Supporting Information

N-Arylation of *NH*-Sulfoximines *via* dual Nickel Photocatalysis

Alexander Wimmer, Burkhard König*

Department of Chemistry and Pharmacy, Institute of Organic Chemistry, University of Regensburg, Universitätsstraße 31, 93051, Regensburg, Germany

Email: Burkhard.koenig@chemie.uni-regensburg.de

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1. Materials and methods:

Starting materials and reagents were purchased from commercial suppliers (Sigma Aldrich, Alfa Aesar, Acros, Fluka or TCI) and were used without further purification. Unless otherwise stated, all reactions were performed in dried and degassed solvents. Solvents were dried over molecular sieve (3Å or 4Å) and degassed by bubbling nitrogen for 15 minutes before used. Unless otherwise stated, yields are generally isolated amounts of products, obtained after automated flash-column chromatography on flash silica gel, using HPLC-grade petrolether or hexane and ethylacetate as eluents. All reactions with oxygen- or moisture-sensitive reagents were carried out in glassware, which was dried before use by heating under vacuum. Dry nitrogen was used as inert gas. Liquid reagents and solvents were transferred *via* syringe, needle and septum technique. All NMR spectra were measured at room temperature, using a Bruker Avance 300 (300 MHz for ^{1}H, 75 MHz for ^{13}C and 282 MHz for ^{19}F) or a Bruker Avance 400 (400 MHz for ^{1}H, 101 MHz for ^{13}C and 376 MHz for ^{19}F) NMR spectrometer. All chemical shifts are reported in δ-scale as parts per million [ppm] (multiplicity, coupling constants *J*, number of protons) relative to the solvent residual peaks as the internal standard.[1] Coupling constants *J* are given in Hertz [Hz]. Abbreviations used for signal multiplicity: ^{1}H-, ^{13}C-NMR: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintet, sept. = septet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, and m = multiplet. ^{13}C NMR: (+) = primary/tertiary, (-) = secondary, (C_q) = quaternary. The mass spectrometrical measurements were performed at the Central Analytical Laboratory of the University of Regensburg. All mass spectra were recorded on a Finnigan MAT 95, ThermoQuest Finnigan TSQ 7000, Finnigan MAT SSQ 710 A or an Agilent Q-TOF 6540 UHD instrument. GC measurements were performed on a GC 7890 from Agilent Technologies. Data acquisition and evaluation was done with Agilent ChemStation Rev.C.01.04.. GC measurements were made and analyzed *via* integration of the signal obtained with respect to the calibration with a suitable internal standard. Analytical TLC was performed on silica gel coated alumina. Visualization was done by UV light (254 or 366 nm). If necessary, potassium permanganate was used for chemical staining. Enantiomeric purity was determined by NP chiral HPLC (Varian 920-LC) analysis with either Daicel Chiralpak AS-H (5 µm, 4.6 x 250 mm) or Phenomenex Lux Cellulose-1 (5 µm, 4.6 x 250 mm) columns, using *n*-heptane and *iso*-propanol as eluents. Melting points were determined of purified solid products, using a MPA100 OptiMelt – automated melting point system – from SRS: Starting operating temperature: 50 °C; Ending operating temperature: 300 °C; Heating gradient: 1 °C/min. The standard photochemical set-up for experiments in regular scale consists of 455 nm LEDs (OSRAM Oslon SSL 80 royal-blue, 455 nm (±15 nm), radiant power 500 mW, 2.9 V, 350 mA) which illuminate from the bottom and a custom made aluminum cooling block connected to a thermostat which cools from the side (Figure S 1). Large-scale reactions were performed in a self-designed batch-reactor which consists of the following three compartments: **1** A round-bottomed glass cylinder as vessel for the reaction mixture. **2** A second, slightly smaller glass cylinder with connection to cooling water, in order to cool the reaction mixture. By connecting the two glass cylinders a thin film of the reaction mixture is created and facilitates both, illumination and cooling of the reaction mixture. **3** 455 nm LEDs (OSRAM Oslon SSL 80 royal-blue, 455 nm (±15 nm), 500 mW, 2.9 V, 350 mA), generating a total radiant power of 12 W, are placed on the inside of a custom made aluminum cooling-block which surrounds the reaction vessel (Figure S 2).

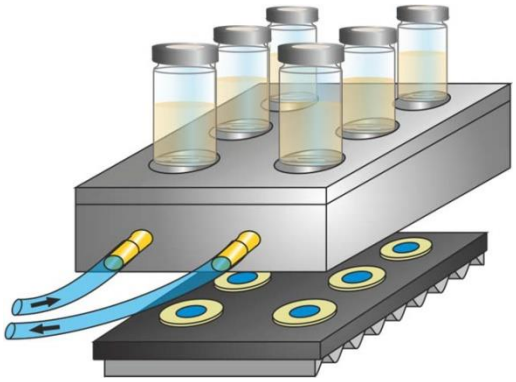


Figure S 1. Standard photochemical set-up for small regular-scale reactions.

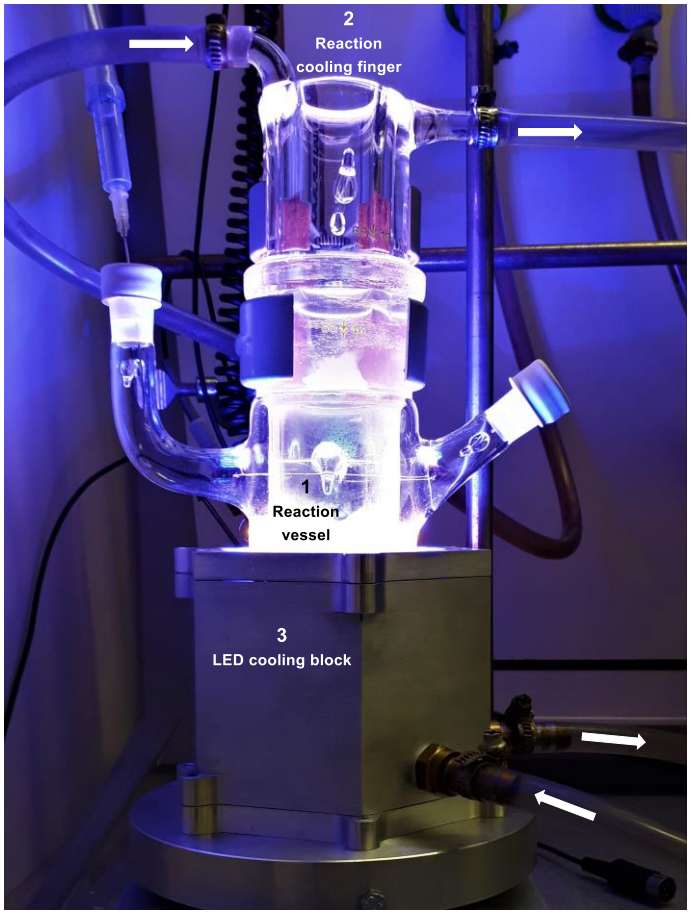


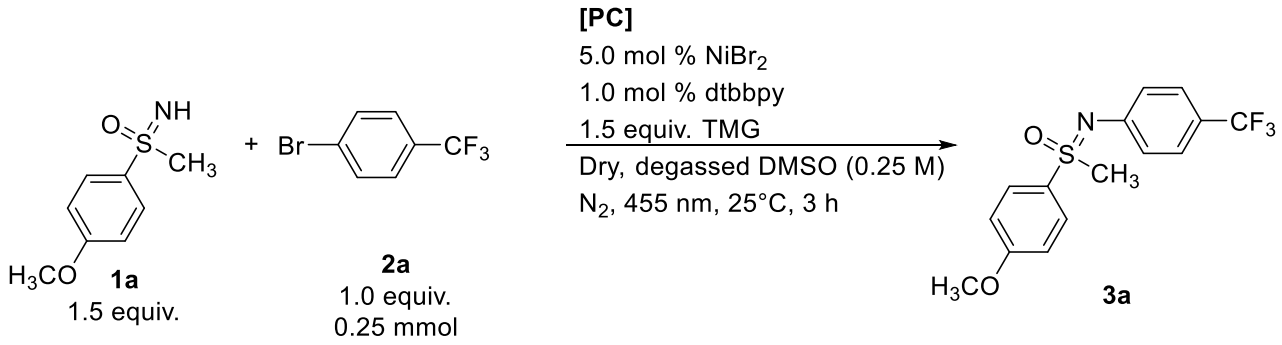
Figure S 2. Reactor for large-scale photoreactions.

2. Optimization of the reaction conditions

A 5 mL crimp vial was equipped with 46.3 mg of **1a** (0.25 mmol, 1.0 equiv.) and a magnetic stirring bar and was capped with a septum. Nitrogen atmosphere was introduced *via* three cycles of vacuum/nitrogen (2 min. at 7 mbar / 2 min. flush with nitrogen atmosphere). 39 µL of **2a** (0.275 mmol, 1.1 equiv.), 50 µL of a 7.5 mM stock solution of $[Ir(ppy)_2(dtbbpy)]PF_6$ (1.125 µmol, 0.15 mol %) in dry and degassed DMSO and 50 µL of a 10 mM stock solution of $[Ni(dtbbpy)]Br_2$ (3.75 µmol, 0.20 mol %) in dry and degassed DMSO were added *via* Hamilton syringes under nitrogen atmosphere. Then, 38 µL tetramethylguanidine (TMG) (0.275 mmol, 1.2 equiv.) was added *via* Hamilton syringe under nitrogen atmosphere. Finally, 1 mL of dry and degassed DMSO (0.25 M) was added *via* syringe under nitrogen atmosphere. The reaction mixture was stirred and irradiated, using a blue LED (455 nm) for 3 hours at 25 °C in a typical irradiation set-up used in our laboratories.

After 3 hours the reaction mixture was diluted in a 1:1 ratio with a stock solution of naphthalene in DMSO as internal standard and the reaction mixture was analyzed *via* calibrated gas chromatography.

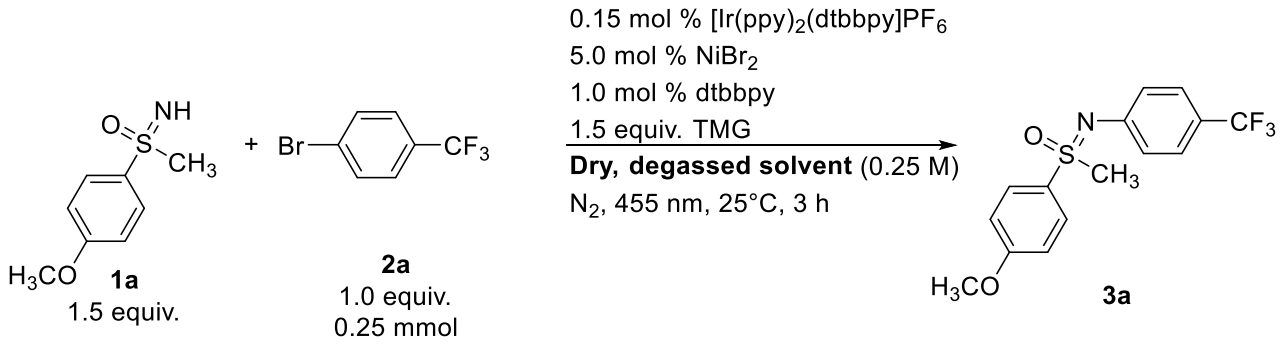
Table S 1. Screening of different photocatalysts.



Entry	[PC]	Yield[a]
1	1.0 mol % $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	17
2	0.15 mol % $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	33
3	1.0 mol % $[Ir(dFppy)_3]$	49
4	0.15 mol % $[Ir(dFppy)_3]$	29
5	1.0 mol % $[Ru(bpy)_3]Cl_2$	51

[a]Yields were determined by GC analysis with naphthalene as internal standard.

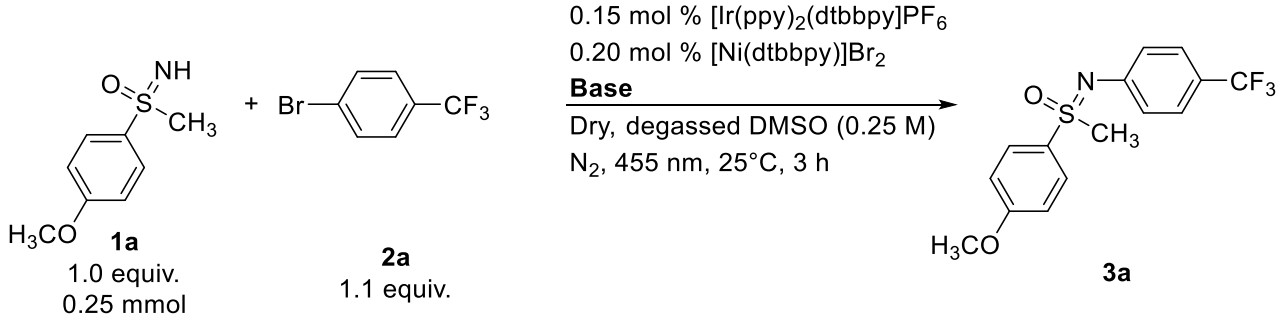
Table S 2. Screening of different solvents.



Entry	Solvent	Yield[a]
1	MeCN	99
2	DMF	99
3	DMAc	97
4	THF	99
5	DCM	4
6	DMSO (not dried)	91

[a]Yields were determined by GC analysis with naphthalene as internal standard.

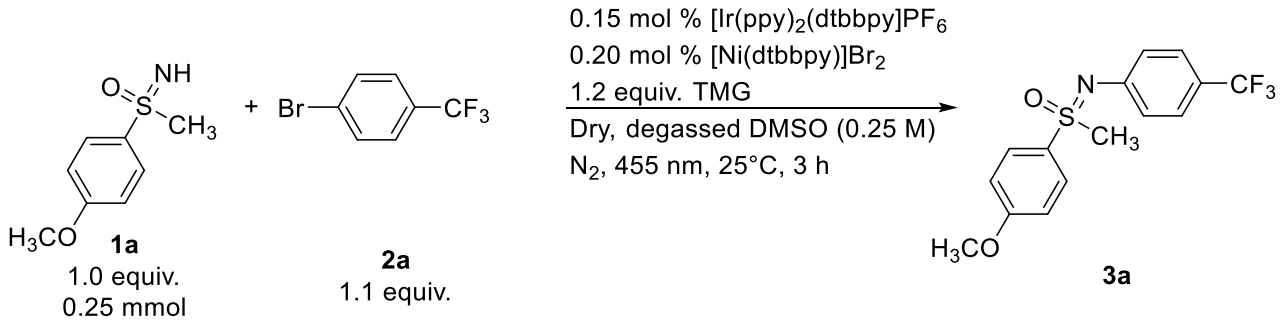
Table S 3. Screening of different bases.



Entry	Base	Yield[a]
1	1.5 equiv. DBU	0
2	1.5 equiv. Quinuclidine	80
3	1.5 equiv. DABCO	60
4	1.5 equiv. DIPEA	0
5	1.5 equiv. KOAc	27
6	1.5 equiv. Cs_2CO_3	0

[a]Yields were determined by GC analysis with naphthalene as internal standard.

Table S 4. Control Reactions.



Entry	Condition	Yield[a]
1	No $[Ir(ppy)_2(dtbbpy)]PF_6$	1
2	No $[Ir(ppy)_2(dtbbpy)]PF_6$, but irradiation at 390nm	46[b]
3	No $[Ni(dtbbpy)]Br_2$	0
4	No TMG	0
5	No Light, reaction in the dark	0
6	No degassing, O_2 atmosphere	14

[a]Yields were determined by GC analysis with naphthalene as internal standard. [b]Isolated yield after purification *via* automated flash-column chromatography.

3. Mechanistic proposal

This mechanistic proposal is based on reported literature for similar type of compounds.[2] A photosensitized reaction pathway is suggested, where the *N*-arylated sulfoximine is produced *via* the reductive elimination from an excited-state nickel species (**A3***). Although the photosensitization mechanism is underlined by the fact that the reaction can proceed in the absence of **[Ir]-Cat** *via* direct excitation with light of 390 nm (Table S 4, entry 2), photo-electron-transfer processes between **[Ir]-Cat** and any nickel species cannot be ruled out.

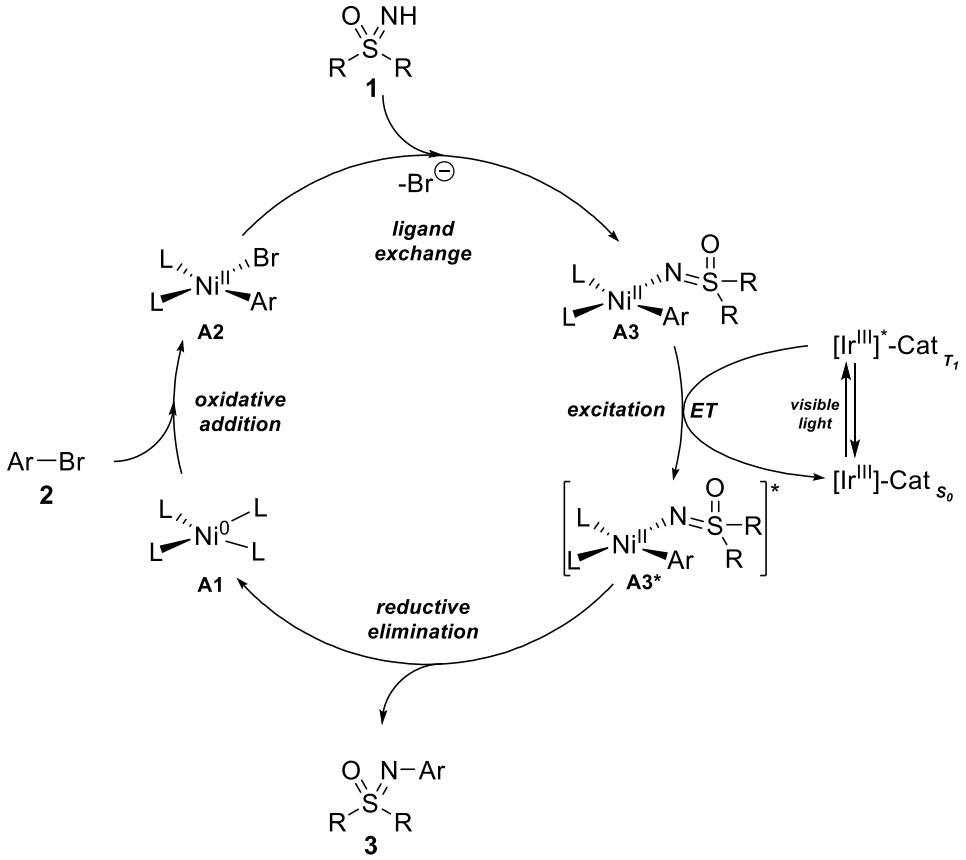


Figure S 3. Mechanistic proposal for the dual-catalytic *N*-arylation of *NH*-sulfoximines.

4. General procedures

4.1.Preparation of metal catalysts – $[Ir(ppy)_2(dtbbpy)]PF_6$ and $[Ni(dtbbpy)]Br_2$

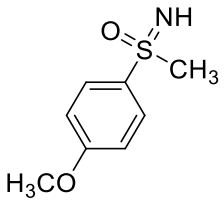
The used $[Ir(ppy)_2(dtbbpy)]PF_6$[3] (**[Ir]-Cat**) and $[Ni(dtbbpy)]Br_2$[4] (**[Ni-2]-Cat**) catalysts were prepared according to literature known procedures.

4.2.Preparation of *NH*-sulfoximines

NH-Sulfoximines **1ar** and ***S*-1at** were purchased from commercial suppliers and used without further purification.

Imino(4-methoxyphenyl)(methyl)-λ^6-sulfanone (1a)

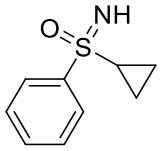
Compound was prepared according to reported literature procedure and ^{1}H-NMR data are matching with the literature known spectra.[5]



^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.05 – 7.79 (m, 2H), 7.06 – 6.86 (m, 2H), 3.82 (s, 3H), 3.03 (s, 1H), 2.75 (s, 3H).

Cyclopropyl(imino)(phenyl)-λ^6-sulfanone (1ai)

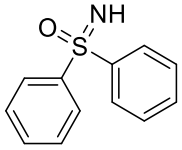
Compound was prepared according to reported literature procedure and ^{1}H-NMR data are matching with the literature known spectra.[6]



^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.99 – 7.87 (m, 2H), 7.63 – 7.43 (m, 3H), 2.69 (s, 1H), 2.50 (tt, *J* = 7.9, 4.8 Hz, 1H), 1.34 (ddt, *J* = 10.2, 7.0, 4.7 Hz, 1H), 1.24 – 1.07 (m, 1H), 1.01 (dddd, *J* = 9.0, 8.0, 6.8, 4.8 Hz, 1H), 0.87 (dddd, *J* = 9.0, 7.9, 6.9, 4.9 Hz, 1H).

Iminodiphenyl-λ^6-sulfanone (1aj)

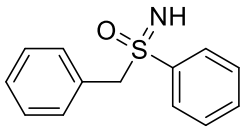
Compound was prepared from the respective sulfoxide according to reported literature procedure and ^{1}H-NMR data are matching with the literature known spectra.[7]



^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.10 – 8.01 (m, 4H), 7.56 – 7.45 (m, 6H), 3.11 (s, 1H).

Benzyl(imino)(phenyl)-λ^6-sulfanone (1ak)

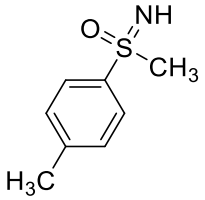
Compound was prepared according to reported literature procedure and ^{1}H-NMR data are matching with the literature known spectra.[8]



^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.80 – 7.73 (m, 2H), 7.62 – 7.53 (m, 1H), 7.50 – 7.40 (m, 2H), 7.34 – 7.23 (m, 3H), 7.14 – 7.07 (m, 2H), 4.36 (q, *J* = 13.4 Hz, 2H), 2.84 (s, 1H).

Imino(methyl)(*p*-tolyl)-λ^6-sulfanone (1al)

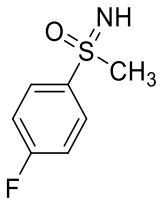
Compound was prepared according to reported literature procedure and ^{1}H-NMR data are matching with the literature known spectra.[5]



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 – 7.80 (m, 2H), 7.34 – 7.28 (m, 2H), 3.05 (s, 3H), 2.57 (s, 1H), 2.40 (s, 3H).

(4-Fluorophenyl)(imino)(methyl)-λ^6-sulfanone (1am)

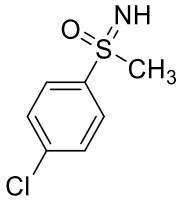
Compound was prepared according to reported literature procedure and ^{1}H-NMR data are matching with the literature known spectra.[8]



^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.07 – 7.95 (m, 2H), 7.25 – 7.15 (m, 2H), 3.09 (s, 3H), 2.77 (s, 1H).

(4-Chlorophenyl)(imino)(methyl)-λ^6-sulfanone (1an)

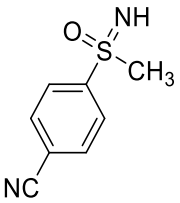
Compound was prepared according to reported literature procedure and ^{1}H-NMR data are matching with the literature known spectra.[8]



^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 – 7.87 (m, 2H), 7.57 – 7.48 (m, 2H), 3.11 (s, 3H), 2.59 (s, 1H).

4-(*S*-Methylsulfonimidoyl)benzonitrile (1ao)

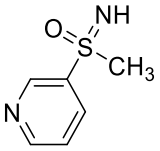
Compound was prepared according to reported literature procedure and ^{1}H-NMR data are matching with the literature known spectra.[5]



^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.14 – 8.08 (m, 2H), 7.86 – 7.81 (m, 2H), 3.10 (s, 3H), 2.83 (s, 1H).

Imino(methyl)(pyridin-3-yl)- λ^6-sulfanone (1ap)

Compound was prepared according to reported literature procedure for similar *NH*-sulfoximines.[8]



Yellowish oil, 140 mg, 24% yield.

Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 90% ethylacetate).

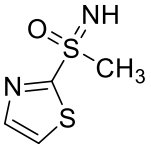
^{1}H NMR (300 MHz, D_6-DMSO) δ = 8.73 – 8.70 (m, 1H), 8.15 – 8.03 (m, 2H), 7.68 – 7.61 (m, 1H), 4.44 (s, 1H), 3.16 (s, 3H).

^{13}C NMR (75 MHz, D_6-DMSO) δ = 161.1 (C_q), 149.5 (+), 138.7 (+), 126.7 (+), 120.2 (+), 41.6 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_6H_8N_2OS$) calc.: 157.0430, found: 157.0433.

Imino(methyl)(thiazol-2-yl)- λ^6-sulfanone (1aq)

Compound was prepared according to reported literature procedure for similar *NH*-sulfoximines.[8]



Yellowish oil, 259 mg, 21% yield.

Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 60% ethylacetate).

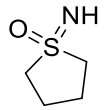
^{1}H NMR (400 MHz, D_6-DMSO) δ = 8.12 (d, *J* = 3.1 Hz, 1H), 8.06 (d, *J* = 3.1 Hz, 1H), 5.08 (s, 1H), 3.26 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (75 MHz, D_6-DMSO) δ = 170.8 (C_q), 144.4 (+), 127.1 (+), 44.3 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_4H_6N_2OS_2$) calc.: 162.9994, found: 162.9997.

1-Iminotetrahydro-1*H*-1λ^6-thiophene 1-oxide (1as)

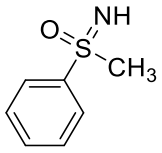
Compound was prepared according to reported literature procedure and ^{1}H-NMR data are matching with the literature known spectra.[8]



^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.03 – 2.96 (m, 5H), 2.11 (td, *J* = 6.8, 3.7 Hz, 4H).

Imino(methyl)(phenyl)-λ^6-sulfanone (1at)

Compound was prepared according to reported literature procedure.[6]

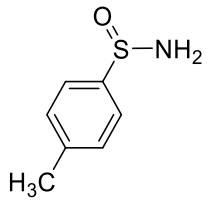


^{1}H NMR (300 MHz, D_6-DMSO) δ = 7.98 – 7.90 (m, 2H), 7.66 – 7.54 (m, 3H), 4.22 (s, 1H), 3.06 (s, 3H).

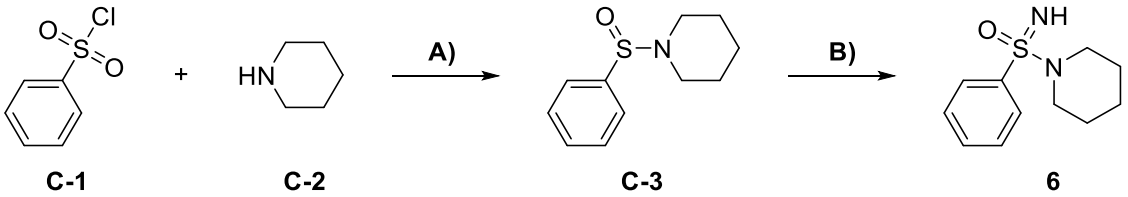
4.3.Preparation of other sulfoximidoyl derivatives

4-Methylbenzenesulfinamide (4)

p-Toluenesulfinamide was purchased from commercial suppliers and used without further purification.



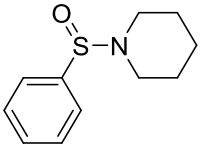
1-(*S*-Phenylsulfonimidoyl)piperidine (6)



Scheme S 1. A) Preparation of the sulfinamide C-3 from the respective sulfonyl chloride and piperidine. B) Preparation of the *NH*-sulfonimidamide 6.

1-(Phenylsulfinyl)piperidine (C-3)

The sulfinamide derivative **C-3** was prepared according to literature known procedure for similar sulfinamides (**A**)[9]) and ^{1}H-NMR data are matching with the literature known spectra.[10]



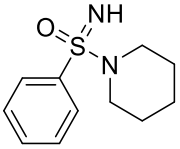
Procedure **A)**:

To a 0.3 M solution of phenyl sulfonyl chloride (1.45 mL, 11.3 mmol, 1.0 equiv.) and triethylamine (3.14 mL, 22.6 mmol, 2.0 equiv.) in anhydrous CH_2Cl_2 at 0 °C under nitrogen atmosphere, was added slowly a 0.3 M solution of piperidine (1.12 mL, 11.3 mmol, 1.0 equiv.) and triphenylphosphine (2.97 g, 11.3 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 *via* a dropping funnel. The reaction mixture was stirred for 18 hours, concentrated under reduced pressure and the crude mixture was purified by automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 30% ethylacetate), affording 655 mg of sulfinamide **C-3** (28%) as a light yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.69 – 7.59 (m, 2H), 7.54 – 7.44 (m, 3H), 3.17 – 3.04 (m, 2H), 2.94 (m, 2H), 1.72 – 1.44 (m, 6H).

1-(*S*-Phenylsulfonimidoyl)piperidine (6)

The sulfonimidamide **6** was prepared according to reported literature procedure (**B)**) and ^{1}H-NMR data are matching with the literature known spectra.[10]

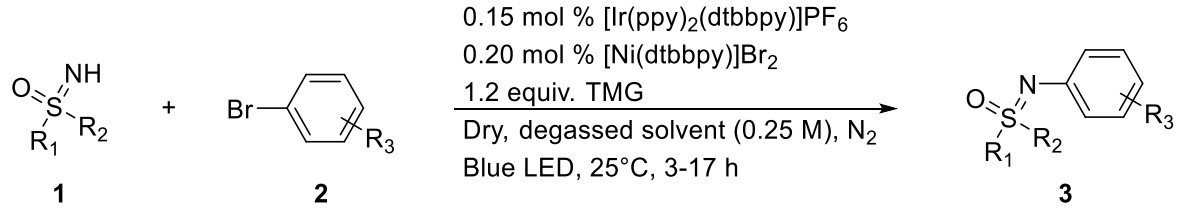


Yellow-orange solid, 264 mg, 38% yield.

Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 30% ethylacetate).

^{1}H NMR (400 MHz, D_6-DMSO) δ = 7.81 – 7.71 (m, 2H), 7.68 – 7.51 (m, 3H), 4.28 (s, 1H), 2.87 – 2.78 (m, 4H), 1.60 – 1.42 (m, 4H), 1.29 (m, 2H).

4.4.General procedure for the *N*-arylation of *NH*-sulfoximines with bromo arenes

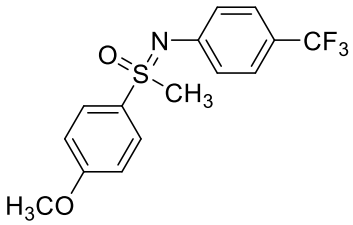


A 5 mL crimp vial was equipped with solid *NH*-sulfoximine (**1**) (0.25 mmol, 1.0 equiv.), solid bromo arene (**2)** (0.275 mmol, 1.1 equiv.) and a magnetic stirring bar and was capped with a septum. All liquid substrates were added *via* syringe after degassing. Nitrogen atmosphere was introduced *via* three cycles of vacuum/nitrogen (2 min. at 7 mbar / 2 min. flush with nitrogen atmosphere). 50 µL of a 7.5 mM stock solution of $[Ir(ppy)_2(dtbbpy)]PF_6$ (1.125 µmol, 0.15 mol %) in dry and degassed DMSO and 50 µL of a 10 mM stock solution of $[Ni(dtbbpy)]Br_2$ (3.75 µmol, 0.20 mol %) in dry and degassed DMSO were added *via* Hamilton syringes under nitrogen atmosphere. Then, 38 µL tetramethylguanidine (TMG) (0.275 mmol, 1.2 equiv.) was added *via* Hamilton syringe under nitrogen atmosphere. Finally, 1 mL of dry and degassed solvent (0.25 M) was added *via* syringe under nitrogen atmosphere. The reaction mixture was stirred and irradiated, using a blue LED (455 nm) for 3-17 hours at 25 °C in a typical irradiation set-up used in our laboratories. The progress of the reaction could be monitored by GC analysis, GC/MS analysis or TLC analysis.

When the reaction was over, the reaction mixture was diluted with brine (10 mL) and extracted three times with ethylacetate (3 x 10 mL). The combined organic layers were dried with Na_2SO_4, filtered and the solvent was removed under reduced pressure. Evaporation of volatiles led to the crude product. Purification was performed *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate/methanol), affording the corresponding *N*-arylated sulfoximine (**3**) as pure product.

The color, shape and yield of the product, the type of used solvent, any deviations from the general reaction procedure and detailed information about purification *via* column chromatography are given for every compound in the respective section.

(4-Methoxyphenyl)(methyl)((4-(trifluoromethyl)phenyl)imino)-λ^6-sulfanone (3a)



White oil, 72.5 mg, 88% yield.

Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 3.5 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 30% ethylacetate).

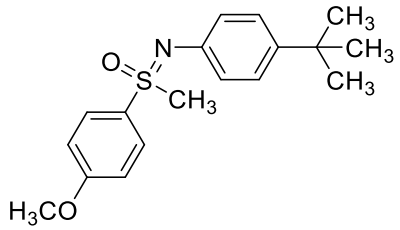
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 – 7.76 (m, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 7.01 – 6.92 (m, 2H), 3.81 (s, 3H), 3.23 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.8 (C_q), 149.1 (C_q), 130.7 (+), 129.7 (C_q), 126.2 (+, q, *J*=3.7), 124.7 (C_q, q, *J*=271.0), 123.0 (C_q, q, *J*=32.3), 122.8 (+), 115.0 (+), 55.6 (+), 46.7 (+).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.2 (s).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{15}H_{14}F_3NO_2S$) calc.: 330.0770, found: 330.0776.

((4-(*tert*-Butyl)phenyl)imino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (3b)



White oil, 78.6 mg, 99% yield.

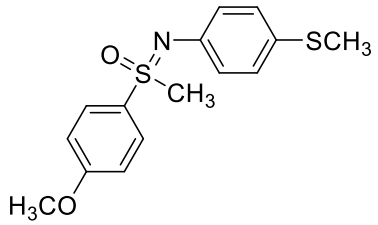
Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 25% ethylacetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93 – 7.88 (m, 2H), 7.17 – 7.10 (m, 2H), 7.01 – 6.96 (m, 2H), 6.95 – 6.89 (m, 2H), 3.85 (s, 3H), 3.20 (s, 3H), 1.23 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.5 (C_q), 144.3 (C_q), 142.1 (C_q), 130.9 (+), 125.9 (+), 122.8 (+), 114.9 (+), 55.8 (+), 46.5 (+), 34.2 (C_q), 31.5 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{18}H_{23}NO_2S$) calc.: 318.1522, found: 318.1527.

(4-Methoxyphenyl)(methyl)((4-(methylthio)phenyl)imino)-λ^6-sulfanone (3c)



White oil, 70.1 mg, 92% yield.

0.5 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 1.0 mol % $[Ni(dtbbpy)]Br_2$; Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (hexane/ethylacetate, 40% ethylacetate).

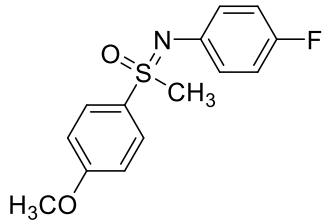
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 – 7.79 (m, 2H), 7.08 – 7.00 (m, 2H), 6.99 – 6.88 (m, 4H), 3.80 (s, 3H), 3.19 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.5 (C_q), 143.4 (C_q), 130.8 (+), 130.3 (C_q), 129.8 (C_q), 128.9 (+) 123.8 (+), 114.8 (+), 55.7 (+), 46.4 (+), 17.3 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{15}H_{17}NO_2S_2$) calc.: 308.0773, found: 308.0779.

((4-Fluorophenyl)imino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (3d)

^{1}H-NMR data are matching with the literature known spectra.[11]



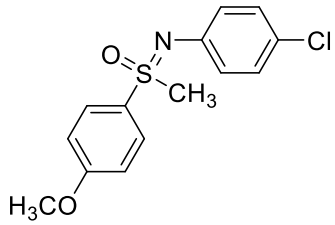
White oil, 69.1 mg, 99% yield.

0.5 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 1.0 mol % $[Ni(dtbbpy)]Br_2$; Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 30% ethylacetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 – 7.79 (m, 2H), 6.99 – 6.88 (m, 4H), 6.84 – 6.72 (m, 2H), 3.81 (s, 3H), 3.18 (s, 3H).

((4-Chlorophenyl)imino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (3e)

^{1}H-NMR data are matching with the literature known spectra.[11]

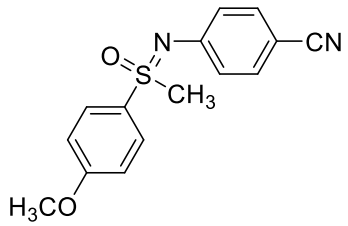


White oil, 66.6 mg, 90% yield.

0.2 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 1.0 mol % $[Ni(dtbbpy)]Br_2$; Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 35% ethylacetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87 – 7.78 (m, 2H), 7.08 – 6.99 (m, 2H), 6.99 – 6.86 (m, 4H), 3.81 (s, 3H), 3.19 (s, 3H).

4-(((4-Methoxyphenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)benzonitrile (3f)



White oil, 70.2 mg, 98% yield.

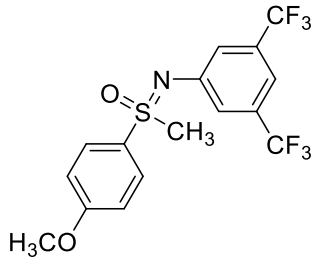
Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (hexane/ethylacetate, 50% ethylacetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 – 7.79 (m, 2H), 7.41 – 7.32 (m, 2H), 7.05 – 6.93 (m, 4H), 3.86 (s, 3H), 3.26 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.0 (C_q), 150.6 (C_q), 133.3 (+), 130.7 (+), 129.4 (C_q), 123.2 (+), 119.8 (C_q), 115.2 (+), 103.9 (C_q), 55.9 (+), 47.1 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{15}H_{14}N_2O_2S$) calc.: 287.0849, found: 287.0851.

((3,5-Bis(trifluoromethyl)phenyl)imino)(4-methoxyphenyl)(methyl)-λ⁶-sulfanone (3g)



White oil, 95.4 mg, 96% yield.

0.5 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 1.0 mol % $[Ni(dtbbpy)]Br_2$; Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 20% ethylacetate).

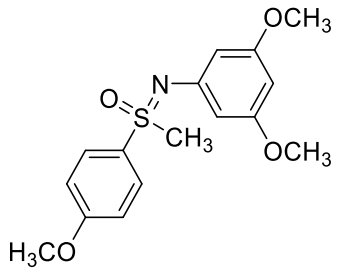
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.90 – 7.80 (m, 2H), 7.38 (s, 2H), 7.29 (s, 1H), 7.04 – 6.94 (m, 2H), 3.81 (s, 3H), 3.26 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 164.0 (C_q), 147.4 (C_q), 132.0 (C_q, q, *J* = 32.8 Hz), 130.7 (+), 129.0 (C_q), 123.5 (C_q, q, *J* = 272.7 Hz), 122.8 (+, d, *J* = 4.0 Hz), 115.1 (+), 114.5 (+, sept., *J* = 4.1 Hz), 55.7 (+), 46.6 (+).

^{19}F NMR (377 MHz, $CDCl_3$) δ = -63.6.

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{16}H_{13}F_6NO_2S$) calc.: 398.0644, found: 398.0652.

((3,5-Dimethoxyphenyl)imino)(4-methoxyphenyl)(methyl)-λ⁶-sulfanone (3h)



White oil, 62.7 mg, 78% yield.

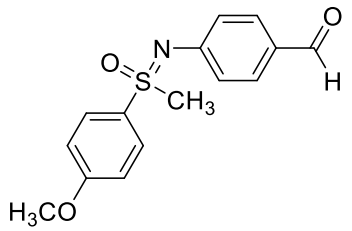
Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 40% ethylacetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 – 7.81 (m, 2H), 6.97 – 6.89 (m, 2H), 6.22 – 6.18 (m, 2H), 6.02 – 5.99 (m, 1H), 3.80 (s, 3H), 3.65 (s, 6H), 3.18 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.5 (C_q), 161.0 (C_q), 147.2 (C_q), 130.7 (+), 130.4 (C_q), 114.8 (+), 101.6 (+), 94.5 (+), 55.7 (+), 55.2 (+), 46.4 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{16}H_{19}NO_4S$) calc.: 322.1108, found: 322.1110.

4-(((4-Methoxyphenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)amino)benzaldehyde (3i)



White oil, 42.6 mg, 59% yield.

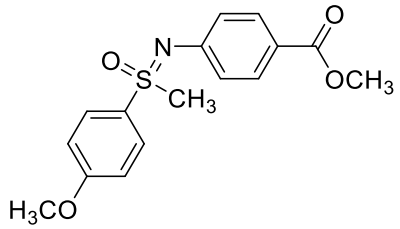
Solvent: 1 mL dry and degassed dimethylacetamide (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (hexane/ethylacetate, 30% ethylacetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.76 (s, 1H), 7.89 – 7.79 (m, 2H), 7.67 – 7.55 (m, 2H), 7.09 – 7.00 (m, 2H), 7.02 – 6.93 (m, 2H), 3.83 (s, 3H), 3.26 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 191.1 (+), 163.9 (C_q), 152.5 (C_q), 131.3 (+), 130.7 (+), 130.0 (C_q), 129.6 (C_q), 122.9 (+), 115.1 (+), 55.8 (+), 47.0 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{15}H_{15}NO_3S$) calc.: 290.0845, found: 290.0853.

Methyl 4-(((4-methoxyphenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)benzoate (3j)



White solid, 79.0 mg, 99% yield.

Melting point: 95 °C

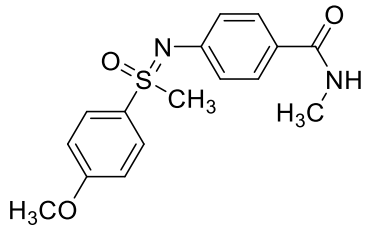
Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 30% ethylacetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85 – 7.79 (m, 2H), 7.78 – 7.72 (m, 2H), 7.00 – 6.89 (m, 4H), 3.78 (s, 3H), 3.78 (s, 3H), 3.22 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.10 (C_q), 163.66 (C_q), 150.61 (C_q), 130.78 (+), 130.64 (+), 129.66 (C_q), 122.67 (C_q), 122.42 (+), 114.93 (+), 55.68 (+), 51.70 (+), 46.75 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{16}H_{17}NO_4S$) calc.: 320.0951, found: 320.0952.

4-(((4-Methoxyphenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)-N-methylbenzamide (3k)



White viscous oil, 75.6 mg, 95% yield.

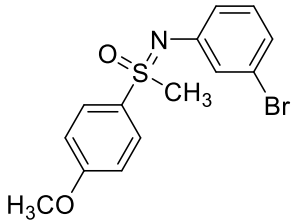
Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (hexane/ethylacetate, 80% ethylacetate).

^{1}H NMR (400 MHz, D_6-DMSO) δ = 8.10 (q, *J* = 4.5 Hz, 1H), 7.88 – 7.80 (m, 2H), 7.60 – 7.51 (m, 2H), 7.19 – 7.05 (m, 2H), 6.90 – 6.75 (m, 2H), 3.82 (s, 3H), 3.38 (s, 3H), 2.70 (d, *J* = 4.5 Hz, 3H).

^{13}C NMR (101 MHz, D_6-DMSO) δ = 166.4 (C_q), 163.0 (C_q), 148.9 (C_q), 130.5 (+), 129.8 (C_q), 128.0 (+), 126.6 (C_q), 121.7 (+), 114.8 (+), 55.7 (+), 45.7 (+), 26.1 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{16}H_{18}N_2O_3S$) calc.: 319.1111, found: 319.1110.

((3-Bromophenyl)imino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (3l)



White oil, 53.9 mg, 66% yield with respect to 1,3-dibromobenzene as limiting reagent.

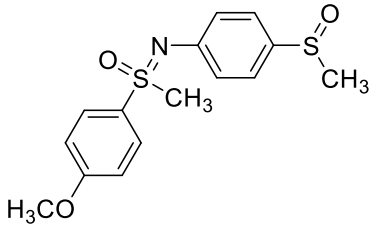
92.6 mg of the *NH*-sulfoximine (0.5 mmol, 2.1 equiv.) was reacted with 30.0 µL of 1,3-dibromobenzene (58.4 mg, 0.24 mmol, 1 equiv.); 0.5 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 2.0 mol % $[Ni(dtbbpy)]Br_2$; Solvent: 2 mL dry and degassed acetonitrile (0.12 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (hexane/ethylacetate, 30% ethylacetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 – 7.78 (m, 2H), 7.20 – 7.13 (m, 1H), 7.01 – 6.85 (m, 5H), 3.82 (s, 3H), 3.20 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.6 (C_q), 147.0 (C_q), 130.7 (+), 130.1 (+), 129.9 (C_q), 126.2 (+), 124.4 (+), 122.5 (C_q), 121.7 (+), 114.9 (+), 55.7 (+), 46.6 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{14}H_{14}BrNO_2S$) calc.: 340.0001, found: 340.0002.

(4-Methoxyphenyl)(methyl)((4-(methylsulfinyl)phenyl)imino)-λ^6-sulfanone (3m)



Yellow oil, 72.0 mg, 89% yield, diastereomeric ration of 1:1.

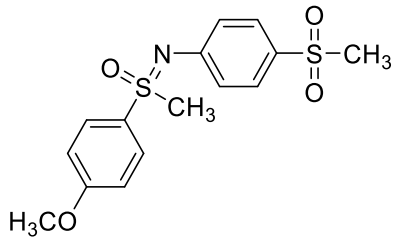
Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (ethylacetate/methanol, 5% methanol).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.90 – 7.82 (m, 2H), 7.43 – 7.37 (m, 2H), 7.16 – 7.08 (m, 2H), 7.03 – 6.94 (m, 2H), 3.85 (s, 3H), 3.30 (d, *J* = 1.9 Hz, 3H), 2.65 (d, *J* = 1.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.0 (C_q, d, *J* = 2.1 Hz), 148.3 (C_q, d, *J* = 3.9 Hz), 137.3 (C_q), 130.9 (+), 129.3 (C_q, d, *J* = 10.0 Hz), 125.1 (+), 123.7 (+, d, *J* = 7.8 Hz), 115.2 (+, d, *J* = 1.7 Hz), 55.9 (+), 46.7 (+), 43.8 (+, d, *J* = 5.4 Hz).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{15}H_{17}NO_3S_2$) calc.: 324.0723, found: 324.0726.

(4-Methoxyphenyl)(methyl)((4-(methylsulfonyl)phenyl)imino)-λ^6-sulfanone (3n)



Yellow oil, 84.0 mg, 99% yield.

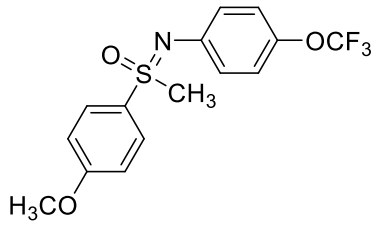
Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 70% ethylacetate).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.87 – 7.80 (m, 2H), 7.67 – 7.59 (m, 2H), 7.09 – 7.02 (m, 2H), 7.03 – 6.95 (m, 2H), 3.85 (s, 3H), 3.27 (s, 3H), 2.96 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 164.0 (C_q), 151.4 (C_q), 132.2 (C_q), 130.7 (+), 129.2 (C_q), 128.7 (+), 123.0 (+), 115.2 (+), 55.9 (+), 47.0 (+), 44.8 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{15}H_{17}NO_4S_2$) calc.: 340.0672, found: 340.0676.

(4-Methoxyphenyl)(methyl)((4-(trifluoromethoxy)phenyl)imino)-λ^6-sulfanone (3o)



Yellow oil, 84.6 mg, 98% yield.

Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (hexane/ethylacetate, 25% ethylacetate).

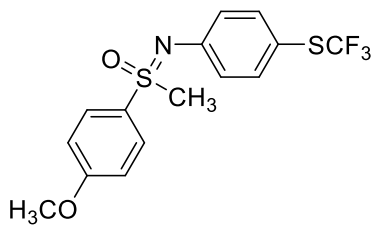
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 – 7.80 (m, 2H), 7.02 – 6.89 (m, 6H), 3.83 (s, 3H), 3.21 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.6 (C_q), 144.1 (C_q), 143.6 (C_q, q, J = 1.9 Hz), 130.7 (+), 130.0 (C_q), 123.9 (+), 121.7 (+), 120.5 (C_q, q, J = 255.9 Hz), 114.9 (+), 55.6 (+), 46.5 (+).

^{19}F NMR (377 MHz, $CDCl_3$) δ = -58.7.

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{15}H_{14}NO_3S$) calc.: 346.0719, found: 346.0722.

(4-Methoxyphenyl)(methyl)((4-((trifluoromethyl)thio)phenyl)imino)-λ^6-sulfanone (3p)



Yellow oil, 75.9 mg, 84% yield.

Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (hexane/ethylacetate, 35% ethylacetate).

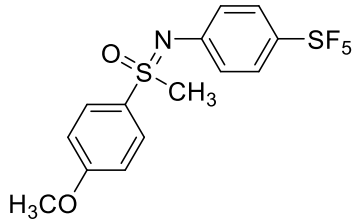
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 – 7.79 (m, 2H), 7.41 – 7.31 (m, 2H), 7.03 – 6.91 (m, 4H), 3.84 (s, 3H), 3.23 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.8 (C_q), 148.7 (C_q), 137.7 (C_q), 130.7 (+), 129.9 (C_q), 129.8 (C_q, q, J = 308.2 Hz), 123.8 (+), 115.2 (C_q, q, J = 1.8 Hz), 115.1 (+), 55.8 (+), 46.9 (+).

^{19}F NMR (282 MHz, $CDCl_3$) δ = -44.2.

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{15}H_{14}F_3NO_2S_2$) calc.: 362.0491, found: 362.0494.

(4-Methoxyphenyl)(methyl)((4-(pentafluoro-λ^6-sulfaneyl)phenyl)imino)-λ^6-sulfanone (3q)



Colorless oil, 29.1 mg, 30% yield.

0.5 mol % [Ni(dtbbpy)]Br_2; Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (hexane/ethylacetate, 15% ethylacetate).

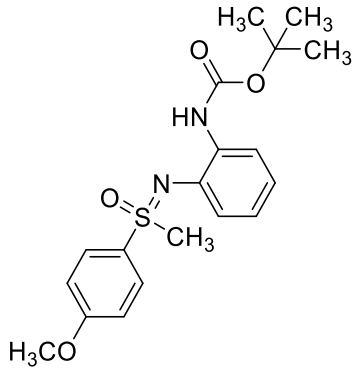
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 – 7.81 (m, 2H), 7.51 – 7.42 (m, 2H), 7.05 – 6.93 (m, 4H), 3.87 (s, 3H), 3.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.9 (C_q), 148.9 (C_q), 147.1 (C_q), 130.8 (+), 129.7 (C_q), 126.9 (+, p, J = 4.4 Hz), 122.3 (+), 115.2 (+), 55.9 (+), 47.0 (+).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -90.5.

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{14}H_{14}F_5NO_2S_2$) calc.: 388.0459, found: 388.0466.

***tert*-Butyl-(2-(((4-methoxyphenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)phenyl)carbamate (3r)**



White oil, 92.2 mg, 98% yield.

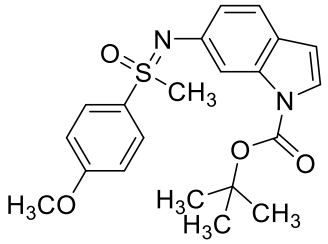
0.5 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 1.0 mol % $[Ni(dtbbpy)]Br_2$; Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (hexane/ethylacetate, 25% ethylacetate).

^{1}H NMR (400 MHz, D_6-DMSO) δ = 8.00 (s, 1H), 7.91 – 7.80 (m, 3H), 7.18 – 7.07 (m, 2H), 6.80 – 6.69 (m, 2H), 6.63 (td, *J* = 7.6, 1.6 Hz, 1H), 3.81 (s, 3H), 3.47 (s, 3H), 1.51 (s, 9H).

^{13}C NMR (101 MHz, D_6-DMSO) δ = 163.0 (C_q), 152.4 (C_q), 134.4 (C_q), 131.7 (C_q), 130.5 (+), 129.4 (C_q), 122.0 (+), 120.7 (+), 119.9 (+), 117.9 (+), 114.8 (+), 79.4 (C_q), 55.7 (+), 45.7 (+), 28.1 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{19}H_{24}N_2O_4S$) calc.: 377.1530, found: 377.1534.

***tert*-Butyl-6-(((4-methoxyphenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)-1H-indole-1-carboxylate (3s)**



Yellowish viscous oil, 85.1 mg, 85% yield.

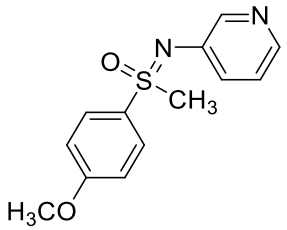
0.5 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 5.0 mol % $[Ni(dtbbpy)]Br_2$; Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 30% ethylacetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 – 7.87 (m, 2H), 7.84 (s, 1H), 7.44 (d, *J* = 3.6 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.01 – 6.90 (m, 3H), 6.41 (d, *J* = 3.6 Hz, 1H), 3.81 (s, 3H), 3.22 (s, 3H), 1.65 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.4 (C_q), 150.0 (C_q), 142.4 (C_q), 136.0 (C_q), 131.0 (+), 130.7 (C_q), 125.5 (C_q), 124.8 (+), 121.0 (+), 119.8 (+), 114.7 (+), 110.0 (+), 107.2 (+), 83.5 (C_q), 55.7 (+), 46.3 (+), 28.4 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{21}H_{24}N_2O_4S$) calc.: 401.1530, found: 401.1538.

(4-Methoxyphenyl)(methyl)(pyridin-3-ylimino)-λ^6-sulfanone (3t)



Dark oil, 64.9 mg, 99% yield.

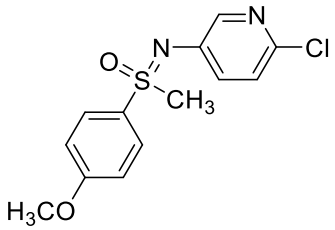
1.0 mol % $[Ni(dtbbpy)]Br_2$; Solvent: 1 mL dry and degassed dimethylacetamide (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 90 % ethylacetate).

^{1}H NMR (400 MHz, D_6-DMSO) δ = 8.11 (d, *J* = 2.6 Hz, 1H), 7.98 (dd, *J* = 4.6, 1.6 Hz, 1H), 7.89 – 7.82 (m, 2H), 7.18 – 7.11 (m, 3H), 7.08 (dd, *J* = 8.2, 4.6 Hz, 1H), 3.82 (s, 3H), 3.41 (s, 3H).

^{13}C NMR (101 MHz, D_6-DMSO) δ = 163.0 (C_q), 144.2 (+), 142.5 (C_q), 141.5 (+), 130.5 (+), 129.5 (C_q), 128.5 (+), 123.6 (+), 114.9 (+), 55.8 (+), 45.5 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{13}H_{14}N_2O_2S$) calc.: 263.0849, found: 263.0849.

((6-Chloropyridin-3-yl)imino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (3u)



White oil, 66.0 mg, 89% yield.

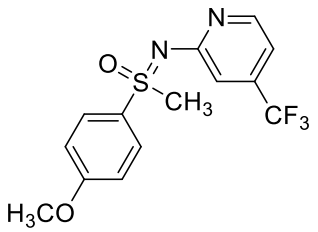
0.5 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 1.0 mol % $[Ni(dtbbpy)]Br_2$; Solvent: 1 mL dry and degassed dimethylacetamide (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 45% ethylacetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (d, *J* = 2.5 Hz, 1H), 7.85 – 7.76 (m, 2H), 7.22 (dd, *J* = 8.5, 2.9 Hz, 1H), 7.03 – 6.93 (m, 3H), 3.84 (s, 3H), 3.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.3 (C_q), 144.4 (+), 143.2 (C_q), 141.4 (C_q), 132.5 (+), 130.8 (+), 129.1 (C_q), 124.0 (+), 115.2 (+), 55.8 (+), 46.7 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{13}H_{13}ClN_2O_2S$) calc.: 297.0459, found: 297.0463.

(4-Methoxyphenyl)(methyl)((4-(trifluoromethyl)pyridin-2-yl)imino)-λ^6-sulfanone (3v)



White oil, 81.8 mg, 99% yield.

0.5 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 1.0 mol % $[Ni(dtbbpy)]Br_2$; Solvent: 1 mL dry and degassed dimethylacetamide (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 30% ethylacetate).

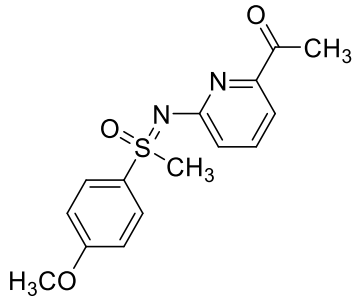
^{1}H NMR (400 MHz, D_6-DMSO) δ = 8.20 (d, *J* = 5.2 Hz, 1H), 7.93 – 7.87 (m, 2H), 7.17 – 7.12 (m, 2H), 7.04 (d, *J* = 5.3 Hz, 1H), 7.01 (s, 1H), 3.84 (s, 3H), 3.46 (s, 3H).

^{13}C NMR (101 MHz, D_6-DMSO) δ = 162.9 (C_q), 160.1 (C_q), 149.2 (+), 138.3 (C_q, q, *J* = 32.8 Hz), 130.7 (C_q), 129.7 (+), 123.0 (C_q, q, *J* = 273.1 Hz), 114.7 (+), 111.7 (+, q, *J* = 3.8 Hz), 110.4 (+, q, *J* = 3.0 Hz), 55.8 (+), 44.9 (+).

^{19}F NMR (376 MHz, D_6-DMSO) δ = -63.3.

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{14}H_{13}F_3N_2O_2S$) calc.: 331.0723, found: 331.0724.

((6-Acetylpyridin-2-yl)imino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (3w)



White viscous oil, 28.2 mg, 37% yield.

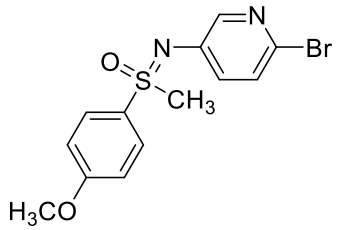
1.0 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 5.0 mol % $[Ni(dtbbpy)]Br_2$; Solvent: 1 mL dry and degassed dimethylacetamide (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 60% ethylacetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 – 7.86 (m, 2H), 7.61 – 7.54 (m, 1H), 7.44 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.04 – 6.96 (m, 3H), 3.86 (s, 3H), 3.32 (s, 3H), 2.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.6 (C_q), 163.3 (C_q), 158.3 (C_q), 151.4 (C_q), 138.4 (+), 131.2 (C_q), 129.9 (+), 120.7 (+), 114.8 (+), 114.0 (+), 55.8 (+), 46.3 (+), 26.0 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{15}H_{16}N_2O_3S$) calc.: 305.0954, found: 305.0958.

((6-Bromopyridin-3-yl)imino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (3x)



White solid, 65.7 mg, 77% yield.

Melting point: 147 °C.

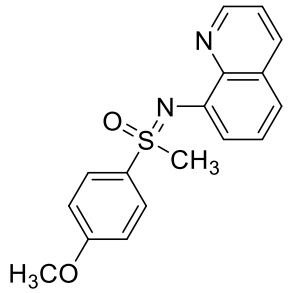
0.5 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 5.0 mol % $[Ni(dtbbpy)]Br_2$; Solvent: 1 mL dry and degassed dimethylacetamide (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (hexane/ethylacetate, 30% ethylacetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.12 (d, *J* = 2.4 Hz, 1H), 7.95 – 7.86 (m, 2H), 7.53 (dd, *J* = 8.7, 2.6 Hz, 1H), 7.04 – 6.95 (m, 2H), 6.75 (d, *J* = 8.7 Hz, 1H), 3.87 (s, 3H), 3.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.6 (C_q), 158.0 (C_q), 148.7 (+), 140.2 (+), 130.9 (C_q), 130.1 (+), 118.4 (+), 114.9 (+), 111.7 (C_q), 55.8 (+), 46.1 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{13}H_{13}BrN_2O_2S$) calc.: 340.9954, found: 340.9959.

(4-Methoxyphenyl)(methyl)(quinolin-8-ylimino)-λ^6-sulfanone (3y)



Orange solid, 21.1 mg, 27% yield.

Melting point: 121 °C.

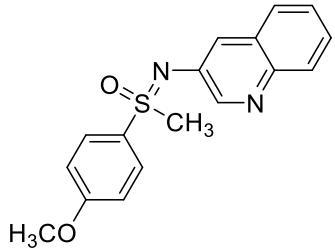
1.0 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 5.0 mol % $[Ni(dtbbpy)]Br_2$; Solvent: 1 mL dry and degassed dimethylacetamide (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 70% ethylacetate).

^{1}H NMR (400 MHz, D_6-DMSO) δ = 8.87 – 8.82 (m, 2H), 7.90 – 7.84 (m, 2H), 7.49 (dd, *J* = 8.1, 4.5 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.38 (dd, *J* = 8.5, 7.4 Hz, 1H), 7.12 – 7.06 (m, 2H), 6.94 (dd, *J* = 7.4, 1.2 Hz, 1H), 3.79 (s, 3H), 3.52 (s, 3H).

^{13}C NMR (101 MHz, D_6-DMSO) δ = 163.0 (C_q), 150.2 (+), 148.8 (C_q), 142.8 (C_q), 132.4 (+), 130.3 (+), 129.7 (C_q), 129.4 (+), 124.6 (C_q), 121.2 (+), 120.3 (+), 115.3 (+), 114.8 (+), 55.7 (+), 45.6 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{17}H_{16}N_2O_2S$) calc.: 313.1005, found: 313.1005.

(4-Methoxyphenyl)(methyl)(quinolin-3-ylimino)-λ^6-sulfanone (3z)



Orange oil, 75.8 mg, 97% yield.

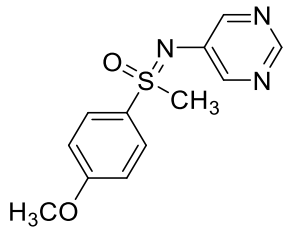
1.0 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 5.0 mol % $[Ni(dtbbpy)]Br_2$; Solvent: 1 mL dry and degassed dimethylacetamide (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (hexane/ethylacetate, 70% ethylacetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.69 (d, *J* = 2.6 Hz, 1H), 7.94 – 7.82 (m, 3H), 7.57 (d, *J* = 2.5 Hz, 1H), 7.53 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.45 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.36 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 6.97 – 6.89 (m, 2H), 3.78 (s, 3H), 3.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.8 (C_q), 149.8 (+), 143.9 (C_q), 139.5 (C_q), 130.9 (+), 129.3 (C_q), 129.0 (C_q), 128.8 (+), 126.8 (+), 126.8 (+), 126.6 (+), 124.2 (+), 115.1 (+), 55.7 (+), 46.7 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{17}H_{16}N_2O_2S$) calc.: 313.1005, found: 313.1009.

(4-Methoxyphenyl)(methyl)(pyrimidin-5-ylimino)-λ^6-sulfanone (3aa)



Yellowish oil, 65.2 mg, 99% yield.

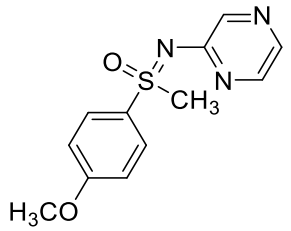
1.0 mol % [Ni(dtbbpy)]Br_2; Solvent: 1 mL dry and degassed dimethylacetamide (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petroleth-er/ethylacetate, 80% ethylacetate).

^{1}H NMR (400 MHz, D_6-DMSO) δ = 8.60 (s, 1H), 8.25 (s, 2H), 7.92 – 7.86 (m, 2H), 7.21 – 7.11 (m, 2H), 3.83 (s, 3H), 3.50 (s, 3H).

^{13}C NMR (101 MHz, D_6-DMSO) δ = 163.3 (C_q), 150.6 (+), 149.5 (+), 141.2 (C_q), 130.5 (+), 128.7 (C_q), 115.1 (+), 55.8 (+), 45.3 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{12}H_{13}N_3O_2S$) calc.: 264.0801, found: 264.0805.

(4-Methoxyphenyl)(methyl)(pyrazin-2-ylimino)-λ^6-sulfanone (3ab)



Yellowish oil, 25.0 mg, 38% yield.

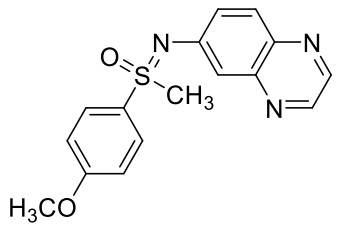
0.5 mol % [Ni(dtbbpy)]Br_2; Solvent: 1 mL dry and degassed dimethylacetamide (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petroleth-er/ethylacetate, 40% ethylacetate).

^{1}H NMR (400 MHz, D_6-DMSO) δ = 8.13 (d, *J* = 1.0 Hz, 1H), 7.97 – 7.94 (m, 2H), 7.92 – 7.87 (m, 2H), 7.19 – 7.10 (m, 2H), 3.84 (s, 3H), 3.48 (s, 3H).

^{13}C NMR (101 MHz, D_6-DMSO) δ = 162.9 (C_q), 155.7 (C_q), 141.4 (+), 139.5 (+), 135.4 (+), 130.4 (C_q), 129.7 (+), 114.7 (+), 55.8 (+), 44.9 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{12}H_{13}N_3O_2S$) calc.: 264.0801, found: 264.0802.

(4-Methoxyphenyl)(methyl)(quinoxalin-6-ylimino)-λ^6-sulfanone (3ac)



Yellowish oil, 19.6 mg, 25% yield.

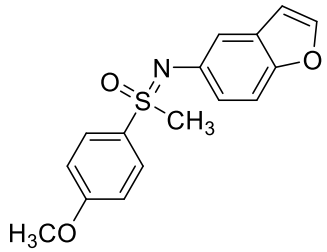
1.0 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 5.0 mol % $[Ni(dtbbpy)]Br_2$; Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 60% ethylacetate).

^{1}H NMR (400 MHz, D_6-DMSO) δ = 8.67 (dd, *J* = 25.4, 1.9 Hz, 2H), 7.95 – 7.88 (m, 2H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.44 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.27 (d, *J* = 2.4 Hz, 1H), 7.17 – 7.09 (m, 2H), 3.80 (s, 3H), 3.49 (s, 3H).

^{13}C NMR (101 MHz, D_6-DMSO) δ = 163.1 (C_q), 148.1 (C_q), 145.3 (+), 143.4 (C_q), 142.5 (+), 138.3 (C_q), 130.5 (+), 129.5 (+), 129.2 (C_q), 129.0 (+), 116.5 (+), 115.0 (+), 55.7 (+), 45.7 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{16}H_{15}N_3O_2S$) calc.: 314.0958, found: 314.0960.

(Benzofuran-5-ylimino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (3ae)



Orange oil, 73.1 mg, 97% yield.

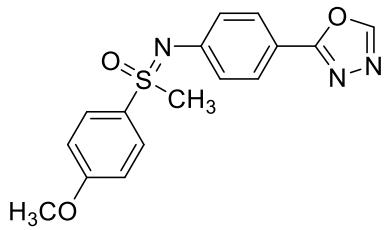
0.5 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 3.0 mol % $[Ni(dtbbpy)]Br_2$; Solvent: 1 mL dry and degassed dimethylacetamide (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (hexane/ethylacetate, 30% ethylacetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 – 7.85 (m, 2H), 7.48 (d, *J* = 2.2 Hz, 1H), 7.26 (d, *J* = 8.7 Hz, 1H), 7.23 (d, *J* = 2.1 Hz, 1H), 7.01 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.99 – 6.91 (m, 2H), 6.58 (dd, *J* = 2.1, 0.9 Hz, 1H), 3.81 (s, 3H), 3.22 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.4 (C_q), 151.1 (C_q), 145.2 (+), 140.5 (C_q), 131.0 (+), 130.6 (C_q), 128.0 (C_q), 121.3 (+), 114.8 (+), 111.5 (+), 106.7 (+), 55.7 (+), 46.3 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{16}H_{15}NO_3S$) calc.: 302.0845, found: 302.0848.

((4-(1,3,4-Oxadiazol-2-yl)phenyl)imino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (3af)



White solid, 81.5 mg, 99% yield.

Melting point: 133 °C

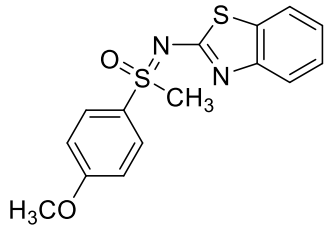
0.5 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 2.0 mol % $[Ni(dtbbpy)]Br_2$; Solvent: 1 mL dry and degassed dimethylacetamide (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 60% ethylacetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.34 (s, 1H), 7.88 – 7.82 (m, 2H), 7.81 – 7.76 (m, 2H), 7.10 – 7.04 (m, 2H), 6.99 – 6.94 (m, 2H), 3.82 (s, 3H), 3.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.0 (C_q), 163.8 (C_q), 152.1 (+), 149.8 (C_q), 130.7 (+), 129.7 (C_q), 128.2 (+), 123.3 (+), 116.1 (C_q), 115.0 (+), 55.8 (+), 46.9 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{16}H_{15}N_3O_3S$) calc.: 330.0907, found: 330.0908.

(Benzo[*d*]thiazol-2-ylimino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (3ag)



Yellowish oil, 35.0 mg, 44% yield.

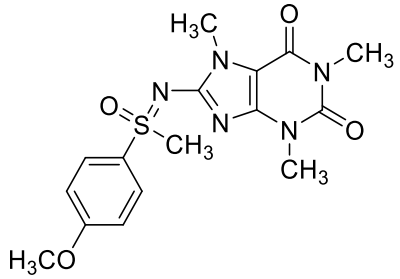
2.0 mol % $[Ni(dtbbpy)]Br_2$; Solvent: 1 mL dry and degassed dimethylacetamide (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 40% ethylacetate).

^{1}H NMR (300 MHz, D_6-DMSO) δ = 7.74 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.47 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.26 (ddd, *J* = 8.2, 7.3, 1.3 Hz, 1H), 7.25 – 7.13 (m, 2H), 7.14 (ddd, *J* = 8.2, 7.4, 1.2 Hz, 1H), 3.85 (s, 3H), 3.63 (s, 3H).

^{13}C NMR (75 MHz, D_6-DMSO) δ = 166.4 (C_q), 163.4 (C_q), 151.5 (C_q), 132.5 (C_q), 130.1 (+), 129.0 (C_q), 125.6 (+), 122.6 (+), 121.2 (+), 119.8 (+), 114.9 (+), 55.9 (+), 44.4 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{15}H_{14}N_2O_2S_2$) calc.: 319.0569, found: 319.0574.

8-(((4-Methoxyphenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)-1,3,7-trimethyl-3,7-dihydro-1*H*-purine-2,6-dione (3ah)



White solid, 27.4 mg, 29% yield.

Melting point: 235 °C

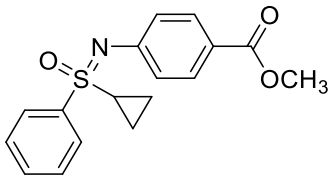
0.15 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 2.0 mol % $[Ni(dtbbpy)]Br_2$; Solvent: 6 mL dry and degassed dimethylacetamide (0.04 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 60% ethylacetate) and subsequent recrystallization in ethanol.

^{1}H NMR (400 MHz, D_6-acetone) δ = 8.09 – 8.02 (m, 2H), 7.23 – 7.17 (m, 2H), 3.94 (s, 3H), 3.71 (s, 3H), 3.65 (s, 3H), 3.33 (s, 3H), 3.24 (s, 3H).

^{13}C NMR (101 MHz, D_6-DMSO) δ = 163.3 (C_q), 153.5 (C_q), 151.3 (C_q), 150.9 (C_q), 147.0 (C_q), 129.9 (+), 129.8 (C_q), 114.7 (+), 102.7 (C_q), 55.9 (+), 43.9 (+), 30.2 (+), 29.3 (+), 27.3 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{16}H_{19}N_5O_4S$) calc.: 378.1231, found: 378.1236.

Methyl 4-((cyclopropyl(oxo)(phenyl)-λ^6-sulfaneylidene)amino)benzoate (3ai)



White solid, 77.3 mg, 98% yield.

Melting point: 158 °C

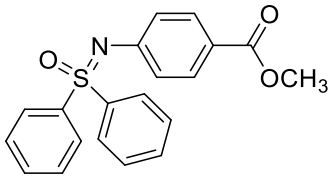
Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (hexane/ethylacetate, 25% ethylacetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 – 7.84 (m, 2H), 7.79 – 7.73 (m, 2H), 7.59 – 7.53 (m, 1H), 7.52 – 7.45 (m, 2H), 7.03 – 6.97 (m, 2H), 3.80 (s, 3H), 2.73 – 2.63 (m, 1H), 1.62 – 1.54 (m, 1H), 1.30 – 1.21 (m, 1H), 1.21 – 1.13 (m, 1H), 1.00 – 0.88 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.2 (C_q), 150.4 (C_q), 139.2 (C_q), 133.3 (+), 130.8 (+), 129.6 (+), 128.7 (+), 122.8 (+), 122.7 (C_q), 51.7 (+), 34.6 (+), 6.8 (-), 5.3 (-).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{17}H_{17}NO_3S$) calc.: 316.1002, found: 316.1002.

Methyl 4-((oxodiphenyl-λ^6-sulfaneylidene)amino)benzoate (3aj)



White solid, 85.2 mg, 97% yield.

Melting point: 158 °C

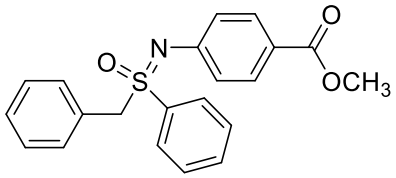
Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (hexane/ethylacetate, 15% ethylacetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ = δ 8.06 – 8.01 (m, 4H), 7.85 – 7.80 (m, 2H), 7.55 – 7.43 (m, 6H), 7.18 – 7.12 (m, 2H), 3.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.2 (C_q), 150.0 (C_q), 140.5 (C_q), 133.1 (+), 130.9 (+), 129.5 (+), 128.5 (+), 123.2 (+), 123.2 (C_q) 51.8 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{20}H_{17}NO_3S$) calc.: 352.1002, found: 352.1009.

Methyl 4-((benzyl(oxo)(phenyl)-λ^6-sulfaneylidene)amino)benzoate (3ak)



Yellowish solid, 80.4 mg, 88% yield.

Melting point: 133 °C

Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (hexane/ethylacetate, 15% ethylacetate).

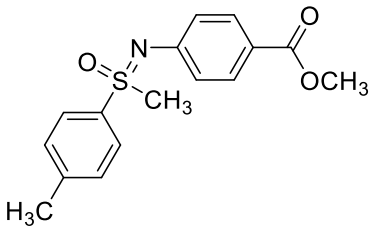
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 – 7.77 (m, 2H), 7.61 – 7.56 (m, 2H), 7.56 – 7.49 (m, 1H), 7.41 – 7.34 (m, 2H), 7.32 – 7.27 (m, 1H), 7.24 – 7.16 (m, 2H), 7.11 – 6.94 (m, 4H), 4.63 – 4.48 (m, 2H), 3.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.2 (C_q), 150.7 (C_q), 136.2 (C_q), 133.6 (+), 131.4 (+), 130.9 (+), 129.7 (+), 129.2 (+), 129.1 (+), 128.5 (+), 127.9 (C_q), 122.9 (C_q), 122.7 (+), 63.9 (-), 51.8 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{21}H_{19}NO_3S$) calc.: 366.1158, found: 366.1160.

Methyl 4-((methyl(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)amino)benzoate (3al)

^{1}H-NMR data are matching with the literature known spectra.[12]

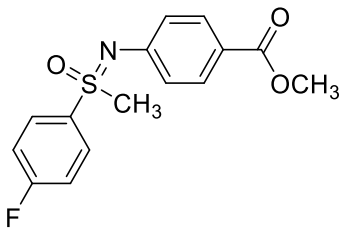


White solid, 75.1 mg, 99% yield.

Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 25% ethylacetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.82 – 7.75 (m, 4H), 7.32 – 7.27 (m, 2H), 7.02 – 6.94 (m, 2H), 3.80 (s, 3H), 3.24 (s, 3H), 2.39 (s, 3H).

Methyl 4-(((4-fluorophenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)benzoate (3am)



Yellowish oil, 76.1 mg, 99% yield.

Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 30% ethylacetate).

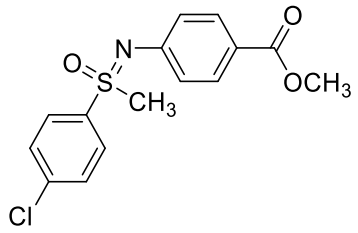
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.00 – 7.90 (m, 2H), 7.84 – 7.76 (m, 2H), 7.24 – 7.16 (m, 2H), 7.03 – 6.92 (m, 2H), 3.82 (s, 3H), 3.28 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.1 (C_q), 165.9 (C_q, d, J = 256.5 Hz), 149.9 (C_q), 134.7 (C_q, d, J = 3.2 Hz), 131.5 (+), 131.4 (+), 131.0 (+), 123.3 (C_q), 122.6 (+), 117.3 (+), 117.0 (+), 51.9 (+), 46.6 (+).

^{19}F NMR (282 MHz, $CDCl_3$) δ = -104.2.

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{15}H_{14}FNO_3S$) calc.: 308.0751, found: 308.0756.

Methyl 4-(((4-chlorophenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)benzoate (3an)



Yellowish oil, 80.1 mg, 99% yield.

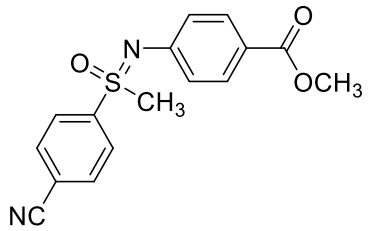
Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 30% ethylacetate).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.92 – 7.85 (m, 2H), 7.84 – 7.78 (m, 2H), 7.54 – 7.46 (m, 2H), 7.03 – 6.94 (m, 2H), 3.83 (s, 3H), 3.29 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.1 (C_q), 149.7 (C_q), 140.6 (C_q), 137.2 (C_q), 131.0 (+), 130.2 (+), 130.2 (+), 123.5 (C_q), 122.6 (+), 51.9 (+), 46.5 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{15}H_{14}ClNO_3S$) calc.: 324.0456, found: 324.0459.

Methyl 4-(((4-cyanophenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)benzoate (3ao)



Yellowish oil, 71.5 mg, 91% yield.

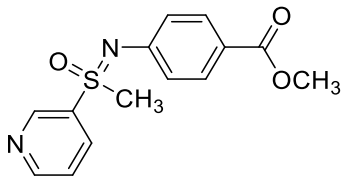
Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 45% ethylacetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 – 8.00 (m, 2H), 7.85 – 7.73 (m, 4H), 7.00 – 6.92 (m, 2H), 3.81 (s, 3H), 3.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.9 (C_q), 149.3 (C_q), 143.5 (C_q), 133.5 (+), 131.0 (+), 129.4 (+), 123.8 (C_q), 122.6 (+), 117.5 (C_q), 117.1 (C_q), 51.9 (+), 46.0 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{16}H_{14}N_2O_3S$) calc.: 315.0798, found: 315.0803.

Methyl 4-((methyl(oxo)(pyridin-3-yl)-λ^6-sulfaneylidene)amino)benzoate (3ap)



Yellowish crystals, 44.3 mg, 61% yield.

Melting point: 144 °C

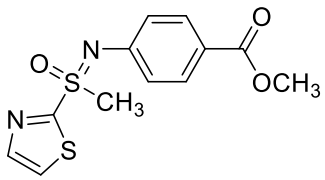
Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 60% ethylacetate).

^{1}H NMR (400 MHz, D_6-DMSO) δ = 8.76 (d, *J* = 4.3 Hz, 1H), 8.19 (dt, *J* = 7.9, 1.1 Hz, 1H), 8.14 (td, *J* = 7.7, 1.7 Hz, 1H), 7.73 – 7.65 (m, 3H), 6.97 – 6.90 (m, 2H), 3.75 (s, 3H), 3.52 (s, 3H).

^{13}C NMR (101 MHz, D_6-DMSO) δ = 166.0 (C_q), 156.2 (C_q), 150.7 (C_q), 150.5 (+), 138.9 (+), 130.4 (+), 127.7 (+), 123.4 (+), 121.9 (+), 121.8 (C_q), 51.7 (+), 41.6 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{14}H_{14}N_2O_3S$) calc.: 291.0798, found: 291.0801

Methyl 4-((methyl(oxo)(thiazol-2-yl)-λ^6-sulfaneylidene)amino)benzoate (3aq)



Yellowish crystals, 34.8 mg, 47% yield.

Melting point: 131 °C

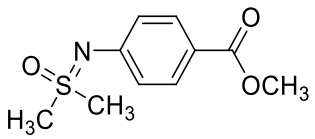
0.5 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 1.0 mol % $[Ni(dtbbpy)]Br_2$; Solvent: 1 mL dry and degassed dimethylacetamide (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 55% ethylacetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 3.1 Hz, 1H), 7.86 – 7.82 (m, 2H), 7.68 (d, *J* = 3.0 Hz, 1H), 7.13 – 7.08 (m, 2H), 3.84 (s, 3H), 3.52 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.1 (C_q), 165.6 (C_q), 148.7 (C_q), 145.2 (+), 131.0 (+), 126.8 (+), 124.5 (C_q), 123.3 (+), 52.0 (+), 44.8 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{12}H_{12}N_2O_3S_2$) calc.: 297.0362, found: 297.0366.

Methyl 4-((dimethyl(oxo)-λ^6-sulfaneylidene)amino)benzoate (3ar)



Colorless oil, 56.3 mg, 99% yield.

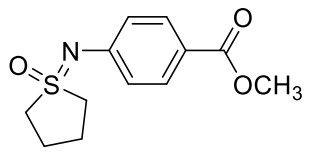
Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 60% ethylacetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 – 7.87 (m, 2H), 7.12 – 7.06 (m, 2H), 3.87 (s, 3H), 3.20 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.2 (C_q), 150.3 (C_q), 131.2 (+), 123.6 (C_q), 122.5 (+), 52.0 (+), 42.5 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{10}H_{13}NO_3S$) calc.: 228.0689, found: 228.0688.

Methyl 4-((1-oxidotetrahydro-1λ^6-thiophen-1-ylidene)amino)benzoate (3as)



Yellowish oil, 60.8 mg, 96% yield.

Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (hexane/ethylacetate, 30% ethylacetate).

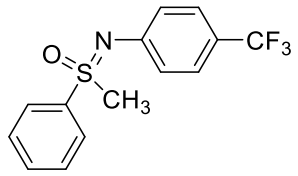
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 – 7.87 (m, 2H), 7.08 – 7.01 (m, 2H), 3.87 (s, 3H), 3.48 – 3.38 (m, 2H), 3.28 – 3.15 (m, 2H), 2.42 – 2.17 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.2 (C_q), 151.2 (C_q), 131.2 (+), 123.1 (C_q), 121.9 (+), 53.1 (+), 51.9 (-), 24.0 (-).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{12}H_{15}NO_3S$) calc.: 254.0845, found: 254.0850.

Methyl(phenyl)((4-(trifluoromethyl)phenyl)imino)-λ^6-sulfanone (3at)

^{1}H-NMR data are matching with the literature known spectra.[13]



Colorless oil, 67.3 mg, 90% yield.

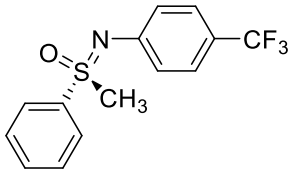
Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 20% ethylacetate).

(Chiralpak AS-H, *n*-heptane/ *iso*-propanol = 95/5, 1.0 mL/min, 254 nm): t_R = 12.00 min, 16.99 min.

For chiral HPLC trace see section 5.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 – 7.91 (m, 2H), 7.66 – 7.49 (m, 3H), 7.38 – 7.31 (m, 2H), 7.12 – 7.01 (m, 2H), 3.26 (s, 3H).

(*S*)-Methyl(phenyl)((4-(trifluoromethyl)phenyl)imino)-λ^6-sulfanone ((*S*)-3at)



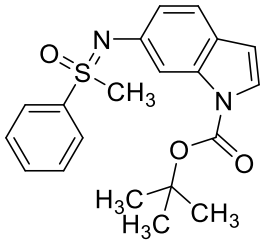
Colorless oil, 59.9 mg, 80% yield.

Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 20% ethylacetate).

(Chiralpak AS-H, *n*-heptane/ *iso*-propanol = 95/5, 1.0 mL/min, 254 nm): t_R = 16.57 min.

For chiral HPLC trace see section 5.

***tert*-Butyl 6-((methyl(oxo)(phenyl)-λ^6-sulfaneylidene)amino)-1*H*-indole-1-carboxylate (3au)**



Colorless oil, 88.9 mg, 96% yield.

0.5 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 5.0 mol % $[Ni(dtbbpy)]Br_2$. Solvent: 1 mL dry and degassed dimethylacetamide (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (hexane/ethylacetate, 30% ethylacetate).

(Chiralpak AS-H, *n*-heptane/ *iso*-propanol = 95/5, 1.0 mL/min, 215 nm): t_R = 16.87 min, 18.91 min.

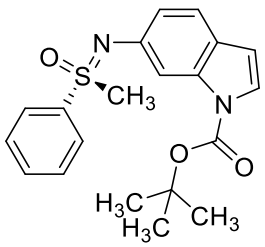
For chiral HPLC trace see section 4.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 – 7.98 (m, 2H), 7.86 (s, 1H), 7.58 – 7.40 (m, 4H), 7.30 (d, *J* = 8.3 Hz, 1H), 6.98 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.41 (dd, *J* = 3.7, 0.8 Hz, 1H), 3.24 (s, 3H), 1.65 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.0 (C_q), 142.2 (C_q), 139.6 (C_q), 135.9 (C_q), 133.2 (+), 129.5 (+), 128.8 (+), 125.6 (C_q), 124.9 (+), 121.0 (+), 119.8 (+), 110.0 (+), 107.2 (+), 83.5 (C_q), 45.9 (+), 28.3 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{20}H_{22}N_2O_3S$) calc.: 371.1424, found: 371.1429.

***tert*-Butyl (*S*)-6-((methyl(oxo)(phenyl)-λ^6-sulfaneylidene)amino)-1*H*-indole-1-carboxylate ((*S*)-3au)**



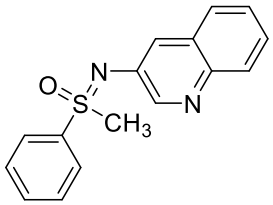
Colorless oil, 71.3 mg, 77% yield.

0.5 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 5.0 mol % $[Ni(dtbbpy)]Br_2$. Solvent: 1 mL dry and degassed dimethylacetamide (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 30% ethylacetate).

(Chiralpak AS-H, *n*-heptane/ *iso*-propanol = 95/5, 1.0 mL/min, 215 nm): t_R = 18.80 min.

For chiral HPLC trace see section 4.

Methyl(phenyl)(quinolin-3-ylimino)-λ^6-sulfanone (3av)



Orange oil, 69.2 mg, 98% yield.

1.0 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 5.0 mol % $[Ni(dtbbpy)]Br_2$. Solvent: 1 mL dry and degassed dimethylacetamide (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (hexane/ethylacetate, 70% ethylacetate).

(Chiralpak AS-H, *n*-heptane/ *iso*-propanol = 70/30 + 0.5v% diethylamine, 0.5 mL/min, 254 nm): t_R = 18.76 min, 22.32 min.

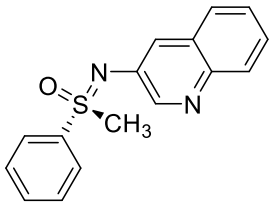
For chiral HPLC trace see section 4.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.71 (d, *J* = 2.6 Hz, 1H), 8.02 – 7.97 (m, 2H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.50 (m, 5H), 7.49 – 7.44 (m, 1H), 7.42 – 7.35 (m, 1H), 3.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 149.8 (+), 144.0 (C_q), 139.2 (C_q), 138.6 (C_q), 133.8 (+), 129.9 (+), 129.0 (+), 128.8 (C_q), 128.7 (+), 127.0 (+), 126.9 (+), 126.7 (+), 124.4 (+), 46.3 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{16}H_{14}N_2OS$) calc.: 283.0900, found: 283.0901.

(*S*)-Methyl(phenyl)(quinolin-3-ylimino)-λ^6-sulfanone ((*S*)-3av)



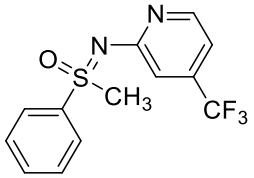
Orange oil, 69.7 mg, 99% yield.

1.0 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 5.0 mol % $[Ni(dtbbpy)]Br_2$. Solvent: 1 mL dry and degassed dimethylacetamide (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 70% ethylacetate).

(Chiralpak AS-H, *n*-heptane/ *iso*-propanol = 70/30 + 0.5v% diethylamine, 0.5 mL/min, 254 nm): t_R = 22.17 min.

For chiral HPLC trace see section 4.

Methyl(phenyl)((4-(trifluoromethyl)pyridin-2-yl)imino)-λ^6-sulfanone (3aw)



White solid, 29.3 mg, 39% yield.

Melting point: 98 °C

0.5 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 1.0 mol % $[Ni(dtbbpy)]Br_2$. Solvent: 1 mL dry and degassed dimethylacetamide (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 25% ethylacetate).

(Chiralpak AS-H, *n*-heptane/ *iso*-propanol = 95/5, 1.0 mL/min, 254 nm): t_R = 15.28 min, 20.47 min.

For chiral HPLC trace see section 4.

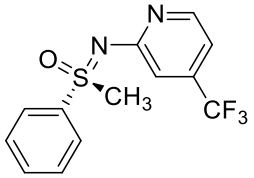
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.18 (d, *J* = 5.3 Hz, 1H), 8.04 – 7.95 (m, 2H), 7.67 – 7.60 (m, 1H), 7.56 (ddt, *J* = 8.3, 6.3, 1.5 Hz, 2H), 7.08 (s, 1H), 6.94 – 6.86 (m, 2H), 3.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.0 (C_q), 148.9 (+), 140.0 (C_q, q, *J* = 33.5 Hz), 139.8 (C_q), 133.4 (+), 129.7 (+), 127.8 (+), 123.1 (C_q, q, *J* = 273.2 Hz), 113.0 (+, q, *J* = 4.0 Hz), 111.4 (+, q, *J* = 3.4 Hz), 45.6 (+).

^{19}F NMR (377 MHz, $CDCl_3$) δ = -65.6.

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{13}H_{11}F_3N_2OS$) calc.: 301.0617, found: 301.0621.

(*S*)-Methyl(phenyl)((4-(trifluoromethyl)pyridin-2-yl)imino)-λ^6-sulfanone ((*S*)-3aw)



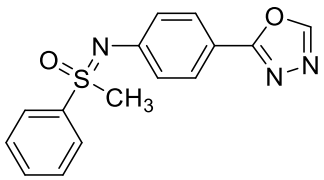
Orange oil, 42.8 mg, 57% yield.

0.5 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 1.0 mol % $[Ni(dtbbpy)]Br_2$. Solvent: 1 mL dry and degassed dimethylacetamide (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 25% ethylacetate).

(Chiralpak AS-H, *n*-heptane/ *iso*-propanol = 95/5, 1.0 mL/min, 254 nm): t_R = 20.25 min.

For chiral HPLC trace see section 4.

((4-(1,3,4-Oxadiazol-2-yl)phenyl)imino)(methyl)(phenyl)-λ^6-sulfanone (3ax)



Orange oil, 72.6 mg, 97% yield.

0.5 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 2.0 mol % $[Ni(dtbbpy)]Br_2$. Solvent: 1 mL dry and degassed dimethylacetamide (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (hexane/ethylacetate, 50% ethylacetate).

(Lux Cellulose-1, *n*-heptane/ *iso*-propanol = 50/50 + 0.5vol% diethylamine, 0.5 mL/min, 254 nm): t_R = 16.46 min, 18.04 min.

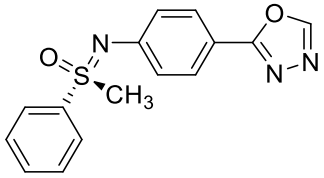
For chiral HPLC trace see section 4.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.35 (s, 1H), 7.99 – 7.93 (m, 2H), 7.85 – 7.79 (m, 1H), 7.65 – 7.58 (m, 1H), 7.57 – 7.49 (m, 2H), 7.12 – 7.05 (m, 2H), 3.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.0 (C_q), 152.1 (+), 149.5 (C_q), 138.8 (C_q), 133.8 (+), 129.9 (+), 128.6 (+), 128.3 (+), 123.4 (+), 116.4 (C_q), 46.5 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{15}H_{13}N_3O_2S$) calc.: 300.0801, found: 300.0810.

(*S*)-((4-(1,3,4-Oxadiazol-2-yl)phenyl)imino)(methyl)(phenyl)-λ^6-sulfanone ((*S*)-3ax)



Orange oil, 73.9 mg, 99% yield.

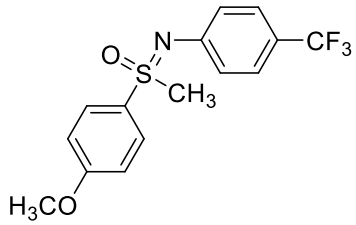
0.5 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 2.0 mol % $[Ni(dtbbpy)]Br_2$. Solvent: 1 mL dry and degassed dimethylacetamide (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 50% ethylacetate).

(Cellulose-1, *n*-heptane/ *iso*-propanol = 50/50 + 0.5vol% diethylamine, 0.5 mL/min, 254 nm): t_R = 17.99 min.

For chiral HPLC trace see section 4.

4.5.Large-scale synthesis of *N*-arylated sulfoximine 3a

(4-Methoxyphenyl)(methyl)((4-(trifluoromethyl)phenyl)imino)-λ^6-sulfanone (3a)



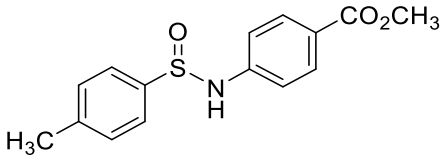
The large-scale synthesis of *N*-arylated sulfoximine **3a** was performed in self-designed batch-reactor, which is depicted in Figure S 2.

Compartment 1 was charged with 5.0 g of *NH*-sulfoximine **1a** (27.0 mmol, 1.0 equiv.), 37.0 mg of $[Ir(ppy)_2(dtbbpy)]PF_6$ (0.04 mmol, 0.15 mol %) and 26.3 mg $[Ni(dtbbpy)]Br_2$ (0.05 mmol, 0.20 mol %) and a magnetic stirring bar. The closed apparatus was degassed *via* three cycles of vacuum/nitrogen (2 min. at 7 mbar / 2 min. flush with nitrogen atmosphere). After that, 4.2 mL bromo arene **2a** (29.7 mmol, 1.1 equiv.), 4.1 mL of tetramethylguanidine (32.4 mmol, 1.2 equiv.) and 108 mL dry and degassed acetonitrile were added *via* syringe under nitrogen atmosphere. The reaction mixture was stirred and irradiated, using blue LEDs (455 nm) for 17 hours at 25 °C. The reaction mixture was diluted with brine (250 mL) and extracted three times with ethylacetate (3 x 150 mL). The combined organic layers were dried with Na_2SO_4, filtered and the solvent was removed under reduced pressure. Evaporation of volatiles led to the crude product. Purification was performed *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 30% ethylacetate), affording 8.8 g of the corresponding *N*-arylated sulfoximine **3a** (99%).

4.6.Procedures for the *N*-arylation of sulfoximidoyl derivatives 4 & 6

Methyl-4-((*p*-tolylsulfinyl)amino)benzoate (5)

p-Toluenesulfinamide (**4**) (38.8 mg, 0.25 mmol, 1.0 equiv.) was used as sulfoximidoyl derivative instead of *NH*-sulfoximines and reacted as described in the general procedure for *NH*-sulfoximines.



White crystals, 67.3 mg, 93% yield.

Melting point: 126 °C

0.5 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 2.0 mol % $[Ni(dtbbpy)]Br_2$. Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 20% ethylacetate).

^{1}H NMR (300 MHz, D_6-DMSO) δ = 9.84 (s, 1H), 7.88 – 7.80 (m, 2H), 7.67 – 7.57 (m, 2H), 7.45 – 7.37 (m, 2H), 7.22 – 7.13 (m, 2H), 3.79 (s, 3H), 2.38 (s, 3H).

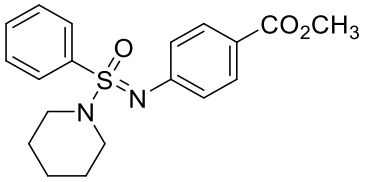
^{13}C NMR (75 MHz, D_6-DMSO) δ = 165.9 (C_q), 146.8 (C_q), 141.4 (C_q), 140.9 (C_q), 130.8 (+), 129.7 (+), 125.5 (+), 122.5 (C_q), 116.2 (+), 51.8 (+), 20.9 (+).

HRMS (ESI) (m/z): $[M + H]^+$ ($C_{15}H_{15}NO_3S$) calc.: 290.0845, found: 290.0848.

Methyl 4-((oxo(phenyl)(piperidin-1-yl)-λ^6-sulfaneylidene)amino)benzoate (7)

^{1}H-NMR data are matching with the literature known spectra.[14]

1-(Phenylsulfonimidoyl)piperidine (**C-3**) (56.1 mg, 0.25 mmol, 1.0 equiv.) was used as sulfoximidoyl derivative instead of *NH*-sulfoximines and reacted as described in the general procedure for *NH*-sulfoximines.



White solid, 86.0 mg, 96% yield.

0.5 mol % $[Ir(ppy)_2(dtbbpy)]PF_6$; 1.0 mol % $[Ni(dtbbpy)]Br_2$. Solvent: 1 mL dry and degassed acetonitrile (0.25 M); reaction time: 17 h; Purified *via* automated flash column chromatography on flash silica gel (petrolether/ethylacetate, 10% ethylacetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 – 7.88 (m, 4H), 7.64 – 7.50 (m, 3H), 7.28 – 7.24 (m, 2H), 3.88 (s, 3H), 3.07 (ddd, *J* = 11.2, 7.0, 3.9 Hz, 2H), 2.98 (ddd, *J* = 11.4, 7.0, 3.9 Hz, 2H), 1.61 – 1.43 (m, 4H), 1.36 (quint., *J* = 5.7 Hz, 2H).

5. Experimental details of the analysis of enantiopure sulfoximines by NP chiral HPLC

Methyl(phenyl)((4-(trifluoromethyl)phenyl)imino)-λ^6-sulfanone (3at)

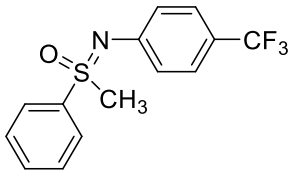
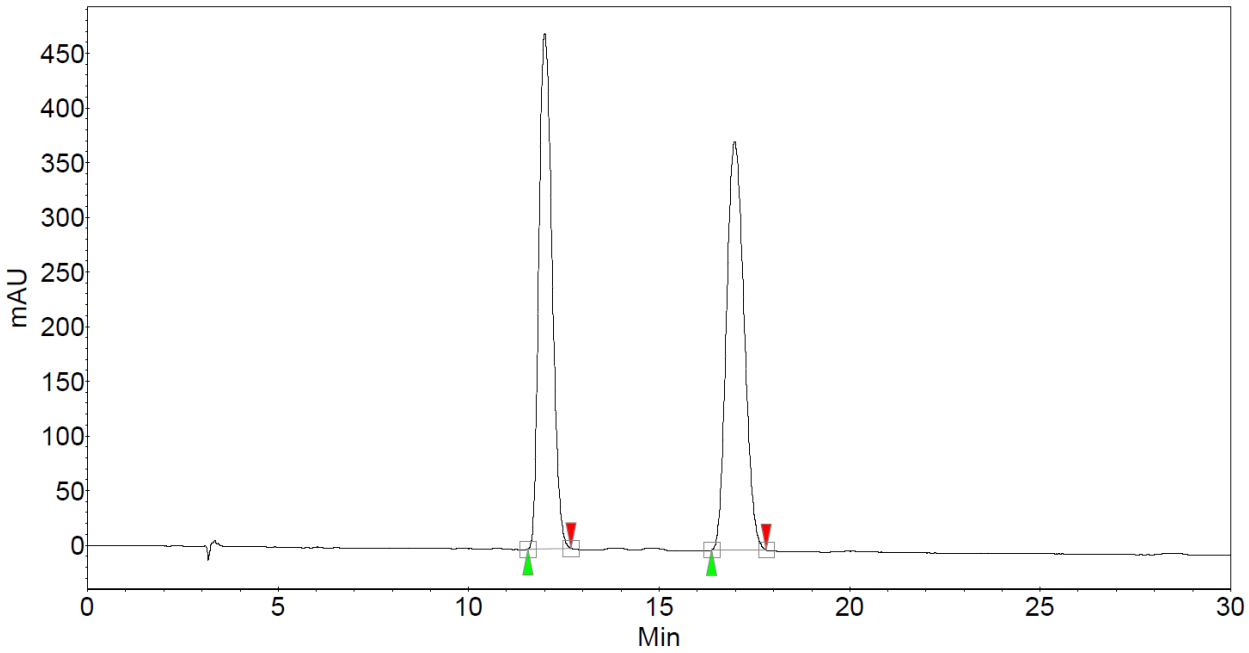


Table S 5. Data for chiral HPLC of 3at

Peak #	Retention Time [min]	Height [mAU]	Area [mAU*min]	Area% [%]
1	12.00	471.1	189.0	49
2	16.99	373.0	199.4	51
Total		844.1	388.4	100

HPLC chromatogram



(*S*)-Methyl(phenyl)((4-(trifluoromethyl)phenyl)imino)-λ^6-sulfanone ((*S*)-3at)

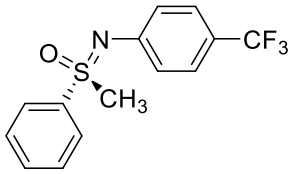
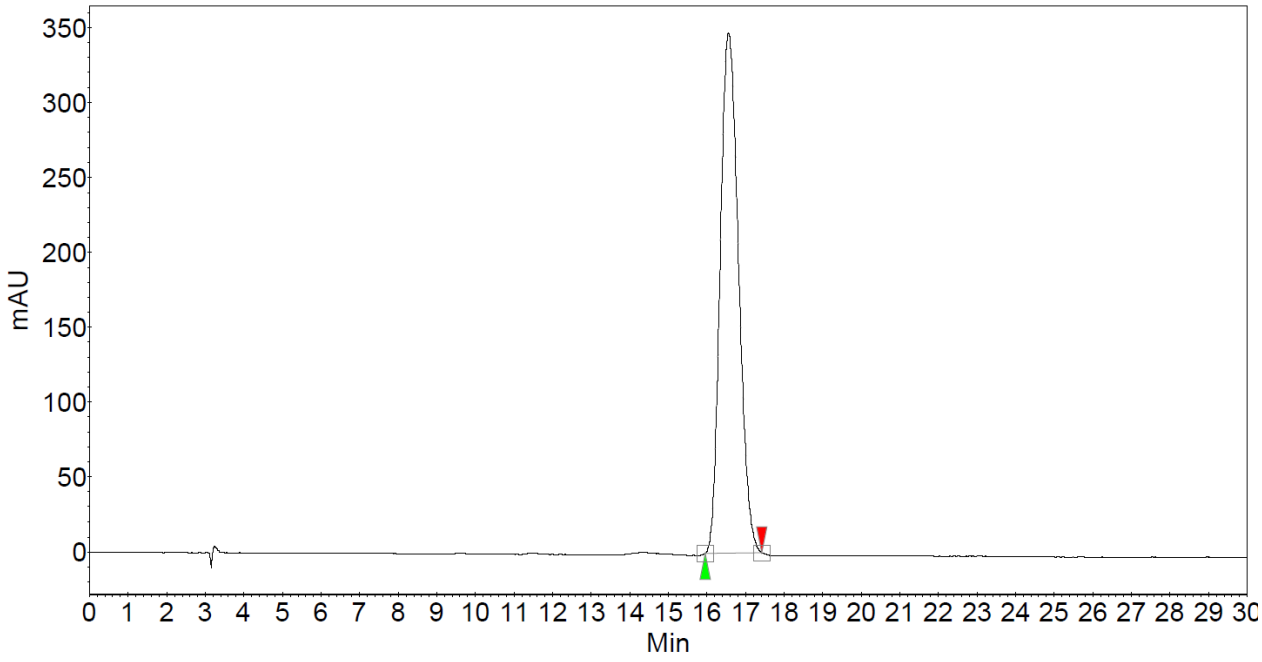


Table S 6. Data for chiral HPLC of *S*-3at

Peak #	Retention Time [min]	Height [mAU]	Area [mAU*min]	Area% [%]
1	16.57	347.3	192.0	100
Total		347.3	192.0	100

HPLC chromatogram



***tert*-butyl 6-((methyl(oxo)(phenyl)-λ^6-sulfaneylidene)amino)-1*H*-indole-1-carboxylate (3au)**

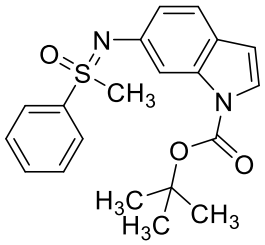
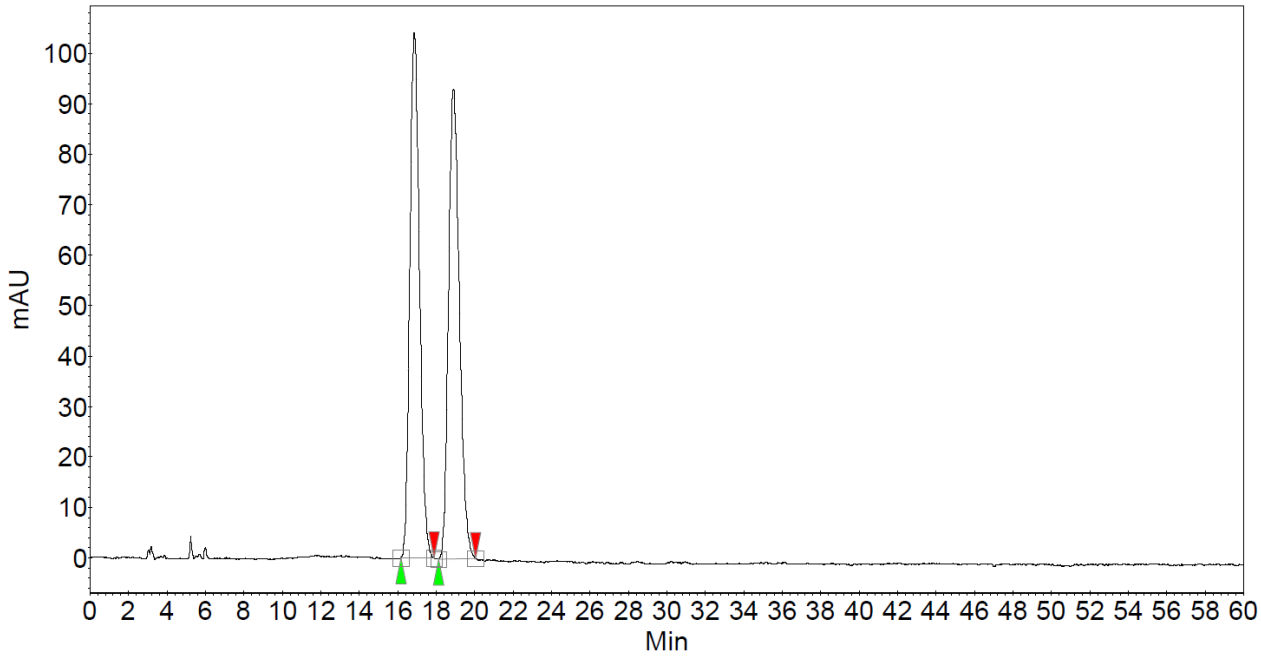


Table S 7. Data for chiral HPLC of 3au

Peak #	Retention Time [min]	Height [mAU]	Area [mAU*min]	Area% [%]
1	16.87	104.0	60.7	50
2	18.91	93.0	61.3	50
Total		197.0	122.0	100

HPLC chromatogram



***tert*-butyl (*S*)-6-((methyl(oxo)(phenyl)-λ^6-sulfaneylidene)amino)-1*H*-indole-1-carboxylate ((*S*)-3au)**

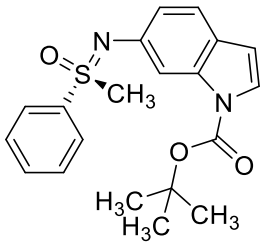
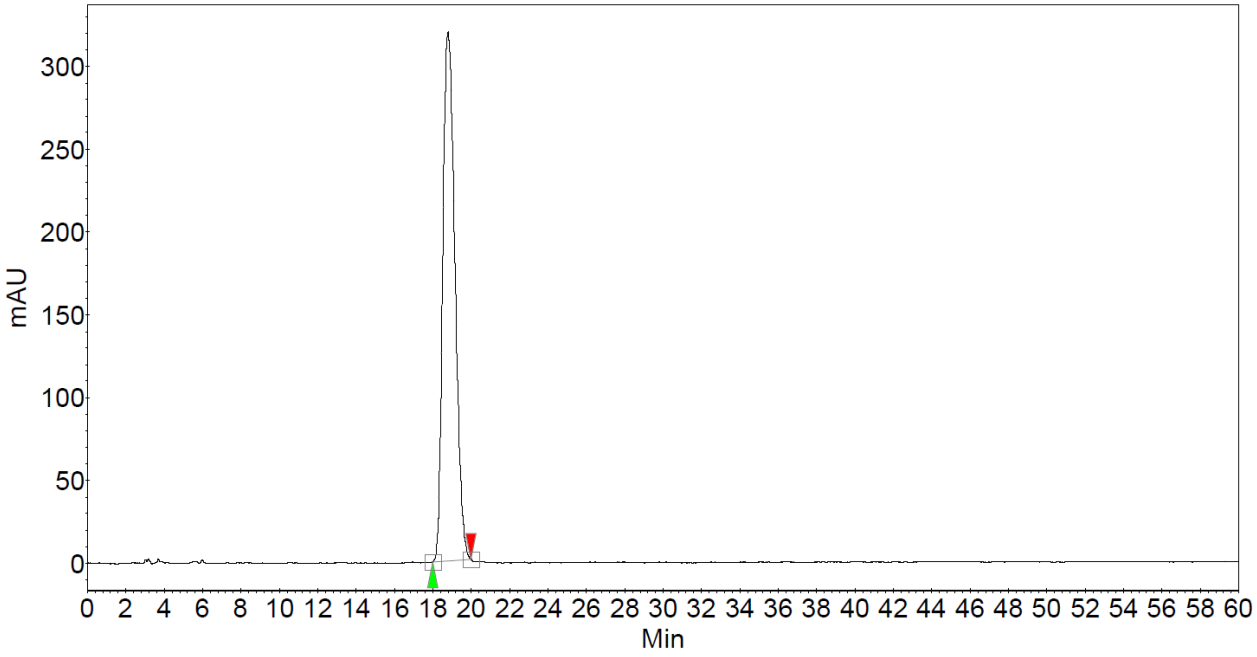


Table S 8. Data for chiral HPLC of *S*-3au

Peak #	Retention Time [min]	Height [mAU]	Area [mAU*min]	Area% [%]
1	18.80	319.5	235.8	100
Total		319.5	235.8	100

HPLC chromatogram



Methyl(phenyl)(quinolin-3-ylimino)-λ^6-sulfanone (3av)

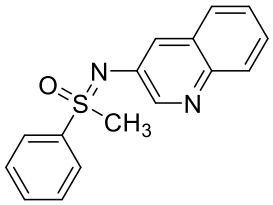
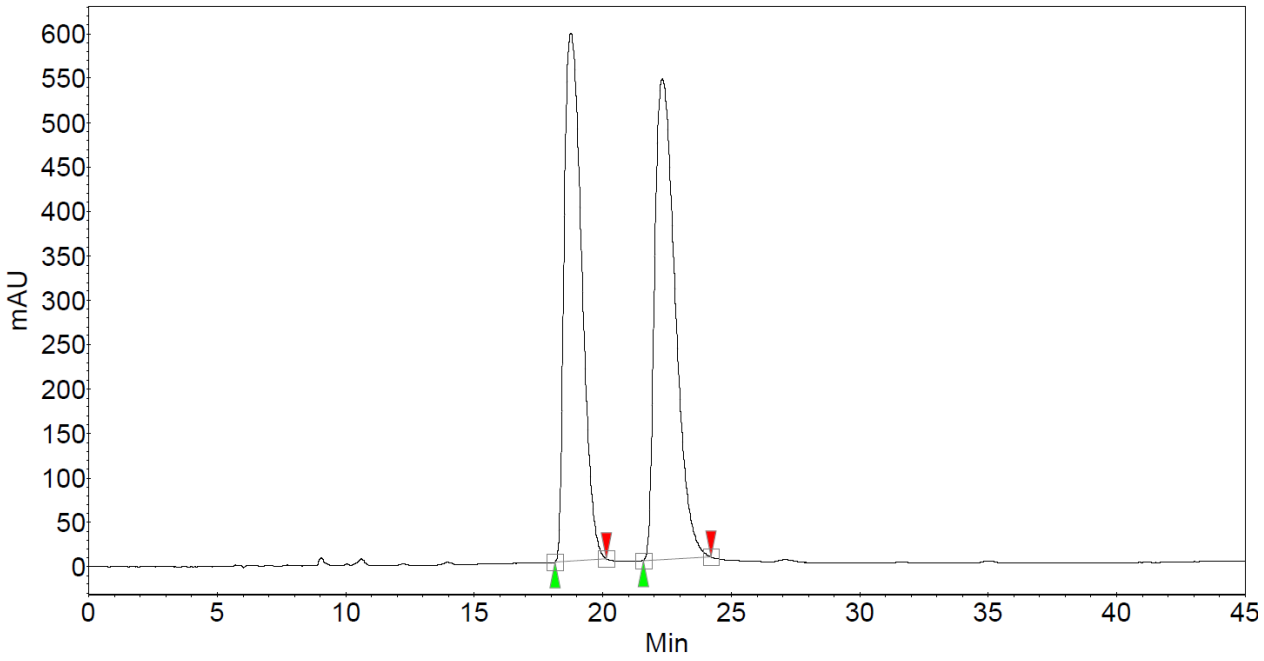


Table S 9. Data for chiral HPLC of 3av

Peak #	Retention Time [min]	Height [mAU]	Area [mAU*min]	Area% [%]
1	18.76	594.3	468.2	48
2	22.32	541.2	503.3	52
Total		1135.6	971.5	100

HPLC chromatogram



(*S*)-Methyl(phenyl)(quinolin-3-ylimino)-λ^6-sulfanone ((*S*)-3av)

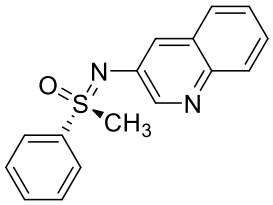
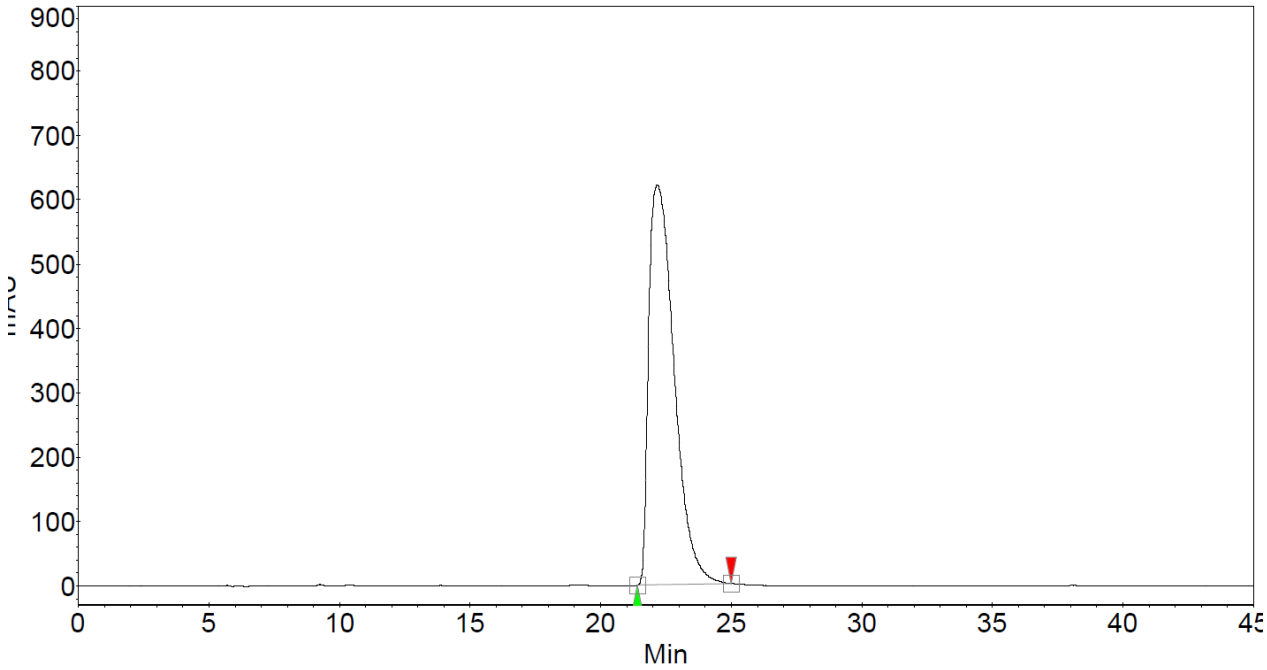


Table S 10. Data for chiral HPLC of S-*3*av

Peak #	Retention Time [min]	Height [mAU]	Area [mAU*min]	Area% [%]
1	22.17	620.7	701.5	100
Total		620.7	701.5	100

HPLC chromatogram



Methyl(phenyl)((4-(trifluoromethyl)pyridin-2-yl)imino)-λ^6-sulfanone (3aw)

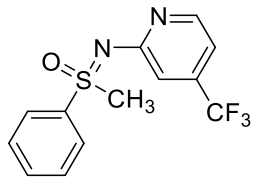
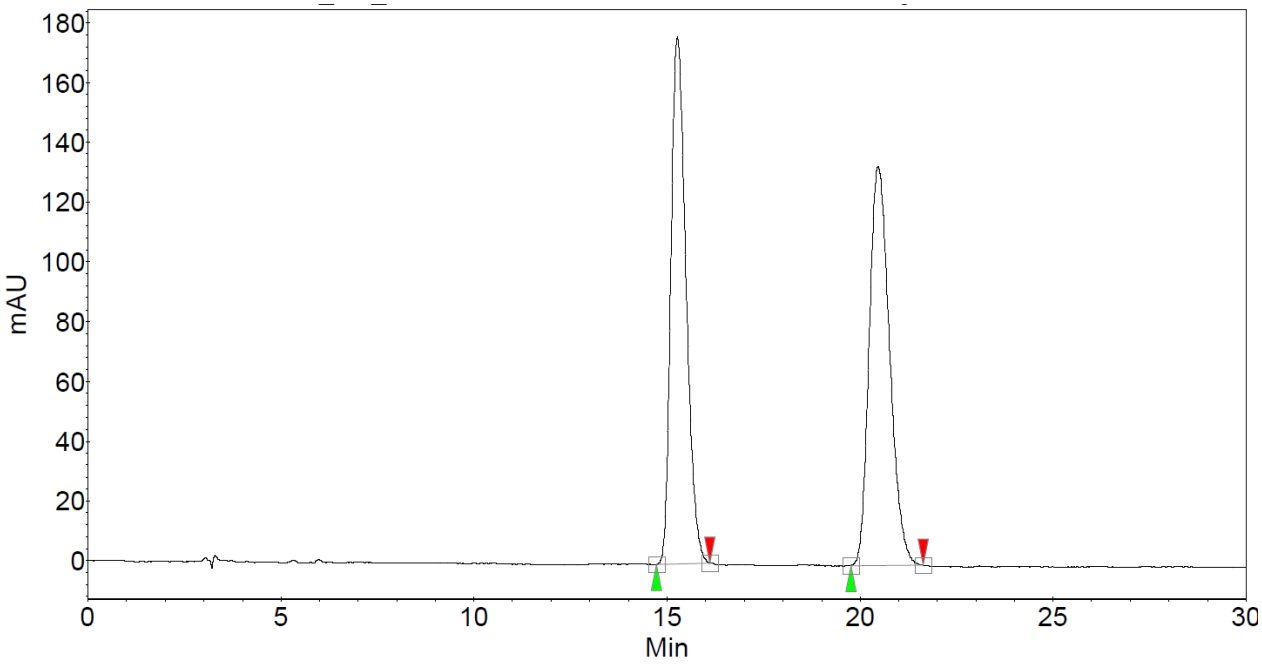


Table S 11. Data for chiral HPLC of 3aw

Peak #	Retention Time [min]	Height [mAU]	Area [mAU*min]	Area% [%]
1	15.28	176.4	80.1	50
2	20.47	133.7	81.7	50
Total		310.1	161.9	100

HPLC chromatogram



(*S*)-Methyl(phenyl)((4-(trifluoromethyl)pyridin-2-yl)imino)-λ^6-sulfanone ((*S*)-3aw

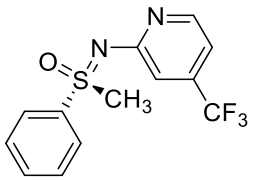
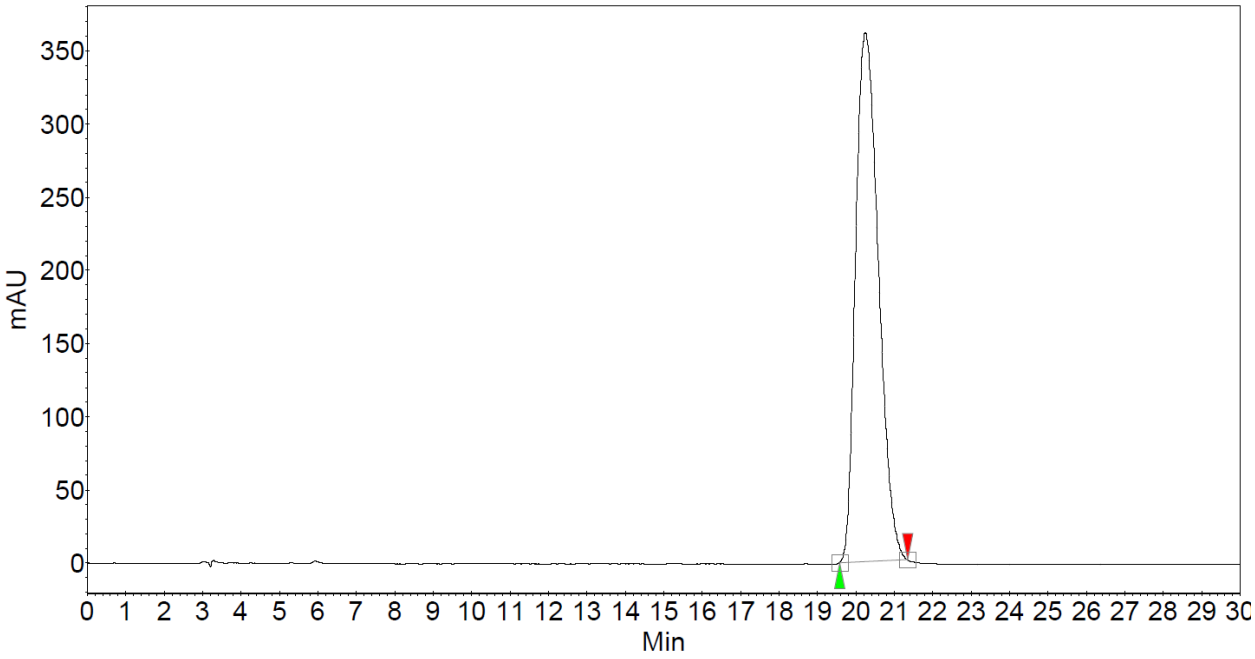


Table S 12. Data for chiral HPLC of *S*-3aw

Peak #	Retention Time [min]	Height [mAU]	Area [mAU*min]	Area% [%]
1	20.25	361.5	248.2	100
Total		361.5	248.2	100

HPLC chromatogram



((4-(1,3,4-Oxadiazol-2-yl)phenyl)imino)(methyl)(phenyl)-λ^6-sulfanone (3ax)

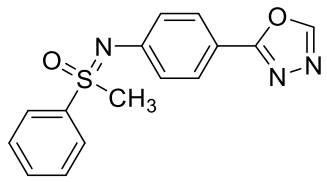
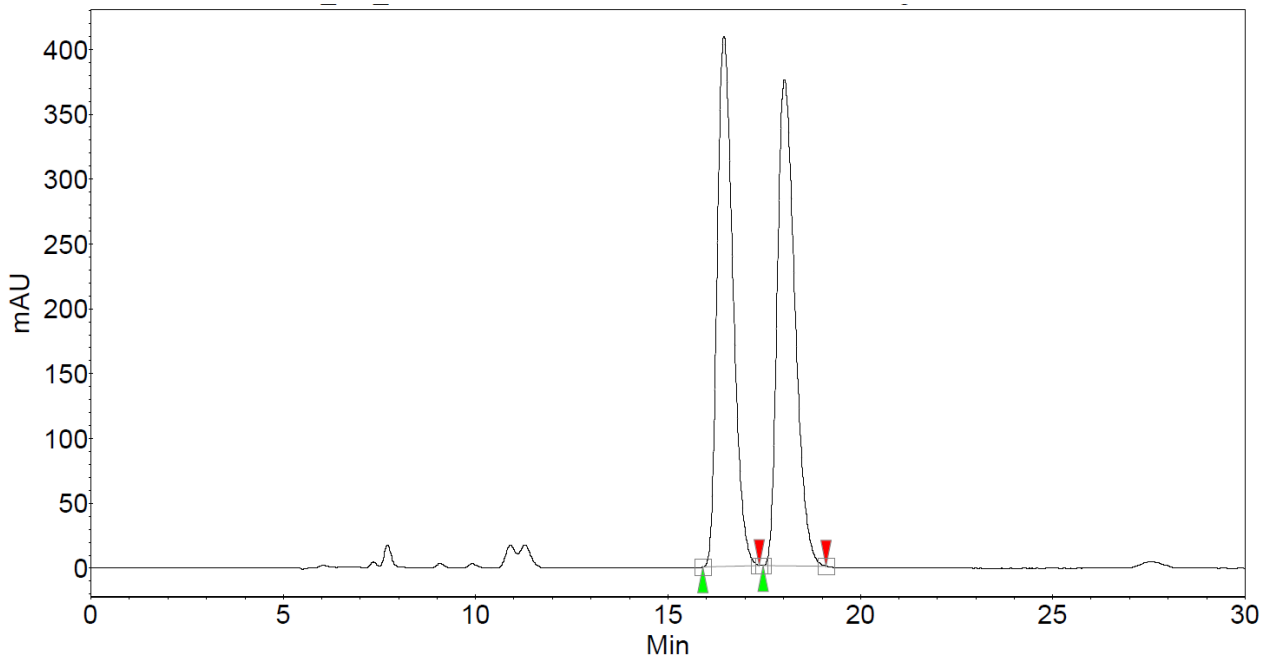


Table S 13. Data for chiral HPLC of 3ax

Peak #	Retention Time [min]	Height [mAU]	Area [mAU*min]	Area% [%]
1	16.46	409.0	196.1	49
2	18.04	375.3	200.5	51
Total		784.3	396.6	100

HPLC chromatogram



(*S*)-((4-(1,3,4-Oxadiazol-2-yl)phenyl)imino)(methyl)(phenyl)-λ^6-sulfanone ((*S*)-3ax)

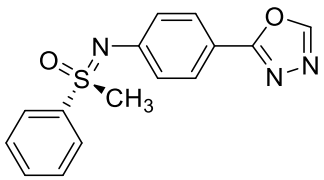
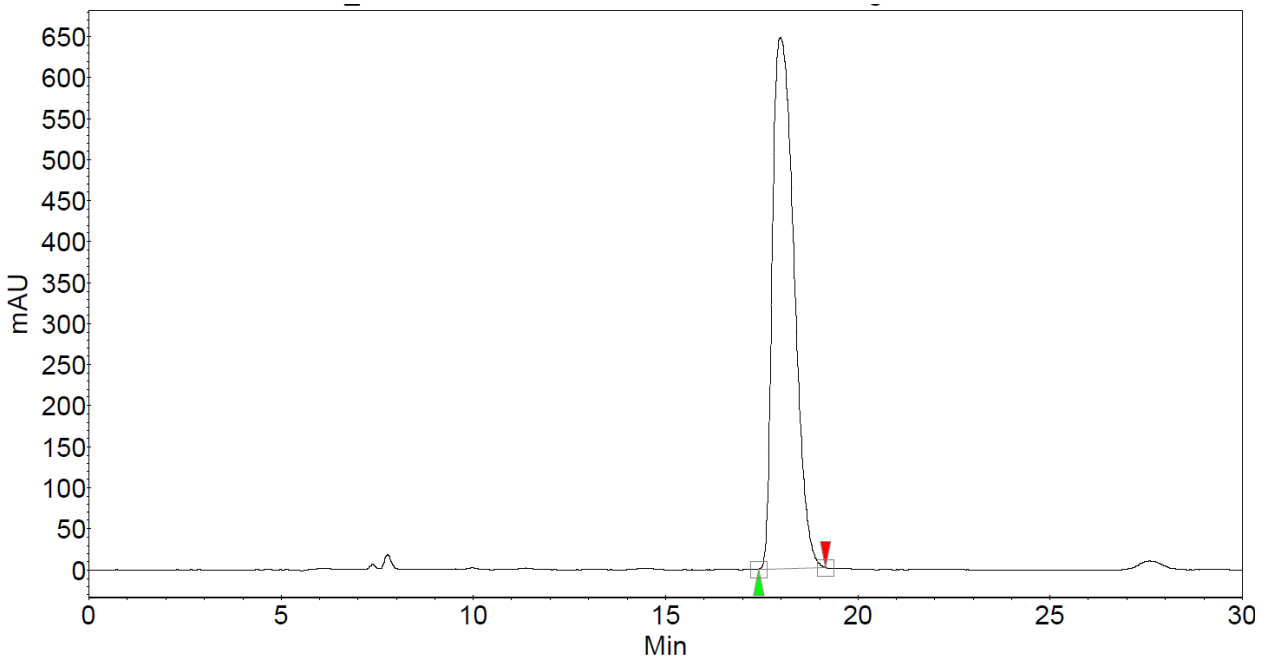


Table S 14. Data for chiral HPLC of *S*-3ax

Peak #	Retention Time [min]	Height [mAU]	Area [mAU*min]	Area% [%]
1	17.99	647.8	423.0	100
Total		647.8	423.0	100

HPLC chromatogram



6. References

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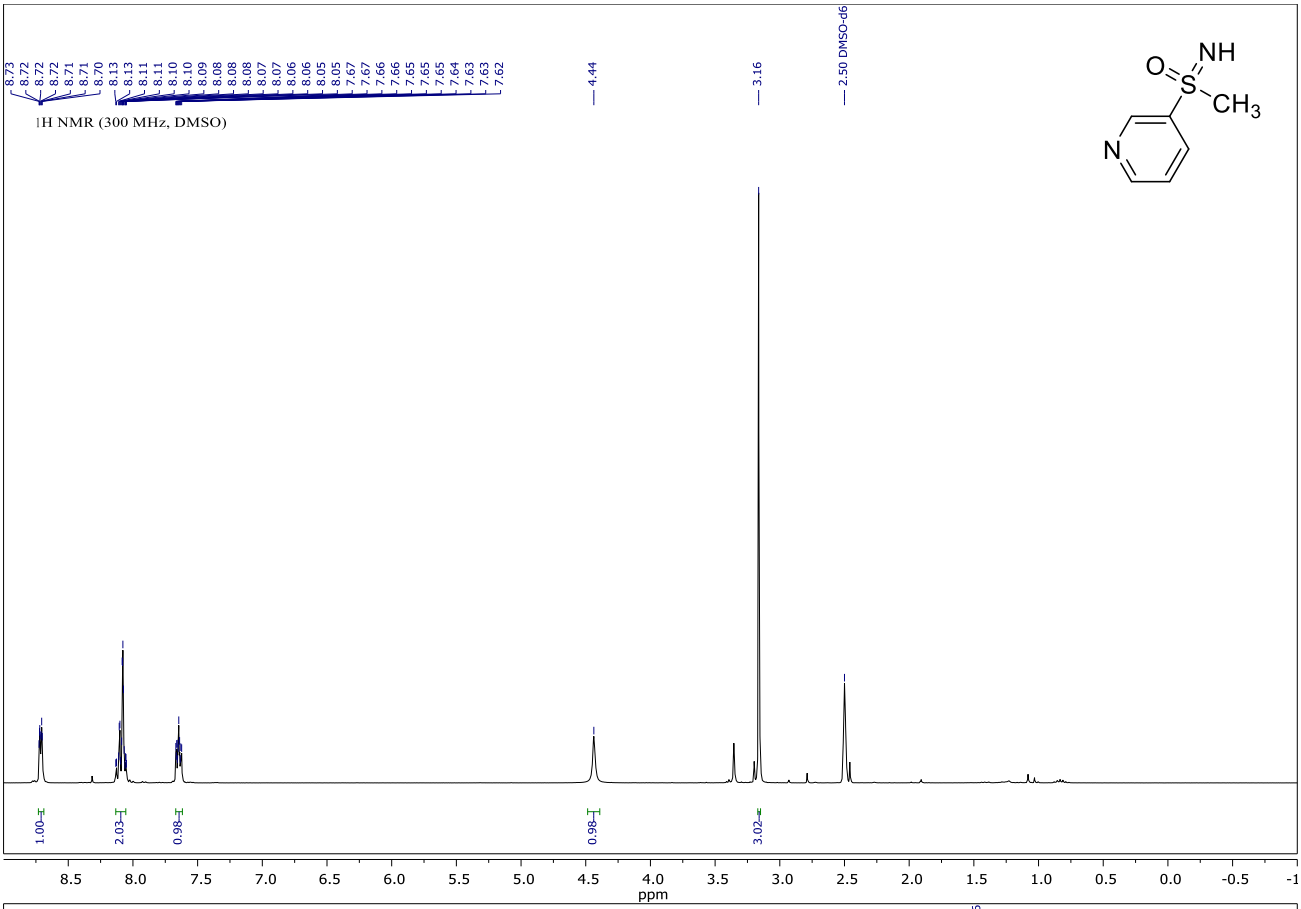
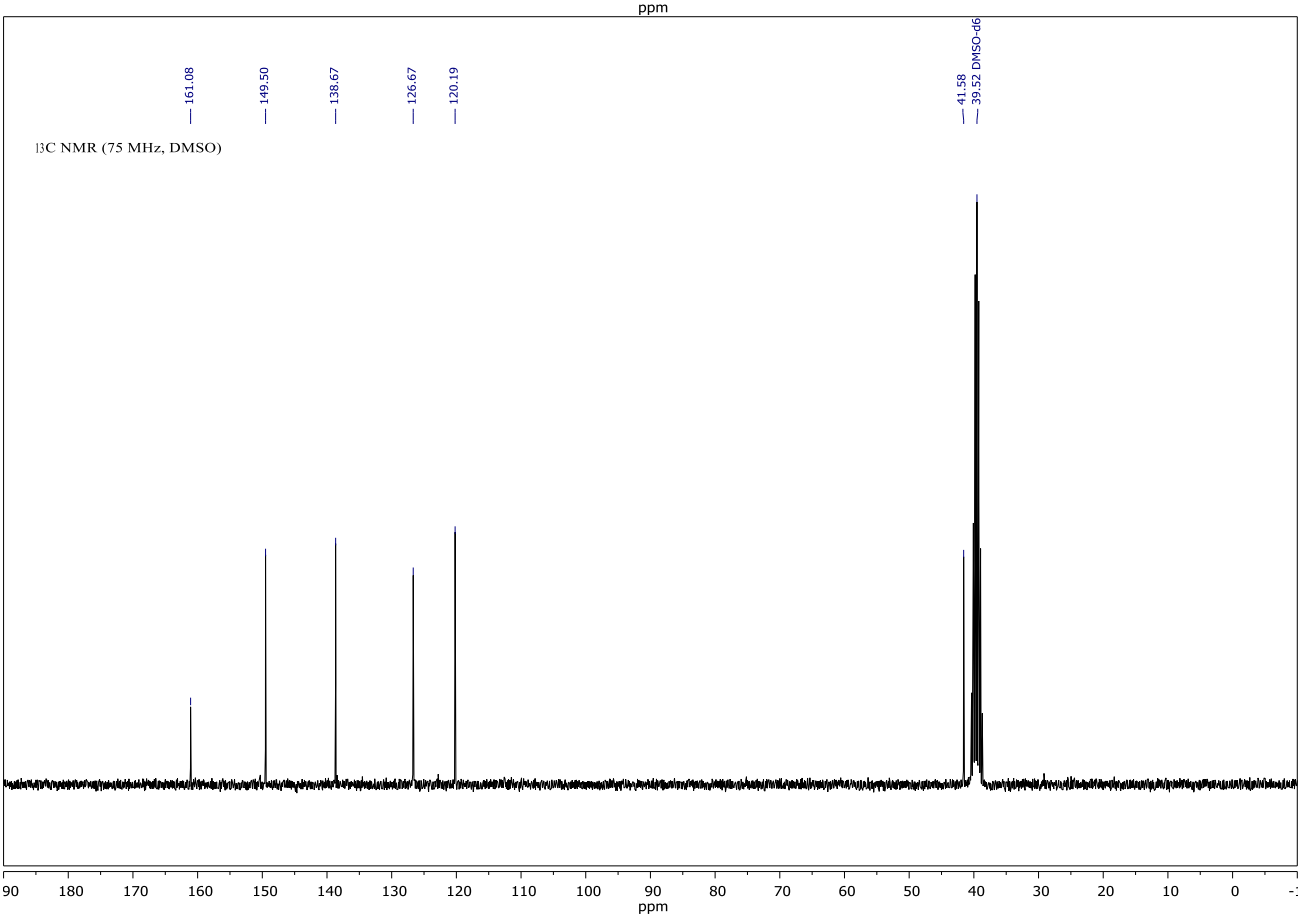
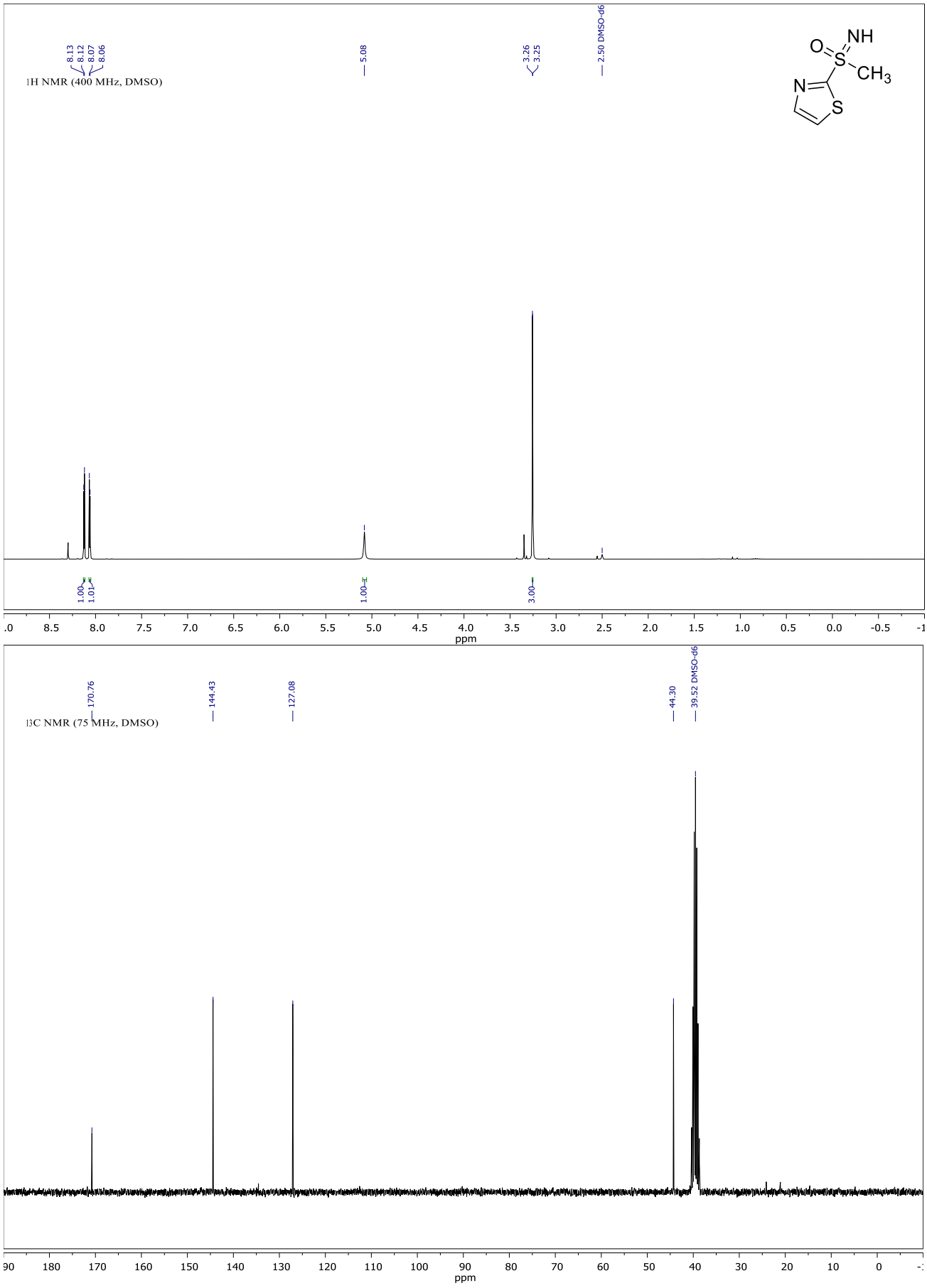
7. ^{1}H-, ^{13}C- and ^{19}F-NMR spectra of products

Imino(methyl)(pyridin-3-yl)-l6-sulfanone (1ap)

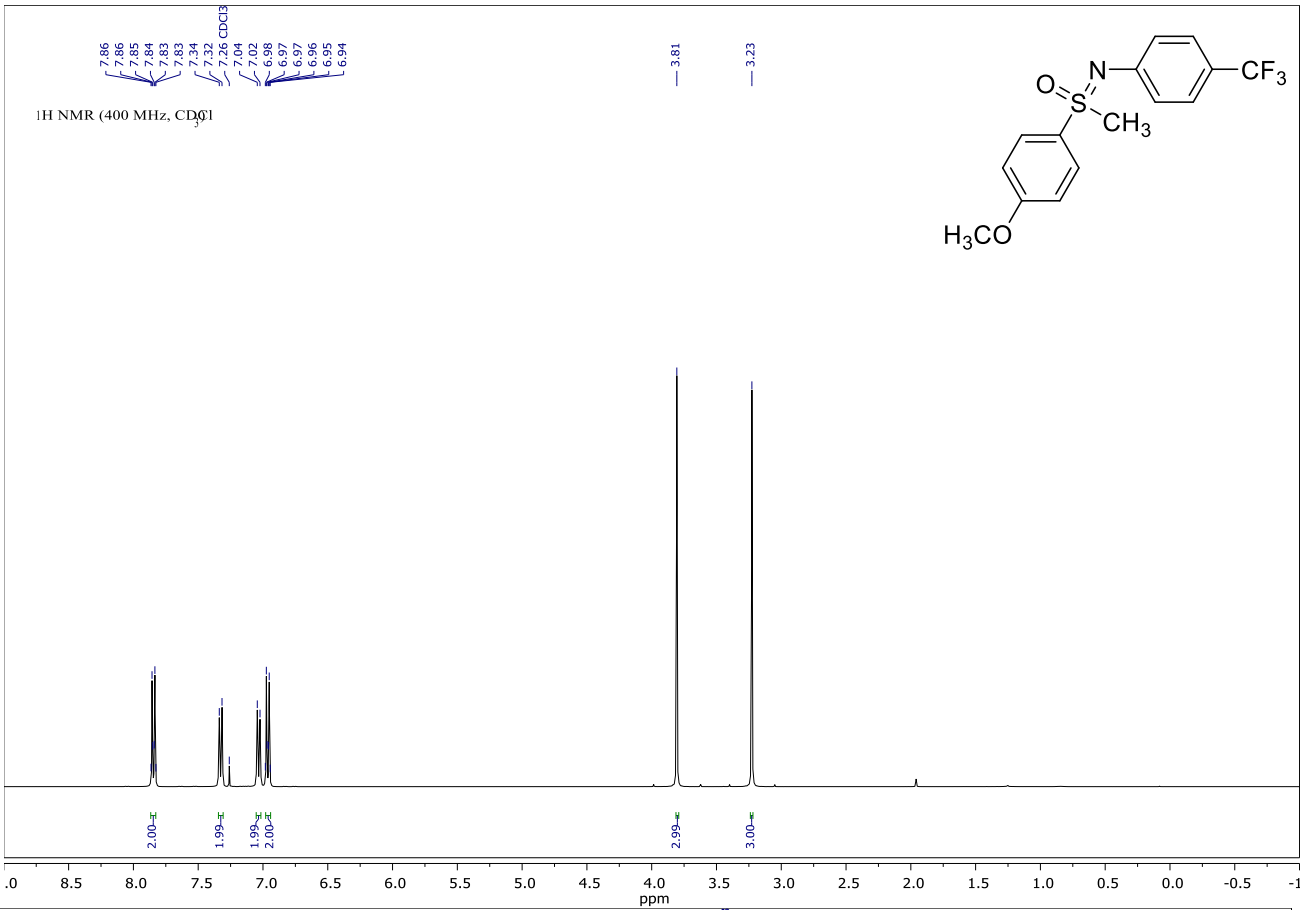


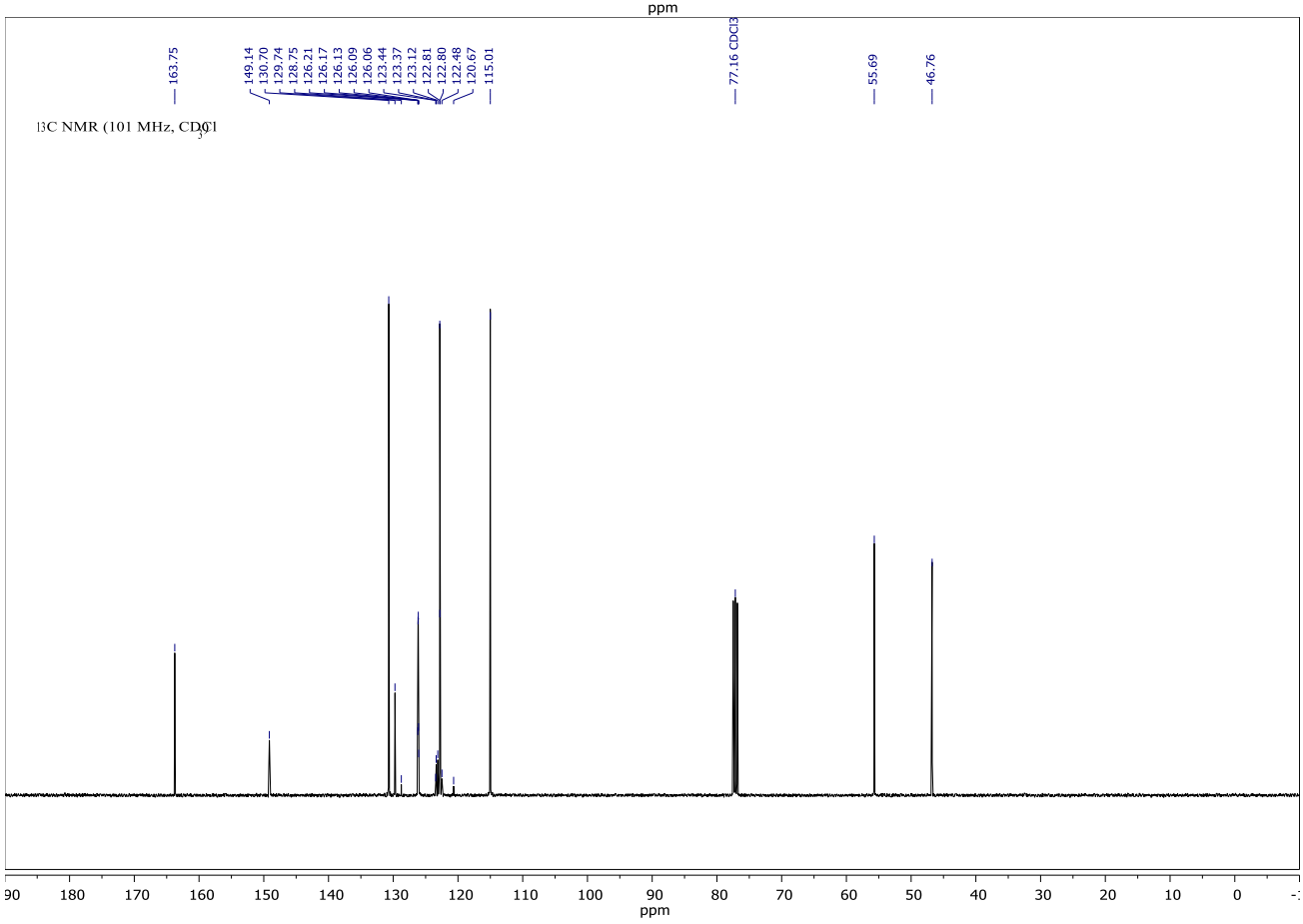


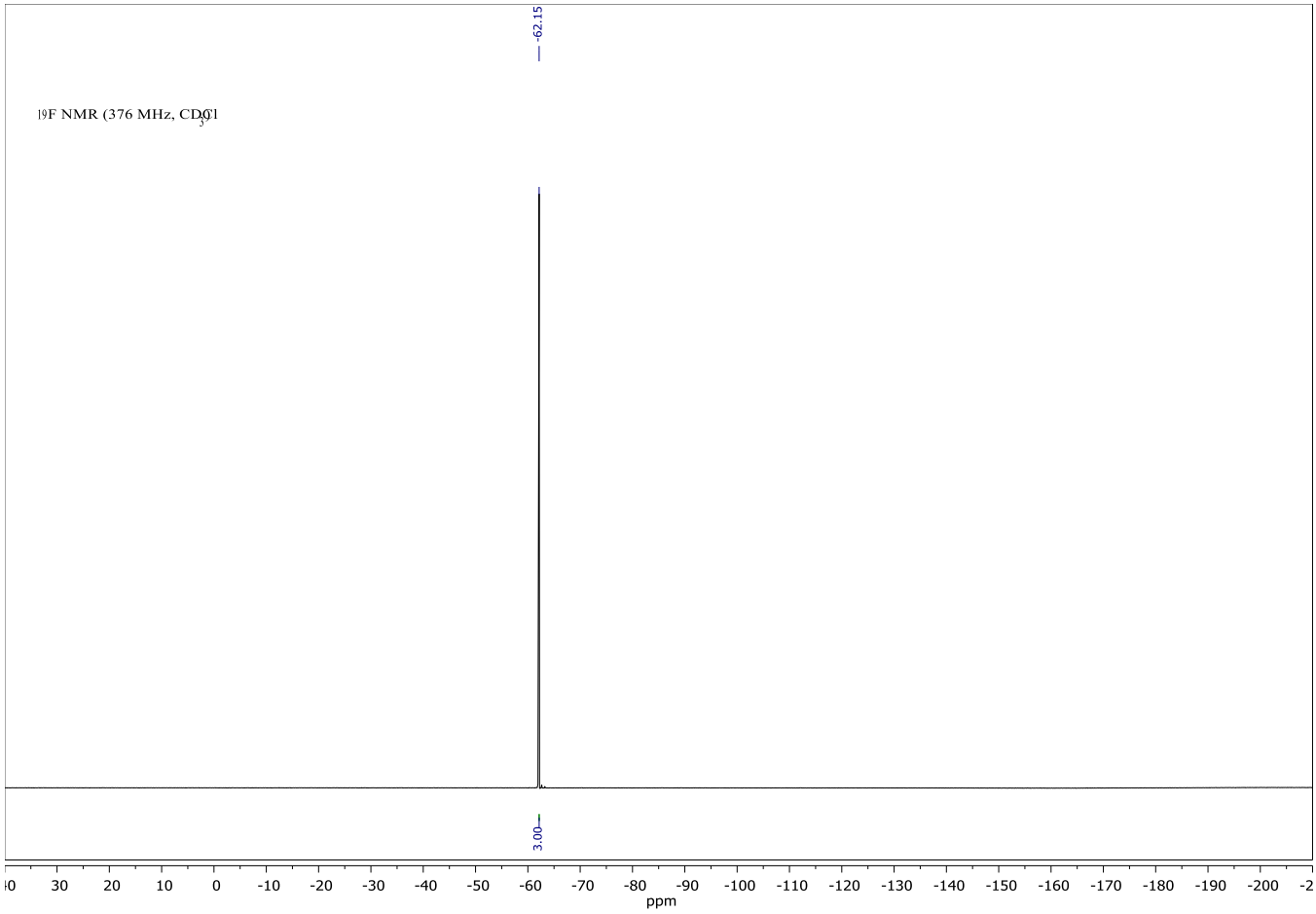
Imino(methyl)(thiazol-2-yl)- λ^6-sulfanone (1aq)



(4-Methoxyphenyl)(methyl)((4-(trifluoromethyl)phenyl)imino)-λ^6-sulfanone (3a)

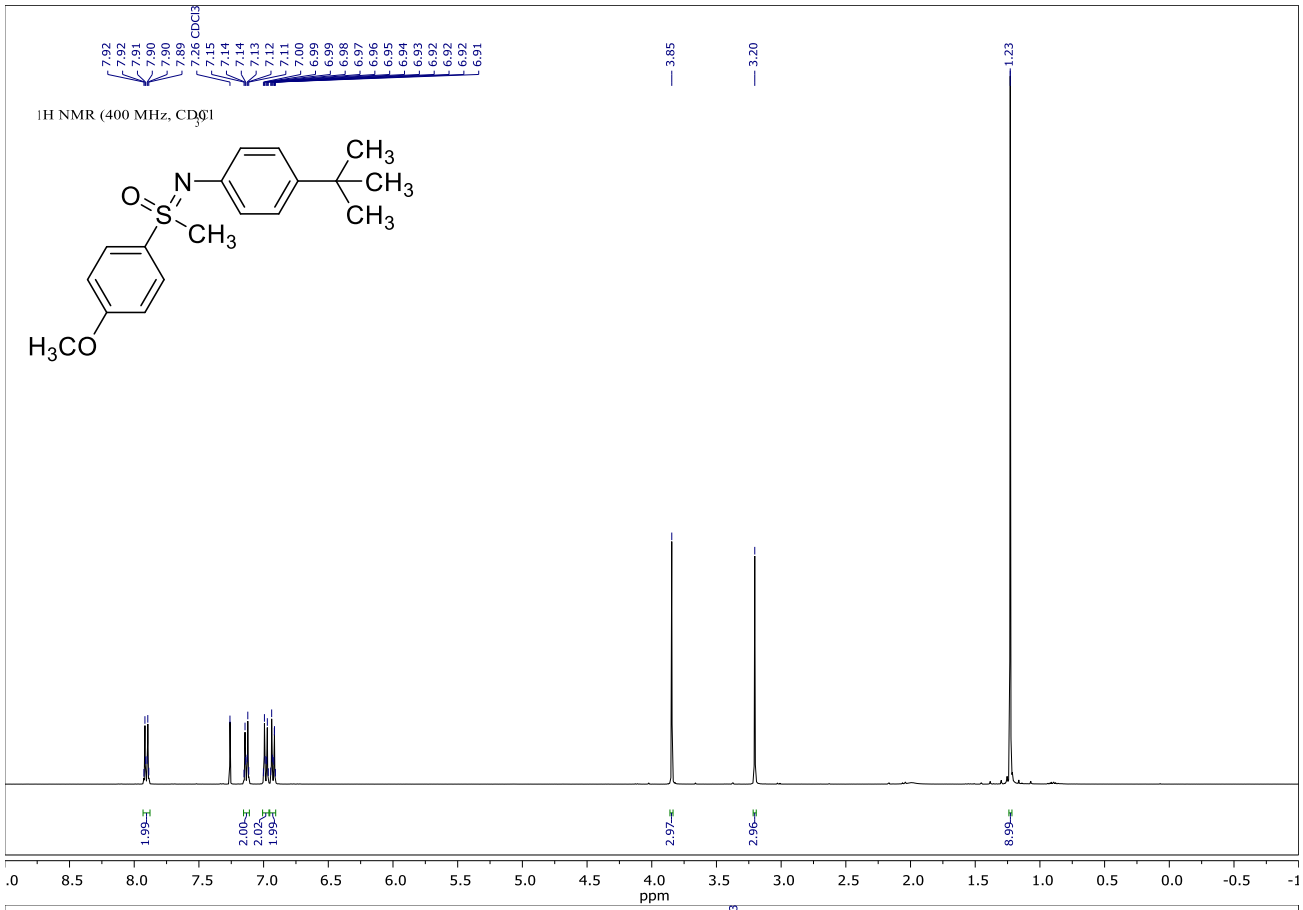


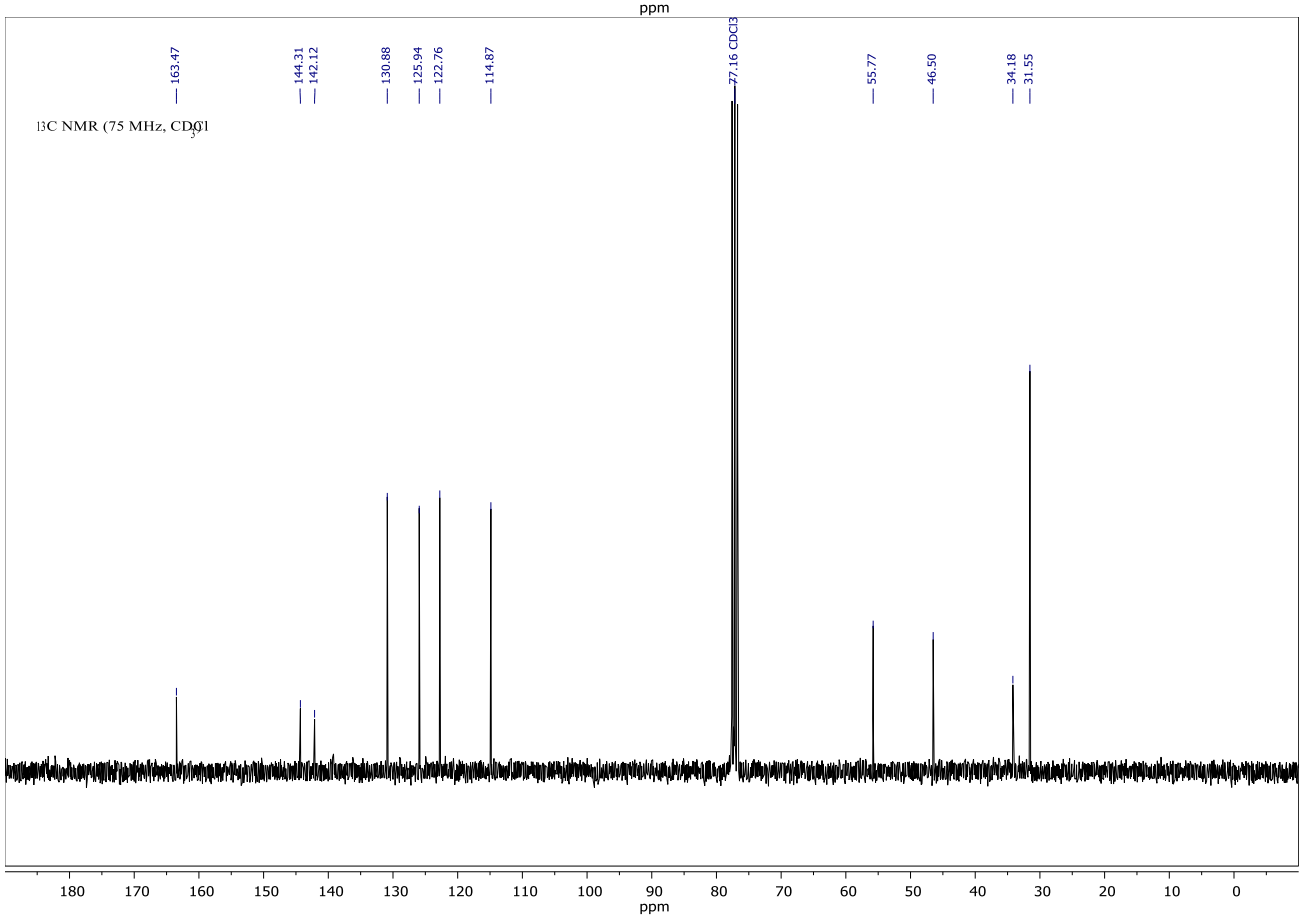




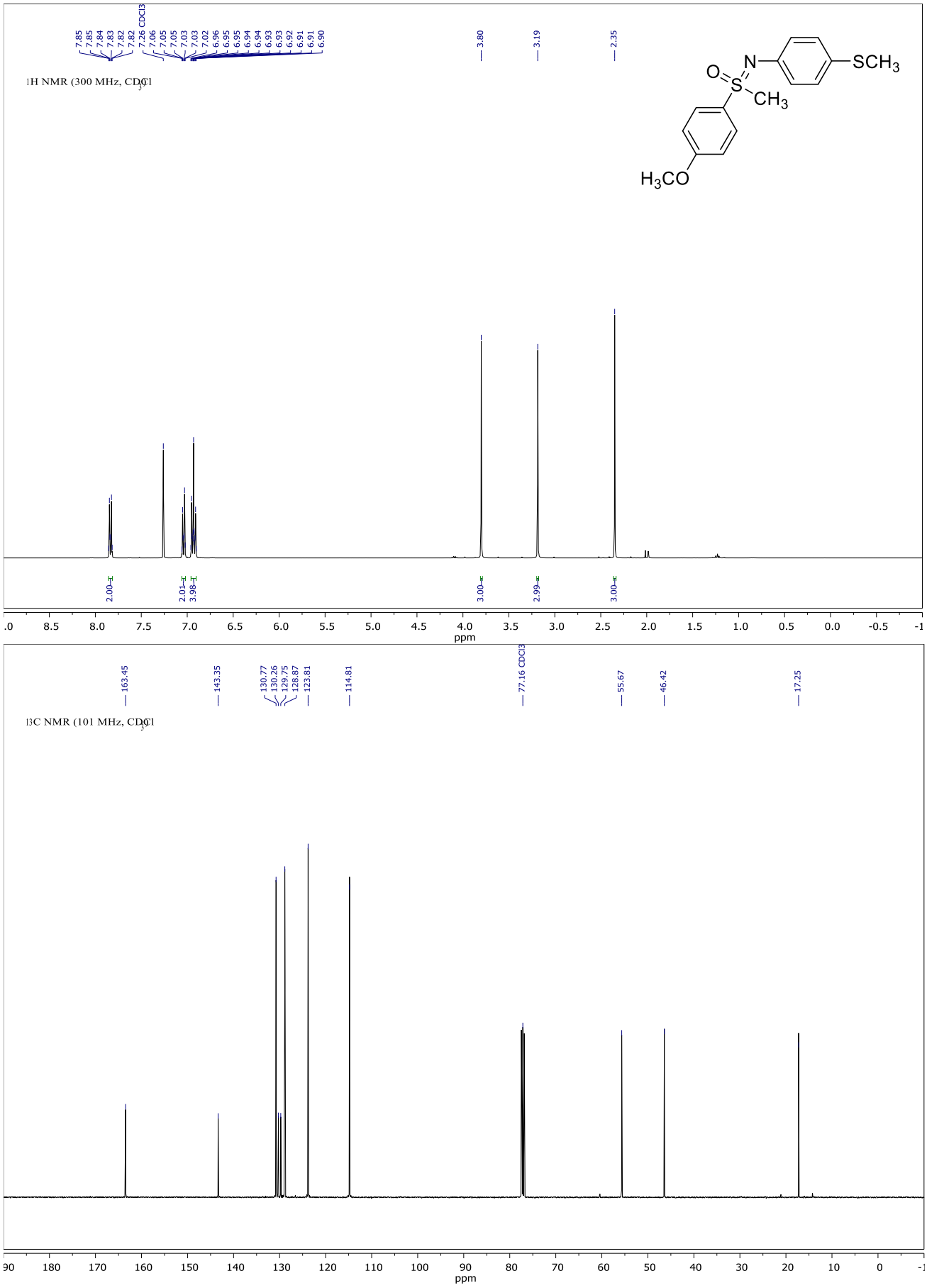
^{19}F NMR (376 MHz, $CDCl_3$)

((4-(*tert*-Butyl)phenyl)imino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (3b)

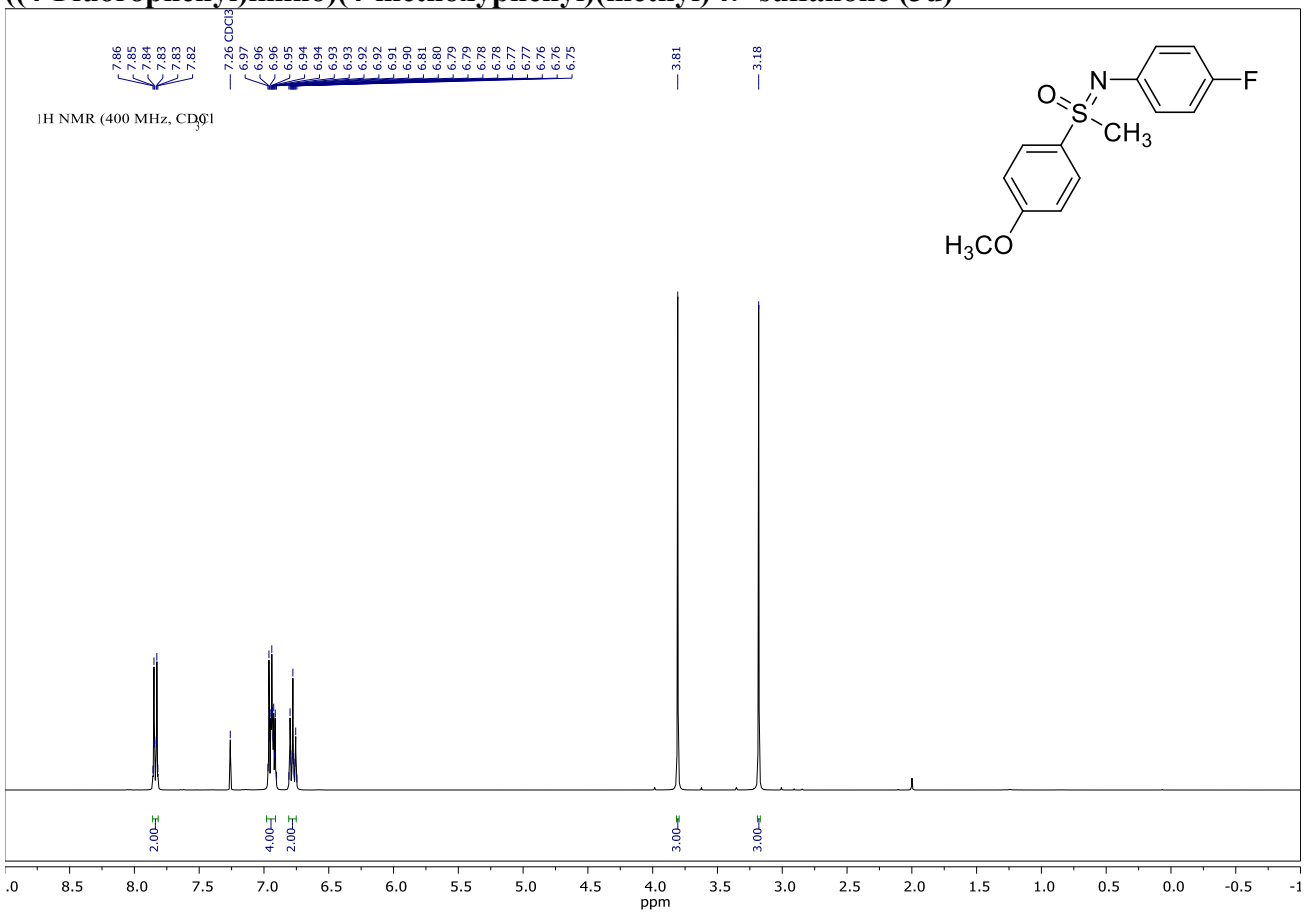




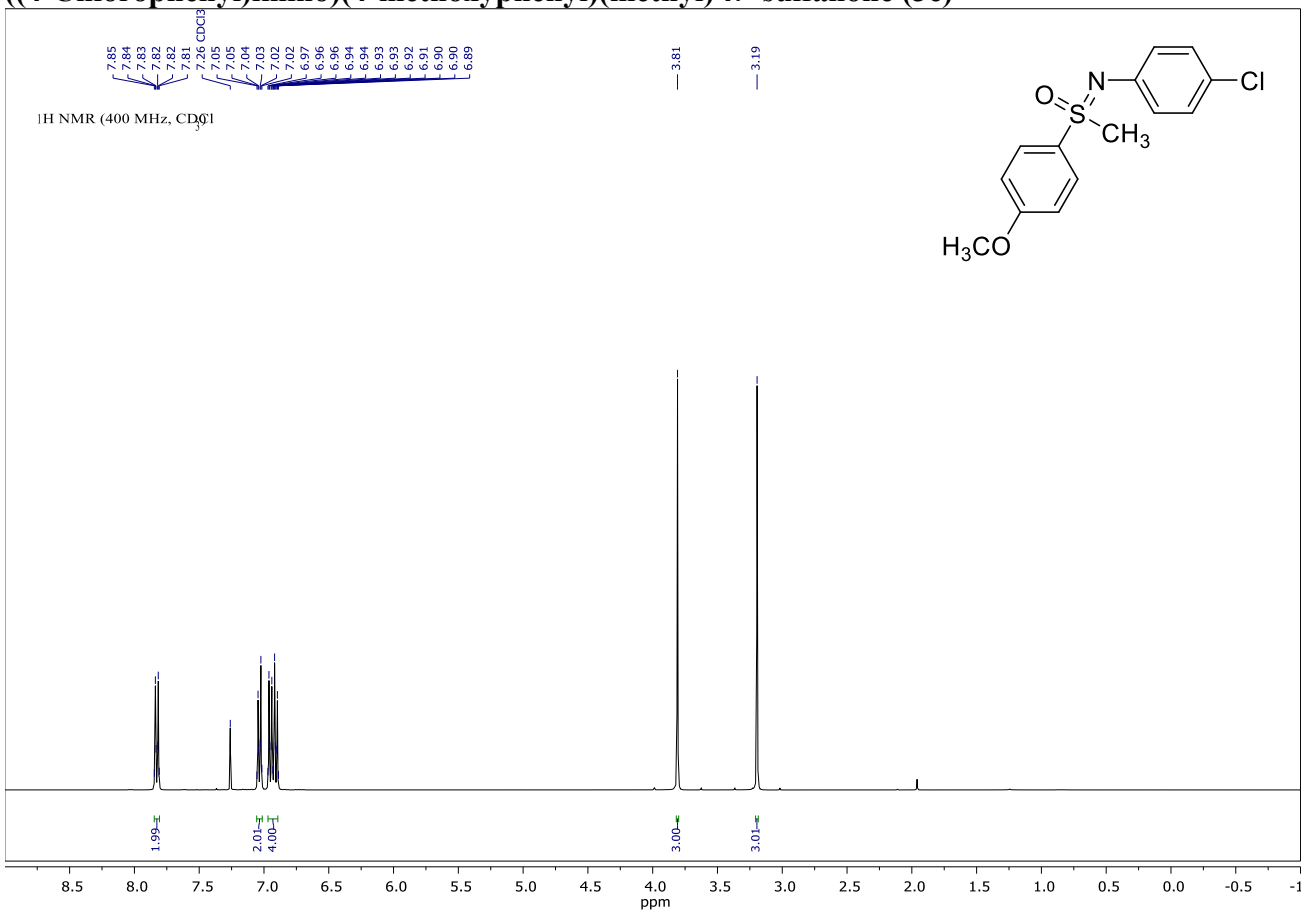
(4-Methoxyphenyl)(methyl)((4-(methylthio)phenyl)imino)-λ^6-sulfanone (3c)



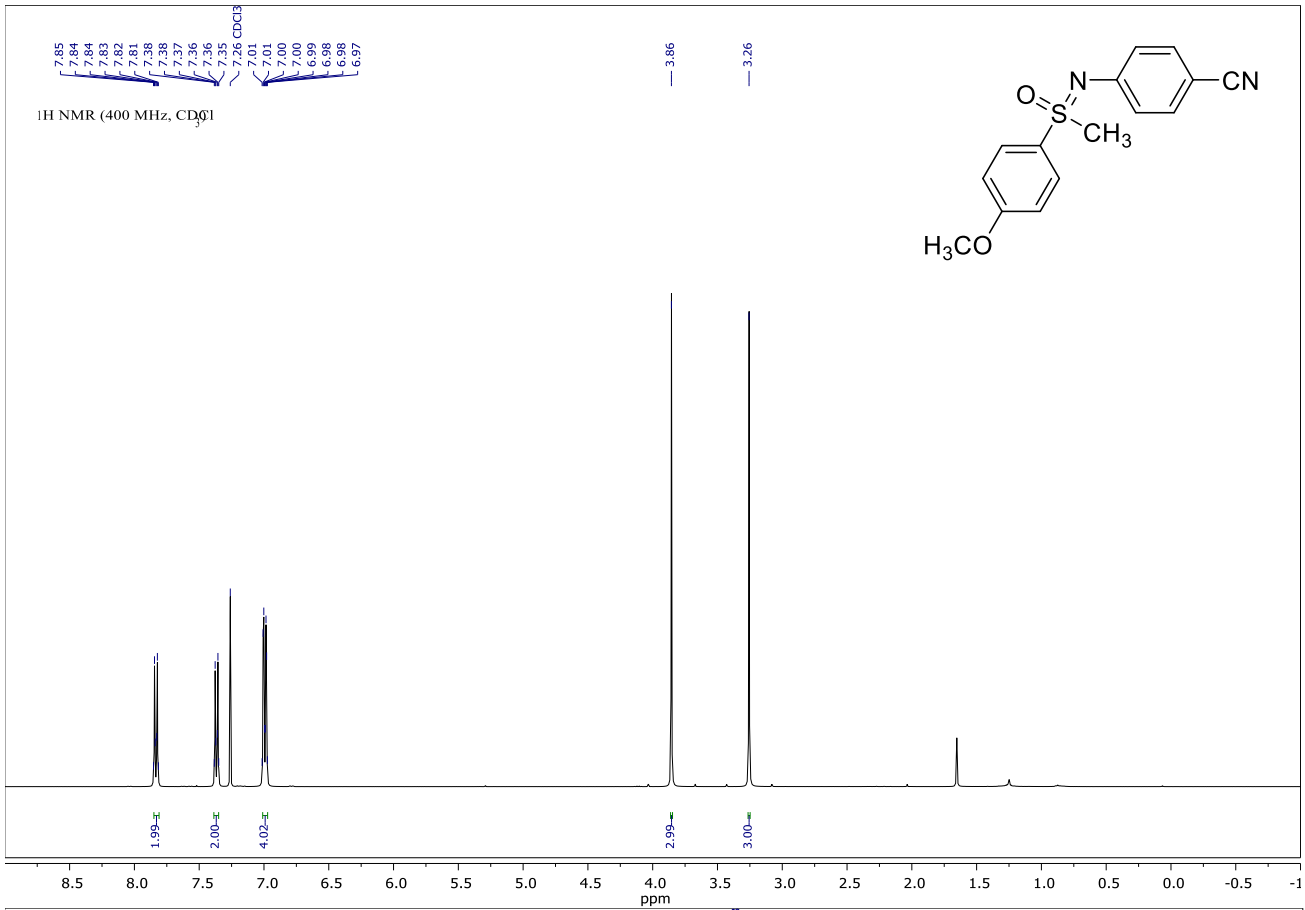
((4-Fluorophenyl)imino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (3d)

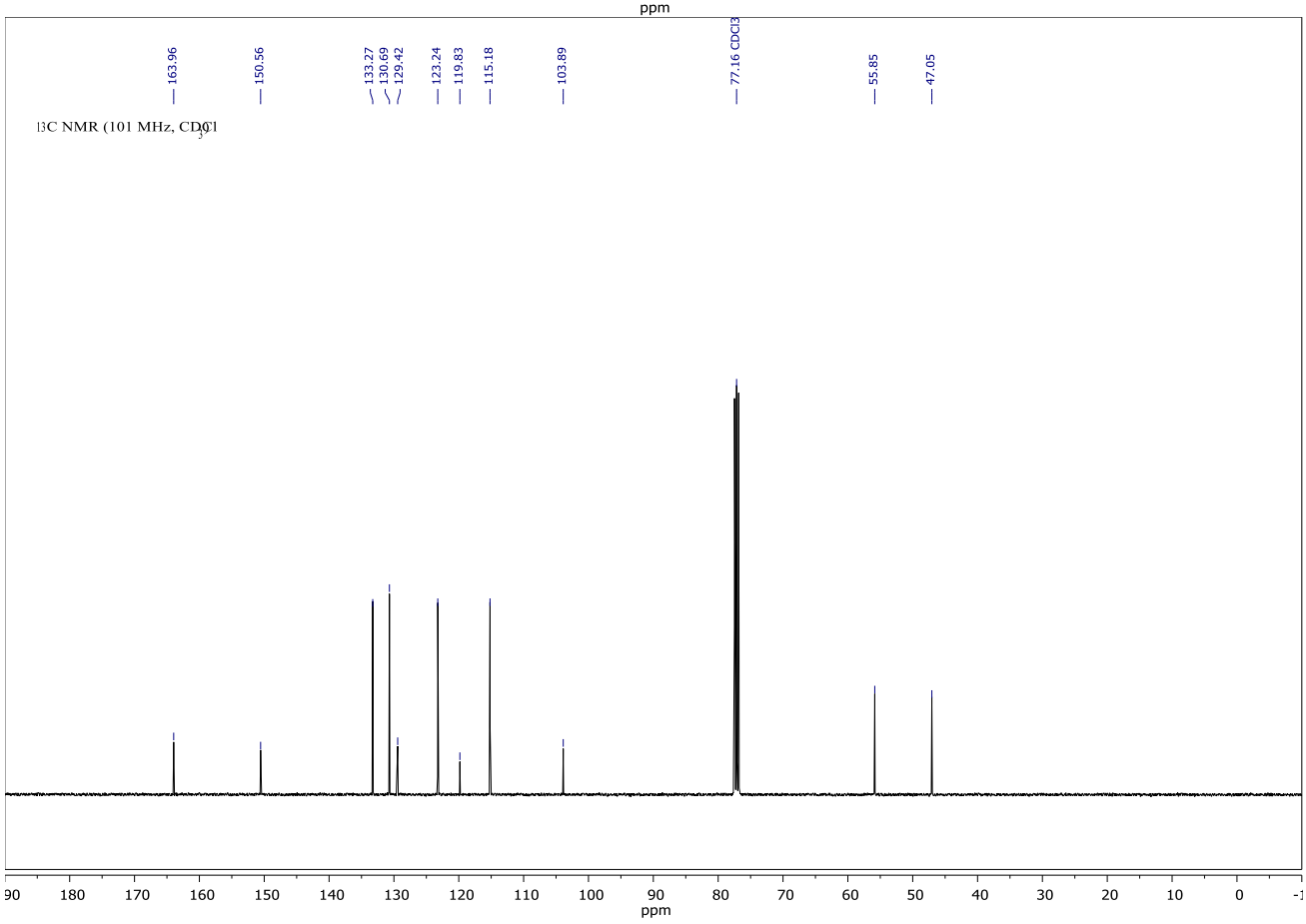


((4-Chlorophenyl)imino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (3e)

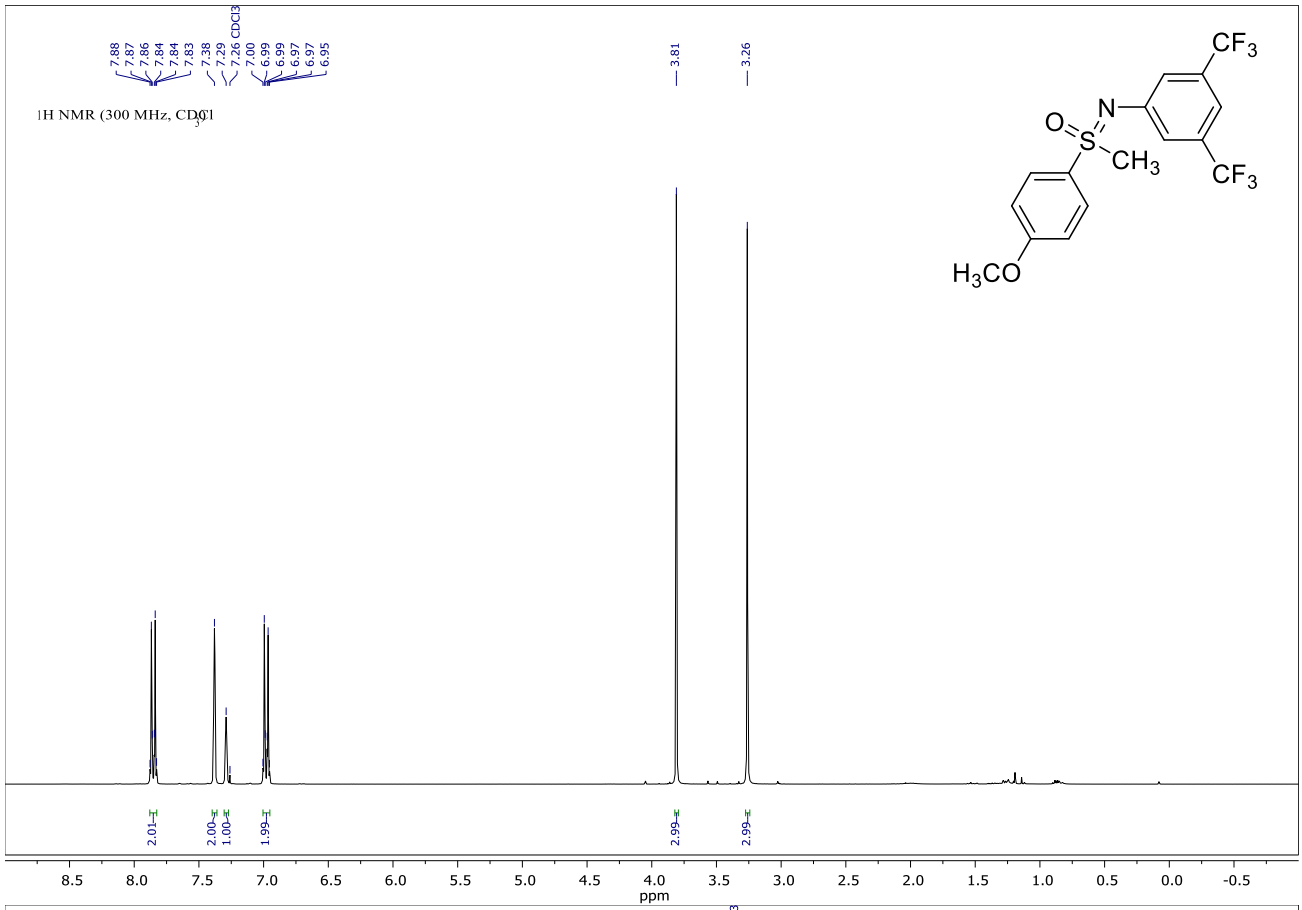


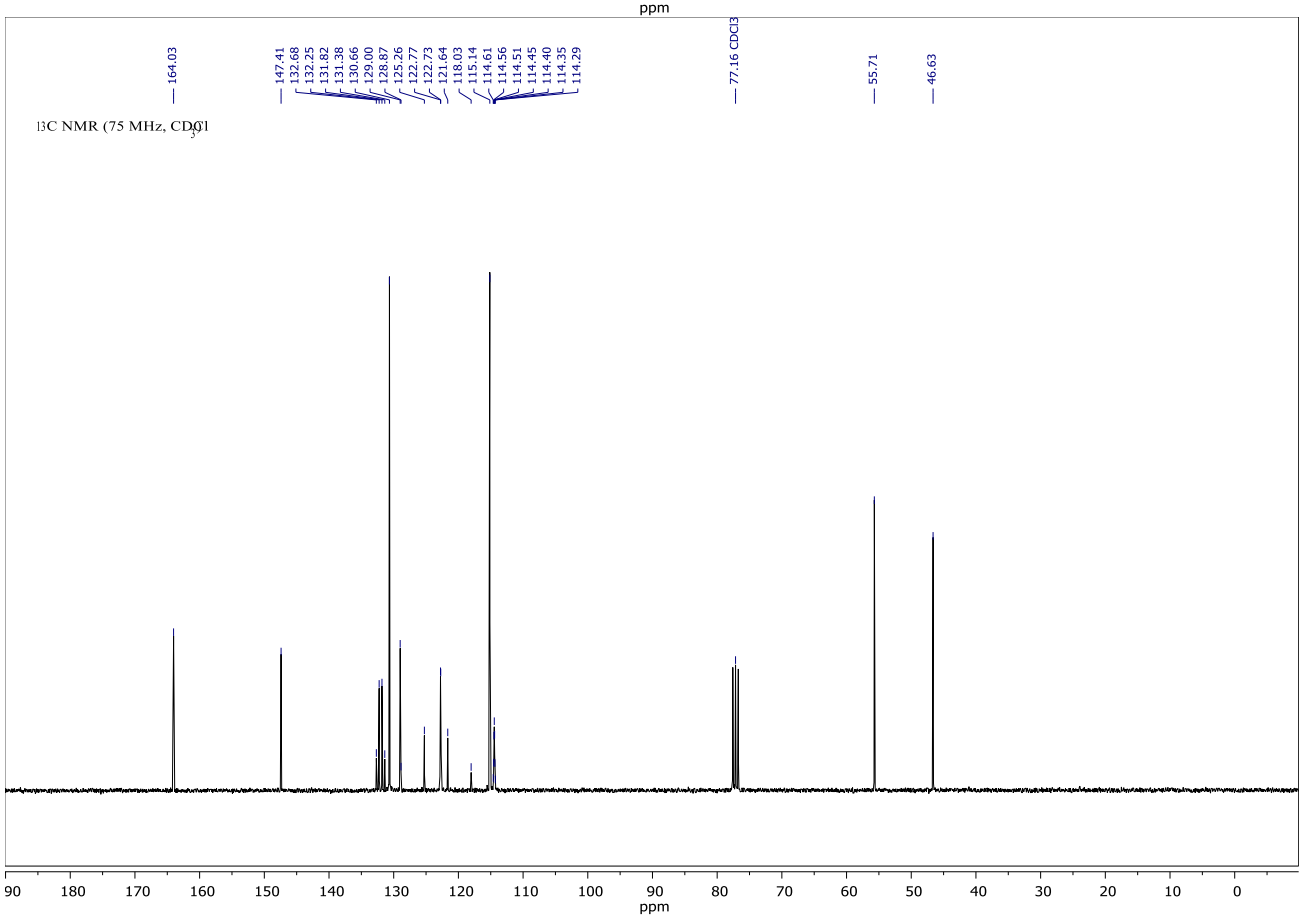
4-(((4-Methoxyphenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)benzonitrile (3f)

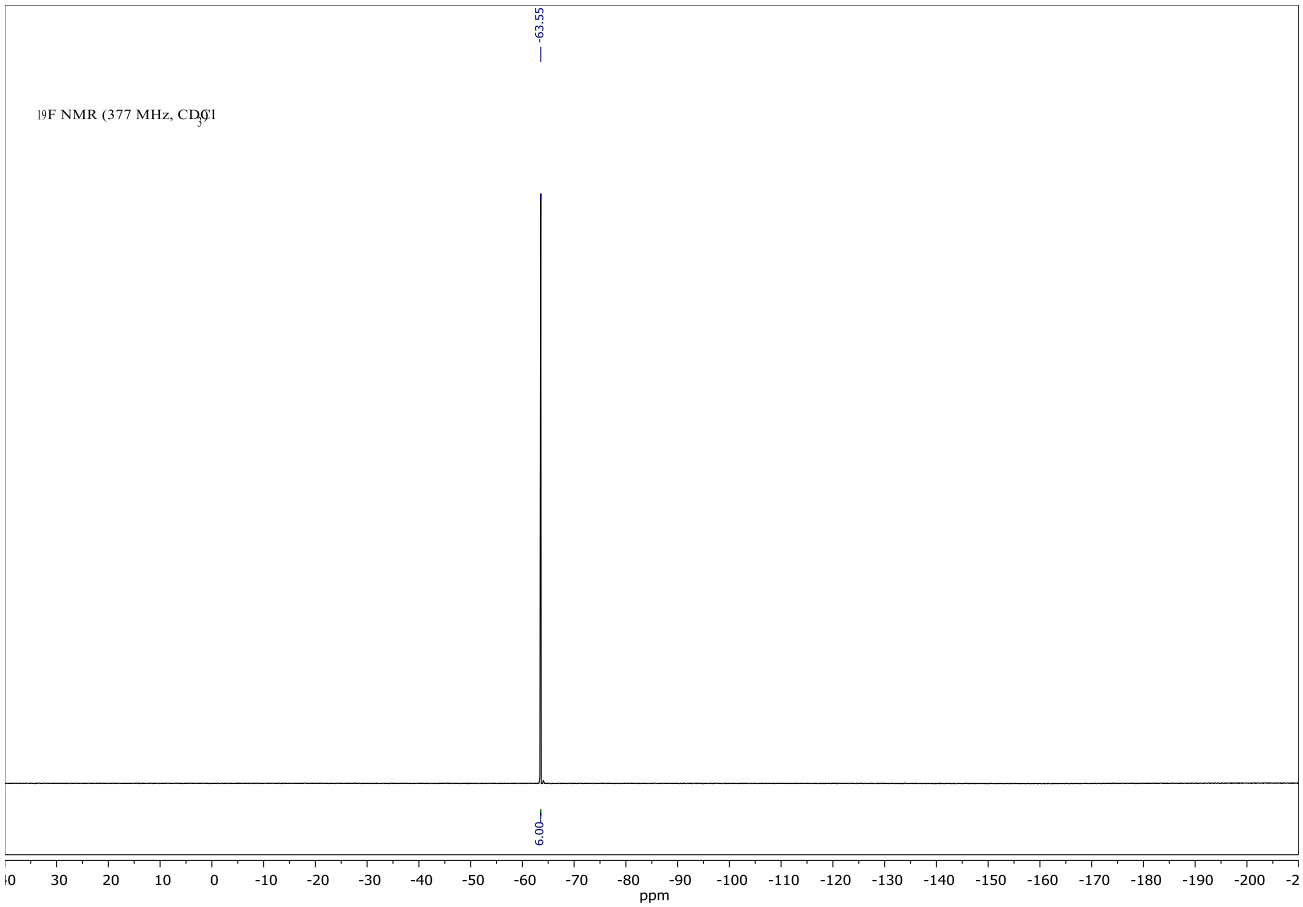




((3,5-Bis(trifluoromethyl)phenyl)imino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (3g)



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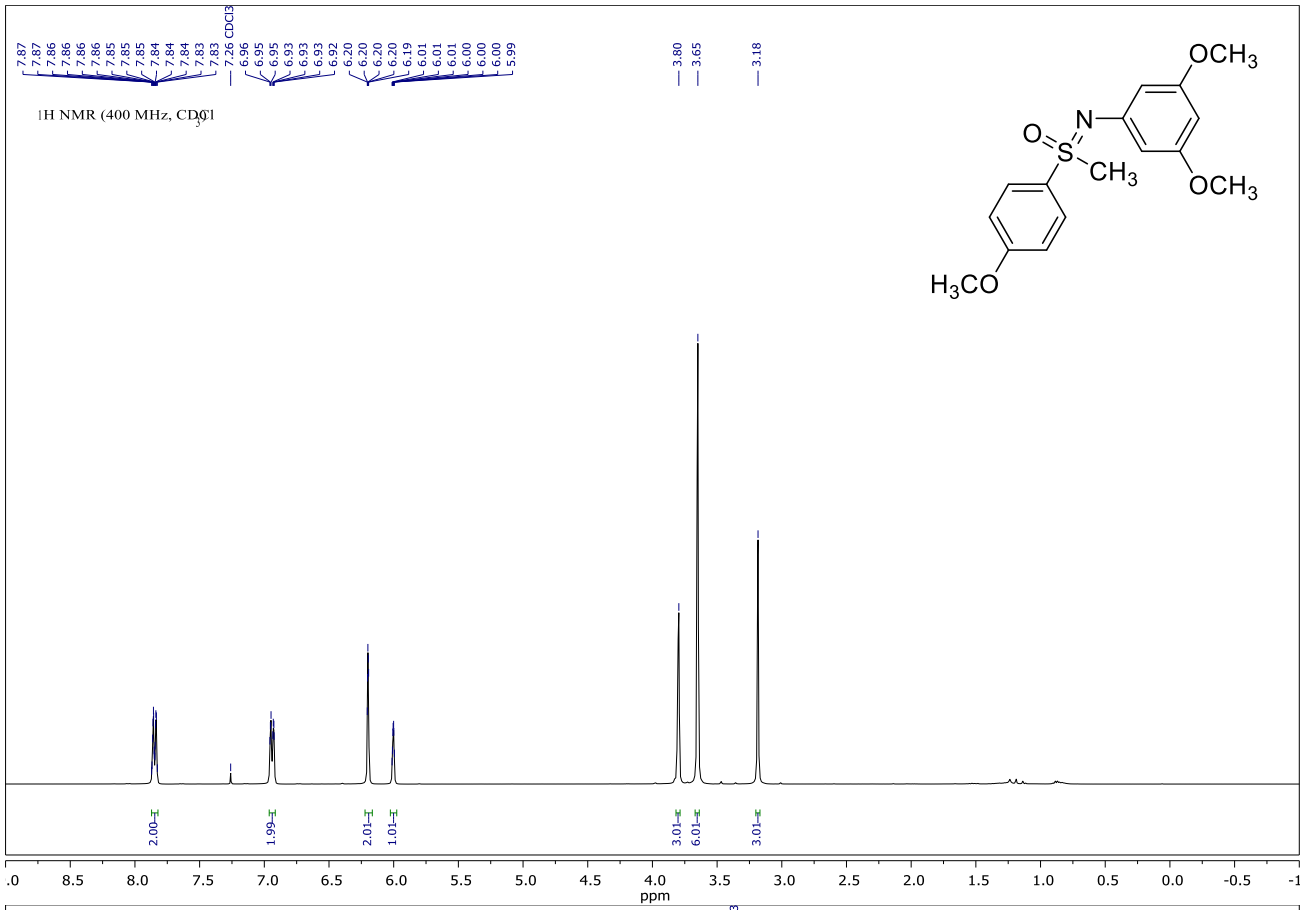
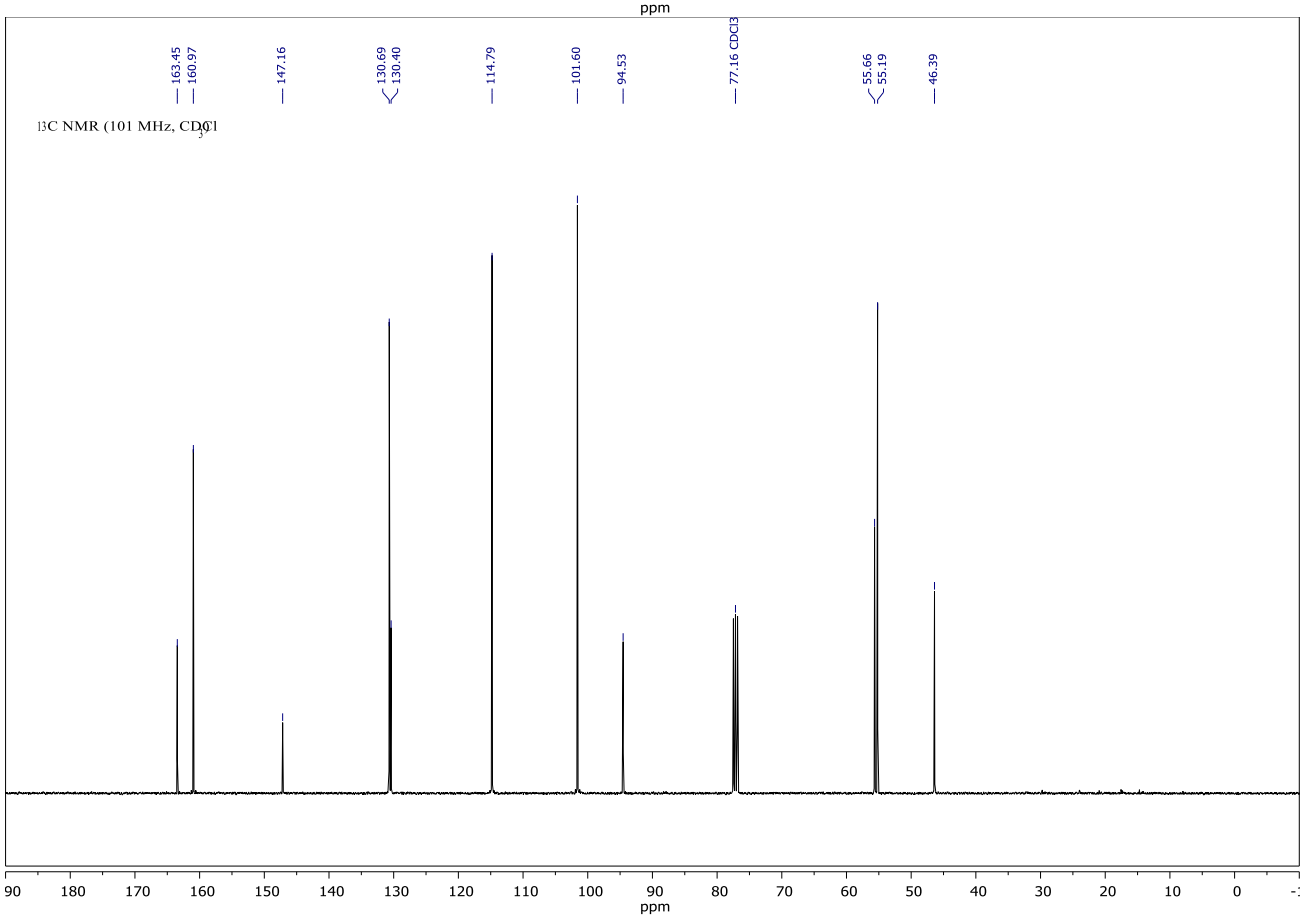
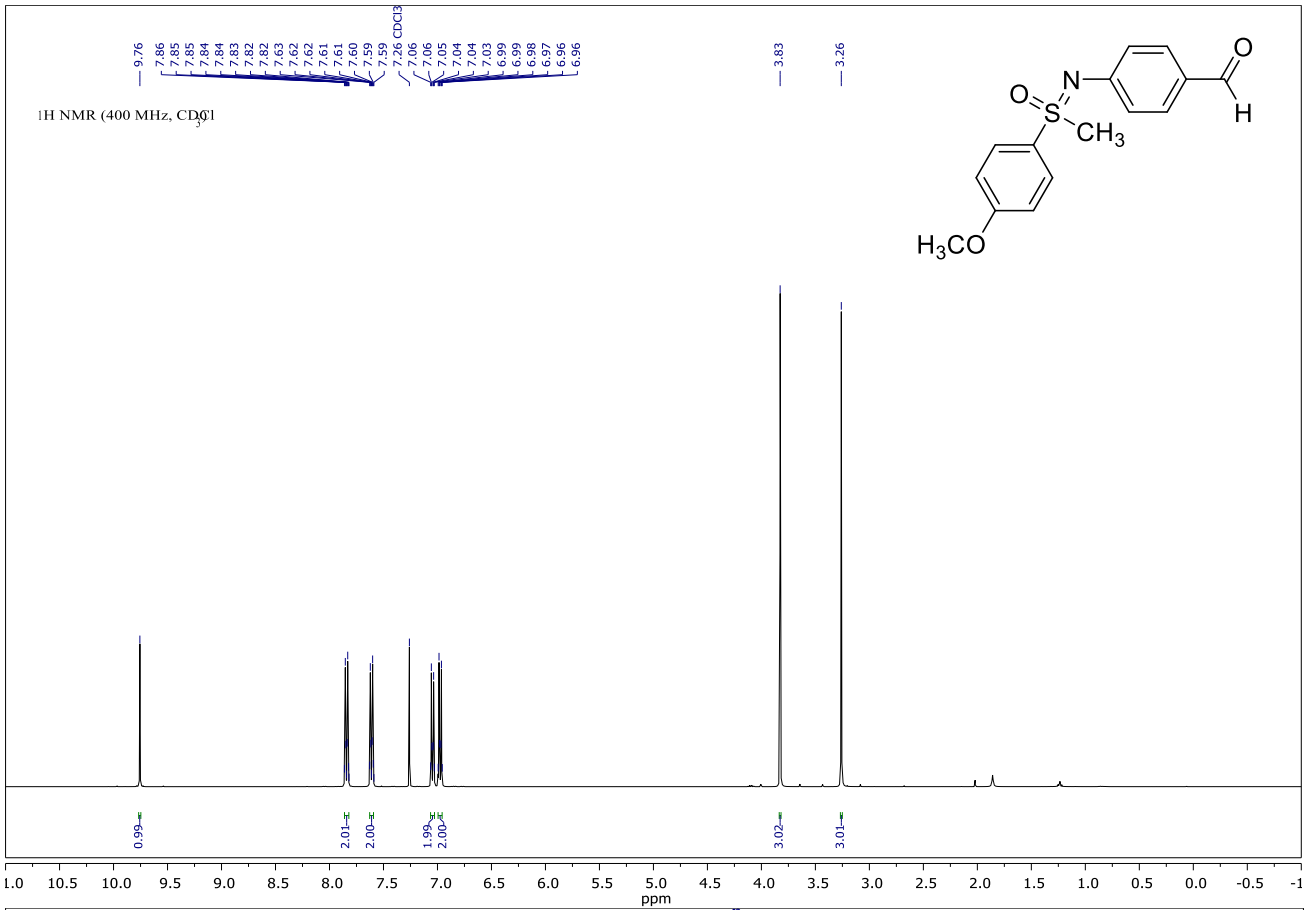
19F NMR (377 MHz, CDCl3)
6.00
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
ppm

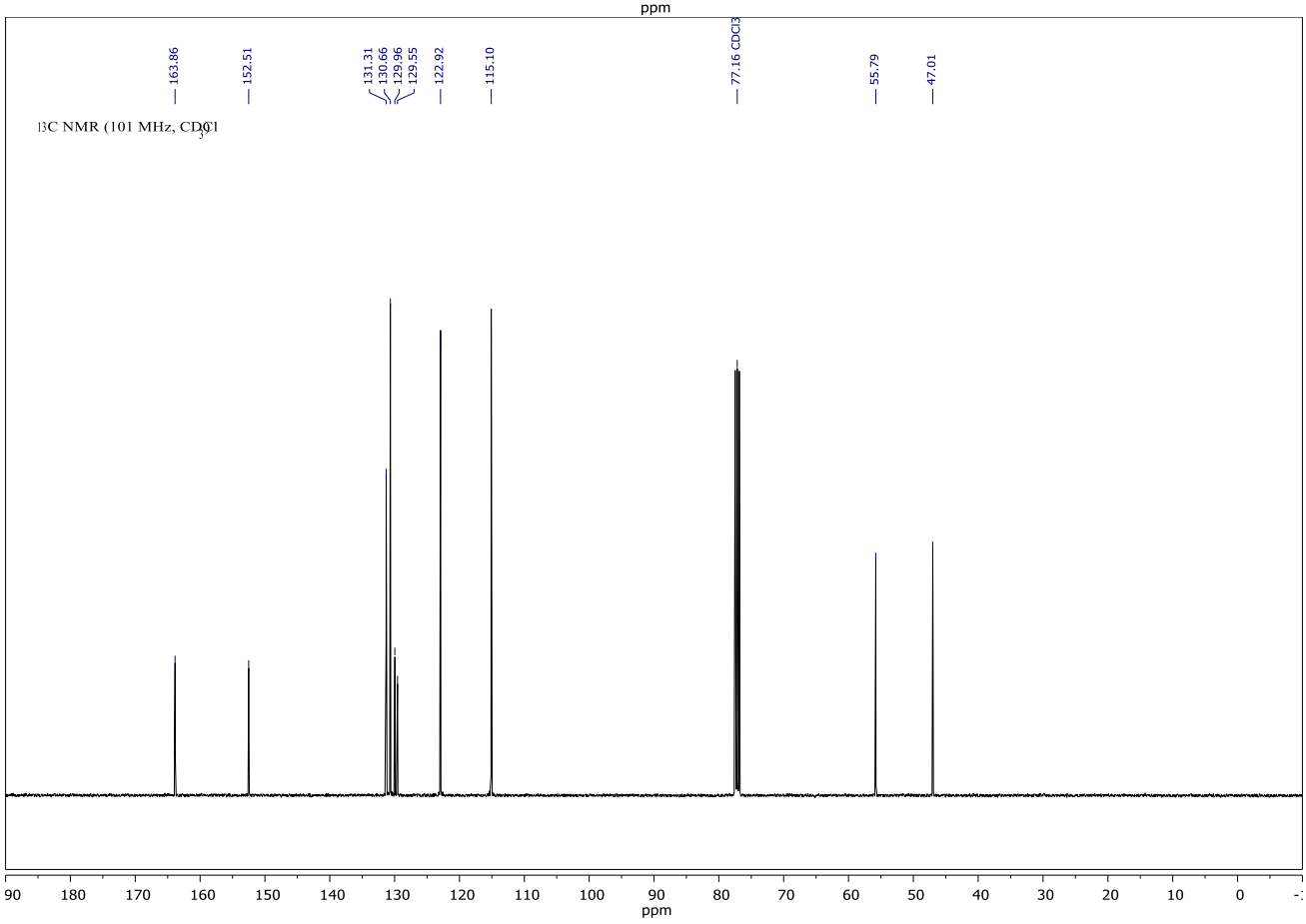
((3,5-Dimethoxyphenyl)imino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (3h)



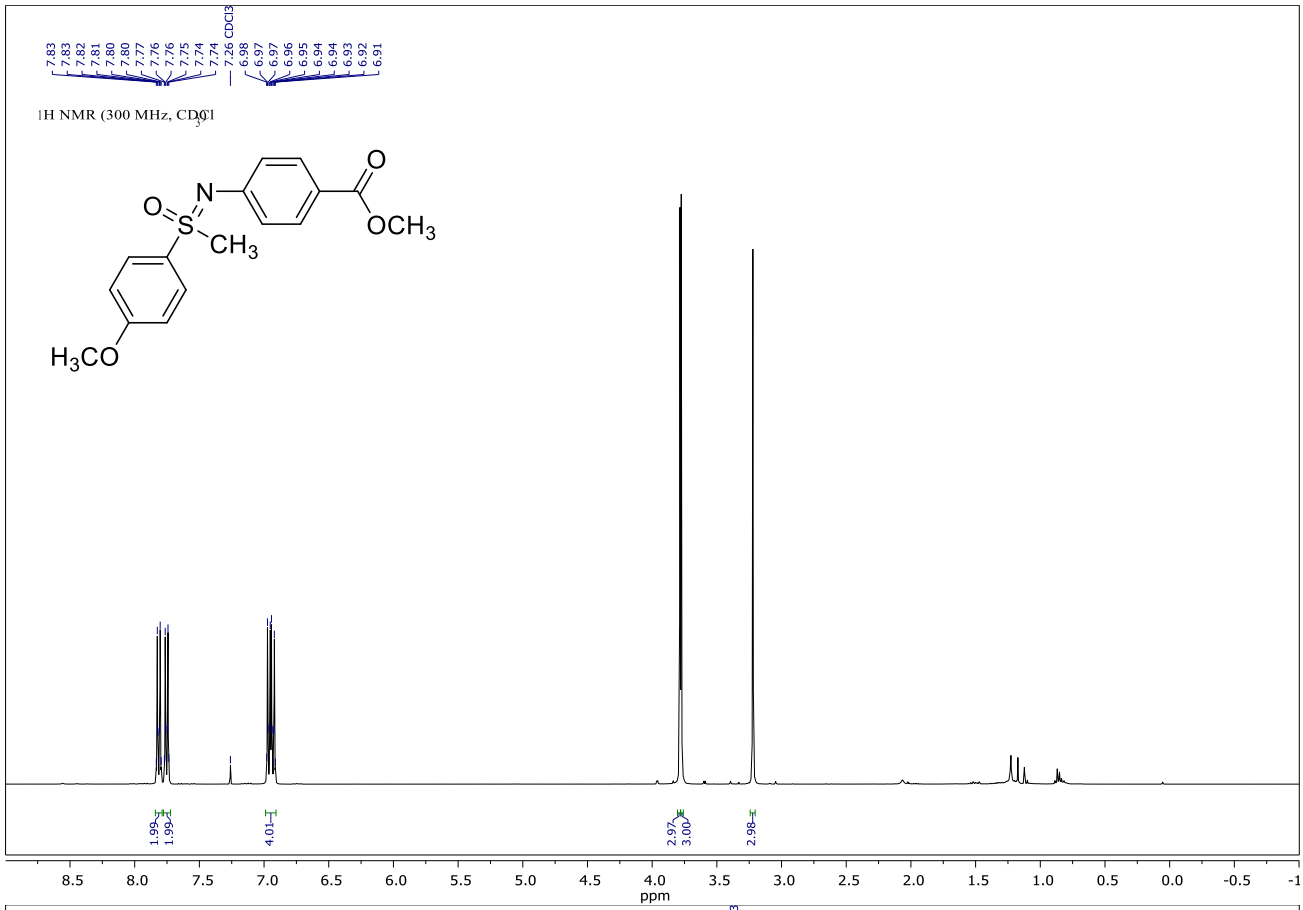


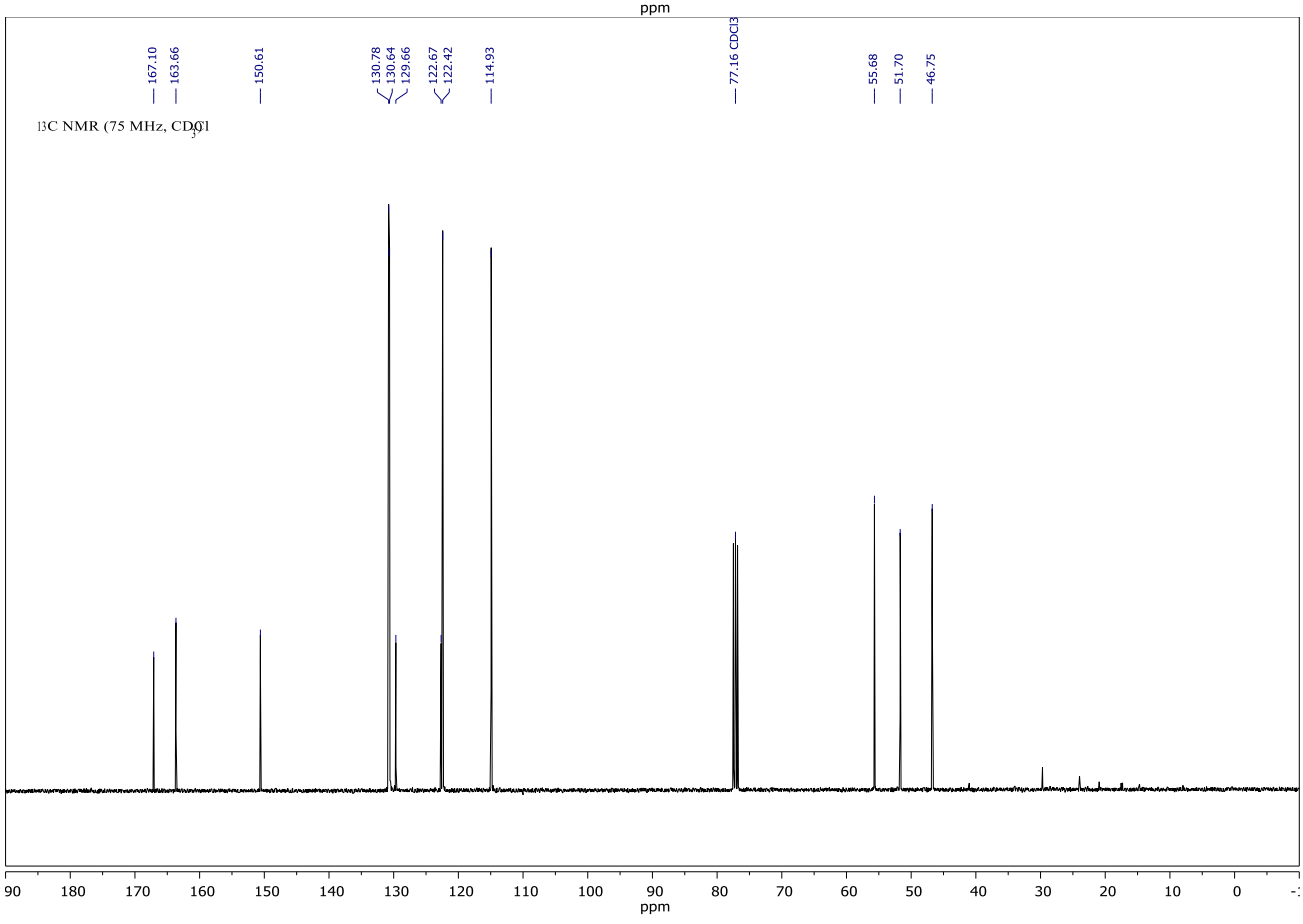
4-(((4-Methoxyphenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)benzaldehyde (3i)



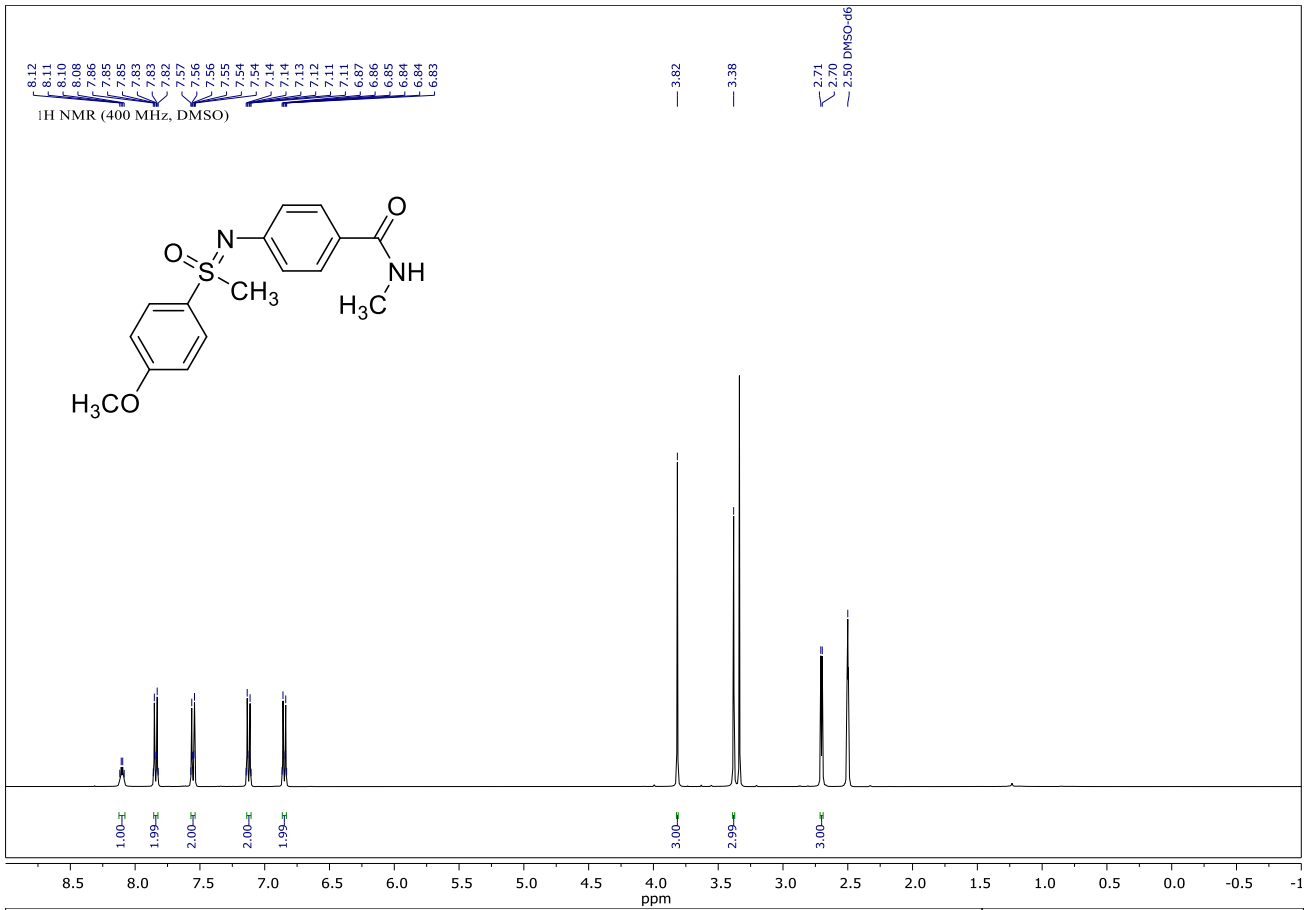


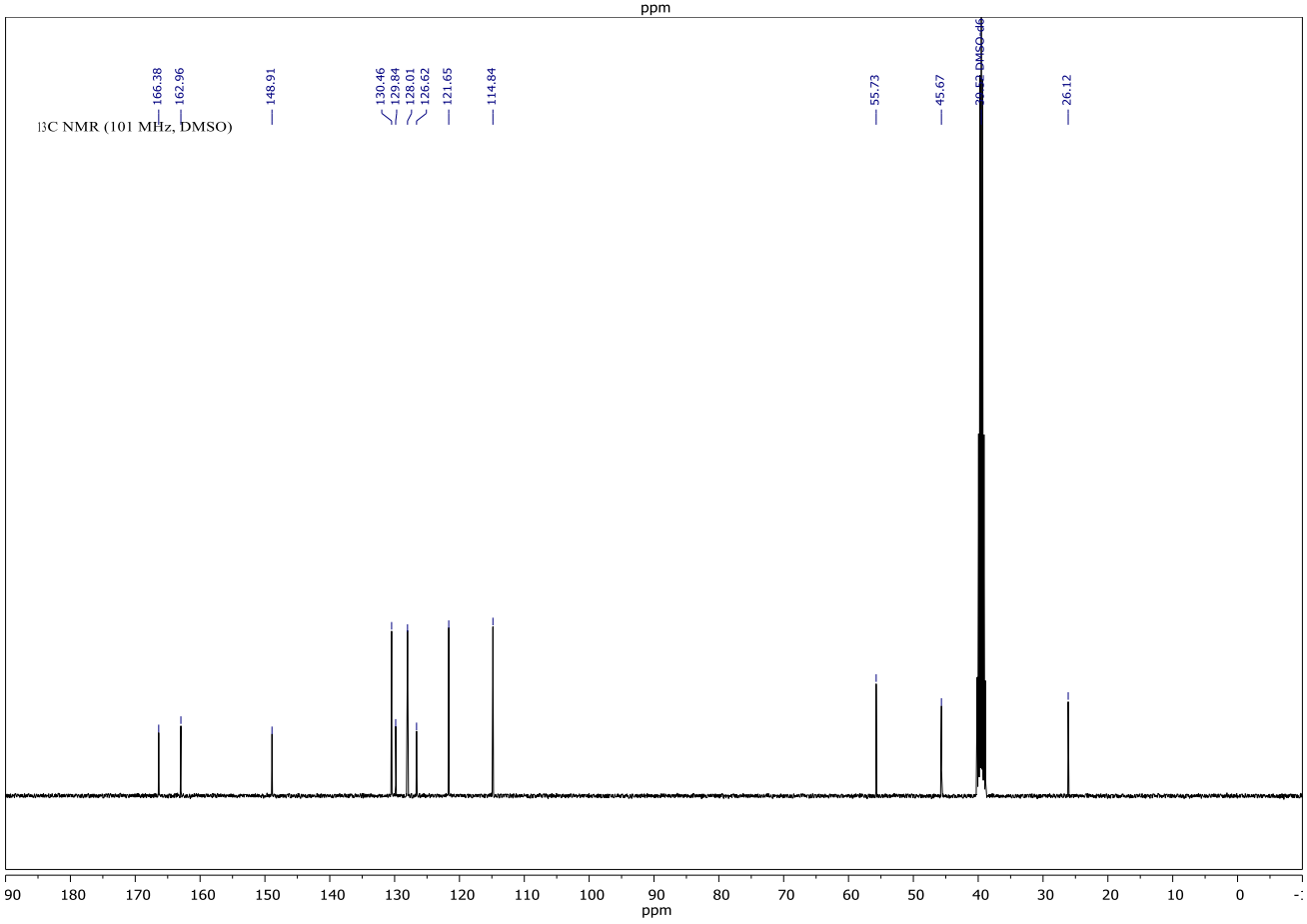
Methyl 4-(((4-methoxyphenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)benzoate (3j)



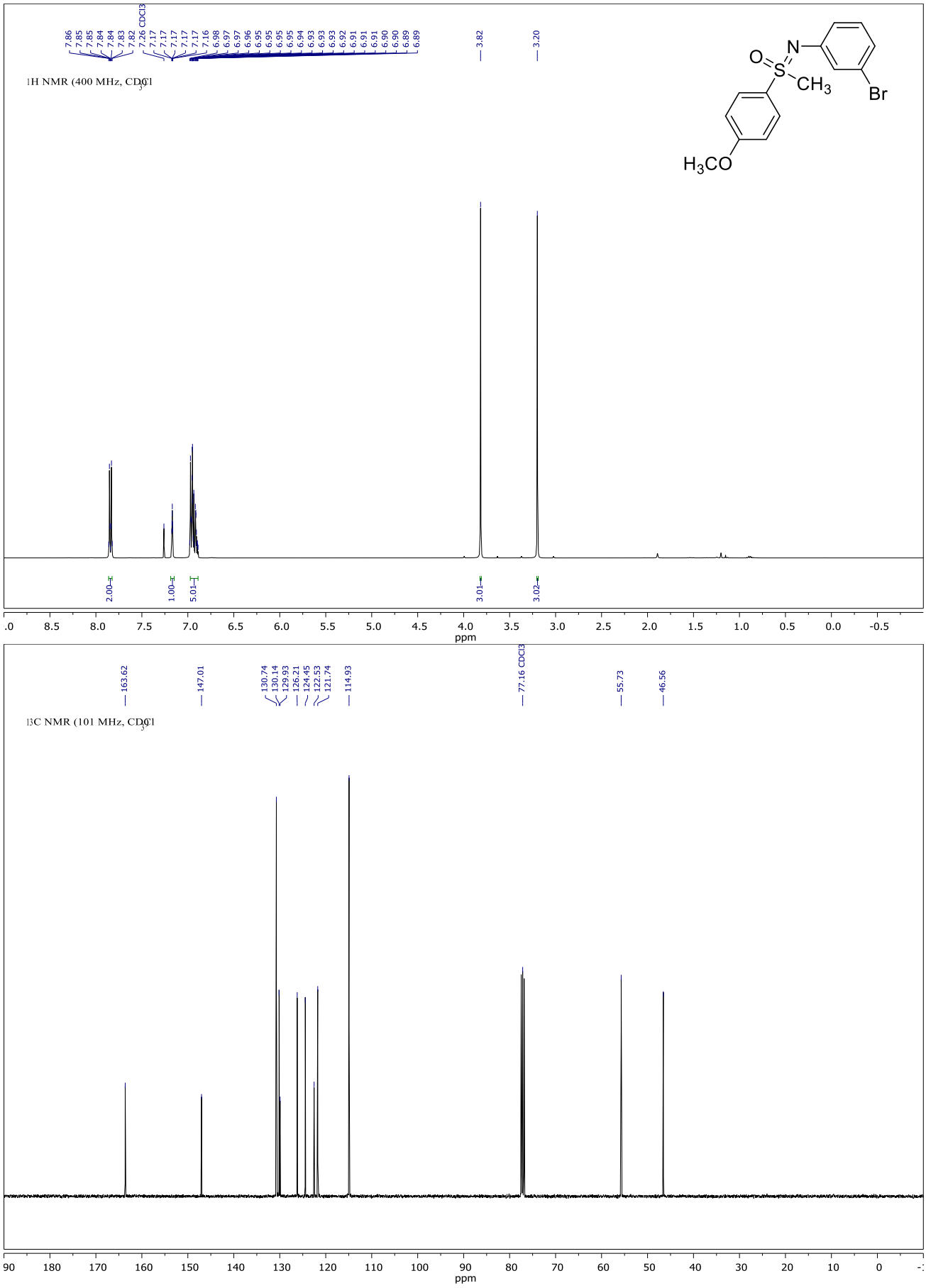


4-(((4-Methoxyphenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)-N-methylbenzamide (3k)

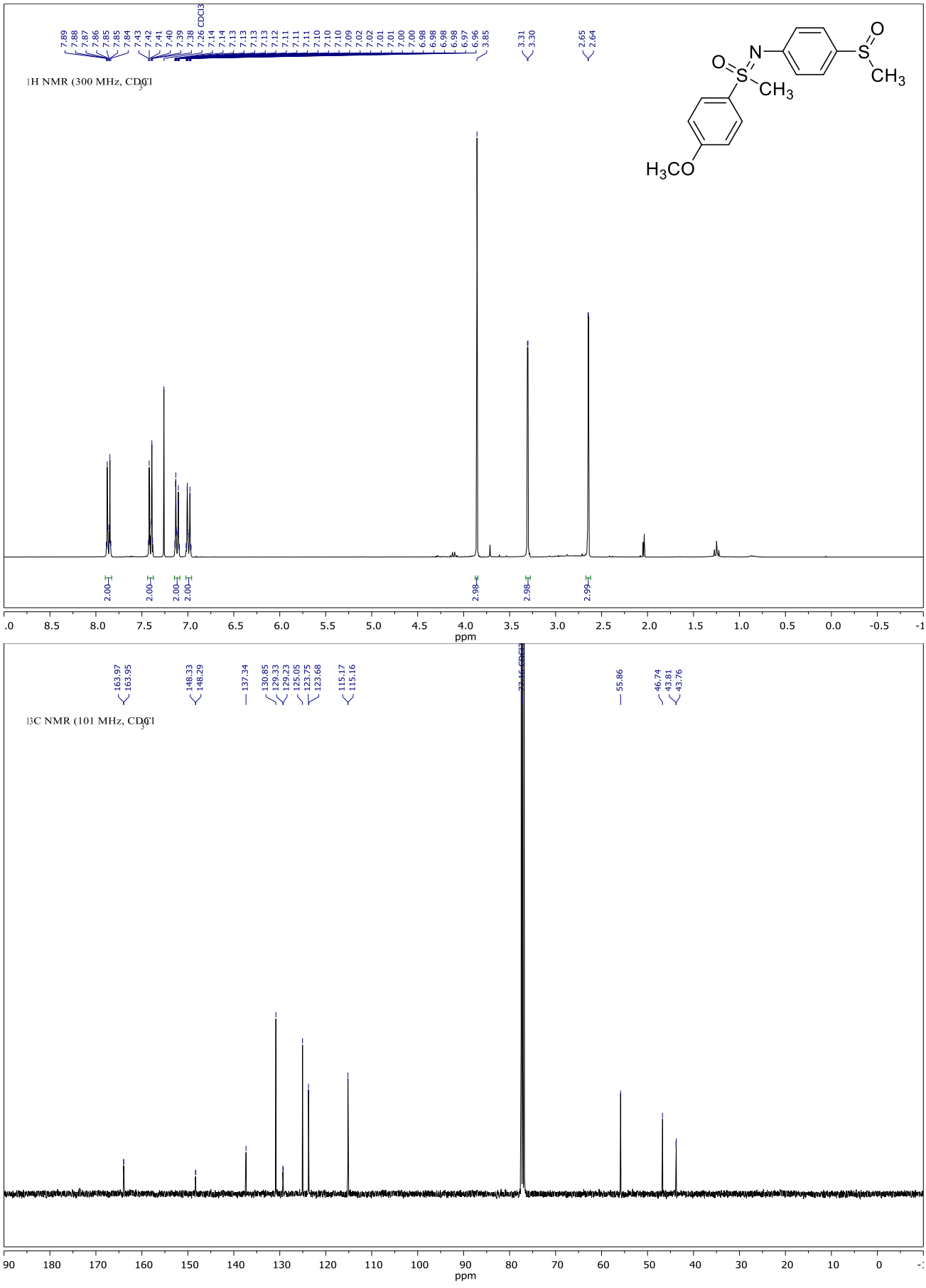




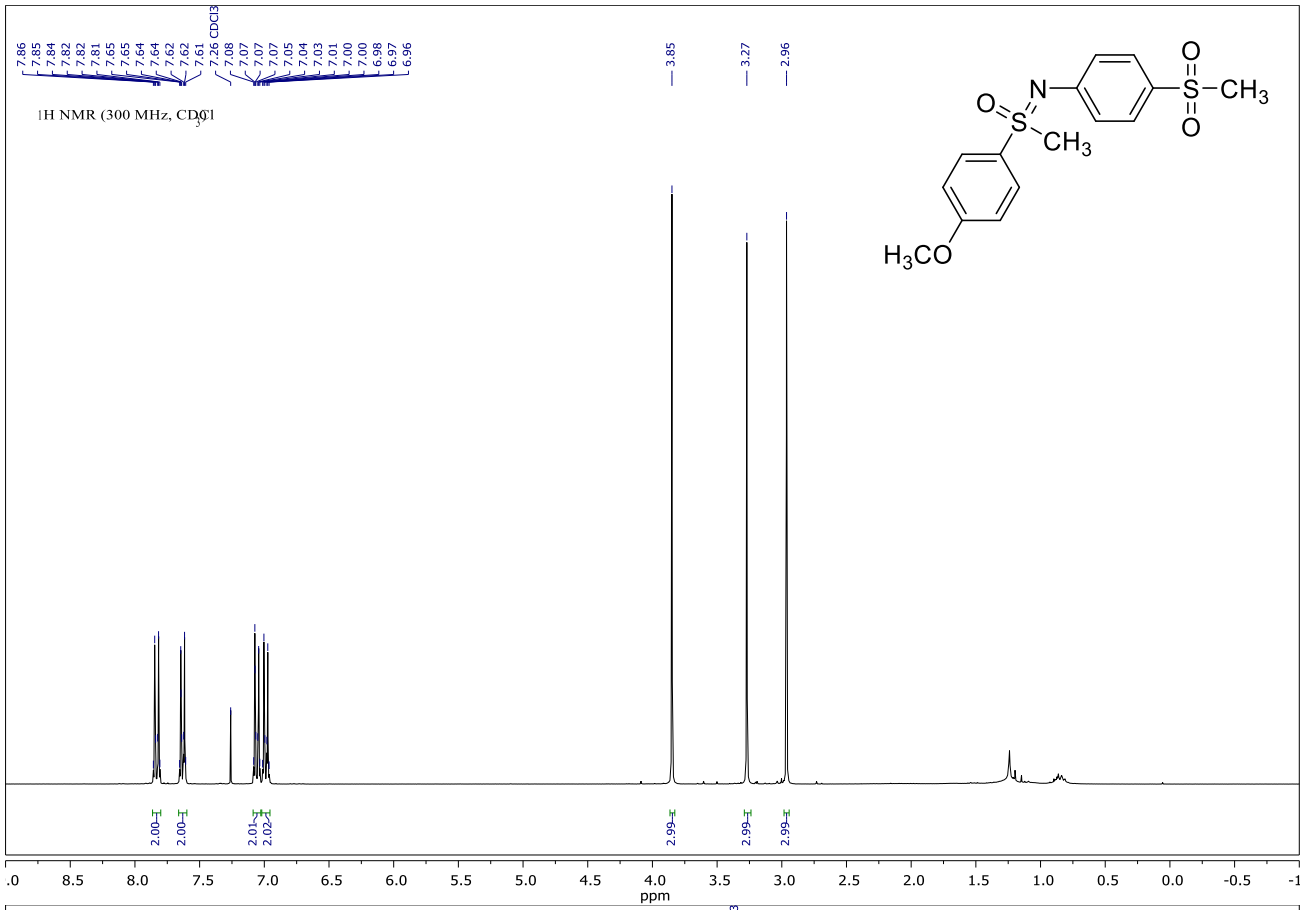
((3-Bromophenyl)imino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (3l)

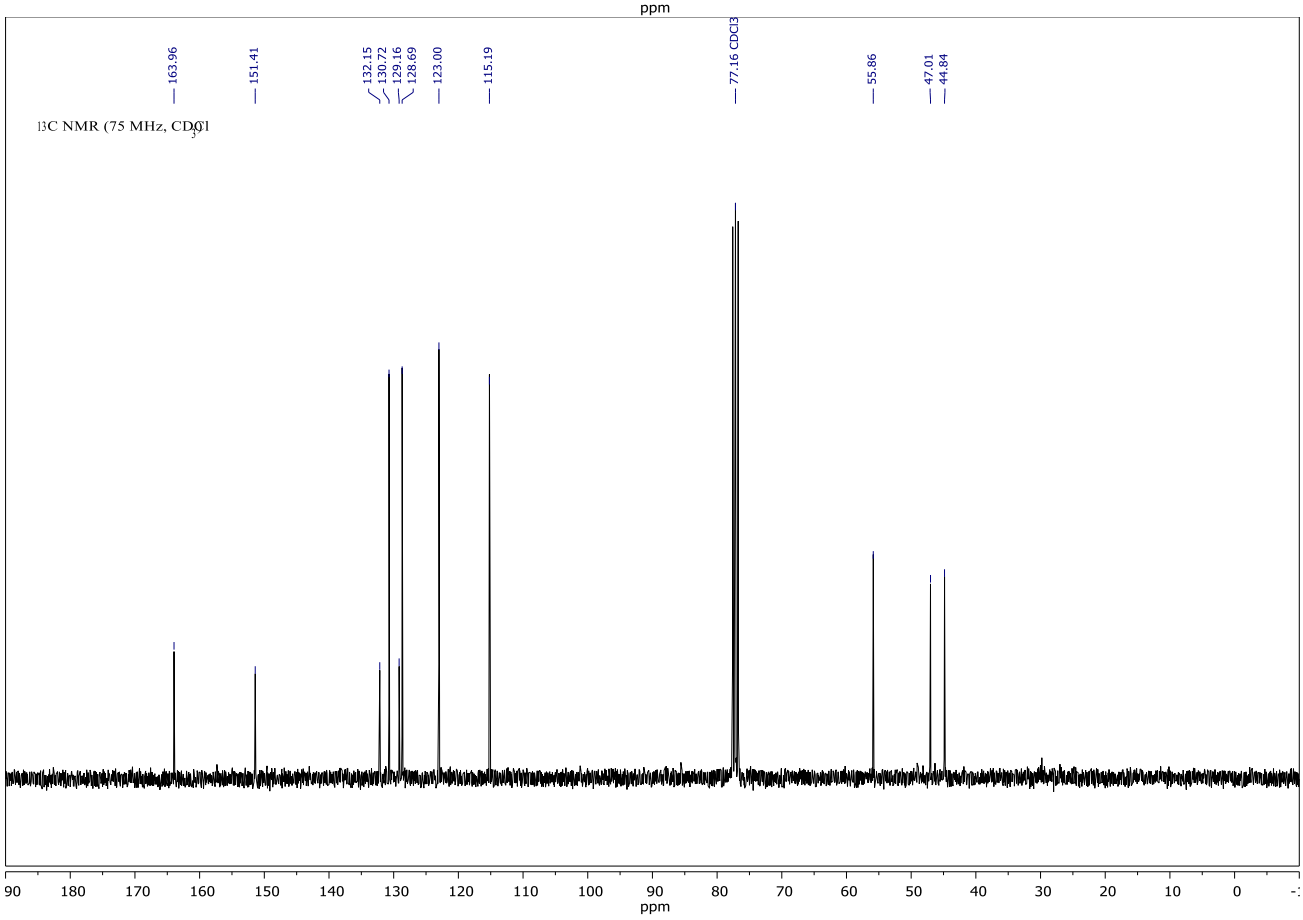


(4-Methoxyphenyl)(methyl)((4-(methylsulfinyl)phenyl)imino)-λ^6-sulfanone (3m)

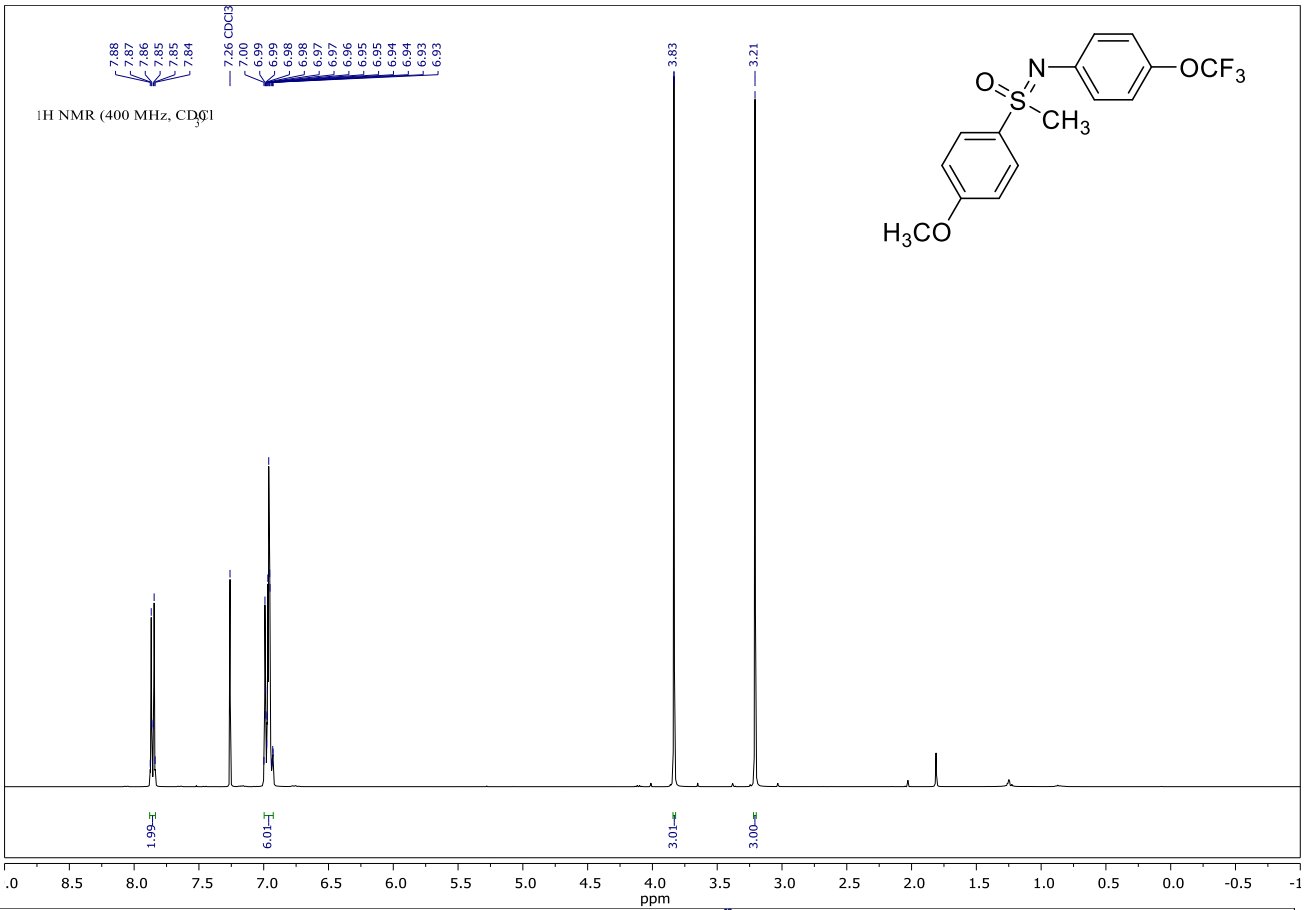


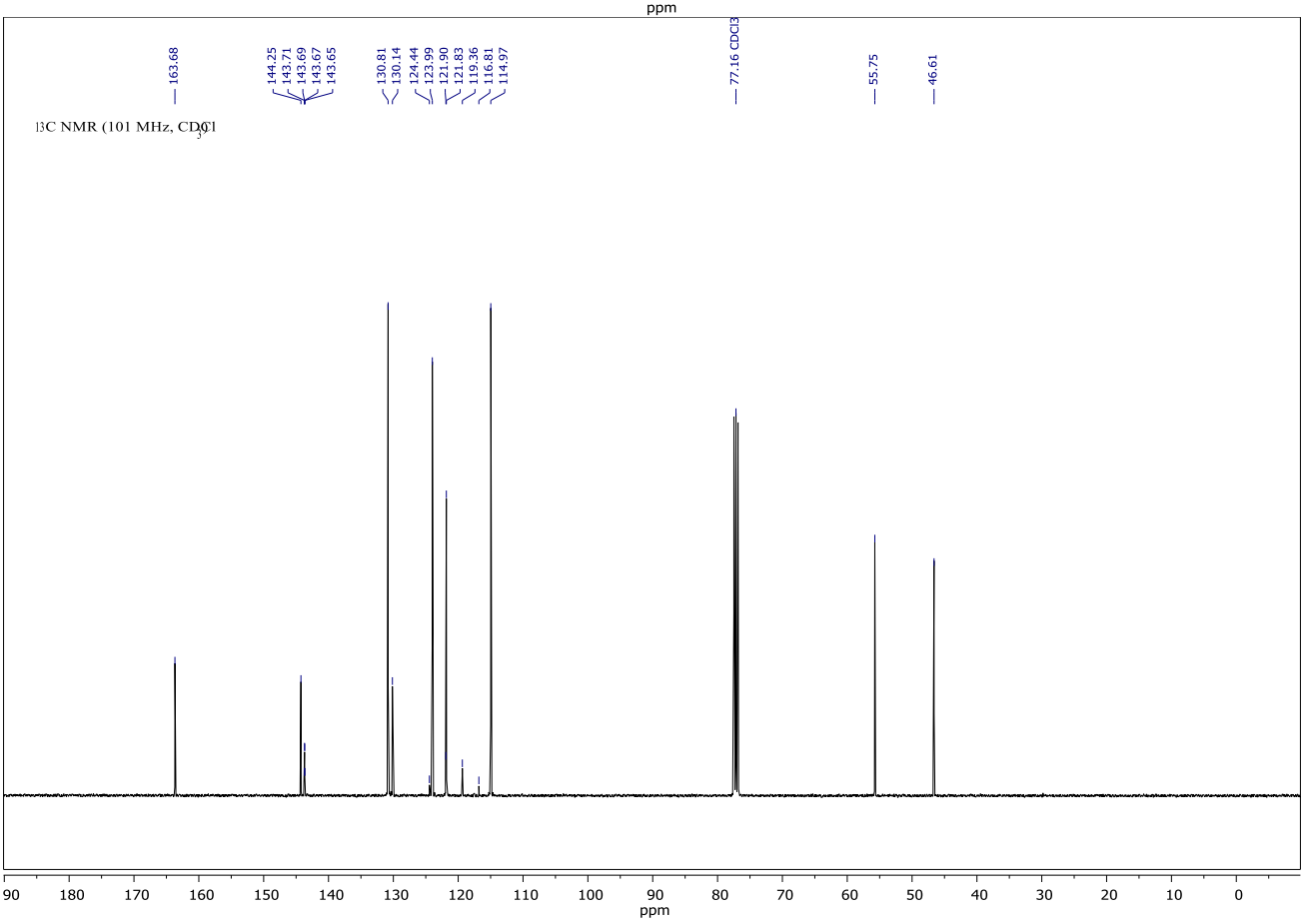
(4-Methoxyphenyl)(methyl)((4-(methylsulfonyl)phenyl)imino)-λ^6-sulfanone (3n)

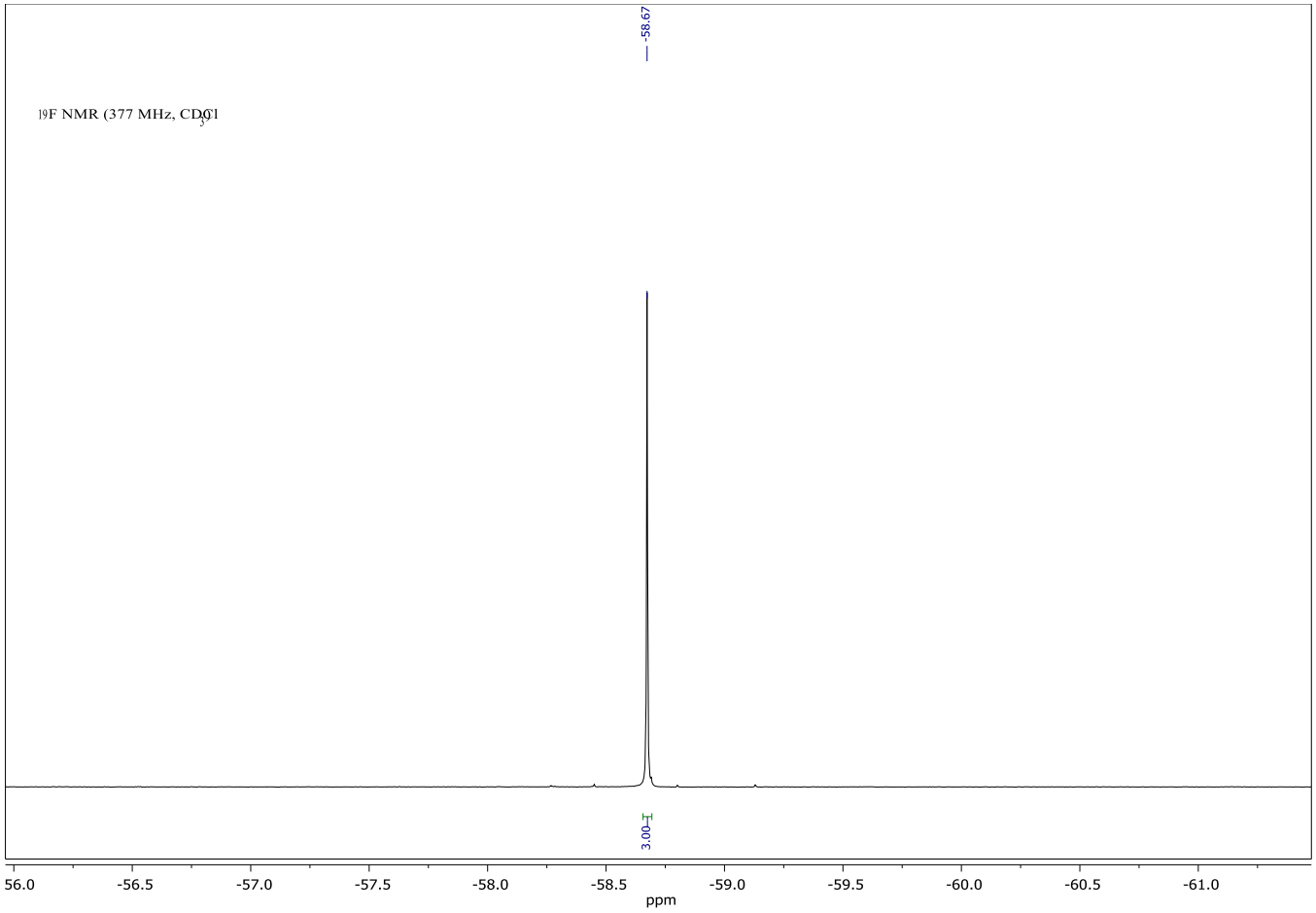




(4-Methoxyphenyl)(methyl)((4-(trifluoromethoxy)phenyl)imino)-λ^6-sulfanone (3o)

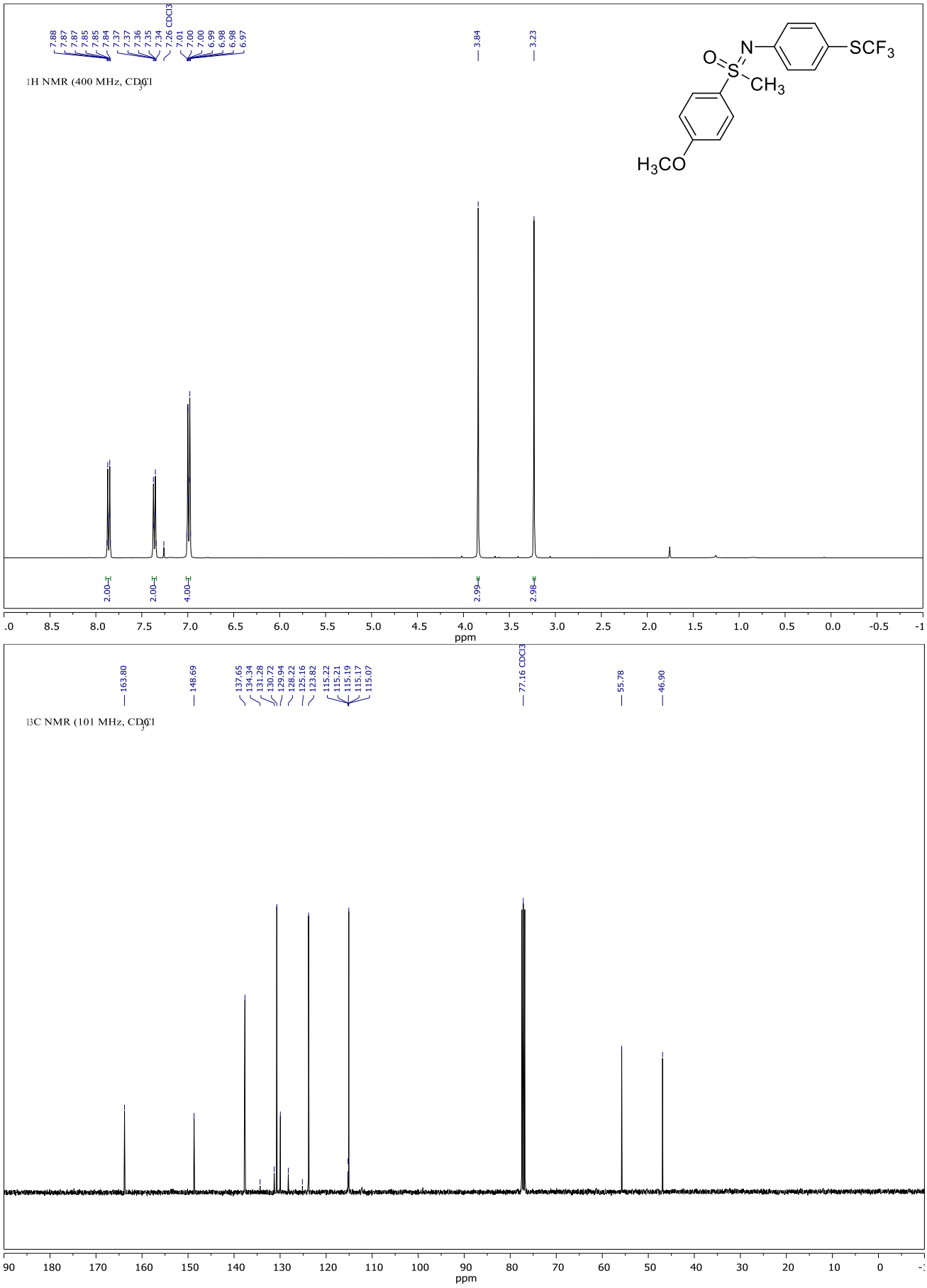


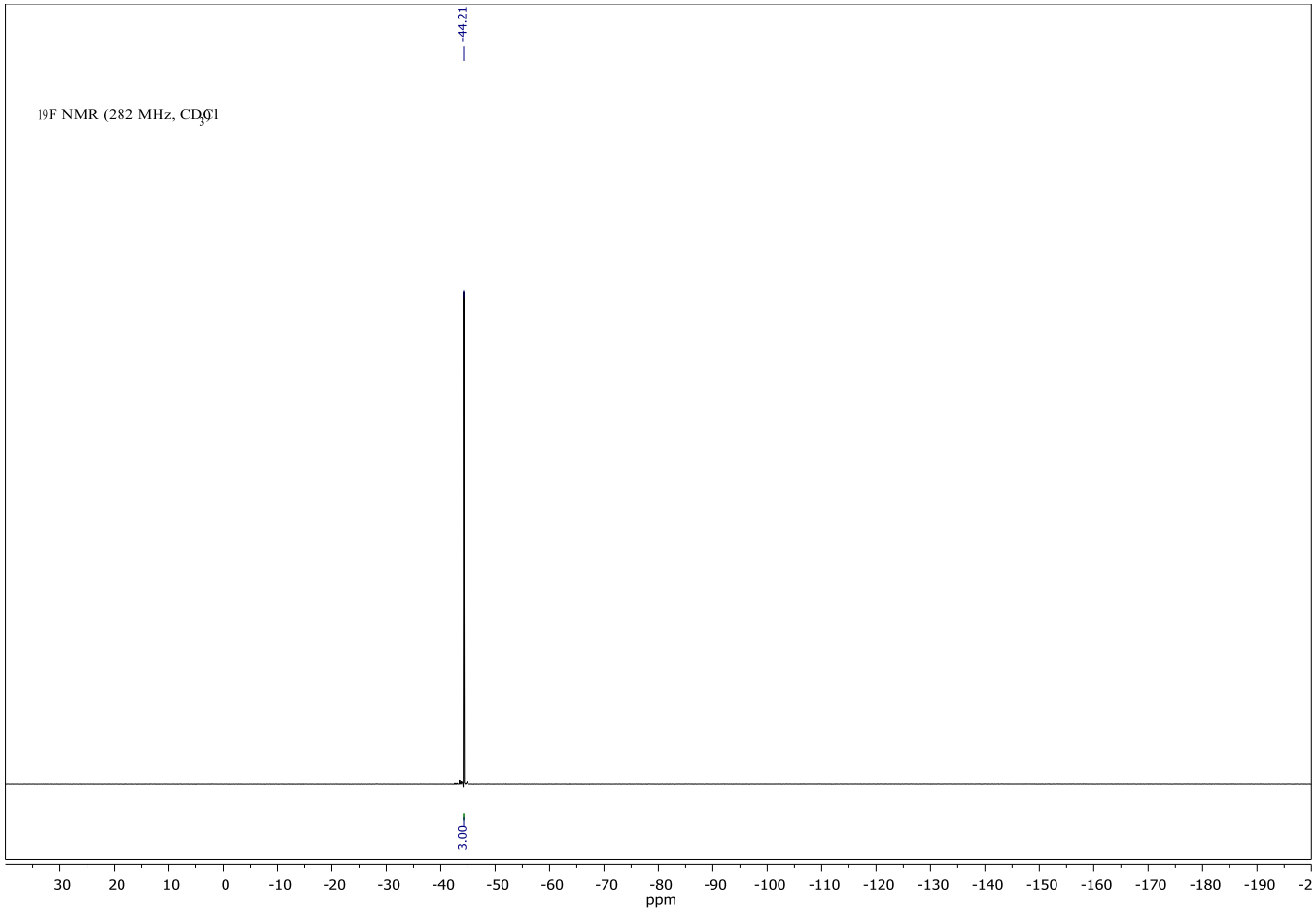




^{19}F NMR (377 MHz, $CDCl_3$)

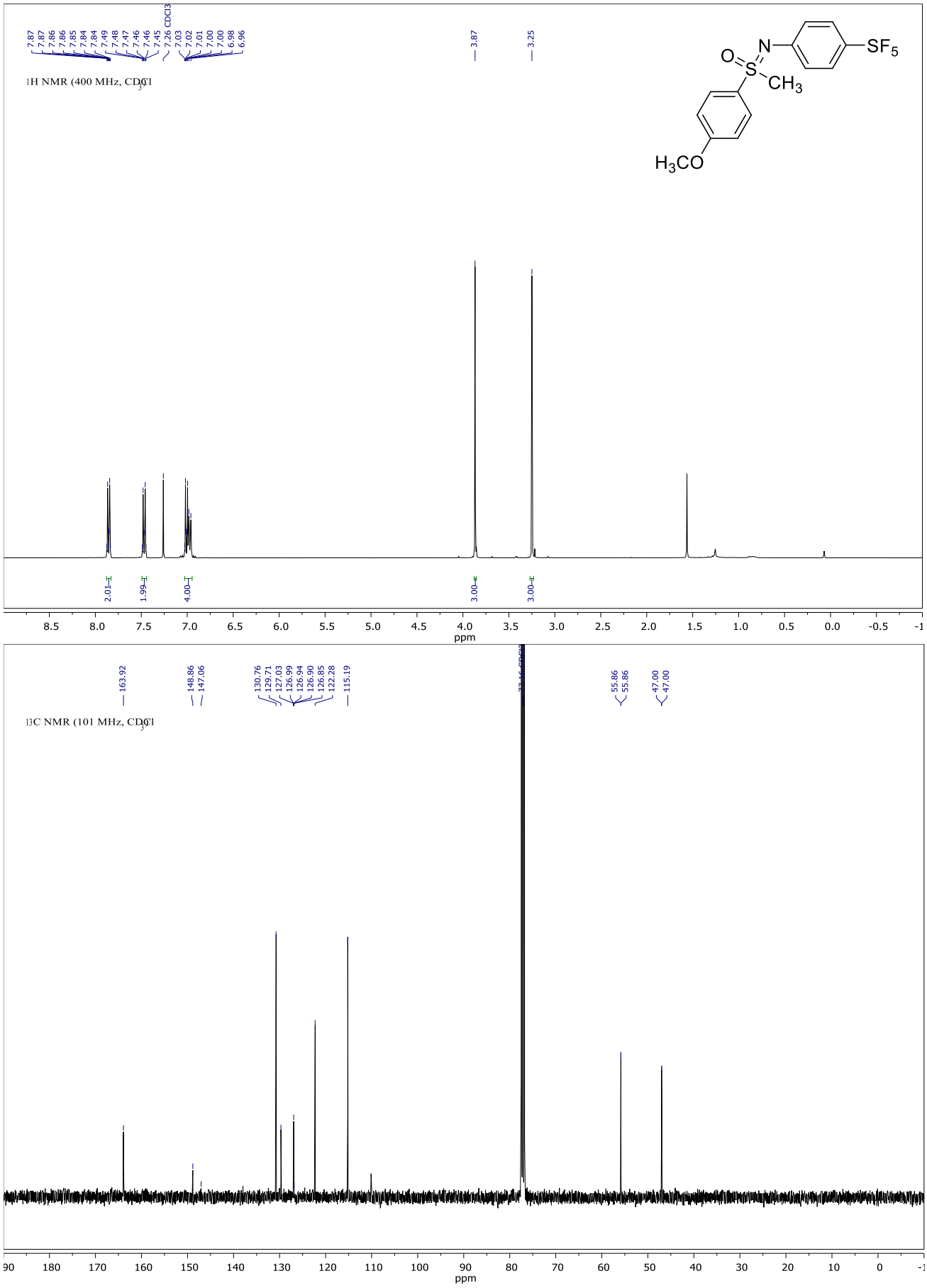
(4-Methoxyphenyl)(methyl)((4-((trifluoromethyl)thio)phenyl)imino)-λ^6-sulfanone (3p)

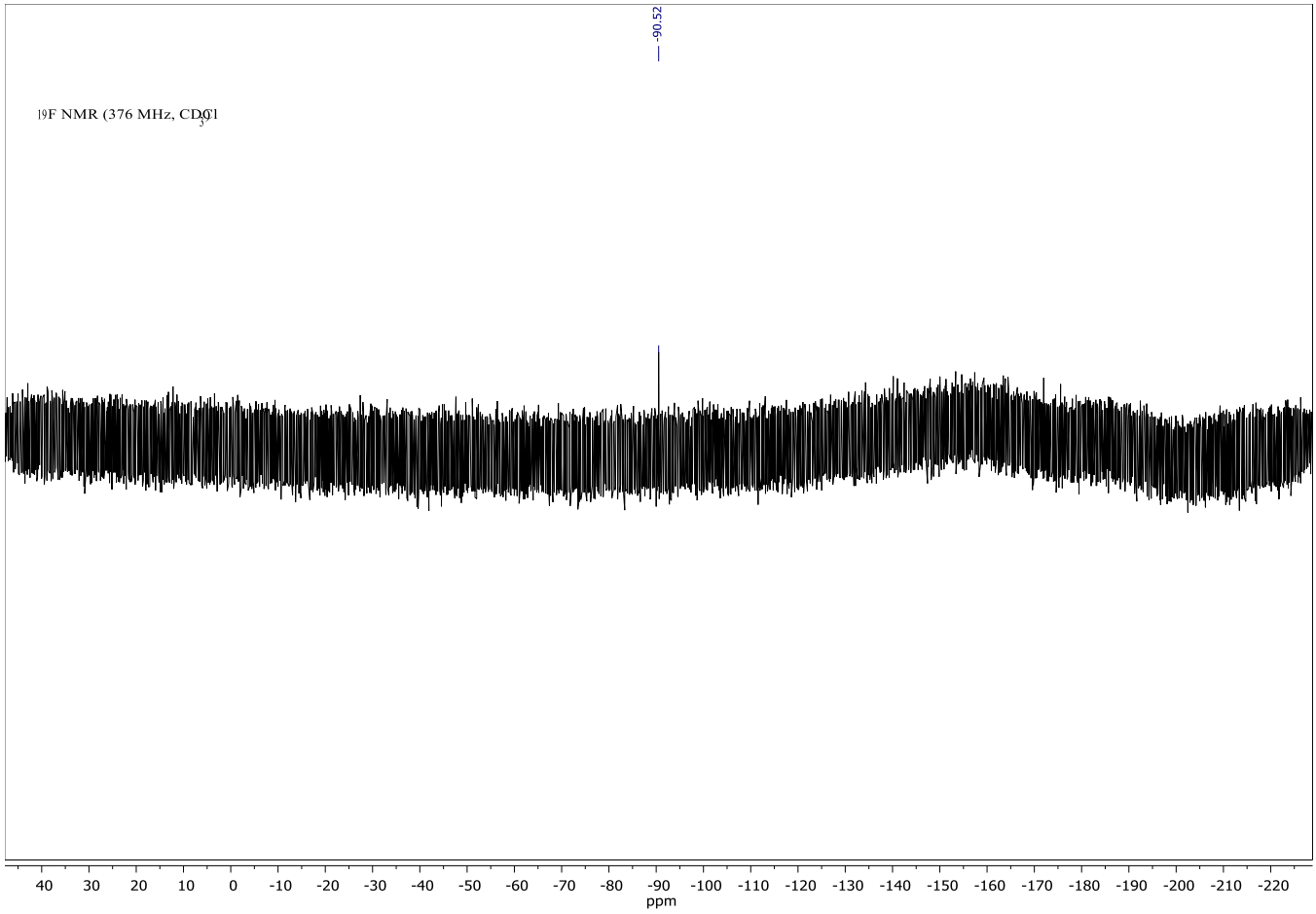




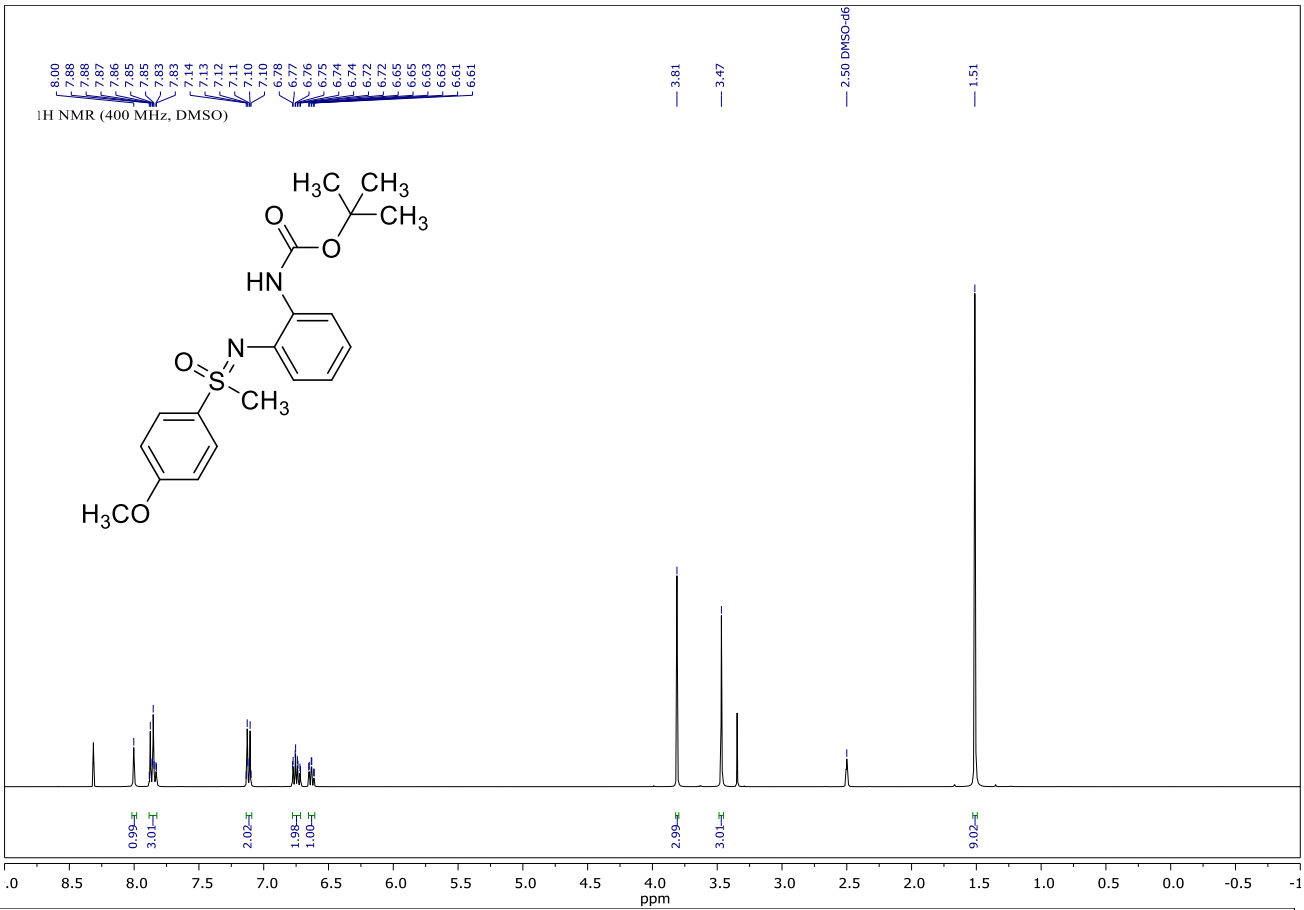
^{19}F NMR (282 MHz, $CDCl_3$)

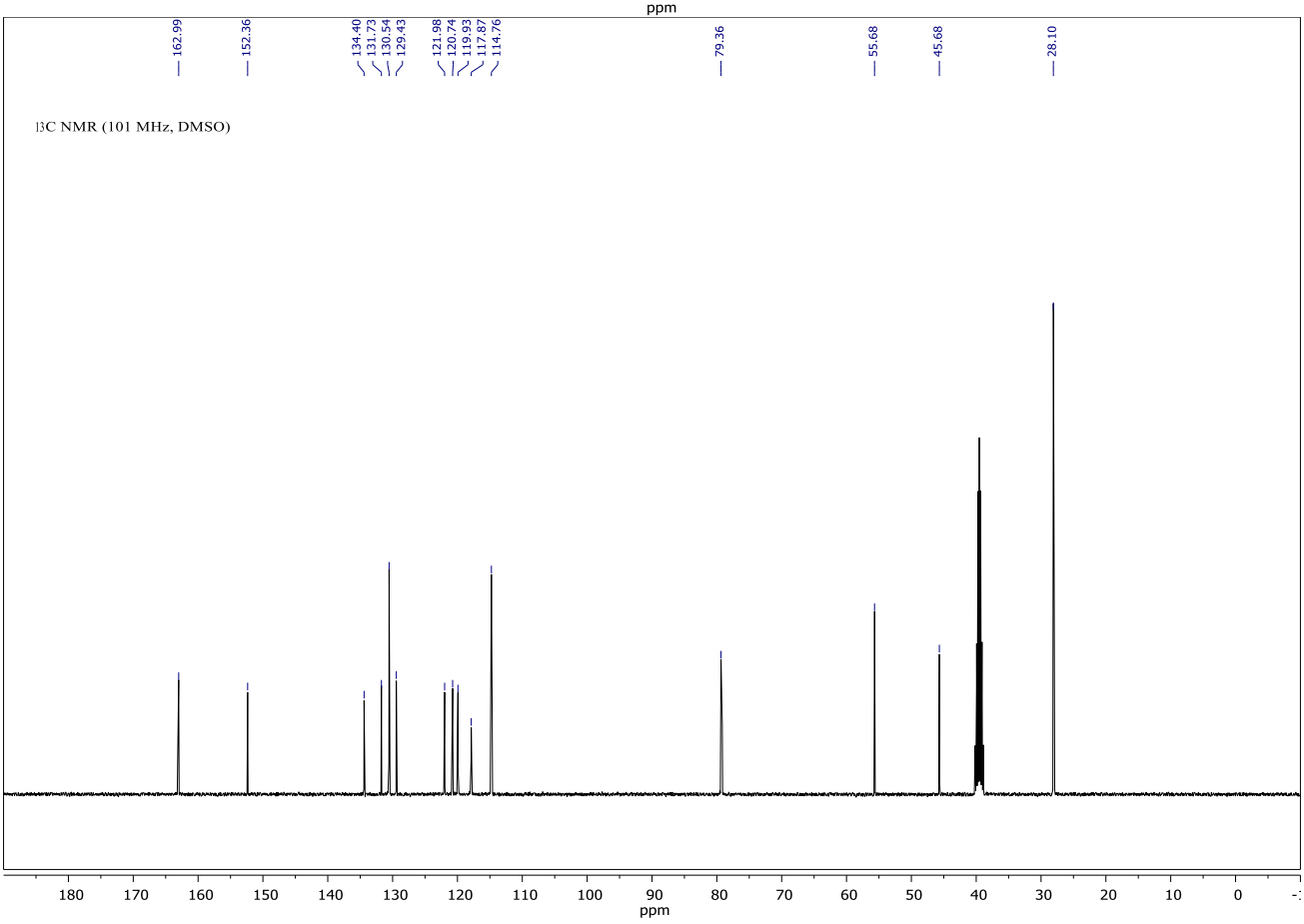
(4-Methoxyphenyl)(methyl)((4-(pentafluoro-λ^6-sulfaneyl)phenyl)imino)-λ^6-sulfanone (3q)



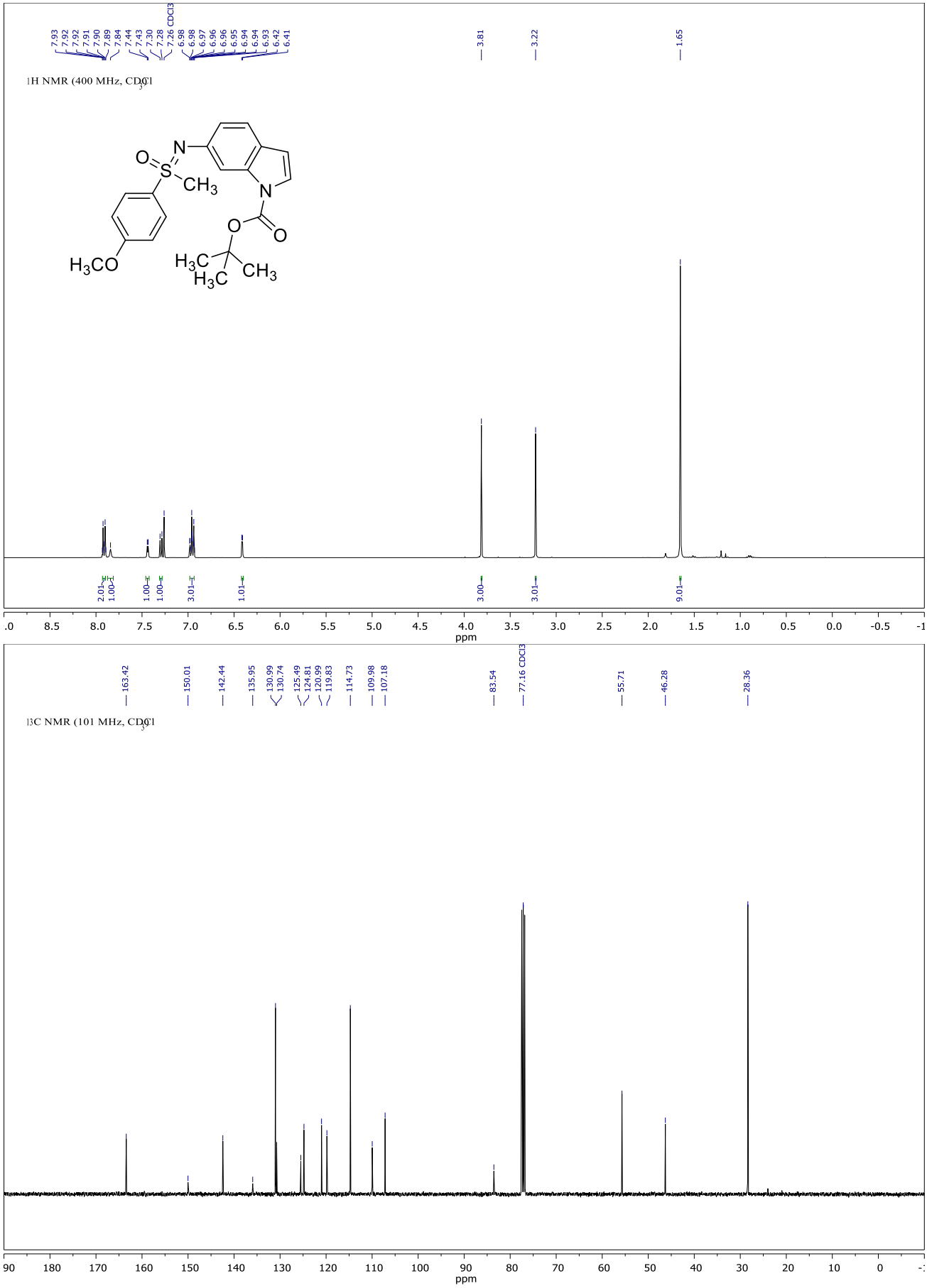

-90.52
19F NMR (376 MHz, CDCl3)
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
ppm

tert-Butyl-(2-(((4-methoxyphenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)phenyl)carbamate (3r)

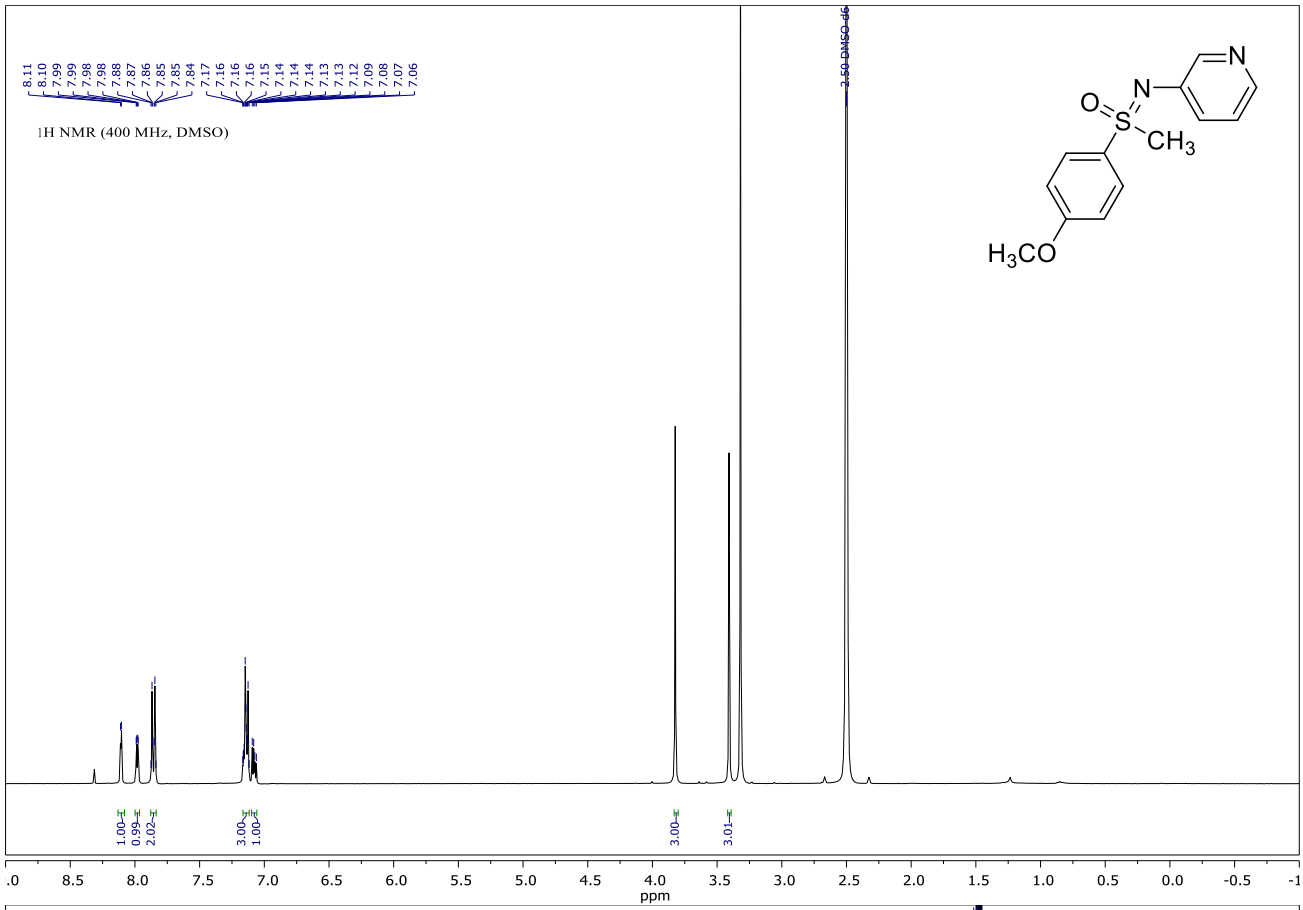


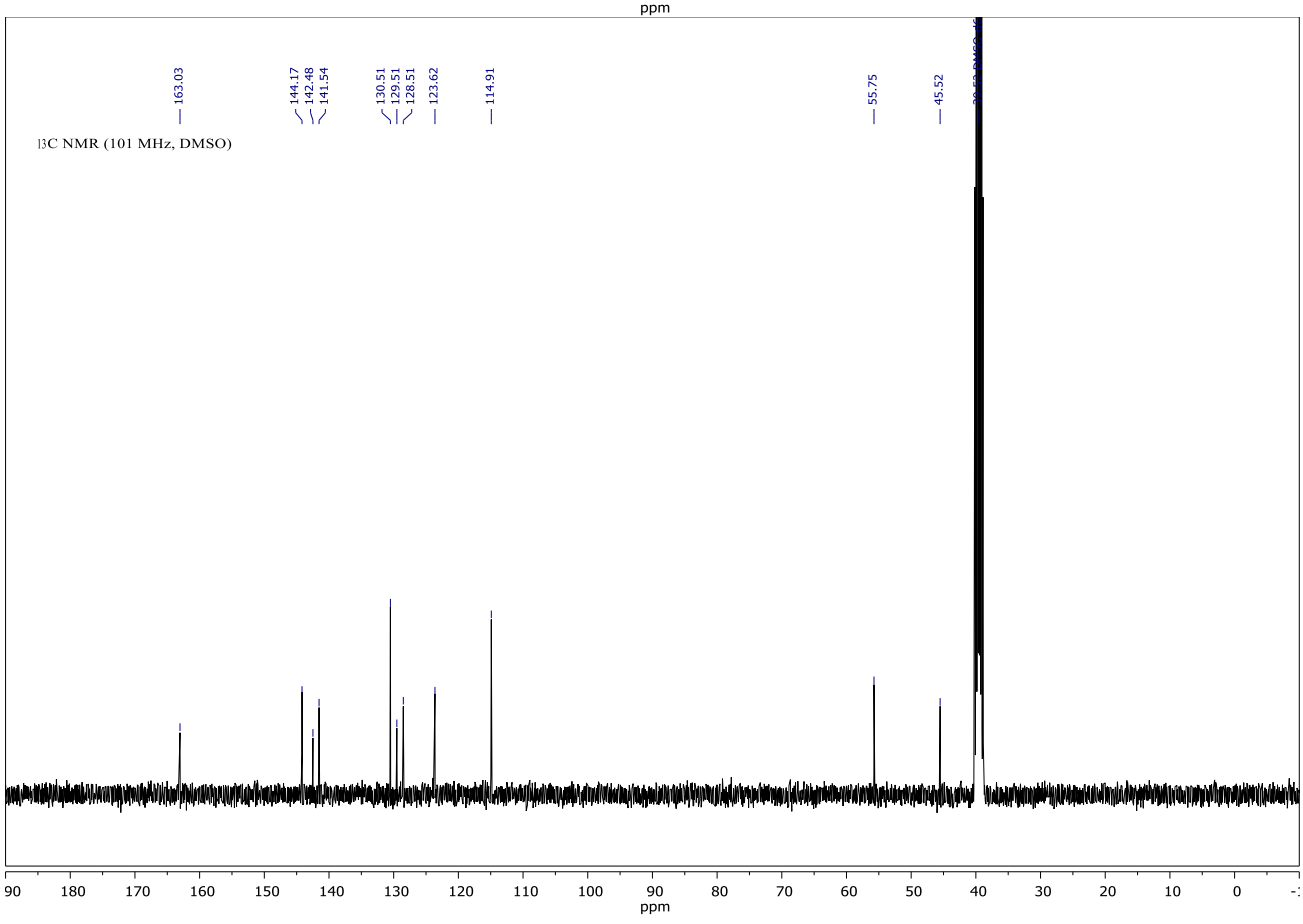


tert-Butyl-6-(((4-methoxyphenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)-1H-indole-1-carboxylate (3s)

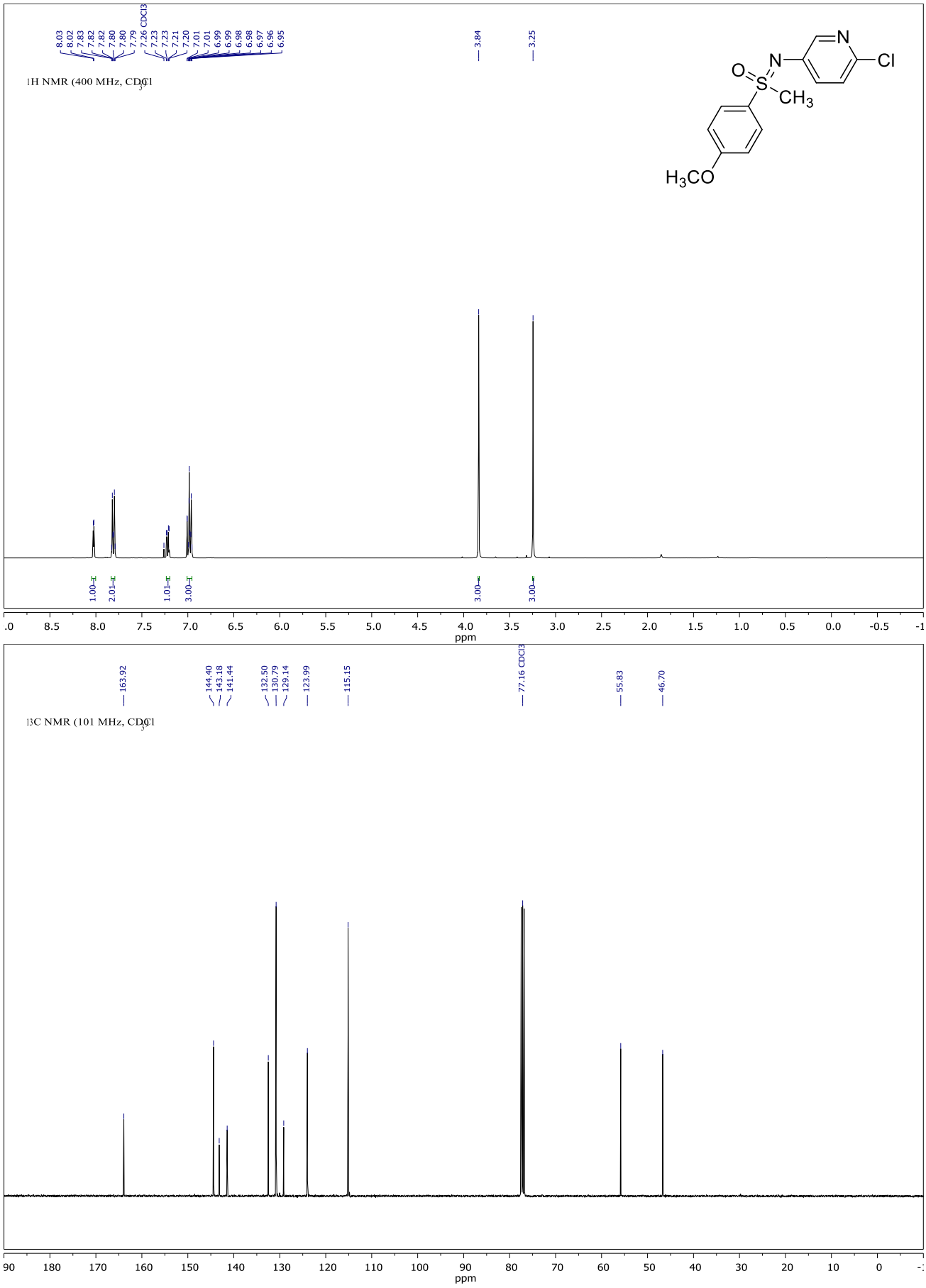


(4-Methoxyphenyl)(methyl)(pyridin-3-ylimino)-λ^6-sulfanone (3t)

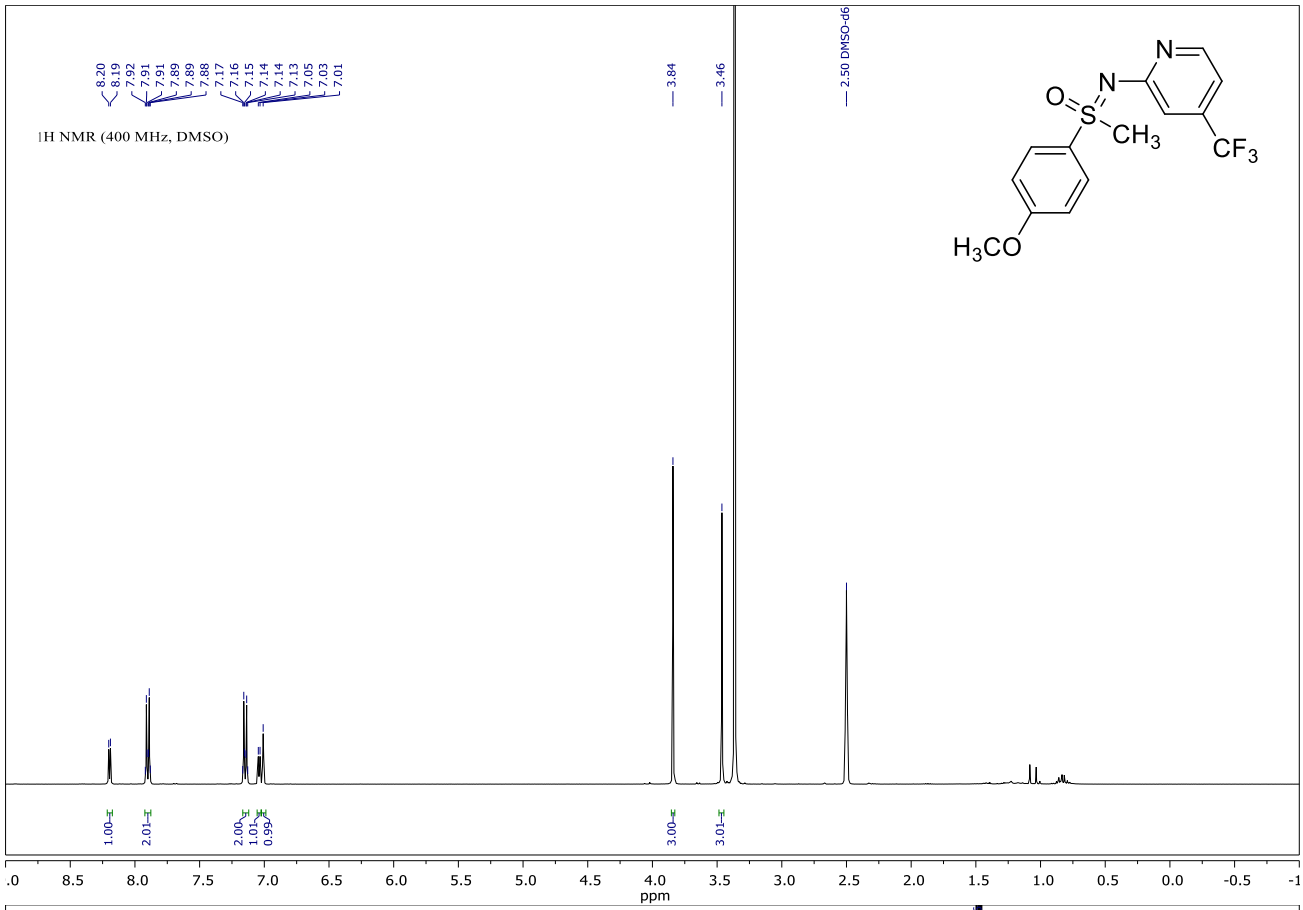


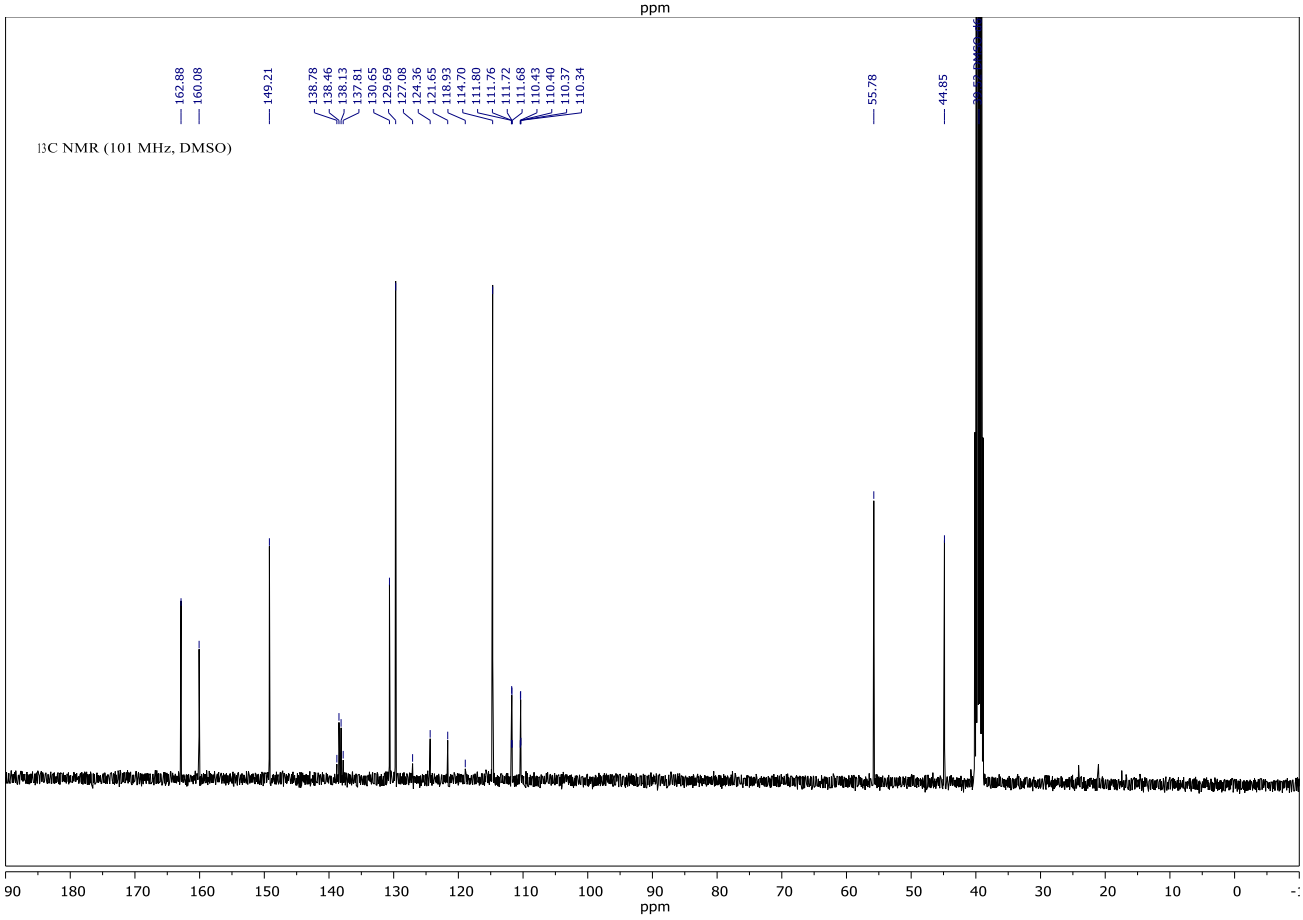


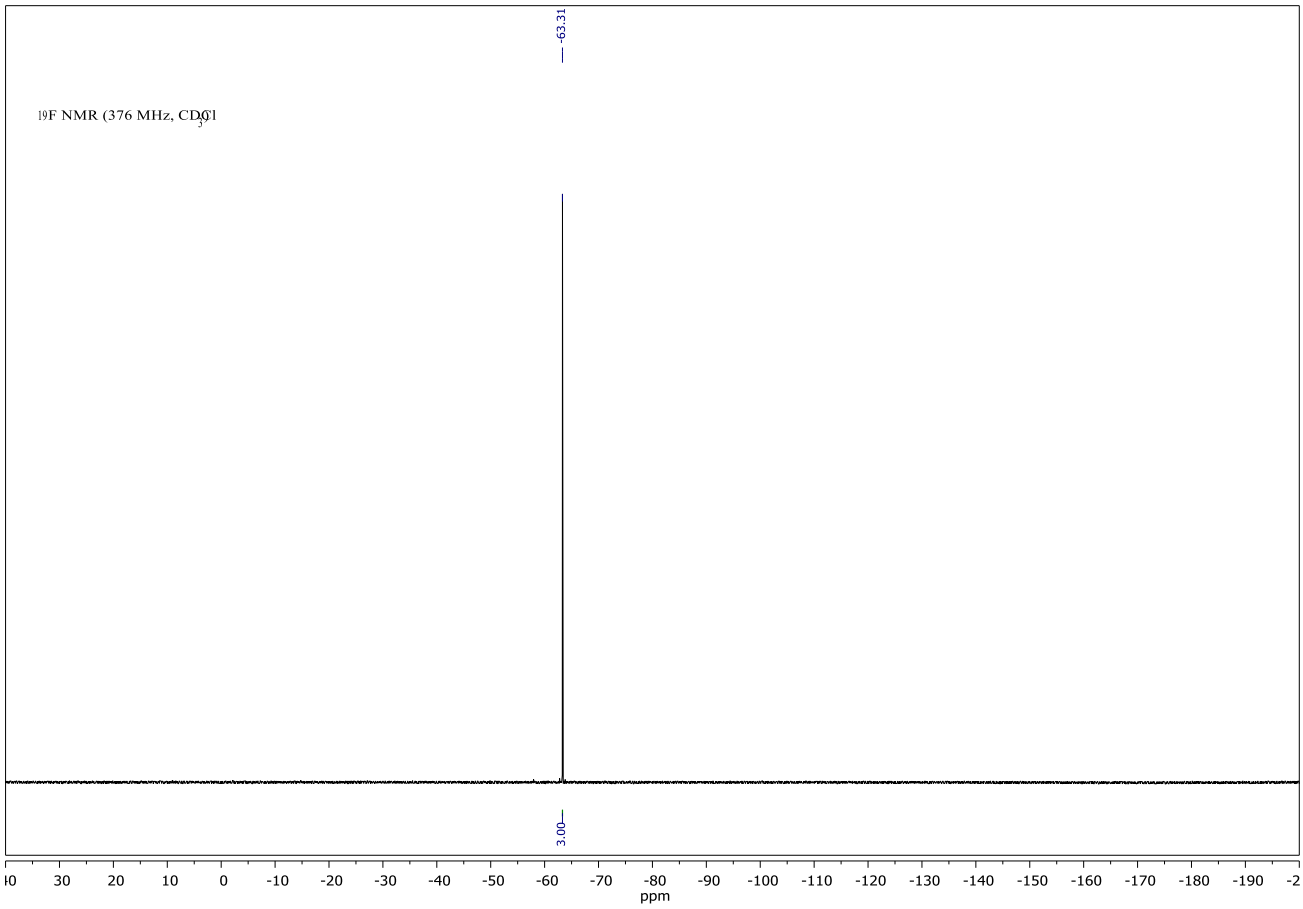
((6-Chloropyridin-3-yl)imino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (3u)



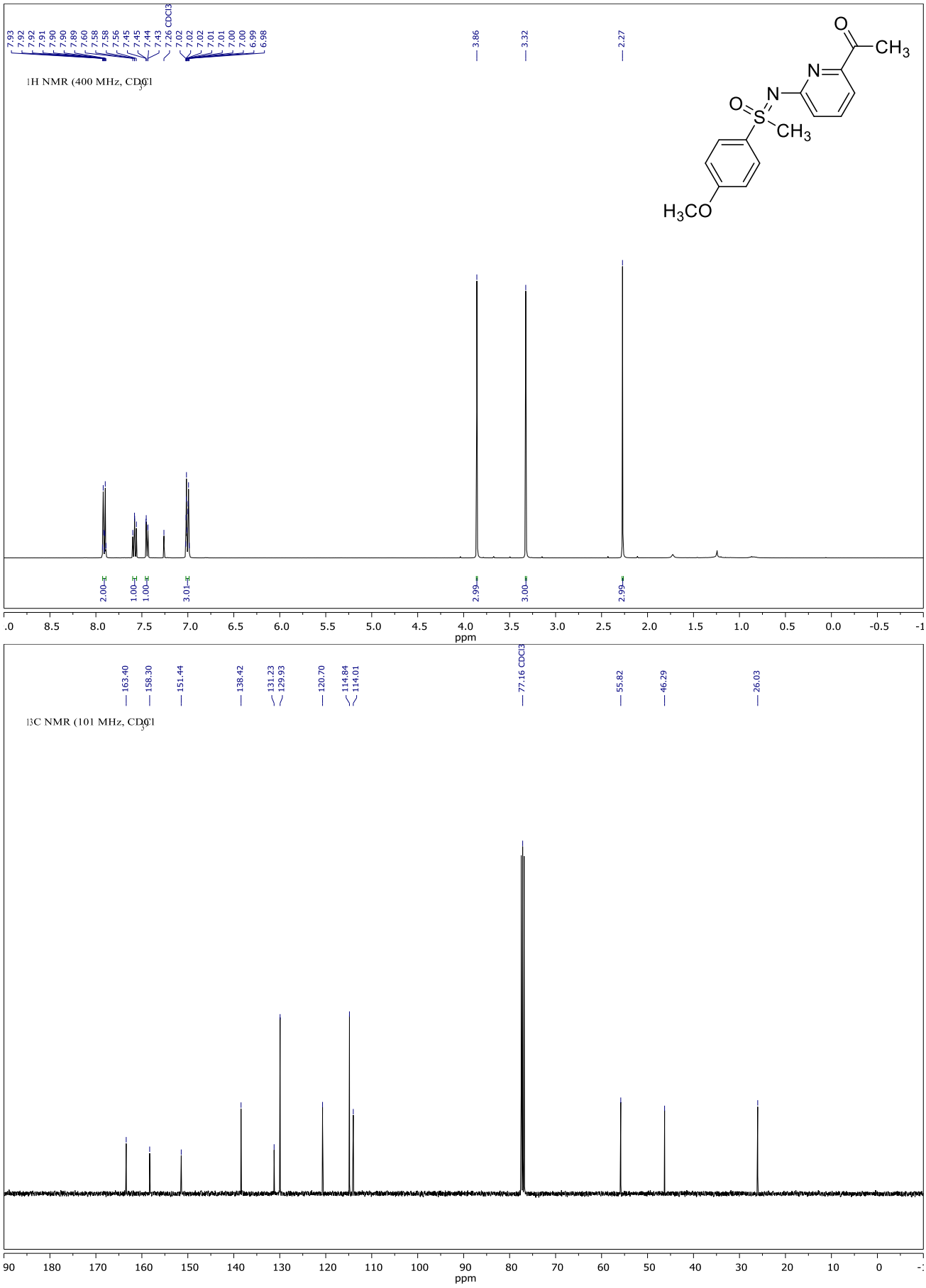
(4-Methoxyphenyl)(methyl)((4-(trifluoromethyl)pyridin-2-yl)imino)-λ^6-sulfanone (3v)



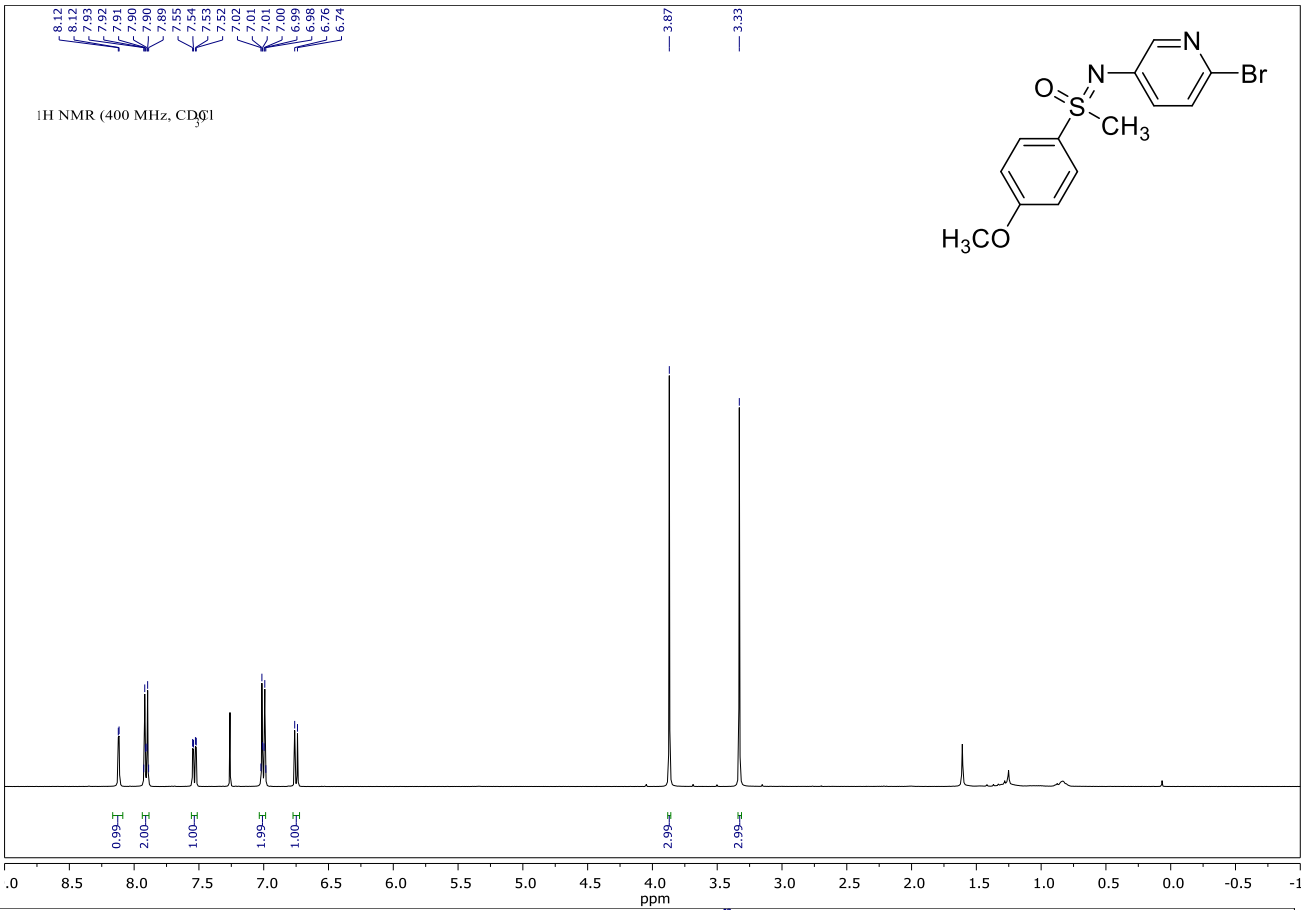


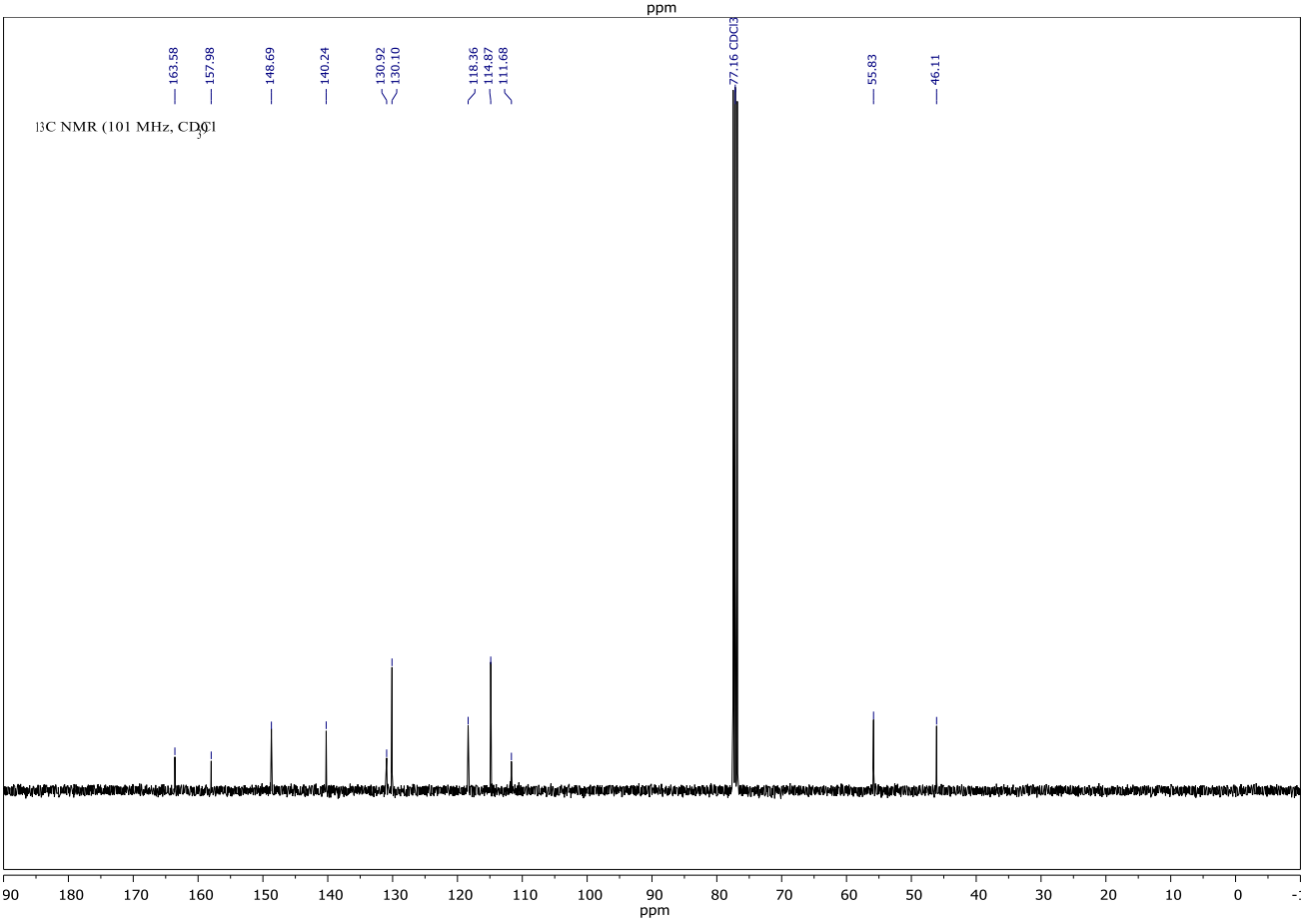

-63.31
19F NMR (376 MHz, CDCl3)
3.00
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm

((6-Acetylpyridin-2-yl)imino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (3w)

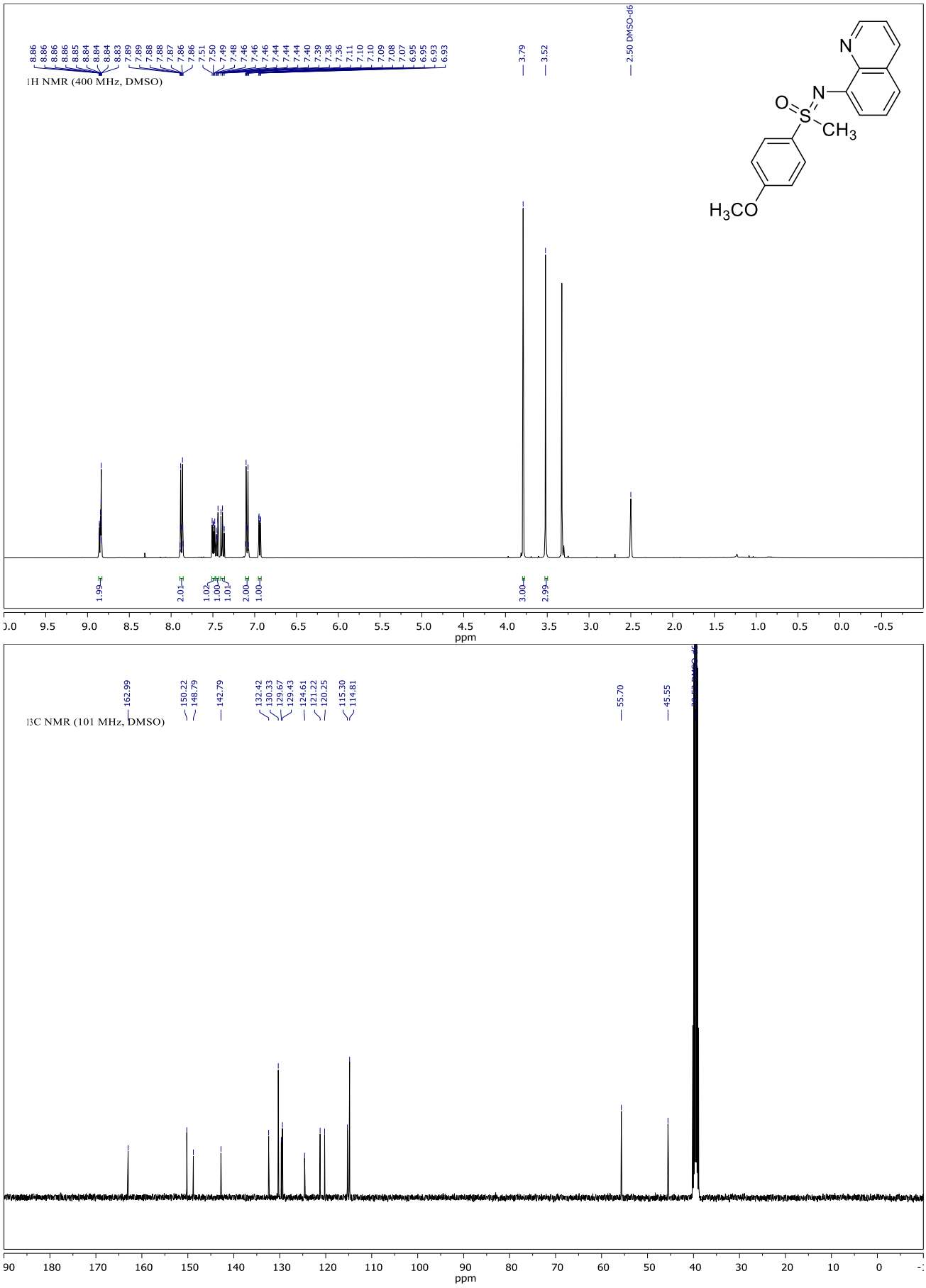


((6-Bromopyridin-3-yl)imino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (3x)

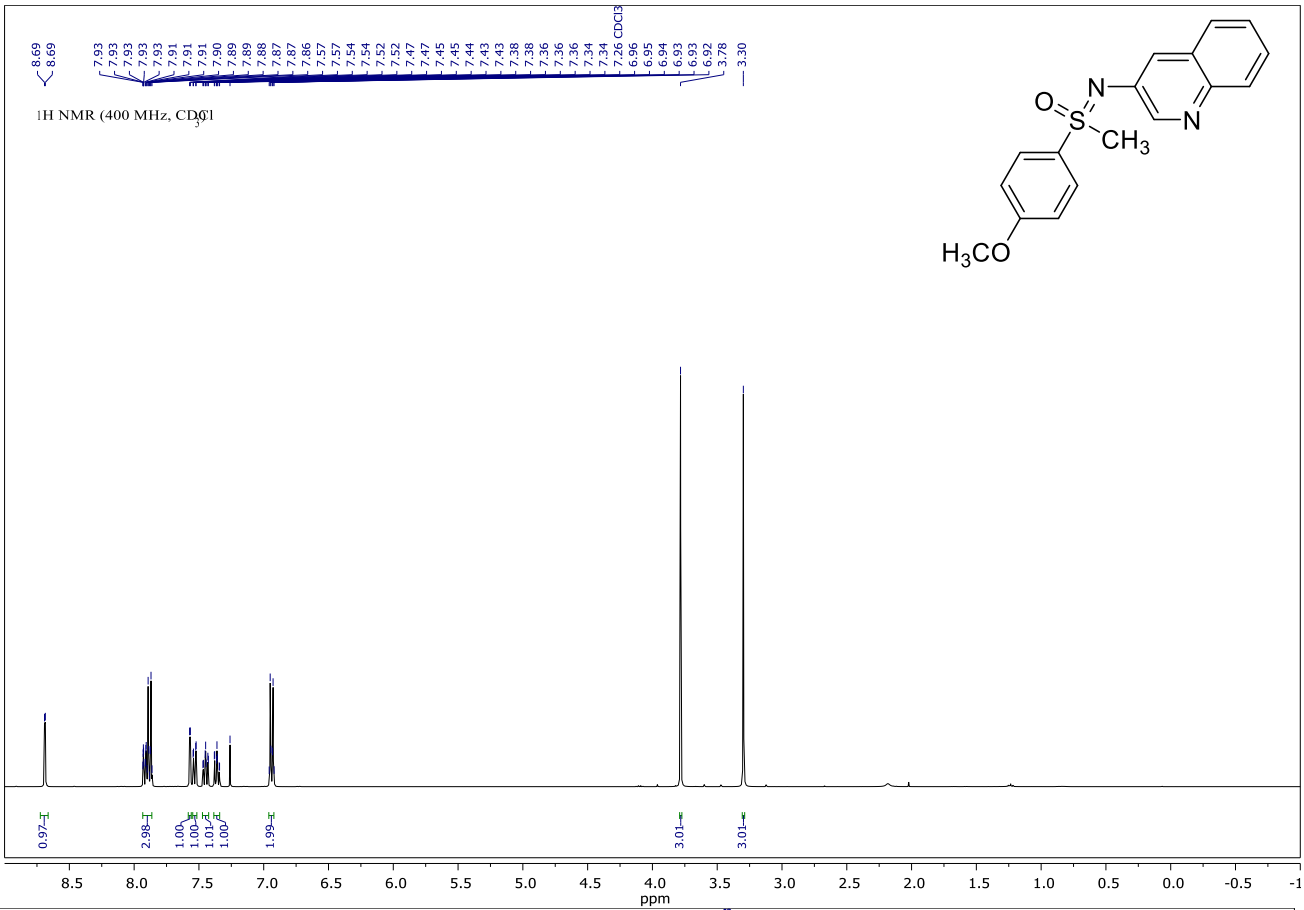


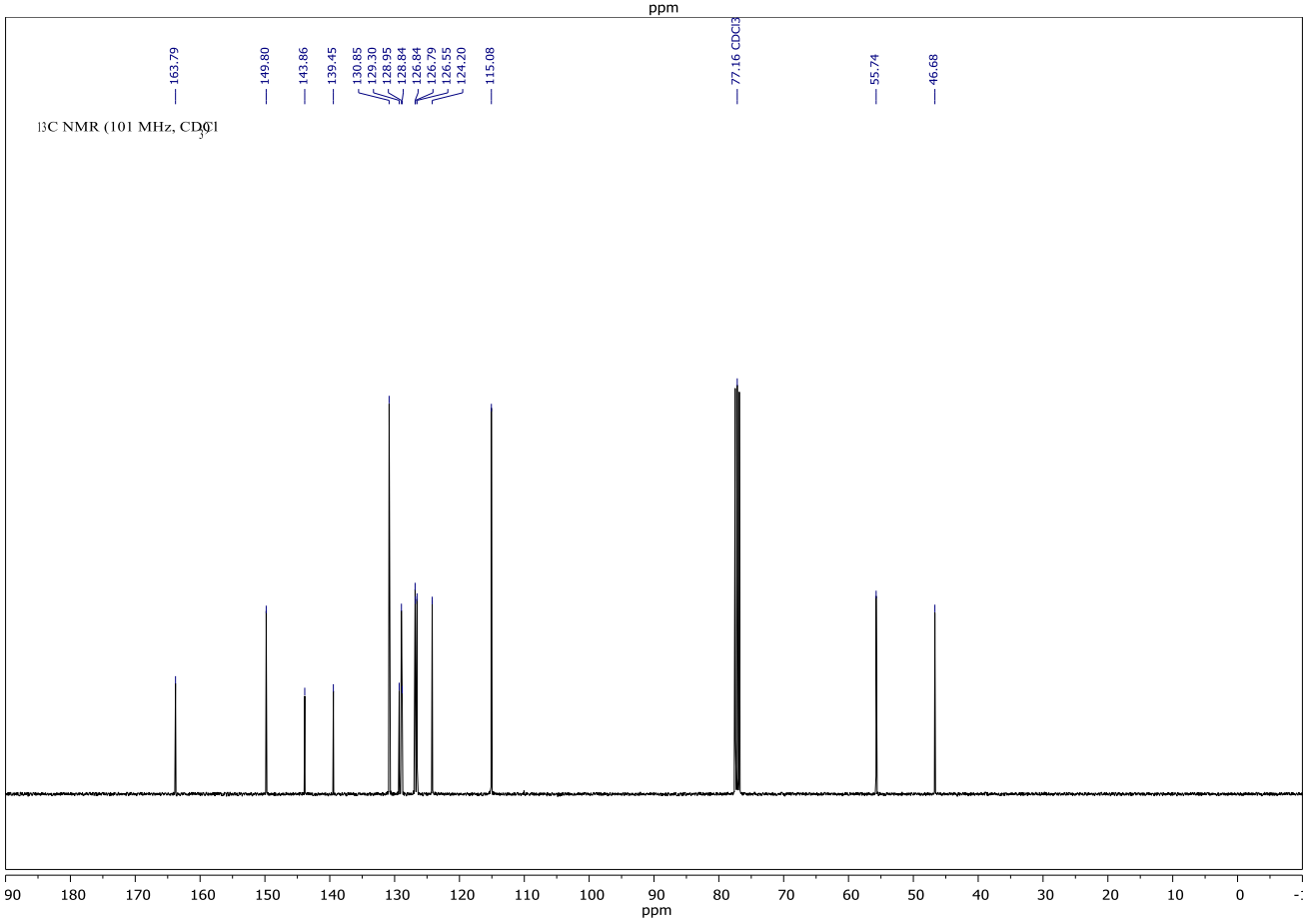


(4-Methoxyphenyl)(methyl)(quinolin-8-ylimino)-λ^6-sulfanone (3y)

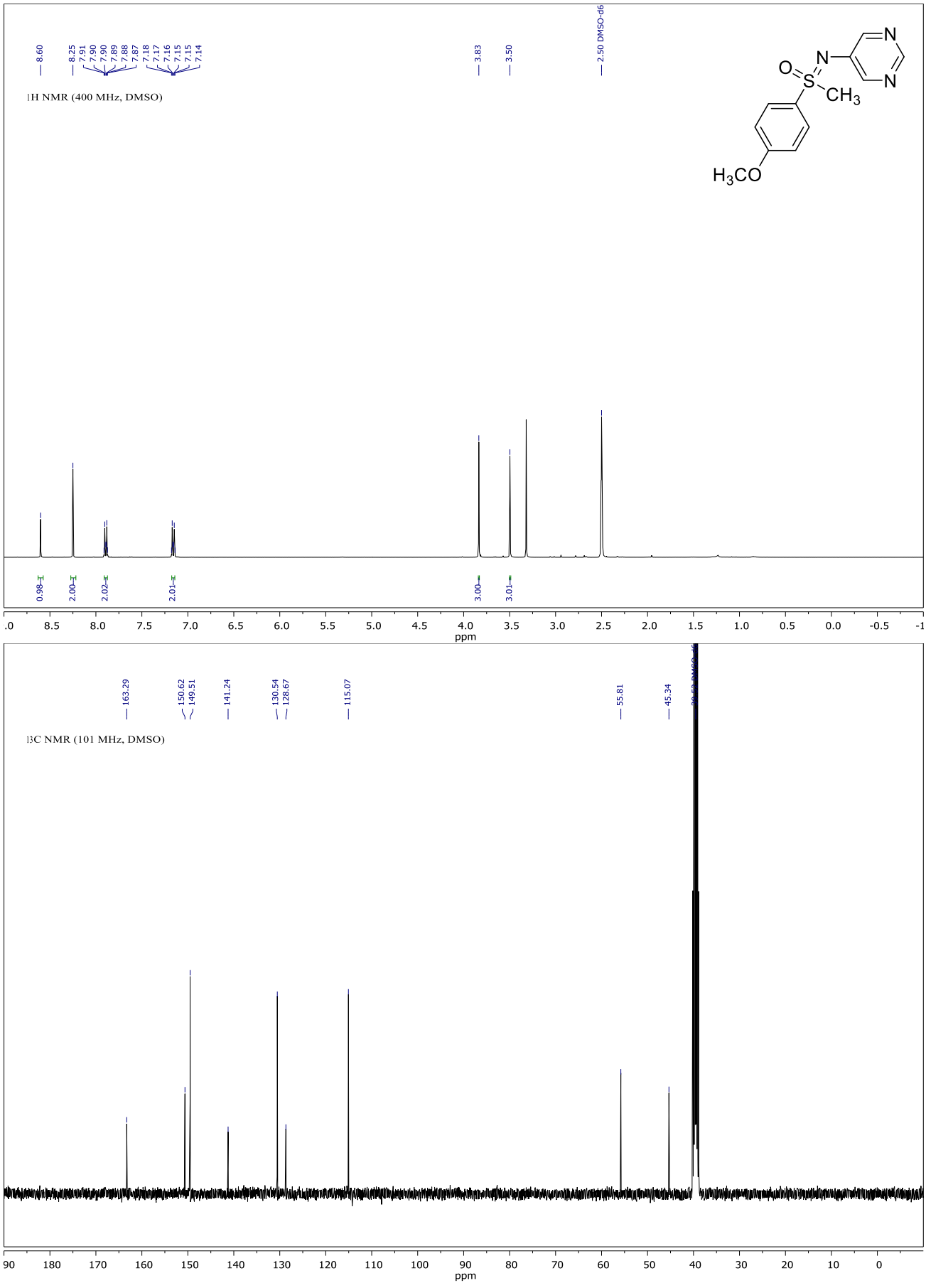


(4-Methoxyphenyl)(methyl)(quinolin-3-ylimino)-λ^6-sulfanone (3z)

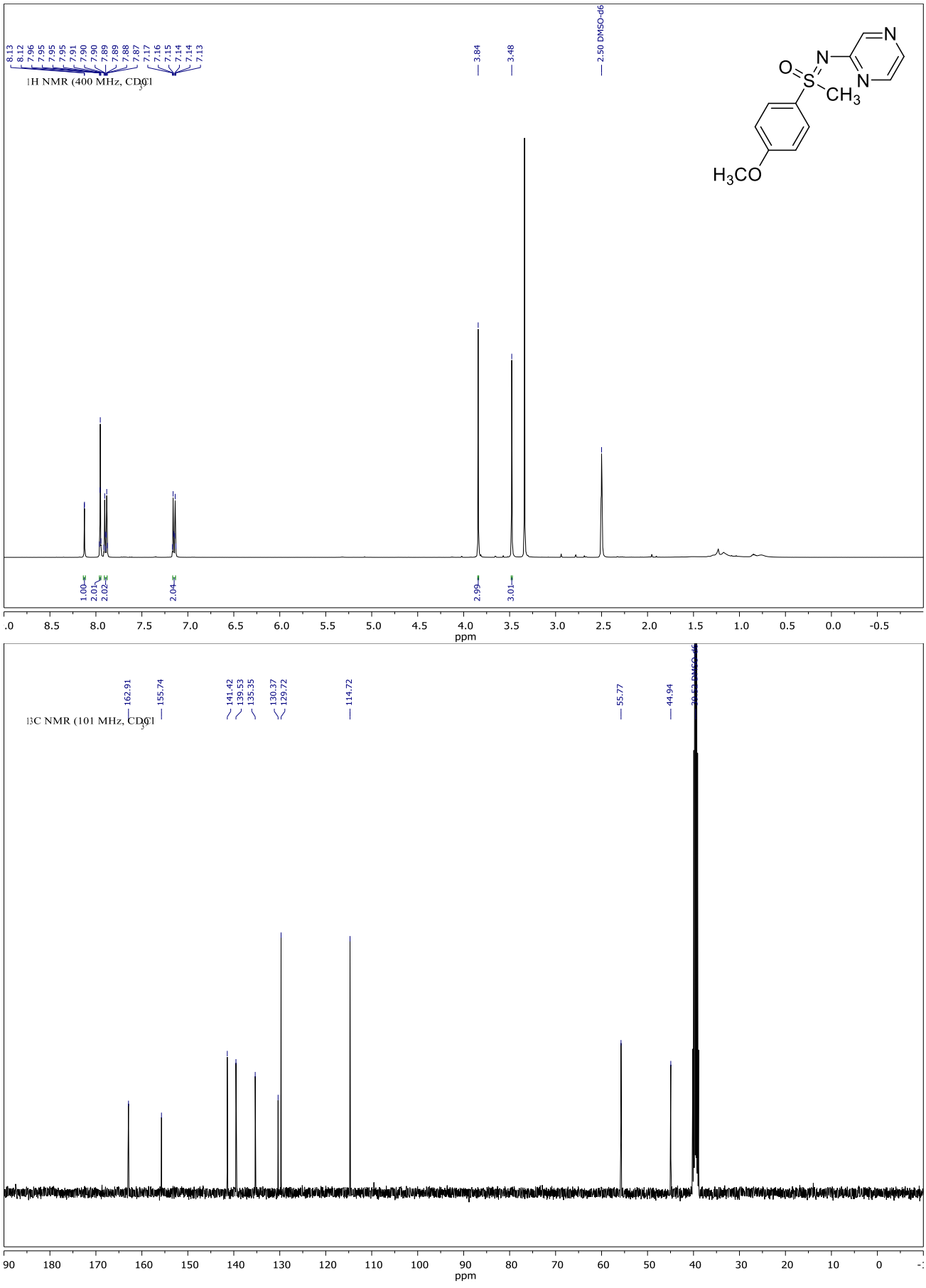




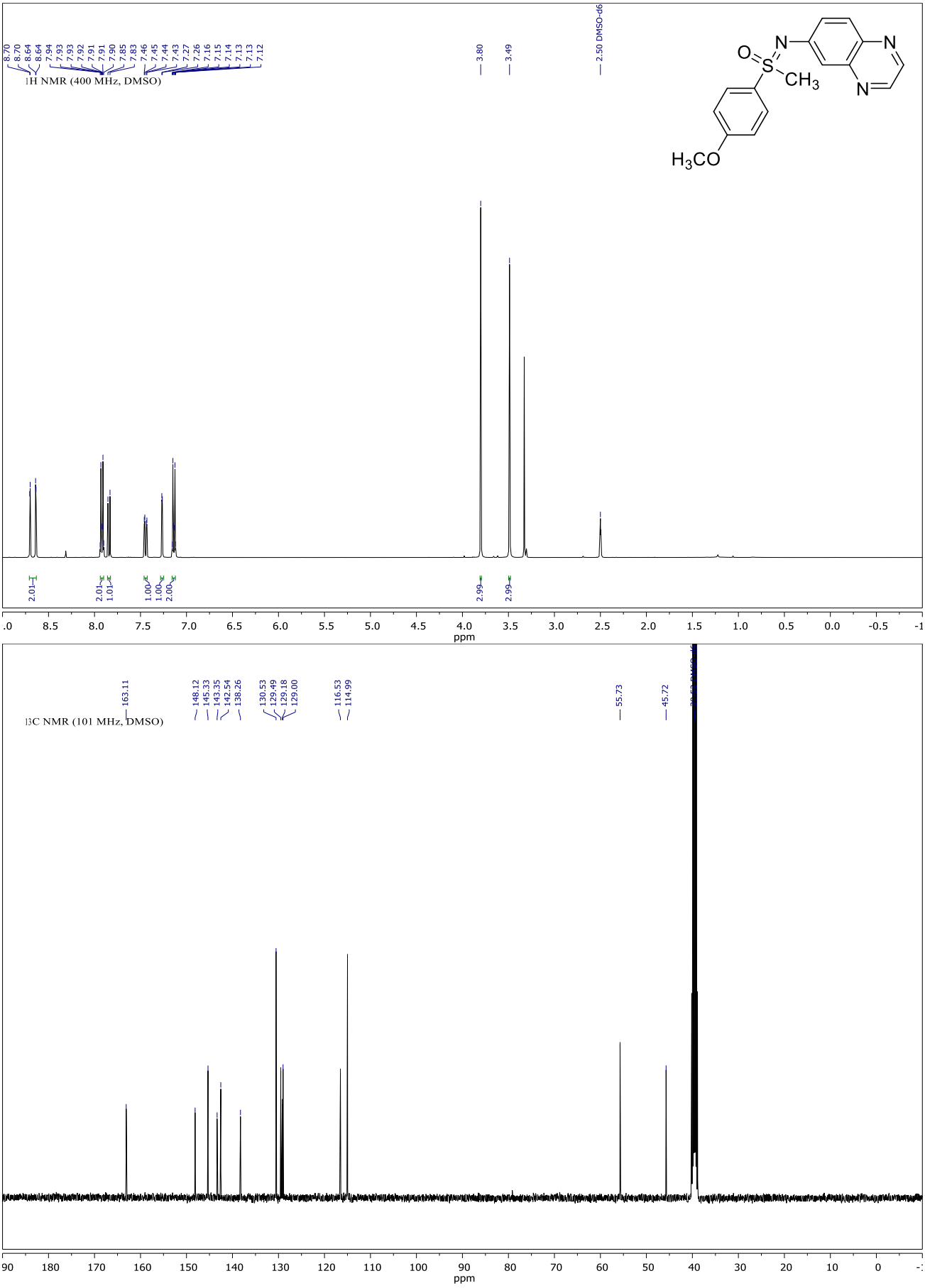
(4-Methoxyphenyl)(methyl)(pyrimidin-5-ylimino)-λ^6-sulfanone (3aa)



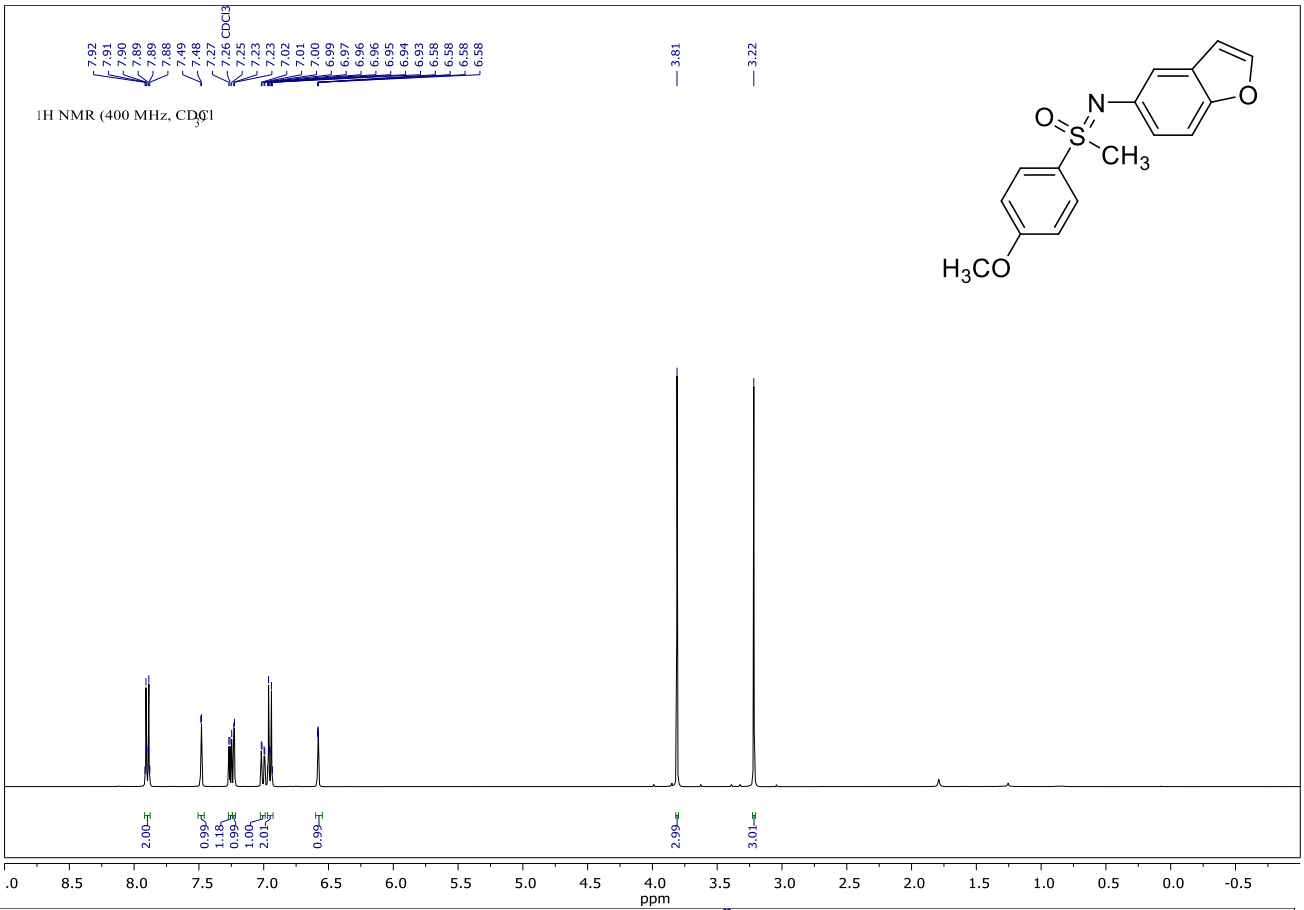
(4-Methoxyphenyl)(methyl)(pyrazin-2-ylimino)-λ^6-sulfanone (3ab)

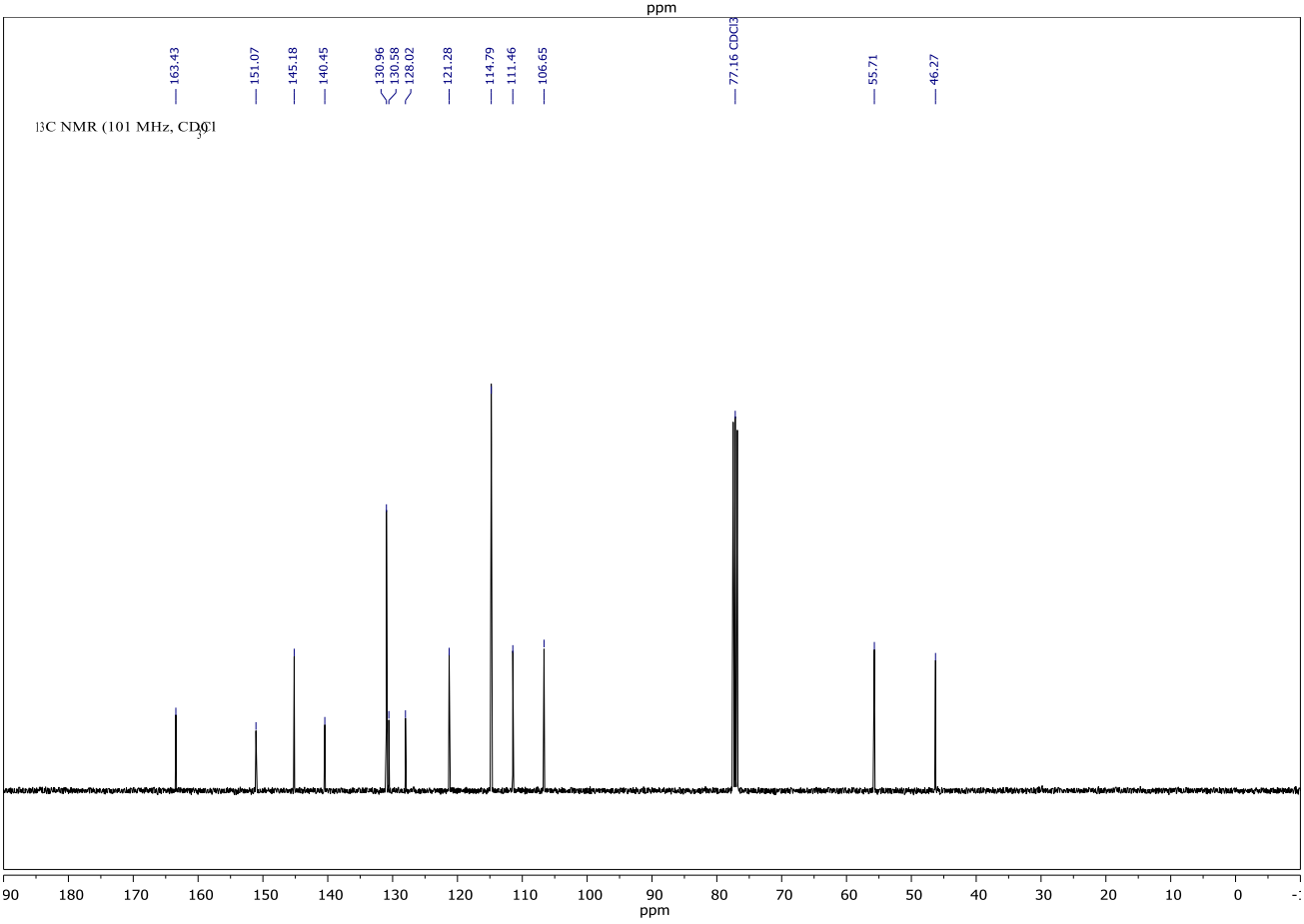


(4-Methoxyphenyl)(methyl)(quinoxalin-6-ylimino)-λ^6-sulfanone (3ac)

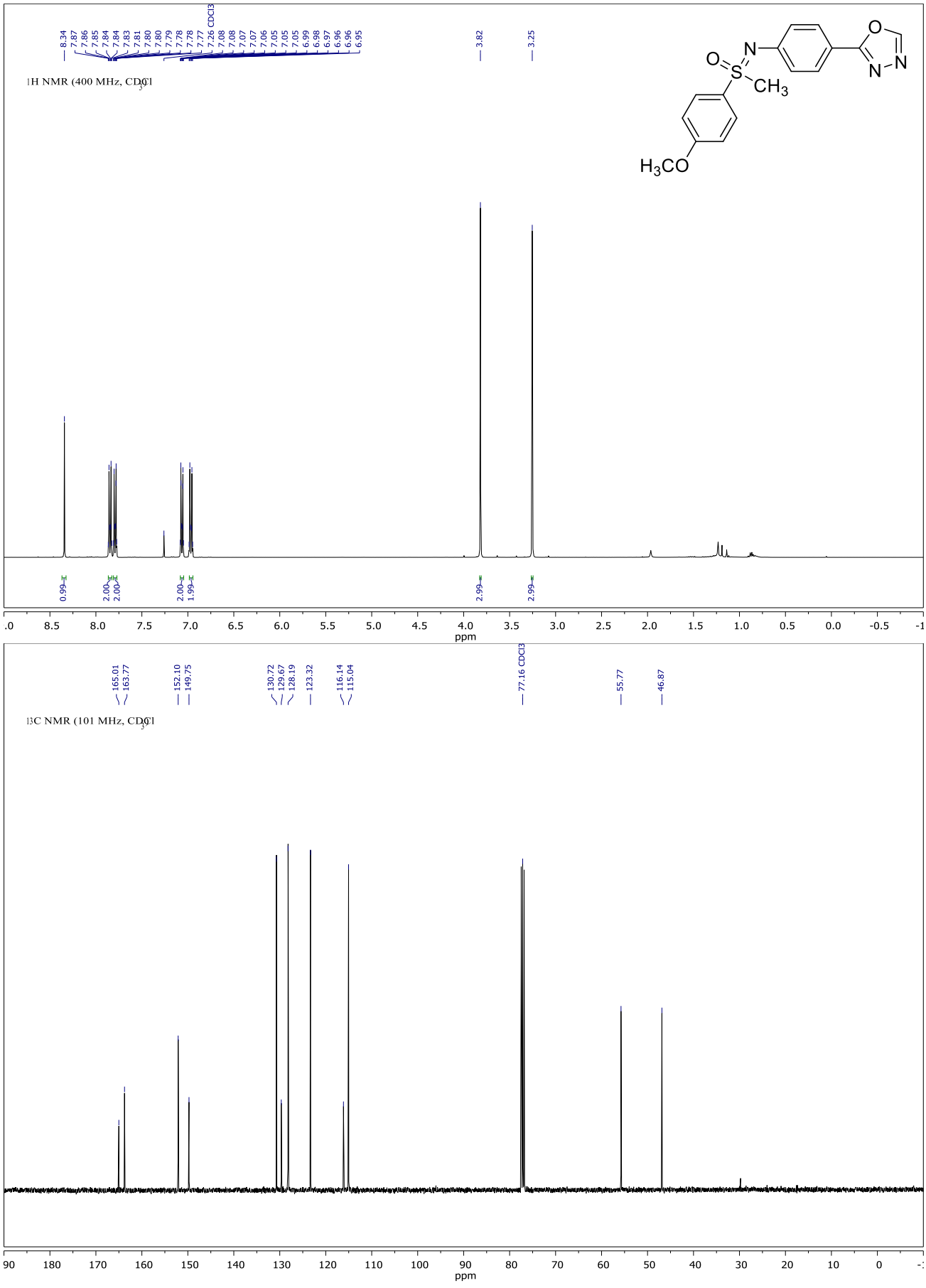


(Benzofuran-5-ylimino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (3ae)

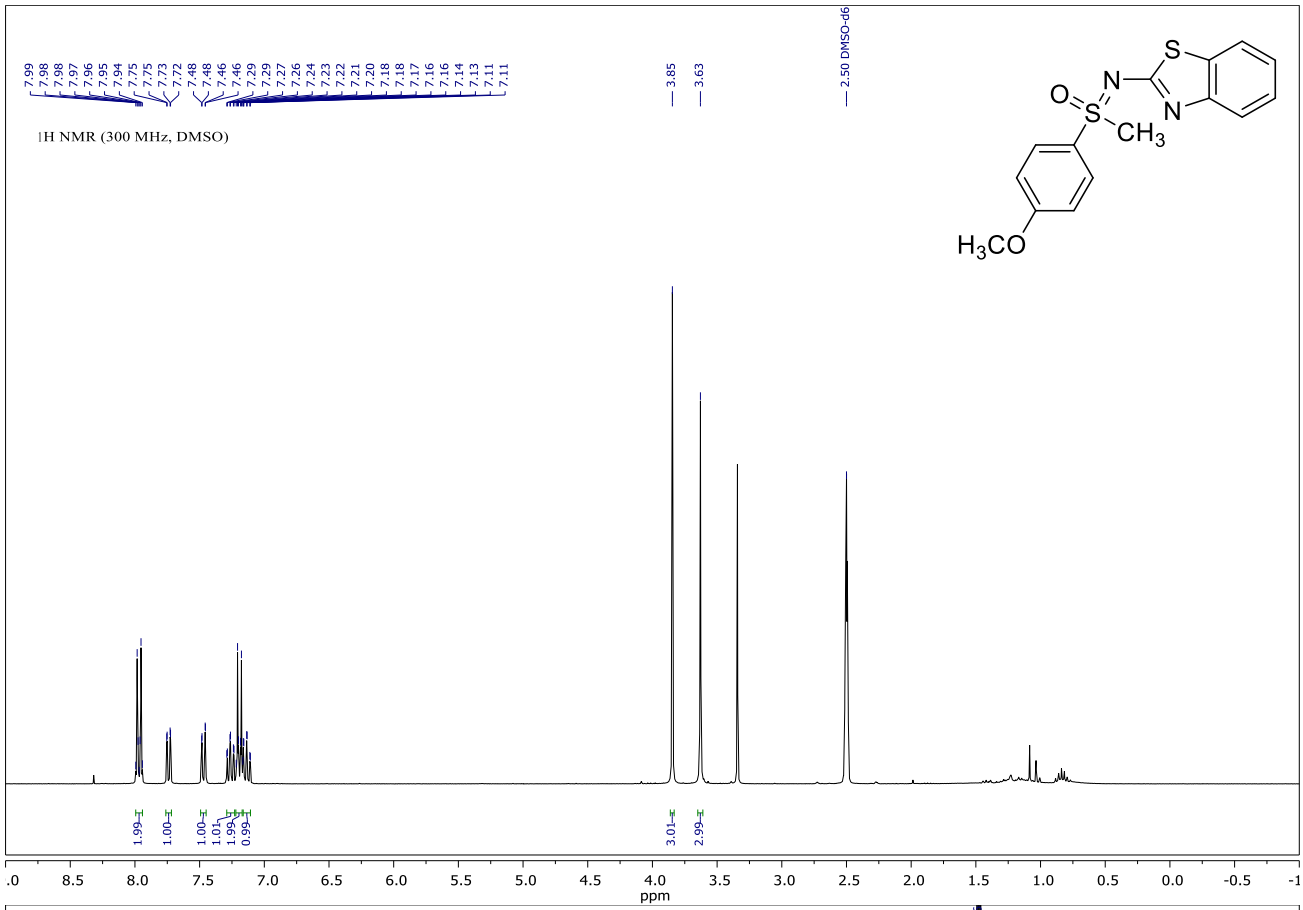


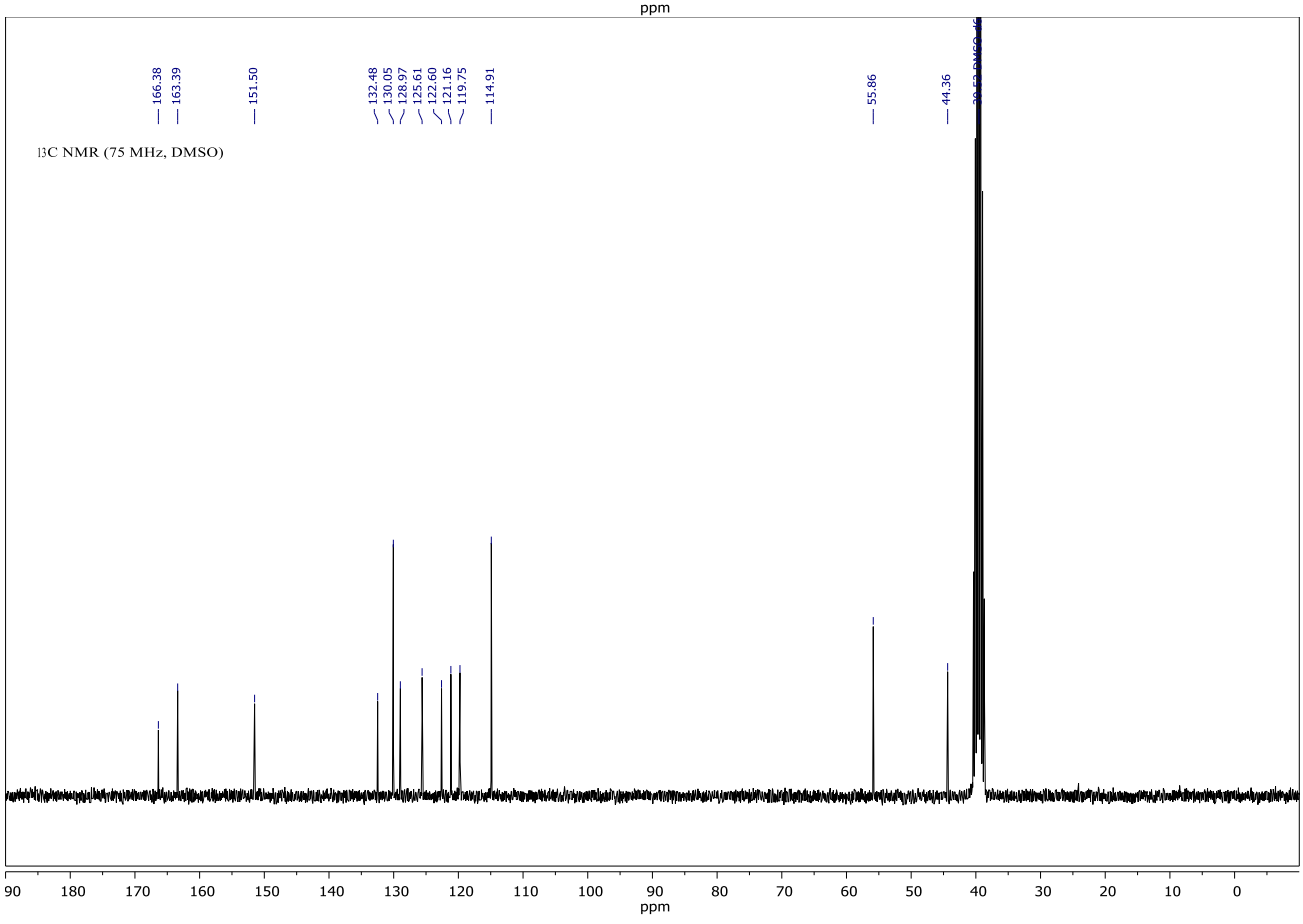


((4-(1,3,4-Oxadiazol-2-yl)phenyl)imino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (3af)

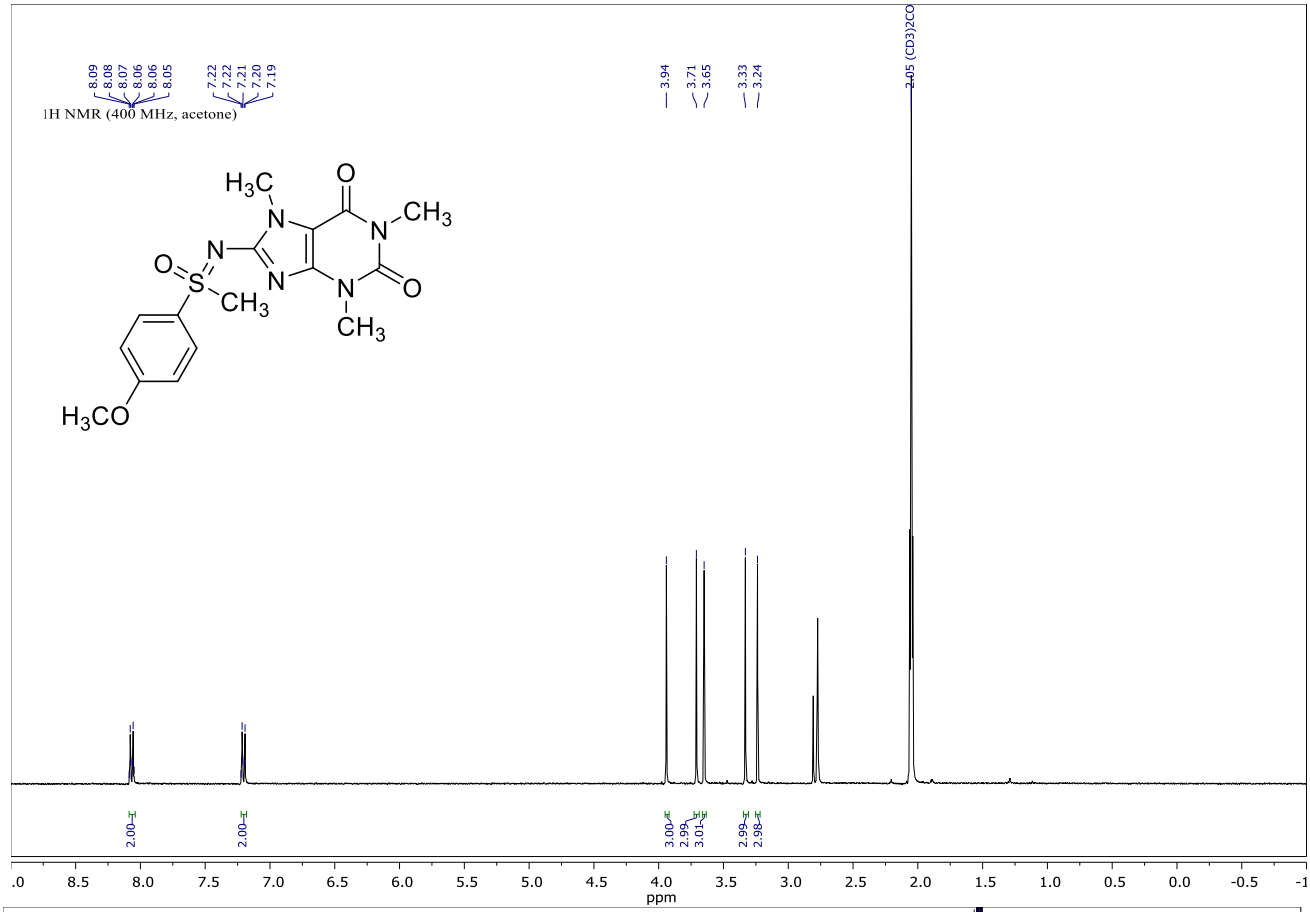


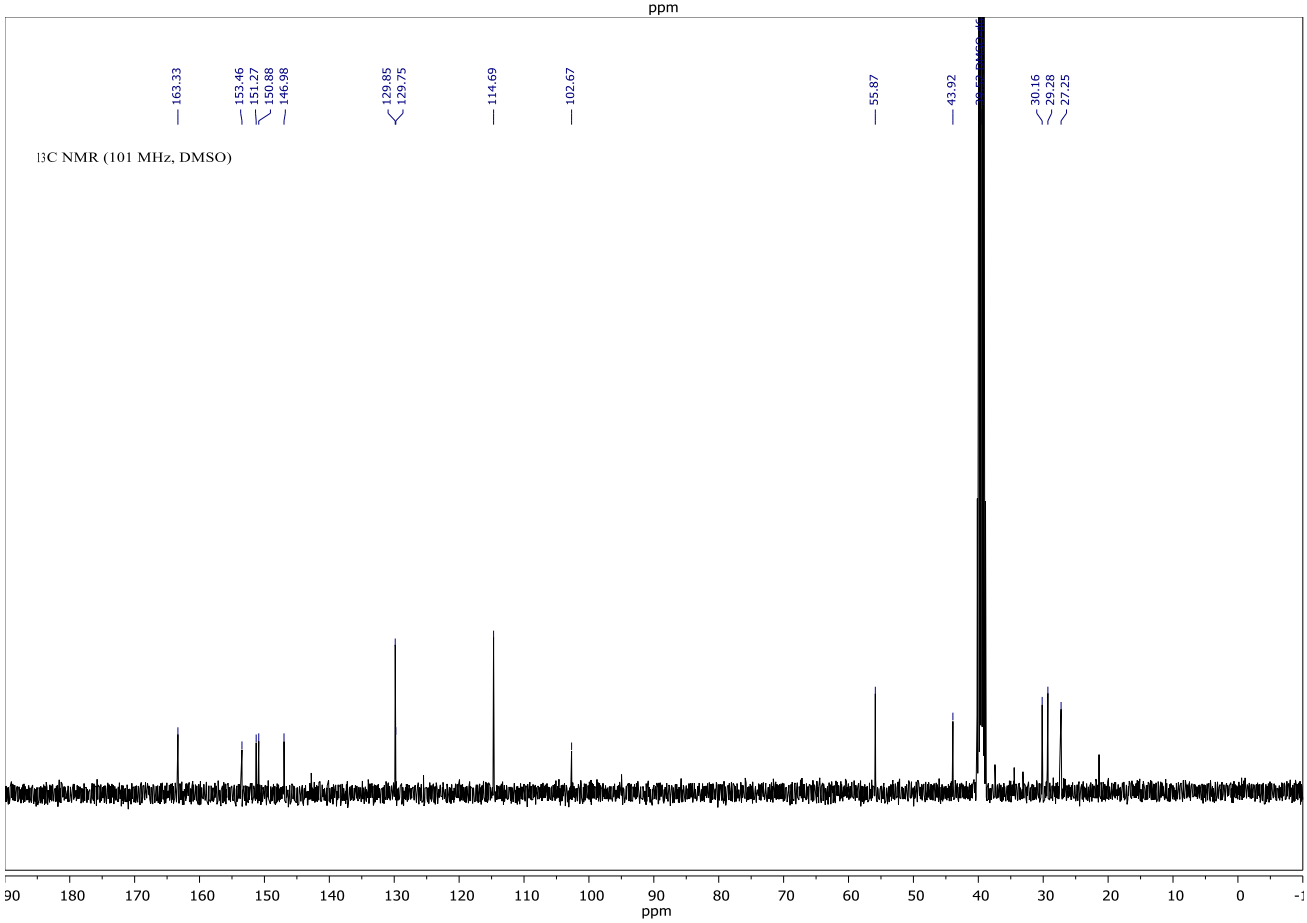
(Benzo[*d*]thiazol-2-ylimino)(4-methoxyphenyl)(methyl)-λ^6-sulfanone (3ag)



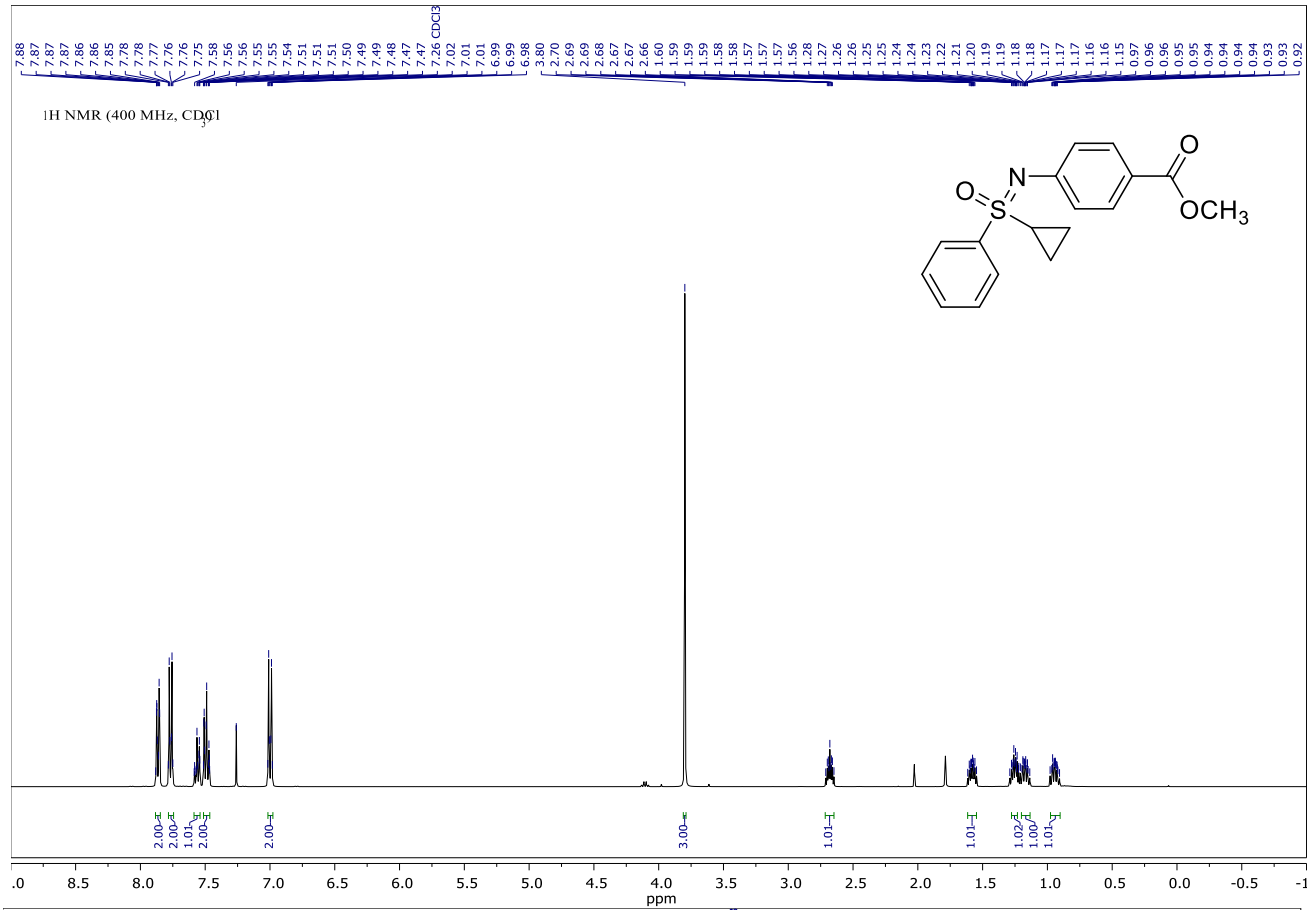


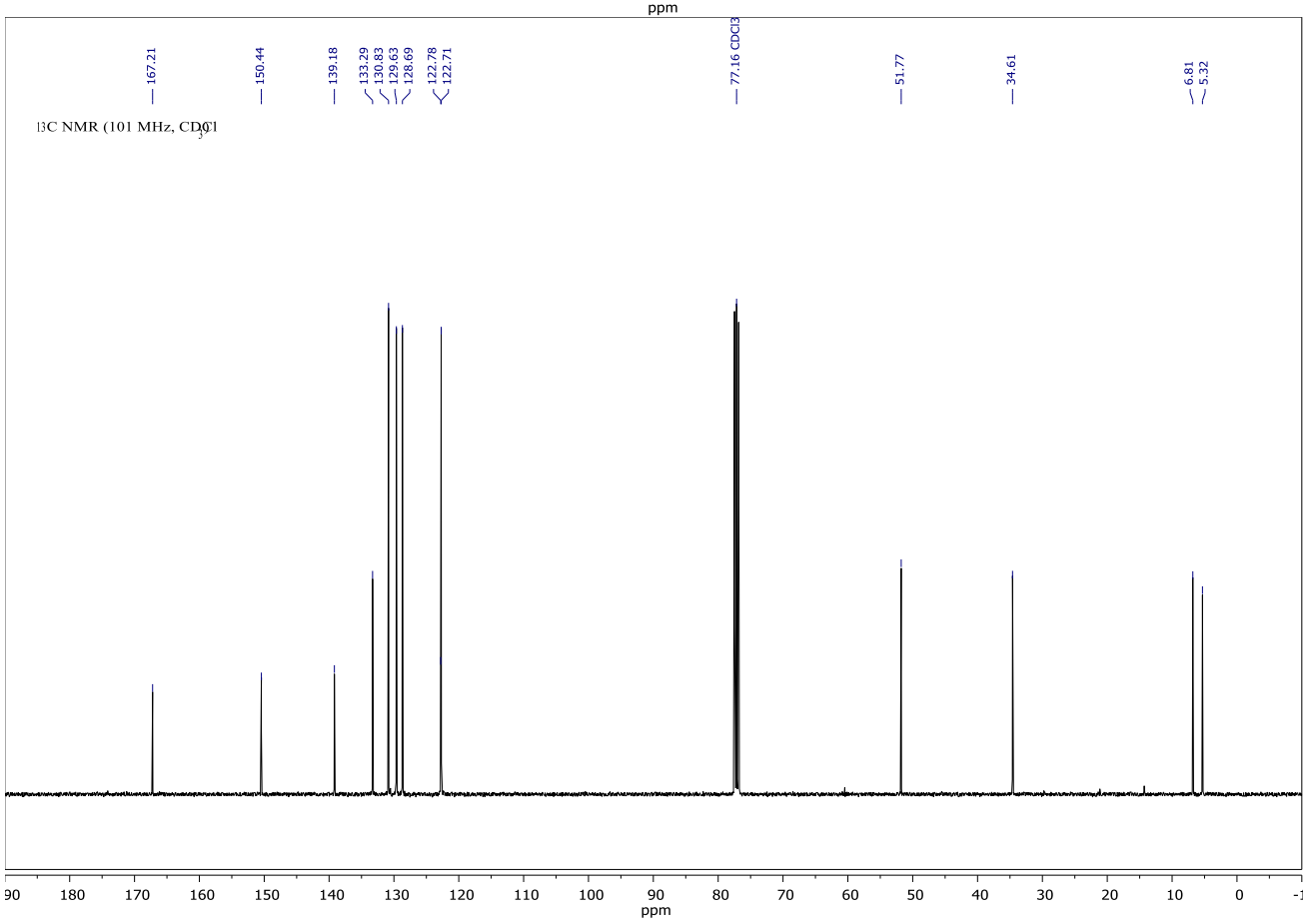
8-(((4-Methoxyphenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)-1,3,7-trimethyl-3,7-dihydro-1*H*-purine-2,6-dione (3ah)



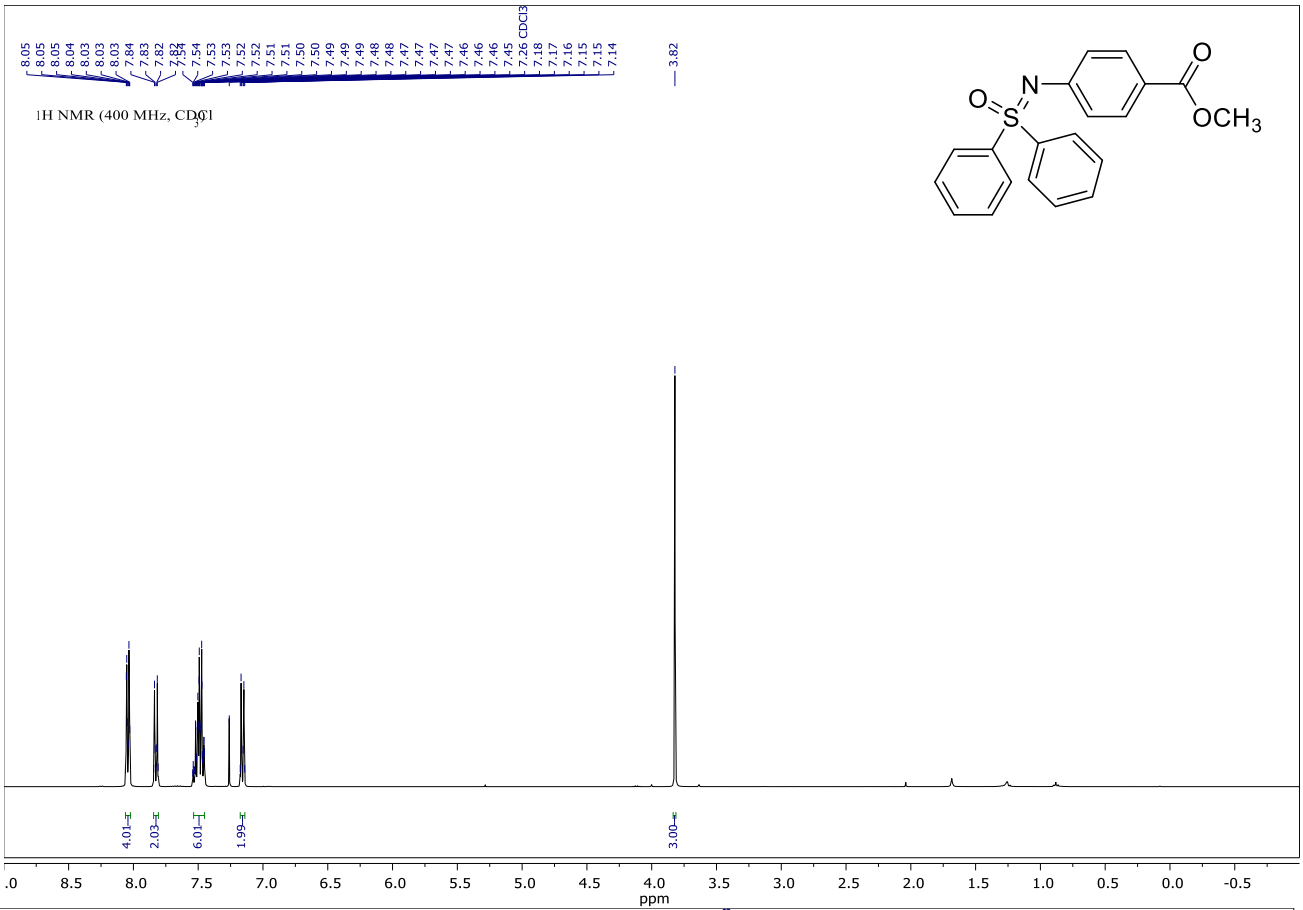


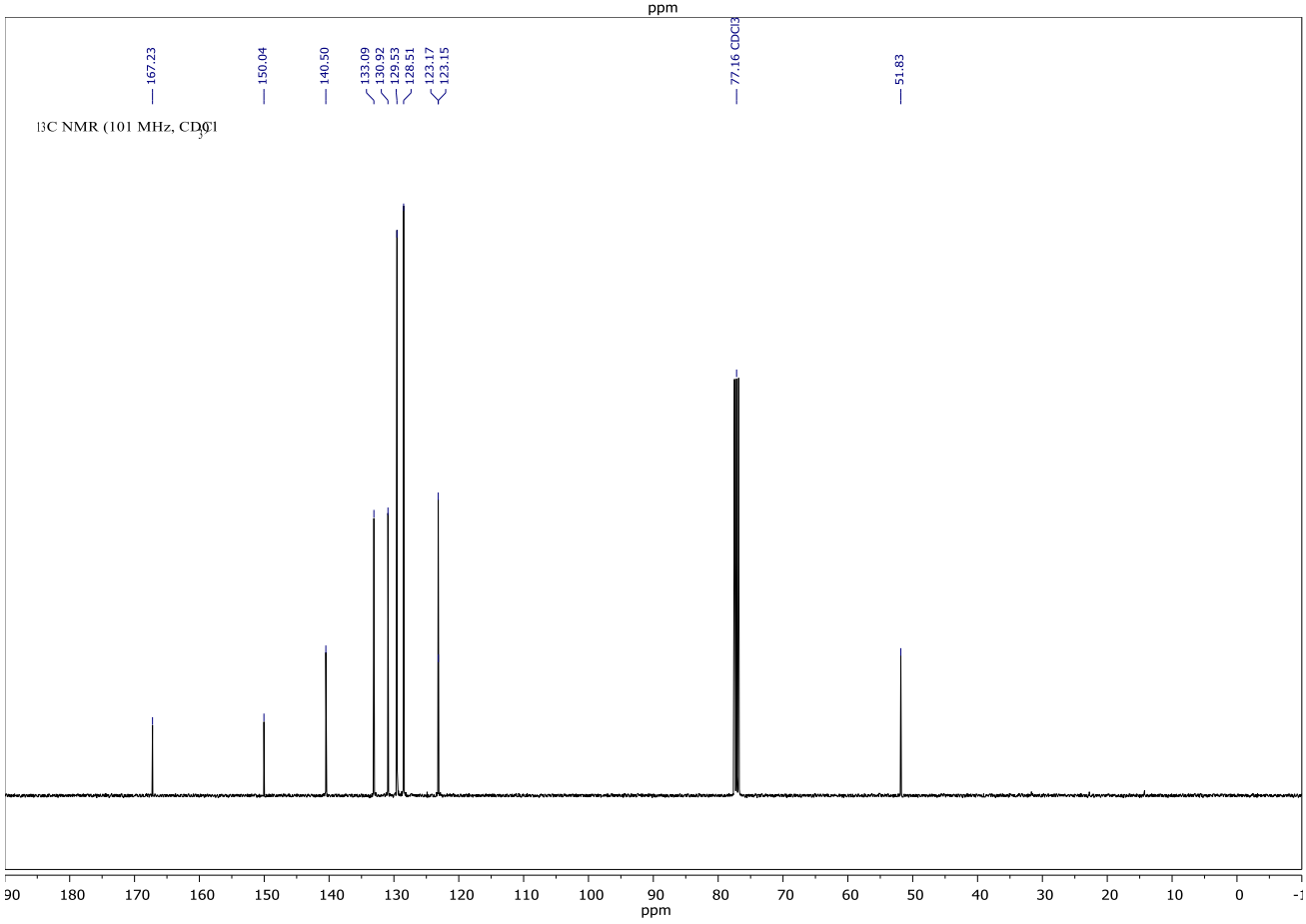
Methyl 4-((cyclopropyl(oxo)(phenyl)-λ^6-sulfaneylidene)amino)benzoate (3ai)



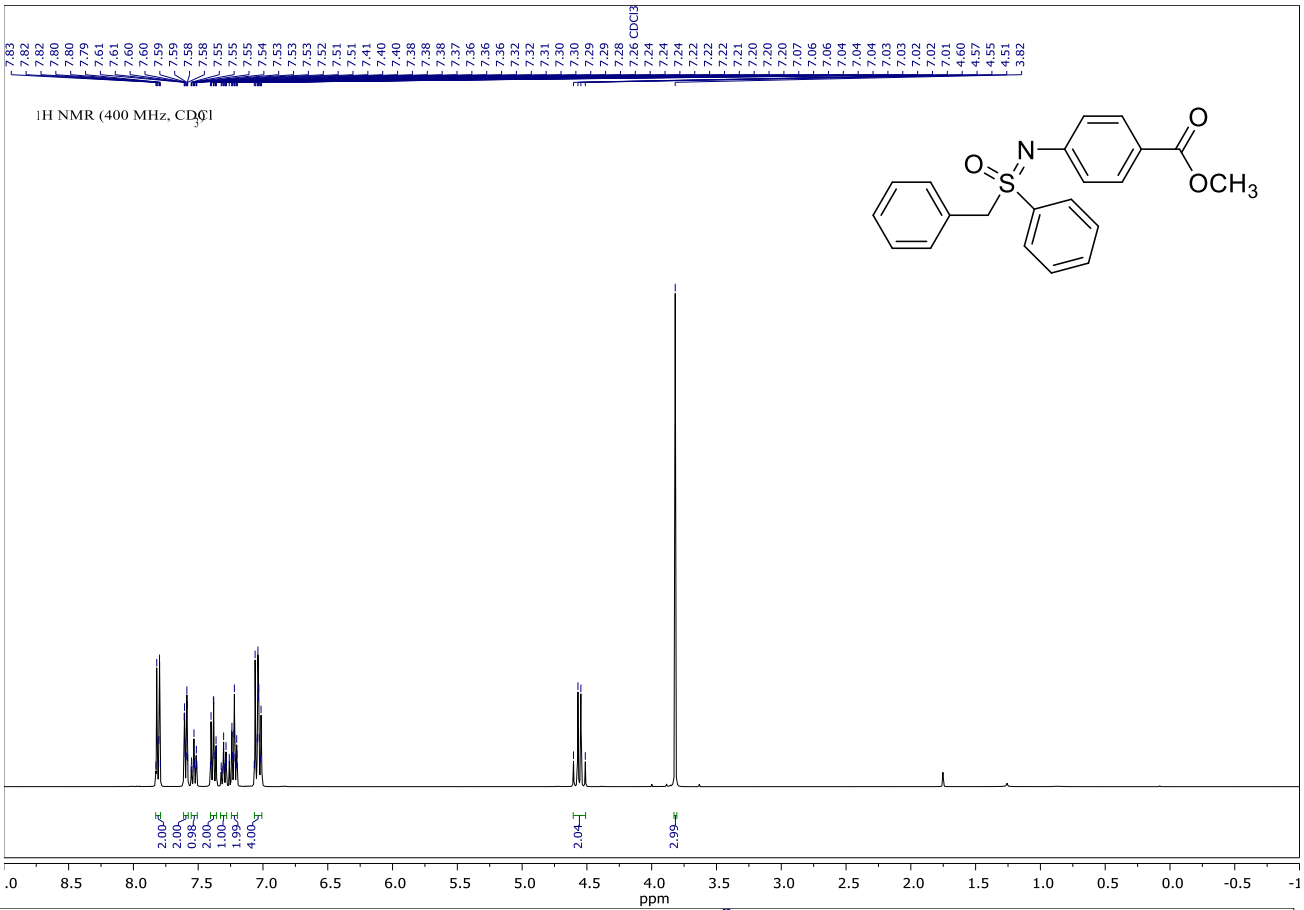


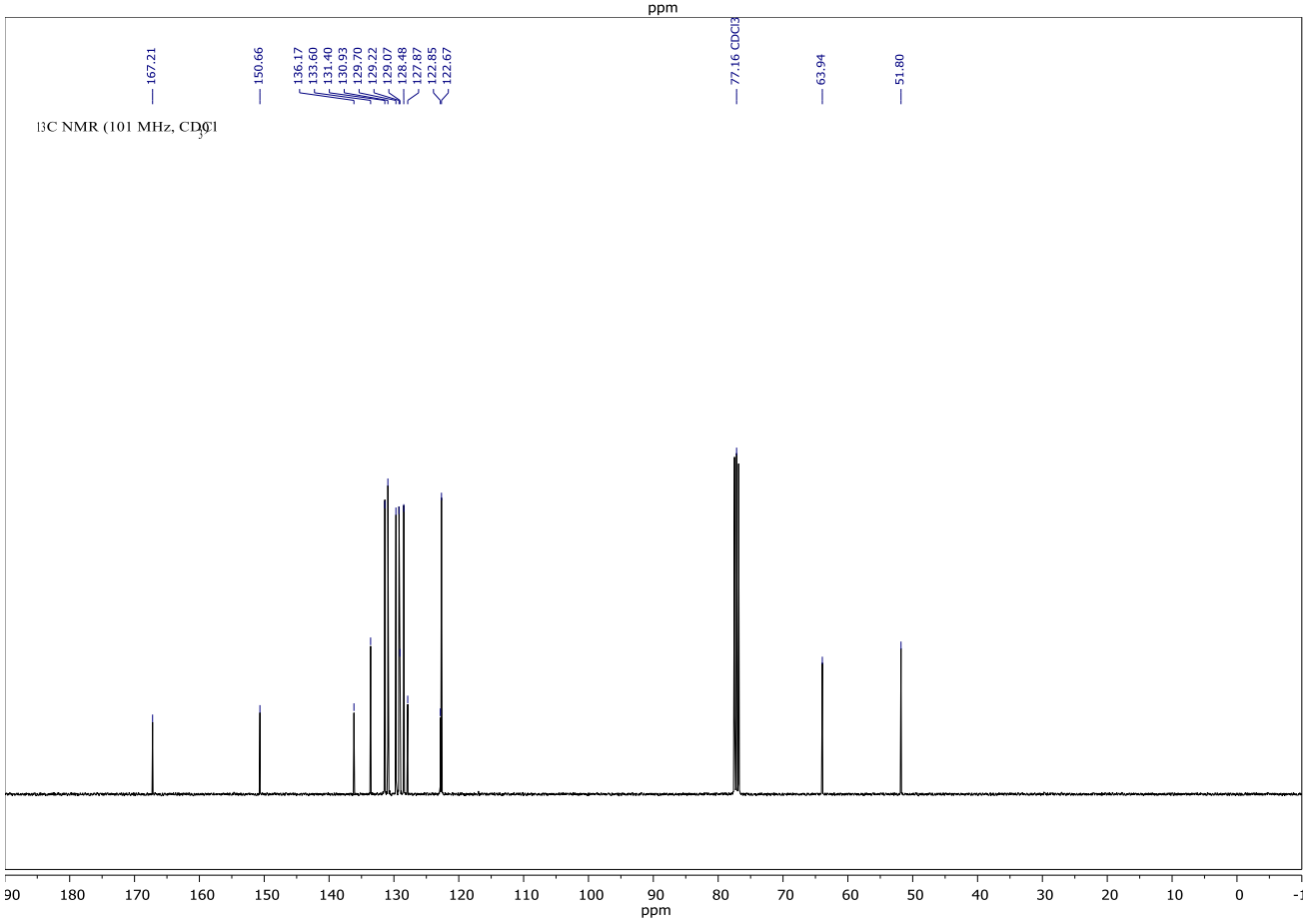
Methyl 4-((oxodiphenyl-λ^6-sulfaneylidene)amino)benzoate (3aj)



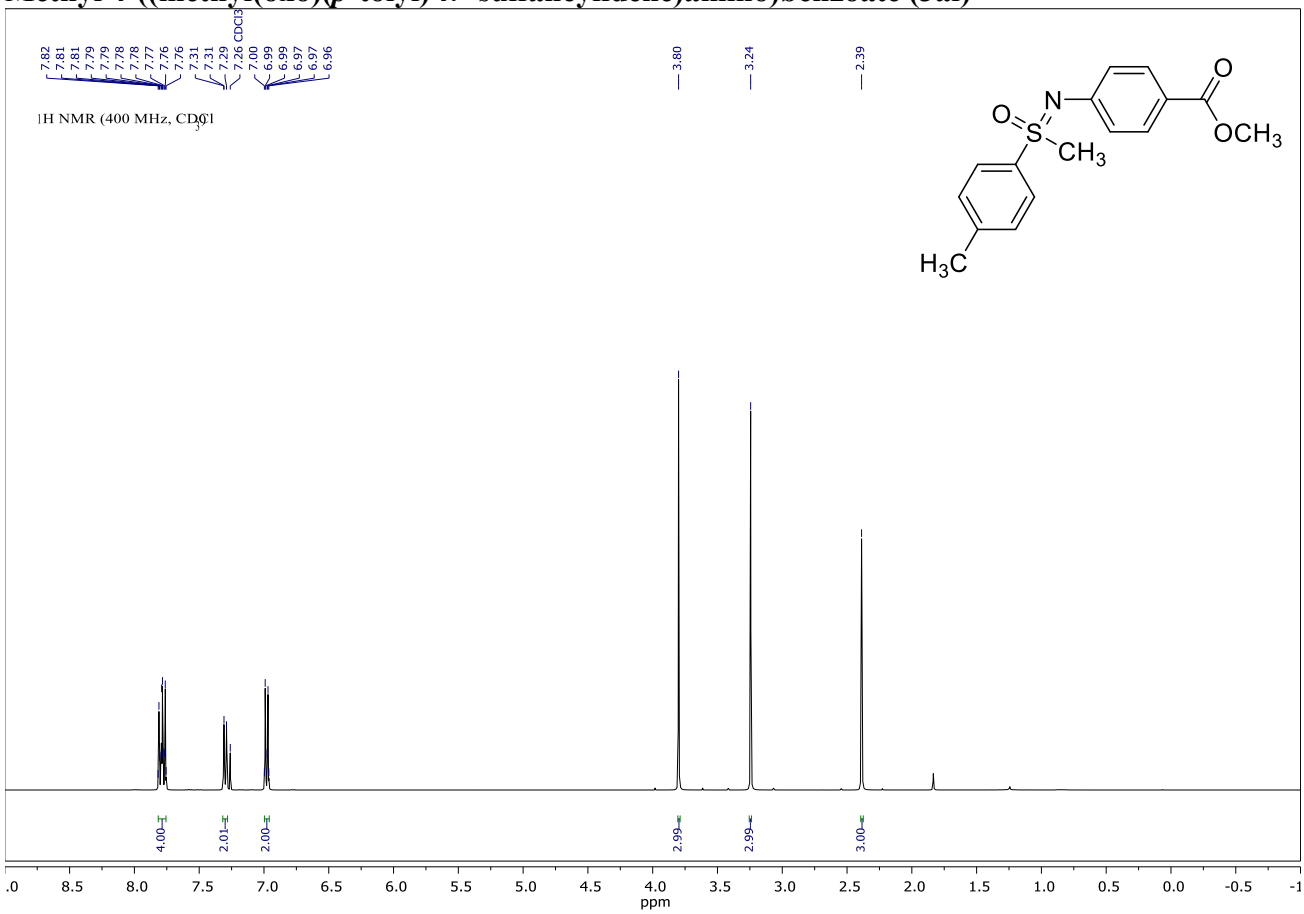


Methyl 4-((benzyl(oxo)(phenyl)-λ^6-sulfaneylidene)amino)benzoate (3ak)

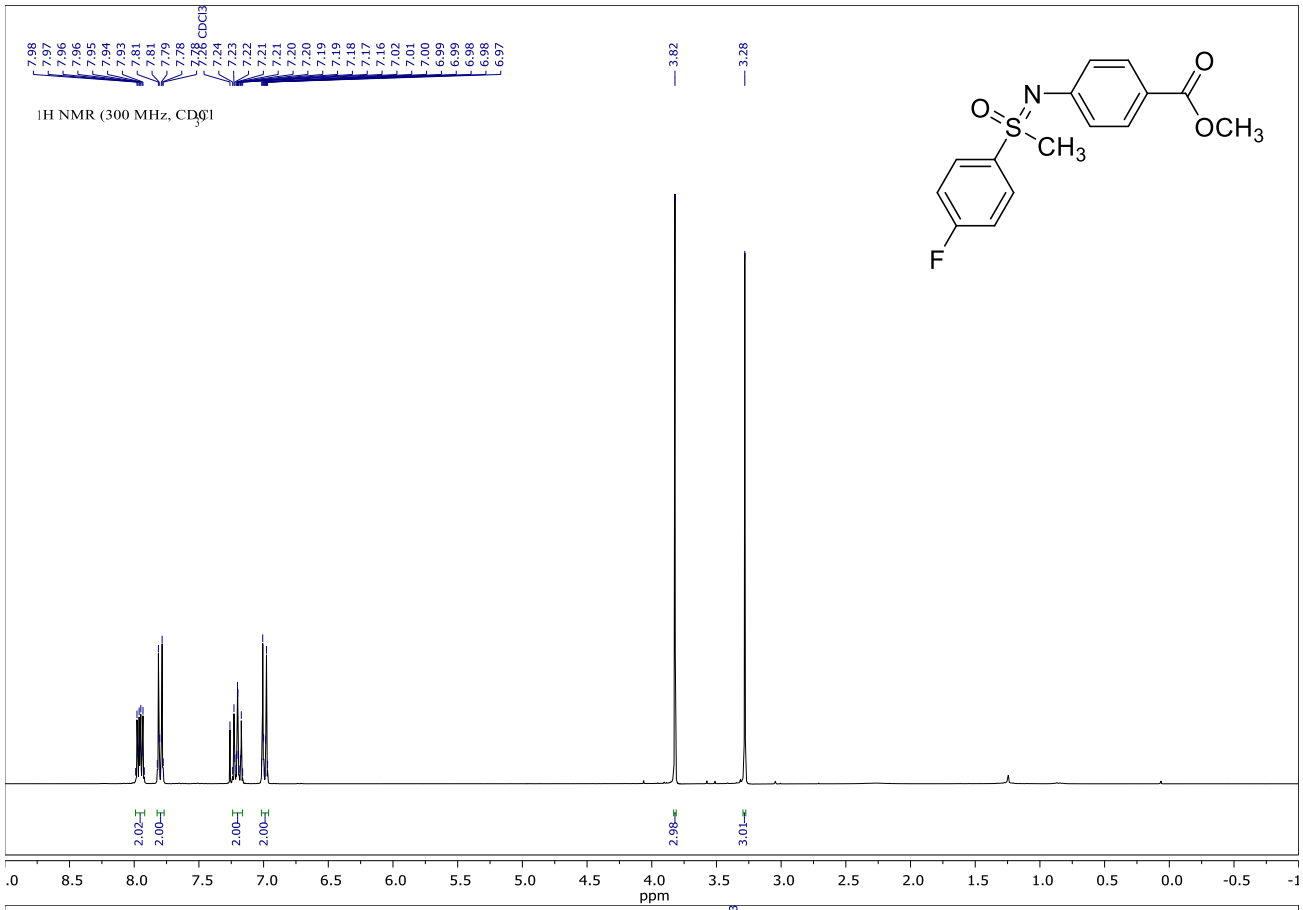


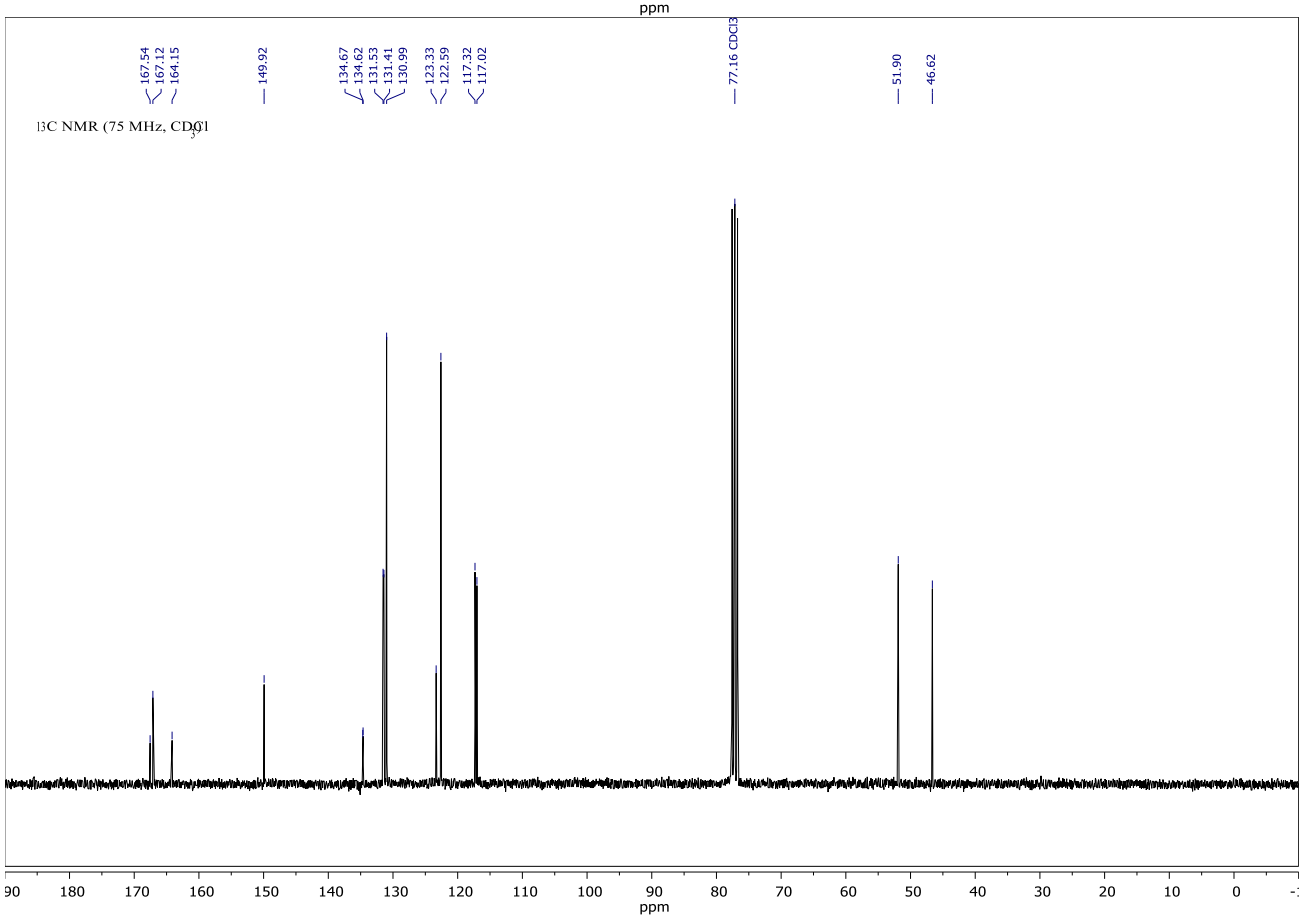


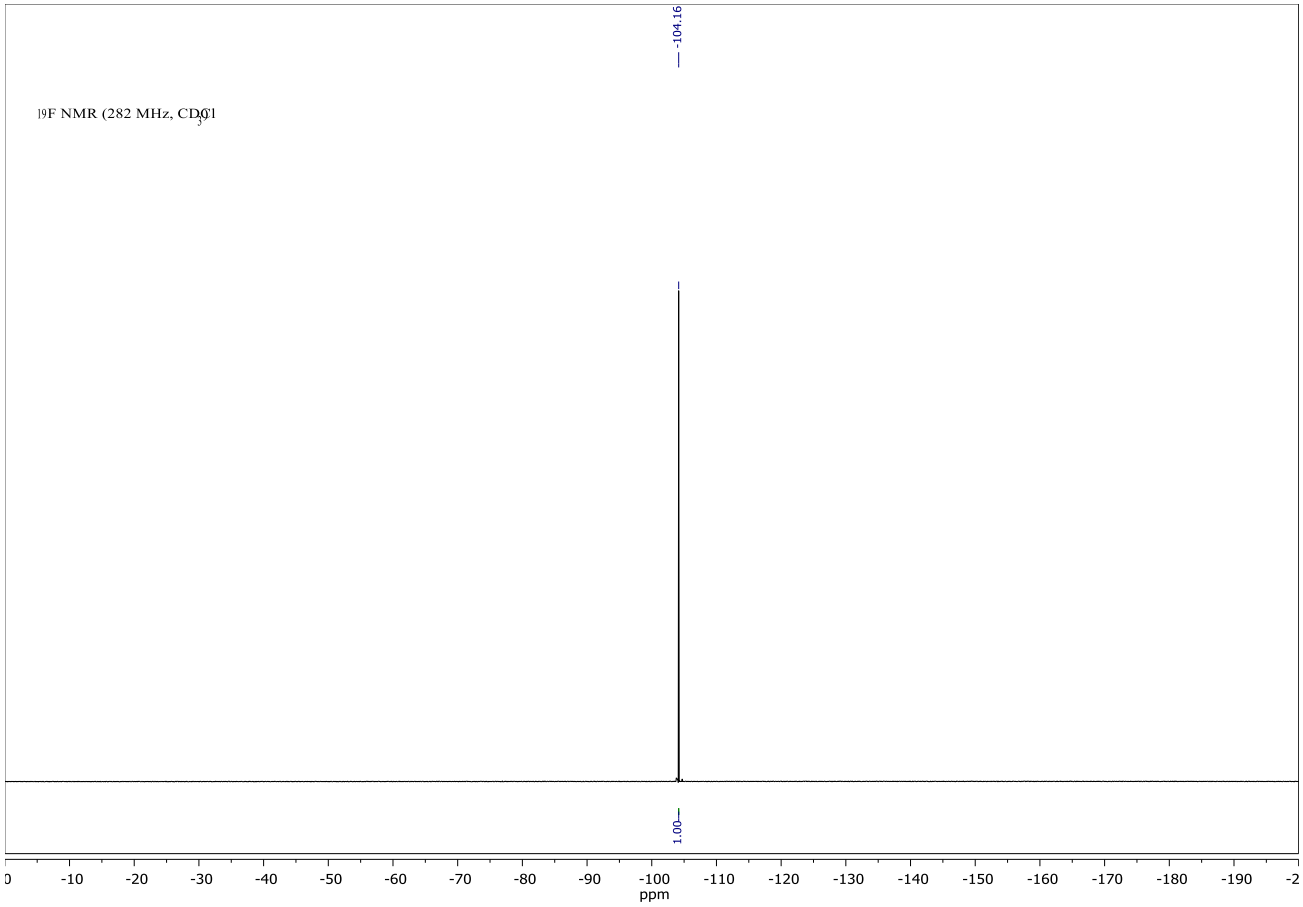
Methyl 4-((methyl(oxo)(*p*-tolyl)-λ^6-sulfaneylidene)amino)benzoate (3al)



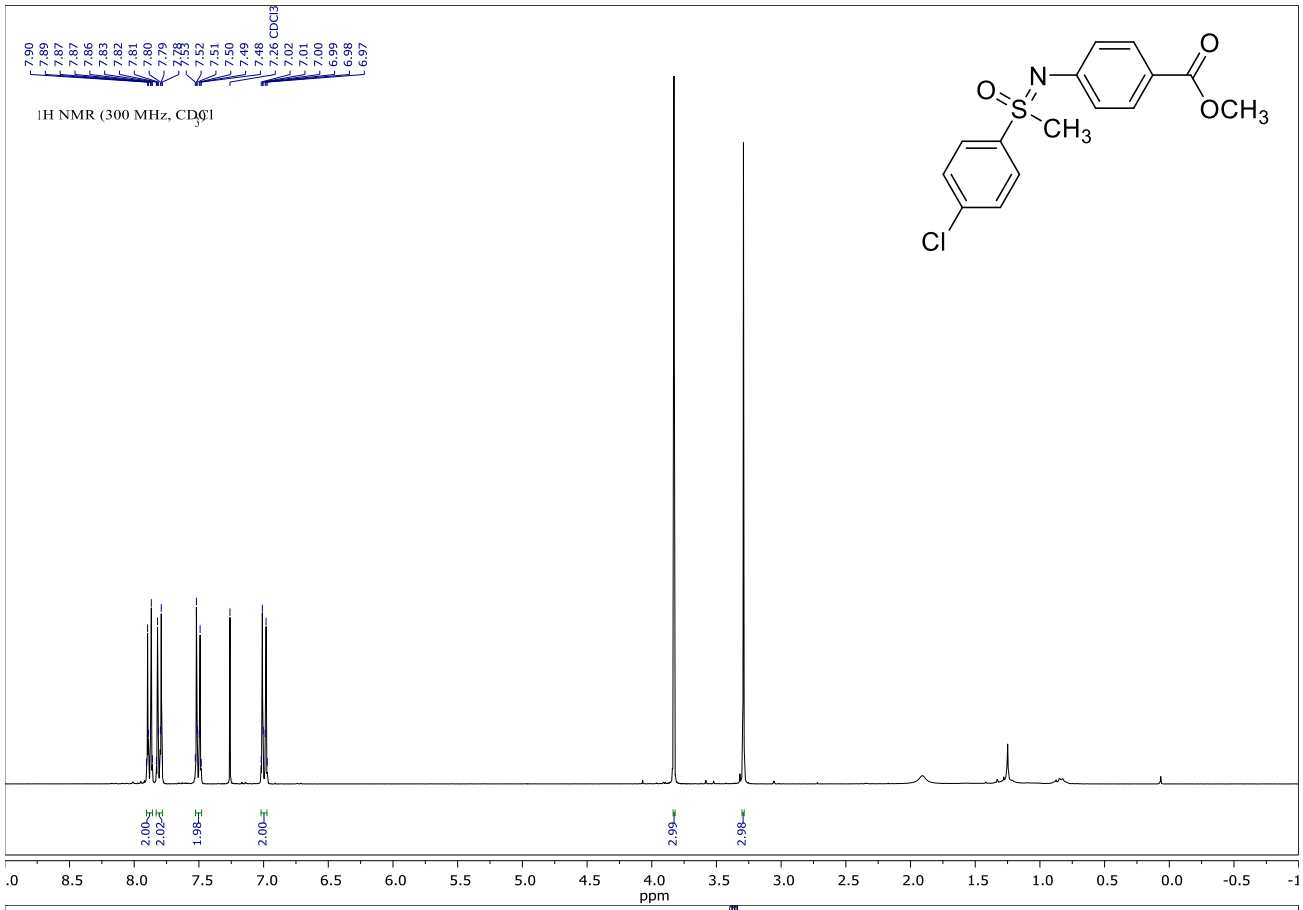
Methyl 4-(((4-fluorophenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)benzoate (3am)

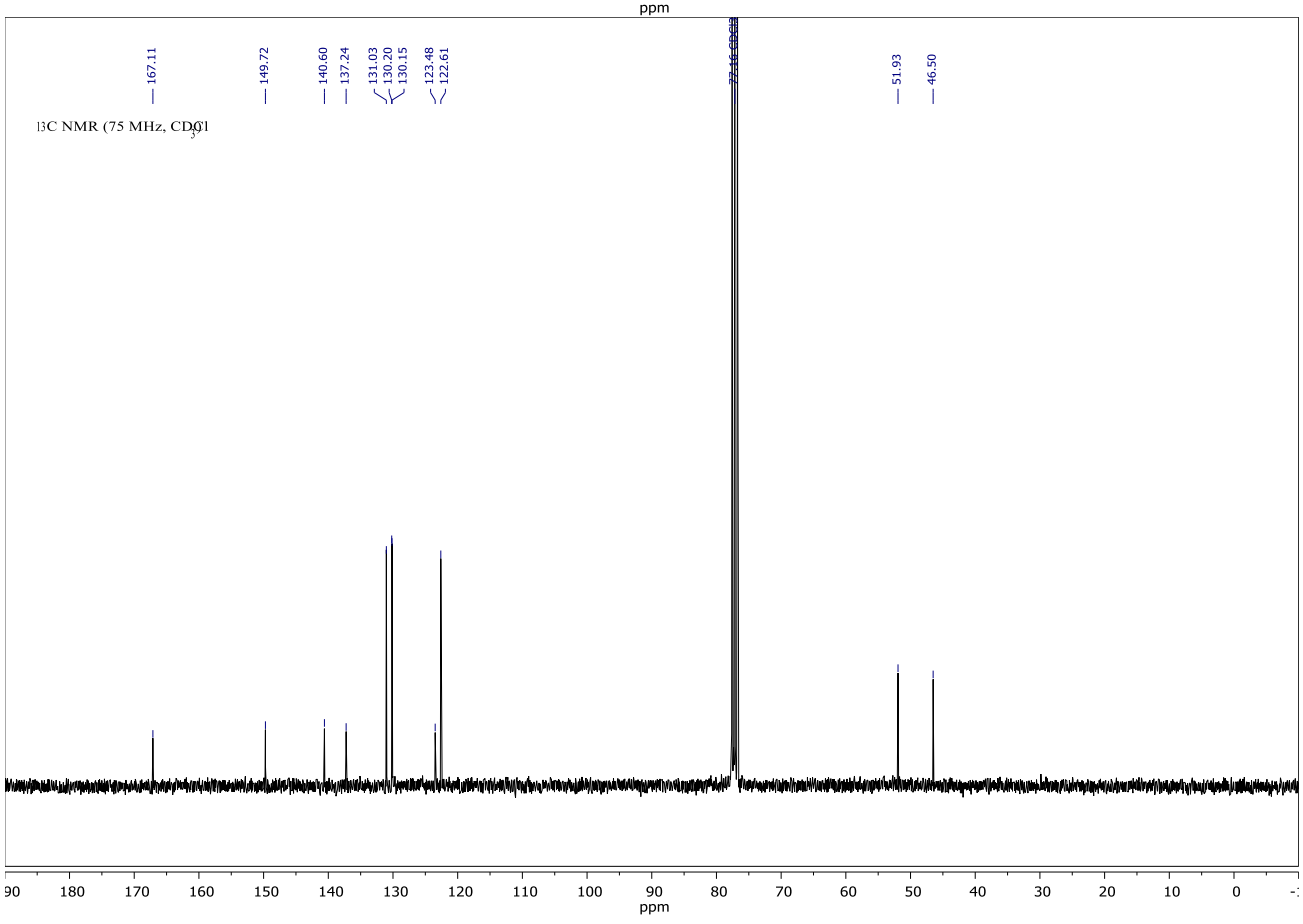




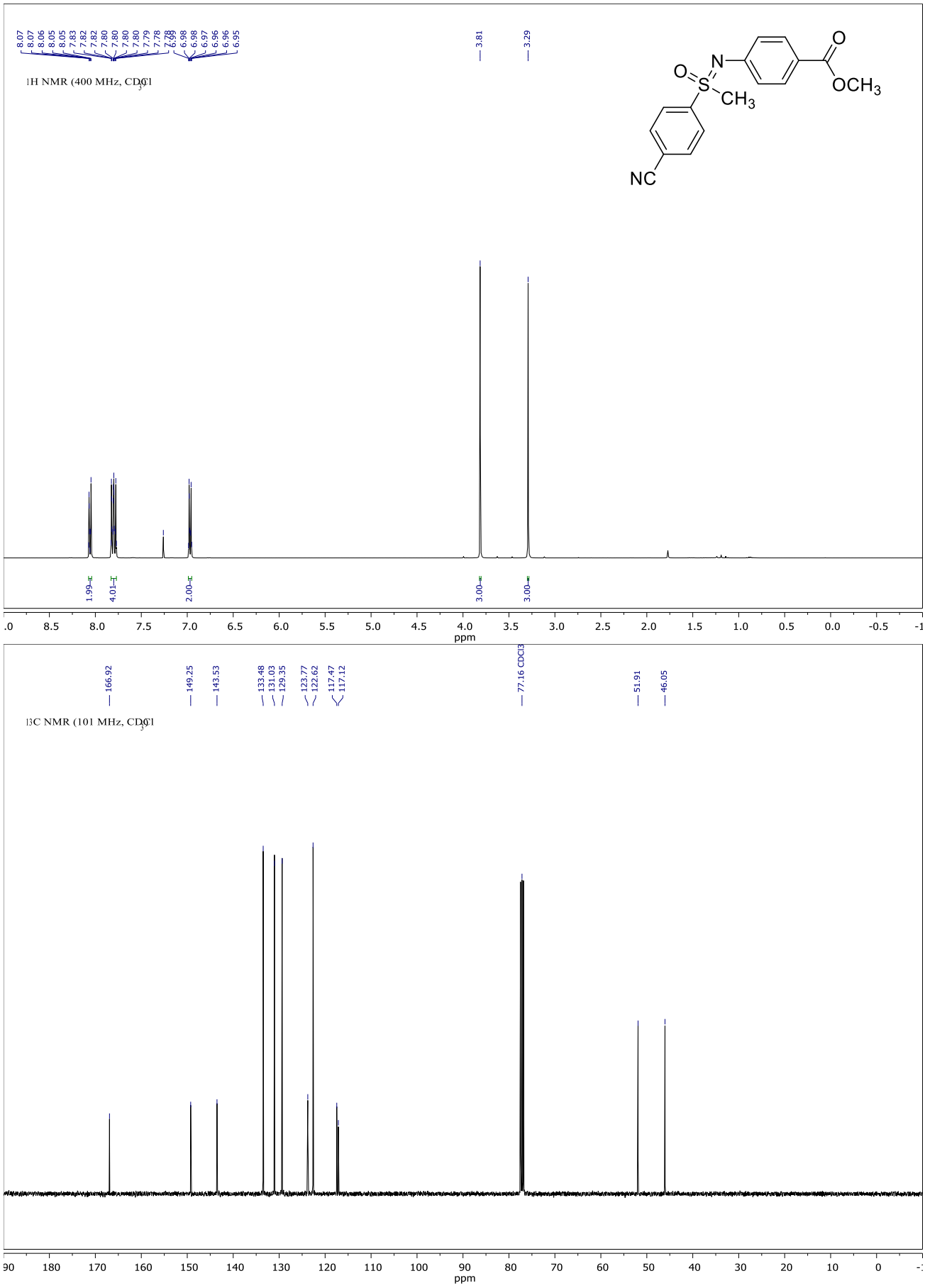

19F NMR (282 MHz, CD3OD)
-104.16
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
ppm

Methyl 4-(((4-chlorophenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)benzoate (3an)

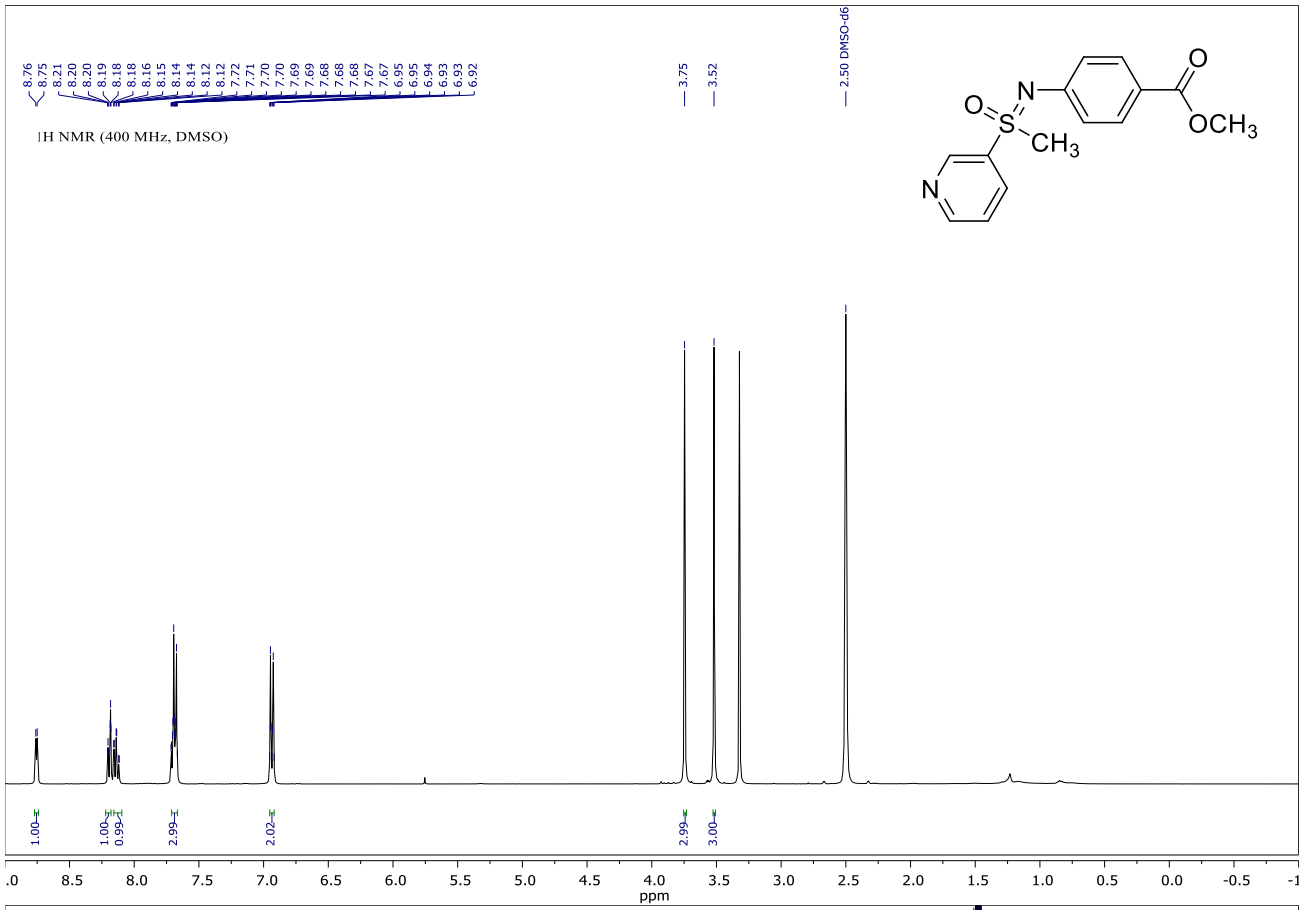


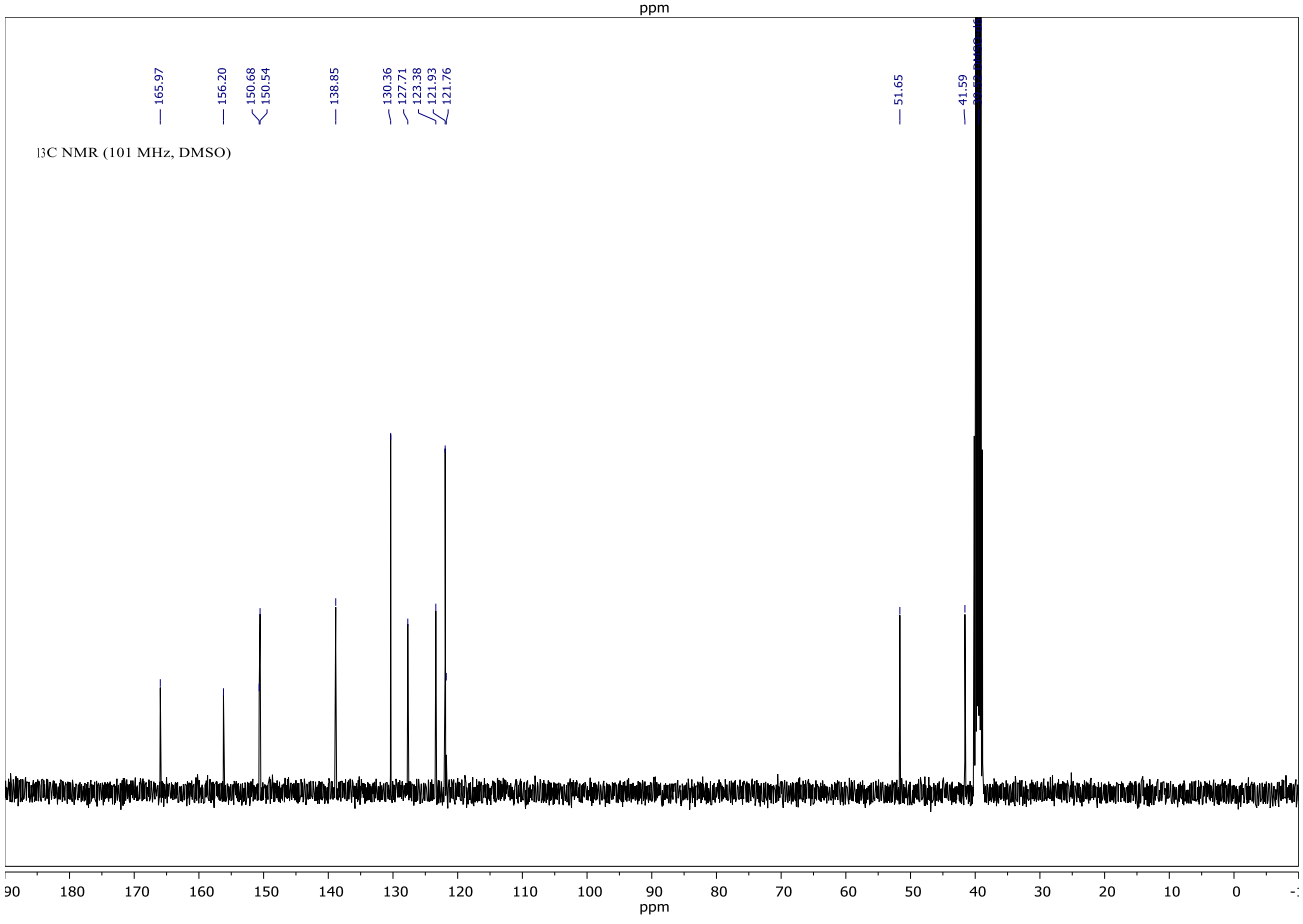


Methyl 4-(((4-cyanophenyl)(methyl)(oxo)-λ^6-sulfaneylidene)amino)benzoate (3ao)

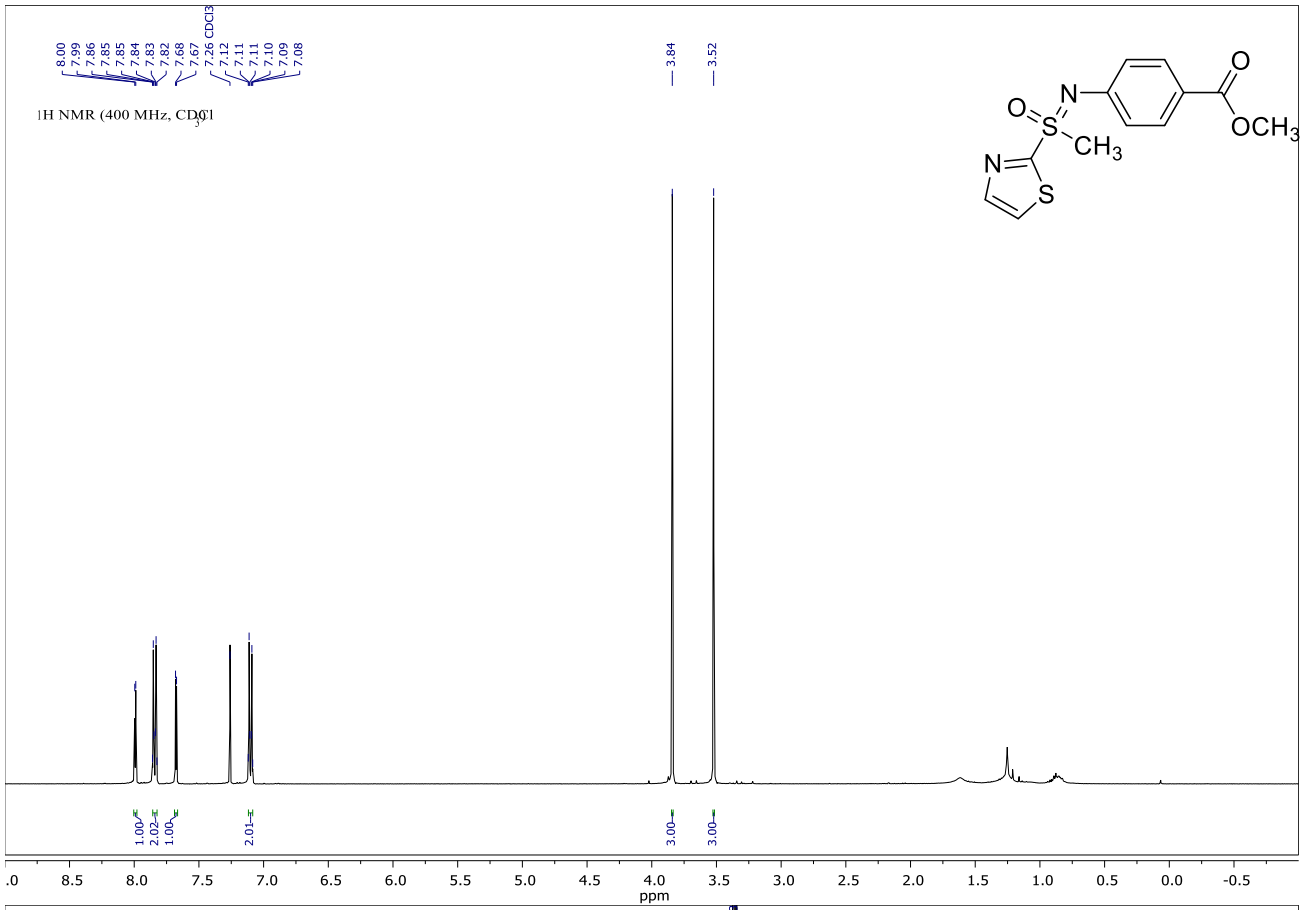


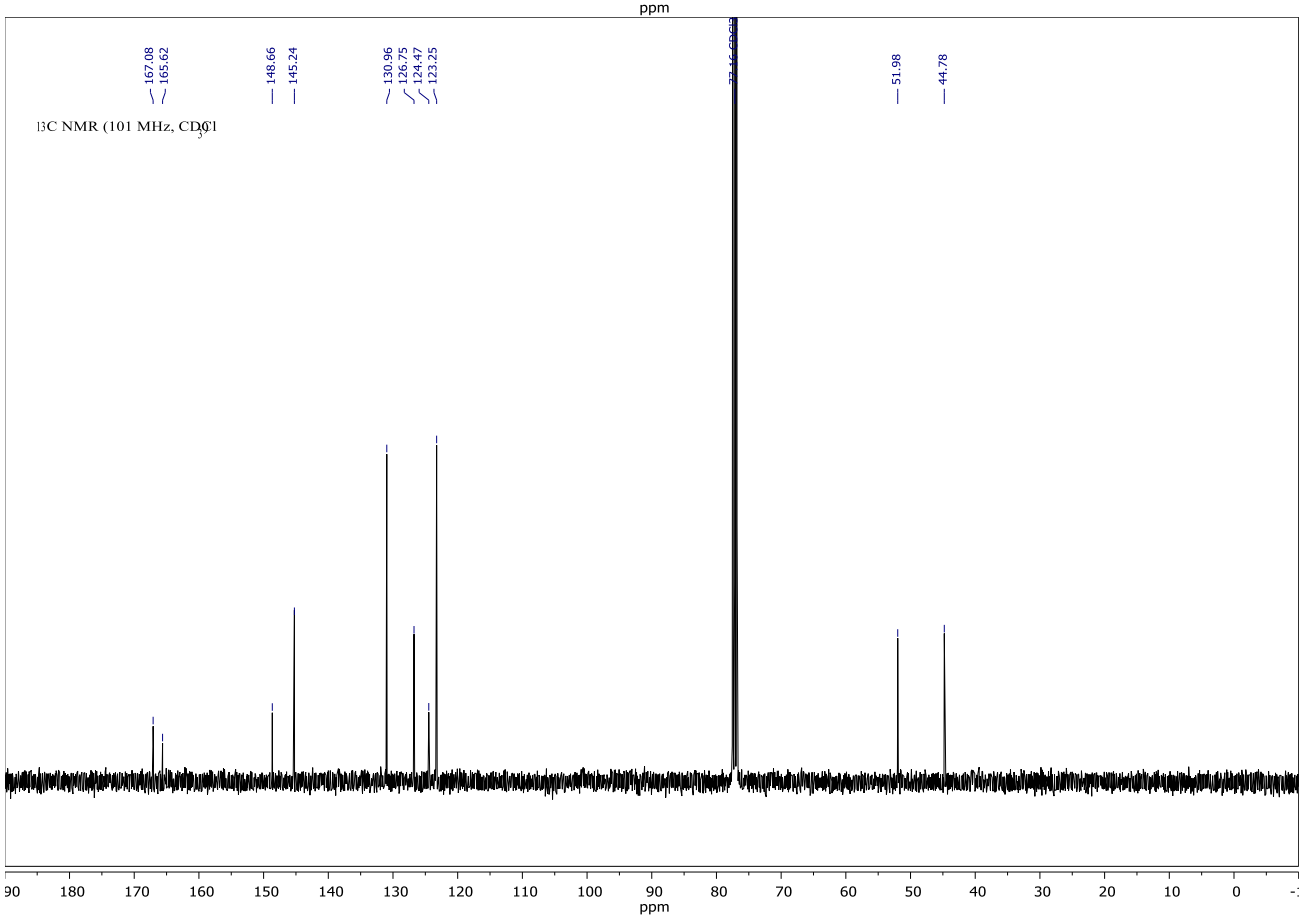
Methyl 4-((methyl(oxo)(pyridin-3-yl)-λ^6-sulfaneylidene)amino)benzoate (3ap)



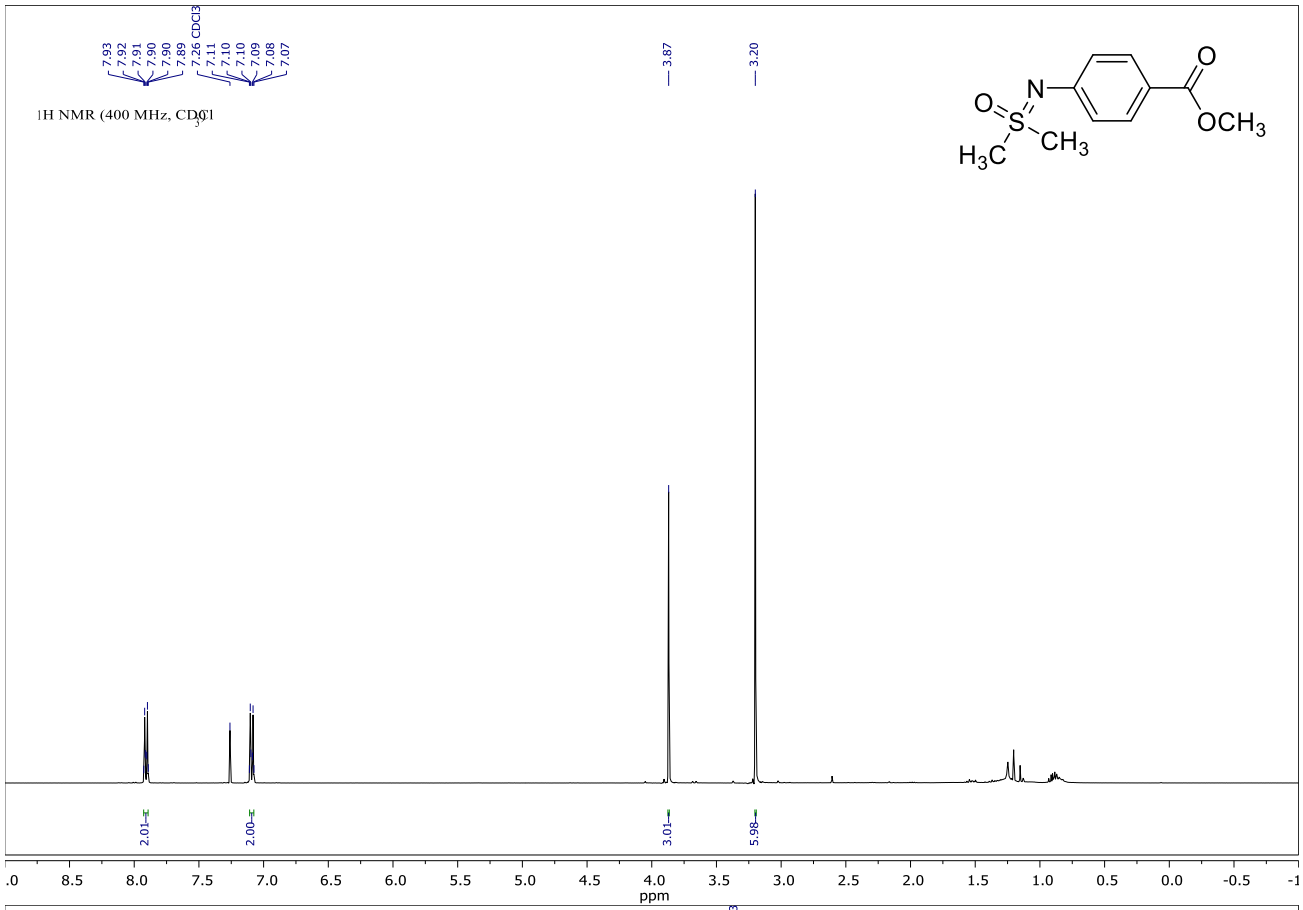


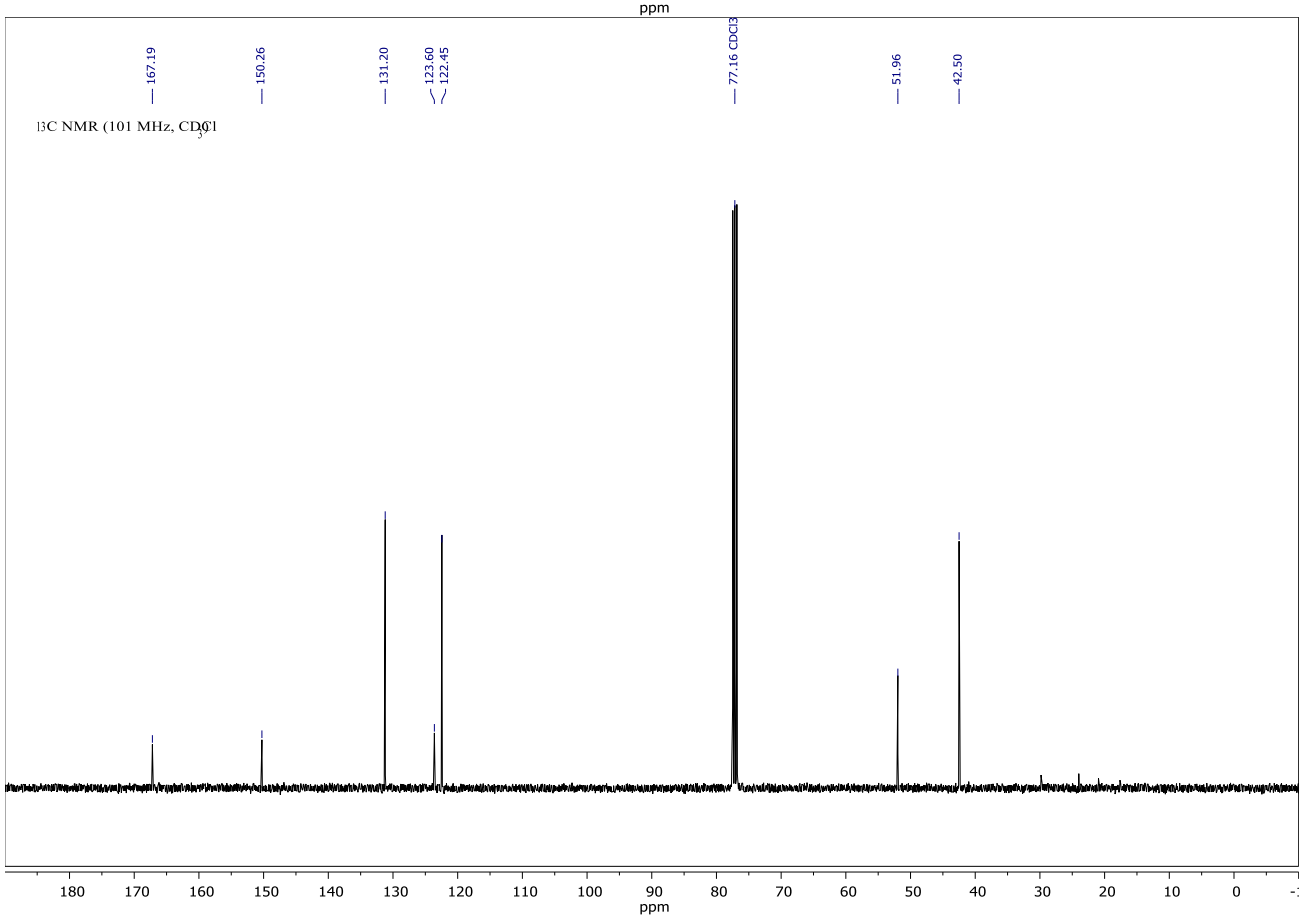
Methyl 4-((methyl(oxo)(thiazol-2-yl)-λ^6-sulfaneylidene)amino)benzoate (3aq)



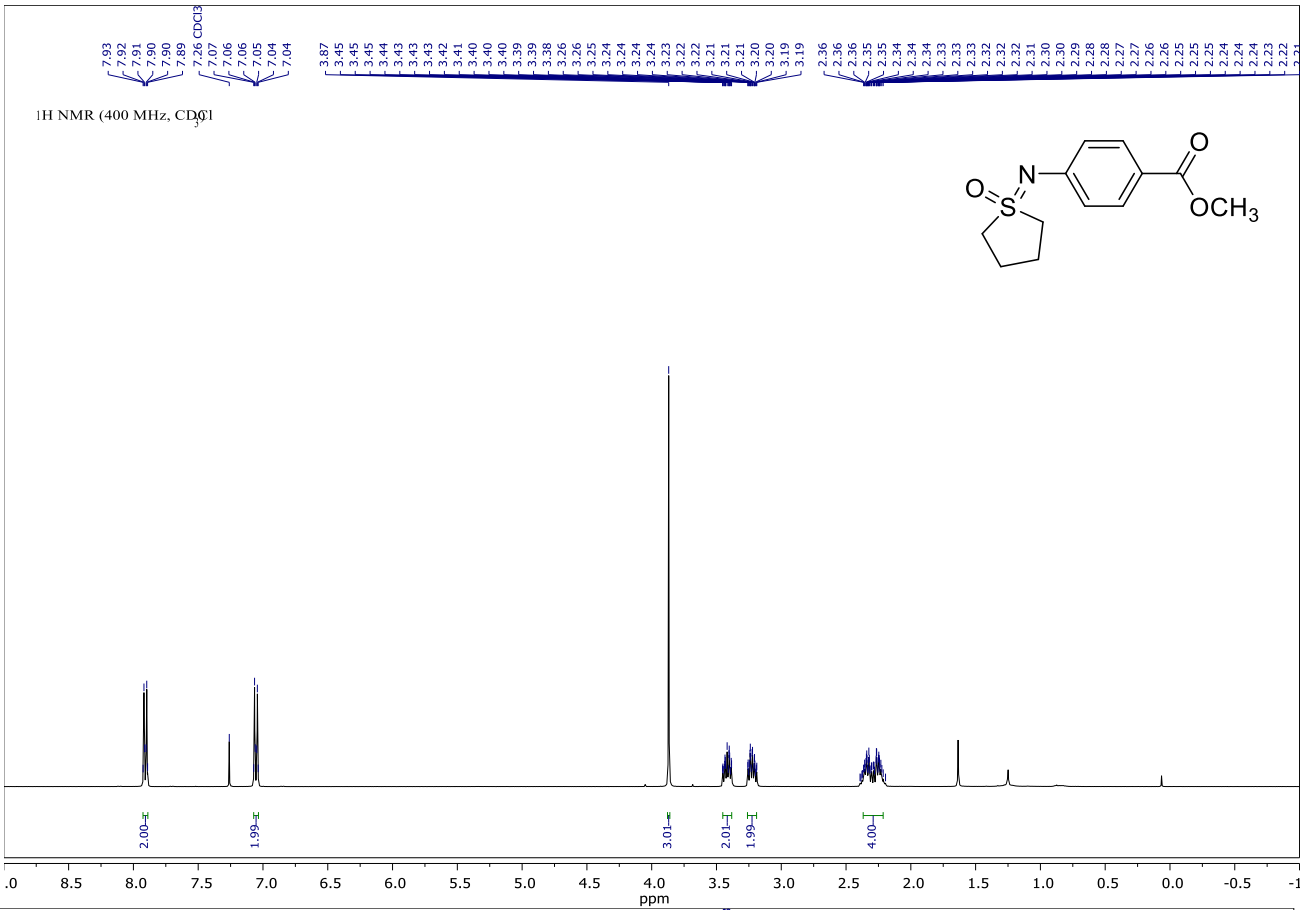


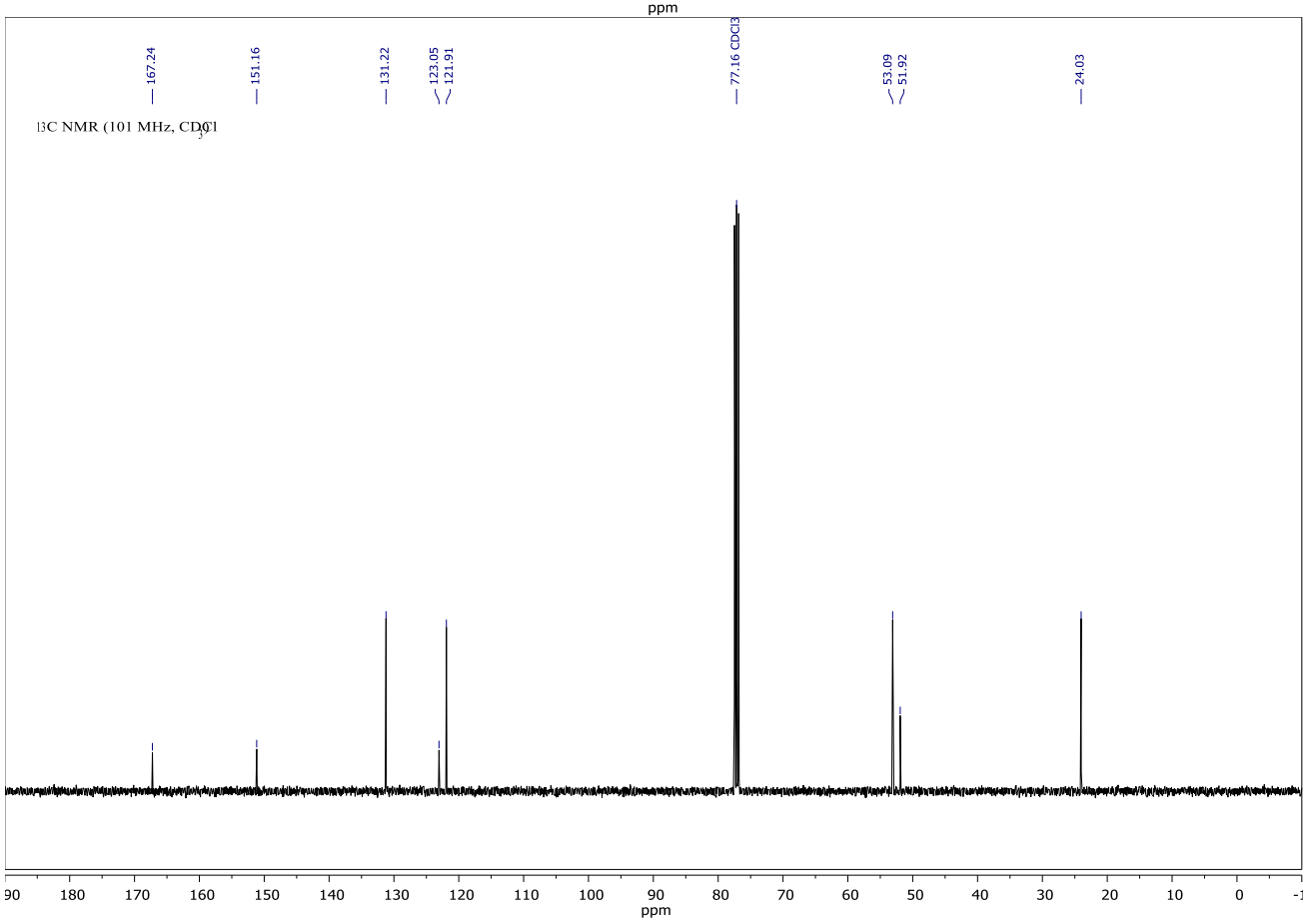
Methyl 4-((dimethyl(oxo)-λ^6-sulfaneylidene)amino)benzoate (3ar)



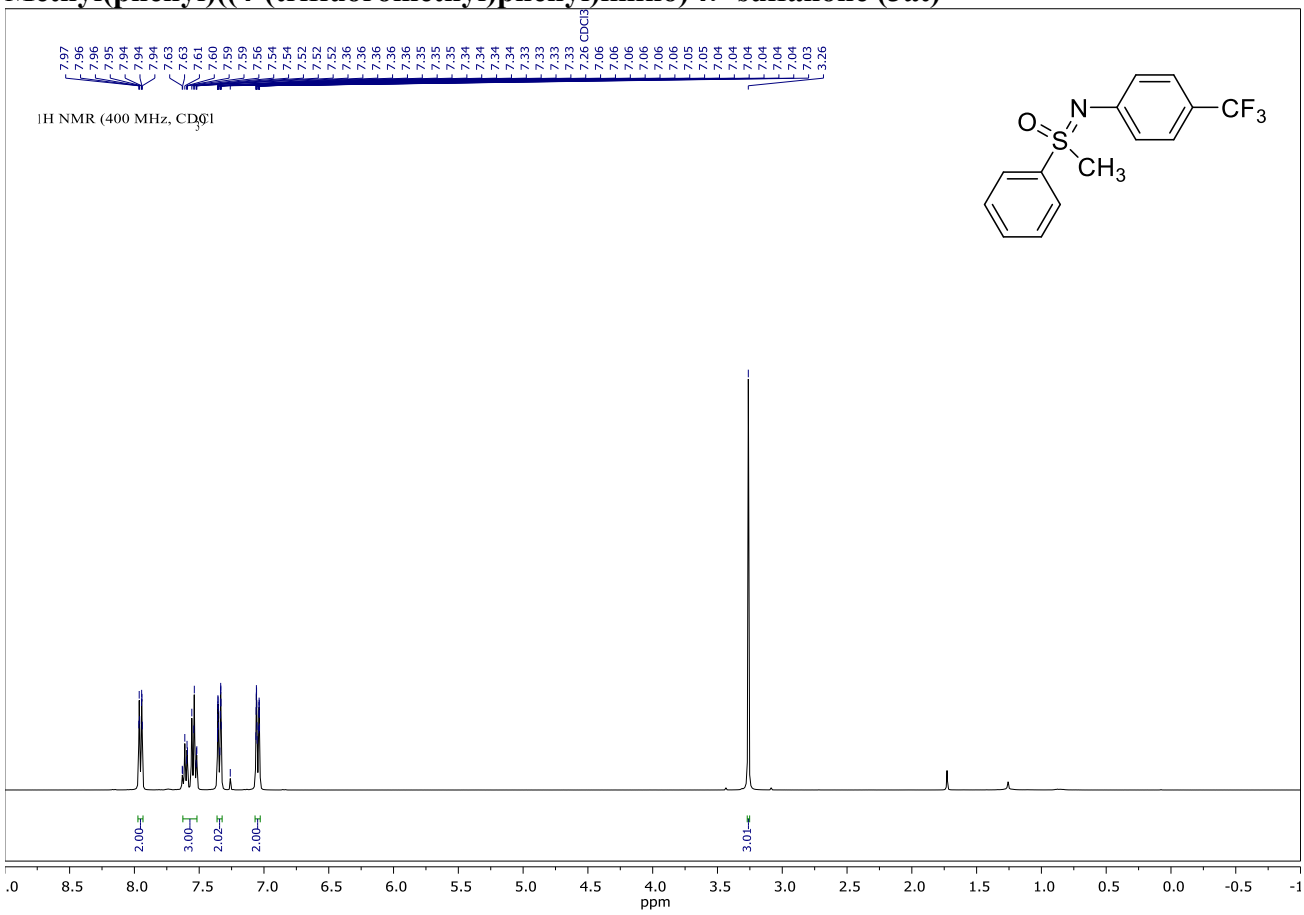


Methyl 4-((1-oxidotetrahydro-1λ^6-thiophen-1-ylidene)amino)benzoate (3as)

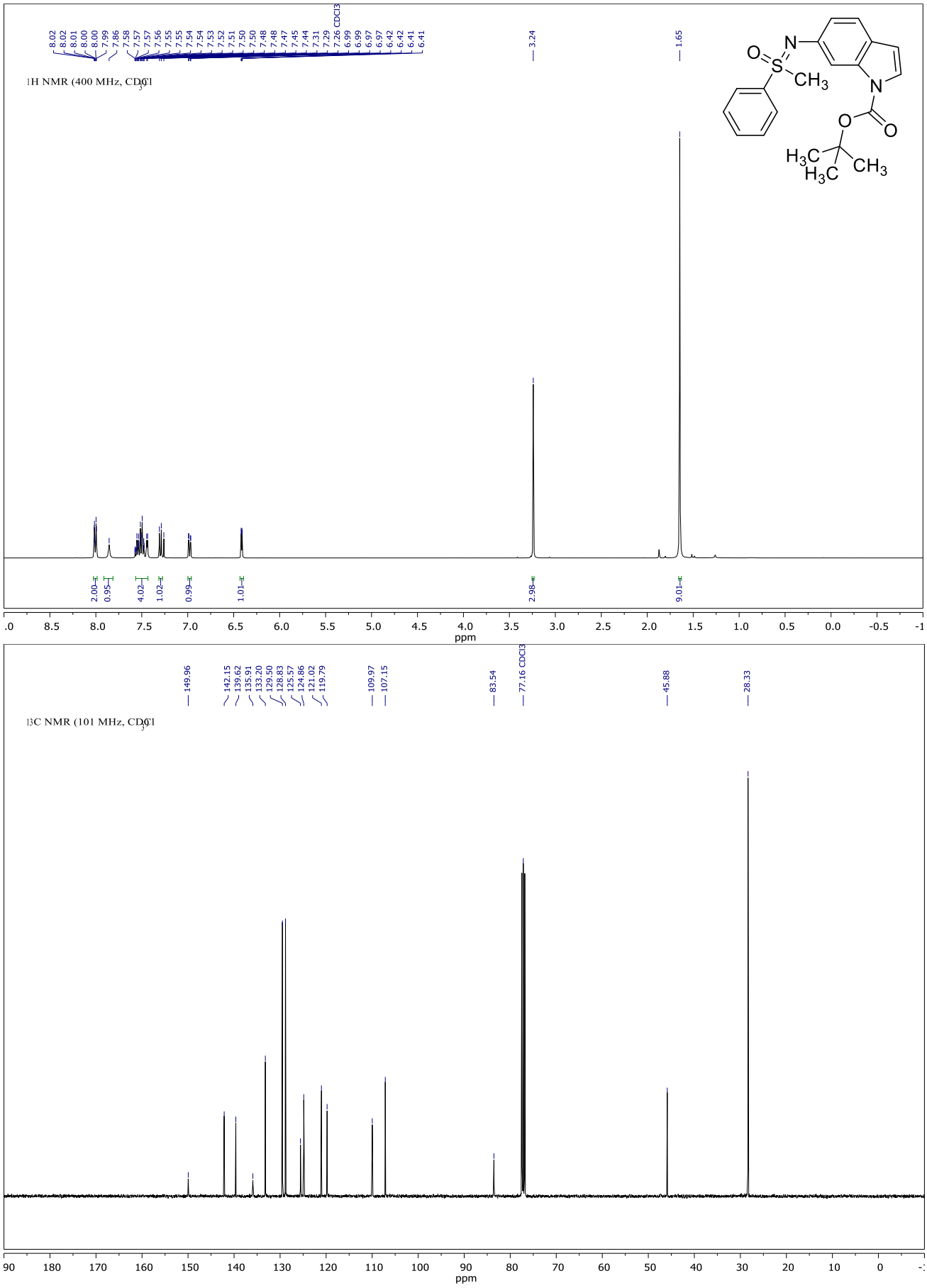




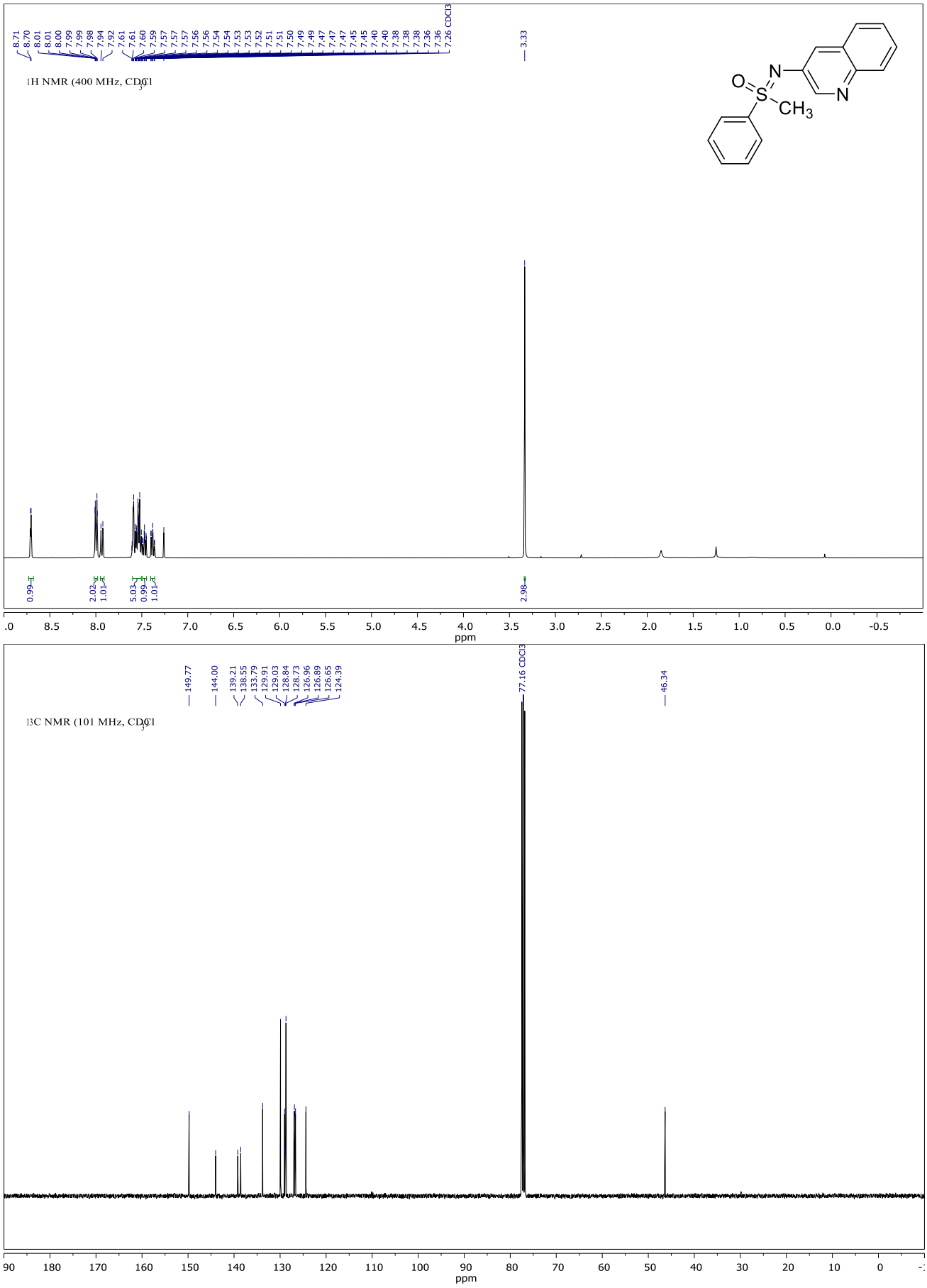
Methyl(phenyl)((4-(trifluoromethyl)phenyl)imino)-λ^6-sulfanone (3at)



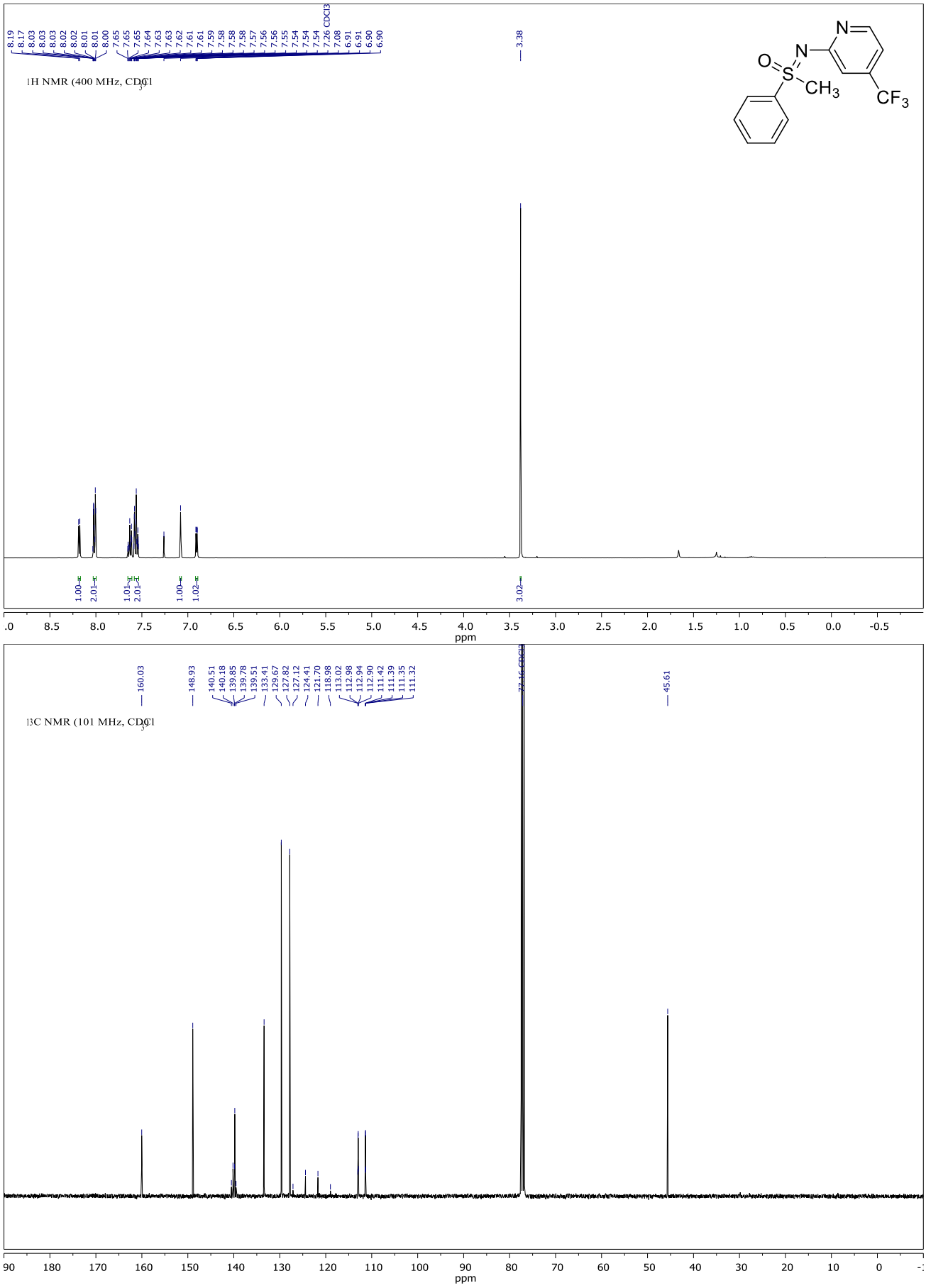
tert-butyl 6-((methyl(oxo)(phenyl)-λ^6-sulfaneylidene)amino)-1_H_-indole-1-carboxylate (3au)

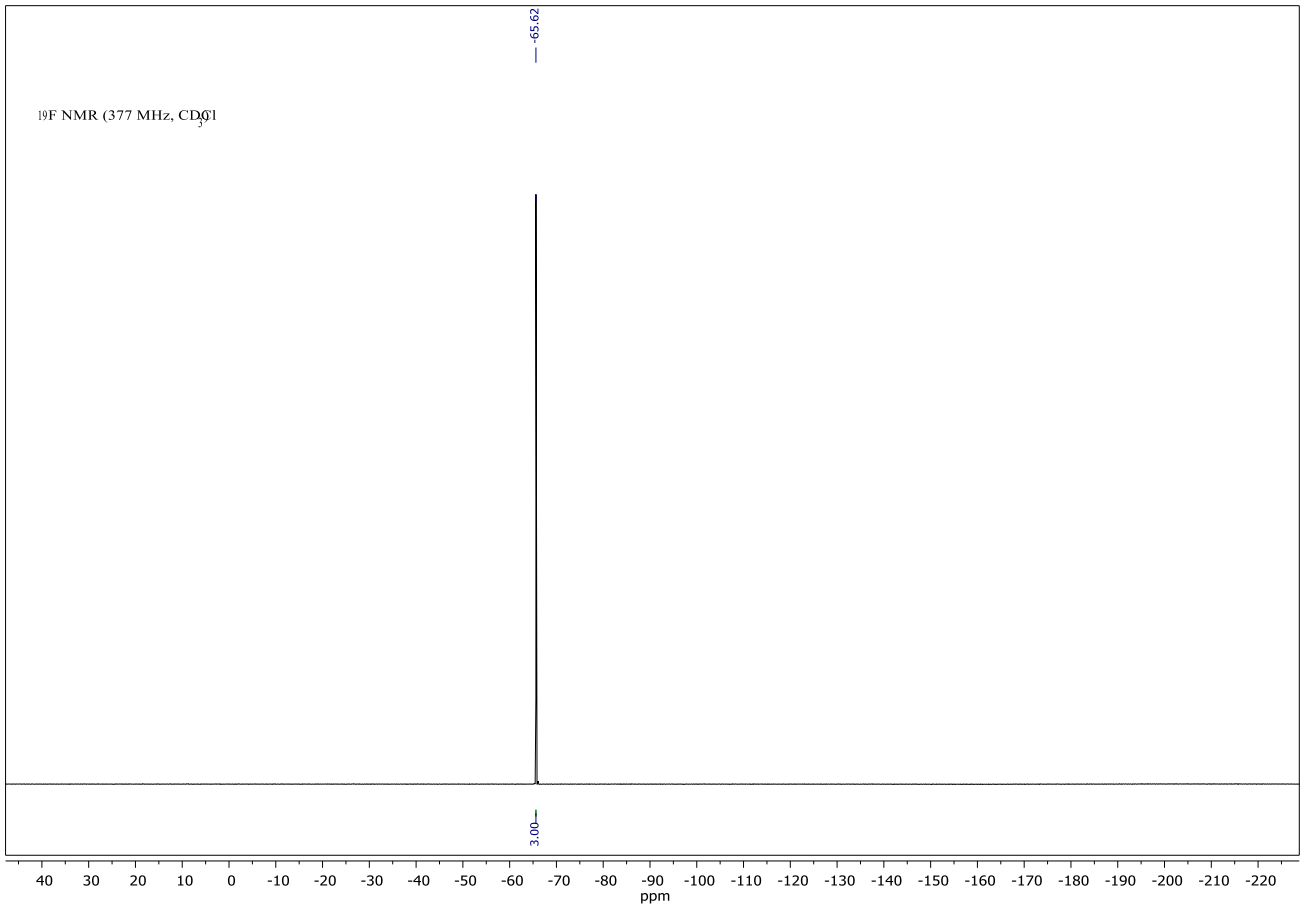


Methyl(phenyl)(quinolin-3-ylimino)-λ^6-sulfanone (3av)

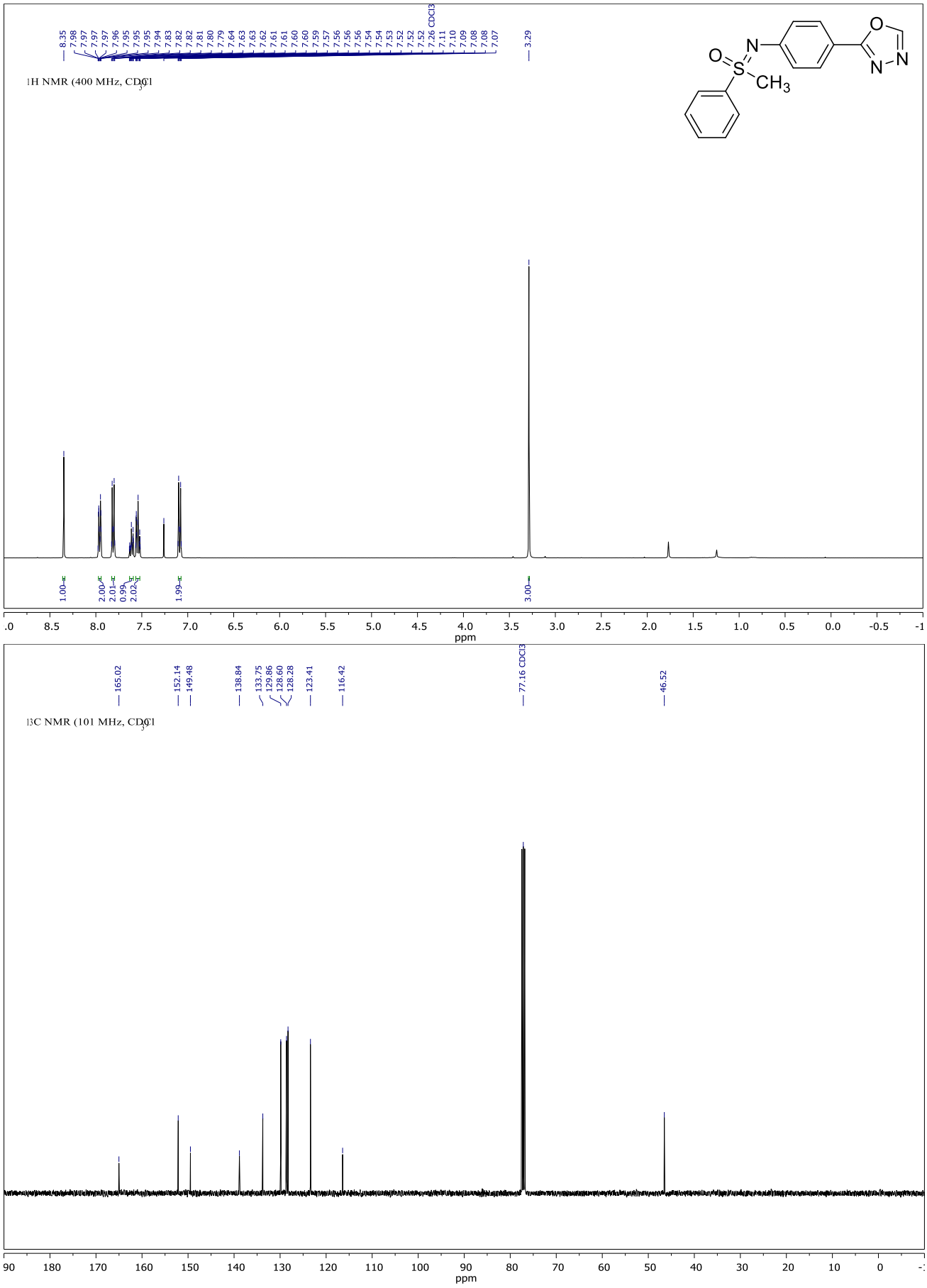


Methyl(phenyl)((4-(trifluoromethyl)pyridin-2-yl)imino)-λ^6-sulfanone (3aw)

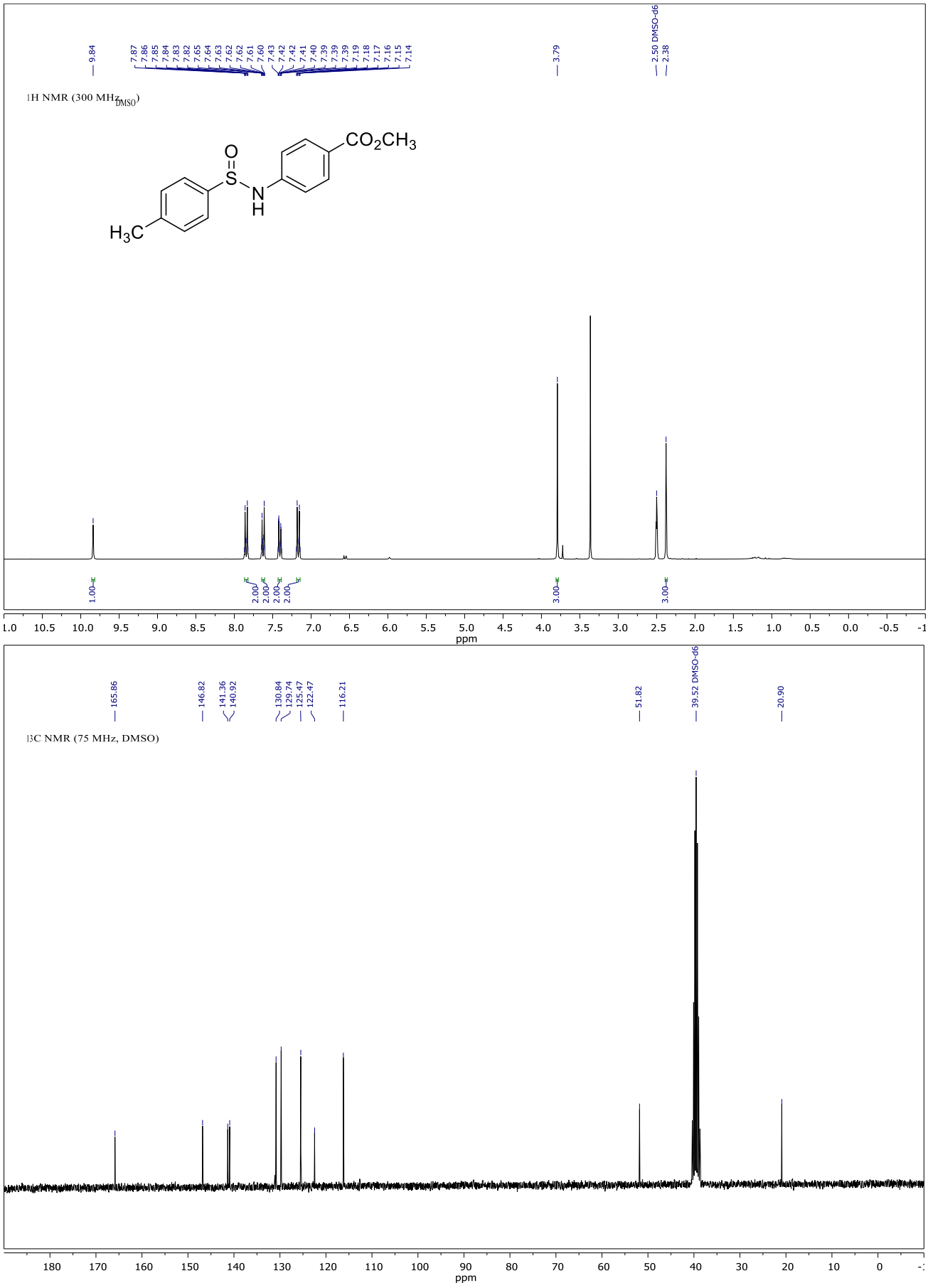



-65.62
19F NMR (377 MHz, CDCl3)
3.00
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
ppm

((4-(1,3,4-Oxadiazol-2-yl)phenyl)imino)(methyl)(phenyl)-λ^6-sulfanone (3ax)



Methyl (*S*)-4-((*p*-tolylsulfinyl)amino)benzoate (5)



Methyl 4-((oxo(phenyl)(piperidin-1-yl)-λ^6-sulfaneylidene)amino)benzoate (7)