Supporting Information

Silver-catalysed double decarboxylative addition-cyclisation-elimination cascade sequence for the synthesis of quinolin-2-ones

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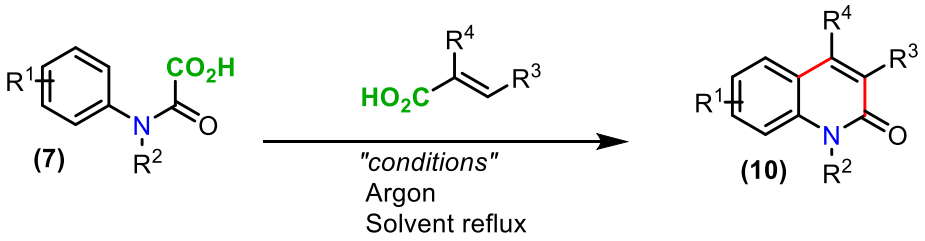
1. General information

Unless otherwise specified, all reagents were purchased from commercial sources and used without further purification. Anhydrous solvents were obtained using a solvent purification system drying over 3Å molecular sieves. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded on Varian Mercury 300 MHz (75.5 MHz for ^{13}C), Bruker 400 MHz (101 MHz for ^{13}C), Bruker 600 MHz (151 MHz for ^{13}C and 377 MHz for ^{19}F) instruments. All spectral data were acquired at 295 K. Chemical shifts are reported in parts per million (ppm, δ), downfield from tetramethyl silane (TMS, δ = 0.00 ppm), and are referenced to residual solvent [$CDCl_3$, δ = 7.26 ppm (^{1}H) and 77.16 ppm (^{13}C)]. Coupling constants (*J*) are reported in Hertz (Hz). The multiplicity abbreviations used are br broad, s singlet, d doublet, t triplet, q quartet, m multiplet, app apparent. Infrared (IR) spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer. High-resolution mass spectra were obtained from the University of Stellenbosch Mass Spectrometry Service and recorded in electrospray positive mode with a time-of-flight analyzer system on a Waters Synapt G2 machine. Thin-layer chromatography was carried out on Merck silica gel 60F_{254} precoated aluminum foil sheets and were visualized using UV light (254 nm) or staining with basic potassium permanganate solution. Flash column chromatography was carried out using silica gel 60 (Merck 7734), eluting with the specified solvent system.

2. Table S1: Reaction optimization for thermal mediated cascade sequence

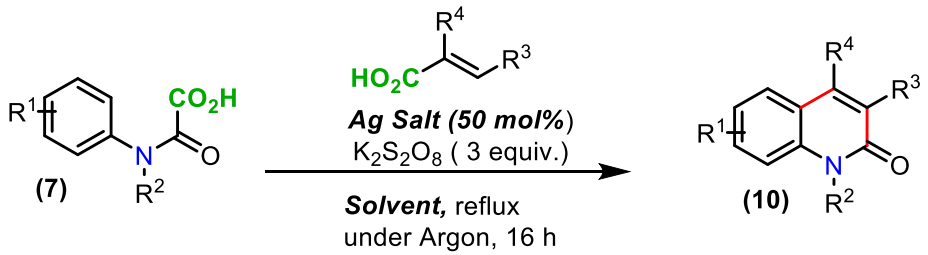


entry	catalyst (mol%)	equiv	oxidant	equiv	solvent (v/v =1)	yield 10 (%)
1	$Mn(OAc)_3.2H_2O$	3	-	-	PhMe	52
2	$Mn(OAc)_3.2H_2O$	1.5	-	-	PhMe	12
3	$Mn(OAc)_3.2H_2O$	1	-	-	PhMe	*no reaction*
4[b]	$Mn(OAc)_3.2H_2O$	0.50	-	-	PhMe	*no reaction*
5	$AgNO_3$	0.50	$K_2S_2O_8$	3	ACN/H_2O	58
6	$Mn(OAc)_3.2H_2O$	0.50	$K_2S_2O_8$	3	ACN/H_2O	16
7	$Fe(OAc)_2$	0.50	$K_2S_2O_8$	3	ACN/H_2O	43
8	$Co(OAc)_2$	0.50	$K_2S_2O_8$	3	ACN/H_2O	36
9	$Cu(OAc)_2.2H_2O$	0.50	$K_2S_2O_8$	3		12
10[e]	$AgNO_3$	0.50	$K_2S_2O_8$	3	ACN/H_2O	*no reaction*
12[e]	-	-	$K_2S_2O_8$	3	ACN/H_2O	*no reaction*
13	-	-	$K_2S_2O_8$	3	ACN/H_2O	35
14	$AgNO_3$	0.10	$K_2S_2O_8$	3	ACN/H_2O	37
15	$AgNO_3$	0.20	$K_2S_2O_8$	3	ACN/H_2O	34
16	$AgNO_3$	0.30	$K_2S_2O_8$	3	ACN/H_2O	40
17	$AgNO_3$	0.80	$K_2S_2O_8$		ACN/H_2O	56
18	$AgNO_3$	1.00	$K_2S_2O_8$	3	ACN/H_2O	58
19[ac]	$AgNO_3$	0.50	$K_2S_2O_8$	3	ACN/H_2O	60
20	$AgNO_3$	0.50	$K_2S_2O_8$	4	ACN/H_2O	27
21	$AgNO_3$	0.50	$K_2S_2O_8$	6	ACN/H_2O	25
22	$AgNO_3$	3	-	-	ACN/H_2O	*no reaction*

23	$AgNO_3$	3	NFSI	3	ACN/H_2O	*no reaction*
24	$AgNO_3$	3	H_2O_2	3	ACN/H_2O	*no reaction*
25	$AgNO_3$	3	TBHP	3	ACN/H_2O	*no reaction*
26	$AgNO_3$	0.50	$Na_2S_2O_8$	3	ACN/H_2O	33
27	$AgNO_3$	0.50	$(NH_4)_2S_2O_8$	3	ACN/H_2O	22

Unless otherwise stated all reactions were performed under argon and all yields were determined by H^1 NMR using trimethoxy benzene as standard for 16hr. [a]Isolated Yields. [b]Open to air. [c]Acid base extracted Michael acceptor. [e]Reaction performed at room temperature.

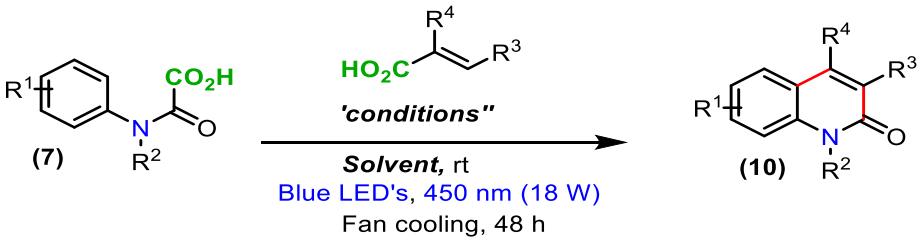
3. Table S2: Solvent and metal salt screen for thermal cascade sequence



entry	solvent (v/v =1)	metal salt	yield
1[a,b]	ACN/H_2O	$AgNO_3$	60
1	ACN/H_2O	$AgNO_3$	58
2	ACOH/H_2O	$AgNO_3$	58
3	DMSO/ H_2O		34
4	DMA/H_2O		5
5	EtOH/H_2O		38
6	PhMe/H_2O		52
7	Acetone/H_2O		38
8	THF/H_2O		23
9	Dioxane/H_2O		31
10	ACN/H_2O	$AgOTF_3$	45
11	ACN/H_2O	Ag_2SO_4	41
12	ACN/H_2O	$AgClO_4$	33
13	ACN/H_2O	$AgOCF_3$	44
14	ACN/H_2O	AgOAc	41

Unless otherwise stated all reactions were performed under argon and all yields were determined by H^1 NMR using trimethoxy benzene as standard for 16hr. [a]Isolated Yields. [b]Acid base extracted Michael acceptor.

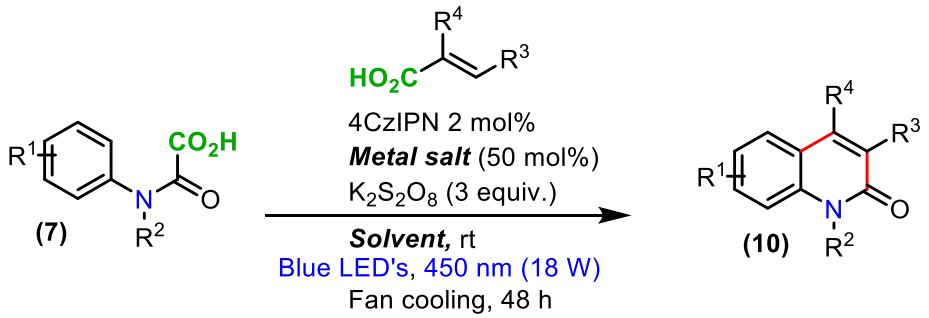
4. Table S3: Reaction optimisation for visible-light mediated cascade sequence.



entry	photocatalyst	Equiv.	Metal Salt	equiv	Oxidant	equiv	Solvent (v/v=1)	Yield
1	-	-	-	-	$K_2S_2O_8$	3.0	ACN/H_2O	**13**
2[c]	-	-	-	-	$K_2S_2O_8$	3.0	ACN/H_2O	**18**
3	-	-	$AgNO_3$	0.50	$K_2S_2O_8$	3.0	ACN/H_2O	**22**
4[b]	Ir[df(CF3)ppy]$_2$ (dtbbpy)PF6)	0.02	-	-	-	-	DMF/H_20	-
5[d]	$Ru(Bpyz)_3(PF6)_2$	0.05	-	-	$K_2S_2O_8$	3.0	ACN/H_2O	54
6	Ir[df(CF3)ppy]$_2$ (dtbbpy)PF6)	0.02	-	-	$K_2S_2O_8$	3.0	ACN/H_2O	-
7	Mes-Acr-Ph	0.20	-	-	$K_2S_2O_8$	3.0	ACN/H_2O	19
8	Cl-CTX	0.20	-	-	$K_2S_2O_8$	3.0	ACN/H_2O	25
9	4CzIPN	0.02	-	-	$K_2S_2O_8$	3.0	ACN/H_2O	25
10[e]	$Ru(Bpyz)_3(PF6)_2$	0.05	$AgNO_3$	0.50	$K_2S_2O_8$	3.0	ACN/H_2O	46
11[e]	Cl-CTX	0.20	$AgNO_3$	0.50	$K_2S_2O_8$	3.0	ACN/H_2O	43
12[a]	4CzIPN	0.02	$AgNO_3$	0.50	$K_2S_2O_8$	3.0	ACN/H_2O	58
13	Mes-Acr-Ph	0.10	$AgNO_3$	0.50	$K_2S_2O_8$	3.0	ACN/H_2O	43
15	Mes-Acr-Ph	0.10	$AgNO_3$	0.50	$(PhS)_2$	3.0	TFE	6
16	Mes-Acr-Ph-*t*Bu	0.10	$AgNO_3$	0.50	$K_2S_2O_8$	3.0	ACN/H_2O	20
17[e]	Ir[df(CF3)ppy]$_2$ (dtbbpy)PF6)	0.02	$AgNO_3$	0.50	$K_2S_2O_8$	3.0	ACN/H_2O	38
18	Cl-4CzIPN	0.02	$AgNO_3$	0.50	$K_2S_2O_8$	3.0	ACN/H_2O	51

Unless otherwise stated all reactions were performed under argon for 48 hr, 450nm LEDs were used and all yields were determined by H^1 NMR using trimethoxy benzene as standard. [a]Isolated Yields. [b]Open to air. [c]380nm LEDs used. [d] Reaction time 72 hr.[e] poor conversion after 48h.

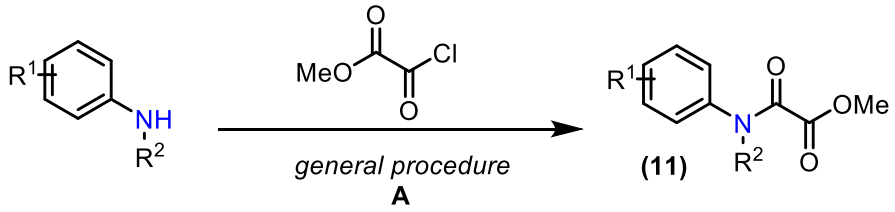
5. Table S4:Solvent and metal salt optimization for visible-light mediated cascade sequence.



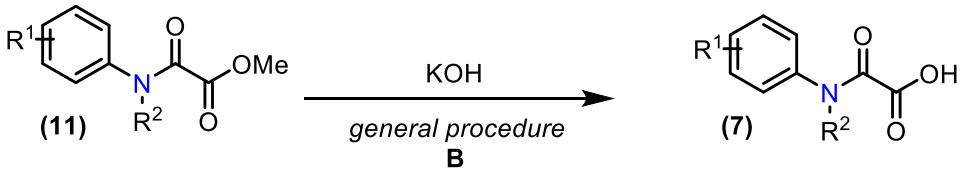
entry	metal salt	solvent	yield
1[a]	$AgNO_3$	ACN/H_2O	58
2	$Cu(OAc).H_2O$	ACN/H_2O	15
3	$Mn(OAc)_3.2H_2O$		7
4	$Fe(OAc)_2$		45
5	$Ni(OAc)_2$		15
6	$Co(OAc)_2$	Acetone/H_2O	33
7	$AgNO_3$	THF/H_2O	42
8		DMF/H_2O	18
9		Dioxane/H_2O	38
10		DMSO/H_2O	40
11		EtOH/H_2O	13
12		DMA/H_2O	23
13		NMP/H_2O	-
14		ACN/H_2O	

Unless otherwise stated all reactions were performed under argon for 48 hr, 450nm LEDs were used and all yields were determined by H^1 NMR using trimethoxy benzene as standard. [a]Isolated Yields. [b]Open to air. [c]380nm LEDs used. [d] Reaction time 72 hr.[e] poor conversion after 4h hr.

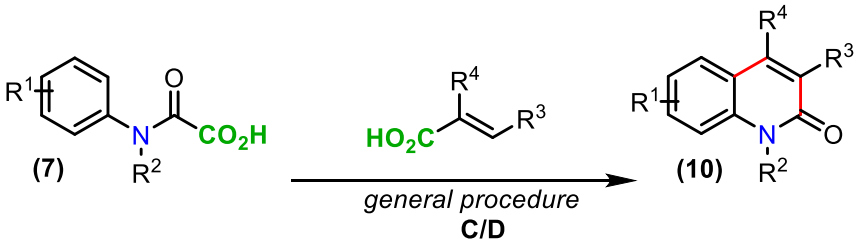
6. General scheme for the synthesis of oxamic esters (11)



7. General scheme for the synthesis of (7)



8. General scheme for the synthesis of (10)



9. General synthetic procedure A: Synthesis of oxamic esters (11)

To a solution of aniline (1.0 equiv.) and triethylamine or *N*, *N*-Diisopropylethylamine (1.2 equiv.) in dry CH_2Cl_2 (3 mL/mmol of aniline) at 0 °C under argon, was added methyl 2-chloro-2-oxoacetate (1.2 equiv.) dropwise and the solution allowed to warm up to room temperature. After TLC analysis indicated full conversion of the starting material (10–12 h) an equal amount of deionized water was added. The layers were separated, and the aqueous layer was reextracted with CH_2Cl_2 (x2). The combined organic extracts were washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, filtered and concentrated in vacuo to give oxamic esters which were typically sufficiently pure to be used without further purification.

10. General synthetic procedure B: Synthesis of oxamic acids (7)

To a solution of oxoester (1 equiv.) in THF, was added KOH (1.5 equiv.), dissolved in deionized water (~4:1 THF/water) and the reaction allowed to stir at room temperature. The resultant mixture was stirred at room temperature until the oxoester was completely consumed by TLC analysis (3–5 h). The reaction mixture was then diluted with an equivalent amount of deionized water and EtOAc. The layers were separated, and the aqueous layer was washed with EtOAc (x2) before being acidified to pH ~2-3 by the dropwise addition of 6M aqueous HCl. Thereafter, the aqueous layer was reextracted with EtOAc (x3), the combined organic extracts dried over $MgSO_4$ and concentrated in vacuo to give the appropriate β-oxoacids which could be purified by column chromatography on silica gel if needed.

11. General synthetic procedure C: Thermal mediated synthesis of quinoline-2-ones (10)

A mixture of oxamic acid (1 equiv.), acrylic acid (3 equiv.), $AgNO_3$ (50 mol%) and $K_2S_2O_8$, (3 equiv.) in a ~1:1 ACN/water was thoroughly degassed using an argon balloon, and the reaction left to stir at reflux temperature until TLC analysis indicated consumption of the starting material (~18 h). An equal amount of brine was then added and the organic layer separated. The aqueous layer was reextracted with or EtOAc (x3). The combined organic extracts washed with saturated aqueous $NaHCO_3$ dried over $MgSO_4$ and concentrated in vacuo. The resulting crude product was

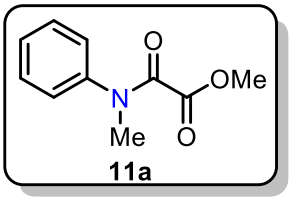
purified by column chromatography on silica gel (Petroleum ether/EtOAc gradient) to afford Quinolin-2-ones (**10**).

12. General synthetic procedure D: Visible-light mediated synthesis of quinoline-2-ones (10)

A mixture of oxamic acid (1 equiv.), acrylic acid (3 equiv.), $AgNO_3$ (50 mol%), $K_2S_2O_8$, (3 equiv.) and photocatalyst (4-CzIPN) (2 mol%) in ~1:1 ACN/water was thoroughly degassed using an argon balloon, the vial was sealed using parafilm, reaction mixture was irradiated with Blue LED's 450 nm and left to stir at room temperature until TLC analysis indicated consumption of the starting material (~48 h). An equal amount of saturated brine was then added, and the organic layer separated. The aqueous layer was reextracted with or EtOAc (x3) and the combined organic extracts washed with saturated aqueous $NaHCO_3$ before being dried over $MgSO_4$ and concentrated in vacuo. The resulting crude product was purified by column chromatography on silica gel (Petroleum ether/EtOAc gradient) to afford the Quinoline-2-ones (**10**).

13. Characterization data for oxamic esters (11)

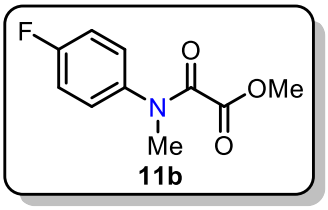
Methyl 2-(methyl(phenyl)amino)-2-oxoacetate (11a)



11a

Prepared according to general procedure **A** using *N*-methylaniline (0.400 g, 2.7 mmol), triethylamine (0.56 mL, 4.0 mmol) and methyl 2-chloro-2-oxoacetate (0.30 mL, 3.2 mmol) in CH_2Cl_2 (20 mL) to afford **11a** as a colourless oil (0.619 g, 98% yield). **IR** (film, ν_{max}/cm^{-1}), 2952, 1741, 1664, 1593, 1496, 1450, 1391, 1229, 774, 699, 550; $\mathbf{R_f}$ = 0.37 (2:3 EtOAc:Petroleum ether); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.41–7.28 (m, 3H), 7.23–7.14 (m, 2H), 3.51 (s, 3H), 3.31 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.9, 161.5, 141.3, 129.6, 128.3, 126.1, 52.2, 36.0; **HRMS** (ESI$^+$) m/z: [M + H] calcd for $C_{10}H_{12}NO_3^+$ 194.0812; found 194.0820.

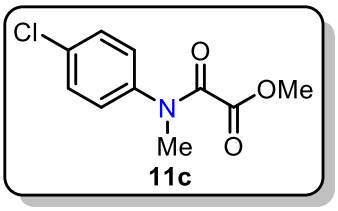
Methyl 2-((4-fluorophenyl)(methyl)amino)-2-oxoacetate (11b)



11b

Prepared according to general procedure **A** using 4-fluoro-*N*-methylaniline (0.500 g, 4.0 mmol), triethylamine (0.84 mL, 6.0 mmol) methyl 2-chloro-2-oxoacetate (0.44 mL, 4.8 mmol) in CH_2Cl_2 (20 mL) to afford **11b** as a colourless solid (0.800 g, 95 yield). $\mathbf{R_f}$ = 0.43 (2:3 EtOAc:Petroleum ether); **M.P.** 73–75 °C; **IR** (film, ν_{max}/cm^{-1}), 3074, 1734, 1667, 1502, 1455, 1399, 1221, 1149, 1113, 958, 851, 791, 553; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.25–7.18 (m, 2H), 7.12–7.04 (m, 2H), 3.58 (s, 3H), 3.32 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.3, 162.1 (d, $J_{C\text{-}F}$ = 249.1 Hz), 161.3, 137.6, 128.6 (d, $J_{C\text{-}F}$ = 8.8 Hz), 116.7 (d, $J_{C\text{-}F}$ = 22.9 Hz), 52.4, 36.5; **HRMS** (ESI$^+$) m/z: [M + H] calcd for $C_{10}H_{11}FNO_3^+$ 212.0717; found 212.0724.

Methyl 2-((4-chlorophenyl)(methyl)amino)-2-oxoacetate (11c)[1]

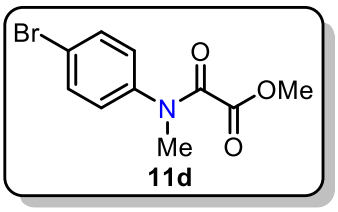


11c

Prepared according to general procedure **A** using 4-Chloro-*N*-methyl aniline (0.500 g, 3.5 mmol), triethylamine (0.74 mL, 5.3 mmol) and methyl 2-chloro-2-oxoacetate (0.39 mL, 4.2 mmol) in CH_2Cl_2 (20 mL) to afford **11c** as a colourless oil (0.745 g, 97 % yield). $\mathbf{R_f}$ = 0.76 (3:7 EtOAc:Petroleum ether); **IR** (film, ν_{max}/cm^{-1}), 2953, 1742, 1666, 1591, 1491, 1228, 1113, 1039, 838; **^{1}H NMR (**300 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 3.60 (s, 3H), 3.32

(s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.8, 161.4, 140.1, 134.4, 130.0, 127.7, 52.6, 36.3; **HRMS** (ESI^+) m/z: [M + H] calcd for $C_{10}H_{11}ClNO_3^+$ 228.0422; found 228.0430.

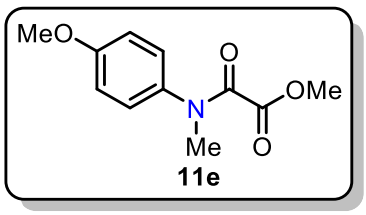
Methyl 2-((4-bromophenyl)(methyl)amino)-2-oxoacetate (11d)



11d

Prepared according to general procedure **A** using 4-Bromo-*N*-methyl aniline (0.500 g, 2.89 mmol), triethylamine (0.59 mL, 4.34 mmol) and methyl 2-chloro-2-oxoacetate (0.30 mL, 3.22 mmol) in CH_2Cl_2 (20 mL) to afford **11d** as a colourless solid (0.753 g, 96 % yield). **R_f** = 0.30 (3:7 EtOAc:Petroleum ether); **M.P.** 49–51 °C; **IR** (film, ν_{max}/cm^{-1}), 2960, 1723, 1666, 1483, 1298, 1234, 1114, 779, 826, 539; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 3.60 (s, 3H), 3.32 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.8, 161.3, 140.6, 133.0, 128.0, 122.3, 52.6, 36.3; **HRMS** (ESI^+) m/z: [M + H] calcd for $C_{10}H_{11}BrNO_3^+$ 271.9917; found 271.9971.

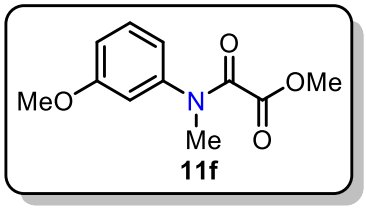
Methyl 2-((4-methoxyphenyl)(methyl)amino)-2-oxoacetate (11e)



11e

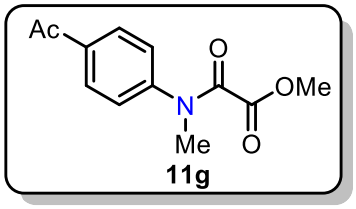
Prepared according to general procedure **A** using 4-Methoxy-*N*-methyl aniline (0.500 g, 3.64 mmol), triethylamine (0.76 mL, 5.46 mmol) and methyl 2-chloro-2-oxoacetate (0.40 mL, 4.37 mmol) in CH_2Cl_2 (20 mL) to afford **11e** as brown solid (0.797 g, 98 % yield). **R_f** = 0.42 (2:3 EtOAc:Petroleum ether); **M.P.** 69–71 °C; **IR** (film, ν_{max}/cm^{-1}) 2953, 2840, 1741, 1661, 1510, 1455, 1392, 1296, 1231, 1114, 1028, 782, 557; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H), 3.55 (s, 3H), 3.28 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.2, 161.9, 159.4, 134.0, 127.9, 114.7, 55.5, 52.2, 36.4; **HRMS** (ESI^+) m/z: [M + H] calcd for $C_{11}H_{14}NO_4^+$ 224.0917; found 224.0927.

Methyl 2-(methyl(phenyl)amino)-2-oxoacetate (11f)



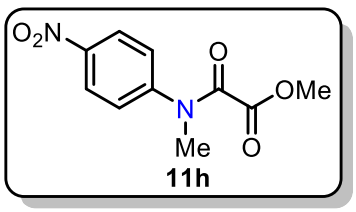
Prepared according to general procedure **A** using 3-methoxy-*N*-methylaniline (0.600 g, 3.46 mmol), triethylamine (1.50 mL, 10.30 mmol) and methyl 2-chloro-2-oxoacetate (0.477 mL, 5.18 mmol) in CH_2Cl_2 (20 mL) to afford **11f** as a yellow oil (0.758 g, 98 yield). $\mathbf{R_f}$ = 0.52 (2:3 EtOAc:Petroleum ether); **IR** (film, ν_{max}/cm^{-1}); 2951, 1831, 1742, 1662, 1596, 1489, 1459, 1220, 1113, 1039, 782, 697; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.27 (t, *J* = 8.1 Hz, 1H), 6.86 (ddd, *J* = 8.4, 2.5, 0.9 Hz, 1H), 6.79 (ddd, *J* = 7.8, 2.0, 0.9 Hz, 1H), 6.74 (t, *J* = 2.2 Hz, 1H), 3.79 (s, 3H), 3.59 (s, 3H), 3.34 (s, 3H) **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.1, 161.7, 160.5, 142.7, 130.4, 118.3, 114.1, 111.9, 55.6, 52.4, 36.2; **HRMS** (ESI$^+$) m/z: [M + H] calcd for $C_{11}H_{14}NO_4^+$ 224.0917; found 224.0920.

Methyl 2-((4-acetylphenyl)(methyl)amino)-2-oxoacetate (11g)



Prepared according to general procedure **A** using 4-Acetal-*N*-methyl aniline (0.400 g, 2.68 mmol), triethylamine (0.560 mL, 4.02 mmol) and methyl 2-chloro-2-oxoacetate (0.296 mL, 3.22 mmol) in CH_2Cl_2 (20 mL) to afford **11g** as a colourless oil (0.619 g, 98% yield). $\mathbf{R_f}$ = 0.37 (2:3 EtOAc:Petroleum ether); **M.P.** 69–71 °C; **IR** (film, ν_{max}/cm^{-1}) 2954, 1877, 1743, 1669, 1598, 1382, 1262, 1229, 1115, 861, 846; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 3.58 (s, 3H), 3.36 (s, 3H), 2.58 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 196.8, 162.6, 161.1, 145.6, 136.4, 129.8, 125.7, 52.6, 36.0, 26.7; **HRMS** (ESI$^+$) m/z: [M + H] calcd for $C_{12}H_{14}NO_4^+$ 236.0917; found 236.0918.

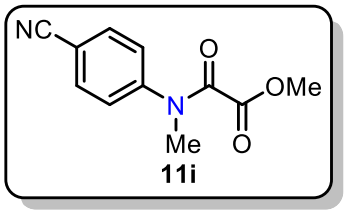
Methyl 2-((4-cyanophenyl)(methyl)amino)-2-oxoacetate (11h)



Prepared according to general procedure **A** using *N*-methyl-4-nitroaniline (0.800 g, 5.26 mmol), DIPEA (2.75 mL, 15.78 mmol) and methyl 2-chloro-2-oxoacetate (0.725 mL, 7.89 mmol), pyridine (0.229 mL, 2.63 mmol) in CH_2Cl_2 (20 mL) to afford **11h** as a light-yellow solid (1.221 g, 97 % yield). $\mathbf{R_f}$ = 0.51 (2:3 EtOAc:Petroleum ether); **M.P.** 94–96 °C; **IR**

(film,ν_{max}/cm^{-1}) 2960, 1725, 1669, 1589, 1514, 1338, 1296, 1235, 1108, 855, 783, 694, 540; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 3.65 (bs, 3H), 3.42 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.3, 161.0, 147.4, 147.0, 126.4, 125.2, 52.9, 36.4; **HRMS** (ESI$^+$) m/z: [M + H] calcd for $C_{10}H_{11}N_2O_5^+$ 239.0662; found 239.0673.

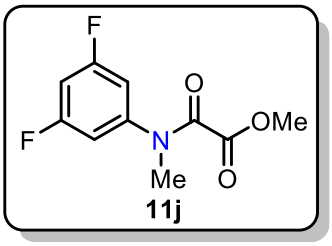
Methyl 2-(methyl(4-nitrophenyl)amino)-2-oxoacetate (11i)



11i

Prepared according to general procedure **A** using 4-(methylamino)benzonitrile (0.800 g, 6.05 mmol), DIPEA (3.20 mL, 15.78 mmol) and methyl 2-chloro-2-oxoacetate (0.84 mL, 9.08 mmol), pyridine (0.244 mL, 3.05 mmol) in CH_2Cl_2 (20 mL) to afford **11i** as a light-yellow solid (1.221 g, 97 % yield). **R_f** = 0.54 (2:3 EtOAc:Petroleum ether); **M.P.** 90–92 °C; **IR** (film, ν_{max}/cm^{-1}) 2959, 2226, 1724, 1672, 1602, 1560, 1237, 1117, 884, 791, 570; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 3.64 (s, 3H), 3.39 (s, 4H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.4, 161.0, 145.8, 133.7, 126.6, 117.9, 112.3, 52.8, 36.2; **HRMS** (ESI$^+$) m/z: [M + H] calcd for $C_{11}H_{11}N_2O_3^+$ 219.0764; found 219.0770.

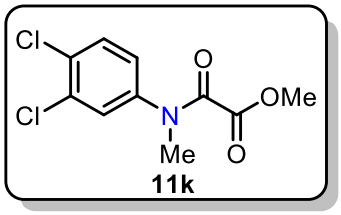
Methyl 2-((3,5-difluorophenyl)(methyl)amino)-2-oxoacetate (11j)



11j

Prepared according to general procedure **A** using 3,5-difluoro-*N*-methylaniline (0.500 g, 3.49 mmol), triethylamine (0.983 mL, 5.24 mmol) and methyl 2-chloro-2-oxoacetate (0.386 mL, 4.19 mmol) in CH_2Cl_2 (20 mL) to afford **11j** as a yellow solid (0.787 g, 98% yield). **R_f** = 0.69 (1:4 EtOAc:Petroleum ether); **M.P.** 78–80 °C; **IR** (film, ν_{max}/cm^{-1}) 3056, 1673, 1607, 1464, 1429, 1394, 1347, 1204, 1118, 980, 872, 843, 685; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -106.99; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.86–6.73 (m, 3H), 3.67 (s, 3H), 3.34 (s, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.2 (dd, J_{C-F} = 251.4, 14.1 Hz), 162.4, 161.1, 143.9 (t, J_{C-F} = 11.9 Hz), 109.6 (d, J_{C-F} = 27.1 Hz), 104.2 (t, J_{C-F} = 25.2 Hz), 52.8, 36.2; **HRMS** (ESI+) m/z: [M + H] calcd for $C_{10}H_{10}F_2NO_3^+$ 230.0623; found 230.0633.

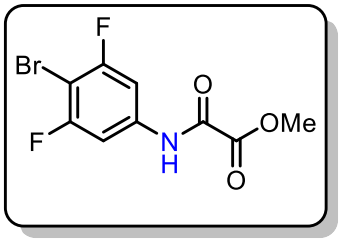
Methyl 2-((3,4-dichlorophenyl)(methyl)amino)-2-oxoacetate (11k)



11k

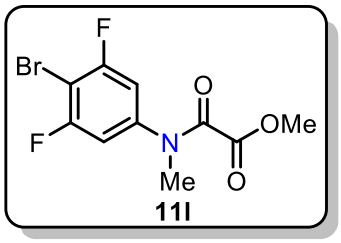
Prepared according to general procedure **A** using 3,4-dichloro-*N*-methylaniline (0.500 g, 2.84 mmol), triethylamine (0.594 mL, 4.26 mmol) and methyl 2-chloro-2-oxoacetate (0.313 mL, 3.41 mmol) in CH_2Cl_2 (20 mL) to afford **11k** as brown solid (0.739 g, 99 % yield). $\mathbf{R_f}$ = 0.85 (2:3 EtOAc:Petroleum ether); **M.P.** 213–215 °C; **IR** (film, ν_{max}/cm^{-1}) 3060, 1746, 1671, 1589, 1467, 1413, 1375, 1226, 1118, 871, 826, 608; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.5 Hz, 1H), 7.35 (d, *J* = 2.5 Hz, 1H), 7.08 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.65 (s, 3H), 3.33 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 162.5, 161.1, 140.9, 133.7, 132.8, 131.4, 128.2, 125.6, 52.8, 36.4; **HRMS** (ESI$^+$) m/z: [M + H] calcd for $C_{10}H_{10}Cl_2NO_3^+$ 262.0032; found 262.0042.

Methyl 2-((4-bromo-3,5-difluorophenyl)(methyl)amino)-2-oxoacetate[9]



Prepared according to general procedure **A** using 4-bromo-3,5-difluoroaniline (0.800 g, 3.85 mmol), triethylamine (1.07 mL, 7.70 mmol) and methyl 2-chloro-2-oxoacetate (0.531 mL, 5.76 mmol) in CH_2Cl_2 (30 mL) to afford methyl 2-((4-bromo-3,5-difluorophenyl)(methyl)amino)-2-oxoacetate as a white solid (0.949 g, 83% yield). $\mathbf{R_f}$ = 0.26 (1:4 EtOAc:Petroleum ether); **M.P.** 174–176 °C; **IR** (film, ν_{max}/cm^{-1}) 3421, 3334, 3118, 3047, 1739, 1686, 1606, 1548, 1423, 1277, 1213, 1033, 872, 579, 534, **^{19}F NMR** (377 MHz, $CDCl_3$) δ -101.42, -103.20; **^{1}H NMR** (300 MHz, $CDCl_3$)(tautomers) δ 8.99 (bs, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 6.0 Hz, 2H), 3.98 (s, 2H), 3.87 (s, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$)(tautomers) δ 160.9, 160.4, 160.3 (dd, $J_{C\text{-}F}$ = 252.3, 5.4 Hz), 160.2 (dd, $J_{C\text{-}F}$ = 247.5, 5.9 Hz), 153.9, 137.0 (t, $J_{C\text{-}F}$ = 12.7 Hz), 134.1 (t, $J_{C\text{-}F}$ = 11.6 Hz), 113.1 (d, $J_{C\text{-}F}$ = 28.4 Hz), 103.9 (dd, $J_{C\text{-}F}$ = 28.2, 3.0 Hz), 101.2 (t, $J_{C\text{-}F}$ = 24.2 Hz), 94.1 (t, $J_{C\text{-}F}$ = 24.6 Hz), 54.5 (d, $J_{C\text{-}F}$ = 4.5 Hz), 54.0 (d, $J_{C\text{-}F}$ = 4.5 Hz).

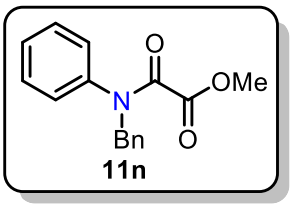
Methyl 2-((4-bromo-3,5-difluorophenyl)(methyl)amino)-2-oxoacetate (11l)



11l

Prepared using oxamic ester methyl 2-((4-bromo-3,5-difluorophenyl)(methyl)amino)-2-oxoacetate 0.899 g, 3.06 mmol), methyl iodide (0.285 mL, 4.56 mmol) and Sodium hydride (0.109 mL, 4.56 mmol) in DMF (30 mL) to afford **11l** as a white solid (0.507 g, 54% yield). **M.P.** 140–142 °C; $\mathbf{R_f}$ = 0.45 (1:4 EtOAc:Petroleum ether); **IR** (film, ν_{max}/cm^{-1}) 3052, 1744, 1671, 1583, 1459, 1406, 1208, 1023, 880, 766, 583; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -101.99, -103.45; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.87 (d, J = 6.9 Hz, 2H), 3.70 (s, 3H), 3.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2, 160.9, 160.3 (dd, J_{C-F} = 250.7, 4.6 Hz), 142.3 (t, J_{C-F} = 11.4 Hz), 110.2 (d, J_{C-F} = 24.9 Hz), 98.2 (q, J_{C-F} = 24.4, 23.7 Hz), 53.0, 36.3; **HRMS** (ESI$^+$) m/z: [M + H] calcd for $C_{10}H_9BrF_2NO_3^+$ 307.9728; found 307.9739.

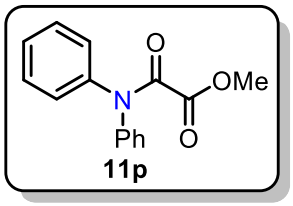
Methyl 2-(benzyl(phenyl)amino)-2-oxoacetate (11n)



11n

Prepared according to general procedure **A** using *N*-benzylaniline (0.500 g, 2.53 mmol), triethylamine (0.529 mL, 3.78 mmol) and methyl 2-chloro-2-oxoacetate (0.278 mL, 3.04 mmol) in CH_2Cl_2 (20 mL) to afford **11n** as a brown oil (0.680 g, 99% yield). $\mathbf{R_f}$ = 0.67 (2:3 EtOAc:Petroleum ether); **IR** (film, ν_{max}/cm^{-1}) 3321, 2924, 1724, 1660, 1433, 1229, 743, 698; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.35–7.27 (m, 6H), 7.26–7.21 (m, 2H), 7.10–7.05 (m, 2H), 4.97 (s, 2H), 3.56 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.0, 161.8, 139.9, 136.0, 129.5, 128.9, 128.7, 128.7, 128.0, 127.2, 52.4, 52.2; **HRMS** (ESI+) m/z: [M + H] calcd for $C_{16}H_{16}NO_3^+$ 270.1125; found 270.1126.

Methyl 2-(diphenylamino)-2-oxoacetate (11p) [2]

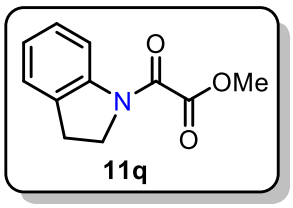


11p

Prepared according to general procedure **A** using diphenylamine (0.508 g, 3.00 mmol), triethylamine (0.627 mL, 4.50 mmol) and methyl 2-chloro-2-oxoacetate (0.332 mL, 3.06 mmol) in CH_2Cl_2 (20 mL) to afford **11p** as a white solid (0.745 g, 97 % yield). $\mathbf{R_f}$ = 0.68 (2:3 EtOAc:Petroleum ether); **M.P.** 103–105 °C; **IR** (film, ν_{max}/cm^{-1}) 3373, 3953, 1735, 1674, 1489, 1377, 1239, 1145, 759, 695; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.38 (t, J = 7.5 Hz, 5H), 7.33–7.24 (m, 5H), 3.61 (s, 3H); **^{13}C**

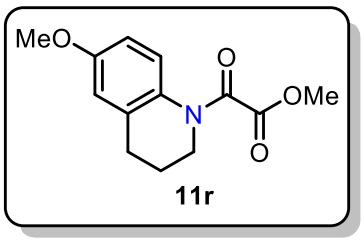
NMR (101 MHz, $CDCl_3$) δ 163.1, 161.1, 140.6, 140.5, 129.8, 129.3, 128.7, 127.9, 127.2, 125.9, 52.5. All recorded data were in accordance with those previously reported.

Methyl 2-(indolin-1-yl)-2-oxoacetate (11q)



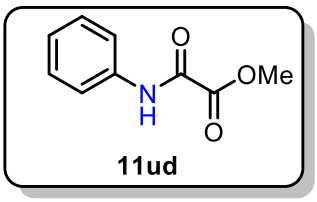
Prepared according to general procedure **A** using indoline (0.500 g, 4.20 mmol), triethylamine (0.880 mL, 6.30 mmol) and methyl 2-chloro-2-oxoacetate (0.463 mL, 5.04 mmol) in CH_2Cl_2 (20 mL) to afford **11q** as a yellow oil (0.788 g, 91 yield). $\mathbf{R_f}$ = 0.64 (2:3 EtOAc:Petroleum ether); **IR** (film, ν_{max}/cm^{-1}) 2955, 1738, 1597, 1484, 1417, 1249, 1097, 973, 759; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.5 Hz, 1H), 7.30–7.22 (m, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 4.31 (t, *J* = 8.3 Hz, 2H)), 3.94 (s, 3H), 3.23 (t, *J* = 8.3 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.2, 157.4, 141.8, 132.2, 127.8, 125.4, 124.9, 118.0, 53.0, 48.7, 28.3; **HRMS** (ESI^+) m/z: [M + H] calcd for $C_{11}H_{12}NO_3^+$ 206.0812; found 206.0813.

Methyl 2-(6-methoxy-3,4-dihydroquinolin-1(2H)-yl)-2-oxoacetate (11r)



Prepared according to general procedure **A** using 6-methoxy-1,2,3,4-tetrahydroquinoline (0.460 g, 2.82 mmol), triethylamine (0.590 mL, 4.23 mmol) and methyl 2-chloro-2-oxoacetate (0.311 mL, 3.38 mmol) in CH_2Cl_2 (20 mL) to afford **11r** as brown solid (0.640 g, 96% yield). $\mathbf{R_f}$ = 0.54 (3:7 EtOAc:Petroleum ether); **M.P.** 65–67 °C; **IR** (film, ν_{max}/cm^{-1}) 2962, 1747, 1644, 1501, 1441, 1403, 1311, 1200, 1157, 1016, 873, 763, 720; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.91 (d, *J* = 8.7 Hz, 1H), 6.78–6.61 (m, 3H), 3.88–3.79 (m, 2H), 3.77 (s, 3H), 3.70 (s, 3H), 2.74 (t, *J* = 6.5 Hz, 2H), 2.06–1.94 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 163.7, 160.9, 157.9, 134.1, 129.9.0, 122.2, 114.2, 111.8, 55.4, 52.6, 42.4, 27.0, 23.1; **HRMS** (ESI^+) m/z: [M + H] calcd for $C_{13}H_{16}NO_4^+$ 250.1074; found 250.1078

Methyl 2-oxo-2-(phenylamino)acetate

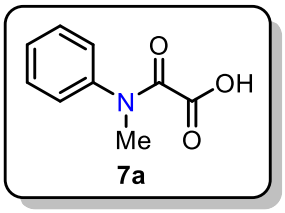


11ud

Prepared according to general procedure **A** aniline (0.600 g, 6.44 mmol), triethylamine (1.80 mL, 12.88 mmol) and methyl 2-chloro-2-oxoacetate (0.711 mL, 7.73 mmol) in CH_2Cl_2 (20 mL) to afford **11ud** as white solid (1.102 g, 95% yield). **M.P.** 102–104 °C; **R_f** = 0.23 (2:3 EtOAc:Petroleum ether); **IR** (film, ν_{max}/cm^{-1}) 3336, 1692, 1587, 1537, 1292, 11169, 758, 708, 547**;** **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.64 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.22–7.14 (m, 1H), 3.94 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 161.5, 153.7, 136.3, 129.3, 125.6, 119.9, 54.1; **HRMS** (ESI$^+$) m/z: [M + H] calcd for $C_9H_{10}NO_3^+$ 180.0665; found 180.0667.

14. Characterization data for oxamic acids (7)

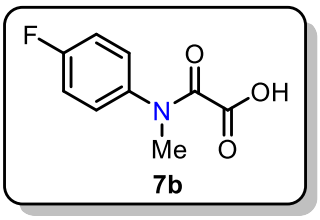
2-(methyl(phenyl)amino)-2-oxoacetic acid (7a)[3]



7a

Prepared according to general procedure **B** using oxamic ester **11a** (0.562 g, 2.92 mmol), potassium hydroxide (0.246 g, 4.38 mL) in THF (30 mL) to afford **7a** as a white solid (0.450 g, 86 % yield). **R_f** = 0.24 (1:4 MeOH:DCM); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 10.19 (s, 1H), 7.40–7.34 (m, 3H), 7.28–7.17 (m, 3H), 3.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.4, 160.9, 141.9, 129.8, 128.7, 126.2, 38.0. All recorded data were in accordance with those previously reported.

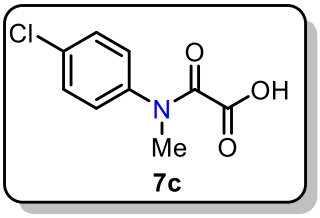
2-((4-fluorophenyl)(methyl)amino)-2-oxoacetic acid (7b)[1]



7b

Prepared according to general procedure **B** using oxamic ester **11b** (0.491 g, 2.32 mmol), potassium hydroxide (0.195 g, 3.48 mL) in THF (30 mL) to afford **7b** as a white solid (0.393 g, 86 % yield). **R_f** = 0.15 (1:4 MeOH:DCM); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.24–7.16 (m, 2H), 7.15–7.06 (m, 2H), 3.37 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.4 (d, $J_{C\text{-}F}$ = 248.9 Hz), 160.0, 159.7, 138.2, 128.2 (d, $J_{C\text{-}F}$ = 8.7 Hz), 116.8 (d, $J_{C\text{-}F}$ = 23.0 Hz), 38.9. All recorded data were in accordance with those previously reported.

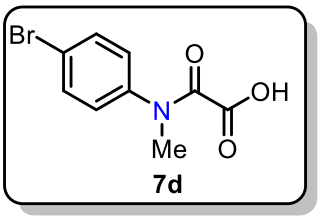
2-((4-chlorophenyl)(methyl)amino)-2-oxoacetic acid (7c)[3]



7c

Prepared according to general procedure **B** using oxamic ester **11c** (0.500 g, 2.20 mmol), potassium hydroxide (0.185 g, 3.29 mL) in THF (30 mL) to afford **7c** as a white solid (0.452 g, 96 % yield). $\mathbf{R_f}$ = 0.68 (1:4 MeOH:DCM); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 3.37 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.9, 159.8, 140.5, 134.5, 129.9, 127.4, 38.5. All recorded data were in accordance with those previously reported.

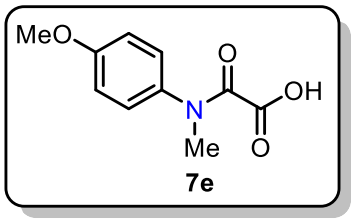
2-((4-bromophenyl)(methyl)amino)-2-oxoacetic acid (7d)[3]



7d

Prepared according to general procedure **B** using oxamic ester **11d** (0.500 g, 1.84 mmol), potassium hydroxide (0.154 g, 2.76 mL) in THF (30 mL) to afford **7d** as a brown solid (0.467 g, 98% yield). $\mathbf{R_f}$ = 0.32 (1:4 MeOH:DCM); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.6 Hz, 3H), 7.10 (d, *J* = 8.6 Hz, 2H), 3.35 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.5, 160.3, 141.0, 133.1, 127.9, 122.6, 38.3. All recorded data were in accordance with those previously reported.

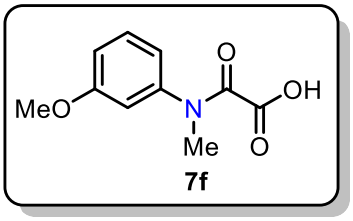
2-((4-methoxyphenyl)(methyl)amino)-2-oxoacetic acid (7e)[1]



7e

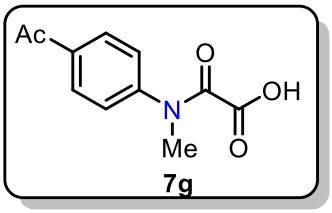
Prepared according to general procedure **B** using oxamic ester **11e** (0.500 g, 2.24 mmol), potassium hydroxide (0.189 g, 3.36 mL) in THF (30 mL) to afford **7e** as a brown solid (0.416 g, 89% yield). $\mathbf{R_f}$ = 0.23 (1:4 MeOH:DCM); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.15 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H), 3.31 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4, 161.7, 159.6, 134.2, 127.7, 114.9, 55.6, 37.7. All recorded data were in accordance with those previously reported.

2-((3-methoxyphenyl)(methyl)amino)-2-oxoacetic acid (7f)



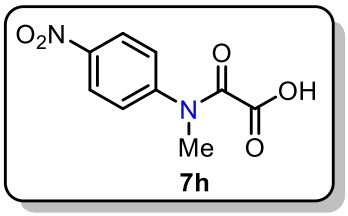
Prepared according to general procedure **B** using oxamic ester **11f** (0.511 g, 2.29 mmol), potassium hydroxide (0.193 g, 3.43 mL) in THF (30 mL) to afford **7f** as a colourless solid (0.422 g, 88 % yield). $\mathbf{R_f}$ = 0.25 (1:4 MEOH:DCM); **M.P.** 40–42 °C; **IR** (film, ν_{max}/cm^{-1}) 3390, 2936, 2481, 1923, 1588, 1651, 1485, 1265, 1219, 1112, 1034,776, 691; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.91 (s, 1H), 7.25 (t, *J* = 8.1 Hz, 1H), 6.88 – 6.84 (m, 1H), 6.82–6.78 (m, 1H), 6.76 (t, *J* = 2.3 Hz, 1H), 3.76 (s, 3H), 3.29 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.8, 162.2, 160.5, 142.5, 130.5, 118.3, 114.5, 111.9, 55.6, 37.0; **HRMS** (ESI$^+$) m/z: [M + H] calcd for $C_{10}H_{12}NO_4^+$ 210.0761; found 210.0767.

2-((4-acetylphenyl)(methyl)amino)-2-oxoacetic acid (7g)



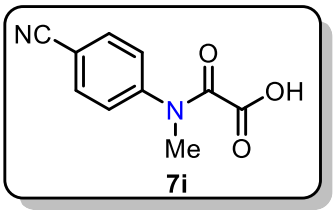
Prepared according to general procedure **B** using oxamic ester **11h** (0.403 g, 1.71 mmol), potassium hydroxide (0.144 g, 2.57 mmol) in THF (30 mL) to afford **7g** as a colourless solid (0.291 g, 77 % yield). $\mathbf{R_f}$ = 0.27 (1:4 MeOH:DCM); **M.P.** 126–128 °C; **IR** (film, ν_{max}/cm^{-1}) 3246, 2176, 1771, 1663, 1597, 1405, 1320, 1354, 1266, 1131, 1080, 754; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 3.39 (s, 3H), 2.61 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 197.6, 161.6, 161.1, 145.9, 136.7, 130.1, 126.0, 37.5, 26.8; **HRMS** (ESI$^+$) m/z: [M + H] calcd for $C_{11}H_{12}NO_4^+$ 222.0761; found 222.0774.

2-(methyl(4-nitrophenyl)amino)-2-oxoacetic acid (7h)[9]



Prepared according to general procedure **B** using oxamic ester **11i** (0.500 g, 2.01 mmol), potassium hydroxide (0.178 g, 3.15 mL) in THF (30 mL) to afford **7h** as a brown solid (0.237 g, 53 % yield). $\mathbf{R_f}$ = 0.15 (1:4 MeOH:DCM); **M.P.** 73–75 °C; **IR** (film, ν_{max}/cm^{-1}) 2962, 1731 1685, 1659, 1617, 1219, 1172, 1116, 984, 562; **^{1}H NMR** (300 MHz, DMSO-d_6) δ 8.28 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 3.32 (s, 3H); **^{13}C NMR** (75 MHz, DMSO-d_6) δ 172.3, 164.1, 162.7 161.1, 126.5, 125.0, 21.3.

2-((4-cyanophenyl)(methyl)amino)-2-oxoacetic acid (7i)

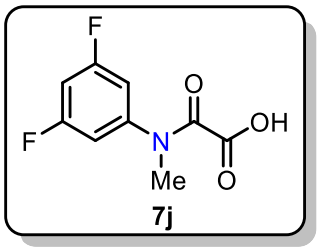


7i

Prepared according to general procedure **B** using **11j** (0.505 g, 2.31 mmol), potassium hydroxide (0.195 g, 3.47 mL) in THF (30 mL) to afford **7i** as a colourless solid (0.336 g, 71% yield). $\mathbf{R_f}$ = 0.29 (1:4 MeOH:DCM); **M.P.** 144–146 °C; **IR** (film, ν_{max}/cm^{-1}), 2924, 2229, 1748, 1625, 1593, 1503, 1405, 1196, 1119, 851, 703, 572; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 7.92 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H), 3.30 (s, 3H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 163.8, 162.4, 160.9, 145.5, 133.4, 126.3, 118.1, 35.0.

4

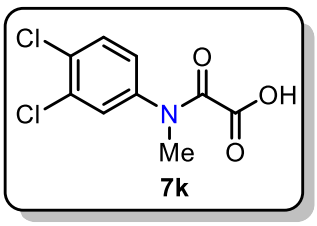
2-((3,5-difluorophenyl)(methyl)amino)-2-oxoacetic acid (7j)



7j

Prepared according to general procedure **B** using **11k** (0.500 g, 2.18 mmol), potassium hydroxide (0.183 g, 3.27 mL) in THF (30 mL) to afford **7j** as a yellow oil (0.401 g, 86% yield). $\mathbf{R_f}$ = 0.30 (1:4 MeOH:DCM); **IR** (film, ν_{max}/cm^{-1}) 3439, 3085, 2925, 1905, 1658, 1605, 1451, 1275, 1218, 1120, 989, 852, 681, 506; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -106.94 (d, J = 14.5 Hz), -107.18 (d, J = 14.5 Hz); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.70 (s, 1H), 6.86–6.68 (m, 3H), 3.31 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.2 (dd, $J_{C\text{-}F}$ = 250.8, 14.0 Hz), 162.9 (d, $J_{C\text{-}F}$ = 48.7 Hz), 162.2, 143.9 (q, $J_{C\text{-}F}$ = 11.8 Hz), 107.6 (dd, $J_{C\text{-}F}$ = 46.7, 17.3 Hz), 103.2 (dt, $J_{C\text{-}F}$ = 208.5, 23.9 Hz), 36.9; **HRMS** (ESI$^+$) m/z: [M + H] calcd for $C_9H_8F_2NO_3^+$ 216.0467; found 216.0473.

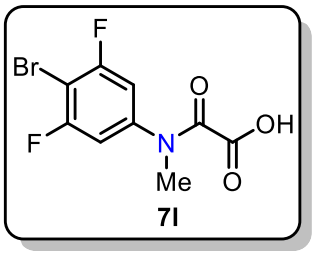
2-((3,4-dichlorophenyl)(methyl)amino)-2-oxoacetic acid (7k)



7k

Prepared according to general procedure **B** using **11l** (0.500 g, 1.91 mmol), potassium hydroxide (0.161 g, 2.86 mL) in THF (30 mL) to afford **7k** as a white solid (0.468 g, 99% yield). $\mathbf{R_f}$ = 0.47 (1:4 MeOH:DCM); **M.P.** 67–69 °C; **IR** (film, ν_{max}/cm^{-1}) 3948, 2925, 2525, 1941, 1722, 1634, 1548, 1466, 1245, 1030, 1113, 601, 561, **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50–7.45 (m, 1H), 7.38–7.33 (m, 1H), 7.11–7.06 (m, 1H), 3.35 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.7, 160.7, 141.1, 133.7, 133.2, 131.5, 128.3, 125.71 38.1; **HRMS** (ESI$^+$) m/z: [M + H] calcd for $C_9H_8Cl_2NO_3^+$ 247.9876; found 247.9882.

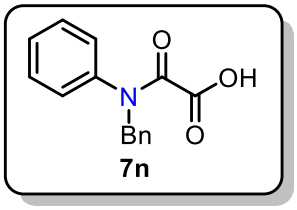
2-((4-bromo-3,5-difluorophenyl)(methyl)amino)-2-oxoacetic acid (7l)



7l

Prepared according to general procedure **B** using **11m** (0.400 g, 1.30 mmol), potassium hydroxide (0.109 g, 1.95 mL) in THF (30 mL) to afford **7l** as a white solid (0.340 g, 89% yield). $\mathbf{R_f}$ = 0.30 (1:4 MeOH:DCM); **IR** (film, ν_{max}/cm^{-1}) 3385, 2923, 1891, 1655, 1595, 1472, 1425, 1283, 1223, 1028, 652, 581, 512; **M.P.** 84–86 °C; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -101.90; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.00 (s, 1H), 6.90 (d, *J* = 7.1 Hz, 2H), 3.33 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 161.5, 161.1, 160.3 (dd, $J_{C\text{-}F}$ = 251.3, 5.7 Hz), 142.1 (t, $J_{C\text{-}F}$ = 11.4 Hz), 110.5 (d, $J_{C\text{-}F}$ = 26.4 Hz), 98.9 (t, $J_{C\text{-}F}$ = 24.5 Hz), 37.6; **HRMS** (ESI$^+$) m/z: [M + H] calcd for $C_9H_7BrF_2NO_3^+$ 293.9572; found 297.9517.

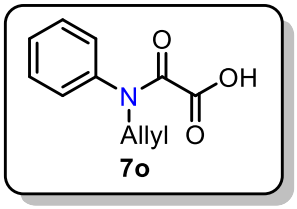
2-(benzyl(phenyl)amino)-2-oxoacetic acid (7n)[3]



7n

Prepared according to general procedure **B** using **11o** (0.504 g, 1.87 mmol), potassium hydroxide (0.158 g, 2.80 mL) in THF (30 mL) to afford **7n** as a brown oil (0.413 g, 87 % yield). $\mathbf{R_f}$ = 0.11 (1:4 MeOH:DCM); **^{1}H NMR** (300 MHz, DMSO-d_6) δ 7.45–7.08 (m, 10H), 4.94 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.1, 161.2, 139.8, 135.4, 129.4, 128.8, 128.7, 128.6, 127.4, 127.4, 53.5. All recorded data were in accordance with those previously reported.

2-(benzyl(phenyl)amino)-2-oxoacetic acid (7o)[4]

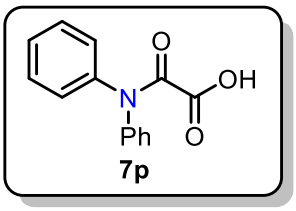


7o

To a stirred solution of *N*-Allylaniline (1.00 g, 7.51 mmol) in THF (20 mL) at -78 °C; oxalyl chloride (3.20 mL, 37.57 mmol) was sringed dropwise slowly over ten minutes, reaction mixture was left to stir at that temperature to which it was allowed to slowly warm to room temperature overnight. The resultant reaction mixture was cooled to 0 °C and mixture was then diluted with an equivalent amount of 2.5M NaOH and EtOAc. The layers were separated, and the aqueous layer was washed with EtOAc (x2) before being acidified to pH ~2-3 by the dropwise addition of 6M aqueous HCl. Thereafter, the aqueous layer was reextracted with EtOAc (x3), the combined organic extracts dried over $MgSO_4$ and concentrated in vacuo to afford **7o** as a

colourless gum (1.12 g, 73% yield). **R_f** = 0.5 (1:4 MeOH:DCM); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.36 (s, 1H), 7.45–7.31 (m, 3H), 7.24–7.16 (m, 2H), 5.92–5.74 (m, 1H), 5.24–5.10 (m, 2H), 4.34 (d, *J* = 6.3 Hz, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 162.6, 161.5, 139.9, 131.1, 129.7, 128.9, 127.2, 119.5, 52.5. All recorded data were in accordance with those previously reported.

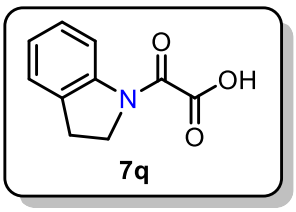
2-(diphenylamino)-2-oxoacetic acid (7p)



7p

Prepared according to general procedure **B** using **11p** (0.502 g, 1.96 mmol), Potassium hydroxide (0.166 g, 0.294 mmol) in THF (30 mL) to afford **7p** as a white solid (0.468 g, 98% yield). **R_f** = 0.27 (1:4 MeOH:DCM); **M.P.** 153–155 °C; **IR** (film, ν_{max}/cm^{-1}) 2864, 2559, 1747, 1620, 1588, 1438, 1491, 1221, 758, 692, 587; **^{1}H NMR** (300 MHz, DMSO-d_6) δ 7.49–7.24 (m, 10H); **^{13}C NMR** (75 MHz, DMSO-d_6) δ 164.1, 162.4, 140.6, 140.5, 129.7, 129.3, 128.5, 128.1, 127.2, 126.5; **HRMS** (ESI$^+$) m/z: [M + H] calcd for $C_{14}H_{12}NO_3^+$ 242.0812; found 242.0815.

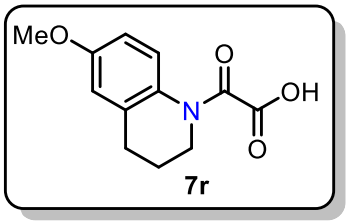
2-(indolin-1-yl)-2-oxoacetic acid (7q)



7q

Prepared according to general procedure **B** using **11q** (0.512 g, 2.49 mmol), potassium hydroxide (0.210 g, 3.74 mL) in THF to afford **7q** as a white solid (0.424 g, 89% yield) . **R_f** = 0.33 (1:4 MeOH:DCM); **M.P.** 126–128 °C; **IR** (film, ν_{max}/cm^{-1}); 3229, 2930, 1766, 1640, 1366, 1290, 1181, 753, 708, 646; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.2 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 4.66 (t, *J* = 8.2 Hz, 2H), 3.27 (t, *J* = 8.2 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.2, 155.9, 142.0, 132.9, 127.9, 126.5, 125.2, 118.7, 50.6, 28.8; **HRMS** (ESI$^+$) m/z: [M + H] calcd for $C_{10}H_{10}NO_3^+$ 192.0655; found 192.0665.

2-(6-methoxy-3,4-dihydroquinolin-1(2H)-yl)-2-oxoacetic acid (7r)

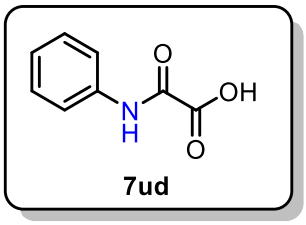


7r

Prepared according to general procedure B using **11r** (0.500 g, 2.00 mmol), potassium hydroxide (1.67 g, 3.0 mL) in THF (30 mL) to afford **7r** as a brown solid (0.420 g, 89 % yield). **R_f** = 0.18 (1:4 MeOH:DCM); **M.P.** 124–126 °C; **IR** (film, ν_{max}/cm^{-1}) 2922, 2848,

2434, 1729, 1572, 1499, 1466, 1427, 1272, 1232, 1180, 801, 411; **^{1}H NMR** (300 MHz, DMSO-d_6) δ 7.02 (d, *J* = 8.7 Hz, 1H), 6.86 – 6.72 (m, 2H), 3.76 – 3.54 (m, 5H), 2.82 (t, *J* = 6.8 Hz, 1H), 2.70 (t, *J* = 6.8 Hz, 1H), 1.98–1.79 (m, 2H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 165.3, 157.6, 125.0, 122.7, 114.4, 114.0, 112.3, 112.1, 46.2, 42.0, 26.8, 23.2; **HRMS** (ESI+) m/z: [M + H] calcd for $C_{12}H_{14}NO_4^+$ 236.0917; found 236.0920

2-oxo-2-(phenylamino)acetic acid (7ud)[1]

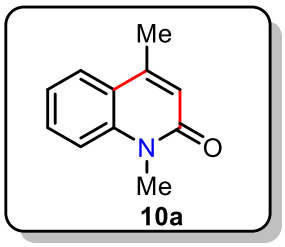


7ud

Prepared according to general procedure **B** using **11ud** (0.510 g, 2.85 mmol), potassium hydroxide (0.240 g, 4.23 mL) in THF (30 mL) to afford **7ud** as a white solid (0.445g, 95% yield). **R_f** = 0.39 (1:4 MeOH:DCM); **M.P.** 141–143 °C; **IR** (film, ν_{max}/cm^{-1}) 3299, 2938, 1762, 1684, 1543, 1347, 1303, 1206, 747, 690; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 1H); **^{13}C NMR (**101 MHz, $CDCl_3$) δ 160.2, 152.0, 135.6, 129.6, 126.5, 120.1. All recorded data were in accordance with those previously reported.

15. Characterization data for quinoline-2-ones (10).

1,4-Dimethylquinolin-2(1H)-one (10a)[5]



10a

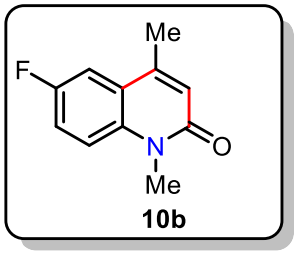
Prepared using general Procedure **C** using **7a** (0.140 g, 0.78 mmol), methacrylic acid (0.201 g, 2.34 mmol), $AgNO_3$ (0.66 g, 0.39 mmol) and $K_2S_2O_8$ (0.632 g, 0.234 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (10–40%) afforded **10a** as a white solid (0.081 g, 60% yield).

Prepared using general Procedure **D** using **7a** (0.100 g, 0.558 mmol), methacrylic acid (0.141 g, 1.67 mmol), $AgNO_3$ (0.043 g, 0.027 mmol), 4-CzIPN (0.009 g, 0.011 mmol) and $K_2S_2O_8$ (0.453 g, 1.67 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (10–40%) afforded **10a** as a white solid (0.056 g, 58% yield).

R_f = 0.18 (2:3 EtOAc:Petroleum ether). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.53 (t, *J* = 8.6 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 1H), 7.22 (t, *J* = 8.1 Hz, 1H), 6.55 (s, 1H), 3.65 (s, 3H),

2.41 (d, J = 1.2 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 162.1, 146.4, 139.7, 130.4, 125.1, 121.9, 121.3, 121.0, 114.4, 29.2, 19.0. All data were in accordance with those previously reported.

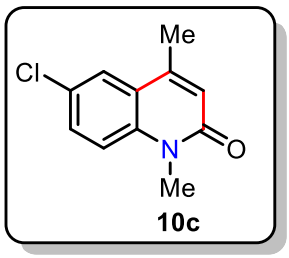
6-Fluoro-1,4-dimethylquinolin-2(1H)-one (10b)[5]



10b

Prepared using general Procedure **C** using **7b** (0.132 g, 0.669 mmol), methacrylic acid (0.169g, 2.01 mmol), $AgNO_3$ (0.055 g, 0.335 mmol) and $K_2S_2O_8$ (0.543 g, 2.01 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (10–15%) afforded **10b** as a white solid (0.071 g, 56% yield). **R_f** = 0.23 (2:3 Pet Ether:Petroleum ether); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.38–7.27 (m, 3H), 6.63 (s, 1H), 3.69 (s, 3H), 2.42 (d, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.9, 157.8 (d, $J_{C\text{-}F}$ = 241.7 Hz), 145.6 (d, J = 3.2 Hz), 136.5, 122.4 (d, $J_{C\text{-}F}$ = 8.0 Hz), 122.4, 118.1 (d, $J_{C\text{-}F}$ = 23.6 Hz), 116.1 (d, $J_{C\text{-}F}$ = 8.1 Hz), 110.8 (d, $J_{C\text{-}F}$= 22.9 Hz), 29.8, 19.1. All data were in accordance with those previously reported.

6-Chloro-1,4-dimethylquinolin-2(1H)-one (10c)[5]

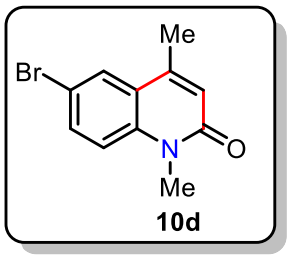


10c

Prepared using general Procedure **C** using **7c** (0.150 g, 0.702 mmol), methacrylic acid (0.181 g, 2.11 mmol), $AgNO_3$ (0.060 g, 0.351 mmol) and $K_2S_2O_8$ (0.570 g, 2.11 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (15–30%) afforded **10c** as a white solid (0.120 g, 82% yield).

R_f = 0.56 (3:7 EtOAc:Petroleum Ether); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.60 (d, J = 2.4 Hz, 1H), 7.47 (dd, J = 9.0, 2.4 Hz, 1H), 7.25 (d, J = 8.9 Hz, 1H), 6.58 (s, 1H), 3.64 (s, 3H), 2.40 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.8, 145.4, 138.4, 130.4, 127.6, 124.7, 122.6, 122.3, 115.9, 29.4, 18.9. All data were in accordance with those previously reported.

6-Bromo-1,4-dimethylquinolin-2(1H)-one (10d) [6]

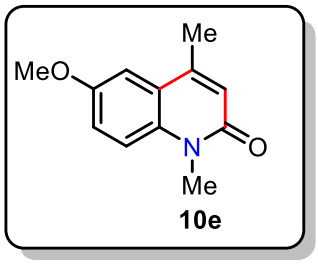


Prepared using general Procedure **C** using **7d** (0.147 g, 0.570 mmol), methacrylic acid (0.147 g, 1.77 mmol), $AgNO_3$ (0.048 g, 0.285mmol) and $K_2S_2O_8$ (0.462 g, 1.71 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (5–30%) afforded **10d** as a colorless solid (0.079 g, 55% yield).

Prepared using general Procedure **D** using **7d** (0.097 g, 0.376 mmol), methacrylic acid (0.097 g, 1.13 mmol), $AgNO_3$ (0.032 g, 0.188 mmol), 4-CzIPN (0.006 g, 0.008 mmol) and $K_2S_2O_8$ (0.305 g, 1.13 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (5–30%) afforded **10d** as colorless solid (0.68 g, 72% yield);

R_f = 0.21 (3:7 EtOAc:Petroleum ether); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 2.2 Hz, 1H), 7.62 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.22 (d, *J* = 9.0 Hz, 1H), 6.59 (s, 1H), 3.66 (s, 3H), 2.42 (d, *J* = 1.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.9, 145.4, 138.8, 133.2, 127.8, 123.1, 122.3, 116.2, 115.1, 29.5, 19.0. All data were in accordance with those previously reported.

6-Methoxy-1,4-dimethylquinolin-2(1H)-one (10e) [5]

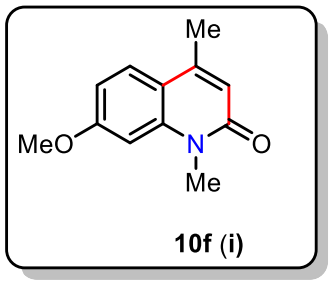


Prepared using general Procedure **C** using **7e** (0.143 g, 0.680 mmol), methacrylic acid (0.176 g, 2.05 mmol), $AgNO_3$ (0.058 g, 0.340 mmol) and $K_2S_2O_8$ (0.554 g, 2.05 mmol). Chromatography on silica gel with EtOAc/ Petroleum ether (40–70%) afforded **10e** as a white solid (0.105 g, 76% yield).

Prepared using general Procedure **D** using **7e** (0.100 g, 0.478 mmol), methacrylic acid (0.123 g, 1.43 mmol), $AgNO_3$ (0.41 g, 0.239 mmol), 4-CzIPN (0.007 g, 0.009 mmol) and $K_2S_2O_8$ (0.388 g, 1.43 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (40–70 %) afforded **10e** as a colorless solid (0.073 g, 75% yield).

R_f = 0.23 (4:1 EtOAc:Petroleum ether); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 9.1 Hz, 1H), 7.17 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.11 (d, *J* = 2.9 Hz, 1H), 6.60 (s, 1H), 3.88 (s, 3H), 3.68 (s, 3H), 2.43 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4, 161.7, 159.6, 134.7, 134.2, 127.7, 126.7, 121.7, 114.9, 55.6, 37.7, 17.4. All data were in accordance with those previously reported.

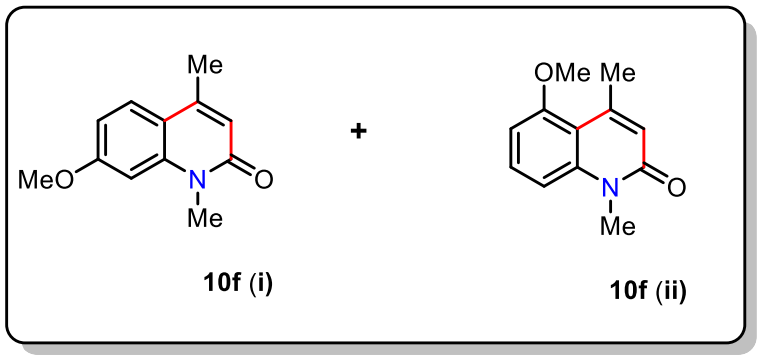
7-Methoxy-1,4-dimethylquinolin-2(1H)-one (10f)[5]



Prepared using general Procedure **C** using **7f** (0.197 g, 1.01 mmol), methacrylic acid (0.261 g, 3.03 mmol), $AgNO_3$ (0.086 g, 0.505 mmol) and $K_2S_2O_8$ (0.819 g, 0.303 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (0–5%) afforded **10f** a white solid (0.032 g, 16 % yield).

10f (i): obtained as a white (0.022 g, 23% yield); $\mathbf{R_f}$ = 0.31 (4:1 EtOAc:Petroleum ether); **^{1}H NMR** (300 MHz, DMSO-d_6) δ 7.69 (d, J = 8.7 Hz, 1H), 6.95–6.87 (m, 2H), 6.34 (d, J = 1.3 Hz, 1H), 3.89 (s, 3H), 3.57 (s, 3H), 2.38 (d, J = 1.3 Hz, 3H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 161.3, 161.2, 146.3, 141.2, 126.8, 117.3, 114.6, 109.4, 98.9, 55.5, 28.8, 18.4. All data were in accordance with those previously reported.

7-Methoxy-1,4-dimethylquinolin-2(1H)-one & 5-methoxy-1,4-dimethylquinolin-2(1H)-one (10f)[5]

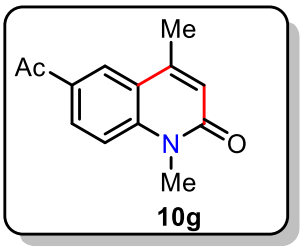


Prepared using general Procedure **D** using **7f** (0.100 g, 0.478 mmol), methacrylic acid (0.123 g, 1.43 mmol), $AgNO_3$ (0.041 g, 0.239 mmol), 4-CzIPN (0.007 g, 0.009 mmol) and $K_2S_2O_8$ (0.388 g, 1.43 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (0–5%) afforded **10f** as a mixture of 1:1.5 separable regioisomers (0.055 g, 57% yield).

10f (i): obtained as a white (0.022 g, 23% yield); $\mathbf{R_f}$ = 0.31 (4:1 EtOAc:Petroleum ether); **^{1}H NMR** (300 MHz, DMSO-d_6) δ 7.69 (d, J = 8.7 Hz, 1H), 6.95 – 6.87 (m, 2H), 6.34 (d, J = 1.3 Hz, 1H), 3.89 (s, 3H), 3.57 (s, 3H), 2.38 (d, J = 1.3 Hz, 3H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 161.3, 161.2, 146.3, 141.2, 126.8, 117.3, 114.6, 109.4, 98.9, 55.5, 28.8, 18.4. All data were in accordance with those previously reported.

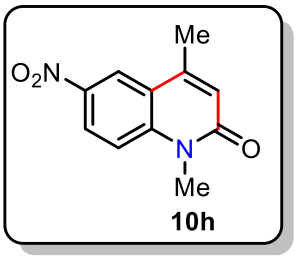
10f(ii): obtained as a white (0.033 g, 34% yield); $\mathbf{R_f}$ = 0.43 (4:1 EtOAc:Petroleum ether); **M.P.** 83–85 °C; **IR** (film, vmax/cm^{-1}) 3421, 2923, 2851, 1726, 1645, 1588, 1452, 1375, 1319, 1231, 1063, 1034, 856, 734 **^{1}H NMR** (300 MHz, DMSO-d_6) δ 7.53 (t, *J* = 8.4 Hz, 1H), 7.09 (d, *J* = 9.5 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 1H), 6.34 (d, *J* = 1.3 Hz, 1H), 3.86 (s, 3H), 3.55 (s, 3H), 2.55 (d, *J* = 1.3 Hz, 3H); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 160.4, 158.3, 146.9, 141.5, 131.2, 120.4, 111.0, 107.7, 104.6, 55.9, 29.4, 24.5; **HRMS** (ESI$^+$) m/z: [M + H] calcd for $C_{12}H_{14}NO_2^+$ 204.1019; found 204.1030.

6-Acetyl-1,4-dimethylquinolin-2(1H)-one (10g)[6]



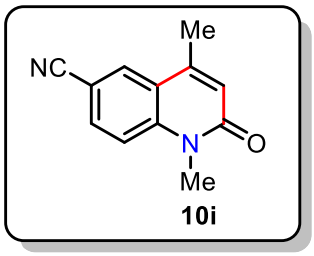
Prepared using general Procedure **C** using **7g** (0.165 g, 0.75 mmol), methacrylic acid (0.189 g, 2.24 mmol), $AgNO_3$ (0.63 g, 0.373 mmol) and $K_2S_2O_8$ (0.605 g, 2.24 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (20–60%) afforded **10g** as a white solid (0.072 g, 72% yield). $\mathbf{R_f}$ = 0.48 (2:3 EtOAc:Petroleum ether); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.26 (d, *J* = 2.0 Hz, 1H), 8.10 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 1H), 6.60 (s, 1H), 3.67 (s, 3H), 2.63 (s, 3H), 2.48 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.7, 162.1, 147.0, 142.9, 130.8, 130.3, 126.1, 121.8, 121.0, 114.5, 29.6, 26.6, 19.0. All data were in accordance with those previously reported.

1,4-Dimethyl-6-nitroquinolin-2(1H)-one (10h)



Prepared using general Procedure **C** using **7h** (0.114 g, 0.509 mmol), methacrylic acid (0.131 g, 1.53 mmol), $AgNO_3$ (0.043 g, 2.55 mmol) and $K_2S_2O_8$ (0.413 g, 1.53 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (15–40%) afforded **10h** as a yellow solid (0.067 g, 60% yield). $\mathbf{R_f}$ = 0.63 (4:1 EtOAc: Petroleum ether); **M.P.** 220–222 °C; **IR** (film, vmax/cm^{-1}) 2925, 1662, 1601, 1517, 1337, 1298, 1115, 908, 738; **^{1}H NMR** (300 MHz, $CDCl_3$)δ 8.60 (d, *J* = 2.6 Hz, 1H), 8.41 (dd, *J* = 9.3, 2.6 Hz, 1H), 7.46 (d, *J* = 9.3 Hz, 1H), 6.71 (s, 1H), 3.75 (s, 3H), 2.54 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.8, 146.4, 144.1, 142.1, 125.3, 123.1, 121.5, 121.3, 115.1, 30.0, 19.1; **HRMS** (ESI$^+$) m/z: [M + H] calcd for $C_{11}H_{11}N_2O_3^+$ 219.0764; found 219.0775.

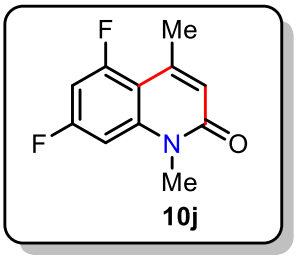
1,4-Dimethyl-2-oxo-1,2-dihydroquinoline-6-carbonitrile (10i)



10i

Prepared using general Procedure **C** using **7i** (0.135 g, 0.66 mmol), methacrylic acid (0.171 g, 1.98 mmol), $AgNO_3$ (0.056 g, 0.33 mmol) and $K_2S_2O_8$ (0.535 g, 1.98 mmol). Chromatography on silica gel with EtOAc/ Petroleum ether (15– 40%) afforded **10i** as a white solid (0.110 g, 84% yield). $\mathbf{R_f}$ = 0.60 (4:1 EtOAc:Petroleum ether); **M.P.** 232–234 °C; **IR** (film, vmax/cm^{-1}) 2932, 2216, 1668, 1584, 1546, 1301, 1065, 917, 813; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 1.9 Hz, 1H), 7.79 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 6.66 (s, 1H), 3.70 (s, 3H), 2.47 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.7, 145.6, 142.6, 133.1, 130.1, 122.9, 121.7, 118.7, 115.39, 105.5, 29.6, 18.9; **HRMS** (ESI^+) m/z: [M + H] calcd for $C_{11}H_{12}N_2O^+$ 199.0866; found 199.0870.

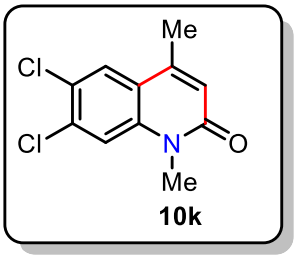
5,7-Difluoro-1,4-dimethylquinolin-2(1H)-one (10j)



10j

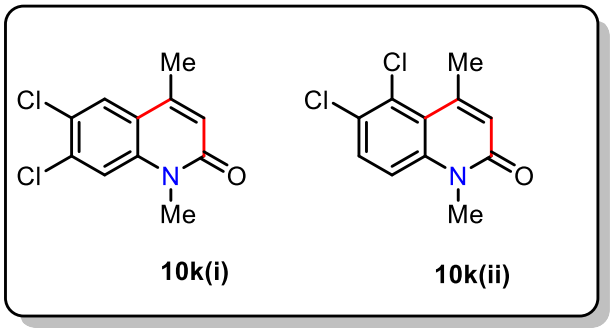
Prepared using general Procedure **C** using **7j** (0.205 g, 0.950 mmol), methacrylic acid (0.246 g, 2.86 mmol), $AgNO_3$ (0.081 g, 0.475 mmol) and $K_2S_2O_8$ (0.773 g, 2.86 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (15– 20%) afforded **10j** as a brown solid (0.090 g, 45% yield). $\mathbf{R_f}$ = 0.41 (3:7 EtOAc:Petroleum ether); **M.P.** 89–91 °C; **IR** (film, vmax/cm^{-1}), 3084, 1662,1631, 1599, 1568, 1442, 1363, 1313, 1111, 1005; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -105.17 (d, *J* = 10.1 Hz), -105.74 (d, *J* = 10.1 Hz); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.89–6.78 (m, 1H), 6.72–6.62 (m, 1H), 6.43 (s, 1H), 3.60 (s, 3H), 2.53 (d, $J_{H\text{-}F}$ = 9.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.1 (dd, $J_{C\text{-}F}$ = 258.5, 14.25 Hz), 161.7, 160.7 (dd, $J_{C\text{-}F}$ = 141.1, 13.9 Hz), 145.0 (dd, $J_{C\text{-}F}$ = 3.6, 1.4 Hz), 142.7 (dd, $J_{C\text{-}F}$ = 13.0, 8.7 Hz), 121.3 (d, $J_{C\text{-}F}$ = 2.7 Hz), 108.0 (dd, $J_{C\text{-}F}$ = 14.3, 3.1 Hz), 98.4 (dd, $J_{C\text{-}F}$ = 27.5, 26.5 Hz), 97.8 (dd, $J_{C\text{-}F}$ = 26.4, 3.9 Hz), 30.1, 22.9 (d, $J_{C\text{-}F}$ = 12.9 Hz). **HRMS** (ESI^+) m/z: [M + H] calcd for $C_{11}H_{10}F_2NO^+$ 210.0725; found 210.0733.

6,7-dichloro-1,4-dimethylquinolin-2(1H)-one (10k)



Prepared using general Procedure **C** using **7k** (0.145 g, 0.580 mmol), methacrylic acid (0.148 g, 1.75 mmol), $AgNO_3$ (0.049 g, 0.290 mmol) and $K_2S_2O_8$ (0.473 g, 1.75 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (15–30%) afforded **10k** as a white solid (0.054 g, 42% yield). $\mathbf{R_f}$ = 0.22 (2:3) EtOAc:Petroleum ether); **M.P.** 181–183 °C; **IR** (film, vmax/cm-1) 2925, 1646, 1577, 1405, 1297, 1147, 1072, 855, 822, 542; 422; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.42 (s, 1H), 6.58 (s, 1H), 3.63 (s, 3H), 2.41 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 161.7, 145.1, 139.1, 134.1, 126.4, 126.0, 122.3, 121.2, 116.2, 29.6, 19.0; **HRMS** (ESI^+) m/z: [M + H] calcd for $C_{11}H_{10}Cl_2NO$ 241.0134; found 242.0140.

6,7-dichloro-1,4-dimethylquinolin-2(1H)-one & 5,6-dichloro-1,4-dimethylquinolin-2(1H)-one (10k(i) & 10(ii))



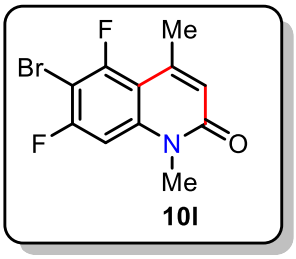
Prepared using general Procedure **D** using **7k** (0.100 g, 0.403 mmol), methacrylic acid (0.104 g, 1.21 mmol), $AgNO_3$ (0.034 g, 0.202 mmol), 4-CzIPN (0.006 g, 0.008 mmol) and $K_2S_2O_8$ (0.327 g, 1.21 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (5– 35 %) afforded **10k** as a mixture of 1:1.1 separable regioisomers (0.052 g, 53% yield).

10k(i): obtained as a white solid (0.027g); $\mathbf{R_f}$ = 0.22 (2:3) EtOAc:Petroleum ether); **M.P.** 181–183 °C; **IR** (film, vmax/cm^{-1}) 2925, 1646, 1577, 1405, 1297, 1147, 1072, 855, 822, 542; 422; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.42 (s, 1H), 6.58 (s, 1H), 3.63 (s, 3H), 2.41 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 161.7, 145.1, 139.1, 134.1, 126.4, 126.0, 122.3, 121.2, 116.2, 29.6, 19.0; **HRMS** (ESI+) m/z: [M + H] calcd for $C_{11}H_{10}Cl_2NO$ 241.0134; found 242.0140.

10l(ii): obtained as a white solid (0.025g); $\mathbf{R_f}$ = 0.74 (2:3) EtOAc:Petroleum ether); **M.P.** 162–164 °C; **IR** (film, vmax/cm^{-1}) 2921, 1649, 1581, 1458, 1406, 1300, 1148, 1075,882; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 9.2 Hz, 1H), 7.27 (d, *J* = 9.2 Hz, 1H), 6.65 (s, 1H), 3.69 (s, 3H), 2.82 (s, 3H); **^{13}C**

NMR (151 MHz, $CDCl_3$) δ 161.0, 146.9, 140.9, 131.8, 131.0, 128.9, 125.7, 121.2, 114.6, 30.3, 26.5; **HRMS** (ESI^+) m/z: [M + H] calcd for $C_{11}H_{10}Cl_2NO^+$ 242.0134; found 242.0140.

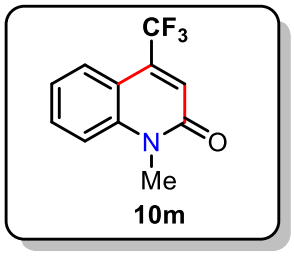
6-Bromo-5,7-difluoro-1,4-dimethylquinolin-2(1H)-one (10l)



Prepared using general Procedure **C** using **7l** (0.139 g, 0.474 mmol), methacrylic acid (0.122 g, 1.42 mmol), $AgNO_3$ (0.040 g, 0.237 mmol) and $K_2S_2O_8$ (0.384 g, 1.42 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (5–30%) afforded **10m** as a white solid (0.059 g, 43% yield).

Prepared using general Procedure **D** using **7l** (0.100 g, 0.341 mmol), methacrylic acid (0.086 g, 1.02 mmol), $AgNO_3$ (0.029 g, 0.171 mmol), 4-CzIPN (0.005 g, 0.007 mmol) and $K_2S_2O_8$ (0.277 g, 1.02 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (5–30%) afforded **10m** as colorless solid (0.053 g, 54% yield). **R_f** = 0.39 (3:7 EtOAc:Petroleum ether); **M.P.** 173–175 °C; **IR** (film, vmax/cm^{-1}) 3070, 1662, 1593, 1555, 1428, 1359, 1304, 1246, 1140, 1044, 862, 582; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -100.20 (d, J = 5.7 Hz), -100.68 (d, J = 5.7 Hz); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.96 (dd, J = 10.3, 2.0 Hz, 1H), 6.48 (s, 1H), 3.62 (s, 3H), 2.56 (d, $J_{H\text{-}F}$ = 8.2, Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) 161.3, δ 160.7 (dd, $J_{(C\text{-}F)}$ = 190.4 , 6.2 Hz), 157.8 (dd, $J_{(C\text{-}F)}$ = 202.6, 6.2 Hz), 144.5, 141.18 (dd, $J_{(C\text{-}F)}$ = 12.3, 8.4 Hz), 122.3, 108.8 (dd, $J_{(C\text{-}F)}$ = 15.3, 2.4 Hz), 98.37 (d, $J_{(C\text{-}F)}$ = 27.5 Hz), 91.8 (t, $J_{(C\text{-}F)}$ = 25.8 Hz), 30.1 (d, $J_{(C\text{-}F)}$ = 3.9 Hz), 22.9 (d, $J_{(C\text{-}F)}$ = 16.2 Hz); **HRMS** (ESI^+) m/z: [M + H] calcd for $C_{11}H_9BrF_2NO^+$ 287.9830; found 287.9839

1-Methyl-4-(trifluoromethyl)quinolin-2(1H)-one (10m)

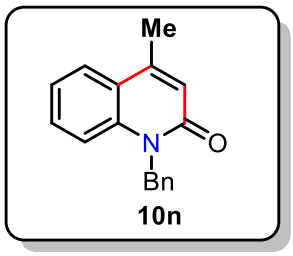


Prepared using general Procedure **C** using **7a** (0.141 g, 0.787 mmol), 2-(trifluoromethyl)acrylic acid (0.331 g, 0.236 mmol), $AgNO_3$ (0.065 g, 0.394 mmol) and $K_2S_2O_8$ (0.638 g, 0.236 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (0–5%) afforded **10m** as a white solid (0.096 g, 54% yield).

Prepared using general Procedure **D** using **7a** (0.100 g, 0.558 mmol), 2-(trifluoromethyl)acrylic acid (0.234 g, 1.67 mmol), $AgNO_3$ (0.047 g, 0.279 mmol), 4-CzIPN (0.009 g, 0.011 mmol) and

$K_2S_2O_8$ (0.453 g, 1.67 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (0–5%) afforded **10m** as colorless solid (0.107 g, 84% yield); **M.P.** 64–66 °C; **R_f** = 0.34 (3:7 EtOAc:Petroleum ether); **IR** (film, vmax/cm-1) 2939, 1663, 1592, 1456, 1262, 1121, 1069, 949, 884, 754, 726; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -63.13; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 1H), 7.67 (t, *J* = 8.2 Hz, 1H), 7.46 (d, *J* = 9.1 Hz, 1H), 7.34 (t, *J* = 8.2 Hz, 1H), 7.12 (s, 1H), 3.76 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.7, 140.7, 137.1 (q, *J* = 31.6 Hz), 131.8, 125.9, 123.9, 123.0, 121.2, 115.3, 115.1, 30.0; **HRMS** (ESI^+) m/z: [M + H] calcd for $C_{11}H_9F_3NO^+$ 228.0631; found 228.0637.

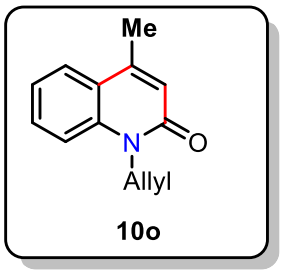
1-Benzyl-4-methylquinolin-2(1H)-one (10n)[5]



10n

Prepared using general Procedure **C** using **7n** (0.102 g, 0.400 mmol), methacrylic acid (0.101 g, 1.20 mmol), $AgNO_3$ (0.033 g, 0.200 mmol) and $K_2S_2O_8$ (0.324 g, 1.20 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (3–7%) afforded **10n** as a colorless solid (0.046 g, 46% yield). **R_f** = 0.50 (1:4 EtOAc:Petroleum ether); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.47–7.38 (m, 1H), 7.30–7.18 (m, 7H), 6.71 (d, *J* = 1.3 Hz, 1H), 5.56 (s, 2H), 2.51 (d, *J* = 1.1 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.3, 147.0, 139.2, 136.6, 130.4, 128.7, 127.2, 126.52, 125.2, 122.0, 121.7, 121.0, 115.3, 45.7, 19.1. All data were in accordance with those previously reported.

1-allyl-4-methylquinolin-2(1H)-one (10o)[7]

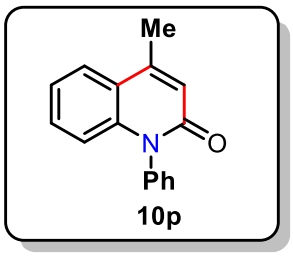


10o

Prepared using general Procedure **C** using **7o** (0.156 g, 0.700 mmol), methacrylic acid (0.196 g, 2.28 mmol), $AgNO_3$ (0.065 g, 0.388 mmol) and $K_2S_2O_8$ (0.617 g, 2.28 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (7–15%) afforded **10o** as a colorless gum (0.068 g, 45% yield). **R_f** = 0.58 (1:4 EtOAc:Petroleum ether); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.9 Hz, 1H), 7.57 (td, *J* = 7.9, 7.3, 1.4 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 6.67 (s, 1H), 6.07 – 5.91 (m, 1H), 5.24 (d, *J* = 10.5 Hz, 1H), 5.11 (d, *J* = 17.3 Hz, 1H), 5.02 – 4.94 (m, 2H), 2.52 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 161.9, 147.0, 139.1, 132.0, 130.5,

125.3, 122.1, 121.7, 121.0, 116.9, 115.2, 44.4, 19.2; All data were in accordance with those previously reported.

4-Methyl-1-phenylquinolin-2(1H)-one (10p)[8]



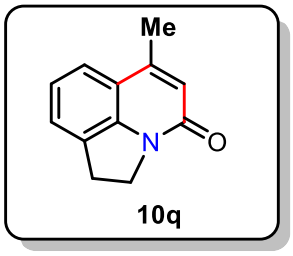
10p

Prepared using general Procedure **C** using **7p** (0.144 g, 0.597 mmol), methacrylic acid (0.154 g, 1.79 mmol), $AgNO_3$ (0.051 g, 0.299 mmol) and $K_2S_2O_8$ (0.484 g, 1.79 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (5–35%) afforded **10p** as a white solid (0.059 g, 42% yield).

Prepared using general Procedure **D** using **7p** (0.100 g, 0.415 mmol), methacrylic acid (0.107 g, 1.24 mmol), $AgNO_3$ (0.035 g, 0.208 mmol), 4-CzIPN (0.007 g, 0.008 mmol) and $K_2S_2O_8$ (0.336 g, 1.24 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (5–35%) afforded **10p** as colorless solid (0.074 g, 76% yield).

R_f = 0.41 (3:7 EtOAc:Petroleum ether**; ^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.64–7.47 (m, 3H), 7.37–7.22 (m, 4H), 6.72–6.63 (m, 2H), 2.54 (d, *J* = 1.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.3, 147.6, 141.0, 137.8, 130.3, 130.1, 129.1, 129.0, 124.9, 122.3, 121.5, 121.2, 116.4, 19.3. All data were in accordance with those previously reported.

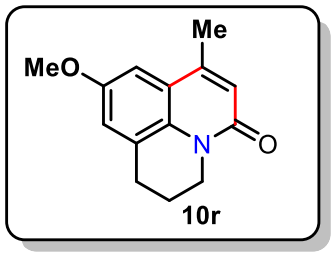
6-Methyl-1,2-dihydro-4H-pyrrolo[3,2,1-ij] quinolin-4-one (10q)



10q

Prepared using general Procedure **C** using **7q** (0.149 g, 0.779mmol), methacrylic acid (0.201 g, 0.234 mmol), $AgNO_3$ (0.066 g, 0.390 mmol) and $K_2S_2O_8$ (0.632 g, 2.34 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (5–15%) afforded **10q** as a white solid (0.064 g, 44% yield). **R_f** = 0.29 (3:7 EtOAc:Petroleum ether); **M.P.** 91–93 °C; **IR** (film, vmax/cm^{-1}) 3302, 2937, 1703, 1627, 1464, 1265, 1152, 1025, 849, 696, 530; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.53 (s, 1H), 4.42 (t, *J* = 8.0 Hz, 2H), 3.42 (t, *J* = 8.0 Hz, 2H), 2.45 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.2, 146.9, 142.3, 131.0, 125.2, 123.2, 122.0, 121.2, 118.1, 46.7, 27.4, 18.0; **HRMS** (ESI^+) m/z: [M + H] calcd for $C_{12}H_{12}NO^+$ 186.0913; found 186.0922

9-Methoxy-7-methyl-2,3-dihydro-1H,5H-pyrido[3,2,1-ij]quinolin-5-one (10r)

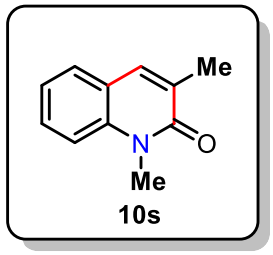


Prepared using general Procedure **C** using **7r** (0.150 g, 0.637 mmol), methacrylic acid (0.169 g, 1.91 mmol), $AgNO_3$ (0.54 g, 0.319 mmol) and $K_2S_2O_8$ (0.516 g, 1.91 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (10–20%) afforded **10r** as a white solid (0.102 g, 70% yield).

Prepared using general Procedure **D** using **7r** (0.100 g, 0.425 mmol), methacrylic acid (0.106 g, 1.26 mmol), $AgNO_3$ (0.036 g, 0.213 mmol), 4-CzIPN (0.007 g, 0.009 mmol) and $K_2S_2O_8$ (0.345 g, 0.213 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (10–20%) afforded **10r** as colourless solid (0.084 g, 82% yield).

R_f = 0.15 (2:3 EtOAc:Petroleum ether); **M.P.** 113–115 °C **IR** (film, vmax/cm^{-1}) 3539, 2923, 2854, 1734, 1643, 1615, 1576, 1264, 1121, 1066, 1073, 742, 625; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.93 (s, 2H), 6.57 (s, 1H), 4.15 (t, *J* = 6.2 Hz, 2H), 3.84 (s, 3H), 2.94 (t, *J* = 6.2 Hz, 2H), 2.41 (s, 3H), 2.06 (p, *J* = 6.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3, 154.1, 145.8, 131.1, 126.8, 122.2, 121.4, 118.0, 105.6, 55.7, 42.1, 28.3, 20.9, 19.3; **HRMS** (ESI^+) m/z: [M + H] calcd for $C_{14}H_{16}NO_2^+$ 230.1176; found 230.1181.

1,3-Dimethylquinolin-2(1H)-one (10s)[5]



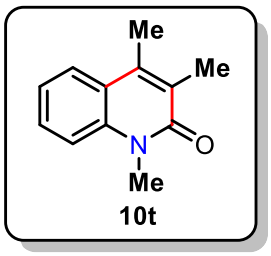
Prepared using general Procedure **C** using oxamic acid **7a** (0.145 g, 0.809 mmol), crotonic acid (0.209 g, 2.43 mmol), $AgNO_3$ (0.069 g, 0.405 mmol) and $K_2S_2O_8$ (0.657 g, 2.43 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (10–25%) afforded **10s** as a colourless solid (0.031 g, 22% yield).

Prepared using general Procedure **D** using **7s** (0.100 g, 0.558 mmol), crotonic acid (0.123 g, 1.67 mmol), $AgNO_3$ (0.041 g, 0.279 mmol), 4-CzIPN (0.007 g, 0.011 mmol) and $K_2S_2O_8$ (0.388 g, 1.67 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (10–25%) afforded **10s** as colourless solid (0.050 g, 52% yield).

R_f = 0.41 (3:7 EtOAc: Petroleum Ether); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.57–7.47 (m, 3H), 7.33 (d, *J* = 8.8 Hz, 1H), 7.21 (td, *J* = 7.4, 1.1 Hz, 1H), 3.75 (s, 3H), 2.26 (d, *J* = 1.3 Hz, 3H); **^{13}C NMR** (151 MHz,

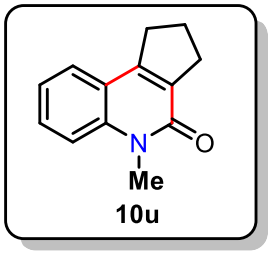
$CDCl_3$) δ 163.1, 139.3, 135.8, 130.2, 129.4, 127.9, 122.1, 120.9, 114.0, 29.8, 17.9. All data were in accordance with those previously reported.

1,3,4-trimethylquinolin-2(1H)-one (10t)



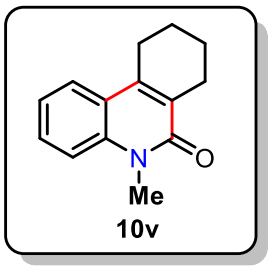
Prepared using general Procedure **C** using oxamic acid **7a** (0.149 g, 0.820 mmol), tiglic acid (0.246 g, 2.46 mmol), $AgNO_3$ (0.068 g, 0.410 mmol) and $K_2S_2O_8$ (0.665 g, 2.46 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (0–7%) afforded **10t** as a yellow solid (0.080 g, 52% yield). $\mathbf{R_f}$ = 0.26 (2:3 EtOAc:Petroleum ether); **M.P.** 67–69 °C; **IR** (film, vmax/cm^{-1}), 2922, 1716, 1626, 1586, 1454, 1315, 1097, 750, 603, 446; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.51 (ddd, *J* = 8.1, 7.1, 1.5 Hz, 1H), 7.35 (d, *J* = 9.7 Hz, 1H), 7.28–7.21 (m, 1H), 3.75 (s, 3H), 2.46 (s, 3H), 2.29 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.6, 140.9, 138.6, 129.3, 127.4, 124.9, 121.9, 121.8, 114.2, 30.0, 15.4, 14.0; **HRMS** (ESI^+) m/z: [M + H] calcd for $C_{12}H_{14}NO^+$ 188.1070; found 188.1070.

5-Methyl-1,2,3,5-tetrahydro-4H-cyclopenta[c]quinolin-4-one (10u)



Prepared using general Procedure **C** using oxamic acid **7a** (0.138 g, 0.770 mmol), cyclopent-1-ene-1-carboxylic acid (0.259 g, 2.31 mmol), $AgNO_3$ (0.650 g, 0.385 mmol) and $K_2S_2O_8$ (0.624 g, 2.31 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (10–20%) afforded **10u** as a colorless solid (0.070 g, 45% yield). $\mathbf{R_f}$ = 0.43 (3:7 EtOAc:Petroleum ether); **M.P.** 116–118 °C; **IR** (film, vmax/cm^{-1}) 2954, 1642, 1619, 1588, 1451, 1400, 1310, 1200, 1036, 758, 416; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.57–7.50 (m, 2H), 7.40–7.35 (m, 1H), 7.28–7.21 (m, 1H), 3.74 (s, 3H), 3.14 (t, *J* = 7.5 Hz, 2H), 2.99 (t, *J* = 7.5 Hz, 2H), 2.19 (p, *J* = 7.5 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.2, 150.2, 140.1, 133.4, 129.6, 125.5, 122.0, 119.8, 114.6, 32.3, 31.5, 29.4, 22.8; **HRMS** (ESI^+) m/z: [M + H] calcd for $C_{13}H_{14}NO^+$ 200.1070; found 200.1080.

5-Methyl-7,8,9,10-tetrahydrophenanthridin-6(5H)-one (10v)

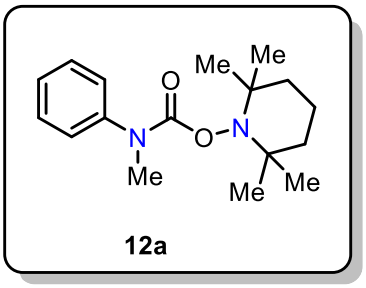


10v

Prepared using general Procedure **C** using oxamic acid **7a** (0.145 g, 0.809 mmol), cyclohex–1–ene–1–carboxylic acid (0.306 g, 2.43 mmol), $AgNO_3$ (0.067 g, 0.404 mmol) and $K_2S_2O_8$ (0.657 g, 2.43 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (5–10%) afforded **10v** as colorless solid (0.101 g, 59% yield).

Prepared using general Procedure **D** using oxamic acid **7a** (0.101 g, 0.56 mmol), cyclohex–1–ene–1–carboxylic acid (0.213 g, 1.69 mmol), $AgNO_3$ (0.048 g, 0.282 mmol), 4-CzIPN (0.009 g, 0.011 mmol) and $K_2S_2O_8$ (0.457 g, 1.69 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (5– 10%) afforded **10v** as colorless solid (0.069 g, 57% yield); **M.P.** 90–91 °C; $\mathbf{R_f}$ = 0.53 (3:7 EtOAc:Petroleum ether); **IR** (film, vmax/cm^{-1}) 2931, 1634, 1589, 1456, 1311, 1091, 956, 752, 587, 515; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 6.6 Hz, 1H), 7.67 (t, *J* = 8.5 Hz, 1H), 7.52 (d, *J* = 9.7 Hz, 1H), 7.40 (t, *J* = 7.0 Hz, 1H), 3.91 (s, 3H), 3.03 (t, *J* = 6.1 Hz, 2H), 2.83 (t, *J* = 6.1 Hz, 2H), 2.08–1.91 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.3, 141.8, 138.1, 129.0, 128.6, 123.6, 121.8, 121.3, 114.1, 29.7, 29.6, 29.6, 25.5, 24.7, 22.0; **HRMS** (ESI^+) m/z: [M + H] calcd for $C_{14}H_{16}NO^+$ 214.1226; found 214.1233

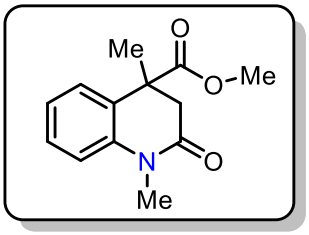
2,2,6,6-tetramethylpiperidin-1-yl methyl(phenyl)carbamate (12a)



12a

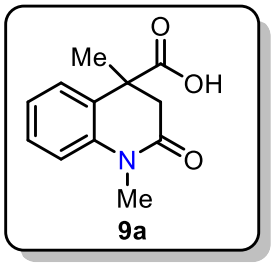
Prepared using general Procedure **D** using oxamic acid **7a** (0.100 g, 0.56 mmol), TEMPO (0.131 g, 0.837 mmol), $AgNO_3$ (0.047 g, 0.28 mmol), 4-CzIPN (0.009 g, 0.011 mmol) and $K_2S_2O_8$ (0.457 g, 1.67 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (5–10%) afforded **12a** as yellow oil (0.103 g, 67% yield). $\mathbf{R_f}$ = 0.67 (3:7 EtOAc:Petroleum ether); **IR** (film, vmax/cm^{-1}), 2394, 1730,1594, 1500, 1460, 1412, 1255, 1291, 957, 700, 555 **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.7 Hz, 2H), 7.24 (s, 3H), 3.31 (s, 3H), 1.69–1.29 (m, 6H), 1.11 (s, 6H), 0.84 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.7, 143.5, 129.0, 126.6, 126.5, 60.2, 39.0, 31.8, 20.7, 17.0; **HRMS** (ESI^+) m/z: [M + H] calcd for $C_{17}H_{27}N_2O_2^+$ 291.2076; found 291.2075.

Methyl 1,4-dimethyl-2-oxo-1,2,3,4-tetrahydroquinoline-4-carboxylate (13)[9]



Prepared using general Procedure **D** using oxamic acid **7a** (0.100 g, 0.56 mmol), methyl methacrylate (0.167 g, 0.178 mmol), $AgNO_3$ (0.047 g, 0.28 mmol), 4-CzIPN (0.009 g, 0.011 mmol) and $K_2S_2O_8$ (0.457 g, 1.67 mmol). Chromatography on silica gel with EtOAc/Petroleum ether (5–10%) afforded **13** as yellow solid (0.052 g, 40% yield). $\mathbf{R_f}$ = 0.43 (3:7 EtOAc:Petroleum ether); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.36–7.26 (m, 2H), 7.09 (td, *J* = 7.7, 1.2 Hz, 1H), 7.01 (d, *J* = 9.3 Hz, 1H), 3.68 (s, 3H), 3.36 (s, 3H), 3.14 (d, *J* = 15.9 Hz, 1H), 2.56 (d, *J* = 15.9 Hz, 1H), 1.60 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4, 168.4, 139.8, 128.8, 126.1, 123.40, 115.3, 52.9, 44.7, 41.7, 29.6, 23.4.

1,4-dimethyl-2-oxo-1,2,3,4-tetrahydroquinoline-4-carboxylic acid (9a)



Prepared according to general procedure **B** using **13** (0.180 g, 0.772 mmol), potassium hydroxide (0.052 g, 0.93 mL) in THF (15 mL) to afford the commercially available 1,4-dimethyl-2-oxo-1,2,3,4-tetrahydroquinoline-4-carboxylic acid **(9a)** as a colorless solid (0.147 g, 87 % yield). $\mathbf{R_f}$ = 0.18 (1:4 MeOH:DCM) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.05 (s, 1H), 7.27 (dq, *J* = 16.4, 7.6 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 3.68 (s, 3H), 3.09 (d, *J* = 16.2 Hz, 1H), 2.55 (d, *J* = 16.2 Hz, 1H), 1.63 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 178.6, 171.7, 136.1, 129.1, 126.6, 125.3, 124.3, 116.7, 44.8, 40.5, 23.31, 21.0.

16. References

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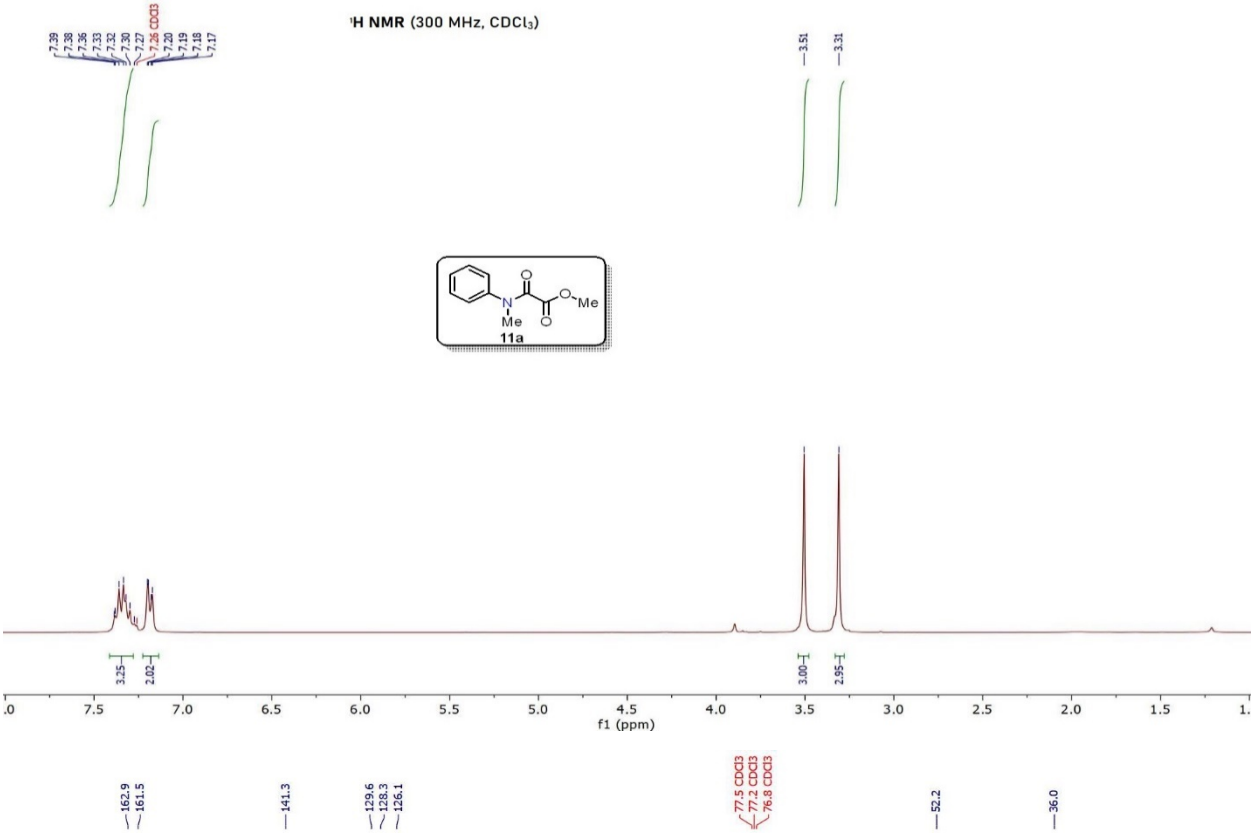
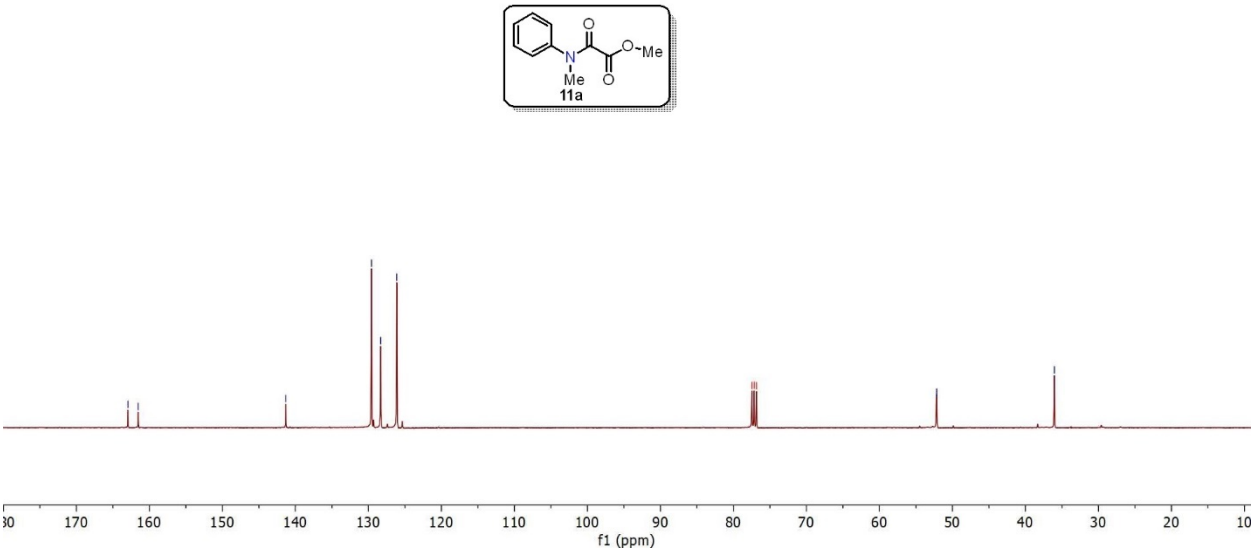
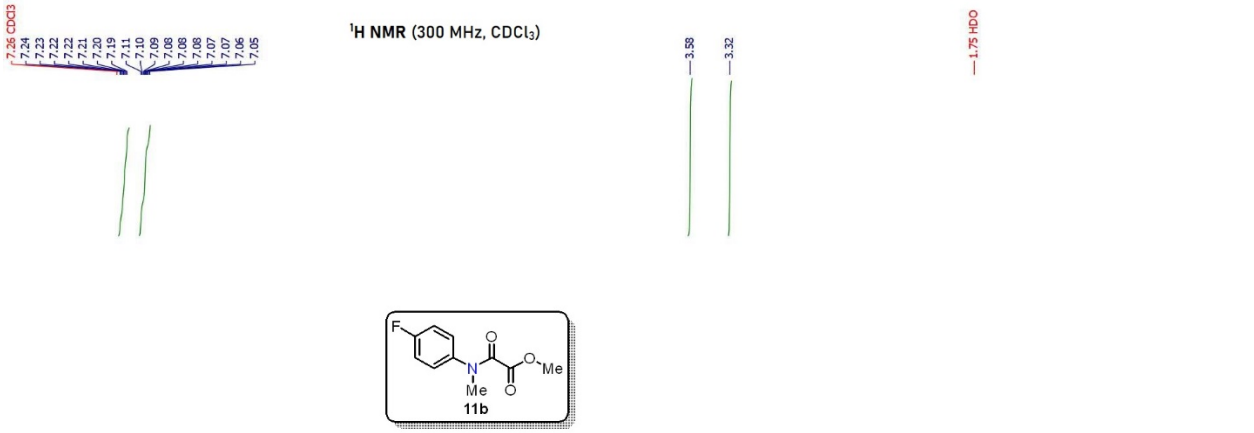
17. NMR SPECTRA



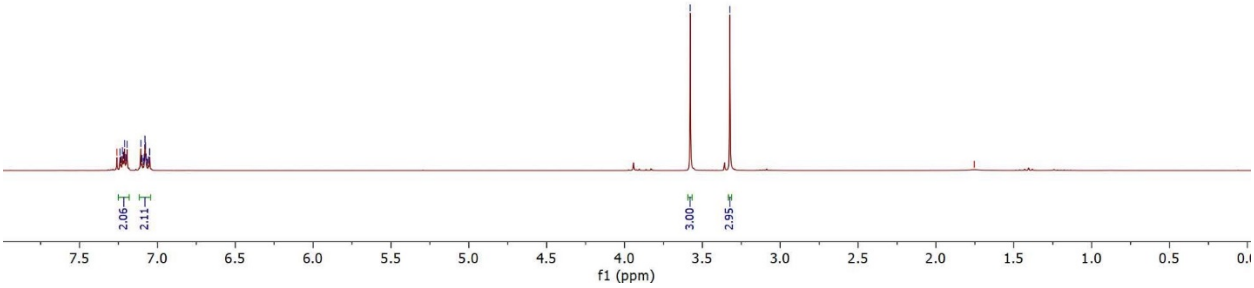
^{13}C NMR (101 MHz, $CDCl_3$)



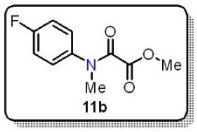


^{1}H NMR (300 MHz, $CDCl_3$)

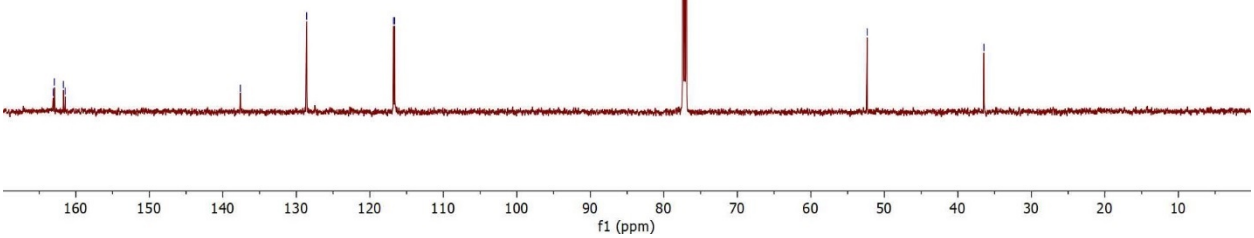
11b

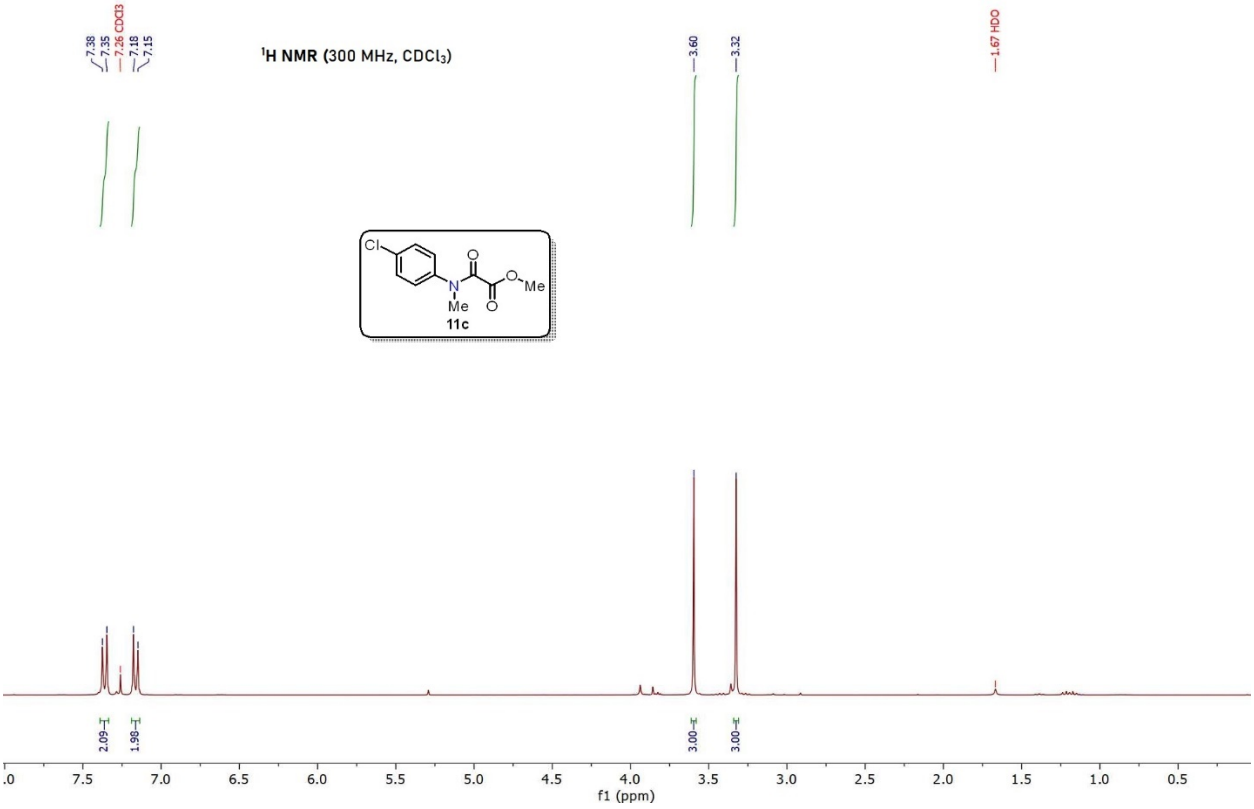


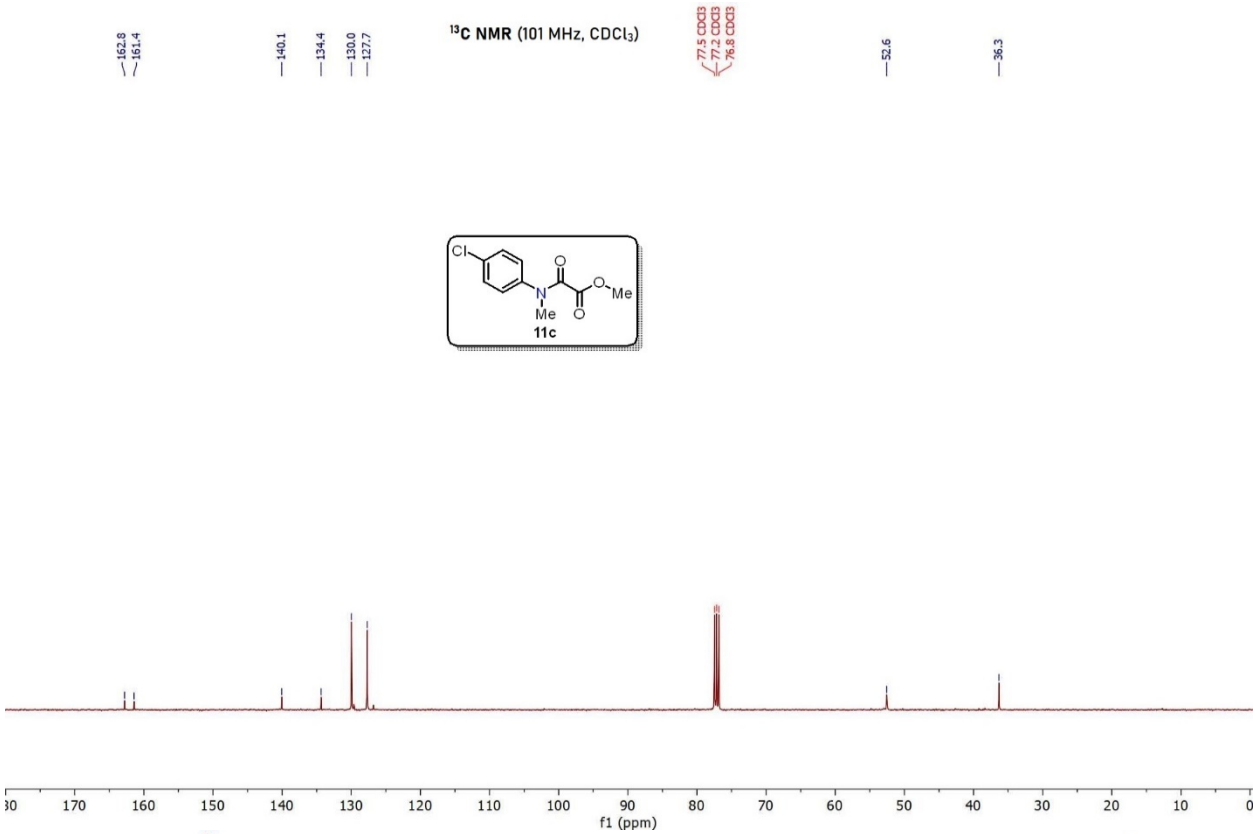
^{13}C NMR (151 MHz, $CDCl_3$)

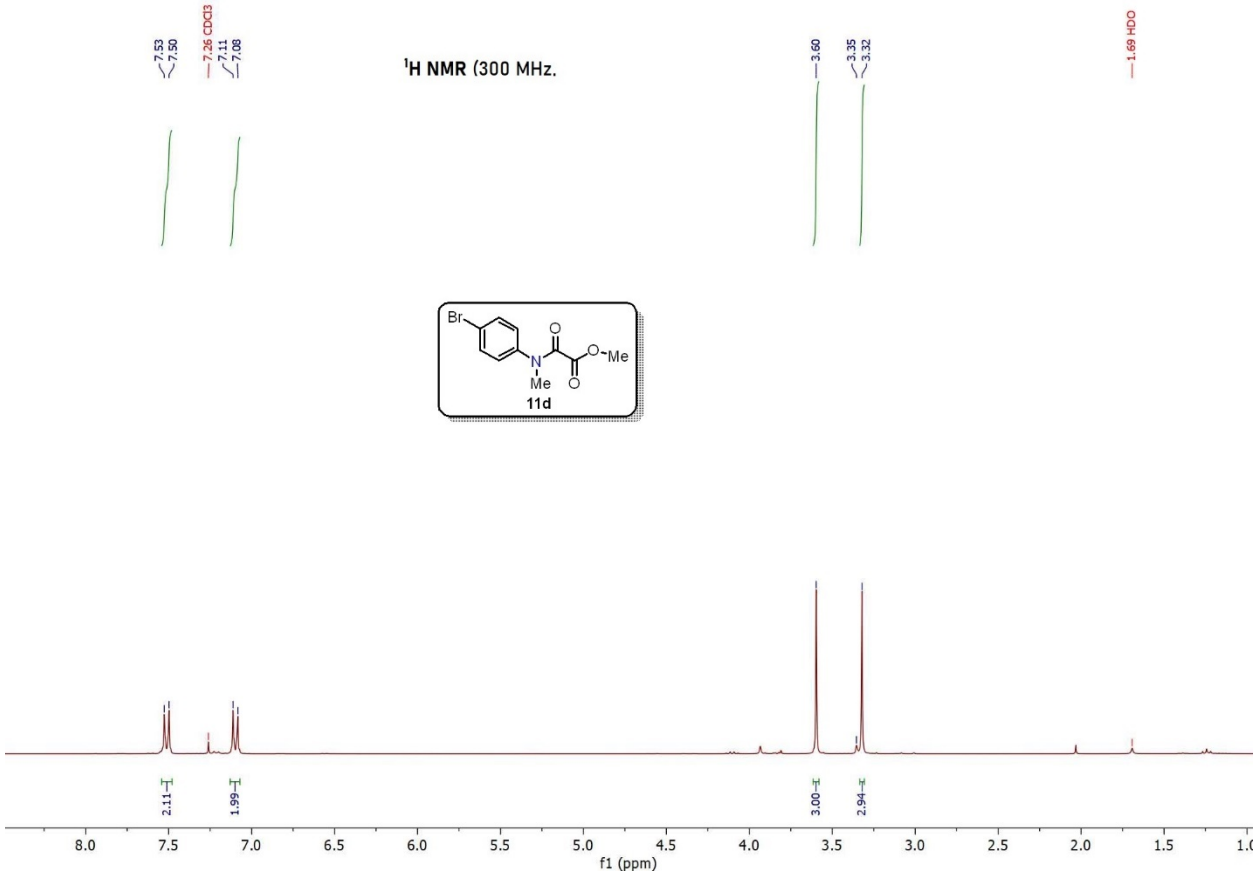


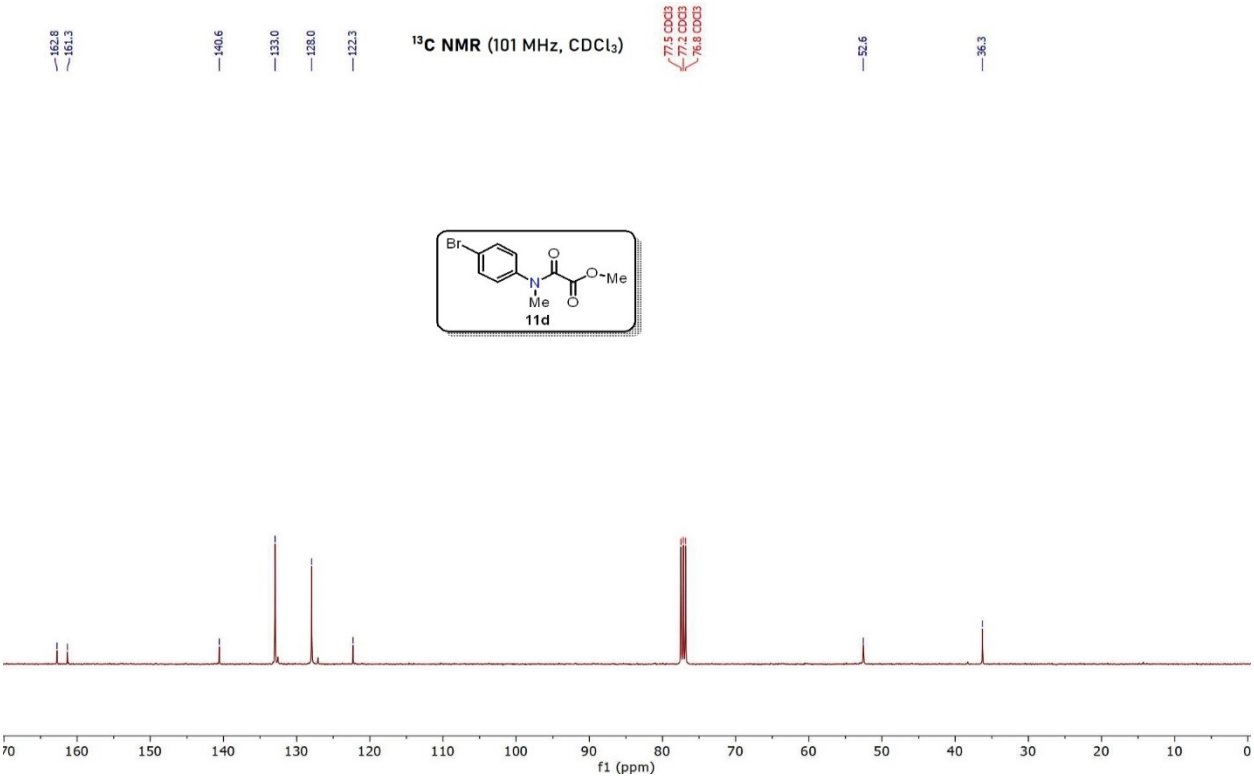
11b

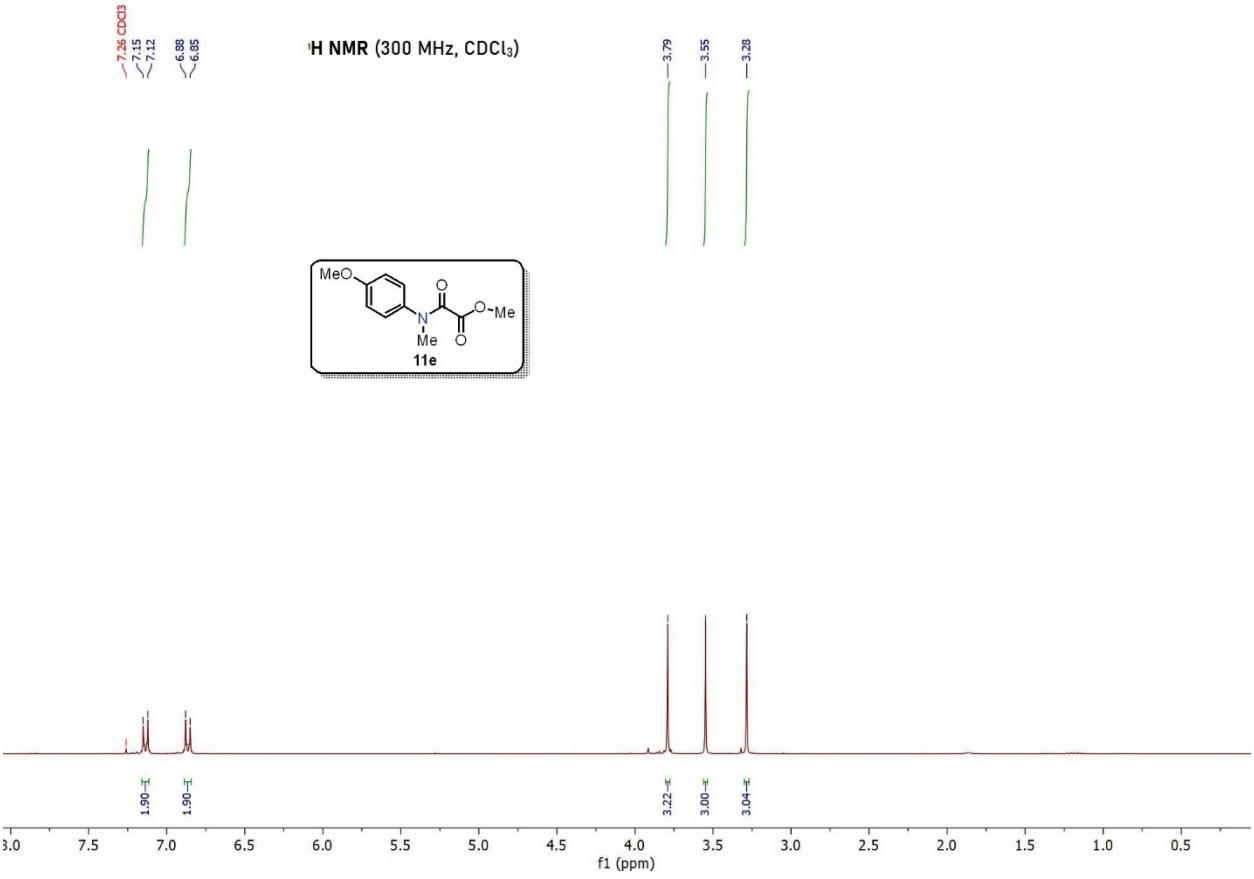


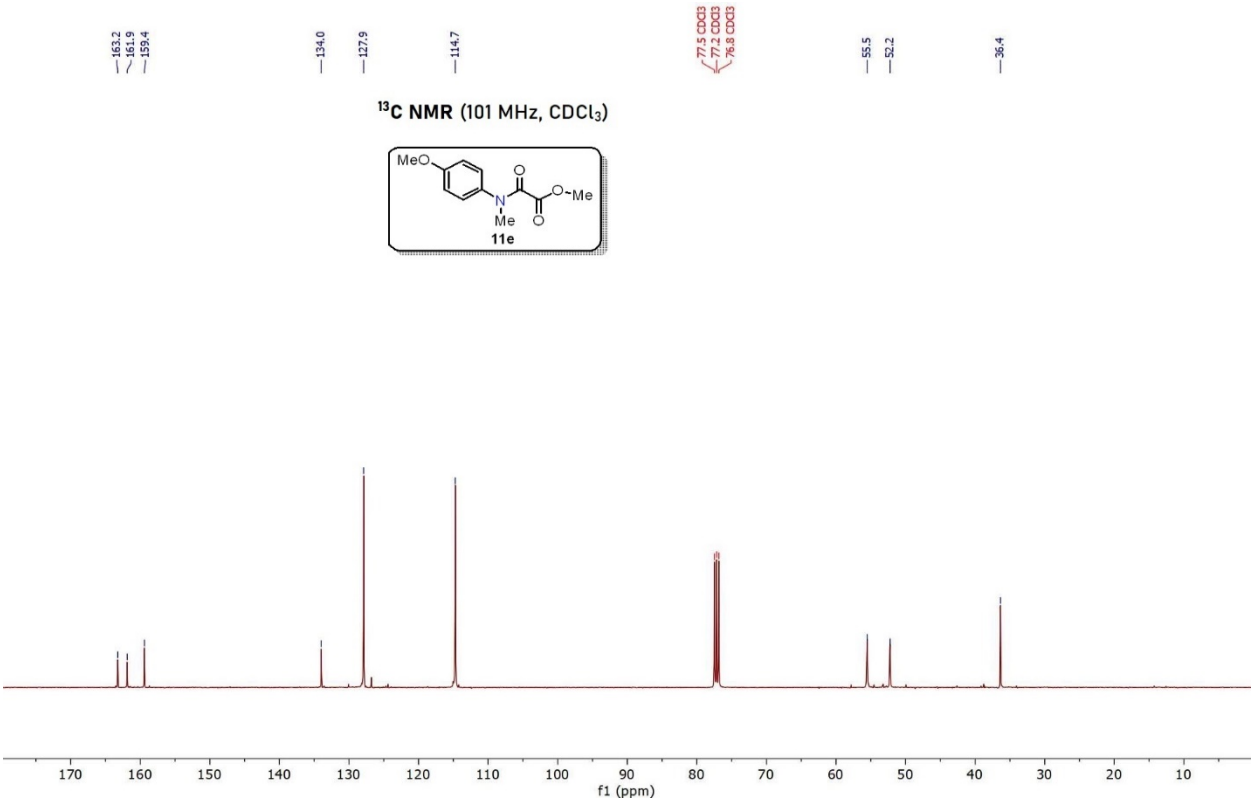

7.38
7.35
7.26 CDCl3
7.18
7.15
1H NMR (300 MHz, CDCl3)
3.60
3.32
1.67 HDO
Cl
O
N
Me
O
O
Me
11c
2.09
1.90
3.00
3.00
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

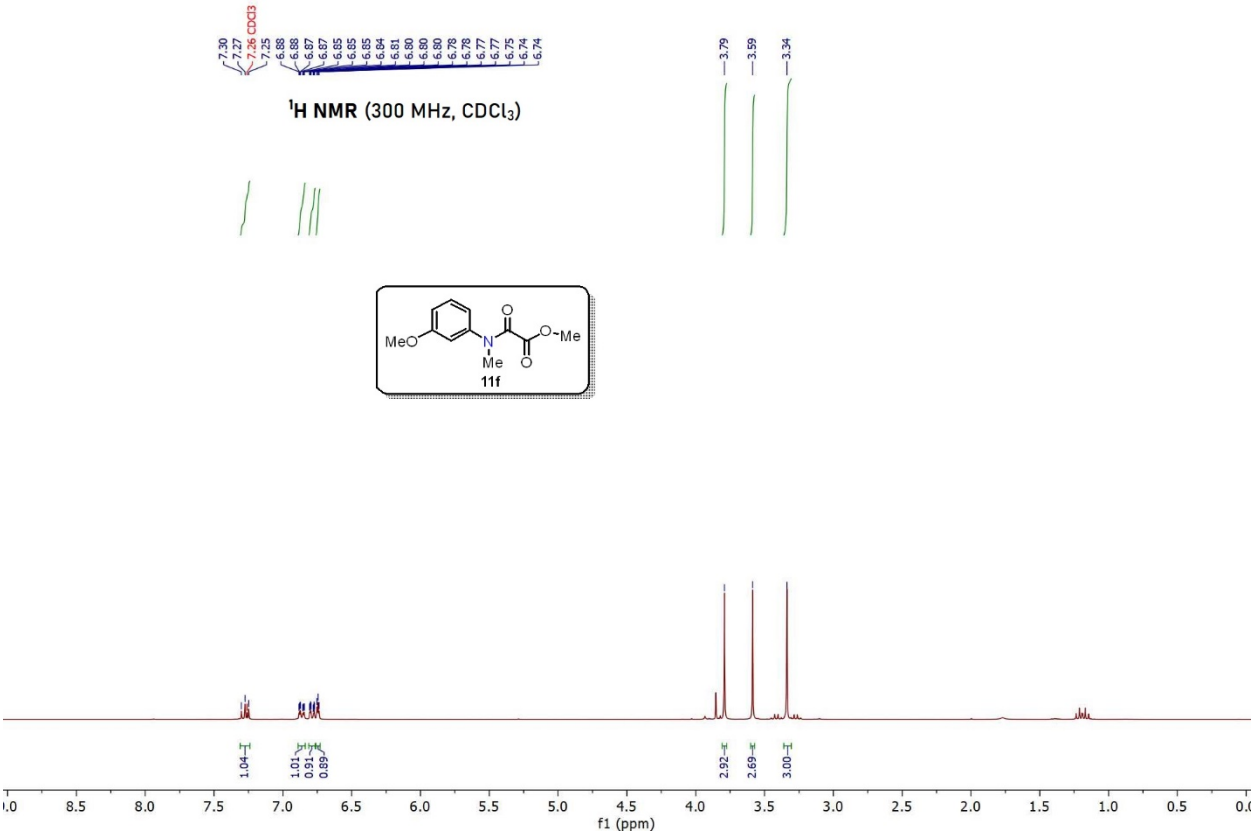

162.8
161.4
140.1
134.4
130.0
127.7
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
52.6
36.3
13C NMR (101 MHz, CDCl3)
Cl
N
Me
O
O
O
Me
Me
11c
f1 (ppm)


7.53
7.50
7.26 CDCl3
7.11
7.08
3.60
3.35
3.32
1.69 HDO
1H NMR (300 MHz.
Br
N
Me
O
O
O
Me
Me
11d
2.11
1.99
3.00
2.94
f1 (ppm)

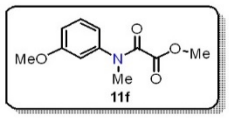

162.8
161.3
140.6
133.0
128.0
122.3
13C NMR (101 MHz, CDCl3)
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
52.6
36.3
Br
N
Me
O
O
O
Me
11d
f1 (ppm)

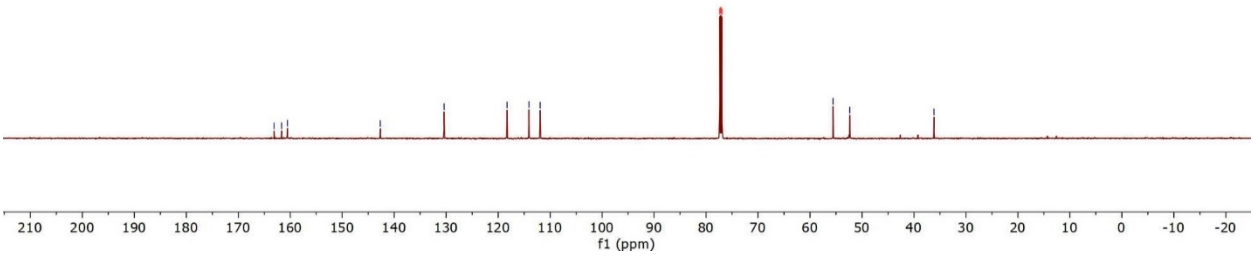

7.26 CDCl3
7.15
7.12
6.88
6.85
1H NMR (300 MHz, CDCl3)
3.79
3.55
3.28
MeO
N
Me
O
O
O
Me
11e
1.90
1.90
3.22
3.00
3.04
f1 (ppm)


163.2
161.9
159.4
134.0
127.9
114.7
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
55.5
52.2
36.4
13C NMR (101 MHz, CDCl3)
MeO
N
Me
O
O
O
Me
11e
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

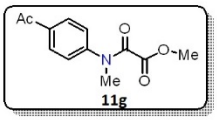

7.30
7.27
7.26 CDCl3
7.25
6.88
6.87
6.85
6.84
6.81
6.80
6.78
6.77
6.75
6.74
3.79
3.59
3.34
1H NMR (300 MHz, CDCl3)
MeO
N
Me
O
O
O
Me
11f
1.04
1.01
0.91
0.89
2.92
2.69
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

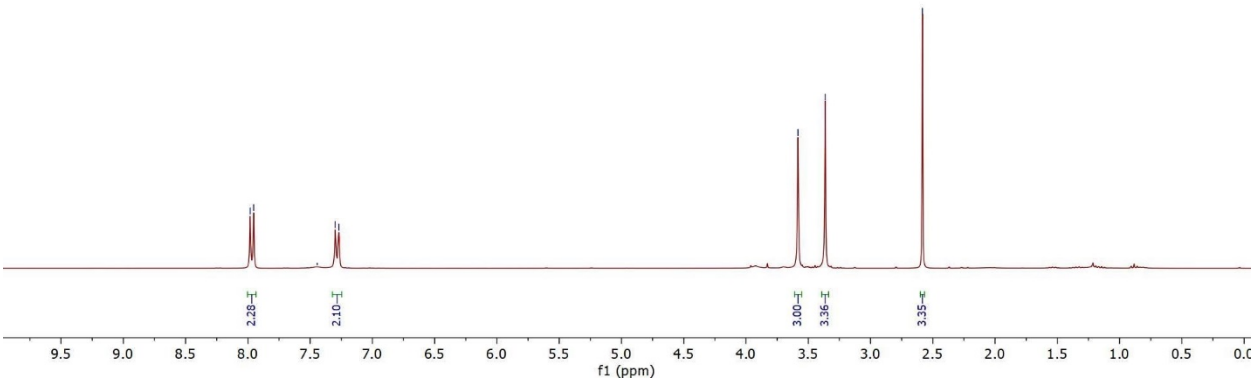
^{13}C NMR (151 MHz, $CDCl_3$)

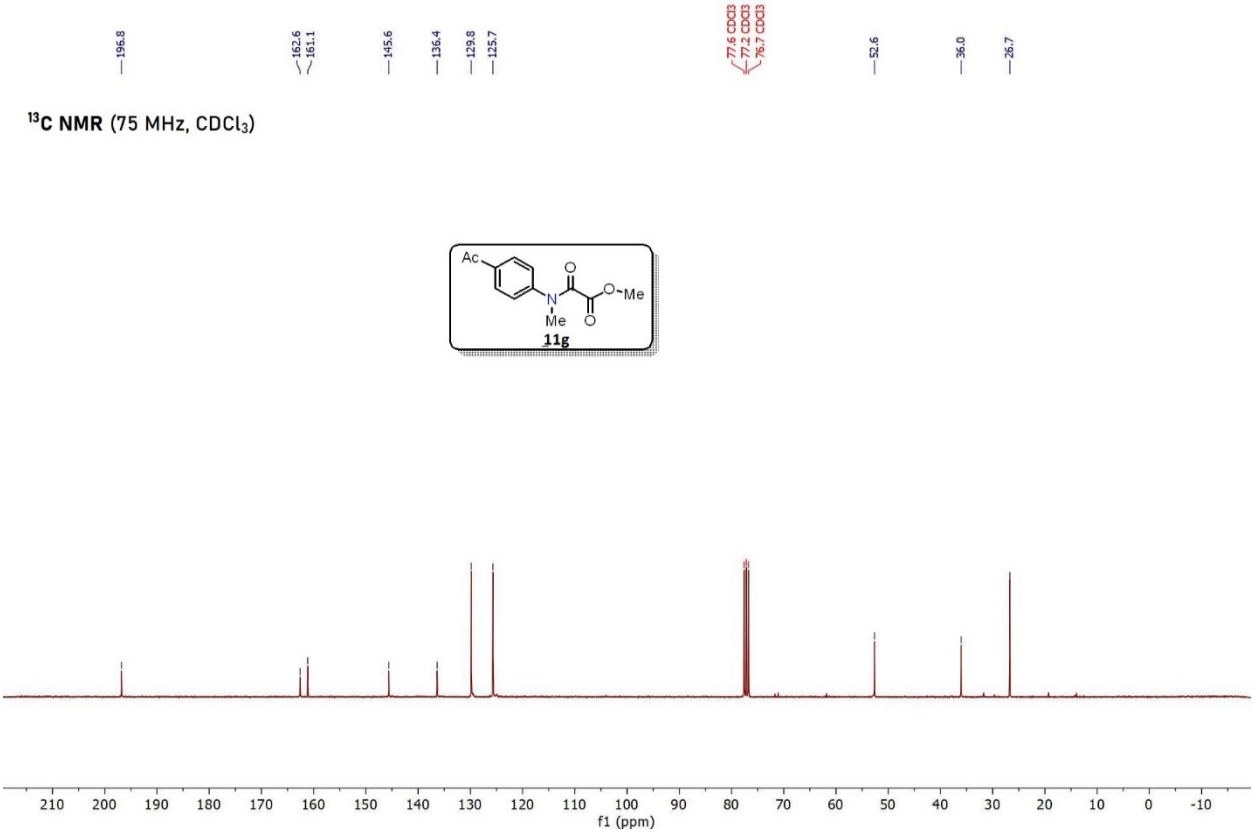


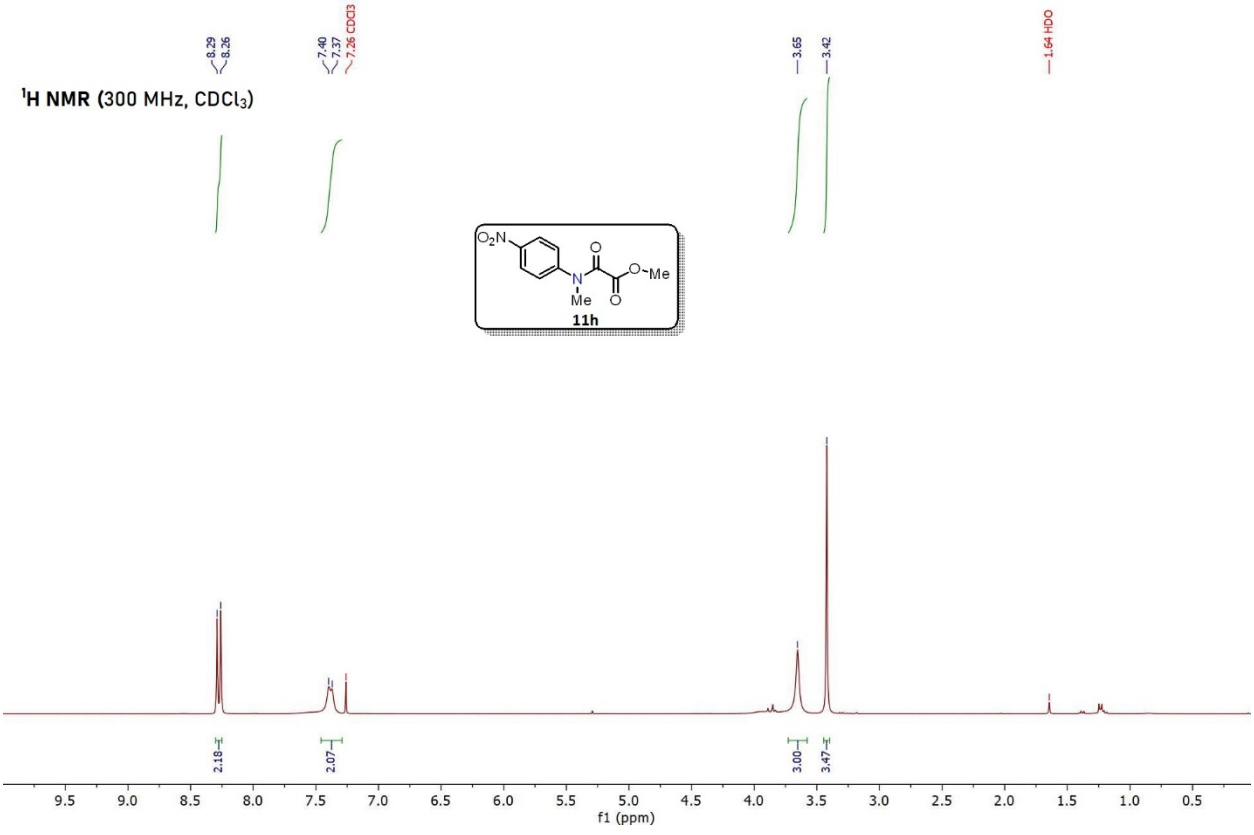


^{1}H NMR (300 MHz, $CDCl_3$)

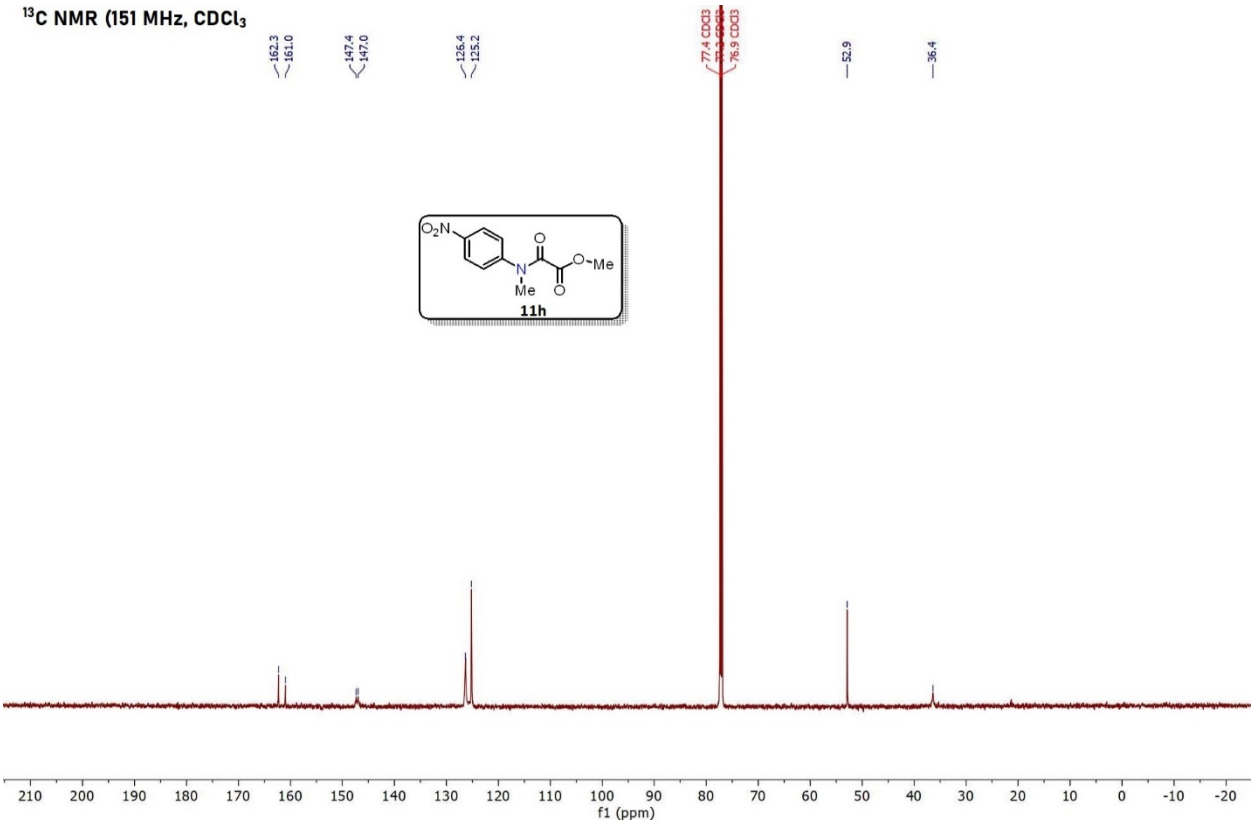




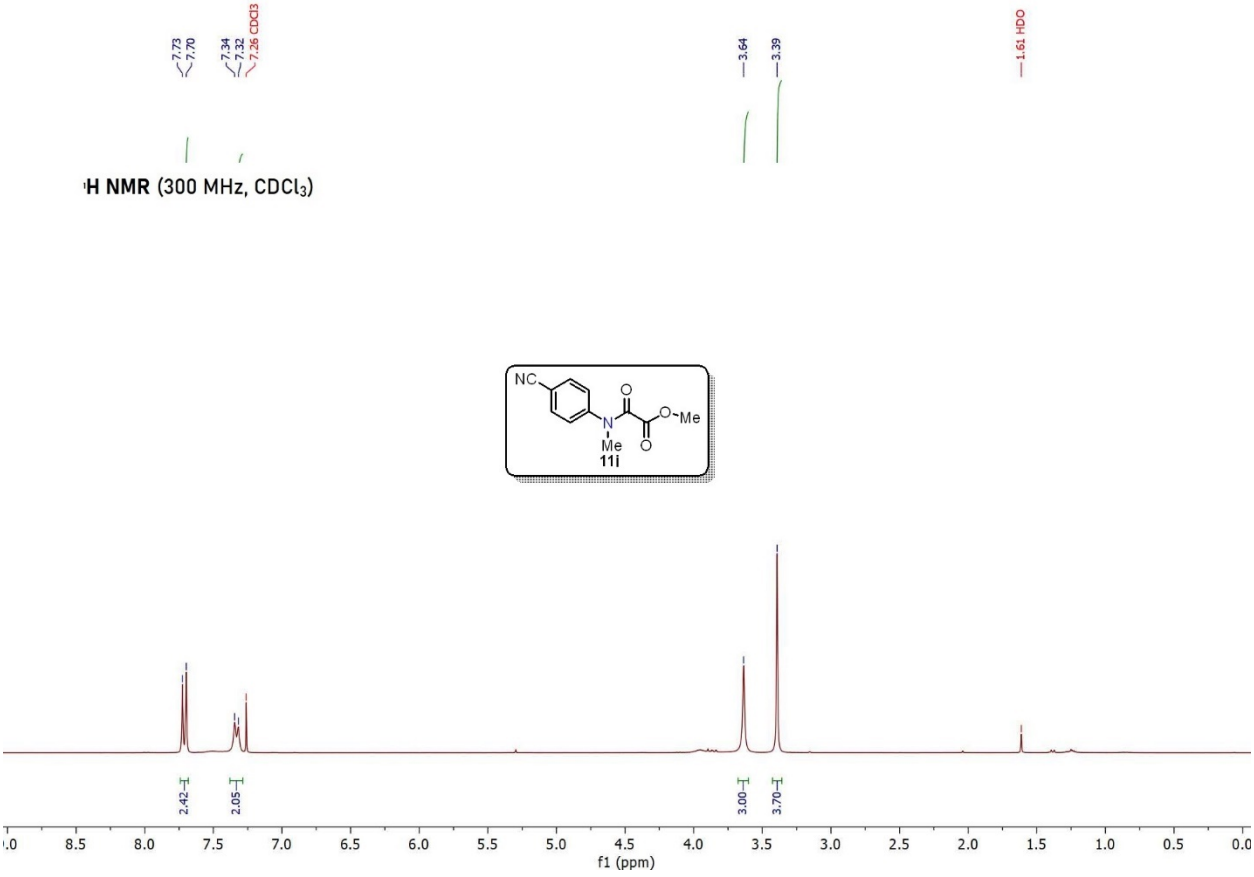

196.8
162.6
161.1
145.6
136.4
129.8
125.7
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
52.6
36.0
26.7
13C NMR (75 MHz, CDCl3)
Ac
O
N
Me
O
O
Me
11g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.29
8.26
7.40
7.37
7.26 CDCl3
3.65
3.42
1.64 HDO
1H NMR (300 MHz, CDCl3)
O2N
O
N
Me
O
O
Me
11h
2.18
2.07
3.00
3.47
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)

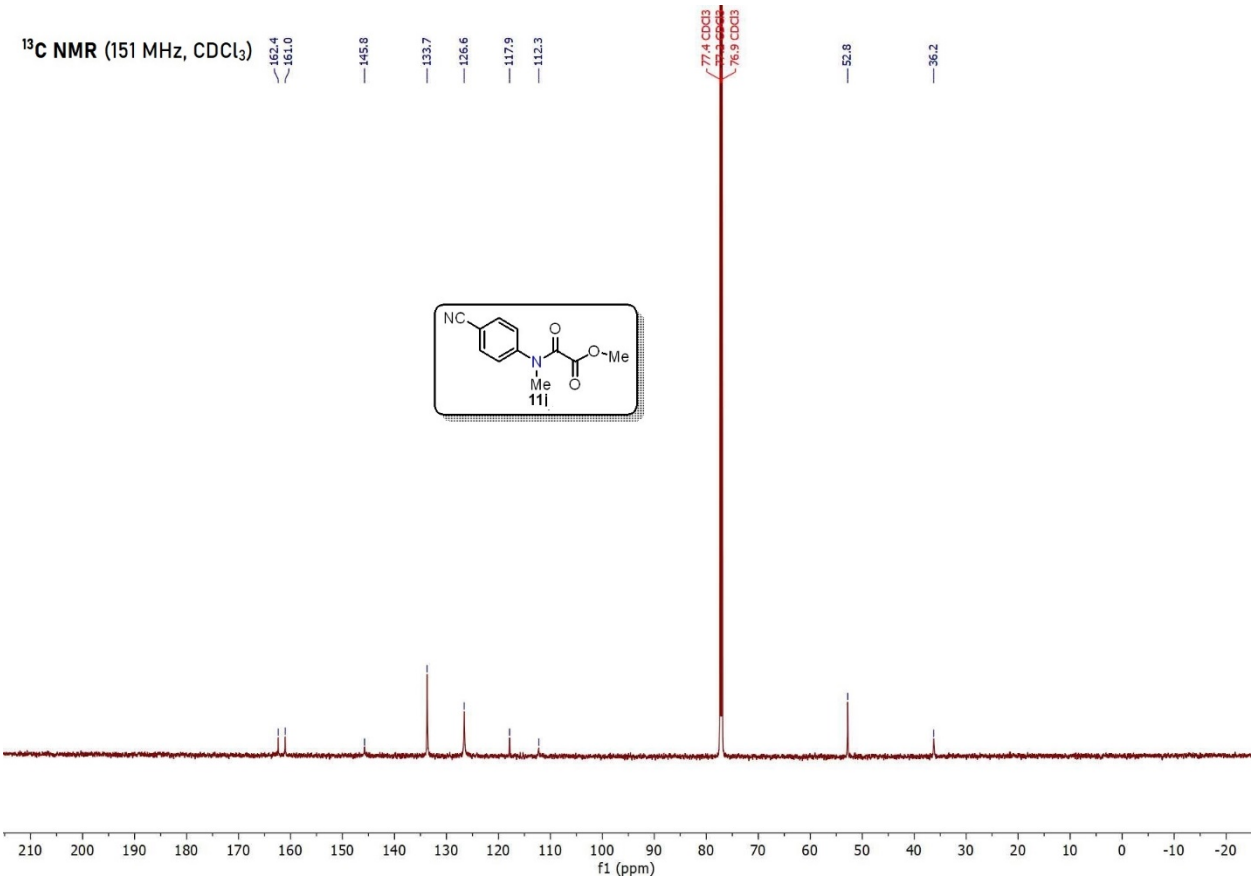
^{13}C NMR (151 MHz, $CDCl_3$)



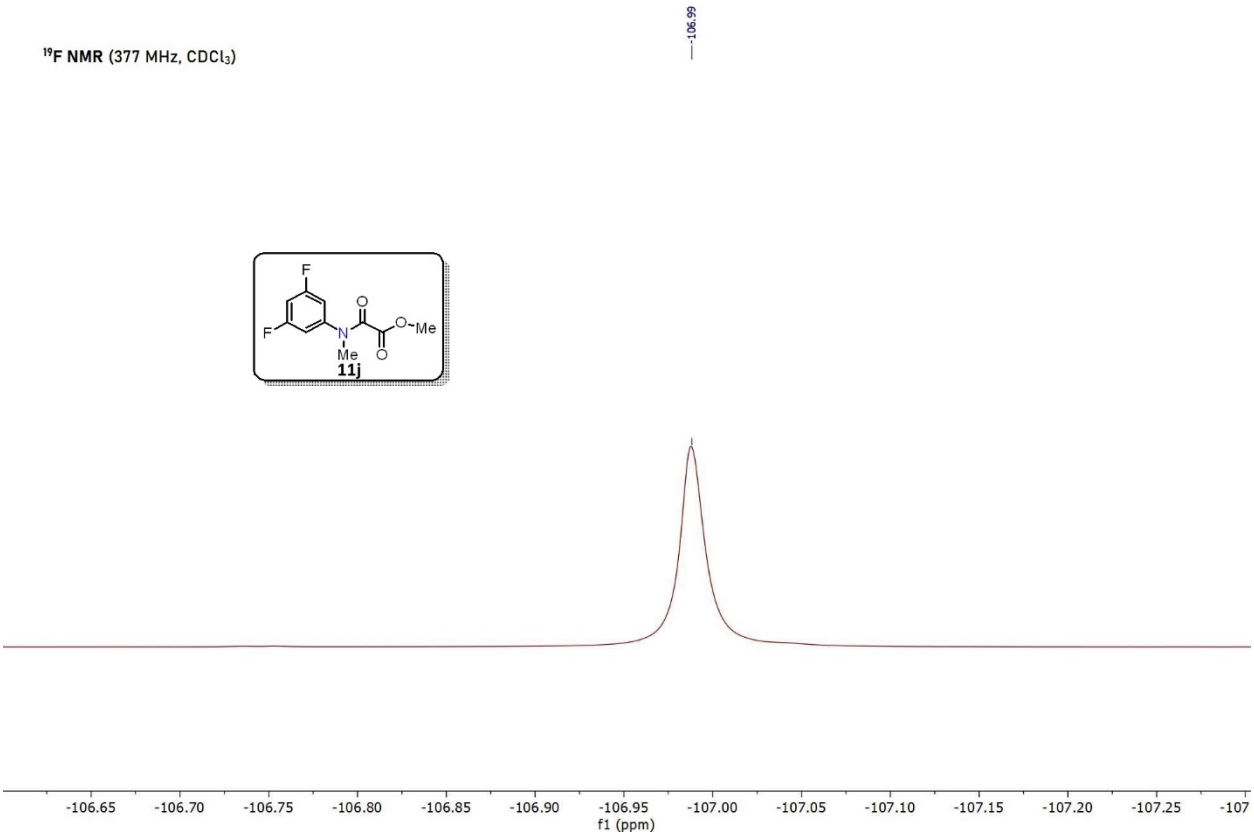
^{1}H NMR (300 MHz, $CDCl_3$)

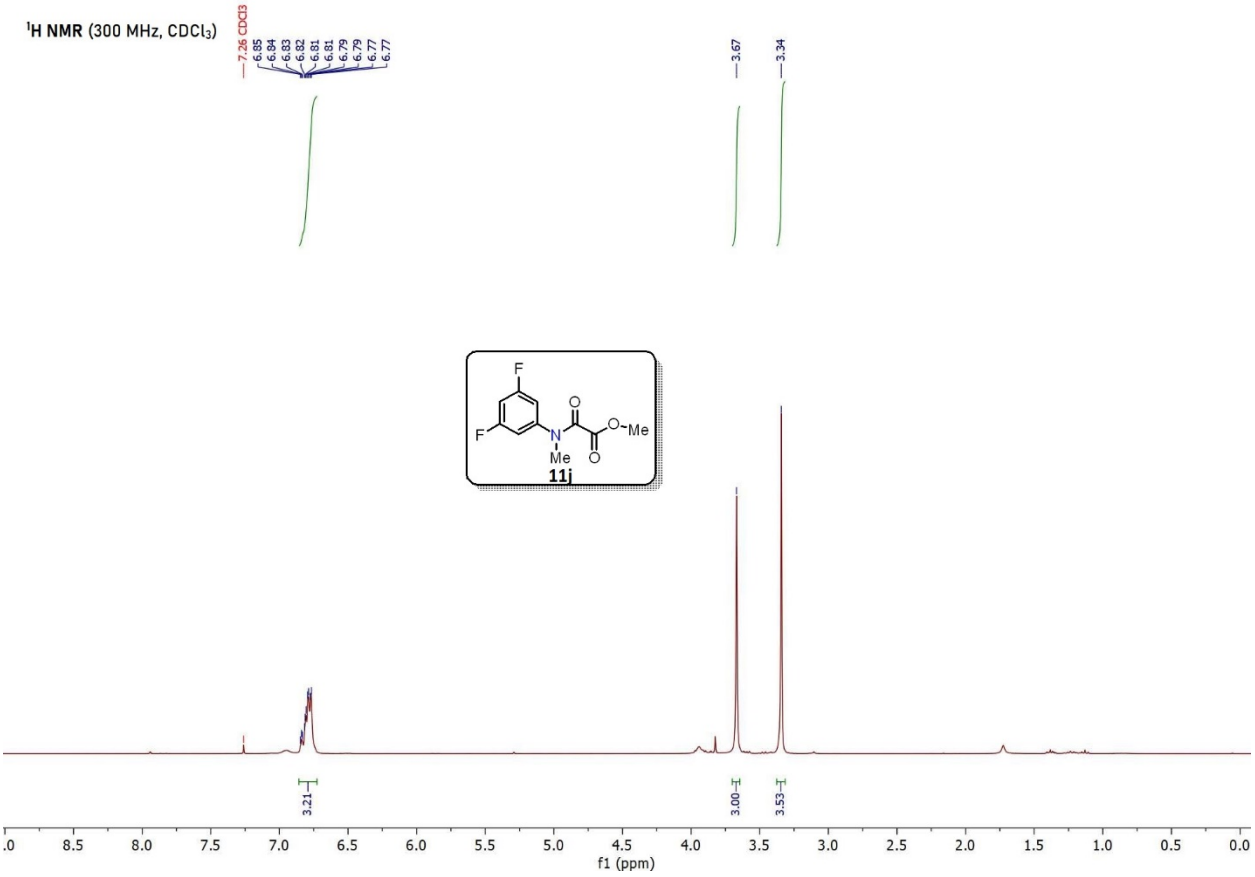


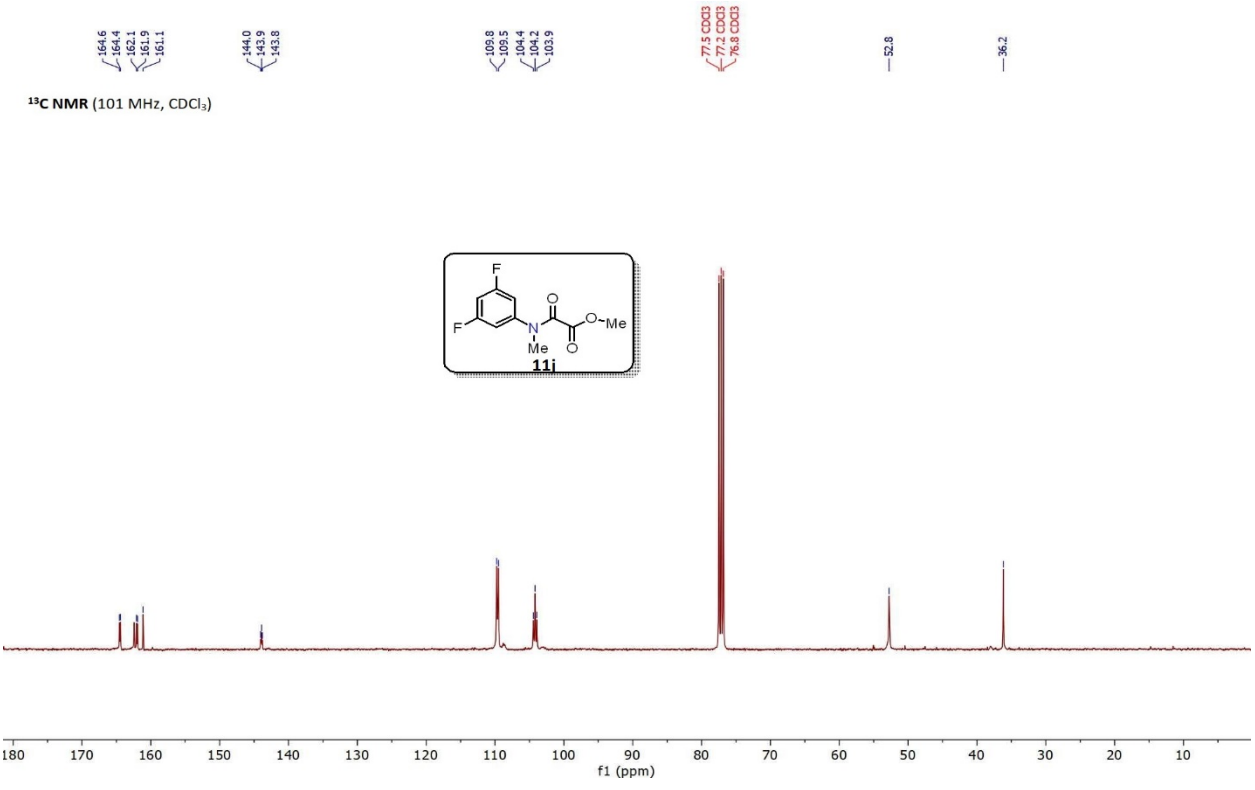
^{13}C NMR (151 MHz, $CDCl_3$)

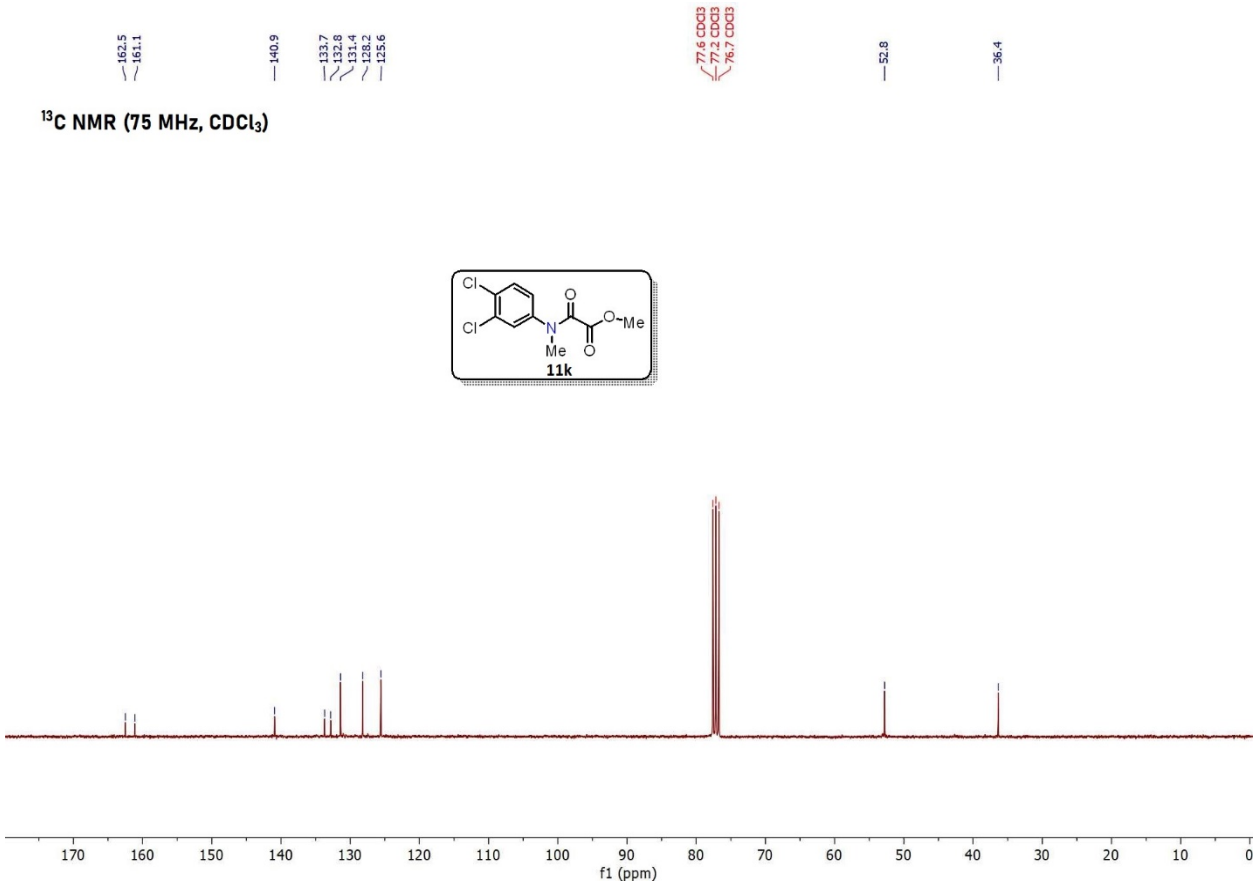


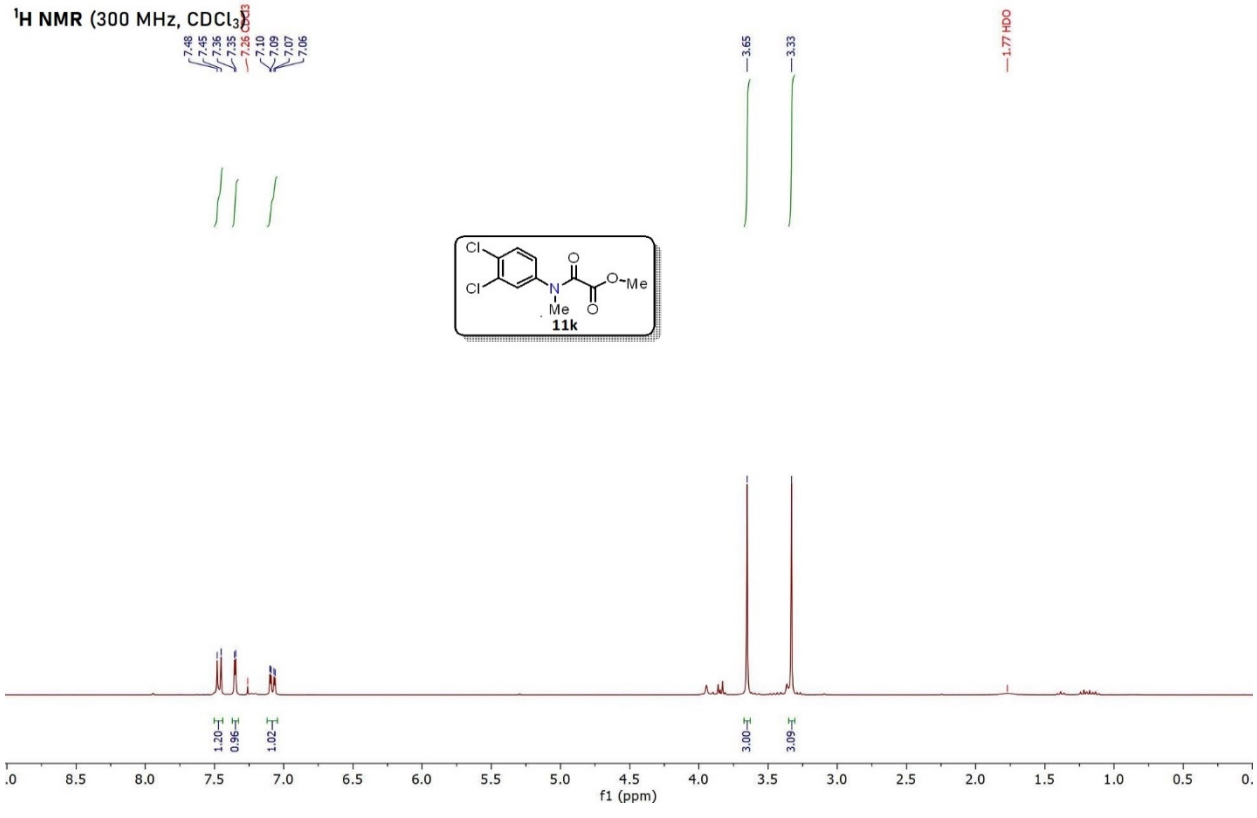
^{19}F NMR (377 MHz, $CDCl_3$)




¹H NMR (300 MHz, CDCl₃)
7.26 CDCl3
6.85
6.84
6.83
6.82
6.81
6.81
6.79
6.79
6.77
6.77
6.77
3.67
3.34
F
F
N
Me
O
O
O
Me
11j
3.21
3.00
3.53
f1 (ppm)


164.6
164.4
162.1
161.9
161.1
144.0
143.9
143.8
109.8
109.5
104.4
104.2
103.9
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
52.8
36.2
¹³C NMR (101 MHz, CDCl₃)
F
F
N
Me
O
O
O
Me
11j
f1 (ppm)


162.5
161.1
140.9
133.7
132.8
131.4
128.2
125.6
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
52.8
36.4
13C NMR (75 MHz, CDCl3)
Cl
Cl
N
Me
O
O
O
Me
11k
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


1H NMR (300 MHz, CDCl3)
7.48
7.45
7.36
7.35
7.26 CDCl3
7.10
7.09
7.07
7.06
3.65
3.33
1.77 HDO
Cl
Cl
N
Me
O
O
O
Me
11k
1.20
0.96
1.02
3.00
3.09
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)

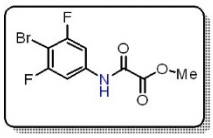
^{19}F NMR (377 MHz, $CDCl_3$)

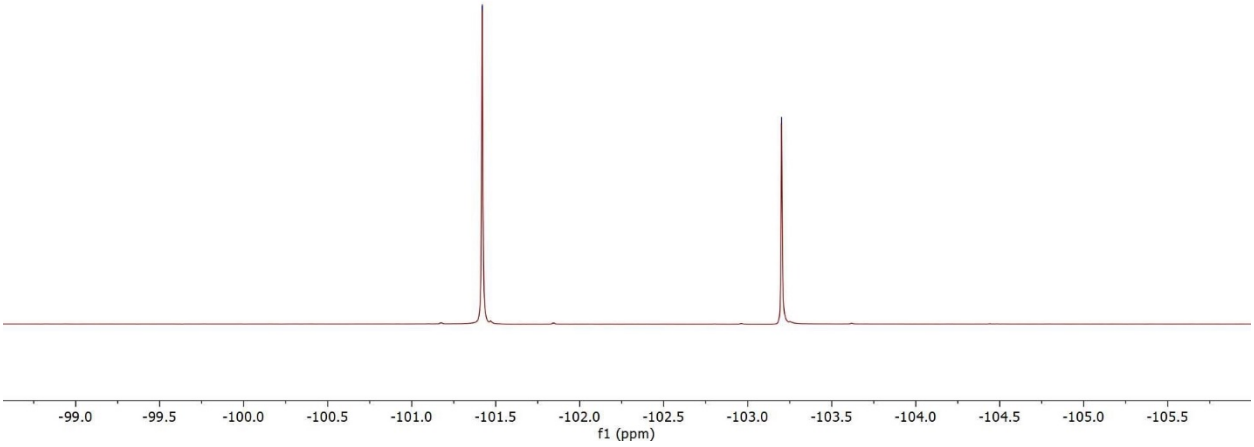
Tautomers

-101.42

-103.20

methyl 2-((4-bromo-3,5-difluorophenyl)amino)-2-oxoacetate





8.99

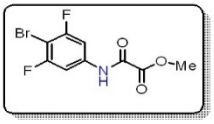
7.40
7.38
7.26 CDCl3
6.95
6.93

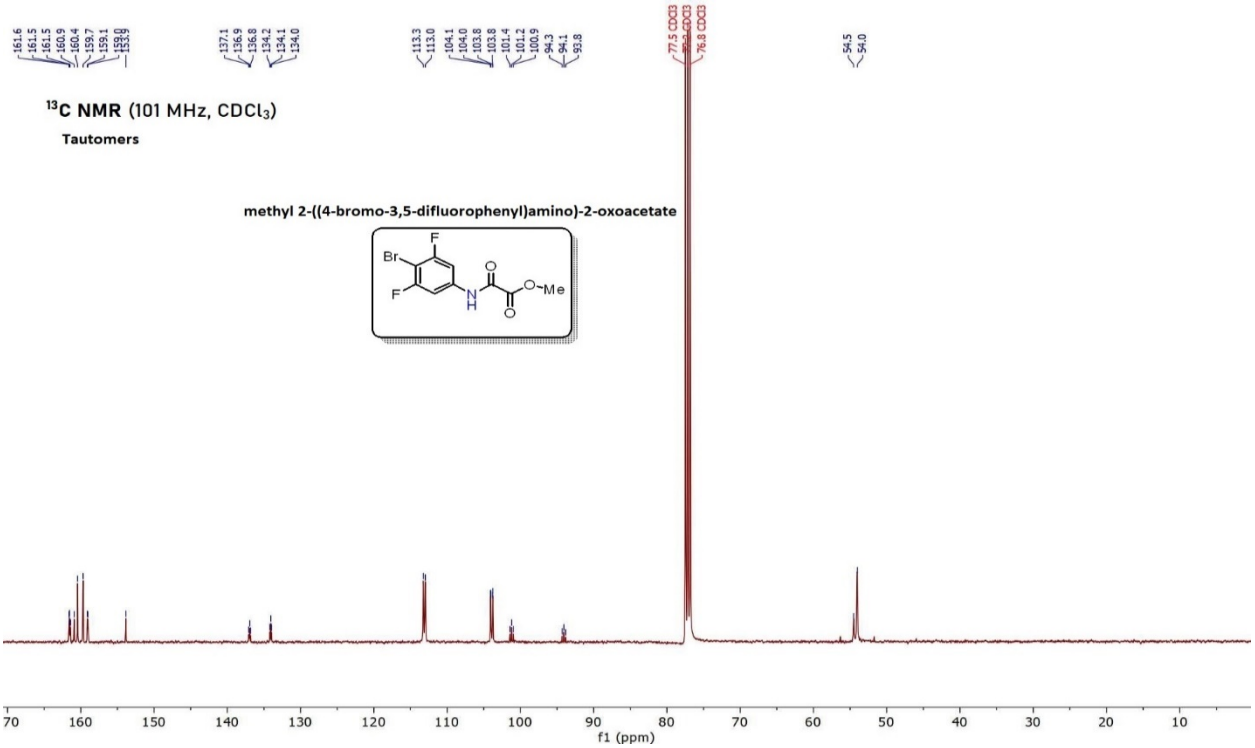
3.98
3.87

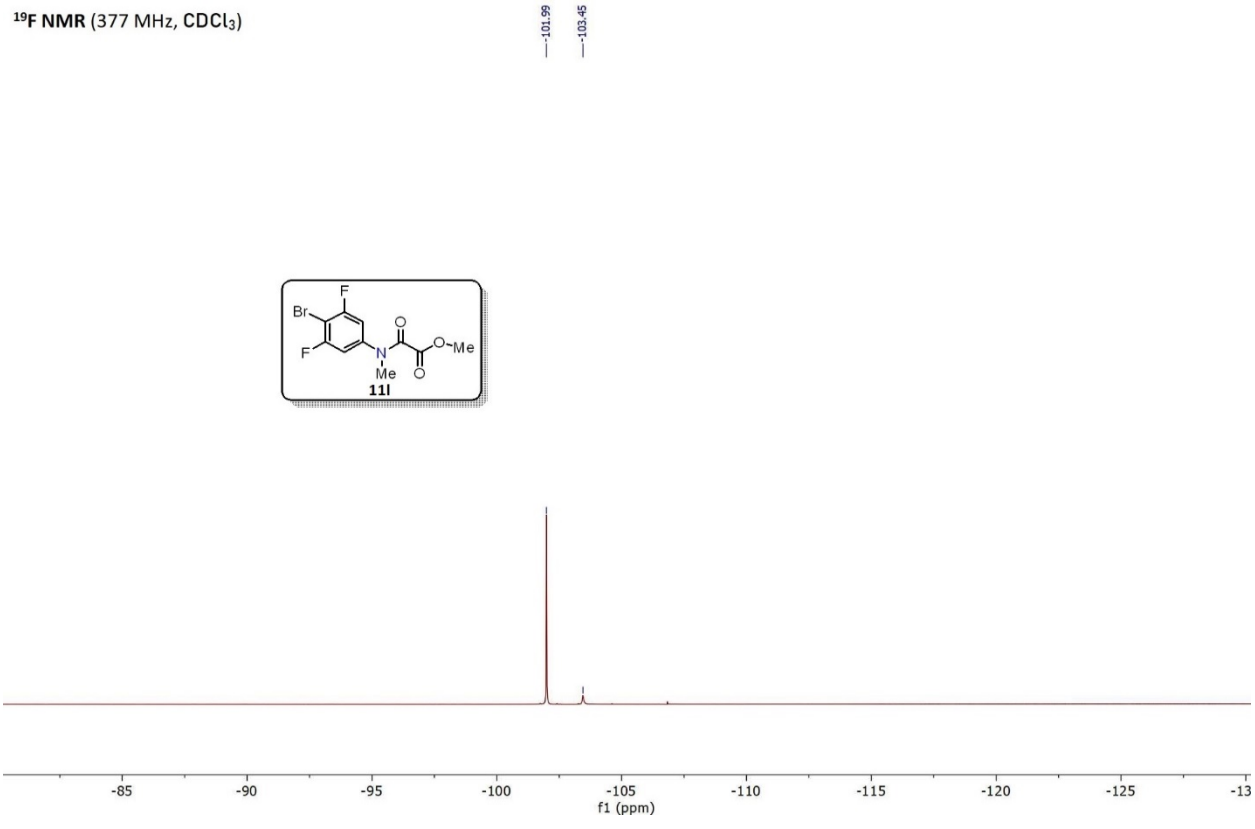
^{1}H NMR (300 MHz, $CDCl_3$)

Tautomers

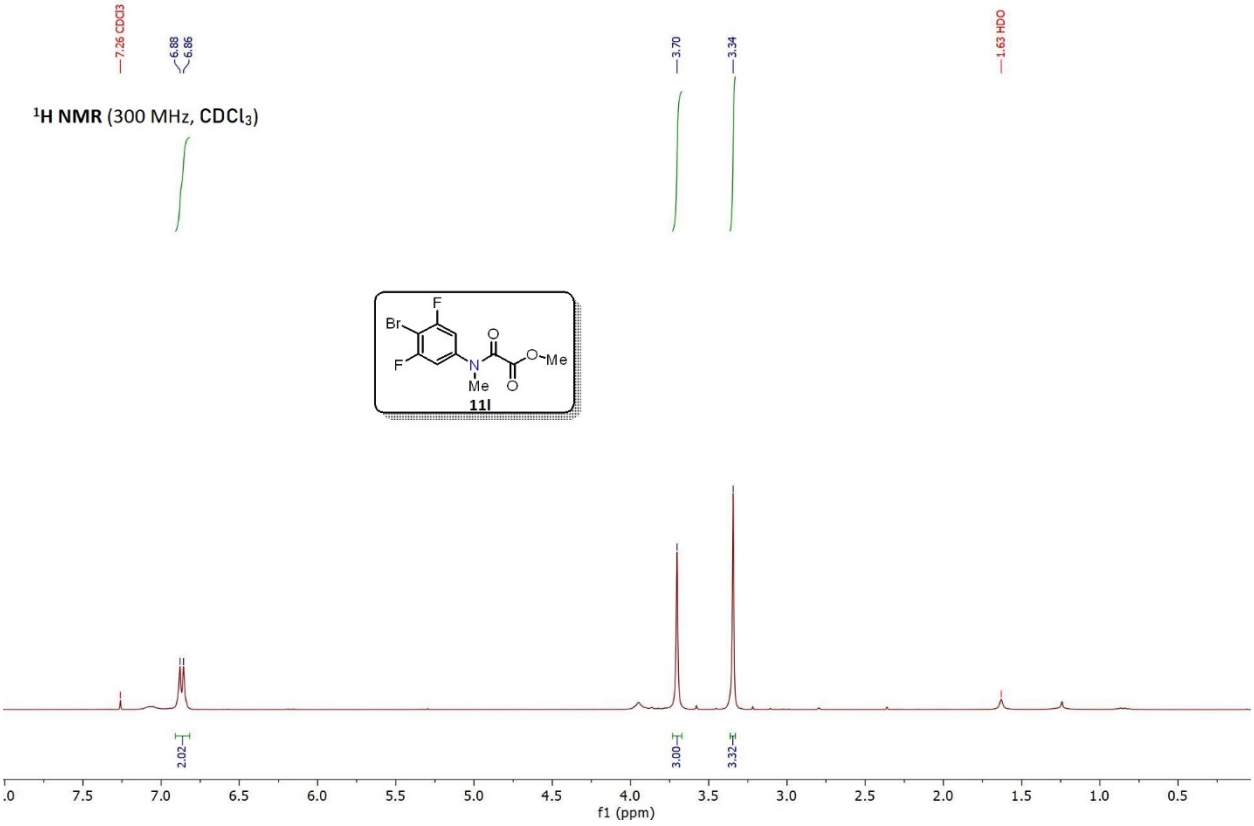
methyl 2-((4-bromo-3,5-difluorophenyl)amino)-2-oxoacetate



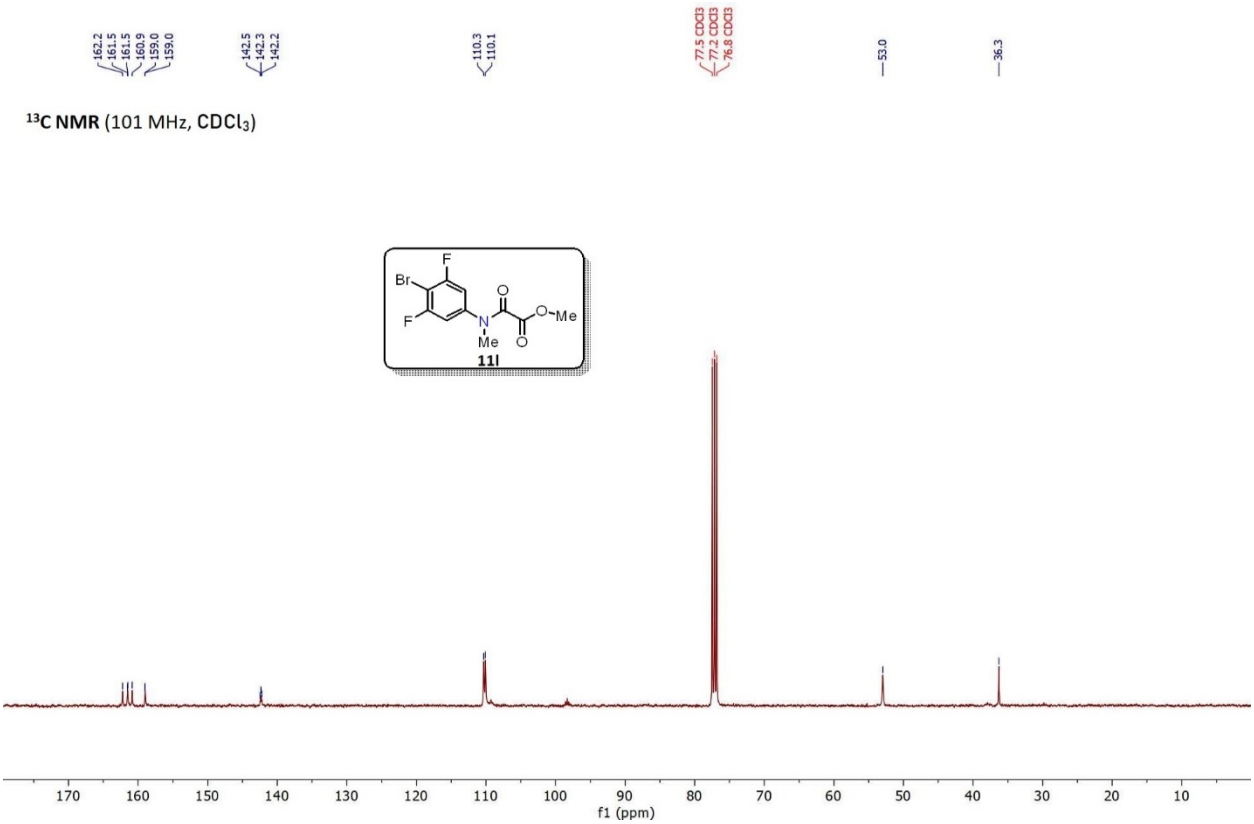

161.6
161.5
161.5
160.9
160.4
159.7
159.1
158.8
137.1
136.9
136.8
134.2
134.1
134.0
113.3
113.0
104.1
104.0
103.8
103.8
101.4
101.2
100.9
94.3
94.1
93.8
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
54.5
54.0
13C NMR (101 MHz, CDCl3)
Tautomers
methyl 2-((4-bromo-3,5-difluorophenyl)amino)-2-oxoacetate
Br
F
F
N
H
O
O
O
Me
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

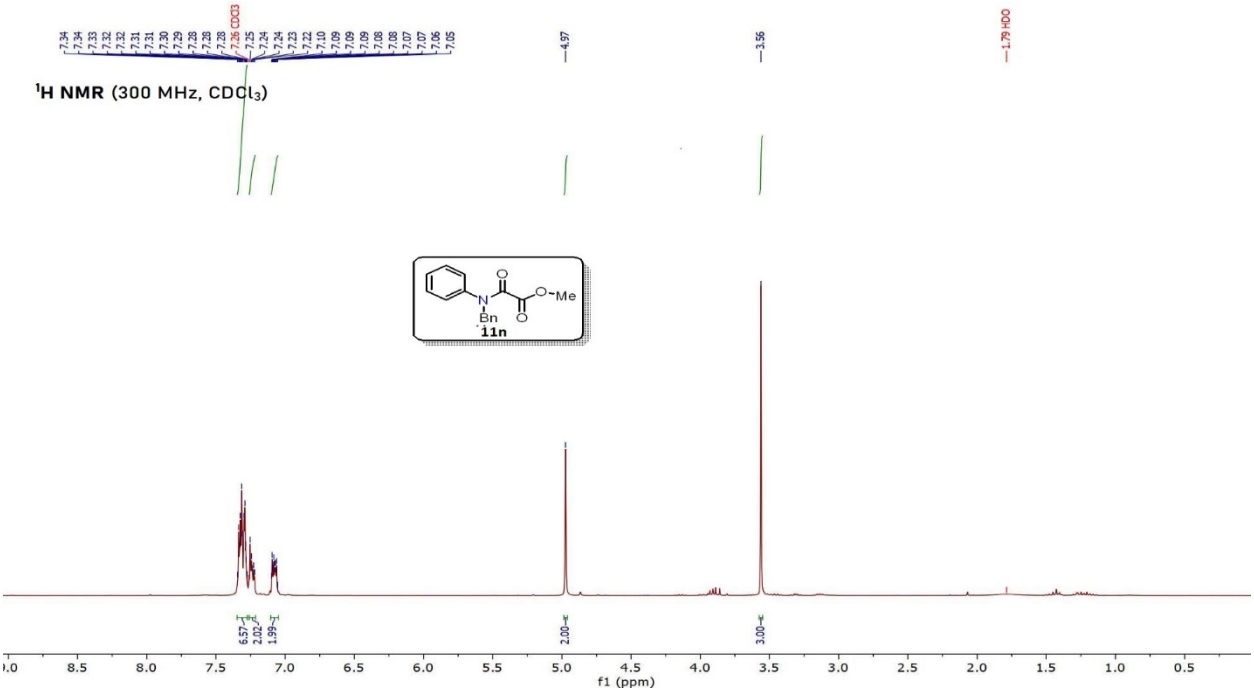

19F NMR (377 MHz, CDCl3)
-101.99
-103.45
Br
F
F
N
Me
O
O
O
Me
11l
-85
-90
-95
-100
-105
-110
-115
-120
-125
-13
f1 (ppm)

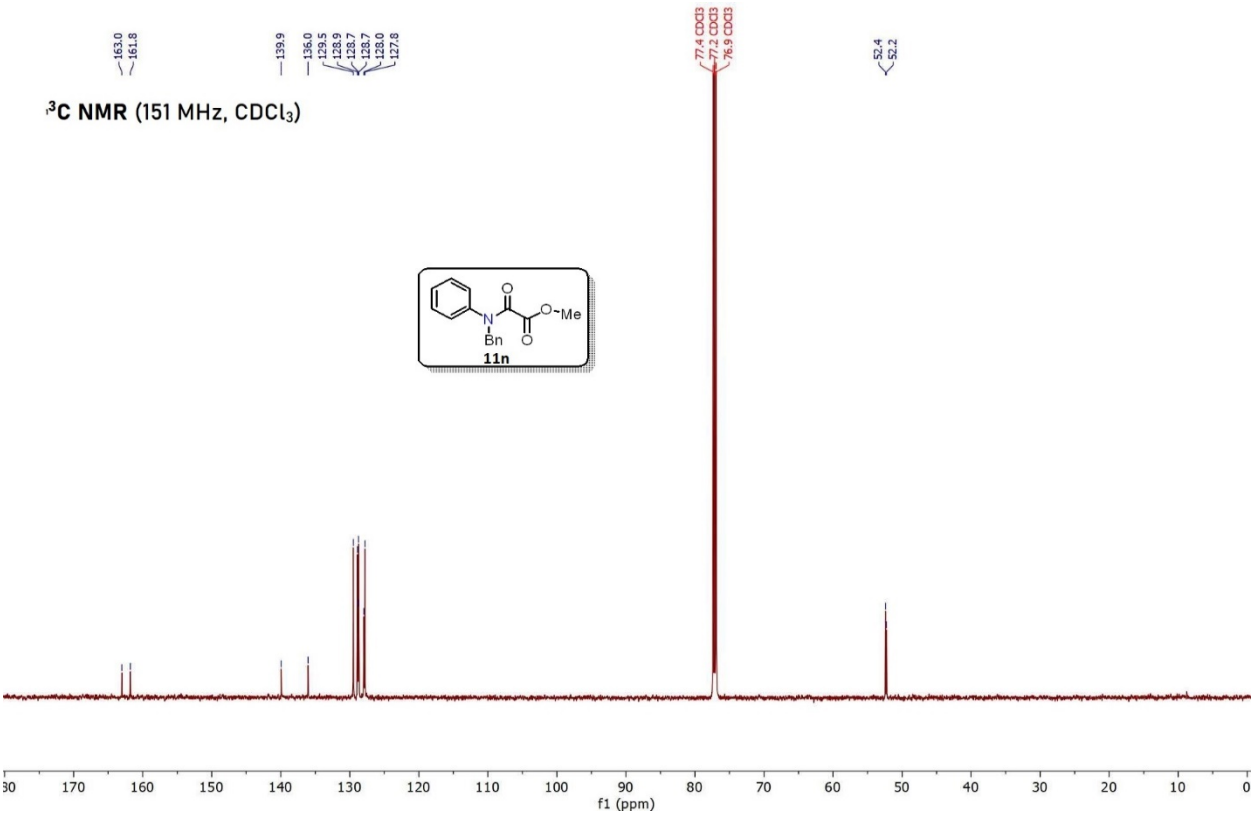
^{1}H NMR (300 MHz, $CDCl_3$)

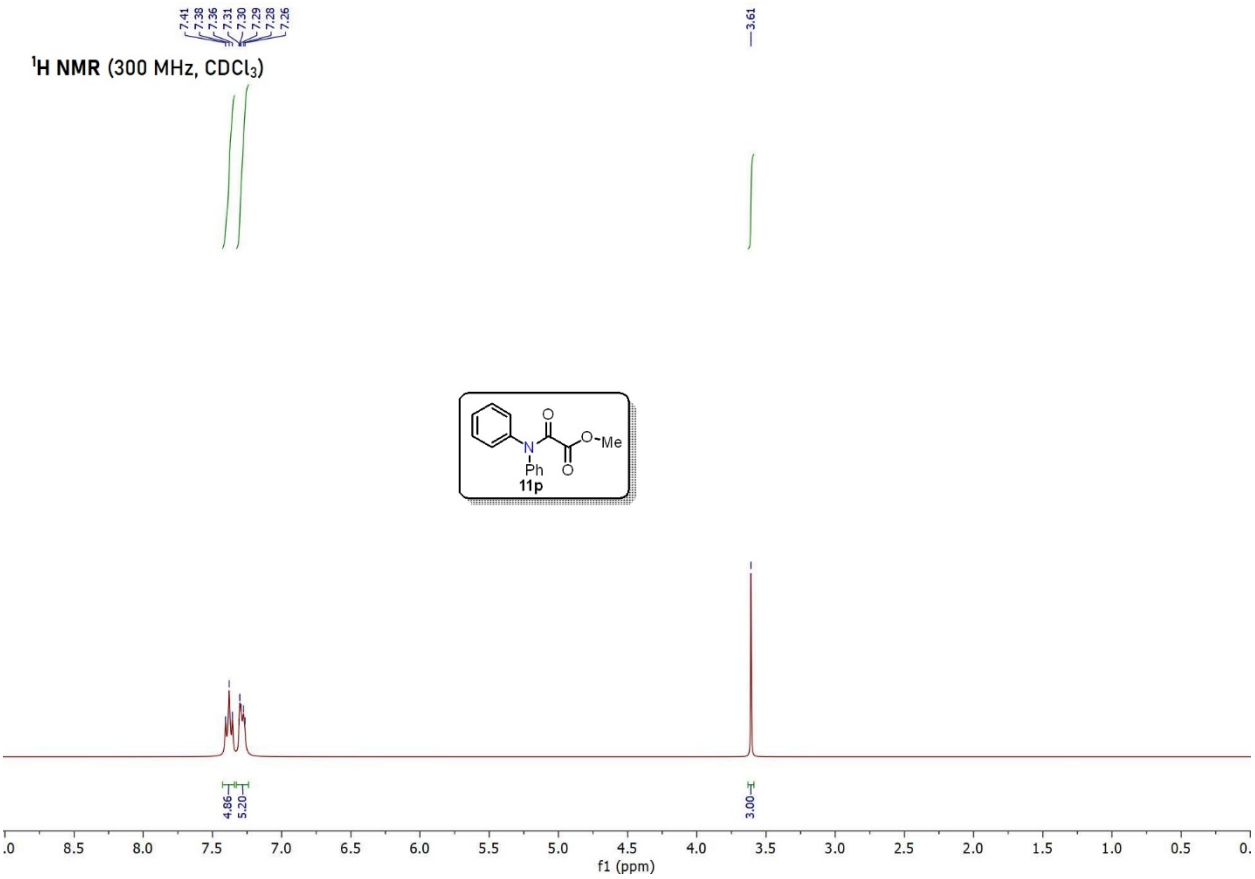


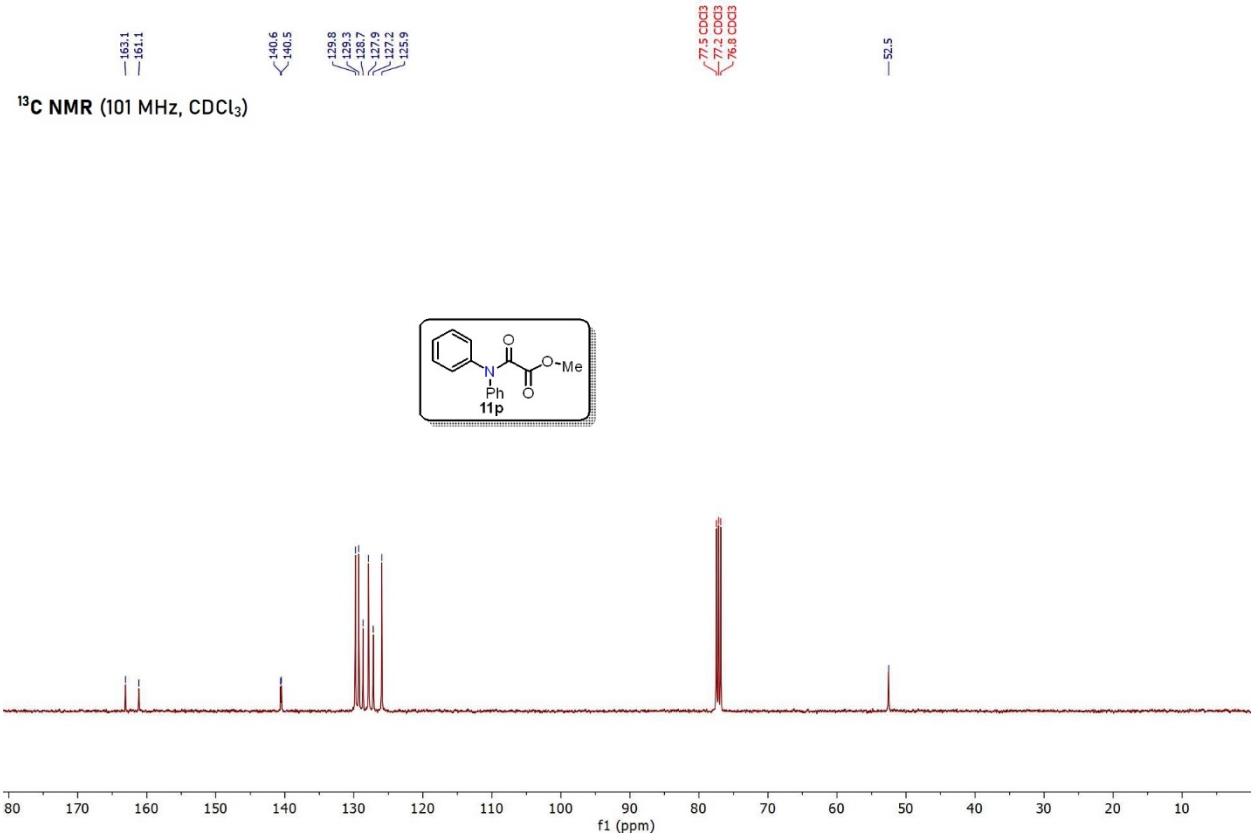
^{13}C NMR (101 MHz, $CDCl_3$)

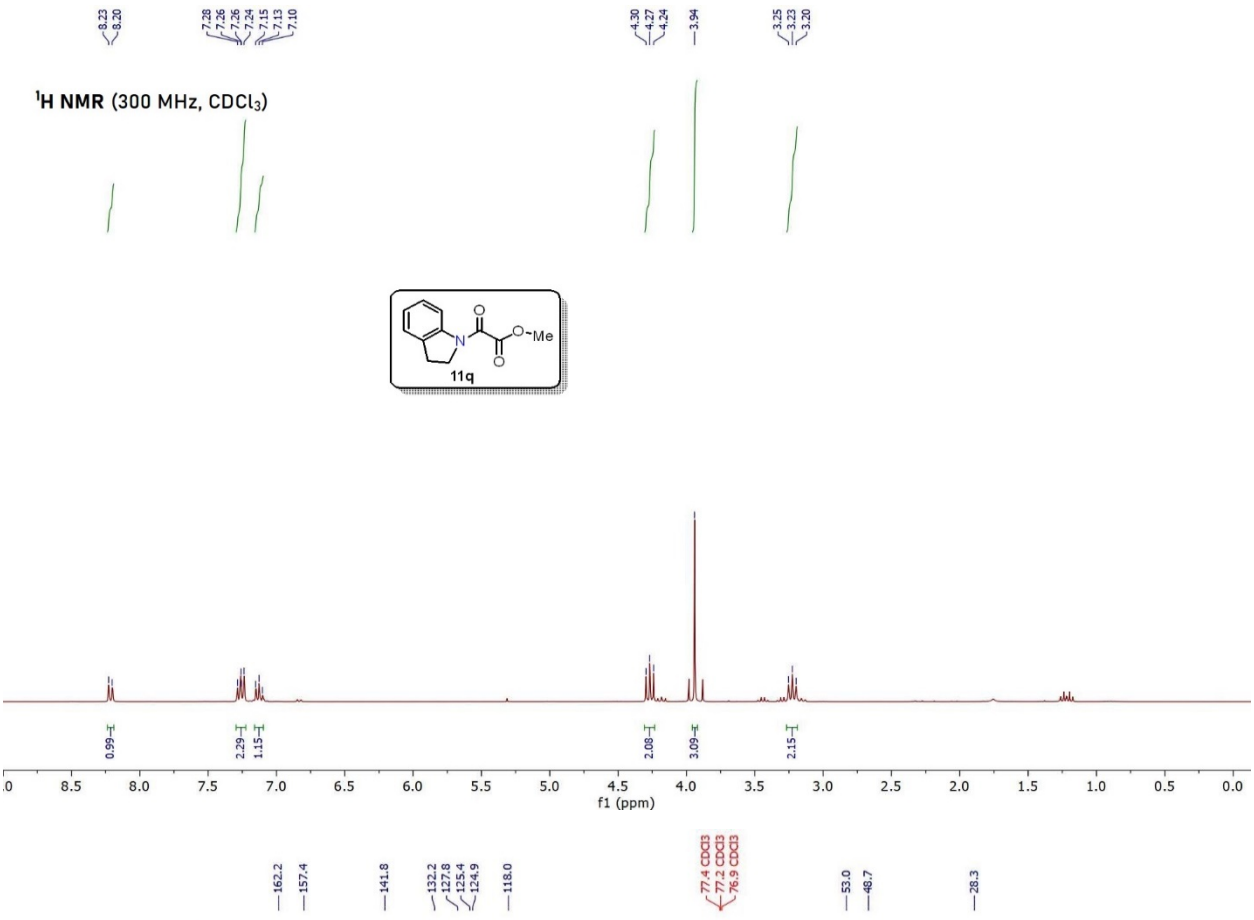


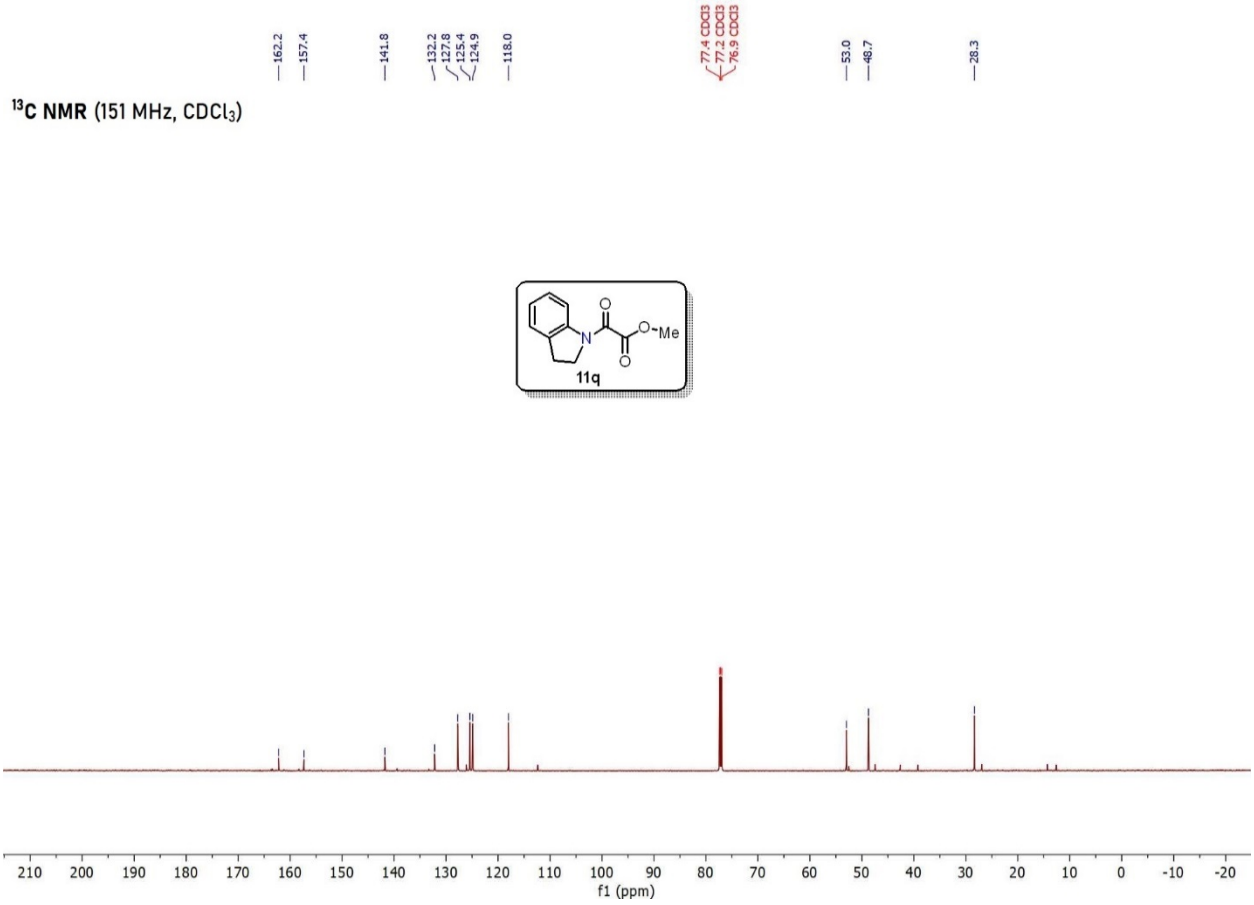

7.34 7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.29 7.28 7.28 7.26 CDCl3 7.25 7.24 7.24 7.23 7.22 7.10 7.09 7.09 7.09 7.08 7.08 7.07 7.07 7.06 7.05
4.97
3.56
1.79 H2O
¹H NMR (300 MHz, CDCl₃)
N
Bn
O
O
O
Me
11n
6.57
2.02
1.99
2.00
3.00
f1 (ppm)

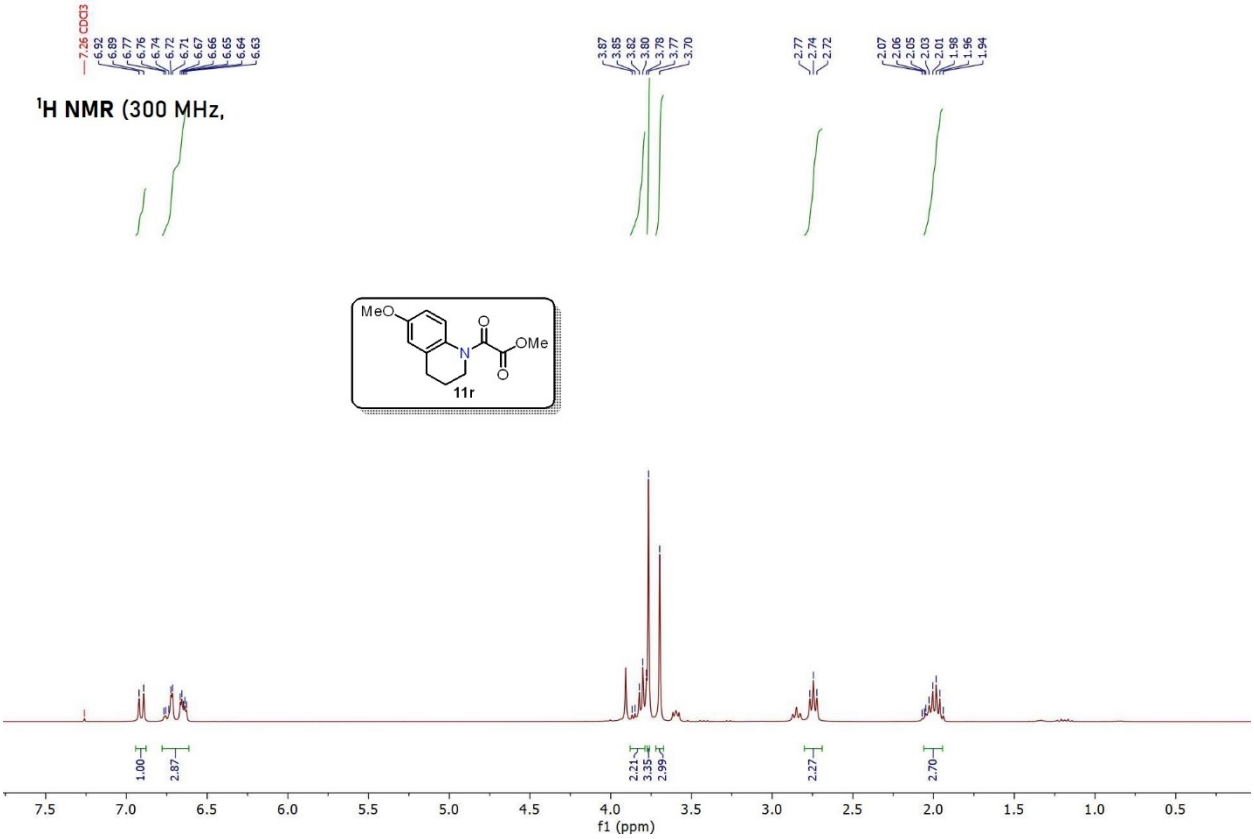

163.0
161.8
139.9
136.0
129.5
128.9
128.7
128.7
128.0
127.8
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
52.4
52.2
¹³C NMR (151 MHz, CDCl₃)
N
Bn
O
O
O
Me
11n
f1 (ppm)

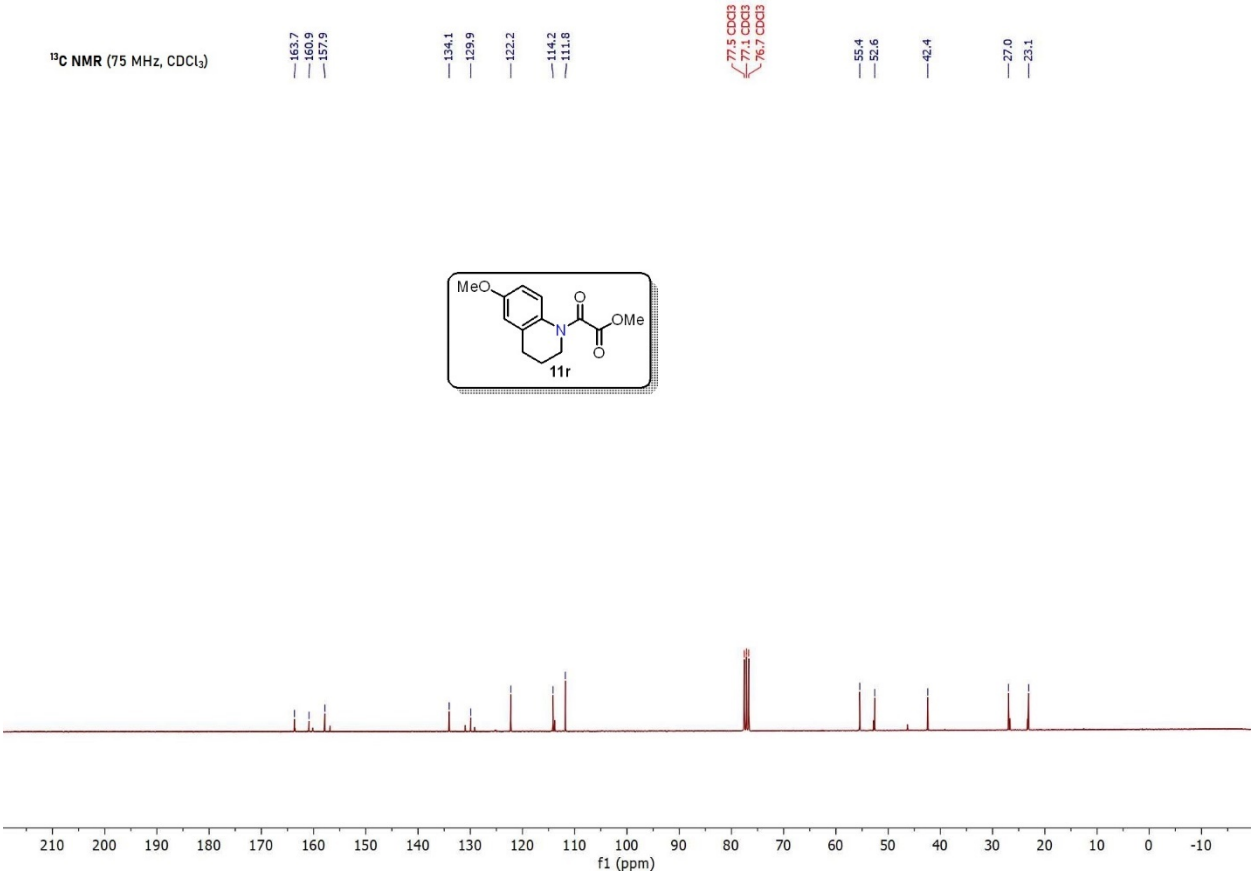

7.41
7.38
7.36
7.31
7.30
7.29
7.28
7.26
3.61
1H NMR (300 MHz, CDCl3)
N
Ph
O
O
O
Me
11p
4.86
5.20
3.00
f1 (ppm)

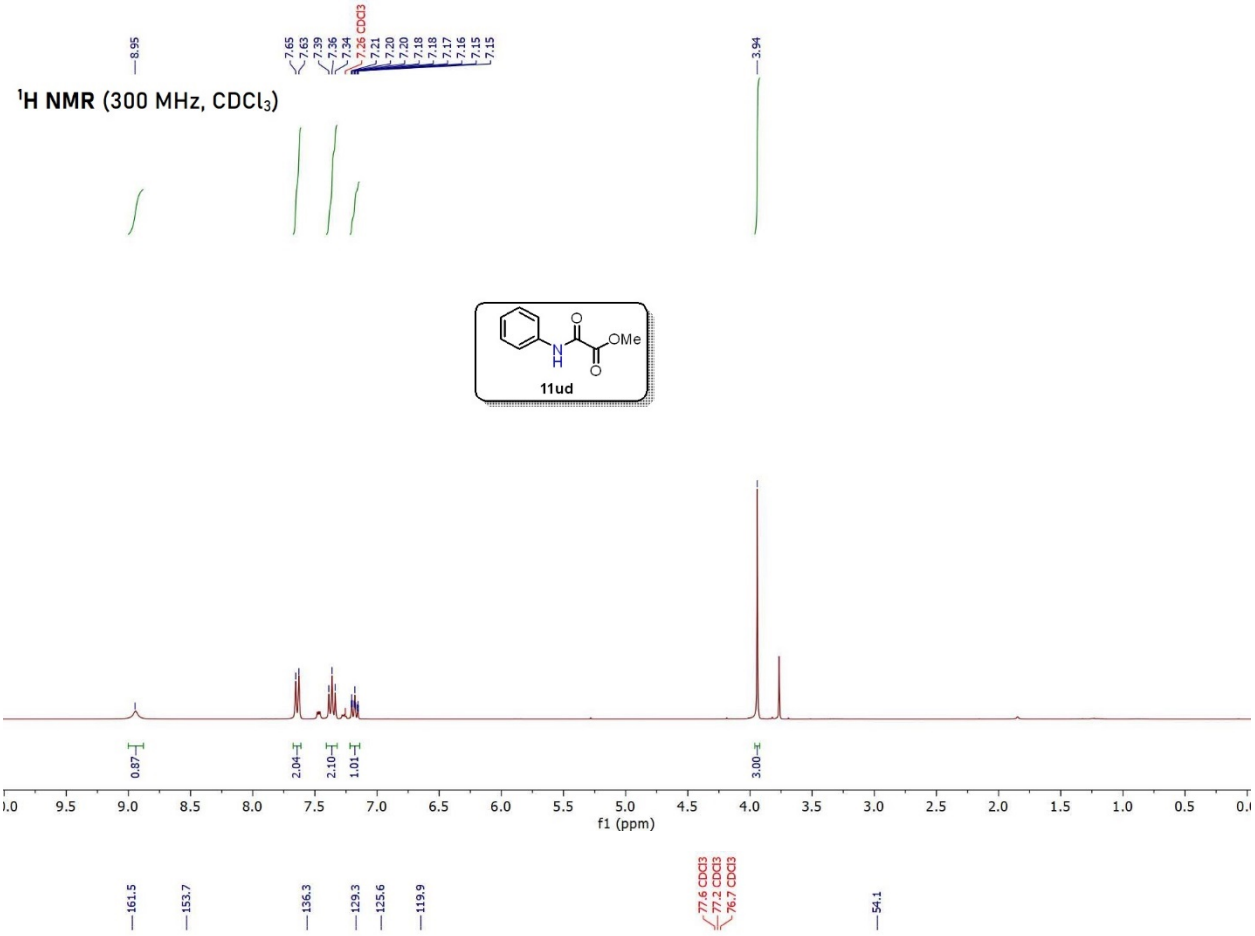

163.1
161.1
140.6
140.5
129.8
129.3
128.7
127.9
127.2
125.9
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
52.5
13C NMR (101 MHz, CDCl3)
N
Ph
O
O
O
Me
11p
f1 (ppm)

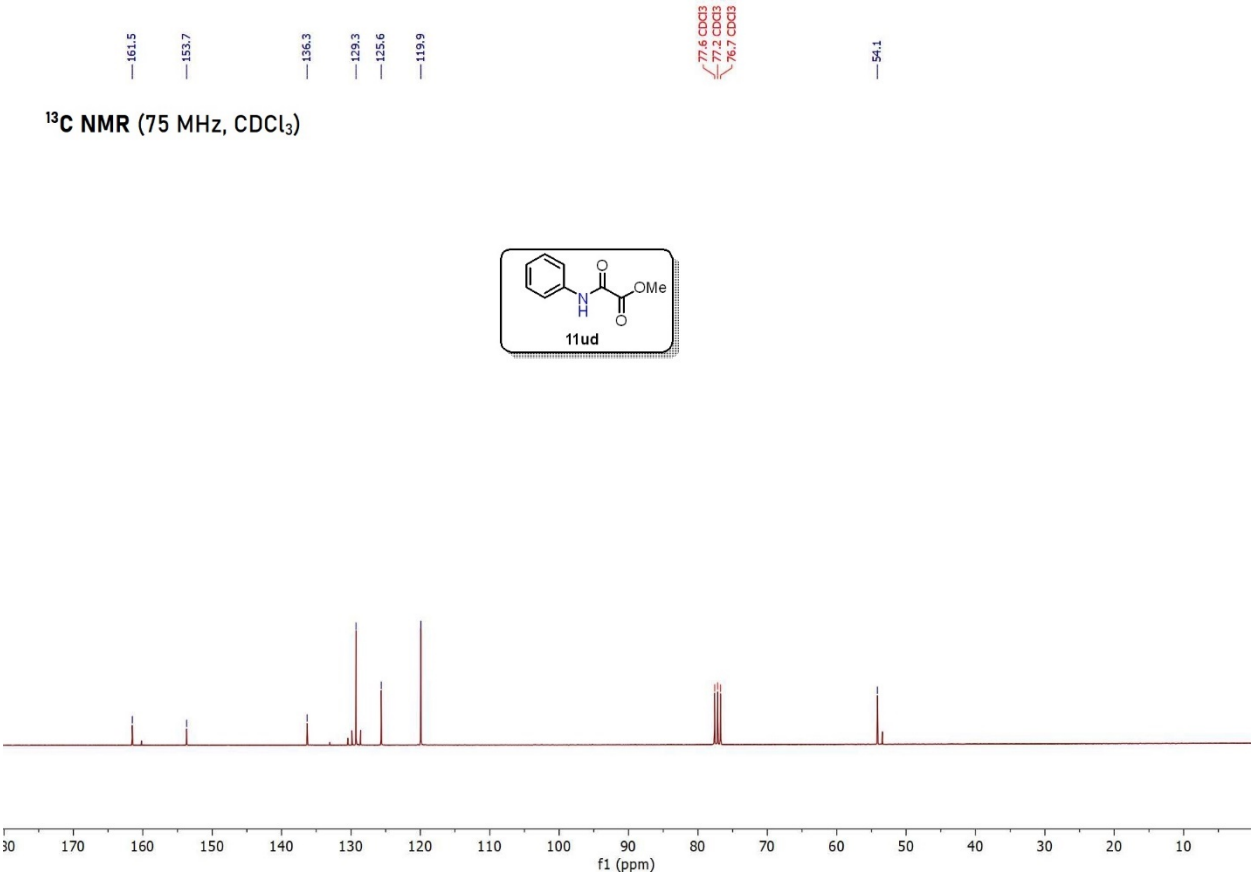

8.23
8.20
7.28
7.26
7.26
7.24
7.15
7.13
7.10
4.30
4.27
4.24
3.94
3.25
3.23
3.20
1H NMR (300 MHz, CDCl3)
N
O
O
O
Me
11q
0.99
2.29
1.15
2.08
3.09
2.15
f1 (ppm)

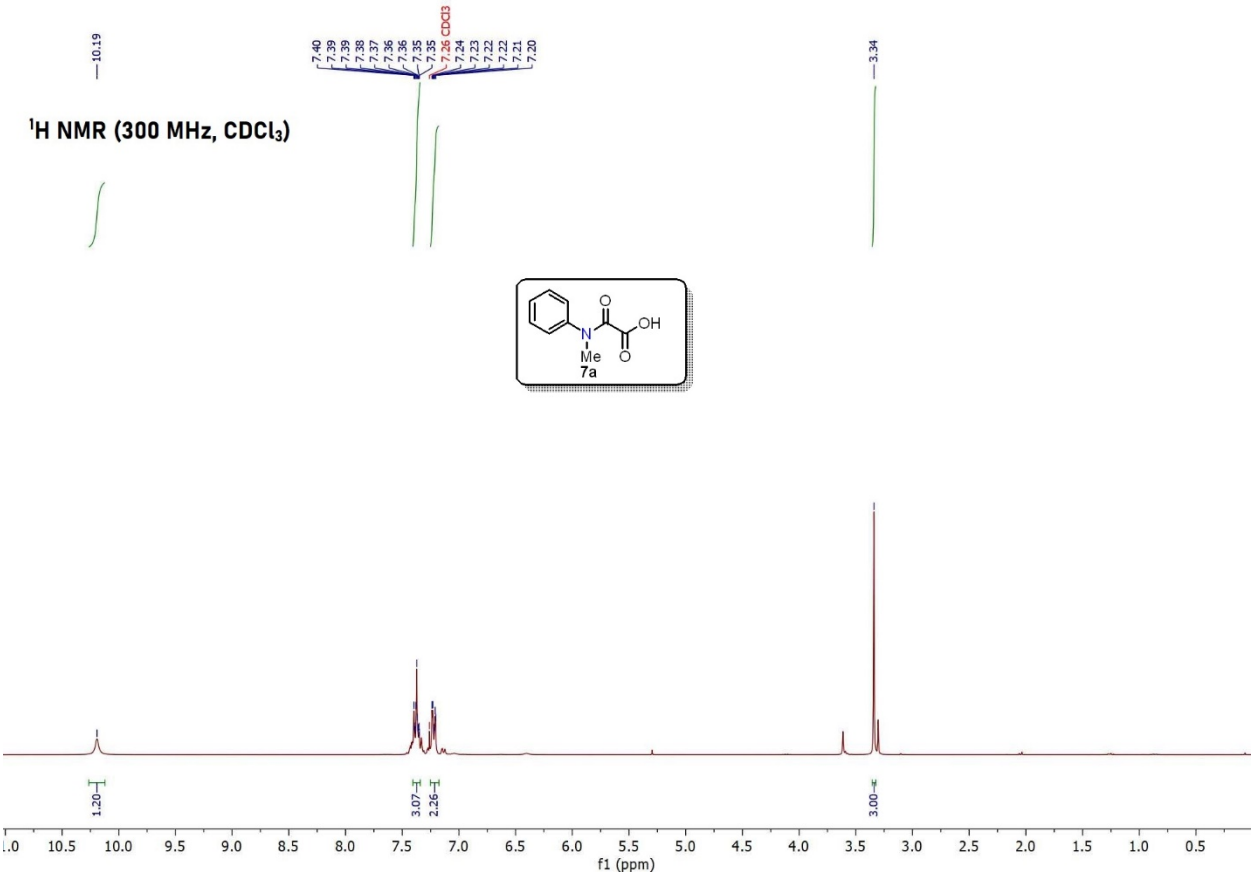

162.2
157.4
141.8
132.2
127.8
125.4
124.9
118.0
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
53.0
46.7
28.3
13C NMR (151 MHz, CDCl3)
N
O
O
O
Me
11q
f1 (ppm)

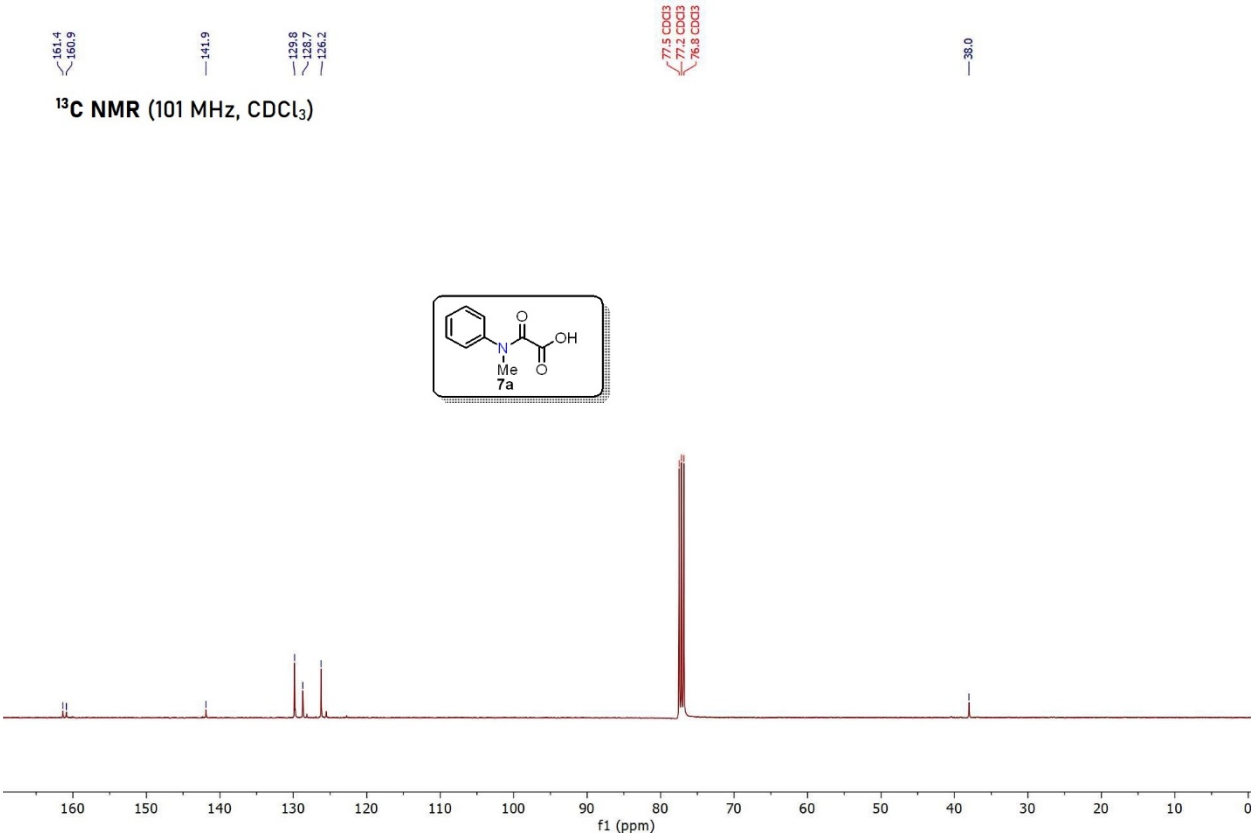

7.26 CDCl3
6.92
6.89
6.77
6.76
6.74
6.72
6.71
6.67
6.66
6.65
6.64
6.63
3.87
3.85
3.82
3.80
3.78
3.77
3.70
2.77
2.74
2.72
2.07
2.06
2.05
2.03
2.01
1.98
1.96
1.94
1H NMR (300 MHz,
MeO
OMe
11r
1.00
2.87
2.21
3.35
2.99
2.27
2.70
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

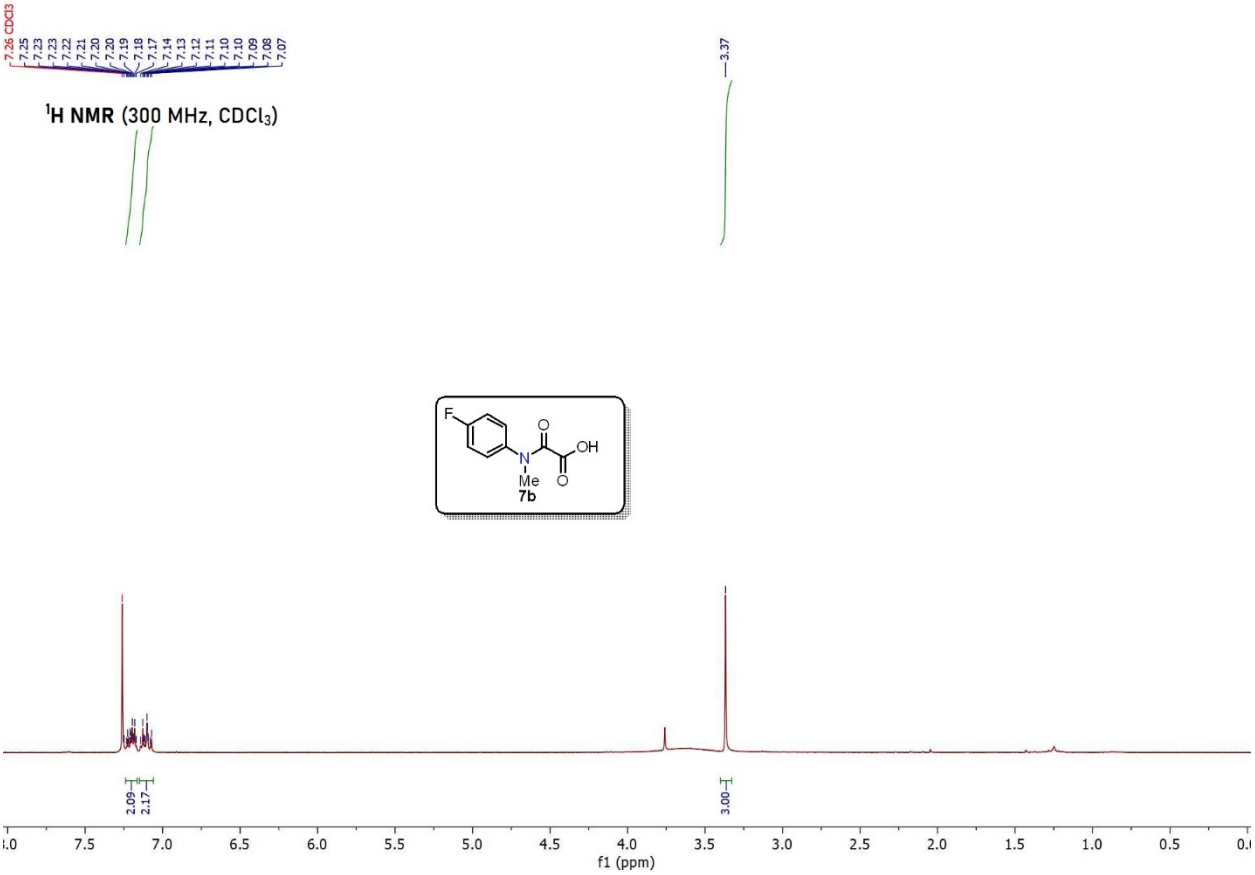

13C NMR (75 MHz, CDCl3)
163.7
160.9
157.9
134.1
129.9
122.2
114.2
111.8
77.5 CDCl3
77.1 CDCl3
76.7 CDCl3
55.4
52.6
42.4
27.0
23.1
MeO
OMe
11r
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

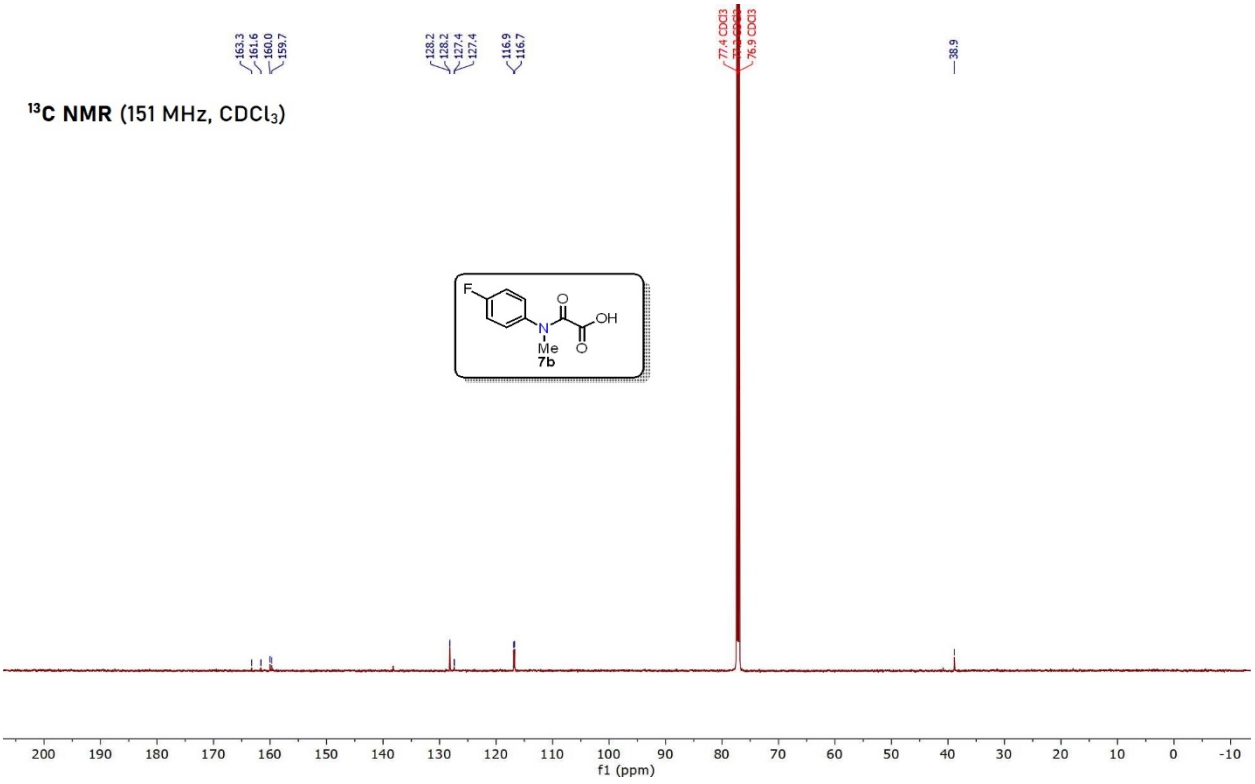

8.95
7.65
7.63
7.39
7.36
7.34
7.26 CDCl3
7.21
7.20
7.20
7.18
7.18
7.17
7.16
7.15
7.15
3.94
1H NMR (300 MHz, CDCl3)
OMe
11ud
0.87
2.04
2.10
1.01
3.00
f1 (ppm)

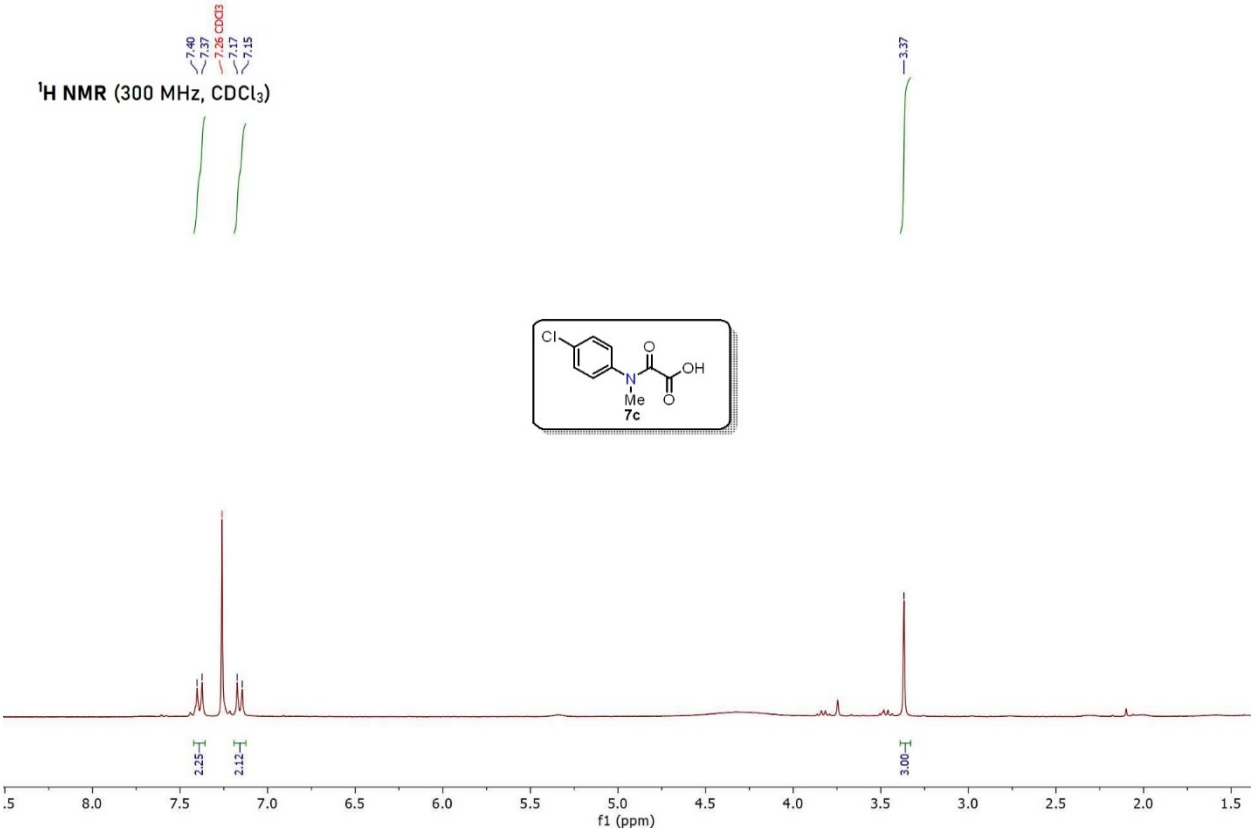

161.5
153.7
136.3
129.3
125.6
119.9
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
54.1
13C NMR (75 MHz, CDCl3)
OMe
11ud
f1 (ppm)


10.19
7.40
7.39
7.39
7.38
7.37
7.36
7.36
7.35
7.35
7.26 CDCl3
7.24
7.23
7.22
7.22
7.21
7.20
3.34
1H NMR (300 MHz, CDCl3)
N
Me
O
OH
O
7a
1.20
3.07
2.26
3.00
f1 (ppm)

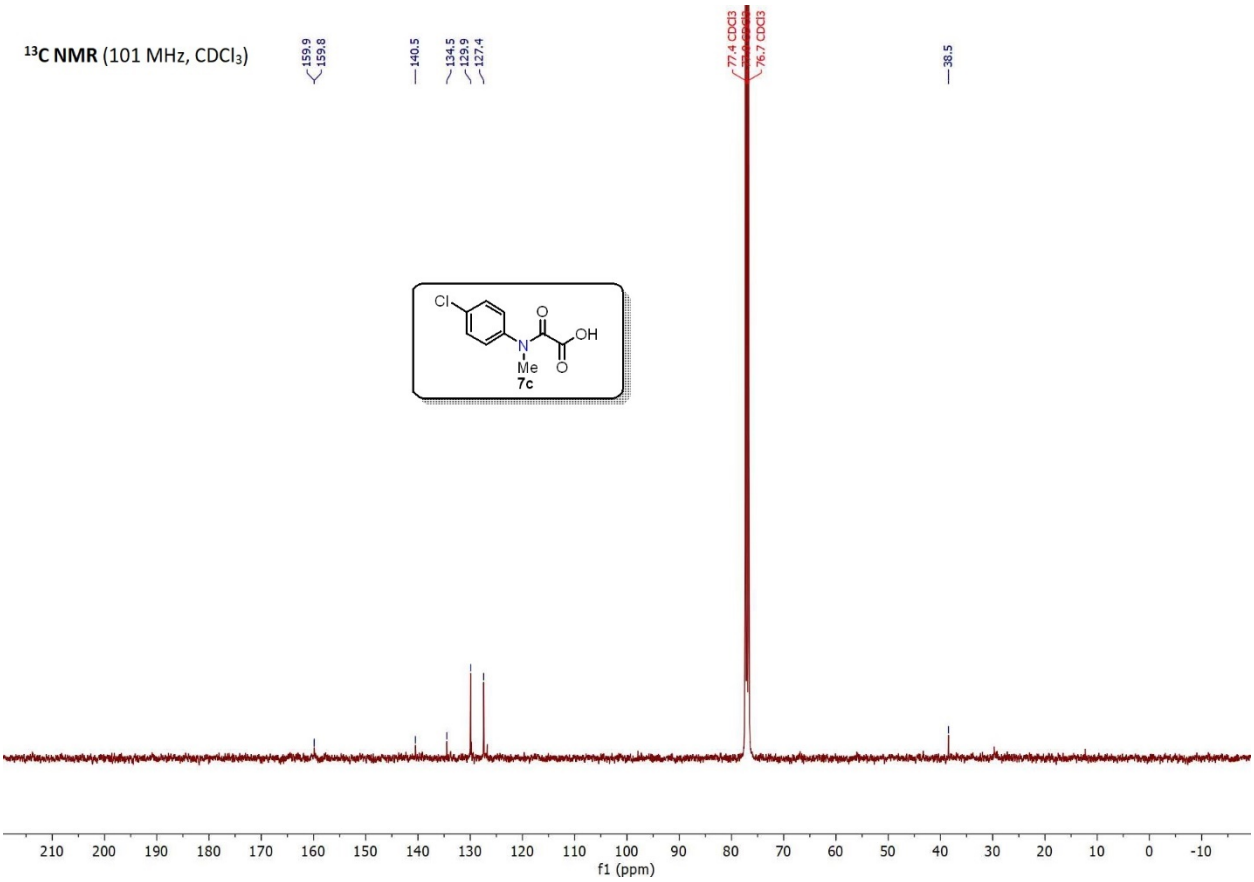

161.4
160.9
141.9
129.8
128.7
126.2
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
38.0
13C NMR (101 MHz, CDCl3)
N
Me
O
OH
O
7a
f1 (ppm)

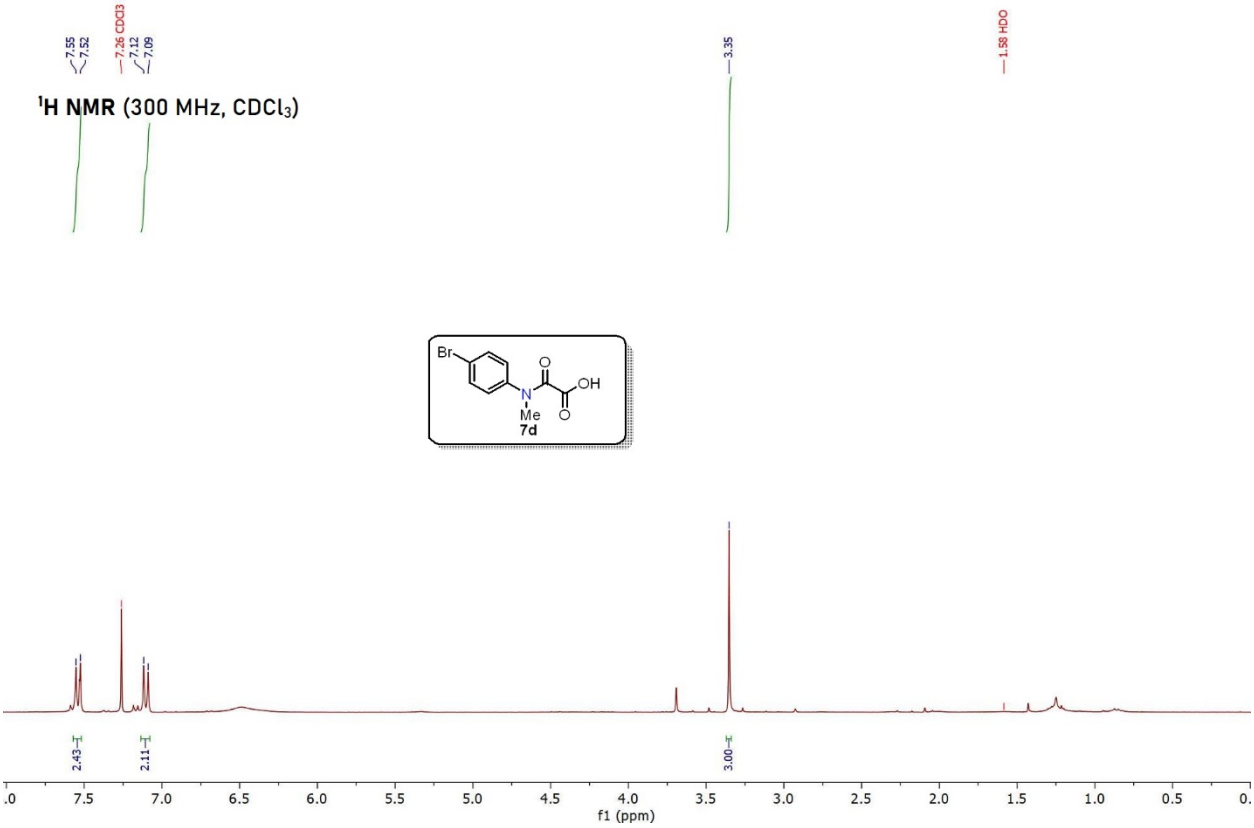

7.26 CDCl3
7.25
7.23
7.23
7.22
7.21
7.20
7.20
7.19
7.18
7.17
7.14
7.13
7.12
7.11
7.10
7.10
7.09
7.08
7.07
3.37
1H NMR (300 MHz, CDCl3)
F
N
Me
OH
O
7b
2.09
2.17
3.00
f1 (ppm)

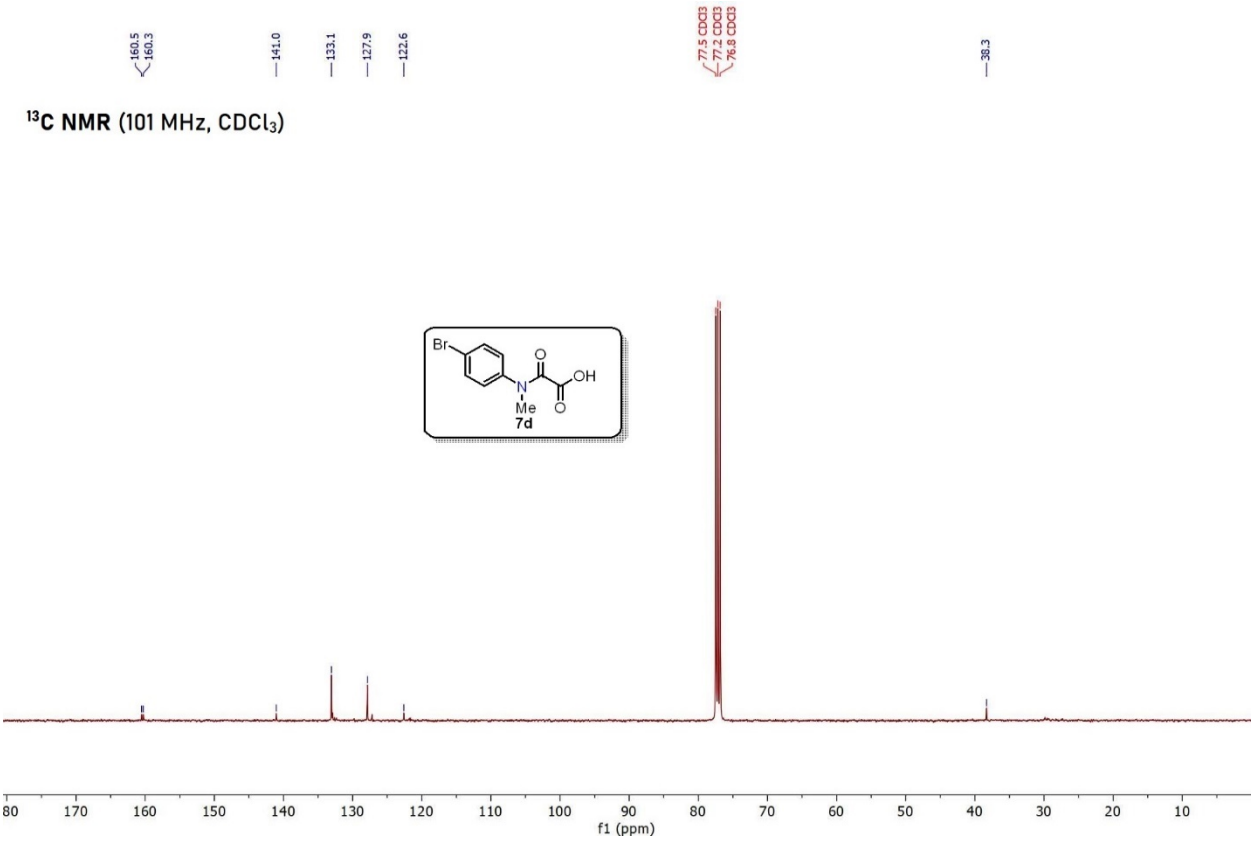

163.3
161.6
160.0
159.7
128.2
128.2
127.4
127.4
116.9
116.7
77.4 CDCl3
76.9 CDCl3
38.9
13C NMR (151 MHz, CDCl3)
F
N
Me
OH
O
7b
f1 (ppm)

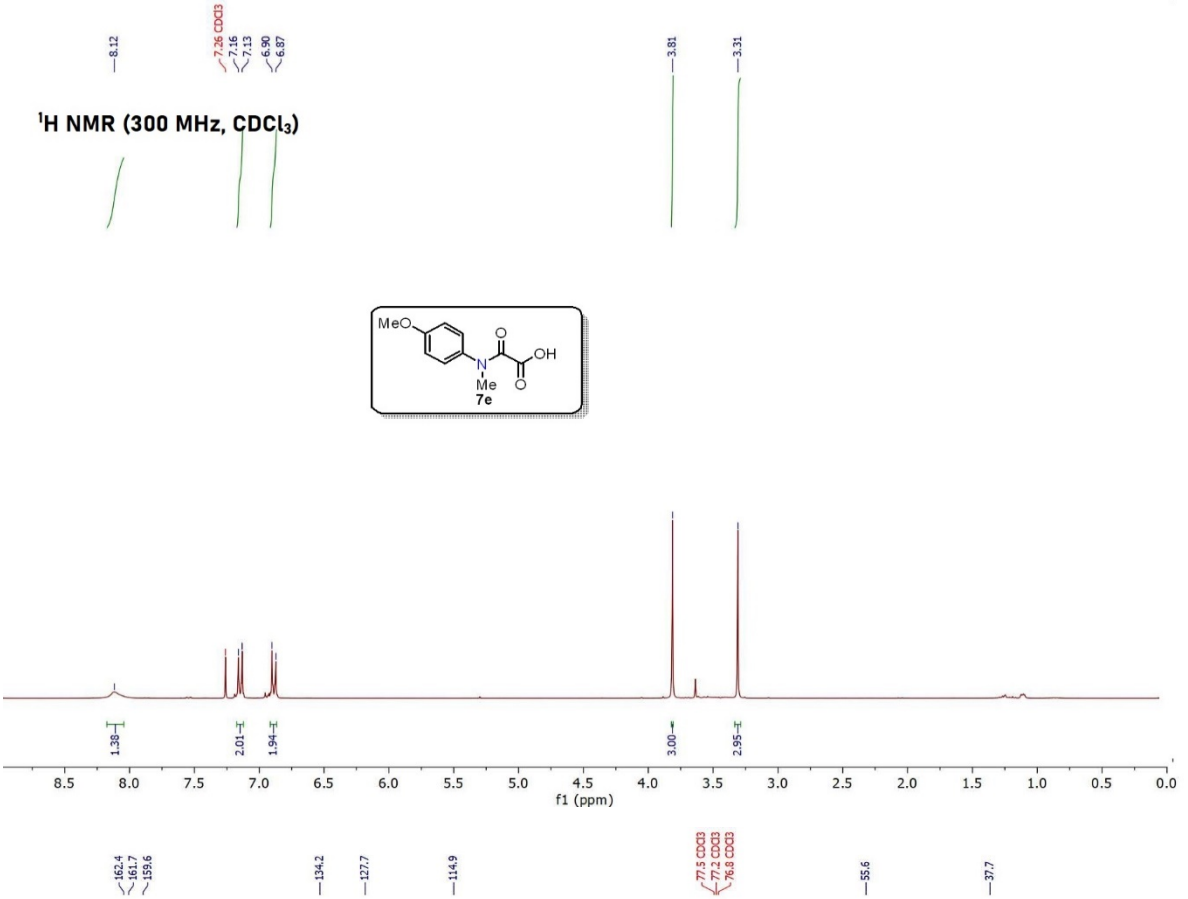


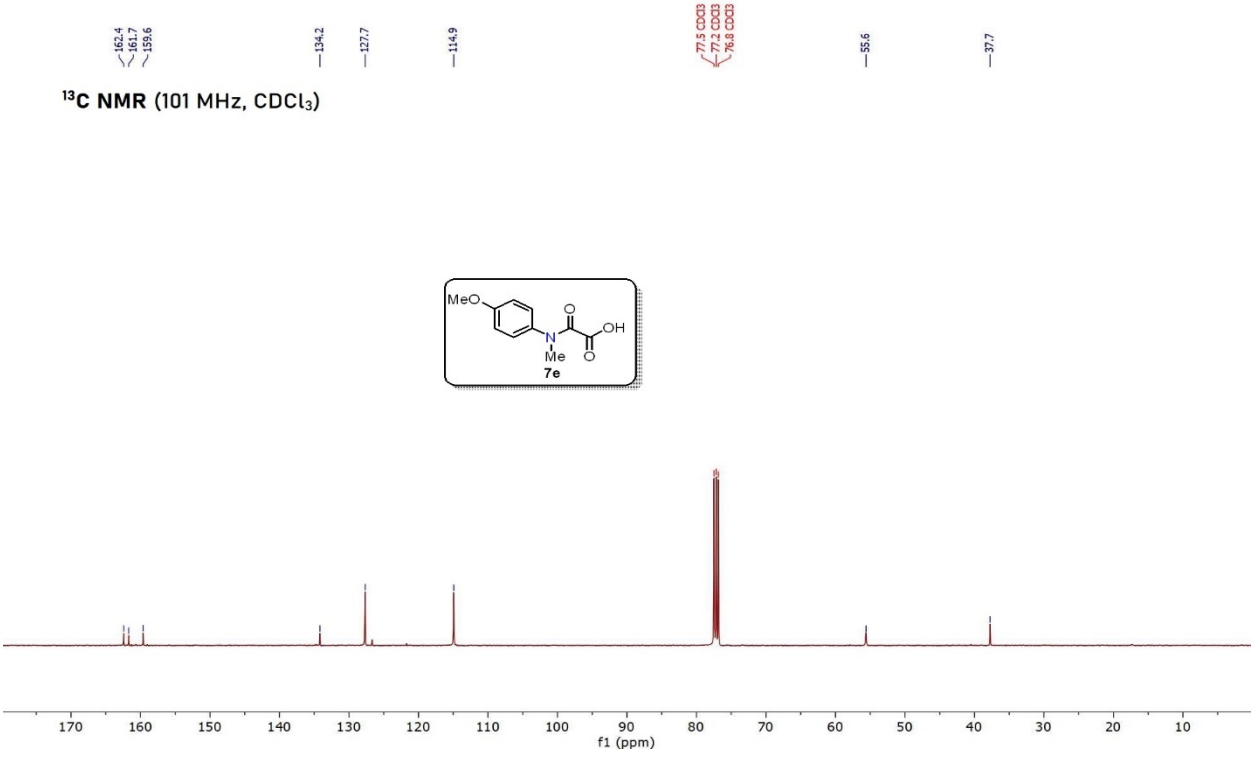
^{13}C NMR ($CDCl_3$)

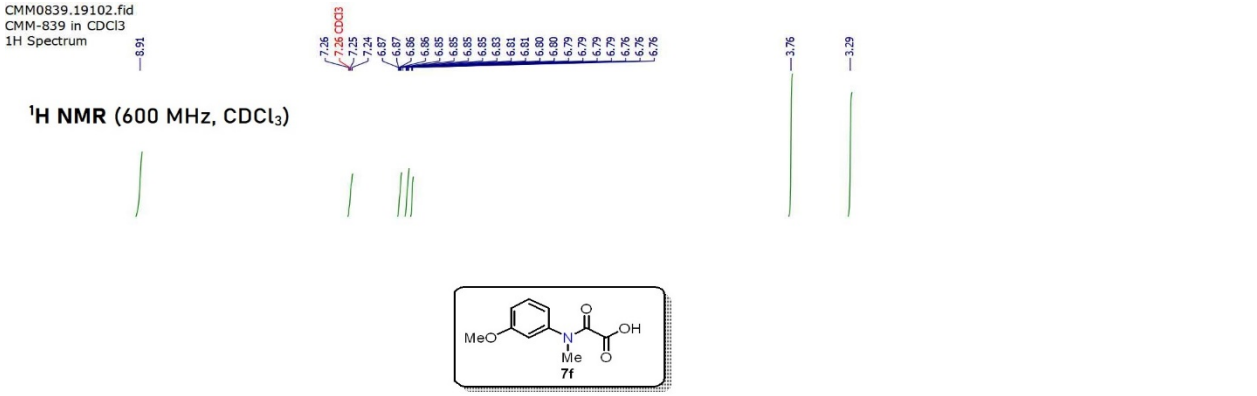



7.55
7.52
7.26 CDCl3
7.12
7.09
3.35
1.58 H2O
¹H NMR (300 MHz, CDCl3)
Br
N
Me
OH
O
7d
2.43
2.11
3.00
f1 (ppm)

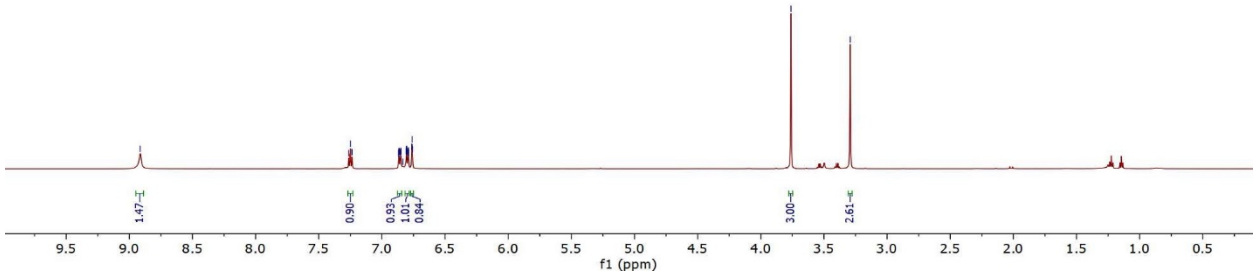

160.5
160.3
141.0
133.1
127.9
122.6
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
38.3
¹³C NMR (101 MHz, CDCl3)
Br
N
Me
OH
O
7d
f1 (ppm)


8.12
7.26 CDCl3
7.16
7.13
6.90
6.87
3.81
3.31
1H NMR (300 MHz, CDCl3)
MeO
N
Me
OH
O
O
7e
1.38
2.01
1.94
3.00
2.95
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

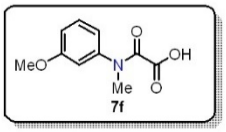

162.4
161.7
159.6
134.2
127.7
114.9
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
55.6
37.7
13C NMR (101 MHz, CDCl3)
MeO
N
Me
OH
O
O
7e
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

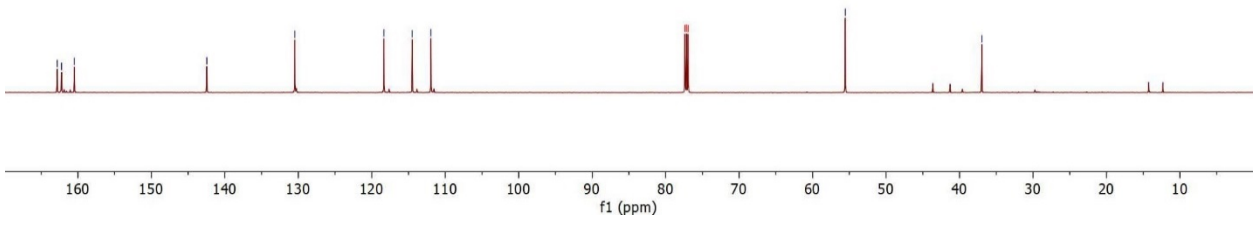


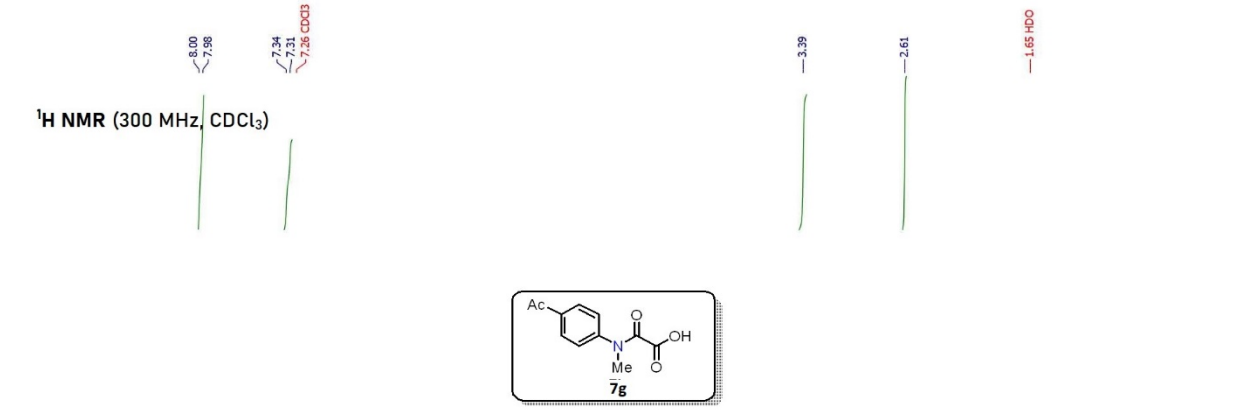
^{1}H NMR (600 MHz, $CDCl_3$)

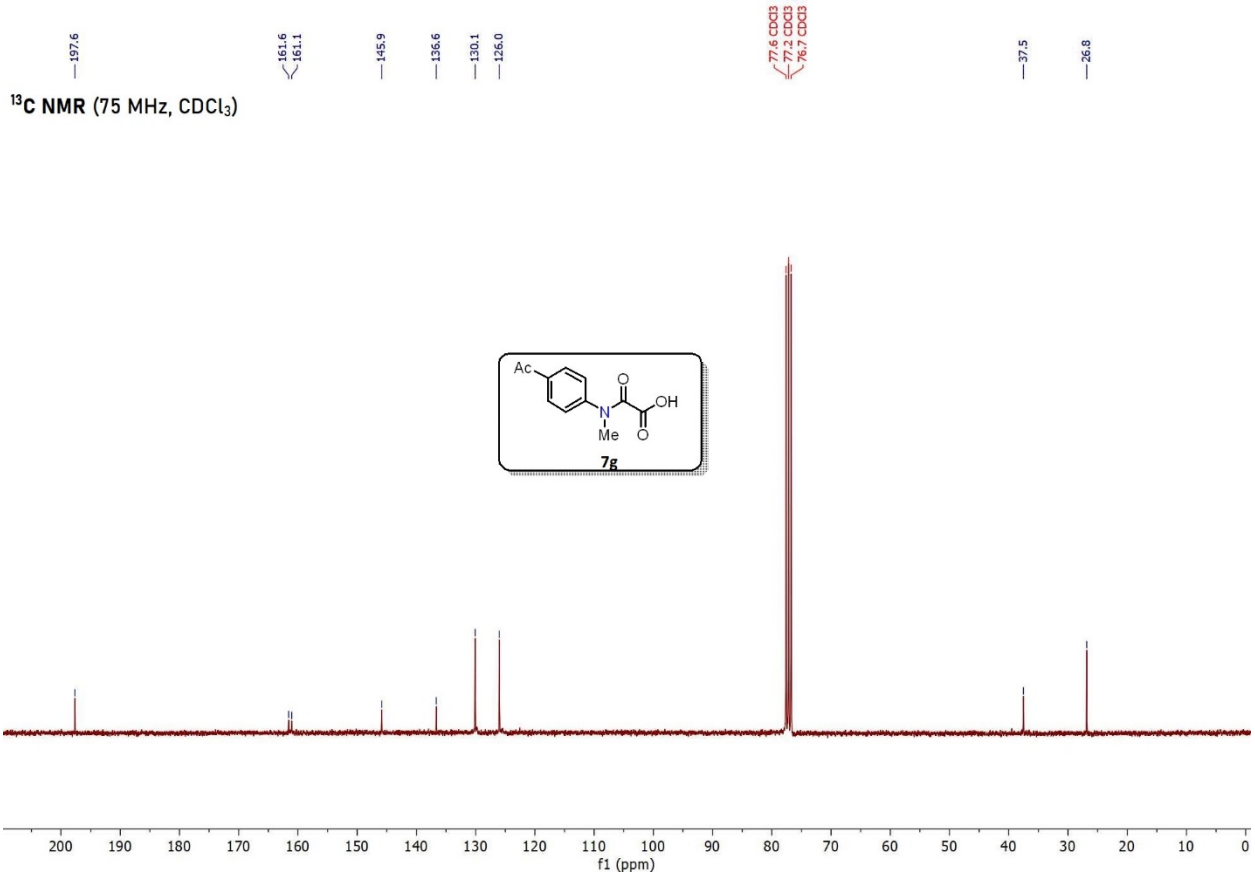


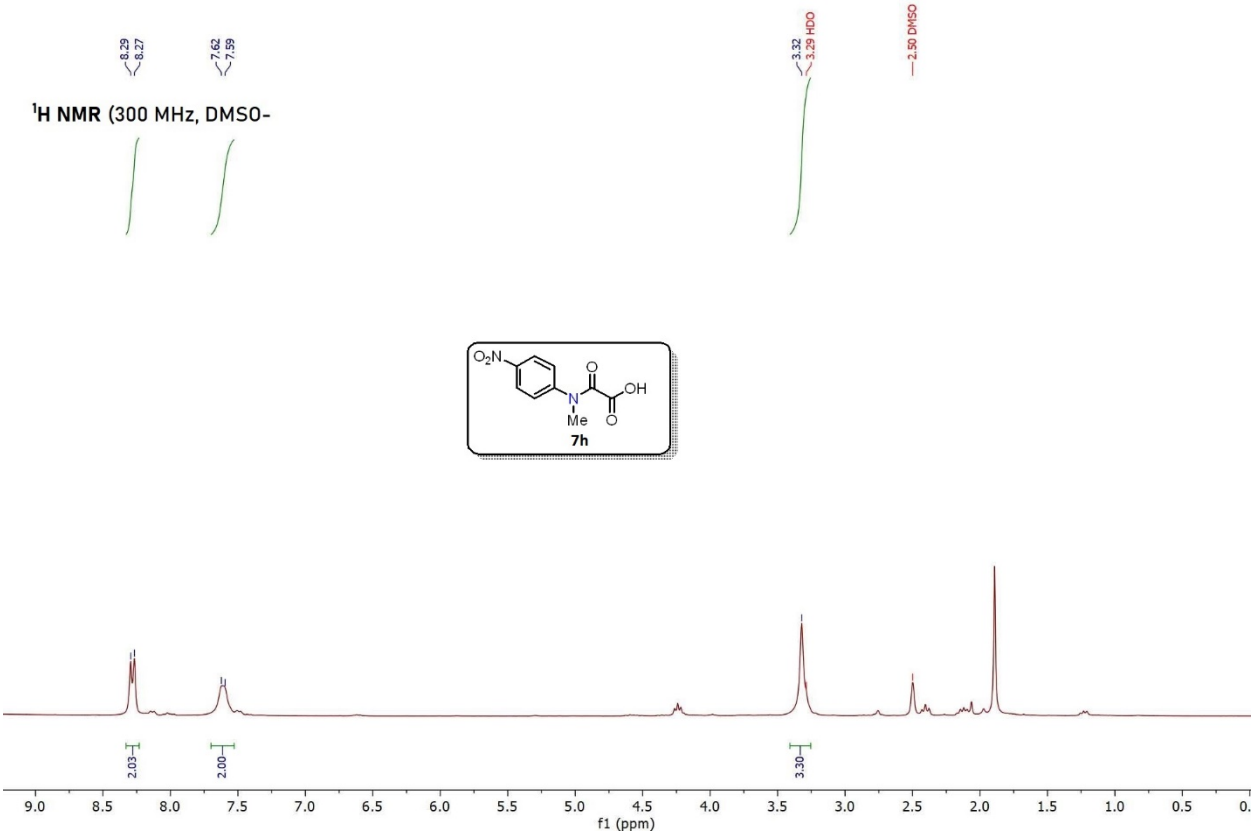
^{13}C NMR (151 MHz, $CDCl_3$)

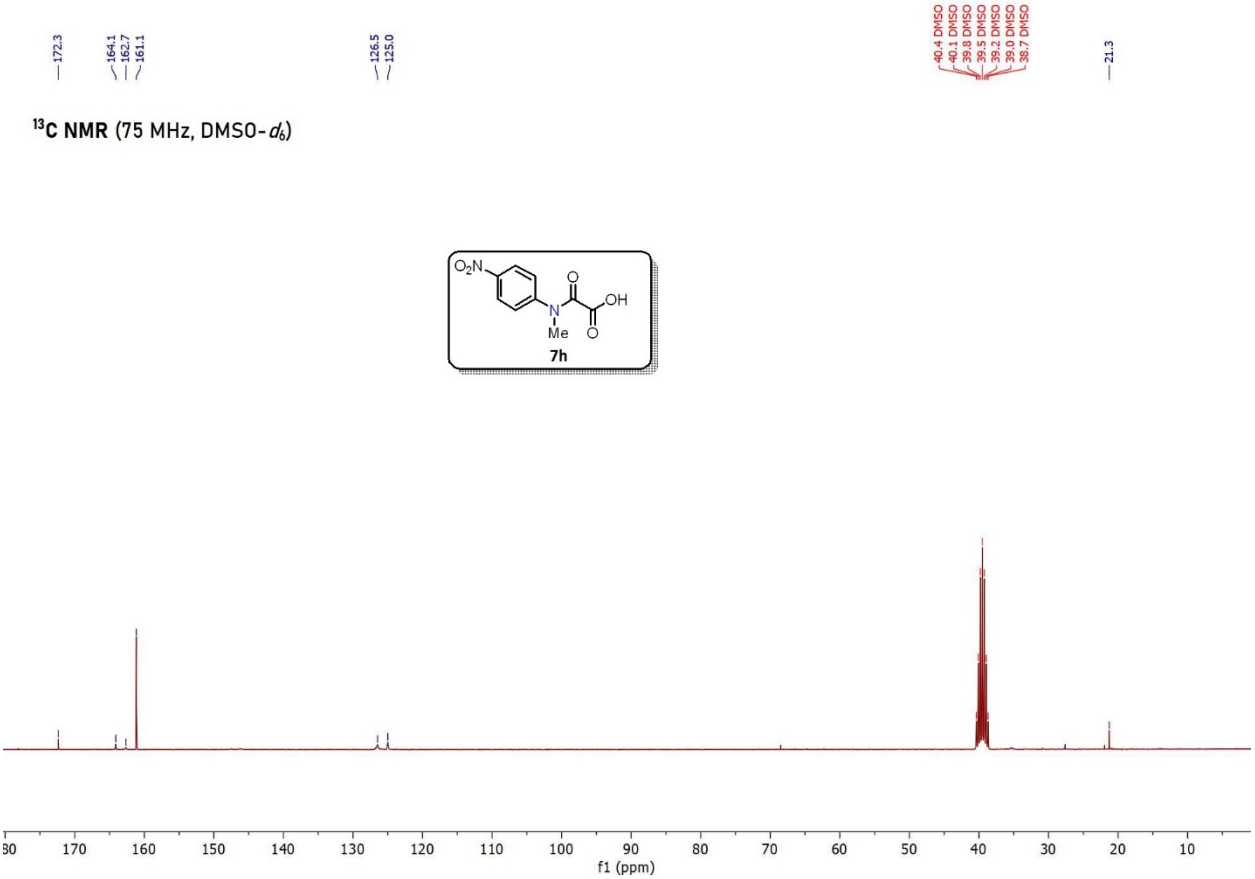


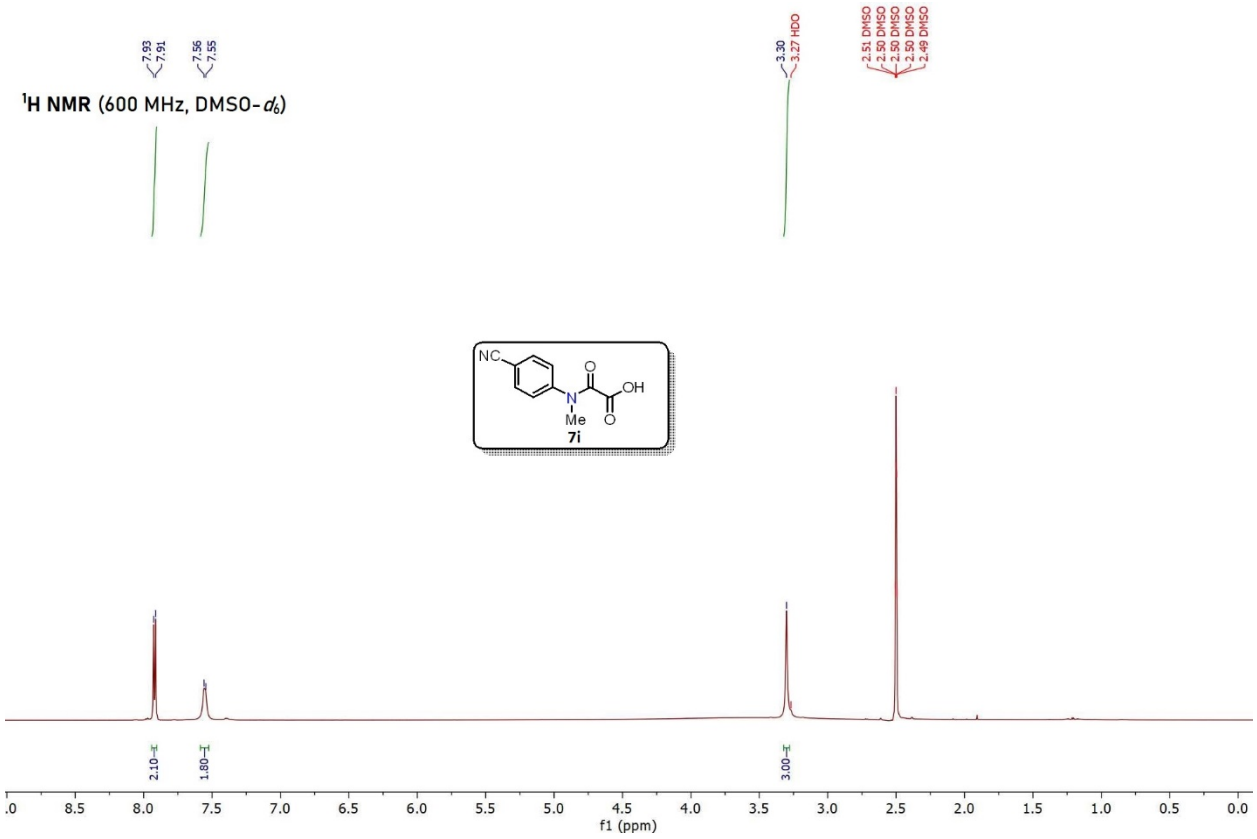



8.00
7.98
7.34
7.31
7.26 CDCl3
3.39
2.61
1.65 HDO
1H NMR (300 MHz, CDCl3)
Ac
N
Me
O
OH
O
7g
2.63
1.77
2.65
3.00
f1 (ppm)

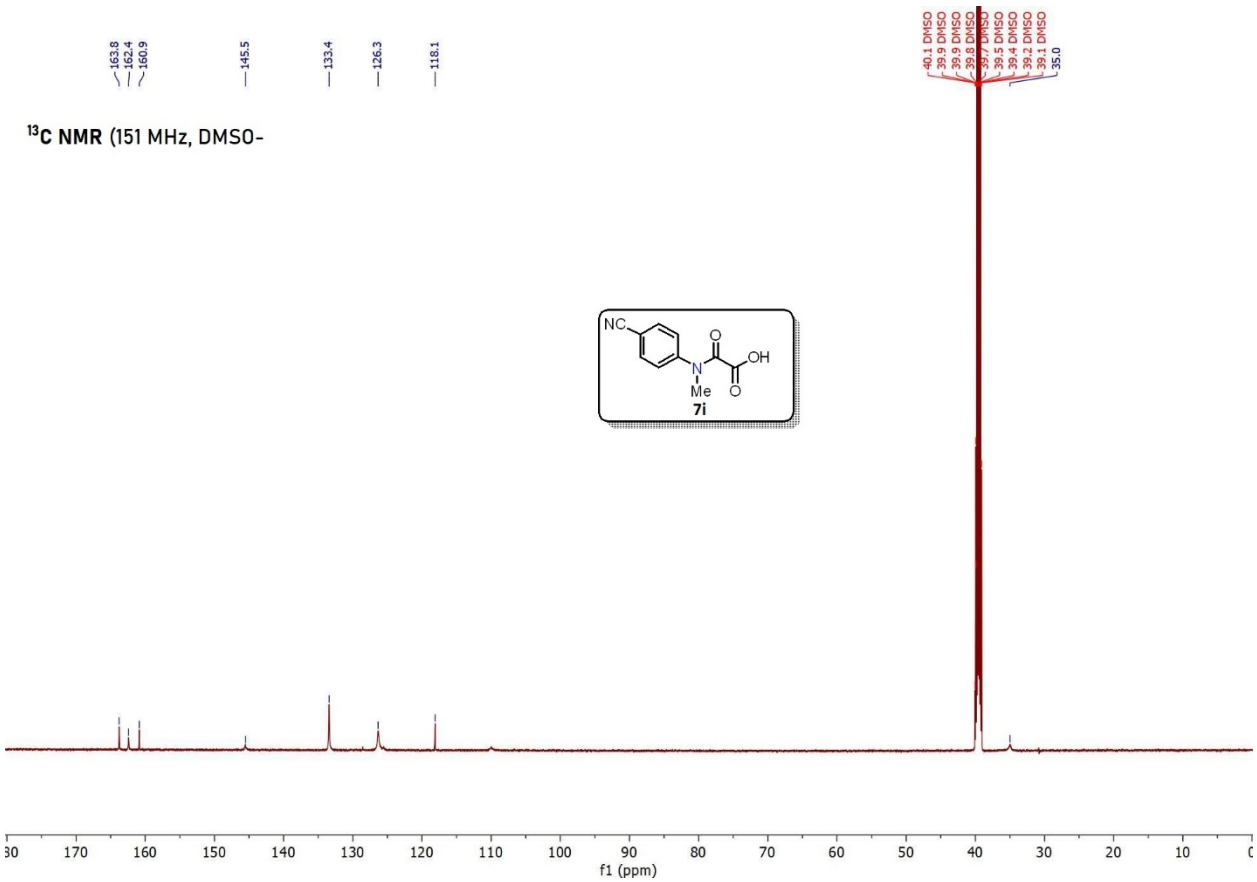

197.6
161.6
161.1
145.9
136.6
130.1
126.0
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
37.5
26.8
13C NMR (75 MHz, CDCl3)
Ac
N
Me
O
OH
O
7g
f1 (ppm)


8.29
8.27
7.62
7.59
3.32
3.29 HDO
2.50 DMSO
¹H NMR (300 MHz, DMSO-
O2N
N
Me
O
OH
7h
2.03
2.00
3.30
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)

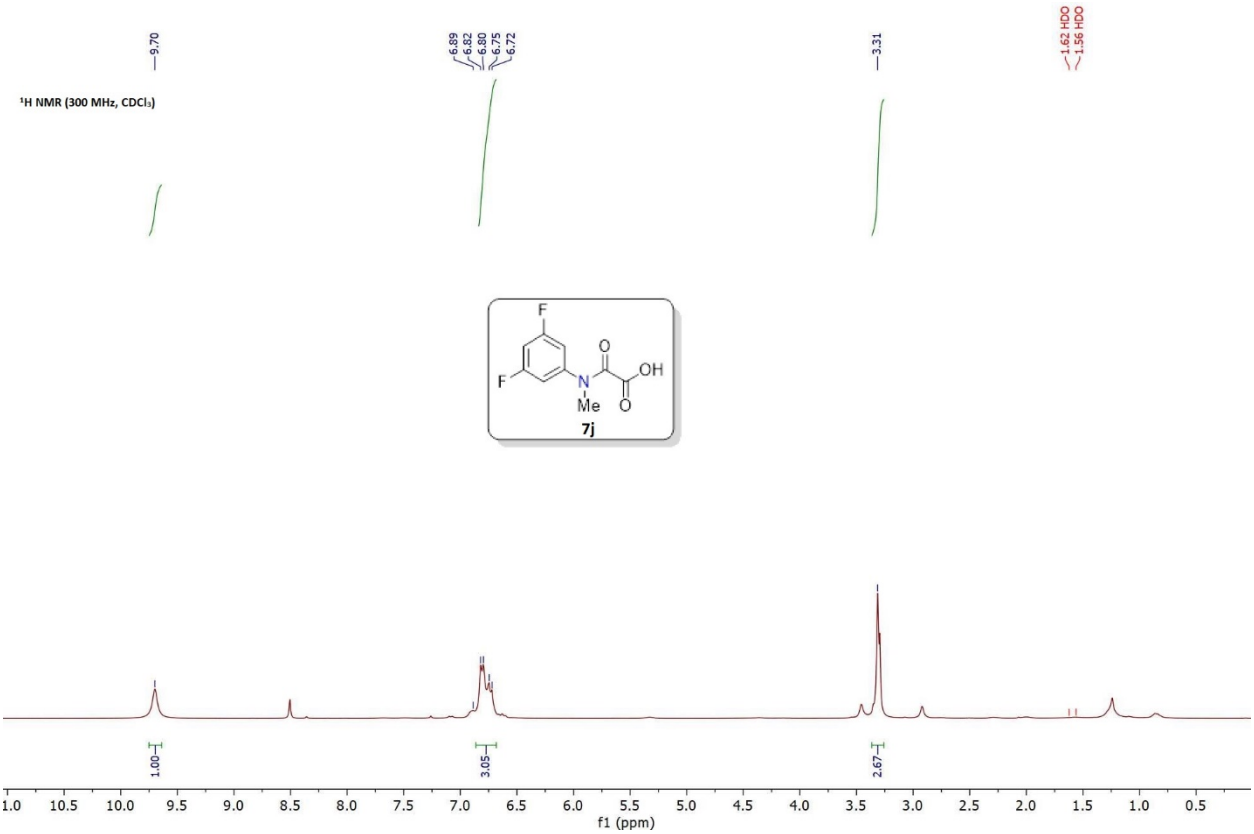

172.3
164.1
162.7
161.1
126.5
125.0
40.4 DMSO
40.1 DMSO
39.8 DMSO
39.5 DMSO
39.2 DMSO
39.0 DMSO
38.7 DMSO
21.3
¹³C NMR (75 MHz, DMSO-d6)
O2N
N
Me
O
OH
7h
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

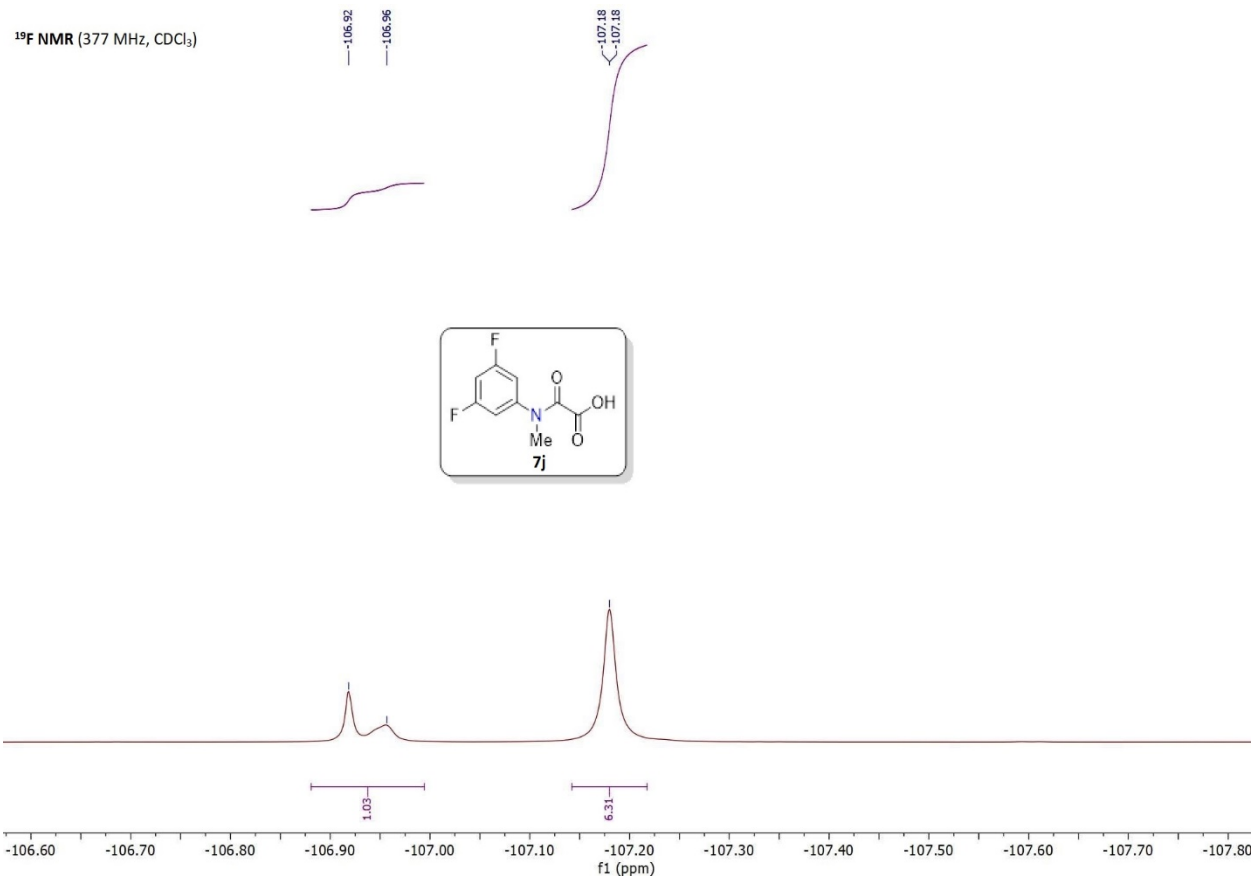


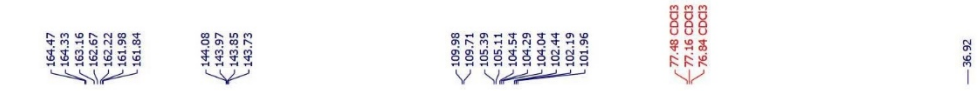
^{1}H NMR (600 MHz, DMSO-d_6)



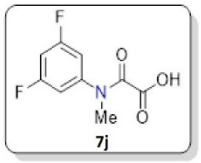
^{13}C NMR (151 MHz, DMSO-


9.70
6.89
6.82
6.80
6.75
6.72
3.31
1.62 HDO
1.56 HDO
¹H NMR (300 MHz, CDCl₃)
F
F
N
Me
O
OH
O
7j
1.00
3.05
2.67
1.0 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
f1 (ppm)

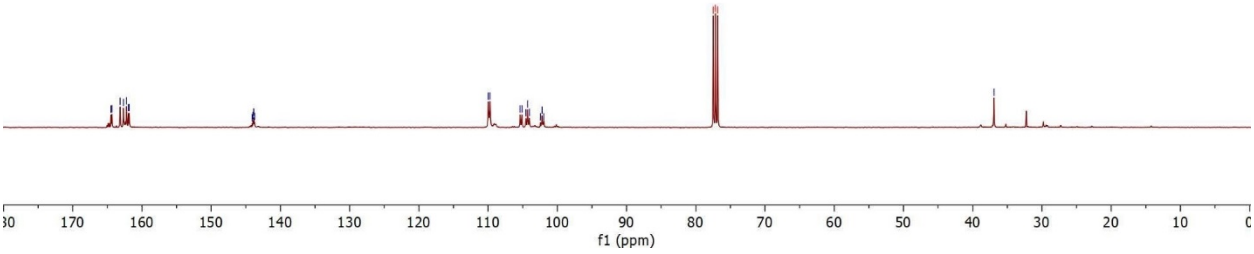

¹⁹F NMR (377 MHz, CDCl₃)
-106.92
-106.96
-107.18
-107.18
F
F
N
Me
O
OH
O
7j
1.03
6.31
-106.60 -106.70 -106.80 -106.90 -107.00 -107.10 -107.20 -107.30 -107.40 -107.50 -107.60 -107.70 -107.80
f1 (ppm)

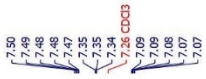


^{13}C NMR (101 MHz, $CDCl_3$)

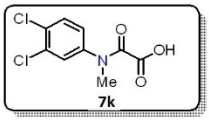


7j

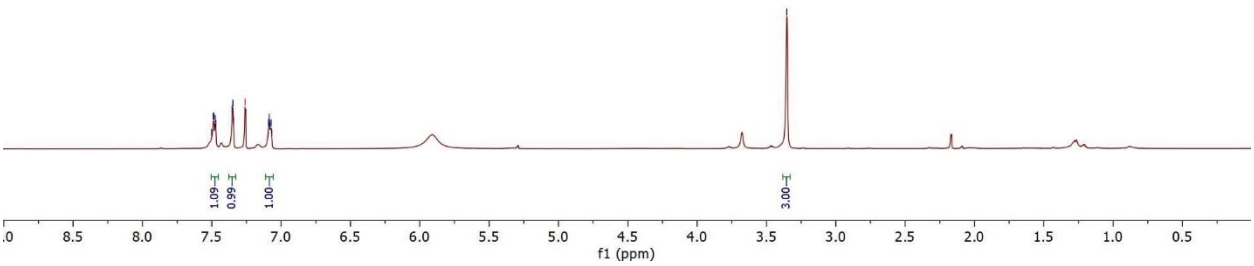


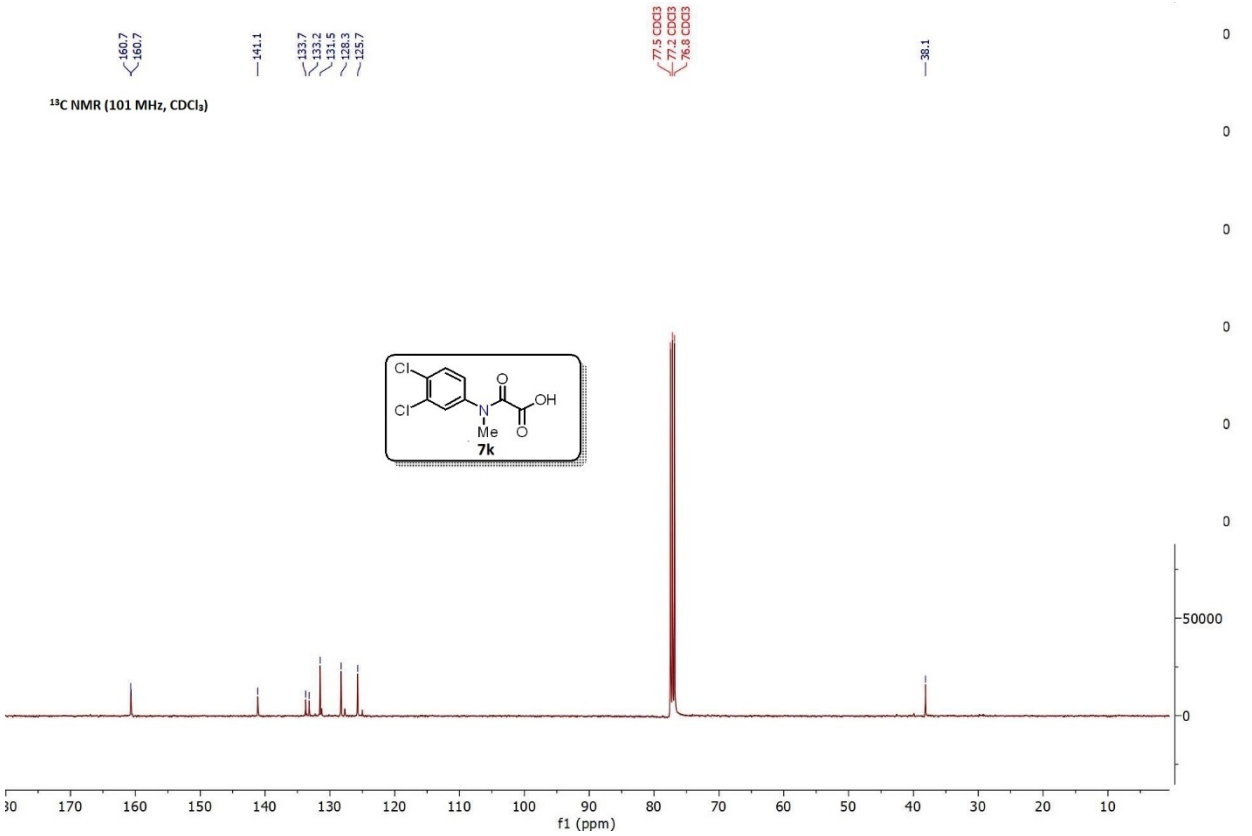


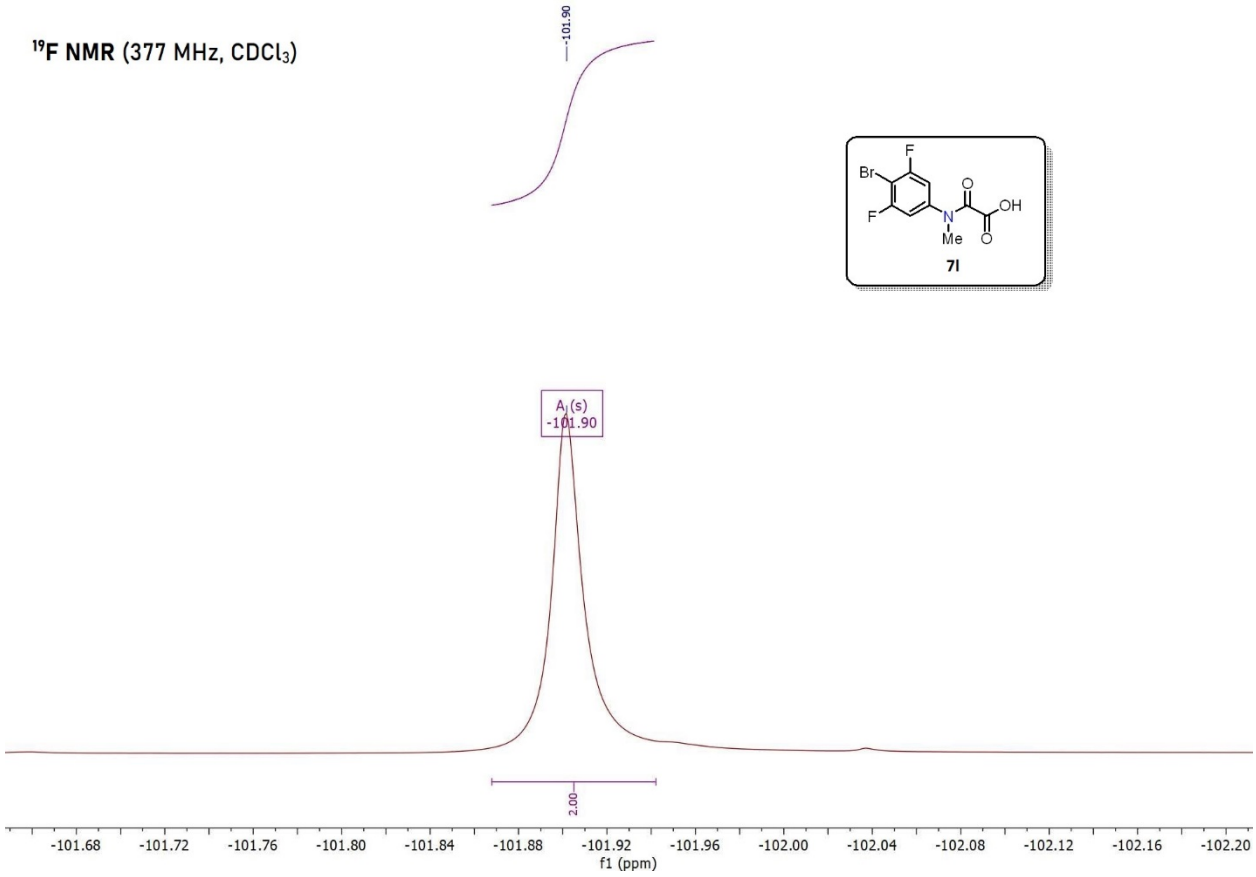
^{1}H NMR (300 MHz, $CDCl_3$)

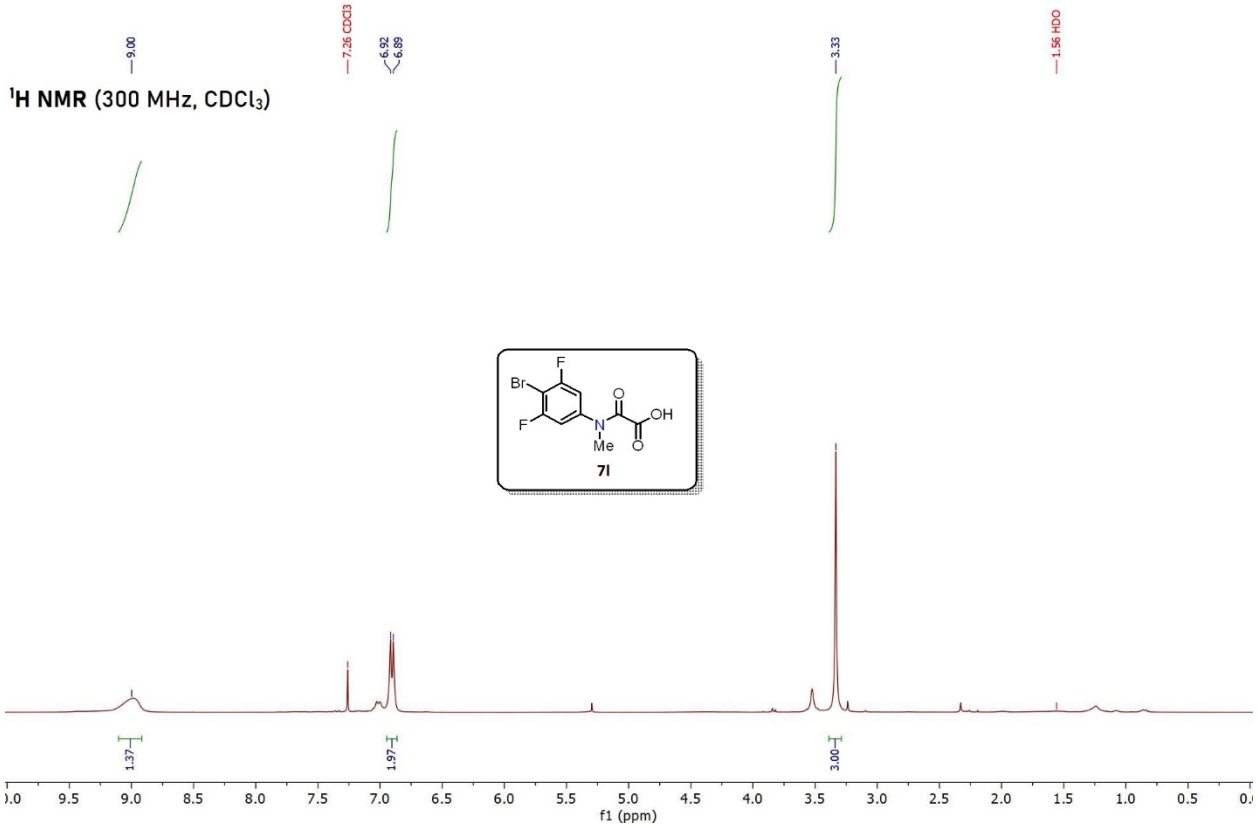


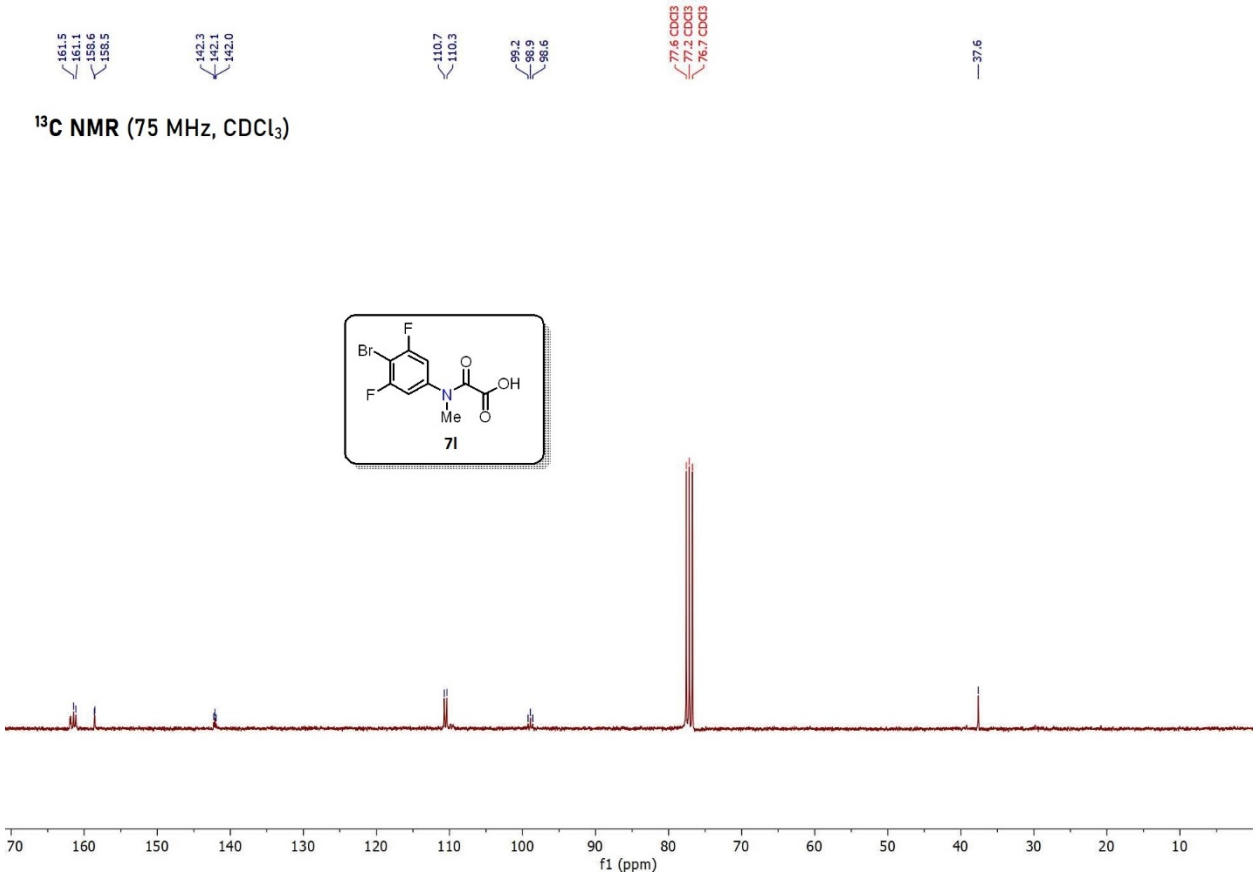
7k

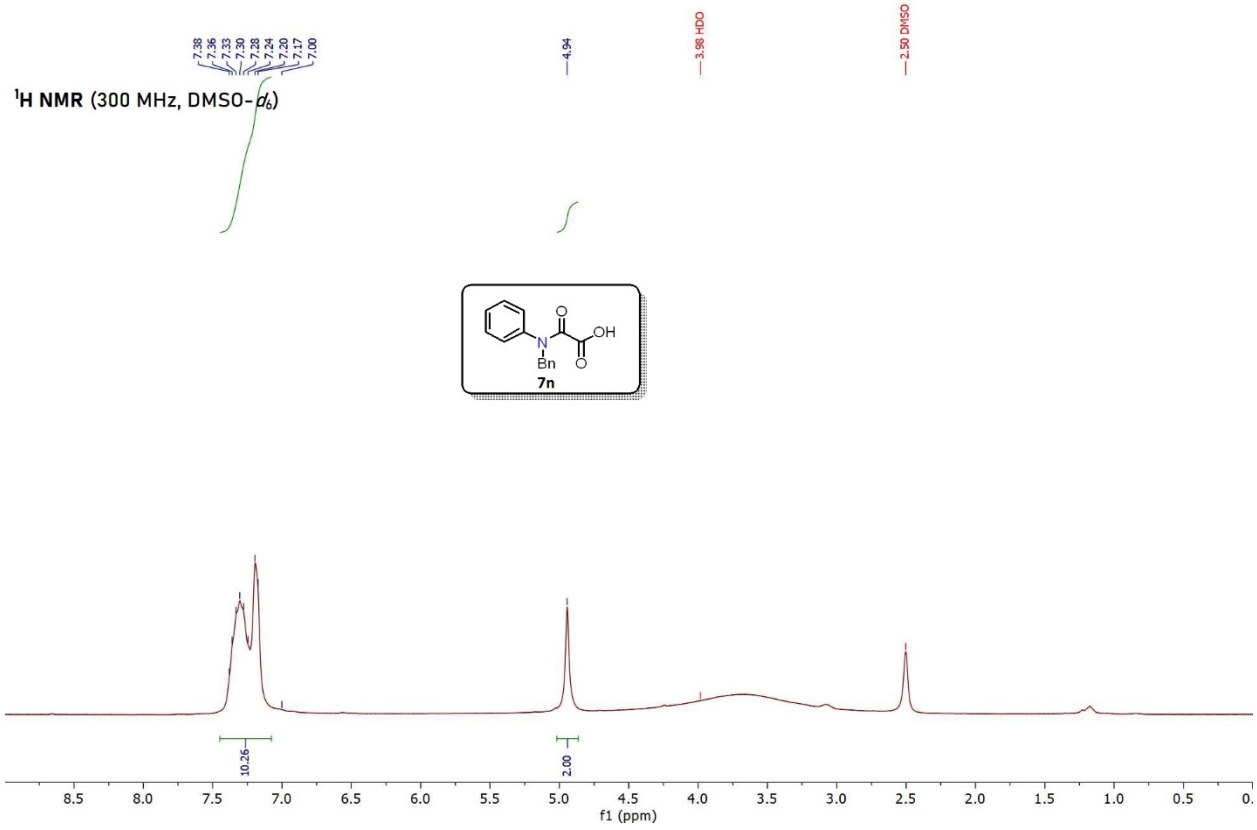


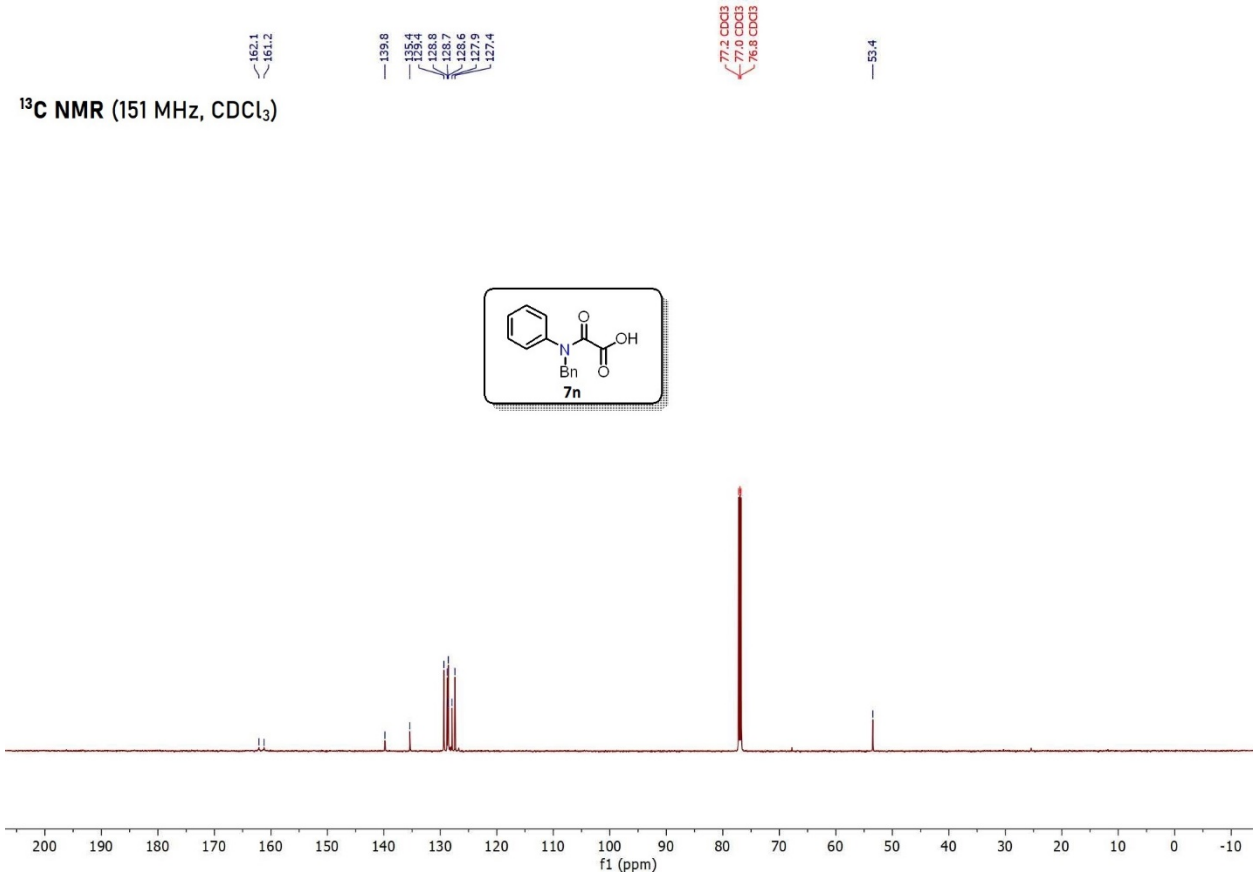

160.7
160.7
141.1
133.7
133.2
131.5
128.3
125.7
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
38.1
13C NMR (101 MHz, CDCl3)
Cl
Cl
N
Me
O
OH
O
7k
50000
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

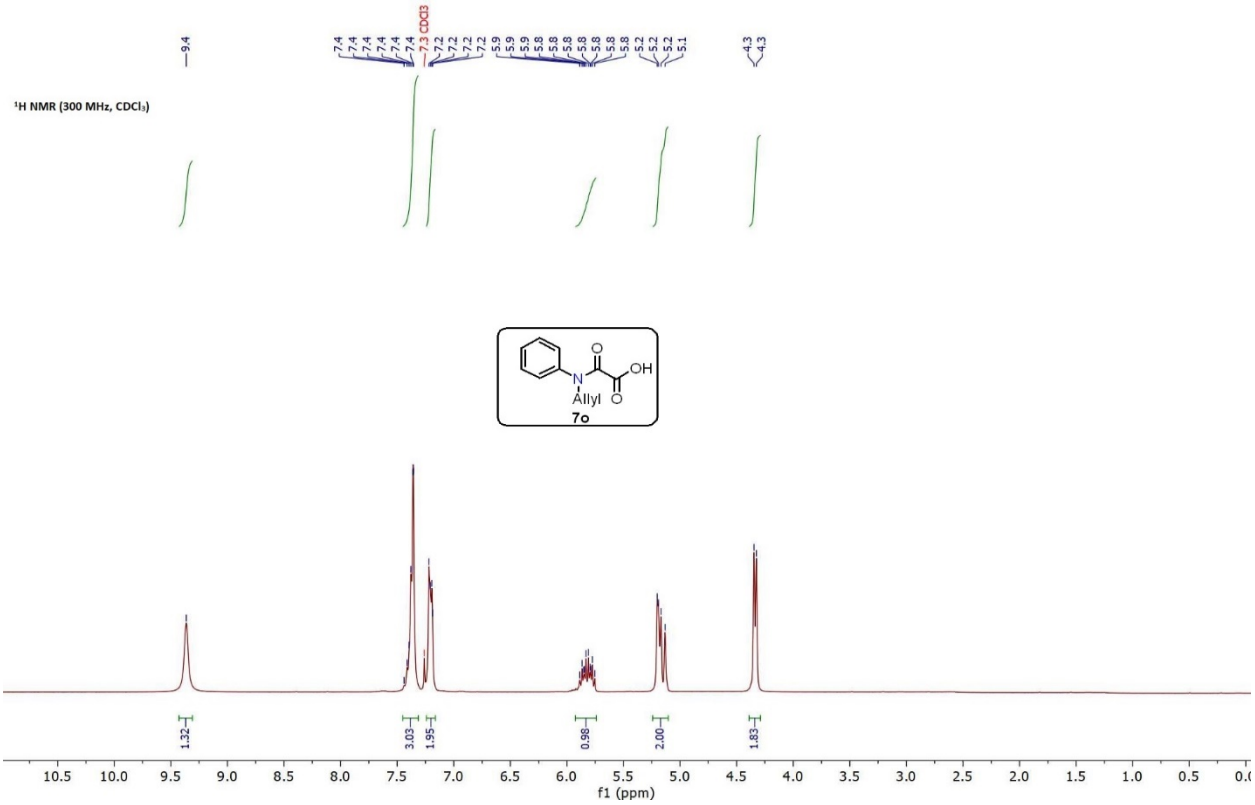

19F NMR (377 MHz, CDCl3)
-101.90
F
Br
F
N
Me
O
OH
O
7l
A (s)
-101.90
2.00
-101.68
-101.72
-101.76
-101.80
-101.84
-101.88
-101.92
-101.96
-102.00
-102.04
-102.08
-102.12
-102.16
-102.20
f1 (ppm)

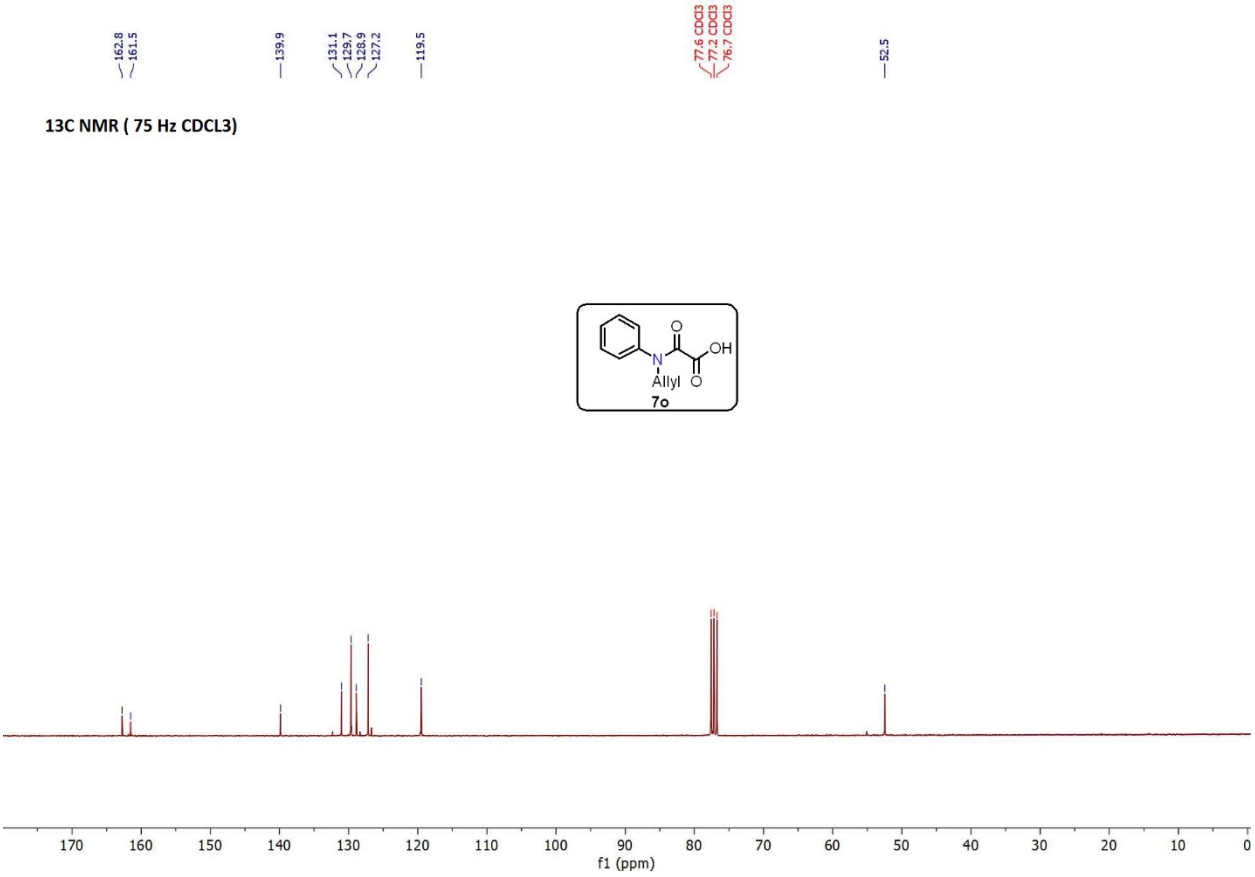

9.00
7.26 CDCl3
6.92
6.89
3.33
1.56 H2O
1H NMR (300 MHz, CDCl3)
F
Br
F
N
Me
O
OH
O
7l
1.37
1.97
3.00
f1 (ppm)

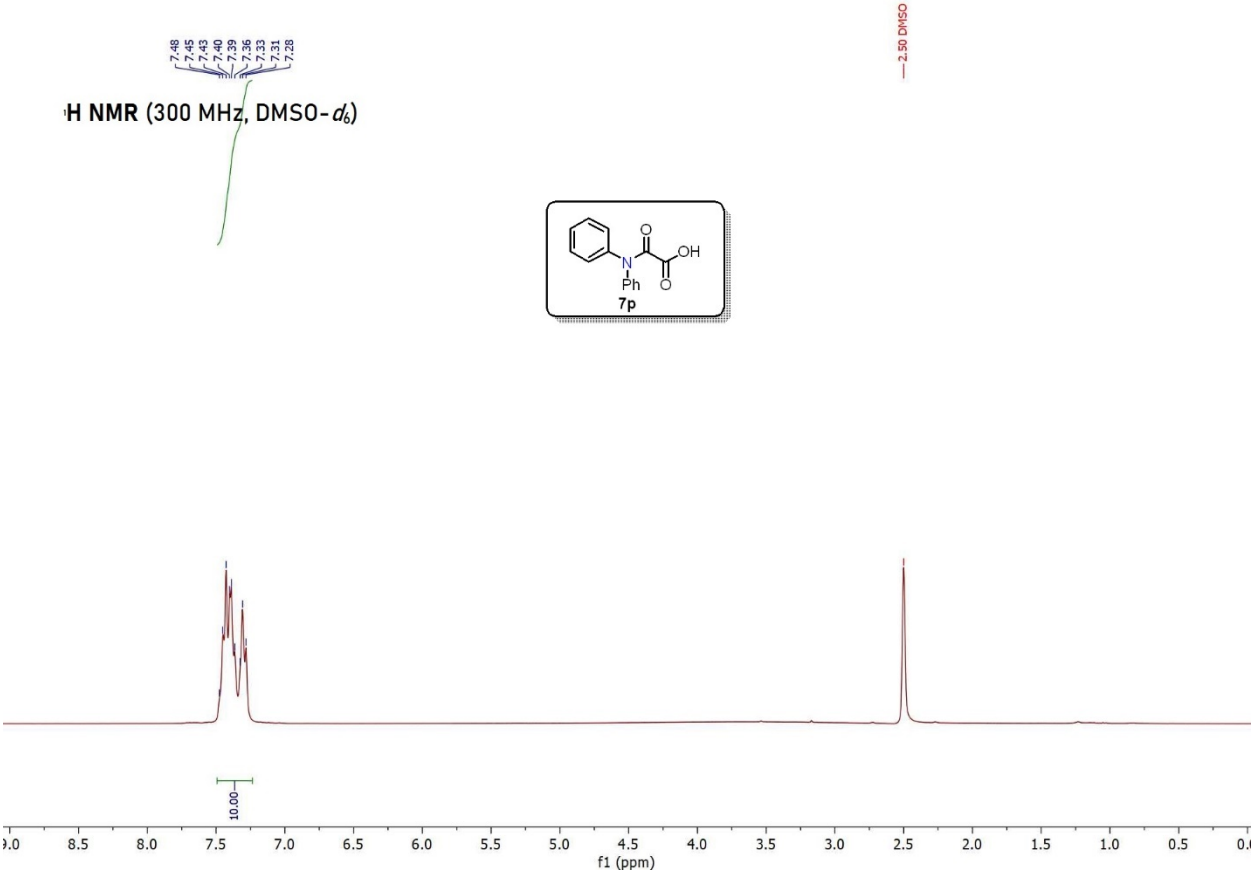

161.5
161.1
158.6
158.5
142.3
142.1
142.0
110.7
110.3
99.2
98.9
98.6
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
37.6
13C NMR (75 MHz, CDCl3)
F
Br
F
N
Me
O
OH
O
7l
f1 (ppm)


7.38
7.36
7.33
7.30
7.28
7.24
7.20
7.17
7.00
4.94
3.98 HDO
2.50 DMSO
1H NMR (300 MHz, DMSO-d6)
OH
N
Bn
O
7n
10.26
2.00
f1 (ppm)

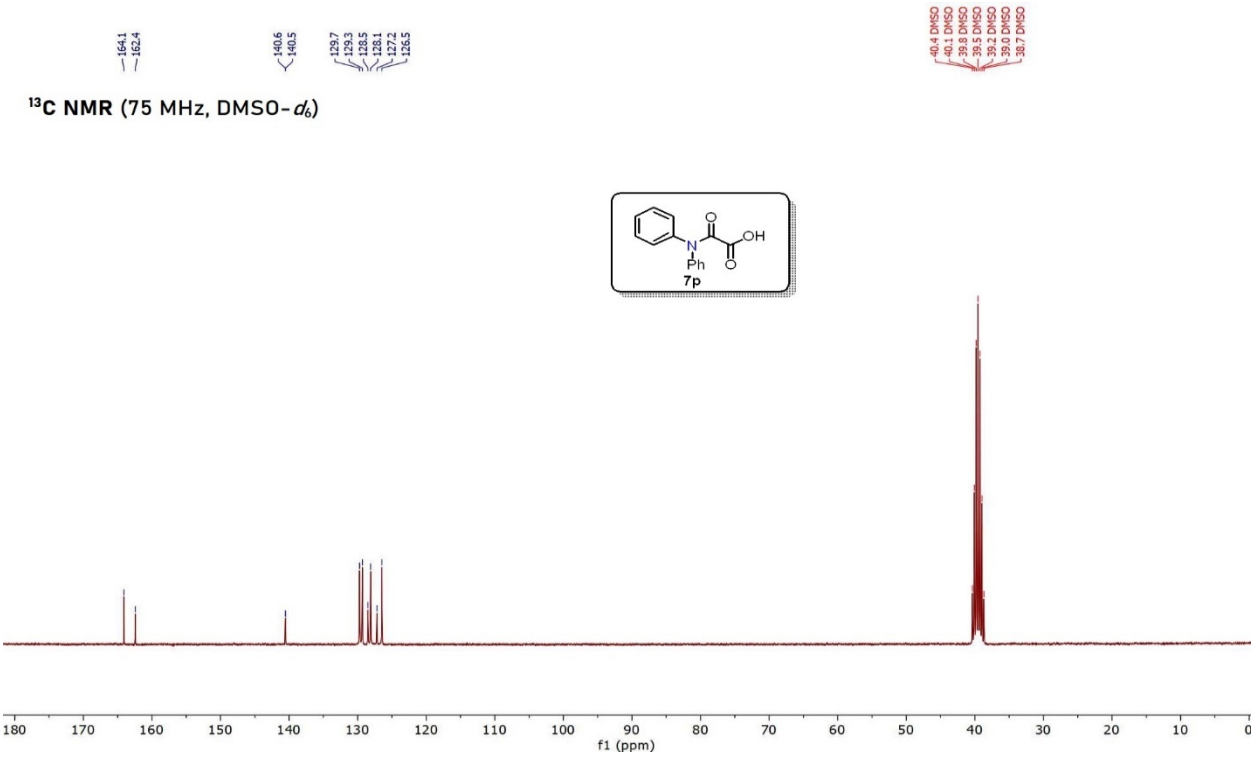

162.1
161.2
139.8
135.4
129.4
128.8
128.7
128.6
127.9
127.4
77.2 CDCl3
77.0 CDCl3
76.8 CDCl3
53.4
13C NMR (151 MHz, CDCl3)
OH
N
Bn
O
7n
f1 (ppm)


¹H NMR (300 MHz, CDCl₃)
9.4
7.4
7.4
7.4
7.4
7.4
7.4
7.3 CDCl3
7.2
7.2
7.2
7.2
5.9
5.9
5.9
5.8
5.8
5.8
5.8
5.8
5.8
5.2
5.2
5.2
5.1
4.3
4.3
N
OH
O
O
Allyl
7o
1.32
3.03
1.95
0.98
2.00
1.83
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
f1 (ppm)

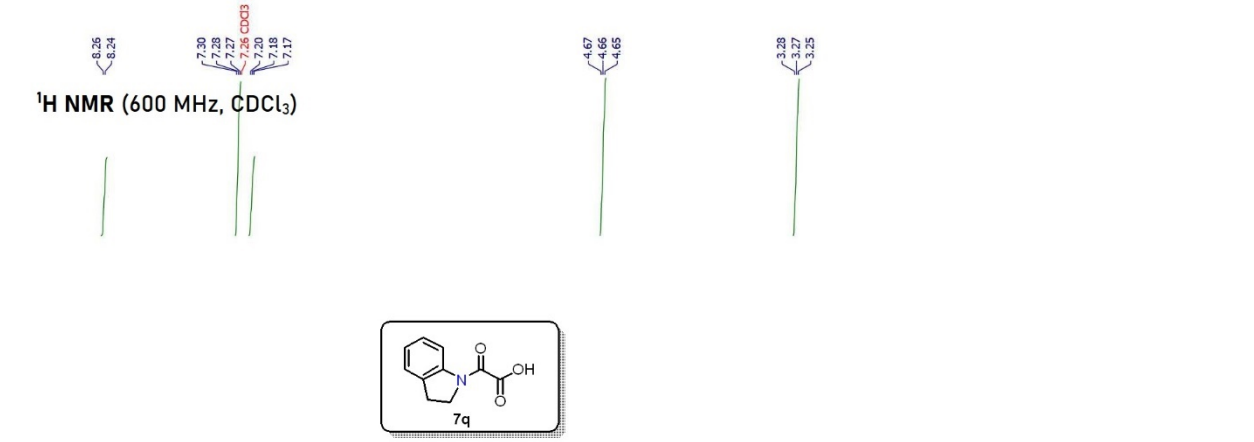

162.8
161.5
139.9
131.1
129.7
128.9
127.2
119.5
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
52.5
13C NMR (75 Hz CDCL3)
N
OH
O
O
Allyl
7o
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

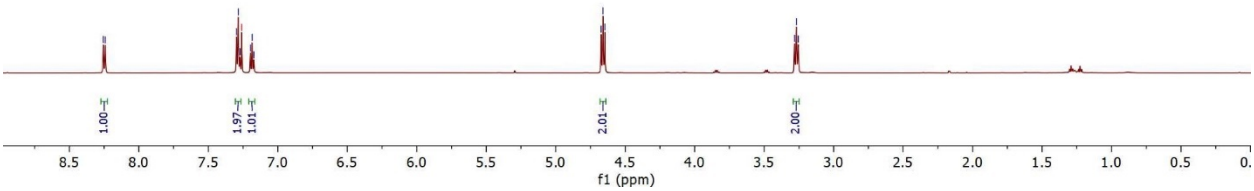


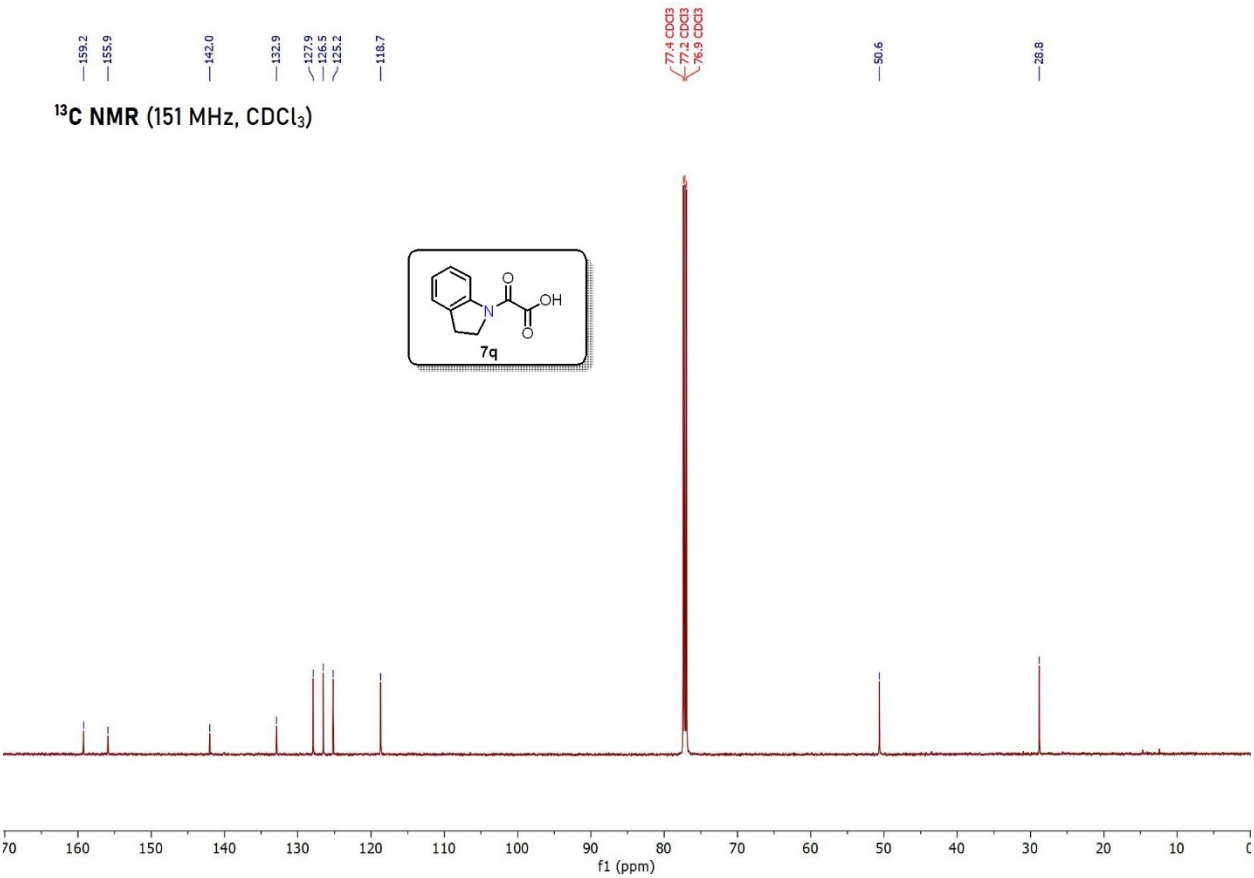
H NMR (300 MHz, DMSO-d_6)



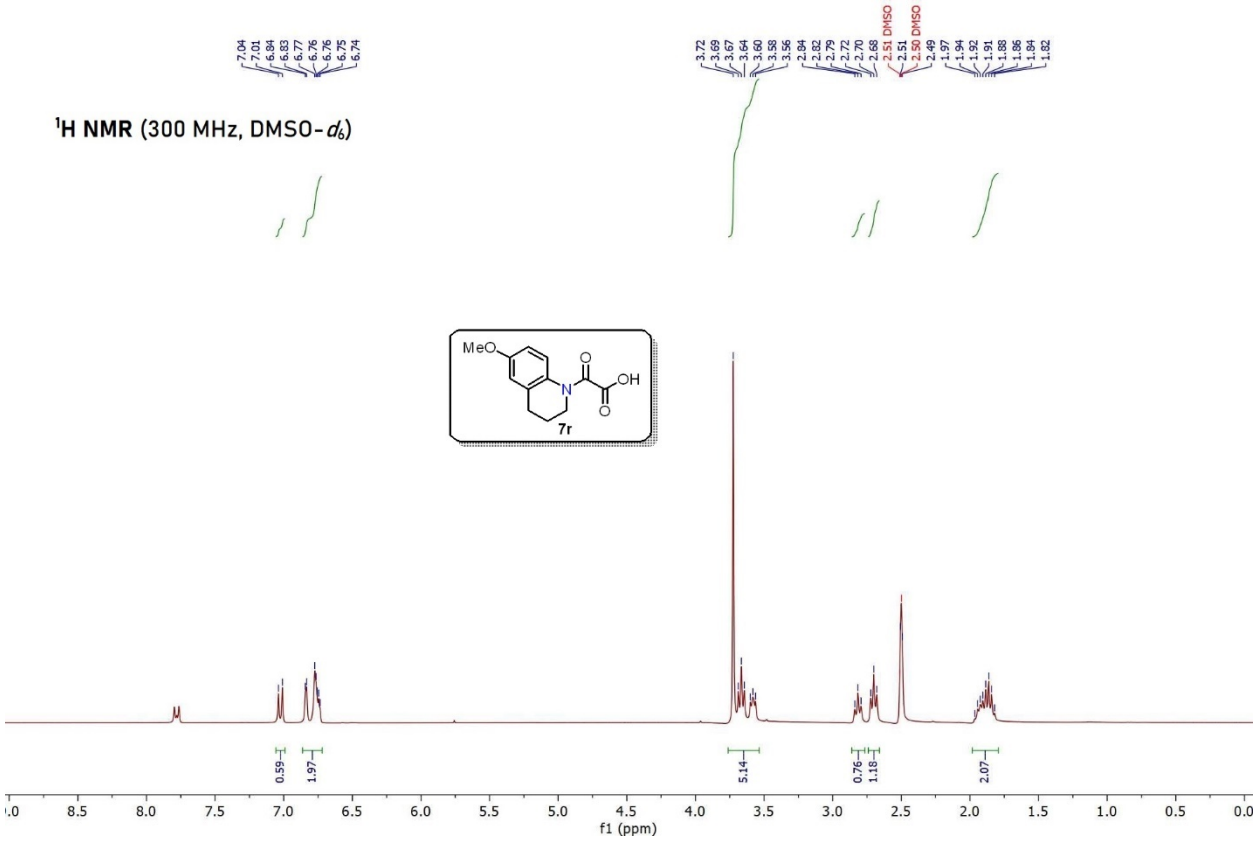
^{13}C NMR (75 MHz, DMSO-d_6)


8.26
8.24
7.30
7.28
7.27
7.26 CDCl3
7.20
7.18
7.17
4.67
4.66
4.65
3.28
3.27
3.25
1H NMR (600 MHz, CDCl3)
OH
N
O
O
7q

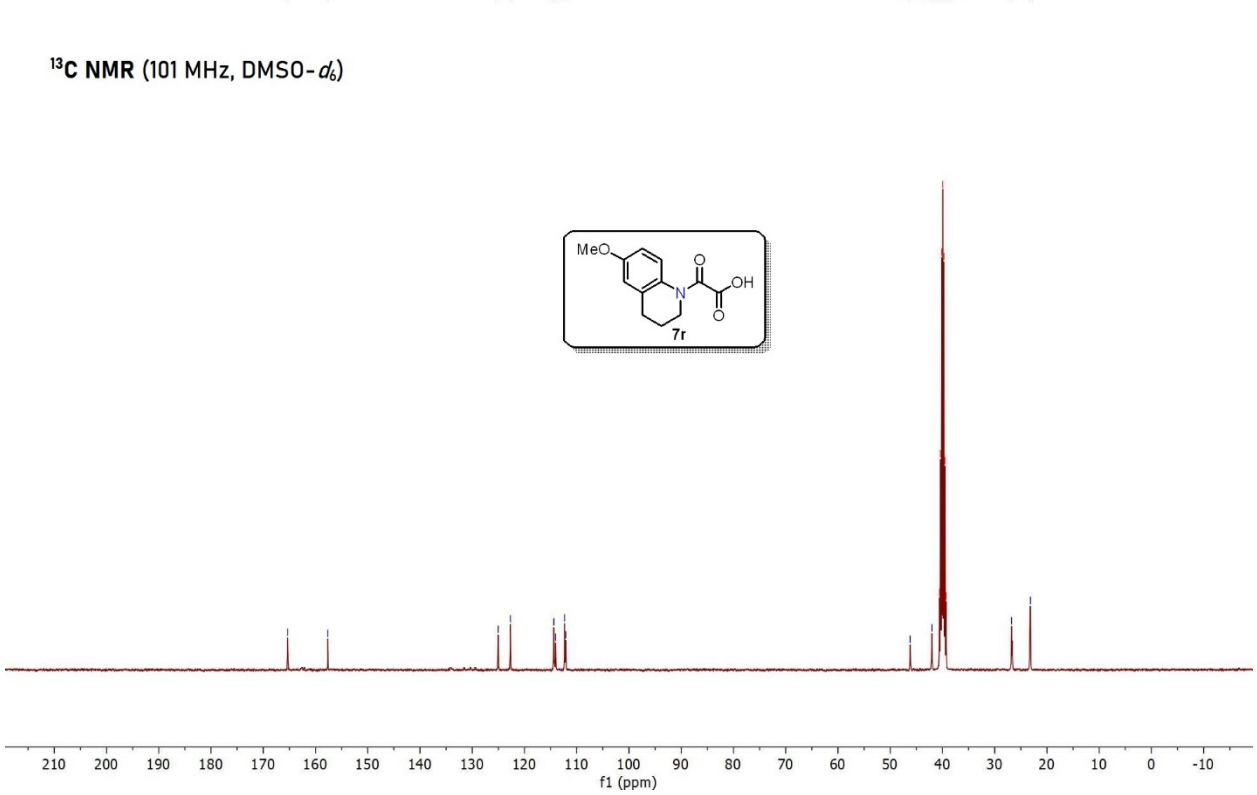

1.00
1.97
1.01
2.01
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

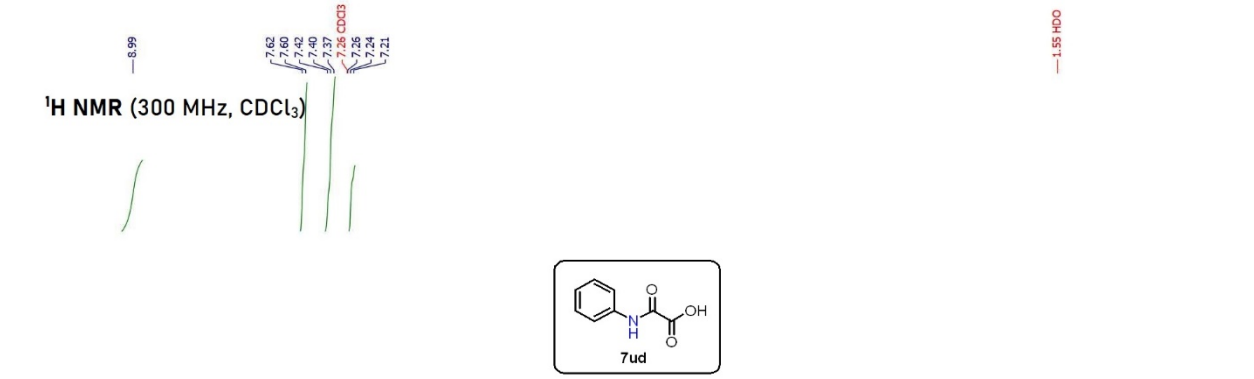

159.2
155.9
142.0
132.9
127.9
126.5
125.2
118.7
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
50.6
28.8
13C NMR (151 MHz, CDCl3)
OH
N
O
O
7q
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

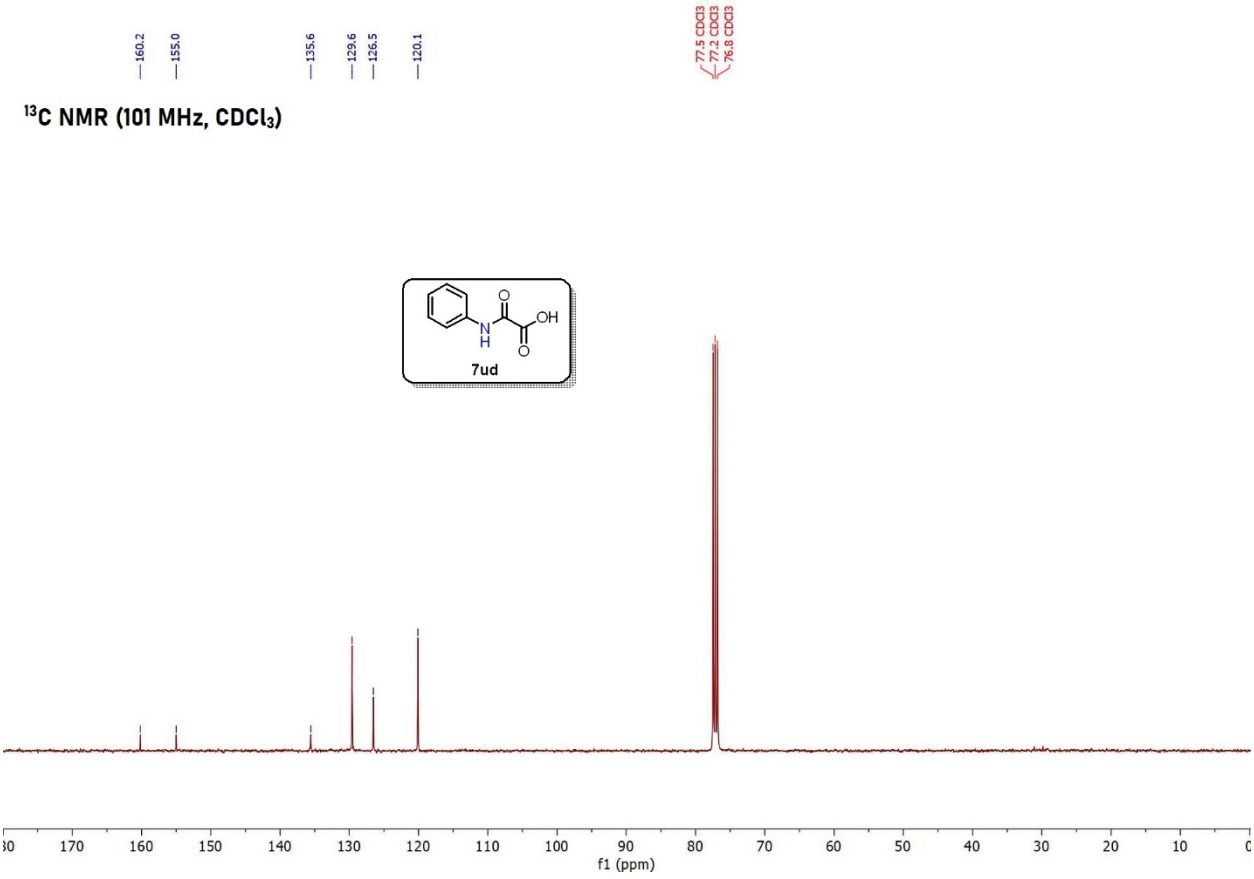
^{1}H NMR (300 MHz, DMSO-d_6)



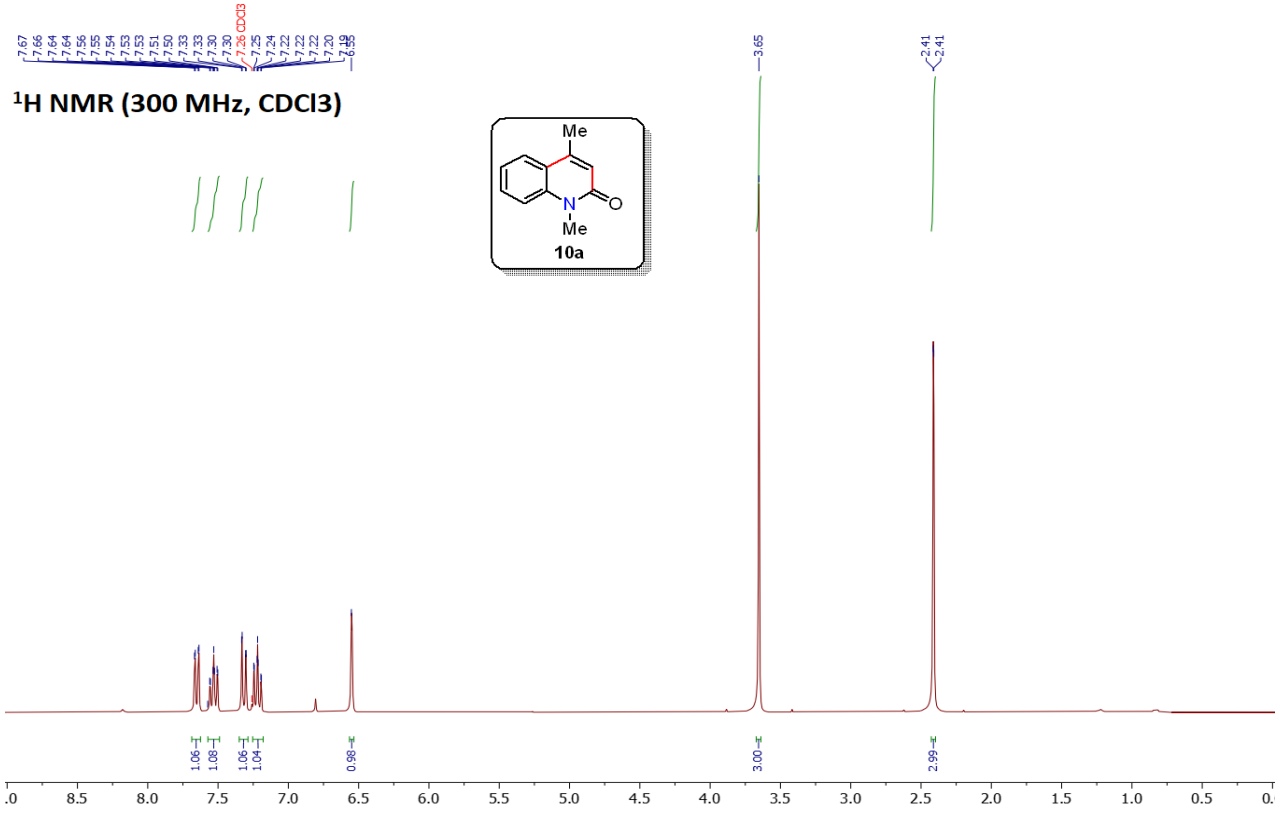
^{13}C NMR (101 MHz, DMSO-d_6)



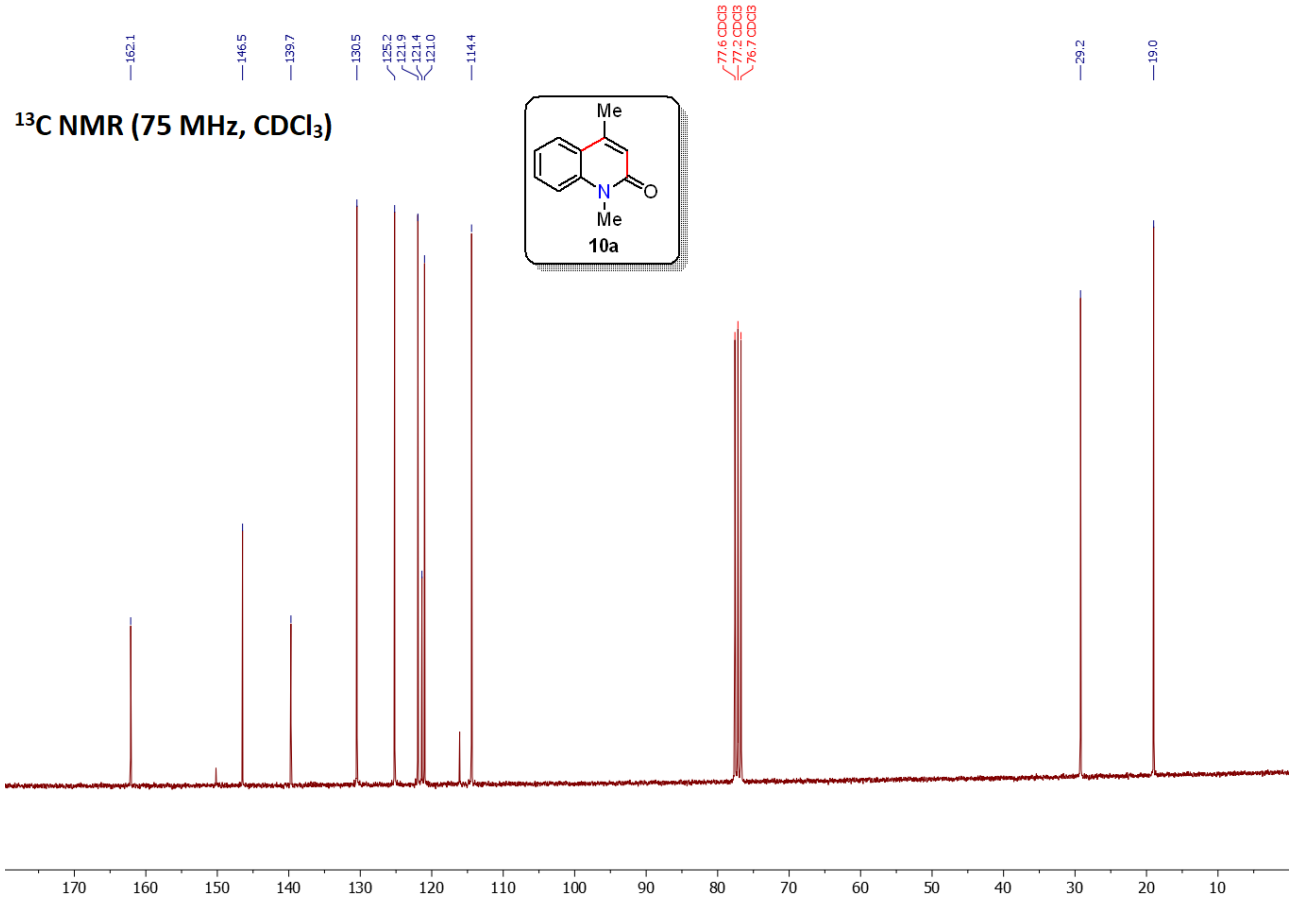

8.99
7.62
7.60
7.42
7.40
7.37
7.26 CDCl3
7.26
7.24
7.21
1.55 HDO
1H NMR (300 MHz, CDCl3)
7ud
1.00
2.08
2.16
0.92
f1 (ppm)

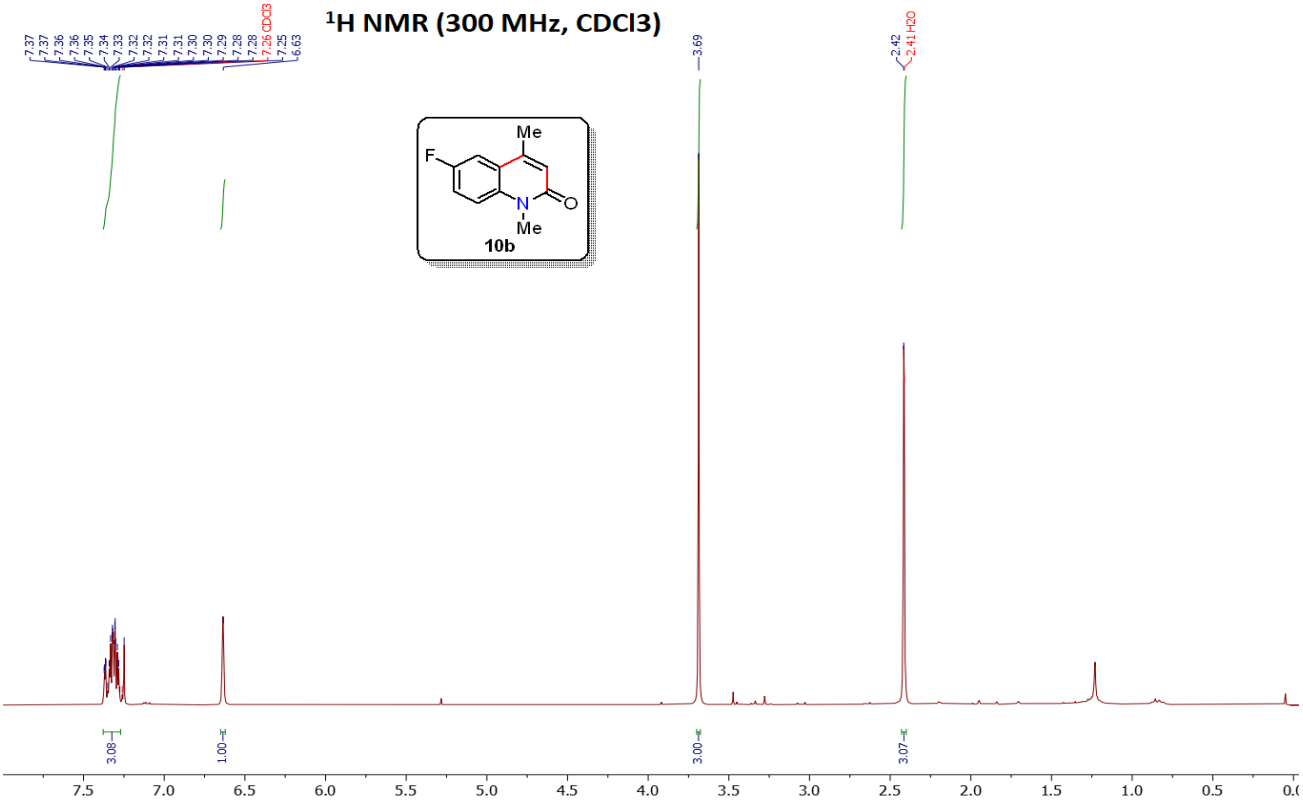

160.2
155.0
135.6
129.6
126.5
120.1
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
13C NMR (101 MHz, CDCl3)
7ud
f1 (ppm)

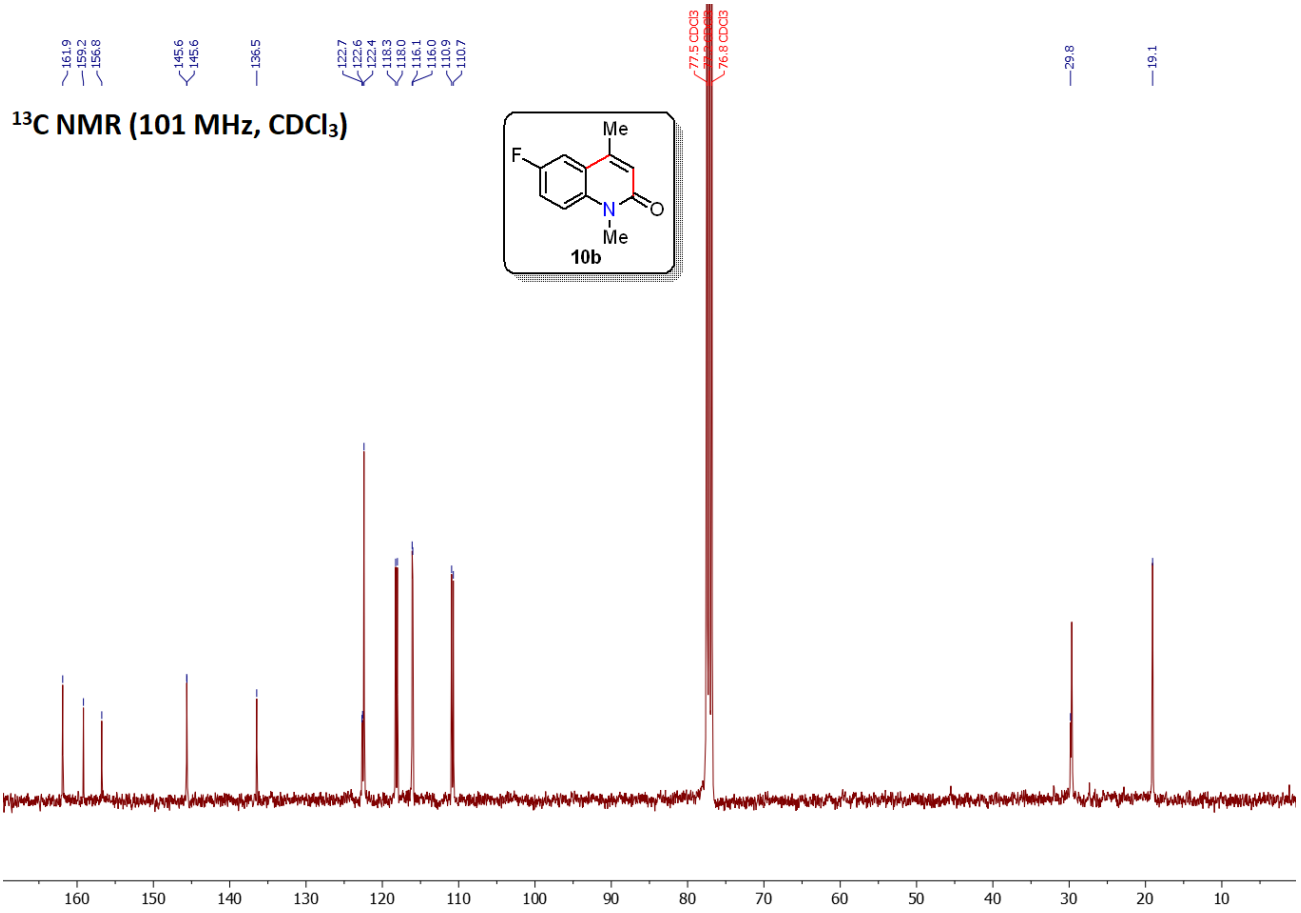
^{1}H NMR (300 MHz, CDCl3)



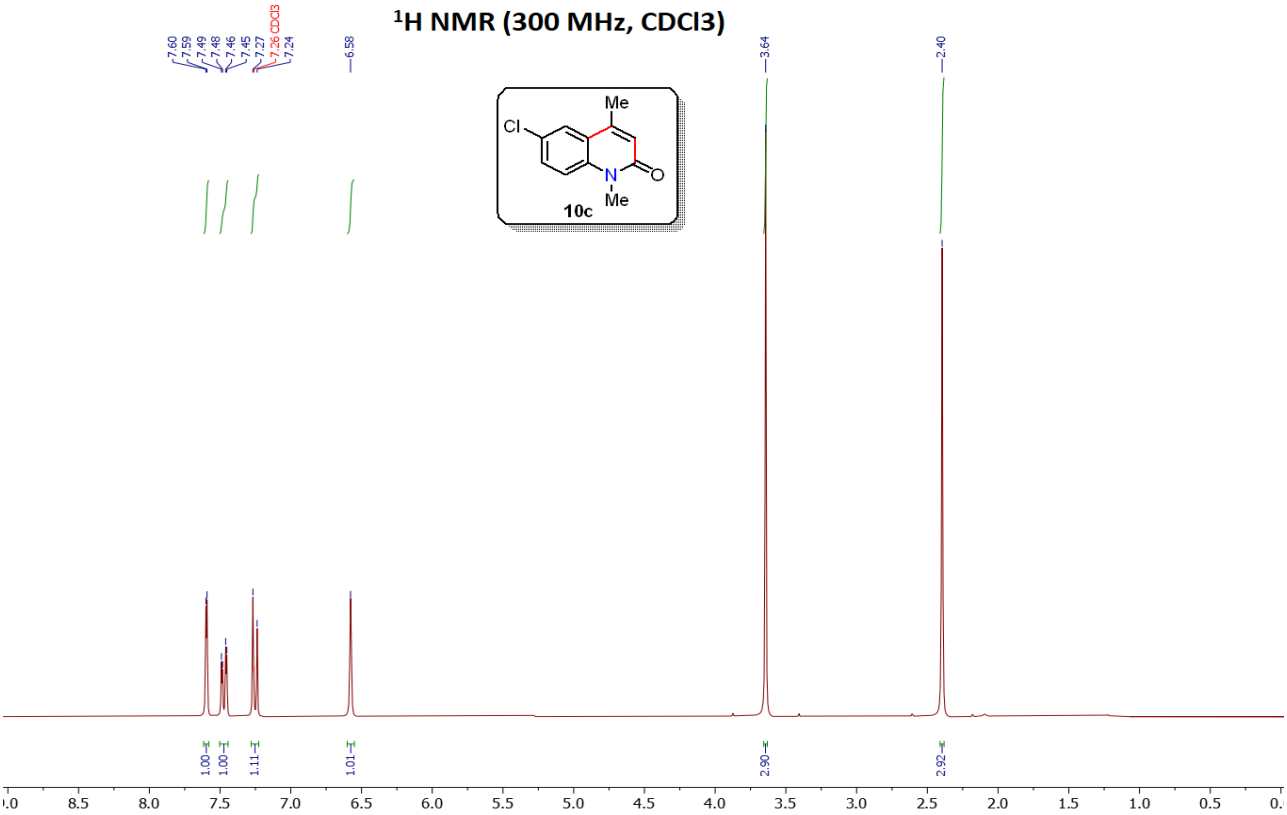
^{13}C NMR (75 MHz, $CDCl_3$)



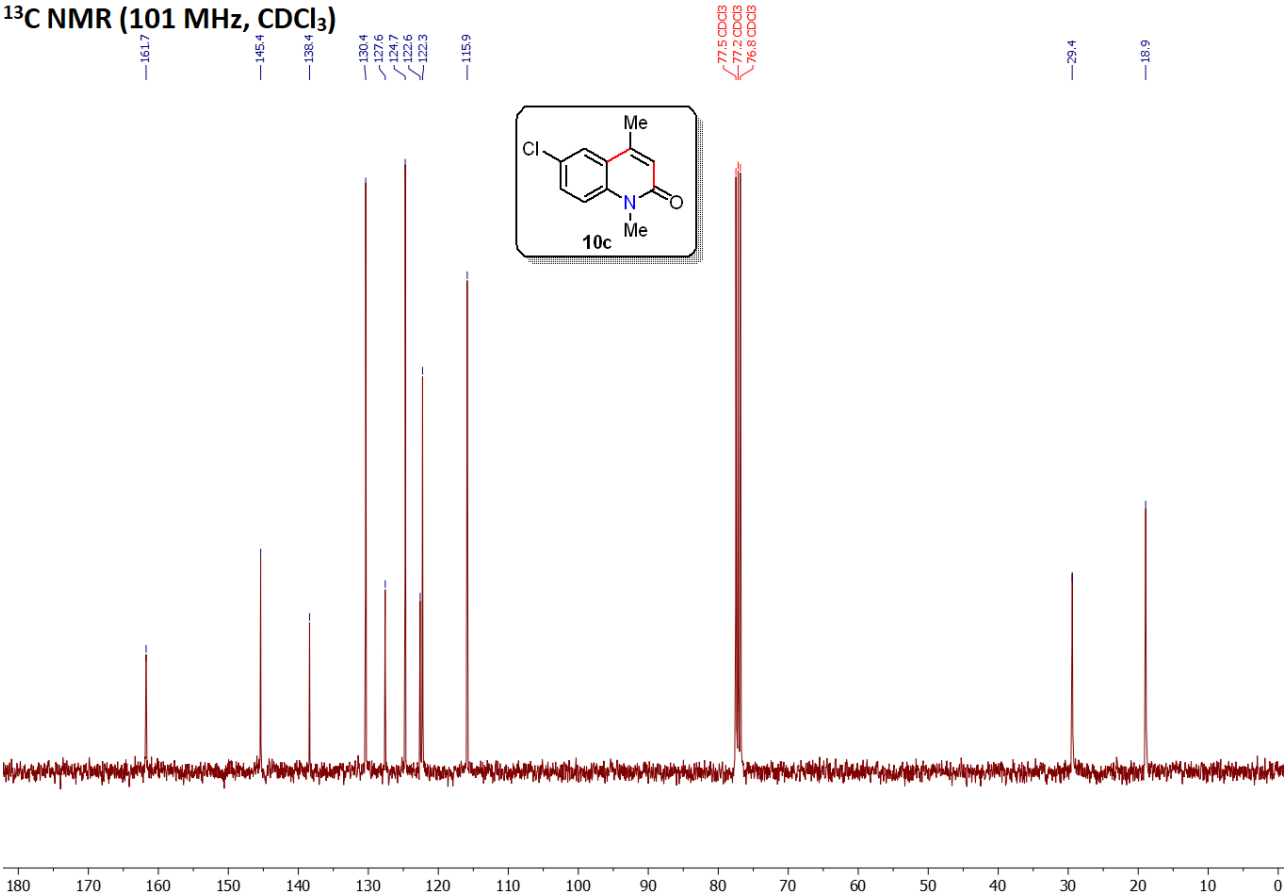

^{1}H NMR (300 MHz, CDCl3)
Me
F
N
O
Me
10b
7.37
7.37
7.36
7.36
7.35
7.34
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.28
7.26 CDCl3
7.25
6.63
3.69
2.42
2.41 H2O
3.08
1.00
3.00
3.07
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

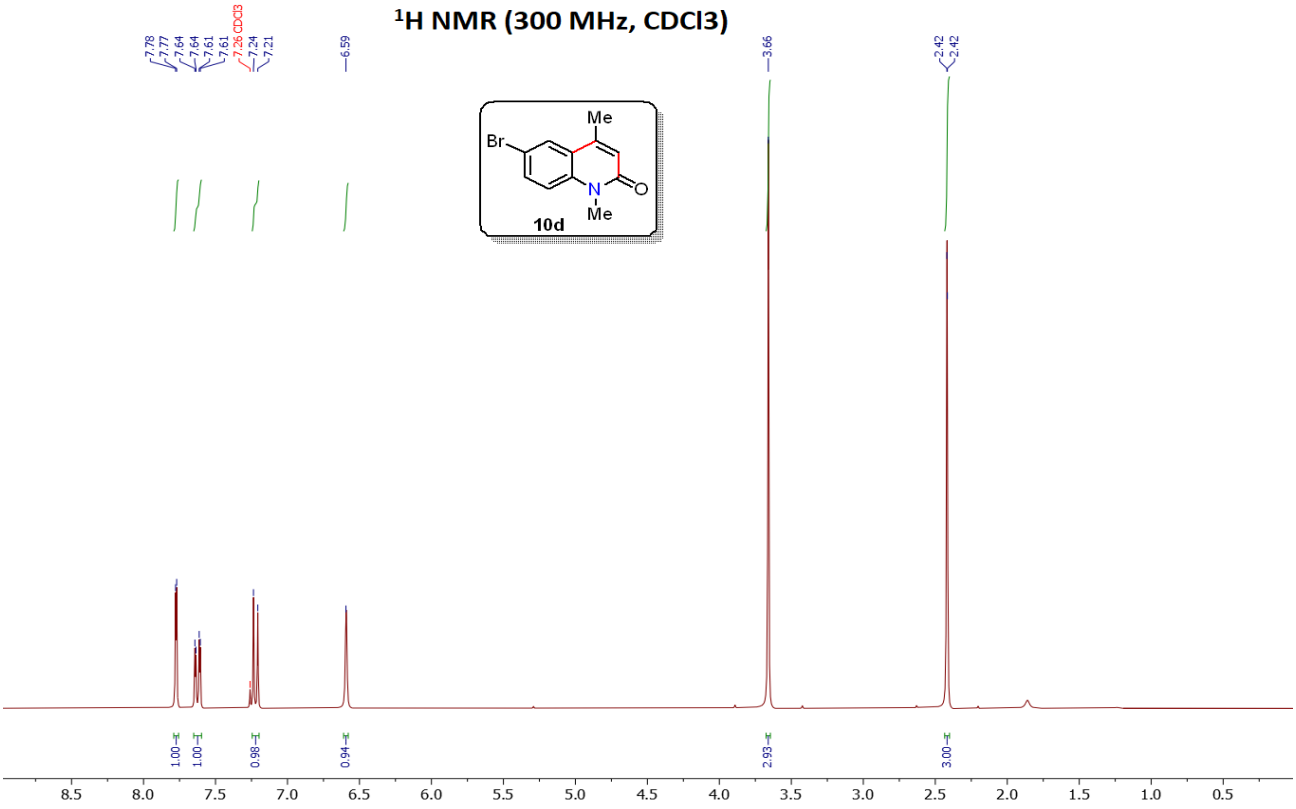

^{13}C NMR (101 MHz, CDCl$_3$)
Me
F
N
O
Me
10b
161.9
159.2
156.8
145.6
145.6
136.5
122.7
122.6
122.4
118.3
118.0
116.1
116.0
110.9
110.7
77.5 CDCl3
76.8 CDCl3
29.8
19.1
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

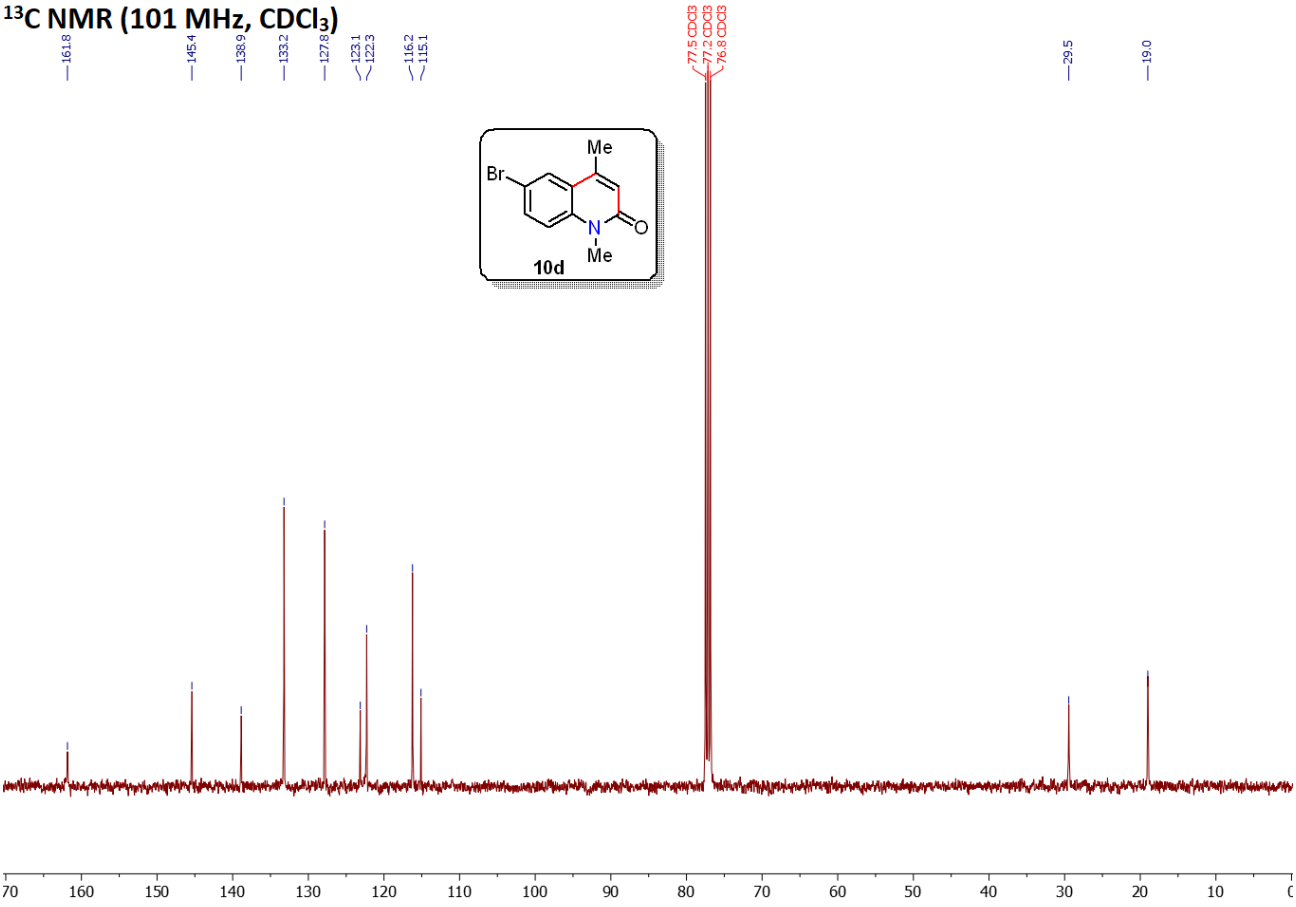
^{1}H NMR (300 MHz, CDCl3)



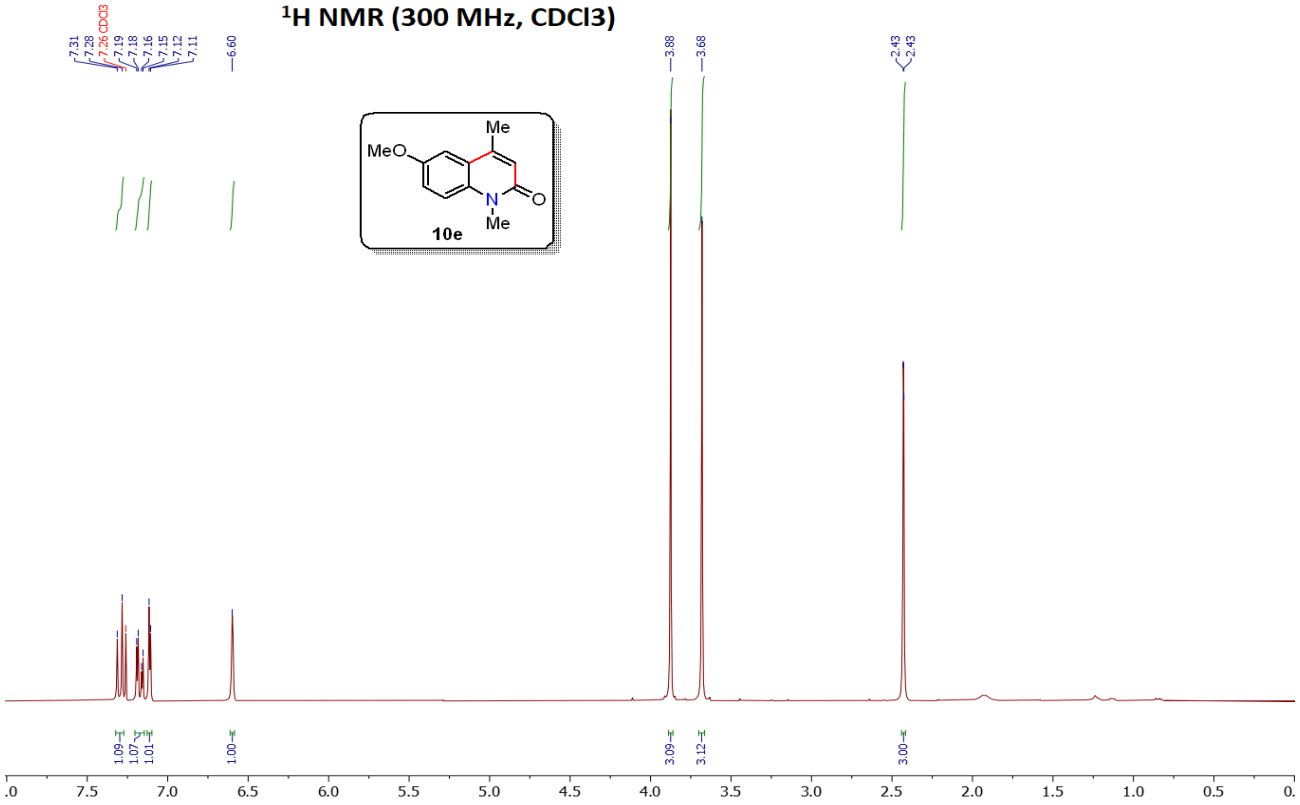
^{13}C NMR (101 MHz, $CDCl_3$)



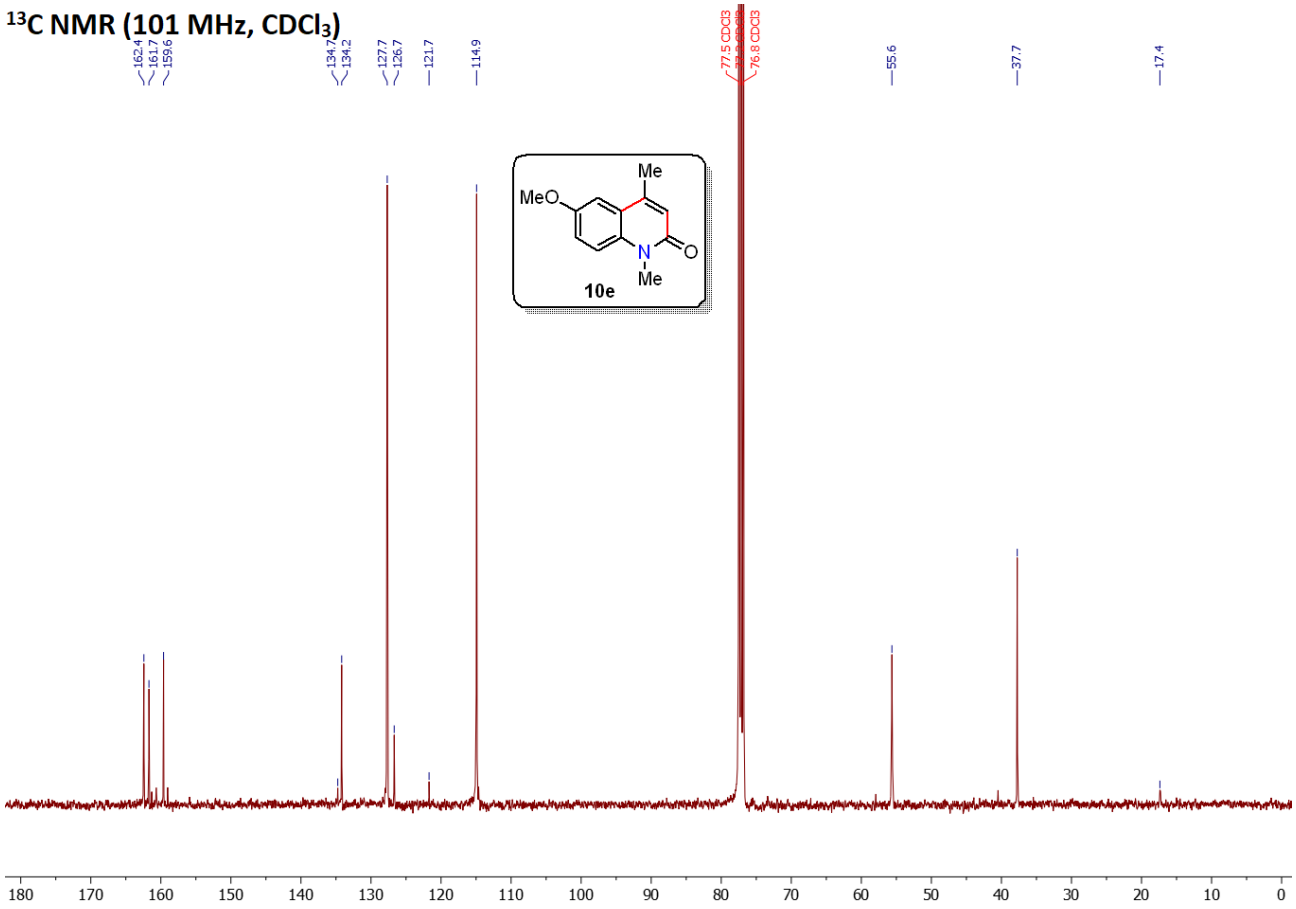

1H NMR (300 MHz, CDCl3)
7.78
7.77
7.64
7.64
7.61
7.61
7.26 CDCl3
7.24
7.21
6.59
3.66
2.42
2.42
Me
Br
N
O
Me
10d
1.00
1.00
0.98
0.94
2.93
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


13C NMR (101 MHz, CDCl3)
161.8
145.4
138.9
133.2
127.8
123.1
122.3
116.2
115.1
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
29.5
19.0
Me
Br
N
O
Me
10d
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

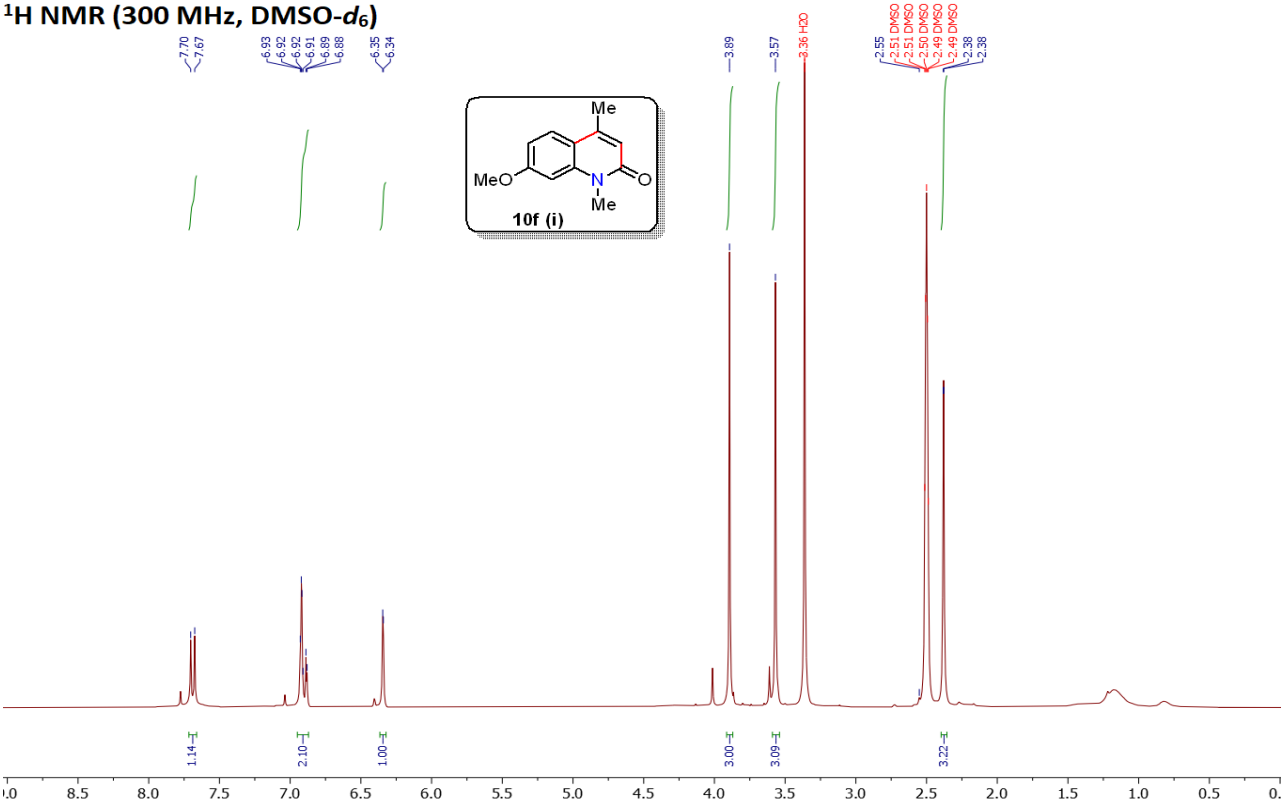
^{1}H NMR (300 MHz, CDCl3)



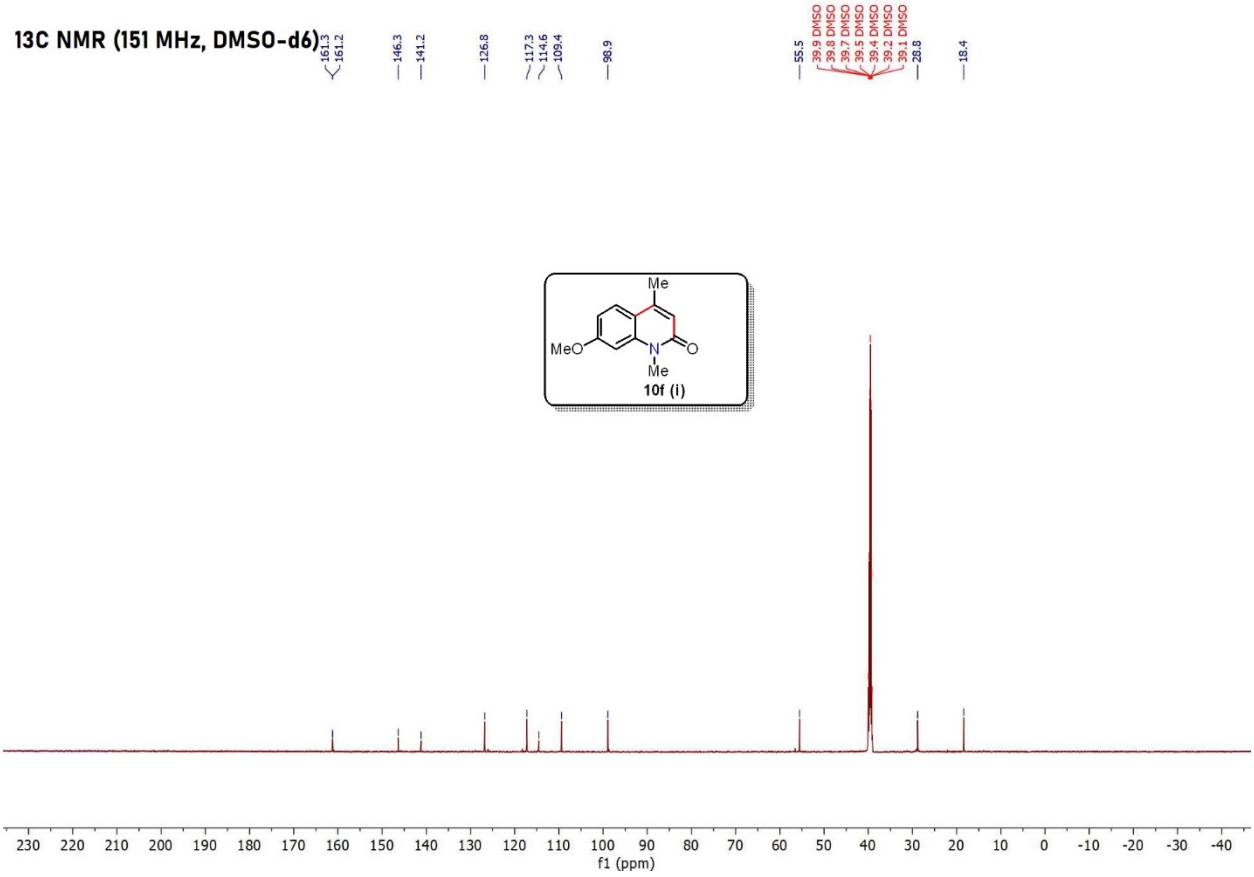
^{13}C NMR (101 MHz, $CDCl_3$)



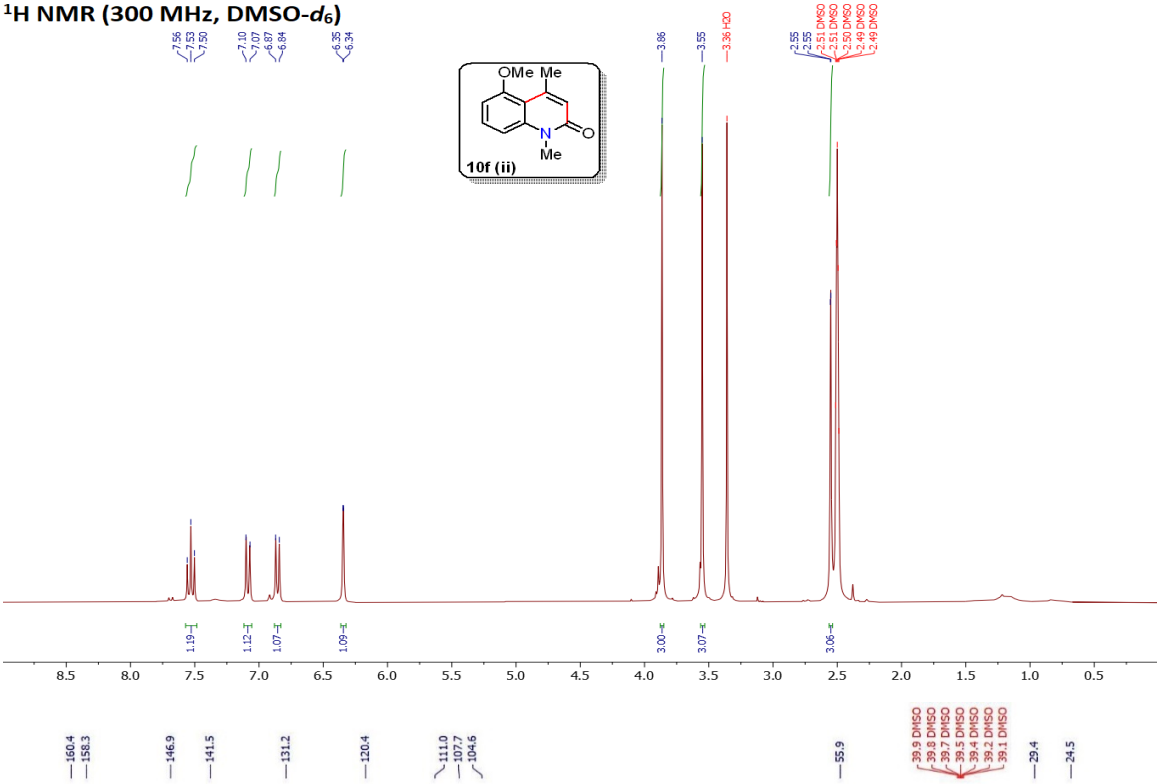
^{1}H NMR (300 MHz, DMSO-d_6)



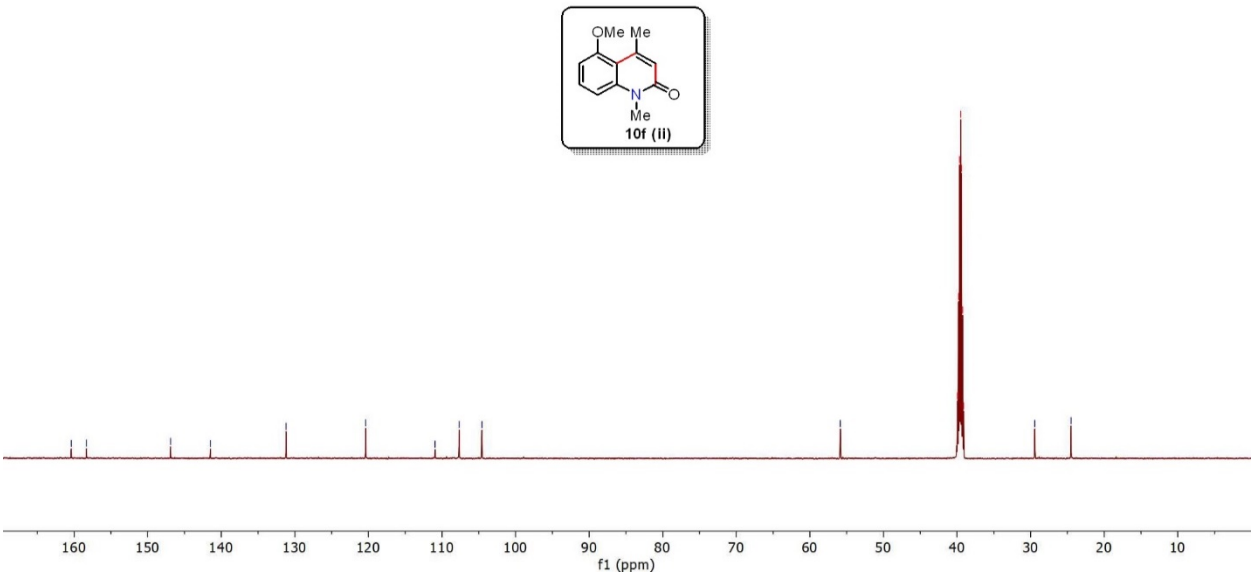
13C NMR (151 MHz, DMSO-d6)

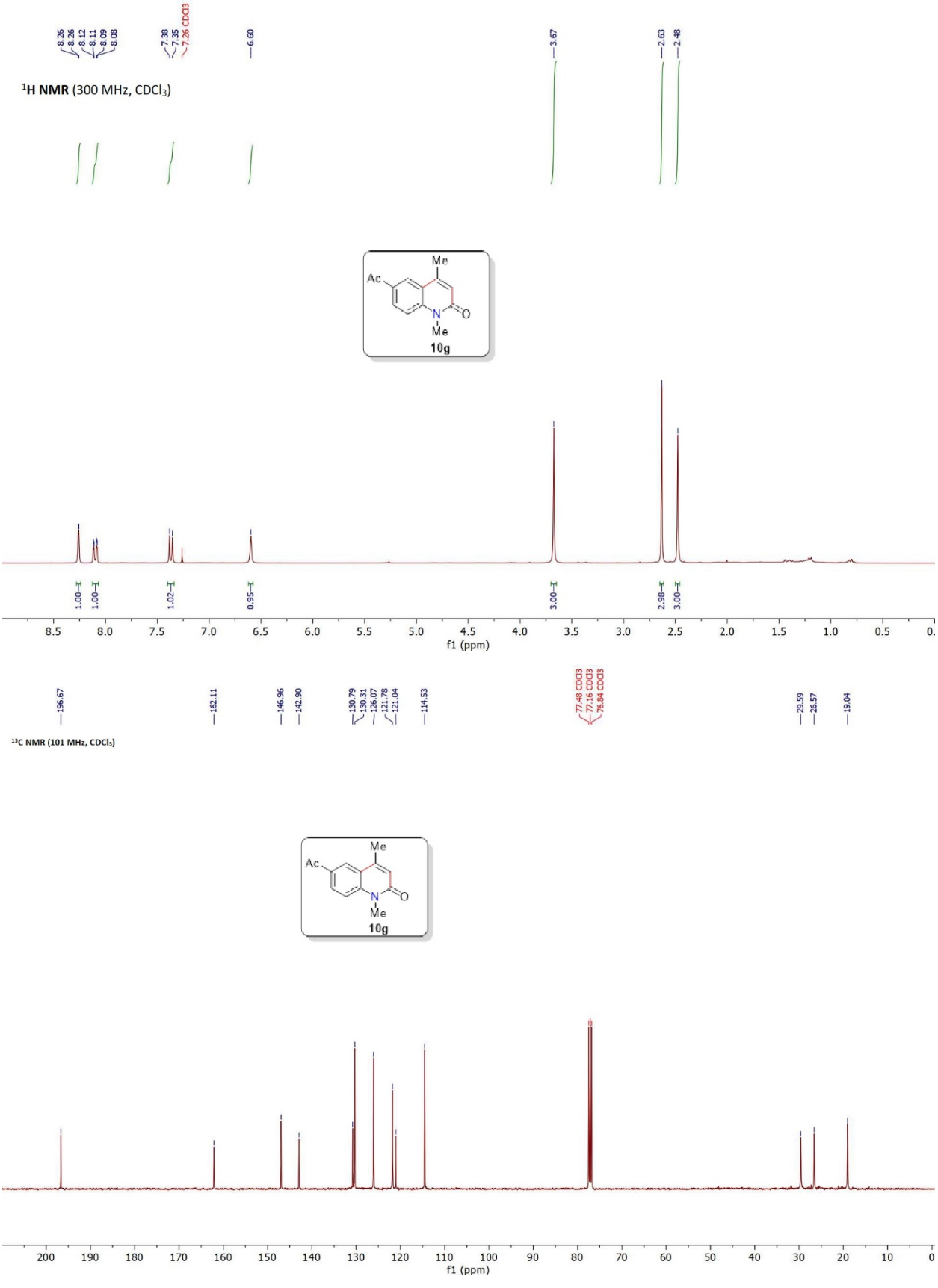


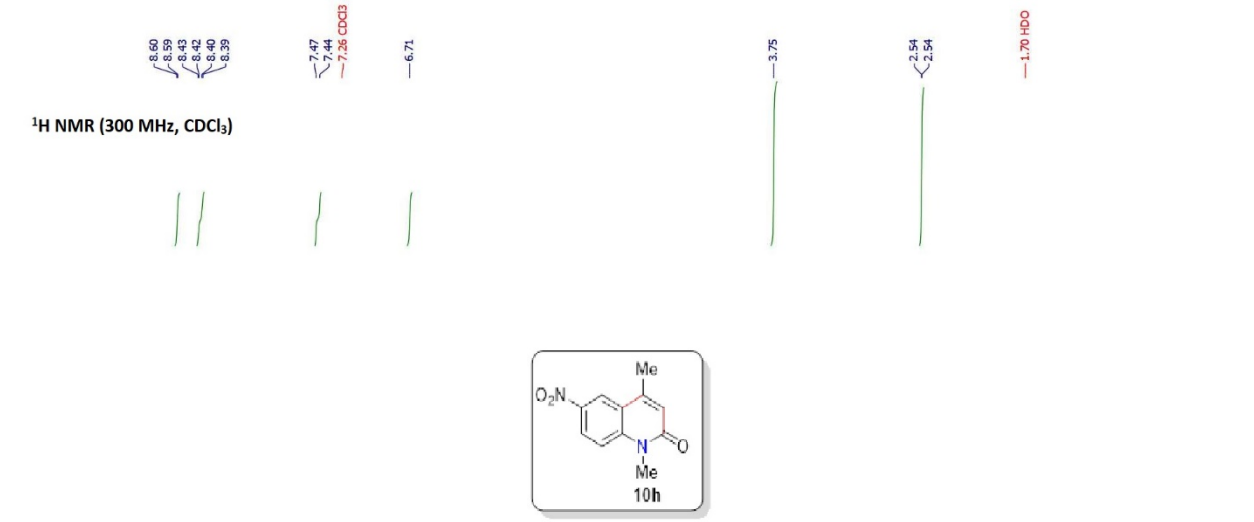
^{1}H NMR (300 MHz, DMSO-d_6)



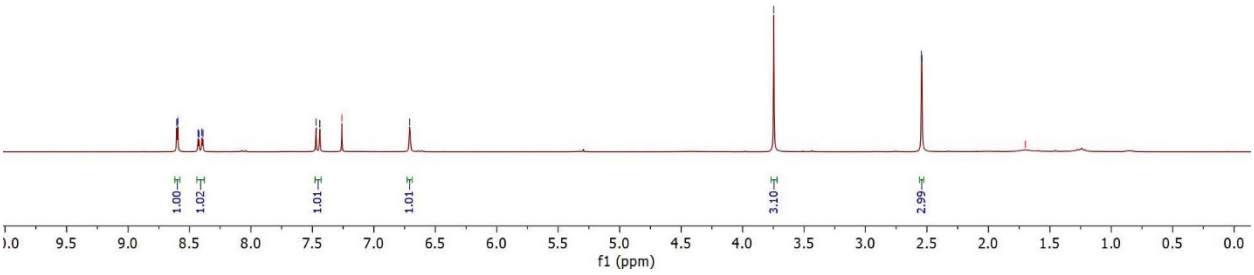
13C NMR (151 MHz, DMSO-d6)



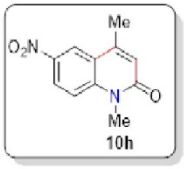

8.26
8.26
8.12
8.11
8.09
8.08
7.38
7.35
7.26 CDCl3
6.60
3.67
2.63
2.48
1H NMR (300 MHz, CDCl3)
Me
Ac
N
O
Me
10g
1.00
1.00
1.02
0.95
3.00
2.98
3.00
f1 (ppm)
196.67
162.11
146.96
142.90
130.79
130.31
126.07
121.78
121.04
114.53
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
29.59
26.57
19.04
13C NMR (101 MHz, CDCl3)
Me
Ac
N
O
Me
10g
f1 (ppm)

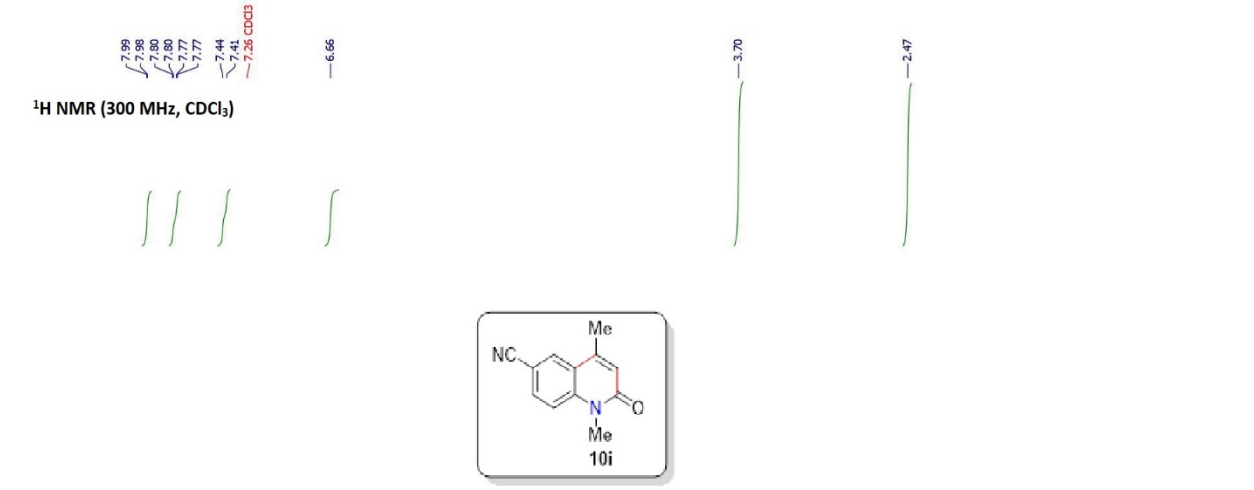


^{1}H NMR (300 MHz, $CDCl_3$)

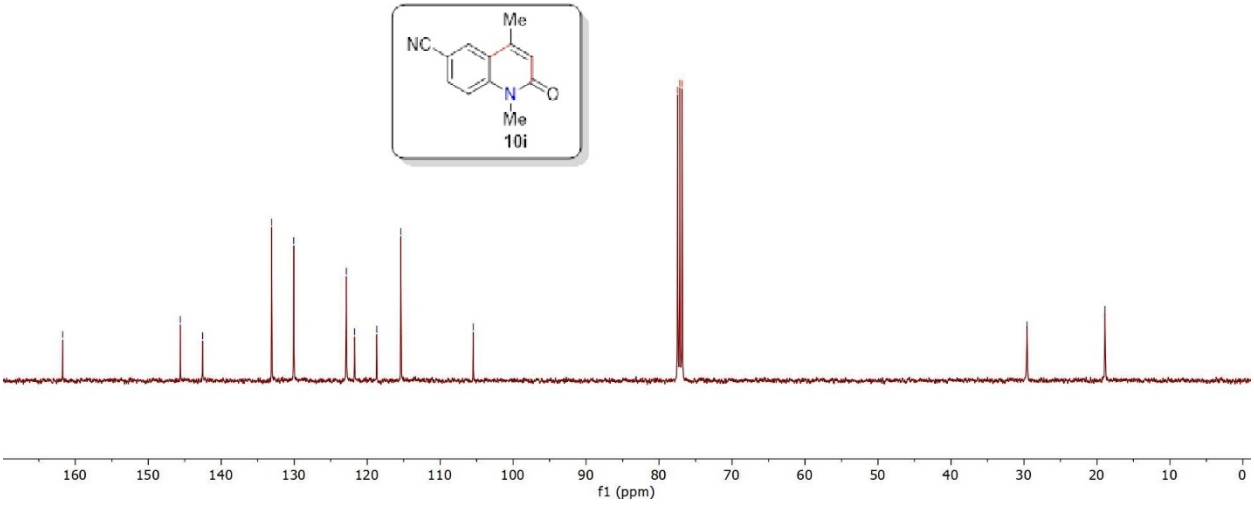


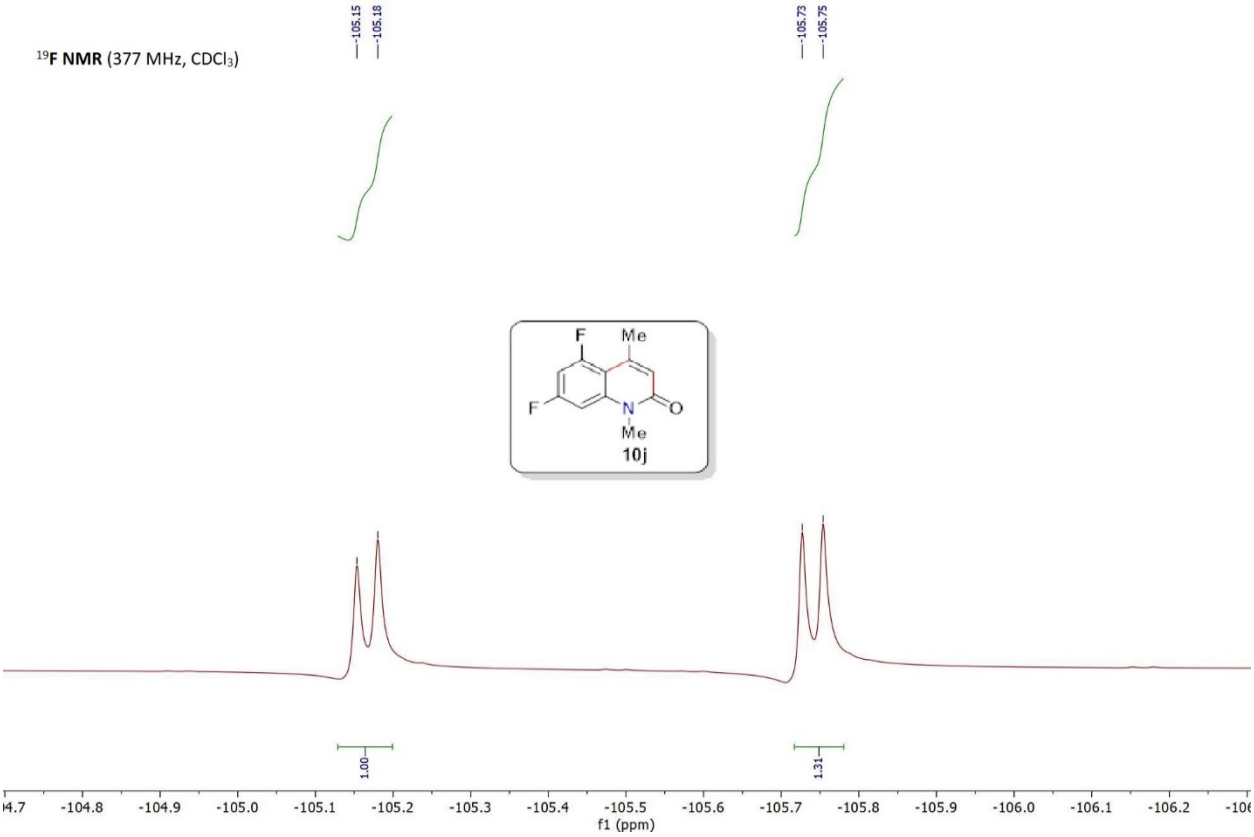
^{13}C NMR ($CDCl_3$)

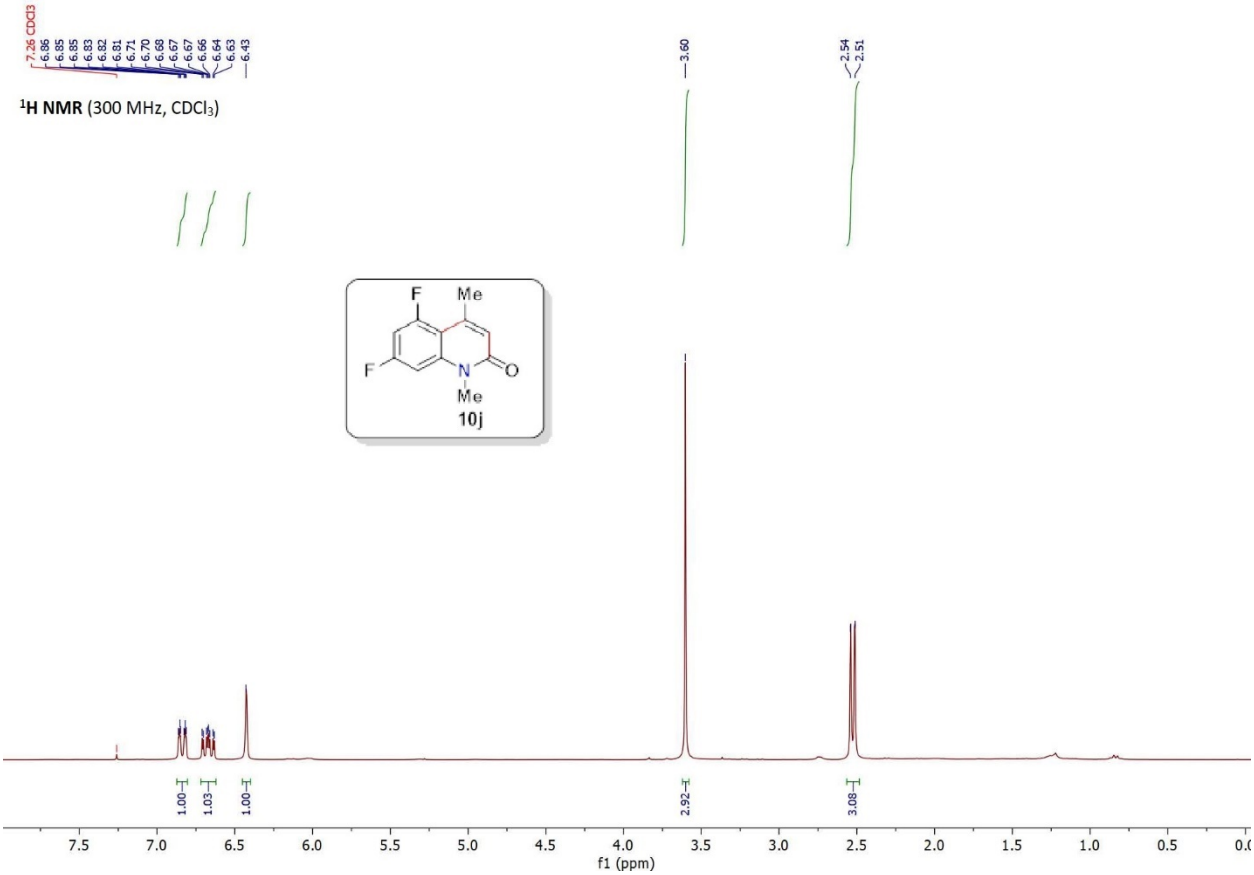



7.99
7.98
7.80
7.80
7.77
7.77
7.44
7.41
7.26 CDCl3
6.66
3.70
2.47
1H NMR (300 MHz, CDCl3)
Me
NC
N
O
Me
10i
1.00
1.01
1.03
1.03
3.00
2.97
f1 (ppm)

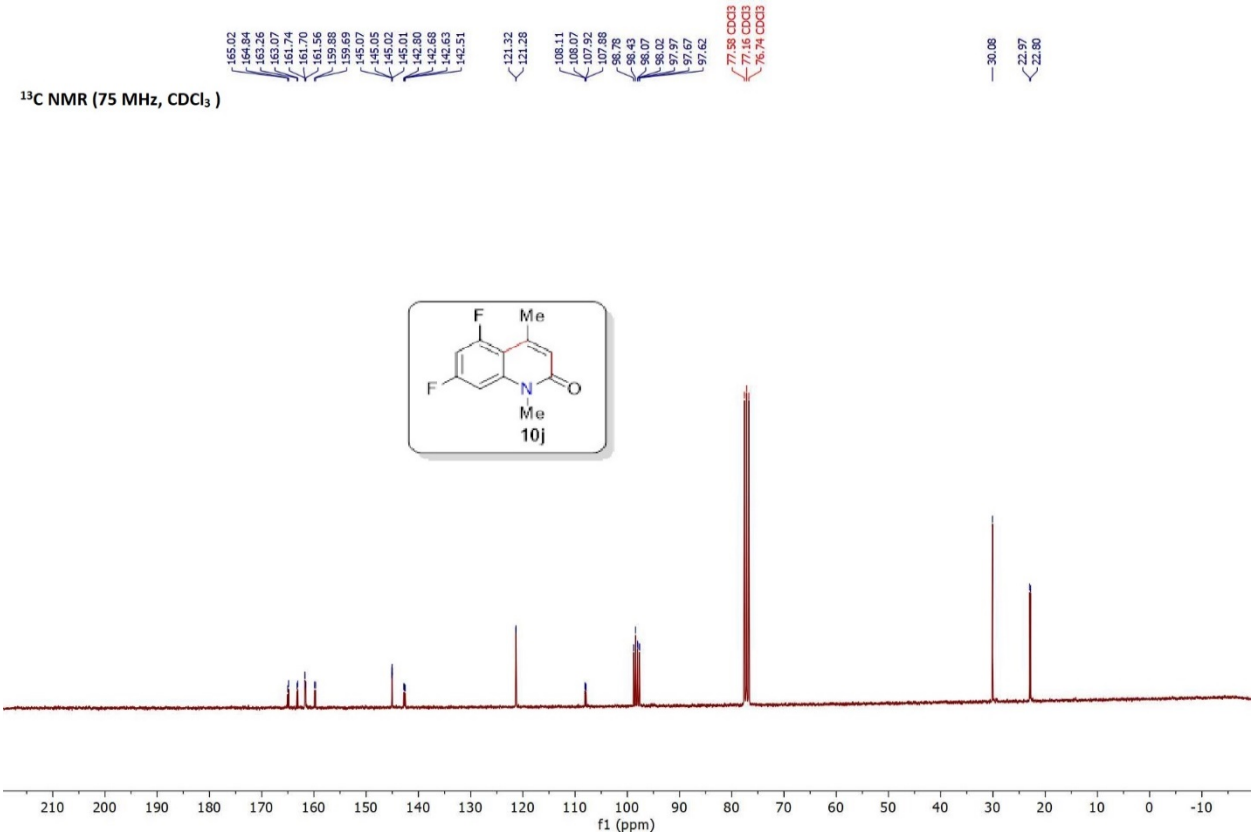

161.74
145.61
142.56
133.09
130.07
122.86
121.73
118.69
115.39
105.47
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
29.59
18.90
13C NMR (101 MHz, CDCl3)


Me
NC
N
O
Me
10i
f1 (ppm)

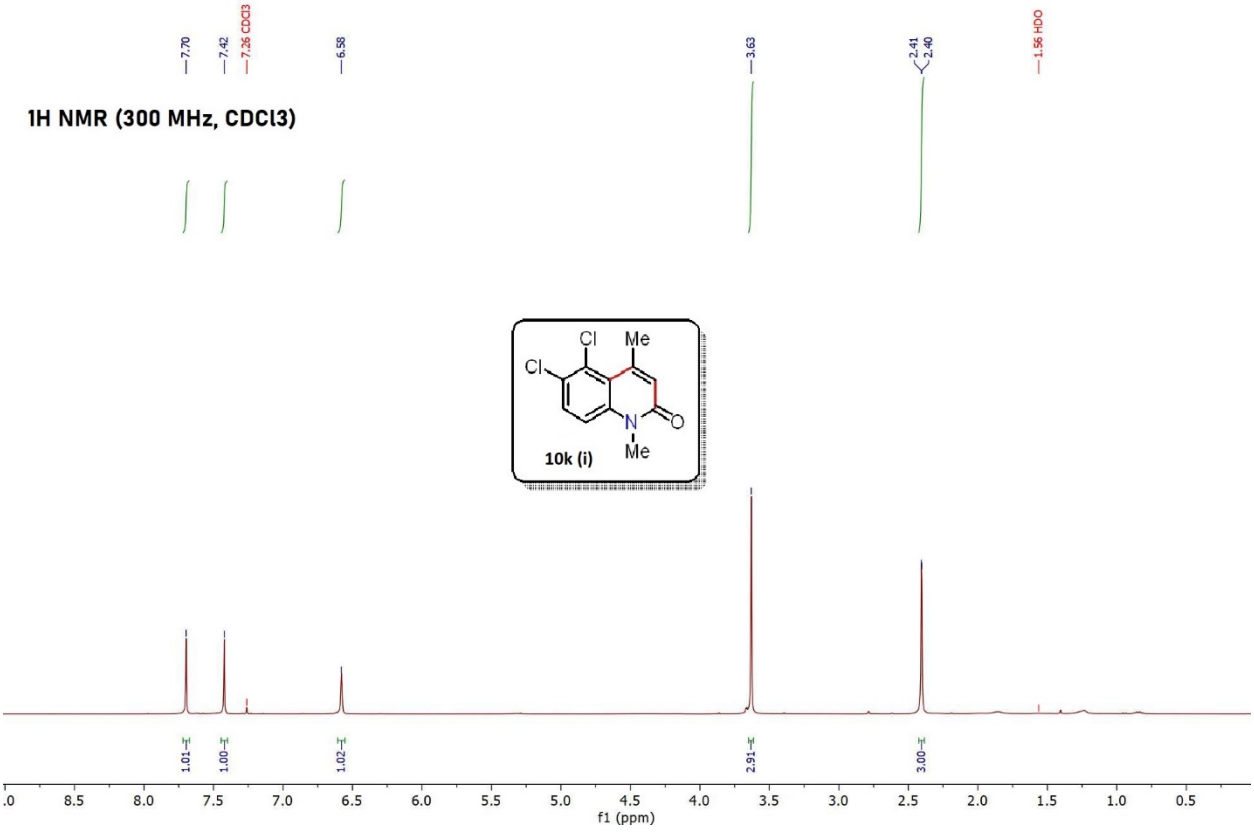

19F NMR (377 MHz, CDCl3)
-105.15
-105.18
-105.73
-105.75
F
Me
F
N
O
Me
10j
1.00
1.31
f1 (ppm)

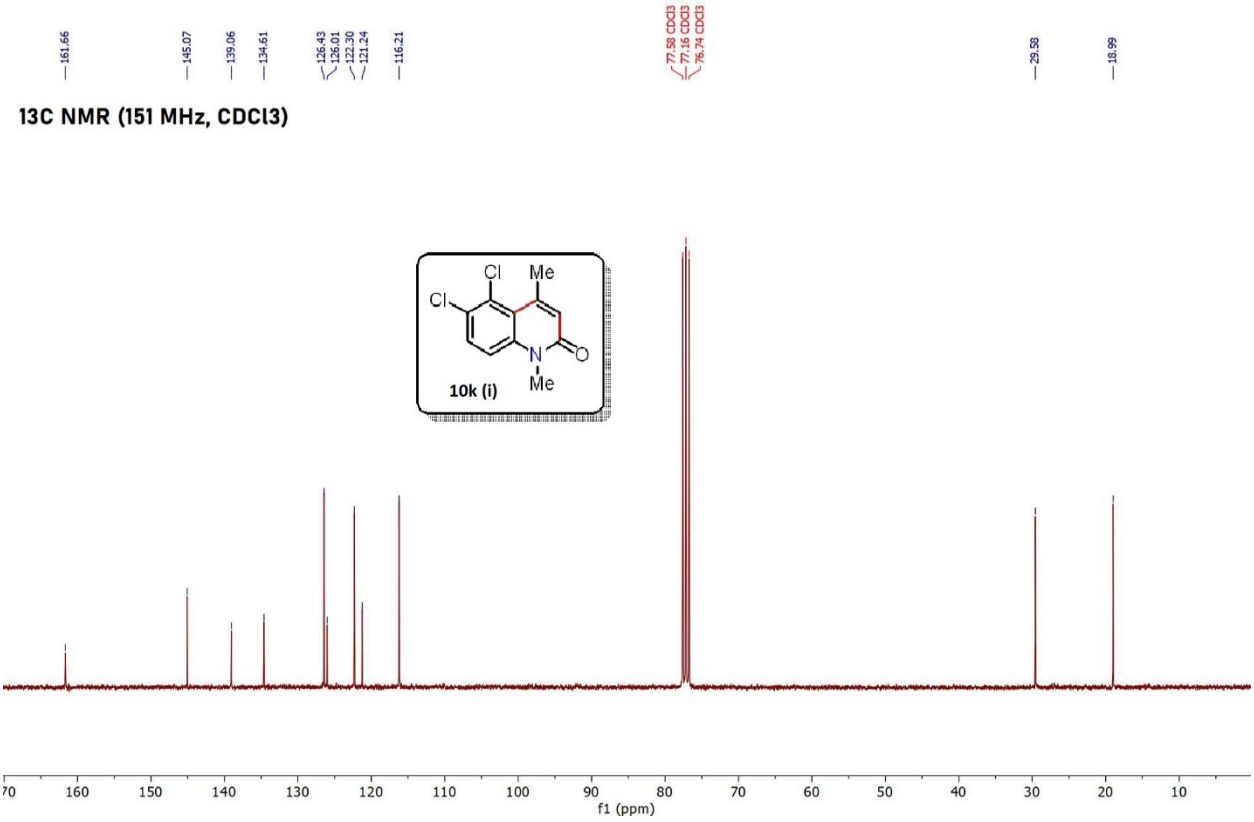

7.26 CDCl3
6.86
6.85
6.85
6.83
6.82
6.81
6.71
6.70
6.68
6.67
6.67
6.66
6.64
6.63
6.43
1H NMR (300 MHz, CDCl3)
3.60
2.54
2.51
F
Me
F
N
O
Me
10j
1.00
1.03
1.00
2.92
3.08
f1 (ppm)

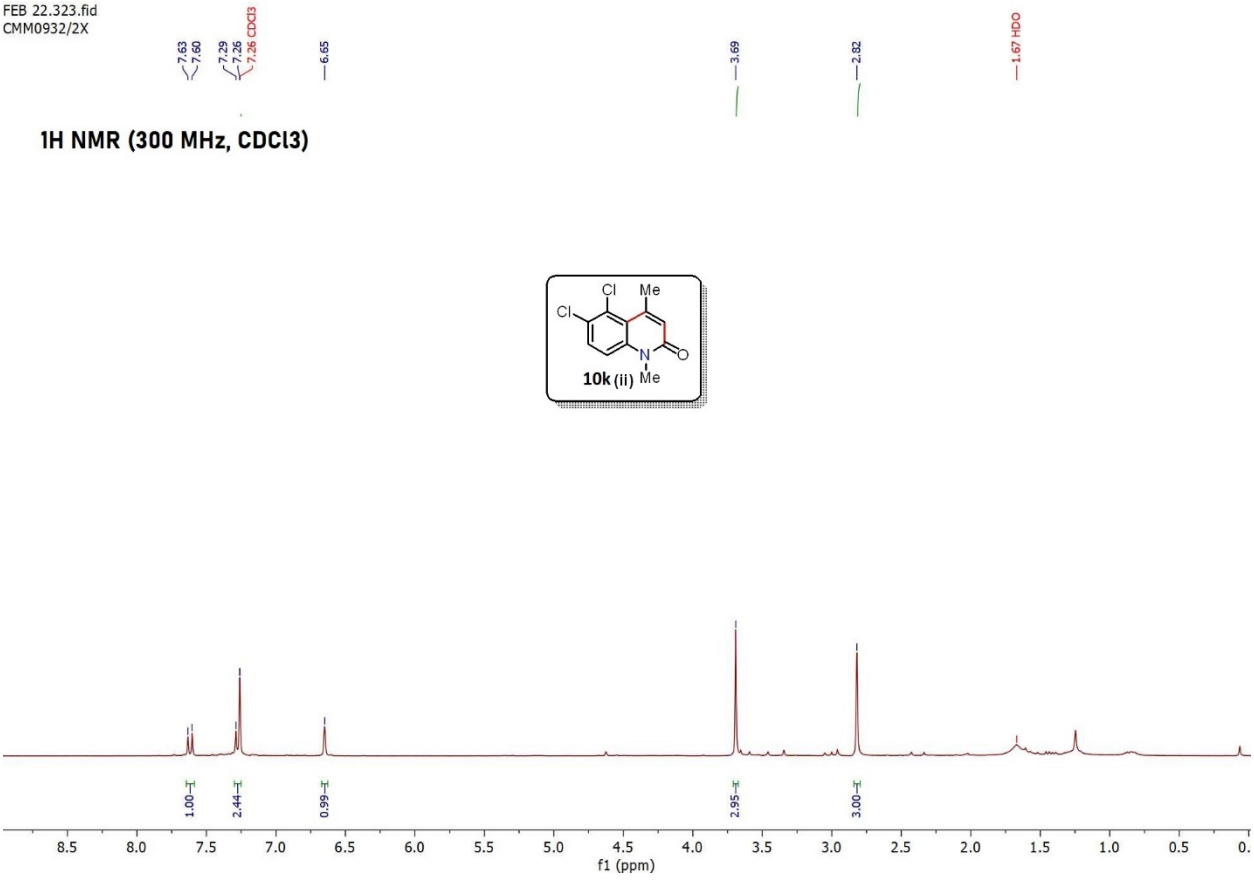
^{13}C NMR (75 MHz, $CDCl_3$)

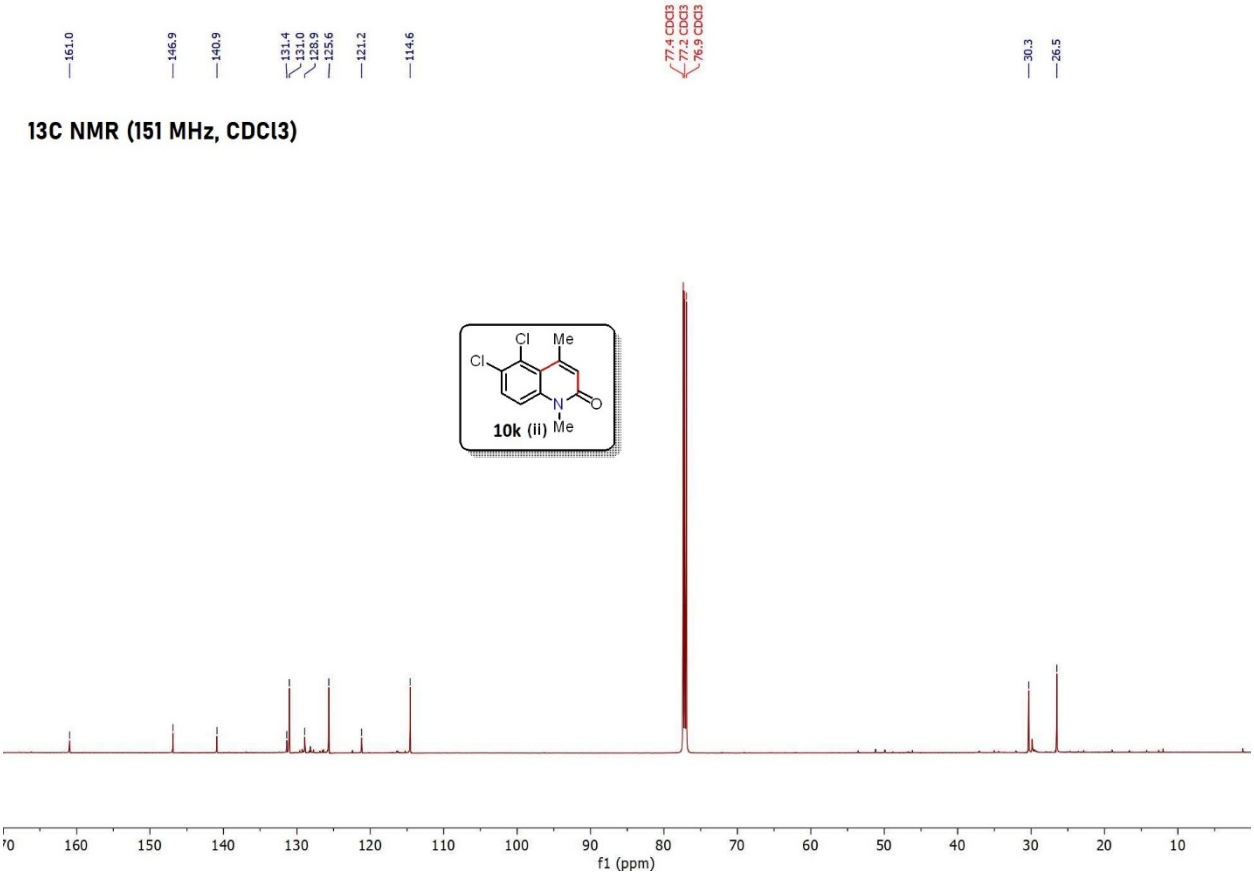


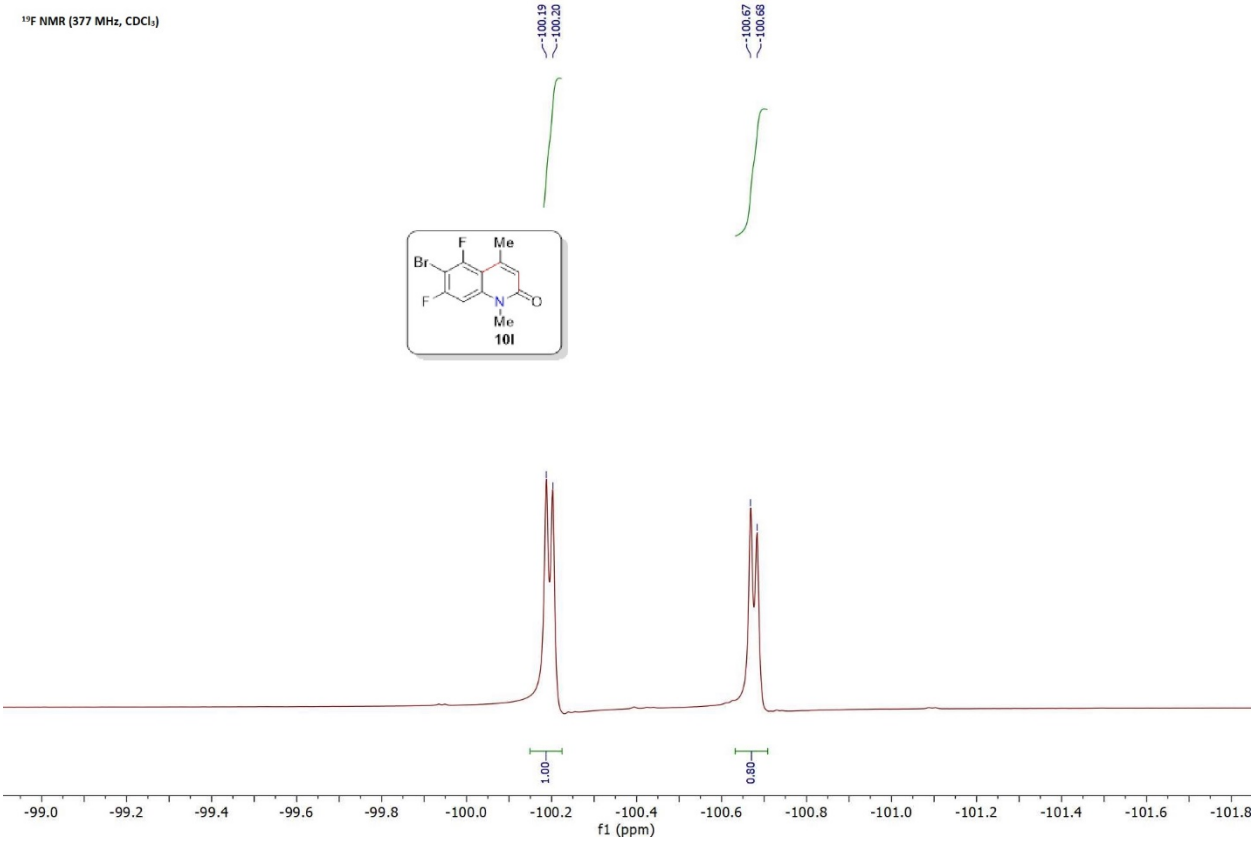
1H NMR (300 MHz, CDCl3)

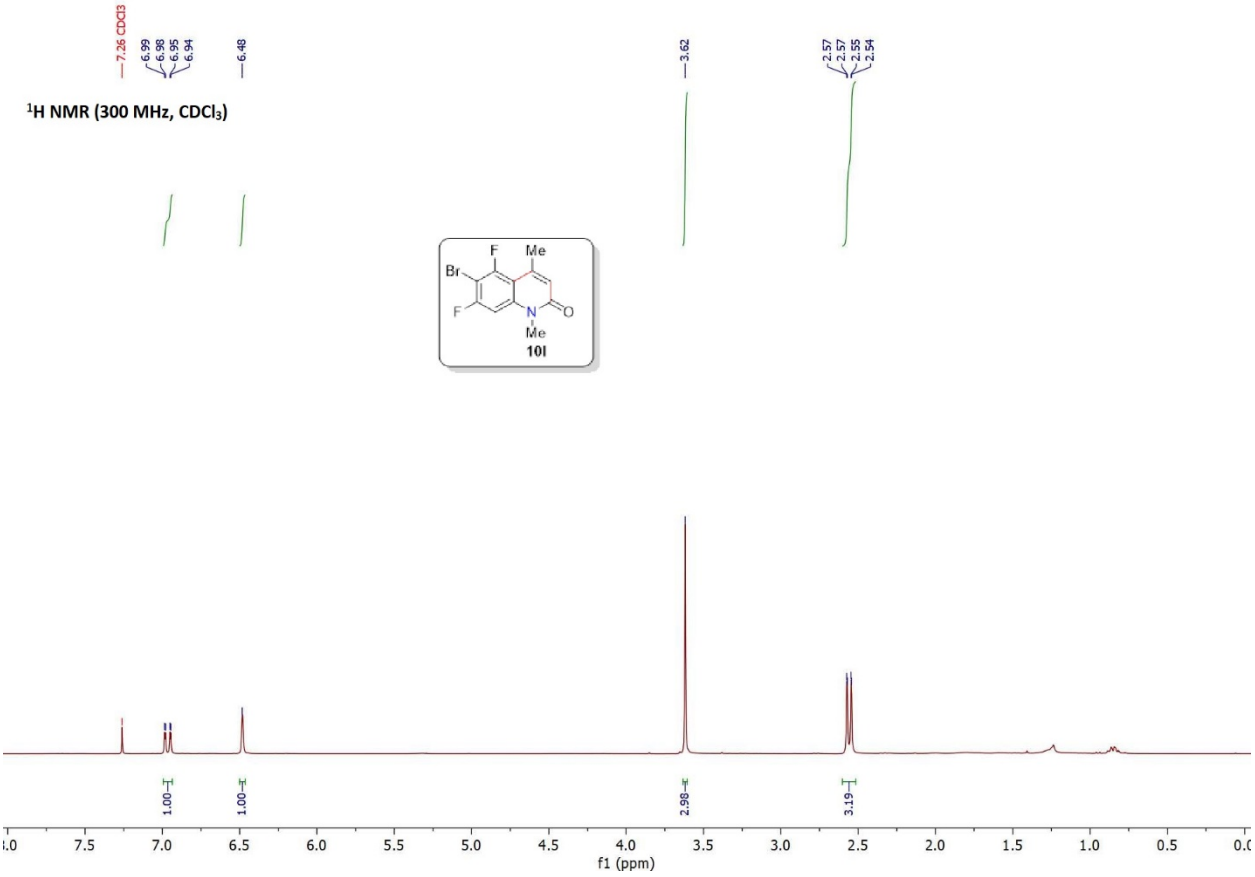


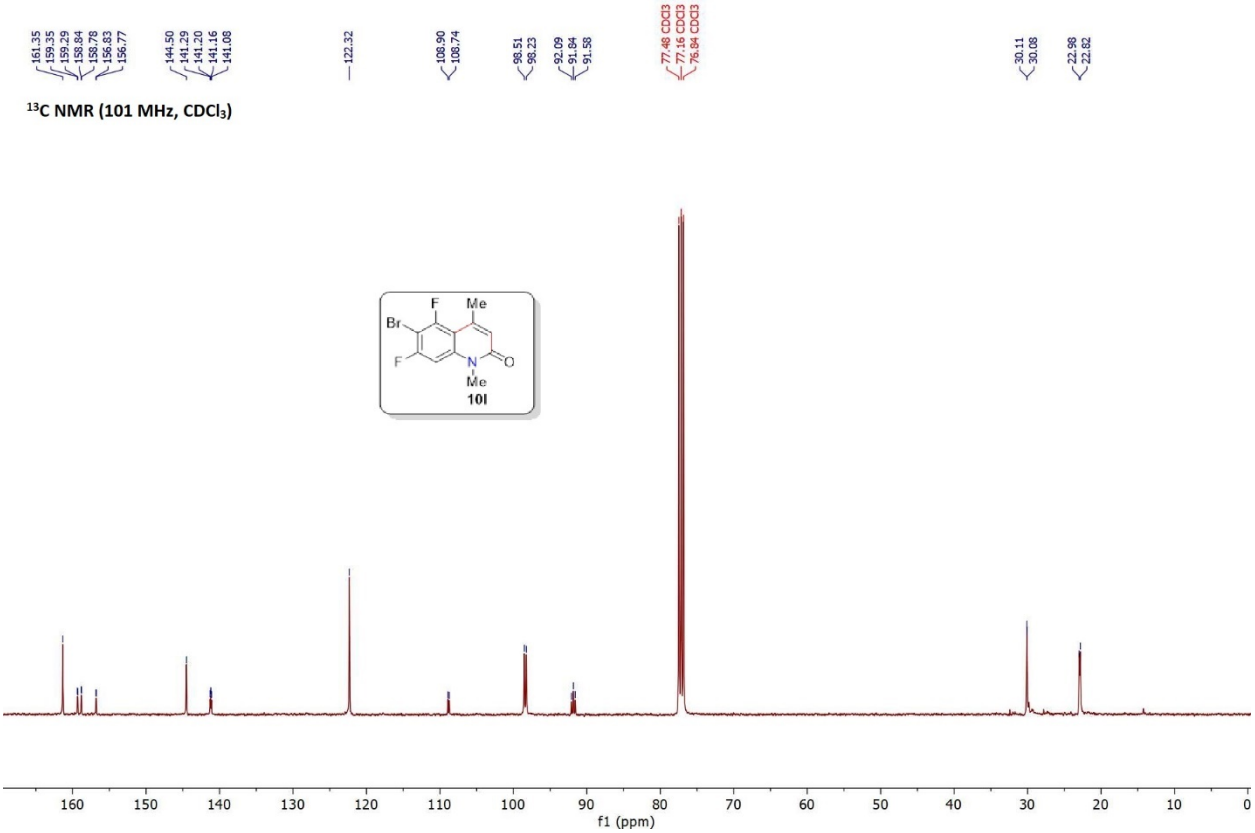

161.66
145.07
139.06
134.61
126.43
126.01
122.30
121.24
116.21
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
29.58
18.99
13C NMR (151 MHz, CDCl3)
Cl
Me
Cl
N
O
Me
10k (i)
f1 (ppm)


FEB 22.323.fid
CMM0932/2X
7.63
7.60
7.29
7.26
7.26 CDCl3
6.65
3.69
2.82
1.67 HDO
1H NMR (300 MHz, CDCl3)
Cl
Me
Cl
N
O
Me
10k (ii)
1.00
2.44
0.99
2.95
3.00
f1 (ppm)

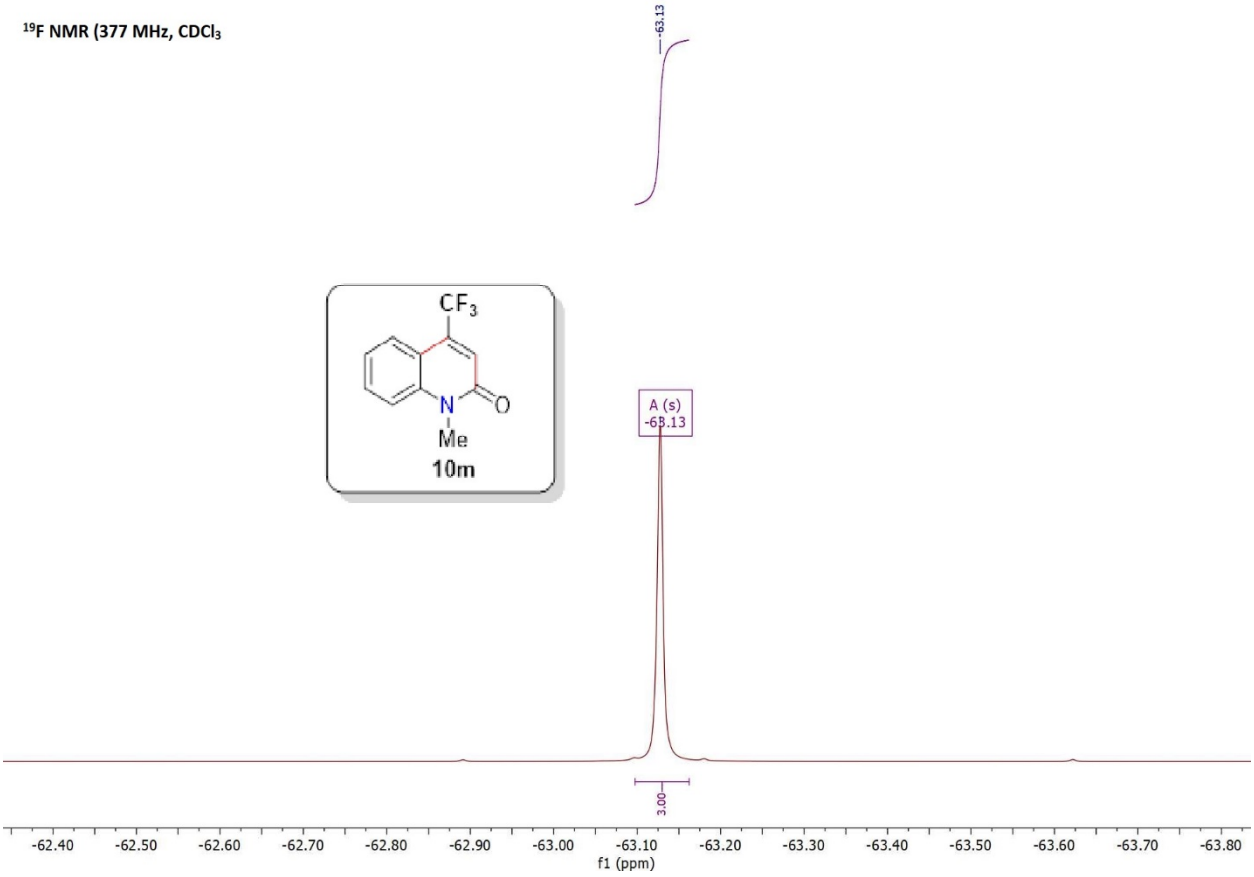

161.0
146.9
140.9
131.4
131.0
128.9
125.6
121.2
114.6
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
30.3
26.5
13C NMR (151 MHz, CDCl3)
Cl
Me
Cl
N
O
Me
10k (ii)
f1 (ppm)


19F NMR (377 MHz, CDCl3)
-100.19
-100.20
-100.67
-100.68
F
Me
Br
F
N
O
Me
10l
1.00
0.80
f1 (ppm)

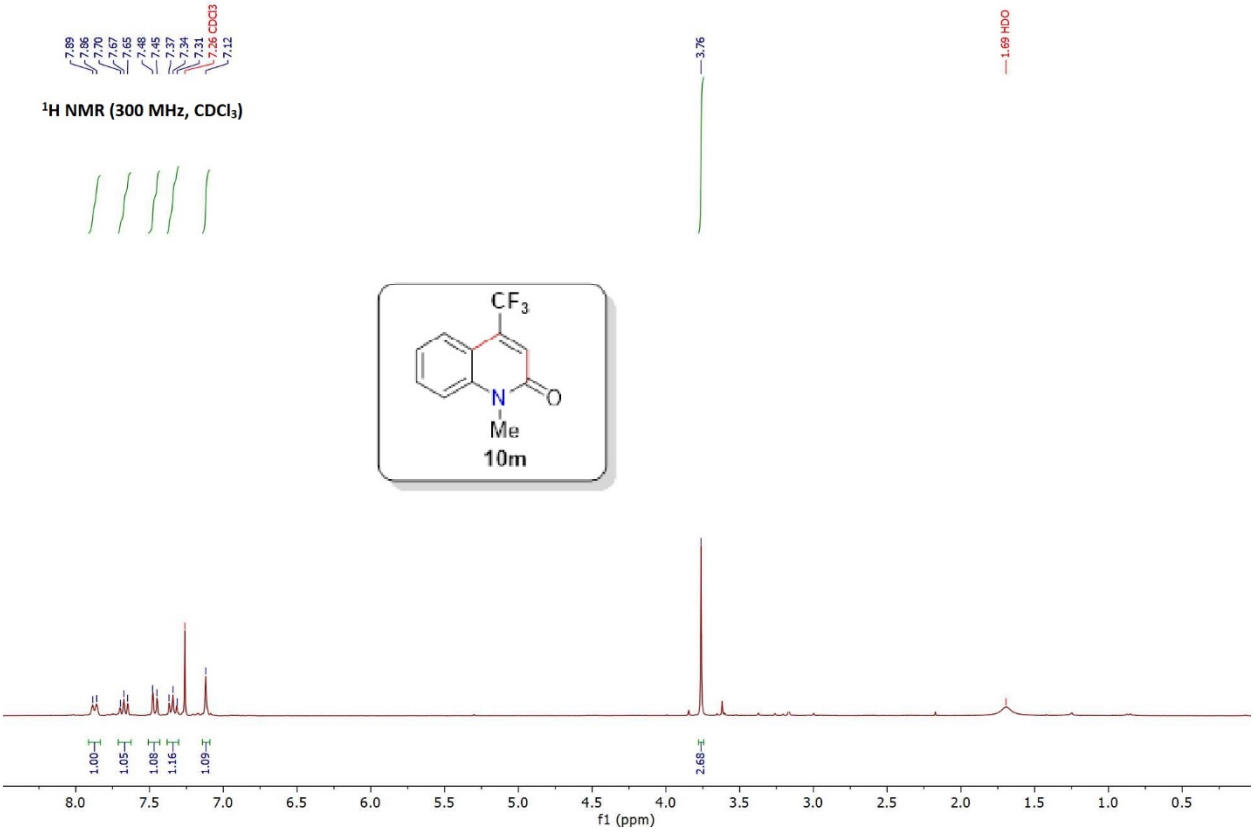

7.26 CDCl3
6.99
6.98
6.95
6.94
6.48
3.62
2.57
2.57
2.55
2.54
1H NMR (300 MHz, CDCl3)
F
Me
Br
F
N
O
Me
10l
1.00
1.00
2.98
3.19
f1 (ppm)


161.35
159.35
159.29
158.84
158.78
156.83
156.77
144.50
141.29
141.20
141.16
141.08
122.32
108.90
108.74
98.51
98.23
92.09
91.84
91.58
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
30.11
30.08
22.98
22.82
13C NMR (101 MHz, CDCl3)
F
Me
Br
F
N
O
Me
10l
f1 (ppm)

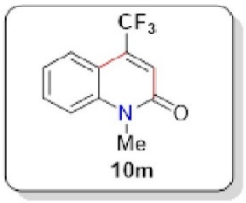
^{19}F NMR (377 MHz, $CDCl_3$

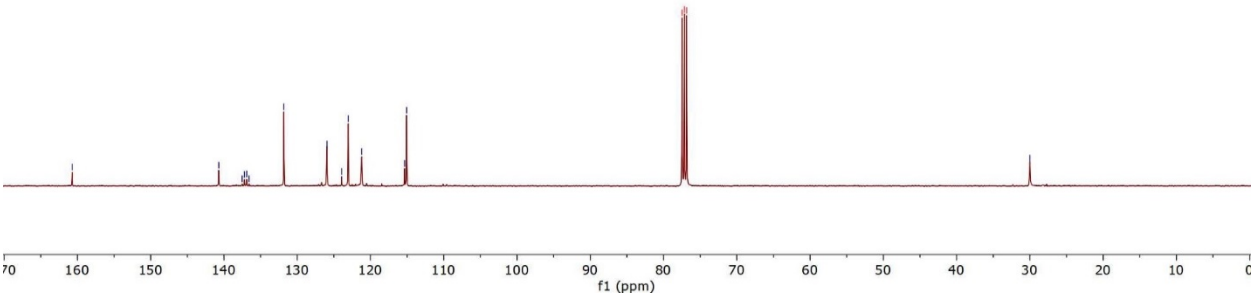


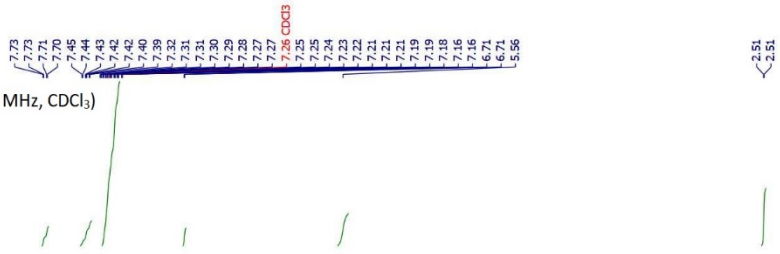
^{1}H NMR (300 MHz, $CDCl_3$)



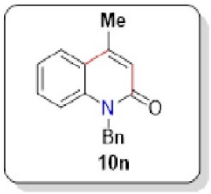
^{13}C NMR (151 MHz, $CDCl_3$)

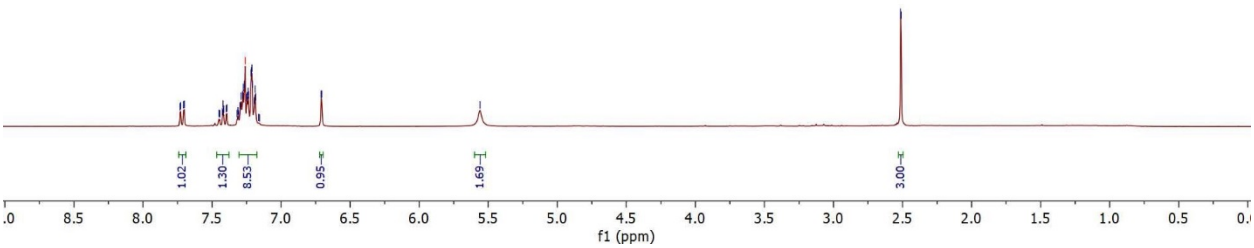


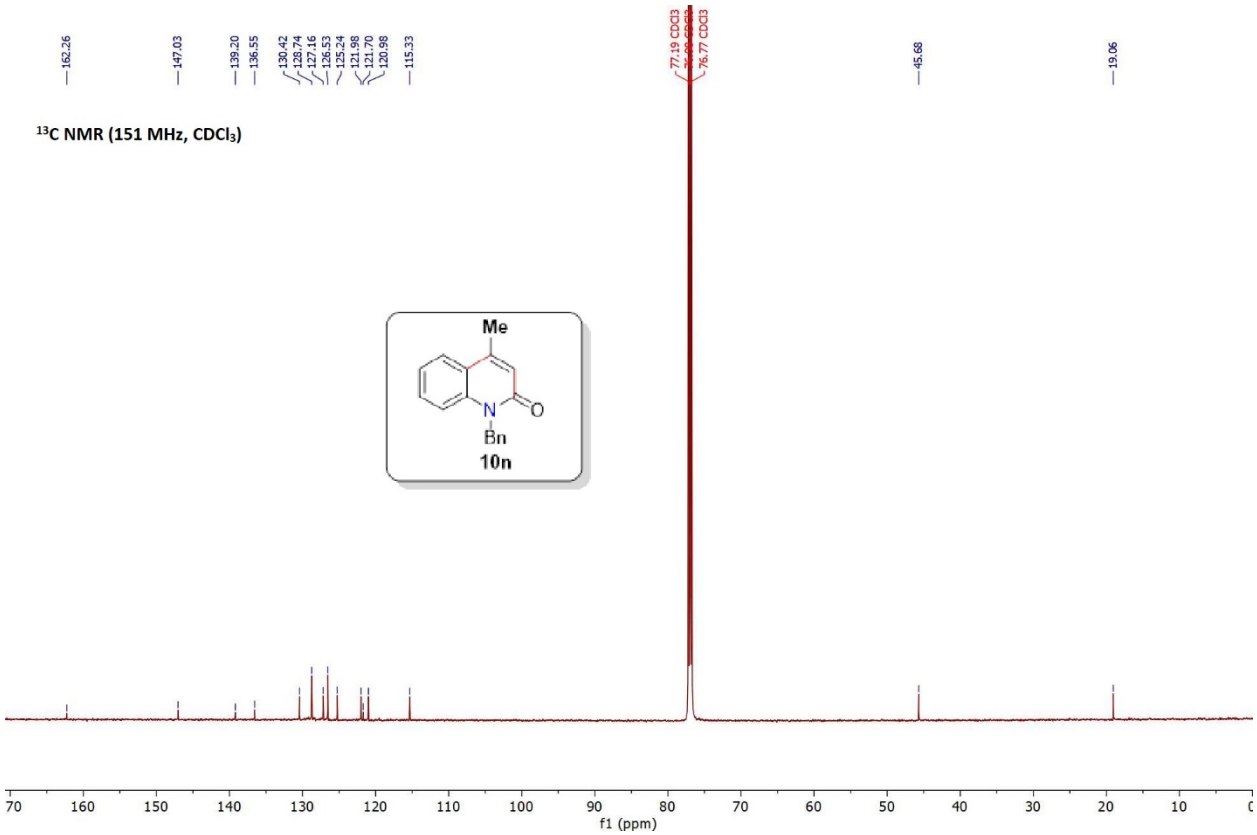


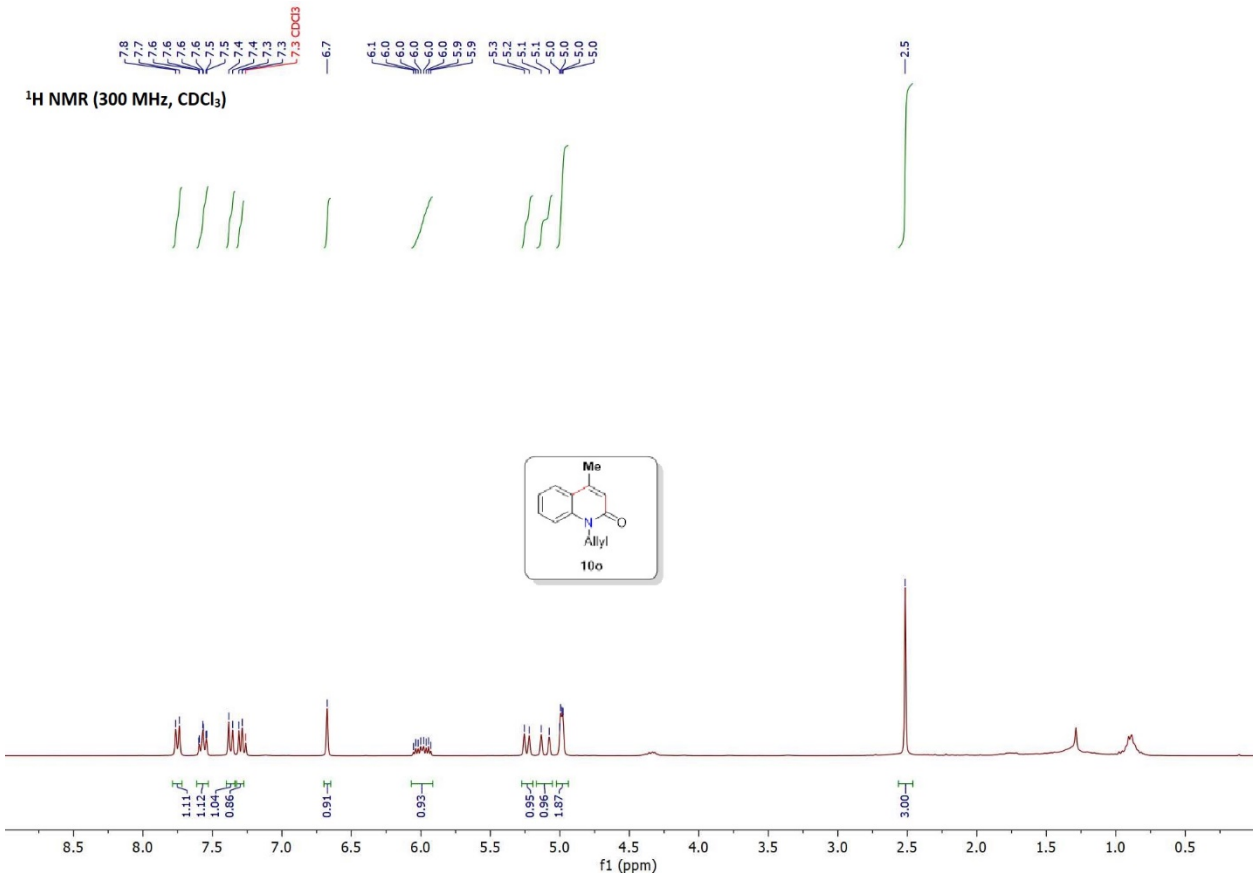


^{1}H NMR (300 MHz, $CDCl_3$)

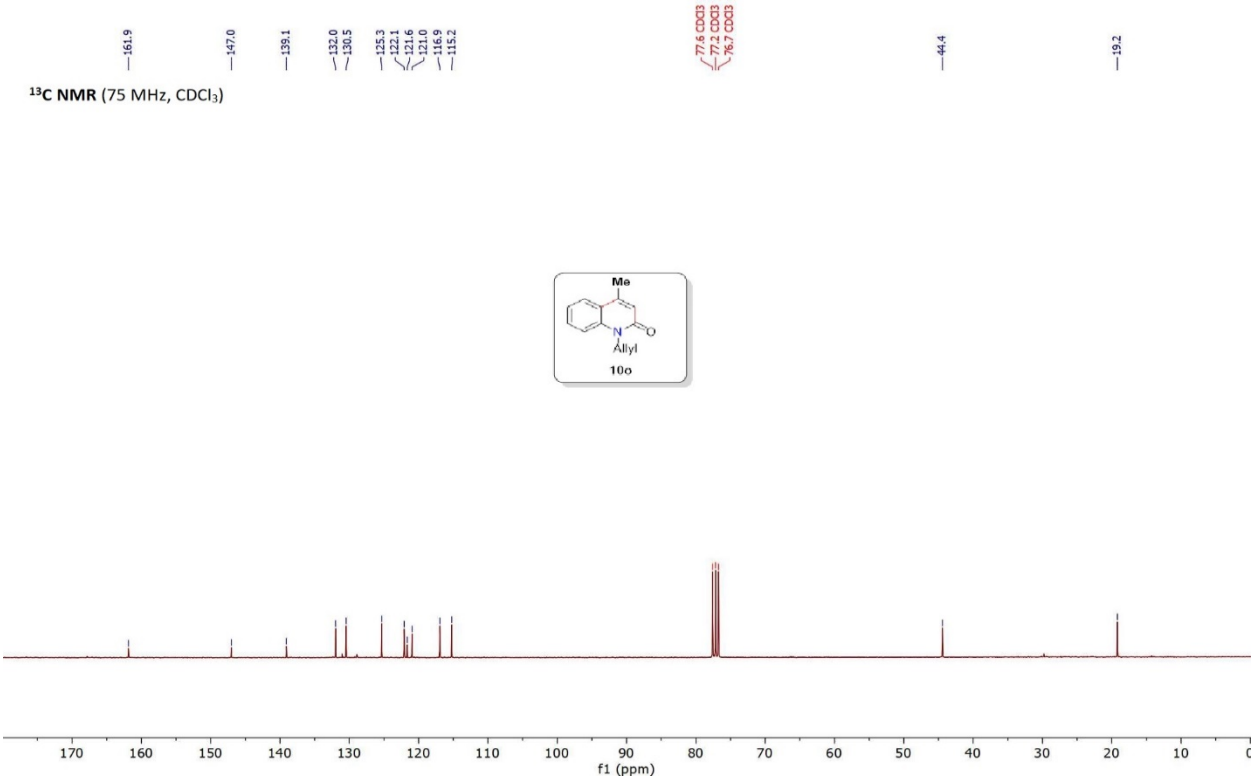




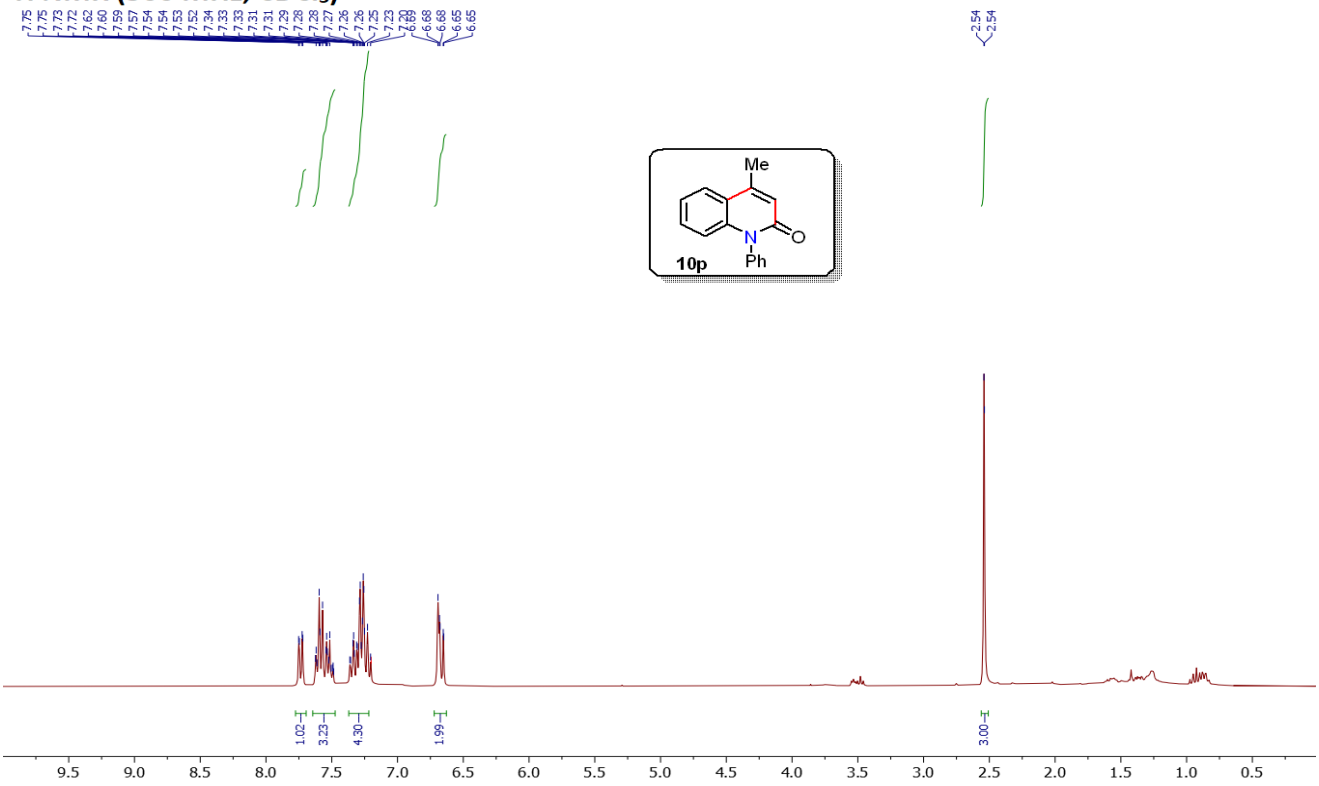

162.26
147.03
139.20
136.55
130.42
128.74
127.16
126.53
125.24
121.98
121.70
120.98
115.33
77.19 CDCl3
76.77 CDCl3
45.68
19.06
13C NMR (151 MHz, CDCl3)
Me
N
O
Bn
10n
f1 (ppm)


7.3 CDCl3
6.7
5.9
5.2
5.1
5.0
2.5
1H NMR (300 MHz, CDCl3)
Me
N
O
Allyl
10o
1.11
1.12
1.04
0.86
0.91
0.93
0.95
0.96
1.87
3.00
f1 (ppm)

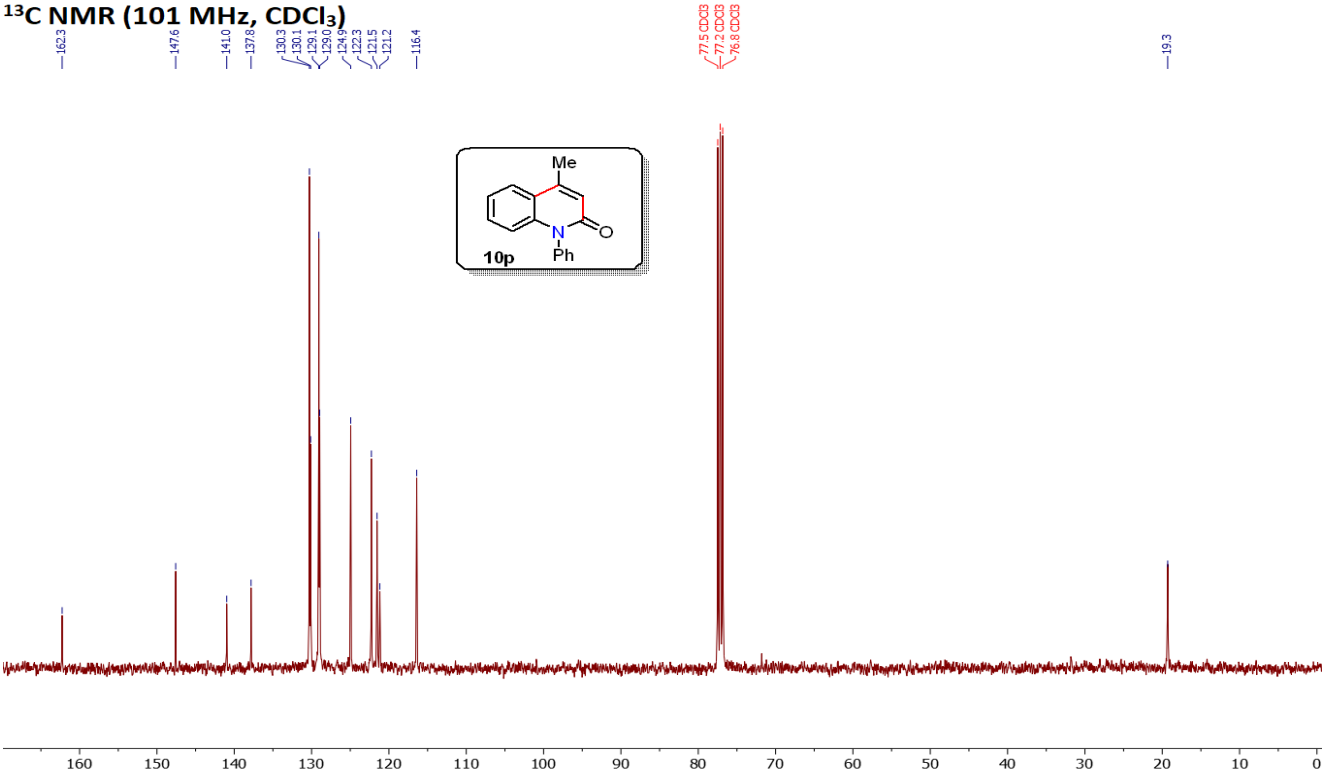
^{13}C NMR (75 MHz, $CDCl_3$)



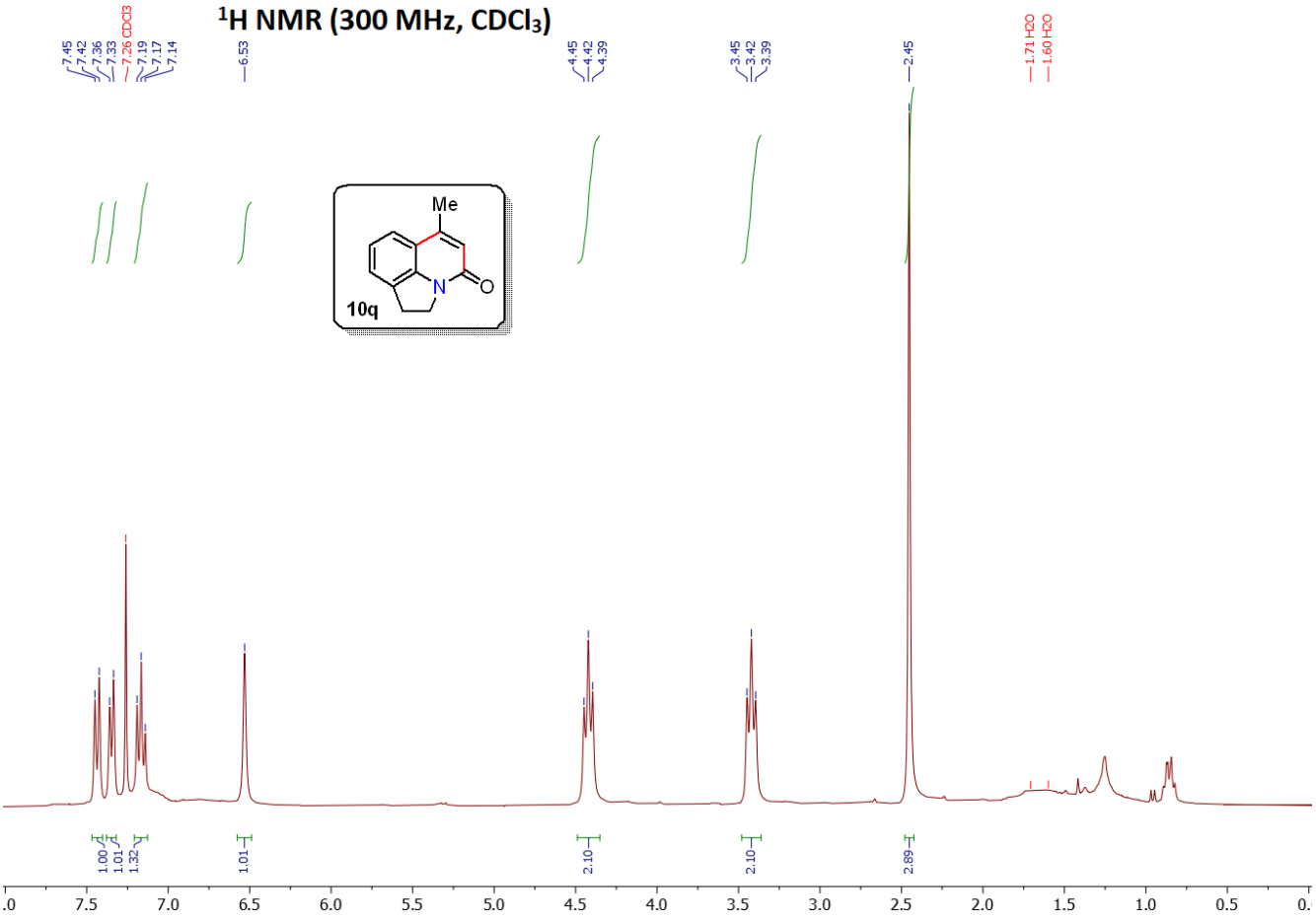
^{1}H NMR (300 MHz, $CDCl_3$)

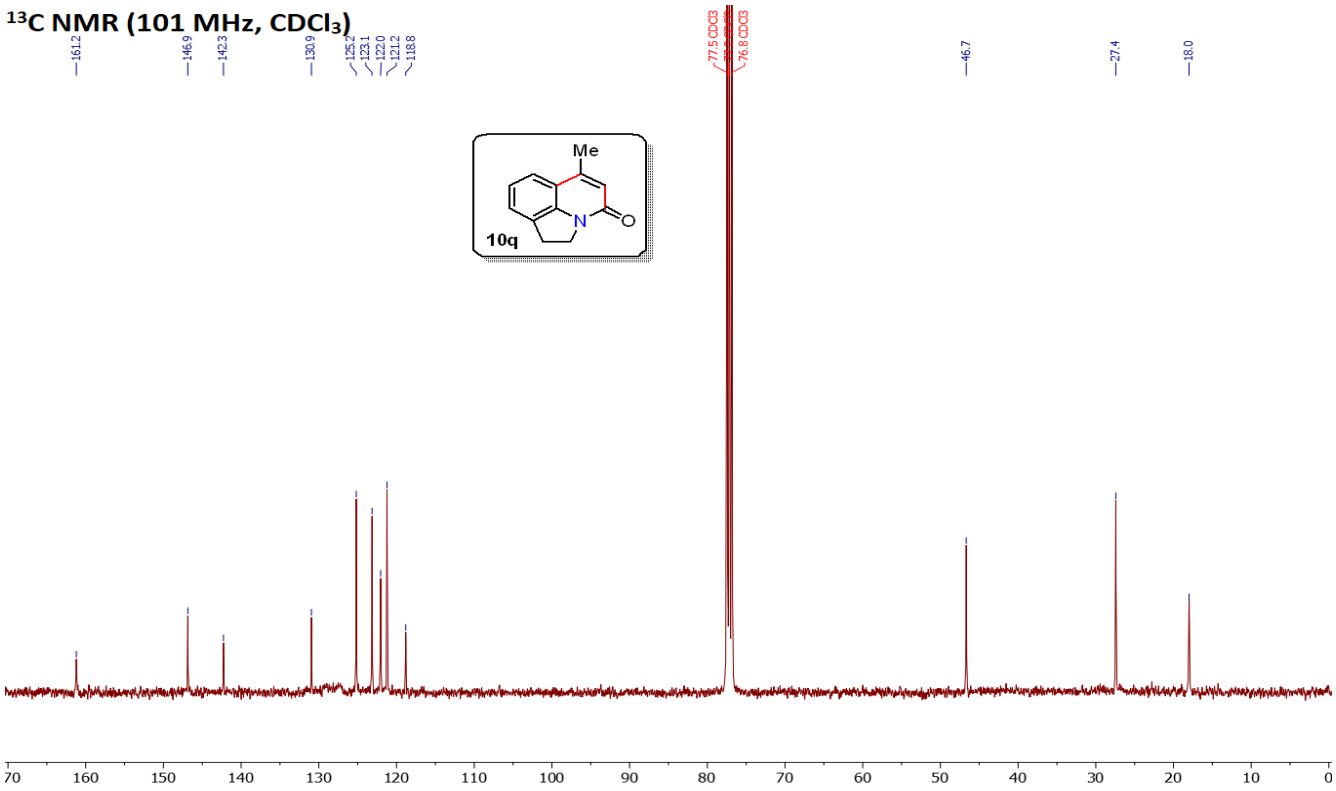


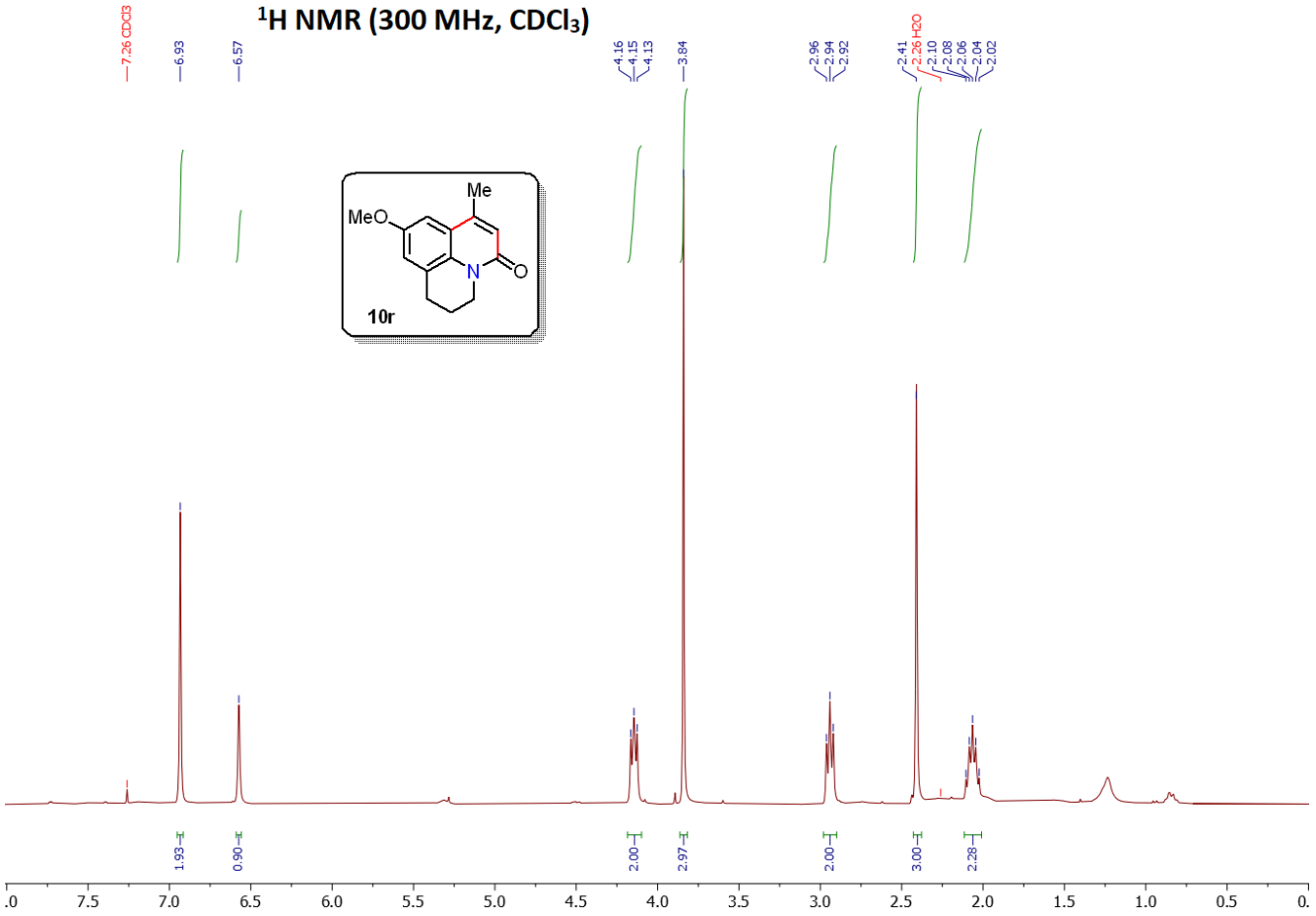
^{13}C NMR (101 MHz, $CDCl_3$)



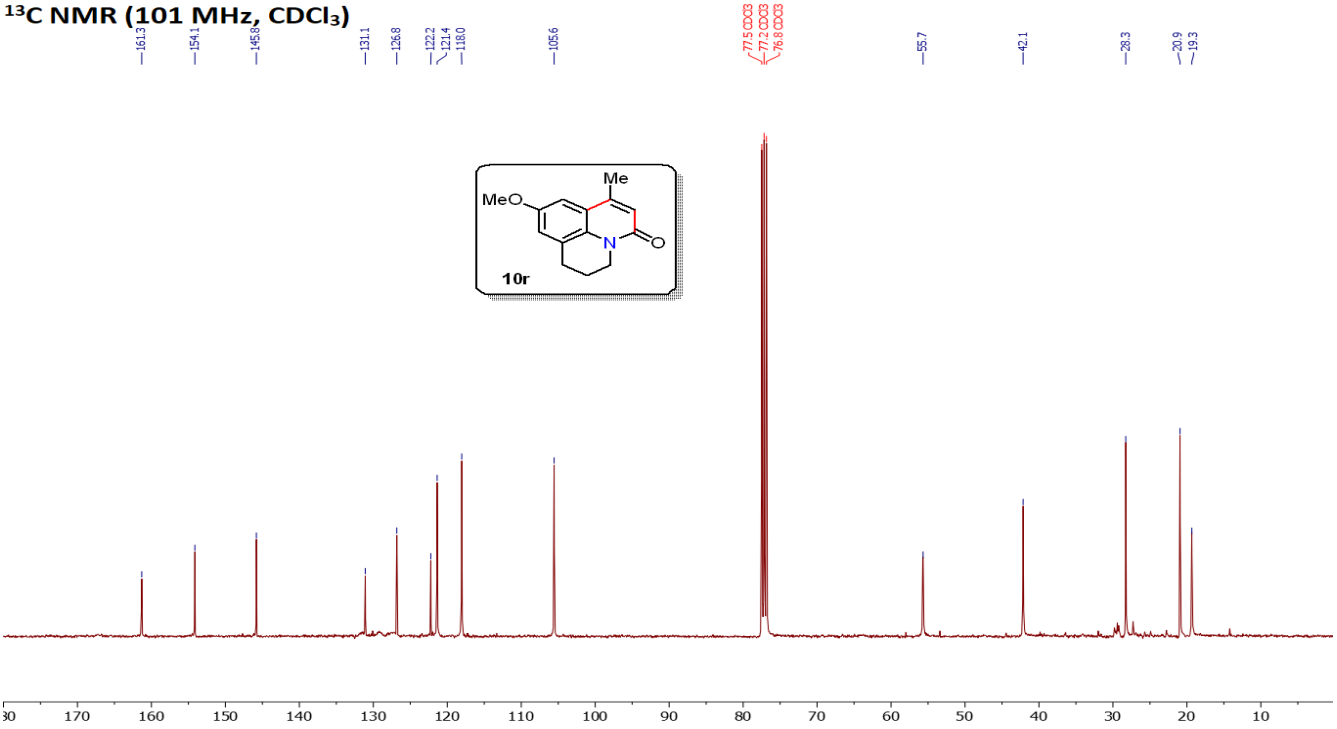
^{1}H NMR (300 MHz, $CDCl_3$)



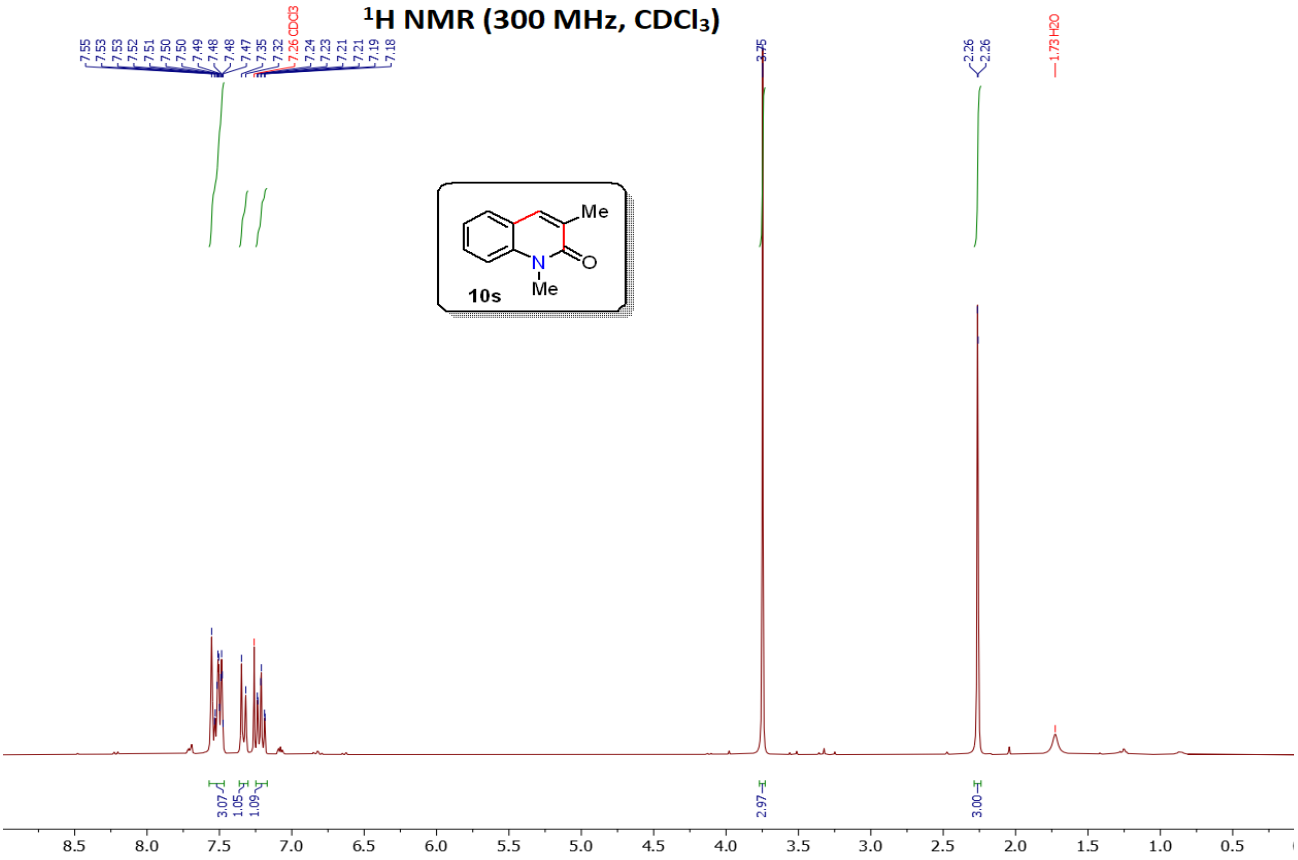

13C NMR (101 MHz, CDCl3)
161.2
146.9
142.3
130.9
125.2
123.1
122.0
121.2
118.8
77.5 CDCl3
76.8 CDCl3
46.7
27.4
18.0
Me
N
O
10q


1H NMR (300 MHz, CDCl3)
7.26 CDCl3
6.93
6.57
4.16
4.15
4.13
3.84
2.96
2.94
2.92
2.41
2.26 H2O
2.10
2.08
2.06
2.04
2.02
Me
MeO
N
O
10r
1.93
0.90
2.00
2.97
2.00
3.00
2.28

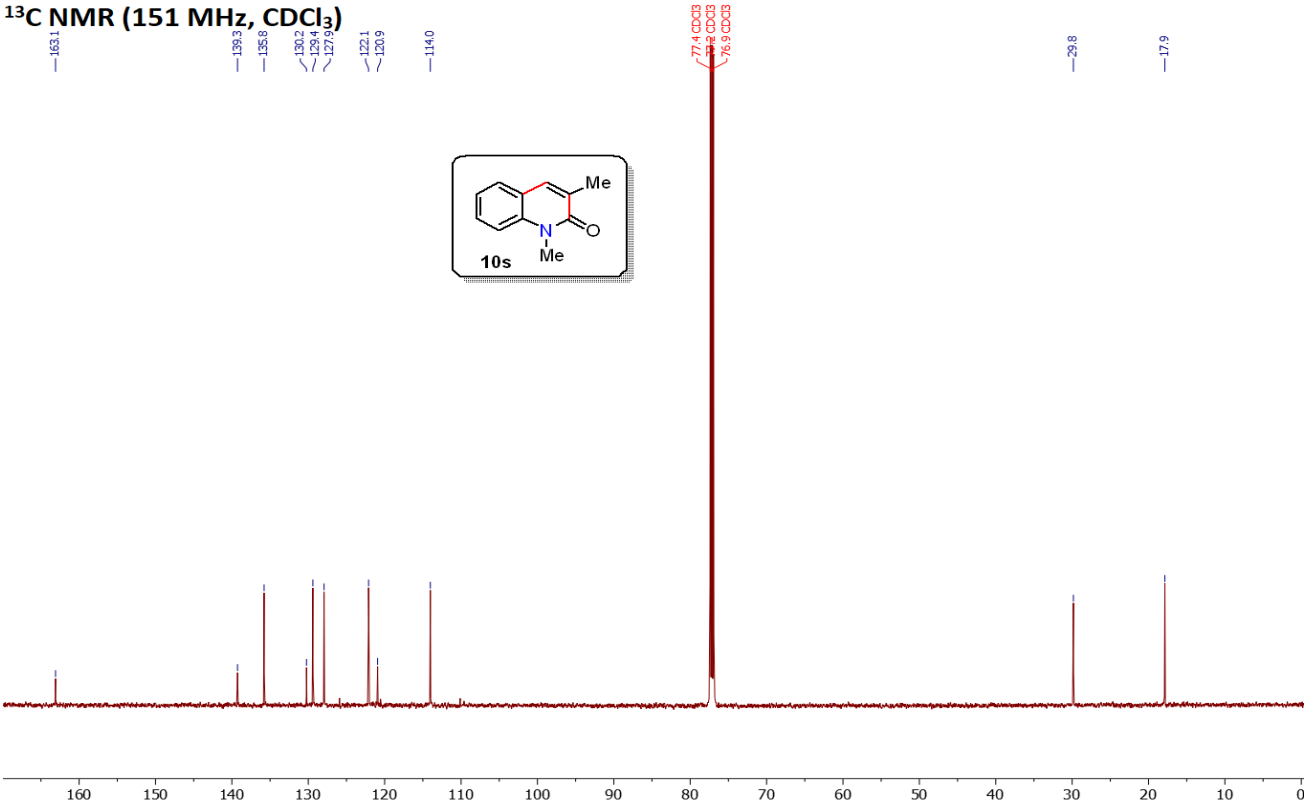
^{13}C NMR (101 MHz, $CDCl_3$)



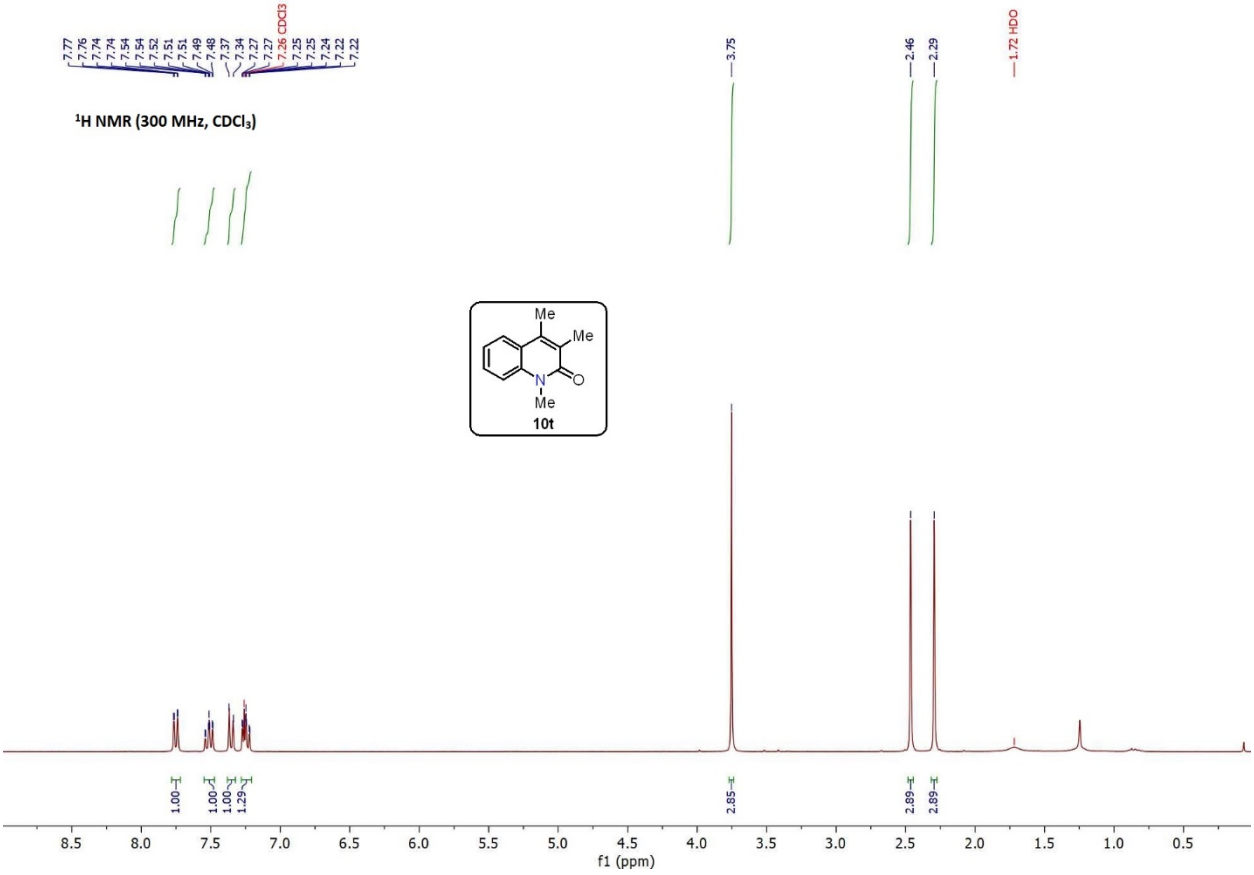
^{1}H NMR (300 MHz, $CDCl_3$)

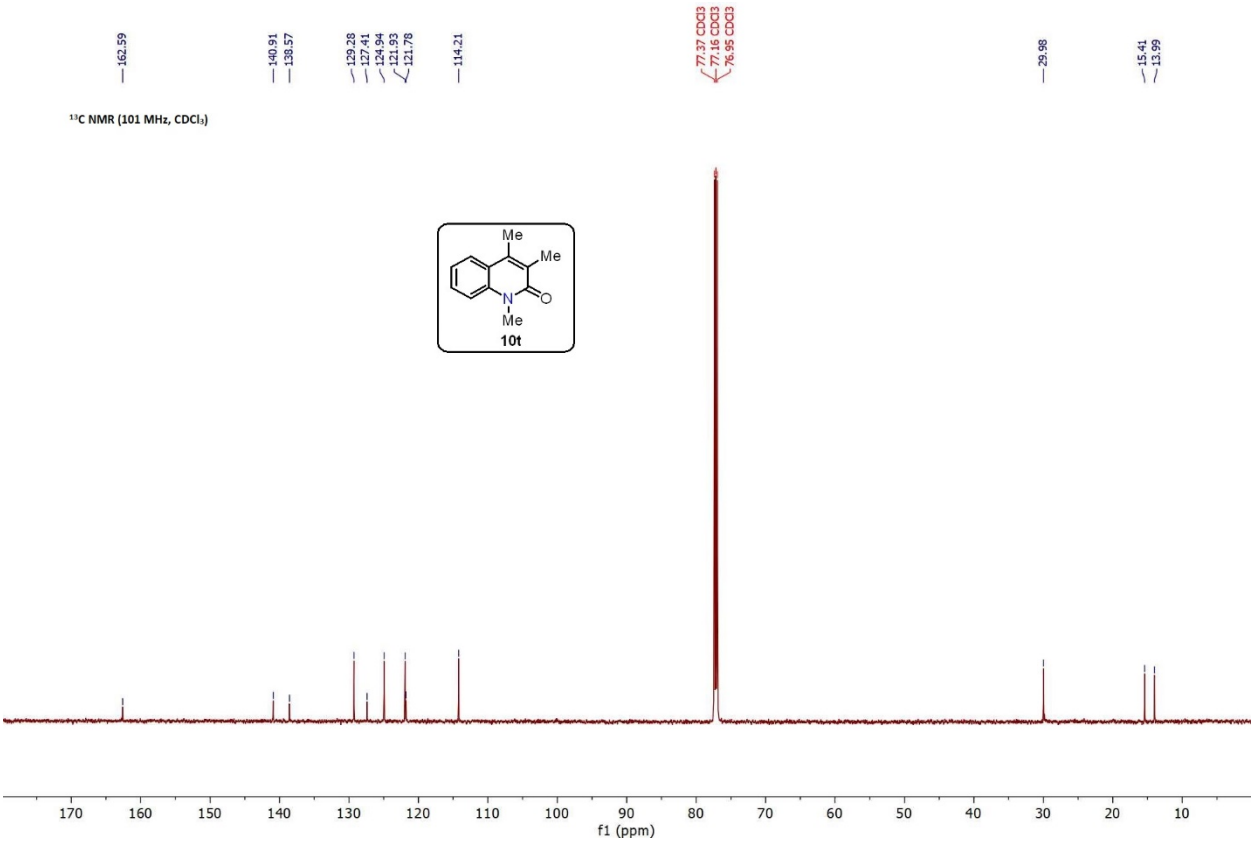


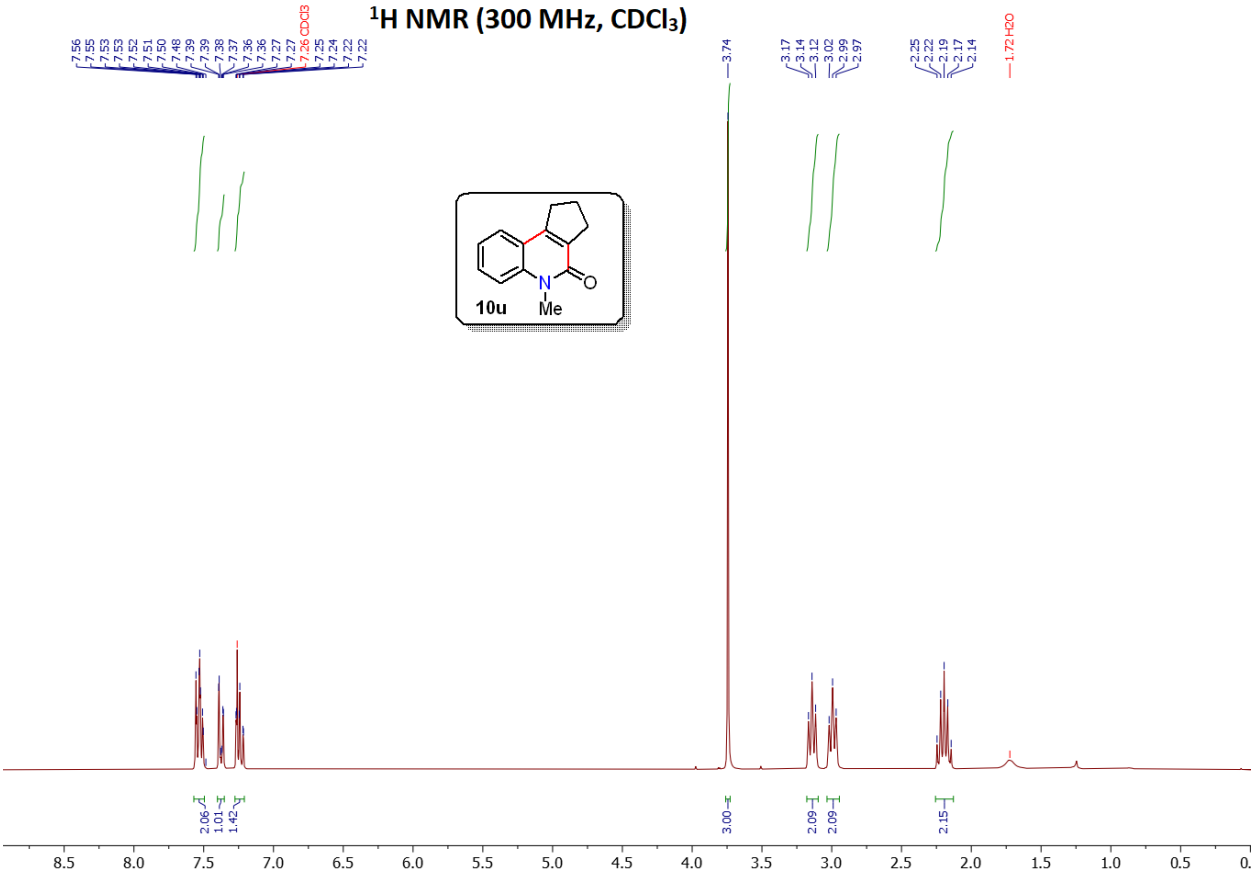
^{13}C NMR (151 MHz, $CDCl_3$)

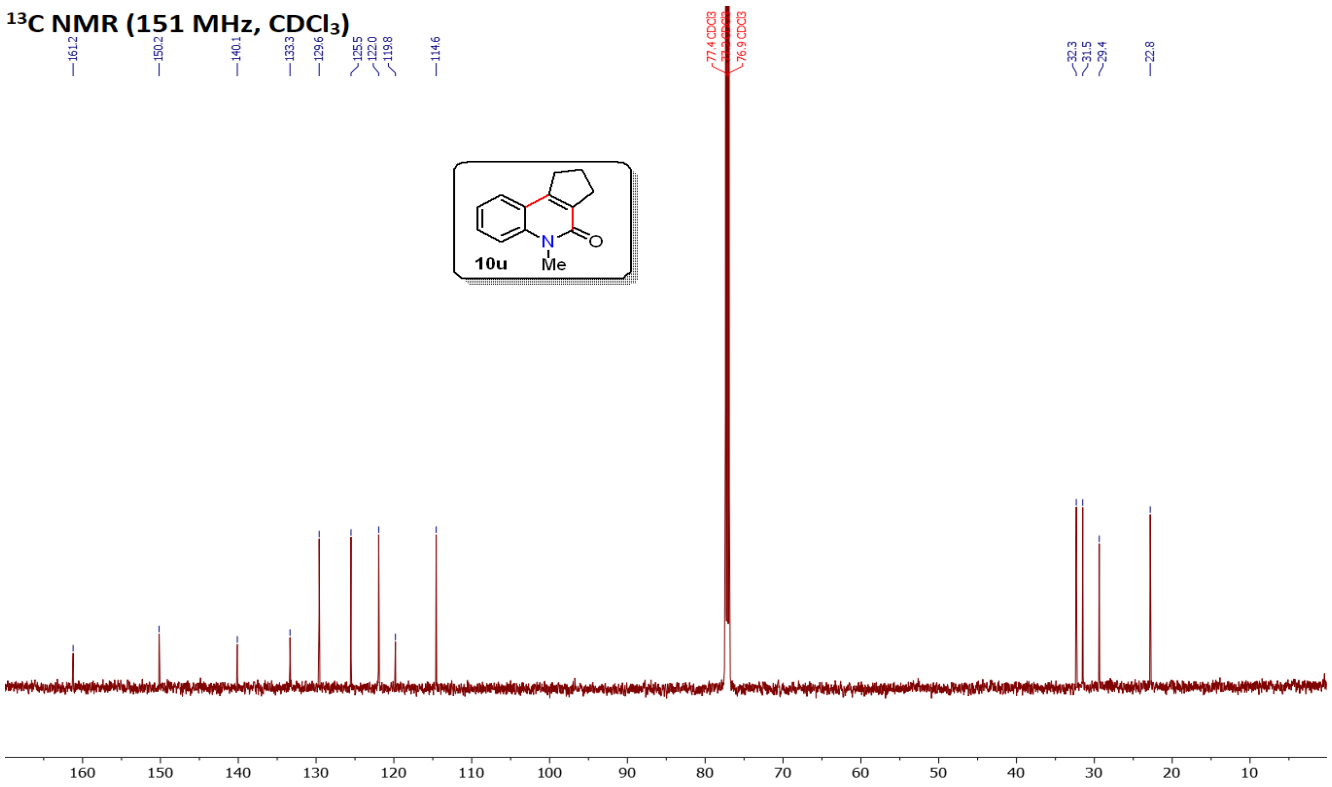


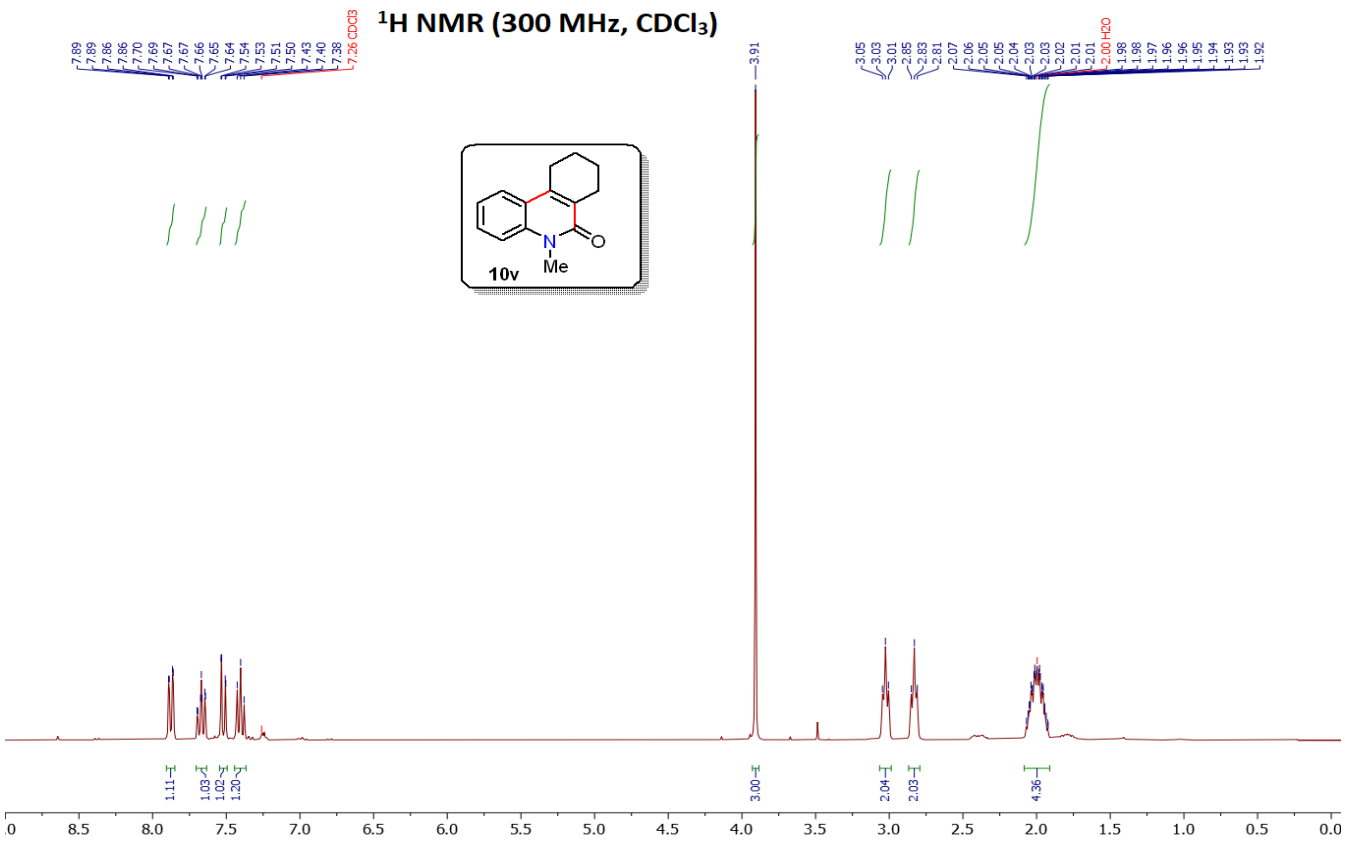
^{1}H NMR (300 MHz, $CDCl_3$)

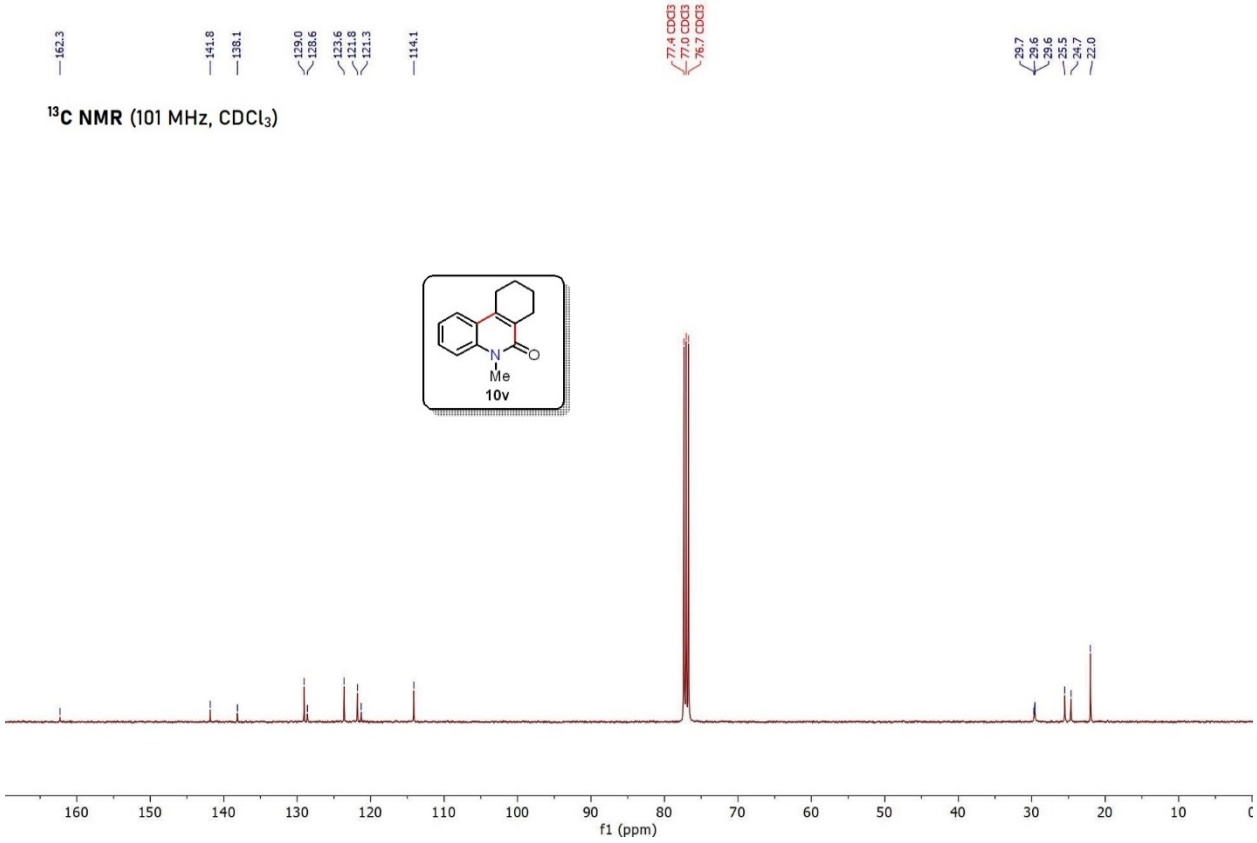


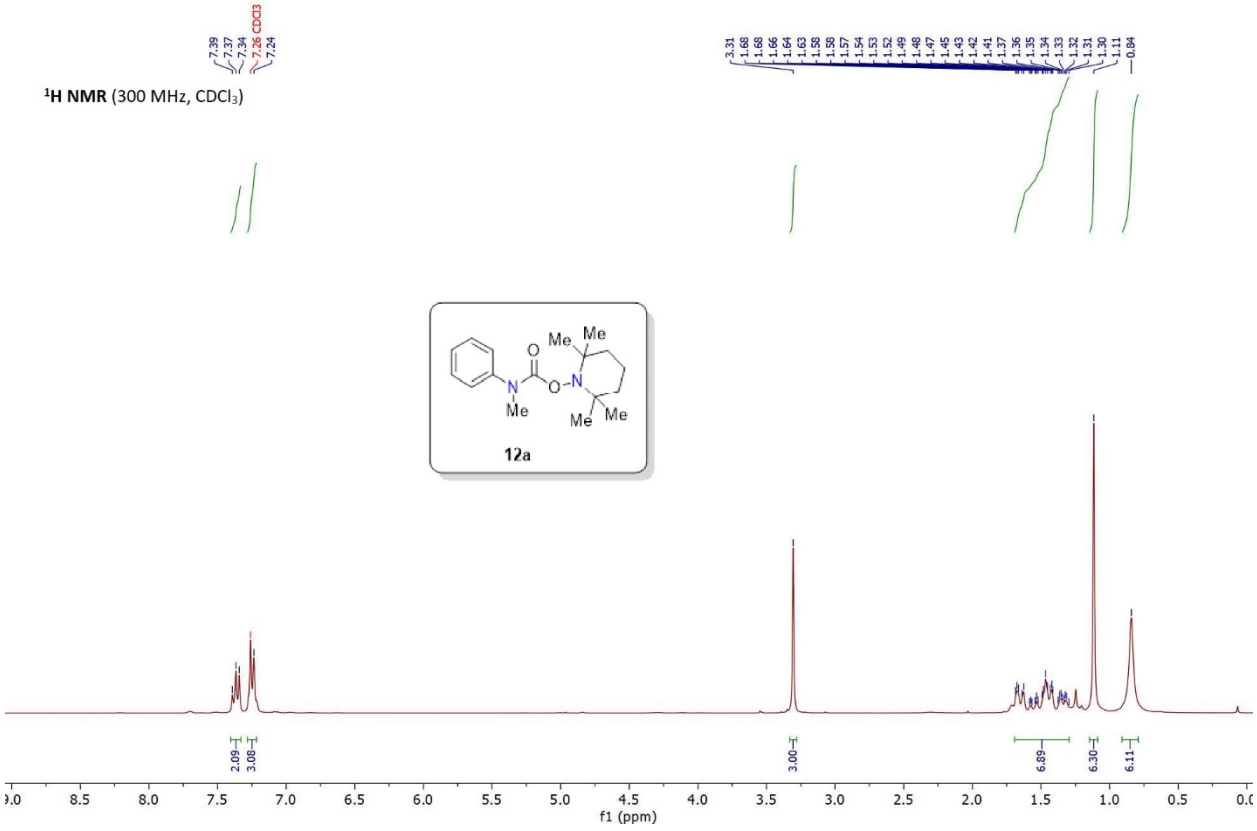

162.59
140.91
138.57
129.28
127.41
124.94
121.93
121.78
114.21
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
29.98
15.41
13.99
13C NMR (101 MHz, CDCl3)
Me
Me
N
O
Me
10t
f1 (ppm)


1H NMR (300 MHz, CDCl3)
7.26 CDCl3
3.74
1.72 H2O
10u
N
O
Me

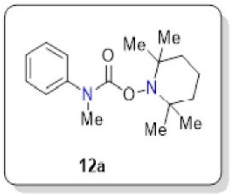

13C NMR (151 MHz, CDCl3)
161.2
150.2
140.1
133.3
129.6
125.5
122.0
119.8
114.6
77.4 CDCl3
76.9 CDCl3
32.3
31.5
29.4
22.8
10u
N
Me
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


1H NMR (300 MHz, CDCl3)
7.89
7.89
7.86
7.86
7.86
7.70
7.69
7.67
7.67
7.66
7.65
7.64
7.54
7.53
7.51
7.50
7.43
7.40
7.38
7.26 CDCl3
3.91
3.05
3.03
3.01
2.85
2.83
2.81
2.07
2.06
2.05
2.05
2.04
2.03
2.03
2.02
2.01
2.01
2.00 H2O
1.98
1.98
1.97
1.96
1.96
1.95
1.94
1.93
1.93
1.92
10v
N
Me
O
1.11
1.03
1.02
1.20
3.00
2.04
2.03
4.36
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

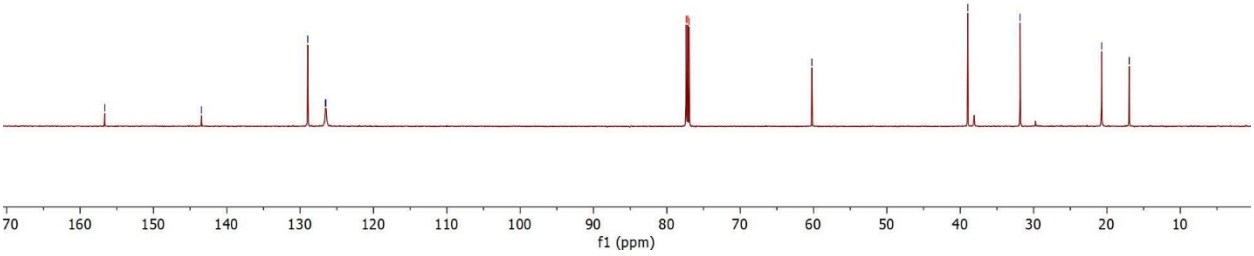

162.3
141.8
138.1
129.0
128.6
123.6
121.8
121.3
114.1
77.4 CDCl3
77.0 CDCl3
76.7 CDCl3
29.7
29.6
29.6
25.5
24.7
22.0
13C NMR (101 MHz, CDCl3)
N
O
Me
10v
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.39
7.37
7.34
7.26 CDCl3
7.24
3.31
1.68
1.68
1.66
1.64
1.63
1.58
1.58
1.57
1.54
1.53
1.52
1.49
1.48
1.47
1.45
1.43
1.42
1.41
1.37
1.36
1.35
1.34
1.33
1.32
1.31
1.30
1.11
0.84
1H NMR (300 MHz, CDCl3)
Me
Me
O
N
O
N
Me
Me
Me
12a
2.09
3.08
3.00
6.89
6.30
6.11
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)

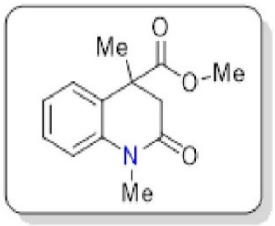
^{13}C NMR (151 MHz, $CDCl_3$)

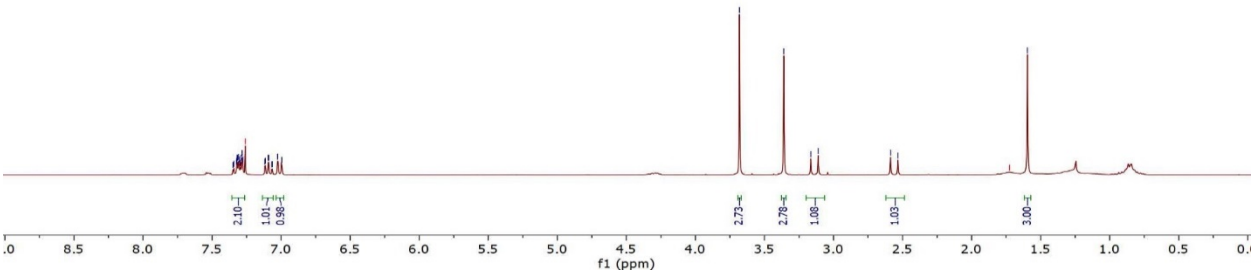


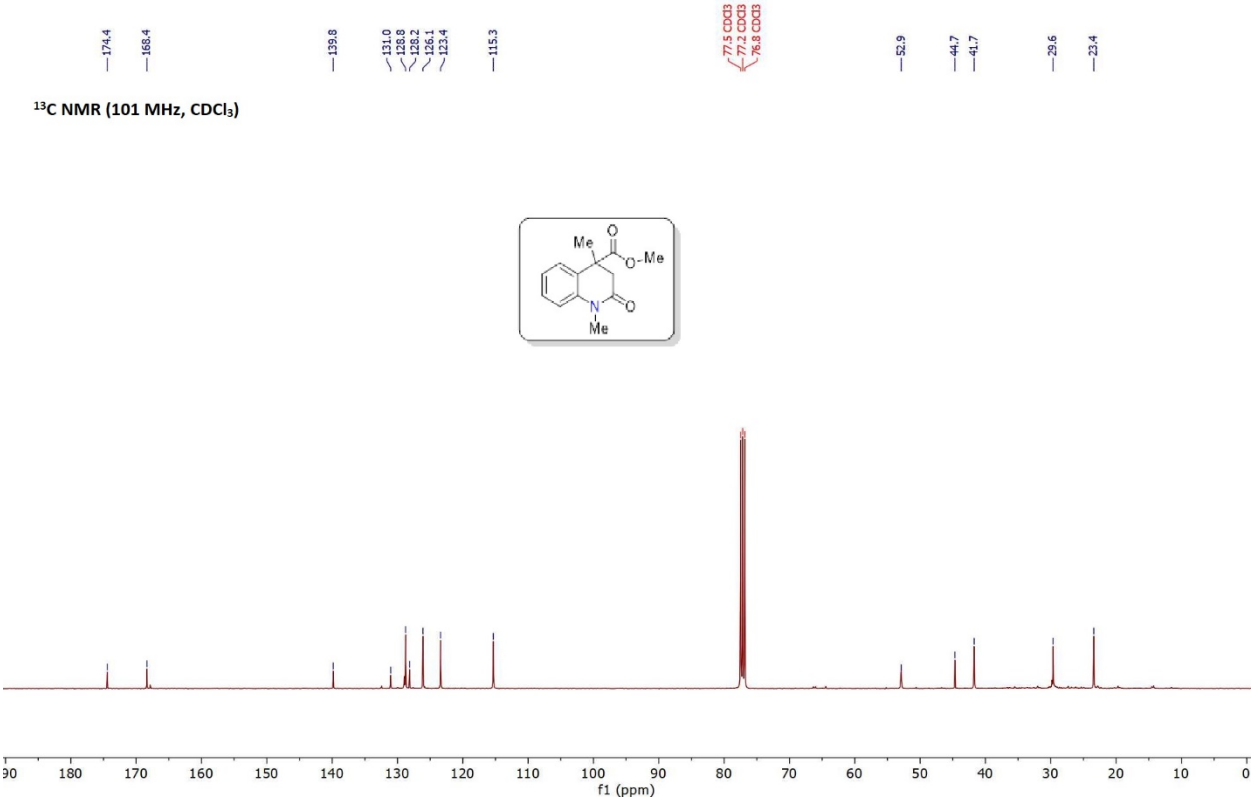
12a

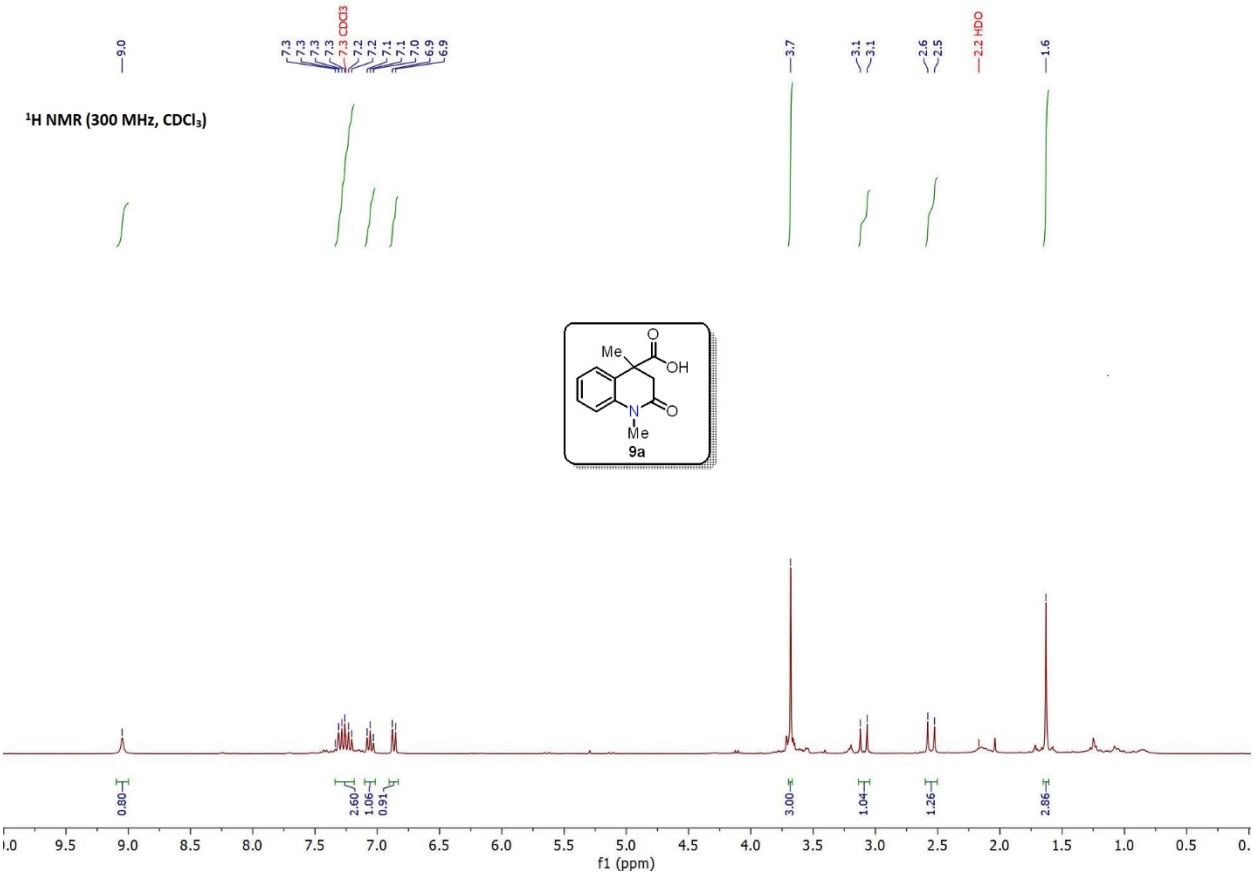


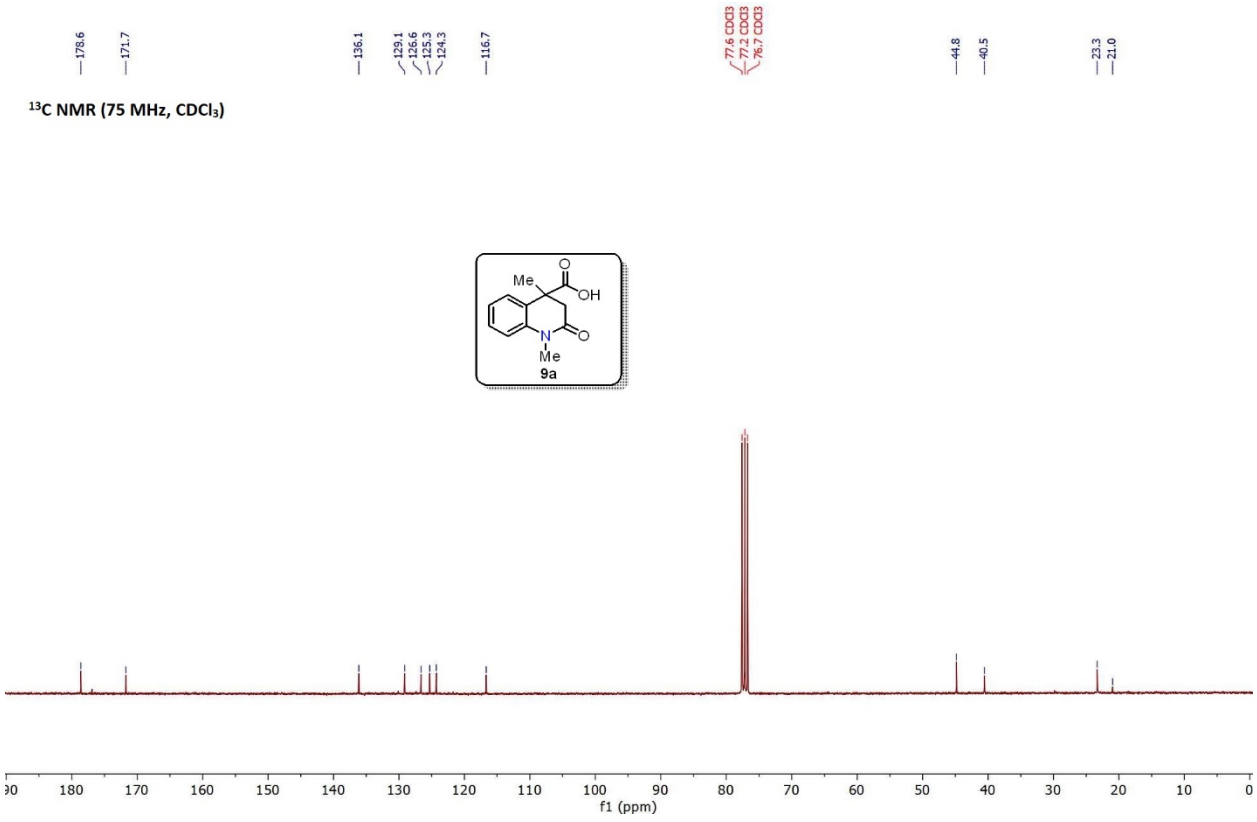
^{1}H NMR (300 MHz, $CDCl_3$)






174.4
168.4
139.8
131.0
128.8
128.2
126.1
123.4
115.3
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
52.9
44.7
41.7
29.6
23.4
13C NMR (101 MHz, CDCl3)
Me
O
O-Me
N
O
Me
f1 (ppm)


9.0
7.3
7.3
7.3
7.3
7.3 CDCl3
7.2
7.2
7.1
7.1
7.0
6.9
6.9
3.7
3.1
3.1
2.6
2.5
2.2 HDO
1.6
1H NMR (300 MHz, CDCl3)
Me
OH
O
N
O
Me
9a
0.80
2.60
1.06
0.91
3.00
1.04
1.26
2.86
f1 (ppm)



^{13}C NMR (75 MHz, $CDCl_3$)