Supporting Information

Access to 4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(4*H*)-ones via amidoxime *O*-heteroarylation/cyclization reactions sequence

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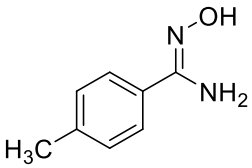
S1. General Information

4-Cyanopyridine-*N*-oxide, 2-phenylpyridine-*N*-oxide, 2-benzylpyridine-*N*-oxide, [2,2'-bipyridine]-1-oxide, 3,5-dimethylpyridine-*N*-oxide, quinoline-*N*-oxide, isoquinoline-*N*-oxide were obtained via oxidation of corresponding azines.[1–3] 4-Methoxypyridine-*N*-oxide was synthesized from 4-nitropyridine-*N*-oxide according to a literature procedure.[1] Acetamidoxime (**1n**), pyridine-*N*-oxide, picoline-*N*-oxides, 4-nitropyridine-*N*-oxide, and all other reagents and solvents were purchased and were used as is. Reactions were monitored by analytical thin layer chromatography (TLC) Macherey–Nagel, TLC plates Silufol UV–254 using UV light for detection. Column chromatography was carried out with silica gel grade 60 (0.040–0.063 mm) 230–400 mesh. NMR spectra were recorded on Bruker Avance DPX 400 (400 MHz, 101 MHz, and 376 MHz for ^{1}H, $^{13}C\{^{1}H\}$, and $^{19}F\{^{1}H\}$ respectively) in DMSO–d_6 or in $CDCl_3$. Chemical shifts are reported as parts per million (δ, ppm); the solvent peaks were used as internal standards: 2.50 ppm for residual ^{1}H, 39.50 ppm for $^{13}C\{^{1}H\}$ in DMSO–d_6; 7.26 ppm for residual ^{1}H, 77.16 ppm for $^{13}C\{^{1}H\}$ in $CDCl_3$. Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad; coupling constants, *J*, are reported in Hertz (Hz). Melting points were determined in open capillary tubes on Electrothermal IA 9300 series Digital Melting Point Apparatus. High–resolution mass spectra (HRMS) were measured on Bruker Maxis HRMS–ESI–qTOF (ESI Ionization).

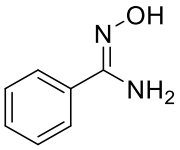
S2. Synthetic procedures and characterization of obtained compounds

S2.1. Synthesis of amidoximes 1

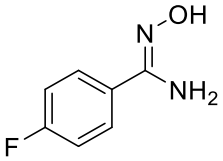
General procedure 1.[4] To a stirred suspension of corresponding nitrile and hydroxylamine hydrochloride (1.5 equiv.) in EtOH (10 mL per gram of nitrile) $NaHCO_3$ (1.5 equiv.) was added. The reaction mixture was stirred under reflux for 6 h. After the reaction had completed, the reaction mixture was concentrated under reduced pressure, and the residue was diluted with cold water (200 mL). The resulting precipitate was filtered off, washed with cold water (50 mL), and dried under reduced pressure (50 mbar) at 50 °C.



***N*'-Hydroxy-4-methylbenzimidamide** (**1a**).[4] White powder, 96% (6.15 g) yield; obtained from 0.043 mol (5.0 g) of *p*-tolunitrile. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.52 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 8.3 Hz, 2H), 4.85 (s, 2H), 2.38 (s, 3H).

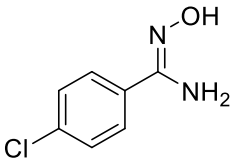


***N*'-hydroxybenzimidamide** (**1b**).[4] White powder, 77% (15.2 g) yield; obtained from 0.145 mol (14.9 g) of benzonitrile. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.60 (s, 1H), 7.62–7.73 (m, 2H), 7.32–7.42 (m, 3H), 5.78 (s, 2H),

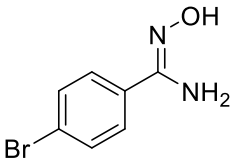


4-Fluoro-*N*'-hydroxybenzimidamide (**1c**).[5] Light green powder, 72% (0.91 g) yield; obtained from 8.3 mmol (1.0 g) of 4-fluorobenzonitrile. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.64 (s, 1H),

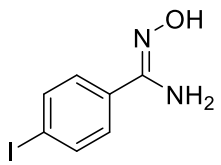
7.77–7.68 (m, 2H), 7.25–7.16 (m, 2H), 5.84 (s, 2H). $^{19}F\{^{1}H\}$ NMR (376 MHz, DMSO-d_6) δ –112.95.



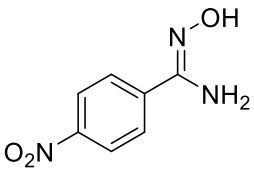
4-Chloro-*N*'-hydroxybenzimidamide (**1d**).[6] White powder, 89% (3.31 g) yield; obtained from 0.022 mol (3.0 g) of 4-chlorobenzonitrile. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.72 (s, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 5.86 (s, 2H).



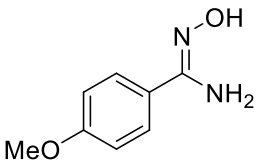
4-Bromo-*N*'-hydroxybenzimidamide (**1e**).[5] Light gray powder, 91% (2.15 g) yield; obtained from 0.011 mol (2.0 g) of 4-bromobenzonitrile. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.73 (s, 1H), 7.66–7.60 (m, 2H), 7.60–7.54 (m, 2H), 5.86 (s, 2H).



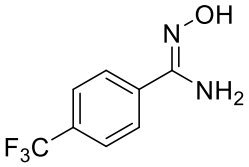
4-Iodo-*N*'-hydroxybenzimidamide (**1f**).[5] Light yellow powder, 73% (0.96 g) yield; obtained from 5 mmol (1.15 g) of 4-iodobenzonitrile. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.72 (s, 1H), 7.74 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 5.83 (s, 2H).



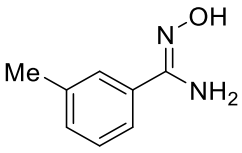
***N*'-Hydroxy-4-nitrobenzimidamide** (**1g**).[6] Light yellow powder, 98% (1.2 g) yield; obtained from 7 mmol (1.04 g) of 4-nitrobenzonitrile. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.11 (s, 1H), 8.23 (d, J = 8.9 Hz, 2H), 7.94 (d, J = 8.9 Hz, 2H), 6.05 (s, 2H).



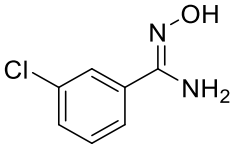
***N*'-Hydroxy-4-methoxybenzimidamide** (**1h**).[6] White powder, 78% (0.97 g) yield; obtained from 8 mmol (1.06 g) of 4-methoxybenzonitrile. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.45 (s, 1H), 7.61 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 5.71 (s, 2H), 3.76 (s, 3H).



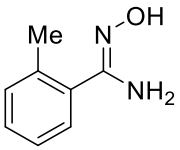
***N*'-Hydroxy-4-(trifluoromethyl)benzimidamide** (**1i**).[4] White powder, 89% (1.06 g) yield; obtained from 6 (1.03 g) mmol of 4-(trifluoromethyl)benzonitrile. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.92 (s, 1H), 7.90 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 5.97 (s, 2H).



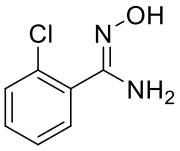
***N*'-Hydroxy-3-methylbenzimidamide** (**1j**).[7] White powder, 66% (0.84 g) yield; obtained from 8.5 mmol of (1.0 g) *m*-tolunitrile. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.57 (s, 1H), 7.51 (s, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.19 (d, J = 7.6 Hz, 1H), 5.75 (s, 2H), 2.32 (s, 3H).



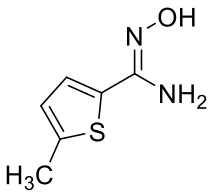
3-Chloro-*N*'-hydroxybenzimidamide (**1k**).[7] White powder, 82% (1.02 g) yield; obtained from 7 mmol (0.96 g) of 3-chlorobenzonitrile. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.78 (s, 1H), 7.74–7.68 (m, 1H), 7.65 (dt, J = 7.2, 1.7 Hz, 1H), 7.47–7.36 (m, 2H), 5.90 (s, 2H).



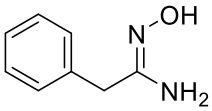
***N*'-Hydroxy-2-methylbenzimidamide** (**1l**).[5] White powder, 75% (1.92 g) yield; obtained from 0.017 mol (2.0 g) of *o*-tolunitrile. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.50–7.18 (m, 4H), 4.81 (s, 2H), 2.47 (s, 3H).



3-Chloro-*N*'-hydroxybenzimidamide (**1m**).[7] White powder, 85% (3.17 g) yield; obtained from 0.022 mol (3.0 g) of 2-chlorobenzonitrile. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.45 (s, 1H), 7.49–7.46 (m, 1H), 7.43–7.39 (m, 2H), 7.35 (ddd, J = 8.0, 6.6, 1.4 Hz, 1H), 5.80 (s, 2H).



***N*'-Hydroxy-5-methylthiophene-2-carboximidamide** (**1o**).[4] Brown powder, 88% (1.12 g) yield; obtained from 8 mmol (1 g) of 5-methylthiophene-2-carbonitrile. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.06 (d, J = 3.6 Hz, 1H), 6.76–6.64 (m, 1H), 4.83 (s, 2H), 2.47 (s, 3H).

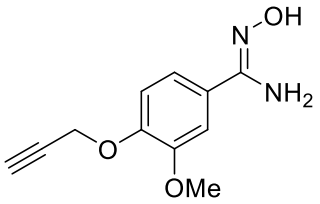


***N*'-Hydroxy-2-phenylacetimidamide** (**1p**).[8] White powder, 63% (1.02 g) yield; obtained from 0.043 mol (5.0 g) of 2-phenylacetonitrile. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.44–7.24 (m, 5H), 4.52 (s, 2H), 3.50 (s, 2H).

Synthesis of *N*'-hydroxy-3-methoxy-4-(prop-2-yn-1-yloxy)benzimidamide (**1q**)

To a stirred suspension of 3-methoxy-4-(prop-2-yn-1-yloxy)benzonitrile (1.0 g, 5.3 mmol) and hydroxylamine hydrochloride (3.17 g, 0.046 mol) in a EtOH/H_2O mixture (20 mL, 1:1 v/v)

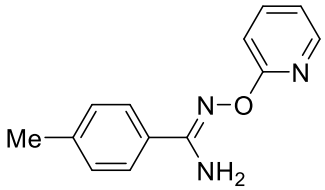
$NaHCO_3$ (3.83 g, 0.046 mol) was added. The reaction mixture was stirred at room temperature for 6 days. After the reaction had completed, the reaction mixture was diluted with H_2O (100 mL) The resulting precipitate was filtered off and washed with cold water (50 mL).



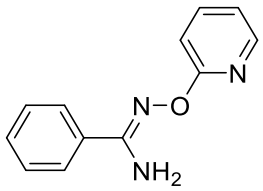
White powder, yield 89% (1.04 g, obtained from 5.34 mmol of. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.50 (s, 1H), 7.29 (d, J = 2.0 Hz, 1H), 7.23 (dd, J = 8.4, 2.0 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 5.76 (s, 2H), 4.80 (d, J = 2.4 Hz, 2H), 3.79 (s, 3H), 3.55 (t, J = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.5, 148.7, 147.1, 127.0, 117.6, 113.4, 109.3, 79.3, 78.3, 56.0, 55.4. HRMS (ESI) calcd for $C_{11}H_{13}N_2O_3^+$ $[M+H]^+$ 221.0921, found 221.0911.

S2.2. Synthesis of *O*-(pyridin-2-yl)amidoximes 3

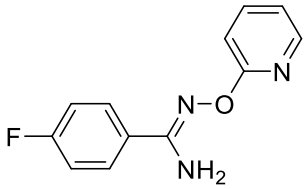
General procedure 2. Amidoxime **1** (1 mmol), pyridine *N*-oxide **2** (1.2 mmol, 1.2 equiv.), DIPEA (525 μL, 3 mmol, 3 equiv.) and acetonitrile (5 mL) were placed in a 10 mL round-bottomed flask. PyBroP (1.2 mmol, 1.2 equiv.) was added and the resulted reaction mixture was stirred at room temperature for 24 h. After this time, the solvent was removed on a rotary evaporator under reduced pressure (45 °C, 200 mbar). Target *O*-(pyridin-2-yl)amidoximes were isolated by column chromatography on silica gel using a hexane/ethyl acetate mixture as eluent (2:1, v/v).



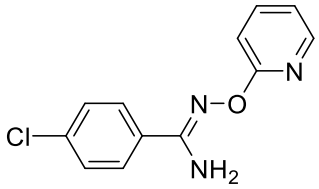
4-Methyl-*N*'-(pyridin-2-yloxy)benzimidamide 3a. White powder, yield 95% (216 mg), mp = 126–127°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (dd, J = 4.8, 1.4 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.64 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.6 Hz, 1H), 7.28 – 7.22 (m, 2H), 6.99 – 6.92 (m, 1H), 5.21 (s, 2H), 2.40 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.6, 154.6, 147.7, 141.0, 139.5, 129.6 (2C), 129.0, 126.4 (2C), 118.0, 108.8, 21.5. HRMS (ESI), m/z: $[M+H]^+$ $C_{13}H_{14}N_3O^+$ calcd. 228.1131; found 228.1132.



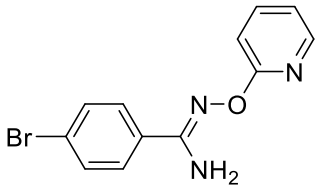
***N*'-(Pyridin-2-yloxy)benzimidamide 3b**. Beige powder, yield 99% (212 mg), mp = 109–110°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, J = 5.0, 2.0 Hz, 1H), 7.79 – 7.73 (m, 2H), 7.73 – 7.66 (m, 1H), 7.52 – 7.39 (m, 4H), 6.96 (ddd, J = 7.4, 5.0, 0.8 Hz, 1H), 5.25 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 165.5, 154.6, 147.6, 139.5, 131.9, 130.7, 128.8 (2C), 126.5 (2C), 118.0, 108.7. HRMS (ESI), m/z: $[M+H]^+$ $C_{12}H_{12}N_3O^+$ calcd. 214.0975; found 214.0977.



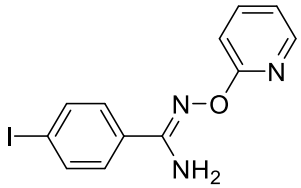
4-Fluoro-*N*'-(pyridin-2-yloxy)benzimidamide 3c. White powder, yield 93% (215 mg), mp = 123–124°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, J = 5.0, 1.4 Hz, 1H), 7.87 – 7.59 (m, 3H), 7.41 (d, J = 8.4 Hz, 1H), 7.21 – 7.06 (m, 2H), 7.03 – 6.89 (m, 1H), 5.22 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.4, 164.3 (d, J = 250.7 Hz), 153.9, 147.7, 139.5, 128.6 (2C, d, J = 8.6 Hz), 128.0 (d, J = 3.3 Hz), 118.2, 116.0 (2C, d, J = 21.9 Hz), 108.7. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –109.66. HRMS (ESI), m/z: $[M+H]^+$ $C_{12}H_{11}FN_3O^+$ calcd. 232.0881; found 232.0883.



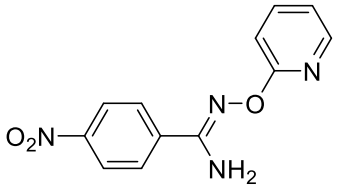
4-Chloro-*N*'-(pyridin-2-yloxy)benzimidamide 3d. White powder, yield 93% (228 mg), mp = 125–126°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 5.4 Hz, 1H), 7.74 – 7.64 (m, 3H), 7.47 – 7.36 (m, 3H), 6.99 – 6.92 (m, 1H), 5.30 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.3, 153.7, 147.7, 139.5, 136.8, 130.3, 129.1 (2C), 127.8 (2C), 118.2, 108.7. HRMS (ESI), m/z: $[M+H]^+$ $C_{12}H_{11}ClN_3O^+$ calcd. 248.0585; found 248.0588.



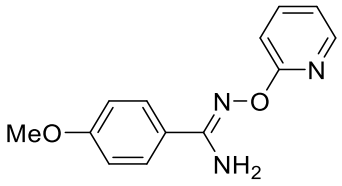
4-Bromo-*N*'-(pyridin-2-yloxy)benzimidamide 3e. White powder, yield 96% (279 mg), mp = 122-123°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, J = 5.0, 1.8 Hz, 1H), 7.71 (ddd, J = 8.8, 7.2, 2.0 Hz, 1H), 7.65 – 7.61 (m, 2H), 7.60 – 7.56 (m, 2H), 7.41 (d, J = 8.4 Hz, 1H), 6.97 (dd, J = 6.8, 5.2 Hz, 1H), 5.22 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.3, 153.7, 147.7, 139.5, 132.1, 132.0 (2C), 130.8, 129.1, 128.0 (2C), 125.1, 118.2, 108.7. HRMS (ESI), m/z: $[M+H]^+$ $C_{12}H_{11}BrN_3O^+$ calcd. 292.0080; found 292.0085.



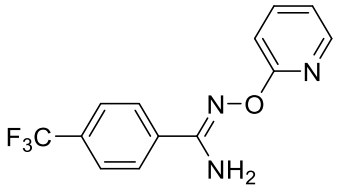
4-Iodo-*N'*-(pyridin-2-yloxy)benzimidamide 3f. White powder, yield 86% (293 mg), mp = 106–107°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, J = 5.0, 2.0 Hz, 1H), 7.81 – 7.75 (m, 2H), 7.70 (ddd, J = 8.8, 7.2, 2.0 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.39 (d, J = 8.4 Hz, 1H), 6.96 (ddd, J = 7.2, 4.9, 1.2 Hz, 1H), 5.29 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.3, 148.8, 142.6, 134.6 (2C), 133.0, 126.4, 123.1 (2C), 113.2, 103.7, 92.0. HRMS (ESI), m/z: $[M+H]^+$ $C_{12}H_{11}IN_3O^+$ calcd. 339.9941; found 339.9947.



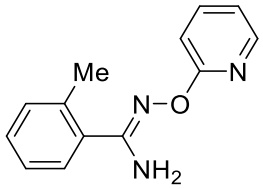
4-Nitro-N'-(pyridin-2-yloxy)benzimidamide 3g. Yellow powder, yield 99% (290 mg), mp = 182–183°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.31 (d, J = 8.8 Hz, 2H), 8.22 (dd, J = 5.0, 2.0 Hz, 1H), 8.09 (d, J = 8.8 Hz, 2H), 7.82 (ddd, J = 8.7, 7.2, 2.0 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.11 – 6.99 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 165.1, 153.0, 148.4, 147.3, 139.6, 138.0, 127.9 (2C), 123.5 (2C), 118.1, 108.4. HRMS (ESI), m/z: $[M+H]^+$ $C_{12}H_{11}N_4O_3^+$ calcd. 259.0826; found 259.0829.



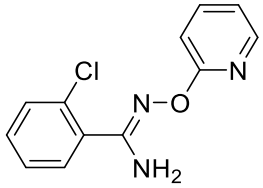
4-Methoxy-*N'*-(pyridin-2-yloxy)benzimidamide 3h. White powder, yield 93% (227 mg), mp = 119–120°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 5.2 Hz, 1H), 7.73 – 7.63 (m, 3H), 7.42 (d, J = 8.4 Hz, 1H), 6.99 – 6.87 (m, 3H), 5.22 (s, 2H), 3.83 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.6, 161.6, 154.5, 147.6, 139.4, 127.9 (2C), 124.2, 117.9, 114.2 (2C), 108.7, 55.5. HRMS (ESI), m/z: $[M+H]^+$ $C_{13}H_{14}N_3O_2^+$ calcd. 244.1081; found 244.1082.



***N*'-(Pyridin-2-yloxy)-4-(trifluoromethyl)benzimidamide 3i**. White powder, yield 52% (146 mg), mp = 122–123°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, J = 4.9, 2.0 Hz, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.77 – 7.65 (m, 3H), 7.41 (d, J = 8.4 Hz, 1H), 6.99 (dd, J = 7.2, 4.9 Hz, 1H), 5.30 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.3, 153.3, 147.7, 139.6, 135.3, 132.6 (q, J = 32.8 Hz), 126.9 (2C), 125.8 (2C, q, J = 3.8 Hz), 123.9 (q, J = 272.4 Hz), 118.39, 108.72. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –62.90. HRMS (ESI), m/z: $[M+H]^+$ $C_{13}H_{11}F_3N_3O^+$ calcd. 282.0849; found 282.0852.

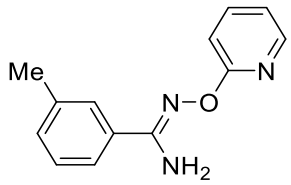


2-Methyl-*N*'-(pyridin-2-yloxy)benzimidamide 3j. Beige powder, yield 77% (174 mg), mp = 131–133°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, J = 5.0, 2.0 Hz, 1H), 7.69 (ddd, J = 8.8, 6.8, 1.9 Hz, 1H), 7.54 – 7.46 (m, 1H), 7.44 – 7.33 (m, 2H), 7.33 – 7.22 (m, 2H), 7.00 – 6.92 (m, 1H), 5.25 (s, 2H), 2.53 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.5, 155.3, 147.6, 139.4, 137.1, 132.0, 130.9, 130.1, 129.1, 126.0, 117.9, 108.7, 19.9. HRMS (ESI), m/z: $[M+H]^+$ $C_{13}H_{14}N_3O^+$ calcd. 228.1131; found 228.1132.

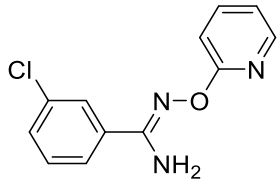


2-Chloro-*N*'-(pyridin-2-yloxy)benzimidamide 3k. Beige powder, yield 91% (225 mg), mp = 125–126°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, J = 4.8, 1.9 Hz, 1H), 7.68 (ddd, J = 9.2, 7.3, 2.0 Hz, 1H), 7.62 (dd, J = 7.5, 1.7 Hz, 1H), 7.47 (dd, J = 7.9, 1.2 Hz, 1H), 7.41 (td, J = 7.6, 1.7 Hz, 1H), 7.38 – 7.31 (m, 2H), 6.96 (ddd, J = 7.4, 5.1, 0.8 Hz, 1H), 5.30 (s, 2H). ^{13}C{^{1}H} NMR

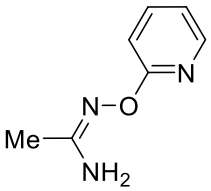
(101 MHz, $CDCl_3$) δ 165.3, 153.9, 147.6, 139.5, 133.0, 131.4, 131.4, 131.2, 130.4, 127.1, 118.1, 108.8. HRMS (ESI), m/z: $[M+H]^+$ $C_{12}H_{11}ClN_3O^+$ calcd. 248.0585; found 248.0587.



3-Methyl-*N*'-(pyridin-2-yloxy)benzimidamide 3l. White powder, yield 84% (192 mg), mp = 107–108°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 4.9, 1.8 Hz, 1H), 7.70 (ddd, *J* = 9.0, 7.2, 2.0 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.56 – 7.50 (m, 1H), 7.44 (dt, *J* = 8.5, 0.9 Hz, 1H), 7.37 – 7.27 (m, 2H), 6.96 (ddd, *J* = 7.2, 4.9, 1.0 Hz, 1H), 5.35 – 5.14 (m, 2H), 2.41 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.5, 154.8, 147.6, 139.45, 138.6, 131.8, 131.5, 128.7, 127.2, 123.5, 118.0, 108.7, 21.5. HRMS (ESI), m/z: $[M+H]^+$ calcd. $C_{13}H_{14}N_3O$ 228.1131; found 228.1128.

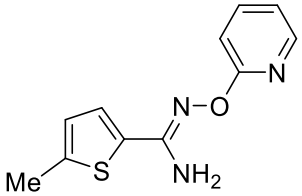


3-Chloro-*N*'-(pyridin-2-yloxy)benzimidamide 3m. White powder, yield 85% (210 mg), mp = 113–114°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 4.8, 2.0 Hz, 1H), 7.77 (t, *J* = 1.8 Hz, 1H), 7.72 (ddd, *J* = 9.0, 7.3, 2.0 Hz, 1H), 7.62 (dt, *J* = 7.5, 1.2 Hz, 1H), 7.46 (dt, *J* = 8.0, 1.8, 1.0 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 6.98 (ddd, *J* = 7.2, 4.9, 1.2 Hz, 1H), 5.23 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.3, 153.4, 147.6, 139.6, 134.9, 133.6, 130.8, 130.1, 126.8, 124.6, 118.3, 108.7. HRMS (ESI), m/z: $[M+H]^+$ $C_{12}H_{11}ClN_3O^+$ calcd. 248.0585; found 248.0589.

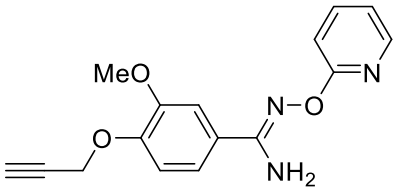


***N*'-(Pyridin-2-yloxy)acetimidamide 3n**. Yield 54% (by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 4.8, 2.0, 1H), 7.68–7.55 (m, 1H), 7.24 – 7.14 (m, 1H), 6.87 (dd, *J* = 7.2, 5.0 Hz,

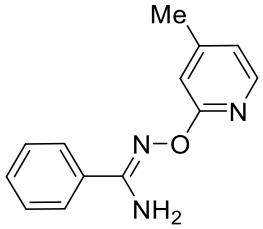
1H), 5.18 (s, 2H), 1.97 (s, 3H). HRMS (ESI), m/z: $[M+H]^+$ $C_7H_{10}N_3O^+$ calcd. 152.0818; found 152.0827.



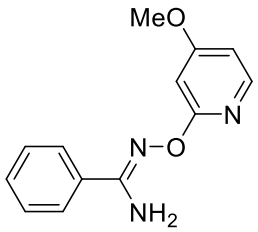
5-Methyl-*N*'-(pyridin-2-yloxy)thiophene-2-carboximidamide 3o. Brown powder, yield 98% (226 mg), mp = 108–110°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, J = 4.8, 1.9 Hz, 1H), 7.74 – 7.65 (m, 1H), 7.41 (d, J = 8.5 Hz, 1H), 7.19 (d, J = 3.6 Hz, 1H), 6.94 (dd, J = 7.4, 5.3 Hz, 1H), 6.72 (d, J = 3.4 Hz, 1H), 5.22 (s, 2H), 2.50 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.4, 150.4, 147.6, 143.0, 139.5, 131.2, 126.4, 125.6, 118.1, 108.7, 15.5. HRMS (ESI), m/z: $[M+H]^+$ $C_{11}H_{12}N_3OS^+$ calcd. 234.0696; found 234.0696.



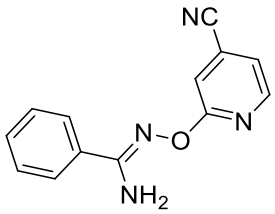
3-Methoxy-4-(prop-2-yn-1-yloxy)-*N*'-(pyridin-2-yloxy)benzimidamide 3p. White powder, yield 44% (132 mg), mp = 92–94°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.19 (dd, J = 4.9, 2.0 Hz, 1H), 7.78 (td, J = 8.8, 7.2, 2.0 Hz, 1H), 7.44 – 7.34 (m, 3H), 7.09 (d, J = 8.2 Hz, 1H), 7.01 (t, J = 7.2, 4.8 Hz, 1H), 6.70 (s, 2H), 4.84 (d, J = 2.4 Hz, 2H), 3.84 (s, 3H), 3.57 (t, J = 2.4 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 165.9, 154.9, 149.3, 148.5, 147.7, 139.9, 125.7, 119.5, 118.1, 113.9, 110.8, 108.8, 79.6, 78.9, 56.5, 56.1. HRMS (ESI), m/z: $[M+H]^+$ $C_{16}H_{16}N_3O_3^+$ calcd. 298.1186; found 298.1172.



***N'*-((4-Methylpyridin-2-yl)oxy)benzimidamide 3q**. White powder, yield 56% (128 mg), mp = 110–111°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 5.0 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.53 – 7.40 (m, 3H), 7.29 – 7.24 (m, 1H), 6.78 (dd, J = 5.1, 1.4 Hz, 1H), 5.25 (s, 2H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.7, 154.6, 151.0, 147.2, 132.0, 130.7, 128.8 (2C), 126.5 (2C), 119.4, 108.9, 21.5. HRMS (ESI), m/z: $[M+H]^+$ $C_{13}H_{14}N_3O^+$ calcd. 228.1131; found 228.1134.

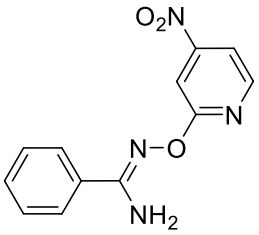


***N'*-((4-Methoxypyridin-2-yl)oxy)benzimidamide 3r**. White powder, yield 99% (240 mg), mp = 87–89°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 5.8 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.53 – 7.41 (m, 3H), 6.97 (d, J = 2.3 Hz, 1H), 6.53 (dd, J = 5.8, 2.3 Hz, 1H), 5.25 (s, 2H), 3.87 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.7, 167.4, 154.6, 148.2, 131.9, 130.8, 128.8 (2C), 126.5 (2C), 106.1, 93.1, 55.5. HRMS (ESI), m/z: $[M+H]^+$ $C_{13}H_{14}N_3O_2^+$ calcd. 244.1081; found 244.1082.

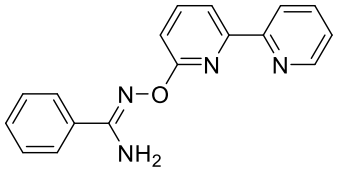


***N'*-((4-Cyanopyridin-2-yl)oxy)benzimidamide 3s**. White powder, yield 6% (14 mg), mp = 143–145°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 5.0 Hz, 1H), 7.79 – 7.70 (m, 3H), 7.56 – 7.44 (m, 3H), 7.18 (dd, J = 5.0, 1.3 Hz, 1H), 5.42 – 5.18 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz,

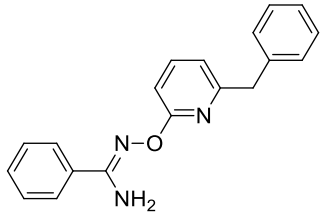
$CDCl_3$) δ 165.8, 155.4, 149.1, 131.2 (2C), 129.1 (2C), 126.6 (2C), 123.3, 119.4, 116.8, 111.6. HRMS (ESI), m/z: $[M+H]^+$ $C_{13}H_{11}N_4O^+$ calcd. 239.0927; found 239.0928.



***N'*-((4-nitropyridin-2-yl)oxy)benzimidamide 3t**. Yield 4% (by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 5.4 Hz, 1H), 8.18 (d, J = 1.8 Hz, 1H), 7.80 – 7.72 (m, 2H), 7.68 (dd, J = 5.4, 1.8 Hz, 1H), 7.57 – 7.43 (m, 3H), 5.34 (s, 2H). HRMS (ESI), m/z: $[M+H]^+$ $C_{12}H_{11}N_4O_3^+$ calcd. 259.0826; found 259.0829.

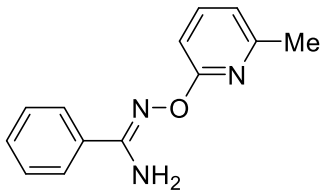


***N'*-([2,2'-Bipyridin]-6-yloxy)benzimidamide 3u**. White powder, yield 40% (115 mg), mp = 132–133°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72 – 8.64 (m, 1H), 8.36 (dt, J = 8.0, 0.9 Hz, 1H), 8.07 (dd, J = 7.5, 0.8 Hz, 1H), 7.90 – 7.73 (m, 4H), 7.57 – 7.40 (m, 4H), 7.30 (ddd, J = 7.4, 4.8, 1.0 Hz, 1H), 5.30 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.3, 156.0, 154.6, 154.4, 149.3, 140.4, 137.0, 131.9, 130.8, 128.9 (2C), 126.5 (2C), 123.8, 121.4, 115.5, 109.0. HRMS (ESI), m/z: $[M+H]^+$ $C_{17}H_{15}N_4O^+$ calcd. 291.1240; found 291.1244.

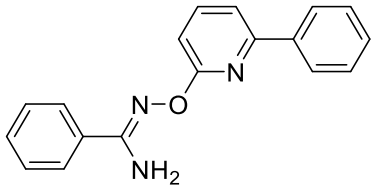


***N'*-((6-Benzylpyridin-2-yl)oxy)benzimidamide 3v**. White powder, yield 28% (85 mg), mp = 110–111°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.69 (m, 2H), 7.60 (t, J = 8.0 Hz, 1H), 7.51 – 7.41 (m, 3H), 7.35 – 7.26 (m, 5H), 7.25 – 7.18 (m, 1H), 6.74 (d, J = 7.3 Hz, 1H), 5.26 (s, 2H), 4.11 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.3, 159.3, 154.3, 140.0, 139.5, 132.0, 130.7,

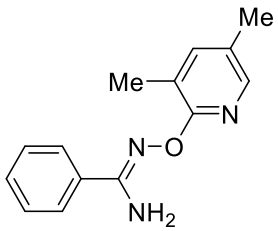
129.3 (2C), 128.9 (2C), 128.6 (2C), 126.5 (3C), 117.3, 106.0, 44.4. HRMS (ESI), m/z: $[M+H]^+$ $C_{19}H_{18}N_3O^+$ calcd. 304.1444; found 304.1432.



***N′*-((6-Methylpyridin-2-yl)oxy)benzimidamide 3w**. White powder, yield 15% (35 mg), mp = 126–128°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 2H), 7.59 (dd, J = 8.7, 7.5 Hz, 1H), 7.51 – 7.39 (m, 3H), 7.28 (d, J = 8.4 Hz, 1H), 6.82 (d, J = 7.3 Hz, 1H), 5.26 (s, 2H), 2.49 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.2, 156.7, 154.2, 139.8, 132.0, 130.7, 128.8 (2C), 126.5 (2C), 117.4, 105.3, 24.2. HRMS (ESI), m/z: $[M+H]^+$ $C_{13}H_{14}N_3O^+$ calcd. 228.1131; found 228.1136.

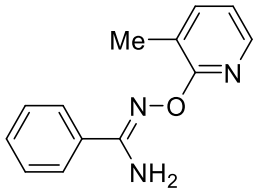


***N′*-((6-Phenylpyridin-2-yl)oxy)benzimidamide 3x**. White powder, yield 66% (192 mg), mp = 120–122°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.6 Hz, 2H), 7.84 – 7.70 (m, 3H), 7.59 – 7.29 (m, 8H), 5.34 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.6, 155.9, 154.5, 140.2, 139.2, 132.0, 130.7, 129.0, 128.9 (2C), 128.8 (2C), 127.2 (2C), 126.5 (2C), 114.9, 107.1. HRMS (ESI), m/z: [M+H]+ $C_{18}H_{16}N_3O^+$ calcd. 290.1288; found 290.1289.

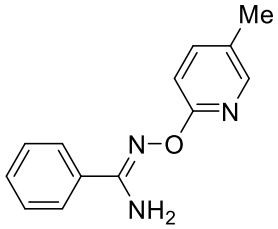


***N′*-((3,5-Dimethylpyridin-2-yl)oxy)benzimidamide 3y**. White powder, yield 58% (140 mg), mp = 115–116°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 2.0 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.45 – 7.35 (m, 3H), 7.27 (d, J = 2.2 Hz, 1H), 5.13 (s, 2H), 2.26 (s, 3H), 2.22 (s, 3H). ^{13}C{^{1}H}

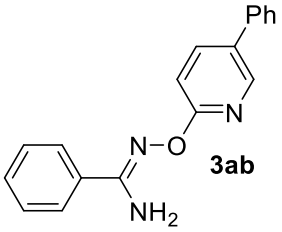
NMR (101 MHz, $CDCl_3$) δ 160.5, 155.6, 144.9, 140.4, 132.1, 130.5, 128.6 (2C), 127.4, 126.8 (2C), 119.4, 17.5, 16.0. HRMS (ESI), m/z: $[M+H]^+$ $C_{14}H_{16}N_3O^+$ calcd. 242.1288; found 242.1288.



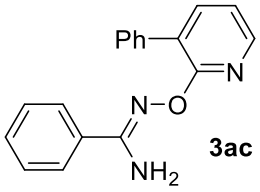
***N′*-((3-Methylpyridin-2-yl)oxy)benzimidamide 3z**. Yellow liquid, yield 40% (90 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, J = 5.0, 1.8 Hz, 1H), 7.79 – 7.72 (m, 2H), 7.47 – 7.36 (m, 4H), 6.87 (dd, J = 7.1, 5.1 Hz, 1H), 5.16 (s, 2H), 2.30 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.1, 155.9, 145.4, 139.3, 132.0, 130.6, 128.7 (2C), 126.9 (2C), 119.8, 118.2, 16.1. HRMS (ESI), m/z: $[M+H]^+$ $C_{13}H_{14}N_3O^+$ calcd. 228.1131; found 228.1136.



***N′*-((5-Methylpyridin-2-yl)oxy)benzimidamide 3aa**. White powder, yield 34% (78 mg), mp. = 133-134°C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 1.8 Hz, 1H), 7.78 – 7.72 (m, 2H), 7.53 – 7.41 (m, 4H), 7.34 (d, J = 8.5 Hz, 1H), 5.22 (s, 2H), 2.28 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 163.8, 154.4, 147.3, 140.2, 132.0, 130.7, 128.9 (2C), 127.1, 126.5 (2C), 108.2, 17.6. HRMS (ESI), m/z: $[M+H]^+$ $C_{13}H_{14}N_3O^+$ calcd. 228.1131; found 228.1132.

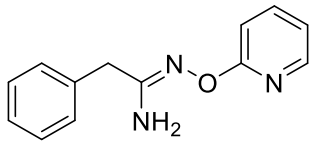


3ab

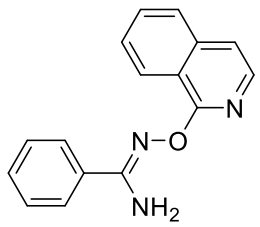


3ac

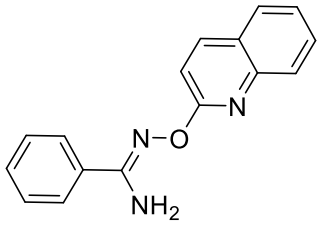
***N*'-((5-phenylpyridin-2-yl)oxy)benzimidamide 3ab + *N*'-((3-phenylpyridin-2-yl)oxy)benzimidamide 3ac**. Yield 6% for **3ab** and 35% for **3ac** (by ^{1}H NMR) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 2.5 Hz, 1H; **3ac**), 7.98 – 7.92 (m, 1H **3ab** + **3ac**), 7.84 – 7.76 (m, 2H; **3ac**), 7.68 – 7.64 (m, 2 H; **3ab**), 7.63 – 7.57 (m, 2H; **2ac**), 7.57 – 7.45 (m, 6H; **3ab**+**3ac**), 7.45 – 7.43 (m, 1H; **3ab**), 7.42 – 7.36 (m, 1H; **3ac**), 5.31 (s, 2H), 4.89 (s, 2H, **2ab**).



2-Phenyl-*N*'-(pyridin-2-yloxy)acetimidamide 3ad. Yellow liquid, yield 79% (179 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.09 (m, 1H), 7.59 (dd, J = 8.7, 7.2, 1.9 Hz, 1H), 7.33 – 7.13 (m, 6H), 6.88 – 6.81 (m, 1H), 5.10 (s, 2H), 3.52 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.9, 155.5, 147.1, 139.0, 135.3, 128.6 (2C), 128.5 (2C), 127.0, 117.4, 108.3, 37.1. HRMS (ESI), m/z: $[M+H]^+$ $C_{13}H_{14}N_3O^+$ calcd. 228.1131; found 228.1131.

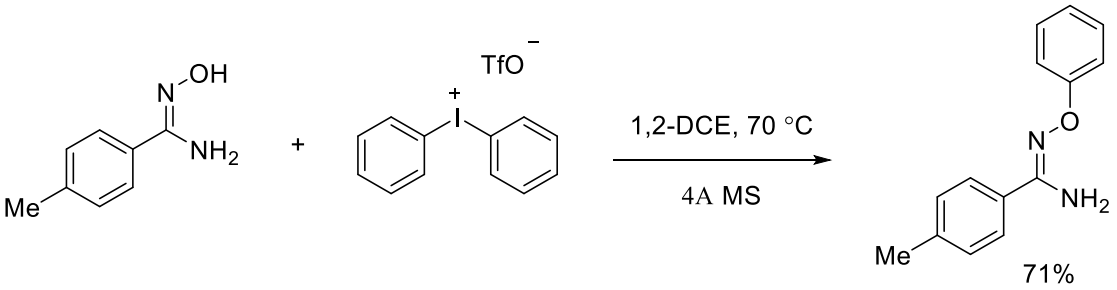


***N*'-(Isoquinolin-1-yloxy)benzimidamide 3ae**. Beige powder, yield 47% (124 mg). mp = 133–135°C ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.3 Hz, 1H), 8.15 (d, J = 5.9 Hz, 1H), 7.86 – 7.80 (m, 2H), 7.79 (d, J = 8.3 Hz, 1H), 7.73 – 7.65 (m, 1H), 7.61 – 7.53 (m, 1H), 7.52 – 7.39 (m, 3H), 7.29 (d, J = 5.8 Hz, 1H), 5.27 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.1, 156.8, 140.6, 138.3, 131.8, 130.8, 130.5, 128.7 (2C), 127.0 (2C), 126.8, 126.5, 123.7, 118.8, 115.9. HRMS (ESI), m/z: $[M+H]^+$ $C_{16}H_{14}N_3O^+$ calcd. 264.1131; found 264.1133.



***N′*-(Quinolin-2-yloxy)benzimidamide 3af**. White powder, yield 22% (57 mg), mp = 142–143°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 9.0 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.85 – 7.70 (m, 4H), 7.70 – 7.61 (m, 1H), 7.56 – 7.37 (m, 4H), 5.34 (s, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 163.9, 154.7, 146.6, 139.9, 131.9, 130.8, 130.0, 128.9 (2C), 127.7, 127.6, 126.6 (2C), 125.9, 124.5, 110.4. HRMS (ESI), m/z: $[M+H]^+$ $C_{16}H_{14}N_3O^+$ calcd. 264.1131; found 264.1134.

S2.3. Synthesis of 4-methyl-*N*'-phenoxybenzimidamide 7

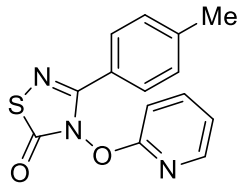


4-Methyl-*N*'-phenoxybenzimidamide (**7**) was synthesized from *p*-tolylamidoxime **1a** following to a literature procedure[9] from *N*'-hydroxy-4-methylbenzimidamide:

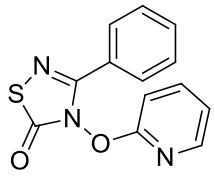
In a Schlenk tube were placed amidoxime **1a** (150 mg, 1 mmol), diphenyliodonium triflate (645 mg, 1.5 mmol, 1.5 equiv.), 1,2-DCE (5 mL), and 3Å MS (1 g) under Ar atmosphere. The reaction mixture was stirred at 70 °C for 36 h. Then 1,2-DCE was removed under reduced pressure and the crude product was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane (1:10) as the eluent. Compound **7** was obtained in 67% (151 mg) yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.2 Hz, 2H), 7.36 – 7.27 (m, 4H), 7.25 (d, J = 7.8 Hz, 2H), 7.03 – 6.94 (m, 1H), 5.06 (s, 2H), 2.40 (s, 3H).

S2.4. Cyclization of *O*-pyridylamidoximes 3 into 4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(*H*)-ones 4

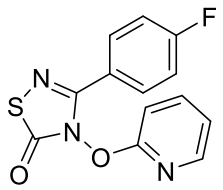
General procedure 3. *O*-(Pyridin-2-yl)amidoxime **3** (0.2 or 0.3 mmol) and Na_2CO_3 (4 equiv.) were placed in a 10 mL round-bottomed flask and CH_2Cl_2 (0.9 mL) was added. The resulting mixture was cooled to 0 °C using an ice bath and (chlorocarbonyl)sulfenyl chloride (2 equiv.) was added dropwise. The reaction mixture was stirred at room temperature for 4 h. Then the reaction mixture was diluted with water (5 mL). The product was extracted with CH_2Cl_2 (3x5 mL). The organic phase was washed with water, dried under Na_2SO_4 for 24 h, and concentrated under vacuum to dryness. The product was isolated by column chromatography on silica gel using a hexane/ethyl acetate mixture as eluent (10:1, v/v).



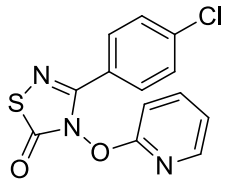
4-(Pyridin-2-yloxy)-3-(*p*-tolyl)-1,2,4-thiadiazol-5(*4H*)-one 4a. White powder, yield 89% (76 mg was obtained from 0.30 mmol of **3a**), mp = 127–128°C ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, J = 4.9, 2.0 Hz, 1H), 7.75 – 7.67 (m, 3H), 7.19 (d, J = 8.0 Hz, 2H), 7.06 (dd, J = 7.2, 4.9 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.4, 160.0, 152.1, 146.5, 141.1, 139.3, 128.5 (2C), 126.8 (2C), 124.5, 120.0, 107.7, 20.6. HRMS (ESI), m/z: $[M+H]^+$ calcd. $C_{14}H_{12}N_3O_2S^+$ 286.0645; found 286.0647.



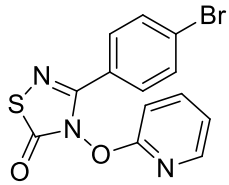
3-Phenyl-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(*4H*)-one 4b. White powder, yield 87% (47 mg was obtained from 0.20 mmol of **3b**), mp = 122–124°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dt, J = 5.0, 2.0, 0.8 Hz, 1H), 7.84 – 7.78 (m, 2H), 7.71 (td, J = 8.3, 7.2, 2.0 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.42 – 7.35 (m, 2H), 7.06 (ddd, J = 7.2, 5.0, 0.8 Hz, 1H), 7.04 – 7.00 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.3, 161.0, 153.7, 147.4, 140.3, 131.5, 128.8 (2C), 128.2, 127.9 (2C), 121.1, 108.7. HRMS (ESI), m/z: $[M+H]^+$ $C_{13}H_{10}N_3O_2S^+$ calcd. 272.0488; found 272.0490.



3-(4-Fluorophenyl)-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(4*H*)-one 4c. White powder, yield 82% (71 mg was obtained from 0.30 mmol of **3c**), mp = 106–108°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.04 (m, 1H), 7.89 – 7.79 (m, 2H), 7.73 (ddd, J = 8.3, 7.2, 2.0 Hz, 1H), 7.12 – 7.01 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.1, 164.6 (d, J = 253.1 Hz), 160.9, 152.7, 147.4, 140.4, 130.2 (2C, d, J = 8.9 Hz), 124.5 (d, J = 3.4 Hz), 121.2, 116.1 (2C, d, J = 22.1 Hz), 108.7. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –107.23. HRMS (ESI), m/z: $[M+H]^+$ $C_{13}H_9FN_3O_2S^+$ calcd. 290.0394; found 290.0397.

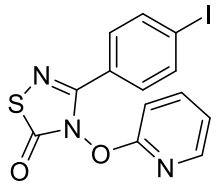


3-(4-Chlorophenyl)-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(*4H*)-one 4d. White powder, yield 88% (54 mg was obtained from 0.20 mmol of **3d**), mp = 120–122°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, J = 4.8, 1.0 Hz, 1H), 7.81 – 7.69 (m, 3H), 7.41 – 7.33 (m, 2H), 7.12 – 7.00 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.1, 160.9, 152.7, 147.5, 140.5, 138.0, 129.2 (4C), 126.7, 121.3, 108.7. HRMS (ESI), m/z: $[M+H]^+$ $C_{13}H_9ClN_3O_2S^+$ calcd. 306.0099; found 306.0095.

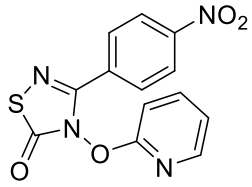


3-(4-Bromophenyl)-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(*4H*)-one 4e. Beige powder, yield 90% (94 mg was obtained from 0.30 mmol of **3e**), mp = 128–129°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 5.0, 1.8 Hz, 1H), 7.77 – 7.66 (m, 3H), 7.57 – 7.49 (m, 2H), 7.11 – 7.06 (m, 1H), 7.04 (d, J = 8.4 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.1, 160.9, 152.8,

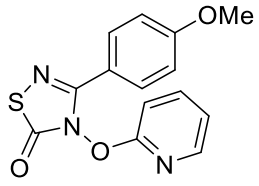
147.5, 140.5, 132.1 (2C), 129.3 (2C), 127.1, 126.4, 121.3, 108.7. HRMS (ESI), m/z: $[M+H]^+$ $C_{13}H_9BrN_3O_2S^+$ calcd. 349.9593; found 349.9588.



3-(4-Iodophenyl)-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(4*H*)-one 4f. White powder, yield 86% (103 mg was obtained from 0.30 mmol of **3f**), mp = 130–131°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 5.1, 1.8 Hz, 1H), 7.78 – 7.70 (m, 3H), 7.58 – 7.52 (m, 2H), 7.08 (ddd, J = 7.2, 5.0, 0.8 Hz, 1H), 7.04 (d, J = 8.3 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.1, 160.9, 153.0, 147.5, 140.5, 138.1 (2C), 129.3 (2C), 127.7, 121.3, 108.7, 98.7. HRMS (ESI), m/z: $[M+H]^+$ $C_{13}H_9IN_3O_2S^+$ calcd. 397.9455; found 397.9447.

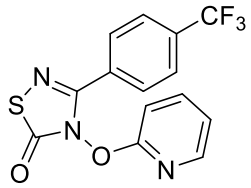


3-(4-Nitrophenyl)-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(*4H*)-one 4g. Light-yellow powder, yield 72% (46 mg was obtained from 0.20 mmol of **3g**), mp = 135–136°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.23 (m, 2H), 8.08 – 8.02 (m, 3H), 7.75 (ddd, J = 8.4, 7.2, 1.8 Hz, 1H), 7.13 – 7.05 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.6, 160.7, 151.8, 149.4, 147.4, 140.7, 133.6, 129.0 (2C), 124.0 (2C), 121.6, 108.8. HRMS (ESI), m/z: $[M+H]^+$ $C_{13}H_9N_4O_4S^+$ calcd. 317.0339; found 317.0339.

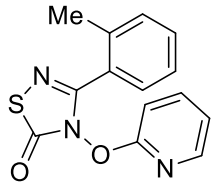


3-(4-Methoxyphenyl)-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(4*H*)-one 4h. White powder, yield 84% (76 mg was obtained from 0.30 mmol of **3h**), mp = 111–112°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (ddd, J = 5.0, 2.0, 0.8 Hz, 1H), 7.82 – 7.75 (m, 2H), 7.72 (ddd, J = 8.3, 7.2, 2.0

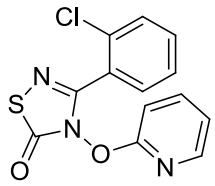
Hz, 1H), 7.09 – 7.01 (m, 2H), 6.91 – 6.85 (m, 2H), 3.80 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 172.5, 162.1, 161.0, 153.3, 147.5, 140.3, 129.5 (2C), 121.0, 120.7, 114.2 (2C), 108.7, 55.5. HRMS (ESI), m/z: $[M+H]^+$ $C_{14}H_{12}N_3O_3S^+$ calcd. 302.0594; found 302.0597.



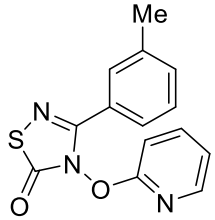
4-(Pyridin-2-yloxy)-3-(4-(trifluoromethyl)phenyl)-1,2,4-thiadiazol-5(*4H*)-one 4i. White powder, yield 73% (74 mg was obtained from 0.30 mmol of **3i**), mp = 119–121°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.04 (m, 1H), 7.96 (d, J = 7.0 Hz, 2H), 7.74 (ddd, J = 8.3, 7.2, 2.0 Hz, 1H), 7.66 (d, J = 8.2 Hz, 2H), 7.09 (ddd, J = 7.2, 5.0, 0.8 Hz, 1H), 7.06 (dt, J = 8.4, 0.9 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 171.9, 160.8, 152.4, 147.5, 140.5, 133.20 (q, J = 32.9 Hz), 131.4, 128.3 (2C), 125.8 (2C, q, J = 3.8 Hz), 123.6 (q, J = 272.5 Hz), 119.6, 108.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.16. HRMS (ESI), m/z: $[M+H]^+$ $C_{14}H_9F_3N_3O_2S^+$ calcd. 340.0362; found 340.0364.



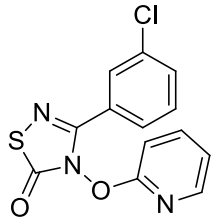
4-(Pyridin-2-yloxy)-3-(*o*-tolyl)-1,2,4-thiadiazol-5(*4H*)-one 4j. Beige powder, yield 82% (70 mg was obtained from 0.30 mmol of **3j**), mp = 95–97°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (ddd, J = 5.0, 2.0, 0.8 Hz, 1H), 7.62 (ddd, J = 8.7, 7.2, 1.9 Hz, 1H), 7.35 – 7.26 (m, 2H), 7.19 (d, J = 7.6 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 7.04 (ddd, J = 7.2, 5.0, 0.9 Hz, 1H), 6.83 (dt, J = 8.4, 0.9 Hz, 1H), 2.42 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 171.8, 161.1, 154.8, 147.0, 140.1, 138.1, 130.9, 130.7, 129.5, 127.9, 125.6, 121.0, 108.5, 19.7. HRMS (ESI), m/z: $[M+H]^+$ $C_{14}H_{12}N_3O_2S^+$ calcd. 286.0645; found 286.0648.



3-(2-Chlorophenyl)-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(*4H*)-one 4k. White powder, yield 76% (70 mg was obtained from 0.30 mmol of **3k**), mp =108–110°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 4.9, 1.8 Hz, 1H), 7.69 – 7.60 (m, 1H), 7.46 – 7.31 (m, 3H), 7.20 (td, *J* = 7.6, 1.2 Hz, 1H), 7.06 (dd, *J* = 6.9, 5.1 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.3, 161.2, 152.7, 147.1, 140.2, 134.0, 132.3, 131.5, 130.0, 128.0, 126.7, 121.1, 108.6. HRMS (ESI), m/z: [M+H]+ $C_{13}H_9ClN_3O_2S^+$ calcd. 306.0099; found 306.0111.

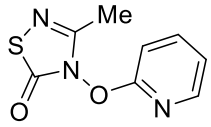


4-(Pyridin-2-yloxy)-3-(*m*-tolyl)-1,2,4-thiadiazol-5(*4H*)-one 4l. White powder, yield 76% (65 mg was obtained from 0.30 mmol of **3l**), mp = 92–94°C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.08 (dd, *J* = 4.9, 1.8 Hz, 1H), 7.76 – 7.68 (m, 1H), 7.63 (s, 1H), 7.61 – 7.53 (m, 1H), 7.27 – 7.23 (m, 3H), 7.06 (ddd, *J* = 7.2, 5.0, 0.8 Hz, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.3, 161.0, 153.9, 147.4, 140.3, 138.7, 132.4, 128.6, 128.6, 128.1, 124.9, 121.1, 108.7, 21.5. HRMS (ESI), m/z: [M+H]+ $C_{14}H_{12}N_3O_2S^+$ calcd. 286.0645; found 286.0645.

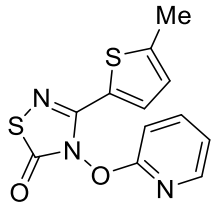


3-(3-Chlorophenyl)-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(*4H*)-one 4m. White powder, yield 68% (68 mg was obtained from 0.30 mmol of **3m**), mp = 112–124°C. ^{1}H NMR (400 MHz, DMSO-d_6) *δ* 8.08 (dd, *J* = 5.0, 1.8 Hz, 1H), 7.83 (t, *J* = 1.9 Hz, 1H), 7.77 – 7.68 (m, 2H), 7.46 – 7.39 (m, 1H), 7.33 (t, *J* = 7.9 Hz, 1H), 7.11 – 7.03 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ*

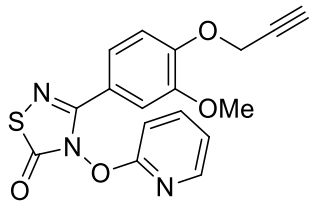
172.0, 160.8, 152.4, 147.5, 140.5, 134.9, 131.7, 130.1, 129.7, 128.1, 125.9, 121.3, 108.7. HRMS (ESI), m/z: $[M+H]^+$ $C_{13}H_9ClN_3O_2S^+$ calcd. 306.0099; found 306.0101.



3-Methyl-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(*4H*)-one 4n. Beige powder, yield 28% (52 mg was obtained from the mixture of **3n (**0.30 mmol) and tri(pyrrolidin-1-yl)phosphine oxide), mp = 117–118°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, J = 5.0, 1.6 Hz, 1H), 7.81 (ddd, J = 8.3, 7.2, 2.0 Hz, 1H), 7.17 (ddd, J = 7.2, 5.0, 0.8 Hz, 1H), 7.12 (d, J = 8.3 Hz, 1H), 2.29 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.4, 161.2, 153.4, 147.5, 140.5, 121.4, 108.8, 16.5. HRMS (ESI), m/z: $[M+H]^+$ $C_8H_8N_3O_2S^+$ calcd. 210.0332; found 210.0331.

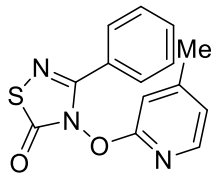


3-(5-Methylthiophen-2-yl)-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(*4H*)-one 4o. Beige powder, yield 85% (74 mg was obtained from 0.30 mmol of **3o**), mp = 137–138°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, J = 4.9, 1.8 Hz, 1H), 7.84 – 7.76 (m, 1H), 7.49 (d, J = 3.8 Hz, 1H), 7.19 – 7.08 (m, 2H), 6.69 (d, J = 3.7 Hz, 1H), 2.47 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.7, 160.9, 148.2, 147.7, 145.9, 140.4, 129.7, 127.1, 126.4, 121.3, 108.8, 15.5. HRMS (ESI), m/z: $[M+H]^+$ $C_{12}H_{10}N_3O_2S_2^+$ calcd. 292.0209; found 292.0204.

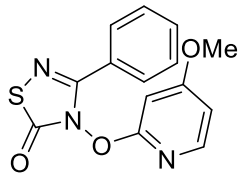


3-(3-Methoxy-4-(prop-2-yn-1-yloxy)phenyl)-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(*4H*)-one 4p. White powder, yield 68% (73 mg was obtained from 0.30 mmol of **3p**), mp = 135–136°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (ddd, J = 5.0, 1.9, 0.8 Hz, 1H), 7.78 – 7.69 (m, 1H), 7.43 (dd, J

= 8.5, 2.0 Hz, 1H), 7.38 (d, *J* = 2.1 Hz, 1H), 7.08 (ddd, *J* = 7.3, 5.0, 0.8 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 1H), 4.76 (d, *J* = 2.4 Hz, 2H), 3.82 (s, 3H), 2.51 (t, *J* = 2.4 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 172.3, 161.0, 153.0, 149.6, 149.5, 147.5, 140.4, 121.8, 121.1, 120.8, 113.3, 111.1, 108.6, 77.8, 76.5, 56.7, 56.0. HRMS (ESI), m/z: $[M+H]^+$ $C_{17}H_{14}N_3O_4S^+$ calcd. 356.0700; found 356.0685.



4-((4-Methylpyridin-2-yl)oxy)-3-phenyl-1,2,4-thiadiazol-5(*4H*)-one 4q. White powder, yield 54% (46 mg was obtained from 0.30 mmol of **3q**), mp = 109–110°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 5.1 Hz, 1H), 7.84 – 7.78 (m, 2H), 7.48 – 7.42 (m, 1H), 7.42 – 7.35 (m, 2H), 6.87 (d, *J* = 5.0 Hz, 1H), 6.83 (s, 1H), 2.34 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 172.4, 161.4, 153.8, 152.2, 146.9, 131.5, 128.8 (2C), 128.3, 127.9 (2C), 122.5, 108.7, 21.2. HRMS (ESI), m/z: $[M+H]^+$ $C_{14}H_{12}N_3O_2S^+$ calcd. 286.0645; found 286.0648.



4-((4-Methoxypyridin-2-yl)oxy)-3-phenyl-1,2,4-thiadiazol-5(*4H*)-one 4r. White powder, yield 84% (76 mg was obtained from 0.30 mmol of **3r**), mp = 109–111°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 5.8 Hz, 1H), 7.83 – 7.78 (m, 2H), 7.48 – 7.43 (m, 1H), 7.43 – 7.37 (m, 2H), 6.60 (dd, *J* = 5.8, 2.1 Hz, 1H), 6.47 (d, *J* = 2.1 Hz, 1H), 3.84 (s, 3H).$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 172.4, 167.0, 162.9, 153.7, 147.8, 131.5, 128.8 (2C), 128.3, 127.9 (2C), 109.6, 92.6, 55.8. HRMS (ESI), m/z: $[M+H]^+$ $C_{14}H_{12}N_3O_3S^+$ calcd. 302.0594; found 302.0581.

S3. X-ray diffraction studies

Singe crystals for X-ray studying were obtained by slow evaporation of solutions of compounds **3k**, **3u**, **3y**, and **4m** in $CDCl_3$ at RT in air. X–ray diffraction data were collected at a Rigaku SuperNova (**3k**, **3u**, **3y**) and XtaLAB Synergy (**4m**) diffractometers using Cu–Kα (λ = 0.154184 nm) radiation. The structures have been solved with the ShelXT[10] structure solution program using Intrinsic Phasing and refined with the ShelXL[11] refinement package incorporated in the OLEX2 program package[12] using Least Squares minimization. Hydrogen atom positions in XRD structures were set according to neutron diffraction data.[13] Supplementary crystallographic data for this paper have been deposited at Cambridge Crystallographic Data Centre and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif. CCDC numbers are presented in **Table S1**.

Table S1. Crystal data and refinement details for crystals structures of **3k**, **3u**, **3y**, **4m**.

Compound	**3k**	**3u**	**3y**	**4m**
Identification code	COB-58	SYN-549	SYN-557	END-088
CCDC number	2474620	2474622	2474623	2474621
Empirical formula	$C_{12}H_{10}ClN_3O$	$C_{17}H_{14}N_4O$	$C_{14}H_{15}N_3O$	$C_{13}H_8ClN_3O_2S$
Formula weight	247.68	290.32	241.29	305.73
Temperature/K	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	trigonal	monoclinic
Space group	$P2_1/c$	C2/c	$P3_2$	P2/n
a/Å	10.6695(2)	21.1399(3)	10.23780(10)	27.1298(12)
b/Å	9.7859(2)	6.21410(10)	10.23780(10)	6.4573(2)
c/Å	11.9081(3)	21.7378(3)	10.7057(2)	8.0989(3)
α/°	90	90	90	90
β/°	113.892(3)	93.6270(10)	90	114.245(5)
γ/°	90	90	120	90
Volume/Å^3	1136.79(5)	2849.88(7)	971.76(3)	1293.67(10)
Z	4	8	3	4
ρ_{calc}g/cm^3	1.447	1.353	1.237	1.570
μ/mm^{-1}	2.867	0.711	0.646	4.178
F(000)	512.0	1216.0	384.0	624.0
Crystal size/mm^3	0.09×0.07×0.04	0.22×0.2×0.18	0.18×0.16×0.15	0.2×0.18×0.12
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.066 to 143.27	8.152 to 143.632	9.976 to 143.056	7.148 to 160.804
Index ranges	$-11 \le h \le 13$, $-11 \le k \le 12$, $-14 \le l \le 14$	$-24 \le h \le 26$, $-7 \le k \le 7$, $-23 \le l \le 26$	$-12 \le h \le 8$, $-12 \le k \le 12$, $-13 \le l \le 13$	$-33 \le h \le 34$, $-8 \le k \le 7$, $-10 \le l \le 10$
Reflections collected	6398	8402	5945	10275
Independent reflections	2212 [R_{int} = 0.0279, R_{sigma} = 0.0300]	2791 [R_{int} = 0.0396, R_{sigma} = 0.0326]	2387 [R_{int} = 0.0243, R_{sigma} = 0.0277]	2716 [R_{int} = 0.0397, R_{sigma} = 0.0247]
Data/restraints/parameters	2212/0/154	2791/0/207	2387/1/170	2716/11/217
Goodness-of-fit on F^2	1.075	1.068	1.054	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0352, wR_2 = 0.0961	R_1 = 0.0424, wR_2 = 0.1142	R_1 = 0.0318, wR_2 = 0.0838	R_1 = 0.0513, wR_2 = 0.1357
Final R indexes [all data]	R_1 = 0.0389, wR_2 = 0.0988	R_1 = 0.0441, wR_2 = 0.1161	R_1 = 0.0323, wR_2 = 0.0845	R_1 = 0.0538, wR_2 = 0.1374
Largest diff. peak/hole / e Å^{-3}	0.47/–0.29	0.19/–0.29	0.17/–0.20	0.44/–0.60
Flack parameter			0.01(12)	

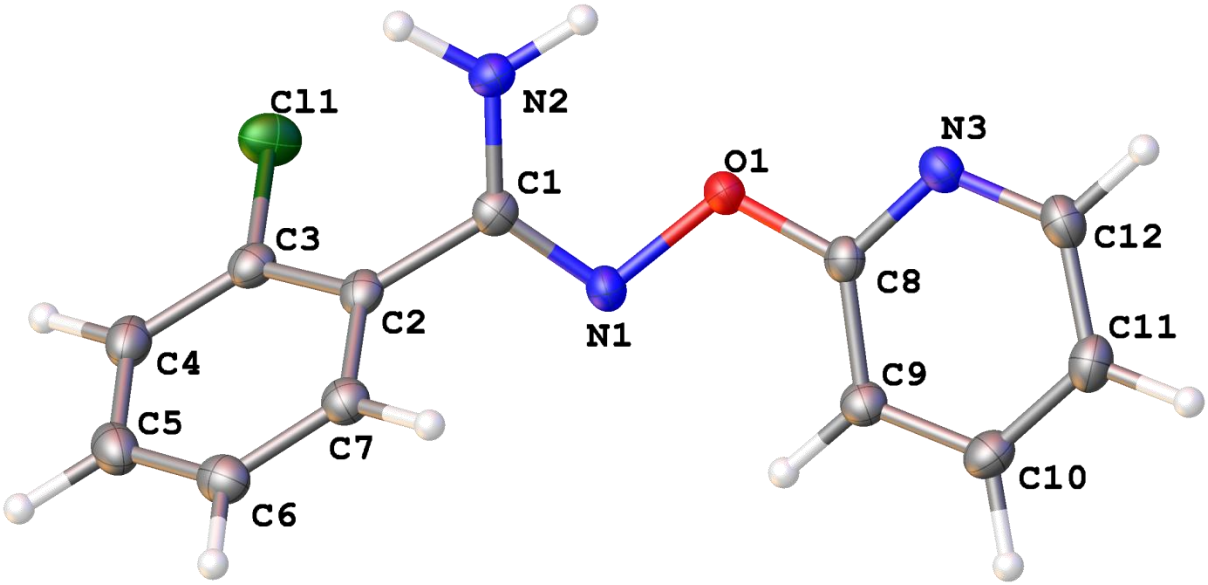


Figure S1. OLEX2 view of the crystal structure of **3k**.

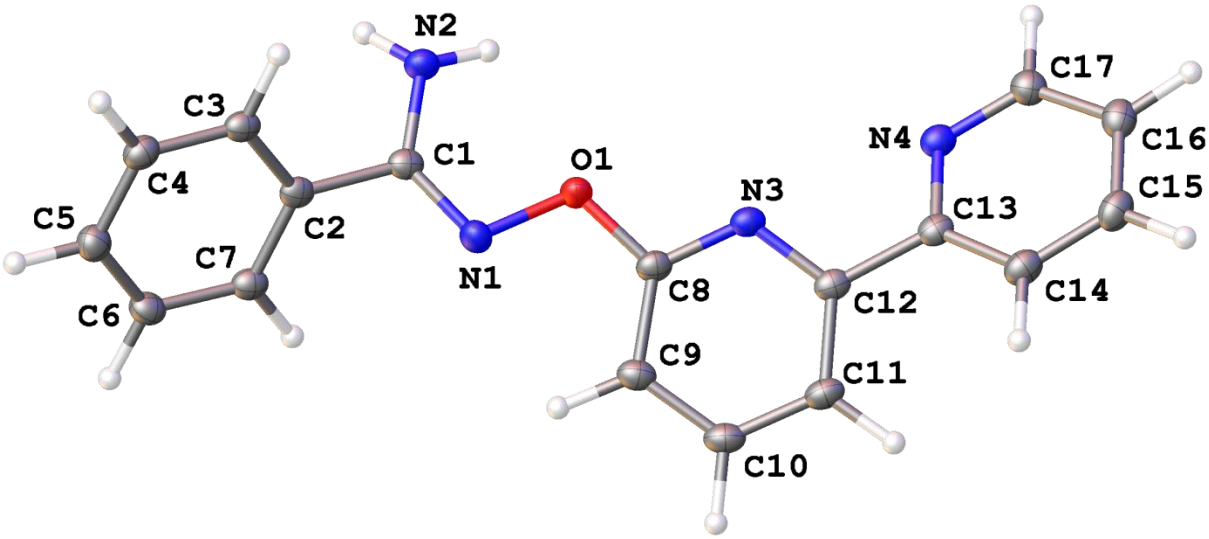


Figure S2. OLEX2 view of the crystal structure of **3u**.

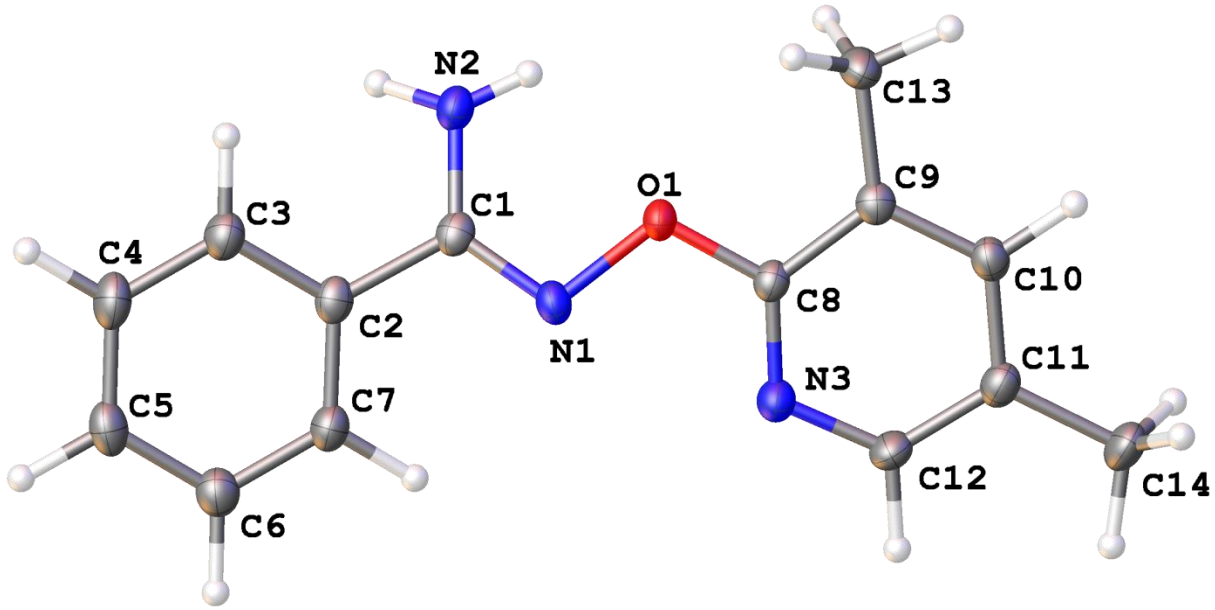


Figure S3. OLEX2 view of the crystal structure of **3y**.

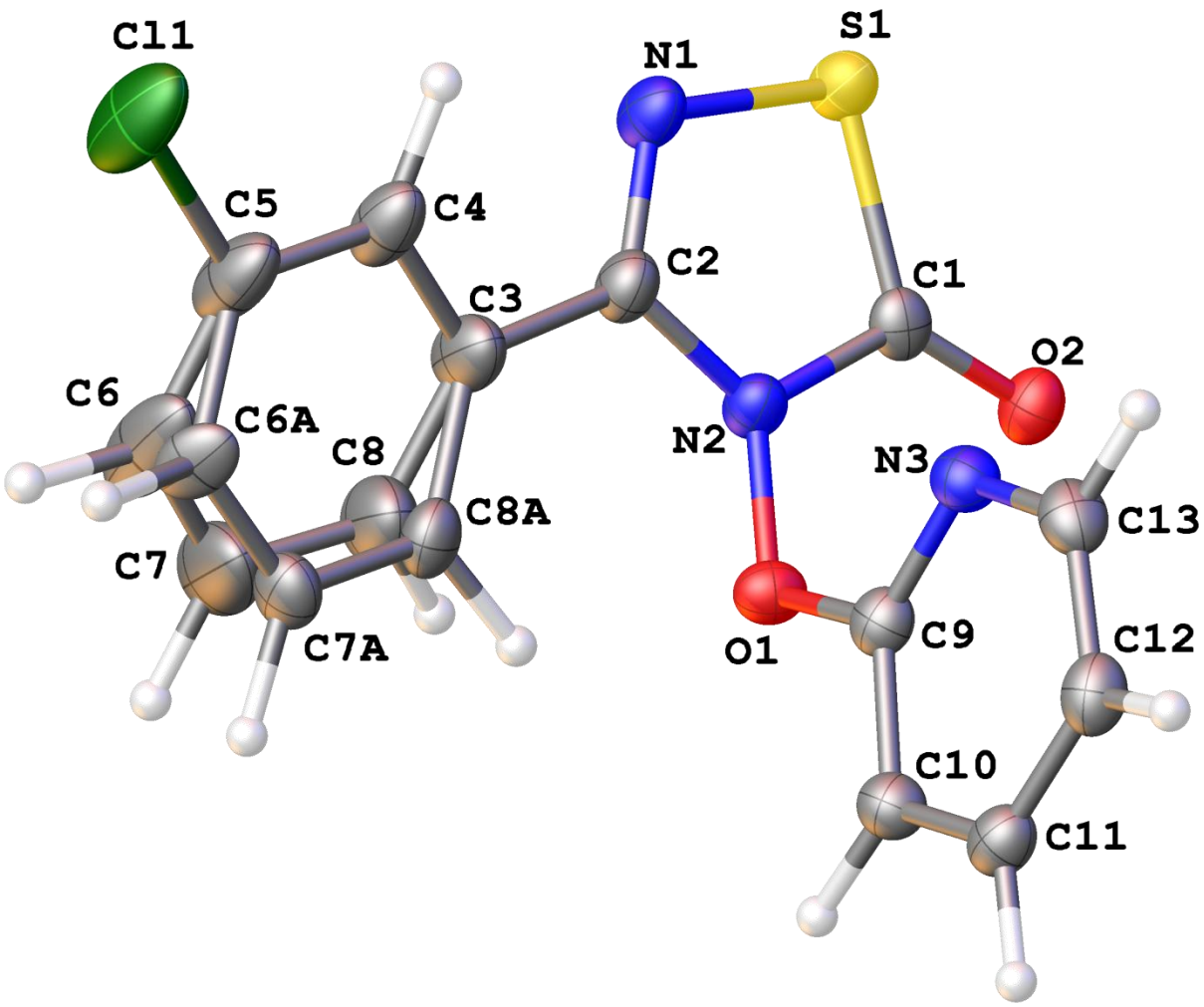
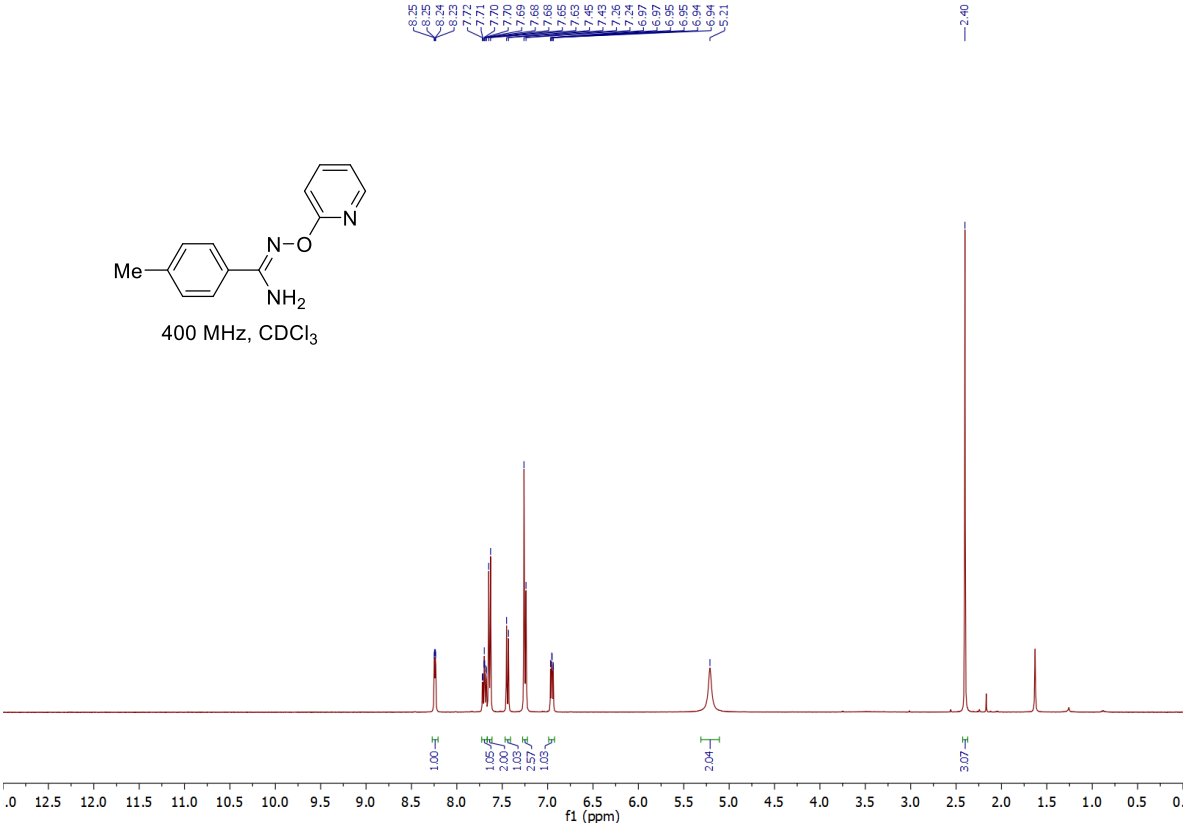
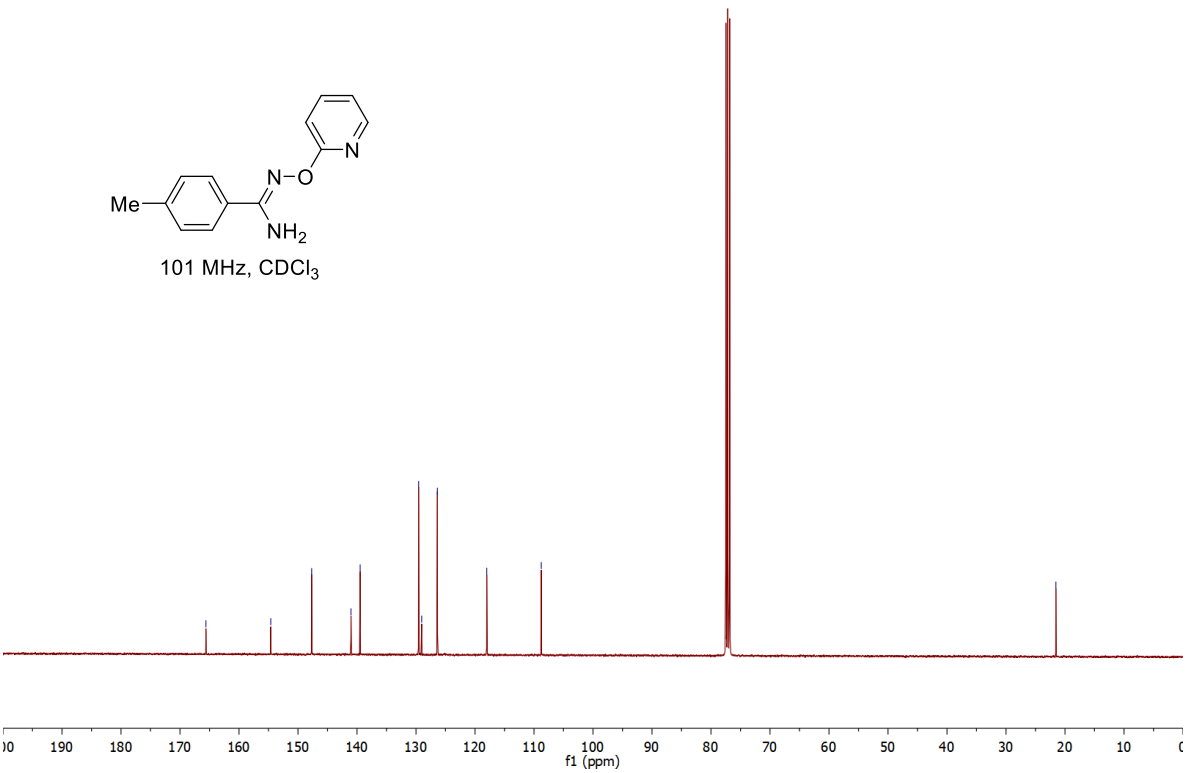


Figure S4. OLEX2 view of the crystal structure of **4m**. The disorder of aromatic ring was solved via splitting.

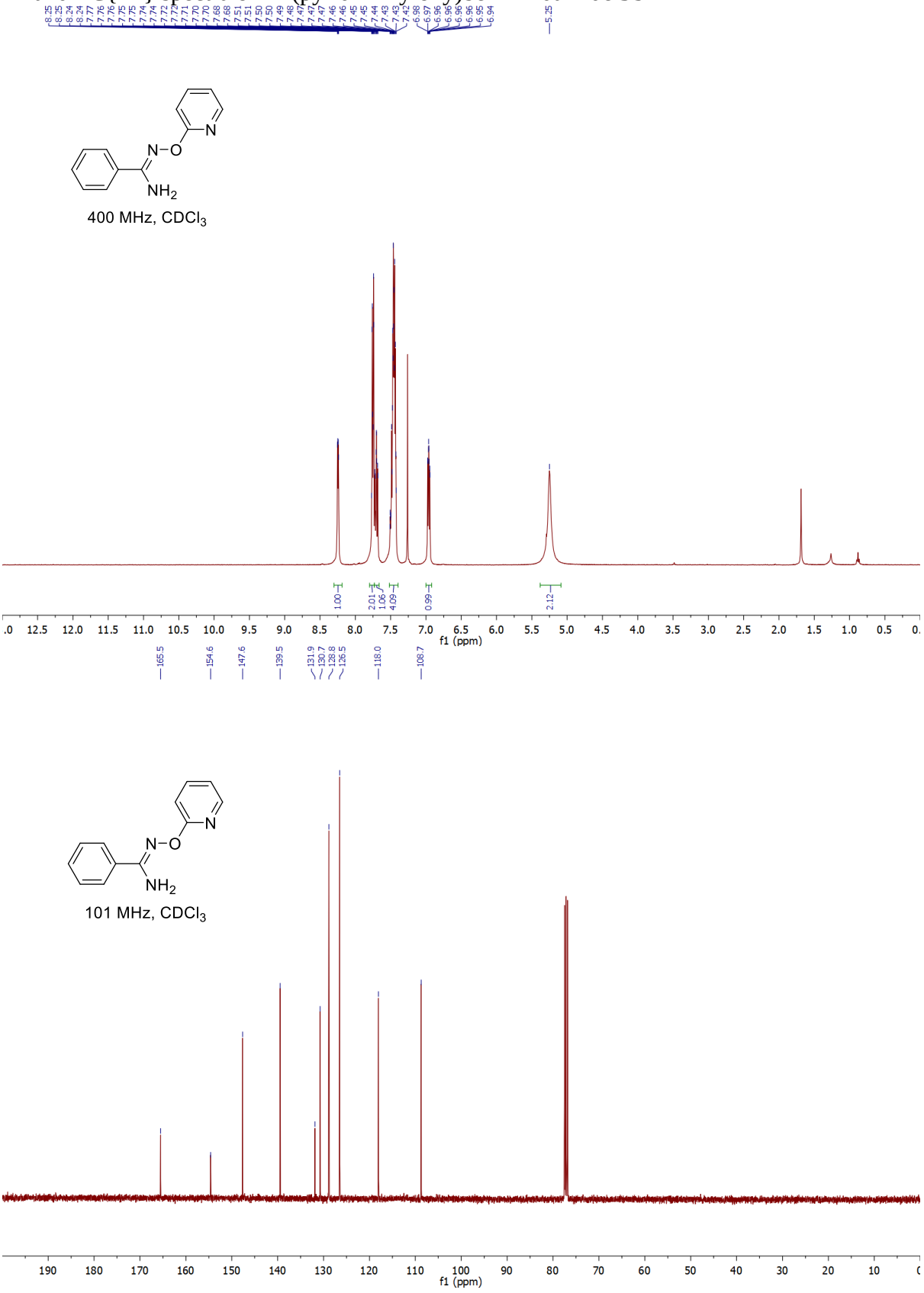
S4. ^{1}H, $^{13}C\{^{1}H\}$, and $^{19}F\{^{1}H\}$ NMR spectra of synthesized compounds

^{1}H and $^{13}C\{^{1}H\}$ spectra of 4-methyl-*N*'-(pyridin-2-yloxy)benzimidamide **3a**

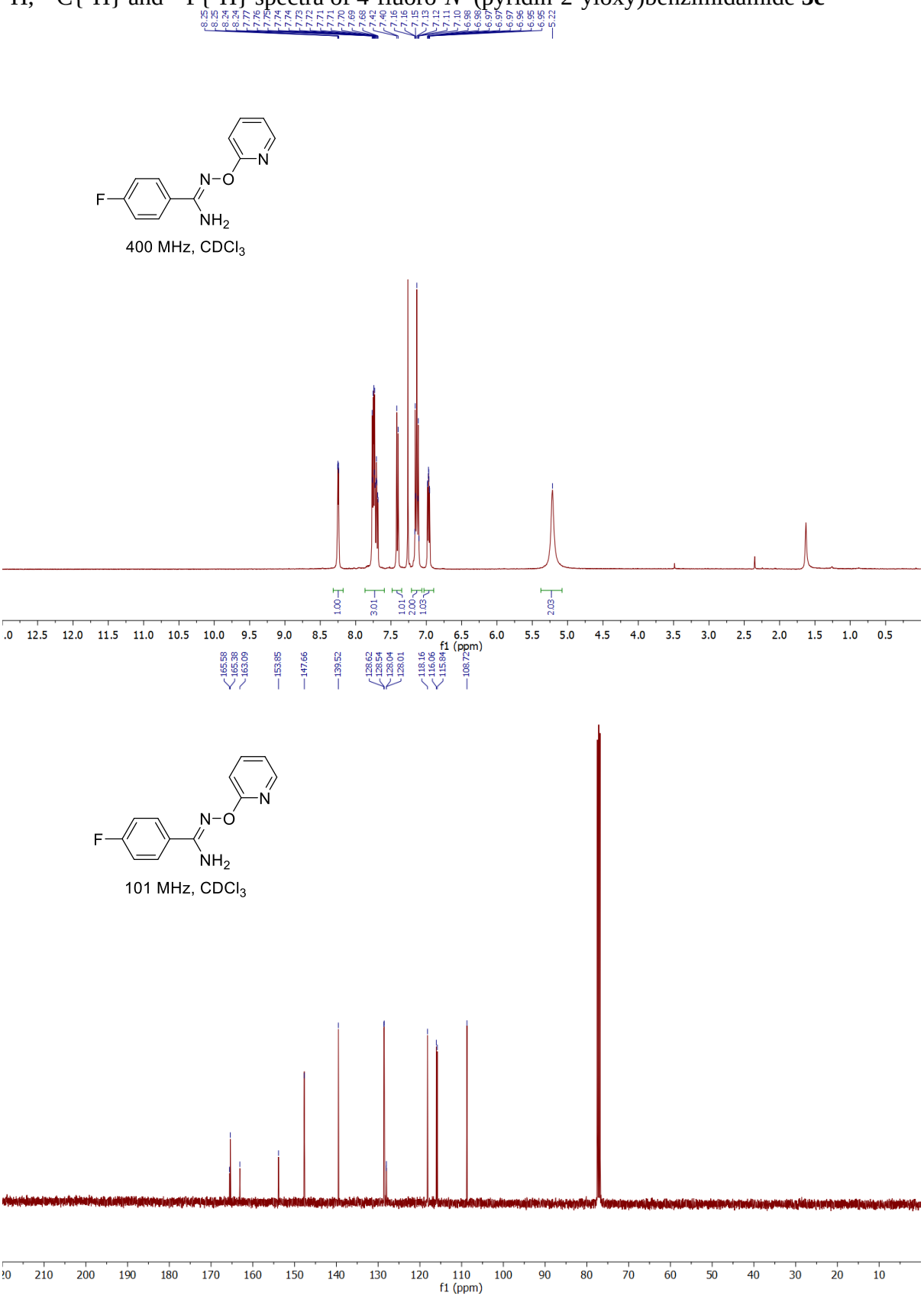


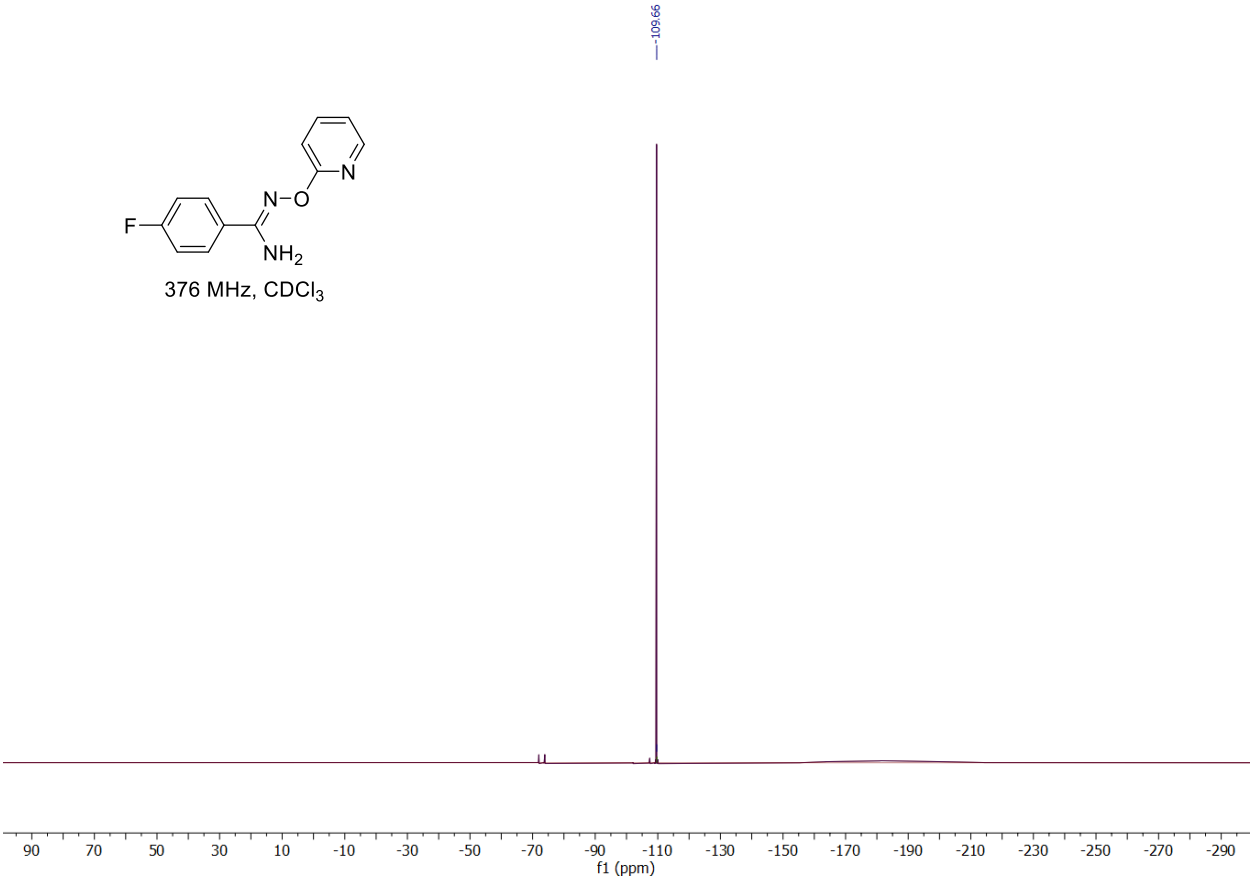


^{1}H and $^{13}C\{^{1}H\}$ spectra of *N*'-(pyridin-2-yloxy)benzimidamide **3b**

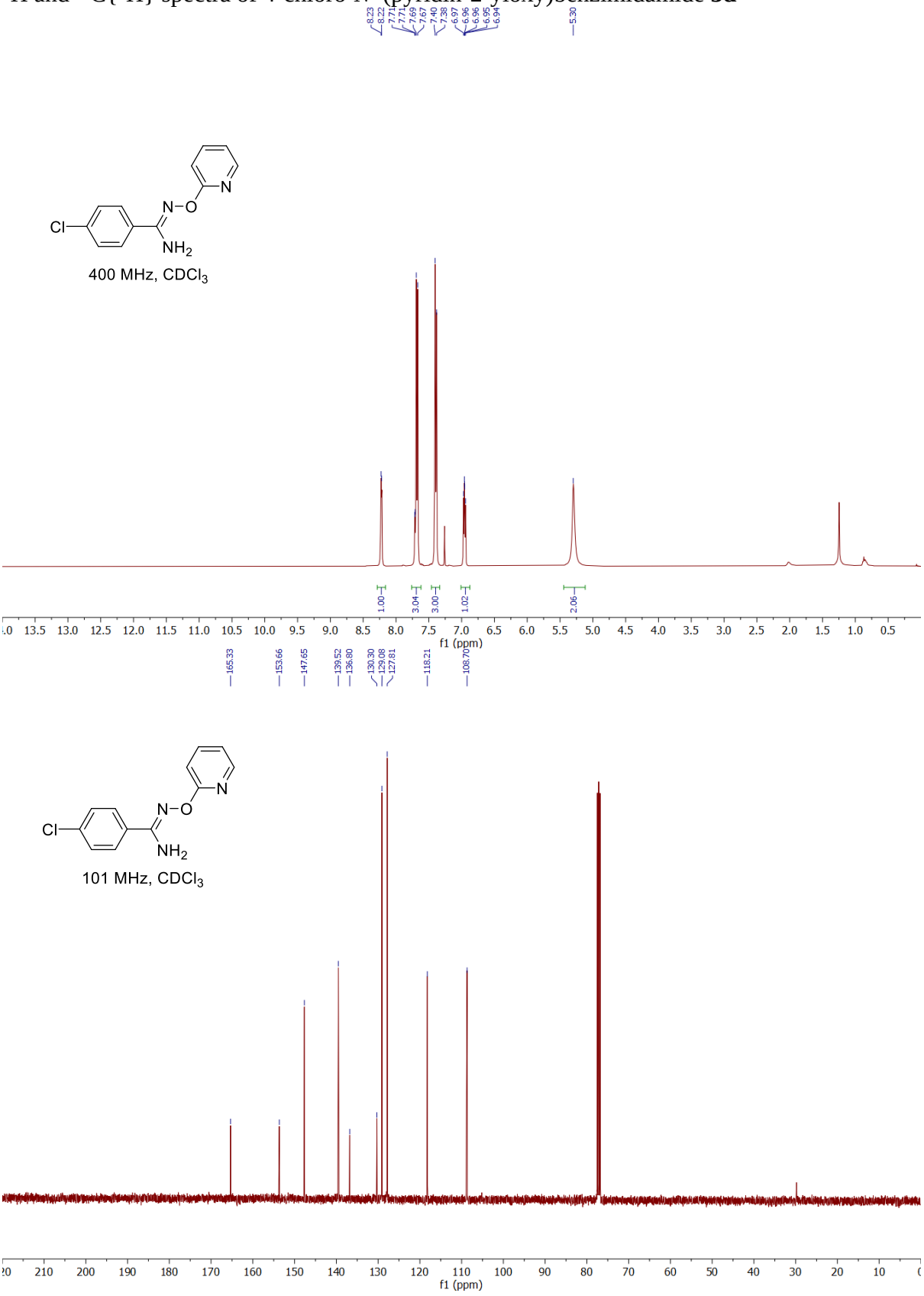


^{1}H, $^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ spectra of 4-fluoro-*N*'-(pyridin-2-yloxy)benzimidamide **3c**

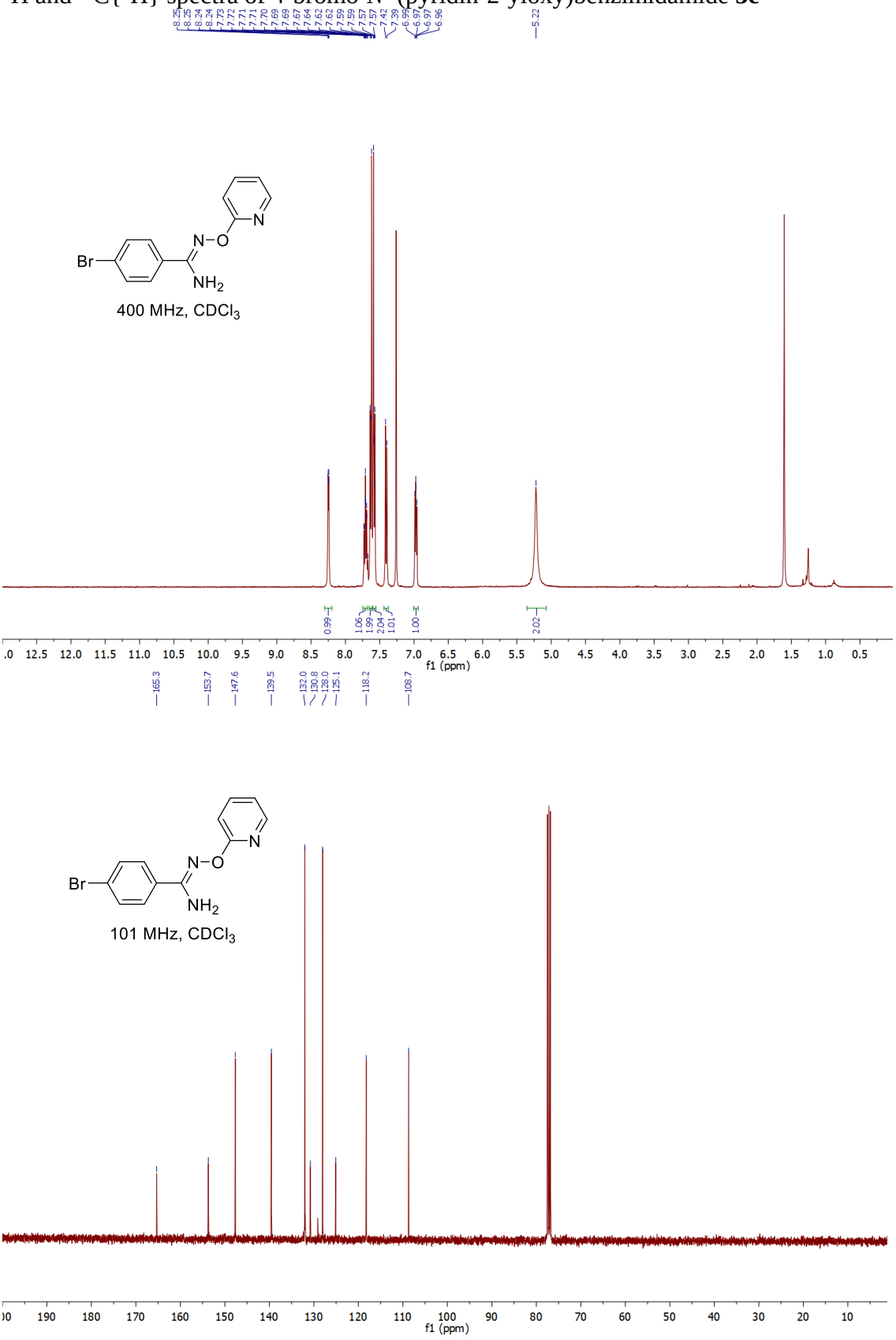



-109.66
F
N
N–O
NH2
376 MHz, CDCl3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

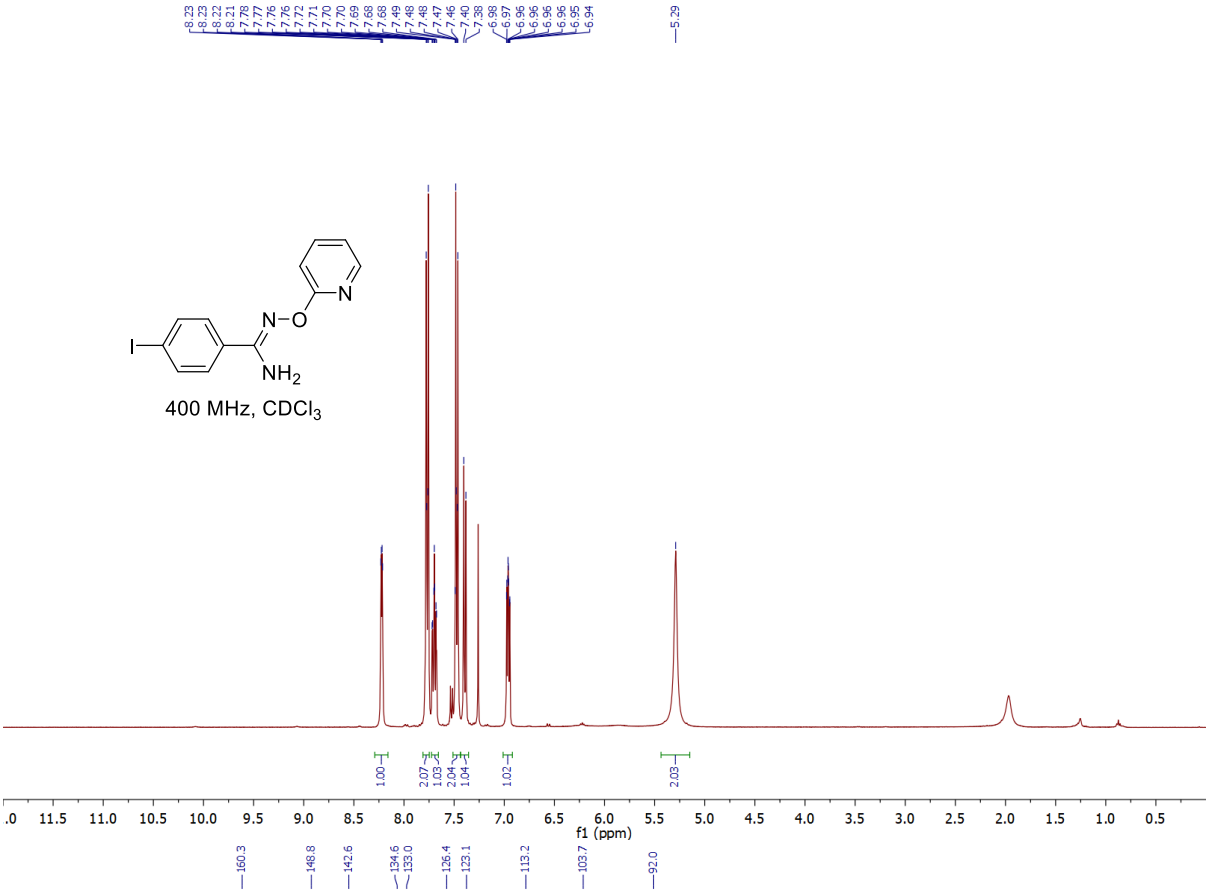
^{1}H and $^{13}C\{^{1}H\}$ spectra of 4-chloro-*N*'-(pyridin-2-yloxy)benzimidamide **3d**

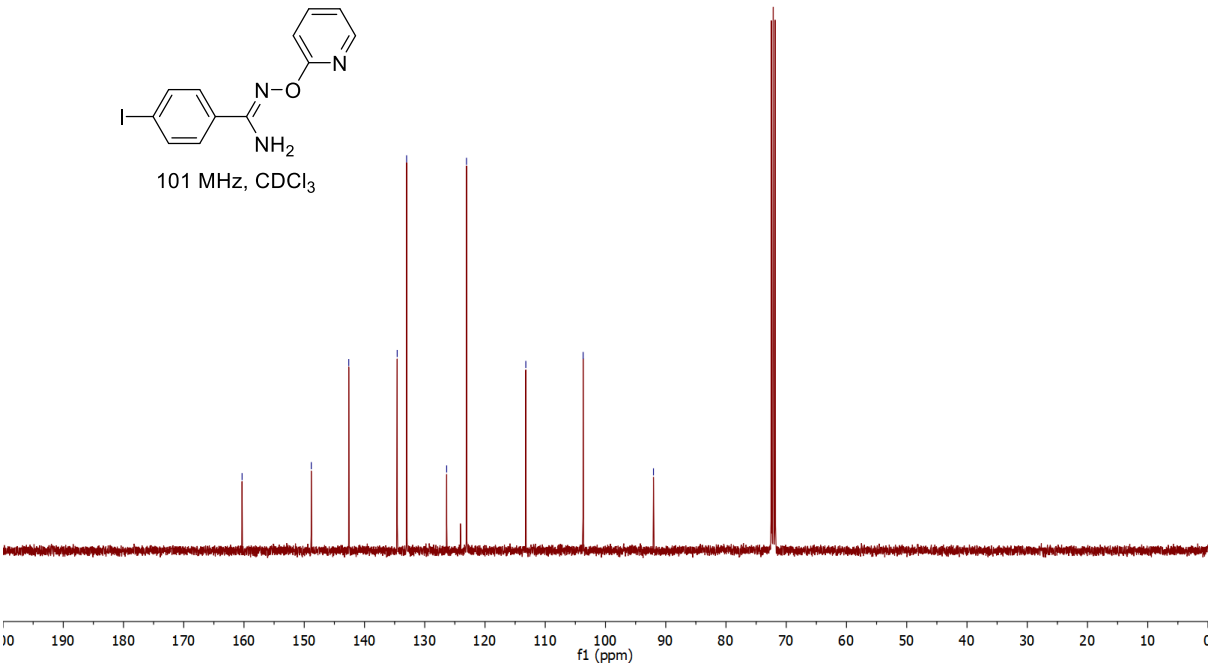


^{1}H and $^{13}C\{^{1}H\}$ spectra of 4-bromo-*N*'-(pyridin-2-yloxy)benzimidamide **3e**

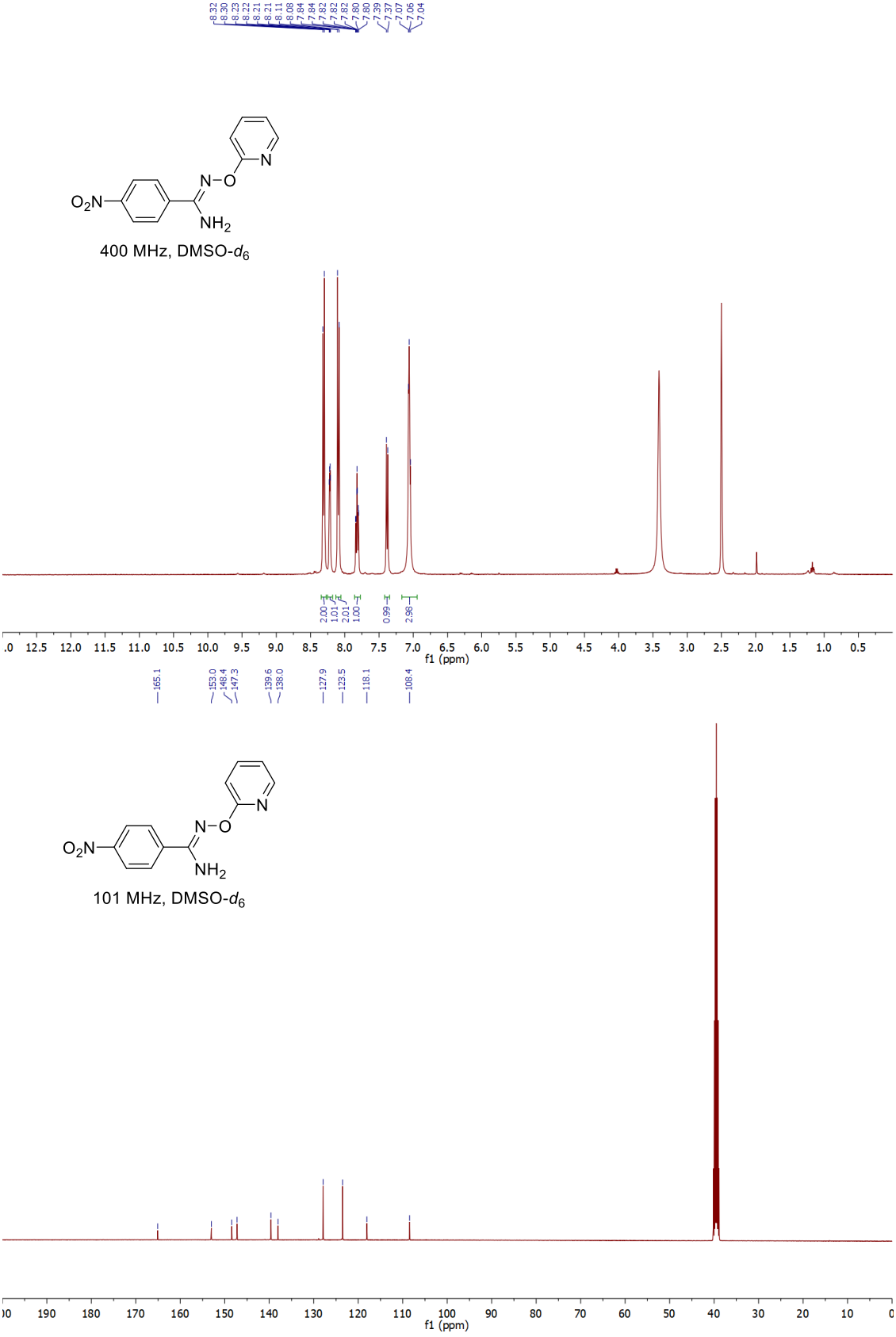


^{1}H and $^{13}C\{^{1}H\}$ 4-iodo-*N'*-(pyridin-2-yloxy)benzimidamide **3f**

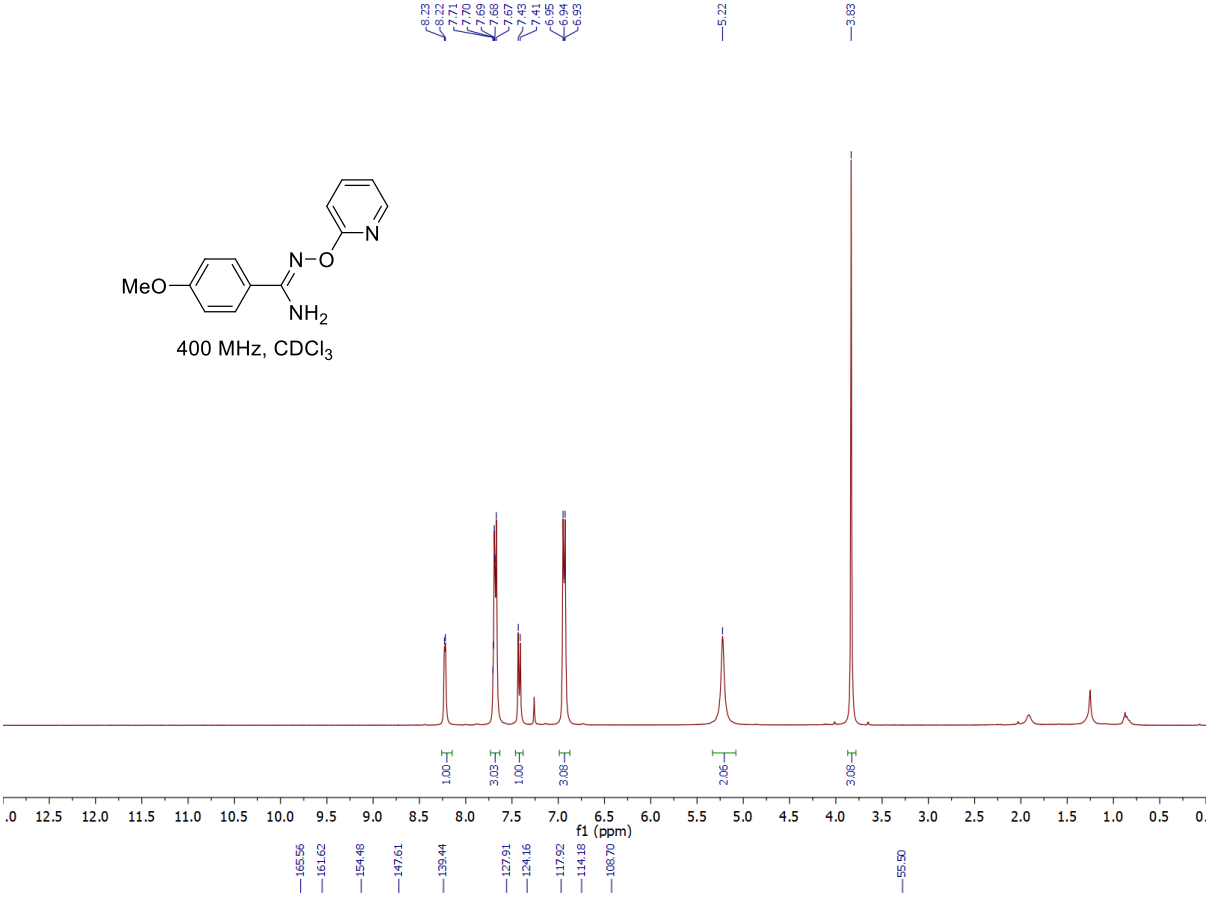


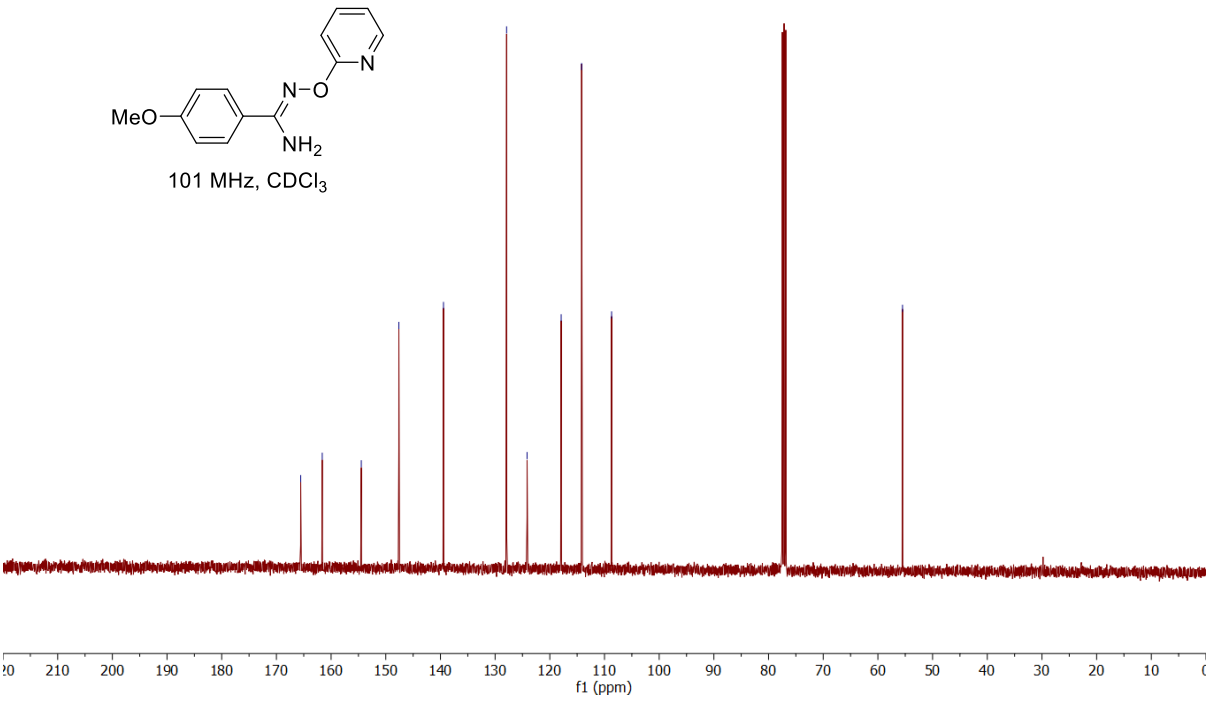


^{1}H and $^{13}C\{^{1}H\}$ spectra of 4-nitro-N'-(pyridin-2-yloxy)benzimidamide **3g**

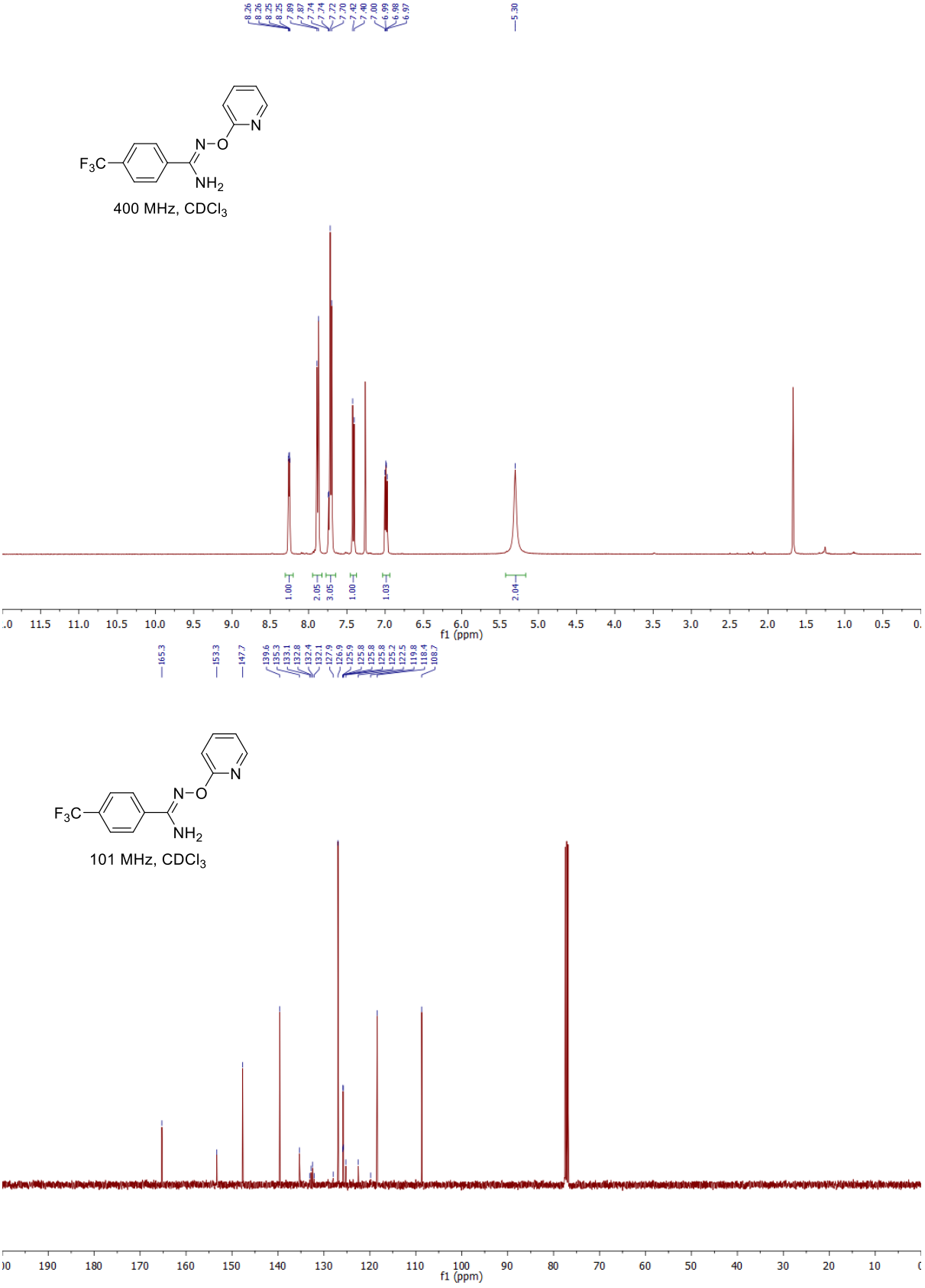


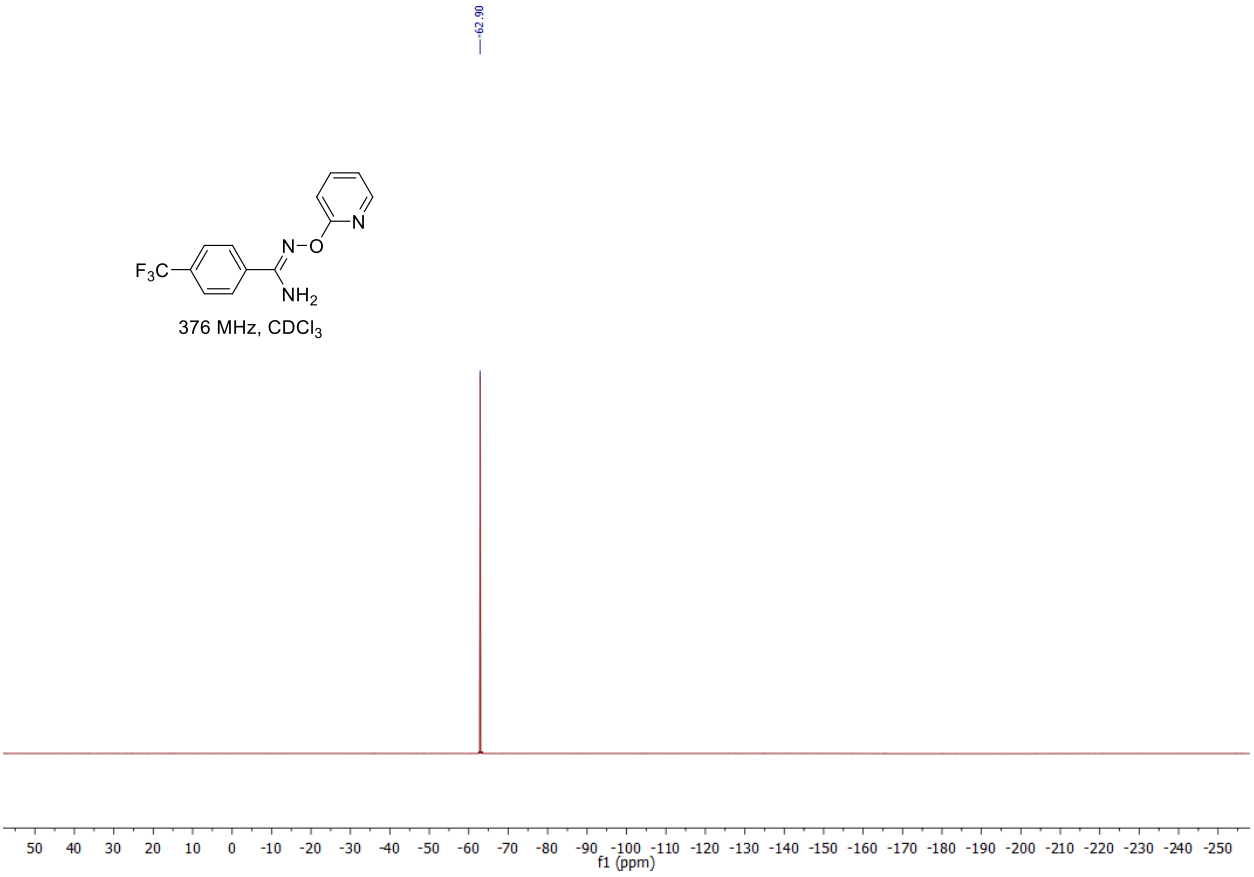
^{1}H and $^{13}C\{^{1}H\}$ spectra of 4-methoxy-N'-(pyridin-2-yloxy)benzimidamide **3h**



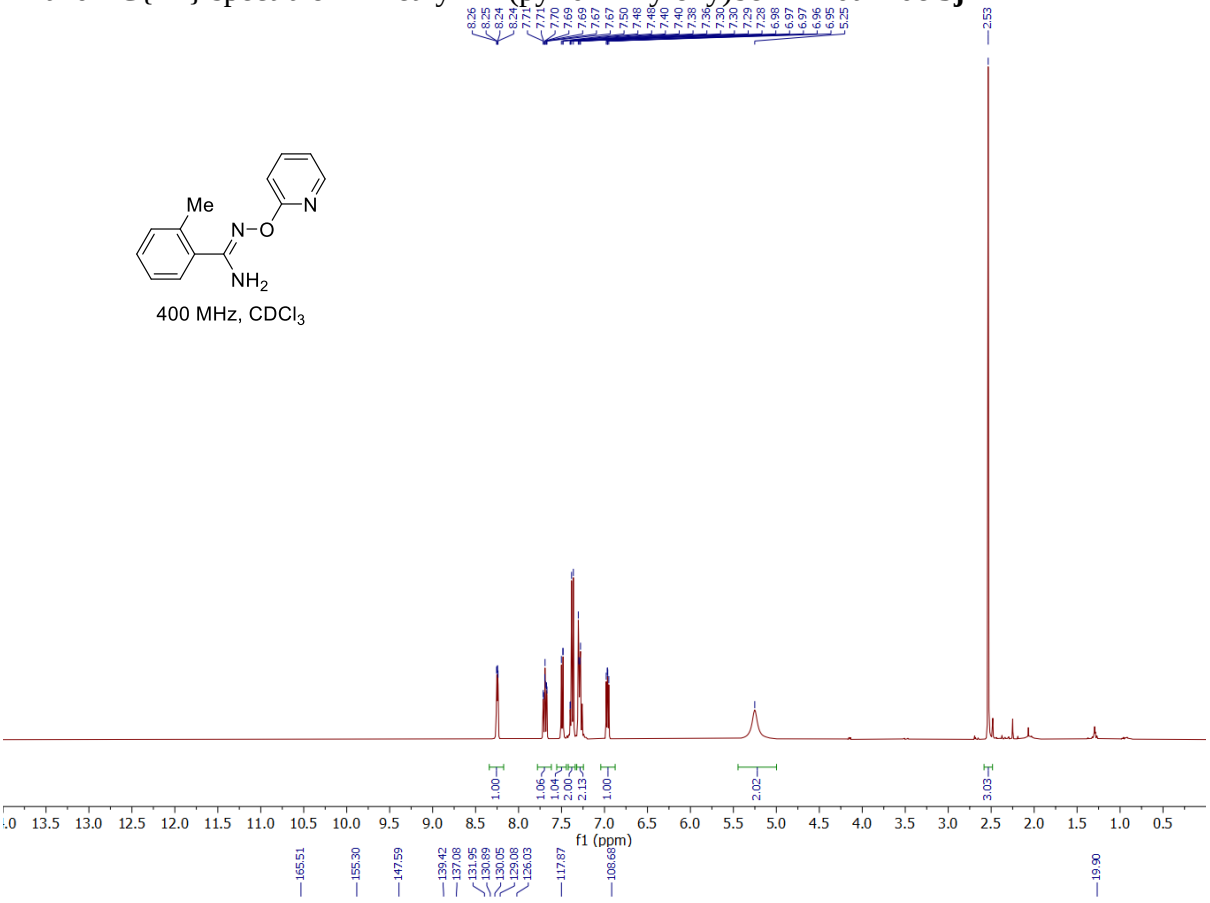


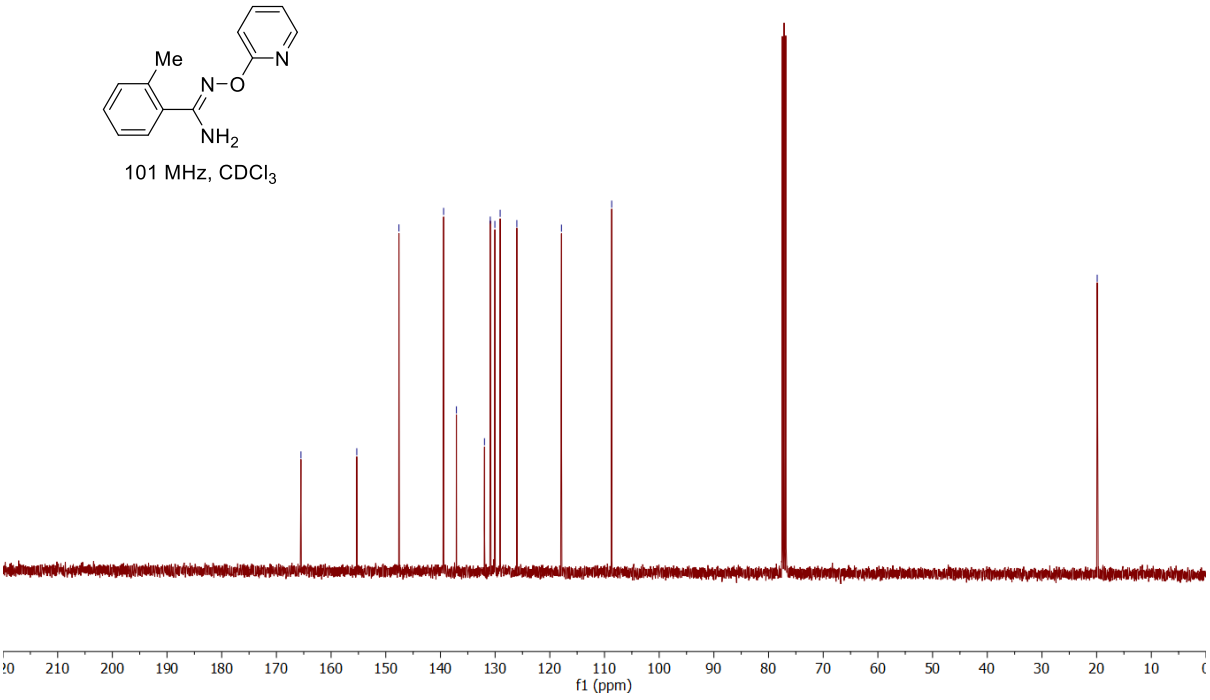
^{1}H, $^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ spectra of *N*'-(pyridin-2-yloxy)-4-(trifluoromethyl)benzimidamide **3i**



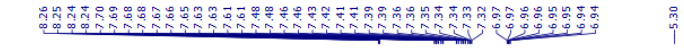

-62.90
F3C
N
O
NH2
376 MHz, CDCl3
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)

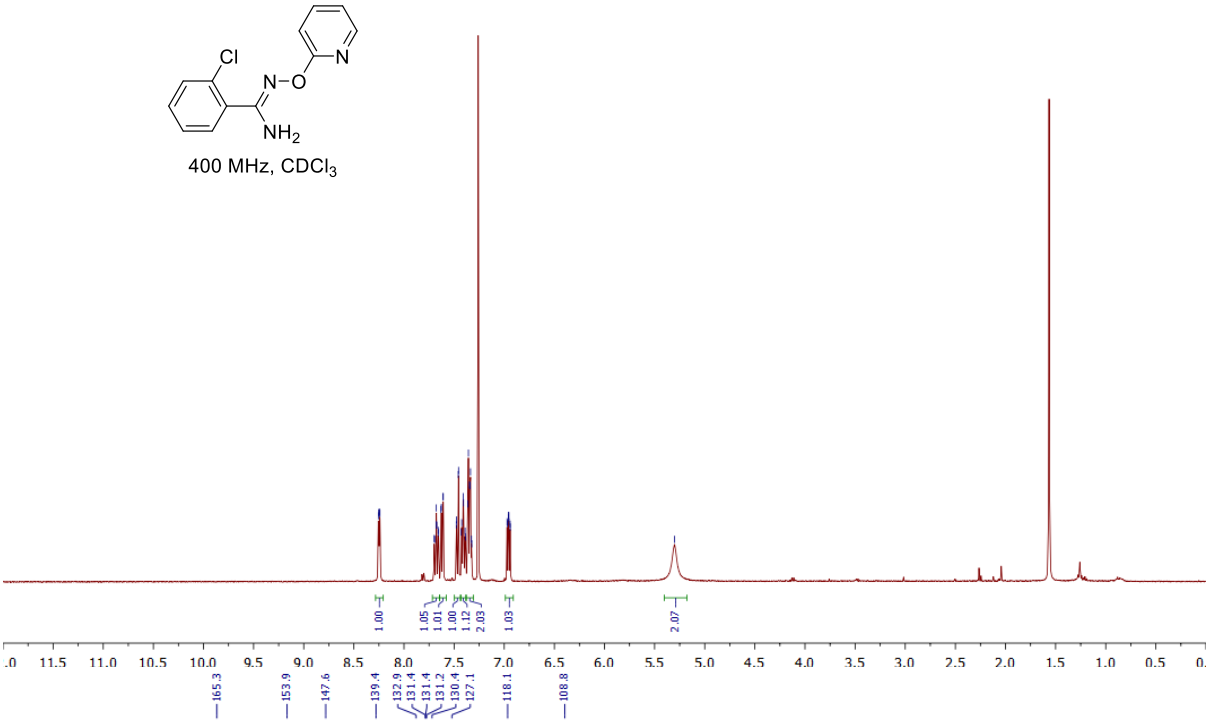
^{1}H and $^{13}C\{^{1}H\}$ spectra of 2-methyl-*N*'-(pyridin-2-yloxy)benzimidamide **3j**

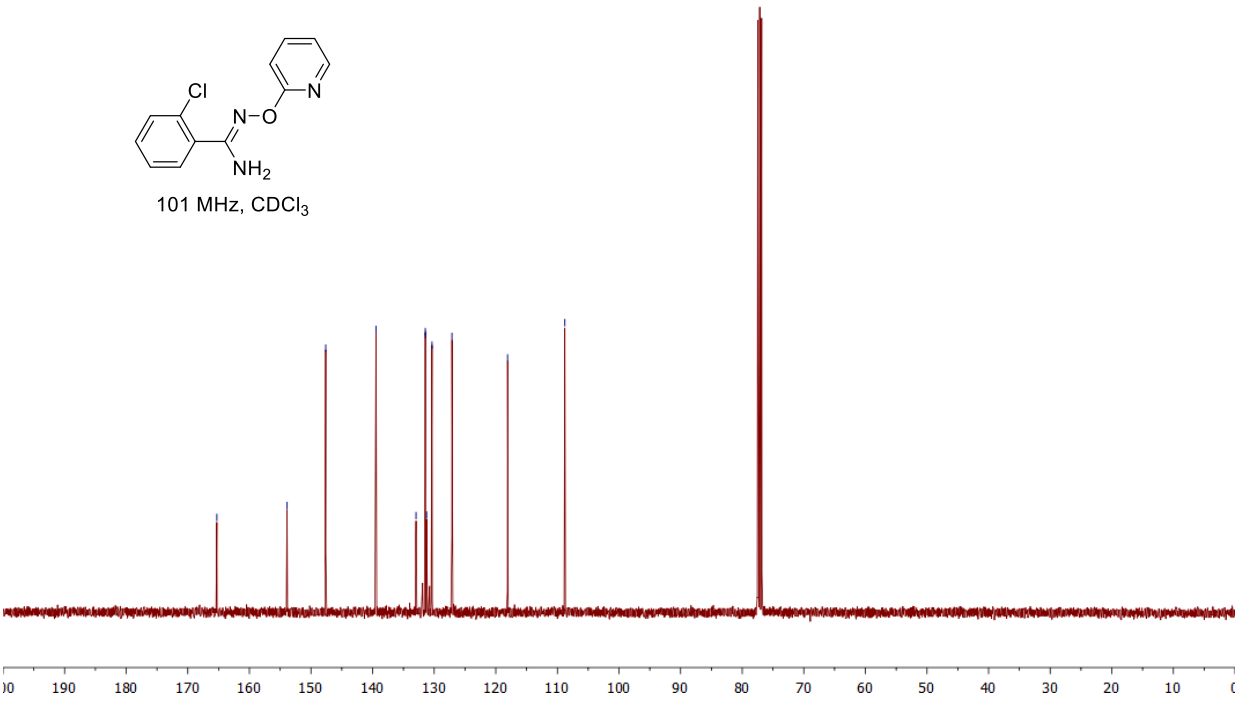




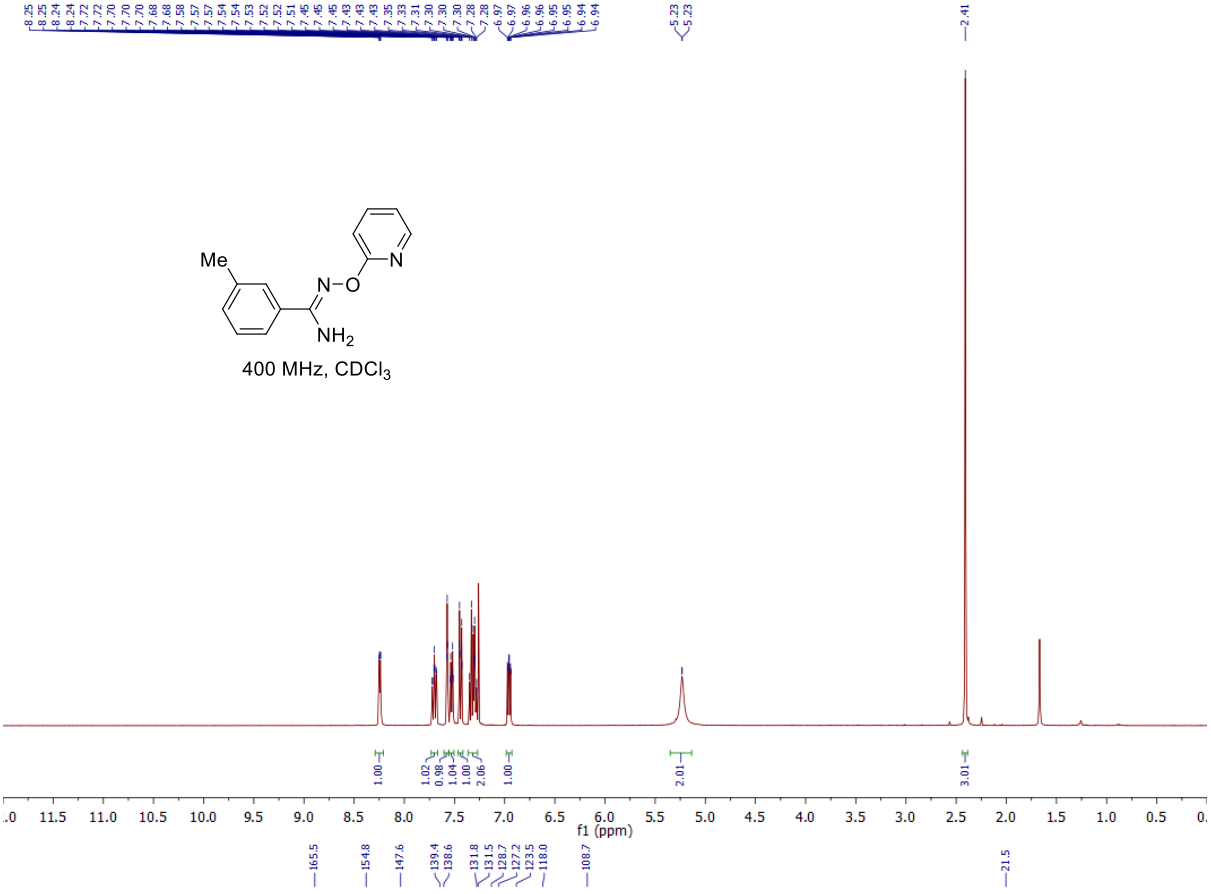
^{1}H and $^{13}C\{^{1}H\}$ spectra of 2-chloro-*N*'-(pyridin-2-yloxy)benzimidamide **3k**

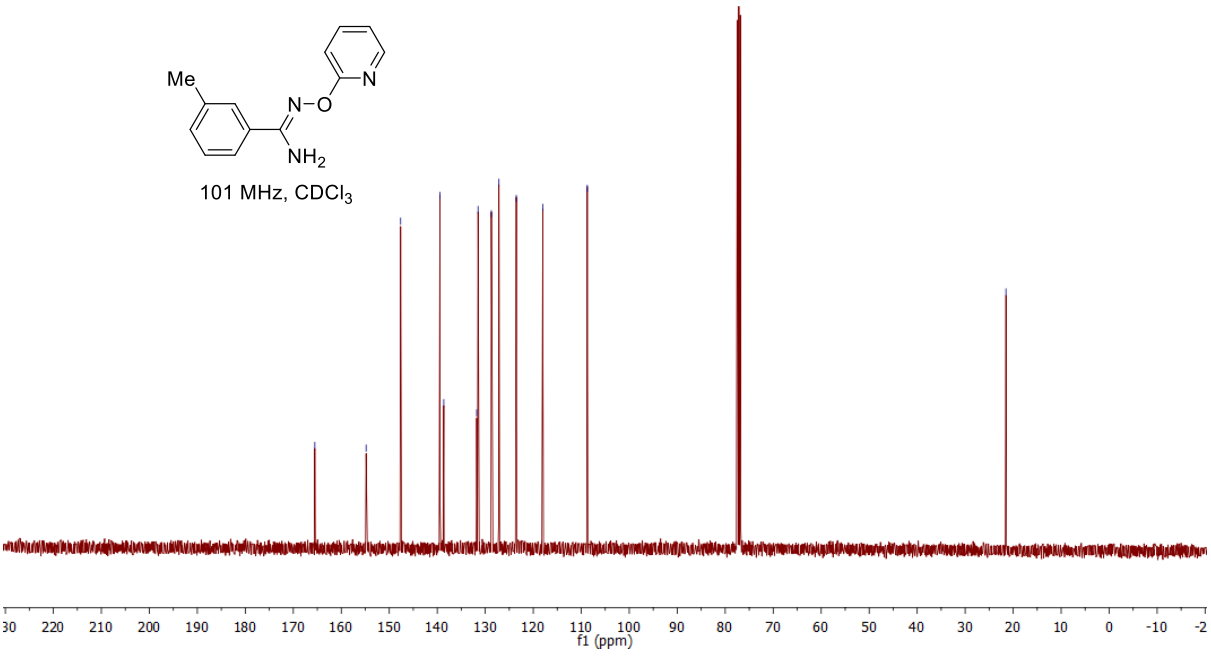




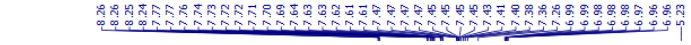


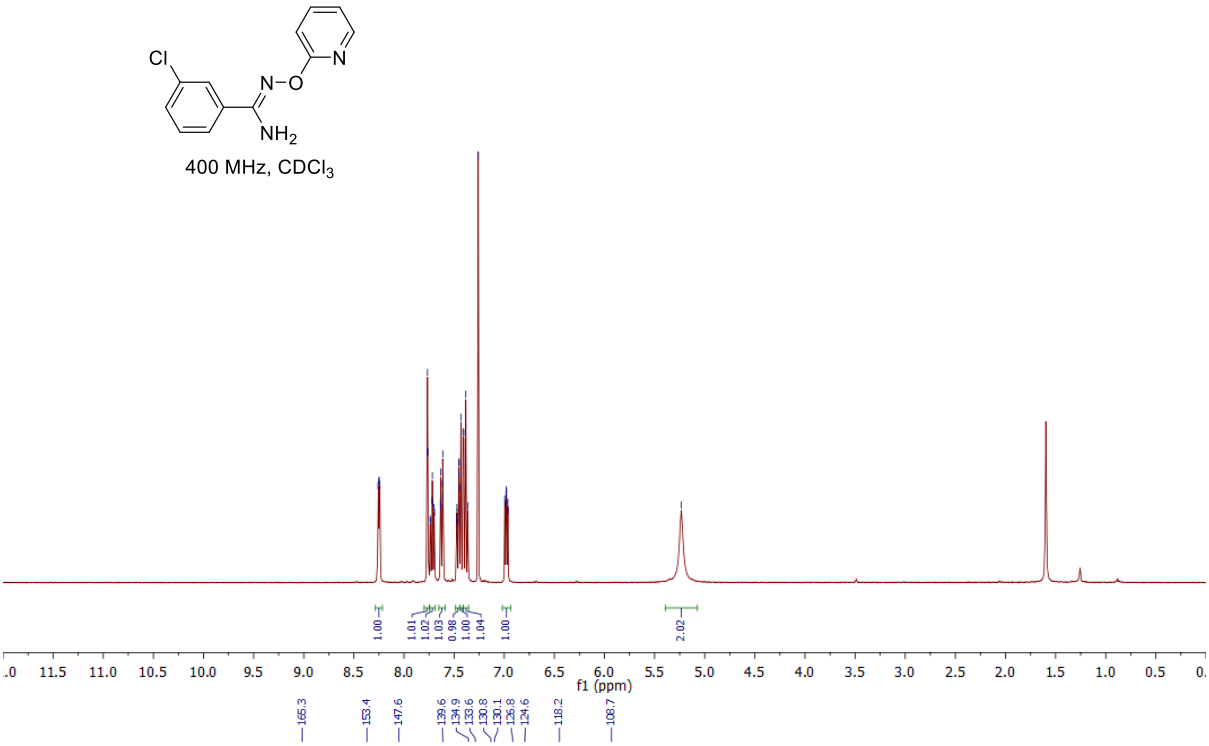
^{1}H and $^{13}C\{^{1}H\}$ spectra of 3-methyl-*N*'-(pyridin-2-yloxy)benzimidamide **3l**

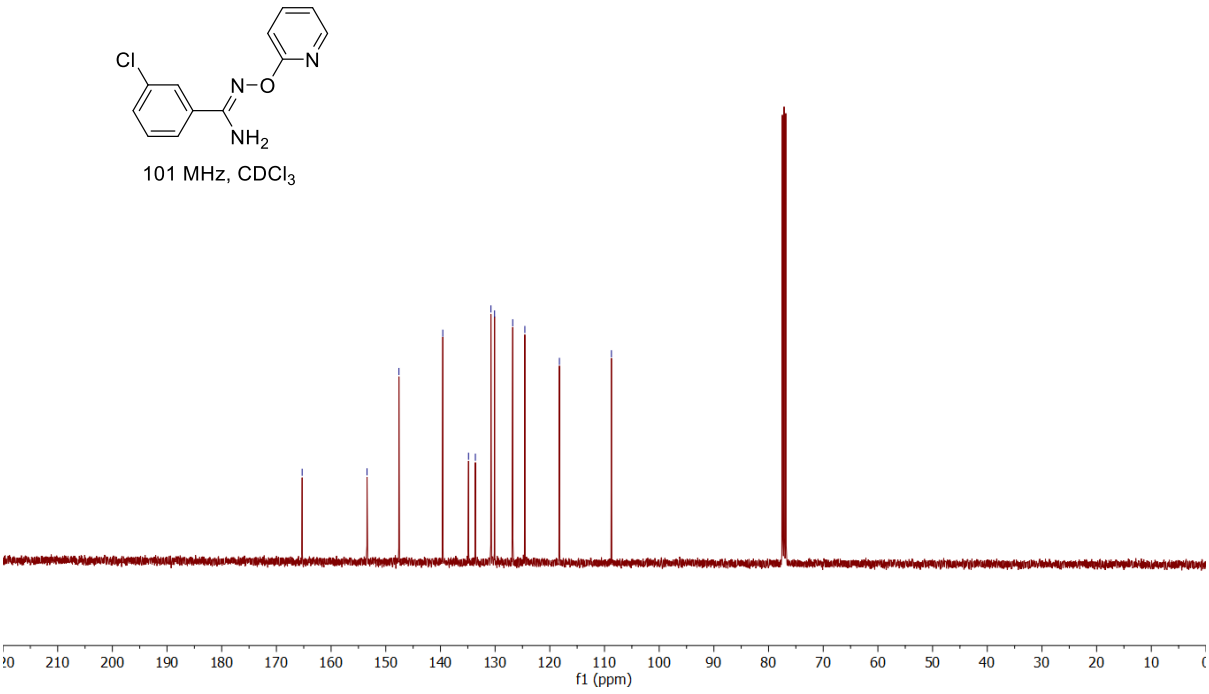




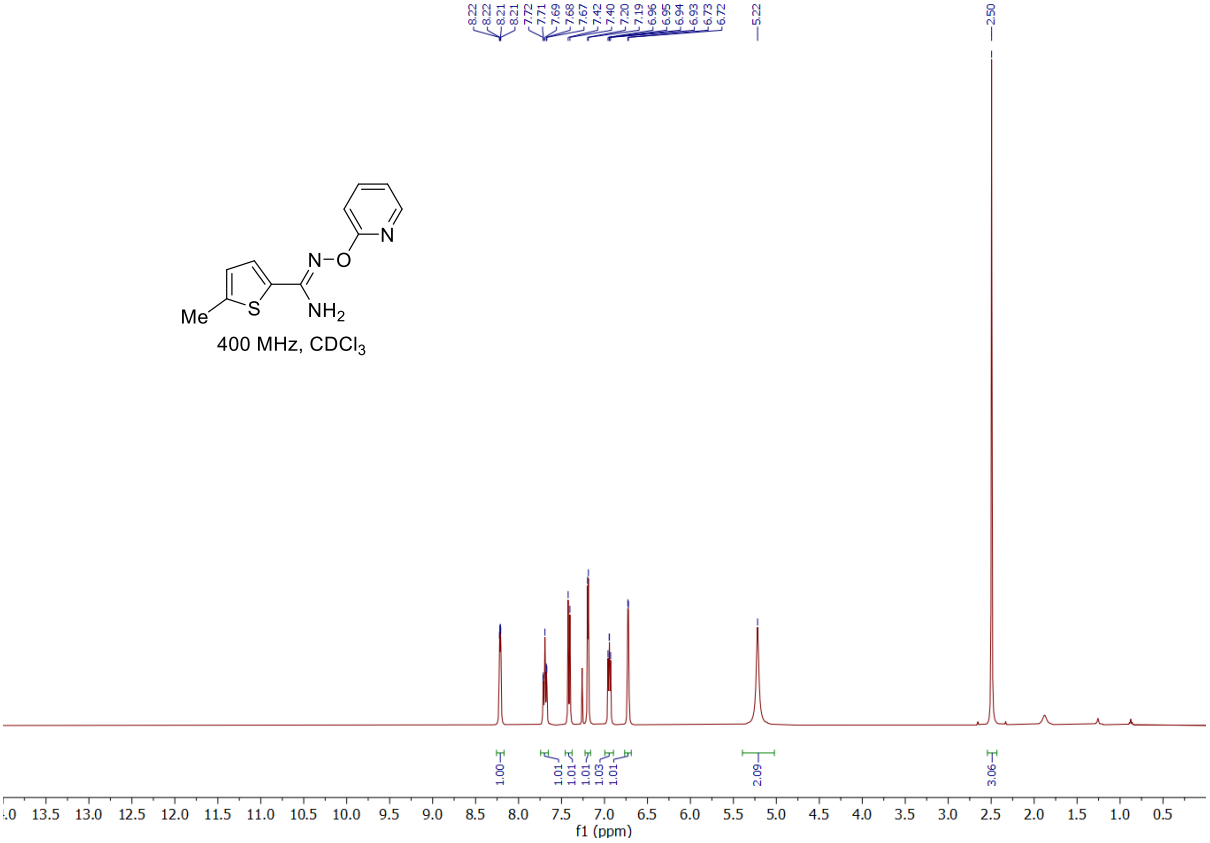
^{1}H and $^{13}C\{^{1}H\}$ spectra of 3-chloro-*N*'-(pyridin-2-yloxy)benzimidamide **3m**

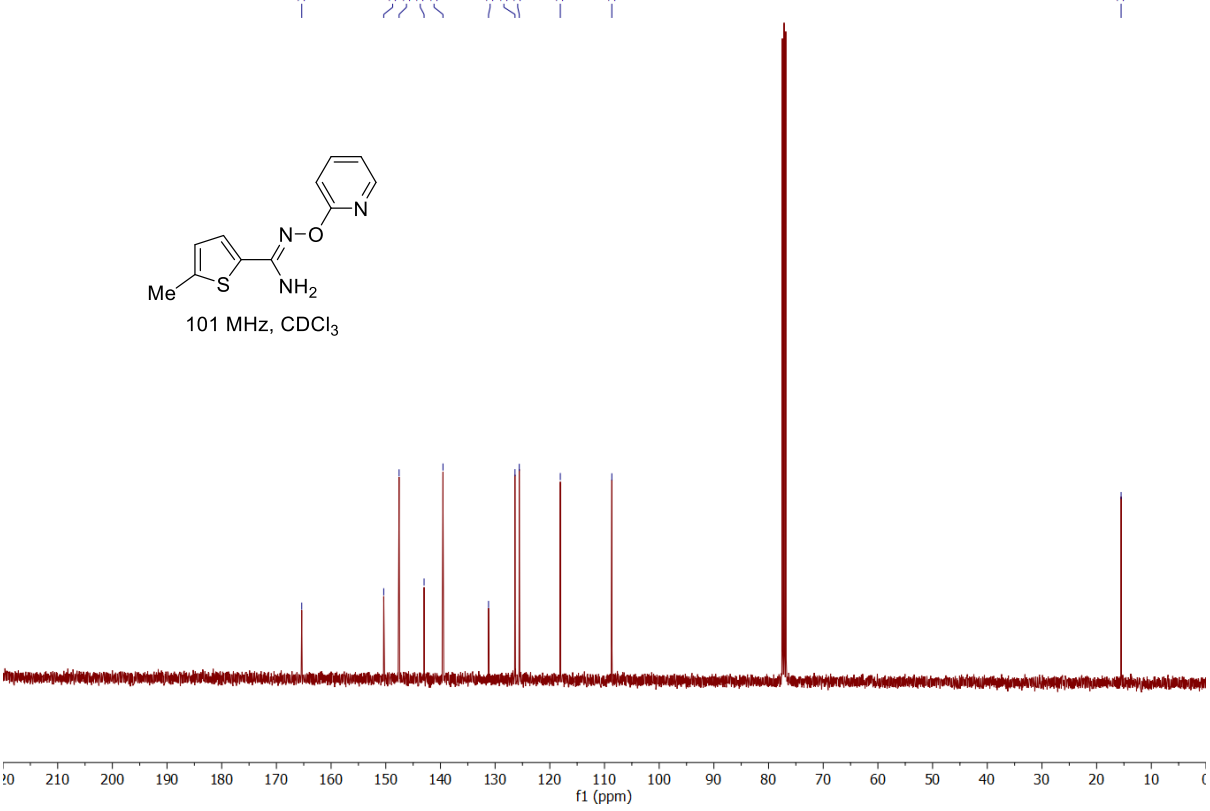




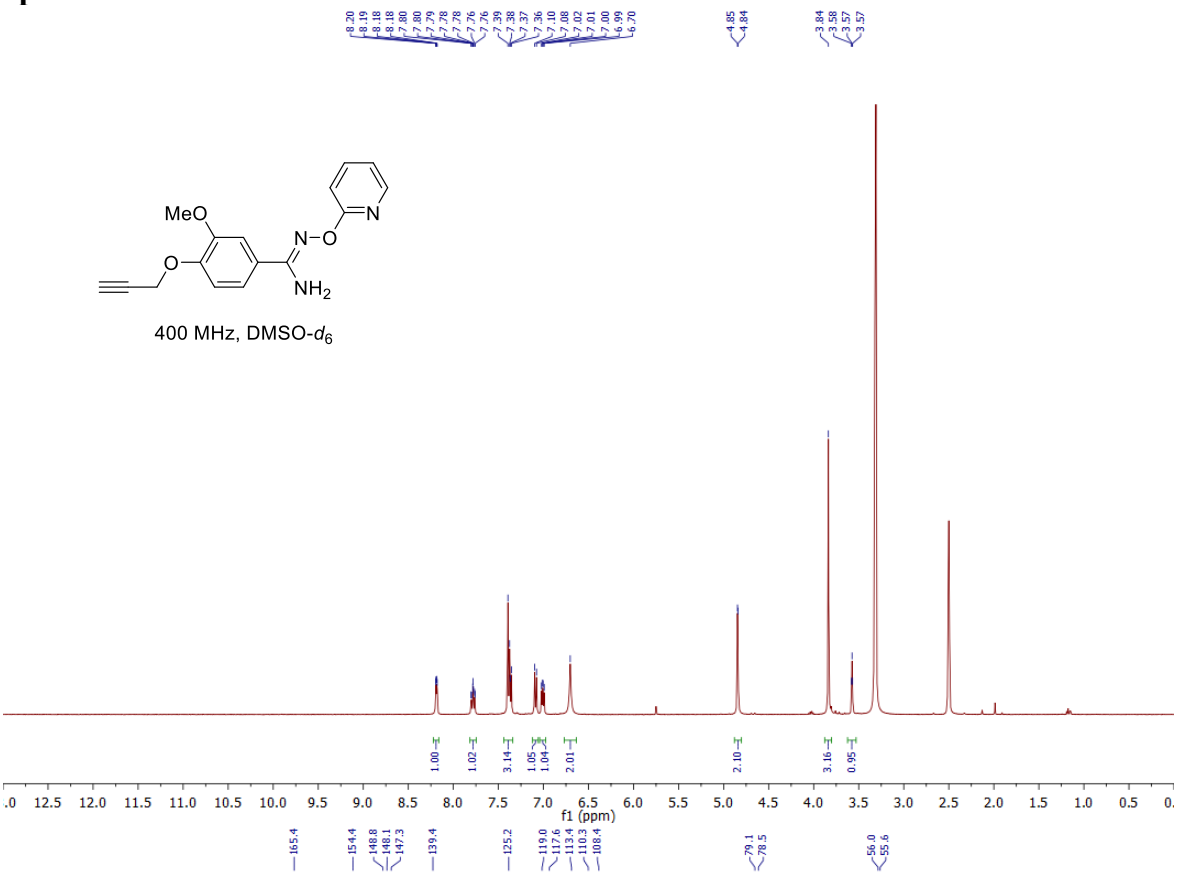


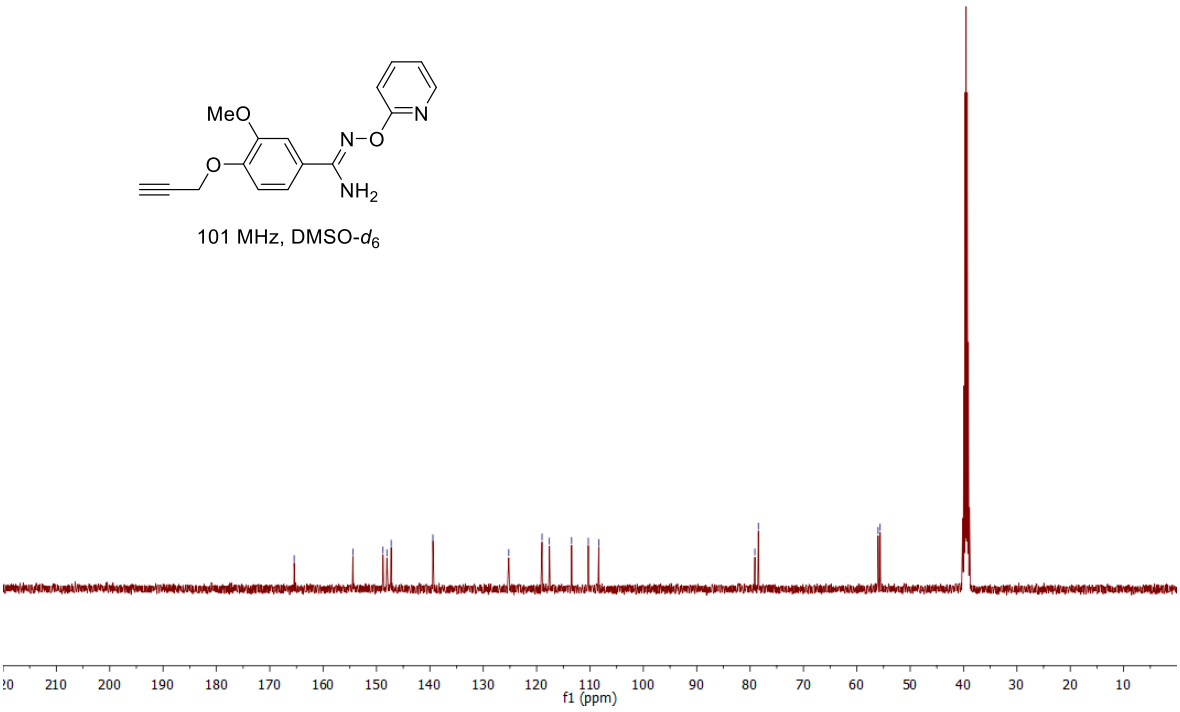
^{1}H and ^{13}C{^{1}H} spectra of 5-methyl-*N*'-(pyridin-2-yloxy)thiophene-2-carboximidamide **3o**



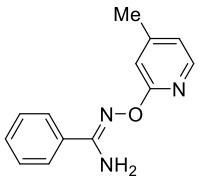


^{1}H and ^{13}C{^{1}H} spectra of 3-methoxy-4-(prop-2-yn-1-yloxy)-*N*'-(pyridin-2-yloxy)benzimidamide **3p**

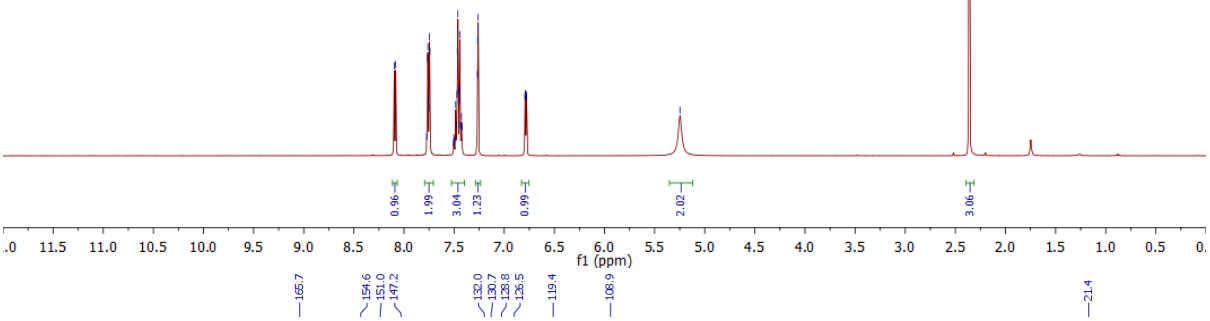


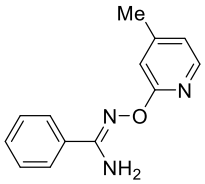


^{1}H and $^{13}C\{^{1}H\}$ spectra of *N*'-((4-methylpyridin-2-yl)oxy)benzimidamide **3q**

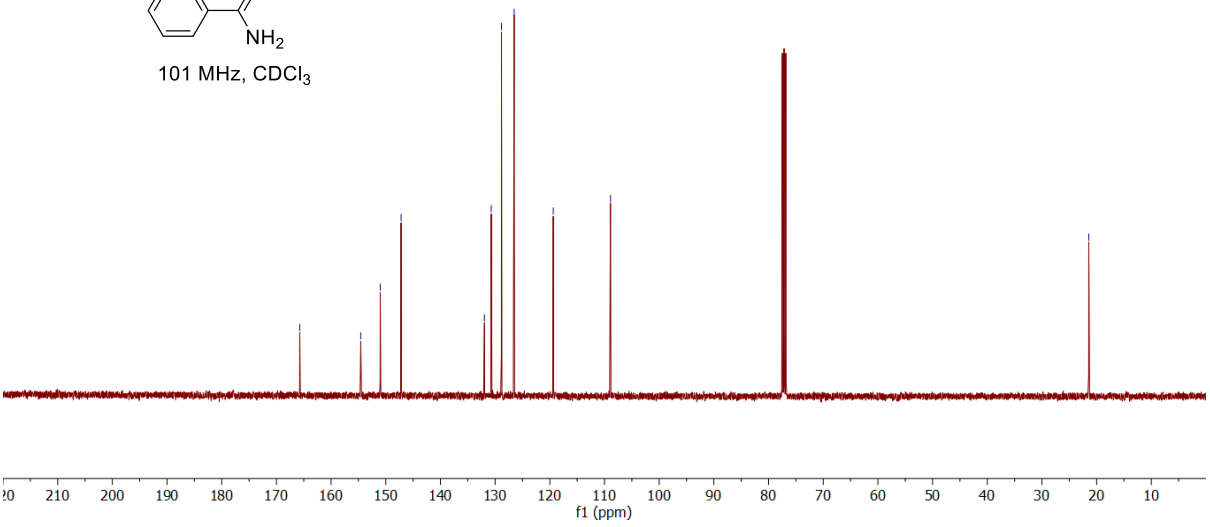


400 MHz, $CDCl_3$

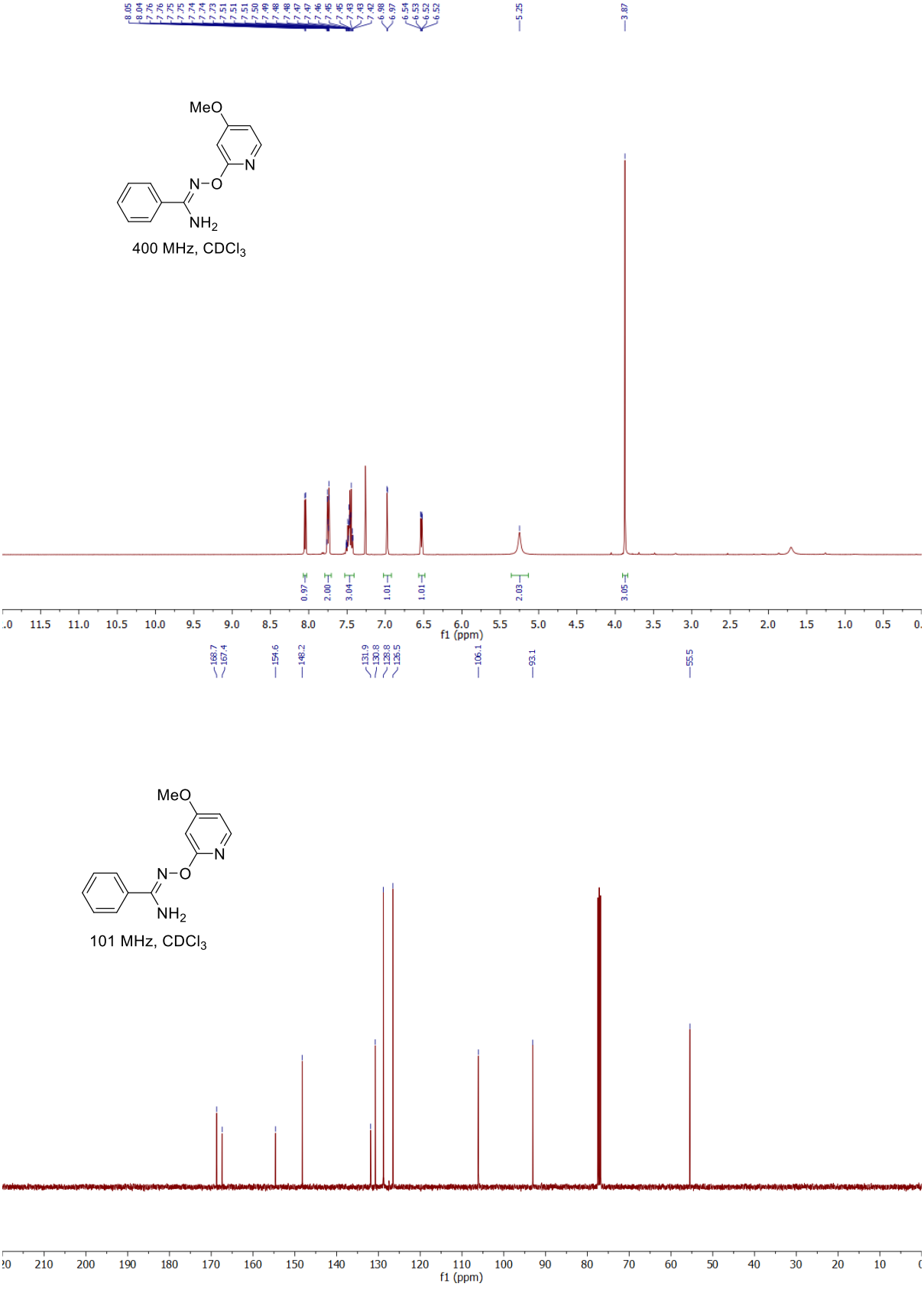




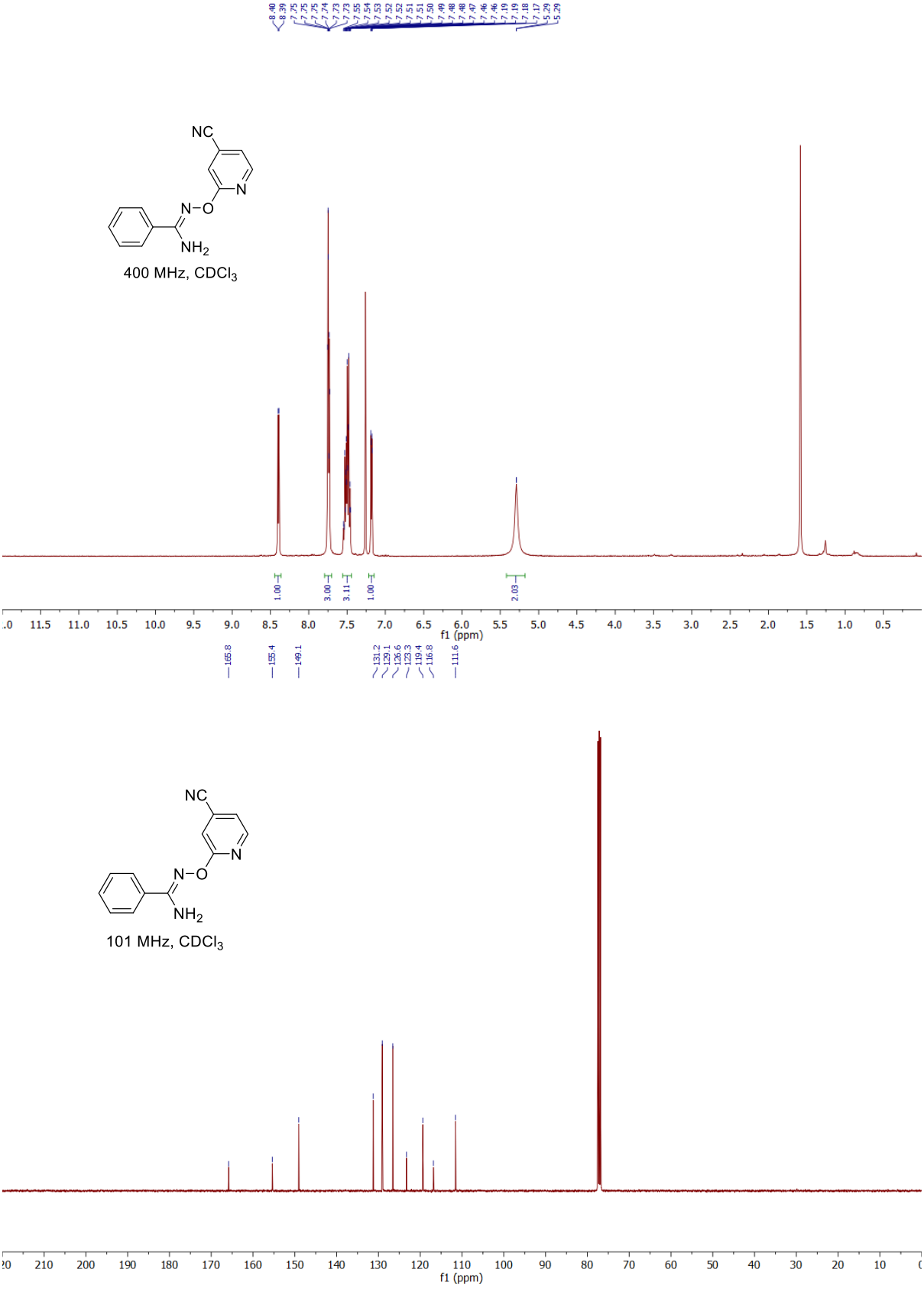
101 MHz, $CDCl_3$



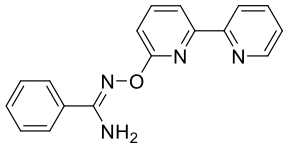
^{1}H and $^{13}C\{^{1}H\}$ spectra of *N'*-((4-methoxypyridin-2-yl)oxy)benzimidamide **3r**



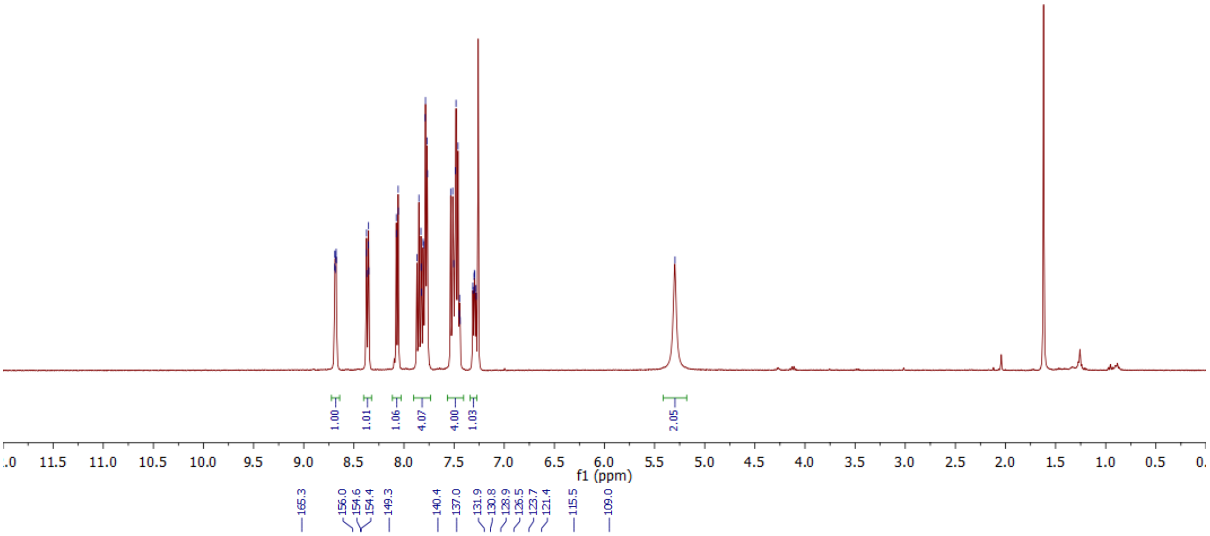
^{1}H and $^{13}C\{^{1}H\}$ spectra of *N*′-((4-cyanopyridin-2-yl)oxy)benzimidamide **3s**

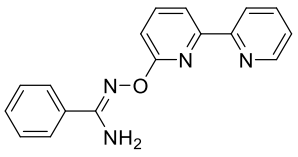


^{1}H and $^{13}C\{^{1}H\}$ spectra of *N'*-([2,2'-bipyridin]-6-yloxy)benzimidamide **3u**

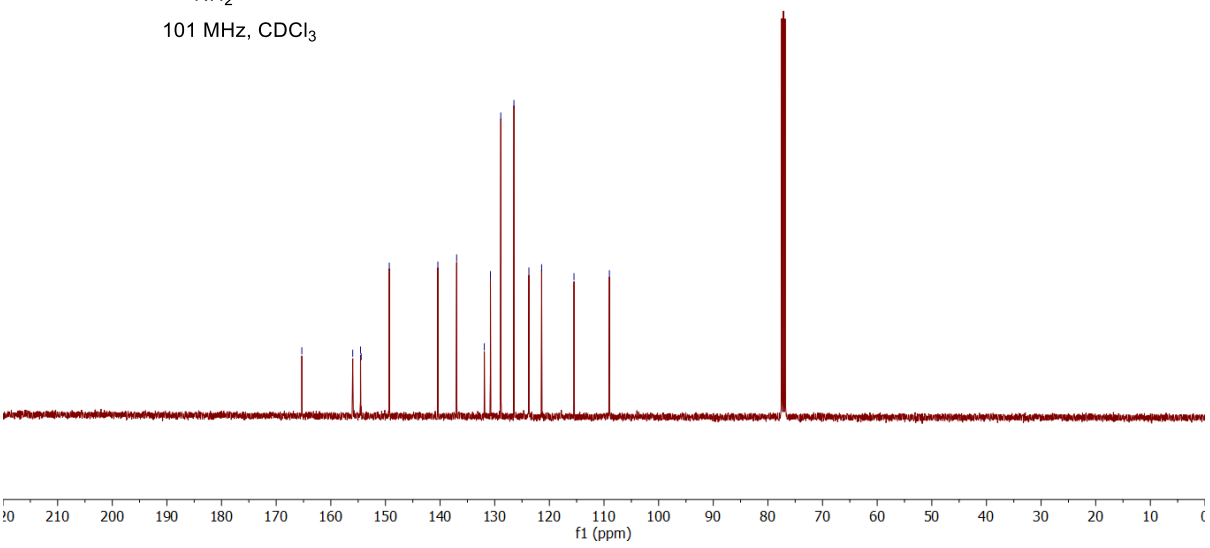


400 MHz, $CDCl_3$

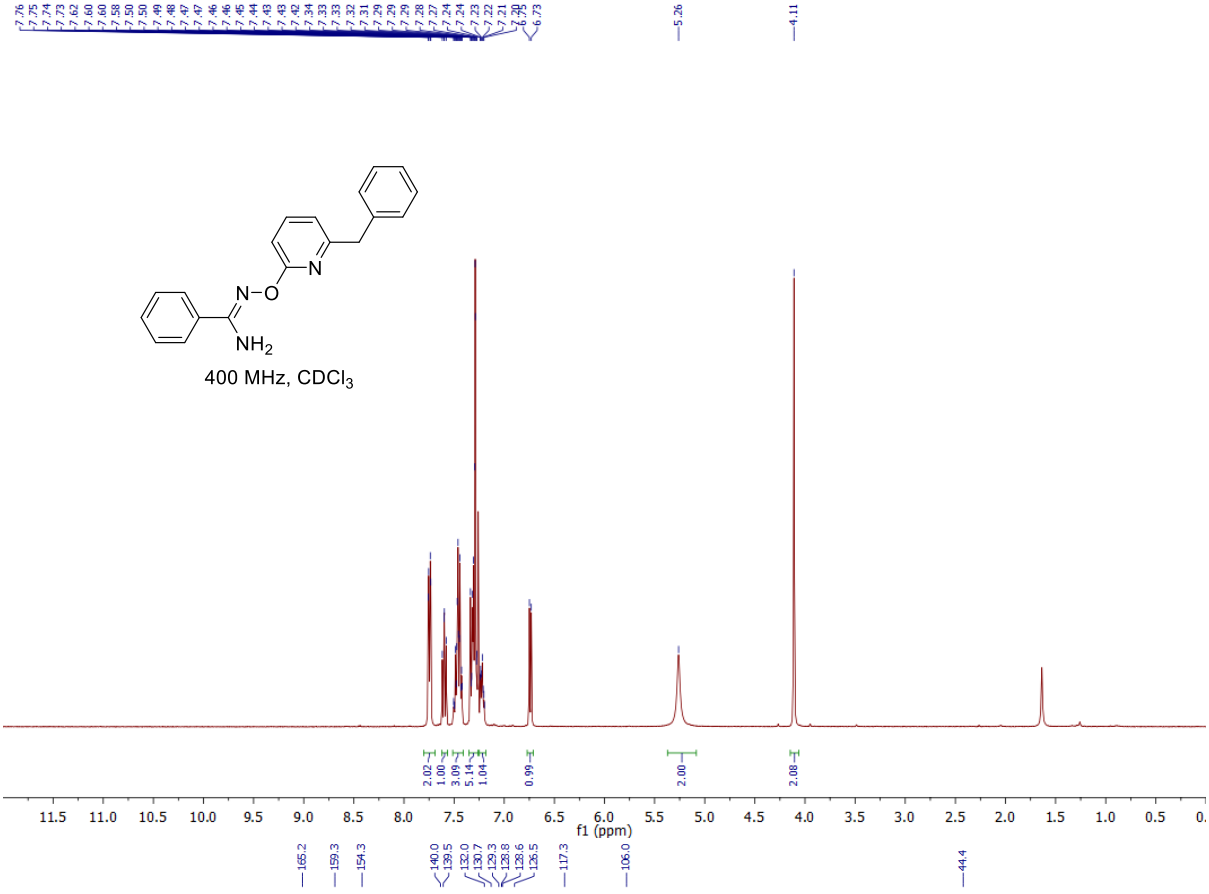


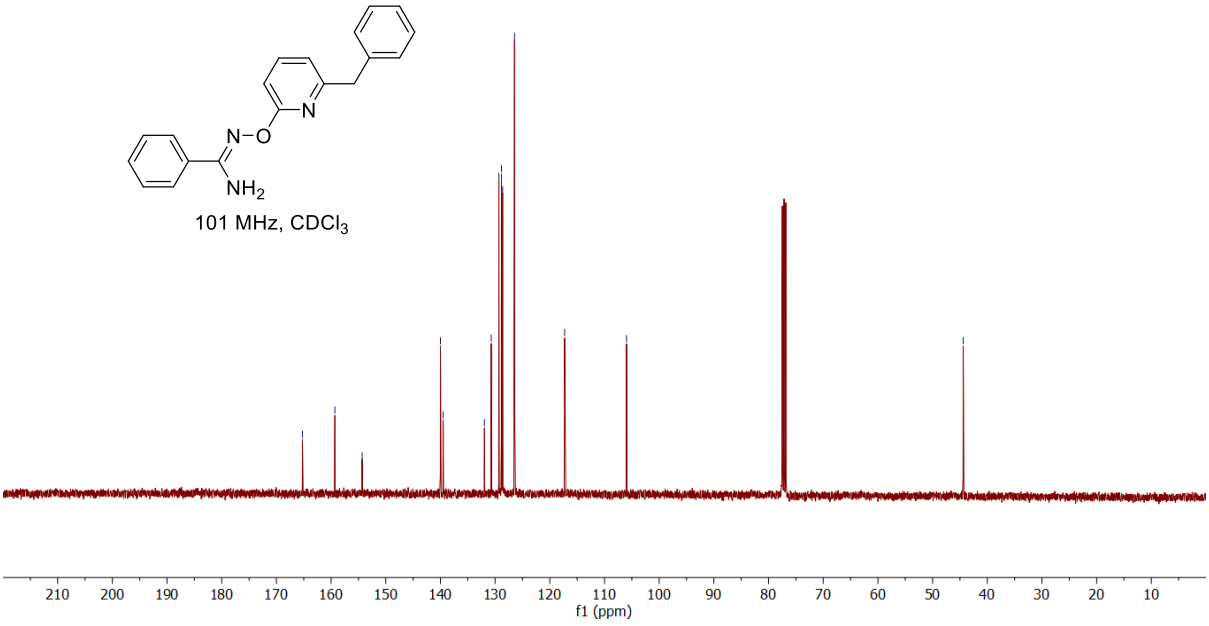


101 MHz, $CDCl_3$

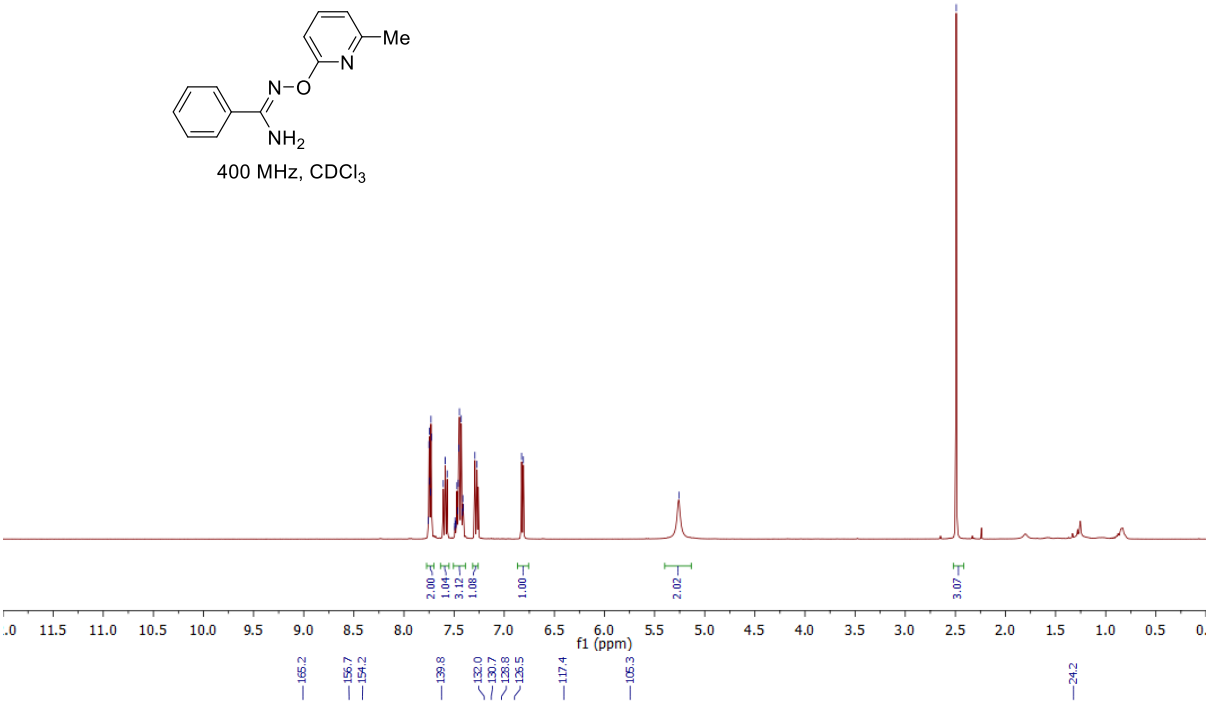


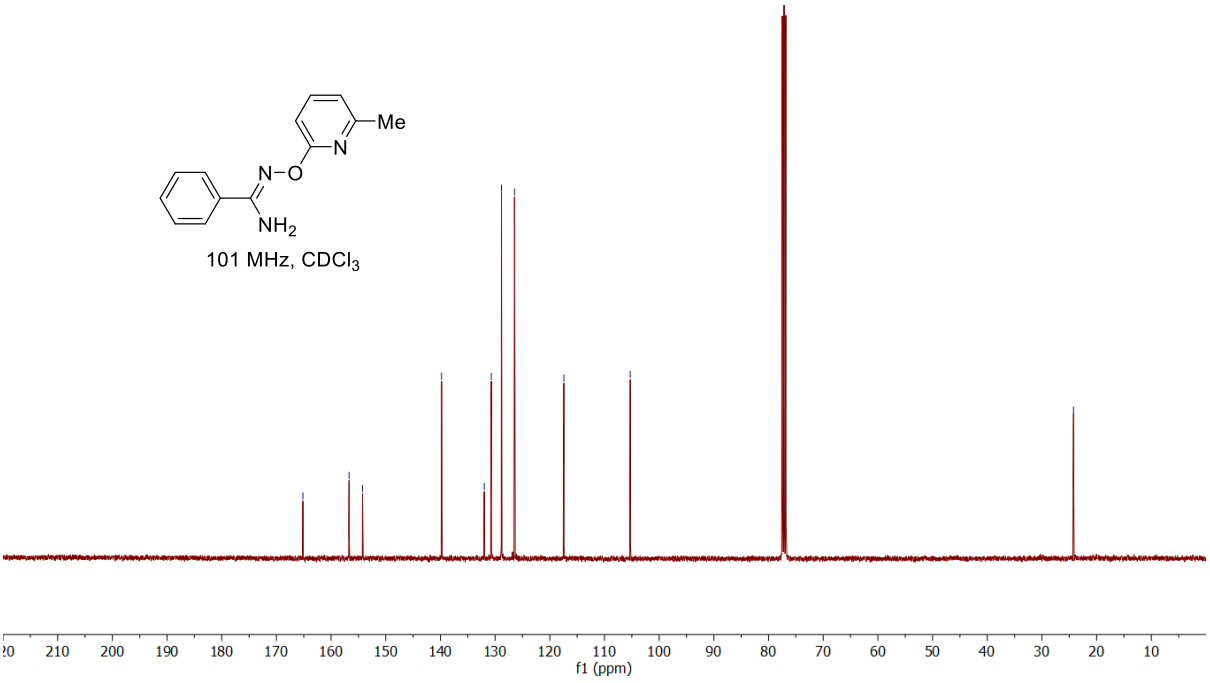
^{1}H and $^{13}C\{^{1}H\}$ spectra of *N*′-((6-benzylpyridin-2-yl)oxy)benzimidamide **3v**



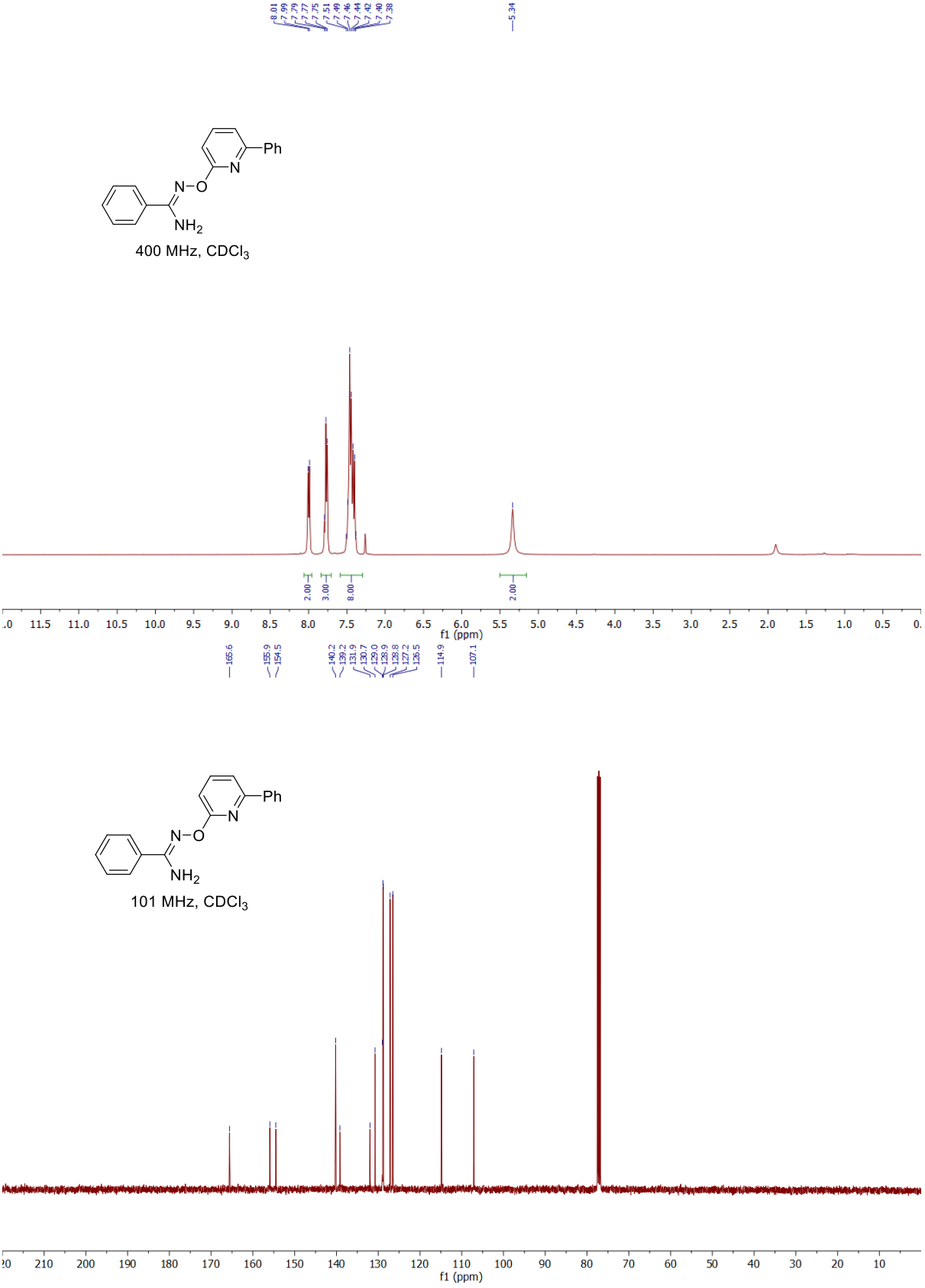


^{1}H and $^{13}C\{^{1}H\}$ spectra of *N'*-((6-methylpyridin-2-yl)oxy)benzimidamide **3w**

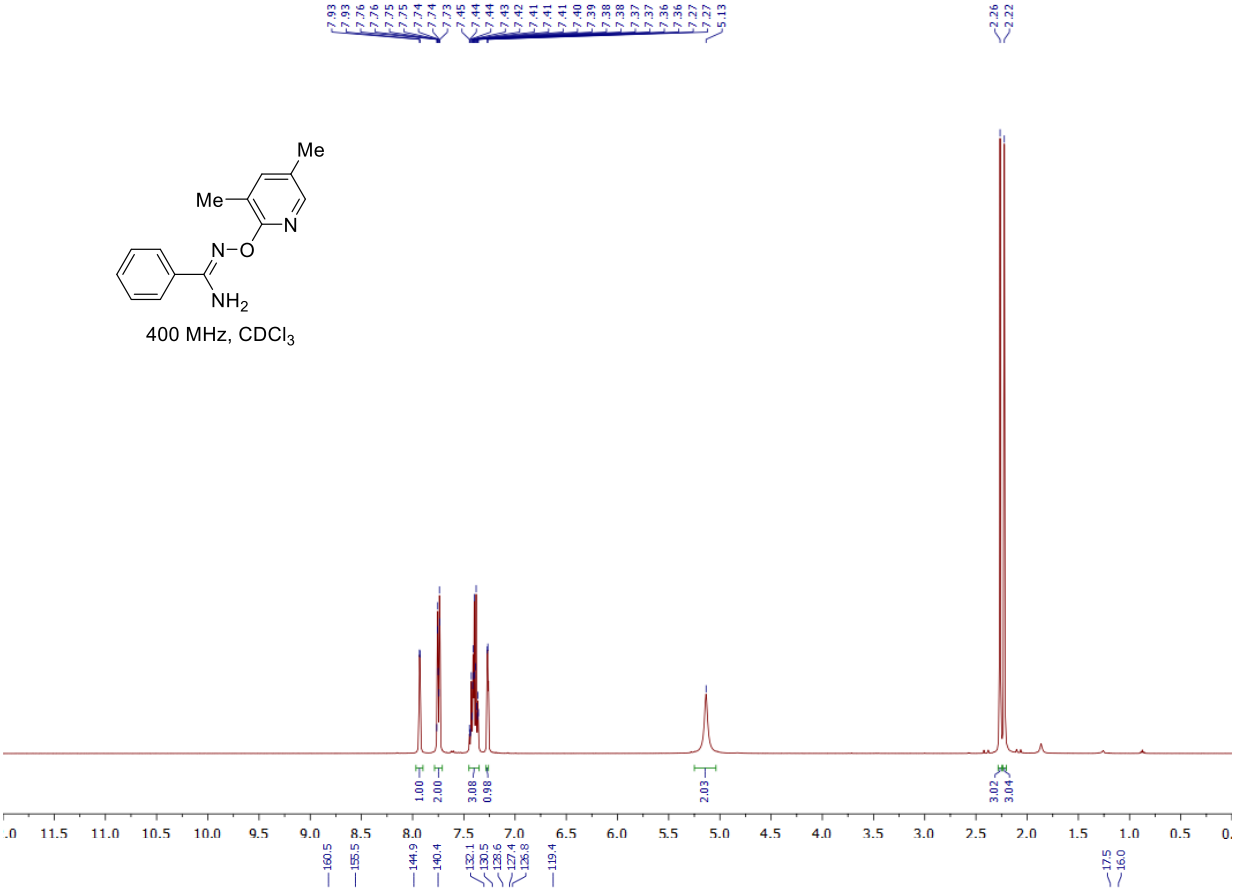


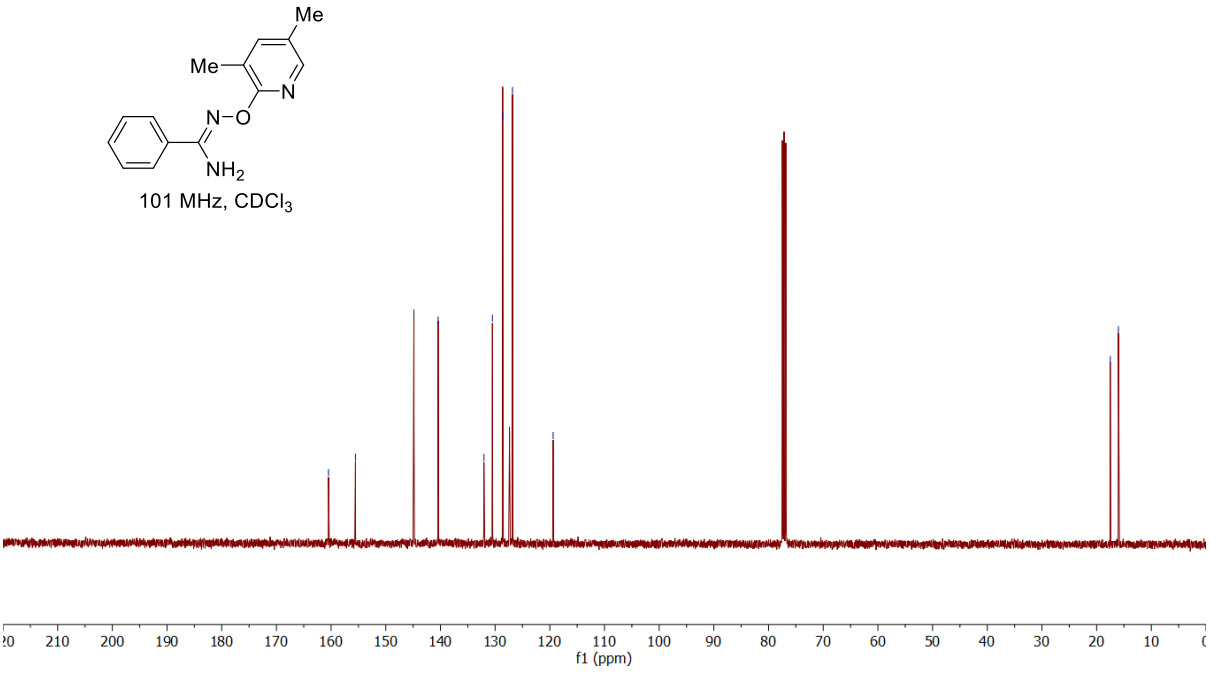


^{1}H and $^{13}C\{^{1}H\}$ spectra of *N'*-((6-phenylpyridin-2-yl)oxy)benzimidamide **3x**

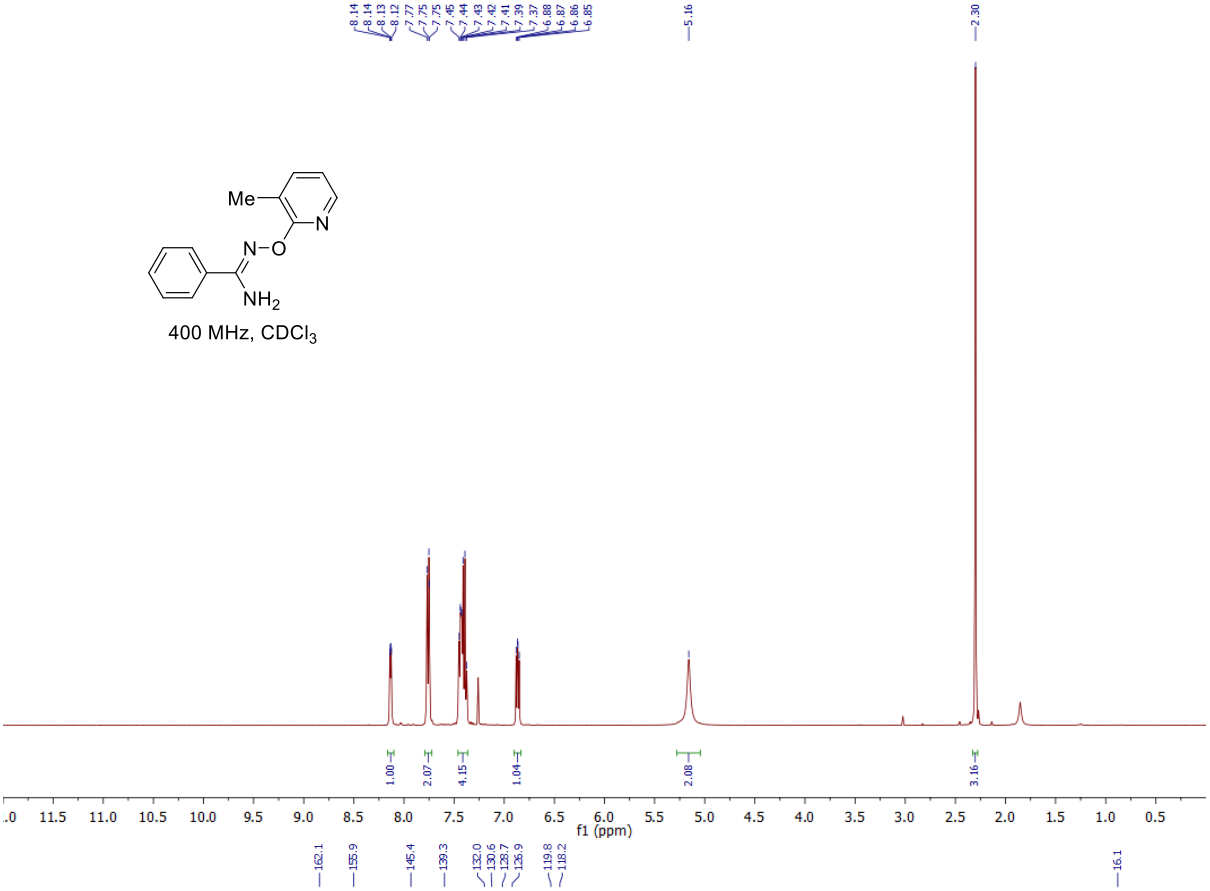


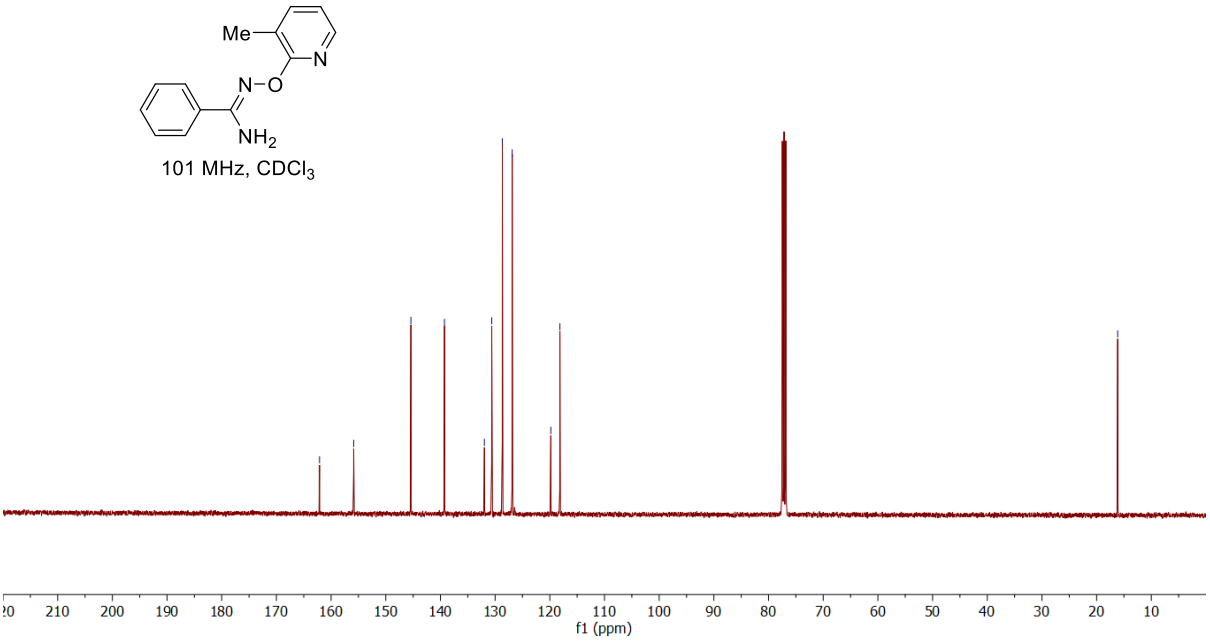
^{1}H and $^{13}C\{^{1}H\}$ spectra of *N*′-((3,5-dimethylpyridin-2-yl)oxy)benzimidamide **3y**



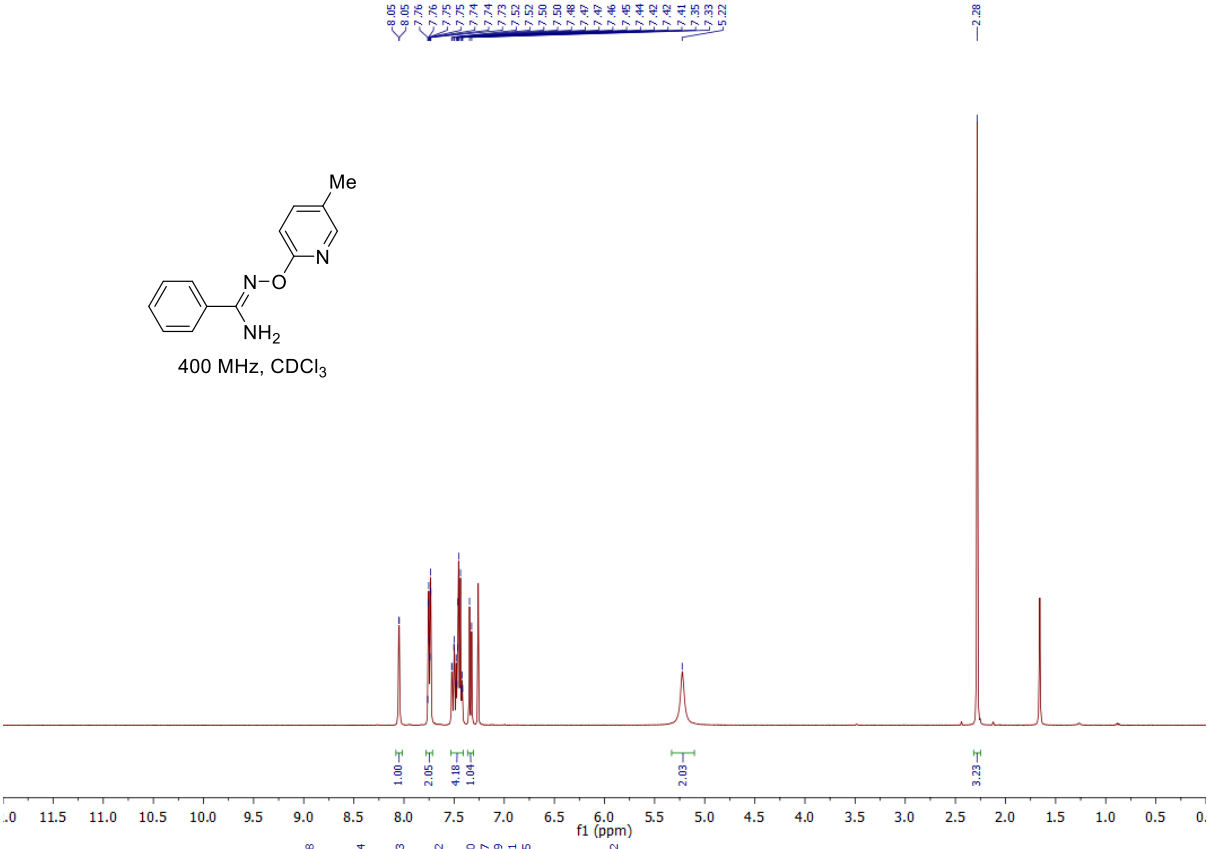


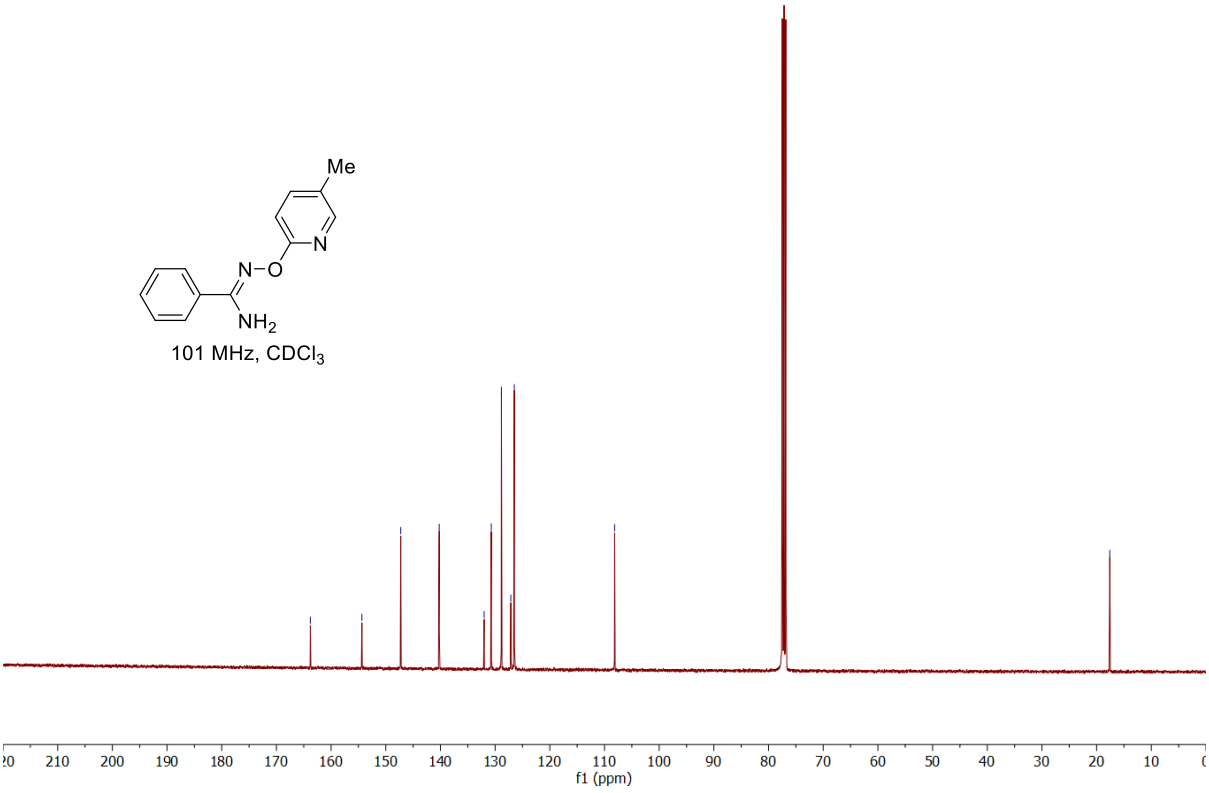
^{1}H and $^{13}C\{^{1}H\}$ spectra of *N*′-((3-methylpyridin-2-yl)oxy)benzimidamide **3z**

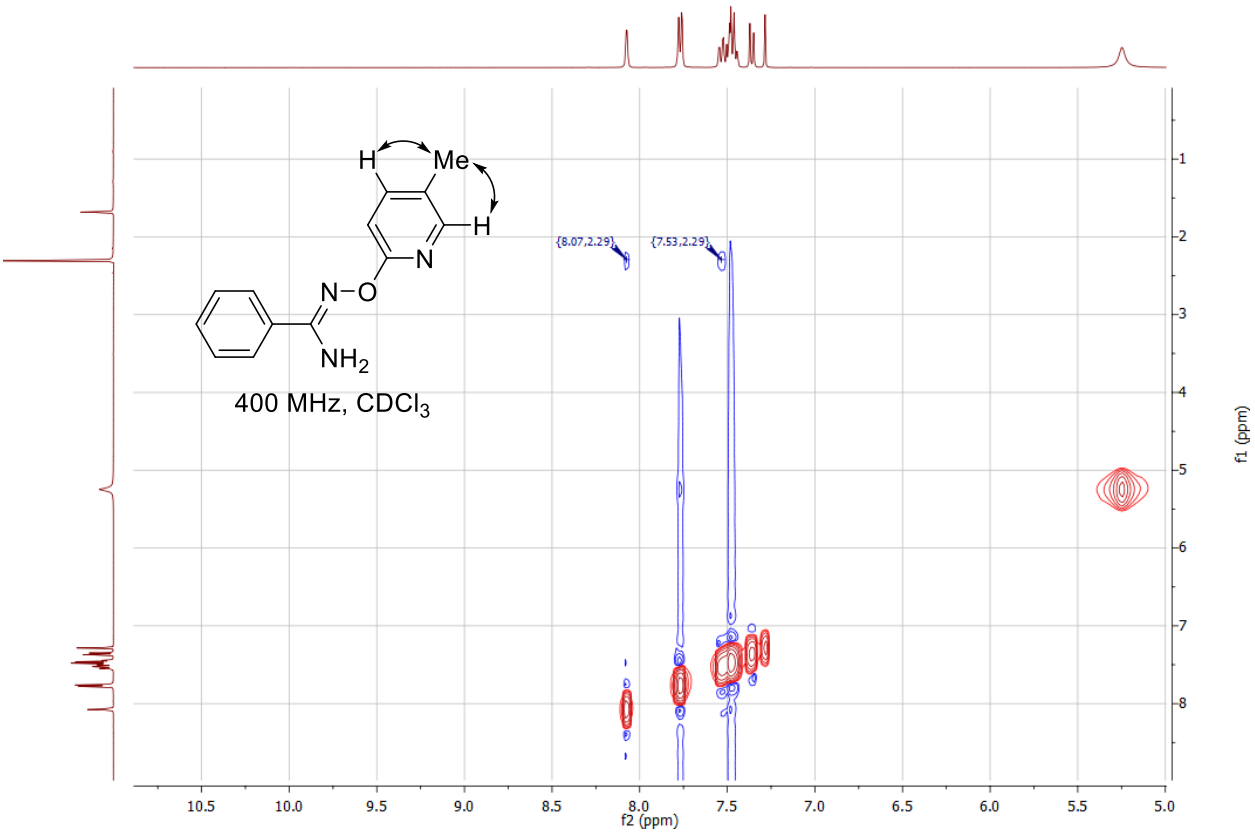




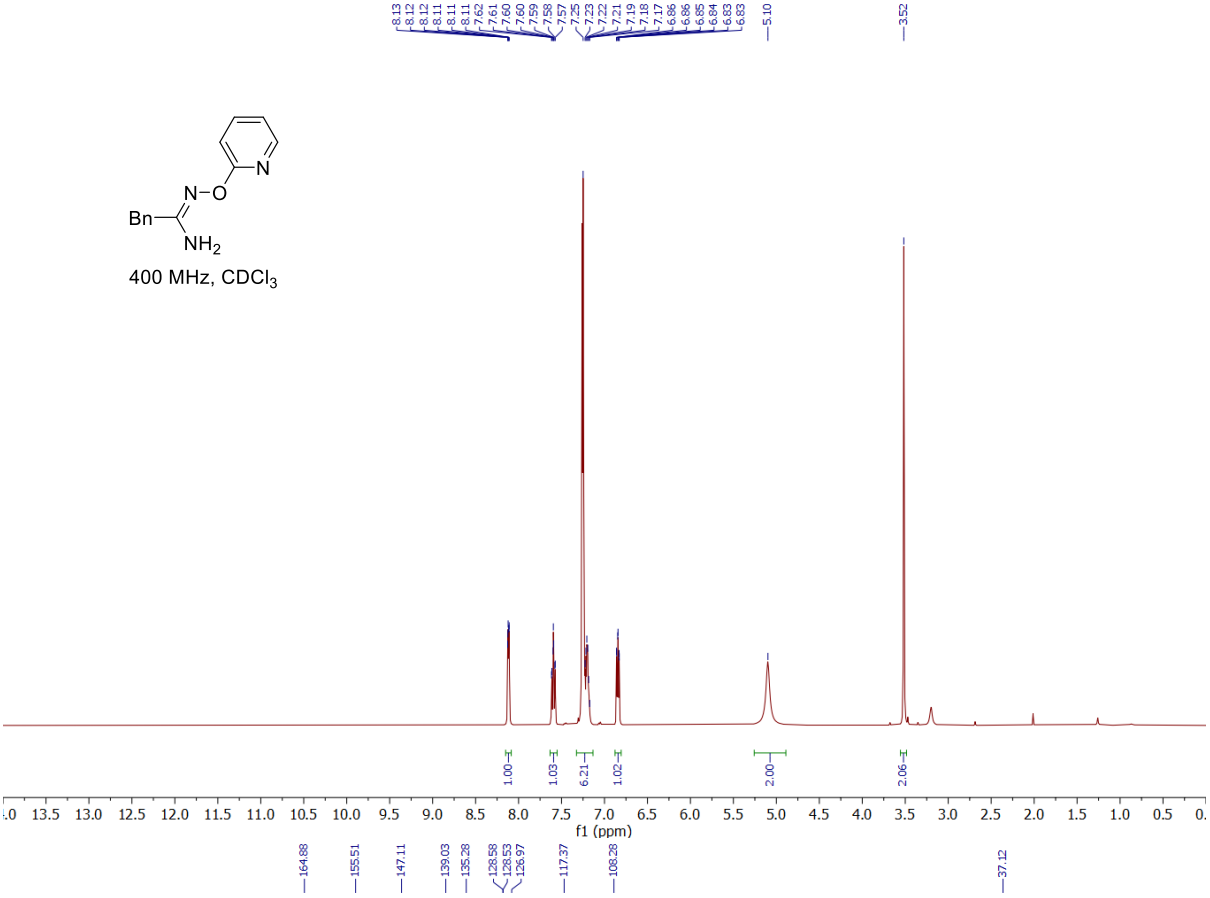
^{1}H, ^{13}C{^{1}H} and ^{1}H-^{1}H NOESY spectra of *N'*-((5-methylpyridin-2-yl)oxy)benzimidamide **3aa**

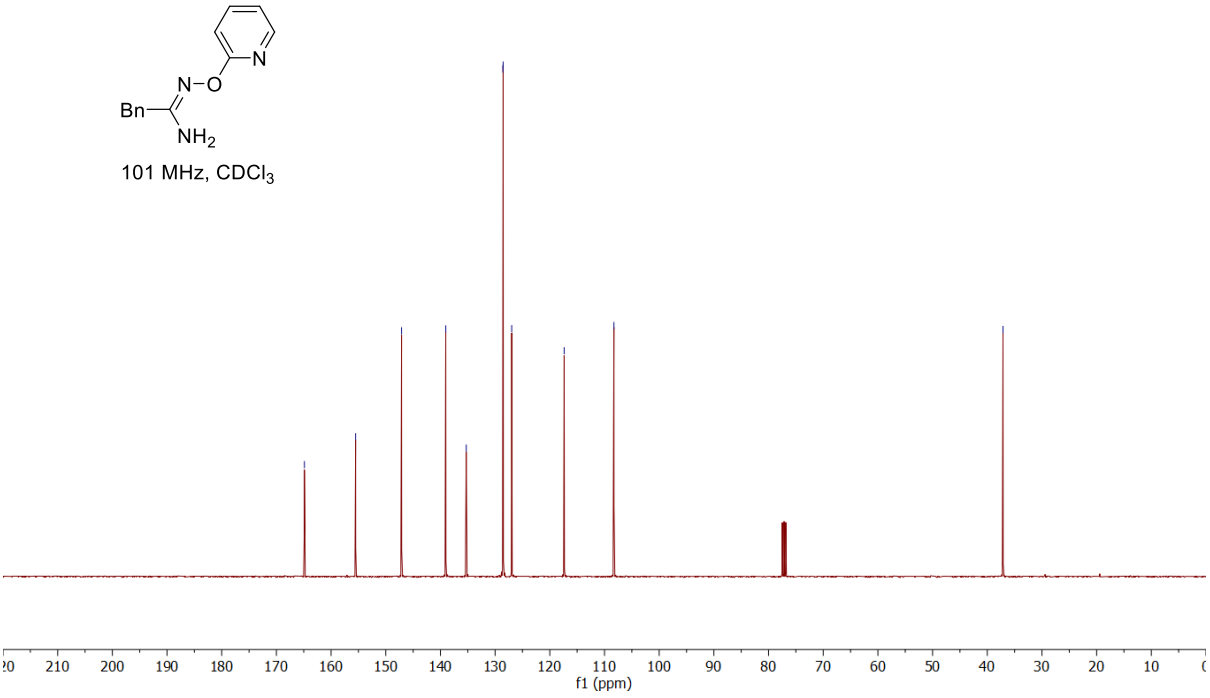




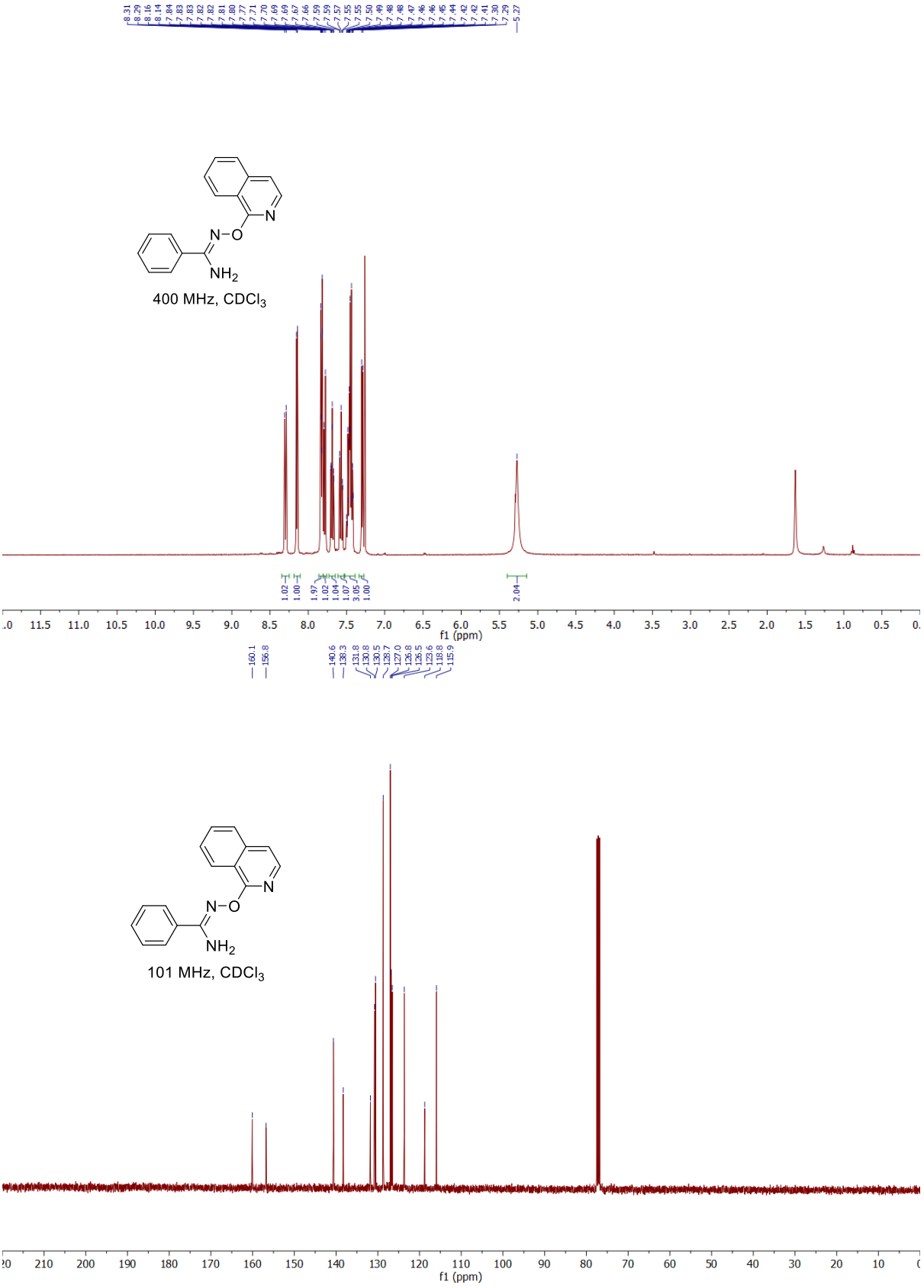

H
Me
H
N
N–O
NH2
400 MHz, CDCl3
{8.07,2.29}
{7.53,2.29}
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
f2 (ppm)
1
2
3
4
5
6
7
8
f1 (ppm)

^{1}H and $^{13}C\{^{1}H\}$ spectra of 2-phenyl-*N*'-(pyridin-2-yloxy)acetimidamide **3ad**

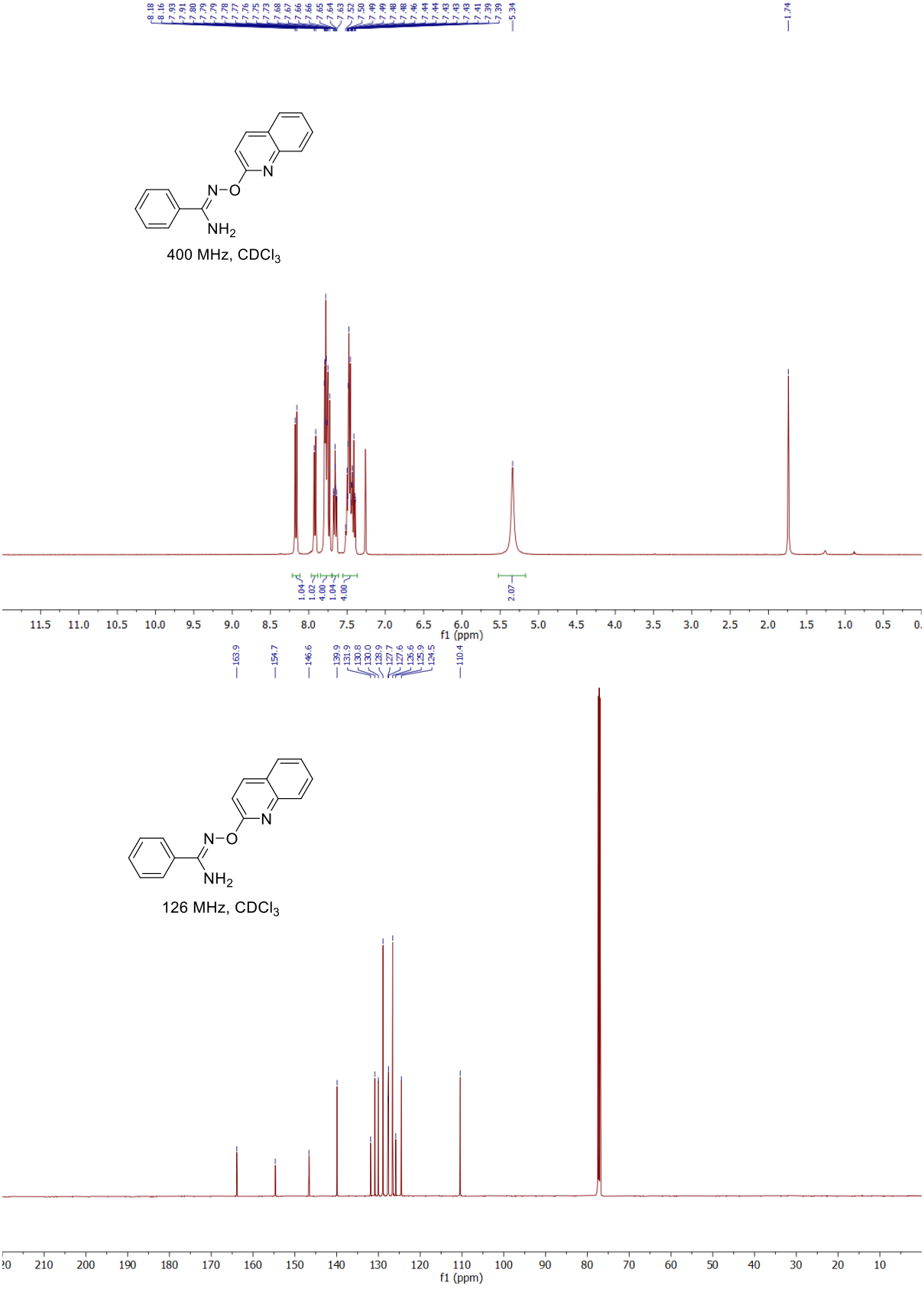




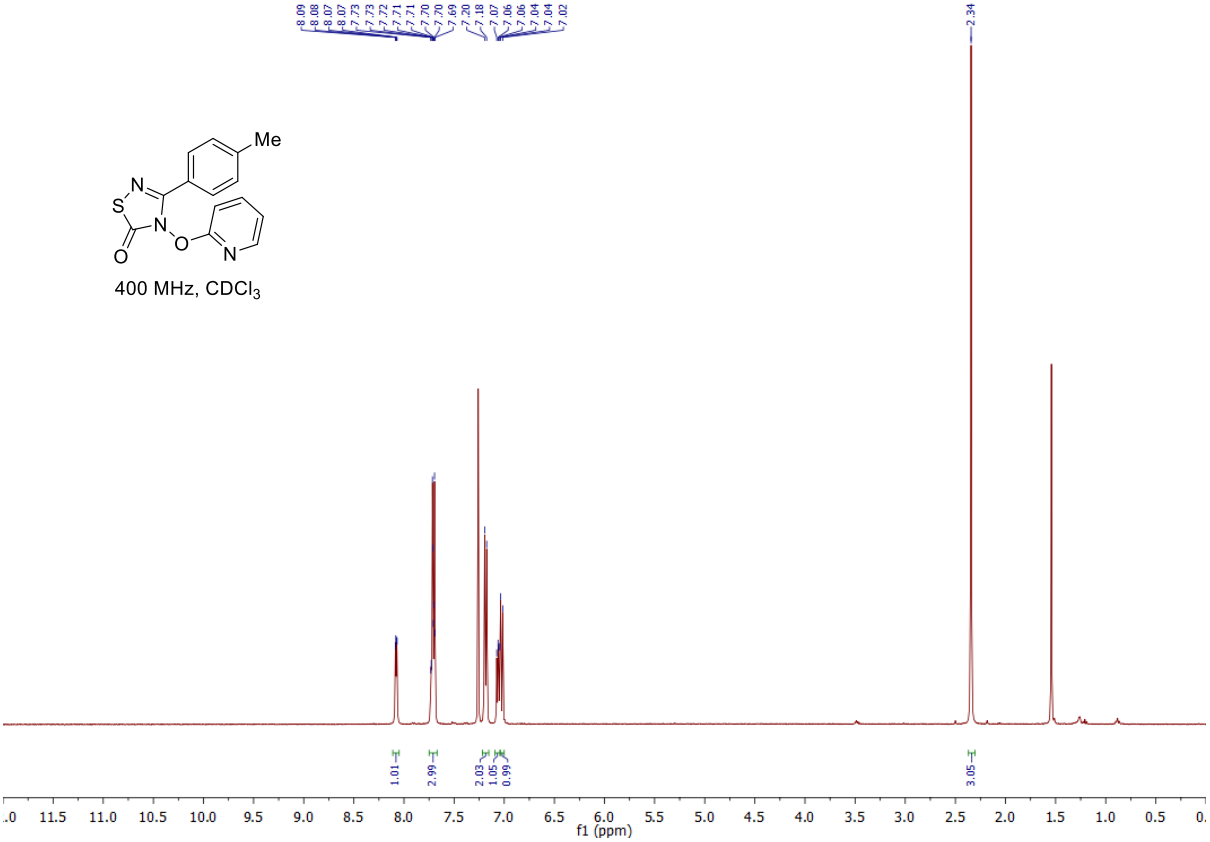
^{1}H and $^{13}C\{^{1}H\}$ spectra of *N'*-(isoquinolin-1-yloxy)benzimidamide **3ae**

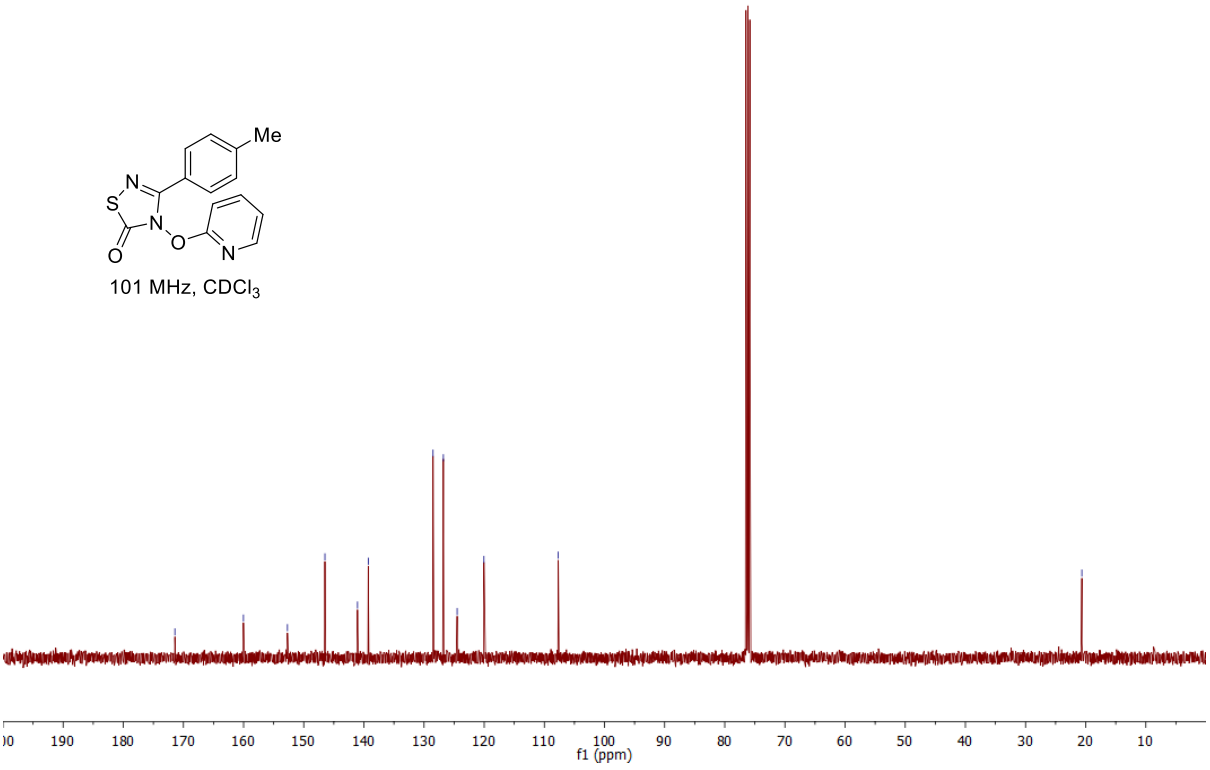


^{1}H and $^{13}C\{^{1}H\}$ spectra of *N'*-(quinolin-2-yloxy)benzimidamide **3af**

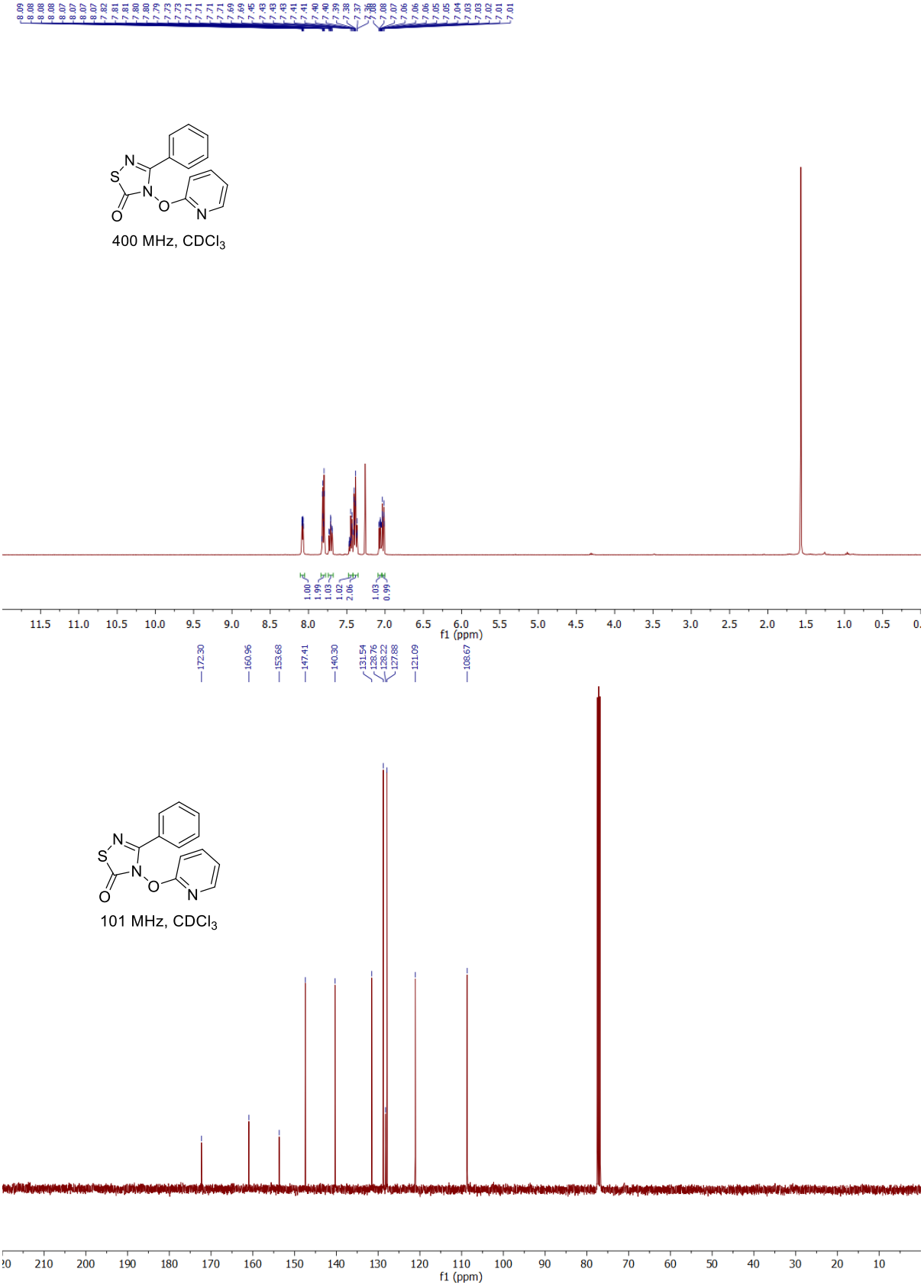


^{1}H and $^{13}C\{^{1}H\}$ spectra of 4-(pyridin-2-yloxy)-3-(p-tolyl)-1,2,4-thiadiazol-5(*4H*)-one **4a**

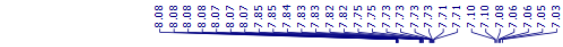


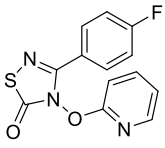


^{1}H and $^{13}C\{^{1}H\}$ spectra of 3-phenyl-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(*4H*)-one **4b**

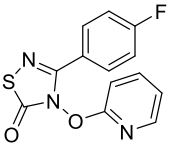


^{1}H, $^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ spectra of 3-(4-fluorophenyl)-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(4*H*)-one **4c**

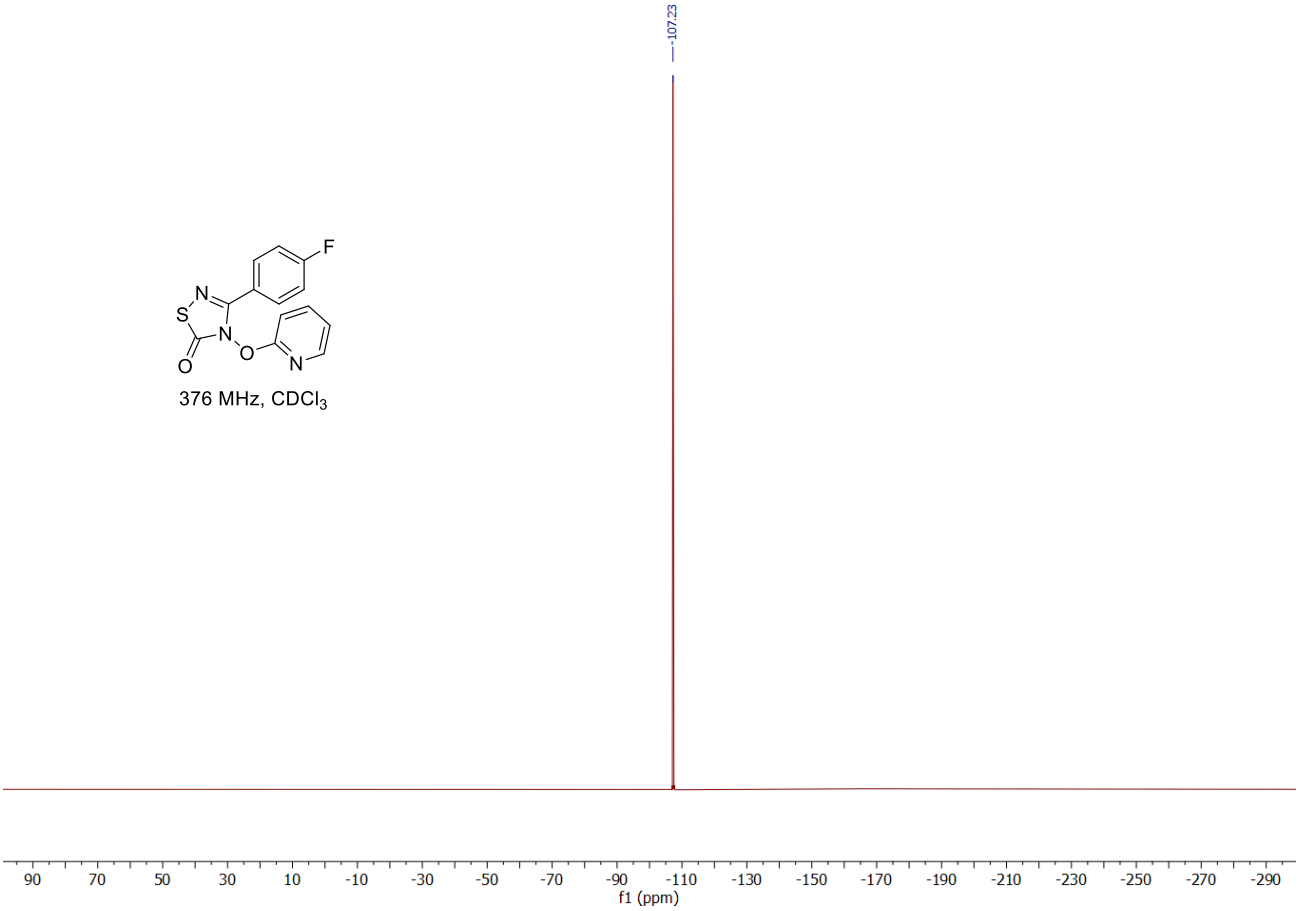




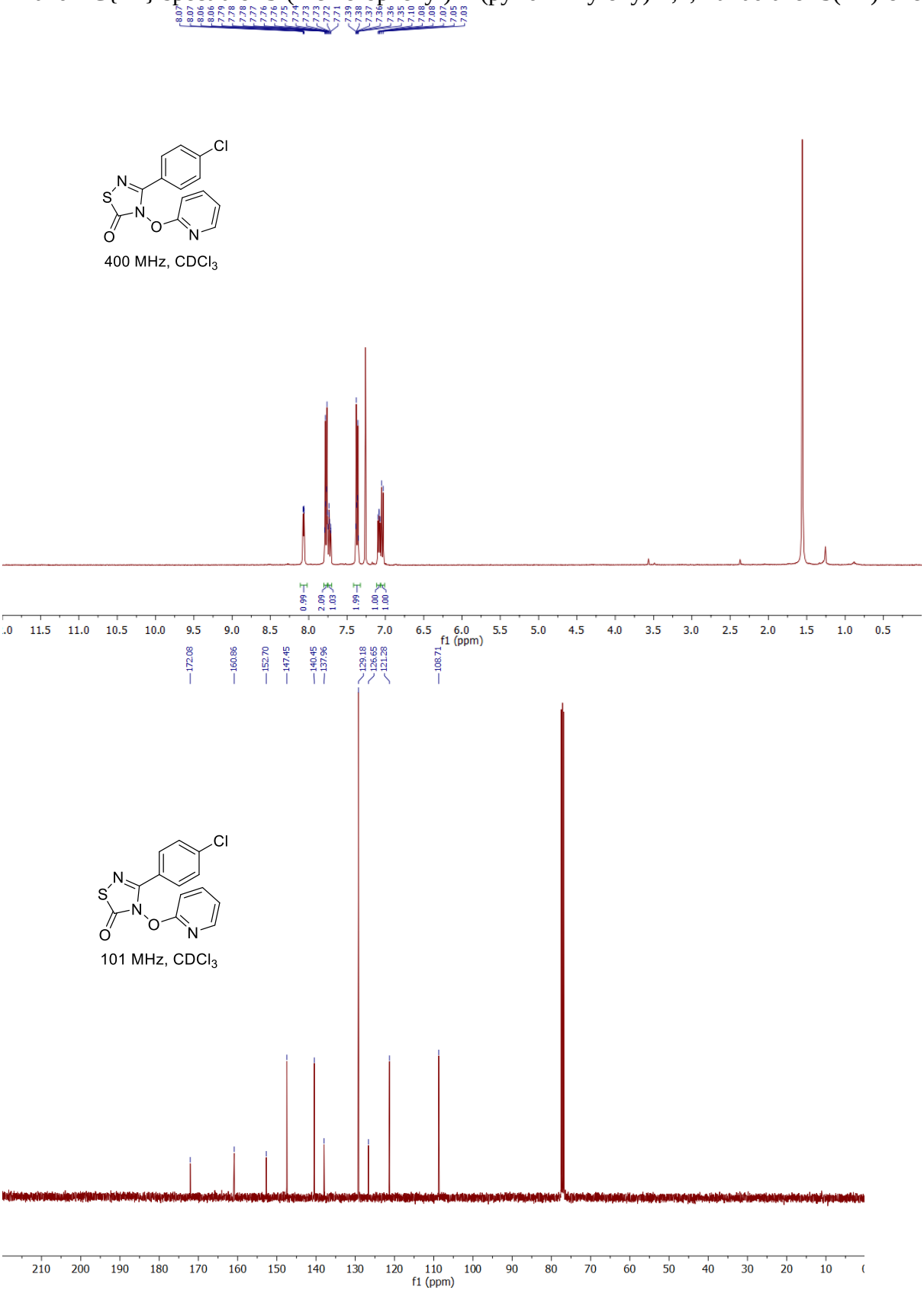
400 MHz, $CDCl_3$



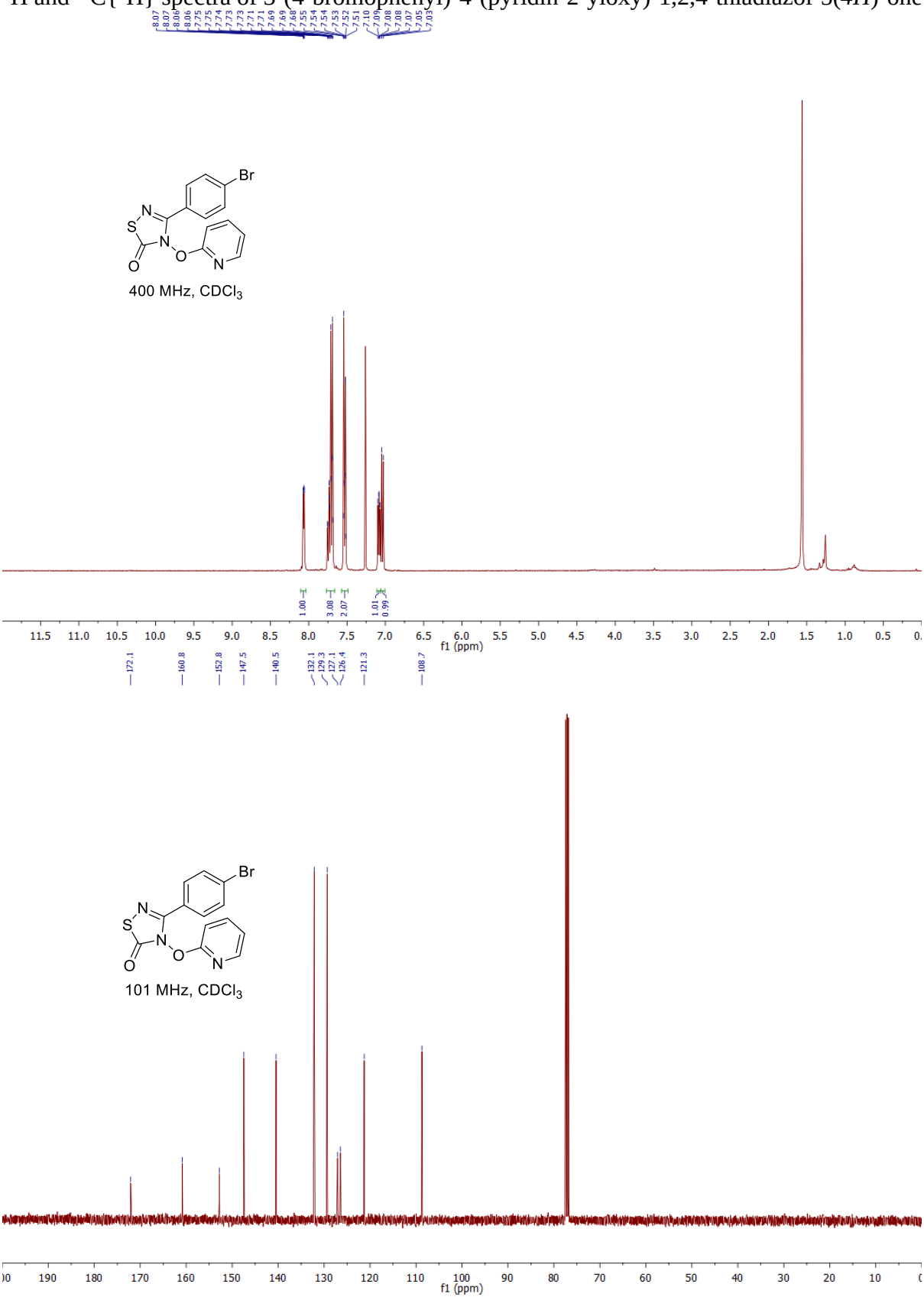
101 MHz, $CDCl_3$


-107.23
F
S
N
N
O
O
N
376 MHz, CDCl3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

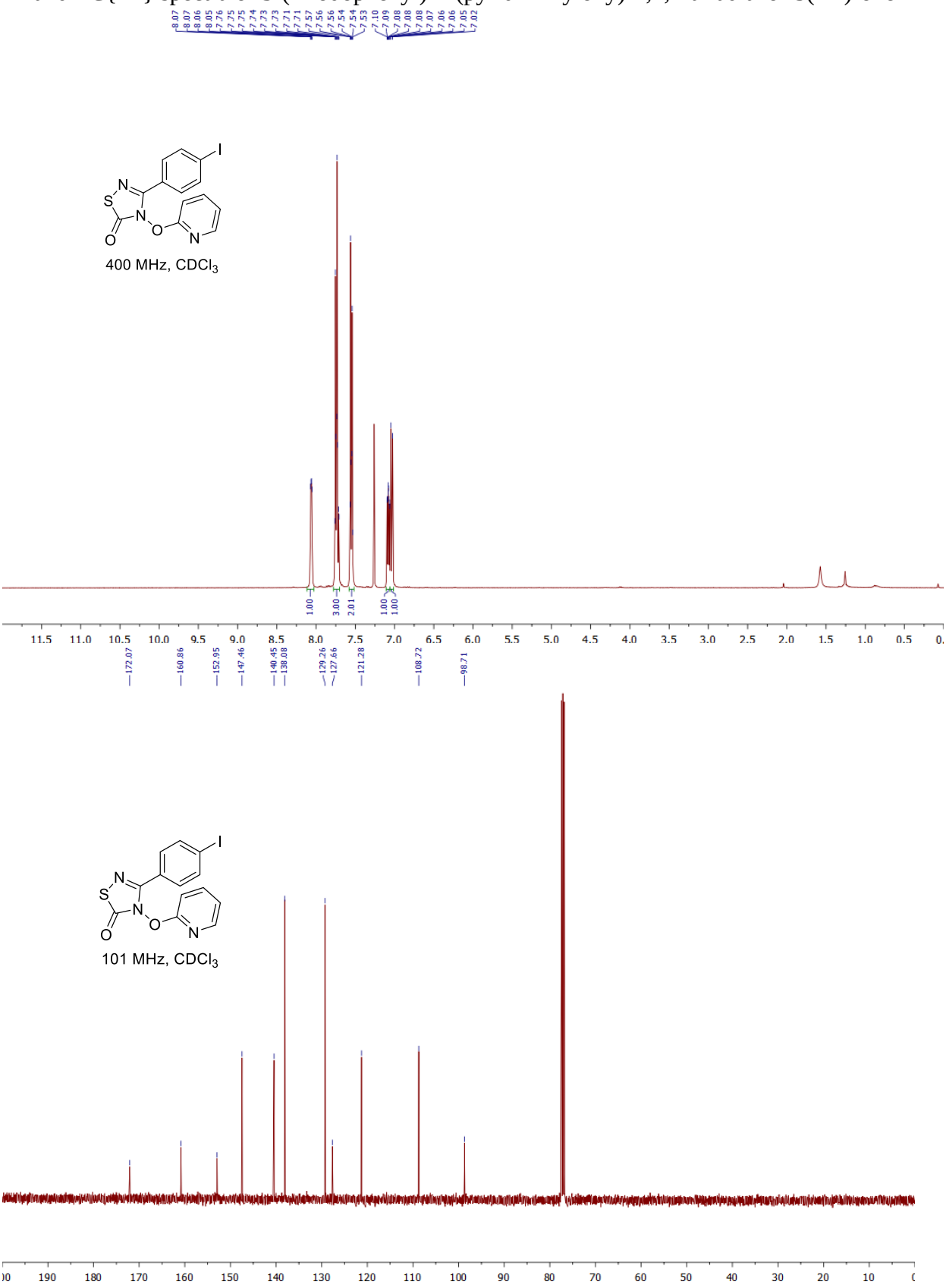
^{1}H and ^{13}C{^{1}H} spectra of 3-(4-chlorophenyl)-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(*4H*)-one **4d**



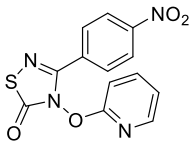
^{1}H and $^{13}C\{^{1}H\}$ spectra of 3-(4-bromophenyl)-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(*4H*)-one **4e**



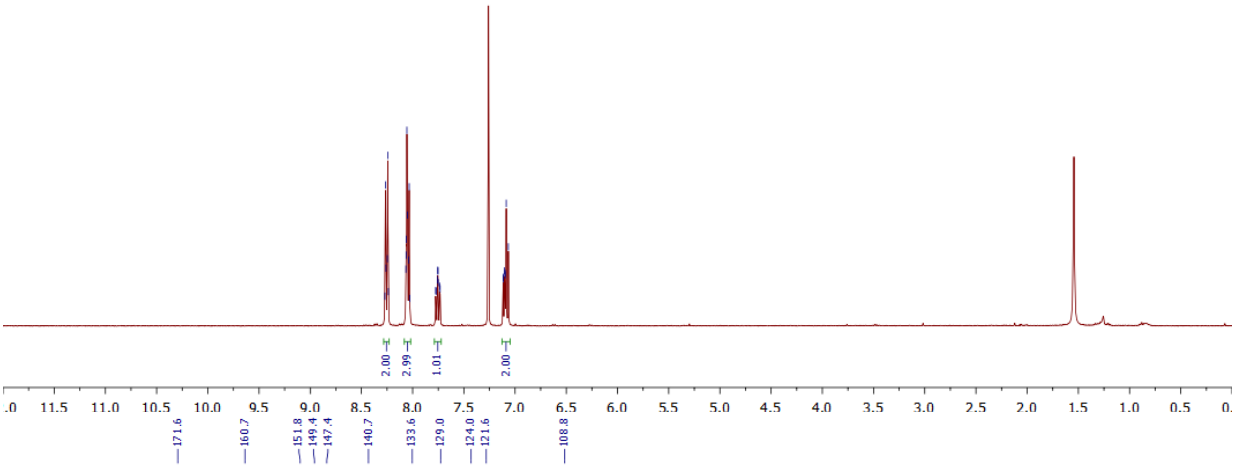
^{1}H and $^{13}C\{^{1}H\}$ spectra of 3-(4-iodophenyl)-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(4*H*)-one **4f**

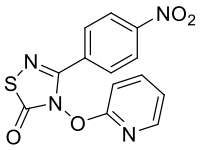


^{1}H and $^{13}C\{^{1}H\}$ spectra of 3-(4-nitrophenyl)-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(*4H*)-one **4g**



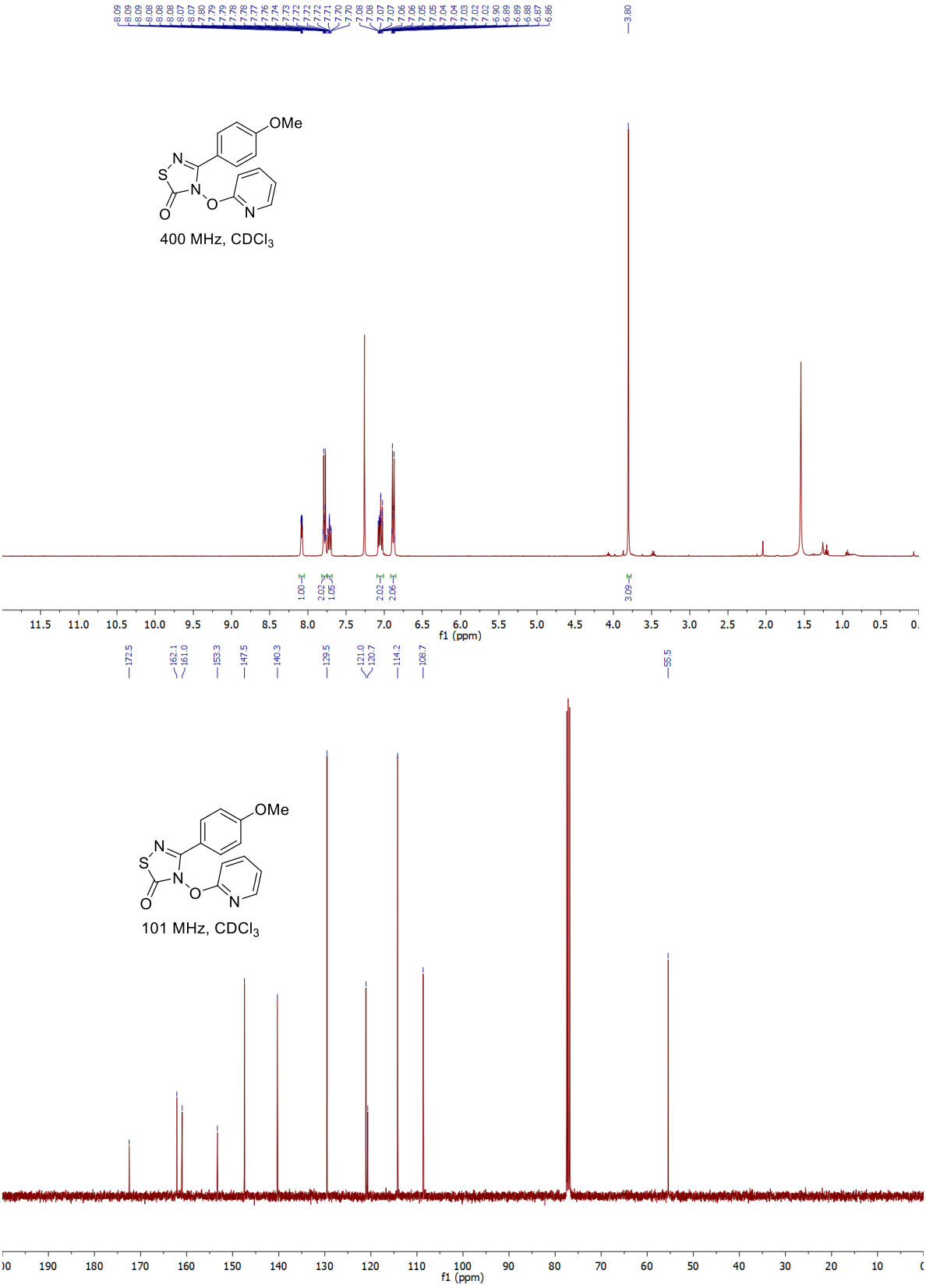
400 MHz, $CDCl_3$



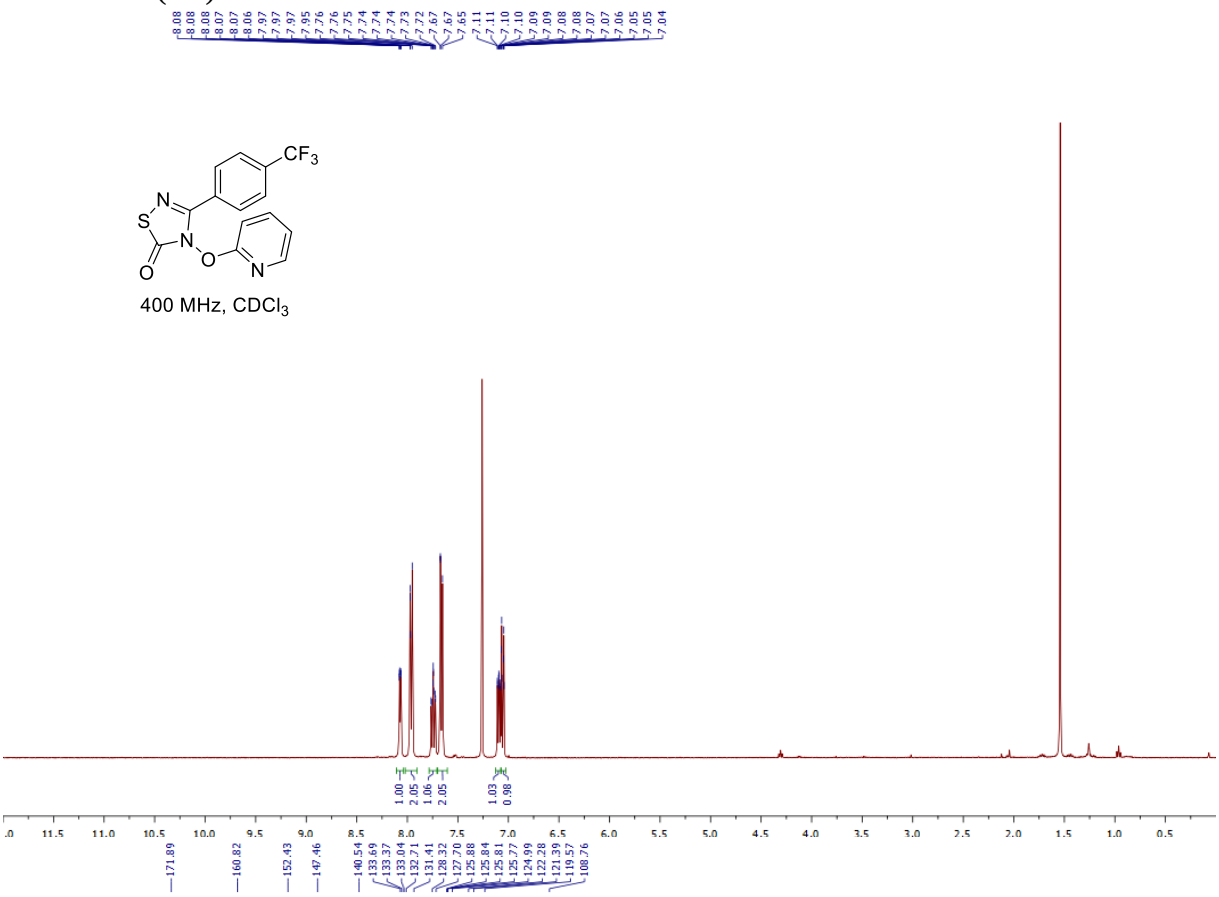


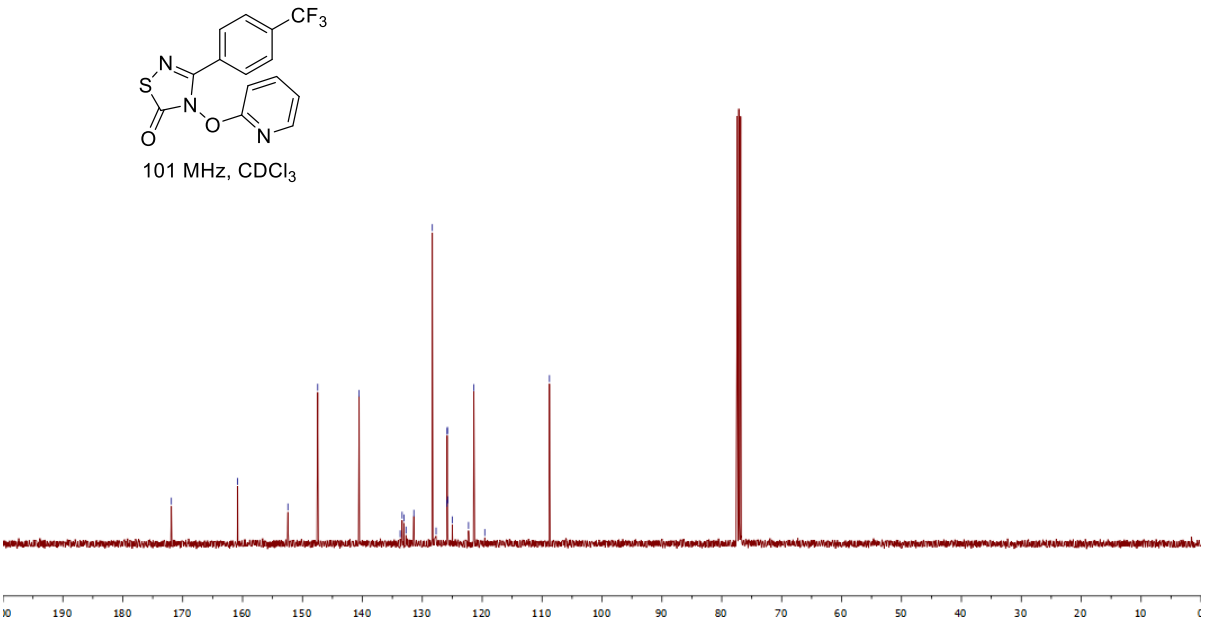
101 MHz, $CDCl_3$

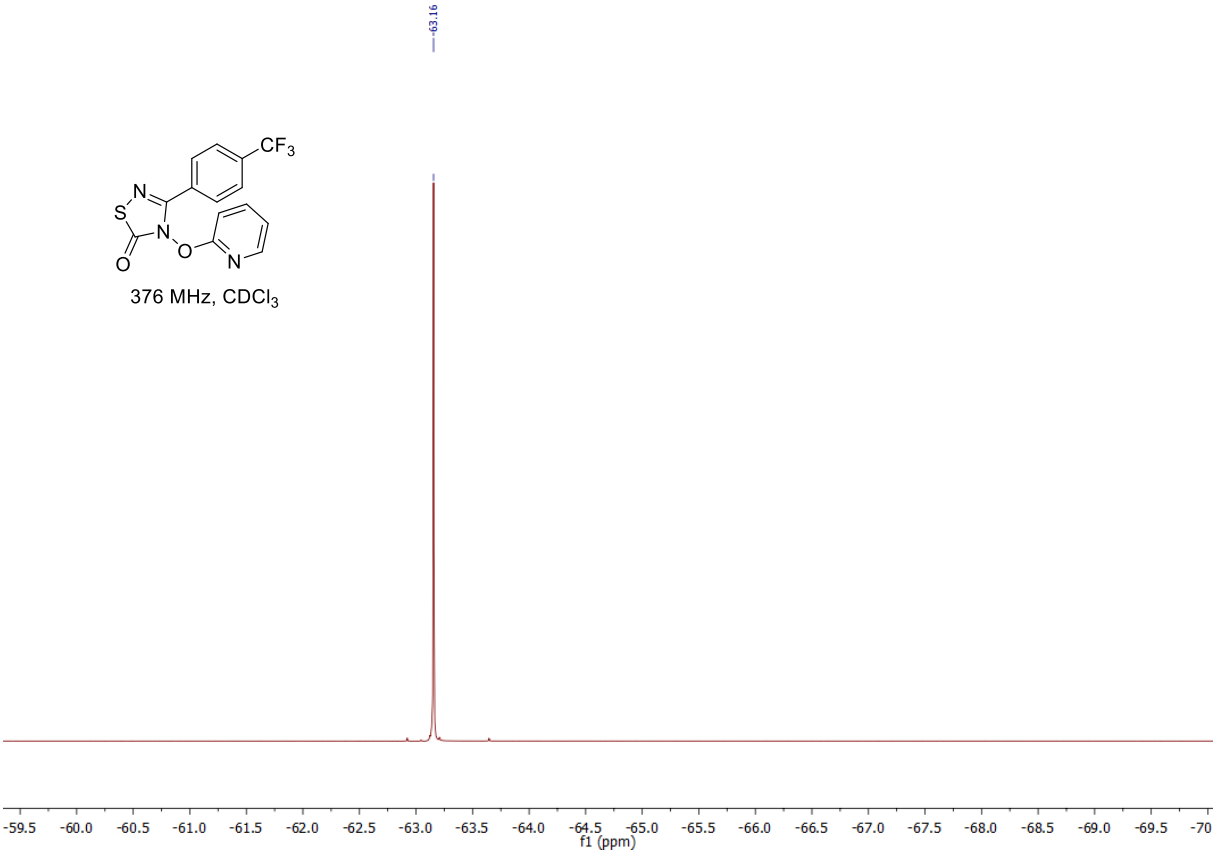
^{1}H and $^{13}C\{^{1}H\}$ spectra of 3-(4-methoxyphenyl)-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(4*H*)-one **4h**



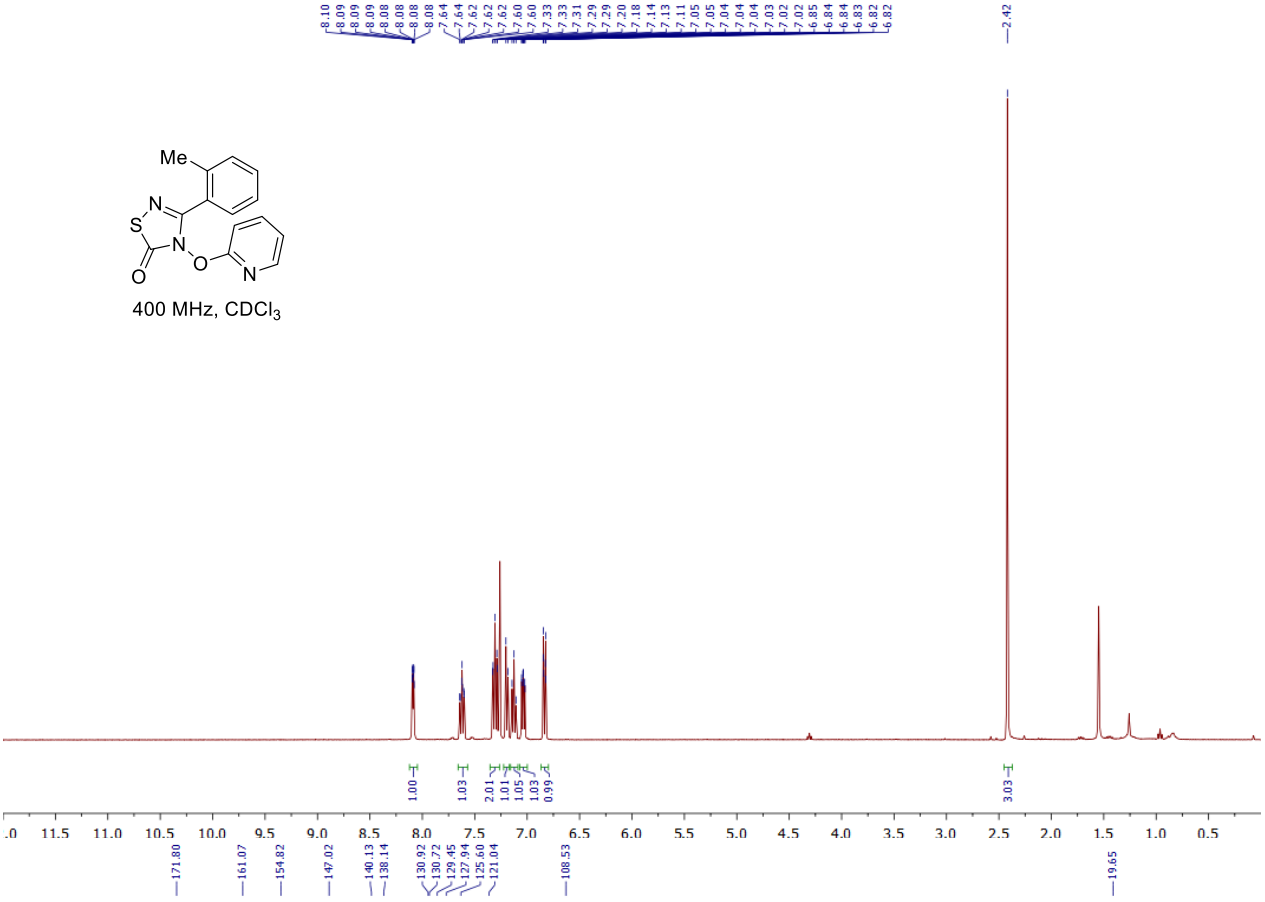
^{1}H, $^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ spectra of 4-(pyridin-2-yloxy)-3-(4-(trifluoromethyl)phenyl)-1,2,4-thiadiazol-5(*4H*)-one **4i**

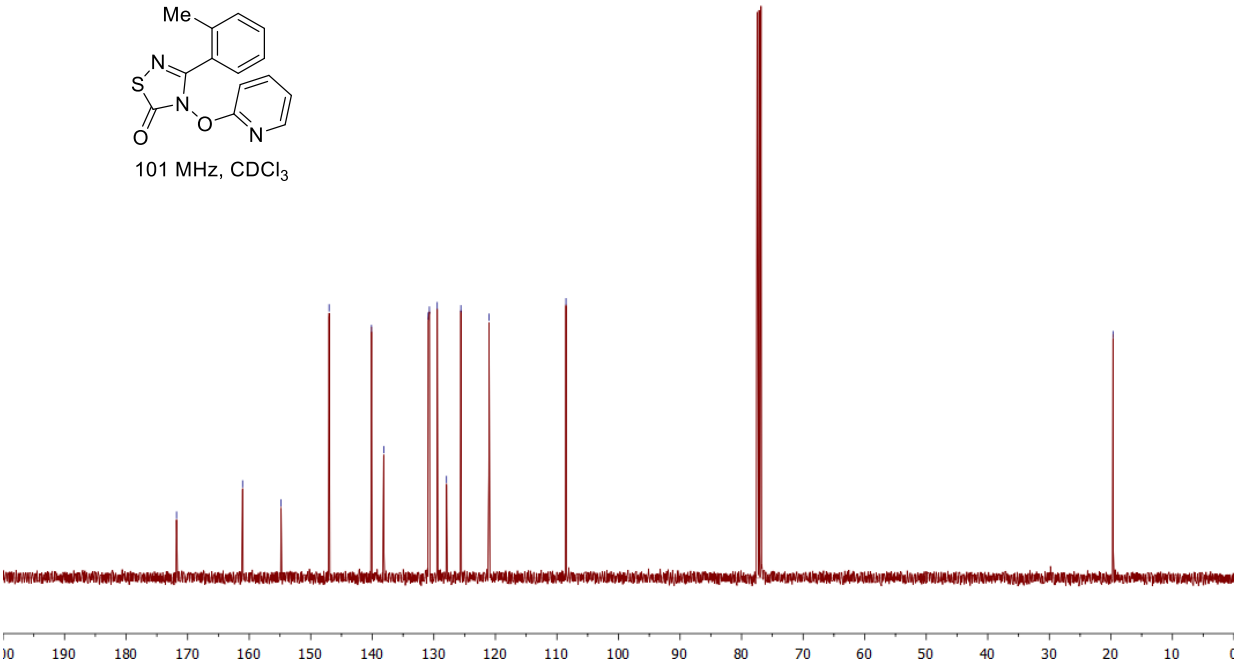




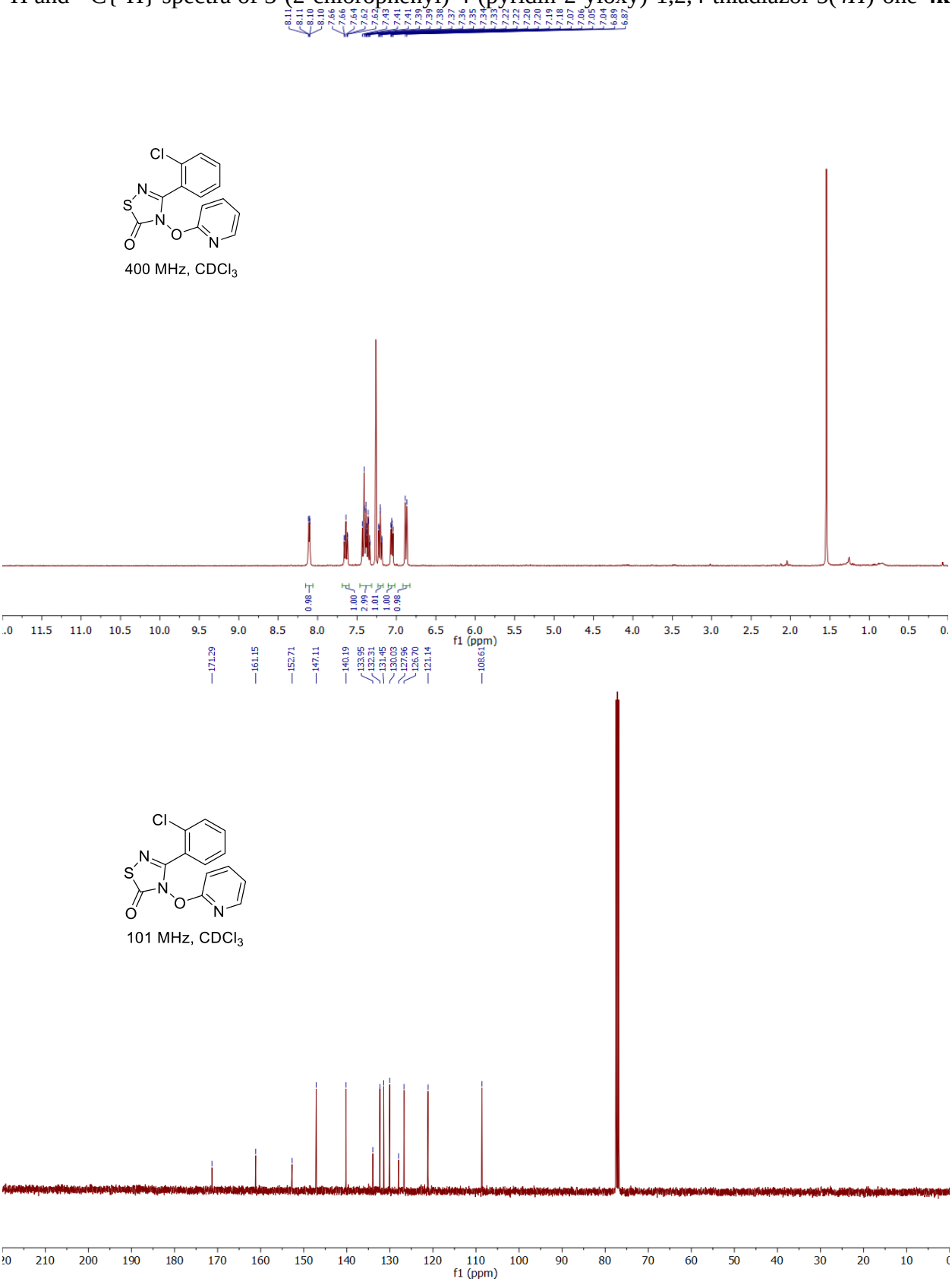

-63.16
CF3
S
N
N
O
O
N
376 MHz, CDCl3
-59.5
-60.0
-60.5
-61.0
-61.5
-62.0
-62.5
-63.0
-63.5
-64.0
-64.5
-65.0
-65.5
-66.0
-66.5
-67.0
-67.5
-68.0
-68.5
-69.0
-69.5
-70
f1 (ppm)

^{1}H and $^{13}C\{^{1}H\}$ spectra of 4-(pyridin-2-yloxy)-3-(o-tolyl)-1,2,4-thiadiazol-5(*4H*)-one **4j**

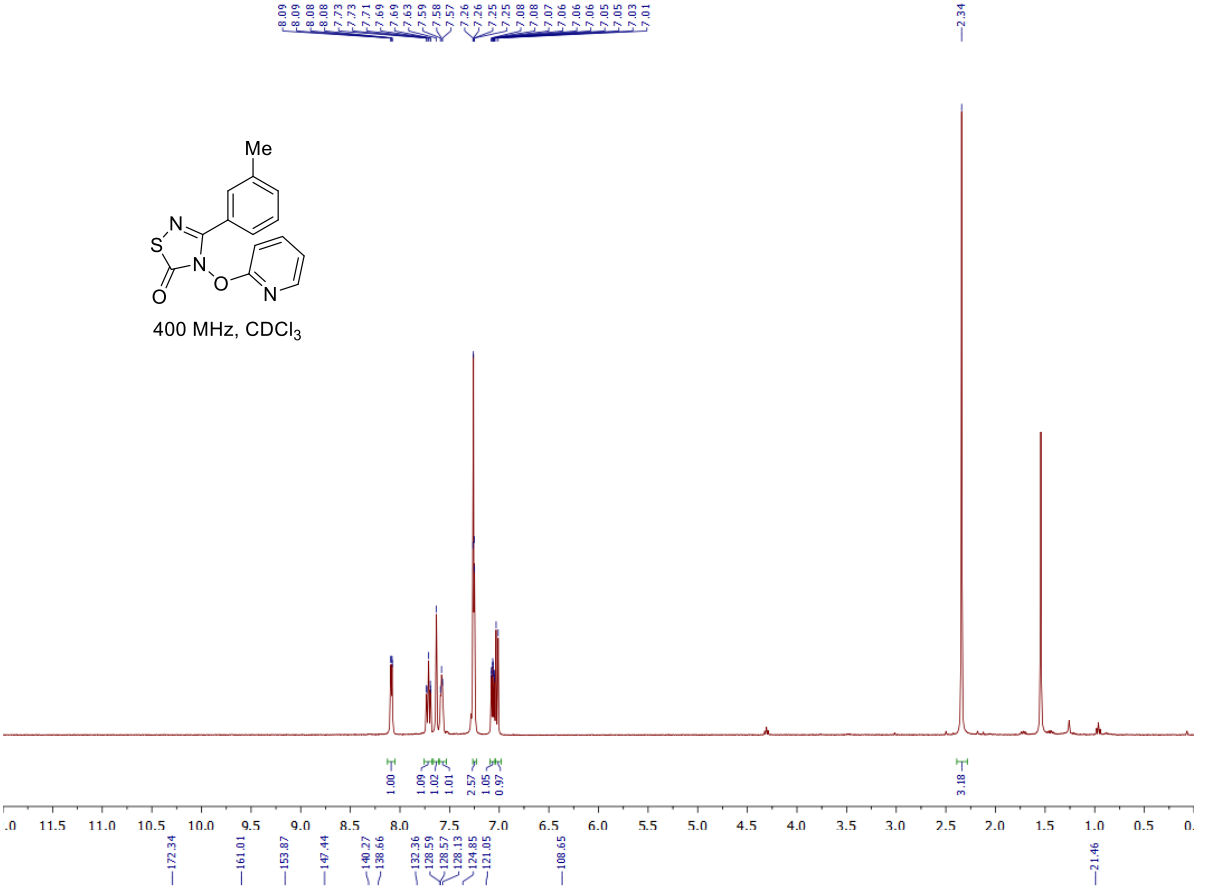


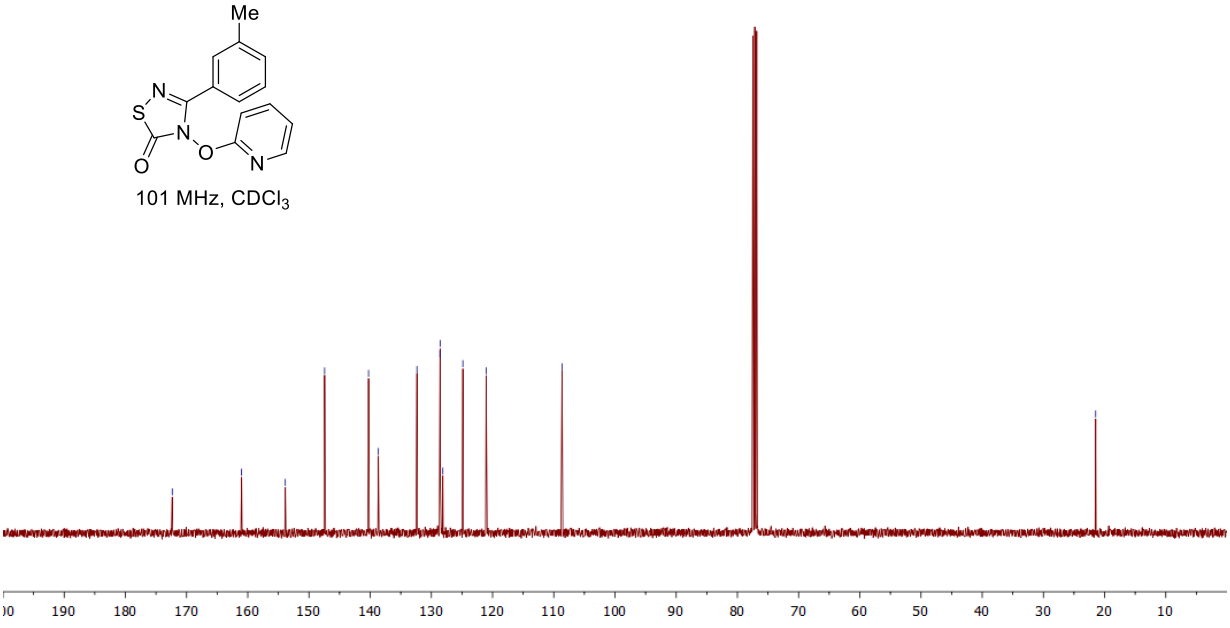


^{1}H and $^{13}C\{^{1}H\}$ spectra of 3-(2-chlorophenyl)-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(*4H*)-one **4k**

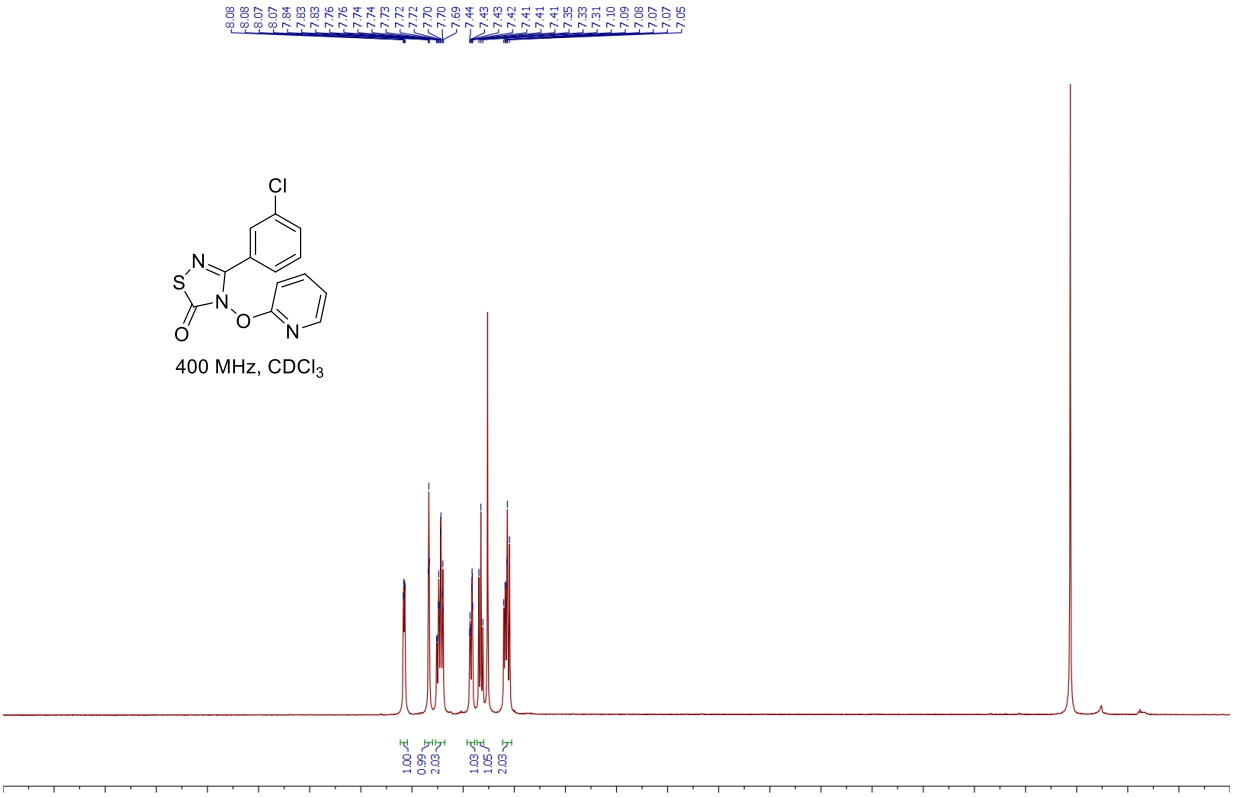


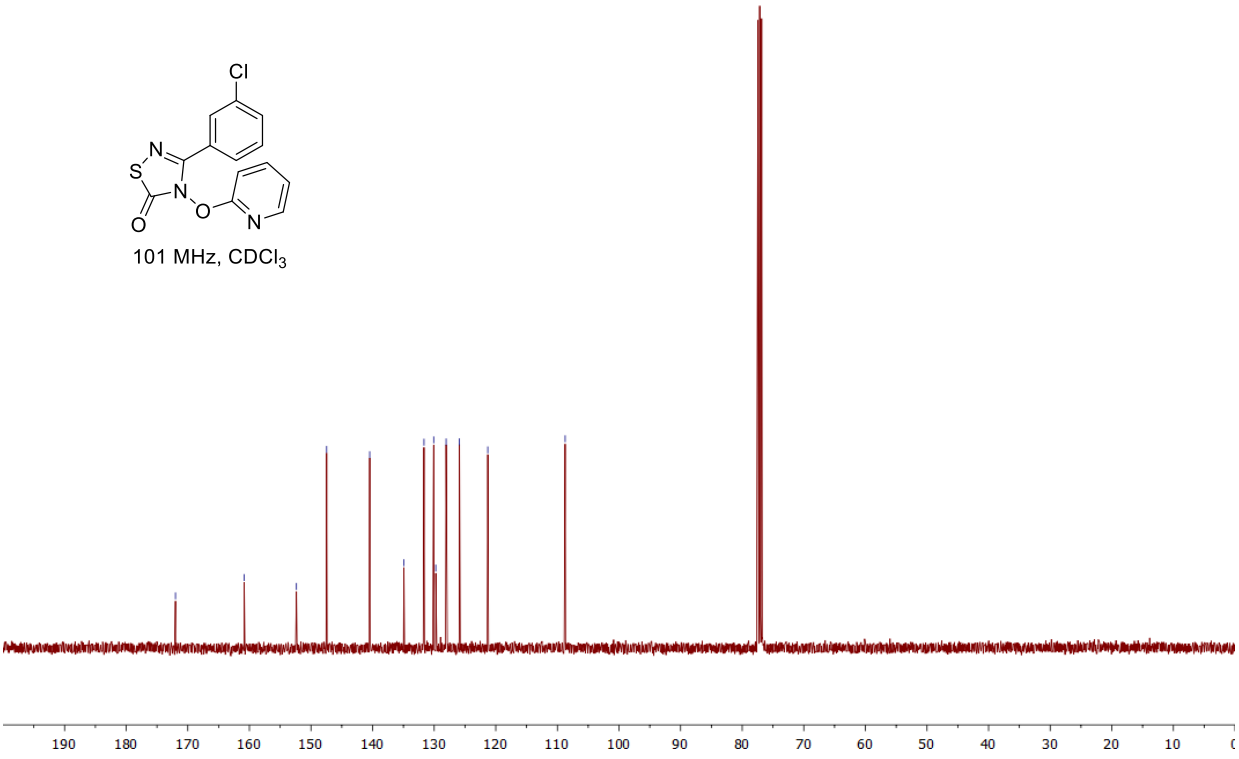
^{1}H and $^{13}C\{^{1}H\}$ spectra of 4-(pyridin-2-yloxy)-3-(*m*-tolyl)-1,2,4-thiadiazol-5(*4H*)-one **4l**



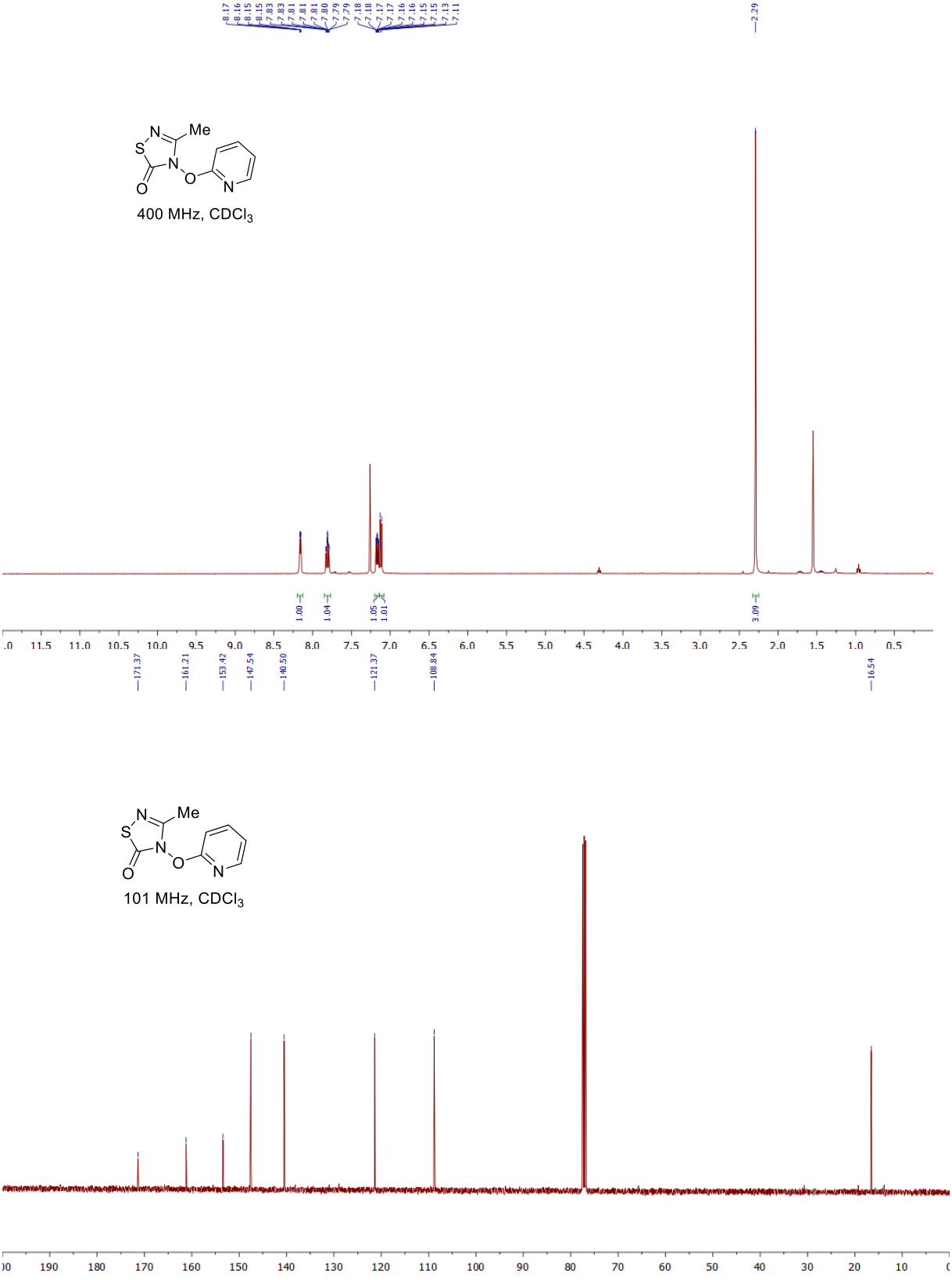


^{1}H and $^{13}C\{^{1}H\}$ spectra of 3-(3-chlorophenyl)-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(*4H*)-one **4m**

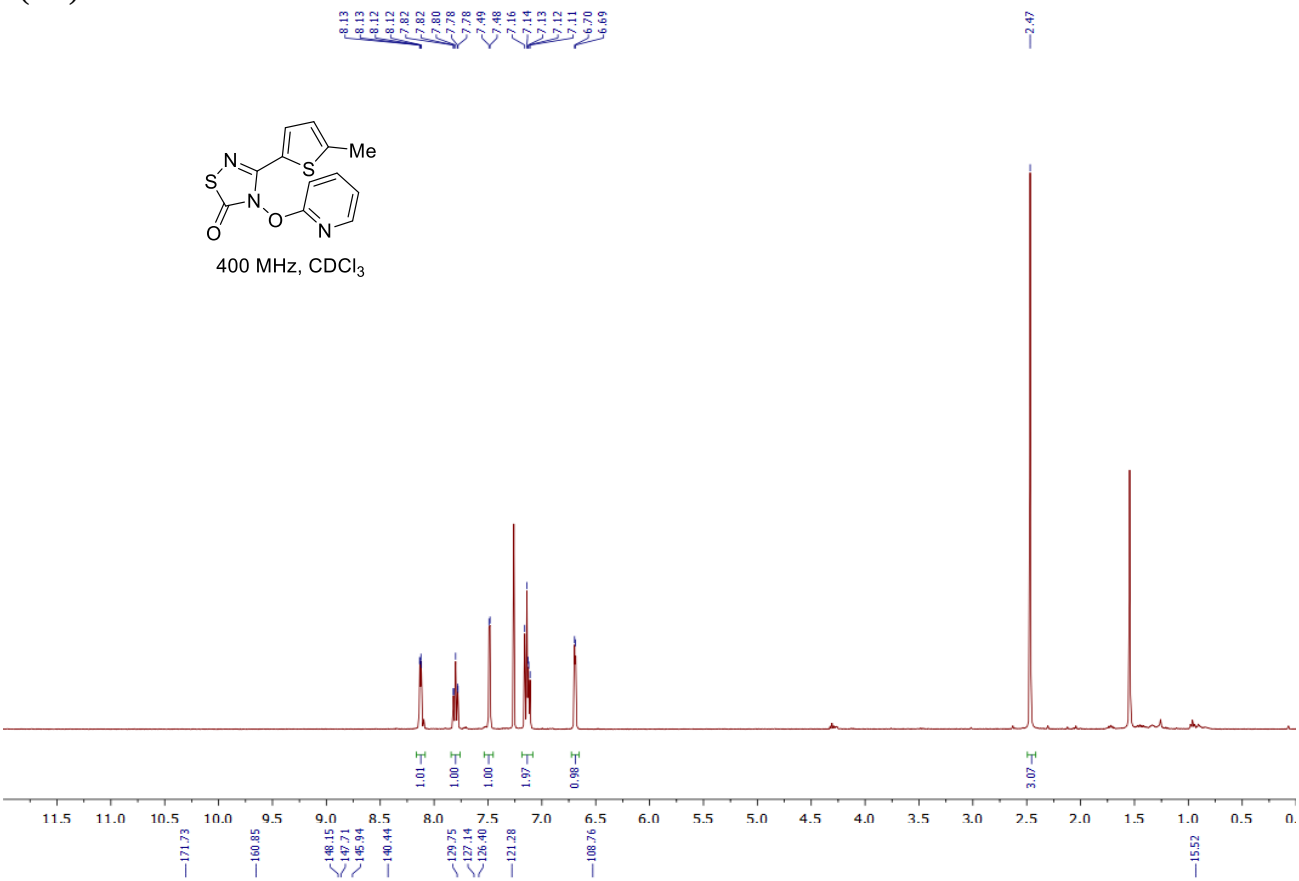


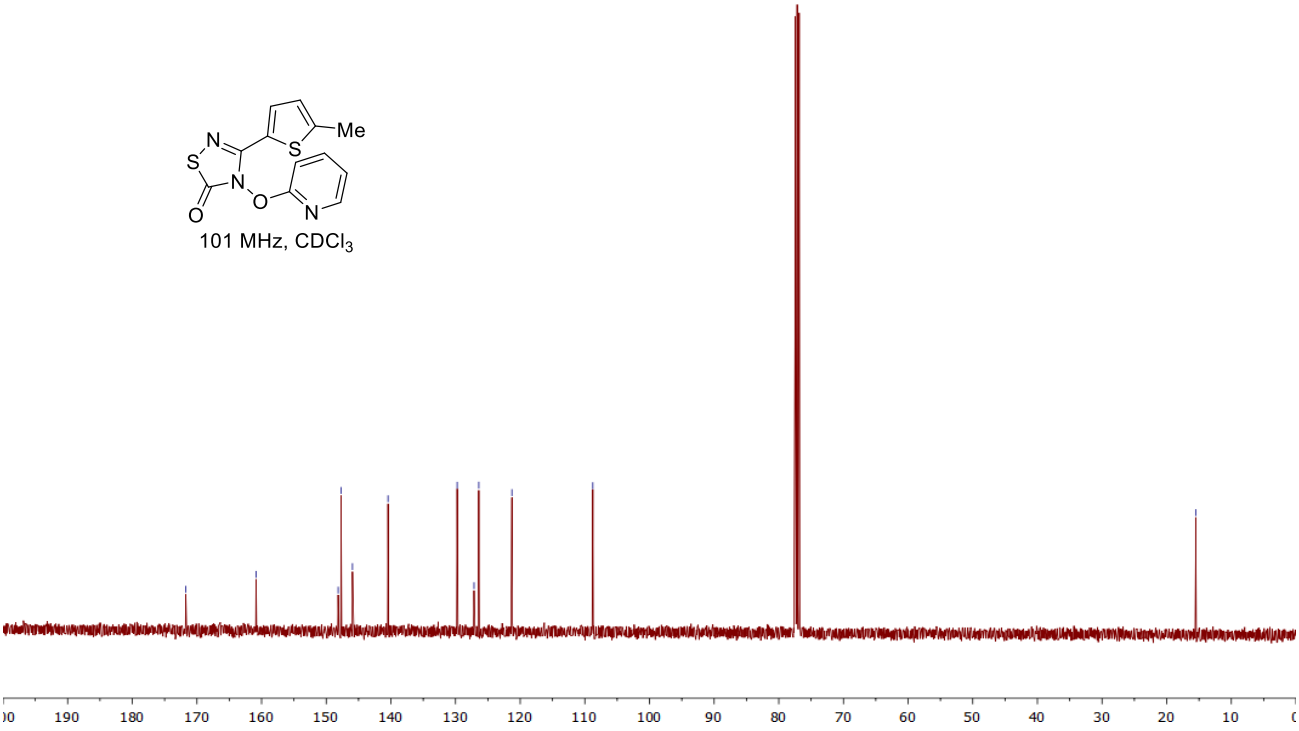


^{1}H and $^{13}C\{^{1}H\}$ spectra of 3-methyl-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(*4H*)-one **4n**

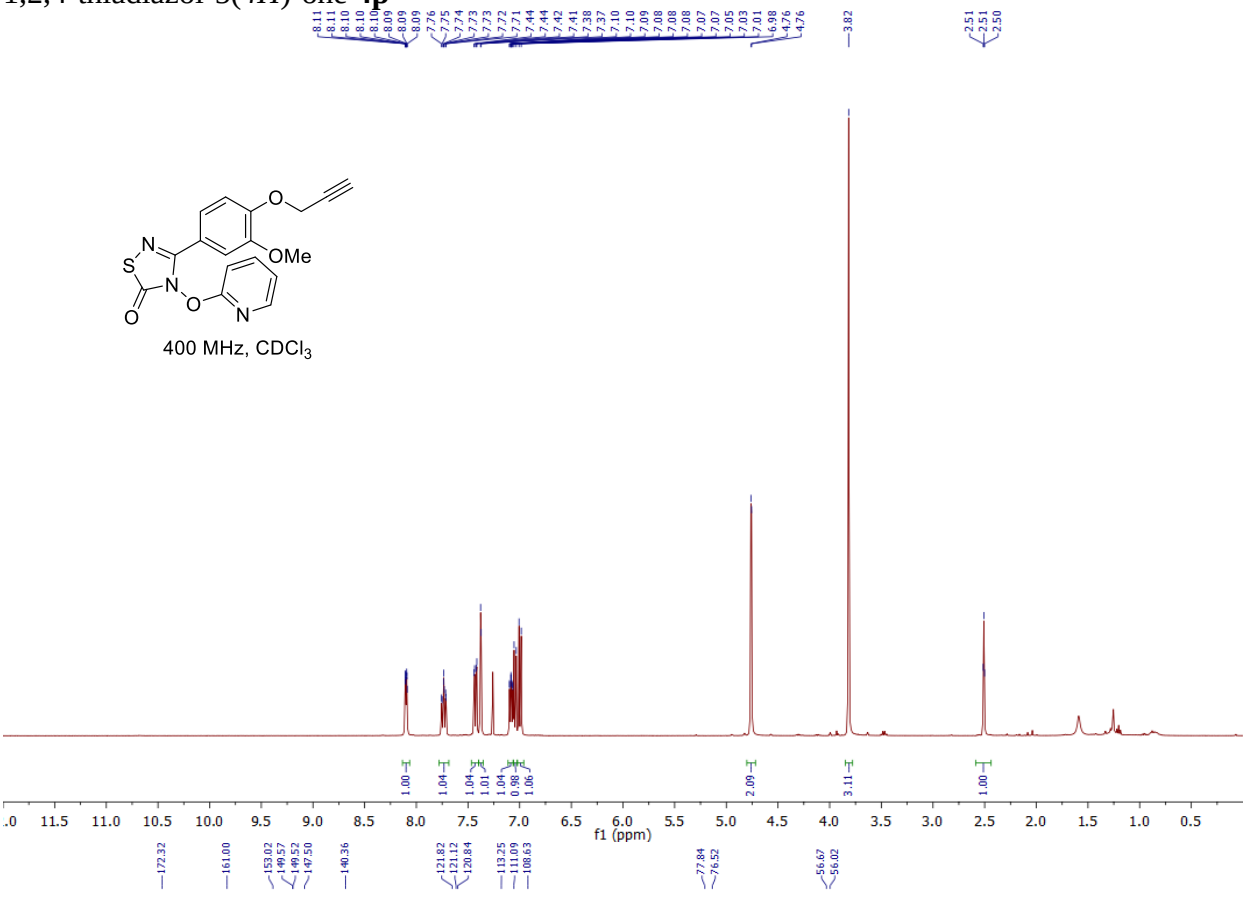


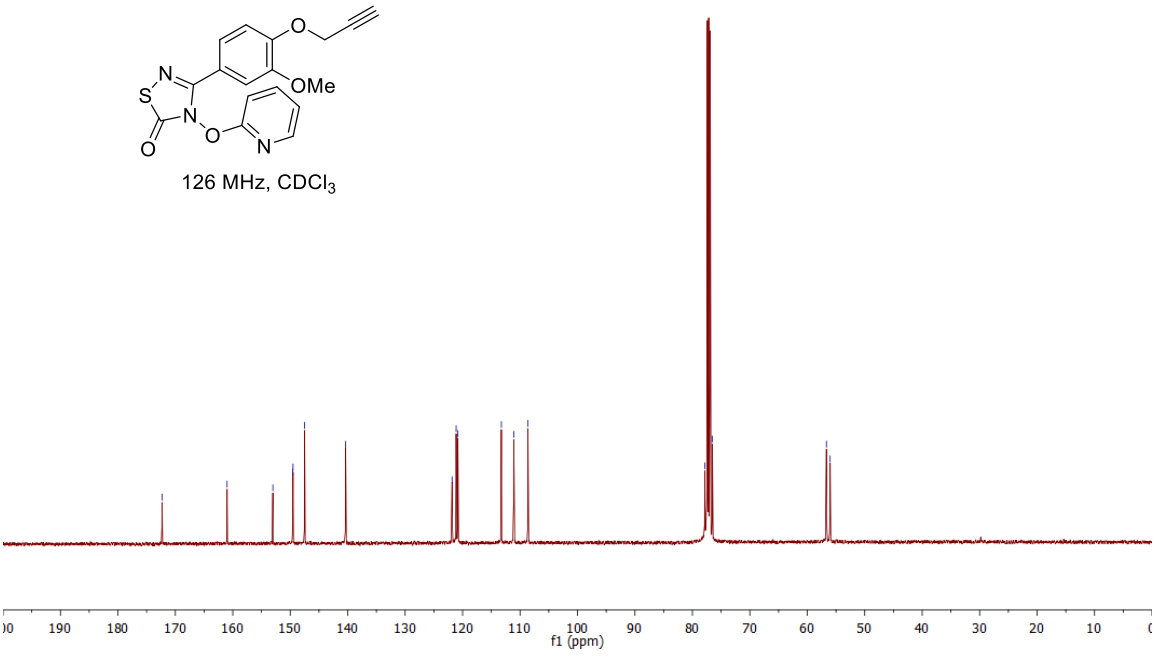
^{1}H and $^{13}C\{^{1}H\}$ spectra of 3-(5-methylthiophen-2-yl)-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(*4H*)-one **4o**



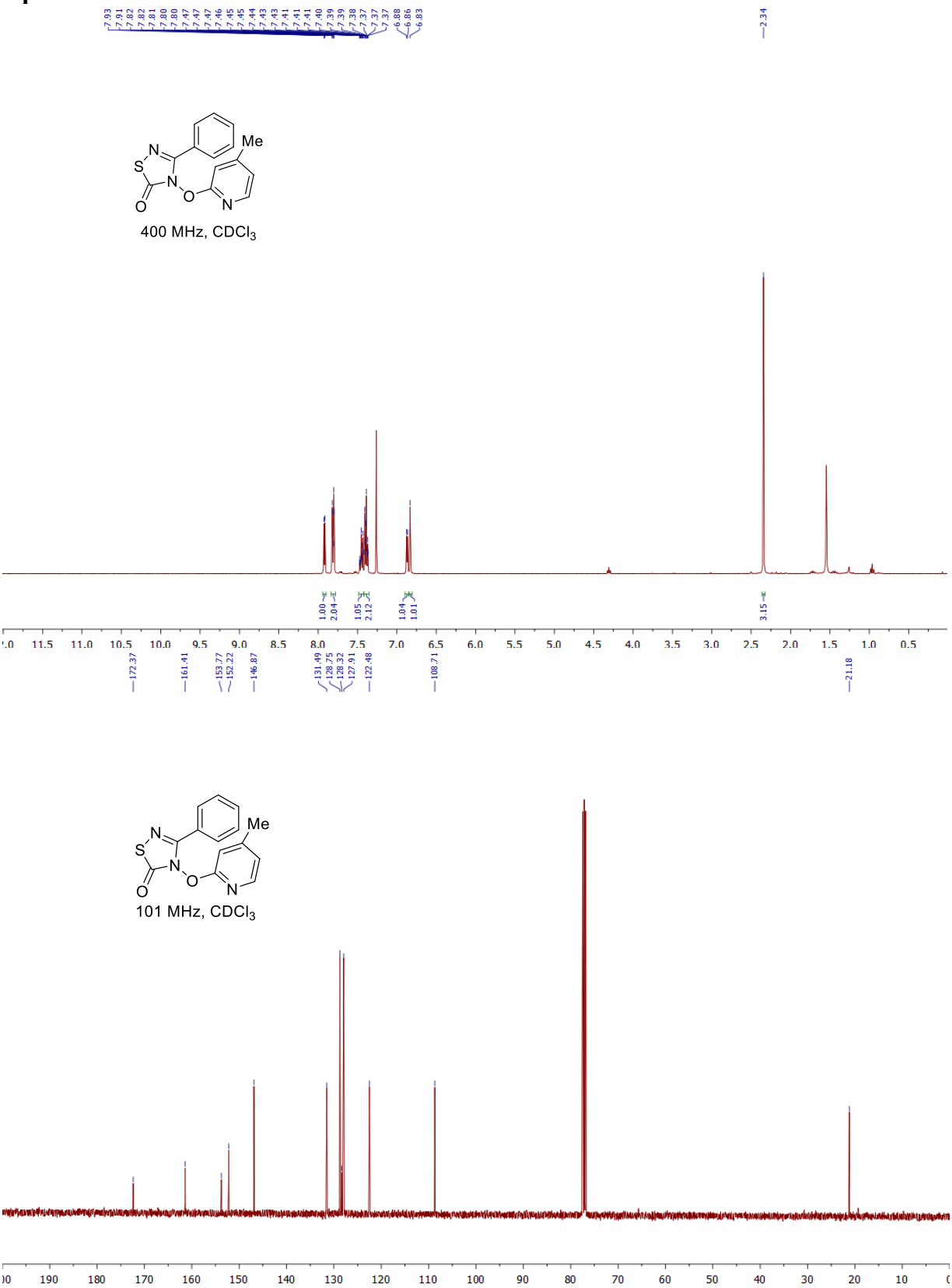


^{1}H and $^{13}C\{^{1}H\}$ spectra of 3-(3-methoxy-4-(prop-2-yn-1-yloxy)phenyl)-4-(pyridin-2-yloxy)-1,2,4-thiadiazol-5(*4H*)-one **4p**

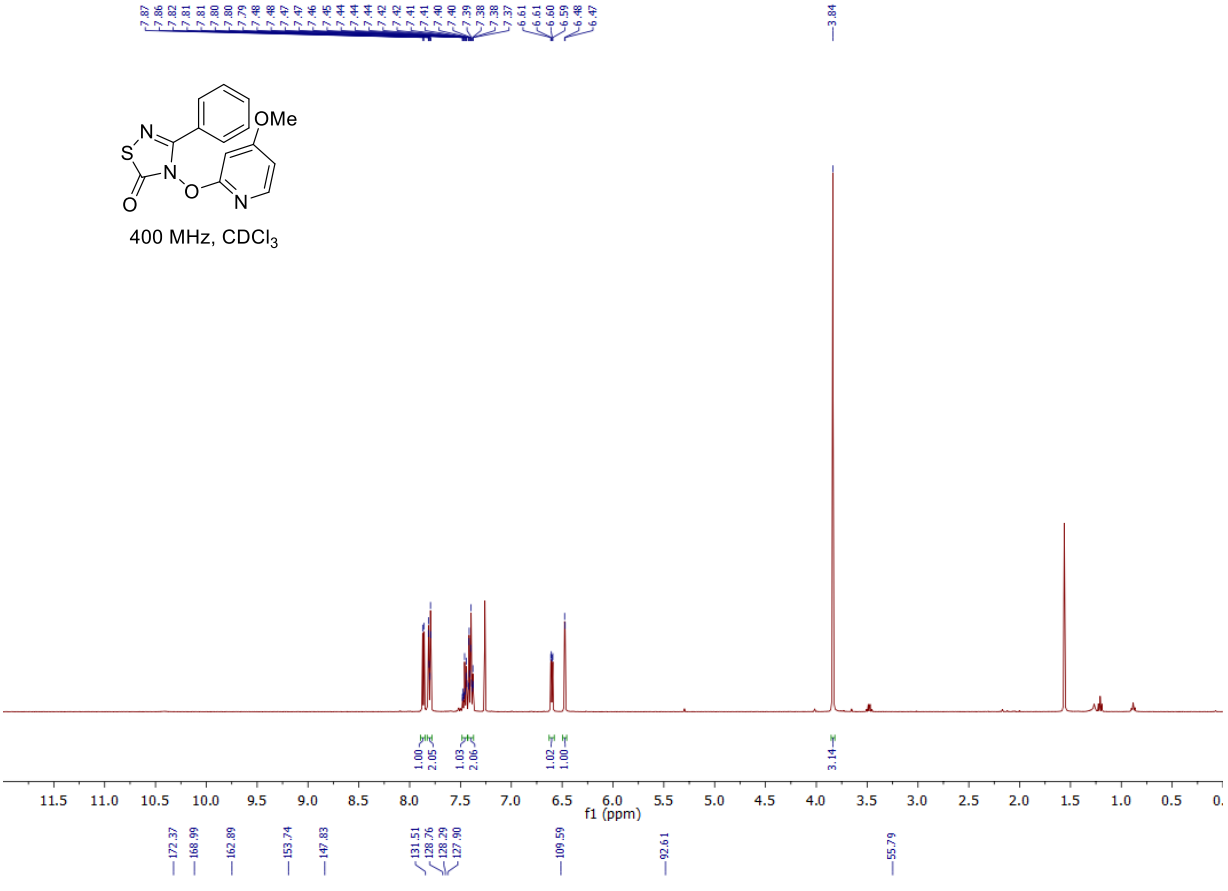


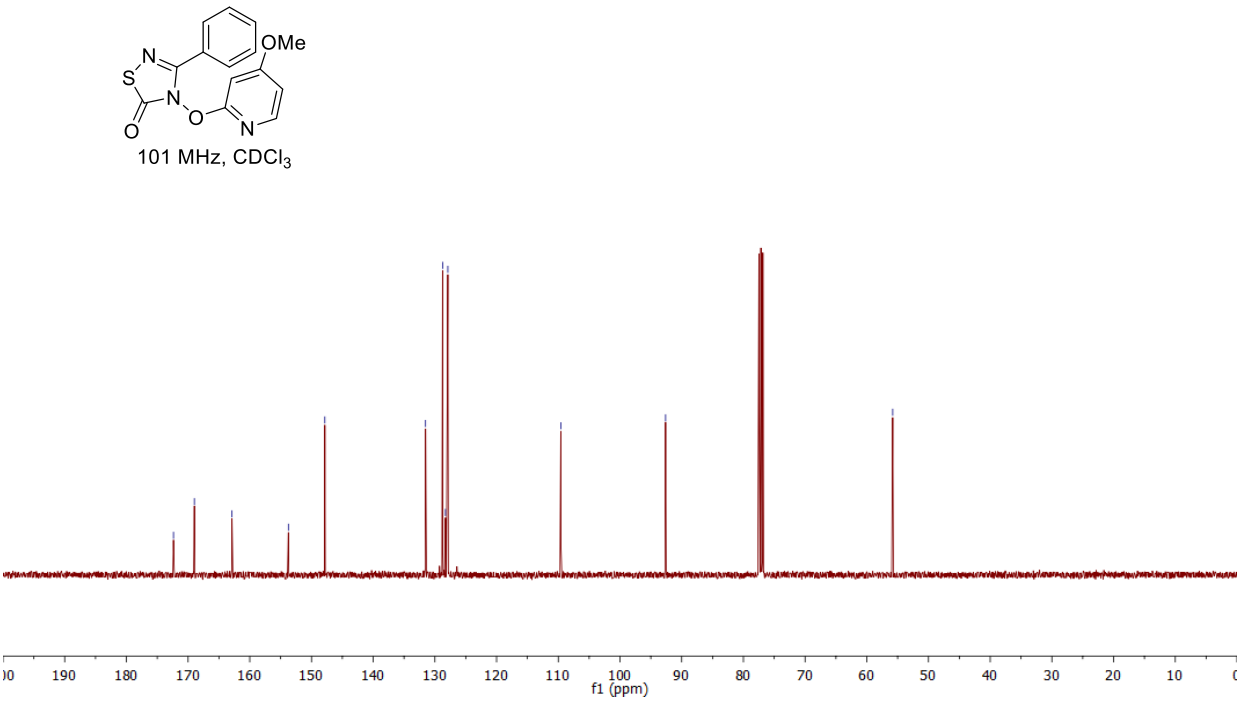


^{1}H and $^{13}C\{^{1}H\}$ spectra of 4-((4-methylpyridin-2-yl)oxy)-3-phenyl-1,2,4-thiadiazol-5(*4H*)-one **4q**

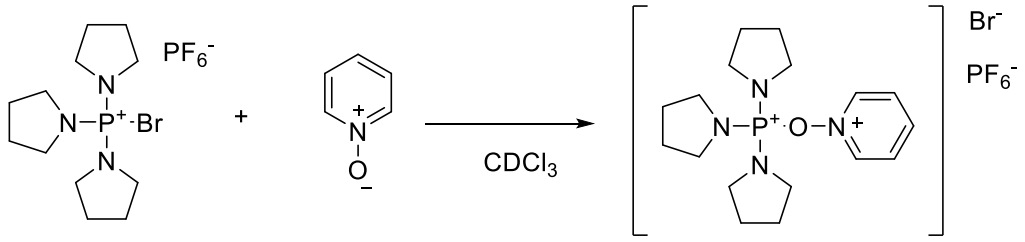


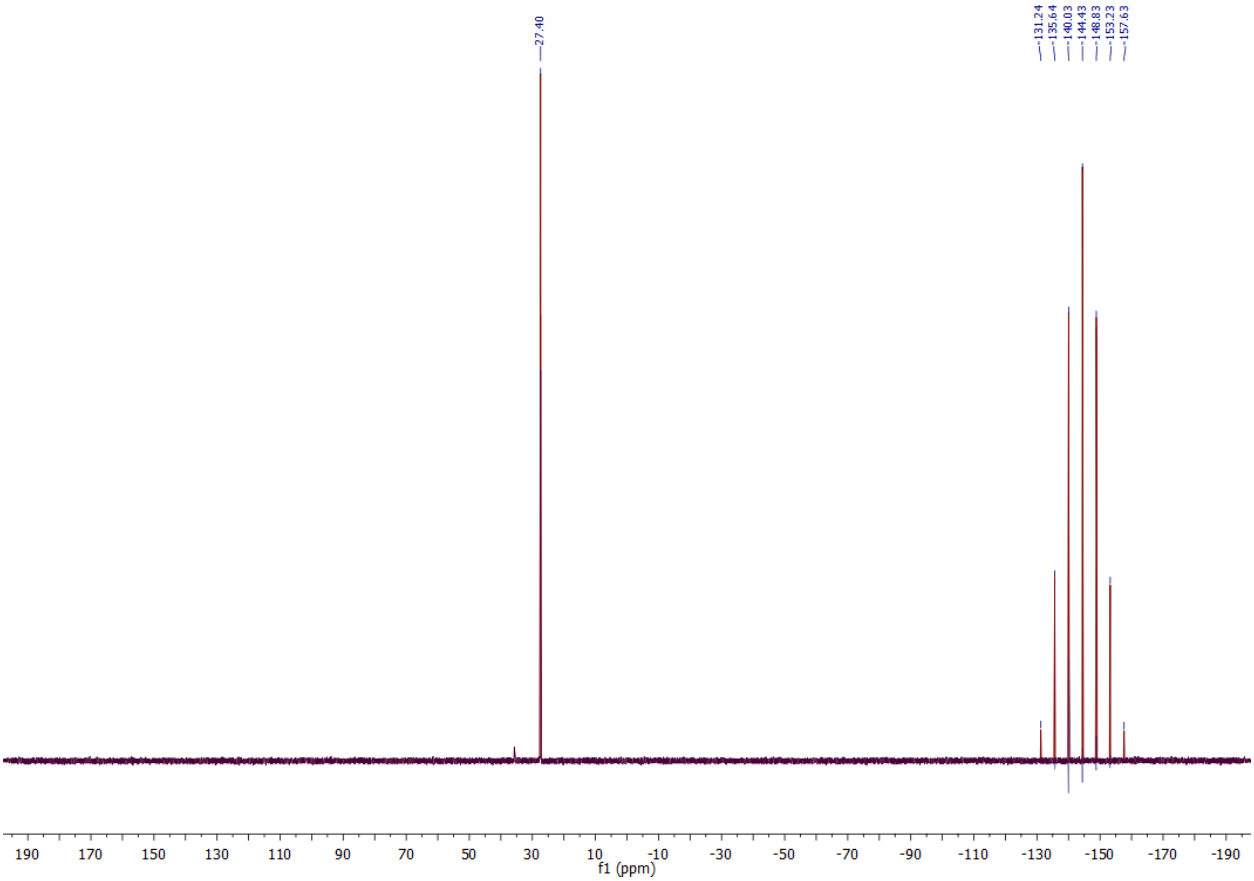
^{1}H and $^{13}C\{^{1}H\}$ spectra of 4-((4-methoxypyridin-2-yl)oxy)-3-phenyl-1,2,4-thiadiazol-5(*4H*)-one **4r**



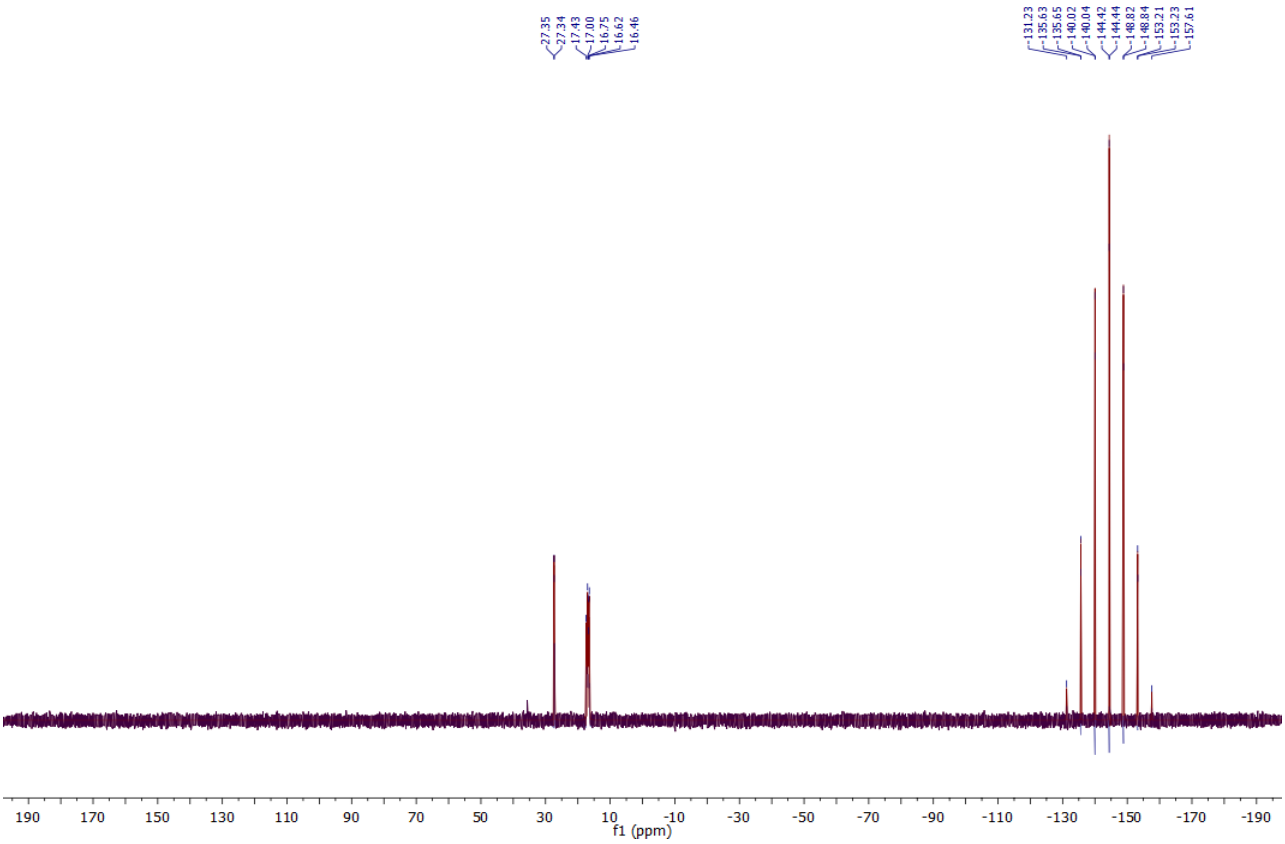


S5. Reaction of PyBroP with pyridine-*N*-oxide in $CDCl_3$

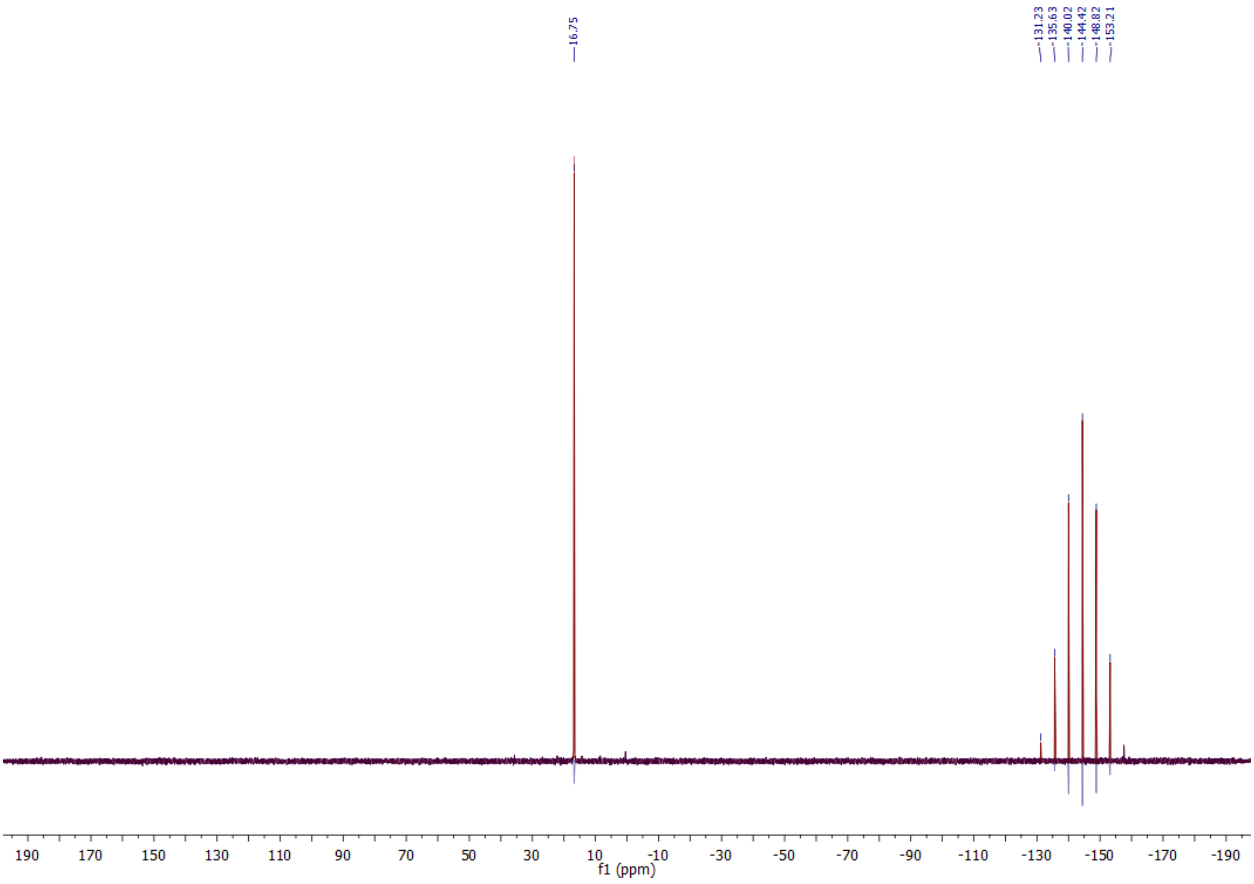




$^{31}P\{^{1}H\}$ spectrum of PyBroP in $CDCl_3$ at RT. P–Br 27.40 ppm, PF_6 –144.43 ppm.



$^{31}P\{^{1}H\}$ NMR spectrum of a mixture of PyBroP and pyridine-*N*-oxide (2 equiv.) in $CDCl_3$ at room temperature, recorded 6 h after the addition of the *N*-oxide.



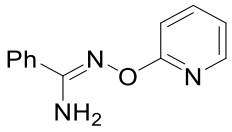
$^{31}P\{^{1}H\}$ NMR spectrum of a mixture of PyBroP and pyridine-*N*-oxide (2 equiv.) in $CDCl_3$ at room temperature, recorded 24 h after the addition of the *N*-oxide.

S6. Computation details

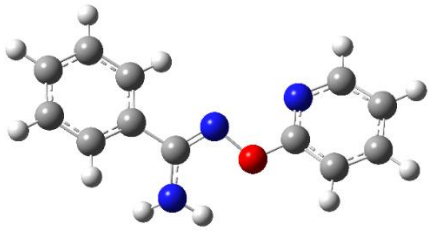
All calculations were performed by using the Gaussian 09 suite of quantum chemical programs.[14] Geometry optimizations and energy calculations for compounds **3b**, **8**–**16**, chlorocarbonylsulfenyl chloride, and transition states TS1–TS7 were performed at the DFT B3LYP/6-31+G(d,p)/LANL2DZ level using PCM model for dichloromethane. Stationary points on the respective potential-energy surfaces were characterized at the same level of theory by evaluating the corresponding Hessian indices. Careful verification of the unique imaginary frequencies for transition states was carried out to check whether the frequency indeed pertains to the desired reaction coordinate. The intrinsic reaction coordinate (IRC) calculations for transition states TS1–TS3, TS6, and TS7 were performed to make sure that the located transition structure connects the related reactant and product.[15] Both structures, TS4 and TS5, have the same imaginary frequency and geometry corresponding to a transition state of rotation around a single C-N bond. However, we were unable to correctly perform an IRC analysis for these conformational transformations.

Table S2. Energies (au) and cartesian coordinates of stationary points for compounds **3b**, **8**–**16**, chlorocarbonylsulfenyl chloride, and transition states TS1–TS7.

Compound **3b**

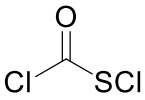


Zero-point correction = 0.211907
Thermal correction to Energy = 0.225177
Thermal correction to Enthalpy = 0.226121
Thermal correction to Gibbs Free Energy = 0.169850
E_0 = -703.177507, E = -703.164237,
H = -703.163293, G = -703.219564.
Imaginary frequency = 0.

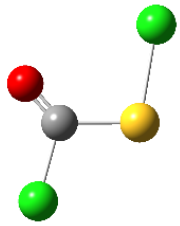


C	1.32858718	-1.09765569	0.21065046
N	0.29957818	-0.40094869	-0.17642154
O	-0.87968682	-1.19991069	-0.00373354
C	2.65883918	-0.44250169	0.09147646
N	1.28174618	-2.39136169	0.65596846
C	3.80585418	-1.20190369	-0.19275354
C	5.05275318	-0.58116369	-0.30154554
C	5.16746818	0.80101231	-0.12882254
C	4.02745918	1.56210931	0.15296746
C	2.78063918	0.94630831	0.26500946
C	-2.05595682	-0.50023069	-0.00978854
C	-3.20563882	-1.27450469	-0.24847554
C	-4.43373282	-0.62850969	-0.22040854
C	-4.47707082	0.75113931	0.02894846
C	-3.27247682	1.41219131	0.24408846
N	-2.07058682	0.80269431	0.23487146
H	2.03205118	-2.71328069	1.25019646
H	0.36689318	-2.76554269	0.86637046
H	3.72439518	-2.27238769	-0.35346154
H	5.93130518	-1.17781369	-0.52809254

(Chlorocarbonyl)sulfenyl chloride



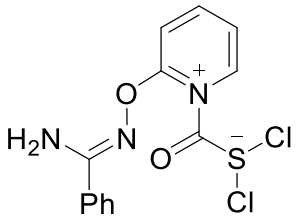
Zero-point correction = 0.011241
Thermal correction to Energy = 0.017143
Thermal correction to Enthalpy = 0.018087
Thermal correction to Gibbs Free Energy = -0.020166
E_0 = -153.292408, E = -153.286507,
H = -153.285562, G = -153.323816.
Imaginary frequency = 0.



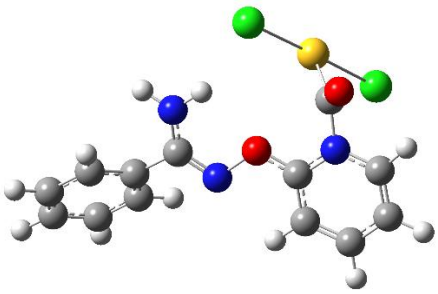
Cl	1.71550947	1.97223871	0.01921172
C	0.14229247	1.01349571	0.01921172
O	-0.92876653	1.50750071	0.01921172
S	0.63913547	-0.73272329	0.01921172
Cl	-1.39451353	-1.71318629	0.01921172

H	6.13748618	1.28204531	-0.21251154	
H	4.11051218	2.63573331	0.29333546	
H	1.89679318	1.53139131	0.49362646	
H	-3.11479782	-2.33604469	-0.44961054	
H	-5.34666982	-1.18841469	-0.39940754	
H	-5.41571982	1.29378131	0.05363646	
H	-3.25614382	2.48165031	0.44087446	

Compound **8**

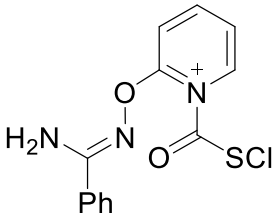


Zero-point correction = 0.226269
Thermal correction to Energy = 0.246791
Thermal correction to Enthalpy = 0.247735
Thermal correction to Gibbs Free Energy = 0.173402
E_0 = -856.485401, E = -856.464879,
H = -856.463935, G = -856.538268.
Imaginary frequency = 0.

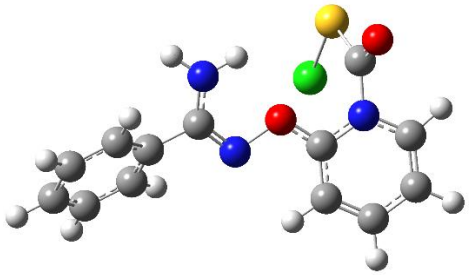


C	-1.09865764	-0.08396553	0.10993215
N	-0.30605664	-1.12746053	0.12211115
O	1.06233036	-0.64849153	0.30542615
C	-2.53484164	-0.40070753	-0.12406285
N	-0.74952664	1.19901947	0.32271715
C	-3.53286664	0.27618947	0.59606815
C	-4.87899164	-0.02108653	0.37272615
C	-5.23802264	-0.99170353	-0.56805485
C	-4.24563664	-1.66801153	-1.28561785
C	-2.89823464	-1.37554153	-1.06691885
C	1.94379936	-1.62740953	0.39404115
C	1.66371236	-3.00113453	0.40307415
C	2.70094636	-3.89808353	0.58860015
C	4.02003736	-3.44415153	0.78202915
C	4.26050736	-2.09595053	0.75745115
N	3.23768436	-1.20757053	0.54560315
H	-1.41259564	1.92668647	0.10098315
H	0.21971236	1.48745047	0.41464315
H	-3.26136764	1.01467047	1.34428915
H	-5.64499364	0.50131847	0.93776315
H	-6.28567864	-1.21917253	-0.74143285

Compound **9**



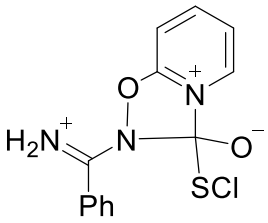
Zero-point correction = 0.225513
Thermal correction to Energy = 0.244116
Thermal correction to Enthalpy = 0.245060
Thermal correction to Gibbs Free Energy = 0.175554
E_0 = -841.316004, E = -841.297402,
H = -841.296458, G = -841.365963.
Imaginary frequency = 0.



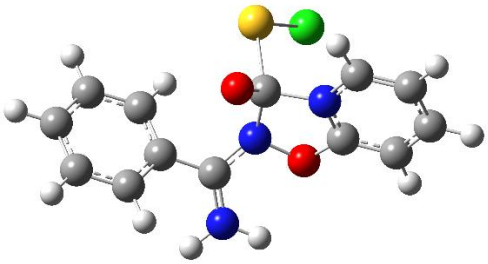
C	-1.19756675	0.38162023	-0.54174367
N	-0.34453175	1.31839723	-0.20582367
O	1.00265725	0.83355423	-0.53017067
C	-2.61517075	0.67374223	-0.19997167
N	-0.91041475	-0.77124377	-1.17573667
C	-3.64253475	0.31050523	-1.08673667
C	-4.97254275	0.58544223	-0.76318467
C	-5.28539275	1.22184423	0.44234133
C	-4.26352975	1.58636423	1.32551033
C	-2.93162975	1.31458623	1.00883533
C	1.92687325	1.76553223	-0.40214467
C	1.73530425	3.12179523	-0.11312467
C	2.83947625	3.95509123	-0.05643767
C	4.13873225	3.45806823	-0.28819567
C	4.29764125	2.12647123	-0.56472967
N	3.19977125	1.29908223	-0.60227567
H	-1.60713275	-1.49745877	-1.24168167
H	0.03849825	-1.00947677	-1.42005467
H	-3.40660675	-0.16037777	-2.03620567
H	-5.76169175	0.30857423	-1.45539467
H	-6.32091975	1.43241623	0.69230433

H	-4.52007664	-2.41740253	-2.02190785	H	-4.50345975	2.07515623	2.26479133
H	-2.12616464	-1.88772753	-1.63070485	H	-2.13745775	1.58285123	1.69689333
H	0.63759536	-3.31442253	0.28147415	H	0.72718525	3.47546423	0.04596133
H	2.48761236	-4.96178653	0.59839515	H	2.69778725	5.00789523	0.16314733
H	4.84227236	-4.13068453	0.93832615	H	5.00812225	4.10208923	-0.25386467
H	5.24031336	-1.65547753	0.88372115	H	5.25257125	1.65330423	-0.75586867
Cl	2.16155536	2.98861247	0.30657115	C	3.42025625	-0.10795377	-0.93739767
C	3.60486136	0.22660347	0.52858415	O	3.70586325	-0.46571477	-2.04145467
O	4.16047636	0.68508547	1.47982115	S	3.35794725	-1.35431377	0.39031733
S	3.23494436	1.13970447	-1.03956585	Cl	2.91237625	-0.15642577	2.24906633
Cl	4.24805936	-0.73393953	-2.39445285				

Compound **10**

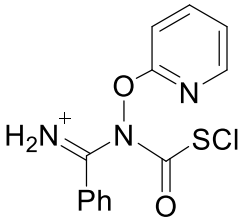


Zero-point correction = 0.226591
Thermal correction to Energy = 0.244400
Thermal correction to Enthalpy = 0.245344
Thermal correction to Gibbs Free Energy = 0.178748
E_0 = -841.317834, E = -841.300025,
H = -841.299081, G = -841.365677.
Imaginary frequency = 0.

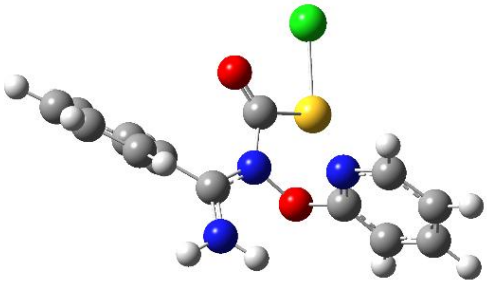


C	-0.84126508	-0.86569964	-0.70533223
N	0.32285792	-0.23083064	-0.47925323
O	1.42941592	-0.82450964	-1.14601023
C	-2.09205508	-0.30242364	-0.17371223
N	-0.87143008	-1.95799964	-1.44687323
C	-3.03387308	-1.17095864	0.40770977
C	-4.24415808	-0.66014564	0.87190577
C	-4.52348108	0.70523036	0.74418877
C	-3.59002508	1.56455936	0.15514577
C	-2.37001608	1.06868336	-0.30156923
C	2.49075292	-0.73639464	-0.31285323
C	3.74310292	-1.27886764	-0.56207223
C	4.69721092	-1.09879864	0.43486077
C	4.38826992	-0.40596264	1.62254977
C	3.12340092	0.11494236	1.79272477
N	2.21045992	-0.06519164	0.80700877
H	-1.76122008	-2.33100964	-1.75188923
H	-0.02637908	-2.39441064	-1.79474723
H	-2.80708708	-2.22568164	0.52678877
H	-4.96494808	-1.32506964	1.33629077

Compound **11**



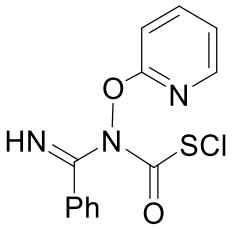
Zero-point correction = 0.226371
Thermal correction to Energy = 0.244456
Thermal correction to Enthalpy = 0.245401
Thermal correction to Gibbs Free Energy = 0.177490
E_0 = -841.320322, E = -841.302236,
H = -841.301292, G = -841.369203.
Imaginary frequency = 0.



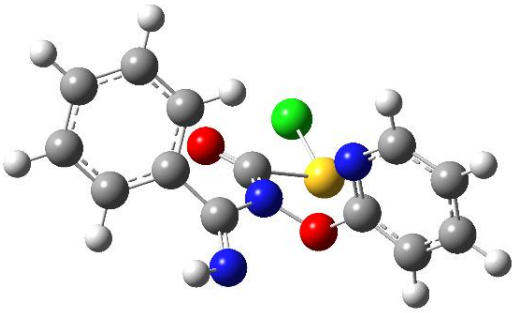
C	-0.65203829	-0.86191064	-0.19729305
N	0.27980171	0.13199936	-0.18215005
O	1.47813471	-0.09100264	-0.85160605
C	-2.05556929	-0.61567064	0.16414695
N	-0.28248429	-2.05745164	-0.58999605
C	-2.69284529	-1.50464764	1.04839895
C	-4.04318929	-1.32460764	1.34433795
C	-4.75825629	-0.28331364	0.74448595
C	-4.12459829	0.58900736	-0.14909705
C	-2.77137629	0.43542836	-0.43623805
C	2.52298871	-0.63145764	-0.02840605
C	3.73740771	-0.83116964	-0.67681405
C	4.75691471	-1.36154664	0.11274895
C	4.50804471	-1.65036364	1.46082495
C	3.23917471	-1.39958564	1.97512795
N	2.24196671	-0.88952664	1.22330995
H	-0.98525029	-2.77396764	-0.72837705
H	0.67451471	-2.28940364	-0.82944605
H	-2.13071829	-2.30111164	1.52591895
H	-4.53351029	-1.99451364	2.04272195

H	-5.46929708	1.09890036	1.10340277	H	-5.81116829	-0.15019264	0.97228195
H	-3.81226708	2.62121636	0.04798277	H	-4.68501429	1.38873836	-0.62168305
H	-1.65131608	1.73175936	-0.76828923	H	-2.28547329	1.10552436	-1.13742005
H	3.93976492	-1.81467364	-1.48195223	H	3.87210271	-0.58464864	-1.72333905
H	5.69238392	-1.50624364	0.29437877	H	5.73467171	-1.54444964	-0.32050805
H	5.12928592	-0.27370164	2.40073177	H	5.28305171	-2.06083264	2.09802895
H	2.78698792	0.66711836	2.66151577	H	2.99635771	-1.60697864	3.01265795
C	0.77234792	0.48179436	0.85168677	C	0.18633771	1.41021336	0.43435995
O	0.10344692	0.31996136	1.87720477	O	-0.64120529	1.73243236	1.22993295
S	0.87357892	2.41661036	0.56544477	S	1.55371771	2.48406136	-0.23893605
Cl	2.11801092	2.72078936	-1.33620723	Cl	1.02905771	4.32803936	0.93353995

Compound **12**

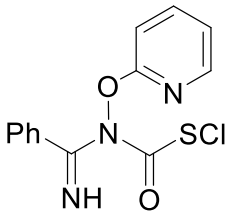


Zero-point correction = 0.213260
Thermal correction to Energy = 0.231146
Thermal correction to Enthalpy = 0.232090
Thermal correction to Gibbs Free Energy = 0.163864
E_0 = -840.904737, E = -840.886851,
H = -840.885907, G = -840.954133.
Imaginary frequency = 0.

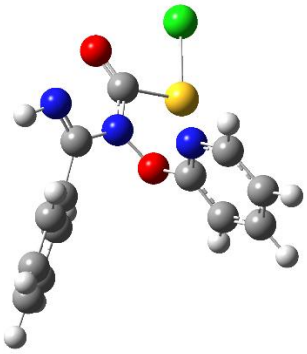


C	-0.61092435	-0.68887561	-0.50000499
N	0.35689265	0.26093439	-0.03552499
O	1.67984265	0.05844239	-0.44088899
C	-1.90412035	-0.69805761	0.23295601
N	-0.24597535	-1.47120861	-1.43692499
C	-3.10176835	-0.81229861	-0.49002299
C	-4.31921335	-0.90577761	0.18666801
C	-4.34599435	-0.89665461	1.58517501
C	-3.15206335	-0.78852661	2.30729501
C	-1.93324535	-0.68104161	1.63694101
C	2.38378465	-0.88925661	0.32682601
C	3.62336465	-1.25770661	-0.19825099
C	4.36208365	-2.17071861	0.54846001
C	3.83332165	-2.66533661	1.74830301
C	2.57778265	-2.22011461	2.15174501
N	1.85349565	-1.32936561	1.44535501
H	-0.97876935	-2.15664661	-1.62303299
H	-3.08174235	-0.80663761	-1.57594699
H	-5.24406335	-0.98053261	-0.37715399

Compound **13**



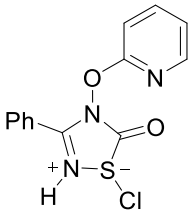
Zero-point correction = 0.213133
Thermal correction to Energy = 0.231073
Thermal correction to Enthalpy = 0.232018
Thermal correction to Gibbs Free Energy = 0.163408
E_0 = -840.901830, E = -840.883889,
H = -840.882945, G = -840.951555.
Imaginary frequency = 0.



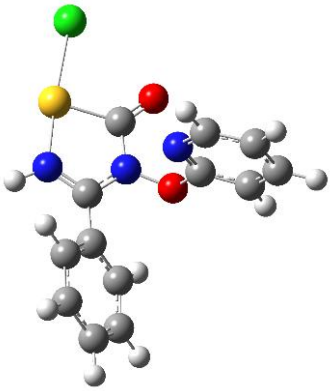
C	1.89288824	-2.30834853	1.30262118
N	0.76031124	-1.77382953	0.60790518
O	0.98506424	-0.83901353	-0.40545782
C	3.17222824	-2.31664253	0.53973218
N	1.69709124	-2.73954553	2.48438718
C	4.35858824	-1.96104053	1.20138418
C	5.58318624	-2.03849353	0.53566918
C	5.63204824	-2.47729953	-0.79138382
C	4.45190024	-2.83277353	-1.45439482
C	3.22403124	-2.74507753	-0.79733382
C	1.26521924	0.47149447	0.04517918
C	1.62644824	1.36698747	-0.96252182
C	1.89068924	2.67210647	-0.55727582
C	1.78986824	3.00481647	0.80050218
C	1.42774924	2.00841047	1.70208118
N	1.16317124	0.74114047	1.32531318
H	2.54779524	-3.17712453	2.84113918
H	4.31950324	-1.60890353	2.22818418
H	6.49509524	-1.75250753	1.05083618

H	-5.29346035	-0.97191361	2.11055101	H	6.58508724	-2.53964653	-1.30822082
H	-3.17019235	-0.78681661	3.39295701	H	4.48735424	-3.17812753	-2.48315582
H	-1.00526335	-0.60338661	2.19423401	H	2.31160524	-3.02203253	-1.31568682
H	3.97553865	-0.84889061	-1.13812399	H	1.69275324	1.05032847	-1.99687582
H	5.33521365	-2.49739861	0.19588301	H	2.17477524	3.41997647	-1.29070682
H	4.38044365	-3.38085161	2.35203001	H	1.99037624	4.01178647	1.14920818
H	2.12400865	-2.57859261	3.07156401	H	1.34078824	2.21562847	2.76489918
C	0.12668065	1.57509839	0.30214901	C	-0.54354476	-2.19248553	0.68238318
O	-0.93159935	2.10457739	0.50728001	O	-1.00997976	-3.04415553	1.38560218
S	1.80949165	2.44471039	0.38423301	S	-1.53534276	-1.21100053	-0.62095682
Cl	1.05249565	4.43476339	1.17090101	Cl	-3.56983376	-2.06161453	-0.10285282

Compound **14**

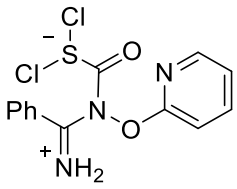


Zero-point correction = 0.214161
Thermal correction to Energy = 0.231703
Thermal correction to Enthalpy = 0.232647
Thermal correction to Gibbs Free Energy = 0.165943
E_0 = -840.927256, E = -840.909714,
H = -840.908770, G = -840.975474.
Imaginary frequency = 0.

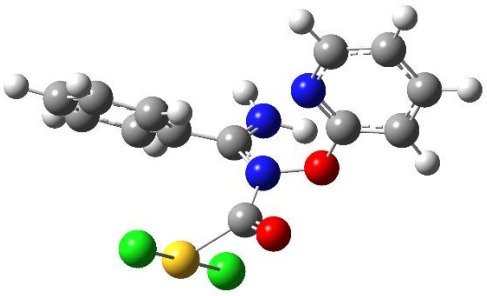


C	0.23319862	-2.73199061	0.32586500
N	-0.38644138	-1.69783161	-0.33248200
O	0.33867962	-0.69822261	-0.93719700
C	1.68633662	-2.95842261	0.28085100
N	-0.62356638	-3.47796561	0.94771800
C	2.33338062	-3.40363661	1.44738000
C	3.69964562	-3.67984261	1.41919700
C	4.42104562	-3.52559461	0.23062000
C	3.77589762	-3.09019761	-0.93204200
C	2.41217462	-2.79973561	-0.91305200
C	0.61448762	0.39962639	-0.09486600
C	1.19967762	1.49635839	-0.72863200
C	1.50576762	2.58281839	0.08538500
C	1.21564662	2.52140739	1.45566400
C	0.62761462	1.36480939	1.95734900
N	0.33124262	0.30082139	1.18341600
H	-0.35308838	-4.35152261	1.38568700
H	1.77800262	-3.50456261	2.37466100

Compound **15**



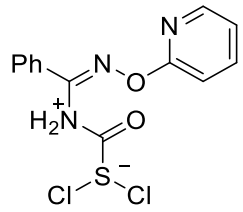
Zero-point correction = 0.227016
Thermal correction to Energy = 0.247235
Thermal correction to Enthalpy = 0.248179
Thermal correction to Gibbs Free Energy = 0.174546
E_0 = -856.481816, E = -856.461597,
H = -856.460653, G = -856.534286.
Imaginary frequency = 0.



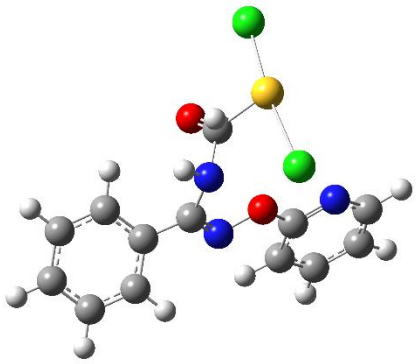
C	-0.67278937	0.35541927	-1.02611694
N	-0.00466437	-0.64053973	-0.37442894
O	1.26480563	-0.92840673	-0.87487594
C	-1.80956937	1.04537227	-0.41180094
N	-0.19610337	0.76289327	-2.17930294
C	-2.90443137	1.42839327	-1.20779394
C	-3.94446837	2.15582227	-0.63553594
C	-3.88925137	2.51267727	0.71769006
C	-2.79514837	2.13807427	1.50496206
C	-1.75441237	1.39811927	0.94897006
C	2.30992963	-0.29336773	-0.16922094
C	3.58552363	-0.79080273	-0.43535394
C	4.63937263	-0.15201373	0.21256406
C	4.37027263	0.91973027	1.07443906
C	3.04695563	1.31260427	1.25122206
N	2.01569863	0.71068127	0.62487706
H	-0.56688737	1.59602127	-2.61787794
H	0.55557863	0.26386927	-2.64198894

H	4.20009762	-4.00946461	2.32400400	H	-2.96156437	1.11637327	-2.24561594
H	5.48457862	-3.74303861	0.21054600	H	-4.80186837	2.43484127	-1.23921194
H	4.33409662	-2.97752161	-1.85597700	H	-4.70235937	3.08088527	1.15894606
H	1.91507362	-2.46925761	-1.81753400	H	-2.75332937	2.41871027	2.55211906
H	1.39265062	1.49015339	-1.79501100	H	-0.89420737	1.12259827	1.54892206
H	1.96037462	3.46987039	-0.34408100	H	3.73093263	-1.63244673	-1.10235394
H	1.43710562	3.35301339	2.11523000	H	5.65777963	-0.49201773	0.05398906
H	0.38012262	1.27007639	3.01073700	H	5.16810863	1.43377827	1.59868906
C	-1.78177338	-1.52983961	-0.26546900	H	2.78780763	2.13535827	1.91144206
O	-2.35746838	-0.61034361	-0.77660200	Cl	-2.16120137	-2.31484473	-2.08270094
S	-2.53211438	-2.92506661	0.72871100	C	-0.48201537	-1.66257273	0.50723606
Cl	-4.90868538	-2.09700661	0.31515600	O	0.30508563	-2.28741873	1.15972006
				S	-2.31335337	-2.02535573	0.47286806
				Cl	-2.44508537	-1.76461873	2.93879506

Compound **16**



Zero-point correction = 0.226164
Thermal correction to Energy = 0.246300
Thermal correction to Enthalpy = 0.247244
Thermal correction to Gibbs Free Energy = 0.172769
E_0 = -856.455002, E = -856.434865,
H = -856.433921, G = -856.508397.
Imaginary frequency = 0.

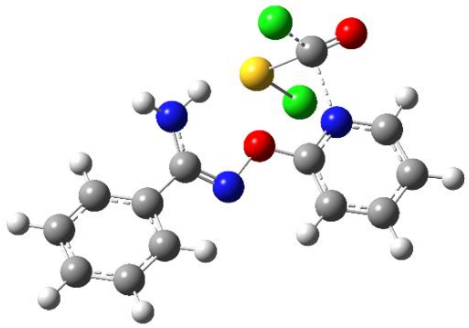


C	-1.40790663	1.93561669	-1.30706066
N	-0.62250163	2.93249369	-1.13856566
O	0.69201137	2.59358369	-1.39954266
C	-2.86390463	2.04937669	-1.15495566
N	-0.84103863	0.63133969	-1.71967666
C	-3.63874963	0.96415869	-0.70735166
C	-5.01785663	1.10930669	-0.55081266
C	-5.63305063	2.33070769	-0.83937666
C	-4.86472863	3.41344469	-1.28361766
C	-3.48813163	3.27703469	-1.44646266
C	1.60878937	3.61898069	-1.14629766
C	1.24367937	4.86831869	-0.64156666
C	2.27857937	5.78137069	-0.44039866
C	3.59423037	5.41648969	-0.74216566
C	3.82197037	4.13398369	-1.23954766
N	2.83974337	3.24014169	-1.44120366
H	-1.60096063	-0.03882731	-1.89277266
H	-0.25578900	-0.93352700	-1.49627200
H	-3.18174263	0.01702369	-0.43446766

H	-5.60692363	0.26960669	-0.19653666
H	-6.70668463	2.43876869	-0.72044766
H	-5.34059663	4.36097669	-1.51581766
H	-2.89154863	4.10686869	-1.80899866
H	0.21395537	5.10965969	-0.41729866
H	2.05448437	6.76864569	-0.04836966
H	4.42017937	6.10361969	-0.59507466
H	4.82590737	3.80036669	-1.48823266
Cl	0.92369337	-0.09756331	-3.96644866
C	0.10284637	-0.00679931	-0.69274466
O	-0.13052363	0.14334869	0.46341134
S	1.44089237	-0.99642431	-1.46603666
Cl	2.14772437	-1.92737631	0.62903634

TS1

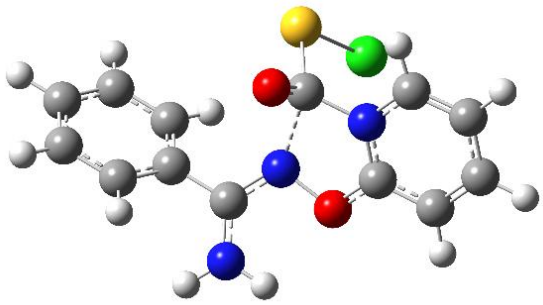
Zero-point correction = 0.224242
Thermal correction to Energy = 0.244449
Thermal correction to Enthalpy = 0.245393
Thermal correction to Gibbs Free Energy = 0.171765
E_0 = -856.454395, E = -856.434188,
H = -856.433244, G = -856.506872.
Imaginary frequency = 1.



C	-2.21418300	-0.36457900	-0.30128300
N	-1.45477600	0.60794800	0.12352000
O	-0.10096400	0.31501800	-0.26503700
C	-3.66625400	-0.24884700	-0.00002300
N	-1.77191600	-1.47963500	-0.94383700
C	-4.42495800	-1.39513400	0.28929100
C	-5.78902700	-1.28293100	0.56966500
C	-6.40697100	-0.02875300	0.56417400
C	-5.65448500	1.11588000	0.27776000
C	-4.29188200	1.00889900	-0.00433000
C	0.73881500	1.36857200	-0.15808500
C	0.33868800	2.67657600	0.15597200
C	1.31607200	3.66505200	0.19046400
C	2.65020600	3.34170800	-0.08594000
C	2.94997400	2.01676200	-0.37603000
N	2.01857600	1.05301100	-0.40421100
H	-2.43367100	-2.02559800	-1.47524500
H	-0.81146500	-1.49926100	-1.26061300
H	-3.94898300	-2.37041000	0.32079200
H	-6.36509800	-2.17446200	0.79885400
H	-7.46777000	0.05661500	0.78079400
H	-6.13049200	2.09191300	0.26619700
H	-3.70907200	1.89289400	-0.23914500
H	-0.70234400	2.88646100	0.35511000
H	1.03605300	4.68676100	0.42851200
H	3.43440800	4.08959800	-0.07222100
H	3.96370600	1.68949100	-0.59054000

TS2

Zero-point correction = 0.225568
Thermal correction to Energy = 0.243102
Thermal correction to Enthalpy = 0.244046
Thermal correction to Gibbs Free Energy = 0.177913
E_0 = -841.315042, E = -841.297508,
H = -841.296564, G = -841.362697.
Imaginary frequency = 1.

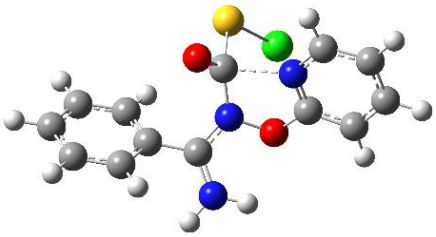


C	-1.10578023	-0.88389664	-0.36046030
N	-0.00622723	-0.14677964	-0.38456330
O	1.11714077	-0.94798864	-0.78532830
C	-2.36201223	-0.17223064	-0.04022830
N	-1.13283423	-2.19613664	-0.60722130
C	-3.32274123	-0.78224564	0.78603470
C	-4.50988023	-0.11166064	1.07906270
C	-4.74653623	1.16163736	0.54873170
C	-3.79242323	1.76797636	-0.27443630
C	-2.59937323	1.10734236	-0.56941530
C	2.22014577	-0.54075464	-0.17100530
C	3.46067777	-1.09189864	-0.50871930
C	4.58201977	-0.66725564	0.17855270
C	4.47001577	0.30409436	1.19642170
C	3.23700977	0.82402136	1.48827470
N	2.12494677	0.40180636	0.79904270
H	-2.01446423	-2.66763864	-0.74940630
H	-0.28451823	-2.70667464	-0.80988530
H	-3.13353023	-1.75957964	1.21910170
H	-5.24593223	-0.57969164	1.72495070
H	-5.67373623	1.67883936	0.77623270
H	-3.97901023	2.75196036	-0.69288430
H	-1.86596023	1.56391736	-1.22401530
H	3.50030477	-1.83448564	-1.29595430
H	5.55205677	-1.08454164	-0.06861730
H	5.33598677	0.64809936	1.74762170
H	3.06206277	1.57454836	2.24840470

Cl	1.81607400	-1.51589700	-2.13591500	C	0.81013877	0.96609336	1.23301570
C	2.94707100	-0.86888700	-0.68864300	O	0.31035977	0.64313136	2.27861270
O	4.07405800	-0.56803400	-0.89361100	S	0.47861677	2.71326936	0.69255270
S	2.23738900	-1.81992800	0.73508500	Cl	1.48341077	2.83946036	-1.33118430
Cl	3.65746600	-1.15917400	2.38115600				

TS3

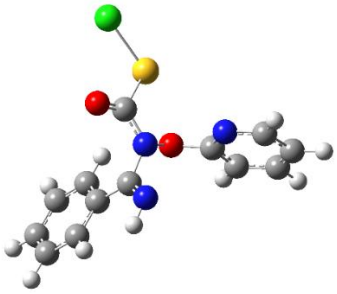
Zero-point correction = 0.226024
Thermal correction to Energy = 0.243303
Thermal correction to Enthalpy = 0.244247
Thermal correction to Gibbs Free Energy = 0.178963
E_0 = -841.307657, E = -841.290378,
H = -841.289434, G = -841.354718.
Imaginary frequency = 1.



C	-0.67796680	-0.73171181	-0.43941968
N	0.43230120	-0.01810881	-0.13270768
O	1.56638520	-0.36665581	-0.87851768
C	-1.99845080	-0.30062581	0.04237532
N	-0.57148280	-1.77053281	-1.24080068
C	-2.90408480	-1.26580781	0.51730032
C	-4.17651680	-0.87006281	0.92530632
C	-4.55165180	0.47549419	0.84599332
C	-3.65271180	1.43243919	0.36184932
C	-2.37305280	1.05240419	-0.03609968
C	2.66368220	-0.57612181	-0.05215868
C	3.82262320	-1.15834681	-0.55143268
C	4.87140520	-1.27522081	0.36012332
C	4.72040020	-0.82260581	1.68054632
C	3.51238620	-0.24989281	2.06067432
N	2.50659520	-0.14067981	1.17571332
H	-1.40643380	-2.21061681	-1.60625268
H	0.32765920	-2.09316281	-1.57885068
H	-2.60601180	-2.30619481	0.59943732
H	-4.87152580	-1.60974781	1.30873232
H	-5.54523680	0.77846619	1.16123032
H	-3.94866980	2.47387719	0.29073732
H	-1.68307780	1.79282819	-0.42621968
H	3.89307120	-1.49159981	-1.57954268
H	5.80721420	-1.72268881	0.04223932
H	5.52767020	-0.91156481	2.39793832
H	3.32694820	0.12898619	3.06036632
C	0.61791120	0.76708319	1.09250232
O	-0.04004680	0.56409219	2.08380932

TS4

Zero-point correction = 0.212846
Thermal correction to Energy = 0.230046
Thermal correction to Enthalpy = 0.230990
Thermal correction to Gibbs Free Energy = 0.164468
E_0 = -840.896231, E = -840.879031,
H = -840.878087, G = -840.944609.
Imaginary frequency = 1.

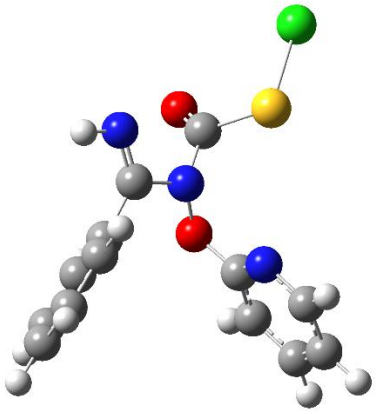


C	-1.01741300	-0.80059900	1.08205200
N	0.03405800	0.05686400	0.53885600
O	0.66568000	-0.43214700	-0.62041300
C	-2.30504500	-0.81478000	0.33706500
N	-0.68404500	-1.43717800	2.13092200
C	-3.42326300	-1.47821700	0.87756000
C	-4.63564700	-1.49845300	0.19226800
C	-4.75439800	-0.85826200	-1.04718500
C	-3.65232000	-0.19586000	-1.59278500
C	-2.43740300	-0.16952900	-0.90546100
C	1.84306500	-1.17318700	-0.37192600
C	2.15095900	-2.12818000	-1.34014300
C	3.34389200	-2.82731100	-1.16263400
C	4.13911000	-2.54993900	-0.04505100
C	3.70719800	-1.57354200	0.85161400
N	2.56680900	-0.87937500	0.68524700
H	-1.44534700	-2.03445600	2.46120000
H	-3.36170800	-1.97051700	1.84306300
H	-5.48927200	-2.00847400	0.62773500
H	-5.70057200	-0.87395200	-1.57958100
H	-3.73462800	0.30433300	-2.55266400
H	-1.59476400	0.34423700	-1.35288700
H	1.48728300	-2.30781700	-2.17798700
H	3.64143000	-3.58451500	-1.88108900
H	5.06963300	-3.07890600	0.12922300
H	4.29075300	-1.32647300	1.73420800
C	0.02470300	1.41248700	0.64652500
O	-0.58910800	2.05872500	1.45782200
S	1.13947500	2.13570700	-0.71058200
Cl	0.98086200	4.30015700	-0.07045500

S	1.10150620	2.57060019	0.93547132	
Cl	2.29033120	2.80902419	-0.98644968	

TS5

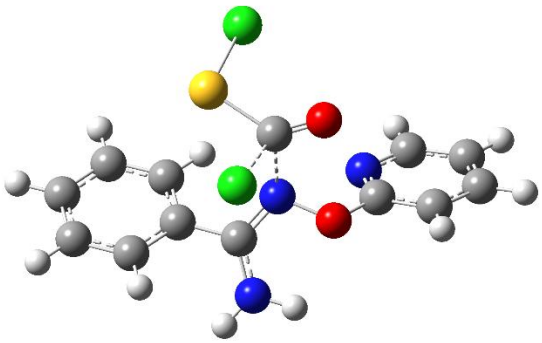
Zero-point correction = 0.212038
Thermal correction to Energy = 0.229483
Thermal correction to Enthalpy = 0.230427
Thermal correction to Gibbs Free Energy = 0.162608
E_0 = -840.887256, E = -840.869812,
H = -840.868868, G = -840.936686.
Imaginary frequency = 1.



C	-1.53057747	-0.29240745	0.08455596
N	-0.69420247	0.78562455	0.48230996
O	-1.23902447	1.76718755	1.32136096
C	-3.00720547	-0.09524545	0.16371496
N	-0.92158747	-1.32094845	-0.36451104
C	-3.76289147	-0.21294545	-1.01390804
C	-5.15522747	-0.11499545	-0.96535104
C	-5.80126647	0.08748655	0.25813996
C	-5.05107647	0.19539155	1.43406696
C	-3.65784847	0.11193855	1.39052396
C	-1.51068547	2.98925755	0.69197696
C	-1.87895347	4.01726755	1.56664396
C	-2.18796647	5.24406455	0.98962496
C	-2.10998147	5.38800955	-0.40303004
C	-1.72344547	4.28616555	-1.15893904
N	-1.42752247	3.08716355	-0.61706804
H	-1.58571747	-2.03415545	-0.66227304
H	-3.26006247	-0.36763045	-1.96394204
H	-5.73223247	-0.19699645	-1.88152204
H	-6.88424747	0.15917155	0.29584496
H	-5.54972947	0.34476155	2.38705596
H	-3.08121347	0.19624155	2.30526396
H	-1.91395047	3.84987855	2.63703296
H	-2.48009547	6.08018155	1.61719896

TS6

Zero-point correction = 0.223817
Thermal correction to Energy = 0.244196
Thermal correction to Enthalpy = 0.245140
Thermal correction to Gibbs Free Energy = 0.170804
E_0 = -856.445949, E = -856.425570,
H = -856.424626, G = -856.498963.
Imaginary frequency = 1.

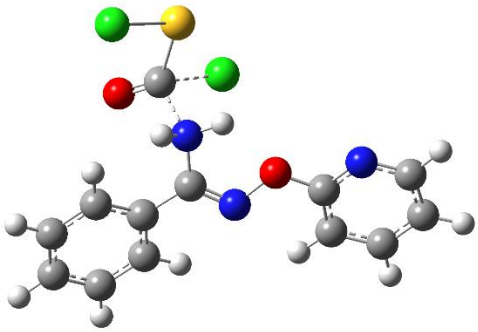


C	0.42548565	-1.45360412	-0.19016344
N	-0.47107035	-0.48246712	-0.23196544
O	-1.68596535	-0.97118412	-0.77565344
C	1.75383265	-1.15972412	0.39651056
N	0.18317765	-2.70036612	-0.61944244
C	2.92272165	-1.65735612	-0.20310844
C	4.16376965	-1.41810412	0.38870856
C	4.24313965	-0.69415812	1.58374756
C	3.07932065	-0.20305712	2.18454356
C	1.83629165	-0.42947912	1.59259956
C	-2.80737735	-0.69829912	-0.01528744
C	-4.02803535	-0.79567812	-0.69958544
C	-5.18682335	-0.58275912	0.03675256
C	-5.08616135	-0.27613912	1.40164656
C	-3.81598635	-0.20364812	1.96473156
N	-2.68091335	-0.42087712	1.27108256
H	0.82050565	-3.45022412	-0.39660144
H	-0.71925435	-2.92976312	-1.01190244
H	2.86521965	-2.20463612	-1.13907544
H	5.06665465	-1.79211012	-0.08409944
H	5.20977365	-0.51423712	2.04497756
H	3.13854365	0.35548788	3.11363456
H	0.92905565	-0.05679012	2.05481656
H	-4.04563435	-1.01937412	-1.76025844
H	-6.15693335	-0.64468912	-0.44698244
H	-5.96761535	-0.09628612	2.00744156

H	-2.34099547	6.33096555	-0.88617304	H	-3.68755835	0.03219488	3.01837056
H	-1.64541147	4.34892255	-2.24100804	Cl	0.82101765	0.60076788	-2.84442044
C	0.66741453	0.50995155	0.87711196	C	-0.27852535	1.31948688	-1.27632844
O	1.04712453	-0.00802245	1.88413396	O	-1.40244135	1.63179988	-1.44872944
S	1.63723353	1.22796555	-0.47965104	S	1.12132465	2.21769188	-0.49990144
Cl	3.76866053	0.75743055	0.17226096	Cl	0.06411765	3.18952988	1.28001956

TS7

Zero-point correction = 0.225351
Thermal correction to Energy = 0.245378
Thermal correction to Enthalpy = 0.246322
Thermal correction to Gibbs Free Energy = 0.171557
E_0 = -856.437641, E = -856.417614,
H = -856.416670, G = -856.491434.
Imaginary frequency = 1.



C	-0.67447414	2.63734458	-0.74469855
N	0.60619586	2.77051358	-0.66171755
O	1.26644086	1.56746158	-0.90169955
C	-1.54035714	3.82046558	-0.56819855
N	-1.27114014	1.35633558	-0.99146955
C	-2.87018114	3.83328858	-1.02219255
C	-3.65455714	4.97961458	-0.87762555
C	-3.12591714	6.12266458	-0.27439255
C	-1.80367414	6.11499658	0.18720845
C	-1.01567614	4.97632958	0.04251345
C	2.64307486	1.63422558	-0.74304255
C	3.30434686	2.73628758	-0.19244155
C	4.69105986	2.64366458	-0.08501055
C	5.34493486	1.48420958	-0.51443355
C	4.56909586	0.45274058	-1.04118855
N	3.23265386	0.52287358	-1.15931155
H	-2.01360414	1.39902658	-1.69168955
H	-0.56126514	0.68561558	-1.29406555
H	-3.31817914	2.96499558	-1.49288855
H	-4.67922614	4.97302858	-1.23561955
H	-3.73914014	7.01117958	-0.15854355
H	-1.38871214	6.99607458	0.66709845
H	0.00446586	4.96921158	0.40895345
H	2.76033586	3.61195858	0.13298745
H	5.25338086	3.47158358	0.33603945
H	6.42204286	1.38087658	-0.44219155
H	5.02814386	-0.46982142	-1.38718855

Cl	-0.50471014	0.12509158	1.60566145	
C	-2.16656114	0.57560158	0.47400645	
O	-2.98348614	1.31019658	0.91984445	
S	-2.37944214	-1.19883442	-0.09674855	
Cl	-4.21665914	-0.92151142	-1.45392455	

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