3H), 4.95 (d, 1H, J = 17.4 Hz), 5.15 (d, 1H, J = 10.5 Hz), 6.73 (dd, 1H, J = 10.5, 17.4 Hz), 6.87-6.90 (m, 2H, Ar), 7.02-7.07 (m, 6H, Ar), 7.24-7.37 (m, 6H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 15.55, 117.99, 125.65, 126.22, 127.18, 127.40, 127.90, 130.88, 131.84,

136.35, 136.63, 138.24, 138.36, 142.23, 142.26, 142.54. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu = 3059$ , 3004, 2970, 2919, 1714, 1422, 1363, 1272, 1222, 1091, 906, 737, 703 cm<sup>-1</sup>; MS (%): m/e = 328 (M<sup>+</sup>, 100), 281 (44.42), 203 (46.37); HRMS Calcd. for C<sub>23</sub>H<sub>20</sub>S (Maldi): 329.1359, Found: 329.1356  $\pm$  0.003 (M+H<sup>+</sup>).



Product **51**. A pale yellow solid, Mp: 110-113 °C, ¹H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta$  = 2.20 (s, 3H), 2.37 (s, 3H), 2.45 (s, 3H), 4.91 (d, 1H, J = 17.4 Hz), 5.11 (d, 1H, J = 10.5 Hz), 6.73 (dd, 1H, J = 10.5, 17.4 Hz), 6.68-6.84 (m, 4H, Ar), 7.07-7.17 (m, 8H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 15.59, 21.12, 21.26, 117.25, 125.70, 128.12, 128.56, 130.83, 131.86, 135.80, 136.05, 136.88, 137.05, 137.52, 138.71, 139.56, 139.73, 142.26. IR (CH<sub>2</sub>Cl<sub>2</sub>): v = 3085, 3045, 3023, 2989, 2920, 2863, 1900, 1804, 1601, 1508, 1489, 1441, 1265, 1113, 1087, 1017, 998, 900, 819, 780, 737 cm<sup>-1</sup>; MS (%): m/e = 356 (M<sup>+</sup>, 100), 341 (29.47), 309 (25.91), 294 (40.31); HRMS Calcd. for C<sub>25</sub>H<sub>24</sub>S (Maldi): 357.1672, Found: 357.1672 ± 0.003 (M+H<sup>+</sup>).



Product **5m**. A pale yellow solid, Mp: 100-101 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, TMS):  $\delta$  = 2.46 (s, 3H), 4.99 (d, 1H, J = 17.1 Hz), 5.21 (d, 1H, J = 10.8 Hz), 6.66 (dd, 1H, J = 10.8, 17.1 Hz), 6.78 (d, 2H, J = 7.5 Hz, Ar), 7.00-7.17 (m, 8H, Ar), 7.27-7.33 (m, 2H, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, TMS):  $\delta$  = 15.40, 119.27, 125.65, 127.79, 128.27, 131.67, 132.19, 132.26, 133.31, 135.92, 137.06, 137.85, 139.30, 139.48, 140.23, 140.63. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  = 3104, 3048, 2920, 2852, 1897, 1589, 1490, 1438, 1398, 1264, 1091, 1015, 916, 831, 804, 739 cm<sup>-1</sup>; MS (%): m/e = 396 (M<sup>+</sup>, 73.25), 314 (100), 278 (55.11), 202 (48.78), 138 (41.52), 137 (43.21); HRMS Calcd. for C<sub>23</sub>H<sub>18</sub>Cl<sub>2</sub>S (Maldi): 397.0579, Found: 397.0573 ± 0.003 (M+H<sup>+</sup>).

