**ELECTRONIC SUPPORTING INFORMATION**

# End-Group Functionalization of a Conjugated Azomethine with Ureas for Property Tailoring

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Table S1. Summary of X-ray crystallographic data.

| | |
|---|---|
| Chemical formula | $2(C_{40}H_{38}N_6O_{10}S_3)\cdot 2(C_3H_6O)\cdot 0.25(H_2O)$ |
| $M_r$ | 1838.54 |
| Crystal system, space group | Monoclinic, $P2_1/n$ |
| Temperature (K) | 105 |
| $a$, $b$, $c$ (Å) | 15.7977 (7), 19.3045 (9), 29.3563 (14) |
| β (°) | 103.172 (3) |
| $V$ (Å$^3$) | 8717.1 (7) |
| $Z$ | 4 |
| Radiation type | Ga $K\alpha$, λ = 1.34139 Å |
| μ (mm$^{-1}$) | 1.38 |
| Crystal size (mm) | 0.2 × 0.06 × 0.04 |
| $R_{int}$ | 0.104 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.651 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.070, 0.219, 1.02 |
| No. of reflections | 19903 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.70, −0.52 |
| $T_{min}$, $T_{max}$ | 0.550, 0.752 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 126439, 19903, 11126 |
| No. of parameters | 1159 |
| No. of restraints | 154 |
| H-atom treatment | H-atom parameters constrained |
| CCDC # | 1858237 |

Computer programs: *APEX* 2 (2013) Bruker AXS Inc., Madison, WI 53719-1173., *SAINT* (2013) V8.34A; Integration Software for Single Crystal Data. Bruker AXS Inc., ShelXT (Sheldrick, 2015), XL (Sheldrick, 2008), Olex2 (Dolomanov *et al.*, 2009).

Table S2. Selected donor•••acceptor hydrogen bond distances and angles of **1b** derived from the X-ray crystallographic structure.

| **Hydrogen bond interaction** | ***D*—H···*A*** | ***D*—H** | **H···*A*** | ***D*···*A*** | ***D*—H···*A*** |
|---|---|---|---|---|---|
| Intermolecular | $N_{16}$—$H_{16}$···$O_{14}^{ii}$ | 0.88 | 2.46 | 3.207 (4) | 143.7 |
| | $N_{23}$—$H_{23}$···$O_{110}^{i}$ | 0.88 | 2.37 | 3.132 (4) | 144.5 |
| | $N_{26}$—$H_{26}$···$O_{25}^{ii}$ | 0.88 | 2.44 | 3.118 (4) | 134.2 |
| | $N_{26}$—$H_{26}$···$O_{29}^{iii}$ | 0.88 | 2.22 | 2.917 (4) | 135.3 |
| Intramolecular | $N_{12}$—$H_{12}$···$O_{12}$ | 0.88 | 2.15 | 2.771 (3) | 127.2 |
| | $N_{15}$—$H_{15}$···$O_{17}$ | 0.88 | 2.07 | 2.718 (4) | 129.3 |
| | $N_{15}$—$H_{15}$···$O_{1}$ | 0.88 | 2.17 | 2.937 (12) | 145.0 |
| | $N_{16}$—$H_{16}$···$O_{1}$ | 0.88 | 2.00 | 2.811 (11) | 152.7 |
| | $N_{22}$—$H_{22}$···$O_{22}$ | 0.88 | 2.07 | 2.710 (4) | 128.7 |
| | $N_{25}$—$H_{25}$···$O_{27}$ | 0.88 | 2.12 | 2.755 (4) | 128.9 |
| With solvent | $N_{13}$—$H_{13}$···$O_{41}^{i}$ | 0.88 | 1.96 | 2.837 (4) | 172.1 |
| | $O_{1}$—$H_{1A}$···$O_{14}^{ii}$ | 0.87 | 1.55 | 2.350 (11) | 152.2 |
| | $O_{1}$—$H_{1B}$···$O_{17}$ | 0.87 | 2.19 | 2.701 (12) | 117.1 |

Symmetry codes: (i) $x-1, y, z$; (ii) $x+1, y, z$; (iii) $-x, -y+1, -z$.

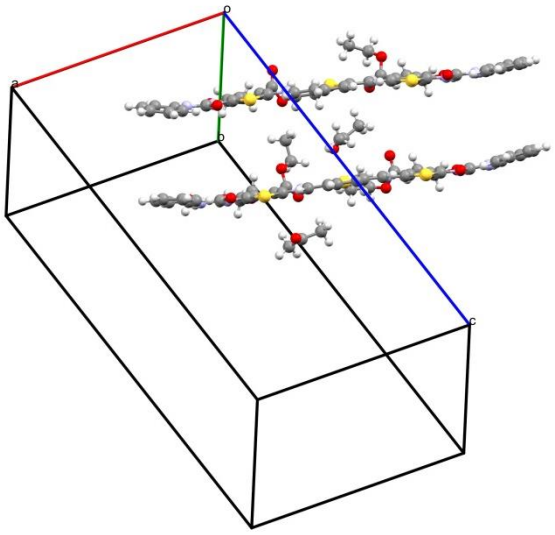


Figure S1. Resolved X-ray crystal structure of **1b** shown with the unit cell along with the cocrystalized solvent molecules.

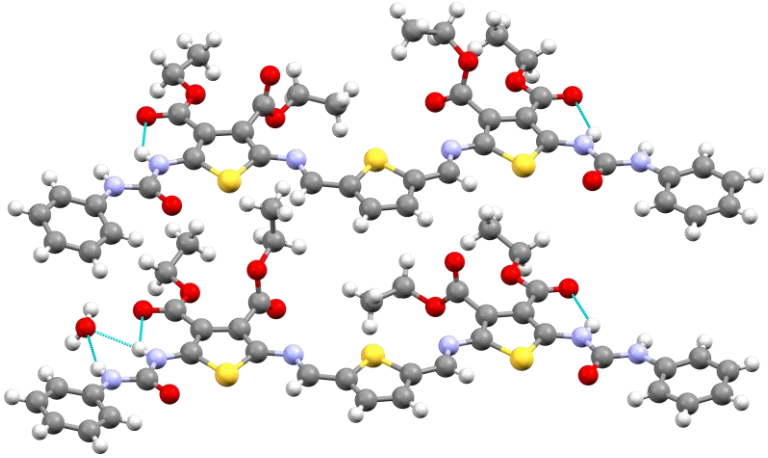


Figure S2. Intramolecular hydrogen bonds, shown as blue lines, of the two molecules of **1b** resolved by X-ray crystallography. The intermolecular hydrogen bonds between **1b** and the cocrystallized water molecule are also shown.

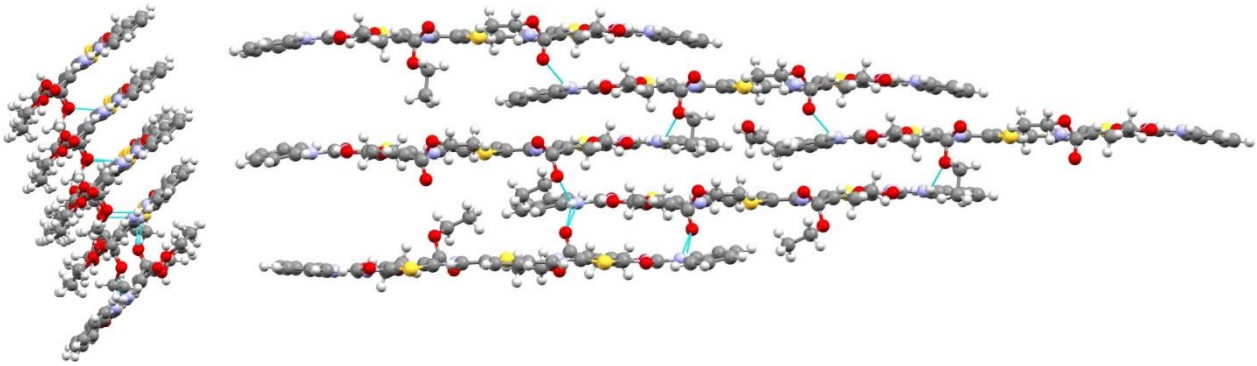


Figure S3. X-ray crystal structure of **1b** shown along the side-on (left) and edge-on (right) views with intermolecular hydrogen bonding illustrated by the blue dotted lines.

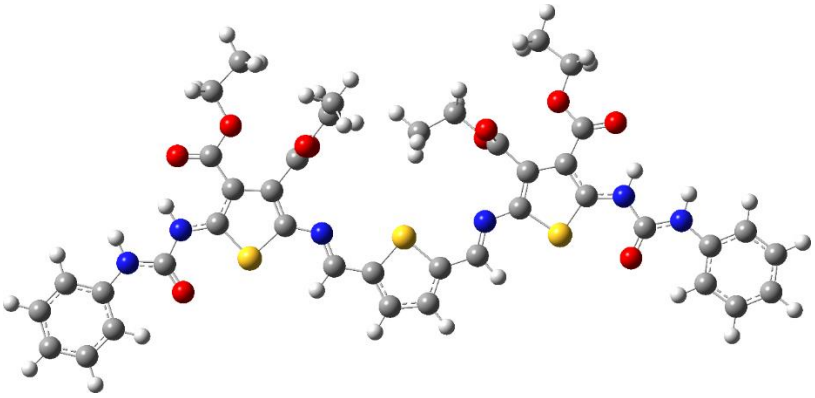


Figure S4. Optimized geometry of **1b** calculated by DFT-ωB97X-D with the 6-31G(d) basis set.

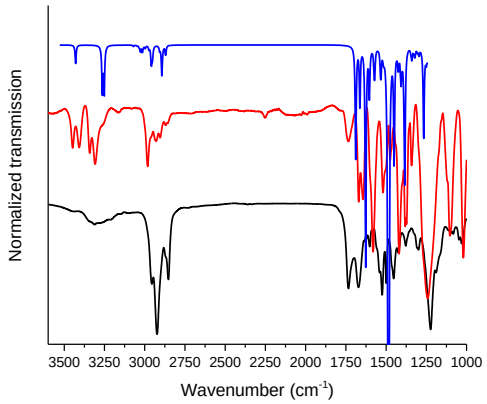



Figure S5. Normalized complete ATR FT-IR spectra of **1b** (black) and **4** (red) as a thin film drop-cast on the ATR crystal. Theoretically calculated IR spectrum by DFT-ωB97X-D (blue) corrected with a basis set dependent scaling factor.

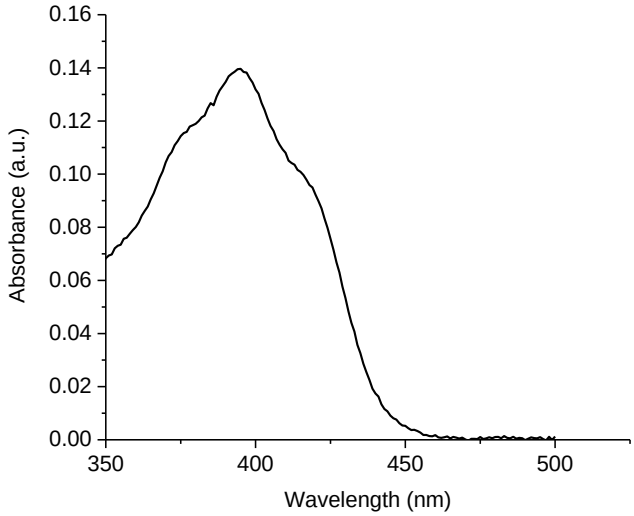


Figure S6. Absorption spectrum of **2** measured in anhydrous dichloromethane.

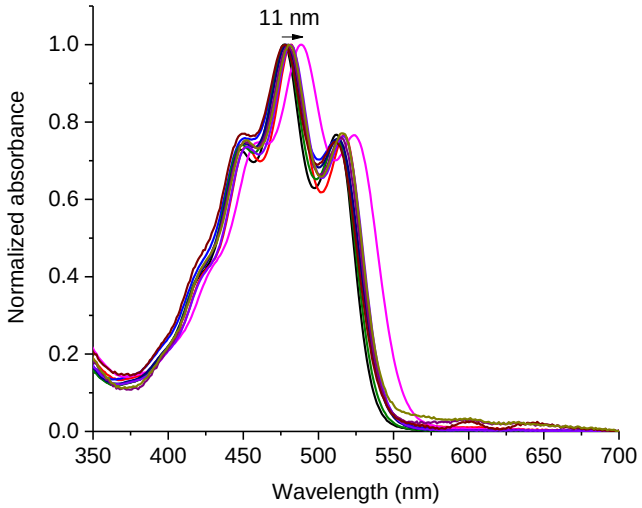



Figure S7. Normalized absorption spectra of **1b** measured in different solvents: ether (—), toluene (—), acetonitrile (—), DMSO (—), ethyl acetate (—), acetone (—), THF (—), EtOH (—), MeOH (—), and *i*-PrOH (—).

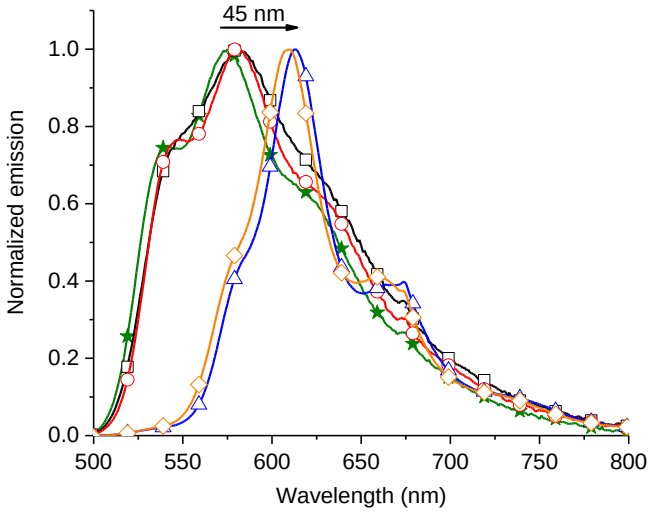



Figure S8. Normalized emission spectra of **1b** measured in ethyl acetate (★), acetone (□), THF (○), ethanol (△), and *i*-propanol (◊).

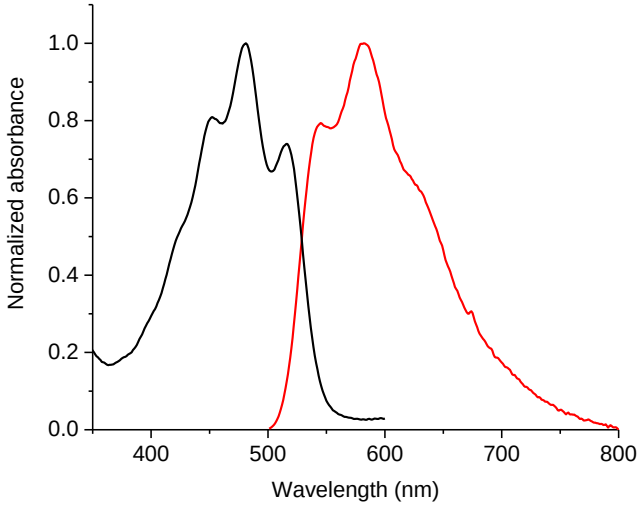



Figure S9. Normalized absorption (—) and emission (—) spectra of **1b** measured in anhydrous dichloromethane.

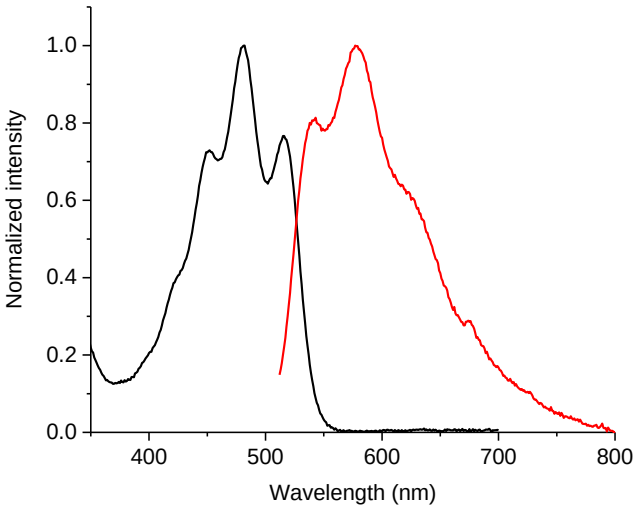



Figure S10. Normalized absorption (—) and emission (—) spectra of **1b** measured in 2-methyl-THF.

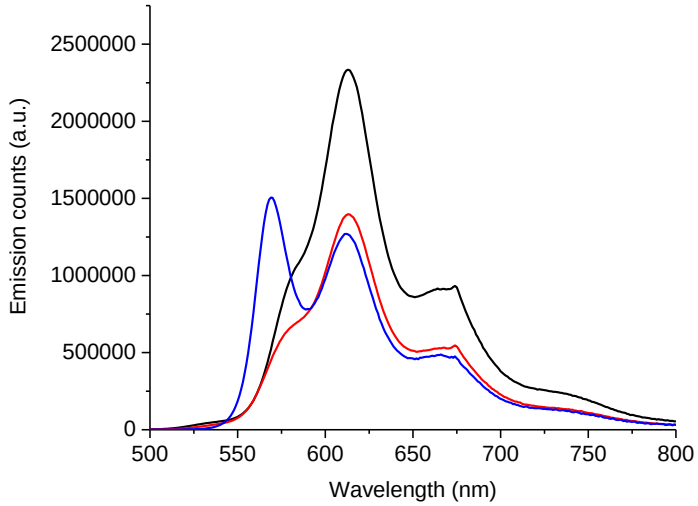



Figure S11. Emission spectra of **1b** measured in ethanol (—) and THF with 70% (—) and 80% (—) volume water added.

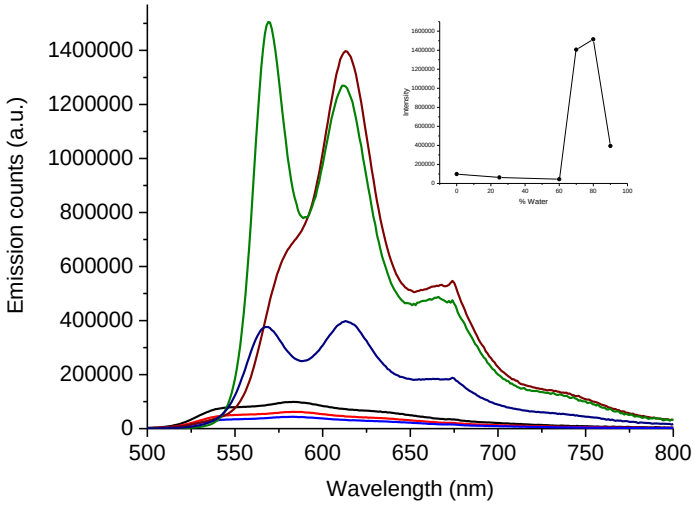



Figure S12. Emission spectra of **1b** measured in THF with different ratios of water: 0 (—), 25 (—), 60 (—), 70 (—), 80 (—) and 90 (—) % volume of water. Inset: change in fluorescence intensity with water volume % added to THF.

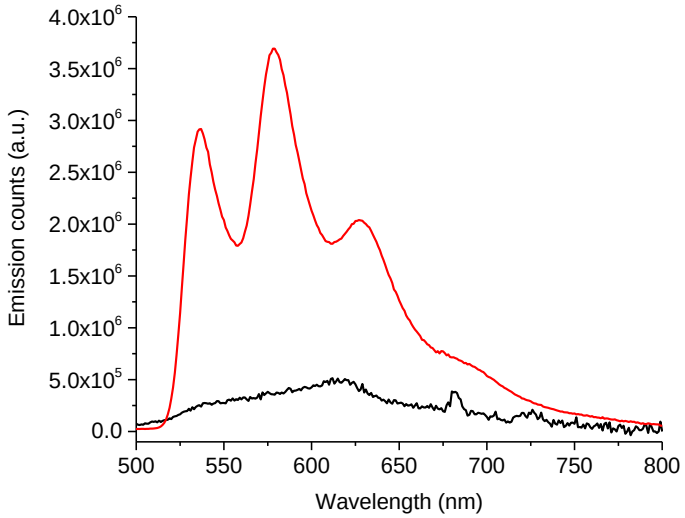



Figure S13. Emission spectra of **1b** in 1:9 ethanol/methanol at 298 K (—) magnified 100 times and 77 (—) K.

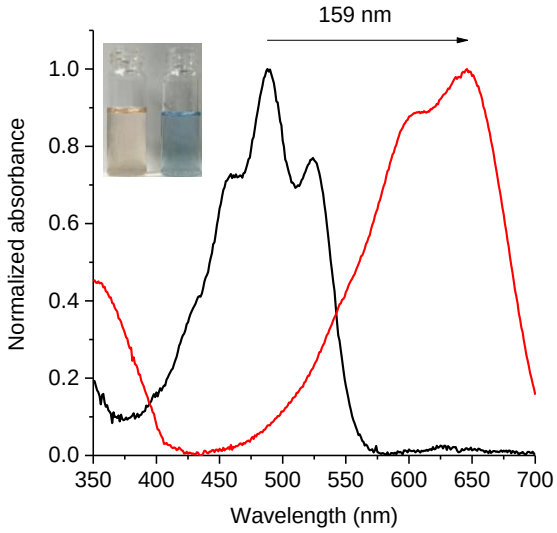



Figure S14. Normalized absorption spectra of **1b** measured in DMSO without (black) and with $PO_3^{4-}$ (red). Inset: photograph of vials of **1b** in DMSO without (left) and with $PO_3^{4-}$ (right).

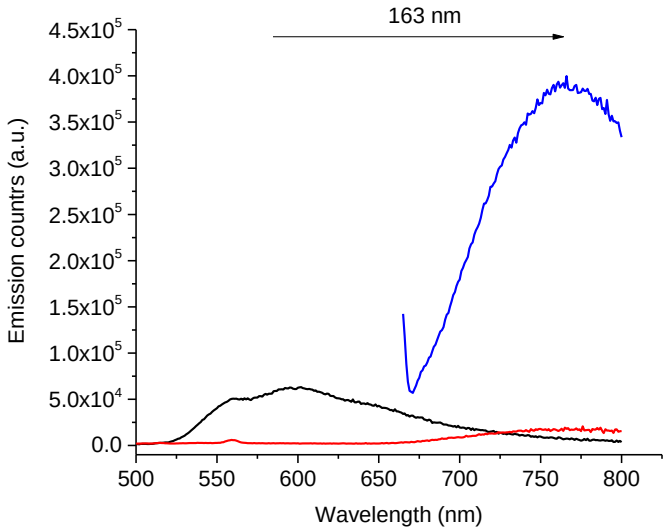



Figure S15. Emission spectra of **1b** measured in DMSO (black) excited at 480 nm, $PO_3^{4-}$ added exciting at 480 nm (red), and exciting at 650 nm (blue).

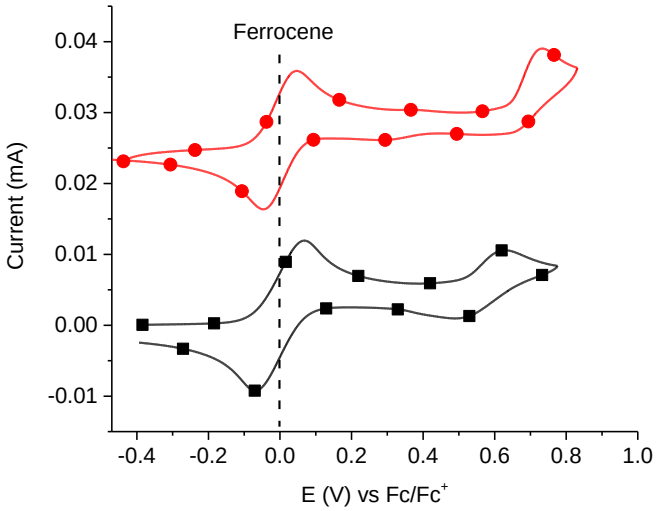



Figure S16. Anodic cyclic voltammograms of **1b** (■) and **2** (●) measured in anhydrous dichloromethane with $TBAPF_6$ as an electrolyte with ferrocene as an internal reference at 100 mV/sec.

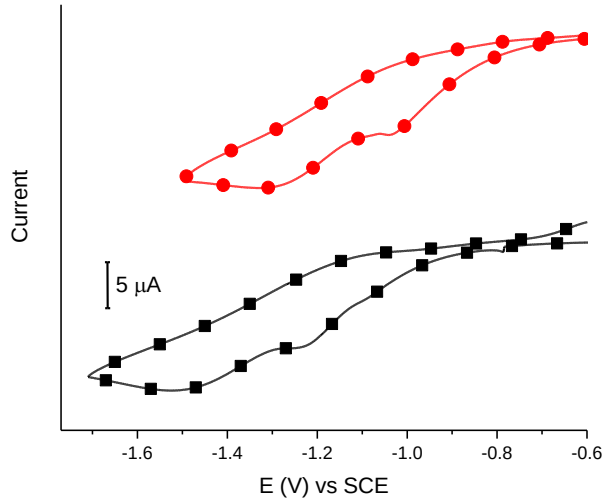



Figure S17. Uncorrected cathodic cyclic voltammogram of **1b** (■) and **2** (●) measured in anhydrous dichloromethane with $TBAPF_6$ as an electrolyte at 100 mV/sec.

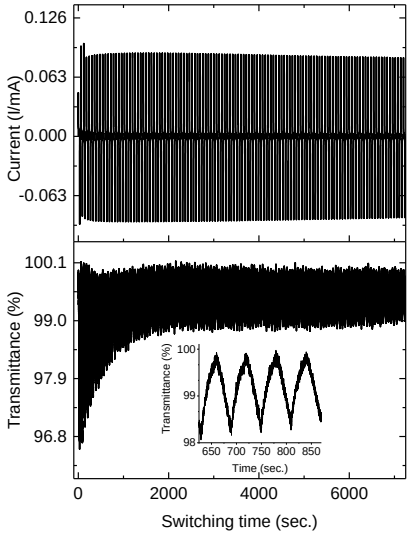



Figure S18. Change in current (top) and transmittance % at 254 nm (bottom) of **1b** with switching of applied potential measured in 0.1 M $TBAFP_6$ in dichloromethane between 0 and 1.1 V at 30 second intervals. Inset: zoom of lower panel between 645 and 860 sec.

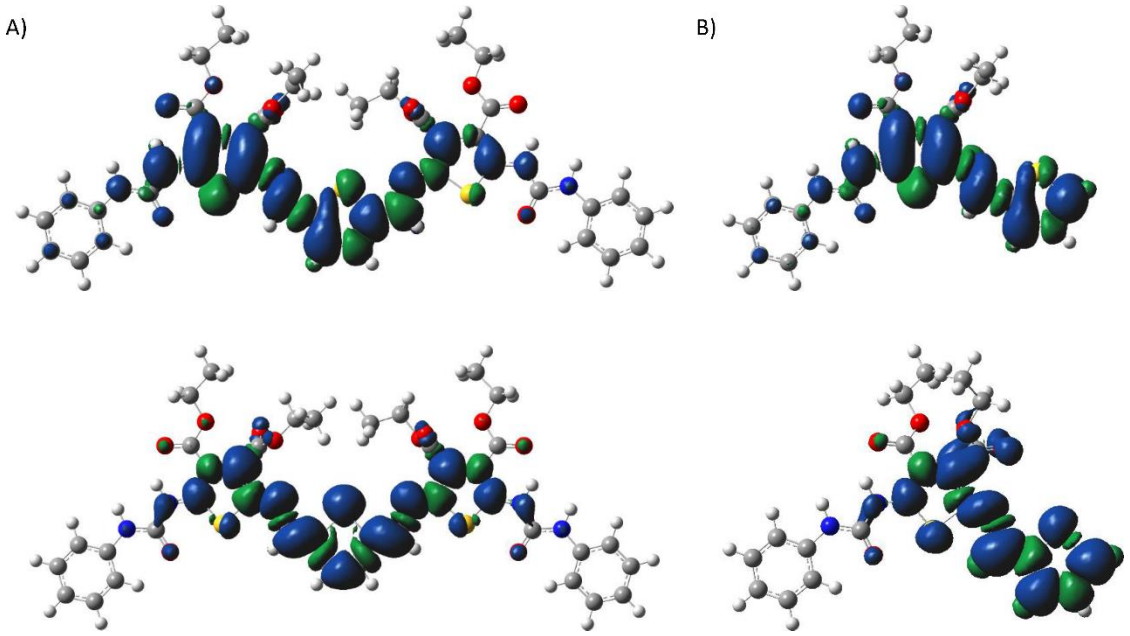


Figure S19. Spin density of the radical cation (top) and the radical anion (bottom) of **1b** (A) and **2** (B).

Table S3. Atomic coordinates of the neutral singlet of **1b** calculated by DFT-ωb97X-D with the 6-31+g(d,p) basis set.

| Atom | x | y | z |
|---|---|---|---|
| S | 0.03999 | -1.14461 | 0.03084 |
| S | 5.7588 | -1.46931 | 0.07984 |
| S | -5.67429 | -1.50148 | -0.06332 |
| O | 8.29999 | -2.49973 | 0.10225 |
| O | 8.09597 | 2.48494 | -0.10877 |
| O | 6.04992 | 3.40944 | -0.25776 |
| O | 3.32729 | 2.54266 | 1.02462 |
| O | 3.27414 | 2.29663 | -1.21681 |
| O | -8.20259 | -2.56199 | -0.08132 |
| O | -8.05773 | 2.42584 | -0.11714 |
| O | -6.0264 | 3.38761 | -0.01847 |
| O | -3.20763 | 2.45401 | -1.14211 |
| O | -3.34469 | 2.42217 | 1.10435 |
| N | 3.04251 | -0.7773 | 0.0497 |
| N | 8.1986 | -0.22489 | 0.02274 |
| H | 8.66935 | 0.68094 | -0.01106 |
| N | 10.24505 | -1.26572 | 0.05037 |
| H | 10.59578 | -0.31907 | 0.0181 |
| N | -2.96692 | -0.78339 | -0.01943 |

| | | | |
|---|---|---|---|
| N | -8.12749 | -0.28489 | -0.10883 |
| H | -8.60866 | 0.61589 | -0.12685 |
| N | -10.16169 | -1.34964 | -0.11507 |
| H | -10.52331 | -0.40658 | -0.12657 |
| C | -1.19422 | -2.36197 | 0.05645 |
| C | -0.66692 | -3.63354 | 0.11093 |
| H | -1.27941 | -4.52722 | 0.13408 |
| C | 0.74782 | -3.63264 | 0.13242 |
| H | 1.36047 | -4.52558 | 0.17332 |
| C | 1.27476 | -2.3604 | 0.09362 |
| C | 2.6778 | -2.00573 | 0.09318 |
| H | 3.38258 | -2.84476 | 0.12744 |
| C | 4.36071 | -0.38538 | 0.03394 |
| C | 4.74103 | 0.92319 | -0.01925 |
| C | 6.16134 | 1.10139 | -0.03224 |
| C | 6.83388 | -0.11209 | 0.02229 |
| C | 8.89006 | -1.4264 | 0.06186 |
| C | 11.24025 | -2.26563 | 0.07945 |
| C | 10.96471 | -3.63642 | 0.11774 |
| H | 9.94148 | -3.98301 | 0.1276 |
| C | 12.02181 | -4.54558 | 0.14318 |
| H | 11.79661 | -5.60713 | 0.17278 |
| C | 13.3455 | -4.11508 | 0.13111 |
| H | 14.15828 | -4.83341 | 0.15126 |
| C | 13.61303 | -2.74684 | 0.09285 |
| H | 14.63745 | -2.38856 | 0.08284 |
| C | 12.57118 | -1.82786 | 0.06713 |
| H | 12.79145 | -0.7642 | 0.03729 |
| C | 6.87213 | 2.37509 | -0.13012 |
| C | 6.62806 | 4.72708 | -0.36513 |
| H | 7.30507 | 4.74038 | -1.22294 |
| H | 7.20713 | 4.92573 | 0.54032 |
| C | 5.48114 | 5.69859 | -0.53089 |
| H | 4.8076 | 5.65537 | 0.3289 |
| H | 4.91131 | 5.4761 | -1.43702 |
| H | 5.8756 | 6.71492 | -0.61156 |
| C | 3.71531 | 2.0142 | 0.00456 |
| C | 2.23222 | 3.29298 | -1.33142 |
| H | 2.33583 | 3.66852 | -2.34986 |
| H | 2.43996 | 4.09972 | -0.62516 |
| C | 0.86627 | 2.6766 | -1.09993 |

| | | | |
|---|---|---|---|
| H | 0.09376 | 3.43518 | -1.25636 |
| H | 0.77783 | 2.29428 | -0.07993 |
| H | 0.68661 | 1.85561 | -1.79858 |
| C | -2.59749 | -2.01068 | 0.0217 |
| H | -3.29954 | -2.85265 | 0.03409 |
| C | -4.28802 | -0.40129 | -0.05087 |
| C | -4.68266 | 0.90391 | -0.07027 |
| C | -6.10544 | 1.06637 | -0.08745 |
| C | -6.76438 | -0.15583 | -0.09034 |
| C | -8.80499 | -1.49495 | -0.10028 |
| C | -11.14519 | -2.36148 | -0.11175 |
| C | -10.85332 | -3.7294 | -0.10455 |
| H | -9.82599 | -4.06382 | -0.10029 |
| C | -11.89948 | -4.65145 | -0.10258 |
| H | -11.66165 | -5.71064 | -0.09696 |
| C | -13.22819 | -4.23658 | -0.10784 |
| H | -14.03235 | -4.96482 | -0.10625 |
| C | -13.51201 | -2.8711 | -0.11523 |
| H | -14.54063 | -2.52494 | -0.11946 |
| C | -12.48121 | -1.93936 | -0.11711 |
| H | -12.71411 | -0.87794 | -0.12277 |
| C | -6.83272 | 2.33436 | -0.08006 |
| C | -6.62811 | 4.69907 | 0.00886 |
| H | -7.33961 | 4.73804 | 0.83727 |
| H | -7.17266 | 4.84863 | -0.92698 |
| C | -5.50525 | 5.69744 | 0.17799 |
| H | -4.97583 | 5.53019 | 1.12001 |
| H | -5.9186 | 6.70933 | 0.19044 |
| H | -4.79204 | 5.62526 | -0.6473 |
| C | -3.67487 | 2.01112 | -0.11448 |
| C | -2.38462 | 3.49795 | 1.18601 |
| H | -2.74792 | 4.33109 | 0.57827 |
| H | -1.43957 | 3.14744 | 0.76378 |
| C | -2.24805 | 3.8757 | 2.64313 |
| H | -1.52258 | 4.68804 | 2.7389 |
| H | -1.8954 | 3.0275 | 3.23538 |
| H | -3.20426 | 4.21655 | 3.04948 |

Table S4. Atomic coordinates of the radical cation of **1b** calculated by DFT-ωb97X-D with the 6-31+g(d,p) basis set.

| atom | x | y | z |
|---|---|---|---|
| S | 0.04116 | -1.25187 | 0.08038 |
| S | 5.72786 | -1.50818 | 0.07256 |
| S | -5.63745 | -1.54661 | -0.00475 |
| O | 8.28645 | -2.43504 | 0.10328 |
| O | 7.90277 | 2.5327 | -0.1999 |
| O | 5.82151 | 3.38264 | -0.30378 |
| O | 3.10016 | 2.38537 | 0.9544 |
| O | 3.14721 | 2.18192 | -1.29327 |
| O | -8.13911 | -2.50115 | -0.07162 |
| O | -7.89177 | 2.46549 | -0.06857 |
| O | -5.84525 | 3.39519 | 0.04307 |
| O | -3.05145 | 2.33574 | -1.07442 |
| O | -3.21221 | 2.36017 | 1.17789 |
| N | 2.99534 | -0.90886 | 0.05362 |
| N | 8.10682 | -0.16741 | -0.02657 |
| H | 8.54308 | 0.75558 | -0.08134 |
| N | 10.18869 | -1.13843 | 0.01845 |
| H | 10.50627 | -0.18108 | -0.03374 |
| N | -2.94331 | -0.84953 | 0.06595 |
| N | -8.00628 | -0.22324 | -0.07457 |
| H | -8.45605 | 0.70046 | -0.09294 |
| N | -10.07033 | -1.24679 | -0.14927 |
| H | -10.40687 | -0.29371 | -0.16003 |
| C | -1.21473 | -2.45789 | 0.14518 |
| C | -0.68978 | -3.75269 | 0.21774 |
| H | -1.31409 | -4.63695 | 0.26535 |
| C | 0.70464 | -3.76376 | 0.22205 |
| H | 1.31495 | -4.65668 | 0.27336 |
| C | 1.24362 | -2.48143 | 0.15058 |
| C | 2.64997 | -2.14386 | 0.12858 |
| H | 3.35649 | -2.978 | 0.17563 |
| C | 4.29046 | -0.47886 | 0.02083 |
| C | 4.61905 | 0.84877 | -0.06126 |
| C | 6.02273 | 1.07995 | -0.08981 |
| C | 6.74445 | -0.11076 | -0.01954 |
| C | 8.84357 | -1.34618 | 0.03754 |
| C | 11.21964 | -2.10236 | 0.07047 |
| C | 10.99291 | -3.48102 | 0.12762 |

| | | | |
|---|---|---|---|
| H | 9.98338 | -3.86573 | 0.13564 |
| C | 12.08242 | -4.35033 | 0.17434 |
| H | 11.89632 | -5.41886 | 0.21847 |
| C | 13.38931 | -3.87132 | 0.16482 |
| H | 14.22761 | -4.55893 | 0.20157 |
| C | 13.60743 | -2.49504 | 0.1072 |
| H | 14.61814 | -2.09998 | 0.09862 |
| C | 12.53298 | -1.6154 | 0.06041 |
| H | 12.71409 | -0.54493 | 0.01544 |
| C | 6.68438 | 2.38173 | -0.19869 |
| C | 6.34654 | 4.72329 | -0.42046 |
| H | 7.00993 | 4.76048 | -1.28789 |
| H | 6.9301 | 4.94378 | 0.47684 |
| C | 5.16047 | 5.64886 | -0.57019 |
| H | 4.50021 | 5.57893 | 0.29807 |
| H | 4.58862 | 5.40584 | -1.4697 |
| H | 5.51455 | 6.67962 | -0.65396 |
| C | 3.54786 | 1.89781 | -0.06061 |
| C | 2.0775 | 3.14658 | -1.43598 |
| H | 2.21768 | 3.55191 | -2.43827 |
| H | 2.22305 | 3.94015 | -0.70025 |
| C | 0.72681 | 2.47534 | -1.2853 |
| H | -0.06827 | 3.21053 | -1.43804 |
| H | 0.61589 | 2.04757 | -0.28577 |
| H | 0.60383 | 1.67836 | -2.02302 |
| C | -2.57557 | -2.1142 | 0.12253 |
| H | -3.29618 | -2.93687 | 0.15773 |
| C | -4.21749 | -0.4782 | 0.02638 |
| C | -4.59214 | 0.88424 | 0.00992 |
| C | -5.96354 | 1.07583 | -0.01749 |
| C | -6.6734 | -0.15988 | -0.03594 |
| C | -8.73536 | -1.4367 | -0.09748 |
| C | -11.08384 | -2.23658 | -0.18413 |
| C | -10.82151 | -3.60873 | -0.21038 |
| H | -9.8041 | -3.97227 | -0.20157 |
| C | -11.89061 | -4.5031 | -0.24816 |
| H | -11.68122 | -5.56773 | -0.26848 |
| C | -13.20706 | -4.05153 | -0.26045 |
| H | -14.02932 | -4.75841 | -0.29018 |
| C | -13.45838 | -2.68008 | -0.23446 |
| H | -14.47785 | -2.30894 | -0.24352 |

| | | | |
|---|---|---|---|
| C | -12.40488 | -1.77526 | -0.19607 |
| H | -12.60975 | -0.70864 | -0.17529 |
| C | -6.6722 | 2.37365 | -0.01982 |
| C | -6.41088 | 4.73213 | 0.05517 |
| H | -7.12341 | 4.79167 | 0.88062 |
| H | -6.94427 | 4.88017 | -0.88649 |
| C | -5.25929 | 5.69557 | 0.21974 |
| H | -4.74242 | 5.52709 | 1.16813 |
| H | -5.64501 | 6.71805 | 0.21595 |
| H | -4.54494 | 5.59326 | -0.601 |
| C | -3.53453 | 1.95213 | -0.03426 |
| C | -2.20571 | 3.4016 | 1.26931 |
| H | -2.52808 | 4.24006 | 0.64682 |
| H | -1.27165 | 3.00469 | 0.86618 |
| C | -2.0823 | 3.78407 | 2.72507 |
| H | -1.32596 | 4.56678 | 2.82547 |
| H | -1.77373 | 2.92793 | 3.32994 |
| H | -3.03016 | 4.16839 | 3.11086 |

Table S5. Atomic coordinates of the radical anion of **1b** calculated by DFT-ωb97X-D with the 6-31+g(d,p) basis set.

| atom | x | y | z |
|---|---|---|---|
| S | -0.01168 | -0.79235 | 0.0723 |
| S | 5.68573 | -1.39639 | 0.07743 |
| S | -5.69342 | -1.39059 | 0.00594 |
| O | 8.17058 | -2.69181 | 0.02943 |
| O | 8.42826 | 2.29433 | 0.01663 |
| O | 6.49189 | 3.42161 | -0.17524 |
| O | 3.7837 | 2.86657 | 1.20023 |
| O | 3.54224 | 2.64314 | -1.02701 |
| O | -8.17734 | -2.67915 | 0.00769 |
| O | -8.4223 | 2.2988 | -0.26193 |
| O | -6.51595 | 3.42102 | 0.1377 |
| O | -3.95405 | 2.89375 | -1.34425 |
| O | -3.28157 | 2.53756 | 0.76927 |
| N | 3.05578 | -0.45119 | 0.09578 |
| N | 8.25552 | -0.41119 | 0.05247 |
| H | 8.81001 | 0.4458 | 0.05748 |
| N | 10.20661 | -1.61234 | 0.01342 |
| H | 10.63085 | -0.69597 | 0.01264 |

| | | | |
|---|---|---|---|
| N | -3.06427 | -0.46323 | 0.01225 |
| N | -8.25719 | -0.40264 | -0.1378 |
| H | -8.80918 | 0.45095 | -0.22907 |
| N | -10.20989 | -1.60294 | -0.12696 |
| H | -10.63344 | -0.6905 | -0.2151 |
| C | -1.26668 | -2.02728 | 0.09668 |
| C | -0.69343 | -3.31704 | 0.14848 |
| H | -1.3012 | -4.21528 | 0.17023 |
| C | 0.68843 | -3.31063 | 0.16614 |
| H | 1.30331 | -4.2036 | 0.20332 |
| C | 1.25197 | -2.01651 | 0.12933 |
| C | 2.61448 | -1.69247 | 0.12968 |
| H | 3.30154 | -2.54792 | 0.15874 |
| C | 4.38472 | -0.17133 | 0.0742 |
| C | 4.91918 | 1.0914 | 0.0649 |
| C | 6.35734 | 1.11361 | 0.05573 |
| C | 6.90122 | -0.15811 | 0.06666 |
| C | 8.83719 | -1.66255 | 0.03096 |
| C | 11.11842 | -2.68545 | -0.01162 |
| C | 10.73841 | -4.03229 | -0.00553 |
| H | 9.69126 | -4.29738 | 0.01888 |
| C | 11.7212 | -5.02129 | -0.03187 |
| H | 11.41355 | -6.06247 | -0.02716 |
| C | 13.07441 | -4.69574 | -0.06324 |
| H | 13.82853 | -5.47551 | -0.08343 |
| C | 13.44708 | -3.35166 | -0.06845 |
| H | 14.49607 | -3.07378 | -0.09266 |
| C | 12.4803 | -2.35405 | -0.04307 |
| H | 12.78326 | -1.31031 | -0.04803 |
| C | 7.19789 | 2.30393 | -0.0273 |
| C | 7.20641 | 4.66929 | -0.259 |
| H | 7.89468 | 4.62201 | -1.10697 |
| H | 7.79024 | 4.79904 | 0.65615 |
| C | 6.1711 | 5.75891 | -0.42956 |
| H | 5.48583 | 5.78022 | 0.42184 |
| H | 5.59169 | 5.604 | -1.3437 |
| H | 6.67092 | 6.72895 | -0.49687 |
| C | 4.03628 | 2.28989 | 0.16073 |
| C | 2.63431 | 3.76334 | -1.05871 |
| H | 2.70277 | 4.13368 | -2.08253 |
| H | 2.99869 | 4.53129 | -0.37245 |

| | | | |
|---|---|---|---|
| C | 1.22002 | 3.33452 | -0.71794 |
| H | 0.55456 | 4.19978 | -0.79767 |
| H | 1.16313 | 2.94528 | 0.30125 |
| H | 0.86915 | 2.56257 | -1.40771 |
| C | -2.62874 | -1.70753 | 0.06746 |
| H | -3.31727 | -2.56176 | 0.09412 |
| C | -4.38682 | -0.17058 | -0.00192 |
| C | -4.91603 | 1.09556 | -0.09301 |
| C | -6.35423 | 1.11814 | -0.1549 |
| C | -6.90226 | -0.15043 | -0.11927 |
| C | -8.84099 | -1.65157 | -0.07855 |
| C | -11.12016 | -2.67754 | -0.10441 |
| C | -10.7458 | -4.01229 | 0.08741 |
| H | -9.70427 | -4.26666 | 0.2216 |
| C | -11.72656 | -5.00348 | 0.10148 |
| H | -11.42329 | -6.03527 | 0.25041 |
| C | -13.07261 | -4.69158 | -0.06924 |
| H | -13.82532 | -5.47287 | -0.05571 |
| C | -13.43991 | -3.35931 | -0.25781 |
| H | -14.48325 | -3.09231 | -0.39324 |
| C | -12.47467 | -2.35998 | -0.27688 |
| H | -12.77267 | -1.32576 | -0.42762 |
| C | -7.19977 | 2.30832 | -0.11355 |
| C | -7.24441 | 4.6627 | 0.18408 |
| H | -7.99894 | 4.5963 | 0.97256 |
| H | -7.75381 | 4.80417 | -0.77281 |
| C | -6.2373 | 5.75827 | 0.45579 |
| H | -5.72923 | 5.5917 | 1.40942 |
| H | -6.75236 | 6.72163 | 0.50204 |
| H | -5.48793 | 5.80324 | -0.33862 |
| C | -4.02649 | 2.26855 | -0.3023 |
| C | -2.27922 | 3.56063 | 0.62099 |
| H | -2.78057 | 4.52 | 0.46067 |
| H | -1.68006 | 3.33228 | -0.26434 |
| C | -1.44037 | 3.56284 | 1.87934 |
| H | -0.66789 | 4.33301 | 1.80041 |
| H | -0.94953 | 2.59588 | 2.01828 |
| H | -2.05296 | 3.77772 | 2.75916 |

Table S6. Atomic coordinates of the neutral **2** calculated by DFT-ωb97X-D with the 6-31+g(d,p) basis set.

| Atom | x | y | z |
|---|---|---|---|
| S | 5.29574 | -2.4877 | -0.10935 |
| S | -0.32006 | -1.2521 | -0.05409 |
| O | -3.03648 | -1.63319 | 0.07201 |
| O | -1.63975 | 3.13825 | -0.31378 |
| O | 0.5684 | 3.55823 | -0.39393 |
| O | 3.04459 | 1.83467 | -1.46313 |
| O | 2.92927 | 2.0706 | 0.77206 |
| N | 2.47953 | -1.25604 | -0.14626 |
| N | -2.38773 | 0.54378 | -0.10719 |
| H | -2.62508 | 1.5352 | -0.17097 |
| N | -4.62401 | 0.03503 | 0.0008 |
| H | -4.73654 | 1.03662 | -0.06513 |
| C | 3.74831 | -3.27501 | -0.07241 |
| C | 3.8856 | -4.64318 | -0.02214 |
| H | 3.03799 | -5.31836 | 0.00672 |
| C | 5.24408 | -5.06077 | -0.01334 |
| H | 5.5635 | -6.09469 | 0.02301 |
| C | 6.1107 | -4.00228 | -0.05679 |
| C | 2.50497 | -2.53733 | -0.09452 |
| H | 1.59748 | -3.15276 | -0.06554 |
| C | 1.2994 | -0.54418 | -0.16359 |
| C | 1.24553 | 0.81429 | -0.2582 |
| C | -0.0912 | 1.3335 | -0.24338 |
| C | -1.03603 | 0.32254 | -0.14019 |
| C | -3.3482 | -0.45036 | -0.00429 |
| C | -5.83002 | -0.68992 | 0.10324 |
| C | -5.89531 | -2.08554 | 0.17051 |
| H | -4.98795 | -2.67162 | 0.14795 |
| C | -7.13963 | -2.70763 | 0.26737 |
| H | -7.17883 | -3.79127 | 0.31914 |
| C | -8.3175 | -1.96641 | 0.29752 |
| H | -9.27895 | -2.46332 | 0.37299 |
| C | -8.24507 | -0.57525 | 0.22925 |
| H | -9.1506 | 0.0226 | 0.25128 |
| C | -7.0131 | 0.06017 | 0.13334 |
| H | -6.96823 | 1.14477 | 0.08254 |
| C | -0.47632 | 2.74127 | -0.32024 |
| C | 0.31112 | 4.97648 | -0.46558 |

| | | | |
|---|---|---|---|
| H | -0.31365 | 5.26011 | 0.38481 |
| H | -0.2396 | 5.18106 | -1.38733 |
| C | 1.65294 | 5.67279 | -0.44026 |
| H | 2.18335 | 5.46 | 0.492 |
| H | 1.50202 | 6.75316 | -0.51059 |
| H | 2.27333 | 5.35487 | -1.28234 |
| C | 2.49387 | 1.62774 | -0.40259 |
| C | 4.11144 | 2.89936 | 0.75313 |
| H | 3.95157 | 3.71129 | 0.0388 |
| H | 4.95212 | 2.29316 | 0.40524 |
| C | 4.32626 | 3.41495 | 2.15794 |
| H | 5.21764 | 4.04771 | 2.17866 |
| H | 4.47221 | 2.59 | 2.86002 |
| H | 3.4717 | 4.01132 | 2.48929 |
| H | 7.19187 | -4.03215 | -0.06154 |

Table S7. Atomic coordinates of the radical cation of **2** calculated by DFT-ωb97X-D with the 6-31+g(d,p) basis set.

| Atom | x | y | z |
|---|---|---|---|
| S | 5.22237 | -2.42922 | -0.04178 |
| S | -0.3712 | -1.28661 | -0.0239 |
| O | -3.03029 | -1.60944 | 0.12039 |
| O | -1.61402 | 3.13835 | -0.26318 |
| O | 0.59557 | 3.55687 | -0.34451 |
| O | 2.96881 | 1.77758 | -1.53599 |
| O | 2.98955 | 1.99812 | 0.71128 |
| N | 2.40809 | -1.25655 | -0.1677 |
| N | -2.35721 | 0.56346 | -0.06066 |
| H | -2.57249 | 1.5668 | -0.11979 |
| N | -4.60763 | 0.06791 | 0.02018 |
| H | -4.70817 | 1.0707 | -0.06058 |
| C | 3.6873 | -3.25255 | -0.11601 |
| C | 3.85609 | -4.63911 | -0.10684 |
| H | 3.02158 | -5.32925 | -0.14687 |
| C | 5.2041 | -5.01761 | -0.04072 |
| H | 5.55607 | -6.04035 | -0.02368 |
| C | 6.04631 | -3.92325 | -0.00068 |
| C | 2.45808 | -2.57213 | -0.16834 |
| H | 1.55805 | -3.1926 | -0.21746 |
| C | 1.25815 | -0.59076 | -0.15972 |

| | | | |
|---|---|---|---|
| C | 1.21583 | 0.82079 | -0.24827 |
| C | -0.06736 | 1.33323 | -0.21521 |
| C | -1.05043 | 0.3038 | -0.10276 |
| C | -3.35716 | -0.43707 | 0.03671 |
| C | -5.82923 | -0.64581 | 0.10471 |
| C | -5.9052 | -2.03919 | 0.17238 |
| H | -5.00626 | -2.6385 | 0.16536 |
| C | -7.15785 | -2.64685 | 0.24918 |
| H | -7.21157 | -3.72946 | 0.30168 |
| C | -8.32574 | -1.88986 | 0.25827 |
| H | -9.29377 | -2.37561 | 0.31808 |
| C | -8.23898 | -0.49968 | 0.18973 |
| H | -9.13842 | 0.107 | 0.19595 |
| C | -6.99889 | 0.12209 | 0.11388 |
| H | -6.93978 | 1.20571 | 0.06321 |
| C | -0.4497 | 2.76223 | -0.27843 |
| C | 0.36086 | 4.98897 | -0.40565 |
| H | -0.25479 | 5.26772 | 0.4521 |
| H | -0.19177 | 5.19896 | -1.32407 |
| C | 1.71445 | 5.65848 | -0.38349 |
| H | 2.24613 | 5.43197 | 0.54448 |
| H | 1.5787 | 6.74104 | -0.44536 |
| H | 2.32248 | 5.33824 | -1.23333 |
| C | 2.48938 | 1.59675 | -0.44062 |
| C | 4.21769 | 2.76984 | 0.65354 |
| H | 4.05484 | 3.61431 | -0.02049 |
| H | 4.99871 | 2.13131 | 0.23396 |
| C | 4.53585 | 3.21559 | 2.06103 |
| H | 5.4578 | 3.80261 | 2.05007 |
| H | 4.6814 | 2.35697 | 2.72113 |
| H | 3.73427 | 3.84023 | 2.46367 |
| H | 7.1272 | -3.93755 | 0.05 |

Table S8. Atomic coordinates of the radical anion of **2** calculated by DFT-ωb97X-D with the 6-31+g(d,p) basis set.

| Atom | x | y | z |
|---|---|---|---|
| S | 5.49866 | -2.45434 | -0.15111 |
| S | -0.03597 | -1.32229 | -0.00705 |
| O | -2.82296 | -1.86813 | 0.02113 |
| O | -1.65244 | 2.97783 | 0.13028 |

| | | | |
|---|---|---|---|
| O | 0.31387 | 3.44301 | -0.84151 |
| O | 3.6476 | 1.68681 | -0.37119 |
| O | 2.23433 | 2.78641 | 0.99217 |
| N | 2.7111 | -1.20333 | -0.117 |
| N | -2.23127 | 0.33888 | 0.12613 |
| H | -2.52487 | 1.3096 | 0.22908 |
| N | -4.44665 | -0.23576 | 0.09976 |
| H | -4.58506 | 0.76423 | 0.08461 |
| C | 3.94036 | -3.26984 | -0.10032 |
| C | 4.12897 | -4.65651 | -0.07747 |
| H | 3.30003 | -5.35475 | -0.04566 |
| C | 5.49346 | -5.03638 | -0.10037 |
| H | 5.83044 | -6.06741 | -0.08829 |
| C | 6.35549 | -3.97007 | -0.14033 |
| C | 2.73094 | -2.54579 | -0.0868 |
| H | 1.81161 | -3.1406 | -0.0568 |
| C | 1.57986 | -0.51568 | -0.10323 |
| C | 1.41055 | 0.87935 | -0.0603 |
| C | 0.01848 | 1.27878 | 0.01819 |
| C | -0.85221 | 0.21447 | 0.07892 |
| C | -3.14724 | -0.68608 | 0.07558 |
| C | -5.63151 | -0.99388 | 0.09026 |
| C | -5.66542 | -2.3906 | 0.17787 |
| H | -4.74243 | -2.94805 | 0.24599 |
| C | -6.8947 | -3.04875 | 0.17161 |
| H | -6.90633 | -4.13235 | 0.23935 |
| C | -8.09243 | -2.34459 | 0.08166 |
| H | -9.04193 | -2.86966 | 0.07788 |
| C | -8.05332 | -0.9529 | -0.00344 |
| H | -8.97387 | -0.382 | -0.07439 |
| C | -6.83645 | -0.28207 | -0.00063 |
| H | -6.81898 | 0.80245 | -0.06986 |
| C | -0.51528 | 2.62677 | -0.19347 |
| C | -0.12953 | 4.79436 | -1.05341 |
| H | -0.39652 | 5.23196 | -0.08688 |
| H | -1.02591 | 4.77799 | -1.67955 |
| C | 1.004 | 5.54431 | -1.71704 |
| H | 1.8898 | 5.56234 | -1.0765 |
| H | 0.69519 | 6.57605 | -1.90638 |
| H | 1.27275 | 5.08244 | -2.67048 |
| C | 2.53449 | 1.78337 | 0.12873 |

| | | | |
|---|---|---|---|
| C | 3.18748 | 3.84592 | 1.10723 |
| H | 3.46151 | 4.19157 | 0.10519 |
| H | 4.09421 | 3.46755 | 1.58955 |
| C | 2.54511 | 4.94912 | 1.92169 |
| H | 3.2439 | 5.78348 | 2.03116 |
| H | 2.27495 | 4.59172 | 2.91916 |
| H | 1.64003 | 5.31807 | 1.43009 |
| H | 7.43639 | -3.98431 | -0.16538 |

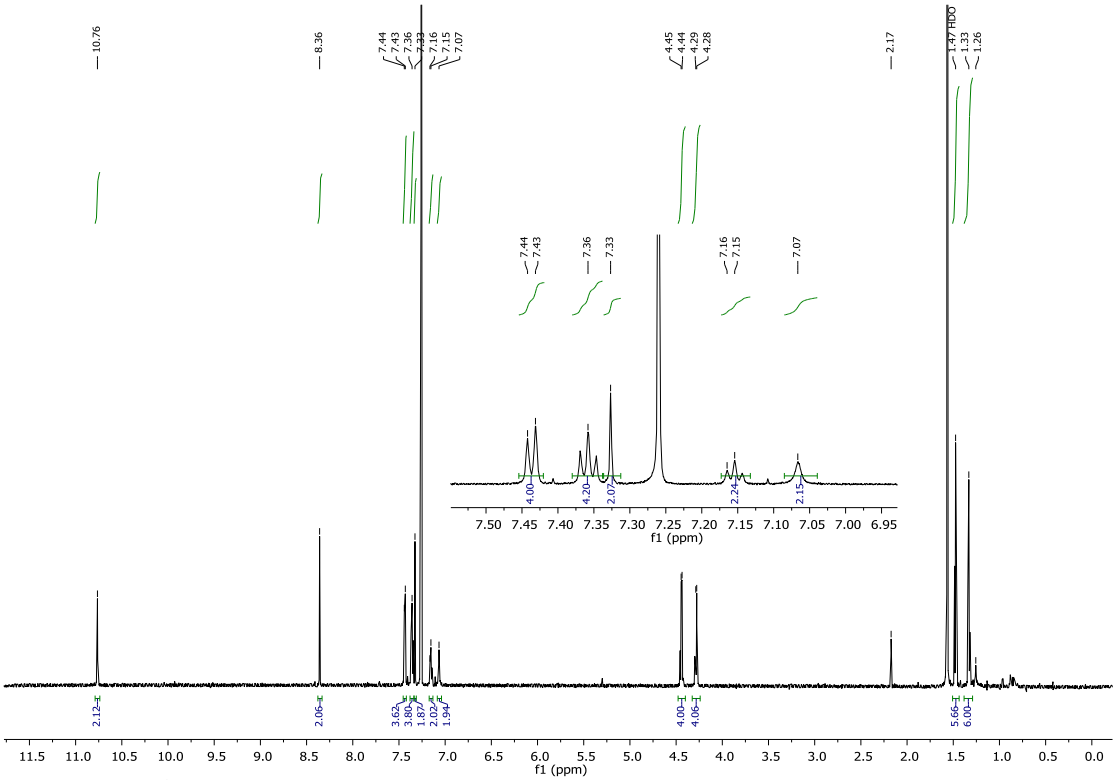


Figure S20. $^{1}$H NMR of **1b** in $CDCl_3$.

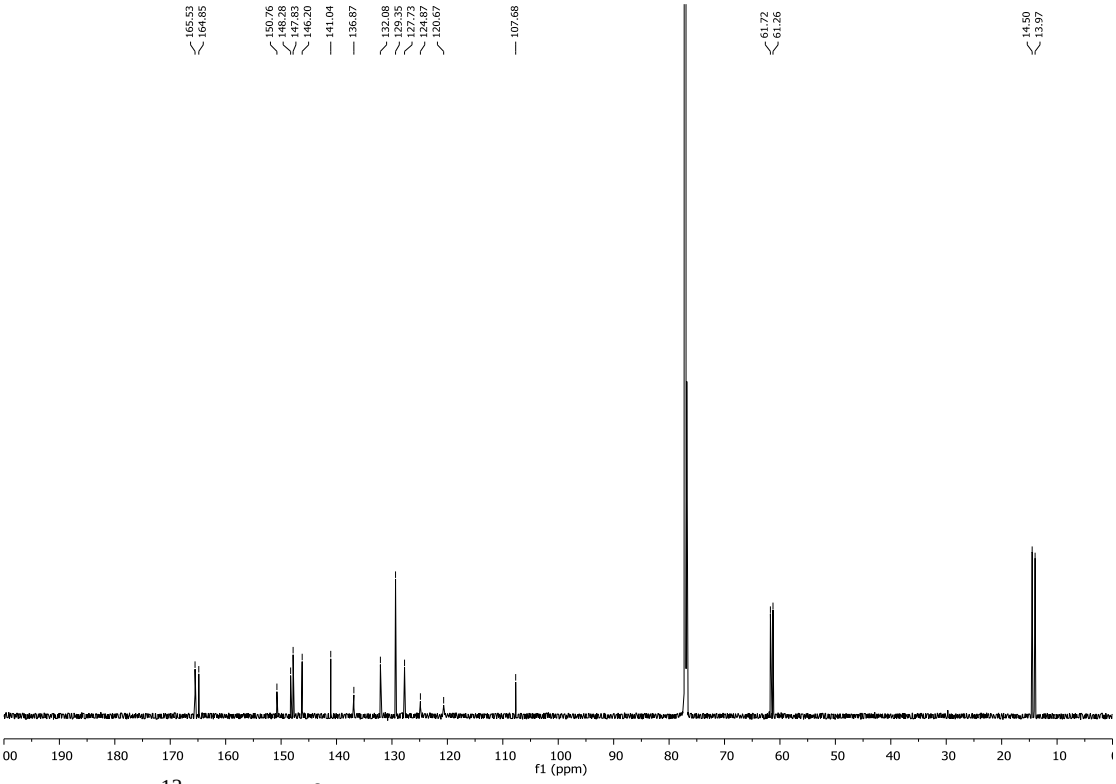
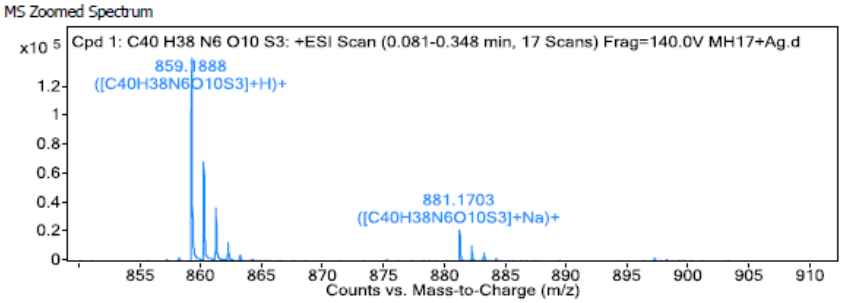


Figure S21. $^{13}$C NMR of **1b** in $CDCl_3$.




**MS Spectrum Peak List**

| Ion | Formula | Abund | *Expe. m/z* | *Calc. m/z* | Diff(ppm) |
|---|---|---|---|---|---|
| (M+H)+ | C40H38N6O10S3 | 141331.58 | 859.1888 | 859.1884 | -0.41 |
| (M+Na)+ | C40H38N6O10S3 | 22245.17 | 881.1703 | 881.1704 | 0.06 |

Figure S22. High-resolution mass spectrometry data of **1b**.

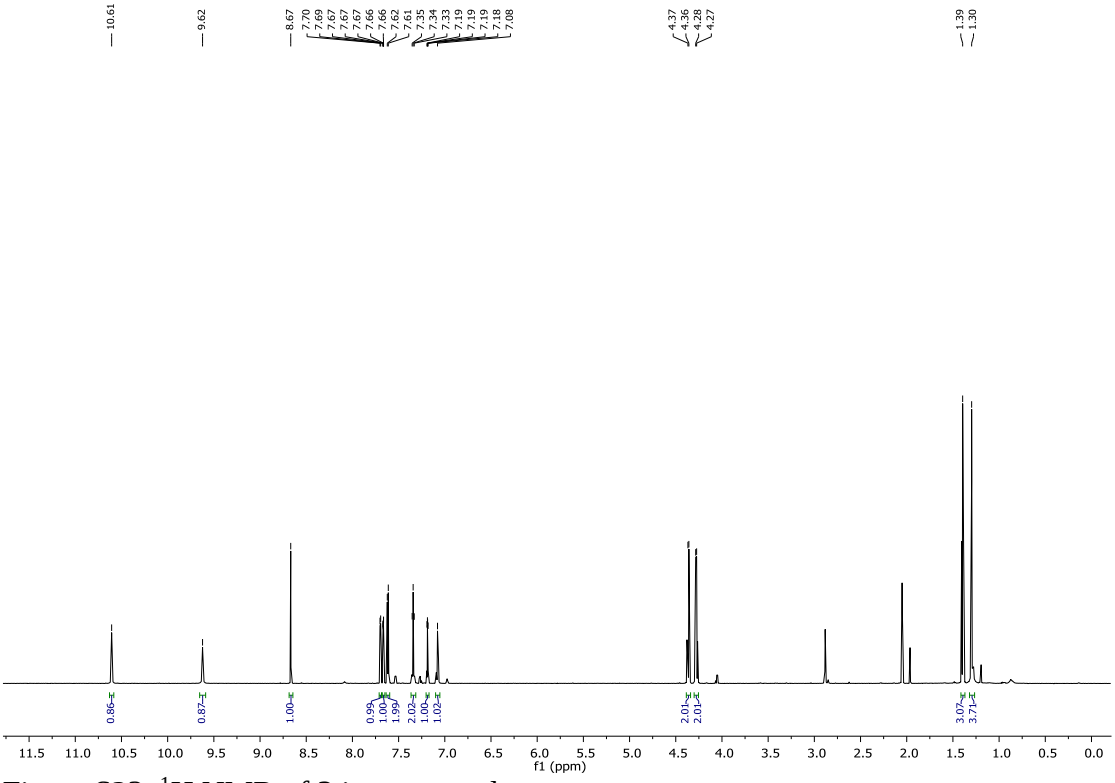



Figure S23. $^{1}$H NMR of **2** in acetone-$d_6$.

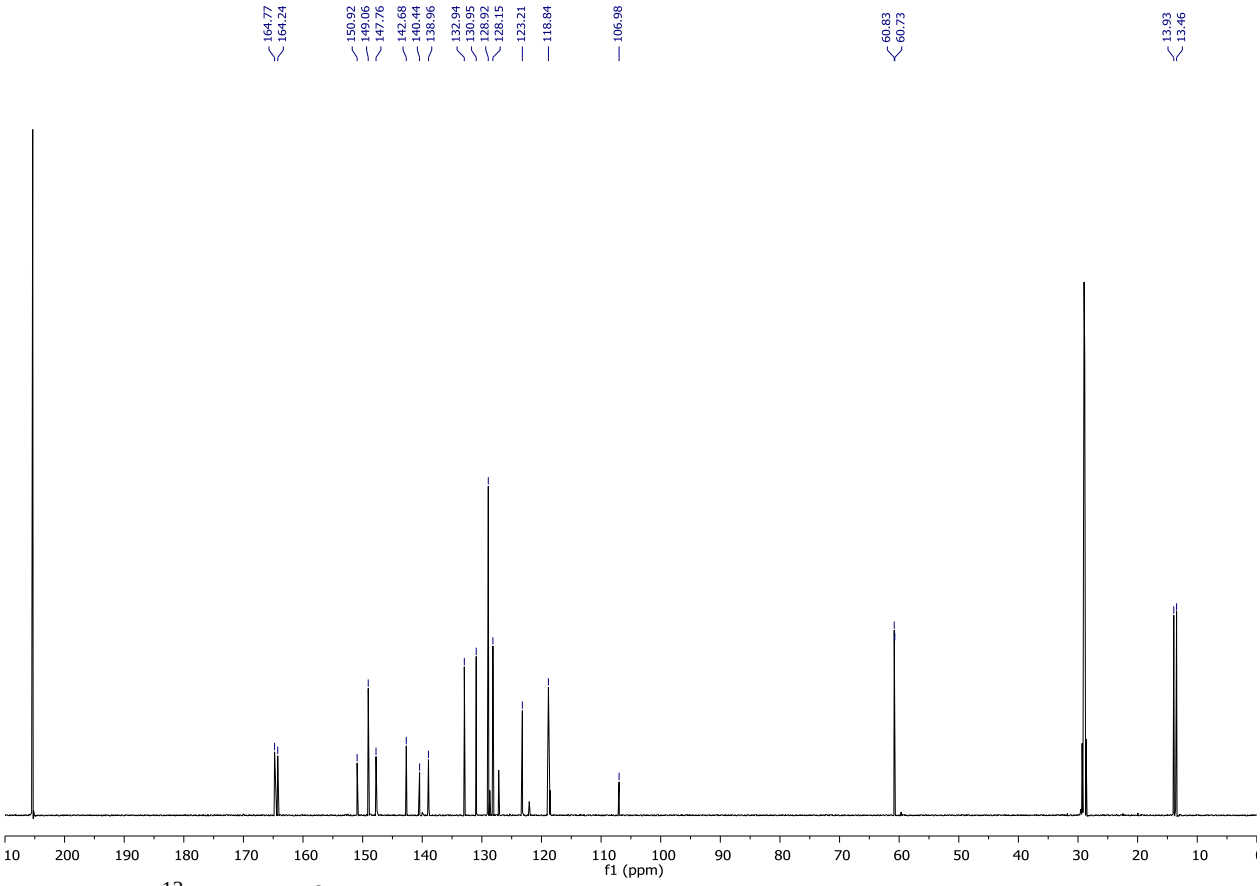



Figure S24. $^{13}C$ NMR of **2** in acetone-$d_6$.

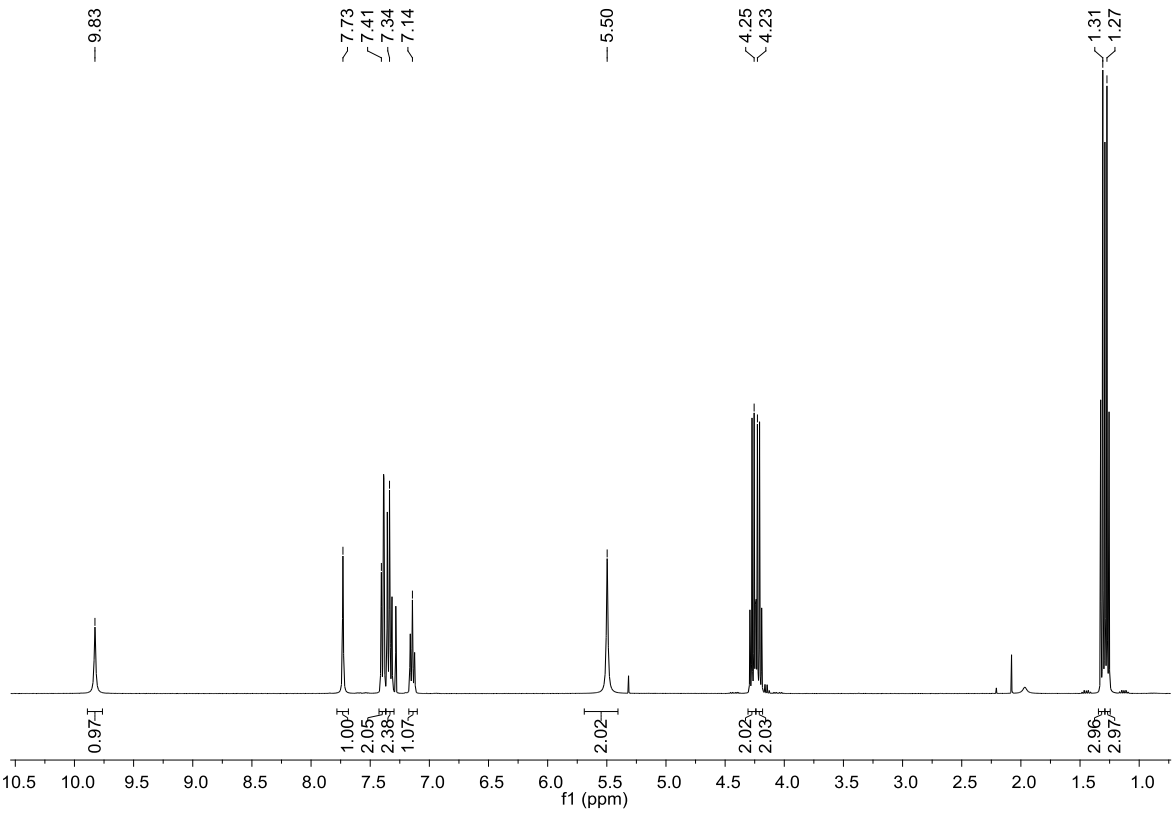



Figure S25. $^{1}H$ NMR of **3** in $CDCl_3$.

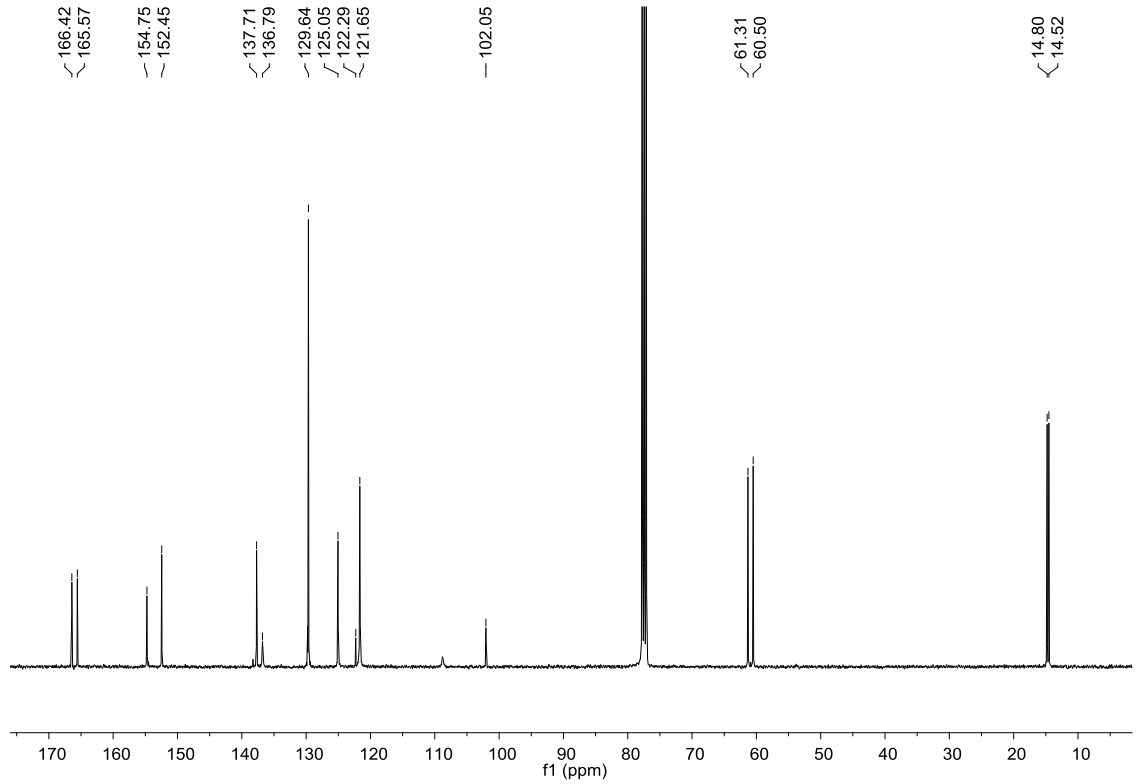



Figure S26. $^{13}C$ NMR of **3** in $CDCl_3$.