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Metal-Free Amidation of Ether sp^3 C–H Bonds with Sulfonamides using $PhI(OAc)_2$

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- Supporting Information –

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1. Experimental details

General. Organic solvents were purified by passing over activated alumina with dry N_2. All chemicals were purchased from major commercial suppliers and used as received. Tetrahydrofuran (THF) and diethylether (Et_2O) were dried either by passing over activated alumina or by distillation from Na/benzophenone giving identical results for the amidation experiments. Additional ether substrates were passed through a small alumina pad and stored under N_2 before use. NMR spectra were recorded on Agilent DD2-400, -500, -600; Varian INOVA 500; Bruker Avance 600; or Bruker AMX-500 spectrometers at ambient probe temperatures. Chemical shifts are reported with respect to residual internal protio solvent for ^1H and $^{13}C\{^1H\}$ NMR spectra. The chemical shift δ is reported in units of parts per million (ppm). MS analyses were performed by the Mass Spectrometry and Proteomics Resource of the W.M. Keck Foundation Biotechnology Resource Laboratory at Yale University. Reactions under microwave irradiation were carried out in a Biotage Initiator Microwave Synthesizer with a Robot Eight automated sampler or in a CEM Discover microwave system with an Intellivent Explorer automated sampler.

General procedure for the amidation of ethers under thermal conditions. In a typical experiment the corresponding sulfonamide (0.2 mmol) and hypervalent iodine oxidant (0.3 to 0.4 mmol) were placed into a reactor vessel (Radleys Carousel 12 Place Reaction Station, RR98030) or sealed Schlenk tube equipped with a stir bar. The solids were suspended in the corresponding ether (2 mL) under N_2 atmosphere, and the reaction mixture heated at 60 ºC for 2 hours. The resulting clear solution was transferred to a round bottom flask, and the solvent was evaporated under reduced pressure to give an oily residue that was redissolved in $CDCl_3$. Conversion and selectivity were obtained by ^1H NMR analysis of the crude mixture after addition of trimethoxybenzene as

internal standard. In the case of THF, the resulting amidated ethers (**2**) could be purified simply by washing the residue several times with pentane and drying under vacuum. The final oils or solids showed excellent purity by ^{1}H NMR spectroscopy and the isolated yield was coincident with the spectroscopic yield calculated by NMR using trimethoxybenzene as internal standard. The other cyclic and acyclic amidated ethers were purified by successive extractions with pentane, concentration under vacuum to a minimum amount of solvent and storage in the freezer for 24 h. Then the organic fraction was discarded and the clear oil washed twice with cold pentane (-60 ºC) and dried under vacuum.

General procedure for the amidation of ethers under microwave conditions. In a typical experiment the corresponding sulfonamide (0.5 mmol), hypervalent iodine oxidant (0.55 mmol) and iodine (0, 0.02 or 0.5 mmol) were placed into a microwave vial (2-5 mL, Biotage Microwave). The solids were suspended in the ether substrate (2 mL) under N_2 atmosphere and then exposed to microwave irradiation (120 ºC, 10 min). The resulting solution was transferred to a round bottom flask, and the solvent was evaporated under reduced pressure to give an oily residue that was redissolved in $CDCl_3$. Conversion and selectivity were obtained by ^{1}H NMR analysis of the crude mixture after addition of trimethoxybenzene as internal standard. The same purification procedure described above was used.

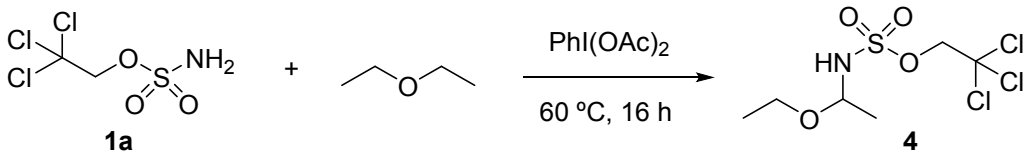
Procedure for Study of the Impact of TEMPO on the Amidation Reaction. 2,2,2-Trichloroethoxysulfonamide (0.1 mmol), $PhI(OAc)_2$ (0.2 mmol), and TEMPO (0.2 mmol) were placed into a microwave cell and suspended in THF (1 mL) under N_2 atmosphere. The reaction mixture was heated in an oil bath at 60 °C for two hours. The solvent was removed by rotary evaporation and the resulting residue was dissolved in

$CDCl_3$ and examined by ^1H NMR spectroscopy. Starting material was still present and no product was observed.

Procedure for Obtaining KIE Results. 2,2,2-Trichloroethoxysulfonamide (0.1 mmol), $PhI(OAc)_2$ (0.2 mmol), and iodine (0 mmol or 0.002 mmol) were placed into a microwave cell and suspended in a mixture of THF (0.500 mL) and THF-d_8 (0.500 mL) under N_2 atmosphere. The reaction mixture was heated in an oil bath at 60 °C for two hours. The contents were placed directly into NMR tubes and analyzed. Values for $k_{H/D}$ were determined by comparison of the average integration of the sulfonamide-related doublets at 4.77 ppm and 4.59 ppm (representing both deuterated and non-deuterated products) to that of the THF-related multiplet at 2.15 ppm (representing the non-deuterated product only). A KIE value of $k_{H/D} = 9.3$ was found for the reaction without added I_2, while a value of $k_{H/D} = 2.2$ was observed for the reaction involving 2 mol% I_2.

2. Screening conditions for the amidation of diethyl ether

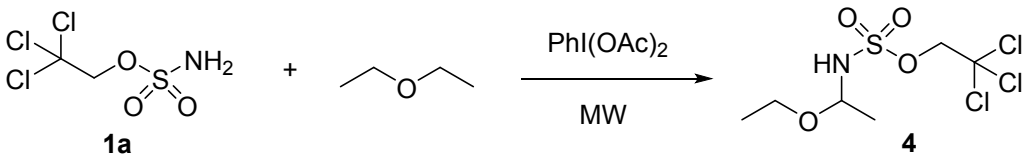
Table S1. Optimization of α-amidation of diethyl ether under thermal conditions[a]



Entry	Solvent	$PhI(OAc)_2$ (equiv.)	Yield (%)[b]
1	Neat	2	16
2	Et_2O / ACN	2	17
3	Et_2O / DCE	2	9
4	Et_2O / DMF	2	0
5	Et_2O / Toluene	2	12
6	Neat	1.1	18
7	Neat	4	6
8	**Et_2O / DCE**	**1.1**	**35**
9	Et_2O / DCE	4	12
10	Neat (+MS 4Å)	2	4

[a]Conditions: **1a** (0.5 mmol, 114 mg), diethyl ether or mixed solvent (2.5 mL), reactions carried out under N_2 atmosphere. [b]Yields were determined by ^1H NMR spectroscopy using trimethoxybenzene as internal standard.

Table S2. Optimization of α-amidation of diethyl ether under microwave irradiation[a]

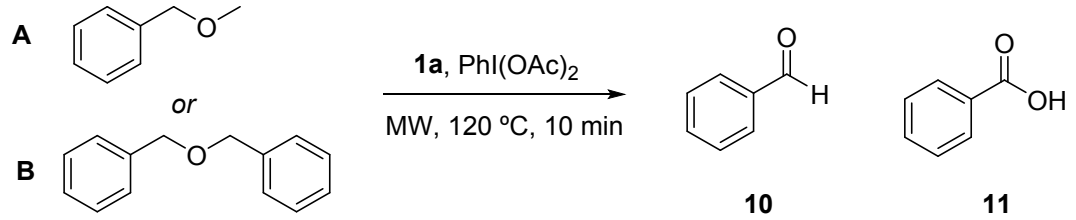


Entry	Solvent	Time (min)	T (ºC)	Oxidant (Equiv)	Yield(%)[b]
1	Neat	10	120	2	38
2	Et_2O / DCE	10	120	2	22
3	Neat	20	120	2	38
4	Neat	30	120	2	39
5	**Neat**	**1**	**120**	**1.1**	**60**
6	Neat	5	120	1.1	53
7	Neat	10	120	1.1	57
8	Neat	5	80	1.1	46
9	Neat	5	100	1.1	53
10	Neat	5 x 2[c]	100	1.1 x 2[c]	35
11	Neat	5 x 3[c]	100	1.1 x 3[c]	33

[a]Conditions: **1a** (0.5 mmol, 114 mg), diethyl ether or mixed solvent (2 mL), reactions carried out under N_2 atmosphere and microwave irradiation. [b]Yields were determined by ^{1}H NMR spectroscopy using trimethoxybenzene as internal standard. [c]Successive additions of $PhI(OAc)_2$ after each reaction cycle.

3. Oxidation of benzylic ethers

Table S3. Screening conditions for the oxidation of benzylic ethers[a]



Entry	Substrate	$PhI(OAc)_2$ (mmol)	1a (mmol)	10 (mmol)[b]	11 (mmol)[b]
1	A	0.55	0.5	0.24	0.31
2	A	0.55	-	0.35	-
3	A	-	-	0.11	-
4	B	0.55	0.5	0.88	0.56
5	B	0.55	-	0.85	0.63
6	B	-	-	0.24	0.14

[a]Conditions: **1a** (0.5 mmol, 114 mg), $PhI(OAc)_2$ (0.55 mmol, 177 mg), benzylic ether (2 mL), reactions carried out under N_2 atmosphere and microwave irradiation. [b]Product formation was quantified by ^1H NMR spectroscopy using trimethoxybenzene as internal standard, and its formation was evidenced by ^1H NMR spectroscopy by addition of authentic samples of **10** and **11**.

4. Spectroscopic characterization of amidated ethers.

Compounds **2c**[1] and **2k**[2] have been previously reported and their ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra are consistent with the data reported here. Compounds **2b** and **2d** have been proposed but no spectroscopic characterization was reported.[3] Compound **2j** has been already synthesized, but only ^{1}H NMR data are available.[4]

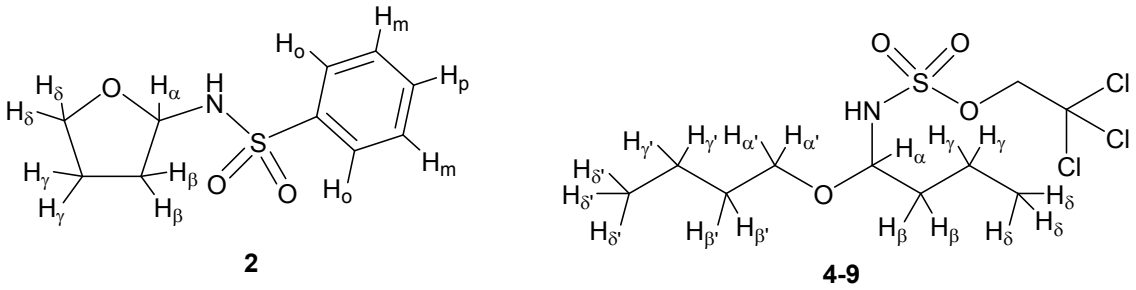
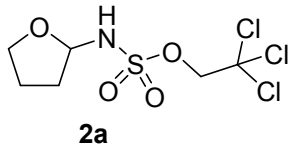
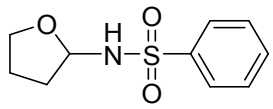


Figure S1. Labeling scheme for ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy assignments.



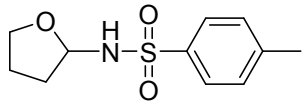
2a

Compound 2a. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.69 (br d, 1H, $^{3}J_{HH}$ = 8.9 Hz, NH), 5.38 (m, 1H, H_α), 4.79 (d, 1H, $^{2}J_{HH}$ = 11.0 Hz, $CH\mathit{H}CCl_3$), 4.65 (d, 1H, $^{2}J_{HH}$ = 11.0 Hz, $C\mathit{H}HCCl_3$), 3.98 (m, 1H, $C\mathit{H}_\delta H_\delta$), 3.88 (m, 1H, $CH_\delta\mathit{H}_\delta$), 2.27 (m, 1H, $C\mathit{H}_\beta H_\beta$), 1.98 (m, 2 H, $CH_{2\gamma}$), 1.88 (m, 1H, $CH_\beta\mathit{H}_\beta$). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 93.5 (CCl_3), 85.5 (CH_α), 78.5 ($\mathit{C}Cl_3$), 67.8 ($CH_{2\delta}$), 32.1 ($CH_{2\beta}$), 24.2 ($CH_{2\gamma}$). HRMS (FT-ICR): calcd. for $C_6H_{10}Cl_3NO_4S$-Na ($M+Na^+$): 319.9294. Found: m/z = 319.9280.



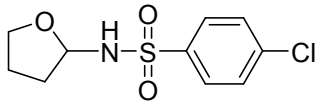
2b

Compound 2b. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.92 (d, 2H, $^{3}J_{HH}$ = 7.7 Hz, H_o), 7.56 (t, 1H, $^{3}J_{HH}$ = 7.7 Hz, H_p), 7.49 (t, 2H, $^{3}J_{HH}$ = 7.7 Hz, H_m), 5.42 (br s, 1H, NH), 5.37 (m, 1H, H_α), 3.68 (m, 2H, $CH_{2\delta}$), 2.17 (m, 1H, CH_βH$_\beta$), 1.87 (m, 2H, $CH_{2\gamma}$), 1.78 (m, 1H, CH$_\beta H_\beta$). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 141.4 (C_{ipso}), 132.6 (C_p), 128.9 (CH_m), 127.0 (CH_o), 85.0 (CH_α), 67.2 ($CH_{2\delta}$), 32.7 ($CH_{2\beta}$), 24.0 ($CH_{2\gamma}$). HRMS (FT-ICR): calcd. for C10H13NO3S-Na (M+Na$^+$): 250.0514. Found: m/z = 250.0506.



2c

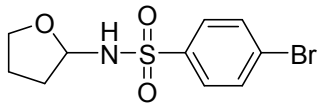
Compound 2c. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.79 (d, 2H, $^{3}J_{HH}$ = 8.3 Hz, H_o), 7.27 (d, 2H, $^{3}J_{HH}$ = 8.3 Hz, H_m), 5.64 (br d, 1H, $^{3}J_{HH}$ = 9.3 Hz, NH), 5.33 (m, 1H, H_α), 3.67 (m, 2H, $CH_{2\delta}$), 2.41 (s, 3H, CH_3), 2.13 (m, 1H, CH_βH$_\beta$), 1.88-1.82 (m, 3H, CH$_\beta H_\beta$, $CH_{2\gamma}$). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 143.2 (C_p), 138.5 (C_{ipso}), 129.5 (CH_m), 127.0 (CH_o), 84.9 (CH_α), 67.2 ($CH_{2\delta}$), 32.6 ($CH_{2\beta}$), 23.9 ($CH_{2\gamma}$). HRMS (FT-ICR): calcd. for $C_{11}H_{15}NO_3S$-Na (M+Na$^+$): 264.0670. Found: m/z = 264.0662.



2d

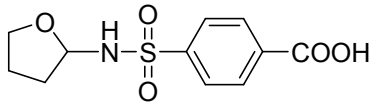
Compound 2d. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, 2H, $^{3}J_{HH}$ = 8.6 Hz, H_o), 7.45 (d, 2H, $^{3}J_{HH}$ = 8.6 Hz, H_m), 5.37 (m, 1H, H_α), 5.14 (br d, 1H, $^{3}J_{HH}$ = 9.1 Hz, NH),

3.67 (t, 2H, $^{3}J_{CHH}$ = 7.0 Hz, $CH_{2\delta}$), 2.19 (m, 1H, CH_{β}H$_{\beta}$), 1.86 (quint, 2H, $^{3}J_{CHH}$ = 7.0 Hz, $CH_{2\gamma}$), 1.75 (m, 1H, CH$_{\beta}H_{\beta}$). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 139.9 (C_p), 139.0 (C_{ipso}), 129.1 (CH_m), 128.6 (CH_o), 85.0 (CH_α), 67.3 ($CH_{2\delta}$), 32.7 ($CH_{2\beta}$), 24.1 ($CH_{2\gamma}$). HRMS (FT-ICR): calcd. for $C_{10}H_{12}ClNO_3S$-Na ($M+Na^+$): 284.0124. Found: m/z = 284.0116.



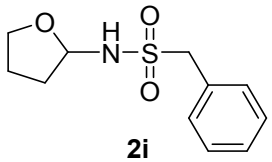
2e

Compound 2e. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.77 (d, 2H, $^{3}J_{HH}$ = 8.6 Hz, H_o), 7.62 (d, 2H, $^{3}J_{HH}$ = 8.6 Hz, H_m), 5.56 (br d, 1H, $^{3}J_{HH}$ = 9.1 Hz, NH), 5.36 (m, 1H, H_α), 3.67 (m, 2H, $CH_{2\delta}$), 2.19 (m, 1H, CH_{β}H$_{\beta}$), 1.87 (m, 2H, $CH_{2\gamma}$), 1.77 (m, 1H, CH$_{\beta}H_{\beta}$). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 140.0 (C_{ipso}), 132.1 (CH_m), 128.7 (CH_o), 127.5 (C_p), 85.0 (CH_α), 67.3 ($CH_{2\delta}$), 32.7 ($CH_{2\beta}$), 24.0 ($CH_{2\gamma}$). HRMS (FT-ICR): calcd. for C10H11BrNO3S ($M-H^-$): 303.9649. Found: m/z = 303.9639.



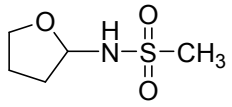
2f

Compound 2f. ^{1}H NMR (400 MHz, dmso-d_6): δ = 8.67 (d, 1H, $^{3}J_{HH}$ = 8.9 Hz, NH), 8.09 (d, 2H, $^{3}J_{HH}$ = 8.7 Hz, H_m), 7.91 (d, 2H, $^{3}J_{HH}$ = 8.7 Hz, H_o), 5.20 (m, 1H, H_α), 3.51 (m, 1H, CH_{δ}H$_{\delta}$), 3.46 (m, 1H, CH$_{\delta}H_{\delta}$), 2.04 (m, 1H, CH_{β}H$_{\beta}$), 1.86 (m, 1H, CH_{γ}H$_{\gamma}$), 1.70 (m, 2H, CH$_{\beta}H_{\beta}$, CH$_{\gamma}H_{\gamma}$). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 166.3 (COOH), 146.3 (C_{ipso}), 133.8 (C_p), 129.8 (CH_m), 126.6 (CH_o), 85.5 (CH_α), 66.2 ($CH_{2\delta}$), 31.3 ($CH_{2\beta}$), 23.7 ($CH_{2\gamma}$). HRMS (FT-ICR): calcd. for $C_{11}H_{13}NO_5S$-Na ($M+Na^+$): 294.0412. Found: m/z = 294.0405.



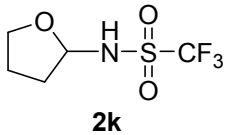
2i

Compound 2i. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45-7.30 (m, 5H, $H_{o,m,p}$), 5.33 (m, 2H, H_α, NH), 4.36 (d, 1H, $^{2}J_{HH}$ = 13.8 Hz, SC*H*H), 4.29 (d, 1H, $^{2}J_{HH}$ = 13.8 Hz, SCH*H*), 3.91 (m, 1H, C$H_\delta H_\delta$), 3.83 (m, 1H, $CH_\delta H_\delta$), 2.17 (m, 1H, C$H_\beta H_\beta$), 1.87 (m, 2H, $CH_{2\gamma}$), 1.68 (m, 1H, $CH_\beta H_\beta$). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 131.0 (CH_o), 130.8 (C_{ipso}), 128.7 (CH_m), 128.6 (C_p), 85.0 (CH_α), 67.4 ($CH_{2\delta}$), 60.3 (SCH_2), 32.2 ($CH_{2\beta}$), 24.4 ($CH_{2\gamma}$). HRMS (FT-ICR): calcd. for $C_{11}H_{16}NO_3S$ ($M+H^+$): 242.0851. Found: m/z = 242.0843.



2j

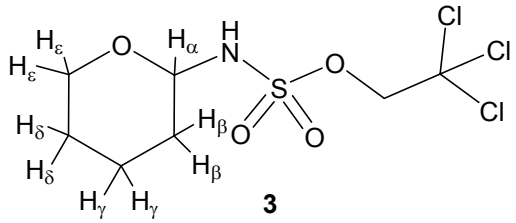
Compound 2j. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.35 (m, 1H, H_α), 5.30 (d, 1H, $^{3}J_{HH}$ = 9.5 Hz, NH), 3.91 (m, 1H, C$H_\delta H_\delta$), 3.84 (m, 1H, $CH_\delta H_\delta$), 3.07 (s, 3H, CH_3), 2.25 (m, 1H, C$H_\beta H_\beta$), 1.94 (m, 2H, $CH_{2\gamma}$), 1.76 (m, 1H, $CH_\beta H_\beta$). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 84.9 (CH_α), 67.2 ($CH_{2\delta}$), 42.8 (CH_3), 32.2 ($CH_{2\beta}$), 24.2 ($CH_{2\gamma}$). HRMS (FT-ICR): calcd. for $C_5H_{11}NO_3S$-Na ($M+Na^+$): 188.0357. Found: m/z = 188.0350.



2k

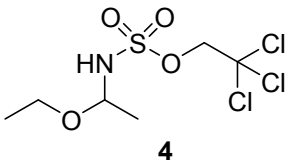
Compound 2k. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.54 (br s, 1H, NH), 5.42 (m, 1H, H_α), 3.99 (m, 1H, C$H_\delta H_\delta$), 3.88 (m, 1H, $CH_\delta H_\delta$), 2.31 (m, 1H, C$H_\beta H_\beta$), 1.99 (m, 2H, $CH_{2\gamma}$), 1.91 (m, 1H, $CH_\beta H_\beta$). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 119.3 (q, $^{1}J_{CF}$ =

321 Hz, CF_3), 85.9 (CH_α), 68.1 ($CH_{2\delta}$), 33.1 ($CH_{2\beta}$), 24.1 ($CH_{2\gamma}$). ^{19}F NMR (375 MHz, $CDCl_3$): δ = -77.7. HRMS (FT-ICR): calcd. for $C_5H_8F_3NO_3S$-Na ($M+Na^+$): 242.0075. Found: m/z = 242. 0043.



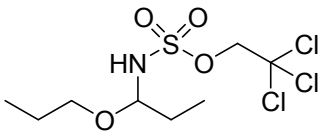
3

Compound 3. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.72 (br d, 1H, $^3J_{HH}$ = 9.5 Hz, NH), 4.77-4.68 (m, 3H, H_α, CH_2CCl_3), 4.03 (d, 1H, $^2J_{HH}$ = 12.4 Hz, CH_εH$_\varepsilon$), 3.59 (m, 1H, CH$_\varepsilon H_\varepsilon$), 1.94 (m, 2H, $CH_{2\gamma}$), 1.71-1.41 (m, 4H, $CH_{2\beta}$, $CH_{2\delta}$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 93.5 (CCl_3), 82.5 (CH_α), 78.6 (CCl_3), 66.8 ($CH_{2\varepsilon}$), 31.4 ($CH_{2\beta}$), 24.6 (CH_δ), 22.5 ($CH_{2\gamma}$). HRMS (FT-ICR): calcd. for $C_7H_{11}Cl_3NO_4S$ ($M-H^-$): 309.9480. Found: m/z = 309.9477.



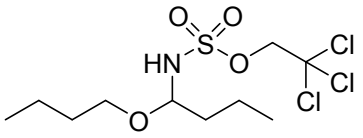
4

Compound 4. ^1H NMR (600 MHz, $CDCl_3$): δ = 5.18 (d, 1H, $^3J_{HH}$ = 9 Hz, NH), 4.89 (m, 1H, CH_α), 4.66 (m, 2H, CH_2CCl_3), 3.82 (m, 1H, C$H_{\alpha'}$CH$_{\alpha'}$), 3.56 (m, 1H, CH$_{\alpha'}$C$H_{\alpha'}$), 1.48 (d, 3H, $^3J_{HH}$ = 5.8 Hz, $CH_{3\beta}$), 1.22 (t, 3H, $^3J_{HH}$ = 7.0 Hz, $CH_{3\beta'}$). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ = 93.4 (CCl_3), 82.9 (CH_2CCl_3), 78.2 (CH_αNH), 63.9 ($CH_{2\alpha}$), 22.4 ($CH_{3\beta}$), 15.0 ($CH_{3\beta'}$). HRMS (FT-ICR): calcd. for $C_6H_{11}Cl_3NO_4S$ ($M-H^-$): 297.9480. Found: m/z = 297.9473.



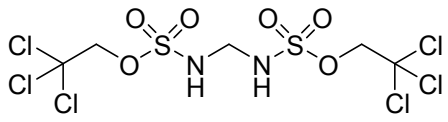
5

Compound 5. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.39 (d, 1H, $^{3}J_{HH}$ = 9.3 Hz, NH), 4.68-4.61 (m, 3H, CH_{α}, CH_2CCl_3), 3.75 (m, 1H, C$H_{\alpha'}$CH$_{\alpha'}$), 3.42 (m, 1H, CH$_{\alpha'}$C$H_{\alpha'}$), 1.74 (m, 2H, $CH_{2\beta}$), 1.58 (m, 2H, $CH_{2\beta'}$), 0.98 (t, 3H, $^{3}J_{HH}$ = 7.2 Hz, $CH_{3\gamma}$), 0.91 (t, 3H, $^{3}J_{HH}$ = 7.6 Hz, $CH_{3\gamma}$). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 94.4 (CCl_3), 87.6 (CH_2CCl_3), 78.1 ($CH_{\alpha}NH$), 70.5 ($CH_{2\alpha'}$), 29.2 ($CH_{2\beta}$), 22.6 ($CH_{2\beta'}$), 10.5 ($CH_{3\gamma'}$), 9.0 ($CH_{3\gamma}$). HRMS (FT-ICR): calcd. for $C_8H_{15}Cl_3NO_4S$ (M-H$^-$): 325.9793. Found: m/z = 325.9603.



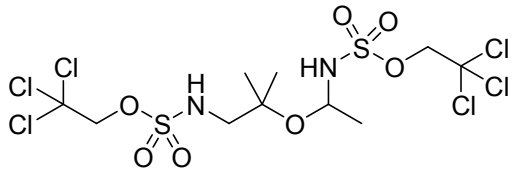
6

Compound 6. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.51 (d, 1H, $^{3}J_{HH}$ = 9.2 Hz, NH), 4.68 (m, 1H, CH_{α}), 4.67 (s, 2H, CH_2CCl_3), 3.78 (m, 1H, C$H_{\alpha'}$CH$_{\alpha'}$), 3.46 (m, 1H, CH$_{\alpha'}$C$H_{\alpha'}$), 1.73-1.63 (m, 2H, $CH_{2\beta}$), 1.54 (m, 2H, $CH_{2\beta'}$), 1.44 (m, 2H, $CH_{2\gamma}$), 1.34 (m, 2H, $CH_{2\gamma'}$), 0.92 (t, 3H, $^{3}J_{HH}$ = 7.2 Hz, $CH_{3\delta}$), 0.89 (t, 3H, $^{3}J_{HH}$ = 7.5 Hz, $CH_{3\delta'}$). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 94.3 (CCl_3), 86.3 (CH_2CCl_3), 78.6 ($CH_{\alpha}NH$), 70.6 ($CH_{2\alpha'}$), 38.0 ($CH_{2\beta}$), 31.5 ($CH_{2\beta'}$), 19.3 ($CH_{2\gamma'}$), 18.0 ($CH_{2\gamma}$), 13.8 ($CH_{3\delta'}$), 13.6 ($CH_{3\delta}$). HRMS (FT-ICR): calcd. for $C_{10}H_{21}Cl_3NO_4S$ (M+H$^+$): 356.0257. Found: m/z = 356.0254.



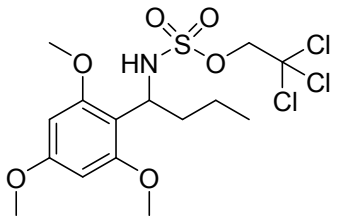
8

Compound 8. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.89 (t, 2H, $^{3}J_{HH}$ = 6.7 Hz, 2NH), 4.70 (m, 2H, NHCH_2NH), 4.68 (s, 4H, CH_2CCl_3). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 92.9 (CCl_3), 78.4 (CH_2CCl_3), 53.3 ($NHCH_2NH$). HRMS (FT-ICR): calcd. for $C_5H_7Cl_6N_2O_6S_2$ ($M\text{-}H^-$): 466.7852. Found: m/z = 466.7833.



9

Compound 9. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.25 (q, 1H, $^{3}J_{HH}$ = 5.3 Hz, CH_α), 5.02 (br s, 2 H, 2NH), 4.66 (s, 2H, $CHCCl_3$), 4.62 (s, 2H, CH_2CCl_3), 3.55 (d, 1H, $^{2}J_{HH}$ = 9.8 Hz, C$H_{\beta'}$H$_{\beta'}$), 3.20 (d, 1H, $^{2}J_{HH}$ = 9.8 Hz, CH$_{\beta'}$$H_{\beta'}$), 1.49 (d, 3H, $^{3}J_{HH}$ = 5.2 Hz, $CH_{3\beta}$), 1.36 (s, 3H, $CH_{3\beta'}$), 1.32 (s, 3H, $CH_{3\beta'}$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 94.5 (2xCCl_3), 87.9 (CH_α), 80.2 ($C_{\alpha'}$) 78.7 (CH_2CCl_3), 77.7 (CH_2CCl_3), 57.9 ($CH_{\alpha'}$), 26.2 ($CH_{3\beta'}$), 24.0 ($CH_{3\beta'}$), 21.6 ($CH_{3\beta}$). HRMS (FT-ICR): calcd. for $C_{10}H_{17}Cl_6N_2O_7S_2$ ($M\text{-}H^-$): 550.8553. Found: m/z = 550.8614.



10

Compound 10. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.13 (s, 2H, CH_{Ar}), 6.06 (d, 1H, $^{3}J_{HH}$ = 10.4 Hz, NH), 5.08 (dt, 1H, $^{3}J_{HH}$ = 10.4, 7.6 Hz, CH_{α}), 4.32 (d, 1H, $^{2}J_{HH}$ = 11.0 Hz, C*H*HCCl$_3$), 4.29 (d, 1H, $^{2}J_{HH}$ = 11.0 Hz, CH*H*CCl$_3$), 3.83 (s, 6H, OMe-*orto*), 3.80 (s, 3H, OMe-*para*), 1.89 (m, 1H, CH_{β}H$_{\beta}$), 1.70 (m, 1H, CH$_{\beta}H_{\beta}$), 1.40 (m, 1H, CH_{γ}H$_{\gamma}$), 1.24 (m, 1H, CH$_{\gamma}H_{\gamma}$), 0.90 (t, 3H, $^{3}J_{HH}$ = 7.4 Hz, $CH_{3\delta}$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 160.8 (C_{orto}, C_{para}), 109.6 (C_{ipso}), 93.5 (CCl_3), 91.0 (CH_{meta}), 77.9 (*C*H$_2$CCl$_3$), 55.8 (OMe-*orto*), 55.4 (OMe-*para*), 50.5 (CH_{α}), 37.6 ($CH_{2\beta}$), 19.5 ($CH_{2\gamma}$), 13.7 ($CH_{2\delta}$). HRMS (FT-ICR): calcd. for $C_{15}H_{23}Cl_3NO_6S$ ($M+H^+$): 450.0312. Found: m/z = 450.0293.

5. Crystallographic details of compounds 2a, 2d, 8 and 12

5.1 Crystallographic details

Low-temperature diffraction data (93K, ω scans) were collected on either a Rigaku R-AXIS RAPID diffractometer coupled to a RAXIS RAPID imaging plate detector with Mo Kα radiation (λ = 0.71073 Å) or a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å). The data frames were processed and scaled using the Rigaku CrystalClear software. The data were corrected for Lorentz and polarization effects. All structures were solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-97. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model, except for those bound to nitrogen which were located in the Fourier difference electron density map and their N-H bond distances restrained using DFIX instruction. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). Complete details of the X-ray analyses reported herein have been deposited at The Cambridge Crystallographic Data Centre (CCDC 1015066 (**2a**), 1015067 (**2d**), 1015068 (**8**) and 1015069 (**12**)).

5.2 Crystal data and structure refinement for 2a

Crystal data

$C_6H_{10}Cl_3NO_4S$	$F(000) = 608$
$M_r = 298.56$	$D_x = 1.775$ Mg m^{-3}
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
$a = 10.97$ (5) Å	Cell parameters from 277 reflections
$b = 11.299$ (4) Å	$\theta = 7.8$–$49.8°$
$c = 9.022$ (4) Å	$\mu = 9.17$ mm^{-1}
$\beta = 92.4$ (3)°	$T = 93$ K
$V = 1117$ (5) Å^3	Plate, colorless
$Z = 4$	0.10 × 0.10 × 0.02 mm

Data collection

Rigaku Saturn 944+ CCD diffractometer	1940 independent reflections
Radiation source: fine-focus sealed tube	1246 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.208$
Detector resolution: 22.2 pixels mm^{-1}	$\theta_{max} = 66.6°$, $\theta_{min} = 4.0°$
ω scans	$h = -13 \rightarrow 13$
Absorption correction: multi-scan Jacobson, R. (1998) Private Communication	$k = -13 \rightarrow 13$
$T_{min} = 0.461$, $T_{max} = 0.838$	$l = -10 \rightarrow 10$
28348 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
$R[F^2 > 2\sigma(F^2)] = 0.078$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.215$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.1086P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
1940 reflections	$(\Delta/\sigma)_{max} < 0.001$
139 parameters	$\Delta\rho_{max} = 0.78$ e Å^{-3}
1 restraint	$\Delta\rho_{min} = -0.43$ e Å^{-3}

5.3 Crystal data and structure refinement for 2d

Crystal data

$C_{10}H_{12}ClNO_3S$	$F(000) = 544$
$M_r = 261.72$	$D_x = 1.525$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 7.9569$ (5) Å	Cell parameters from 6699 reflections
$b = 10.2188$ (4) Å	$\theta = 3.1–25.0°$
$c = 14.1417$ (10) Å	$\mu = 0.51$ mm^{-1}
$\beta = 97.438$ (7)°	$T = 93$ K
$V = 1140.19$ (12) Å^3	Block, colorless
$Z = 4$	0.15 × 0.15 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID imaging plate diffractometer	2018 independent reflections
Radiation source: fine-focus sealed tube	1309 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.071$
Detector resolution: 10 pixels mm^{-1}	$\theta_{max} = 25.0°$, $\theta_{min} = 3.3°$
ω scans	$h = -9 \rightarrow 9$
Absorption correction: multi-scan Jacobson, R. (1998) Private Communication	$k = -12 \rightarrow 12$
$T_{min} = 0.928$, $T_{max} = 0.951$	$l = -16 \rightarrow 16$
10427 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
$R[F^2 > 2\sigma(F^2)] = 0.036$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.094$	H atoms treated by a mixture of independent and constrained refinement
$S = 0.99$	$w = 1/[\sigma^2(F_o^2) + (0.045P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
2018 reflections	$(\Delta/\sigma)_{max} < 0.001$
148 parameters	$\Delta\rho_{max} = 0.40$ e Å^{-3}
1 restraint	$\Delta\rho_{min} = -0.45$ e Å^{-3}

5.4 Crystal data and structure refinement for 8

Crystal data

$C_5H_8Cl_6N_2O_6S_2$	$F(000) = 936$
$M_r = 468.95$	$D_x = 1.916$ Mg m^{-3}
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
$a = 14.4775$ (15) Å	Cell parameters from 6172 reflections
$b = 10.2636$ (7) Å	$\theta = 3.3–67.6°$
$c = 11.6608$ (9) Å	$\mu = 12.31$ mm^{-1}
$\beta = 110.253$ (8)°	$T = 93$ K
$V = 1625.6$ (2) Å^3	Plate, colorless
$Z = 4$	0.3 × 0.3 × 0.01 mm

Data collection

Rigaku Saturn 944+ CCD diffractometer	2861 independent reflections
Radiation source: fine-focus sealed tube	1883 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.279$
Detector resolution: 22.2 pixels mm^{-1}	$\theta_{max} = 66.6°$, $\theta_{min} = 3.3°$
ω scans	$h = -17\rightarrow17$
Absorption correction: multi-scan Jacobson, R. (1998) Private Communication	$k = -12\rightarrow11$
$T_{min} = 0.460$, $T_{max} = 1.000$	$l = -13\rightarrow13$
43520 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
$R[F^2 > 2\sigma(F^2)] = 0.097$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.285$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.13$	$w = 1/[\sigma^2(F_o^2) + (0.1312P)^2 + 3.3223P]$ where $P = (F_o^2 + 2F_c^2)/3$
2861 reflections	$(\Delta/\sigma)_{max} = 0.001$
198 parameters	$\Delta\rho_{max} = 1.18$ e Å^{-3}
2 restraints	$\Delta\rho_{min} = -0.63$ e Å^{-3}

5.5 Crystal data and structure refinement for 12

Crystal data

$C_{15}H_{22}Cl_3NO_6S$	$F(000) = 936$
$M_r = 450.75$	$D_x = 1.452$ Mg m^{-3}
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
$a = 10.2017$ (2) Å	Cell parameters from 8958 reflections
$b = 13.6673$ (4) Å	$\theta = 3.0–66.6°$
$c = 16.8782$ (14) Å	$\mu = 5.25$ mm^{-1}
$\beta = 118.800$ (5)°	$T = 93$ K
$V = 2062.23$ (19) Å^3	Block, colorless
$Z = 4$	0.3 × 0.3 × 0.2 mm

Data collection

Rigaku Saturn 944+ CCD diffractometer	3583 independent reflections
Radiation source: fine-focus sealed tube	3456 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.063$
Detector resolution: 22.2 pixels mm^{-1}	$\theta_{max} = 66.7°$, $\theta_{min} = 4.4°$
ω scans	$h = -12 \rightarrow 12$
Absorption correction: multi-scan Jacobson, R. (1998) Private Communication	$k = -14 \rightarrow 15$
$T_{min} = 0.703$, $T_{max} = 1.000$	$l = -20 \rightarrow 20$
34944 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
$wR(F^2) = 0.123$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.05$	$w = 1/[\sigma^2(F_o^2) + (0.065P)^2 + 2.8299P]$ where $P = (F_o^2 + 2F_c^2)/3$
3583 reflections	$(\Delta/\sigma)_{max} = 0.001$
243 parameters	$\Delta\rho_{max} = 0.66$ e Å^{-3}
1 restraint	$\Delta\rho_{min} = -0.55$ e Å^{-3}

6. Crystallographic geometric parameters for compounds 2a, 2d, 8 and 12

6.1 Geometric parameters (Å, º) for compound 2a

N1—C4	1.472 (8)	C1—H1A	0.9900
N1—S1	1.561 (6)	C1—H1B	0.9900
N1—H1	0.89 (2)	C2—C3	1.525 (10)
O1—C1	1.404 (9)	C2—H2A	0.9900
O1—C4	1.439 (8)	C2—H2B	0.9900
O2—S1	1.422 (5)	C3—C4	1.488 (8)
O3—S1	1.422 (5)	C3—H3A	0.9900
O4—C5	1.456 (8)	C3—H3B	0.9900
O4—S1	1.559 (6)	C4—H4	1.0000
Cl1—C6	1.740 (7)	C5—C6	1.492 (10)
Cl2—C6	1.780 (7)	C5—H5A	0.9900
Cl3—C6	1.742 (6)	C5—H5B	0.9900
C1—C2	1.488 (9)		

C4—N1—S1	122.5 (4)	C4—C3—H3A	111.5
C4—N1—H1	119 (4)	C2—C3—H3A	111.5
S1—N1—H1	119 (4)	C4—C3—H3B	111.5
C1—O1—C4	109.2 (5)	C2—C3—H3B	111.5
C5—O4—S1	118.8 (4)	H3A—C3—H3B	109.3
O3—S1—O2	121.0 (3)	O1—C4—N1	112.4 (5)
O3—S1—O4	108.7 (3)	O1—C4—C3	105.2 (6)
O2—S1—O4	102.5 (3)	N1—C4—C3	109.8 (5)
O3—S1—N1	108.4 (3)	O1—C4—H4	109.8
O2—S1—N1	110.9 (3)	N1—C4—H4	109.8
O4—S1—N1	103.9 (4)	C3—C4—H4	109.8
O1—C1—C2	106.3 (5)	O4—C5—C6	107.5 (5)
O1—C1—H1A	110.5	O4—C5—H5A	110.2
C2—C1—H1A	110.5	C6—C5—H5A	110.2
O1—C1—H1B	110.5	O4—C5—H5B	110.2
C2—C1—H1B	110.5	C6—C5—H5B	110.2
H1A—C1—H1B	108.7	H5A—C5—H5B	108.5
C1—C2—C3	106.7 (5)	C5—C6—Cl1	110.0 (5)
C1—C2—H2A	110.4	C5—C6—Cl3	109.4 (5)
C3—C2—H2A	110.4	Cl1—C6—Cl3	110.7 (3)
C1—C2—H2B	110.4	C5—C6—Cl2	110.0 (4)
C3—C2—H2B	110.4	Cl1—C6—Cl2	108.0 (4)
H2A—C2—H2B	108.6	Cl3—C6—Cl2	108.7 (3)
C4—C3—C2	101.5 (5)		

C5—O4—S1—O3	-49.1 (5)	C1—O1—C4—C3	-32.4 (6)
C5—O4—S1—O2	-178.2 (4)	S1—N1—C4—O1	78.2 (6)
C5—O4—S1—N1	66.2 (5)	S1—N1—C4—C3	-165.1 (4)
C4—N1—S1—O3	178.7 (4)	C2—C3—C4—O1	32.5 (6)
C4—N1—S1—O2	-46.3 (5)	C2—C3—C4—N1	-88.7 (6)
C4—N1—S1—O4	63.2 (5)	S1—O4—C5—C6	163.5 (4)
C4—O1—C1—C2	17.3 (8)	O4—C5—C6—Cl1	-60.5 (6)
O1—C1—C2—C3	4.1 (8)	O4—C5—C6—Cl3	61.3 (6)
C1—C2—C3—C4	-22.4 (7)	O4—C5—C6—Cl2	-179.4 (4)
C1—O1—C4—N1	87.0 (6)		

6.2 Geometric parameters (Å, º) for compound 2d

S1—O3	1.4297 (18)	C1—H1A	1.0000
S1—O2	1.4377 (19)	C6—C7	1.386 (4)
S1—N1	1.612 (2)	C6—H6	0.9500
S1—C5	1.765 (3)	C2—C3	1.517 (4)
Cl1—C8	1.741 (3)	C2—H2A	0.9900
O1—C1	1.400 (3)	C2—H2B	0.9900
O1—C4	1.435 (4)	C9—H9	0.9500
C8—C7	1.372 (4)	C7—H7	0.9500
C8—C9	1.377 (4)	C3—C4	1.515 (4)
C5—C6	1.379 (3)	C3—H3A	0.9900
C5—C10	1.383 (4)	C3—H3B	0.9900
C10—C9	1.386 (4)	C4—H4A	0.9900
C10—H10	0.9500	C4—H4B	0.9900
C1—N1	1.470 (4)	N1—H1	0.876 (17)
C1—C2	1.514 (4)		

O3—S1—O2	119.17 (12)	C1—C2—H2A	111.3
O3—S1—N1	108.02 (11)	C3—C2—H2A	111.3
O2—S1—N1	105.18 (11)	C1—C2—H2B	111.3
O3—S1—C5	107.68 (12)	C3—C2—H2B	111.3
O2—S1—C5	107.22 (11)	H2A—C2—H2B	109.2
N1—S1—C5	109.30 (12)	C8—C9—C10	118.8 (2)
C1—O1—C4	108.3 (2)	C8—C9—H9	120.6
C7—C8—C9	121.6 (3)	C10—C9—H9	120.6
C7—C8—Cl1	119.0 (2)	C8—C7—C6	119.6 (2)
C9—C8—Cl1	119.4 (2)	C8—C7—H7	120.2
C6—C5—C10	120.6 (2)	C6—C7—H7	120.2
C6—C5—S1	119.9 (2)	C4—C3—C2	104.0 (3)
C10—C5—S1	119.4 (2)	C4—C3—H3A	111.0

C5—C10—C9	120.0 (2)	C2—C3—H3A	111.0
C5—C10—H10	120.0	C4—C3—H3B	111.0
C9—C10—H10	120.0	C2—C3—H3B	111.0
O1—C1—N1	112.5 (2)	H3A—C3—H3B	109.0
O1—C1—C2	105.1 (3)	O1—C4—C3	107.3 (3)
N1—C1—C2	110.3 (2)	O1—C4—H4A	110.3
O1—C1—H1A	109.6	C3—C4—H4A	110.3
N1—C1—H1A	109.6	O1—C4—H4B	110.3
C2—C1—H1A	109.6	C3—C4—H4B	110.3
C5—C6—C7	119.4 (2)	H4A—C4—H4B	108.5
C5—C6—H6	120.3	C1—N1—S1	121.60 (18)
C7—C6—H6	120.3	C1—N1—H1	118 (2)
C1—C2—C3	102.4 (2)	S1—N1—H1	111.8 (19)

O3—S1—C5—C6	-2.4 (3)	C7—C8—C9—C10	0.5 (4)
O2—S1—C5—C6	126.9 (2)	Cl1—C8—C9—C10	-178.6 (2)
N1—S1—C5—C6	-119.5 (2)	C5—C10—C9—C8	-0.7 (4)
O3—S1—C5—C10	179.0 (2)	C9—C8—C7—C6	0.6 (4)
O2—S1—C5—C10	-51.6 (2)	Cl1—C8—C7—C6	179.7 (2)
N1—S1—C5—C10	61.9 (2)	C5—C6—C7—C8	-1.5 (4)
C6—C5—C10—C9	-0.2 (4)	C1—C2—C3—C4	24.9 (3)
S1—C5—C10—C9	178.3 (2)	C1—O1—C4—C3	-16.8 (3)
C4—O1—C1—N1	-86.8 (3)	C2—C3—C4—O1	-6.4 (4)
C4—O1—C1—C2	33.3 (3)	O1—C1—N1—S1	-58.6 (3)
C10—C5—C6—C7	1.3 (4)	C2—C1—N1—S1	-175.6 (2)
S1—C5—C6—C7	-177.3 (2)	O3—S1—N1—C1	-42.0 (2)
O1—C1—C2—C3	-36.0 (3)	O2—S1—N1—C1	-170.3 (2)
N1—C1—C2—C3	85.6 (3)	C5—S1—N1—C1	74.9 (2)

6.3 Geometric parameters (Å, º) for compound 8

C1—N1	1.465 (11)	C4—H4B	0.9900
C1—N2	1.469 (10)	C5—Cl5	1.769 (10)
C1—H1A	0.9900	C5—Cl6	1.770 (10)
C1—H1B	0.9900	C5—Cl4	1.787 (11)
C2—O3	1.423 (11)	N1—S1	1.598 (7)
C2—C3	1.523 (13)	N1—H1	0.91 (2)
C2—H2A	0.9900	N2—S2	1.603 (7)
C2—H2B	0.9900	N2—H2	0.91 (2)
C3—Cl1	1.760 (11)	O1—S1	1.415 (6)
C3—Cl3	1.767 (10)	O2—S1	1.416 (6)
C3—Cl2	1.783 (10)	O3—S1	1.575 (6)
C4—O6	1.437 (11)	O4—S2	1.415 (6)

C4—C5	1.504 (13)	O5—S2	1.425 (5)
C4—H4A	0.9900	O6—S2	1.571 (6)
N1—C1—N2	115.0 (7)	C4—C5—Cl6	110.6 (7)
N1—C1—H1A	108.5	Cl5—C5—Cl6	109.6 (5)
N2—C1—H1A	108.5	C4—C5—Cl4	109.6 (7)
N1—C1—H1B	108.5	Cl5—C5—Cl4	110.3 (5)
N2—C1—H1B	108.5	Cl6—C5—Cl4	109.2 (5)
H1A—C1—H1B	107.5	C1—N1—S1	123.9 (5)
O3—C2—C3	109.0 (7)	C1—N1—H1	130 (7)
O3—C2—H2A	109.9	S1—N1—H1	102 (6)
C3—C2—H2A	109.9	C1—N2—S2	118.7 (5)
O3—C2—H2B	109.9	C1—N2—H2	118 (9)
C3—C2—H2B	109.9	S2—N2—H2	119 (9)
H2A—C2—H2B	108.3	C2—O3—S1	119.0 (6)
C2—C3—Cl1	110.1 (7)	C4—O6—S2	118.5 (5)
C2—C3—Cl3	106.2 (7)	O1—S1—O2	119.7 (4)
Cl1—C3—Cl3	110.8 (5)	O1—S1—O3	101.1 (4)
C2—C3—Cl2	110.1 (7)	O2—S1—O3	110.5 (3)
Cl1—C3—Cl2	109.4 (6)	O1—S1—N1	108.2 (4)
Cl3—C3—Cl2	110.1 (5)	O2—S1—N1	107.5 (4)
O6—C4—C5	109.6 (7)	O3—S1—N1	109.6 (4)
O6—C4—H4A	109.7	O4—S2—O5	121.0 (4)
C5—C4—H4A	109.7	O4—S2—O6	103.0 (3)
O6—C4—H4B	109.7	O5—S2—O6	109.3 (3)
C5—C4—H4B	109.7	O4—S2—N2	110.3 (4)
H4A—C4—H4B	108.2	O5—S2—N2	106.9 (3)
C4—C5—Cl5	107.5 (6)	O6—S2—N2	105.2 (3)
O3—C2—C3—Cl1	-61.6 (9)	C2—O3—S1—O2	41.2 (7)
O3—C2—C3—Cl3	178.4 (6)	C2—O3—S1—N1	-77.1 (7)
O3—C2—C3—Cl2	59.2 (9)	C1—N1—S1—O1	-154.7 (6)
O6—C4—C5—Cl5	176.2 (6)	C1—N1—S1—O2	-24.2 (7)
O6—C4—C5—Cl6	56.5 (9)	C1—N1—S1—O3	95.9 (7)
O6—C4—C5—Cl4	-63.9 (8)	C4—O6—S2—O4	175.6 (6)
N2—C1—N1—S1	-102.0 (8)	C4—O6—S2—O5	45.8 (6)
N1—C1—N2—S2	-78.3 (8)	C4—O6—S2—N2	-68.7 (6)
C3—C2—O3—S1	-136.6 (7)	C1—N2—S2—O4	35.2 (7)
C5—C4—O6—S2	142.8 (6)	C1—N2—S2—O5	168.5 (6)
C2—O3—S1—O1	168.9 (6)	C1—N2—S2—O6	-75.3 (6)

6.4 Geometric parameters (Å, º) for compound 12

C1—N1	1.490 (3)	C9—C10	1.383 (4)
C1—C7	1.512 (3)	C9—H9	0.9500
C1—C2	1.529 (3)	C10—O6	1.375 (3)
C1—H1A	1.0000	C10—C11	1.392 (4)
C2—C3	1.522 (4)	C11—C12	1.392 (4)
C2—H2A	0.9900	C11—H11	0.9500
C2—H2B	0.9900	C12—O4	1.368 (3)
C3—C4	1.522 (4)	C13—O5	1.428 (3)
C3—H3A	0.9900	C13—H13A	0.9800
C3—H3B	0.9900	C13—H13B	0.9800
C4—H4A	0.9800	C13—H13C	0.9800
C4—H4B	0.9800	C14—O6	1.430 (3)
C4—H4C	0.9800	C14—H14A	0.9800
C5—O3	1.438 (3)	C14—H14B	0.9800
C5—C6	1.520 (4)	C14—H14C	0.9800
C5—H5A	0.9900	C15—O4	1.431 (3)
C5—H5B	0.9900	C15—H15A	0.9800
C6—Cl3	1.764 (3)	C15—H15B	0.9800
C6—Cl2	1.765 (3)	C15—H15C	0.9800
C6—Cl1	1.773 (3)	N1—S1	1.5936 (19)
C7—C8	1.394 (3)	N1—H1	0.883 (18)
C7—C12	1.406 (3)	O1—S1	1.4175 (18)
C8—O5	1.375 (3)	O2—S1	1.4305 (18)
C8—C9	1.400 (3)	O3—S1	1.6010 (18)

N1—C1—C7	111.77 (19)	C10—C9—H9	121.1
N1—C1—C2	109.02 (19)	C8—C9—H9	121.1
C7—C1—C2	114.2 (2)	O6—C10—C9	123.6 (2)
N1—C1—H1A	107.2	O6—C10—C11	114.6 (2)
C7—C1—H1A	107.2	C9—C10—C11	121.8 (2)
C2—C1—H1A	107.2	C10—C11—C12	118.9 (2)
C3—C2—C1	113.6 (2)	C10—C11—H11	120.6
C3—C2—H2A	108.9	C12—C11—H11	120.6
C1—C2—H2A	108.9	O4—C12—C11	123.4 (2)
C3—C2—H2B	108.9	O4—C12—C7	115.0 (2)
C1—C2—H2B	108.9	C11—C12—C7	121.5 (2)
H2A—C2—H2B	107.7	O5—C13—H13A	109.5
C4—C3—C2	112.6 (2)	O5—C13—H13B	109.5
C4—C3—H3A	109.1	H13A—C13—H13B	109.5
C2—C3—H3A	109.1	O5—C13—H13C	109.5
C4—C3—H3B	109.1	H13A—C13—H13C	109.5

C2—C3—H3B	109.1	H13B—C13—H13C	109.5
H3A—C3—H3B	107.8	O6—C14—H14A	109.5
C3—C4—H4A	109.5	O6—C14—H14B	109.5
C3—C4—H4B	109.5	H14A—C14—H14B	109.5
H4A—C4—H4B	109.5	O6—C14—H14C	109.5
C3—C4—H4C	109.5	H14A—C14—H14C	109.5
H4A—C4—H4C	109.5	H14B—C14—H14C	109.5
H4B—C4—H4C	109.5	O4—C15—H15A	109.5
O3—C5—C6	109.4 (2)	O4—C15—H15B	109.5
O3—C5—H5A	109.8	H15A—C15—H15B	109.5
C6—C5—H5A	109.8	O4—C15—H15C	109.5
O3—C5—H5B	109.8	H15A—C15—H15C	109.5
C6—C5—H5B	109.8	H15B—C15—H15C	109.5
H5A—C5—H5B	108.3	C1—N1—S1	120.16 (16)
C5—C6—Cl3	107.68 (18)	C1—N1—H1	119 (2)
C5—C6—Cl2	111.0 (2)	S1—N1—H1	114 (2)
Cl3—C6—Cl2	109.47 (14)	C5—O3—S1	117.56 (15)
C5—C6—Cl1	111.26 (18)	C12—O4—C15	117.1 (2)
Cl3—C6—Cl1	108.97 (15)	C8—O5—C13	117.96 (19)
Cl2—C6—Cl1	108.44 (15)	C10—O6—C14	117.7 (2)
C8—C7—C12	117.1 (2)	O1—S1—O2	119.96 (11)
C8—C7—C1	122.4 (2)	O1—S1—N1	110.26 (11)
C12—C7—C1	120.5 (2)	O2—S1—N1	107.66 (10)
O5—C8—C7	114.5 (2)	O1—S1—O3	102.45 (10)
O5—C8—C9	122.7 (2)	O2—S1—O3	108.22 (10)
C7—C8—C9	122.8 (2)	N1—S1—O3	107.62 (10)
C10—C9—C8	117.8 (2)		

N1—C1—C2—C3	-63.6 (3)	C10—C11—C12—C7	-2.4 (4)
C7—C1—C2—C3	170.6 (2)	C8—C7—C12—O4	-178.5 (2)
C1—C2—C3—C4	-177.2 (3)	C1—C7—C12—O4	0.3 (3)
O3—C5—C6—Cl3	-179.56 (17)	C8—C7—C12—C11	1.7 (3)
O3—C5—C6—Cl2	60.6 (3)	C1—C7—C12—C11	-179.5 (2)
O3—C5—C6—Cl1	-60.2 (3)	C7—C1—N1—S1	-96.8 (2)
N1—C1—C7—C8	-59.6 (3)	C2—C1—N1—S1	135.95 (18)
C2—C1—C7—C8	64.7 (3)	C6—C5—O3—S1	127.25 (19)
N1—C1—C7—C12	121.6 (2)	C11—C12—O4—C15	5.5 (3)
C2—C1—C7—C12	-114.0 (3)	C7—C12—O4—C15	-174.4 (2)
C12—C7—C8—O5	-179.0 (2)	C7—C8—O5—C13	177.3 (2)
C1—C7—C8—O5	2.2 (3)	C9—C8—O5—C13	-2.1 (4)
C12—C7—C8—C9	0.4 (4)	C9—C10—O6—C14	-16.1 (4)
C1—C7—C8—C9	-178.4 (2)	C11—C10—O6—C14	164.9 (2)

O5—C8—C9—C10	177.7 (2)	C1—N1—S1—O1	-46.9 (2)
C7—C8—C9—C10	-1.7 (4)	C1—N1—S1—O2	-179.46 (17)
C8—C9—C10—O6	-178.0 (2)	C1—N1—S1—O3	64.09 (19)
C8—C9—C10—C11	1.0 (4)	C5—O3—S1—O1	179.96 (18)
O6—C10—C11—C12	-179.9 (2)	C5—O3—S1—O2	-52.4 (2)
C9—C10—C11—C12	1.0 (4)	C5—O3—S1—N1	63.7 (2)
C10—C11—C12—O4	177.8 (2)		

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