Supporting Information

for

Rasta resin–triphenylphosphine oxides and their use as recyclable heterogeneous reagent precursors in halogenation reactions

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General experimental details

All reagents were obtained from the Acros, Aldrich, and Alfa Aesar companies, and were used as received. All reactions were carried out in dry glassware under a N₂ atmosphere, and were monitored by TLC analysis using GF₂₅₄ silica gel coated plates. ¹H and ¹³C NMR spectra were recorded in CDCl₃ on a Bruker DRX-300 or DRX-400 spectrometer operating at 300/400 MHz for ¹H and 75/100 MHz for ¹³C analysis. Gel-phase ³¹P NMR analysis was performed on a Brucker DRX-400 spectrometer operating at 162 MHz. Chemical shift data is expressed in ppm with reference to TMS. Elemental analysis was performed at the Shanghai Institute of Organic Chemistry. EIMS data was recorded on a Finnigan MAT 96 mass spectrometer. X-ray diffraction data was collected on a Bruker Smart Apex II CCD.

Synthesis of 16

Rasta resin-PPh₃ 14 [1] (25.0 g, 24.3 mmol) was added to dichloromethane (50 mL) and 50% hydrogen peroxide (50 mL). The reaction mixture was magnetically stirred at room temperature for 1 h. The resin was then filtered, washed sequentially with CH₂Cl₂ (3 × 100 mL), methanol (3 × 100 mL), THF (3 × 100 mL), diethyl ether (3 × 100 mL) and hexane (3 × 100 mL), and then dried under vacuum at 60 °C for 16 h to afford 16 as white free-flowing beads (100% yield). Elemental analysis was used to determine the phosphine content (3.0%), and thus a loading level of 0.97 mmol PPh₃/g. A peak at δ 29.4 was observed by gel-phase ³¹P NMR analysis.
Synthesis of 18

Rasta resin-NBniPr₂-PPh₃ 19 [2] (20.0 g, 18.8 mmol) was added to dichloromethane (50 mL) and 50% hydrogen peroxide (50 mL). The reaction mixture was magnetically stirred at room temperature for 1 h. The resin was then filtered, washed sequentially with CH₂Cl₂ (3 × 100 mL), methanol (3 × 100 mL), THF (3 × 100 mL), diethyl ether (3 × 100 mL) and hexane (3 × 100 mL) and then dried under vacuum at 60 ºC for 16 h to afford 18 as white free-flowing beads (100% yield). Elemental analysis was used to determine the phosphine content (3.3%), and nitrogen content (1.5%), and thus loading levels of 1.07 mmol PPh₃/g, 1.06 mmol NiPr₂/g. A peak at δ 29.8 was observed by gel-phase ³¹P NMR analysis.

General procedure for Appel reactions using 16

To 16 (0.6 g, 0.6 mmol) was added dichloromethane (5 mL) in a round-bottom flask. After 10 min, oxalyl chloride or oxalyl bromide was added (0.6 mmol). The reaction mixture was magnetically stirred at room temperature. Upon cessation of gas evolution, 4 was added (0.5 mmol), and the reaction mixture was heated to reflux. After the reaction was complete according to TLC analysis, the mixture was cooled to room temperature and filtered. The solid on the funnel was washed with dichloromethane (3 × 10 mL), and the filtrate was concentrated under reduced pressure to afford the desired product 5 in an essentially pure state based on ¹H and ¹³C NMR spectroscopic analyses.
1-Bromo-4-(chloromethyl)benzene (5Aa, Table 1, entry 1) [3]. Isolated yield: 98%. $^1$H-NMR (400 MHz, CDCl$_3$) δ 4.52 (s, 2H), 7.25 (d, 2H, $J$ = 8.4 Hz), 7.48 (d, 2H, $J$ = 8.4 Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 45.5, 122.6, 130.4, 132.0, 136.6; MS for C$_7$H$_6$BrCl: calcd 204.0, found 204.0.

1-Bromo-4-(bromomethyl)benzene (5Ab, Table 1, entry 2) [4]. Isolated yield: 92%. $^1$H-NMR (300 MHz, CDCl$_3$) δ 4.44 (s, 2H), 7.27 (d, 2H, $J$ = 8.4 Hz), 7.47 (d, 2H, $J$ = 8.4 Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 32.5, 122.6, 130.8, 132.1, 136.9; MS for C$_7$H$_6$Br$_2$: calcd 247.9, found 247.9.

1-(Chloromethyl)-3-nitrobenzene (5Ba, Table 1, entry 3) [3]. Isolated yield: 93%. $^1$H-NMR (300 MHz, CDCl$_3$) δ 4.67 (s, 2H), 7.56 (t, 1H, $J$ = 7.8 Hz), 7.74 (d, 1H, $J$ = 7.6 Hz) 8.20 (d, 1H, $J$ = 8.2 Hz) 8.28 (s, 1H); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 44.7, 123.5, 123.6, 130.0, 134.6, 148.5; MS for C$_7$H$_6$ClNO$_2$: calcd 171.0, found 171.0.

1-(Bromomethyl)-3-nitrobenzene (5Bb, Table 1, entry 4) [4]. Isolated yield: 91%. $^1$H-NMR (400 MHz, CDCl$_3$) δ 4.55 (s, 2H), 7.55 (t, 1H, $J$ = 7.9 Hz), 7.74 (d, 1H, $J$ = 7.7 Hz), 8.16 (d, 1H, $J$ = 8.2 Hz), 8.26 (s, 1H); $^{13}$C-NMR
(100 MHz, CDCl$_3$) $\delta$ 31.4, 123.4, 124.1, 130.1, 135.2, 139.9, 148.5; MS for C$_7$H$_6$BrNO$_2$: calcd 216.0, found 215.0.

1,3-Dichloro-2-(chloromethyl)benzene (5Ca, Table 1, entry 5) [5]. Isolated yield: 93%. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 4.88 (s, 2H), 7.19-7.35 (m, 3H); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 40.9, 128.7, 130.4, 133.6, 136.3; MS for C$_7$H$_5$BrNO$_2$: calcd 216.0, found 215.0.

2-(Bromomethyl)-1,3-dichlorobenzene (5Cb, Table 1, entry 6) [5]. Isolated yield: 90%. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 4.76 (s, 2H), 7.17-7.34 (m, 3H); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 27.6, 128.7, 130.2, 133.8, 136.1; MS for C$_7$H$_6$BrCl$_2$: calcd 237.9, found 237.9.

2-(Chloromethyl)-1,3,5-trimethylbenzene (5Da, Table 1, entry 7) [5]. Isolated yield: 98%. $^1$H-NMR (300 MHz, CDCl$_3$) $\delta$ 2.26 (s, 3H), 2.39 (s, 6H), 4.65 (s, 2H), 6.87 (s, 2H); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 19.3, 21.2, 41.3, 129.4, 131.2, 137.6, 138.6; MS for C$_{10}$H$_{13}$Cl: calcd 168.1, found 168.1.
2-(Bromomethyl)-1,3,5-trimethylbenzene (5Db, Table 1, entry 8) [6]. Isolated yield: 93%. $^1$H-NMR (300 MHz, CDCl$_3$) δ 2.26 (s, 3H), 2.38 (s, 6H), 4.56 (s, 2H), 6.85 (s, 2H); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 19.3, 21.2, 29.9, 129.4, 131.2, 137.6, 138.7; MS for C$_{10}$H$_{13}$Br: calcd 212.0, found 212.0.

(1-Chloroethyl)benzene (5Ea, Table 1, entry 9) [7]. Isolated yield: 85%. $^1$H-NMR (400 MHz, CDCl$_3$) δ 1.86 (d, 3H, $J$ = 6.8 Hz), 5.10 (q, 1H, $J$ = 6.8 Hz), 7.30-7.43 (m, 5H); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 26.6, 58.9, 126.6, 128.4, 128.7, 142.9; MS for C$_8$H$_9$(C$_8$H$_9$Cl): calcd 105.1, found 105.1.

(1-Bromoethyl)benzene (5Eb, Table 1, entry 10) [5]. Isolated yield: 89%. $^1$H-NMR (400 MHz, CDCl$_3$) δ 2.04 (d, 3H, $J$ = 6.9 Hz), 5.21 (q, 1H, $J$ = 6.9 Hz), 7.24-7.44 (m, 5H); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 27.0, 49.8, 127.0, 128.5, 128.8, 143.4; MS for C$_8$H$_9$(C$_8$H$_9$Br): calcd 105.1, found 105.1.

(3-Chloropropyl)benzene (5Fa, Table 1, entry 11) [5]. Isolated yield: 95%. $^1$H-NMR (400 MHz, CDCl$_3$) δ 2.05-2.12 (m, 2H), 2.78 (t, 2H, $J$ = 7.2 Hz), 3.53 (t, 2H, $J$ = 6.3 Hz), 7.19-7.31 (m, 5H); $^{13}$C-NMR (100 MHz,
CDCl\textsubscript{3} δ 32.9, 34.1, 44.4, 126.3, 128.6, 128.7, 140.8; MS for C\textsubscript{9}H\textsubscript{11}Cl: calcd 154.1, found 154.1.

![5Fb](image)

(3-Bromopropyl)benzene (5Fb, Table 1, entry 12) [8]. Isolated yield: 90%. \textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}) δ 2.12-2.21 (m, 2H), 2.78 (t, 2H, J = 7.2 Hz), 3.39 (t, 2H, J = 6.6 Hz), 7.18-7.32 (m, 5H); \textsuperscript{13}C-NMR (100 MHz, CDCl\textsubscript{3}) δ 33.3, 34.1, 34.3, 126.3, 128.6, 128.7, 140.7; MS for C\textsubscript{9}H\textsubscript{11}Br: calcd 198.0, found 198.0.

![5Ga](image)

(4-Chlorobutyl)benzene (5Ga, Table 1, entry 13) [9]. Isolated yield: 98%. \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) δ 1.78-1.80 (m, 4H), 2.64 (t, 2H, J = 7.0 Hz), 3.54 (m, 2H), 7.17-7.20 (m, 3H), 7.26-7.30 (m, 2H); \textsuperscript{13}C-NMR (100 MHz, CDCl\textsubscript{3}) δ 28.8, 32.3, 35.3, 45.1, 126.1, 126.2, 128.6, 142.1; MS for C\textsubscript{10}H\textsubscript{13}Cl: calcd 168.1, found 168.1.

![5Gb](image)

(4-Bromobutyl)benzene (5Gb, Table 1, entry 14) [10]. Isolated yield: 92%. \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) δ 1.75-1.81 (m, 2H), 1.86-1.91 (m, 2H), 2.64 (t, 2H, J = 7.5 Hz), 3.42 (t, 2H, J = 6.7 Hz), 7.17-7.30 (m, 5H); \textsuperscript{13}C-NMR (100 MHz, CDCl\textsubscript{3}) δ 30.0, 32.4, 33.8, 35.1, 126.1, 128.5, 128.5, 141.9; MS for C\textsubscript{10}H\textsubscript{13}Br: calcd 212.0, found 212.0.
(3-Chlorobutyl)benzene (5Ha, Table 1, entry 15 and 17, Table 4) [11]. Isolated yields: 95% for entry 15 and 92% for entry 17. \(^{1}\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 1.53 (d, 3H, \(J = 6.5\) Hz), 1.98-2.05 (m, 2H), 2.72-2.86 (m, 2H), 3.96-4.03 (m, 1H), 7.20-7.32 (m, 5H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\) 25.6, 33.1, 42.1, 58.1, 126.3, 128.6, 128.7, 141.3; MS for C\(_{10}\)H\(_{13}\)Cl: calcd 168.1, found 168.1.

(3-Bromobutyl)benzene (5Hb, Table 1, entry 16) [12]. Isolated yield: 91%. \(^{1}\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.73 (d, 3H, \(J = 6.6\) Hz), 2.03-2.15 (m, 2H), 2.74-2.86 (m, 2H), 4.06-4.09 (m, 1H), 7.18-7.31 (m, 5H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) \(\delta\) 26.7, 34.1, 42.8, 51.1, 126.4, 128.6, 128.7, 141.1; MS for C\(_{10}\)H\(_{13}\)Br: calcd 212.0, found 212.0.

**General procedure for aldehyde halogenation reactions using 16**

To 16 (0.3 g, 0.3 mmol) was added chloroform (3 mL) in a round-bottom flask. After 10 min, oxalyl chloride or oxalyl bromide was added (0.3 mmol). The reaction mixture was magnetically stirred at room temperature. Upon cessation of gas evolution, 6 was added (0.1 mmol) and the reaction mixture was heated to reflux. After 72 h, the reaction mixture was cooled to room temperature and then filtered. The solid on funnel was washed with dichloromethane (3 × 5 mL). The filtrate was concentrated under reduced pressure to afford the crude product. The crude product was purified by flash silica gel column chromatography using 5% ethyl acetate in hexanes as the eluent.
(Dichloromethyl)benzene (7Aa, Table 2, entry 1) [13]. Isolated yield: 54%. $^1$H-NMR (400 MHz, CDCl$_3$) δ 6.73 (s, 1H), 7.39-7.42 (m, 3H), 7.58-7.60 (m, 2H); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 71.9, 126.2, 128.9, 130.0, 140.5; MS for C$_7$H$_6$Cl: calc 125.0, found 125.0.

(Dibromomethyl)benzene (7Ab, Table 2, entry 2) [14]. Isolated yield: 75%. $^1$H-NMR (400 MHz, CDCl$_3$) δ 6.66 (s, 1H), 7.32-7.39 (m, 3H), 7.57 (d, 2H, $J = 7.3$ Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 41.2, 126.6, 128.7, 130.0, 142.0; MS for C$_7$H$_6$Br: calc 170.0, found 170.0.

1-Bromo-4-(dichloromethyl)benzene (7Ba, Table 2, entry 3) [13]. Isolated yield: 65%. $^1$H-NMR (400 MHz, CDCl$_3$) δ 6.66 (s, 1H), 7.44 (d, 2H, $J = 8.5$ Hz), 7.54 (d, 2H, $J = 8.5$ Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 71.0, 124.2, 127.9, 132.1, 139.5; MS for C$_7$H$_5$BrCl: calc 237.9, found 237.9.

1-Bromo-4-(dibromomethyl)benzene (7Bb, Table 2, entry 4) [15]. Isolated yield: 83%. $^1$H-NMR (400 MHz, CDCl$_3$) δ 6.59 (s, 1H), 7.45 (d, 2H, $J = 8.4$ Hz), 7.51 (d, 1H, $J = 8.4$ Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 39.7.
124.0, 128.3, 132.0, 141.1; MS for C$_7$H$_4$Br$_2$ (C$_7$H$_4$Br$_3$): calc 247.9, found 247.1.

1-(Dichloromethyl)-4-nitrobenzene (7Ca, Table 2, entry 5) [13]. Isolated yield: 64%. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 6.77 (s, 1H), 7.76 (d, 2H, $J = 8.7$ Hz), 8.26 (d, 2H, $J = 8.7$ Hz). $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 69.9, 124.2, 127.5, 148.6; MS for C$_7$H$_5$ClNO$_2$ (C$_7$H$_5$ClNO$_2$): calc 170.0, found 170.0.

1-(Dibromomethyl)-4-nitrobenzene (7Cb, Table 2, entry 6). Isolated yield: 89%. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 6.67 (s, 1H), 7.75 (d, 2H, $J = 8.7$ Hz), 8.25 (d, 2H, $J = 8.7$ Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 38.3, 124.2, 127.9, 148.0; HRMS for C$_7$H$_4$BrNO$_2$ (C$_7$H$_3$Br$_2$NO$_2$): calc 213.9504, found 214.0910.

1-Chloro-4-(dibromomethyl)-2-nitrobenzene (7Da, Table 2, entry 7). Isolated yield: 61%. $^1$H-NMR (300 MHz, CDCl$_3$) $\delta$ 6.72 (s, 1H), 7.63 (d, 1H, $J = 8.4$ Hz), 7.76 (dd, 1H, $J_1 = 8.4$ Hz, $J_2 = 2.3$ Hz), 8.1 (d, 1H, $J = 2.3$ Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 69.1, 123.6, 128.7, 130.8, 132.6, 138.2, 140.3; MS for C$_7$H$_4$Cl$_2$NO$_2$ (C$_7$H$_4$Cl$_2$NO$_2$): calc 203.9, found 203.9.
1-Chloro-4-(dibromomethyl)-2-nitrobenzene (7Db, Table 2, entry 8) [14]. Isolated yield: 93%. $^1$H-NMR (400 MHz, CDCl$_3$) δ 6.63 (s, 1H), 7.59 (d, 1H, $J = 8.4$ Hz), 7.76 (d, 1H, $J = 8.4$ Hz), 8.09 (s, 1H); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 36.9, 123.9, 128.4, 131.3, 132.6, 141.9, 147.6; MS for C$_7$H$_4$BrClNO$_2^+$ (C$_7$H$_4$Br$_2$ClNO$_2$): calc 247.9, found 248.1.

1-(Dichloromethyl)-4-methoxybenzene (7Ea, Table 2, entry 9) [13]. Isolated yield: 94%. $^1$H-NMR (400 MHz, CDCl$_3$) δ 3.83 (s, 3H), 6.71 (s, 1H), 6.92 (d, 2H, $J = 8.7$ Hz), 7.51 (d, 2H, $J = 8.7$ Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 55.5, 71.9, 114.1, 127.7, 132.8, 160.7; MS for CH$_3$ClO$^+$ (C$_8$H$_8$Cl$_2$O): calc 155.0, found 155.0.

1-(Dibromomethyl)-4-methoxybenzene (7Eb, Table 2, entry 10). NMR yield: 5%. $^1$H-NMR (400 MHz, CDCl$_3$) δ 3.76 (s, 3H), 6.63 (s, 1H), 6.81 (d, 2H, $J = 8.5$ Hz), 7.46 (d, 2H, $J = 8.5$ Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 40.9, 55.4, 113.7, 121.2, 127.9, 160.4; MS for C$_8$H$_8$BrO$^+$ (C$_8$H$_8$Br$_2$O): calc 199.0, found 199.0
1-(Dichloromethyl)-4-methylbenzene (7Fa, Table 2, entry 11) [13]. Isolated yield: 85%. $^1$H-NMR (400 MHz, CDCl$_3$) δ 2.37 (s, 3H), 6.68 (s, 1H), 7.20 (d, 2H, $J = 8.0$ Hz), 7.45 (d, 2H, $J = 8.0$ Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 21.4, 72.0, 126.1, 129.5, 137.7, 140.2; MS for C$_8$H$_8$Cl$^+$ (C$_8$H$_8$Cl$_2$): calc 139.0, found 139.0.

1-(Dibromomethyl)-4-methylbenzene (7Fb, Table 2, entry 12). Isolated yield: 77%. $^1$H-NMR (400 MHz, CDCl$_3$) δ 2.36 (s, 3H), 6.63 (s, 1H), 7.16 (d, 2H, $J = 8.0$ Hz), 7.45 (d, 2H, $J = 8.0$ Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 21.4, 41.3, 126.6, 129.4, 139.4, 140.2; MS for C$_8$H$_8$Br$^+$ (C$_8$H$_8$Br$_2$): calc 183.0, found 182.9.

General procedure for aziridine halogenation reactions using 16

To 16 (0.6 g, 0.6 mmol) was added dichloromethane (5 mL) in round-bottom flask. After 10 min, oxalyl chloride or oxalyl bromide was added (0.6 mmol). The reaction mixture was magnetically stirred at room temperature. Upon cessation of gas evolution, 8 was added (0.5 mmol), and the reaction mixture was heated to reflux. After the reaction was complete according to TLC analysis, the mixture was cooled to room temperature and filtered. The solid on funnel was washed with dichloromethane (3 × 10 mL), and the filtrate was concentrated to afford the desired product 9 in an essentially pure state based on $^1$H and $^{13}$C NMR spectroscopic analyses.
N-(2-Chlorocyclopentyl)-4-methylbenzenesulfonamide (9Aa, Table 3, entry 1) [16]. Isolated yield: 95%.

\[ ^1H\text{-NMR (400 MHz, CDCl}_3 \delta 1.41-1.43 (m, 1H), 1.72-1.85 (m, 3H), 2.11-2.18 (m, 2H), 2.44 (s, 3H), 3.57-3.59 (m, 1H), 4.06-4.10 (m, 1H), 5.28 (d, 1H, } J = 5.9 \text{ Hz), 7.33 (d, 2H, } J = 8.0 \text{ Hz), 7.79 (d, 2H, } J = 8.0 \text{ Hz); } ^{13}C\text{-NMR (100 MHz, CDCl}_3 \delta 20.9, 21.8, 30.7, 33.6, 62.8, 63.8, 127.4, 130.0, 137.1, 144.0; MS for C}_{12}H_{16}ClNO_2S: \text{ calcd 273.1, found 273.1.} \]

N-(2-Bromocyclopentyl)-4-methylbenzenesulfonamide (9Ab, Table 3, entry 2) [17]. Isolated yield: 93%.

\[ ^1H\text{-NMR (400 MHz, CDCl}_3 \delta 1.26-1.42 (m, 1H), 1.63-1.82 (m, 2H), 1.93-1.96 (m, 1H), 2.16-2.28 (m, 2H), 2.45 (s, 3H), 3.65-3.80 (m, 1H), 4.10-4.11 (m, 1H), 5.25 (d, 1H, } J = 4.2 \text{ Hz), 7.34 (d, 2H, } J = 7.4 \text{ Hz), 7.80 (d, 2H, } J = 7.4 \text{ Hz); } ^{13}C\text{-NMR (100 MHz, CDCl}_3 \delta 21.5, 21.7, 30.8, 34.2, 54.4, 63.1, 127.4, 130.0, 136.9, 143.9; MS for C}_{12}H_{16}BrNO_2S: \text{ calcd 317.0, found 317.0.} \]

N-(2-Chlorocyclohexyl)-4-methylbenzenesulfonamide (9Ba, Table 3, entry 3 and 5, Table 5) [18]. Isolated yields: 89% for entry 3, and 95% for entry 5. \[ ^1H\text{-NMR (400 MHz, CDCl}_3 \delta 1.23-1.32 (m, 4H), 1.58-1.71 (m, 2H), 2.16-2.24 (m, 2H), 2.43 (s, 3H), 3.08-3.10 (m, 1H), 3.71 (dt, 1H, } J_1 = 9.6 \text{ Hz, } J_2 = 4.1 \text{ Hz), 4.98-5.10 (m, 1H), 7.31 (d, 2H, } J = 8.2 \text{ Hz), 7.78 (d, 2H, } J = 8.2 \text{ Hz); } ^{13}C\text{-NMR (100 MHz, CDCl}_3 \delta 21.4, 23.2, 24.0, 32.1, 34.7, 58.4, 61.9, 82.3; MS for C}_{12}H_{16}ClNO_2S: \text{ calcd 273.1, found 273.1.} \]
127.1, 129.5, 137.5, 143.2; MS for C$_{13}$H$_{16}$ClNO$_2$S: calcd 287.1, found 287.1.

N-(2-Bromocyclohexyl)-4-methylbenzenesulfonamide (9Bb, Table 3, entry 4) [17]. Isolated yield: 92%.

$^1$H-NMR (300 MHz, CDCl$_3$) δ 1.25-1.44 (m, 3H), 1.65-1.82 (m, 3H), 2.27-2.32 (m, 2H), 2.43 (s, 3H), 3.14-3.17 (m, 1H), 3.84 (dt, 1H, $J_1$ = 9.6 Hz, $J_2$ = 5.7 Hz), 4.78-4.90 (m, 1H), 7.31 (d, 2H, $J$ = 8.0 Hz), 7.78 (d, 2H, $J$ = 8.3 Hz);

$^{13}$C-NMR (100 MHz, CDCl$_3$) δ 21.7, 23.6, 25.5, 33.0, 35.9, 55.2, 58.8, 127.5, 129.7, 137.3, 143.6; MS for C$_{13}$H$_{18}$BrNO$_2$S: calcd 331.0, found 331.0.

N-(2-Chlorocycloheptyl)-4-methylbenzenesulfonamide (9Ca, Table 3, entry 6). Isolated yield: 96%. $^1$H-NMR (400 MHz, CDCl$_3$) δ 1.45-1.60 (m, 7H), 2.00-2.05 (m, 3H), 2.43 (s, 3H), 3.36-3.38 (m, 1H), 3.92-3.94 (m, 1H), 5.03-5.08 (m, 1H), 7.31 (d, 2H, $J$ = 8.1 Hz), 7.78 (d, 2H, $J$ = 8.1 Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 21.8, 22.8, 22.9, 27.4, 31.0, 34.2, 61.9, 65.7, 127.6, 129.8, 137.1, 143.8; HRMS for C$_{14}$H$_{20}$ClNO$_2$S: calcd 301.0903, found 301.0899.
N-(2-Bromocycloheptyl)-4-methylbenzenesulfonamide (9Cb, Table 3, entry 7). Isolated yield: 98%. $^1$H-NMR (400 MHz, CDCl$_3$) δ 1.48-1.61 (m, 7H), 2.03-2.15 (m, 3H), 2.43 (s, 3H), 3.48-3.50 (m, 1H), 4.04-4.09 (m, 1H), 4.92-4.99 (m, 1H), 7.31 (d, 2H, J = 8.0 Hz), 7.78 (d, 2H, J = 8.2 Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 21.8, 22.8, 24.0, 27.5, 31.3, 34.9, 58.8, 62.2, 127.6, 129.9, 137.0, 143.8; HRMS for C$_{14}$H$_{20}$BrNO$_2$S: calcd 345.0398, found 345.0393.

N-(2-Chlorocyclooctyl)-4-methylbenzenesulfonamide (9Da, Table 3, entry 8). Isolated yield: 93%. $^1$H-NMR (400 MHz, CDCl$_3$) δ 1.26-1.35 (m, 2H), 1.47-1.49 (m, 2H), 1.63-1.67 (m, 2H), 1.70-1.77 (m, 5H), 1.94-2.14 (m, 3H), 2.43 (s, 3H), 3.37-3.39 (m, 1H), 3.93-3.96 (m, 1H), 4.90-4.97 (m, 1H), 7.31 (d, 2H, J = 8.1 Hz), 7.77 (d, 2H, J = 8.1 Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 21.7, 24.0, 25.5, 25.7, 29.8, 31.3, 32.0, 60.7, 65.8, 127.6, 129.7, 136.7, 143.6; HRMS for C$_{15}$H$_{22}$ClNO$_2$S: calcd 315.1060, found 315.1053.

N-(2-Bromocyclooctyl)-4-methylbenzenesulfonamide (9Db, Table 3, entry 9) [19]. Isolated yield: 92%. $^1$H-NMR (400 MHz, CDCl$_3$) δ 1.26-1.33 (m, 2H), 1.48 (s, 2H), 1.67-1.74 (m, 5H), 1.99-2.11 (m, 2H), 2.11-2.43 (m,
1H), 2.48 (s, 3H), 3.50 (s, 1H), 4.05-4.08 (m, 1H), 4.95-5.03 (m, 1H), 7.31 (d, 2H, J = 7.8 Hz), 7.78 (d, 2H, J = 7.8 Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 21.7, 25.0, 25.4, 25.5, 25.8, 31.8, 32.2, 59.7, 61.0, 127.7, 129.6, 136.5, 143.6; MS for C$_{15}$H$_{22}$BrNO$_2$S: calcd 360.0, found 360.0.

![9Ea](image)

$N$-(2-Chloro-2-phenylethyl)-4-methylbenzenesulfonamide (9Ea, Table 3, entry 10) [20]. Isolated yield: 91%.

$^1$H-NMR (400 MHz, CDCl$_3$) δ 2.44 (s, 3H), 3.39-3.52 (m, 2H), 4.76 (t, 1H, J = 6.0 Hz), 4.87 (dd, 1H, J$_1$ = 8.2Hz, J$_2$ = 5.9Hz), 7.27-7.36 (m, 7H), 7.73 (d, 2H, J = 8.3Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 21.6, 50.4, 61.7, 127.1, 127.3, 129.0, 129.1, 130.0, 137.0, 137.9, 143.9; MS for C$_{15}$H$_{16}$ClNO$_2$S: calcd 309.1, found 309.1.

![9Eb](image)

$N$-(2-Bromo-2-phenylethyl)-4-methylbenzenesulfonamide (9Eb, Table 3, entry 11) [21]. Isolated yield: 93%.

$^1$H-NMR (400 MHz, CDCl$_3$) δ 2.45 (s, 3H), 3.54-3.60 (m, 2H), 4.83 (t, 1H, J = 5.9 Hz), 4.90 (t, 1H, J = 7.0 Hz), 7.27-7.33 (m, 7H), 7.73 (d, 2H, J = 8.1 Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 21.7, 50.2, 52.7, 127.2, 127.7, 129.2, 129.3, 130.0, 137.1, 138.3, 144.0; Ms for C$_{15}$H$_{16}$BrNO$_2$S: calcd 353.0, found 353.0.

![9Fa](image)

$N$-(2-(4-Bromophenyl)-2-chloroethyl)-4-methylbenzenesulfonamide (9Fa, Table 3, entry 12) [22]. Isolated yield: 93%. $^1$H-NMR (400 MHz, CDCl$_3$) δ 2.44 (s, 3H), 3.39-3.44 (m, 2H), 4.85 (t, 1H, J = 7.7 Hz), 4.92 (t, 1H, J =
\[6.5 \text{ Hz}, 7.16 (d, 2H, J = 8.3 \text{ Hz}), 7.31 (d, 2H, J = 8.3 \text{ Hz}), 7.46 (d, 2H, J = 8.3 \text{ Hz}), 7.70 (d, 2H, J = 8.3 \text{ Hz});\]

\[^{13}\text{C-NMR (100 MHz, CDCl}_3\text{)} \delta 21.7, 50.4, 61.0, 123.3, 127.1, 129.0, 130.0, 132.2, 136.9, 137.0, 144.1; \text{MS for}\]

C\text{\textsubscript{15}H\textsubscript{12}BrClNO\textsubscript{2}S}: calcd 387.0, found 387.0.

\[N-(2\text{-Bromo-2-(4-bromophenyl)ethyl})-4\text{-methylbenzenesulfonamide (9Fb, Table 3, entry 13). Isolated yield:}\]

95\%. \[^1\text{H-NMR (400 MHz, CDCl}_3\text{)} \delta 2.45 (s, 3H), 4.88 (t, 2H, J = 7.3 \text{ Hz}), 7.16 (d, 2H, J = 8.3 \text{ Hz}), 7.32 (d, 2H, J = 8.3 \text{ Hz}); \text{^13C-NMR (100 MHz, CDCl}_3\text{)} \delta 21.7, 50.1, 51.6, 123.3, 127.1, 129.4, 130.0, 132.3, 137.0, 137.4, 144.1; \text{HRMS for C}_{15}\text{H}_{15}\text{Br}_{2}\text{NO}_{2}\text{S: calcd 430.9190, found 430.9189.}\]

**General procedure for epoxide halogenation reactions using 18**

To 18 (1.3 g, 1.2 mmol) was added chloroform (10 mL) in a round-bottom flask. After 10 min, oxalyl chloride or oxalyl bromide was added (1.1 mmol). The reaction mixture was magnetically stirred at room temperature. Upon cessation of gas evolution, 10 was added (0.5 mmol) and the reaction mixture was heated to reflux. After the reaction was completed as monitored by TLC, the mixture was cooled to room temperature and filtered. The solid on funnel was washed with dichloromethane (3 \times 10 \text{ mL}). The solvent of filtrate was removed to afford the desired product 11 in an essentially pure state based on \[^1\text{H and } ^{13}\text{C NMR spectroscopic analyses.}\]
(1,2-Dichloroethyl)benzene (11Aa, Table 6, entry 1) [23]. Isolated yield: 95%. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$
3.90-4.02 (m, 2H), 5.01 (t, 1H, $J$ = 7.3 Hz), 7.35-7.42 (m, 5H); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 48.5, 61.9, 127.5, 129.0, 129.3, 138.1; MS for C$_8$H$_8$Cl$_2$: calcd 174.0, found 174.0.

(1,2-Dibromoethyl)benzene (11Ab, Table 6, entry 2) [24]. Isolated yield: 93%. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$
3.40-4.1 (m, 2H), 5.11-5.15 (dd, 1H, $J_1$ = 10.6 Hz, $J_2$ = 5.5 Hz), 7.24-7.32 (m, 5H); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$
35.1, 51.0, 127.7, 128.9, 129.3, 138.7; MS for C$_8$H$_8$Br$_2$: calcd 261.9, found 261.9.

(2,3-Dichloropropyl)benzene (11Ba, Table 6, entry 3) [23]. Isolated yield: 89%. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$
3.12 (dd, 1H, $J_1$ = 14.2 Hz, $J_2$ = 7.3 Hz), 3.37 (dd, 1H, $J_1$ = 14.2 Hz, $J_2$ = 5.7 Hz), 3.69-3.81 (m, 2H), 4.29-4.34 (m, 1H), 7.30-7.42 (m, 5H); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 41.1, 47.6, 61.1, 127.3, 128.7, 129.7, 136.4; MS for C$_9$H$_{10}$Cl$_2$: calcd 188.0, found 188.0.
(2,3-Dibromopropyl)benzene (11Bb, Table 6, entry 4) [25]. Isolated yield: 92%. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 3.12 (dd, 1H, $J_1 = 14.5$ Hz, $J_2 = 7.8$ Hz), 3.38 (dd, 1H, $J_1 = 14.5$ Hz, $J_2 = 4.8$ Hz), 3.61 (dd, 1H, $J_1 = 10.4$ Hz, $J_2 = 9.0$ Hz), 3.81 (dd, 1H, $J_1 = 10.5$ Hz, $J_2 = 4.2$ Hz), 4.32-4.35 (m, 1H), 7.22-7.35 (m, 5H); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 36.2, 42.1, 52.5, 127.3, 128.6, 129.6, 136.9; MS for C$_9$H$_{10}$Br$_2$: calcd 275.9, found 275.9.

(2,3-Dichloropropoxy)benzene (11Ca, Table 6, entry 5) [26]. Isolated yield: 95%. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 3.88-3.99 (m, 2H), 4.27 (d, 2H, $J = 6.0$ Hz), 4.34-4.39 (m, 1H), 6.93 (d, 2H, $J = 7.9$ Hz), 6.94-7.01 (m, 1H), 7.28-7.32 (m, 2H); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 45.2, 57.5, 68.3, 114.9, 121.8, 129.8, 158.1; MS for C$_9$H$_{10}$Cl$_2$O: calcd 204.0, found 204.0.

(2,3-Dibromopropoxy)benzene (11Cb, Table 6, entry 6) [27]. Isolated yield: 96%. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 3.88-3.97 (m, 2H), 4.35-4.40 (m, 2H), 4.42-4.46 (m, 1H), 6.95 (d, 2H, $J = 8.2$ Hz), 7.02 (t, 1H, $J = 7.4$ Hz), 7.29-7.34 (m, 2H); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 32.9, 47.9, 69.1, 115.0, 121.8, 129.7, 158.1; MS for C$_9$H$_{10}$Br$_2$O: calcd 291.9, found 291.9.
(3,4-Dichlorobutyl)benzene (11Da, Table 6, entry 7). Isolated yield: 98%. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 2.01-2.05 (m, 1H), 2.28-2.33 (m, 1H), 2.74-2.80 (m, 1H), 2.88-2.92 (m, 1H), 3.66 (dd, 1H, $J_1 = 11.3$ Hz, $J_2 = 7.4$ Hz), 3.77 (dd, 1H, $J_1 = 11.3$ Hz, $J_2 = 5.1$ Hz), 3.98-4.00 (m, 1H), 7.20-7.22 (m, 3H), 7.28-7.32 (m, 2H); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 32.1, 36.8, 48.4, 60.3, 126.4, 128.6, 128.7, 140.5; HRMS for $\text{C}_{10}\text{H}_{12}\text{Cl}_2$: calcd 202.0316, found 202.0321.

(3,4-Dibromobutyl)benzene (11Db, Table 6, entry 8). Isolated yield: 92%. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 2.08-2.11 (m, 1H), 2.46-2.50 (m, 1H), 2.74-2.79 (m, 1H), 2.91-2.94 (m, 1H), 3.65 (t, 1H, $J = 10.2$ Hz), 3.87 (dd, 1H, $J_1 = 10.3$ Hz, $J_2 = 4.4$ Hz), 4.09-4.13 (m, 1H), 7.20-7.24 (m, 3H), 7.30-7.33 (m, 2H); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 33.1, 36.4, 37.8, 52.2, 126.4, 128.7, 128.7, 140.4; HRMS for $\text{C}_{10}\text{H}_{12}\text{Br}_2$: calcd 289.9306, found 289.9300.
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16

After 8 cycles
$S_{24}$
5Ca
$5Db$
$\text{Br}$

$5\text{Hb}$
11Cb
X-ray Structure Details

X-ray structure of N-(2-chlorocyclohexyl)-4-methylbenzenesulfonamide

X-ray structure of N-(2-bromocyclohexyl)-4-methylbenzenesulfonamide
Refinement

The structures were solved by direct methods, \textit{SHELXS-97} (Sheldrick, 2008). All non-H atoms were refined anisotropically.

All of the C-bound H atoms were observable from difference Fourier map but were all placed at geometrical positions with C—H = 0.93, 0.96, 0.97 and 0.98Å for phenyl, methyl, methylene and methine H-atoms. The N-bound H atom was located from difference Fourier map. All H-atoms were refined using riding model with \( U_{	ext{iso}}(H) = 1.2U_{	ext{eq}}(	ext{Carrier}) \).

Highest peak is 0.44 at (0.5145, 0.9409, 0.6173) [0.96Å from Cl1] Deepest hole is -0.48 at (0.2792, 0.0893, 0.3290) [0.70Å from Cl1]

Computing details

Data collection: \textit{APEX} (Bruker AXS Inc, 2007); cell refinement: \textit{SAINT} v7.34A (Bruker AXS Inc, 2007); data reduction: \textit{CrystalStructure} (Rigaku/MSC and Rigaku Corporation, 2006); program(s) used to solve structure: \textit{SHELXS97} (Sheldrick, 2008); program(s) used to refine structure: \textit{SHELXL97} (Sheldrick, 2008); molecular graphics: Mercury (Macrae et al., 2008); software used to prepare material for publication: \textit{SHELXL97} (Sheldrick, 2008).

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X-ray report of N-(2-chlorocyclohexyl)-4-methylbenzenesulfonamide

The compound N-(2-chlorocyclohexyl)-4-methylbenzenesulfonamide crystallized in a centrosymmetric triclinic primitive space group, $P1$ (#2). There are two complex molecules in the unit cell. The cyclo-hexyl ring is in the chair form with the puckering amplitude ($Q$) of 0.535(4) Å, $\theta$ value of 176.3(4)$^\circ$ and $\phi$ value of 35(6)$^\circ$. Both the chloride and the sulphonamide groups are at axial positions. The compound is racemic. The atoms C1 and C2 are of the same configuration.

All the bond parameters are comparable to its bromide analogue. C—Cl is 1.818(3) Å, S=O is 1.4268(18)–1.4365(18) Å; S—N is 1.616(2) Å.

There are only very weak $\pi\cdots\pi$ inter-actions between the neighbouring tolyl rings. The complementary pair of inter-molecular N1—H1N···O2 H-bonding inter-actions link the molecules into dimers. There is no residual solvent accessible void volume found in the unit cell.

Experimental

A colourless block crystal of, C$_{13}$H$_{18}$ClNO$_2$S, having approximate dimensions of 0.38 mm x 0.56 mm x 0.56 mm was mounted in glass capillary. All measurements were made on a Bruker Apex CCD detector with graphite monochromated Mo—K$\alpha$ radiation.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions: $a = 6.9260(2)$ Å, $b = 9.4804(3)$ Å, $c = 11.6065(4)$ Å, $V = 714.23(4)$ Å$^3$, $\alpha = 73.524(2)^\circ$, $\beta = 77.837(2)^\circ$, $\gamma = 87.759(2)^\circ$.

For $Z = 2$ and F.W. = 287.79, the calculated density is 1.338 g/cm$^3$. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be: $P1$ (#2)

The data were collected at a temperature of 23(1)$^\circ$C to a maximum 2$\theta$ value of 25.02$^\circ$.

Of the 11110 reflections that were collected, 2480 reflections were unique. ($R_{int} = 0.0275$); equivalent reflections were merged.
Figure 1 The compound shown at 50% probability thermal ellipsoids with the atom numbering scheme.

Figure 2 The packing diagram of the unit cell was projected along the $a$ axis, shown at 50% probability thermal ellipsoids. The cyan dotted lines represent the complementary pair of intermolecular N1-H1N···O2 H-bonding interactions linking the molecules into dimers.
Crystal data

| Formula          | C_{13}H_{18}ClNO_{2}S |
|------------------|-----------------------|
| Mr.             | 287.79                |
| F(000)          | 304                   |
| Triclinic, $P\bar{1}$ | $D_x = 1.338 \text{ Mg m}^{-3}$ |
| Hall symbol     | -P 1                  |
| Mo Kα radiation | $\lambda = 0.71073 \text{ Å}$ |
| $a = 6.9260(2)\text{Å}$ | Cell parameters from 11110 reflections |
| $b = 9.4804(3)\text{Å}$ | $\theta = 1.9^\circ$ - $25.0^\circ$ |
| $c = 11.6065(4)\text{Å}$ | $\mu = 0.41 \text{ mm}^{-1}$ |
| $\alpha = 73.524(2)^\circ$ | $T = 296 \text{ K}$ |
| $\beta = 77.837(2)^\circ$ | Block, colourless |
| $\gamma = 87.759(2)^\circ$ | |
| $V = 714.23(4)\text{Å}^3$ | |

Data collection

| Instrument       | Bruker APEX CCD diffractometer |
|------------------|--------------------------------|
| 2480 reflections | 2480 independent reflections |
| Radiation source | fine-focus sealed tube |
| Graphite         | 2119 reflections with $I > 2\sigma(I)$ |
| $\omega$ & $\phi$ scans | $R_{int} = 0.028$ |
| $\theta_{max} = 25.0^\circ$, $\theta_{min} = 1.9^\circ$ | Absorption correction: multi-scan SADABS (Sheldrick, 2008) |
| $h = -8 \rightarrow 8$ | $k = -11 \rightarrow 11$ |
| $l = -13 \rightarrow 13$ | 11110 measured reflections |

Refinement

| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
|---------------------|-------------------------------------------------------------|
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.045$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.127$ | H-atom parameters constrained |
| $S = 1.06$ | $w = 1/[\sigma^2(F_o^2) + (0.0607P)^2 + 0.4124P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 2480 reflections | $(\Delta/\sigma)_{max} = 0.006$ |
| 164 parameters | $\Delta \varphi_{max} = 0.44 \text{ e Å}^{-3}$ |
| 0 restraints | $\Delta \varphi_{min} = -0.48 \text{ e Å}^{-3}$ |
Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating $R$-factors(gt) etc. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\AA^2$)

|     | x          | y          | z          | $U_{eq}$/$U_{eq1}$ |
|-----|------------|------------|------------|-------------------|
| Cl1 | 0.63511 (16) | 0.92618 (12) | 0.64754 (11) | 0.1109 (4)       |
| S1  | 0.28780 (9)  | 0.46056 (6)  | 0.87910 (6)  | 0.0428 (2)       |
| O1  | 0.4977 (3)   | 0.4550 (2)   | 0.84511 (18) | 0.0566 (5)       |
| O2  | 0.1860 (3)   | 0.37354 (19) | 0.99763 (16) | 0.0521 (5)       |
| N1  | 0.2296 (3)   | 0.6289 (2)   | 0.87325 (19) | 0.0461 (5)       |
| H1N | 0.0941      | 0.6362      | 0.9106      | 0.055*           |
| C1  | 0.3156 (4)   | 0.7518 (3)   | 0.7656 (2)   | 0.0487 (6)       |
| H1  | 0.3512      | 0.7157      | 0.6929      | 0.058*           |
| C2  | 0.5015 (4)   | 0.8056 (3)   | 0.7917 (3)   | 0.0621 (7)       |
| H2  | 0.5832      | 0.7209      | 0.8187      | 0.075*           |
| C3  | 0.4571 (6)   | 0.8854 (4)   | 0.8886 (3)   | 0.0798 (10)      |
| H3A | 0.5790      | 0.9275      | 0.8943      | 0.096*           |
| H3B | 0.4052      | 0.8154      | 0.9674      | 0.096*           |
| C4  | 0.3092 (6)   | 1.0073 (4)   | 0.8630 (4)   | 0.0861 (11)      |
| H4A | 0.2784      | 1.0499      | 0.9313      | 0.103*           |
| H4B | 0.3672      | 1.0843      | 0.7899      | 0.103*           |
|   | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$   | $U^{13}$   | $U^{23}$   |
|---|------------|------------|------------|------------|------------|------------|
| C1 | 0.0846 (7) | 0.0878 (7) | 0.1249 (9) | -0.0193 (5) | 0.0215 (6) | -0.0025 (6) |
| S1 | 0.0387 (4) | 0.0433 (3) | 0.0469 (4) | 0.0074 (2)  | -0.0075 (3) | -0.0155 (3) |
| O1 | 0.0388 (10)| 0.0639 (12)| 0.0721 (13)| 0.0100 (8)  | -0.0116 (9) | -0.0283 (10)|
| O2 | 0.0547 (11)| 0.0511 (10)| 0.0458 (10)| 0.0072 (8)  | -0.0090 (8) | -0.0082 (8) |
| N1 | 0.0435 (12)| 0.0427 (11)| 0.0515 (12)| 0.0032 (9)  | -0.0023 (9) | -0.0182 (9) |
| C1 | 0.0539 (15)| 0.0502 (14)| 0.0452 (14)| 0.0029 (12) | -0.0098 (12)| -0.0192 (11)|
| C2 | 0.0540 (17)| 0.0529 (16)| 0.077 (2)   | 0.0019 (13) | -0.0178 (14)| -0.0117 (14)|
| C3 | 0.101 (3)  | 0.067 (2)  | 0.089 (2)   | -0.0015 (18)| -0.051 (2)  | -0.0276 (18)|
| C4 | 0.128 (3)  | 0.0575 (18)| 0.086 (2)   | 0.009 (2)   | -0.032 (2)  | -0.0351 (18)|

Atomic displacement parameters (Å²)
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| C5 | 0.086 (2) | 0.0538 (17) | 0.081 (2) | 0.0253 (16) | -0.0157 (18) |
| C6 | 0.0635 (18) | 0.0592 (17) | 0.0641 (18) | 0.0080 (14) | -0.0281 (14) |
| C7 | 0.0411 (13) | 0.0354 (12) | 0.0458 (13) | 0.0062 (10) | -0.0072 (10) |
| C8 | 0.0422 (14) | 0.0623 (16) | 0.0510 (15) | 0.0070 (12) | -0.0053 (11) |
| C9 | 0.0444 (15) | 0.0625 (17) | 0.0648 (17) | 0.0019 (12) | -0.0129 (13) |
| C10 | 0.0658 (18) | 0.0428 (13) | 0.0532 (15) | 0.0041 (12) | -0.0183 (13) |
| C11 | 0.0670 (19) | 0.0608 (17) | 0.0505 (16) | 0.0057 (14) | -0.0015 (13) |
| C12 | 0.0441 (15) | 0.0547 (15) | 0.0543 (16) | 0.0035 (12) | -0.0015 (12) |
| C13 | 0.094 (2) | 0.070 (2) | 0.074 (2) | 0.0020 (18) | -0.0320 (19) |

Geometric parameters (Å, °)

|   |   |   |   |   |   |
|---|---|---|---|---|---|
| Cl1—C2 | 1.818 (3) | C5—H5A | 0.9700 |
| S1—O1 | 1.4268 (18) | C5—H5B | 0.9700 |
| S1—O2 | 1.4365 (18) | C6—H6A | 0.9700 |
| S1—N1 | 1.616 (2) | C6—H6B | 0.9700 |
| S1—C7 | 1.767 (2) | C7—C8 | 1.383 (3) |
| N1—C1 | 1.480 (3) | C7—C12 | 1.388 (3) |
| N1—H1N | 0.9561 | C8—C9 | 1.374 (4) |
| C1—C2 | 1.520 (4) | C8—H8 | 0.9300 |
| C1—C6 | 1.525 (4) | C9—C10 | 1.389 (4) |
| C1—H1 | 0.9800 | C9—H9 | 0.9300 |
| C2—C3 | 1.501 (5) | C10—C11 | 1.379 (4) |
| C2—H2 | 0.9800 | C10—C13 | 1.506 (4) |
| C3—C4 | 1.521 (5) | C11—C12 | 1.383 (4) |
| C3—H3A | 0.9700 | C11—H11 | 0.9300 |
| C3—H3B | 0.9700 | C12—H12 | 0.9300 |
| C4—C5 | 1.499 (5) | C13—H13A | 0.9600 |
| C4—H4A | 0.9700 | C13—H13B | 0.9600 |
| C4—H4B | 0.9700 | C13—H13C | 0.9600 |
| C5—C6 | 1.516 (4) |   |   |
| O1—S1—O2 | 119.78 (11) | C6—C5—H5A | 109.4 |
| Bond          | Distance (Å) | Angle (°) |
|---------------|--------------|-----------|
| O1—S1—N1     | 108.11 (11)  | 109.4     |
| O2—S1—N1     | 105.61 (11)  | 109.4     |
| O1—S1—C7     | 107.50 (11)  | 108.0     |
| O2—S1—C7     | 107.29 (11)  | 112.5 (2) |
| N1—S1—C7     | 108.09 (11)  | 109.1     |
| C1—N1—S1     | 121.06 (16)  | 109.1     |
| C1—N1—H1N    | 116.9        | 109.1     |
| S1—N1—H1N    | 111.7        | 109.1     |
| N1—C1—C2     | 107.4 (2)    | 107.8     |
| N1—C1—C6     | 110.0 (2)    | 120.1 (2) |
| C2—C1—C6     | 111.9 (2)    | 119.70 (19) |
| N1—C1—H1     | 109.2        | 120.18 (19) |
| C2—C1—H1     | 109.2        | 119.5 (2) |
| C6—C1—H1     | 109.2        | 120.2     |
| C3—C2—C1     | 112.6 (3)    | 120.2     |
| C3—C2—C11    | 110.5 (2)    | 121.7 (3) |
| C1—C2—C11    | 107.0 (2)    | 119.2     |
| C3—C2—H2     | 108.9        | 119.2     |
| C1—C2—H2     | 108.9        | 117.8 (2) |
| C11—C2—H2    | 108.9        | 121.7 (3) |
| C2—C3—C4     | 113.0 (3)    | 120.6 (3) |
| C2—C3—H3A    | 109.0        | 121.9 (2) |
| C4—C3—H3A    | 109.0        | 119.1     |
| C2—C3—H3B    | 109.0        | 119.1     |
| C4—C3—H3B    | 109.0        | 119.0 (2) |
| H3A—C3—H3B   | 107.8        | 120.5     |
| C5—C4—C3     | 110.9 (3)    | 120.5     |
| C5—C4—H4A    | 109.5        | 109.5     |
| C3—C4—H4A    | 109.5        | 109.5     |
| C5—C4—H4B    | 109.5        | 109.5     |
| C3—C4—H4B    | 109.5        | 109.5     |
| H4A—C4—H4B   | 108.0        | 109.5     |
| Bond                  | Angle     | Bond                  | Angle     |
|----------------------|-----------|----------------------|-----------|
| C4—C5—C6            | 111.4 (3) | H13B—C13—H13C       | 109.5     |
| C4—C5—H5A           | 109.4     |                      |           |

Hydrogen-bond geometry (Å, °)

| D—H···A   | D—H   | H···A   | D···A   | D—H···A |
|-----------|-------|--------|--------|--------|
| N1—H1N···O2<sup>i</sup> | 0.96  | 2.00   | 2.949 (3) | 172.9  |
| C2—H2···O1   | 0.98  | 2.53   | 3.204 (3) | 126    |
| C12—H12···O1 | 0.93  | 2.54   | 2.903 (3) | 104    |

Symmetry code: (i) -x, -y+1, -z+2.

**X-ray report of N-(2-bromocyclohexyl)-4-methylbenzenesulfonamide**

The compound N-(2-bromocyclohexyl)-4-methylbenzenesulfonamide crystallized in a centrosymmetric monoclinic primitive space group, P 2<sub>1</sub>/c (# 14). There are a total of four complex molecules in the unit cell. The cyclo-hexyl ring is in the chair form with the puckering amplitude (Q) of 0.529(9)Å, θ value of 176.1(10)<sup>°</sup> and ϕ value of 59(12)<sup>°</sup>. Both the bromide and the sulphonamide groups are at axial positions. The compound is racemic. The atoms C1 and C2 are of the same configuration.

All the bond parameters are comparable within normal ranges. C—Br is 1.985(7)Å, S=O is 1.429(5)–1.441(4)Å; S–N is 1.615(5)Å.

There are weak π···π inter-actions between the neighbouring tolyl rings. Inter-molecular H-bonding inter-actions present. There is no residual solvent accessible void volume found in the unit cell.

**Experimental**

A colourless plate crystal of, C<sub>13</sub>H<sub>18</sub>BrNO<sub>2</sub>S, having approximate dimensions of 0.14 mm x 0.26 mm x 0.38 mm was mounted in glass capillary. All measurements were made on a Bruker Apex CCD detector with graphite monochromated Mo—Kα radiation.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions: a = 10.8559(4)Å, b = 13.6017(5)Å, c = 10.5811(4)Å, V = 1482.46(10)Å<sup>3</sup> β = 108.406(2)<sup>°</sup>.  

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For $Z = 4$ and F.W. = 332.25, the calculated density is 1.489 g/cm$^3$. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be: $P 2_1/c$ (#14)

The data were collected at a temperature of 23(1)$^\circ$C to a maximum 2$\theta$ value of 66.1$^\circ$.

Of the 17462 reflections that were collected, 2616 reflections were unique. ($R_{\text{int}} = 0.0738$); equivalent reflections were merged.

Figure 3 The ORTEP plot of the compound was shown at 50% probability thermal ellipsoids with the atom numbering scheme.
Figure 4 The packing diagram of the unit cell was shown at 50% probability thermal ellipsoids. The cyan dotted line represent the complementary pair of intermolecular N1-H1N···O2 H-bonding interactions linking the molecules into dimers.

Crystal data

| Chemical Formula | Formula Weight | Density |
|------------------|----------------|---------|
| C_{13}H_{18}BrNO_2S | 332.25 g/mol | 1.489 g/cm³ |

Hall symbol: -P 2ybc

Cell parameters from 17462 reflections

| Parameter | Value |
|-----------|-------|
| a         | 10.8559(4) Å |
| b         | 13.6017(5) Å |
| c         | 10.5811(4) Å |
| α         | 90° |
| β         | 108.406(2)° |
| γ         | 90° |

Volume: 1482.46(10) Å³

Plate, colourless

Z = 4
Data collection

|                            | Value                        |
|---------------------------|------------------------------|
| Bruker APEX CCD diffractometer | 2616 independent reflections |
| Radiation source: fine-focus sealed tube | 1601 reflections with $I > 2\sigma(I)$ |
| graphite                  | $R_{int} = 0.074$            |
| $\omega$ & $\phi$ scans  | $\theta_{max} = 25.0^\circ$, $q_{min} = 2.0^\circ$ |
| Absorption correction: multi-scan SADABS (Sheldrick, 2008) | $h = -11\rightarrow 12$ |
| $T_{min} = 0.405$, $T_{max} = 0.686$ | $k = -16\rightarrow 16$ |
| 17462 measured reflections| $l = -12\rightarrow 12$     |

Refinement

| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
|---------------------|---------------------------------------------------------------|
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.068$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.201$ | H-atom parameters constrained |
| $S = 1.04$ | $w = 1/[\sigma^2(F_o^2) + (0.0872P)^2 + 3.5474P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 2616 reflections | $(\Delta/\sigma)_{max} = 0.019$ |
| 164 parameters | $\Delta\rho_{max} = 1.55$ e Å$^{-3}$ |
| 0 restraints    | $\Delta\rho_{min} = -0.81$ e Å$^{-3}$ |

Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Refinement of $F^2$ against ALL reflections. The weighted R-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional R-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating $R$-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$-factors based on ALL data will be even larger.
Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|     | x               | y               | z               | \(U_{iso}/U_{eq}\) |
|-----|-----------------|-----------------|-----------------|---------------------|
| Br1 | 1.05259 (9)     | 0.31013 (9)     | 0.63054 (10)    | 0.1096 (5)          |
| S1  | 0.58845 (16)    | 0.39459 (12)    | 0.38391 (16)    | 0.0520 (5)          |
| O1  | 0.6280 (5)      | 0.2988 (3)      | 0.3570 (5)      | 0.0646 (12)         |
| O2  | 0.4575 (4)      | 0.4086 (3)      | 0.3858 (4)      | 0.0632 (12)         |
| N1  | 0.6808 (5)      | 0.4284 (4)      | 0.5293 (5)      | 0.0537 (13)         |
| H1N | 0.6400          | 0.4783          | 0.5605          | 0.064*              |
| C1  | 0.8245 (7)      | 0.4251 (5)      | 0.5627 (6)      | 0.0612 (18)         |
| H1  | 0.8472          | 0.4297          | 0.4803          | 0.073*              |
| C2  | 0.8705 (7)      | 0.3288 (5)      | 0.6279 (7)      | 0.0683 (19)         |
| H2  | 0.8172          | 0.2766          | 0.5735          | 0.082*              |
| C3  | 0.8607 (9)      | 0.3220 (6)      | 0.7644 (8)      | 0.084 (2)           |
| H3A | 0.9024          | 0.2618          | 0.8056          | 0.101*              |
| H3B | 0.7698          | 0.3180          | 0.7584          | 0.101*              |
| C4  | 0.9212 (9)      | 0.4070 (8)      | 0.8520 (7)      | 0.094 (3)           |
| H4A | 0.9050          | 0.4007          | 0.9367          | 0.113*              |
| H4B | 1.0144          | 0.4059          | 0.8691          | 0.113*              |
| C5  | 0.8689 (9)      | 0.5011 (7)      | 0.7901 (8)      | 0.091 (3)           |
| H5A | 0.9133          | 0.5546          | 0.8471          | 0.109*              |
| H5B | 0.7774          | 0.5051          | 0.7816          | 0.109*              |
| C6  | 0.8855 (8)      | 0.5124 (6)      | 0.6535 (8)      | 0.081 (2)           |
| H6A | 0.9772          | 0.5163          | 0.6630          | 0.097*              |
| H6B | 0.8447          | 0.5730          | 0.6129          | 0.097*              |
| C7  | 0.6156 (6)      | 0.4763 (5)      | 0.2655 (5)      | 0.0485 (15)         |
| C8  | 0.5881 (7)      | 0.5746 (5)      | 0.2724 (7)      | 0.0647 (19)         |
| H8  | 0.5562          | 0.5977          | 0.3387          | 0.078*              |
| C9  | 0.6087 (7)      | 0.6380 (5)      | 0.1799 (7)      | 0.0677 (19)         |
| H9  | 0.5903          | 0.7044          | 0.1843          | 0.081*              |
| C10 | 0.6559 (7)      | 0.6054 (6)      | 0.0807 (6)      | 0.0620 (18)         |
| C11 | 0.6824 (7)      | 0.5081 (6)      | 0.0772 (7)      | 0.071 (2)           |
| H11 | 0.7148          | 0.4853          | 0.0111          | 0.085*              |
|       | U<sub>11</sub>  | U<sub>12</sub>  | U<sub>13</sub>  | U<sub>21</sub>  | U<sub>22</sub>  | U<sub>23</sub>  |
|-------|----------------|----------------|----------------|----------------|----------------|----------------|
| Br1   | 0.0643 (6)     | 0.1545 (11)    | 0.1021 (8)     | 0.0326 (6)     | 0.0149 (5)     | -0.0239 (6)   |
| S1    | 0.0471 (9)     | 0.0586 (10)    | 0.0518 (9)     | 0.0023 (7)     | 0.0177 (7)     | -0.0078 (8)   |
| O1    | 0.069 (3)      | 0.057 (3)      | 0.071 (3)      | 0.001 (2)      | 0.028 (2)      | -0.007 (2)    |
| O2    | 0.046 (3)      | 0.079 (3)      | 0.065 (3)      | -0.002 (2)     | 0.019 (2)      | -0.013 (2)    |
| N1    | 0.046 (3)      | 0.074 (4)      | 0.043 (3)      | 0.008 (3)      | 0.015 (2)      | -0.002 (2)    |
| C1    | 0.061 (4)      | 0.081 (5)      | 0.043 (4)      | 0.006 (4)      | 0.018 (3)      | 0.003 (3)     |
| C2    | 0.058 (4)      | 0.072 (5)      | 0.065 (5)      | -0.007 (4)     | 0.007 (3)      | -0.006 (4)    |
| C3    | 0.083 (6)      | 0.089 (6)      | 0.080 (6)      | -0.011 (5)     | 0.024 (4)      | 0.021 (5)     |
| C4    | 0.095 (7)      | 0.136 (9)      | 0.052 (5)      | 0.010 (6)      | 0.025 (4)      | 0.000 (5)     |
| C5    | 0.099 (7)      | 0.101 (7)      | 0.063 (5)      | 0.008 (5)      | 0.010 (5)      | -0.023 (5)    |
| C6    | 0.073 (5)      | 0.063 (5)      | 0.091 (6)      | -0.013 (4)     | 0.005 (4)      | 0.015 (4)     |
| C7    | 0.042 (3)      | 0.062 (4)      | 0.039 (3)      | 0.002 (3)      | 0.010 (3)      | -0.006 (3)    |
| C8    | 0.085 (5)      | 0.059 (5)      | 0.058 (4)      | 0.017 (4)      | 0.033 (4)      | -0.008 (3)    |
| C9    | 0.079 (5)      | 0.056 (4)      | 0.069 (5)      | 0.014 (4)      | 0.025 (4)      | 0.003 (4)     |
| C10   | 0.055 (4)      | 0.076 (5)      | 0.048 (4)      | 0.002 (4)      | 0.007 (3)      | 0.008 (4)     |
| C11   | 0.081 (5)      | 0.084 (6)      | 0.060 (4)      | 0.010 (4)      | 0.040 (4)      | -0.001 (4)    |
| C12   | 0.073 (5)      | 0.058 (4)      | 0.067 (4)      | 0.012 (3)      | 0.034 (4)      | -0.010 (4)    |
| C13   | 0.099 (7)      | 0.097 (6)      | 0.071 (5)      | 0.001 (5)      | 0.029 (5)      | 0.013 (5)     |

Geometric parameters (Å, °)

|       |       |       |
|-------|-------|-------|
| Br1   | C2    | 1.985 (7) |
| C5    | H5A   | 0.9700  |

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| Bond                  | Distance (Å) | Angles (°) |
|----------------------|--------------|------------|
| S1—O1                | 1.429 (5)    | C5—H5B    | 0.9700    |
| S1—O2                | 1.441 (4)    | C6—H6A    | 0.9700    |
| S1—N1                | 1.615 (5)    | C6—H6B    | 0.9700    |
| S1—C7                | 1.768 (6)    | C7—C8     | 1.377 (9) |
| N1—C1                | 1.488 (8)    | C7—C12    | 1.380 (8) |
| N1—H1N              | 0.9264       | C8—C9     | 1.375 (9) |
| C1—C2                | 1.491 (10)   | C8—H8     | 0.9300    |
| C1—C6                | 1.539 (10)   | C9—C10    | 1.378 (10)|
| C1—H1               | 0.9800       | C9—H9     | 0.9300    |
| C2—C3                | 1.485 (11)   | C10—C11   | 1.357 (10)|
| C2—H2               | 0.9800       | C10—C13   | 1.517 (10)|
| C3—C4                | 1.497 (12)   | C11—C12   | 1.375 (10)|
| C3—H3A              | 0.9700       | C11—H11   | 0.9300    |
| C3—H3B              | 0.9700       | C12—H12   | 0.9300    |
| C4—C5                | 1.468 (12)   | C13—H13A  | 0.9600    |
| C4—H4A             | 0.9700       | C13—H13B  | 0.9600    |
| C4—H4B             | 0.9700       | C13—H13C  | 0.9600    |
| C5—C6                | 1.520 (11)   |            |           |
| O1—S1—O2            | 118.9 (3)    | C6—C5—H5A | 109.3     |
| O1—S1—N1            | 108.3 (3)    | C4—C5—H5B | 109.3     |
| O2—S1—N1            | 105.5 (3)    | C6—C5—H5B | 109.3     |
| O1—S1—C7            | 107.7 (3)    | H5A—C5—H5B | 108.0    |
| O2—S1—C7            | 108.2 (3)    | C5—C6—C1  | 111.1 (6) |
| N1—S1—C7            | 107.7 (3)    | C5—C6—H6A | 109.4     |
| C1—N1—S1            | 120.4 (4)    | C1—C6—H6A | 109.4     |
| C1—N1—H1N           | 121.4        | C5—C6—H6B | 109.4     |
| S1—N1—H1N           | 109.0        | C1—C6—H6B | 109.4     |
| N1—C1—C2            | 108.0 (6)    | H6A—C6—H6B | 108.0    |
| N1—C1—C6            | 109.7 (6)    | C8—C7—C12 | 120.6 (6)|
| C2—C1—C6            | 111.9 (6)    | C8—C7—S1  | 119.0 (5)|
| N1—C1—H1            | 109.1        | C12—C7—S1 | 120.4 (5)|
| Bond                  | Angle (°) | Bond                  | Angle (°) |
|----------------------|-----------|----------------------|-----------|
| C2—C1—H1            | 109.1     | C9—C8—C7             | 119.0 (6) |
| C6—C1—H1            | 109.1     | C9—C8—H8             | 120.5     |
| C3—C2—C1            | 112.9 (6) | C7—C8—H8             | 120.5     |
| C3—C2—Br1           | 110.8 (5) | C8—C9—C10            | 121.6 (7) |
| C1—C2—Br1           | 107.8 (5) | C8—C9—H9             | 119.2     |
| C3—C2—H2            | 108.4     | C10—C9—H9            | 119.2     |
| C1—C2—H2            | 108.4     | C11—C10—C9           | 117.9 (7) |
| Br1—C2—H2           | 108.4     | C11—C10—C13          | 122.6 (7) |
| C2—C3—C4            | 113.7 (7) | C9—C10—C13           | 119.5 (7) |
| C2—C3—H3A           | 108.8     | C10—C11—C12          | 122.6 (6) |
| C4—C3—H3A           | 108.8     | C10—C11—H11          | 118.7     |
| C2—C3—H3B           | 108.8     | C12—C11—H11          | 118.7     |
| C4—C3—H3B           | 108.8     | C11—C12—C7           | 118.4 (6) |
| H3A—C3—H3B          | 107.7     | C11—C12—H12          | 120.8     |
| C5—C4—C3            | 111.4 (7) | C7—C12—H12           | 120.8     |
| C5—C4—H4A           | 109.3     | C10—C13—H13A         | 109.5     |
| C3—C4—H4A           | 109.3     | C10—C13—H13B         | 109.5     |
| C5—C4—H4B           | 109.3     | H13A—C13—H13B        | 109.5     |
| C3—C4—H4B           | 109.3     | C10—C13—H13C         | 109.5     |
| H4A—C4—H4B          | 108.0     | H13A—C13—H13C        | 109.5     |
| C4—C5—C6            | 111.5 (7) | H13B—C13—H13C        | 109.5     |
| C4—C5—H5A           | 109.3     |                       |           |

Hydrogen-bond geometry (Å, º)

| D—H···A   | D—H  | H···A  | D···A  | D—H···A  |
|-----------|------|--------|--------|----------|
| N1—H1N···O2i | 0.93 | 2.05   | 2.971 (7) | 175.5    |
| C2—H2···O1  | 0.98 | 2.57   | 3.248(9)  | 127      |
| C12—H12···O1 | 0.93 | 2.54   | 2.906(8)  | 104      |

Symmetry code: (i) -x+1, -y+1, -z+1.