Supporting Information

Regioselective 5-*exo-dig* (halo)cyclization of N-propargyloxycarbonyl guanidine derivatives under mild condition

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1. Methods and materials

All chemicals were used as received unless otherwise stated. ^{1}H NMR and ^{13}C NMR spectra were collected on Bruker AVANCE III HD400. Proton chemical shifts of NMR spectra were calibrated with TMS as internals reference. HRMS spectral data were recorded on Aglient 7250 and JEOL-JMS-T100LPAccuTOF devices. Analytical thin-layer chromatography (TLC) analysis was performed on TLC silica gel plates (0.2 ± 0.03 mm) and visualized with ultraviolet light (254 nm) to monitor the reaction progression.

2. X-ray crystal structure analysis

Procedure

The single crystals of compounds **3a**, **3i, 4m, 5b** and **6g** were obtained by slow evaporation of their solution in DCM / PE (2:5), DCM / PE (3:10), Et_2O/ DCM/ PE (1:2:20), MeOH/ PE (1:5) and Et_2O/ DCM/ PE (5:3:10) at room temperature, respectively. The X-ray crystallographic data were collected on BrukerD8 VENTURE METALJET Ga-Target SC-XRD, and deposited in Cambridge Crystallographic Data Centre (CCDC) with deposition numbers of 2251361, 2251367, 2251362, 2251368 and 2251364, respectively. These data can be obtained free of charge from CCDC via https://www.ccdc.cam.ac.uk/structures/

2.1. Crystallographic Information for Compound 3a

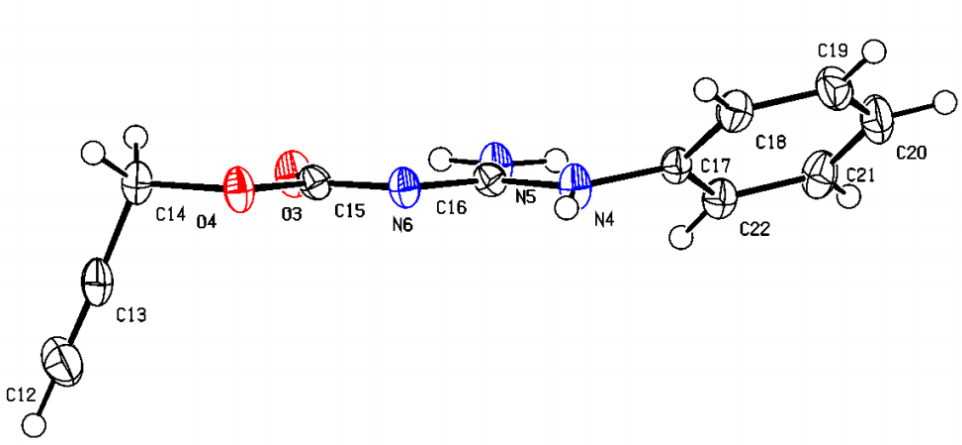


Figure S1. ORTEP of **3a** (at 50% level).

Table S1 Crystal data and structure refinement for compound **3a** (CDCC2251361).

Identification code	**3a**
Empirical formula	$C_{11}H_{11}N_3O_2$
Formula weight	217.23
Temperature/K	298.00
Crystal system	triclinic
Space group	P-1
a/Å	8.7766(8)
b/Å	9.6982(9)

c/Å	13.2431(13)
α/°	99.818(4)
β/°	98.950(4)
γ/°	101.433(4)
Volume/Å^3	1067.53(18)
Z	4
ρ_{calc}g/cm^3	1.352
μ/mm^{-1}	0.096
F(000)	456.0
Crystal size/mm^3	0.15 × 0.12 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.38 to 54.98
Index ranges	-11 ≤ h ≤ 10, -12 ≤ k ≤ 12, -17 ≤ l ≤ 17
Reflections collected	14132
Independent reflections	4746 [R_{int} = 0.0493, R_{sigma} = 0.0524]
Data/restraints/parameters	4746/0/289
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0442, wR_2 = 0.1135
Final R indexes [all data]	R_1 = 0.0589, wR_2 = 0.1217
Largest diff. peak/hole / e Å^{-3}	0.36/-0.32

2.2. Crystallographic Information for Compound 3i

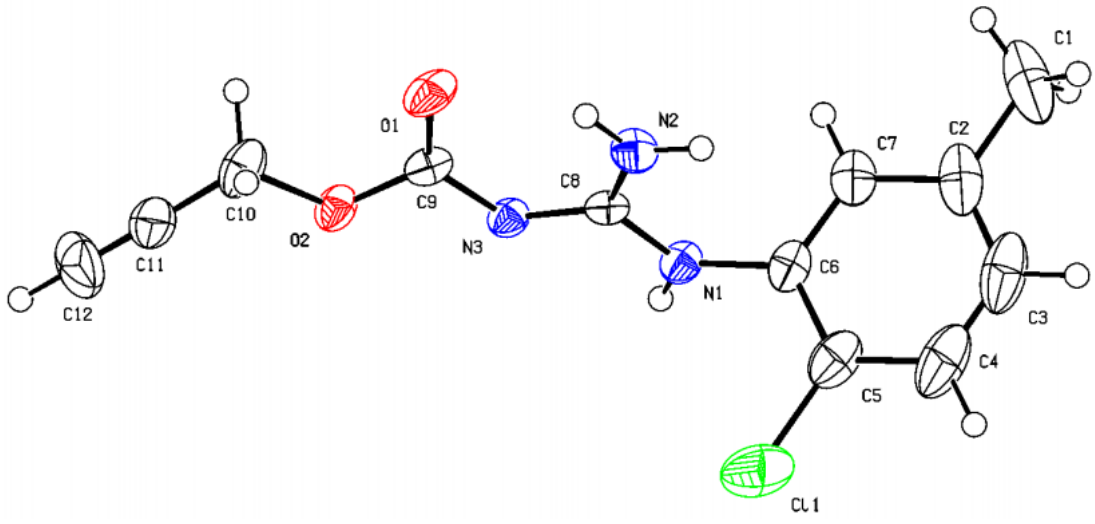


Figure S2. ORTEP of **3i** (at 50% level).

Table S2 Crystal data and structure refinement for compound **3i** (CDCC2251367).

Identification code	**3i**

Empirical formula	$C_{12}H_{13}ClN_3O_2$
Formula weight	266.70
Temperature/K	150.00
Crystal system	tetragonal
Space group	$P4_12_12$
a/Å	9.38970(10)
b/Å	9.38970(10)
c/Å	28.9002(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2548.03(8)
Z	8
ρ_{calc}g/cm^3	1.390
μ/mm^{-1}	0.298
F(000)	1112.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.562 to 54.874
Index ranges	-12 ≤ h ≤ 12, -11 ≤ k ≤ 11, -24 ≤ l ≤ 36
Reflections collected	23658
Independent reflections	2838 [R_{int} = 0.0579, R_{sigma} = 0.0283]
Data/restraints/parameters	2838/0/164
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0441, wR_2 = 0.1101
Final R indexes [all data]	R_1 = 0.0499, wR_2 = 0.1133
Largest diff. peak/hole / e Å^{-3}	0.14/-0.57
Flack parameter	-0.95(4)

2.3. Crystallographic Information for Compound 4m

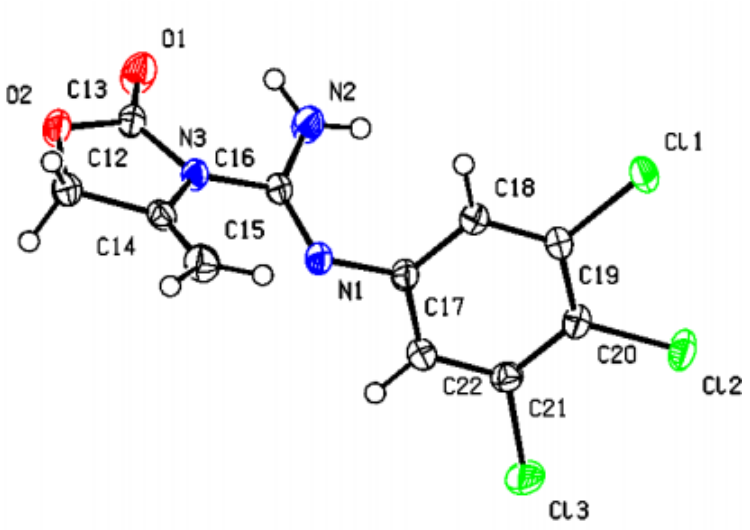


Figure S3. ORTEP of **4m** (at 50% level).

Table S3 Crystal data and structure refinement for compound **4m** (CDCC2251362).

Identification code	**4m**
Empirical formula	$C_{11}H_8Cl_3N_3O_2$
Formula weight	320.55
Temperature/K	200.00
Crystal system	triclinic
Space group	P-1
a/Å	7.5748(3)
b/Å	12.5331(4)
c/Å	13.9255(5)
α/°	91.8130(10)
β/°	97.6170(10)
γ/°	102.8260(10)
Volume/Å^3	1275.11(8)
Z	4
ρ_{calc}g/cm^3	1.670
μ/mm^{-1}	0.718
F(000)	648.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.956 to 59.21
Index ranges	-10 ≤ h ≤ 9, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19
Reflections collected	20912

Independent reflections	6864 [R_{int} = 0.0476, R_{sigma} = 0.0534]
Data/restraints/parameters	6864/0/343
Goodness-of-fit on F^2	0.991
Final R indexes [I>=2σ (I)]	R_1 = 0.0423, wR_2 = 0.1151
Final R indexes [all data]	R_1 = 0.0452, wR_2 = 0.1177
Largest diff. peak/hole / e $Å^{-3}$	0.53/-0.50

2.4. Crystallographic Information for Compound 5b

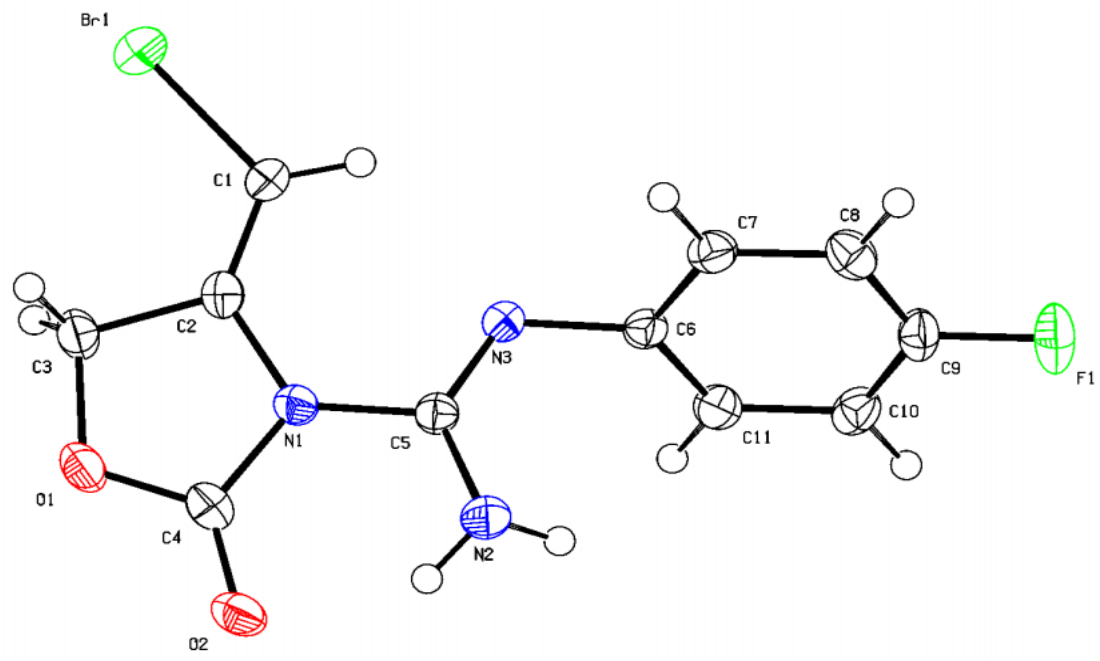


Figure S4. ORTEP of **5b** (at 50% level).

Table S4 Crystal data and structure refinement for compound **5b** (CDCC2251368).

Identification code	**5b**
Empirical formula	$C_{11}H_9BrFN_3O_2$
Formula weight	314.12
Temperature/K	298.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.3126(16)
b/Å	6.7487(10)
c/Å	16.077(2)
α/°	90
β/°	109.264(5)
γ/°	90
Volume/$Å^3$	1158.7(3)

Z	4
ρ_{calc}g/cm^3	1.801
μ/mm^{-1}	3.558
F(000)	624.0
Crystal size/mm^3	0.2 × 0.16 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.368 to 52.744
Index ranges	-14 ≤ h ≤ 14, -8 ≤ k ≤ 7, -20 ≤ l ≤ 14
Reflections collected	9147
Independent reflections	2340 [R_{int} = 0.0457, R_{sigma} = 0.0460]
Data/restraints/parameters	2340/0/164
Goodness-of-fit on F^2	1.131
Final R indexes [I>=2σ (I)]	R_1 = 0.0361, wR_2 = 0.1091
Final R indexes [all data]	R_1 = 0.0388, wR_2 = 0.1118
Largest diff. peak/hole / e Å^{-3}	0.49/-0.77

2.5. Crystallographic Information for Compound 6g

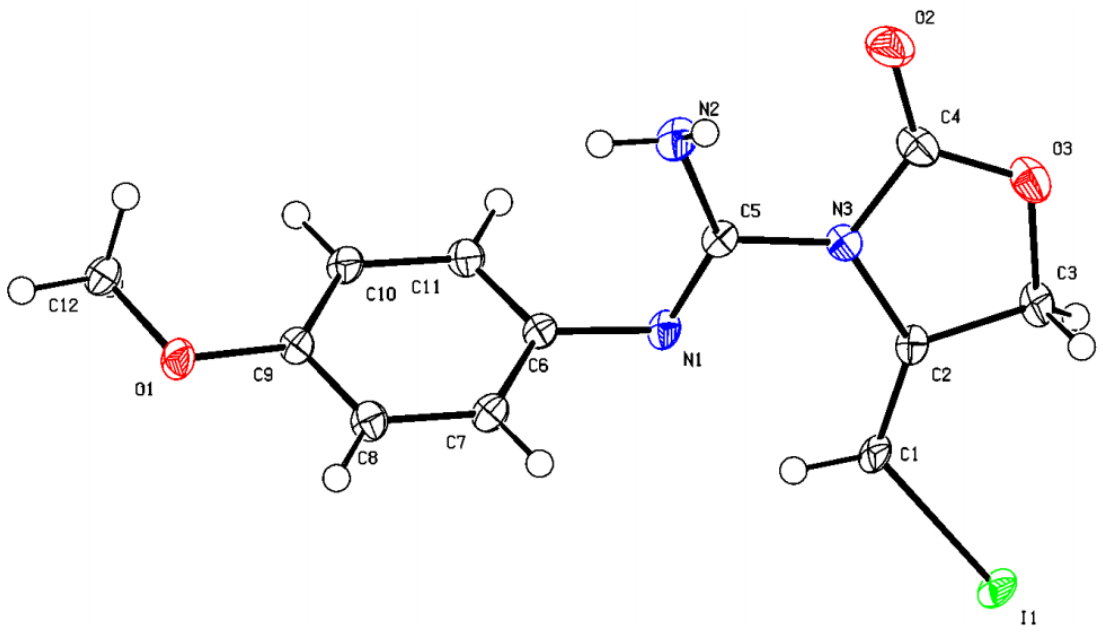


Figure S5. ORTEP of **6g** (at 50% level).

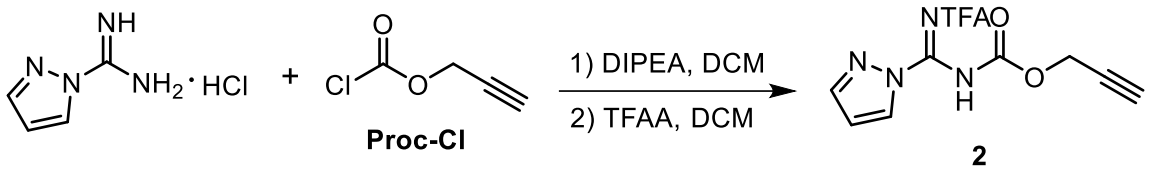
Table S5 Crystal data and structure refinement for compound **6g** (CDCC2251364).

Identification code	**6g**
Empirical formula	$C_{12}H_{12}IN_3O_3$
Formula weight	373.15

Temperature/K	150.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.4737(4)
b/Å	7.2411(2)
c/Å	15.4718(5)
α/°	90
β/°	106.0440(10)
γ/°	90
Volume/Å^3	1343.03(7)
Z	4
ρ_{calc}g/cm^3	1.845
μ/mm^{-1}	2.392
F(000)	728.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.728 to 54.962
Index ranges	$-15 \leq h \leq 15$, $-6 \leq k \leq 9$, $-19 \leq l \leq 19$
Reflections collected	9658
Independent reflections	2930 [R_{int} = 0.0619, R_{sigma} = 0.0678]
Data/restraints/parameters	2930/253/174
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	R_1 = 0.0542, wR_2 = 0.1479
Final R indexes [all data]	R_1 = 0.0633, wR_2 = 0.1549
Largest diff. peak/hole / e Å^{-3}	1.43/-2.42

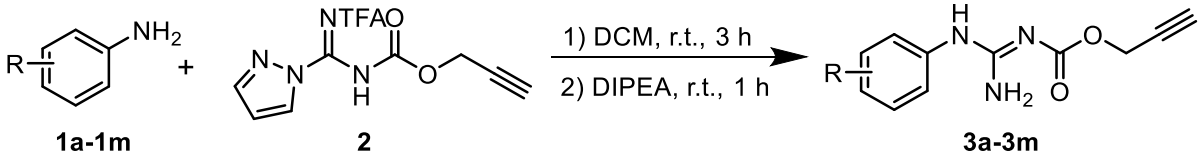
3. Compound Synthesis

3.1. Synthesis of Compound 2

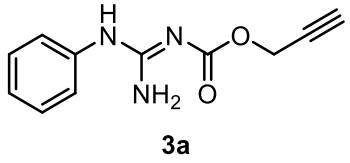


General procedure: Compound **2** was synthesized via literature procedure with modifications. [1] A solution of 1H-pyrazole-1-carboxamidine hydrochloride (1.0 equiv) and DIPEA (N,N-diisopropylethylamine, 3.0 equiv) in DCM was stirred at room temperature for approximately 20 min. Then **Proc-Cl** (propargyloxycarbonyl chloride, 2.0 equiv) was added in, and it was further stirred for approximately 1 h. The reaction mixture was diluted with DCM, washed with H_2O and brine, dried over anhydrous Na_2SO_4, and concentrated under vacuum. Then, a solution of the obtained condensed crude (1.0 equiv) and TFAA (trifluoroacetic anhydride, 2.0 equiv) in DCM was stirred at room temperature for approximately 30 min. The reaction mixture was diluted with DCM, and washed with H_2O and brine. After being dried over anhydrous Na_2SO_4, the obtained crude was concentrated under vacuum to afford compound **2**. Due to the instability of compound **2** over silica gel, it was used directly in the next step without further purification.

3.2. Synthesis of Compounds 3a-3m

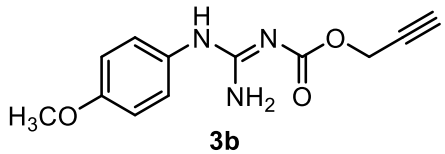


General procedure: A solution of aromatic amine **1a−1m** (1.0 equiv) and compound **2** (1.5 equiv) in DCM was stirred at room temperature for approximately 3 h. Then DIPEA (3.0 equiv) was added in, and the mixture was stirred for additional 1 h. The reaction mixture was diluted with DCM, washed with H_2O and brine, and dried over anhydrous Na_2SO_4. The obtained crude was concentrated under vacuum and purified by silica gel column chromatography to afford the target compounds **3a-3m.**



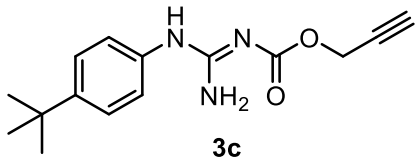
1-Propargyloxycarbonyl-2-phenylguanidine (compound **3a**) was obtained as a white solid after purification through silica gel column chromatography (PE/EtOAc 2:1). ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.41 (m, 2H), 7.29 (m, 3H), 4.45 (d, J = 2.4 Hz, 2H), 2.33 (t, J = 2.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.9, 160.9, 136.2, 129.8, 127.0, 126.2, 79.1, 73.6, 51.7; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{12}N_3O_2$ 218.0924; found 218.0928.



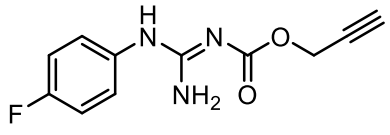
3b

1-Propargyloxycarbonyl-2-(4'-methoxyphenyl)guanidine (compound **3b**) was obtained as a white solid after purification through silica gel column chromatography (PE/EtOAc 1:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (m, 2H), 6.93 (m, 2H), 4.49 (d, J = 2.4 Hz, 2H), 3.82 (s, 3H), 2.35 (t, J = 2.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 163.0, 161.5, 158.8, 128.3, 128.1, 115.0, 79.2, 73.5, 55.5, 51.8; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{14}N_3O_3$ 248.1030; found 248.1026.



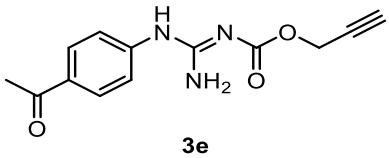
3c

1-Propargyloxycarbonyl-2-(4'-(tert-butyl)phenyl)guanidine (compound **3c**) was obtained as a white solid after purification through silica gel column chromatography (PE/EtOAc 3:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (m, 2H), 7.24 (m, 2H), 4.51 (d, J = 2.4 Hz, 2H), 2.36 (t, J = 2.4 Hz, 1H), 1.35 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 163.0, 161.1, 150.2, 133.2, 126.7, 125.7, 79.2, 73.5, 51.7, 34.6, 31.3; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{20}N_3O_2$ 274.1550; found 274.1548.



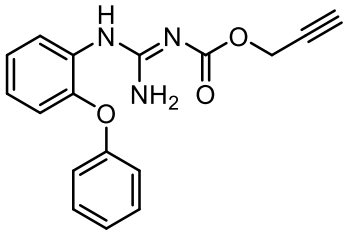
3d

1-Propargyloxycarbonyl-2-(4'-fluorophenyl)guanidine (compound **3d**) was obtained as a white solid after purification through silica gel column chromatography (PE/EtOAc 1:1). ^1H NMR (400 MHz, d_6-DMSO) δ 9.07 (br, 1H), 7.44 (m, 2H), 7.15 (m, 2H), 4.58 (d, J = 2.4 Hz, 2H), 3.42 (t, J = 2.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, d_6-DMSO) δ 162.8, 160.1, 158.9 (d, J = 241.1Hz), 135.0 (d, J = 2.9 Hz), 124.4 (d, J = 8.4 Hz), 115.8 (d, J = 22.6 Hz), 80.4, 77.0, 52.1; ^{19}F NMR (376 MHz, d_6-DMSO) δ -119.31 (s, 1F); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{11}FN_3O_2$ 236.0830; found 236.0825.



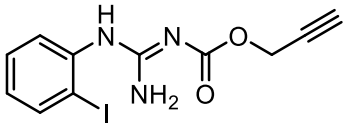
3e

1-Propargyloxycarbonyl-2-(4'-acetylphenyl)guanidine (compound **3e**) was obtained as a white solid after purification through silica gel column chromatography (PE/EtOAc 1:1). ^{1}H NMR (400 MHz, d_6-DMSO) δ 9.36 (br, 1H), 7.89 (m, 2H), 7.64 (m, 2H), 4.63 (d, J = 2.4 Hz, 2H), 3.43 (t, J = 2.8 Hz, 1H), 2.52 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, d_6-DMSO) δ 197.0, 162.6, 159.4, 143.8, 131.7, 129.8, 120.2, 80.3, 77.1, 52.4, 26.9; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{14}N_3O_3$ 260.1030; found 260.1021.



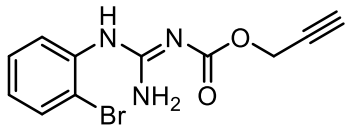
3f

1-Propargyloxycarbonyl-2-(2'-phenoxyphenyl)guanidine (compound **3f**) was obtained as a yellow liquid after purification through silica gel column chromatography (PE/EtOAc 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, J = 7.6, 4.0 Hz, 1H), 7.32 (m, 2H), 7.24 (m, 1H), 7.17 (m, 1H), 7.11 (t, J = 7.2 Hz, 1H), 6.98 (m, 3H), 4.55 (d, J = 2.4 Hz, 2H), 2.37 (t, J = 2.4 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.7, 160.3, 156.4, 151.4, 129.8, 128.0, 127.6, 127.4, 124.2, 123.8, 119.7, 118.6, 79.0, 73.7, 51.9; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}N_3O_3$ 310.1186; found 310.1191.



3g

1-Propargyloxycarbonyl-2-(2'-iodophenyl)guanidine (compound **3g**) was obtained as a white solid after purification through silica gel column chromatography (PE/EtOAc 1:1). ^{1}H NMR (400 MHz, d_6-DMSO) δ 9.02 (br, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.38 (m, 2H), 6.97 (m, 1H), 4.56 (d, J = 2.4 Hz, 2H), 3.42 (t, J = 2.4 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, d_6-DMSO) δ 161.8, 158.7, 141.0, 139.3, 129.4, 128.1, 127.8, 97.8, 80.2, 77.1, 52.1; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{11}IN_3O_2$ 343.9890; found 343.9880.

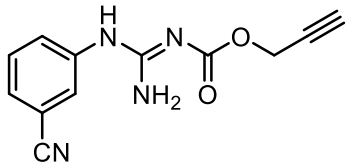


3h

1-Propargyloxycarbonyl-2-(2'-bromophenyl)guanidine (compound **3h**) was obtained as a brown solid after purification through silica gel column chromatography (PE/EtOAc 1:1). ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.91 (br, 1H), 7.65 (dd, J = 8.0, 1.6 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.36 (m, 1H), 7.11 (m, 1H), 4.57 (d, J = 2.4 Hz, 2H), 3.43 (t, J = 2.4 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, d_6-DMSO) δ 161.9, 159.0, 137.4, 133.1, 128.6, 128.2, 127.1, 119.1, 80.2, 77.1, 52.1; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{11}BrN_3O_2$ 296.0029; found 296.0023.

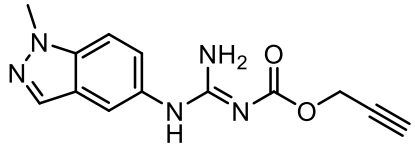
3i

1-Propargyloxycarbonyl-2-(2'-chloro-5'-methylphenyl)guanidine (compound **3i**) was obtained as a white solid after purification through silica gel column chromatography (PE/EtOAc 3:1). ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.94 (br, 1H), 7.46 (s, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.00 (dd, J = 8.0, 2.0 Hz, 1H), 4.58 (d, J = 2.4 Hz, 2H), 3.43 (t, J = 2.4 Hz, 1H), 2.29 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, d_6-DMSO) δ 162.0, 159.4, 137.6, 135.4, 129.5, 128.2, 127.4, 125.0, 80.3, 77.1, 52.2, 20.4; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{13}ClN_3O_2$ 266.0691; found 266.0687.



3j

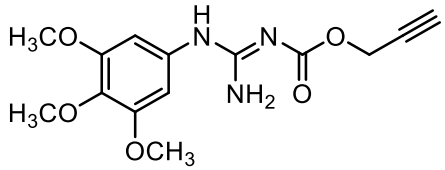
1-Propargyloxycarbonyl-2-(3'-cyanophenyl)guanidine (compound **3j**) was obtained as a white solid after purification through silica gel column chromatography (PE/EtOAc 1:1). ^{1}H NMR (400 MHz, d_6-DMSO) δ 9.31 (br, 1H), 8.05 (s, 1H), 7.67 (m, 1H), 7.50 (m, 2H), 4.61 (d, J = 2.4 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, d_6-DMSO) δ 162.5, 159.4, 140.2, 130.5, 127.0, 126.1, 124.3, 119.3, 111.9, 80.3, 77.1, 52.3; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{11}N_4O_2$ 243.0877; found 243.0869.



3k

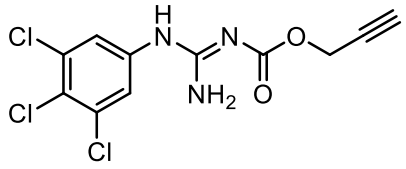
1-Propargyloxycarbonyl-2-(1'-methyl-1H-indazol-5'-yl)guanidine (compound **3k**) was

obtained as a white solid after purification through silica gel column chromatography (EtOAc). ^{1}H NMR (400 MHz, d_6-DMSO) δ 9.15 (br, 1H), 8.01 (s, 1H), 7.79 (d, J = 2.0 Hz 1H), 7.60 (d, J = 9.2 Hz, 1H), 7.31 (dd, J = 8.8, 2.0 Hz, 1H), 4.57 (d, J = 2.4 Hz, 2H), 4.03 (s, 3H), 3.41 (t, J = 2.4 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, d_6-DMSO) δ 162.5, 160.7, 137.8, 132.7,131.1, 124.0, 123.9, 114.7, 110.4, 80.6, 76.9, 52.0, 35.9; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{13}H_{14}N_5O_2$ 272.1142; found 272.1133.



3l

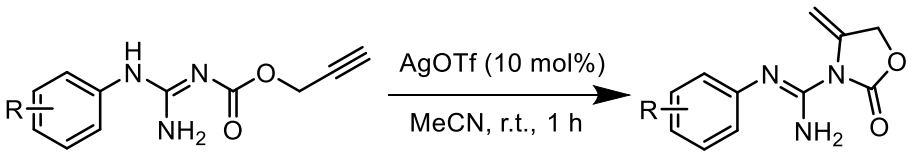
1-Propargyloxycarbonyl-2-(3',4',5'-trimethoxyphenyl)guanidine (compound **3l**) was obtained as a white solid after purification through silica gel column chromatography (PE/EtOAc 1:1). ^{1}H NMR (400 MHz, d_6-DMSO) δ 9.17 (br, 1H), 6.70 (s, 2H), 4.60 (d, J = 2.4 Hz, 2H), 3.76 (s, 6H), 3.64 (s, 3H), 3.40 (t, J = 2.4 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, d_6-DMSO) δ 162.8, 160.1, 153.3, 134.7, 134.2, 100.9, 80.5, 76.9, 60.5, 56.3, 52.2; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{14}H_{18}N_3O_5$ 308.1241; found 308.1249.



3m

1-Propargyloxycarbonyl-2-(3',4',5'-trichlorophenyl)guanidine (compound **3m**) was obtained as a brown solid after purification through silica gel column chromatography (PE/EtOAc 2:1). ^{1}H NMR (400 MHz, d_6-DMSO) δ 9.42 (br, 1H), 7.77 (s, 2H), 4.64 (d, J = 2.4 Hz, 2H), 3.47 (t, J = 2.4 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, d_6-DMSO) δ 162.0, 158.6, 140.6, 133.0, 123.3, 121.4, 80.1, 77.4, 52.4; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{11}H_9Cl_3N_3O_2$ 319.9755; found 319.9752.

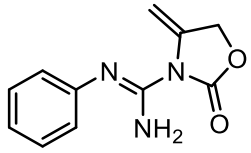
3.3. Synthesis of Compounds 4a-4m



3a-3m **4a-4m**

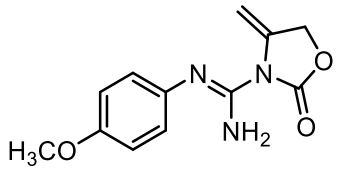
General procedure: A solution of compound **3a−3m** (1.0 equiv) and AgOTf (0.1 equiv) in MeCN was stirred at room temperature for 1 h. Then the reaction mixture was concentrated under vacuum, and the obtained crude was purified by silica gel column chromatography to

afford the target compound **4a-4m**.



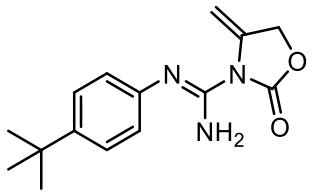
4a

4-Methylene-2-oxo-N'-phenyloxazolidine-3-carboximidamide (compound **4a**) was obtained in 94% yield (198 mg, 0.97 mmol) as a white liquid after purification through silica gel column chromatography (PE/EtOAc 7:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 2H), 7.07 (m, 1H), 6.94 (m, 2H), 6.09 (q, *J* = 2.4 Hz, 1H), 5.85 (br, 2H), 4.95 (t, *J* = 2.4 Hz, 2H), 4.66 (q, *J* = 2.0 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.3, 146.9, 145.2, 135.7, 129.7, 123.4, 121.8, 93.4, 67.3; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{12}N_3O_2$ 218.0924; found 218.0918.



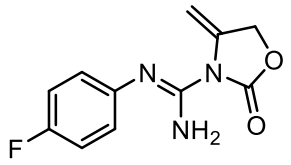
4b

N'-(4'-methoxyphenyl)-4-methylene-2-oxooxazolidine-3-carboximidamide (compound **4b**) was obtained in 78% yield (194 mg, 1.01 mmol) as a white liquid after purification through silica gel column chromatography (PE/EtOAc 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (m, 4H), 6.07 (q, *J* = 2.4 Hz, 1H), 5.84 (br, 2H), 4.94 (t, *J* = 2.4 Hz, 2H), 4.64 (q, *J* = 2.0 Hz, 1H), 3.79 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.3, 155.8, 145.6, 139.9, 135.8, 122.6, 115.0, 93.2, 67.3, 55.5; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{14}N_3O_3$ 248.1030; found 248.1033.



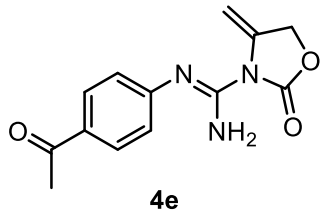
4c

N'-(4'-(tert-butyl)phenyl)-4-methylene-2-oxooxazolidine-3-carboximidamide (compound **4c**) was obtained in 80% yield (218 mg, 1.00 mmol) as a white liquid after purification through silica gel column chromatography (PE/EtOAc 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (m, 2H), 6.88 (m, 2H), 6.09 (q, *J* = 2.4 Hz, 1H), 5.86 (br, 2H), 4.94 (t, *J* = 2.4 Hz, 2H), 4.64 (q, *J* = 2.0 Hz, 1H), 1.32 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.3, 146.2, 145.2, 144.1, 135.8, 126.5, 121.2, 93.3, 67.3, 34.3, 31.5; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{20}N_3O_2$ 274.1550; found 274.1546.



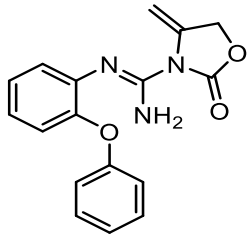
4d

N'-(4'-fluorophenyl)-4-methylene-2-oxooxazolidine-3-carboximidamide (compound **4d**) was obtained in 76% yield (177 mg, 0.99 mmol) as a white liquid after purification through silica gel column chromatography (PE/EtOAc 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (m, 2H), 6.89 (m, 2H), 6.06 (q, *J* = 2.4Hz, 1H), 5.87 (br, 2H), 4.95 (t, *J* = 2.4 Hz, 2H), 4.66 (q, *J* = 2.0 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.4, 157.1 (d, *J* = 180.8 Hz), 145.7, 142.8 (d, *J* = 2.9 Hz), 135.7, 122.9 (d, *J* = 8.0 Hz), 116.4 (d, *J* = 22.6 Hz), 93.5, 67.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.63 (s, 1F); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{11}FN_3O_2$ 236.0830; found 236.0825.



4e

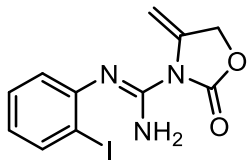
N'-(4'-acetylphenyl)-4-methylene-2-oxooxazolidine-3-carboximidamide (compound **4e**) was obtained as a white solid after purification through silica gel column chromatography (PE/EtOAc 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (m, 2H), 7.00 (m, 2H), 6.05 (s, 1H), 5.97 (br, 2H), 4.95 (t, *J* = 1.6 Hz, 2H), 4.66 (q, *J* = 2.4 Hz, 1H), 2.56 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.2, 156.1, 151.9, 144.9, 135.5, 132.5, 130.4, 121.9, 93.9, 67.3, 26.4; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{14}N_3O_3$ 260.1030; found 260.1022.



4f

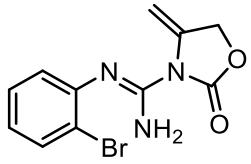
4-Methylene-2-oxo-N'-(2'-phenoxyphenyl)oxazolidine-3-carboximidamide (compound **4f**) was obtained in 99% yield (313 mg, 1.02 mmol) as a white solid after purification through silica gel column chromatography (PE/EtOAc 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (m, 2H), 7.16 (m, 1H), 7.08 (m, 2H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.99 (m, 1H), 6.89 (m, 2H), 5.90 (br, 2H), 5.56 (q, *J* = 2.4 Hz, 1H), 4.82 (t, *J* = 2.4 Hz, 2H), 4.36 (q, *J* = 2.0 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.0, 156.1, 147.3, 144.8, 138.7, 135.1, 129.5, 125.4, 124.6, 123.8, 122.3, 121.9, 117.0, 93.4, 67.2; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}N_3O_3$ 310.1186; found

310.1189.



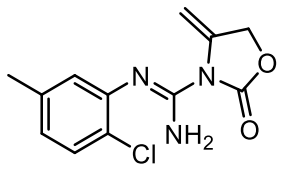
4g

N'-(2'-iodophenyl)-4-methylene-2-oxooxazolidine-3-carboximidamide (compound **4g**) was obtained in 85% yield (289 mg, 0.99 mmol) as a white liquid after purification through silica gel column chromatography (PE/EtOAc 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.32 (m, 1H), 6.94 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.79 (m, 1H), 6.37 (q, *J* = 2.0 Hz, 1H), 5.90 (br, 2H), 4.96 (t, *J* = 2.4 Hz, 2H), 4.70 (q, *J* = 1.6 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.3, 148.7, 145.4, 139.7, 135.2, 129.6, 125.0, 121.7, 94.8, 93.1, 67.4; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{11}IN_3O_2$ 343.9890; found 343.9886.



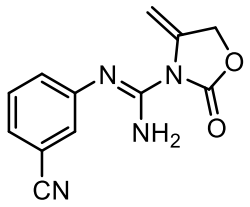
4h

N'-(2'-bromophenyl)-4-methylene-2-oxooxazolidine-3-carboximidamide (compound **4h**) was obtained in 91% yield (273 mg, 1.01 mmol) as a white liquid after purification through silica gel column chromatography (PE/EtOAc 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.30 (m, 1H), 6.97 (m, 2H), 6.30 (q, *J* = 2.4 Hz, 1H), 5.89 (br, 2H), 4.99 (t, *J* = 2.4 Hz, 2H), 4.72 (q, *J* = 2.0 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.2, 145.4, 145.2, 135.3, 133.5, 128.7, 124.7, 122.9, 116.9, 94.3, 67.4; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{11}BrN_3O_2$ 296.0029; found 296.0023.



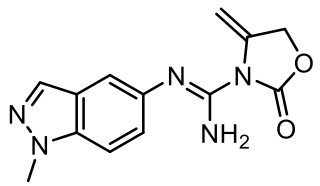
4i

N'-(2'-chloro-5'-methylphenyl)-4-methylene-2-oxooxazolidine-3-carboximidamide (compound **4i**) was obtained in 91% yield (241 mg, 1.00 mmol) as a white liquid after purification through silica gel column chromatography (PE/EtOAc 7:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.0 Hz, 1H), 6.81 (m, 2H), 6.21 (q, *J* = 2.4 Hz, 1H), 5.84 (br, 2H), 4.96 (t, *J* = 2.4 Hz, 2H), 4.68 (q, *J* = 2.0 Hz, 1H), 2.30 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.2, 145.0, 143.5, 138.0, 135.4, 130.0, 125.3, 123.6, 122.9, 94.0, 67.4, 20.9; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{13}ClN_3O_2$ 266.0691; found 266.0689.



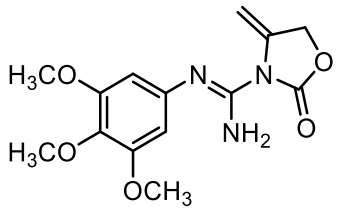
4j

N'-(3'-cyanophenyl)-4-methylene-2-oxooxazolidine-3-carboximidamide (compound **4j**) was obtained as a white solid after purification through silica gel column chromatography (PE/EtOAc 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (t, J = 8.0 Hz, 1H), 7.34 (m, 1H), 7.22 (t, J = 8.0 Hz, 2H), 7.17 (m, 1H), 6.03 (s, 1H), 5.97 (br, 2H), 4.95 (t, J = 2.4 Hz, 2H), 4.67 (q, J = 2.4 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.1, 147.8, 145.8, 135.4, 130.6, 126.9, 126.8, 125.4, 118.7, 113.6, 94.1, 67.3; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{11}N_4O_2$ 243.0877; found 243.0867.



4k

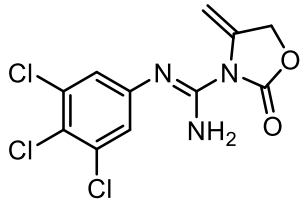
N'-(1'-methyl-1H-indazol-5'-yl)-4-methylene-2-oxooxazolidine-3-carboximidamide (compound **4k**) was obtained as a white solid after purification through silica gel column chromatography (PE/EtOAc 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.35 (d, J = 8.8 Hz, 1H), 7.20 (d, J = 2.4 Hz, 1H), 7.02 (dd, J = 8.8, 2.0 Hz, 1H), 6.09 (s, 1H), 5.91 (br, 2H), 4.93 (t, J = 2.4 Hz, 2H), 4.65 (q, J = 2.4 Hz, 1H), 4.62 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.2, 145.9, 140.0, 137.3, 135.8, 132.0, 124.8, 122.7, 111.5, 110.2, 93.2, 67.3, 35.6; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{14}N_5O_2$ 272.1142; found 272.1133.



4l

4-Methylene-2-oxo-N'-(3',4',5'-trimethoxyphenyl)oxazolidine-3-carboximidamide (compound **4l**) was obtained in 90% yield (264 mg, 0.96 mmol) as a white solid after purification through silica gel column chromatography (PE/EtOAc 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (s, 2H), 6.07 (q, J = 2.4 Hz, 1H), 5.94 (br, 2H), 4.94 (t, J = 2.4 Hz, 2H), 4.66 (q, J = 2.0 Hz, 1H), 3.82 (s, 6H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.2, 154.1, 145.7, 143.0, 135.7, 133.9, 99.1, 93.5, 67.3, 61.0, 56.1; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{18}N_3O_5$ 308.1241;

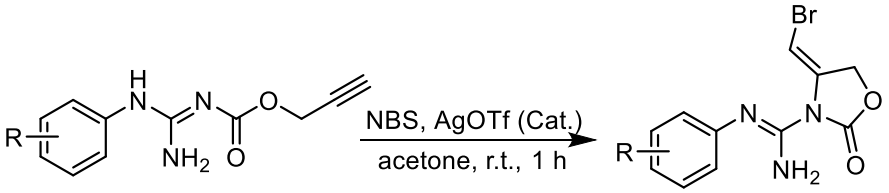
found 308.1236.



4m

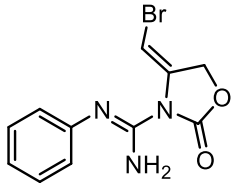
4-Methylene-2-oxo-N'-(3',4',5'-trichlorophenyl)oxazolidine-3-carboximidamide (compound **4m**) was obtained in 69% yield (221 mg, 1.00 mmol) as a white solid after purification through silica gel column chromatography (PE/EtOAc 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (s, 2H), 6.01 (br, 3H), 4.95 (t, J = 2.4 Hz, 2H), 4.67 (q, J = 2.0 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 156.1, 146.4, 146.0, 135.2, 134.8, 125.6, 122.5, 94.3, 67.3; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_9Cl_3N_3O_2$ 319.9755; found 319.9724.

3.4. Synthesis of Compounds 5a-5e



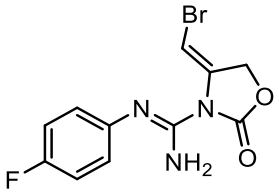
3 **5**

General procedure: A solution of compound **3** (1.0 equiv), NBS (1.2 equiv) and AgOTf (0.1 equiv) in acetone was stirred at room temperature for 1 h. The reaction mixture was diluted with DCM, and washed with H_2O and brine. After being dried over anhydrous Na_2SO_4, the organic was concentrated and purified via silica gel column chromatography to afford the target compound **5a-5e**.



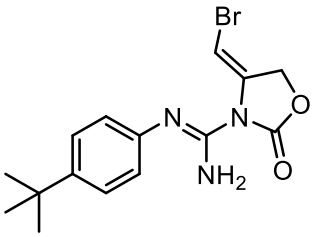
5a

4-(Bromomethylene)-2-oxo-N'-phenyloxazolidine-3-carboximidamide (compound **5a**) was obtained in 77% yield (228 mg, 1.00 mmol) as a white solid after purification through silica gel column chromatography (PE/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, J = 2.8 Hz, 1H), 7.38 (m, 2H), 7.11 (t, J = 7.6 Hz, 1H), 6.94 (m, 2H), 5.96 (br, 2H), 4.97 (d, J = 2.8 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 156.1, 146.3, 145.0, 132.3, 129.8, 123.7, 121.8, 90.8, 68.1; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{11}BrN_3O_2$ 296.0029; found 296.0032.



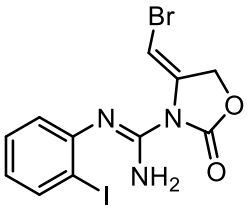
5b

4-(Bromomethylene)-N'-(4'-fluorophenyl)-2-oxooxazolidine-3-carboximidamide (compound **5b)** was obtained in 73% yield (228 mg, 1.00 mmol) as a white solid after purification through silica gel column chromatography (PE/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (t, *J* = 2.8 Hz, 1H), 7.05 (m, 2H), 6.86 (m, 2H), 5.95 (br, 2H), 4.95 (d, *J* = 2.8 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.5, 157.1 (d, *J* = 212.6 Hz), 145.5, 142.2 (d, *J* = 2.9 Hz), 132.3, 123.0 (d, *J* = 8.0 Hz), 116.5 (d, *J* = 22.3 Hz), 90.9, 68.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.15 (s, 1F); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{10}FBrN_3O_2$ 313.9935; found 313.9938.



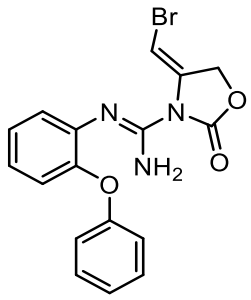
5c

4-(Bromomethylene)-N'-(4'-(tert-butyl)phenyl)-2-oxooxazolidine-3-carboximidamide (compound **5c**) was obtained in 82% yield (288 mg, 1.00 mmol) as a yellow liquid after purification through silica gel column chromatography (PE/EtOAc 15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (t, *J* = 2.8 Hz, 1H), 7.37 (m, 2H), 6.86 (m, 2H), 5.95 (br, 2H), 4.95 (d, *J* = 2.8 Hz, 1H), 1.32 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.1, 146.5, 145.0, 143.4, 132.4, 126.6, 121.2, 90.8, 68.1, 34.3, 31.5; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{19}BrN_3O_2$ 352.0655; found 352.0661.



5d

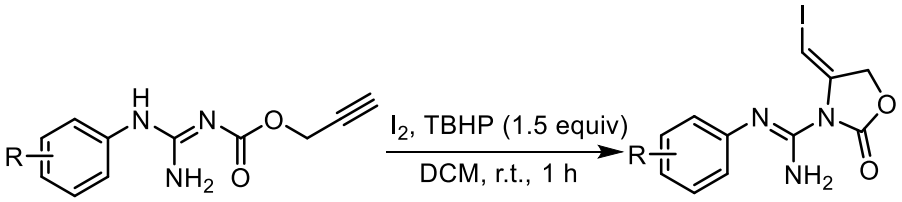
4-(Bromomethylene)-N'-(2'-iodophenyl)-2-oxooxazolidine-3-carboximidamide (compound **5d**) was obtained in 56% yield (237 mg, 1.00 mmol) as a white solid after purification through silica gel column chromatography (PE/EtOAc 13:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.66 (t, *J* = 2.8 Hz, 1H), 7.33 (m, 1H), 6.93 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.81 (m, 1H), 5.96 (br, 2H), 4.98 (d, *J* = 2.8 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.0, 148.0, 145.1, 139.8, 131.9, 129.7, 125.3, 121.6, 93.3, 91.7, 68.2; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{10}BrIN_3O_2$ 421.8996; found 421.8984.



5e

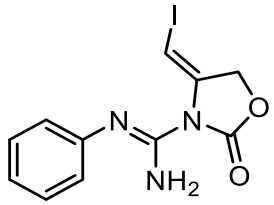
4-(Bromomethylene)-2-oxo-N'-(2'-phenoxyphenyl)oxazolidine-3-carboximidamide (compound **5e**) was obtained in 70% yield (293 mg, 1.09 mmol) as a white liquid after purification through silica gel column chromatography (PE/EtOAc 12:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (m, 2H), 7.18 (m, 1H), 7.11 (m, 2H), 7.01 (m, 2H), 6.86 (m, 2H), 6.79 (t, J = 2.8 Hz, 1H), 5.99 (br, 2H), 4.82 (d, J = 2.8 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.8, 155.9, 147.3, 144.6, 138.1, 131.6, 129.5, 125.5, 124.9, 123.7, 122.6, 122.3, 116.6, 90.8, 68.0; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}BrN_3O_3$ 388.0291; found 388.0297.

3.5. Synthesis of Compounds 6a-6g



3 **6**

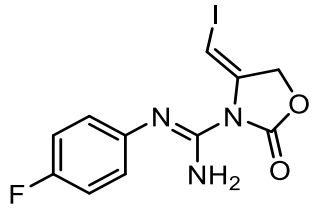
General procedure: A solution of compound **3** (1.0 equiv), I_2 (1.5 equiv) and TBHP (1.5 equiv) in DCM was stirred at room temperature for 1 h. Then the reaction mixture was diluted with DCM and quenched with $Na_2S_2O_3$ aqueous solution. After being washed with brine and dried over anhydrous Na_2SO_4, the organic was concentrated under vacuum and purified by silica gel column chromatography to afford the target compound **6**.



6a

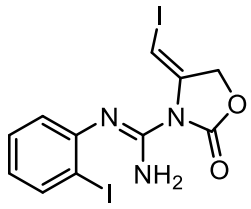
4-(Iodomethylene)-2-oxo-N'-phenyloxazolidine-3-carboximidamide (compound **6a**) was obtained in 85% yield (292 mg, 1.00 mmol) as a white solid after purification through silica gel column chromatography (PE/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, J = 2.4 Hz, 1H), 7.36 (m, 2H), 7.09 (t, J = 7.6 Hz, 1H), 6.92 (dd, J = 8.4, 1.2 Hz, 2H), 5.91 (br, 2H), 4.86 (d, J = 2.8 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.5, 146.3, 145.2, 134.6, 129.8, 123.7, 121.8, 71.7, 60.7; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{11}IN_3O_2$ 343.9890; found

343.9878.



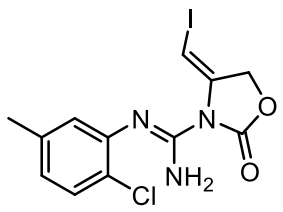
6b

N'-(4'-fluorophenyl)-4-(iodomethylene)-2-oxooxazolidine-3-carboximidamide (compound **6b**) was obtained in 85% yield (305 mg, 1.00 mmol) as a white solid after purification through silica gel column chromatography (PE/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 2.8 Hz, 1H), 7.05 (m, 2H), 6.87 (m, 2H), 5.92 (br, 2H), 4.86 (d, *J* = 2.8 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.5, 157.3 (d, *J* = 171.4 Hz), 145.7, 142.2 (d, *J* = 2.6 Hz), 134.5, 123.0 (d, *J* = 7.7 Hz), 116.5 (d, *J* = 22.3 Hz), 71.7, 60.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.13 (s, 1F); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{10}FIN_3O_2$ 361.9796; found 361.9799.



6c

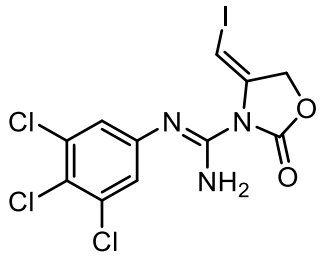
4-(Iodomethylene)-N'-(2'-iodophenyl)-2-oxooxazolidine-3-carboximidamide (compound **6c**) was obtained in 91% yield (425 mg, 1.00 mmol) as a white solid after purification through silica gel column chromatography (PE/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.61 (t, *J* = 2.8 Hz, 1H), 7.32 (m, 1H), 6.93 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.81 (m, 1H), 5.93 (br, 2H), 4.88 (d, *J* = 2.8 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.4, 148.0, 145.3, 139.8, 134.1, 129.7, 125.2, 121.6, 93.3, 71.7, 61.8 ; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{10}I_2N_3O_2$ 469.8857; found 469.8844.



6d

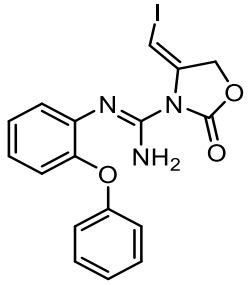
N'-(2'-chloro-5'-methylphenyl)-4-(iodomethylene)-2-oxooxazolidine-3-carboximidamide (compound **6d**) was obtained in 90% yield (355 mg, 1.01 mmol) as a white solid after purification through silica gel column chromatography (PE/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, *J* = 2.8 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 6.85 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.78

(d, J = 2.0 Hz, 1H), 5.89 (br, 2H), 4.87 (d, J = 2.8 Hz, 2H), 2.30 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 156.4, 145.0, 142.9, 138.1, 134.3, 130.0, 125.5, 123.6, 123.4, 71.7, 61.0, 20.9; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{12}ClIN_3O_2$ 391.9657; found 391.9649.



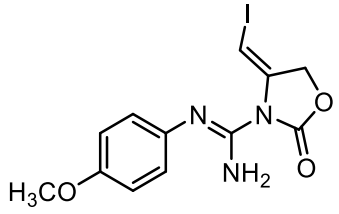
6e

4-(Iodomethylene)-2-oxo-N'-(3',4',5'-trichlorophenyl)oxazolidine-3-carboximidamide (compound **6e**) was obtained in 81% yield (363 mg, 1.00 mmol) as a white solid after purification through silica gel column chromatography (PE/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, J = 2.8 Hz, 1H), 6.98 (s, 2H), 6.08 (br, 2H), 4.87 (d, J = 2.8 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 156.3, 146.0, 145.7, 134.9, 134.0, 125.9, 122.5, 71.7, 61.1; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_8Cl_3N_3O_2$ 445.8721; found 445.8712.



6f

4-(Iodomethylene)-2-oxo-N'-(2'-phenoxyphenyl)oxazolidine-3-carboximidamide (compound **6f**) was obtained in 83% yield (363 mg, 1.00 mmol) as a white liquid after purification through silica gel column chromatography (PE/EtOAc 13:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (m, 2H), 7.18 (m, 1H), 7.12 (m, 2H), 7.03 (m, 2H), 6.86 (m, 2H), 6.72 (t, J = 2.8 Hz, 2H), 5.95 (br, 2H), 4.72 (d, J = 2.8 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 157.8, 156.3, 147.2, 144.8, 138.2, 133.7, 129.5, 125.6, 124.9, 123.8, 122.7, 122.4, 116.6, 71.5, 60.6; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}IN_3O_3$ 436.0153; found 436.0146.

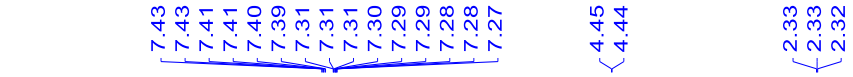


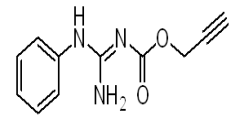
6g

4-(Iodomethylene)-N'-(4'-methoxyphenyl)-2-oxooxazolidine-3-carboximidamide (compound

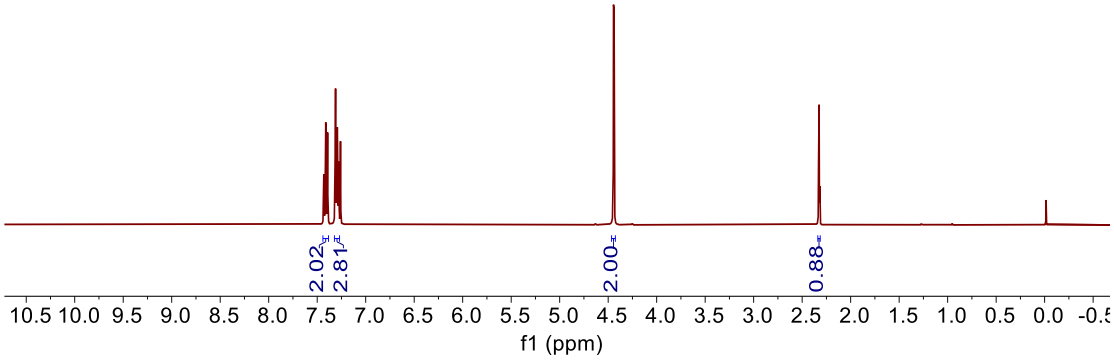
6g) was obtained in 71% yield (265 mg, 1.00 mmol) as a white solid after purification through silica gel column chromatography (PE/EtOAc 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 2.8 Hz, 1H), 6.88 (m, 4H), 5.90 (br, 2H), 4.86 (d, *J* = 2.8 Hz, 2H), 3.80 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 156.5, 156.0, 145.6, 139.2, 134.6, 122.6, 115.1, 71.7, 60.6, 55.6; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{13}IN_3O_3$ 373.9996; found 373.9989.

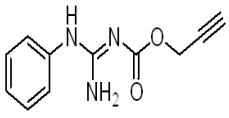
4. NMR spectra



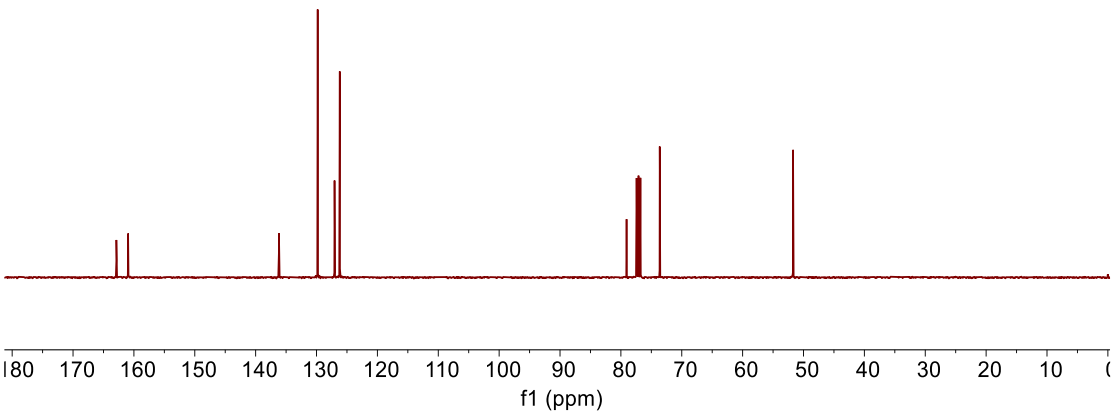


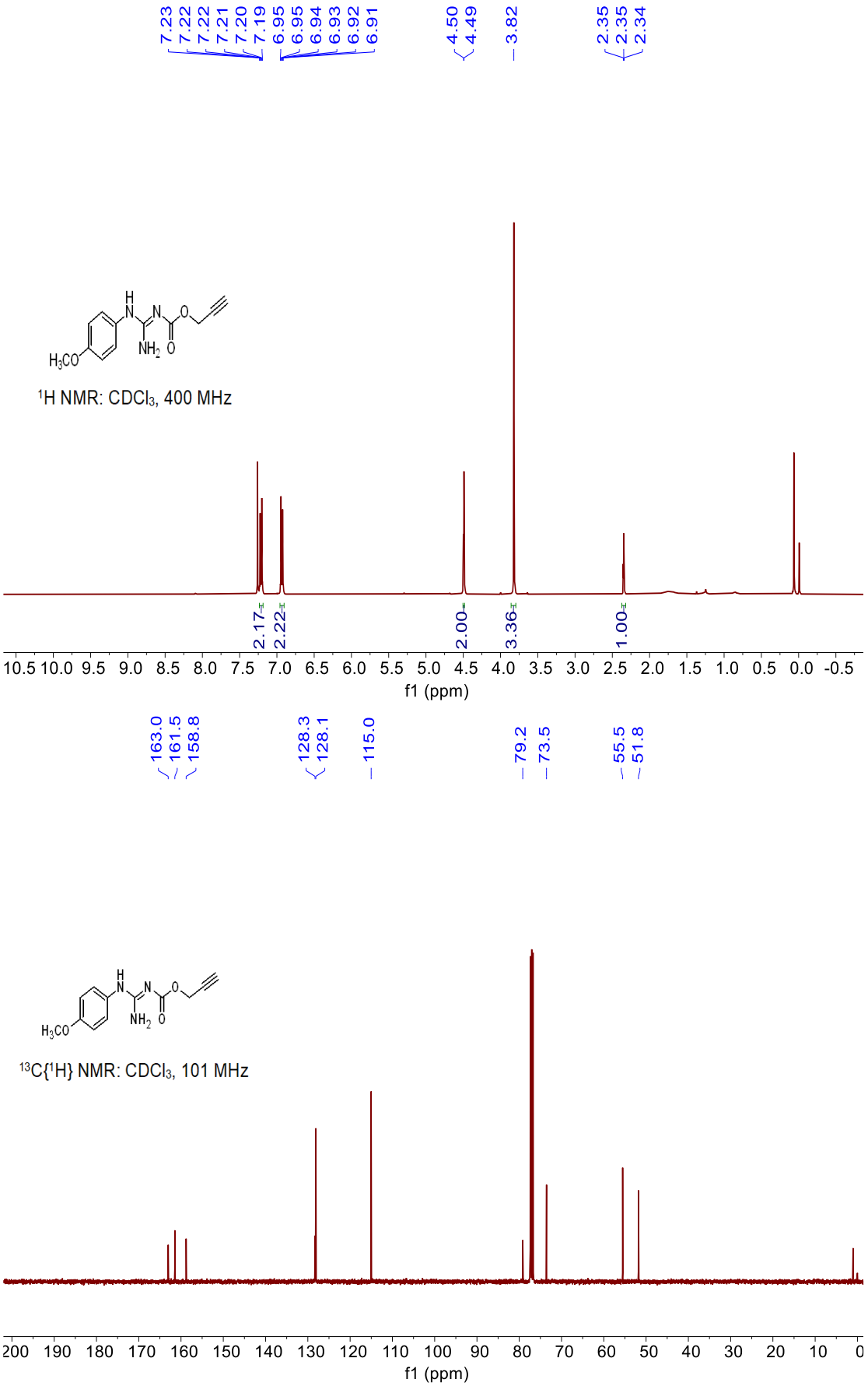
^{1}H NMR: $CDCl_3$, 400 MHz

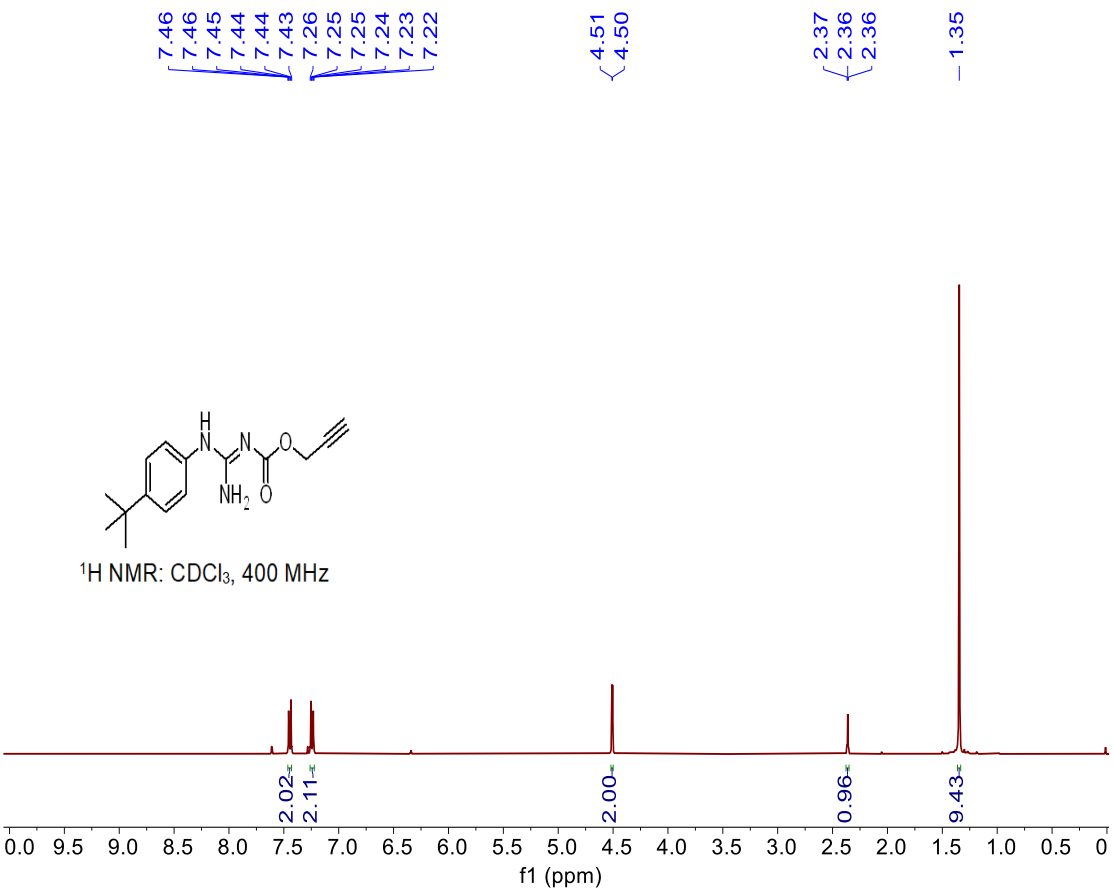




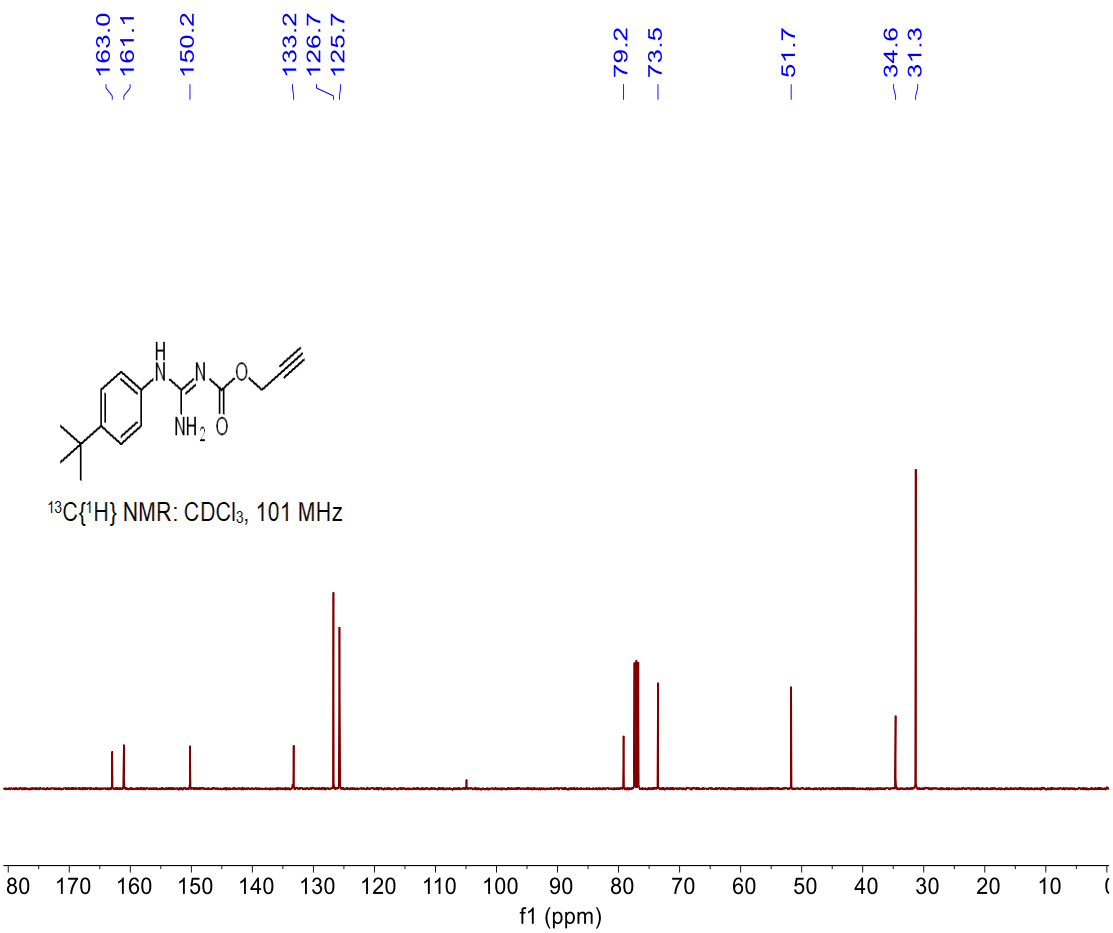
^{13}C{^{1}H} NMR: $CDCl_3$, 101 MHz



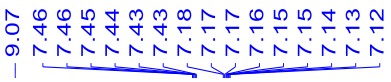

7.23
7.22
7.22
7.21
7.20
7.19
6.95
6.95
6.94
6.93
6.92
6.91
4.50
4.49
3.82
2.35
2.35
2.34
1H NMR: CDCl3, 400 MHz
2.17
2.22
2.00
3.36
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
163.0
161.5
158.8
128.3
128.1
115.0
79.2
73.5
55.5
51.8
13C{1H} NMR: CDCl3, 101 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

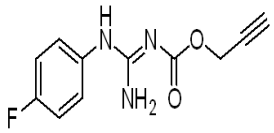


^{1}H NMR: $CDCl_3$, 400 MHz

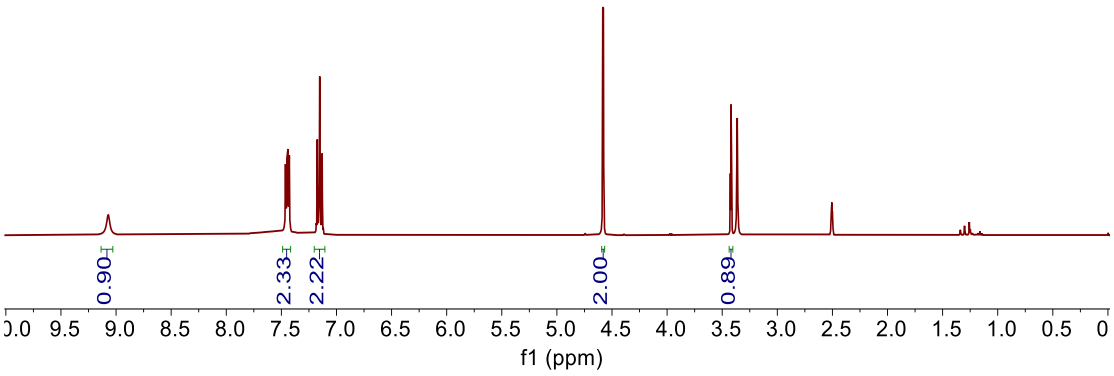


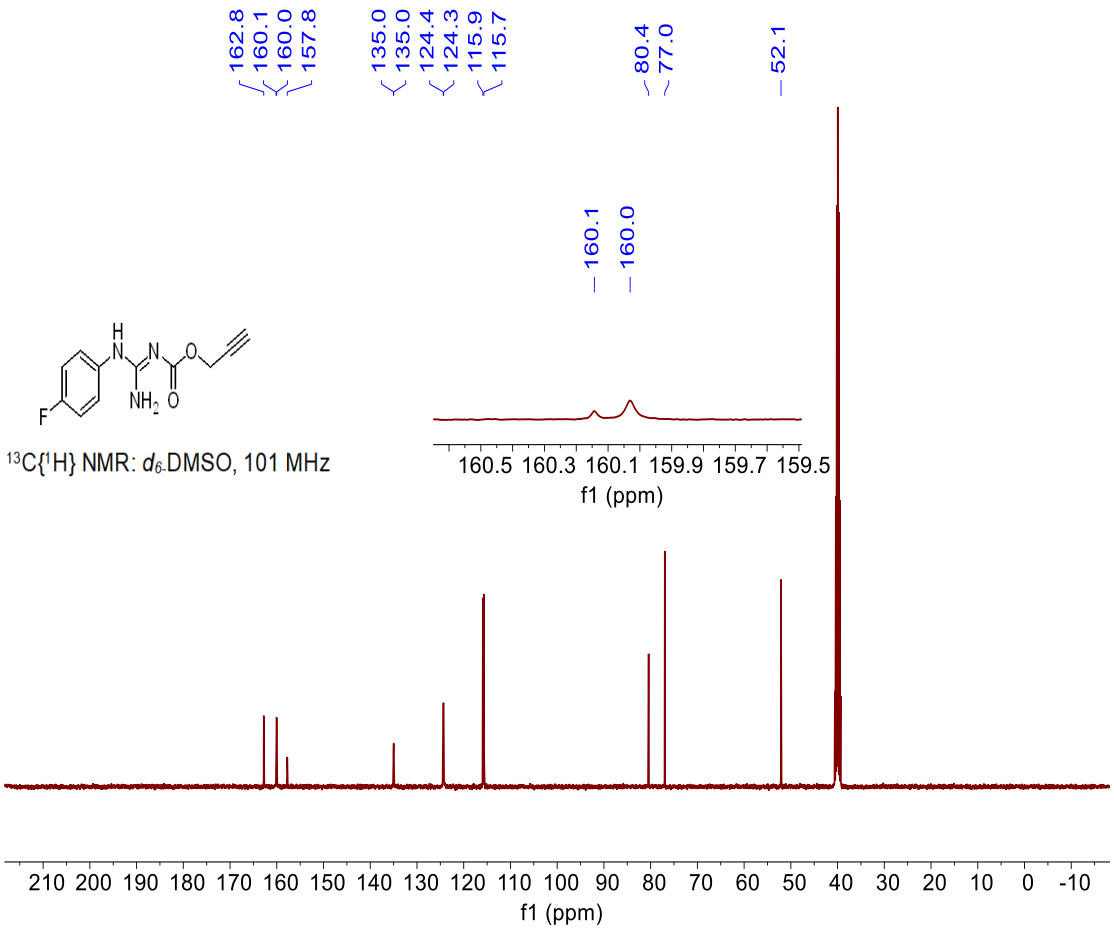
^{13}C{^{1}H} NMR: $CDCl_3$, 101 MHz



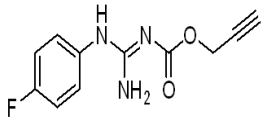


^{1}H NMR: d_6-DMSO, 400 MHz

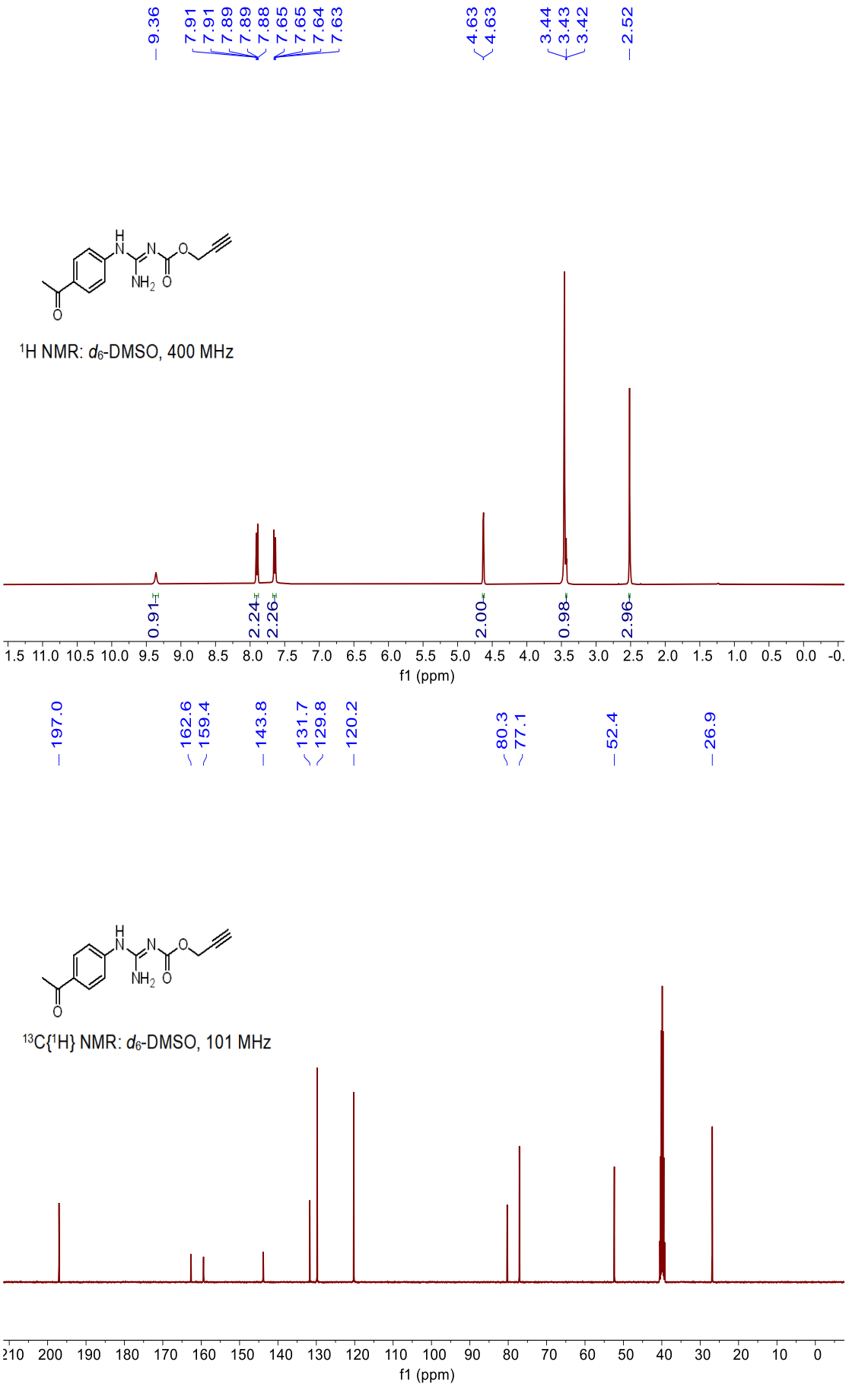


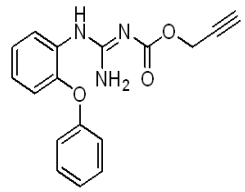


^{13}C{^{1}H} NMR: d_6-DMSO, 101 MHz

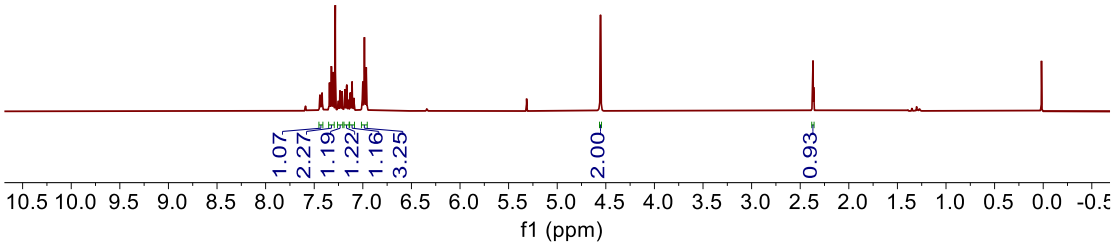


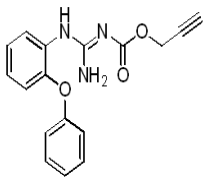
^{19}F NMR: d_6-DMSO, 376 MHz


9.36
7.91
7.91
7.89
7.89
7.88
7.65
7.65
7.64
7.63
4.63
4.63
3.44
3.43
3.42
2.52
1H NMR: d6-DMSO, 400 MHz
0.91
2.24
2.26
2.00
0.98
2.96
f1 (ppm)
197.0
162.6
159.4
143.8
131.7
129.8
120.2
80.3
77.1
52.4
26.9
13C{1H} NMR: d6-DMSO, 101 MHz
f1 (ppm)

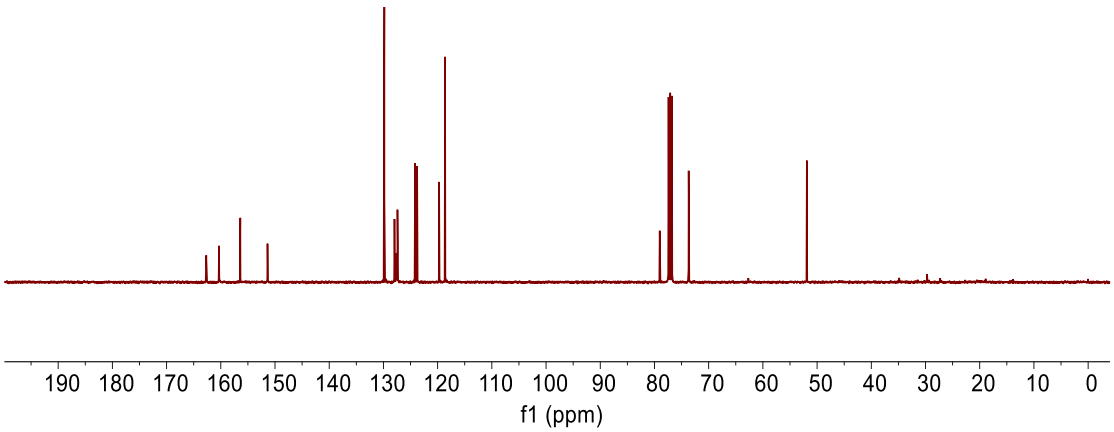


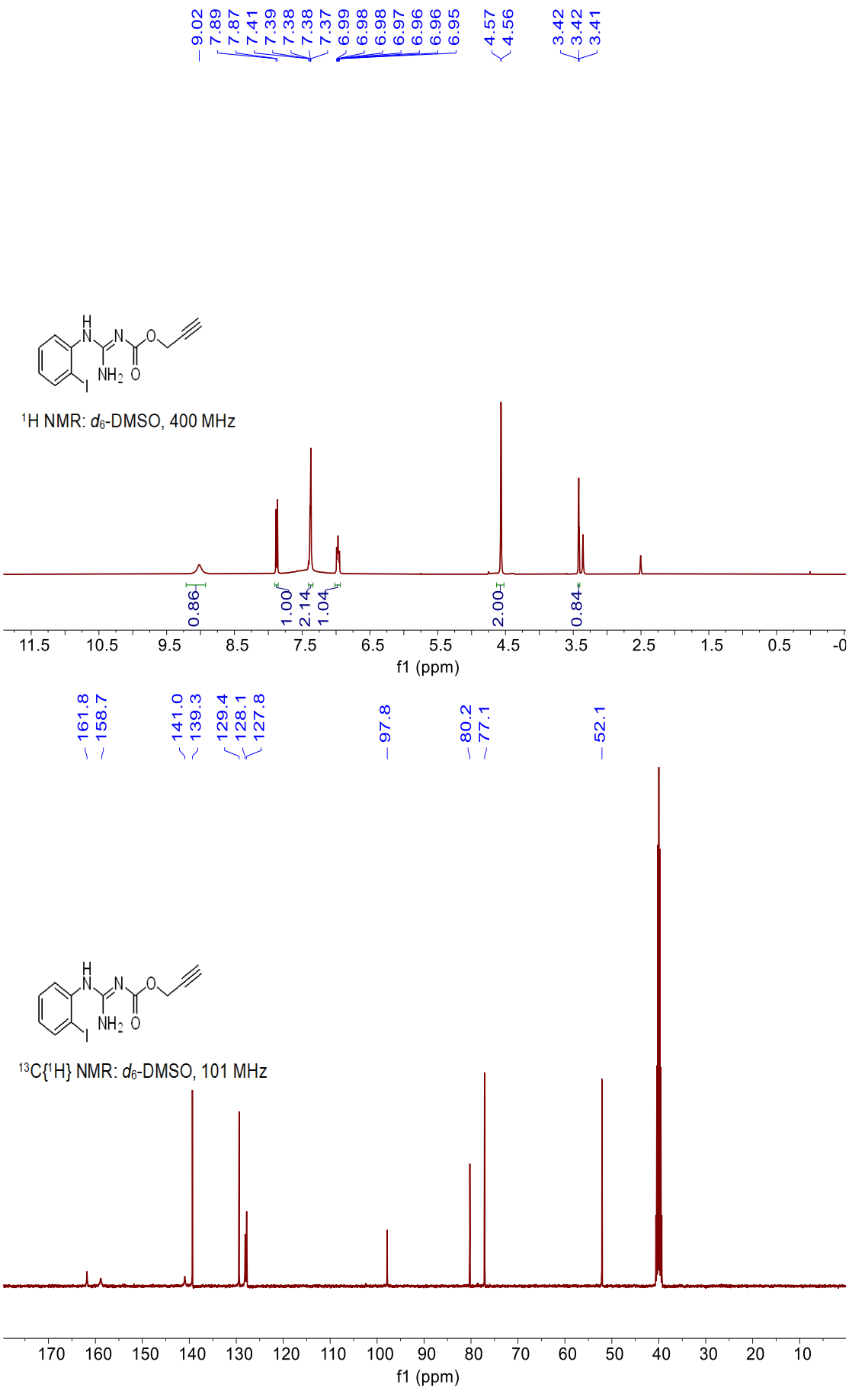
^{1}H NMR: $CDCl_3$, 400 MHz

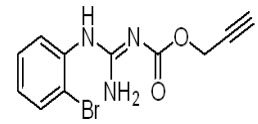




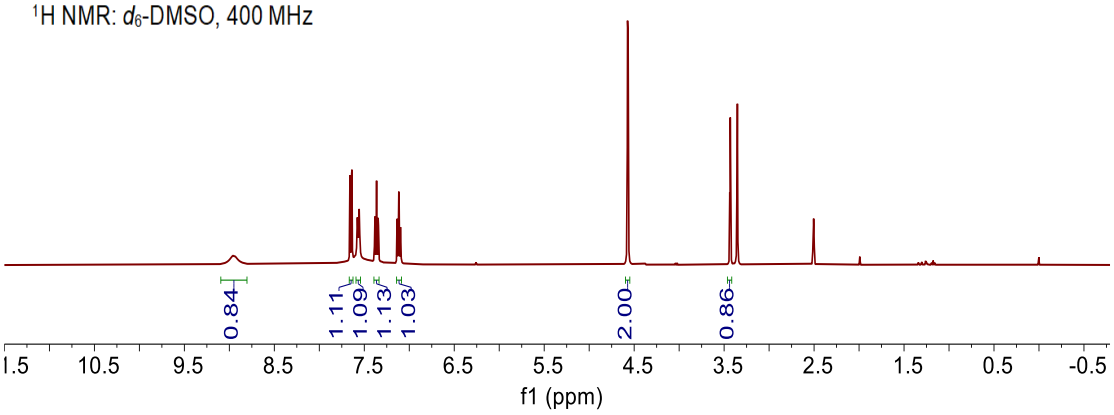
^{13}C{^{1}H} NMR: $CDCl_3$, 101 MHz

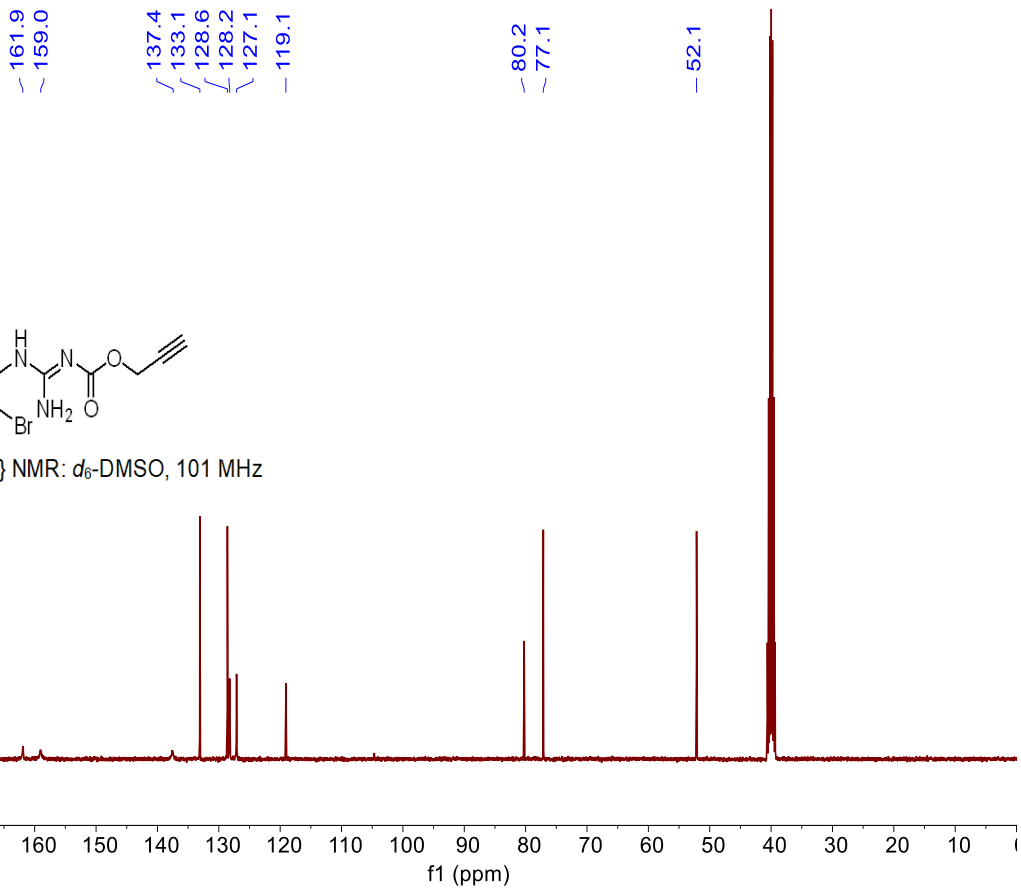



9.02
7.89
7.87
7.41
7.39
7.38
7.38
7.37
6.99
6.98
6.98
6.97
6.96
6.96
6.95
4.57
4.56
3.42
3.42
3.41
1H NMR: d6-DMSO, 400 MHz
0.86
1.00
2.14
1.04
2.00
0.84
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)
161.8
158.7
141.0
139.3
129.4
128.1
127.8
97.8
80.2
77.1
52.1
13C{1H} NMR: d6-DMSO, 101 MHz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

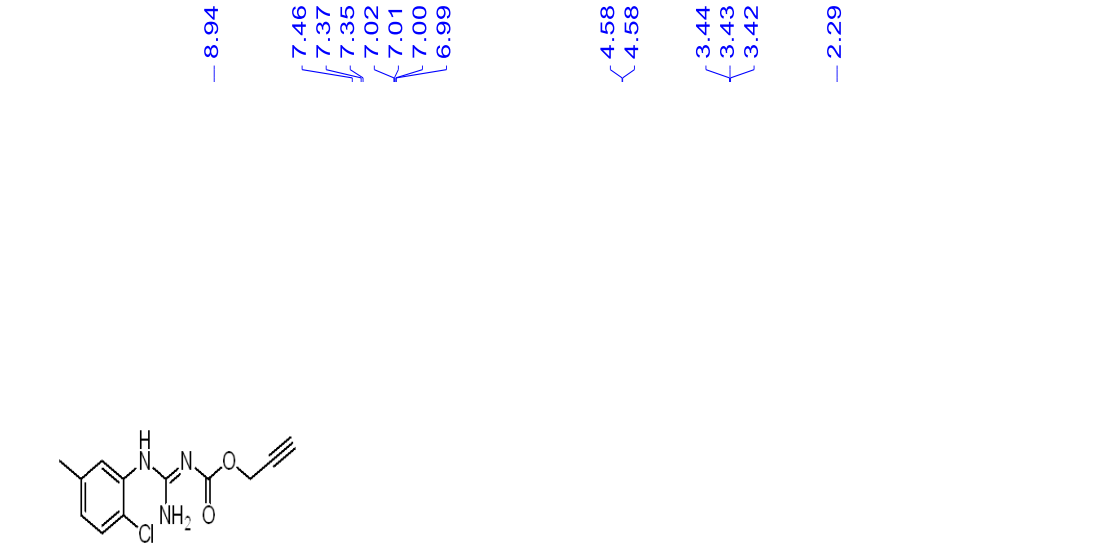


^{1}H NMR: d_6-DMSO, 400 MHz

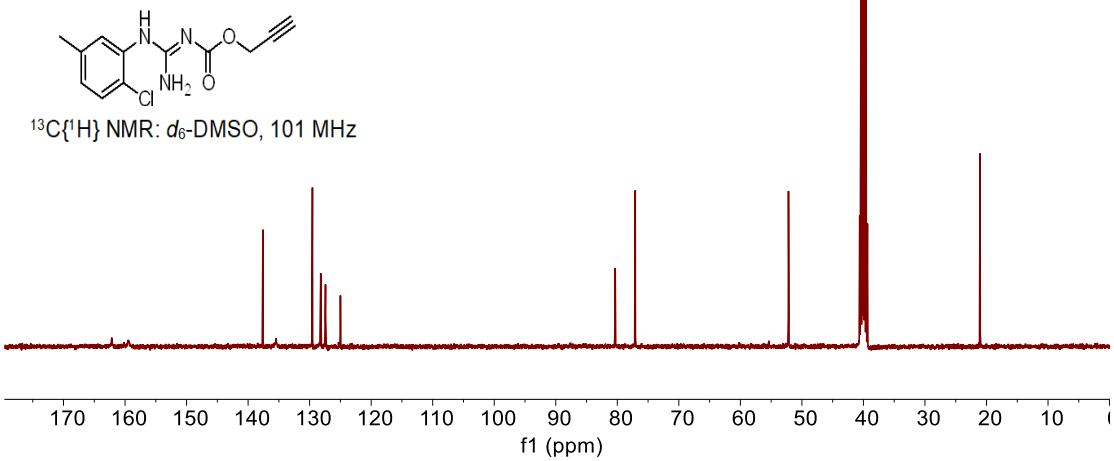




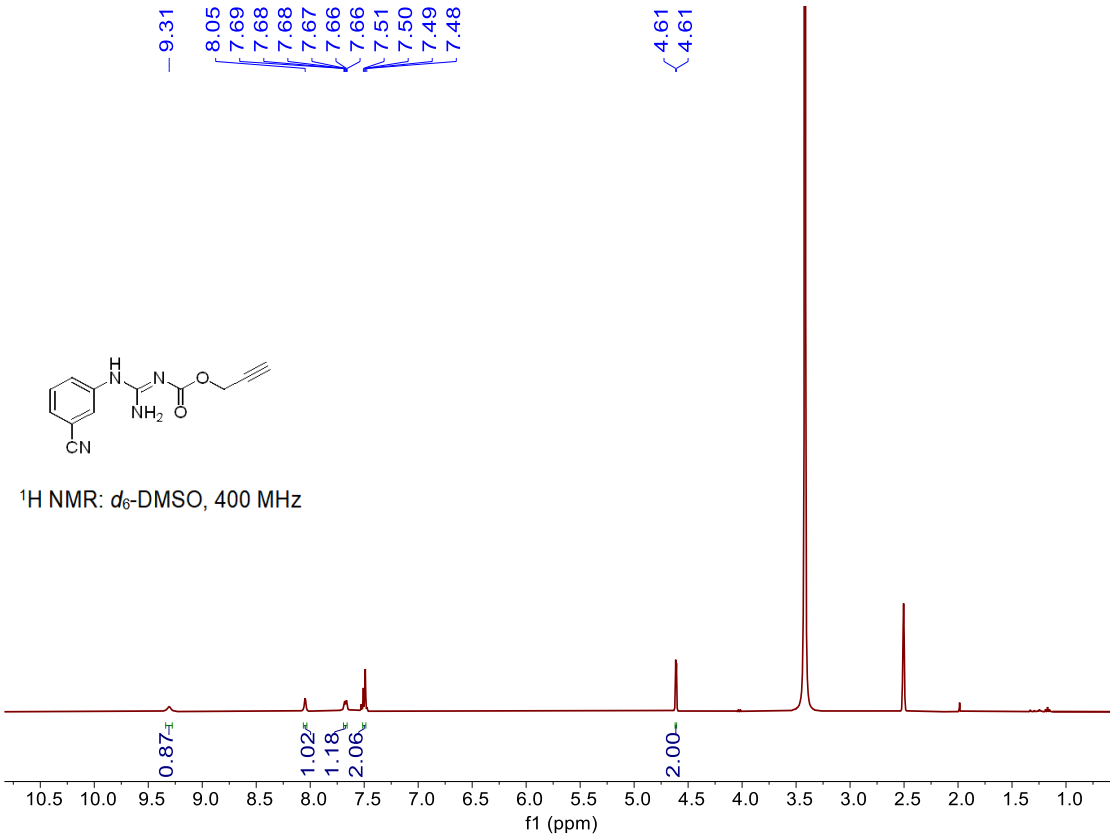
^{13}C{^{1}H} NMR: d_6-DMSO, 101 MHz



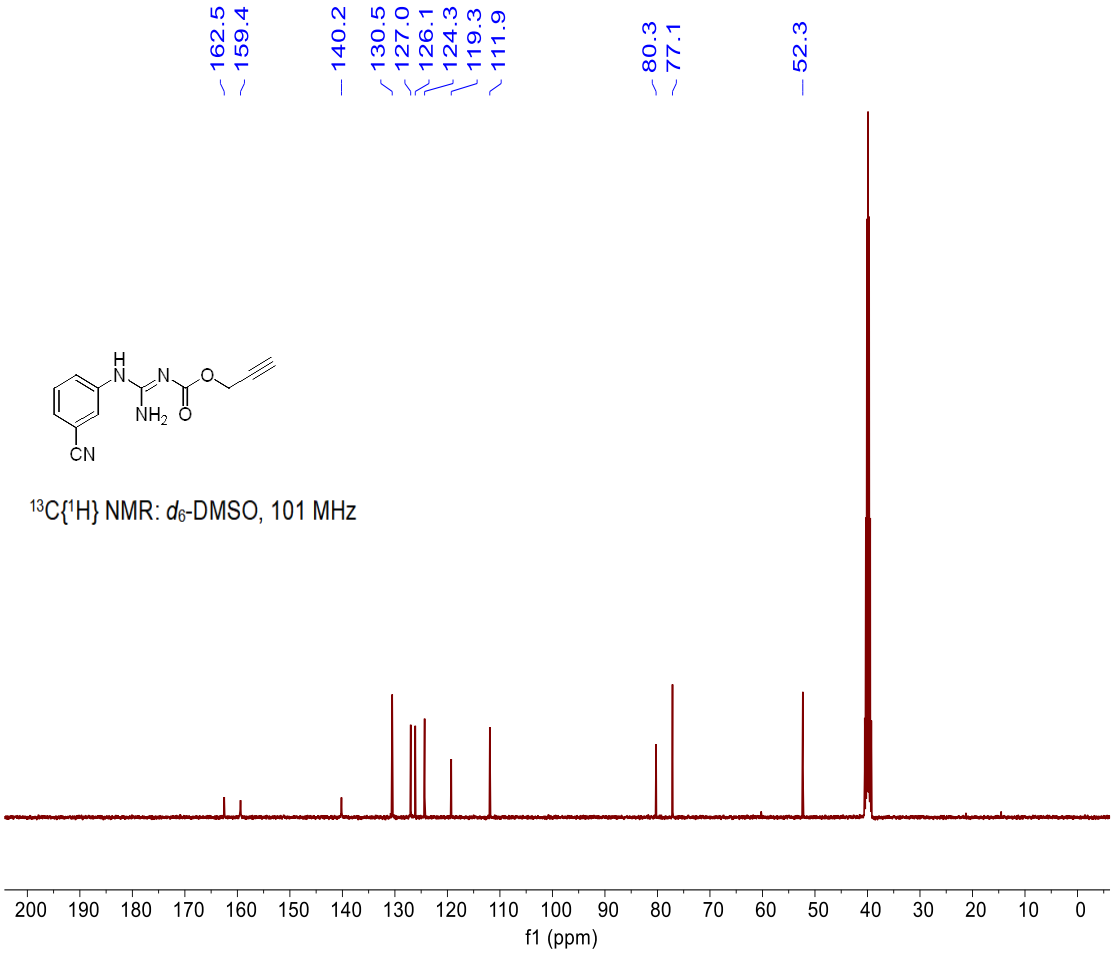
^{1}H NMR: d_6-DMSO, 400 MHz



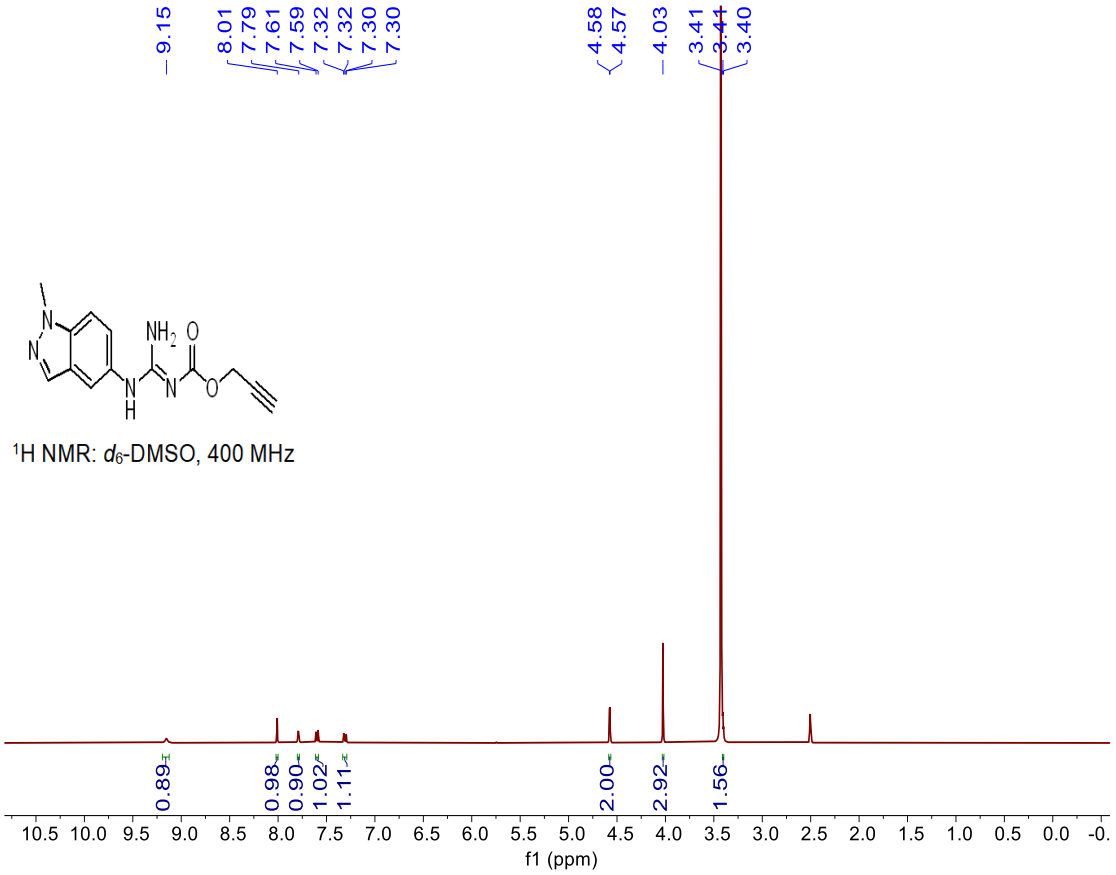
^{13}C{^{1}H} NMR: d_6-DMSO, 101 MHz



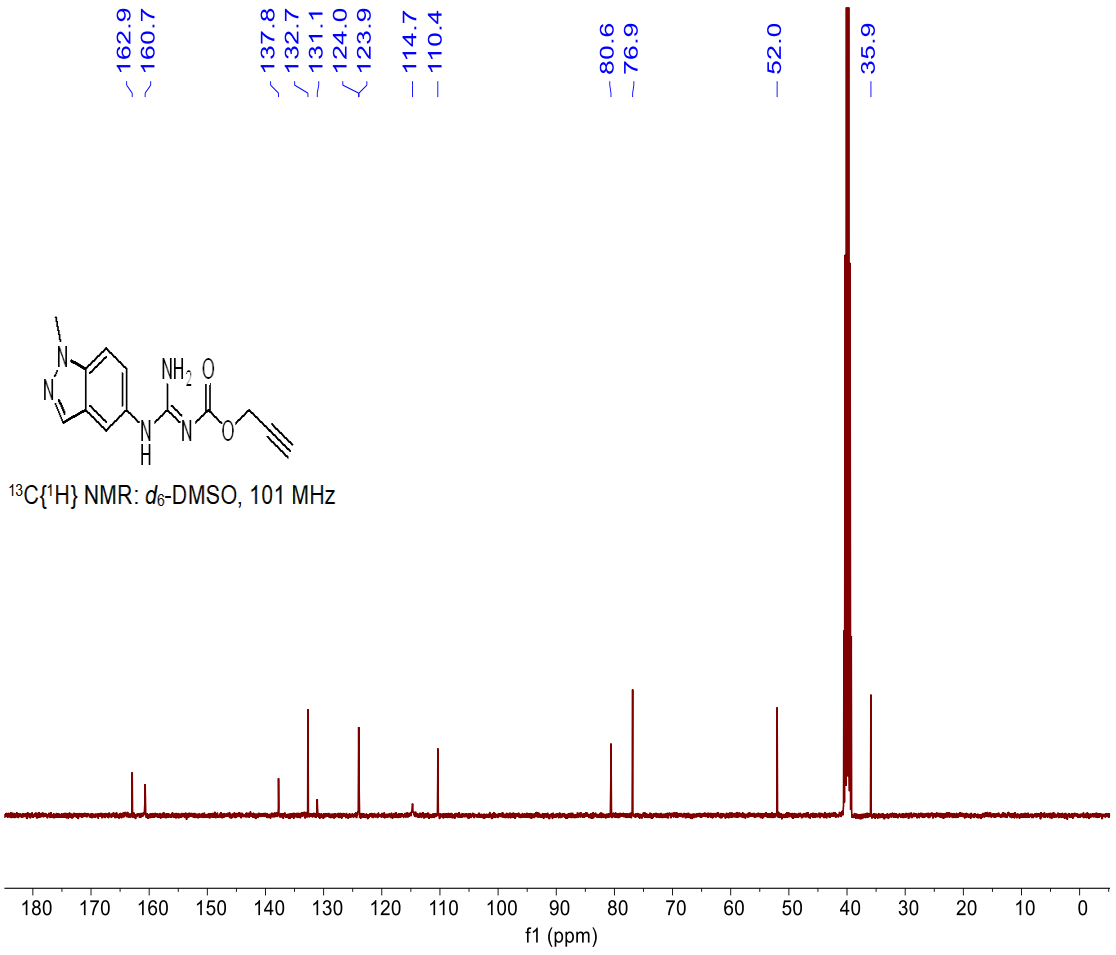
^{1}H NMR: d_6-DMSO, 400 MHz



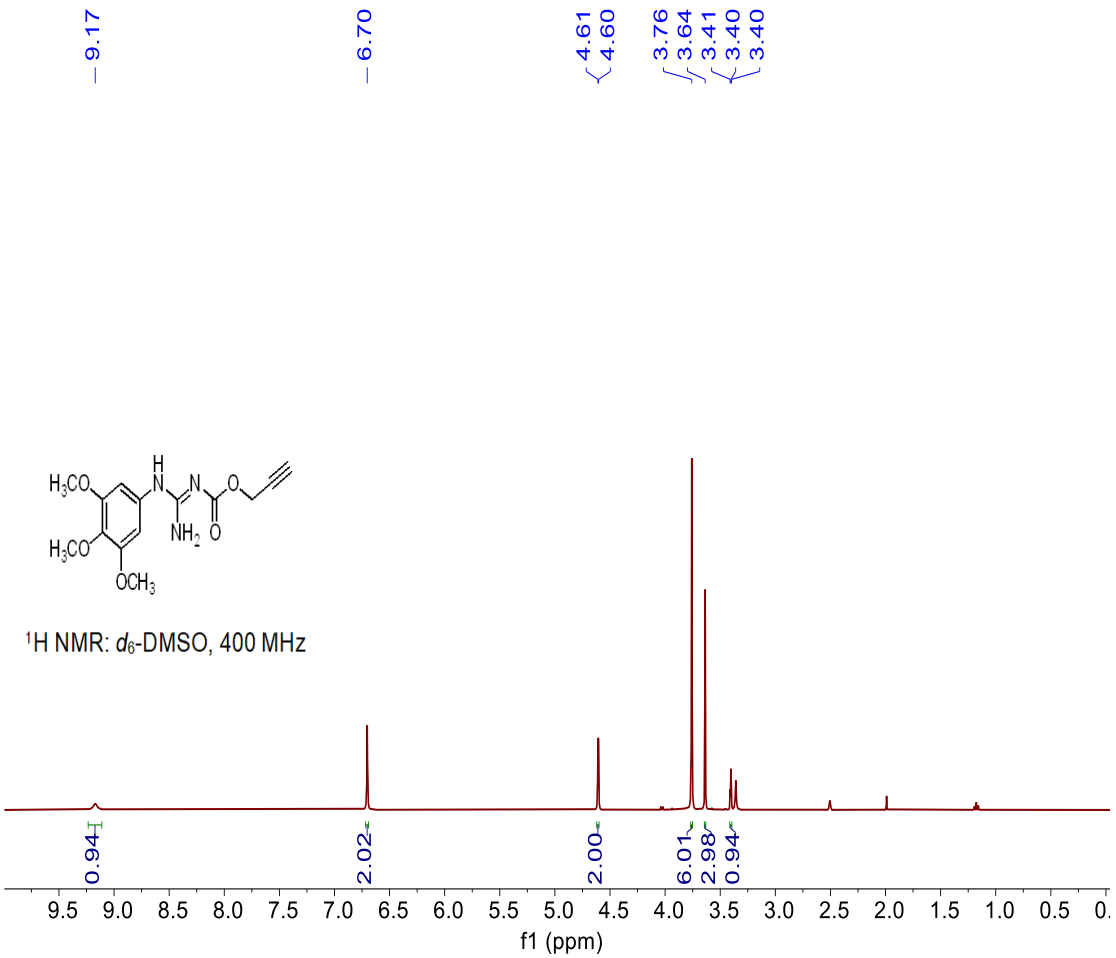
^{13}C{^{1}H} NMR: d_6-DMSO, 101 MHz

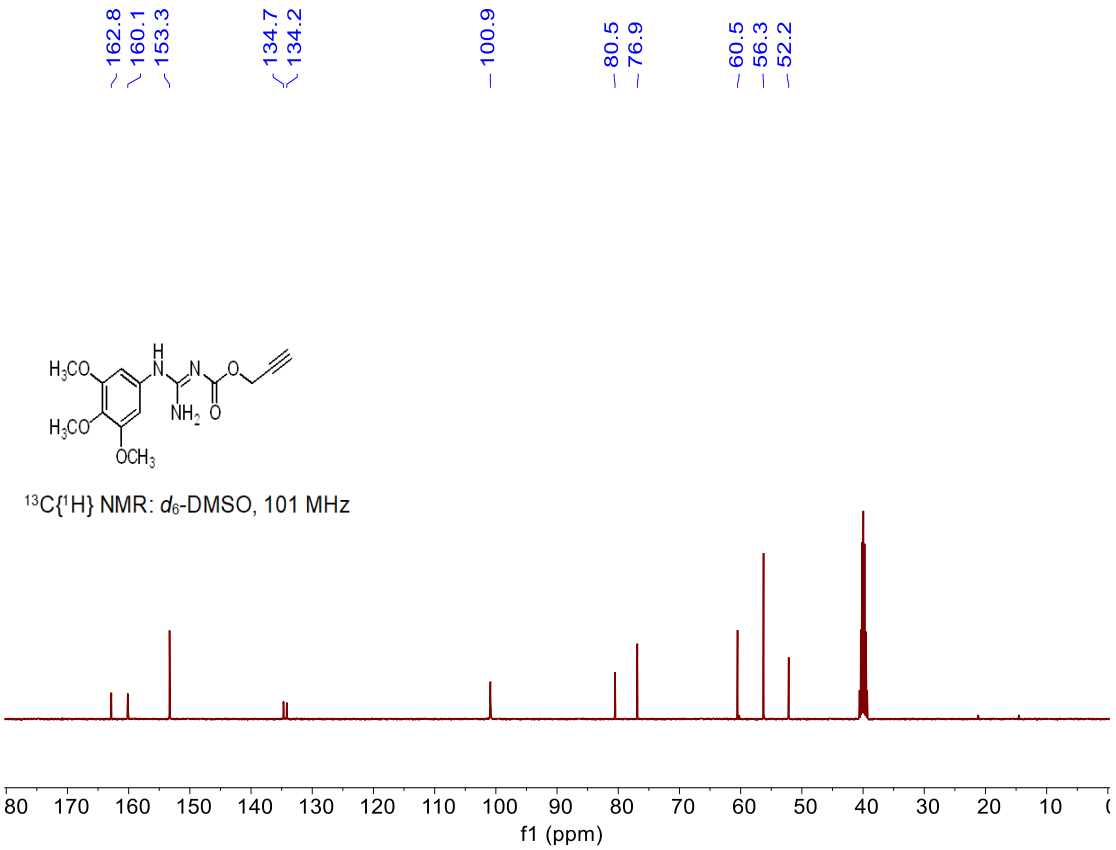


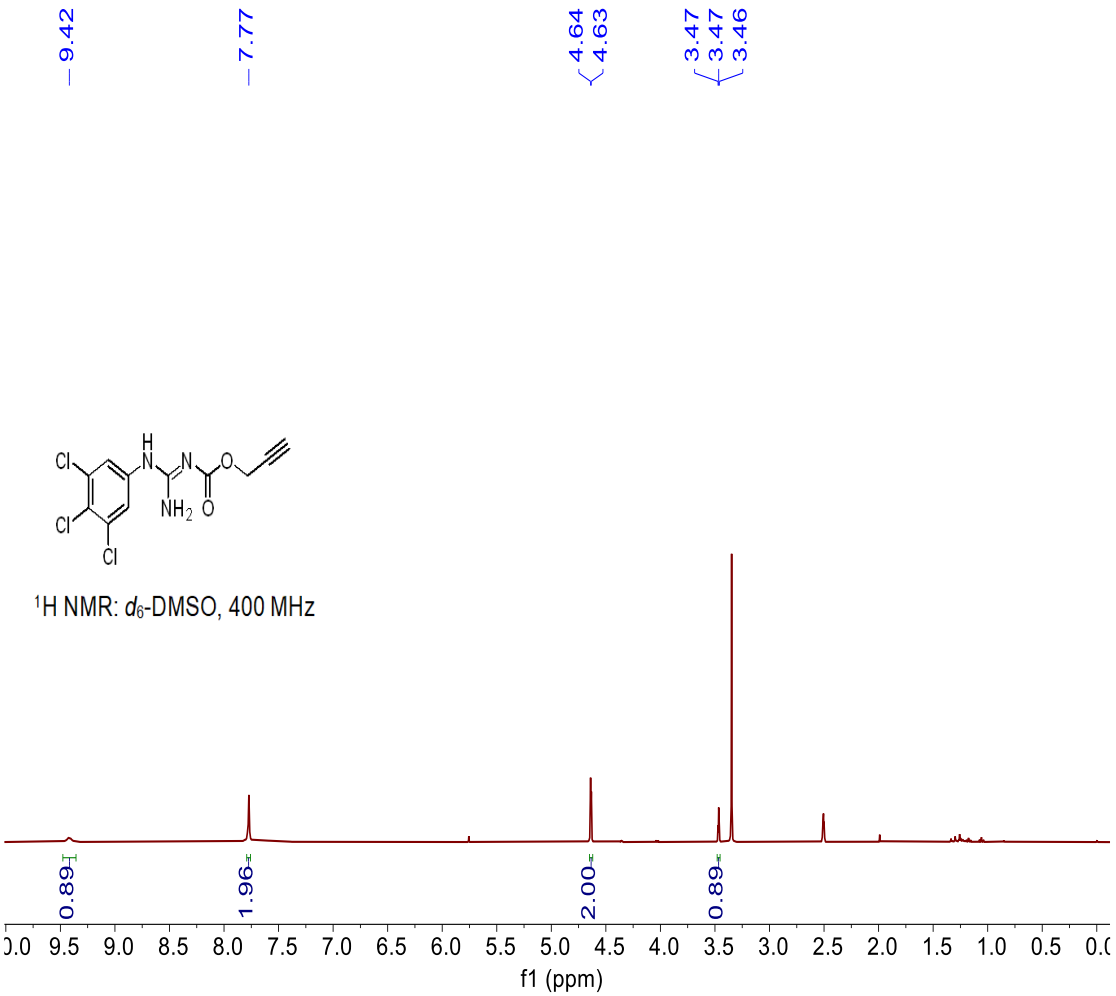
^{1}H NMR: d_6-DMSO, 400 MHz

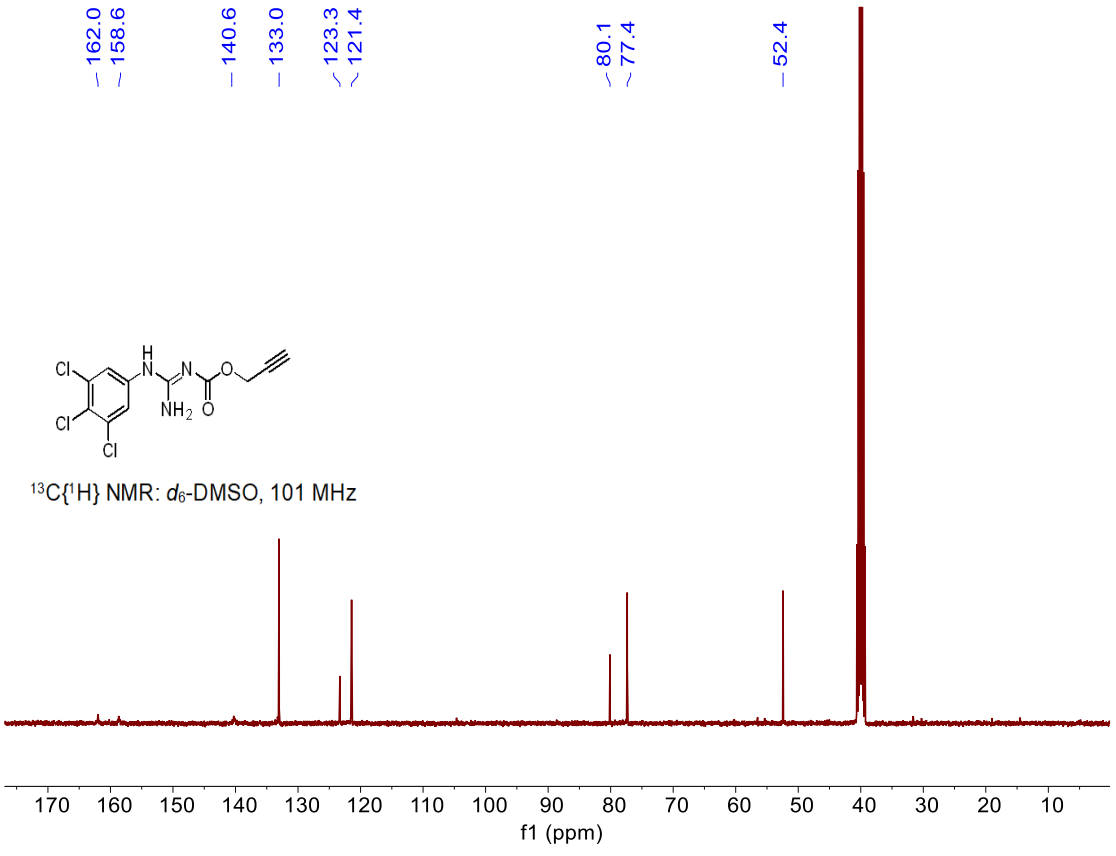


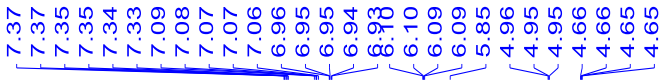
^{13}C{^{1}H} NMR: d_6-DMSO, 101 MHz

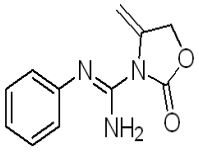

9.17
6.70
4.61
4.60
3.76
3.64
3.41
3.40
3.40
H3CO
H3CO
OCH3
NH2
O
1H NMR: d6-DMSO, 400 MHz
0.94
2.02
2.00
6.01
2.98
0.94
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


162.8
160.1
153.3
134.7
134.2
100.9
80.5
76.9
60.5
56.3
52.2
H3CO
H3CO
OCH3
NH2
O
13C{1H} NMR: d6-DMSO, 101 MHz
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

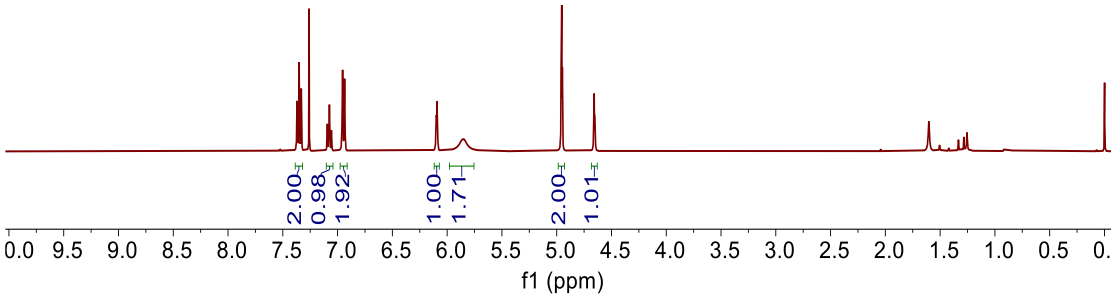

9.42
7.77
4.64
4.63
3.47
3.47
3.46
Cl
Cl
Cl
H
N
N
O
NH2
O
1H NMR: d6-DMSO, 400 MHz
0.89
1.96
2.00
0.89
f1 (ppm)

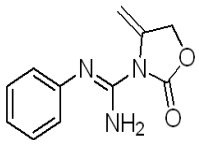

162.0
158.6
140.6
133.0
123.3
121.4
80.1
77.4
52.4
Cl
Cl
Cl
H
N
N
O
NH2
O
13C{1H} NMR: d6-DMSO, 101 MHz
f1 (ppm)



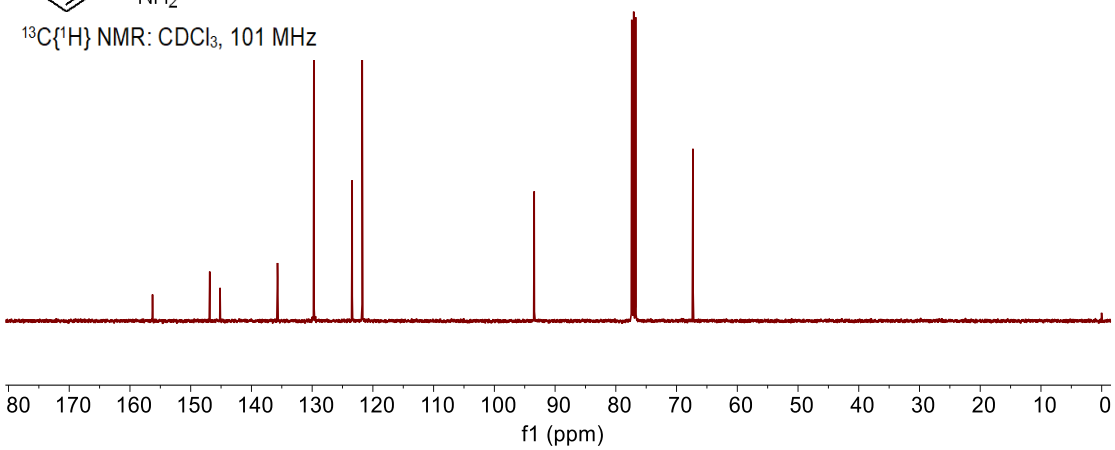


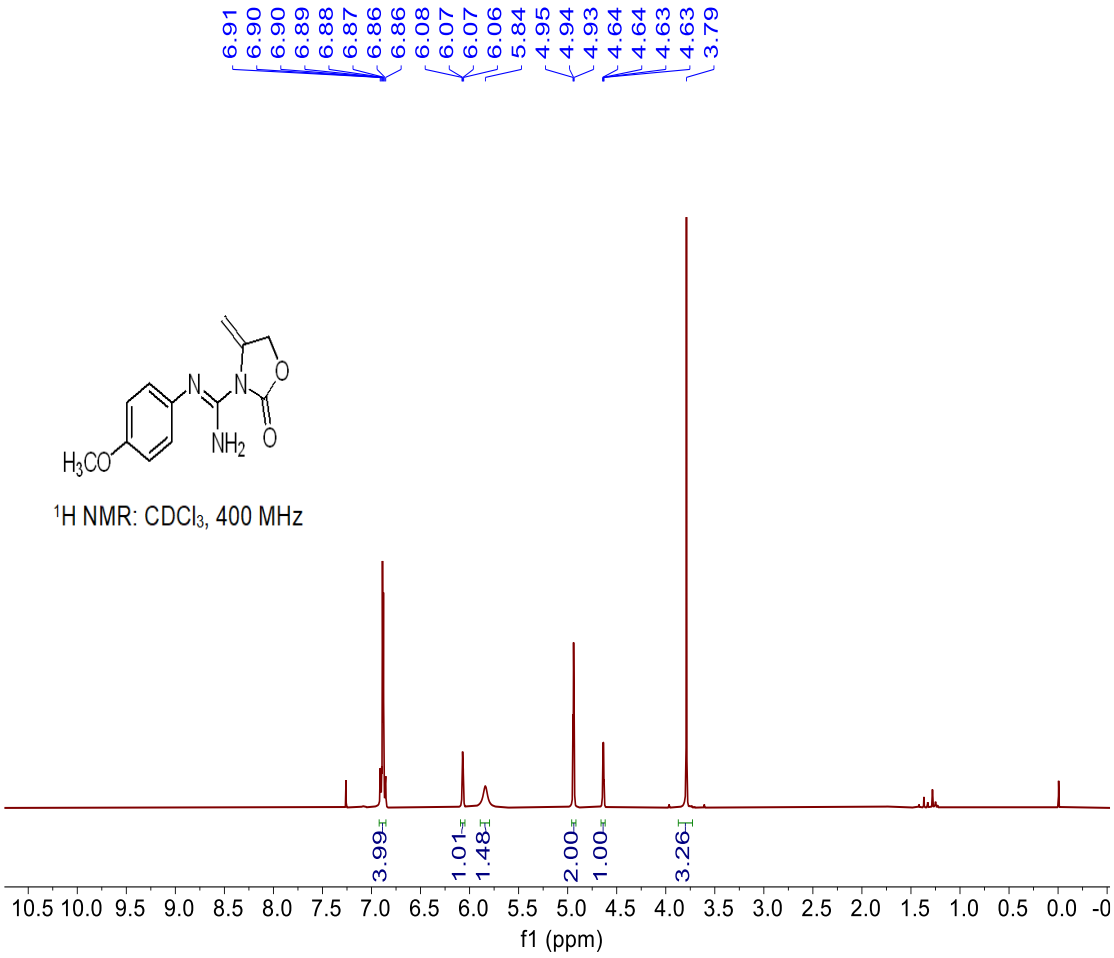
^{1}H NMR: $CDCl_3$, 400 MHz

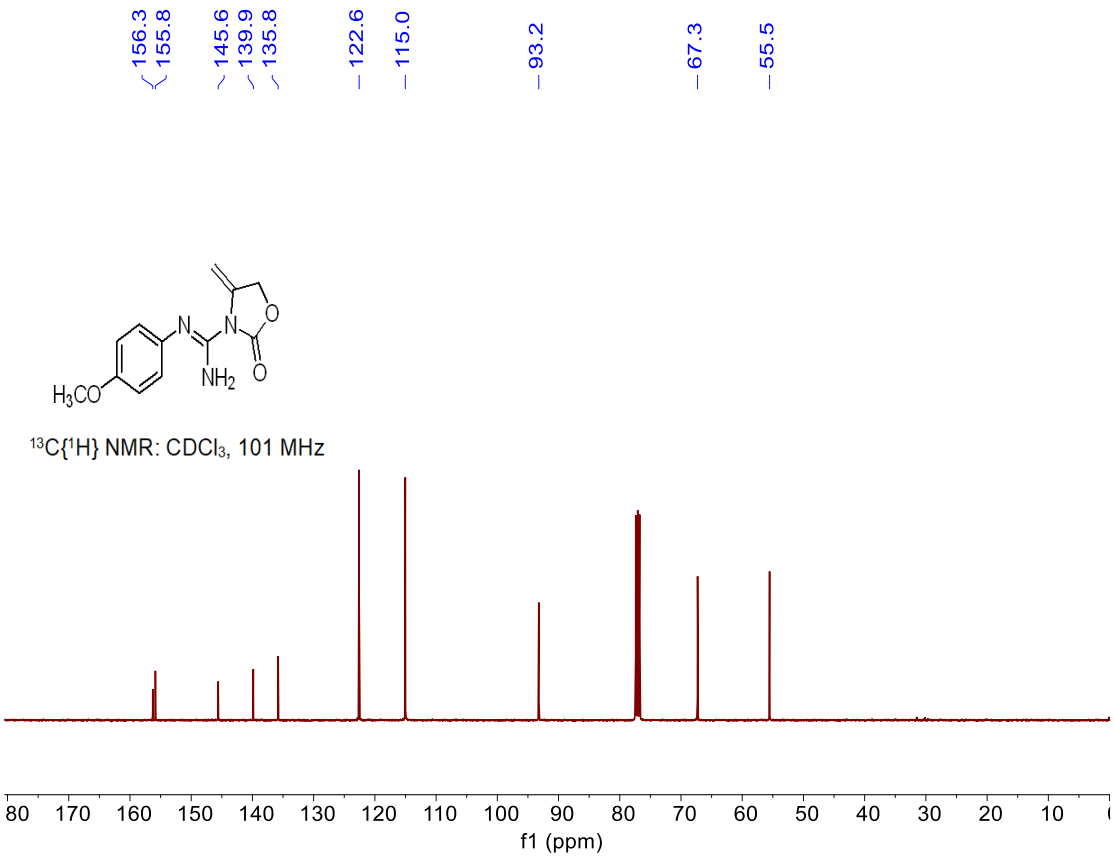


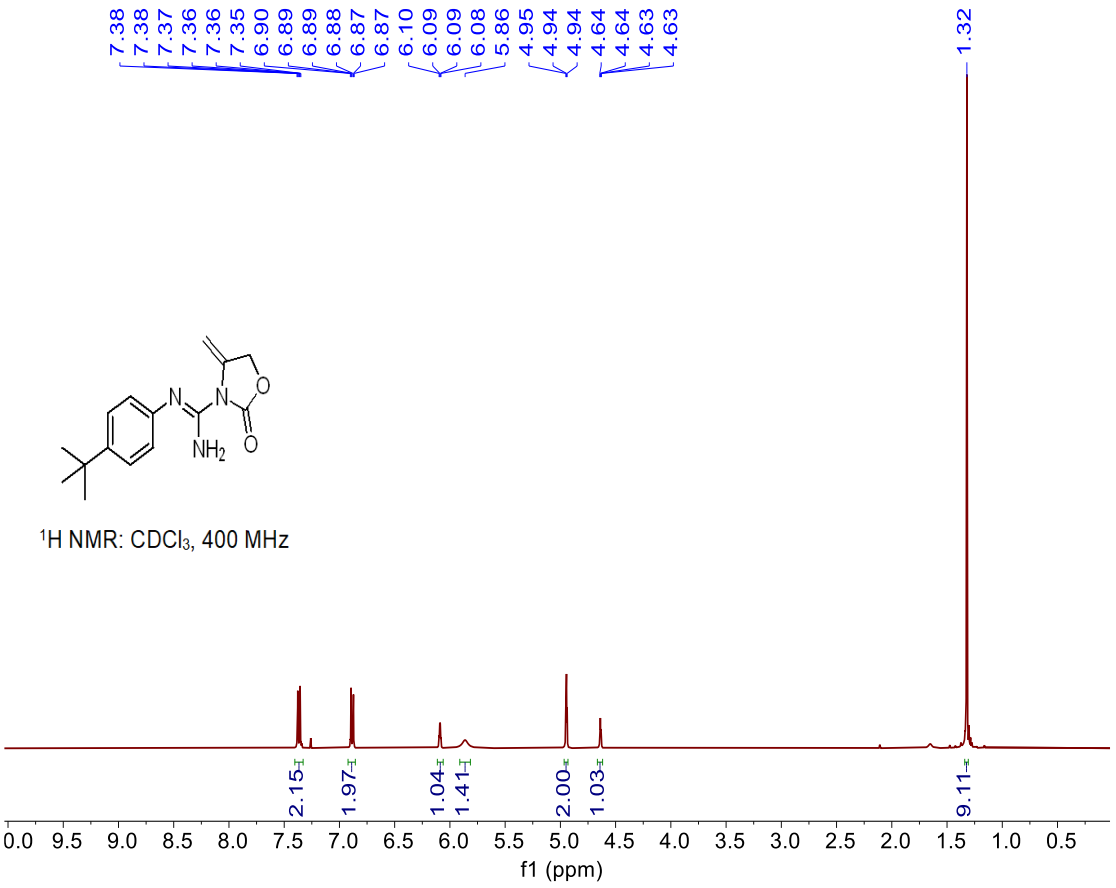


$^{13}C\{^{1}H\}$ NMR: $CDCl_3$, 101 MHz

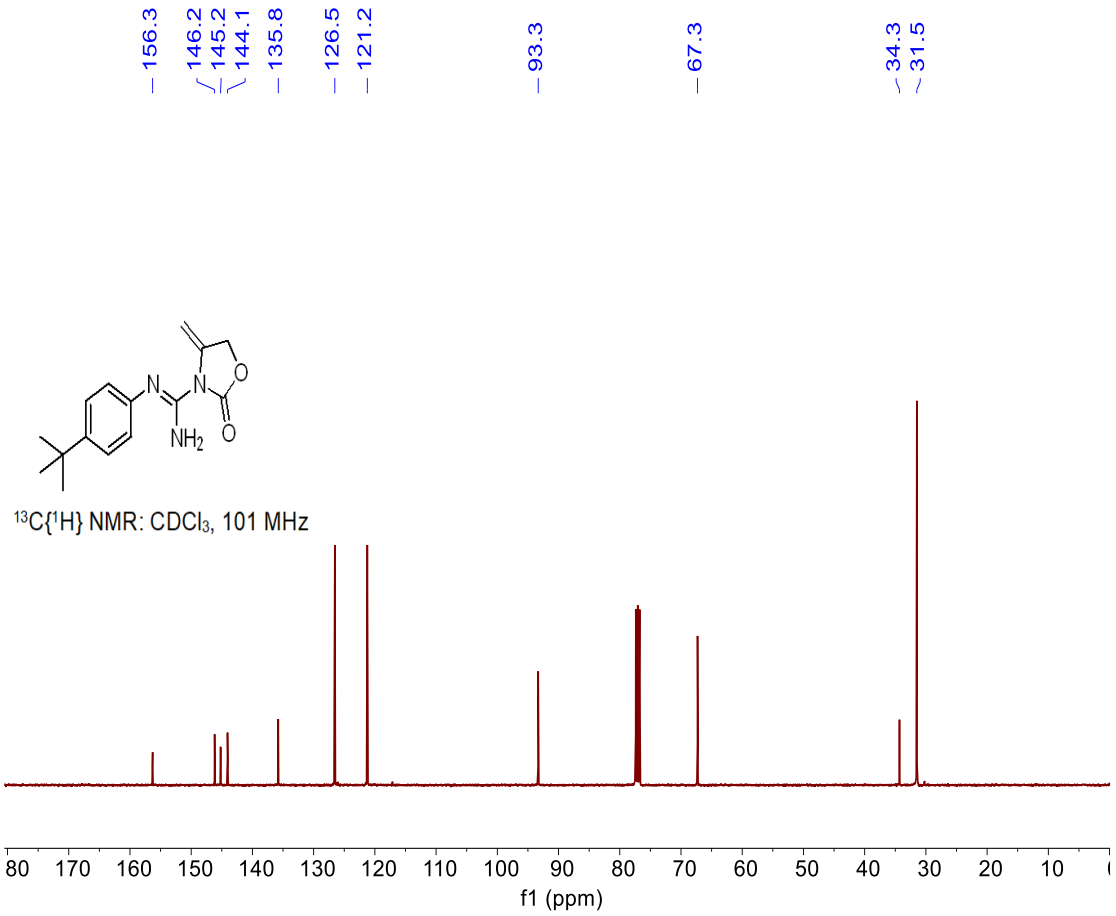



6.91
6.90
6.90
6.89
6.88
6.87
6.86
6.86
6.08
6.07
6.07
6.06
5.84
4.95
4.94
4.93
4.64
4.64
4.63
4.63
3.79
H3CO
NH2
1H NMR: CDCl3, 400 MHz
3.99
1.01
1.48
2.00
1.00
3.26
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

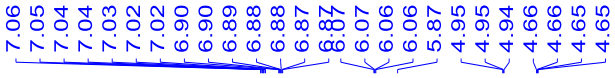

156.3
155.8
145.6
139.9
135.8
122.6
115.0
93.2
67.3
55.5
H3CO
NH2
13C{1H} NMR: CDCl3, 101 MHz
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

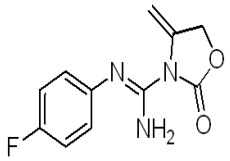


^{1}H NMR: $CDCl_3$, 400 MHz

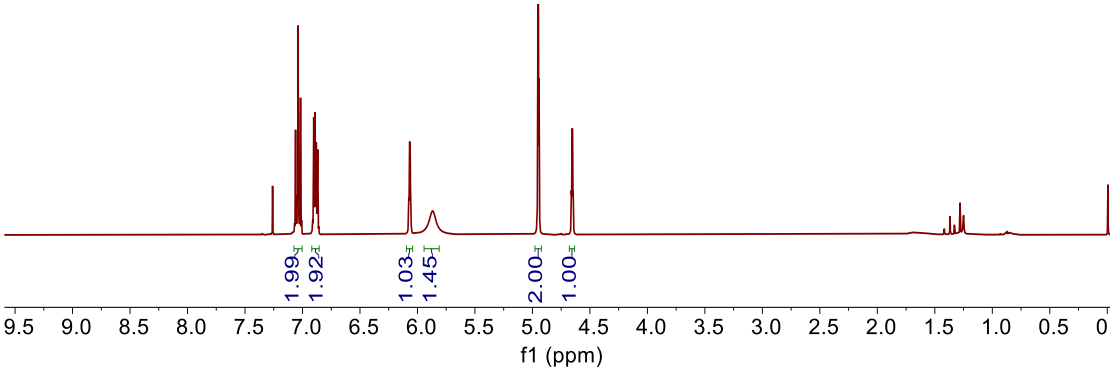


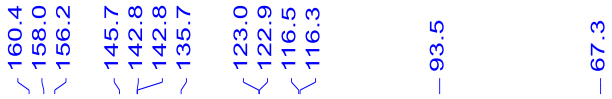
^{13}C{^{1}H} NMR: $CDCl_3$, 101 MHz

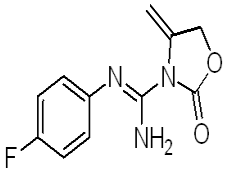




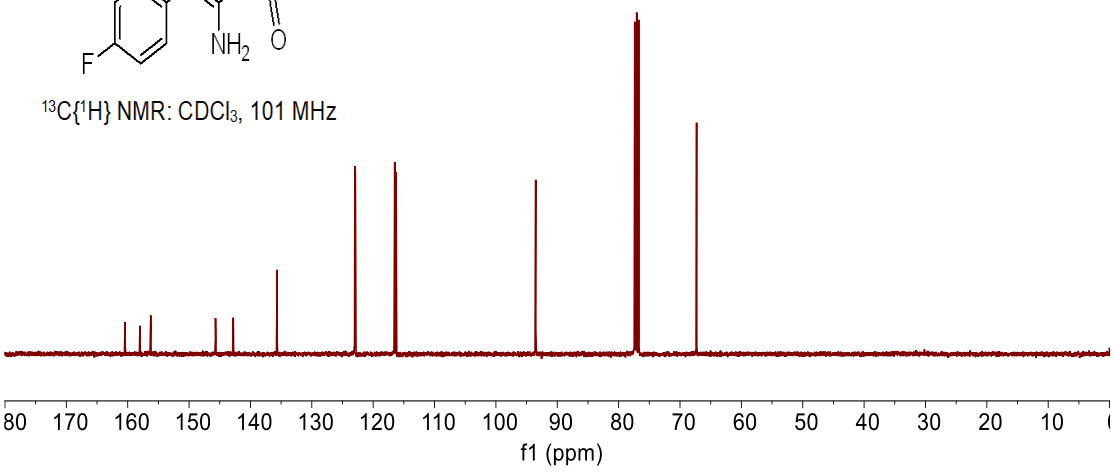
^{1}H NMR: $CDCl_3$, 400 MHz

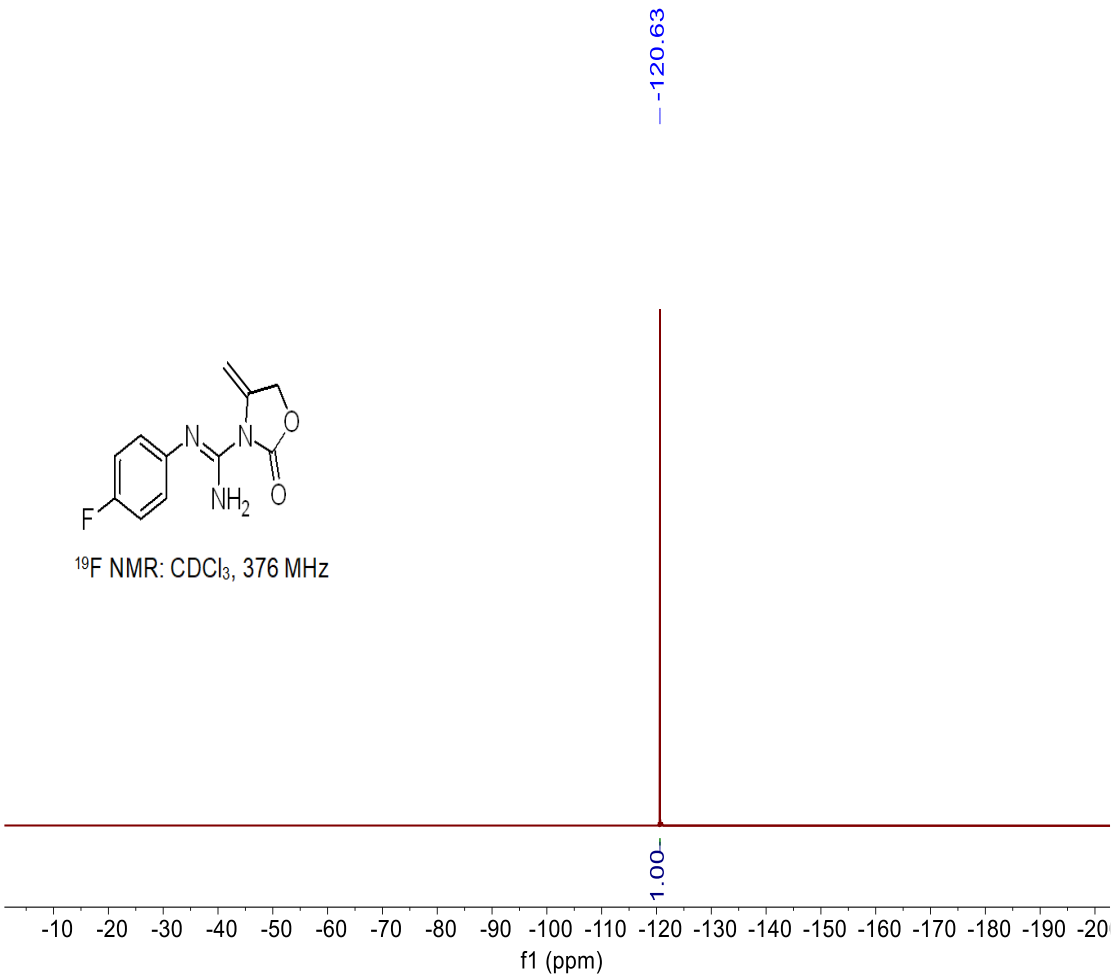




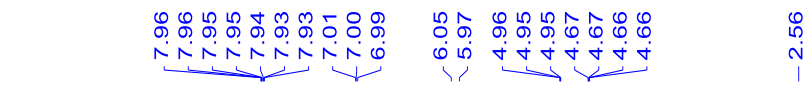


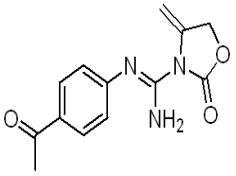
^{13}C{^{1}H} NMR: $CDCl_3$, 101 MHz



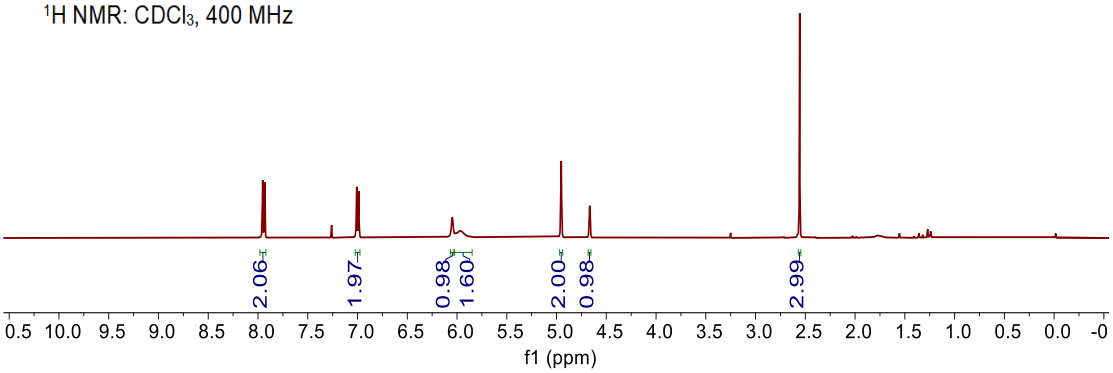


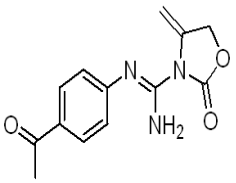
^{19}F NMR: $CDCl_3$, 376 MHz



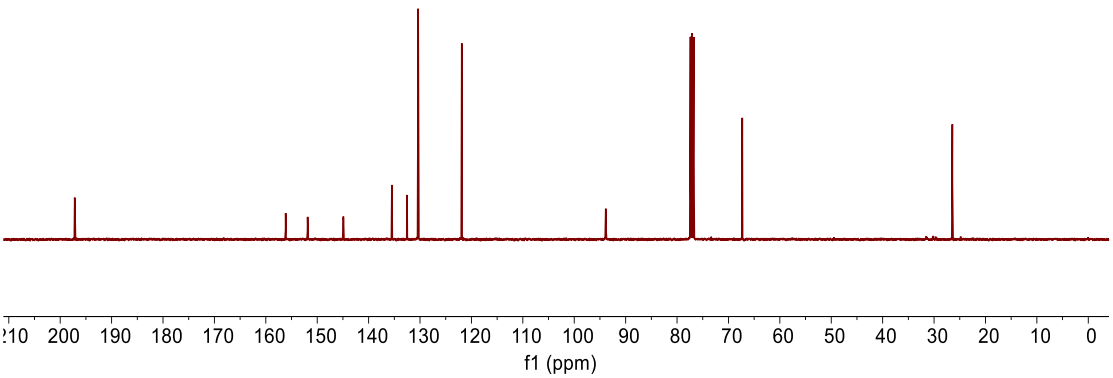


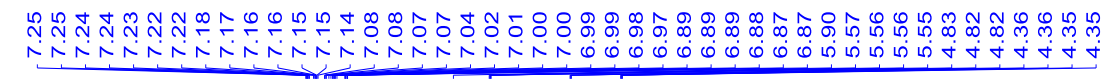
^{1}H NMR: $CDCl_3$, 400 MHz

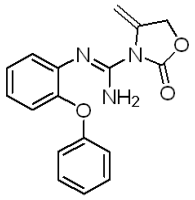




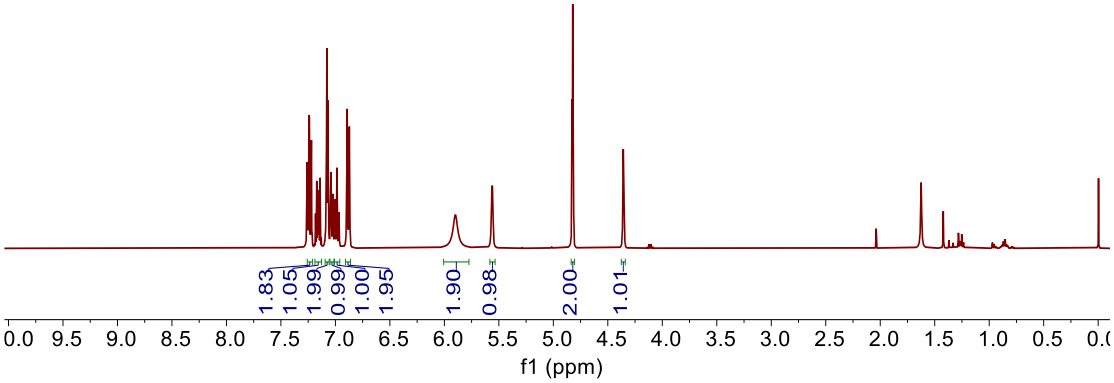
^{13}C{^{1}H} NMR: $CDCl_3$, 101 MHz

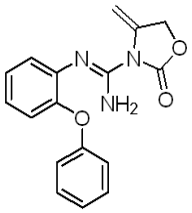




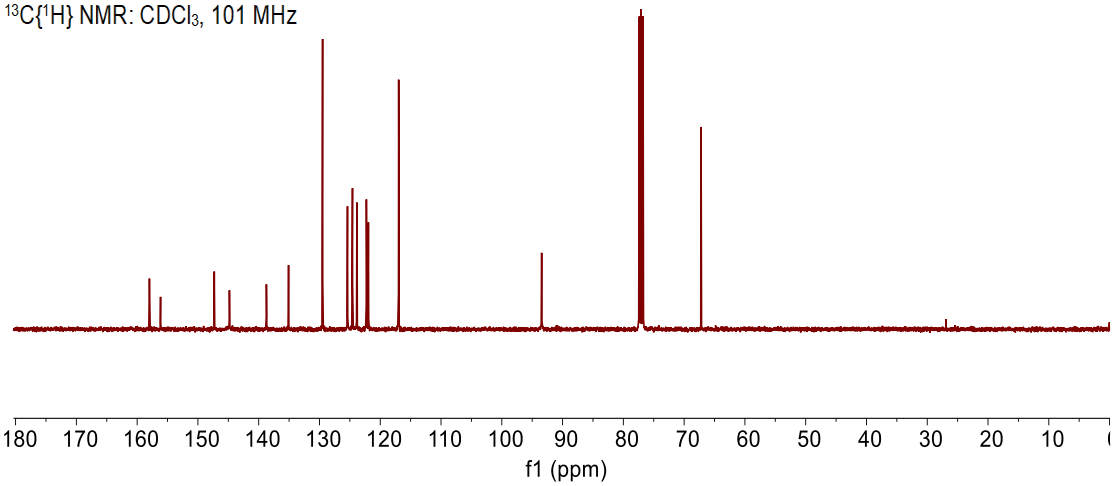


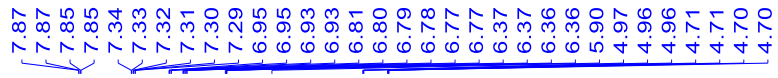
^{1}H NMR: $CDCl_3$, 400 MHz

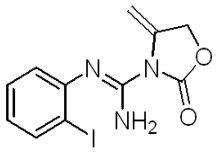




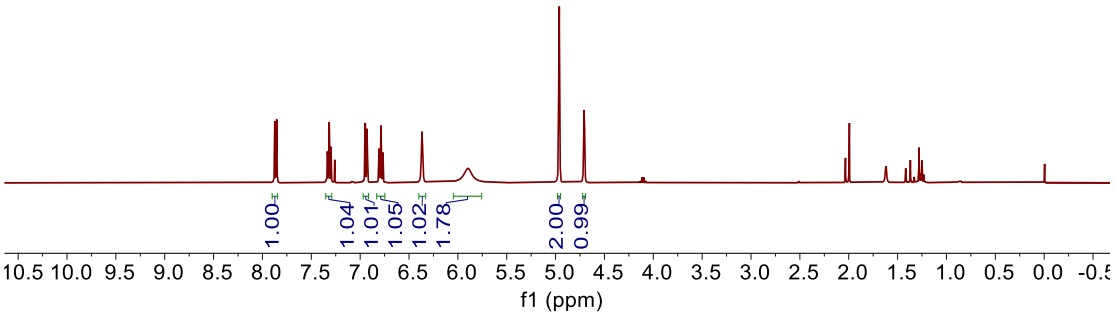
^{13}C{^{1}H} NMR: $CDCl_3$, 101 MHz

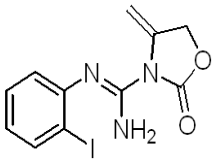




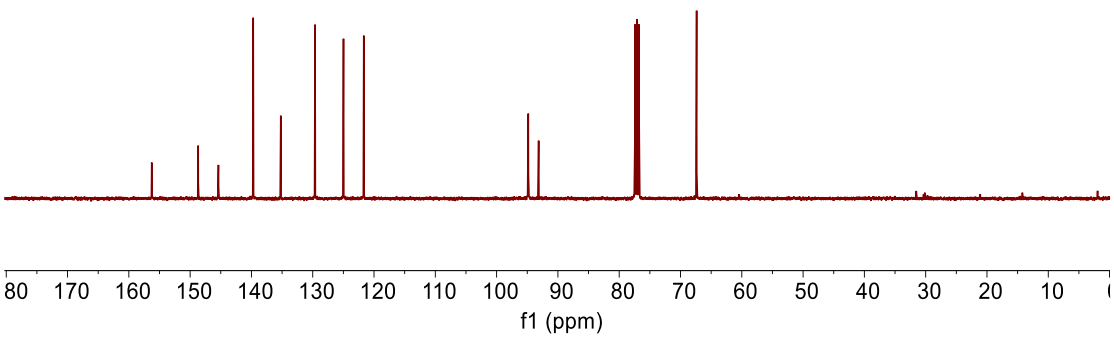


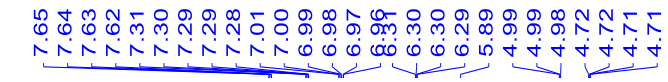
^{1}H NMR: $CDCl_3$, 400 MHz

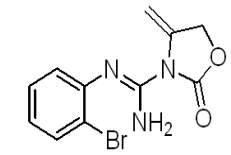




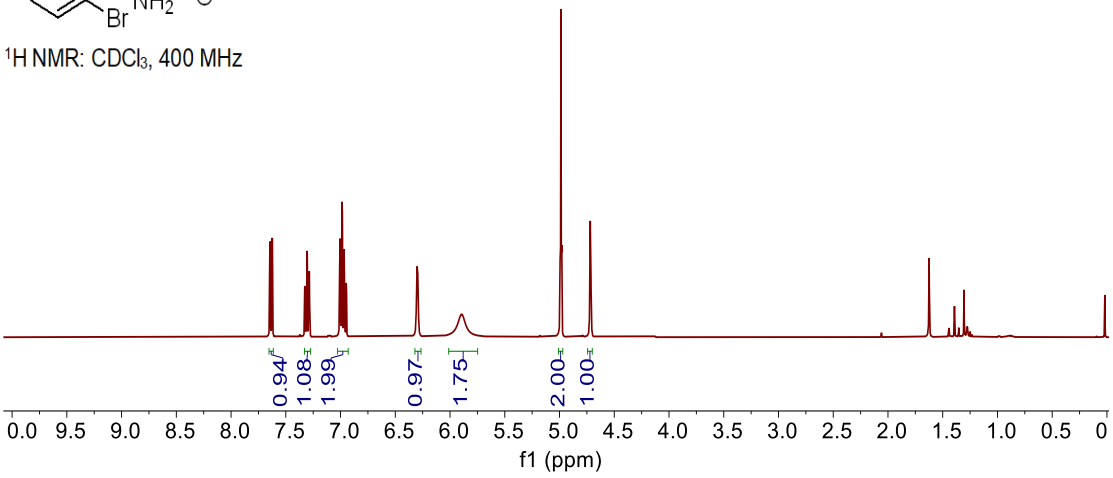
^{13}C{^{1}H} NMR: $CDCl_3$, 101 MHz

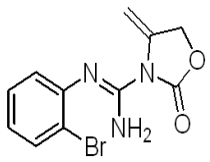




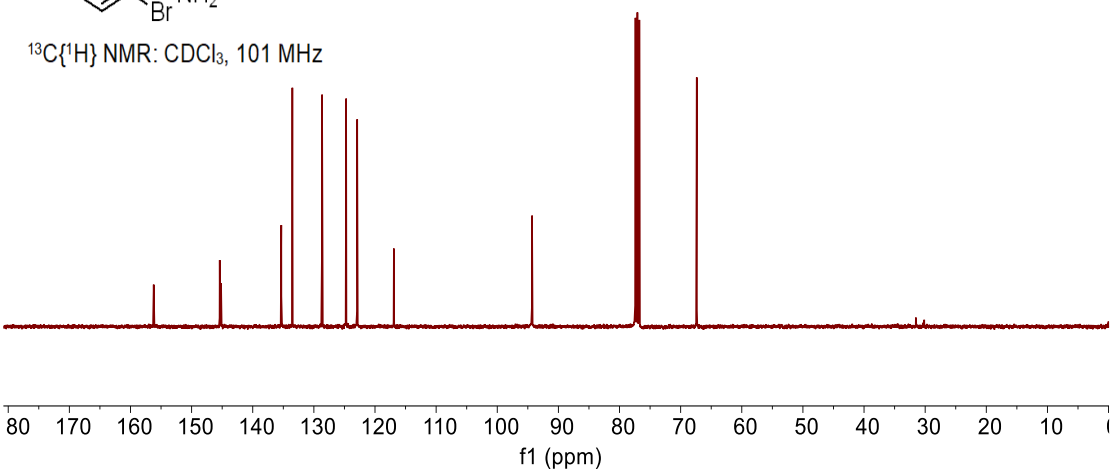


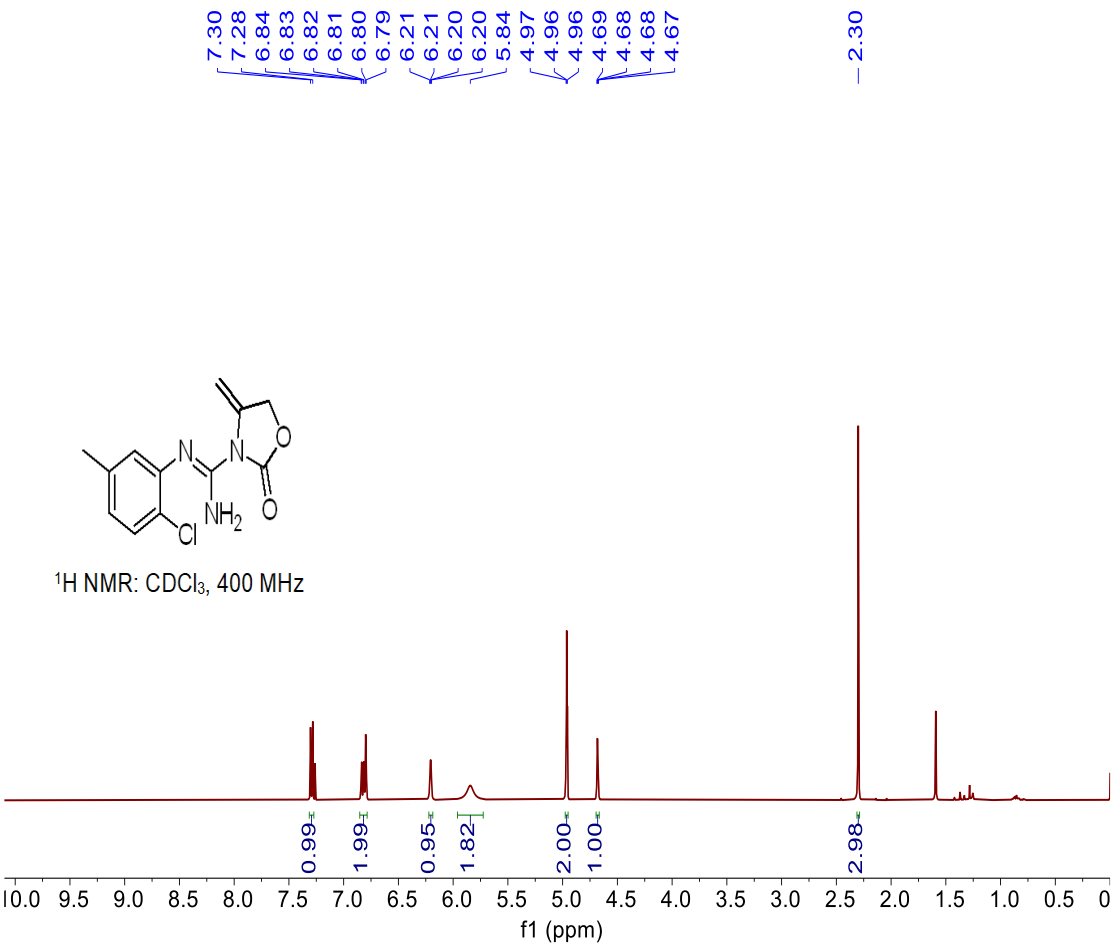
^{1}H NMR: $CDCl_3$, 400 MHz

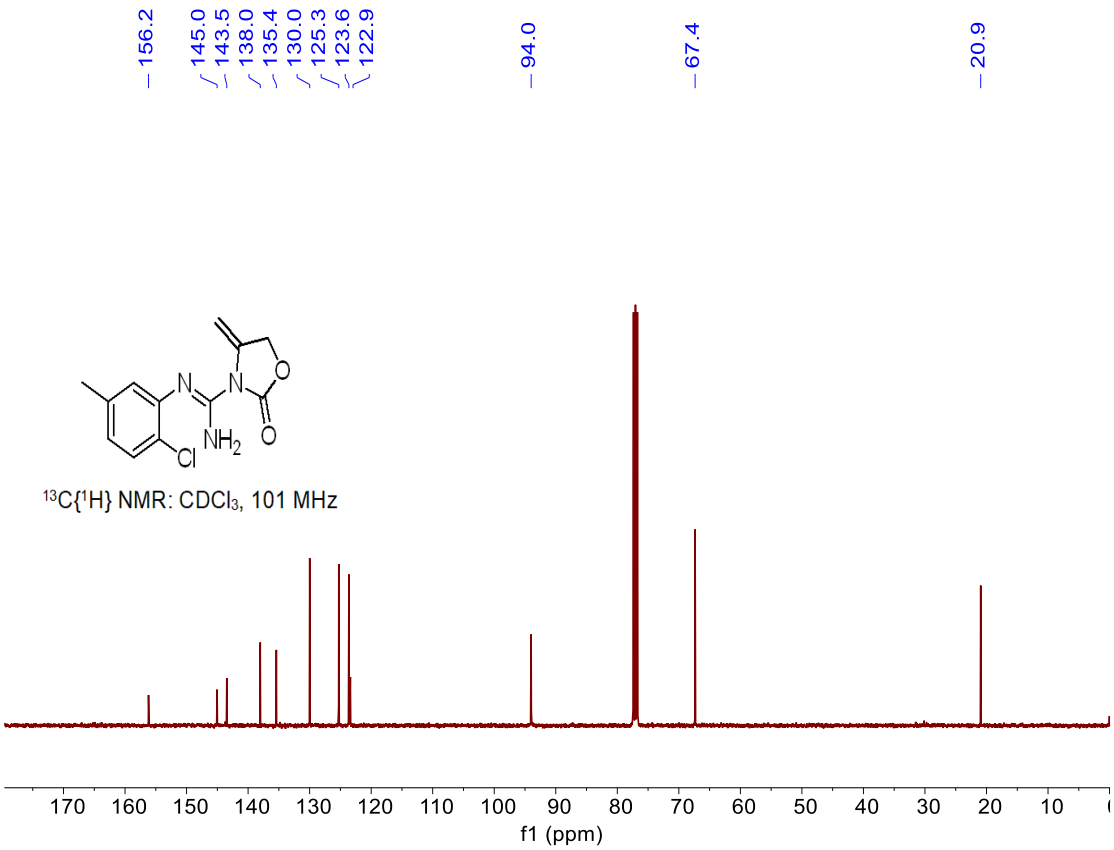


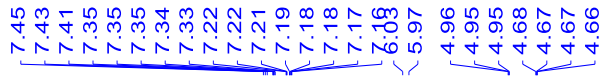


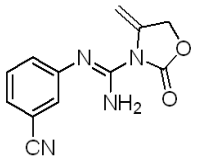
^{13}C{^{1}H} NMR: $CDCl_3$, 101 MHz



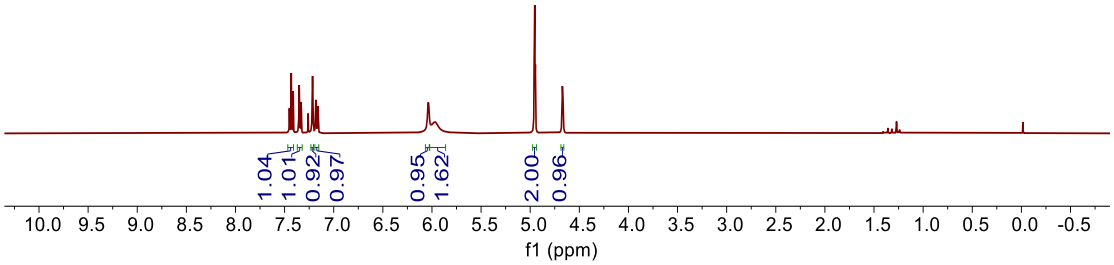

7.30
7.28
6.84
6.83
6.82
6.81
6.80
6.79
6.21
6.21
6.20
6.20
5.84
4.97
4.96
4.96
4.69
4.68
4.68
4.67
2.30
Cl
NH2
O
O
N
N
O
1H NMR: CDCl3, 400 MHz
0.99
1.99
0.95
1.82
2.00
1.00
2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

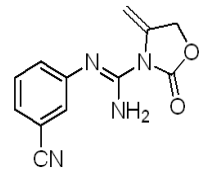

156.2
145.0
143.5
138.0
135.4
130.0
125.3
123.6
122.9
94.0
67.4
20.9
Cl
NH2
O
O
N
N
O
13C{1H} NMR: CDCl3, 101 MHz
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



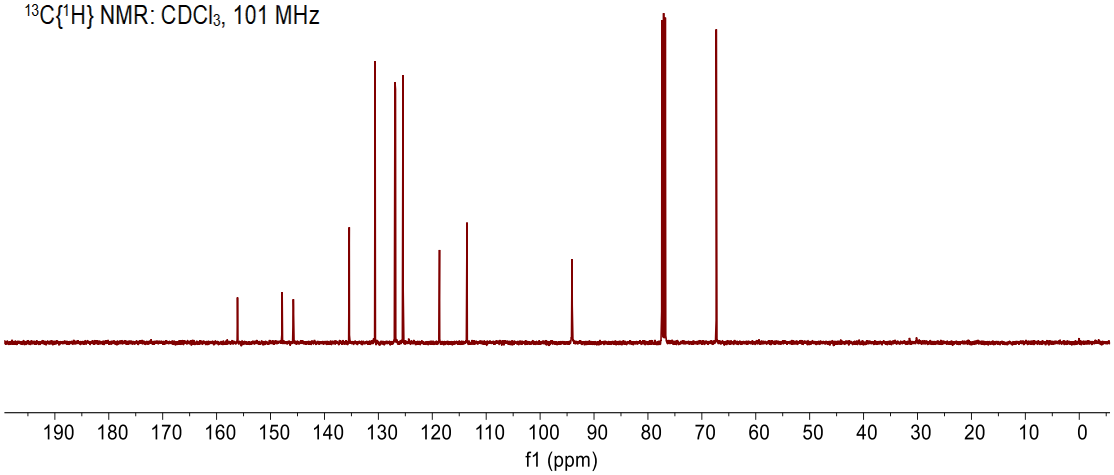


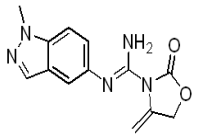
^{1}H NMR: $CDCl_3$, 400 MHz



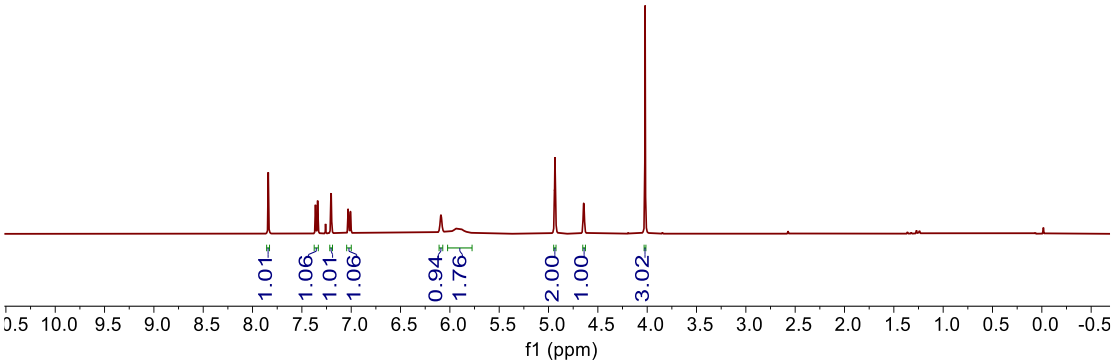


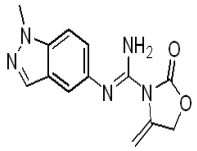
^{13}C{^{1}H} NMR: $CDCl_3$, 101 MHz



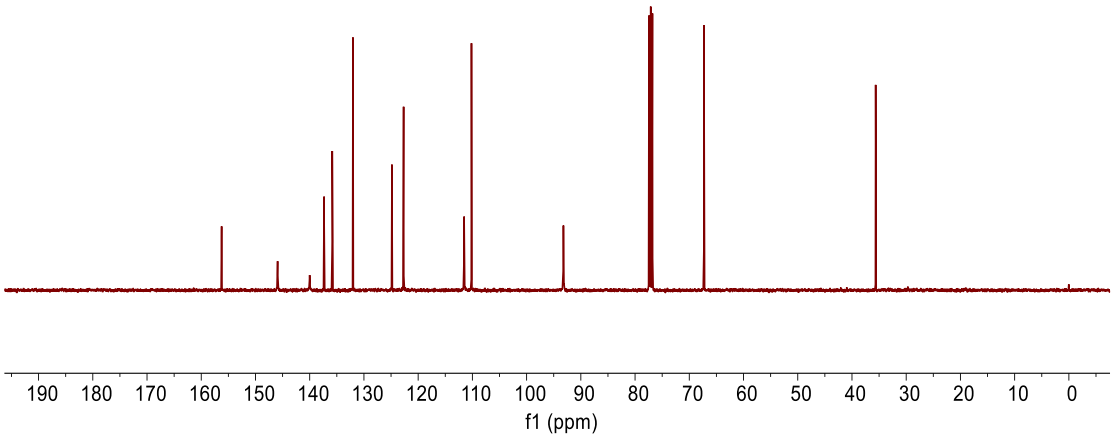


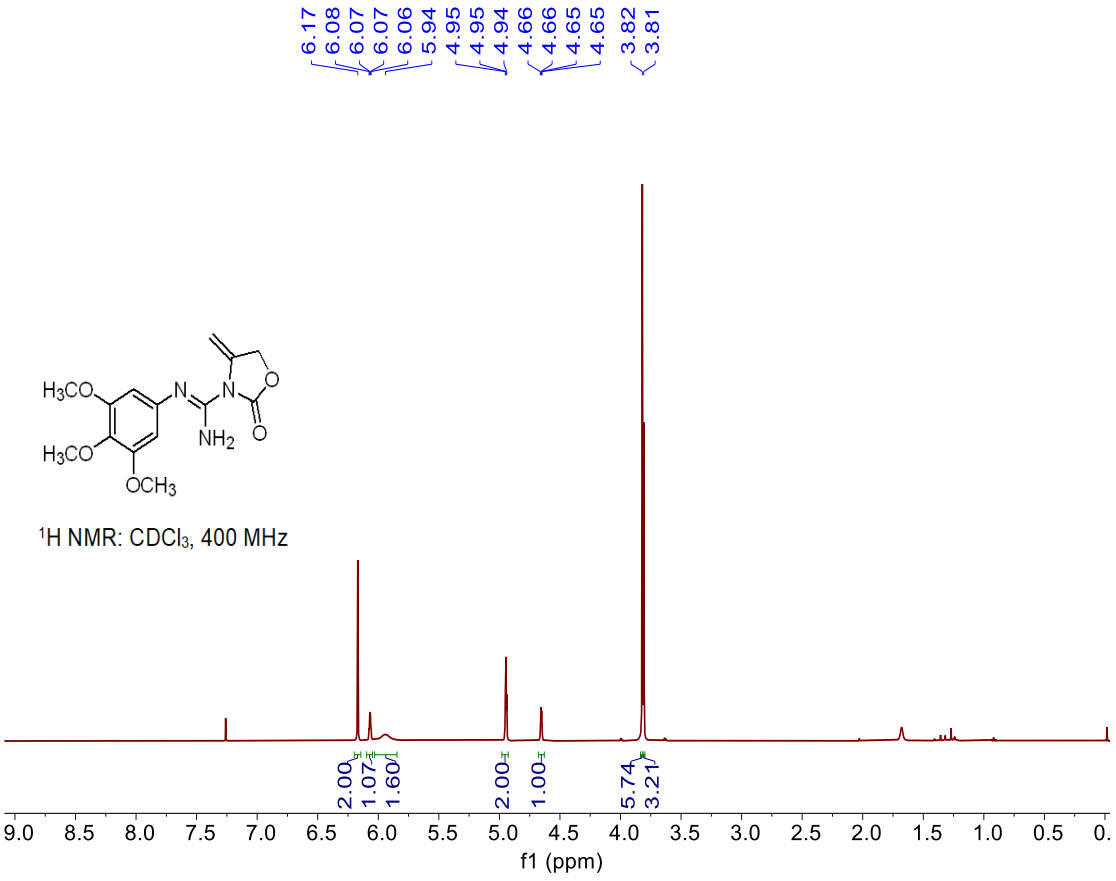
^{1}H NMR: $CDCl_3$, 400 MHz

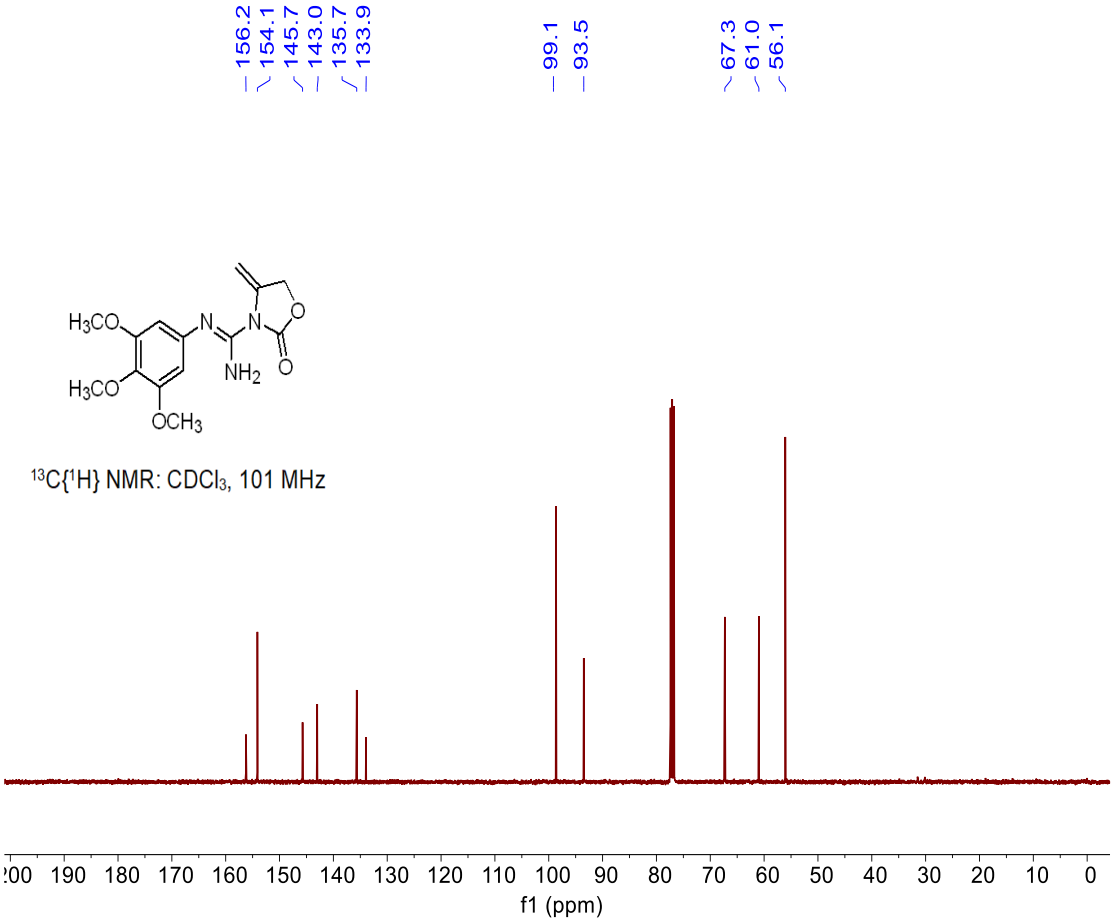


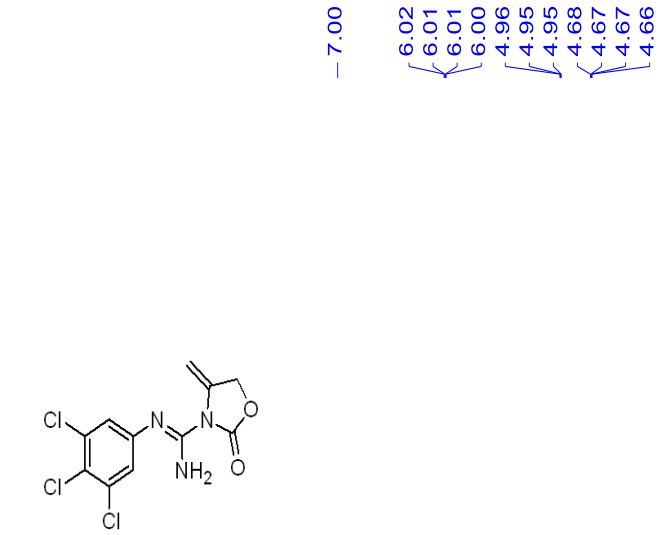


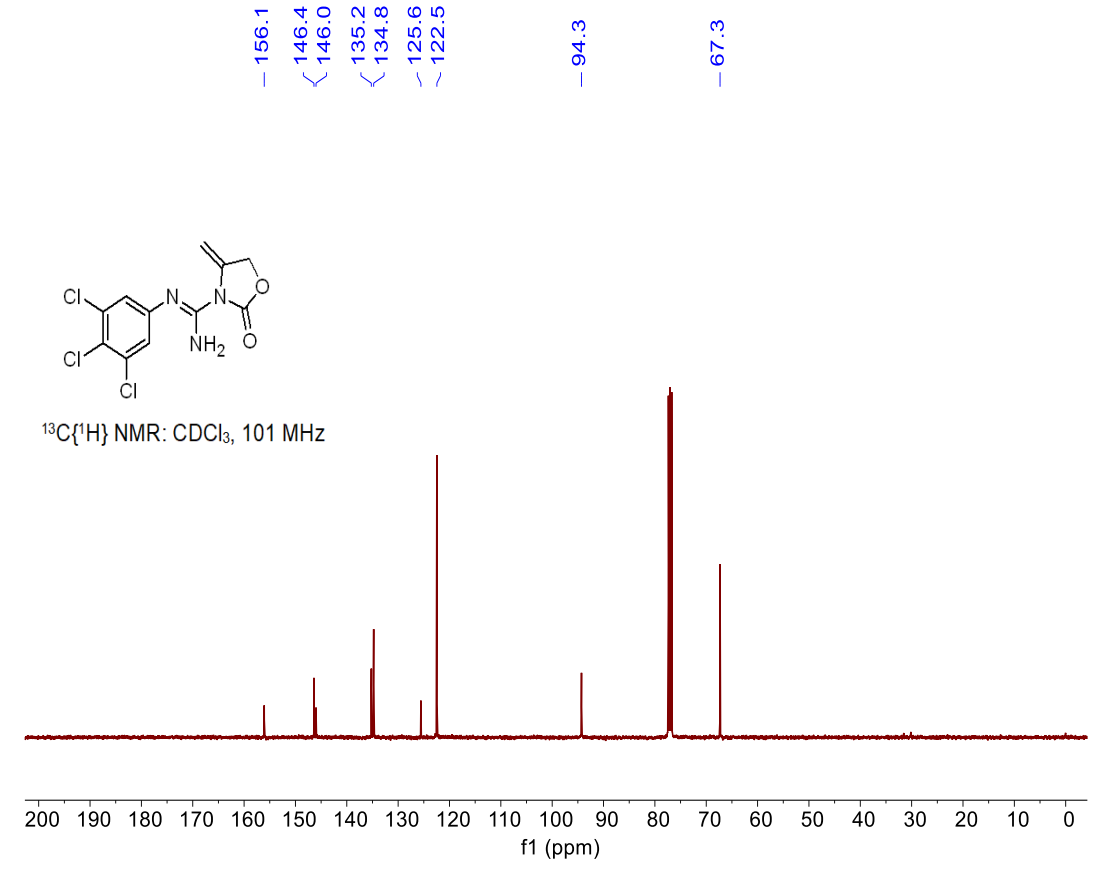
^{13}C{^{1}H} NMR: $CDCl_3$, 101 MHz

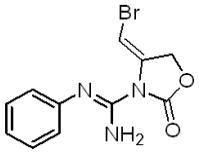



6.17
6.08
6.07
6.07
6.06
5.94
4.95
4.95
4.94
4.66
4.66
4.65
4.65
3.82
3.81
H3CO
H3CO
OCH3
N
N
O
O
NH2
1H NMR: CDCl3, 400 MHz
2.00
1.07
1.60
2.00
1.00
5.74
3.21
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

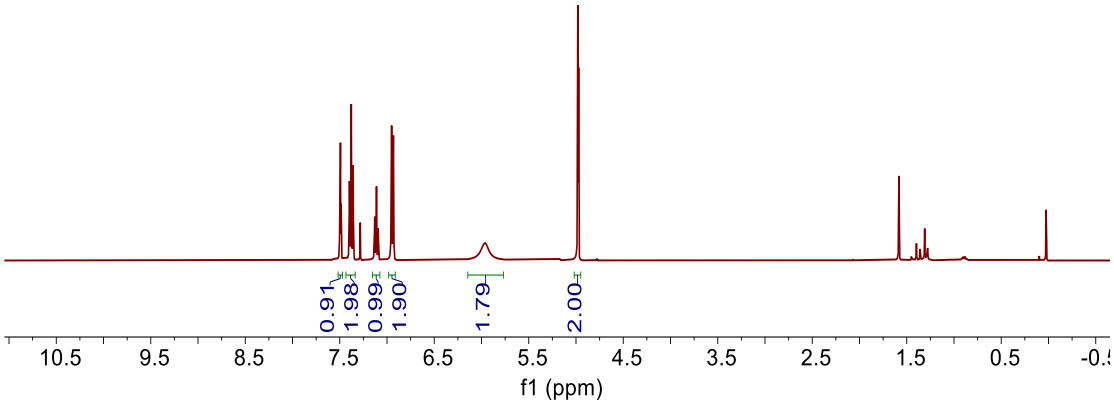

156.2
154.1
145.7
143.0
135.7
133.9
99.1
93.5
67.3
61.0
56.1
H3CO
H3CO
OCH3
N
N
O
O
NH2
13C{1H} NMR: CDCl3, 101 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

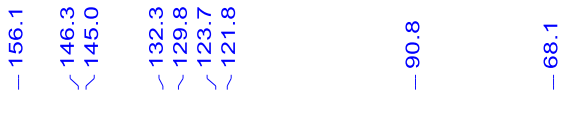

7.00
6.02
6.01
6.01
6.00
4.96
4.95
4.95
4.68
4.67
4.67
4.66
Cl
Cl
Cl
N
N
O
O
NH2
1H NMR: CDCl3, 400 MHz
1.82
2.68
2.00
0.98
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

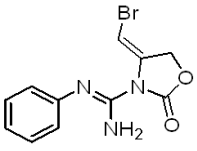

156.1
146.4
146.0
135.2
134.8
125.6
122.5
94.3
67.3
Cl
Cl
Cl
N
N
O
O
NH2
13C{1H} NMR: CDCl3, 101 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



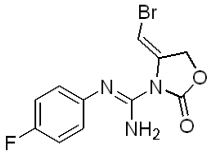
^{1}H NMR: $CDCl_3$, 400 MHz



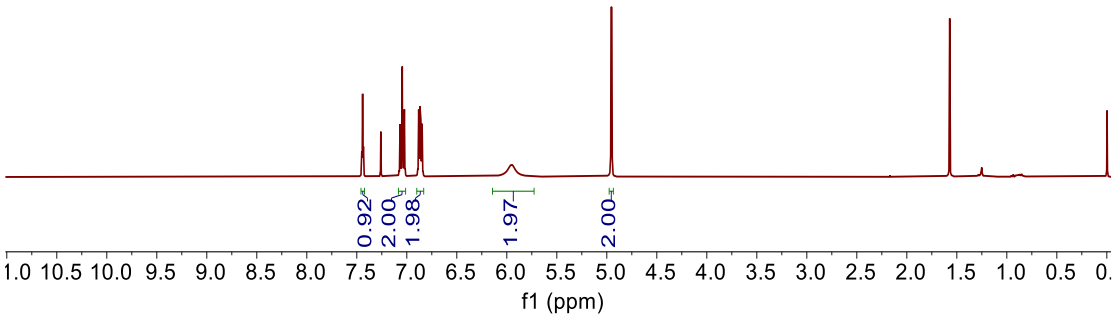


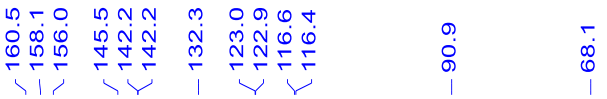


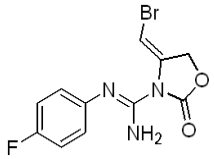
^{13}C{^{1}H} NMR: $CDCl_3$, 101 MHz



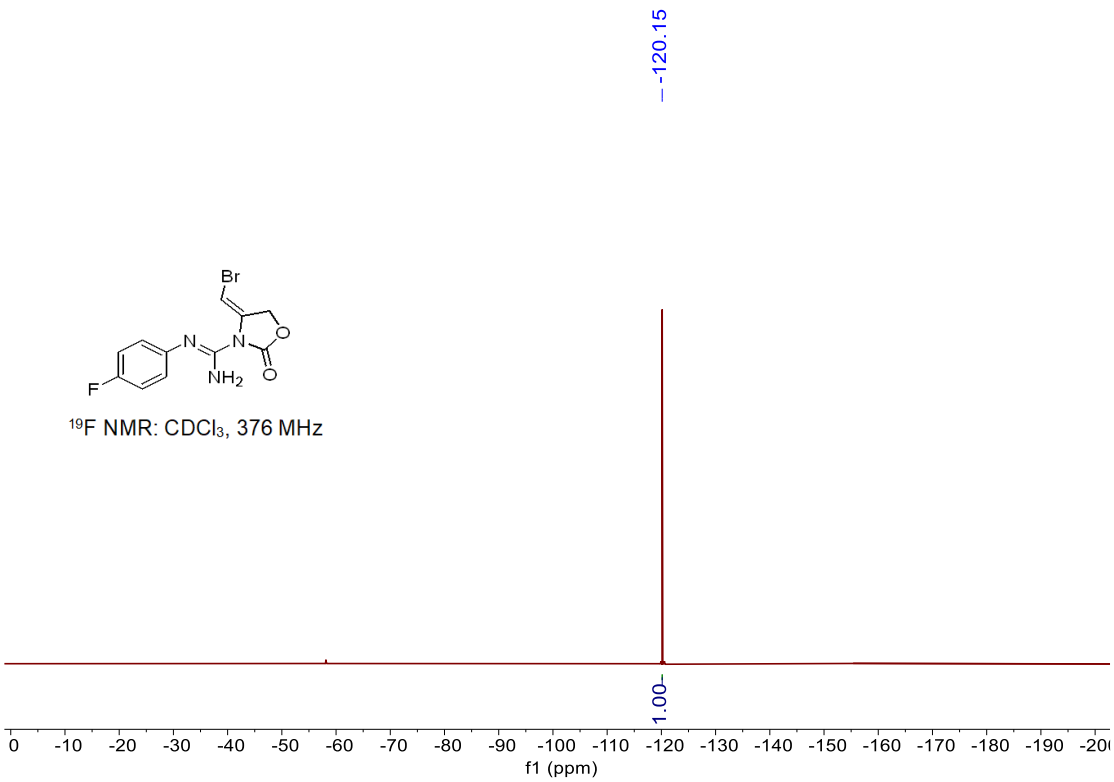
^{1}H NMR: $CDCl_3$, 400 MHz

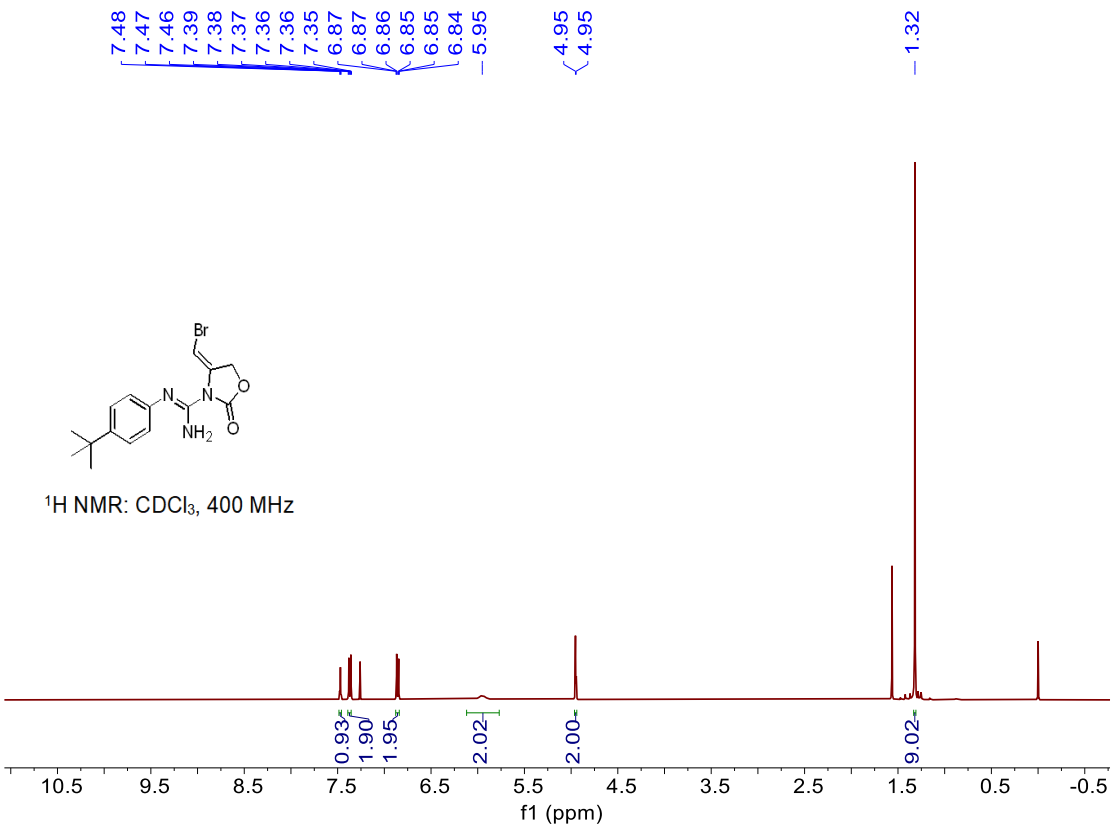




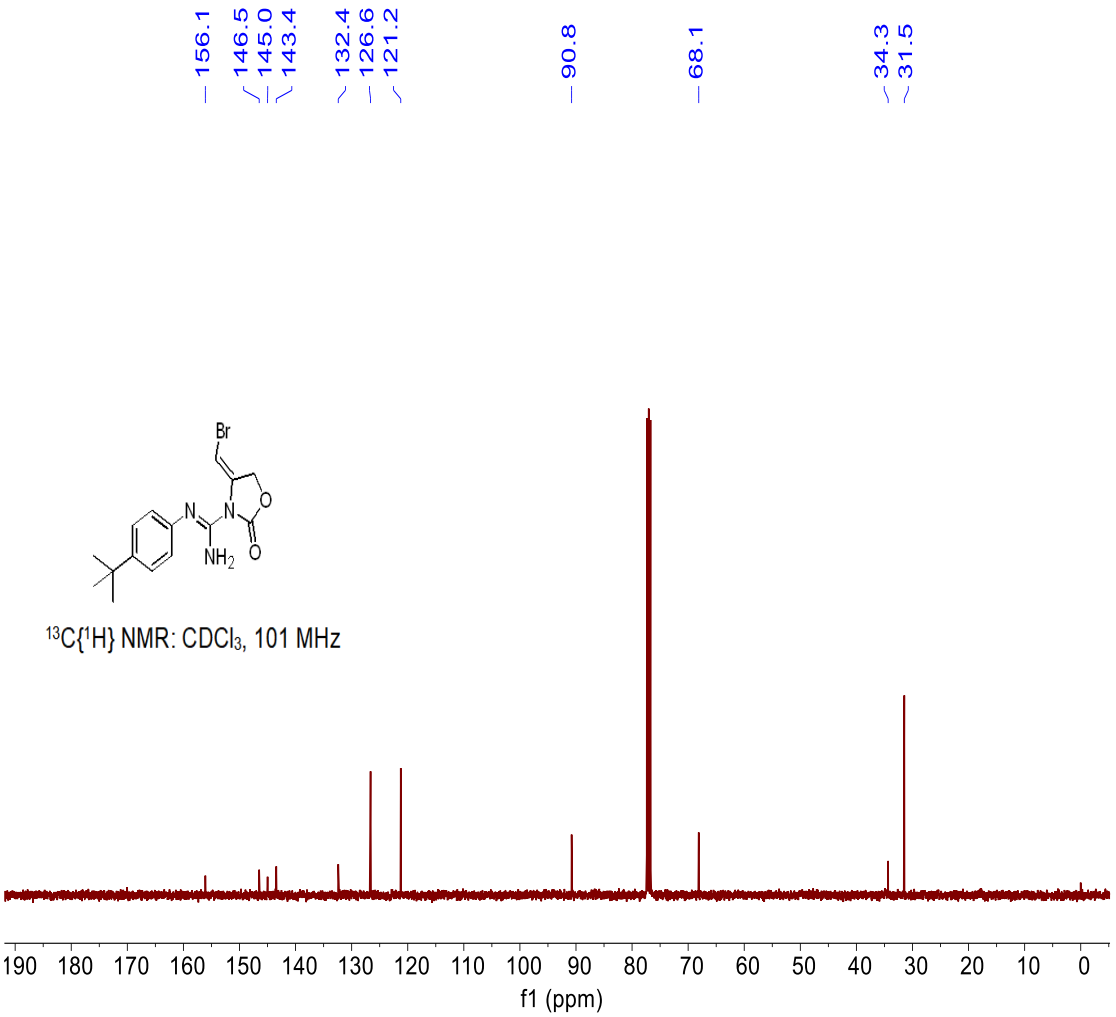


^{13}C{^{1}H} NMR: $CDCl_3$, 101 MHz

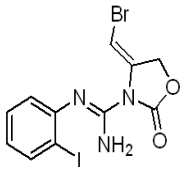

-120.15
Br
N
N
O
O
NH2
F
19F NMR: CDCl3, 376 MHz
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)



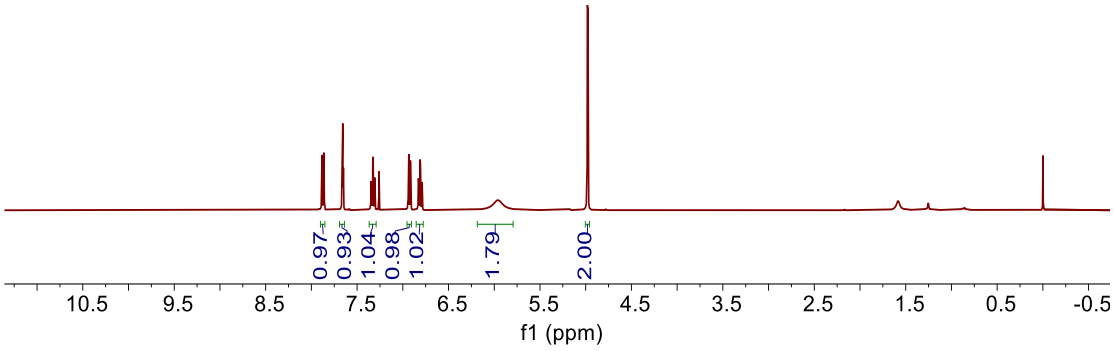
^{1}H NMR: $CDCl_3$, 400 MHz

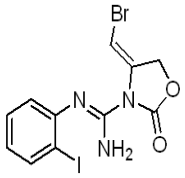


^{13}C{^{1}H} NMR: $CDCl_3$, 101 MHz



^{1}H NMR: $CDCl_3$, 400 MHz





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


7.29
7.28
7.28
7.26
7.25
7.24
7.24
7.20
7.19
7.18
7.18
7.17
7.16
7.16
7.13
7.12
7.11
7.10
7.10
7.04
7.02
7.01
7.00
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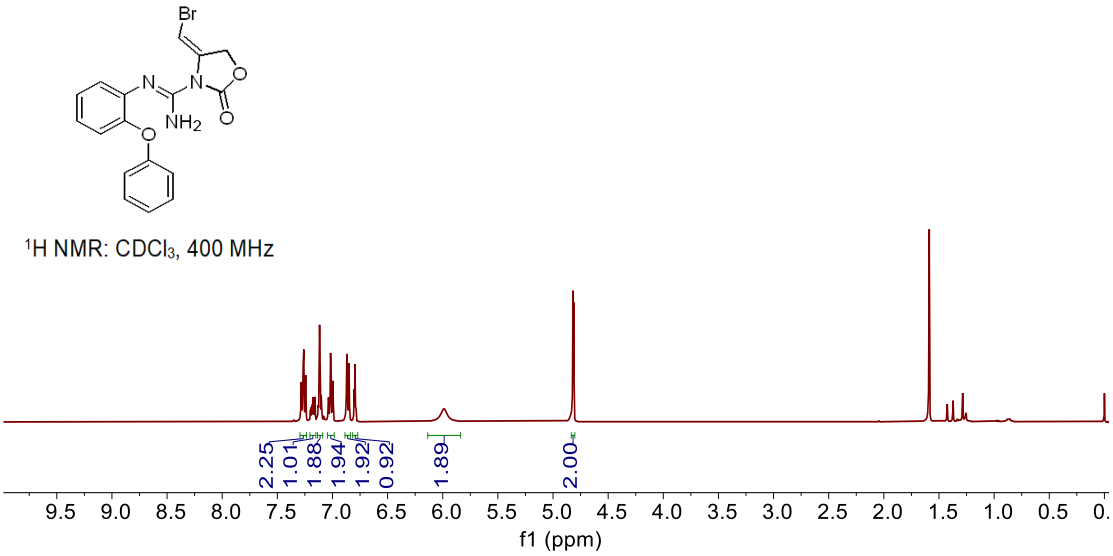
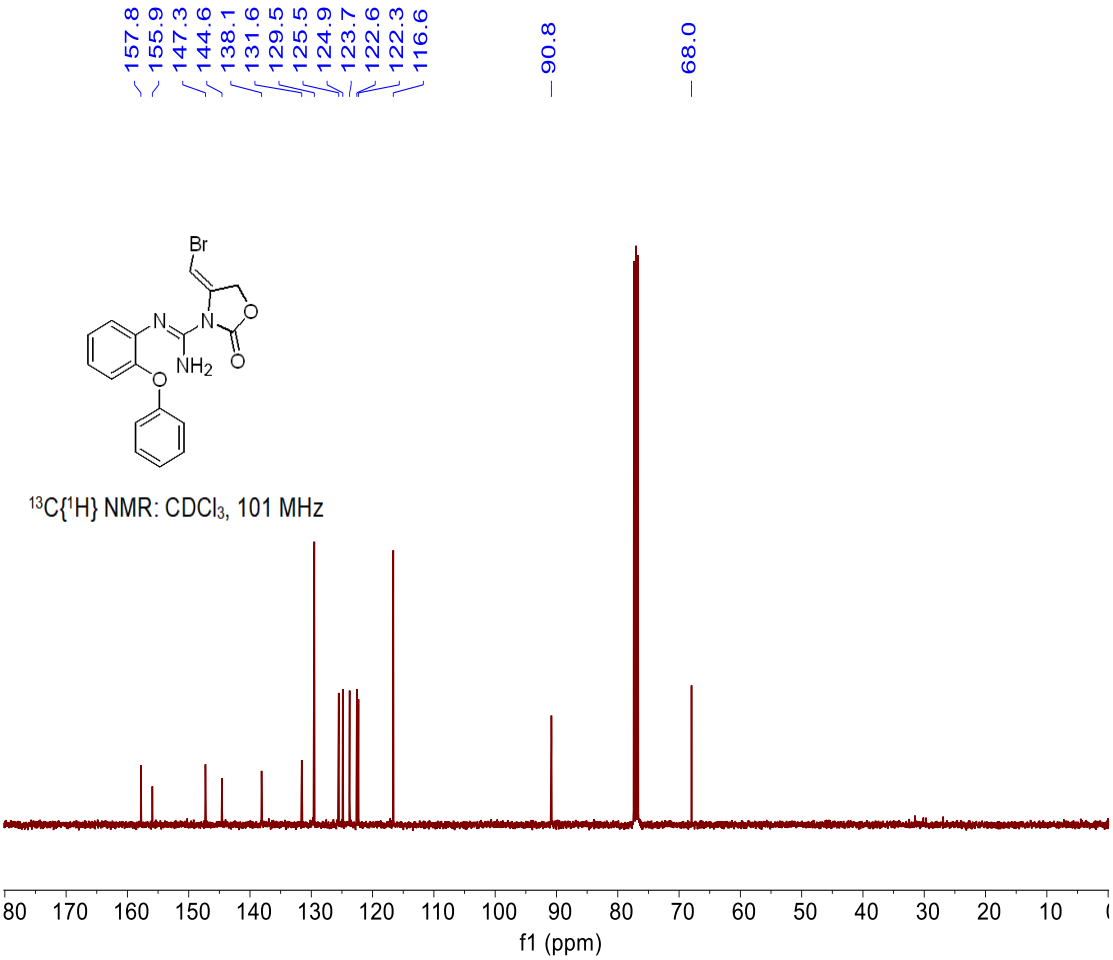
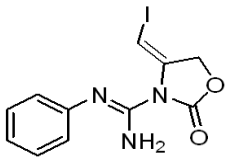
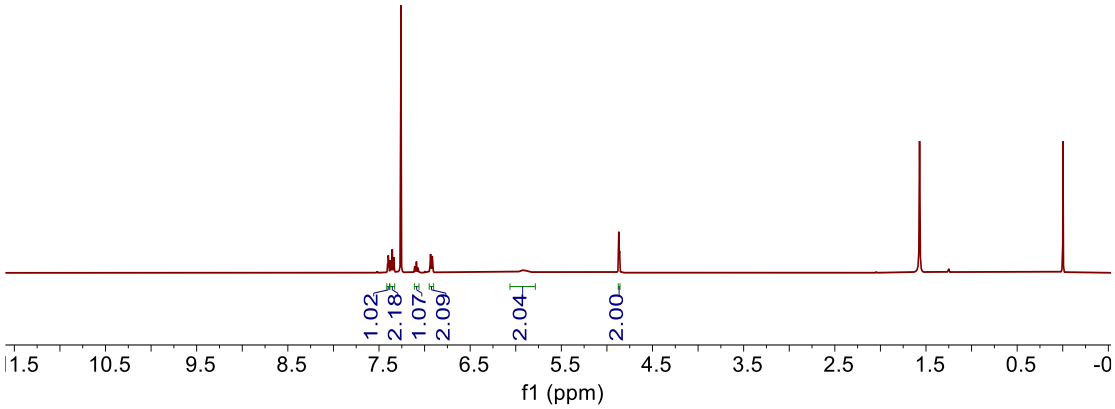
6.80
6.79
6.79
5.99
4.82
4.81

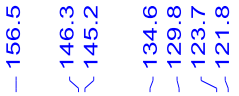

Br
N
N
O
O
NH2
O
1H NMR: CDCl3, 400 MHz
2.25
1.01
1.88
1.94
1.92
0.92
1.89
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

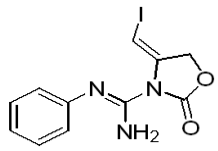

157.8
155.9
147.3
144.6
138.1
131.6
129.5
125.5
124.9
123.7
122.6
122.3
116.6
90.8
68.0
Br
N
N
O
O
NH2
O
13C{1H} NMR: CDCl3, 101 MHz
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



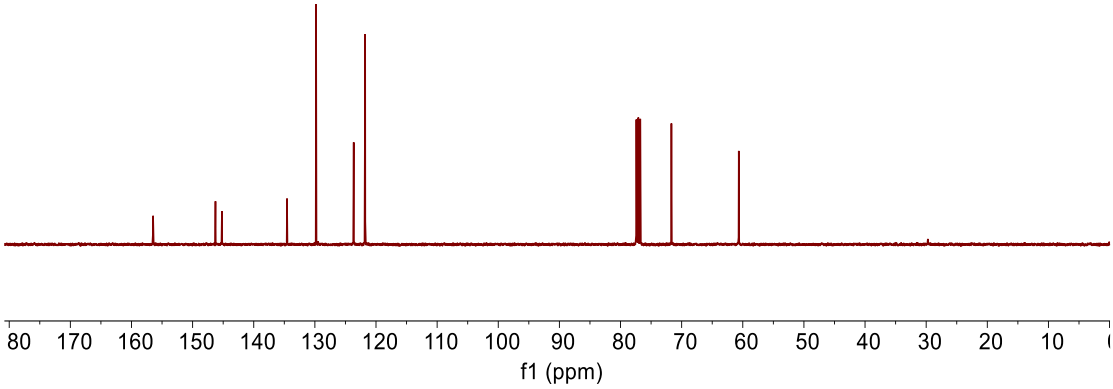
^{1}H NMR: $CDCl_3$, 400 MHz







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




7.38
7.38
7.37
7.07
7.06
7.05
7.05
7.04
7.04
7.03
7.03
6.90
6.89
6.88
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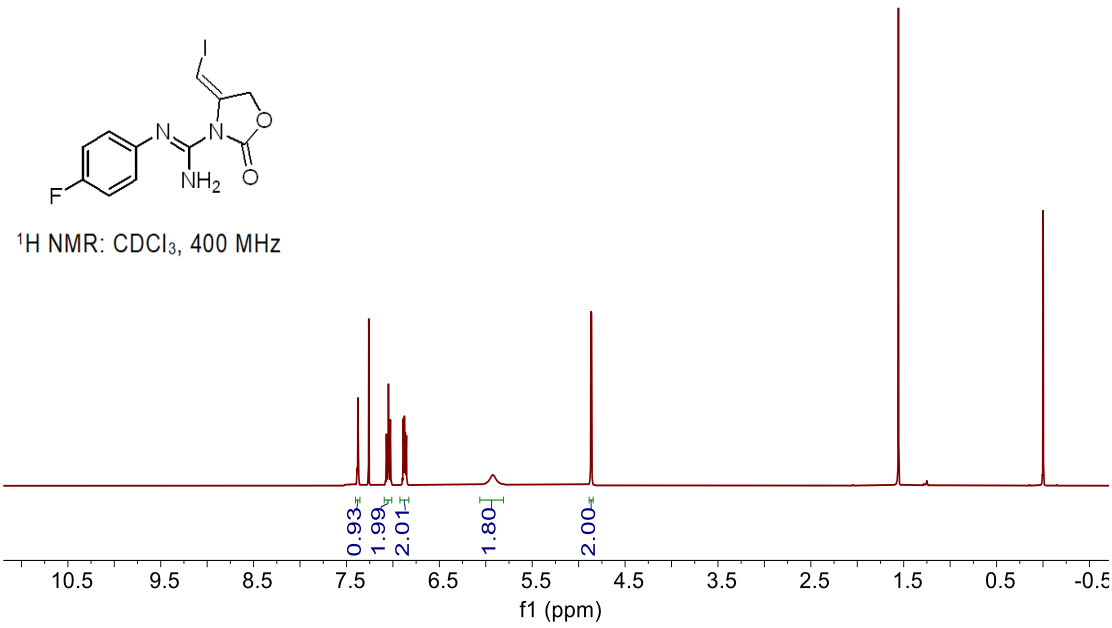
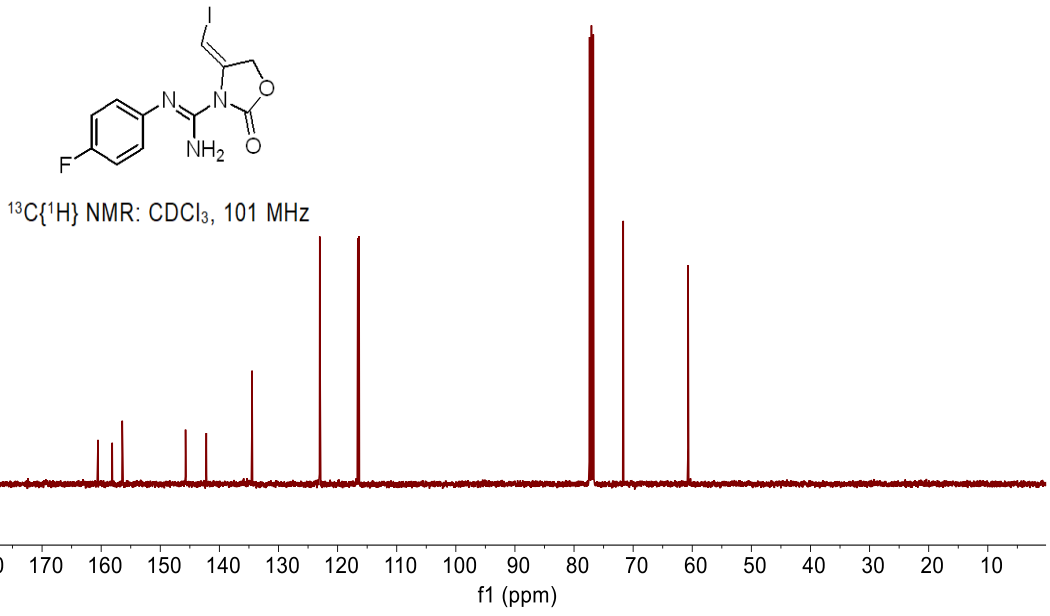
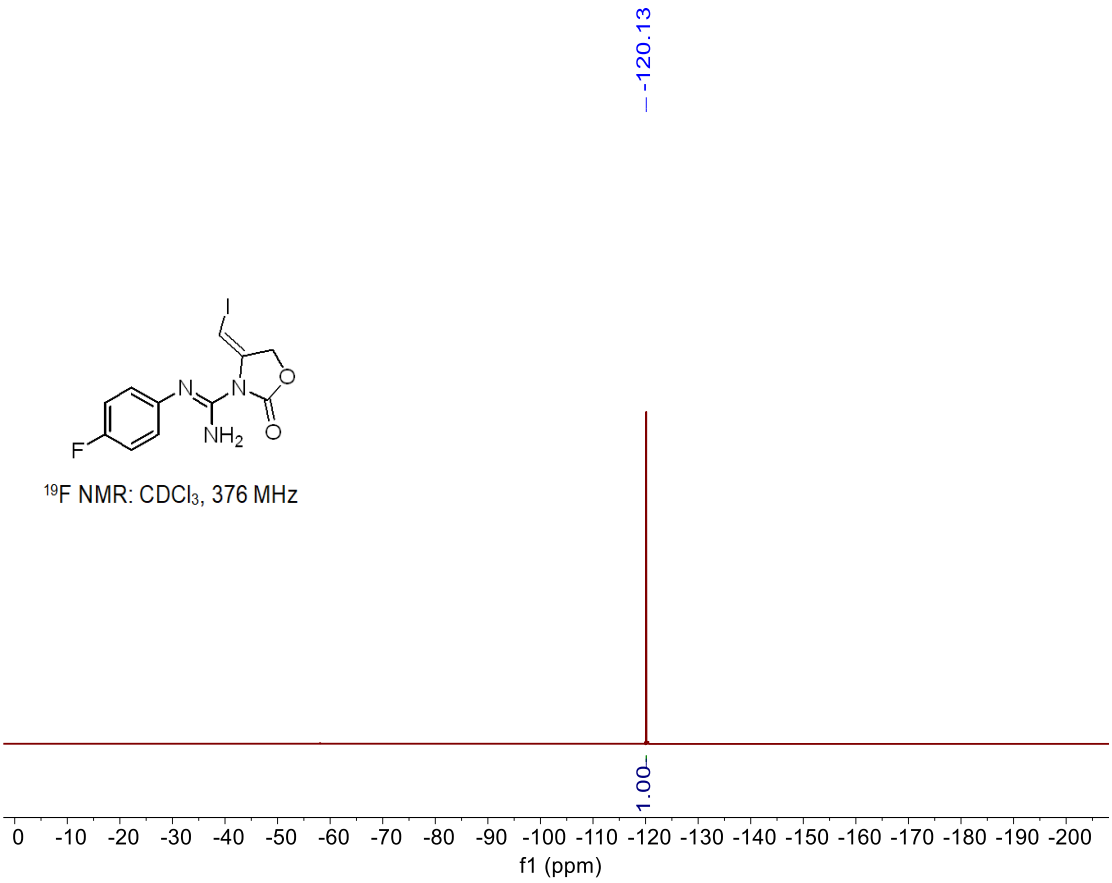
6.87
6.87
6.86
6.85
5.92
4.87
4.86

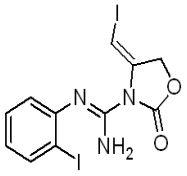

I
N
N
O
O
NH2
F
1H NMR: CDCl3, 400 MHz
0.93
1.99
2.01
1.80
2.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


160.5
158.1
156.4
145.7
142.2
142.2
134.5
123.0
122.9
116.6
116.4
71.7
60.7

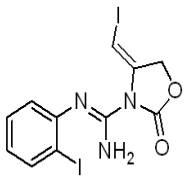

I
N
N
O
O
NH2
F
13C{1H} NMR: CDCl3, 101 MHz
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



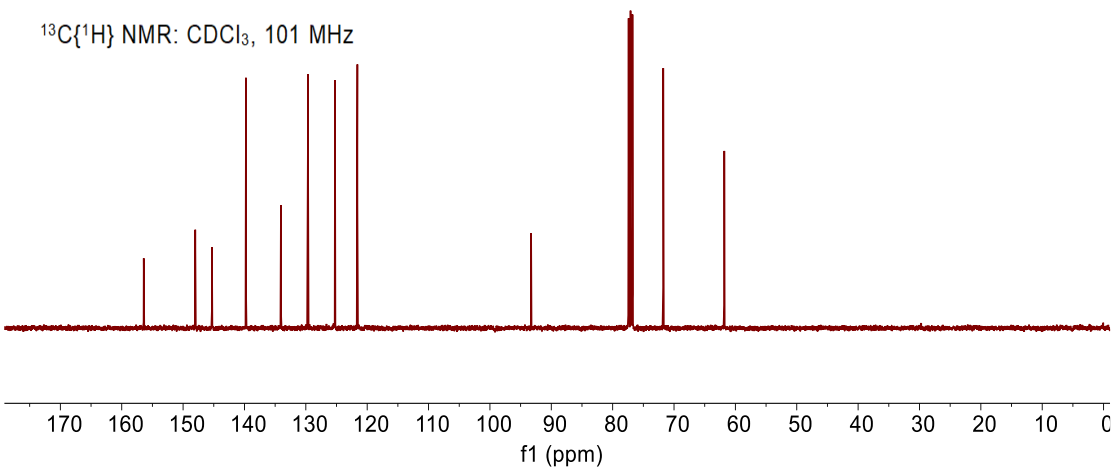
^{19}F NMR: $CDCl_3$, 376 MHz

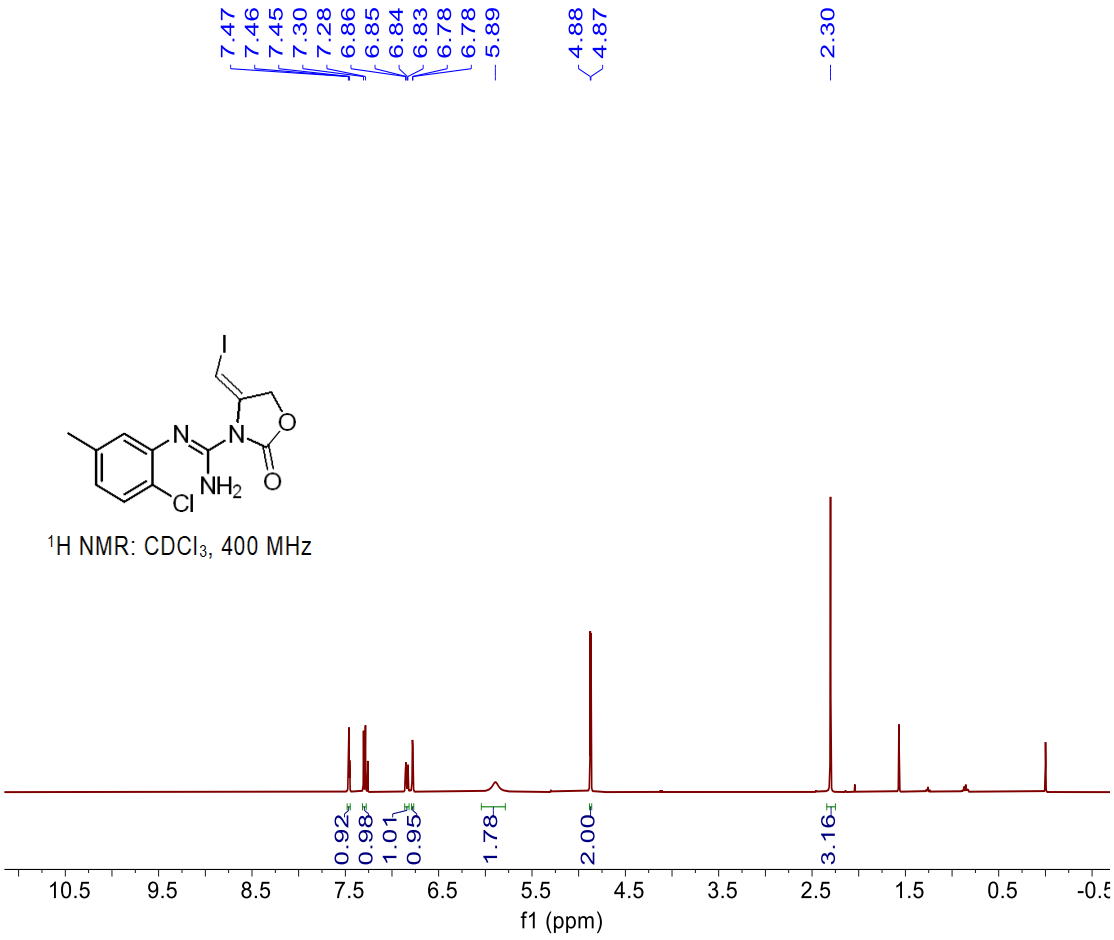


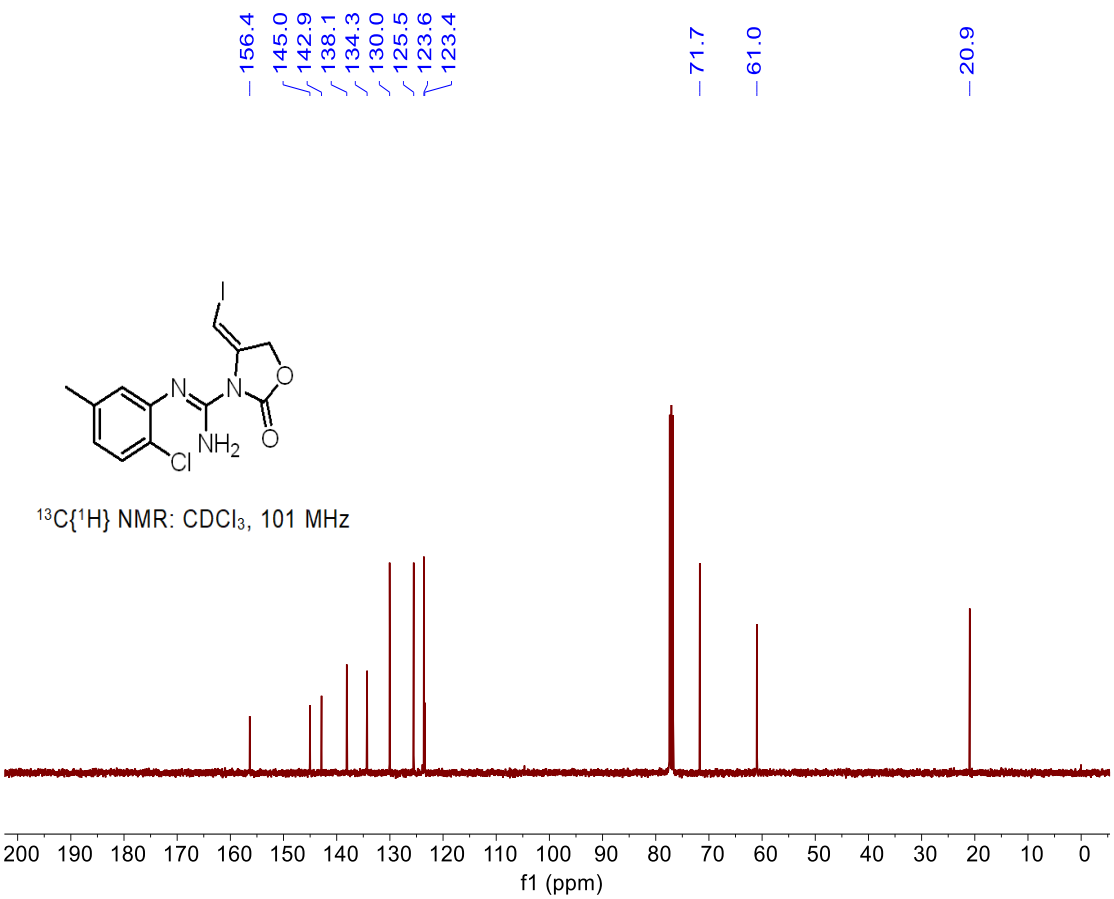
^{1}H NMR: $CDCl_3$, 400 MHz

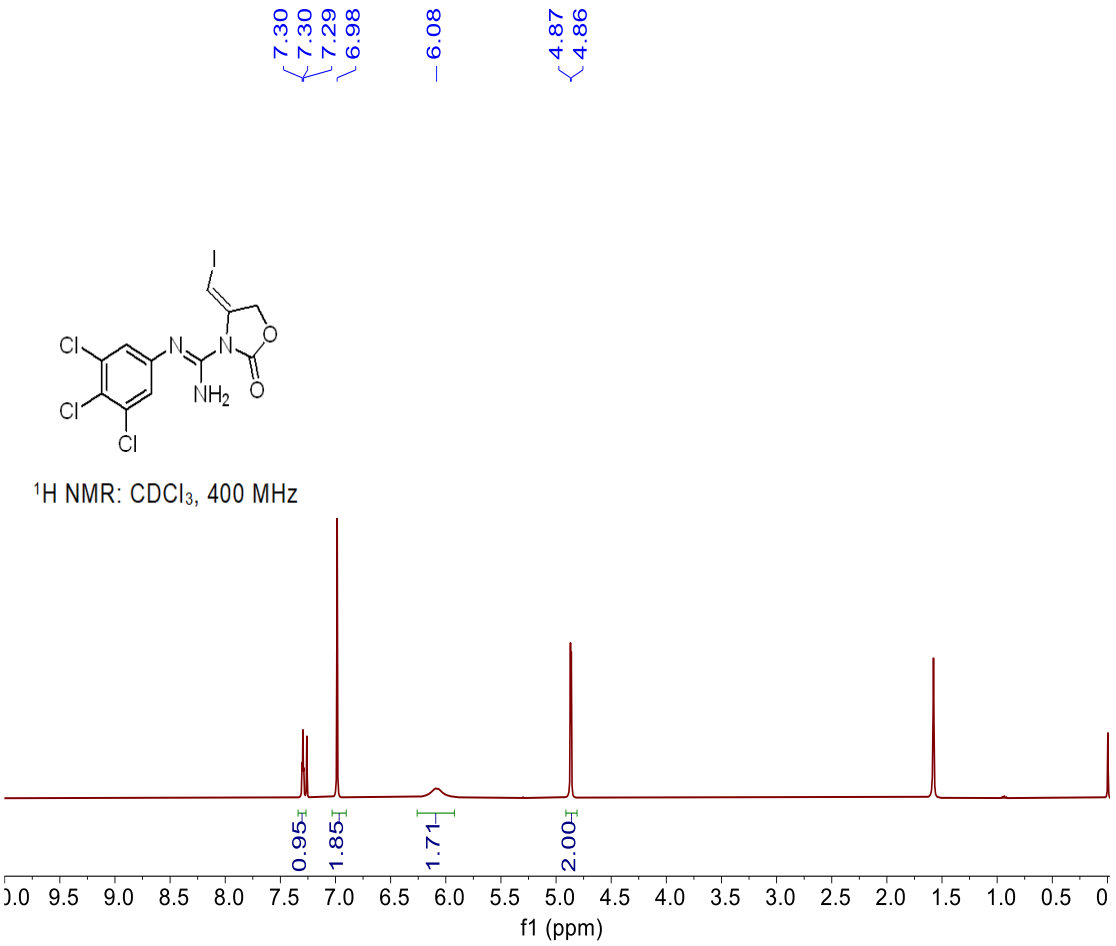


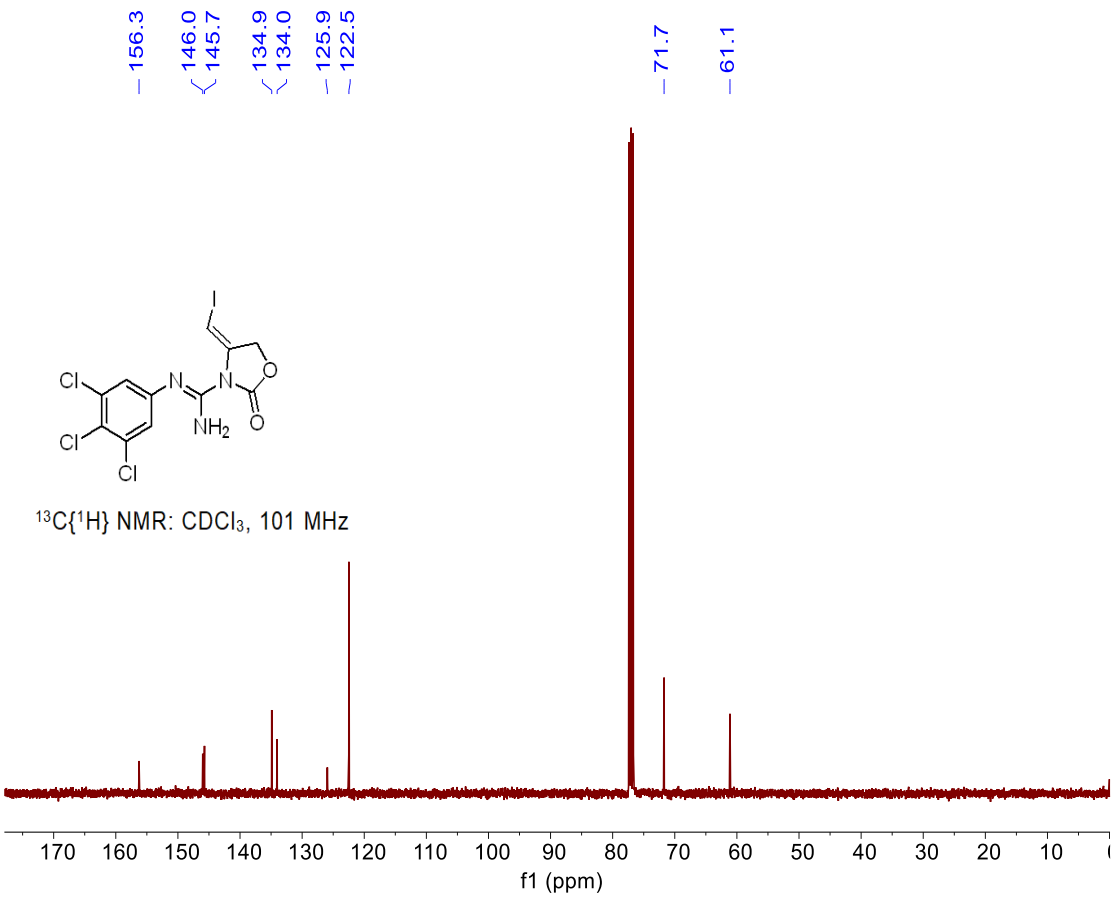
^{13}C{^{1}H} NMR: $CDCl_3$, 101 MHz

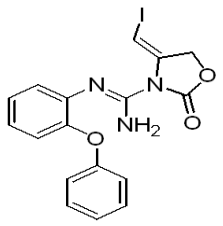



7.47
7.46
7.45
7.30
7.28
6.86
6.85
6.84
6.83
6.78
6.78
5.89
4.88
4.87
2.30
I
N
N
O
O
NH2
Cl
1H NMR: CDCl3, 400 MHz
0.92
0.98
1.01
0.95
1.78
2.00
3.16
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

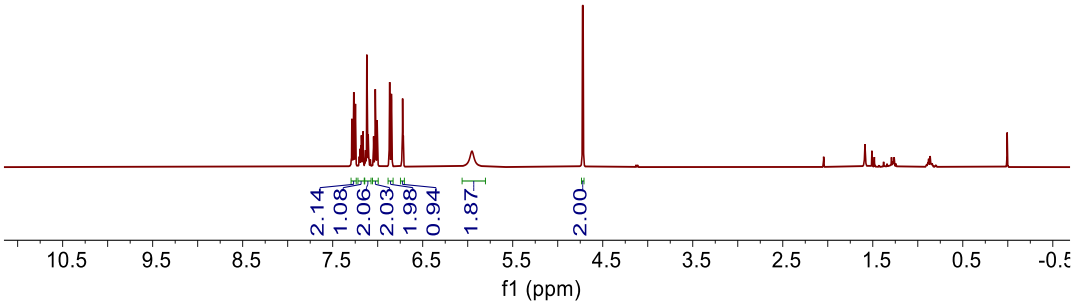

156.4
145.0
142.9
138.1
134.3
130.0
125.5
123.6
123.4
71.7
61.0
20.9
I
N
N
O
O
NH2
Cl
13C{1H} NMR: CDCl3, 101 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

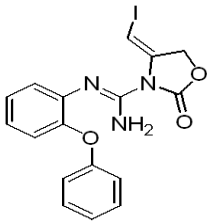

7.30
7.30
7.29
6.98
6.08
4.87
4.86
Cl
Cl
Cl
N
N
O
O
NH2
I
1H NMR: CDCl3, 400 MHz
0.95
1.85
1.71
2.00
f1 (ppm)


156.3
146.0
145.7
134.9
134.0
125.9
122.5
71.7
61.1
Cl
Cl
Cl
N
N
O
O
NH2
I
13C{1H} NMR: CDCl3, 101 MHz
f1 (ppm)

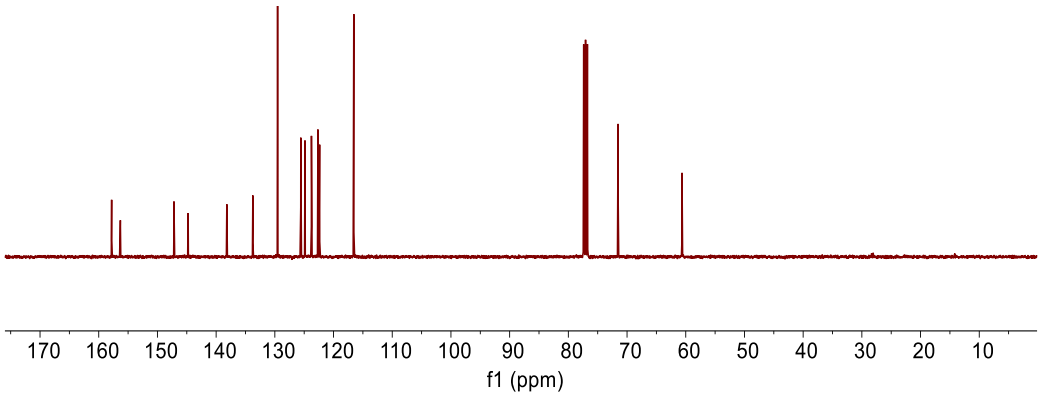


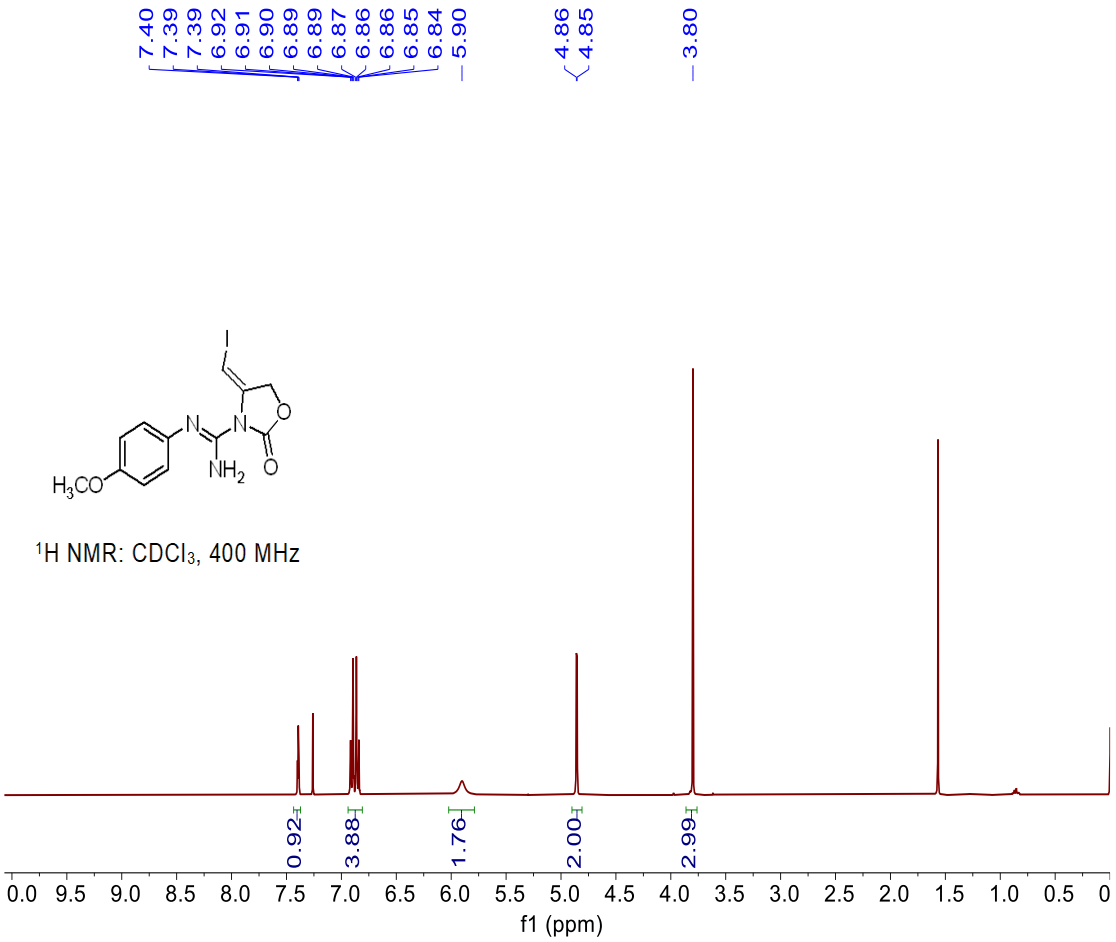
^{1}H NMR: $CDCl_3$, 400 MHz

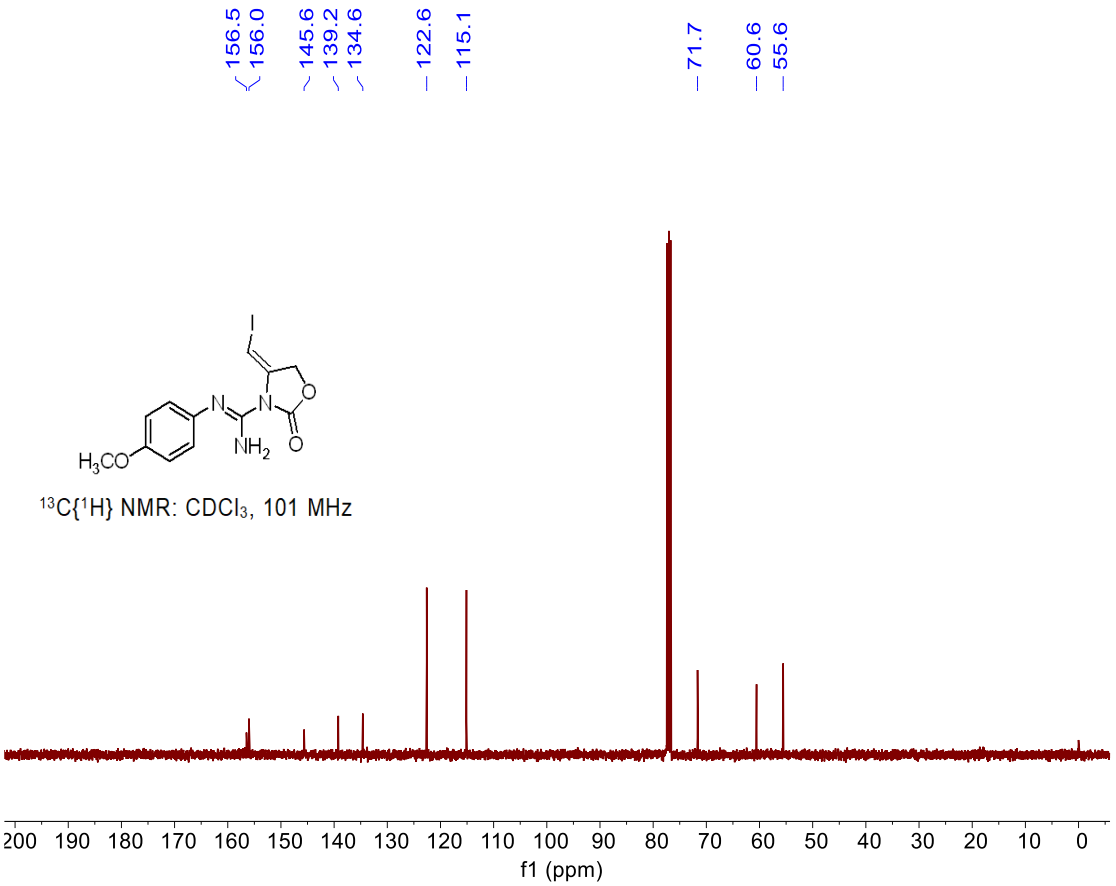




^{13}C{^{1}H} NMR: $CDCl_3$, 101 MHz




7.40
7.39
7.39
6.92
6.91
6.90
6.89
6.89
6.87
6.86
6.86
6.85
6.84
5.90
4.86
4.85
3.80
I
N
N
O
O
NH2
H3CO
1H NMR: CDCl3, 400 MHz
0.92
3.88
1.76
2.00
2.99
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)


156.5
156.0
145.6
139.2
134.6
122.6
115.1
71.7
60.6
55.6
I
N
N
O
O
NH2
H3CO
13C{1H} NMR: CDCl3, 101 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Reference:

[1] Tian, M.; Yan, M.; Baran, P. S. 11-Step total synthesis of Araiosamines. *J. Am. Chem. Soc.* 2016, *138*, 14234−14237.