Electronic Supplementary Information (ESI)

Diethyl phosphite-mediated switchable synthesis of bis(imidazoheterocycles)disulfanes using imidazoheterocycles and octasulfur

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General Experimental

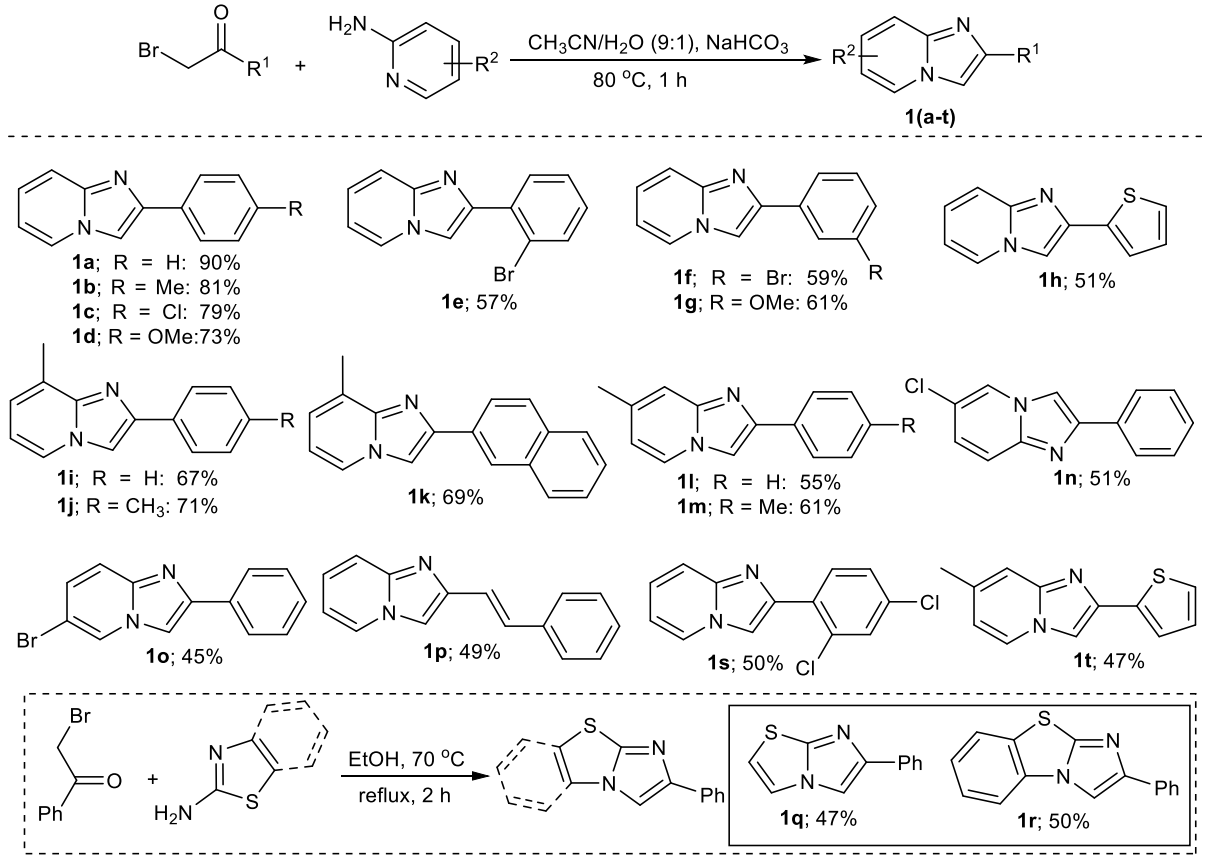
All reagents were purchase from Sigma-Aldrich (Merck), Alfa Aesar, Acros, SDFine, Spectrochem or AVRA and used without further purification unless otherwise stated. For all reactions carried out under inert atmosphere, solvents were dried over activated 4 Å molecular sieves. Silicon oil baths on stirrer hotplates were employed with temperature control via thermometer. Reaction progress was monitored by Thin Layer Chromatography (TLC) performed using TLC Silica gel 60 F254. TLC plate's visualization was achieved by a combination of ultraviolet light (254 nm), potassium permanganate solution, iodine treatment or p-anisaldehyde stains. Flash column chromatography was performed using silica gel (100-200 mesh) as a stationary phase. Melting points were measured in open capillaries using DBK digital melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR's were recorded using Bruker AVIII400 (^{1}H = 400 MHz and ^{13}C = 101 MHz) with the spectrometers at 300 K. Chemical shifts (δ) are given in ppm relative to TMS and coupling constants (J) are quoted in Hz to one decimal place. For spectra recorded in chloroform-d ($CDCl_3$) the δ 7.26 ppm resonance of residual $CHCl_3$ for proton spectra and δ 77.16 ppm resonance of $CDCl_3$ for carbon spectra were used as internal references. Spectral data for ^{1}H NMR spectroscopy is reported as follows: Chemical shift (multiplicity, coupling constant, number of protons); and for ^{13}C NMR spectroscopy: Chemical shift. The following abbreviations were used for multiplicity in ^{1}H NMR: s (singlet), d (doublet), t (triplet), q (quadruplet), dd (doublet of doublets), td (triplet of doublets), quin (quintuplet), bs (broad singlet), m (multiplet), app. (apparent). All NMR spectrums are processed using MestReNova version 6.0.2(v). Mass spectra were analysed by Electrospray Ionization (ESI) method that were obtained on a Shimadzu LCMS-2020 mass spectrometer. High resolution mass spectroscopy (HRMS) were recorded using ESI-TOF techniques and was obtained using a Thermo scientific ExactiveTM Orbitrap mass spectrometer or Q STAR XL Hybrid MS/MS to adjust the calibrated mass scale.

The single crystal X-ray diffraction measurements for all the components were performed at 100 K using APEX2 (Bruker, 2016; Bruker D8 VENTURE Kappa Duo PHOTON II CPAD) diffractometer having graphite-monochromatized (MoKα = 0.71073 Å). The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of unit cell parameters and an orientation matrix were calculated from 36 frames, and the cell refinement was performed by SAINT-Plus (Bruker, 2016). An optimized strategy used for data collection consisted of different sets of φ and ω scans with 0.5^{0} steps φ/ω. The data were collected with a time frame of 10 sec for all four components by setting the sample to detector distance fixed at 40 cm. All the data points were corrected for Lorentzian, polarization, and absorption effects using SAINT-Plus and SADABS programs (Bruker, 2016). SHELXS-97 (Sheldrick, 2008) was used for structure solution, and full-matrix least-squares refinement on F^2. The molecular graphics of ORTEP diagrams were performed by Mercury software. The crystal symmetry of all four components was cross-checked by running the cif files through PLATON (Spek, 2020) software and notified that no additional symmetry was observed. The Encifer software was used to correct the cif files.

Synthesis of Starting Materials

Synthesis of imidazoheterocycles (1a-v):

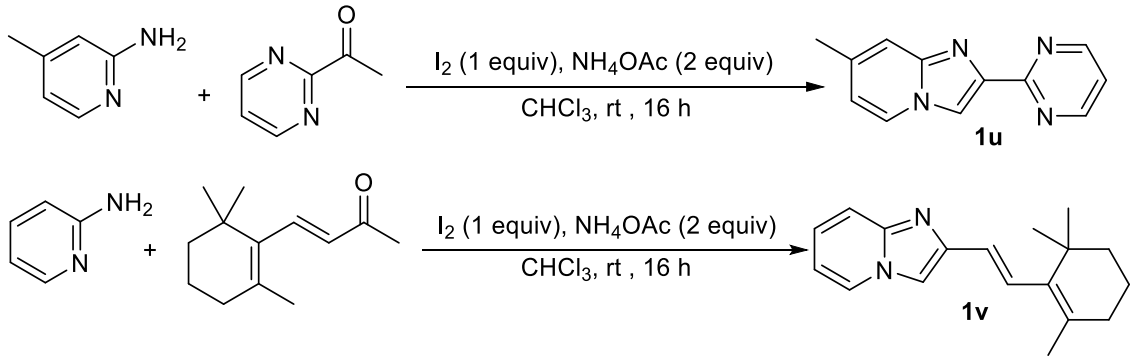
Method-A: *According to known procedure (Scheme S1),*[1] a heat gun-dried round bottle flask was charged β-keto bromides (5 mmol, 1.0 equiv), various 2-aminopyridines (7.5 mmol, 1.5 equiv) and sodium bicarbonates (7.5 mmol, 1.5 equiv) in CH_3CN/H_2O (9:1 mL, 10 mL). The reaction mixture was stirred at 80 °C for 1 h and monitored by TLC either complete or appeared to be proceeding no further progress. The mixture was quenched by addition of water (30 mL) followed by extraction with EtOAc (3x40 mL). The combined organic layers were washed with brine (2x30 mL), dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The resulting residue was subjected to flash column chromatography (silica gel 60-120 mesh, eluted with 20-30% ethyl acetate/petether) to afford desired of imidazoheterocycles **1a-t**.



Scheme S1*: Synthesis of imidazoheterocycles* ***1a-t****.*

Method-B: *According to known procedure (Scheme S2),*[2] a heat gun-dried round bottle flask was charged 1-(pyrimidin-2-yl)ethan-1-one or (*E*)-4-(2,6,6-trimethylcyclohex-1-en-1-yl)but-3-en-2-one (4.0 mmol, 1.0 equiv)], 4-methylpyridin-2-amine or pyridin-2-amine (4.8 mmol, 1.2 equiv), iodine (4 mmol, 1 equiv), and ammonium acetate (8 mmol, 2 equiv) in $CHCl_3$ (15 mL). The reaction mixture was stirred at room temperature for 16 h and monitored by TLC either complete or appeared to be proceeding no further progress. The mixture was quenched by addition of 10% sodium thiosulfate solution (10 mL) and water (20 mL) followed by extraction with EtOAc (2x40 mL). The combined organic layers were washed with brine (2x10 mL) dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The resulting residue was subjected to

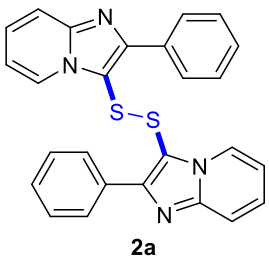
flash chromatography (silica gel 100-200 mesh, eluted with 25-30% ethyl acetate/petether) to afford desired product imidazopyridines **1u** and **1v**.



Scheme S2*: Synthesis of imidazo[1,2-a]pyridines* ***1u*** *and* ***1v****.*

General Procedure-1 (GP1) for the synthesis of bis(imidazoheterocycle)disulfanes:
A heat gun-dried Schlenk tube was charged imidazoheterocycles (0.5 mmol, 1.0 equiv), S_8 (5.0 mmol, 10 equiv) and diethyl phosphite (0.25 mmol, 0.5 equiv) in DMSO (2.5 mL). The reaction mixture was stirred at 120 °C for 22 h and monitored by TLC either complete or appeared to be preceding no further progress. The mixture was quenched by addition of water (10 mL) followed by extraction with EtOAc (3x10 mL). The combined organic layers were washed with brine (2x10 mL), dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The resulting residue was subjected to flash column chromatography (silica gel 100-200 mesh, eluted with 40-50% ethyl acetate/petether) to afford desired bis(imidazoheterocycle)disulfanes.

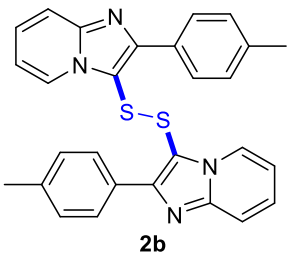
1,2-Bis(2-phenylimidazo[1,2-a]pyridin-3-yl)disulfane (2a):



Following ***GP1*** using 2-phenylimidazo[1,2-*a*]pyridine **1a** (97.1 mg, 0.5 mmol), S_8 (160.0 mg, 5.0 mmol) and diethyl phosphite (34.5 mg, 32 µL, 0.25 mmol) for 22 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **2a** as a yellow solid (189.2 mg, 84%); **mp**: 239-241 °C [Lit.[3] 242-243 °C]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 6.6 Hz, 2H), 7.63 (app. bs, 4H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 2H), 7.13–7.09 (m, 6H), 6.74 (td, *J* = 6.8, 0.7 Hz, 2H); **LCMS** (ESI, *M+H*$^+$): 451.15. *These data are consistent with literature values.*[3]

Gram-Scale Reaction: *Following* ***GP1*** *using 2-phenylimidazo[1,2-a]pyridine* ***1a*** *(1.16 g, 6.0 mmol,* S_8 *(1.92 g, 60.0 mmol) and diethylphosphite (414.0 mg, 386.0 µL, 3.0 mmol) in DMSO (25 mL) for 24 h. Purification by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound* ***2a*** *(1.71 g, 63%) as a yellow solid.*

1,2-Bis[2-(p-tolyl)imidazo[1,2-a]pyridin-3-yl]disulfane (2b):

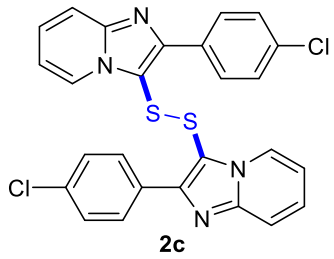


Following ***GP1*** using 2-(*p*-tolyl)imidazo[1,2-*a*]pyridine **1b** (104.1 mg, 0.5 mmol), S_8 (160.0 mg, 5 mmol) and diethylphosphite (34.5 mg, 32 µL, 0.25 mmol) for 22 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **2b** as a white solid (181.9 mg, 76%); **mp**: 201-203 °C [Lit.[3] 203-204 °C]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 6.5 Hz, 2H), 7.53 (app. bs, 4H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.19–7.14 (m, 2H),

6.87 (d, *J* = 6.6 Hz, 4H), 6.74 (t, *J* = 6.8 Hz, 2H), 2.27 (s, 6H); **LCMS** (ESI, *M+H*$^+$): 479.15. *These data are consistent with literature values.*[3]

Gram-Scale Reaction: *Following* ***GP1*** *using 2-(p-tolyl)imidazo[1,2-a]pyridine* ***1b*** *(1.05 g, 5.0 mmol, S_8 (1.60 mg, 50.0 mmol) and diethyl phosphite (345.0 mg, 322 μL, 2.5 mmol) DMSO (20 mL) for 24 h. Purification by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound* ***2b*** *(1.44 g, 60%) as a colorless solid.*

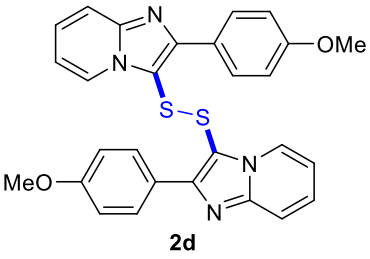
1,2-Bis[2-(4-chlorophenyl)imidazo[1,2-a]pyridin-3-yl]disulfane(2c):



2c

Following ***GP1*** using 2-(4-chlorophenyl)imidazo[1,2-*a*]pyridine **1c** (114.3 mg, 0.5 mmol), S_8 (160.0 mg, 5.0 mmol) and diethyl phosphite (34.5 mg, 32 μL, 0.25 mmol) for 22 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **2c** as a yellow solid (148.0 mg, 57%); **mp**: 213-215 ^{o}C [Lit.[3] 210-212 ^{o}C]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (s, 2H), 7.43 (app. bs, 4H), 7.28 (d, *J* =4.1 Hz, 4H), 6.96–6.86 (m, 6H); **LCMS** (ESI, *M*$^+$): 519.10. *These data are consistent with literature values.*[3]

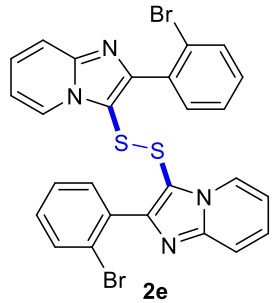
1,2-Bis[2-(4-methoxyphenyl)imidazo[1,2-a]pyridin-3-yl]disulfane (2d):



2d

Following ***GP1*** using 2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridine **1d** (112.1 mg, 0.5 mmol), S_8 (160.0 mg, 5 mmol) and diethyl phosphite (34.5 mg, 32 μL, 0.25 mmol) for 22 h. Purified by flash column chromatography (silica gel, 50% EtOAc in petether) yielded title compound **2d** as a yellow solid (168.5 mg, 66%); **mp**:209-211 ^{o}C [Lit.[3] 211-213 ^{o}C]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 6.1 Hz, 2H), 7.59 (app. bs, 4H), 7.32 (d, *J* = 7.4 Hz, 2H), 7.21–7.16 (m, 2H), 6.76 (t, *J* = 6.7 Hz, 2H), 6.60 (d, *J* = 6.3 Hz, 4H), 3.78 (s, 6H); **LCMS** (ESI, *M+H*$^+$): 511.20. *These data are consistent with literature values.*[3]

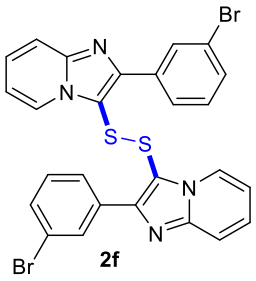
1,2-Bis[2-(2-bromophenyl)imidazo[1,2-a]pyridin-3-yl]disulfane (2e):



2e

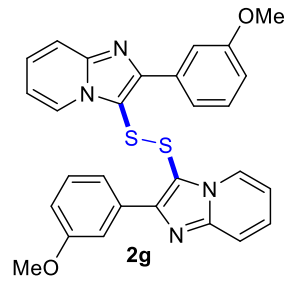
Following ***GP1*** using 2-(2-bromophenyl)imidazo[1,2-*a*]pyridine **1e** (136.5 mg, 0.5 mmol), S_8 (160.0 mg, 5.0 mmol) and diethyl phosphite (34.5 mg, 32 μL, 0.25 mmol) for 22 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **2e** as a yellow solid (164.2 mg, 54%); **mp**: 235-237 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 6.4 Hz, 2H), 7.64 (app. bs, 4H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 7.28 Hz, 2H), 7.14–7.08 (m, 4H), 6.75 (t, *J* = 6.5 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.4, 132.1, 128.3, 128.0(3C) 127.8(2C), 127.1, 124.5, 117.8(2C), 113.1; **HRMS** (ESI-TOF) calculated for $C_{26}H_{17}Br_2N_4S_2$ [M+H]$^+$: *m/z* 606.9256; found 606.9261.

1,2-Bis[2-(3-bromophenyl)imidazo[1,2-a]pyridin-3-yl]disulfane (2f):



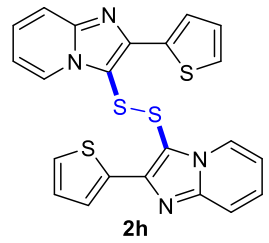
Following ***GP1*** using 2-(3-bromophenyl)imidazo[1,2-*a*]pyridine **1f** (136.5 mg, 0.5 mmol), S_8 (160.0 mg, 5.0 mmol) and diethyl phosphite (34.5 mg, 32 μL, 0.25 mmol) for 22 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **2f** as a yellow solid (206.8 mg, 68%); **mp**: 150-152 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (s, 2H), 7.64 (s, 2H), 7.49 (s, 2H), 7.35 (s, 2H), 7.26 (t, *J* = 7.2 Hz, 2H), 7.18 (s, 2H), 6.89 (d, *J* = 5.7 Hz, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.5, 133.7, 131.0, 130.4, 129.2, 127.7(2C), 126.5, 124.7, 121.8, 117.8, 113.8(2C); **HRMS** (ESI-TOF) calculated for $C_{26}H_{17}Br_2N_4S_2$ $[M+H]^+$: *m/z* 606.9256; found 606.9255.

1,2-Bis[2-(3-methoxyphenyl)imidazo[1,2-a]pyridin-3-yl]disulfane (2g):



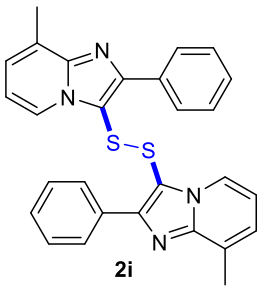
Following ***GP1*** using 2-(3-methoxyphenyl)imidazo[1,2-*a*]pyridine **1g** (112.1 mg, 0.5 mmol), S_8 (160.0 mg, 5.0 mmol) and diethyl phosphite (34.5 mg, 32 μL, 0.25 mmol) for 22 h. Purified by flash column chromatography (silica gel, 50% EtOAc in petether) yielded title compound **2g** as a yellow solid (160.1 mg, 63%); **mp**: 141-143 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 6.5 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.23–7.19 (m, 6H), 6.97 (t, *J* = 6.9 Hz, 2H), 6.75 (td, *J* = 6.8, 1.0 Hz, 2H), 6.67 (d, *J* = 7.3 Hz, 2H), 3.81 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.8, 147.4, 133.2, 128.6, 127.2, 124.5, 120.7, 117.6(2C), 114.8, 113.1, 112.6, 55.2(2C); **HRMS** (ESI-TOF) calculated for $C_{28}H_{23}N_4O_2S_2$ $[M+H]^+$: *m/z* 511.1262, found 511.1244.

1,2-Bis[2-(thiophen-2-yl)imidazo[1,2-a]pyridin-3-yl]disulfane (2h):



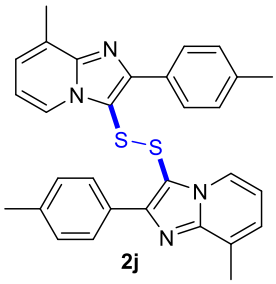
Following ***GP1*** using 2-(thiophen-2-yl)imidazo[1,2-*a*]pyridine **1h** (100.1 mg, 0.5 mmol), S_8 (160.0 mg, 5.0 mmol) and diethyl phosphite (34.5 mg, 32 μL, 0.25 mmol) for 22 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **2h** as a yellow color solid (171.2 mg, 74%); **mp**: 179-181 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 6.7 Hz, 2H), 7.60–7.49 (m, 2H), 7.40 (s, 2H), 7.25–7.20 (m, 2H), 7.17–7.07 (m, 2H), 6.74 (t, *J* = 6.7 Hz,4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.7, 127.5, 127.3, 126.8, 126.5, 124.4(3C), 117.4, 113.4(2C); **HRMS** (ESI-TOF) calculated for $C_{22}H_{15}N_4S_4$ $[M+H]^+$: *m/z* 463.0180; found 463.0174.

1,2-Bis(8-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)disulfane (2i):



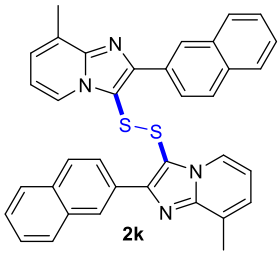
Following ***GP1*** using 8-methyl-2-phenylimidazo[1,2-*a*]pyridine **1i** (104.1 mg, 0.5 mmol), S_8 (160.0 mg, 5 mmol) and diethyl phosphite (34.5 mg, 32 μL, 0.25 mmol) for 22 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **2i** as a yellow color solid (196.2 mg, 82%); **mp**: 137-139 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 5.7 Hz, 2H), 7.55 (app. bs, 4H), 7.07–6.99 (m, 6H), 6.96 (d, *J* = 6.9 Hz, 2H), 6.67 (t, *J* = 6.8 Hz, 2H), 2.47 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.5, 147.7, 132.3, 127.9, 127.6, 127.5, 127.3, 126.0(2C), 122.5, 113.0(2C), 16.9(2C); **HRMS** (ESI-TOF) calculated for $C_{28}H_{23}N_4S_2$ $[M+H]^+$: *m/z* 479.1364; found 479.1351.

1,2-Bis(8-methyl-2-(p-tolyl)imidazo[1,2-a]pyridin-3-yl)disulfane(2j):



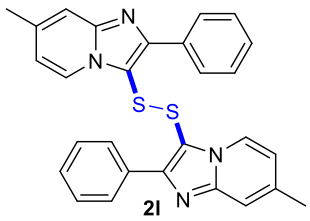
Following ***GP1*** using 8-methyl-2-(*p*-tolyl)imidazo[1,2-*a*]pyridine **1j** (111.1 mg, 0.5 mmol), S_8 (160.0 mg, 5.0 mmol) and diethyl phosphite (34.5 mg, 32 μL, 0.25 mmol) for 22 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **2j** as a yellow solid (169.7 mg, 67%); **mp**: 177-179 °C [Lit.[3] 178-180 °C]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 4.7 Hz, 2H), 7.45 (app. bs, 4H), 6.92 (d, *J* = 6.6 Hz, 2H), 6.81 (d, *J* = 5.1 Hz, 4H), 6.68 (t, *J* = 6.7 Hz, 2H), 2.46 (s, 6H), 2.23 (s, 6H)*;* **LCMS** (ESI, *M+H*$^+$): 507.20. *These data are consistent with literature values.*[3]

1,2-Bis(8-methyl-2-(naphthalen-2-yl)imidazo[1,2-a]pyridin-3-yl)disulfane (2k):



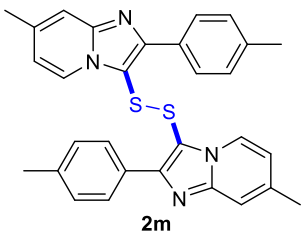
Following ***GP1*** using 8-methyl-2-(naphthalen-2-yl)imidazo[1,2-*a*]pyridine **1k** (129.1 mg, 0.5 mmol), S_8 (160.0 mg, 5.0 mmol) and diethyl phosphite (34.5 mg, 32 μL, 0.25 mmol) for 22 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **2k** as a yellow solid (173.6 mg, 60 %); **mp**: 195-197°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 16.6 Hz, 4H), 7.79 (d, *J* = 6.6 Hz, 2H), 7.70 (d, *J* = 7.4 Hz, 4H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.41 (app. bs, 4H), 6.52 (t, *J* = 6.7 Hz, 2H), 6.41 (bs, 2H), 2.03 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.4, 133.0, 132.7, 129.5, 128.8, 127.30(2C), 127.28, 126.9, 126.7, 126.1(2C), 126.0, 125.6, 125.5, 122.2, 113.1, 16.3; **HRMS** (ESI-TOF) calculated for $C_{36}H_{27}N_4S_2$ $[M+H]^+$: *m/z* 579.1677; found 579.1663.

1,2-Bis(7-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)disulfane (2l):



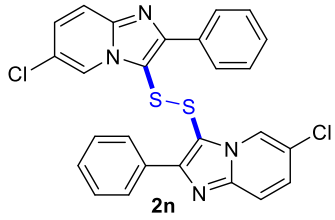
Following ***GP1*** using 7-methyl-2-phenylimidazo[1,2-*a*]pyridine **1l** (104.1 mg, 0.5 mmol), S_8 (160.0 mg, 5.0 mmol) and diethyl phosphite (34.5 mg, 32 μL, 0.25 mmol) for 22 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **2l** as a yellow color solid (186.6 mg, 78%); **mp**: 219-225 °C [Lit.[3] 224-225 °C]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 6.8 Hz, 2H), 7.63 (app. bs, 4H), 7.16–7.04 (m, 8H), 6.53 (dd, *J* = 6.9, 1.2 Hz, 2H), 2.36 (s, 6H); **LCMS** (ESI, M+H$^+$): 479.15. *These data are consistent with literature values.* [3]

1,2-Bis(7-methyl-2-(p-tolyl)imidazo[1,2-a]pyridin-3-yl)disulfane (2m):



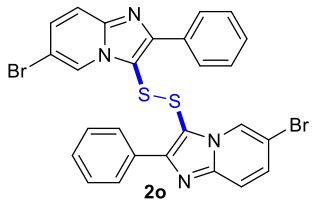
Following ***GP1*** using 7-methyl-2-(*p*-tolyl)imidazo[1,2-*a*]pyridine **1m** (111.1 mg, 0.5 mmol), S_8 (160.0 mg, 5.0 mmol) and diethyl phosphite (34.5 mg, 32 μL, 0.25 mmol) for 22 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **2m** as a Yellow solid (220.4 mg, 87%); **mp**: 216-218 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 6.4 Hz, 2H), 7.56 (app. bs, 4H), 7.07 (s, 2H), 6.89 (d, *J* = 4.7 Hz, 4H), 6.55 (d, *J* = 6.4 Hz, 2H), 2.37 (s, 6H), 2.28 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.8, 138.2, 137.9, 129.4, 128.3, 127.8(3C), 123.8, 116.1, 115.4, 21.5(2C), 21.4(2C); **HRMS** (ESI-TOF) calculated for $C_{30}H_{27}N_4S_2$ $[M+H]^+$: *m/z* 507.1677; found 507.1663.

1,2-Bis(6-chloro-2-phenylimidazo[1,2-a]pyridin-3-yl)disulfane (2n):



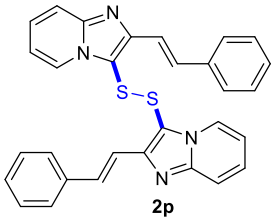
Following ***GP1*** using 6-chloro-2-phenylimidazo[1,2-*a*]pyridine **1n** (114.3 mg, 0.5 mmol), S_8 (160.0 mg, 5.0 mmol) and diethyl phosphite (34.5 mg, 32 μL, 0.25 mmol) for 22 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **2n** as a light yellow solid (155.8 mg, 60%); **mp**: 241-243 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (s, 2H), 7.59–7.44 (app. bs, 4H), 7.21–7.03 (m, 10H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.8, 131.2, 128.4(2C), 127.9(2C), 127.73, 127.71, 122.8, 121.7, 118.2(3C); **HRMS** (ESI-TOF) calculated for $C_{26}H_{17}Cl_2N_4S_2$ $[M+H]^+$: *m/z* 519.0272; found 519.0259.

1,2-Bis(6-bromo-2-phenylimidazo[1,2-a]pyridin-3-yl)disulfane (2o):



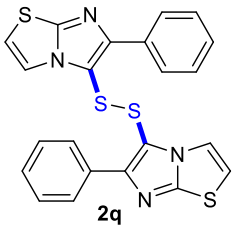
Following ***GP1*** using 6-bromo-2-phenylimidazo[1,2-*a*]pyridine **1o** (136.5 mg, 0.5 mmol), S_8 (160.0 mg, 5.0 mmol) and diethyl phosphite (34.5 mg, 32 μL, 0.25 mmol) for 22 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **2o** in traces, instead corresponding sulfide **3o** was isolated.

1,2-Bis(2-((E)-styryl)imidazo[1,2-a]pyridin-3-yl)disulfane (2p):



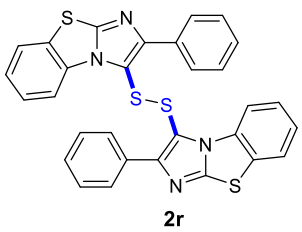
Following ***GP1*** using (*E*)-2-styrylimidazo[1,2-*a*]pyridine **1p** (110.1 mg, 0.5 mmol), S_8 (160.0 mg, 5.0 mmol) and diethyl phosphite (34.5 mg, 32 μL, 0.25 mmol) for 22 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **2p** in traces and undesired product was isolated.

1,2-Bis(6-phenylimidazo[2,1-b]thiazol-5-yl)disulfane (2q):



Following ***GP1*** using 6-phenylimidazo[2,1-*b*]thiazole **1q** (100.1 mg, 0.5 mmol), S_8 (160.0 mg, 5.0 mmol) and diethyl phosphite (34.5 mg, 32 μL, 0.25 mmol)for 22 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **2q** as a light yellow solid (120.2 mg, 52 %); **mp**: 179-181 °C [Lit.[3] 177-179 °C]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78–7.76 (m, 4H), 7.28–7.23 (m, 6H), 7.12 (d, *J* = 4.4 Hz, 2H), 6.68 (d, *J* = 4.4 Hz, 2H); **LCMS** (ESI, $M+H^+$): 463.00. *These data are consistent with literature values.*[3]

1,2-Bis(2-phenylbenzo[d]imidazo[2,1-b]thiazol-3-yl)disulfane (2r):

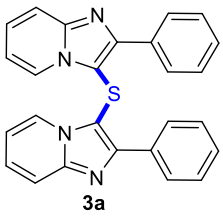


Following ***GP1*** using 2-phenylbenzo[*d*]imidazo[2,1-*b*]thiazole **1r** (100.1 mg, 0.5 mmol), S_8 (160.0 mg, 5.0 mmol) and diethyl phosphite (34.5 mg, 32 μL, 0.25 mmol)for 22 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **2r** was isolated as a impure (<20%).

General Procedure-2 (GP2) for synthesis of bis(imidazoheterocycle)-sulfanes:

A heat gun-dried Schlenk tube was charged imidazoheterocycles (0.5 mmol, 1.0 equiv), S_8 (0.5 mmol, 1.0 equiv) and diethyl phosphite (0.5 mmol, 1.0 equiv) in DMSO (2.5 mL). The reaction mixture was stirred at 120 °C for 5 h and monitored by TLC either complete or appeared to be proceeding no further progress. The mixture was quenched by addition of water (10 mL) followed by extraction with EtOAc (3x10 mL). The combined organic layers were washed with brine (2x10 mL), dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The resulting residue was subjected to flash chromatography (silica gel, eluted with 30-40% ethyl acetate/petether) to afford the corresponding sulfanes.

Bis[2-phenylimidazo[1,2-a]pyridin-3-yl]sulfane (3a):

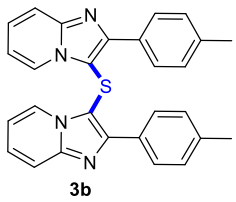


3a

Following ***GP2*** using 2-phenylimidazo[1,2-*a*]pyridine **1a** (97.1 mg, 0.5 mmol), S_8 (16.0 mg, 0.5 mmol) and diethyl phosphite (69.0 mg, 65 µL, 0.5 mmol) for 5 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **3a** as a light yellow solid (171.5 mg, 82%); **mp**: 253-255 °C [Lit.[4] 251-252 °C]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12–8.08 (m, 4H), 7.64–7.59 (m, 4H), 7.58–7.54 (m, 4H), 7.51–7.49 (m, 2H), 7.12–7.08 (m, 2H), 6.34 (td, *J* = 6.8, 1.1 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.9, 146.6, 133.9, 129.6(2C), 129.0, 128.7(2C), 126.4, 125.4, 117.4, 112.6, 107.5; **LCMS** (ESI, *M+H*$^+$): 419.10. *These data are consistent with literature values.* [4]

Gram-Scale Reaction: *Following **GP2** using 2-phenylimidazo[1,2-a]pyridine **1a** (1.16 g, 6.0 mmol, S_8 (192 mg, 6.0 mmol) and diethyl phosphite (828.0 mg, 0.77 mL, 6.0 mmol) in DMSO (25 mL) for 6 h. Purification by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **2a** (1.97 g, 78%) as a light yellow solid.*

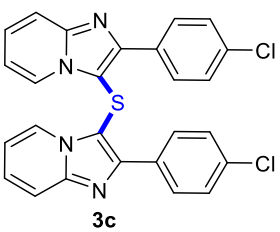
Bis[2-(p-tolyl)imidazo[1,2-a]pyridin-3-yl]sulfane (3b):



3b

Following ***GP2*** using 2-(*p*-tolyl) imidazo[1,2-*a*]pyridine **1b** (104.1 mg, 0.5 mmol), S_8 (16.0 mg, 0.5 mmol) and diethyl phosphite (69.0 mg, 0.5 mmol) for 5 h. Purified by flash column chromatography (silica gel, 30% EtOAc in petether) yielded title compound **3b** as a light yellow solid (177.1 mg, 77%); **mp**: 259-261 °C [Lit.[4] 263-264 °C]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 4H), 7.59 (d, *J* = 6.9 Hz, 2H), 7.48 (d, *J* = 9.0 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 4H), 7.10–7.06 (m, 2H), 6.35 (td, *J* = 6.8, 1.1 Hz, 2H), 2.51 (s, 6H). LCMS (ESI, M$^+$): 446.11. *These data are consistent with literature values.* [4]

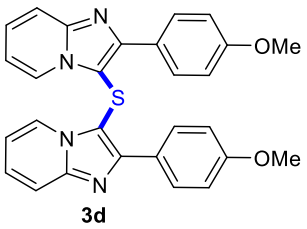
Bis[2-(4-chlorophenyl)imidazo[1,2-a]pyridin-3-yl]sulfane (3c):



3c

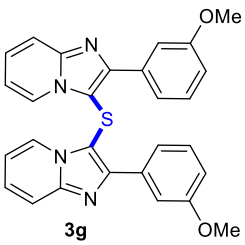
Following ***GP2*** using 2-(4-chlorophenyl)imidazo[1,2-*a*]pyridine **1c** (114.3 mg, 0.5 mmol), S_8 (16.0 mg, 0.5 mmol) and diethyl phosphite (69.0 mg, 0.5 mmol) for 5 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **3c** as a light yellow color solid (155.9 mg, 64%); **mp**: 293-295 °C [Lit.[4] 296-297 °C]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 4H), 7.61–7.57 (m, 6H), 7.52 (d, *J* = 9.0 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 2H), 6.46 (t, *J* = 6.7 Hz, 2H); **LCMS** (ESI, *M*$^+$*):* 487.10. *These data are consistent with literature values.* [4]

Bis[2-(4-methoxyphenyl)imidazo[1,2-a]pyridin-3-yl]sulfane (3d):



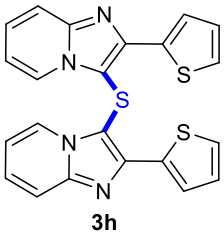
Following ***GP2*** using 2-(4-methoxyphenyl)imidazo[1,2-a]pyridine **1d** (112.1 mg, 0.5 mmol), S_8 (16.0 mg, 0.5 mmol) and diethyl phosphite (69.0 mg, 65 µL, 0.5 mmol) for 5 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **3d** as a brown solid (155.5 mg, 65%); mp: 222-224 °C [Lit.[4] 224-225 °C]; **^{1}H NMR** (400 MHz, CDCl3) δ 8.09–8.07 (m, 4H), 7.61 (d, *J* = 6.9 Hz, 2H), 7.47 (d, *J* = 9.0 Hz, 2H), 7.15–7.11 (m, 4H), 7.10–7.06 (m, 2H), 6.39 (td, *J* = 6.9, 1.0 Hz, 2H), 3.94 (s, 6H); **LCMS** (ESI, *M+H⁺):* 479.13. *These data are consistent with literature values.*[4]

Bis[2-(3-methoxyphenyl)imidazo[1,2-a]pyridin-3-yl]sulfane (3g):



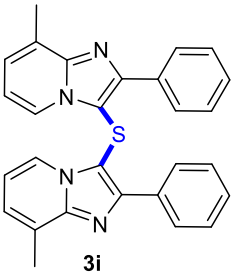
Following ***GP2*** using 2-(3-methoxyphenyl)imidazo[1,2-*a*]pyridine **1g** (112.1 mg, 0.5 mmol), S_8 (16.0 mg, 0.5 mmol) and diethyl phosphite (69.0 mg, 65 µL, 0.5 mmol) for 5 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **3g** as a yellow color solid (186.6 mg, 78%); **mp**: 149-151°C [Lit.[4] 153-154 °C]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.5 Hz, 2H), 7.65–7.60 (m, 4H), 7.54–7.49 (m, 4H), 7.12–7.09 (m, 4H), 6.39 (t, *J* = 6.7 Hz, 2H), 3.94 (s, 6H). **LCMS** (ESI, *M+H⁺):* 479.19. *These data are consistent with literature values.* [4]

Bis[2-(thiophen-2-yl)imidazo[1,2-a]pyridin-3-yl]sulfane (3h):



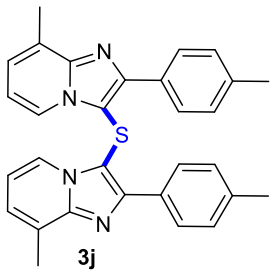
Following ***GP2*** using 2-(thiophen-2-yl)imidazo[1,2-*a*]pyridine **1h** (100.1 mg, 0.5 mmol), S_8 (16.0 mg, 0.5 mmol) and diethyl phosphite (69.0 mg, 65 µL, 0.5 mmol) for 5 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **3h** as a yellow color solid (157.1 mg, 73%); **mp**: 211-213 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 3.5 Hz, 2H), 7.93 (d, *J* = 6.8 Hz, 2H), 7.55–7.49 (m, 4H), 7.28 (t, *J* = 4.2 Hz, 2H), 7.12 (t, *J* = 7.7 Hz, 2H), 6.54 (t, *J* = 6.8 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.9, 145.3, 136.6, 128.0, 127.5(2C), 126.8, 125.3, 117.4, 113.3, 104.6; **HRMS** (ESI-TOF) calculated for $C_{22}H_{15}N_4S$ $[M+H]^+$: *m/z* 431.0459; found 431.0443.

Bis(8-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)sulfane (3i):



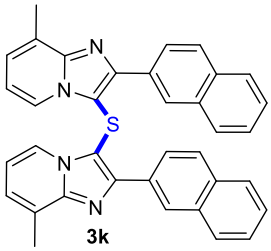
Following ***GP2*** using 8-methyl-2-phenylimidazo[1,2-*a*]pyridine **1i** (104.1 mg, 0.5 mmol), S_8 (16.0 mg, 0.5 mmol) and diethyl phosphite (69.0 mg, 65 µL, 0.5 mmol) for 5 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **3i** as a brown color solid (136.2 mg, 61%); **mp**: 214-216 °C [Lit.[4] 216-217 °C]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 4H), 7.59 (d, *J* = 6.9 Hz, 2H), 7.48 (d, *J* = 9.0 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 4H), 7.09–7.05 (m, 2H), 6.35 (td, *J* = 6.8, 0.9 Hz, 2H), 2.51 (s, 6H); **LCMS** (ESI, *M+H⁺*): 447.20. *These data are consistent with literature values.* [4]

Bis[8-methyl-2-(p-tolyl)imidazo[1,2-a]pyridin-3-yl]sulfane (3j):



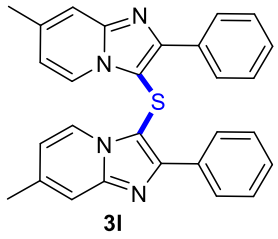
Following ***GP2*** using 8-methyl-2-(*p*-tolyl)imidazo[1,2-*a*]pyridine **1j** (111.1 mg, 0.5 mmol), S_8 (16.0 mg, 0.5 mmol) and diethyl phosphite (69.0 mg, 65 μL, 0.5 mmol) for 5 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **3j** as a white color solid (151.7 mg, 64%); **mp**: 236-238 °C [Lit.[4] 239-240 °C]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 4H), 7.46 (d, *J* = 6.8 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 4H), 6.86 (d, *J* = 6.9 Hz, 2H), 6.27 (t, *J* = 6.9 Hz, 2H), 2.51 (s, 12H); **LCMS** (ESI, *M+H*$^+$): 475.20. *These data are consistent with literature values.* [4]

Bis[8-methyl-2-(naphthalen-2-yl)imidazo[1,2-a]pyridin-3-yl]sulfane (3k):



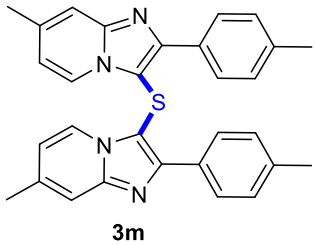
Following ***GP2*** using 8-methyl-2-(naphthalen-2-yl)imidazo[1,2-*a*]pyridine **1k** (129.1 mg, 0.5 mmol), S_8 (16.0 mg, 0.5 mmol) and diethyl phosphite (69.0 mg, 65 μL, 0.5 mmol) for 5 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **3k** as a yellow color (224.1 mg, 82%); **mp**: 199-201°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (s, 2H), 8.28 (dd, *J* = 8.5, 1.7 Hz, 2H), 8.08 (d, *J* = 8.6 Hz, 2H), 8.06–8.02 (m, 2H), 8.01–7.97 (m, 2H), 7.61–7.58 (m, 4H), 7.42 (d, *J* = 6.8 Hz, 2H), 6.83 (d, *J* = 6.9 Hz, 2H), 6.06 (t, *J* = 6.9 Hz, 2H), 2.53 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.4, 147.0, 133.53, 133.47, 131.7, 129.1, 128.8, 128.3, 128.0, 127.5, 127.4, 126.7, 126.5, 125.3, 123.3, 112.7, 107.9, 16.9; **HRMS** (ESI-TOF) calculated for $C_{36}H_{27}N_4S$ [M+H]$^+$: *m/z* 547.1956; found 547.1948.

Bis(7-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)sulfane (3l):



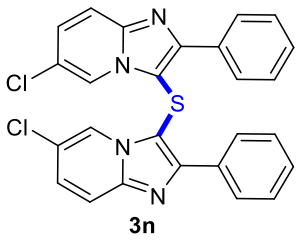
Following ***GP2*** using 7-methyl-2-phenylimidazo[1,2-*a*]pyridine **1l** (104.1 mg, 0.5 mmol), S_8 (16.0 mg, 0.5 mmol) and diethyl phosphite (69.0 mg, 65 μL, 0.5 mmol) for 5 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **3l** as a yellow solid (196.4 mg, 88%); **mp**: 199-201 °C [Lit.[4] 197-198 °C]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11–8.08 (m, 4H), 7.62–7.58 (m, 4H), 7.55–7.51 (m, 2H), 7.40 (tt, *J* = 7.2, 1.32 Hz, 2H), 7.24 (s, 2H), 6.17 (dd, *J* = 7.0, 1.6 Hz, 2H), 2.25 (s, 6H); **LCMS** (ESI, *M+H*$^+$): 447.15. *These data are consistent with literature values.* [4]

Bis[7-methyl-2-(p-tolyl)imidazo[1,2-a]pyridin-3-yl]sulfane (3m):



Following ***GP2*** using 7-methyl-2-(*p*-tolyl)imidazo[1,2-*a*]pyridine **1m** (111.1 mg, 0.5 mmol), S_8 (16.0 mg, 0.5 mmol) and diethyl phosphite (69.0 mg, 65 μL, 0.5 mmol) for 5 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **3m** as a yellow color solid (161.3 mg, 68%); **mp**: 227-229 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 4H), 7.44 (d, *J* = 7.1 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 4H), 7.23 (s, 2H), 6.19 (dd, *J* = 7.0, 1.6 Hz, 2H), 2.51 (s, 6H), 2.26 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.7, 147.0, 138.7, 137.5, 131.1, 129.39(2C), 129.36(2C), 124.7, 115.9, 115.2, 106.3, 21.6, 21.3; **HRMS** (ESI-TOF) calculated for $C_{30}H_{27}N_4S$ [M+H]$^+$: *m/z* 475.1956; found 475.1945.

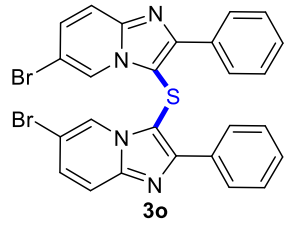
Bis(6-chloro-2-phenylimidazo[1,2-a]pyridin-3-yl)sulfane (3n):



3n

Following ***GP2*** using 6-chloro-2-phenylimidazo[1,2-*a*]pyridine **1n** (114.3 mg, 0.5 mmol), S_8 (16.0 mg, 0.5 mmol) and diethyl phosphite (69.0 mg, 65 µL, 0.5 mmol) for 5 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **3n** as a white solid (155.9 mg, 64 %); **mp**: 239-241 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.1 Hz, 4H), 7.65 (t, *J* = 7.3 Hz, 4H), 7.59 (d, *J* = 7.3 Hz, 2H), 7.57 (d, *J* = 1.2 Hz, 2H), 7.45 (d, *J* = 9.4 Hz, 2H), 7.08 (dd, *J* = 9.4, 1.9 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.0, 145.1, 133.1, 129.6, 129.4(2C), 129.2(2C), 128.1, 123.8, 121.4, 117.9, 107.8; **HRMS** (ESI-TOF) calculated for $C_{26}H_{17}Cl_2N_4S$ $[M+H]^+$: *m/z* 487.0551; found 487.0539.

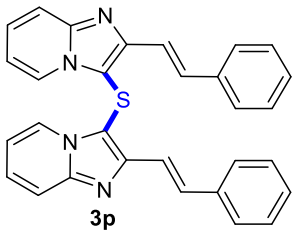
Bis(6-bromo-2-phenylimidazo[1,2-a]pyridin-3-yl)sulfane (3o):



3o

Following **GP1** using 6-bromo-2-phenyl-imidazo[1,2-*a*]pyridine **1o** (136.5 mg, 0.5 mmol, S_8 (16.0 mg, 0.5 mmol) and diethyl phosphite (69.0 mg, 65 µL, 0.5 mmol) for 5 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **3o** as a white solid; (169.2 mg, 59%); **mp**: 250-252 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.1 Hz, 4H), 7.73 (d, *J* = 1.1 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 4H), 7.40 (tt, *J* = 7.6, 1.2, 2H), 7.41 (d, *J* = 9.8 Hz, 2H), 7.19 (dd, *J* = 9.4, 1.8 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.7, 145.2, 133.0, 130.3, 129.7, 129.4(2C), 129.3(2C), 126.0, 118.2, 107.9, 107.4; **HRMS** (ESI-TOF) calculated for $C_{26}H_{17}Br_2N_4S$ $[M+H]^+$: m/z 573.9462; found 574.9535.

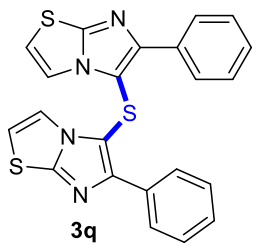
Bis[2-[(E)-styryl]imidazo[1,2-a]pyridin-3-yl]sulfane (3p):



3p

Following ***GP2*** using (*E*)-2-styrylimidazo[1,2-*a*]pyridine **1p** (110.1 mg, 0.5 mmol), S_8 (16.0 mg, 0.5 mmol) and diethyl phosphite (69.0 mg, 65 µL, 0.5 mmol) for 5 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **3p** as a yellow color solid (152.9 mg, 65%); **mp**: 237-239 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 6.4 Hz, 2H), 7.81 (q, *J* = 16.0 Hz, 4H), 7.69 (d, *J* = 6.6 Hz, 4H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 7.3 Hz, 6H), 7.22 (t, *J* = 7.8 Hz, 2H), 6.78 (t, *J* = 6.5 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.7, 147.3, 136.9, 133.8, 129.0(2C), 128.6, 127.2(2C), 127.0, 124.4, 117.59, 117.56, 113.3, 107.6; **HRMS** (ESI-TOF) calculated for $C_{30}H_{23}N_4S$ $[M+H]^+$: *m/z*471.1643; found 471.1643.

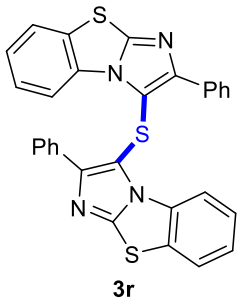
Bis(6-phenylimidazo[2,1-b]thiazol-5-yl)sulfane (3q):



3q

Following ***GP2*** using 6-phenylimidazo[2,1-*b*]thiazole **1q** (100.1 mg, 0.5 mmol), S_8 (16.0 mg, 0.5 mmol) and diethyl phosphite (69.0 mg, 65 µL, 0.5 mmol) for 5 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **3q** as a light yellow solid (137.7 mg, 64%); **mp**: 227-229°C [Lit.[4] 230-231°C]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08–8.06 (m, 4H), 7.56–7.53 (m, 4H), 7.46 (tt, *J* = 7.4, 1.2 Hz, 2H), 6.52 (d, *J* = 4.5 Hz, 2H), 6.48 (d, *J* = 4.5 Hz, 2H); **LCMS** (ESI, *M+H*$^+$): 431.05. *These data are consistent with literature values.*[4]

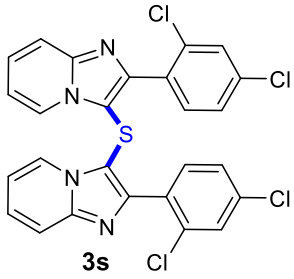
Bis(2-phenylbenzo[d]imidazo[2,1-b]thiazol-3-yl)sulfane (3r):



3r

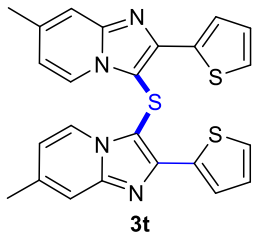
Following ***GP2*** using 2-phenylbenzo[*d*]imidazo[2,1-*b*]thiazole **1r** (125.1 mg, 0.5 mmol), S_8 (16.0 mg, 0.5 mmol) and diethyl phosphite (69.0 mg, 65 µL, 0.5 mmol) for 5 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **3r** as a light yellow solid (111.4 mg, 42%); **mp**: 251-253 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 2H), 7.76–7.72 (m, 4H), 7.59 (dd, *J* = 8.0, 0.7 Hz, 2H), 7.28–7.26 (m, 6H), 7.24 (dd, *J* = 8.0, 1.1 Hz, 2H), 7.04 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.6, 149.7, 133.3, 133.2, 129.8, 128.8(2C), 128.5, 128.3(2C), 126.0, 124.9, 123.9, 114.9, 112.0; **HRMS** (ESI-TOF) calculated for $C_{30}H_{19}N_4S_3$ $[M+H]^+$: *m/z* 531.0772; found 531.0762.

Bis[2-(2,4-dichlorophenyl)imidazo[1,2-a]pyridin-3-yl]sulfane (3s):



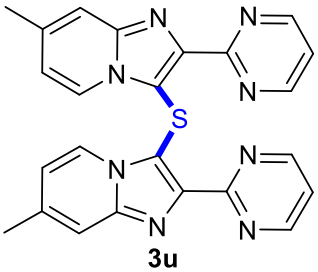
Following ***GP2*** using 2-(2,4-dichlorophenyl)imidazo[1,2-*a*]pyridine **1s** (131.5 mg, 0.5 mmol), S_8 (16.0 mg, 0.5 mmol) and diethyl phosphite (69.0 mg, 65 µL, 0.5 mmol) for 5 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **3s** as a light yellow solid (170.1 mg, 61%); **mp**: 157-159 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61–7.58 (m, 4H), 7.56 (d, *J* = 9.0 Hz, 2H), 7.37 (d, *J* = 1.1 Hz, 4H), 7.25–7.21 (m, 2H), 6.63 (td, *J* = 6.8, 1.1 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.0, 146.3, 135.7, 135.1, 133.5, 131.6, 129.9, 127.1, 126.4, 124.2, 117.9, 113.2, 109.9; **HRMS** (ESI-TOF) calculated for $C_{26}H_{15}Cl_4N_4S$ $[M+H]^+$: *m/z* 554.9766; found 554.9772.

Bis[7-methyl-2-(thiophen-2-yl)imidazo[1,2-a]pyridin-3-yl]sulfane (3t):



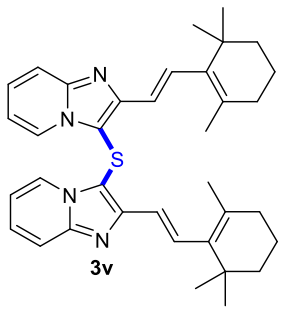
Following ***GP2*** using 7-methyl-2-(thiophen-2-yl)imidazo[1,2-*a*]-pyridine **1t** (107.1 mg, 0.5 mmol), S_8 (16.0 mg, 0.5 mmol) and diethyl phosphite (69.0 mg, 65 µL, 0.5 mmol) for 5 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **3t** as a yellow color solid (126.1 mg, 55%); **mp**: 183-185 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (s, 2H), 7.78 (d, *J* = 6.7 Hz, 2H), 7.53 (d, *J* = 4.4 Hz, 2H), 7.27 (app. bs, 4H), 6.38 (d, *J* = 6.6 Hz, 2H), 2.26 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.3, 145.0, 138.1, 136.8, 128.0, 127.24, 127.20, 124.5, 115.9(2C), 104.1, 21.4; **HRMS** (ESI-TOF) calculated for $C_{24}H_{19}N_4S_3$ $[M+H]^+$: *m/z* 459.0772; found 459.0756.

Bis[7-methyl-2-(pyrimidin-2-yl)imidazo[1,2-a]pyridin-3-yl]sulfane (3u):



Following ***GP2*** using 7-methyl-2-(pyrimidin-2-yl)imidazo[1,2-*a*]pyridine **1u** (105.1 mg, 0.5 mmol), S_8 (16.0 mg, 0.5 mmol) and diethyl phosphite (69.0 mg, 65 µL, 0.5 mmol) for 5 h. Purified by flash column chromatography (silica gel, 50% EtOAc in petether) yielded title compound **3u** as a yellow color solid (123.8 mg, 55%); **mp**: 226-228 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.48 (d, *J* = 1.2 Hz, 2H), 8.63 (s, 2H), 8.58 (d, *J* = 2.4 Hz, 2H), 8.54 (d, *J* = 7.1 Hz, 2H), 7.33 (s, 2H), 6.51 (d, *J* = 7.0 Hz, 2H), 2.32 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.1, 147.2, 145.2, 145.0, 143.6, 143.5, 138.3, 125.3, 116.5, 116.1, 109.1, 21.4; **HRMS** (ESI-TOF) calculated for $C_{24}H_{19}N_8S$ $[M+H]^+$: *m/z* 451.1453; found 451.1442.

Bis{2-((E)-2-(2,6,6-trimethylcyclohex-1-en-1-yl)vinyl)imidazo[1,2-a]pyridin-3-yl}-sulfane (3v):

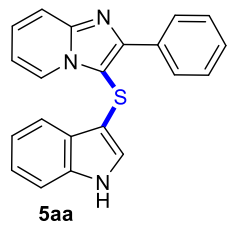


Following ***GP2*** using (*E*)-2-(2-(2,6,6-trimethylcyclohex-1-en-1-yl)vinyl) imidazo[1,2-*a*]pyridine **1v** (133.1 mg, 0.5 mmol), S_8 (16.0 mg, 0.5 mmol), diethyl phosphite (69.0 mg, 65 μL, 0.5 mmol) for 5 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **3v** as a yellow color solid (132.2 mg, 47%); **mp**: 197-199 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 6.8 Hz, 2H), 7.52 (d, *J* = 9.0 Hz, 2H), 7.45 (d, *J* = 16.0 Hz, 2H), 7.20–7.16 (m, 2H), 7.09 (d, *J* = 16.0 Hz, 2H), 6.68 (td, *J* = 6.8, 1.0 Hz, 2H), 2.13 (t, *J* = 6.0 Hz, 4H), 1.94 (s, 6H), 1.70 (quintet, *J* = 6.4 Hz, 4H), 1.59–1.54 (m, 4H), 1.20 (s, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.1, 147.2, 138.1, 133.6, 130.8, 126.6, 124.8, 122.5, 117.3, 112.7, 105.8, 39.7, 34.5, 33.2, 29.2(2C), 22.1, 19.4; **HRMS** (ESI-TOF) calculated for $C_{36}H_{43}N_4S$ $[M+H]^+$: *m/z* 563.3208; found 563.3212.

General Procedure-3 (GP3) for the synthesis of imidazo[1,2-a]pyridine-indole derived sulfanes:

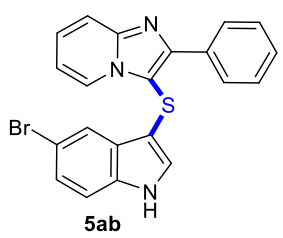
A heat gun-dried Schlenk tube was charged 1,2-bis(2-phenylimidazo[1,2-*a*]pyridin-3-yl)disulfane (0.5 mmol, 1.0 equiv), substituted indoles (0.75 mmol, 1.5 equiv) and diethyl phosphite (0.5 mmol, 1.0 equiv) in DMSO (2.5 mL). The reaction mixture was stirred at 120 ^{o}C for 15 h and monitored by TLC either complete or appeared to be proceeding no further progress. The mixture was quenched by addition of water (10 mL) followed by extraction with EtOAc (3x10 mL). The combined organic layers was washed with brine (2x10 mL), dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The resulting residue was subjected to flash chromatography (silica gel, eluted with 30-40% ethyl acetate/petether) to afford the corresponding imidazo[1,2-*a*]pyridine-indole derived thioethers.

3-*[(1H-Indol-3-yl)thio]-2-phenylimidazo[1,2-a]pyridine (5aa):*



Following ***GP3*** using 1,2-bis(2-phenylimidazo[1,2-*a*]pyridin-3-yl)disulfane **2a** (225.3 mg, 0.5 mmol), 1*H*-indole **4a** (87.8 mg, 0.75 mmol) and diethyl phosphite (69.0 mg, 65 μL, 0.5 mmol) for 15 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **5aa** as a light yellow solid (126.3 mg, 74%); **mp**: 220-222 ^{o}C; [Lit.[5] 219-221 ^{o}C]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.60 (dt, *J* = 6.8, 1.1 Hz, 1H), 8.36–8.34 (m, 2H), 8.27 (s, 1H), 7.62 (d, *J* = 9.0 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.46–7.42 (m, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.24–7.21 (m, 1H), 7.19 (d, *J* = 2.6 Hz, 1H), 7.16–7.12 (m, 1H), 7.02–6.98 (m, 1H), 6.87 (td, *J* = 6.8, 1.1 Hz, 1H); **HRMS** (ESI-TOF) calculated for $C_{21}H_{16}N_3S$ $[M+H]^+$: *m/z* 342.1059; found 342.1052. *These data are consistent with literature values.* [5]

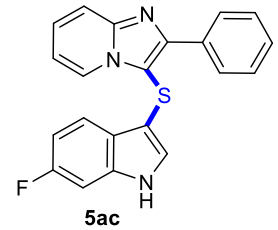
3-[(5-Bromo-1H-indol-3-yl)thio]-2-phenylimidazo[1,2-a]pyridine (5ab):



5ab

Following ***GP3*** using 1,2-bis(2-phenylimidazo[1,2-*a*]pyridin-3-yl)disulfane **2a** (225.3 mg, 0.5 mmol), 5-bromo-1*H*-indole **4b** (147.0 mg, 0.75 mmol) and diethyl phosphite (69.0 mg, 65 μL, 0.5 mmol) for 15 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **5ab** as a light yellow solid (102.9 mg, 49%); **mp**: 227-229 °C [Lit.[5] 228-230°C]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (dt, *J* = 6.8, 1.0 Hz, 1H), 8.41 (s, 1H), 8.29–8.24 (m, 2H), 7.62 (d, *J* = 9.0 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 2H), 7.50–7.45 (m, 1H), 7.38 (d, *J* = 1.8 Hz, 1H), 7.21–7.17 (m, 2H), 7.11 (d, *J* = 8.6 Hz, 1H), 6.91 (td, *J* = 6.8, 1.1 Hz, 1H); **HRMS** (ESI-TOF) calculated for $C_{21}H_{15}BrN_3S$ $[M+H]^+$: *m/z* 420.0165; found 420.1053. *These data are consistent with literature values.* [5]

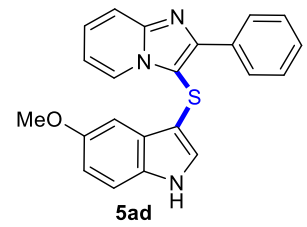
3-[(6-Fluoro-1H-indol-3-yl)thio]-2-phenylimidazo[1,2-a]pyridine (5ac):



5ac

Following ***GP3*** using 1,2-bis(2-phenylimidazo[1,2-*a*]pyridin-3-yl)disulfane **2a** (225.3 mg, 0.5 mmol), 6-fluoro-1*H*-indole **4c** (101.3 mg, 0.75 mmol) and diethyl phosphite (69.0 mg, 0.5 mmol) for 15 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **5ac** as a light yellow solid (53.4 mg, 74%); **mp**: 206-208 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.50 (s, 1H), 8.87 (d, *J* = 6.8 Hz, 1H), 8.33 (d, *J* = 7.2 Hz, 2H), 7.86 (d, *J* = 2.5 Hz, 1H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.40–7.35 (m, 1H), 7.12–7.05 (m, 2H), 6.91 (dd, *J* = 8.7, 5.4 Hz, 1H), 6.64 (td, *J* = 9.7, 2.3 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 159.0 (d, *J* = 236.0 Hz), 147.9, 145.3, 136.1 (d, *J* = 12.8 Hz), 133.8, 131.0, 128.44(2C), 128.39(2C), 126.5, 125.0, 124.3, 119.2, 119.1, 117.0, 113.1, 109.8, 108.3 (d, *J* = 24.6 Hz),101.0, 98.2 (d, *J* = 25.8 Hz); **HRMS** (ESI-TOF) calculated for $C_{21}H_{15}N_3SF$ $[M+H]^+$: *m/z* 360.0965; found 360.0965.

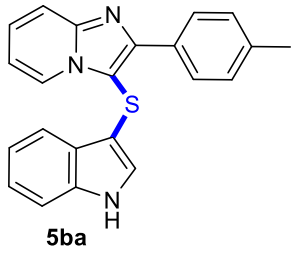
3-[(5-Methoxy-1H-indol-3-yl)thio]-2-phenylimidazo[1,2-a]pyridine (5ad):



5ad

Following ***GP3*** using 1,2-bis(2-phenylimidazo[1,2-*a*]pyridin-3-yl)disulfane **2a** (225.3 mg, 0.5 mmol), 5-methoxy-1*H*-indole **4d** (110.3 mg, 0.75 mmol) and diethyl phosphite (69.0 mg, 65 μL, 0.5 mmol) for 15 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **5ad** as a light yellow solid (131.9 mg, 71%); **mp**: 186-188°C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.31 (s, 1H), 8.94 (d, *J* = 6.3 Hz, 1H), 8.46 (d, *J* = 7.2 Hz, 2H), 7.93 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.50–7.33 (m, 3H), 7.18 (d, *J* = 8.6 Hz, 1H), 7.10–7.05 (m, 1H), 6.59 (d, *J* = 8.1 Hz, 1H), 6.44 (s, 1H), 3.15 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 153.9, 147.5, 145.3, 134.0, 131.0, 129.0, 128.6, 128.44(2C), 128.39(2C), 128.32, 128.2, 126.4, 125.1, 117.0, 113.0, 112.7, 110.1, 99.9, 99.1, 54.4; **HRMS** (ESI-TOF) calculated for $C_{22}H_{18}N_3SO$ $[M+H]^+$: *m/z* 372.1171; found 372.1165.

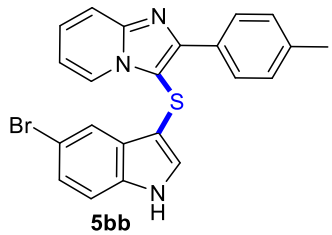
3-[(1H-Indol-3-yl)thio]-2-(p-tolyl)imidazo[1,2-a]pyridine (5ba):



5ba

Following ***GP3*** using 1,2-bis(2-(*p*-tolyl)imidazo[1,2-*a*]pyridin-3-yl)disulfane **2b** (239.3 mg, 0.5 mmol), 1*H*-indole **4a** (87.8 mg, 0.75 mmol) and diethyl phosphite (69.0 mg, 65 µL, 0.5 mmol) for 15 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **5ba** as a yellow solid (142.1 mg, 80%); **mp**: 190-192 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.44 (s, 1H), 8.86 (d, *J* = 6.6 Hz, 1H), 8.30 (d, *J* = 7.7 Hz, 2H), 7.85 (s, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.41–7.31 (m, 4H), 7.07–6.99 (m, 3H), 6.79 (t, *J* = 7.3 Hz, 1H), 2.42 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 147.8, 145.2, 137.7, 136.2, 131.1, 130.2, 129.0(2C), 128.3(2C), 127.7, 126.3, 124.9, 121.9, 119.7, 118.2, 116.9, 112.9, 112.1, 109.7, 100.6, 21.0; **HRMS** (ESI-TOF) calculated for $C_{22}H_{18}N_3S$ $[M+H]^+$: *m/z* 356.1216; found 356.1222.

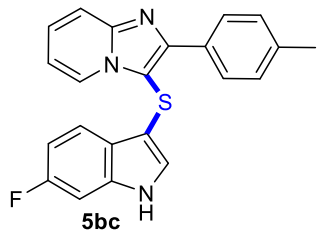
3-[(5-Bromo-1H-indol-3-yl)thio]-2-(p-tolyl)imidazo[1,2-a]pyridine (5bb):



5bb

Following ***GP3*** using 1,2-bis(2-(*p*-tolyl)imidazo[1,2-*a*]-pyridin-3-yl)disulfane **2b** (239.3 mg, 0.5 mmol), 5-bromo-1*H*-indole **4b** (147.0 mg, 0.75 mmol) and diethyl phosphite (69 mg, 65 µL, 0.5 mmol) for 15 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **5bb** as a light yellow solid (175.9 mg, 81%); **mp**: 210-212°C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.59 (s, 1H), 8.88 (d, *J* = 5.9 Hz, 1H), 8.14 (d, *J* = 7.3 Hz, 2H), 7.93 (s, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.43–7.35 (m, 3H), 7.25 (d, *J* = 8.4 Hz, 1H), 7.12–7.05 (m, 2H), 6.94 (s, 1H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 148.7, 145.3, 137.8, 134.8, 131.8, 130.9, 129.5, 129.0 (2C), 128.5 (2C), 126.4, 124.9, 124.5, 120.9, 116.9, 114.0, 113.0, 112.5, 109.6, 100.7, 21.0; **HRMS** (ESI-TOF) calculated for $C_{22}H_{17}BrN_3S$ $[M+H]^+$: *m/z* 434.0321; found 434.0321.

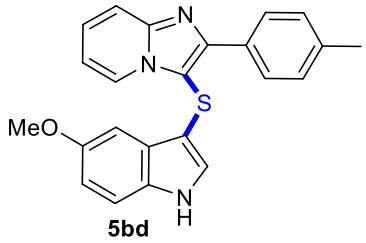
3-[(6-Fluoro-1H-indol-3-yl)thio]-2-(p-tolyl)imidazo[1,2-a]pyridine (5bc):



5bc

Following ***GP3*** using 1,2-bis(2-(*p*-tolyl)imidazo[1,2-*a*]pyridin-3-yl)disulfane **2b** (239.3 mg, 0.5 mmol), 6-fluoro-1*H*-indole **4c** (141.9 mg, 0.75 mmol) and diethyl phosphite (69.0 mg, 65 µL, 0.5 mmol) for 15 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **5bc** as a light yellow solid (141.9 mg, 76%); **mp**: 198-200°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (dt, *J* = 6.8, 1.2 Hz, 1H), 8.22 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 9.0 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.24–7.19 (m, 2H), 7.17 (d, *J* = 2.6 Hz, 1H), 6.92 (dd, *J* = 9.3, 2.2 Hz, 1H), 6.86 (td, *J* = 6.8, 1.1 Hz, 1H), 6.76–6.71 (m, 1H), 2.45 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ159.0 (d, *J* = 240.9 Hz), 147.9, 145.3, 137.7, 136.1 (d, *J* = 12.8 Hz), 130.9 (d, *J* = 15.5 Hz), 129.0(2C), 128.3(2C), 126.3, 124.9, 124.4, 119.2 (d, *J* = 10.3 Hz), 116.9, 113.0, 109.3, 108.3 (d, *J* = 24.7 Hz), 101.1,98.2 (d, *J* = 25.8 Hz), 20.9 (*one quaternary aromatic resonance could not be identified*); **HRMS** (ESI-TOF) calculated for $C_{22}H_{17}FN_3S$ $[M+H]^+$: *m/z* 374.1122; found 374.1121.

3-[(5-Methoxy-1H-indol-3-yl)thio]-2-(p-tolyl)imidazo[1,2-a]pyridine (5bd):



5bd

Following ***GP3*** using 1,2-bis(2-(*p*-tolyl)imidazo[1,2-*a*]-pyridin-3-yl)disulfane **2b** (239.3 mg, 0.5 mmol), 5-methoxy-1*H*-indole **4d** (110.3 mg, 0.75 mmol) and diethyl phosphite (69.0 mg, 65 μL, 0.5 mmol) for 15 h. Purified by flash column chromatography (silica gel, 40% EtOAc in petether) yielded title compound **5bd** as a light yellow solid (165.7 mg, 86%); **mp**: 166-168^{o}C; **^{1}H NMR** (400 MHz, 4:1 DMSO-d$_6$:DCM$^{\#}$) δ 11.32 (s, 1H), 8.93 (d, *J* = 6.8 Hz, 1H), 8.37 (d, *J* = 8.1 Hz, 2H), 7.92 (d, *J* = 2.6 Hz, 1H), 7.61 (d, *J* = 9.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.37–7.32 (m, 1H), 7.19 (d, *J* = 8.7 Hz, 1H), 7.05 (td, *J* = 6.8, 0.8 Hz, 1H), 6.61 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.48 (d, *J* = 2.2 Hz, 1H), 3.18 (s, 3H), 2.38 (s, 3H); **^{13}C NMR** (101 MHz, 4:1 DMSO-d$_6$:DCM$^{\#}$) δ 153.9, 147.7, 145.2, 137.7, 131.2, 131.0, 130.9, 128.9(2C), 128.4(3C), 126.3, 125.0, 116.9, 112.9, 112.8, 112.7, 109.8, 100.2, 99.2, 54.2, 20.8; **HRMS** (ESI-TOF) calculated for $C_{23}H_{20}N_3OS$ $[M+H]^+$: *m/z* 386.1322; found 386.1321. *$^{\#}$A mixture of DCM:DMSO-d$_6$ (4:1) used for the clear solubility and recorded the NMR for better resolution of the spectra.*

Table S1: Crystal data and structure refinement for 2i and 3a

DATA_2i		**CCDC**		**2128914**
Bond precision:		C-C = 0.0090 A		Wavelength=0.71073
Cell:	a=12.800(2)	b=13.044(2)	c=28.611(5)	
	alpha=90	beta=90	gamma=90	
Temperature:	100 K			
	Calculated		**Reported**	
Volume	4777.0(13)		4776.8(13)	
Space group	P 21 21 21		P 21 21 21	
Hall group	P 2ac 2ab		P 2ac 2ab	
Moiety formula	C28 H22 N4 S2		C28 H22 N4 S2	
Sum formula	C28 H22 N4 S2		C28 H22 N4 S2	
Mr	478.62		478.61	
Dx,g cm-3	1.331		1.331	
Z	8		8	
Mu (mm-1)	0.248		0.248	
F000	2000.0		2000.0	
F000'	2002.57			
h,k,lmax	15,15,34		15,15,34	
Nref	8422[4698]		8420	
Tmin,Tmax	0.971,0.980		0.619,0.746	
Tmin'	0.959			

Correction method= # Reported T Limits: Tmin=0.619 Tmax=0.746
AbsCorr = MULTI-SCAN				

Data completeness= 1.79/1.00		Theta(max)= 24.999		
R(reflections)= 0.0559(8354)			wR2(reflections)= 0.1503(8420)	
S = 1.263	Npar= 600			

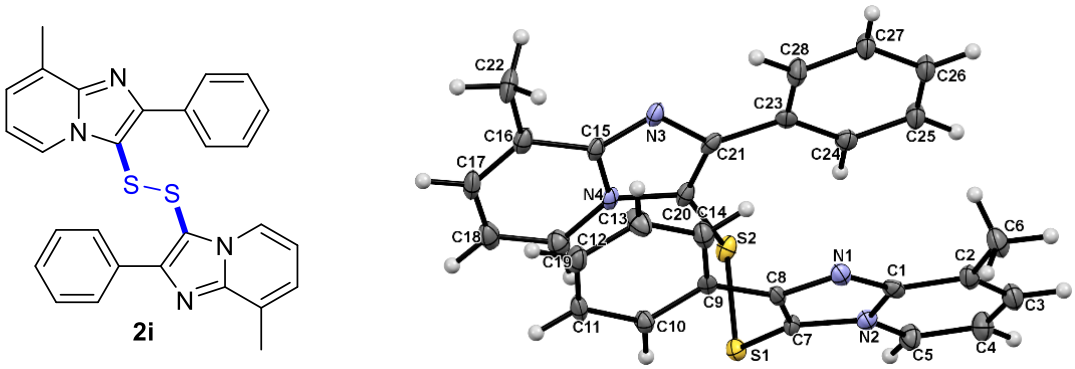


Figure S1: *ORTEP diagram of compound* ***2i****, the asymmetric unit contains two molecules for clarity one of the molecules was deleted. Herein, the ellipsoids are drawn with a 50% probability level. [Crystallization was performed by taking 30 mg of* ***2i*** *in a conical flask followed by slow addition of 20% EtOAc in petroleum ether until dissolving the compound* ***2i.*** *The obtained clear solution was kept at ambient temperature to evaporate petroleum ether and formed single-crystals as desired.]*

DATA_3a	**CCDC**	**2128915**
Bond precision:	C-C = 0.0020 A	Wavelength=0.71073
Cell:	a=11.9878(11)	b=13.8358(16)	c=12.5210(14)
	alpha=90	beta=101.924(4)	gamma=90
Temperature:	100 K		

	Calculated	Reported
Volume	2031.9(4)	2031.9(4)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C26 H18 N4 S	C26 H18 N4 S
Sum formula	C26 H18 N4 S	C26 H18 N4 S
Mr	418.50	418.50
Dx,g cm-3	1.368	1.368
Z	4	4
Mu (mm-1)	0.181	0.181
F000	872.0	872.0
F000'	872.77	
h,k,lmax	15,17,15	15,17,15
Nref	4436	4429
Tmin,Tmax	0.979,0.986	0.696,0.746
Tmin'	0.966	

Correction method= # Reported T Limits: Tmin=0.696 Tmax=0.746
AbsCorr = MULTI-SCAN	

Data completeness= 0.998	Theta(max)= 27.000
R(reflections)= 0.0409(4142)	wR2(reflections)= 0.1206(4429)
S = 1.202	Npar= 281

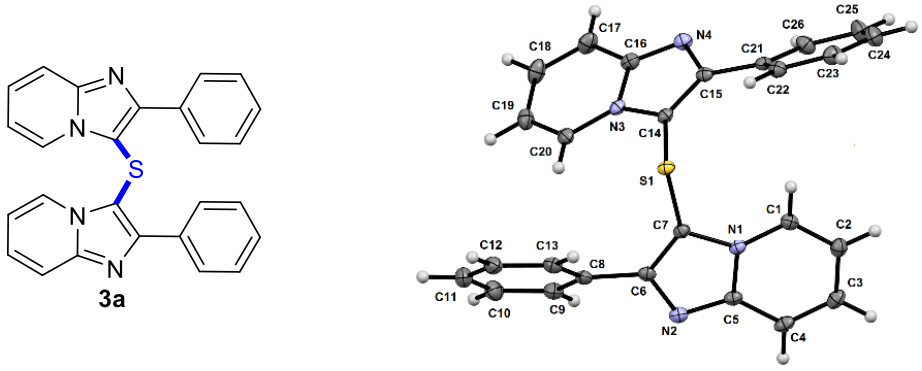


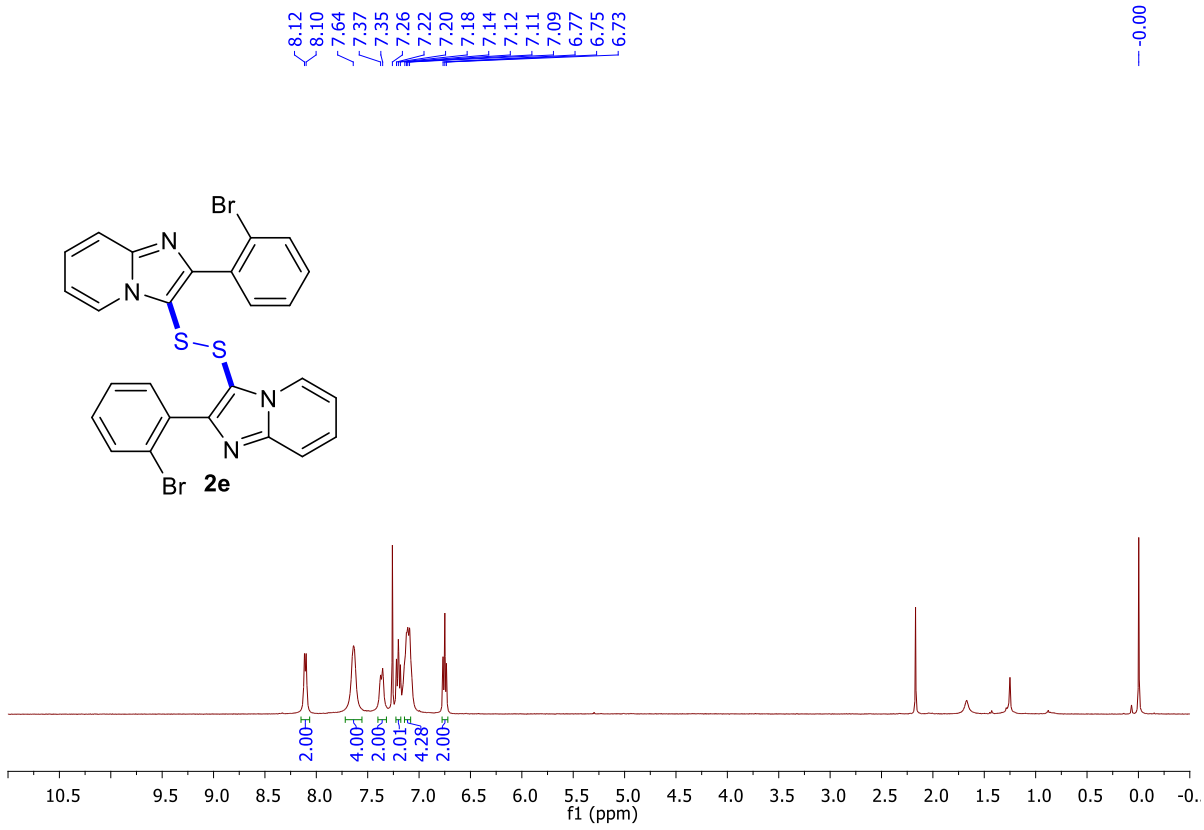
Figure S2: *ORTEP diagram of* ***3a*** *drawn at the 50% probability level.*
[Crystallization was performed by taking 30 mg of ***3a*** *in a conical flask followed by slow addition of 20% EtOAc in petroleum ether until dissolving the compound* ***3a.*** *The obtained clear solution was kept at ambient temperature to evaporate petroleum ether and formed single-crystals as desired.]*

References

1. M. H. Fisher and A. Lusi, *J. Med. Chem*., 1972, **15**, 982.
2. D. Kour, R. Khajuria and K. K. Kapoor, *Tetrahedron Lett.,* 2016, **57**, 4464.
3. S. M. A. Shakoor, D. S. Agarwal, S. Khullar, S. K. Mandal and R. Sakhuja, *Chem.–Asian J.,* 2017, **12**, 3061.
4. L.-L. Tian, S. Lu, Z.-H. Zhang, E.-L. Huang, H.-T. Yan, X. Zhu, X.-Q. Hao and M.-P. Song, *J. Org. Chem.*, 2019, **84**, 5213.
5. T. Guo, X.-N. Wei, M. Zhang, Y. Liu, L.-M. Zhu and Y.-H. Zhao, *Chem. Commun.,* 2020, **56**, 5751.

Unknown Compounds Spectra ^{1}H and ^{13}C NMR Spectra

(Note: Common laboratory solvents as trace impurities, peaks at δ 1.25 and δ 1.58 refers to grease and moisture respectively in a ***^{1}H NMR*** *recorded in $CDCl_3$ and DMSO. In a* ***^{13}C NMR*** *recorded in $CDCl_3$ a peak at δ 29.7 represents to grease; Ref. H. E. Gottlie, V. Kotlyar, A. Nudelman, J. Org. Chem., 1997, 62, 7512).*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8.10
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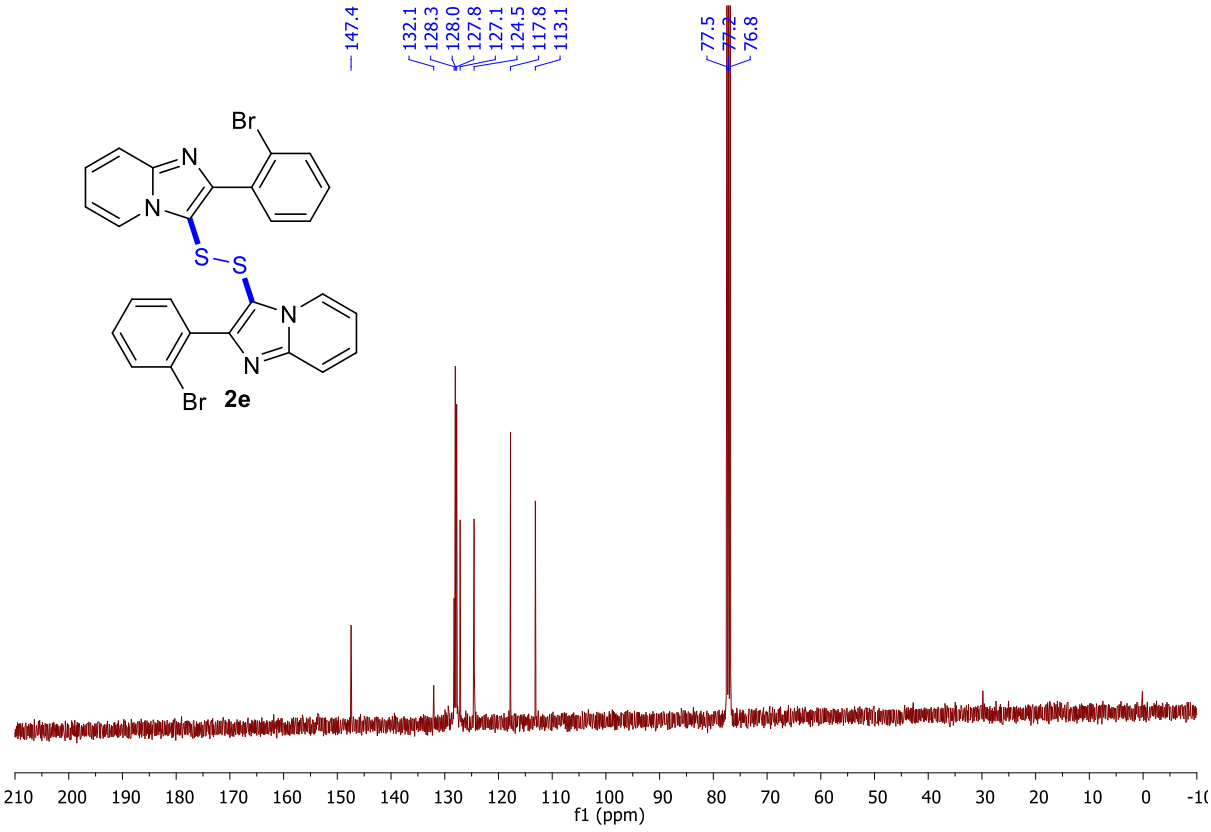
7.35
7.26
7.22
7.20
7.18
7.14
7.12
7.11
7.09
6.77
6.75
6.73
-0.00
Br
N
N
S
S
N
N
Br
2e
2.00
4.00
2.00
2.01
4.28
2.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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127.1
124.5
117.8
113.1
77.5
77.2
76.8
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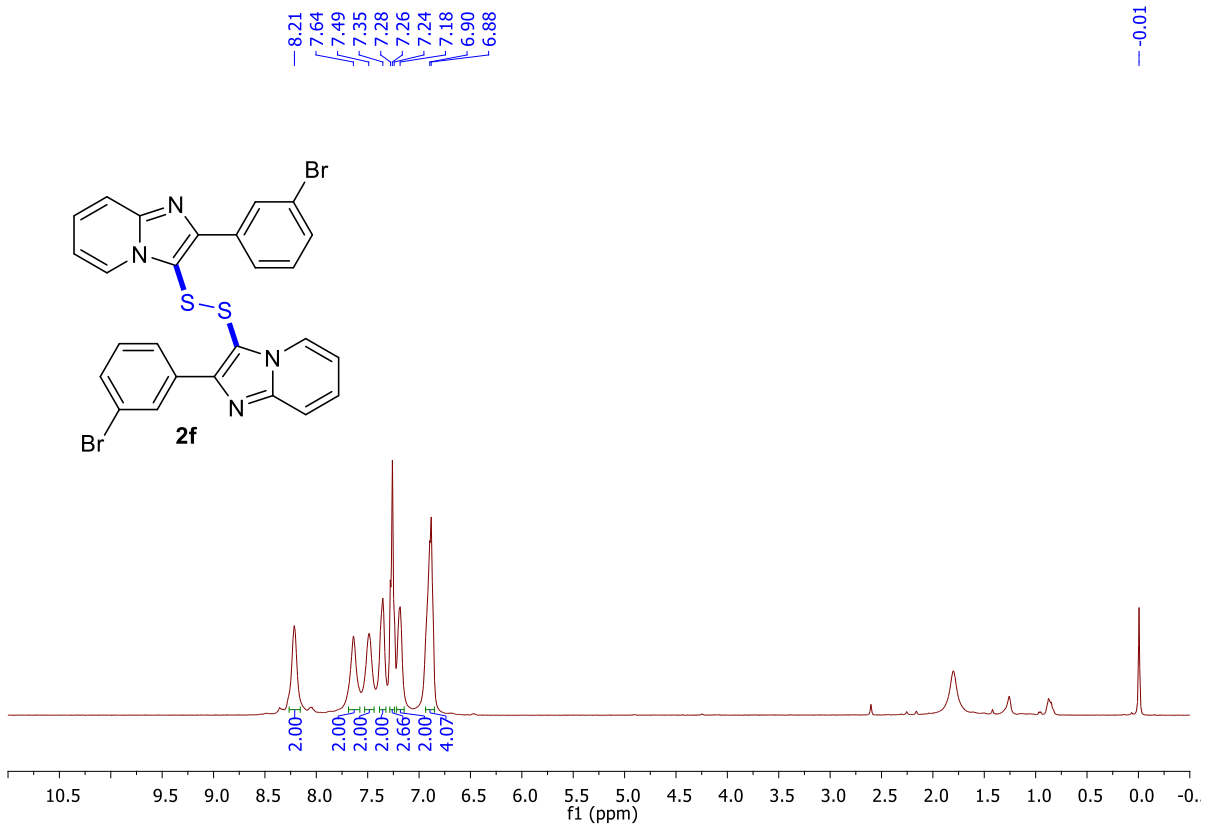
N
N
S
S
N
N
Br
2e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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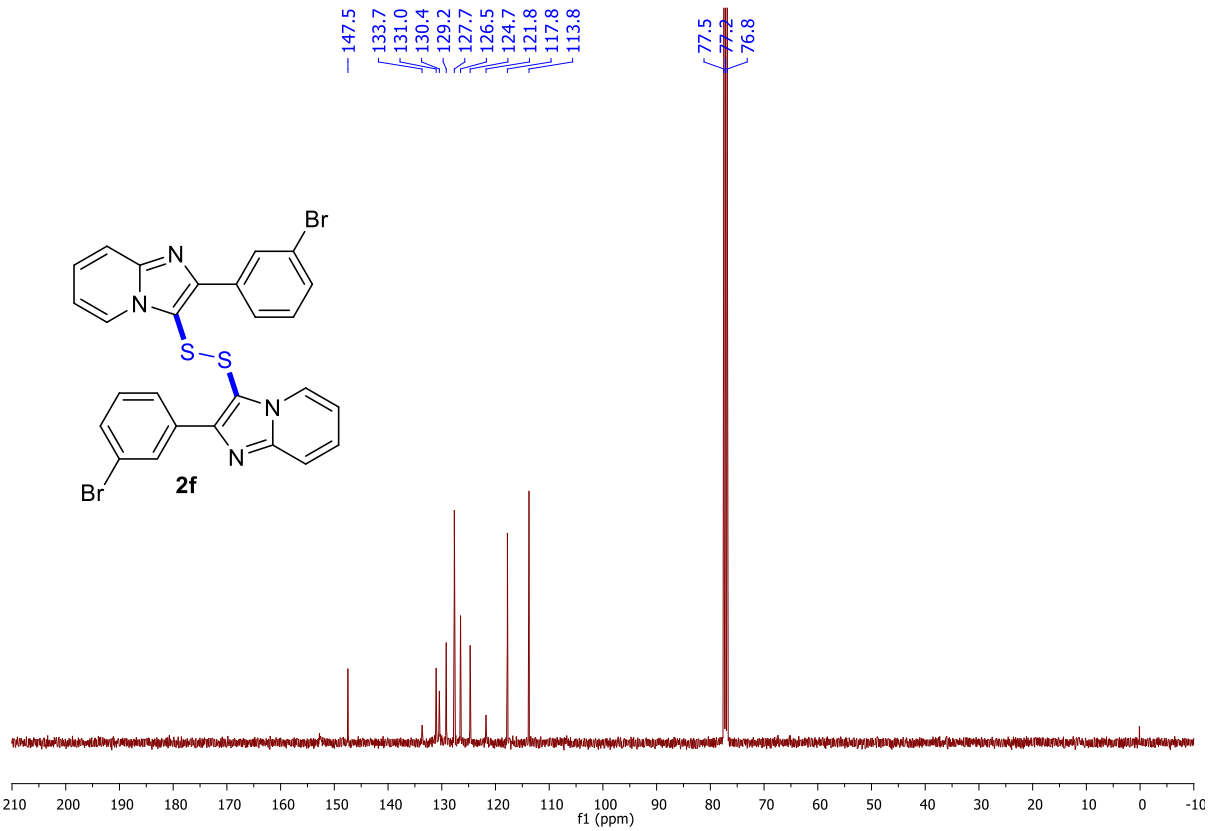
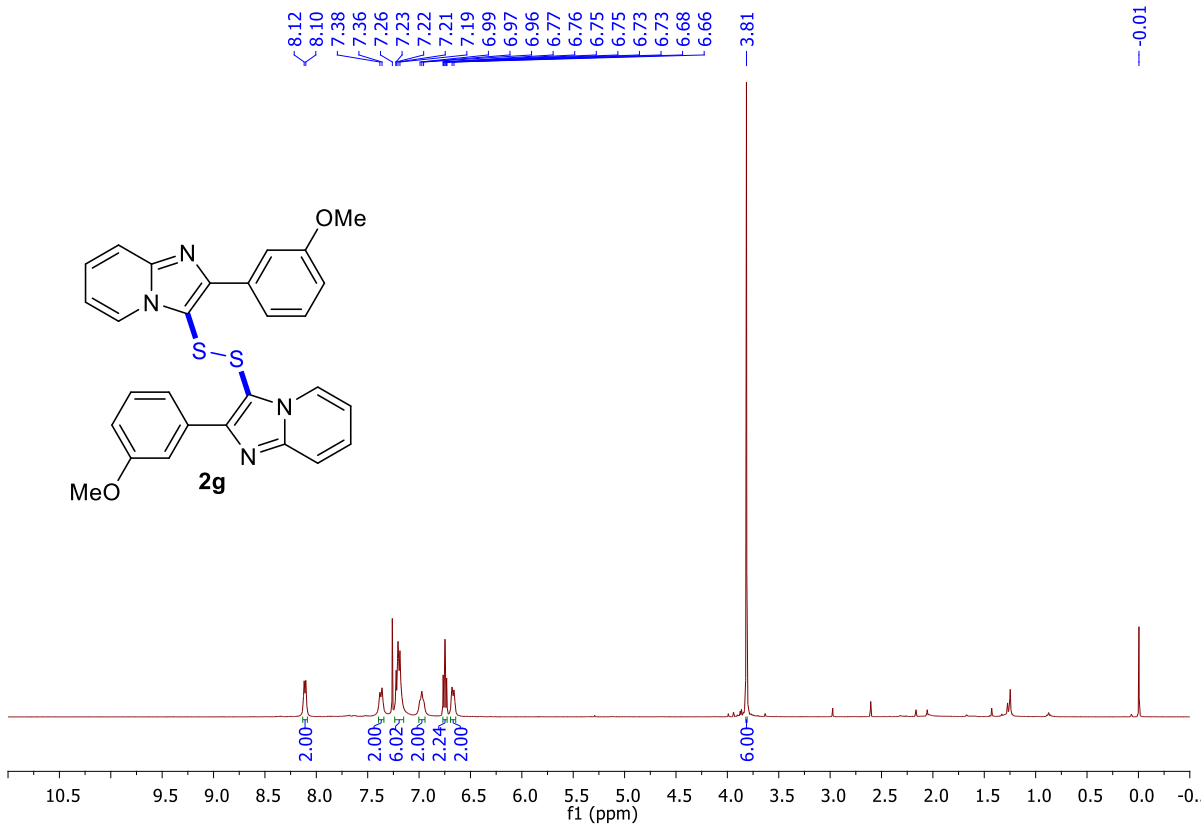
7.64
7.49
7.35
7.28
7.26
7.24
7.18
6.90
6.88
-0.01
Br
N
N
S
S
N
N
Br
2f
2.00
2.00
2.00
2.00
2.66
2.00
4.07
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


147.5
133.7
131.0
130.4
129.2
127.7
126.5
124.7
121.8
117.8
113.8
77.5
77.2
76.8
Br
N
N
S
S
N
N
Br
2f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.10
7.38
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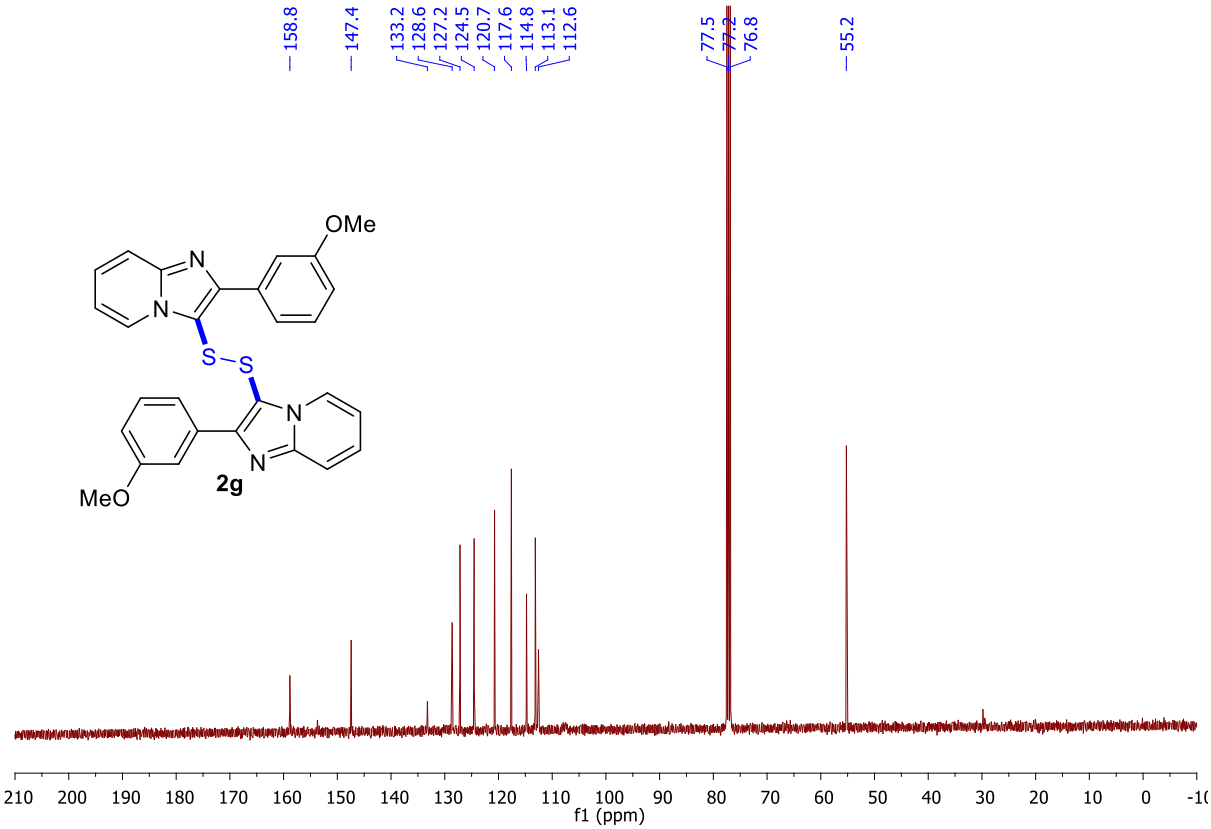
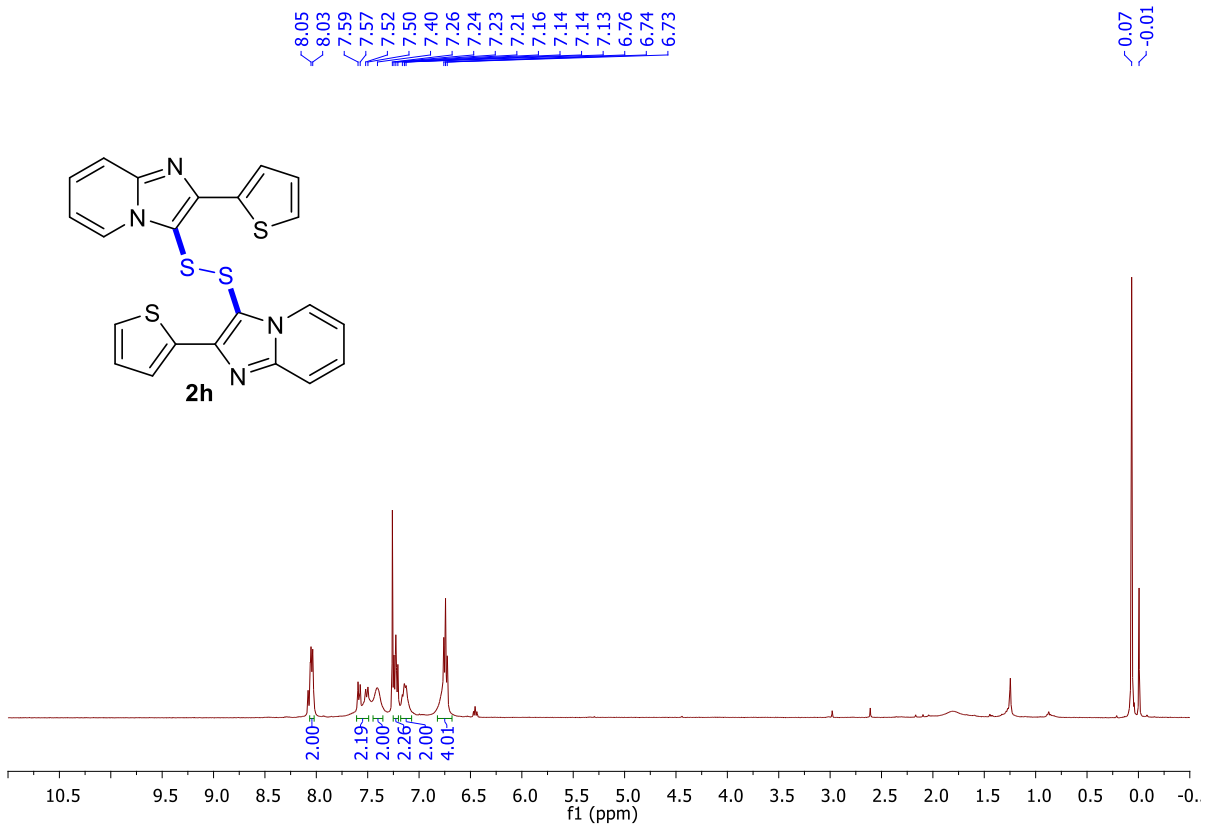
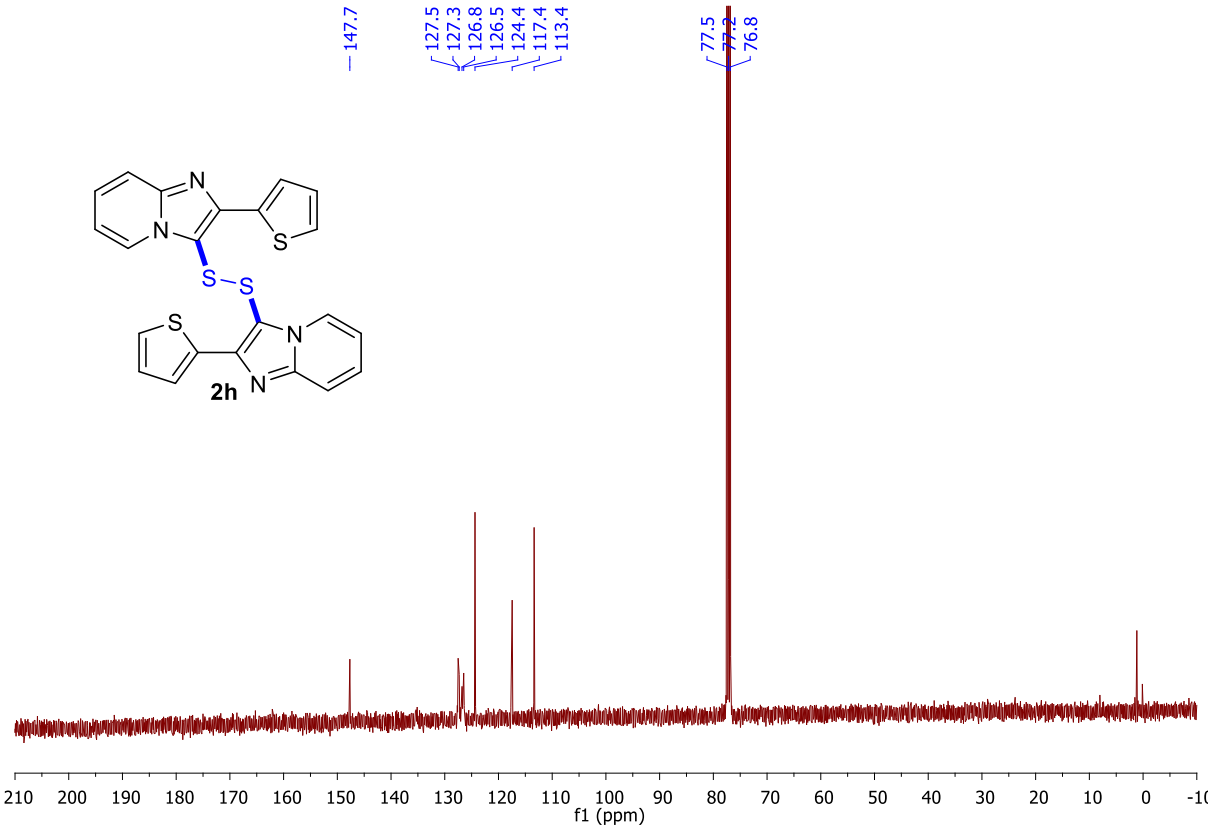
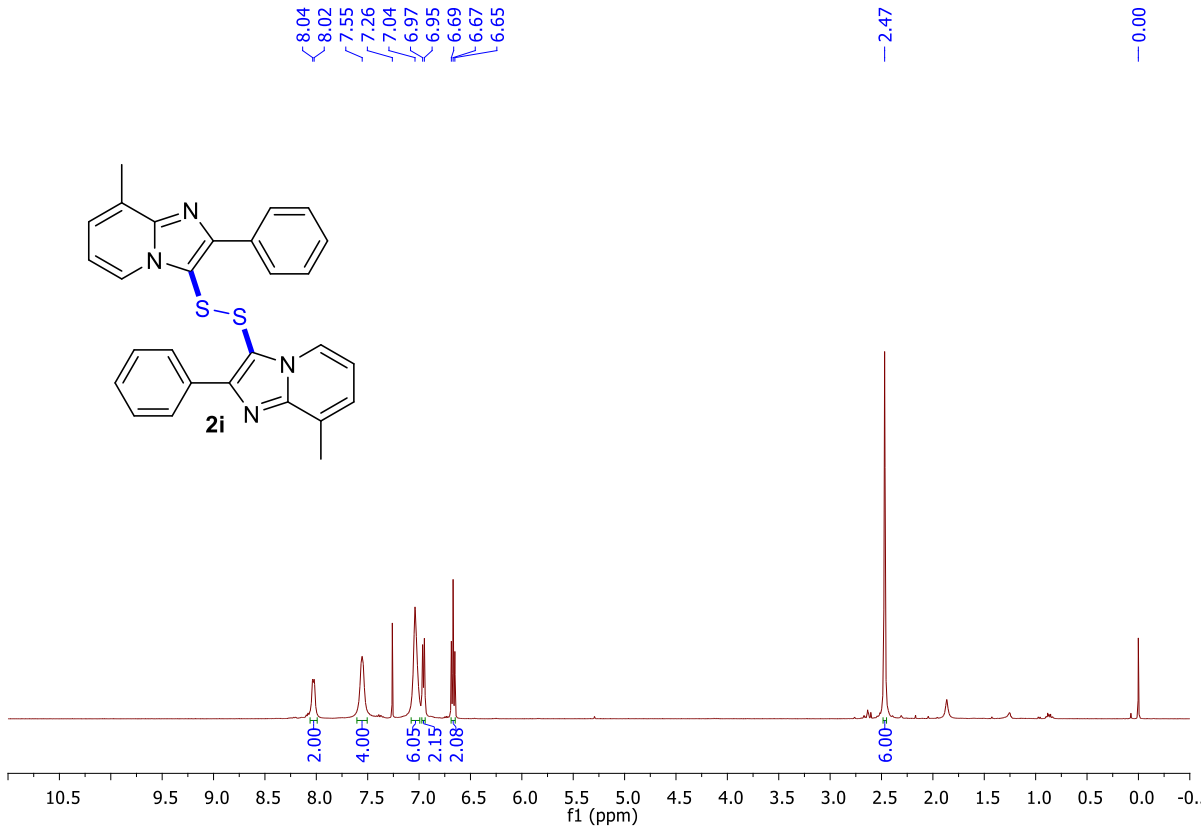
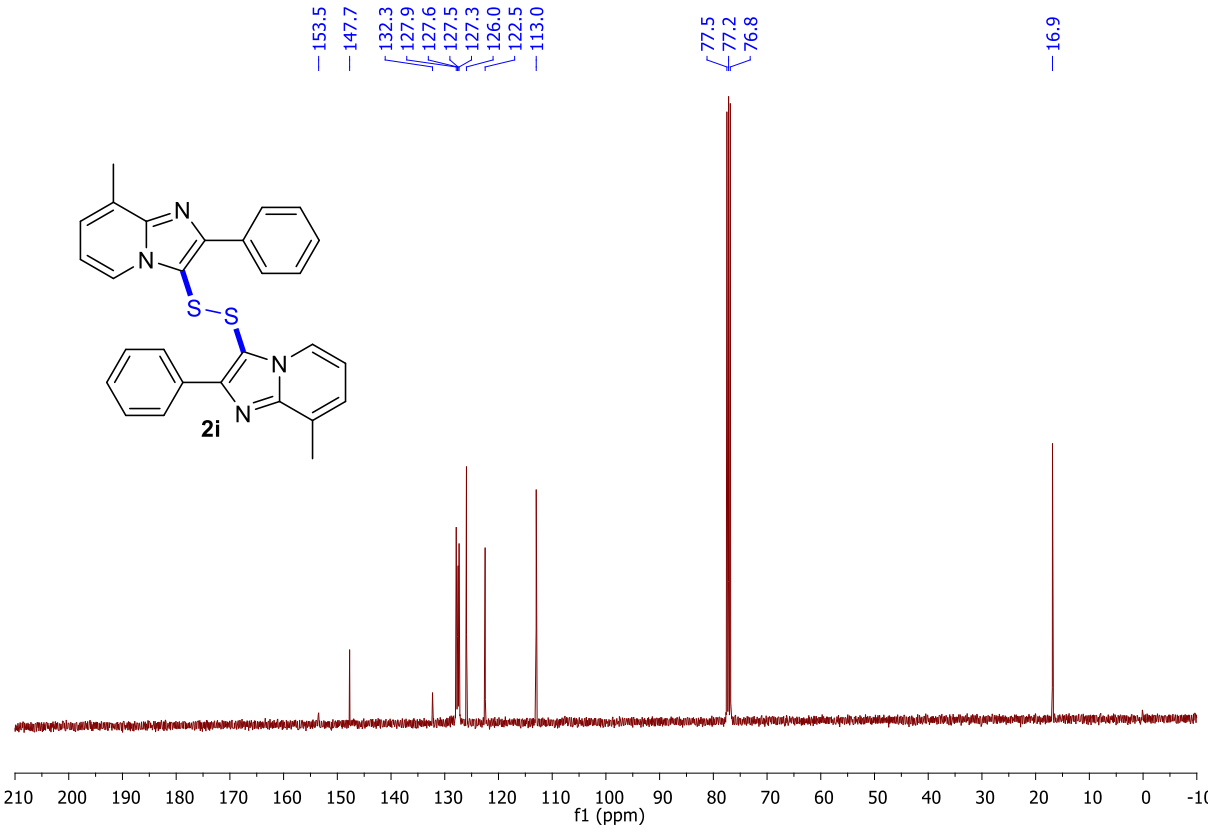
7.23
7.22
7.21
7.19
6.99
6.97
6.96
6.77
6.76
6.75
6.75
6.73
6.73
6.68
6.66
3.81
-0.01
OMe
N
N
S
S
N
N
MeO
2g
2.00
2.00
6.02
2.00
2.24
2.00
6.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

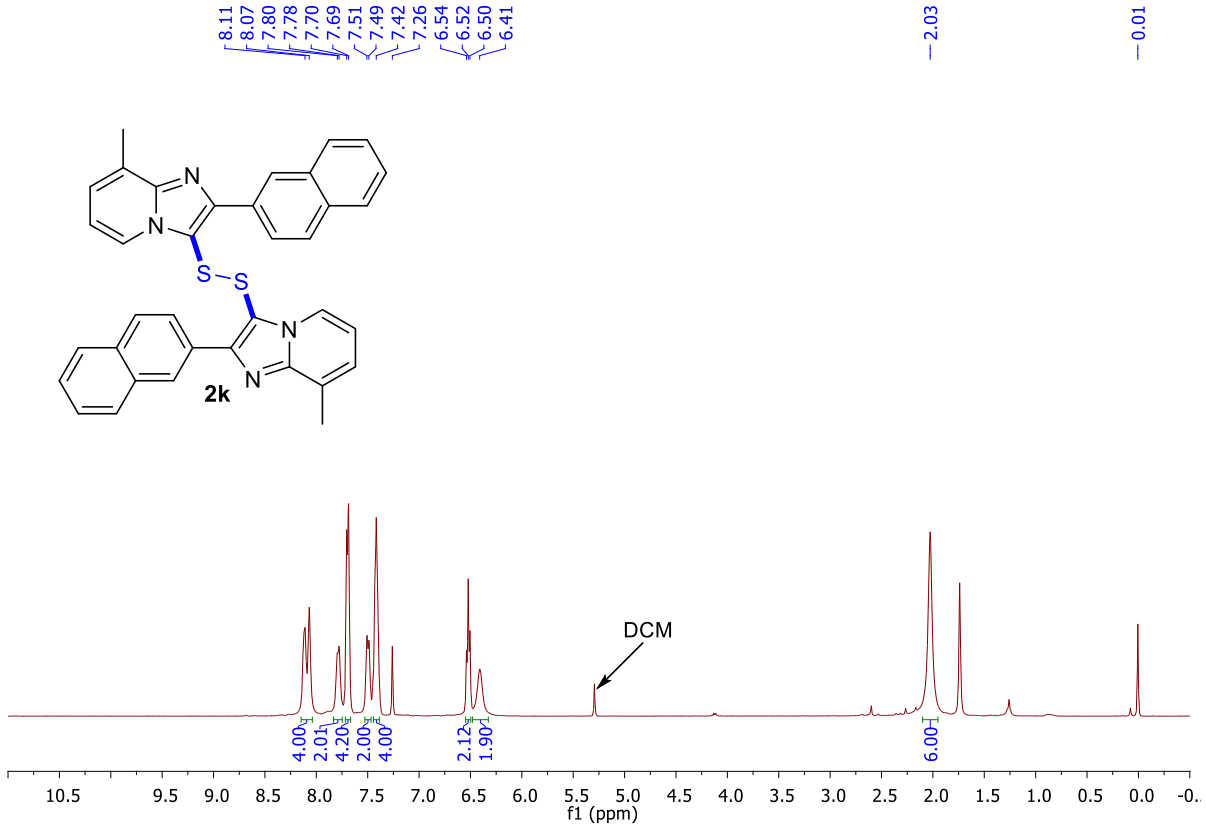

158.8
147.4
133.2
128.6
127.2
124.5
120.7
117.6
114.8
113.1
112.6
77.5
77.2
76.8
55.2
OMe
N
N
S
S
N
N
MeO
2g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

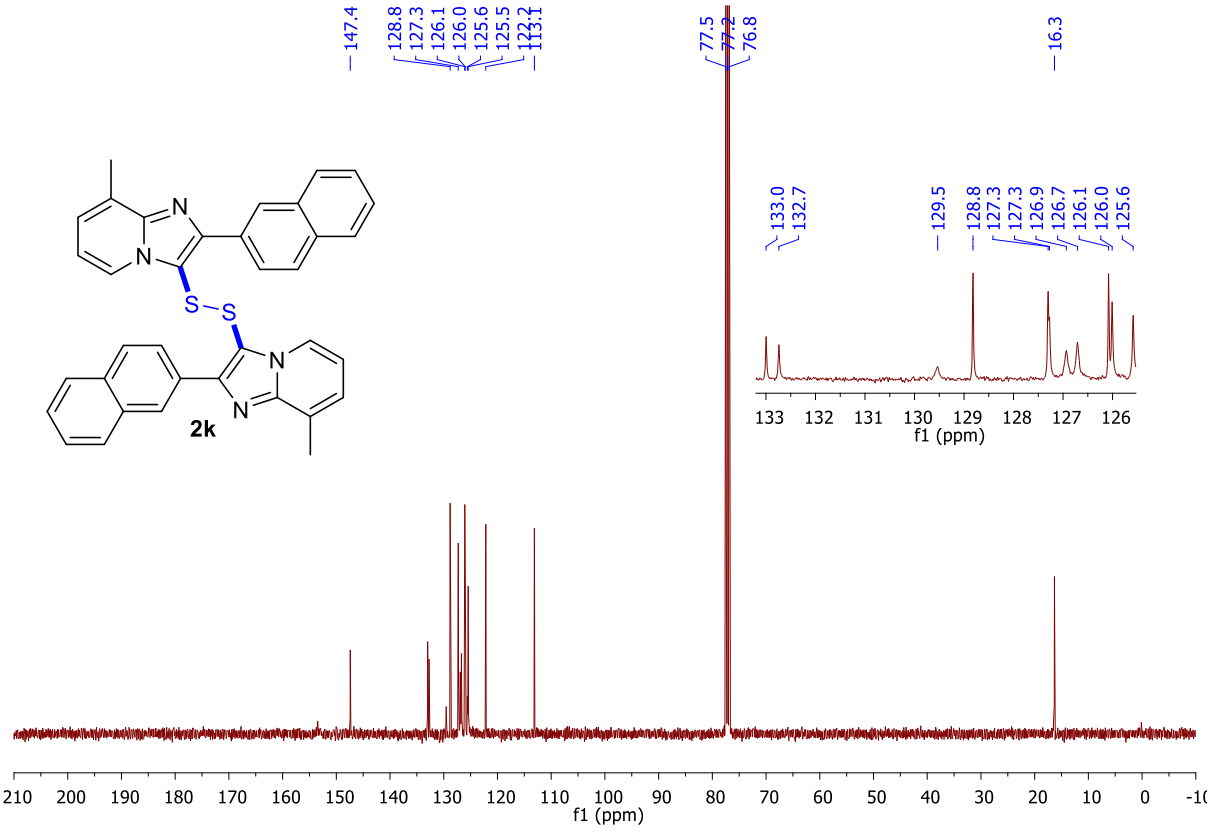

8.05
8.03
7.59
7.57
7.52
7.50
7.40
7.26
7.24
7.23
7.21
7.16
7.14
7.14
7.13
6.76
6.74
6.73
0.07
-0.01
2h
2.00
2.19
2.00
2.26
2.00
4.01
f1 (ppm)

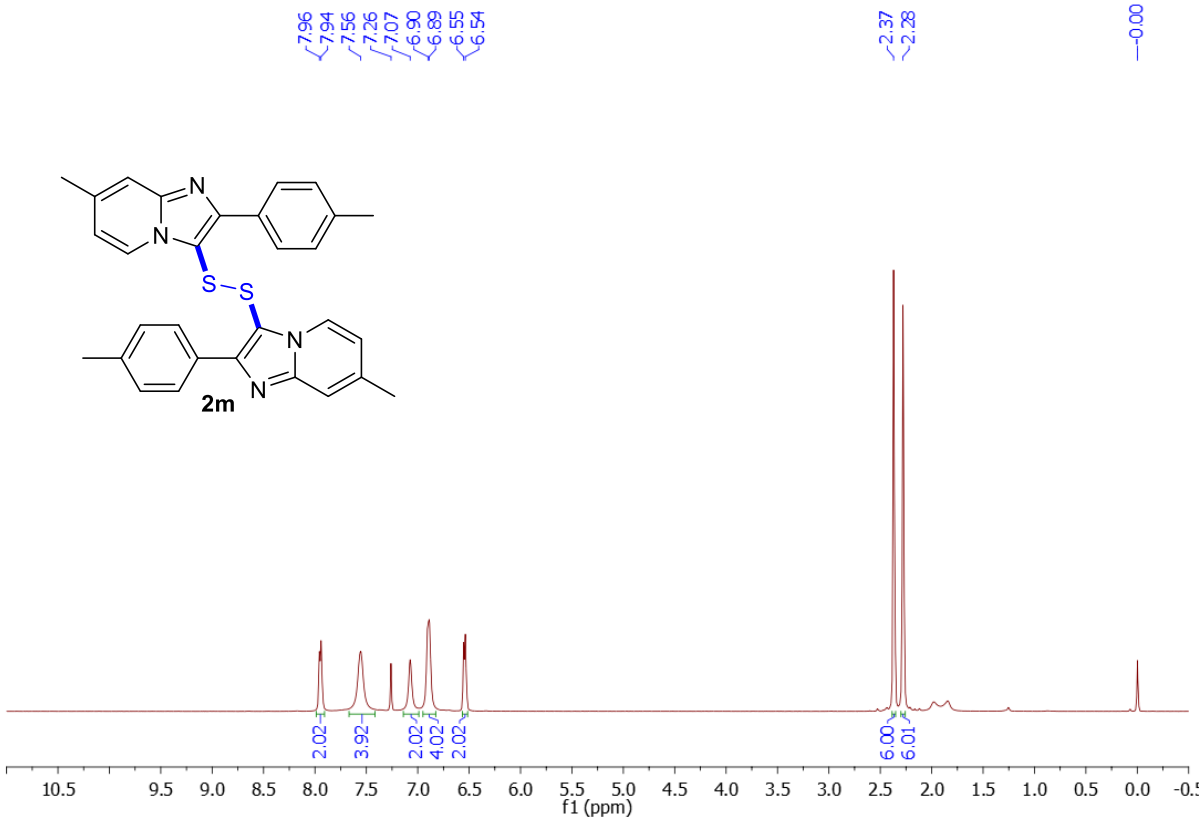

147.7
127.5
127.3
126.8
126.5
124.4
117.4
113.4
77.5
77.2
76.8
2h
f1 (ppm)

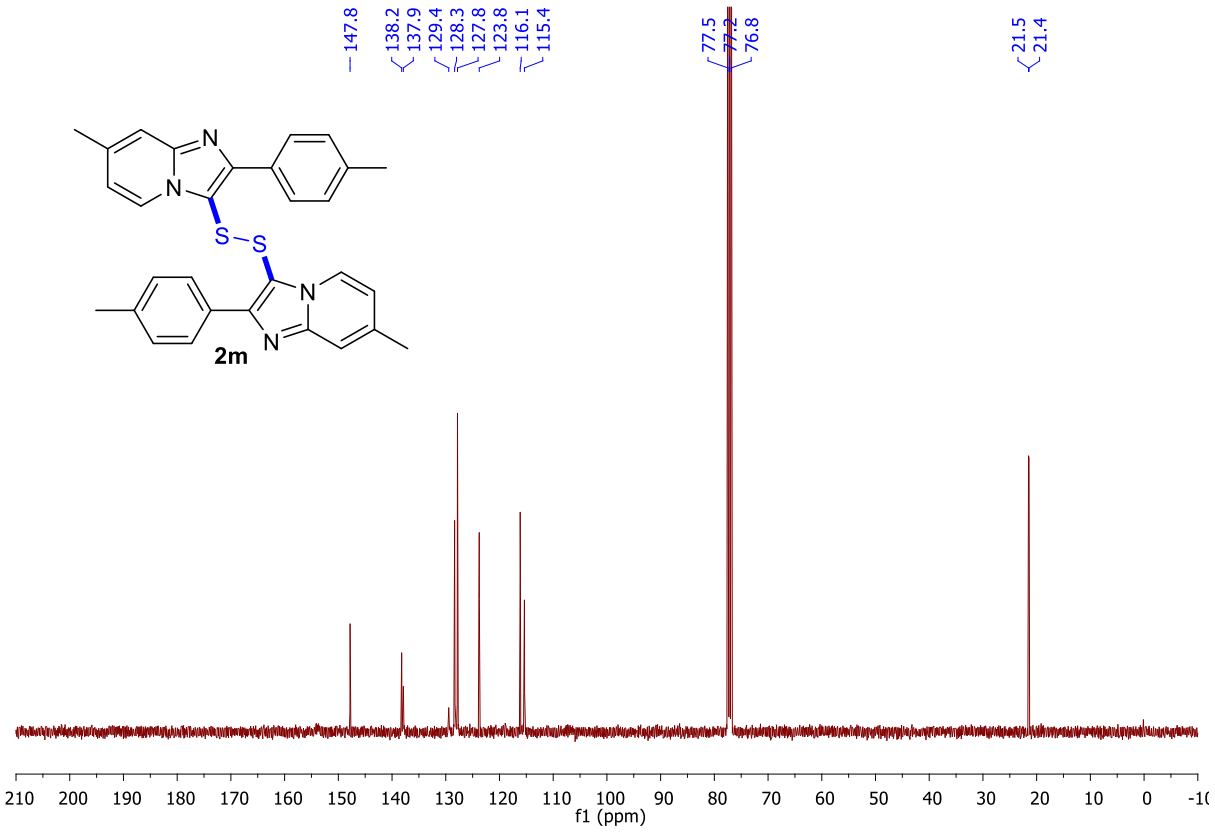

8.04
8.02
7.55
7.26
7.04
6.97
6.95
6.69
6.67
6.65
2.47
0.00
2i
2.00
4.00
6.05
2.15
2.08
6.00
f1 (ppm)

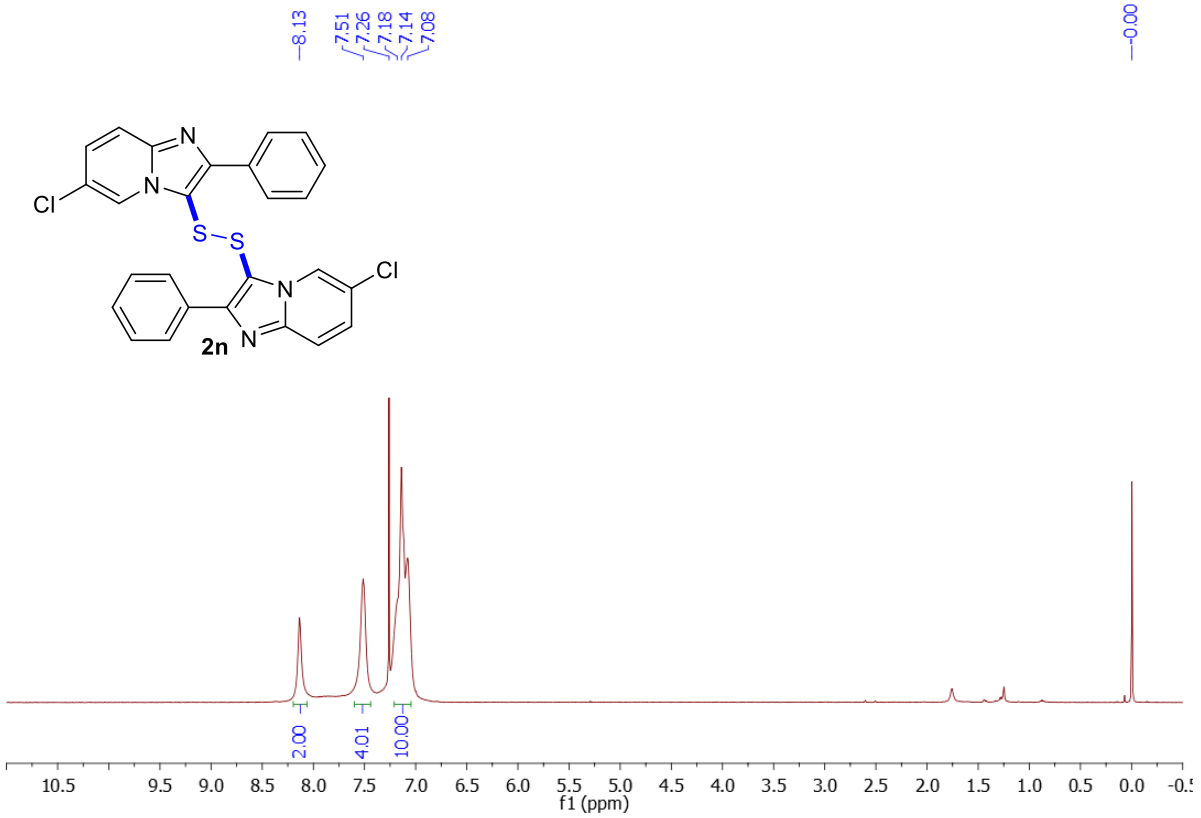

153.5
147.7
132.3
127.9
127.6
127.5
127.3
126.0
122.5
113.0
77.5
77.2
76.8
16.9
2i
f1 (ppm)

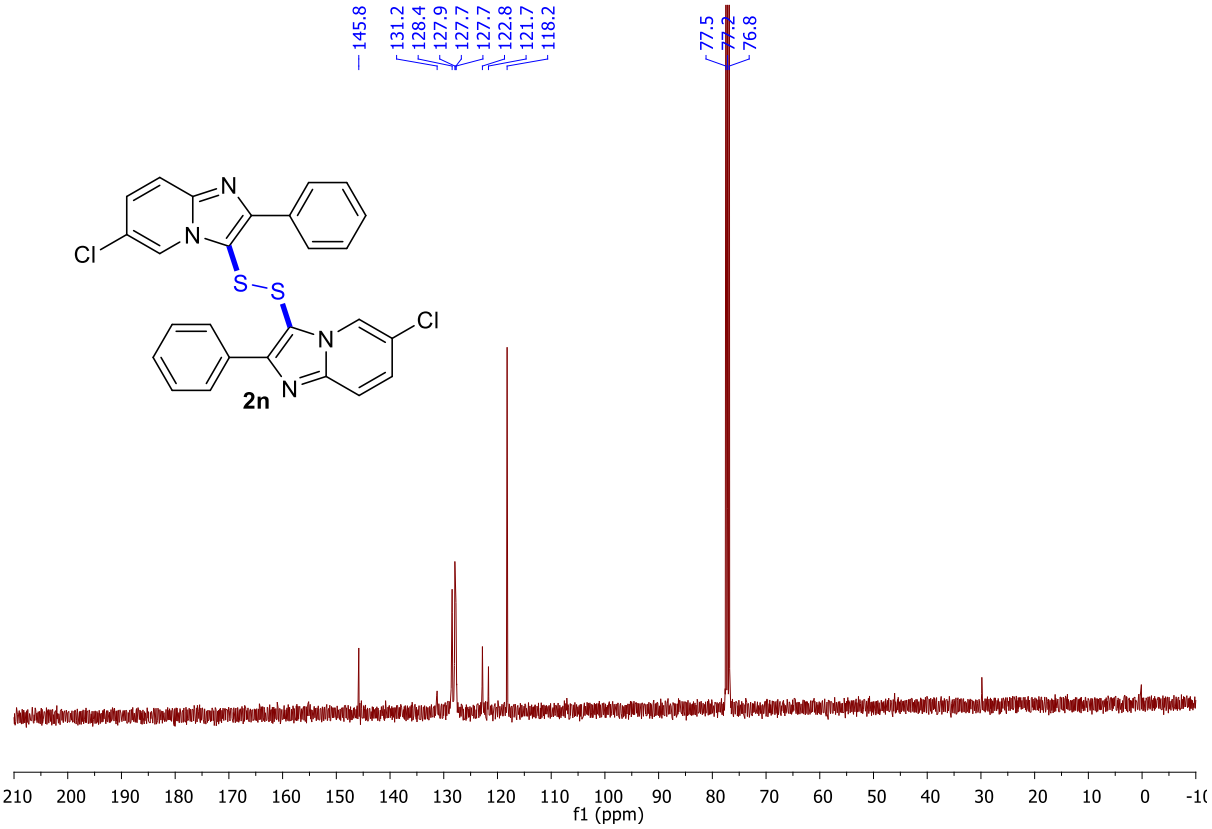

8.11
8.07
7.80
7.78
7.70
7.69
7.51
7.49
7.42
7.26
6.54
6.52
6.50
6.41
2.03
0.01
2k
DCM
4.00
2.01
4.20
2.00
4.00
2.12
1.90
6.00
f1 (ppm)


147.4
128.8
127.3
126.1
126.0
125.6
125.5
122.2
113.1
77.5
77.2
76.8
16.3
133.0
132.7
129.5
128.8
127.3
127.3
126.9
126.7
126.1
126.0
125.6
2k
f1 (ppm)

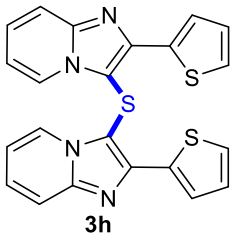

7.96
7.94
7.56
7.26
7.07
6.90
6.89
6.55
6.54
2.37
2.28
0.00
2m
2.02
3.92
2.02
4.02
2.02
6.00
6.01
f1 (ppm)


147.8
138.2
137.9
129.4
128.3
127.8
123.8
116.1
115.4
77.5
77.2
76.8
21.5
21.4
2m
f1 (ppm)

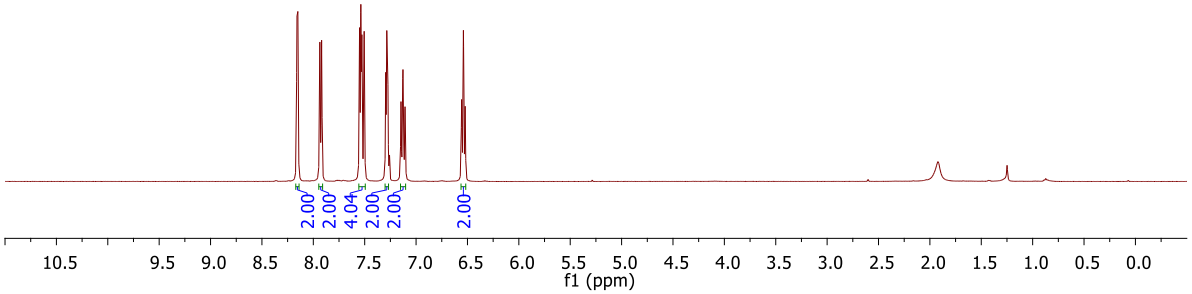

8.13
7.51
7.26
7.18
7.14
7.08
0.00
Cl
N
N
S
S
Cl
N
N
2n
2.00
4.01
10.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

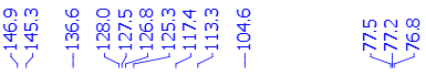

145.8
131.2
128.4
127.9
127.7
127.7
122.8
121.7
118.2
77.5
77.2
76.8
Cl
N
N
S
S
Cl
N
N
2n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

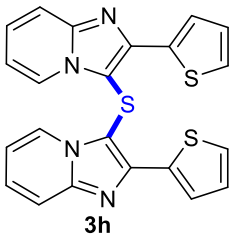

8.16
8.15
7.94
7.92
7.55
7.54
7.53
7.50
7.30
7.28
7.27
7.26
7.15
7.13
7.11
6.56
6.54
6.52


N
N
S
S
N
S
N

3h

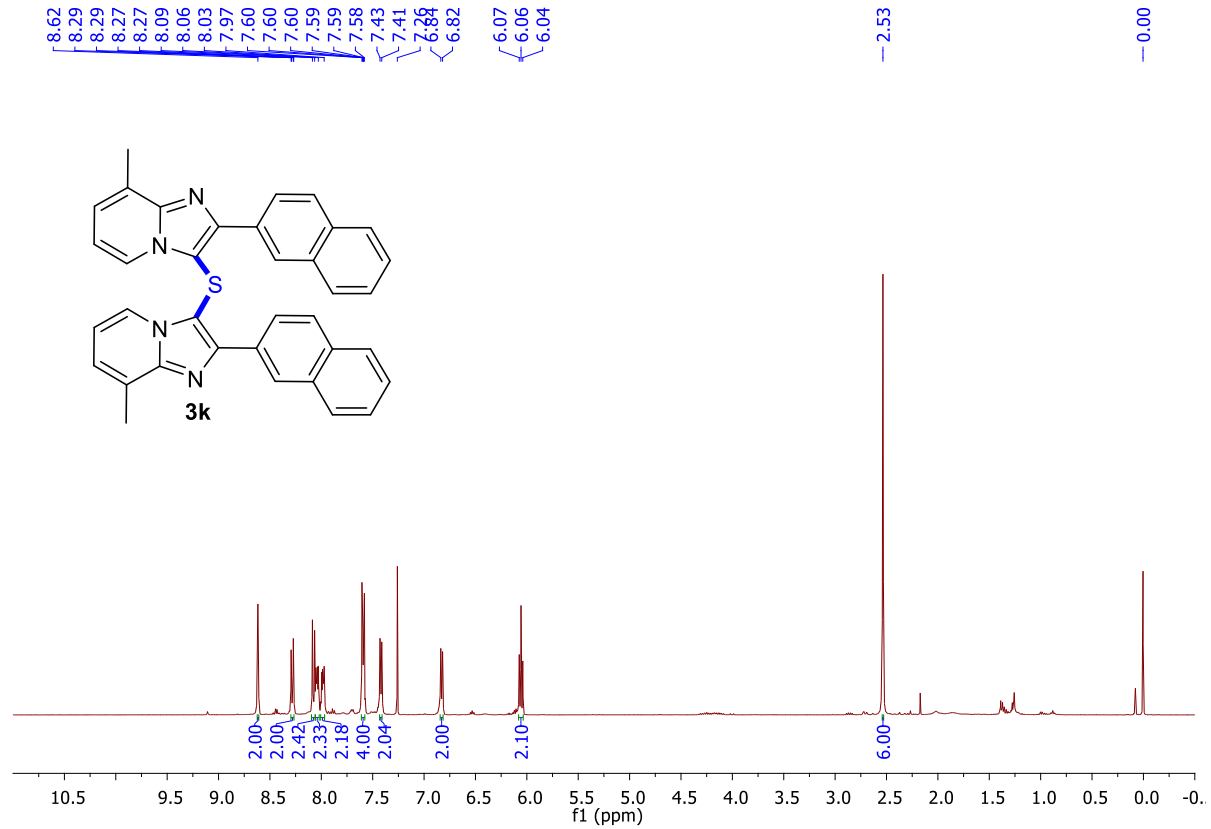

2.00
2.00
4.04
2.00
2.00
2.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

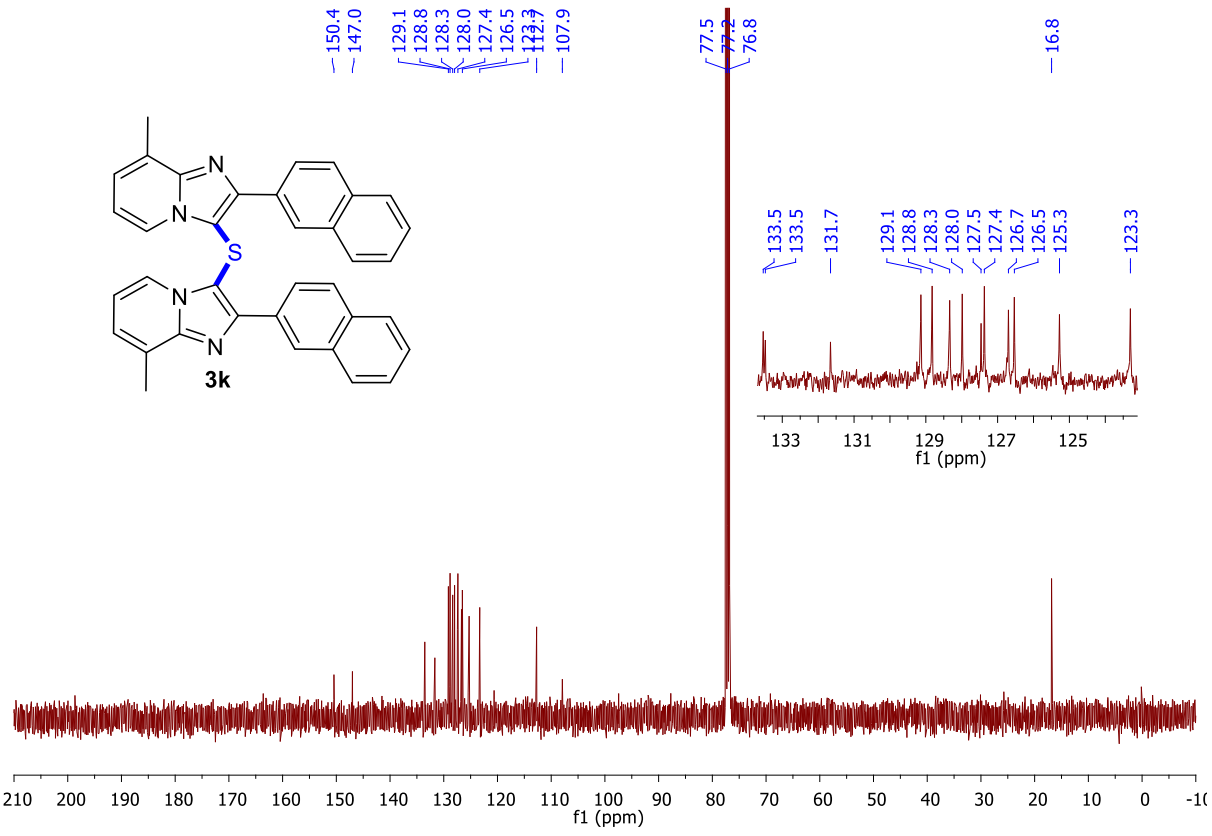

146.9
145.3
136.6
128.0
127.5
126.8
125.3
117.4
113.3
104.6
77.5
77.2
76.8

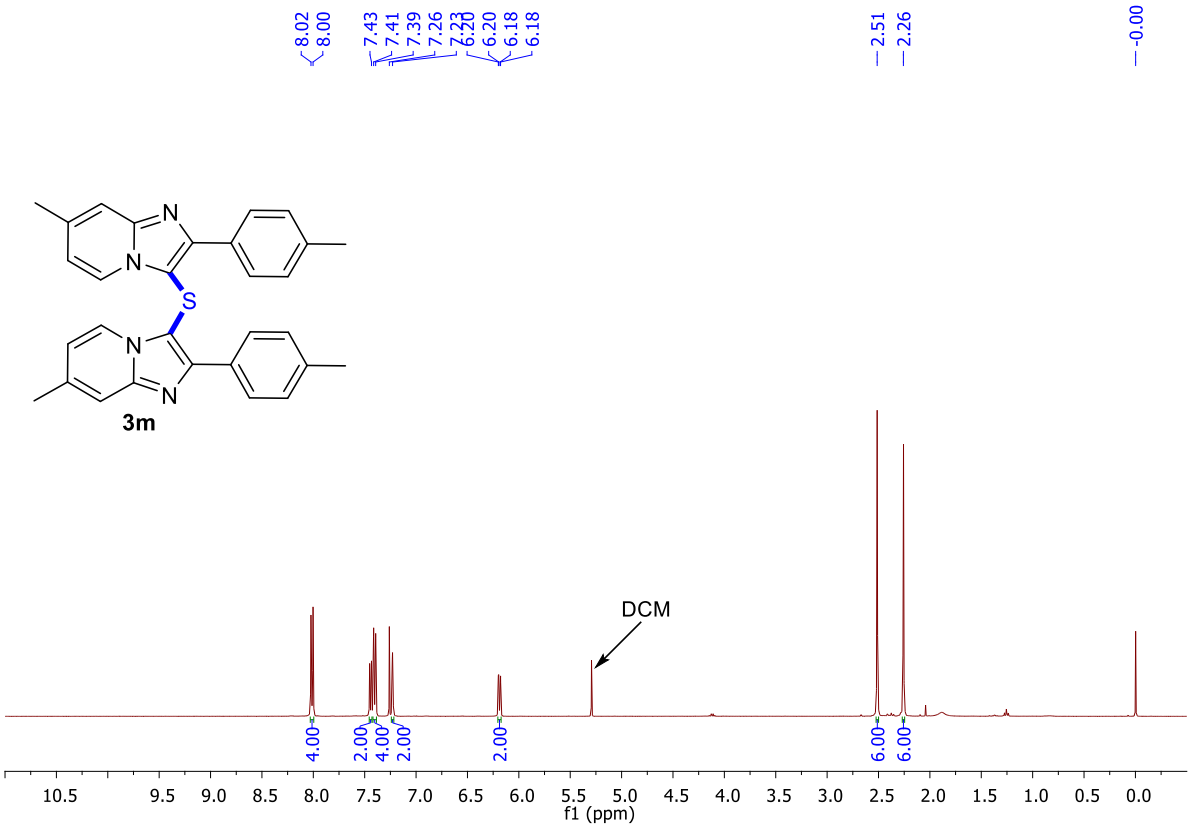

N
N
S
S
N
S
N

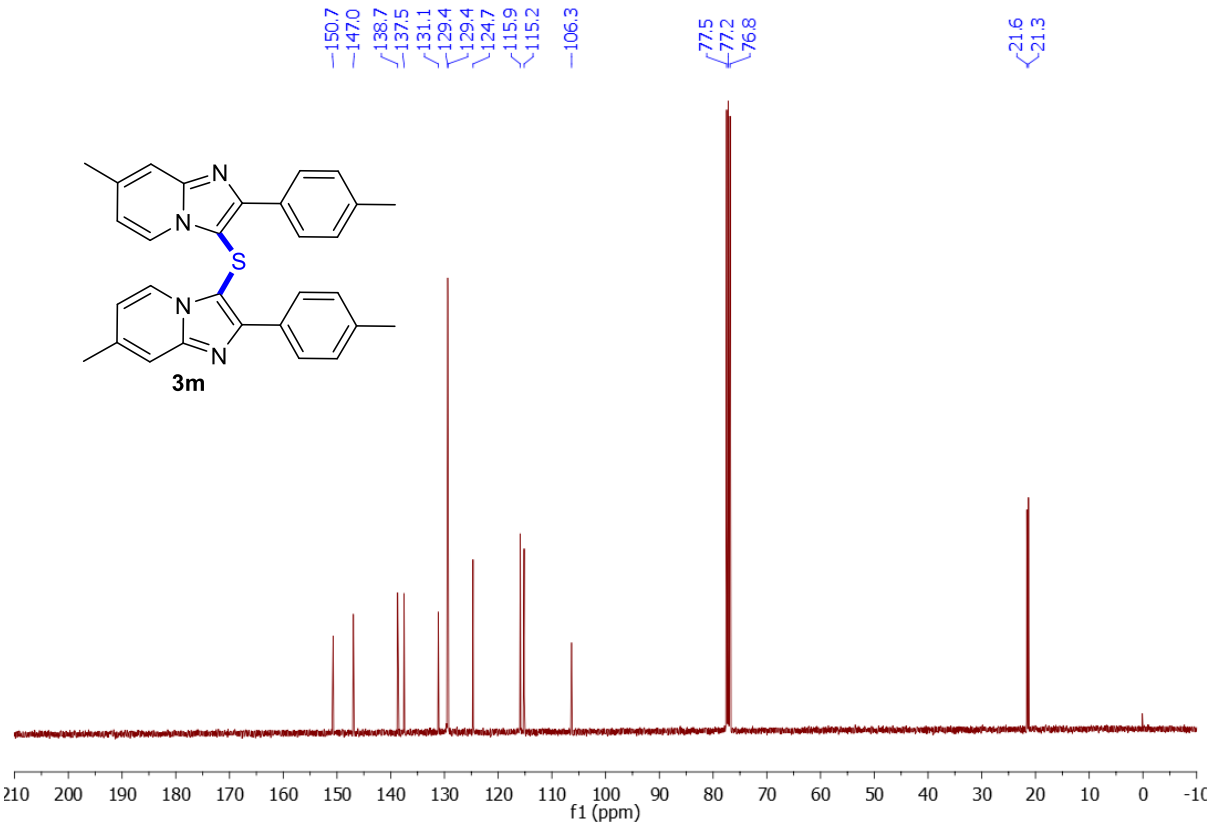
3h

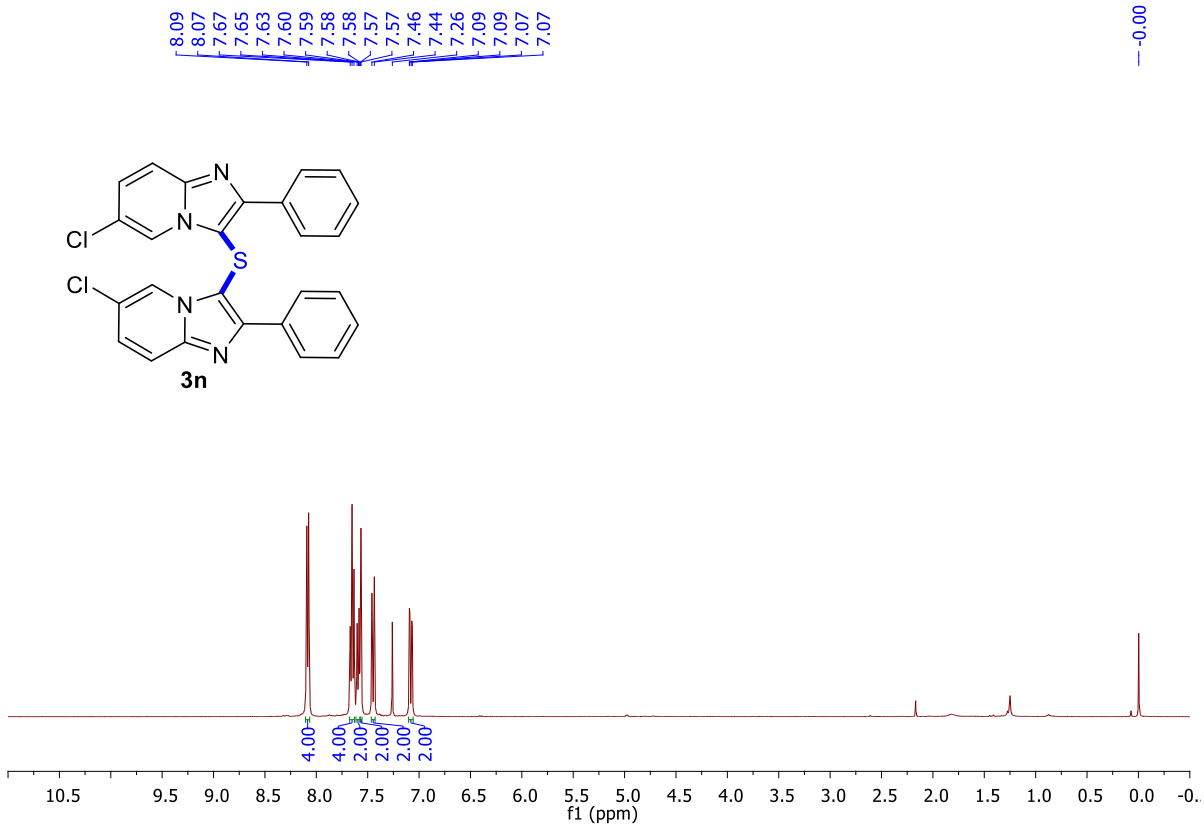
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.62
8.29
8.29
8.27
8.27
8.09
8.06
8.03
7.97
7.60
7.60
7.60
7.59
7.59
7.58
7.43
7.41
7.26
6.84
6.82
6.07
6.06
6.04
2.53
0.00
N
N
S
N
N
3k
2.00
2.00
2.42
2.33
2.18
4.00
2.04
2.00
2.10
6.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


150.4
147.0
129.1
128.8
128.3
128.0
127.4
126.5
107.9
77.5
76.8
16.8
N
N
S
N
N
3k
133.5
133.5
131.7
129.1
128.8
128.3
128.0
127.5
127.4
126.7
126.5
125.3
123.3
133
131
129
127
125
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.02
8.00
7.43
7.41
7.39
7.26
7.23
6.20
6.18
6.18
2.51
2.26
-0.00
3m
DCM
4.00
2.00
4.00
2.00
2.00
6.00
6.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


150.7
147.0
138.7
137.5
131.1
129.4
129.4
124.7
115.9
115.2
106.3
77.5
77.2
76.8
21.6
21.3
3m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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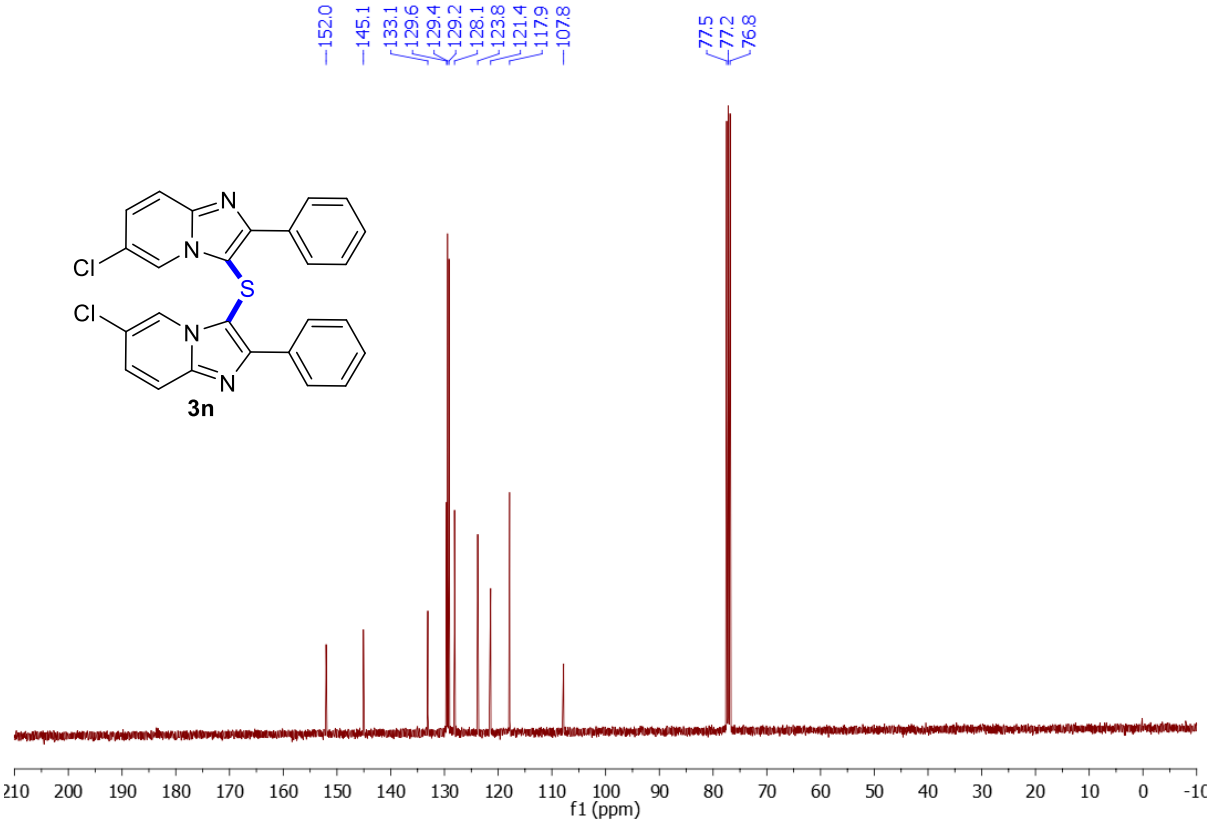
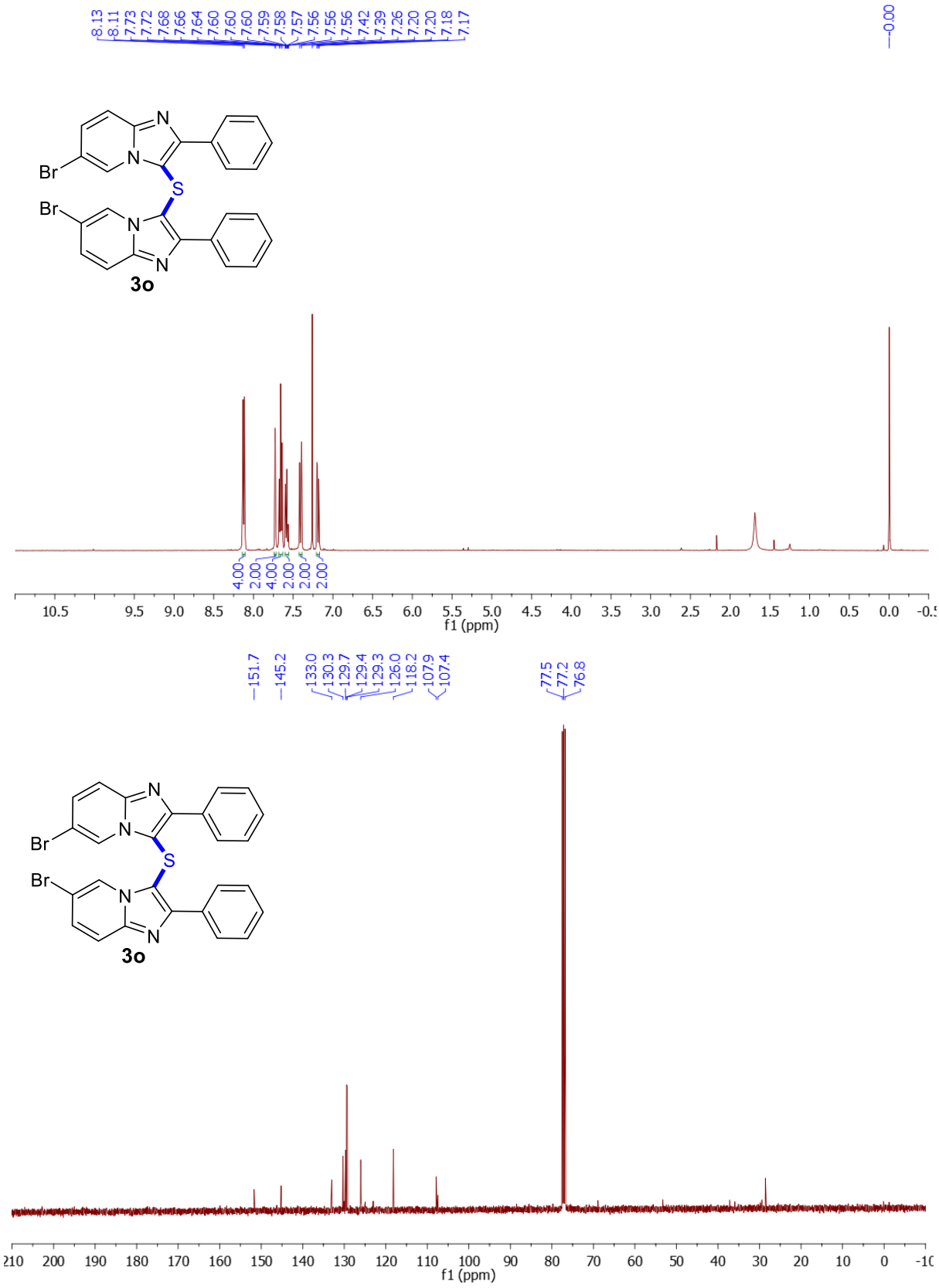
7.63
7.60
7.59
7.58
7.58
7.57
7.57
7.46
7.44
7.26
7.09
7.09
7.07
7.07
-0.00
Cl
N
N
S
Cl
N
N
3n
4.00
4.00
2.00
2.00
2.00
2.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


152.0
145.1
133.1
129.6
129.4
129.2
128.1
123.8
121.4
117.9
107.8
77.5
77.2
76.8
Cl
N
N
S
Cl
N
N
3n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.13
8.11
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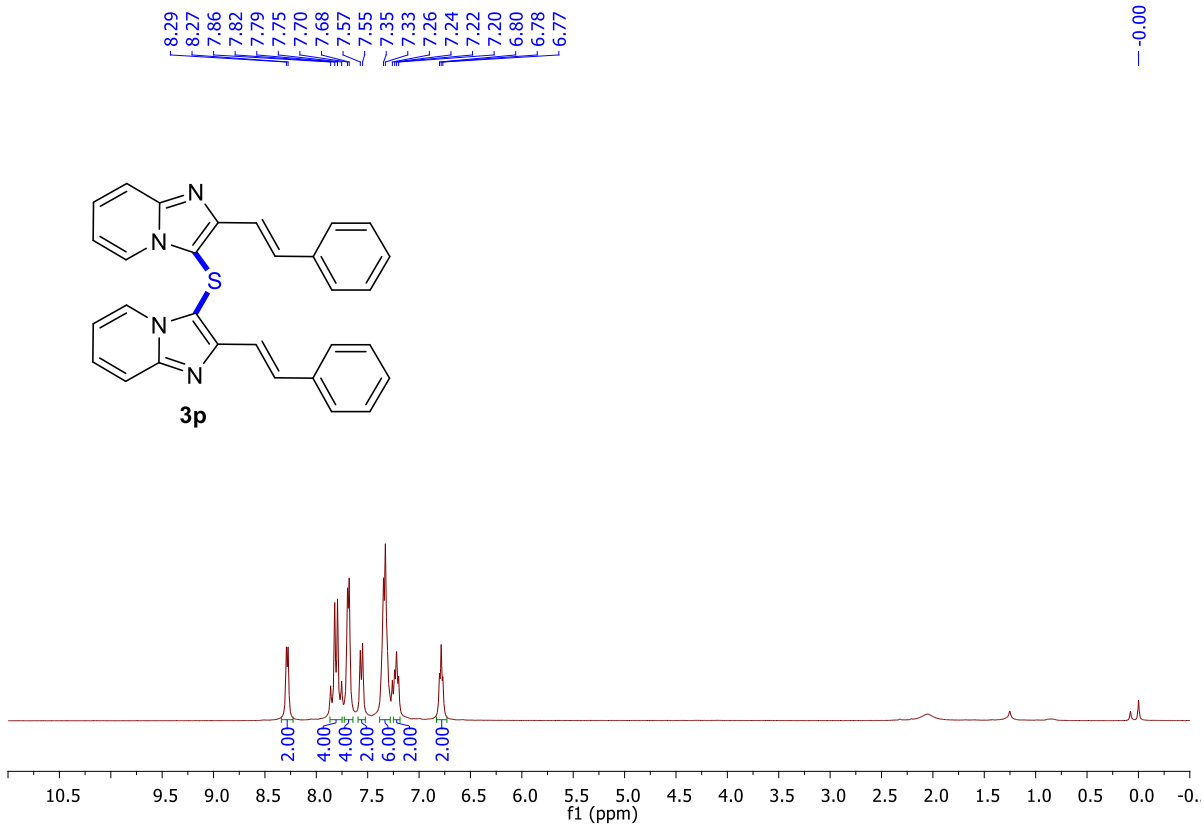
7.68
7.66
7.64
7.60
7.60
7.60
7.59
7.58
7.57
7.56
7.56
7.56
7.42
7.39
7.26
7.20
7.20
7.18
7.17
0.00
Br
N
N
S
Br
N
N
3o
4.00
2.00
4.00
2.00
2.00
2.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
151.7
145.2
133.0
130.3
129.7
129.4
129.3
126.0
118.2
107.9
107.4
77.5
77.2
76.8
Br
N
N
S
Br
N
N
3o
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.29
8.27
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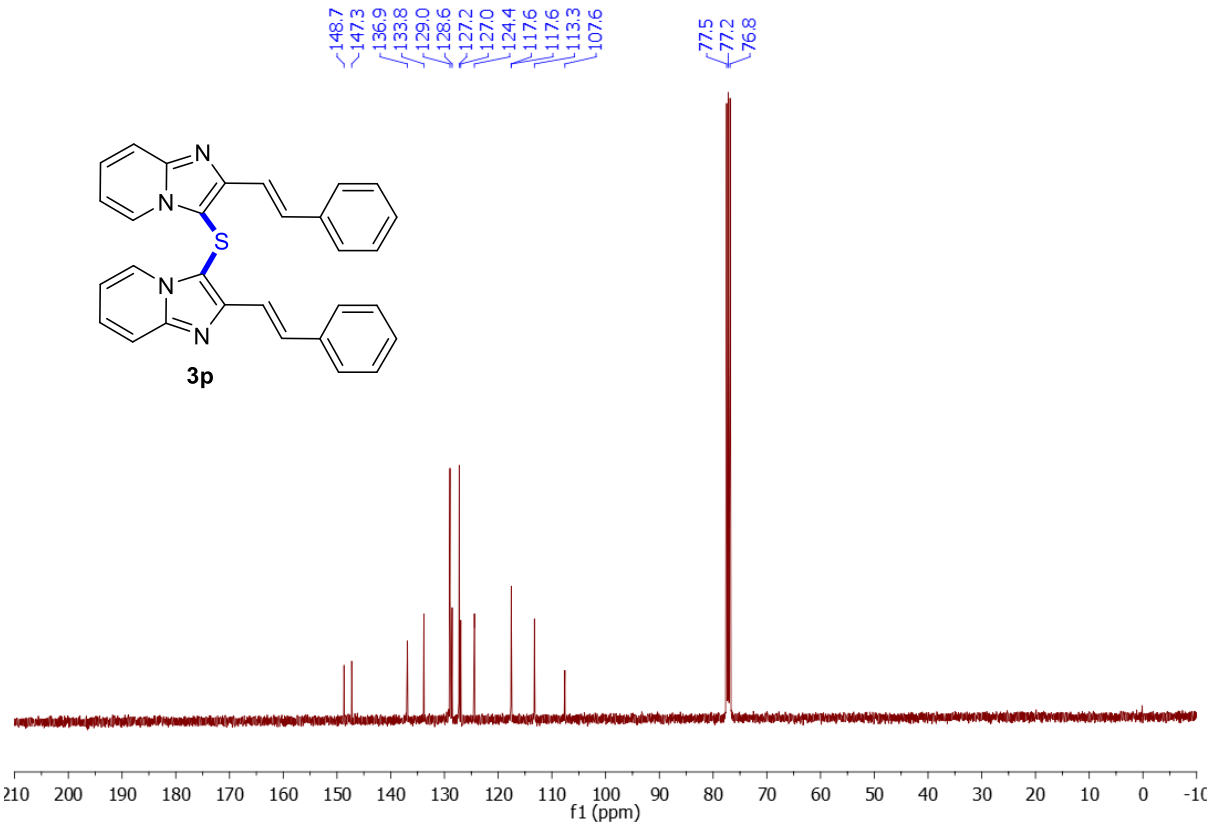
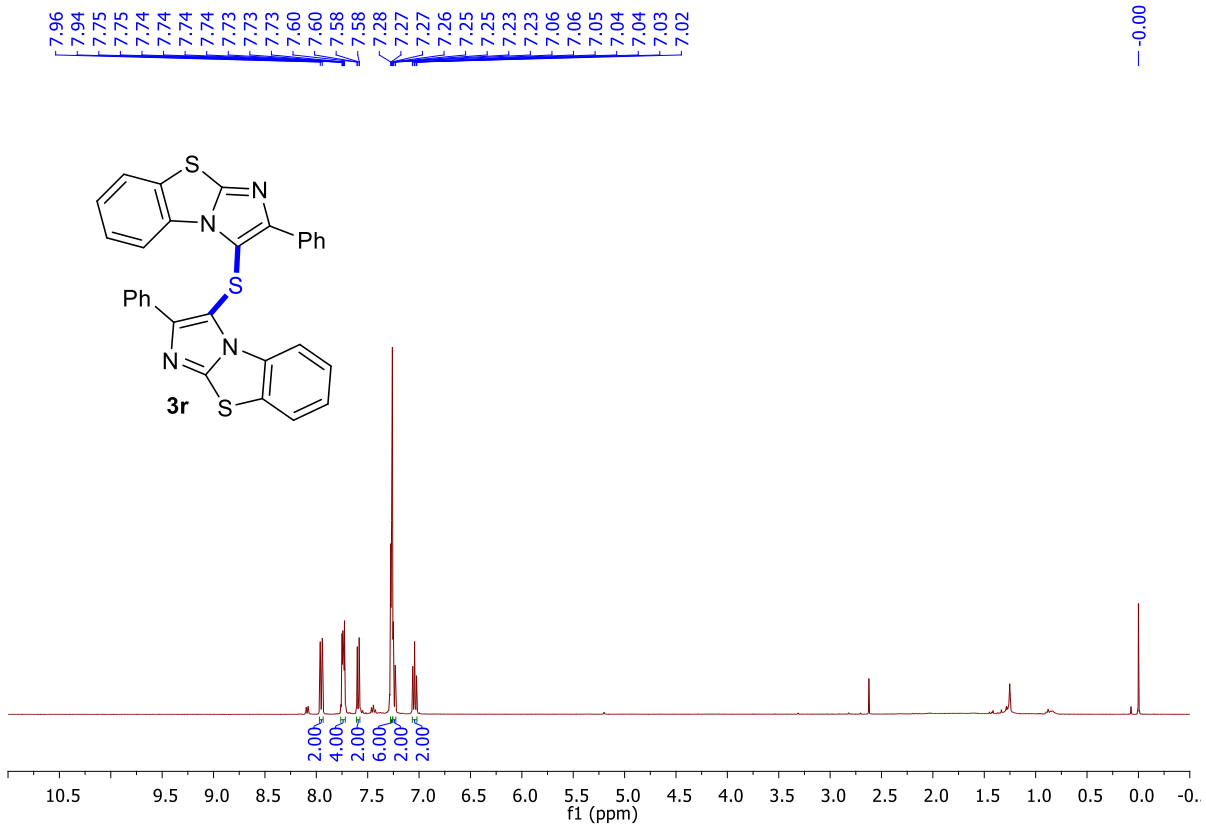
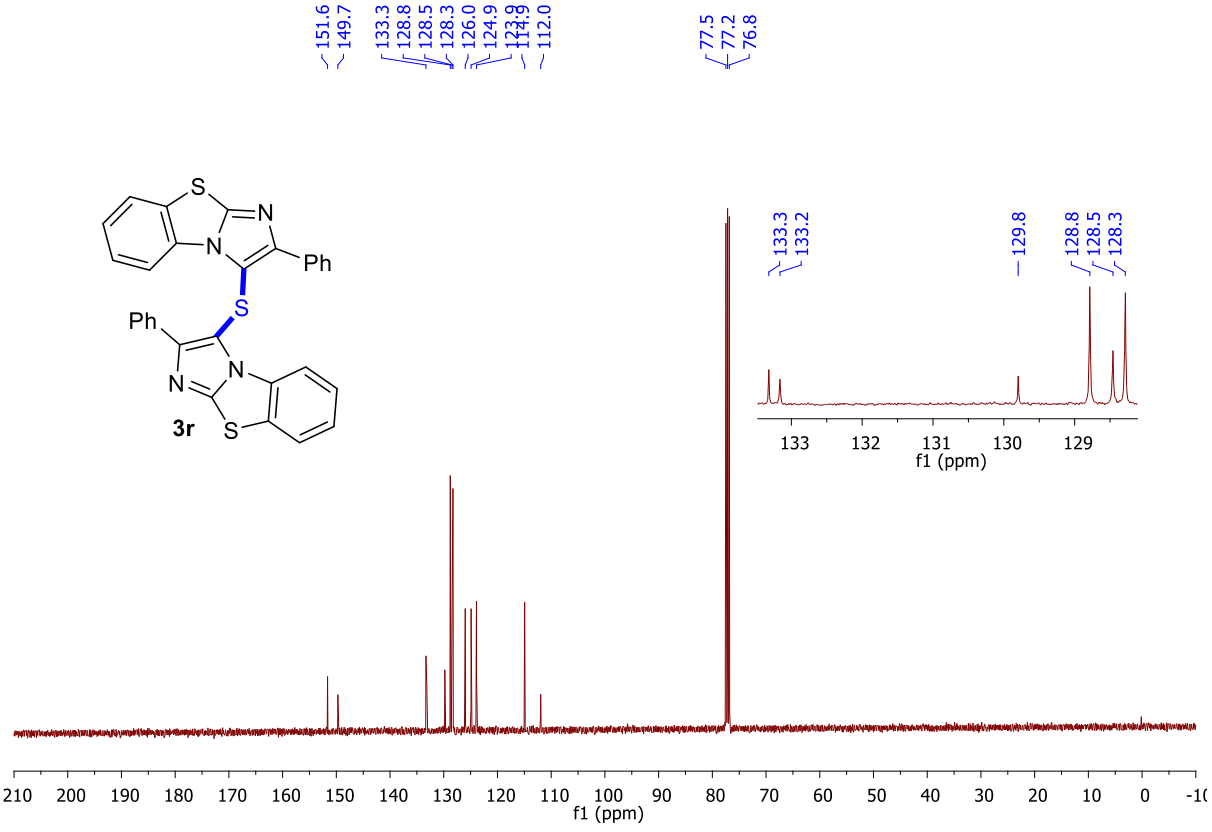
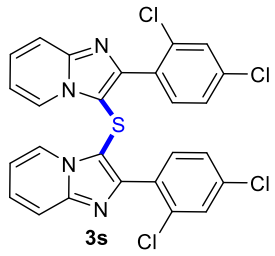
7.82
7.79
7.75
7.70
7.68
7.57
7.55
7.35
7.33
7.26
7.24
7.22
7.20
6.80
6.78
6.77
-0.00
3p
2.00
4.00
4.00
2.00
6.00
2.00
2.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

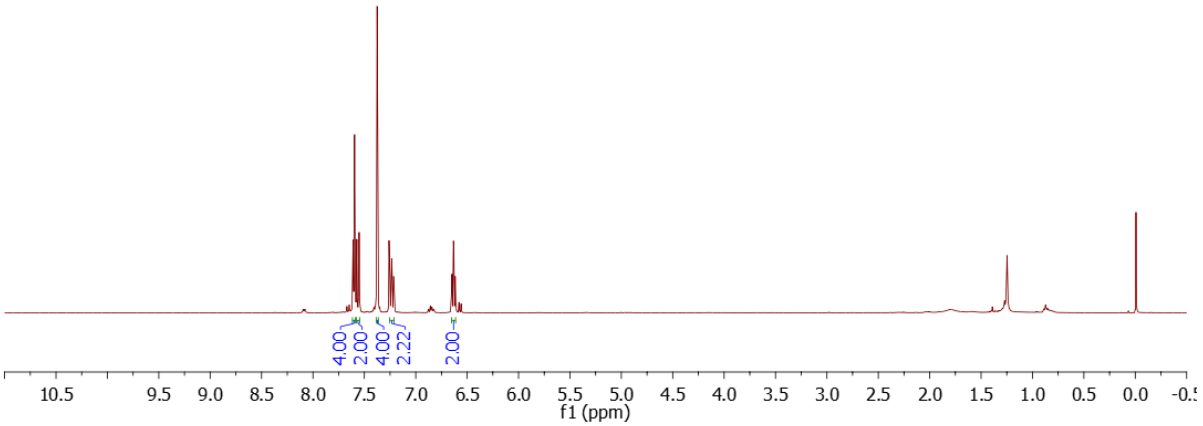

148.7
147.3
136.9
133.8
129.0
128.6
127.2
127.0
124.4
117.6
117.6
113.3
107.6
77.5
77.2
76.8
3p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.96 7.94 7.75 7.75 7.74 7.74 7.74 7.74 7.73 7.73 7.73 7.60 7.58 7.58 7.28 7.27 7.27 7.26 7.25 7.25 7.23 7.23 7.06 7.06 7.05 7.04 7.04 7.03 7.02
-0.00
Ph
Ph
3r
2.00 4.00 2.00 6.00 2.00 2.00
f1 (ppm)

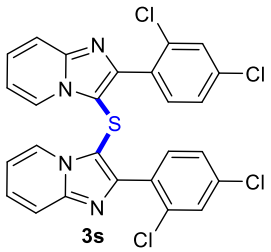

151.6 149.7 133.3 128.8 128.5 128.3 126.0 124.9 112.0
77.5 77.2 76.8
Ph
Ph
3r
133.3 133.2 129.8 128.8 128.5 128.3
133 132 131 130 129
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

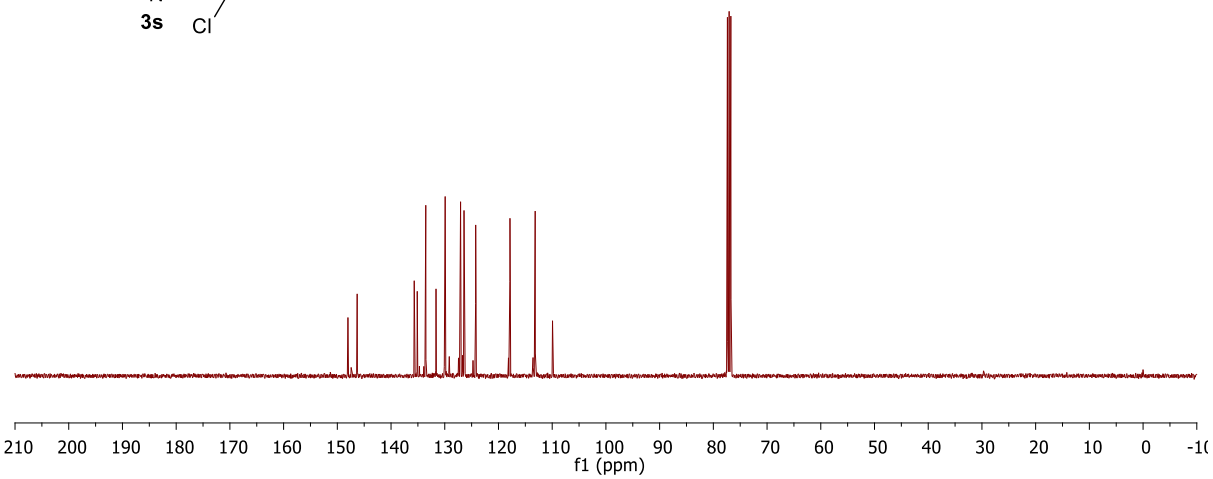

7.61
7.61
7.60
7.60
7.59
7.57
7.55
7.38
7.37
7.26
7.25
7.25
7.24
7.23
7.23
7.23
7.22
7.21
6.65
6.65
6.63
6.63
6.62
6.61
0.01

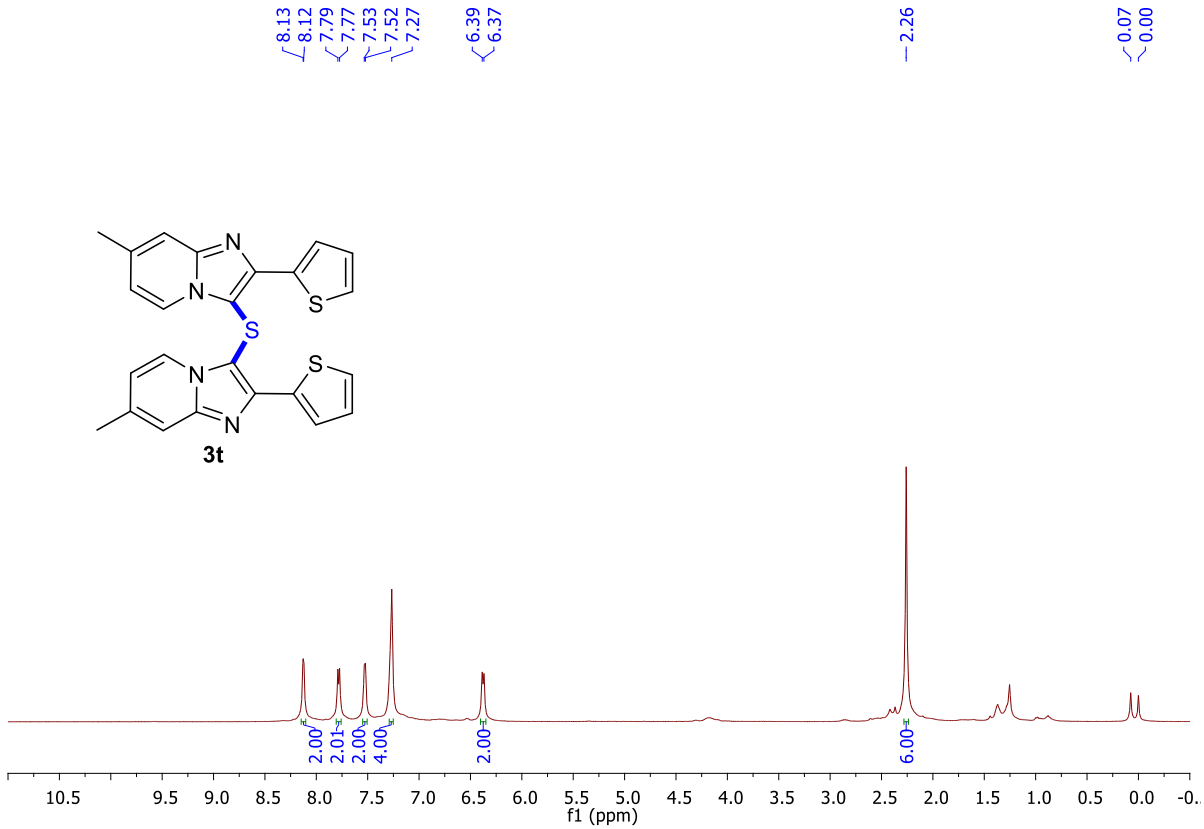

Cl
N
N
S
N
N
Cl
Cl
Cl
3s

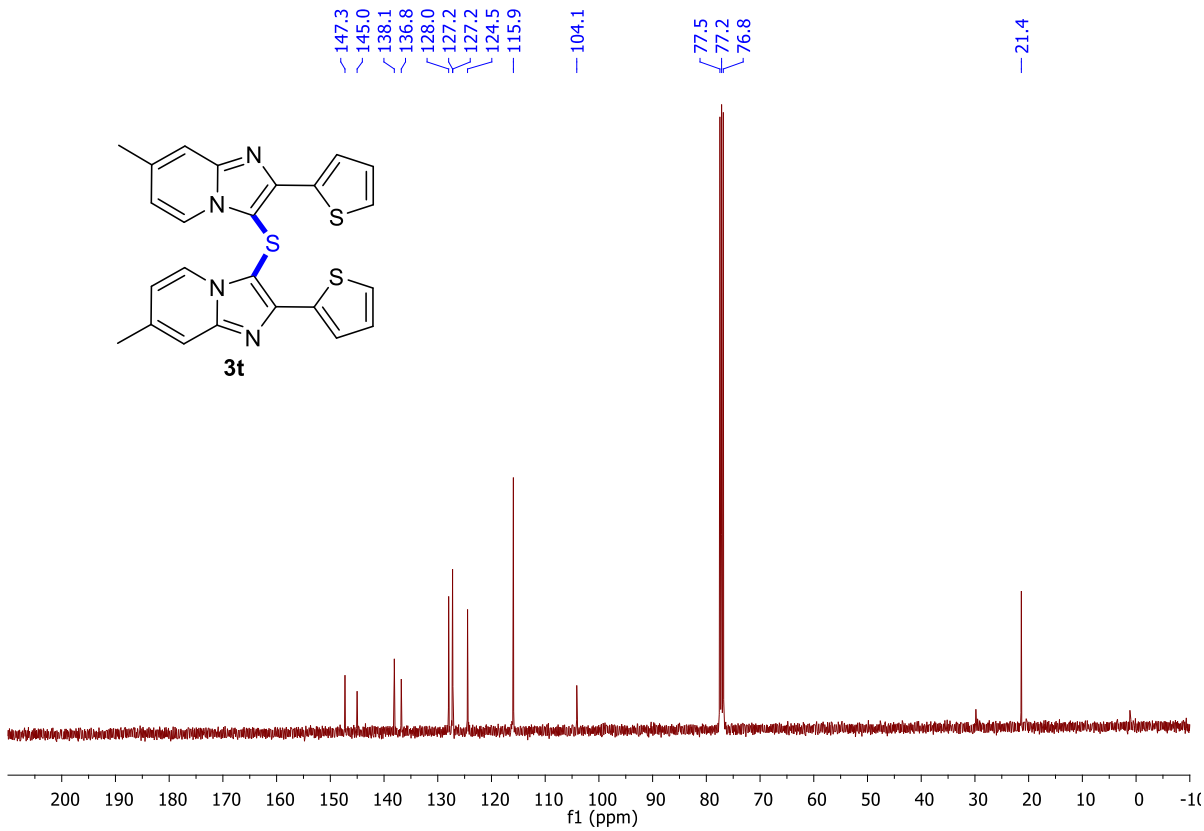

4.00
2.00
4.00
2.22
2.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

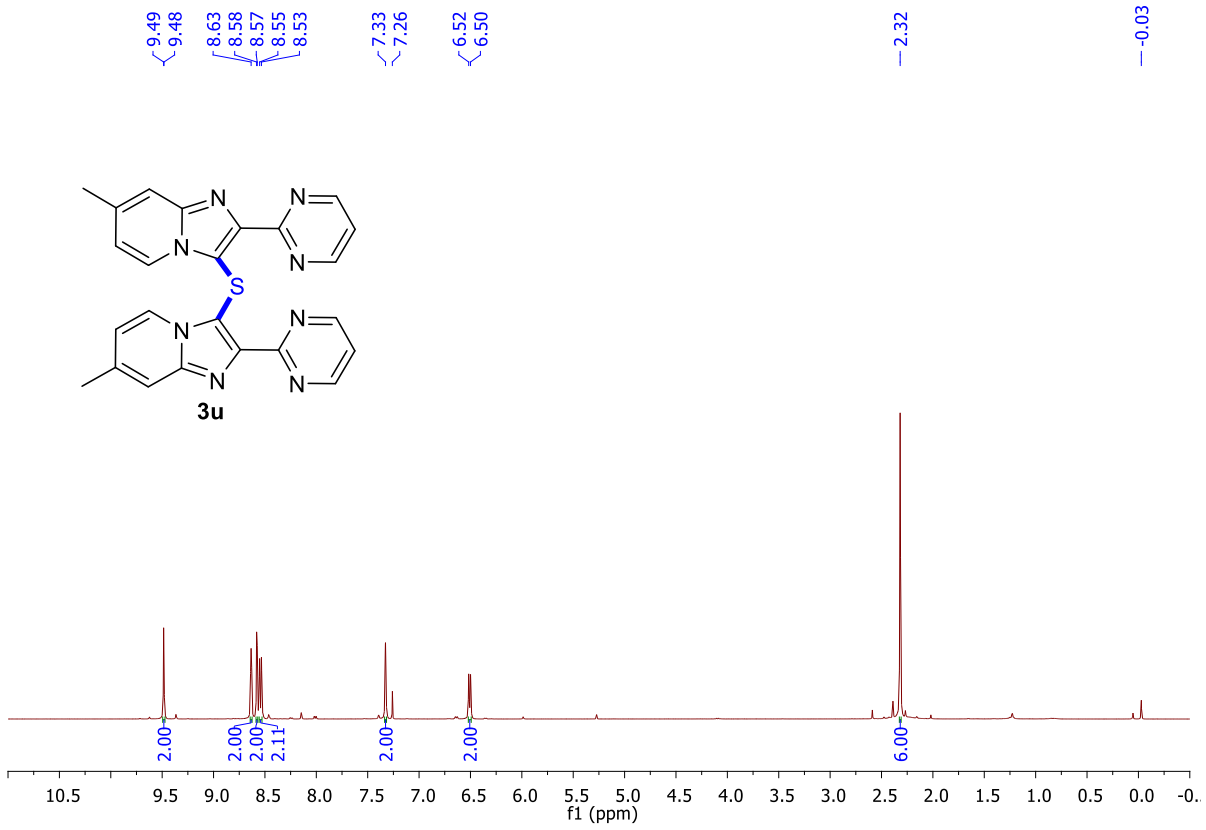

148.0
146.3
135.7
135.1
133.5
131.6
129.9
127.1
126.4
124.2
117.9
113.2
109.9
77.4
77.1
76.7

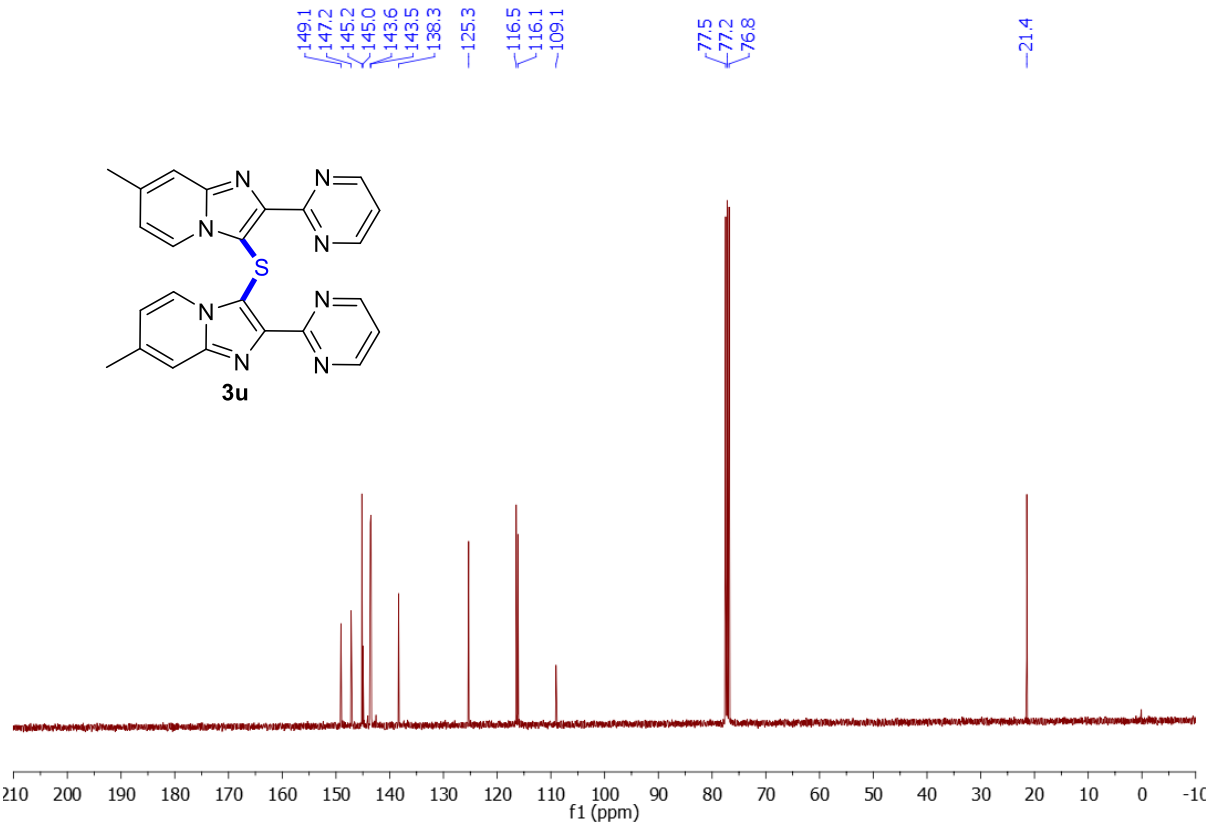

Cl
N
N
S
N
N
Cl
Cl
Cl
3s

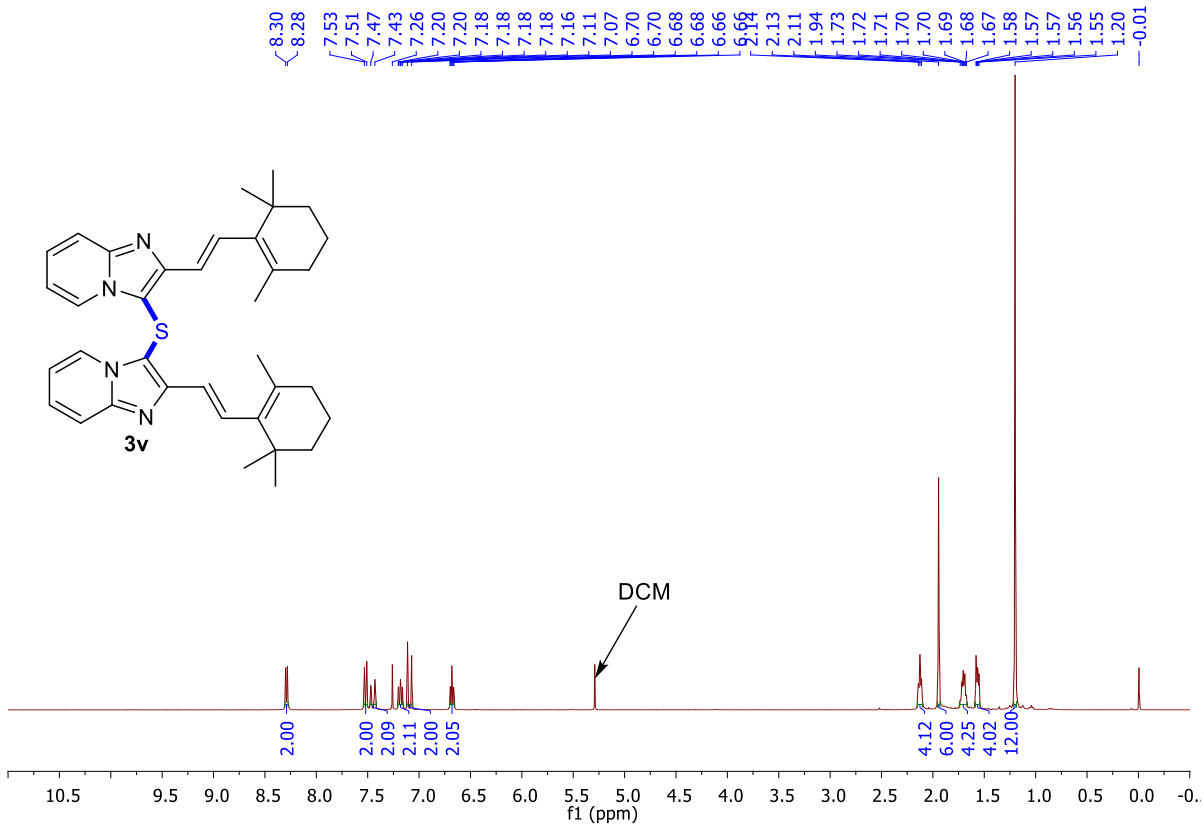

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

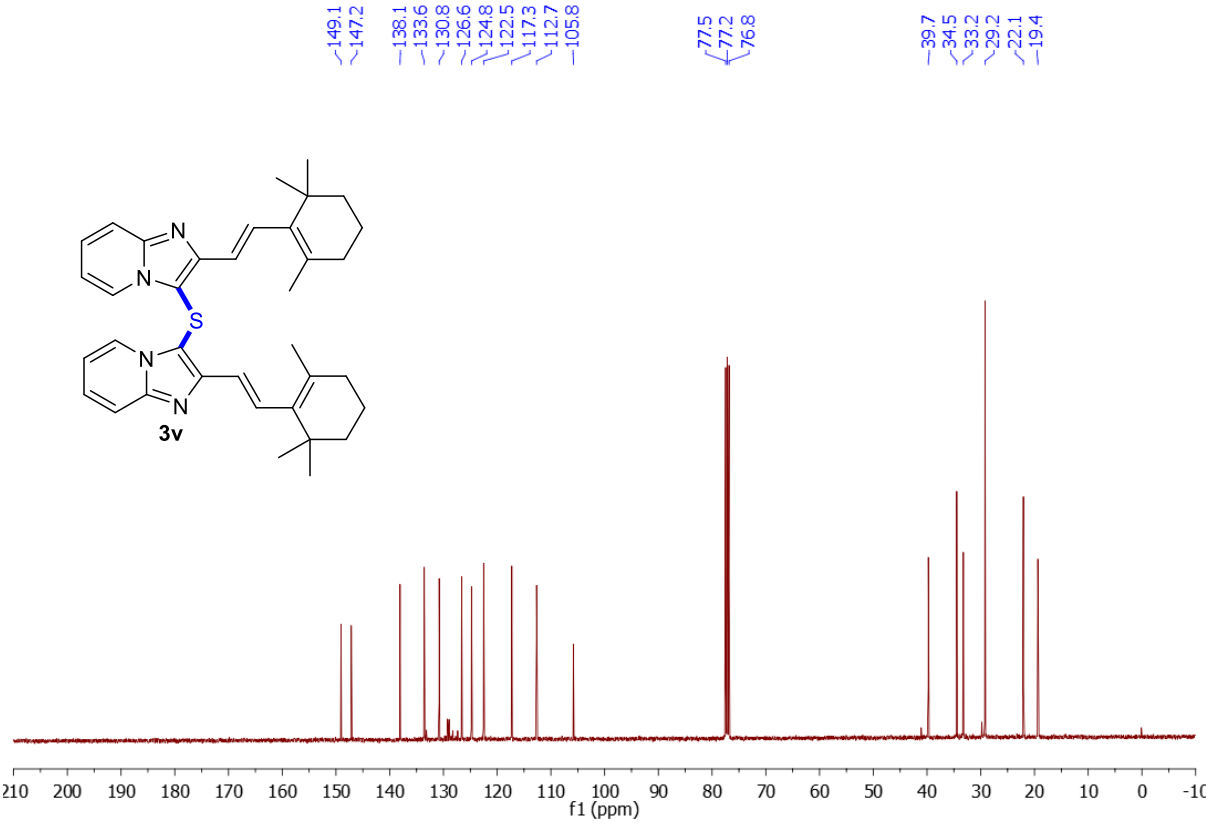

8.13
8.12
7.79
7.77
7.53
7.52
7.27
6.39
6.37
2.26
0.07
0.00
3t
2.00
2.01
2.00
4.00
2.00
6.00
f1 (ppm)

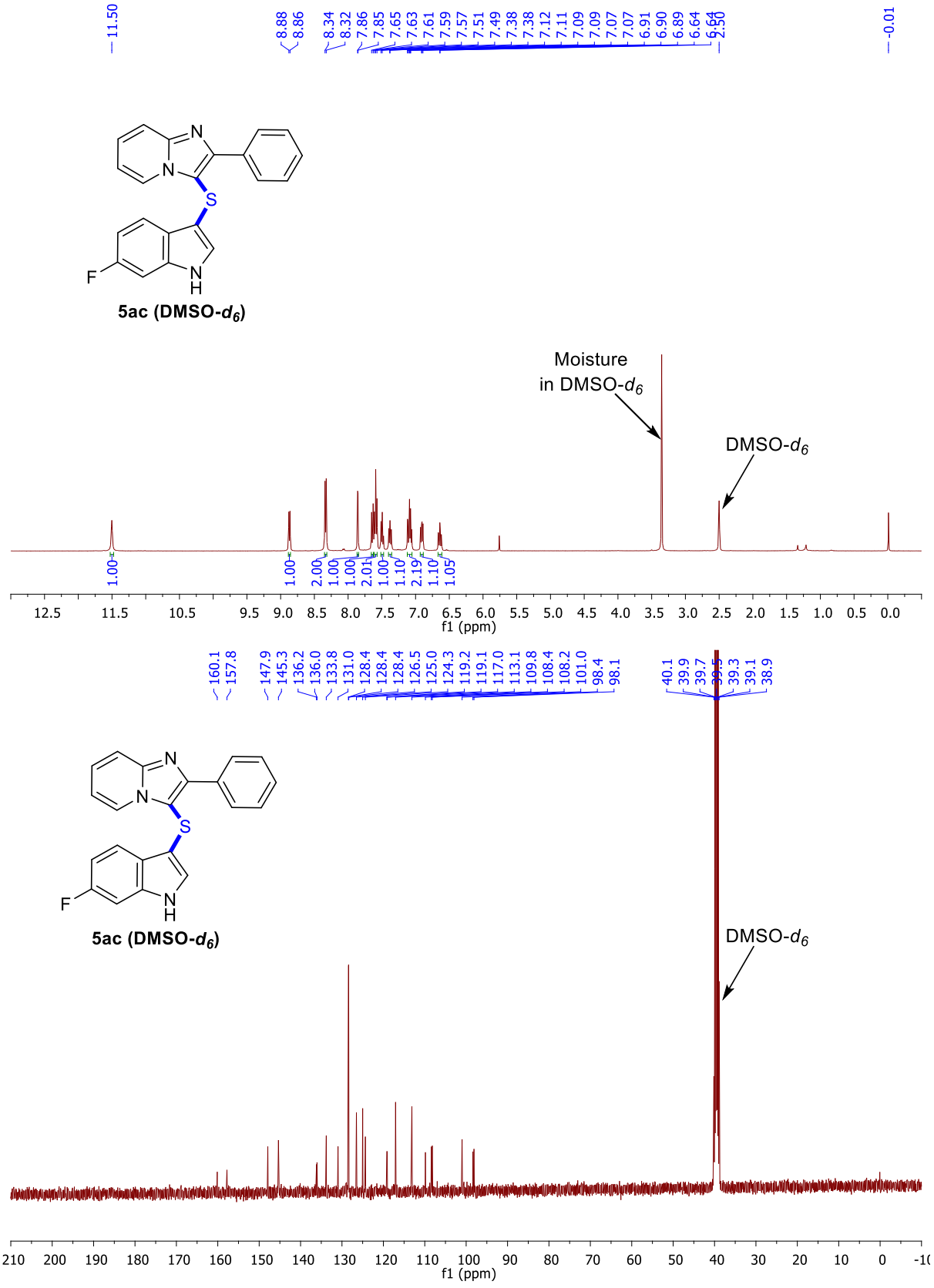

147.3
145.0
138.1
136.8
128.0
127.2
127.2
124.5
115.9
104.1
77.5
77.2
76.8
21.4
3t
f1 (ppm)

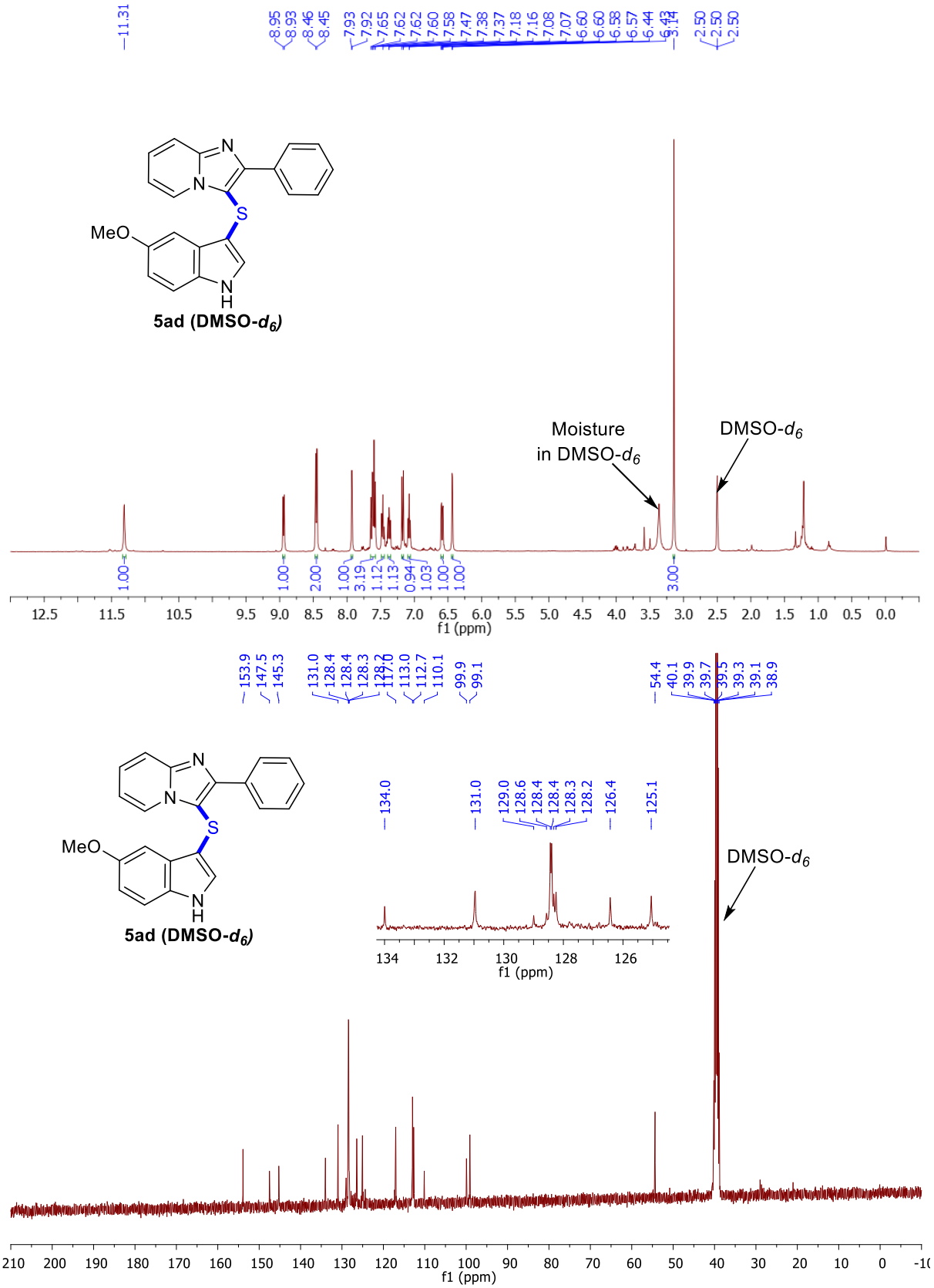

9.49
9.48
8.63
8.58
8.57
8.55
8.53
7.33
7.26
6.52
6.50
2.32
-0.03
3u
2.00
2.00
2.00
2.11
2.00
2.00
6.00
f1 (ppm)

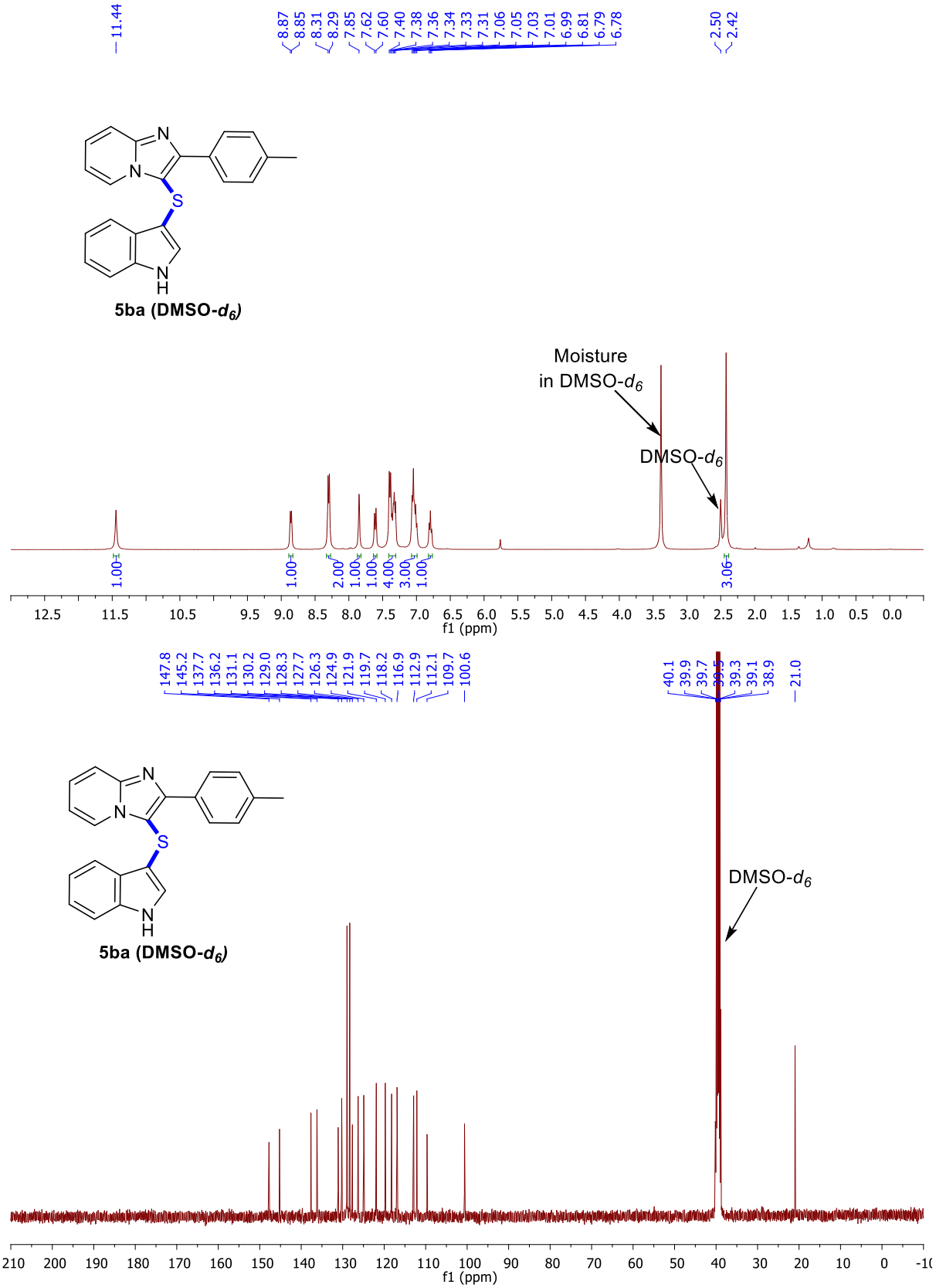

149.1
147.2
145.2
145.0
143.6
143.5
138.3
125.3
116.5
116.1
109.1
77.5
77.2
76.8
21.4
3u
f1 (ppm)

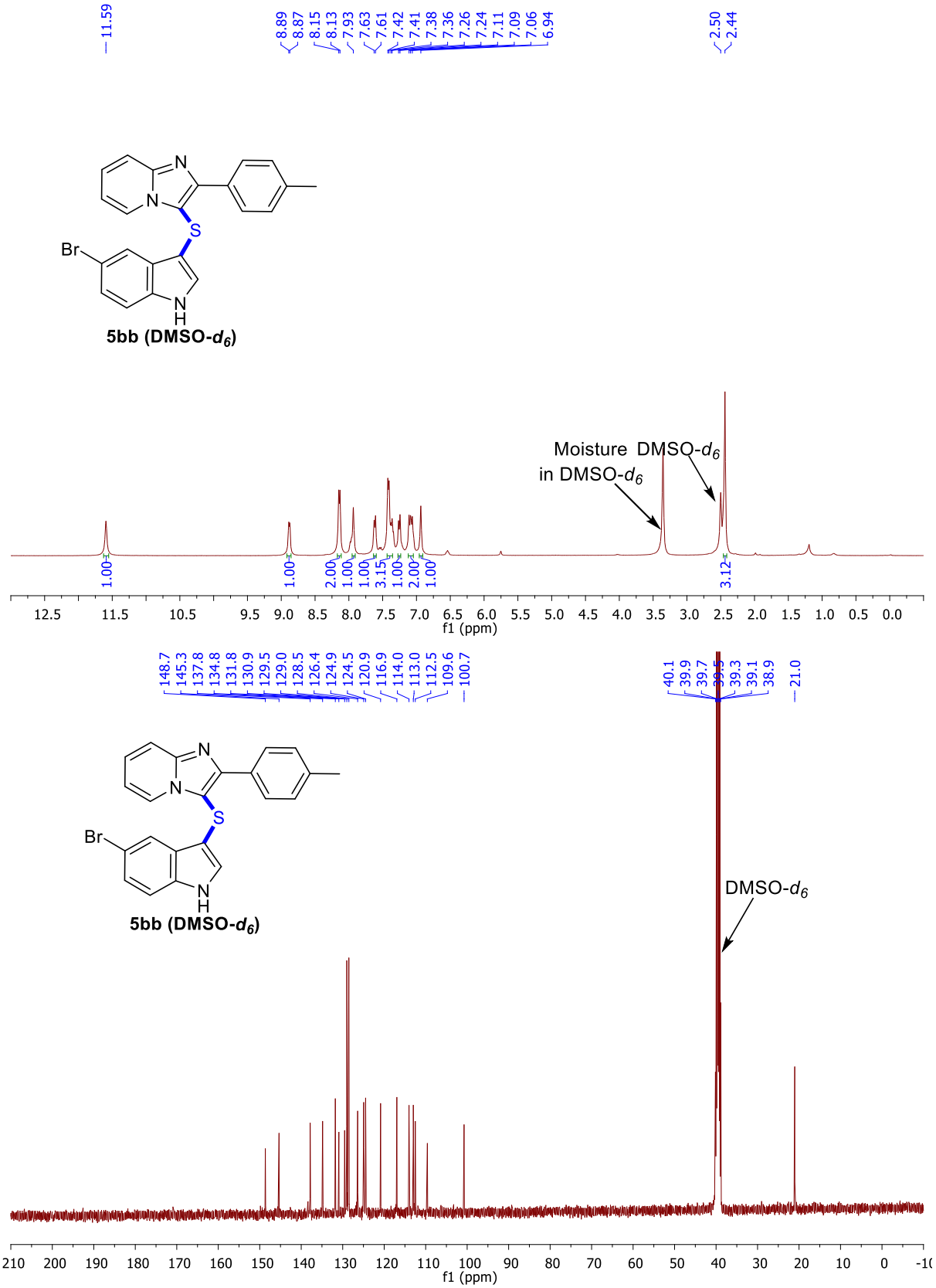

8.30
8.28
7.53
7.51
7.47
7.43
7.26
7.20
7.20
7.18
7.18
7.18
7.16
7.11
7.07
6.70
6.70
6.68
6.68
6.66
6.66
2.14
2.13
2.11
1.94
1.73
1.72
1.71
1.70
1.70
1.69
1.68
1.67
1.58
1.57
1.57
1.56
1.55
1.20
-0.01
3v
DCM
2.00
2.00
2.09
2.11
2.00
2.05
4.12
6.00
4.25
4.02
12.00
f1 (ppm)

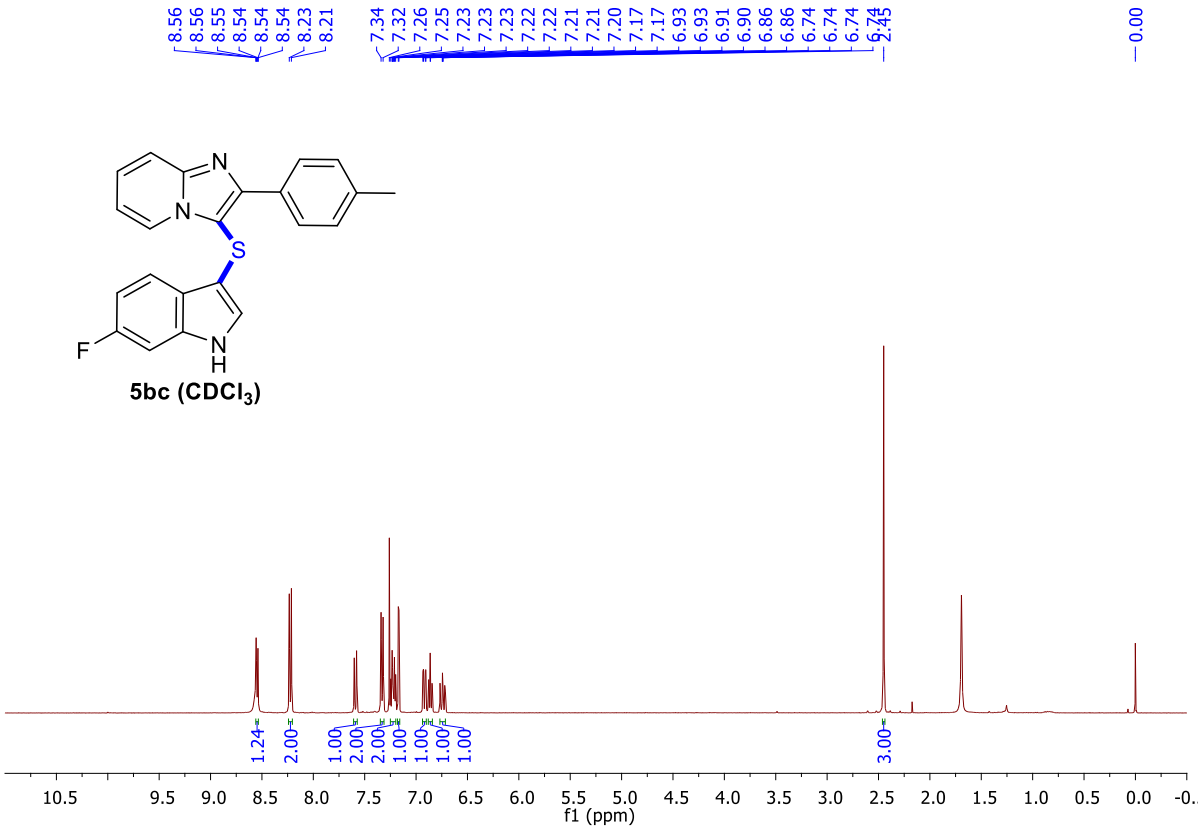

149.1
147.2
138.1
133.6
130.8
126.6
124.8
122.5
117.3
112.7
105.8
77.5
77.2
76.8
39.7
34.5
33.2
29.2
22.1
19.4
3v
f1 (ppm)

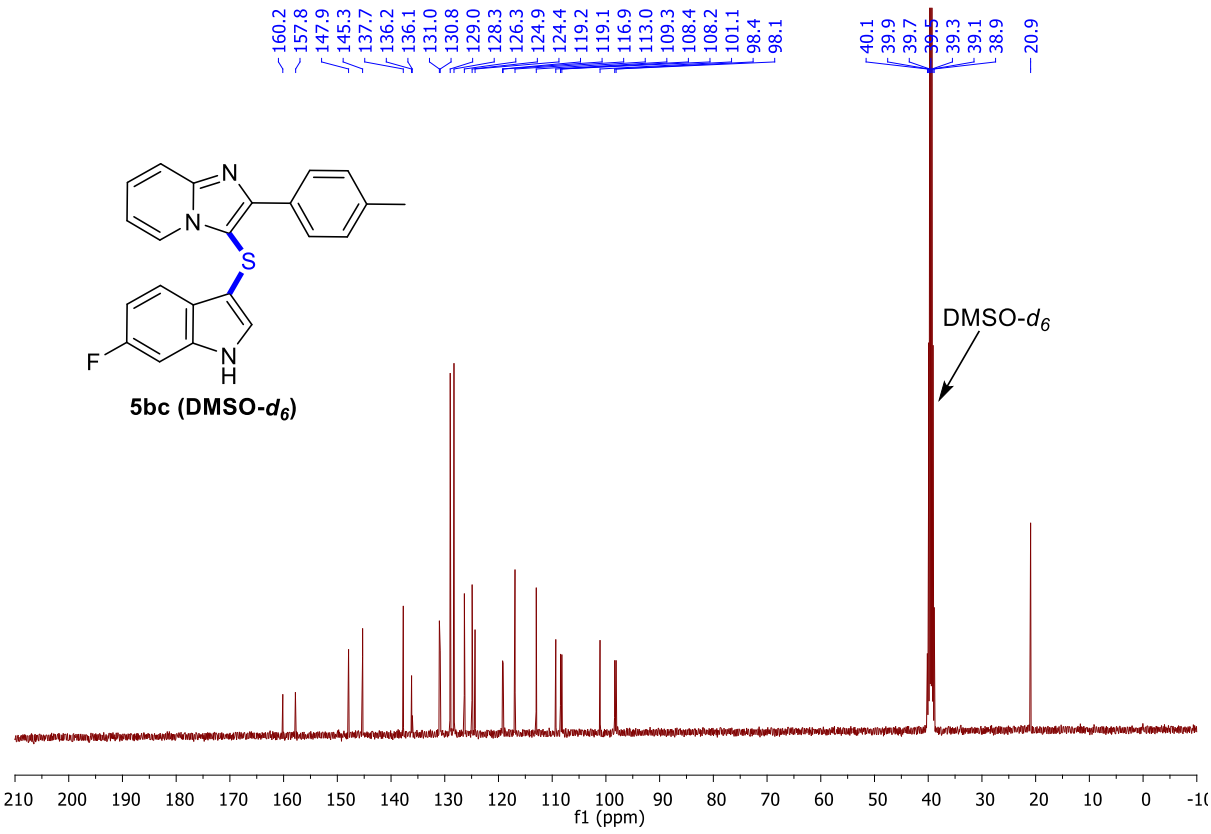

11.50
8.88
8.86
8.34
8.32
7.86
7.85
7.65
7.63
7.61
7.59
7.57
7.51
7.49
7.38
7.38
7.12
7.11
7.09
7.09
7.07
7.07
6.91
6.90
6.89
6.64
6.64
2.50
-0.01
5ac (DMSO-d_6)
Moisture
in DMSO-d_6
DMSO-d_6
1.00
1.00
2.00
1.00
1.00
2.01
1.00
1.10
2.19
1.10
1.05
f1 (ppm)
160.1
157.8
147.9
145.3
136.2
136.0
133.8
131.0
128.4
128.4
128.4
126.5
125.0
124.3
119.2
119.1
117.0
113.1
109.8
108.4
108.2
101.0
98.4
98.1
40.1
39.9
39.7
39.5
39.3
39.1
38.9
5ac (DMSO-d_6)
DMSO-d_6
f1 (ppm)

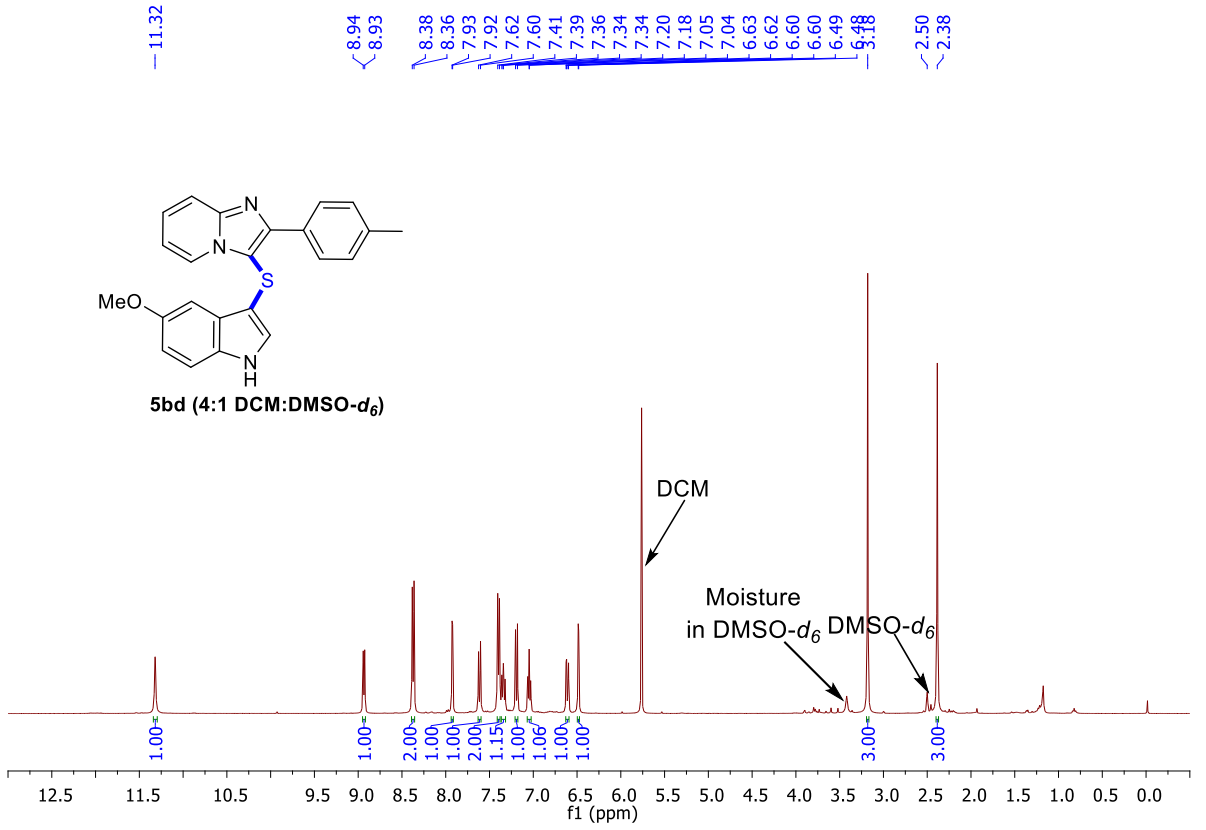

11.31
8.95
8.93
8.46
8.45
7.93
7.92
7.65
7.62
7.62
7.60
7.58
7.47
7.38
7.37
7.18
7.16
7.08
7.07
6.60
6.60
6.58
6.57
6.44
6.43
5.14
2.50
2.50
2.50
MeO
S
N
H
5ad (DMSO-d_6)
Moisture
in DMSO-d_6
DMSO-d_6
1.00
1.00
2.00
1.00
3.19
1.12
1.13
0.94
1.03
1.00
1.00
3.00
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
153.9
147.5
145.3
131.0
128.4
128.4
128.3
128.2
117.0
113.0
112.7
110.1
99.9
99.1
54.4
40.1
39.9
39.7
39.5
39.3
39.1
38.9
MeO
S
N
H
5ad (DMSO-d_6)
134.0
131.0
129.0
128.6
128.4
128.4
128.3
128.2
126.4
125.1
DMSO-d_6
134
132
130
128
126
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

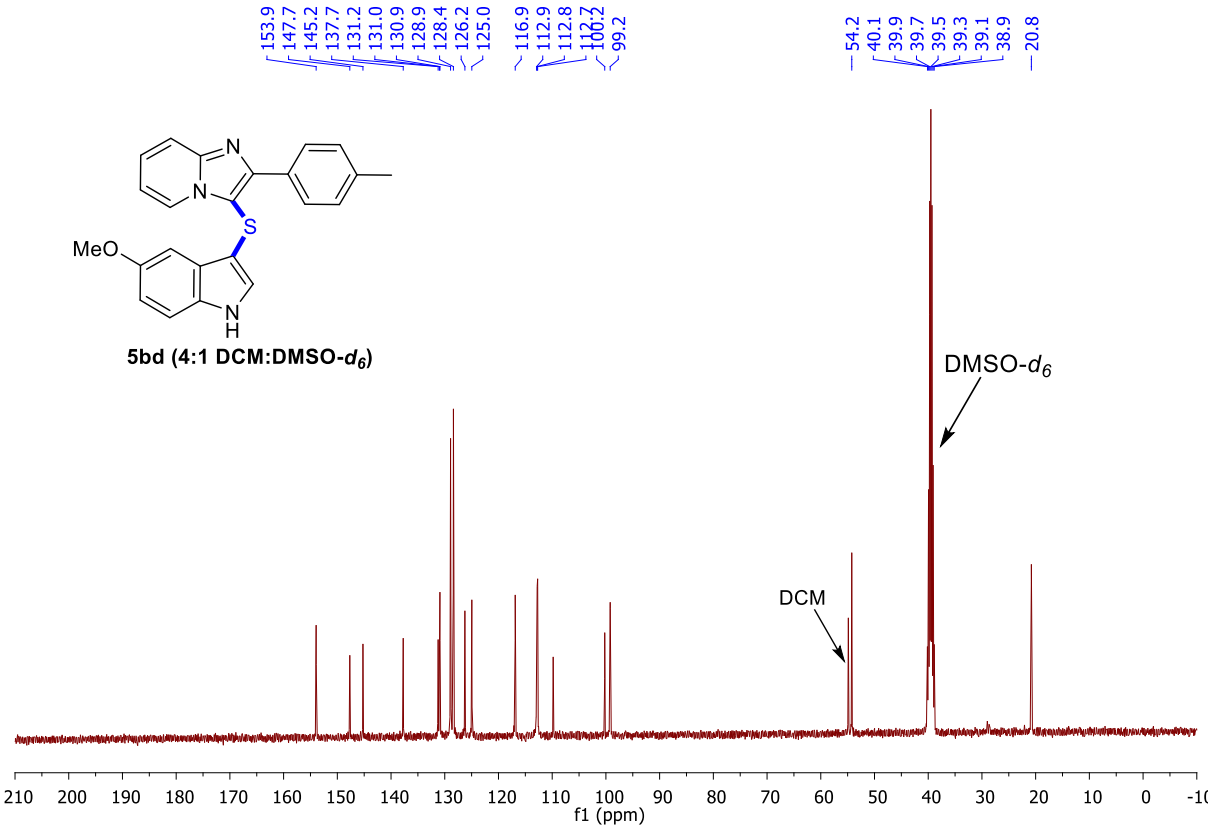

11.44
8.87
8.85
8.31
8.29
7.85
7.62
7.60
7.40
7.38
7.36
7.34
7.33
7.31
7.06
7.05
7.03
7.01
6.99
6.81
6.79
6.78
2.50
2.42
5ba (DMSO-d6)
Moisture
in DMSO-d6
DMSO-d6
1.00
1.00
2.00
1.00
1.00
4.00
3.00
1.00
3.06
f1 (ppm)
147.8
145.2
137.7
136.2
131.1
130.2
129.0
128.3
127.7
126.3
124.9
121.9
119.7
118.2
116.9
112.9
112.1
109.7
100.6
40.1
39.9
39.7
39.5
39.3
39.1
38.9
21.0
5ba (DMSO-d6)
DMSO-d6
f1 (ppm)


11.59
8.89
8.87
8.15
8.13
7.93
7.63
7.61
7.42
7.41
7.38
7.36
7.26
7.24
7.11
7.09
7.06
6.94
2.50
2.44
Br
5bb (DMSO-d_6)
Moisture DMSO-d_6
in DMSO-d_6
1.00
1.00
2.00
1.00
1.00
3.15
1.00
2.00
1.00
3.12
f1 (ppm)
148.7
145.3
137.8
134.8
131.8
130.9
129.5
129.0
128.5
126.4
124.9
124.5
120.9
116.9
114.0
113.0
112.5
109.6
100.7
40.1
39.9
39.7
39.5
39.3
39.1
38.9
21.0
Br
5bb (DMSO-d_6)
DMSO-d_6
f1 (ppm)


8.56
8.56
8.55
8.54
8.54
8.54
8.23
8.21
7.34
7.32
7.26
7.25
7.23
7.23
7.23
7.22
7.22
7.21
7.21
7.20
7.17
7.17
6.93
6.93
6.91
6.90
6.86
6.86
6.74
6.74
6.74
6.74
2.45
0.00
F
N
H
5bc (CDCl3)
1.24
2.00
1.00
2.00
2.00
1.00
1.00
1.00
3.00
f1 (ppm)


160.2
157.8
147.9
145.3
137.7
136.2
136.1
131.0
130.8
129.0
128.3
126.3
124.9
124.4
119.2
119.1
116.9
113.0
109.3
108.4
108.2
101.1
98.4
98.1
40.1
39.9
39.7
39.5
39.3
39.1
38.9
20.9
DMSO-d6
F
N
H
5bc (DMSO-d6)
f1 (ppm)


11.32
8.94
8.93
8.38
8.36
7.93
7.92
7.62
7.60
7.41
7.39
7.36
7.34
7.34
7.20
7.18
7.05
7.04
6.63
6.62
6.60
6.60
6.49
6.48
3.18
2.50
2.38
MeO
N
H
5bd (4:1 DCM:DMSO-d_6)
DCM
Moisture
in DMSO-d_6
DMSO-d_6
1.00
1.00
2.00
1.00
1.00
2.00
1.15
1.00
1.06
1.00
1.00
3.00
3.00
f1 (ppm)


153.9
147.7
145.2
137.7
131.2
131.0
130.9
128.9
128.4
126.2
125.0
116.9
112.9
112.8
99.2
54.2
40.1
39.9
39.7
39.5
39.3
39.1
38.9
20.8
MeO
N
H
5bd (4:1 DCM:DMSO-d_6)
DMSO-d_6
DCM
f1 (ppm)