Supporting Information for

Unprecedented CO₂-Promoted Aminochlorination of Olefins with Chloramine-T

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Experimental

General Methods. Melting points were determined on a Yanaco melting point apparatus and are uncorrected. Infrared spectra were obtained on a JASCO FT/IR-410 infrared spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL FT-NMR JNM EX 270 spectrometer (^1H NMR, 270 MHz; ^{13}C NMR, 68 MHz) using tetramethylsilane as an internal standard. Mass spectra were measured on a JEOL JMS-DX303HF mass spectrometer. Elemental analyses were performed at the Analytical Center, Faculty of Engineering, Osaka University. Products were purified by chromatography on silica gel BW-300 (Fuji Silysia Chemical Co.). Analytical thin-layer chromatography was performed on precoated silica gel glass plates (silica gel 60 F₂₅₄, 0.25 mm thickness) (Merck Co.). Compounds were visualized by UV light or treatment with an ethanolic solution of phosphomolybdic acid followed by heating. Since the minor regioisomers **2d**, **1g**, **2h** and **2i** could not be isolated in pure form, the structures were determined by some spectral data, mainly ^1H -NMR and Mass, in a form of mixture with the corresponding major regioisomers.

Typical Procedure for Aminochlorination of Olefins with Chloramine-T under CO₂

A magnetic stirring bar, Chloramine-T (281 mg, 1 mmol), styrene (104 mg, 1 mmol), and benzene (3 mL) were placed in a 50-mL stainless steel autoclave lined with a glass liner. The autoclave was closed, purged three times with carbon dioxide, pressurized with 10 atm of CO₂ and then stirred at room temperature for 6 h. After discharging excess CO₂, aqueous Na₂S₂O₃ (0.5 M, 20 mL) was added to the reaction mixture. The solution was then extracted with CH₂Cl₂ (10 mL x 3). The combined organic extracts were dried over Na₂SO₄ and concentrated to give the crude product. Purification by flash column chromatography (silica gel; 30% ethyl acetate in hexane) gave **2a** (247 mg, 80%).

1-Chloro-1-phenyl-2-(*p*-toluenesulfonamido)ethane (1a)¹

1a Colorless solid (247 mg, 80%); Mp: 95-96 °C; IR (KBr, cm⁻¹) 3265 (NH), 1334, 1155 (S=O); ¹H-NMR (CDCl₃, 270 MHz) δ 2.44 (s, 3H, Ar-CH₃), 3.36-3.53 (m, 2H, CH₂-NH), 4.87 (dd, 1H, *J* = 5.9, 7.1 Hz, CH-Cl), 4.87 (br t, 1H, NH, D₂O exchangeable), 7.11-7.43 (m, 7H, ArH), 7.73 (d, 2H, *J* = 8.4 Hz, ArH); ¹³C NMR (CDCl₃, 68 MHz) δ 21.3, 50.0, 61.4, 126.6, 126.9, 128.4, 128.5, 129.4, 136.4, 137.6, 143.3; MS (CI, methane): *m/z* (relative intensity, %) 310 ([M+1]⁺, 28), 274 ([M-Cl]⁺, 100); HRMS (CI, methane): *m/z* Calcd for C₁₅H₁₇ClNO₂S (M+H) 310.0669, found 310.0664; Anal. Calcd for C₁₅H₁₆ClNO₂S: C, 58.15; H, 5.21; N, 4.52. Found: C, 58.26; H, 5.06; N, 4.43.

2-Chloro-1-phenyl-1-(*p*-toluenesulfonamido)ethane (2a)

2a Colorless solid (40.3 mg, 13%); Mp: 173-174 °C; IR (KBr, cm⁻¹) 3257 (NH), 1313, 1161 (S=O); ¹H-NMR (CDCl₃, 270 MHz) δ 2.39 (s, 3H, Ar-CH₃), 3.72 (d, 2H, *J* = 5.9 Hz, CH₂-Cl), 4.56 (t, 1H, *J* = 5.9 Hz, CH-NH), 5.22 (br d, 1H, NH, D₂O exchangeable), 7.03-7.30 (m, 7H, ArH), 7.73 (d, 2H, *J* = 8.4 Hz, ArH); ¹³C NMR (CDCl₃, 68 MHz) δ 21.6, 47.9, 58.4, 126.7, 127.1, 128.2, 128.5, 129.4, 136.8, 143.4; MS (CI, isobutane): *m/z* (relative intensity, %) 310 ([M+1]⁺, 100), 274 ([M-Cl]⁺, 24); HRMS (CI, isobutane): *m/z* Calcd for C₁₅H₁₇ClNO₂S (M+H) 310.0669, found 310.0674; Anal. Calcd for C₁₅H₁₆ClNO₂S: C, 58.15; H, 5.21; N, 4.52. Found: C, 58.12; H, 4.96; N, 4.43.

1-Chloro-1-(4-nitrophenyl)-2-(*p*-toluenesulfonamido)ethane (1b)

1b Yellow solid (251 mg, 71%); Mp: 111-113 °C; IR (KBr, cm⁻¹) 3278 (NH), 1522, 1346 (NO₂), 1163 (S=O); ¹H-NMR (CDCl₃, 270 MHz) δ 2.43 (s, 3H, Ar-CH₃), 3.38-3.54 (m, 2H, CH₂-NH), 5.00 (t, 1H, *J* = 6.8 Hz, CH-Cl), 5.20 (t, 1H, *J* = 6.5 Hz, NH, D₂O exchangeable), 7.29 (d, 2H, *J* = 8.1 Hz, ArH), 7.49 (d, 2H, *J* = 8.6 Hz, ArH), 7.68 (d, 2H, *J* = 8.1 Hz, ArH), 8.15 (d, 2H, *J* = 8.6 Hz, ArH); ¹³C NMR (CDCl₃, 68 MHz) δ 21.4, 49.8, 59.6, 123.7, 126.6, 128.3, 129.6, 136.1, 143.8, 144.6, 147.5; MS (CI, isobutane): *m/z* (relative intensity, %) 355 ([M+1]⁺, 81), 319 ([M-Cl]⁺, 100); HRMS (CI, isobutane): *m/z* Calcd for C₁₅H₁₆ClN₂O₄S (M+H) 355.0520, found 355.0523; Anal. Calcd for C₁₅H₁₅ClN₂O₄S: C, 50.78; H, 4.26; N, 7.90. Found: C, 50.77; H, 4.12; N, 7.74.

1-Chloro-1-(4-chlorophenyl)-2-(*p*-toluenesulfonamido)ethane (1c)

Colorless solid (254 mg, 74%); Mp: 100-102 °C; IR (KBr, cm^{-1}) 3282 (NH), 1325, 1153 (S=O); $^1\text{H-NMR}$ (CDCl_3 , 270 MHz) δ 2.44 (s, 3H, Ar-CH₃), 3.33-3.50 (m, 2H, CH₂-NH), 4.81 (br t, 1H, NH, D₂O exchangeable), 4.87 (dd, 1H, J = 6.2, 7.8 Hz, CH-Cl), 7.20-7.35 (m, 6H, ArH), 7.71 (d, 2H, J = 8.4 Hz, ArH); $^{13}\text{C NMR}$ (CDCl_3 , 68 MHz) δ 21.5, 50.0, 60.5, 126.7, 128.5, 128.7, 129.6, 134.4, 136.2, 137.3, 143.5; MS (CI, isobutane): m/z (relative intensity, %) 344 ($[\text{M}+1]^+$, 7), 308 ($[\text{M}-\text{Cl}]^+$, 100); HRMS (CI, isobutane): m/z Calcd for $\text{C}_{15}\text{H}_{16}\text{Cl}_2\text{NO}_2\text{S}$ (M+H) 344.0280, found 344.0285; Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{Cl}_2\text{NO}_2\text{S}$: C, 52.33; H, 4.39; N, 4.07. Found: C, 52.37; H, 4.27; N, 4.04.

1-Chloro-1-(4-methylphenyl)-2-(*p*-toluenesulfonamido)ethane (1d)

Colorless solid (174 mg, 54%); Mp: 119-121 °C; IR (KBr, cm^{-1}) 3245 (NH), 1325, 1159 (S=O); $^1\text{H-NMR}$ (CDCl_3 , 270 MHz) δ 2.34 (s, 3H, Ar-CH₃), 2.44 (s, 3H, Ar-CH₃), 3.37-3.49 (m, 2H, CH₂-NH), 4.77 (br t, 1H, NH, D₂O exchangeable), 4.83 (dd, 1H, J = 6.5, 8.1 Hz, CH-Cl), 6.97-7.25 (m, 4H, ArH), 7.32 (d, 2H, J = 8.4 Hz, ArH), 7.72 (d, 2H, J = 8.4 Hz, ArH); $^{13}\text{C NMR}$ (CDCl_3 , 68 MHz) δ 21.1, 21.5, 50.2, 61.5, 126.9, 129.4, 129.6, 134.7, 136.7, 138.8, 143.5; MS (CI, isobutane): m/z (relative intensity, %): 324 ($[\text{M}+1]^+$, 4), 288 ($[\text{M}-\text{Cl}]^+$, 100); HRMS (CI, isobutane): m/z Calcd for $\text{C}_{16}\text{H}_{19}\text{ClNO}_2\text{S}$ (M+H) 324.0826, found 324.0816; Anal.: Calcd for $\text{C}_{16}\text{H}_{18}\text{ClNO}_2\text{S}$: C, 59.34; H, 5.60; N, 4.33. Found: C, 59.32; H, 5.52; N, 4.28.

2-Chloro-1-(4-methoxyphenyl)-1-(*p*-toluenesulfonamido)ethane (2e)

Colorless solid (257 mg, 76%); Mp: 120-121 °C; IR (KBr, cm^{-1}) 3274 (NH), 1325 (S=O), 1251 (MeO), 1162 (S=O); $^1\text{H-NMR}$ (CDCl_3 , 270 MHz) δ 2.40 (s, 3H, Ar-CH₃), 3.66-3.71 (m, 2H, CH₂-Cl), 3.77 (s, 3H, CH₃-O), 4.50 (t, 1H, J = 5.9 Hz, CH-NH), 5.15 (br d, 1H, NH, D₂O exchangeable), 6.76 (d, 2H, J = 8.6 Hz, ArH), 7.03 (d, 2H, J = 8.6 Hz, ArH), 7.21 (d, 2H, J = 8.1 Hz, ArH), 7.62 (d, 2H, J = 8.1 Hz, ArH); $^{13}\text{C NMR}$ (CDCl_3 , 68 MHz) δ 21.5, 47.7, 55.1, 58.0, 113.7, 126.9, 127.9, 129.1, 129.3, 136.7, 143.2, 159.1; MS (EI): m/z (relative intensity, %) 339 ($[\text{M}]^+$, 1), 290 ($[\text{M}-\text{CH}_2\text{Cl}]^+$, 100); HRMS (EI): m/z Calcd for $\text{C}_{16}\text{H}_{18}\text{ClNO}_3\text{S}$ (M) 339.0696, found 339.0699; Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{ClNO}_3\text{S}$: C, 56.55; H, 5.34; N, 4.12. Found: C, 56.34; H, 5.17; N, 4.05.

1-Chloro-1-phenyl-2-(*p*-toluenesulfonamido)propane (**1f**)²

Colorless solid (168 mg, 52% for the reaction from *trans*- β -methylstyrene); Mp: 72-74 °C; IR (KBr, cm^{-1}) 3264 (NH), 1336, 1165 (S=O); $^1\text{H-NMR}$ (CDCl_3 , 270 MHz) δ 1.02 (d, 3H, J = 6.8 Hz, $\text{CH}_3\text{-CH}$), 2.43 (s, 3H, Ar- CH_3), 3.70-3.82 (m, 1H, $\text{CH}_2\text{-NH}$), 4.91 (d, 1H, J = 9.2 Hz, NH , D_2O exchangeable), 5.02 (d, 1H, J = 6.2 Hz, CH-Cl), 7.24-7.36 (m, 7H, ArH), 7.77 (d, 2H, J = 8.4 Hz, ArH); $^{13}\text{C NMR}$ (CDCl_3 , 68 MHz) δ 15.2, 21.5, 55.3, 68.0, 127.0, 127.2, 128.4, 128.5, 129.8, 137.4, 137.9, 143.6; MS (CI, isobutane): m/z (relative intensity, %) 324 ($[\text{M}+1]^+$, 20), 288 ($[\text{M-Cl}]^+$, 100); HRMS (CI, isobutane): m/z Calcd for $\text{C}_{16}\text{H}_{19}\text{ClNO}_2\text{S}$ (M+H) 324.0826, found 324.0818; Anal.: Calcd for $\text{C}_{16}\text{H}_{18}\text{ClNO}_2\text{S}$: C, 59.34; H, 5.60; N, 4.33. Found: C, 59.29; H, 5.47; N, 4.28.

2-Chloro-2-phenyl-1-(*p*-toluenesulfonamido)propane (**1h**)

Colorless solid (177 mg, 55%); Mp: 78-80 °C; IR (KBr, cm^{-1}) 3275 (NH), 1325, 1161 (S=O); $^1\text{H-NMR}$ (CDCl_3 , 270 MHz) δ 1.98 (s, 3H, $\text{CH}_3\text{-CCl}$), 2.43 (s, 3H, Ar- CH_3), 3.37-3.52 (m, 2H, $\text{CH}_2\text{-NH}$), 4.71 (t, 1H, J = 6.2 Hz, NH , D_2O exchangeable), 7.26-7.37 (m, 5H, ArH), 7.47 (d, 2H, J = 8.4 Hz, ArH), 7.68 (d, 2H, J = 8.4 Hz, ArH); $^{13}\text{C NMR}$ (CDCl_3 , 68 MHz) δ 21.6, 29.0, 55.4, 71.8, 126.0, 126.8, 128.1, 128.4, 129.6, 136.6, 141.6, 143.4; MS (CI, isobutane): m/z (relative intensity, %): 324 ($[\text{M}+1]^+$, 3), 288 ($[\text{M-Cl}]^+$, 100); HRMS (CI, isobutane): m/z Calcd for $\text{C}_{16}\text{H}_{19}\text{ClNO}_2\text{S}$ (M+H) 324.0826, found 324.0824; Anal.: Calcd for $\text{C}_{16}\text{H}_{18}\text{ClNO}_2\text{S}$: C, 59.34; H, 5.60; N, 4.33. Found: C, 59.14; H, 5.53; N, 4.39.

1-Chloro-2-(*p*-toluenesulfonamido)indane (**1i**)

Brown solid (202 mg, 63%); Mp: 106-109 °C; IR (KBr, cm^{-1}) 3265 (NH), 1329, 1161 (S=O); $^1\text{H-NMR}$ (CDCl_3 , 270 MHz) δ 2.45 (s, 3H, Ar- CH_3), 2.74 (dd, 1H, J = 4.9, 16.2 Hz, $\text{CH}_2\text{-CH-NH}$), 3.39 (dd, 1H, J = 7.0, 16.2 Hz, $\text{CH}_2\text{-CH-NH}$), 4.03-4.30 (m, 1H, CH-NH), 4.99 (d, 1H, J = 7.6 Hz, NH , D_2O exchangeable), 5.08 (d, 1H, J = 4.6 Hz, CH-Cl), 7.06-7.35 (m, 6H, ArH), 7.79 (d, 2H, J = 8.4 Hz, ArH); $^{13}\text{C NMR}$ (CDCl_3 , 68 MHz) δ 21.8, 37.8, 63.3, 65.3, 124.9, 125.3, 127.2, 127.7, 129.4, 129.8, 136.7, 139.3, 139.4, 143.8; MS (CI, isobutane): m/z (relative intensity, %): 322 ($[\text{M}+1]^+$, 7), 286 ($[\text{M-Cl}]^+$, 100); HRMS (CI, isobutane): m/z Calcd for $\text{C}_{16}\text{H}_{17}\text{ClNO}_2\text{S}$ (M+H) 322.0669, found 322.0659; Anal.: Calcd for $\text{C}_{16}\text{H}_{16}\text{ClNO}_2\text{S}$: C, 59.71; H, 5.01; N, 4.35. Found: C, 59.81; H, 4.96; N, 4.15.

1-Chloro-2-(*p*-toluenesulfonamido)-3,4-dihydronaphthalene (**1j**)

Brown solid (178 mg, 53%); Mp: 106-108 °C; IR (KBr, cm^{-1}) 3280 (NH), 1329, 1155 (S=O); $^1\text{H-NMR}$ (CDCl_3 , 270 MHz) δ 1.66-1.77 (m, 1H, $\text{CH}_2\text{-CH}_2\text{-CH-NH}$), 2.38-2.51 (m, 1H, $\text{CH}_2\text{-CH}_2\text{-CH-NH}$), 2.47 (s, 3H, Ar- CH_3), 2.73-2.93 (m, 2H, $\text{CH}_2\text{-CH}_2\text{-CH-NH}$), 3.82-3.89 (m, 1H, CH-NH), 4.82 (d, 1H, $J = 7.8$ Hz, NH , D_2O exchangeable), 4.91 (d, 1H, $J = 4.1$ Hz, CH-Cl), 7.26-7.37 (m, 4H, ArH), 7.47 (d, 2H, $J = 8.4$ Hz, ArH), 7.68 (d, 2H, $J = 8.4$ Hz, ArH); $^{13}\text{C NMR}$ (CDCl_3 , 68 MHz) δ 21.7, 23.0, 23.8, 54.5, 58.5, 126.6, 126.8, 128.6, 128.9, 129.7, 130.9, 132.6, 134.8, 136.9, 143.5; MS (CI, isobutane): m/z (relative intensity, %) 336 ($[\text{M}+1]^+$, 4), 300 ($[\text{M-Cl}]^+$, 100); HRMS (CI, isobutane): m/z Calcd for $\text{C}_{17}\text{H}_{19}\text{ClNO}_2\text{S}$ (M+H) 336.0826, found 336.0827

2-Chloro-1-(*p*-toluenesulfonamido)-3,4-dihydronaphthalene (**2j**)

Brown solid (50 mg, 15%); Mp: 164-165 °C; IR (KBr, cm^{-1}) 3277 (NH), 1331, 1152 (S=O); $^1\text{H-NMR}$ (CDCl_3 , 270 MHz) δ 2.07-2.13 (m, 1H, $\text{CH}_2\text{-CH}_2\text{-CH-Cl}$), 2.31-2.45 (m, 1H, $\text{CH}_2\text{-CH}_2\text{-CH-Cl}$), 2.50 (s, 3H, Ar- CH_3), 2.71-2.80 (m, 1H, $\text{CH}_2\text{-CH}_2\text{-CH-Cl}$), 3.00-3.13 (m, 1H, $\text{CH}_2\text{-CH}_2\text{-CH-Cl}$), 4.38 (m, 1H, CH-Cl), 4.55-4.59 (m, 1H, CH-NH), 4.59 (br d, 1H, NH , D_2O exchangeable), 6.52 (d, 1H, $J = 7.6$ Hz, ArH), 7.01-7.21 (m, 3H, ArH), 7.40 (d, 2H, $J = 8.4$ Hz, ArH), 7.84 (d, 2H, $J = 8.4$ Hz, ArH); $^{13}\text{C NMR}$ (CDCl_3 , 68 MHz) δ 21.8, 23.6, 24.7, 56.8, 58.4, 126.7, 127.3, 128.2, 129.0, 129.6, 129.8, 131.2, 135.7, 136.7, 143.9; MS (CI, isobutane): m/z (relative intensity, %) 336 ($[\text{M}+1]^+$, 100), 300 ($[\text{M-Cl}]^+$, 82), HRMS (CI, isobutane): m/z Calcd for $\text{C}_{17}\text{H}_{19}\text{ClNO}_2\text{S}$ (M+H) 336.0826, found 336.0828; Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{ClNO}_2\text{S}$: C, 60.80; H, 5.40; N, 4.17. Found: C, 60.99; H, 5.43; N, 4.10.

3-Chloro-4-(*p*-toluenesulfonamido)hexane (**1k**) Stereochemistry was determined by the conversion of product **1k** to a known aziridine.³

Colorless solid (81 mg, 28%); Mp: 95-97 °C; IR (KBr, cm^{-1}) 3278 (NH), 1323, 1168 (S=O); $^1\text{H-NMR}$ (CDCl_3 , 270 MHz) δ 0.79 (t, 3H, $J = 7.4$ Hz, $\text{CH}_3\text{-CH}_2$), 0.94 (t, 3H, $J = 7.4$ Hz, $\text{CH}_3\text{-CH}_2$), 1.36-1.71 (m, 4H, $\text{CH}_3\text{-CH}_2\text{-CH-CH-CH}_2\text{-CH}_3$), 2.43 (s, 3H, Ar- CH_3), 3.27-3.37 (m, 1H, CH-NH), 3.70-3.76 (m, 1H, CH-Cl), 4.81 (br d, 1H, NH , D_2O exchangeable), 7.30 (d, 2H, $J = 8.4$ Hz, ArH), 7.76 (d, 2H, $J = 8.4$ Hz, ArH); $^{13}\text{C NMR}$ (CDCl_3 , 68 MHz) δ 10.2, 11.6, 21.6, 21.8, 28.4, 59.0, 69.2, 126.8, 129.5, 137.9, 143.3; MS (CI, isobutane): m/z (relative intensity, %) 290 ($[\text{M}+1]^+$, 100), 254 ($[\text{M-Cl}]^+$, 8); HRMS (CI, isobutane): m/z Calcd for $\text{C}_{13}\text{H}_{21}\text{ClNO}_2\text{S}$ (M+H) 290.0982, found 290.0989; Anal. Calcd for $\text{C}_{13}\text{H}_{20}\text{ClNO}_2\text{S}$: C, 53.87; H, 6.96; N, 4.83. Found: C, 53.98; H, 6.78; N, 4.78.

1-Chloro-2-(*p*-toluenesulfonamido)cyclohexane (**1l**)⁴

Colorless solid (77 mg, 27%); Mp: 99-101 °C; IR (KBr, cm⁻¹) 3255 (NH), 1334, 1155 (S=O); ¹H-NMR (CDCl₃, 270 MHz) δ 1.23-1.31 (m, 3H, CH₂-CHH), 1.54-1.72 (m, 3H, CH₂-CHH), 1.36-1.71 (m, 2H, CH₂-CHH, CH₂-CHH), 2.43 (s, 3H, Ar-CH₃), 3.27-3.37 (m, 1H, CH-NH), 3.70-3.76 (m, 1H, CH-Cl), 4.81 (br d, 1H, NH, D₂O exchangeable), 7.30 (d, 2H, *J* = 8.4 Hz, ArH), 7.76 (d, 2H, *J* = 8.4 Hz, ArH); ¹³C NMR (CDCl₃, 68 MHz) δ 21.6, 23.4, 24.3, 32.4, 34.9, 58.6, 62.1, 127.1, 129.4, 137.0, 143.3; MS (CI, isobutane): *m/z* (relative intensity, %) 288 ([M+1]⁺, 100), 252 ([M-Cl]⁺, 23); HRMS (CI, isobutane): *m/z* Calcd for C₁₃H₁₉ClNO₂S (M+H) 288.0826, found 288.0829; Anal. Calcd for C₁₃H₁₈ClNO₂S: C, 54.25; H, 6.30; N, 4.87. Found: C, 54.50; H, 6.05; N, 4.82.

2-Chloro-1-*n*-butoxy-1-(*p*-toluenesulfonamido)ethane (**1m**)

Brown solid (174 mg, 57%); Mp: 91-94 °C; IR (neat, cm⁻¹) 3271 (NH), 1336, 1162 (S=O); ¹H-NMR (CDCl₃, 270 MHz) δ 0.83 (t, 3H, *J* = 7.3 Hz, CH₃-CH₂), 1.15-1.31 (m, 2H, CH₃-CH₂), 1.34-1.44 (m, 2H, CH₃-CH₂-CH₂), 2.42 (s, 3H, Ar-CH₃), 3.26-3.35 (m, 1H, CHH-Cl), 3.41-3.55 (m, 3H, CH₂O, CHH-Cl), 4.74-4.88 (m, 1H, CH-NH), 5.76 (d, 1H, *J* = 9.5 Hz, NH, D₂O exchangeable), 7.30 (d, 2H, *J* = 8.4 Hz, ArH), 7.78 (d, 2H, *J* = 8.4 Hz, ArH); ¹³C NMR (CDCl₃, 68 MHz) δ 13.7, 19.0, 21.5, 31.1, 46.0, 68.2, 83.1, 126.6, 129.5, 137.9, 143.5. MS (FAB): *m/z* (relative intensity, %) 304 ([M-1]⁺, 84); HRMS (FAB): *m/z* Calcd for C₁₃H₁₉ClNO₃S (M-H) 304.0772, found 304.0770.

1-Chloro-4-(*p*-toluenesulfonamido)-2-cyclooctene (**1n**)

Colorless solid (157 mg, 70%); Mp: 93-94 °C; IR (KBr, cm⁻¹) 3259 (NH), 1328, 1161 (S=O); ¹H-NMR (CDCl₃, 270 MHz) δ 1.31-1.88 (m, 6H, (CH₂)₃-CH₂), 1.95-2.19 (m, 2H, (CH₂)₃-CH₂), 2.42 (s, 3H, Ar-CH₃), 4.57-4.73 (m, 2H, CH-NH, CH-Cl), 4.64 (br, 1H, NH, D₂O exchangeable), 5.18 (dd, 1H, *J* = 6.8, 11.9 Hz, CH-CHCl), 5.65 (dd, 1H, *J* = 6.5, 11.9 Hz, CH-CHNH), 7.30 (d, 1H, *J* = 8.1 Hz, ArH), 7.78 (d, 2H, *J* = 8.1 Hz, ArH); ¹³C NMR (CDCl₃, 68 MHz) δ 21.5, 22.5, 23.4, 34.5, 37.2, 51.1, 57.6, 127.1, 129.4, 130.2, 132.0, 137.1, 143.1; MS (CI, isobutane): *m/z* (relative intensity, %) 314 ([M+1]⁺, 3), 278 ([M-Cl]⁺, 100), HRMS (CI, isobutane): *m/z* Calcd for C₁₅H₂₁ClNO₂S (M+H) 314.0982, found 314.0991; Anal. Calcd for C₁₅H₂₀ClNO₂S: C, 57.40; H, 6.42; N, 4.46. Found: C, 57.29; H, 6.25; N, 4.42.

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1a (^1H -nmr)

2a (¹H-nmr)

△ EtOAc

1b (^{13}C -nmr)

1c (^1H -nmr)

1c (¹³C-nmr)

1d (^1H -nmr)

1d (^{13}C -nmr)

2e (^1H -nmr)

2e (^{13}C -nmr)

1f (¹H-nmr)

1f (^{13}C -nmr)

DFILE C:\WINNMR95\TEMPDATA\AUTO2E
 COMNT 5-34 5h
 DATIM Sun Feb 29 02:20:31 2004
 OBNUC ^{13}C
 EXMOD BCM
 OBFRQ 67.80 MHz
 OBSET 135.00 KHz
 OBFIN 5200.0 Hz
 POINT 32768
 FREQU 18348.6 Hz
 SCANS 1200
 ACQTM 1.786 sec
 PD 1.214 sec
 PW1 5.0 us
 IRNUC ^1H
 CTEMP 23.2 c
 SLVNT CDCL₃
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 32

1h (^1H -nmr)

1h (^{13}C -nmr)

1i (^1H -nmr)

1i (^{13}C -nmr)

1j (^1H -nmr)

1j (^{13}C -nmr)

2j (^1H -nmr)

2j (^{13}C -nmr)

1k (^1H -nmr)

1k (^{13}C -nmr)

11 (^1H -nmr)

11 (^{13}C -nmr)

1m (1H-nmr)

1m (^{13}C -nmr)

1n (^1H -nmr)

1n (^{13}C -nmr)