A Short Versatile Route Towards Benzothiadiazinyl Radicals
Supporting Information

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1. General Experimental Considerations
All manipulations were carried out under an atmosphere of Argon using standard Schlenk line\(^1\) and glovebox techniques unless otherwise stated. All solvents were purchased from Fisher Scientific and dried before use following the methods specified. DCM and MeCN were dried by reflux over CaH\(_2\) and stored over activated molecular sieves. THF was dried by reflux over potassium and stored over activated molecular sieves. \(^1\)Hexane and Et\(_2\)O were dried by reflux over sodium/benzophenone and stored over potassium mirrors. Toluene was dried by reflux over sodium and stored over activated molecular sieves. \(^1\)BuLi was purchased from ACROS as a 2.5 M solution in hexanes. Pyridine, Et\(_3\)N and Pr\(_2\)EtN were vacuum distilled over CaH\(_2\) and stored over activated molecular sieves. Ferrocene and DABCO were purified by vacuum sublimation. Ph\(_3\)P was recrystallised from DCM and \(^1\)hexane. NaBAr\(_{Cl}\) and (4-methoxy)benzonitrile were prepared according to literature procedures.\(^2,3\) All other compounds were used as supplied by the manufacturer.

NMR spectra were recorded on either a JEOL ECS 400 MHz NMR spectrometer, a Bruker AV II 400 MHz spectrometer, or a Bruker NEO 400 MHz spectrometer. The spectra are reported in ppm and referenced to appropriate residual solvent peaks; spectra recorded in SOCl\(_2\) were arbitrarily referenced to residual DMSO-d\(_5\) in the insert capillary. EPR spectra were recorded on a continuous wave X-band ADANI CMS 8400 spectrometer at ambient temperature. EPR spectral simulation and analysis were performed using the EasySpin computational package.\(^4\) Single crystal X-ray diffraction data were recorded on either an Agilent SuperNova Dual diffractometer or a Nonius Kappa CCD diffractometer, with Mo-K\(_\alpha\) (\(\lambda = 0.71073\) Å) or Cu-K\(_\alpha\) (\(\lambda = 1.54184\) Å) radiation. Electrochemical studies were performed with a Biologic potentiostat and carried out in a three-electrode electrochemical cell with a glassy carbon working electrode, a platinum wire counter electrode, and a silver wire pseudo-reference electrode. Magnetic studies were performed using a Quantum Design MPMS-7 magnetometer. Elemental Analysis was performed by Stephen Boyer via the London Metropolitan University service.
2. Synthetic Details

2.1. Synthesis of N-Arylamidines

The substituted N-arylamidines 1a-o,t were prepared via standard methods through condensation of lithiated anilines with suitable carbonitriles, followed by aqueous work-up.\(^5\) Compound 1f was synthesised in the absence of light. Compound 1p was synthesised by Lewis-acid mediated condensation in the melt.\(^6\) The syntheses of 1a and 1p are given as exemplars. All amidines were isolated as colourless crystalline solids in good yields.

\(\text{Aniline (4.56 cm}^3, 50 \text{mmol) was dissolved in THF (50 cm}^3) \text{and } \text{nBuLi (2.5 M in hexanes, 20 cm}^3, 50 \text{mmol) was added dropwise at 0 °C. The reaction mixture was allowed to slowly warm to room temperature and stir for 1 hour. Benzonitrile (4.84 cm}^3, 50 \text{mmol) was then added yielding a straw-coloured solution thick with off-white precipitate. After 12 hours of stirring, the mixture was quenched with ice water (50 cm}^3) \text{and the organic products extracted into DCM (3 x 50 cm}^3) \text{under air. The combined organic extracts were washed with water and brine (50 cm}^3 \text{each), dried over MgSO}_4, \text{filtered, and evaporated to dryness. The crude residue was recrystallised from DCM and hexanes at -20 °C. The colourless microcrystalline solid was collected by filtration, washed with cold hexanes, and dried in vacuo to give 1a (8.80 g, 44.8 mmol, 90%). }\)

\(^{1}H\text{ NMR (400 MHz, DCM, 19.8 °C): }\delta 7.87 (\text{bs, 2H}), 7.45 (\text{m, 3H}), 7.35 (\text{t, } J = 7.3 \text{ Hz, 2H}), 7.04 (\text{t, } J = 7.3 \text{ Hz, 1H}), 6.94 (\text{d, } J = 7.3 \text{ Hz, 2H}), 3.91 (\text{s, 2H}). \(^{13}C\{^{1}H\}\text{ NMR (100.5 MHz, DCM, 18.4 °C): }\delta 154.4, 150.2, 136.0, 129.6, 128.5, 126.8, 122.9, 121.5.\)

Analytical data in accordance with the literature.\(^7-9\)

\(1b:\)

\(\text{Colourless needles, 71% yield. }^{1}H\text{ NMR (400 MHz, DCM, 19.3 °C): }\delta 7.89 (\text{d, } J = 6.4 \text{ Hz, 2H}), 7.46 (\text{m, 3H}), 7.22 (\text{d, } J = 7.3 \text{ Hz, 1H}), 7.17 (\text{t, } J = 7.3, 7.8 \text{ Hz, 1H}), 6.97 (\text{t, } J = 7.3 \text{ Hz, 1H}), 6.82 (\text{d, } J = 7.8 \text{ Hz}), 4.76 (\text{bs, 2H}), 2.15 (\text{s, 3H}). \(^{13}C\{^{1}H\}\text{ NMR (100.5 MHz, DCM, 18.5 °C): }\delta 153.5, 148.5, 135.9, 130.8, 130.5, 129.6, 128.5, 126.9, 126.8, 123.0, 120.8, 17.5.\)

Analytical data in accordance with the literature.\(^9,10\)
1c:

![Structure of 1c]

Colourless needles, 87% yield. $^1$H NMR (400 MHz, DCM, 19.8 °C): $\delta$ 7.90 (d, $J = 6.4$ Hz, 2H), 7.47 (m, 3H), 7.05 (t, $J = 7.3$, 7.8 Hz, 1H), 6.87 (d, $J = 7.3$ Hz, 1H), 6.68 (d, $J = 7.8$ Hz, 1H), 4.72 (bs, 2H), 2.28 (s, 3H), 2.07 (s, 3H). $^{13}$C{$^1$H} NMR (100.5 MHz, DCM, 18.4 °C): $\delta$ 153.5, 148.3, 138.1, 136.0, 128.5, 128.0, 126.8, 126.2, 124.6, 118.5, 20.3, 13.4.

Analytical data in accordance with the literature.$^8,^1^1$

1d:

![Structure of 1d]

Colourless needles, 79% yield. $^1$H NMR (400 MHz, DCM, 19.8 °C): $\delta$ 7.89 (d, $J = 6.9$ Hz, 2H), 7.46 (m, 3H), 7.09 (d, $J = 7.8$ Hz, 1H), 6.79 (d, $J = 7.3$ Hz, 1H), 6.65 (s, 1H), 4.75 (bs, 1H), 2.29 (s, 3H), 2.10 (s, 3H). $^{13}$C{$^1$H} NMR (100.5 MHz, DCM, 18.3 °C): $\delta$ 153.5, 148.3, 136.6, 136.0, 130.6, 130.5, 128.5, 126.3, 123.7, 121.4, 20.9, 17.0.

Analytical data in accordance with the literature.$^8$

1e:

![Structure of 1e]

Colourless needles, 78% yield. $^1$H NMR (400 MHz, DCM, 19.9 °C): $\delta$ 7.85 (d, $J = 6.9$ Hz, 2H), 7.45 (m, 3H), 6.70 (s, 1H), 6.55 (s, 2H), 4.89 (bs, 2H), 2.29 (s, 6H). $^{13}$C{$^1$H} NMR (100.5 MHz, DCM, 18.4 °C): $\delta$ 154.2, 150.0, 139.3, 136.1, 130.5, 128.5, 126.8, 126.3, 123.7, 21.2.

Analytical data in accordance with the literature.$^8,^9$

1f:
Colourless microcrystalline solid, 65% yield. $^1$H NMR (400 MHz, DCM, 17.1 °C): $\delta$ 7.86 (d, $J = 5.7$ Hz, 2H), 7.46 (m, 3H), 7.24 (t, $J = 8.0$ Hz, 1H), 6.60 (d, $J = 7.8$ Hz, 1H), 6.52 (d, $J = 8.7$ Hz, 2H), 4.93 (bs, 2H), 3.78 (s, 3H). $^{13}$C($^1$H) NMR (100.5 MHz, DCM, 18.4 °C): $\delta$ 161.0, 154.3, 151.7, 135.9, 130.6, 130.4, 128.5, 126.8, 113.7, 108.7, 107.0, 55.3.

Analytical data in accordance with the literature.$^{11,12}$

1g:

![1g structure](image)

Colourless micro-crystalline solid, 63% yield. $^1$H NMR (400 MHz, DCM, 18.7 °C): $\delta$ 7.28 (m, 6H), 6.95 (bs, 3H), 4.84 (bs, 2H), 2.50 (bs, 3H). $^{13}$C($^1$H) NMR (100.5 MHz, DCM, 18.8 °C): $\delta$ 156.2, 149.6, 137.2, 135.7, 130.7, 129.3, 129.1, 127.9, 125.7, 122.6, 121.6, 19.6.

Analytical data in accordance with the literature.$^9$

1h:

![1h structure](image)

Colourless microcrystalline solid, 66% yield. Anal. Calc. for C$_{16}$H$_{18}$N$_2$: C, 80.6; H, 7.61; N, 11.8. Found: C, 80.39; H, 7.76; N, 11.8. $^1$H NMR (400 MHz, DCM, 18.8 °C): $\delta$ 7.49 (bs, 1H), 7.28 (m, 3H), 7.06 (bs, 1H), 6.87 (bs, 1H), 6.73 (bs, 1H), 2.55 (s, 3H), 2.30 (s, 3H), 2.14 (s, 3H). $^{13}$C($^1$H) NMR (100.5 MHz, DCM, 19.0 °C): $\delta$ 155.3, 148.1, 138.0, 137.4, 135.9, 130.8, 129.1, 128.0, 126.3, 125.8, 124.5, 118.6, 20.3, 19.8, 13.6.

1i:

![1i structure](image)

Colourless microcrystalline solid, 77% yield. $^1$H NMR (400 MHz, DCM, 19.6 °C): $\delta$ 7.82 (d, $J = 6.9$ Hz, 2H), 7.33 (t, $J = 6.6$, 7.1 Hz, 2H), 7.03 (t, $J = 6.6$, 7.3 Hz, 1H), 6.93 (t, $J = 7.3$, 8.2 Hz, 4H), 4.81 (bs, 2H), 3.84 (s, 3H). $^{13}$C($^1$H) NMR (100.5 MHz, DCM, 19.2 °C): $\delta$ 161.6, 153.7, 150.4, 129.6, 128.3, 122.7, 121.6, 113.7, 55.5.

Analytical data in accordance with the literature.$^5$
1j:

Colourless microcrystalline solid, 74% yield. Anal. Calc. for C₁₆H₁₈N₂O: C, 75.6; H, 7.13; N, 11.0. Found: C, 75.6; H, 7.24; N, 11.0. ¹H NMR (400 MHz, DCM, 18.3 °C): δ 7.85 (d, J = 8.2 Hz, 2H), 7.04 (t, J = 7.6, 7.8 Hz, 1H), 6.94 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 7.3 Hz, 1H), 6.66 (d, J = 7.6 Hz, 1H), 4.68 (bs, 2H), 3.84 (s, 3H), 2.28 (s, 3H), 2.06 (s, 3H). ¹³C(¹H) NMR (100.5 MHz, DCM, 19.3 °C): δ 161.6, 153.0, 148.5, 138.0, 128.3, 128.1, 126.2, 124.4, 118.7, 113.7, 55.5, 20.3, 13.4.

1k:

Colourless microcrystalline solid, 88% yield. Anal. Calc. for C₁₂H₁₁N₃: C, 73.1 H, 5.62; N, 21.3. Found: C, 73.0; H, 5.75; N, 21.4. ¹H NMR (400 MHz, DCM, 18.4 °C): δ 8.68 (d, J = 4.6 Hz, 2H), 7.73 (d, J = 4.6 Hz, 2H), 7.36 (t, J = 6.4, 6.9 Hz, 2H), 7.07 (t, J = 6.9 Hz, 1H), 6.93 (d, J = 6.9 Hz, 2H), 5.01 (bs, 2H). ¹³C(¹H) NMR (100.5 MHz, DCM, 18.7 °C): δ 152.4, 150.4, 149.5, 143.2, 129.7, 123.4, 121.2, 121.0.

1l:

Colourless microcrystalline solid, 85% yield. Anal. Calc. for C₁₄H₁₅N₃: C, 74.6; H, 6.71; N, 18.7. Found: C, 74.8; H, 6.74; N, 18.6. ¹H NMR (400 MHz, DCM, 18.8 °C): δ 8.68 (d, J = 4.6 Hz, 2H), 7.76 (d, J = 4.6 Hz, 2H), 7.06 (t, J = 7.3, 7.8 Hz, 1H), 6.89 (d, J = 7.3 Hz, 1H), 6.67 (d, J = 7.8 Hz, 1H), 4.87 (bs, 2H), 2.29 (s, 3H), 2.05 (s, 3H). ¹³C(¹H) NMR (100.5 MHz, DCM, 18.8 °C): δ 151.6, 150.4, 147.6, 143.1, 138.2, 127.8, 126.3, 125.0, 121.0, 118.1, 20.2, 13.4.

1m:

Colourless needles, 71% yield. ¹H NMR (400 MHz, DCM, 19.3 °C): δ 7.89 (d, J = 6.4 Hz, 2H), 7.46 (m, 3H), 7.22 (d, J = 7.3 Hz, 1H), 7.17 (t, J = 7.3, 7.8 Hz, 1H), 6.97 (t, J = 7.3 Hz, 1H), 6.82 (d, J = 7.8 Hz, 1H), 4.91 (bs, 2H), 2.16 (s, 3H). ¹³C(¹H) NMR (100.5 MHz, DCM, 19.3 °C): δ 153.5, 148.5, 135.9, 130.8, 130.5, 129.6, 128.5, 126.9, 126.8, 123.0, 120.8, 17.5.

Analytical data in accordance with the literature.⁹,¹¹

1n:
Colourless needles, 73% yield. \textsuperscript{1}H NMR (400 MHz, DCM, 18.9 °C): \(\delta 7.87\) (d, \(J = 7.1\) Hz, 2H), 7.45 (m, 3H), 7.06 (s, 1H), 6.99 (d, \(J = 7.9\) Hz, 1H), 6.71 (d, \(J = 7.8\) Hz, 1H), 4.78 (bs, 2H), 2.31 (s, 3H), 2.13 (s, 3H). \textsuperscript{13}C{\textsuperscript{1}H} NMR (100.5 MHz, DCM, 18.9 °C): \(\delta 153.8, 145.7, 136.0, 132.3, 131.5, 130.4, 129.3, 128.5, 127.5, 126.8, 120.7, 20.7, 17.5\).

Analytical data in accordance with the literature.\textsuperscript{9}

Colourless needles, 68% yield. Anal. Calc. for C\textsubscript{19}H\textsubscript{16}N\textsubscript{2}: C, 83.8; H, 5.92; N, 10.3. Found: C, 83.6; H, 5.90; N, 10.3. \textsuperscript{1}H NMR (400 MHz, DCM, 19.3 °C): \(\delta 7.70\) (d, \(J = 7.2\) Hz, 2H), 7.50 (d, \(J = 7.4\) Hz, 2H), 7.46-7.29 (m, 7H), 7.24 (t, \(J = 7.3, 7.4\) Hz, 1H), 7.16 (t, \(J = 7.4\) Hz, 1H), 6.98 (d, \(J = 7.6\) Hz, 1H), 4.81 (bs, 2H). \textsuperscript{13}C{\textsuperscript{1}H} NMR (100.5 MHz, DCM, 19.7 °C): \(\delta 153.7, 147.4, 140.4, 135.9, 133.9, 130.9, 130.5, 129.1, 128.7, 128.5, 127.9, 126.8, 126.7, 123.5, 122.1\).

\textbf{1p:}

Aniline (2.05 cm\textsuperscript{3}, 22.5 mmol), pivalonitrile (2.49 cm\textsuperscript{3}, 22.5 mmol) and AlCl\textsubscript{3} (3.00 g, 22.5 mmol) were combined and heated to 130 °C. After 1 hour, the molten mixture was poured into a 12.5 % aqueous NaOH (50 cm\textsuperscript{3}) and ice (50 g) mixture, and allowed to stir for 15 minutes. The suspension was extracted into DCM (3 x 50 cm\textsuperscript{3}), dried over MgSO\textsubscript{4}, filtered, and evaporated to dryness. The crude residue was recrystallised from DCM and hexanes at -20 °C. The colourless needles were collected by filtration, washed with cold hexanes and dried in vacuo to give 1p (1.63 g, 9.3 mmol, 41%). \textsuperscript{1}H NMR (400 MHz, DCM, 25.0 °C): \(\delta 7.28\) (t, \(J = 7.6, 8.0\) Hz, 2H), 6.97 (t, \(J = 7.4\) Hz, 1H), 6.77 (d, \(J = 7.4\) Hz, 2H), 4.38 (bs, 2H), 1.26 (s, 9H). \textsuperscript{13}C{\textsuperscript{1}H} NMR (100.5 MHz, DCM, 25.0 °C): \(\delta 164.1, 150.9, 129.5, 122.3, 121.4, 36.9, 28.4\).

Analytical data in accordance with the literature.\textsuperscript{13}

\textbf{1t:}

\begin{align*}
\text{N} & \text{N} \\
\text{NH} & \text{NH}_2
\end{align*}
Colourless needles, 85% yield. $^1H$ NMR (400 MHz, DCM, 18.0 °C): $\delta$ 7.84 (bs, 2H), 7.50-7.41 (m, 3H), 7.30 (d, $J$ = 8.1 Hz, 2H), 6.87 (d, $J$ = 8.1 Hz, 2H), 4.96 (bs, 2H). $^{13}$C($^1H$) NMR (100.5 MHz, DCM, 19.6 °C): $\delta$ 154.8, 148.9, 135.7, 130.7, 129.6, 128.5, 127.8, 126.8, 123.8.

Analytical data in accordance with the literature.$^{14}$

2.2. Synthesis of 1,2,4-Benzothiadiazine 1-Chlorides

The S(IV) heterocycles were prepared by treatment of the corresponding $N$-arylamidine in neat, excess thionyl chloride at reflux. The synthesis of 2a is given as exemplar. Single crystals suitable for X-ray diffraction studies were grown via slow diffusion of $n$-hexane into a saturated solution of the product in SOCl$_2$, or by slow cooling of saturated SOCl$_2$ solutions. NMR spectra were recorded in SOCl$_2$ and arbitrarily referenced to residual DMSO-$d_5$ in the insert capillary (fixed at 2.50 ppm).

2a:

$^{1}H$ NMR (400 MHz, SOCl$_2$, 19.4 °C): $\delta$ 8.46 (d, $J$ = 7.3 Hz, 2H), 7.92 (s, 1H), 7.52 (m, 3H).

$^{13}C$($^1H$) NMR (100.5 MHz, SOCl$_2$, 18.7 °C): $\delta$ 158.3, 140.4, 139.5, 135.3, 134.6, 132.9, 132.6, 129.2, 128.7, 122.1, 116.5.

Synthesis from 1t gave the same product in slightly reduced yield (37%) as confirmed by NMR.

2b:

Orange crystalline solid, 61% yield. Anal. Calc. for C$_{14}$H$_8$Cl$_4$N$_2$S: C, 44.5; H, 2.1; N, 7.4. Found: C, 44.3; H, 2.1; N, 7.5. $^1H$ NMR (400 MHz, SOCl$_2$, 18.4 °C): $\delta$ 8.43 (d, $J$ = 7.1 Hz, 2H), 8.01 (s, 1H), 7.53 (m, 3H), 5.36 (s, 2H). $^{13}$C($^1H$) NMR (100.5 MHz, SOCl$_2$, 18.6 °C): $\delta$ 141.7, 141.4, 136.6, 135.6, 132.7, 132.6, 129.0, 128.8, 124.3, 116.3, 37.2.
2c:

Orange crystalline solid, 76% yield. Anal. Calc. for C₁₅H₁₀Cl₄N₂S: C, 45.9; H, 2.6; N, 7.1. Found: C, 45.8; H, 2.4; N, 7.2. ¹H NMR (400 MHz, SOCl₂, 19.6 °C): δ 8.44 (d, J = 8.2 Hz, 2H), 7.97 (s, 1H), 7.52 (m, 3H), 5.38 (s, 2H), 4.96 (s, 2H). ¹³C{¹H} NMR (100.5 MHz, SOCl₂, 19.6 °C): δ 157.5, 142.4, 141.3, 137.9, 135.6, 134.0, 132.6, 129.0, 128.7, 124.4, 118.1, 38.6, 35.2.

Although this compound appears clean by NMR spectroscopy, SCXRD analysis shows a small (< 4%) disordered component of 2c' in which the benzo-fused ring is fully chlorinated in the lattice.

2d:

Pale yellow crystalline solid, 31% yield. Anal. Calc. for C₁₅H₁₀Cl₄N₂S: C, 45.9; H, 2.6; N, 7.1. Found: C, 45.7; H, 2.6; N, 7.2. ¹H NMR (400 MHz, SOCl₂, 16.6 °C): δ 8.44 (d, J = 7.3 Hz, 2H), 7.52 (m, 3H), 5.37 (s, 2H), 2.85 (s, 3H). ¹³C{¹H} NMR (100.5 MHz, SOCl₂, 19.1 °C): δ 157.5, 141.8, 141.6, 135.5, 133.9, 133.5, 133.0, 132.7, 129.0, 128.8, 116.8, 37.7, 16.7.

2e:

Orange fibrous solid, 40% yield. Anal. Calc. for C₁₅H₁₀Cl₄N₂S: C, 45.9; H, 2.6; N, 7.1. Found: C, 45.8; H, 2.4; N, 7.3. ¹H NMR (400 MHz, SOCl₂, 17.7 °C): δ 8.49 (d, J = 7.3 Hz, 2H), 7.55 (m, 3H), 5.07 (s, 2H), 2.81 (s, 3H). ¹³C{¹H} NMR (100.5 MHz, SOCl₂, 18.7 °C): δ 157.6, 140.6, 139.6, 135.2, 134.3, 133.4, 132.8, 130.7, 129.1, 128.8, 119.0, 41.3, 16.0.
2f:

Red crystalline solid, 46% yield. Anal. Calc. for C_{14}H_{8}Cl_{4}N_{2}OS: C, 42.7; H, 2.0; N, 7.1. Found: C, 42.5; H, 1.9; N, 7.2. \(^1\)H NMR (400 MHz, SOCl₂, 18.5 °C): \(\delta\) 8.47 (d, \(J = 8.0\) Hz, 2H), 7.52 (m, 3H), 4.24 (s, 3H). \(^{13}\)C\{\(^1\)H\} NMR (100.5 MHz, SOCl₂, 18.3 °C): \(\delta\) 159.1, 149.3, 140.6, 140.4, 135.4, 132.8, 129.2, 128.7, 124.7, 112.5, 62.4.

2g:

Pale orange crystalline solid, 46% yield. Anal. Calc. for C_{14}H_{8}Cl_{4}N_{2}S: C, 44.5; H, 2.1; N, 7.4. Found: C, 44.4; H, 2.1; N, 7.5. \(^1\)H NMR (400 MHz, SOCl₂, 18.4 °C): \(\delta\) 8.02 (d, \(J = 7.3\) Hz, 1H), 7.95 (s, 1H), 7.43 (t, \(J = 6.4, 7.3\) Hz, 1H), 7.33 (t, \(J = 6.0, 7.3\) Hz, 2H), 2.76 (s, 3H). \(^{13}\)C\{\(^1\)H\} NMR (100.5 MHz, SOCl₂, 18.9 °C): \(\delta\) 160.3, 139.6, 139.4, 135.2, 134.3, 132.8, 132.0, 131.6, 131.5, 126.1, 122.1, 116.1, 22.4.

2h:

Turmeric-coloured crystalline solid, 53% yield. Anal. Calc. for C_{16}H_{12}Cl_{4}N_{2}S: C, 47.3; H, 3.0; N, 6.9. Found: C, 47.2; H, 2.9; N, 6.7. \(^1\)H NMR (400 MHz, SOCl₂, 18.5 °C): \(\delta\) 8.00 (s, 1H), 7.96 (d, \(J = 7.8\) Hz, 1H), 7.41 (t, \(J = 7.3, 7.6\) Hz, 1H), 7.33 (t, \(J = 6.0, 7.3\) Hz, 2H), 5.32 (s, 2H), 4.98 (s, 2H), 2.71 (s, 3H). \(^{13}\)C\{\(^1\)H\} NMR (100.5 MHz, SOCl₂, 19.2 °C): \(\delta\) 159.9, 142.5, 140.9, 138.8, 138.0, 136.0, 134.4, 131.8, 131.5, 131.3, 126.1, 124.5, 117.4, 38.7, 35.4, 22.0.

2i:

Dark red crystalline solid, 81% yield. Anal. Calc. for C_{14}H_{8}Cl_{4}N_{2}OS: C, 42.7; H, 2.1; N, 7.1. Found: C, 42.3; H, 2.1; N, 7.1. \(^1\)H NMR (400 MHz, SOCl₂, 18.5 °C): \(\delta\) 8.44 (d, \(J = 8.6\) Hz, 2H), 7.92 (s, 1H), 7.01 (d, \(J = 8.6\) Hz, 2H), 3.88 (s, 3H). \(^{13}\)C\{\(^1\)H\} NMR (100.5 MHz, SOCl₂, 19.2 °C): \(\delta\) 163.5, 158.1, 140.6, 139.4, 134.2, 131.8, 131.3, 127.8, 122.1, 116.6, 114.1, 55.3.

2j:
To avoid concomitant formation of \(2q\), the time at reflux time must be reduced to 12 hours. Red crystalline solid, 63% yield. Anal. Calc. for C\(_{16}\)H\(_{12}\)Cl\(_4\)N\(_2\)OS: C, 45.5; H, 2.9; N, 6.6. Found: C, 45.4; H, 2.8; N, 6.8. \(^1\)H NMR (400 MHz, SOCl\(_2\), 18.0 °C): \(\delta\) 8.42 (d, \(J = 8.8\) Hz, 2H), 7.97 (s, 1H), 7.02 (d, \(J = 8.8\) Hz, 2H), 5.39 (s, 2H), 4.97 (s, 2H), 3.88 (s, 3H). \(^{13}\)C\(({^1}\)H\}) NMR (100.5 MHz, SOCl\(_2\), 19.0 °C): \(\delta\) 163.4, 157.4, 142.4, 141.5, 137.6, 133.5, 131.2, 128.1, 124.5, 118.3, 114.2, 55.4, 38.7, 35.4.

**Synthesis of 3:2 1,5,7-trichloro-3-(\(p\)-pyridinium)-benzo-1,2,4-thiadiazine chloride, 2k', and 1,5,6,7-tetrachloro-3-(\(p\)-pyridinium)-benzo-1,2,4-thiadiazine chloride, 2k'':**

Yellow solid, 72 % yield based on 3:2 ratio of 2k': 2k'' species, assuming chloride salt formation. The solid was near insoluble even in hot SOCl\(_2\), and only \(^1\)H NMR data could be obtained, which nevertheless permitted unambiguous assignment of the products, consistent with the SCXRD data for 3k. 2k' \(^1\)H NMR (400 MHz, SOCl\(_2\), 19.1 °C) \(\delta\): 8.88 (bs, 2H), 8.73 (bs, 2H), 7.99 (bs, 1H), 7.82 (bs 1H). 2k'' \(^1\)H NMR (400 MHz, SOCl\(_2\), 19.1 °C) \(\delta\): 8.88 (bs, 2H), 8.73 (bs, 2H), 7.96 (bs, 1H).

\(2l.H[\text{HCl}_2]\):

Yellow crystalline solid, 87% yield. Elemental analysis results are between those expected for \([2l.H]\text{Cl}\) and \([2l.H][\text{HCl}_2]\) salts even after recrystallisation; this is likely due to the tendency of the \([\text{HCl}_2]\) anion to lose HCl although the concomitant formation of the Cl\(^-\) and [HCl\(_2\)]\(^-\) cannot be ruled out. Anal. Calc. for C\(_{14}\)H\(_{11}\)Cl\(_6\)N\(_3\)S: C, 36.1, H, 2.38, N, 9.02. Anal. Calc. for C\(_{14}\)H\(_{10}\)Cl\(_5\)N\(_3\)S: C, 39.2, H, 2.35, N, 9.78. Found: C, 37.3, H, 2.10, N, 9.14. \(^1\)H NMR (400 MHz, SOCl\(_2\), 18.1 °C): \(\delta\) 8.82 (dd, \(J = 5.3, 33.2\) Hz, 4H), 8.03 (s, 1H), 5.33 (s, 2H), 4.96 (s, 2H).

\(^{13}\)C\(({^1}\)H\}) NMR (100.5 MHz, SOCl\(_2\), 19.0 °C): \(\delta\) 152.2, 151.7, 143.0, 141.1, 139.8, 138.3, 136.8, 125.4, 124.8, 116.3, 38.4, 35.1.

**Attempted Synthesis of 2p**

Reaction of 1p under standard conditions gave a low yield of pale peach solid (37% assuming complete conversion to desired product). Attempted recrystallisation of this from boiling SOCl\(_2\) was not successful in obtaining a single product, though a very low quality crystal did afford a connectivity map for \(1p.H\text{Cl}\) below, indicating that ortho-chlorination is rapid for this species.

The \(^1\)H NMR of the crystals remained a mixture with broad peaks commensurate with \(1p.H\text{Cl}\) as the major product but with 40% of the remaining aromatic integrals corresponding to other
species; no 1p remained. The \(^1\)H NMR is reported here for reference, but as this is a mixture, these data should be regarded as indicative only.

\(^1\)H NMR (400 MHz, SOCl\(_2\), 25.0 °C): \(\delta\) 8.39 (bs, 1H), 7.60 (bs, 2H), 1.51 (bs, 9H).

**NMR parameters for 1,7-dichloro-5,6-bis(chloromethyl)-3-(3-chloro-4-methoxyphenyl)benzo-1,2,4-thiadiazine, 2q:**

![Structural diagram]

Formed concomitantly with 2j on prolonged heating in SOCl\(_2\). \(^1\)H NMR (400 MHz, SOCl\(_2\), 18.7 °C): \(\delta\): 8.45 (s, 1H), 8.36 (m, 1H), 7.97 (s, 1H), 7.08 (d, \(J = 8.7\) Hz, 1H), 5.39 (s, 2H), 4.98 (s, 2H), 3.96 (s, 3H). \(^{13}\)C\{\(^1\)H\} NMR (100.5 MHz, SOCl\(_2\), 18.3 °C): \(\delta\): 158.8, 156.7, 142.8, 138.0, 133.9, 131.1, 129.9, 129.4, 124.9, 123.2, 118.4, 112.3, 56.6, 39.1, 35.7.

### 2.3. Synthesis of 1,2,4-Benzothiadiazinyl Radicals

The 1,2,4-benzothiadiazinyl radicals 3a-j were prepared by treating the S(IV) 1-chlorides with Ph\(_3\)P in MeCN. The synthesis of 3a is given as exemplar. Although deeply coloured solids that appeared to be homogenous were obtained in all cases, samples pure by combustion analysis could only be isolated for 3c, 3d and 3e. It is unknown if this is due to true sample impurity or degradation of these highly sensitive materials; reported yields are therefore indicative only.

**3a:**

2a (0.40 g, 1.1 mmol) was suspended in MeCN (5 cm\(^3\)), degassed with three freeze-pump-thaw cycles, and backfilled with argon. A solution of Ph\(_3\)P (0.15 g, 0.6 mmol) in degassed MeCN (5 cm\(^3\)) was added resulting in an immediate darkening of colour. After 5 minutes of rapid stirring, the supernatant was removed via filter cannula and the dark purple solids were washed with MeCN (5 cm\(^3\)) and dried *in vacuo* to give 3a (0.25 g, 0.8 mmol, 69%).

**3b:**

Dark blue powder, 51% yield.

**3c:**
Dark purple powder, 72% yield. Anal. Calc. for C_{15}H_{10}Cl_{3}N_{2}S: C, 50.5; H, 2.8; N, 7.9. Found: C, 50.4; H, 2.7; N, 8.0

![Chemical structure 3d](image)

3d: Dark purple powder, 60% yield. Anal. Calc. for C_{15}H_{10}Cl_{3}N_{2}S: C, 50.5; H, 2.8; N, 7.9. Found: C, 50.5; H, 2.9; N, 8.0.

![Chemical structure 3e](image)

3e: Dark purple powder, 68% yield. Anal. Calc. for C_{15}H_{10}Cl_{3}N_{2}S: C, 50.5; H, 2.8; N, 7.9. Found: C, 50.3; H, 2.7; N, 7.9.

![Chemical structure 3f](image)

3f: Dark purple/green powder, 58% yield.

![Chemical structure 3g](image)

3g: Dark green powder, 64% yield.
3h: Dark purple powder, 57% yield.

3i: Dark blue powder, 49% yield.

3j: Dark blue powder, 68% yield.

3k:

\[
\text{SNCl} \quad \text{X} = 4:1 \text{ H, Cl}
\]

Attempts to recrystallise crude \(2k\) (50 mg, 0.13 mmol) from hot pyridine (1 cm\(^3\)) gave rapid discolouration to a murky, dark solution. On storage at -20 °C, a few dark purple, low quality crystals suitable for SCXRD were isolated.

2.4. Test Synthesis of 1,2,4-Benzothiadiazinyl Cation

Halide abstraction was achieved by treating the 1,2,4-benzothiadiazine 1-chloride \(2a\) with \(\text{GaCl}_3\) in DCM.

\[
\begin{array}{c}
\text{Cl} \quad \text{Cl} \\
\text{Cl} \quad \text{N} \\
\text{Cl} \quad \text{S} \\
\text{Cl} \quad \text{N} \\
\text{Cl}
\end{array}
\quad \text{GaCl}_3
\quad \text{DCM}
\quad 25 \degree \text{C}
\]

\[
\begin{array}{c}
\text{Cl} \quad \text{Cl} \\
\text{Cl} \quad \text{N} \\
\text{Cl} \quad \text{S}^+ \\
\text{Cl} \quad \text{N} \\
\text{Cl}
\end{array}
\quad \text{[4a][GaCl}_4]^{-}
\]
2a (30 mg, 0.08 mmol) was suspended in DCM (5 cm³) and GaCl₃ (14.5 mg, 0.08 mmol) added, giving a dark purple solution. After 5 minutes of stirring, the reaction mixture was filtered to remove undissolved material, and the filtrate was layered with “hexane (10 cm³). After 1 week, dark purple crystals of [4a][GaCl₄] were isolated by filtration, washed with “hexane (2 x 2.5 cm³), and dried in vacuo (27 mg, 0.05 mmol, 63% yield). ¹H NMR (400 MHz, DCM, 25.0 °C): δ 8.92 (s, 1H), 8.70 (d, J = 7.4 Hz, 2H), 7.84 (t, J = 7.4, 7.6 Hz, 1H), 7.73 (t, J = 7.4, 7.6 Hz, 2H). ¹³C{¹H} NMR (100.6 MHz, DCM, 25.0 °C): δ 166.4, 150.7, 148.7, 148.6, 145.0, 140.4, 135.8, 130.1, 129.8, 122.2. The compound was unstable in solution and in the solid state, and satisfactory elemental analysis could not be obtained.

3. Single-Crystal X-Ray Diffraction Data
Single crystal X-ray diffraction data were recorded on either an Agilent SuperNova Dual diffractometer or a Nonius Kappa CCD diffractometer, with Mo-Kα (λ = 0.71073 Å) or Cu-Kα (λ = 1.54184 Å) radiation. Single crystals were mounted on nylon cryloops or MiTeGen microloops. Unit cell determination, data reduction and absorption corrections were performed using CrysAlisPro 38.41. Using the Olex2 GUI, the structures were solved with the SHELXT structure solution program via intrinsic phasing and refined with the SHELXL refinement package using least squares minimisation. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included using a riding model unless otherwise stated. Crystal structure images were made using Mercury with thermal ellipsoids shown at 50% probability.

Supplementary crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CDCC) under the deposition numbers: 2101061; 2101062; 2101063; 2101064; 2101065; 2101066; 2101067; 2101068; 2101069; 2101070; 2101071; 2101072; 2101073; 2101074; 2101075; 2101076; 2101077; 2101078.

3.1. Crystallographic Data and Unit Cell Parameters

Figure S1 Crystal structure of 2a - Front view.
| Compound | 2b |
|----------|----|
| **Empirical formula** | C_{14}H_{8}Cl_{4}N_{2}S |
| **Formula weight** | 378.08 |
| **Temperature/K** | 150.00(10) |
| **Crystal system** | triclinic |
| **Space group** | P1  |
| a/Å | 8.9856(5) |
| b/Å | 9.2182(3) |
| c/Å | 9.3740(6) |
| α/° | 103.868(4) |
| β/° | 94.530(7) |
| γ/° | 95.061(4) |
| **Volume/Å³** | 2857.0(3) |
| **Z** | 8 |
| **ρ_{calc} g/cm³** | 1.693 |
| **μ/mm⁻¹** | 0.962 |
| **F(000)** | 1456.0 |
| **Crystal size/mm³** | 0.28 × 0.28 × 0.18 |
| **Radiation** | MoKα (λ = 0.71073) |
| **2θ range for data collection/°** | 5.62 to 50.06 |
| **Index ranges** | -17 ≤ h ≤ 17, -16 ≤ k ≤ 16, -19 ≤ l ≤ 19 |
| **Reflections collected** | 26565 |
| **Independent reflections** | 5023 [R_{int} = 0.0674] |
| **Data/restraints/parameters** | 5023/0/361 |
| **Goodness-of-fit on F²** | 1.029 |
| **Final R indexes [I>=2σ (I)]** | R_{I} = 0.0484, wR_{I} = 0.098 |
| **Final R indexes [all data]** | R_{I} = 0.0866, wR_{I} = 0.1119 |
| **Largest diff. peak/hole / e Å⁻³** | 0.65/-0.33 |

**Flack parameter**

**Figure S2** Crystal structure of 2a - Side view.
**2b:**

| Parameter                      | Value          |
|--------------------------------|----------------|
| Volume/Å³                      | 746.84(7)      |
| Z                              | 2              |
| ρcalc/g/cm³                    | 1.681          |
| μ/mm⁻¹                         | 8.456          |
| F(000)                         | 380            |
| Crystal size/mm³               | 0.239 × 0.125 × 0.119 |
| Radiation                      | CuKα (λ = 1.54184) |
| 2Θ range for data collection   | 9.772 to 130.764 |
| Index ranges                   | -10 ≤ h ≤ 9, -10 ≤ k ≤ 10, -11 ≤ l ≤ 10 |
| Reflections collected          | 7792           |
| Independent reflections        | 2562 [Rint = 0.0194, Rsigma = 0.0186] |
| Data/restraints/parameters      | 2562/0/190     |
| Goodness-of-fit on F²          | 1.066          |
| Final R indexes [I>=2σ (I)]    | R₁ = 0.0267, wR² = 0.0724 |
| Final R indexes [all data]     | R₁ = 0.0275, wR² = 0.0730 |
| Largest diff. peak/hole / e Å⁻³ | 0.38/-0.34     |
| Flack parameter                |                |

**Figure S3** - Crystal structure of **2b** - Front view.

**Figure S4** - Crystal structure of **2b** - Side view.
**2c:**

![Figure S5 - Crystal structure of 2c - Front view.](image1)

**Figure S5 - Crystal structure of 2c - Front view.**

![Figure S6 - Crystal structure of 2c - Side view.](image2)

**Figure S6 - Crystal structure of 2c - Side view.**

| Compound | 2c |
|----------|----|
| Empirical formula | C_{15}H_{9.97}Cl_{4.03}N_{2}S |
| Formula weight | 393.31 |
| Temperature/K | 100.0(5) |
| Crystal system | triclinic |
| Space group | P̅1 |
| a/Å | 7.3043(3) |
| b/Å | 9.0923(3) |
| c/Å | 12.6109(5) |
| α/° | 80.349(3) |
| β/° | 86.679(3) |
| γ/° | 72.338(3) |
| Volume/Å³ | 786.73(5) |
| Z | 2 |
| ρ_{calc} g/cm³ | 1.66 |
| μ/mm⁻¹ | 8.097 |
| F(000) | 397 |
| Crystal size/mm³ | 0.267 × 0.168 × 0.053 |
| Radiation | CuKα (λ = 1.54184) |
| 2θ range for data collection/° | 7.11 to 137.166 |
| Index ranges | -8 ≤ h ≤ 8, -10 ≤ k ≤ 10, -15 ≤ l ≤ 15 |
| Reflections collected | 15042 |
| Independent reflections | 2891 [R(int) = 0.0370, R(sigma) = 0.0213] |
| Data/restraints/parameters | 2891/0/212 |
| Goodness-of-fit on F² | 1.028 |
| Final R indexes [I>=2σ (I)] | R₁ = 0.0360, wR₂ = 0.0943 |
| Final R indexes [all data] | R₁ = 0.0368, wR₂ = 0.0950 |
| Largest diff. peak/hole / e Å⁻³ | 1.29/-0.49 |
| Flack parameter | }
**2d-α:**

![Crystal structure of 2d-α](image)

**Figure S7** - Crystal structure of 2d-α - Front view.

![Crystal structure of 2d-α](image)

**Figure S8** - Crystal structure of 2d-α - Side view.

**Compound**

| Property               | Value                      |
|------------------------|----------------------------|
| Empirical formula      | C_{15}H_{10}Cl_{4}N_{2}S   |
| Formula weight         | 392.11                     |
| Temperature/K          | 100.0(5)                   |
| Crystal system         | monoclinic                 |
| Space group            | P2_1/c                     |
| a/Å                    | 7.38990(10)                |
| b/Å                    | 10.5325(2)                 |
| c/Å                    | 20.5855(4)                 |
| α/°                    | 90                         |
| β/°                    | 96.598(2)                  |
| γ/°                    | 90                         |
| Volume/Å³              | 1591.64(5)                 |
| Z                      | 4                          |
| ρ_{calc}/g/cm³         | 1.636                      |
| μ/mm⁻¹                 | 7.949                      |
| F(000)                 | 792                        |
| Crystal size/mm³       | 0.377 × 0.042 × 0.038       |
| Radiation              | CuKα (λ = 1.54184)         |
| 2Θ range for data collection/° | 8.648 to 146.978 |
| Index ranges           | -9 ≤ h ≤ 6, -13 ≤ k ≤ 13, -25 ≤ l ≤ 25 |
| Reflections collected  | 19045                      |
| Independent reflections| 3201 [R_{int} = 0.0386, R_{sigma} = 0.0244] |
| Data/restraints/parameters | 3201/0/200               |
| Goodness-of-fit on F²  | 1.057                      |
| Final R indexes [I>2σ (I)] | R₁ = 0.0456, wR₂ = 0.1183 |
| Final R indexes [all data] | R₁ = 0.0475, wR₂ = 0.1198 |
| Largest diff. peak/hole / e Å⁻³ | 1.26/-0.51 |
| Flack parameter        | 1.26/-0.51                 |
2d-β:

**Figure S9** - Crystal structure of 2d-β - Front view.

**Figure S10** - Crystal structure of 2d-β - Side view.

| Compound | 2d-β |
|----------|------|
| Empirical formula | $C_{15}H_{10}Cl_4N_2S$ |
| Formula weight | 392.11 |
| Temperature/K | 180(2) |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 9.1703(4) |
| b/Å | 13.7683(7) |
| c/Å | 12.5807(6) |
| $\alpha^\circ$ | 90 |
| $\beta^\circ$ | 96.799(3) |
| $\gamma^\circ$ | 90 |
| Volume/Å$^3$ | 1577.26(13) |
| Z | 4 |
| $\rho_{\text{calc}}$/g/cm$^3$ | 1.651 |
| $\mu$/mm$^{-1}$ | 0.878 |
| F(000) | 792 |
| Crystal size/mm$^3$ | 0.42 x 0.23 x 0.23 |
| Radiation | MoKα ($\lambda=0.71073$) |
| 2θ range for data collection/° | 2.61 to 25.03 |
| Index ranges | -10 ≤ h ≤ 10, -15 ≤ k ≤ 16, -14 ≤ l ≤ 14 |
| Reflections collected | 11297 |
| Independent reflections | 2778 [Rint = 0.1127] |
| Data/restraints/parameters | 2778/0/200 |
| Goodness-of-fit on $F^2$ | 1.036 |
| Final R indexes [I>=2σ (I)] | $R_1 = 0.0738$, $wR_2 = 0.2026$ |
| Final R indexes [all data] | $R_1 = 0.1020$, $wR_2 = 0.2238$ |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.450/-0.668 |
| Flack parameter |
**2f:**

| Compound | 2f |
|----------|----|
| Empirical formula | C_{14}H_{8}Cl_{4}N_{2}O_{S} |
| Formula weight | 394.08 |
| Temperature/K | 100.00(10) |
| Crystal system | triclinic |
| Space group | P̅1 |
| a/Å | 7.10603(16) |
| b/Å | 7.22142(17) |
| c/Å | 15.6955(4) |
| α/° | 83.2406(19) |
| β/° | 78.4301(19) |
| γ/° | 71.106(2) |
| Volume/Å³ | 745.33(3) |
| Z | 2 |
| ρ(calc) g/cm³ | 1.756 |
| μ/mm⁻¹ | 8.544 |
| F(000) | 396 |
| Crystal size/mm³ | 0.367 × 0.197 × 0.115 |
| Radiation | CuKα (λ = 1.54184) |
| 2θ range for data collection/° | 5.756 to 142.51 |
| Index ranges | -8 ≤ h ≤ 8, -8 ≤ k ≤ 8, -19 ≤ l ≤ 19 |
| Reflections collected | 14538 |
| Independent reflections | 2893 [R(int) = 0.0297, R(sigma) = 0.0191] |
| Data/restraints/parameters | 2893/0/230 |
| Goodness-of-fit on F² | 1.055 |
| Final R indexes [I>=2σ(I)] | R₁ = 0.0269, wR₂ = 0.0769 |
| Final R indexes [all data] | R₁ = 0.0277, wR₂ = 0.0778 |
| Largest diff. peak/hole / e Å⁻³ | 0.36/-0.33 |
| Flack parameter | |

**Figure S11** - Crystal structure of 2f - Front view. Only one orientation of the OMe group is shown for clarity.

**Figure S12** - Crystal structure of 2f - Side view. Only one orientation of the OMe group is shown for clarity.
**2g:**

| Compound | 2g |
|----------|----|
| Empirical formula | C_{28}H_{16}Cl_{8}N_{4}S_{2} |
| Formula weight | 756.17 |
| Temperature/K | 100.0(6) |
| Crystal system | monoclinic |
| Space group | P2_1 |
| a/Å | 9.0246(3) |
| b/Å | 13.7857(5) |
| c/Å | 12.0756(4) |
| α/° | 90 |
| β/° | 98.513(3) |
| γ/° | 90 |
| Volume/Å³ | 1485.78(9) |
| Z | 2 |
| ρcalc/g/cm³ | 1.69 |
| μ/mm⁻¹ | 8.491 |
| F(000) | 760 |
| Crystal size/mm³ | 0.216 × 0.077 × 0.048 |
| Radiation | CuKα (λ = 1.54184) |
| 2θ range for data collection/° | 7.402 to 142.134 |
| Index ranges | -11 ≤ h ≤ 11, -15 ≤ k ≤ 16, -14 ≤ l ≤ 14 |
| Reflections collected | 54843 |
| Independent reflections | 5617 [Rw = 0.0805, Rsigma = 0.0293] |
| Data/restraints/parameters | 5617/1/381 |
| Goodness-of-fit on F² | 1.093 |
| Final R indexes [I>=2σ (I)] | R₁ = 0.0766, wR₂ = 0.2049 |
| Final R indexes [all data] | R₁ = 0.0769, wR₂ = 0.2058 |
| Largest diff. peak/hole / e Å⁻³ | 1.10/-0.69 |
| Flack parameter | 0.06(3) |

**Figure S13** - Crystal structure of 2g - Front view. Only one molecule in the asymmetric unit is shown for clarity.

**Figure S14** - Crystal structure of 2g - Side view. Only one molecule in the asymmetric unit is shown for clarity.
### 2h:

| Compound | 2h |
|----------|----|
| Empirical formula | C_{16}H_{12}Cl_{4}N_{2}S |
| Formula weight | 406.14 |
| Temperature/K | 100.00(10) |
| Crystal system | orthorhombic |
| Space group | Pbc a |
| a/Å | 14.2979(4) |
| b/Å | 14.0607(3) |
| c/Å | 16.3174(4) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å^3 | 3280.41(15) |
| Z | 8 |
| ρ_{calc} g/cm^3 | 1.645 |
| μ/mm⁻¹ | 7.736 |
| F(000) | 1648 |
| Crystal size/mm³ | 0.424 × 0.235 × 0.177 |
| Radiation | CuKα (λ = 1.54184) |
| 2θ range for data collection/° | 10.356 to 142.54 |
| Index ranges | -17 ≤ h ≤ 17, -13 ≤ k ≤ 17, -20 ≤ l ≤ 20 |
| Reflections collected | 63211 |
| Independent reflections | 3183 [R_{int} = 0.0724, R_{aggr} = 0.0183] |
| Data/restraints/parameters | 3183/0/237 |
| Goodness-of-fit on F² | 1.108 |
| Final R indexes [I>=2σ (I)] | R₁ = 0.0399, wR₂ = 0.0977 |
| Final R indexes [all data] | R₁ = 0.0400, wR₂ = 0.0977 |
| Largest diff. peak/hole / e Å⁻³ | 1.00/-0.47 |
| Flack parameter | |

**Figure S15** - Crystal structure of 2h - Front view.

**Figure S16** - Crystal structure of 2h - Side view.
**2i:**

![Crystal structure of 2i - Front view.](image1)

**Figure S17 - Crystal structure of 2i - Front view.**

![Crystal structure of 2i - Side view.](image2)

**Figure S18 - Crystal structure of 2i - Side view.**

| Compound | 2i |
|----------|----|
| Empirical formula | C_{14}H_{8}Cl_{4}N_{2}O_{2} |
| Formula weight | 394.08 |
| Temperature/K | 100.0(5) |
| Crystal system | triclinic |
| Space group | P\(\bar{1}\) |
| \(a/\text{Å}\) | 7.0073(5) |
| \(b/\text{Å}\) | 9.6628(6) |
| \(c/\text{Å}\) | 12.0172(7) |
| \(\alpha/°\) | 95.257(5) |
| \(\beta/°\) | 106.738(6) |
| \(\gamma/°\) | 101.231(6) |
| Volume/Å³ | 754.78(9) |
| \(Z\) | 2 |
| \(\rho_{\text{calc}}/\text{g/cm}³\) | 1.734 |
| \(\mu/\text{mm}⁻¹\) | 8.438 |
| \(F(000)\) | 396 |
| Crystal size/Å³ | 0.222 × 0.040 × 0.035 |
| Radiation | CuK\(\alpha\) (\(\lambda = 1.54184\)) |
| 2\(\theta\) range for data collection/° | 7.78 to 144.244 |
| Index ranges | \(-8 \leq h \leq 7, -11 \leq k \leq 10, -14 \leq l \leq 14\) |
| Reflections collected | 11718 |
| Independent reflections | 2964 [\(R_{\text{int}} = 0.0508, R_{\text{sigma}} = 0.0319\)] |
| Data/restraints/parameters | 2964/0/200 |
| Goodness-of-fit on \(F\)² | 1.028 |
| Final R indexes [\(I \geq 2\sigma(I)\)] | \(R_1 = 0.0387, wR_2 = 0.1048\) |
| Final R indexes [all data] | \(R_1 = 0.0408, wR_2 = 0.1073\) |
| Largest diff. peak/hole / e Å⁻³ | 0.64/-0.39 |
| Flack parameter | |
**2j:**

![Crystal structure of 2j - Front view.](image1)

**Figure S19** - Crystal structure of 2j - Front view.

![Crystal structure of 2j - Side view.](image2)

**Figure S20** - Crystal structure of 2j - Side view.

| Compound | 2j |
|----------|----|
| Empirical formula | C_{16}H_{12}Cl_{4}N_{2}O_{5} |
| Formula weight | 422.14 |
| Temperature/K | 99.9(6) |
| Crystal system | triclinic |
| Space group | P1 |
| a/Å | 7.4264(7) |
| b/Å | 11.9574(11) |
| c/Å | 11.9660(9) |
| α/° | 115.075(9) |
| β/° | 91.228(8) |
| γ/° | 95.201(8) |
| Volume/Å³ | 956.37(16) |
| Z | 2 |
| ρ.calc | 1.466 |
| μ/mm⁻¹ | 6.697 |
| F(000) | 428 |
| Crystal size/mm³ | 0.415 x 0.042 x 0.028 |
| Radiation | CuKα (λ = 1.54184) |
| 2Θ range for data collection/° | 8.176 to 134.15 |
| Index ranges | -6 ≤ h ≤ 8, -14 ≤ k ≤ 13, -14 ≤ l ≤ 14 |
| Reflections collected | 6147 |
| Independent reflections | 3403 [R(int) = 0.0440, Rsigma = 0.0492] |
| Data/restraints/parameters | 3403/0/218 |
| Goodness-of-fit on F² | 1.056 |
| Final R indexes [I>2σ (I)] | R₁ = 0.0546, wR₂ = 0.1486 |
| Final R indexes [all data] | R₁ = 0.0611, wR₂ = 0.1565 |
| Largest diff. peak/hole / e Å⁻³ | 0.81/-0.84 |
| Flack parameter |
**2l.H[\text{HCl}_2]:**

![Crystal structure of 2l.H[\text{HCl}_2] - Front view. Anion omitted for clarity.](image)

**Figure S21** - Crystal structure of 2l.H[\text{HCl}_2] - Front view. Anion omitted for clarity.

![Crystal structure of 2l.H[\text{HCl}_2] - Side view. Anion omitted for clarity.](image)

**Figure S22** - Crystal structure of 2l.H[\text{HCl}_2] - Side view. Anion omitted for clarity.
2r:

**Empirical formula**

| Compound          | 2r |
|-------------------|----|
| Empirical formula | C₁₆H₁₀.₄₂Cl₅.₅₈N₂OS |
| Formula weight    | 476.64 |
| Temperature/K     | 100.00(13) |
| Crystal system    | monoclinic |
| Space group       | P2₁/n |
| a/Å               | 6.5698(7) |
| b/Å               | 16.562(2) |
| c/Å               | 16.941(3) |
| α/°               | 90 |
| β/°               | 93.510(12) |
| γ/°               | 90 |
| Volume/Å³         | 1839.8(5) |
| Z                 | 4 |
| ρ calc g/cm³      | 1.721 |
| μ/mm⁻¹            | 9.11 |
| F(000)            | 957 |
| Crystal size/mm³  | 0.056 × 0.028 × 0.018 |
| Radiation         | CuKα (λ = 1.54184) |
| 2θ range for data collection/° | 7.472 to 136.154 |
| Index ranges      | -4 ≤ h ≤ 7, -19 ≤ k ≤ 19, -20 ≤ l ≤ 19 |
| Reflections collected | 6606 |
| Independent reflections | 3350 [R_w = 0.0626, R_{wmax} = 0.0882] |
| Data/restraints/parameters | 3350/0/241 |
| Goodness-of-fit on F² | 1.145 |
| Final R indexes [I>=2σ (I)] | R₁ = 0.1055, wR₂ = 0.2644 |
| Final R indexes [all data] | R₁ = 0.1319, wR₂ = 0.2818 |
| Largest diff. peak/hole / e Å⁻³ | 0.77/-0.96 |
| Flack parameter   | 0.77/-0.96 |

**Figure S23** - Crystal structure of 2r - Front view. Shown in partial chlorination ortho to the OMe group.

**Figure S24** - Crystal structure of 2r - Side view. Shown with partial chlorination ortho to the OMe group.
**2s:**

| Compound | 2s |
|----------|----|
| Empirical formula | $C_{15}H_{9.88}Cl_{4.12}N_2S$ |
| Formula weight | 396.33 |
| Temperature/K | 100.0(6) |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| $a/$Å | 7.8074(3) |
| $b/$Å | 15.8724(4) |
| $c/$Å | 13.5003(4) |
| $\alpha^\circ$ | 90 |
| $\beta^\circ$ | 105.795(3) |
| $\gamma^\circ$ | 90 |
| Volume/Å$^3$ | 1609.82(9) |
| $Z$ | 4 |
| $\rho$/g/cm$^3$ | 1.635 |
| $\mu$/mm$^{-1}$ | 8.049 |
| $F(000)$ | 800 |
| Crystal size/mm$^3$ | $0.315 \times 0.066 \times 0.03$ |
| Radiation | CuKα ($\lambda = 1.54184$) |
| 2Θ range for data collection" | 8.796 to 135.814 |
| Index ranges | $-9 \leq h \leq 9, -19 \leq k \leq 19, -16 \leq l \leq 16$ |
| Reflections collected | 22798 |
| Independent reflections | 2931 [R(int) = 0.0463, R(sigma) = 0.0202] |
| Data/restraints/parameters | 2931/0/210 |
| Goodness-of-fit on $F^2$ | 1.318 |
| Final R indexes [$I>2\sigma(I)$] | $R_1 = 0.0744, wR_2 = 0.1732$ |
| Final R indexes [all data] | $R_1 = 0.0748, wR_2 = 0.1733$ |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.16/-0.73 |

**Figure S25** - Crystal structure of 2s - Front view. Shown with partial chlorination at C6.

**Figure S26** - Crystal structure of 2s - Side view. Shown with partial chlorination at C6.
3a:

**Empirical formula**

\[ \text{C}_{13.5}\text{H}_{7}\text{Cl}_{4}\text{N}_{2}\text{S} \]

**Formula weight**

371.07

**Temperature/K**

100.0(7)

**Crystal system**

orthorhombic

**Space group**

\( \text{Pbcn} \)

\[ a/\text{Å} = 16.7712(3) \]

\[ b/\text{Å} = 13.1359(2) \]

\[ c/\text{Å} = 13.0495(2) \]

\[ \alpha/° = 90 \]

\[ \beta/° = 90 \]

\[ \gamma/° = 90 \]

**Volume/Å\(^3\)**

2874.87(8)

**Z**

8

**\( \rho_{\text{calc}} \) g/cm\(^3\)**

1.715

**\( \mu \text{ mm}^{-1} \)**

8.764

**F(000)**

1488

**Crystal size/mm\(^3\)**

\( 0.257 \times 0.084 \times 0.08 \)

**Radiation**

CuK\( \alpha \) (\( \lambda = 1.54184 \))

**\( 2\theta \) range for data collection/°**

8.55 to 142.028

**Index ranges**

\(-20 \leq h \leq 20, -16 \leq k \leq 16, -16 \leq l \leq 12 \)

**Reflections collected**

72177

**Independent reflections**

2779 \([R_{\text{int}} = 0.0861, R_{\text{sigma}} = 0.0305]\)

**Data/restraints/parameters**

2779/0/186

**Goodness-of-fit on \( F^2 \)**

1.237

**Final R indexes \([I>=2\sigma(I)]\)**

\( R_1 = 0.0615, wR_2 = 0.1453 \)

**Final R indexes \([\text{all data}]\)**

\( R_1 = 0.0638, wR_2 = 0.1454 \)

**Largest diff. peak/hole / e Å\(^3\)**

1.15I-0.68

**Flack parameter**

Figure S27 - Crystal structure of 3a - Front view. Solvent of crystallisation (DCM) omitted for clarity.

Figure S28 - Crystal structure of 3a - Side view of radical dimerisation. Solvent of crystallisation (DCM) omitted for clarity.
**3c:**

![3c Crystal Structure](image)

**Figure S29** - Crystal structure of 3c - Front view.

![3c Crystal Structure](image)

**Figure S30** - Crystal structure of 3c - Side view of radical dimerisation.

| Compound | 3c |
|----------|----|
| Empirical formula | C_{15}H_{10}Cl_{3}N_{2}S |
| Formula weight | 356.66 |
| Temperature/K | 149.99(10) |
| Crystal system | monoclinic |
| Space group | P2_1/n |
| a/Å | 11.5111(15) |
| b/Å | 7.7055(8) |
| c/Å | 16.9368(18) |
| α/° | 90 |
| β/° | 104.127(12) |
| γ/° | 90 |
| Volume/Å³ | 1456.8(3) |
| Z | 4 |
| \(\rho_{\text{calc}}\)/g/cm³ | 1.626 |
| μ/mm⁻¹ | 6.972 |
| F(000) | 724 |
| Crystal size/mm² | 0.132 × 0.041 × 0.028 |
| Radiation | CuKα (λ = 1.54184) |
| 2Θ range for data collection/° | 8.42 to 131.946 |
| Index ranges | -13 ≤ h ≤ 13, -9 ≤ k ≤ 8, -20 ≤ l ≤ 14 |
| Reflections collected | 7614 |
| Independent reflections | 2532 [R_{int} = 0.0574, R_{sigma} = 0.0513] |
| Data/restraints/parameters | 2532/0/190 |
| Goodness-of-fit on F² | 1.053 |
| Final R indexes [I≥2σ (I)] | R₁ = 0.0388, wR₂ = 0.1031 |
| Final R indexes [all data] | R₁ = 0.0454, wR₂ = 0.1076 |
| Largest diff. peak/hole / e Å⁻³ | 0.38/-0.58 |
| Flack parameter | |

S31
3e:

**Empirical formula**: $C_{30}H_{20}Cl_6N_4S_2$

**Formula weight**: 713.32

**Temperature/K**: 100.00(10)

**Crystal system**: triclinic

**Space group**: $P \bar{1}$

- $a/\text{Å}$: 9.9369(4)
- $b/\text{Å}$: 12.2664(4)
- $c/\text{Å}$: 13.3652(5)
- $\alpha^\circ$: 91.036(3)
- $\beta^\circ$: 107.068(4)
- $\gamma^\circ$: 109.355(3)

**Volume/Å$^3$**: 1457.25(10)

**Z**: 2

**$\rho_{calcd}$, g/cm$^3$**: 1.626

**$\mu$, mm$^{-1}$**: 6.97

**$F(000)$**: 724

**Crystal size/mm$^3$**: $0.273 \times 0.17 \times 0.048$

**Radiation**: CuK$\alpha$ ($\lambda = 1.54184$)

**2$\Theta$ range for data collection/$^\circ$**: 6.976 to 142.122

**Index ranges**: $-12 \leq h \leq 12, -14 \leq k \leq 15, -16 \leq l \leq 16$

**Reflections collected**: 29597

**Independent reflections**: 5631 [R(int) = 0.0638, R(sigma) = 0.0358]

**Data/restraints/parameters**: 5631/0/381

**Goodness-of-fit on $F^2$**: 1.08

**Final R indexes [I>=2$\sigma$ (I)]**: $R_1 = 0.0679, wR_2 = 0.1871$

**Final R indexes [all data]**: $R_1 = 0.0708, wR_2 = 0.1907$

**Largest diff. peak/hole / e Å$^3$**: 2.23/-0.49

**Flack parameter**: 0.05(3)

**Figure S31** - Crystal structure of 3e - Front view. Only one molecule of the asymmetric unit is shown for clarity.

**Figure S32** - Crystal structure of 3e - Side view of radical dimerisation.
**3k:**

**Figure S33** - Crystal structure of 3e - Front view. Only one molecule of the asymmetric unit is shown for clarity.

**Figure S34** - Crystal structure of 3k - Side view of radical dimerisation.

**Compound 3k**
- **Empirical formula**: $\text{C}_{13}\text{H}_8\text{N}_3\text{SCl}_2$
- **Formula weight**: 300.84
- **Temperature/K**: 99.98(10)
- **Crystal system**: monoclinic
- **Space group**: $P2_1/c$
- **Volume/Å³**: 1190.83(11)
- **Z**: 4
- **$\rho_{\text{calc}}$/g/cm³**: 1.725
- **$\mu$/mm⁻¹**: 6.430
- **F(000)**: 628.0
- **Cryst size/mm³**: 0.304 × 0.079 × 0.053
- **Radiation**: CuKα ($\lambda = 1.54184$)
- **2θ range for data collection/°**: 9.502 to 152.66
- **Index ranges**: -9 ≤ h ≤ 9, -23 ≤ k ≤ 23, -11 ≤ l ≤ 11
- **Reflections collected**: 23707
- **Independent reflections**: 2489 [Rint = 0.0543, Rsigma = 0.0168]
- **Data/restraints/parameters**: 2489/8/177
- **Goodness-of-fit on $F^2$**: 1.095
- **Final R indexes [I>2σ (I)]**: $R_1 = 0.0467$, $wR_2 = 0.1182$
- **Final R indexes [all data]**: $R_1 = 0.0468$, $wR_2 = 0.1183$
- **Largest diff. peak/hole / e Å⁻³**: 0.91/-0.51
[4a][GaCl₄]:

**Figure S35** - Crystal structure of [4a][GaCl₄] - Front view.

**Figure S36** - Crystal structure of [4a][GaCl₄] - Side view.
4. EPR Spectroscopy

EPR spectra were recorded on a continuous wave X-band ADANI CMS 8400 spectrometer at ambient temperature with a spectral width of 7.5 mT and a modulation amplitude of 100 μT. EPR spectral simulation and analysis were performed using the EasySpin computational package. The 1,2,4-benzothiadiazinyl radicals 3a-j were prepared in situ by combining a solution of S(IV) 1-chloride (0.005 mmol) in toluene (100 μL) with a 50 mM solution of ferrocene in toluene (100 μL, 0.005 mmol). 50 μL of the dark blue/green solution was transferred to a sealed quartz EPR tube for analysis.

4.1. EPR Spectra of 1,2,4-Benzothiadiazinyl Radicals

![EPR Spectra of 3a](image)

Figure S37 - EPR spectra of 3a. \(g\)-value = 2.00369, line width = 0.27 MHz, \(a_{N2}\) = 15.56 MHz, \(a_{N4}\) = 13.13 MHz.
**Figure S38** - EPR spectra of 3b. $g$-value = 2.00346, line width = 0.26 MHz, $a_{N2} = 15.64$ MHz, $a_{N4} = 13.51$ MHz.

**Figure S39** - EPR spectra of 3c. $g$-value = 2.00341, line width = 0.31 MHz, $a_{N2} = 15.80$ MHz, $a_{N4} = 13.60$ MHz.
**Figure S40** - EPR spectra of 3d. \( g \)-value = 2.00431, line width = 0.31 MHz, \( a_{N2} = 15.10 \) MHz, \( a_{N4} = 13.10 \) MHz.

**Figure S41** - EPR spectra of 3e. \( g \)-value = 2.00463, line width = 0.37 MHz, \( a_{N2} = 14.69 \) MHz, \( a_{N4} = 13.30 \) MHz.
Figure S42 - EPR spectra of 3f. $g$-value = 2.00453, line width = 0.33 MHz, $a_{N2} = 14.56$ MHz, $a_{N4} = 13.23$ MHz.

Figure S43 - EPR spectra of 3g. $g$-value = 2.00461, line width = 0.27 MHz, $a_{N2} = 15.88$ MHz, $a_{N4} = 13.35$ MHz.
Figure S44 - EPR spectra of 3h. $g$-value = 2.00449, line width = 0.34 MHz, $a_{N2} = 15.61$ MHz, $a_{N4} = 13.71$ MHz.

Figure S45 - EPR spectra of 3i. $g$-value = 2.00410, line width = 0.29 MHz, $a_{N2} = 15.82$ MHz, $a_{N4} = 12.89$ MHz.
Figure S46 - EPR spectra of 3j. $g$-value = 2.00411, line width = 0.38 MHz, $a_{N2}$ = 14.73 MHz, $a_{N4}$ = 13.98 MHz.
5. Cyclic Voltammetry

Electrochemical studies were performed with a Biologic multichannel potentiostat and carried out in a three-electrode electrochemical cell consisting of a glassy carbon working electrode, a platinum wire counter-electrode, and a silver wire pseudo-reference electrode. The glassy carbon working electrode was polished prior to use with a 3 μm and 1 μm diamond suspension, followed by a 0.05 μm alumina suspension. All cyclic voltammetry studies were performed under an atmosphere of argon with 2 mM concentration of analyte unless otherwise stated, and a 50 mM concentration of [t-Bu₄N][PF₆] supporting electrolyte in 10 cm³ of anhydrous DCM. All experiments were performed at 100 mV s⁻¹ unless otherwise stated. Ferrocene was added during the final measurements as an internal reference. Cyclic voltammograms were corrected in situ for uncompensated Ohmic loss using positive feedback at the 85% level relative to the measured solution resistance prior to the experiment. Data were processed with the EC Lab software and plotted with Matlab.

5.1. Cyclic Voltammograms of 1,2,4-Benzothiadiazine 1-Chlorides

![Cyclic voltammogram of 2a.](image)

Figure S47 - Cyclic voltammogram of 2a.
Figure S48 - Cyclic voltammogram of 2b.

Figure S49 - Cyclic voltammogram of 2c.
Figure S50 - Cyclic voltammogram of 2d.

Figure S51 - Cyclic voltammogram of 2e.
**Figure S52** - Cyclic voltammogram of 2f.

**Figure S53** - Cyclic voltammogram of 2g.
**Figure S54** - Cyclic voltammogram of 2h.

**Figure S55** - Cyclic voltammogram of 2i.
5.2. Variable Concentration Studies
Variable concentration cyclic voltammetry studies were performed on 2a to qualitatively assess the radical monomer-dimer equilibrium (Figure S57).
5.3. Variable Scan Rate Studies

Variable scan rate studies on 2f were performed to gain further insight into the electrochemical behaviour of the 1,2,4-benzothiadiazine 1-chlorides. The cyclic voltammograms can be superimposed upon one another (Figure S58), although the peak-to-peak separation increases with scan-rate, suggesting that the redox chemistry for the S(III)/S(IV) couple is quasi-reversible.\textsuperscript{19} The S(II)/S(III) couple is believed to be associated with an $E_{rC_i}$ process; a reversible electron transfer followed by an irreversible chemical reaction. For a typical $E_{rC_i}$ mechanism, the ratio of the anodic to cathodic peak currents decreases because the reduced species (\textit{i.e.} the S(II) anion) is consumed by a subsequent chemical reaction (\textit{i.e.} comproportionation), resulting in fewer species to oxidise on the anodic scan. As the scan rate is increased, the time scale of the experiment competes with the time scale of the chemical step. This results in relatively more reduced species left for reoxidation, and for sufficiently fast scan rates, the electrochemical feature will regain reversibility. No evidence of quasi-reversibility was observed for the S(II)/S(III) couple for scan rates up to 2 V s$^{-1}$, indicating that the comproportionation reaction is extremely rapid.

\textbf{Figure S58} - Cyclic voltammograms of 2f at various scan rates.
A plot for each of the maximum and minimum peak currents against the square root of the scan rate gave a linear correlation with $R^2$ values close to 1. The plots for the S(III)/S(IV) dimer redox couple are shown in Figure S59. This indicates an electrochemically reversible electron transfer process involving a freely diffusing redox species according to the Randles-Sevcik equation, and confirms that the analyte is not adsorbed to the electrode surface.\textsuperscript{20}

![Figure S59 - Randles-Sevcik plot for 3f.](image-url)
6. Magnetometric Studies
Magnetometric studies on 3c and 3e were performed using a Quantum Design MPMS 7 magnetometer and recorded between 2-300 K in either a 1000 Oe or 10000 Oe applied magnetic field. Samples were finely ground under inert atmosphere in a Glove Box and placed in gelatin capsules enclosed inside a pierced straw with a uniform diamagnetic background. Diamagnetic corrections were applied according to literature procedures.\textsuperscript{21} Curie-Weiss analysis provided Curie constants of 0.145 and 0.021 emu.K.Oe\textsuperscript{-1}.mol\textsuperscript{-1} for 3c and 3e respectively, consistent with essentially diamagnetic species with significant residual S = ½ defects arising from grinding the samples. The Weiss constants were found to be -998 and -101 K respectively, again consistent with strong antiferromagnetic coupling. The low temperature magnetic data clearly show the antiferromagnetic transition of trace O\textsubscript{2} within the sample at 50 K.\textsuperscript{22} There is evidence for some magnetic phase change leading to increased susceptibility at 82 K and 75 K for 3c and 3e respectively; it not known if this small effect is due to trace impurity, structural phase transition, or a purely magnetic phase transition. Further study is hampered by the extreme difficulty in obtaining large samples of sufficient purity for examination, which will therefore require additional optimisation of the syntheses.

6.1 Curie-Weiss Plots

![Curie-Weiss plot](image)

Figure S60 – Curie-Weiss plot for 3c, recorded in a field of 1000 Oe.
Figure S61 – Curie-Weiss for 3e, recorded in a field of 1000 Oe.
7. Computational Chemistry
7.1. EPR and Electronic Studies

Calculations were performed using the Gaussian 16 suite of programs. Structures were optimised in the gas-phase, from single-crystal X-ray diffraction data where available, at the DFT UB3LYP/6-31g level of theory. All structures were confirmed as minima by frequency analysis and the absence of imaginary frequencies. Single-point calculations for the EPR parameters were performed at the UB3LYP/cc-pVDZ level of theory from the UB3LYP/6-31g optimised geometry. Orbital visualisations were made using the VMD molecular graphics viewer.

Many studies on the redox properties of sulphur-nitrogen radicals have found good correlation between the \( E_{1/2} \) potentials for the 0/1\(^{+} \) couple with both the calculated energies of the LUMO of the S(IV) cations, and the SOMO of the radical. Optimised geometries of the 1,2,4-benzothiadiazine 1-chlorides 2a-j were calculated, along with their corresponding free radicals 3a-j. The results, summarised in Table S1, were found to give poor correlation with experimental electrochemical results although systems bearing electron-withdrawing groups did tend to have SOMOs with lower (more negative) energies, whilst those bearing electron-donating groups had SOMOs with higher (less negative) energies. As with the \( E_{1/2} \) potentials for the S(III)/S(IV) couple, the range of values observed for the calculated LUMO and SOMO energies was small, further indicating that the substituents on the benzo-fused and pendant aryl ring have only a minor influence on the electronic structure of the radical.

|      | LUMO Energy / eV | SOMO Energy / eV | \( E_{1/2} / \) V |
|------|-----------------|-----------------|------------------|
| a    | -4.5013         | -6.1177         | 0.096            |
| b    | -4.5165         | -6.1231         | -0.014           |
| c    | -4.4951         | -6.0913         | -0.020           |
| d    | -4.4836         | -6.0477         | -0.024           |
| e    | -4.4733         | -6.0447         | 0.057            |
| f    | -4.2687         | -6.0371         | 0.014            |
| g    | -4.4997         | -6.0872         | 0.108            |
| h    | -4.4970         | -6.0700         | 0.041            |
| i    | -4.3974         | -6.0273         | 0.086            |
| j    | -4.5413         | -6.0037         | -0.018           |

Table S1 - Calculated LUMO and SOMO energies for the 1,2,4-benzothiadiazine 1-chlorides 2a-j and corresponding radicals 3a-j. Potentials referenced against the Fc/Fc\(^{+} \) couple.

Systematic and comprehensive studies of sulphur-nitrogen radicals have shown that DFT calculations gives excellent correlation to experimental EPR parameters. However, the absolute accuracy of the calculated hyperfine coupling constants are typically poor and show significant basis set sensitivity. As such, appropriate scaling factors have been developed for each nuclei and basis set. Calculations were performed following established methods for 1,2,4-benzothiadiazinyl radicals. The hyperfine coupling constants were found to be significantly overestimated even after scaling (0.73 for \(^{14}\)N) whilst the ratio of \( a_{N2} \) to \( a_{N4} \) was inconsistent and gave poor correlation to experimental data. A table of unscaled calculated hyperfine coupling constants and the estimated spin densities on N2, N4 and S1 are shown in Table S2.
Dimerisation Energy Calculations were performed in a manner reported in the literature, including an explicit dispersion correction.\textsuperscript{33,34} Dimerisation energies were obtained by comparing the energies of the dimer of the parent radical with that of the monomer according to the following equation:

$$\Delta E_{\text{dim}} = E_{\text{dimer}} - 2E_{\text{monomer}}$$

The dimer energies were calculated as unrestricted singlets at the UM062X-D3/6-311++G(d,p) level whilst the monomer was calculated as an unrestricted doublet at the same level. The starting geometries for the calculations were derived from the crystal structure geometries of 3a (suprafacial), 3c (trans-antarafacial), and 3e (trans-suprafacial) which were trimmed down to remove all substituents and halides, replacing them with protons where appropriate.

In the case of suprafacial dimerisation, no minimum could be located on the potential energy surface, and the calculations instead converged to transition state corresponding to the formation of an S-N single bond and breaking of the pancake dimer system. Given the need for electron withdrawing groups to stabilise the radicals which was observed experimentally, the calculation for the suprafacial geometry was repeated for the full compound 3a, again using the crystal geometry for the initial calculation; this too did not converge and an equivalent transition state was located.

The calculated energies are shown in Table S3 below.

| Compound                                  | Dimerisation Mode | Dimerisation Energy |
|-------------------------------------------|-------------------|---------------------|
|                                           |                   | Hartree             |
|                                           |                   | kj.mol\(^{-1}\)     |
|                                           |                   | kcal.mol\(^{-1}\)   |
| 3-phenyl-benzo-1,2,4-thiadazinyl          | Suprafacial\*     | -0.02451            |
|                                           |                   | -64.354             |
|                                           |                   | -15.381             |
|                                           | Trans-antarafacial| -0.02279            |
|                                           |                   | -59.827             |
|                                           |                   | -14.299             |
|                                           | Trans-suprafacial | -0.02353            |
|                                           |                   | -61.775             |
|                                           |                   | -14.764             |
| 5,6,7-trichloro-3-phenyl-benzo-1,2,4-thiadazinyl | Suprafacial\*     | -0.0384             |
|                                           |                   | -100.81             |
|                                           |                   | -24.095             |

Table S3 – Dimerisation Energies for 3-phenyl-benzothiadiazinyl radical pancake bonding modes.

7.3. Magnetic Exchange Interactions

Single-point exchange energies were performed on the Gaussian 16 suite of programs\textsuperscript{23} and calculated at the UB3LYP/6-311g(d,p) level of theory\textsuperscript{27} with a simple dinuclear nearest-neighbour exchange model from pairwise combinations of radicals.\textsuperscript{35,36} Atomic coordinates...
were taken from crystallographic data. The individual pairwise exchange energies, $J$, were estimated in terms of the difference between the total energies of the triplet (TS) and broken symmetry single (BSS) states and the respective expectation values of the two states according to the expression:

$$J = -\frac{(E_{TS} - E_{BSS})}{\langle S^2 \rangle_{TS} - \langle S^2 \rangle_{BSS}}$$

![Figure S62 - Magnetic exchange pathways in 3c.](image)

| $E_{TS}$ / Hartrees | $\langle S^2 \rangle_{TS}$ | $E_{BSS}$ / Hartrees | $\langle S^2 \rangle_{BSS}$ | $J$ / cm$^{-1}$ |
|---------------------|--------------------------|----------------------|--------------------------|----------------|
| $J_{1}$             | -4931.92924166           | 2.0329               | -4931.93785381           | 0.9984         | -1827.115    |
| $J_{2}$             | -4931.94238034           | 2.0330               | -4931.94253497           | 0.9996         | -32.841      |
| $J_{3}$             | -4931.94504518           | 2.0348               | -4931.94504480           | 1.0000         | 0.081        |
| $J_{4}$             | -4931.94527360           | 2.0347               | -4931.94527371           | 1.0000         | -0.023       |

**Table S4** - Calculated exchange energies for 3c.

3e:

| $E_{TS}$ / Hartrees | $\langle S^2 \rangle_{TS}$ | $E_{BSS}$ / Hartrees | $\langle S^2 \rangle_{BSS}$ | $J$ / cm$^{-1}$ |
|---------------------|--------------------------|----------------------|--------------------------|----------------|
| $J_{1}$             | -4931.83391003           | 2.0309               | -4931.85623662           | 0.9934         | -4723.013    |
| $J_{2}$             | -4931.89695375           | 2.0319               | -4931.89802333           | 0.9987         | -227.203     |
| $J_{3}$             | -4931.81925623           | 2.0310               | -4931.81968459           | 0.9989         | -91.090      |
| $J_{4}$             | -4931.86338358           | 2.0330               | -4931.86338389           | 1.0000         | -0.066       |
| $J_{5}$             | -4931.82426099           | 2.0324               | -4931.82426100           | 1.0000         | -0.002       |

**Table S5** - Calculated exchange energies for 3e.
Figure S63 - Exchange pathways for 3e.
7.4. Cartesian Coordinates for Optimised Geometries

Full Cartesian coordinates and total energies for all optimised geometries are given below:

2a:

| Center Number | Atomic Number | Atomic Type | X (Angstroms) | Y (Angstroms) | Z (Angstroms) |
|---------------|---------------|-------------|---------------|---------------|---------------|
| 1             | 16            | 0           | 1.441607      | 7.238480      | 8.519775      |
| 2             | 17            | 0           | 1.416780      | 7.329372      | 11.064734     |
| 3             | 17            | 0           | 6.709794      | 8.263969      | 7.176513      |
| 4             | 17            | 0           | 6.165360      | 11.413797     | 7.548903      |
| 5             | 17            | 0           | 3.226106      | 12.426335     | 8.422110      |
| 6             | 7             | 0           | 4.338111      | 6.581157      | 7.684833      |
| 7             | 7             | 0           | 2.085870      | 5.718973      | 8.009575      |
| 8             | 6             | 0           | 4.049804      | 7.898677      | 7.854102      |
| 9             | 6             | 0           | 3.428829      | 5.601719      | 7.750811      |
| 10            | 6             | 0           | 2.776948      | 8.412314      | 8.217039      |
| 11            | 6             | 0           | 3.882369      | 4.219691      | 7.491581      |
| 12            | 6             | 0           | 2.531955      | 9.776361      | 8.402779      |
| 13            | 1             | 0           | 1.558285      | 10.132721     | 8.715429      |
| 14            | 6             | 0           | 5.088761      | 8.864222      | 7.648981      |
| 15            | 6             | 0           | 5.211204      | 3.986655      | 7.087153      |
| 16            | 1             | 0           | 5.879892      | 4.833172      | 6.978518      |
| 17            | 6             | 0           | 4.851993      | 10.219633     | 7.812321      |
| 18            | 6             | 0           | 3.001869      | 3.130620      | 7.640072      |
| 19            | 1             | 0           | 1.983127      | 3.312244      | 7.958272      |
| 20            | 6             | 0           | 3.563783      | 10.671731     | 8.193441      |
| 21            | 6             | 0           | 5.649104      | 2.688049      | 6.836143      |
| 22            | 1             | 0           | 6.674586      | 2.516603      | 6.526209      |
| 23            | 6             | 0           | 3.447025      | 1.832479      | 7.385693      |
| 24            | 1             | 0           | 2.764673      | 0.997620      | 7.505204      |
| 25            | 6             | 0           | 4.769523      | 1.607051      | 6.983246      |
| 26            | 1             | 0           | 5.113244      | 0.596337      | 6.787693      |

Total energy $E(UB3LYP) = -2847.12972313$ Hartrees
2b:

---

Center     Atomic      Atomic             Coordinates (Angstroms)
Number     Number       Type             X           Y           Z
---
1          17           0        7.317996    6.799277    7.292015
2          16           0        6.738006    0.908202    4.916811
3          17           0        9.046558    4.360726    8.503876
4          17           0        6.319687    6.892489    3.529507
5          17           0        5.271316   -0.041658    6.769585
6           7           0        5.264526    3.439336    3.951648
7           7           0        5.777360    1.105287    3.491726
8           6           0        6.131554    3.610985    4.989637
9           6           0        6.246488    4.934705    5.547097
10          6           0        5.134336    2.294461    3.268691
11          6           0        7.135852    5.144246    6.592022
12          6           0        4.232369    2.283770    2.096011
13          6           0        5.406740    6.019556    4.969179
14          1           0        5.191294    6.817365    5.672163
15          1           0        4.512015    5.617962    4.506204
16          1           0        7.907134    4.087977    7.135196
17          6           0        6.927209    2.582035    5.553262
18          6           0        3.861084    1.068923    1.488216
19          1           0        4.237225    0.137740    1.892684
20          6           0        7.799333    2.808122    6.623160
21          1           0        8.376360    2.000055    7.055994
22          6           0        3.744695    3.497549    1.576106
23          1           0        4.047296    4.428593    2.038309
24          6           0        3.007974    1.072195    0.383522
25          1           0        2.719693    0.132392   -0.075262
26          6           0        2.894268    3.493427    0.470114
27          1           0        2.525305    4.432863    0.072245
28          6           0        2.522362    2.282086   -0.128246
29          1           0        1.859664    2.281732   -0.987716
---

Total energy E(UB3LYP) = -2886.44928161 Hartrees
2c:

```
Center     Atomic      Atomic             Coordinates (Angstroms)
Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
 1         17           0        5.069510    1.884385    3.627555
 2         16           0        2.980081    3.320418    3.923627
 3         17           0        4.578637    6.439213   -0.288167
 4         17           0        3.993752    9.737949    1.286108
 5         17           0        3.674616    9.282836    5.243824
 6         7           0        2.724870    3.596869    5.611955
 7         6           0        4.050203    5.854892    4.265851
 8         6           0        3.285649    4.695545    6.208193
 9         6           0        3.819463    5.058785    1.943947
10        6           0        3.536403    4.287404    1.238464
11        6           0        4.642346    7.073407    3.772743
12        6           0        4.790342    7.275900    2.392368
13        6           0        3.114313    4.739821    7.676769
14        6           0        3.647986    4.880591    3.320195
15        6           0        3.355379    5.938374    8.374974
16        6           0        3.652443    6.820333    7.821610
17        6           0        2.705260    3.593918    8.380484
18        6           0        2.522557    2.673946    7.845157
19        6           0        2.549139    3.648010    9.772054
20        6           0        2.240821    2.759588    10.312929
21        6           0        3.194627    5.985906    9.760103
22        6           0        3.377090    6.914390   10.290852
23        6           0        4.374605    6.242574    1.504816
24        6           0        5.081542    8.067329    4.795949
25        6           0        5.897419    8.708382    4.478181
26        6           0        5.306821    7.576460    5.736788
27        6           0        2.793055    4.841826    10.462587
28        6           0        2.669862    4.881368    11.540173
29        6           0        5.368493    8.538282    1.833925
30        6           0        5.946722    8.365057    0.930664
31        6           0        5.949032    9.107504    2.551149
---------------------------------------------------------------------
Total energy E(UB3LYP) =  -2925.75973149 Hartrees
```
| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|--------------|--------------|-------------|------------------------|
|              |              |             | X          | Y          | Z          |
| 1            | 17           | 0           | 5.114392   | 1.885218   | 3.656962   |
| 2            | 16           | 0           | 3.003736   | 3.325893   | 3.930355   |
| 3            | 17           | 0           | 4.573405   | 6.582082   | -0.267685  |
| 4            | 17           | 0           | 3.601751   | 9.310635   | 5.201712   |
| 5            | 7            | 0           | 3.912534   | 5.722758   | 5.624374   |
| 6            | 7            | 0           | 2.752905   | 3.589924   | 5.618298   |
| 7            | 6            | 0           | 4.045437   | 5.861449   | 4.274344   |
| 8            | 6            | 0           | 3.299792   | 4.691635   | 6.218023   |
| 9            | 6            | 0           | 4.619588   | 7.091107   | 3.798861   |
| 10           | 6            | 0           | 4.746121   | 7.266920   | 2.428314   |
| 11           | 6            | 0           | 3.134234   | 4.731008   | 7.687015   |
| 12           | 6            | 0           | 3.656486   | 4.891050   | 3.316198   |
| 13           | 6            | 0           | 3.376034   | 5.927619   | 8.388121   |
| 14           | 6            | 0           | 3.670360   | 6.811466   | 7.836461   |
| 15           | 6            | 0           | 3.730644   | 3.581798   | 8.394010   |
| 16           | 6            | 0           | 2.548229   | 2.663070   | 7.850921   |
| 17           | 6            | 0           | 2.579857   | 3.631021   | 9.780768   |
| 18           | 6            | 0           | 2.275734   | 2.740184   | 10.31986   |
| 19           | 6            | 0           | 3.220784   | 5.970263   | 9.774047   |
| 20           | 1            | 0           | 3.404299   | 6.897109   | 10.307196  |
| 21           | 6            | 0           | 4.353820   | 6.270354   | 1.500714   |
| 22           | 6            | 0           | 5.042079   | 8.111362   | 4.795536   |
| 23           | 1            | 0           | 5.834591   | 8.760182   | 4.438177   |
| 24           | 1            | 0           | 5.275485   | 7.654048   | 5.750621   |
| 25           | 6            | 0           | 2.824130   | 4.823095   | 10.474248  |
| 26           | 1            | 0           | 2.705472   | 4.858725   | 11.552447  |
| 27           | 6            | 0           | 3.810206   | 5.057228   | 1.920647   |
| 28           | 6            | 0           | 3.412248   | 3.945013   | 0.981042   |
| 29           | 1            | 0           | 3.539749   | 4.231426   | -0.060542  |
| 30           | 1            | 0           | 4.025121   | 3.054948   | 1.170443   |
| 31           | 1            | 0           | 2.361922   | 3.665224   | 1.126785   |
| 32           | 17           | 0           | 5.433075   | 8.819312   | 1.807177   |

Total energy $E(UB3LYP) = -2925.75928790$ Hartrees
| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|------------------------|
| 1             | 17            | 0           | 5.117940 1.858223 3.670225 |
| 2             | 16            | 0           | 3.006183 3.305436 3.936486 |
| 3             | 17            | 0           | 4.619052 6.537357 -0.262588 |
| 4             | 7             | 0           | 3.882221 5.713190 5.632863 |
| 5             | 7             | 0           | 2.750009 3.566328 5.620911 |
| 6             | 6             | 0           | 4.029659 5.847490 4.287465 |
| 7             | 6             | 0           | 3.289521 4.670860 6.224801 |
| 8             | 6             | 0           | 4.579895 7.061717 3.776606 |
| 9             | 6             | 0           | 4.766971 7.280612 2.417564 |
| 10            | 6             | 0           | 3.140582 4.703302 7.695719 |
| 11            | 6             | 0           | 3.667590 4.870845 3.322145 |
| 12            | 6             | 0           | 3.532047 5.851467 8.410332 |
| 13            | 1             | 0           | 3.937668 6.694558 7.865414 |
| 14            | 6             | 0           | 2.613243 3.598127 8.390979 |
| 15            | 1             | 0           | 2.320345 2.714599 7.837986 |
| 16            | 6             | 0           | 2.479795 3.645095 9.779580 |
| 17            | 1             | 0           | 2.075904 2.789009 10.309620 |
| 18            | 6             | 0           | 3.396800 5.890405 9.798439 |
| 19            | 1             | 0           | 3.700980 6.777883 10.343405 |
| 20            | 6             | 0           | 4.381268 6.241351 1.518750 |
| 21            | 6             | 0           | 2.869998 4.789358 10.486805 |
| 22            | 1             | 0           | 2.766286 4.822475 11.566680 |
| 23            | 6             | 0           | 3.841389 5.026693 1.928042 |
| 24            | 6             | 0           | 3.462044 3.905290 0.991359 |
| 25            | 1             | 0           | 3.613960 4.181055 -0.049886 |
| 26            | 1             | 0           | 4.066484 3.014734 1.202579 |
| 27            | 1             | 0           | 2.407176 3.631056 1.113949 |
| 28            | 17            | 0           | 5.028235 8.333700 4.975916 |
| 29            | 6             | 0           | 5.348729 8.561858 1.913412 |
| 30            | 1             | 0           | 5.886152 8.441131 0.978892 |
| 31            | 1             | 0           | 5.958702 9.060984 2.658359 |
| 32            | 17            | 0           | 3.969639 9.816457 1.509648 |

Total Energy E(UB3LYP) = -2925.75684163 Hartrees
| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|--------------|-------------|-------------------------|
|               |              |             | X          | Y          | Z          |
| 1             | 16           | 0           | 1.446734  | 7.223536  | 8.427569  |
| 2             | 17           | 0           | 1.465630  | 7.186049  | 10.957944 |
| 3             | 17           | 0           | 6.76622   | 8.229599  | 7.276682  |
| 4             | 17           | 0           | 6.182444  | 11.376091 | 7.545914  |
| 5             | 17           | 0           | 3.272801  | 12.414003 | 8.335738  |
| 6             | 7            | 0           | 4.379787  | 6.542431  | 7.725085  |
| 7             | 7            | 0           | 2.108941  | 5.698753  | 7.947318  |
| 8             | 6            | 0           | 4.083509  | 7.863978  | 7.848103  |
| 9             | 6            | 0           | 3.457471  | 5.571616  | 7.752520  |
| 10            | 6            | 0           | 2.791643  | 8.375237  | 8.121295  |
| 11            | 6            | 0           | 3.913299  | 4.186512  | 7.501053  |
| 12            | 6            | 0           | 2.505739  | 9.750741  | 8.235887  |
| 13            | 6            | 0           | 5.122861  | 8.827736  | 7.661058  |
| 14            | 6            | 0           | 5.255735  | 3.947183  | 7.150776  |
| 15            | 1            | 0           | 5.933863  | 4.787659  | 7.073279  |
| 16            | 6            | 0           | 4.857962  | 10.181730 | 7.774266  |
| 17            | 6            | 0           | 3.020143  | 3.103433  | 7.610131  |
| 18            | 1            | 0           | 1.991182  | 3.292385  | 7.888820  |
| 19            | 6            | 0           | 3.554141  | 10.652038 | 8.076093  |
| 20            | 6            | 0           | 5.694537  | 2.644128  | 6.913382  |
| 21            | 1            | 0           | 6.730760  | 2.466325  | 6.645295  |
| 22            | 6            | 0           | 3.465904  | 1.802856  | 7.369180  |
| 23            | 1            | 0           | 2.773445  | 0.972417  | 7.458387  |
| 24            | 6            | 0           | 4.802126  | 1.569052  | 7.020290  |
| 25            | 1            | 0           | 5.146460  | 0.556415  | 6.835598  |
| 26            | 8            | 0           | 1.204031  | 10.036140 | 8.572814  |
| 27            | 6            | 0           | 0.416524  | 11.098525 | 7.916630  |
| 28            | 1            | 0           | -0.610462 | 10.738796 | 7.964369  |
| 29            | 1            | 0           | 0.518976  | 12.034013 | 8.463710  |
| 30            | 1            | 0           | 0.730264  | 11.225571 | 6.877343  |

Total Energy E(UB3LYP) = -2961.60478588 Hartrees
2g:

```
Center     Atomic      Atomic             Coordinates (Angstroms)
Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
1         16           0        1.344517    7.426041    8.045327
2         17           0        0.854436    7.381120   10.552427
3         17           0        6.816270    8.119685    7.674848
4         17           0        6.417535   11.286889    8.085817
5         17           0        3.444104   12.472938    8.507454
6          7           0        4.293500    6.590298    7.730159
7          7           0        1.975317    5.873522    7.592812
8          6           0        4.062346    7.918265    7.886768
9          6           0        3.327759    5.666026    7.60319
10         6           0        2.780237    8.509185    8.047930
11         6           0        3.758677    4.266447    7.377646
12         6           0        2.595241    9.881160    8.250386
13         6           0        5.180708    8.816756    7.896425
14         6           0        1.606985   10.295029    8.407936
15         6           0        5.041296    4.084960    6.815416
16         6           0        5.612084    4.965157    6.593555
17         6           0        5.059578   10.178639    8.076038
18         6           0        2.966100    3.132038    7.709110
19         6           0        3.702358    10.707378    8.257402
20         6           0        5.543268    2.813977    6.553479
21         6           0        6.527812    2.698953    6.113207
22         6           0        3.505847    1.861216    7.440452
23         6           0        2.916392    0.987081    7.699561
24         6           0        4.766643    1.692805    6.865669
25         6           0        5.142543    0.693381    6.670882
26         6           0        1.602051    3.197691    8.362143
27         6           0        1.576860    3.897841    9.202502
28         6           0        0.833294    3.533423    7.659620
29         6           0        1.320992    2.207271    8.733362
---------------------------------------------------------------------
Total energy E(UB3LYP) =  -2886.43218800 Hartrees
```
Total energy $E(UB3LYP) = -2965.06307593$ Hartrees
| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X           | Y           | Z           |
| 1             | 17            | 0           | 4.974897    | 1.870553    | 3.748893    |
| 2             | 16            | 0           | 2.913754    | 3.376450    | 3.900513    |
| 3             | 17            | 0           | 4.834940    | 6.322388    | -0.301758   |
| 4             | 17            | 0           | 4.250859    | 9.684155    | 1.141104    |
| 5             | 17            | 0           | 3.686384    | 9.353336    | 5.087153    |
| 6             | 7             | 0           | 3.821349    | 5.798154    | 5.575628    |
| 7             | 7             | 0           | 2.572545    | 3.708147    | 5.559756    |
| 8             | 6             | 0           | 4.033263    | 5.890753    | 4.231685    |
| 9             | 6             | 0           | 3.134265    | 4.807014    | 6.161626    |
| 10            | 6             | 0           | 3.913872    | 5.030500    | 1.923372    |
| 11            | 1             | 0           | 3.651339    | 4.244668    | 1.225964    |
| 12            | 6             | 0           | 4.683074    | 7.079454    | 3.736798    |
| 13            | 6             | 0           | 4.915063    | 7.235489    | 2.361854    |
| 14            | 6             | 0           | 2.890103    | 4.891560    | 7.610010    |
| 15            | 6             | 0           | 3.659984    | 4.898952    | 3.291945    |
| 16            | 6             | 0           | 3.153007    | 6.091971    | 8.306762    |
| 17            | 1             | 0           | 3.521675    | 6.948905    | 7.757650    |
| 18            | 6             | 0           | 2.388705    | 3.787774    | 8.324185    |
| 19            | 1             | 0           | 2.187239    | 2.864664    | 7.795346    |
| 20            | 6             | 0           | 2.160982    | 3.866843    | 9.697673    |
| 21            | 1             | 0           | 1.783139    | 2.999718    | 10.224245   |
| 22            | 6             | 0           | 2.926305    | 6.179711    | 9.671824    |
| 23            | 1             | 0           | 3.116442    | 7.094488    | 10.219924   |
| 24            | 6             | 0           | 4.524003    | 6.186109    | 1.482293    |
| 25            | 6             | 0           | 5.087862    | 8.093812    | 4.753451    |
| 26            | 1             | 0           | 5.934297    | 8.708055    | 4.464165    |
| 27            | 1             | 0           | 5.248289    | 7.626770    | 5.719352    |
| 28            | 6             | 0           | 2.430880    | 5.066266    | 10.375112   |
| 29            | 6             | 0           | 5.558382    | 8.464833    | 1.801218    |
| 30            | 1             | 0           | 6.180925    | 8.249367    | 0.937440    |
| 31            | 1             | 0           | 6.113306    | 9.040400    | 2.533462    |
| 32            | 8             | 0           | 2.242353    | 5.255337    | 11.730418   |
| 33            | 6             | 0           | 1.724973    | 4.160100    | 12.537305   |
| 34            | 1             | 0           | 2.402814    | 3.299653    | 12.514903   |
| 35            | 1             | 0           | 1.666214    | 4.558352    | 13.548938   |
| 36            | 1             | 0           | 0.728219    | 3.857239    | 12.197994   |

Total energy E(UB3LYP) = -3040.24578786 Hartrees
3a:

| Center Number | Atomic Number | Atomic Type | X (Angstroms) | Y (Angstroms) | Z (Angstroms) |
|---------------|---------------|-------------|--------------|--------------|--------------|
| 1             | 16            | 0           | 1.377408     | 7.275125     | 8.482359     |
| 2             | 17            | 0           | 6.676776     | 8.230900     | 7.118504     |
| 3             | 17            | 0           | 6.210369     | 11.385620    | 7.556857     |
| 4             | 17            | 0           | 3.282176     | 12.438391    | 8.464905     |
| 5             | 7             | 0           | 4.282453     | 6.583468     | 7.615383     |
| 6             | 7             | 0           | 2.080180     | 5.671990     | 8.131903     |
| 7             | 6             | 0           | 4.014959     | 7.908023     | 7.818922     |
| 8             | 6             | 0           | 3.379281     | 5.589979     | 7.766559     |
| 9             | 6             | 0           | 2.756463     | 8.431951     | 8.216548     |
| 10            | 6             | 0           | 3.863097     | 4.209427     | 7.498315     |
| 11            | 6             | 0           | 2.546103     | 9.795595     | 8.408367     |
| 12            | 1             | 0           | 1.578135     | 10.175477    | 8.711954     |
| 13            | 6             | 0           | 5.069162     | 8.852071     | 7.621642     |
| 14            | 6             | 0           | 5.199101     | 4.000734     | 7.110204     |
| 15            | 1             | 0           | 5.854871     | 4.856595     | 7.013496     |
| 16            | 6             | 0           | 4.868346     | 10.215391    | 7.810882     |
| 17            | 6             | 0           | 2.999909     | 3.105159     | 7.627877     |
| 18            | 1             | 0           | 1.972220     | 3.269794     | 7.926834     |
| 19            | 6             | 0           | 3.599036     | 10.679630    | 8.205646     |
| 20            | 6             | 0           | 5.661480     | 2.707626     | 6.856413     |
| 21            | 1             | 0           | 6.693590     | 2.555770     | 6.557523     |
| 22            | 6             | 0           | 3.468470     | 1.815243     | 7.372691     |
| 23            | 1             | 0           | 2.796241     | 0.969507     | 7.474955     |
| 24            | 6             | 0           | 4.799573     | 1.611628     | 6.986385     |
| 25            | 1             | 0           | 5.161428     | 0.607544     | 6.788555     |

Total energy $E(\text{UB3LYP}) = -2386.96710162$ Hartrees
3b:

| Center Number | Atomic Number | Atomic Type | X (Angstroms) | Y (Angstroms) | Z (Angstroms) |
|---------------|---------------|-------------|---------------|---------------|---------------|
| 1             | 17            | 0           | 7.247433      | 6.817043      | 7.309422      |
| 2             | 16            | 0           | 6.839585      | 0.889498      | 4.895722      |
| 3             | 17            | 0           | 8.988317      | 4.392485      | 8.559115      |
| 4             | 17            | 0           | 6.377162      | 6.905935      | 3.530429      |
| 5             | 7             | 0           | 5.327195      | 3.423619      | 3.913511      |
| 6             | 7             | 0           | 5.708827      | 1.047608      | 3.523262      |
| 7             | 6             | 0           | 6.172495      | 3.601662      | 4.977186      |
| 8             | 6             | 0           | 6.256496      | 4.925727      | 5.530998      |
| 9             | 6             | 0           | 5.154970      | 2.251925      | 3.261310      |
| 10            | 6             | 0           | 7.114039      | 5.154148      | 6.608532      |
| 11            | 6             | 0           | 4.233140      | 2.265428      | 2.093781      |
| 12            | 6             | 0           | 5.424412      | 6.002348      | 4.928107      |
| 13            | 1             | 0           | 5.170529      | 6.792625      | 5.627001      |
| 14            | 1             | 0           | 4.556129      | 5.591370      | 4.425351      |
| 15            | 6             | 0           | 7.880498      | 4.113944      | 7.160954      |
| 16            | 6             | 0           | 6.956548      | 2.576212      | 5.564139      |
| 17            | 6             | 0           | 3.847582      | 1.063881      | 1.469734      |
| 18            | 1             | 0           | 4.228717      | 0.124943      | 1.851437      |
| 19            | 6             | 0           | 7.805219      | 2.826787      | 6.640173      |
| 20            | 1             | 0           | 8.404489      | 2.036705      | 7.076739      |
| 21            | 6             | 0           | 3.744386      | 3.487380      | 1.597351      |
| 22            | 1             | 0           | 4.056012      | 4.409665      | 2.070325      |
| 23            | 6             | 0           | 2.982779      | 1.087706      | 0.374264      |
| 24            | 1             | 0           | 2.687832      | 0.156053      | -0.097522     |
| 25            | 6             | 0           | 2.882390      | 3.505312      | 0.498699      |
| 26            | 1             | 0           | 2.515533      | 4.453692      | 0.119872      |
| 27            | 6             | 0           | 2.496843      | 2.307123      | -0.114770     |
| 28            | 1             | 0           | 1.825736      | 2.323240      | -0.067702     |

Total energy $E_{(UB3LYP)} = -2426.28581316$ Hartrees
| Center Number | Atomic Number | Atomic Type | X (Angstroms) | Y (Angstroms) | Z (Angstroms) |
|---------------|---------------|-------------|---------------|---------------|---------------|
| 1             | 16            | 0           | 2.884716      | 3.319212      | 3.868381      |
| 2             | 17            | 0           | 4.651132      | 6.444569      | -0.291774     |
| 3             | 17            | 0           | 4.062383      | 9.771314      | 1.280322      |
| 4             | 17            | 0           | 3.613427      | 9.298375      | 5.205034      |
| 5             | 7             | 0           | 3.836220      | 5.719280      | 5.598607      |
| 6             | 7             | 0           | 2.777373      | 3.523829      | 5.639254      |
| 7             | 6             | 0           | 4.003607      | 5.853341      | 4.243197      |
| 8             | 6             | 0           | 3.254430      | 4.657683      | 6.198911      |
| 9             | 6             | 0           | 3.824021      | 5.069769      | 1.925822      |
| 10            | 1             | 0           | 3.533718      | 4.316381      | 1.203581      |
| 11            | 6             | 0           | 4.608683      | 7.068785      | 3.772034      |
| 12            | 6             | 0           | 4.801937      | 7.280231      | 2.391303      |
| 13            | 6             | 0           | 3.109807      | 4.721855      | 7.678404      |
| 14            | 6             | 0           | 3.626872      | 4.874189      | 3.291121      |
| 15            | 6             | 0           | 3.364131      | 5.926644      | 8.358312      |
| 16            | 1             | 0           | 3.654050      | 6.800803      | 7.789575      |
| 17            | 6             | 0           | 2.709821      | 3.587972      | 8.410438      |
| 18            | 1             | 0           | 2.509948      | 2.663200      | 7.883677      |
| 19            | 6             | 0           | 2.575898      | 3.659371      | 9.798114      |
| 20            | 1             | 0           | 2.271373      | 2.778773      | 10.354355     |
| 21            | 6             | 0           | 3.224529      | 5.993219      | 9.746347      |
| 22            | 1             | 0           | 3.416699      | 6.929209      | 10.260699     |
| 23            | 6             | 0           | 4.404990      | 6.254887      | 1.501238      |
| 24            | 6             | 0           | 5.021004      | 8.062744      | 4.805653      |
| 25            | 1             | 0           | 5.852077      | 8.696696      | 4.513265      |
| 26            | 1             | 0           | 5.207379      | 7.574258      | 5.755892      |
| 27            | 6             | 0           | 2.833012      | 4.860802      | 10.470927     |
| 28            | 1             | 0           | 2.726347      | 4.914434      | 11.549776     |
| 29            | 6             | 0           | 5.404020      | 8.539047      | 1.855836      |
| 30            | 1             | 0           | 5.998901      | 8.367552      | 0.963199      |
| 31            | 1             | 0           | 5.974693      | 9.098104      | 2.589098      |

Total energy $E_{UB3LYP} = -2465.59604853$ Hartrees
Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | X     | Y     | Z     |
|---------------|---------------|-------------|-------------------------|-------|-------|-------|
| 1             | 16            | 0           |                         | 2.926148 | 3.314008 | 3.882421 |
| 2             | 17            | 0           |                         | 4.678699 | 6.572571 | -0.263549 |
| 3             | 17            | 0           |                         | 3.553929 | 9.334520 | 5.143822 |
| 4             | 7             | 0           |                         | 3.838899 | 5.722320 | 5.613434 |
| 5             | 7             | 0           |                         | 2.820012 | 3.512868 | 5.651587 |
| 6             | 6             | 0           |                         | 4.006780 | 5.856730 | 4.259269 |
| 7             | 6             | 0           |                         | 3.276013 | 4.651596 | 6.214795 |
| 8             | 6             | 0           |                         | 4.597992 | 7.083006 | 3.803337 |
| 9             | 6             | 0           |                         | 4.775693 | 7.262228 | 2.433674 |
| 10            | 6             | 0           |                         | 3.131624 | 4.712424 | 7.694222 |
| 11            | 6             | 0           |                         | 3.647779 | 4.882995 | 3.295911 |
| 12            | 6             | 0           |                         | 3.384171 | 5.915743 | 8.377179 |
| 13            | 1             | 0           |                         | 3.673764 | 6.791232 | 7.810451 |
| 14            | 6             | 0           |                         | 2.734226 | 3.575843 | 8.423439 |
| 15            | 1             | 0           |                         | 2.536300 | 2.652078 | 7.894134 |
| 16            | 6             | 0           |                         | 2.600518 | 3.643376 | 9.811300 |
| 17            | 1             | 0           |                         | 2.297833 | 2.760772 | 10.365392 |
| 18            | 6             | 0           |                         | 3.245069 | 5.978500 | 9.765452 |
| 19            | 1             | 0           |                         | 3.436638 | 6.913260 | 10.282252 |
| 20            | 6             | 0           |                         | 4.403501 | 6.273923 | 1.503205 |
| 21            | 6             | 0           |                         | 4.990696 | 8.105410 | 4.809426 |
| 22            | 1             | 0           |                         | 5.807036 | 8.740953 | 4.482661 |
| 23            | 1             | 0           |                         | 5.171696 | 7.653150 | 5.777929 |
| 24            | 6             | 0           |                         | 2.855677 | 4.843550 | 10.487170 |
| 25            | 1             | 0           |                         | 2.749515 | 4.894119 | 11.566225 |
| 26            | 6             | 0           |                         | 3.827251 | 5.063318 | 1.912915 |
| 27            | 6             | 0           |                         | 3.408683 | 3.972539 | 0.956202 |
| 28            | 1             | 0           |                         | 3.552540 | 4.264094 | -0.082201 |
| 29            | 1             | 0           |                         | 3.987565 | 3.057094 | 1.133441 |
| 30            | 1             | 0           |                         | 2.349702 | 3.722308 | 1.094620 |
| 31            | 17            | 0           |                         | 5.503885 | 8.611392 | 1.838511 |

Total energy E(UB3LYP) = -2465.59426778 Hartrees
### Molecular Structure

![Molecular Structure Image](image)

### Molecular Information

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 16            | 0           | X: 2.920541  Y: 3.293032  Z: 3.885030 |
| 2             | 17            | 0           | X: 4.705361  Y: 6.529517  Z: -0.259643 |
| 3             | 7             | 0           | X: 3.777686  Y: 5.719224  Z: 5.618465 |
| 4             | 7             | 0           | X: 2.823428  Y: 3.480270  Z: 5.656313 |
| 5             | 6             | 0           | X: 3.965105  Y: 5.847553  Z: 4.268929 |
| 6             | 6             | 0           | X: 3.295530  Y: 4.629468  Z: 6.219639 |
| 7             | 6             | 0           | X: 4.524577  Y: 7.059658  Z: 3.776207 |
| 8             | 6             | 0           | X: 4.761941  Y: 7.285607  Z: 2.419436 |
| 9             | 6             | 0           | X: 3.131622  Y: 4.683813  Z: 7.700946 |
| 10            | 6             | 0           | X: 3.645124  Y: 4.862167  Z: 3.300558 |
| 11            | 6             | 0           | X: 3.541944  Y: 5.836817  Z: 8.394449 |
| 12            | 1             | 0           | X: 3.943191  Y: 6.69834  Z: 7.831375 |
| 13            | 6             | 0           | X: 2.606989  Y: 3.593886  Z: 8.420468 |
| 14            | 1             | 0           | X: 2.291782  Y: 2.708344  Z: 7.882696 |
| 15            | 6             | 0           | X: 2.496305  Y: 3.659303  Z: 9.810500 |
| 16            | 1             | 0           | X: 2.090639  Y: 2.814380  Z: 10.357526 |
| 17            | 6             | 0           | X: 3.428319  Y: 5.895960  Z: 9.785178 |
| 18            | 1             | 0           | X: 3.746645  Y: 6.789660  Z: 10.312130 |
| 19            | 6             | 0           | X: 4.411055  Y: 6.246682  Z: 1.519941 |
| 20            | 6             | 0           | X: 2.906081  Y: 4.809344  Z: 10.497548 |
| 21            | 1             | 0           | X: 2.818622  Y: 4.857870  Z: 11.578432 |
| 22            | 6             | 0           | X: 3.854186  Y: 5.028441  Z: 1.919458 |
| 23            | 6             | 0           | X: 3.476554  Y: 3.917644  Z: 0.968691 |
| 24            | 1             | 0           | X: 3.695693  Y: 4.174832  Z: -0.065654 |
| 25            | 1             | 0           | X: 4.020756  Y: 2.996144  Z: 1.210616 |
| 26            | 1             | 0           | X: 2.404883  Y: 3.693495  Z: 1.040201 |
| 27            | 17            | 0           | X: 4.928599  Y: 8.342279  Z: 4.985341 |
| 28            | 6             | 0           | X: 5.356534  Y: 8.566709  Z: 1.937231 |
| 29            | 1             | 0           | X: 5.919385  Y: 8.450725  Z: 1.017165 |
| 30            | 1             | 0           | X: 5.943722  Y: 9.065678  Z: 2.700426 |
| 31            | 17            | 0           | X: 3.995736  Y: 9.836099  Z: 1.492464 |

Total energy $E_{UB3LYP} = -2465.59278462$ Hartrees
| Center Number | Atomic Number | Atomic Type | X (Angstroms) | Y (Angstroms) | Z (Angstroms) |
|---------------|---------------|-------------|---------------|---------------|---------------|
| 1             | 16            | 0           | 1.403019      | 7.311891      | 8.477996      |
| 2             | 17            | 0           | 6.750398      | 8.236210      | 7.239622      |
| 3             | 17            | 0           | 6.273991      | 11.386937     | 7.679885      |
| 4             | 17            | 0           | 3.353815      | 12.451619     | 8.527337      |
| 5             | 7             | 0           | 4.332615      | 6.591805      | 7.664455      |
| 6             | 7             | 0           | 2.103567      | 5.712262      | 8.110807      |
| 7             | 6             | 0           | 4.066842      | 7.918739      | 7.858631      |
| 8             | 6             | 0           | 3.408889      | 5.611659      | 7.760500      |
| 9             | 6             | 0           | 2.797951      | 8.443514      | 8.206527      |
| 10            | 6             | 0           | 3.877229      | 4.227747      | 7.497522      |
| 11            | 6             | 0           | 2.570579      | 9.811105      | 8.375806      |
| 12            | 6             | 0           | 5.127822      | 8.858880      | 7.692059      |
| 13            | 6             | 0           | 5.217017      | 4.002994      | 7.132087      |
| 14            | 1             | 0           | 5.888097      | 4.849520      | 7.061271      |
| 15            | 6             | 0           | 4.916630      | 10.220522     | 7.877124      |
| 16            | 6             | 0           | 2.994449      | 3.135829      | 7.594730      |
| 17            | 1             | 0           | 1.964415      | 3.313615      | 7.877688      |
| 18            | 6             | 0           | 3.638237      | 10.699519     | 8.224811      |
| 19            | 6             | 0           | 5.663665      | 2.706329      | 6.868328      |
| 20            | 1             | 0           | 6.698926      | 2.542002      | 6.587350      |
| 21            | 6             | 0           | 3.447177      | 1.842232      | 7.329566      |
| 22            | 1             | 0           | 2.759907      | 1.005975      | 7.407274      |
| 23            | 6             | 0           | 4.782055      | 1.622636      | 6.965668      |
| 24            | 1             | 0           | 5.131741      | 0.615715      | 6.760329      |
| 25            | 8             | 0           | 1.300713      | 10.207296     | 8.777464      |
| 26            | 6             | 0           | 0.428855      | 10.849239     | 7.769315      |
| 27            | 1             | 0           | -0.515205     | 11.009358     | 8.286985      |
| 28            | 1             | 0           | 0.851106      | 11.802730     | 7.446991      |
| 29            | 1             | 0           | 0.285949      | 10.181033     | 6.914923      |

Total energy $E_{(UB3LYP)} = -2501.44354252$ Hartrees
3g:

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Center | Atomic Number | Atomic Number | Type | Coordinates (Angstroms) | X | Y | Z
---|---|---|---|---|---|---|---
1 | 16 | 0 | 1.302255 | 7.477658 | 8.124250
2 | 17 | 0 | 6.781885 | 8.099536 | 7.502890
3 | 17 | 0 | 6.466700 | 11.269948 | 7.962356
4 | 17 | 0 | 3.522544 | 12.500137 | 8.516446
5 | 7 | 0 | 4.245148 | 6.608597 | 7.657101
6 | 7 | 0 | 1.945374 | 5.830608 | 7.825415
7 | 6 | 0 | 4.035834 | 7.941973 | 7.847928
8 | 6 | 0 | 3.272132 | 5.661313 | 7.603665
9 | 6 | 0 | 2.771666 | 8.544447 | 8.089549
10 | 6 | 0 | 3.734874 | 4.261662 | 7.424756
11 | 6 | 0 | 2.627245 | 9.915378 | 8.290050
12 | 1 | 0 | 1.654316 | 10.354595 | 8.474059
13 | 6 | 0 | 5.166013 | 8.818351 | 7.811800
14 | 6 | 0 | 5.037208 | 4.109383 | 6.901213
15 | 1 | 0 | 5.618755 | 5.003033 | 6.717755
16 | 6 | 0 | 5.030518 | 10.187799 | 8.009974
17 | 6 | 0 | 2.953974 | 3.103574 | 7.698964
18 | 6 | 0 | 3.752815 | 10.729478 | 8.250677
19 | 6 | 0 | 5.571272 | 2.852651 | 6.629518
20 | 1 | 0 | 6.572683 | 2.767058 | 6.221077
21 | 6 | 0 | 3.524759 | 1.847788 | 7.421409
22 | 1 | 0 | 2.938638 | 0.959199 | 7.635138
23 | 6 | 0 | 4.808109 | 1.710730 | 6.890320
24 | 1 | 0 | 5.208171 | 0.722149 | 6.687720
25 | 6 | 0 | 1.559586 | 3.120243 | 8.287219
26 | 1 | 0 | 1.500843 | 3.736301 | 9.189753
27 | 1 | 0 | 0.829181 | 3.539550 | 7.588996
28 | 1 | 0 | 1.252967 | 2.100921 | 8.542843
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Total energy E(UB3LYP) = -2426.26898651 Hartrees
Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | X | Y | Z
---|---|---|---|---|---|---
1 | 16 | 0 | 2.541636 | 3.491537 | 3.716797
2 | 17 | 0 | 4.643213 | 6.596914 | -0.302828
3 | 17 | 0 | 4.396085 | 9.897680 | 1.437784
4 | 17 | 0 | 3.840512 | 9.256270 | 5.33837
5 | 7 | 0 | 3.772438 | 5.676047 | 5.549308
6 | 7 | 0 | 2.461711 | 3.622679 | 5.506451
7 | 6 | 0 | 3.935537 | 5.861735 | 4.201318
8 | 6 | 0 | 3.083738 | 4.634390 | 6.112590
9 | 6 | 0 | 3.673880 | 5.213294 | 1.850682
10 | 1 | 0 | 3.306240 | 4.530216 | 1.094596
11 | 6 | 0 | 4.655905 | 7.034493 | 3.785043
12 | 6 | 0 | 4.872949 | 7.288710 | 2.415631
13 | 6 | 0 | 2.969098 | 4.690764 | 7.599312
14 | 6 | 0 | 3.455984 | 4.974230 | 3.206116
15 | 6 | 0 | 2.992919 | 5.964907 | 8.203430
16 | 1 | 0 | 3.095127 | 6.835384 | 7.566968
17 | 6 | 0 | 2.843665 | 3.530764 | 8.409685
18 | 6 | 0 | 2.744721 | 3.711166 | 9.800950
19 | 1 | 0 | 2.662010 | 2.830389 | 10.430601
20 | 6 | 0 | 2.879574 | 6.113892 | 9.584126
21 | 1 | 0 | 2.888644 | 7.105302 | 10.024432
22 | 6 | 0 | 4.375479 | 6.350466 | 1.480362
23 | 6 | 0 | 5.150809 | 7.937802 | 4.864502
24 | 1 | 0 | 6.026303 | 8.521747 | 4.599659
25 | 1 | 0 | 5.297793 | 7.389700 | 5.789111
26 | 6 | 0 | 2.754592 | 4.977536 | 10.389322
27 | 1 | 0 | 2.669585 | 5.074309 | 11.467183
28 | 6 | 0 | 5.601923 | 8.502493 | 1.937305
29 | 1 | 0 | 6.171019 | 8.314512 | 1.031356
30 | 1 | 0 | 6.232817 | 8.959626 | 2.691646
31 | 6 | 0 | 2.835749 | 2.115198 | 7.873596
32 | 1 | 0 | 1.894699 | 1.882493 | 7.366364
33 | 1 | 0 | 3.629011 | 1.948020 | 7.138078
34 | 1 | 0 | 2.973268 | 1.403979 | 8.694354

Total energy \( E(UB3LYP) = -2504.89884282 \) Hartrees
| Center | Atomic Number | Atomic Type | Coordinates (Angstroms) | X       | Y       | Z       |
|--------|---------------|-------------|-------------------------|---------|---------|---------|
| 1      | 16            | 0           |                         | 1.370122| 7.298982| 8.341416|
| 2      | 17            | 0           |                         | 6.727186| 8.336599| 7.304629|
| 3      | 17            | 0           |                         | 6.242303| 11.449390|7.966973 |
| 4      | 17            | 0           |                         | 3.278080| 12.440631|8.818341 |
| 5      | 7             | 0           |                         | 4.311272| 6.650384|7.558817 |
| 6      | 7             | 0           |                         | 2.084550| 5.725254 |7.899441 |
| 7      | 6             | 0           |                         | 4.035315| 7.970108 |7.853082 |
| 8      | 6             | 0           |                         | 3.402657| 5.665142 |7.588499 |
| 9      | 6             | 0           |                         | 2.760294| 8.467353 |8.231808 |
| 10     | 6             | 0           |                         | 3.894860| 4.313922 |7.236639 |
| 11     | 6             | 0           |                         | 2.541692| 9.812696 |8.520188 |
| 12     | 1             | 0           |                         | 1.560664| 10.171316|8.807379 |
| 13     | 6             | 0           |                         | 5.097708| 8.923112 |7.779897 |
| 14     | 6             | 0           |                         | 5.250398| 4.122269 |6.894146 |
| 15     | 1             | 0           |                         | 5.914324| 4.977144 |6.894920 |
| 16     | 6             | 0           |                         | 4.888942| 10.268119|8.065965 |
| 17     | 6             | 0           |                         | 3.032432| 3.204200 |7.235769 |
| 18     | 1             | 0           |                         | 1.991122| 3.345173 |7.497768 |
| 19     | 6             | 0           |                         | 3.603021| 10.705616|8.436646 |
| 20     | 6             | 0           |                         | 5.723623| 2.859983 |6.562198 |
| 21     | 1             | 0           |                         | 6.761343| 2.696824 |6.297075 |
| 22     | 6             | 0           |                         | 3.499989| 1.931966 |6.903299 |
| 23     | 1             | 0           |                         | 2.813135| 1.094928 |6.910830 |
| 24     | 6             | 0           |                         | 4.850721| 1.758721 |6.565113 |
| 25     | 8             | 0           |                         | 5.419802| 0.543940 |6.219692 |
| 26     | 6             | 0           |                         | 4.586187| -0.646572|6.197131 |
| 27     | 1             | 0           |                         | 5.253728| -1.454460|5.900911 |
| 28     | 1             | 0           |                         | 4.167375| -0.855695|7.188124 |
| 29     | 1             | 0           |                         | 3.775212| -0.540826|5.466457 |

Total energy $E(\text{UB3LYP}) = -2501.45226718$ Hartrees
| Center | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|--------|---------------|-------------|------------------------|
| 1      | 16            | 0           | X: 2.833199 Y: 3.368964 Z: 3.827814 |
| 2      | 17            | 0           | X: 4.911921 Y: 6.340564 Z: -0.300994 |
| 3      | 17            | 0           | X: 4.316766 Y: 9.720496 Z: 1.146933 |
| 4      | 17            | 0           | X: 3.631529 Y: 9.365722 Z: 5.050739 |
| 5      | 7             | 0           | X: 3.744510 Y: 5.789184 Z: 5.550402 |
| 6      | 7             | 0           | X: 2.629286 Y: 3.619794 Z: 5.582458 |
| 7      | 6             | 0           | X: 3.990499 Y: 5.884624 Z: 4.204133 |
| 8      | 6             | 0           | X: 3.103119 Y: 4.758068 Z: 6.14072 |
| 9      | 6             | 0           | X: 3.924323 Y: 5.045220 Z: 1.899536 |
| 10     | 1             | 0           | X: 3.657107 Y: 4.279699 Z: 1.181098 |
| 11     | 6             | 0           | X: 4.650746 Y: 7.073212 Z: 3.737386 |
| 12     | 6             | 0           | X: 4.927805 Y: 7.243477 Z: 2.365182 |
| 13     | 6             | 0           | X: 2.878383 Y: 4.861442 Z: 7.604679 |
| 14     | 6             | 0           | X: 3.644905 Y: 4.890498 Z: 3.255734 |
| 15     | 6             | 0           | X: 3.155344 Y: 6.065965 Z: 8.285134 |
| 16     | 1             | 0           | X: 3.522293 Y: 6.914571 Z: 7.722686 |
| 17     | 6             | 0           | X: 2.378708 Y: 3.771365 Z: 8.338035 |
| 18     | 1             | 0           | X: 2.159298 Y: 2.845282 Z: 7.821309 |
| 19     | 6             | 0           | X: 2.166081 Y: 3.867274 Z: 9.714020 |
| 20     | 1             | 0           | X: 1.784733 Y: 3.009343 Z: 10.253451 |
| 21     | 6             | 0           | X: 2.943635 Y: 6.171764 Z: 9.653296 |
| 22     | 1             | 0           | X: 3.145129 Y: 7.092804 Z: 10.186961 |
| 23     | 6             | 0           | X: 4.557774 Y: 6.204537 Z: 1.479501 |
| 24     | 6             | 0           | X: 5.027377 Y: 8.084746 Z: 4.761713 |
| 25     | 1             | 0           | X: 5.890275 Y: 8.690237 Z: 4.508584 |
| 26     | 1             | 0           | X: 5.144620 Y: 7.618789 Z: 5.739052 |
| 27     | 6             | 0           | X: 2.450410 Y: 5.071724 Z: 10.375056 |
| 28     | 6             | 0           | X: 5.590878 Y: 8.473098 Z: 1.834219 |
| 29     | 1             | 0           | X: 6.233049 Y: 8.263813 Z: 0.983364 |
| 30     | 1             | 0           | X: 6.130334 Y: 9.039161 Z: 2.585494 |
| 31     | 8             | 0           | X: 2.277219 Y: 5.277301 Z: 11.733855 |
| 32     | 6             | 0           | X: 1.755505 Y: 4.194937 Z: 12.551935 |
| 33     | 1             | 0           | X: 2.423756 Y: 3.326413 Z: 12.532942 |
| 34     | 1             | 0           | X: 1.706914 Y: 4.600738 Z: 13.561378 |
| 35     | 1             | 0           | X: 0.753386 Y: 3.897483 Z: 12.222711 |

Total energy $E_{UB3LYP} = -2580.08115172$ Hartrees
The following geometries were used for the dimerization energy calculations. Parent 1,2,4-benzothiadiazinyl monomer:

| Center Number | Atomic Number | Atomic Type | X       | Y       | Z       |
|---------------|---------------|-------------|---------|---------|---------|
| 1             | 16            | 0           | 7.215861| 4.835470| 8.582726|
| 2             | 7             | 0           | 9.070689| 7.197400| 8.061054|
| 3             | 7             | 0           | 8.822108| 4.818768| 8.265270|
| 4             | 6             | 0           | 10.964761| 5.749536| 7.779614|
| 5             | 6             | 0           | 9.509281| 5.946255| 8.055522|
| 6             | 6             | 0           | 11.785479| 6.854662| 7.545860|
| 7             | 1             | 0           | 11.348876| 7.844224| 7.568769|
| 8             | 6             | 0           | 7.754866| 7.481434| 8.303314|
| 9             | 6             | 0           | 6.758342| 6.515161| 8.563739|
| 10            | 6             | 0           | 13.139183| 6.677414| 7.288883|
| 11            | 1             | 0           | 13.769304| 7.540293| 7.108534|
| 12            | 6             | 0           | 7.360738| 8.837056| 8.293026|
| 13            | 6             | 0           | 13.685237| 5.397738| 7.262864|
| 14            | 1             | 0           | 14.741452| 5.261093| 7.062234|
| 15            | 6             | 0           | 11.516172| 4.466784| 7.752750|
| 16            | 1             | 0           | 10.875481| 3.613898| 7.934599|
| 17            | 6             | 0           | 12.870184| 4.293888| 7.495366|
| 18            | 1             | 0           | 13.290002| 3.295187| 7.476285|
| 19            | 6             | 0           | 5.079230| 8.219003| 8.785319|
| 20            | 6             | 0           | 5.430674| 6.882976| 8.802770|
| 21            | 1             | 0           | 4.686954| 6.118467| 8.999932|
| 22            | 6             | 0           | 6.052342| 9.197501| 8.528736|
| 23            | 1             | 0           | 4.052254| 8.508750| 8.969896|
| 24            | 1             | 0           | 5.770759| 10.243381| 8.516350|
| 25            | 1             | 0           | 8.129025| 9.573728| 8.092796|

Total energy E(UM062X) = -1008.356542 Hartree
Suprafacial Dimer:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) | X   | Y   | Z   |
|---------------|---------------|-------------|------------------------|-----|-----|-----|
| 1             | 16            | 0           | 7.168933               | 4.832242 | 8.658536 |
| 2             | 7             | 0           | 9.001882               | 7.191306 | 8.046684 |
| 3             | 7             | 0           | 8.765684               | 4.815940 | 8.333171 |
| 4             | 6             | 0           | 10.889698              | 5.750751 | 7.770406 |
| 5             | 6             | 0           | 9.436806               | 5.955267 | 8.046495 |
| 6             | 6             | 0           | 11.691212              | 6.841088 | 7.424404 |
| 7             | 1             | 0           | 11.228822              | 7.814711 | 7.326451 |
| 8             | 6             | 0           | 7.685246               | 7.477075 | 8.322420 |
| 9             | 6             | 0           | 6.702506               | 6.510428 | 8.614200 |
| 10            | 6             | 0           | 13.056729              | 6.673410 | 7.241410 |
| 11            | 1             | 0           | 13.672456              | 7.524037 | 6.973059 |
| 12            | 6             | 0           | 7.288387               | 8.827067 | 8.315324 |
| 13            | 6             | 0           | 13.637268              | 5.417449 | 7.407581 |
| 14            | 1             | 0           | 14.704838              | 5.289536 | 7.271097 |
| 15            | 6             | 0           | 11.470785              | 4.490800 | 7.919014 |
| 16            | 1             | 0           | 10.841965              | 3.648019 | 8.178727 |
| 17            | 6             | 0           | 12.841312              | 4.327111 | 7.743824 |
| 18            | 1             | 0           | 13.286305              | 3.346865 | 7.867250 |
| 19            | 6             | 0           | 5.012798               | 8.202619 | 8.833347 |
| 20            | 6             | 0           | 5.374304               | 6.869408 | 8.867503 |
| 21            | 1             | 0           | 4.643674               | 6.103508 | 9.108946 |
| 22            | 6             | 0           | 5.978015               | 9.182089 | 8.563319 |
| 23            | 16            | 0           | 9.001882               | 7.191306 | 8.046684 |
| 24            | 7             | 0           | 7.176934               | 7.191313 | 11.527668 |
| 25            | 7             | 0           | 8.005509               | 6.815962 | 11.241044 |
| 26            | 6             | 0           | 5.881503               | 5.750768 | 11.803857 |
| 27            | 6             | 0           | 7.334400               | 5.955283 | 11.527791 |
| 28            | 6             | 0           | 5.079982               | 6.841107 | 12.149835 |
| 29            | 1             | 0           | 5.542369               | 7.814731 | 12.247789 |
| 30            | 6             | 0           | 9.085969               | 7.477088 | 11.251897 |
| 31            | 6             | 0           | 10.068706              | 6.510444 | 10.960097 |
| 32            | 6             | 0           | 3.714462               | 6.673429 | 12.333074 |
| 33            | 1             | 0           | 3.098729               | 7.524058 | 12.601137 |
| 34            | 6             | 0           | 9.482817               | 8.827082 | 11.258971 |
| 35            | 6             | 0           | 3.133926               | 5.417467 | 12.166630 |
| 36            | 1             | 0           | 2.066354               | 5.289555 | 12.303094 |
| 37            | 6             | 0           | 5.300420               | 4.490095 | 11.655250 |
| 38            | 1             | 0           | 5.929246               | 3.648030 | 11.395653 |
| 39            | 6             | 0           | 3.929889               | 4.327127 | 11.830413 |
| 40            | 1             | 0           | 3.484900               | 3.346878 | 11.706988 |
| 41            | 6             | 0           | 11.758394              | 8.202648 | 10.740885 |
| 42            | 6             | 0           | 11.396897              | 6.869434 | 10.706751 |
| 43            | 1             | 0           | 12.127527              | 6.103537 | 10.465294 |
| 44            | 6             | 0           | 10.793180              | 9.182114 | 11.010934 |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
|45|1|0|3.986708|8.485781|9.032818|
|46|1|0|5.692582|10.227218|8.549448|
|47|1|0|8.719490|9.566837|11.468453|
|48|1|0|8.051715|9.566827|8.105858|
|49|1|0|11.078605|10.227245|11.024788|
|50|1|0|12.784477|8.485815|10.541382|

Total energy $E_{\text{UM062X}} = -2016.737595$ Hartree. N.B. This energy corresponds to a transition state for the formation of an S-N bond, and is not a minimum on the potential energy surface.
Trans-antarafacial Dimer:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X           | Y           | Z           |
| 1             | 16            | 0           | 3.134183    | 2.574078    | 6.546637    |
| 2             | 7             | 0           | 3.003758    | 2.642545    | 9.584647    |
| 3             | 7             | 0           | 1.909073    | 3.079555    | 7.493228    |
| 4             | 6             | 0           | 4.050696    | 1.964843    | 9.019652    |
| 5             | 6             | 0           | 2.001448    | 3.083636    | 8.813837    |
| 6             | 6             | 0           | 4.244149    | 1.799469    | 7.630781    |
| 7             | 6             | 0           | 0.847357    | 3.697654    | 9.533057    |
| 8             | 6             | 0           | 6.206963    | 0.465109    | 7.994427    |
| 9             | 6             | 0           | 5.004712    | 1.379524    | 9.881130    |
| 10            | 6             | 0           | 6.058616    | 0.648613    | 9.379679    |
| 11            | 6             | 0           | -0.260408   | 4.168868    | 8.825454    |
| 12            | 1             | 0           | -0.291507   | 4.039298    | 7.751219    |
| 13            | 6             | 0           | 5.306847    | 1.041475    | 7.123152    |
| 14            | 1             | 0           | 5.429525    | 0.936587    | 6.050531    |
| 15            | 6             | 0           | -1.288211   | 4.819699    | 9.493704    |
| 16            | 1             | 0           | -2.144427   | 5.184850    | 8.938498    |
| 17            | 6             | 0           | 0.906262    | 3.870359    | 10.916994   |
| 18            | 1             | 0           | 1.766186    | 3.490393    | 11.453825   |
| 19            | 6             | 0           | -1.217613   | 5.012145    | 10.872008   |
| 20            | 1             | 0           | -2.018327   | 5.526318    | 11.390946   |
| 21            | 6             | 0           | -0.121342   | 4.531773    | 11.581598   |
| 22            | 1             | 0           | -0.067462   | 4.687002    | 12.655386   |
| 23            | 16            | 0           | 4.241710    | 5.129544    | 9.877286    |
| 24            | 7             | 0           | 4.374447    | 5.064725    | 6.839512    |
| 25            | 7             | 0           | 5.467206    | 4.606361    | 8.931288    |
| 26            | 6             | 0           | 3.327386    | 5.742217    | 7.404410    |
| 27            | 6             | 0           | 5.375400    | 4.621488    | 7.610391    |
| 28            | 6             | 0           | 3.132758    | 5.905838    | 8.793342    |
|   |   |   |          |          |          |
|---|---|---|----------|----------|----------|
| 29| 6 | 0 | 6.529481 | 4.007060 | 6.891568 |
| 30| 6 | 0 | 1.170513 | 7.241010 | 8.429894 |
| 31| 6 | 0 | 2.374570 | 6.329412 | 6.542898 |
| 32| 6 | 0 | 1.320393 | 7.059837 | 7.044491 |
| 33| 6 | 0 | 7.637206 | 3.536203 | 7.599449 |
| 34| 1 | 0 | 7.668273 | 3.666279 | 8.673622 |
| 35| 6 | 0 | 2.069582 | 6.663028 | 9.301169 |
| 36| 1 | 0 | 1.945707 | 6.106556 | 4.213350 | 4.970697 |
| 37| 6 | 0 | 8.665090 | 2.885120 | 6.931529 |
| 38| 1 | 0 | 9.521334 | 2.520323 | 7.486923 |
| 39| 6 | 0 | 6.470596 | 3.833666 | 5.507713 |
| 40| 1 | 0 | 5.610656 | 4.213350 | 4.970697 |
| 41| 6 | 0 | 8.594522 | 2.692005 | 5.553336 |
| 42| 1 | 0 | 9.395278 | 2.177639 | 5.034655 |
| 43| 6 | 0 | 7.498212 | 3.171946 | 4.843479 |
| 44| 1 | 0 | 7.444350 | 3.034433 | 3.769766 |
| 45| 1 | 0 | 7.037993 | -0.110590 | 7.606276 |
| 46| 1 | 0 | 6.778507 | 0.207768 | 10.058796 |
| 47| 1 | 0 | 4.865140 | 1.523550 | 10.945832 |
| 48| 1 | 0 | 0.339116 | 7.816136 | 8.818104 |
| 49| 1 | 0 | 0.601417 | 7.502117 | 6.365336 |
| 50| 1 | 0 | 2.515169 | 6.187072 | 5.478110 |

Total energy $E_{(UM062X)} = -2016.735871$ Hartree
Trans-Suprafacial Dimer:

---

Center     Atomic      Atomic             Coordinates (Angstroms)
Number     Number       Type             X           Y           Z
---
1         16           0        5.388993    0.054993    5.481318
2          7           0        2.758128    1.242187    6.424909
3          7           0        4.746002    0.005116    6.970849
4          6           0        2.998937    1.255579    5.079961
5          6           0        3.603089    0.651625    7.249555
6          6           0        1.989695    1.755116    4.225528
7          6           0        3.260230    0.688174    8.700222
8          6           0        2.190730    1.845255    2.868190
9          6           0        4.408131    0.927479    3.092209
10          6           0        3.986392   -0.065731    9.622974
11          1           0        4.775796   -0.715476    9.267581
12          6           0        2.249166    1.540950    9.145961
13          1           0        1.702420    2.123469    8.415083
14          6           0        4.195928    0.818460    4.473488
15          6           0        3.410900    1.445332    2.293482
16          6           0        3.709469    0.040809   10.980201
17          1           0        4.275239   -0.547935   11.693062
18          6           0        2.713212    0.905766   11.425077
19          1           0        2.502721    0.993153   12.484884
20          6           0        1.982784    1.653028   10.504570
21          1           0        1.204715    2.325260   10.847237
22          16          0        6.754169    2.432018    5.845706
23          7           0        4.350752    3.798630    7.101681
24          7           0        5.645512    3.370873    5.121585
25          6           0        3.557383    4.500615    4.953678
26          6           0        4.588917    3.839903    5.803883
27          6           0        2.305956    4.795355    5.496731
28          1           0        2.130304    4.579179    6.542831
29          6           0        5.244651    3.209573    7.950896
30          6           0        7.210626    1.825297    8.463904
31          6           0        5.025794    3.333193    9.341903
32          6           0        3.805488    4.760480    3.605330
---
|   | E(UM062X) |   |   |   |   |   |   |
|---|-----------|---|---|---|---|---|---|
|33 | 1         | 0 | 4.775918 | 4.517670 | 3.191874 |
|34 | 6         | 0 | 6.372651 | 2.466898 | 7.541454 |
|35 | 6         | 0 | 6.949924 | 1.945751 | 9.812310 |
|36 | 6         | 0 | 5.858221 | 2.718772 | 10.247731 |
|37 | 6         | 0 | 1.552388 | 5.577503 | 3.343771 |
|38 | 1         | 0 | 0.771494 | 5.992962 | 2.717088 |
|39 | 6         | 0 | 1.305959 | 5.325618 | 4.691030 |
|40 | 1         | 0 | 0.331772 | 5.542115 | 5.113879 |
|41 | 6         | 0 | 2.806408 | 5.301180 | 2.805574 |
|42 | 1         | 0 | 3.004341 | 5.502650 | 1.759094 |
|43 | 1         | 0 | 5.349523 | 0.599875 | 2.663874 |
|44 | 1         | 0 | 3.566831 | 1.539485 | 1.226063 |
|45 | 1         | 0 | 1.407855 | 2.247793 | 2.236633 |
|46 | 1         | 0 | 1.067947 | 2.084636 | 4.688694 |
|47 | 1         | 0 | 8.057175 | 1.245758 | 8.111055 |
|48 | 1         | 0 | 7.587469 | 1.449123 | 10.533047 |
|49 | 1         | 0 | 5.659075 | 2.814562 | 11.308373 |
|50 | 1         | 0 | 4.164399 | 3.908426 | 9.657862 |

Total energy E(UM062X) = -2016.736613 Hartree
3a optimised for dimerization calculation:

```
| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
| 1             | 17            | 0           | 8.569219 10.037802 7.972789 |
| 2             | 16            | 0           | 7.212371 4.839071 8.585537 |
| 3             | 17            | 0           | 3.442647 8.644224 9.084929 |
| 4             | 17            | 0           | 5.593758 10.871467 8.509903 |
| 5             | 7             | 0           | 9.071744 7.184290 8.060955 |
| 6             | 7             | 0           | 8.816365 4.809443 8.268480 |
| 7             | 6             | 0           | 10.961826 5.738946 7.780384 |
| 8             | 6             | 0           | 9.509462 5.930473 8.056629 |
| 9             | 6             | 0           | 11.773702 6.850984 7.545974 |
| 10            | 1             | 0           | 11.330194 7.838179 7.569352 |
| 11            | 6             | 0           | 7.769645 7.478864 8.300631 |
| 12            | 6             | 0           | 6.765551 6.523258 8.563448 |
| 13            | 6             | 0           | 13.127815 6.680847 7.287894 |
| 14            | 1             | 0           | 13.752927 7.546982 7.106781 |
| 15            | 6             | 0           | 7.372018 8.844857 8.289667 |
| 16            | 6             | 0           | 13.680383 5.403799 7.261820 |
| 17            | 1             | 0           | 14.737172 5.273378 7.060248 |
| 18            | 6             | 0           | 11.518681 4.458497 7.753680 |
| 19            | 1             | 0           | 10.883679 3.601398 7.936179 |
| 20            | 6             | 0           | 12.873226 4.294097 7.495107 |
| 21            | 1             | 0           | 13.299698 3.298359 7.475623 |
| 22            | 6             | 0           | 5.089962 8.218605 8.785123 |
| 23            | 6             | 0           | 5.442995 6.885275 8.802792 |
| 24            | 1             | 0           | 4.687314 6.135267 9.002657 |
| 25            | 6             | 0           | 6.055147 9.213437 8.527418 |
```

Total energy E(UM062X) = -2387.14465 Hartree
3a dimer optimised for dimerization calculation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) |
|---------------|---------------|-------------|-------------------------|
|               |               |             | X           | Y           | Z           |
| 1             | 17            | 0           | 8.632963    | 10.047575  | 8.032659    |
| 2             | 16            | 0           | 7.176579    | 4.876507   | 8.644425    |
| 3             | 17            | 0           | 3.522501    | 8.761198   | 9.344386    |
| 4             | 17            | 0           | 5.718172    | 10.942969  | 8.763462    |
| 5             | 7             | 0           | 9.068911    | 7.182044   | 8.052243    |
| 6             | 7             | 0           | 8.771463    | 4.816756   | 8.326647    |
| 7             | 6             | 0           | 10.921694   | 5.704100   | 7.770855    |
| 8             | 6             | 0           | 9.474568    | 5.933484   | 8.041892    |
| 9             | 6             | 0           | 11.744773   | 6.788607   | 7.453692    |
| 10            | 1             | 0           | 11.303205   | 7.774748   | 7.373457    |
| 11            | 6             | 0           | 7.775504    | 7.506747   | 8.338351    |
| 12            | 6             | 0           | 6.763981    | 6.572070   | 8.629837    |
| 13            | 6             | 0           | 13.107477   | 6.597226   | 7.273239    |
| 14            | 1             | 0           | 13.740962   | 7.443056   | 7.034812    |
| 15            | 6             | 0           | 7.417159    | 8.876724   | 8.373725    |
| 16            | 6             | 0           | 13.660768   | 5.326307   | 7.413533    |
| 17            | 1             | 0           | 14.726356   | 5.180809   | 7.280468    |
| 18            | 6             | 0           | 11.475847   | 4.428551   | 7.896961    |
| 19            | 1             | 0           | 10.830357   | 3.593004   | 8.136323    |
| 20            | 6             | 0           | 12.843173   | 4.243753   | 7.723474    |
| 21            | 1             | 0           | 13.269428   | 3.253368   | 7.827854    |
| 22            | 6             | 0           | 5.140547    | 8.300091   | 8.949134    |
| 23            | 6             | 0           | 5.458334    | 6.957614   | 8.923553    |
| 24            | 1             | 0           | 4.697782    | 6.221183   | 9.159032    |
| 25            | 6             | 0           | 6.121603    | 9.273357   | 8.685615    |
| 26            | 17            | 0           | 8.138235    | 10.047581  | 11.541620   |
| 27            | 16            | 0           | 9.594650    | 4.876510   | 10.929927   |
| 28            | 17            | 0           | 13.248683   | 8.761220   | 10.229829   |
| 29            | 17            | 0           | 11.053011   | 10.942986  | 10.810770   |
| 30            | 7             | 0           | 7.702308    | 7.182048   | 11.522104   |
| 31            | 7             | 0           | 7.999728    | 4.816771   | 11.247572   |
| 32            | 6             | 0           | 5.849508    | 5.704112   | 11.803411   |
| 33            | 6             | 0           | 7.296637    | 5.933496   | 11.532396   |
| 34            | 6             | 0           | 5.026423    | 6.786619   | 12.120559   |
Total energy $E(\text{UM062X}) = -4774.327698$ Hartree. N.B. This energy corresponds to a transition state for the formation of an S-N bond, and is not a minimum on the potential energy surface.
8. References

1. A. M. Borys, The Schlenk Line Survival Guide, https://schlenklinesurvivalguide.com.
2. R. Anulewicz-Ostrowska, T. Kliś, D. Krajewski, B. Lewandowski and J. Serwatowski, Tetrahedron Lett., 2003, 44, 7329–7331.
3. C. S. Chang, Y. T. Lin, S. R. Shih, C. C. Lee, Y. C. Lee, C. L. Tai, S. N. Tseng and J. H. Chern, J. Med. Chem., 2005, 48, 3522–3535.
4. S. Stoll and A. Schweiger, J. Magn. Reson., 2006, 178, 42–55.
5. I. K. Khanna, Y. Yu, R. M. Huff, R. M. Weier, X. Xu, F. J. Koszyk, P. W. Collins, J. N. Cogburn, C. M. Koboldt, J. L. Masferrer, K. Seibert, A. W. Veenhuizen, J. Yuan, D. Yang and Y. Y. Zhang, Synthesis, 2000, 3168–3185.
6. P. Oxley and W. F. Short, J. Chem. Soc., 1953, 255–260.
7. M. Cortes-Salva, C. Garvin and J. C. Antilla, J. Org. Chem., 2011, 76, 1456–1459.
8. T. B. Nguyen, L. Ermolenko and A. Al-Mourabit, Heterocycles, 2012, 86, 555–563.
9. Y. Wang, H. Wang, J. Peng and Q. Zhu, Org. Lett., 2011, 13, 4604–4607.
10. J. I. Clodt, V. D. Hack, R. Fröhlich and E. U. Würthwein, Synthesis, 2010, 1485–1492.
11. B. L. Korbad and S. Lee, Bull. Korean Chem. Soc., 2013, 34, 1266–1268.
12. T. Yao, Tetrahedron Lett., 2015, 56, 4623–4626.
13. J. C. Zhuo, A. H. Soloway, J. C. Beeson, W. Ji, B. A. Barnum, F. G. Rong, W. Tjarks, G. T. Jordan IV, J. Liu and S. G. Shore, J. Org. Chem., 1999, 64, 9566–9574.
14. M. Q. Tran, T. B. Nguyen, W. R. Sawadogo, L. Ermolenko, S. Song, P. Retailleau, M. Diederich and A. Al-Mourabit, European J. Org. Chem., 2018, 2018, 5878–5884.
15. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Crystallogr., 2009, 42, 339–341.
16. G. M. Sheldrick, Acta Crystallogr. Sect. A Found. Crystallogr., 2015, 71, 3–8.
17. G. M. Sheldrick, Acta Crystallogr. Sect. C Struct. Chem., 2015, 71, 3–8.
18. G. Gritzner and J. Kuta, Int. Union Pure Appl. Chem., 1984, 1, 462–466.
19. N. Elgrishi, K. J. Rountree, B. D. McCarthy, E. S. Rountree, T. T. Eisenhart and J. L. Dempsey, J. Chem. Educ., 2018, 95, 197–206.
20. A. J. Bard and L. R. Faulkner, Electrochemical Methods: Fundamental and Applications, John Wiley & Sons, NJ, 2nd edn., 2001.
21. G. A. Bain and J. F. Berry, J. Chem. Educ., 2008, 85, 532.
22. N. Feeder, R. J. Less, J. M. Rawson, P. Oliete and F. Palacio, Chem. Commun., 2000, 2, 2449–2450.
23. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, G. A. Cheeseman, J. R. Scalmani, G.; Barone, V. Petersson, X. Nakatsuji, H.; Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F.; Lipparini, F. Egidio, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. Montgomery, J. A., J. E. Peralta, F. Ogliaro, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, G. A. Cheeseman, J. R. Scalmani, G.; Barone, V. Petersson, X. Nakatsuji, H.; Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F.; Lipparini, F. Egidio, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. Montgomery, J. A., J. E. Peralta, F. Ogliaro, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, G. A. Cheeseman, J. R. Scalmani, G.; Barone, V. Petersson, X. Nakatsuji, H.; Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F.; Lipparini, F. Egidio, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. Montgomery, J. A., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, 2016.
24. R. G. Parr and W. Yang, Density-functional theory of atoms and molecules, Oxford University Press, 1989.
25. R. Ditchfield, W. J. Hehre and J. A. Pople, J. Chem. Phys., 1971, 54, 724–728.
26. T. H. Dunning, J. Chem. Phys., 1989, 100, 1007–1023.
27. A. D. McLean and G. S. Chandler, J. Chem. Phys., 1980, 72, 5639–5648.
28. W. Humphrey, A. Dalke and K. Schulten, J. Mol. Graph., 1996, 14, 33–38.
29. R. T. Boeré, K. H. Moock and M. Parvez, ZAAC - J. Inorg. Gen. Chem., 1994, 620, 1589–1598.
30. P. Kaszynski, J. Phys. Chem. A, 2001, 105, 7615–7625.
31. P. Kaszynski, J. Phys. Chem. A, 2001, 105, 7626–7633.
32 J. Zienkiewicz, P. Kaszynski and V. G. Young, J. Org. Chem., 2004, 69, 7525–7536.
33 M. A. Nascimento, E. Heyer, R. J. Less, C. M. Pask, A. Arauzo, J. Campo and J. M. Rawson, Cryst. Growth Des., 2020, 20, 4313–4324.
34 R. L. Melen, R. J. Less, C. M. Pask and J. M. Rawson, Inorg. Chem., 2016, 55, 11747–11759.
35 L. Noodleman, J. Chem. Phys., 1981, 74, 5737–5743.
36 L. Noodleman and E. R. Davidson, Chem. Phys., 1986, 109, 131–143.