Supplementary Material (ESI) for Organic & Biomolecular Chemistry

The Influence of Reaction Conditions on the Diels-Alder Cycloadditions of 2-Thio-3-Chloroacrylamides; Investigation of Thermal, Catalytic and Microwave Conditions

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Supporting Information

Synthesis of Sulfoxide Adducts

2-*exo*-Benzenesulfinyl-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid *p*-tolylamide 4a-*endo* and 2-*endo*-Benzenesulfinyl-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid *p*-tolylamide 4a-*exo*

Freshly distilled cyclopentadiene (353 mg, 0.41 mL, 5.35 mmol) was added to a solution of **3a** (340 mg, 1.07 mmol) in dichloromethane (7 mL). The reaction solution was then heated at reflux for 18 hours. The solvent and most of the excess diene were evaporated at reduced pressure to give the crude adduct **4a** as a mixture of inseparable diastereomers. A ^{1}H NMR spectrum was recorded of the crude reaction product (crude ratio of **4a-*exo*** : **4a-*endo*** = 1: 1.3) before purification by chromatography on silica gel using ethyl acetate-hexane (40:60) as eluent to give the adduct (383 mg, 93%) as a colourless solid with a ratio of **4a-*exo*** : **4a-*endo*** of 1: 1.40; mp 134-142^{o}C; Found C, 65.35; H, 5.12; N, 3.59; Cl, 7.84; S, 9.68. $C_{21}H_{20}NClO_2S$ requires C, 65.36; H, 5.22; N, 3.63; Cl, 8.31; S, 9.19; ν_{max}/cm^{-1} (KBr) 1675, 1517, 1374, 1042, 749; The NMR signals for each diastereomer could be distinguished:

Major Diastereomer **4a-*endo***: δ_H (270 MHz, $CDCl_3$) 1.95-2.00 (1H, H_A of ABq, *J* 10, one of CH_2-7), 2.28 (3H, s, $ArCH_3$), 2.68-2.72 (1H, H_B of ABq, *J* 10, one of CH_2-7), 3.33 (1H, b s, H-4), 3.89 (1H, b s, H-1), 4.89 (1H, d, *J* 2, H-3), 6.16-6.21 (1H, m, H-5), 6.35-6.41 (1H, m, H-6), 6.98-7.42 (4H, m, ArH), 7.30-7.41 (3H, m, ArH), 8.82-8.94 (2H, m, ArH), 9.34 (1H, bs, NH); δ_C (67.8 MHz, $CDCl_3$) 21.5 (*C*H_3, $ArCH_3$), 45.5 (*C*H_2, C-7), 50.3 (*C*H, C-4), 54.2 (*C*H, C-1), 59.4 (*C*H, C-3), C-2 obscured by $CDCl_3$ signals at 76.7-77.5, 120.3 (*C*H, aromatic CH), 126.3 (*C*H, aromatic CH), 128.8 (*C*H, aromatic CH), 129.3 (*C*H, aromatic CH), 131.3 (*C*H, aromatic CH), 134.1 (*C*, aromatic C), 134.5 (*C*, aromatic C), 135.3 (*C*H, C-5), 138.7 (*C*H, C-6), 164.1 (*C*, CO).

Minor Diastereomer **4a-*exo***: δ_H (270 MHz, $CDCl_3$) 1.72-1.90 (2H, ABq, *J* 10, CH_2-7), 2.28 (3H, s, $ArCH_3$), 3.45 (1H, b s, H-4), 3.65 (1H, b s, H-1), 5.63 (1H, d, *J* 4, H-3), 6.62-6.68 (1H, m, H-5), 6.80-6.88 (1H, m, H-6), 6.98-7.42 (4H, m, ArH), 7.30-7.41 (3H, m, ArH), 8.82-8.94 (2H, m, ArH), 9.87 (1H, bs, NH); δ_C (67.8 MHz, $CDCl_3$) 21.5 (*C*H_3, $ArCH_3$), 45.2 (*C*H_2, C-7), 50.6 (*C*H, C-4), 54.8 (*C*H, C-1), 59.2 (*C*H, C-3), 79.5 (*C*, C-2), 120.3 (*C*H, aromatic CH), 126.3 (*C*H, aromatic CH), 128.8 (*C*H, aromatic CH), 129.3 (*C*H, aromatic CH), 131.1 (*C*H, aromatic CH), 134.1 (*C*, aromatic C), 134.5 (*C*, aromatic C), 134.9 (*C*H, C-6), 140.0 (*C*H, C-5), 165.1 (*C*, CO).

MS *m/z* 385 (M^+, 21%), 260 (100, M^+-SOPh), 224 (64, M^+-SOPh-Cl), 125 (38, $[SOPh]^+$), 91 (77); isotopic Cl pattern observed; 385, 387 (3:1 ratio ^{35}Cl:^{37}Cl); Found (HRMS, EI) *m/z* 385.0893. $C_{21}H_{20}N^{35}ClO_2S$ requires 385.0903.

2-*exo*-Benzenesulfinyl-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid benzylamide 4c-*endo* and 2-*endo*-Benzenesulfinyl-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid benzylamide 4c-*exo*

The title compound was prepared as described for **4a** using freshly distilled cyclopentadiene (825 mg, 1.00 mL, 12.50 mmol) and **3c** (800 mg, 2.50 mmol) in dichloromethane (16 mL). The reaction solution was then heated at reflux for 18 hours. The solvent and most of the excess diene were evaporated at reduced pressure to give the crude adduct **4c** as a mixture of inseparable diastereomers. A ^1H NMR spectrum was recorded of the crude reaction product (crude ratio of **4c-*exo*** : **4c-*endo*** = 1: 1.3) before purification by chromatography on silica gel using ethyl acetate-hexane (20:80) as eluent to give the adduct (803 mg, 84%) as a colourless solid; mp 122-5^{o}C; Found C, 65.22; H, 5.34; N, 3.45; Cl, 9.50; S, 8.04. $C_{21}H_{20}NClO_2S$ requires C, 65.36; H, 5.22; N, 3.63; Cl, 9.19; S, 8.31; ν_{max}/cm^{-1} (KBr) 3349 (br NH), 1675, 1509, 1032; The NMR signals for each diastereomer could be distinguished. The sample of the adduct used for characterisation had an altered diastereomeric ratio (**4c-*exo*** : **4c-*endo*** = 1 : 3) to that of the crude (**4c-*exo*** : **4c-*endo*** = 1 : 1.3) due to chromatography:

Major Diastereomer **4c-*endo*:** δ_H (270 MHz, $CDCl_3$) 1.84-1.92 (1H, H_A of ABq, *J* 10, H-7'), 2.60-2.66 (1H, H_B of ABq, *J* 10, H-7), 3.28 (1H, b s, H-4), 3.62-3.82 (2H, m, one of NCH_2, H-1), 4.07-4.31 (1H, m, one of NCH_2), 4.88 (1H, d, *J* 2, H-3), 6.06-6.11 (1H, m, H-5), 6.37-6.41 (1H, m, H-6), 6.72-6.86 (1H, b s, NH), 7.02-7.18 (2H, m, ArH), 7.20-7.37 (3H, m, ArH), 7.38-7.52 (3H, m, ArH), 7.75-7.90 (2H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 43. 6 (NCH_2), 45.7 (C-7), 50.3 (C-4), 53.9 (C-1), 59.8 (C-3), 76.7 (C-2), 126.3 (aromatic CH), 127.7 (aromatic CH), 127.9 (aromatic CH), 128.3 (aromatic CH), 128.7 (aromatic CH), 131.0 (aromatic CH), 135.7 (C-5), 138.6 (C-6), 137.6 (aromatic C), 141.1 (aromatic C), 166.2 (CO).

Minor Diastereomer **4c-*exo***: δ_H (270 MHz, $CDCl_3$) 1.60-1.66 (1H, H_A of ABq, *J* 10, H-7), 1.73-1.80 (1H, H_B of ABq, *J* 10, H-7'), 3.42 (1H, b s, H-4), 3.52 (1H, b s, H-1), 3.62-3.82

(1H, m, one of NCH_2), 4.07-4.31 (1H, m, one of NCH_2), 5.63 (1H, d, *J* 4, H-3), 6.55-6.63 (1H, m, H-5), 6.72-6.90 (1H, m, H-6), 7.02-7.18 (2H, m, ArH), 7.20-7.37 (4H, m, NH, ArH), 7.38-7.52 (3H, m, ArH), 7.75-7.90 (2H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 43.7 (NCH_2), 45.3 (C-7), 50.6 (C-4), 54.9 (C-1), 59.6 (C-3), 78.9 (C-2), 126.3 (aromatic CH), 127.7 (aromatic CH), 127.9 (aromatic CH), 128.3 (aromatic CH), 128.7 (aromatic CH), 130.9 (aromatic CH), 135.5 (C-6), 139.7 (C-5), 137.6, 140.8 (aromatic C), 167.3 (CO).

MS *m/z* 385 (M^+, 1%), 260 (37, M^+-Cl), 224 (17, M^+-SOPh, HCl), 91 (100); isotopic Cl pattern observed on expansion; 385, 387 (3:1 ratio ^{35}Cl:^{37}Cl).

2-*exo*-Benzenesulfinyl-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid isopropylamide 4d-*endo* and 2-*endo*-Benzenesulfinyl-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid isopropylamide 4d-*exo*

The title compound was prepared as described for **4a** using freshly distilled cyclopentadiene (485 mg, 0.58 mL, 7.35 mmol) and **3d** (400 mg, 1.47 mmol) in dichloromethane (6 mL). The reaction solution was then heated at reflux for 18 hours. The solvent and most of the excess diene were evaporated at reduced pressure to give the crude adduct **4d** as a mixture of inseparable diastereomers. A ^1H NMR spectrum was recorded of the crude reaction product (crude ratio of **4d-*exo*** : **4d-*endo*** = 1: 1.2) before purification by chromatography on silica gel using ethyl acetate-hexane (20:80) as eluent to give the adduct (440 mg, 89%) as a colourless solid; mp 142-145^{o}C; Found C, 60.03; H, 5.93; N, 4.13; Cl, 10.50; S, 9.51. $C_{17}H_{20}NClO_2S$ requires C, 60.43; H, 5.97; N, 4.15; Cl, 10.52; S, 9.51; ν_{max}/cm^{-1} (KBr) 3340 (br NH), 1652, 1531, 1074, 1037, 744; The NMR signals for each diastereomer could be distinguished:

Major Diastereomer **4d-*endo***: δ_H (270 MHz, $CDCl_3$) 0.70 (3H, d, *J* 7, one of -CH(C*H*$_3$)$_2$), 0.95 (3H, d, *J* 7, one of -CH(C*H*$_3$)$_2$), 1.87-1.92 (1H, H_A of ABq, dd, *J* 10, 2, H-7'), 2.60-2.67 (1H, H_B of ABq, *J* 10, H-7), 3.28 (1H, b s, H-4), 3.38-3.64 (1H, m, NCH), 3.74 (1H, b s, H-1), 4.91 (1H, d, *J* 2, H-3), 6.06-6.13 (1H, m, H-5), 6.26-6.41 (2H, m, H-6, NH), 7.42-7.49 (3H, m, ArH), 7.80-7.91 (2H, m, ArH) ; δ_C (67.8 MHz, $CDCl_3$) 22.0 (one of CH(*C*H$_3$)$_2$), 22.3 [one of CH(*C*H$_3$)$_2$], 41.6 (NCH), 45.2 (C-7), 50.5 (C-4), 54.0 (C-1), 59.7 (C-3), 75.6 (C-2), 126.4 (aromatic CH), 128.8 (aromatic CH), 130.8 (aromatic CH), 135.3 (C-5), 139.6 (C-6), 141.1 (aromatic C), 165.2 (CO).

Minor Diastereomer **4d-*exo***: δ_H (270 MHz, $CDCl_3$) 0.58 (3H, d, *J* 7, one of -CH(C*H*$_3$)$_2$), 0.98 (3H, d, *J* 7, one of -CH(C*H*$_3$)$_2$), 1.58-1.64 (1H, H_A of ABq, *J* 10, one of CH_2-7), 1.76-1.82 (1H, H_B of ABq, *J* 10, one of CH_2-7), 3.38-3.64 (3H, m, NCH, H-4, H-1), 5.66 (1H, d, *J* 4, H-3), 6.56-6.63 (1H, m, H-5), 6.76-6.87 (2H, m, H-6, NH), 7.42-7.49 (3H, m, ArH), 7.80-7.91 (2H, m, ArH) ; δ_C (67.8 MHz, $CDCl_3$) 21.5 (one of CH(*C*H$_3$)$_2$), 22.0 (one of CH(*C*H$_3$)$_2$), 41.8 (NCH), 45.6 (C-7), 50.4 (C-4), 55.3 (C-1), 59.9(C-3), 77.9 (C-2), 126.4 (aromatic CH), 128.6

(aromatic CH), 130.6 (aromatic CH), 135.3 (C-6), 138.6 (C-5), 141.8 (aromatic C), 166.4 (CO).

MS *m/z* 337 (M^+, 1%), 242 (15), 212 (15, M^+-SOPh), 173 (20), 155(100), 125 (15, $[SOPh]^+$), 91 (50), 77 (60); isotopic Cl pattern observed; 337, 339 (3:1 ratio ^{35}Cl:^{37}Cl); Found (HRMS, EI) *m/z* 337.0897. $C_{17}H_{20}N^{35}ClO_2S$ requires 337.0903.

2-*exo*-Benzenesulfinyl-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid *n*-butylamide 4e-*endo* and 2-*endo*-Benzenesulfinyl-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid *n*-butylamide 4e-*exo*

The title compound was prepared as described for **4a** using freshly distilled cyclopentadiene (162 mg, 0.20 mL, 7.00 mmol) and **3e** (400 mg, 1.4 mmol) in dichloromethane (6 mL). The reaction solution was then heated at reflux for 18 hours. The solvent and most of the excess diene were evaporated at reduced pressure to give the crude adduct **4e** as a mixture of inseparable diastereomers. A ^1H NMR spectrum was recorded of the crude reaction product (crude ratio of **4e-*exo*** : **4e-*endo*** = 1: 1.2) before purification by chromatography on silica gel using ethyl acetate-hexane (20:60) as eluent to give the adduct (373 mg, 76%) as a colourless solid; mp 102-106^{o}C; Found C, 61.10; H, 6.39; N, 3.96; Cl, 10.61; S, 9.13. $C_{18}H_{22}NClO_2S$ requires C, 61.44; H, 6.30; N, 3.98; Cl, 10.07; S, 9.11; ν_{max}/cm^{-1} (KBr) 3346 (br NH), 1660, 1528, 1035, 748; (Not all of the ^1H NMR signals for the two diastereomers could be distinguished, hence the ^1H NMR has been assigned as a mixture) δ_H (270 MHz, $CDCl_3$) 0.68-0.90 (3H, m, -CH_3-4'), 1.00-1.28 (4H, m, -C*H*$_2$-C*H*$_2$-), 1.57-1.62 (0.47H, H_A of ABq, *J* 10, one of CH_2-7b), 1.68-1.94 (1H, m, one of CH_2-7b, H-7a'), 2.54-2.80 (1.53H, m, H-7a, one of SCH_2), 2.81-3.03 (1H, m, one of SCH_2), 3.28 (0.53H, b s, H-4a), 3.40 (0.47H, b s, H-4b), 3.48 (0.47H, b s, H-1b), 3.74 (0.53H, b s, H-1a), 4.87 (0.53H, d, *J* 2, H-3a), 5.63 (0.47H, d, *J* 4, H-3b), 6.02-6.14 (0.53H, m, H-5a), 6.29-6.39 (0.53H, m, H-6a), 6.48 (0.53H, b s, NHa), 6.54-6.64 (0.47H, m, H-5b), 6.71-6.82 (0.47H, m, H-6b), 6.95 (0.47H, b s, NHb), 7.36-7.56 (3H, m, ArH), 7.74-7.94 (2H, m, ArH);

Major Diastereomer **4e-*endo***: δ_C (67.8 MHz, $CDCl_3$) 13.6 (-CH_3-4'), 20.1 (-CH_2-3'), 31.1 (-CH_2-3'), 39.3 (SCH_2-), 45.6 (C-7), 50.2 (C-4), 53.9 (C-1), 59.8 (C-3), 78.6 (C-2), 126.2 (aromatic CH), 128.6 (aromatic CH), 130.9 (aromatic CH), 135.2 (C-5), 138.5 (C-6), 140.9 (aromatic C), 166.1 (CO).

Minor Diastereomer **4e-*exo***: δ_C (67.8 MHz, $CDCl_3$) 13.6 (-CH_3-4'), 20.0 (-CH_2-3'), 31.0 (-CH_2-2'), 39.4 (SCH_2-), 45.3 (C-7), 50.5 (C-4), 55.0 (C-1), 59.6 (C-3), 76.3 (C-2), 126.2 (aromatic CH), 128.6 (aromatic CH), 130.7 (aromatic CH), 135.4 (C-6), 139.7 (C-5), 141.4 (aromatic C), 167.2 (CO).

MS *m/z* 351 (M+, 5%), 226 (100, M^+-SOPh), 190 (38, M^+-SOPh-HCl), 125 (72, [SOPh]+), 91 (93), 57 (95); isotopic Cl pattern observed; 351, 353 (3:1 ratio ^{35}Cl: ^{37}Cl).

2-*exo*-Benzenesulfinyl-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid allylamide 4f-*endo* and 2-*endo*-Benzenesulfinyl-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid allylamide 4f-*exo*

The title compound was prepared as described for **4a** using freshly distilled cyclopentadiene (488 mg, 0.59 mL, 7.40 mmol) and **3f** (400 mg, 1.48 mmol) in dichloromethane (6 mL). The reaction solution was then heated at reflux for 18 hours. The solvent and most of the excess diene were evaporated at reduced pressure to give the crude adduct **4f** as a mixture of inseparable diastereomers. A ^1H NMR spectrum was recorded of the crude reaction product (crude ratio of **4f-*exo*** : **4f-*endo*** = 1 : 1.3) before purification by chromatography on silica gel using ethyl acetate-hexane (20:80) as eluent to give the adduct (392 mg, 79%) as a colourless solid; Found C, 60.60; H, 5.41; N, 4.14; Cl, 10.84; S, 9.44. $C_{21}H_{20}NClO_2S$ requires C, 60.79; H, 5.40; N, 4.17; Cl, 10.56; S, 9.55; ν_{max}/cm^{-1} (KBr); 3350 (NH), 1660 (CO), 1525, 1076, 1041, 748; (Not all of the ^1H NMR signals for the two diastereomers could be distinguished, hence the ^1H NMR has been assigned as a mixture): δ_H (270 MHz, $CDCl_3$) 1.53-1.60 (0.3H, H_A of ABq, *J* 11, one of CH_2-7b), 2.00-2.07 (1H, m, H-7a', one of CH_2-7b), 2.74 (0.7H, H_B of ABq, *J* 11, H-7a), 3.18-3.66 (3.3H, m, NCH_2, H-1b, H-4b, H-4a), 3.75 (0.7H, b s, H-1a), 4.86 (0.75H, d, *J* 2, H-3a), 4.96-5.12 (2H, m, $=CH_2$), 5.36-5.58 (1H, m, CH=), 5.61 (0.3H, d, *J* 4, H-3b), 6.09-6.17 (0.7H, m, H-5a), 6.30-6.38 (0.7H, m, H-6a), 6.49-6.63 (1H, m, NHa, H-5b), 6.76-6.81 (0.3H, m, H-6b), 7.03 (0.3H, b s, NHb), 7.41-7.58 (3H, m, ArH), 7.80-7.92 (2H, m, ArH). The ^{13}C NMR signals for each diastereomer could be distinguished:

Major Diastereomer **4f-*endo***: δ_C (67.8 MHz, $CDCl_3$) 42.0 (NCH_2), 45.6 (C-7), 50.1 (C-4), 53.9 (C-1), 59.7 (C-3), 76.7 (C-2), 116.8 ($=CH_2$), 126.2 (aromatic CH), 128.6 (aromatic CH), 131.0 (aromatic CH), 133.4 (CH=), 135.5 (C-5), 138.6 (C-6), 140.7 (aromatic C), 166.1 (CO).

Minor Diastereomer **4f-*exo***: δ_C (67.8 MHz, $CDCl_3$) 42.2 (NCH_2), 45.3 (C-7), 50.5 (C-4), 54.8 (C-1), 59.5 (C-3), 79.0 (C-2), 116.6 ($=CH_2$), 126.2 (aromatic CH), 128.6 (aromatic CH), 130.8 (aromatic CH), 133.3 (CH=), 135.1 (C-6), 139.6 (C-5), 141.2 (aromatic C), 167.1 (CO).

MS m/z 335 (M^+, 5%), 210 (79, M^+-SOPh), 174 (27, M^+-SOPh, HCl), 125 (63, $[SOPh]^+$), 91 (85), 41 (100); isotopic Cl pattern observed; 335, 337 (3:1 ^{35}Cl: ^{37}Cl).

2-*exo*-Benzenesulfinyl-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid amide 4g-*endo* and 2-*endo*-Benzenesulfinyl-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid amide 4g-*exo*

The title compound was prepared as described for **4a** using freshly distilled cyclopentadiene (290 mg, 0.35 mL, 4.40 mmol) and **3g** (100 mg, 0.44 mmol) in dichloromethane (2 mL). The reaction solution was then heated at reflux for 18 hours. The solvent and most of the excess diene were evaporated at reduced pressure to give the crude adduct **4g** as a mixture of inseparable diastereomers. A ^{1}H NMR spectrum was recorded of the crude reaction product (crude ratio of **4g-*exo***: **4g-*endo*** = 1: 1.6) before purification by chromatography on silica gel using ethyl acetate-hexane (40:60) as eluent to give the adduct (96 mg, 74%) as a colourless solid; mp 145-147^{o}C; Found C, 57.10; H, 4.98; N, 5.00; Cl, 11.84; S, 10.45. $C_{14}H_{14}NClO_2S$ requires C, 56.85; H, 4.77; N, 4.74; Cl, 11.99; S, 10.84; ν_{max}/cm^{-1} (KBr) 3381 (br NH), 1680, 1617, 1374, 1042, 749; The NMR signals for each diastereomer could be distinguished:

Major Diastereomer **4g-*endo***: δ_H (270 MHz, $CDCl_3$) 1.87-1.94 (1H, H_A of ABq, *J* 9, H-7'), 2.62-2.68 (1H, H_B of ABq, *J* 9, H-7), 3.28 (1H, b s, H-4), 3.72 (1H, b s, H-1), 4.76 (1H, d, *J* 2, H-3), 5.14 (1H, b s, NH), 6.12-6.24 (1H, m, H-5), 6.32-6.42 (1H, m, H-6), 6.47 (1H, b s, NH), 7.36-7.56 (3H, m, ArH), 7.84-8.04 (2H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 45.6 (C-7), 50.1 (C-4), 53.9 (C-1), 59.5 (C-3), 77.6 (C-2), 126.3 (aromatic CH), 128.7 (aromatic CH), 131.2 (aromatic CH), 135.9 (C-5), 138.4 (C-6), 140.8 (aromatic C), 167.8 (CO).

Minor Diastereomer **4g-*exo***: δ_H (270 MHz, $CDCl_3$) 1.53-1.81 (2H, ABq, *J* 10, CH_2-7), 3.41 (1H, b s, H-4), 3.51 (1H, b s, H-1), 5.31 (1H, b s, NH), 5.51 (1H, d, *J* 4, H-3), 6.56-6.66 (1H, m, H-5), 6.74-6.84 (1H, m, H-6), 6.89 (1H, b s, NH), 7.36-7.56 (3H, m, ArH), 7.84-8.04 (2H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 45.4 (C-7), 50.5 (C-4), 54.6 (C-1), 59.3 (C-3), 79.6 (C-2), 126.3 (aromatic CH), 128.7 (aromatic CH), 131.0 (aromatic CH), 135.0 (C-6), 139.8 (C-5), 141.1 (aromatic C), 168.8 (CO).

MS *m/z* 295 (M^+, 9%), 260 (2, M^+-Cl), 170 (91, M^+-SOPh), 135 (60, M^+-Cl, SOPh), 134 (65, $[PhS{=}C{=}CH]^+$), 125 (84, $[SOPh]^+$), 109 (70), 91 (100); isotopic Cl pattern observed; 295, 297 (3:1 ratio ^{35}Cl:^{37}Cl); Found (HRMS, EI) *m/z* 295.0401, $C_{14}H_{14}N^{35}ClO_2S$ requires 295.0434.

2-*exo*-Benzenesulfinyl-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid 4'-fluorophenylamide 4h-*endo* and 2-*endo*-Benzenesulfinyl-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid 4'-fluorophenylamide 4h-*exo*

The title compound was prepared as described for **4a** using freshly distilled cyclopentadiene (512 mg, 0.60 mL, 7.75 mmol) and **3h** (500 mg, 1.55 mmol) in dichloromethane (10 ml). The reaction solution was then heated at reflux for 18 hours. The solvent and most of the excess diene was evaporated at reduced pressure to give the crude adduct **4h** as a mixture of

inseparable diastereomers. A ^{1}H NMR spectrum was recorded of the crude reaction product (crude ratio of **4h-***exo* : **4h-***endo* = 1 : 1.7) before purification by chromatography on silica gel using ethyl acetate-hexane (20:80) as eluent to give the adduct (578 mg, 96%) as a colourless solid (ratio of **4h-***exo* : **4h-***endo* = 1 : 1.8); mp 113-116^{o}C; Found C, 61.64; H, 4.56; N, 3.41; Cl, 9.55; F, 5.30; S, 8.33. $C_{20}H_{17}NClFO_2S$ requires C, 61.61; H, 4.40; N, 3.59; Cl, 9.09; F, 4.87; S, 8.22; ν_{max}/cm^{-1} (KBr) 1670 (CO), 1531, 1507, 1035, 748; With the exception of the aromatic region of the ^{1}H NMR spectrum, the NMR signals for each diastereomer could be distinguished:

Major Diastereomer **4h-***endo*: δ_H (270 MHz, $CDCl_3$) 1.90-1.99 (1H, dd, H_A of ABq, *J* 2,10, H-7'), 2.67-2.73 (1H, H_B of ABq, *J* 10, H-7), 3.33 (1H, b s, H-4), 3.91 (1H, b s, H-1), 4.88 (1H, d, *J* 2, H-3), 6.16-6.21 (1H, m, H-5), 6.38-6.43 (1H, m, H-6), 8.41 (1H, b s, NH); δ_C (67.8 MHz, $CDCl_3$) 45.8 (*C*H_2, C-7), 50.4 (*C*H, C-4), 54.2 (*C*H, C-1), 59.4 (C-3), C-2 obscured by $CDCl_3$ at 76.6-77.6, 115.5 (*C*H, d, $^3J_{CF}$ 22, aromatic CH, ArC-3), 122.1 (*C*H, d, $^2J_{CF}$ 9, aromatic CH, ArC-2), 126.3 (*C*H, aromatic CH), 128.8 (*C*H, aromatic CH), 131.3 (*C*H, aromatic CH), 133.3 (*C*, aromatic C), 135.3 (*C*H, C-5), 138.9 (*C*H, C-6), 140.2 (*C*, aromatic C), 159.5 (*C*, d, $^4J_{CF}$ 244, aromatic C, ArC-4), 164.4 (CO).

Minor Diastereomer **4h-***exo*: δ_H (270 MHz, $CDCl_3$) 1.61-1.88 (2H, ABq, *J* 10, CH_2-7), 3.68 (1H, b s, H-4), 3.78 (1H, b s, H-1), 5.63 (1H, d, *J* 4, H-3), 6.62-6.68 (1H, m, H-5), 6.81-6.88 (1H, m, H-6), 8.93 (1H, b s, NH); δ_C (67.8 MHz, $CDCl_3$) 45.4 (*C*H_2, C-7), 50.7 (*C*H, C-4), 54.9 (*C*H, C-1), 59.2 (*C*H, C-3), 79.7 (*C*, C-2), 115.5 (*C*H, d, $^3J_{CF}$ 22, aromatic CH, ArC-3), 122.1 (*C*H, d, $^2J_{CF}$ 9, aromatic CH, ArC-2), 126.3 (*C*H, aromatic CH), 128.8 (*C*H, aromatic CH), 131.3 (*C*H, aromatic CH), 133.2 (*C*, aromatic C), 135.0 (*C*H, C-6), 140.1 (*C*H, C-5), 140.6 (*C*, aromatic C), 159.5 (*C*, d, $^4J_{CF}$ 244, aromatic C, ArC-4), 165.4 (CO).

The aromatic signals for each diastereomer in the 1H NMR spectrum were indistinguishable: δ_H (270 MHz, $CDCl_3$) 6.92 (2H, overlapping dd, *J* 8, 8, C-3 ArH), 7.08-7.18 (2H, m, ArH), 7.30-7.40 (3H, m, ArH), 7.80-7.90 (2H, m, ArH).

MS *m/z* 389 (M^+, 1%), 264 (30, M^+-SOPh), 228 (35, M^+-SOPh-Cl), 119 (57), 91 (100).

2-*exo*-(4'-Methoxybenzenesulfinyl)-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid *p*-tolylamide 4i-*endo* and 2-*endo*-(4'-Methoxybenzenesulfinyl)-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid *p*-tolylamide 4i-*exo*

The title compound was prepared as described for **4a** using freshly distilled cyclopentadiene (146 mg, 0.18 mL, 2.20 mmol) and **3i** (148 mg, 0.44 mmol) in dichloromethane (3 mL). The reaction solution was then heated at reflux for 18 hours. The solvent and most of the excess diene were evaporated at reduced pressure to give the crude adduct **4i** as a mixture of inseparable diastereomers. An NMR was recorded of the crude reaction product (crude ratio

of **4i-*exo*** : **4i-*endo*** = 1 : 1.3). No further purification was carried out. After dissolution in ether and evaporation, the adduct was isolated (172 mg, 98%) as a colourless solid; mp 141-5°C (with decomposition); Found C, 63.54; H, 5.48; N, 3.47; Cl, 8.48; S, 7.63. $C_{22}H_{22}NClO_3S$ requires C, 63.53; H, 5.33; N, 3.37; Cl, 8.52; S, 7.71; ν_{max}/cm^{-1} (KBr) 3700-2800 (b NH), 1664 (CO), 1592, 1496, 1259, 1306, 1174, 1032, 829; Not all of the ^1H NMR signals for the two diastereomers could be distinguished, hence the ^1H NMR has been assigned as a mixture: δ_H (270 MHz, $CDCl_3$) 1.62-1.66 (0.44H, H_A of ABq, *J* 11, one of CH_2-7b), 1.78-1.83 (0.44H, H_B of ABq, *J* 11, one of CH_2-7b), 1.90-1.95 (0.56H, H_A of ABq, *J* 11, H-7a'), 2.28 (3H, s, Ar CH_3), 2.65-2.71 (0.56H, H_B of ABq, *J* 11, H-7a), 3.29 (0.56H, b s, H-4a), 3.42 (0.44H, b s, H-4b), 3.64 (0.44H, b s, H-1b), 3.74 (3H, s, -OCH_3), 3.87 (0.56H, b s, H-1a), 4.85 (0.56H, d, *J* 2, H-3a), 5.60 (0.44H, d, *J* 4, H-3b), 6.17-6.23 (0.56H, m, H-5a), 6.37-6.42 (0.56H, m, H-6a), 6.61-6.68 (0.44H, m, H-5b), 6.80-6.91 (2.44H, m, ArH, H-6b), 7.02-7.11 (2H, m, ArH), 7.12-7.26 (2H, m, ArH), 7.73-7.87 (2H, m, ArH), 8.49 (0.56H, b s, NHa), 9.02 (0.44H, b s, NHb). The ^{13}C NMR signals for each diastereomer could be distinguished:

Major Diastereomer **4i-*endo***: δ_C (67.8 MHz, $CDCl_3$) 20.8 (Ar *C*H_3), 45.3 (C-7), 50.4 (C-4), 54.0 (C-1), 55.3 (-O*C*H_3), 59.5 (C-3), C-2 obscured by $CDCl_3$ at 76.5-77.5, 114.3 (aromatic CH), 120.3 (aromatic CH), 129.3 (aromatic CH), 129.4 (aromatic CH), 132.0 (aromatic C), 134.1 (aromatic C), 135.5 (C-5), 136.0 (aromatic C), 138.5 (C-6), 162.1 (C-OMe), 165.3 (CO).

Minor Diastereomer **4i-*exo***: δ_C (67.8 MHz, $CDCl_3$) 20.8 (Ar *C*H_3), 45.2 (C-7), 50.6 (C-4), 54.7 (C-1), 55.3 (-O*C*H_3), 59.2 (C-3), 79.2 (C-2), 114.3 (aromatic CH), 120.3 (aromatic CH), 129.3 (aromatic CH), 129.4 (aromatic CH), 132.0 (aromatic C), 134.7 (aromatic C), 134.9 (C-6), 136.0 (aromatic C), 139.8 (C-5), 161.9 (C-OMe), 164.4 (CO).

MS *m/z* 415 (M^+, 3%), 260 (6, M^+-SOAr), 224 (9, M^+-SOAr-HCl), 84 (100); isotopic Cl pattern observed on expansion; 415, 417 (3:1 ratio ^{35}Cl:^{37}Cl); Found (HRMS, EI) *m/z* 415.1011. $C_{22}H_{22}N^{35}ClO_3S$ requires 415.1009.

2-*exo*-(4'-Methoxybenzenesulfinyl)-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid benzylamide 4j-*endo* and 2-*endo*-(4'-Methoxybenzenesulfinyl)-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid benzylamide 4j-*exo*

The title compound was prepared as described for **4a** using freshly distilled cyclopentadiene (136 mg, 0.16 mL, 2.20 mmol) and **3j** (137 mg, 0.41 mmol) in dichloromethane (3 mL). The reaction solution was then heated at reflux for 18 hours. The solvent and most of the excess diene were evaporated at reduced pressure to give the crude adduct **4j** as a mixture of inseparable diastereomers. A ^1H NMR spectrum was recorded of the crude reaction product (crude ratio of **4j-*exo*** : **4j-*endo*** = 1 : 1.1). No further purification was carried out. After

dissolution in ether and evaporation, the adduct was isolated (156 mg, 89%) as a colourless solid; Found C, 63.17; H, 5.35; N, 4.20. $C_{22}H_{22}NClO_3S$ requires C, 63.53; H, 5.33; N, 3.37; ν_{max}/cm^{-1} (KBr) 3500-2900 (b NH), 1645 (CO), 1593, 1226, 1076, 1036; Not all of the ^1H NMR signals for the two diastereomers could be distinguished, hence the ^1H NMR has been assigned as a mixture: δ_H (270 MHz, $CDCl_3$) 1.56-1.61 (0.47H, H_A of ABq, *J* 10, one of CH_2-7b), 1.72-1.91 (1H, m, H-7a', one of CH_2-7b), 2.59-2.66 (0.53H, H_B of ABq, *J* 10, H-7a), 3.24 (0.53H, b s, H-4a), 3.39 (0.47H, b s, H-4b), 3.51 (0.47H, b s, H-1b), 3.72 (0.53H, b s, H-1a), 3.80-3.98 (4H, m, -OCH_3, one of NCH_2), 4.18-4.38 (1H, m, one of NCH_2), 4.85 (0.53H, d, *J* 2, H-3a), 5.60 (0.47H, d, *J* 4, H-3b), 6.02-6.11 (0.53H, m, H-5a), 6.31-6.39 (0.53H, m, H-6a), 6.56-6.62 (0.47H, m, H-5b), 6.72-6.79 (0.47H, m, H-6b), 6.84-7.81 (10H, m, ArH, both NHs). The ^{13}C NMR signals for each diastereomer could be distinguished:

Major Diastereomer **4j-***endo*: δ_C (67.8 MHz, $CDCl_3$) 43.8 (N*C*H_2), 45.6 (C-7), 50.3 (C-4), 53.9 (C-1), 55.4 (-O*C*H_3), 59.8 (C-3), C-2 obscured by $CDCl_3$ at 76.5-77.5, 114.2 (aromatic CH), 127.2 (aromatic CH), 128.0 (aromatic CH), 128.1 (aromatic CH), 128.6 (aromatic CH), 135.6 (C-5), 137.6 (aromatic C), 138.4 (C-6), 161.9 (C-OMe), 167.4 (CO).

Minor Diastereomer **4j-***exo*: δ_C (67.8 MHz, $CDCl_3$) 43.9 (N*C*H_2), 45.3 (C-7), 50.5 (C-4), 54.8 (C-1), 55.4 (-O*C*H_3), 59.6 (C-3), 78.7 (C-2), 114.2 (aromatic CH), 127.2 (aromatic CH), 128.0 (aromatic CH), 128.1 (aromatic CH), 128.6 (aromatic CH), 135.1 (C-6), 137.5 (aromatic C), 139.6 (C-5), 161.7 (C-OMe), 166.4 (CO).

MS *m/z* 415 (M^+, 18%), 260 (33, M^+-SOAr), 225 (13, M^+-SOAr-Cl), 155 (29, $[SOAr]^+$), 91 (100); isotopic Cl pattern observed; 415, 417 (3:1 ratio ^{35}Cl:^{37}Cl); Found (HRMS, EI) *m/z* 415.1013. $C_{22}H_{22}N^{35}ClO_3S$ requires 415.1009.

2-*exo*-(4'-Methoxybenzenesulfinyl)-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid ethylamide 4k-*endo* and 2-*endo*-(4'-Methoxybenzenesulfinyl)-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid ethylamide 4k-*exo*

The title compound was prepared as described for **4a** using freshly distilled cyclopentadiene (343 mg, 5.20 mmol) and **3k** (300 mg, 1.04 mmol) in dichloromethane (6 mL). The reaction solution was then heated at reflux for 18 hours. The solvent and most of the excess diene were evaporated at reduced pressure to give the crude adduct **4k** as a mixture of inseparable diastereomers. A ^1H NMR spectrum was recorded of the crude reaction product (crude ratio of **4k-***exo* : **4k-***endo* = 1 : 1.2) before purification by chromatography on silica gel using ethyl acetate-hexane (gradient elution 20-40% ethyl acetate) as eluent to give the adduct (273 mg, 74%) as a colourless solid; mp 103-4^{o}C; Found C, 57.36; H, 5.50; N, 3.81; Cl, 10.43; S, 8.61. $C_{17}H_{20}NClO_3S$ requires C, 57.70; H, 5.70; N, 3.96; Cl, 10.02; S, 9.06; ν_{max}/cm^{-1} (KBr) 3700-2800 (b NH), 1662 (CO), 1593, 1533, 1494, 1258, 1031; Not all of the ^1H NMR signals for the two diastereomers could be distinguished, hence the ^1H NMR has been assigned as a

mixture: δ_H (270 MHz, $CDCl_3$) 0.88-0.98 (3H, s, 2 overlapping t, *J* 7, 7, -CH_3), 1.56-1.61 (0.47H, H_A of ABq, *J* 11, one of CH_2-7b), 1.75-1.80 (0.47H, H_B of ABq, *J* 11, one of CH_2-7b), 1.86-1.90 (0.53H, H_A of ABq, *J* 11, H-7a'), 2.63-2.68 (0.53H, H_B of ABq, *J* 11, H-7a), 2.77-3.12 (2H, m, NCH_2), 3.25 (0.53H, b s, H-4a), 3.39 (0.47H, b s, H-4b), 3.48 (0.47H, b s, H-1b), 3.72 (0.53H, b s, H-1a), 3.82 (3H, s, -OCH_3), 4.84 (0.57H, d, *J* 2, H-3a), 5.60 (0.47H, d, *J* 4, H-3b), 6.08-6.15 (0.57H, m, H-5a), 6.34-6.39 (0.57H, m, H-6a), 6.49-6.62 (0.94H, m, H-5b, NHb), 6.74-6.80 (0.47H, m, H-6b), 6.92-7.03 (2.53H, m, 2 of ArH, NHa), 7.70-7.82 (2H, m, ArH). The ^{13}C NMR signals for each diastereomer could be distinguished:

Major Diastereomer **4k-*endo***: δ_C (67.8 MHz, $CDCl_3$) 14.6 (-*C*H_3), 34.9 (N*C*H_2), 45.6 (C-7), 50.4 (C-4), 54.2 (C-1), 55.7 (-O*C*H_3), 60.0 (C-3), 76.6 (C-2), 114.7 (aromatic CH), 128.3 (aromatic CH), 131.7 (aromatic C), 135.9 (C-5), 138.6 (C-6), 162.2 (C-OMe), 166.5 (CO).

Minor Diastereomer **4k-*exo***: δ_C (67.8 MHz, $CDCl_3$) 14.4 (-*C*H_3), 34.7 (N*C*H_2), 45.8 (C-7), 50.8 (C-4), 55.1 (C-1), 55.7 (-O*C*H_3), 60.2 (C-3), 78.9 (C-2), 114.7 (aromatic CH), 128.3 (aromatic CH), 132.2 (aromatic C), 135.5 (C-6), 139.8 (C-5), 162.1 (C-OMe), 167.5 (CO).

MS *m/z* 353 (M^+, 18%), 272 (26), 198 (100, M^+-SOR), 155 (70, $[SOR]^+$), 91 (90); isotopic Cl pattern observed; 353, 355 (3:1 ratio ^{35}Cl:^{37}Cl); Found (HRMS, EI) *m/z* 353.0852. $C_{17}H_{20}N^{35}ClO_3S$ requires 353.0852.

2-*exo*-(4-Nitrobenzenesulfinyl)-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid *p*-tolylamide 4l-*endo* and 2-*endo*-(4-Nitrobenzenesulfinyl)-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid *p*-tolylamide 4l-*exo*

The title compound was prepared as described for **4a** using freshly distilled cyclopentadiene (182 mg, 2.75 mmol) and **3l** (200 mg, 0.55 mmol) in dichloromethane (4 mL). The reaction solution was then heated at reflux for 18 hours. The solvent and most of the excess diene was evaporated at reduced pressure to give the crude adduct **4l** as a mixture of inseparable diastereomers. An NMR was recorded of the crude reaction product (crude ratio = 1: 1.3) before purification by trituration using diethyl ether-hexane as solvent to give the adduct **4l** (186 mg, 79%) as an off-white solid; mp 179-79.5^oC (with decomposition); Found C, 59.00; H, 4.57; N, 6.03; Cl, 8.72; S, 7.80. $C_{21}H_{19}N_2ClO_4S$ requires C, 58.53; H, 4.44; N, 6.50; Cl, 8.23; S, 7.44; ν_{max}/cm^{-1} (KBr) 1674 (CO), 1526 (very strong), 1348, 1043; The NMR signals for each diastereomer could be distinguished:

Major diastereomer **4l-*endo***: δ_H (270 MHz, $CDCl_3$) 2.02 (1H, d, *J* 10, $H_{7'}$), 2.27 (3H, s, $ArCH_3$), 2.70 (1H, d, *J* 10, H_7), 3.68 (1H, s, H_4), 3.90 (1H, s, H_1), 4.90 (1H, d, *J* 2, H_3), 6.18-6.24 (1H, m, H_5), 6.41-6.47 (1H, m, H_6), 6.99-7.10 (4H, m, ArH), 8.02-8.23 (5H, m, ArH, NH); δ_C (67.8 MHz, $CDCl_3$) 20.8 (*C*H_3, $ArCH_3$), 45.8 (*C*H, C_7), 50.2 (*C*H, C_4), 54.0 (*C*H, C_1), 59.4 (*C*H, C_3), 78.7 (*C*, C_2), 120.0 (*C*H, aromatic CH), 123.6 (*C*H, aromatic CH), 127.62

(*C*H, aromatic CH), 129.6 (*C*H, aromatic CH), 134.2 (*C*, aromatic C), 135.2 (*C*H, C_5), 139.1 (*C*H, C_6), 147.9 (*C*, aromatic C), 149.6 (*C*, aromatic C), 163.4 (CO).

Minor diastereomer **4l-*exo***: δ_H (270 MHz, $CDCl_3$) 1.67 (1H, d, *J* 10, $H_{7'}$), 1.91 (1H, d, *J* 10, H_7), 2.27 (3H, s, $ArCH_3$), 3.50 (1H, s, H_4), 3.67 (1H, s, H_1), 5.65 (1H, d, *J* 4, H_3), 6.67-6.72 (1H, m, H_5), 6.81-6.87 (1H, m, H_6), 6.99-7.10 (4H, m, ArH), 8.02-8.23 (5H, m, ArH), 8.63 (1H, b s, NH); δ_C (67.8 MHz, $CDCl_3$) 20.8 (*C*H_3, $ArCH_3$), 45.6 (*C*H, C_7), 50.6 (*C*H, C_4), 54.8 (*C*H, C_1), 59.2 (*C*H, C_3), 80.8 (*C*, C_2), 120.0 (*C*H, aromatic CH), 123.6 (*C*H, aromatic CH), 127.6 (*C*H, aromatic CH), 129.6 (*C*H, aromatic CH), 134.2 (*C*, aromatic C), 134.8 (*C*H, C_6), 140.5 (*C*H, C_5), 148.3 (*C*, aromatic C), 149.4 (*C*, aromatic C), 163.4 (CO).

MS *m/z* 430 (M^+, 10%), 395 (2, M^+-Cl), 260 (84, M^+-SOAr), 224 (79, M^+-SOAr-HCl), 91 (100); isotopic Cl pattern observed; 430, 432 (3:1 ^{35}Cl:^{37}Cl). Found (HRMS, EI) *m/z* 430.0705. $C_{21}H_{19}N_2{}^{35}ClO_4S$ requires 430.0754.

2-*exo*-(*n*-Butylsulfinyl)-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid *p*-tolylamide 4m-*endo* and 2-*endo*-(*n*-Butylsulfinyl)-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid *p*-tolylamide 4m-*exo*

The title compound was prepared as described for **4a** using freshly distilled cyclopentadiene (551 mg, 0.66 mL, 8.35 mmol) and **3m** (500 mg, 1.67 mmol) in dichloromethane (10 mL). The reaction solution was then heated at reflux for 18 hours. The solvent and most of the excess diene were evaporated at reduced pressure to give the crude adduct **4m** as a mixture of inseparable diastereomers. A ^1H NMR spectrum was recorded of the crude reaction product (crude ratio of **4m-*exo*** : **4m-*endo*** = 1 : 1.04) before purification by chromatography on silica gel using ethyl acetate-hexane (10:90) as eluent to give the adduct (531 mg, 87%) as a colourless oil; Found C, 62.00; H, 6.76; N, 3.97; Cl, 9.88; S, 8.52. $C_{19}H_{24}NClO_2S$ requires C, 62.36; H, 6.61; N, 3.83; Cl, 9.69; S, 8.76; ν_{max}/cm^{-1} (film) 3700-2600 (b NH), 1680, 1604, 1538, 1515, 1315, 1021; Not all of the ^1H NMR signals for the two diastereomers could be distinguished, hence the ^1H NMR has been assigned as a mixture: δ_H (270 MHz, $CDCl_3$) 0.85-0.97 (3H, 2 overlapping t, *J* 7,7, -CH_3), 1.32-1.60 (2H, m, -CH_2-3'), 1.62-1.95 (3.5H, m, -CH_2-2', H-7a', both of CH_2-7b), 2.31 (1.5H, s, one of Ar CH_3), 2.33 (1.5H, s, one of Ar CH_3), 2.48-2.64 (1.5H, m, H-7a, one of SCH_2), 3.09-3.30 (1.5H, m, one of SCH_2, H-4a), 3.38 (0.5H, b s, H-4b), 3.52 (0.5H, b s, H-1b), 3.67 (0.5H, b s, H-1a), 4.89 (0.5H, d, *J* 2, H-3a), 5.60 (0.5H, d, *J* 4, H-3b), 6.15-6.20 (0.5H, m, H-5a), 6.35-6.40 (0.5H, m, H-6a), 6.45-6.53 (0.5H, m, H-5b), 6.65-6.72 (0.5H, m, H-6b), 7.08-7.20 (2H, m, ArH), 7.33-7.48 (2H, m, ArH), 8.90 (0.5H, b s, NHa), 9.54 (0.5H, b s, NHb). The ^{13}C NMR signals for each diastereomer could be distinguished:

Major Diastereomer **4m-*endo***: δ_C (67.8 MHz, $CDCl_3$) 14.0 (*C*H_3, CH_3-4'), 21.2 (*C*H_3, Ar CH_3), 22.3 (*C*H_2, -CH_2-3'), 26.4 (*C*H_2, -CH_2-2'), 45.4 (*C*H_2, C-7), 49.7 (*C*H_2, SCH_2), 50.0

(*C*H, C-4), 53.9 (*C*H, C-1), 59.6 (*C*H, C-3), 71.6 (*C*, C-2), 121.0 (*C*H, aromatic CH), 129.9 (*C*H, aromatic CH), 134.7 (*C*, aromatic C), 135.4 (*C*, aromatic C), 135.6 (*C*H, C-5), 138.6 (*C*H, C-6), 166.4 (CO).

Minor Diastereomer **4m-***exo*: δ_C (67.8 MHz, $CDCl_3$) 14.0 (*C*H_3, CH_3-4'), 21.2 (*C*H_3, Ar CH_3), 22.3 (*C*H_2, -CH_2-3'), 26.6 (*C*H_2, -CH_2-2'), 45.8 (*C*H_2, C-7), 50.8 (*C*H, C-4), 51.6 (*C*H_2, SCH_2), 53.9 (*C*H, C-1), 59.5 (*C*H, C-3), 73.8 (*C*, C-2), 121.0 (*C*H, aromatic CH), 129.9 (*C*H, aromatic CH), 134.7 (*C*, aromatic C), 135.4 (*C*, aromatic C), 135.5 (*C*H, C-6), 138.3 (*C*H, C-5), 165.4 (CO).

MS *m/z* 365 (M^+, 11%), 330 (4, M^+-Cl) 260 (46, M^+-SOR), 224 (35, M^+-SOR-HCl), 91 (100); isotopic Cl pattern observed; 365, 367 (3:1 ratio ^{35}Cl:^{37}Cl). Found (HRMS, EI) 365.1216. $C_{19}H_{24}N^{35}ClO_2S$ requires 365.1216.

2-*exo*-(*n*-Butylsulfinyl)-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid benzylamide 4n-*endo* and 2-*endo*-(*n*-Butylsulfinyl)-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid *n*-butylamide 4n-*exo*

The title compound was prepared as described for **4a** using freshly distilled cyclopentadiene (551 mg, 0.66 mL, 8.35 mmol) and **3n** (500 mg, 1.67 mmol) in dichloromethane (10 mL). The reaction solution was then heated at reflux for 18 hours. The solvent and most of the excess diene were evaporated at reduced pressure to give the crude adduct **4n** as a mixture of inseparable diastereomers. A ^1H NMR spectrum was recorded of the crude reaction product (crude ratio of **4n-***endo* : **4n-***exo* = 1: 1.1) before purification by chromatography on silica gel using ethyl acetate-hexane (10:90) as eluent to give the adduct (512 mg, 84%) as a colourless oil; Found C, 62.37; H, 6.86; N, 3.70; Cl, 9.95; S, 9.15. $C_{19}H_{24}NClO_2S$ requires C, 62.36; H, 6.61; N, 3.83; Cl, 9.69; S, 8.76; ν_{max}/cm^{-1} (film) 3315 (NH), 1677 (CO), 1604, 1535, 1316, 1026, 817; Not all of the ^1H NMR signals for the two diastereomers could be distinguished, hence the ^1H NMR has been assigned as a mixture: δ_H (270 MHz, $CDCl_3$) 0.84-0.95 (3H, 2 overlapping triplets, *J* 7, 7, -CH_3), 1.24-1.50 (2H, m, -CH_2-3'), 1.58-1.88 (3.53H, m, -CH_2-2', H-7a, H-7a', one of CH_2-7b), 2.22-2.37 (1H, m, one of SCH_2), 2.46-2.52 (0.47H, H_B of ABq, *J* 10, H-7b), 2.92-3.12 (1H, m, one of SCH_2), 3.15 (0.47H, b s, H-4a), 3.33 (0.53H, b s, H-4b), 3.39 (0.53H, b s, H-1b), 3.54 (0.47H, b s, H-1a), 4.39-4.55 (2H, m, NCH_2), 4.82 (0.47H, d, *J* 2, H-3a), 5.55 (0.53H, d, *J* 4, H-3b), 6.04-6.08 (0.47H, m, H-5a), 6.30-6.35 (0.47H, m, H-6a), 6.42-6.48 (0.53H, m, H-5b), 6.60-6.65 (0.53H, m, H-6b), 7.22-7.43 (5.47H, m, ArH, NHa), 7.83 (0.53H, b s, NHb). The ^{13}C NMR signals for each diastereomer could be distinguished:

Major Diastereomer **4n-***exo*: δ_C (67.8 MHz, $CDCl_3$) 13.6 (*C*H_3, CH_3-4'), 21.8 (*C*H_2, -CH_2-3'), 26.1 (*C*H_2, -CH_2-2'), 43.8 (*C*H_2, NCH_2), 45.3 (*C*H_2, C-7), 49.3 (*C*H, C-4), 50.5 (*C*H_2, SCH_2), 53.3 (*C*H, C-1), 59.6 (*C*H, C-3), 70.7 (*C*, C-2), 127.5 (*C*H, aromatic CH), 128.2 (*C*H,

aromatic CH), 128.9 (*C*H, aromatic CH), 135.2 (*C*H, C-5), 137.8 (*C*H, C-6), 138.0 (*C*, aromatic C), 167.0 (CO).

Minor Diastereomer **4n-*endo***: δ_C (67.8 MHz, $CDCl_3$) 13.6 (*C*H_3, CH_3-4'), 21.8 (*C*H_2, -CH_2-3'), 25.8 (*C*H_2, -CH_2-2'), 43.9 (*C*H_2, NCH_2), 44.9 (*C*H_2, C-7), 48.6 (*C*H_2, SCH_2), 50.2 (*C*H, C-4), 53.4 (*C*H, C-1), 59.4 (*C*H, C-3), 72.9 (*C*, C-2), 127.5 (*C*H, aromatic CH), 128.2 (*C*H, aromatic CH), 128.9 (*C*H, aromatic CH), 135.2 (*C*H, C-6), 138.0 (*C*, aromatic C), 138.7 (*C*H, C-5), 168.0 (CO).

MS *m/z* 365 (M^+, 6%), 260 (81, M^+-SOR), 224 (34, M^+-SOR-HCl), 91 (100); isotopic Cl pattern observed; 365, 367 (3:1 ratio ^{35}Cl:^{37}Cl).

2-*exo*-(*n*-Butylsulfinyl)-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid 4'-fluorophenylamide 4o-*endo* and 2-*endo*-(*n*-Butylsulfinyl)-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid 4'-fluorophenylamide 4o-*exo*

The title compound was prepared as described for **4a** using freshly distilled cyclopentadiene (545 mg, 0.63 mL, 8.25 mmol) and **3o** (500 mg, 1.55 mmol) in dichloromethane (10 mL). The reaction solution was then heated at reflux for 18 hours. The solvent and most of the excess diene was evaporated at reduced pressure to give the crude adduct **4o** as a mixture of inseparable diastereomers. Purification by chromatography on silica gel using ethyl acetate-hexane (15:85) as eluent to give the adduct (582 mg, 95%) as a colourless solid (ratio of **4o-*exo*** : **4o-*endo*** of 1 : 1.1); mp 70-73^oC; Found C, 58.56; H, 5.52; N, 3.76; Cl, 9.13; F, 5.44; S, 8.75. $C_{18}H_{21}NClFO_2S$ requires C, 58.45; H, 5.72; N, 3.79; Cl, 9.58; F, 5.14; S, 8.67; ν_{max}/cm^{-1} (KBr) 1682 (CO), 1615, 1549, 1510, 1219, 1027, 834; Not all the ^1H NMR signals for the two diastereomers could be distinguished, hence the ^1H NMR has been assigned as a mixture: δ_H (270 MHz, $CDCl_3$) 0.88-0.98 (3H, overlapping triplets, *J* 7, 7, CH_3-4'), 1.36-1.95 (5.47H, m, CH_2-2', CH_2-3', CH_2-7b, H-7'a), 2.45-2.61 (1.53H, m, one of SCH_2, H-7a), 3.09-3.31 (1.53H, m, one of SCH_2, H-4a), 3.39 (0.47H, b s, H-4b), 3.52 (0.47H, b s, H-1b), 3.68 (0.53H, b s, H-1a), 4.88 (0.53H, d, *J* 2, H-3a), 5.59 (0.47H, d, *J* 4, H-3b), 6.17-6.21 (0.53H, m, H-5a), 6.38-6.43 (0.53H, m, H-6a), 6.50-6.56 (0.47H, m, H-5b), 6.68-6.73 (0.47H, m, H-6b), 6.98-7.09 (2H, m, ArH), 7.41-7.58 (2H, m, ArH), 8.98 (0.53H, b s, NHa), 9.64 (0.47H, b s, NHb); The ^{13}C signals for each diastereomer could be distinguished:

Major Diastereomer **4o-*endo***: δ_C (67.8 MHz, $CDCl_3$) 13.5 (*C*H_3, CH_3-4), 21.8 (*C*H_2, CH_2-3'), 26.1 (*C*H_2, CH_2-2'), 45.4 (*C*H_2, C-7), 49.0 (*C*H_2, $SOCH_2$), 50.3 (*C*H, C-4), 53.1 (*C*H, C-1), 58.9 (*C*H, C-3), 71.1 (*C*, C-2), 115.6 (*C*H, d, $^3J_{CF}$ 22, aromatic CH, ArC-3), 122.1 (*C*H, aromatic CH, ArC-2), 133.6 (*C*, aromatic C, ArC-1), 135.0 (*C*H, C-5), 138.2 (*C*H, C-6), 159.5 (*C*, d, $^4J_{CF}$ 244, aromatic C, ArC-4), 166.1 (*C*, CO).
Minor Diastereomer **4o-*exo***: δ_C (67.8 MHz, $CDCl_3$) 13.5 (*C*H_3, CH_3-4), 21.8 (*C*H_2, CH_2-3'), 25.9 (*C*H_2, CH_2-2'), 44.9 (*C*H_2, C-7), 49.2 (*C*H, C-4), 51.2 (*C*H_2, $SOCH_2$), 53.1 (*C*H, C-1),

59.1 (*C*H, C-3), 73.3 (*C*, C-2), 115.6 (*C*H, d, $^{3}J_{CF}$ 22, aromatic CH, ArC-3), 122.1 (*C*H, aromatic CH, ArC-2), 133.4 (*C*, aromatic C, ArC-1), 134.9 (*C*H, C-6), 138.9 (*C*H, C-5), 159.5 (*C*, d, $^{4}J_{CF}$ 244, aromatic C, ArC-4), 165.1 (*C*, CO).

Diels-Alder reaction of (-)-3o with cyclopentadiene

The title compound was prepared as described for **4a** using freshly distilled cyclopentadiene (109 mg, 0.13 mL, 1.65 mmol) and (-)-**3o** (100 mg, 0.33 mmol, 53% ee, $[\alpha]_D$ –98 (*c* 1.3 in dichloromethane) in dichloromethane (2 mL). The reaction solution was then heated at reflux for 18 hours. The solvent and most of the excess diene was evaporated at reduced pressure to give the crude adduct (-)-**4o** as a mixture of inseparable diastereomers. Purification by chromatography on silica gel using ethyl acetate-hexane (gradient elution 10-20% ethyl acetate) as eluent to give the adduct (86 mg, 79%) as a colourless solid (ratio of (-)-**4o**-*exo* : (-)-**4o**-*endo* of 1 : 1.1); $[\alpha]_D$ –58 (*c* 1.6 in dichloromethane). Spectroscopic characteristics were as described above.

Diels-Alder reaction of (+)-3o with cyclopentadiene

The title compound was prepared as described for **4a** using freshly distilled cyclopentadiene (55 mg, 0.07 mL, 0.83 mmol) and (+)-**3o** (50 mg, 0.17 mmol, 53% ee, [α] +94 (*c* 1.7 in dichloromethane) in dichloromethane (1 mL). The reaction solution was then heated at reflux for 18 hours. The solvent and most of the excess diene was evaporated at reduced pressure to give the crude adduct (+)-**4o** as a mixture of inseparable diastereomers. Purification by chromatography on silica gel using ethyl acetate-hexane (gradient elution 10-20% ethyl acetate) as eluent to give the adduct (+)-**4o** (42 mg, 75%) as a colourless solid (ratio of (+)-**4o**-*exo* : (+)-**4o**-*endo* of 1: 1.1); [α] + 57 (*c* 1.2 in DCM). Spectroscopic characteristics were as reported previously.

2-*exo*-(Benzylsulfinyl)-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid *N*-benzylamide 4p-*endo* and 2-*endo*-(benzylsulfinyl)-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid *N*-benzylamide 4p-*exo*

The title compound was prepared as described for **4a** using freshly distilled cyclopentadiene (20 mL) and **3p** (2.21 g, 6.6 mmol) in dichloromethane (50 mL) and the reaction solution was then heated at reflux for 24 h. The solvent and most of the excess cyclopentadiene was evaporated at reduced pressure. The mixture was then applied to a column of silica and the remaining cyclopentadiene was eluted with hexane. The product was then eluted with hexane-ethyl acetate (60:40) to give the adduct as a white solid (2.35 g, 88%) and an inseparable mixture of diastereomers (ratio of **4p**-*endo*: **4p**-*exo* of 1 : 1.4), mp 126-129 °C; (Found C, 66.05; H, 5.55; N, 3.46; S, 8.42; Cl, 8.76. $C_{22}H_{22}ClNO_2S$ requires C, 66.07; H,

5.54; N, 3.50; S, 8.02; Cl, 8.86%); ν_{max}/cm^{-1} (KBr) 3330 (NH), 3031 (CH), 2934 (CH), 1663 (CO), 1533 (NH bend), 1029 (SO);

Major diastereomer **4p-*exo***: δ_H (300 MHz, $CDCl_3$) 1.63 [1H, d, A of AB system, J_{AB} 9.6, one of C(7)H_2], 1.80 [1H, d, B of AB system, J_{AB} 9.6 one of C(7)H_2], 3.36 (1H, d, A of AB system, J_{AB} 12.8, one of SCH_2), 3.39 [1H, br s, C(1)*H* or C(4)*H*], 3.44 [1H, br s, C(1)*H* or C(4)*H*], 4.30 (1H, d, B of AB system, J_{AB} 12.4, one of SCH_2), 4.49 (1H, dd, A of ABX, J_{AB} 14.4, J_{AX} 5.2, one of NHCH_2), 4.67 (1H, dd, B of ABX, J_{AB} 14.4, J_{BX} 6.8, one of NHCH_2), 5.69 [1H, d, *J* 3.6, C(3)*H*], 6.47 [1H, dd, *J* 5.6, 2.8, C(5)*H* or C(6)*H*], 6.58 [1H, dd, *J* 5.6, 2.8, C(5)*H* or C(6)*H*], 7.07-7.14 (2H, m, Ar*H*), 7.24-7.46 (8H, m, Ar*H*)*, 7.99 (1H, br t, *J* 5.6, N*H*); δ_C (75.5 MHz, $CDCl_3$) 44.1, 44.9 [2 × CH_2, NHCH_2 & *C*(7)H_2], 50.3, 53.6 [2 × CH, *C*(1)H & *C*(4)H], 55.1 (CH_2, S*C*H_2), 59.7 [CH, *C*(3)H], 73.0 [C, *C*(2)], 128.3, 128.4, 128.8, 128.9, 130.0 (5 × CH, 5 signals for 6 carbons, 5 × aromatic *C*H), 131.6 (C, aromatic *C*), 135.0 [CH, *C*(5)H or *C*(6)H], 138.1 (C, aromatic *C*), 138.9 [CH, *C*(5)H or *C*(6)H], 167.8 (C, *C*O).

Minor diastereomer **4p-*endo***: δ_H (300 MHz, $CDCl_3$) 1.83 [1H, d, A of AB system, J_{AB} 9.6, one of C(7)H_2], 2.46 [1H, d, B of AB system, J_{AB} 10.0, one of C(7)H_2], 3.22 [1H, br s, C(1)*H* or C(4)*H*], 3.33 (1H, d, A of AB system, J_{AB} 12.8, one of SCH_2), 3.57 [1H, br s, C(1)*H* or C(4)*H*], 4.40 (1H, d, B of AB system, J_{AB} 12.8, one of SCH_2), 4.44 (1H, dd, A of ABX, J_{AB} 14.4, J_{AX} 5.6, one of NHCH_2), 4.54 (1H, dd, B of ABX, J_{AB} 14.4, J_{BX} 6.8, one of NHCH_2), 4.95 [1H, d, *J* 2.0, C(3)*H*], 6.12 [1H, dd, *J* 5.6, 3.2, C(6)*H* or C(5)*H*], 6.37 [1H, dd, *J* 5.6, 3.2, C(6)*H* or C(5)*H*], 7.16-7.22 (2H, m, Ar*H*), 7.24-7.46 (9H, m, N*H* & Ar*H*)*; δ_C (75.5 MHz, $CDCl_3$) 44.0, 45.3 [2 × CH_2, NHCH_2 & *C*(7)H_2], 49.4, 53.3 [2 × CH, *C*(1)H & *C*(4)H], 57.1 (CH_2, S*C*H_2), 59.9 [CH, *C*(3)H], 71.0 [C, *C*(2)], 127.73, 127.75, 128.3, 128.82, 128.85 (5 × CH, 5 signals for 6 carbons, 5 × aromatic *C*H), 131.6 (C, aromatic *C*), 135.3, 138.0 [2 × CH, *C*(5)H & *C*(6)H], 138.1 (C, aromatic *C*), 166.9 (C, *C*O).

*These signals were indistinguishable for the two diastereomers.

HRMS (ES+): Exact mass calculated for $C_{22}H_{23}NO_2S^{35}Cl$ $[M+H]^+$ 400.1138. Found 400.1139; m/z (ES+) 402.0 {[($C_{22}H_{22}NO_2S^{37}Cl$)+H^+], 44%}, 400.0 {[($C_{22}H_{22}NO_2S^{35}Cl$)+H^+], 100%}.

2-*exo*-(Benzylsulfinyl)-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid *N*-(4-fluorophenyl)amide 4q-*endo* and 2-*endo*-(benzylsulfinyl)-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid *N*-(4-fluorophenyl)amide 4q-*exo*

Method A: Thermal conditions

The title compound was prepared as described for **4a** using freshly distilled cyclopentadiene (0.12 mL, 1.5 mmol) and **3q** (0.10 g, 0.3 mmol) in dichloromethane (10 mL) and the reaction solution was then heated at reflux for 18 h. The solvent and most of the excess cyclopentadiene was evaporated at reduced pressure to give the crude adduct as a brown solid (ratio of **4q-*endo*: 4q-*exo*** of 1 : 1.2). Following recrystallisation from dichloromethane-

hexane, the pure adduct was isolated as a white solid (0.11 g, 90%) and as a mixture of inseparable diastereomers (ratio of **4q-*endo*: 4q-*exo*** of 1 : 1.2); ν_{max}/cm^{-1} (KBr) 3303 (NH), 2973 (CH), 1669 (CO), 1612, 1537 (NH bend), 1508, 1025 (SO);

Major diastereomer **4q-*exo***: δ_H (300 MHz, $CDCl_3$) 1.71 [1H, d, A of AB system, J_{AB} 9.9, one of C(7)H_2], 1.85 [1H, d, B of AB system, J_{AB} 9.9, one of C(7)H_2], 3.45 [1H, br s, C(1)*H* or C(4)*H*], 3.55 [1H, br s, C(1)*H* or C(4)*H*], 3.61 or 3.66 (1H, d, A of AB system, J_{AB} 12.9, one of SCH_2)*, 4.48 or 4.56 (1H, d, B of AB system, J_{AB} 12.9, one of SCH_2)*, 5.71 [1H, d, *J* 3.6, C(3)*H*], 6.53 [1H, dd, *J* 5.4, 2.7, C(5)*H* or C(6)*H*], 6.65 [1H, dd, *J* 5.4, 2.7, C(5)*H* or C(6)*H*], 6.99-7.41 (7H, m, Ar*H*)*, 7.58-7.67 (2H, m, Ar*H*), 9.70 (1H, br s, N*H*).

Minor diastereomer **4q-*endo***: δ_H (300 MHz, $CDCl_3$) 1.91 [1H, d, A of AB system, J_{AB} 9.6, one of C(7)H_2], 2.53 [1H, d, B of AB system, J_{AB} 9.6, one of C(7)H_2], 3.29 [1H, br s, C(1)*H* or C(4)*H*], 3.61 or 3.66 (1H, d, A of AB system, J_{AB} 12.6, one of SCH_2)*, 3.70 [1H, br s, C(1)*H* or C(4)*H*], 4.48 or 4.56 (1H, d, B of AB system, J_{AB} 12.9, one of SCH_2)*, 5.00 [1H, d, *J* 1.8, C(3)*H*], 6.22 [1H, dd, *J* 5.7, 3.0, C(6)*H* or C(5)*H*], 6.43 [1H, dd, *J* 5.4, 3.3, C(6)*H* or C(5)*H*], 6.99-7.41 (7H, m, Ar*H*)*, 7.46-7.58 (2H, m, Ar*H*), 9.04 (1H, br s, N*H*).

*These signals could not be distinguished for the two diastereomers.

Method B: Microwave conditions

An excess of freshly distilled cyclopentadiene (0.08 mL, 1.2 mmol) and **3q** (0.08 g, 0.2 mmol) were placed in a sealed microwave reaction vessel with stirring and heated for 5 min at 300 W at 100 °C. The crude reaction mixture was applied to a column of silica gel and the excess cyclopentadiene was eluted with hexane. The product was then eluted with hexane-ethyl acetate (gradient elution 2-5% ethyl acetate), to give the cycloadduct as a white solid (0.06 g, 69%) and a mixture of inseparable diastereomers (ratio of **4q-*endo*: 4q-*exo*** of 1.1 : 1), mp 119-120 °C; ν_{max}/cm^{-1} (KBr) 3304 (NH), 2993 (CH), 1669 (CO), 1612, 1508, 1536 (NH bend), 1406 (CN stretch), 1024 (SO);

Minor diastereomer **4q-*exo***: δ_H (300 MHz, $CDCl_3$) 1.71 [1H, d, A of AB system, J_{AB} 9.9, one of C(7)H_2], 1.85 [1H, d, B of AB system, J_{AB} 9.9, one of C(7)H_2] 3.45 [1H, br s, C(1)*H* or C(4)*H*], 3.55 [1H, br s, C(1)*H* or C(4)*H*], 3.61 or 3.66 (1H, d, A of AB system, J_{AB} 12.6, one of SCH_2)*, 4.48 or 4.56 (1H, d, B of AB system, J_{AB} 12.6, one of SCH_2)*, 5.71 [1H, d, *J* 3.6, C(3)*H*], 6.53 [1H, dd, *J* 5.7, 3.0, C(5)*H* or C(6)*H*], 6.65 [1H, dd, *J* 5.7, 3.0, C(5)*H* or C(6)*H*], 6.99-7.41 (7H, m, Ar*H*)*, 7.58-7.67 (2H, m, Ar*H*), 9.71 (1H, br s, N*H*); δ_C (75.5 MHz, $CDCl_3$) 45.0 [CH_2, *C*(7)H_2], 50.4, 53.5 [2 × CH, *C*(1)H & *C*(4)H], 55.8 or 57.8 (CH_2, S*C*H_2)*, 59.1 [CH, *C*(3)H], 73.5 [C, *C*(2)], 115.9 [CH, d, $^2J_{CF}$ 23, aromatic *C*(3′)H], 122.1 [CH, d, $^3J_{CF}$ 8, aromatic *C*(2′)H], 128.6, 129.0, 130.1 (3 × CH, 3 × aromatic *C*H), 133.3, 133.6 (2 × C, 2 × aromatic *C*), 135.0, 139.2 [2 × CH, *C*(5)H & *C*(6)H], 159.6 [C, d, $^1J_{CF}$ 243, aromatic *C*(4′)], 165.1 (C, *C*O).

Major diastereomer **4q-*endo***: δ_H (300 MHz, $CDCl_3$) 1.91 [1H, d, A of AB system, J_{AB} 9.6, one of C(7)H_2], 2.53 [1H, d, B of AB system, J_{AB} 9.9, one of C(7)H_2], 3.28 [1H, br s, C(1)*H*

or C(4)*H*], 3.61 or 3.66 (1H, d, A of AB system, J_{AB} 12.9, one of SCH_2)*, 3.70 [1H, br s, C(1)*H* or C(4)*H*], 4.48 or 4.56 (1H, d, B of AB system, J_{AB} 12.9, one of SCH_2)*, 5.00 [1H, d, *J* 1.8, C(3)*H*], 6.22 [1H, dd, *J* 5.7, 2.7, C(6)*H* or C(5)*H*], 6.43 [1H, dd, *J* 5.7, 3.3, C(6)*H* or C(5)*H*], 6.99-7.41 (7H, m, Ar*H*)*, 7.46-7.58 (2H, m, Ar*H*), 9.04 (1H, br s, N*H*); δ_C (75.5 MHz, $CDCl_3$) 45.5 [CH_2, *C*(7)H_2], 49.7, 53.6 [2 × CH, *C*(1)H & *C*(4)H], 55.8 or 57.8 (CH_2, S*C*H_2)*, 59.4 [CH, *C*(3)H], 71.5 [C, *C*(2)], 115.8 [CH, d, $^2J_{CF}$ 22, aromatic *C*(3′)H], 122.0 [CH, d, $^3J_{CF}$ 8, aromatic *C*(2′)H], 128.7, 129.0, 130.1 (3 × CH, 3 × aromatic *C*H), 131.10, 131.13 (2 × C, 2 × aromatic *C*), 134.9, 138.4 [2 × CH, *C*(5)H & *C*(6)H], 159.6 [C, d, $^1J_{CF}$ 243, aromatic *C*(4′)], 165.9 (C, *C*O).

*These signals could not be distinguished for the two diastereomers.

HRMS (ES+): Exact mass calculated for $C_{21}H_{20}NOSF^{35}Cl$ $[M+H]^+$ 404.0887. Found 404.0902; m/z (ES+) 406.2 {[($C_{21}H_{19}NOSF^{37}Cl$)+H^+], 40%}, 404.2 {[($C_{21}H_{19}NOSF^{35}Cl$)+H^+], 100%}.

2-*exo*-(*S*s)-(Benzylsulfinyl)-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid (*R*)-phenylethylamide 4r-*endo* and 2-*endo*-(*S*s)-(benzylsulfinyl)-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid (*R*)-phenylethylamide 4r-*exo*

The title compound was prepared as described for **4a** using freshly distilled cyclopentadiene (10 mL) was added to a solution of **3r** (0.43 g, 1.2 mmol) in dichloromethane (10 mL) and the reaction solution was then heated at reflux for 24 h. The solvent and most of the excess cyclopentadiene was evaporated at reduced pressure. The mixture was then applied to a column of silica gel and the remaining cyclopentadiene was eluted with hexane. The product was then eluted with hexane-ethyl acetate (90:10) to give the adduct as a clear oil (0.34 g, 66%)* and an inseparable mixture of diastereomers (ratio of **4r-*endo***: **4r-*exo*** of 1 : 1.3); ν_{max}/cm^{-1} (film) 3326 (NH), 2974 (CH), 1662 (CO), 1528 (NH bend), 1030 (SO);

Major diastereomer **4r-*exo***: δ_H (300 MHz, $CDCl_3$) 1.57 [3H, d, *J* 6.0, CH(CH_3)], 1.65 [1H, d, A of AB system, J_{AB} 9.9, one of C(7)H_2], 1.82 [1H, d, B of AB system, J_{AB} 9.6, one of C(7)H_2], 3.05 or 3.10 (1H, d, A of AB system, J_{AB} 12.9, one of SCH_2), 3.39 [1H, br s, C(1)*H* or C(4)*H*], 3.47 [1H, br s, C(1)*H* or C(4)*H*], 4.09 (1H, d, B of AB system, J_{AB} 12.9, one of SCH_2), 5.20-5.31 (1H, m, NHC*H*), 5.64 [1H, d, *J* 3.6, C(3)*H*], 6.46 [1H, dd, *J* 5.7, 3.0, C(5)*H* or C(6)*H*], 6.59 [1H, dd, *J* 5.7, 3.0, C(5)*H* or C(6)*H*], 6.92-7.02 (2H, m, Ar*H*), 7.17-7.58* (8H, m, Ar*H*), 7.98 (1H, br d, *J* 9.0, N*H*); δ_C (75.5 MHz, $CDCl_3$) 22.2 [CH_3, C(*C*H_3)], 44.9 [CH_2, *C*(7)H_2], 49.7, 50.3, 53.7 [3 × CH, *C*(1)H, *C*(4)H & NH*C*H], 54.2 (CH_2, S*C*H_2), 59.6 [CH, *C*(3)H], 72.5 [C, *C*(2)], 126.9, 127.8, 128.2, 128.7, 128.9, 129.9 (6 × CH, 6 × aromatic *C*H), 131.7 (C, aromatic *C*), 135.0, 138.9 [2 × CH, *C*(5)H & *C*(6)H], 143.0 (C, aromatic *C*), 166.9 (C, *C*O).

Minor diastereomer **4r-*endo***: δ_H (300 MHz, $CDCl_3$) 1.54 [3H, d, *J* 7.2, CH(CH_3)], 1.85 [1H, d, A of AB system, J_{AB} 9.9, one of C(7)H_2], 2.46 [1H, d, B of AB system, J_{AB} 9.9, one of

C(7)H_2], 3.05 or 3.10 (1H, d, A of AB system, J_{AB} 12.9, one of SCH_2), 3.21 [1H, br s, C(1)*H* or C(4)*H*], 3.62 [1H, br s, C(1)*H* or C(4)*H*], 4.19 (1H, d, B of AB system, J_{AB} 12.9, one of SCH_2), 4.92 [1H, d, *J* 2.1, C(3)*H*], 5.08-5.18 (1H, m, NHC*H*), 6.22 [1H, dd, *J* 5.7, 3.0, C(5)*H* or C(6)*H*], 6.39 [1H, dd, *J* 5.7, 3.0, C(5)*H* or C(6)*H*], 7.02-7.13 (2H, m, Ar*H*), 7.17-7.58* (9H, m, Ar*H* & N*H*); δ_C (75.5 MHz, $CDCl_3$) 22.3 [CH_3, C(CH_3)], 45.4 [CH_2, *C*(7)H_2], 49.4, 49.6, 53.4 [3 × CH, *C*(1)H, *C*(4)H & NH*C*H], 56.2 (CH_2, S*C*H_2), 59.8 [CH, *C*(3)H], 70.6 [C, *C*(2)], 126.9, 127.7, 128.3, 128.7, 128.8, 129.9 (6 × CH, 6 × aromatic *C*H), 131.8 (C, aromatic *C*), 135.3, 138.0 [2 × CH, *C*(5)H & *C*(6)H], 143.1 (C, aromatic *C*), 166.0 (C, *C*O).

*These signals were indistinguishable for the two diastereomers.

HRMS (ES+): Exact mass calculated for $C_{23}H_{25}NO_2S^{35}Cl$ $[M+H]^+$ 414.1295. Found 414.1293; m/z (ES+) 416.0 {[($C_{23}H_{24}NO_2S^{37}Cl$)+H^+], 44%}, 414.0 {[($C_{23}H_{24}NO_2S^{35}Cl$)+H^+], 100%}.

*A yield of 94% was obtained for a batch that was synthesised later.

2-*exo*-(Methylsulfinyl)-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid 4'-fluorophenylamide 4s-*endo* and 2-*endo*-(methylsulfinyl)-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid 4'-fluorophenylamide 4s-*exo*

Method A: Thermal conditions

The title compound was prepared as described for **4a** using freshly distilled cyclopentadiene (31.0g, 47 mL, 470 mmol) and **3s** (26.6g, 94 mmol) in dichloromethane (492 mL). The reaction solution was heated at reflux for 18 hours. The solvent and most of the excess diene was evaporated at reduced pressure to give the crude adduct **4s** as a mixture of inseparable diastereomers. Purification by chromatography on silica gel using ethyl acetate-hexane (20:80) as the eluent gave adduct **4s** in a ratio of **4s-*endo***: **4s-*exo*** = 1:1 (by ^{1}H NMR spectroscopy) as a white solid (28.7g, 93%); mp 196-198^{o}C; Found C, 54.81; H, 4.44; N, 4.31; S, 10.10. $C_{15}H_{15}NClFO_2S$ requires C, 54.96; H, 4.61; N, 4.27; S, 9.78; ν_{max}/cm^{-1} (KBr) 1676, 1547, 1032, 833; The ^{1}H NMR signals for the two diastereomers were distinguishable, hence the ^{1}H NMR signals have been assigned separately;

4s-*endo*: δ_H (300 MHz, $CDCl_3$) 1.64 (1H, H_A of AB_q, *J* 9.8, H-7'), 1.85 (1H, H_B of AB_q, *J* 9.8, H-7), 2.72 (3H, s, SCH_3), 3.41 (1H, bs, H-4), 3.51 (1H, bs, H-1), 5.58 (1H, d, *J* 2, H-3), 6.48-6.56 (1H, m, H-5), 6.62-6.71 (1H, m, H-6), 9.48 (1H, bs, NH).

4s-*exo:* δ_H (300 MHz, $CDCl_3$) 1.90 (1H, H_A of AB_q, *J* 9.0, H-7'), 1.85 (1H, H_B of AB_q, *J* 9.0, H-7), 2.77 (3H, s, SCH_3), 3.23 (1H, bs, H-4), 3.66 (1H, bs, H-1), 4.87 (1H, d, *J* 3.9, H-3), 6.15-6.24 (1H, m, H-5), 6.38-6.45 (1H, m, H-6), 9.48 (1H, bs, NH).

The aromatic signals for each diastereomer in the ^{1}H NMR spectrum were indistinguishable and are reported here as a mixture: δ_H 6.94-7.09 (4H, m, ArH), 7.38-7.58 (4H, m, ArH).The majority of ^{13}C NMR signals for each diastereomer could be distinguished;

4s-*endo*: δ_C (75.5 MHz, $CDCl_3$) 35.2 (CH_3, SCH_3), 45.1 (CH_2, C-7), 49.4 (CH, C-4), 53.3 (CH, C-1), 58.7 (CH, C-3), 73.9 (C, C-2), 115.9 (CH, d, $^2J_{CF}$ 22.12, aromatic CH, ArC-3), 122.1 (CH, d, $^3J_{CF}$ 8.00, aromatic CH, ArC-2), 133.3 (C, d, $^4J_{CF}$ 2.00, aromatic C, ArC-1), 134.9 (CH, C-5), 165.8 (CO).

4s-*exo:* δ_C (75.5 MHz, $CDCl_3$) 36.8 (CH_3, SCH_3), 45.5 (CH_2, C-7), 50.3 (CH, C-4), 53.4 (CH, C-1), 58.9 (CH, C-3), 71.8 (C, C-2), 115.6 (CH, d, $^2J_{CF}$ 22.10, aromatic CH, ArC-3), 122.0 (CH, d, $^3J_{CF}$ 8.00, aromatic CH, ArC-2), 133.5 (C, d, $^4J_{CF}$ 2.23, aromatic C, ArC-1), 135.0 (CH, C-5), 165.8 (CO).

Some of the aromatic signals for each diastereomer in the ^{13}C NMR spectrum were indistinguishable and are reported here as a mixture: 138.4 (CH, C-6), 159.5 (C, d, $^1J_{CF}$ 244.42, quaternary aromatic C, ArC-4); MS *m/z*; 327 (M^+, 30%), 264 (100%), 276 (5%), 228 (65%), 91 (90%); isotopic Cl pattern observed; 327, 329 (3:1 ^{35}Cl : ^{37}Cl).

Method B – Microwave conditions

Freshly distilled cyclopentadiene (12.6g, 19.1 mL, 191 mmol) was added to a solution of **3s** (10.0g, 38.2 mmol) in dichloromethane (30 mL). The reaction solution was heated to 100°C under pressure and held at this temperature for 10 minutes. TLC analysis showed that there was a substantial amount of starting material remaining. The reaction was re-exposed to the reaction conditions for a further 10 minutes when the solvent and most of the excess diene was evaporated at reduced pressure to give the crude adduct **4s** as a mixture of inseparable diastereomers. Purification by chromatography on silica gel using ethyl acetate-hexane (20:80) as eluent to give adduct **4s** in ratio of **4s-*endo***: **4s-*exo*** = 1:1 (by ^{1}H NMR spectroscopy) as a white solid (12.1g, 97%). Spectroscopic characteristics were consistent with those outlined above.

2-*exo*-(*iso*-Propyl sulfinyl)-3-*exo*-chlorobicyclo [2.2.1] hept-5-ene-2-*endo*-carboxylic acid 4'-fluorophenylamide 4t-*endo* and 2-*endo*-(*iso*-propyl sulfinyl)-3-*endo*-chlorobicyclo [2.2.1] hept-5-ene-2-*exo*-carboxylic acid 4'-fluorophenylamide 4t-*exo*

Freshly distilled cyclopentadiene (2.9 g, 3.7 mL, 45 mmol) was added to a solution of **3t** (2.6g, 8.9 mmol) in dichloromethane (60 mL). The reaction solution was heated at reflux for 18 hours. The solvent and most of the excess diene was evaporated at reduced pressure to give the crude adduct **4t** as a mixture of inseparable diastereomers. Purification by chromatography on silica gel using ethyl acetate-hexane (20:80) as eluent to give the adduct in a ratio of **4t-*endo***: **4t-*exo*** = 1.4:1(by ^{1}H NMR spectroscopy) as a white solid (2.8g, 87%); mp 220-222 °C; Found C, 57.30; H, 5.39; N, 4.07; S, 8.77 $C_{17}H_{19}NClFO_2S$ requires C, 57.38; H, 5.38; N, 3.94; S, 9.01; ν_{max}/cm^{-1} (KBr)1679; The ^{1}H NMR signals for the two diastereomers were indistinguishable, hence the ^{1}H NMR has been assigned for the mixture

δ_H (300 MHz, $CDCl_3$) 0.92-1.25 [3.5H, m, $CH(CH_3)_2$ major], 1.35 [0.41H, d, *J* 7.2, $CH(CH_3)_2$ minor], 1.43 [0.41H, d, *J* 7.2, $CH(CH_3)_2$ minor], 1.63 (0.59H, H_A of AB_q, *J* 9.8, H-7' major), 1.79 (0.59H, H_A of AB_q, *J* 9.8, H-7 major), 1.88 (0.41H, H_a of AB_q, *J* 9.8, H-7' minor), 2.58 (0.41H, H_a of AB_q, *J* 9.8, H-7 minor), 3.22 (0.59H, bs, H-4 major), 3.28-3.59 (1.82H, contains $CH(CH_3)_2$ major and minor, H-1 minor and H-4 of minor), 3.64 (0.59H, bs, H-1 of major), 4.88 (0.59H, *J* 1.9, H-3 major), 5.61 (0.41H, *J* 3.8, H-3 minor), 6.15-6.23 (0.59 H, m, H-5 major), 6.35-6.42 (0.59H, m, H-6 major), 6.50-6.59 (0.41H, m, H-5 minor), 6.68-6.79 (0.41H, m, H-6 minor), 6.92-7.18 (2H, m, ArH major and minor), 7.34-7.68 (2H, m, ArH major and minor), 8.67 (0.59H, bs, NH major), 9.31 (0.59H, bs, NH minor).

The majority of ^{13}C signals for each diastereomer could be distinguished;

Major diastereomer **4t-*endo***: δ_C (75.5 MHz, $CDCl_3$) 12.9 [CH_3, $CH(CH_3)_2$], 20.3 [CH_3, $CH(CH_3)_2$], 45.2 (CH_2, C-7), 48.5 (CH, C-4), 50.4 (CH, C-1), 53.5 (CH, C-3), 59.1 [CH_3, $CH(CH_3)_2$], 71.3 (C, C-2), 115.9 (CH, d, $^2J_{CF}$ 22.80, aromatic CH, ArC-3), 133.5 (C, d, $^4J_{CF}$ 2.00, aromatic C, ArC-1), 135.2 (CH, C-5), 138.3 (CH, C-6) 165.4 (CO).

Minor diastereomer **4t-*exo***: δ_C (75.5 MHz, $CDCl_3$) 12.9 [CH_3, $CH(CH_3)_2$], 20.4 [CH_3, $CH(CH_3)_2$], 45.5 (CH_2, C-7), 48.2 (CH, C-4), 50.1 (CH, C-1), 54.3 (CH, C-3), 59.4 [CH_3, $CH(CH_3)_2$], 73.5 (C, C-2), 115.8 (CH, d, $^2J_{CF}$ 19.53, aromatic CH, ArC-3), 133.7 (C, d, $^4J_{CF}$ 2.87, aromatic C, ArC-1), 134.8 (CH, C-5), 139.1 (CH, C-5), 166.1 (CO).

Some of the aromatic signals for each diastereomer in the ^{13}C NMR spectrum were indistinguishable: 159.4 (C, d, $^{1}J_{CF}$ 244.20, quaternary aromatic C, ArC-4); MS *m/z*; 355 (M^+, 2%), 313 (5%), 277 (100%), 264 (90%); isotopic Cl pattern observed; 355, 357 (3:1 ^{35}Cl: ^{37}Cl).

Cu(II) Catalysed Cycloadditions

$CuCl_2$ Catalysed Cycloadditions at Room Temperature

$CuCl_2$ Catalysed cycloaddition of 3a with cyclopentadiene

Sulfoxide **3a** (100 mg, 0.31 mmol) was reacted with cyclopentadiene (266 mg, 4.03 mmol) in the presence of a catalytic amount of $CuCl_2$ (1% by weight *cf* the sulphoxide) in dichloromethane (1 mL) as outlined in Method A. Following chromatography of the reaction mixture on silica gel using ethyl acetate-hexane (20:80) as eluent, a mixture consisting of both adduct diastereomers was isolated (no detectable starting material) in a ratio **4a-***exo* : **4a-***endo* of 1 : 1.7. Spectroscopic characteristics were as previously reported.

$CuCl_2$ Catalysed cycloaddition of 3b with cyclopentadiene

Sulfoxide **3b** (50 mg, 0.19 mmol) was reacted with cyclopentadiene (2 additions of 106 mg, 1.60 mmol) in the presence of a catalytic amount of $CuCl_2$ (1% by weight *cf* the sulphoxide) in dichloromethane (1 mL) as outlined in Method B. Following chromatography of the reaction mixture on silica gel using ethyl acetate-hexane (20:80) as eluent, a mixture consisting of both adduct diastereomers was isolated (no detectable starting material) in a ratio of **4b-***exo* : **4b-***endo* of 1:1.4. No attempt was made to separate the adduct diastereomers. Spectroscopic characteristics were as previously reported.

$CuCl_2$ Catalysed cycloaddition of 3c with cyclopentadiene

Sulfoxide **3c** (50 mg, 0.16 mmol) was reacted with cyclopentadiene (0.10 mL, 1.30 mmol) in the presence of a catalytic amount of $CuCl_2$ (1% by weight *cf* the sulphoxide) in dichloromethane (1 mL) as outlined in Method A. Following chromatography of the reaction mixture on silica gel using ethyl acetate-hexane (20:80) as eluent, a mixture consisting of unreacted sulphoxide **3c** (50% conversion by NMR) and both adduct diastereomers in a ratio

of **4c-***exo* : **4c-***endo* of 1 : 1.3 was isolated. Spectroscopic characteristics were as previously reported.

$CuCl_2$ Catalysed cycloaddition of 3e with cyclopentadiene

Sulfoxide **3e** (50 mg, 0.18 mmol) was reacted with cyclopentadiene (0.10 mL, 1.30 mmol) in the presence of a catalytic amount of $CuCl_2$ (1% by weight *cf* the sulphoxide) in dichloromethane (1 mL) as outlined in Method A. Following chromatography of the reaction mixture on silica gel using ethyl acetate-hexane (gradient elution: 0-20% ethyl acetate) as eluent, a mixture consisting of unreacted sulphoxide **3e** (63% conversion by NMR) and both adduct diastereomers in a ratio of **4e-***exo* : **4e-***endo* of 1:1.4 was isolated. Spectroscopic characteristics were as previously reported.

$CuCl_2$ Catalysed cycloaddition of 3f with cyclopentadiene

Sulfoxide **3f** (50 mg, 0.18 mmol) was reacted with cyclopentadiene (0.10 mL, 1.30 mmol) in the presence of a catalytic amount of $CuCl_2$ (1% by weight *cf* the sulphoxide) in dichloromethane (1 mL) as outlined in Method A. Following chromatography of the reaction mixture on silica gel using ethyl acetate-hexane (gradient elution: 0-20% ethyl acetate) as eluent, a mixture consisting of unreacted sulphoxide **3f** (55% conversion by NMR) and both adduct diastereomers in a ratio **4f-***exo* : **4f-***endo* of 1:1.5 was isolated. Spectroscopic characteristics were as previously reported.

$CuCl_2$ Catalysed cycloaddition of 3g with cyclopentadiene

Sulfoxide **3g** (50 mg, 0.18 mmol) was reacted with cyclopentadiene (2 additions of 0.10 m1, 1.30 mmol) in the presence of a catalytic amount of $CuCl_2$ (1% by weight *cf* the sulphoxide) in dichloromethane (1 mL) as outlined in Method B. Following chromatography of the reaction mixture on silica gel using ethyl acetate-hexane (gradient elution: 20-50% ethyl acetate) as eluent, a mixture consisting of both adduct diastereomers was isolated (no detectable starting material) in a ratio of **4g-***exo* : **4g-***endo* of 1:2.3. Spectroscopic characteristics were as previously reported.

$CuCl_2$ Catalysed cycloaddition of 3s with cyclopentadiene

Sulfoxide **3s** (50 mg, 0.19 mmol) was reacted with cyclopentadiene (0.10 mL, 1.36 mmol) in the presence of a catalytic amount of $CuCl_2$ (1% by weight *cf* the sulfoxide) in dichloromethane (1 mL) at room temperature. Following chromatography of the reaction

mixture on silica gel using ethyl acetate-hexane (gradient elution: 0-30%) as eluent, a mixture consisting of both adduct diastereomers was isolated (no detectable starting material) in a ratio **4s-***endo*: **4s-***exo* of 1:1. Spectroscopic characteristics were as reported above.

$CuCl_2$ Catalysed Cycloadditions at Reflux

$CuCl_2$ Catalysed cycloaddition of 3b with cyclopentadiene

Sulfoxide **3b** (50 mg, 0.19 mmol) was reacted with cyclopentadiene (0.10 mL, 1.36 mmol) in the presence of a catalytic amount of $CuCl_2$ (1% by weight *cf* the sulfoxide) in dichloromethane (1 mL) as described for **3a.** Following chromatography of the reaction mixture on silica gel using ethyl acetate-hexane (20:80) as eluent, a mixture consisting of both adduct diastereomers was isolated (no detectable starting material) in a ratio **4b-***endo*: **4b-***exo* of 2.1:1. Spectroscopic characteristics were as reported above.

$CuCl_2$ Catalysed cycloaddition of 3d with cyclopentadiene

Sulfoxide **3d** (50 mg, 0.18 mmol) was reacted with cyclopentadiene (0.10 mL, 1.36 mmol) in the presence of a catalytic amount of $CuCl_2$ (1% by weight *cf* the sulfoxide) in dichloromethane (1 mL) as described for **3a.** Following chromatography of the reaction mixture on silica gel using ethyl acetate-hexane (gradient elution: 0-30%) as eluent, a mixture consisting of both adduct diastereomers was isolated (no detectable starting material) in a ratio **4d-***endo*: **4d-***exo* of 2.0:1. Spectroscopic characteristics were as reported above.

$CuCl_2$ Catalysed cycloaddition of 3g with cyclopentadiene

Sulfoxide **3g** (50 mg, 0.2 mmol) was reacted with cyclopentadiene (0.12 mL, 1.52 mmol) in the presence of a catalytic amount of $CuCl_2$ (1% by weight *cf* the sulfoxide) in dichloromethane (1 mL) as described for **3a.** Following chromatography of the reaction mixture on silica gel using ethyl acetate-hexane (gradient elution: 0-30%) as eluent, a mixture

consisting of both adduct diastereomers was isolated (no detectable starting material) in a ratio **4g-***endo*: **4g-***exo* of 2.4:1. Spectroscopic characteristics were as reported above.

$CuCl_2$ Catalysed cycloaddition of 3s with cyclopentadiene

Sulfoxide **3s** (50 mg, 0.19 mmol) was reacted with cyclopentadiene (0.10 mL, 1.36 mmol) in the presence of a catalytic amount of $CuCl_2$ (1% by weight *cf* the sulfoxide) in dichloromethane (1 mL) as described for **3a**. Following chromatography of the reaction mixture on silica gel using ethyl acetate-hexane (gradient elution: 0-30%) as eluent, a mixture consisting of both adduct diastereomers was isolated (no detectable starting material) in a ratio **4s-***endo*: **4s-***exo* of 1:1. Spectroscopic characteristics were as reported earlier.

$Cu(OTf)_2$ Catalysed Cycloadditions at Room Temperature

$Cu(OTf)_2$ Catalysed cycloaddition of 3b with cyclopentadiene

Sulfoxide **3b** (50 mg, 0.19 mmol) was reacted with cyclopentadiene (0.10 mL, 1.36 mmol) in the presence of a catalytic amount of $Cu(OTf)_2$ (1% by weight *cf* the sulfoxide) in dichloromethane (1 mL) as described for **3a.** After stirring for 2 hours the reaction mixture was black in colour. A ^{1}H NMR spectrum was recorded at this time, which showed the formation of both adduct diastereomers in a ratio **4b-***endo*: **4b-***exo* of 5.5:1. Spectroscopic characteristics were as reported above.

$Cu(OTf)_2$ Catalysed cycloaddition of 3d with cyclopentadiene

Sulfoxide **3d** (50 mg, 0.18 mmol) was reacted with cyclopentadiene (0.10 mL, 1.36 mmol) in the presence of a catalytic amount of $Cu(OTf)_2$ (1% by weight *cf* the sulfoxide) in dichloromethane (1 mL) as described for **3a.** Following chromatography of the reaction mixture on silica gel using ethyl acetate-hexane (gradient elution: 0-30%) as eluent, a mixture consisting of both adduct diastereomers was isolated in a ratio **4d-***endo*: **4d-***exo* of 5.4:1. Spectroscopic characteristics were as reported above.

$Cu(OTf)_2$ Catalysed cycloaddition of 3g with cyclopentadiene

Sulfoxide **3g** (50 mg, 0.2 mmol) was reacted with cyclopentadiene (0.12 mL, 1.52 mmol) in the presence of a catalytic amount of $Cu(OTf)_2$ (1% by weight *cf* the sulfoxide) in dichloromethane (1 mL) as described for **3a.** Following chromatography of the reaction mixture on silica gel using ethyl acetate-hexane (gradient elution: 0-30%) as eluent, a mixture consisting of both adduct diastereomers was isolated (no detectable starting material) in a ratio **4g-***endo*: **4g-***exo* of 2.4:1 Spectroscopic characteristics were as reported above.

$Cu(OTf)_2$ Catalysed cycloaddition of 3s with cyclopentadiene

Sulfoxide **3s** (50 mg, 0.19 mmol) was reacted with cyclopentadiene (0.10 ml, 1.36 mmol) in the presence of a catalytic amount of $Cu(OTf)_2$ (1% by weight *cf* the sulfoxide) in dichloromethane (1 mL) at room temperature as described for **3a.** Following chromatography of the reaction mixture on silica gel using ethyl acetate-hexane (gradient elution: 0-30%) as eluent, a mixture consisting of both adduct diastereomers was isolated (no detectable starting material) in a ratio **4s-***endo*: **4s-***exo* of 1:1. Spectroscopic characteristics were as reported above.

$Cu(OTf)_2$ Catalysed Cycloadditions at Reflux

$Cu(OTf)_2$ Catalysed cycloaddition of 3a with cyclopentadiene

Sulfoxide **3a** (50 mg, 0.18 mmol) was reacted with cyclopentadiene (172 mg, 2.61 mmol) in the presence of a catalytic amount of $Cu(OTf)_2$ (1% by weight *cf* the sulphoxide) in dichloromethane (1.5 mL) as described for **3c**. The reaction solution was refluxed overnight with the blue colour forming within 10 minutes at reflux. Following chromatography of the reaction mixture on silica gel using ethyl acetate-hexane (20:80) as eluent, a mixture consisting of both adduct diastereomers was isolated (no detectable starting material) in a ratio of **4a-***exo* : **4a-***endo* of 1:4.2. Spectroscopic characteristics were as previously reported.

This reaction was also conducted at room temperature for 2 days. NMR analysis of the product showed no sulfoxide remaining and an adduct ratio of **4a-***exo* : **4a-***endo* of 1:1.8.

When the reaction was conducted at reflux for 3 hours, a trace (<5%) of the sulfoxide was seen by NMR analysis, with an adduct ratio of **4a-***exo* : **4a-***endo* of 1:2.5.

$Cu(OTf)_2$ Catalysed cycloaddition of 3b with cyclopentadiene

Sulfoxide **3b** (200 mg, 0.78 mmol) was reacted with cyclopentadiene (257 mg, 3.90 mmol) in the presence of a catalytic amount of $Cu(OTf)_2$ (1% by weight *cf* the sulphoxide) in dichoromethane (4 mL) as described for **3c**. The reaction solution was refluxed for 1 hour. Following chromatography of the reaction mixture on silica gel using ethyl acetate-hexane (gradient elution: 20-50% ethyl acetate) as eluent, a mixture consisting of both adduct diastereomers was isolated (no detectable starting material) in a ratio of **4b-***exo* : **4b-***endo* of 1 : 5.2. Spectroscopic characteristics were as previously reported.

This reaction was also carried out (0.2mmol of **3b**) allowing the reaction solution to reflux for 16 hours. Following chromatography, the adduct diastereomers were isolated in a ratio of **4b-***exo* : **4b-***endo* of 1:5.2.

$Cu(OTf)_2$ Catalysed cycloaddition of 3d with cyclopentadiene

Sulfoxide **3d** (50 mg, 0.18 mmol) was reacted with cyclopentadiene (172 mg, 2.61 mmol) in the presence of a catalytic amount of $Cu(OTf)_2$ (1% by weight *cf* the sulphoxide) in dichloromethane (1.5 mL) as described for **3c**. The reaction solution was refluxed for 2 hours. Following chromatography of the reaction mixture on silica gel using ethyl acetate-hexane (gradient elution: 10-30% ethyl acetate) as eluent, a mixture consisting of both adduct diastereomers was isolated (no detectable starting material) in a ratio of **4d-***exo* : **4d-***endo* of 1 : 5.3. Spectroscopic characteristics were as previously reported.

$Cu(OTf)_2$ Catalysed cycloaddition of 3e with cyclopentadiene

Sulfoxide **3e** (50 mg, 0.18 mmol) was reacted with cyclopentadiene (172 mg, 2.61 mmol) in the presence of a catalytic amount of $Cu(OTf)_2$ (1% by weight *cf* the sulphoxide) in dichloromethane (1 mL) as described for **3c**. The reaction solution was refluxed for 2 hours, with the blue colour developing within 5 minutes at reflux. Following chromatography of the reaction mixture on silica gel using ethyl acetate-hexane (gradient elution: 10-30% ethyl acetate) as eluent, a mixture consisting of both adduct diastereomers was isolated (no detectable starting material) in a ratio of **4e-***exo* : **4e-***endo* of 1 : 4.8. Spectroscopic characteristics were as previously reported.

$Cu(OTf)_2$ Catalysed cycloaddition of 3f with cyclopentadiene

Sulfoxide **3f** (50 mg, 0.18 mmol) was reacted with cyclopentadiene (172 mg, 2.61 mmol) in the presence of a catalytic amount of $Cu(OTf)_2$ (1% by weight *cf* the sulphoxide) in dichloromethane (1 mL) as described for **3c**. The reaction solution was refluxed for 2 hours. Following chromatography of the reaction mixture on silica gel using ethyl acetate-hexane (gradient elution: 10-30% ethyl acetate) as eluent, a mixture consisting of both adduct diastereomers was isolated (no detectable starting material) in a ratio of **4e-***exo* : **4e-***endo* of 1 : 4.5. Spectroscopic characteristics were as previously reported.

$Cu(OTf)_2$ Catalysed cycloaddition of 3i with cyclopentadiene

Sulfoxide **3i** (60 mg, 0.18 mmol) was reacted with cyclopentadiene (60 mg, 0.90 mmol) in the presence of a catalytic amount of $Cu(OTf)_2$ (1% by weight *cf* the sulfoxide) in dichloromethane (1 ml) as described for **3c**. The reaction solution was refluxed for 2 hours. Following chromatography of the reaction mixture on silica gel using ethyl acetate-hexane (30:70) as eluent, a mixture consisting of both adduct diastereomers was isolated (no detectable starting material) in a ratio of **4i-***exo* : **4i-***endo* of 1 : 3.5. Spectroscopic characteristics were as previously reported.

$Cu(OTf)_2$ Catalysed cycloaddition of 3j with cyclopentadiene

Sulfoxide **3j** (60 mg, 0.18 mmol) was reacted with cyclopentadiene (60 mg, 0.90 mmol) in the presence of a catalytic amount of $Cu(OTf)_2$ (1% by weight *cf* the sulfoxide) in dichloromethane (1 mL) as described for **3c**. The reaction solution was refluxed for 2 hours. Following chromatography of the reaction mixture on silica gel using ethyl acetate-hexane (30:70) as eluent, a mixture consisting of both adduct diastereomers was isolated (no detectable starting material) in a ratio of **4j-***exo* : **4j-***endo* of 1 : 5.7. Spectroscopic characteristics were as previously reported.

$Cu(OTf)_2$ Catalysed cycloaddition of 3k with cyclopentadiene

Sulfoxide **3k** (40 mg, 0.14 mmol) was reacted with cyclopentadiene (46 mg, 0.70 mmol) in the presence of a catalytic amount of $Cu^{II}(OTf)_2$ (1% by weight *cf* the sulfoxide) in dichloromethane (1 mL) as described for **3c**. The reaction solution was refluxed for 1 hour. Following chromatography of the reaction mixture on silica gel using ethyl acetate-hexane (40:60) as eluent, a mixture consisting of both adduct diastereomers was isolated (no detectable starting material) in a ratio of **4k-***exo* : **4k-***endo* of 1 : 5.2. Spectroscopic characteristics were as previously reported.

$Cu(OTf)_2$ Catalysed cycloaddition of 3s with cyclopentadiene

Sulfoxide **3s** (50 mg, 0.19 mmol) was reacted with cyclopentadiene (0.10 ml, 1.36 mmol) in the presence of a catalytic amount of $Cu^{II}(OTf)_2$ (1% by weight *cf* the sulfoxide) in dichloromethane (1 mL) at reflux**.** Following chromatography of the reaction mixture on silica gel using ethyl acetate-hexane (gradient elution: 0-30%) as eluent, a mixture consisting of both adduct diastereomers was isolated (no detectable starting material) in a ratio **4s-***endo*: **4s-***exo* of 1:1. Spectroscopic characteristics were as reported above.

Synthesis of Sulfide Adducts

2-*exo*-Phenylthio-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid ethylamide 6b-*endo* and 2-*endo*-Phenylthio-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid ethylamide 6b-*exo*

The title compound was prepared from **5b** (750 mg, 3.11 mmol), $CuCl_2$ (628 mg, 4.67 mmol) and freshly distilled cyclopentadiene (2 mL) in dichloromethane (15 mL) as described for **6a**. Freshly distilled cyclopentadiene (1 mL lots) were added every 48 hours for 10 days to give the crude product mixture (27% conversion, diastereomeric ratio of **6b-***endo* : **6b-***exo* of 1.3 : 1) which was isolated by chromatography on silica gel of the reaction mixture. The crude product was treated with morpholine (488 mg, 5.7 mmol) as described for **6a** and, after chromatography on silica gel using ethyl acetate-hexane (gradient elution 10-30% ethyl acetate) as eluent, the adduct was isolated as separable diastereomers:

Major Diastereomer **6b-*endo*** as a colourless solid (160 mg, 17%): mp 99-101 °C; Found C, 62.21; H, 5.93; N, 4.52; Cl, 11.61; S, 10.29. $C_{16}H_{18}NClOS$ requires C, 62.43; H, 5.89; N, 4.55; Cl, 11.52; S, 10.42; ν_{max}/cm^{-1} (KBr) 1652 (CO), 1536, 1438, 1285; δ_H (270 MHz, $CDCl_3$) 0.94 (3H, t, *J* 7, CH_2CH_3), 1.78-1.84 (1H, dd, H_A of ABq, *J* 9, 2, H-7'), 2.51-2.57 (1H, H_B of ABq, *J* 9, H-7), 3.01 (1H, b s, H-4), 3.07-3.20 (3H, m, H-1, NCH_2), 4.65 (1H, d, *J* 2, H-3), 5.90 (1H, b s, NH), 6.10-6.20 (2H, symmetrical m, H-5, H-6), 7.22-7.34 (3H, m, ArH), 7.36-7.48 (2H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 14.5 (CH_2CH_3), 34.8 (NCH_2), 46.3 (C-7), 52.5 (C-1 or C-4), 53.5 (C-1 or C-4), 64.8 (C-3), 65.9 (C-2), 128.2 (aromatic CH), 128.9 (aromatic CH), 133.1 (aromatic CH), 133.3 (aromatic C), 135.8 (C-5), 137.5 (C-6), 171.0 (CO); MS *m/z* 307 (M^+, 12%), 272 (100, M^+-Cl), 198 (61, M^+-SPh), 162 (25, M^+-SPh-Cl), 109 (80, $[SPh]^+$), 91 (86), 65 (90); isotopic Cl pattern observed; 307, 309 (3:1 ratio ^{35}Cl:^{37}Cl); Found (HRMS, EI) *m/z* 307.0797. $C_{16}H_{18}N^{35}ClOS$ requires 307.0798.

Minor Diastereomer **6b-*exo*** as a colourless solid (90 mg, 9%): mp 97-99 °C; Found C, 62.12; H, 6.00; N, 4.36; Cl, 11.56; S, 10.89. $C_{16}H_{18}NClOS$ requires C, 62.43; H, 5.89; N, 4.55; Cl, 11.52; S, 10.42; ν_{max}/cm^{-1} (KBr) 1639 (CO), 1534, 1438, 1281, 1067, 746, 690; δ_H (270 MHz, $CDCl_3$) 0.90 (3H, t, *J* 7, CH_2CH_3), 1.64-1.81 (2H, ABq, *J* 10, CH_2-7), 3.08-3.31 (4H, m, NCH_2, H-1, H-4), 5.29 (1H, d, *J* 4, H-3), 6.39-6.45 (1H, m, H-5 or H-6), 6.46-6.51 (1H, m, H-5 or H-6), 6.57 (1H, b s, NH), 7.20-7.35 (5H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 14.4

(CH_2CH_3), 35.2 (NCH_2), 45.9 (C-7), 50.0 (C-1 or C-4), 53.1 (C-1 or C-4), 65.5 (C-3), 67.1 (C-2), 127.3 (aromatic CH), 128.9 (aromatic CH), 131.0 (aromatic CH), 133.8 (aromatic C), 136.6 (C-5 or C-6), 136.7 (C-5 or C-6), 171.8 (CO); MS *m/z* 307 (M^+, 5%), 272 (35, M^+-Cl), 198 (17, M^+-SPh), 162 (17, M^+-SPh-Cl), 134 (50), 109 (98, $[SPh]^+$), 91 (100), 65 (97); isotopic Cl pattern observed; 307, 309 (3:1 ratio ^{35}Cl:^{37}Cl).

2-*exo*-Phenylthio-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid benzyl-amide 6c-*endo* and 2-*endo*-Phenylthio-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid benzylamide 6c-*exo*

The title compound was prepared from **5c** (500 mg, 1.65 mmol), $CuCl_2$ (332 mg, 2.48 mmol) and freshly distilled cyclopentadiene (1.5 mL) in dichloromethane (10 mL) as described for **6a**. Freshly distilled cyclopentadiene (0.5 mL lots) were added every 48 hours for 10 days to give the crude product mixture (43% conversion, diastereomeric ratio of **6c-***endo* : **6c-***exo* of 1.7 : 1) which was isolated by chromatography on silica gel of the reaction mixture. The crude product was treated with morpholine (213 mg, 2.47 mmol) as described for **6a** and, after chromatography on silica gel using ethyl acetate-hexane (20:80) as eluent the adduct was isolated (238 mg, 39%, ratio of **6c-***endo* : **6c-***exo* of 1.5:1) as a colourless solid. The adduct diastereomers were inseparable by chromatography; mp 82-86 °C; Found C, 68.21; H, 5.29; N, 3.78; Cl, 9.96; S, 8.46. $C_{21}H_{20}NClOS$ requires C, 68.19; H, 5.45; N, 3.79; Cl, 9.58; S, 8.67; ν_{max}/cm^{-1} (KBr) 1654 (CO), 1514, 1264, 758, 696; Not all of the ^1H NMR signals for the two diastereomers could be distinguished, hence the ^1H NMR spectrum has been assigned as a mixture: δ_H (270 MHz, $CDCl_3$) 1.60-1.84 (1.41H, m, H-7a', both of CH_2-7b), 2.51-2.56 (0.59H, H_B of ABq, *J* 10, H-7a), 3.00 (0.59H, b s, H-4a), 3.10 (0.59H, b s, H-1a), 3.26-3.31 (0.82H, overlapping b s, H-1b, H-4b), 4.12-4.32 (2H, m, NCH_2), 4.69 (0.59H, d, *J* 2, H-3a), 5.32 (0.41H, d, *J* 4, H-3b), 6.09-6.22 (1.18H, symmetrical m, H-5a, H-6a), 6.25 (0.59H, b t, NH), 6.37-6.50 (0.82H, symmetrical m, H-5b, H-6b), 6.92 (0.41H, b t, NH), 6.97-7.10 (2H, m, ArH), 7.13-7.38 (8H, m, ArH); The signals for each diastereomer could be distinguished on the ^{13}C NMR spectrum:

Major Diastereomer **6c-***endo*: δ_C (67.8 MHz, $CDCl_3$) 44.2 (*C*H_2, NCH_2), 46.4 (*C*H_2, C-7), 52.5 (*C*H, C-4), 53.6 (*C*H, C-1), 64.7 (*C*H, C-3), 65.9 (*C*, C-2), 127.5 (*C*H, aromatic CH), 128.0 (*C*H, aromatic CH), 128.7 (*C*H, aromatic CH), 128.9 (*C*H, aromatic CH), 130.9 (*C*H, aromatic CH), 133.0 (*C*H, aromatic CH), 133.1 (*C*, aromatic C), 135.9 (*C*H, C-5), 137.5 (*C*H, C-6), 137.9 (*C*, aromatic C), 171.1 (*C*, CO).

Minor Diastereomer (amide *exo*) **6c-***exo*: δ_C (67.8 MHz, $CDCl_3$) 44.6 (*C*H_2, NCH_2), 45.9 (*C*H_2, C-7), 50.2 (*C*H, C-1 or C-4), 53.1 (*C*H, C-1 or C-4), 65.4 (*C*H, C-3), 67.0 (*C*, C-2), 127.3 (*C*H, aromatic CH), 127.8 (*C*H, aromatic CH), 128.7 (*C*H, aromatic CH), 128.9 (*C*H,

aromatic CH), 130.9 (*C*H, aromatic CH), 133.0 (*C*H, aromatic CH), 134.1 (*C*, aromatic C), 136.6 (*C*H, C-5 or C-6), 136.7 (*C*H, C-5 or C-6), 137.7 (*C*, aromatic C), 172.0 (*C*, CO).

MS *m/z* 369 (M^+, 2%), 334 (16, M^+-Cl), 260 (5, M^+-SPh), 158 (14), 109 (30, $[SPh]^+$), 91 (100); isotopic Cl pattern observed; 369, 371 (3:1 ratio ^{35}Cl:^{37}Cl).

2-*exo*-Phenylthio-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid isopropylamide 6d-*endo* and 2-*endo*-Phenylthio-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid isopropylamide 6d-*exo*

The title compound was prepared from **5d** (500 mg, 1.96 mmol), $CuCl_2$ (395 mg, 2.94 mmol) and freshly distilled cyclopentadiene (1.5 mL) in dichloromethane (10 mL) as described for **6a**. Freshly distilled cyclopentadiene (0.5 mL lots) were added every 48 hours for 10 days to give the crude product mixture (22% conversion, diastereomeric ratio of **6d-*endo*** : **6d-*exo*** of 1.5 : 1) which was isolated by chromatography on silica gel of the reaction mixture. The crude product was treated with morpholine (332 mg, 3.82 mmol) as described for **6a** and, after chromatography on silica gel using ethyl acetate-hexane (gradient elution 5-30% ethyl acetate) as eluent, the adduct was isolated as separable diastereomers:

Major Diastereomer **6d-*endo*** as an off-white solid (106 mg, 17%): (note: this compound also contained approx. 5% of the minor diastereomer) mp 118-120 °C; Found C, 63.28; H, 6.30; N, 4.20; Cl, 11.21; S, 9.64. $C_{17}H_{20}NClOS$ requires C, 63.44; H, 6.26; N, 4.35; Cl, 11.01; S, 9.96; ν_{max}/cm^{-1} (KBr) 1636 (CO), 1520, 755; δ_H (270 MHz, $CDCl_3$) 0.83 (3H, d, *J* 7, one of $CH(CH_3)_2$), 1.08 (3H, d, *J* 7, one of $CH(CH_3)_2$), 1.74-1.81 (1H, dd, H_A of ABq, *J* 2,10, H-7'), 2.47-2.53 (1H, H_B of ABq, *J* 10, H-7), 3.01 (1H. b s, H-4), 3.10 (1H, b s, H-1), 3.72-3.91 (1H, m, NCH), 4.73 (1H, d, *J* 2, H-3), 5.71-5.83 (1H, b d, NH), 6.09-6.16 (1H, m, H-5 or H-6), 6.19-6.24 (1H, m, H-5 or H-6), 7.20-7.31 (3H, m, ArH), 7.33-7.45 (2H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 22.2 (one of $CH(CH_3)_2$), 22.5 (one of $CH(CH_3)_2$), 41.9 (N*C*H), 46.5 (C-7), 53.1 (C-1 or C-4), 53.6 (C-1 or C-4), 64.6 (C-3), 65.8 (C-2), 127.8 (aromatic CH), 128.8 (aromatic CH), 132.4 (aromatic CH), 133.5 (aromatic C), 136.1 (C-5), 137.0 (C-6), 169.9 (CO); MS *m/z* 321 (M^+, 3%), 286 (39, M^+-Cl), 212 (28, M^+-SPh), 134 (40), 109 (100, $[SPh]^+$), 91 (52), 65 (87), 43 (98); isotopic Cl pattern observed; 321, 323 (3:1 ratio ^{35}Cl:^{37}Cl).

Minor Diastereomer **6d-*exo*** as an off-white solid (51 mg, 8%): mp 114-116 °C; Found C, 63.08; H, 6.05; N, 4.24; Cl, 11.26; S, 10.21. $C_{17}H_{20}NClOS$ requires C, 63.44; H, 6.26; N, 4.35; Cl, 11.01; S, 9.96; ν_{max}/cm^{-1} (KBr) 1638 (CO), 1519, 1027, 755; δ_H (270 MHz, $CDCl_3$) 0.79 (3H, d, *J* 7, one of $CH(CH_3)_2$), 1.07 (3H, d, *J* 7, one of $CH(CH_3)_2$), 1.60-1.81 (2H, ABq, *J* 10, CH_2-7), 3.21-3.29 (2H, overlapping b s, H-1, H-4), 3.78-3.95 (1H, m, NCH), 5.37 (1H, d, *J* 4, H-3), 6.31-6.49 (3H, m, H-5, H-6, NH), 7.12-7.38 (5H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 22.0 [one of $CH(CH_3)_2$], 22.5 [one of $CH(CH_3)_2$], 42.3 (NCH), 45.8 (C-7), 50.2 (C-1 or C-4), 53.6 (C-1 or C-4), 65.3 (C-3), 67.3 (C-2), 127.0 (aromatic CH), 128.8 (aromatic CH),

130.5 (aromatic CH), 134.1 (aromatic C), 136.3 (C-5 or C-6), 136.9 (C-5 or C-6), 170.8 (CO); MS *m/z* 321 (M^+, 8%), 286 (57, M^+-Cl), 212 (15, M^+-SPh), 199 (25, M^+-SPh-HCl), 134 (73), 91 (80), 43 (100); isotopic Cl pattern observed; 321, 323 (3:1 ratio ^{35}Cl:^{37}Cl).

2-*exo*-Phenylthio-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid *n*-butylamide 6e-*endo* and 2-*endo*-Phenylthio-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid *n*-butylamide 6e-*exo*

The title compound was prepared from **5e** (400 mg, 1.48 mmol), $CuCl_2$ (300 mg, 2.22 mmol) and freshly distilled cyclopentadiene (1.5 mL) in dichloromethane (8 mL) as described for **6a**. Freshly distilled cyclopentadiene (0.5 mL lots) were added every 48 hours for 10 days to give the crude product mixture (34% conversion, diastereomeric ratio of **6e-*endo*** : **6e-*exo*** of 1.9:1) which was isolated by chromatography on silica gel of the reaction mixture. The crude product was treated with morpholine (213 mg, 2.45 mmol) as described for **6a** and, after chromatography on silica gel using ethyl acetate-hexane (20:80) as eluent the adduct was isolated (124 mg, 25%, ratio of **6e-*endo*** : **6e-*exo*** of 2.0 : 1) as a yellow oil. The adduct diastereomers were inseparable by chromatography; Found C, 64.51; H, 6.67; N, 4.08; Cl, 10.90; S, 9.40. $C_{18}H_{22}NClOS$ requires C, 64.36; H, 6.60; N, 4.17; Cl, 10.55; S, 9.55; ν_{max}/cm^{-1} (film) 1648, 1523, 1439, 1252, 739, 687; Not all of the ^1H NMR signals for the two diastereomers could be distinguished, hence the ^1H NMR spectrum has been assigned as a mixture: δ_H (270 MHz, $CDCl_3$) 0.75-0.88 (3H, overlapping t, *J* 7, 7, CH_3-4'), 1.07-1.36 (4H, m, -CH_2CH_2-), 1.62-1.70 (0.33H, H_A of ABq, *J* 9, one of CH_2-7b), 1.74-1.84 (1H, m, H-7a', one of CH_2-7b), 2.47-2.55 (0.67H, H_B of ABq, *J* 9, H-7a), 2.97-3.30 (4H, m, NCH_2, H-1a, H-4a, H-1b, H-4b), 4.67 (0.67H, d, *J* 2, H-3a), 5.31 (0.33H, d, *J* 4, H-3b), 5.98 (0.67H, b t, NHa), 6.11-6.21 (1.34H, symmetrical m, H-5a, H-6a), 6.35-6.50 (0.66H, symmetrical m, H-5b, H-6b), 6.63 (0.33H, b t, NHb), 7.15-7.43 (5H, m, ArH); The signals for each diastereomer could be distinguished on the ^{13}C NMR spectrum:

Major diastereomer **6e-*endo***: δ_C (67.8 MHz, $CDCl_3$) 13.6 (CH_3-4'), 20.0 (CH_2-3'), 31.3 (CH_2-2'), 39.7 (NCH_2), 46.3 (C-7), 52.6 (C-1 or C-4), 53.5 (C-1 or C-4), 64.7 (C-3), 65.9 (C-2), 128.0 (aromatic CH), 129.1 (aromatic CH), 132.7 (aromatic CH), 133.4 (aromatic C), 135.8 (C-5), 137.3 (C-6), 171.0 (CO).

Minor diastereomer **6e-*exo***: δ_C (67.8 MHz, $CDCl_3$) 13.6 (CH_3-4'), 20.0 (CH_2-3'), 31.3 (CH_2-2'), 40.0 (NCH_2), 45.8 (C-7), 50.2 (C-1 or C-4), 53.1 (C-1 or C-4), 65.4 (C-3), 67.1 (C-2), 127.1 (aromatic CH), 129.1 (aromatic CH), 130.6 (aromatic CH), 133.9 (aromatic C), 136.5 (C-5 or C-6), 136.6 (C-5 or C-6), 171.9 (CO).

MS *m/z* 335 (M^+, 2%), 300 (37, M^+-Cl), 226 (21, M^+-SPh), 134 (36), 109 (100, $[SPh]^+$), 91 (50), 39 (88); isotopic Cl pattern observed; 335, 337 (3:1 ratio ^{35}Cl:^{37}Cl).

2-*exo*-Phenylthio-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid allylamide 6f-*endo* and 2-*endo*-Phenylthio-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid allylamide 6f-*exo*

The title compound was prepared from **5e** (400 mg, 1.58 mmol), $Cu^{II}Cl_2$ (320 mg, 2.37 mmol) and freshly distilled cyclopentadiene (1.5 mL) in dichloromethane (8 mL) as described for **6a**. Freshly distilled cyclopentadiene (0.5 mL lots) were added every 48 hours for 10 days to give the crude product mixture (46% conversion, diastereomeric ratio of **6f-*endo*** : **6f-*exo*** of 2.0 : 1) which was isolated by chromatography on silica gel of the reaction mixture. The crude product was treated with morpholine (190 mg, 2.18 mmol) as described for **6a** and, after chromatography on silica gel using ethyl acetate-hexane (gradient elution 5-30% ethyl acetate) as eluent the adduct **6f** was isolated (154 mg, 31%, ratio of **6f-*endo*** : **6f-*exo*** of 1.8 : 1) as a yellow oil. The adduct diastereomers were inseparable by chromatography; Found C, 63.84; H, 5.70; N, 4.28; Cl, 11.08; S, 10.03. $C_{17}H_{18}NClOS$ requires C, 63.84; H, 5.67; N, 4.38; Cl, 11.08; S, 10.02; ν_{max}/cm^{-1} (film) 1654, 1525, 1416, 1282, 741, 690; The NMR signals for each diastereomer could be distinguished:

Major diastereomer **6f-*endo***: δ_H (270 MHz, $CDCl_3$) 1.77-1.87 (1H, H_A of ABq, *J* 9, H-7'), 2.51-2.57 (1H, H_B of ABq, *J* 9, H-7), 3.02 (1H, b s, H-4), 3.09 (1H, b s, H-1), 3.61-3.82 (2H, m, NCH_2), 4.63 (1H, d, *J* 2, H-3), 4.98-5.12 (2H, m, $=CH_2$), 5.50-5.70 (1H, m, CH=), 6.07 (1H, b s, NH), 6.15-6.24 (2H, m, H-5, H-6), 7.20-7.43 (5H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 42.4 (*C*H_2, NCH_2), 46.3 (*C*H_2, C-7), 52.3 (*C*H, C-1 or C-4), 53.5 (*C*H, C-1 or C-4), 64.9 (*C*H, C-3), 66.0 (*C*, C-2), 116.8 (*C*H_2, $=CH_2$), 128.3 (*C*H, aromatic CH), 128.9 (*C*H, aromatic CH), 133.1 (*C*H, aromatic CH), 133.3 (*C*, aromatic C), 133.9 (*C*H, CH=), 135.8 (*C*H, C-5), 137.6 (*C*H, C-6), 171.0 (*C*, CO).

Minor diastereomer **6f-*exo***: δ_H (270 MHz, $CDCl_3$) 1.67-1.76 (1H, H_A of ABq, *J* 9, one of CH_2-7), 1.77-1.87 (1H, H_B of ABq, *J* 9, one of CH_2-7), 3.24-3.32 (2H, overlapping b s, H-1, H-4), 3.61-3.82 (2H, m, NCH_2), 4.98-5.12 (2H, m, $=CH_2$), 5.27 (1H, d, *J* 4, H-3), 5.50-5.70 (1H, m, CH=), 6.37-6.50 (2H, symmetrical m, H-5, H-6), 6.70 (1H, b s, NH), 7.20-7.43 (5H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 42.7 (*C*H_2, NCH_2), 45.9 (*C*H_2, C-7), 50.2 (*C*H, C-1 or C-4), 52.8 (*C*H, C-1 or C-4), 65.6 (*C*H, C-3), 67.1 (*C*, C-2), 116.8 (*C*H_2, $=CH_2$), 127.4 (*C*H, aromatic CH), 128.9 (*C*H, aromatic CH), 131.2 (*C*H, aromatic CH), 133.6 (*C*, aromatic C), 133.9 (*C*H, CH=), 136.6 (*C*H, C-5 or C-6), 136.6 (*C*H, C-5 or C-6), 172.0 (*C*, CO).

MS *m/z* 319 (M^+, 3%), 284 (26, M^+-Cl), 210 (13, M^+-SPh), 134 (20), 109 (63, $[SPh]^+$), 91 (40), 41 (100); isotopic Cl pattern observed; 319, 321 (3:1 ratio ^{35}Cl:^{37}Cl); Found (HRMS, EI) *m/z* 319.0785. $C_{17}H_{18}N^{35}ClOS$ requires 319.0798.

2-*exo*-(4-Nitrobenzenethio)-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid *p*-tolylamide 6g-*endo* and 2-*endo*-(4-Nitrobenzenethio)-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid *p*-tolylamide 6g-*exo*

The title compound was prepared from **5g** (600 mg, 1.72 mmol), $Cu^{II}Cl_2$ (347 mg, 2.22 mmol) and freshly distilled cyclopentadiene (2 mL) in dichloromethane (12 mL) as described for **6a**. Freshly distilled cyclopentadiene (1 mL lots) were added every 48 hours for 10 days to give the crude product mixture (% conversion could not be determined due to β-H being obscured by aromatic protons, diastereomeric ratio of **6g-*endo*** : **6g-*exo*** of 2.7 : 1) which was isolated by chromatography on silica gel of the reaction mixture. The crude product was treated with an excess of morpholine (300 mg, 3.45 mmol) as described for **6a** and, after chromatography on silica gel using ethyl acetate-hexane (gradient elution 10-40% ethyl acetate) as eluent the adduct **337** was isolated (386 mg, 54%, ratio of **6g-*endo*** : **6g-*exo*** of 2.3 : 1) as a yellow solid. The adduct diastereomers were inseparable by chromatography; mp 66-68 °C; Found C, 60.59; H, 4.77; N, 6.50; Cl, 8.17; S, 7.44. $C_{21}H_{19}N_2ClO_3S$ requires C, 60.79; H, 4.62; N, 6.75; Cl, 8.54; S, 7.73; ν_{max}/cm^{-1} (KBr) 1676 (CO), 1586, 1578, 1517 (vs), 1338 (vs), 853; The NMR signals for each diastereomer could be distinguished:

Major diastereomer **6g-*endo***: δ_H (270 MHz, $CDCl_3$) 1.86-1.92 (1H, H_A of ABq, *J* 10, H-7'), 2.29 (3H, s, Ar CH_3), 2.45-2.51 (1H, H_B of ABq, *J* 10, H-7), 3.18-3.21 (2H, overlapping b s, H-1, H-4), 4.98 (1H, d, *J* 2, H-3), 6.19-6.26 (1H, m, H-5 or H-6), 6.32-6.39 (1H, m, H-5 or H-6), 7.02-7.21 (4H, m, ArH), 7.42-7.51 (2H, m, ArH), 8.00-8.11 (3H, m, ArH, NH); δ_C (67.8 MHz, $CDCl_3$) 20.8 (*C*H_3, Ar *C*H_3), 46.9 (*C*H_2, C-7), 53.9 (*C*H, C-1 or C-4), 54.1 (*C*H, C-1 or C-4), 63.3 (*C*H, C-3), 67.2 (*C*, C-2), 120.4 (*C*H, aromatic CH), 123.9 (*C*H, aromatic CH), 129.7 (*C*H, aromatic CH), 130.3 (*C*H, aromatic CH), 134.6 (*C*, aromatic C), 134.8 (*C*, aromatic C), 136.1 (*C*H, C-5), 137.2 (*C*H, C-6), 143.3 (*C*, aromatic C), 146.7 (*C*, aromatic C), 168.3 (*C*, CO).

Minor diastereomer **6g-*exo***: δ_H (270 MHz, $CDCl_3$) 1.70-1.77 (1H, H_A of ABq, *J* 10, one of CH_2-7), 1.85-1.93 (1H, H_B of ABq, *J* 10, one of CH_2-7), 2.29 (3H, s, Ar CH_3), 3.37 (1H, b s, H-1 or H-4), 3.44 (1H, b s, H-1 or H-4), 5.64 (1H, d, *J* 4, H-3), 6.45-6.51 (2H, m, H-5, H-6), 7.02-7.21 (4H, m, ArH), 7.35-7.43 (2H, m, ArH), 8.00-8.11 (2H, m, ArH), 8.39 (1H, b s, NH); δ_C (67.8 MHz, $CDCl_3$) 20.8 (*C*H_3, Ar *C*H_3), 45.9 (*C*H_2, C-7), 50.5 (*C*H, C-1 or C-4), 64.1 (*C*H, C-3), 68.6 (*C*, C-2), 120.4 (*C*H, aromatic CH), 123.9 (*C*H, aromatic CH), 129.1 (*C*H, aromatic CH), 129.7 (*C*H, aromatic CH), 134.6 (*C*, aromatic C), 134.8 (*C*, aromatic C), 135.5 (*C*H, C-5 or C-6), 137.9 (*C*H, C-5 or C-6), 143.8 (*C*, aromatic C), 146.4 (*C*, aromatic C), 169.2 (*C*, CO). *Note*: one CH observed for 2 carbons (C-1 and C-4) with the second peak under the signals at 53.93-54.07.

MS *m/z* 414 (M^+, 11), 379 (93, M^+-Cl), 260 (37, M^+-SAr), 224 (36, M^+-SAr-HCl), 91 (100); isotopic Cl pattern observed; 414, 416 (3:1 ratio ^{35}Cl:^{37}Cl); Found (HRMS, EI) *m/z* 414.0802; $C_{21}H_{19}N_2{}^{35}ClO_3S$ requires 414.0805.

2-*exo*-(*n*-Butanethio)-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid *p*-tolylamide 6h-*endo* and 2-*endo*-(*n*-Butanethio)-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid *p*-tolylamide 6h-*exo*

The title compound was prepared from **5h** (500 mg, 1.76 mmol), $Cu^{II}Cl_2$ (356 mg, 2.65 mmol) and freshly distilled cyclopentadiene (2 mL) in dichloromethane (10 mL) as described for **6a**. Freshly distilled cyclopentadiene (1 mL lots) were added every 48 hours for 10 days to give the crude product mixture (% conversion and crude ratio could not be determined due to broadening of NMR signals) which was isolated by chromatography on silica gel of the reaction mixture. The crude product was treated with morpholine (200 mg, 2.30 mmol) as described for **6a** and, after chromatography on silica gel using ethyl acetate-hexane (gradient elution 5-20% ethyl acetate) as eluent the adduct **6h** was isolated (200 mg, 33%, ratio of **6h-*endo*** : **6h-*exo*** of 4.0 : 1) as a yellow oil. The adduct diastereomers were inseparable by chromatography; Found C, 65.34; H, 6.75. $C_{19}H_{24}NClOS$ requires C, 65.22; H, 6.91; ν_{max}/cm^{-1} (film) 1675 (CO, m, b), 1519 (v s), 1314; Not all of the ^1H NMR signals for the two diastereomers could be distinguished, hence the ^1H NMR spectrum has been assigned as a mixture: δ_H (270 MHz, $CDCl_3$) 0.79-0.90 (3H, overlapping t, *J* 7, 7, -CH_3-4'), 1.21-1.80 (5.2H, m, $(CH_2)_2$, CH_2-7b, H-7a'), 2.31 (3H, s, Ar-CH_3), 2.38-2.78 (2.8H, m, SCH_2, H-7a), 3.03 (1.6H, overlapping b s, H-1a, H-4a), 3.23 (0.2H, b s, one of H-1b or H-4b), 3.34 (0.2H, b s, one of H-1b or H-4b), 4.71 (0.8H, d, *J* 2, H-3a), 5.25 (0.2H, d, *J* 4, H-3b), 6.16-6.28 (1.6H, symmetrical m, H-5a, H-6a), 6.31-6.42 (0.4H, symmetrical m, H-5b, H-6b), 7.08-7.18 (2H, m, ArH), 7.30-7.41 (2H, m, ArH), 8.06 (0.8H, b s, NH), 8.58 (0.2H, b s, NH); The signals for each diastereomer could be distinguished on the ^{13}C NMR:

Major Diastereomer **6h-*endo***: δ_C (67.8 MHz, $CDCl_3$) 13.5 (*C*H_3, CH_3-4'), 20.8(*C*H_3, Ar-CH_3), 22.0 (*C*H_2, CH_2-3'), 30.8 (*C*H_2, CH_2-2'), 31.5 (*C*H_2, SCH_2), 46.7 (*C*H_2, C-7), 53.5 (*C*H, C-1 or C-4), 54.0 (*C*H, C-1 or C-4), 64.2 (*C*H, C-3), 64.9 (*C*, C-2), 119.9 (*C*H, aromatic CH), 129.5 (*C*H, aromatic CH), 134.1 (*C*, aromatic C), 134.1 (*C*, aromatic C), 136.0 (*C*H, C-5), 137.1 (*C*H, C-6), 169.7 (*C*, CO).

Minor Diastereomer **6h-*exo***: δ_C (67.8 MHz, $CDCl_3$) 13.5 (*C*H_3, CH_3-4'), 20.8 (*C*H_3, Ar-CH_3), 22.0 (*C*H_2, CH_2-3'), 30.5 (*C*H_2, CH_2-2'), 31.5 (*C*H_2, SCH_2), 45.8 (*C*H_2, C-7), 50.1 (*C*H, C-1 or C-4), 52.0 (*C*H, C-1 or C-4), 65.1 (*C*H, C-3), 65.9 (*C*, C-2), 119.9 (*C*H, aromatic CH), 129.5 (*C*H, aromatic CH), 134.1 (*C*, aromatic C), 134.1 (*C*, aromatic C), 136.4 (*C*H, C-5 or C-6), 170.7 (*C*, CO). *Note*: one CH observed for 2 carbons (C-5 and C-6).

2-*exo*-(*n*-Butanethio)-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid benzylamide 6i-*endo* and 2-*endo*-(*n*-Butanethio)-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid benzylamide 6i-*exo*

The title compound was prepared from **5i** (500 mg, 1.76 mmol), $Cu^{II}Cl_2$ (356 mg, 2.65 mmol) and freshly distilled cyclopentadiene (2 mL) in dichloromethane (10 mL) as described for **6a**. Freshly distilled cyclopentadiene (1 mL lots) were added every 48 hours for 10 days to give the crude product mixture (% conversion and crude ratio could not be determined due to broadening of NMR signals) which was isolated by chromatography on silica gel of the reaction mixture. The crude product was treated with morpholine (200 mg, 2.30 mmol) as described for **6a** and, after chromatography on silica gel using ethyl acetate-hexane (gradient elution 5-20% ethyl acetate) as eluent, the adduct **6i** was isolated (280 mg, 46%, ratio of **6i-***endo* : **6i-***exo* of 2.7 : 1) as a yellow oil. The adduct diastereomers were inseparable by chromatography; Found C, 62.99; H, 6.41; N, 3.55. $C_{19}H_{24}NClOS$ requires C, 65.22; H, 6.91; N, 4.00; ν_{max}/cm^{-1} (film) 1648 (CO), 1522, 1283; Not all of the ^1H NMR signals for the two diastereomers could be distinguished, hence the ^1H NMR spectrum has been assigned as a mixture: δ_H (270 MHz, $CDCl_3$) 0.79-0.91 (3H, overlapping t, *J* 7, 7, -CH_3-4'), 1.19-1.78 (5.27H, m, $(CH_2)_2$, H-7a', CH_2-7b), 2.22-2.65 (2.73H, m, CH_2S, H-7a), 2.95 (0.73H, b s, H-4a), 3.02 (0.73H, H-1a), 3.22 (0.27H, b s, H-4b), 3.28 (0.27H, b s, H-1b), 4.30-4.55 (2H, m, NCH_2), 4.62 (0.73H, d, *J* 2, H-3a), 5.18 (0.27H, d, *J* 4, H-3b), 6.14-6.21 (1.46H, symmetrical m, H-5a, H-6a), 6.29-6.39 (0.54H, symmetrical m, H-5b, H-6b), 6.62 (0.73H, b t, NHa), 7.11 (0.23H, b t, NHb), 7.21-7.40 (5H, m, ArH); The signals for each diastereomer could be distinguished on the ^{13}C NMR:

Major Diastereomer **6i-***endo*: δ_C (67.8 MHz, $CDCl_3$) 13.6 (*C*H_3, CH_3-4'), 22.1 (*C*H_2, CH_2-3'), 30.7 (*C*H_2, CH_2-2'), 31.3 (*C*H_2, SCH_2), 44.0 (*C*H_2, NCH_2), 46.5 (*C*H_2, C-7), 52.7(*C*H, C-1 or C-4), 53.4 (*C*H, C-1 or C-4), 64.1 (*C*, C-2), 64.7 (*C*H, C-3), 127.8 (*C*H, aromatic CH), 128.0 (*C*H, aromatic CH), 128.7 (*C*H, aromatic CH), 135.6 (*C*H, C-5), 137.5 (*C*H, C-6), 138.3 (*C*, aromatic C), 171.8 (*C*, CO).

Minor Diastereomer **6i-***exo*: δ_C (67.8 MHz, $CDCl_3$) 13.6 (*C*H_3, CH_3-4'), 21.7 (*C*H_2, CH_2-3'), 30.7 (*C*H_2, CH_2-2'), 33.1 (*C*H_2, SCH_2), 44.1 (*C*H_2, NCH_2), 45.8 (*C*H_2, C-7), 50.1 (*C*H, C-1 or C-4), 52.0 (*C*H, C-1 or C-4), 65.0 (*C*, C-2), 65.3 (*C*H, C-3), 127.8 (*C*H, aromatic CH), 128.0 (*C*H, aromatic CH), 128.7 (*C*H, aromatic CH), 135.9 (*C*H, C-5), 136.4 (*C*H, C-6), 138.3 (*C*, aromatic C), 172.8 (*C*, CO).

2-*exo*-(Benzylthio)-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid *N*-(4-fluorophenyl)amide 6j-*endo* and 2-*endo*-(benzylthio)-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid *N*-(4-fluorophenyl)amide 6j-*exo*

Method: Microwave Conditions

An excess of freshly distilled cyclopentadiene (2.0 mL, 23.0 mmol) and **5j** (0.14 g, 0.4 mmol) were placed in a sealed microwave reaction vessel with stirring and subsequently heated for 10 min at 300 W at 150 °C. The crude reaction mixture was applied to a column of silica gel

and the excess cyclopentadiene was eluted with hexane. The product was then eluted with hexane-ethyl acetate (90:10), to give the cycloadduct as a clear oil (0.14 g, 88%), as an inseparable mixture of diastereomers (ratio of **6j-***endo*: **6j-***exo* of 3.1 : 1); ν_{max}/cm^{-1} (film) 3335 (NH), 3065 (CH), 2985 (CH), 1665 (CO), 1611, 1509, 1406 (CN stretch);

Major diastereomer **6j-***endo*: δ_H (300 MHz, $CDCl_3$) 1.81 [1H, d, A of AB system, J_{AB} 9.6, one of C(7)H_2], 2.43 [1H, d, B of AB system, J_{AB} 9.3, one of C(7)H_2], 3.07 [1H, br s, C(1)*H* or C(4)*H*], 3.12 [1H, br s, C(1)*H* or C(4)*H*], 3.67 (1H, d, A of AB system, J_{AB} 11.7, one of SCH_2), 3.99 (1H, d, B of AB system, J_{AB} 11.7, one of SCH_2), 4.78 [1H, d, *J* 2.1, C(3)*H*], 6.22-6.28 [2H, sym m, C(5)*H* & C(6)*H*], 6.95-7.33 (7H, m, Ar*H*)*, 7.33-7.40 (2H, m, Ar*H*), 8.06 (1H, br s, N*H*); δ_C (75.5 MHz, $CDCl_3$) 36.7 (CH_2, SCH_2), 46.8 [CH_2, *C*(7)H_2], 53.0, 53.5 [2 × CH, *C*(1)H & *C*(4)H], 64.0 [CH, *C*(3)H], 65.6 [C, *C*(2)], 115.7 [CH, d, $^2J_{CF}$ 23, aromatic *C*(3′)H], 122.5 [CH, d, $^3J_{CF}$ 8, aromatic *C*(2′)H], 127.4, 128.6, 129.0 (3 × CH, 3 × aromatic *C*H), 133.5, 133.6 (2 × C, 2 × aromatic *C*), 136.4, 136.9 [2 × CH, *C*(5)H & *C*(6)H], 159.5 [C, d, $^1J_{CF}$ 244, aromatic *C*(4′)], 169.6 (C, *C*O).

Minor diastereomer **6j-***exo*: δ_H (300 MHz, $CDCl_3$) 1.71-1.77 [2H, m, C(7)H_2], 3.29 [1H, br s, C(1)*H* or C(4)*H*], 3.34 [1H, br s, C(1)*H* or C(4)*H*], 3.61 (1H, d, A of AB system, J_{AB} 12.3, one of SCH_2), 3.87 (1H, d, B of AB system, J_{AB} 12.3, one of SCH_2), 5.28 [1H, d, *J* 3.6, C(3)*H*], 6.31-6.40 [2H, sym m, C(5)*H* & C(6)*H*], 6.95-7.33 (7H, m, Ar*H*)*, 7.41-7.48 (2H, m, Ar*H*), 8.57 (1H, br s, N*H*); δ_C (75.5 MHz, $CDCl_3$) 35.8 (CH_2, SCH_2), 45.9 [CH_2, *C*(7)H_2], 50.1, 52.0 [2 × CH, *C*(1)H & *C*(4)H], 64.8 [CH, *C*(3)H], 66.4 [C, *C*(2)], 115.8 [CH, d, $^2J_{CF}$ 22, aromatic *C*(3′)H], 122.4 [CH, d, $^3J_{CF}$ 8, aromatic *C*(2′)H], 127.4, 128.9, 129.0 (3 × CH, 3 × aromatic *C*H), 133.71, 133.75 (2 × C, 2 × aromatic *C*), 136.2, 136.3 [2 × CH, *C*(5)H & *C*(6)H], 159.5 [C, d, $^1J_{CF}$ 244, aromatic *C*(4′)], 170.6 (C, *C*O).

*These aromatic signals were indistinguishable for the two diastereomers.

Synthesis of Sulfone adducts

2-*exo*-Benzenesulfonyl-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid isopropylamide 7d-*endo* and 2-*endo*-Benzenesulfonyl-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid isopropylamide 7d-*exo* and 6-*endo*-Benzenesulfonyl-7-*endo*-chloro-3-oxatricyclo[3.2.1.$0^{2,1}$]octane-6-*exo*-carboxylic acid isopropylamide 8d-*exo*

The sulfone adduct was prepared as outlined for **7a** using the sulfoxide adduct **4d** (150 mg, 0.44 mmol) in dichloromethane (3 mL). A representative sample (0.3 mL, 15 mg) was removed for estimation of the ratio of **4d-***endo* : **4d-***exo* at 1.2 : 1 by ^{1}H NMR spectroscopy. A solution of *m*CPBA (149 mg of 70% pure material, 0.6 mmol) in dichloromethane (3 mL) was then added to the remaining adduct solution (135 mg, 0.4 mmol) in dichloromethane (2.7 mL). After stirring for 18 hours, the reaction mixture was worked-up as outlined for **7a** to give the crude product (134 mg, 95%) with a ratio of **7d-***endo* : **7d-***exo* of 1.2 : 1. Evidence

for over-oxidation of the minor adduct diastereomer to the epoxide was observed. The level of over-oxidation to the epoxide **8d-*exo*** was estimated at 30% of the minor diastereomer by ^{1}H NMR spectroscopy. Purification by chromatography on silica gel using ethyl acetate-hexane (30:70) as eluent gave **7d** (118 mg, 84%) as a colourless solid; Found C, 57.30; H, 5.55; N, 4.13; Cl, 10.34; S, 8.80. $C_{17}H_{20}NClO_3S$ requires C, 57.70; H, 5.70; N, 4.13; Cl, 10.02; S, 9.06; ; Not all of the ^{1}H NMR signals for the two diastereomers could be distinguished, hence the ^{1}H NMR spectrum has been assigned as a mixture: δ_H (270 MHz, $CDCl_3$) 1.11-1.29 [6H, m, $CH(CH_3)_2$], 1.40-1.71 (0.78H, ABq, *J* 9, CH_2-7b), 1.79-1.87 (0.61H, H_A or ABq, *J* 9, H-7'a), 2.88-2.98 (0.61H, H_B of ABq, H-7a), 3.08 (0.61H, b s, H-4a), 3.31 (0.39H, b s, H-4b), 3.52 (0.39H, b s, H-1b), 3.79 (0.61H, b s, H-1a), 3.83-4.03 (1H, m, NCH), 4.72 (0.61H, d, *J* 2, H-3a), 5.29 (0.39H, d, *J* 4, H-3b), 6.12-6.21 (0.61H, m, H-5a), 6.23-6.32 (0.61H, m, H-6a), 6.46-6.50 (0.39H, m, H-5b), 6.59 (0.61H, b d, NHa), 6.63-6.68 (0.39H, m, H-6b), 6.81 (0.39H, b d, NHb), 7.42-7.68 (3H, m, ArH), 7.87-7.98 (2H, m, ArH); The signals for each diastereomer could be distinguished on the ^{13}C NMR spectrum:

Major Diastereomer **7d-*endo***: δ_C (67.8 MHz, $CDCl_3$) 42.8 (*C*H, NCH), 47.5 (*C*H_2, C-7), 50.6 (*C*H, C-1 or C-4), 53.2 (*C*H, C-1 or C-4), 59.7 (*C*H, C-3), 82.4 (*C*, C-2), 128.4 (*C*H, aromatic CH), 130.1 (*C*H, aromatic CH), 134.0 (*C*H, aromatic CH), 137.1 (*C*H, C-5 or C-6), 138.2 (*C*, aromatic C), 138.7 (*C*H, C-5 or C-6), 165.1 (*C*, CO).

Minor Diastereomer **7d-*exo***: δ_C (67.8 MHz, $CDCl_3$) 43.0 (*C*H, NCH), 46.8 (*C*H_2, C-7), 50.7 (*C*H, C-1 or C-4), 52.1 (*C*H, C-1 or C-4), 62.4 (*C*H, C-3), 82.2 (*C*, C-2), 128.7 (*C*H, aromatic CH), 129.5 (*C*H, aromatic CH), 134.3 (*C*H, aromatic CH), 135.7 (*C*H, C-5 or C-6), 135.8 (*C*H, C-5 or C-6), 138.2 (*C*, aromatic C), 166.1 (*C*, CO).

The isopropyl CH_3 signals for both diastereomers were seen as overlapping singlets at δ_C 21.4-22.5 [*C*H_3, overlapping $CH(CH_3)_2$],

Characteristic signals for the epoxide **8d-*exo*** were seen at δ_H (270 MHz, $CDCl_3$) 0.71-0.78 (1H, H_A of ABq, *J* 9, one of CH_2-7), 1.55-1.63 (1H, H_B of ABq, *J* 9, one of CH_2-7), 4.11-4.18 (1H, m, H-5 or H-6), 6.71 (1H, b d, NH); δ_C (67.8 MHz, $CDCl_3$) 23.7 (*C*H_2, C-7), 44.8 (*C*H, NCH), 48.7 (*C*H, C-1 or C-4), 49.0 (*C*H, C-1 or C-4), 164.9 (*C*, CO).

2-*exo*-Benzenesulfinyl-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid ethylamide 7b-*endo*

A solution of *m*CPBA (44 mg of 70% pure material, 0.18 mmol) in dichloromethane (2 mL) was added to a solution of the sulfide adduct **6b-*endo*** (50 mg, 0.16 mmol) in dichloromethane (5 ml). Before addition of the *m*CPBA solution, an NMR of a representative sample of the starting material was recorded. This NMR showed no trace of the minor diastereomer **6b-*exo*** present. After stirring for 18 hrs, 0.5 mL of the reaction

solution was removed and the solvent evaporated at reduced pressure. NMR analysis (^{1}H NMR spectroscopy) of this sample showed 82% conversion of the sulfide adduct **6b-***endo* to the corresponding sulfoxide adduct **4b-***endo* with 18% sulfone adduct **7b-***endo*. A solution of *m*CPBA (50 mg of 70% pure material, 0.20 mmol) in dichloromethane (1 mL) was added to the reaction solution before stirring for a further 18 hours when a sample (1 mL) was removed and analysed by ^{1}H NMR spectroscopy which showed complete conversion to the sulfone adduct **7b-***endo* which was purified by chromatography on silica gel using ethyl acetate-hexane (30:70) as eluent to give the sulfone adduct **7b-***endo* as a colourless solid which was still contaminated with approximately 25% mCPBA; δ_H (270 MHz, $CDCl_3$) 1.22 (3H, t, *J* 7, $-CH_3$), 1.79-1.86 (1H, H_A of ABq, *J* 9, H-7'), 2.90-2.98 (1H, H_B of ABq, *J* 9, H-7), 3.09 (1H, b s, H-4), 3.18-3.42 (2H, m, NCH_2), 3.78 (1H, b s, H-1), 4.69 (1H, d, *J* 2, H-3), 6.13-6.29 (2H, symmetrical m, H-5, H-6), 6.74 (1H, b s, NH), 7.44-7.68 (3H, m, ArH), 7.85-7.93 (2H, m, ArH), 8.09-8.15. All other spectroscopic details were as previously reported.

2-*endo*-Benzenesulfinyl-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid ethylamide 7b-*exo* and 6-*endo*-Benzenesulfonyl-7-*endo*-chloro-3-oxatricyclo[3.2.1.0^{2,1}]-octane-6-*exo*-carboxylic acid ethylamide 8b-*exo*

A solution of *m*CPBA (44 mg of 70% pure material, 0.18 mmol) in dichloromethane (2 mL) was added to a solution of the sulfide adduct **6b-***exo* (50 mg, 0.16 mmol) in dichloromethane (5 mL). Before addition of the *m*CPBA solution, an NMR of a representative sample of the starting material was recorded. This NMR showed no trace of the major diastereomer **7b-***endo*. After stirring for 18 hrs, 0.5 mL of the reaction solution was removed and the solvent evaporated at reduced pressure. NMR analysis (^{1}H NMR spectroscopy) of this sample showed 50% conversion to the sulfoxide adduct **4b-***exo* and 50% conversion to the corresponding sulfone adduct **7b-***exo*. A solution of *m*CPBA (50 mg of 70% pure material, 0.20 mmol) in dichloromethane (1 mL) was added to the reaction solution before stirring for a further 18 hours when a sample (1 mL) was removed and analysed by ^{1}H NMR spectroscopy which showed complete conversion to the epoxide of the sulfone adduct **8b-***exo*. All spectroscopic details were as reported above.

Synthesis of acrylate adducts

2-*exo*-Phenylthio-3-*exo*-chlorobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid methyl ester 11a-*endo* and 2-*endo*-Phenylthio-3-*endo*-chlorobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid methyl ester 11a-*exo*

Cyclopentadiene (4 mL) was added to **10a** (600 mg, 2.63 mmol) in a round bottom flask. No solvent was added and the two reagents were heated at 50 °C for 16 hours. After cooling to

room temperature, the reaction mixture was applied directly to a column of silica gel prepared using 100% hexane. The excess cyclopentadiene was eluted using 100% hexane (300 mL) before the product **11a** was recovered using 5% ethyl acetate-hexane. The crude adduct was then purified by chromatography on silica gel using ethyl acetate-hexane (5:95) as eluent to give the adduct **11a** (668 mg, 86%) as a clear oil with a ratio of **11a-***endo* : **11a-***exo* of 4.0 : 1; Found C, 61.26; H, 4.90; Cl, 12.06; S, 11.13. $C_{15}H_{15}ClO_2S$ requires C, 61.11; H, 5.13; Cl, 12.03; S, 10.88. ν_{max}/cm^{-1} (film) 1730 (CO), 1248, 1230, 753; The NMR signals for each diastereomer could be distinguished:

Major Diastereomer **11a-***endo*: δ_H (270 MHz, $CDCl_3$) 1.78-2.60 (2H, ABq, *J* 9, CH_2-7), 3.05 (2H, b s, H-1, H-4), 3.50 (3H, s, OCH_3), 4.46 (1H, d, *J* 2, H-3), 6.03-6.18 (2H, symmetrical m, H-5, H-6), 7.30-7.53 (5H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 44.99 (*C*H_2, C-7), 50.25 (*C*H, C-1 or C-4), 51.92 (*C*H_3, OCH_3), 53.05 (*C*H, C-1 or C-4), 64.73 (*C*H, C-3), 65.17 (*C*, C-2), 128.67 (*C*H, aromatic CH), 129.57 (*C*H, aromatic CH), 131.88 (*C*, aromatic C), 136.17 (*C*H, aromatic CH or H-5 or H-6), 136.85 (*C*H, aromatic CH or H-5 or H-6), 138.48 (*C*H, aromatic CH or H-5 or H-6), 171.41 (*C*, CO).

Minor Diastereomer **11a-***exo*: δ_H (270 MHz, $CDCl_3$) 1.31-1.78 (2H, ABq, *J* 11, CH_2-7), 3.26 (1H, b s, H-1 or H-4), 3.42 (1H, b s, H-1 or H-4), 3.53 (3H, s, OCH_3), 5.06 (1H, d, *J* 4, H-3), 6.39-6.43 (1H, m, H-5 or H-6), 6.53-6.59 (1H, m, H-5 or H-6), 7.30-7.53 (5H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 46.01 (*C*H_2, C-7), 49.96 (*C*H, C-1 or C-4), 50.89 (*C*H, C-1 or C-4), 52.43 (*C*H_3, OCH_3), 65.36 (*C*H, C-3), 67.14 (*C*, C-2), 128.67 (*C*H, aromatic CH), 129.06 (*C*H, aromatic CH), 131.88 (*C*, aromatic C), 135.64 (*C*H, aromatic CH or H-5 or H-6), 135.95 (*C*H, aromatic CH or H-5 or H-6), 136.45 (*C*H, aromatic CH or H-5 or H-6), 172.02 (*C*, CO).

MS *m/z* 294, 296 (M^+, 17%), 259 (38, M^+-Cl), 228 (100, $[105]^+$), 149 (41, M^+-HCl-SPh), 109 (41, $[SPh]^+$), 66 (56), 65 (57); isotopic Cl pattern observed; 294, 296 (3:1 ^{35}Cl:^{37}Cl); Found (HRMS, EI) *m/z* 294.0471. $C_{15}H_{15}{}^{35}ClO_2S$ requires 294.0481.

2-*exo*-Phenylthio-3-*exo*-bromobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid methyl ester 11b-*endo* and 2-*endo*-Phenylthio-3-*endo*-bromobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylic acid methyl ester 11b-*exo*

The adduct was prepared as outlined for **11a** using **10b** (400 mg, 1.47 mmol) and cyclopentadiene (4 mL). After heating at 50 °C for 16 hours, the reaction solution was cooled to room temperature and applied directly to a column of silica gel prepared using 100% hexane. The excess cyclopentadiene was eluted using 100% hexane (300 mL) before the product **11b** was recovered using 5% ethyl acetate-hexane with a ratio of **11b-***endo* : **11b-***exo* of 4.3 : 1. The crude adduct was then purified by chromatography on silica gel using ethyl acetate-hexane (5:95) as eluent to give the adduct **11b** (424 mg, 85%) as a clear oil;

Found C, 55.17; H, 4.71. $C_{15}H_{15}BrO_2S$ requires C, 53.10; H, 4.71; ν_{max}/cm^{-1} (film) 1729 (CO), 1246, 1036, 745; The NMR signals for each diastereomer could be distinguished:

Major Diastereomer **11b-***endo*: δ_H (270 MHz, $CDCl_3$) 1.81-2.66 (2H, ABq, *J* 9, CH_2-7), 3.02 (1H, b s, H-1 or H-4), 3.18 (1H, b s, H-1 or H-4), 3.53 (3H, s, OCH_3), 4.50 (1H, d, *J* 2, H-3), 6.02-6.17 (2H, symmetrical m, H-5, H-6), 7.30-7.53 (5H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 45.00 (*C*H_2, C-7), 50.30 (*C*H, C-1 or C-4), 51.95 (*C*H_3, OCH_3), 53.88 (*C*H, C-1 or C-4), 56.34 (*C*H, C-3), 63.84 (*C*, C-2), 127.75 (*C*H, aromatic CH), 129.18 (*C*H, aromatic CH), 132.30 (*C*, aromatic C), 136.17 (*C*H, aromatic CH or H-5 or H-6), 136.59 (*C*H, aromatic CH or H-5 or H-6), 138.15 (*C*H, aromatic CH or H-5 or H-6), 171.28 (*C*, CO).

Minor Diastereomer **11b-***exo*: δ_H (270 MHz, $CDCl_3$) 1.30-1.79 (2H, ABq, *J* 11, CH_2-7), 3.30 (1H, b s, H-1 or H-4), 3.37 (1H, b s, H-1 or H-4), 3.55 (3H, s, OCH_3), 5.05 (1H, d, *J* 3, H-3), 6.33-6.39 (1H, m, H-5 or H-6), 6.51-6.57 (1H, m, H-5 or H-6), 7.30-7.53 (5H, m, ArH); δ_C (67.8 MHz, $CDCl_3$) 46.38 (*C*H_2, C-7), 50.08 (*C*H, C-1 or C-4), 52.47 (*C*H_3, OCH_3), 53.05 (*C*H, C-1 or C-4), 57.36 (*C*H, C-3), 65.23 (*C*, C-2), 127.75 (*C*H, aromatic CH), 128.48 (*C*H, aromatic CH), 132.30 (*C*, aromatic C), 135.75 (*C*H, aromatic CH or H-5 or H-6), 135.88 (*C*H, aromatic CH or H-5 or H-6), 137.33 (*C*H, aromatic CH or H-5 or H-6), 171.80 (*C*, CO).

MS *m/z* 340, 338 (M^+, 7%), 259 (100, M^+-Br), 227 (93), 199 (61), 161 (25), 110 (72), 66 (59); isotopic Br pattern observed; 340, 338 (1:1 ^{79}Br: ^{81}Br); Found (HRMS, EI) *m/z* 337.9973. $C_{15}H_{15}{}^{79}BrO_2S$ requires 337.9976. Found (HRMS, EI) *m/z* 339.9953. $C_{15}H_{15}{}^{81}BrO_2S$ requires 339.9956.

Cycloadditions with 2,3-dimethyl-1,3-butadiene

N-Benzyl-3,4-dimethylbenzamide 12b

a) Prepared from N-benzyl-Z-3-chloro-2-(benzylsulfinyl)propenamide **3p**

The title compound was prepared as described for **12a** using 2,3-dimethyl-1,3-butadiene (0.71 mL, 6.1 mmol) and **3p** (0.20 g, 0.6 mmol). The excess diene was then evaporated at reduced pressure to give the crude product as a brown oil. Signals in the ^{1}H NMR spectrum of the crude product (~ 46%) at δ_H 1.72 (3H, s, one of C*H*$_3$), 1.77 (3H, s, one of C*H*$_3$), 2.42 [1H, br d, *J* 18.3, one of C(2)*H*$_2$], 2.49-2.66 [1H, m, one of C(2)*H*$_2$], 2.90 [1H, br d, *J* 16.8, one of C(5)*H*$_2$], 3.47 [1H, br d, *J* 16.8, one of C(5)*H*$_2$], 3.96 [1H, dd, *J* 10.2, 4.2, C(6)*H*], were consistent with the cyclohexene intermediate **13c**. Following purification by column chromatography using hexane-ethyl acetate 80:20 as eluent, the trisubstituted aromatic product **12b** was obtained as a white solid (0.04 g, 53%), mp 102-104 °C; (Found C, 79.37;

H, 7.14; N, 5.79. $C_{16}H_{17}NO$ requires C, 80.30; H, 7.16; N, 5.85%); ν_{max}/cm^{-1} (KBr) 3329 (NH), 2919 (CH), 1638 (CO), 1547, 1495; δ_H (300 MHz, $CDCl_3$) 2.30 (6H, s, 2 × ArC*H*$_3$), 4.65 (2H, d, *J* 5.7, NHC*H*$_2$), 6.33 (1H, br s, N*H*), 7.18 [1H, d, *J* 7.7, aromatic C(5)*H*], 7.28-7.41 (5H, m, Ar*H*), 7.50 [1H, dd, *J* 7.7, 1.9, aromatic C(6)*H*], 7.59 [1H, d, *J* 1.9, aromatic C(2)*H*]; δ_C (75.5 MHz, $CDCl_3$) 20.16, 20.22 (2 × CH_3, 2 × Ar*C*H$_3$), 44.5 (CH_2, NH*C*H$_2$), 124.7, 128.0, 128.3, 128.7, 129.2, 130.2 (6 × CH, 6 × aromatic *C*H), 132.2, 137.4, 138.8, 141.1 (4 × C, 4 × aromatic *C*), 167.9 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{16}H_{18}NO$ $[M+H]^+$ 240.1388. Found 240.1390; m/z (ES+) 240.2 {[($C_{16}H_{17}NO$)+H^+], 100%}.

b) Prepared from N-benzyl-Z-3-chloro-2-(butylsulfinyl)propenamide **3n**

The title compound was also prepared from 2,3-dimethyl-1,3-butadiene (0.46 mL, 4.0 mmol) and *N*-benzyl-*Z*-3-chloro-2-(butylsulfinyl)propenamide **3n** (0.12 g, 0.4 mmol). The excess diene was then evaporated at reduced pressure to give the crude product as an orange oil, with no evidence of the cyclohexene intermediate in the ^{1}H NMR spectrum of the crude product. Following purification by column chromatography using hexane-ethyl acetate as eluent (gradient elution 5-10% ethyl acetate), the trisubstituted aromatic product **12b** was obtained as a white solid (0.04 g, 39%), mp 102-104 °C, with IR, ^{1}H NMR and ^{13}C NMR spectroscopic details identical to above.

N-(4-Fluorophenyl)-3,4-dimethylbenzamide 12c

2,3-Dimethyl-1,3-butadiene (0.35 mL, 3.0 mmol) and *N*-(4-fluorophenyl)-*Z*-3-chloro-2-(benzylsulfinyl)propenamide **3q** (0.10 g, 0.3 mmol) were placed in a sealed microwave reaction vessel with stirring and subsequently heated for 30 min at 300 W at 100 °C. The excess diene was then evaporated at reduced pressure to give the crude product as an orange solid (~63% **12c**). Signals in the ^{1}H NMR spectrum of the crude product (~ 37%) at δ_H 1.72 (3H, s, one of C*H*$_3$), 1.76 (3H, s, one of C*H*$_3$), 2.42 [1H, br d, *J* 17.1, one of C(2)*H*$_2$], 2.50-2.67 [1H, m, one of C(2)*H*$_2$], 2.90 [1H, br d, *J* 17.1, one of C(5)*H*$_2$], 3.47 [1H, br d, *J* 16.8, one of C(5)*H*$_2$], 3.96 [1H, dd, *J* 9.9, 4.2, C(6)*H*], were consistent with the cyclohexene intermediate **13b**. Following purification by column chromatography using hexane-ethyl acetate as eluent (gradient elution 2-5% ethyl acetate), the trisubstituted aromatic product **12c** was obtained as a white solid (0.06 g, 83%), mp 139-141 °C; ν_{max}/cm^{-1} (KBr) 3332 (NH), 2920 (CH), 1656 (CO), 1612, 1508; δ_H (300 MHz, $CDCl_3$) 2.33 (3H, s, one of ArC*H*$_3$), 2.34

(3H, s, one of ArC*H*$_3$), 7.02-7.12 (2H, m, Ar*H*), 7.55-7.63 [4H, m, Ar*H*, contains aromatic C(5)*H* and aromatic C(6)*H*], 7.65 [1H, s, aromatic C(2)*H*], 7.74 (1H, br s, N*H*); δ_C (75.5 MHz, $CDCl_3$) 20.2, 20.3 (2 × CH_3, 2 × Ar*C*H$_3$), 116.1 [CH, d, $^2J_{CF}$ 22, aromatic *C*(3′)H], 122.5 [CH, d, $^3J_{CF}$ 8, aromatic *C*(2′)H], 124.8, 128.7, 130.3 (3 × CH, 3 × aromatic *C*H), 132.6 (C, aromatic *C*), 134.5 [C, d, $^4J_{CF}$ 3, aromatic *C*(1′)], 137.6, 141.6 (2 × C, 2 × aromatic *C*), 159.8 [C, d, $^1J_{CF}$ 244, aromatic *C*(4′)], 166.3 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{15}H_{14}NOFNa$ $[M+Na]^+$ 266.0957. Found 266.0965; m/z (ES+) 244.1 {[($C_{15}H_{14}NOF$)+H^+], 100%}.

_N_,3,4-Trimethylbenzamide 12d

2,3-Dimethyl-1,3-butadiene (1.5 mL, 12.8 mmol) and **3v** (0.33 g, 1.3 mmol) were placed in a sealed microwave reaction vessel with stirring and subsequently heated for 60 min at 300 W at 100 °C. The excess diene was then evaporated at reduced pressure to give the crude product as a yellow oil (~50% **12d**). Signals in the ^{1}H NMR spectrum of the crude product (~ 48%) at δ_H 1.72 (3H, s, one of C*H*$_3$), 1.77 (3H, s, one of C*H*$_3$), 2.42 [1H, br d, *J* 18.6, one of C(2)*H*$_2$], 2.50-2.61 [1H, m, one of C(2)*H*$_2$], 2.91 [1H, br d, *J* 17.5, one of C(5)*H*$_2$], 2.99 (3H, d, *J* 4.8, NHC*H*$_3$), 3.46 [1H, br d, *J* 18.9, one of C(5)*H*$_2$], 3.96 [1H, dd, *J* 10.2, 4.2, C(6)*H*], were consistent with the cyclohexene intermediate **13d**. Following purification by column chromatography using hexane-ethyl acetate 60:40 as eluent, the trisubstituted aromatic product **12d** was obtained as a white solid (0.05 g, 21%)*, mp 99-102 °C; ν_{max}/cm^{-1} (KBr) 3345 (NH), 2918 (CH), 1635 (CO), 1546, 1497; δ_H (300 MHz, $CDCl_3$) 2.30 (6H, s, 2 × ArC*H*$_3$), 3.00 (3H, d, *J* 4.8, NHC*H*$_3$), 6.10 (1H, br s, N*H*), 7.17 [1H, d, *J* 7.8, aromatic C(5)*H*], 7.46 [1H, dd, *J* 7.8, 1.7, aromatic C(6)*H*], 7.56 [1H, d, *J* 1.7, aromatic C(2)*H*]; δ_C (75.5 MHz, $CDCl_3$) 20.16, 20.18 (2 × CH_3, 2 × Ar*C*H$_3$), 27.2 (CH_3, NH*C*H$_3$), 124.5, 128.6, 130.1 (3 × CH, 3 × aromatic *C*H), 132.5, 137.3, 140.8 (3 × C, 3 × aromatic *C*), 168.8 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{10}H_{14}NO$ $[M+H]^+$ 164.1075. Found 164.1070; m/z (ES+) 164.1 {[($C_{10}H_{13}NO$)+H^+], 100%}.

*A yield of 42% was obtained in a repeat experiment.

_N_-Phenyl-3,4-dimethylbenzamide 12e

The title compound was prepared as described for **12a** using 2,3-dimethyl-1,3-butadiene (0.36 mL, 3.1 mmol) and **3w** (0.10 g, 0.3 mmol). The excess diene was then evaporated at reduced pressure to give the crude product as a brown oil (~57% **12e**). Signals in the ^{1}H NMR spectrum of the crude product (~ 43%) at δ_H 1.72 (3H, s, one of C*H*$_3$), 1.77 (3H, s, one of C*H*$_3$), 2.42 [1H, br d, *J* 16.8, one of C(2)*H*$_2$], 2.50-2.65 [1H, m, one of C(2)*H*$_2$], 2.90 [1H, br d, *J* 17.1, one of C(5)*H*$_2$], 3.47 [1H, br d, *J* 17.1, one of C(5)*H*$_2$], 3.96 [1H, dd, *J* 9.9, 4.2, C(6)*H*], were consistent with the cyclohexene intermediate. Following purification by column chromatography using hexane-ethyl acetate as eluent (gradient elution 2-10% ethyl acetate), the trisubstituted aromatic product **12e** was obtained as a white solid (0.04 g, 53%), mp 102-104 °C; (Found C, 78.83; H, 6.09; N, 6.69. $C_{15}H_{15}NO$ requires C, 79.97; H, 6.71; N, 6.22%); ν_{max}/cm^{-1} (KBr) 3336 (NH), 3058 (CH), 2916 (CH), 1652 (CO), 1597, 1522; δ_H (300 MHz, $CDCl_3$) 2.29 (3H, s, one of ArC*H*$_3$), 2.30 (3H, s, one of ArC*H*$_3$), 7.06-7.23 (2H, m, Ar*H*), 7.30-7.41 (2H, m, Ar*H*), 7.57 [1H, dd, *J* 7.8, 1.8, aromatic C(6)*H*], 7.60-7.69 (3H, m, Ar*H*), 7.96 (1H, br s, N*H*); δ_C (75.5 MHz, $CDCl_3$) 20.2, 20.3 (2 × CH_3, 2 × Ar*C*H$_3$), 120.6, 124.7, 124.8, 128.8, 129.4, 130.3 (6 × CH, 6 × aromatic *C*H), 132.8, 137.6, 138.5, 141.4 (4 × C, 4 × aromatic *C*), 166.4 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{15}H_{16}NO$ $[M+H]^+$ 226.1232. Found 226.1240; m/z (ES+) 226.1 {[($C_{15}H_{15}NO$)+H^+], 100%}.

(1*R,6*R**)-1-(Benzylthio)-6-chloro-*N*-(4-fluorophenyl)-3,4-dimethylcyclohex-3-enecarboxamide 13b**

2,3-Dimethyl-1,3-butadiene (0.45 mL, 3.9 mmol) and *N*-(4-fluorophenyl)-*Z*-3-chloro-2-(benzylthio)propenamide **5j** (0.13 g, 0.4 mmol) were placed in a sealed microwave reaction vessel with stirring and subsequently heated for 120 min at 300 W at 140 °C. The excess diene was then evaporated at reduced pressure to give the crude product as a pale yellow solid. The ^{1}H NMR spectrum of the crude product was very clean. Following purification by column chromatography using hexane-ethyl acetate 98:2 as eluent, the substituted cyclohexene **13b** was obtained as a white solid (0.16 g, 98%), mp 119-121 °C; ν_{max}/cm^{-1} (KBr) 3252 (NH), 3030 (CH), 2920 (CH), 1666 (CO), 1609, 1512; δ_H (300 MHz, $CDCl_3$) 1.59 (3H, s, one of C*H*$_3$), 1.67 (3H, s, one of C*H*$_3$), 2.37 [1H, br d, A of AB system, J_{AB} 18.8, one of C(2)*H*$_2$], 2.58 [1H, br dd, A of ABX, J_{AB} 16.8, J_{AX} 5.9, one of C(5)*H*$_2$], 2.65-2.84 [1H, m, one of C(5)*H*$_2$], 3.03 [1H, br d, B of AB system, J_{AB} 18.8, one of C(2)*H*$_2$], 3.85 (1H, d, A of AB system, J_{AB} 12.6, one of SC*H*$_2$), 3.90 (1H, d, B of AB system, J_{AB} 12.6, one of SC*H*$_2$),

4.72 [1H, dd, X of ABX, J_{BX} 9.6, J_{AX} 5.9, C(6)*H*], 6.98-7.07 (2H, m, Ar*H*), 7.21-7.33 (5H, m, Ar*H* of benzyl), 7.39-7.47 (2H, m, Ar*H*), 9.27 (1H, br s, N*H*); δ_C (75.5 MHz, $CDCl_3$) 18.6, 18.8 (2 × CH_3, 2 × *C*H_3), 34.9 (CH_2, S*C*H_2), 40.0, 40.4 [2 × CH_2, *C*(2)H_2 & *C*(5)H_2], 61.6 [CH, *C*(6)H], 62.5 [C, *C*(1)], 116.0 [CH, d, $^2J_{CF}$ 23, aromatic *C*(3′)H], 122.1 [CH, d, $^3J_{CF}$ 7.9, aromatic *C*(2′)H], 122.5, 124.6 [2 × C, *C*(3) & *C*(4)], 128.0, 129.2, 129.3 (3 × CH, 3 × aromatic *C*H), 133.9, 137.4 (2 × C, 2 × aromatic *C*), 160.0 [C, d, $^1J_{CF}$ 244, aromatic *C*(4′)], 169.8 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{22}H_{24}NOS^{35}ClF$ $[M+H]^+$ 404.1251. Found 404.1251; m/z (ES+) 406.1 {[($C_{22}H_{23}NOS^{37}ClF$)+H^+], 42%}, 404.2 {[($C_{22}H_{23}NOS^{35}ClF$)+H^+], 100%}.

(1*R,6*R**)-*N*-Benzyl-1-(benzylthio)-6-chloro-3,4-dimethylcyclohex-3-enecarboxamide 13c**

2,3-Dimethyl-1,3-butadiene (0.70 mL, 6.1 mmol) and *N*-benzyl-*Z*-3-chloro-2-(benzylsulfinyl)propenamide **5k** (0.19 g, 0.6 mmol) were placed in a sealed microwave reaction vessel with stirring and subsequently heated for 120 min at 300 W at 180 °C. The excess diene was then evaporated at reduced pressure to give the crude product as a pale yellow solid. The ^{1}H NMR spectrum of the crude product was very clean. Following purification by column chromatography using hexane-ethyl acetate 85:15 as eluent, the substituted cyclohexene **13c** was obtained as a white solid (0.16 g, 98%), mp 118-120 °C; ν_{max}/cm^{-1} (KBr) 3354 (NH), 3029 (CH), 2915 (CH), 1652 (CO), 1516; δ_H (300 MHz, $CDCl_3$) 1.57 (3H, s, one of C*H*$_3$), 1.65 (3H, s, one of C*H*$_3$), 2.33 [1H, br d, A of AB system, J_{AB} 17.6, one of C(2)*H*$_2$], 2.50-2.76 [2H, m, C(5)*H*$_2$], 2.91 [1H, br d, B of AB system, J_{AB} 18.5, one of C(2)*H*$_2$], 3.73 (1H, d, A of AB system, *J* 12.2, one of SC*H*$_2$), 3.80 (1H, d, B of AB system, *J* 12.3, one of SC*H*$_2$), 4.40 (1H, dd, A of ABX, J_{AB} 14.7, J_{AX} 5.8, one of NHC*H*$_2$), 4.48 (1H, dd, B of ABX, J_{AB} 14.7, J_{BX} 5.8, one of NHC*H*$_2$), 4.73 [1H, dd, *J* 8.8, 5.9, C(6)*H*], 7.08-7.17 (2H, m, Ar*H*), 7.19-7.41 (8H, m, Ar*H*), 7.61 (1H, br s, N*H*); δ_C (75.5 MHz, $CDCl_3$) 18.7, 18.8 (2 × CH_3, 2 × *C*H_3), 34.7 (CH_2, S*C*H_2), 39.8, 40.2 [2 × CH_2, *C*(2)H_2 & *C*(5)H_2], 44.7 (CH_2, NH*C*H_2), 61.4 [C, *C*(1)], 61.5 [CH, *C*(6)H], 122.5, 124.4 [2 × C, *C*(3) & *C*(4)], 127.8, 128.0, 128.2, 129.1, 129.17, 129.23 (6 × CH, 6 × aromatic *C*H), 137.3, 138.4 (2 × C, 2 × aromatic *C*), 171.3 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{23}H_{27}NOS^{35}Cl$ $[M+H]^+$ 400.1502. Found 400.1520; m/z (ES+) 402.2 {[($C_{23}H_{26}NOS^{37}Cl$)+H^+], 42%}, 400.2 {[($C_{23}H_{26}NOS^{35}Cl$)+H^+], 100%}.

(1*R,6*R**)-1-(Benzylthio)-6-chloro-*N*,3,4-dimethylcyclohex-3-enecarboxamide 13d**

2,3-Dimethyl-1,3-butadiene (0.95 mL, 8.2 mmol) and *N*-methyl-*Z*-3-chloro-2-(benzylthio)propenamide **5l** (0.20 g, 0.8 mmol) were placed in a sealed microwave reaction vessel with stirring and subsequently heated for 120 min at 300 W at 180 °C. The excess diene was then evaporated at reduced pressure to give the crude product as a pale yellow solid. The ^{1}H NMR spectrum of the crude product was very clean. Following purification by column chromatography using hexane-ethyl acetate 80:20 as eluent, the substituted cyclohexene product **13d** was obtained as a clear oil (0.16 g, 58%); ν_{max}/cm^{-1} (film) 3437 (NH), 3293, 2916 (CH), 1642 (CO), 1525; δ_H (300 MHz, $CDCl_3$) 1.55 (3H, s, one of C*H*$_3$), 1.64 (3H, s, one of C*H*$_3$), 2.28 [1H, br d, A of AB system, J_{AB} 18.0, one of C(2)*H*$_2$], 2.47-2.75 [2H, m, C(5)*H*$_2$], 2.79 (3H, d, *J* 4.8, NHC*H*$_3$), 2.93 [1H, br d, B of AB system, J_{AB} 18.3, one of C(2)*H*$_2$], 3.77 (1H, d, A of AB system, *J* 12.6, one of SC*H*$_2$), 3.83 (1H, d, B of AB system, *J* 12.6, one of SC*H*$_2$), 4.68 [1H, dd, *J* 9.6, 5.7, C(6)*H*], 7.22-7.37 (6H, m, Ar*H* & N*H*); δ_C (75.5 MHz, $CDCl_3$) 18.2, 18.4 (2 × CH_3, 2 × *C*H$_3$), 26.9 (CH_3, NH*C*H$_3$), 34.3 (CH_2, S*C*H$_2$), 39.5, 39.8 [2 × CH_2, *C*(2)H$_2$ & *C*(5)H$_2$], 61.2 [C, *C*(1)], 61.3 [CH, *C*(6)H], 122.2, 124.0 [2 × C, *C*(3) & *C*(4)], 127.4, 128.7, 128.8 (3 × CH, 3 × aromatic *C*H), 137.2 (C, aromatic *C*), 171.7 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{23}NOS^{35}Cl$ $[M+H]^+$ 324.1189. Found 324.1175; m/z (ES+) 326.2 {[($C_{17}H_{22}NOS^{37}Cl$)+H^+], 40%}, 324.2 {[($C_{17}H_{22}NOS^{35}Cl$)+H^+], 100%}.