

Electronic Supplementary Information

Synthesis of novel synthetic intermediates from the reaction of benzimidazole and triazole carbenes with ketenimines and their application in the construction of spiro-pyrroles

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1. The preparation of 2-(2-alkoxycarbonyl-1-arylamino-1-propenyl)benzimidazolium salts **3** or 5-(2-alkoxycarbonyl-1-arylamino-1-propenyl)triazolium salts **5** from the reaction of benzimidazole or triazole carbenes with ketenimines.

Under nitrogen atmosphere and at $-20\text{ }^{\circ}\text{C}$, benzimidazolium chloride or bromide salts **1** (0.5 mmol) or triazolium chloride salts **4** (0.5 mmol) were mixed with *t*-BuOK (0.5 mmol) in dry THF (30 mL) and stirred for 5 min. Keteneimines **2** (0.5 mmol) were added to the reaction mixture and the mixture were stirred at $-20\text{ }^{\circ}\text{C}$ for 1 h. After removal of solvent under vacuum at room temperature, the residue was chromatographed on a neutral Al_2O_3 column eluting with a mixture of acetone and methanol (5:1). The eluent was evaporated and the 2-(2-alkoxycarbonyl-1-arylamino-1-propenyl)benzimidazolium chlorides or bromides **3** or 5-(2-alkoxycarbonyl-1-arylamino-1-propenyl)triazolium chlorides **5** were isolated in 68-93% or 68-81% yields, respectively. The benzimidazolium or triazolium chlorides or bromides **3** or **5** were converted into tetrafluoroborate salts by treatment with NH_4BF_4 in methanol.

(E)-1,3-diethyl-2-(2-methoxycarbonyl-1-phenylamino-1-propenyl)benzimidazolium bromide (3a): 85%, yellow crystals (ethyl acetate and petroleum ether), mp $179\text{--}181\text{ }^{\circ}\text{C}$; $\nu_{\text{max}}/\text{cm}^{-1}$ 3342, 2729, 1688, 1590, 1546, 1514; δ_{H} (500 MHz, CDCl_3) 10.34 (brs, 1H), 7.69-7.73 (m, 2H), 7.61 (dd, $J = 6.0, 2.8\text{ Hz}$, 2H), 7.31 (t, $J = 8.1\text{ Hz}$, 2H), 7.13 (d, $J = 7.9\text{ Hz}$, 2H), 7.03 (t, $J = 7.4\text{ Hz}$, 1H), 4.40-4.51 (m, 4H), 3.63 (s, 3H), 1.96 (s, 3H), 1.54 (t, $J = 7.3\text{ Hz}$, 6H); δ_{C} (125 MHz, CDCl_3) 168.1, 147.3, 139.9, 131.4, 131.1, 129.0, 126.9, 123.0, 119.3, 113.3, 113.0, 52.1, 42.3, 16.4, 13.9; MS (ESI): 364 (M^+). Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{BrN}_3\text{O}_2$: C 59.46, H 5.90, N 9.46; Found: C 59.55, H 6.04, N 9.60.

(E)-1,3-dibutyl-2-(2-methoxycarbonyl-1-phenylamino-1-propenyl)benzimidazolium tetrafluoroborate (3b): 80%, white crystals (ethyl acetate and petroleum ether), mp $155\text{--}157\text{ }^{\circ}\text{C}$; $\nu_{\text{max}}/\text{cm}^{-1}$ 2722, 1698, 1615, 1589, 1543, 1514; δ_{H} (400 MHz, CDCl_3) 7.87 (s, 1H), 7.65-7.68 (m, 2H), 7.58-7.62 (m, 2H), 7.27 (t, $J = 7.2\text{ Hz}$, 2H), 7.01 (t, $J = 7.4\text{ Hz}$, 1H), 6.95 (d, $J = 7.6\text{ Hz}$, 2H), 4.29 (t, $J = 8.0\text{ Hz}$, 4H), 3.62 (s, 3H), 1.98 (s, 3H), 1.68-1.92 (m, 4H), 1.36-1.45 (m, 4H), 0.92 (t, $J = 7.3\text{ Hz}$, 6H); δ_{C} (100 MHz, CDCl_3) 167.9, 146.9, 139.4, 131.5, 131.1, 129.2, 127.0, 123.5, 119.2, 114.3, 113.3, 52.2, 46.6, 30.7, 20.1, 15.8, 13.5; MS (ESI): 420 (M^+). Anal. Calcd for $\text{C}_{26}\text{H}_{34}\text{BF}_4\text{N}_3\text{O}_2$: C 61.55, H 6.75, N 8.28; Found: C 61.47, H 6.50, N 8.27.

(E)-1,3-dibenzyl-2-(2-methoxycarbonyl-1-(*p*-methoxyphenyl)amino-1-propenyl)benzimidazolium chloride (3c): 85%, yellow crystals (ethyl acetate and petroleum ether), mp $191\text{--}193\text{ }^{\circ}\text{C}$; $\nu_{\text{max}}/\text{cm}^{-1}$ 3431, 1688, 1611, 1594, 1579, 1523, 1508; δ_{H} (400 MHz, CDCl_3) 11.15 (brs, 1H), 7.29-7.42 (m, 14H), 7.02 (d, $J = 8.5\text{ Hz}$, 2H), 6.78 (dd, $J = 8.8, 1.2\text{ Hz}$, 2H), 5.72 (d, $J = 16.2\text{ Hz}$, 2H), 5.59 (d, $J = 16.2\text{ Hz}$, 2H), 3.76 (s, 3H), 3.41 (s, 3H), 1.73 (s, 3H); δ_{C} (100 MHz, CDCl_3) 168.6, 155.7, 150.2, 133.3, 132.9, 132.3, 132.0, 129.2, 128.7, 127.9, 126.8, 121.4, 114.3, 114.2, 109.1, 55.6, 51.9, 51.4, 16.1; MS (ESI): 518 (M^+). Anal. Calcd for $\text{C}_{33}\text{H}_{32}\text{ClN}_3\text{O}_3$: C 71.53, H 5.82, N 7.58; Found: C 71.30, H 5.85, N 7.56.

(E)-1,3-di(*p*-methylbenzyl)-2-(2-methoxycarbonyl-1-phenylamino-1-propenyl)benzimidazolium chloride (3d): 92%, white crystals (ethyl acetate and petroleum ether), mp $174\text{--}176\text{ }^{\circ}\text{C}$; $\nu_{\text{max}}/\text{cm}^{-1}$ 3491, 3430, 1681, 1607, 1591, 1511; δ_{H} (400 MHz, CDCl_3) 11.13 (s, 1H), 7.31-7.33 (m, 2H), 7.24-7.26 (m, 2H), 7.15-7.21 (m, 6H), 7.07 (d, $J = 7.8\text{ Hz}$, 4H), 6.98 (d, $J = 8.0\text{ Hz}$, 2H), 6.89 (t, $J = 7.3\text{ Hz}$, 1H), 5.60 (d, $J = 16.0\text{ Hz}$, 2H), 5.48 (d, $J = 16.0\text{ Hz}$, 2H), 3.34 (s, 3H), 2.24 (s, 3H), 1.69 (s, 3H); δ_{C} (100 MHz, CDCl_3) 168.1, 149.8, 140.0, 138.5, 132.0, 131.6, 129.8, 129.7, 128.7, 127.7, 126.6, 122.6, 119.2, 114.2, 112.2, 51.8, 51.2, 21.1, 16.5; HRMS (TOF-EI): 515.2578 (M^+-1); Anal. Calcd for $\text{C}_{34}\text{H}_{33}\text{N}_3\text{O}_2$: 515.2567 (M^+-1).

(E)-1,3-di(*p*-chlorobenzyl)-2-(2-methoxycarbonyl-1-phenylamino-1-propenyl)benzimidazolium chloride (3e): 74%, white crystals (ethyl acetate and petroleum ether), mp 188-190 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 3491, 3430, 1687, 1610, 1592, 1528, 1512; δ_{H} (500 MHz, CDCl_3) 11.21 (brs, 1H), 7.48 (dd, $J = 6.2, 3.1$ Hz, 2H), 7.32-7.37 (m, 10H), 7.26 (t, $J = 7.7$ Hz, 2H), 6.98-7.02 (m, 3H), 5.71 (d, $J = 16.4$ Hz, 2H), 5.58 (d, $J = 16.4$ Hz, 2H), 3.47 (s, 3H), 1.76 (s, 3H); δ_{C} (125 MHz, CDCl_3) 168.3, 150.1, 139.7, 134.7, 131.8, 131.3, 131.2, 129.4, 129.0, 128.9, 127.1, 122.9, 119.0, 114.1, 112.4, 52.0, 50.6, 16.5; HRMS (TOF-EI): 555.1486 (M^+-1); Anal. Calcd for $\text{C}_{32}\text{H}_{27}\text{Cl}_2\text{N}_3\text{O}_2$: 555.1475 (M^+-1).

(E)-1,3-di(*p*-chlorobenzyl)-2-(1-(*p*-chlorophenyl)amino-2-ethoxycarbonyl-1-propenyl)benzimidazolium chloride (3f): 72%, white crystals (ethyl acetate and petroleum ether), mp 200-202 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 3421, 1681, 1608, 1588, 1492; δ_{H} (500 MHz, CDCl_3) 11.34 (brs, 1H), 7.48-7.50 (m, 2H), 7.32-7.37 (m, 10H), 7.21 (d, $J = 8.6$ Hz, 2H), 6.93 (d, $J = 8.6$ Hz, 2H), 5.68 (d, $J = 16.4$ Hz, 2H), 5.56 (d, $J = 16.4$ Hz, 2H), 3.86 (q, $J = 7.1$ Hz, 2H), 1.76 (s, 3H), 1.17 (t, $J = 7.1$ Hz, 3H); δ_{C} (100 MHz, CDCl_3) 167.5, 150.0, 138.5, 134.8, 131.8, 131.0, 130.8, 129.4, 129.0, 128.8, 127.5, 127.2, 119.8, 114.0, 113.9, 61.3, 50.6, 16.6, 14.0; MS (EI): 480 (75), 482 (100), 604 (M^+ , 20%), 606 (20). Anal. Calcd for $\text{C}_{33}\text{H}_{29}\text{Cl}_4\text{N}_3\text{O}_2$: C 61.79, H 4.56, N 6.55; Found: C 61.72, H 4.52, N 6.36.

(E)-1,3-di(*p*-bromobenzyl)-2-(2-methoxycarbonyl-1-phenylamino-1-propenyl)benzimidazolium tetrafluoroborate (3g): 68%, white crystals (ethyl acetate and petroleum ether), mp 251-253 °C, $\nu_{\text{max}}/\text{cm}^{-1}$ 3341, 1687, 1617, 1598, 1579; δ_{H} (400 MHz, CDCl_3) 7.89 (s, 1H), 7.46 (dd, $J = 6.3, 3.1$ Hz, 2H), 7.40 (d, $J = 8.3$ Hz, 4H), 7.33 (dd, $J = 6.2, 3.1$ Hz, 2H), 7.17 (d, $J = 7.8$ Hz, 2H), 7.08 (d, $J = 8.2$ Hz, 4H), 6.94 (t, $J = 7.1$ Hz, 1H), 6.82 (d, $J = 8.0$ Hz, 2H), 5.53 (d, $J = 16.4$ Hz, 2H), 5.41 (d, $J = 16.4$ Hz, 2H), 3.33 (s, 3H), 1.72 (s, 3H); δ_{C} (100 MHz, CDCl_3) 167.9, 149.2, 139.1, 132.4, 131.8, 131.4, 130.3, 129.2, 129.1, 127.5, 123.6, 123.0, 119.1, 114.9, 114.0, 52.1, 50.2, 16.2; HRMS (TOF-EI): 643.0477 (M^+-1), Anal. Calcd for $\text{C}_{32}\text{H}_{27}\text{Br}_2\text{N}_3\text{O}_2$: 643.0470 (M^+-1).

(E)-5-(2-methoxycarbonyl-1-phenylamino-1-propenyl)-1,3,4-triphenyl-1,2,4-triazolium chloride (5a): 81%, yellow crystals (ethyl acetate and petroleum ether), mp 171-173 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 2698, 1676, 1589, 1541, 1496, 1451; δ_{H} (400 MHz, CDCl_3) 11.96 (s, 1H), 7.98 (dd, $J = 8.0, 2.0$ Hz, 2H), 7.70-8.10 (br, 1H), 7.60 (d, $J = 7.4$ Hz, 2H), 7.30-7.51 (m, 10H), 7.02 (t, $J = 7.7$ Hz, 2H), 6.82 (t, $J = 7.3$ Hz, 1H), 6.44 (d, $J = 7.8$ Hz, 2H), 3.63 (s, 3H), 1.33 (s, 3H); δ_{C} (100 MHz, CDCl_3) 168.7, 153.5, 150.8, 139.7, 135.1, 131.9, 131.8, 131.24, 131.18, 130.6, 129.8, 129.52, 129.45, 128.8, 128.2, 127.8, 125.8, 123.0, 122.5, 119.2, 112.5, 52.1, 15.6; MS (EI): 194 (100), 296 (60), 486 (M^+-1 , 6%), 487 (M^+ , 3%). Anal. Calcd for $\text{C}_{31}\text{H}_{27}\text{ClN}_4\text{O}_2$: C 71.19, H 5.20, N 10.71; Found: C 70.92, H 5.09, N 10.42.

(E)-5-(1-(*p*-chlorophenyl)amino-2-ethoxycarbonyl-1-propenyl)-1,3,4-triphenyl-1,2,4-triazolium tetrafluoroborate (5b): 68%, yellow crystals (ethyl acetate and petroleum ether), mp 212-214 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 3329, 1686, 1584, 1541, 1493; δ_{H} (400 MHz, CDCl_3) 7.74 (s, 1H), 7.70 (dd, $J = 7.8, 1.9$ Hz, 2H), 7.37-7.51 (m, 9H), 7.33 (t, $J = 8.1$ Hz, 2H), 7.28 (t, $J = 7.8$ Hz, 2H), 6.91 (d, $J = 8.8$ Hz, 2H), 6.24 (d, $J = 8.8$ Hz, 2H), 3.99 (dq, $J = 7.0, 0.6$ Hz, 2H), 1.32 (s, 3H), 1.11 (t, $J = 7.1$ Hz, 3H); δ_{C} (100 MHz, $\text{DMSO}-d_6$) 166.3, 153.4, 149.8, 138.3, 133.9, 132.8, 131.9, 131.8, 130.54, 130.47, 130.3, 129.5, 129.0, 128.4, 127.3, 126.7, 126.0, 124.0, 121.7, 119.4, 117.8, 61.5, 15.6, 13.8; MS (EI): 75 (100), 193 (80), 296 (45), 534 (M^+-1 , 7%), 535 (M^+ , 4%). Anal. Calcd for $\text{C}_{32}\text{H}_{28}\text{BClF}_4\text{N}_4\text{O}_2$: C 61.71, H 4.53, N 9.00; Found: C 61.78, H 4.51, N 8.92.

(E)-5-(2-methoxycarbonyl-1-(*p*-methoxyphenyl)amino-1-propenyl)-1,3,4-triphenyl-1,2,4-triazolium chloride (5c): 70%, yellow crystals (ethyl acetate and petroleum ether), mp 192-193 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 2750, 1671, 1610, 1588, 1508; δ_{H} (400 MHz, CDCl_3) 10.85 (s, 1H), 7.97 (d, $J = 7.3$ Hz, 2H), 7.70-8.10 (br, 1H), 7.60 (d, $J = 7.8$ Hz, 2H), 7.39-7.51 (m, 8H), 7.32 (t, $J = 7.7$ Hz, 2H), 6.57 (d, $J = 8.8$ Hz, 2H), 6.39 (d, $J = 8.8$ Hz, 2H), 3.69 (s, 3H), 3.61 (s, 3H), 1.27 (s, 3H); δ_{C} (100 MHz, CDCl_3) 169.0, 155.6, 153.5, 150.9, 135.2, 133.0, 132.0, 131.7, 131.5, 131.2, 131.1, 129.8, 129.5, 129.4, 128.7, 127.8, 125.8, 123.0, 121.5, 113.5, 109.2, 55.4, 51.9, 15.0; MS (ESI): 517 (M^+), 518 (M^++1). Anal. Calcd for $\text{C}_{32}\text{H}_{29}\text{ClN}_4\text{O}_3$: C 69.49, H 5.29, N 10.13; Found: C 69.26, H 5.36, N 10.05.

(E)-5-(2-methoxycarbonyl-1-(*p*-methylphenyl)amino-1-propenyl)-1,3,4-triphenyl-1,2,4-triazolium tetrafluoroborate (5d): 74%, yellow crystals (ethyl acetate and petroleum ether), mp 226-227 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 3329, 1688, 1606, 1542, 1514, 1501; δ_{H} (400 MHz, CDCl_3) 7.78-7.81 (m, 3H), 7.50-7.70 (br, 1H), 7.59 (dd, $J = 8.5, 1.2$ Hz, 2H), 7.52-7.55 (m, 4H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.42 (t, $J = 7.6$ Hz, 2H), 7.35 (t, $J = 7.8$ Hz, 2H), 6.84 (d, $J = 8.2$ Hz, 2H), 6.32 (d, $J = 8.3$ Hz, 2H), 3.61 (s, 3H), 2.20 (s, 3H), 1.34 (s, 3H); δ_{C} (100 MHz, CDCl_3) 168.6, 154.3, 150.3, 136.8, 134.8, 132.8, 131.9, 131.5, 131.4, 130.1, 129.8, 129.7, 129.6, 129.0, 128.8, 127.4, 125.3, 122.7, 119.4, 114.2, 52.2, 20.7, 15.9; MS (ESI): 501 (M^+), 502 (M^++1). Anal. Calcd for

C₃₂H₂₉BF₄N₄O₂: C 65.32, H 4.97, N 9.52; Found: C 65.13, H 5.05, N 9.30.

2. General procedure for the reaction of 2-(2-alkoxycarbonyl-1-arylamino-1-propenyl)benzimidazolium salts 3 or 5-(2-alkoxycarbonyl-1-arylamino-1-propenyl)triazolium salts 5 with ethyl propiolate or DMAD.

Under nitrogen atmosphere and at room temperature, benzimidazolium salts **3** (0.5 mmol) or triazolium salts **5** (0.5 mmol) were mixed with *t*-BuOK (0.6 mmol) in dry toluene. After the temperature was elevated to 80 °C, ethyl propiolate or DMAD (0.6 mmol) was added to the mixture. The reaction mixture was stirred at 80 °C for half an hour and then the solvent was removed under vacuum. The products **11**, **12**, **14** or **15** were isolated by chromatography on a silica gel column eluting with a mixture of petroleum ether (60-90 °C) and ethyl acetate (5:1).

(E)-Ethyl

1,3-dibenzyl-2'-(1-methoxycarbonylethylidene)-1'-(*p*-methoxyphenyl)-1,1',2',3-tetrahydrospiro[benzimidazole-2,3'-pyrrole]-4'-carboxylate (11c**):** 53%, orange crystals (ethyl acetate and petroleum ether), mp 172-173 °C; $\nu_{\max}/\text{cm}^{-1}$ 1713, 1687, 1612, 1598, 1506; δ_{H} (400 MHz, CDCl₃) 7.38 (d, *J* = 6.7 Hz, 4H), 7.27-7.29 (m, 6H), 7.09 (s, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 6.49 (dd, *J* = 5.2, 3.2 Hz, 2H), 6.15 (dd, *J* = 5.4, 3.2 Hz, 2H), 4.36 (d, *J* = 16.0 Hz, 2H), 4.30 (d, *J* = 16.0 Hz, 2H), 3.89 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.09 (s, 3H), 1.59 (s, 3H), 0.88 (t, *J* = 7.1 Hz, 3H); δ_{C} (100 MHz, CDCl₃) 170.2, 163.6, 157.8, 148.3, 147.7, 140.4, 138.6, 134.2, 128.3, 128.1, 126.9, 124.9, 117.7, 114.5, 114.0, 108.2, 103.3, 96.0, 59.3, 55.5, 52.0, 49.2, 17.7, 13.7; MS (EI): 90 (100), 395 (60), 615 (M⁺, 20%). Anal. Calcd for C₃₈H₃₇N₃O₅: C 74.13, H 6.06, N 6.82; Found: C 73.80, H 6.22, N 6.73.

(E)-Ethyl

1,3-di(*p*-methylbenzyl)-2'-(1-methoxycarbonylethylidene)-1'-phenyl-1,1',2',3-tetrahydrospiro[benzimidazole-2,3'-pyrrole]-4'-carboxylate (11d**):** 61%, red crystals (ethyl acetate and petroleum ether), mp 161-163 °C; $\nu_{\max}/\text{cm}^{-1}$ 1693, 1619, 1593, 1505; δ_{H} (400 MHz, CDCl₃) 7.31 (t, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 4H), 7.20 (s, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 4H), 6.89 (d, *J* = 8.1 Hz, 2H), 6.48 (dd, *J* = 5.3, 3.2 Hz, 2H), 6.15 (dd, *J* = 5.3, 3.2 Hz, 2H), 4.33 (d, *J* = 15.9 Hz, 2H), 4.26 (d, *J* = 15.9 Hz, 2H), 3.89 (q, *J* = 7.2 Hz, 2H), 3.09 (s, 3H), 2.32 (s, 6H), 1.43 (s, 3H), 0.89 (t, *J* = 7.2 Hz, 3H); δ_{C} (100 MHz, CDCl₃) 170.0, 163.5, 148.2, 147.0, 141.2, 140.4, 136.4, 135.4, 129.4, 128.7, 128.2, 125.9, 122.9, 117.6, 114.8, 109.5, 103.3, 96.0, 59.4, 52.0, 48.9, 21.0, 18.3, 13.7; MS (EI): 105 (100), 423 (80), 613 (M⁺, 10%). Anal. Calcd for C₃₉H₃₉N₃O₄: C 76.32, H 6.40, N 6.85; Found: C 76.42, H 6.48, N 6.73.

(E)-Ethyl

1,3-di(*p*-chlorobenzyl)-2'-(1-methoxycarbonylethylidene)-1'-phenyl-1,1',2',3-tetrahydrospiro[benzimidazole-2,3'-pyrrole]-4'-carboxylate (11e**):** 58%, red crystals (ethyl acetate and petroleum ether), mp 129-131 °C; $\nu_{\max}/\text{cm}^{-1}$ 1709, 1687, 1610, 1591, 1508, 1496; δ_{H} (400 MHz, CDCl₃) δ (ppm) 7.29-7.35 (m, 6H), 7.19-7.25 (m, 5H), 6.86 (td, *J* = 7.6, 1.2 Hz, 2H), 6.51 (dd, *J* = 5.4, 3.2 Hz, 2H), 6.13 (dd, *J* = 5.4, 3.2 Hz, 2H), 4.32 (d, *J* = 16.0 Hz, 2H), 4.25 (d, *J* = 16.0 Hz, 2H), 3.90 (q, *J* = 7.1 Hz, 2H), 3.08 (s, 3H), 1.43 (s, 3H), 0.92 (t, *J* = 7.1 Hz, 3H); δ_{C} (100 MHz, CDCl₃) δ (ppm) 169.9, 163.3, 147.5, 147.4, 140.9, 139.9, 136.9, 132.7, 129.6, 128.2, 126.2, 122.8, 118.1, 115.2, 108.7, 103.5, 95.9, 59.6, 52.1, 48.5, 18.3, 13.8; MS (EI): 125 (100), 463 (25), 653 (M⁺, 10%). Anal. Calcd for C₃₇H₃₃Cl₂N₃O₄: C 67.89, H 5.08, N 6.42; Found: C 68.01, H 5.31, N 6.34.

(E)-Ethyl

1,3-di(*p*-chlorobenzyl)-1'-(chlorophenyl)-2'-(1-ethoxycarbonylethylidene)-1,1',2',3-tetrahydrospiro[benzimidazole-2,3'-pyrrole]-4'-carboxylate (11f**):** 47%, red crystals (ethyl acetate and petroleum ether), mp 145-146 °C; $\nu_{\max}/\text{cm}^{-1}$ 1688, 1614, 1590, 1503, 1492; δ_{H} (400 MHz, CDCl₃) 7.40-7.44 (m, 6H), 7.35 (s, 1H), 7.28 (td, *J* = 8.5, 2.0 Hz, 4H), 7.13 (td, *J* = 8.9, 2.2 Hz, 2H), 6.46 (dd, *J* = 5.0, 3.2 Hz, 2H), 6.17 (dd, *J* = 5.4, 3.2 Hz, 2H), 4.40 (d, *J* = 16.4 Hz, 2H), 4.32 (d, *J* = 16.4 Hz, 2H), 3.84 (q, *J* = 7.1 Hz, 2H), 3.46 (q, *J* = 7.1 Hz, 2H), 1.47 (s, 3H), 0.98 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.1 Hz, 3H); δ_{C} (100 MHz, CDCl₃) 169.8, 163.5, 148.3, 146.9, 141.0, 140.9, 138.6, 133.0, 131.5, 130.9, 130.2, 128.9, 125.6, 118.4, 116.4, 109.9, 104.0, 96.8, 61.8, 59.8, 48.9, 18.8, 14.4, 14.2; MS (EI): 125 (100), 463 (25), 701 (M⁺, 3%). Anal. Calcd for C₃₈H₃₄Cl₃N₃O₄: C 64.92, H 4.87, N 5.98; Found: C 65.09, H 4.73, N 5.83.

(E)-Ethyl

1,3-di(*p*-bromobenzyl)-2'-(1-methoxycarbonylethylidene)-1'-phenyl-1,1',2',3-tetrahydrospiro[benzimidazole-2,3'-pyrrole]-4'-carboxylate (11g**):** 54%, red crystals (ethyl acetate and petroleum ether), mp 151-153 °C; $\nu_{\max}/\text{cm}^{-1}$ 1698, 1619, 1593, 1504, 1491; δ_{H} (400 MHz, CDCl₃) 7.38 (td, *J* = 8.4, 1.8 Hz, 4H), 7.34 (t, *J* =

7.6 Hz, 2H), 7.25 (d, J = 8.4 Hz, 4H), 7.20 (t, J = 7.5 Hz, 1H), 7.19 (s, 1H), 6.84 (d, J = 7.4 Hz, 2H), 6.52 (dd, J = 5.2, 3.2 Hz, 2H), 6.13 (dd, J = 5.4, 3.2 Hz, 2H), 4.30 (d, J = 16.2 Hz, 2H), 4.23 (d, J = 16.2 Hz, 2H), 3.90 (q, J = 7.1 Hz, 2H), 3.08 (s, 3H), 1.43 (s, 3H), 0.93 (t, J = 7.1 Hz, 3H); δ_{C} (100 MHz, CDCl_3) 169.9, 163.3, 147.5, 147.4, 140.8, 139.9, 137.4, 131.2, 130.0, 129.6, 126.2, 122.8, 120.8, 118.1, 115.2, 108.6, 103.5, 95.9, 59.6, 52.1, 48.6, 18.3, 13.8; MS (EI): 169 (100), 171 (95), 551 (20), 553 (35), 555 (20), 741 (M^+ , 2%), 743 (4). Anal. Calcd for $\text{C}_{37}\text{H}_{33}\text{Br}_2\text{N}_3\text{O}_4$: C 59.77, H 4.47, N 5.65; Found: C 59.67, H 4.50, N 5.58.

(E)-Ethyl

1'-(*p*-chlorophenyl)-2'-(1-ethoxycarbonylethylidene)-1,3,4-triphenyl-1,1',2',4-tetrahydrospiro[1,2,4-triazole-2,3'-pyrrole]-4'-carboxylate (12b): 56%, red crystals (ethyl acetate and petroleum ether), mp 134-136 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1716, 1613, 1593, 1493; δ_{H} (400 MHz, CDCl_3) 7.47 (dd, J = 7.7, 1.3 Hz, 2H), 7.44 (s, 1H), 7.15-7.29 (m, 12H), 7.07 (d, J = 8.0 Hz, 2H), 6.80 (t, J = 7.1 Hz, 1H), 6.60 (d, J = 8.7 Hz, 2H), 4.11-4.15 (m, 1H), 3.95-4.06 (m, 3H), 1.52 (s, 3H), 1.05 (t, J = 7.1 Hz, 3H), 1.01 (t, J = 7.1 Hz, 3H); δ_{C} (100 MHz, CDCl_3) 168.4, 163.1, 148.2, 146.1, 143.8, 143.3, 139.4, 138.8, 131.3, 129.4, 128.8, 128.7, 128.6, 128.5, 128.3, 128.1, 128.0, 126.7, 123.8, 119.1, 118.1, 114.3, 111.1, 94.2, 61.5, 59.7, 17.7, 14.2, 13.9; MS (EI): 180 (100), 632 (M^+ , 15%). Anal. Calcd for $\text{C}_{37}\text{H}_{33}\text{ClN}_4\text{O}_4$: C 70.19, H 5.25, N 8.85; Found: C 70.39, H 5.59, N 8.41.

(E)-Ethyl

2'-(1-methoxycarbonylethylidene)-1'-(*p*-methoxyphenyl)-1,3,4-triphenyl-1,1',2',4-tetrahydrospiro[1,2,4-triazole-2,3'-pyrrole]-4'-carboxylate (12c): 68%, orange crystals (ethyl acetate and petroleum ether), mp 160-162 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1713, 1687, 1595, 1511, 1493; δ_{H} (400 MHz, CDCl_3) 7.49 (dd, J = 7.4, 1.9 Hz, 2H), 7.33 (s, 1H), 7.16-7.28 (m, 11H), 7.10 (d, J = 7.6 Hz, 2H), 6.83 (d, J = 9.2 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 3.97-4.02 (m, 2H), 3.81 (s, 3H), 3.59 (s, 3H), 1.54 (s, 3H), 1.08 (t, J = 7.1 Hz, 3H); δ_{C} (100 MHz, CDCl_3) 169.4, 163.2, 158.0, 148.9, 146.32, 146.28, 143.4, 138.9, 133.9, 128.72, 128.68, 128.4, 128.11, 128.05, 127.9, 126.5, 124.9, 119.1, 115.9, 114.6, 114.2, 108.7, 94.4, 59.6, 55.5, 52.7, 17.3, 14.3; MS (EI): 180 (100), 614 (M^+ , 10%). Anal. Calcd for $\text{C}_{37}\text{H}_{34}\text{N}_4\text{O}_5$: C 72.30, H 5.58, N 9.11; Found: C 72.14, H 5.30, N 9.18.

(E)-Ethyl

2'-(1-methoxycarbonylethylidene)-1'-(*p*-methylphenyl)-1,3,4-triphenyl-1,1',2',4-tetrahydrospiro[1,2,4-triazole-2,3'-pyrrole]-4'-carboxylate (12d): 57%, red crystals (ethyl acetate and petroleum ether), mp 191-193 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1712, 1687, 1614, 1594, 1513, 1492; δ_{H} (400 MHz, CDCl_3) 7.49 (dd, J = 8.0, 1.5 Hz, 2H), 7.39 (s, 1H), 7.24-7.28 (m, 3H), 7.16-7.21 (m, 7H), 7.10 (t, J = 7.9 Hz, 4H), 6.81 (t, J = 7.2 Hz, 1H), 6.77 (d, J = 8.2 Hz, 2H), 3.95-4.03 (m, 2H), 3.60 (s, 3H), 2.35 (s, 3H), 1.56 (s, 3H), 1.08 (t, J = 7.1 Hz, 3H); δ_{C} (100 MHz, CDCl_3) 169.3, 163.1, 148.7, 146.3, 146.27, 143.4, 138.9, 138.3, 136.2, 130.0, 128.7, 128.66, 128.4, 128.0, 127.9, 126.5, 123.04, 122.99, 119.2, 116.4, 114.2, 109.2, 94.4, 59.6, 52.72, 52.67, 20.9, 17.7, 14.2; MS (EI): 76 (100), 180 (90), 598 (M^+ , 25%). Anal. Calcd for $\text{C}_{37}\text{H}_{34}\text{N}_4\text{O}_4$: C 74.23, H 5.72, N 9.36; Found: C 74.28, H 5.70, N 9.24.

(E)-Dimethyl

1,3-dibutyl-2'-(1-methoxycarbonylethylidene)-1'-phenyl-1,1',2',3-tetrahydrospiro[benzimidazole-2,3'-pyrrole]-4',5'-dicarboxylate (14b): 70%, red crystals (ethyl acetate and petroleum ether), mp 128-129 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1747, 1716, 1690, 1610, 1515, 1492; δ_{H} (400 MHz, CDCl_3) 7.41 (t, J = 7.7 Hz, 2H), 7.33 (t, J = 7.0 Hz, 1H), 7.28 (d, J = 7.7 Hz, 2H), 6.49 (brs, 2H), 6.14 (dd, J = 5.0, 3.2 Hz, 2H), 3.68 (s, 3H), 3.46 (s, 3H), 3.14 (brs, 4H), 2.98 (s, 3H), 1.49-1.66 (m, 4H), 1.42 (s, 3H), 1.31-1.39 (m, 4H), 0.94 (t, J = 7.4 Hz, 6H); δ_{C} (100 MHz, CDCl_3) 170.1, 163.3, 162.3, 148.6, 147.3, 139.6, 139.4, 129.6, 127.9, 126.4, 117.0, 115.3, 104.9, 101.6, 94.9, 52.9, 52.0, 51.0, 44.2, 30.1, 20.6, 17.0, 13.9; MS (EI): 44 (100), 313 (40), 502 (45), 561 (M^+ , 10%). Anal. Calcd for $\text{C}_{32}\text{H}_{39}\text{N}_3\text{O}_6$: C 68.43, H 7.00, N 7.48; Found: C 68.66, H 6.93, N 7.47.

(E)-Dimethyl

1,3-di(*p*-methylbenzyl)-2'-(1-methoxycarbonylethylidene)-1'-phenyl-1,1',2',3-tetrahydrospiro[benzimidazole-2,3'-pyrrole]-4',5'-dicarboxylate (14d): 69%, red crystals (ethyl acetate and petroleum ether), mp 171-172 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1747, 1711, 1611, 1587, 1508, 1493; δ_{H} (400 MHz, CDCl_3) 7.31 (d, J = 7.8, 4H), 7.25-7.27 (m, 3H), 7.10 (d, J = 7.9 Hz, 4H), 6.87-6.89 (m, 2H), 6.51 (brs, 2H), 6.20 (dd, J = 5.2, 3.2 Hz, 2H), 4.33 (s, 4H), 3.60 (s, 3H), 3.37 (s, 3H), 3.08 (s, 3H), 2.34 (s, 6H), 1.24 (s, 3H); δ_{C} (100 MHz, CDCl_3) 170.1, 162.9, 161.9, 149.2, 147.1, 140.0, 139.1, 136.5, 135.1, 129.3, 128.8, 128.6, 127.9, 126.6, 117.7, 114.9, 104.0, 103.4, 95.3, 52.7, 52.0, 51.0, 48.8, 21.1, 17.1; MS (EI): 105 (100), 657 (M^+ , 25%). Anal. Calcd for $\text{C}_{40}\text{H}_{39}\text{N}_3\text{O}_6$: C 73.04, H 5.98, N 6.39; Found: C 73.13, H 6.09, N 6.28.

(E)-Dimethyl

1,3-di(*p*-chlorobenzyl)-2'-(1-methoxycarbonylethylidene)-1'-phenyl-1,1',2',3-tetrahydrospiro[benzimidazole-2,3'-pyrrole]-4',5'-dicarboxylate (14e): 58%, red crystals (ethyl acetate and petroleum ether), mp 208-210 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1744, 1716, 1706, 1610, 1593, 1508, 1492; δ_{H} (400 MHz, CDCl_3) 7.28 (d, $J = 8.4$ Hz, 4H), 7.17-7.23 (m, 7H), 6.75 (dd, $J = 8.2, 1.4$ Hz, 2H), 6.47 (brs, 2H), 6.13 (brs, 2H), 4.24 (brs, 4H), 3.52 (s, 3H), 3.31 (s, 3H), 3.00 (s, 3H), 1.15 (s, 3H); δ_{C} (100 MHz, CDCl_3) 169.9, 162.5, 161.6, 149.3, 146.5, 139.7, 138.8, 136.6, 132.8, 130.1, 129.5, 128.3, 128.1, 126.5, 118.2, 115.2, 103.6, 103.5, 95.1, 52.8, 52.1, 51.1, 48.5, 17.0; MS (EI): 125 (100), 388 (15), 697 (M^+ , 3%). Anal. Calcd for $\text{C}_{38}\text{H}_{33}\text{Cl}_2\text{N}_3\text{O}_6$: C 65.33, H 4.76, N 6.01; Found: C 65.46, H 4.61, N 5.90.

(E)-Dimethyl

1,3-di(*p*-bromobenzyl)-2'-(1-methoxycarbonylethylidene)-1'-phenyl-1,1',2',3-tetrahydrospiro[benzimidazole-2,3'-pyrrole]-4',5'-dicarboxylate (14g): 58%, red crystals (ethyl acetate and petroleum ether), mp 191-194 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1743, 1719, 1705, 1608, 1592, 1508, 1490; δ_{H} (400 MHz, CDCl_3) 7.34 (dd, $J = 8.4, 1.9$ Hz, 4H), 7.21-7.24 (m, 7H), 6.72-6.75 (m, 2H), 6.47 (dd, $J = 5.4, 3.2$ Hz, 2H), 6.13 (dd, $J = 5.4, 3.2$ Hz, 2H), 4.22 (s, 4H), 3.52 (s, 3H), 3.32 (s, 3H), 3.00 (s, 3H), 1.14 (s, 3H); δ_{C} (100 MHz, CDCl_3) 169.9, 162.5, 161.6, 149.3, 146.5, 139.7, 138.7, 137.1, 131.2, 130.5, 129.5, 128.2, 126.6, 121.0, 118.2, 115.2, 103.6, 103.4, 95.1, 52.8, 52.1, 51.1, 48.6, 17.0; MS (ESI): 785 (45%, M^+), 787 (100), 789 (65). Anal. Calcd for $\text{C}_{38}\text{H}_{33}\text{Br}_2\text{N}_3\text{O}_6$: C 57.96, H 4.22, N 5.34; Found: C 57.73, H 4.22, N 5.18.

(E)-Dimethyl

2'-(1-methoxycarbonylethylidene)-1,1'3,4-tetraphenyl-1,1',2',4-tetrahydrospiro[1,2,4-triazole-2,3'-pyrrole]-4',5'-dicarboxylate (15a): 71%, red crystals (ethyl acetate and petroleum ether), mp 159-160 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1748, 1713, 1620, 1593, 1493; δ_{H} (400 MHz, CDCl_3) 7.48 (dd, $J = 6.4, 1.7$ Hz, 2H), 7.34 (dd, $J = 6.4, 1.8$ Hz, 2H), 7.21-7.29 (m, 11H), 7.13 (d, $J = 7.7$ Hz, 2H), 6.85 (t, $J = 7.2$ Hz, 1H), 6.61-6.63 (m, 2H), 3.70 (s, 3H), 3.64 (s, 3H), 3.55 (s, 3H), 1.35 (s, 3H); δ_{C} (100 MHz, CDCl_3) 169.0, 162.8, 161.7, 150.5, 146.2, 143.9, 143.0, 138.7, 138.3, 129.3, 129.0, 128.9, 128.5, 128.3, 128.12, 128.07, 127.9, 126.9, 126.1, 119.4, 117.6, 114.1, 106.2, 93.7, 53.1, 52.7, 51.3, 16.5; MS (EI): 180 (100), 628 (M^+ , 15%). Anal. Calcd for $\text{C}_{37}\text{H}_{32}\text{N}_4\text{O}_6$: C 70.69, H 5.13, N 8.91; Found: C 70.56, H 4.85, N 8.76.

(E)-Dimethyl

2'-(1-ethoxycarbonylethylidene)-1'-(*p*-chlorophenyl)-1,3,4-triphenyl-1,1',2',4-tetrahydrospiro[1,2,4-triazole-2,3'-pyrrole]-4',5'-dicarboxylate (15b): 58%, orange crystals (ethyl acetate and petroleum ether), mp 197-198 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1751, 1710, 1623, 1595, 1492; δ_{H} (400 MHz, CDCl_3) 7.37 (dd, $J = 6.7, 1.7$ Hz, 2H), 7.33 (dd, $J = 8.0, 2.0$ Hz, 2H), 7.12-7.21 (m, 8H), 7.05 (d, $J = 8.9$ Hz, 2H), 7.01 (d, $J = 7.8$ Hz, 2H), 6.75 (t, $J = 7.3$ Hz, 1H), 6.31 (d, $J = 8.3$ Hz, 2H), 4.05-4.09 (m, 1H), 3.93-3.97 (m, 1H), 3.68 (s, 3H), 3.47 (s, 3H), 1.27 (s, 3H), 0.93 (t, $J = 7.2$ Hz, 3H); δ_{C} (100 MHz, CDCl_3) 168.2, 162.7, 161.7, 150.3, 146.1, 143.0, 142.5, 138.3, 137.4, 133.4, 129.4, 129.1, 129.0, 128.9, 128.5, 128.3, 128.2, 128.1, 127.3, 127.0, 119.3, 118.6, 114.1, 107.2, 93.5, 61.5, 53.2, 51.4, 16.5, 13.9; MS (EI): 180 (100), 676 (M^+ , 1%). Anal. Calcd for $\text{C}_{38}\text{H}_{33}\text{ClN}_4\text{O}_6$: C 67.40, H 4.91, N 8.27; Found: C 67.54, H 5.03, N 8.11.

(E)-Dimethyl

2'-(1-methoxycarbonylethylidene)-1'-(*p*-methoxyphenyl)-1,3,4-triphenyl-1,1',2',4-tetrahydrospiro[1,2,4-triazole-2,3'-pyrrole]-4',5'-dicarboxylate (15c): 61%, red crystals (ethyl acetate and petroleum ether), mp 207-209 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1754, 1716, 1705, 1618, 1594, 1509, 1493; δ_{H} (400 MHz, CDCl_3) 7.47 (dd, $J = 8.0, 1.6$ Hz, 2H), 7.34 (dd, $J = 8.0, 1.2$ Hz, 2H), 7.22-7.30 (m, 8H), 7.12 (d, $J = 8.0$ Hz, 2H), 6.84 (t, $J = 7.1$ Hz, 1H), 6.72 (d, $J = 9.1$ Hz, 2H), 6.59 (d, $J = 7.4$ Hz, 2H), 3.78 (s, 3H), 3.69 (s, 3H), 3.63 (s, 3H), 3.54 (s, 3H), 1.36 (s, 3H); δ_{C} (100 MHz, CDCl_3) 169.1, 162.7, 161.7, 159.0, 150.9, 146.2, 144.0, 143.0, 138.3, 131.2, 128.9, 128.8, 128.6, 128.5, 128.4, 128.09, 128.06, 126.8, 119.3, 116.7, 114.3, 114.1, 105.3, 93.6, 55.4, 52.9, 52.6, 51.2, 16.1; MS (EI): 180 (100), 658 (M^+ , 2%). Anal. Calcd for $\text{C}_{38}\text{H}_{34}\text{N}_4\text{O}_7$: C 69.29, H 5.20, N 8.51; Found: C 68.93, H 5.52, N 8.07.

(E)-Dimethyl

2'-(1-methoxycarbonylethylidene)-1'-(*p*-methylphenyl)-1,3,4-triphenyl-1,1',2',4-tetrahydrospiro[1,2,4-triazole-2,3'-pyrrole]-4',5'-dicarboxylate (15d): 64%, red crystals (ethyl acetate and petroleum ether), mp 195-196 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1755, 1716, 1709, 1619, 1595, 1509, 1493; δ_{H} (400 MHz, CDCl_3) 7.47 (dd, $J = 7.7, 1.4$ Hz, 2H), 7.33 (dd, $J = 8.0, 1.8$ Hz, 2H), 7.22-7.29 (m, 8H), 7.12 (d, $J = 7.8$ Hz, 2H), 7.01 (d, $J = 8.2$ Hz, 2H), 6.84 (t, $J = 7.2$ Hz, 1H), 6.52 (d, $J = 7.6$ Hz, 2H), 3.71 (s, 3H), 3.63 (s, 3H), 3.54 (s, 3H), 2.30 (s, 3H), 1.35 (s, 3H); δ_{C} (100 MHz, CDCl_3) 169.1, 162.8, 161.7, 150.7, 146.2, 144.0, 143.0, 138.3, 138.0, 136.0, 129.9, 128.9, 128.8, 128.51, 128.50, 128.4, 128.09, 128.08, 126.8, 126.1, 119.4, 117.2, 114.1, 105.7, 93.6, 53.0, 52.7, 51.3, 21.0, 16.4; MS (EI): 180 (100), 642 (M^+ , 37%). Anal. Calcd for $\text{C}_{38}\text{H}_{34}\text{N}_4\text{O}_6$: C 71.01, H

5.33, N 8.72; Found: C 70.75, H 5.34, N 8.52.

3. General procedure for the reaction of 2-(2-alkoxycarbonyl-1-arylamino-1-propenyl)benzimidazolium salts **3** or 5-(2-alkoxycarbonyl-1-arylamino-1-propenyl)triazolium salts **5** with allenes **16**.

Method A: Under nitrogen atmosphere, benzimidazolium salts **3** (0.5 mmol) or triazolium salts **5** (0.5 mmol) were mixed with *t*-BuOK (0.6 mmol) in dry toluene at room temperature. When the temperature was elevated to 60 °C, allenes **16** (0.5 mmol) was added to the reaction mixture, and the mixture was stirred for 3-5 h at 60 °C. After removal of solvent under vacuum, the products **17**, or **19-I** and **19-II** were isolated, respectively, by chromatography on a silica gel column eluting with a mixture of petroleum ether (60-90 °C) and ethyl acetate (7:1). **19-I** and **19-II** can be converted into **20** by stand in deuterium chloroform for a few days.

Method B: Under nitrogen atmosphere and at room temperature, benzimidazolium salts **3** (0.5 mmol) were mixed with *t*-BuOK (0.6 mmol) in dry toluene. After allenes **16** (0.5 mmol) was added, the reaction mixture stirred for 48 h in refluxing toluene. The solvent was removed under vacuum, and the compounds **18** and **17** were isolated as major and minor products by chromatography on a silica gel column eluting with a mixture of petroleum ether (60-90 °C) and ethyl acetate (7:1).

(*E,E*)-Methyl

2-(1,3-di(*p*-chlorobenzyl)-4'-ethyl-5'-methoxycarbonylmethylidene-1'-phenyl-1,3-dihydrospiro[benzimidazole-2,3'-pyrrolidine]-2'-ylidene)propanoate (17a**):** 58% from method A, yellow crystals (ethyl acetate and petroleum ether), mp 197-199 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1701, 1640, 1601, 1503, 1490; δ_{H} (400 MHz, CDCl₃) 7.43 (t, *J* = 8.0 Hz, 2H), 7.24-7.36 (m, 9H), 7.06 (d, *J* = 7.6 Hz, 2H), 6.58 (dt, *J* = 7.6, 1.0 Hz, 1H), 6.49 (dt, *J* = 7.6, 1.0 Hz, 1H), 6.09 (d, *J* = 7.3 Hz, 1H), 5.88 (d, *J* = 7.3 Hz, 1H), 4.76 (s, 1H), 4.63 (d, *J* = 17.9 Hz, 1H), 4.56 (d, *J* = 17.2 Hz, 1H), 4.51 (d, *J* = 17.2 Hz, 1H), 4.26 (d, *J* = 17.9 Hz, 1H), 4.21-4.23 (m, 1H), 3.49 (s, 3H), 2.86 (s, 3H), 1.97-2.05 (m, 1H), 1.52-1.58 (m, 1H), 1.41 (s, 3H), 0.83 (t, *J* = 7.4 Hz, 3H); δ_{C} (100 MHz, CDCl₃) 170.5, 167.1, 162.2, 146.2, 139.9, 139.8, 138.7, 138.0, 136.8, 132.6, 132.3, 129.9, 128.6, 128.5, 128.1, 127.9, 127.1, 119.0, 117.8, 106.9, 104.9, 103.0, 96.4, 91.3, 56.7, 52.1, 50.6, 50.4, 49.7, 22.1, 17.1, 10.8; MS (EI): 125 (100), 681 (M⁺, 2%). Anal. Calcd for C₃₉H₃₇Cl₂N₃O₄: C 68.62, H 5.46, N 6.16; Found: C 68.67, H 5.45, N 5.97.

(*E,E*)-Methyl

2-(1,3-di(*p*-chlorobenzyl)-4'-benzyl-5'-methoxycarbonylmethylidene-1'-phenyl-1,3-dihydrospiro[benzimidazole-2,3'-pyrrolidine]-2'-ylidene)propanoate (17b**):** 62% (method A), 14% (method B), yellow crystals (ethyl acetate and petroleum ether), mp 178-179 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1698, 1601, 1509, 1496; δ_{H} (400 MHz, CDCl₃) 7.24-7.35 (m, 7H), 7.16-7.22 (m, 2H), 7.03-7.13 (m, 5H), 6.91 (br, 2H), 6.90 (d, *J* = 6.8 Hz, 2H), 6.51 (t, *J* = 7.6 Hz, 1H), 6.44 (t, *J* = 7.5 Hz, 1H), 6.01 (d, *J* = 7.4 Hz, 1H), 5.83 (d, *J* = 7.4 Hz, 1H), 4.67 (d, *J* = 18.0 Hz, 1H), 4.57 (s, 1H), 4.50 (d, *J* = 16.9 Hz, 1H), 4.39-4.45 (m, 2H), 4.24 (d, *J* = 18.0 Hz, 1H), 3.88 (dd, *J* = 12.5, 3.7 Hz, 1H), 2.95 (s, 3H), 2.80 (s, 3H), 2.35 (t, *J* = 12.0 Hz, 1H), 1.38 (s, 3H); δ_{C} (100 MHz, CDCl₃) 170.5, 166.1, 159.6, 146.1, 140.0, 139.9, 138.7, 137.7, 137.6, 136.5, 132.6, 130.0, 129.8, 128.7, 128.6, 128.2, 128.1, 127.9, 127.7, 126.3, 119.3, 118.0, 107.2, 105.2, 103.6, 96.4, 93.0, 57.6, 52.1, 50.8, 50.4, 50.2, 36.1, 17.1; MS (TOF-ESI): 744 (M+1). Anal. Calcd for C₄₄H₃₉Cl₂N₃O₄: C 70.96, H 5.28, N 5.64; Found: C 71.07, H 5.20, N 5.54.

(*E*)-Methyl

1,3-di(*p*-chlorobenzyl)-2'-(1-methoxycarbonylethylidene)-5'-phenethyl-1'-phenyl-1,1',2',3-tetrahydrospiro[benzimidazole-2,3'-pyrrole]-4'-carboxylate (18b**):** 53% from method B, yellow crystals (ethyl acetate and petroleum ether), mp 135-136 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1712, 1693, 1620, 1592, 1493; δ_{H} (400 MHz, CDCl₃) 7.38-7.40 (m, 3H), 7.36 (d, *J* = 7.4 Hz, 4H), 7.25 (d, *J* = 8.8 Hz, 4H), 7.12-7.16 (m, 3H), 6.80-6.83 (m, 4H), 6.52 (brs, 2H), 6.17 (brs, 2H), 4.30 (s, 4H), 3.46 (s, 3H), 3.05 (s, 3H), 2.59-2.63 (m, 2H), 2.32-2.36 (m, 2H), 1.18 (s, 3H); δ_{C} (100 MHz, CDCl₃) 170.6, 164.5, 160.4, 146.6, 140.4, 140.3, 138.9, 137.3, 132.7, 129.9, 129.5, 129.0, 128.5, 128.4, 128.14, 128.07, 126.2, 117.7, 112.0, 103.0, 101.8, 94.9, 52.0, 50.4, 48.5, 33.9, 28.6, 16.6; MS (ESI): 744 (M+1, 100%), 746 (65). Anal. Calcd for C₄₄H₃₉Cl₂N₃O₄: C 70.96, H 5.28, N 5.64; Found: C 70.96, H 5.58, N 5.43.

(*E,E*)-Ethyl

2-(1,3-di(*p*-chlorobenzyl)-4'-benzyl-5'-methoxycarbonylmethylidene-1'-(*p*-chlorophenyl)-1,3-dihydrospiro[benzimidazole-2,3'-pyrrolidine]-2'-ylidene)propanoate (17c**):** 53% from method A, yellow crystals (ethyl acetate and petroleum ether), mp 174-175 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1712, 1695, 1644, 1601, 1513, 1490; δ_{H} (400 MHz, C₆D₆) 7.32 (d, *J* = 8.4 Hz, 2H), 7.16-7.21 (m, 6H), 7.11 (d, *J* = 7.3 Hz, 3H), 7.03 (d, *J* = 8.4 Hz, 2H),

6.92 (d, J = 8.7 Hz, 2H), 6.76 (t, J = 7.2 Hz, 1H), 6.69 (t, J = 7.2 Hz, 1H), 6.48 (brs, 2H), 6.20 (d, J = 6.9 Hz, 1H), 6.01 (d, J = 6.9 Hz, 1H), 4.76-4.94 (m, 4H), 4.93 (dd, J = 10.8, 4.2 Hz, 1H), 4.91 (s, 1H), 4.88 (d, J = 18.3 Hz, 1H), 4.78 (d, J = 17.2 Hz, 1H), 4.64 (d, J = 18.3 Hz, 1H), 4.58 (d, J = 17.2 Hz, 1H), 4.22-4.27 (m, 1H), 3.57 (dd, J = 12.6, 4.2 Hz, 1H), 3.19 (s, 3H), 2.92-2.97 (m, 1H), 2.54 (dd, J = 12.4, 11.0 Hz, 1H), 1.59 (s, 3H), 0.89 (t, J = 7.1 Hz, 3H); δ_C (100 MHz, $CDCl_3$) 170.2, 166.1, 159.6, 144.8, 139.5, 139.4, 137.6, 137.5, 137.2, 136.5, 133.7, 132.7, 132.6, 130.1, 129.8, 128.8, 128.6, 128.2, 127.9, 127.7, 126.3, 119.1, 118.0, 107.7, 105.0, 103.5, 95.5, 92.2, 61.8, 56.5, 50.5, 50.4, 49.2, 35.8, 17.5, 14.1; MS (TOF-ESI): 792 ($M+1$, 100%), 794 (95). Anal. Calcd for $C_{45}H_{40}Cl_3N_3O_4$: C 68.14, H 5.08, N 5.30; Found: C 68.45, H 5.46, N 4.92.

(*E,E*)-Methyl

2-(1,3-di(*p*-bromobenzyl)-4'-ethyl-5'-methoxycarbonylmethylidene-1'-phenyl-1,3-dihydrospiro[benzimidazole-2,3'-pyrrolidine]-2'-ylidene)propanoate (17d): 48% from method A, yellow crystals (ethyl acetate and petroleum ether), mp 189-191 °C; ν_{max}/cm^{-1} 1701, 1600, 1503, 1488; δ_H (400 MHz, $CDCl_3$) 7.40 (d, J = 8.4 Hz, 2H), 7.31-7.37 (m, 4H), 7.26 (t, J = 7.4 Hz, 1H), 7.16 (d, J = 6.2 Hz, 2H), 7.14 (d, J = 6.4 Hz, 2H), 6.97 (d, J = 7.6 Hz, 2H), 6.51 (dt, J = 7.6, 0.9 Hz, 1H), 6.41 (dt, J = 7.6, 1.0 Hz, 1H), 6.02 (d, J = 7.4 Hz, 1H), 5.80 (d, J = 7.4 Hz, 1H), 4.68 (s, 1H), 4.53 (d, J = 18.0 Hz, 1H), 4.47 (d, J = 17.2 Hz, 1H), 4.41 (d, J = 17.2 Hz, 1H), 4.13-4.18 (m, 2H), 3.42 (s, 3H), 2.78 (s, 3H), 1.89-1.96 (m, 1H), 1.44-1.53 (m, 1H), 1.33 (s, 3H), 0.75 (t, J = 7.4 Hz, 3H); δ_C (100 MHz, $CDCl_3$) 170.5, 167.1, 162.2, 146.2, 139.9, 139.8, 138.7, 138.5, 137.3, 131.5, 131.4, 129.9, 128.5, 128.3, 128.1, 127.1, 120.6, 120.4, 119.1, 117.8, 106.9, 104.9, 103.0, 96.3, 91.3, 56.6, 52.1, 50.7, 50.4, 49.7, 22.1, 17.1, 10.7; MS (TOF-ESI): 770 ($M+1$, 55%), 772 (100). Anal. Calcd for $C_{39}H_{37}Br_2N_3O_4$: C 60.71, H 4.83, N 5.45; Found: C 60.94, H 4.69, N 5.24.

(*E,E*)-Methyl

2-(1,3-di(*p*-bromobenzyl)-4'-benzyl-5'-methoxycarbonylmethylidene-1'-phenyl-1,3-dihydrospiro[benzimidazole-2,3'-pyrrolidine]-2'-ylidene)propanoate (17e): 51% (method A), 15% (method B), yellow crystals (ethyl acetate and petroleum ether), mp 172-174 °C; ν_{max}/cm^{-1} 1698, 1601, 1513, 1490; δ_H (400 MHz, $CDCl_3$) 7.50 (d, J = 8.4 Hz, 2H), 7.43 (t, J = 7.4 Hz, 2H), 7.34-7.37 (m, 5H), 7.12-7.24 (m, 5H), 7.00 (br, 2H), 6.99 (d, J = 6.8 Hz, 2H), 6.61 (t, J = 7.2 Hz, 1H), 6.53 (t, J = 7.4 Hz, 1H), 6.10 (d, J = 7.0 Hz, 1H), 5.92 (d, J = 6.9 Hz, 1H), 4.75 (d, J = 18.0 Hz, 1H), 4.66 (s, 1H), 4.47-4.59 (m, 3H), 4.32 (d, J = 18.0 Hz, 1H), 3.46 (dd, J = 12.5, 3.9 Hz, 1H), 3.05 (s, 3H), 2.89 (s, 3H), 2.44 (t, J = 12.0 Hz, 1H), 1.47 (s, 3H); δ_C (100 MHz, $CDCl_3$) 170.5, 166.1, 159.5, 146.1, 140.0, 139.9, 138.7, 138.2, 137.6, 137.1, 131.7, 131.5, 130.0, 129.8, 128.6, 128.3, 128.1, 127.7, 126.3, 120.7, 120.6, 119.3, 118.0, 107.2, 105.2, 103.6, 96.4, 92.9, 57.5, 52.1, 50.9, 50.5, 50.2, 36.1, 17.1; MS (EI): 91 (100), 169 (68), 171 (71), 831 (M^+ , 2%), 833 (4). Anal. Calcd for $C_{44}H_{39}Br_2N_3O_4$: C 63.40, H 4.72, N 5.04; Found: C 63.56, H 4.98, N 4.95.

(*E*)-Methyl

1,3-di(*p*-bromobenzyl)-2'-(1-methoxycarbonylethylidene)-5'-phenethyl-1'-phenyl-1,1',2',3'-tetrahydrospiro[benzimidazole-2,3'-pyrrole]-4'-carboxylate (18e): 46% from method B, yellow crystals (ethyl acetate and petroleum ether), mp 134-135 °C; ν_{max}/cm^{-1} 1710, 1692, 1617, 1592, 1500; δ_H (400 MHz, $CDCl_3$) 7.38-7.41 (m, 7H), 7.29 (d, J = 8.4 Hz, 4H), 7.12-7.17 (m, 3H), 6.77-6.81 (m, 4H), 6.52 (brs, 2H), 6.16 (brs, 2H), 4.27 (brs, 4H), 3.46 (s, 3H), 3.04 (s, 3H), 2.57-2.62 (m, 2H), 2.30-2.34 (m, 2H), 1.16 (s, 3H); δ_C (100 MHz, $CDCl_3$) 170.7, 164.5, 160.5, 146.7, 140.4, 140.2, 138.7, 137.7, 131.1, 130.3, 129.5, 128.9, 128.6, 128.4, 128.1, 126.2, 120.8, 117.8, 112.0, 103.1, 101.6, 94.8, 52.0, 50.5, 48.6, 33.8, 28.6, 16.6; MS (ESI): 831 (M^+ , 45%), 833 (100), 835 (55). Anal. Calcd for $C_{44}H_{39}Br_2N_3O_4$: C 63.40, H 4.72, N 5.04; Found: C 63.13, H 4.95, N 4.84.

(2'*E*,5'*E*,3'*S*,4'*R*) or (2'*E*,5'*E*,3'*R*,4'*S*)-Methyl

2'-(1-methoxycarbonylethylidene)-1,1',3,4-tetraphenyl-5'-propylidene-1,4-dihydrospiro[1,2,4-triazole-2,3'-pyrrolidine]-4'-carboxylate (19a-I): 49 %, yellow crystals (ethyl acetate and petroleum ether), mp 164-166 °C; ν_{max}/cm^{-1} 1744, 1715, 1653, 1594, 1493; δ_H (400 MHz, CD_3COCD_3 , 40°C) 7.72 (t, J = 3.7 Hz, 2H), 7.47 (d, J = 6.3 Hz, 2H), 7.24-7.33 (m, 13H), 6.85-6.88 (m, 1H), 6.59 (br, 2H), 4.92 (s, 1H), 4.70 (dt, J = 7.6, 2.4 Hz, 1H), 3.52 (s, 3H), 3.51 (s, 3H), 1.97-2.01 (m, 1H), 1.81-1.88 (m, 1H), 1.07 (s, 3H), 0.94 (t, J = 7.3 Hz, 3H); δ_C (100 MHz, CD_3COCD_3) 170.2, 169.5, 148.5, 143.2, 143.0, 140.5, 139.9, 137.8, 130.5, 130.4, 129.95, 129.8, 129.5, 129.49, 129.46, 129.0, 128.7, 128.1, 127.2, 120.6, 116.5, 105.0, 103.4, 94.7, 52.5, 51.8, 50.0, 22.5, 16.2, 14.8; MS (ESI): 613 ($M+1$). Anal. Calcd for $C_{38}H_{36}N_4O_4$: C 74.49, H 5.92, N 9.14; Found: C 74.46, H 5.49, N 9.09.

(2'*E*,5'*E*,3'*R*,4'*R*) or (2'*E*,5'*E*,3'*S*,4'*S*)-Methyl

2'-(1-methoxycarbonylethylidene)-1,1',3,4-tetraphenyl-5'-propylidene-1,4-dihydrospiro[1,2,4-triazole-2,3'-pyrrolidine]-4'-carboxylate (19a-II): 14 %, yellow crystals (ethyl acetate and petroleum ether), mp

147-149 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1753, 1719, 1594; δ_{H} (400 MHz, CD_3COCD_3) 7.41 (t, $J = 7.8$ Hz, 4H), 7.27-7.36 (m, 11H), 7.17 (t, $J = 7.2$ Hz, 2H), 7.01 (br, 2H), 6.82 (t, $J = 7.2$ Hz, 1H), 4.54 (dt, $J = 7.6, 2.4$ Hz, 1H), 4.39 (s, 1H), 3.48 (s, 3H), 3.35 (s, 3H), 1.82-1.88 (m, 1H), 1.76-1.80 (m, 1H), 1.22 (s, 3H), 0.83 (t, $J = 7.3$ Hz, 3H); δ_{C} (100 MHz, CDCl_3) 174.8, 173.1, 152.9, 150.9, 148.2, 145.3, 143.6, 143.3, 134.5, 134.4, 134.3, 134.1, 133.9, 133.8, 133.2, 133.0, 132.9, 132.6, 132.5, 124.7, 121.7, 108.9, 107.5, 99.3, 60.7, 56.8, 56.4, 26.6, 21.1, 18.9; MS (ESI): 613 (M+1). Anal. Calcd for $\text{C}_{38}\text{H}_{36}\text{N}_4\text{O}_4$: C 74.49, H 5.92, N 9.14; Found: C 74.29, H 5.74, N 9.04.

(2'E,5'E,3'S,4'R) or (2'E,5'E,3'R,4'S)-Methyl

2'-(1-methoxycarbonylethylidene)-1'-(*p*-methoxyphenyl)-1,3,4-triphenyl-5'-propylidene-1,4-dihydrospiro[1,2,4-triazole-2,3'-pyrrolidine]-4'-carboxylate (19b-I): 26%, orange crystals (ethyl acetate and petroleum ether), mp 161-162 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1746, 1707, 1595, 1509, 1493; δ_{H} (400 MHz, CD_3COCD_3 , 40°C) 7.70 (t, $J = 3.4$ Hz, 2H), 7.47 (dd, $J = 7.7, 1.4$ Hz, 2H), 7.23-7.33 (m, 10H), 6.83-6.87 (m, 3H), 6.53 (br, 2H), 4.89 (t, $J = 1.2$ Hz, 1H), 4.62 (dt, $J = 7.6, 2.4$ Hz, 1H), 3.80 (s, 3H), 3.51 (s, 3H), 3.50 (s, 3H), 1.94-2.03 (m, 1H), 1.77-1.89 (m, 1H), 1.09 (s, 3H), 0.94 (t, $J = 7.3$ Hz, 3H); δ_{C} (100 MHz, CD_3COCD_3) 170.2, 169.5, 159.5, 148.5, 143.1, 143.0, 139.8, 138.4, 132.9, 130.7, 130.4, 129.9, 129.5, 129.4, 129.0, 128.9, 128.7, 127.1, 120.5, 116.4, 114.9, 104.9, 102.7, 94.6, 55.8, 52.4, 51.7, 50.0, 22.4, 15.9, 14.8; MS (ESI): 643 (M+1). Anal. Calcd for $\text{C}_{39}\text{H}_{38}\text{N}_4\text{O}_5$: C 72.88, H 5.96, N 8.72; Found: C 72.53, H 5.81, N 8.47.

(2'E,5'E,3'R,4'R) or (2'E,5'E,3'S,4'S)-Methyl

2'-(1-methoxycarbonylethylidene)-1'-(*p*-methoxyphenyl)-1,3,4-triphenyl-5'-propylidene-1,4-dihydrospiro[1,2,4-triazole-2,3'-pyrrolidine]-4'-carboxylate (19b-II): 24%, yellow crystals (ethyl acetate and petroleum ether), mp 156-158 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1756, 1698, 1596, 1509, 1493; δ_{H} (400 MHz, CD_3COCD_3) 7.41 (d, $J = 7.2$ Hz, 2H), 7.27-7.35 (m, 10H), 7.18 (t, $J = 7.6$ Hz, 2H), 6.95 (br s, 4H), 6.82 (t, $J = 7.2$ Hz, 1H), 4.49 (t, $J = 7.5$ Hz, 1H), 4.36 (s, 1H), 3.84 (s, 3H), 3.49 (s, 3H), 3.34 (s, 3H), 1.80-1.89 (m, 1H), 1.71-1.79 (m, 1H), 1.25 (s, 3H), 0.83 (t, $J = 7.4$ Hz, 3H); δ_{C} (100 MHz, CD_3COCD_3) 170.6, 168.9, 159.7, 148.5, 146.6, 143.9, 139.6, 139.3, 133.5, 130.6, 130.2, 129.9, 129.8, 129.7, 128.9, 128.7, 128.5, 128.1, 120.3, 117.4, 115.2, 104.5, 102.6, 95.0, 56.3, 55.8, 52.5, 52.1, 22.3, 16.6, 14.6; MS (ESI): 643 (M+1). Anal. Calcd for $\text{C}_{39}\text{H}_{38}\text{N}_4\text{O}_5$: C 72.88, H 5.96, N 8.72; Found: C 72.88, H 5.87, N 8.65.

(2'E,5'E,3'S,4'R) or (2'E,5'E,3'R,4'S)-Methyl

2'-(1-methoxycarbonylethylidene)-1'-(*p*-methylphenyl)-1,3,4-triphenyl-5'-propylidene-1,4-dihydrospiro[1,2,4-triazole-2,3'-pyrrolidine]-4'-carboxylate (19c-I): 38%, yellow solid, mp 80-84 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1747, 1707, 1595, 1512, 1493; δ_{H} (400 MHz, CD_3COCD_3 , 40°C) 7.70 (t, $J = 3.6$ Hz, 2H), 7.47 (d, $J = 6.6$ Hz, 2H), 7.24-7.35 (m, 10H), 7.10 (d, $J = 8.1$ Hz, 2H), 6.85 (t, $J = 6.6$ Hz, 1H), 6.47 (br, 2H), 4.90 (s, 1H), 4.68 (dt, $J = 7.5, 2.3$ Hz, 1H), 3.51 (s, 3H), 3.50 (s, 3H), 2.31 (s, 3H), 1.96-2.02 (m, 1H), 1.80-1.88 (m, 1H), 1.08 (s, 3H), 0.94 (t, $J = 7.4$ Hz, 3H); δ_{C} (100 MHz, CD_3COCD_3) 169.3, 168.6, 147.6, 142.2, 142.1, 138.9, 137.1, 137.0, 136.9, 129.6, 129.4, 129.0, 128.6, 128.5, 128.4, 128.1, 128.0, 127.8, 126.3, 119.6, 115.5, 104.0, 102.2, 93.8, 51.5, 50.8, 49.1, 21.5, 20.1, 15.2, 13.8; HRMS (ESI-TOF): 627.2966 (M+1); $\text{C}_{39}\text{H}_{39}\text{N}_4\text{O}_4$ required 627.2971 (M+1).

(2'E,5'E,3'R,4'R) or (2'E,5'E,3'S,4'S)-Methyl

2'-(1-methoxycarbonylethylidene)-1'-(*p*-methylphenyl)-1,3,4-triphenyl-5'-propylidene-1,4-dihydrospiro[1,2,4-triazole-2,3'-pyrrolidine]-4'-carboxylate (19c-II): 21%, yellow solid, mp 73-77 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1747, 1707, 1595, 1512, 1493; δ_{H} (400 MHz, CDCl_3) 7.51-7.53 (m, 3H), 7.30-7.37 (m, 9H), 7.27 (t, $J = 7.2$ Hz, 3H), 7.18-7.21 (m, 3H), 6.85 (t, $J = 7.2$ Hz, 1H), 4.79 (d, $J = 2.3$ Hz, 1H), 4.17 (dt, $J = 8.1, 2.2$ Hz, 1H), 3.55 (s, 3H), 3.48 (s, 3H), 2.51-2.56 (m, 1H), 2.40-2.46 (m, 1H), 2.33 (s, 3H), 1.04 (s, 3H), 0.90 (t, $J = 7.4$ Hz, 3H); δ_{C} (100 MHz, CDCl_3) 170.2, 167.9, 164.0, 148.7, 143.1, 140.9, 139.9, 139.6, 136.8, 130.9, 130.0, 129.5, 129.47, 129.36, 129.1, 129.1, 128.8, 127.2, 120.4, 119.1, 116.4, 108.3, 95.1, 90.9, 52.0, 50.8, 47.2, 21.4, 21.1, 15.5, 14.3; HRMS (ESI-TOF): 627.2959 (M+1); $\text{C}_{39}\text{H}_{39}\text{N}_4\text{O}_4$ required 627.2971 (M+1).

(E)-Methyl

2'-(1-methoxycarbonylethylidene)-1,1',3,4-tetraphenyl-5'-propyl-1,1',2',4-tetrahydrospiro[1,2,4-triazole-2,3'-pyrrole]-4'-carboxylate (20a): orange crystals (ethyl acetate and petroleum ether), mp 166-168 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1717, 1689, 1609, 1592, 1493; δ_{H} (400 MHz, CD_3COCD_3) 7.47-7.49 (m, 5H), 7.28-7.33 (m, 8H), 7.09-7.18 (m, 6H), 6.73 (t, $J = 7.0$ Hz, 1H), 3.49 (s, 3H), 3.47 (s, 3H), 2.48-2.55 (m, 1H), 2.34-2.41 (m, 1H), 1.26 (s, 3H), 1.12-1.24 (m, 2H), 0.63 (t, $J = 7.3$ Hz, 3H); δ_{C} (100 MHz, CD_3COCD_3) 170.3, 164.5, 164.0, 147.0, 146.0, 144.5, 139.8, 139.7, 130.4, 130.3, 130.2, 129.7, 129.6, 129.5, 129.4, 129.0, 128.9, 128.8, 127.6, 119.4, 114.9, 113.9, 102.0, 94.6, 52.6, 50.5, 28.4, 21.9, 16.3, 14.4; MS (ESI): 613 (M+1). Anal. Calcd for $\text{C}_{38}\text{H}_{36}\text{N}_4\text{O}_4$: C 74.49, H 5.92, N 9.14; Found: C 74.39, H 6.04, N 9.15.

(E)-Methyl

2'-(1-methoxycarbonylethylidene)-1'-(*p*-methoxyphenyl)-1,3,4-triphenyl-5'-propyl-1,1',2',4-tetrahydros piro[1,2,4-triazole-2,3'-pyrrole]-4'-carboxylate (20b): orange crystals (ethyl acetate and petroleum ether), mp 217-219 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1717, 1692, 1594, 1510, 1493; δ_{H} (400 MHz, CD_3COCD_3) 7.48 (dd, $J = 8.0, 1.9$ Hz, 2H), 7.25-7.33 (m, 9H), 7.09-7.18 (m, 5H), 7.02 (d, $J = 7.6$ Hz, 2H), 6.73 (t, $J = 7.0$ Hz, 1H), 3.86 (s, 3H), 3.49 (s, 3H), 3.46 (s, 3H), 2.46-2.53 (m, 1H), 2.30-2.37 (m, 1H), 1.31 (s, 3H), 1.12-1.23 (m, 2H), 0.64 (t, $J = 7.3$ Hz, 3H); δ_{C} (100 MHz, CD_3COCD_3) 170.4, 164.5, 164.4, 160.7, 147.0, 146.1, 144.6, 139.8, 131.9, 131.4, 130.4, 129.7, 129.5, 129.4, 129.0, 128.9, 128.7, 127.5, 119.3, 115.4, 114.9, 113.4, 101.4, 94.5, 55.9, 52.6, 50.3, 21.9, 16.2, 14.4; MS (ESI): 643 (M+1). Anal. Calcd for $\text{C}_{39}\text{H}_{38}\text{N}_4\text{O}_5$: C 72.88, H 5.96, N 8.72; Found: C 72.91, H 6.06, N 8.69.