Supporting Information

Pd(II) and Pd(0) Co-catalyzed Reactions of Sulfonamides with MCPs

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Experimental Procedures

General Methods. Melting points are uncorrected. ¹H and ¹³C NMR spectra were recorded at 300 and 75 MHz, respectively. Mass spectra were recorded by EI methods, and HRMS was measured on a Finnigan MA⁺ mass spectrometer. Organic solvents used were dried by standard methods when necessary. All solid compounds reported in this paper gave satisfactory CHN microanalyses. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. The starting methylenecyclopropanes were prepared according to the literature.¹

Ref. 1. Utimoto, K.; Tamura, M.; Sisido, K. *Tetrahedron*. **1973**, 29, 1169.

***N,N*-Di-[2-(diphenylmethyl)propenyl]-*p*-toluenesulfonamide (4a):** To a mixture of diphenylmethylenecyclopropane **1a** (0.185 g, 0.9 mmol), *p*-toluenesulfonamide **2a** (0.051 g, 0.3 mmol), Pd(PPh₃)₄ (0.035 g, 10 mol%), Pd(OAc)₂ (0.003 g, 5 mol%) and PPh₃ (0.032 g, 40 mol%) was added dry toluene (4 mL), and the resulting mixture was heated at 110 °C for 3 h with stirring. Removal of the solvent gave a crude oil that was purified

by flash chromatography using EtOAc / hexane (1 : 10) as the eluant to yield **4a** (0.174 g, 100%) as colorless solid. mp. 142-144 °C; ¹H NMR (300 MHz, CDCl₃) δ 2.37 (s, 3H, CH₃), 3.82 (s, 4H, CH₂), 4.63 (s, 4H, =CH+CH), 5.15 (s, 2H, =CH), 7.00-7.27 (m, 22H, Ar), 7.57 (d, 2H, *J* = 8.0 Hz, Ar); ¹³C NMR (75 MHz, CDCl₃) δ 21.604, 52.352, 54.602, 117.762, 126.607, 127.434, 128.410, 129.295, 129.647, 137.409, 141.423, 143.208, 145.995; MS (EI) *m/z*: 583 (M⁺, 10.75), 428 (85.70), 205 (76.51), 167 (60.46), 91 (100); Anal. Calcd. for C₃₉H₃₇NO₂S (%): C, 80.24; H, 6.39; N, 2.40. Found: C, 80.18; H, 6.46; N, 2.35; IR (neat): ν 3084, 3025, 2925, 2857, 1644, 1597, 1493, 1450, 1347 cm⁻¹.

***N*-[2-(Diphenylmethyl)propenyl]-*p*-toluenesulfonamide (3a):** To a mixture of diphenylmethylenecyclopropane **1a** (0.062 g, 0.3 mmol), *p*-toluenesulfonamide **2a** (0.051 g, 0.3 mmol), Pd(PPh₃)₄ (0.035 g, 10 mol%), Pd(OAc)₂ (0.003 g, 5 mol%) and PPh₃ (0.032 g, 40 mol%) was added dry toluene (4 mL), and the resulting mixture was heated at 90 °C for 1 h with stirring. Removal of the solvent gave a crude oil that was purified by flash chromatography using EtOAc / hexane (1 : 10) as the eluant to yield **3a** (0.057 g, 50%) as colorless solid. mp. 121-123 °C; ¹H NMR (300 MHz, CDCl₃) δ 2.43 (s, 3H, CH₃), 3.55 (d, 2H, *J* = 6.2 Hz, CH₂), 4.62 (s, 1H, CH), 4.76 (s, 1H, =CH), 4.82 (t, 1H, *J* = 6.1 Hz, NH), 5.29 (s, 1H, =CH), 7.05-7.29 (m, 12H, Ar), 7.70 (d, 2H, *J* = 8.1 Hz, Ar); ¹³C NMR (75 MHz, CDCl₃) δ 21.616, 48.083, 54.936, 117.372, 127.355, 127.885, 129.188, 129.844, 130.428, 137.673, 141.827, 144.260, 147.935; MS (EI) *m/z*: 222 (39.79), 220 (65.93), 207 (18.51), 206 (100), 91 (69.66), 77 (6.11); Anal. Calcd. for C₂₃H₂₃NO₂S (%): C, 73.18; H, 6.14; N, 3.71. Found: C, 72.98; H, 6.21; N, 3.59; IR (neat): ν 3282, 3060, 2925, 2853, 1655, 1598, 1494, 1450, 1326 cm⁻¹.

***N,N*-Di-[2-(*o*-chlorobenzophenylmethyl)propenyl]-*p*-toluenesulfonamide (4b) and *N*-[2-(*o*-chlorobenzophenylmethyl)propenyl]-*p*-toluenesulfonamide (3b):** To a mixture of 2-chlorobenzophenylmethylenecyclopropane **1b** (0.216 g, 0.9 mmol), *p*-toluenesulfonamide **2a** (0.051 g, 0.3 mmol), Pd(PPh₃)₄ (0.035 g, 10 mol%), Pd(OAc)₂ (0.003 g, 5 mol%) and PPh₃ (0.032 g, 40 mol%) was added dry toluene (4 mL), and the resulting mixture was heated at 110 °C for 17 h with stirring. Removal of the solvent gave a crude oil that was purified by flash chromatography using EtOAc / hexane (1 : 10) as

the eluant to yield **4b** (0.138 g, 71%) as colorless liquid and **3b** (0.033 g, 27%) as colorless solid. **4b**: ^1H NMR (300 MHz, CDCl_3) δ 2.40 (s, 3H, CH_3), 3.86 (d, 1H, $J = 6.9$ Hz, CH), 3.93 (s, 2H, CH_2), 3.98 (d, 1H, $J = 6.9$ Hz, CH), 4.51 (s, 2H, CH), 4.95 (s, 1H, =CH), 4.97 (s, 1H, =CH), 5.10 (s, 1H, =CH), 5.15 (s, 1H, =CH), 6.94-7.39 (m, 20H, Ar), 7.59 (d, 2H, $J = 8.2$ Hz, Ar); ^{13}C NMR (75 MHz, CDCl_3) δ 21.532, 51.204, 51.275, 51.840, 51.933, 116.905, 117.009, 126.587, 126.600, 126.801, 127.332, 127.890, 128.385, 128.395, 129.449, 129.464, 129.740, 129.755, 130.188, 130.220, 134.633, 137.719, 137.783, 139.322, 139.432, 139.745, 139.788, 143.002, 143.020, 144.472, 144.520; MS (EI) m/z : 651 (M^+ , 6.12), 496 (47.90), 460 (40.17), 165 (42.29), 91 (100); HRMS (MALDI) Calcd. for $[\text{C}_{39}\text{H}_{35}\text{Cl}_2\text{NO}_2\text{SNa}]^+$: 674.1663, Found: 674.1658; IR (neat): ν 3061, 3027, 2923, 2851, 1654, 1599, 1494, 1442, 1340 cm^{-1} . **3b**: mp. 139-141 $^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 2.42 (s, 3H, CH_3), 3.58 (t, 2H, $J = 5.9$ Hz, CH_2), 4.53 (s, 1H, CH), 4.70 (t, 1H, $J = 6.0$ Hz, NH), 5.07 (s, 1H, =CH), 5.30 (s, 1H, =CH), 6.90-7.38 (m, 11H, Ar), 7.69 (d, 2H, $J = 8.0$ Hz, Ar); ^{13}C NMR (75 MHz, CDCl_3) δ 21.424, 47.648, 51.142, 116.462, 126.540, 126.783, 127.032, 127.871, 128.366, 129.251, 129.573, 129.657, 130.075, 134.416, 136.740, 139.030, 139.391, 143.266, 145.523; MS (EI) m/z : 411 (M^+ , 0.63), 256 (49.28), 240 (100), 91 (88.21); Anal. Calcd. for $\text{C}_{23}\text{H}_{22}\text{ClNO}_2\text{S}$ (%): C, 67.06; H, 5.38; N, 3.40. Found: C, 67.01; H, 5.37; N, 3.35; IR (neat): ν 3243, 3026, 2929, 2850, 1652, 1597, 1493, 1465 cm^{-1} .

***N,N*-Di-{2-[di-(*p*-methoxyphenyl)methyl]propenyl}-*p*-toluenesulfonamide (4c)**: To a mixture of [di(*p*-methoxyphenyl)]methylenecyclopropane **1c** (0.240 g, 0.9 mmol), *p*-toluenesulfonamide **2a** (0.051 g, 0.3 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.035 g, 10 mol%), $\text{Pd}(\text{OAc})_2$ (0.003 g, 5 mol%) and PPh_3 (0.032 g, 40 mol%) was added dry toluene (4 mL), and the resulting mixture was heated at 115 $^\circ\text{C}$ for 3 h with stirring. Removal of the solvent gave a crude oil that was purified by flash chromatography using EtOAc / hexane (1 : 4) as the eluant to yield **4c** (0.211 g, 100%) as colorless solid. mp. 129-131 $^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 2.41 (s, 3H, CH_3), 3.79 (s, 12H, OCH_3), 3.82 (s, 4H, CH_2), 4.51 (s, 2H, CH), 4.62 (s, 2H, =CH), 5.12 (s, 2H, =CH), 6.79 (d, 8H, $J = 8.4$ Hz, Ar), 6.92 (d, 8H, $J = 8.4$ Hz, Ar), 7.21 (d, 2H, $J = 8.4$ Hz, Ar), 7.59 (d, 2H, $J = 8.4$ Hz, Ar); ^{13}C NMR (75 MHz, CDCl_3) δ 21.474, 52.126, 52.881, 55.160, 113.594, 116.987, 127.306, 129.489, 130.015,

133.778, 137.381, 143.014, 146.505, 158.065; MS (EI) m/z : 703 (M^+ , 0.52), 548 (17.53), 265 (100), 227 (29.25), 91 (55.19); Anal. Calcd. for $C_{43}H_{45}NO_6S$ (%): C, 73.37; H, 6.44; N, 1.99. Found: C, 72.98; H, 6.35; N, 1.98; IR (neat): ν 3003, 2932, 2835, 1649, 1609, 1582, 1510 cm^{-1} .

***N,N*-Di-[2-(1-methyloctyl)propenyl]-*p*-toluenesulfonamide (4d):** To a mixture of methylheptylmethylenecyclopropane **1d** (0.150 g, 0.9 mmol), *p*-toluenesulfonamide **2a** (0.051 g, 0.3 mmol), $Pd(PPh_3)_4$ (0.035 g, 10 mol%), $Pd(OAc)_2$ (0.003 g, 5 mol%) and PPh_3 (0.032 g, 40 mol%) was added dry toluene (4 mL), and the resulting mixture was heated at 110 °C for 8 h with stirring. Removal of the solvent gave a crude oil that was purified by flash chromatography using EtOAc / hexane (1 : 10) as the eluant to yield **4d** (0.151 g, 100%) as colorless liquid. 1H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, 6H, J = 6.6 Hz, CH_3), 0.96 (d, 6H, J = 6.7 Hz, CH_3), 1.11-1.45 (m, 24H, CH_2), 1.98-2.01 (m, 2H, CH), 2.42 (s, 3H, CH_3), 3.79 (s, 4H, CH_2), 4.76 (s, 2H, =CH), 4.83 (s, 2H, =CH), 7.29 (d, 2H, J = 8.2 Hz, Ar), 7.72 (d, 2H, J = 8.2 Hz, Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.070, 19.588, 21.432, 22.649, 27.248, 29.289, 29.740, 31.858, 35.452, 36.376, 50.397, 110.762, 127.188, 129.374, 137.877, 142.846, 148.452; MS (EI) m/z : 503 (M^+ , 2.99), 404 (100), 348 (20.37), 91 (17.58); HRMS (EI) Calcd. for $C_{31}H_{53}NO_2S$: 503.3797, Found: 503.3752, IR (neat): ν 2957, 2926, 2855, 1648, 1599, 1498 cm^{-1} .

***N*-[2-(3-phenylpropyl)propenyl]-*p*-toluenesulfonamide (3e):** To a mixture of 3-phenylpropylmethylenecyclopropane **1e** (0.142 g, 0.9 mmol), *p*-toluenesulfonamide **2a** (0.051 g, 0.3 mmol), $Pd(PPh_3)_4$ (0.035 g, 10 mol%), $Pd(OAc)_2$ (0.003 g, 5 mol%) and PPh_3 (0.032 g, 40 mol%) was added dry toluene (4 mL), and the resulting mixture was heated at 90 °C for 10 h with stirring. Removal of the solvent gave a crude oil that was purified by flash chromatography using EtOAc / hexane (1 : 4) as the eluant to yield **3e** (0.055 g, 56%) as colorless liquid. 1H NMR (300 MHz, $CDCl_3$) δ 1.63-1.73 (m, 2H, CH_2), 2.01 (t, 2H, J = 8.0 Hz, CH_2), 2.42 (s, 3H, CH_3), 2.55 (t, 2H, J = 7.4 Hz, CH_2), 3.50 (d, 2H, J = 7.3 Hz, CH_2), 4.57 (t, 1H, J = 6.0 Hz, NH), 4.84 (s, 1H, =CH), 4.92 (s, 1H, =CH), 7.12-7.31 (m, 7H, Ar), 7.74 (d, 2H, J = 8.8 Hz, Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.477, 28.980, 33.044, 33.315, 47.802, 112.159, 125.756, 127.100, 128.271, 128.336, 128.455,

128.554, 129.649, 136.824, 141.972, 143.407, 144.128; MS (EI) *m/z*: 224 (4.46), 174 (8.36), 155 (17.59), 104 (45.78), 91 (100); HRMS (EI) Calcd. for C₁₉H₂₃NO₂S: 329.1449, Found: 329.1461; IR (neat): ν 3287, 3026, 2927, 2858, 1641, 1599, 1495 cm⁻¹.

***N,N*-Di-(2-cyclohexylpropenyl)-*p*-toluenesulfonamide (4f):** To a mixture of cyclohexylmethylenecyclopropane **1f** (0.110 g, 0.9 mmol), *p*-toluenesulfonamide **2a** (0.051 g, 0.3 mmol), Pd(PPh₃)₄ (0.035 g, 10 mol%), Pd(OAc)₂ (0.003 g, 5 mol%) and PPh₃ (0.032 g, 40 mol%) was added dry toluene (4 mL), and the resulting mixture was heated at 110 °C for 24 h with stirring. Removal of the solvent gave a crude oil that was purified by flash chromatography using EtOAc / hexane (1 : 10) as the eluant to yield **4f** (0.106 g, 85%) as colorless liquid. ¹H NMR (300 MHz, CDCl₃) δ 0.98-1.20 (m, 12H, CH₂), 1.58-1.76 (m, 10H, CH₂, CH), 2.40 (s, 3H, CH₃), 3.73 (s, 4H, CH₂), 4.76 (s, 2H, =CH), 4.82 (s, 2H, =CH), 7.27 (d, 2H, *J* = 8.5 Hz, Ar), 7.69 (d, 2H, *J* = 8.5 Hz, Ar); ¹³C NMR (75 MHz, CDCl₃) δ 21.420, 26.232, 26.568, 32.178, 40.585, 51.118, 110.965, 127.168, 129.451, 137.411, 142.914, 148.955; MS (EI) *m/z*: 415 (M⁺, 36.94), 261 (100), 155 (48.76), 91 (77.21); HRMS (EI) Calcd. for C₂₅H₃₇NO₂S: 415.2545, Found: 415.2523; IR (neat): ν 2926, 2852, 1645, 1599, 1498 cm⁻¹.

***N,N*-Di-[2-(*p*-phenylcyclohexyl)propenyl]-*p*-toluenesulfonamide (4g) and *N*-[2-(*p*-phenylcyclohexyl)propenyl]-*p*-toluenesulfonamide (3g):** To a mixture of *p*-phenylcyclohexylmethylenecyclopropane **1g** (0.178 g, 0.9 mmol), *p*-toluenesulfonamide **2a** (0.051 g, 0.3 mmol), Pd(PPh₃)₄ (0.035 g, 10 mol%), Pd(OAc)₂ (0.003 g, 5 mol%) and PPh₃ (0.032 g, 40 mol%) was added dry toluene (4 mL), and the resulting mixture was heated at 110 °C for 19 h with stirring. Removal of the solvent gave a crude oil that was purified by flash chromatography using EtOAc / hexane (1 : 10) as the eluant to yield **4g** (*trans* and *cis*-mixture) (0.105 g, 62%) as colorless liquid, and **3g** (*trans* and *cis*-mixture) (0.015g, 14%) as colorless liquid. *trans* or *cis*-**4g**: ¹H NMR (300 MHz, CDCl₃) δ 1.22-1.49 (m, 4H, CH₂), 1.63-1.79 (m, 4H, CH₂), 1.80-1.98 (m, 8H, CH₂), 2.42 (s, 3H, CH₃), 2.43-2.54 (m, 2H, CH), 2.71-2.80 (m, 2H, CH), 3.81 (s, 2H, CH₂),

3.86 (s, 2H, CH₂), 4.90 (s, 1H, =CH), 4.93 (s, 1H, =CH), 4.96 (s, 1H, =CH), 5.03 (s, 1H, =CH), 7.14-7.36 (m, 12H, Ar), 7.75 (d, 2H, *J* = 8.2 Hz, Ar); *cis* or *trans*-**4g**: ¹H NMR (300 MHz, CDCl₃) δ 1.22-1.49 (m, 8H, CH₂), 1.63-1.79 (m, 4H, CH₂), 1.80-1.98 (m, 6H, CH₂, CH), 2.16-2.23 (m, 2H, CH), 2.42 (s, 3H, CH₃), 3.78 (s, 2H, CH₂), 3.83 (s, 2H, CH₂), 4.86 (s, 1H, =CH), 4.90 (s, 1H, =CH), 4.96 (s, 1H, =CH), 5.00 (s, 1H, =CH), 7.14-7.36 (m, 12H, Ar), 7.73 (d, 2H, *J* = 8.2 Hz, Ar); MS (EI) *m/z*: 567 (M⁺, 8.50), 412 (26.53), 155 (22.24), 91 (100); HRMS (EI) Calcd. for C₃₇H₄₅NO₂S: 567.3171, Found: 567.3164; IR (neat): ν 3026, 2923, 2853, 1639, 1599, 1493 cm⁻¹. *trans* or *cis*-**3g**: ¹H NMR (300 MHz, CDCl₃) δ 1.29-1.51 (m, 2H, CH₂), 1.61-1.98 (m, 6H, CH₂), 2.44 (s, 3H, CH₃), 2.45-2.52 (m, 1H, CH), 2.65-2.74 (m, 1H, CH), 3.58 (d, 2H, *J* = 6.5 Hz, CH₂), 4.52 (t, 1H, *J* = 6.3 Hz, NH), 4.92 (s, 1H, =CH), 5.05 (s, 1H, =CH), 7.20-7.38 (m, 7H, Ar), 7.79 (d, 2H, *J* = 8.0 Hz, Ar); *cis* or *trans*-**3g**: ¹H NMR (300 MHz, CDCl₃) δ 1.29-1.51 (m, 4H, CH₂), 1.61-1.98 (m, 5H, CH₂, CH), 2.23-2.32 (m, 1H, CH), 2.44 (s, 3H, CH₃), 3.55 (d, 2H, *J* = 6.5 Hz, CH₂), 4.50 (t, 1H, *J* = 6.3 Hz, NH), 4.92 (s, 1H, =CH), 5.05 (s, 1H, =CH), 7.20-7.38 (m, 7H, Ar), 7.77 (d, 2H, *J* = 8.0 Hz, Ar); MS (EI) *m/z*: 369 (M⁺, 2.19), 214 (71.77), 198 (100), 155 (60.54), 91 (100); HRMS (EI) Calcd. for C₂₂H₂₇NO₂S: 369.1762, Found: 369.1763; IR (neat): ν 3287, 2925, 2855, 1639, 1599, 1498 cm⁻¹.

***N*-[2-(Diphenylmethyl)propenyl]-methanesulfonamide (5b):** To a mixture of diphenylmethylenecyclopropane **1a** (0.185 g, 0.9 mmol), methanesulfonamide **2b** (0.029 g, 0.3 mmol), Pd(PPh₃)₄ (0.035 g, 10 mol%), Pd(OAc)₂ (0.003 g, 5 mol%) and PPh₃ (0.032 g, 40 mol%) was added dry toluene (4 mL), and the resulting mixture was heated at 110 °C for 1 d with stirring. Removal of the solvent gave a crude oil that was purified by flash chromatography using EtOAc / hexane (1 : 2) as the eluant to yield **5b** (0.082 g, 91%) as colorless solid. mp. 136-138 °C; ¹H NMR (300 MHz, CDCl₃) δ 2.86 (s, 3H, CH₃), 3.72 (d, 2H, *J* = 6.2 Hz, CH₂), 4.73 (s, 1H, CH), 4.77 (t, 1H, *J* = 6.4 Hz, NH), 4.86 (s, 1H, =CH), 5.40 (s, 1H, =CH), 7.15-7.34 (m, 10H, Ar); ¹³C NMR (75 MHz, CDCl₃) δ 40.925, 47.986, 55.125, 116.819, 127.052, 128.799, 129.366, 141.227, 147.601; MS (EI) *m/z*: 301 (M⁺, 5.74), 222 (47.56), 220 (100), 206 (100), 191 (72.70), 165 (65.86), 115 (63.26), 91 (67.94); Anal. Calcd. for C₁₇H₁₉NO₂S (%): C, 67.74; H, 6.35; N, 4.65. Found:

C, 67.76; H, 6.47; N, 4.45; IR (neat): ν 3292, 3059, 3027, 2927, 1649, 1599, 1493 cm^{-1} .

***N*-[2-(diphenylmethyl)propenyl]-*m*-nitrophenylsulfonamide (5d):** To a mixture of diphenylmethylenecyclopropane **1a** (0.185 g, 0.9 mmol), *m*-nitrobenzenesulfonamide **2d** (0.061 g, 0.3 mmol), Pd(PPh₃)₄ (0.035 g, 10 mol%), Pd(OAc)₂ (0.003 g, 5 mol%) and PPh₃ (0.032 g, 40 mol%) was added dry toluene (4 mL), and the resulting mixture was heated at 120 °C for 2 d with stirring. Removal of the solvent gave a crude oil that was purified by flash chromatography using EtOAc / hexane (1 : 4) as the eluant to yield **5d** (0.073 g, 60%) as brown liquid. ¹H NMR (300 MHz, CDCl₃) δ 3.64 (d, 2H, *J* = 6.2 Hz, CH₂), 4.64 (s, 1H, CH), 4.73 (s, 1H, =CH), 5.28 (t, 1H, *J* = 6.1 Hz, NH), 5.30 (s, 1H, =CH), 7.00-7.29 (m, 10H, Ar), 7.69 (t, 1H, *J* = 7.9 Hz, Ar), 8.14 (d, 1H, *J* = 8.0 Hz, Ar), 8.40 (d, 1H, *J* = 8.0 Hz, Ar), 8.64 (s, 1H, Ar); ¹³C NMR (75 MHz, CDCl₃) δ 47.828, 54.684, 117.113, 122.309, 126.781, 127.091, 128.477, 128.956, 130.448, 132.565, 140.457, 142.207, 146.401, 148.529; MS (EI) *m/z*: 408(M⁺, 1.63), 222 (20.17), 220 (32.84), 206 (100), 186 (5.50), 91 (30.70); HRMS (EI) Calcd. for C₂₂H₂₀N₂O₄S: 408.1144, Found: 408.1151; IR (neat): ν 3300, 3084, 2921, 2851, 1655, 1604, 1534, 1493, 1450 cm^{-1} .

***N,N*-Di-[2-(diphenylmethyl)propenyl]-*p*-nitrophenylsulfonamide (6c):** To a mixture of diphenylmethylenecyclopropane **1a** (0.185 g, 0.9 mmol), *p*-nitrobenzenesulfonamide **2c** (0.061 g, 0.3 mmol), Pd(PPh₃)₄ (0.035 g, 10 mol%), Pd(OAc)₂ (0.003 g, 5 mol%) and PPh₃ (0.032 g, 40 mol%) was added dry toluene (4 mL), and the resulting mixture was heated at 120 °C for 1 d with stirring. Removal of the solvent gave a crude oil that was purified by flash chromatography using EtOAc / hexane (1 : 4) as the eluant to yield **6c** (0.184 g, 100%) as colorless solid. mp. 175-177 °C; ¹H NMR (300 MHz, CDCl₃) δ 3.93 (s, 4H, CH₂), 4.58 (s, 2H, CH), 4.67 (s, 2H, =CH), 5.13 (s, 2H, =CH), 6.95-7.30 (m, 20H, Ar), 7.85 (d, 2H, *J* = 8.9 Hz, Ar), 8.22 (d, 2H, *J* = 8.9 Hz, Ar); ¹³C NMR (75 MHz, CDCl₃) δ 52.170, 54.577, 118.166, 124.274, 126.812, 128.493, 128.521, 129.135, 140.989, 145.298, 146.012, 149.873; MS (EI) *m/z*: 614(M⁺, 4.85), 428 (27.01), 207 (43.95), 205

(54.37), 167 (78.06), 91 (100); Anal. Calcd. for $C_{38}H_{34}N_2O_4S$ (%): C, 74.24; H, 5.57; N, 4.56. Found: C, 74.29; H, 5.77; N, 4.34; IR (neat): ν 3025, 2921, 2857, 1650, 1595, 1530, 1493, 1451, 1344 cm^{-1} .

[2-(diphenylmethyl)propenyl]amine (9): To a solution of *N,N*-Di-[2-(diphenylmethyl)propenyl]-*p*-nitrophenylsulfonamide (**6c**) (0.052 g, 0.084 mmol), PhSH (0.018 g, 0.168 mmol) in anhydrous DMF (2 mL) was added anhydrous K_2CO_3 (0.035 g, 0.252 mmol). The reaction mixture was stirred for 2 h at 32 °C, then was exacted with $NaHCO_3$ aq (12 mL) and diethyl ether (13 mL). The organic layer was dried over $MgSO_4$. The solvent was evaporated to give a crude oil that was purified by flash chromatography using EtOAc / hexane (1 : 10) as eluant to yield **9** (0.026 g, 72%) as colorless liquid. 1H NMR (300 MHz, $CDCl_3$) δ 1.42 (broad, 1H, NH), 3.20 (s, 4H, CH_2), 4.56 (s, 2H, CH), 4.91 (s, 2H, =CH), 5.26 (s, 2H, =CH), 7.12-7.31 (m, 20H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.639, 54.866, 115.032, 126.270, 128.211, 129.207, 142.087, 149.426; MS (EI) m/z : 429 (M^+ , 4.61), 205 (49.80), 191 (32.09), 165 (31.03), 91 (59.49), 57 (100); HRMS (EI) Calcd. for $C_{32}H_{31}N$: 429.2456, Found: 429.2446; IR (neat): ν 3293, 3059, 3026, 2924, 2852, 1678, 1598, 1494, 1450 cm^{-1} .

[2-(diphenylmethyl)propenyl]benzylamine (7): To a mixture of diphenylmethylenecyclopropane **1a** (0.062 g, 0.3 mmol), *p*-nitrobenzenesulfonamide **2c** (0.061 g, 0.3 mmol), $Pd(PPh_3)_4$ (0.035 g, 10 mol%), $Pd(OAc)_2$ (0.003 g, 5 mol%) and PPh_3 (0.032 g, 40 mol%) was added dry toluene (4 mL), and the resulting mixture was heated at 100 °C for 10 h with stirring. Removal of the solvent gave a crude oil that was purified by flash chromatography using EtOAc / hexane (1 : 10) as the eluant to yield *N*-[2-(diphenylmethyl)propenyl]-*p*-nitrobenzenesulfonamide (0.076 g, 62%). Then to a mixture of *N*-[2-(diphenylmethyl)propenyl]-*p*-nitrobenzenesulfonamide (0.040 g, 0.098 mmol), benzylbromide (0.018 g, 0.108 mmol) and anhydrous K_2CO_3 (0.027 g, 0.196 mmol) was added anhydrous DMF (1 mL), and the resulting mixture was stirred 1 h at 27 °C then exacted with $NaHCO_3$ aq. (12 mL) and diethyl ether (13 mL). The organic

layer was dried over MgSO_4 . The solvent was evaporated to give a crude oil that was purified by flash chromatography using EtOAc / hexane (1 : 10) as the eluant to yield ***N*-[2-(diphenylmethyl)propenyl]-*N*-benzyl-*p*-nitrobenzenesulfonamide** (0.036 g, 74%). To a solution of **[2-(diphenylmethyl)propenyl]-*N*-benzyl-*p*-nitrobenzenesulfonamide** (0.030 g, 0.060 mmol), PhSH (0.013 g, 0.120 mmol) in anhydrous DMF (2 mL) was added anhydrous K_2CO_3 (0.025 g, 0.180 mmol). The reaction mixture was stirred for 2 h at 32 °C, then was exacted with NaHCO_3 aq (12 mL) and diethyl ether (13 mL). The organic layer was dried over MgSO_4 . The solvent was evaporated to give a crude oil that was purified by flash chromatography using EtOAc / hexane (1 : 4) as eluant to yield **7** (0.010 g, 53%) as colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ 1.57 (broad, 1H, NH), 3.27 (s, 2H, CH_2), 3.78 (s, 2H, CH_2), 4.65 (s, 1H, CH), 4.99 (s, 1H, =CH), 5.35 (s, 1H, =CH), 7.18-7.34 (m, 15H, Ar); ^{13}C NMR (75 MHz, CDCl_3) δ 53.254, 54.126, 55.349, 115.187, 126.572, 127.116, 128.310, 128.514, 128.592, 129.507, 142.384, 150.428; MS (EI) m/z : 313 (M^+ , 11.88), 299 (37.24), 222 (13.72), 206 (45.53), 165 (16.40), 91 (100); HRMS (EI) Calcd. for $\text{C}_{23}\text{H}_{23}\text{N}$: 313.1830, Found: 303.1829; IR (neat): ν 3315, 3060, 3026, 2924, 2863, 1647, 1600, 1494, 1451 cm^{-1} .

[2-(diphenylmethyl)propenyl](*n*-hexyl)amine (8): to a mixture of ***N*-[2-(diphenylmethyl)propenyl]-*p*-nitrobenzenesulfonamide** (0.030 g, 0.073 mmol), 1-bromohexane (0.018 g, 0.110 mmol) and anhydrous K_2CO_3 (0.030 g, 0.220 mmol) was added anhydrous DMF (2 mL), and the resulting mixture was stirred 2 h at 64 °C then exacted with NaHCO_3 aq (12 mL) and diethyl ether (13 mL). The organic layer was dried over MgSO_4 . The solvent was evaporated to give a crude oil that was purified by flash chromatography using EtOAc / hexane (1 : 10) as the eluant to yield ***N*-[2-(diphenylmethyl)propenyl]-*N*-(*n*-hexyl)-*p*-nitrobenzenesulfonamide** (0.030 g, 83%). To a solution of **[2-(diphenylmethyl)propenyl]-*N*-(*n*-hexyl)-*p*-nitrobenzenesulfonamide** (0.030 g, 0.061 mmol), PhSH (0.014 g, 0.122 mmol) in anhydrous DMF (2 mL) was added anhydrous K_2CO_3 (0.025 g, 0.183 mmol). The reaction mixture was stirred for 2 h at 32

°C, then was extracted with NaHCO₃ aq (12 mL) and diethyl ether (13 mL). The organic layer was dried over MgSO₄. The solvent was evaporated to give a crude oil that was purified by flash chromatography using EtOAc / hexane (1 : 10) as eluant to yield **8** (0.017 g, 91%) as colorless liquid.. ¹H NMR (300 MHz, CDCl₃) δ 0.89 (t, 3H, *J* = 6.8 Hz, CH₃), 1.26-1.29 (m, 6H, CH₂), 1.30-1.46 (m, 3H, CH₂, NH), 2.56 (t, 2H, *J* = 7.1 Hz, CH₂), 3.22 (s, 2H, CH₂), 4.61 (s, 1H, CH), 4.89 (s, 1H, =CH), 5.28 (s, 1H, =CH), 7.17-7.32 (m, 10H, Ar); ¹³C NMR (75 MHz, CDCl₃) δ 14.303, 22.866, 27.268, 30.173, 32.000, 49.484, 54.661, 55.544, 114.757, 126.556, 128.461, 129.473, 142.380, 150.134; MS (EI) *m/z*: 307 (M⁺, 33.48), 292 (71.80), 222 (13.24), 206 (72.74), 191 (42.47), 165 (32.58), 91 (73.43); HRMS (EI) Calcd. for C₂₂H₂₉N: 307.2300, Found: 307.2254; IR (neat): ν 3309, 3060, 3026, 2927, 2856, 1677, 1599, 1494, 1450 cm⁻¹.

The preparation of deuterated *p*-toluenesulfonamide (TsND₂).

The synthetic method was shown above.² Deuterium oxide (D₂O) (2.5 mL) was added into TsNH₂ (0.5 g) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 24 h. After filtration, TsND₂ (75% D) was isolated in 0.51 g (100%). ¹H NMR (300 MHz, CDCl₃) δ 2.44 (s, 3H, CH₃), 4.88 (br. s, 0.5 H, NH), 7.32 (d, 2H, *J* = 8.1 Hz, Ar), 7.82 (d, 2H, *J* = 8.1 Hz, Ar).

The ring-opening reaction of MCP **1a** with deuterated *p*-toluenesulfonamide TsND₂ was carried out under the same conditions as those described above for 24 h.

4a-d: ¹H NMR (300 MHz, CDCl₃) δ 2.37 (s, 3H, CH₃), 3.82 (s, 4H, CH₂), 4.63 (s, 2.98H, =CH+CH), 5.15 (s, 2H, =CH), 7.00-7.27 (m, 22H, Ar), 7.57 (d, 2H, *J* = 8.0 Hz, Ar). MS (EI) *m/z*: 585 (M⁺, 11.51), 584 (M⁺-1, 16.36), 583 (M⁺-2, 8.96), 428 (74.36), 206 (89.57), 167 (60.60), 91 (100).

Ref. 2. (a) Smith, J. K.; Bergbreiter, D. E.; Newcomb, M. *J. Org. Chem.* **1985**, *50*, 4549. (b) Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 1048.

MCP₅-(C₆D₆)-RT

MCPs-Pd II-(C₆D₆)-RT

MCPs-(CD₃)₂-70°C

MCPs-Pd II (C₆D₆) - 70°C

MCP₃-(CDCl₃)-RT

¹³C OBSERVE

Archive directory: /export/home/shi-m/vnmrSYS/data

Sample directory:

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: cy06-57-C-C

Mercury-300BB "QMC300"

Relax. delay 1.000 sec

Pulse program

Time 1.000 sec

Width 18867.9 Hz

124 repetitions

OBSERVE C13, 75.4421068 MHz

DECOUPLE H1, 300.0234696 MHz

Post-acquisition

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FI size 65536

Total time 13 hr, 1 min, 7 sec

MCPs - PdI (CDCl₃) - RT