Electronic Supplementary Material (ESI) for Chemical Science.

A Short Versatile Route Towards Benzothiadiazinyl Radicals

Supporting Information

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1. General Experimental Considerations

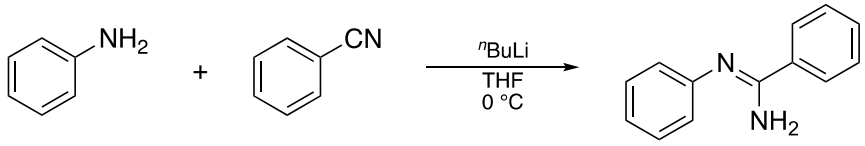
All manipulations were carried out under an atmosphere of Argon using standard Schlenk line[1] and glovebox techniques unless otherwise stated. All solvents were purchased from Fisher Scientific and dried before use following the methods specified. DCM and MeCN were dried by reflux over CaH_2 and stored over activated molecular sieves. THF was dried by reflux over potassium and stored over activated molecular sieves. ^{n}Hexane and Et_2O 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. ^{n}BuLi was purchased from ACROS as a 2.5 M solution in hexanes. Pyridine, Et_3N and $^{i}Pr_2EtN$ were vacuum distilled over CaH_2 and stored over activated molecular sieves. Ferrocene and DABCO were purified by vacuum sublimation. Ph_3P was recrystallised from DCM and ^{n}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-Kα (λ = 0.71073 Å) or Cu-Kα (λ = 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.



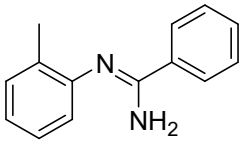
1a

1a:

Aniline (4.56 cm^3, 50 mmol) was dissolved in THF (50 cm^3) and ^{n}BuLi (2.5 M in hexanes, 20 cm^3, 50 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 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) and the organic products extracted into DCM (3 x 50 cm^3) under air. The combined organic extracts were washed with water and brine (50 cm^3 each), dried over $MgSO_4$, 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 NMR** (400 MHz, DCM, 19.8 °C): δ 7.87 (bs, 2H), 7.45 (m, 3H), 7.35 (t, *J* = 7.3 Hz, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 7.3 Hz, 2H), 3.91 (s, 2H). **^{13}C{^{1}H} NMR** (100.5 MHz, DCM, 18.4 °C): δ 154.4, 150.2, 136.0, 130.6, 129.6, 128.5, 126.8, 122.9, 121.5.

Analytical data in accordance with the literature.[7–9]

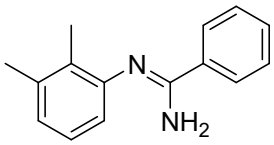
1b:



Colourless needles, 71% yield. **^{1}H 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), 4.76 (bs, 2H), 2.15 (s, 3H). **^{13}C{^{1}H} NMR** (100.5 MHz, DCM, 18.5 °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.[9,10]

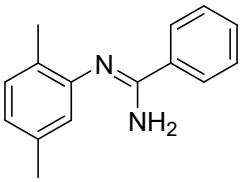
1c:



Colourless needles, 87% yield. **^{1}H NMR** (400 MHz, DCM, 19.8 °C): δ 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): δ 153.5, 148.3, 138.1, 136.0, 130.5, 128.5, 128.0, 126.8, 126.2, 124.6, 118.5, 20.3, 13.4.

Analytical data in accordance with the literature.[8,11]

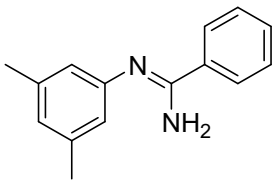
1d:



Colourless needles, 79% yield. **^{1}H NMR** (400 MHz, DCM, 19.8 °C): δ 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): δ 153.5, 148.3, 136.6, 136.0, 130.6, 130.5, 128.5, 126.8, 126.3, 123.7, 121.4, 20.9, 17.0.

Analytical data in accordance with the literature.[8]

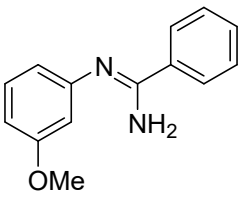
1e:



Colourless needles, 78% yield. **^{1}H NMR** (400 MHz, DCM, 19.9 °C): δ 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): δ 154.2, 150.0, 139.3, 136.1, 130.5, 128.5, 126.8, 124.6, 119.0, 21.2.

Analytical data in accordance with the literature.[8,9]

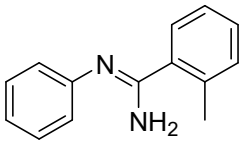
1f:



Colourless microcrystalline solid, 65% yield. **^{1}H NMR** (400 MHz, DCM, 17.1 °C): δ 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): δ 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]

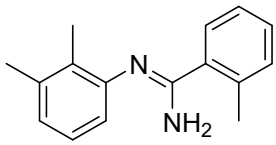
1g:



Colourless micro-crystalline solid, 63% yield. **^{1}H NMR** (400 MHz, DCM, 18.7 °C): δ 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): δ 156.2, 149.6, 137.2, 135.7, 130.7, 129.3, 129.1, 127.9, 125.7, 122.6, 121.6, 19.6.

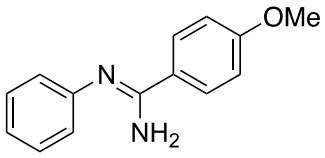
Analytical data in accordance with the literature.[9]

1h:



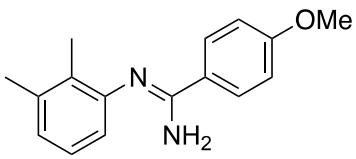
Colourless microcrystalline solid, 66% yield. *Anal.* Calc. for $C_{16}H_{18}N_2$: C, 80.6; H, 7.61; N, 11.8. Found: C, 80.39; H, 7.76; N, 11.8. **^{1}H NMR** (400 MHz, DCM, 18.8 °C): δ 7.49 (bs, 1H), 7.28 (m, 3H), 7.06 (bs, 1H), 6.87 (bs, 1H), 6.73 (bs, 1H), 2.55 (s, 3H), 2.30 (s, 3H), 2.14 (s, 3H). **^{13}C{^{1}H} NMR** (100.5 MHz, DCM, 19.0 °C): δ 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:



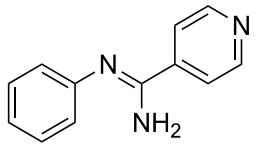
Colourless microcrystalline solid, 77% yield. **^{1}H NMR** (400 MHz, DCM, 19.6 °C): δ 7.82 (d, *J* = 6.9 Hz, 2H), 7.33 (t, *J* = 6.6, 7.1 Hz, 2H), 7.03 (t, *J* = 6.6, 7.3 Hz, 1H), 6.93 (t, *J* = 7.3, 8.2 Hz, 4H), 4.81 (bs, 2H), 3.84 (s, 3H). **^{13}C{^{1}H} NMR** (100.5 MHz, DCM, 19.2 °C): δ 161.6,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

Analytical data in accordance with the literature.[5]



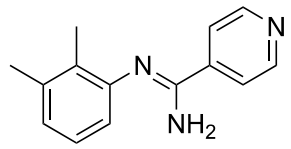
1j:

Colourless microcrystalline solid, 74% yield. *Anal.* Calc. for $C_{16}H_{18}N_2O$: C, 75.6; H, 7.13; N, 11.0. Found: C, 75.6; H, 7.24; N, 11.0. **^{1}H 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). **^{13}C{^{1}H} 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:

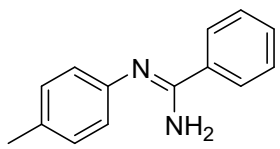
Colourless microcrystalline solid, 88% yield. *Anal.* Calc. for $C_{12}H_{11}N_3$: C, 73.1 H, 5.62; N, 21.3. Found: C, 73.0; H, 5.75; N, 21.4. **^{1}H NMR** (400 MHz, DCM, 18.4 °C): δ 8.68 (d, *J* = 4.6 Hz, 2H), 7.73 (d, *J* = 4.6 Hz, 2H), 7.36 (t, *J* = 6.4, 6.9 Hz, 2H), 7.07 (t, *J* = 6.9 Hz, 1H), 6.93 (d, *J* = 6.9 Hz, 2H), 5.01 (bs, 2H). **^{13}C{^{1}H} 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 $C_{14}H_{15}N_3$: C, 74.6; H, 6.71; N, 18.7. Found: C, 74.8; H, 6.74; N, 18.6. **^{1}H 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). **^{13}C{^{1}H} 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.

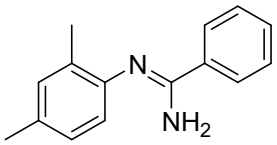
1m:



Colourless needles, 71% yield. **^{1}H 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). **^{13}C{^{1}H} 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.

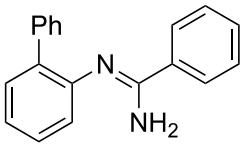
Analytical data in accordance with the literature.[9,11]

1n:



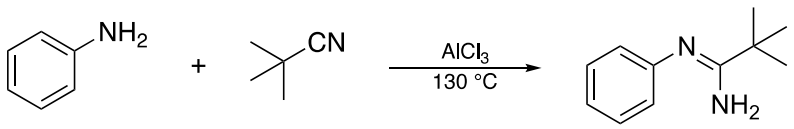
Colourless needles, 73% yield. **^{1}H NMR** (400 MHz, DCM, 18.9 °C): δ 7.87 (d, *J* = 7.1 Hz, 2H), 7.45 (m, 3H), 7.06 (s, 1H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 4.78 (bs, 2H), 2.31 (s, 3H), 2.13 (s, 3H). **^{13}C{^{1}H} NMR** (100.5 MHz, DCM, 18.9 °C): δ 153.8, 145.7, 136.0, 132.3, 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.[9]



1o:

Colourless needles, 68% yield. *Anal.* Calc. for $C_{19}H_{16}N_2$: C, 83.8; H, 5.92; N, 10.3. Found: C, 83.6; H, 5.90; N, 10.3. **^{1}H NMR** (400 MHz, DCM, 19.3 °C): δ 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). **^{13}C{^{1}H} NMR** (100.5 MHz, DCM, 19.7 °C): δ 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.



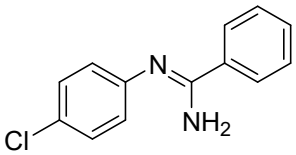
1p

1p:

Aniline (2.05 cm^3, 22.5 mmol), pivalonitrile (2.49 cm^3, 22.5 mmol) and $AlCl_3$ (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^3) and ice (50 g) mixture, and allowed to stir for 15 minutes. The suspension was extracted into DCM (3 x 50 cm^3), dried over $MgSO_4$, 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%). **^{1}H NMR** (400 MHz, DCM, 25.0 °C): δ 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). **^{13}C{^{1}H} NMR** (100.5 MHz, DCM, 25.0 °C): δ 164.1, 150.9, 129.5, 122.3, 121.4, 36.9, 28.4.

Analytical data in accordance with the literature.[13]

1t:



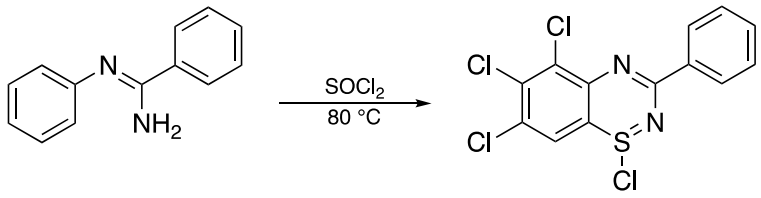
Colourless needles, 85% yield. **^{1}H NMR** (400 MHz, DCM, 18.0 °C): δ 7.84 (bs, 2H), 7.50-7.41 (m, 3H), 7.30 (d, J = 8.1 Hz, 2H), 6.87 (d, J = 8.1 Hz, 2H), 4.96 (bs, 2H). **^{13}C{^{1}H} NMR** (100.5 MHz, DCM, 19.6 °C): δ 154.8, 148.9, 135.7, 130.7, 129.6, 128.5, 127.8, 126.8, 123.8.

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 slowing 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:

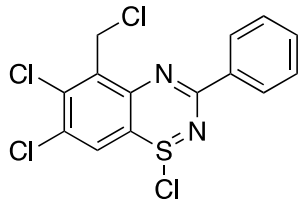


1a **2a**

1a (1.50 g, 7.6 mmol) was degassed, flushed with argon, and cooled to -95 °C. $SOCl_2$ (15 cm^3, 207 mmol) was added slowly and the reaction mixture was gradually warmed to room temperature then heated at reflux overnight (~16 hours). Once cooled to room temperature, ^{n}hexane (30 cm^3) was carefully layered onto the $SOCl_2$ solution. After 1 week, once diffusion and crystallisation were complete, the supernatant was removed *via* filter cannula and the deep orange crystals were washed with ^{n}hexane (2 x 10 cm^3) then dried *in vacuo* to give **2a** (1.98 g, 5.4 mmol, 71%). *Anal.* Calc. for $C_{13}H_6Cl_4N_2S$: C, 42.9; H, 1.7; N, 7.7. Found: C, 42.7; H, 1.8; N, 7.4. **^{1}H NMR** (400 MHz, $SOCl_2$, 19.4 °C): δ 8.46 (d, *J* = 7.3 Hz, 2H), 7.92 (s, 1H), 7.52 (m, 3H). **^{13}C{^{1}H} NMR** (100.5 MHz, $SOCl_2$, 18.7 °C): δ 158.3, 140.4, 139.5, 135.3, 134.6, 132.9, 132.6, 129.2, 128.7, 122.1, 116.5.

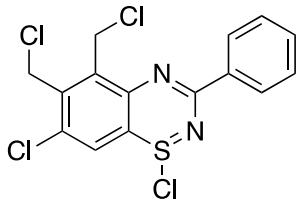
Synthesis from **1t** gave the same product in slightly reduced yield (37%) as confirmed by NMR.

2b:



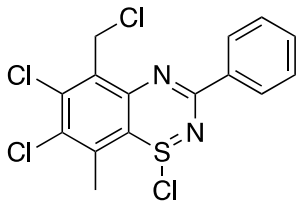
Orange crystalline solid, 61% yield. *Anal.* Calc. for $C_{14}H_8Cl_4N_2S$: C, 44.5; H, 2.1; N, 7.4. Found: C, 44.3; H, 2.1; N, 7.5. **^{1}H NMR** (400 MHz, $SOCl_2$, 18.4 °C): δ 8.43 (d, *J* = 7.1 Hz, 2H), 8.01 (s, 1H), 7.53 (m, 3H), 5.36 (s, 2H). **^{13}C{^{1}H} NMR** (100.5 MHz, $SOCl_2$, 18.6 °C): δ 141.7, 141.4, 136.6, 135.6, 132.7, 132.6, 129.0, 128.8, 124.3, 116.3, 37.2.

2c:



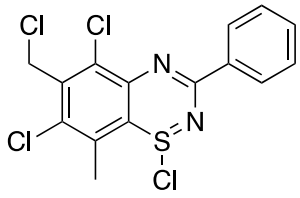
Orange crystalline solid, 76% yield. *Anal.* Calc. for $C_{15}H_{10}Cl_4N_2S$: C, 45.9; H, 2.6; N, 7.1. Found: C, 45.8; H, 2.4; N, 7.2. **^{1}H NMR** (400 MHz, $SOCl_2$, 19.6 °C): δ 8.44 (d, *J* = 8.2 Hz, 2H), 7.97 (s, 1H), 7.52 (m, 3H), 5.38 (s, 2H), 4.96 (s, 2H). **^{13}C{^{1}H} NMR** (100.5 MHz, $SOCl_2$, 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.



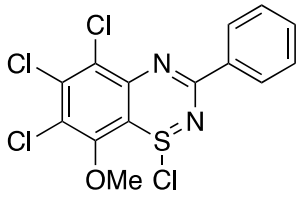
2d:

Pale yellow crystalline solid, 31% yield. *Anal.* Calc. for $C_{15}H_{10}Cl_4N_2S$: C, 45.9; H, 2.6; N, 7.1. Found: C, 45.7; H, 2.6; N, 7.2. **^{1}H NMR** (400 MHz, $SOCl_2$, 16.6 °C): δ 8.44 (d, *J* = 7.3 Hz, 2H), 7.52 (m, 3H), 5.37 (s, 2H), 2.85 (s, 3H). **^{13}C{^{1}H} NMR** (100.5 MHz, $SOCl_2$, 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:

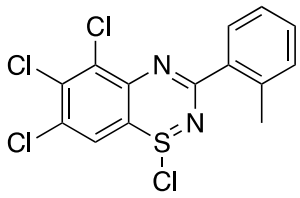
Orange fibrous solid, 40% yield. *Anal.* Calc. for $C_{15}H_{10}Cl_4N_2S$: C, 45.9; H, 2.6; N, 7.1. Found: C, 45.8; H, 2.4; N, 7.3. **^{1}H NMR** (400 MHz, $SOCl_2$, 17.7 °C): δ 8.49 (d, *J* = 7.3 Hz, 2H), 7.55 (m, 3H), 5.07 (s, 2H), 2.81 (s, 3H). **^{13}C{^{1}H} NMR** (100.5 MHz, $SOCl_2$, 18.7 °C): 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:

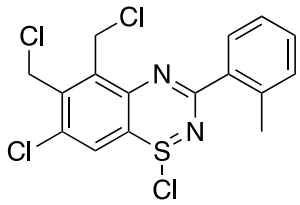
Red crystalline solid, 46% yield. *Anal.* Calc. for $C_{14}H_8Cl_4N_2OS$: C, 42.7; H, 2.0; N, 7.1. Found: C, 42.5; H, 1.9; N, 7.2. **^{1}H NMR** (400 MHz, $SOCl_2$, 18.5 °C): δ 8.47 (d, *J* = 8.0 Hz, 2H), 7.52 (m, 3H), 4.24 (s, 3H). **^{13}C{^{1}H} NMR** (100.5 MHz, $SOCl_2$, 18.3 °C): δ 159.1, 149.3, 140.6, 140.4, 135.4, 132.8, 129.2, 128.7, 124.7, 112.5, 62.4.

2g:



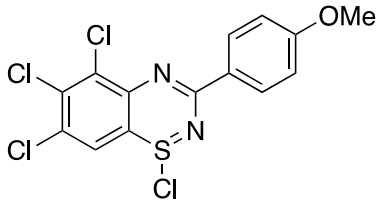
Pale orange crystalline solid, 46% yield. *Anal.* Calc. for $C_{14}H_8Cl_4N_2S$: C, 44.5; H, 2.1; N, 7.4. Found: C, 44.4; H, 2.1; N, 7.5. **^{1}H NMR** (400 MHz, $SOCl_2$, 18.4 °C): δ 8.02 (d, *J* = 7.3 Hz, 1H), 7.95 (s, 1H), 7.43 (t, *J* = 6.4, 7,3 Hz, 1H), 7.33 (t, *J* = 6.0 Hz, 7.3 Hz, 2H), 2.76 (s, 3H). **^{13}C{^{1}H} NMR** (100.5 MHz, $SOCl_2$, 18.9 °C): δ 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:



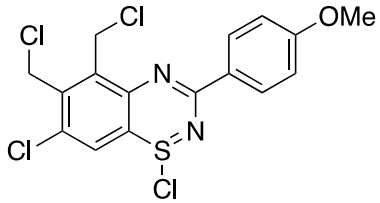
Turmeric-coloured crystalline solid, 53% yield. *Anal.* Calc. for $C_{16}H_{12}Cl_4N_2S$: C, 47.3: H, 3.0; N, 6.9. Found: C, 47.2; H, 2.9: N, 6.7. **^{1}H NMR** (400 MHz, $SOCl_2$, 18.5 °C): δ 8.00 (s, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.3, 7.6 Hz, 1H), 7.33 (t, *J* = 6.0, 7.3 Hz, 2H), 5.32 (s, 2H), 4.98 (s, 2H), 2.71 (s, 3H). **^{13}C{^{1}H} NMR** (100.5 MHz, $SOCl_2$, 19.2 °C): δ 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:



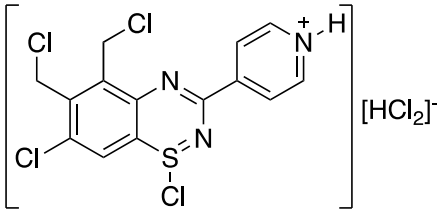
Dark red crystalline solid, 81% yield. *Anal.* Calc. for $C_{14}H_8Cl_4N_2OS$: C, 42.7; H, 2.1; N, 7.1. Found: C, 42.3; H, 2.1; N, 7.1. **^{1}H NMR** (400 MHz, $SOCl_2$, 18.5 °C): δ 8.44 (d, *J* = 8.6 Hz, 2H), 7.92 (s, 1H), 7.01 (d, *J* = 8.6 Hz, 2H), 3.88 (s, 3H). **^{13}C{^{1}H} NMR** (100.5 MHz, $SOCl_2$, 19.2 °C): δ 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 $C_{16}H_{12}Cl_4N_2OS$: 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): δ 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): δ 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.

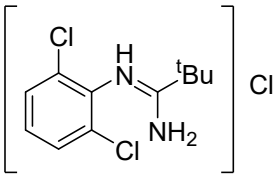
Synthesis of 3:2 1,5,7-trichloro-3-(*p*-pyridinium)-benzo-1,2,4-thiadiazine chloride, 2k', and 1,5,6,7-tetrachloro-3-(*p*-pyridinium)-benzo-1,2,4-thiadiazine chloride, 2k'':
Yellow solid, 72 % yield based on 3:2 ratio of **2k'**: **2k''** species, assuming chloride salt formation. The solid was near 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) δ: 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) (400 MHz, $SOCl_2$, 19.1 °C) δ: 8.88 (bs, 2H), 8.73 (bs, 2H), 7.96 (bs, 1H).



2l.H[HCl_2]:

Yellow crystalline solid, 87% yield. Elemental analysis results are between those expected for [**2l**.H]Cl and [**2l**.H][HCl_2] salts even after recrystallisation; this is likely due to the tendency of the $[HCl_2]^-$ anion to lose HCl although the concomitant formation of the Cl^- and $[HCl_2]^-$ cannot be ruled out. *Anal*. Calc. for $C_{14}H_{11}Cl_6N_3S$: C, 36.1, H, 2.38, N, 9.02. *Anal*. Calc. for $C_{14}H_{10}Cl_5N_3S$: 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): δ 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): δ 152.2, 151.7, 143.0, 141.1, 139.8, 138.3, 136.8, 125.4, 124.8, 116.3, 38.4, 35.1.

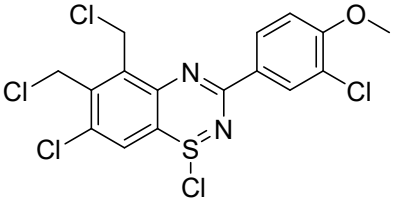
Attempted Synthesis of 2p
Reaction of **1p** under standard conditions gave a low yield of pale peach solid (37% assuming complete conversion to desired product). Attempted recrystalisation of this from boiling $SOCl_2$ was not successful in obtaining a single product, though a very low quality crystal did afford a connectivity map for **1p.HCl** 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.HCl** 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): δ 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:

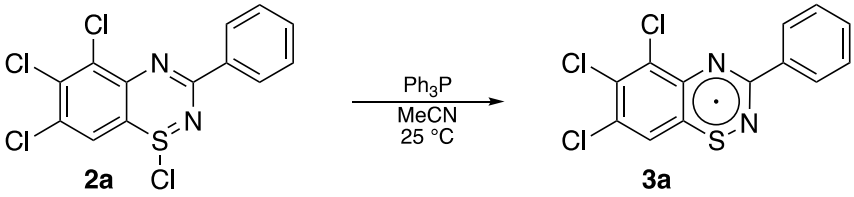


Formed concomitantly with **2j** on prolonged heating in $SOCl_2$. **^{1}H NMR** (400 MHz, $SOCl_2$, 18.7 °C) δ: 8.45 (s, 1H), 8.36 (m, 1H), 7.97 (s, 1H), 7.08 (d, *J* = 8.7 Hz, 1H), 5.39 (s, 2H), 4.98 (s, 2H), 3.96 (s, 3H). **^{13}C{^{1}H} NMR** (100.5 MHz, $SOCl_2$, 18.3 °C) δ: 158.8, 156.7, 142.8, 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_3P 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.

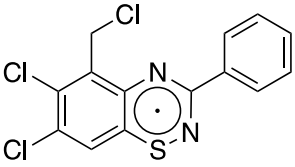
3a:



2a **3a**

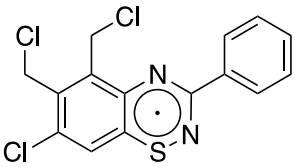
2a (0.40 g, 1.1 mmol) was suspended in MeCN (5 cm^3), degassed with three freeze-pump-thaw cycles, and backfilled with argon. A solution of Ph_3P (0.15 g, 0.6 mmol) in degassed MeCN (5 cm^3) was added resulting in an immediate darkening of colour. After 5 minutes of rapid stirring, the supernatant was 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:

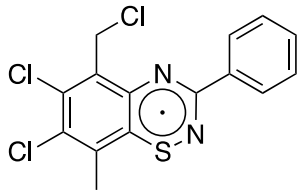


Dark blue powder, 51% yield.

3c:

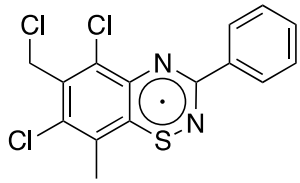


Dark purple powder, 72% yield. *Anal.* Calc. for $C_{15}H_{10}Cl_3N_2S$: C, 50.5; H, 2.8; N, 7.9. Found: C, 50.4; H, 2.7; N, 8.0



3d:

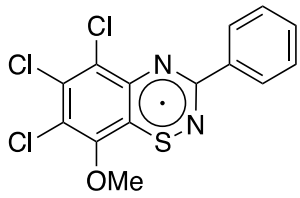
Dark purple powder, 60% yield. *Anal.* Calc. for $C_{15}H_{10}Cl_3N_2S$: C, 50.5; H, 2.8; N, 7.9. Found: C, 50.5; H, 2.9; N, 8.0.



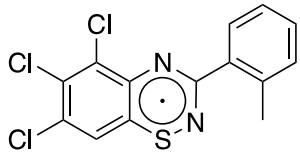
3e:

Dark purple powder, 68% yield. *Anal.* Calc. for $C_{15}H_{10}Cl_3N_2S$: C, 50.5; H, 2.8; N, 7.9. Found: C, 50.3; H, 2.7; N, 7.9.

3f:

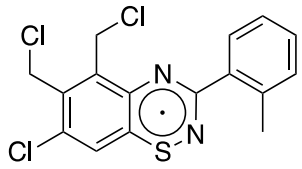


Dark purple/green powder, 58% yield.



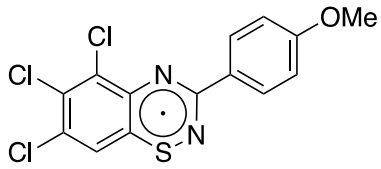
3g:

Dark green powder, 64% yield.



3h:

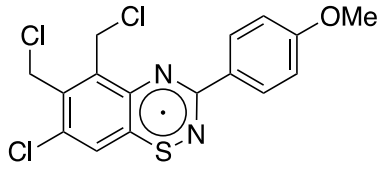
Dark purple powder, 57% yield.



3i:

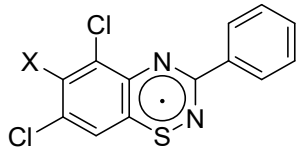
Dark blue powder, 49% yield.

3j:



Dark blue powder, 68% yield.

3k:

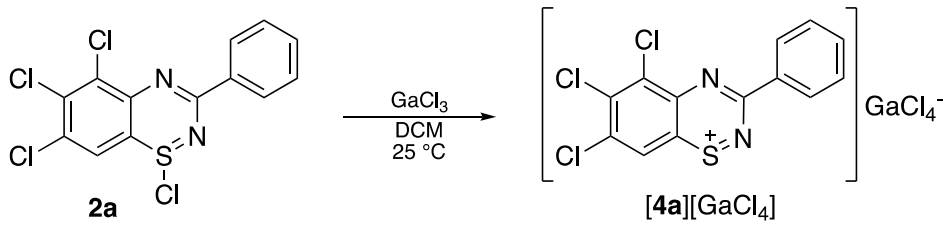


X = 4:1 H, Cl

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 $GaCl_3$ in DCM.



2a [**4a**][$GaCl_4$]

2a (30 mg, 0.08 mmol) was suspended in DCM (5 cm^3) and $GaCl_3$ (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 ^{n}hexane (10 cm^3). After 1 week, dark purple crystals of [**4a**][$GaCl_4$] were isolated by filtration, washed with ^{n}hexane (2 x 2.5 cm^3), and dried *in vacuo* (27 mg, 0.05 mmol, 63% yield). **^{1}H 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). $^{13}C\{^1H\}$ 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,[15] the structures were solved with the SHELXT structure solution program *via* intrinsic phasing[16] and refined with the SHELXL refinement package using least squares minimisation.[17] 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

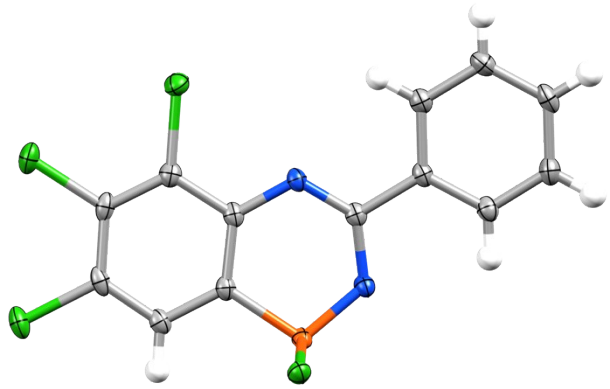


Figure S1 Crystal structure of **2a** - Front view.

2a:

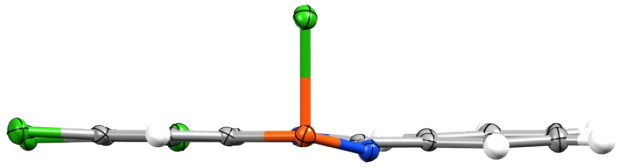


Figure S2 Crystal structure of **2a** - Side view.

Compound	**2b**	**2a**
Empirical formula	$C_{14}H_8Cl_4N_2S$	$C_{14}H_6Cl_4N_2S$
Formula weight	378.08	364.06
Temperature/K	150.00(10)	180(2)
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a/Å	8.9856(5)	14.4699(8)
b/Å	9.2182(3)	8.6411(7)
c/Å	9.3740(6)	16.045(1)
α/°	103.868(4)	90
β/°	94.530(5)	115.564(2)
γ/°	95.061(4)	90
Volume/Å^3		2857.0(3)
Z		8
ρ_{calc}g/cm^3		1.693
μ/mm^{-1}		0.962
F(000)		1456.0
Crystal size/mm^3		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 F^2		1.029
Final R indexes [I>=2σ (I)]		R_1 = 0.0484, wR_2 = 0.098
Final R indexes [all data]		R_1 = 0.0866, wR_2 = 0.1119
Largest diff. peak/hole / e Å^{-3}		0.65/-0.33
Flack parameter		

2b:

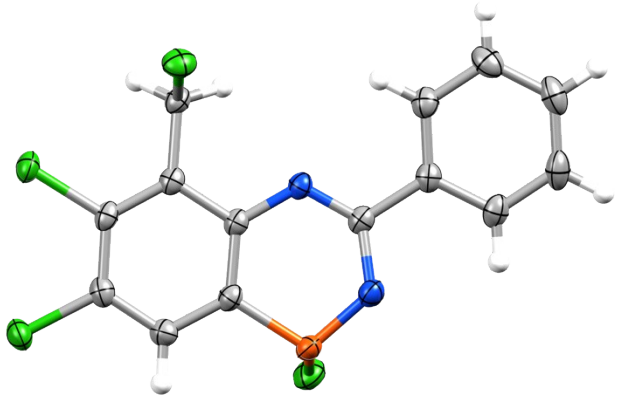


Figure S3 - Crystal structure of **2b** - Front view.

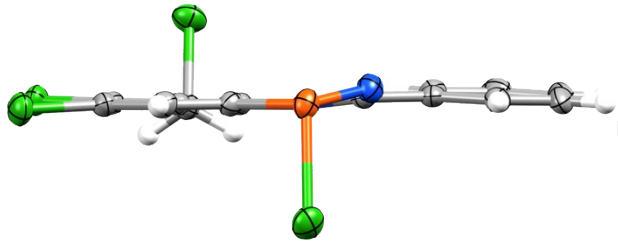


Figure S4 - Crystal structure of **2b** - Side view.

Volume/Å^3	746.84(7)
Z	2
ρ_{calc}g/cm^3	1.681
μ/mm^{-1}	8.456
F(000)	380
Crystal size/mm^3	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 [R_{int} = 0.0194, R_{sigma} = 0.0186]
Data/restraints/parameters	2562/0/190
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0267, wR_2 = 0.0724
Final R indexes [all data]	R_1 = 0.0275, wR_2 = 0.0730
Largest diff. peak/hole / e Å^{-3}	0.38/-0.34
Flack parameter	

2c:

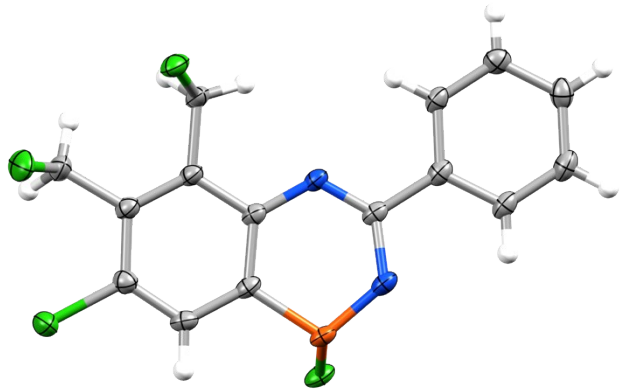


Figure S5 - Crystal structure of **2c** - Front view.

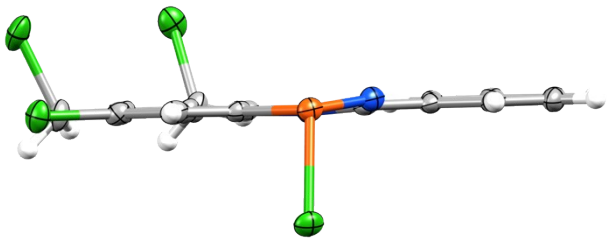


Figure S6 - Crystal structure of **2c** - Side view.

Compound	**2c**
Empirical formula	$C_{15}H_{9.97}Cl_{4.03}N_2S$
Formula weight	393.31
Temperature/K	100.0(5)
Crystal system	triclinic
Space group	$P\bar{1}$
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/Å^3	786.73(5)
Z	2
ρ_{calc}g/cm^3	1.66
μ/mm^{-1}	8.097
F(000)	397
Crystal size/mm^3	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 F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0360, wR_2 = 0.0943
Final R indexes [all data]	R_1 = 0.0368, wR_2 = 0.0950
Largest diff. peak/hole / e Å^{-3}	1.29/-0.49
Flack parameter	

2d-α:

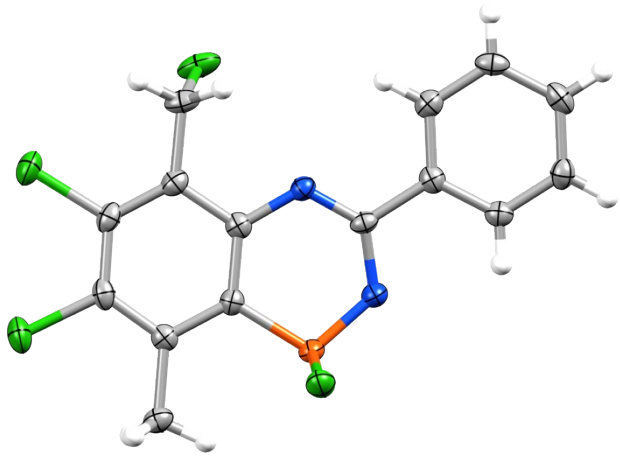


Figure S7 - Crystal structure of **2d-α** - Front view.

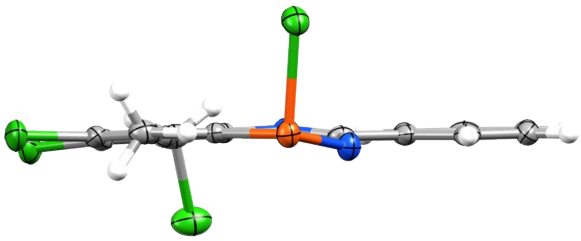


Figure S8 - Crystal structure of **2d-α** - Side view.

Compound	**2d-α**
Empirical formula	$C_{15}H_{10}Cl_4N_2S$
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/Å^3	1591.64(5)
Z	4
ρ_{calc}g/cm^3	1.636
μ/mm^{-1}	7.949
F(000)	792
Crystal size/mm^3	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 F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0456, wR_2 = 0.1183
Final R indexes [all data]	R_1 = 0.0475, wR_2 = 0.1198
Largest diff. peak/hole / e Å^{-3}	1.26/-0.51
Flack parameter	

2d-β:

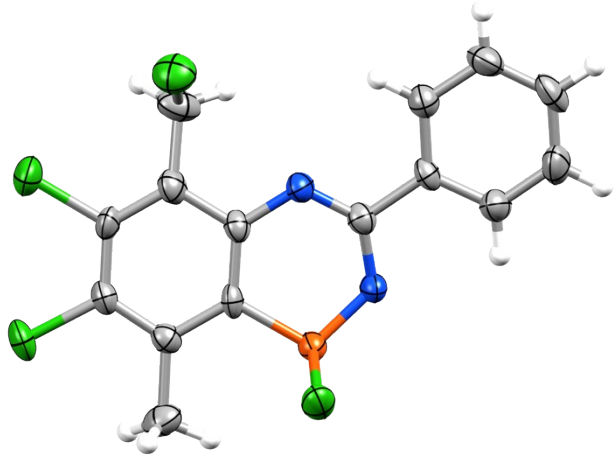


Figure S9 - Crystal structure of **2d-β** - Front view.

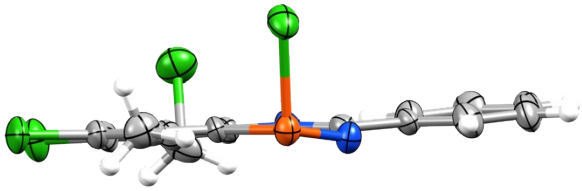


Figure S10 - Crystal structure of **2d-β** - Side view.

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)
α/°	90
β/°	96.799(3)
γ/°	90
Volume/Å^3	1577.26(13)
Z	4
ρ_{calc}g/cm^3	1.651
μ/mm^{-1}	0.878
F(000)	792
Crystal size/mm^3	0.42 x 0.23 x 0.23
Radiation	MoKα (λ =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 [R_{int} = 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:

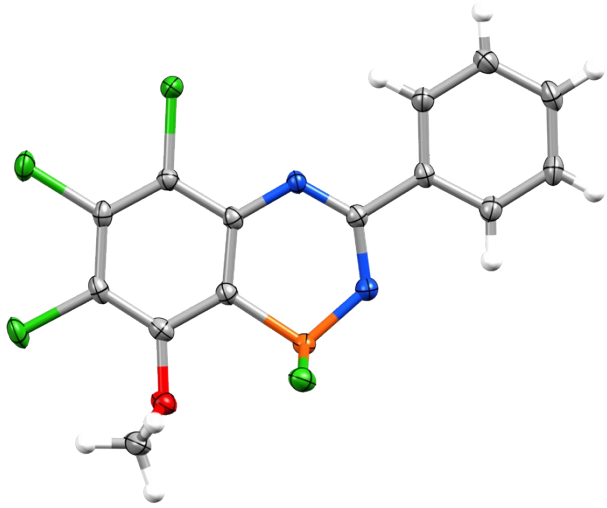


Figure S11 - Crystal structure of **2f** - Front view. Only one orientation of the OMe group is shown for clarity.

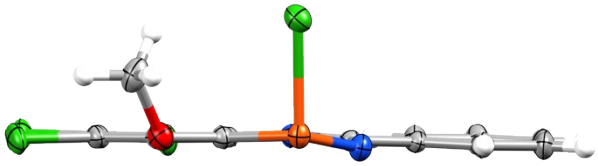


Figure S12 - Crystal structure of **2f** - Side view. Only one orientation of the OMe group is shown for clarity.

Compound	**2f**
Empirical formula	$C_{14}H_8Cl_4N_2OS$
Formula weight	394.08
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	$P\bar{1}$
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/Å^3	745.33(3)
Z	2
ρ_{calc}g/cm^3	1.756
μ/mm^{-1}	8.544
F(000)	396
Crystal size/mm^3	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 F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0269, wR_2 = 0.0769
Final R indexes [all data]	R_1 = 0.0277, wR_2 = 0.0778
Largest diff. peak/hole / e Å^{-3}	0.36/-0.33
Flack parameter	

2g:

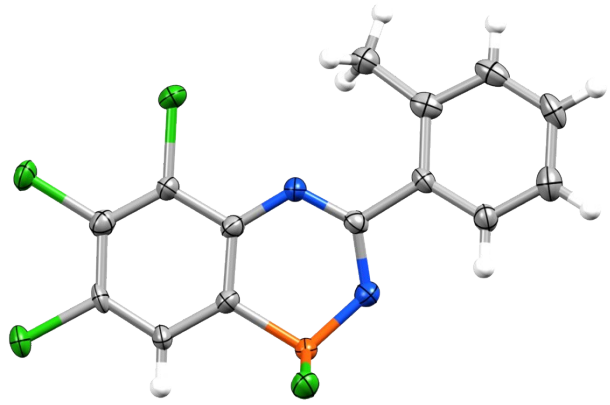


Figure S13 - Crystal structure of **2g** - Front view. Only one molecule in the asymmetric unit is shown for clarity.

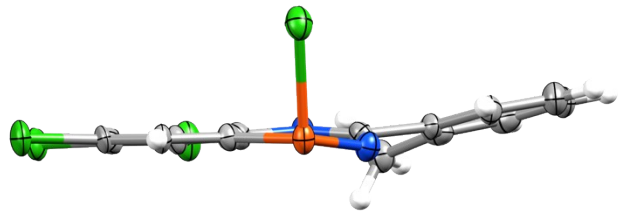


Figure S14 - Crystal structure of **2g** - Side view. Only one molecule in the asymmetric unit is shown for clarity.

Compound	**2g**
Empirical formula	$C_{28}H_{16}Cl_8N_4S_2$
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/Å^3	1485.78(9)
Z	2
ρ_{calc}g/cm^3	1.69
μ/mm^{-1}	8.491
F(000)	760
Crystal size/mm^3	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 [R_{int} = 0.0805, R_{sigma} = 0.0293]
Data/restraints/parameters	5617/1/381
Goodness-of-fit on F^2	1.093
Final R indexes [I>=2σ (I)]	R_1 = 0.0766, wR_2 = 0.2049
Final R indexes [all data]	R_1 = 0.0769, wR_2 = 0.2058
Largest diff. peak/hole / e Å^{-3}	1.10/-0.69
Flack parameter	0.06(3)

2h:

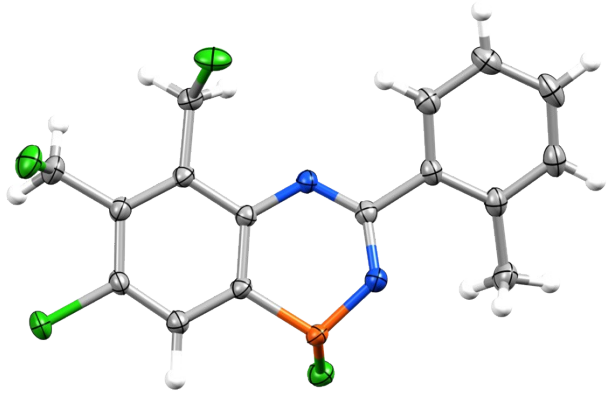


Figure S15 - Crystal structure of **2h** - Front view.

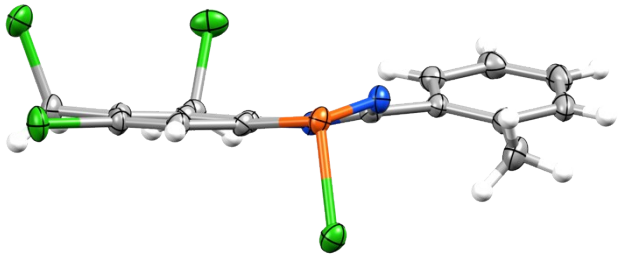


Figure S16 - Crystal structure of **2h** - Side view.

Compound	**2h**
Empirical formula	$C_{16}H_{12}Cl_4N_2S$
Formula weight	406.14
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	*Pbca*
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/mm^3	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_{sigma} = 0.0183]
Data/restraints/parameters	3183/0/237
Goodness-of-fit on F^2	1.108
Final R indexes [I>=2σ (I)]	R_1 = 0.0399, wR_2 = 0.0977
Final R indexes [all data]	R_1 = 0.0400, wR_2 = 0.0977
Largest diff. peak/hole / e Å^{-3}	1.00/-0.47
Flack parameter	

2i:

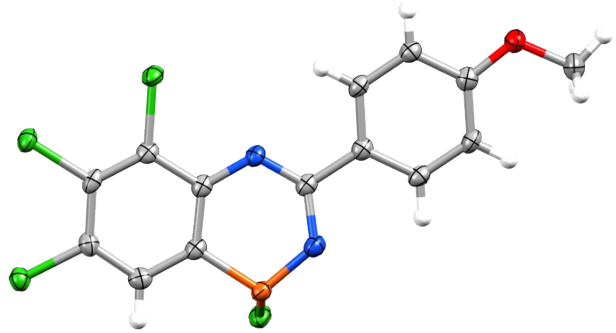


Figure S17 - Crystal structure of **2i** - Front view.

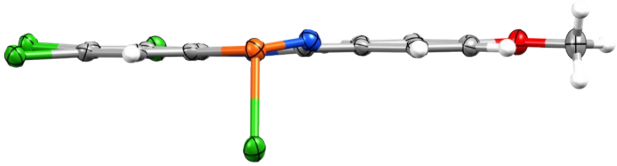


Figure S18 - Crystal structure of **2i** - Side view.

Compound	**2i**
Empirical formula	$C_{14}H_8Cl_4N_2OS$
Formula weight	394.08
Temperature/K	100.0(5)
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	7.0073(5)
b/Å	9.6628(6)
c/Å	12.0172(7)
α/°	95.257(5)
β/°	106.738(6)
γ/°	101.231(6)
Volume/Å^3	754.78(9)
Z	2
ρ_{calc}g/cm^3	1.734
μ/mm^{-1}	8.438
F(000)	396
Crystal size/mm^3	0.222 × 0.040 × 0.035
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.78 to 144.244
Index ranges	-8 ≤ h ≤ 7, -11 ≤ k ≤ 10, -14 ≤ l ≤ 14
Reflections collected	11718
Independent reflections	2964 [R_{int} = 0.0508, R_{sigma} = 0.0319]
Data/restraints/parameters	2964/0/200
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (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:

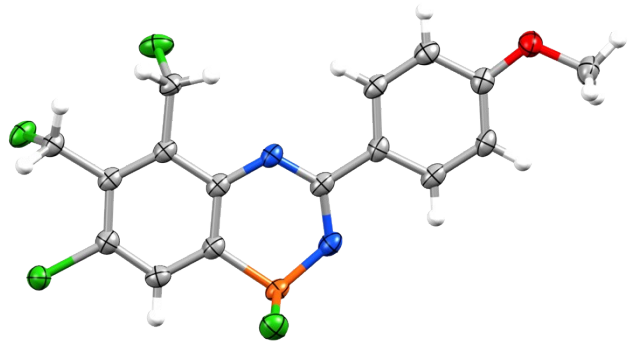


Figure S19 - Crystal structure of **2j** - Front view.

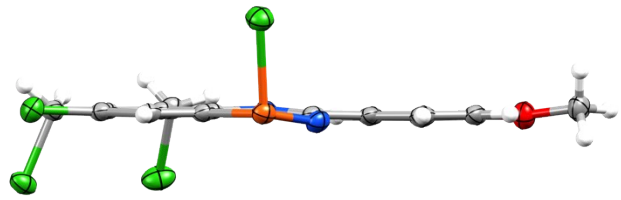


Figure S20 - Crystal structure of **2j** - Side view.

Compound	**2j**
Empirical formula	$C_{16}H_{12}Cl_4N_2OS$
Formula weight	422.14
Temperature/K	99.9(6)
Crystal system	triclinic
Space group	$P\bar{1}$
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/Å^3	956.37(16)
Z	2
ρ_{calc}g/cm^3	1.466
μ/mm^{-1}	6.697
F(000)	428
Crystal size/mm^3	0.415 × 0.042 × 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, R_{sigma} = 0.0492]
Data/restraints/parameters	3403/0/218
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0546, wR_2 = 0.1486
Final R indexes [all data]	R_1 = 0.0611, wR_2 = 0.1565
Largest diff. peak/hole / e Å^{-3}	0.81/-0.84
Flack parameter	

2l.H[HCl$_2$]:

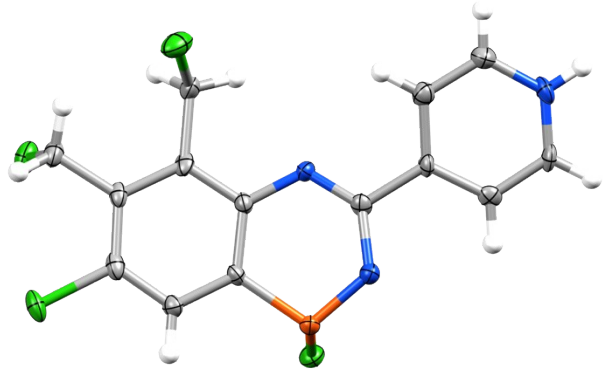


Figure S21 - Crystal structure of **2l**.H[HCl$_2$] - Front view. Anion omitted for clarity.

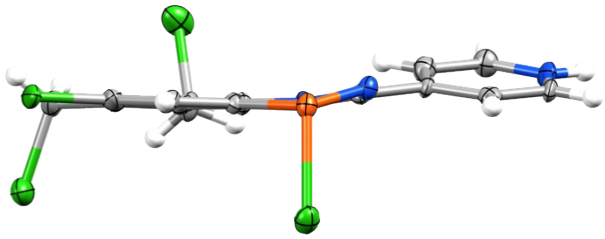


Figure S22 - Crystal structure of **2l**.H[HCl$_2$] - Side view. Anion omitted for clarity.

Compound	**2l.H[HCl$_2$]**
Empirical formula	$C_{14}H_{11}Cl_6N_3S$
Formula weight	466.02
Temperature/K	100.0(5)
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	8.1354(2)
b/Å	9.2414(2)
c/Å	12.9459(6)
α/°	90.608(3)
β/°	101.838(3)
γ/°	105.699(2)
Volume/Å^3	914.81(5)
Z	2
ρ_{calc}g/cm^3	1.692
μ/mm^{-1}	9.662
F(000)	468
Crystal size/mm^3	0.393 × 0.097 × 0.043
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.994 to 139.01
Index ranges	-9 ≤ h ≤ 8, -11 ≤ k ≤ 11, -15 ≤ l ≤ 15
Reflections collected	17679
Independent reflections	3432 [R_{int} = 0.0586, R_{sigma} = 0.0322]
Data/restraints/parameters	3432/0/221
Goodness-of-fit on F^2	1.209
Final R indexes [I>=2σ (I)]	R_1 = 0.1019, wR_2 = 0.2915
Final R indexes [all data]	R_1 = 0.1028, wR_2 = 0.2917
Largest diff. peak/hole / e Å^{-3}	1.33/-0.97
Flack parameter	

2r:

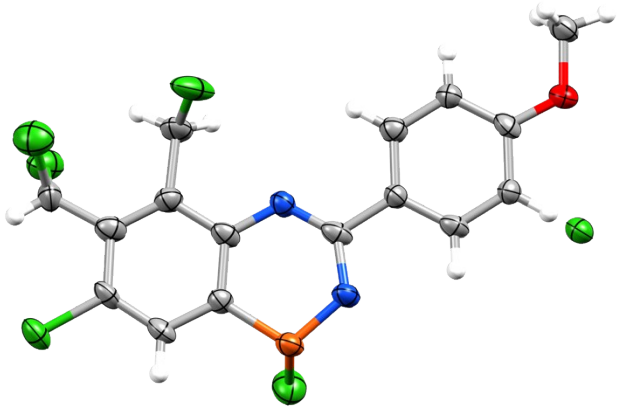


Figure S23 - Crystal structure of **2r** - Front view. Shown in partial chlorination *ortho* to the OMe group.

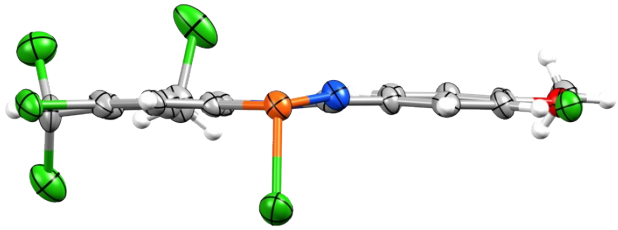


Figure S24 - Crystal structure of **2r** - Side view. Shown with partial chlorination *ortho* to the OMe group.

Compound	**2r**
Empirical formula	$C_{16}H_{10.42}Cl_{5.58}N_2OS$
Formula weight	476.64
Temperature/K	100.00(13)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	6.5698(7)
b/Å	16.562(2)
c/Å	16.941(3)
α/°	90
β/°	93.510(12)
γ/°	90
Volume/Å^3	1839.8(5)
Z	4
ρ_{calc}g/cm^3	1.721
μ/mm^{-1}	9.11
F(000)	957
Crystal size/mm^3	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_{int} = 0.0626, R_{sigma} = 0.0882]
Data/restraints/parameters	3350/0/241
Goodness-of-fit on F^2	1.145
Final R indexes [I>=2σ (I)]	R_1 = 0.1055, wR_2 = 0.2644
Final R indexes [all data]	R_1 = 0.1319, wR_2 = 0.2818
Largest diff. peak/hole / e Å^{-3}	0.77/-0.96
Flack parameter	

2s:

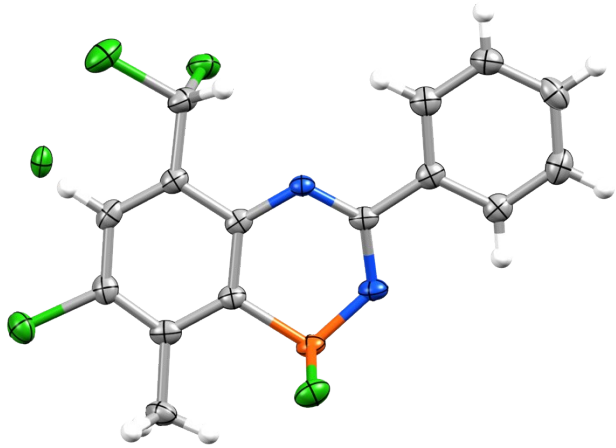


Figure S25 - Crystal structure of **2s** - Front view. Shown with partial chlorination at C6.

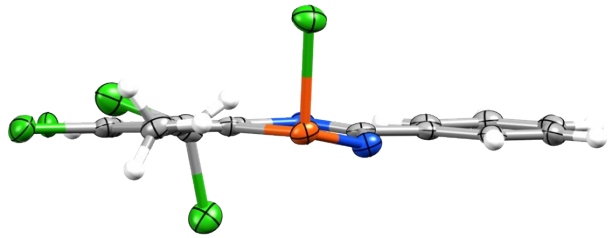


Figure S26 - Crystal structure of **2s** - Side view. Shown with partial chlorination at C6.

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)
α/°	90
β/°	105.795(3)
γ/°	90
Volume/Å^3	1609.82(9)
Z	4
ρ_{calc}g/cm^3	1.635
μ/mm^{-1}	8.049
F(000)	800
Crystal size/mm^3	0.315 × 0.066 × 0.03
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.796 to 135.814
Index ranges	-9 ≤ h ≤ 9, -19 ≤ k ≤ 19, -16 ≤ l ≤ 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>=2σ (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
Flack parameter	

3a:

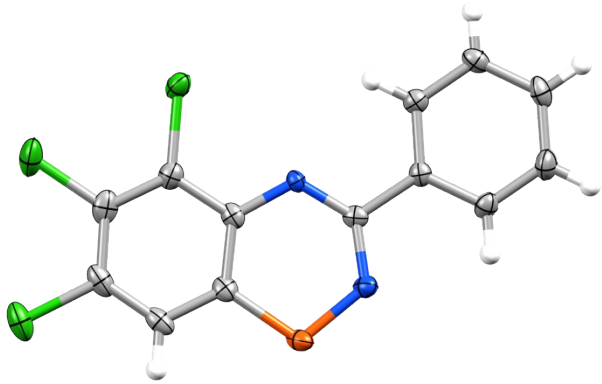


Figure S27 - Crystal structure of **3a** - Front view. Solvent of crystallisation (DCM) omitted for clarity.

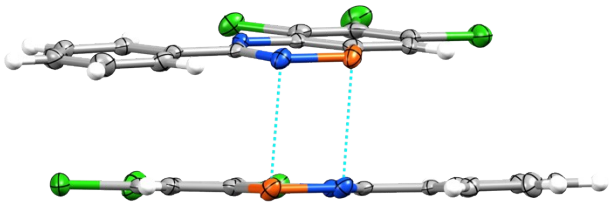


Figure S28 - Crystal structure of **3a** - Side view of radical dimerisation. Solvent of crystallisation (DCM) omitted for clarity.

Compound	**3a**
Empirical formula	$C_{13.5}H_7Cl_4N_2S$
Formula weight	371.07
Temperature/K	100.0(7)
Crystal system	orthorhombic
Space group	*Pbcn*
a/Å	16.7712(3)
b/Å	13.1359(2)
c/Å	13.0495(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2874.87(8)
Z	8
ρ_{calc}g/cm^3	1.715
μ/mm^{-1}	8.764
F(000)	1488
Crystal size/mm^3	0.257 × 0.084 × 0.08
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.55 to 142.028
Index ranges	-20 ≤ h ≤ 20, -16 ≤ k ≤ 16, -16 ≤ l ≤ 12
Reflections collected	72177
Independent reflections	2779 [R_{int} = 0.0861, R_{sigma} = 0.0305]
Data/restraints/parameters	2779/0/186
Goodness-of-fit on F^2	1.237
Final R indexes [I>=2σ (I)]	R_1 = 0.0615, wR_2 = 0.1453
Final R indexes [all data]	R_1 = 0.0638, wR_2 = 0.1454
Largest diff. peak/hole / e Å^{-3}	1.15/-0.68
Flack parameter	

3c:

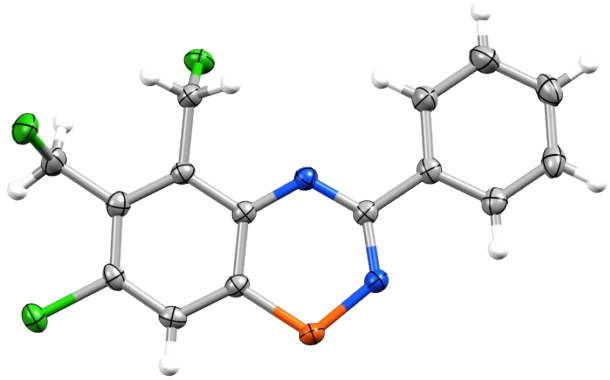


Figure S29 - Crystal structure of **3c** - Front view.

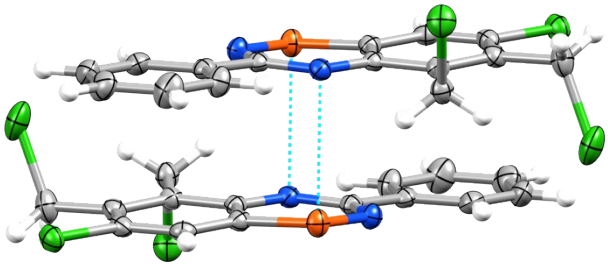


Figure S30 - Crystal structure of **3c** - Side view of radical dimerisation.

Compound	**3c**
Empirical formula	$C_{15}H_{10}Cl_3N_2S$
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/Å^3	1456.8(3)
Z	4
ρ_{calc}g/cm^3	1.626
μ/mm^{-1}	6.972
F(000)	724
Crystal size/mm^3	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 F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0388, wR_2 = 0.1031
Final R indexes [all data]	R_1 = 0.0454, wR_2 = 0.1076
Largest diff. peak/hole / e Å^{-3}	0.38/-0.58
Flack parameter	

3e:

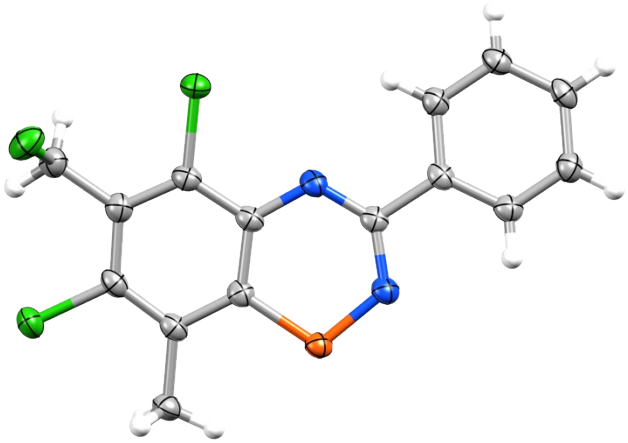


Figure S31 - Crystal structure of **3e** - Front view. Only one molecule of the asymmetric unit is shown for clarity.

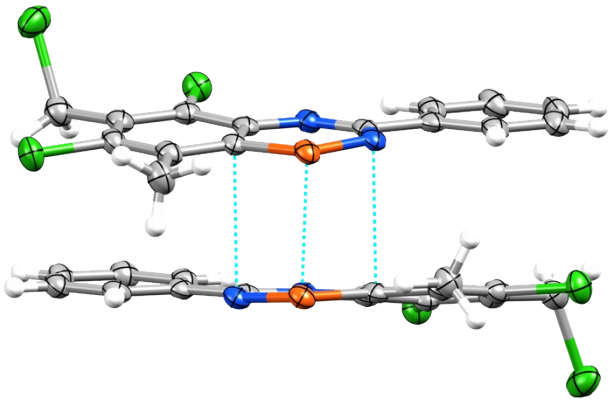


Figure S32 - Crystal structure of **3e** - Side view of radical dimerisation.

Compound	**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/Å	9.9369(4)
b/Å	12.2664(4)
c/Å	13.3652(5)
α/°	91.036(3)
β/°	107.068(4)
γ/°	109.355(3)
Volume/Å^3	1457.25(10)
Z	2
ρ_{calc}g/cm^3	1.626
μ/mm^{-1}	6.97
F(000)	724
Crystal size/mm^3	0.273 × 0.17 × 0.048
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.976 to 142.122
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 15, -16 ≤ l ≤ 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>=2σ (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	

3k:

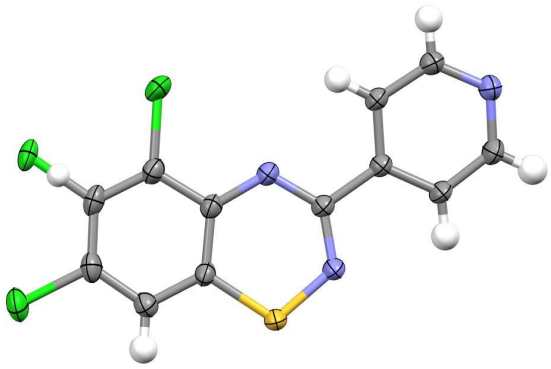


Figure S33 - Crystal structure of **3e** - Front view. Only one molecule of the asymmetric unit is shown for clarity.

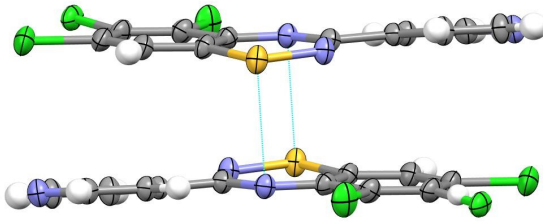


Figure S34 - Crystal structure of **3k** - Side view of radical dimerisation.

Compound	**3k**
Empirical formula	$C_{13}H_8N_3SCl_2$
Formula weight	300.84
Temperature/K	99.98(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.4291(4)
b/Å	18.6148(9)
c/Å	9.0438(5)
α/°	90
β/°	107.796(6)
γ/°	90
Volume/Å^3	1190.83(11)
Z	4
ρ_{calc}g/cm^3	1.725
μ/mm^{-1}	6.430
F(000)	628.0
Crystal size/mm^3	0.304 × 0.079 × 0.053
Radiation	CuKα (λ = 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 [R_{int} = 0.0543, R_{sigma} = 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][$GaCl_4$]:

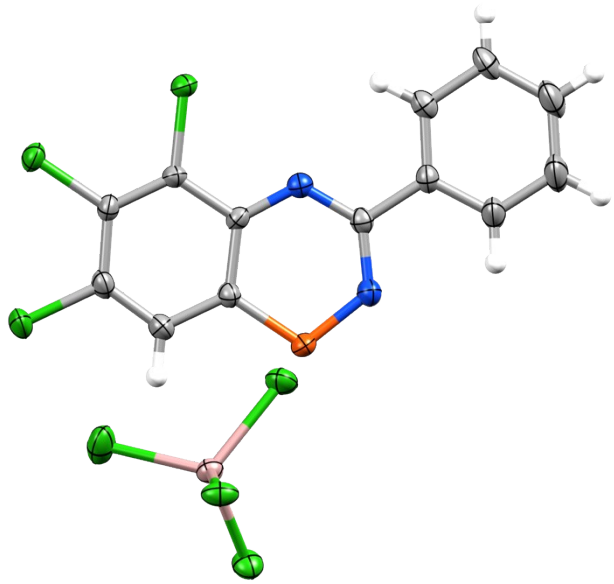


Figure S35 - Crystal structure of **[4a][$GaCl_4$]** - Front view.

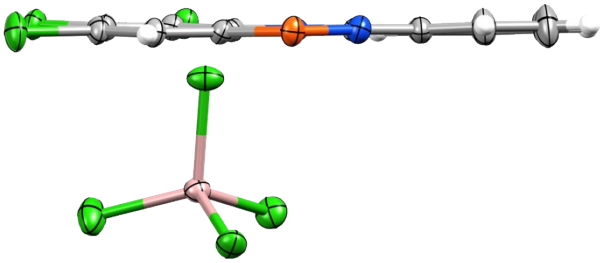


Figure S36 - Crystal structure of **[4a][$GaCl_4$]** - Side view.

Compound	**[4a][$GaCl_4$]**
Empirical formula	$C_{13}H_6Cl_7GaN_2S$
Formula weight	540.13
Temperature/K	100.0(4)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.5753(4)
b/Å	9.8718(4)
c/Å	20.0990(7)
α/°	90
β/°	94.444(3)
γ/°	90
Volume/Å^3	1894.16(13)
Z	4
ρ_{calc}g/cm^3	1.894
μ/mm^{-1}	12.113
F(000)	1056
Crystal size/mm^3	0.209 × 0.197 × 0.061
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.826 to 142.102
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -24 ≤ l ≤ 23
Reflections collected	36088
Independent reflections	3657 [R_{int} = 0.1269, R_{sigma} = 0.0384]
Data/restraints/parameters	3657/0/217
Goodness-of-fit on F^2	1.135
Final R indexes [I>=2σ (I)]	R_1 = 0.0617, wR_2 = 0.1632
Final R indexes [all data]	R_1 = 0.0617, wR_2 = 0.1632
Largest diff. peak/hole / e Å^{-3}	0.92/-0.94
Flack parameter	

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.[4] 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

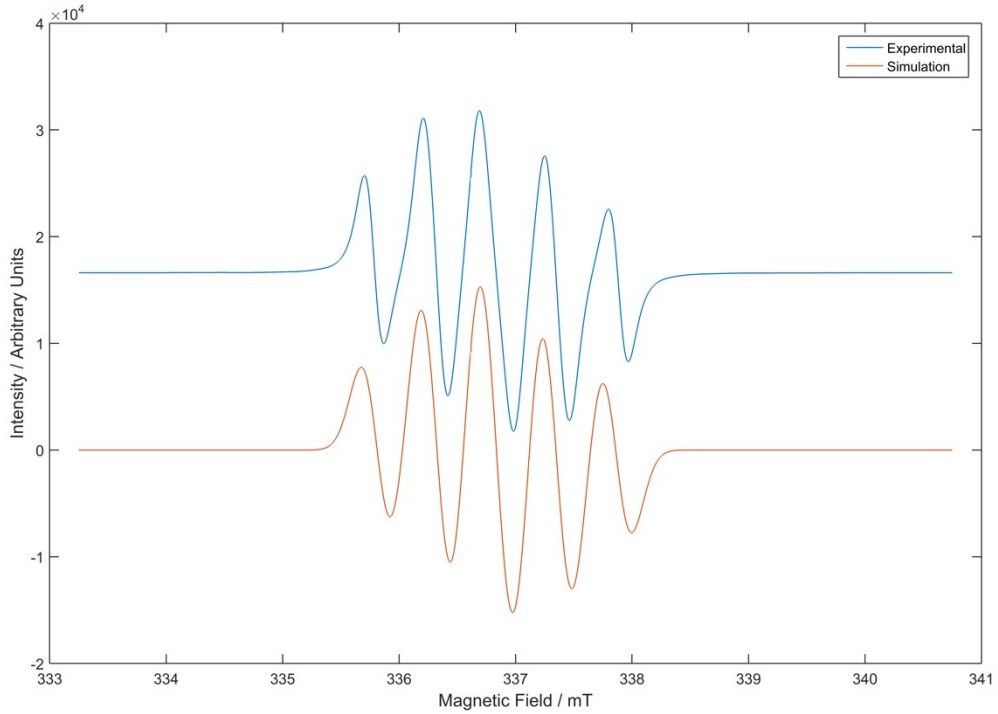


Figure S37 - EPR spectra of **3a**. *g*-value = 2.00369, line width = 0.27 MHz, a_{N2} = 15.56 MHz, a_{N4} = 13.13 MHz.

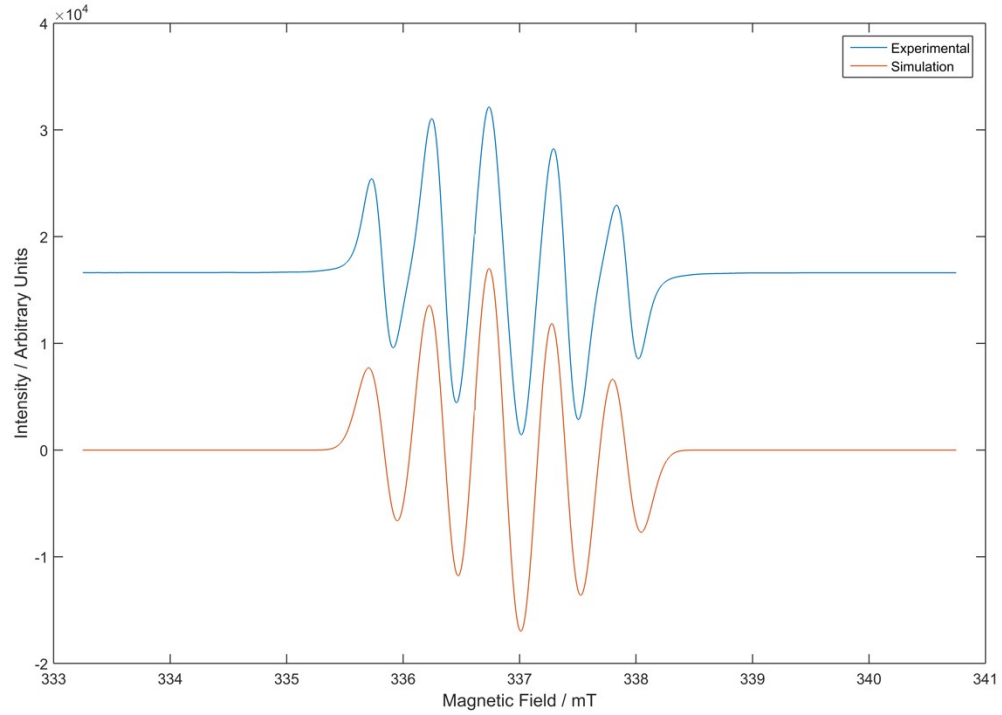


Figure S38 - EPR spectra of **3b**. *g*-value = 2.00346, line width = 0.26 MHz, a_{N2} = 15.64 MHz, a_{N4} = 13.51 MHz.

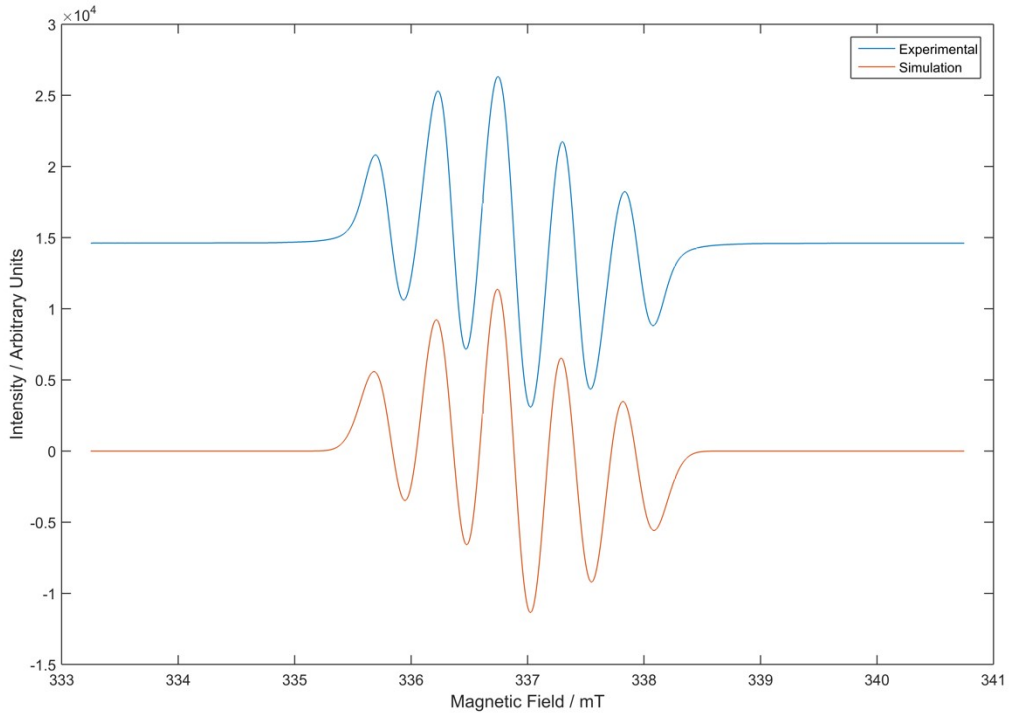


Figure S39 - EPR spectra of **3c**. *g*-value = 2.00341, line width = 0.31 MHz, a_{N2} = 15.80 MHz, a_{N4} = 13.60 MHz.

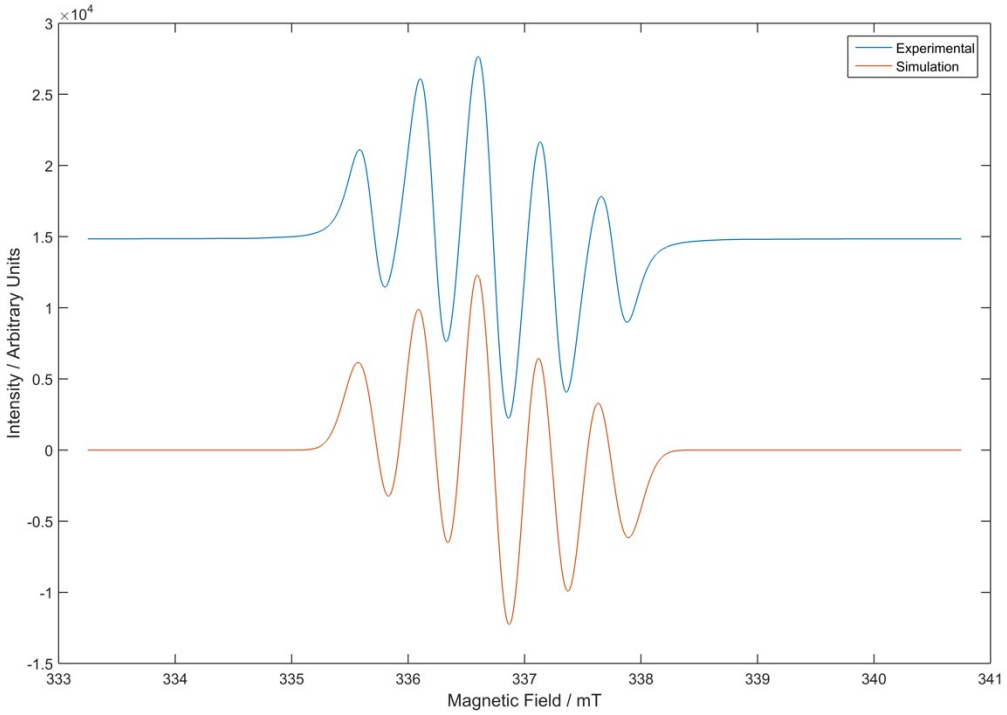


Figure S40 - EPR spectra of **3d**. *g*-value = 2.00431, line width = 0.31 MHz, a_{N2} = 15.10 MHz, a_{N4} = 13.10 MHz.

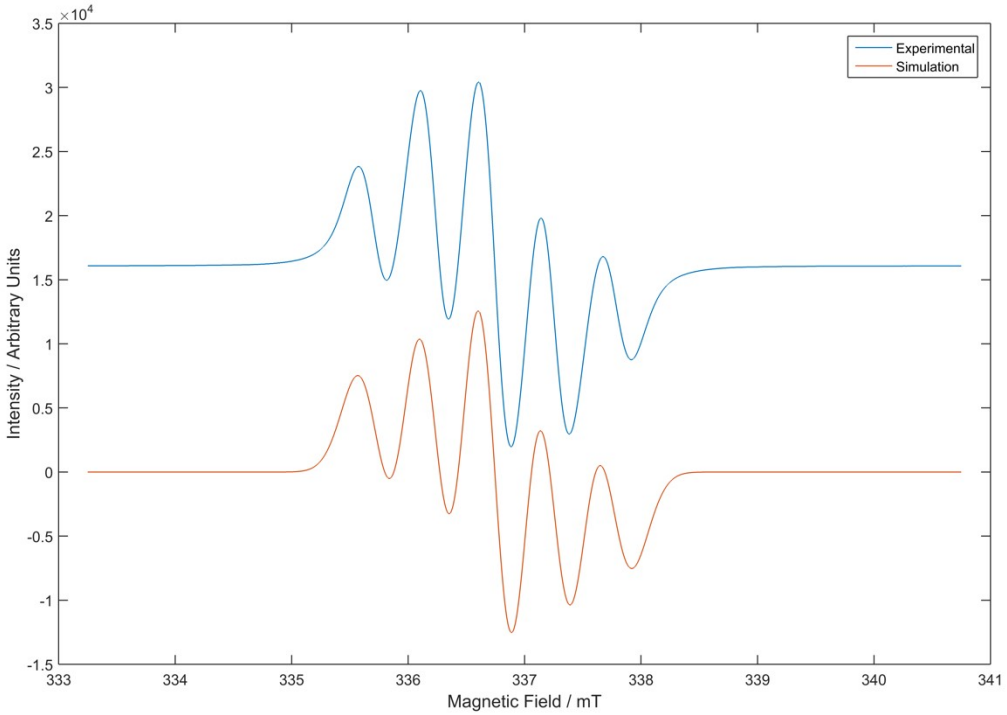


Figure S41 - EPR spectra of **3e**. *g*-value = 2.00463, line width = 0.37 MHz, a_{N2} = 14.69 MHz, a_{N4} = 13.30 MHz.

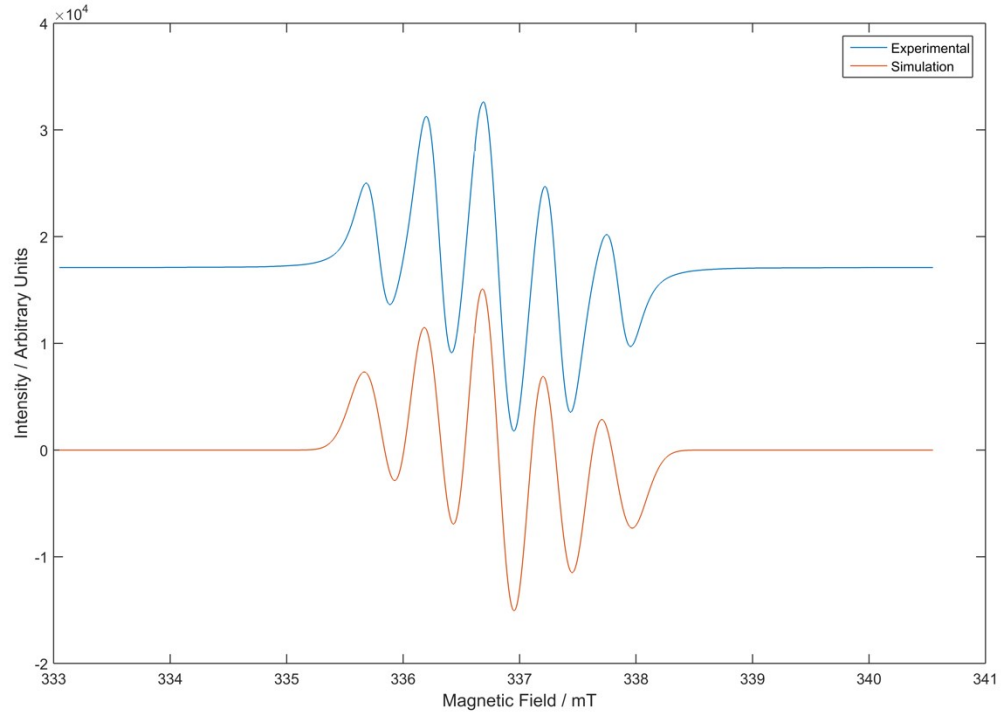


Figure S42 - EPR spectra of **3f**. *g*-value = 2.00453, line width = 0.33 MHz, a_{N2} = 14.56 MHz, a_{N4} = 13.23 MHz.

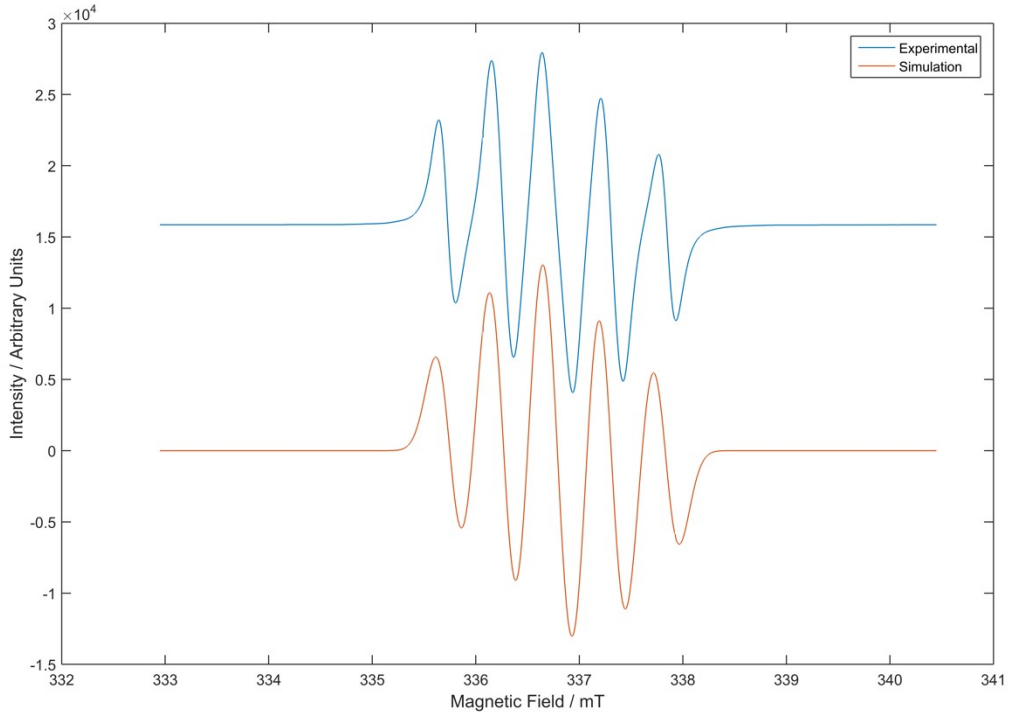


Figure S43 - EPR spectra of **3g**. *g*-value = 2.00461, line width = 0.27 MHz, a_{N2} = 15.88 MHz, a_{N4} = 13.35 MHz.

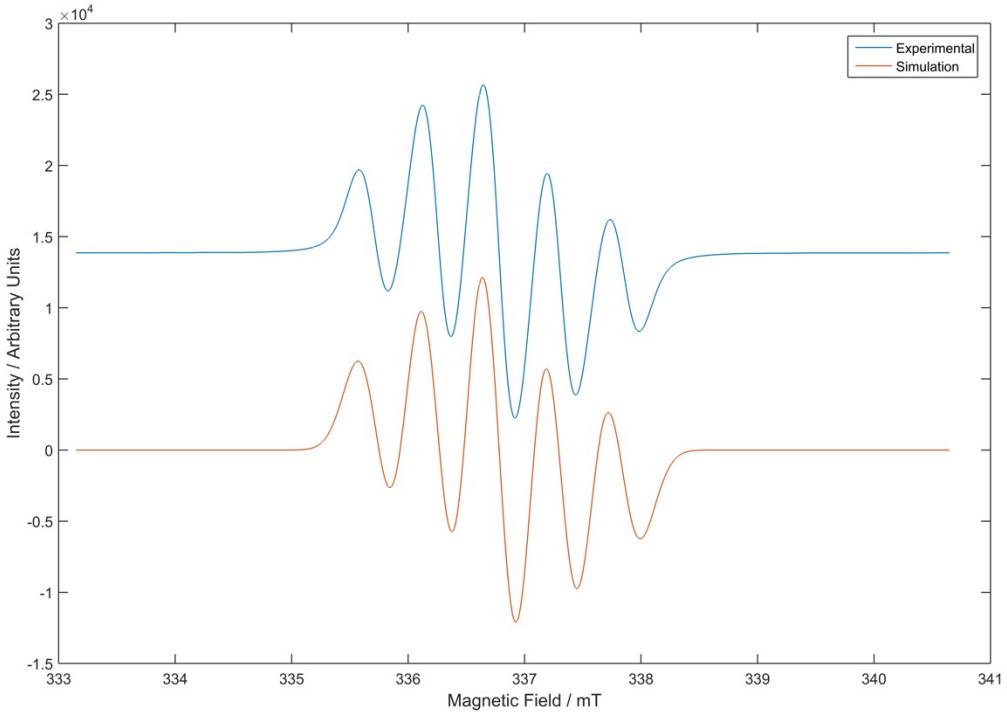


Figure S44 - EPR spectra of **3h**. *g*-value = 2.00449, line width = 0.34 MHz, a_{N2} = 15.61 MHz, a_{N4} = 13.71 MHz.

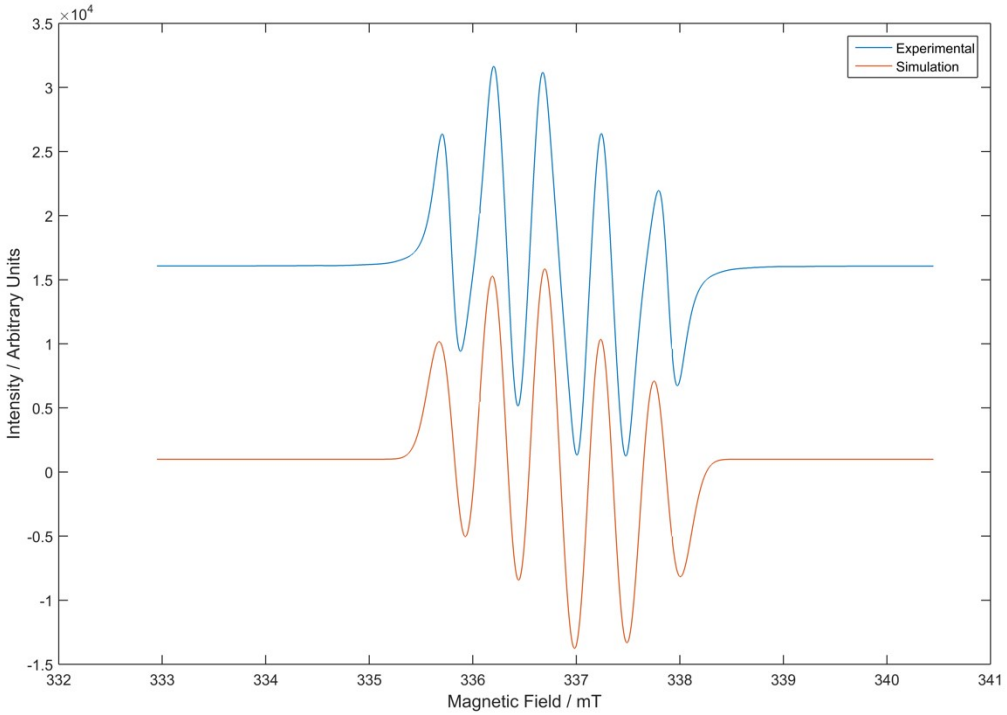


Figure S45 - EPR spectra of **3i**. *g*-value = 2.00410, line width = 0.29 MHz, a_{N2} = 15.82 MHz, a_{N4} = 12.89 MHz.

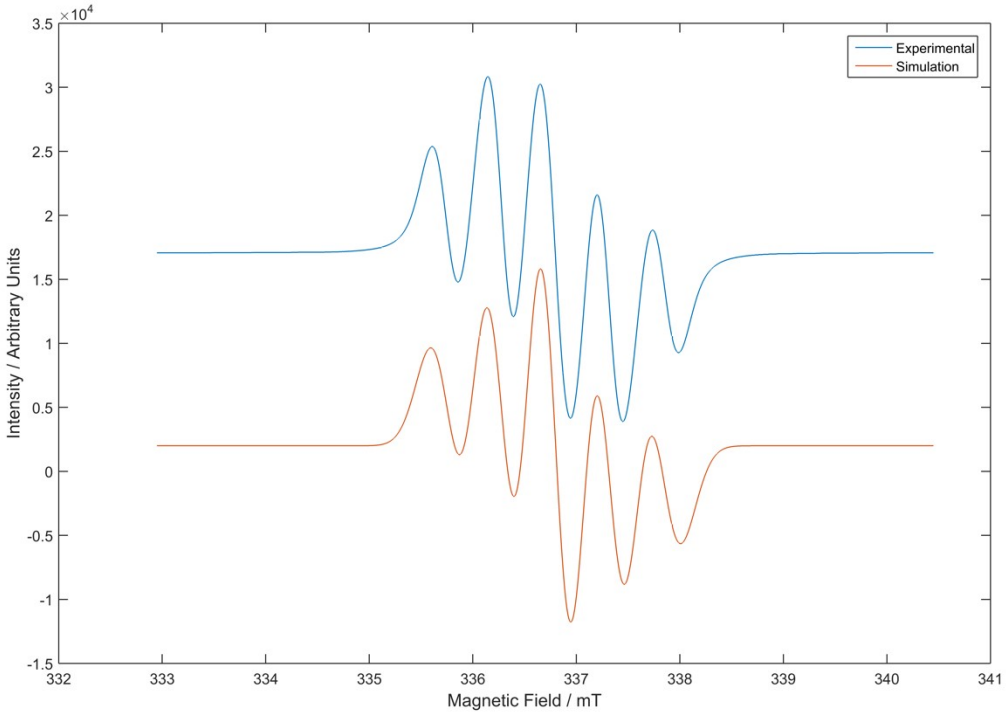


Figure S46 - EPR spectra of **3j**. *g*-value = 2.00411, line width = 0.38 MHz, a_{N2} = 14.73 MHz, a_{N4} = 13.98 MHz.

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 [^{n}Bu$_4$N][PF$_6$] supporting electrolyte in 10 cm^3 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.[18] 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

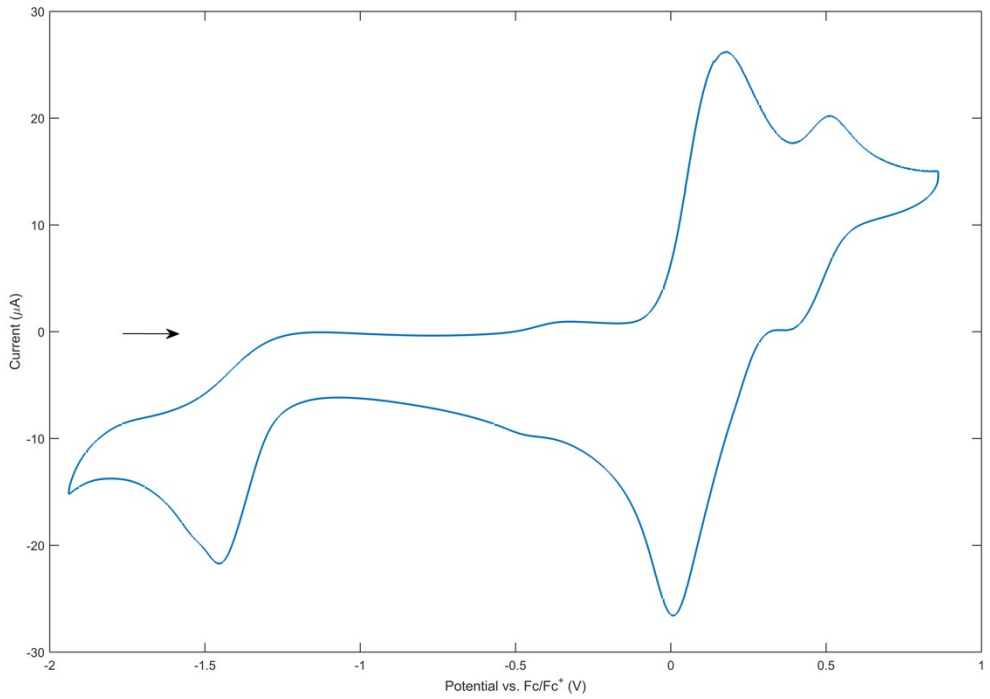


Figure S47 - Cyclic voltammogram of **2a**.

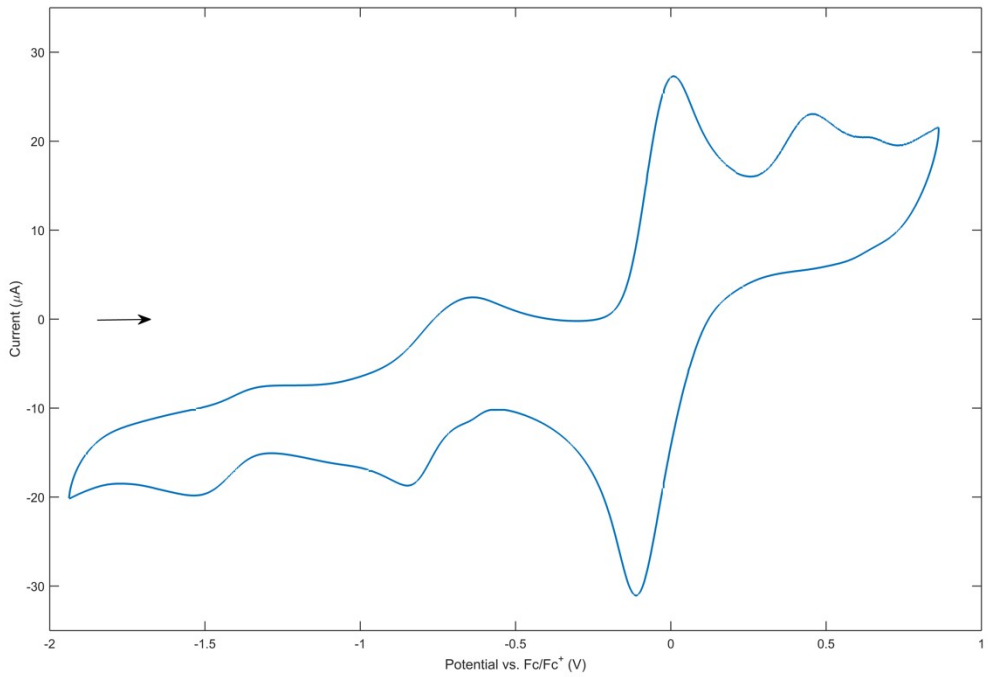


Figure S48 - Cyclic voltammogram of **2b**.

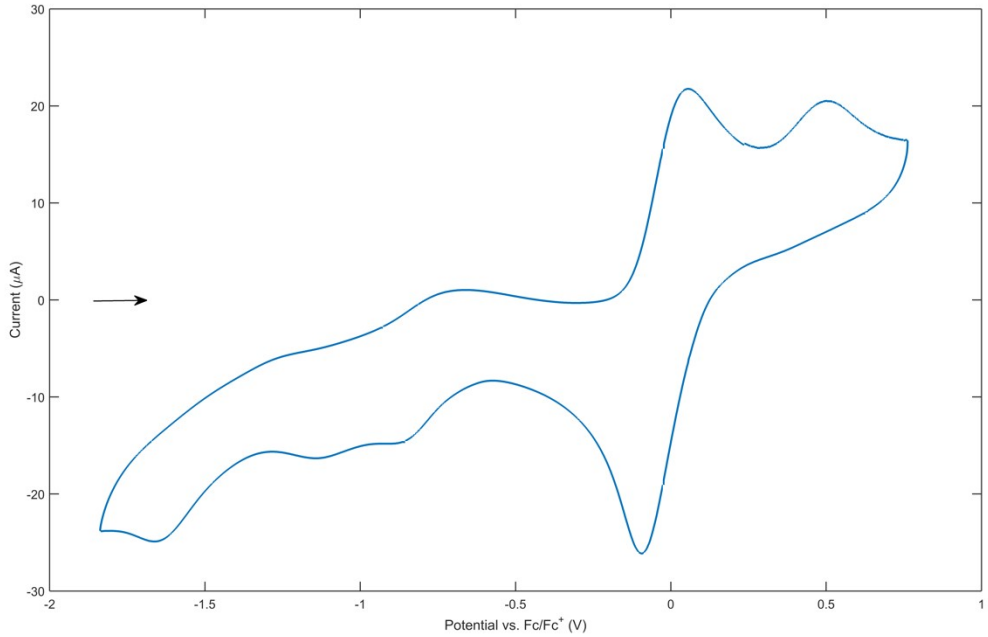


Figure S49 - Cyclic voltammogram of **2c**.

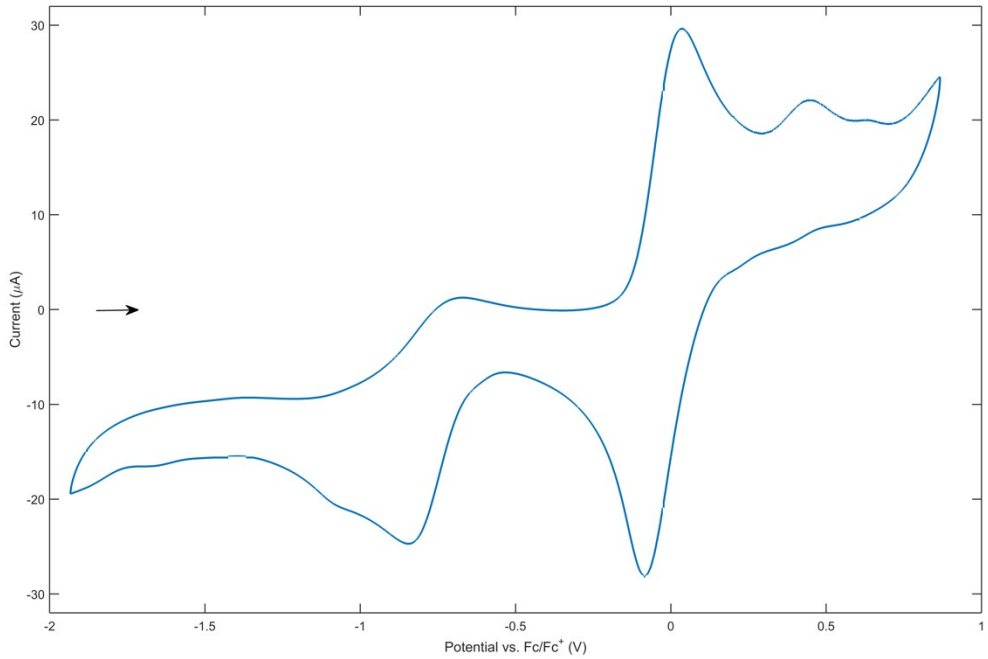


Figure S50 - Cyclic voltammogram of **2d**.

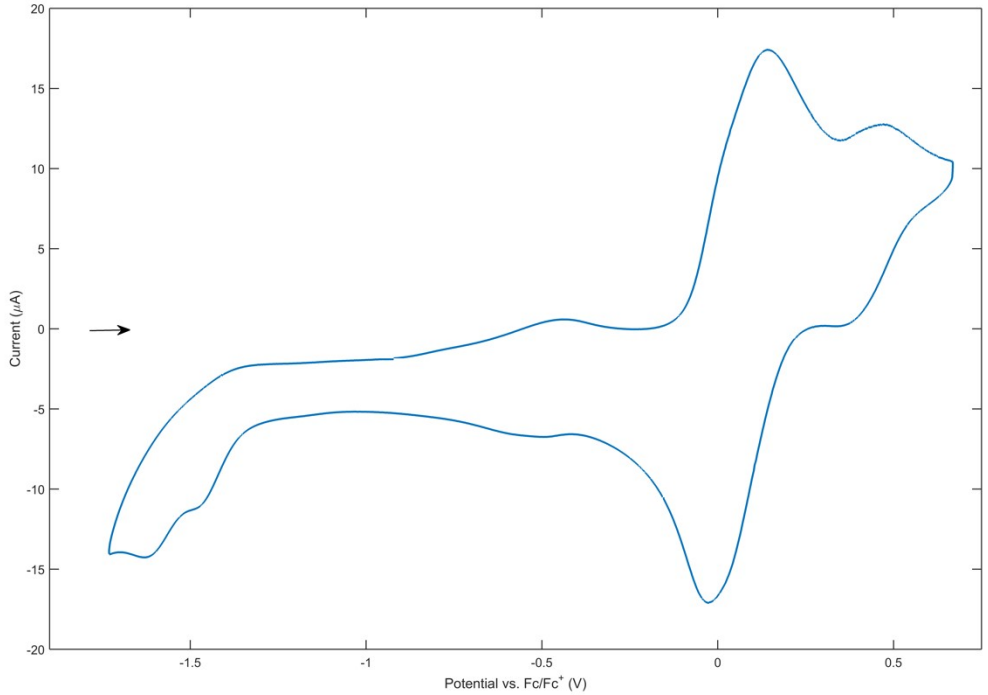


Figure S51 - Cyclic voltammogram of **2e**.

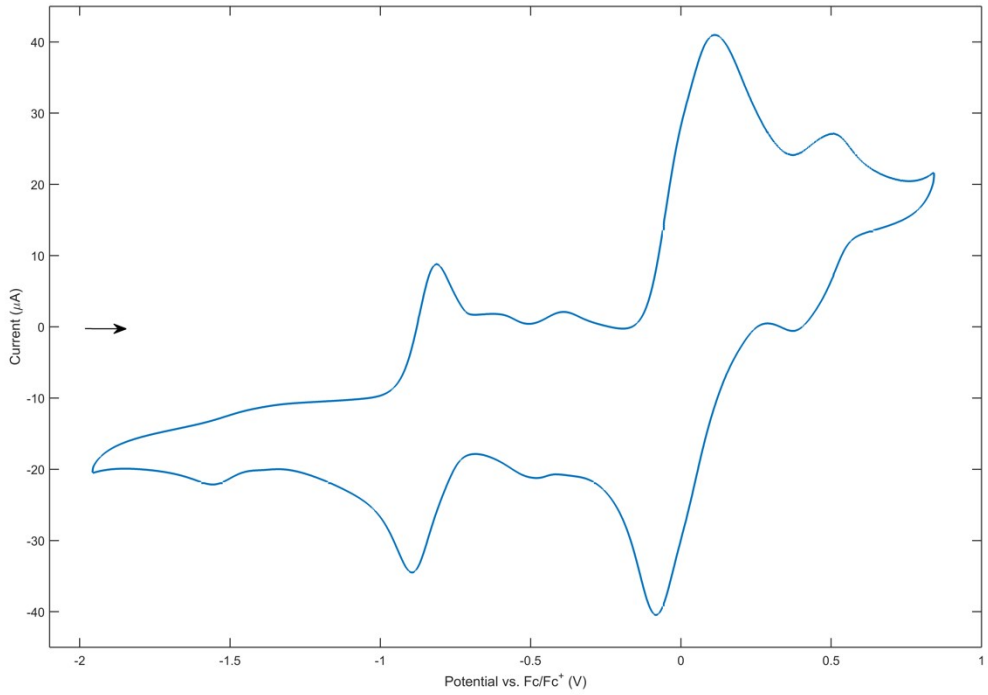


Figure S52 - Cyclic voltammogram of **2f**.

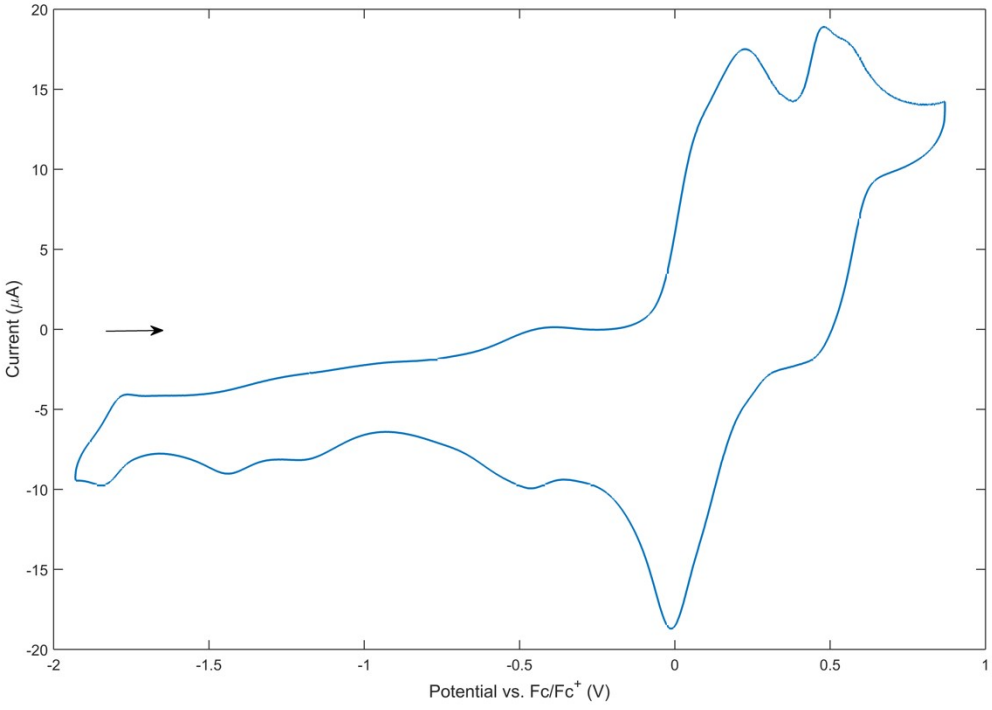


Figure S53 - Cyclic voltammogram of **2g**.

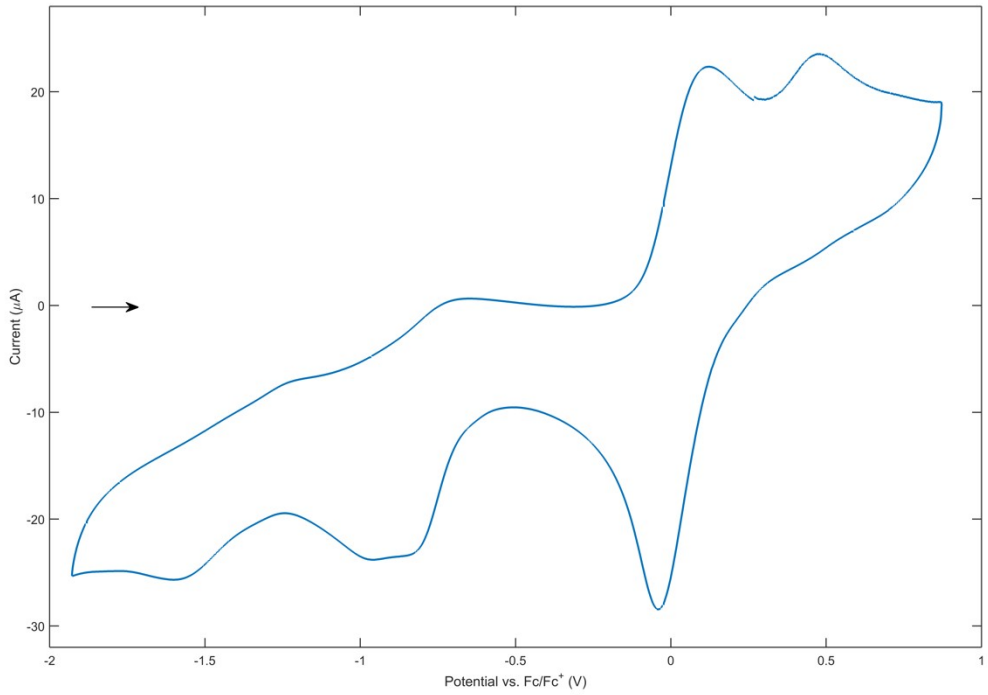


Figure S54 - Cyclic voltammogram of **2h**.

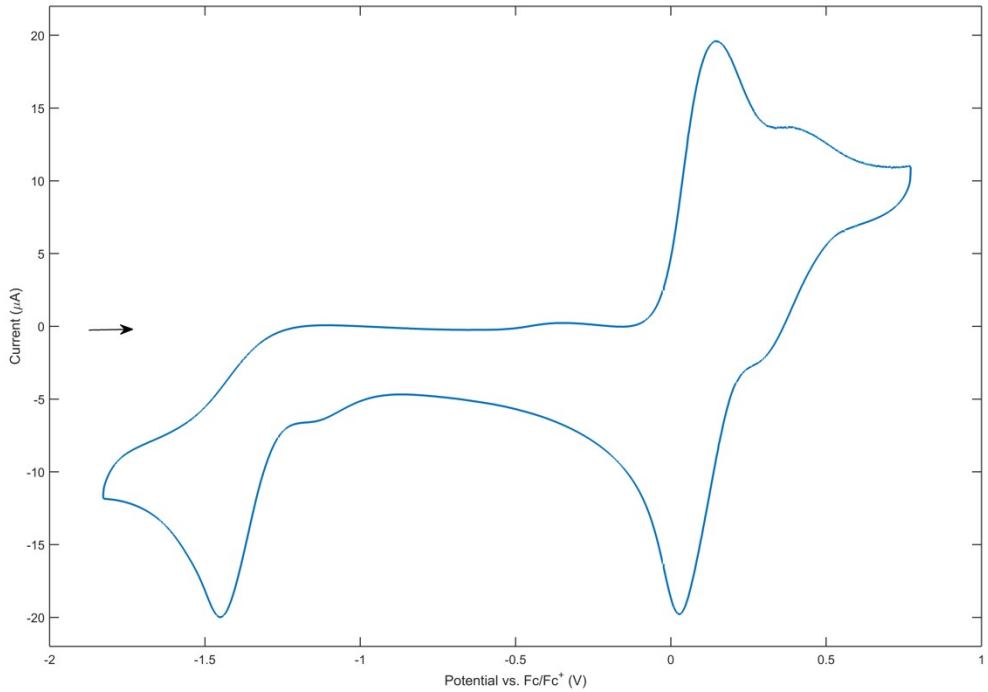


Figure S55 - Cyclic voltammogram of **2i**.

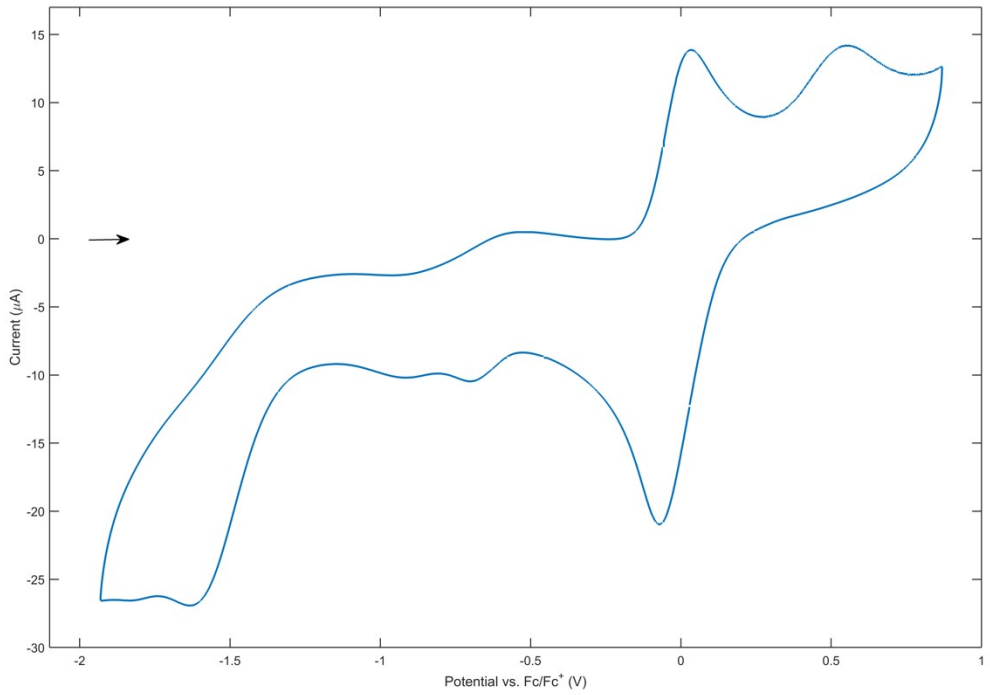


Figure S56 - Cyclic voltammogram of **2j**.

5.2. Variable Concentration Studies

Variable concentration cyclic voltammetry studies were performed on **2a** to qualitatively assess the radical monomer-dimer equilibrium (**Figure S57**).

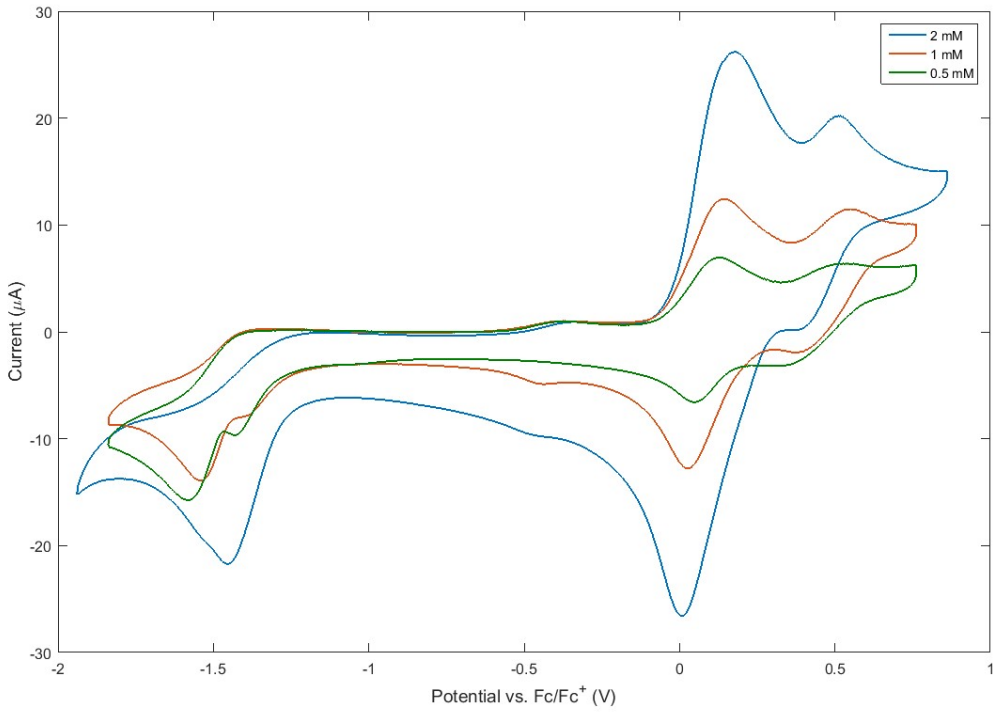


Figure S57 - Cyclic voltammograms of **2a** at various concentrations.

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.[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 (*i.e.* the S(II) anion) is consumed by a subsequent chemical reaction (*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.

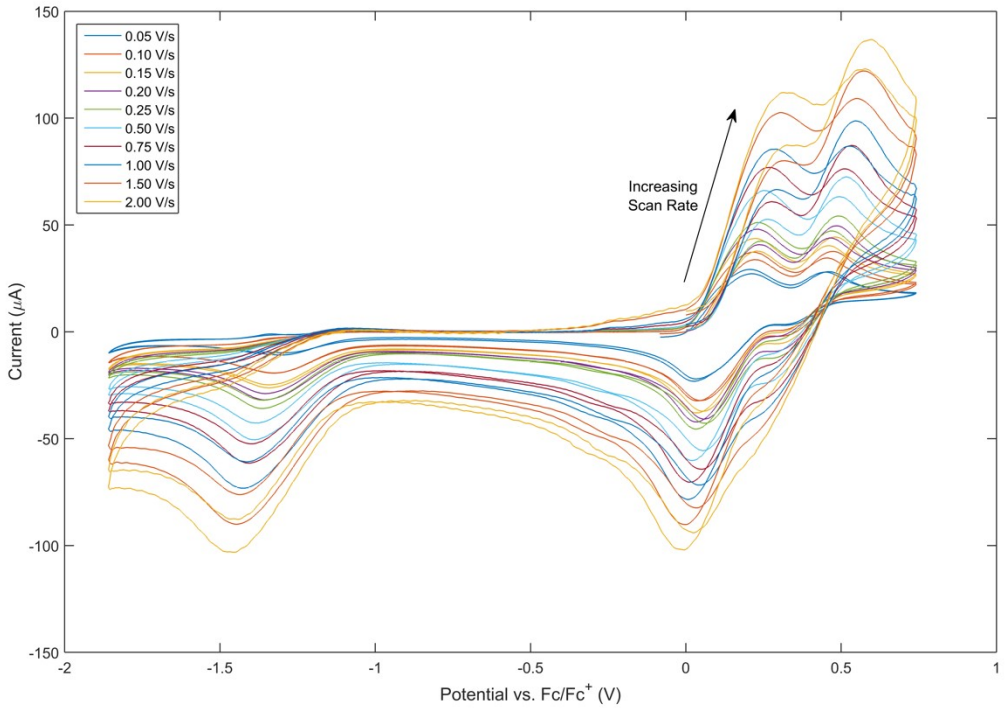


Figure S58 - Cyclic voltammograms of **2f** at various scan rates.

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.[20]

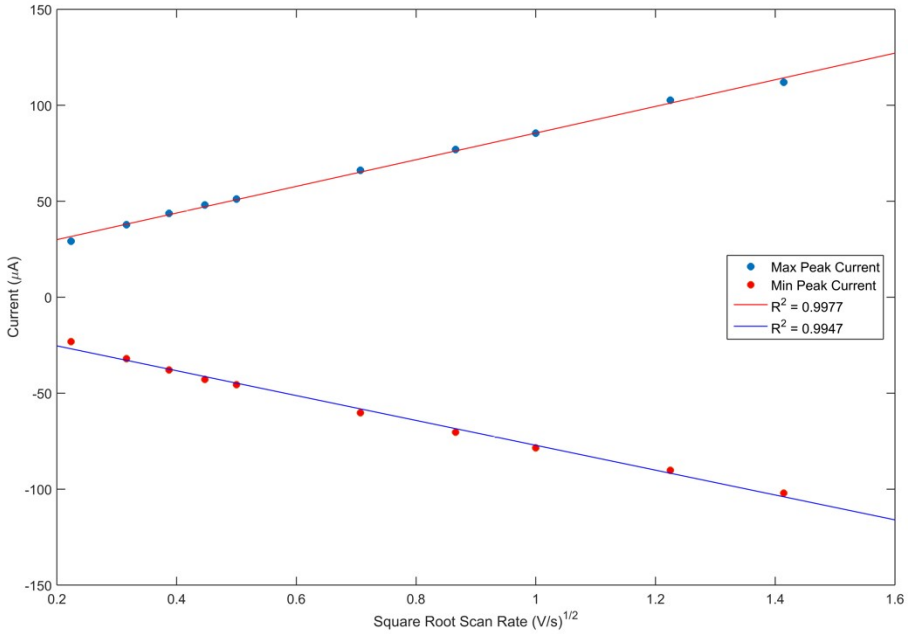


Figure S59 - Randles-Sevcik plot for **3f**.

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.[21] Curie-Weiss analysis provided Curie constants of 0.145 and 0.021 emu.K.Oe^{-1}.mol^{-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_2 within the sample at 50 K.[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

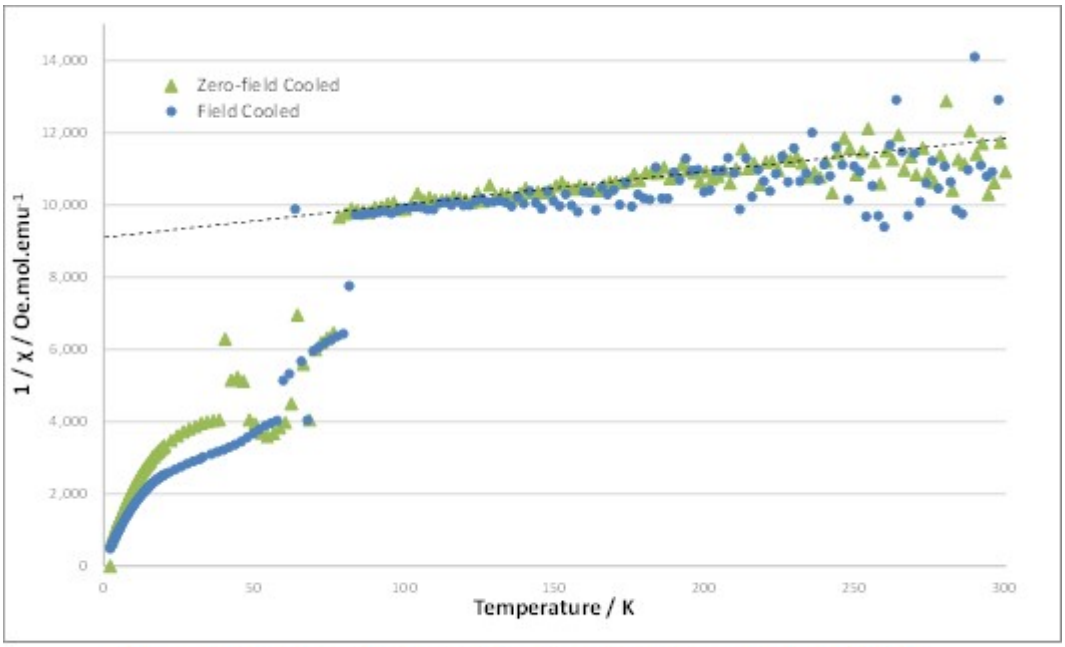


Figure S60 – Curie-Weiss plot for **3c**, recorded in a field of 1000 Oe.

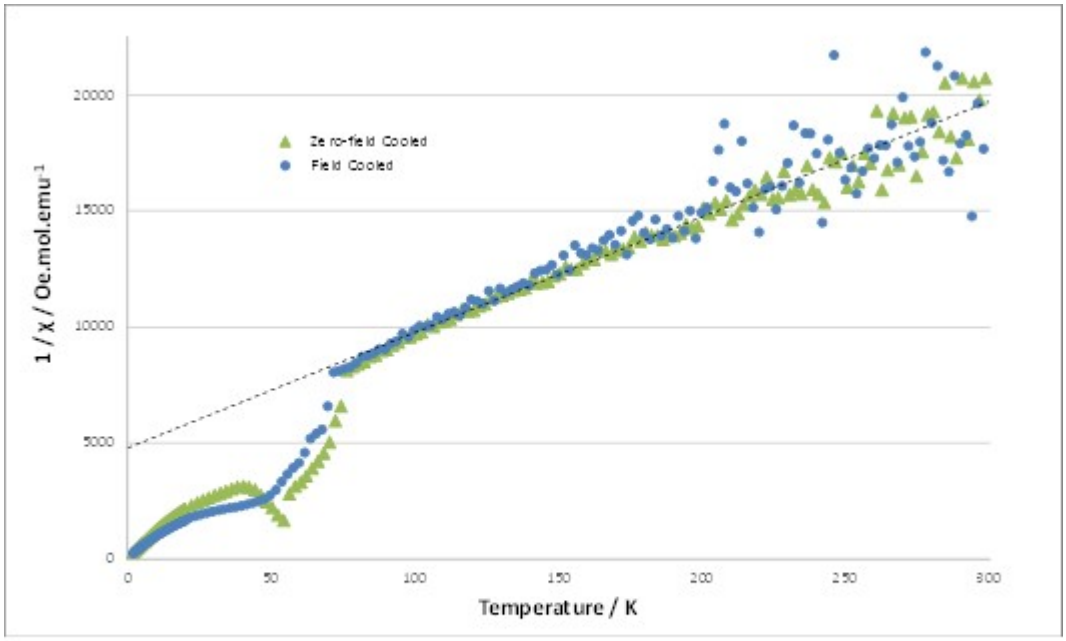


Figure S61 – Curie-Weiss for **3e**, recorded in a field of 1000 Oe.

7. Computational Chemistry

7.1. EPR and Electronic Studies

Calculations were performed using the Gaussian 16 suite of programs.[23] Structures were optimised in the gas-phase, from single-crystal X-ray diffraction data where available, at the DFT[24] UB3LYP/6-31g level of theory.[25] 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[26] from the UB3LYP/6-31g optimised geometry.[27] Orbital visualisations were made using the VMD molecular graphics viewer.[28]

Many studies on the redox properties of sulphur-nitrogen radicals have found good correlation between the *E1/2* 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.[29] 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 *E½* 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.[30,31] 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.[32] 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**.

	a_{N2} / MHz	a_{N4} / MHz	Spin Densities		
			N2	N4	S1
3a	23.181	20.460	0.3766	0.3359	0.2389
3b	22.772	20.328	0.3694	0.3293	0.2427
3c	23.043	20.633	0.3750	0.3348	0.2358
3d	22.604	20.437	0.3679	0.3313	0.2359
3e	23.320	20.851	0.3810	0.3432	0.2261
3f	23.122	20.436	0.3752	0.3361	0.2457
3g	21.362	21.433	0.3500	0.3514	0.2323
3h	21.922	21.269	0.3588	0.3449	0.2302
3k	23.949	19.921	0.3886	0.3272	0.2396
3l	23.787	20.144	0.3866	0.3269	0.2364

Table S2 - Calculated hyperfine coupling constants and spin densities for the 1,2,4-benzothiadiazinyl radicals.

7.2. Dimerisation Energy Calculations

Dimerisation Energy Calculations were performed in a manner reported in the literature, including an explicit dispersion correction.[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:

$$\Delta E_{Dim} = E_{dimer} - 2E_{monomer}$$

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[23] and calculated at the UB3LYP/6-311g(d,p) level of theory[27] with a simple dinuclear nearest-neighbour exchange model from pairwise combinations of radicals.[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:

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

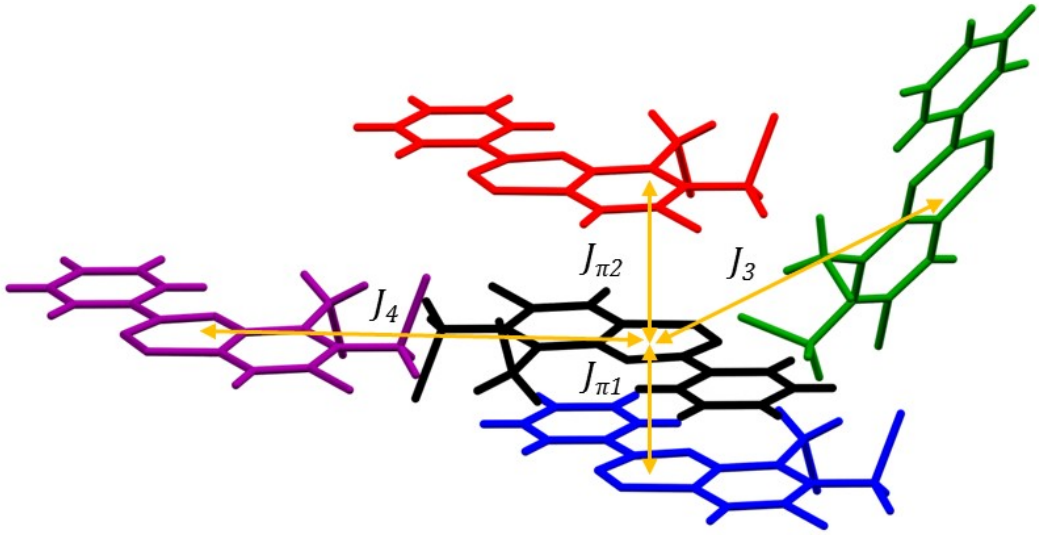


Figure S62 - Magnetic exchange pathways in **3c**.

	E_{TS} / Hartrees	$\langle S^2 \rangle_{TS}$	E_{BSS} / Hartrees	$\langle S^2 \rangle_{BSS}$	J / cm^{-1}
$J_{\pi 1}$	-4931.92924166	2.0329	-4931.93785381	0.9984	-1827.115
$J_{\pi 2}$	-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}
$J_{\pi 1}$	-4931.83391003	2.0309	-4931.85623662	0.9934	-4723.013
$J_{\pi 2}$	-4931.89695375	2.0319	-4931.89802333	0.9987	-227.203
$J_{\pi 3}$	-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**.

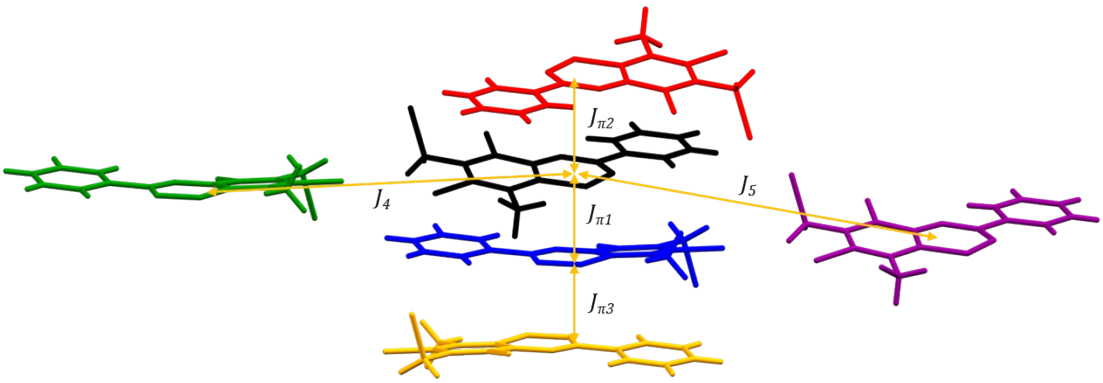
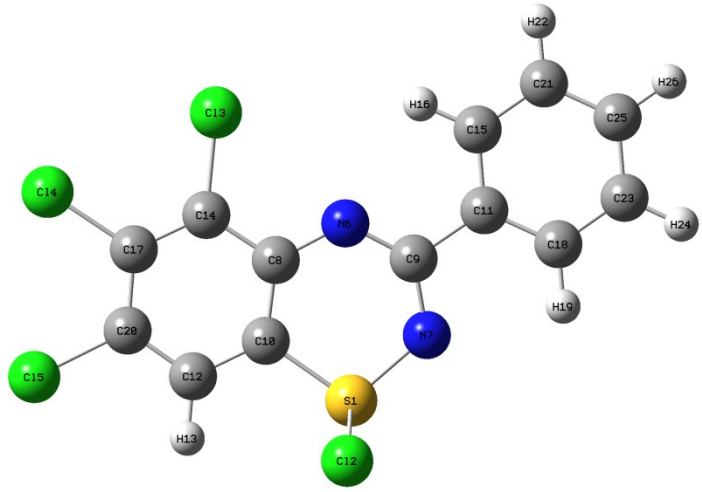


Figure S63 - Exchange pathways for **3e**.

7.4. Cartesian Coordinates for Optimised Geometries

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

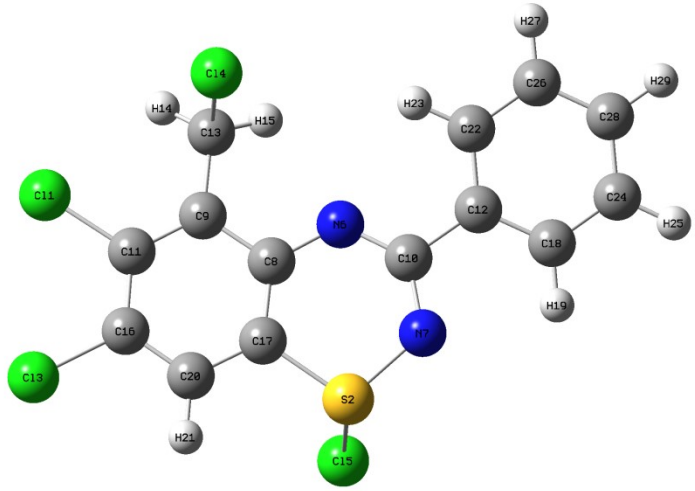
2a:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	1.441607	7.238480	8.519775
2	17	0	1.416780	7.329372	11.064734
3	17	0	6.709794	8.263989	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	7.758081
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	3.988655	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

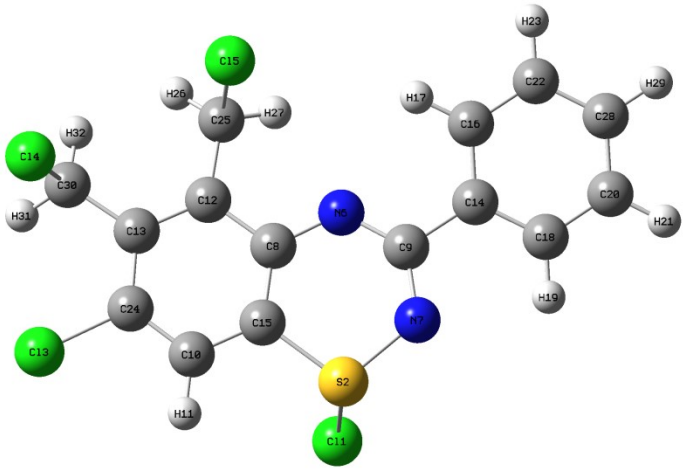
2b:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) 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	6.595202
12	6	0	4.233269	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	6	0	7.907134	4.087977	7.135196
17	6	0	6.927209	2.582035	5.553326
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

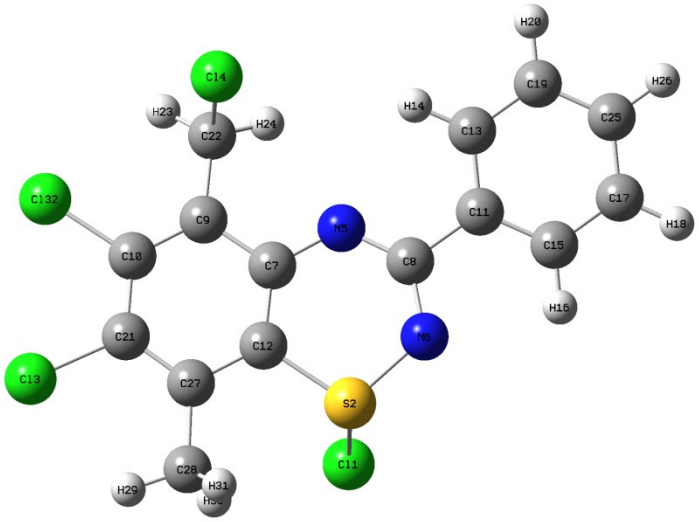
2c:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) 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	3.913668	5.719641	5.616809
7	7	0	2.724870	3.596869	5.611955
8	6	0	4.050203	5.854892	4.265851
9	6	0	3.285649	4.695545	6.208193
10	6	0	3.819463	5.058785	1.943947
11	1	0	3.536403	4.287404	1.238464
12	6	0	4.642346	7.073407	3.772743
13	6	0	4.790342	7.275900	2.392368
14	6	0	3.114313	4.739821	7.676769
15	6	0	3.647986	4.880591	3.320195
16	6	0	3.355379	5.938374	8.374974
17	1	0	3.652443	6.820333	7.821610
18	6	0	2.705260	3.593918	8.386048
19	1	0	2.522557	2.673946	7.845157
20	6	0	2.549139	3.648010	9.772054
21	1	0	2.240821	2.759588	10.312929
22	6	0	3.194627	5.985906	9.760103
23	1	0	3.377090	6.914390	10.290852
24	6	0	4.374605	6.242574	1.504816
25	6	0	5.081542	8.067329	4.795949
26	1	0	5.897419	8.708382	4.478181
27	1	0	5.306821	7.576460	5.736788
28	6	0	2.793055	4.841826	10.462587
29	1	0	2.669862	4.881368	11.540173
30	6	0	5.368493	8.538282	1.833925
31	1	0	5.946722	8.365057	0.930664
32	1	0	5.949032	9.107504	2.551149

Total energy E(UB3LYP) = -2925.75973149 Hartrees

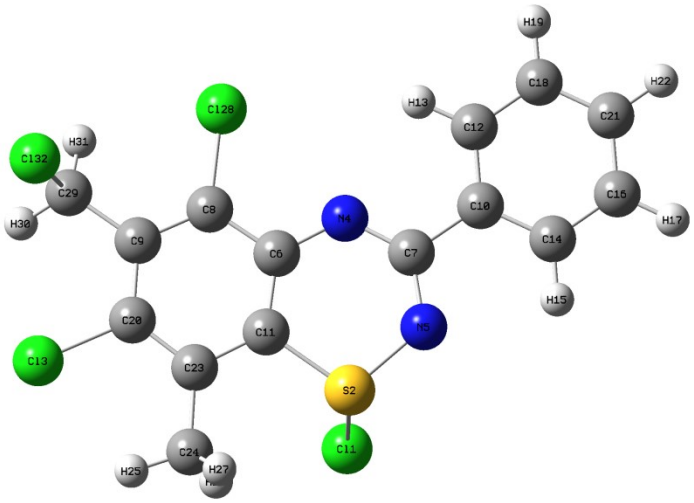
2d:



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	1	0	3.670360	6.811466	7.836461
15	6	0	2.730644	3.581798	8.394010
16	1	0	2.548229	2.663070	7.850921
17	6	0	2.579857	3.631021	9.780768
18	1	0	2.275734	2.740184	10.319986
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

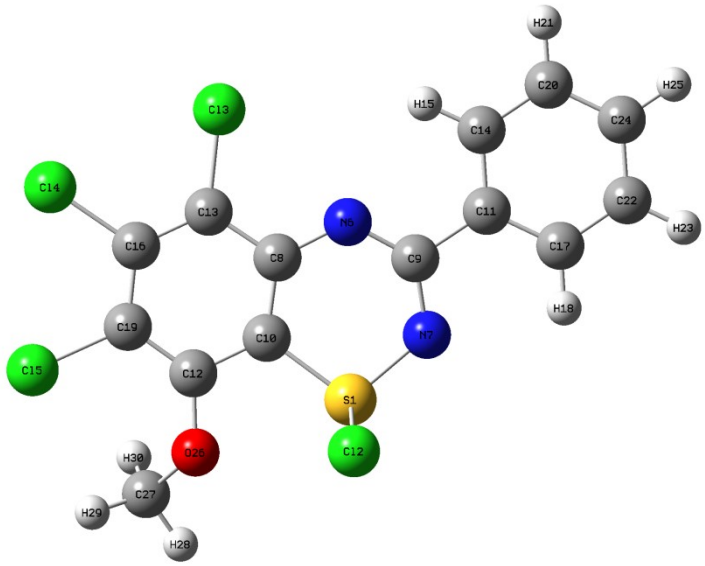
2e:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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

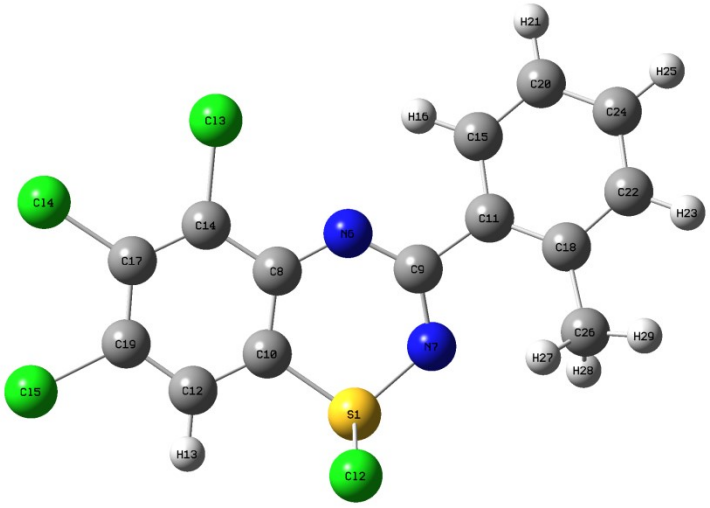
2f:



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	6.769622	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

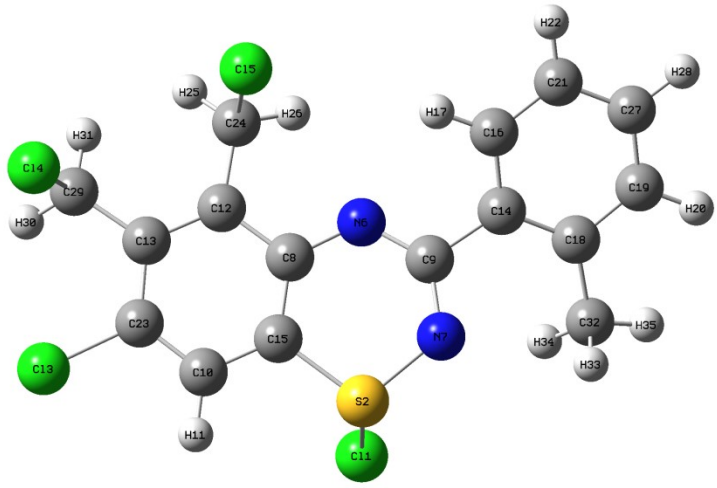
2g:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) 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	8.504754
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	7.606319
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	1	0	1.606985	10.295029	8.407936
14	6	0	5.180708	8.816756	7.896425
15	6	0	5.041296	4.084960	6.815416
16	1	0	5.631208	4.965157	6.593355
17	6	0	5.005957	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	1	0	6.527812	2.698953	6.113207
22	6	0	3.505487	1.861216	7.440452
23	1	0	2.916392	0.987081	7.699561
24	6	0	4.766643	1.692805	6.865869
25	1	0	5.142543	0.693381	6.670882
26	6	0	1.602051	3.197691	8.362143
27	1	0	1.576860	3.897841	9.202502
28	1	0	0.833294	3.533423	7.659620
29	1	0	1.320992	2.207271	8.733362

Total energy E(UB3LYP) = -2886.43218800 Hartrees

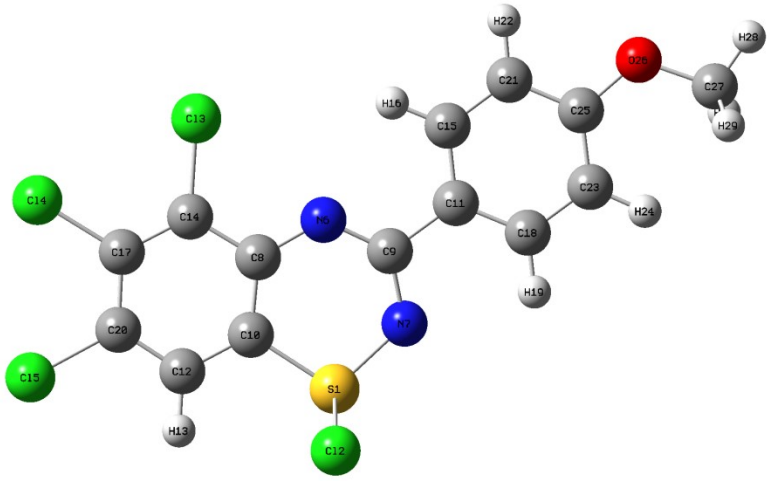
2h:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	4.556548	1.811706	3.475745
2	16	0	2.639022	3.480072	3.786505
3	17	0	4.599391	6.567510	-0.293639
4	17	0	4.319813	9.851085	1.412854
5	17	0	3.873386	9.249849	5.346044
6	7	0	3.840621	5.678658	5.574162
7	7	0	2.414766	3.711331	5.494349
8	6	0	3.978562	5.861785	4.230702
9	6	0	3.113032	4.698947	6.131851
10	6	0	3.684679	5.185740	1.877993
11	1	0	3.330247	4.475736	1.141082
12	6	0	4.683237	7.040203	3.788334
13	6	0	4.863760	7.279160	2.418495
14	6	0	2.971471	4.715322	7.607166
15	6	0	3.484053	4.971568	3.245991
16	6	0	3.000221	5.979717	8.233247
17	1	0	3.116621	6.860776	7.613414
18	6	0	2.826871	3.538439	8.391047
19	6	0	2.710486	3.694912	9.783468
20	1	0	2.614396	2.804131	10.396452
21	6	0	2.870358	6.103153	9.613962
22	1	0	2.882532	7.084902	10.074832
23	6	0	4.358958	6.323896	1.489131
24	6	0	5.192504	7.952778	4.853876
25	1	0	6.054733	8.545604	4.567083
26	1	0	5.370825	7.408136	5.775258
27	6	0	2.723136	4.950937	10.394020
28	1	0	2.623881	5.028272	11.472150
29	6	0	5.566414	8.499626	1.912300
30	1	0	6.129002	8.306730	1.003287
31	1	0	6.197480	8.978417	2.652586
32	6	0	2.825834	2.134377	7.825318
33	1	0	1.876600	1.900353	7.333652
34	1	0	3.607179	1.986880	7.073631
35	1	0	2.984553	1.408731	8.629049

Total energy E(UB3LYP) = -2965.06307593 Hartrees

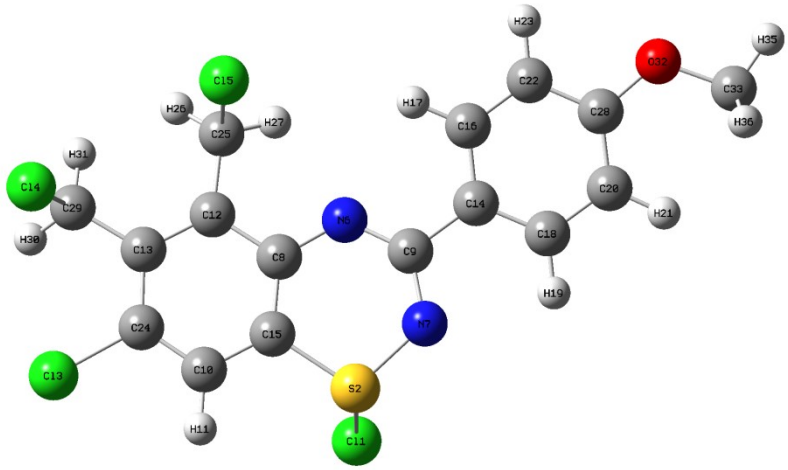
2i:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	1.433747	7.249040	8.360912
2	17	0	1.267296	7.136511	10.905424
3	17	0	6.755540	8.380470	7.354115
4	17	0	6.185928	11.487205	7.972145
5	17	0	3.208361	12.423493	8.802606
6	7	0	4.370066	6.661124	7.616884
7	7	0	2.103836	5.780247	7.755509
8	6	0	4.069576	7.959070	7.881167
9	6	0	3.461218	5.677309	7.565878
10	6	0	2.780404	8.442273	8.229243
11	6	0	3.927211	4.326800	7.218193
12	6	0	2.523575	9.785054	8.521997
13	1	0	1.535986	10.113441	8.821481
14	6	0	5.113123	8.939179	7.805308
15	6	0	5.277893	4.116269	6.860648
16	1	0	5.953041	4.962451	6.848442
17	6	0	4.865432	10.275444	8.074478
18	6	0	3.049145	3.227583	7.237830
19	1	0	2.014847	3.382612	7.518168
20	6	0	3.560842	10.694414	8.436945
21	6	0	5.730354	2.847193	6.534097
22	1	0	6.762407	2.667199	6.258506
23	6	0	3.496847	1.948338	6.910231
24	1	0	2.801658	1.118893	6.937964
25	6	0	4.841764	1.756228	6.556509
26	8	0	5.390865	0.535572	6.215400
27	6	0	4.547534	-0.650667	6.216757
28	1	0	5.206036	-1.465239	5.919585
29	1	0	4.142700	-0.845088	7.216043
30	1	0	3.728113	-0.552649	5.496098

Total energy E(UB3LYP) = -2961.61586995 Hartrees

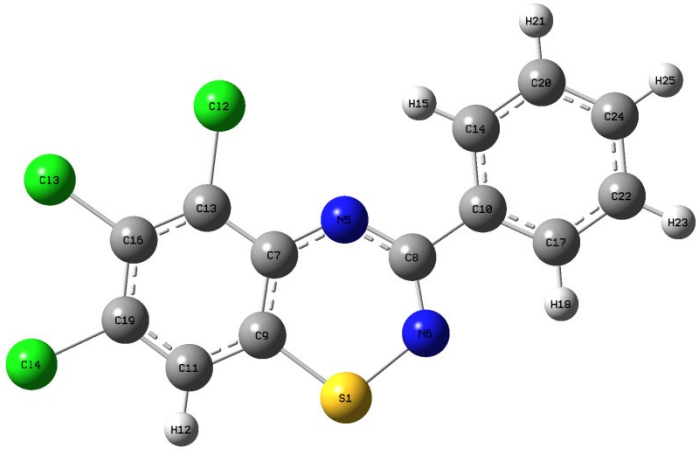
2j:



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	5.255357	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

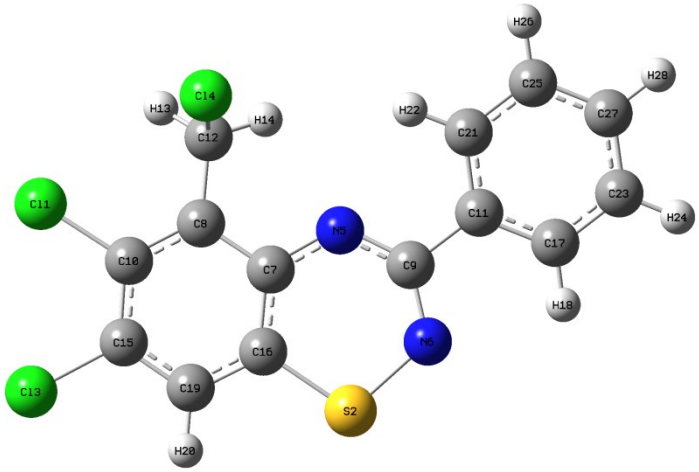
3a:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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	3.285176	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(UB3LYP) = -2386.96710162 Hartrees

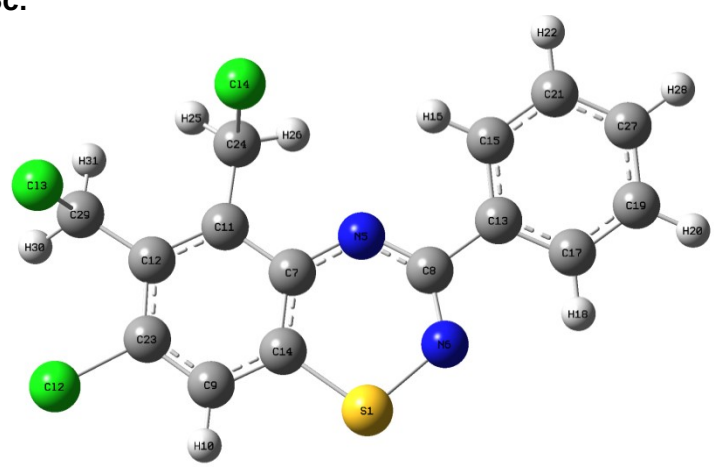
3b:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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	-0.967702

Total energy E(UB3LYP) = -2426.28581316 Hartrees

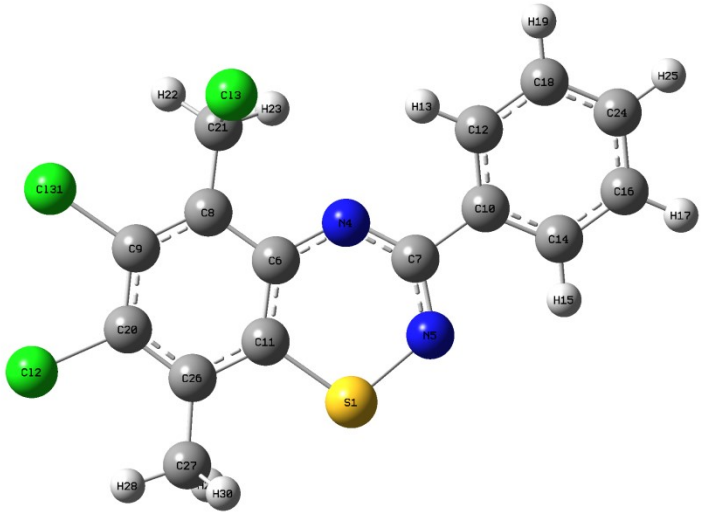
3c:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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	4.513325
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

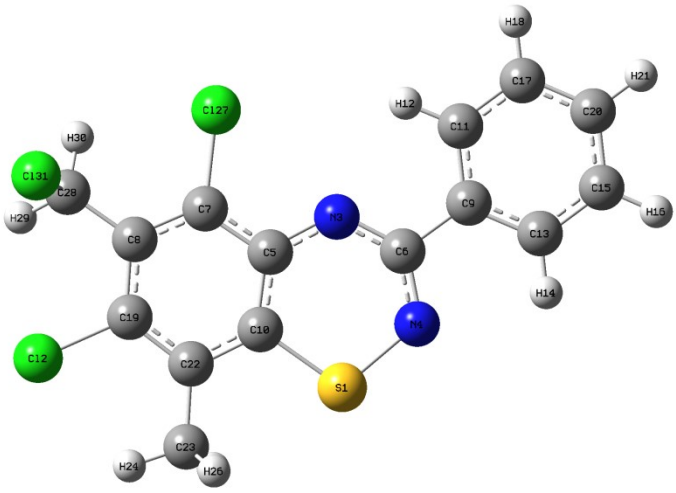
3d:



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	8.811392	1.838511

Total energy E(UB3LYP) = -2465.59426778 Hartrees

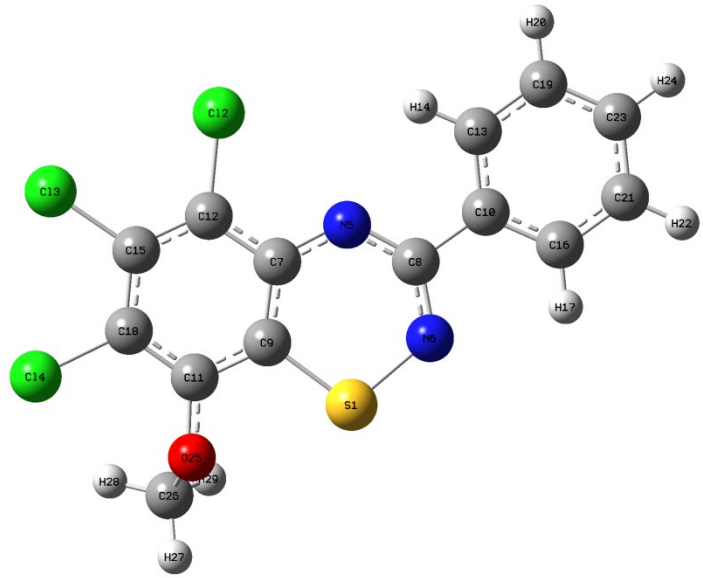
3e:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	2.920541	3.293032	3.885030
2	17	0	4.705361	6.529517	-0.259643
3	7	0	3.777686	5.719224	5.618465
4	7	0	2.823428	3.480270	5.656313
5	6	0	3.965105	5.847553	4.268929
6	6	0	3.255530	4.629468	6.219639
7	6	0	4.524577	7.059658	3.776207
8	6	0	4.761941	7.285607	2.419436
9	6	0	3.131622	4.683813	7.700946
10	6	0	3.645124	4.862167	3.300558
11	6	0	3.541944	5.836817	8.394449
12	1	0	3.943191	6.669834	7.831375
13	6	0	2.606989	3.593886	8.420468
14	1	0	2.291782	2.708344	7.882696
15	6	0	2.496305	3.659303	9.810500
16	1	0	2.090639	2.814380	10.357526
17	6	0	3.428319	5.895960	9.785178
18	1	0	3.746645	6.789660	10.312130
19	6	0	4.411055	6.246682	1.519941
20	6	0	2.906081	4.809344	10.497548
21	1	0	2.818622	4.857870	11.578432
22	6	0	3.854186	5.028441	1.919458
23	6	0	3.476554	3.917644	0.968691
24	1	0	3.695693	4.174832	-0.065654
25	1	0	4.020756	2.996144	1.210616
26	1	0	2.404883	3.693495	1.040201
27	17	0	4.928599	8.342279	4.985341
28	6	0	5.356534	8.566709	1.937231
29	1	0	5.919385	8.450725	1.017165
30	1	0	5.943722	9.065678	2.700426
31	17	0	3.995736	9.836099	1.492646

Total energy E(UB3LYP) = -2465.59278462 Hartrees

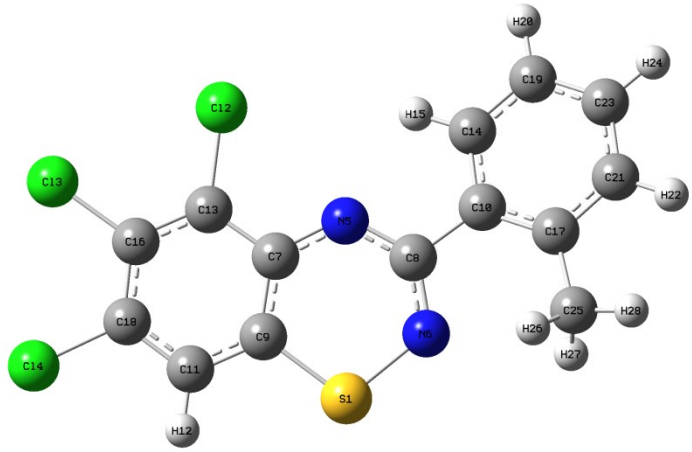
3f:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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	7.776050
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

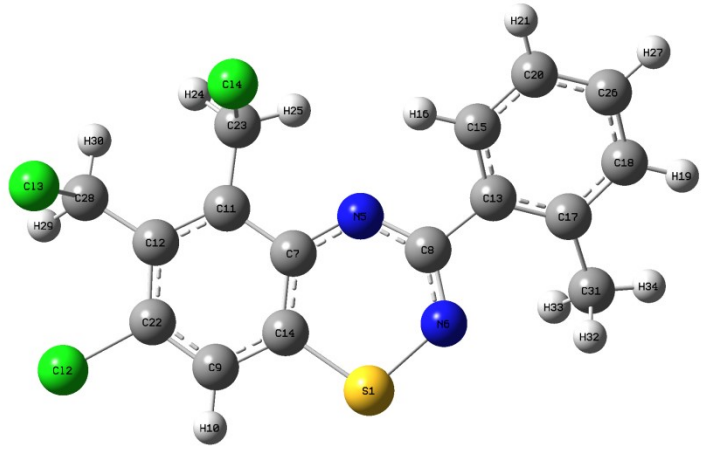
3g:



Center Number	Atomic Number	Atomic 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	7.660365
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

Total energy E(UB3LYP) = -2426.26898651 Hartrees

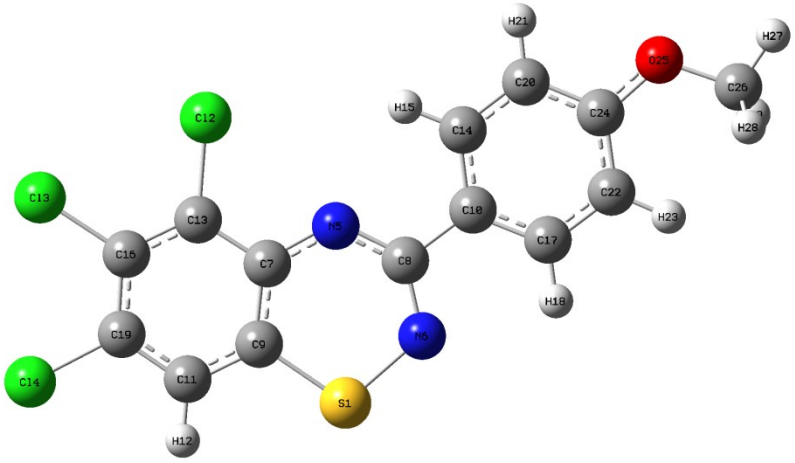
3h:



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	5.333837
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	4.653490	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

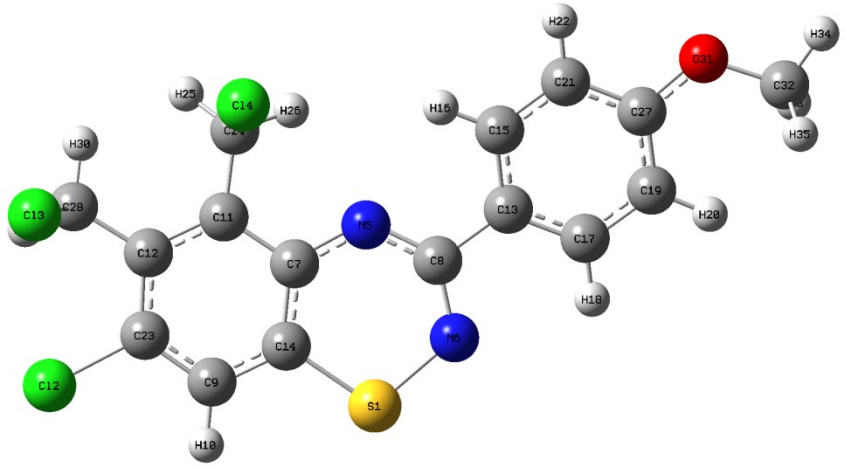
3i:



Center Number	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	6.665038	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	-0.548426	5.466457

Total energy E(UB3LYP) = -2501.45226718 Hartrees

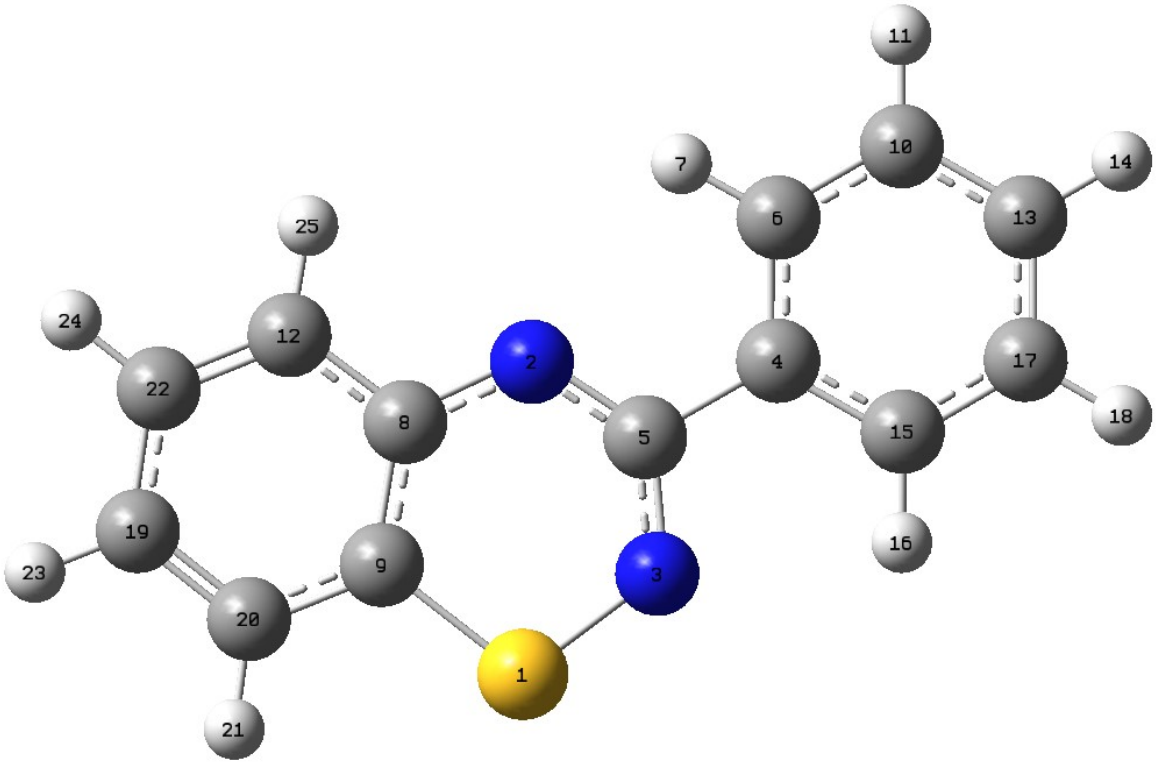
3j:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	2.833199	3.368964	3.827814
2	17	0	4.911921	6.340564	-0.300994
3	17	0	4.316766	9.720496	1.146933
4	17	0	3.631529	9.365722	5.050739
5	7	0	3.744510	5.789184	5.550402
6	7	0	2.629286	3.619794	5.582458
7	6	0	3.990499	5.884624	4.204133
8	6	0	3.103119	4.758068	6.144072
9	6	0	3.924323	5.045220	1.899536
10	1	0	3.657107	4.279699	1.181098
11	6	0	4.650746	7.073212	3.737386
12	6	0	4.927805	7.243477	2.365182
13	6	0	2.878383	4.861442	7.604679
14	6	0	3.644905	4.890498	3.255734
15	6	0	3.155344	6.065965	8.285134
16	1	0	3.522293	6.914571	7.722686
17	6	0	2.378708	3.771365	8.338035
18	1	0	2.159298	2.845282	7.821309
19	6	0	2.166081	3.867274	9.714020
20	1	0	1.784733	3.009343	10.253451
21	6	0	2.943635	6.171764	9.653296
22	1	0	3.145129	7.092804	10.186961
23	6	0	4.557774	6.204537	1.479501
24	6	0	5.027377	8.084746	4.767173
25	1	0	5.890275	8.690237	4.508584
26	1	0	5.144620	7.617899	5.739052
27	6	0	2.450410	5.071724	10.375056
28	6	0	5.590878	8.473098	1.834219
29	1	0	6.233049	8.263813	0.983364
30	1	0	6.130334	9.039161	2.585494
31	8	0	2.277219	5.277301	11.733855
32	6	0	1.755505	4.194937	12.551935
33	1	0	2.423756	3.326413	12.532942
34	1	0	1.706914	4.600738	13.561378
35	1	0	0.753386	3.897483	12.222711

Total energy E(UB3LYP) = -2580.08115172 Hartrees

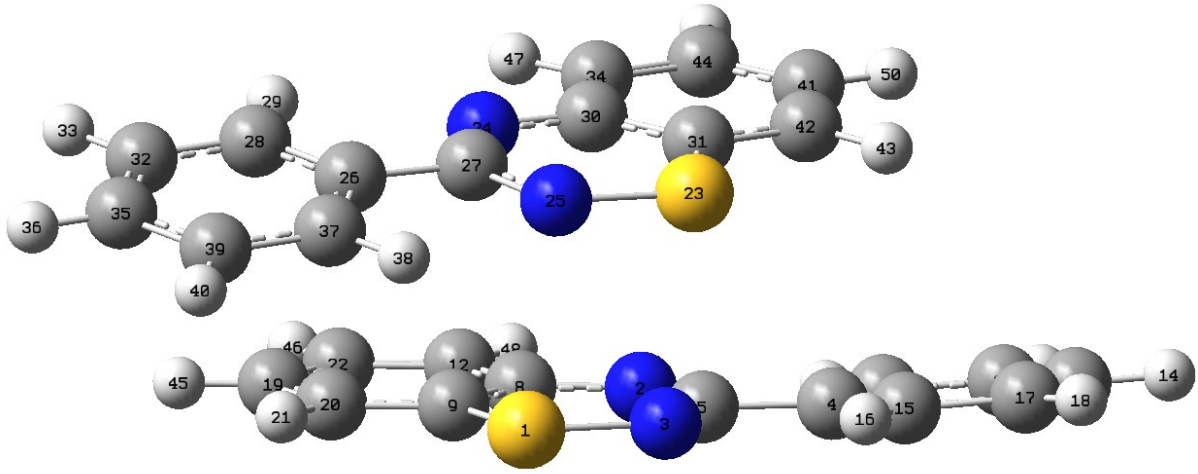
The following geometries were used for the dimerization energy calculations.
Parent 1,2,4-benzothiadiazinyl monomer:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) 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:

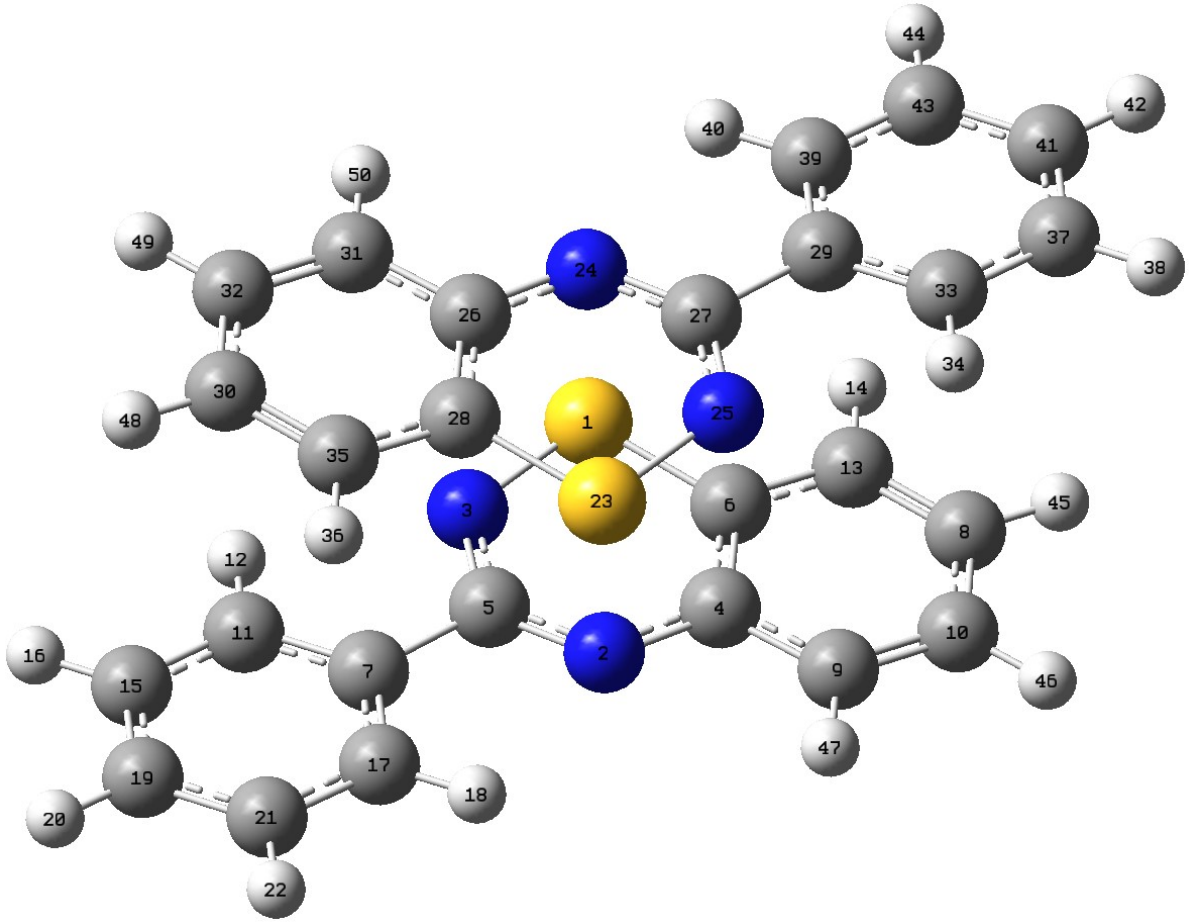


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	7.168933	4.832242	8.658536
2	7	0	9.001882	7.191306	8.046684
3	7	0	8.765684	4.815940	8.333171
4	6	0	10.889698	5.750751	7.770406
5	6	0	9.436806	5.955267	8.046495
6	6	0	11.691212	6.841088	7.424404
7	1	0	11.228822	7.814711	7.326451
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	7.241140
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	4.490080	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	9.602297	4.832249	10.915812
24	7	0	7.769340	7.191313	11.527668
25	7	0	8.005509	4.815962	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	11.395563
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(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
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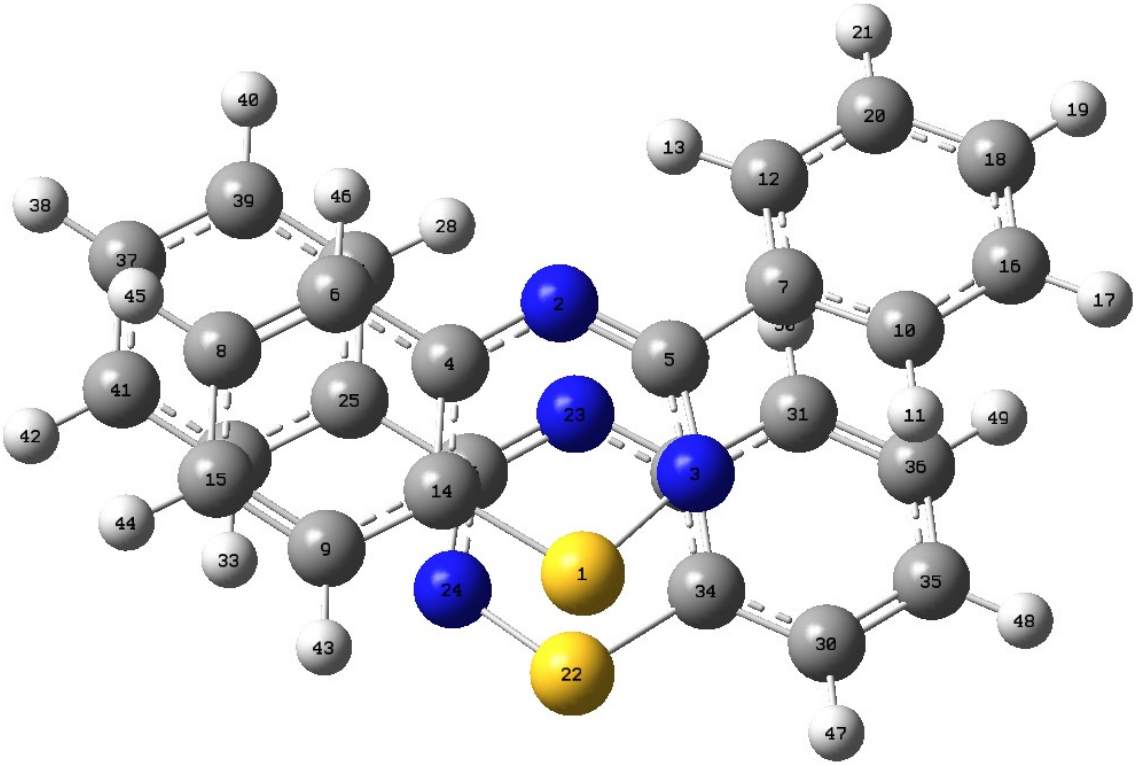
3	7	0	1.909073	3.097955	7.493228
4	6	0	4.050696	1.964843	9.019652
5	6	0	2.001448	3.083636	8.813837
6	6	0	4.244149	1.799469	7.630781
7	6	0	0.847357	3.697654	9.533057
8	6	0	6.206963	0.465109	7.994427
9	6	0	5.004712	1.379524	9.881130
10	6	0	6.058616	0.648613	9.379679
11	6	0	-0.260408	4.168868	8.825454
12	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	4.668702	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	6.766058	10.373839
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**:

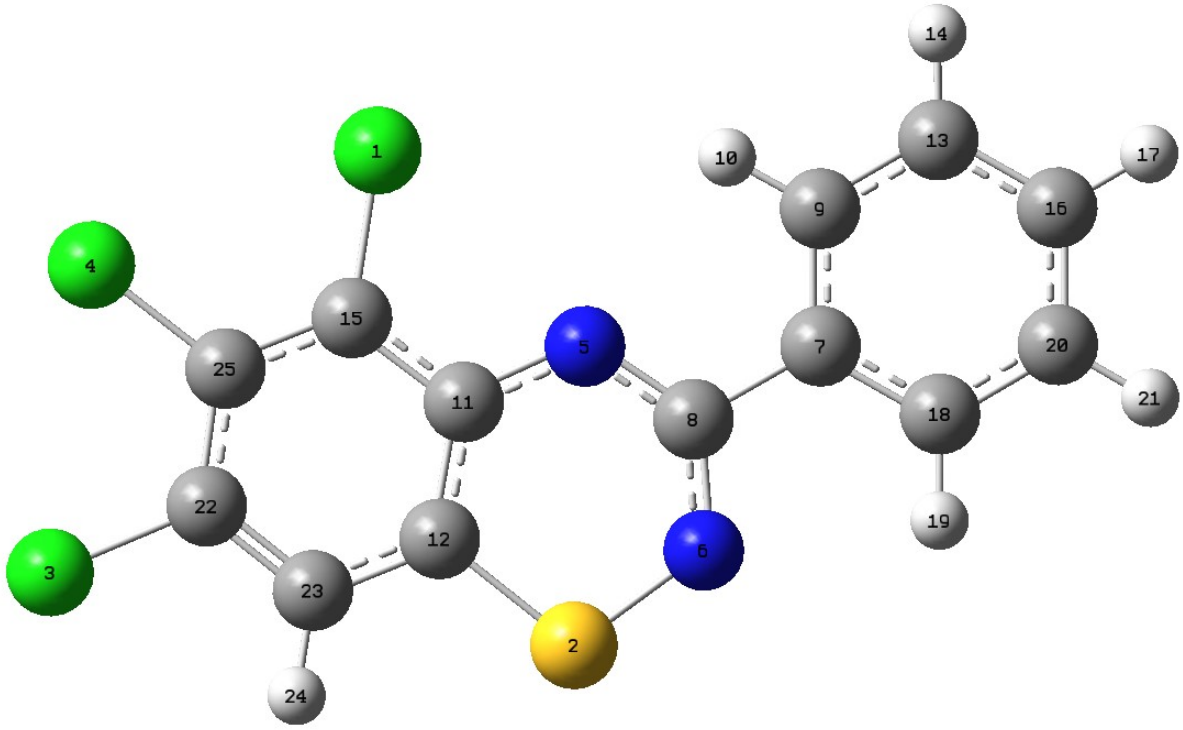


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	5.388993	0.054993	5.481318
2	7	0	2.758128	1.242187	6.424909
3	7	0	4.746002	0.005116	6.970849
4	6	0	2.998937	1.255579	5.079961
5	6	0	3.603089	0.651625	7.249555
6	6	0	1.989695	1.755116	4.225528
7	6	0	3.260230	0.688174	8.700222
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	9.145591
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

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

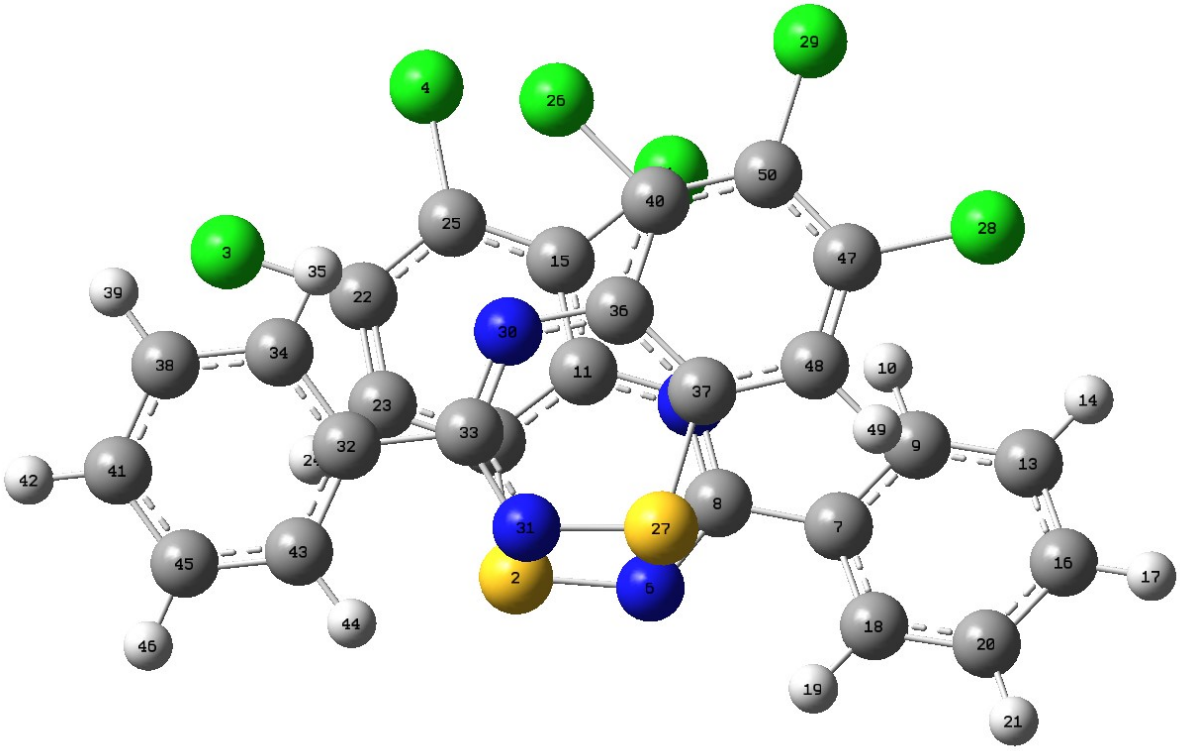
3a optimised for dimerization calculation:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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	3.253168	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	6.788619	12.120559

35	1	0	5.467990	7.774760	12.200799
36	6	0	8.995711	7.506755	11.235961
37	6	0	10.007231	6.572080	10.944466
38	6	0	3.663715	6.597239	12.300987
39	1	0	3.030227	7.443069	12.539402
40	6	0	9.354043	8.876733	11.200559
41	6	0	3.110426	5.326319	12.160684
42	1	0	2.044836	5.180823	12.293729
43	6	0	5.295356	4.428562	11.677299
44	1	0	5.940851	3.593013	11.437958
45	6	0	3.928027	4.243765	11.850760
46	1	0	3.501774	3.253180	11.746376
47	6	0	11.630646	8.300110	10.625116
48	6	0	11.312868	6.957629	10.650717
49	1	0	12.073420	6.221202	10.415231
50	6	0	10.649591	9.273372	10.888642

Total energy E(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.

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