Combining Organometallic Reagents, the Sulfur Dioxide Surrogate DABSO, and Amines: A One-Pot Preparation of Sulfonamides, Amenable to Array Synthesis**

Alex S. Deeming, Claire J. Russell, and Michael C. Willis*

anie_201409283_sm_misellaneous_information.pdf
Supporting Information

1. Experimental
   1.1 General Considerations..........................................................................................S2
   1.2 Initial screening and optimisation for formation of sulfonamide (2) using morpholine and sodium hypochlorite..............................................................................................S3
   1.3 Characterisation data for compounds prepared in Tables 2 and 3.............................S3
2. Array Synthesis...........................................................................................................S17
   2.1 Sulfonamide Data from Array Synthesis.................................................................S18
3. References..................................................................................................................S33
4. NMR Spectra – General Scope..................................................................................S34
5. Chiral HPLC..............................................................................................................S63
6. NMR Spectra – Array Synthesis................................................................................S67
7. LC-MS – Array Synthesis.........................................................................................S75
8. Fungicide, Herbicide and Insecticide Assay..............................................................S261
Experimental

1.1 General considerations

Chemicals were purchased from Sigma Aldrich, Alfa Aesar or Acros and used without further purification with the exception of DABCO which was sublimed (50 °C, 1 mbar) prior to use and starting materials for organometallic reagent preparation were purified by distillation or re-crystallisation as appropriate. All solvents were purchased from Sigma Aldrich, Fisher Scientific or Rathburn and used directly without further purification. ‘Petrol’ refers to the fraction of light petroleum ether boiling in the range 40-60 °C. DABSO was prepared from DABCO and SO₂ gas as described in a previous Willis group publication.¹ DABSO was dried under vacuum (10 mbar) for 20 minutes prior to use. 4-Trimethylsilylbromobenzene² and 2-(4-bromobenzyl)-2-methyl-1,3-dioxolane³ were prepared according to literature procedures. Grignard reagents were titrated with salicylaldehyde phenylhydrazone prior to use. Organolithium reagents were titrated against a 1.0 M solution of 2-propanol in toluene with 0.2% 1,10-phenanthroline as the indicator prior to use. The concentration of aqueous sodium hypochlorite was determined by standard sodium thiosulfate/iodine titration.

Reactions were performed with continuous magnetic stirring, under an atmosphere of nitrogen (passed through a Drierite® filled tube), unless otherwise stated, using standard Schlenk techniques and all glassware was dried in an oven (>200 °C, overnight) and allowed to cool under vacuum (10 mbar) prior to use. Microwave heating was carried out using a CEM Discover-S unit. Flash column chromatography was performed using Apollo scientific silica gel 60 (particle size 0.040-0.063 nm) with the indicated eluents. Crude reaction mixtures were dry-loaded and pressure was applied at the column head with hand bellows. Thin Layer Chromatography (TLC) analysis was carried out on Merck Kieselgel 60 PF254 pre-coated aluminium backed sheets and visualised either by UV fluorescence (254 nm) and/or by staining with potassium permanganate (KMnO₄).

NMR spectra were recorded at ambient temperature on a Bruker DPX400 (400 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) and referenced relative to the residual solvent peak(s) (as specified). Coupling constants (J) are given in Hertz (Hz) and rounded to the nearest 0.5 Hz. Assignments were made on the basis of chemical shifts, coupling constants, COSY, HSQC and comparison with spectra of related compounds. Signal multiplicities are denoted as: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sext, sextet; m, multiplet; br, broad; app, apparent. multiplicities are reported as observed.

Melting points were measured using a Leica Gallen III hot-stage microscope. Low resolution mass spectra were recorded on a Fisons Platform spectrometer (ESI). High resolution mass spectra were measured by the internal service at the University of Oxford using a Bruker Daltronics microTOF spectrometer. m/z ratio values are reported in Daltons; high resolution values are calculated to four decimal places from the molecular formula, all found within a tolerance of 5 ppm. Infrared spectra were
determined neat using a Bruker Tensor 27 FT spectrometer with an internal range of 600-4000 cm⁻¹. Enantiomeric excess (ee) was determined by HPLC using a Chiralpak AD-H column.

1.2 Initial screening and optimisation for formation of sulfonamide (2) using morpholine and sodium hypochlorite

![Chemical Structure](image)

**Reaction conditions:**
- DABSO (0.6 equiv.)
- THF
- -40 °C to rt
- 3-MeO-C6H4-MgBr (1 equiv.), DABSO (0.6 equiv.), THF
- 40 °C then amine, solvent and NaOCl at 0 °C, followed by overnight stirring at rt
- [b] 2.0 equiv. of DMAP added; [c] 4.0 equiv. of pyridine added.

| Entry | Solvent               | Amine equiv. | NaOCl equiv. | Yield |
|-------|-----------------------|--------------|--------------|-------|
| 1     | THF/H2O 1:1           | 2.0          | 1.2          | 38%   |
| 2     | H2O                   | 2.0          | 1.2          | 51%   |
| 3     | H2O                   | 3.0          | 2.0          | 60%   |
| 4     | H2O                   | 4.0          | 2.0          | 66%   |
| 5     | H2O                   | 5.0          | 3.0          | 78%   |
| 6     | H2O                   | 5.0          | 4.0          | 78%   |
| 7     | H2O                   | 7.5          | 5.0          | 79%   |
| 8     | H2O                   | 5.0          | 3.0          | 79%   |
| 9     | H2O                   | 5.0          | 3.0          | 73%   |
| 10    | THF/H2O 1:1           | 5.0          | 3.0          | 67%   |

[a] Reaction conditions: 3-MeO-C6H4-MgBr (1 equiv.), DABSO (0.6 equiv.), THF -40 °C then amine, solvent and NaOCl at 0 °C, followed by overnight stirring at rt; [b] 2.0 equiv. of DMAP added; [c] 4.0 equiv. of pyridine added.

1.3 Characterisation data for compounds prepared in Tables 2 and 3

**General procedure for the synthesis of sulfonamides from organometallic reagent, DABSO, NaOCl and amines, as exemplified by the preparation of 4-[(3-methoxyphenyl)sulfonyl]morpholine**

To a reaction tube was added DABSO (36 mg, 0.15 mmol) and THF (1 mL) and the resulting suspension flushed with nitrogen gas for 2 mins. After cooling to -40 °C 3-methoxyphenylmagnesium bromide (0.97 M in THF, 258 µL, 0.25 mmol) was added dropwise and the mixture stirred at this temp for 30 mins. On warming to room temp a strong flow of nitrogen gas was applied to remove the solvent before addition of water (1.5 mL) and morpholine (109 µL, 1.25 mmol). The resulting mixture was cooled to 0-5 °C (ice-water bath) and NaOCl (15.8% aqueous solution, 296 µL, 0.75 mmol) was added dropwise before allowing the reaction to warm to room temp (Note: addition of NaOCl to mixtures containing anilines results in coloured oxidation products which can be flushed off with 100% CH2Cl2 on chromatography). After stirring for 16 hrs, sat. Na2S2O3(aq) (10 mL) was added and the mixture stirred for a further 20 mins. The aqueous mixture was then extracted with CH2Cl2 (3 × 15 mL) and the combined organic extracts subsequently washed with 1M HCl(aq) (1 × 30 mL). The organic layer was dried (MgSO4), filtered and the solvent removed in vacuo. Purification by flash column chromatography (petrol/Et2O 3:2) afforded the
titled sulfonamide as a white solid (50 mg, 79%); mp 128-129 °C (CH₂Cl₂) [lit.⁴ mp 132 °C]; ¹H NMR (400 MHz, CDCl₃) δ 7.40 (app t, J 8.0, 1H, Ar-H), 7.26 (d, J 8.0, 1H, Ar-H) 7.18 (app t, J 2.0, 1H, Ar-H); 7.08 (dd, J 8.0, 1.5, 1.0, 1H, Ar-H); 3.80 (s, 3H, OMe); 3.68 (t, J 4.5, 4H, NCH₂CH₂); 2.95 (t, J 4.5, 4H, NCH₂CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 160.0, 136.2, 130.2, 120.0, 119.1, 112.8, 66.1, 55.7, 46.0; IR νmax (neat)/cm⁻¹ 2986, 1582, 1426, 1336 (SO₂); LRMS (ESI) m/z 221 (10%, [M+H]⁺), 244 (100%, [M+Na]⁺); HRMS (ESI) found m/z 244.0976 [M+Na]⁺, C₈H₁₅NO₃SNa requires m/z 244.0978.

4-(Butylsulfonyl)morpholine (Entry 1, Table 2)

Prepared according to general procedure using n-butylmagnesium chloride (2.1 M, 119 µL, 0.25 mmol). Flash column chromatography (petrol/Et₂O 2:3) afforded the titled sulfonamide as a white solid (42 mg, 82%); mp 42-43 °C (CH₂Cl₂) [lit.⁵ mp 40-45 °C]; ¹H NMR (400 MHz, CDCl₃) δ 3.69 (t, J 4.5, 4H, NCH₂CH₂), 3.20 (t, J 4.5, 4H, NCH₂CH₂), 2.84 (t, J 8.0, 2H, SCh₂), 1.78-1.70 (m, 2H, SCh₂CH₂), 1.40 (sext., J 7.5, 2H, CH₂CH₃), 0.89 (t, J 7.5, 3H, CH₃CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 66.6, 48.6, 45.8, 24.9, 21.8, 13.6; IR νmax (neat)/cm⁻¹ 2965, 2863, 1454, 1322 (SO₂); LRMS (ESI) m/z 230 (70%, [M+H]⁺), 230 (100%, [M+Na]⁺); HRMS (ESI) found m/z 230.0830 [M+Na]⁺, C₈H₁₅NO₃SNa requires m/z 230.0821. Data in accordance with that previously reported.⁵

4-(Pentylsulfonyl)morpholine (Entry 4, Table 2)

Prepared according to general procedure using n-pentylzinc bromide (0.50 M, 250 µL, 0.25 mmol). The aqueous acid wash gave the pure titled sulfonamide as an off-white solid (36 mg, 64%) without further purification; mp 39-40 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 3.69 (t, J 4.5, 4H, NCH₂CH₂), 3.20 (t, J 4.5, 4H, NCH₂CH₂), 2.84 (t, J 8.0, 2H, SCh₂), 1.80-1.72 (m, 2H, SCh₂CH₂), 1.38-1.24 (m, 4H, CH₂CH₂CH₂), 0.85 (t, J 7.0, 3H, CH₃CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 66.6, 48.8, 45.8, 30.6, 22.6, 22.2, 13.8; IR νmax (neat)/cm⁻¹ 2965, 2863, 1454, 1322 (SO₂), 1259, 1110 (SO₂); LRMS (ESI) m/z 221 (10%, [M+H]⁺), 244 (100%, [M+Na]⁺); HRMS (ESI) found m/z 244.0976 [M+Na]⁺, C₉H₁₈NO₃SNa requires m/z 244.0978.
4-[(4-methoxyphenyl)sulfonyl]morpholine (Entry 5, Table 2)

Prepared according to general procedure using 4-methoxyphenylmagnesium bromide (0.51 M in THF, 490 µL, 0.25 mmol). Flash column chromatography (petrol/Et₂O 1:1) afforded the titled sulfonamide as an off-white solid (55 mg, 86%); mp 109-110 °C (CH₂Cl₂) [lit. mp 110-111 °C]; ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, J 9.0, 2H, Ar-H), 6.95 (d, J 9.0, 2H, Ar-H), 3.82 (s, 3H, OMe), 3.68 (t, J 4.5, 4H, NCH₂C₆H₄), 2.91 (t, J 4.5, 4H, NCH₂CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 163.3, 130.0, 126.7, 114.3, 66.1, 55.7, 46.0; LRMS (ESI) m/z 258 (90%, [M+H]+), 280 (100%, [M+Na]+); HRMS (ESI) found m/z 280.0606 [M+Na]+, C₁₁H₁₅N₄O₄SNa requires m/z 280.0614. Data in accordance with that previously reported.⁶

4-[(2-methoxyphenyl)sulfonyl]morpholine (Entry 6, Table 2)

Prepared according to general procedure using 2-methoxyphenylmagnesium bromide (1.0 M in THF, 250 µL, 0.25 mmol). Flash column chromatography (petrol/Et₂O 2:3) afforded the titled sulfonamide as an off-white solid (54 mg, 84%); mp 85-86 °C (CH₂Cl₂) [lit. mp 86-87 °C]; ¹H NMR (400 MHz, CDCl₃) δ 7.89 (dd, J 4.0, 1.5, 1H, Ar-H), 7.55-7.51 (m, 1H, Ar-H), 7.06-7.02 (m, 2H, Ar-H), 3.93 (s, 3H, OMe), 3.72 (t, J 4.5, 4H, NCH₂CH₂), 3.24 (t, J 4.5, 4H, NCH₂CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 157.0, 134.8, 131.9, 125.8, 120.5, 112.4, 66.8, 56.0, 46.1; LRMS (ESI) m/z 258 (20%, [M+H]+), 280 (20%, [M+Na]+), 537 (100%, [2M+Na]+); HRMS (ESI) found m/z 280.0621 [M+Na]+, C₁₁H₁₅NO₄SNa requires m/z 280.0614. Data in accordance with that previously reported.⁶

4-[(1,1′-biphenyl)-4-ylsulfonyl]morpholine (Entry 7, Table 2)

Prepared according to general procedure using (1,1′-biphenyl)-4-ylmagnesium bromide (0.25 mmol). The aryl Grignard reagent was generated in situ by dropwise addition of cyclopentylmagnesium chloride (2.0
M, 150 μL, 0.30 mmol) to a solution of 4-iodobiphenyl (70 mg, 0.25 mmol) in THF (1 mL) at -40 °C. The solution was allowed to warm to room temp and was stirred for 1 h before use. Flash column chromatography (petrol/Et₂O 2:3) afforded the titled sulfonamide as an off-white solid (54 mg, 71%); mp 206-207 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J 8.5, 2H, Ar-H), 7.68 (d, J 8.5, 2H, Ar-H), 7.56-7.53 (m, 2H, Ar-H), 7.46-7.40 (m, 2H, Ar-H), 3.70 (t, J 4.5, 4H, NCH₂C₂H₅), 2.98 (t, J 4.5, 4H, NCH₂CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 146.1, 139.2, 133.6, 129.1, 128.6, 128.4, 127.8, 127.4, 66.1, 46.0; IR νmax (neat)/cm⁻¹ 1451, 1346, 1330 (SO₂), 1261, 1108 (SO₂); LRMS (ESI) m/z 304 (60%, [M+H]+), 326 (100%, [M+Na]+), 629 (60%, [2M+Na]⁺); HRMS (ESI) found m/z 326.0822 [M+Na]+, C₁₆H₁₇NO₃SNa requires m/z 326.0821.

4-[(4-chlorophenyl)sulfonyl]morpholine (Entry 8, Table 2)

Prepared according to general procedure using 4-chlorophenylmagnesium bromide (1.0 M in THF, 250 μL, 0.25 mmol). Flash column chromatography (petrol/Et₂O 2:3) afforded the titled sulfonamide as an off-white solid (43 mg, 68%); mp 143-144 °C (CH₂Cl₂) [lit.⁷ mp 146-147 °C]; ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, J 8.5, 2H, Ar-H), 7.47 (d, J 8.5, 2H, Ar-H), 3.68 (t, J 4.5, 4H, NCH₂C₂H₅), 2.93 (t, J 4.5, 4H, NCH₂CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 139.8, 133.7, 129.5, 129.2, 66.1, 45.9; LRMS (ESI) m/z 284 (100%, [M+Na]+); HRMS (ESI) found m/z 262.0296 [M+H]+, C₁₀H₁₃ClNO₃S requires m/z 262.0299. Data in accordance with that previously reported.⁷

Methyl 4-(morpholinosulfonyl)benzoate (Entry 9, Table 2)

Prepared according to general procedure using 4-[(methoxycarbonyl)phenyl]magnesium bromide (0.25 mmol). The aryl Grignard solution was prepared in situ by dropwise addition of isopropylmagnesium bromide (1.85M in THF, 151 μL, 0.28 mmol) to a solution of methyl-4-iodobenzoate (66 mg, 0.25 mmol) in THF (0.8 mL) at -40 °C. The solution was stirred at this temp for 1 h before being transferred via syringe to a DABSO-THF suspension. Flash column chromatography (petrol/Et₂O 2:3) afforded the titled sulfonamide as an off-white solid (36 mg, 51%); mp 143-144 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, J 8.5, 2H, Ar-H), 7.84 (d, J 8.5, 2H, Ar-H), 3.98 (s, 3H, CO₂Me), 3.76 (t, J 4.5, 4H, NCH₂CH₂), 3.03 (t, J 4.5, 4H, NCH₂CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 160.0, 130.2, 120.0, 119.1, 112.8, 66.1,
55.7, 46.0; IR $\nu_{\text{max}}$ (neat)/cm$^{-1}$ 2849, 1726 (CO), 1450, 1349 (SO$_2$), 1260, 1110 (SO$_2$); LRMS (ESI) $m/z$ 286 (30%, [M+H$^+$]), 308 (100%, [M+Na$^+$]); HRMS (ESI) found $m/z$ 308.0559 [M+Na$^+$], C$_{12}$H$_{13}$NO$_3$SNa requires $m/z$ 308.0563.

4-[4-(Trimethylsilyl)phenylsulfonyl]morpholine (Entry 10, Table 2)

Prepared according to general procedure using 4-[[trimethylsilyl]phenyl]lithium (0.25 mmol). The aryl lithium solution was generated in situ by dropwise addition of n-butyllithium (1.78 M in hexane, 157 $\mu$L, 0.28 mmol) to a solution of 4-trimethylsilyl bromobenzene (57 mg, 0.25 mmol) in THF (0.8 mL) at -78 °C. The solution was stirred at this temp for 1 h before being transferred via syringe to a DABSO-THF suspension. Flash column chromatography (petrol/Et$_2$O 1:1) afforded the titled sulfonamide as an off-white solid (54 mg, 72%); mp 144 °C (CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.65-7.60 (m, 4H, Ar-H), 3.68 (t, $J$ 4.5, 4H, NCH$_2$CH$_2$), 2.94 (t, $J$ 4.5, 4H, NCH$_2$CH$_2$) 0.23 (s, 9H, SiMe$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 148.9, 136.5, 135.3, 128.1, 67.5, 47.3, 0.0; IR $\nu_{\text{max}}$ (neat)/cm$^{-1}$ 1449, 1348 (SO$_2$), 1259, 1111 (SO$_2$), 1085; LRMS (ESI) $m/z$ 300 (100%, [M+H$^+$]), 322 (60%, [M+Na$^+$]), 621 (40%, [2M+Na$^+$]) ; HRMS (ESI) found $m/z$ 322.0906 [M+Na$^+$], C$_{13}$H$_{12}$NO$_3$SSiNa requires $m/z$ 322.0904.

4-[(4-(2-Methyl-1,3-dioxolan-2-yl)methyl)phenylsulfonyl]morpholine (Entry 11, Table 2)

Prepared according to general procedure using 4-[[2-methyl-1,3-dioxolan-2-yl)methyl]phenyl]lithium (0.25 mmol). The aryl lithium solution was generated in situ by dropwise addition of n-butyllithium (1.8 M in hexane, 153 $\mu$L, 0.28 mmol) to a solution of 2-(4-bromobenzyl)-2-methyl-1,3-dioxolane (64 mg, 0.25 mmol) in THF (0.8 mL) at -78 °C. The solution was stirred at this temp for 1 h before being transferred via syringe to a DABSO-THF suspension. Flash column chromatography (petrol/Et$_2$O 2:3) afforded the titled sulfonamide as an off-white solid (59 mg, 62%); mp 115-116 °C (CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (d, $J$ 8.5, 2H, Ar-H), 7.40 (d, $J$ 8.5, 2H, Ar-H), 3.85-3.82 (m, 2H, COCH$_2$), 3.68 (t, $J$ 4.5, 4H, NCH$_2$CH$_2$), 3.62-3.59 (m, 2H, COCH$_2$), 2.94 (s, 2H, CCH$_2$), 2.92 (t, $J$ 4.5, 4H, NCH$_2$CH$_2$), 1.26 (s, 3H, CMe); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.8, 133.0, 131.3, 127.5, 109.2, 66.1, 64.9, 46.0, 45.2, 24.7; IR $\nu_{\text{max}}$ (neat)/cm$^{-1}$ 1408, 1329 (SO$_2$), 1224, 1111 (SO$_2$), 1038; LRMS (ESI) $m/z$ 328 (100%, [M+H$^+$]), 350 (20%, [M+Na$^+$]); HRMS (ESI) found $m/z$ 350.1032 [M+Na$^+$], C$_{15}$H$_{21}$NO$_3$SNa requires $m/z$ 350.1033.
**Ethyl 4-(morphinosulfonyl)benzoate** (Entry 12, Table 2)

![Ethyl 4-(morphinosulfonyl)benzoate](image)

Prepared according to the general procedure using 4-[(ethoxycarbonyl)phenyl]zinc iodide. Flash column chromatography (CH$_2$Cl$_2$/Et$_2$O 0-5%) afforded the titled sulfonamide as an off-white solid (46 mg, 62%); mp 82-83 °C (CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.15 (d, J = 8.5, 2H, Ar-H), 7.75 (d, J = 8.5, 2H, Ar-H), 4.38 (q, J = 7.0, 2H, OCH$_2$CH$_3$), 3.68 (t, J = 4.5, 4H, NCH$_2$C$_2$H$_5$), 2.95 (t, J = 4.5, 4H, NCH$_2$CH$_3$), 1.36 (t, J = 7.0, 3H, OCH$_2$C$_2$H$_5$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.1, 139.1, 134.6, 130.3, 127.8, 66.1, 61.8, 46.0, 14.3; IR ν$_{max}$ (neat)/cm$^{-1}$ 2855, 1713 (CO), 1451, 1296 (SO$_2$), 1273, 1108 (SO$_2$); LRMS (ESI) m/z 300 (20%, [M+H]$^+$), 322 (100%, [M+Na]$^+$); HRMS (ESI) found m/z 300.0897 [M+H]$^+$, C$_{13}$H$_{18}$NO$_5$S requires m/z 300.0900.

**4-(Thiophen-2-ylsulfonyl)morpholine** (Entry 13, Table 2)

![4-(Thiophen-2-ylsulfonyl)morpholine](image)

Prepared according to general procedure using 2-thienylmagnesium bromide (0.85 M in THF, 294 µL, 0.25 mmol). Flash column chromatography (petrol/Et$_2$O 2:3) afforded the titled sulfonamide as an off-white solid (52 mg, 89%); mp 102-103 °C (CH$_2$Cl$_2$) [lit. mp 104-105 °C]; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.59 (dd, J = 5.0, 1.5, 1H, Ar-H), 7.48 (dd, J = 3.5, 1.5, 1H, Ar-H), 7.11 (dd, J = 5.0, 3.5, 1H, Ar-H), 3.71 (t, J = 4.5, 4H, NCH$_2$CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 135.4, 132.8, 132.5, 127.8, 66.0, 46.0; IR ν$_{max}$ (neat)/cm$^{-1}$ 1450, 1401, 1299 (SO$_2$), 1220, 1112 (SO$_2$); LRMS (ESI) m/z 234 (10%, [M+H]$^+$), 256 (100%, [M+Na]$^+$); HRMS (ESI) found m/z 256.0078 [M+Na]$^+$, C$_8$H$_{11}$NO$_3$S$_2$Na requires m/z 256.0073. Data in accordance with that previously reported.

**4-[(1-Methyl-1H-indol-2-yl)sulfonyl]morpholine** (Entry 15, Table 2)

![4-[(1-Methyl-1H-indol-2-yl)sulfonyl]morpholine](image)

Prepared according to general procedure using 2-lithio-N-methylindole (0.31 M in THF, 806 µL, 0.25 mmol). The aryl lithium was prepared as a stock solution by dropwise addition of t-butyllithium (1.88 M in hexane, 2.34 mL, 4.40 mmol) to a solution of N-methylindole (500 µL, 4.0 mmol) in THF (10 mL) at -78 °C. The mixture was then warmed to room temp and stirred for 1 h before use. Flash column
chromatography (petrol/Et₂O 2:3) afforded the titled sulfonyamide as an off-white solid (46 mg, 65%); mp 123-124 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, J 8.0, 1H, Ar-H), 7.37-7.30 (m, 2H, Ar-H), 7.14 (ddd, J 8.0, 6.0, 2.0, 1H, Ar-H), 7.09 (s, 1H, Ar-H), 3.91 (s, 3H, NMe), 3.67 (t, J 4.5, 4H, NCH₂C₂H₅), 3.11 (t, J 4.5, 4H, NCH₂C₂H₅); ¹³C NMR (100 MHz, CDCl₃) δ 139.4, 130.2, 125.6, 125.1, 122.6, 121.3, 111.0, 110.4, 46.3, 31.6; IR νmax (neat)/cm⁻¹ 2855, 1502, 1451, 1349 (SO₂), 1260, 1112 (SO₂); LRMS (ESI) m/z 281 (40%, [M+H]⁺), 303 (100%, [M+Na]⁺), 583 (80%, [2M+Na]⁺); HRMS (ESI) found m/z 303.0774 [M+Na]+, C₁₃H₁₆N₂O₃SNa requires m/z 303.0774.

4-(Prop-1-en-2-ylsulfonyl)morpholine (Entry 16, Table 2)

Prepared according to general procedure using isopropenylmagnesium bromide (0.52 M, 480 µL, 0.25 mmol). The acid wash afforded the pure titled sulfonyamide as a clear oil (24 mg, 50%) without further purification; ¹H NMR (400 MHz, CDCl₃) δ 5.91 (m, 1H, CH₂CMe), 5.64 (app q, J 1.5, 1H, CH₂CMe), 3.68 (t, J 4.5, 4H, NCH₂C₂H₅), 3.15 (t, J 4.5, 4H, NC₂H₅), 2.00 (dd, J 1.5, 1.0, CH₂CMe); ¹³C NMR (100 MHz, CDCl₃) δ 142.69, 124.7, 66.6, 45.7, 17.7; IR νmax (neat)/cm⁻¹ 2859, 1449, 1338 (SO₂), 1261, 1219, 1113 (SO₂); LRMS (ESI) m/z 214 (100%, [M+Na]⁺); HRMS (ESI) found m/z 192.0688 [M+H]⁺, C₇H₁₄NO₃S requires m/z 192.0689.

N-[(3-Methoxyphenyl)sulfonyl]pyrrolidine (Entry 1, Table 3)

Prepared according to general procedure using 3-methoxyphenylmagnesium bromide (0.97 M in THF, 258 µL, 0.25 mmol) and pyrrolidine (104 µL, 1.25 mmol). Flash column chromatography (petrol/Et₂O 2:3) afforded the titled sulfonyamide as an off-white solid (47 mg, 79%); mp 117-118 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.39-7.32 (m, 2H, Ar-H), 7.28-7.26 (m, 1H, Ar-H), 7.04 (app dt, J 7.5, 2.0, 1H, Ar-H), 3.80 (s, 3H, OMe), 3.21-3.17 (m, 4H, NCH₂C₂H₅), 1.72-1.68 (m, 4H, NCH₂C₂H₅); ¹³C NMR (100 MHz, CDCl₃) δ 159.9, 138.1, 130.1, 119.6, 118.8, 112.4, 55.7, 48.0, 25.3; IR νmax (neat)/cm⁻¹ 2977, 1591, 1477, 1333 (SO₂), 1287, 1152 (SO₂); LRMS (ESI) m/z 242 (20%, [M+H]⁺), 264 (10%, [M+Na]⁺), 505 (100%, [2M+Na]⁺); HRMS (ESI) found m/z 264.0667 [M+Na]⁺, C₁₁H₁₄NO₃SNa requires m/z 264.0665.
(S)-Methyl-N-[(3-methoxyphenyl)sulfonyl]-pyrrolidine-2-carboxylate (Entry 2, Table 3)

![Chemical Structure](image)

Prepared according to general procedure using 3-methoxyphenylmagnesium bromide (0.97 M in THF, 258 µL, 0.25 mmol) and (L)-proline methyl ester hydrochloride (207 mg, 1.25 mmol). Flash column chromatography (petrol/EtO 1:3) afforded the titled sulfonamide as a light yellow oil (51 mg, 68%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.40-7.36 (m, 2H, Ar-H), 7.34-7.32 (m, 1H, Ar-H), 7.05 (app dt, \(J\) 7.5, 2.0, 1H, Ar-H), 4.26 (dd, \(J\) 8.0, 4.0, 1H, NCH\(_2\)Me), 3.80 (s, 3H, OMe), 3.65 (s, 3H, CO\(_2\)Me), 3.46-3.41 (m, 1H, NCH\(_2\)), 3.30-3.24 (m, 1H, NCH\(_2\)), 2.00-1.87 (overlapping m, 3H, NCH\(_2\)×2 and NCH\(_2\)C\(_2\)), 1.75-1.67 (m, 1H, NCH\(_2\)), 1.59-1.53 (m, 2H, CH\(_2\)), 1.48-1.40 (m, 1H, CH\(_2\)), 1.22-0.99 (m, 5H, CH\(_2\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 172.5, 159.9, 139.3, 130.1, 119.6, 119.1, 112.2, 60.4, 55.7, 52.4, 48.6, 30.9, 24.7; IR \(\nu\)\(_{max}\) (neat)/cm\(^{-1}\) 2954, 1750 (CO), 1596, 1480, 1343 (SO\(_2\)), 1153 (SO\(_2\)); LRMS (ESI) \(m/z\) 300 (50%, [M+H]\(^+\)), 621 (100%, [2M+Na]\(^+\)); HRMS (ESI) found \(m/z\) 322.0718 [M+Na]\(^+\), \(C_{13}H_{17}NO_5SNa\) requires \(m/z\) 322.0720; ee > 99% (Major = 18.31 mins : Minor = 16.43 mins, \(n\)-hexane/IPA 90:10, 1 ml/min); 
\([\alpha]_D\) = -97.13 (0.01 g/mL, CHCl\(_3\))

\(N\)-cyclohexyl-3-methoxybenzenesulfonamide (Entry 3, Table 3)

![Chemical Structure](image)

Prepared according to general procedure using 3-methoxyphenylmagnesium bromide (0.97 M in THF, 258 µL, 0.25 mmol) and cyclohexylamine (143 µL, 1.25 mmol). Flash column chromatography (petrol/EtO 2:3) afforded the titled sulfonamide as an off-white solid (51 mg, 76%); mp 40 °C (CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.40 (app dt, 1H, \(J\) 7.5, 1.5. Ar-H), 7.35-7.31 (m, 2H, Ar-H), 7.05 (ddd, \(J\) 8.5, 2.5, 1.0, 1H, Ar-H), 4.62 (d, \(J\) 7.5, 1H, NH), 3.79 (s, 3H, OMe), 3.12-3.04 (m, 1H, NHCH\(_2\)), 1.72-1.65 (m, 2H, CH\(_2\)), 1.59-1.53 (m, 2H, CH\(_2\)), 1.48-1.40 (m, 1H, CH\(_2\)), 1.22-0.99 (m, 5H, CH\(_2\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 159.9, 142.6, 130.1, 119.1, 118.8, 111.6, 55.7, 52.7, 33.9, 25.1, 24.6; IR \(\nu\)\(_{max}\) (neat)/cm\(^{-1}\) 3288 (NH), 2930, 1597, 1476, 1326 (SO\(_2\)), 1156 (SO\(_2\)); LRMS (ESI) \(m/z\) 270 (20%, [M+H]\(^+\)), 292 (10%, [M+Na]\(^+\)), 561 (100%, [2M+Na]\(^+\)); HRMS (ESI) found \(m/z\) 292.0975 [M+Na]\(^+\), \(C_{13}H_{19}NO_3NaS\) requires \(m/z\) 292.0978.
**N-benzyl-3-methoxybenzenesulfonamide** (Entry 4, Table 3)

![Structure](image)

Prepared according to general procedure using 3-methoxyphenylmagnesium bromide (0.97 M in THF, 258 µL, 0.25 mmol) and benzylamine (137 µL, 1.25 mmol). Flash column chromatography (petrol/Et₂O 2:3) afforded the titled sulfonamide as an off-white solid (57 mg, 78%); mp 77-78 °C (CH₂Cl₂) [lit.¹⁰ mp 80 °C]; <sup>1</sup>H NMR (400 MHz, CDCl₃) δ 7.39 (app dt, 1H, J 7.5, 1.5, Ar-H), 7.34 (app t, J 8.0, 1H, Ar-H), 7.29 (t, J 2.0, 1H, Ar-H), 7.23-7.17 (m, 3H, Ar-H), 7.14-7.11 (m, 2H, Ar-H), 7.03 (ddd, J 8.0, 2.5, 1.5, 1H, Ar-H), 4.71 (t, J 6.0, 1H, NH), 4.08 (d, J 6.0, 1H, CH₂NH), 3.76 (s, 3H, OMe); <sup>13</sup>C NMR (100 MHz, CDCl₃) δ 160.0, 141.0, 136.2, 130.2, 128.7, 128.0, 127.9, 119.3, 119.2, 111.8, 55.7, 47.4; LRMS (ESI) m/z 278 (40%, [M+H]<sup>+</sup>), 300 (100%, [M+Na]<sup>+</sup>), 577 (100%, [2M+Na]<sup>+</sup>); HRMS (ESI) found m/z 300.0665 [M+Na]<sup>+</sup>, C₁₄H₁₅NOSNa requires m/z 300.0665. Data in accordance with that previously reported.¹⁰

**3-Methoxy-N-(thiophen-2-ylmethyl)benzenesulfonamide** (Entry 5, Table 3)

![Structure](image)

Prepared according to general procedure using 3-methoxyphenylmagnesium bromide (0.97 M in THF, 258 µL, 0.25 mmol) and 2-thiophenemethylamine (120 µL, 1.25 mmol). Flash column chromatography (petrol/Et₂O 1:1) afforded the titled sulfonamide as a white solid (59 mg, 83%); mp 70-71 °C (CH₂Cl₂); <sup>1</sup>H NMR (400 MHz, CDCl₃) δ 7.49 (app dt, 1H, J 8.0, 1.5, Ar-H), 7.45 (app t, J 8.0, 1H, Ar-H), 7.39 (app t, J 2.5, 1H, Ar-H), 7.23 (dd, J 5.0, 1.5, 1H, Ar-H), 7.14 (ddd, J 8.0, 2.5, 1.5, 1H, Ar-H), 6.92-6.88 (overlapping m, 2H, Ar-H), 4.80 (t, J 6.0, 1H, NH), 4.40 (d, J 6.0, 2H, CH₂NH), 3.88 (s, 3H, OMe); <sup>13</sup>C NMR (100 MHz, CDCl₃) δ 160.0, 140.9, 138.8, 130.2, 126.9, 126.6, 125.9, 119.4, 119.3, 111.7, 55.7, 42.2; IR ν<sub>max</sub> (neat)/cm⁻¹ 3288 (NH), 1597, 1485, 1417, 1314 (SO₂), 1150 (SO₂); LRMS (ESI) m/z 306 (100%, [M+Na]<sup>+</sup>), 589 (90%, [2M+Na]<sup>+</sup>); HRMS (ESI) found m/z 306.0227 [M+Na]<sup>+</sup>, C₁₂H₁₃NO₃S₂Na requires m/z 306.0229.
**N-[(3-Methoxyphenyl)sulfonyl]indoline (Entry 6, Table 3)**

Prepared according to general procedure using 3-methoxyphenylmagnesium bromide (0.97 M in THF, 258 µL, 0.25 mmol) and indoline (149 mg, 1.25 mmol). Flash column chromatography (Et₂O / CH₂Cl₂ 0-5%) afforded the titled sulfonamide as an off-white solid (46 mg, 64%); mp 97 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, J 8.0, 1H, Ar-H), 7.31 (app dt, J 7.5, 1.5, 1H, Ar-H), 7.27 (app t, J 8.0, 1H, Ar-H), 7.16 (app t, J 2.0, 1H, Ar-H), 7.13 (app t, J 8.0, 1H, Ar-H), 7.03-6.98 (overlapping m, 2H, Ar-H), 6.92 (app td, J 7.5, 1.0, 1H, Ar-H), 3.86 (t, J 8.5, 2H, NC₂H₂), 3.66 (s, 3H, OMe), 2.81 (t, J 8.5, 2H, NC₂H₂); ¹³C NMR (100 MHz, CDCl₃) δ 159.8, 142.0, 138.0, 132.0, 130.0, 127.7, 125.2, 124.0, 119.7, 119.4, 115.2, 111.8, 55.5, 50.0, 27.9; IR νmax (neat)/cm⁻¹ 1578, 1480, 1435, 1349 (SO₂), 1292, 1150 (SO₂); LRMS (ESI) m/z 290 (40%, [M+H]⁺), 312 (80%, [M+Na]⁺), 601 (100%, [2M+Na]⁺); HRMS (ESI) found m/z 312.0667 [M+Na]⁺, C₁₅H₁₅N₂O₃SNa requires m/z 312.0665.

**N-(3-fluorophenyl)-3-methoxybenzenesulfonamide (Entry 7, Table 3)**

Prepared according to general procedure using 3-methoxyphenylmagnesium bromide (0.97 M in THF, 258 µL, 0.25 mmol), acetic acid (70 µL, 1.25 mmol) and 3-fluoroaniline (120 µL, 1.25 mmol). Flash column chromatography (Et₂O / CH₂Cl₂ 0-5%) afforded the titled sulfonamide as an off-white solid (51 mg, 73%); mp 87 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.41-7.34 (m, 2H, Ar-H), 7.29 (br s, 1H, NH), 7.20 (app td, J 8.5, 6.5, 1H, Ar-H), 7.08 (app dt, J 7.5, 2.0, 1H, Ar-H), 6.91 (app dt, J 10.0, 2.0, 1H, Ar-H), 6.83-6.80 (m, 3H, Ar-H), 3.78 (s, 3H, OMe); ¹³C NMR (100 MHz, CDCl₃) δ 159.9, 139.8, 138.0 (d, JᵣF 247.0), 159.9, 139.8, 138.0 (d, JᵣF 10.0), 130.6 (d, JᵣF 9.5), 130.2, 119.9, 119.3, 116.6 (d, JᵣF 3.0), 112.2 (d, JᵣF 21.0), 111.7, 108.5 (d, JᵣF 25.0), 55.6; ¹⁹F NMR (377 MHz, CDCl₃) δ -110.8; IR νmax (neat)/cm⁻¹ 3287 (NH), 1599, 1488, 1324 (SO₂), 1162 (SO₂); LRMS (ESI) m/z 282 (10%, [M+H]⁺), 304 (100%, [M+Na]⁺); HRMS (ESI) found m/z 304.0416 [M+Na]⁺, C₁₃H₁₂FNO₂SNa requires m/z 304.0414.
**N-(4-cyanophenyl)-3-methoxybenzenesulfonamide** (Entry 8, Table 3)

Prepared according to general procedure using 3-methoxyphenylmagnesium bromide (0.97 M in THF, 258 µL, 0.25 mmol), acetic acid (70 µL, 1.25 mmol) and 4-aminobenzonitrile (148 mg, 1.25 mmol). Flash column chromatography (Et₂O/CH₂Cl₂ 0-5%) afforded the titled sulfonamide as an off-white solid (59 mg, 81%); mp 156-157 °C (CH₂Cl₂); ¹H NMR (400 MHz, CD₃CN) δ 8.44 (br s, 1H, NH), 7.62 (d, J 9.0, 2H, Ar-H), 7.49-7.42 (m, 2H, Ar-H), 7.38-7.35 (m, 1H, Ar-H), 7.29 (d, J 9.0, 2H, Ar-H), 3.83 (s, 3H, OMe); ¹³C NMR (100 MHz, CD₃CN) δ 165.3, 147.0, 145.4, 138.9, 135.9, 124.8, 124.6, 124.4, 123.7, 117.2, 112.4, 60.8; IR νmax (neat)/cm⁻¹ 3223 (NH), 2232 (CN), 1597, 1430, 1315 (SO₂), 1288, 1150 (SO₂); LRMS (ESI) m/z 289 (100%, [M+H]+), 311 (100%, [M+Na]+); HRMS (ESI) found m/z 287.0497 [M-H]-, C₁₄H₁₁N₂O₃S requires m/z 287.0496.

**N-(benzothiazol-6-yl)-3-methoxybenzenesulfonamide** (Entry 9, Table 3)

Prepared according to general procedure using 3-methoxyphenylmagnesium bromide (0.97 M in THF, 258 µL, 0.25 mmol) and 6-aminobenzothiazole (188 mg, 1.25 mmol). Flash column chromatography (Et₂O/CH₂Cl₂ 0-5%) afforded the titled sulfonamide as an off-white solid (46 mg, 57%); mp 130-131 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 8.93 (s, 1H, Ar-H), 8.09 (br s, 1H, NH), 7.84 (d, J 9.0, 1H, Ar-H), 7.76 (d, J 2.0, 1H, Ar-H), 7.29 (app t, J 8.0, 1H, Ar-H), 7.24 (app dt, J 8.0, 1.5, 1H, Ar-H), 7.19-7.15 (m, 2H, Ar-H), 7.01 (ddd, J 8.0, 2.5, 1.5, 1H, Ar-H), 3.66 (s, 3H, OMe); ¹³C NMR (100 MHz, CDCl₃) δ 160.4, 155.6, 151.3, 140.7, 135.6, 135.4, 130.9, 124.1, 121.2, 121.1(8), 119.7, 114.9, 112.4, 55.9; IR νmax (neat)/cm⁻¹ 3198 (NH), 1595, 1466, 1323 (SO₂), 1245, 1151 (SO₂); LRMS (ESI) m/z 321 (100%, [M+H]+), 343 (60%, [M+Na]+), 663 (10%, [2M+Na]+); HRMS (ESI) found m/z 321.0360 [M+H]+, C₁₄H₁₁N₂O₂S₂ requires m/z 321.0362.
1-[(3-Methoxyphenyl)sulfonyl]piperidine-2-carboxylic acid (Entry 10, Table 3)

Prepared according to general procedure using 3-methoxyphenylmagnesium bromide (0.97 M in THF, 258 µL, 0.25 mmol) and (D)-(L) pipercolinic acid (161 mg, 1.25 mmol). The aqueous acid wash gave the pure titled sulfonamide as an off-white solid (62 mg, 83%) without further purification; mp 122-123 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 8.65 (br s, 1H, CO₂H), 7.34-7.30 (m, 2H, Ar-H), 7.27-7.25 (m, 1H, Ar-H), 7.04-7.00 (m, 1H, Ar-H), 4.71 (app d, J 5.0, 1H, CHCO₂H), 3.78 (s, 3H, OMe), 3.72-3.66 (app d, J 12.5, 1H, NCH₂), 3.16 (td, J 12.5, 3.0, 1H, NCH₂), 2.14-2.07 (m, 1H, CHCH₂), 1.81-1.76 (m, 1H, CHCH₂), 1.71-1.59 (overlapping m, 2H, NCH₂CH₂ and CHCH₂CH₂), 1.44-1.23 (overlapping m, 2H, NCH₂CH₂ and CHCH₂CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 176.7, 159.8, 141.0, 130.0, 119.3, 118.9, 111.9, 55.6, 54.9, 42.7, 27.5, 24.4, 20.0; IR νmax (neat)/cm⁻¹ 2726 (OH), 1706 (CO), 1599, 1488, 1318 (SO₂), 1112 (SO₂); LRMS (ESI) m/z 300 (100%, [M+H]^+), 621 (50%, [2M+Na]^+); HRMS (ESI) found m/z 300.0894 [M+H]^+, C₁₃H₁₈N₂O₅S requires m/z 300.0900.

(S)-[(3-methoxyphenyl)sulfonyl]alanine (Entry 11, Table 3)

Prepared according to general procedure using 3-methoxyphenylmagnesium bromide (0.97 M in THF, 258 µL, 0.25 mmol) and (L) alanine (111 mg, 1.25 mmol). The aqueous acid wash gave the pure titled sulfonamide as a white solid (47 mg, 73%) without further purification; mp 126-127 °C (CH₂Cl₂); ¹H NMR (400 MHz, CD₂OD) δ 7.36-7.30 (m, 2H, Ar-H), 7.29-7.27 (m, 1H, Ar-H) 7.04 (app dt, J 7.0, 2.5, 1H, Ar-H), 3.80 (q, J 7.0, 1H, CHNH), 3.75 (s, 3H, OMe), 1.20 (d, J 7.0, 3H, CHMe); ¹³C NMR (100 MHz, CD₂OD) δ 173.9, 160.0, 142.0, 129.8, 118.7, 118.4, 111.5, 54.7, 51.4, 18.2; IR νmax (neat)/cm⁻¹ 3257 (NH), 1709 (CO), 1476, 1334 (SO₂), 1138 (SO₂); LRMS (ESI) m/z 260 (20%, [M+H]^+), 282 (100%, [M+Na]^+), 541 (60%, [2M+Na]^+); HRMS (ESI) found m/z 260.0581 [M+H]^+, C₁₀H₁₄NO₂S requires m/z 260.0587; ee > 99% (Major = 17.97 mins, n-hexane/IPA 60:40, 1 ml/min); [α]D = +29.5 (0.01 g/mL, CHCl₃).
2-[(3-Methoxyphenyl)sulfonamido]benzamide (Entry 12, Table 3)

Prepared according to general procedure using 3-methoxyphenylmagnesium bromide (0.97 M in THF, 258 µL, 0.25 mmol), acetic acid (70 µL, 1.25 mmol) and anthranilamide (170 mg, 1.25 mmol). Flash column chromatography (Et₂O/CH₂Cl₂ 0-5%) afforded the titled sulfonamide as an off-white solid (39 mg, 51%); mp 128-129 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 10.88 (s, 1H, SO₂NH), 7.65 (dd, J 8.5, 1.0, 1H, Ar-H), 7.39-7.32 (overlapping m, 3H, Ar-H), 7.26-7.22 (overlapping m, 2H, Ar-H), 7.00 (app td, J 8.0, 1.0, 1H, Ar-H), 6.95 (ddd, J 8.5, 2.5, 1.0, 1H, Ar-H), 5.92-5.62 (overlapping br s, 2H, CONH₂), 3.72 (s, 3H, OMe); ¹³C NMR (100 MHz, CDCl₃) δ 170.5, 159.8, 140.6, 139.5, 133.4, 130.0, 127.5, 123.5, 121.3, 119.6(3), 119.5, 111.6, 55.6; IR ν_max (neat)/cm⁻¹ 3419 (CONH), 3201 (NH), 1671 (CO), 1484, 1380, 1350 (SO₂), 1113 (SO₂); LRMS (ESI) m/z 307 (80%, [M+H]+), 329 (100%, [M+Na]+), 635 (40%, [2M+Na]+); HRMS (ESI) found m/z 307.0741 [M+H]+, C₁₄H₁₄N₂O₄S requires m/z 307.0747.

8-[(4-Aminophenyl)sulfonyl]-8-azabicyclo[3.2.1]octane-3-carbonitrile (D4)

Prepared according to general procedure using 4-[Bis(trimethylsilyl)amino]phenylmagnesium bromide (0.48 M in THF, 520 µL, 0.25 mmol) and exo-8-azabicyclo[3.2.1]octane-3-carbonitrile (170 mg, 1.25 mmol). Flash column chromatography (petrol/EtOAc 1:1) afforded the titled sulfonamide as an off-white solid (40 mg, 54%); mp 181-182 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, J 9.0, 2H, Ar-H), 6.69 (d, J 9.0, 2H, Ar-H), 4.87 (br s, 2H, NH₂), 4.19-4.15 (m, 2H, NCH), 2.96 (tt, J 11.5, 6.5, 1H, CHCN), 2.00-1.89 (m, 4H, CNCH₂CH₂), 1.55-1.44 (m, 4H, NCHCH₂CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 153.2, 129.9, 126.6, 122.6, 113.9, 56.5, 36.2, 27.7, 20.8; IR ν_max (neat)/cm⁻¹ 3542, 3362, 3251, 2968, 1636, 1348 (SO₂), 1148 (SO₂); LRMS (ESI) m/z 292 (100%, [M+H]+), 314 (50%, [M+Na]+); HRMS (ESI) found m/z 292.1110 [M+H]+, C₁₄H₁₄N₃O₂S requires m/z 292.1114.
5-Bromo-N-mesityl-2,6-dimethoxypyridine-3-sulfonamide (G6)

Prepared according to general procedure using 3-bromo-2,6-dimethoxypyridinyl-5-magnesium chloride lithium chloride (0.25 mmol) and 2,4,6-trimethylaniline (181 µL, 1.25 mmol). The aryl Grignard reagent was generated in situ by dropwise addition of isopropylmagnesium chloride. LiCl solution (1.17 M in THF, 214 µL, 0.275 mmol) to a solution of 3,5-dibromo-2,6-dimethoxypyridine (89 mg, 0.25 mmol) in THF (1 mL) at 0 °C. The mixture was stirred at room temp for 1 h before being transferred to a DABSO-THF suspension. Flash column chromatography (CH₂Cl₂/Et₂O 0-5%) afforded the titled sulfonamide as an off-white solid (40 mg, 39%); mp 213-214 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 8.03 (s, 1H, Ar-H), 6.78 (s, 2H, Ar-H), 6.25 (s, 1H, NH), 4.07 (s, 3H, OMe), 4.01 (s, 3H, OMe), 2.17 (s, 3H, ArMe), 2.05 (s, 6H, 2 × ArMe); ¹³C NMR (100 MHz, CDCl₃) δ 161.2, 158.0, 143.2, 138.0, 137.5, 129.9, 129.5, 117.7, 95.5, 55.3, 54.9, 20.9, 18.8; IR ν max (neat)/cm⁻¹ 3273, 2995, 1567, 1311 (SO₂), 1160 (SO₂); LRMS (ESI) m/z 415 (90%, [M+H]+), 417 (100%, [M+H]+), 437 (90%, [M+Na]+), 439 (100%, [M+Na]+); HRMS (ESI) found m/z 415.0316 [M+H]+ and 417.0294 [M+H]+, C₁₆H₂₀BrN₂O₄S requires m/z 415.0322 and 417.0301.
2. Array Synthesis

The array synthesis of sulfonamides was performed as a matrix using a Mettler-Toledo-Bohdan XT block equipped with an inert/purging manifold. The experiments were conducted in two runs using the same ten amines each time with 4 organometallic reagents in the first run and three in the second (1 × 40 combinations and 1 × 30 combinations). Non-commercially available organometallic reagents were prepared as stock solutions. 2,4-Dimethoxypyrimidin-5-ylmagnesium chloride was prepared from 5-iodo-2,4-dimethoxy-pyrimidine and LiCl.\(^\text{11}\) \(d_5\)-Ethylmagnesium bromide was prepared from \(d_5\)-bromoethane and Mg turnings.\(^\text{12}\) 3-Lithio-1-(triisopropysilyl)pyrrole was prepared from 3-bromo-1-(triisopropysilyl)pyrrole and BuLi. 3-Acetoxypropylzinc iodide was prepared from 3-acetoxypropyl iodide and activated Zn dust.\(^\text{13}\) 3-Bromo-2,6-dimethoxypyridinyl-5-magnesium chloride was prepared from 3,5-dibromo-2,6-dimethoxypyridine and \(\text{PrMgCl}_2\text{LiCl}\).\(^\text{14}\)

Typical Run:

Oven-dried test tubes were placed in the block reactor which was connected to a manifold and the tubes were cooled by flushing with nitrogen gas. DABSO (36 mg, 0.15 mmol) was added to each of the tubes which were subsequently flushed with nitrogen for 2 mins. THF (0.5 mL) was added to the tubes which were then cooled to -40 °C followed by addition of the corresponding organometallic reagent (0.25 mmol). The resulting mixtures were stirred at this temp for 30 mins before being allowed to warm to room temp. To each of the tubes was added sequentially, H\(_2\)O (1 mL), amine (1.25 mmol) and NaOCl (15.8% aqueous solution, 296 µL, 0.75 mmol). The resulting mixtures were stirred at room temp for 16 h before being transferred to glass vials containing sat. Na\(_2\)S\(_2\)O\(_3\) (aq) (10 mL) and stirred for a further 30 mins. EtOAc (10 mL) was added to each of the vials which were vigorously shaken (robotic assisted agitation) for 1 min before automated extraction of the organic layer via syringe. This process was repeated 3 times before removing the solvent by flushing with hot air (40 °C). The resulting crude reaction mixtures were purified using automated preparative liquid chromatography-mass spectrometry to deliver the desired sulfonamides as identified by LC-MS (retention times given in minutes). Representative \(^1\)H NMR spectra were obtained for certain examples where LC-MS data contained discrepancies and as confirmation of purity. The four examples that failed by purity were judged to have done so by LC-MS and \(^1\)H NMR Spectroscopy.

Purification of samples:

Compounds were purified by mass directed prep HPLC using a mixed trigger of UV with ES+ on a Waters Fraction Lynx system comprising a 2767 injector/collector with a 2525 gradient pump, pump control module two 515 isocratic pumps, CFO, 2996 photodiode array, 2420 ELSD and Micromass
ZQ2000. A Waters XBridge dC18 5micron 19x10mm guard column was used with an XBridge dC18 5micron OBD 30x100mm prep column. The preparative HPLC was conducted employing a generic 11.4 minute run time using H₂O with 10mM ammonium acetate (solvent A) and CH₃CN (solvent B). Isolated compounds were transferred to individual vials by dissolving in DMSO.

Reaction set-up: XT reactor block

2.1 Sulfonamide Data from Array Synthesis

Product obtained as a yellow solid (20 mg, 23%). LC-MS data – Ret. time 0.64: MS ES+ m/z 347 (100%, [M+H]+); MS ES- m/z 345 ([M-H]-); ¹H NMR (400 MHz, CDCl₃) δ 9.58 (br s, 1H, SO₂NH), 8.81 (dd, J 4.0, 1.5, 1H, Ar-H), 8.77 (s, 1H, Ar-H), 8.13 (dd, J 8.5, 1.5, 1H, Ar-H), 7.81 (dd, J 7.0, 2.0, 1H, Ar-H), 7.53-7.40 (m, 3H, Ar-H), 3.99 (s, 3H, OMe), 3.95 (s, 3H, OMe).
Product obtained as an off-white solid (36 mg, 44%). LC-MS data – Ret. time 0.36: MS ES+ \textit{m/z} 331 (100%, [M+H]^+), 353 (40%, [M+Na]^+).

Product obtained as an off-white solid (22 mg, 28%). LC-MS data – Ret. time 0.51: MS ES+ \textit{m/z} 320 (100%, [M+H]^+), 342 (20%, [M+Na]^+).

Product obtained as an off-white solid (34 mg, 40%). LC-MS data – Ret. time 0.49: MS ES+ \textit{m/z} 339 (100%, [M+H]^+), 361 (20%, [M+Na]^+).

Product obtained as a yellow solid (28 mg, 36%). LC-MS data – Ret. time 0.28: MS ES+ \textit{m/z} 311 (100%, [M+H]^+); MS ES- \textit{m/z} 309 (100%, [M-H]^-).

Product obtained as an off-white solid (27 mg, 32%). LC-MS data – Ret. time 0.65: MS ES+ \textit{m/z} 338 (100%, [M+H]^+); MS ES- \textit{m/z} 336 (100%, [M-H]^-).
Product obtained as an off-white solid (22 mg, 24%). LC-MS data – Ret. time 0.65: MS ES+ m/z 364 (100%, [M+H]+); MS ES- m/z 362 (100%, [M-H]).

Product obtained as an off-white solid (26 mg, 40%). LC-MS data – Ret. time 0.42: MS ES+ m/z 260 (100%, [M+H]+); MS ES- m/z 258 (100%, [M-H]).

Product obtained as a white solid (28 mg, 35%). LC-MS data – Ret. time 0.55: MS ES+ m/z 324 (100%, [M+H]+), 346 (100%, [M+Na]+); MS ES- m/z 322 (100%, [M-H]).

Product obtained as an off-white solid (28 mg, 36%). LC-MS data – Ret. time 0.68: MS ES+ m/z 316 (100%, [M+H]+); MS ES- m/z 314 (100%, [M-H]).

Product obtained as an off-white solid (26 mg, 46%). LC-MS data – Ret. time 0.30: MS ES+ m/z 226 (100%, [M+H]+), 248 (40%, [M+Na]+); 1H NMR (400 MHz, CDCl3) δ 3.71 (t, J 5.0, 2H, N(COMe)CH2),
3.55 (t, J 5.0, 2H, N(COMe)CH₂), 3.32 (t, J 5.0, 2H, N(COMe)CH₂CH₂), 3.28 (t, J 5.0, 2H, N(COMe)CH₂CH₂), 2.12 (s, 3H, COMe).

Product obtained as an off-white solid (26 mg, 45%). LC-MS data – Ret. time 0.42: MS ES+ m/z 234 (100%, [M+H⁺]), 256 (25%, [M+Na⁺]).

Product obtained as an off-white solid (27 mg, 53%). LC-MS data – Ret. time 0.25: MS ES+ m/z 205 (100%, [M+H⁺]); MS ES- m/z 203 (80%, [M-H]).

Product obtained as an off-white solid (29 mg, 50%). LC-MS data – Ret. time 0.58: MS ES+ m/z 255 (20%, [M+Na⁺]); MS ES- m/z 231 (20%, [M-H]); ¹H NMR (400 MHz, CDCl₃) δ 6.84 (s, 2H, Ar-H), 5.61 (br s, 1H, NH), 2.31 (s, 6H, 2 × ArMe), 2.20 (s, 3H, ArMe).

Product obtained as a yellow oil (25 mg, 39%). LC-MS data – Ret. time 0.59: MS ES+ m/z 259 (50%, [M+H⁺]); MS ES- m/z 257 (100%, [M-H]); ¹H NMR (400 MHz, CDCl₃) δ 7.53-7.40 (m, 4H, Ar-H), 7.02 (br s, 1H, NH).
Product obtained as a white solid (18 mg, 47%). LC-MS data – Ret. time 0.34: MS ES+ m/z 155 (100%, [M+H]+); 1H NMR (400 MHz, CDCl₃) δ 4.70 (br s, 1H, NH), 2.65-2.51 (m, 1H, NHCH), 0.77-0.65 (m, 4H, CH₂CH₂).

Product obtained as an off-white solid (29 mg, 53%). LC-MS data – Ret. time 0.50: MS ES- m/z 217 (60%, [M-H]-); 1H NMR (400 MHz, CDCl₃) δ 7.43-7.29 (m, 5H, Ar-H), 4.80-4.57 (overlapping br s, 1H, NH and q, J 7.0, 1H, CH₂Me), 1.57 (d, J 7.0, 3H, CH₂Me).

Product obtained as a light brown oil (32 mg, 33%). LC-MS data – Ret. time 0.85: MS ES+ m/z 385 (100%, [M+H]+), 407 (20%, [M+Na]+); MS ES- m/z 383 (100%, [M-H]-).

Product obtained as a yellow solid (47 mg, 51%). LC-MS data – Ret. time 0.53: MS ES+ m/z 369 (95%, [M+H]+), 391 (70%, [M+Na]+).

Product obtained as a clear oil (46 mg, 51%). LC-MS data – Ret. time 0.74: MS ES+ m/z 358 (90%, [M+H]+), 380 (95%, [M+Na]+).
Product obtained as a yellow solid (46 mg, 49%). LC-MS data – Ret. time 0.71: MS ES+ m/z 377 (90%, [M+H]+), 399 (100%, [M+Na]+).

Product obtained as an off-white solid (45 mg, 52%). LC-MS data – Ret. time 0.37: MS ES+ m/z 349 (100%, [M+H]+), 371 (10%, [M+Na]+); MS ES- m/z 347 (100%, [M-H]+).

Product obtained as an off-white solid (41 mg, 44%). LC-MS data – Ret. time 0.85: MS ES+ m/z 376 (25%, [M+H]+), 398 (30%, [M+Na]+); MS ES- m/z 374 (100%, [M-H]+).

Product obtained as an off-white solid (42 mg, 42%). LC-MS data – Ret. time 0.82: MS ES- m/z 400 (100%, [M-H]+).

Product obtained as an off-white solid (39 mg, 53%). LC-MS data – Ret. time 0.65: MS ES+ m/z 298 (60%, [M+H]+), 320 (25%, [M+Na]+); MS ES- m/z 296 (100%, [M-H]+).
Product obtained as an off-white solid (49 mg, 54%). LC-MS data – Ret. time 0.77: MS ES+ m/z 384 (100%, [M+Na]+); MS ES- m/z 360 (100%, [M-H]).

Product obtained as a white solid (52 mg, 59%). LC-MS data – Ret. time 0.87: MS ES+ m/z 354 (90%, [M+H]+), 376 (30%, [M+Na]+); MS ES- m/z 352 (100%, [M-H]).

Product obtained as an off-white solid (20 mg, 27%). LC-MS data – Ret. time 0.55: MS ES+ m/z 300 (100%, [M+H]+); MS ES- m/z 298 (100%, [M-H]).

Product obtained as a yellow oil (32 mg, 45%). LC-MS data – Ret. time 0.33: MS ES+ m/z 284 (100%, [M+H]+), 306 (20%, [M+Na]+); MS ES- m/z 282 (50%, [M-H]).

Product obtained as an off-white solid (25 mg, 37%). LC-MS data – Ret. time 0.45: MS ES+ m/z 273 (100%, [M+H]+), 295 (20%, [M+Na]+).
Product obtained as an off-white solid (31 mg, 43%). LC-MS data – Ret. time 0.44: MS ES+ m/z 292 (100%, [M+H]+), 314 (20%, [M+Na]+); MS ES- m/z 290 (70%, [M-H]).

Product obtained as a yellow oil (20 mg, 30%). LC-MS data – Ret. time 0.26: MS ES+ m/z 264 (100%, [M+H]+); MS ES- m/z 262.0 (100%, [M-H]).

Product obtained as an off-white solid (24 mg, 33%). LC-MS data – Ret. time 0.60: MS ES+ m/z 291 (80%, [M+H]+), 313 (45%, [M+Na]+); MS ES- m/z 289 (100%, [M-H]).

Product obtained as an off-white solid (24 mg, 30%). LC-MS data – Ret. time 0.58: MS ES+ m/z 317 (100%, [M+H]+); MS ES- m/z 315 (100%, [M-H]).

Product obtained as a clear oil (22 mg, 42%). LC-MS data – Ret. time 0.38: MS ES+ m/z 213 (90%, [M+H]+).
Product obtained as an off-white solid (30 mg, 43%). LC-MS data – Ret. time 0.50: MS ES+ m/z 277 (100%, [M+H]+); ES MS- m/z 275 (100%, [M-H]−); 1H NMR (400 MHz, CDCl3) δ 7.30 (d, J 9.0, 2H, Ar-H), 7.12-7.08 (m, 5H, Ar-H), 6.47 (d, J 9.0, 2H, Ar-H), 4.20 (q, J 7.0, 1H, NHCH), 1.20 (d, J 7.0, 3H, CHMe).

Product obtained as an off-white solid (28 mg, 42%). LC-MS data – Ret. time 0.60: MS ES+ m/z 269 (100%, [M+H]+), 291 (10%, [M+Na]+); ES MS- m/z 267 (100%, [M-H]-).

Product obtained as an off-white solid (26 mg, 40%). LC-MS data – Ret. time 0.31: MS ES+ m/z 258 (100%, [M+H]+), 280 (30%, [M+Na]+); MS ES- m/z 256 (100%, [M-H]-); 1H NMR (400 MHz, CD3OD) δ 7.32 (app t, J 2.0, 1H, Ar-H), 6.93 (dd, J 3.0, 2.0, 1H, Ar-H), 6.42 (dd, J 3.0, 2.0, 1H, Ar-H), 3.72-3.62 (m, 4H, N(COMe)C2H5), 3.03-2.91 (m, 4H, N(COMe)C2H5C2H5), 2.09 (s, 3H, COMe).

Product obtained as an off-white solid (20 mg, 33%). LC-MS data – Ret. time 0.39: MS ES+ m/z 247 (100%, [M+H]+), 269 (40%, [M+Na]+); ES MS- m/z 245 (100%, [M-H]-).

Product obtained as an off-white solid (29 mg, 44%). LC-MS data – Ret. time 0.39: MS ES+ m/z 266 (100%, [M+H]+), 288 (40%, [M+Na]+); MS ES- m/z 264 (100%, [M-H]-).
Product obtained as a white solid (19 mg, 32%). LC-MS data – Ret. time 0.26: MS ES+ m/z 238 (100%, [M+H]⁺); ES MS- m/z 236 (100%, [M-H]⁻).

Product obtained as an off-white solid (27 mg, 41%). LC-MS data – Ret. time 0.55: MS ES+ m/z 265 (10%, [M+H]⁺), 287 (20%, [M+Na]⁺); ES MS- m/z 263 (25%, [M-H]⁻).

Product obtained as an off-white solid (23 mg, 32%). LC-MS data – Ret. time 0.55: MS ES- m/z 289 (70%, [M-H]⁻).

Product obtained as an off-white solid (20 mg, 43%). LC-MS data – Ret. time 0.33: MS ES+ m/z 187 (30%, [M+H]⁺), 209 (30%, [M+Na]⁺); ¹H NMR (400 MHz, CDCl₃) δ 8.72 (br s, 1H, ArNH), 7.38-7.36 (m, 1H, Ar-H), 6.84 (dd, J 3.0, 2.5, 1H, Ar-H), 6.54-6.52 (m, 1H, Ar-H), 4.75 (br s, 1H, NH), 2.34-2.29 (m, 1H, NHCH), 0.68-0.63 (m, 2H, CHCH₂), 0.62-0.56 (m, 2H, CHCH₂).

Product obtained as a yellow oil (24 mg, 38%). LC-MS data – Ret. time 0.47: MS ES+ m/z 273 (90%, [M+Na]⁺); MS ES- m/z 249 (100%, [M-H]⁻); ¹H NMR (400 MHz, CDCl₃) δ 8.46 (br s, ArNH), 7.21-7.09 (overlapping m, 6H, Ar-H), 6.70 (dd, J 4.5, 2.0, 1H, Ar-H), 6.33-6.31 (m, 1H, Ar-H), 4.56 (br s, 1H, NH), 4.43-4.35 (m, 1H, NHCH), 1.40 (d, J 7.0, 3H, CHMe).
Product obtained as an off-white solid (25 mg, 41%). LC-MS data – Ret. time 0.55: MS ES+ m/z 243 (100%, [M+H]+), 265 (40%, [M+Na]+); MS ES- m/z 241 (100%, [M-H]); 1H NMR (400 MHz, CDCl3) δ 8.73 (br s, 1H, ArN), 7.24-7.22 (m, 1H, Ar-H), 6.76 (dd, J 5.0, 2.5, 1H, Ar-H), 6.43-6.41 (m, 1H, Ar-H), 4.27 (br s, 1H, NH), 2.71 (d, J 6.5, 2H, NHCH2), 1.65-1.58 (m, 5H, CH2), 1.42-1.32 (m, 1H, CH), 1.18-1.00 (m, 3H, CH2), 0.86-0.75 (m, 2H, CH2).

Product obtained as an off-white solid (31 mg, 42%). LC-MS data – Ret. time 0.32: MS ES+ m/z 293 (100%, [M+H]+), 315 (30%, [M+Na]+); 1H NMR (400 MHz, CDCl3) δ 4.18 (t, J 6.0, 2H, OCH2), 3.72 (t, J 5.0, 2H, N(COMe)CH2), 3.57 (t, J 5.0, 2H, N(COMe)CH2), 3.32 (t, J 5.0, 2H, N(COMe)CH2CH2), 3.28 (t, J 5.0, 2H, N(COMe)CH2CH2), 3.02-2.98 (m, 2H, SCHR2), 2.19-2.13 (m, 2H, OCHR2CH2), 2.12 (s, 3H, NCOMe), 2.07 (s, 3H, OCOMe).

Product obtained as a yellow oil (25 mg, 36%). LC-MS data – Ret. time 0.46: MS ES+ m/z 282 (50%, [M+H]+), 304 (80%, [M+Na]+).

Product obtained as a yellow oil (31 mg, 41%). LC-MS data – Ret. time 0.44: MS ES+ m/z 301 (75%, [M+H]+), 323 (65%, [M+Na]+).

Product obtained as a light brown oil (27 mg, 40%). LC-MS data – Ret. time 0.26: MS ES+ m/z 273 (100%, [M+H]+), 295 (10%, [M+Na]+).
Product obtained as an off-white solid (30 mg, 40%). LC-MS data – Ret. time 0.60: MS ES+ m/z 322 (75%, [M+Na]+); MS ES- m/z 298 (60%, [M-H]-); 1H NMR (400 MHz, CDCl3) δ 6.85 (s, 2H, Ar-H), 5.68 (br s, 1H, NH), 4.14 (t, J 6.0, 2H, OCH2), 3.19-3.14 (m, 2H, SCH2), 2.30 (s, 6H, ArMe x 2), 2.23-2.15 (overlapping s, 3H, ArMe and m, 2H, OCH2CH2), 2.00 (s, 3H, OCOMe).

Product obtained as a light brown oil (33 mg, 40%). LC-MS data – Ret. time 0.59: MS ES+ m/z 348 (80%, [M+Na]+); MS ES- m/z 324 (70%, [M-H]-); 1H NMR (400 MHz, CDCl3) δ 7.44-7.35 (m, 4H, Ar-H), 7.14 (br s, 1H, NH), 4.10 (t, J 6.0, 2H, OCH2), 3.18-3.14 (m, 2H, SCH2), 2.14-2.03 (m, 2H, OCH2CH2), 1.93 (s, 3H, OCOMe).

Product obtained as a light yellow oil (28 mg, 51%). LC-MS data – Ret. time 0.37: MS ES+ m/z 222 (10%, [M+H]+), 244 (80%, [M+Na]+).

Product obtained as an off-white solid (27 mg, 38%). LC-MS data – Ret. time 0.51: MS ES+ m/z 308 (100%, [M+Na]+).

Product obtained as an off-white solid (30 mg, 43%). LC-MS data – Ret. time 0.60: MS ES+ m/z 278 (75%, [M+H]+), 300 (85%, [M+Na]+).
Product obtained as an off-white solid (27 mg, 25%). LC-MS data – Ret. time 0.87: MS ES+ m/z 424 (75%, [M\(^{79}\text{Br}+\text{H}]^+\)), 426 (100%, [M\(^{81}\text{Br}+\text{H}]^+\)); MS ES- m/z 422 (85%, [M\(^{79}\text{Br}-\text{H}]\)), 424 (100%, [M\(^{81}\text{Br}-\text{H}]\)).

Product obtained as an off-white solid (36 mg, 35%). LC-MS data – Ret. time 0.54: MS ES+ m/z 408 (75%, [M\(^{79}\text{Br}+\text{H}]^+\)), 410 (100%, [M\(^{81}\text{Br}+\text{H}]^+\)).

Product obtained as a yellow oil (28 mg, 28%). LC-MS data – Ret. time 0.72: MS ES+ m/z 397 (75%, [M\(^{79}\text{Br}+\text{H}]^+\)), 399 (100%, [M\(^{81}\text{Br}+\text{H}]^+\)), 319 (50%, [M\(^{79}\text{Br}+\text{Na}]\)), 321 (60%, [M\(^{81}\text{Br}+\text{Na}]\)).

Product obtained as a white solid (30 mg, 29%). LC-MS data – Ret. time 0.71: MS ES+ m/z 416 (75%, [M\(^{79}\text{Br}+\text{H}]^+\)), 418 (100%, [M\(^{81}\text{Br}+\text{H}]^+\)), 438 (40%, [M\(^{79}\text{Br}+\text{Na}]\)), 440 (50%, [M\(^{81}\text{Br}+\text{Na}]\)).

Product obtained as an off-white solid (30 mg, 31%). LC-MS data – Ret. time 0.37: MS ES+ m/z 388 (75%, [M\(^{79}\text{Br}+\text{H}]^+\)), 390 (100%, [M\(^{81}\text{Br}+\text{H}]^+\)); MS ES- m/z 386 (80%, [M\(^{79}\text{Br}-\text{H}]\)), 388 (100%, [M\(^{81}\text{Br}-\text{H}]\)).
Product obtained as an off-white solid (35 mg, 34%). LC-MS data – Ret. time 0.85: MS ES+ m/z 415 (10%, [M(\textsuperscript{79}Br)+H]+), 417 (10%, [M(\textsuperscript{81}Br)+H]+); MS MS ES- m/z 413 (80%, [M(\textsuperscript{79}Br)-H]-), 415 (100%, [M(\textsuperscript{81}Br)-H]-).

Product obtained as an off-white solid (29 mg, 26%). LC-MS data – Ret. time 0.82: MS ES+ m/z 441 (25%, [M(\textsuperscript{79}Br)+H]+), 443 (30%, [M(\textsuperscript{81}Br)+H]+); MS ES- m/z 439 (80%, [M(\textsuperscript{79}Br)-H]-), 441 (100%, [M(\textsuperscript{81}Br)-H]-).

Product obtained as an off-white solid (27 mg, 32%). LC-MS data – Ret. time 0.66: MS ES+ m/z 337 (65%, [M(\textsuperscript{79}Br)+H]+), 339 (75%, [M(\textsuperscript{81}Br)+H]+); MS ES- m/z 335 (95%, [M(\textsuperscript{79}Br)-H]-), 337 (100%, [M(\textsuperscript{81}Br)-H]-); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.23 (s, 1H, Ar-H), 5.20 (br s, 1H, NH), 4.04 (s, 3H, OMe), 4.00 (s, 3H, OMe), 2.07-2.00 (m, 1H, NHCH), 0.66-0.63 (m, 2H, CHCH\textsubscript{2}), 0.55-0.51 (m, 2H, CHCH\textsubscript{2}).

Product obtained as an off-white solid (31 mg, 31%). LC-MS data – Ret. time 0.87: MS ES+ m/z 423 (25%, [M(\textsuperscript{79}Br)+Na\textsuperscript{+}]), 425 (30%, [M(\textsuperscript{81}Br)+Na\textsuperscript{+}]); MS ES- m/z 399 (80%, [M(\textsuperscript{79}Br)-H]-), 401 (100%, [M(\textsuperscript{81}Br)-H]-).
Product obtained as an off-white solid (32 mg, 33%). LC-MS data – Ret. time 0.90: MS ES+ m/z 393 (75%, [M(\textsuperscript{79}Br)+H]+), 395 (100%, [M(\textsuperscript{81}Br)+H]+); MS ES- m/z 391 (85%, [M(\textsuperscript{79}Br)-H]-), 393 (100%, [M(\textsuperscript{81}Br)-H]-).
3. References

1) B. Nguyen, E. J. Emmett, M. C. Willis, *J. Am. Chem. Soc.* **2010**, *132*, 16372
2) K. Itami, K. Terakawa, J-I. Yoshida, O. Kajimoto, *J. Am. Chem. Soc.* **2003**, *125*, 6058
3) M. S. Cloonan, J. J. Keating, S. G. Butler, A. J. S. Knox, A. M. Jorgensen, G. H. Peters, D. Rai, D. Corrigan, D. G. Lloyd, C. Williams, M. J. Meegan, *Eur. J. Med. Chem.* **2009**, *44*, 4862
4) A. Lube, W. P. Neumann, M. Niestroj, *Chem. Ber.* **1995**, 128, 1195
5) H. Woolven, C. Gonzalez-Rodriguez, I. Marco, A. L. Thompson, M. C. Willis, *Org Lett.* **2011**, 13, 4876
6) J. R. DeBergh, N. Niljianskul, S. L. Buchwald, *J. Am. Chem. Soc.* **2013**, *135*, 10638
7) E. L. Clennan, H. Zhang, *J. Am. Chem. Soc.* **1995**, *117*, 4218
8) A. Krasovskiy, V. Malakhov, A. Gavryushin, P. Knochel, *Angew. Chem. Int. Ed.* **2006**, *45*, 6040
9) R. J. Cremlyn, *Phosphorous, Sulfur Silicon Relat. Elem.* **1981**, 10, 111
10) X. Cui, F. Shi, M. K. Tse, D. Goerdes, K. Thurow, M. Beller, Y. Deng, *Adv. Synth. Catal.* **2009**, 351, 2949
11) G. Manolikakes, P. Knochel, *Angew. Chem. Int. Ed.* **2008**, 48, 205
12) E. Johansson, P. T. Hurley, B. S. Brunschwig, N. S. Lewis, *J. Phys. Chem. C* **2009**, *113*, 15239
13) Y. Sasaki, A. Niida, T. Tsuji, A. Shigenaga, N. Fujii, A. Otaka, *J. Org. Chem.* **2006**, *71*, 4969
14) S. Yamada, A. Gavryushin, P. Knochel, *Angew. Chem. Int. Ed.* **2010**, *122*, 2261
4. NMR Spectra – General Scope

![NMR Spectra Diagram]
Entry 4, Table 2
Entry 5, Table 2
Entry 6, Table 2
Entry 7, Table 2

![Chemical Structure Image]
Entry 8, Table 2

![Chemical Structure Image]

![NMR Spectra Image]
Entry 10, Table 2

![Chemical Structure Image]

[Detailed Chemical Structure Image]

**Entry 10, Table 2**

[Chemical Structure Diagram]
Entry 12, Table 2
Entry 13, Table 2
Entry 15, Table 2
Entry 16, Table 2
Entry 1, Table 3
Entry 2, Table 3
Entry 3, Table 3
Entry 4, Table 3
Entry 5, Table 3
Entry 6, Table 3
Entry 7, Table 3
Entry 8, Table 3
Entry 9, Table 3
Entry 10, Table 3
Entry 11, Table 3
Entry 12, Table 3
Control Examples

D4
Entry 2, Table 3

Sample Name: product  
Injection Volume: 10.0
Vial Number: GB1  
Channel: UV_VIS_1
Sample Type: unknown  
Wavelength: 225
Control Program: Col_A 10% isocratic  
Bandwidth: 1
Quantif. Method: Standard  
Dilution Factor: 1.0000
Recording Time: 21/8/2014 11:35  
Sample Weight: 1.0000
Run Time (min): 30.00  
Sample Amount: 1.0000

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount | Type |
|-----|----------------|-----------|--------------|----------------|--------------|--------|------|
| 1   | 16.42          | n.a.      | 0.245        | 0.091          | 0.02         | n.a.   | BMB  |
| 2   | 18.31          | n.a.      | 924.277      | 394.542        | 99.98        | n.a.   | BMB  |

Total: 924.522 394.633 100.00 0.000
**Entry 2, Table 3 (racemic)**

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount | Type |
|-----|----------------|-----------|--------------|----------------|--------------|--------|------|
| 1   | 16.02          | n.a.      | 695.013      | 258.757        | 46.84        | n.a.   | BM * |
| 2   | 17.86          | n.a.      | 713.852      | 293.697        | 53.16        | n.a.   | MB * |
| Total |                |           | 1408.865     | 552.454        | 100.00       | 0.000  |      |

Sample Name: rac  
Injection Volume: 10.0  
Vial Number: GA1  
Channel: UV_VIS_1  
Sample Type: unknown  
Wavelength: 225  
Control Program: Col_A 10% isocratic  
Bandwidth: 1  
Quantif. Method: Standard  
Dilution Factor: 1.0000  
Recording Time: 22/8/2014 17:25  
Sample Weight: 1.0000  
Run Time (min): 30.00
### Entry 11, Table 3

| Sample Name: | AD336-pure IC 40% 50min | Injection Volume: | 20.0 |
|------------|-------------------------|-----------------|------|
| Vial Number: | GC12 | Channel: | UV_VIS_1 |
| Sample Type: | unknown | Wavelength: | 225 |
| Control Program: | col a 1% 1 5 ml 30min | Bandwidth: | 1 |
| Quantif. Method: | Ph-pent | Dilution Factor: | 1.0000 |
| Recording Time: | 14/3/2014 14:16 | Sample Weight: | 1.0000 |
| Run Time (min): | 50.00 | Sample Amount: | 1.0000 |

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount | Type |
|-----|---------------|-----------|--------------|----------------|--------------|--------|------|
| 1   | 17.97         | n.a.      | 159.298      | 295.202        | 100.00       | n.a.   | BMB  |
| Total: | | | 159.298 | 295.202 | 100.00 | 0.000 |

---

![Graph of AD336 #8](attachment:image.png)

WVL: 225 nm
Entry 11, Table 3 (racemic)

| Sample Name: | AD336-rac IC 40% 60min | Injection Volume: | 20.0 |
|--------------|------------------------|------------------|------|
| Vial Number: | GC12                   | Channel:         | UV_VIS_1 |
| Sample Type: | unknown                | Wavelength:      | 225  |
| Control Program: | col a 1% 1 5 ml 30min | Bandwidth:      | 1    |
| Quantif. Method: | Ph-pent             | Dilution Factor: | 1.0000 |
| Recording Time: | 14/3/2014 13:32       | Sample Weight:  | 1.0000 |
| Run Time (min): | 41.28                | Sample Amount:  | 1.0000 |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|--------------|------------|--------|------|
| 1   | 20.21        | n.a.      | 13.998     | 42.054       | 48.38      | n.a.   | BM * |
| 2   | 28.81        | n.a.      | 13.796     | 44.863       | 51.62      | n.a.   | MB*  |
| Total: |            |           | 27.794     | 86.917       | 100.00     | 0.000  |      |

No. 1 - 20.212  
No. 2 - 28.811
6. Array Synthesis $^1$H NMR and LC-MS

A1

B2
3: UV Detector: TIC

1: MS ES+: TIC

2: MS ES-: TIC

(1) Corona Detector

(1) 0.24
(2) 0.63
(3) 0.65
(4) 0.90
(5) 0.98
(6) 1.00

ID: A1

File: 13zp545l1
Vial: 5:50

Range: 1.309

Range: 172.724

Range: 198.730
3: UV Detector: TIC

1: MS ES+: TIC

2: MS ES-: TIC

(1) Corona Detector

(1)
Peak ID | Time | 1 : (Time: 0.35) Combine (125:140-(43:50+231:238)) 1 : MS ES+ 1.2e+008

Peak ID | Time | 1 : (Time: 0.36) Combine (126:141-(42:49+227:234)) 2 : MS ES- 1.5e+005
Peak ID  Time  
1  0.51  
1: (Time: 0.52) Combine (188:203-(106:113+282:290))  
1: MS ES+  
1.6e+008  

Peak ID  Time  
1  0.51  
1: (Time: 0.52) Combine (187:202-(105:113+282:289))  
2: MS ES-  
1.1e+005  

Peak ID  Time  
4  1.00  
4: (Time: 1.00) Combine (368:383-271:278)  
1: MS ES+  
2.6e+007
1: MS ES+ : TIC

3.3e+008

Range: 5.484

2: MS ES- : TIC

6.6e+006

Range: 980.336

1: Corona Detector

(1) Corona Detector

999.160
| Peak ID | Time  |
|---------|-------|
| 1       | 0.25  |
| 2       | 0.34  |
| 3       | 0.49  |

**1:**
- (Time: 0.25) Combine (87:101-(2:9+183:190))
- 1:MS ES+
  - 1.0e+007

**2:**
- (Time: 0.34) Combine (119:134-(31:38+216:223))
- 2:MS ES-
  - 7.2e+005

**3:**
- (Time: 0.50) Combine (181:196-(99:107+277:284))
  - 1:MS ES+
    - 1.6e+008
  - 2:MS ES-
    - 2.2e+005

---

File:13zp5691l
Vial:5:53
ID:A4
Method:C:MASSLYNX\1minLC_MS.olp

---
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector

(1) 0.30

Range: 5.66e-1

(1) 0.28

Range: 9.0e+07

(1) 0.29

Range: 2.9e+06

(3) 0.88

Range: 114.990

(1) 0.28

Range: 102.118

(2) 0.82

(4) 0.92
Peak ID  Time
1  0.28
1: (Time: 0.28) Combine (98:113-(17:24+199:206)) 1:MS ES+ 3.2e+007

Peak ID  Time
1  0.28
1: (Time: 0.30) Combine (104:119-(20:28+200:208)) 2:MS ES- 4.9e+005

Peak ID  Time
3  0.88
3: (Time: 0.88) Combine (323:337-(243:250+407:413)) 2:MS ES- 3.1e+004
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector

Range: 4.32e-1

Time -0.0 0.2 0.4 0.6 0.8 1.0

AU

0.0 1.0e-1 2.0e-1 3.0e-1

Range: 4.24e-1

Time -0.0 0.2 0.4 0.6 0.8 1.0

(1) 0.24

(2) 0.28

(3) 0.66

(4) 0.90

(5) 0.99

Range: 1.8e+008

Time -0.0 0.2 0.4 0.6 0.8 1.0

% 0 20 40 60 80 100

Range: 9.9e+006

Time -0.0 0.2 0.4 0.6 0.8 1.0

% 0 20 40 60 80 100

mV 50.000 100.000 150.000

Range: 154.568

Time -0.0 0.2 0.4 0.6 0.8 1.0

mV 50.000 100.000 150.000

Range: 176.880

Time -0.0 0.2 0.4 0.6 0.8 1.0

S86
Peak ID Time
1  0.24
1: (Time: 0.24) Combine (84:98-(3:10+175:182))

2  0.28
2: (Time: 0.28) Combine (99:114-187:194)

3  0.65
3: (Time: 0.66) Combine (240:255-(157:165+337:345))
Peak ID | Time | m/z | Method: C:\MASSLYNX\1minLC_MS.olp
--- | --- | --- | ---
3 | 0.65 | 336.2 | 2:MS ES-
3: | | 2.2e+007 | 1:MS ES+
5 | 0.99 | 144.1 | 2.2e+007
5: | | 124.1 | 1:MS ES+
### Peak 1
- **Peak ID:** 1
- **Time:** 0.43
- **m/z:**
  - 100.0
  - 200.0
  - 300.0
  - 400.0
  - 500.0
  - 600.0
  - 700.0
- **%:**
  - 0
  - 50
  - 100
- **Method:** 1:MS ES+
- **Intensity:** 7.5e+006

Combine (154:169-(72:79+246:253))

![Peak 1 Diagram](#)

### Peak 2
- **Peak ID:** 2
- **Time:** 0.65
- **m/z:**
  - 100.0
  - 200.0
  - 300.0
  - 400.0
  - 500.0
  - 600.0
  - 700.0
- **%:**
  - 0
  - 50
  - 100
- **Method:** 1:MS ES+
- **Intensity:** 1.7e+008

Combine (239:254-(157:164+335:342))

![Peak 2 Diagram](#)

### Peak 3
- **Peak ID:** 3
- **Time:** 0.72
- **m/z:**
  - 100.0
  - 200.0
  - 300.0
  - 400.0
  - 500.0
  - 600.0
  - 700.0
- **%:**
  - 0
  - 50
  - 100
- **Method:** 2:MS ES-
- **Intensity:** 3.7e+007

Combine (233:248-(151:158+338:345))

![Peak 3 Diagram](#)
Peak ID | Time | 2: (Time: 0.42) Combine (150:166-(69:76+260:267))
2: (Time: 0.43) Combine (155:170-(73:80+251:259))
3: (Time: 0.65) Combine (235:250-(154:161+326:333))
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector

(1) 0.55

Time

Range: 4.531

3.4e+008

2.8e+007

999.170

Range: 980.915
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector

Range: 3.975

Range: 3.1e+008

Range: 2.2e+007

Range: 999.160

Range: 999.160

Range: 981.105
Peak ID | Time  
---|---
1 | 0.68

1: (Time: 0.69) Combine (252:267-(170:177+347:355))

1:MS ES+  
1.8e+008

Peak ID | Time  
---|---
1 | 0.68

1: (Time: 0.68) Combine (247:262-(165:172+347:354))

2:MS ES−  
2.8e+006

Peak ID | Time  
---|---
2 | 0.73

2: (Time: 0.73) Combine (268:283-(189:196+374:381))

1:MS ES+  
3.1e+007

Peak ID | Time  
---|---
3 | 0.99

3: (Time: 0.99) Combine (365:380-273:280)

1:MS ES+  
2.5e+007
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector
Peak ID | Time | 1:MS ES+ | 1.9e+005
5: (Time: 0.73) Combine (267:282-(180:188+364:372)) | 140.2, 156.1, 214.2, 257.3, 326.2, 391.3, 413.3, 477.4, 631.0, 648.0, 683.0

Peak ID | Time | 2:MS ES- | 1.9e+004
5: (Time: 0.73) Combine (267:282-(180:187+364:371)) | 130.0, 249.0, 265.1, 317.3, 374.6, 433.0, 450.9, 505.0, 641.1, 662.8, 690.7
| Peak ID | Time | m/z     | %   |
|---------|------|---------|-----|
| 1       | 0.28 | 100.0   | 8.4e+005 |
| 2       | 0.34 | 100.0   | 2.0e+006 |
| 3       | 0.37 | 100.0   | 2.9e+006 |

1:MS ES+
2:MS ES-
3:MS ES+
| Peak ID | Time  |
|--------|-------|
| 4      | 0.43  |

4: (Time: 0.43) Combine (153:168-(67:74+257:264))

1: MS ES+
1.1e+008

| Peak ID | Time  |
|--------|-------|
| 5      | 0.53  |

5: (Time: 0.53) Combine (190:204-(110:117+279:286))

2: MS ES-
2.6e+005

| Peak ID | Time  |
|--------|-------|
| 6      | 0.57  |

6: (Time: 0.57) Combine (209:224-(128:136+307:314))

1: MS ES+
7.1e+005

| Peak ID | Time  |
|--------|-------|
| 6      | 0.57  |

6: (Time: 0.57) Combine (208:223-(128:135+306:314))

2: MS ES-
2.6e+005
Peak ID   Time
7        0.65
7: (Time: 0.65) Combine (237:252-(157:164+335:342)) 1:MS ES+ 3.3e+06

Peak ID   Time
9        1.00
9: (Time: 1.00) Combine (368:382-270:277) 1:MS ES+ 2.5e+07
3: UV Detector: TIC

1: MS ES+: TIC

2: MS ES-: TIC

(1) Corona Detector

Range: 5.794

Range: 3.7e+008

Range: 4.0e+006

Range: 834.180

Range: 813.776
Peak ID | Time | m/z
--- | --- | ---
1 | 0.25 | 100.0 200.0 300.0 400.0 500.0 600.0 700.0

1: MS ES+ 1.8e+008

1: (Time: 0.26) Combine (91:106-(6:13+187:194))

Peak ID | Time | m/z
--- | --- | ---
1 | 0.25 | 100.0 200.0 300.0 400.0 500.0 600.0 700.0

2: MS ES- 1.4e+005

2: (Time: 0.26) Combine (91:106-(5:13+186:194))

Peak ID | Time | m/z
--- | --- | ---
2 | 0.31 | 100.0 200.0 300.0 400.0 500.0 600.0 700.0

1: MS ES+ 1.5e+007

2: (Time: 0.31) Combine (107:123-(30:37+208:215))

Peak ID | Time | m/z
--- | --- | ---
3 | 0.43 | 100.0 200.0 300.0 400.0 500.0 600.0 700.0

1: MS ES+ 1.1e+007

3: (Time: 0.43) Combine (153:168-(73:80+253:260))

13zn227l3 Vial:5:51 ID:B5 Method:C:\MASSLYNX\1minLC_MS.olp
Peak ID  Time
4      0.59

4: (Time: 0.59) Combine (213:227-(128:135+305:312))

2: MS ES-  2.0e+005
3: UV Detector: TIC

Time

1: MS ES+: TIC

Time

2: MS ES- :TIC

Time

Corona Detector

(1) Corona Detector

Time
File:13zn2334 Vial:5:52 ID:B6 Method:C:\MASSLYNX\1minLC_MS.olp

Peak ID  Time
1 0.27
1:(Time: 0.27) Combine (92:107-(9:16+185:192)) 1:MS ES+ 1.2e+007

Peak ID  Time
2 0.34
2:(Time: 0.34) Combine (122:137-(34:42+219:227)) 1:MS ES+ 6.4e+005

Peak ID  Time
2 0.34
2:(Time: 0.34) Combine (122:137-(35:42+220:227)) 2:MS ES- 1.1e+004

Peak ID  Time
3 0.41
3:(Time: 0.41) Combine (147:162-(69:76+251:258)) 1:MS ES+ 9.9e+006
Peak ID | Time | 4: (Time: 0.58) Combine (209:224-(129:136+311:318))
--- | --- | ---
4 | 0.58 | 1: MS ES+ 1.1e+008

---

Peak ID | Time | 4: (Time: 0.58) Combine (210:225-(129:136+305:312))
--- | --- | ---
4 | 0.58 | 2: MS ES− 1.4e+006

---

Peak ID | Time | 5: (Time: 0.64) Combine (235:249-(154:161+340:347))
--- | --- | ---
5 | 0.64 | 1: MS ES+ 3.7e+007

---

Peak ID | Time | 5: (Time: 0.65) Combine (238:253-(157:164+328:335))
--- | --- | ---
5 | 0.65 | 2: MS ES− 1.8e+004
| Peak ID | Time | Formula                  | Charge | Mass/Charge | Intensity |
|--------|------|--------------------------|--------|-------------|-----------|
| 4      | 0.58 | (212:227-(130:137+322:329)) | ES−    | 2.3e+007    |           |
| 5      | 0.63 | (229:244-(150:158+316:324)) | ES+    | 9.8e+005    |           |
| 5      | 0.63 | (229:244-(150:157+316:323)) | ES−    | 2.4e+006    |           |
| 6      | 0.65 | (237:252-(159:166+330:337)) | ES+    | 9.8e+005    |           |
Peak ID  Time
6        0.65
6: (Time: 0.65) Combine (237:252-(158:166+329:337))

Peak ID  Time
9        0.99
9: (Time: 0.99) Combine (366:381-282:289)
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector

Range: 1.173e-1

Range: 2.0e+008

Range: 2.0e+006

Range: 71.620

Range: 52.210
Peak ID | Time | m/z
---|---|---
8 | 0.77 | 328.8
 | | 330.7
 | | 332.9
 | | 384.9
 | | 441.4
 | | 516.9
 | | 563.2
 | | 623.0
 | | 694.2

8: (Time: 0.77) Combine (282:297-(204:211+370:377))

Peak ID | Time | m/z
---|---|---
9 | 0.99 | 111.1
 | | 117.0
 | | 179.1
 | | 247.0
 | | 293.1
 | | 369.0
 | | 383.3
 | | 421.5
 | | 504.6
 | | 523.3
 | | 571.5
 | | 650.8
 | | 678.3

9: (Time: 0.99) Combine (364:379-288:295)
Peak ID | Time | Peak ID | Time
-------|------|--------|------
1      | 0.24 | 2      | 0.33 |
1:     |      | 2:     |      |
---     |   ---| ---     |   ---|
1:MS   | ES+  | 2:MS   | ES-  |
1.6e+07|      | 4.0e+05|

1: (Time: 0.24) Combine (82:96-(2:9+185:192))

2: (Time: 0.33) Combine (116:131-(30:37+207:214))

3: (Time: 0.72) Combine (264:279-(174:181+362:369))

4: (Time: 0.76) Combine (278:292-(197:204+369:376))

---

S125
Peak ID | Time | 
|-------|-----| 
| 5     | 0.82| 

5: (Time: 0.84) Combine (307:322)-(218:226+407:413))

1: MS ES+
1.8e+008

Peak ID | Time | 
|-------|-----| 
| 5     | 0.82| 

5: (Time: 0.84) Combine (307:322)-(218:225+407:413))

2: MS ES-
2.7e+006

Peak ID | Time | 
|-------|-----| 
| 6     | 1.03| 

6: (Time: 1.03) Combine (378:393-267:274)

1: MS ES+
2.5e+007
3: UV Detector: TIC

1: MS ES+: TIC

2: MS ES-: TIC

(1) Corona Detector

(1) 0.33
(2) 0.53
(2) 0.57
(2) 0.61
(2) 0.54
(2) 0.57
(3) 0.56

Range: 7.503
Range: 5.8e+008
Range: 7.0e+006
Range: 999.180
Range: 980.046
Peak ID  Time
1  0.33  
1:(Time: 0.33) Combine (117:132-(35:42+216:223))  
2:MS ES-  
   6.2e+005

Peak ID  Time
2  0.53  
2:(Time: 0.53) Combine (193:207-(110:117+318:325))  
1:MS ES+  
   1.3e+008

Peak ID  Time
2  0.53  
2:(Time: 0.54) Combine (196:211-(114:122+292:300))  
2:MS ES-  
   5.4e+005
3: UV Detector: TIC

1: MS ES+ : TIC

2: MS ES- : TIC

(1) Corona Detector

(1) 0.43
(2) 0.59
(3) 0.70
(4) 0.78

Range: 3.059

Range: 5.6e+008

Range: 7.3e+006

Range: 935.860

Range: 914.953
Peak ID | Time  | 3 0.72
3: (Time: 0.74) Combine (269:284-(182:189+364:372))

Peak ID | Time  | 4 0.77
4: (Time: 0.77) Combine (283:297-(205:212+380:387))
3: UV Detector: TIC

Time
-0.0 0.2 0.4 0.6 0.8 1.0
AU
0.0 1.0 1.5 1.997
Range: 2.007

1: MS ES+ :TIC

Time
-0.0 0.2 0.4 0.6 0.8 1.0
% 0 20 40 60 80 100
3.9e+008

2: MS ES- :TIC

Time
-0.0 0.2 0.4 0.6 0.8 1.0
% 0 20 40 60 80 100
3.9e+006

(1) Corona Detector

Time
-0.0 0.2 0.4 0.6 0.8 1.0
mV 200.000 400.000 600.000
672.340
Range: 653.158
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector

999.190

Range: 981.934

(1) 0.37

Range: 1.231e+1

(1) 0.36

(2) 0.43

(3) 0.76

(1) 0.36

(2) 0.43

(3) 0.76

(1) 0.38

(3) 0.76

mV

200.000

400.000

600.000

800.000

200.000

400.000

600.000

800.000
| Peak ID | Time | m/z 100.0 | m/z 200.0 | m/z 300.0 | m/z 400.0 | m/z 500.0 | m/z 600.0 | m/z 700.0 | % | Method |
|--------|------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|----|--------|
| 1      | 0.28 | 134.0     | 152.1     | 349.2     | 136.1     | 152.1     |           |           |    | ES+    |
| 2      | 0.39 | 134.0     | 152.1     | 349.2     |           |           |           |           |    | ES+    |
| 3      | 0.85 | 135.1     | 270.3     | 308.3     | 376.2     | 439.2     |           |           |    | ES+    |

**Peak 1:**
- Time: 0.28
- Combinations: (99:115-(20:27+207:214))
- Spectrum: 1:MS ES+ 4.3e+007

**Peak 2:**
- Time: 0.39
- Combinations: (138:153-(57:64+233:240))
- Spectrum: 1:MS ES+ 6.9e+007

**Peak 3:**
- Time: 0.85
- Combinations: (316:331-232:240)
- Spectrum: 1:MS ES+ 1.4e+008

**Peak 3 (continued):**
- Time: 0.85
- Combinations: (312:327-230:237)
- Spectrum: 2:MS ES- 1.6e+007
Peak ID | Time  | 4: (Time: 0.96) Combine (352:366-272:279)  

4:  

1: MS ES+  

2.5e+007
3: UV Detector: TIC

4.446

Range: 4.454

1: MS ES+ :TIC

1.4e+008

2: MS ES- :TIC

9.2e+007

(1) Corona Detector

873.110

Range: 848.104
**Peak ID**  |  **Time**  |  **m/z**  |  **%**  
--- | --- | --- | ---  
4 | 1.04 | 100 | 0 
4: (Time: 1.04) Combine (383:397-302:309) | 1:MS ES+ | 2.7e+007

**m/z**

124.1  
144.9  
251.1  
267.2  

---

**Method:** C:\MASSLYNX\1minLC_MS.olp
Peak ID  Time
1   0.39
1: (Time: 0.39) Combine (139:153-(55:63+230:237))

Peak ID  Time
2   0.44
2: (Time: 0.44) Combine (157:172-(75:82+255:262))

Peak ID  Time
3   0.64
3: (Time: 0.65) Combine (237:252-(153:160+333:341))

Peak ID  Time
3   0.64
3: (Time: 0.65) Combine (237:252-(152:160+333:340))
3: UV Detector: TIC

Time

0.0 0.2 0.4 0.6 0.8 1.0

AU

0.0 1.0 2.0

Range: 2.941

1: MS ES+ :TIC

Time

0.0 0.2 0.4 0.6 0.8 1.0

% 0 20 40 60 80 100

5.1e+008

2: MS ES- :TIC

Time

0.0 0.2 0.4 0.6 0.8 1.0

% 0 20 40 60 80 100

2.3e+007

(1) Corona Detector

Time

0.0 0.2 0.4 0.6 0.8 1.0

mV

200.000 400.000 600.000 800.000

999.170

Range: 980.485
Peak ID | Time | m/z
--- | --- | ---
1 | 0.43 | 141.0, 237.1
2 | 0.76 | 105.1, 241.0

Peak ID | Time | m/z
--- | --- | ---
2 | 0.78 | 156.9, 241.0
2 | 0.77 | 182.0, 241.0, 360.3

Method: C:\MASSLYNX\1minLC_MS.olp

ID: C9
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector

(1) 0.59
(2) 0.80
(3) 0.87
(4) 0.88

Range: 7.814

Range: 6.9e+008

Range: 1.8e+007

Range: 999.170

Range: 973.252

ID: C10
**Peak ID** | **Time**  
---|---  
1 | 0.59  

1: (Time: 0.59) Combine (213:228-(133:140+306:313))  

2 | 0.79  

2: (Time: 0.79) Combine (290:304-(208:215+388:395))  

2 | 0.80  

2: (Time: 0.80) Combine (294:308-(210:217+389:396))  

3 | 0.87  

3: (Time: 0.88) Combine (323:338-241:249)
Peak ID | Time
---|---
3 | 0.87

3: (Time: 0.88) Combine (323:338-241:248)

2: MS ES-
4.2e+006
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector
Peak ID | Time  
---|---
1 | 0.32

1: (Time: 0.32) Combine (114:129-(33:40+218:225))

|m/z | % |
---|---|---|
100.0 | 0 |
200.0 | 50 |
300.0 | 100 |
400.0 |
500.0 |
600.0 |
700.0 |

1: MS ES+ 1.1e+008

Peak ID | Time  
---|---
1 | 0.34

1: (Time: 0.34) Combine (119:134-(27:34+215:222))

|m/z | % |
---|---|---|
100.0 | 0 |
200.0 |
300.0 |
400.0 |
500.0 |
600.0 |
700.0 |

2: MS ES- 2.3e+005

Peak ID | Time  
---|---
2 | 0.58

2: (Time: 0.58) Combine (212:226-(133:140+299:306))

|m/z | % |
---|---|---|
100.0 | 0 |
200.0 |
300.0 |
400.0 |
500.0 |
600.0 |
700.0 |

2: MS ES- 1.1e+005
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector

5.749
Range: 5.75

5.0e+008

4.5e+006

634.740
Range: 617.462

S154
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector

(1) 0.23

(2) 0.44

(2) 0.43

(2) 0.45

(3) 1.00

573.590

Range: 559.267

5.8e+006

Range: 4.206

0.43

0.44

0.44

200.000

400.000

573.590

Range: 559.267

3.5e+008

S156
Peak ID | Time
1 | 0.23
1: (Time: 0.23) Combine (81:95-(1:5+182:189))

1: MS ES+
3.2e+006

110.1

137.1

141.9

183.0

Peak ID | Time
2 | 0.43
2: (Time: 0.44) Combine (160:175-(77:85+256:264))

1: MS ES+
9.5e+007

292.3

156.0

154.9

156.0

107.1

172.0

186.0

262.3

320.2

345.0

396.3

460.5

475.1

539.2

579.1

594.3

640.8

656.3

Peak ID | Time
2 | 0.43
2: (Time: 0.43) Combine (155:170-(75:82+257:264))

2: MS ES−
2.4e+005

Peak ID | Time
3 | 1.00
3: (Time: 1.00) Combine (366:381-278:285)

1: MS ES+
2.5e+007

124.1

144.9

413.3

425.3
### Peak ID 1 Time 0.25

1: (Time: 0.27) Combine (93:108-(12:20+188:196))

| m/z | "1:"MS ES+ |
|-----|--------------|
| 264.4 | 1.6e+008    |

### Peak ID 1 Time 0.25

1: (Time: 0.25) Combine (87:102-(7:14+198:205))

| m/z | "1:"MS ES- |
|-----|-------------|
| 264.1 | 2.2e+006    |

### Peak ID 2 Time 0.30

2: (Time: 0.30) Combine (106:121-(28:35+208:215))

| m/z | "1:"MS ES+ |
|-----|-------------|
| 264.1 | 2.7e+007    |

### Peak ID 3 Time 0.43

3: (Time: 0.43) Combine (152:168-(71:78+250:257))

| m/z | "1:"MS ES+ |
|-----|-------------|
| 237.1 | 6.1e+006    |
### Peak 1
- **Time:** 0.24 s
- **m/z:** 100.0, 200.0, 300.0, 400.0, 500.0, 600.0, 700.0
- **%:** 50
- **Method:** 1:MS ES+
- **Intensity:** 1.8e+007

### Peak 2
- **Time:** 0.39 s
- **m/z:** 110.0, 136.1
- **Method:** 1:MS ES+
- **Intensity:** 8.6e+007

### Peak 3
- **Time:** 0.59 s
- **m/z:** 134.9, 291.3, 332.3, 444.2
- **Method:** 1:MS ES+
- **Intensity:** 1.6e+008

### Peak 3 (MS-)
- **Time:** 0.59 s
- **m/z:** 156.0, 289.2
- **Method:** 2:MS ES-
- **Intensity:** 5.1e+006
Peak ID | Time
---|---
3 | 0.61

3: (Time: 0.61) Combine (222:237-(146:154+312:320))

2: MS ES- 6.3e+006
3: UV Detector: TIC

1: MS ES+: TIC

2: MS ES-: TIC

(1) Corona Detector

(1)
File:13zp583l1  Vial:5:51  ID:D9
Method:C:\MASSLYNX\1minLC_MS.olp

**Peak ID | Time | 1:MS ES+ | 2:MS ES-**
--- | --- | --- | ---
1 | 0.50 | 1.2e+008 | 2.1e+006

**Peak ID | Time | 1:(Time: 0.50) Combine (181:196-(99:106+301:308))**
--- | --- | ---
1 | 0.50 | 181:196-(99:106+301:308)

**M/z**
---
100.0 155.9 215.1 340.2 575.2

**%**
---
0 50 100

**Peak ID | Time | 2:MS ES-**
--- | --- | ---
2 | 0.53 | 2.6e+006

**Peak ID | Time | 2:(Time: 0.53) Combine (192:206-(114:121+296:303))**
--- | --- | ---
2 | 0.53 | 192:206-(114:121+296:303)
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector

(1)
| Peak ID | Time |
|--------|------|
| 1      | 0.60 |

1: (Time: 0.60) Combine (217:231-(135:142+318:325))

Method: C:\MASSLYNX\1minLC_MS.olp

- MS ES+ 1.5e+008

Peak ID | Time |
|--------|------|
| 1      | 0.60 |

1: (Time: 0.60) Combine (219:234-(136:143+327:334))

- MS ES- 3.1e+005
3: UV Detector: TIC

1.129e-1
Range: 1.22e-1

1: MS ES+ :TIC

1.8e+008

2: MS ES- :TIC

1.7e+007

(1) Corona Detector

376.350
Range: 358.914
| Peak ID | Time | 1:MS ES+ |
|--------|------|----------|
| 1      | 0.25 | 9.1e+007 |

1: (Time: 0.25) Combine (86:101-(2:9+169:176))

2: (Time: 0.26) Combine (92:107-(12:19+184:191))

3: (Time: 0.31) Combine (107:122-(27:34+206:213))

| Peak ID | Time | 2:MS ES- |
|--------|------|----------|
| 3      | 0.31 | 3.9e+006 |

3: (Time: 0.31) Combine (107:122-(25:32+212:219))

| Peak ID | Time | 2:MS ES+ |
|--------|------|----------|
| 4      | 0.31 | 1.3e+007 |

4: (Time: 0.31) Combine (107:122-(27:34+206:213))
Peak ID | Time | m/z | %
---|---|---|---
4 | 0.37 | 145.0 | 100.0
5 | 0.39 | 145.0 | 100.0

**MS ES+**

2.2e+006

---

Peak ID | Time | m/z | %
---|---|---|---
4 | 0.37 | 145.0 | 100.0
5 | 0.39 | 145.0 | 100.0

**MS ES-**

8.9e+004

---

Peak ID | Time | m/z | %
---|---|---|---
4 | 0.37 | 145.0 | 100.0
5 | 0.39 | 145.0 | 100.0

**MS ES+**

2.2e+006

---

Peak ID | Time | m/z | %
---|---|---|---
4 | 0.37 | 145.0 | 100.0
5 | 0.39 | 145.0 | 100.0

**MS ES-**

4.0e+004
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector
Peak ID | Time
--- | ---
1 | 0.25

1: (Time: 0.25) Combine (89:103-(9:16+194:201))

```
1: MS ES+
8.9e+006
```

Peak ID | Time
--- | ---
2 | 0.31

2: (Time: 0.31) Combine (107:122-(26:34+193:200))

```
1: MS ES+
3.8e+006
```

Peak ID | Time
--- | ---
2 | 0.31

2: (Time: 0.31) Combine (107:122-(26:33+192:200))

```
2: MS ES-
7.8e+003
```

Peak ID | Time
--- | ---
3 | 0.33

3: (Time: 0.33) Combine (116:131-(35:43+209:217))

```
1: MS ES+
2.3e+006
```
Peaks Summary:

**Peaks with Mass Spectrometry Details:**

3: (Time: 0.33) Combine (115:130-(35:42+209:216))
- M/Z: 163.1
- 2:MS ES- 9.6e+003

4: (Time: 0.39) Combine (138:153-(52:59+221:228))
- 1:MS ES+ 4.3e+007

4: (Time: 0.39) Combine (138:153-(51:59+220:228))
- 2:MS ES- 1.7e+006

5: (Time: 0.40) Combine (144:160-(58:65+260:267))
- 1:MS ES+ 8.4e+007
Peak ID | Time
---|---
5 | 0.40

5: (Time: 0.41) Combine (146:161-(60:67+253:260))

2: MS ES-
3.2e+006

m/z

129.0
131.0
245.1
264.1
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector

(1) 0.24
(2) 0.26
(3) 0.32
(4) 0.39
(5) 0.73
(6) 0.83
(7) 1.00

1.15e-1
Range: 1.254e-1

1.6e+008

1.9e+007

253.110
Range: 235.906

S179
| Peak ID | Time | m/z | Method |
|--------|------|-----|--------|
| 4      | 0.39 | 4: (Time: 0.39) Combine (140:156-(59:66+240:247)) | 1: MS ES+ 3.8e+007 |
|        |      |     |        |
| 4      | 0.39 | 4: (Time: 0.39) Combine (141:155-(59:66+242:249)) | 2: MS ES- 6.0e+006 |
| 5      | 0.73 | 5: (Time: 0.73) Combine (268:283-(175:182+363:371)) | 1: MS ES+ 1.4e+005 |
| 5      | 0.73 | 5: (Time: 0.73) Combine (268:283-(174:182+363:370)) | 2: MS ES- 1.5e+004 |
Peak ID  Time
7  1.00
7: (Time: 1.00) Combine (367:382-281:288)

1: MS ES+
2.8e+007

124.0
144.9 211.1 413.3 425.3

m/z
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector

(1) 0.25

(2) 0.26

(1) 0.31

(1) 0.32

Range: 1.83

Range: 3.5e+008

Range: 4.6e+006

Range: 490.600

Range: 472.718
**Peak ID** | **Time** | **m/z**
--- | --- | ---
5: | 0.55 | 2:MS ES- 2.3e+006

5: (Time: 0.55) Combine (198:212-(116:123+297:304))

---

**Peak ID** | **Time** | **m/z**
--- | --- | ---
6: | 0.96 | 1:MS ES+ 2.2e+006

6: (Time: 0.96) Combine (355:369-269:277)
| Peak ID | Time | m/z 1 | m/z 2 | m/z 3 | m/z 4 |
|--------|------|-------|-------|-------|-------|
| 1      | 0.24 | 110.0 | 113.9 | 130.7 | 183.0 |
| 2      | 0.27 | 120.0 | 157.0 | 165.5 | 166.8 |
| 3      | 0.54 | 129.9 | 147.9 | 204.1 | 291.0 |
|        |      |       |       |       | 313.0 |

**Peak ID 1:** MS ES+, 4.9e+006

**Peak ID 2:** (Time: 0.24) Combine (82:96-(2:9+169:176))

**Peak ID 2:** MS ES+, 8.0e+006

**Peak ID 3:** (Time: 0.54) Combine (196:211-(110:117+297:304))

**Peak ID 3:** MS ES+, 4.0e+007

**Peak ID 3:** (Time: 0.54) Combine (196:209-(115:123+279:286))

**Peak ID 3:** MS ES-, 6.1e+006
Peak ID | Time  | 4  | 0.54 |
4: (Time: 0.56) Combine (202:217-(122:129+299:306)) | 1: MS ES+ 4.1e+007 |

Peak ID | Time  | 4  | 0.54 |
4: (Time: 0.54) Combine (197:211-(116:123+295:302)) | 2: MS ES- 7.0e+006 |

Peak ID | Time  | 7  | 1.00 |
7: (Time: 1.00) Combine (366:381-287:294) | 1: MS ES+ 2.7e+007 |
3: UV Detector: TIC

1.145e-1
Range: 1.217e-1

1: MS ES+ : TIC

1.1e+008

2: MS ES- : TIC

2.3e+006

(1) Corona Detector

Range: 92.410

(1) Corona Detector

Range: 92.410
Peak ID  Time
5  0.73
5: (Time: 0.73) Combine (268:283-(174:182+362:369))

Peak ID  Time
6  0.83
6: (Time: 0.83) Combine (306:320-(225:232+393:400))

Peak ID  Time
7  0.86
7: (Time: 0.86) Combine (315:329-(237:244+402:409))

Peak ID  Time
8  0.96
8: (Time: 0.96) Combine (351:366-274:281)
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector

(1) Corona Detector
### Peak 1

| Peak ID | Time | m/z |
|---------|------|-----|
| 1       | 0.24 | 110.1 |

#### Mass Spectrum
- m/z: 110.1

### Peak 2

| Peak ID | Time | m/z |
|---------|------|-----|
| 2       | 0.27 | 120.0 |

#### Mass Spectrum
- m/z: 120.0

### Peak 3

| Peak ID | Time | m/z |
|---------|------|-----|
| 3       | 0.34 | 120.0 |

#### Mass Spectrum
- m/z: 120.0

---

### Peak ID 1

| Peak ID | Time | m/z |
|---------|------|-----|
| 1       | 0.24 | 110.1 |

#### Mass Spectrum
- m/z: 110.1

### Peak ID 2

| Peak ID | Time | m/z |
|---------|------|-----|
| 2       | 0.27 | 120.0 |

#### Mass Spectrum
- m/z: 120.0

### Peak ID 3

| Peak ID | Time | m/z |
|---------|------|-----|
| 3       | 0.34 | 120.0 |

#### Mass Spectrum
- m/z: 120.0

---

### Peak ID 1

| Peak ID | Time | m/z |
|---------|------|-----|
| 1       | 0.24 | 110.1 |

#### Mass Spectrum
- m/z: 110.1

### Peak ID 2

| Peak ID | Time | m/z |
|---------|------|-----|
| 2       | 0.27 | 120.0 |

#### Mass Spectrum
- m/z: 120.0

### Peak ID 3

| Peak ID | Time | m/z |
|---------|------|-----|
| 3       | 0.34 | 120.0 |

#### Mass Spectrum
- m/z: 120.0

---

### Peak ID 1

| Peak ID | Time | m/z |
|---------|------|-----|
| 1       | 0.24 | 110.1 |

#### Mass Spectrum
- m/z: 110.1

### Peak ID 2

| Peak ID | Time | m/z |
|---------|------|-----|
| 2       | 0.27 | 120.0 |

#### Mass Spectrum
- m/z: 120.0

### Peak ID 3

| Peak ID | Time | m/z |
|---------|------|-----|
| 3       | 0.34 | 120.0 |

#### Mass Spectrum
- m/z: 120.0
Peak ID | Time | m/z | 1:MS ES+ | 5.2e+006
--- | --- | --- | --- | ---
4 | 0.40 | 253.2 | 334.3 | 100.0

Peak ID | Time | m/z | 1:MS ES+ | 4.4e+007
--- | --- | --- | --- | ---
5 | 0.47 | 105.1 | 273.1 | 100.0

Peak ID | Time | m/z | 2:MS ES- | 1.3e+006
--- | --- | --- | --- | ---
5 | 0.47 | 249.1 | 129.0 | 143.9

Peak ID | Time | m/z | 1:MS ES+ | 2.1e+005
--- | --- | --- | --- | ---
6 | 0.73 | 156.0 | 205.9 | 142.9

S198
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector

(6) 0.55

Range: 1.25e-1
Peak ID | Time  | m/z   | Intensity |
---     | ---   | ---   | ----      |
1       | 0.27  | 114.1 | 1.3e+007  |
2       | 0.32  | 120.0 | 2.3e+006  |
3       | 0.42  | 223.3 | 9.7e+006  |
4       | 0.46  | 223.3 | 2.6e+006  |
Peak ID    Time
5         0.50
5: (Time: 0.50) Combine (179:194-(99:106+271:278))

6         0.55
6: (Time: 0.55) Combine (197:212-(116:123+299:306))

6         0.55
6: (Time: 0.55) Combine (198:212-(117:124+299:306))

7         0.59
7: (Time: 0.59) Combine (214:229-(123:131+310:317))
Peak ID | Time  | m/z
---|---|---
7  | 0.59 | 100.0
2:MS ES- | 4.1e+005 |

7:(Time: 0.59) Combine (213:228-(123:130+309:317))

Peak ID | Time  | m/z
---|---|---
8  | 0.73 | 100.0
1:MS ES+ | 1.7e+006 |

8:(Time: 0.73) Combine (268:283-(172:179+365:372))

---

**129.0** | **176.1** | **241.2** | **242.3** | **307.1** | **363.0** | **368.4** | **382.3** | **507.5**
---

**125.4** | **156.1** | **206.0** | **235.9** | **321.3** | **322.3** | **410.4** | **411.5**
---
3: UV Detector: TIC

1: MS ES⁺ :TIC

2: MS ES⁻ :TIC

(1) Corona Detector

S204
Peak ID  Time
3 0.31
3: (Time: 0.30) Combine (107:122-(24:32+194:202)) 2: MS ES-
3.5e+004

Peak ID  Time
4 0.33
4: (Time: 0.35) Combine (125:140-(46:53+213:220)) 1: MS ES+
9.3e+006

Peak ID  Time
4 0.33
4: (Time: 0.33) Combine (118:132-(28:35+216:223)) 2: MS ES-
2.3e+005

Peak ID  Time
5 0.41
5: (Time: 0.41) Combine (146:161-(55:63+229:236)) 1: MS ES+
4.8e+005
Peak ID	Time	
6	0.43

6: (Time: 0.43) Combine (152:167-(71:79+246:253))

1: MS ES+
3.5e+005

2: MS ES-
8.6e+003
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector

(1) 0.25  (6) 0.75

(4) 0.46

(6) 0.74

Range: 282.433
| Peak ID | Time |
|---------|------|
| 3       | 0.42 |
| 4       | 0.46 |
| 5       | 0.60 |
| 6       | 0.74 |

**Peak 3**

| m/z       | %  |
|-----------|----|
| 107.0     | 100.0 |
| 115.9     | 100.0 |
| 190.6     | 100.0 |
| 213.9     | 100.0 |

**Peak 4**

| m/z       | %  |
|-----------|----|
| 108.0     | 100.0 |
| 222.1     | 100.0 |
| 304.1     | 100.0 |

**Peak 5**

| m/z       | %  |
|-----------|----|
| 119.9     | 100.0 |
| 155.8     | 100.0 |
| 211.0     | 100.0 |

**Peak 6**

| m/z       | %  |
|-----------|----|
| 125.2     | 100.0 |
| 257.3     | 100.0 |
| 343.6     | 100.0 |

Method: C:\MASSLYNX\1minLC_MS.olp
Peak ID | Time
---|---
6 | 0.74

6: (Time: 0.74) Combine (270:284-(191:198+354:361))

2: MS ES- 3.1e+004

Peak ID | Time
---|---
7 | 0.82

7: (Time: 0.82) Combine (302:317-(223:230+386:393))

2: MS ES- 5.8e+004
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector

(1) 0.24
(6) 0.45
(8) 0.74
Peak ID | Time | m/z
---|---|---
1 | 0.23 | 100.0
| | | 200.0
| | | 300.0
| | | 400.0
| | | 500.0
| | | 600.0
| | | 700.0
| | | 0
| | | 50
| | | 100

1:MS ES+
3.9e+006

1:(Time: 0.23) Combine (78:93-(1:6+165:172))

Peak ID | Time | m/z
---|---|---
2 | 0.25 | 100.0
| | | 200.0
| | | 300.0
| | | 400.0
| | | 500.0
| | | 600.0
| | | 700.0
| | | 0
| | | 50
| | | 100

1:MS ES+
8.6e+006

2:(Time: 0.25) Combine (88:103-(8:15+196:203))

Peak ID | Time | m/z
---|---|---
3 | 0.34 | 100.0
| | | 200.0
| | | 300.0
| | | 400.0
| | | 500.0
| | | 600.0
| | | 700.0
| | | 0
| | | 50
| | | 100

1:MS ES+
1.5e+006

3:(Time: 0.34) Combine (122:137-(26:33+205:212))

Peak ID | Time | m/z
---|---|---
3 | 0.34 | 100.0
| | | 200.0
| | | 300.0
| | | 400.0
| | | 500.0
| | | 600.0
| | | 700.0
| | | 0
| | | 50
| | | 100

2:MS ES-
1.4e+004

3:(Time: 0.34) Combine (122:137-(25:33+204:212))
Peak ID | Time  |
---|---|
7 | 0.56 |

7: (Time: 0.56) Combine (205:220-(76:83+287:295))

1:MS ES+ | 1.9e+005 |

Peak ID | Time  |
---|---|
9 | 0.99 |

9: (Time: 0.99) Combine (366:380-287:294)

1:MS ES+ | 2.8e+007 |
Peak ID Time
1 0.26
1: (Time: 0.26) Combine (90:105-(10:17+194:201))

1: MS ES+
1.0e+008

Peak ID Time
1 0.27
1: (Time: 0.27) Combine (94:109-(13:20+191:198))

2: MS ES−
3.6e+004

Peak ID Time
2 0.69
2: (Time: 0.69) Combine (250:264-(173:180+339:346))

2: MS ES−
4.4e+004

Peak ID Time
3 0.71
3: (Time: 0.71) Combine (260:274-(182:189+344:351))

2: MS ES−
7.3e+004
Peak ID | Time |
4 | 0.82 |
4: (Time: 0.82) Combine (298:313-(222:229+385:392)) 2: MS ES- 3.3e+004

Peak ID | Time | m/z
113.0
130.0
142.0
247.0
249.0
291.2
317.0
369.0
400.1
426.9
473.0
521.0
549.4
617.2
656.0
691.0

Peak ID | Time | m/z
5 | 0.90 |
5: (Time: 0.90) Combine (329:344-250:257) 2: MS ES- 4.3e+004

Peak ID | Time | m/z
129.9
181.0
233.1
293.3
353.4
397.5
429.1
441.4
505.5
578.8
632.5
657.2
689.9
3: UV Detector: TIC

1: MS ES+: TIC

2: MS ES-: TIC

(1) Corona Detector

(1) 0.26 0.38
(3) 0.39
(4) 0.60 0.61 0.63
(5) 0.97

Range: 747.118

4.0e+006

4.5e+008

763.230

Range: 747.118

Range: 1.244e-1

1.149e-1

File: 13zo375l2

Vial: 5:48

ID: F6
Peak ID | Time | Method: C:\MASSLYNX\1minLC_MS.olp

1: (Time: 0.27) Combine (93:108-(13:21+182:189))

1: MS ES+ 9.2e+006

Peak ID | Time | Method: C:\MASSLYNX\1minLC_MS.olp

2: (Time: 0.34) Combine (120:135-(34:42+202:210))

2: MS ES+ 1.3e+006

S220
Peak ID | Time | m/z | Method
---|---|---|---
3 | 0.38 | 136.1 | 1:MS ES+ 6.2e+007

3: (Time: 0.38) Combine (135:150-(54:61+231:238))

233.1 245.0 260.9

118.9 129.7

Peak ID | Time | m/z | Method
---|---|---|---
3 | 0.39 | 118.9 129.7 | 2:MS ES- 1.0e+004

3: (Time: 0.39) Combine (139:154-(54:61+235:243))

233.1 245.0 260.9

118.9 129.7

Peak ID | Time | m/z | Method
---|---|---|---
4 | 0.60 | 135.1 236.3 322.1 | 1:MS ES+ 8.0e+007

4: (Time: 0.60) Combine (216:231-(120:127+325:332))

135.1 236.3 322.1

176.1 307.3 338.1

Peak ID | Time | m/z | Method
---|---|---|---
4 | 0.60 | 134.1 256.2 298.2 | 2:MS ES- 2.1e+005

4: (Time: 0.60) Combine (218:233-(134:141+318:325))

134.1 256.2 298.2

187.1 198.4 257.3 298.9

366.1 435.0 485.9 496.5 555.5 600.7 659.2 697.8

S221
Peak ID | Time
---|---
5 | 0.97

5: (Time: 0.97) Combine (359:374-271:278)

1: MS ES+
2.2e+007

124.0
148.1
211.1
413.3
425.3

m/z

File: 13zo375l2
Vial: 5:48
ID: F6
Method: C:\MASSLYNX\1minLC_MS.olp
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector

(3) 0.61

(2) 0.27

(4) 0.66

(5) 0.86

Range: 2.323e-1

Range: 2.249e-1

Time

%
Peak ID | Time | %
-------|-----|---
1 | 0.26 | 7.8e+006
1: (Time: 0.26) Combine (90:105-(10:17+200:207))

Peak ID | Time | %
-------|-----|---
2 | 0.27 | 8.6e+006
2: (Time: 0.27) Combine (95:110-(16:24+183:191))

Peak ID | Time | %
-------|-----|---
2 | 0.27 | 1.9e+004
2: (Time: 0.27) Combine (95:110-(16:23+183:190))

Peak ID | Time | %
-------|-----|---
3 | 0.61 | 2.3e+007
3: (Time: 0.61) Combine (220:235-(138:146+314:322))

S224
Peak ID | Time  
---|---
3 | 0.59

3: (Time: 0.59) Combine (214:229-(133:140+315:322))

2: MS ES- 2.7e+006

---

Peak ID | Time  
---|---
4 | 0.64

4: (Time: 0.64) Combine (235:249-(155:162+328:335))

1: MS ES+ 3.7e+006

---

Peak ID | Time  
---|---
4 | 0.66

4: (Time: 0.66) Combine (239:254-(157:165+333:341))

2: MS ES- 1.4e+005

---

Peak ID | Time  
---|---
5 | 0.84

5: (Time: 0.86) Combine (315:330-229:237)

1: MS ES+ 2.4e+007
Peak ID | Time
--- | ---
5 | 0.84
5: (Time: 0.86) Combine (314:329-229:236) | 2: MS ES-
 | 7.5e+004

| m/z | 100.0 | 200.0 | 300.0 | 400.0 | 500.0 | 600.0 | 700.0 |
|--- | --- | --- | --- | --- | --- | --- | --- |
| % | 0 | 50 | 100 | 0 | 50 | 100 | 0 |

Peak ID | Time
--- | ---
6 | 0.99
6: (Time: 0.99) Combine (364:378-280:287) | 1: MS ES+
 | 2.6e+007

| m/z | 100.0 | 200.0 | 300.0 | 400.0 | 500.0 | 600.0 | 700.0 |
|--- | --- | --- | --- | --- | --- | --- | --- |
| % | 0 | 50 | 100 | 0 | 50 | 100 | 0 |
3: UV Detector: TIC

1: MS ES+ : TIC

2: MS ES- : TIC

(1) Corona Detector

1.129e-1
Range: 1.222e-1

2.2e+008

2.3e+006

151.800
Range: 134.077
Peak ID | Time | 
|-------|------|
| 1     | 0.24 |

1: (Time: 0.24) Combine (82:96-(1:8+167:174))

1: MS ES+ 3.5e+006

---

Peak ID | Time | 
|-------|------|
| 2     | 0.26 |

2: (Time: 0.28) Combine (97:112-185:192)

1: MS ES+ 8.6e+006

---

Peak ID | Time | 
|-------|------|
| 2     | 0.26 |

2: (Time: 0.28) Combine (96:111-184:192)

2: MS ES- 1.1e+004

---

Peak ID | Time | 
|-------|------|
| 3     | 0.29 |

3: (Time: 0.29) Combine (102:117-(26:33+189:196))

2: MS ES- 1.3e+004

---

S228
Peak ID | Time | mz
---|---|---
4 | 0.37 | 162.0 244.1
5 | 0.56 | 119.9 227.0 257.2
6 | 0.59 | 136.5 160.1 223.1 264.0 282.0 325.1
9 | 0.90 | 165.0 163.1 167.0 231.2 283.3 317.0 385.1

**Method:** C:\MASSLYNX\1minLC_MS.olp

**Peak 4:**
4:(Time: 0.37) Combine (131:146-(50:57+231:238))  1:MS ES+  4.4e+007

**Peak 5:**
5:(Time: 0.56) Combine (204:219-(28:36+287:294))  1:MS ES+  1.5e+005

**Peak 6:**
6:(Time: 0.59) Combine (213:228-(134:141+303:310))  2:MS ES-  6.3e+004

**Peak 9:**
9:(Time: 0.90) Combine (331:345-254:261)  2:MS ES-  6.5e+004
Peak ID | Time
---|---
10 | 0.96

10: (Time: 0.96) Combine (352:366-275:282) 2: MS ES-

165.0

50%

111.0 119.0 249.0 339.8 353.0 369.0 409.2 481.2 527.0 588.6 640.8 652.8 697.2

Peak ID | Time
---|---
11 | 1.00

11: (Time: 1.00) Combine (370:384-281:288) 1: MS ES+

124.0

50%

144.9 425.3

m/z
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector

Range: 1.239e-1

Range: 985.392
| Peak ID | Time  |
|--------|-------|
| 3      | 0.96  |

3: (Time: 0.96) Combine (354:368-275:282)

2: MS ES-

1.6e+005

---

**m/z**

- 100.0
- 200.0
- 300.0
- 400.0
- 500.0
- 600.0
- 700.0

**%**

- 0
- 50
- 100
3: UV Detector: TIC

1: MS ES+: TIC

2: MS ES-: TIC

(1) Corona Detector
| Peak ID | Time | m/z |
|--------|------|-----|
| 3      | 0.87 | 422.1 |

3: (Time: 0.87) Combine (318:333-235:242)

2: MS ES-

2.6e+006

File: 13zp867l1
Vial: 5:47
ID: G1
Method: C:\MASSLYNX\1minLC_MS.olp
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector

Range: 1.051e+1

Range: 8.4e008

Range: 6.1e006

Range: 999.160

Range: 981.295
Peak ID | Time  
---|---
1 | 0.26 

1: (Time: 0.26) Combine (92:106-(3:10+192:199)) 

1: MS ES+ 
7.3e+007 

Peak ID | Time  
---|---
2 | 0.70 

2: (Time: 0.72) Combine (262:277-(177:184+358:366)) 

1: MS ES+ 
5.7e+007 

Peak ID | Time  
---|---
2 | 0.70 

2: (Time: 0.71) Combine (257:272-(176:183+349:356)) 

2: MS ES- 
5.4e+004
Peak ID | Time | Time (ms) | Intensity
---|---|---|---
6 | 1.00 | (Time: 1.00) Combine (367:383-282:289) | 2.9e+07

m/z

124.0

144.9

425.3

S248
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector

(1) 0.26
(2) 0.85
(3) 0.99

Range: 1.944

Range: 2.8e+008

Range: 3.3e+007

Range: 568.330

Range: 550.001
| Peak ID | Time |
|---------|------|
| 1       | 0.23 |

1: (Time: 0.23) Combine (81:95-(1:7+166:173))

1:MS ES+ 4.0e+06

| m/z   |
|-------|
| 110.1 |
| 157.1 |
| 165.4 |

| Peak ID | Time |
|---------|------|
| 2       | 0.26 |

2: (Time: 0.26) Combine (90:105-(9:16+194:201))

1:MS ES+ 7.9e+06

| m/z   |
|-------|
| 120.0 |
| 157.1 |
| 165.5 |
| 166.7 |
| 217.1 |

| Peak ID | Time |
|---------|------|
| 3       | 0.83 |

3: (Time: 0.84) Combine (307:322-(225:233+403:410))

1:MS ES+ 3.8e+07

| m/z   |
|-------|
| 281.9 |
| 109.0 |
| 211.1 |
| 227.0 |
| 299.9 |
| 413.4 |
| 484.8 |

| Peak ID | Time |
|---------|------|
| 3       | 0.83 |

3: (Time: 0.82) Combine (302:317-(219:226+408:413))

2:MS ES- 4.2e+07

| m/z   |
|-------|
| 441.0 |
| 439.0 |
| 412.0 |
| 362.0 |
Peak ID | Time | m/z
--- | --- | ---
4 | 0.99 | 124.0
4 | (Time: 0.99) Combine (366:380-285:292) | 124.0
4 | (Time: 0.99) Combine (366:380-285:292) | 267.2
4 | (Time: 0.99) Combine (366:380-285:292) | 425.3
5 | 1.04 | 124.0
5 | (Time: 1.04) Combine (383:399-304:311) | 124.0
5 | (Time: 1.04) Combine (383:399-304:311) | 267.2
5 | (Time: 1.04) Combine (383:399-304:311) | 425.3
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector

Range: 658.193
Peak ID Time
1 0.26
1: (Time: 0.26) Combine (92:107-(12:19+203:210)) 1:MS ES+ 7.6e+006

Peak ID Time
2 0.65
2: (Time: 0.66) Combine (242:257-(160:167+337:344)) 1:MS ES+ 4.5e+007

Peak ID Time
2 0.65
2: (Time: 0.66) Combine (241:256-(159:167+336:344)) 2:MS ES- 3.6e+005

Peak ID Time
3 0.83
3: (Time: 0.83) Combine (303:317-(219:226+399:406)) 2:MS ES- 1.5e+006
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector

(1) 0.26
(2) 0.76
(3) 0.83

999.180
Range: 981.215

4.1e+007

4.5e+008

6.997
Range: 7.006
Peak ID | Time | m/z
---|---|---
1 | 0.26 | 105.1

1:(Time: 0.26) Combine (92:107-(12:19+203:210))

1:MS ES+
1.5e+007

Peak ID | Time | m/z
---|---|---
2 | 0.78 | 105.1

2:(Time: 0.78) Combine (285:300-(202:210+381:388))

1:MS ES+
9.1e+007

Peak ID | Time | m/z
---|---|---
2 | 0.76 | 401.1

2:(Time: 0.78) Combine (284:299-(202:209+380:388))

2:MS ES-
7.8e+006

Peak ID | Time | m/z
---|---|---
3 | 0.83 | 441.0

3:(Time: 0.83) Combine (303:318-(222:229+392:399))

2:MS ES-
4.9e+005
Peak ID  Time
4        0.99

4: (Time: 0.99) Combine (363:378-270:277)  

1: MS ES+  
2.6e+007

```
| Peak ID | Time |
|---------|------|
| 4       | 0.99 |

4: (Time: 0.99) Combine (363:378-270:277)

1: MS ES+  
2.6e+007
```
3: UV Detector: TIC

1: MS ES+ :TIC

2: MS ES- :TIC

(1) Corona Detector

(1) 0.27
(2) 0.79
(3) 0.91

Range: 4.581

4.4e+008

2.4e+007

999.160

Range: 975.949

4.571

4.4e+008

999.160
### 8. Fungicide, Herbicide and Insecticide Assay

Scores are given for numbered replicates, and average scores (avg) for the replicates. *Avg* scores.

| Compound ID | Smiles | Rep 1 | Rep 2 | Rep 3 | Avg |
|-------------|--------|-------|-------|-------|-----|
| D30         | F3A8D6  | 0     | 0     | 0     | 0   |
| D6          | F3A8D6  | 0     | 0     | 0     | 0   |
| D7          | F3A8D6  | 0     | 0     | 0     | 0   |
| D1          | F3A8D6  | 0     | 0     | 0     | 0   |
| D3          | O-CEDEE=O  | 0     | 0     | 0     | 0   |
| D9          | O-CEDEE=O  | 0     | 0     | 0     | 0   |
| D8          | O-Sig7=O=Si  | 0     | 0     | 0     | 0   |
| D20         | O-CEDEE=O  | 0     | 0     | 0     | 0   |
| D2          | O-Sig7=O=Si  | 0     | 0     | 0     | 0   |
| A9          | O-Sig7=O=Si  | 0     | 0     | 0     | 0   |
| A5          | CDln1=O=CDn1  | 0     | 0     | 0     | 0   |
| A6          | O-CEDEE=O  | 0     | 0     | 0     | 0   |
| A7          | PCF6P=FS=Si  | 0     | 0     | 0     | 0   |
| A8          | CDln1=O=CDn1  | 0     | 0     | 0     | 0   |
| A10         | CDln1=O=CDn1  | 0     | 0     | 0     | 0   |
| B2          | O-Sig7=O=Si  | 0     | 0     | 0     | 0   |
| B6          | CEN2/NC1234CC  | 0     | 0     | 0     | 0   |
| B9          | CEDEE=O=CDn1  | 0     | 0     | 0     | 0   |
| B10         | CEDEE=O=CDn1  | 0     | 0     | 0     | 0   |
| B1          | CEDEE=O=CDn1  | 0     | 0     | 0     | 0   |
| B8          | O-Sig7=O=Si  | 0     | 0     | 0     | 0   |
| B20         | CEDEE=O=CDn1  | 0     | 0     | 0     | 0   |
| C1          | O-Sig7=O=Si  | 0     | 0     | 0     | 0   |
| C2          | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C10         | NAC1=O=NCn1  | 0     | 0     | 0     | 0   |
| C6          | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C7          | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C8          | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C11         | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C12         | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C13         | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C4          | NAC1=O=NCn1  | 0     | 0     | 0     | 0   |
| C5          | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C9          | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C14         | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C15         | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C16         | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C17         | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C18         | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C19         | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C20         | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C21         | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C22         | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C23         | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C24         | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C25         | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C26         | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C27         | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C28         | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C29         | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |
| C30         | O-CHN1=O=CHn1  | 0     | 0     | 0     | 0   |

**Note:** All activities are given, no activity, NC data not captured for this replicate.
Materials and Methods

Methodology

Fungicide assays: The compounds were evaluated in mycelial growth tests in artificial media against *Pythium dissimile*, *Alternaria solani*, *Botryotinia fuckeliana* and *Gibberella zeae*, at rates of 20 ppm.

| Test species                  | Media         | Rate (ppm) |
|-------------------------------|---------------|------------|
| *Pythium dissimile*           | Semi-solid    | 20         |
| *Alternaria solani*           | Semi-solid    | 20         |
| *Botryotinia fuckeliana*      | Semi-solid    | 20         |
| (*Botrytis cinerea*)          |               |            |
| *Gibberella zeae*             | Semi-solid    | 20         |
| (*Fusarium graminearum*)      |               |            |

The compounds were also evaluated against several pathogens on leaf-piece assays at the rate of 100 ppm for *Uromyces viciae-fabae* on bean and *Zymoseptoria tritici* on wheat, and at the rate of 200 ppm for *Phytophthora infestans* on tomato. The compounds were applied prior to inoculation with the pathogens.

| Test species                  | Host          | Rate (ppm) |
|-------------------------------|---------------|------------|
| *Zymoseptoria tritici*        | Wheat         | 100        |
| *Phytophthora infestans*      | Tomato        | 200        |
| *Uromyces viciae-fabae*       | Bean          | 100        |

Mycelial growth or disease inhibition was assessed visually and scored using a 3 band system (0, 55 and 99 where 99 = total inhibition of hyphal growth/disease development, 55 = partial inhibition, 0 = no inhibition), 4-14 d after inoculation depending on the assay.

Herbicide plate assays:

The compounds were tested for herbicidal activity against *Arabidopsis thaliana* at 10 ppm and *Poa annua* at 32 ppm. Test plates were stored for seven days in a controlled environment cabinet. They were scored as 0 or 99, where 99 = herbicidal effect, and 0 = no effect.

| Test species                  | Treatment timing | Rate (ppm) |
|-------------------------------|------------------|------------|
| *Arabidopsis thaliana*        | Pre-emergence    | 10         |
| *Poa annua*                   | Pre-emergence    | 32         |

Insecticide assays: The compound was tested for activity against an aphid species and *Heliothis virescens* at 1000 ppm on a leaf-piece based assay, and against *Plutella xylostella* and *Diabrotica balteata* at 500 ppm in artificial diet assays. Chemicals were applied to feeding aphids, or prior to infestation with *P. xylostella*, *H. virescens* and *D. balteata* larvae.

Mortality was assessed relative to control wells using a 2 band system (0 or 99 where 99 = significant mortality, 0 = no effect), 3-6 d after the treatments depending on the assay.

| Test species                  | Treatment type   | Media      | Rate (ppm) |
|-------------------------------|------------------|------------|------------|
| Aphid species                 | Feeding/contact  | Leaf disc  | 1000       |
| Species                  | Method            | Control       | Concentration |
|-------------------------|-------------------|---------------|---------------|
| *Plutella xylostella*    | Feeding/contact   | Artificial    | 500           |
| *Heliothis virescens*    | Feeding/contact   | Leaf disc     | 1000          |
| *Diabrotica balteata*    | Feeding/contact   | Artificial    | 500           |

*Note: Test 1 used Heliothis virescens as the Lepidoptera species. Test 2 used Plutella xylostella as the Lepidoptera species.*

**Positive controls:** In addition to the test compounds, positive control compounds were included in each test: azoxystrobin and prochloraz for fungicide assays, thiamethoxam and indoxacarb for insecticide assays and norflurazon for herbicide assays.

For all screens, data were recorded for replicates and averaged.