SUPPORTING INFORMATION

Copper-catalyzed radical 1,2-oxysulfoximination of *β,γ*-unsaturated oximes for the synthesis of sulfoximine-substituted isoxazolines

Kishor R. Thete, [a,b] *Vijay Vara,* [a,b] *Raj Y. Patel,* [a] *and M. Muthukrishnan* *[a,b]

[a]Division of Organic Chemistry, CSIR-National Chemical Laboratory, Pune - 411008, India.
[b]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India

E-mail: m.muthukrishnan.ncl@csir.res.in

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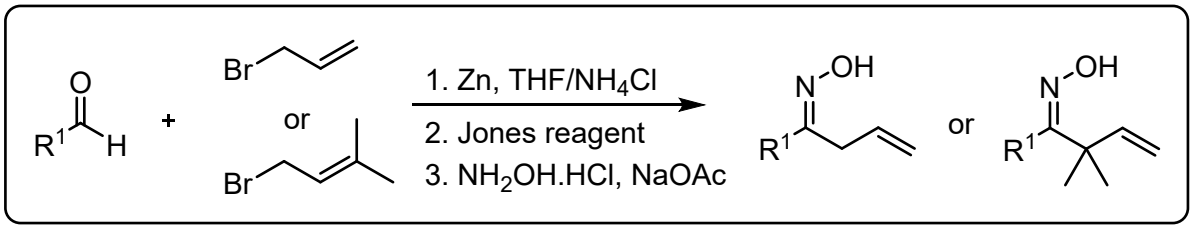
1. General information

Most of the reagents and starting materials used were purchased from commercial sources and used as such. Commercially available dry DMSO was used without further distillation. Melting points are uncorrected and recorded using digital Buchi Melting Point Apparatus B-540. 1H, ^{13}C, DEPT and ^{19}F NMR spectra were recorded on Bruker AV 400/500, AV 100/125 & AV 376 MHz spectrometers, respectively, in $CDCl_3$ using TMS as internal standard, and the chemical shifts are shown in δ scale. Multiplicities of 1H NMR signals are designated as s (singlet), d (doublet), dd (doublet of doublet), t (triplet), quin (quintet), spt (septet) br.s. (broad signal), m (multiplet) etc. Thin layer chromatography was performed on Merck silica gel 60 F254 TLC plates using EtOAc/ pet ether as an eluent. Column chromatography was carried out through silica gel (100-200 mesh) using ethyl acetate/pet ether as an eluent. High-resolution mass spectra (HRMS) were recorded on a Q Exactive Hybrid Quadrupole Orbitrap Mass Spectrometer, where the mass analyzer used for analysis is orbitrap.

2. Experimental section:

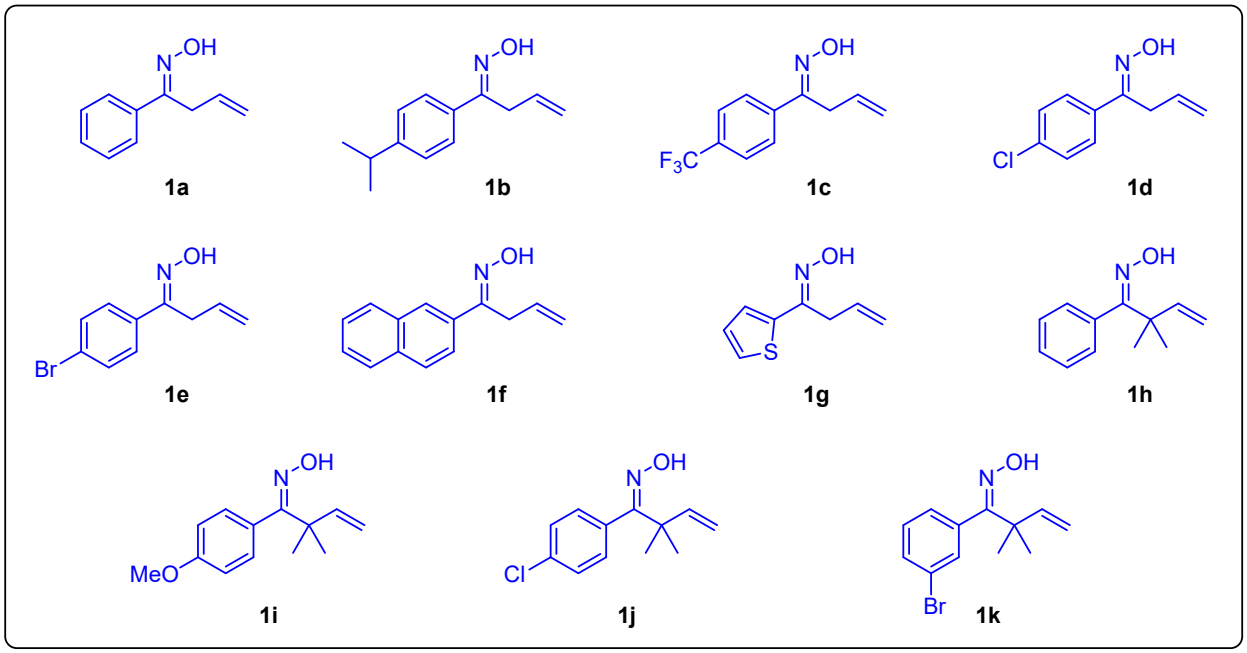
2.1. Experimental procedure for the synthesis of *β,γ*-unsaturated oximes[1-3]



1) To a solution of allyl bromide (2.0 equiv) in anhydrous THF, zinc dust (2.0 equiv) was slowly added at 0 ℃. Aldehyde (1.0 equiv) was dissolved in anhydrous THF and added to the solution. The resulting suspension was stirred overnight at this temperature. The reaction was quenched with NH_4Cl (aq.) carefully at 0 °C, filtered, and extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude homoallylic alcohol product was directly used in the next step without further purification.

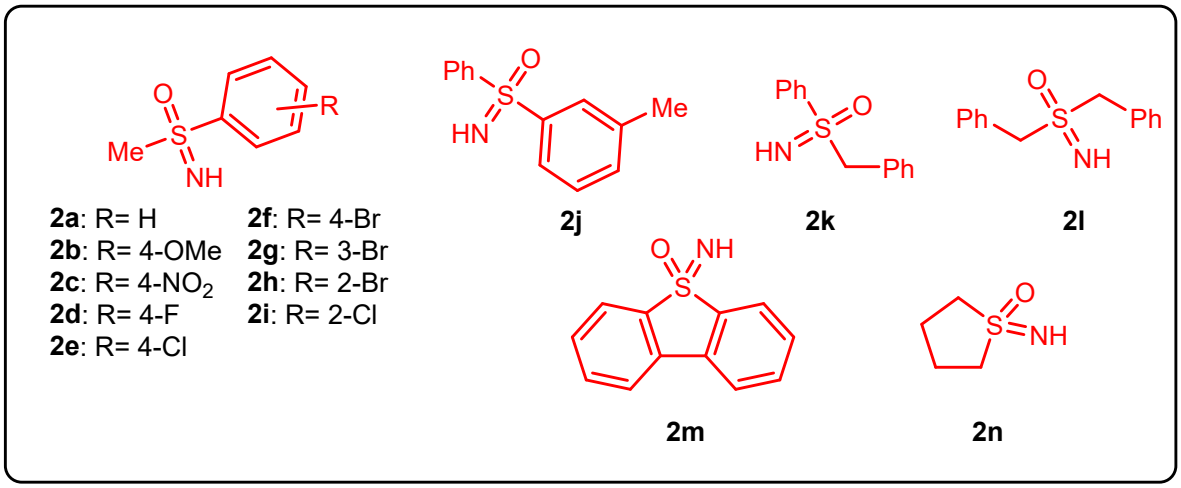
2) A solution of the homoallylic alcohol in diethyl ether was stirred at 0 ℃ while Jones reagent (2.0-4.0 equiv) was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred for 1 hour. The diethyl ether layer was then separated from the aqueous layer, which was extracted with ethyl acetate for 3 times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude ketone product was directly used in the next step without further purification.

3) To a solution of sodium acetate (7.0 equiv) in ethanol, hydroxylamine hydrochloride (5.0 equiv, dissolved in H_2O) was added. The mixture was stirred at room temperature while the ketone (dissolved in ethanol) was added. The mixture was stirred overnight and then extracted with ethyl acetate 3 times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude material was purified by flash chromatography on silica gel to afford the corresponding unsaturated oxime.

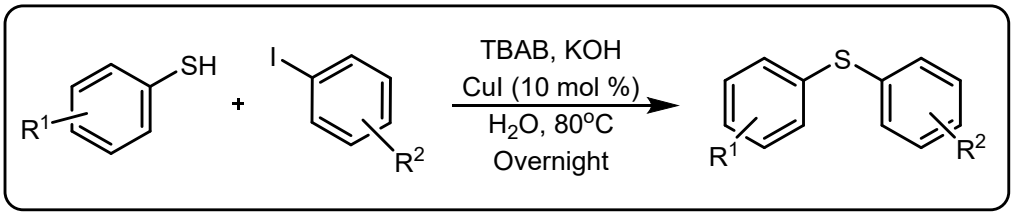


2.2. Experimental procedure for the synthesis of sulfoximines[4-6]

Sulfoximines **2a-2i and 2k-2n** were synthesized in a single step from commercially available sulfides according to the known literature procedure.[5,6] And *sulfoximine* **2j** were synthesized in two steps from corresponding aryl iodide and thiols according to the known literature procedure[4] followed by the synthesis of *NH*-sulfoximines from sulfide.[5]

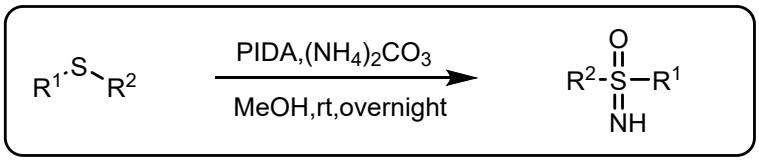


2.2.1 Experimental procedure for the synthesis of sulfides[4]



According to the modified literature procedure[4] the corresponding aryl iodide (11 mmol, 1.1 equiv.), tetra-*n*-butylammonium bromide (TBAB, 10 mmol, 3225 mg, 1.0 equiv.), KOH (15 mmol, 842 mg, 1.5 equiv.), CuI (1.0 mmol, 190 mg, 0.1 equiv.), and the corresponding thiols (10 mmol, 1.0 equiv.) were suspended in H_2O (10 mL). The resulting suspension was stirred overnight at 80 °C in an aluminium block. After cooling down to room temperature, Et_2O (100 mL) was added, and the separated aqueous layer was extracted with Et_2O (3x 30 mL). The combined organic layers were washed with H_2O (20 mL) and brine (20 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography on silica gel (*n*-pentane: EtOAc 80:1) afforded the desired disulfide.

2.2.2 Experimental procedure for the synthesis of sulfoximines[5-6]



According to the modified literature[5-6] in a closed screw cap reaction tube, the corresponding disulfide (1.0 mmol), ammonium carbonate (1.5 mmol, 144 mg, 1.5 equiv.), and (diacetoxyiodo)benzene (PIDA, 2.3 mmol, 741 mg, 2.3 equiv.) were suspended in MeOH (10 mL) and stirred overnight at room temperature. SiO_2 was added, the solvents were removed under reduced pressure, and the product was purified by column chromatography on silica (*n*-pentane: EtOAc 1:0 → 4:1 → 0:1).

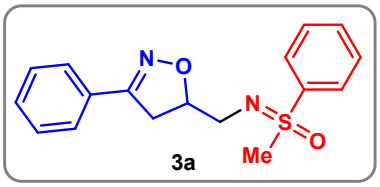
2.3 Experimental procedure for the synthesis of 3a:

An oven-dried 10 ml Schlenk tube equipped with a magnetic stir bar was charged with *β,γ*-unsaturated oximes **1a** (0.31 mmol, 1.0 equiv.), sulfoximine **2a** (0.37 mmol, 1.2 equiv.), $Cu(OAc)_2$ (0.06 mmol, 20 mol%), and K_2CO_3 (0.31 mmol, 1.0 equiv.). Anhydrous DMSO (2 mL) was added to the resulting mixture, which was then stirred at room temperature under an argon atmosphere for 24 h until complete consumption of the starting material, as monitored by TLC. Upon completion, the reaction mixture was diluted with ethyl acetate (5 ml) and washed with water (3 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude material was purified by silica gel column chromatography using petroleum ether/ethyl acetate as the eluent to afford the desired product **3a**.

The same general procedure was followed for the preparation of compounds **3b-3n** and **4a-4l**. For unsymmetrical chiral S(VI) sulfoximines, the products were obtained as inseparable diastereomeric mixtures, with diastereomeric ratios ranging from 1.1:1 to 2:1, as determined by ^{1}H NMR analysis.

3. Characterization Data of 3 & 4:

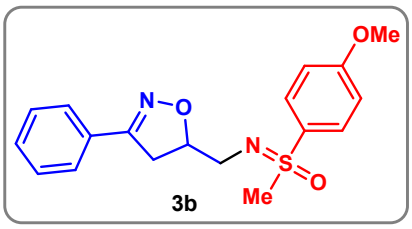
methyl(phenyl)(((3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)imino)-λ⁶-sulfanone (3a):



3a

The product **3a** was obtained in 81% yield (79 mg, off White solid), (dr 2:1); **mp** = 118-120 °C; R_f = 0.25 (petroleum ether/ethyl acetate = 50/50); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = δ 7.91 (t, *J* = 8.9 Hz, 2H), 7.72 – 7.62 (m, 2H), 7.62 – 7.49 (m, 3H), 7.38 (s, 3H), 4.96 – 4.80 (m, 1H), 3.54 – 3.27 (m, 2H), 3.26 – 3.04 (m, 5H).; **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ** = 156.7, 156.5, 139.2, 139.1, 133.0, 129.9, 129.8, 129.7, 129.5, 129.4, 128.7, 128.6, 128.5, 126.7, 81.7, 81.6, 47.0, 46.4, 45.2, 44.8, 38.3, 37.7.; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ calcd for $C_{17}H_{19}O_2N_2S$ 315.1162; found 315.1165.

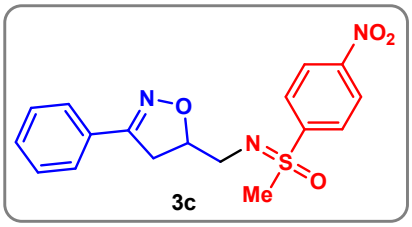
(4-methoxyphenyl)(methyl)(((3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)imino)-λ⁶-sulfanone (3b):



3b

The product **3b** was obtained in 66% yield (71 mg, Light brown solid), (dr 1.2:1); **mp** = 92-94 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 50/50); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = δ 7.82 (t, *J* = 8.8 Hz, 2H), 7.71 – 7.61 (m, 2H), 7.36 (dd, *J* = 7.2, 4.7 Hz, 3H), 6.99 (dd, *J* = 13.0, 8.9 Hz, 2H), 4.94 – 4.78 (m, 1H), 3.84 (d, *J* = 5.0 Hz, 3H), 3.52 – 3.12 (m, 3H), 3.06 (d, *J* = 20.8 Hz, 4H).; **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ** = 163.3, 156.7, 156.5, 130.8, 130.7, 129.8, 129.8, 129.7, 129.7, 128.5, 126.6, 114.6, 114.6, 81.7, 81.6, 55.6, 46.9, 46.3, 45.4, 45.1, 38.3, 37.6.; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ calcd for $C_{18}H_{21}O_3N_2S$ 345.1267; found 345.1275.

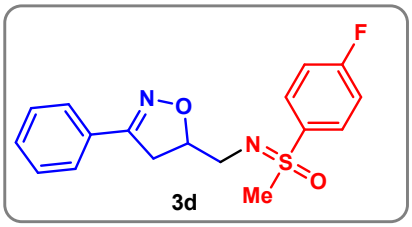
methyl(4-nitrophenyl)(((3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)imino)-λ⁶-sulfanone (3c):



3c

The product **3c** was obtained in 64% yield (71 mg, Off white solid), (dr 1.2:1); **mp** = 114-116 °C; R_f = 0.35 (petroleum ether/ethyl acetate = 50/50); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 8.36 (dd, *J* = 20.8, 8.6 Hz, 2H), 8.13 (t, *J* = 8.4 Hz, 2H), 7.73 – 7.61 (m, 2H), 7.40 (dd, *J* = 7.3, 4.1 Hz, 3H), 4.96 – 4.80 (m, 1H), 3.54 – 3.20 (m, 3H), 3.19 – 3.04 (m, 4H).; **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ** = 156.8, 156.6, 150.5, 150.5, 145.6, 145.6, 130.2, 130.0, 130.0, 129.9, 129.7, 129.5, 128.7, 128.6, 126.6, 126.6, 124.5, 124.5, 81.4, 81.2, 47.0, 46.1, 45.1, 44.5, 38.1, 37.3.; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ calcd for $C_{17}H_{18}O_4N_3S$ 360.1013; found 360.1011.

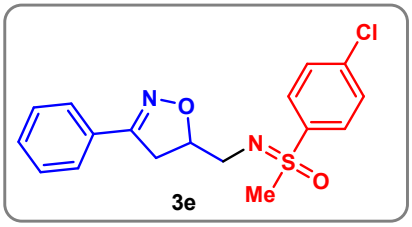
(4-fluorophenyl)(methyl)(((3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)imino)-λ⁶-sulfanone (3d):



3d

The product **3d** was obtained in 78% yield (80 mg, Off white solid), (dr ratio 1.7:1); **mp** = 95-97 °C; R_f = 0.35 (petroleum ether/ethyl acetate = 50/50); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 7.99 – 7.87 (m, 2H), 7.74 – 7.62 (m, 2H), 7.39 (s, 3H), 7.22 (dt, *J* = 17.2, 5.8 Hz, 2H), 4.97 – 4.80 (m, 1H), 3.54 – 3.23 (m, 2H), 3.22 – 3.03 (m, 5H).; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ** =165.5 (d, *J* = 255.1 Hz), 165.5 (d, *J* = 255.1 Hz), 156.7, 156.5, 135.1, 135.0, 131.5 (d, *J* = 14.6 Hz), 131.4 (d, *J* = 14.7 Hz), 129.9, 129.8, 129.6, 128.6, 126.7, 126.7, 116.7 (d, *J* = 22.4 Hz), 116.6 (d, *J* = 22.5 Hz), 81.6, 81.5, 47.0, 46.3, 45.4, 45.0, 38.2, 37.5.; **^{19}F NMR (376 MHz, CDCl$_3$) δ** = -105.06, -105.10; **HRMS (ESI-TOF)** *m/z*: [M + H]$^+$ calcd for $C_{17}H_{18}O_2N_2FS$ 333.1068; found 333.1070.

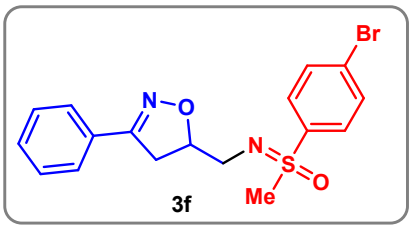
(4-chlorophenyl)(methyl)(((3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)imino)-λ⁶-sulfanone (3e):



3e

The product **3e** was obtained in 67% yield (73 mg, Off white solid), (dr 1.1:1); **mp** = 112-114 °C; R_f = 0.35 (petroleum ether/ethyl acetate = 50/50); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 7.89 – 7.82 (m, 2H), 7.72 – 7.63 (m, 2H), 7.55 – 7.46 (m, 2H), 7.39 (dt, *J* = 5.2, 3.7 Hz, 3H), 4.95 – 4.80 (m, 1H), 3.53 – 3.13 (m, 3H), 3.13 – 3.04 (m, 4H).; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ** = 156.7, 156.5, 139.8, 137.7, 137.7, 130.3, 130.1, 129.9, 129.8, 129.8, 129.8, 129.7, 129.6, 128.6, 128.6, 126.7, 126.7, 81.6, 81.4, 47.0, 46.3, 45.3, 44.8, 38.2, 37.5.; **HRMS (ESI-TOF)** *m/z*: [M + H]$^+$ calcd for $C_{17}H_{18}O_2N_2ClS$ 349.0772; found 349.0768.

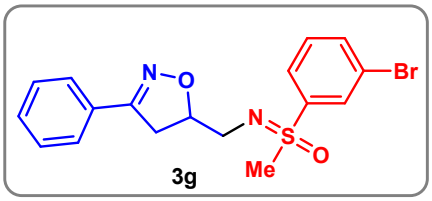
(4-bromophenyl)(methyl)(((3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)imino)-λ⁶-sulfanone (3f):



3f

The product **3f** was obtained in 70% yield (85 mg, Off white solid), (dr 1.2:1); **mp** = 119-121 °C; R_f = 0.35 (petroleum ether/ethyl acetate = 50/50); **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 7.78 (t, *J* = 9.3 Hz, 2H), 7.73 – 7.62 (m, 4H), 7.46 – 7.34 (m, 3H), 4.95 – 4.79 (m, 1H), 3.53 – 3.16 (m, 3H), 3.15 – 3.03 (m, 4H).; **^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ** = 156.7, 156.5, 138.3, 138.2, 132.7, 132.7, 130.4, 130.2, 129.9, 129.8, 129.8, 129.6, 128.6, 128.3, 126.7, 81.6, 81.4, 47.0, 46.3, 45.2, 44.8, 38.2, 37.5.; **HRMS (ESI-TOF)** *m/z*: [M + H]$^+$ calcd for $C_{17}H_{18}O_2N_2BrS$ 393.0267; found 393.0274.

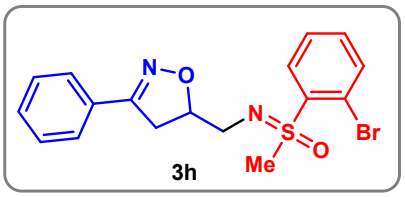
(3-bromophenyl)(methyl)(((3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)imino)-λ⁶-sulfanone (3g):



3g

The product **3g** was obtained in 75% yield (92 mg, Off white solid), (dr 1.4:1); **mp** = 86-88 °C; R_f = 0.35 (petroleum ether/ethyl acetate = 50/50)); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 8.18 – 8.02 (m, 1H), 7.96 – 7.82 (m, 1H), 7.77 – 7.63 (m, 3H), 7.42 (ddd, *J* = 14.6, 7.3, 2.8 Hz, 4H), 4.95 – 4.80 (m, 1H), 3.51 – 3.16 (m, 3H), 3.14 – 3.06 (m, 4H).; **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ** = 156.7, 156.5, 141.4, 141.3, 136.1, 136.1, 131.7, 131.5, 131.0, 130.9, 130.8, 130.7, 129.9, 129.8, 129.8, 129.6, 128.6, 128.6, 127.2, 127.0, 126.7, 126.2, 123.5, 123.5, 81.5, 81.4, 46.9, 46.3, 45.2, 44.8, 38.3, 37.6.; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ calcd for $C_{17}H_{18}O_2N_2BrS$ 393.0267; found 393.0271.

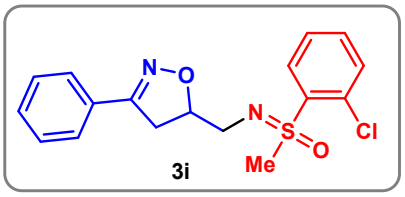
(2-bromophenyl)(methyl)(((3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)imino)-λ⁶-sulfanone (3h):



3h

The product **3h** was obtained in 68% yield (83 mg, Light yellow sticky solid), (dr 1.3:1); R_f = 0.35 (petroleum ether/ethyl acetate = 50/50); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 8.20 (dd, *J* = 12.6, 4.5 Hz, 1H), 7.78 – 7.70 (m, 1H), 7.65 (d, *J* = 3.0 Hz, 2H), 7.51 (dd, *J* = 15.6, 7.8 Hz, 1H), 7.46 – 7.33 (m, 4H), 4.92 – 4.80 (m, 1H), 3.51 – 3.36 (m, 2H), 3.31 (d, *J* = 7.6 Hz, 3H), 3.22 – 2.90 (m, 2H).; **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ** = 156.5, 156.5, 138.0, 137.9, 135.6, 135.5, 134.2, 133.3, 133.2, 129.8, 129.8, 129.8, 129.7, 128.5, 128.3, 128.3, 126.7, 126.6, 120.7, 120.6, 81.4, 81.3, 46.7, 42.6, 42.5, 38.6, 38.1.; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ calcd for $C_{17}H_{18}O_2N_2BrS$ 393.0267; found 393.0269.

(2-chlorophenyl)(methyl)(((3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)imino)-λ⁶-sulfanone (3i):

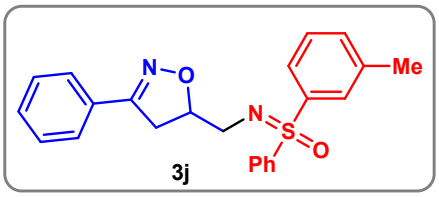


3i

The product **3i** was obtained in 72% yield (78 mg, Light yellow sticky solid), (dr 1.2:1); R_f = 0.35 (petroleum ether/ethyl acetate = 50/50); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 8.16 (dd, *J* = 12.3, 4.4 Hz, 1H), 7.70 – 7.61 (m, 2H), 7.51 (dd, *J* = 10.5, 2.3 Hz, 2H), 7.49 – 7.42 (m, 1H), 7.40 – 7.33 (m, 3H), 4.88 – 4.78 (m, 1H), 3.47 – 3.34 (m, 2H), 3.30 (d, *J* = 7.2 Hz, 3H), 3.23 – 2.89 (m, 2H).; **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ** = 156.5,

156.5, 136.3, 136.2, 134.2, 134.2, 133.0, 132.9, 132.2, 132.2, 132.0, 131.9, 129.8, 129.8, 129.7, 128.5, 127.6, 127.6, 126.7, 126.6, 81.4, 81.3, 46.7, 43.0, 42.9, 38.5, 38.1.; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ calcd for $C_{17}H_{18}O_2N_2ClS$ 349.0772; found 349.0770.

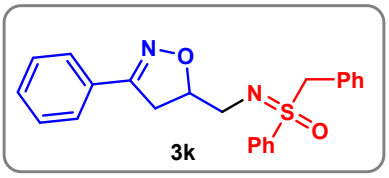
phenyl(((3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)imino)(m-tolyl)-λ⁶-sulfanone (3j):



3j

The product **3j** was obtained in 61% yield (74 mg, Off white solid); (dr 2:1); **mp** = 102-104 °C; R_f = 0.35 (petroleum ether/ethyl acetate = 50/50); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 7.97 (dd, *J* = 22.0, 7.0 Hz, 2H), 7.76 (dd, *J* = 25.8, 7.6 Hz, 4H), 7.48 (dd, *J* = 13.8, 7.2 Hz, 2H), 7.43 – 7.26 (m, 6H), 5.00 (td, *J* = 10.5, 5.9 Hz, 1H), 3.62 – 3.40 (m, 2H), 3.29 (ddd, *J* = 18.8, 12.7, 5.2 Hz, 2H), 2.33 (d, *J* = 47.1 Hz, 3H).; **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ** = 156.7, 140.7, 140.4, 140.1, 139.9, 139.4, 139.3, 133.4, 133.3, 132.45, 132.4, 129.9, 129.8, 129.2, 129.1, 128.9, 128.8, 128.6, 128.5, 126.7, 125.9, 125.6, 81.7, 81.6, 46.9, 46.8, 38.1, 38.0, 21.3, 21.2.; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ calcd for $C_{23}H_{23}O_2N_2S$ 391.1475; found 391.1479.

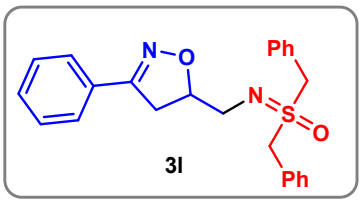
benzyl(phenyl)(((3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)imino)-λ⁶-sulfanone (3k):



3k

The product **3k** was obtained in 54% yield (65 mg, Off white solid), (dr 2:1); **mp** = 113-115 °C; R_f = 0.35 (petroleum ether/ethyl acetate = 50/50); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 7.94 (d, *J* = 7.4 Hz, 1H), 7.69 (dd, *J* = 19.0, 5.4 Hz, 3H), 7.61 – 7.49 (m, 3H), 7.43 (dd, *J* = 18.9, 11.2 Hz, 4H), 7.19 (dd, *J* = 16.7, 8.1 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 9.0 Hz, 2H), 4.99 – 4.82 (m, 1H), 4.51 – 4.22 (m, 2H), 3.57 – 3.15 (m, 4H).; **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ** = 156.7, 156.5, 142.2, 136.9, 136.7, 133.0, 132.6, 131.2, 131.1, 130.0, 129.9, 129.8, 129.6, 129.0, 128.9, 128.6, 128.6, 128.5, 128.5, 128.5, 128.2, 128.1, 126.7, 126.7, 126.3, 81.8, 81.6, 63.2, 62.9, 47.0, 46.2, 38.3, 37.4.; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ calcd for $C_{23}H_{23}O_2N_2S$ 391.1475; found 391.1480.

dibenzyl(((3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)imino)-λ⁶-sulfanone (3l):

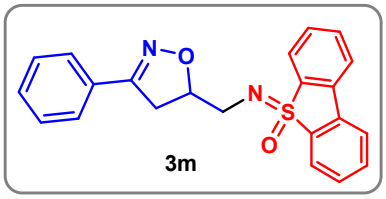


3l

The product **3l** was obtained in 47% yield (59 mg, Light brown solid); **mp** = 105-107 °C; R_f = 0.35 (petroleum ether/ethyl acetate = 50/50); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 7.60 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.41 – 7.35 (m, 8H), 7.32 – 7.28 (m, 2H), 7.24

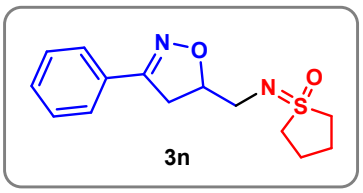
(t, J = 7.0 Hz, 3H), 4.76 – 4.67 (m, 1H), 4.24 (q, J = 13.5 Hz, 2H), 4.17 (s, 2H), 3.15 (dd, J = 4.8, 3.2 Hz, 2H), 3.08 (d, J = 9.0 Hz, 2H).; **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ** = 156.5, 131.1, 131.1, 129.9, 129.8, 128.7, 128.7, 128.6, 128.5, 128.1, 126.7, 81.8, 59.4, 45.4, 37.3.; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ calcd for $C_{24}H_{25}O_2N_2S$ 405.1631; found 405.1626.

5-(((3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)imino)-5H-5λ⁴-dibenzo[b,d]thiophene 5-oxide (3m):



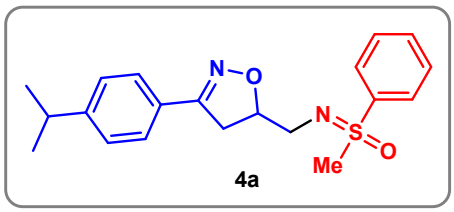
The product **3m** was obtained in 45 % yield (52 mg, Light yellow sticky gum); R_f = 0.3 (petroleum ether/ethyl acetate = 50/50); **^1H NMR (400 MHz, $CDCl_3$) δ** = 7.77 (dd, J = 17.4, 7.4 Hz, 4H), 7.63 (dd, J = 26.1, 3.0 Hz, 4H), 7.47 (dd, J = 14.5, 7.1 Hz, 2H), 7.39 (s, 3H), 4.90 (dd, J = 12.6, 7.5 Hz, 1H), 3.55 (dd, J = 12.1, 4.2 Hz, 1H), 3.50 – 3.31 (m, 3H).; **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ** = 156.6, 138.6, 138.5, 133.2, 133.1, 132.5, 132.1, 131.9, 130.1, 129.9, 129.7, 129.5, 128.6, 127.5, 126.7, 122.5, 121.6, 121.6, 81.4, 47.0, 38.3.; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ calcd for $C_{22}H_{19}O_2N_2S$ 375.1162; found 375.1166.

1-(((3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)imino)tetrahydro-1H-1λ⁶-thiophene 1-oxide (3n):



The product **3n** was obtained in 70 % yield (61 mg, Light yellow sticky gum); R_f = 0.35 (petroleum ether/ethyl acetate = 50/50); **^1H NMR (400 MHz, $CDCl_3$) δ** = 7.67 – 7.61 (m, 2H), 7.38 – 7.33 (m, 3H), 4.89 – 4.80 (m, 1H), 3.32 (dd, J = 9.8, 7.0 Hz, 4H), 3.28 – 3.11 (m, 2H), 3.02 – 2.91 (m, 2H), 2.23 – 2.06 (m, 4H).; **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ** = 156.7, 129.8, 129.6, 128.5, 126.5, 81.6, 52.5, 52.1, 47.2, 37.5, 23.5, 23.3.; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ calcd for $C_{14}H_{19}O_2N_2S$ 279.1162; found 279.1157.

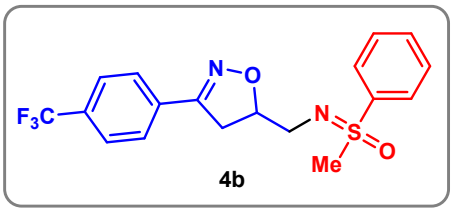
(((3-(4-isopropylphenyl)-4,5-dihydroisoxazol-5-yl)methyl)imino)(methyl)(phenyl)-λ⁶-sulfanone (4a):



The product **4a** was obtained in 65% yield (57 mg, Light yellow sticky solid), (dr 1.2:1); R_f = 0.3 (petroleum ether/ethyl acetate = 50/50); **^1H NMR (400 MHz, $CDCl_3$) δ** = 7.93 (t, J = 8.7 Hz, 2H), 7.61 (dd, J = 12.0, 8.2 Hz, 3H), 7.54 (dd, J = 14.1, 6.6 Hz, 2H), 7.28 – 7.22 (m, 2H), 4.94 – 4.78 (m, 1H), 3.52 – 3.18 (m, 3H), 3.14 – 3.08 (m, 4H), 2.99 – 2.88 (m, 1H), 1.26 (dd, J = 6.7, 4.4 Hz, 6H).; **$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ** = 156.6, 156.5, 151.0, 150.9, 139.1, 139.0, 133.1, 129.5, 129.5, 129.3, 128.7, 128.6, 127.6, 127.4, 127.2, 126.8, 126.7, 81.5, 81.4, 47.0, 46.4, 45.1, 44.8, 38.5, 37.9,

34.0, 23.8.; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ calcd for $C_{20}H_{25}O_2N_2S$ 357.1631; found 357.1634.

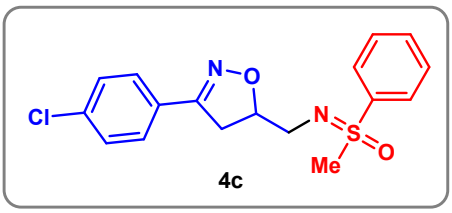
methyl(phenyl)(((3-(4-(trifluoromethyl)phenyl)-4,5-dihydroisoxazol-5-yl)methyl)imino)-λ⁶-sulfanone (4b):



4b

The product **4b** was obtained in 71% yield (59 mg, Light brown solid), (dr 1.6:1); **mp** = 112-114 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 50/50); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 7.95 – 7.87 (m, 2H), 7.79 (dd, *J* = 13.1, 8.2 Hz, 2H), 7.67 – 7.50 (m, 5H), 4.94 (ddd, *J* = 18.9, 12.6, 6.1 Hz, 1H), 3.56 – 3.29 (m, 2H), 3.15 (dd, *J* = 51.4, 17.2 Hz, 5H).; **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ** = 155.7, 155.5, 133.1, 129.5, 129.5, 128.7, 128.5, 126.9, 125.5 (q, *J* = 3.6 Hz), 82.3, 82.2, 46.8, 46.4, 45.2, 44.9, 37.9, 37.2.; **^{19}F NMR (376 MHz, $CDCl_3$) δ** = -62.84, -62.86.; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ calcd for $C_{18}H_{18}O_2N_2F_3S$ 383.1036; found 383.1036.

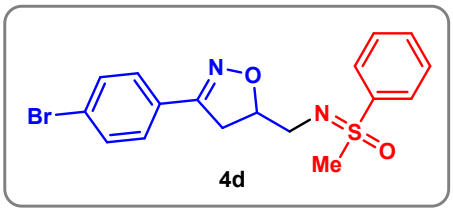
(((3-(4-chlorophenyl)-4,5-dihydroisoxazol-5-yl)methyl)imino)(methyl)(phenyl)-λ⁶-sulfanone (4c):



4c

The product **4c** was obtained in 62% yield (55 mg, Light brown solid), (dr 1.6:1); **mp** = 103-105 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 50/50); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 7.96 – 7.86 (m, 2H), 7.58 (tt, *J* = 14.8, 7.8 Hz, 5H), 7.36 (dd, *J* = 8.4, 6.7 Hz, 2H), 4.91 (dt, *J* = 16.7, 6.5 Hz, 1H), 3.52 – 3.25 (m, 2H), 3.09 (d, *J* = 21.6 Hz, 5H).; **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ** = 155.8, 155.6, 135.8, 135.7, 133.1, 129.5, 129.5, 128.9, 128.7, 128.5, 128.4, 128.3, 127.9, 82.0, 82.0, 46.9, 46.4, 45.2, 44.9, 38.2, 37.5.; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ calcd for $C_{17}H_{18}O_2N_2ClS$ 349.0772; found 349.0768.

(((3-(4-bromophenyl)-4,5-dihydroisoxazol-5-yl)methyl)imino)(methyl)(phenyl)-λ⁶-sulfanone (4d):

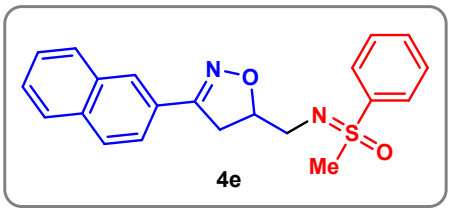


4d

The product **4d** was obtained in 66% yield (54 mg, Off white solid), (dr 1.6:1); **mp** = 107-109 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 50/50); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 7.90 (t, *J* = 8.7 Hz, 2H), 7.65 – 7.46 (m, 7H), 4.97 – 4.80 (m, 1H), 3.52 – 3.25 (m, 2H), 3.15 (dd, *J* = 49.8, 17.5 Hz, 5H).; **^{13}C{^{1}H} NMR**

(101 MHz, $CDCl_3$) δ = 155.9, 155.7, 139.1, 139.0, 133.1, 131.8, 129.5, 129.5, 128.8, 128.7, 128.5, 128.1, 124.1, 124.0, 82.0, 81.9, 46.9, 46.4, 45.2, 44.9, 38.1, 37.4.; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ calcd for $C_{17}H_{18}O_2N_2BrS$ 393.0267; found 393.0278.

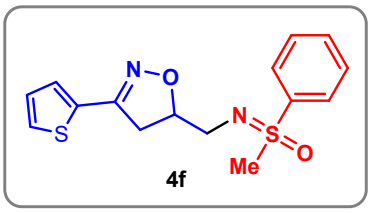
methyl(((3-(naphthalen-2-yl)-4,5-dihydroisoxazol-5-yl)methyl)imino)(phenyl)-λ⁶-sulfanone (4e):



4e

The product **4e** was obtained in 71% yield (61 mg, Off white solid), (dr 1.4:1); **mp** = 103-105 °C; R_f = 0.25 (petroleum ether/ethyl acetate = 50/50); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 7.97 (ddd, *J* = 15.2, 14.0, 6.4 Hz, 4H), 7.89 – 7.80 (m, 3H), 7.59 (dt, *J* = 19.4, 6.8 Hz, 2H), 7.52 (t, *J* = 6.1 Hz, 3H), 5.04 – 4.86 (m, 1H), 3.53 (dddd, *J* = 32.3, 23.7, 16.5, 7.1 Hz, 2H), 3.30 – 3.07 (m, 5H).; **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ** = 156.8, 156.7, 139.2, 139.1, 133.9, 133.1, 133.0, 133.0, 129.5, 129.5, 129.3, 128.7, 128.6, 128.4, 127.8, 127.7, 127.5, 127.3, 127.0, 126.9, 126.9, 126.6, 123.7, 123.6, 81.9, 81.8, 47.1, 46.5, 45.2, 44.8, 38.3, 37.6.; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ calcd for $C_{21}H_{21}O_2N_2S$ 365.1318; found 365.1320.

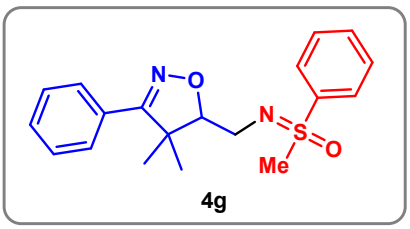
methyl(phenyl)(((3-(thiophen-2-yl)-4,5-dihydroisoxazol-5-yl)methyl)imino)-λ⁶-sulfanone (4f):



4f

The product **4f** was obtained in 51% yield (49 mg, Light brown solid), (dr 1.6:1); **mp** = 97-99 °C; R_f = 0.35 (petroleum ether/ethyl acetate = 50/50); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 7.91 (t, *J* = 8.6 Hz, 2H), 7.64 – 7.49 (m, 3H), 7.39 – 7.31 (m, 1H), 7.20 (dd, *J* = 11.2, 2.7 Hz, 1H), 7.09 – 7.00 (m, 1H), 4.95 – 4.78 (m, 1H), 3.55 – 3.28 (m, 2H), 3.25 – 3.05 (m, 5H).; **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ** = 152.5, 152.3, 139.1, 139.0, 133.1, 132.4, 132.2, 129.5, 129.4, 128.7, 128.5, 128.3, 128.2, 127.9, 127.8, 127.2, 81.9, 81.8, 46.86, 46.3, 45.2, 44.7, 39.1, 38.5.; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ calcd for $C_{15}H_{17}O_2N_2S_2$ 321.0726; found 321.0728.

(((4,4-dimethyl-3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)imino)(methyl)(phenyl)-λ⁶-sulfanone (4g):

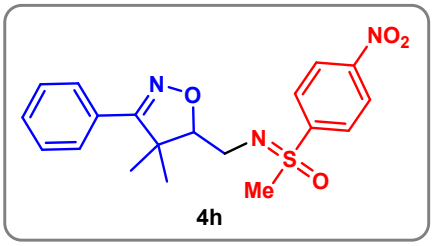


4g

The product **4g** was obtained in 67% yield (61 mg, Off white solid), (dr 1.1:1); **mp** = 111-113 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 50/50); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 8.01 – 7.94 (m, 2H), 7.60 (ddd, *J* = 10.6, 7.6, 2.8 Hz, 5H), 7.41 – 7.35 (m, 3H), 4.37 – 4.27 (m, 1H), 3.34 (ddd, *J* = 17.6, 12.9,

5.7 Hz, 1H), 3.21 – 3.06 (m, 4H), 1.44 (d, *J* = 3.8 Hz, 3H), 1.26 (d, *J* = 42.4 Hz, 3H).; **$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ** = 165.1, 165.0, 139.2, 138.8, 133.1, 133.0, 129.5, 129.5, 129.4, 129.4, 128.9, 128.5, 128.5, 127.5, 127.4, 91.1, 90.7, 50.9, 50.8, 45.4, 44.8, 42.5, 42.2, 25.2, 24.9, 19.2, 19.1.; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ calcd for $C_{19}H_{23}O_2N_2S$ 343.1475; found 343.1478.

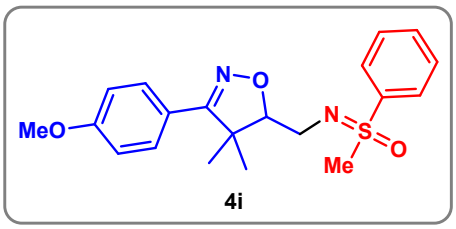
(((4,4-dimethyl-3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)imino)(methyl)(4-nitrophenyl)-λ⁶-sulfanone (4h):



4h

The product **4h** was obtained in 64% yield (66 mg, Light yellow liquid), (dr 1.1:1); ***R*$_f$** = 0.35 (petroleum ether/ethyl acetate = 50/50); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 8.42 (d, *J* = 8.7 Hz, 2H), 8.20 (t, *J* = 9.4 Hz, 2H), 7.64 – 7.55 (m, 2H), 7.38 (t, *J* = 6.1 Hz, 3H), 4.37 – 4.24 (m, 1H), 3.34 (ddd, *J* = 16.7, 13.0, 5.0 Hz, 1H), 3.17 (d, *J* = 5.8 Hz, 3H), 3.15 – 2.96 (m, 1H), 1.43 (s, 3H), 1.26 (d, *J* = 58.1 Hz, 3H).; **$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ** = 165.0, 165.0, 150.6, 150.5, 145.7, 145.3, 130.4, 130.0, 129.7, 129.6, 129.3, 129.2, 128.5, 127.5, 127.4, 124.6, 124.5, 91.0, 90.5, 50.9, 50.8, 45.2, 44.7, 42.6, 42.4, 25.6, 25.0, 19.1, 19.0.; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ calcd for $C_{19}H_{22}O_4N_3S$ 388.1326; found 388.1326.

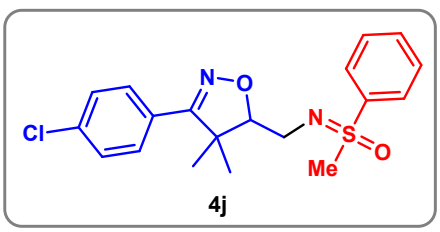
(((3-(4-methoxyphenyl)-4,4-dimethyl-4,5-dihydroisoxazol-5-yl)methyl)imino)(methyl)(phenyl) -λ⁶-sulfanone (4i):



4i

The product **4i** was obtained in 47% yield (40 mg, Sticky yellow gum), (dr 1.2:1); ***R*$_f$** = 0.35 (petroleum ether/ethyl acetate = 50/50); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 8.00 (s, 2H), 7.63 – 7.56 (m, 5H), 6.90 (dd, *J* = 8.0, 4.9 Hz, 2H), 4.39 – 4.20 (m, 1H), 3.82 (d, *J* = 2.3 Hz, 3H), 3.54 – 2.89 (m, 5H), 1.45 (d, *J* = 3.8 Hz, 3H), 1.26 (d, *J* = 41.0 Hz, 3H).; **$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ** = 160.6, 133.1, 133.1, 129.7, 129.6, 128.9, 128.8, 128.8, 128.6, 121.8, 121.7, 113.9, 55.4, 55.2, 25.2, 24.9, 19.3, 19.2.; **HRMS (ESI-TOF)** *m/z*: $[M + H]^+$ calcd for $C_{20}H_{25}O_3N_2S$ 373.1580; found 373.1577.

(((3-(4-chlorophenyl)-4,4-dimethyl-4,5-dihydroisoxazol-5-yl)methyl)imino)(methyl)(phenyl)-λ⁶-sulfanone (4j):

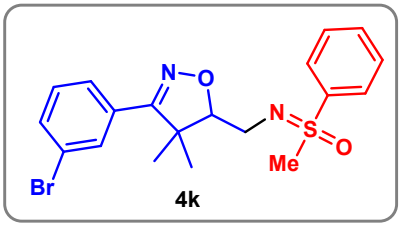


4j

The product **4j** was obtained in 61% yield (52 mg, Sticky yellow gum), (dr 1.2:1); ***R*$_f$** = 0.35 (petroleum ether/ethyl

acetate = 50/50); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 7.97 (t, *J* = 8.0 Hz, 2H), 7.64 – 7.52 (m, 5H), 7.35 (ddd, *J* = 8.6, 4.2, 2.1 Hz, 2H), 4.32 (dt, *J* = 23.8, 6.1 Hz, 1H), 3.45 – 3.07 (m, 5H), 1.42 (d, *J* = 2.8 Hz, 3H), 1.24 (d, *J* = 41.6 Hz, 3H).; **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ** = 164.1, 135.6, 135.6, 133.1, 133.1, 129.6, 129.5, 128.9, 128.8, 128.7, 128.6, 128.6, 128.0, 127.9, 91.3, 90.9, 50.6, 45.3, 44.8, 25.2, 24.8, 19.2, 19.1.; **HRMS (ESI-TOF)** *m/z*: [M + H]$^+$ calcd for $C_{19}H_{22}O_2N_2ClS$ 377.1085; found 377.1095.

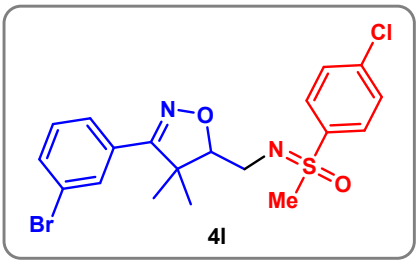
(((3-(3-bromophenyl)-4,4-dimethyl-4,5-dihydroisoxazol-5-yl)methyl)imino)(methyl)(phenyl)-λ^6-sulfanone (4k):



4k

The product **4k** was obtained in 64% yield (50 mg, Sticky white solid), (dr 1.2:1); ***R$_f$*** = 0.35 (petroleum ether/ethyl acetate = 50/50); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 7.97 (t, *J* = 7.9 Hz, 2H), 7.77 (d, *J* = 6.2 Hz, 1H), 7.67 – 7.50 (m, 5H), 7.26 (dt, *J* = 7.9, 4.9 Hz, 1H), 4.40 – 4.26 (m, 1H), 3.33 (ddd, *J* = 17.6, 12.9, 5.6 Hz, 1H), 3.22 – 3.05 (m, 4H), 1.44 (d, *J* = 4.1 Hz, 3H), 1.26 (d, *J* = 43.4 Hz, 3H).; **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ** = 163.9, 163.9, 139.1, 138.8, 133.1, 133.0, 132.5, 132.4, 131.6, 131.5, 130.4, 130.3, 130.0, 129.6, 129.5, 128.9, 128.5, 125.9, 125.8, 122.6, 91.4, 91.0, 50.7, 50.6, 45.3, 44.9, 42.4, 42.1, 25.2, 24.9, 19.2, 19.1.; **HRMS (ESI-TOF)** *m/z*: [M + H]$^+$ calcd for $C_{19}H_{22}O_2N_2BrS$ 421.0580; found 421.0591.

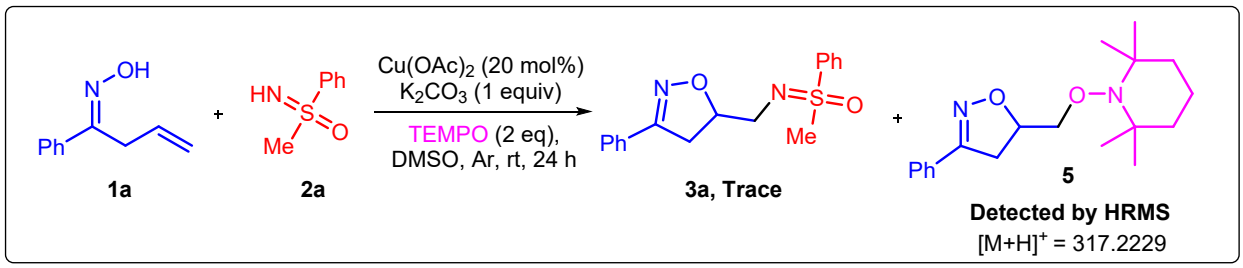
(((3-(3-bromophenyl)-4,4-dimethyl-4,5-dihydroisoxazol-5-yl)methyl)imino)(4-chlorophenyl)(methyl)-λ^6-sulfanone (4l):



4l

The product **4l** was obtained in 60% yield (51 mg, Off White solid), (dr 1.5:1); **mp** = 109-111 °C; ***R$_f$*** = 0.35 (petroleum ether/ethyl acetate = 50/50); **^{1}H NMR (400 MHz, $CDCl_3$) δ** = 7.97 – 7.86 (m, 2H), 7.77 (d, *J* = 6.7 Hz, 1H), 7.62 – 7.47 (m, 4H), 7.30 – 7.22 (m, 1H), 4.38 – 4.25 (m, 1H), 3.32 (ddd, *J* = 17.1, 13.0, 5.3 Hz, 1H), 3.21 – 3.01 (m, 4H), 1.43 (s, 3H), 1.26 (d, *J* = 50.5 Hz, 3H).; **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ** = 163.8, 163.8, 139.8, 139.8, 137.7, 137.3, 132.5, 132.5, 131.5, 131.4, 130.4, 130.4, 130.3, 130.1, 130.0, 129.9, 129.7, 125.9, 125.8, 122.6, 122.6, 91.4, 90.9, 50.7, 50.6, 45.4, 45.0, 42.5, 42.2, 25.4, 24.9, 19.1, 19.0.; **HRMS (ESI-TOF)** *m/z*: [M + H]$^+$ calcd for $C_{19}H_{21}O_2N_2BrClS$ 455.0190; found 455.0201.

4. Mechanistic studies:



In a 10 mL two-neck RB flask, β,γ-unsaturated ketoxime **1a** (0.31 mmol), methyl phenyl sulfoximine **2a** (0.37 mmol, 58 mg), $Cu(OAc)_2$ (20 mol%, 11 mg), K_2CO_3 (1 equiv, 0.31 mmol, 43 mg), TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) (0.62 mmol, 97 mg) and 2 mL DMSO was added. After stirring at room temperature under an argon atmosphere for 24 hours, the mixture was then analyzed by ESI-HRMS. As shown in Figure S1, **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ calcd for $C_{19}H_{29}O_2N_2$ 317.2224; found 317.2229, which may correspond to TEMPO trapped adduct **5** with C-centered radical derived from **1a.**

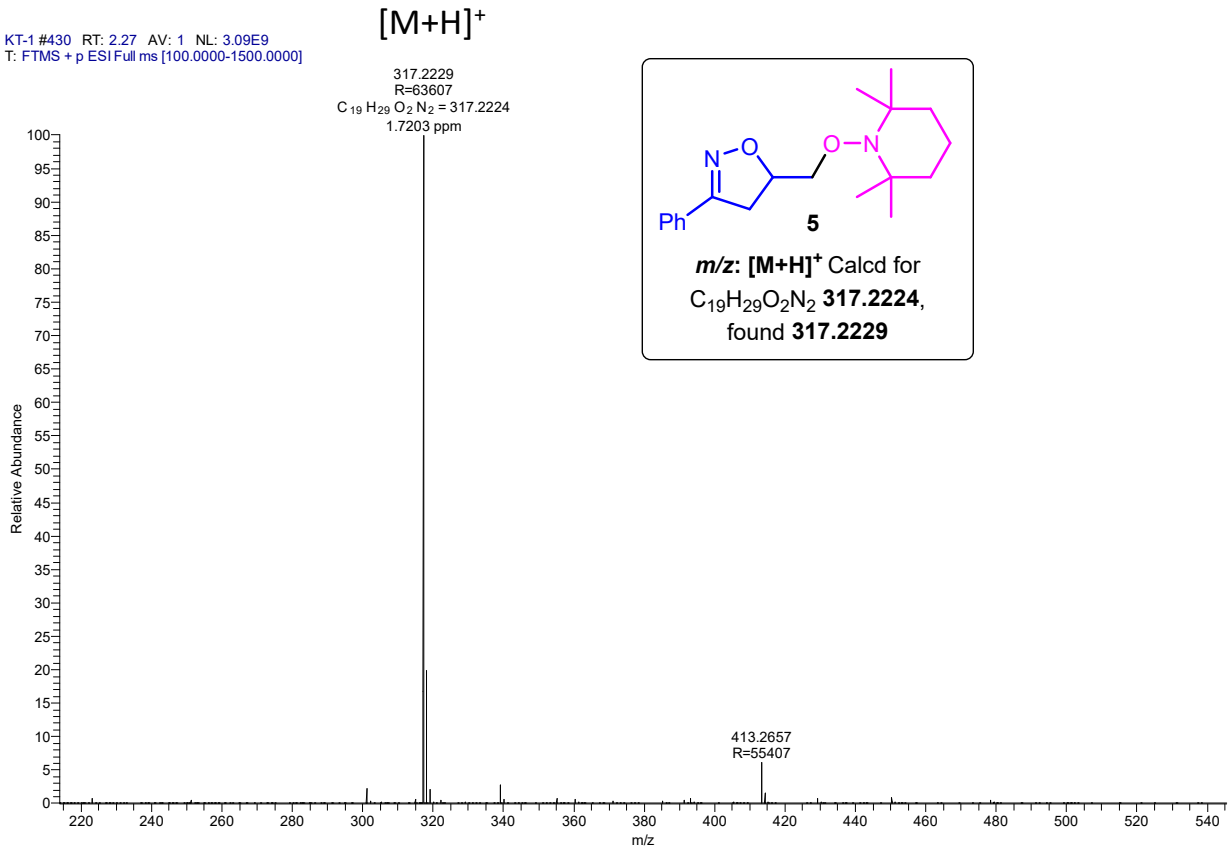
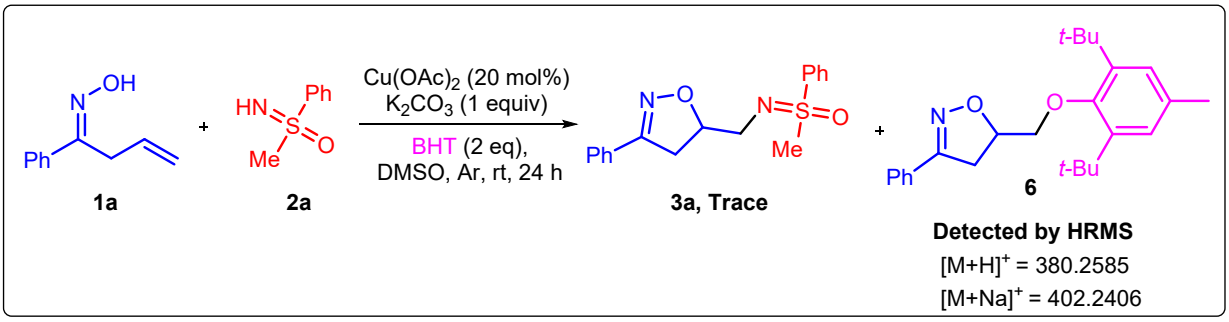


Figure S1. HRMS spectrum of the reaction mixture.



In a 10 mL two-neck RB flask, β,γ-unsaturated ketoxime **1a** (0.31 mmol), methyl phenyl sulfoximine **2a** (0.37 mmol, 58 mg), $Cu(OAc)_2$ (20 mol%, 11 mg), K_2CO_3 (1 equiv, 0.31 mmol, 43 mg), BHT (2,6-di-tert-butyl-4-methyl-phenol) (0.62 mmol, 136 mg) and 2 mL DMSO was added. After stirring at room temperature under an argon atmosphere for 24 hours, the mixture was then analyzed by ESI-HRMS. As shown in Figure S2, **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ calcd for $C_{25}H_{34}O_2N$ 380.2584; found 380.2585, and $[M+Na]^+$ calcd for $C_{25}H_{33}O_2NNa$ 402.2404; found 402.2406, which may correspond to BHT trapped adduct **6** with C-centered radical derived from **1a.**

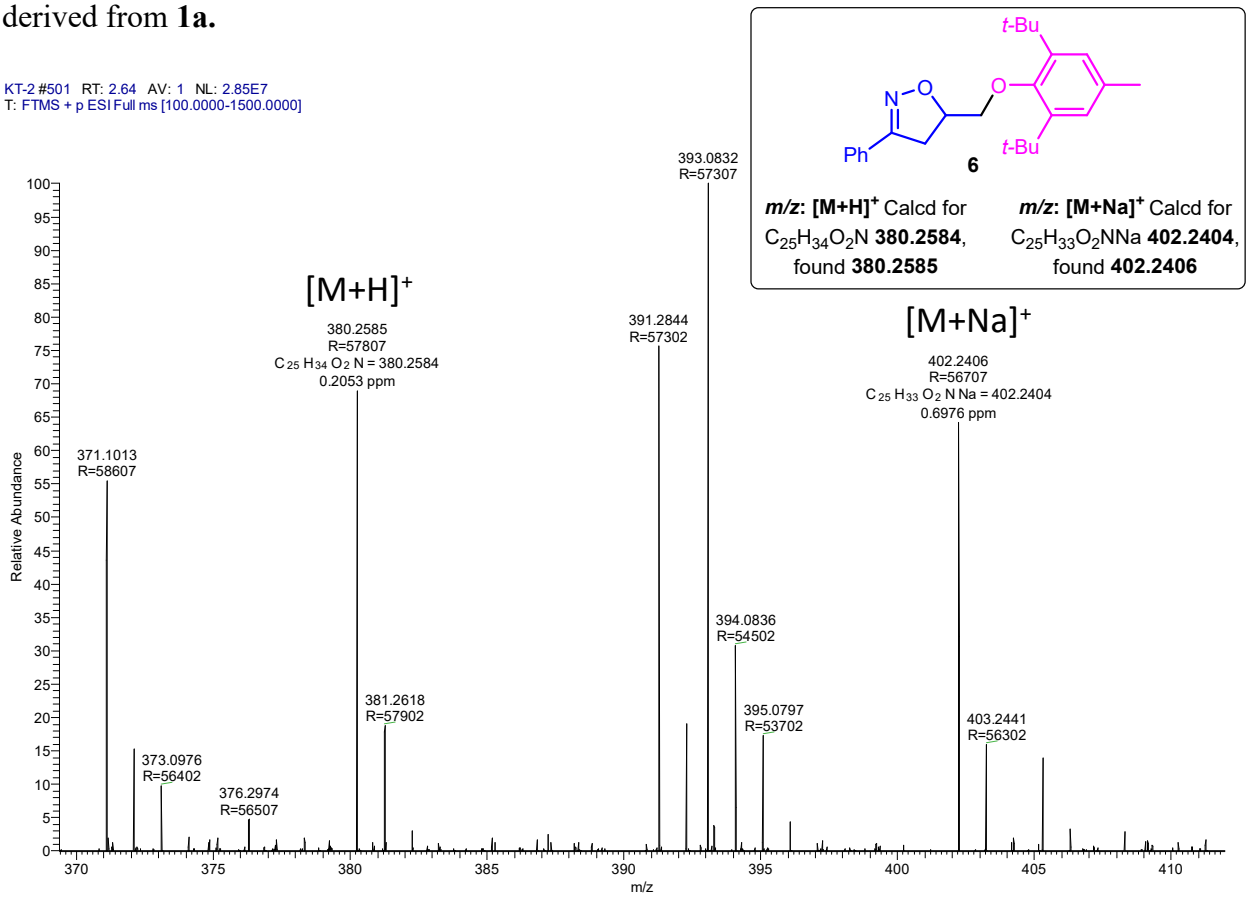
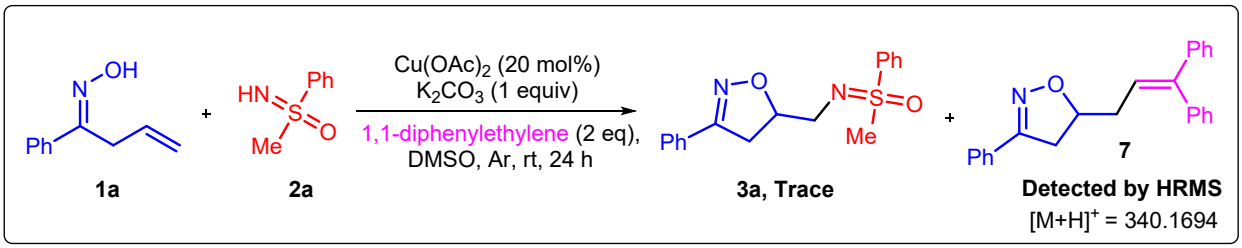


Figure S2. HRMS spectrum of the reaction mixture.



In a 10 mL two-neck RB flask, β,γ-unsaturated ketoxime **1a** (0.31 mmol), methyl phenyl sulfoximine **2a** (0.37 mmol, 58 mg), $Cu(OAc)_2$ (20 mol%, 11 mg), K_2CO_3 (1 equiv, 0.31 mmol, 43 mg), DPE (1,1-diphenylethylene) (0.62 mmol, 112 mg) and 2 mL DMSO was added. After stirring at room temperature under an argon atmosphere for 24 hours, the mixture was then analyzed by ESI-HRMS. As shown in Figure S3, **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ calcd for $C_{24}H_{22}ON$ 340.1696; found 340.1694, which may correspond to DPE trapped adduct **7** with C-centered radical derived from **1a.**

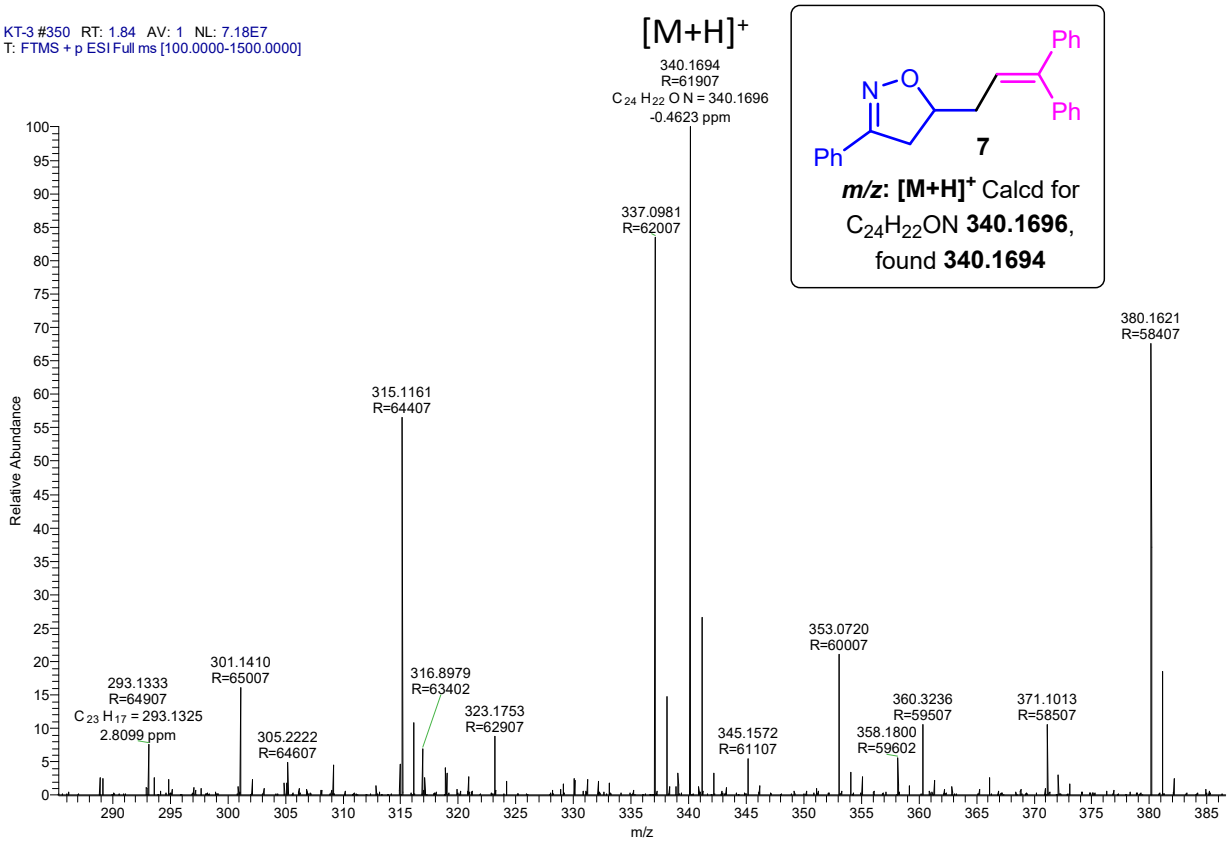


Figure S3. HRMS spectrum of the reaction mixture.

5. References:

(1) L. Wang, K. Zhang, Y. Wang, W. Li, M. Chen and J. Zhang, *Angew. Chem., Int. Ed.*, 2020, **59**, 4421–4427.

(2) 1 W. Yu, P.-L. Wang, K. Xu and H. Li, *Asian J. Org. Chem.*, 2021, **10**, 831–837.

(3) I. Triandafillidi and C. G. Kokotos, *Org. Lett.*, 2017, **19**, 106–109.

(4) L. Rout, P. Saha, S. Jammi and T. Punniyamurthy, *Eur. J. Org. Chem.*, **2008**, 640–643.

(5) Y. Xie, B. Zhou, S. Zhou, S. Zhou, W. Wei, J. Liu, Y. Zhan, D. Cheng, M. Chen, Y. Li, B. Wang, X. Xue and Z. Li, *Chem.Select*, 2017, **2**, 1620–1624.

(6) (a) M. Zenzola, R. Doran, L. Degennaro, R. Luisi and J. A. Bull, *Angew. Chem., Int. Ed.*, 2016, **55**, 7203–7207. (b) R. Hommelsheim, H. M. Núñez Ponce, K.-N. Truong, K. Rissanen and C. Bolm, *Org. Lett.*, 2021, **23**, 3415–3420.

6. X-ray crystallographic study:

Single Crystal-XRD Data: The single-crystal structures of component **3a** were obtained from the ethanol-water (v/v) solvent by the slow evaporation method. The single-crystal structures of component **3a** were determined using X-ray intensity data collected on a Bruker D8-VENTURE Kappa Duo diffractometer equipped with a PHOTON II CPAD detector and Incoatech multilayer mirror optics. The X-ray generator operated at 50 kV and 1.4 mA. Intensity measurements were performed using a Mo Kα radiation source (λ = 0.71073 Å) from a microfocus sealed tube at a temperature of 100(2) K. Initial unit cell parameters were established from 36 matrix frames. Complete intensity data were acquired using an optimized data collection strategy, involving various sets of ω, ϕ, and 2θ scans with a step width of 0.5°, while maintaining a fixed sample-to-detector distance of 5.00 cm. Exposure times varied depending on crystal quality. Data acquisition was controlled and monitored using the APEX4 program suite (Bruker, 2016).[1] Collected data were corrected for Lorentz-polarization and absorption effects using the SAINT and SADABS programs in the APEX3 suite. Structure solution was carried out using direct methods with SHELXS-97,[2] and refinement was performed by full-matrix least-squares on F^2 using SHELXL-2013.[3] All non-hydrogen atoms were refined anisotropically, while hydrogen atoms bonded to carbon were placed in geometrically idealized positions and refined using isotropic displacement parameters. Molecular graphics were generated using the Mercury software.[4] Geometric analyses were performed using SHELXTL (Bruker, 2016) and PLATON.[5] Crystallographic information files (CIFs) have been deposited with the Cambridge Crystallographic Data Centre (**CCDC No. 2502392**) and can be accessed via www.ccdc.cam.ac.uk/data.

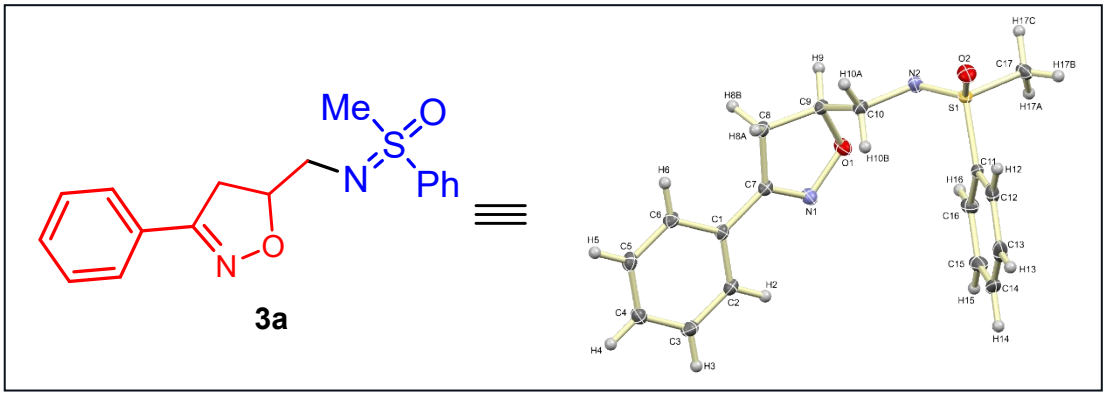


Figure S4: ORTEP diagram of **methyl(phenyl)(((3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)imino)-λ⁶-sulfanone (3a)** with 50% ellipsoid probability (**CCDC 2502392**).

Table S1. Sample and crystal data for 3a.

Identification code	**3a**	
Chemical formula	$C_{17}H_{18}N_2O_2S$	
Formula weight	314.39 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.130 x 0.180 x 0.230 mm	
Crystal system	triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 5.5177(2) Å	α = 85.431(2)°
	b = 8.2099(3) Å	β = 84.675(2)°
	c = 17.2362(8) Å	γ = 80.4690(10)°
Volume	765.05(5) $Å^3$	
Z	2	
Density (calculated)	1.365 g/cm^3	
Absorption coefficient	0.220 mm^{-1}	
F(000)	332	

Table S2. Data collection and structure refinement for 3a.

Theta range for data collection	2.38 to 28.39°
Index ranges	-7<=h<=7, -10<=k<=10, -22<=l<=23
Reflections collected	41860
Independent reflections	3803 [R(int) = 0.0673]
Coverage of independent reflections	99.1%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9720 and 0.9510
Structure solution technique	direct methods
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)

Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3803 / 0 / 200	
Goodness-of-fit on F^2	1.061	
Δ/σ_{max}	0.001	
Final R indices	3470 data; I>2σ(I)	R1 = 0.0397, wR2 = 0.1013
	all data	R1 = 0.0442, wR2 = 0.1047
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0444P)^2+0.6141P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.810 and -0.491 eÅ^{-3}	
R.M.S. deviation from mean	0.059 eÅ^{-3}	

Table S3. Bond lengths (Å) for 3a.

S1-O2	1.4574(11)	S1-N2	1.5194(13)
S1-C17	1.7517(15)	S1-C11	1.7844(14)
O1-N1	1.4151(16)	O1-C9	1.4669(17)
N1-C7	1.2851(18)	N2-C10	1.4706(18)
C1-C6	1.3980(19)	C1-C2	1.4006(19)
C1-C7	1.4691(19)	C2-C3	1.385(2)
C3-C4	1.394(2)	C4-C5	1.385(2)
C5-C6	1.394(2)	C7-C8	1.5048(19)
C8-C9	1.5231(19)	C9-C10	1.516(2)
C11-C12	1.387(2)	C11-C16	1.393(2)
C12-C13	1.390(2)	C13-C14	1.386(3)
C14-C15	1.390(3)	C15-C16	1.390(2)

Table S4. Bond angles (°) for 3a.

O2-S1-N2	120.96(7)	O2-S1-C17	108.64(7)
N2-S1-C17	104.65(7)	O2-S1-C11	106.02(7)
N2-S1-C11	110.89(7)	C17-S1-C11	104.54(7)
N1-O1-C9	108.65(10)	C7-N1-O1	109.37(12)
C10-N2-S1	116.56(10)	C6-C1-C2	118.87(13)
C6-C1-C7	120.24(13)	C2-C1-C7	120.89(12)
C3-C2-C1	120.65(13)	C2-C3-C4	120.09(14)
C5-C4-C3	119.81(14)	C4-C5-C6	120.34(14)
C5-C6-C1	120.23(13)	N1-C7-C1	121.05(13)
N1-C7-C8	113.91(13)	C1-C7-C8	125.00(12)
C7-C8-C9	100.62(11)	O1-C9-C10	108.96(11)
O1-C9-C8	104.51(11)	C10-C9-C8	112.85(12)
N2-C10-C9	108.52(12)	C12-C11-C16	121.71(13)
C12-C11-S1	119.22(11)	C16-C11-S1	119.06(11)
C11-C12-C13	119.04(15)	C14-C13-C12	119.84(15)
C13-C14-C15	120.76(14)	C16-C15-C14	120.00(16)
C15-C16-C11	118.65(15)		

Table S5. Torsion angles (°) for 3a.

C9-O1-N1-C7	10.79(15)	O2-S1-N2-C10	-64.21(13)
C17-S1-N2-C10	172.96(11)	C11-S1-N2-C10	60.78(12)
C6-C1-C2-C3	-0.1(2)	C7-C1-C2-C3	-179.73(13)
C1-C2-C3-C4	0.9(2)	C2-C3-C4-C5	-0.5(2)
C3-C4-C5-C6	-0.6(2)	C4-C5-C6-C1	1.4(2)
C2-C1-C6-C5	-1.0(2)	C7-C1-C6-C5	178.62(13)
O1-N1-C7-C1	178.03(12)	O1-N1-C7-C8	0.32(16)
C6-C1-C7-N1	-171.97(13)	C2-C1-C7-N1	7.7(2)
C6-C1-C7-C8	5.5(2)	C2-C1-C7-C8	-174.90(13)
N1-C7-C8-C9	-10.49(16)	C1-C7-C8-C9	171.90(13)
N1-O1-C9-C10	104.02(13)	N1-O1-C9-C8	-16.86(14)
C7-C8-C9-O1	15.66(13)	C7-C8-C9-C10	-102.59(13)
S1-N2-C10-C9	-163.34(10)	O1-C9-C10-N2	65.56(14)
C8-C9-C10-N2	-178.82(11)	O2-S1-C11-C12	-8.06(13)
N2-S1-C11-C12	-141.10(12)	C17-S1-C11-C12	106.64(12)
O2-S1-C11-C16	170.91(11)	N2-S1-C11-C16	37.87(13)
C17-S1-C11-C16	-74.39(13)	C16-C11-C12-C13	-0.5(2)
S1-C11-C12-C13	178.43(11)	C11-C12-C13-C14	0.4(2)
C12-C13-C14-C15	0.2(2)	C13-C14-C15-C16	-0.7(2)
C14-C15-C16-C11	0.6(2)	C12-C11-C16-C15	0.0(2)
S1-C11-C16-C15	-178.92(11)		

Table S6. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for 3a.

	x/a	y/b	z/c	U(eq)
H2	0.1283	0.3812	0.5056	0.020000
H3	0.1978	0.5057	0.3811	0.023000
H4	0.5797	0.4391	0.3097	0.022000
H5	0.8924	0.2504	0.3643	0.023000
H6	0.8288	0.1312	0.4910	0.020000
H8A	0.7691	0.1056	0.6368	0.019000
H8B	0.6727	-0.0548	0.6096	0.019000
H9	0.5058	-0.0869	0.7326	0.018000
H10A	0.7323	0.1087	0.7793	0.019000
H10B	0.5173	0.2561	0.7553	0.019000
H12	0.4893	0.5594	0.9219	0.023000
H13	0.3110	0.8219	0.8720	0.032000
H14	-0.0208	0.8470	0.7950	0.034000
H15	-0.1799	0.6133	0.7677	0.030000

H16	0.0003	0.3494	0.8157	0.022000
H17A	0.0289	0.1811	0.9639	0.029000
H17B	0.1809	0.2458	1.0266	0.029000
H17C	0.2477	0.0582	1.0026	0.029000

Table S7. Hydrogen bond distances (Å) and angles (°) for 3a.

	Donor-H	**Acceptor-H**	**Donor-Acceptor**	**Angle**
C8-H8A···N1#2	0.99	2.61	3.5782(19)	165.5
C17-H17A···O2#1	0.98	2.27	3.2265(19)	163.8

*Symmetry transformations used to generate equivalent atoms:

#1	*x*-1, *y*, *z*
#2	*x*+1, *y*, *z*

References:

1) Bruker APEX3. SAINT-Plus and SADABS; Bruker AXS Inc: Madison, Wisconsin, USA, 2016.

2) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.

3) G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3–8.

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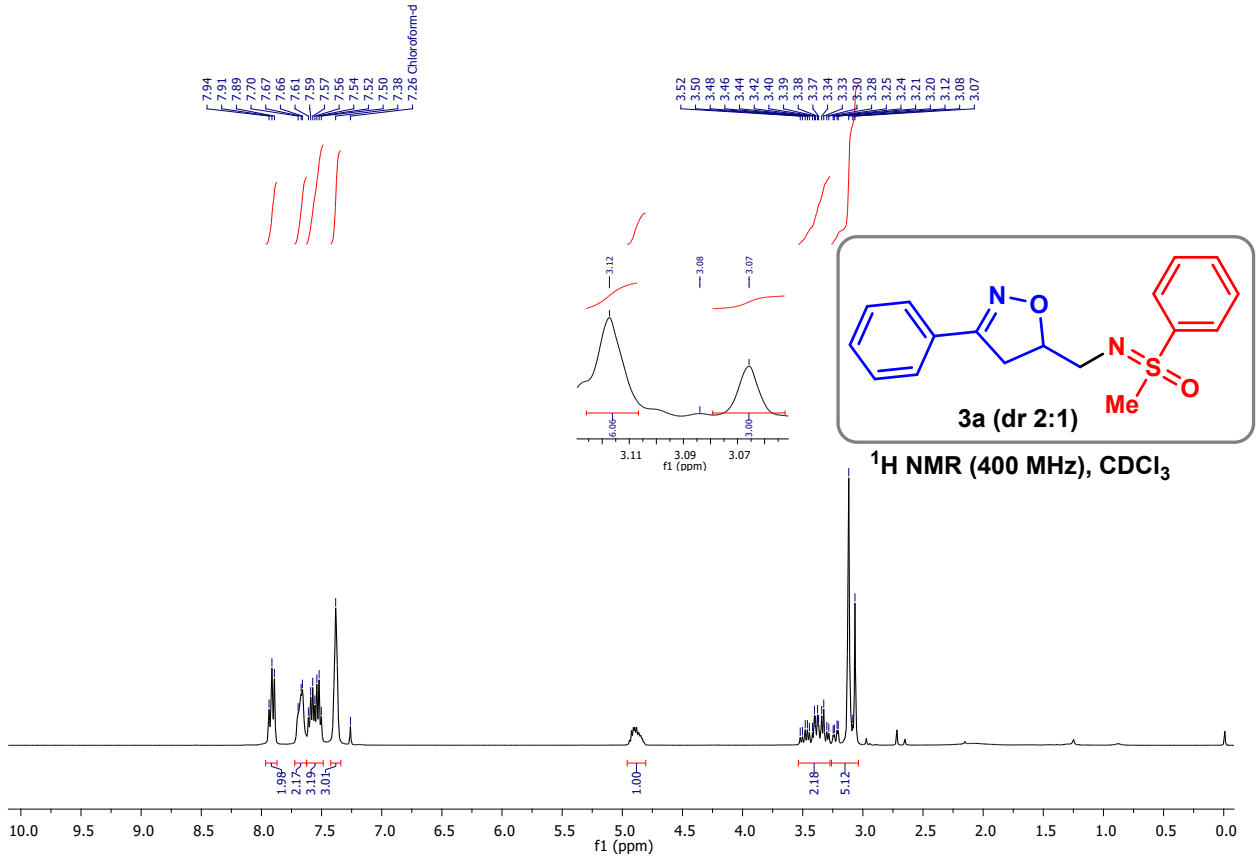
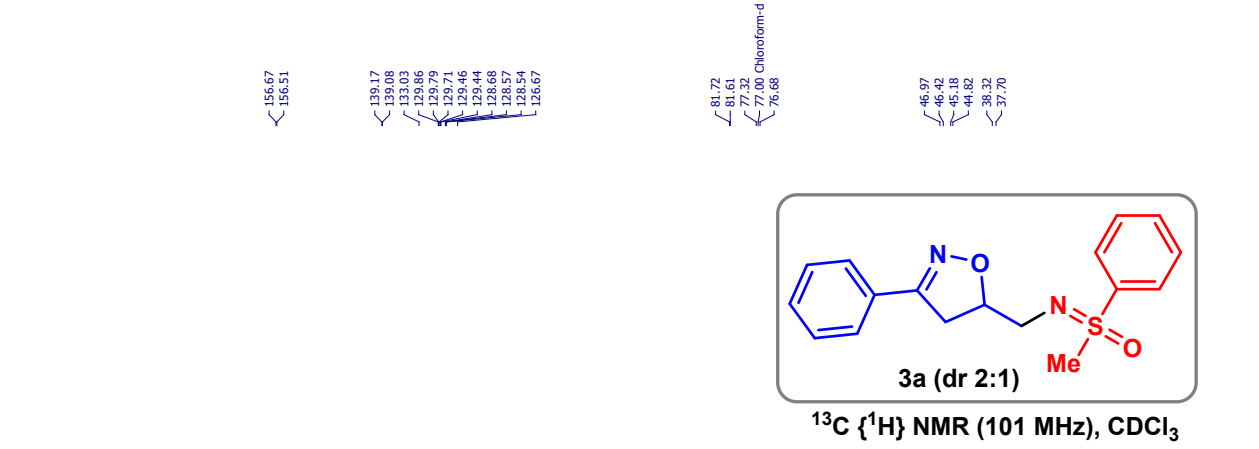
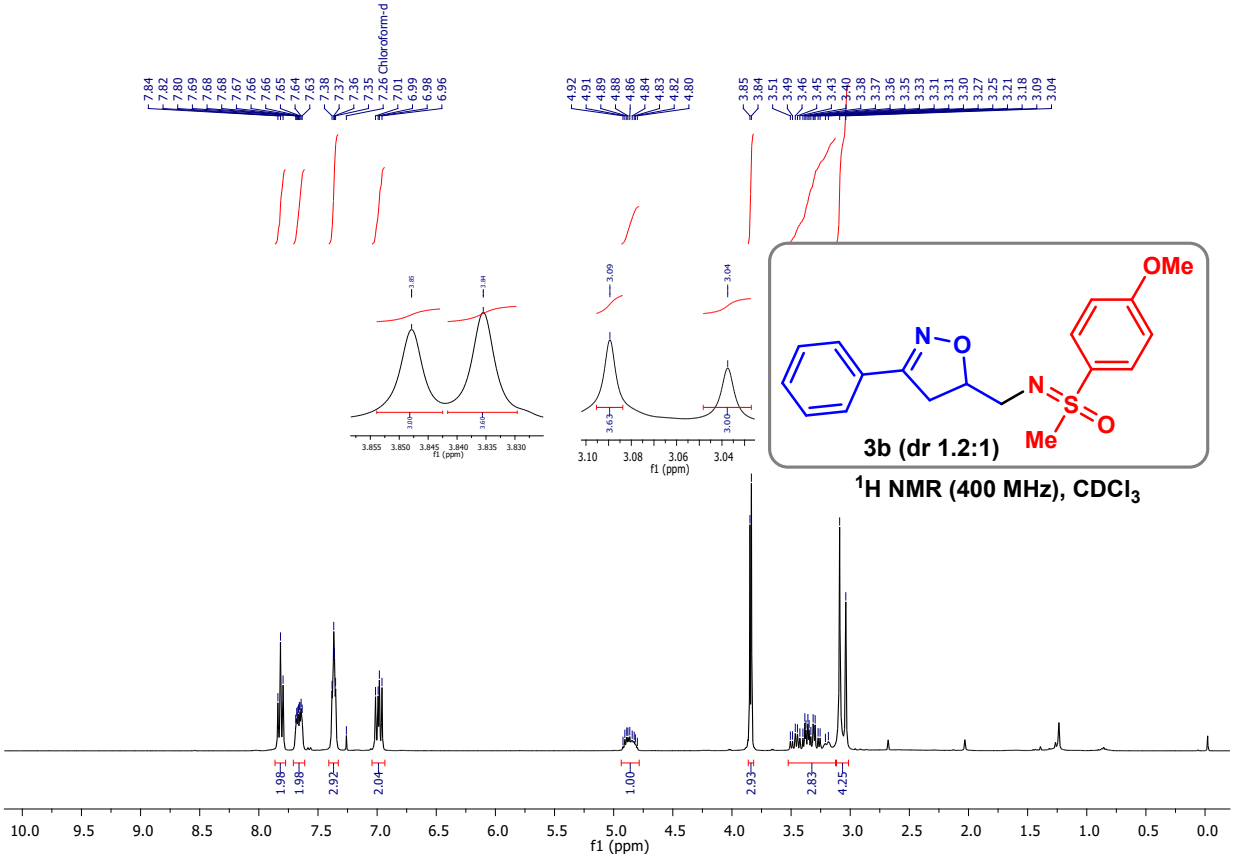
5) A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7–13.

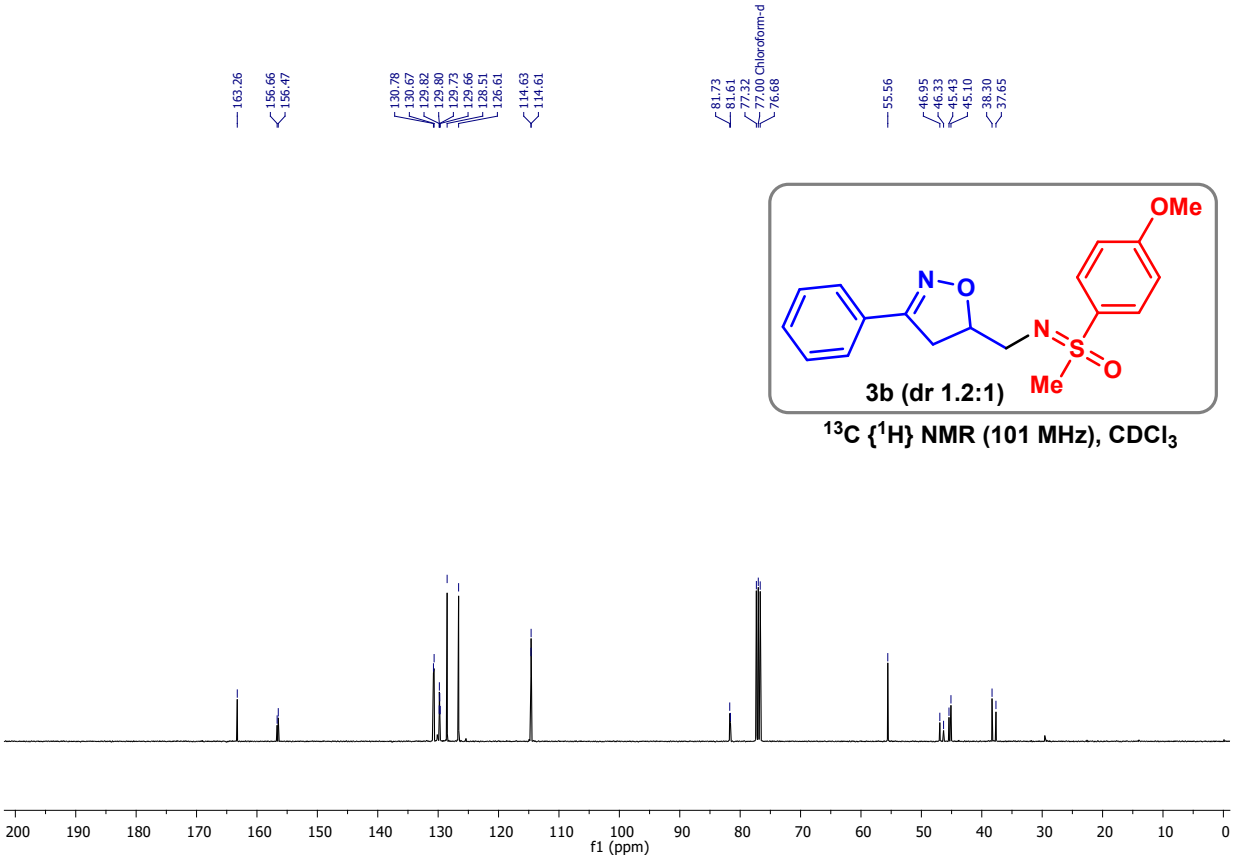
7. Spectral Data:



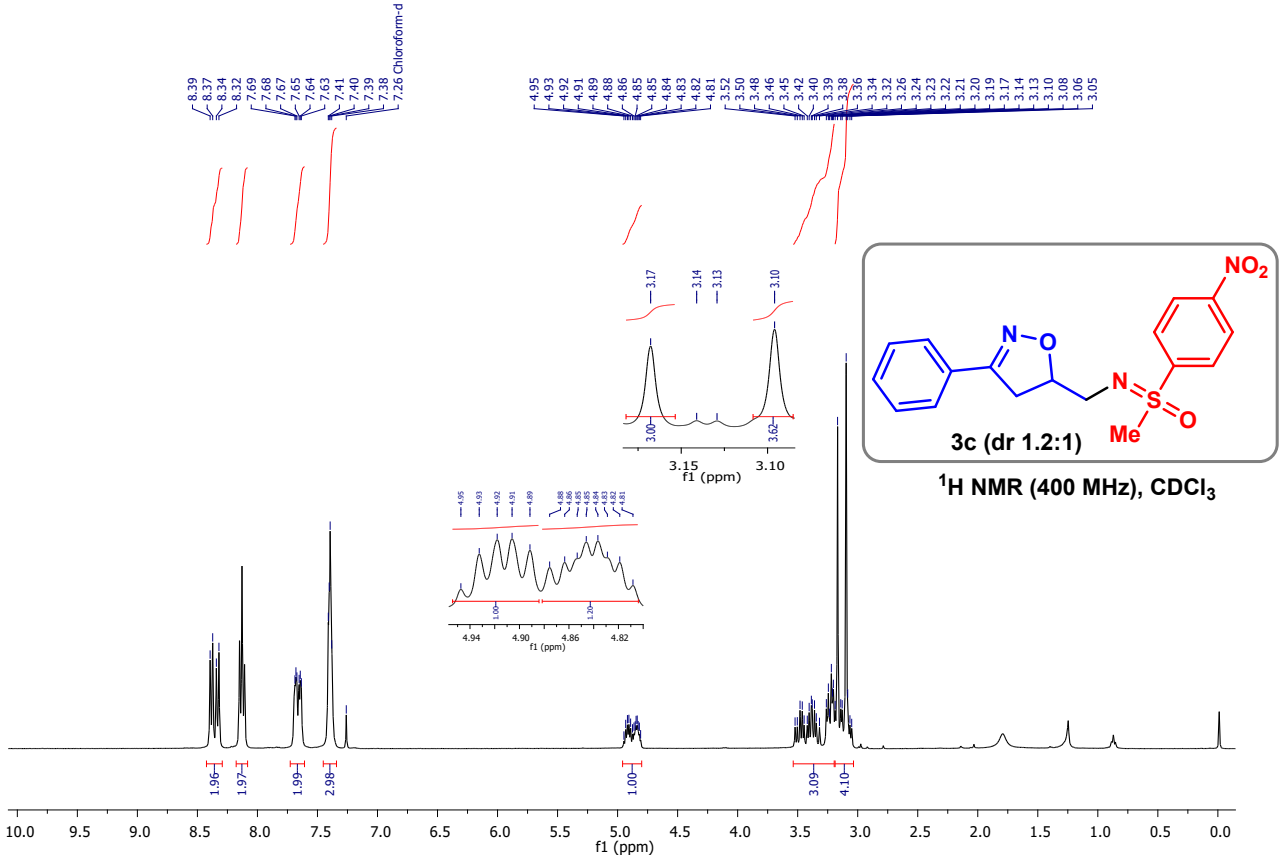


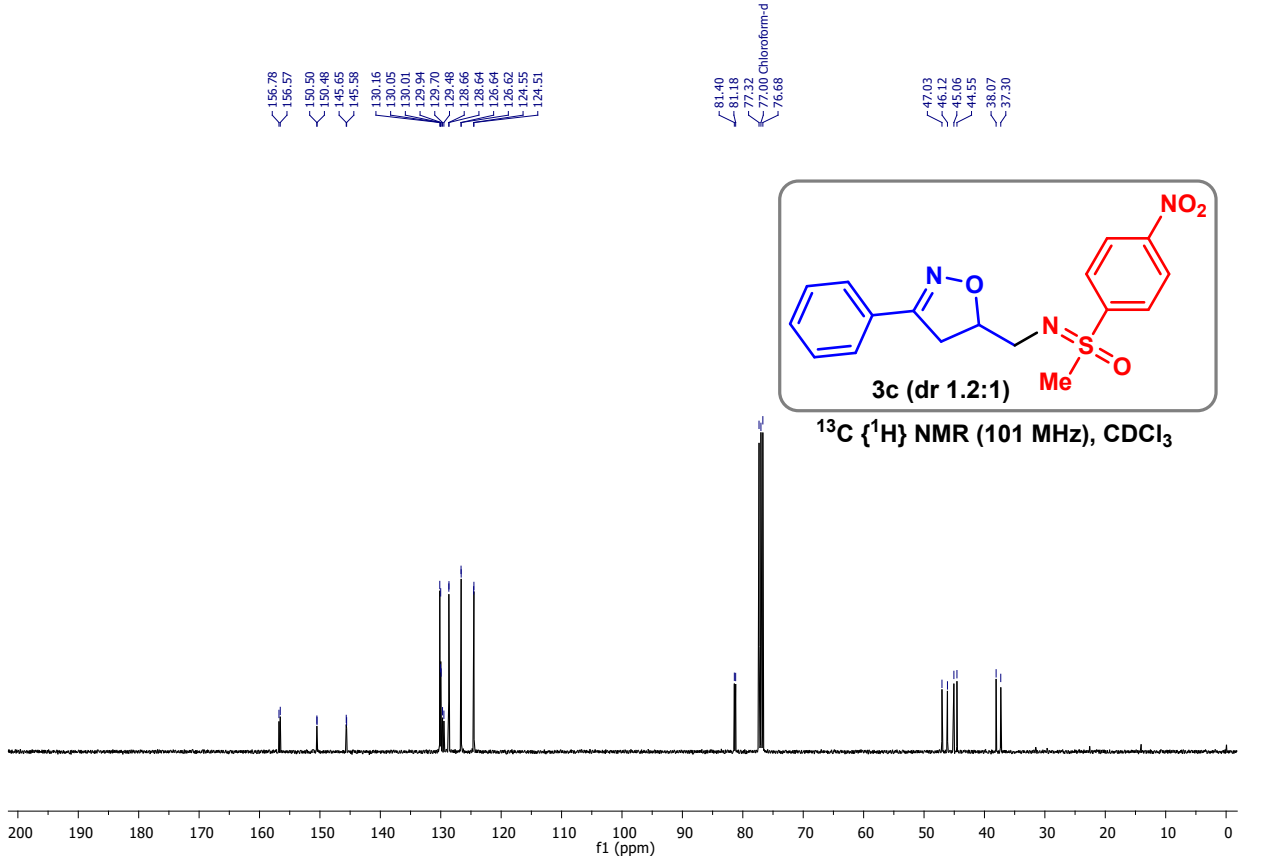


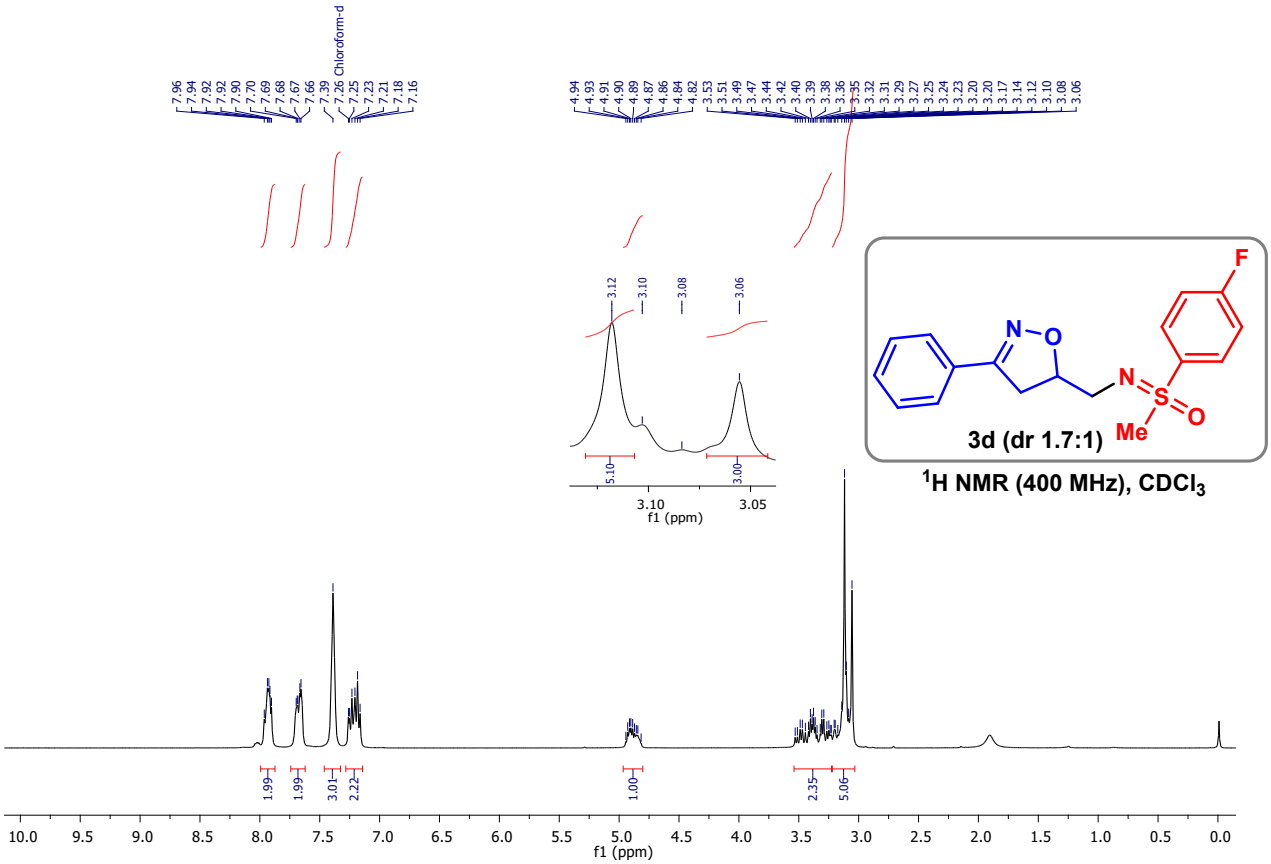
^{1}H NMR (400 MHz), $CDCl_3$



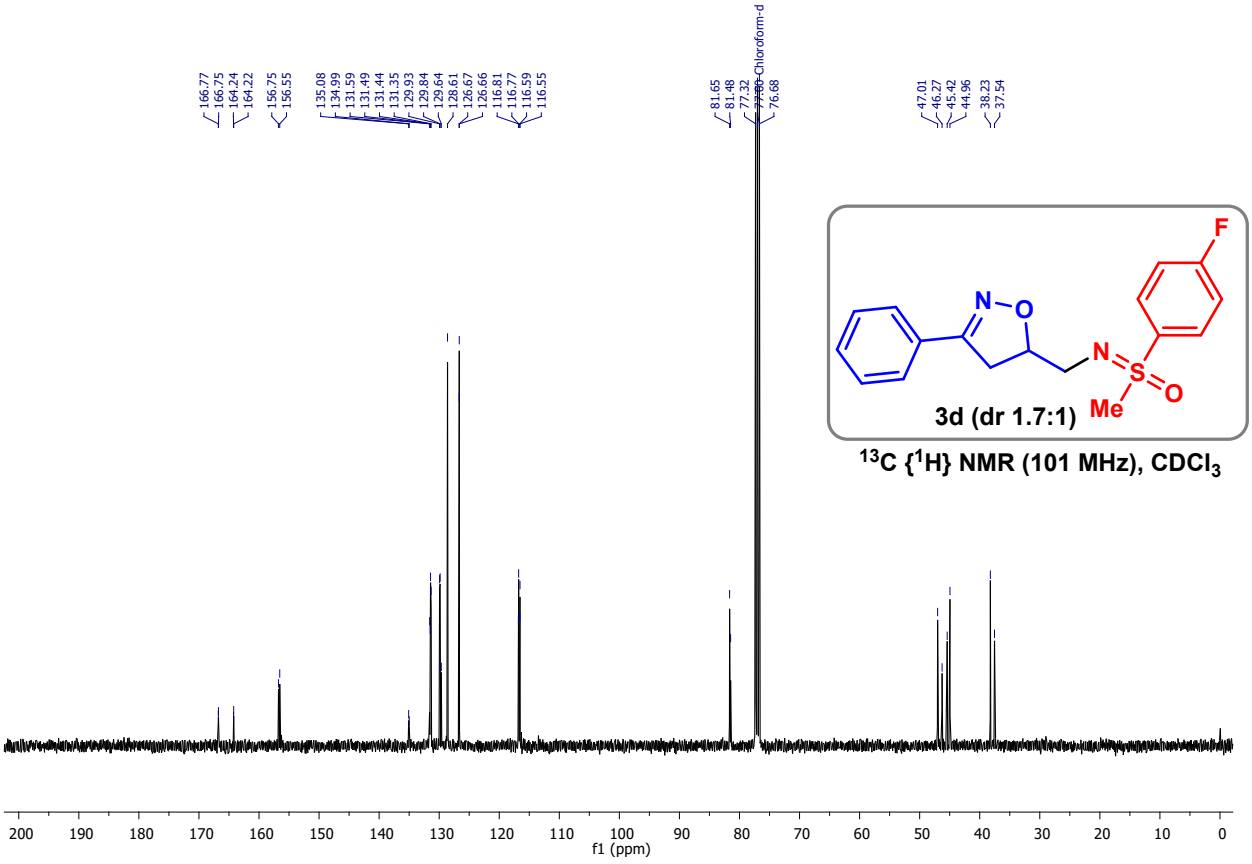
^{13}C {^{1}H} NMR (101 MHz), $CDCl_3$


3c (dr 1.2:1)
^{1}H NMR (400 MHz), CDCl$_3$
f1 (ppm)

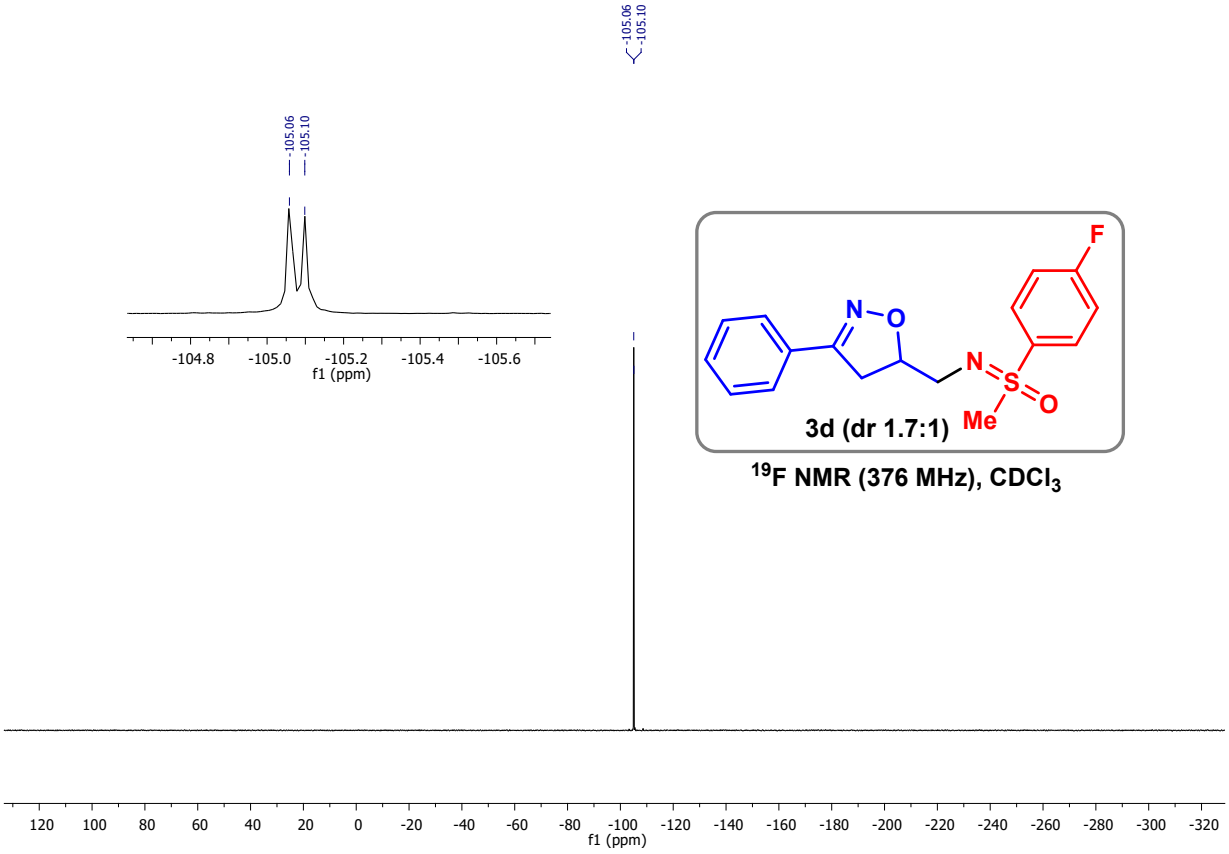

3c (dr 1.2:1)
^{13}C {^{1}H} NMR (101 MHz), CDCl$_3$
f1 (ppm)



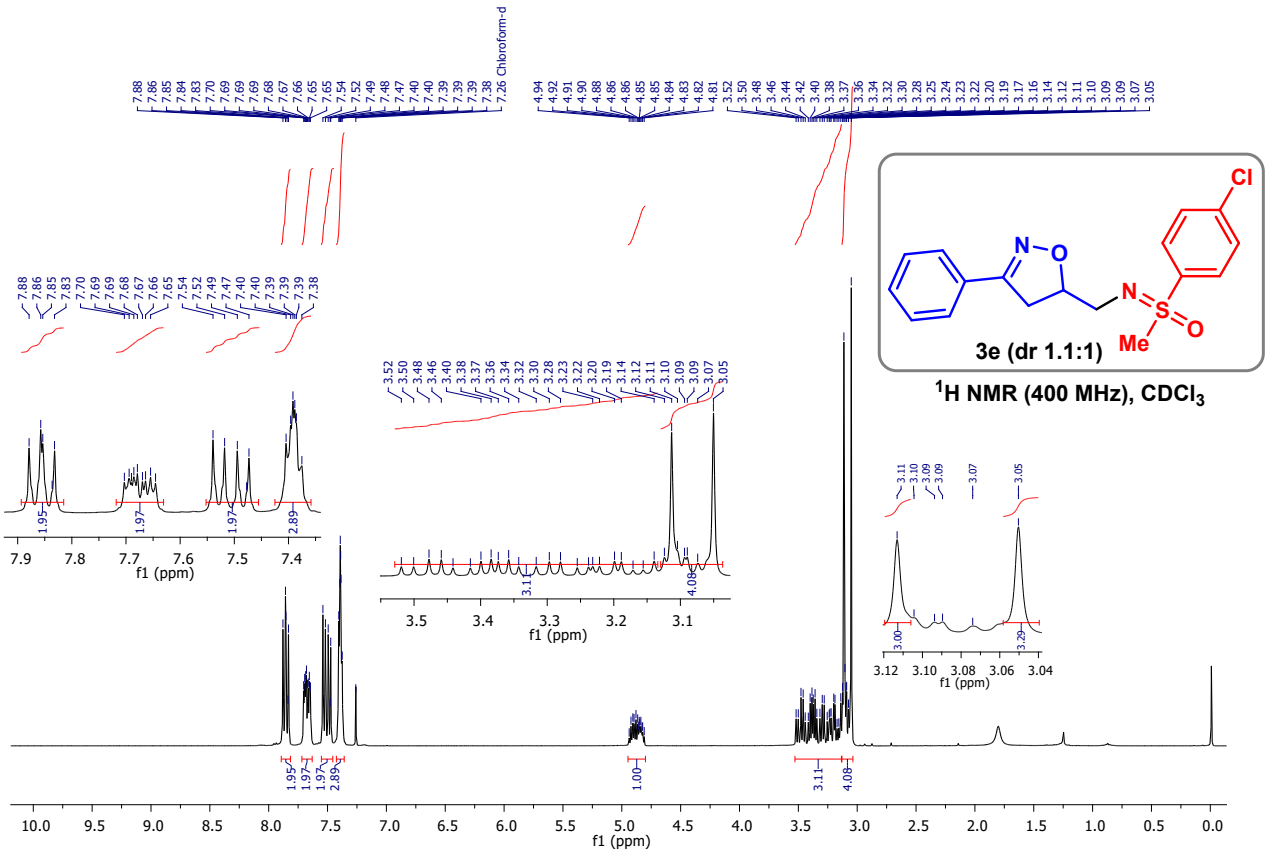
^{1}H NMR (400 MHz), $CDCl_3$



^{13}C {^{1}H} NMR (101 MHz), $CDCl_3$



^{19}F NMR (376 MHz), $CDCl_3$



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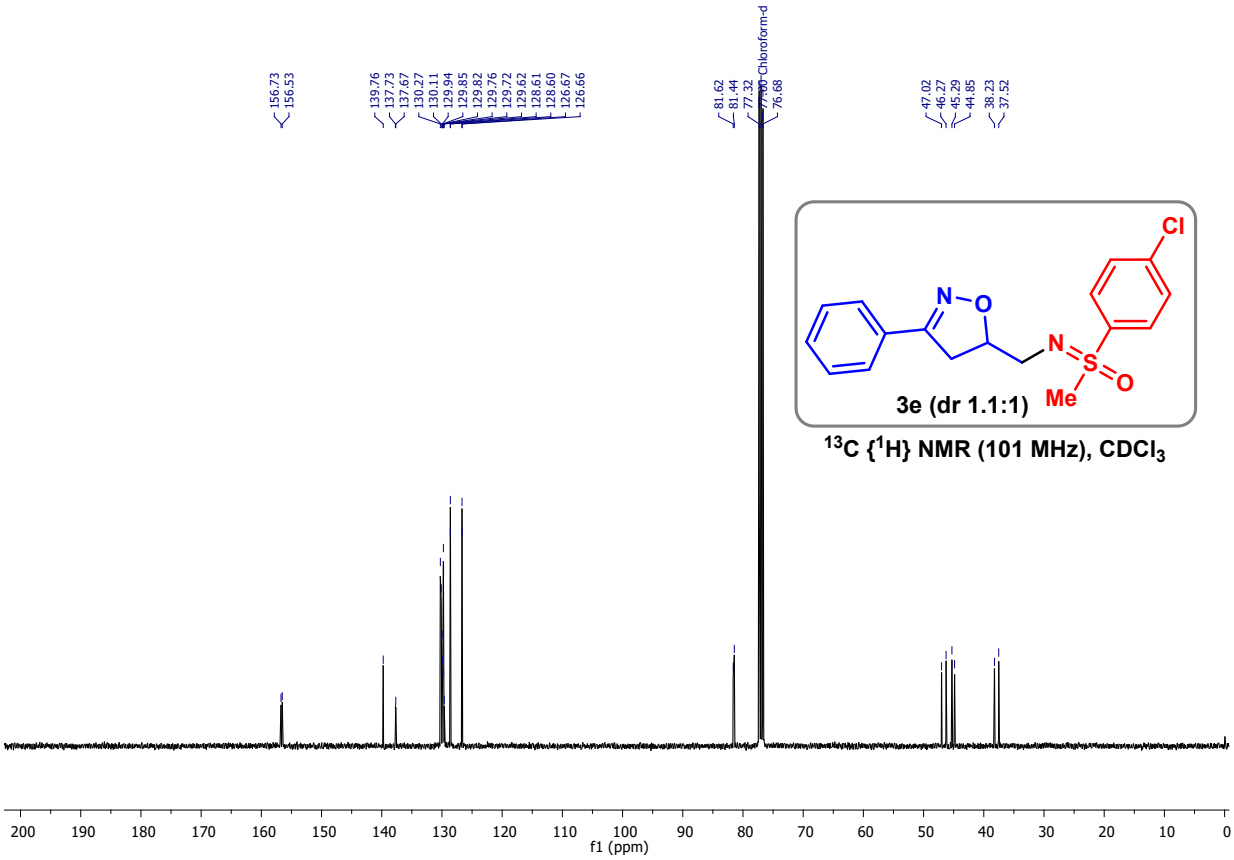
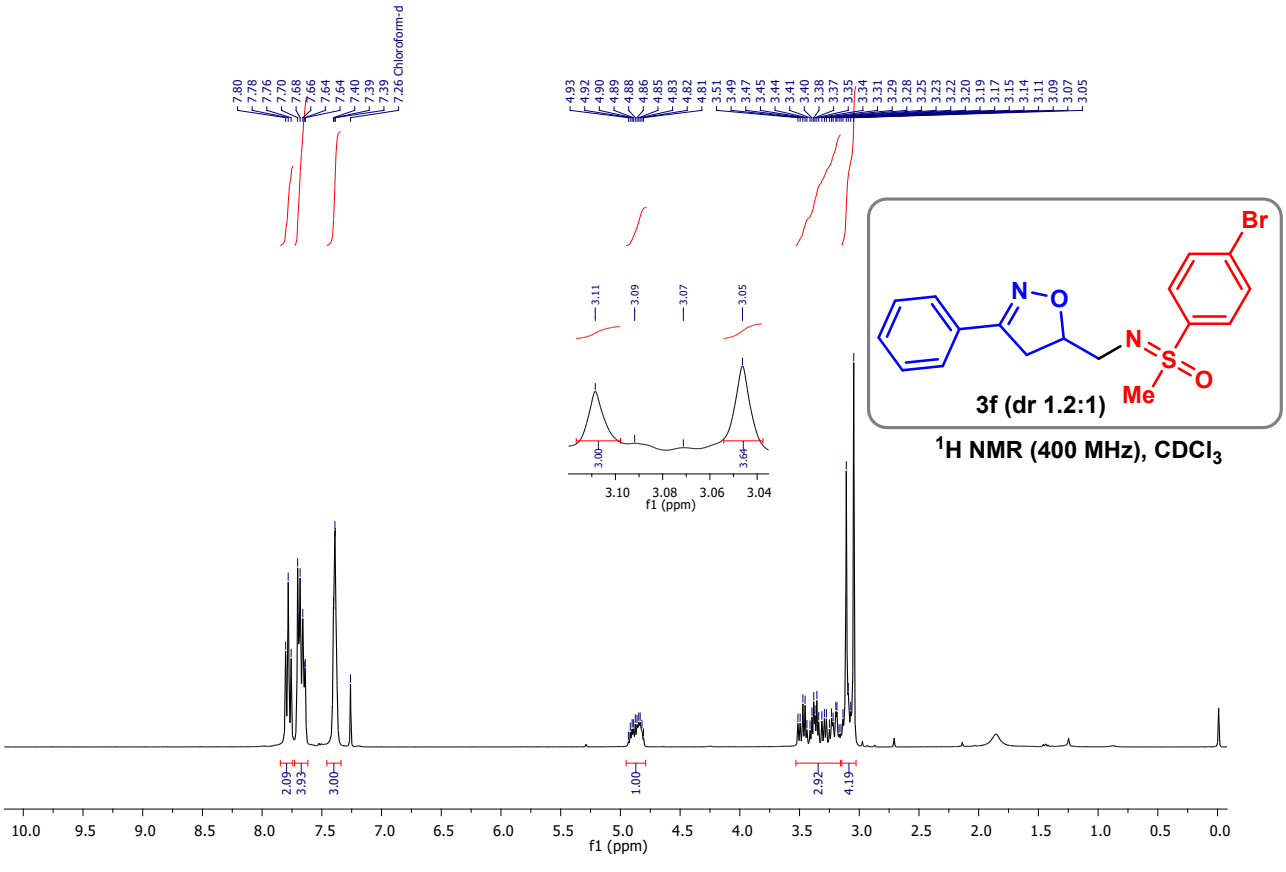
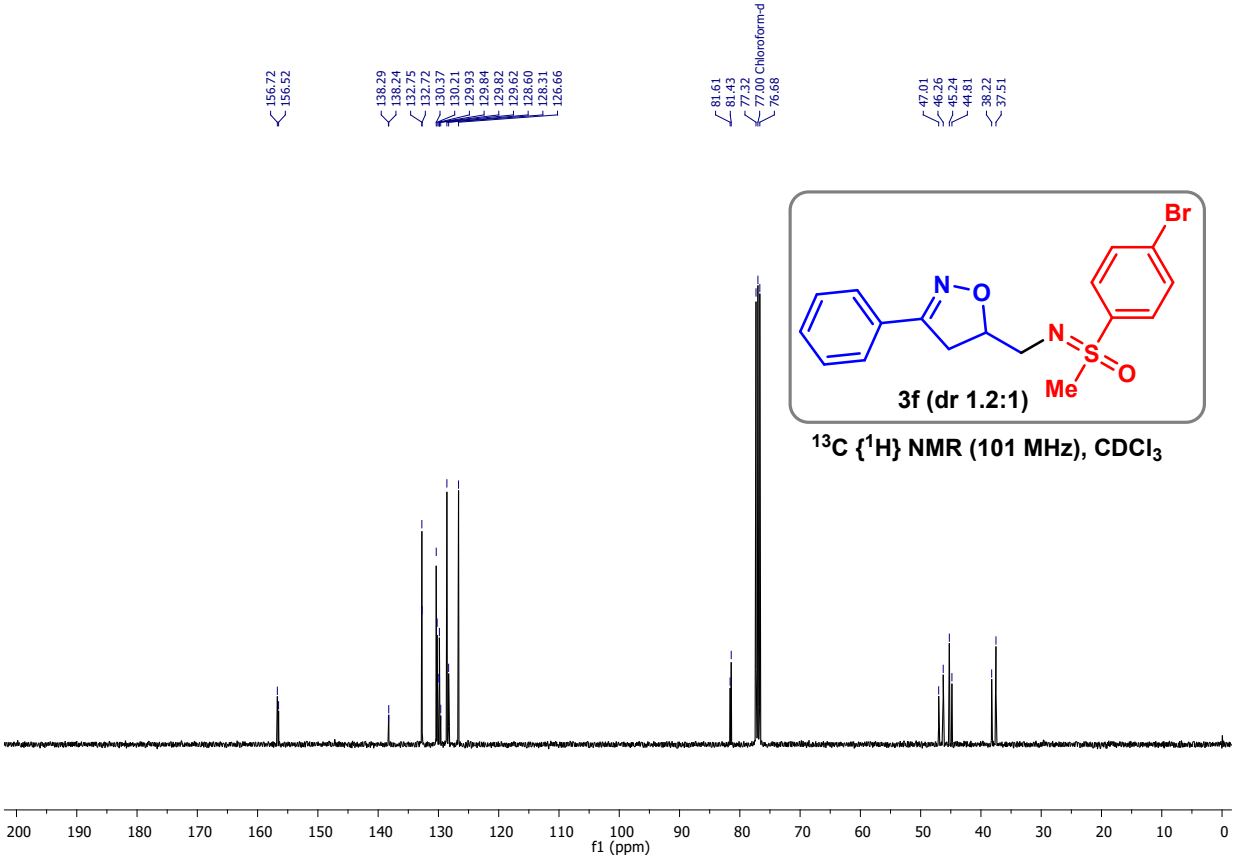


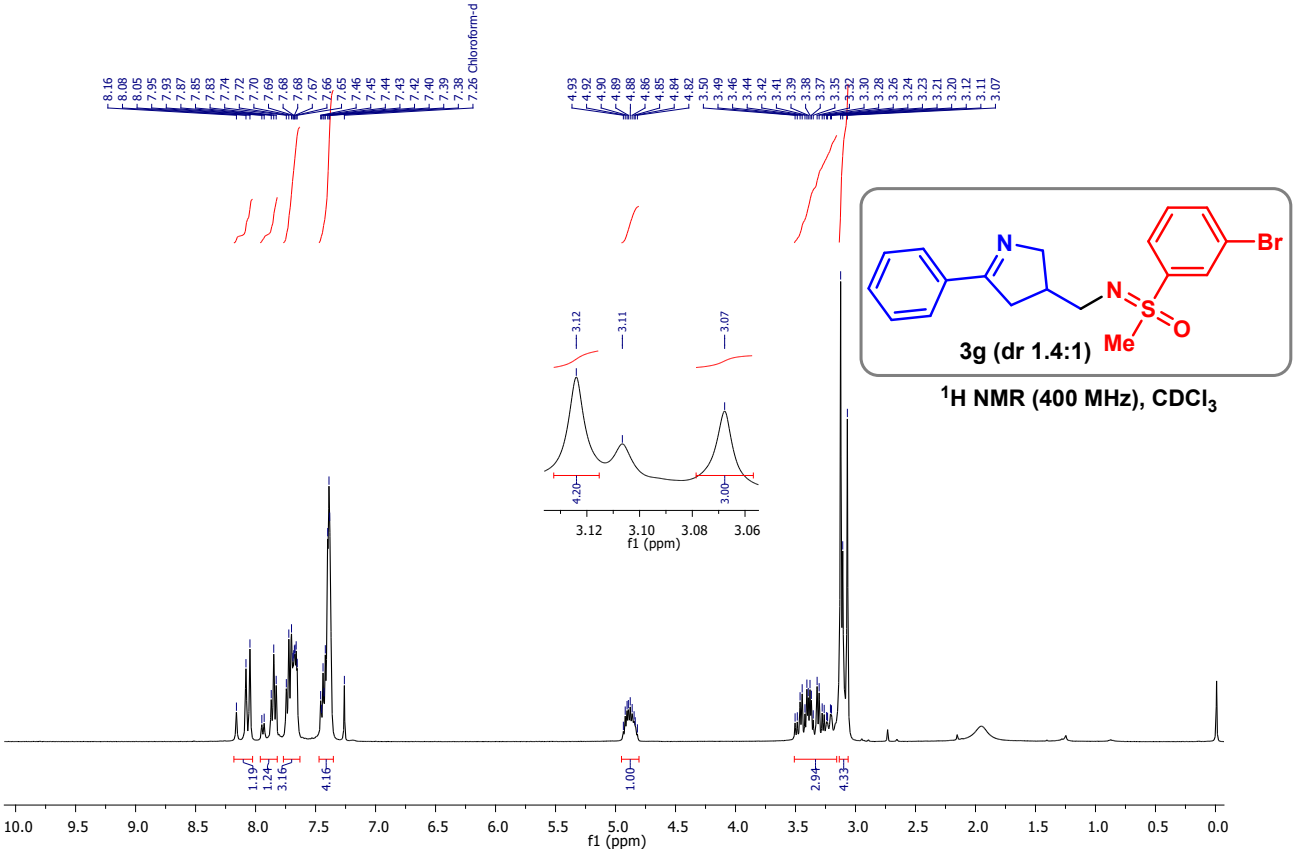
^{13}C {^{1}H} NMR (101 MHz), $CDCl_3$



^{1}H NMR (400 MHz), $CDCl_3$



^{13}C {^{1}H} NMR (101 MHz), $CDCl_3$



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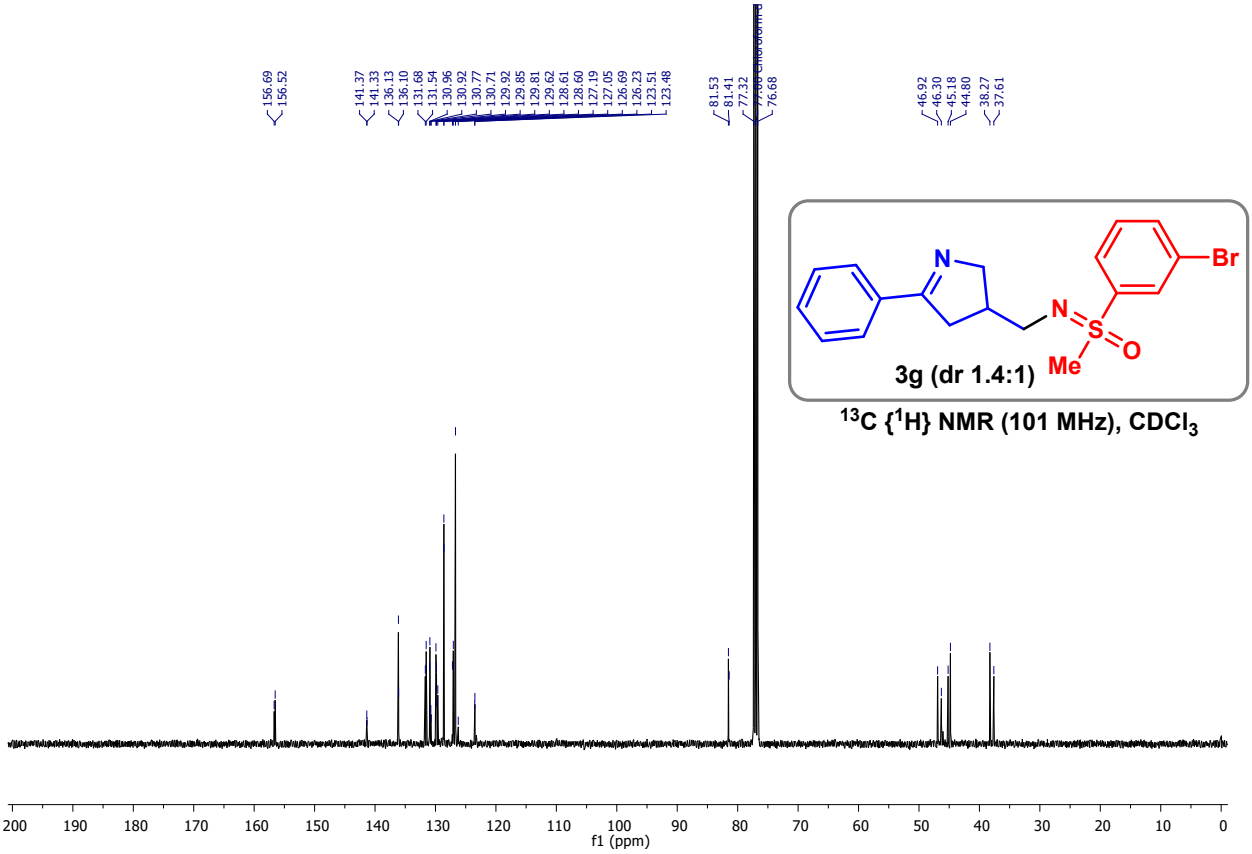
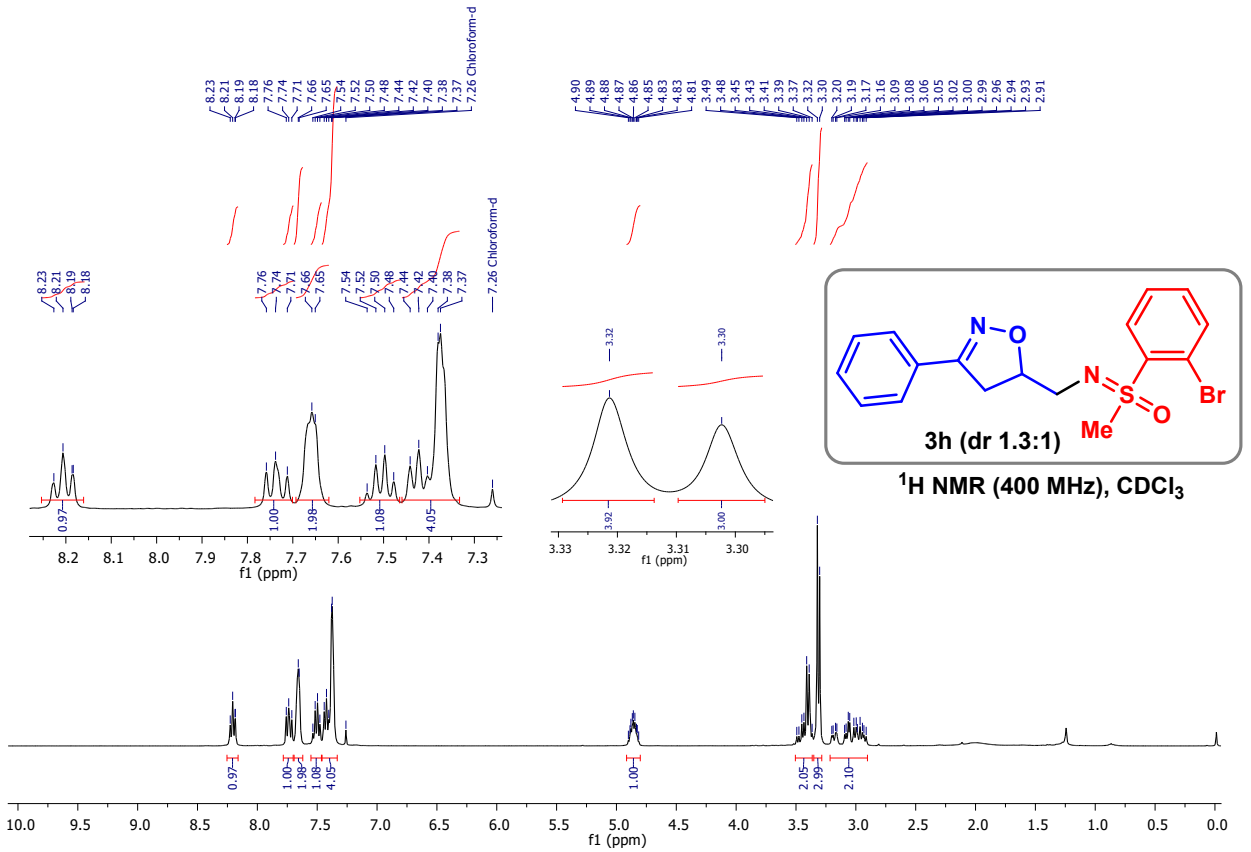
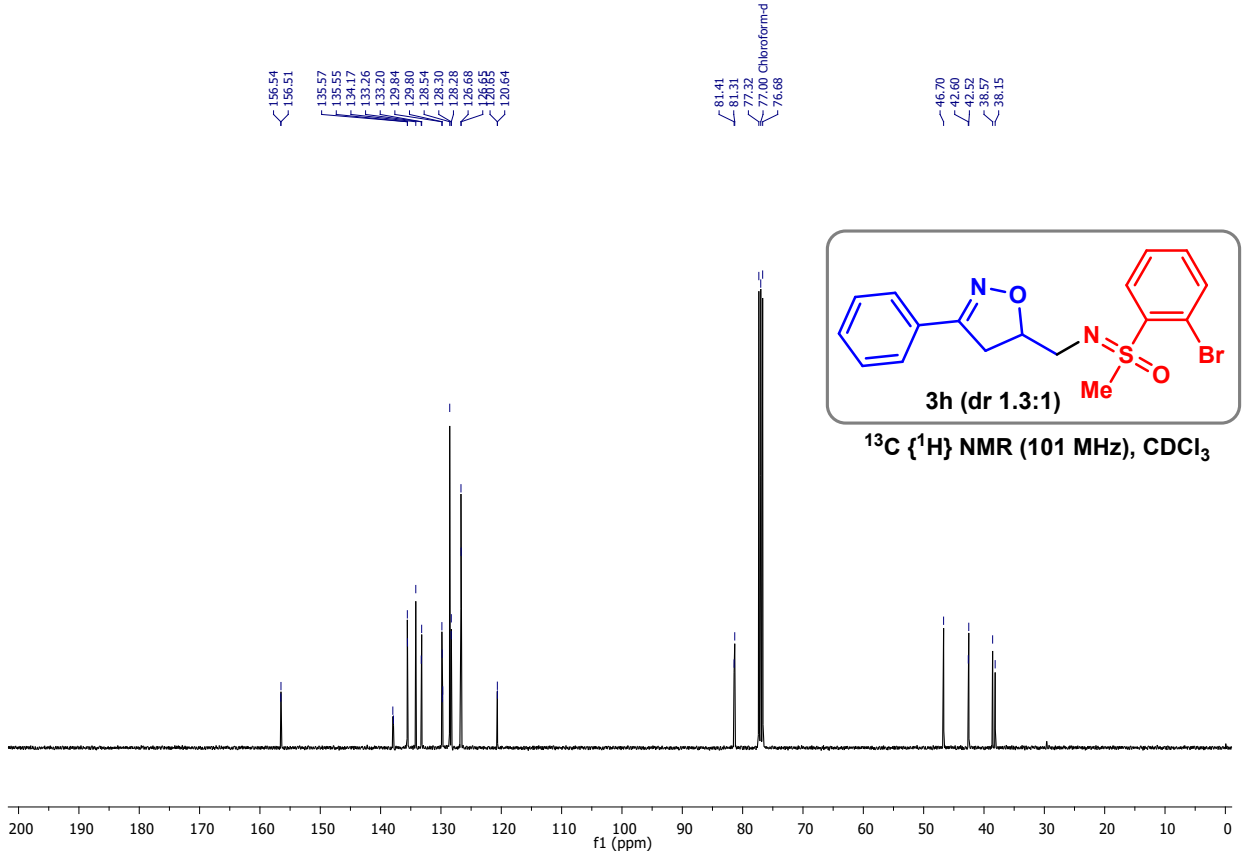


^{13}C {^{1}H} NMR (101 MHz), $CDCl_3$



^{1}H NMR (400 MHz), $CDCl_3$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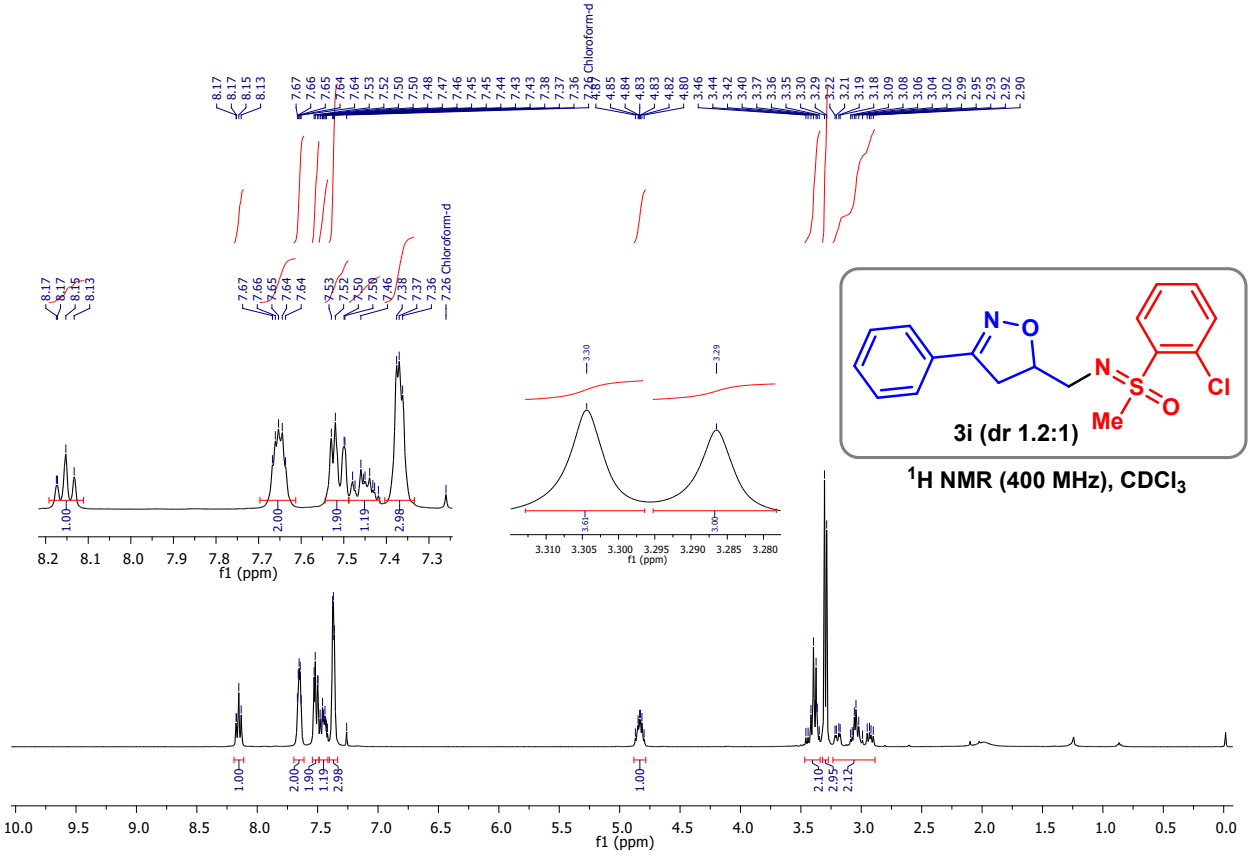
81.41
81.31
77.32
77.00 Chloroform-d
76.68
46.70
42.60
42.52
38.57
38.15
N
O
N
S
O
Me
Br
3h (dr 1.3:1)
^{13}C {^{1}H} NMR (101 MHz), CDCl$_3$
f1 (ppm)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7.50
7.48
7.47
7.46
7.45
7.45
7.44
7.43
7.43
7.38
7.37
7.36
7.26 Chloroform-d
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4.85
4.84
4.83
4.83
4.82
4.80
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3.42
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3.36
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3.22
3.21
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3.18
3.09
3.08
3.06
3.04
3.02
2.99
2.95
2.93
2.92
2.90
1.00
2.00
1.90
1.19
2.98
3.30
3.29
3.61
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N
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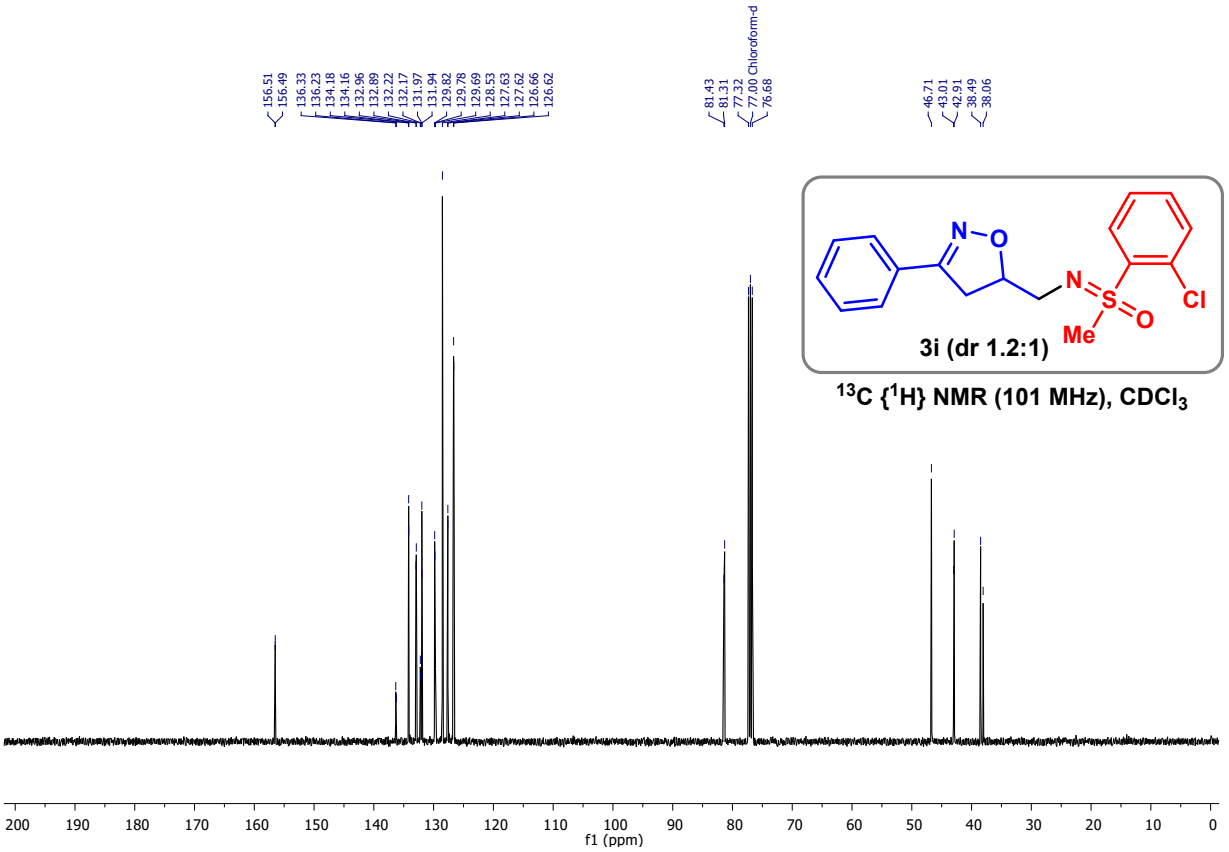
N
S
O
Me
Cl
3i (dr 1.2:1)
^{1}H NMR (400 MHz), CDCl$_3$
f1 (ppm)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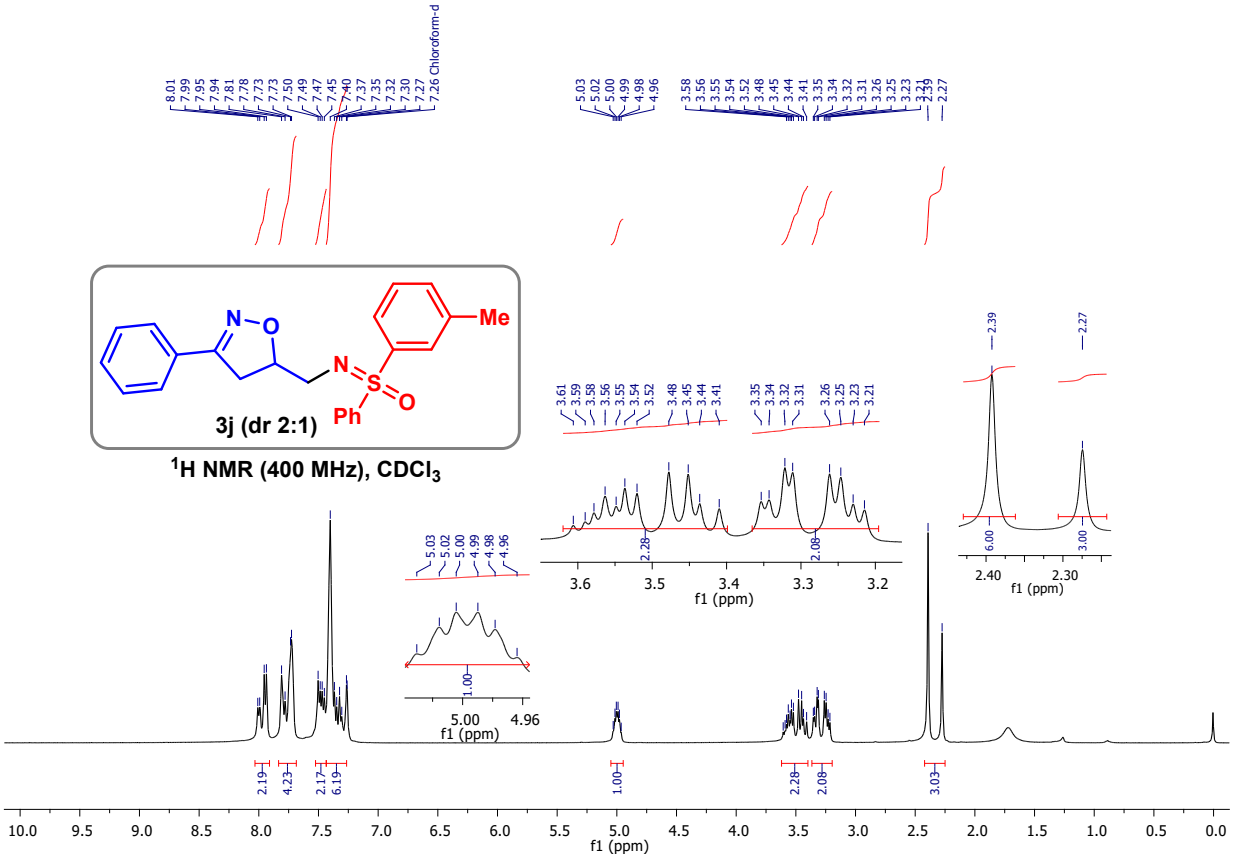
129.69
128.53
127.63
127.62
126.66
126.62
81.43
81.31
77.32
77.00 Chloroform-d
76.68
46.71
43.01
42.91
38.49
38.06
N
O
N
S
O
Cl
Me
3i (dr 1.2:1)
^{13}C {^{1}H} NMR (101 MHz), CDCl$_3$
f1 (ppm)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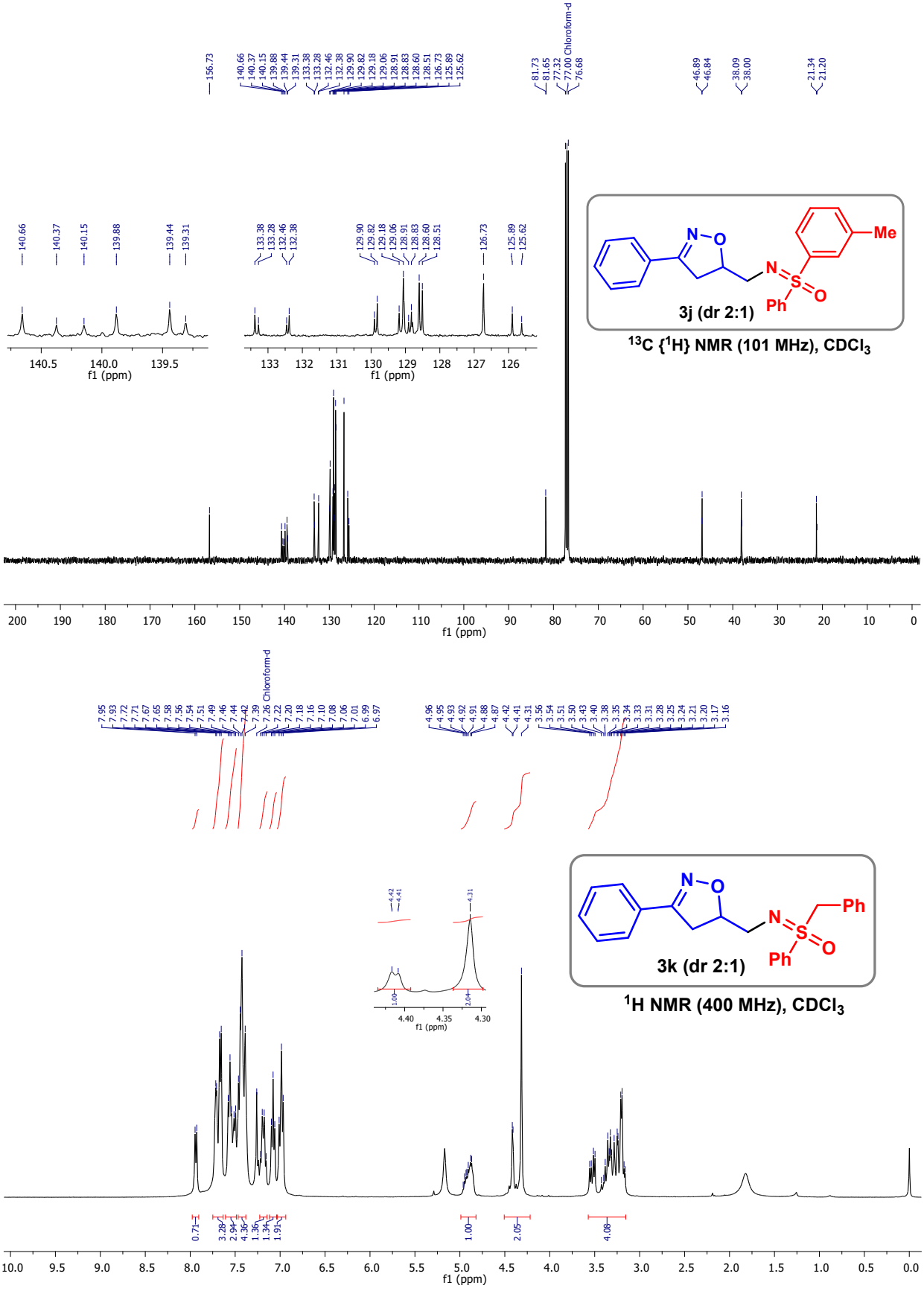
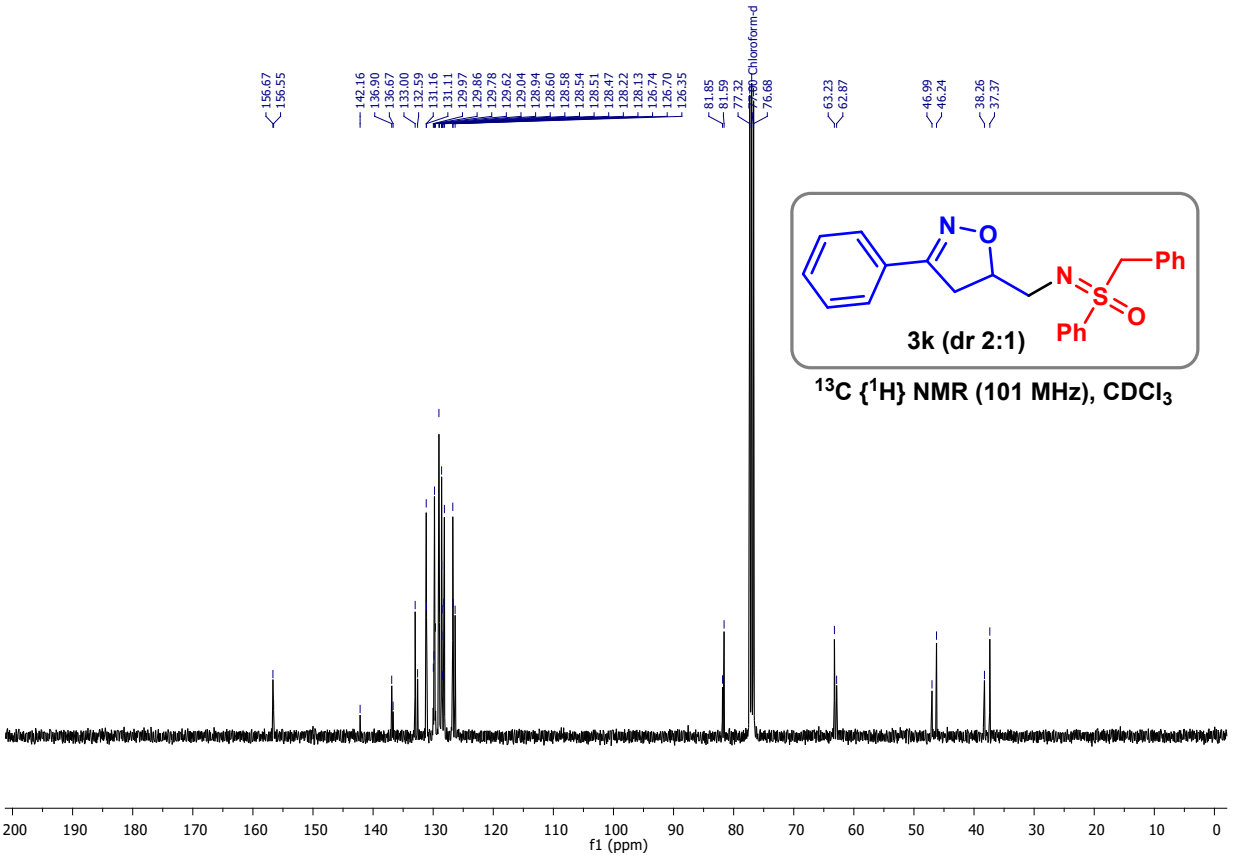
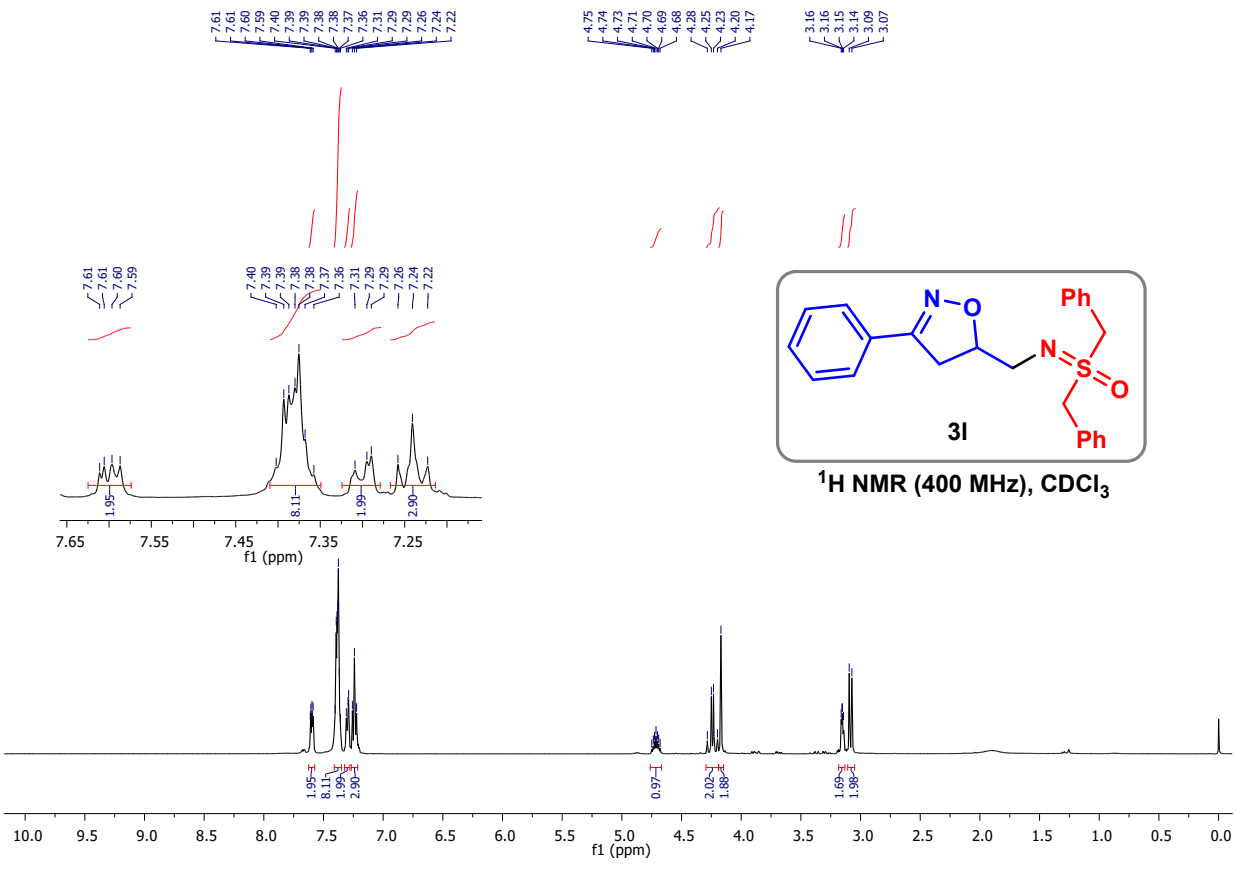
7.37
7.35
7.32
7.30
7.27
7.26 Chloroform-d
5.03
5.02
5.00
4.99
4.98
4.96
3.58
3.56
3.55
3.54
3.52
3.48
3.45
3.44
3.41
3.35
3.34
3.32
3.31
3.26
3.25
3.23
3.21
2.39
2.27
N
O
N
S
O
Me
Ph
3j (dr 2:1)
^{1}H NMR (400 MHz), CDCl$_3$
2.19
4.23
2.17
6.19
1.00
2.28
2.08
3.03
f1 (ppm)

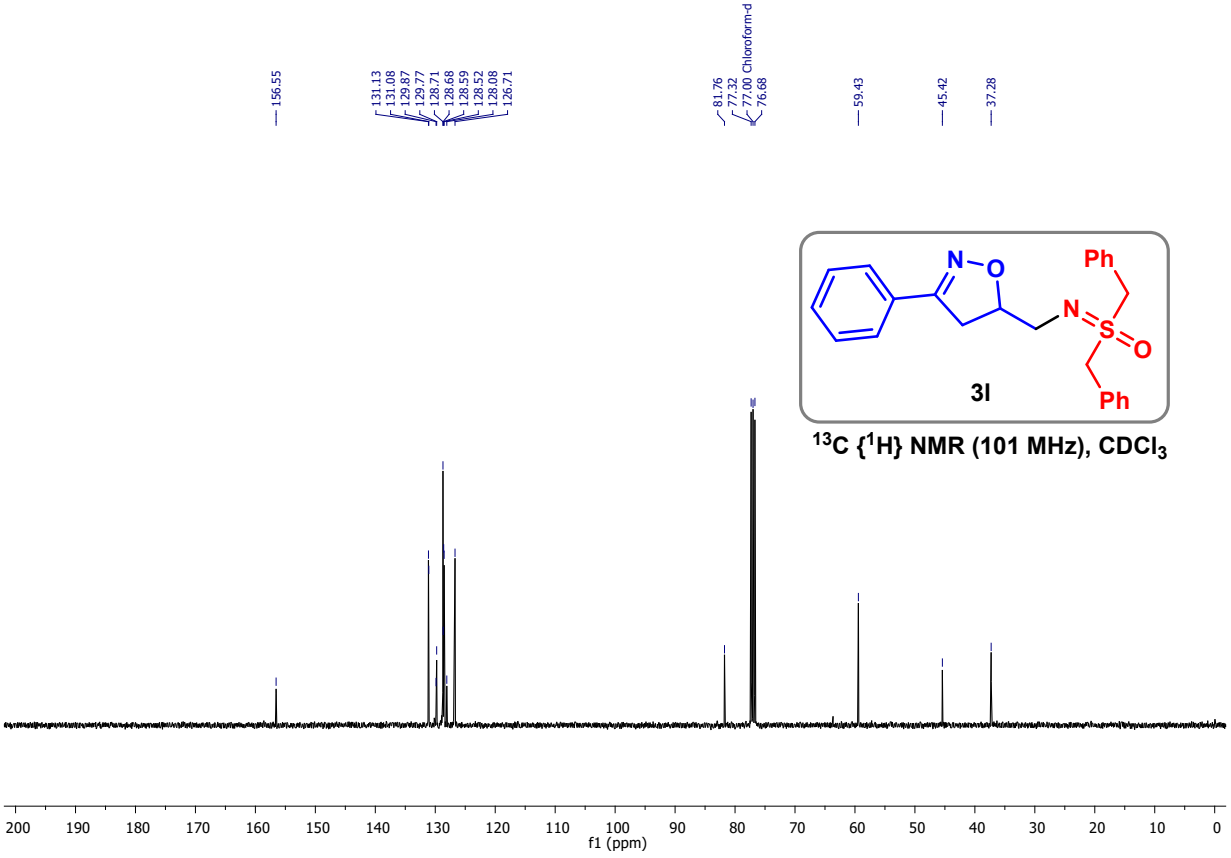

3j (dr 2:1)
^{13}C {^{1}H} NMR (101 MHz), CDCl$_3$
3k (dr 2:1)
^{1}H NMR (400 MHz), CDCl$_3$
f1 (ppm)



^{13}C {^{1}H} NMR (101 MHz), $CDCl_3$



^{1}H NMR (400 MHz), $CDCl_3$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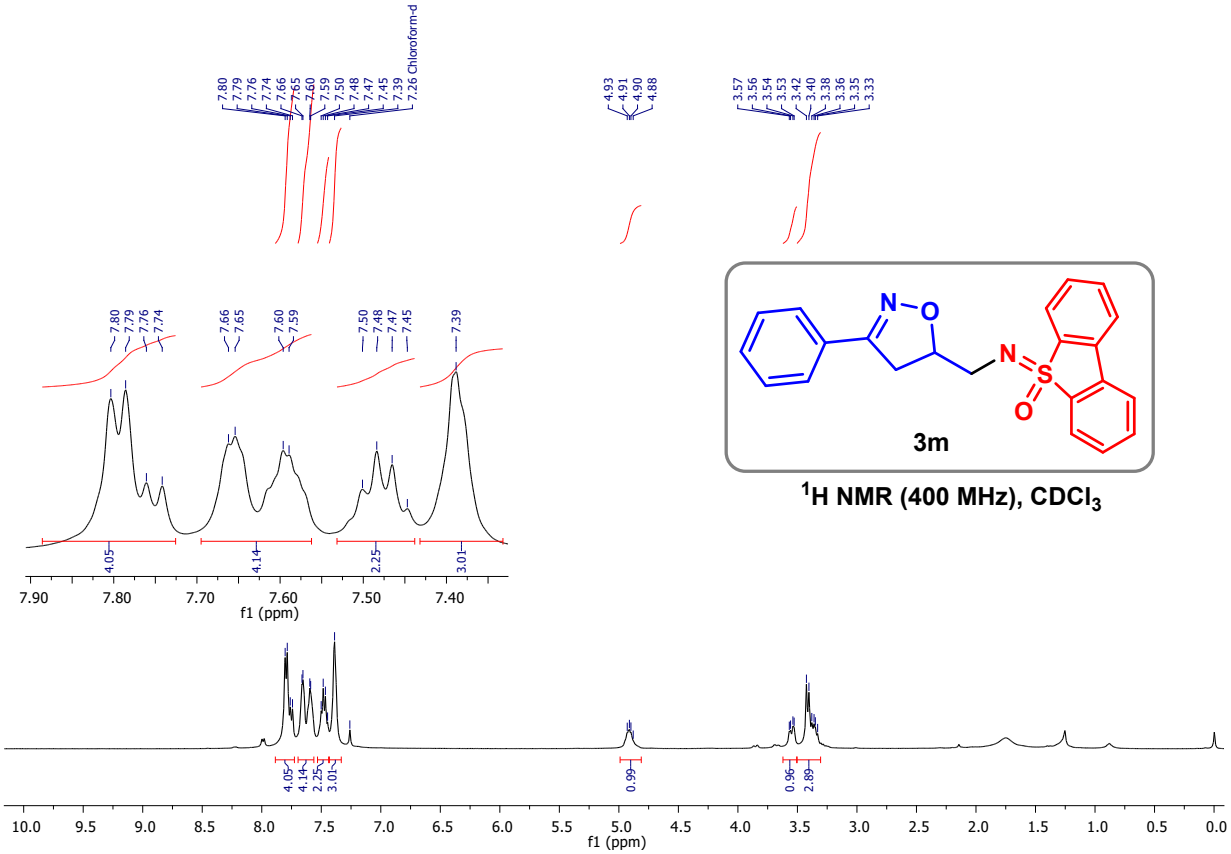
13C {1H} NMR (101 MHz), CDCl3
f1 (ppm)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7.59
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7.48
7.47
7.45
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7.26 Chloroform-d
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4.91
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3.54
3.53
3.42
3.40
3.38
3.36
3.35
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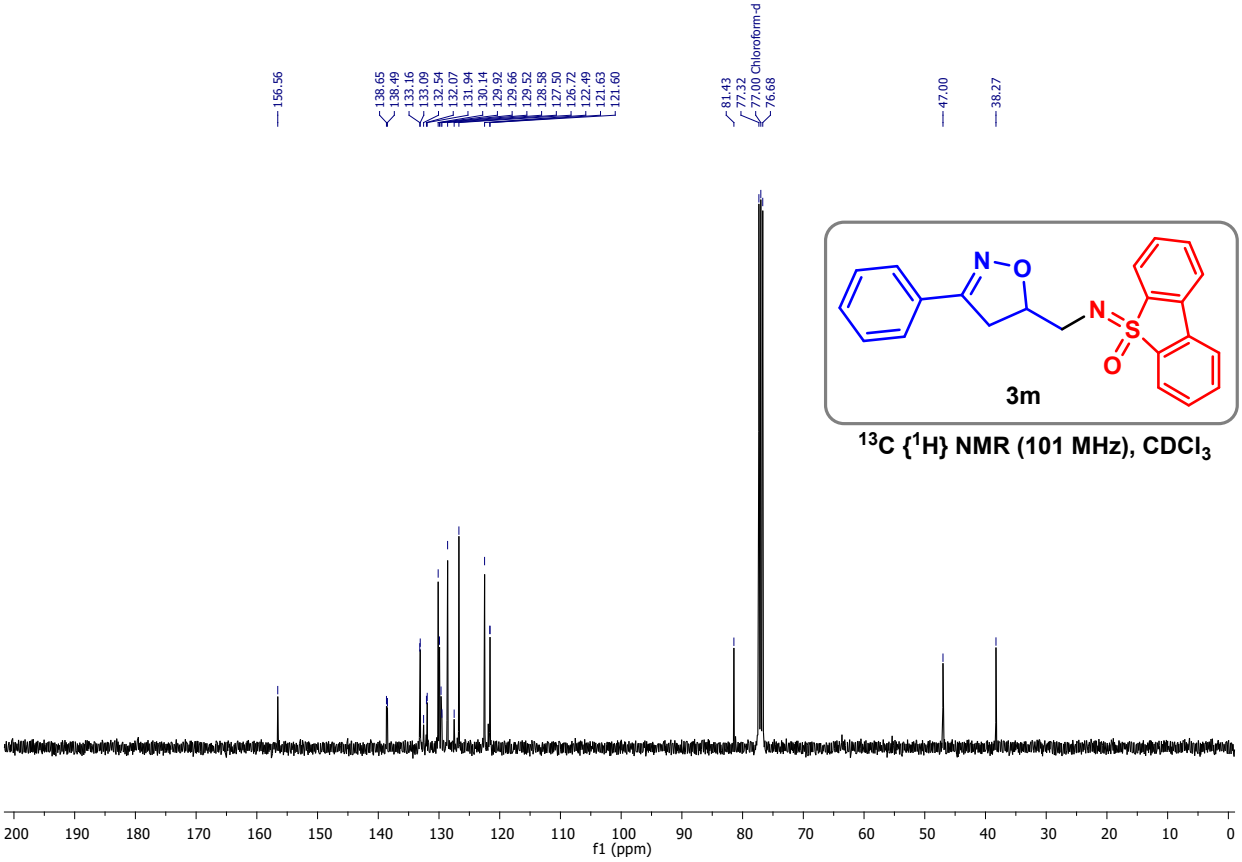
3m
1H NMR (400 MHz), CDCl3
f1 (ppm)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127.50
126.72
122.49
121.63
121.60
81.43
77.32
77.00 Chloroform-d
76.68
47.00
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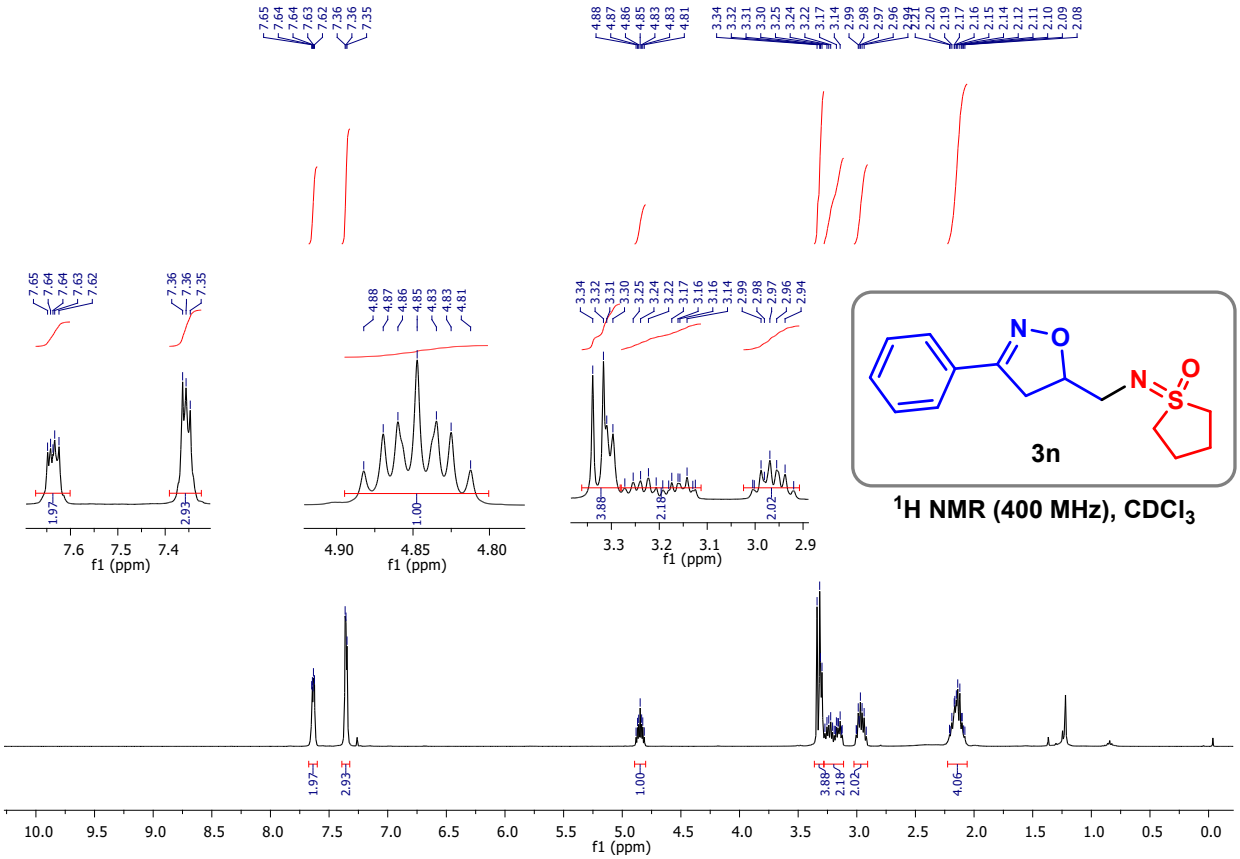
N
O
N
S
O
3m
^{13}C {^{1}H} NMR (101 MHz), CDCl$_3$
f1 (ppm)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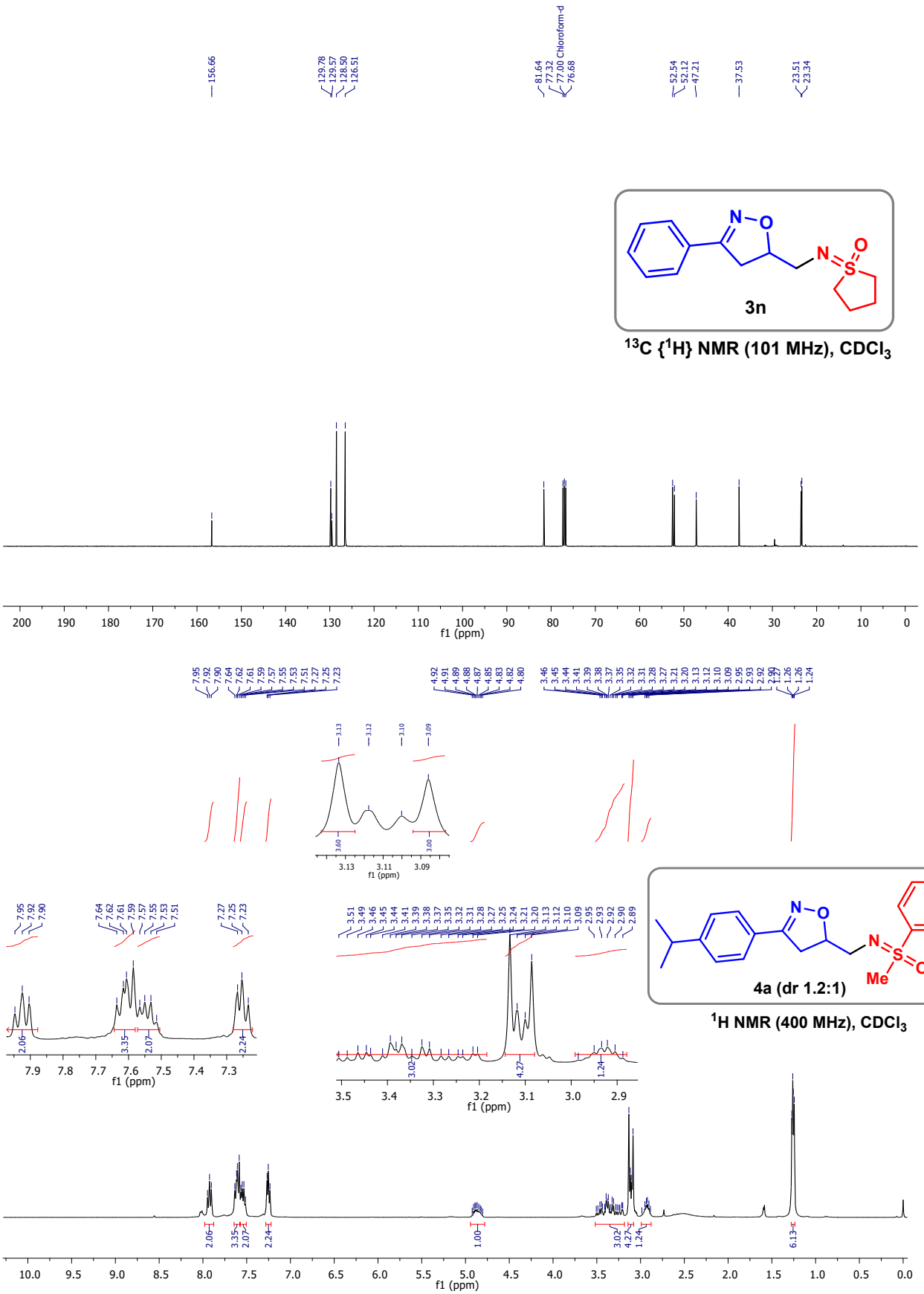
^{1}H NMR (400 MHz), CDCl$_3$
f1 (ppm)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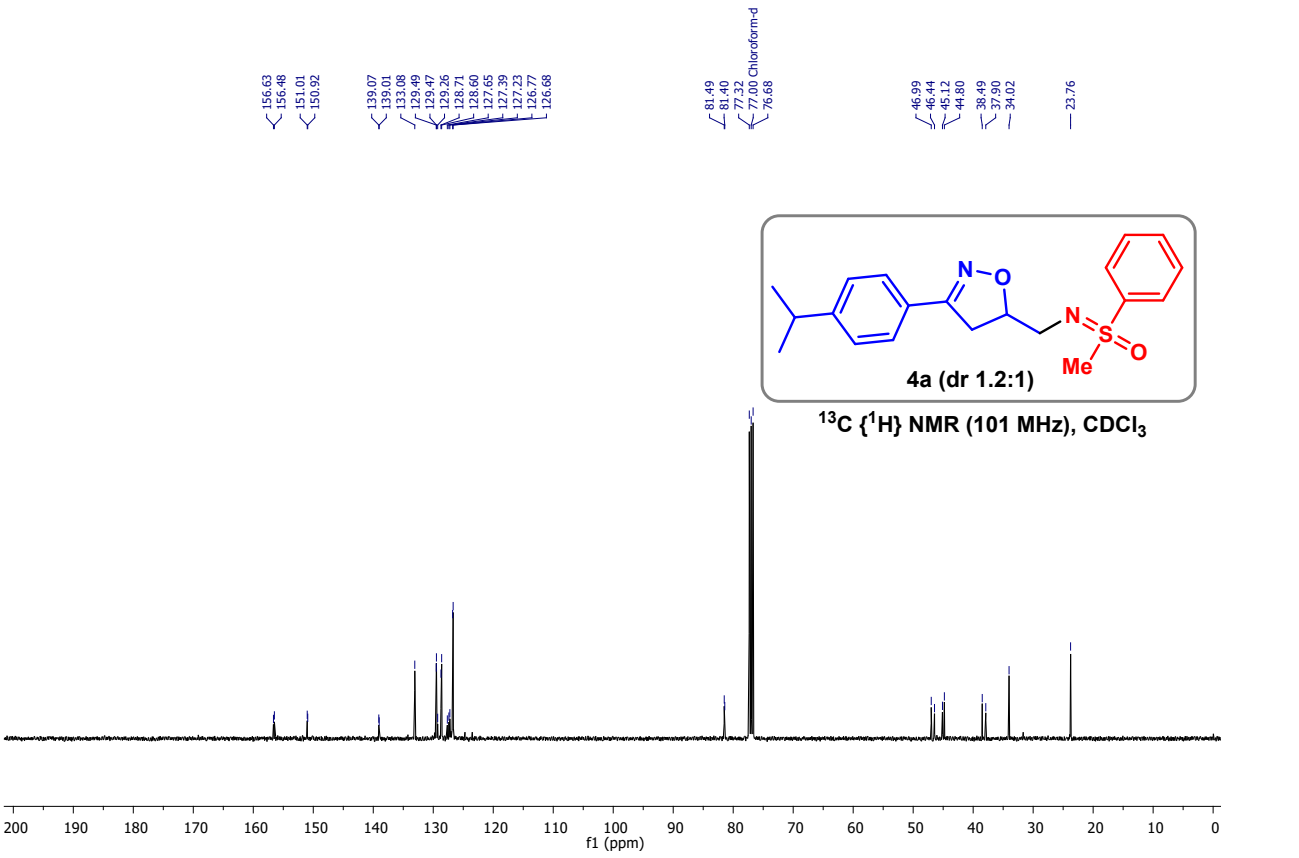
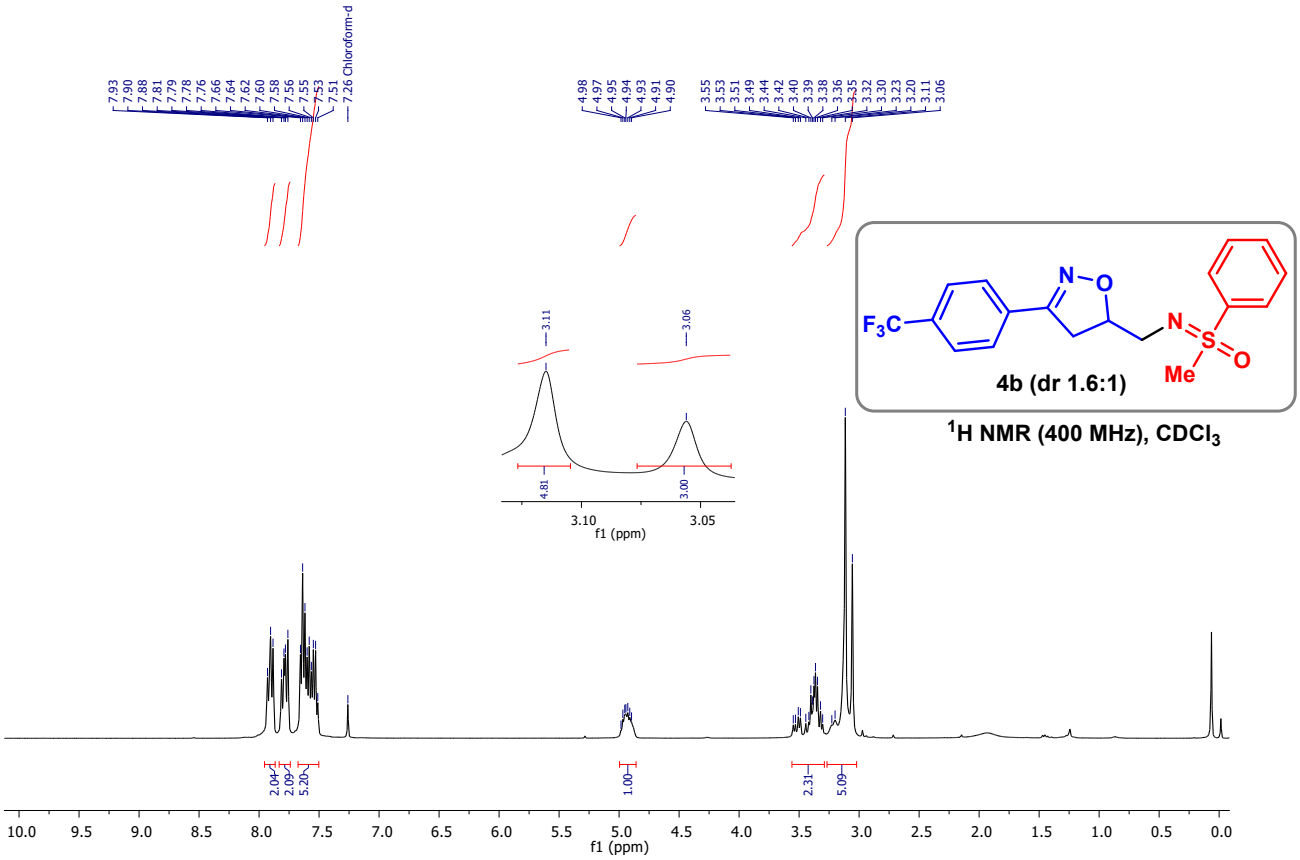
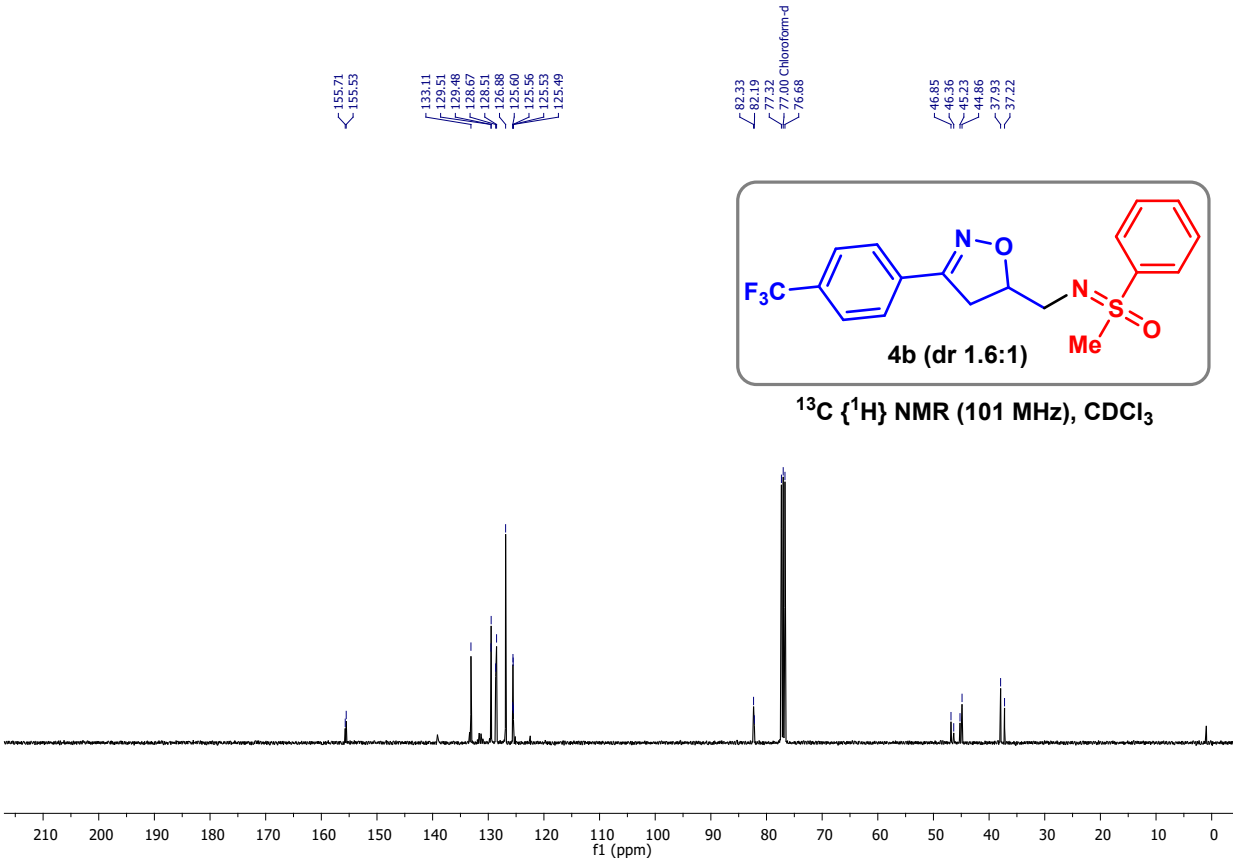
77.32
77.00 Chloroform-d
76.68
52.54
52.12
47.21
37.53
23.51
23.34
3n
13C {1H} NMR (101 MHz), CDCl3
f1 (ppm)
4a (dr 1.2:1)
1H NMR (400 MHz), CDCl3
Me



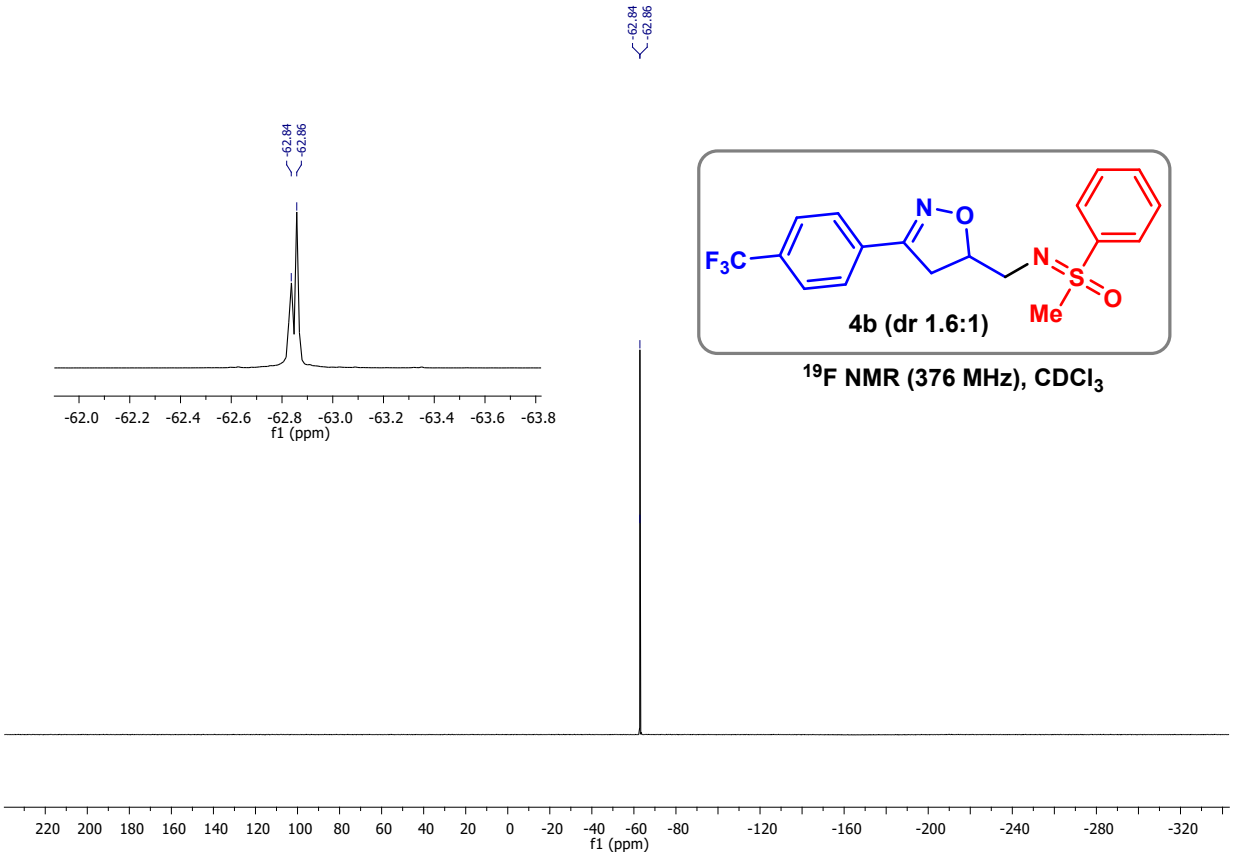
^{13}C {^{1}H} NMR (101 MHz), $CDCl_3$



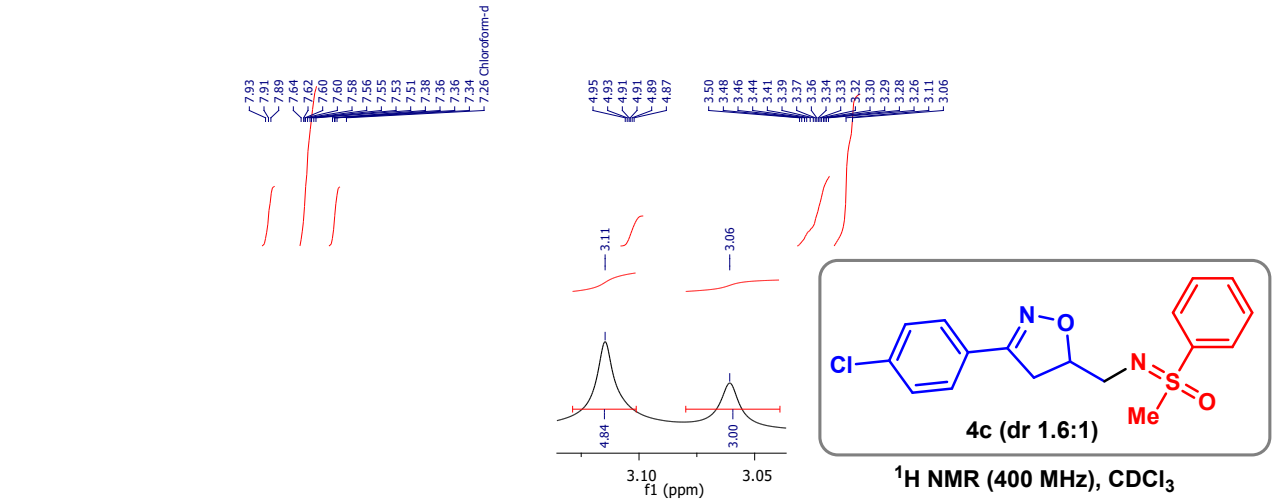
^{1}H NMR (400 MHz), $CDCl_3$



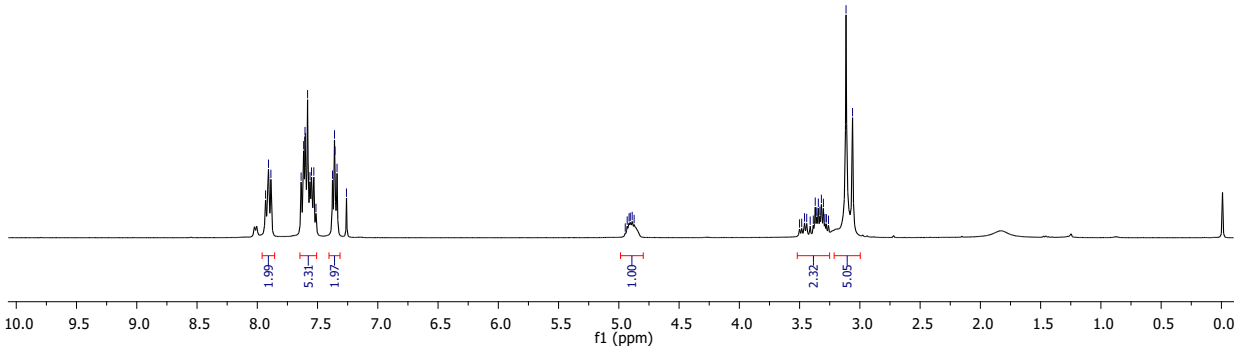
^{13}C {^{1}H} NMR (101 MHz), $CDCl_3$

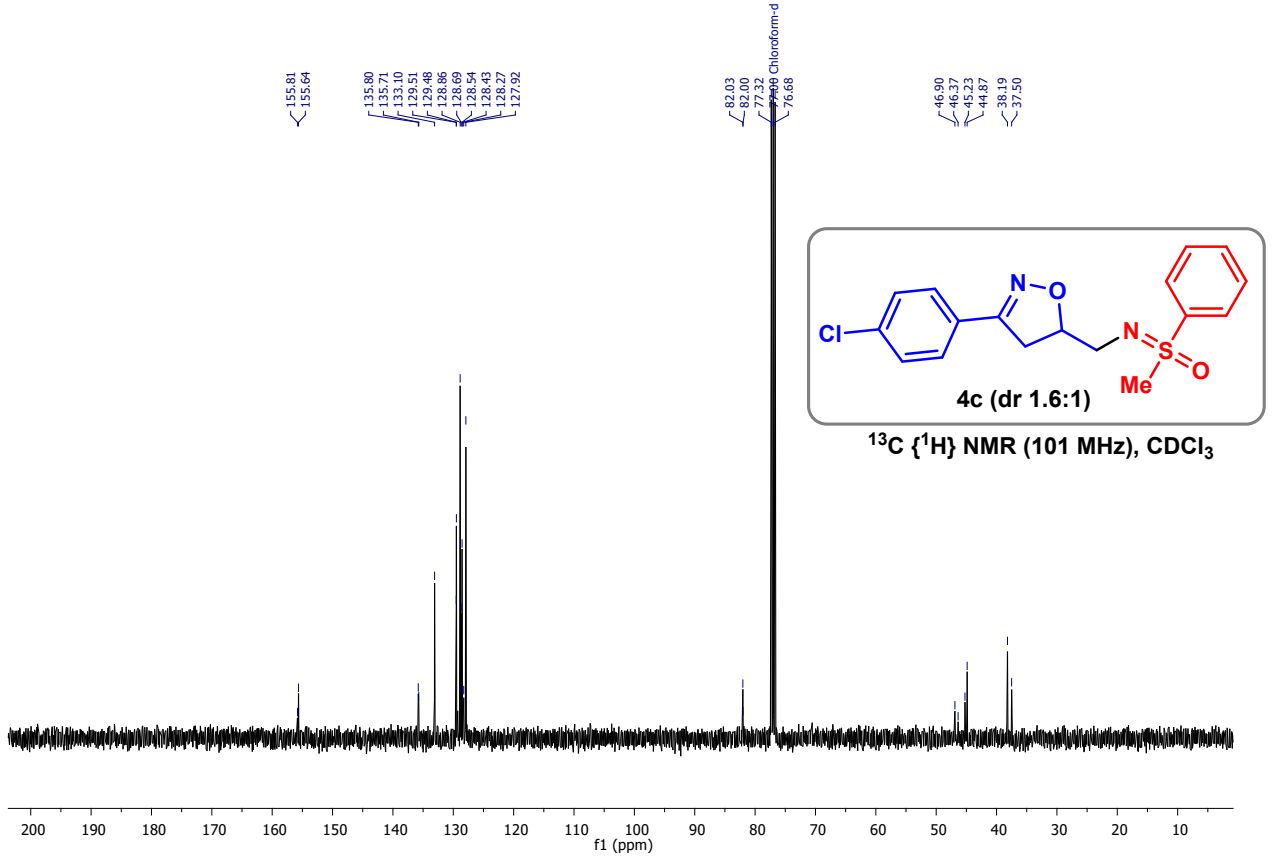


^{19}F NMR (376 MHz), $CDCl_3$

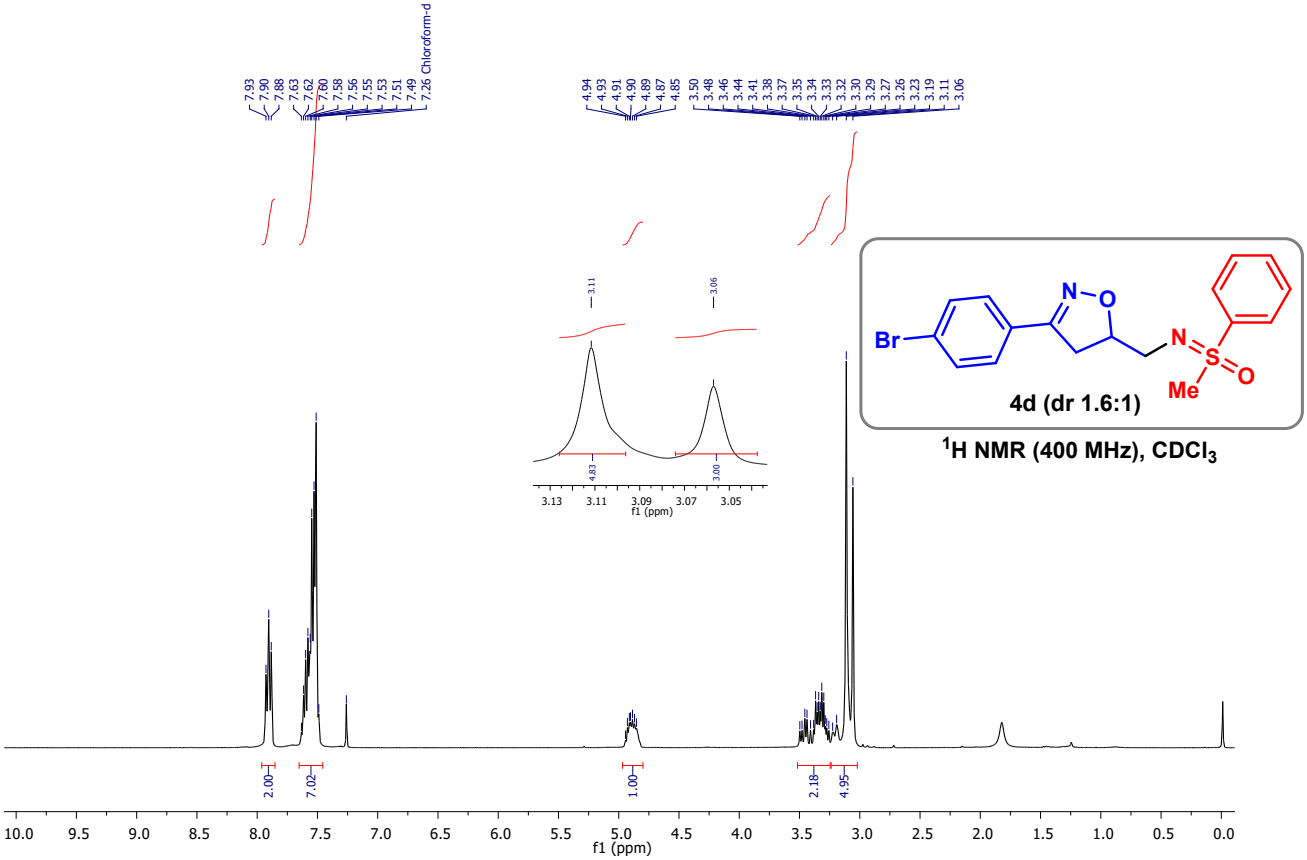


^{1}H NMR (400 MHz), $CDCl_3$





^{13}C {^{1}H} NMR (101 MHz), $CDCl_3$



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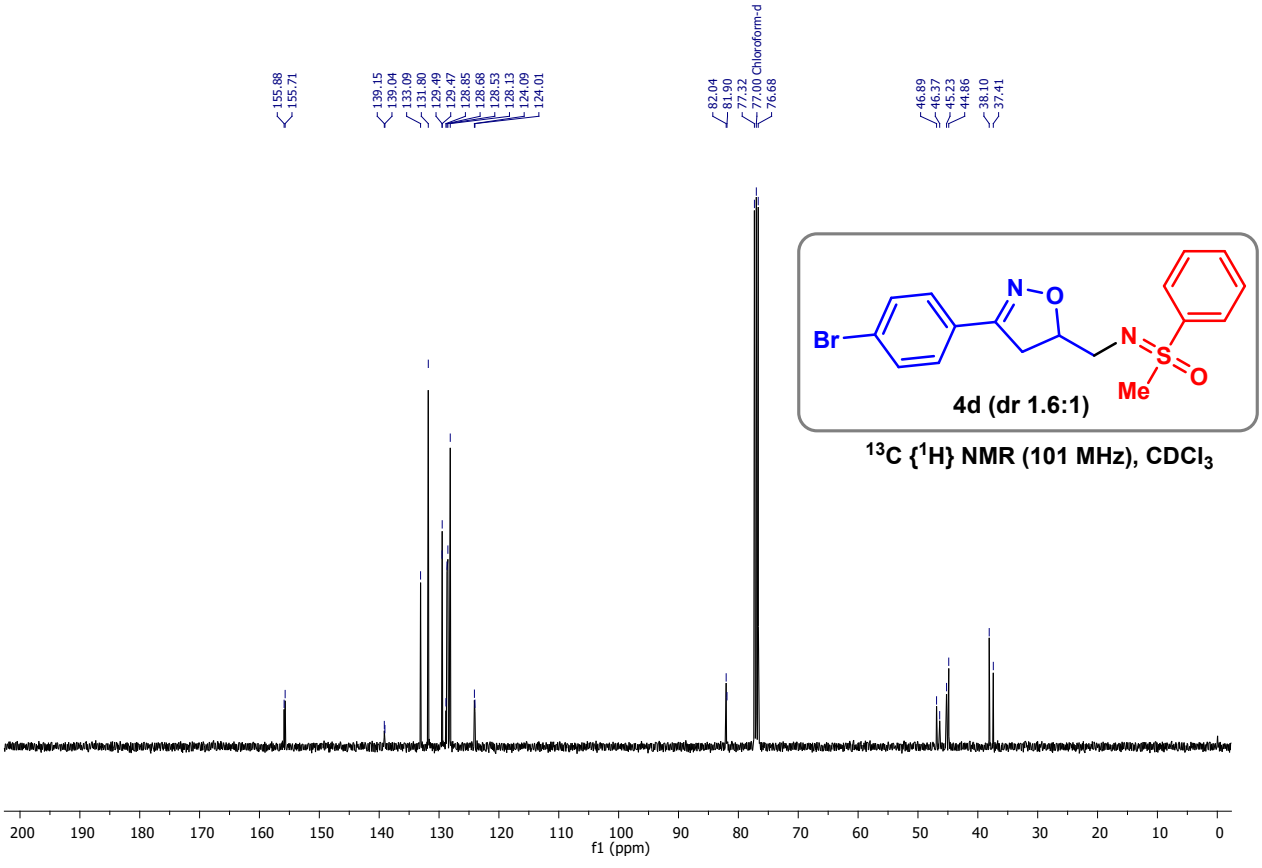
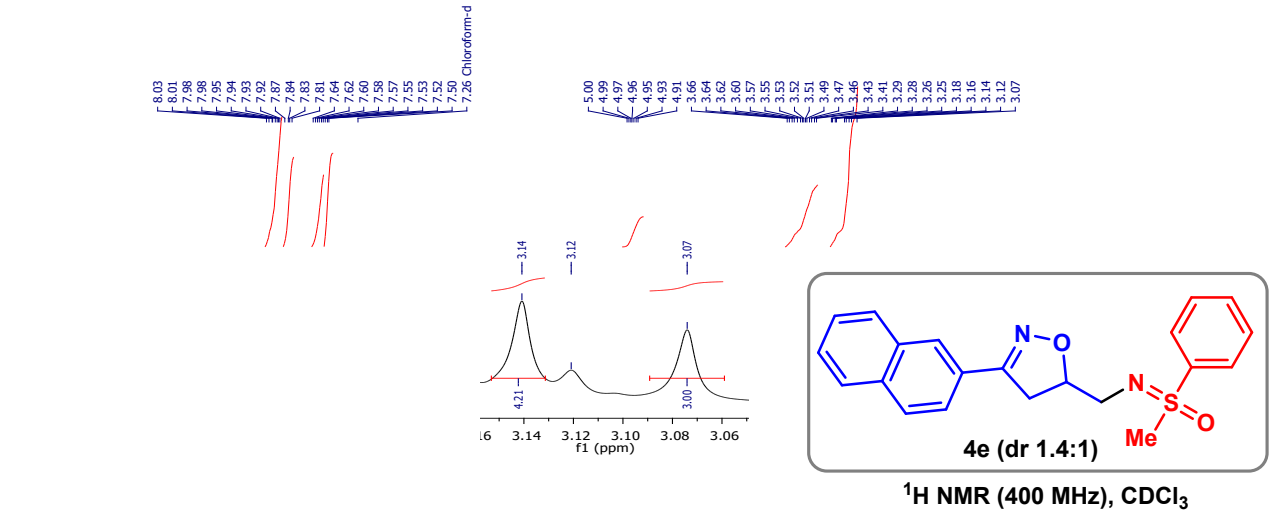
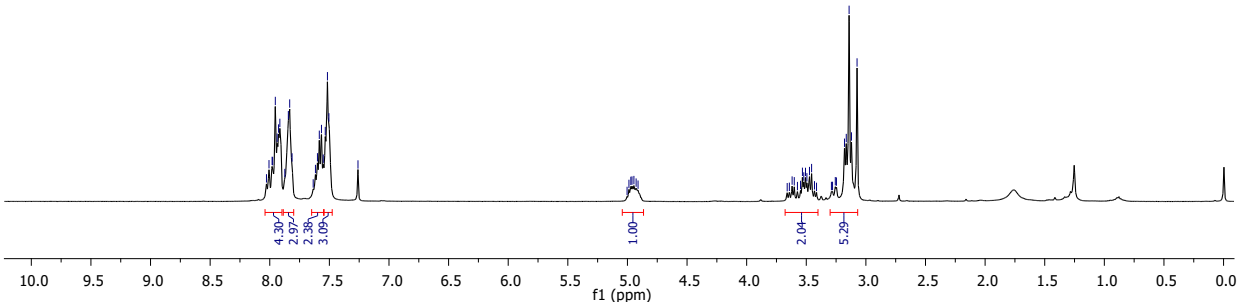
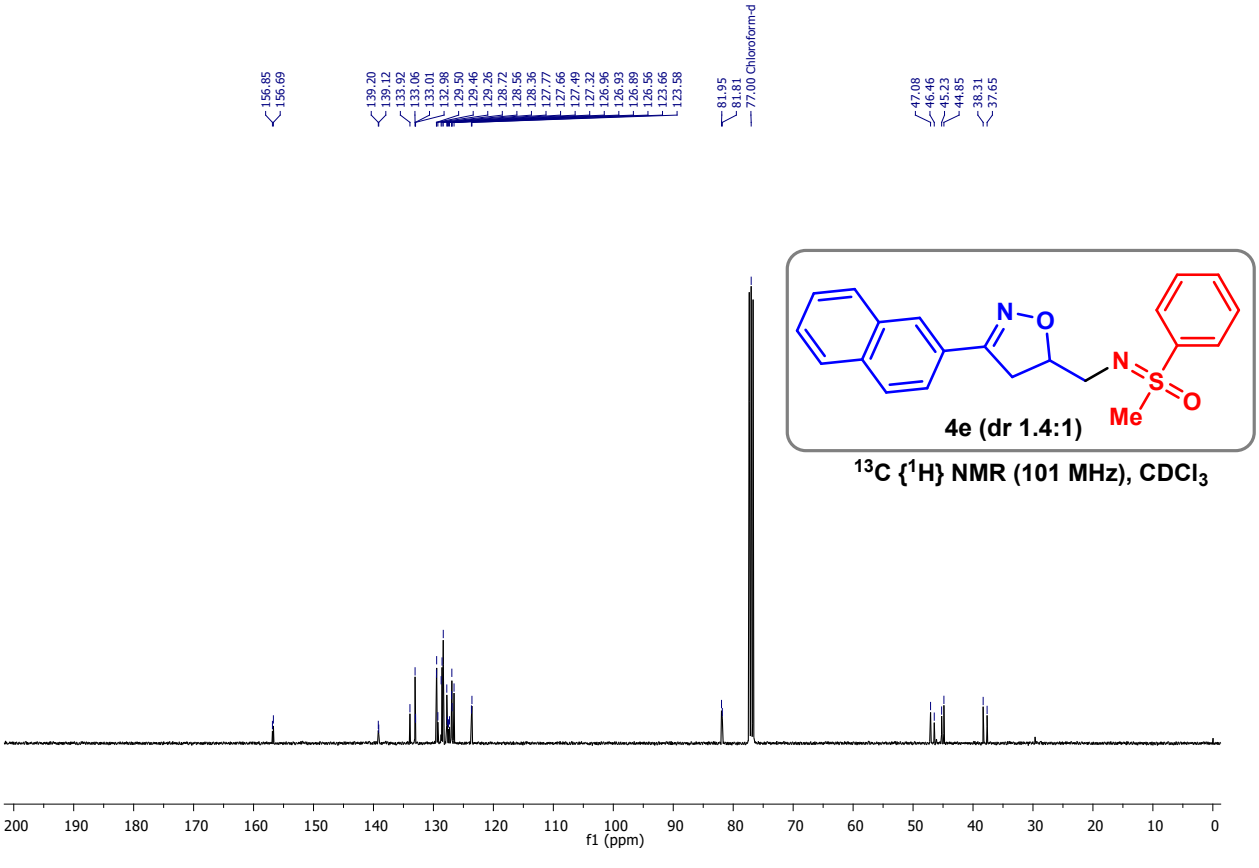


^{13}C {^{1}H} NMR (101 MHz), $CDCl_3$

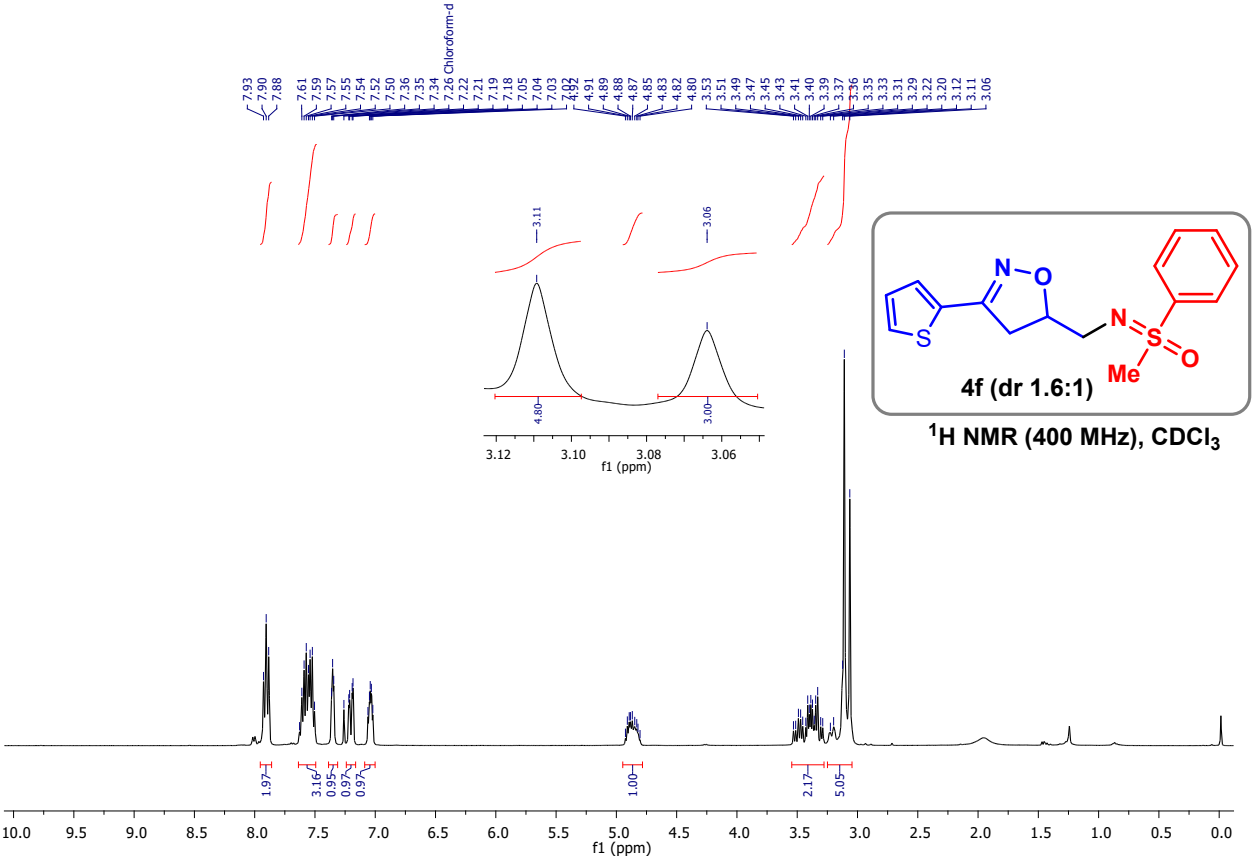


^{1}H NMR (400 MHz), $CDCl_3$





^{13}C {^{1}H} NMR (101 MHz), $CDCl_3$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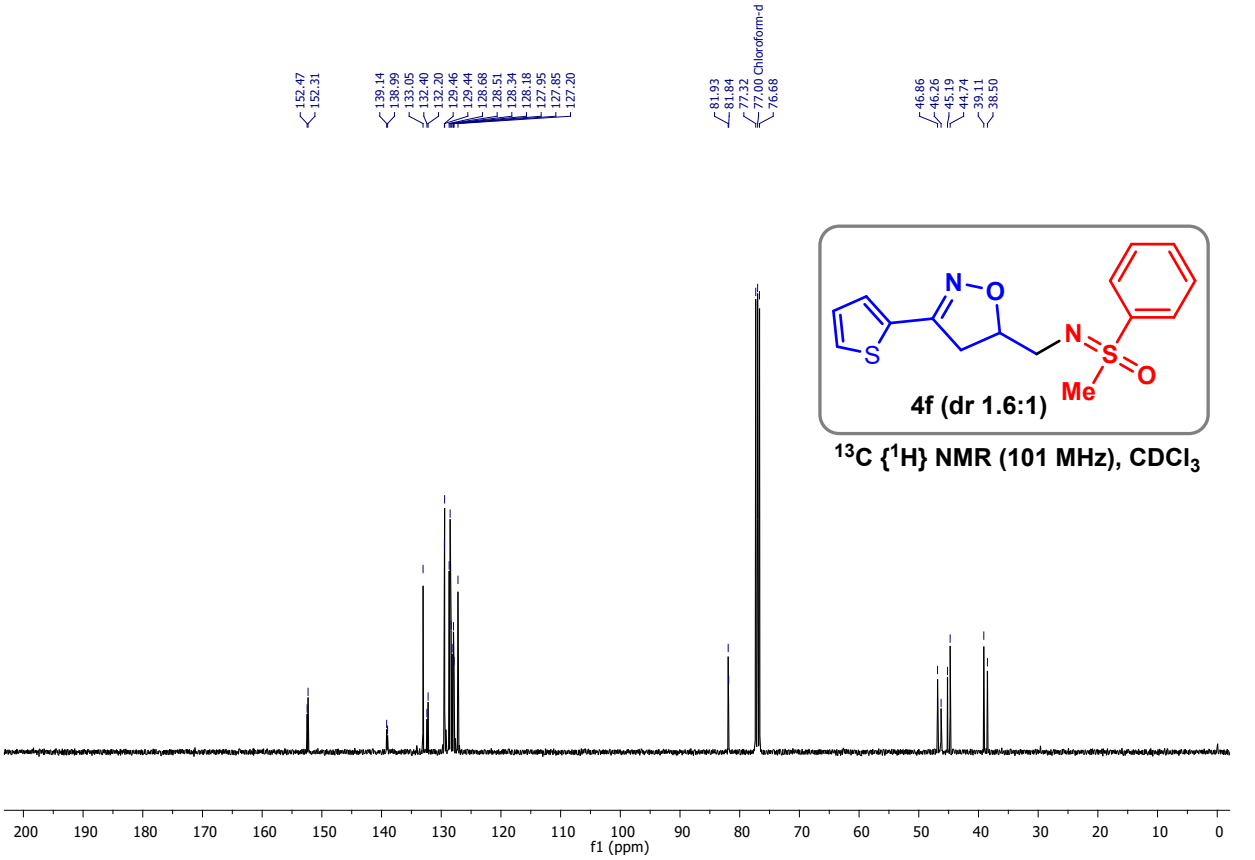
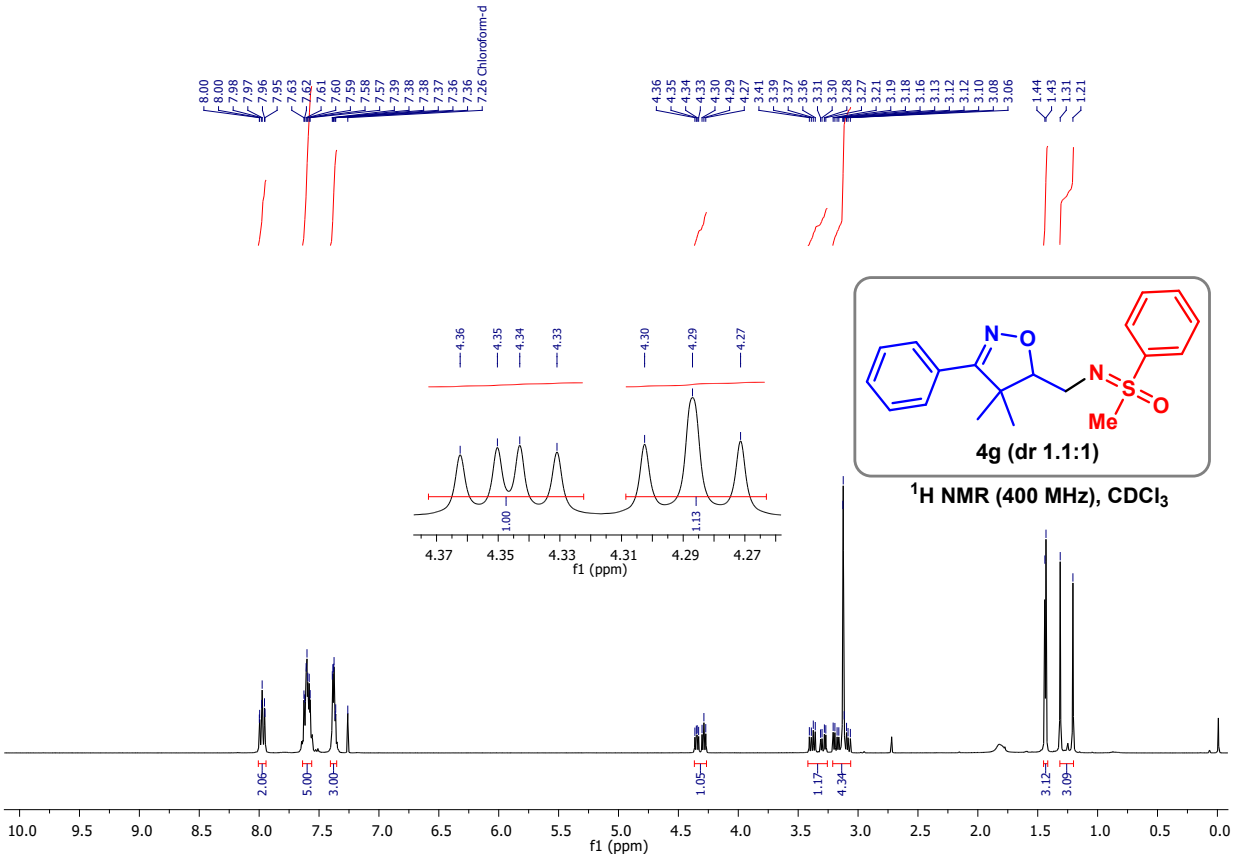
^{1}H NMR (400 MHz), CDCl$_3$
f1 (ppm)


4f (dr 1.6:1)
^{13}C {^{1}H} NMR (101 MHz), CDCl$_3$
f1 (ppm)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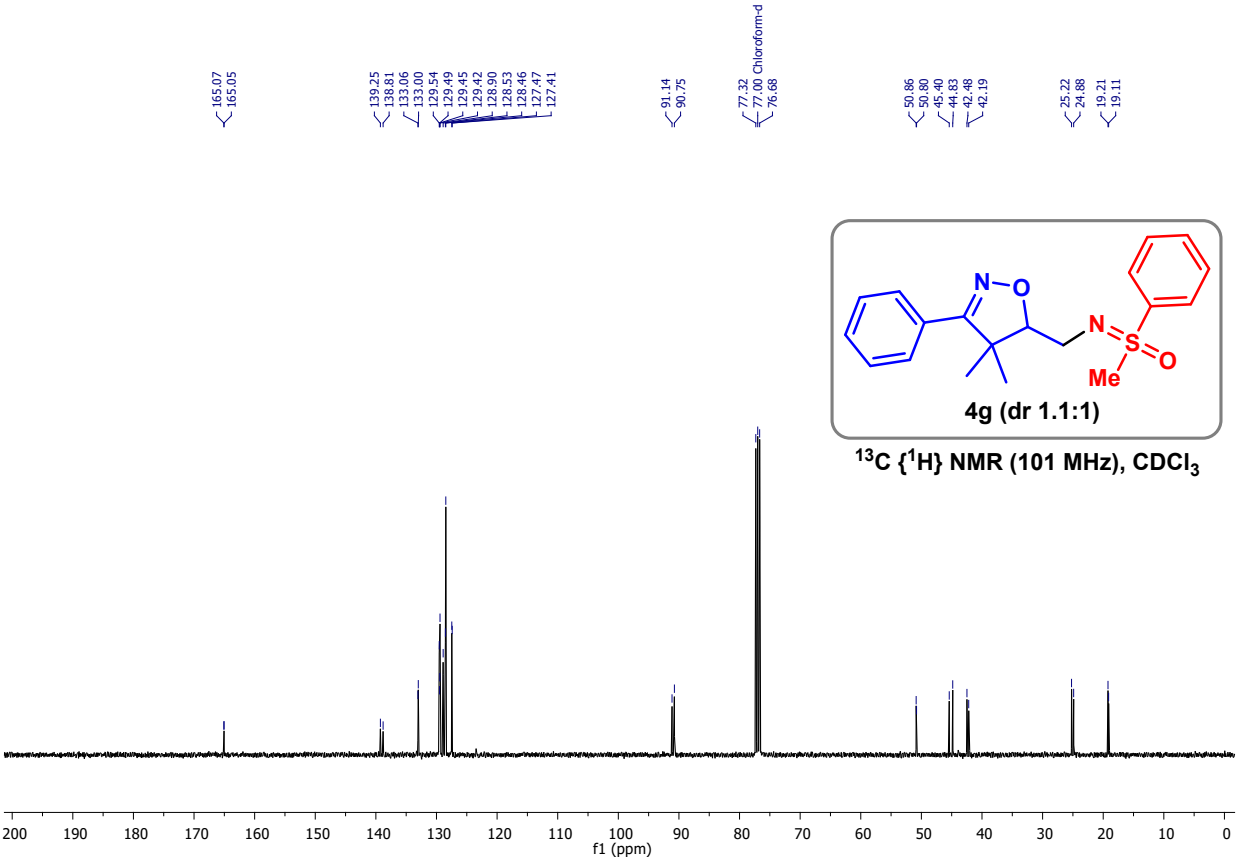
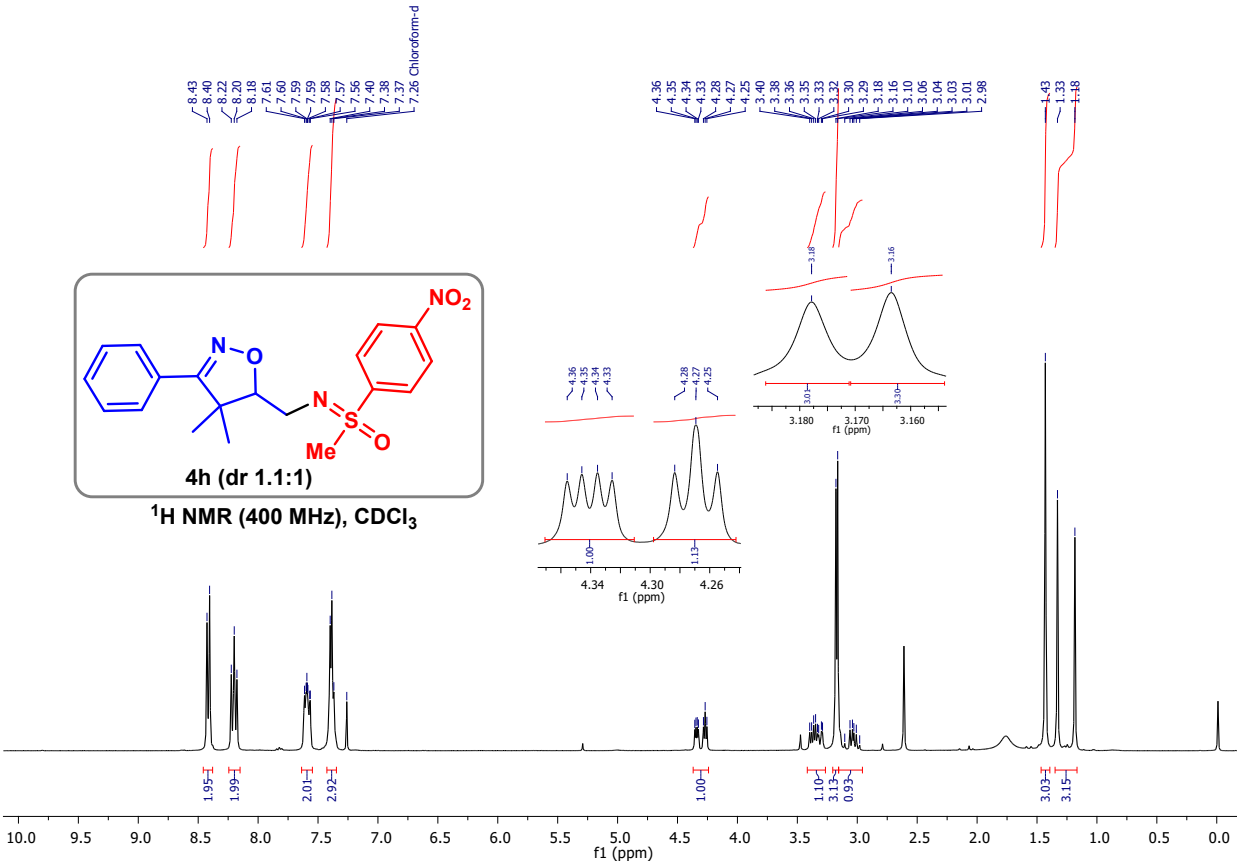
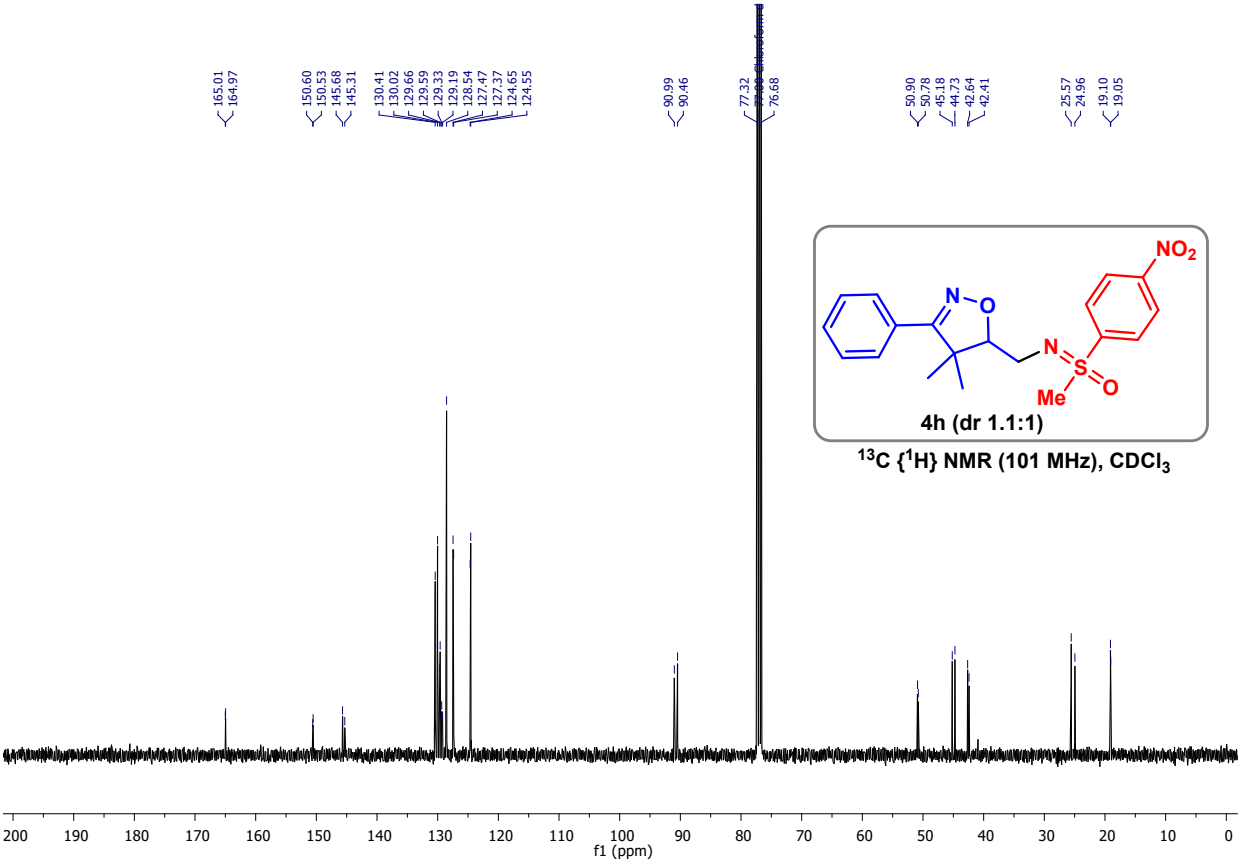
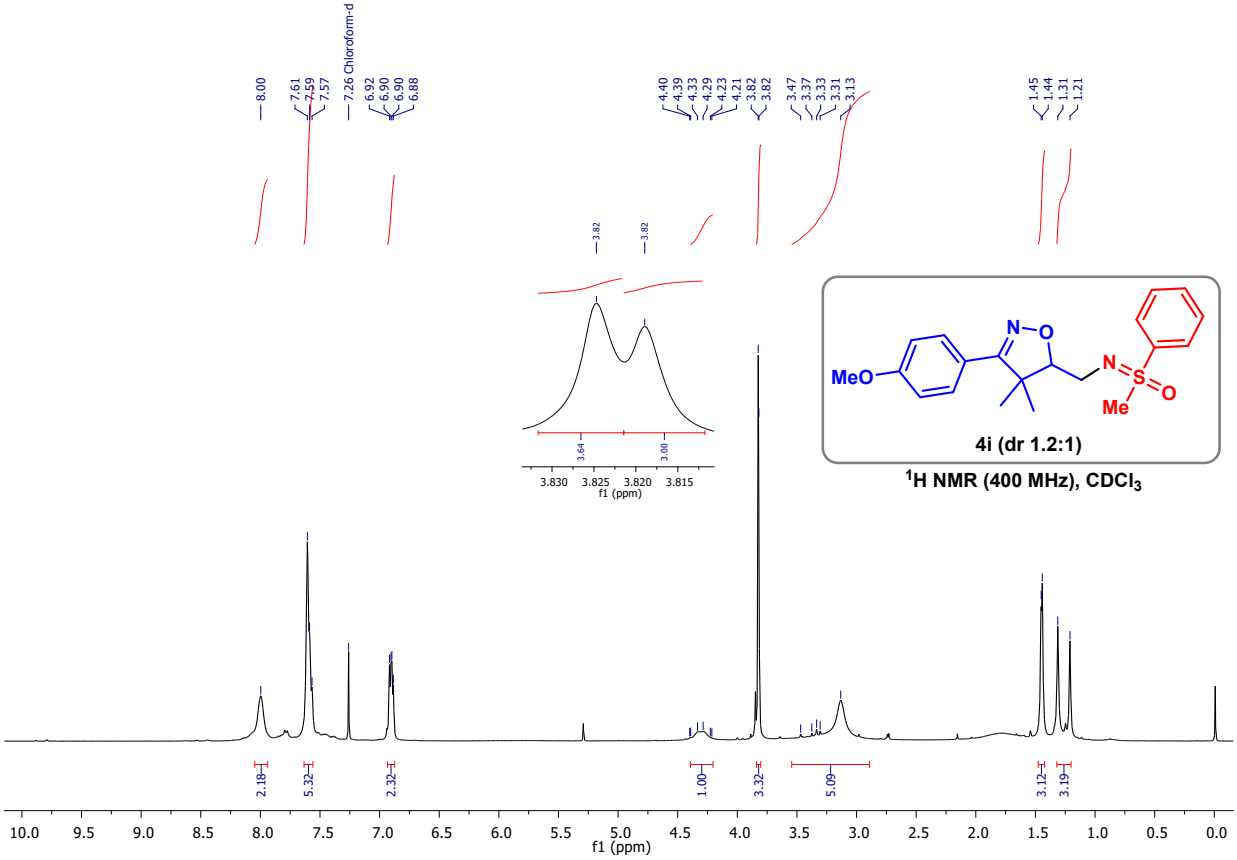
^{1}H NMR (400 MHz), CDCl$_3$
f1 (ppm)

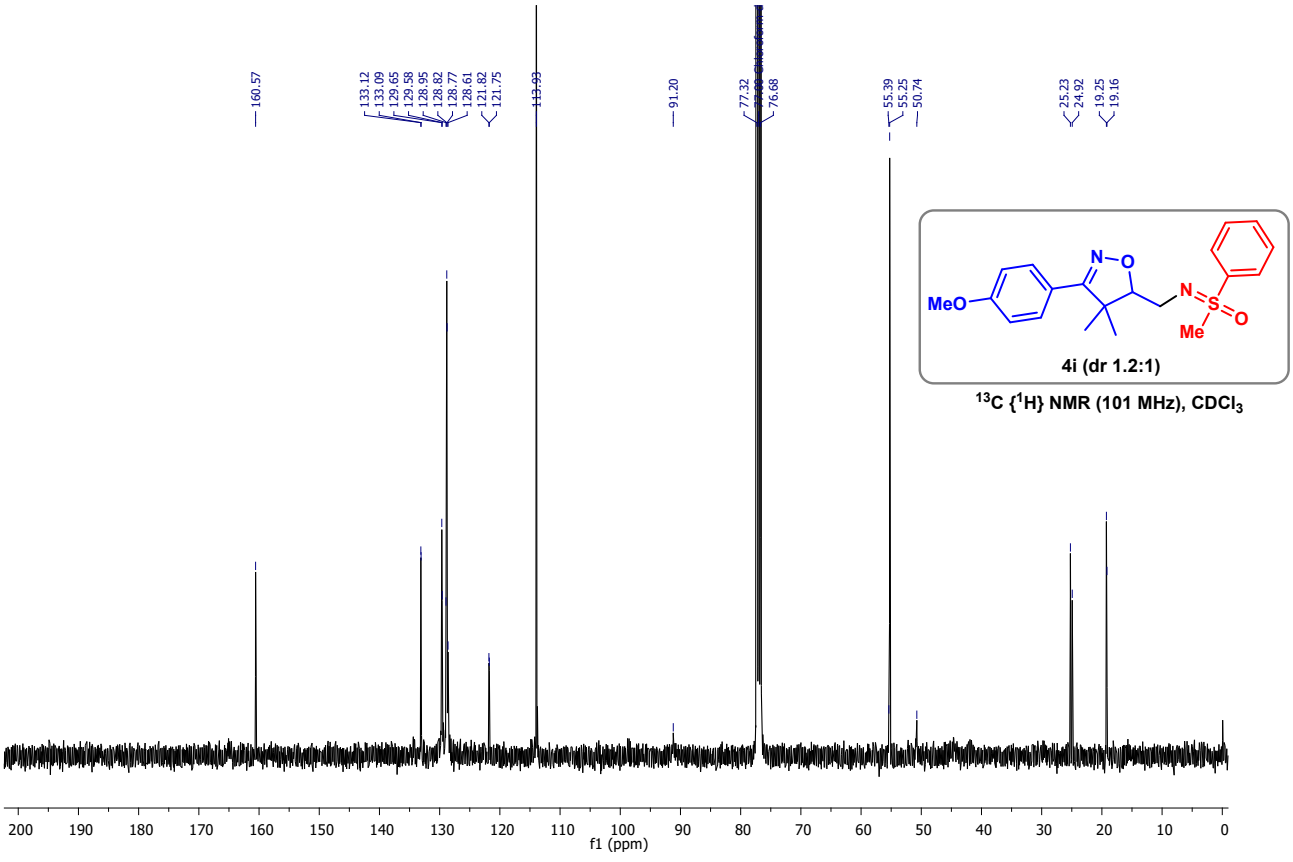

4g (dr 1.1:1)
^{13}C {^{1}H} NMR (101 MHz), CDCl$_3$
f1 (ppm)


4h (dr 1.1:1)
^{1}H NMR (400 MHz), CDCl$_3$
f1 (ppm)

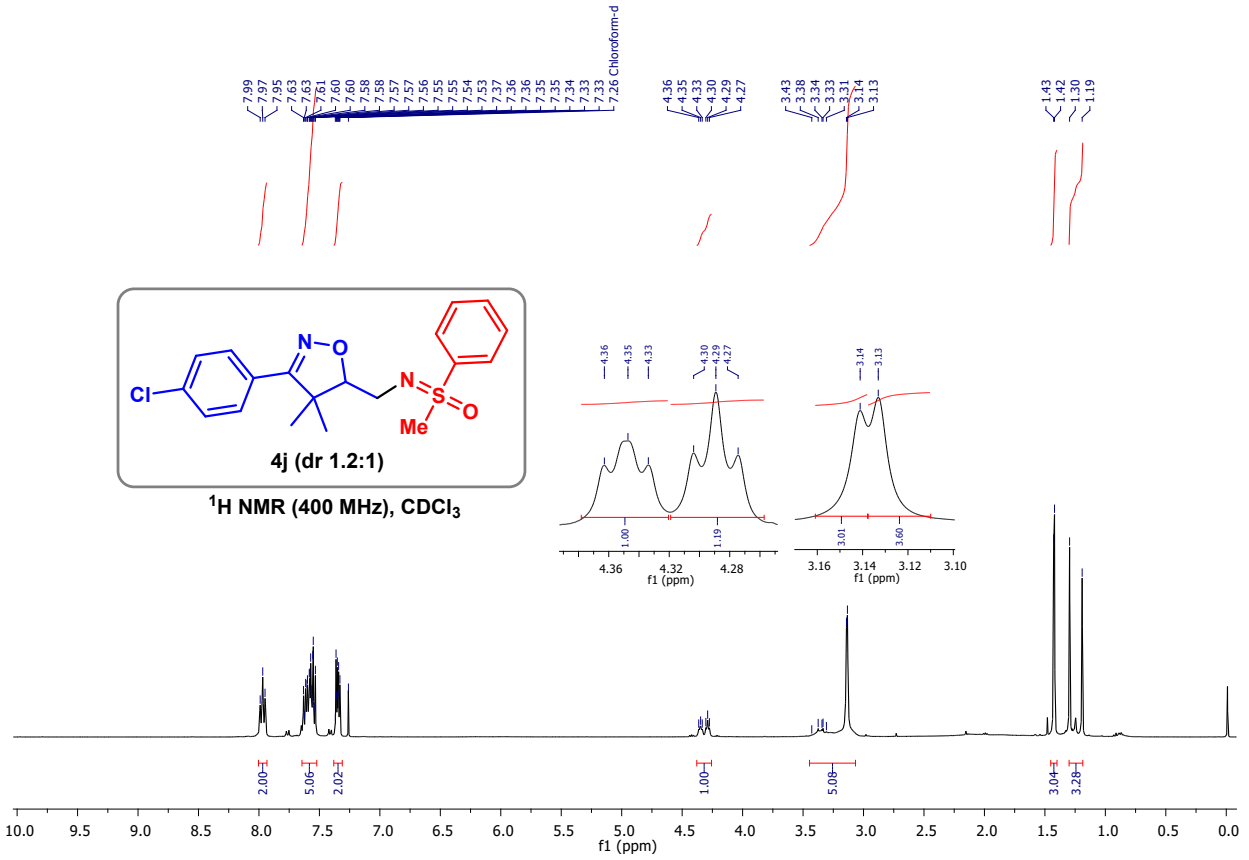

4h (dr 1.1:1)
^{13}C {^{1}H} NMR (101 MHz), CDCl$_3$
f1 (ppm)

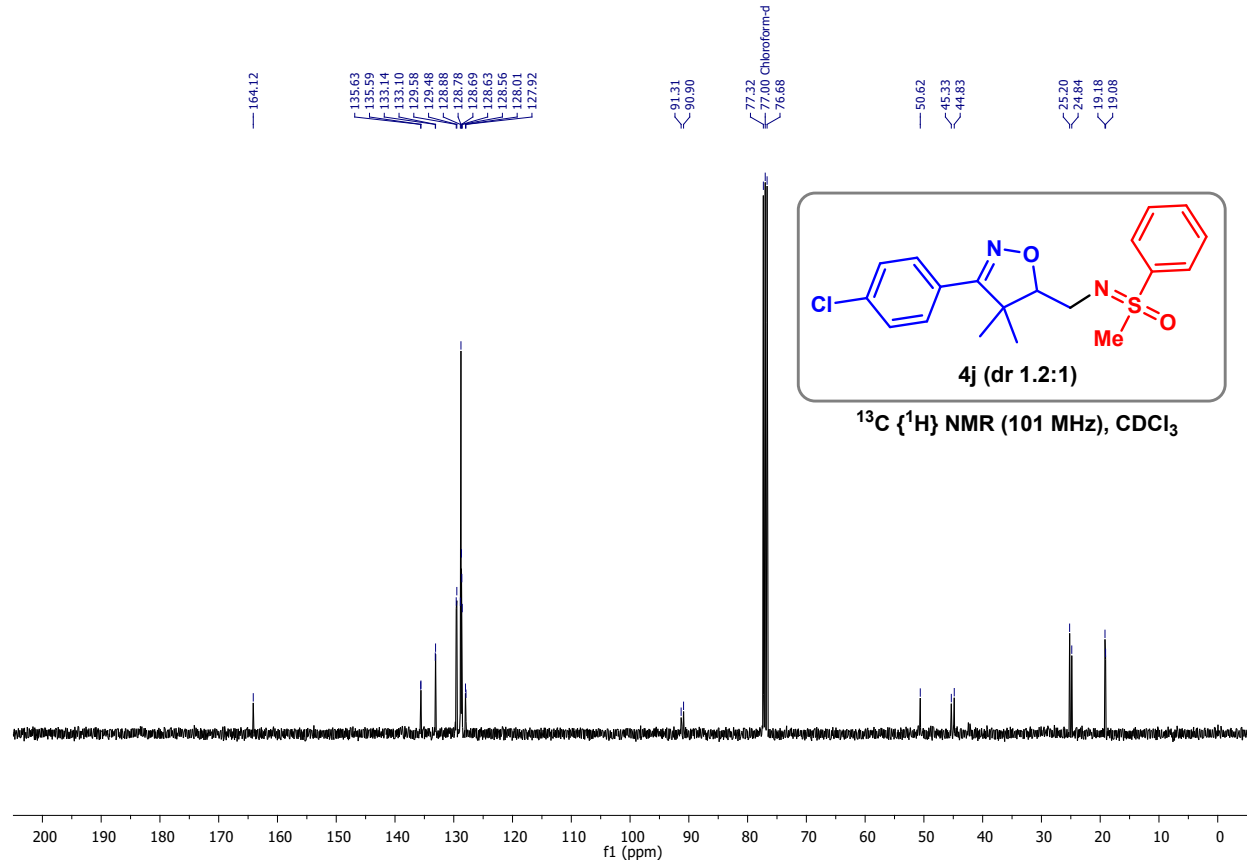


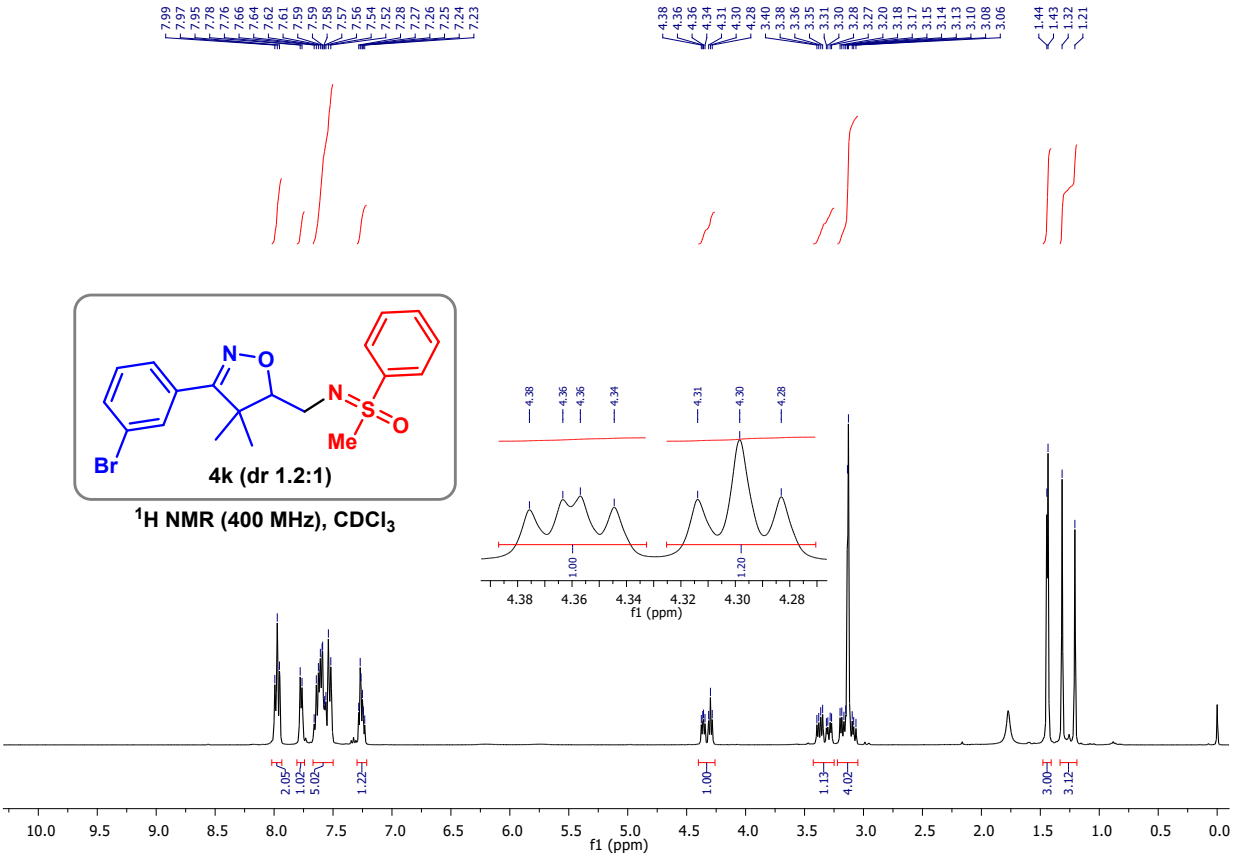
^{1}H NMR (400 MHz), $CDCl_3$

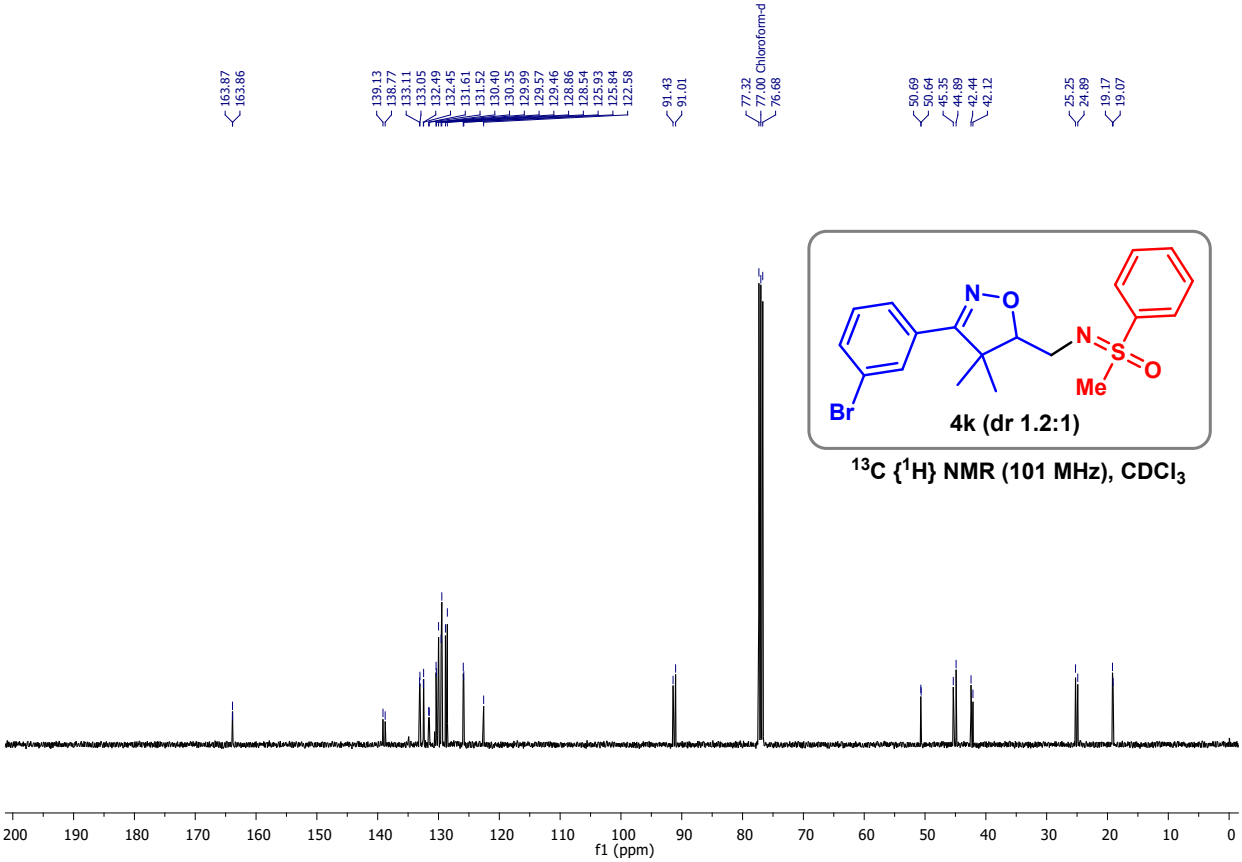


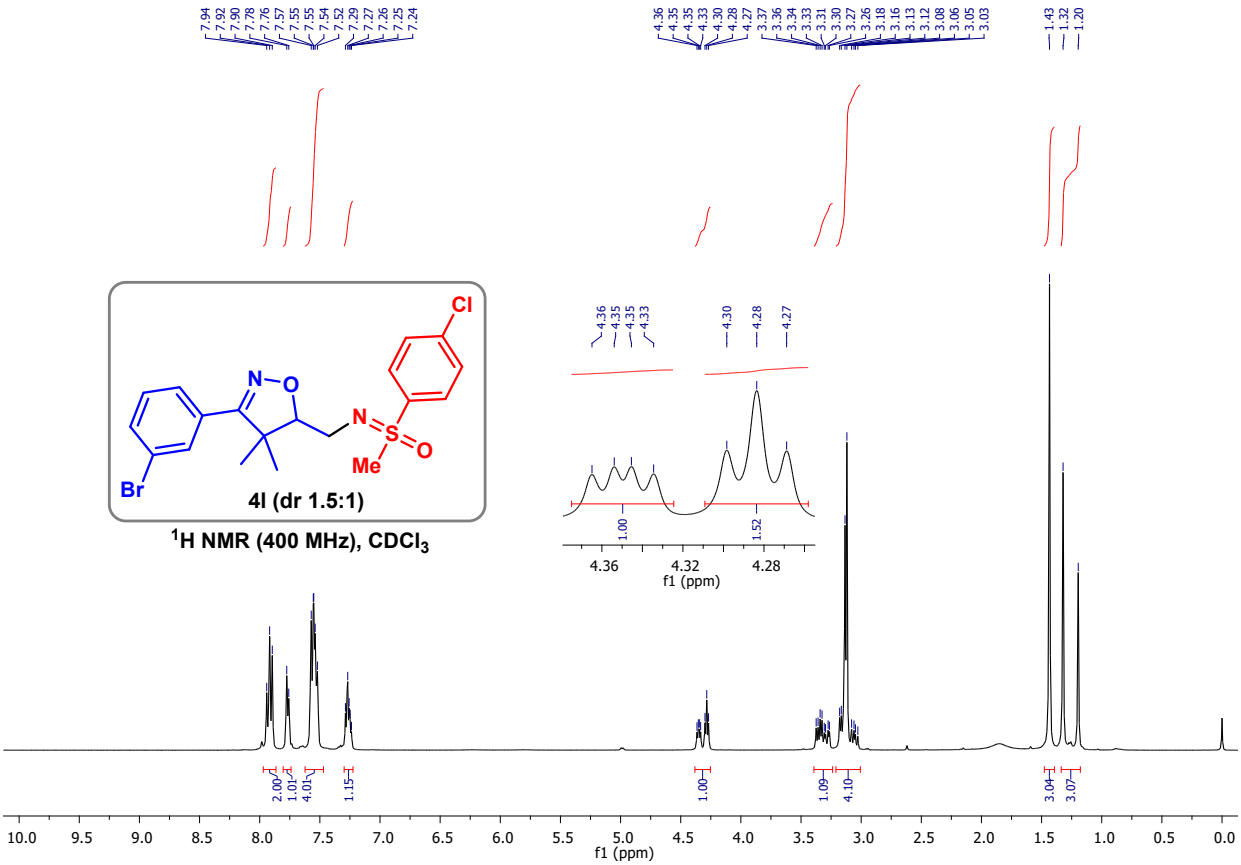
^{13}C {^{1}H} NMR (101 MHz), $CDCl_3$

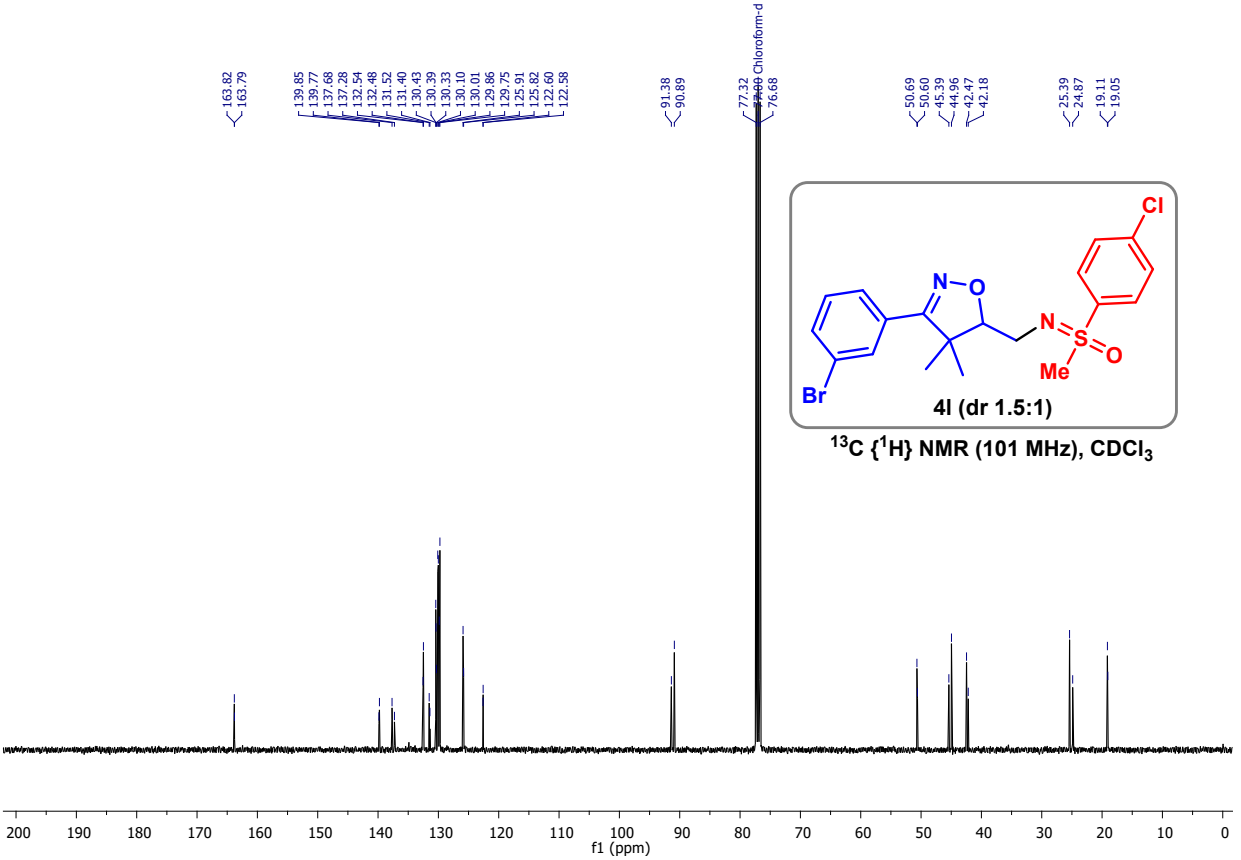

4j (dr 1.2:1)
1H NMR (400 MHz), CDCl3
f1 (ppm)


4j (dr 1.2:1)
13C {1H} NMR (101 MHz), CDCl3
f1 (ppm)


4k (dr 1.2:1)
^{1}H NMR (400 MHz), CDCl$_3$
f1 (ppm)


4k (dr 1.2:1)
^{13}C {^{1}H} NMR (101 MHz), CDCl$_3$
f1 (ppm)


Cl
N
O
N
S
O
Me
Br
4l (dr 1.5:1)
1H NMR (400 MHz), CDCl3
f1 (ppm)


Cl
N
O
N
S
O
Me
Br
4l (dr 1.5:1)
13C {1H} NMR (101 MHz), CDCl3
Chloroform-d
f1 (ppm)