Supporting Information

Palladium-Catalyzed Aminoallylation of Activated Olefins with Allylic Halides and Phthalimine

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General Information. ^1H NMR and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, in CDCl_3 . The chemical shifts are reported in δ units relative to internal tetramethylsilane. IR spectra were obtained in KBr on a FT spectrophotometer. All commercially supplied chemicals were used without further purification. Column chromatography was performed with silica gel 60 (70-230 mesh).

Allyl-1-[(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-benzyl]-malononitrile(3a): colorless crystal; IR (KBr) 3003, 2256, 1724, 1363 cm^{-1} . ^1H NMR (CDCl_3) δ 7.89 (m, 2H), 7.76 (m, 4H), 7.41 (m, 3H), 5.95 (m, 1H), 5.63 (s, 1H), 5.46 (d, $J = 10.0$ Hz, 1H), 5.40 (d, $J = 17.0$ Hz, 1H), 2.84 (dd, $J = 6.8, 14.0$ Hz, 1H), 2.72 (dd, $J = 7.8, 14.0$ Hz, 1H). ^{13}C NMR (CDCl_3) δ 167.55, 135.14, 132.76, 132.74, 131.26, 130.45, 130.00, 129.49, 128.35, 128.33, 124.32, 113.92, 113.91, 58.51, 42.14, 41.67. HRMS (EI) calcd for $\text{C}_{21}\text{H}_{15}\text{N}_3\text{O}_2$: m/z 341.1165. Found: m/z 341.1158. Anal. Calcd for $\text{C}_{21}\text{H}_{15}\text{N}_3\text{O}_2$: C, 73.89; H, 4.43; N, 12.31. Found: C, 73.91; H, 4.49; N, 12.05.

Allyl-1-[(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-4-nitrobenzyl]-malononitrile (3b): colorless crystal; IR (KBr) 3089, 2255, 1724, 1516, 1348 cm^{-1} . ^1H NMR (CDCl_3) δ 8.26 (d, $J = 8.5$ Hz, 2H), 7.99 (d, $J = 8.5$ Hz, 2H), 7.91 (m, 2H), 7.79 (m, 2H), 5.94 (m, 1H), 5.75 (s, 1H), 5.49 (d, $J = 10.0$ Hz, 1H), 5.41 (d, $J = 17.0$ Hz, 1H), 2.84 (dd, $J = 6.8, 14.0$ Hz, 1H), 2.76 (dd, $J = 7.7, 14.0$ Hz, 1H). ^{13}C NMR (CDCl_3) δ 167.04, 138.95, 135.19, 131.00, 130.77, 127.47, 124.55, 124.33, 124.31, 113.46, 113.02, 57.20, 41.50, 41.20. HRMS (EI) calcd for $\text{C}_{21}\text{H}_{14}\text{N}_4\text{O}_4$: m/z 386.1016. Found: m/z 386.1016. Anal. Calcd for $\text{C}_{21}\text{H}_{14}\text{N}_4\text{O}_4$: C, 65.28; H, 3.65; N, 14.50. Found: C, 65.43; H, 3.75; N, 14.31.

Allyl-1-[(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-4-fluorobenzyl]-malononitrile (3c): colorless crystal; IR (KBr) 3089, 2255, 1724, 1516, 1348 cm^{-1} . ^1H NMR (CDCl_3) δ 7.89 (m, 2H), 7.78 (m, 4H), 7.10 (m, 2H), 5.94 (m, 1H), 5.62 (s, 1H), 5.46 (d, $J = 10.0$ Hz, 1H), 5.39 (d, $J = 17.0$ Hz, 1H), 2.81 (dd, $J = 6.8, 14.0$ Hz, 1H), 2.71 (dd, $J = 7.8, 14.0$ Hz, 1H). ^{13}C NMR (CDCl_3) δ 167.21, 163.47 ($J_{\text{CF}} = 235$ Hz), 134.91, 134.25, 132.00, 130.97, 128.36, 127.84, 124.19, 123.51, 116.34 ($^2J_{\text{CF}} = 21$ Hz), 113.81, 113.43, 57.47, 41.93, 41.39. HRMS (EI) calcd for $\text{C}_{21}\text{H}_{14}\text{N}_3\text{O}_2\text{F}$: m/z 359.1070. Found: m/z 359.1074.

Allyl-1-[(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-4-methoxycarbonylbenzyl]-malononitrile (3d): colorless crystal; IR (KBr) 2954, 2256, 1770, 1722, 1392 cm^{-1} . ^1H NMR (CDCl_3) δ 8.07 (d, $J = 8.5$ Hz, 2H), 7.89 (m, 2H), 7.84 (d, $J = 8.5$ Hz, 2H), 7.77 (m, 2H), 5.94 (m, 1H), 5.69 (s, 1H), 5.46 (d, $J = 10.0$ Hz, 1H), 5.38 (d, $J = 17.0$ Hz, 1H), 3.88 (s, 3H), 2.82 (dd, $J = 6.5, 14.0$ Hz, 1H), 2.72 (dd, $J = 7.5, 14.0$ Hz, 1H). ^{13}C NMR (CDCl_3) δ 167.05, 165.98, 136.86, 134.97, 131.81, 130.94, 130.38, 129.82, 127.74, 124.32, 124.20, 113.66, 113.32, 57.77, 52.36, 41.63, 41.40. HRMS (EI) calcd for $\text{C}_{23}\text{H}_{17}\text{N}_3\text{O}_4$: m/z 399.1219. Found: m/z 399.1220. Anal. Calcd for $\text{C}_{23}\text{H}_{17}\text{N}_3\text{O}_4$: C, 69.17; H, 4.29; N, 10.52. Found: C, 69.19; H, 4.68; N, 10.19.

Allyl-1-[(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-4-methylbenzyl]-malononitrile (3e): colorless crystal; IR (KBr) 2954, 2256, 1770, 1722, 1392 cm^{-1} . ^1H NMR (CDCl_3) δ 7.90 (m, 2H), 7.77 (m, 2H), 7.66 (d, $J = 8.2$ Hz, 2H), 7.23 (d, $J = 8.2$ Hz, 2H), 5.96 (m, 1H), 5.61 (s, 1H), 5.47 (d, $J = 10.0$ Hz, 1H), 5.41 (d, $J = 17.0$ Hz, 1H), 2.84 (dd, $J = 6.5, 14.0$ Hz, 1H), 2.73 (dd, $J = 7.0, 14.0$ Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (CDCl_3) δ 167.32, 140.40, 134.78, 131.14, 129.91, 129.68, 129.42, 128.09, 124.07, 124.05, 114.01, 113.69, 58.19, 41.96, 41.55, 21.19. HRMS (EI) calcd for $\text{C}_{22}\text{H}_{17}\text{N}_3\text{O}_2$: m/z 355.1321. Found: m/z 355.1326.

Allyl-1-[(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-4-methoxybenzyl]-malononitrile (3f): colorless crystal; IR (KBr) 3008, 2256, 1720, 1610, 1515 cm^{-1} . ^1H NMR (CDCl_3) δ 7.87 (m, 2H), 7.74 (m, 2H), 7.70 (d, $J = 8.7$ Hz, 2H), 6.90 (d, $J = 8.7$ Hz, 2H), 5.94 (m, 1H), 5.56 (s, 1H), 5.44 (d, $J = 10.0$ Hz, 1H), 5.37 (d, $J = 17.0$ Hz, 1H), 3.78 (s, 3H), 2.81 (dd, $J = 6.8, 14.0$ Hz, 1H), 2.70 (dd, $J = 7.9, 14.0$ Hz, 1H). ^{13}C NMR (CDCl_3) δ 167.26, 160.74, 134.74, 131.24, 131.65, 128.06, 124.27, 124.00, 123.94, 114.45, 114.01, 113.66, 57.78, 55.26, 42.07, 41.47. HRMS (EI) calcd for $\text{C}_{22}\text{H}_{17}\text{N}_3\text{O}_3$: m/z 371.1270. Found: m/z 371.1269. Anal. Calcd for $\text{C}_{22}\text{H}_{17}\text{N}_3\text{O}_3$: C, 71.15; H, 4.61; N, 11.31. Found: C, 71.09; H, 4.74; N, 11.02.

Allyl-1-[(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-*t*-butyl-methyl]-malononitrile (3g): colorless crystal; IR (KBr) 2974, 2254, 1718, 1389 cm^{-1} . ^1H NMR (CDCl_3) δ 7.87 (m, 2H), 7.77 (m, 2H), 5.82 (ddd, $J = 7.0, 10.0, 17.0$ Hz, 1H), 5.32 (d, $J = 10.0$ Hz, 1H), 5.24 (d, $J = 17.0$ Hz, 1H), 4.45 (s, 1H), 2.65 (d, $J = 7.0$ Hz, 2H), 1.24 (s, 9H). ^{13}C NMR (CDCl_3) δ 168.41, 167.52, 134.96, 134.76, 130.76, 130.61, 127.97, 123.98, 123.54, 134.11, 115.37, 114.22, 61.20, 41.72, 38.84, 37.81, 28.70. HRMS (EI) calcd for $\text{C}_{19}\text{H}_{19}\text{N}_3\text{O}_2$: m/z 321.1477. Found: m/z 321.1479. Anal. Calcd for $\text{C}_{19}\text{H}_{19}\text{N}_3\text{O}_2$: C, 71.01; H, 5.96; N, 13.08. Found: C, 70.93; H, 6.06; N, 12.95.

2-[(5-Allyl-2,2-dimethyl-4,6-dioxo-[1,3]dioxan-5-yl)-benzyl]-isoindole-1,3-dione (3h): colorless crystal; IR (KBr) 2945, 1769, 1736, 1713, 1371 cm^{-1} . ^1H NMR (CDCl_3) δ 7.75 (m, 2H), 7.61 (m, 4H), 7.25 (m, 3H), 5.84 (s, 1H), 5.60 (m, 1H), 5.17 (d, $J = 17.0$ Hz, 1H), 5.12 (d, $J = 10.0$ Hz, 1H), 2.84 (d, $J = 7.5$ Hz, 2H), 1.59 (s, 3H), 1.54 (s, 3H). ^{13}C NMR (CDCl_3) δ 167.53, 167.03, 164.91, 134.40, 133.80, 131.26, 131.18, 130.60, 129.15, 128.07, 123.58, 122.52, 106.41, 61.70, 57.11, 42.09, 31.26, 27.93. HRMS (EI) calcd for $\text{C}_{24}\text{H}_{21}\text{NO}_6$: m/z 419.1376. Found: m/z 419.1369. Anal. Calcd for $\text{C}_{24}\text{H}_{21}\text{NO}_6$: C, 68.73; H, 5.05; N, 3.34. Found: C, 68.17; H, 5.04; N, 3.30.

2-[(5-Allyl-2,2-dimethyl-4,6-dioxo-[1,3]dioxan-5-yl)-4-nitrobenzyl]-isoindole-1,3-dione (3i): colorless crystal; ^1H NMR (CDCl_3) δ 8.13 (d, $J = 8.0$ Hz, 2H), 7.80 (m, 2H), 7.75 (d, $J = 8.0$ Hz, 2H), 7.70 (m, 2H), 5.62 (m, 1H), 5.90 (s, 1H), 5.22 (d, $J = 17.5$ Hz, 1H), 5.21 (d, $J = 10.0$ Hz, 1H), 2.76 (dd, $J = 7.0, 13.0$ Hz, 1H), 2.76 (dd, $J = 7.0, 13.0$ Hz, 1H), 1.64 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (CDCl_3) δ 167.40, 164.42, 141.15, 134.74, 132.02, 131.67, 129.88, 123.88, 123.14, 106.98, 62.02, 56.31, 42.81, 31.25, 29.77, 28.24. HRMS (EI) calcd for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_8$ (-Me): m/z 450.7240. Found: m/z 450.7243.

2-[(5-Allyl-2,2-dimethyl-4,6-dioxo-[1,3]dioxan-5-yl)-4-methylbenzyl]-isoindole-1,3-dione (3j): colorless crystal; IR (KBr) 2976, 1771, 1739, 1710, 1371 cm^{-1} . ^1H NMR (CDCl_3) δ 7.76 (m, 2H), 7.67 (m, 2H), 7.53 (d, $J = 8.2$ Hz, 2H), 7.09 (d, $J = 8.2$ Hz, 2H), 5.86 (s, 1H), 5.65 (m, 1H), 5.22 (d, $J = 17.4$ Hz, 1H), 5.17 (d, $J = 10.3$ Hz, 1H), 2.89 (d, $J = 7.5$ Hz, 2H), 2.29 (s, 3H), 1.65 (s, 3H), 1.60 (s, 3H). ^{13}C NMR (CDCl_3) δ 167.58, 165.02, 139.15, 134.38, 131.35, 131.12, 130.80, 123.73, 128.81, 123.59, 122.49, 106.41, 61.59, 57.21, 42.09, 31.33, 27.95, 21.11. HRMS (EI) calcd for $\text{C}_{25}\text{H}_{23}\text{NO}_6$: m/z 433.1524. Found: m/z 433.1526.

2-[(5-Allyl-2,2-dimethyl-4,6-dioxo-[1,3]dioxan-5-yl)-*t*-butyl-methyl]-isoindole-1,3-dione (3k): colorless crystal; IR (KBr) 2978, 1769, 1736, 1716, 1371 cm^{-1} . ^1H NMR (CDCl_3) δ 7.84 (m, 2H), 7.72 (m, 2H), 5.62 (m, 1H), 5.21 (d, $J = 17.0$ Hz, 1H), 5.16 (d, $J = 10.0$ Hz, 1H), 4.79 (s, 1H), 3.20 (dd, $J = 8.5, 13.0$ Hz, 1H), 3.02 (dd, $J = 7.5, 13.0$ Hz, 1H), 1.72 (s, 3H), 1.62 (s, 3H), 1.21 (s, 9H). ^{13}C NMR (CDCl_3) δ 168.66, 168.20, 166.89, 166.14, 134.49, 134.30, 131.58, 131.56, 130.94, 123.96, 123.38, 122.50, 106.41, 64.63, 58.71, 41.03, 19.52, 31.45, 30.06, 28.09. Anal. Calcd for $\text{C}_{27}\text{H}_{25}\text{NO}_6$: C, 66.15; H, 6.31; N, 3.31. Found: C, 65.66; H, 6.12; N, 3.45.

Di-*tert*-butyl 2-[(1,3-dioxo-1,3-dihydro-isoindol-2-yl)methyl]malonate (3l): colorless crystal; IR (KBr) 2980, 1776, 1717, 1396, 1369 cm^{-1} . ^1H NMR (CDCl_3) δ 7.81 (m, 2H), 7.69 (m, 2H), 4.11 (d, $J = 8.0$ Hz, 2H), 3.75 (t, $J = 8.0$ Hz, 1H), 1.40 (s, 18H). ^{13}C NMR (CDCl_3) δ 167.72, 166.50, 134.02, 131.94, 123.31, 51.84, 36.40, 27.75. HRMS (FAB) calcd for $\text{C}_{20}\text{H}_{25}\text{NO}_6$ (-*t*-Bu) m/z 281.1160. Found: m/z 281.1165.

[(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-benzyl]-2-(2-methyl-allyl)malononitrile (3m): colorless crystal; IR (KBr) 2945, 1769, 2255, 1728, 1458, 1348 cm^{-1} . ^1H NMR (CDCl_3) δ 7.88 (m, 2H), 7.76 (m, 4H), 7.41 (m, 3H), 5.67 (s, 1H), 5.16 (s, 1H), 5.06 (s, 1H), 2.77 (d, $J = 14.0$ Hz,

1H), 2.70 (d, $J = 14.0$ Hz, 1H), 1.95 (s, 3H). ^{13}C NMR (CDCl_3) δ 167.25, 136.60, 134.79, 134.22, 131.03, 129.86, 129.16, 124.06, 123.48, 119.53, 114.16, 114.11, 59.22, 44.73, 41.10, 22.98. HRMS (EI) calcd for $\text{C}_{22}\text{H}_{17}\text{N}_3\text{O}_2$: m/z 355.1328. Found: m/z 355.1320. Anal. Calcd for $\text{C}_{22}\text{H}_{17}\text{N}_3\text{O}_2$: C, 74.35; H, 4.82; N, 11.82. Found: C, 74.52; H, 4.94; N, 11.77.

[(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-benzyl]-2-(3-methyl-but-2-enyl)-malononitrile (3n): colorless crystal; IR (KBr) 2978, 1789, 1774, 1722, 1362 cm^{-1} . ^1H NMR (CDCl_3) δ 7.95 (m, 4H), 7.83 (m, 2H), 7.47 (m, 3H), 5.82 (s, 1H), 5.37 (t, $J = 7.5$ Hz, 1H), 3.12 (dd, $J = 7.6, 14.0$ Hz, 1H), 2.88 (dd, $J = 7.2, 14.0$ Hz, 1H), 1.80 (s, 3H), 1.66 (s, 3H). ^{13}C NMR (CDCl_3) δ 168.24, 141.57, 136.01, 135.01, 134.50, 132.20, 130.72, 130.65, 129.81, 124.62, 123.75, 115.69, 115.41, 115.29, 59.20, 43.18, 36.79, 26.05, 18.52. HRMS (EI) calcd for $\text{C}_{23}\text{H}_{19}\text{N}_3\text{O}_2$: m/z 369.1475. Found: m/z 369.1477.

[(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-benzyl]-2-(3-trans-phenyl-allyl)-malononitrile (3o): colorless crystal; IR (KBr) 3061, 2251, 1720, 1366 cm^{-1} . ^1H NMR (d_6 -acetone) δ 7.94 (m, 6H), 7.87 (m, 5H), 7.47 (m, 3H), 6.82 (d, $J = 16.0$ Hz, 1H), 6.39 (dt, $J = 7.5, 16.0$ Hz, 1H), 5.87 (s, 1H), 3.32 (dd, $J = 7.5, 14.5$ Hz, 1H), 3.11 (dd, $J = 7.5, 14.5$ Hz, 1H). ^{13}C NMR (d_6 -acetone) δ 168.22, 138.75, 137.02, 135.98, 134.36, 132.11, 130.77, 130.69, 129.86, 129.52, 129.14, 127.48, 124.63, 120.52, 115.16, 115.00, 59.14, 43.42, 41.24. HRMS (EI) calcd for $\text{C}_{27}\text{H}_{19}\text{N}_3\text{O}_2$: m/z 417.1477. Found: m/z 417.1483. Anal. Calcd for $\text{C}_{27}\text{H}_{19}\text{N}_3\text{O}_2$: C, 77.6; H, 4.59; N, 10.07. Found: C, 77.2; H, 4.81; N, 10.01.

[(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-benzyl]-2-(3-trans-methoxycarbonyl-allyl)-malononitrile (3p): colorless crystal; IR (KBr) 3061, 2251, 1720, 1366 cm^{-1} . ^1H NMR (CDCl_3) δ 7.82 (m, 2H), 7.71 (m, 4H), 7.36 (m, 2H), 6.90 (dt, $J = 7.5, 15.5$ Hz, 1H), 6.02 (d, $J = 15.5$ Hz, 1H), 5.59 (s, 1H), 3.67 (s, 3H), 2.93 (dd, $J = 7.5, 14.0$ Hz, 1H), 2.84 (dd, $J = 7.5, 14.0$ Hz, 1H). ^{13}C NMR (CDCl_3) δ 167.17, 165.00, 136.42, 134.90, 131.96, 130.91, 130.35, 129.71, 129.64, 129.33, 128.58, 124.13, 113.27, 113.13, 58.69, 51.89, 41.17, 39.65. HRMS (EI) calcd for $\text{C}_{23}\text{H}_{17}\text{N}_3\text{O}_4$: m/z 399.1219. Found: m/z 399.1219.

(2S*,4R*)-3,3-dicyano-2-phenyl-1-(4-toluenesulfonyl)-4-vinyl-pyrrolidine (11a): *cis* isomer: colorless needle; IR (KBr) 2926, 2252, 1500, 1469, 1344 cm^{-1} . ^1H NMR (CDCl_3) δ 7.56 (d, $J = 8.5$ Hz, 2H), 7.37 (m, 5H), 7.27 (d, $J = 8.5$ Hz, 2H), 5.77 (ddd, $J = 7.8, 10.0, 17.0$ Hz, 1H), 5.46 (d, $J = 10.0$ Hz, 1H), 5.44 (d, $J = 17.0$ Hz, 1H), 5.09 (s, 1H), 4.16 (dd, $J = 7.8, 12.0$ Hz, 1H), 3.64 (t, $J = 12.0$ Hz, 1H), 3.02 (dd, $J = 7.8, 12.0$ Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (CDCl_3) δ 144.93, 133.84, 133.11, 130.00, 129.94, 128.80, 127.67, 127.19, 124.12, 112.57, 110.29, 70.75, 51.69, 51.43, 49.89, 21.59. HRMS (FAB) calcd for $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_2\text{S}$: m/z 377.1198. Found: m/z 377.1206. Anal. Calcd for $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_2\text{S}$: C, 66.82; H, 5.07; N, 11.13; S, 8.50. Found: C, 66.60; H, 5.08; N, 11.04; S, 8.51; *trans* isomer: colorless needle; IR (KBr) 2925, 2255, 1596, 1454, 1344 cm^{-1} . ^1H NMR (CDCl_3) δ 7.69 (d, $J = 8.5$ Hz, 2H), 7.37 (m, 5H), 7.30 (d, $J = 8.5$ Hz, 2H), 5.71 (ddd, $J = 7.5, 10.5, 17.0$ Hz, 1H), 5.45 (d, $J = 10.5$ Hz, 1H), 5.44 (d, $J = 17.0$ Hz, 1H), 5.32 (s, 1H), 4.02 (dd, $J = 6.8, 12.0$ Hz, 1H), 3.46 (t, $J = 10.0$ Hz, 1H), 3.36 (dt, $J = 6.8, 10.0$ Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (CDCl_3) δ 144.90, 134.79, 133.29, 130.05, 129.97, 128.99, 127.83, 127.61, 127.30, 124.37, 111.20, 69.51, 50.08, 48.80, 46.93, 21.62. HRMS (FAB) calcd for $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_2\text{S}$: m/z 377.1198. Found: m/z 377.1211. Anal. Calcd for $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_2\text{S}$: C, 66.82; H, 5.07; N, 11.13; S, 8.50. Found: C, 66.80; H, 5.14; N, 11.07; S, 8.52.

(2S*,4R*)-3,3-dicyano-2-(4-fluorophenyl)-1-(4-toluenesulfonyl)-4-vinyl-pyrrolidine (11b): *cis* isomer: colorless needle; IR (KBr) 2825, 2255, 1607, 1512, 1338 cm^{-1} . ^1H NMR (CDCl_3) δ 7.54 (d, $J = 8.5$ Hz, 2H), 7.39 (m, 2H), 7.29 (d, $J = 8.5$ Hz, 2H), 7.05 (m, 2H), 5.77 (ddd, $J = 7.8, 10.0, 17.0$ Hz, 1H), 5.49 (d, $J = 10.0$ Hz, 1H), 5.45 (d, $J = 17.0$ Hz, 1H), 5.05 (s, 1H), 4.15 (dd, $J = 7.8, 12.5$ Hz, 1H), 3.64 (t, $J = 12.0$ Hz, 1H), 3.03 (dd, $J = 7.8, 12.0$ Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (CDCl_3) δ 163.58 ($J_{\text{CF}} = 248$ Hz), 145.13, 133.75, 130.08, 129.95, 129.14, 128.94, 128.89, 127.90, 127.66, 124.24, 115.95 ($^2J_{\text{CF}} = 22$ Hz), 112.40, 110.25, 70.16, 51.51, 51.37, 49.90, 21.60. HRMS (FAB) calcd for $\text{C}_{21}\text{H}_{18}\text{F}\text{N}_3\text{O}_2\text{S}$: m/z 395.1104. Found: m/z 395.1099. Anal. Calcd for $\text{C}_{21}\text{H}_{18}\text{F}\text{N}_3\text{O}_2\text{S}$: C, 63.78; H, 4.59; N, 10.63; S, 8.11. Found: C, 64.07; H, 4.77; N, 10.57; S, 8.13; *trans* isomer: colorless needle; IR (KBr) 2923, 2252, 1600, 1511,

1366 cm^{-1} . ^1H NMR (CDCl_3) δ 7.67 (d, J = 8.5 Hz, 2H), 7.34 (m, 4H), 7.10 (m, 2H), 5.70 (m, 1H), 5.45 (d, J = 10.0 Hz, 1H), 5.43 (d, J = 17.0 Hz, 1H), 5.29 (s, 1H), 4.01 (dd, J = 7.0, 10.0 Hz, 1H), 3.45 (t, J = 10.0 Hz, 1H), 3.32 (m, 1H), 2.44 (s, 3H). ^{13}C NMR (CDCl_3) δ 163.45 (J_{CF} = 248 Hz), 145.07, 133.05, 130.70, 129.32, 129.20, 127.66, 127.60, 124.47, 116.12 (J_{CF} = 22 Hz), 11.73, 11.18, 68.84, 50.09, 48.77, 46.96, 21.61. HRMS (FAB) calcd for $\text{C}_{21}\text{H}_{18}\text{N}_3\text{O}_2\text{SF}$: m/z 395.1104. Found: m/z 395.1100. Anal. Calcd for $\text{C}_{21}\text{H}_{18}\text{N}_3\text{O}_2\text{SF}$: C, 63.78; H, 4.59; N, 10.63; S, 8.11. Found: C, 64.06; H, 4.76; N, 10.56; S, 8.13.

(2S*,4R*)-3,3-dicyano-2-(4-methylcarboxyphenyl)-1-(4-toluenesulfonyl)-4-vinylpyrrolidine (11c): *cis* isomer: colorless needle; IR (KBr) 2957, 2254, 1717, 1364, 1169 cm^{-1} . ^1H NMR (CDCl_3) δ 8.04 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 8.5 Hz, 1H), 7.50 (d, J = 8.7 Hz, 2H), 7.29 (d, J = 8.5 Hz, 1H), 5.76 (ddd, J = 7.5, 10.0, 17.0 Hz, 1H), 5.49 (d, J = 10.0 Hz, 1H), 5.46 (d, J = 17.0 Hz, 1H), 5.15 (s, 1H), 4.15 (dd, J = 7.5, 12.0 Hz, 1H), 3.92 (s, 3H), 3.64 (t, J = 12.0 Hz, 1H), 3.04 (dt, J = 7.5, 12.0 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (CDCl_3) δ 166.27, 145.28, 133.10, 133.61, 131.68, 130.16, 130.10, 127.73, 127.68, 124.41, 112.32, 110.04, 70.29, 52.31, 51.85, 51.44, 49.52, 21.62. HRMS (FAB) calcd for $\text{C}_{23}\text{H}_{21}\text{N}_3\text{O}_4\text{S}$: m/z 435.1253. Found: m/z 435.1252. Anal. Calcd for $\text{C}_{23}\text{H}_{21}\text{N}_3\text{O}_4\text{S}$: C, 63.43; H, 4.86; N, 9.65; S, 7.36. Found: C, 63.21; H, 4.94; N, 9.58; S, 7.39; *trans* isomer: colorless needle; IR (KBr) 2926, 2252, 1716, 1437, 1469, 1336, 1169 cm^{-1} . ^1H NMR (CDCl_3) δ 8.08 (d, J = 8.7 Hz, 2H), 7.68 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.7 Hz, 2H), 7.33 (d, J = 8.5 Hz, 2H), 5.70 (ddd, J = 8.0, 10.0, 17.0 Hz, 1H), 5.46 (d, J = 10.0 Hz, 1H), 5.42 (d, J = 17.0 Hz, 1H), 5.34 (s, 1H), 4.04 (dd, J = 7.5, 12.0 Hz, 1H), 3.92 (s, 3H), 3.46 (t, J = 10.0 Hz, 1H), 3.33 (m, 1H), 2.43 (s, 3H). HRMS (FAB) calcd for $\text{C}_{23}\text{H}_{21}\text{N}_3\text{O}_4\text{S}$: m/z 435.1253. Found: m/z 435.1251. Anal. Calcd for $\text{C}_{23}\text{H}_{21}\text{N}_3\text{O}_4\text{S}$: C, 63.43; H, 4.86; N, 9.65; S, 7.36. Found: C, 63.20; H, 4.94; N, 9.56; S, 7.39.

(2S*,4R*)-3,3-dicyano-2-(4-tolyl)-1-(4-toluenesulfonyl)-4-vinylpyrrolidine (11d): *cis* isomer: colorless needle; IR (KBr) 2924, 2255, 1719, 1597, 1336, 1160 cm^{-1} . ^1H NMR (CDCl_3) δ 7.55 (d, J = 8.5 Hz, 2H), 7.28 (m, 4H), 7.16 (d, J = 8.5 Hz, 2H), 5.77 (ddd, J = 8.0, 10.0, 17.0 Hz, 1H), 5.46 (d, J = 10.0 Hz, 1H), 5.42 (d, J = 17.0 Hz, 1H), 5.01 (s, 1H), 4.12 (dd, J = 7.5, 12.0 Hz, 1H), 3.63 (t, J = 12.0 Hz, 1H), 2.99 (dd, J = 7.5, 12.0 Hz, 1H), 2.43 (s, 3H), 2.35 (s, 1H). ^{13}C NMR (CDCl_3) δ 144.88, 140.02, 133.83, 129.99, 129.51, 128.13, 127.70, 127.13, 124.03, 112.65, 110.40, 70.72, 51.58, 51.43, 49.98, 21.61, 21.28. HRMS (FAB) calcd for $\text{C}_{22}\text{H}_{21}\text{N}_3\text{O}_2\text{S}$: m/z 391.1354. Found: m/z 391.1371; *trans* isomer: colorless needle; IR (KBr) 2923, 2252, 1597, 1356, 1159 cm^{-1} . ^1H NMR (CDCl_3) δ 7.70 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 8.5 Hz, 2H), 7.23 (m, 4H), 5.71 (m, 1H), 5.46 (d, J = 10.0 Hz, 1H), 5.44 (d, J = 17.0 Hz, 1H), 5.31 (s, 1H), 4.02 (dd, J = 6.0, 9.5 Hz, 1H), 3.45 (t, J = 9.5 Hz, 1H), 3.37 (m, 1H), 2.44 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (CDCl_3) δ 144.81, 139.98, 133.24, 131.90, 130.00, 129.64, 127.88, 127.59, 127.17, 124.26, 111.96, 111.29, 69.39, 50.00, 48.71, 46.97, 21.59, 21.21. HRMS (FAB) calcd for $\text{C}_{22}\text{H}_{21}\text{N}_3\text{O}_2\text{S}$: m/z 391.1354. Found: m/z 391.1359.

(2S*,4R*)-3,3-dicyano-2-(*t*-butyl)-1-(4-toluenesulfonyl)-4-vinylpyrrolidine (11e): *cis* isomer: colorless needle; IR (KBr) 2995, 2255, 1740, 1358, 1163 cm^{-1} . ^1H NMR (CDCl_3) δ 7.76 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.5 Hz, 1H), 5.72 (ddd, J = 8.0, 10.0, 17.0 Hz, 1H), 5.39 (d, J = 10.0 Hz, 1H), 5.20 (d, J = 17.0 Hz, 1H), 4.41 (s, 1H), 3.75 (dd, J = 6.0, 13.0 Hz, 1H), 3.09 (t, J = 13.0 Hz, 1H), 2.68 (m, 1H), 2.45 (s, 3H), 1.26 (s, 9H). ^{13}C NMR (CDCl_3) δ 145.13, 135.14, 1310.29, 128.11, 127.83, 123.74, 115.20, 113.16, 76.34, 54.98, 53.33, 42.36, 37.19, 26.99, 21.62. HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{23}\text{N}_3\text{O}_2\text{S}$: m/z 357.1511. Found: m/z 357.1519. Anal. Calcd for $\text{C}_{19}\text{H}_{23}\text{N}_3\text{O}_2\text{S}$: C, 63.84; H, 6.49; N, 11.75; S, 8.97. Found: C, 63.79; H, 6.60; N, 11.63; S, 8.95; *trans* isomer: colorless needle; IR (KBr) 2966, 2252, 1739, 1357, 1163 cm^{-1} . ^1H NMR (CDCl_3) δ 7.73 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 5.66 (m, 1H), 5.45 (d, J = 10.0 Hz, 1H), 5.43 (d, J = 17.0 Hz, 1H), 4.39 (s, 1H), 3.66 (t, J = 8.0 Hz, 1H), 3.57 (dd, J = 8.0, 16.0 Hz, 1H), 3.39 (t, J = 8.0 Hz, 1H), 2.41 (s, 3H), 1.22 (s, 9H). ^{13}C NMR (CDCl_3) δ 144.73, 133.87, 129.84, 128.80, 128.45, 123.96, 113.42, 112.64, 75.42, 52.06, 50.12, 42.50, 37.67, 28.14, 21.59. HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{23}\text{N}_3\text{O}_2\text{S}$: m/z 357.1511. Found: m/z 357.1506. Anal. Calcd for $\text{C}_{19}\text{H}_{23}\text{N}_3\text{O}_2\text{S}$: C, 63.84; H, 6.49; N, 11.75; S, 8.97. Found: C, 63.78; H, 6.59; N, 11.62; S, 8.95.

(1S*,4R*)-8,8-dimethyl-1-phenyl-2-(4-toluenesulfonyl)-4-vinyl-7,9-dioxa-2-aza-

spiro[4,5]decane-6,10-dione (11f): *cis* isomer: colorless needle; IR (KBr) 2923, 1774, 1742, 1597, 1350 cm^{-1} . ^1H NMR (CDCl_3) δ 7.62 (d, $J = 8.0$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 1H), 7.23 (m, 5H), 5.50 (dt, $J = 9.5, 17.0$ Hz, 1H), 5.27 (s, 1H), 5.17 (d, $J = 9.5$ Hz, 1H), 5.16 (d, $J = 17.0$ Hz, 1H), 4.08 (t, $J = 9.5$ Hz, 1H), 3.93 (dd, $J = 9.5, 12.0$ Hz, 1H), 3.20 (m, 1H), 2.41 (s, 3H), 1.43 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (CDCl_3) δ 167.05, 162.77, 144.00, 135.10, 133.76, 130.26, 129.71, 128.90, 128.32, 127.80, 127.71, 122.21, 106.05, 66.11, 53.43, 52.84, 29.85, 28.74, 21.66. HRMS (FAB) calcd for $\text{C}_{24}\text{H}_{20}\text{NO}_6\text{S}$ (-Me): m/z 440.1169. Found: m/z 440.1189; *trans* isomer: colorless needle; IR (KBr) 2895, 1778, 1747, 1589, 1352 cm^{-1} . ^1H NMR (CDCl_3) δ 7.52 (d, $J = 8.0$ Hz, 2H), 7.24 (m, 3H), 7.19 (d, $J = 8.0$ Hz, 2H), 7.15 (m, 2H), 5.47 (ddd, $J = 8.0, 10.0, 17.0$ Hz, 1H), 5.17 (d, $J = 17.0$ Hz, 1H), 5.16 (s, 1H), 5.08 (d, $J = 10.0$ Hz, 1H), 3.84 (m, 3H), 2.35 (s, 3H), 1.67 (s, 3H), 1.48 (s, 3H). ^{13}C NMR (CDCl_3) δ 165.89, 163.46, 143.62, 136.72, 134.35, 130.56, 129.35, 128.75, 128.27, 127.55, 127.35, 121.98, 105.46, 71.50, 71.40, 64.17, 52.23, 49.35, 29.72, 29.05, 21.60. HRMS (FAB) calcd for $\text{C}_{24}\text{H}_{20}\text{NO}_6\text{S}$: m/z 455.1406. Found: m/z 455.1417.

3,3-bisbenzenesulfonyl-1-(4-toluenesulfonyl)-4-vinyl-pyrrolidine(11g): colorless needle; IR (KBr) 3070, 1595, 1330, 1167 cm^{-1} . ^1H NMR (CDCl_3) δ 7.96 (d, $J = 8.0$ Hz, 2H), 7.77 (d, $J = 8.0$ Hz, 1H), 7.61 (m, 4H), 7.49 (m, 4H), 7.34 (d, $J = 8.0$ Hz, 2H), 5.91 (m, 1H), 4.95 (d, $J = 10.0$ Hz, 1H), 4.79 (d, $J = 17.0$ Hz, 1H), 4.11 (d, $J = 8.0$ Hz, 1H), 3.69 (d, $J = 13.0$ Hz, 1H), 3.56 (m, 2H), 3.35 (m, 1H), 2.41 (s, 3H). ^{13}C NMR (CDCl_3) δ 144.45, 136.83, 135.58, 135.22, 135.06, 132.57, 131.71, 131.62, 129.92, 129.70, 128.91, 128.55, 127.89, 120.29, 91.65, 52.42, 51.78, 49.64, 21.62. MS (EI) calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_4\text{S}_2$ (-HSO₂Ph): m/z 389.0752. Found: m/z 389.0755. Anal. Calcd for $\text{C}_{25}\text{H}_{25}\text{NO}_6\text{S}_3$: C, 56.48; H, 4.74; N, 2.63. Found: C, 55.63; H, 4.61; N, 2.62; *trans* isomer: