Electronic Supplementary Material (ESI) for ChemComm.

Hydrogen-Free Palladium-Catalyzed Intramolecular *anti*-Markovnikov Hydroaminocarbonylation of 2-(1-Methylvinyl)anilines

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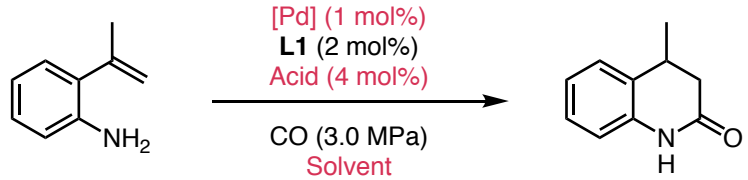
1. Supporting Tables and Schemes.

Table S1. Effect of Pd precursors, acids and solvents. [a]

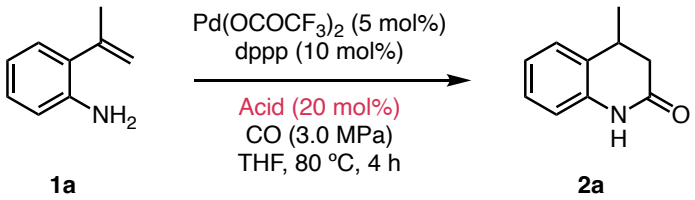


1a **2a**

Entry	Pd	Solvent	Acid	Yield (%)
1	$PdCl_2$	THF	TsOH	n.d.
2	$PdBr_2$	THF	TsOH	n.d.
3[c]	$Pd(dppf)Cl_2$	THF	TsOH	5
4	$Pd(OCOCF_3)_2$	Toluene	TsOH	27
5	$Pd(OCOCF_3)_2$	EtOAc	TsOH	>95
6	$Pd(OCOCF_3)_2$	DCE	TsOH	17
7	$Pd(OCOCF_3)_2$	THF	Benzoic acid	n.d.
8	$Pd(OCOCF_3)_2$	THF	CF_3COOH	n.d.
9	$Pd(OCOCF_3)_2$	THF	H_2SO_4	n.d.
10	$Pd(OCOCF_3)_2$	THF	HCl	n.d.

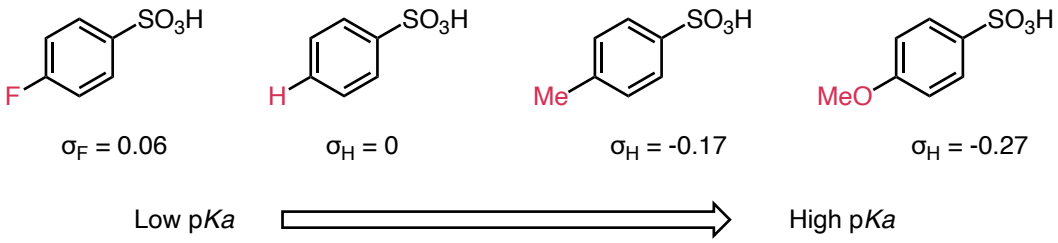
[a] Reactions were performed with **1a** (0.25 mmol) with Pd (1.0 mol%), dppp (2 mol%) and acid (4.0 mol%) in corresponding solvent (2.0 ml), 24 h [b] Yields were determined by GC analysis using mesitylene as an internal standard. [c] no ligand.

Table S2. Effect of TsOH concentration.[a]



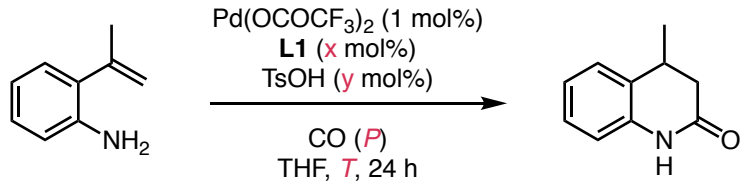
1a **2a**

Entry	Acid	Yield (%)[a]
1	4-F-benzenesulfonic acid	84
2	benzenesulfonic acid	84
3	TsOH	85
4	4-OMe-benzenesulfonic acid	91



[a] Reactions were performed with **1a** (0.25 mmol) with $Pd(OCOCF_3)_2$ (1 mol%), dppp (1 mol%) and TsOH (z mol%) in THF (2.0 ml), 8 h. [b] Yields of **2a** were determined by GC analysis using mesitylene as an internal standard.

Table S3. Screen of reaction conditions (ratio/temperature/pressure). [a]

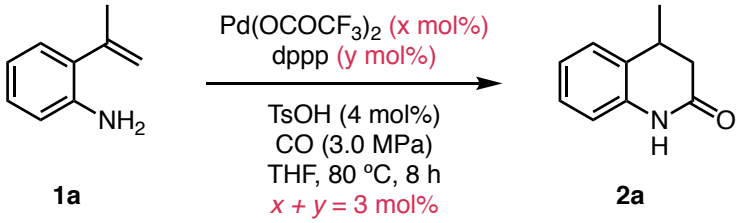


1a **2a**

Entry	X	Y	*P* (MPa)	*T* (C°)	Yield (%)[b]
1	1	4	3.0	80	60
2	3	4	3.0	80	98
3	4	4	3.0	80	68
4[c]	2	1	3.0	80	34
5[c]	2	2	3.0	80	38
6[c]	2	4	3.0	80	57
7[c]	2	8	3.0	80	64
8	2	4	1.0	80	33
9	2	4	2.0	80	77
10	2	4	4.0	80	>95
11	2	4	3.0	60	13
12	2	4	3.0	100	>95

[a] Reactions were performed with **1a** (0.25 mmol) with Pd(OCOCF3) (1 mol%), dppp (X mol%) and TsOH (Y mol%) in THF (2.0 ml), 24 h [b] Yields were determined by GC analysis using mesitylene as an internal standard. [c] 12 h.

Table S4. Effect of catalyst concentration (Pd/L ratio).[a]

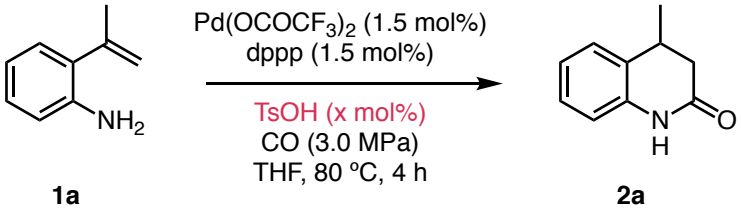


1a **2a**

Entry	x	y	x:y	Yield (%)[b]
1	0.6	2.4	1:4	20
2	1	2	1:2	38
3	1.5	1.5	1:1	55
4	2	1	2:1	28
5	2.4	0.6	4:1	4

[a] Reactions were performed with **1a** (0.25 mmol) with $Pd(OCOCF_3)_2$ (x mol%), dppp (y mol%) and TsOH (4.0 mol%) in THF (2.0 ml), 8 h. [b] Yields of **2a** were determined by GC analysis using mesitylene as an internal standard.

Table S5. Effect of TsOH concentration.[a]

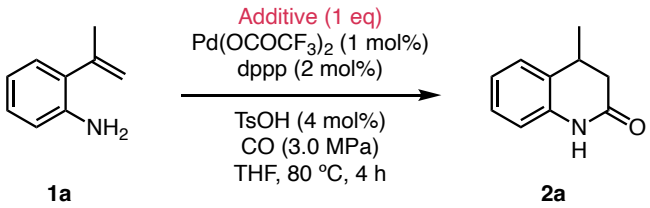


1a **2a**

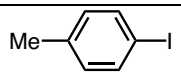
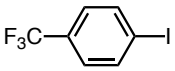
Entry	x	Yield (%)[b]
1	0.5	n.d
2	1.0	n.d
3	1.5	8
4	2.0	8
5	4.0	21
6	6.0	32
7	8.0	35

[a] Reactions were performed with **1a** (0.25 mmol) with $Pd(OCOCF_3)_2$ (1 mol%), dppp (1 mol%) and TsOH (z mol%) in THF (2.0 ml), 8 h. [b] Yields of **2a** were determined by GC analysis using mesitylene as an internal standard.

Table S6. Compatibility of aryl iodides.

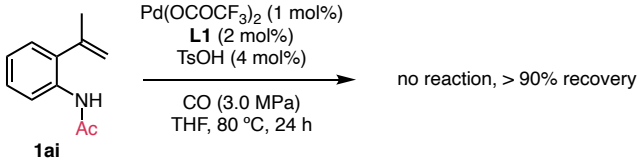


1a **2a**

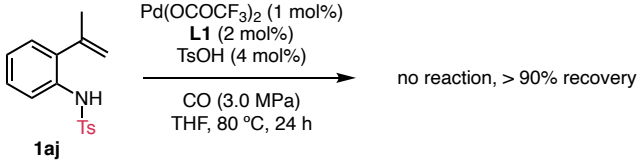
Entry	Additive	Conv. of **1a** (%)	Conv. of Additive (%)	Yield of **2a**
1		12	19	n.d.
2		14	17	n.d.

[a] Reactions were performed with **1a** (0.25 mmol) with $Pd(OCOCF_3)_2$ (1 mol%), dppp (1 mol%) and TsOH (z mol%) in THF (2.0 ml), 8 h. [b] Yields and conversions of **2a** were determined by GC analysis using mesitylene as an internal standard.

Scheme S1. Unsuccessful substrates.

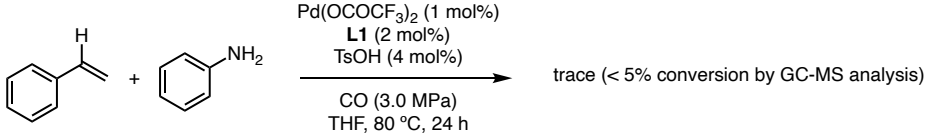


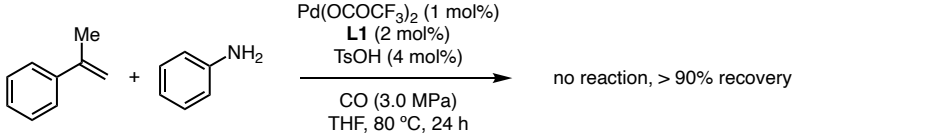
1ai



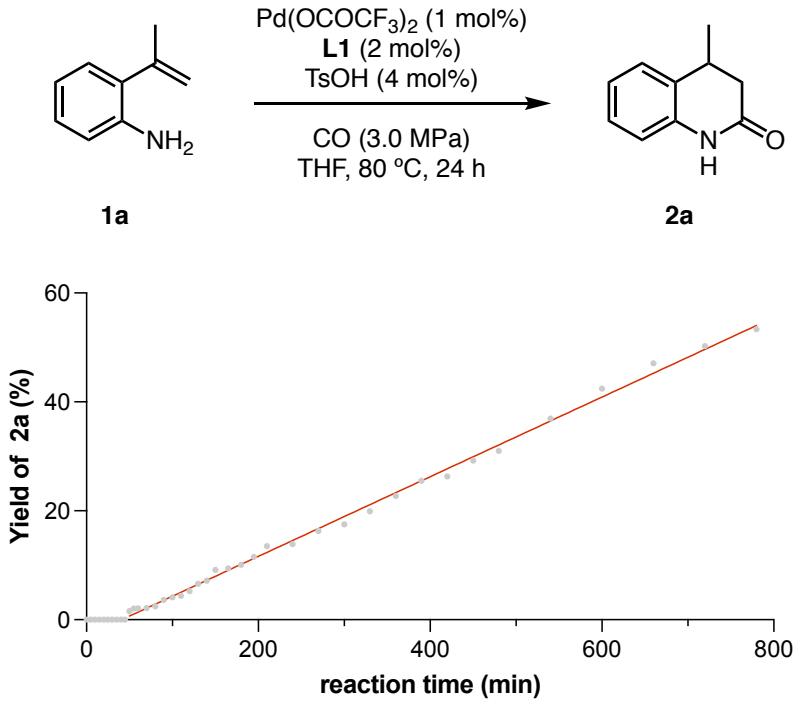
1aj

Scheme S2. Attempts of three component reactions. Products from hydroaminocarbonylation were not detected.

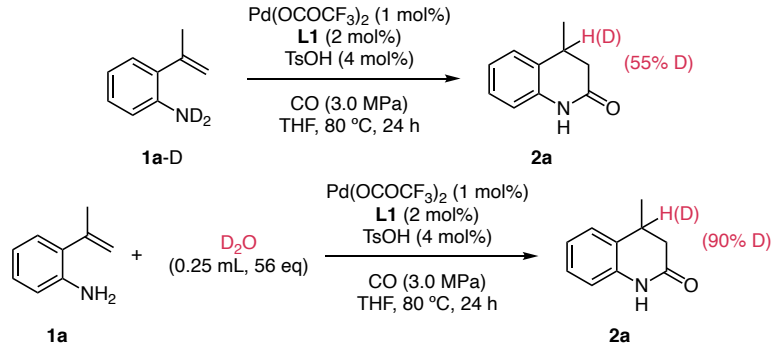




Scheme S3. Analysis of reaction progress

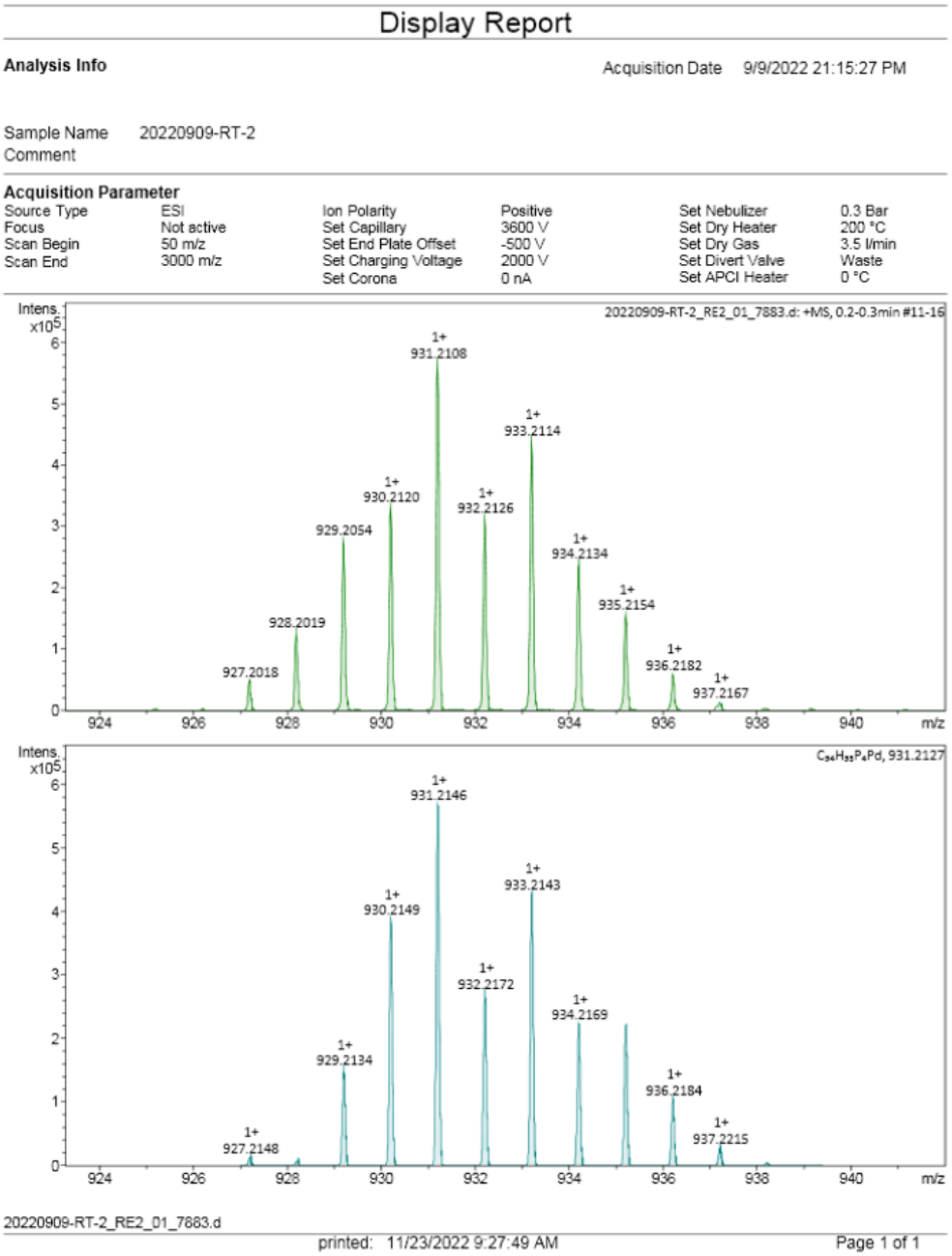


Scheme S4. Deuterium labelling experiments with additional D_2O.



Note: The deuterium incorporation for **1a-**D in the reaction is significantly lower than the theoretical limit. This deviation was attributed to the presence of residual water (H_2O) in the reaction medium.

Figure. S1 HRMS-ESI spectrum of $[H(dppp)_2Pd]^+$.



Note: HRMS-ESI (m/z): $[M]^+$ calcd for $[C_{54}H_{53}P_4Pd]^+$: 931.2127, found: 931.2108.

2. General information

Commercial reagents and solvents were ordered from TCI, Bidepharm and Wohua. Reagents and solvents were used as received unless otherwise stated. When necessary, solvents were dried with standard procedures[1], degassed with N_2 and transferred by syringe. Column chromatography was performed on silica gel (100-200 mesh). Thin layer chromatography (TLC) was performed on EM reagents 0.25 mm silica 60-F plates. NMR spectra were recorded on Bruker ADVANCE III (400 MHz) spectrometer. $CDCl_3$ was the solvent used for the NMR analysis, with tetramethylsilane as the internal standard. Chemical shifts were reported relative to TMS (0.00 ppm) for ^1H NMR and relative to $CDCl_3$ (77.16 ppm) for ^{13}C NMR. Data are reported as follows: chemical shift [integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant(s) in Hertz]. GC-MS analysis was carried out on Angilent 7820A GC system and Angilent 5977B MSD. Melting points were acquired on a Hanon MP450 melting point apparatus. All new products were further characterized by ESI-HRMS. High-resolution mass spectra (HRMS) were recorded on a Bruker microTOF Q III spectrometer with electronspray ionization (ESI).

3. General procedure for hydroaminocarbonlyation

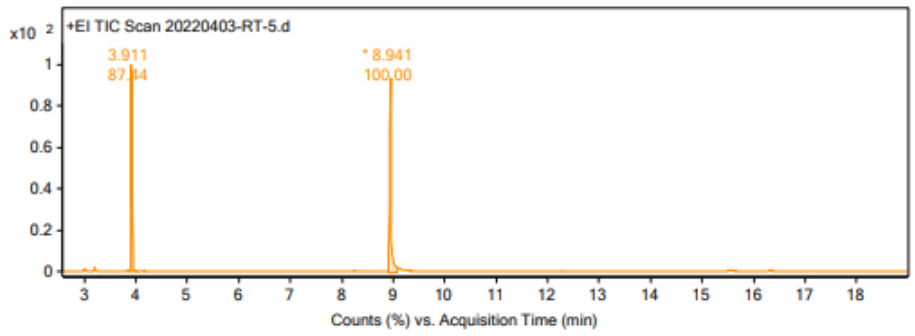
The hydroaminocarbonlyation reactions were conducted in a batch reactor (Shaanxi Wattcas). In a typical run, $Pd(OCOCF_3)_2$ (0.83 mg, 2.5×10^{-3} mmol, 1.0 mol%), 1,3-bis(diphenylphosphino)propane (dppp, 2.06 mg, 5.0×10^{-3} mmol, 2.0 mol%, Rh/L = 1:2), *p*-toluenesulfonic acid (TsOH, 1.72 mg, 0.01 mmol, 4.0 mol%, Rh/acid = 1:4) was dissolved in 2.0 ml of tetrahydrofuran (THF). Substrate (0.25 mmol) was added, and the reactor was flushed with carbon monoxide for three times and then charged with 3.0 MPa carbon monoxide. The mixture was stirred for 24 h at 80 °C. The products were analyzed by GC-MS with mesitylene as an internal standard. The solvents were removed under reduced pressure and the residues were purified by column chromatography (eluent: 20% ethyl acetate in petroleum ether).

Qualitative Analysis Report

Data File	20220403-RT-5.D	**Sample Name**	20220403-RT-5
Sample Type		**Position**	9
Instrument Name	5977B	**User Name**	
Acq Method	GEN-01.M	**Acquired Time**	4/3/2022 3:31:02 PM (UTC+08:00)
IRM Calibration Status	Not Applicable	**DA Method**	00-20220301.m
Comment			
Expected Barcode		**Sample Amount**	
Dual Inj Vol	1	**TuneName**	ATUNE.U
TunePath	D:\MassHunter\GCMS\1\5977\	**TuneDateStamp**	2022-03-03T09:04:44+08:00
MSFirmwareVersion	6.00.34	**OperatorName**	
RunCompletedFlag	True	**Acquisition Time (Local)**	4/3/2022 3:31:02 PM (UTC+08:00)
Acquisition SW Version	MassHunter GC/MS Acquisition B.07.06.2704 18-Jul-2017 Copyright © 1989-2017 Agilent Technologies, Inc.	**SingleQuadrupole Driver Version**	7.6.0.0
SingleQuadrupole Firmware Version	6.00.34		

Chromatograms

Fragmentor Voltage **Collision Energy** 0 **Ionization Mode** EI



Integration Peak List

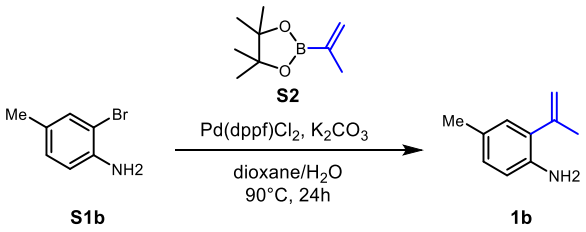
Peak	Start	RT	End	Height	Area	Area %
1	3.883	3.911	4.034	3120451.89	4924193.88	87.44
2	8.894	8.941	9.074	2934303.81	5631776.18	100

--- End Of Report ---

Figure. S2 GC-MS spectrum of curde reaction mixture.

4. Synthesis of Substrate

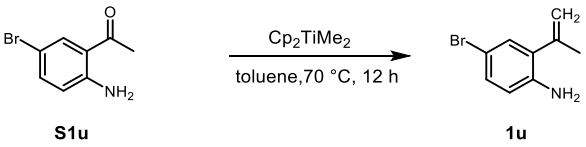
4.1 General Procedure for synthesis of **1b-1s, 1u-1z**



2-Bromoaniline **S1b** (925 mg, 5 mmol, 1.0 eq) was added to a suspension of potassium carbonate (2.07 g, 15 mmol, 3.0 eq), isopropenylboronic acid pinacol ester **S2** (924 mg, 5.5 mmol, 1.1 eq) and $Pd(dppf)Cl_2$ (91mg, 0.25mmol, 0.025 eq) in a mixture of dioxane (20ml) and H_2O (10ml) via syringe. The mixture of reaction was stirred for 24 h at 90 ºC. After cooling to room temperature, the mixture was extracted with ethyl acetate (15 ml × 2). The organic phases were combined, washed with brine, and dried over anhydride Na_2SO_4. The solvent was removed under reduced pressure, and the crude material was purified by silica gel column chromatography (eluent = 20% ethyl acetate in petroleum ether) to give **1b** (640 mg, yield 87%).

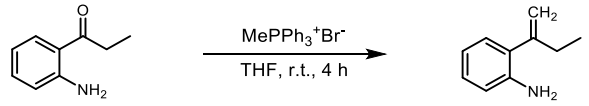
1c-1t, **1v-1z** and **1aa** were prepared following the same procedure as **1b**.

4.2 Synthesis of **1t**



To the solution of freshly prepared Cp_2TiMe_2 in toluene [2] (0.5 M, 20 ml, 2.0 eq), 1-(2-amino-5-bromophenyl) ethenone **S1u** (1.07 g, 5 mmol, 1.0 eq) was added under nitrogen atmosphere. Then the mixture was heated to 70 ℃ and stirred for 12 h. Water (10 mL) was added, and the mixture was extracted with ethyl acetate (20 ml ×2). The organic layers were combined and dried over anhydride Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (eluent: 2% ethyl acetate in petroleum ether) to give 4-bromo-2-(prop-1-en-2-yl) aniline **1u** (360 mg, yield 35%).

4.3 General procedure for synthesis of **1ab**, **1ac**, and **1ae**-**1ah**.

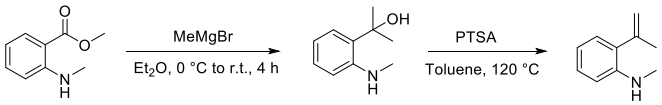


S1ab **1ab**

To a solution of *t*-BuOK (672 mg, 6 mmol, 1.2 eq) in THF (20 ml) at 0 ℃, methyltriphenylphosphonium bromide (2.14 g, 6 mmol 1.2 eq) was added. The mixture was stirred under nitrogen atmosphere for 0.5 h. After that, 2-aminophenones **S1ab** (735 mg, 5 mmol, 1.0 eq) in 2.0 ml THF was added via syringe. The reaction was stirred at room temperature until the complete consumption of the starting material as monitored by thin layer chromatography (about 4 h). The solution was concentrated under reduced pressure, and the residue was purified by chromatography on silica gel (eluent: 2% ethyl acetate in petroleum ether) to give the **1ab** (475 mg, yield 66%).

1ac, 1ae-1ah. were prepared following the same procedure as **1ab**.

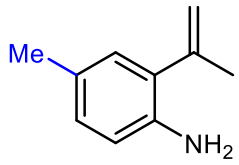
4.4 Synthesis of **1ad**



S1ad-1 **S1ad-2** **1ad**

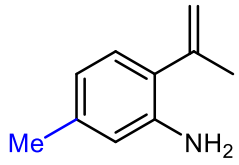
To a solution of methyl 2-(methylamino) benzoate **S1ad-1** (825 mg, 5 mmol, 1.0 eq) in diethyl ether at 0 ℃, methylmagnesium bromide (3.0M in diethyl ether, 12.5 mmol, 4.2 ml, 2.5 eq) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 4 h. The reaction was quenched by saturated $NaHCO_3$, extract with ethyl acetate and washed with brine. The combined organic phases were dried over Na_2SO_4 and concentrated to give the crude 2-(methylamino) α-dimethyl-benzylalcoho **S1ad-2**. TsOH (17.2 mg, 0.1 mmol, 0.02 eq) was added to the solution of the crude 2-(methylamino) *α*-dimethyl-benzylalcoho **S1ad-2** in toluene (20 ml) and the mixture was refluxed overnight. The solvent was removed by vacuum and the residue was subjected to silica gel chromatography (eluent: 2% ethyl acetate in petroleum ether) to give the N-methyl-2-(prop-1-en-2-yl) aniline (**1ad**) (530 mg, 2-step yield: 72%).

5. Characterization data of substrates



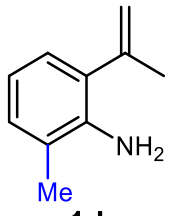
1b

4-Methyl-2-(prop-1-en-2-yl)aniline (**1b**) [3]: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92-6.89 (2H, m), 6.65 (1H, d, *J* = 7.8 Hz), 5.31-5.30 (1H, m). 5.07-5.06 (1H, m), 3.74 (2H, brs), 2.27 (3H, s), 2.10-2.09 (3H, m).



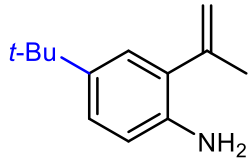
1c

5-Methyl-2-(prop-1-en-2-yl)aniline (**1c**) [4]: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (1H, d, *J* = 7.7 Hz), 6.59 (1H, d, *J* = 7.7 Hz), 6.56 (1H, s), 5.30-5.29 (1H, m), 5.06 (1H, dd, *J* = 2.2, 0.9 Hz), 3.82 (2H, brs), 2.28 (3H, s), 2.08 (3H, dd, *J* = 1.4, 0.9 Hz).



1d

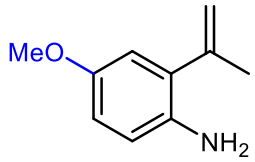
6-Methyl-2-(prop-1-en-2-yl)aniline (**1d**) [3]: light yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (1H, d, *J* = 7.4 Hz), 6.98 (1H, d, *J*= 7.6 Hz), 6.74 (1H, t, *J* = 7.5 Hz), 5.36 (1H, dd, *J* = 2.1, 1.6 Hz), 5.11 (1H, dd, *J* = 2.1, 0.9 Hz), 3.85 (2H, brs), 2.23 (3H, s), 2.13 (3H, s).



1e

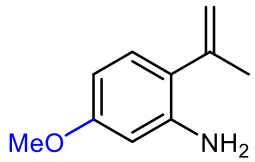
4-(*tert*-butyl)-2-(prop-1-en-2-yl)aniline (**1e**) [5]: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (1H, dd, *J* = 8.3, 2.4 Hz), 7.11 (1H, d, *J* = 2.3 Hz), 6.71 (1H, d, *J* = 8.3

Hz), 5.34 (1H, d, J = 0.6 Hz), 5.11 (1H, s), 3.78 (2H, brs), 2.14 (3H, s), 1.33 (9H, s).



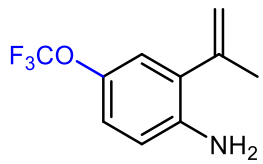
1f

4-Methoxy-2-(prop-1-en-2-yl)aniline (**1f**) [4]: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.68-6.65 (3H, m), 5.30 (1H, s), 5.06 (1H, dd, J = 2.1, 0.9 Hz), 3.75 (3H, s), 3.59 (2H, brs), 2.08-2.07 (3H, m).



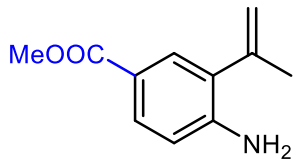
1g

5-Methyloxy-2-(prop-1-en-2-yl)aniline (**1g**) [4]: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (1H, d J = 8.4 Hz), 6.34 (1H, dd, J = 8.4, 2.5 Hz), 6.28 (1H, d, J = 2.5 Hz), 5.29 (1H, s), 5.06 (1H, s), 3.93 (2H, brs), 3.78 (3H, s), 2.08 (3H, s).



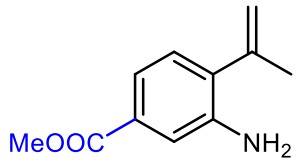
1h

4-Trifluoromethyloxy-2-(prop-1-en-2-yl)aniline (**1h**) [6]: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94-6.91 (2H, m), 6.65 (1H, d, J = 8.2 Hz), 5.34 (1H, s), 5.10 (1H, d, J = 0.7 Hz), 3.87 (2H, brs), 2.06 (3H, s).



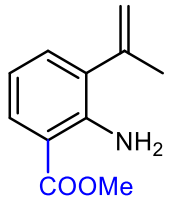
1i

4-Methoxycarbonyl-2-(prop-1-en-2-yl)aniline (**1i**) [7]: light yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.72 (2H, m), 6.65 (1H, d, J = 8.9 Hz), 5.32 (1H, d, J = 1.3 Hz), 5.06 (1H, d, J = 0.8 Hz), 4.31 (2H, brs), 3.84 (3H, s), 2.06 (3H, s).



1j

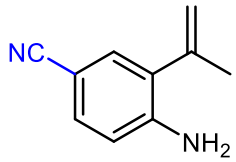
5-Methoxycarbonyl-2-(prop-1-en-2-yl)aniline (**1j**) [7]: colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.37 (2H, m), 7.07 (1H, dd, *J* = 7.6, 0.5 Hz), 5.33-5.32 (1H, m), 5.08 (1H, s), 3.95 (2H, brs), 3.88 (3H, s), 2.06 (3H, s).



1k

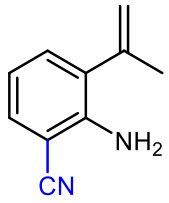
6-Methoxycarbonyl-2-(prop-1-en-2-yl)aniline (**1k**): yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (1H, dd, *J* = 8.1, 1.6 Hz), 7.13 (1H, dd, *J* = 7.3, 1.6 Hz), 6.62 (1H, dd, *J* = 8.0, 7.3 Hz), 6.06 (2H, brs), 5.34-5.33 (1H, m), 5.06 (1H, dd, *J* = 2.0, 1.0 Hz), 3.87 (3H, s), 2.05 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 147.2, 142.9, 132.8, 130.6, 130.2, 116.5, 115.4, 110.6, 51.7, 23.9.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_{11}H_{13}NNaO_2]^+$: 214.0838, found: 214.0842.



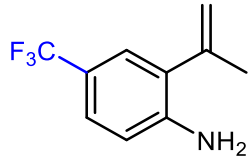
1l

4-Cyano-2-(prop-1-en-2-yl)aniline (**1l**) [5]: light yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.27 (2H, m), 6.68 (1H, d, *J* = 8.3 Hz), 5.36-5.35 (1H, m), 5.08 (1H, dd, *J* = 1.7, 0.9 Hz), 4.41 (2H, brs), 2.04 (3H, m).



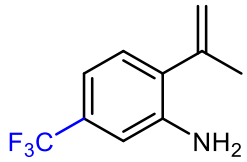
1m

6-Cyano-2-(prop-1-en-2-yl)aniline (**1m**) [8]: colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (1H, dd, *J* =7.8, 1.5 Hz), 7.18 (1H, dd, *J* = 7.5, 1.5 Hz), 6.70 (1H, t, *J* = 7.7 Hz), 5.37-5.36 (1H, m), 5.08 (1H, dd, *J* = 1.4, 1.0 Hz), 4.63 (2H, brs), 2.05-2.04 (3H, m).



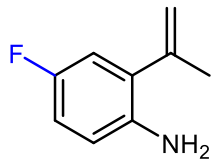
1n

4-Trifluoromethyl-2-(prop-1-en-2-yl)aniline (**1n**) [4]: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.28 (2H, overlapped m), 6.71 (1H, d, *J* = 8.2 Hz), 5.36-5.35 (1H, m), 5.10 (1H, d, *J* = 1.9, 0.9 Hz), 4.14 (2H, brs), 2.08-2.07 (3H, m).



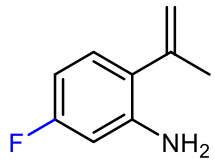
1o

5-Trifluoromethyl-2-(prop-1-en-2-yl)aniline (**1o**) [4]: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (1H, d, *J* = 7.9 Hz), 6.97 (1H, d, *J* = 7.9 Hz), 6.92 (1H, s), 5,36-5.35 (1H, m), 5.10-5.09 (1H, m), 4.01 (2H, brs), 2.08-2.07 (3H, dd, *J* = 1.4, 1.0 Hz).



1p

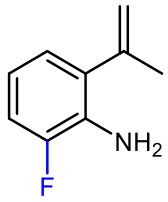
4-Fluoro-2-(prop-1-en-2-yl)aniline (**1p**) [3]: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80-6.76 (2H, m), 6.65-6.61 (1H, m), 5.33-5.32 (1H, m), 5.08 (1H, dd, *J* = 1.9, 0.9 Hz), 3.71 (2H, brs), 2.06 (3H, dd, *J* = 1.4, 1.0 Hz).



1q

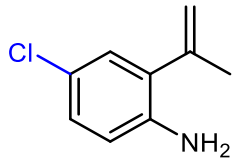
5-Fluoro-2-(prop-1-en-2-yl)aniline (**1q**) [5]: light yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (1H, dd, *J* = 8.4, 6.5 Hz), 6.46-6.38 (2H, m), 5.32-5.31 (1H, m), 5.05

(1H, dd, *J* = 2.0, 0.9 Hz), 3.96 (2H, brs), 2.06 (3H, dd, *J* = 1.4, 0.9 Hz).



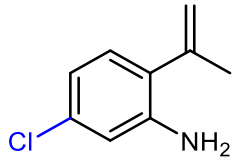
1r

6-Fluoro-2-(prop-1-en-2-yl)aniline (**1r**) [9]: colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (1H, ddd, *J* = 10.9, 8.1, 1.3 Hz), 6.84 (1H, d, *J* = 7.7 Hz), 6.66 (1H, td, *J* =7.9, 5.4 Hz), 5.34-5.33 (1H, m), 5.11-5.10 (1H, dd, *J* = 1.9, 0.9 Hz), 3.91 (2H, brs), 2.08 (3H, dd, *J* = 1.4, 1.0 Hz).



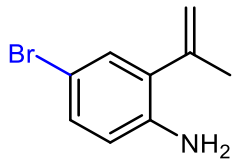
1s

4-Chloro-2-(prop-1-en-2-yl)aniline (**1s**) [4]: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03-7.00 (2H, m), 6.63-6.61 (1H, m), 5.32-5.31 (1H, m), 5.07 (1H, dd, 1.9, 0.9 Hz), 3.83 (2H, brs), 2.05 (3H, s).



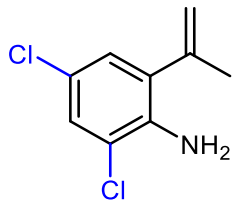
1t

5-Chloro-2-(prop-1-en-2-yl)aniline (**1t**) [3]: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (1H, dd, *J* =7.8, 0.5 Hz), 6.71-6.68 (2H, m), 5.32-5.31 (1H, m), 5.05 (1H, 2.0, 1.0 Hz), 3.91 (2H, brs), 2.05 (3H, dd, *J* = 1.4, 1.0 Hz).



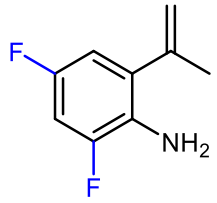
1u

4-Bromo-2-(prop-1-en-2-yl)aniline (**1u**) [3]: light yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.12 (2H, m), 6.57 (1H, d, *J* = 9.1 Hz), 5.31-5.30 (1H, m), 5.05 (1H, dd, *J* = 1.9, 0.9 Hz), 3.83 (1H, brd), 2.04 (3H, s).



1v

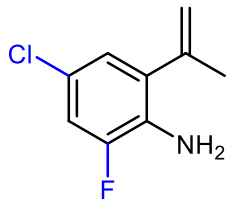
4, 6-Dichloro-2-(prop-1-en-2-yl)aniline (**1v**) [10]: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (1H, d, *J* = 2.4 Hz), 6.92 (1H, d, *J* = 2.4 Hz), 5.35-5.34 (1H, m), 5.08 (1H, d, *J* = 1.8, 0.9 Hz), 4.22 (2H, brs), 2.04 (3H, s).



1w

4, 6-Difluoro-2-(prop-1-en-2-yl)aniline (**1w**): yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69 (1H, ddd, *J* = 11.1, 8.4, 2.8 Hz), 6.61 (1H, ddd, *J* = 9.2, 2.8, 1.7 Hz), 5.35 (1H, s), 5.11 (1H, dd, 1.8, 0.9 Hzz), 3.74 (2H, brs), 2.05 (3H, dd, *J* = 1.5, 1.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6 (dd, *J* = 238.0, 12.4 Hz), 151.2 (dd, *J* = 241.0, 12.4 Hz), 141.7, 131.3 (dd, *J* = 8.2, 4.4 Hz), 127.9 (dd, *J* = 12.6, 3.2 Hz), 116.6, 109.9 (dd, *J* = 22.0, 3.4 Hz), 102.2 (dd, *J* = 26.4, 23.5 Hz), 23.5. ^{19}F NMR (375 MHz, $CDCl_3$) δ -125.2 (d, *J* = 1.3 Hz), -130.1 (d, *J* = 1.3 Hz).

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_9H_9F_2NNa]^+$: 192.0596, found: 192.0601.

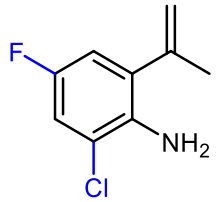


1x

4-Chloro-6-fluoro-2-(prop-1-en-2-yl)aniline (**1x**): colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (1H, dd, *J* = 10.6, 2.3 Hz), 6.83 (1H, m), 5.36-5.34 (1H, m), 5.10 (1H, dd, *J* = 1.8, 0.9 Hz),3.87 (2H, brs), 2.05 (3H, dd, *J* = 1.4, 1.0 Hz). ^{13}C NMR (100

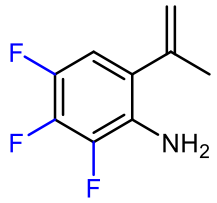
MHz, $CDCl_3$) δ 151.4 (d, *J* = 242.0 Hz), 141.4 (d, *J* = 3.0 Hz), 131.8 (d, *J* = 4.0 Hz), 130.5 (d, *J* = 12.5 Hz), 123.5 (d, *J* = 3.0 Hz), 121.7 (d, *J* = 10.6 Hz), 116.8, 114.3 (d, *J* = 22.6 Hz), 23.6. ^{19}F NMR (375 MHz, $CDCl_3$) δ -131.6.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_9H_9ClFNNa]^+$: 208.0300, found:208.0301.



1y

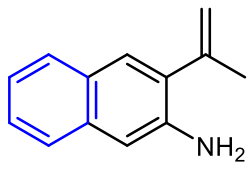
4-Fluoro-6-chloro-2-(prop-1-en-2-yl)aniline (**1y**) [11]: yellow oil, ^1H NMR (400 MHz, $CDCl_3$) δ 6.95 (1H, dd, *J* = 8.1, 2.9 Hz), 6.71 (1H, dd, *J* = 8.9, 2.9 Hz), 5.35-5.34 (1H, m), 5.09 (1H, dd, *J* = 1.7, 0.9 Hz), 4.05 (2H, brs), 2.05-2.04 (3H, m).



1z

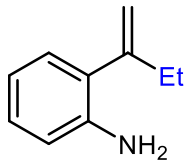
4, 5, 6-Trifluoro-2-(prop-1-en-2-yl)aniline (**1z**): colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 6.68 (1H, ddd, *J* = 10.6, 7.9, 2.4 Hz), 5.36-5.35 (1H, m), 5.09 (1H, s), 3.83 (2H, brs), 2.03 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3 (ddd, *J* = 239.0, 10.3, 3.3 Hz), 140.93 (dt, *J* = 2.4,1.2 Hz), 140.6 (ddd, *J* = 241.4, 12.0, 3.6 Hz), 139.2 (ddd, 247.6, 16.2, 13.8 Hz), 129.2 (dd, *J* = 9.8, 2.4 Hz), 124.2 (m), 117.1, 110.5 (dd, *J* = 17.9, 3.3 Hz), 23.6. ^{19}F NMR (375 MHz, $CDCl_3$) δ -150.4 (d, *J* = 21.7 Hz), -154.8 (d, *J* = 19.7 Hz), -162.5 (m).

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_9H_8F3NNa]^+$: 210.0501, found:210.0498.



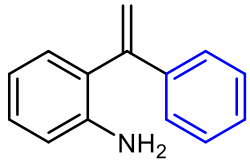
1aa

3-(Prop-1-en-2-yl)naphthalen-2-amine (**1aa**) [12]: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (1H, d, *J* = 8.1 Hz), 7.55 (1H, d, *J* = 8.3 Hz), 7.50 (1H, s), 7.32 (1H, ddd, *J* = 8.2, 6.8, 1.2 Hz), 7.20 (1H, ddd, *J* = 8.1, 6.8, 1.1 Hz), 6.97 (1H, s), 5.35 (1H, dd, *J* = 2.0, 1.6 Hz), 5.12 (1H, dd, *J* = 2.0, 0.9 Hz), 3.97 (2H, brs), 2.15-2.14 (3H, m).



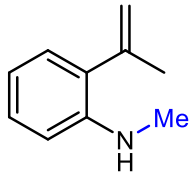
1ab

2-(But-1-en-2-yl)aniline (**1ab**) [6]: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (1H, td, *J* = 7.8, 1.6 Hz), 6.98 (1H, dd, *J* = 7.6, 1.5 Hz), 6.72 (2H, m), 5.27 (1H, d, 3.5, 1.6 Hz), 5.04 (1H, s), 3.84 (2H, brs), 2.37 (2H, q, *J* = 7.4 Hz), 1.06 (3H, t, *J* = 7.4 Hz).



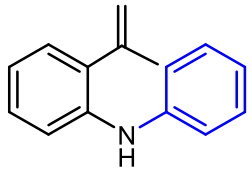
1ac

2-(1-Phenylethenyl)aniline (**1ac**) [5]: white solid, m.p. = 77.2-77.5 C°, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.37 (2H, m), 7.35-7.31 (2H, m), 7.20-7.15 (1H, m), 7.13 (1H, dd, *J* = 7.5, 1.5 Hz), 6.80 (1H, td, *J* = 7.4, 1.1 Hz), 6.71 (1H, dd, *J* = 8.0, 0.9 Hz), 5.81 (1H, d, *J* = 1.4 Hz), 5.37 (1H, d, *J* = 1.4 Hz), 3.56 (2H, brs).



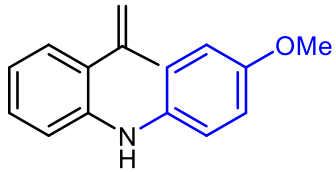
1ad

***N*-methyl-2-(prop-1-en-2-yl)aniline** (**1ad**) [3]: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (1H, ddd, *J* =8.1, 7.5, 1.6 Hz), 7.05 (1H, dd, *J* = 7.4, 1.6 Hz), 6.72 (1H, td, *J* = 7.4, 1.1 Hz), 6.66 (1H, d, *J* = 8.2 Hz), 5.33-5.31 (1H, m), 5.06 (1H, dd, *J* = 2.2, 0.9 Hz), 4.20 (1H, brs), 2.86 (3H, s), 2.08 (3H, dd, *J* = 1.4, 1.0 Hz).



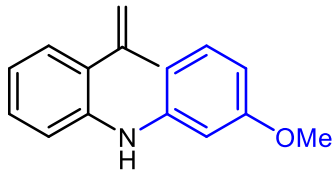
1ae

***N*-phenyl-2-(prop-1-en-2-yl)aniline** (**1ae**) [13]: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.30 (3H, m), 7.25-7.21 (2H, m), 7.14-7.12 (2H, m), 7.00-6.95 (2H, m), 5.93 (1H, brs), 5.36 (1H, s), 5.13 (1H, s), 2.13 (3H, s).



1af

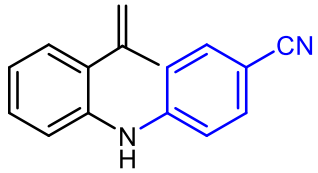
***N*-(4-methoxyphenyl)-2-(prop-1-en-2-yl)aniline** (**1af**) [13]: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14-7.06 (5H, m), 6.90-6.86 (2H, m), 6.83 (1H, td, *J* = 7.4, 1.5 Hz), 5.77 (1H, brs), 5.34-5.33 (1H, m), 5.12-5.11 (1H, m), 3.81 (3H, s), 2.11 (3H, m).



1ag

***N*-(3-methoxyphenyl)-2-(prop-1-en-2-yl)aniline** (**1ag**): light yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.38 (1H, m), 7.24-7.19 (3H, m), 6.99-6.95 (1H, m), 6.70-6.68 (1H, m), 6.54-6.51 (1H, m), 5.90 (1H, brs), 5.34 (1H, d, *J* = 1.5 Hz), 5.11-5.10 (1H, m), 3.82 (3H, s), 2.11 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 144.0, 139.1, 134.1, 130.2, 128.9, 127.8, 121.1, 118.1, 116.3, 110.4, 106.1, 103.4, 55.3, 24.0.

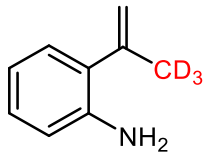
HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_{16}H_{14}N_2Na]^+$: 262.3072, found: 262.3077.



1ah

4-((2-(Prop-1-en-2-yl)phenyl)amino)benzonitrile (**1ah**): yellow oil, ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.49-7.45 (2H, m), 7.34 (1H, dd, *J* = 8.0, 1.1 Hz), 7.26-7.22 (2H, m), 7.10 (1H, td, *J* = 7.5, 1.3 Hz), 6.97-6.93 (2H, m), 6.07 (1H, brs), 5.28-5.27 (1H, m), 5.00 (1H, dd, *J* = 1.9, 0.9 Hz), 2.01 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 143.5, 136.9, 136.4, 133.9, 129.4, 128.1, 124.1, 121.5, 120.1, 116.7, 115.0, 101.6, 24.0. HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_{16}H_{14}N_2Na]^+$: 257.1049, found: 257.1046.

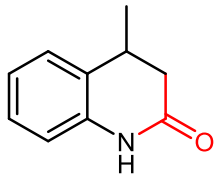


84% D

1a-CD_3

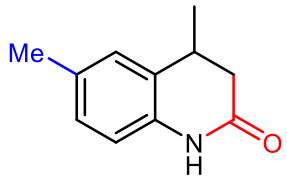
2-(Prop-1-en-2-yl-3,3,3-*d3*)-aniline (1a-CD_3): **1a-CD_3** was prepared following the literature procedure [9]. ^1H NMR (400 MHz, $CDCl_3$) δ 7.06–7.01 (2H, m), 6.74–6.65 (2H, m), 5.27 (1H, s), 5.08 (1H, d, *J* = 2.0 Hz), 3.75 (brs, 2H), 2.02 (0.48H, s).

6. Characterization data of 4-Methyl-3,4-dihydroquinolin-2(1*H*)-one



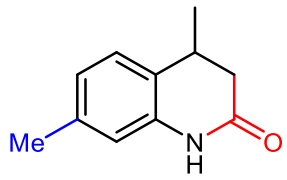
2a

4-Methyl-3,4-dihydroquinolin-2(1*H*)-one (2a) [15]**:** white solid, m.p. = 113.4-115.0 C°, 38.3 mg, 95%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (1H, brs), 7.20-7.15 (2H, m), 7.02 (1H, t, *J* = 7.4 Hz), 6.89 (1H, d, *J* =7.7 Hz), 3.16-3.11 (1H, m), 2.74 (1H, dd, *J* = 16.1, 5.5 Hz), 2.44 (1H, dd, *J* = 16.1, 7.1 Hz), 1.31 (3H, d, *J* = 5.9 Hz), ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 136.6, 128.7, 127.6, 126.6, 123.4, 115.9, 38.4, 30.8, 19.9.



2b

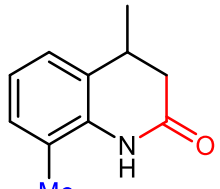
4,6-Dimethyl-3,4-dihydroquinolin-2(1*H*)-one (2b) [15]**:** white solid, m.p. = 120.5-122.0 C°, 31.4 mg, 72%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (1H, s), 6.98 (2H, m), 6.77 (2H, d, *J* = 7.8 Hz), 3.08 (1H, m), 2.72 (1H, dd, *J* = 16.1, 5.8 Hz), 2.41 (2H, dd, *J* = 16.1, 7.1 Hz), 2.30 (3H, s), 1.30 (3H, d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 134.1, 132.9, 128.7, 128.0, 127.2, 115.8, 38.5, 30.8, 21.0, 20.0.



2c

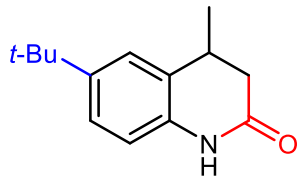
4,7-dimethyl-3,4-dihydroquinolin-2(1*H*)-one (2c) [15]**:** white solid, m.p. = 111.6-113.2 C°, 38.0 mg, 87%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (1H, brs), 7.07 (1H, d, *J* = 7.6 Hz), 6.83 (1H, d, *J* = 7.6 Hz), 6.73 (1H, s), 3.12-3.07 (1H, m), 2.73 (1H, dd, *J* = 16.1, 5.8 Hz), 2.42 (2H, dd, *J* = 16.1, 7.3, Hz), 2.30 (3H, s), 1.30 (3H, d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 137.6, 136.5, 126.3, 125.8, 124.1, 116.5, 38.6,

30.4, 21.1, 20.0.



2d

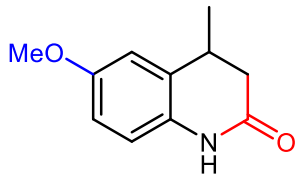
4,9-Dimethyl-3,4-dihydroquinolin-2(1*H*)-one (2d) [16]: white solid, m.p. = 127.5-128.8 ℃, 39.3 mg, 90%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (1H, brs), 7.06-7.03 (2H, m), 6.93 (1H, d, *J* = 7.5 Hz), 3.15-3.08 (1H, m), 2.71 (1H, dd, *J* = 15.9, 5.7 Hz), 2.42 (2H, dd, *J* = 15.9, 6.9 Hz), 2.28 (3H, s), 1.29 (3H, d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 134.8, 129.1, 128.9, 124.5, 123.3, 123.0, 38.4, 31.1, 19.8, 17.1.



2e

6-(*Tert*-butyl)-4-methyl-3,4-dihydroquinolin-2(1*H*)-one (2e): white solid, m.p. = 121.0-122.2 ℃, 33.5 mg, 62%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (1H, brs), 7.20-7.18 (2H, m), 6.80 (1H, d, *J* = 8.7 Hz), 3.16-3.08 (1H, m), 2.74 (1H, dd, *J* = 16.1, 5.9 Hz), 2.44 (1H, dd, *J* = 16.1, 6.7 Hz), 1.31 (3H. d, *J* = 7.0 Hz), 1.31 (9H, s), ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 146.4, 134.0, 128.3, 124.4, 123.6, 115.5, 38.5, 34.5, 31.6, 31.2, 20.1.

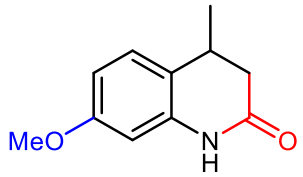
HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_{14}H_{19}NNaO]^+$: 240.1359, found: 240.1360.



2f

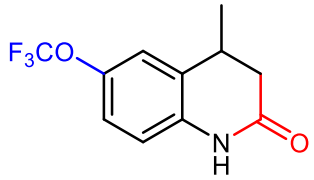
6-Methoxy-4-methyl-3,4-dihydroquinolin-2(1*H*)-one (2f) [16]: white solid, m.p.= 135.2-136.8 ℃, 41.6 mg, 86%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (1H, brs), 6.81-6.69 (3H, m), 3.78 (3H, s), 3.11-3.05 (1H, m), 2.70 (1H, dd, *J* = 16.1, 5.7 Hz), 2.40 (1H, dd,

J = 16.1,7.3 Hz), 1.30 (3H. d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 155.9, 130.3, 130.2, 116.6, 112.8, 112.1, 55.7, 38.3, 31.1, 19.8.



2g

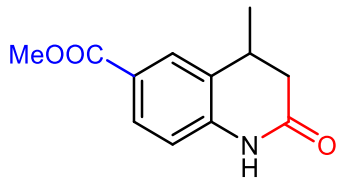
7-Methoxy-4-methyl-3,4-dihydroquinolin-2(1*H*)-one (2g) [16]: white solid, m.p. = 109.0-111.0 C°, 35.8 mg, yield 75%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (1H, brs), 7.08 (1H, d, *J* = 8.4 Hz), 6.56 (1H, d, *J* = 8.3 Hz), 6.41 (1H, s), 3.78 (3H, s), 3.09-3.04 (1H, m), 2.71 (1H, dd, *J* = 16.1, 5.8 Hz), 2.40 (1H, dd, *J* = 16.1, 7.5 Hz), 1.29 (3H. d, *J* = 6.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 159.3, 137.6, 127.4, 121.1, 108.6, 101.8, 55.5, 38.8, 30.1, 20.1.



2h

4-Methyl-6-(trifluoromethoxy)-3,4-dihydroquinolin-2(1*H*)-one (2h): white solid, m.p. = 113.3-115.3 C°, 55.0 mg, 90%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (1H, brs), 7.06-7.03 (2H, m), 6.89 (1H, d, *J* = 8.4 Hz), 3.16-3.11 (1H, m), 2.74 (1H, dd, *J* = 16.2, 5.9 Hz), 2.43 (1H, dd, *J* = 16.2, 7.6 Hz), 1.32 (3H. d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 144.8, 135.3, 130.3, 120.5 (q, *J* = 256.7Hz), 120.3, 119.7 116.7, 37.8, 30.7, 19.5. ^{19}F NMR (375 MHz, $CDCl_3$) δ -58.2.

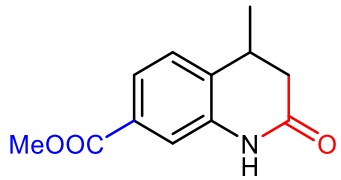
HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_{11}H_{10}F_3NNaO_2]^+$: 268.0556, found: 268.0558.



2i

Methyl 4-methyl-2-oxo-1,2,3,4-tetrahydroquinoline-6-carboxylate (2i): white solid, m.p. = 184.0-185.8 C°, 47.0 mg, 85%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (1H, brs), 7.88 (1H, s), 7.86 (1H, d, *J* = 8.6 Hz), 6.91 (1H, d, *J* = 8.1 Hz), 3.89 (3H, s), 3.20-3.15 (1H, m), 2.76 (1H, dd, *J* = 16.3,5.7 Hz), 2.45 (1H, dd, *J* = 16.2, 7.2 Hz), 1.33 (3H. d, *J* = 7.0 Hz), ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 166.8, 140.7, 129.6, 128.5, 128.4, 125.1, 115.7, 52.2, 38.2, 30.6, 19.8.

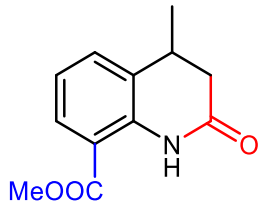
HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_{12}H_{13}NNaO_3]^+$: 242.0788, found:242.0788.



2j

Methyl 4-methyl-2-oxo-1,2,3,4-tetrahydroquinoline-7-carboxylate (2j): white solid, m.p. = 159.0-160.5 C°, 48.5 mg, 89%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (1H, brs), 7.68 (1H, dd, *J* = 7.9, 1.6 Hz), 7.54 (1H, d, *J* = 1.6 Hz), 7.25 (1H, d, *J* = 7.9 Hz), 3.90 (3H, s), 3.19-3.14 (1H, m), 2.75 (1H, dd, *J* = 16.2, 5.9 Hz), 2.45 (1H, dd, *J* = 16.2, 7.2 Hz), 1.32 (3H. d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 166.7, 136.9, 133.9, 129.7, 126.7, 124.7, 116.7, 52.4, 38.0, 31.0, 19.7.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_{12}H_{13}NNaO_3]^+$: 242.0788, found:242.0787.

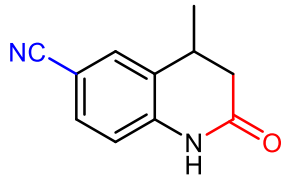


2k

Methyl 4-methyl-2-oxo-1,2,3,4-tetrahydroquinoline-8-carboxylate (2k): white

solid, m.p. = 41.1-42.1 C°, 21.0 mg, 39%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.49 (1H, brs), 7.87 (1H, dd, *J* = 8.0,1.3 Hz), 7.36 (1H, d, *J* = 7.4 Hz), 7.01 (1H, t, *J* = 7.8 Hz), 3.90 (3H, s), 3.17-3.12 (1H, m), 2.71 (1H, dd, *J* = 16.2, 5.9 Hz), 2.42 (1H, dd, *J* = 16.2, 6.7 Hz), 1.30 (3H. d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 167.7, 139.5, 131.8, 129.9, 129.5, 121.9, 113.4, 52.4, 37.8, 31.1, 20.0.

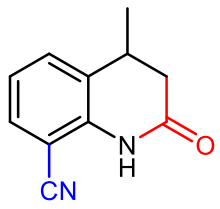
HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_{12}H_{13}NNaO_3]^+$: 242.0788, found: 242.0792.



2l

4-Methyl-2-oxo-1,2,3,4-tetrahydroquinoline-6-carbonitrile (2l): white solid, m.p. = 241.1-242.6 C°, 40.5 mg, 87%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (1H, brs), 7.50-7.48 (2H, m), 6.92-6.90 (1H, m), 3.22-3.14 (1H, m), 2.76 (1H, dd, *J* = 16.4, 5.9 Hz), 2.47 (1H, dd, *J* = 16.4, 7.6 Hz), 1.34 (3H. d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 140.5, 132.2, 130.8, 129.7, 119.1, 116.3, 106.7, 37.9, 30.6, 19.6.

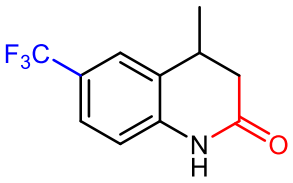
HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_{11}H_{10}N_2NaO]^+$: 209.0685, found: 209.0688.



2m

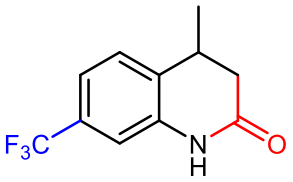
4-Methyl-2-oxo-1,2,3,4-tetrahydroquinoline-8-carbonitrile (2m): white solid, m.p. = 145.6-147.4 C°, 20.5 mg, 44%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (1H, brs), 7.46-7.41 (2H, m), 7.08 (1H, t, *J* = 7.7 Hz), 3.21-3.16 (1H, m), 2.77 (1H, dd, *J* = 16.3, 5.81 Hz), 2.48 (1H, dd, *J* = 16.3, 7.1 Hz), 1.32 (3H. d, *J* = 7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 139.5, 131.5, 130.9, 130.0, 123.3, 115.8, 98.7, 37.9, 31.0, 19.7.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_{11}H_{10}N_2NaO]^+$: 209.0685, found: 209.0687.



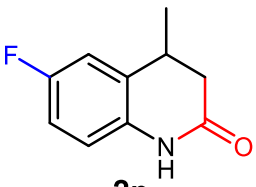
2n

4-Methyl-6-(trifluoromethyl)-3,4-dihydroquinolin-2(1*H*)-one (2n) [17]: white solid, m.p. = 113.8-115.0 ℃, 49.8 mg, 87%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (1H, brs), 7.44-7.42 (2H, m), 6.98 (1H, d, *J* = 8.2 Hz), 3.23-3.15 (1H, m), 2.77 (1H, dd, *J* = 16.3, 5.9 Hz), 2.47 (1H, dd, *J* = 16.3, 7.3 Hz), 1.35 (3H. d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 139.6, 129.1, 125.5 (q, *J* = 32.6 Hz), 125.0 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 271.6 Hz), 123.8 (q, *J* = 3.7 Hz), 116.0, 38.0, 30.7, 19.7. ^{19}F NMR (400 MHz, $CDCl_3$) δ -61.8.



2o

4-Methyl-7-(trifluoromethyl)-3,4-dihydroquinolin-2(1*H*)-one (2o) [18]: white solid, m.p. = 163.6-165.4 ℃, 49.9 mg, 87%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (1H, brs), 7.31-7.26 (2H, m), 7.13 (1H, s), 3.22-3.17 (1H, m), 2.77 (1H, dd, *J* = 5.9, 16.3 Hz), 2.47 (1H, dd, *J* = 7.1, 16.3 Hz), 1.34 (3H, d, *J* = 7.1 Hz), ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 137.2, 132.6, 130.1 (q, *J* = 32.8Hz), 127.2, 123.9 (q, *J* = 272.1 Hz), 120.1 (q, *J* = 3.9 Hz), 112.7 (q, *J* = 3.7 Hz), 37.9, 30.8, 19.7. ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.5

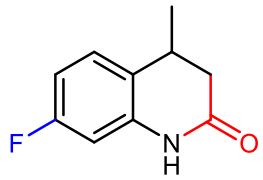


2p

6-Fluoro-4-methyl-3,4-dihydroquinolin-2(1*H*)-one (2p): white solid, m.p. = 152.3-

153.8 ℃, 41.1 mg, 92%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (1H, brs), 6.91-6.84 (3H, m), 3.13-3.08 (1H, m), 2.71 (1H, dd, *J* = 16.2, 5.7 Hz), 2.40 (1H, dd, *J* = 16.2, 7.7 Hz), 1.3 (3H, d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 159.1 (d, *J* = 241.8 Hz), 132.8 (d, *J* = 2.4 Hz), 130.7 (d, *J* = 7.2 Hz), 116.9 (d, *J* = 8.2 Hz), 114.1 (d, *J* = 22.8 Hz), 113.5 (d, *J* = 23.3 Hz), 38.0, 30.8, 19.6. ^{19}F NMR (375 MHz, $CDCl_3$) δ -119.8.

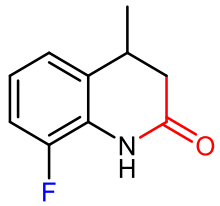
HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_{10}H_{10}FNNaO]^+$: 202.0639, found: 202.0641.



2q

7-Fluoro-4-methyl-3,4-dihydroquinolin-2(1*H*)-one (2q): white solid, m.p. = 100.0-101.9 ℃, 39.6 mg, 91%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (1H, brs), 7.12 (1H, t, *J* = 7.0 Hz), 6.70 (1H, t, *J* = 8.4 Hz), 6.63 (1H, d, *J* = 9.4 Hz), 3.13-3.08 (1H, m), 2.73 (1H, d, *J* = 16.2, 5.7 Hz), 2.42 (1H, *J* = 16.2, 7.2 Hz), 1.29 (3H, d, *J* = 6.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 162.2 (d, *J* = 244.4 Hz), 138.0 (d, *J* = 10.5 Hz), 127.8 (d, *J* = 9.3 Hz), 124.4 (d, *J* = 3.1 Hz), 109.8 (d, *J* = 21.2 Hz), 103.4 (d, *J* = 25.4 Hz), 38.4, 30.2, 20.0. ^{19}F NMR (375 MHz, $CDCl_3$) δ -114.8.

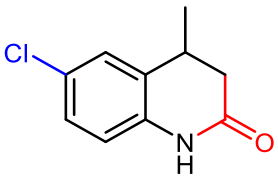
HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_{10}H_{10}FNNaO]^+$: 202.0639, found: 202.0642.



2r

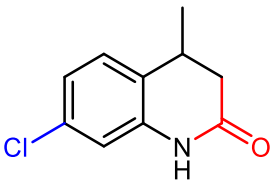
8-Fluoro-4-methyl-3,4-dihydroquinolin-2(1*H*)-one (2r) [19]:white solid, m.p. = 133.9-135.4 ℃, 40.2mg, 90%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (1H, brs), 6.95 (3H, m), 3.18-3.13 (1H, m), 2.74 (1H, d, *J* = 16.2, 5.8 Hz), 2.44 (1H, *J* = 16.2, 7.3 Hz), 1.29 (3H, d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 150.0 (d, *J* = 243.8 Hz), 131.1,

125.0 (d, J = 12.0 Hz), 123.1 (d, J = 7.4 Hz), 121.8 (d, J = 3.2 Hz), 113.9 (d, J = 18.3 Hz), 38.2, 30.9, 19.8. ^{19}F NMR (375 MHz, $CDCl_3$) δ -134.3.



2s

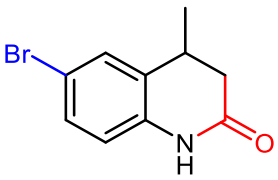
6-Chloro-4-methyl-3,4-dihydroquinolin-2(1*H*)-one (2s) [20]: white solid, m.p. = 167.2-167.9 C°, 42.5 mg, 87%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (1H,br s), 7.16 (1H, s), 7.13 (1H, d, J = 8.6 Hz), 6.83 (1H, d, J = 8.2 Hz), 3.12-3.08 (1H, m), 2.71 (1H, dd, J = 16.1, 5.4 Hz), 2.41 (1H, dd, J = 16.1, 7.3 Hz), 1.30 (3H. d, J = 6.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 135.3, 130.4, 128.4, 127.5, 126.7, 117.1, 38.1, 30.7, 19.7.



2t

7-Chloro-4-methyl-3,4-dihydroquinolin-2(1*H*)-one (2t): white solid, m.p. = 139.4-141.2 C°, 41.5 mg, 86%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (1H, brs), 7.10 (1H, d, J = 8.1 Hz), 6.97 (1H, dd, J = 8.1, 2.0 Hz), 6.89 (1H, d, J = 2.0 Hz), 3.15-3.06 (1H, m), 2.73 (1H, dd, J = 16.2, 5.9 Hz), 2.43 (1H, dd, J = 16.2, 7.3 Hz), 1.29 (3H. d, J = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 137.7, 133.1, 127.7, 127.2, 123.3, 115.9, 38.2, 30.4, 19.8.

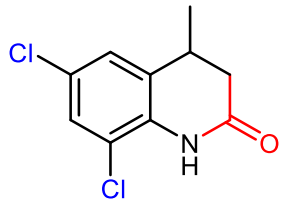
HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_{10}H_{10}ClNNaO]^+$: 218.0343, found: 218.0339.



2u

6-Bromo-4-methyl-3,4-dihydroquinolin-2(1*H*)-one (2u) [16]: white solid, m.p. =

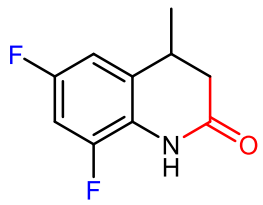
172.0-174.0 C°, 42.5 mg, yield 39%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (1H, brs), 7.32 (1H, d, *J* = 2.0 Hz), 7.29 (1H, dd, *J* = 8.3, 2.1 Hz), 6.70 (1H, d, *J* = 8.3 Hz), 3.16-3.07 (1H, m), 2.71 (1H, dd, *J* = 16.2, 5.8 Hz), 2.41 (1H, dd, *J* = 16.2, 7.4 Hz), 1.30 (3H. d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 135.7, 131.0, 130.5, 129.7, 117.2, 115.9, 38.1, 30.8, 19.7.



2v

6,8-Dichloro-4-methyl-3,4-dihydroquinolin-2(1*H*)-one (2v): white solid, m.p. = 109.9-111.2 C°, 48.5 mg, 85%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (1H, brs), 7.25 (1H, d, *J* = 2.2 Hz), 7.10 (1H, d, *J* = 2.2 Hz), 3.17-3.09 (1H, m), 2.71 (1H, dd, *J* = 16.2, 5.8 Hz), 2.43 (1H, dd, *J* = 16.2, 7.2 Hz), 1.30 (3H. d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 132.2, 131.7, 128.2, 127.5, 125.6, 120.3, 37.9, 31.4, 19.6.

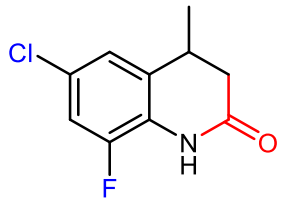
HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_{10}H_{10}Cl_2NNaO]^+$: 251.9953, found: 251.9960.



2w

6,8-Difluoro-4-methyl-3,4-dihydroquinolin-2(1*H*)-one (2w): white solid, m.p. = 177.9-178.9 C°, 44.4 mg, yield 90%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (1H, brs), 6.77-6.72 (2H, m), 3.17-3.09 (1H, m), 2.72 (1H, dd, *J* = 16.2, 5.7 Hz), 2.43 (1H, dd, *J* = 16.2, 7.8 Hz), 1.30 (3H. d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 158.0 (dd, *J* = 244.4, 11.5 Hz), 149.6 (dd, *J* = 246.6, 12.4 Hz), 132.0 (dd, *J* = 8.3, 2.7 Hz), 121.4 (dd, *J* = 12.1, 3.5 Hz), 109.0 (dd, *J* = 23.0, 3.5 Hz), 102.3 (dd, *J* = 26.8, 22.4 Hz). ^{19}F NMR (400 MHz, $CDCl_3$) δ -117.2 (d, *J* = 2.9 Hz), -130.4 (d, *J* = 2.9 Hz).

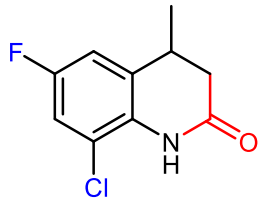
HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_{10}H_9F_2NNaO]^+$: 220.0544, found: 220.0548.



2x

6-Chloro-8-fluoro-4-methyl-3,4-dihydroquinolin-2(1*H*)-one (2x): white solid, m.p. = 179.9-181.1 ℃, 31.5 mg, 59%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (1H, brs), 7.02 (1H, dd, *J* = 9.8, 2.1 Hz), 6.99 (1H, brs), 3.17-3.12 (1H, m), 2.73 (1H, dd, *J* = 16.3, 5.8 Hz), 2.44 (1H, dd, *J* = 16.3, 7.6 Hz), 1.31 (3H. d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 149.6 (d, *J* = 247.2 Hz), 132.1 (d, *J* =2.2 Hz), 127.8 (d, *J* = 9.7 Hz), 123.9 (d, *J* = 12.1 Hz), 122.3 (d, *J* = 3.3 Hz), 114.7 (d, *J* = 21.8 Hz), 38.1, 31.1 (d, *J* =2.3 Hz), 19.6. ^{19}F NMR (375 MHz, $CDCl_3$) δ -131.8.

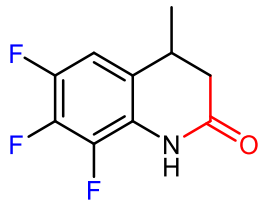
HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_{10}H_9ClFNNaO]^+$: 236.0249, found: 236.0252.



2y

8-Chloro-6-fluoro-4-methyl-3,4-dihydroquinolin-2(1*H*)-one (2y): white solid, m.p. = 131.3-133.1 ℃, 37.0 mg, 70%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (1H, brs), 7.00 (1H, dd, *J* = 8.0, 2.7 Hz), 6.87 (1H, dd, *J* = 8.5, 2.6 Hz), 3.16-3.10 (1H, m), 2.71 (1H, dd, *J* = 16.2, 5.7 Hz), 2.42 (1H, dd, *J* = 16.2, 7.5 Hz), 1.30 (3H. d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 158.0 (d, *J* = 245.4 Hz), 131.9 (d, *J* = 7.6 Hz), 129.9 (d, *J* = 3.1 Hz), 120.0 (d, *J* = 10.8 Hz), 114.9 (d, *J* = 26.0 Hz), 112.7 (d, *J* = 23.0 Hz), 37.9, 31.5, 19.4. ^{19}F NMR (375 MHz, $CDCl_3$) δ -118.1.

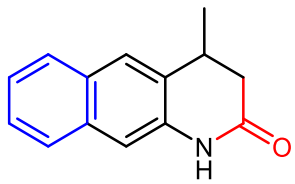
HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_{10}H_9ClFNNaO]^+$: 236.0249, found: 236.0251.



2z

6,7,8-Trifluoro-4-methyl-3,4-dihydroquinolin-2(1*H*)-one (2z): white solid, m.p. = 138.5-140.2 C°, 47.0 mg, 87%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (1H, brs), 6.84 (1H, ddd, *J* = 9.7, 7.3, 2.0 Hz), 3.14-3.09 (1H, m), 2.73 (1H, dd, *J* = 16.3,5.7 Hz), 2.43 (1H, dd, *J* = 16.3, 7.9 Hz), 1.30 (3H. d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 146.6 (ddd, *J* = 245.7, 10.2, 2.8 Hz), 139.3 (ddd, *J* = 248.0, 13.0, 3.6 Hz), 139.0 (ddd, *J* = 249.9, 16.7, 13.2 Hz), 124.7 (ddd, *J* = 5.9, 4.1, 1.0 Hz) 122.6 (dd, *J* = 9.5, 3.1 Hz), 109.6 (dd, *J* = 19.0, 3.5 Hz), 38.1, 30.8, 19.5. ^{19}F NMR (375 MHz, $CDCl_3$) δ -141.9 (dd, *J* = 1.4, 21.1 Hz), -153.4 (dd, *J* = 1.5, 19.8 Hz), -161.4 (dd, *J* = 20.0, 21.0 Hz).

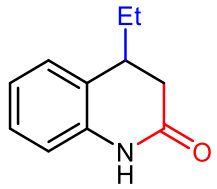
HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_{10}H_8F_3NNaO]^+$: 238.0450, found: 238.0453.



2aa

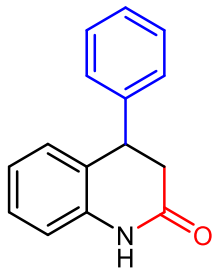
4-Methyl-3,4-dihydrobenzo[*g*]quinolin-2(1*H*)-one (2aa): white solid, m.p. = 163.5-163.9 C°, 47.5 mg, 90%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (1H, brs), 7.76 (1H, d, *J* = 8.3 Hz), 7.73 (1H, d, *J* = 8.4 Hz), 7.65 (1H, s), 7.44-7.35 (2H, m), 7.26 (1H, s), 3.36-3.28 (1H, m), 2.83 (1H, dd, *J* = 16.1, 5.5 Hz), 2.52 (1H, dd, *J* = 16.1, 7.8 Hz), 1.44 (3H. d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 135.1, 133.1, 130.5, 129.8, 127.6, 126.9, 126.4, 125.4, 124.8, 111.7, 38.7, 31.2, 20.1.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_{14}H_{13}NNaO]^+$: 234.0895, found: 234.0896.



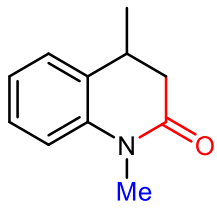
2ab

4-Ethyl-3,4-dihydroquinolin-2(1*H*)-one (2ab) [21]: white solid, m.p. = 125.6-127.1 C°, 27.0 mg, 60% ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (1H, brs), 7.20-7.14 (2H, m), 7.00 (1H, td, *J* = 7.4, 1.1 Hz), 6.84 (1H, d, *J* =7.8 Hz), 2.88-2.82 (1H, m), 2.77 (1H, dd, *J* = 16.0, 6.2 Hz), 2.56 (1H, dd, *J* = 16.0, 3.8 Hz), 1.72-1.54 (2H, m), 0.94 (3H, t, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 136.6, 128.1, 127.6, 127.5, 123.1, 115.9, 38.0, 35.9, 27.1, 11.5.



2ac

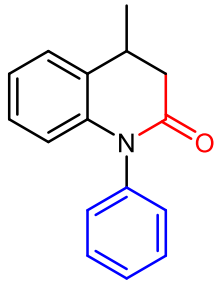
4-Phenyl-3,4-dihydroquinolin-2(1*H*)-one (2ac) [21]: white solid, m.p. 173.2-173.9 C°, 32.0 mg, 58%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (1H, brs), 7.36-7.32 (2H, m), 7.30-7.27 (1H, m), 7.23-7.19 (3H, m), 6.99-6.91 (3H, m), 4.31 (1H, t, *J* = 7.5 Hz), 2.95 (2H, dd, *J* = 7.5, 2.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 141.6, 137.2, 129.0, 128.4, 128.1, 127.9, 127.3, 126.7, 123.5, 116.0, 42.1, 38.5.



2ad

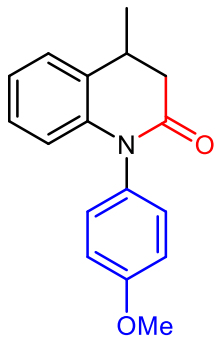
1,4-Dimethyl-3,4-dihydroquinolin-2(1*H*)-one (2ad) [22]: colorless oil, 22.8 mg, 53%,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.24 (1H, m), 7.20 (1H, d, *J* = 7.4 Hz), 7.05 (1H, d, *J* = 7.5, 1.1 Hz), 6.99 (1H, d, *J* = 8.1 Hz), 3.37 (3H, s), 3.08-3.03 (1H, m), 2.73 (1H, dd, *J* = 15.8, 5.5 Hz), 2.45 (1H, dd, *J* = 15.8, 7.6 Hz), 1.28 (3H. d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 139.8, 131.1, 127.4, 126.2, 123.1, 114.8, 39.2, 30.3, 29.5, 19.3.



2ae

4-Methyl-1-phenyl-3,4-dihydroquinolin-2(1*H*)-one (2ae) [23]: white solid, m.p. = 102.0-102.9 C°, 46.2 mg, 78%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.50 (2H, m), 7.45-7.41 (1H, m), 7.27-7.24 (3H, m), 7.08-7.01 (2H, m), 6.41-6.39 (1H, m), 3.27-3.19 (1H, m), 2.94 (1H, dd, *J* = 15.6, 5.4 Hz), 2.65 (1H, dd, *J* = 15.6, 7.1 Hz), 1.42 (3H. d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 140.9, 138.5, 130.8, 129.9, 129.1, 128.2, 127.2, 126.4, 123.3, 117.4, 39.6, 30.8, 19.7.

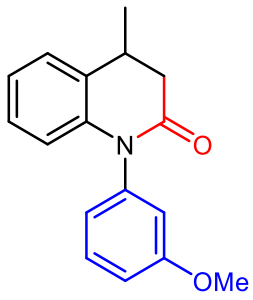


2af

1-(4-Methoxyphenyl)-4-methyl-3,4-dihydroquinolin-2(1*H*)-one (2af): white solid, m.p. = 108.0-109.8 C°, 21.8 mg, 42%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.23 (1H, m), 7.16-7.12 (2H, m), 7.08-7.00 (4H, m), 6.43 (1H, dd, *J* = 7.8, 1.5 Hz), 3.86 (3H, s),

3.23-3.18 (1H, m), 2.91 (1H, dd, J = 15.6, 5.4 Hz), 2.63 (1H, dd, J = 15.6, 7.2 Hz), 1.40 (3H. d, J = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 159.3, 141.1, 131.0, 130.7, 130.0, 127.2, 126.4, 123.2, 117.3, 115.3, 55.6, 39.7, 30.8, 19.8.

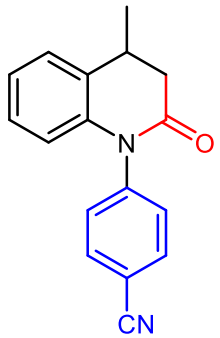
HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_{17}H_{17}NNaO_2]^+$: 290.1151, found: 290.1148.



2ag

1-(3-Methoxyphenyl)-4-methyl-3,4-dihydroquinolin-2(1*H*)-one (2ag): colorless oil, 18.3 mg, 29%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (1H, t, J = 8.1 Hz), 7.26-7.23 (1H, m), 7.08-7.01 (2H, m), 6.97 (1H, ddd, J = 8.4, 2.4, 0.7 Hz), 6.83-6.81 (1H, m), 6.77 (1H, t, J = 2.1 Hz), 6.43 (1H, dd, J = 7.7, 1.5 Hz), 3.81 (3H, s), 3.24-3.19 (1H, m), 2.92 (1H, dd, J = 15.6, 5.4 Hz), 2.64 (1H, dd, J = 15.6, 7.2 Hz), 1.41 (3H. d, J = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 160.9, 140.8, 139.6, 130.7, 130.6, 127.2, 126.4, 123.4, 121.2, 117.4, 114.6, 114.3, 55.5, 39.7, 30.8, 19.8.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_{17}H_{17}NNaO_2]^+$: 290.1151, found: 290.1149.

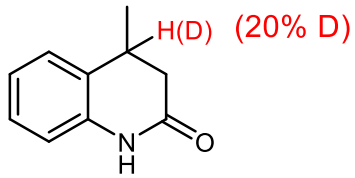


2ah

4-(4-methyl-2-oxo-3,4-dihydroquinolin-1(2*H*)-yl)benzonitrile (2ah): white solid, m.p. = 96.4-98.1 C°, 16.1 mg, 25%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.78 (2H, m), 7.41-7.38 (2H, m), 7.28-7.27 (1H, m), 7.09-7.07 (2H, m), 6.36-6.34 (1H, m), 3.27-3.18

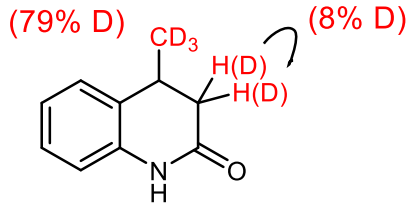
(1H, m), 2.91 (1H, dd, J = 15.6, 5.3 Hz), 2.63 (1H, dd, J = 15.6, 7.1 Hz), 1.40 (3H. d, J = 7.0 Hz), ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 143.0, 140.0, 133.7, 131.4, 130.1, 127.5, 126.8, 124.2, 118.3, 117.5, 112.0, 39.7, 30.8, 19.7.

HRMS–ESI (m/z): $[M+Na]^+$ calcd for $[C_{17}H_{14}N_2NaO_2]^+$: 285.0998, found: 285.0997.



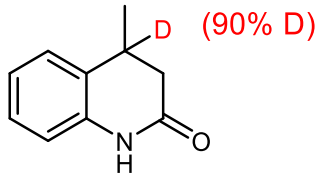
3a

4-Methyl-3, 4-dihydro-2(1H)-quinolinone (3a): white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (1H, brs), 7.19-7.15 (2H, m), 7.01 (1H, td, J = 1.0, 7.4 Hz), 6.86 (1H, d, J =7.8 Hz), 3.12 (0.8H, m), 2.73 (1H, dd, J = 16.1, 5.7 Hz), 2.45-2.39 (1H, m), 1.31 (3H, d, J = 7.1 Hz).



4a

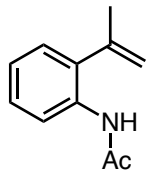
4-Methyl-3, 4-dihydro-2(1H)-quinolinone (4a): white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (1H, brs), 7.21-7.16 (2H, m), 7.03 (1H, td, J =1.1, 7.4 Hz), 6.79 (1H, d, J =7.9 Hz), 3.13-3.10 (1H, m), 2.73 (0.92H, dd, J = 16.1, 5.8 Hz), 2.43 (0.92H, dd, J = 16.1, 7.3 Hz), 1.31 (0.63H, d, J = 7.1 Hz).



5a

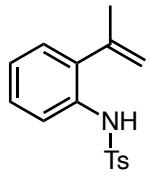
4-Methyl-3, 4-dihydro-2(1H)-quinolinone (5a): white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.37 (1H, brs), 7.20-7.16 (2H, m), 7.02 (1H, t, J = 7.4 Hz), 6.87 (1H, d, J =7.8

Hz), 3.16-3.11 (0.1H, m), 2.74 (1H, d, J = 16.1 Hz), 2.44 (1H, d, J = 16.1 Hz), 1.30 (3H, s).



1ai

N-[2-(1-Methylethenyl)phenyl]acetamide (**1ai**): white solid, m.p. = 49.5-50.6 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (1H, d, J = 8.2 Hz), 7.55 (1H, brs), 7.28-7.23 (1H, m), 7.14-7.05 (2H, m), 5.38 (1H, s), 5.02 (1H, s), 2.15 (3H, s), 2.07 (3H, s).



1aj

4-Methyl-*N*-[2-(1-methylethenyl)phenyl]benzenesulfonamide (**1aj**): white solid, m.p. = 75.8-77.0 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.61 (3H, m), 7.22-7.18 (3H, m), 7.08 (1H, brs), 7.06-6.99 (2H, m), 5.25 (1H, s), 4.67 (1H, d, J = 0.7 Hz), 2.34 (3H, s), 1.69 (3H, s).

7. Gram-scale hydroaminocarbonylaion

The hydroaminocarbonlyation reactions were conducted in a batch reactor (50 ml, Shanghai Yanzheng). Palladium(II) trifluoroacetate (33.2 mg, 0.1 mmol, 1.0 mol%), dppp (1,3-bis(diphenylphosphino)propane) (82.4 mg, 0.2mmol, 2.0 mmol%), TsOH (*p*-toluenesulfonic acid) (68.8mg, 0.4 mmol, 4.0 mmol%) was dissolved in 20 ml THF. 2-(Prop-1-en-2-yl) aniline **1a** (1.36 ml, 10 mmol) was added. After that, the reactor was flushed with carbon monoxide for three times and then charged with 3.0 MPa carbon monoxide for 24 h at 80 °C. The products were analyzed with GC-MS with mesitylene as internal standard. The solvent was removed under reduced pressure and the residue

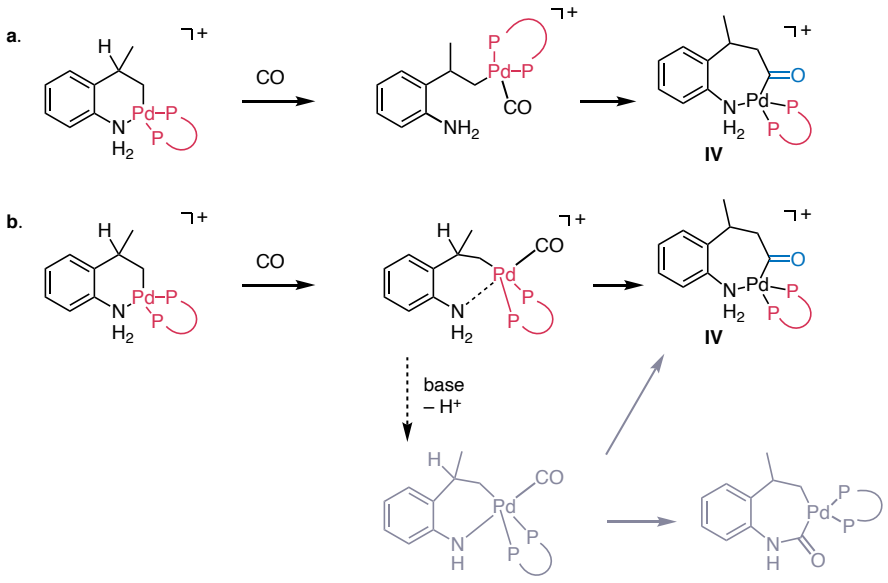
was purified by column chromatography (eluent: 20% ethyl acetate in petroleum ether) to give 4-methyl-3, 4-dihydro-2(1*H*)-quinolinone (**2a**) (1.50 g, 93% yield).

8. Discussions on the alternative CO migratory insertion into the Pd-N bond.

While a definitive proof of acylpalladacycle **IV** has yet to be obtained, we proposed the mechanism as shown in **Scheme 4** based on the reported literature.[24] To our knowledge, examples of CO migratory insertion into the Pd-N bond are scarce, especially for the Pd complexes that can undergo competitive insertion into the Pd-C bonds.

For the migratory insertion of CO in Pd complexes with chelating phosphines, many different pathways have been proposed.[25] The reaction could occur via **(a)** a four-coordinate intermediate and **(b)** a five-coordinate intermediate, as shown in the scheme below. In the four-coordinate pathway, CO would probably displace the aniline -NH_2. For the five-coordinate pathway, deprotonation of aniline -NH_2 is necessary before the migratory insertion into the Pd-N bond can operate. This deprotonation step is usually achieved by utilizing strong bases such as *t*BuONa and LiHMDS,[26] and should be sluggish under the current reaction conditions. Given the rapid migratory insertion of CO into the Pd-C bond, we assume that the reaction is most likely to occur through the acylpalladacycle (**IV**) pathway.

Scheme S5. CO migratory insertion.



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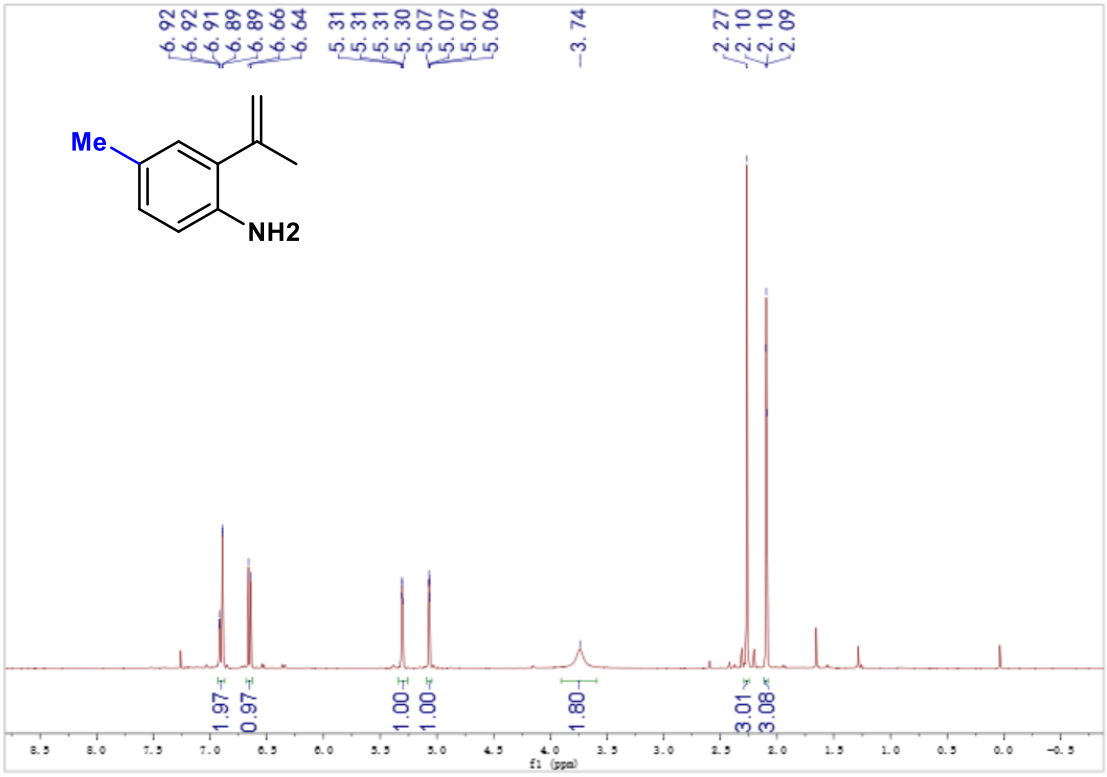
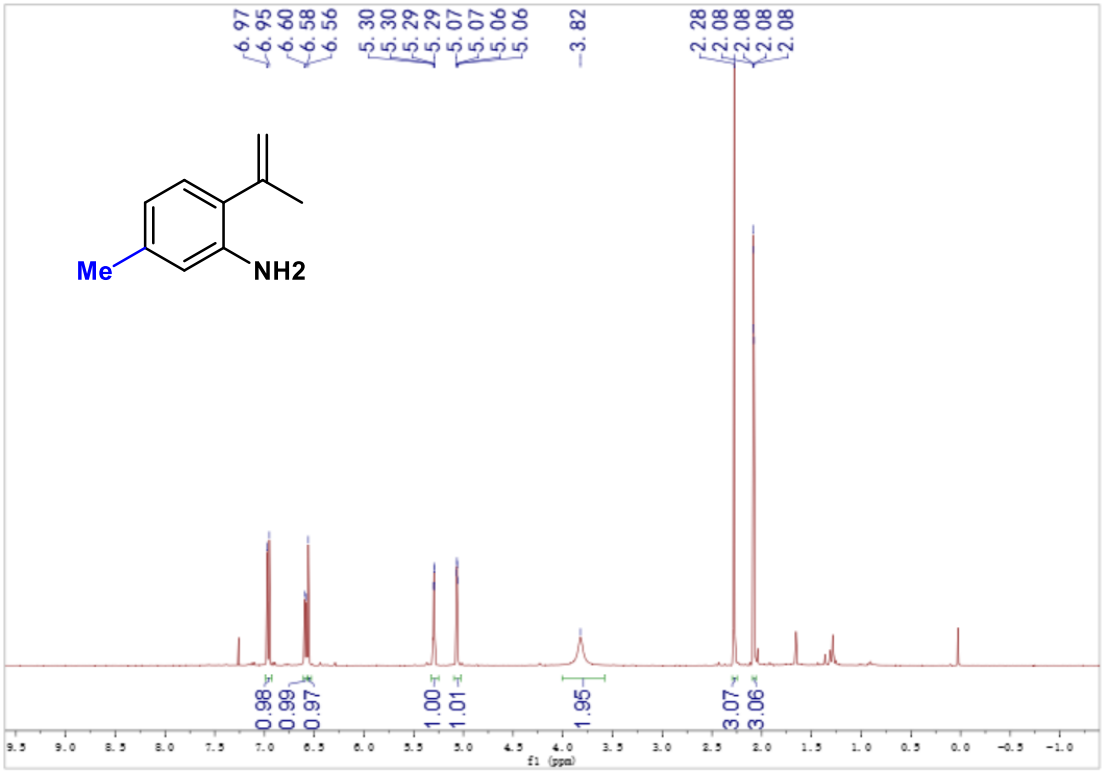
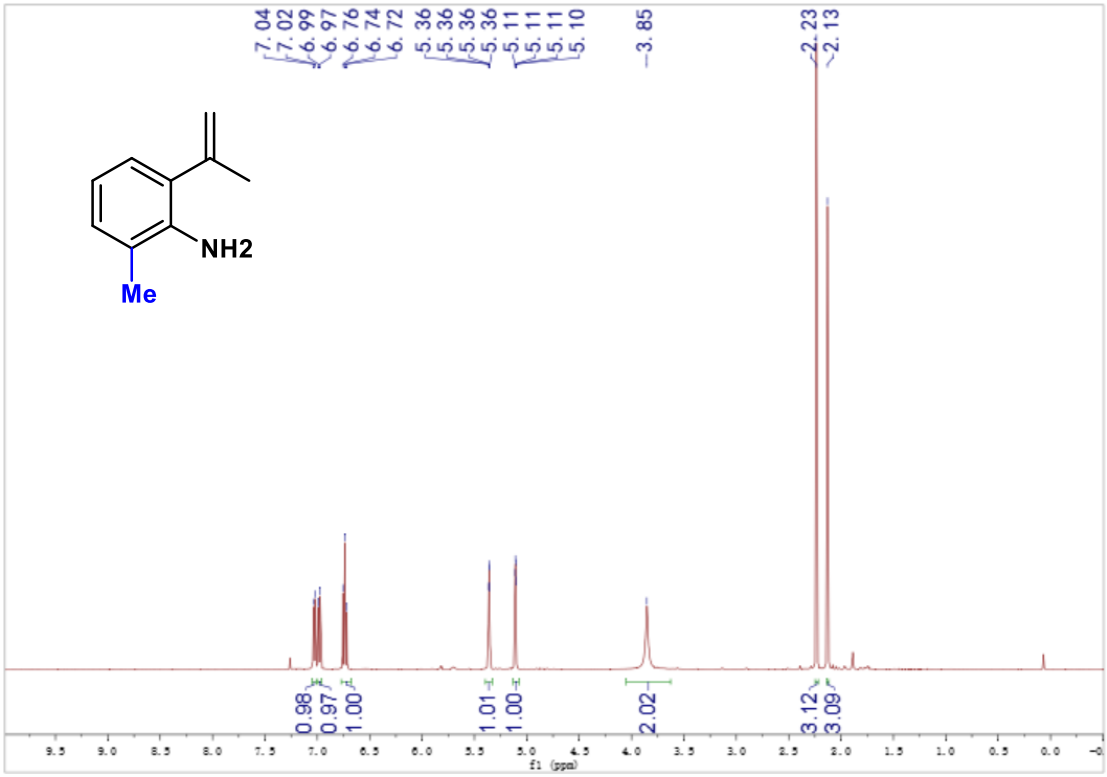
10. NMR spectra



^{1}H NMR of **1b**



^{1}H NMR of **1c**



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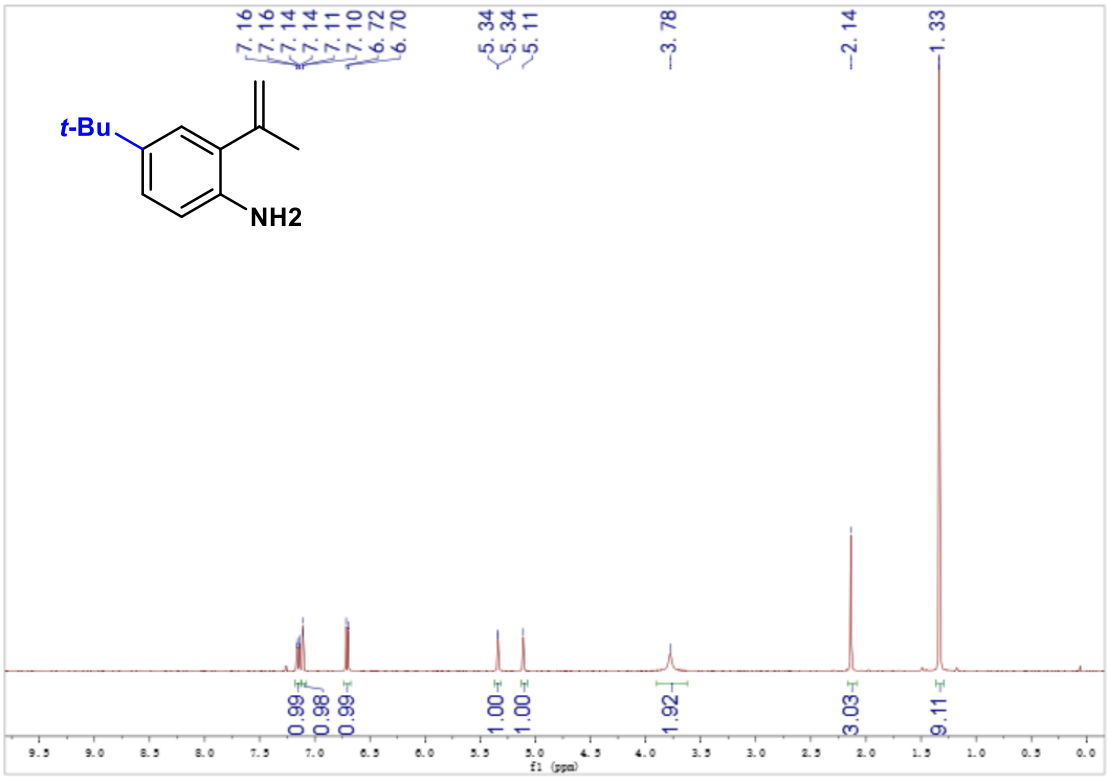

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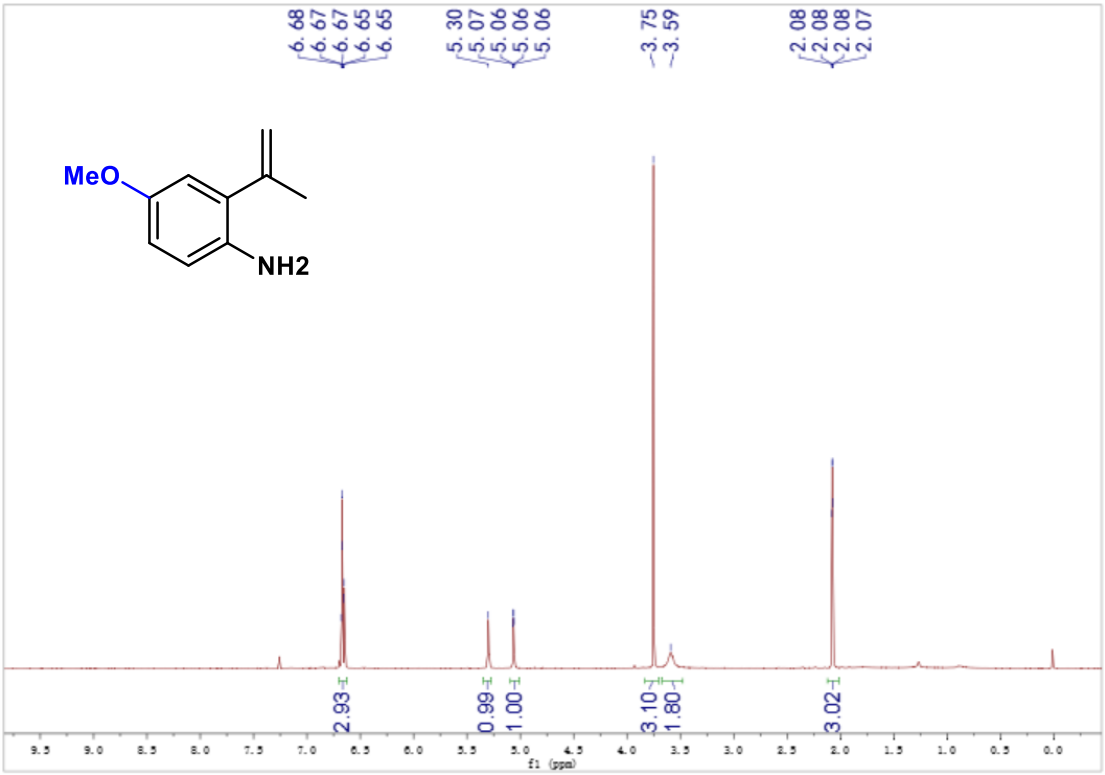
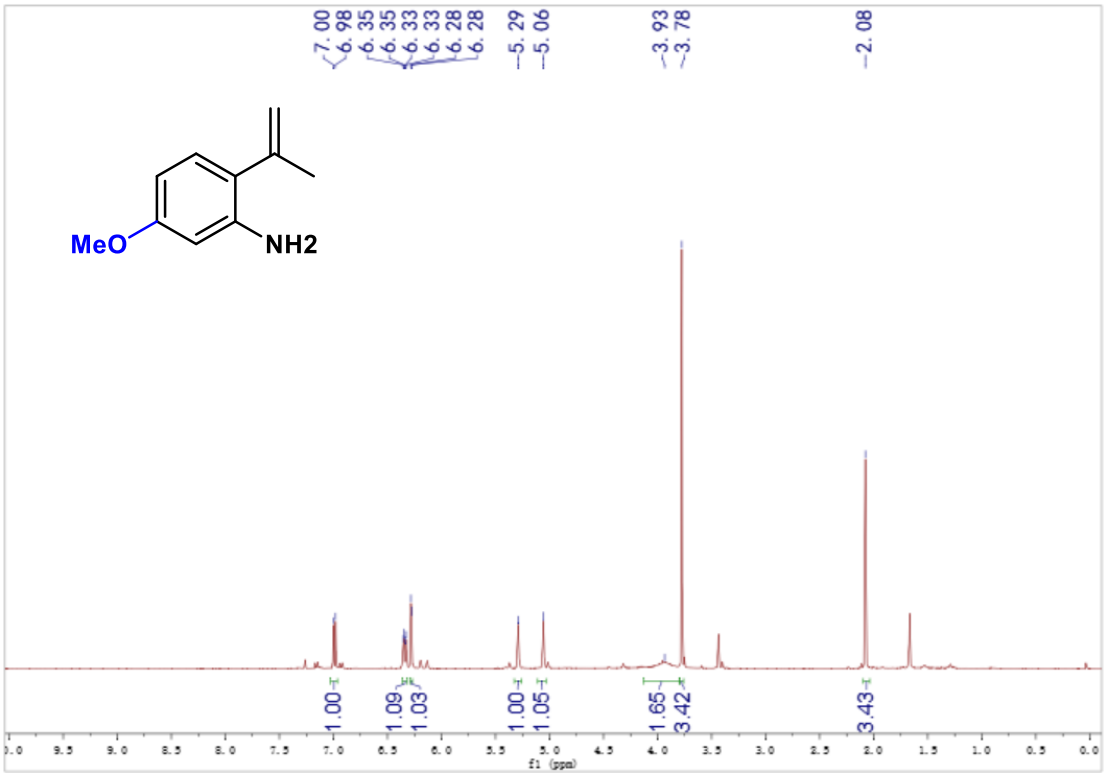
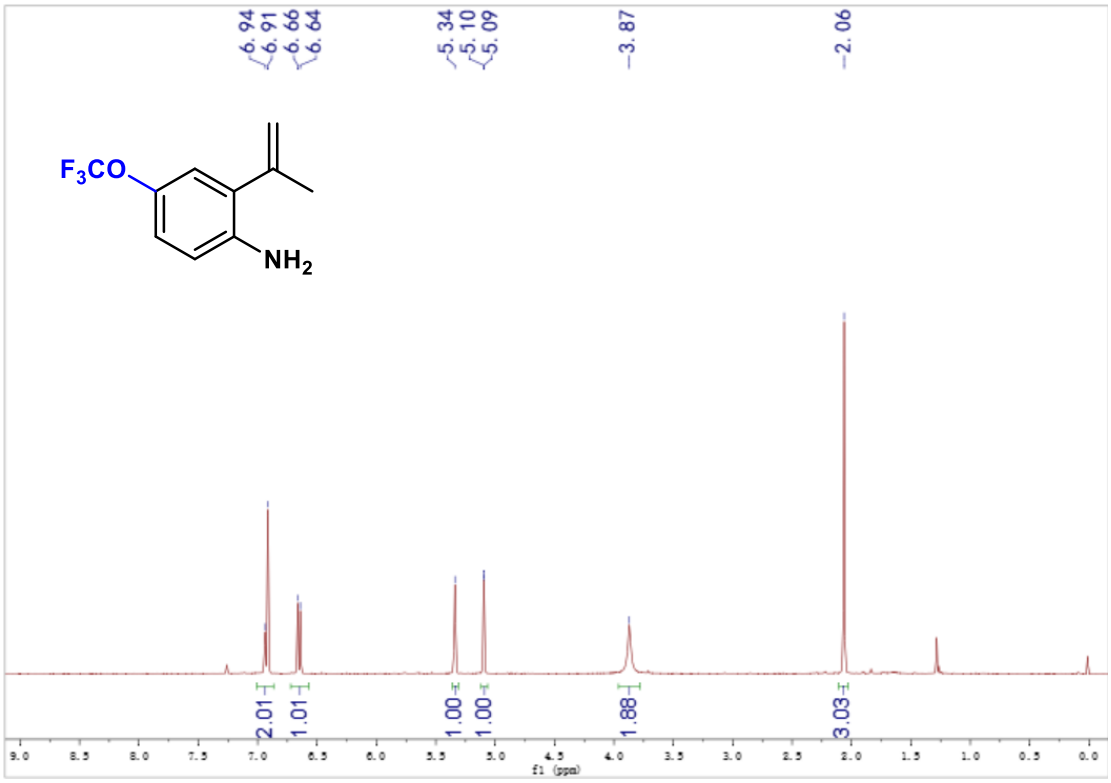


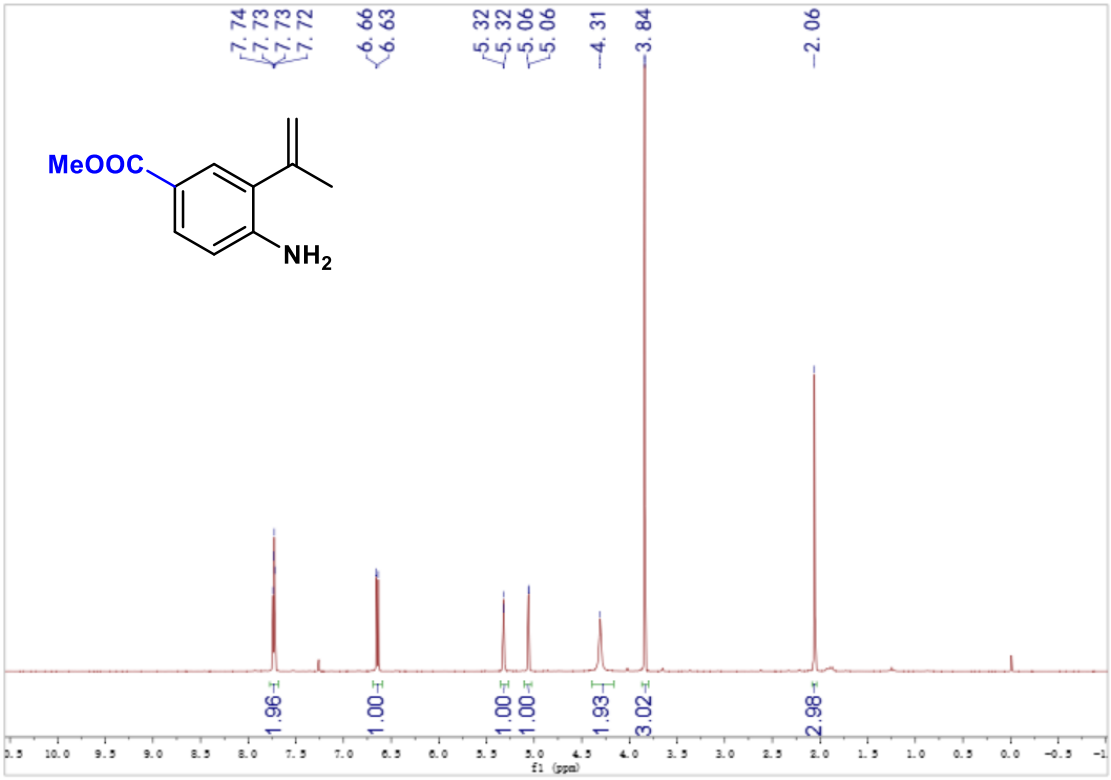
^{1}H NMR of **1f**



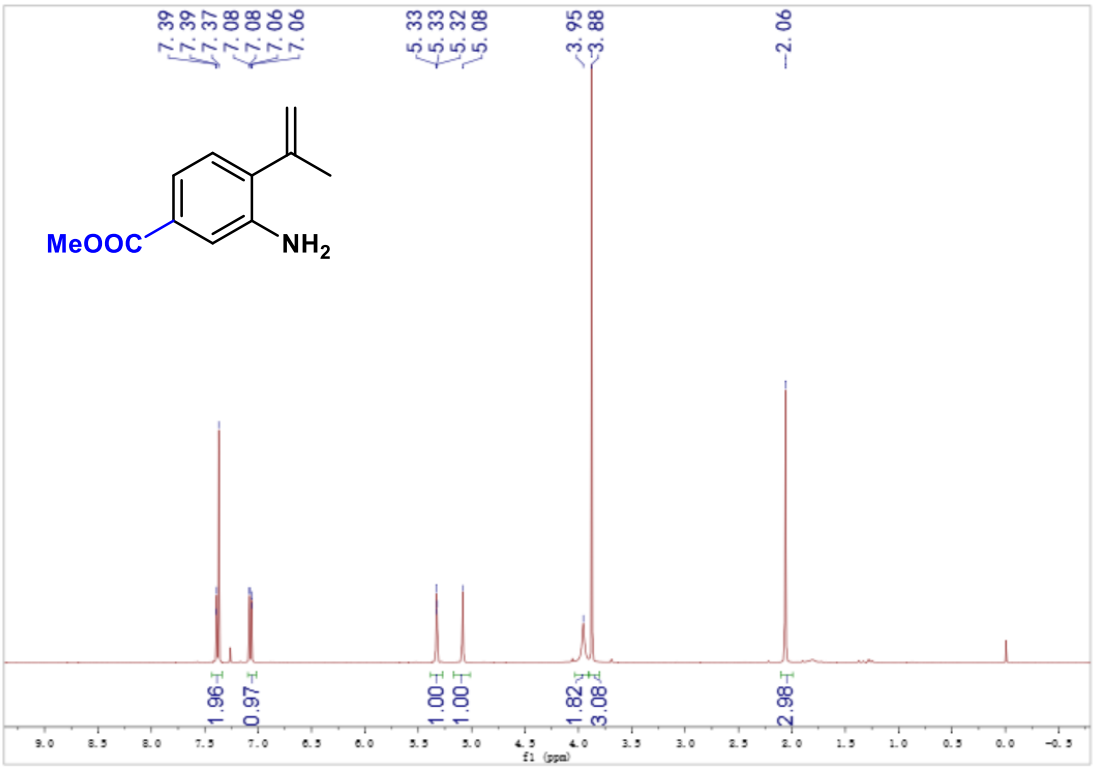
^{1}H NMR of **1g**



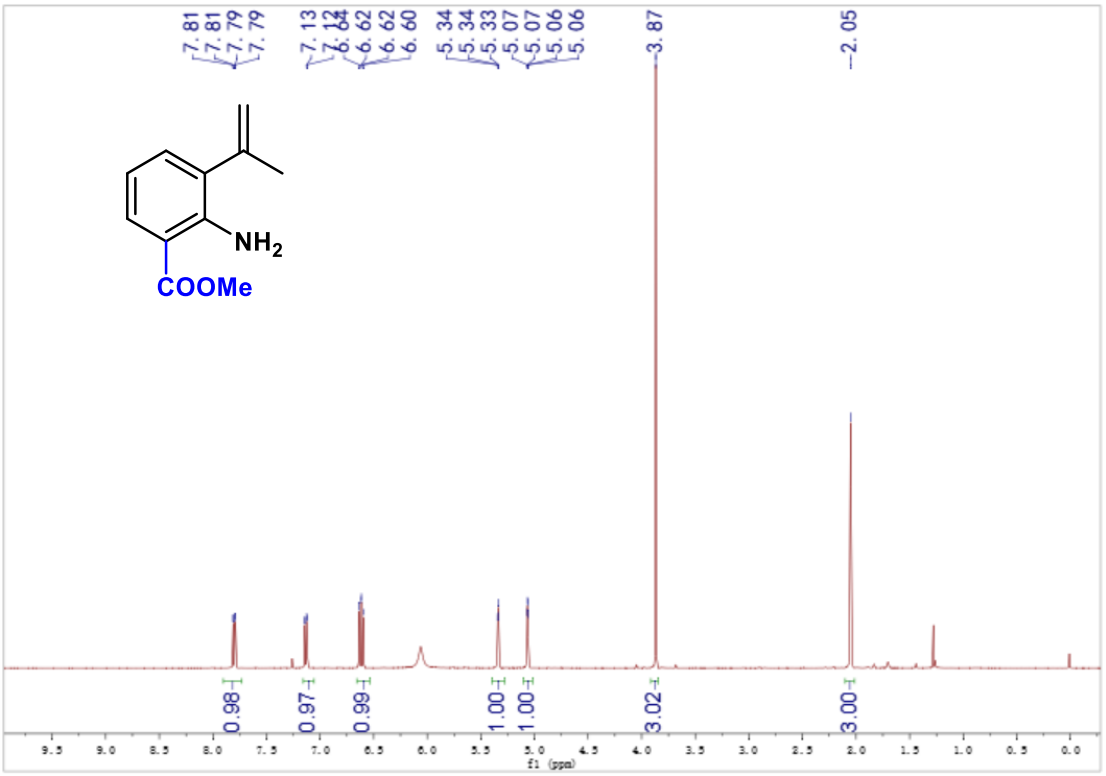
^{1}H NMR of **1h**



^{1}H NMR of **1i**



^{1}H NMR of **1j**



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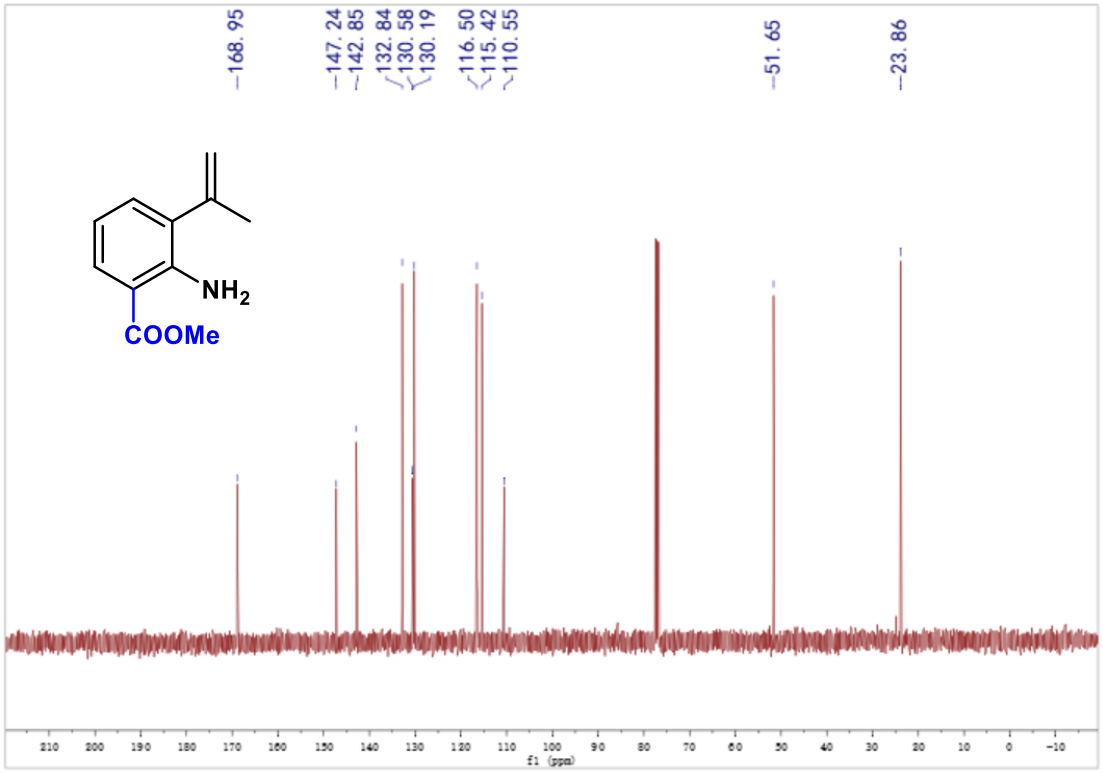
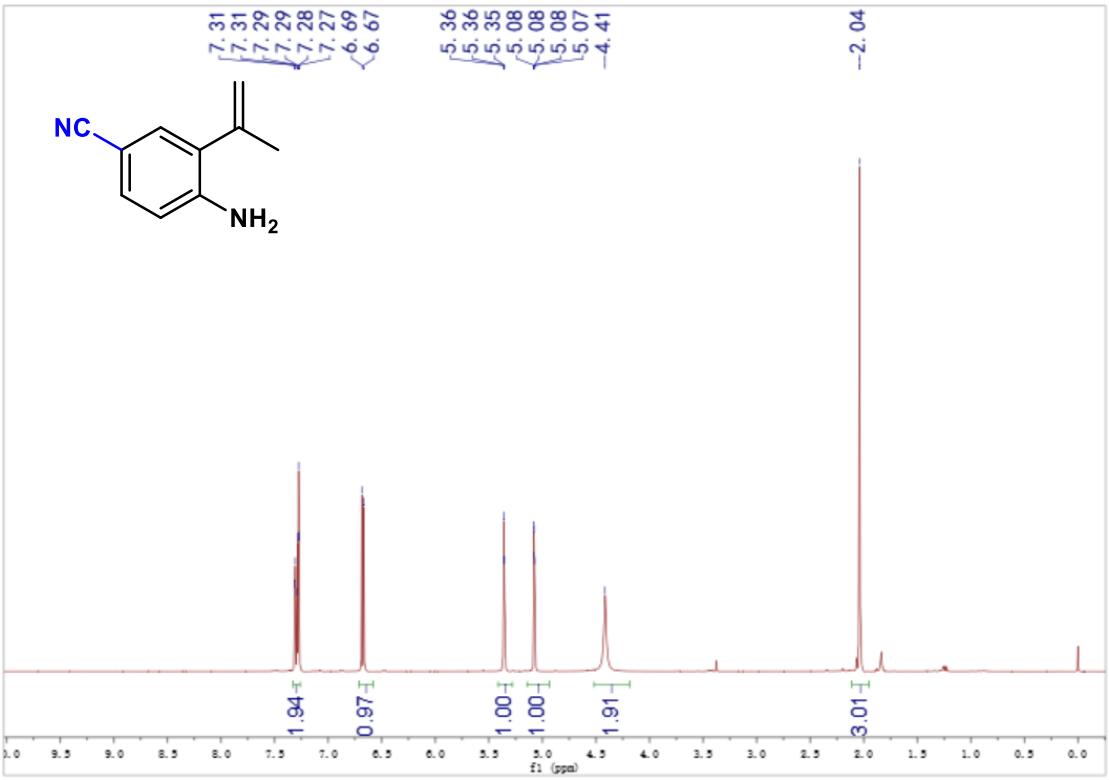
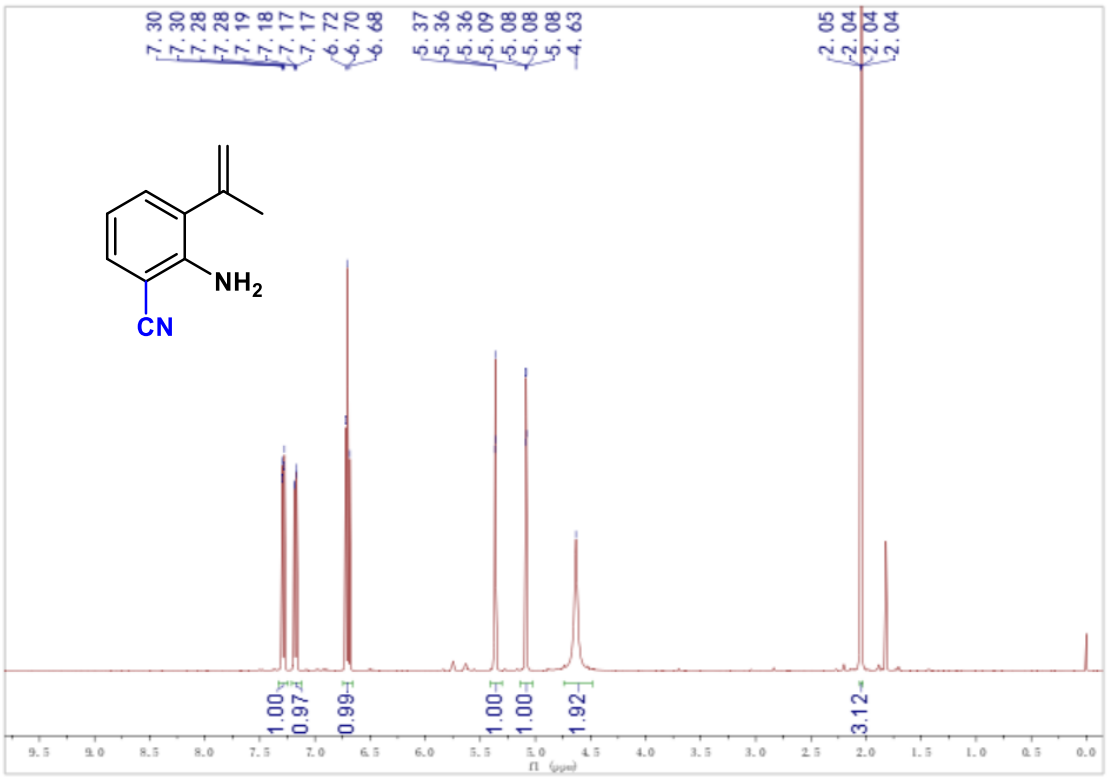


^{13}C NMR of **1k**



^{1}H NMR of **1l**



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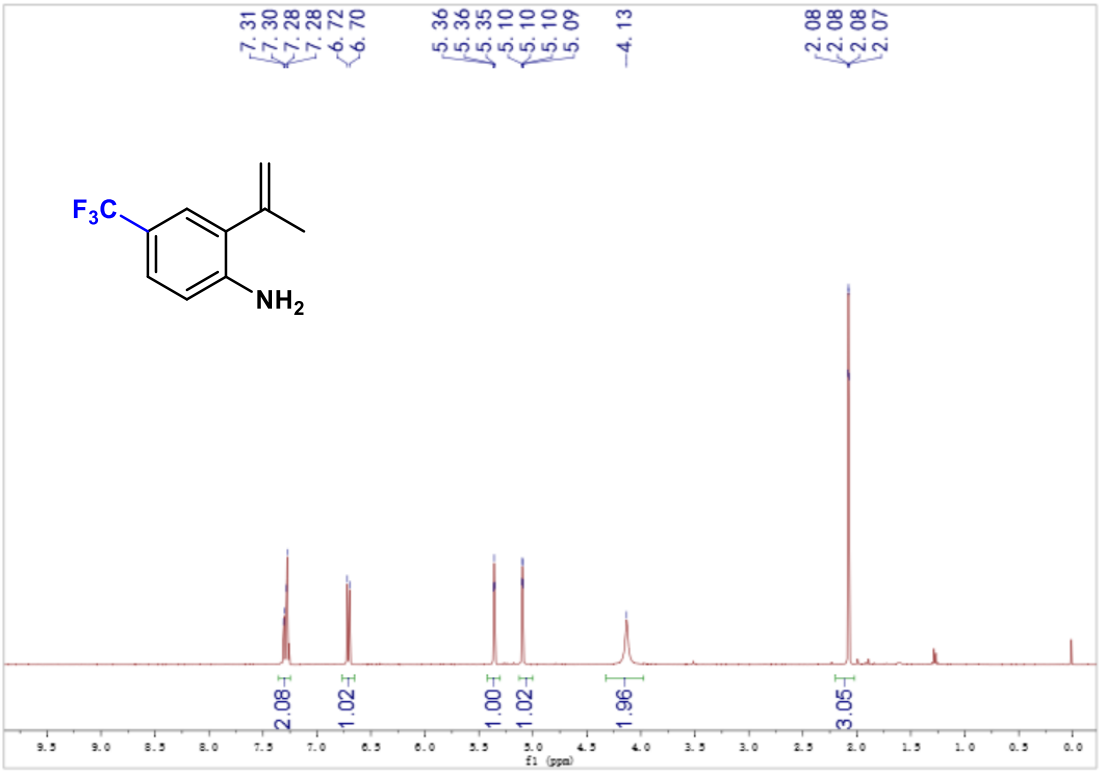

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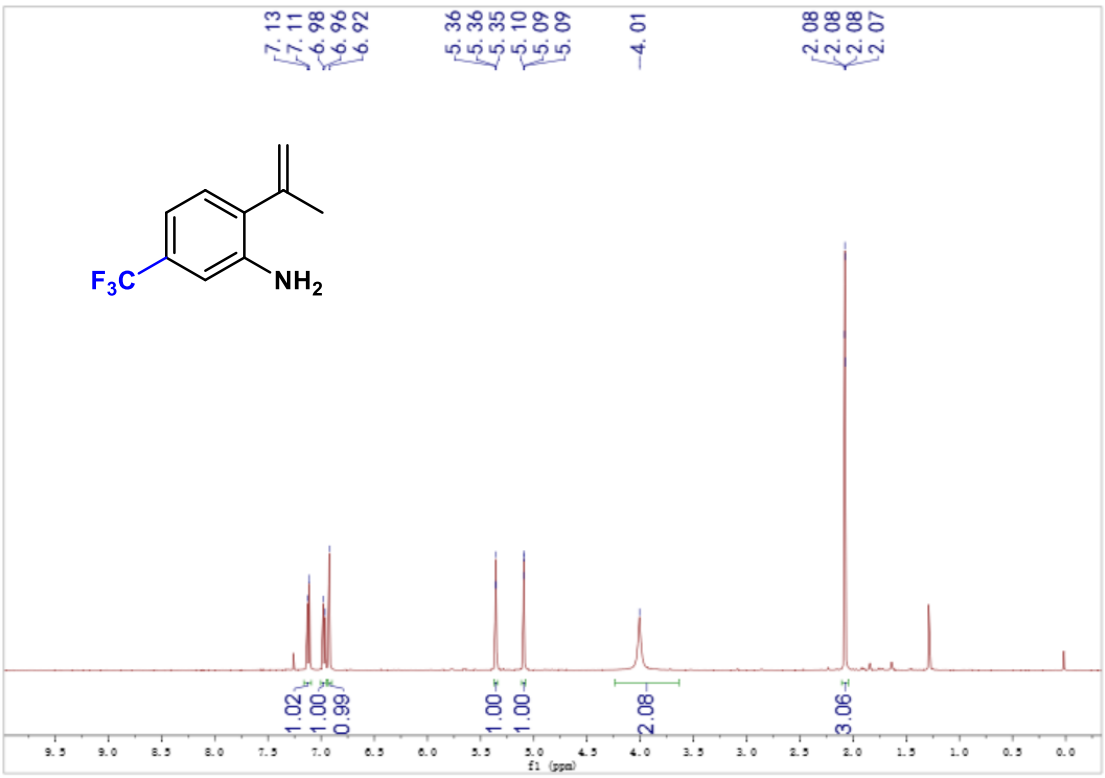

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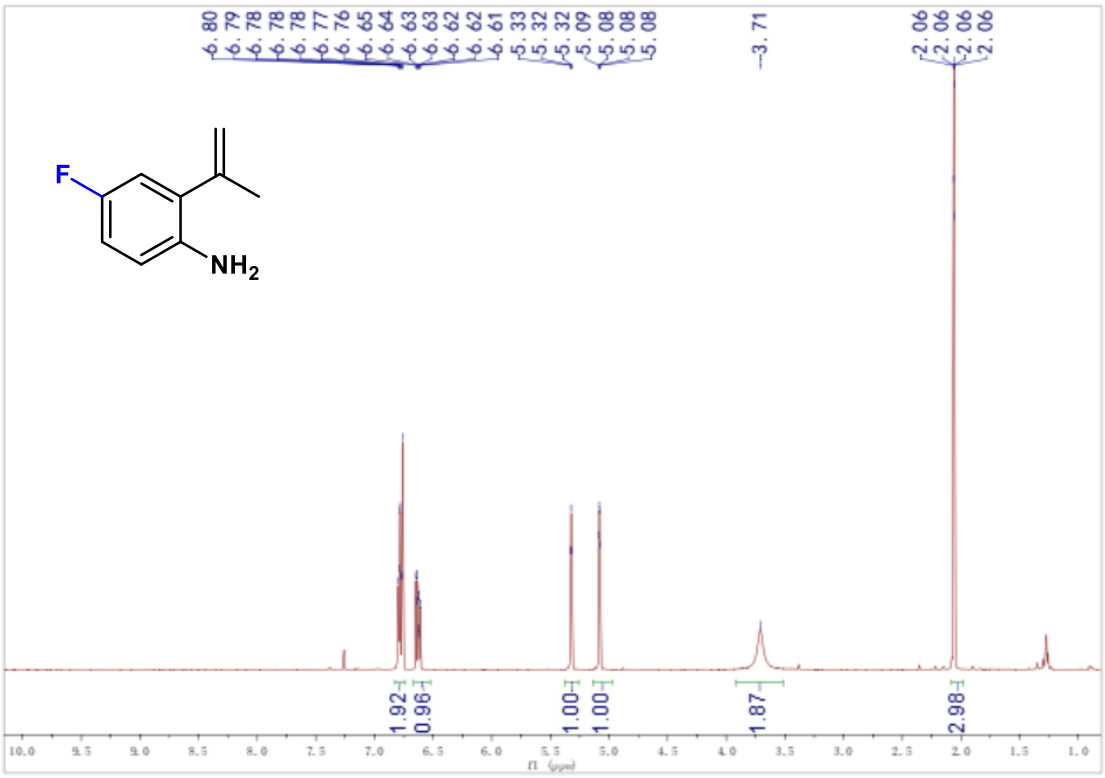

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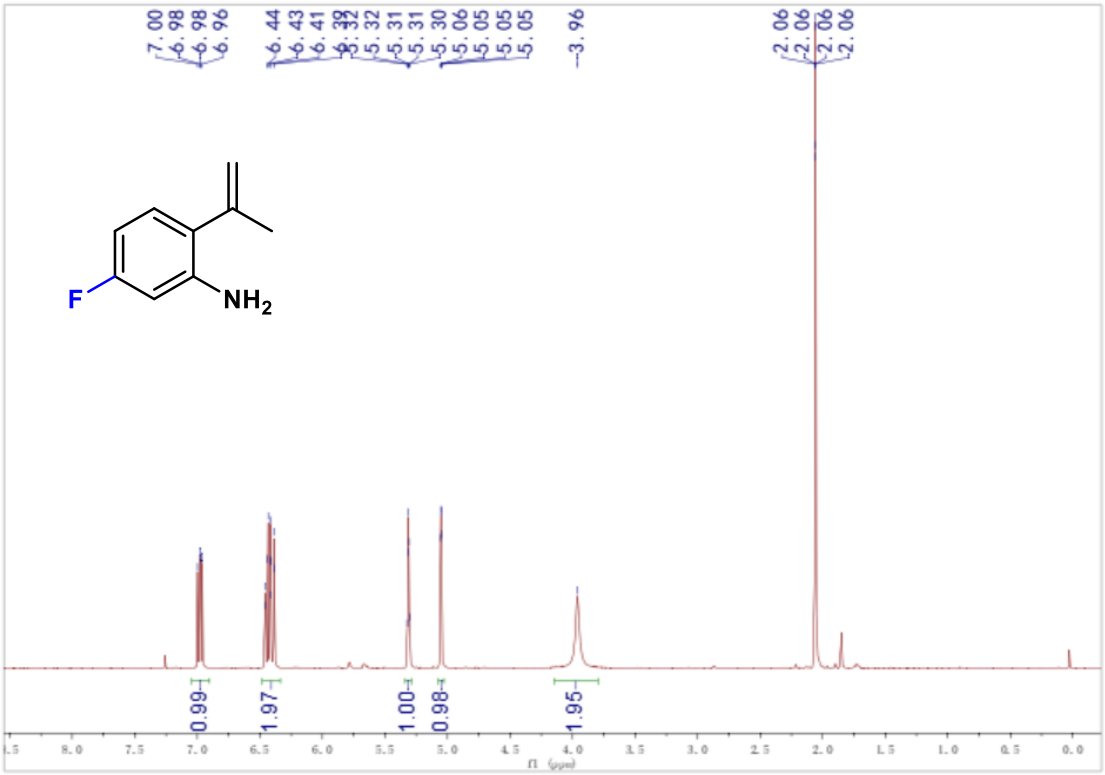
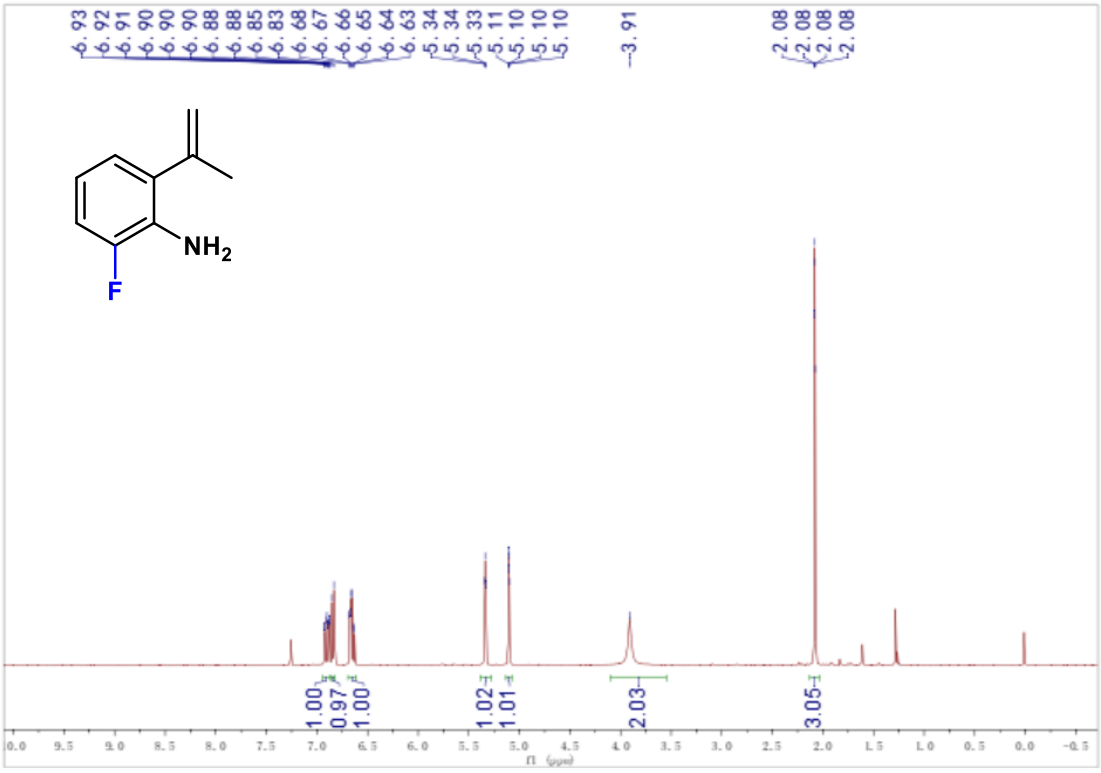
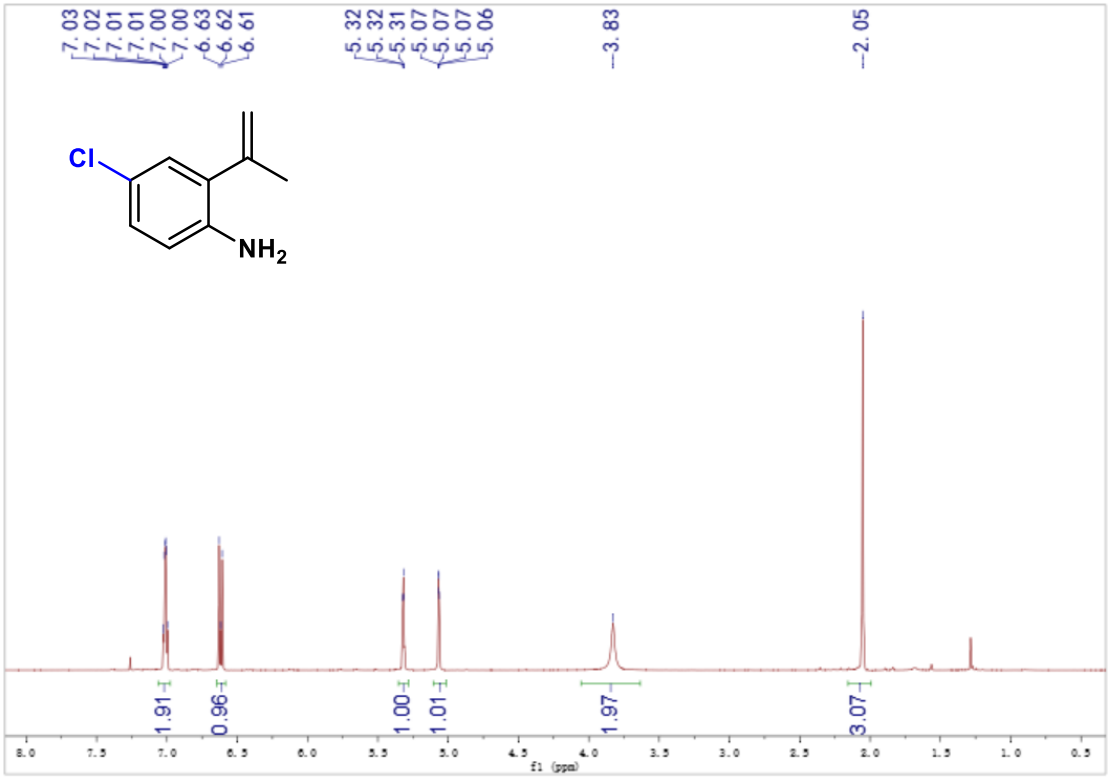


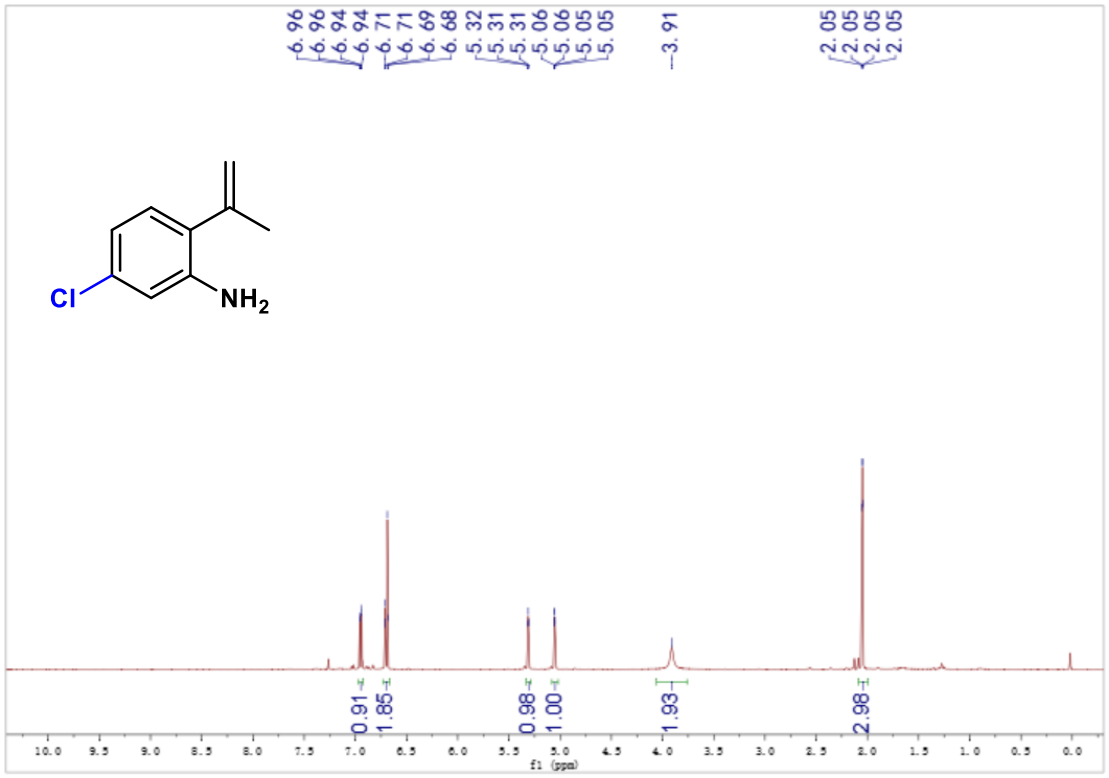
^{1}H NMR of **1q**



^{1}H NMR of **1r**



^{1}H NMR of **1s**



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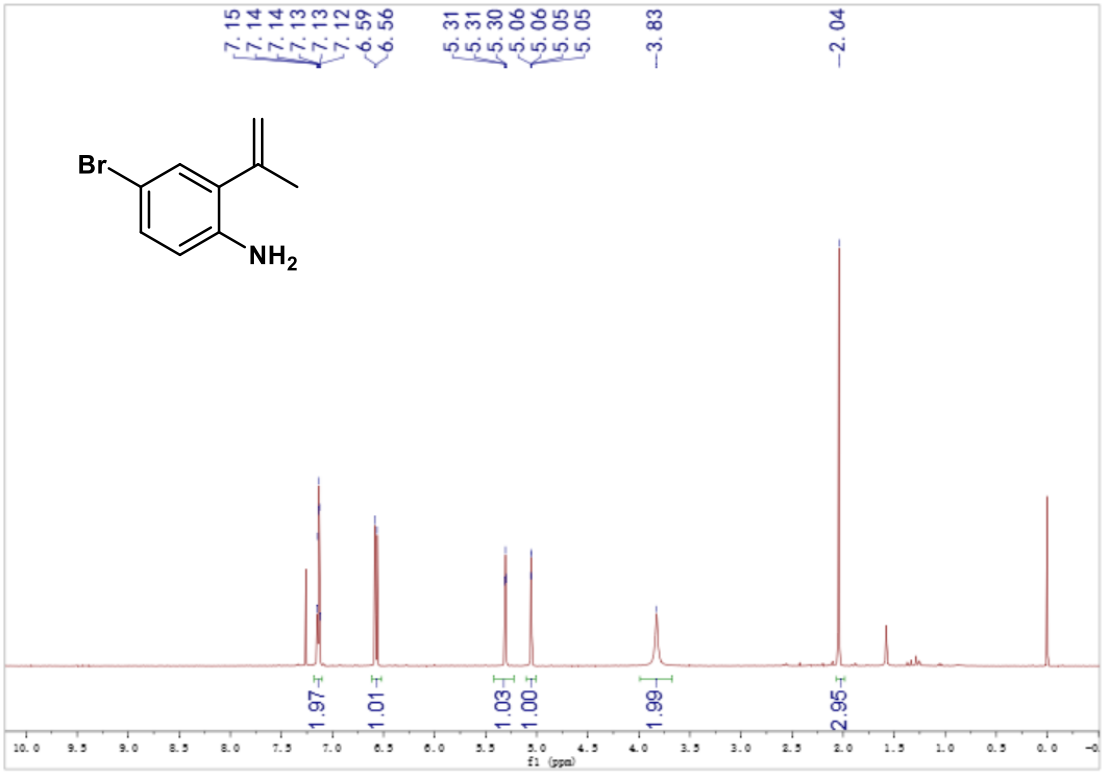
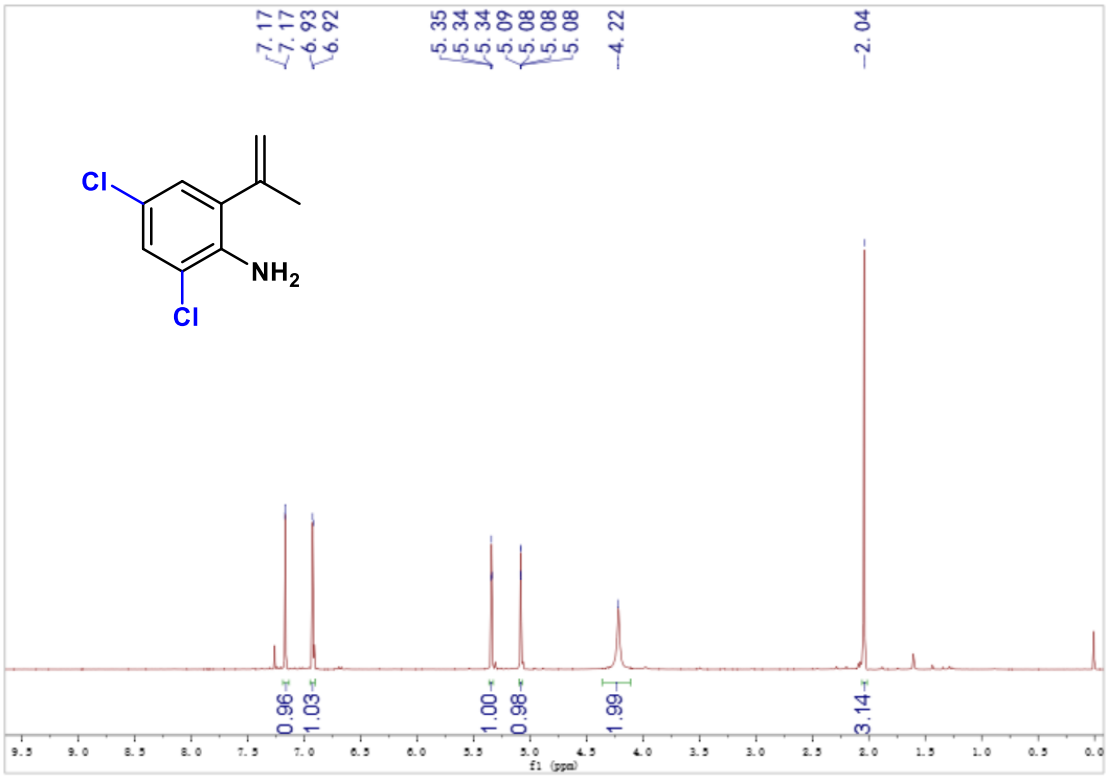
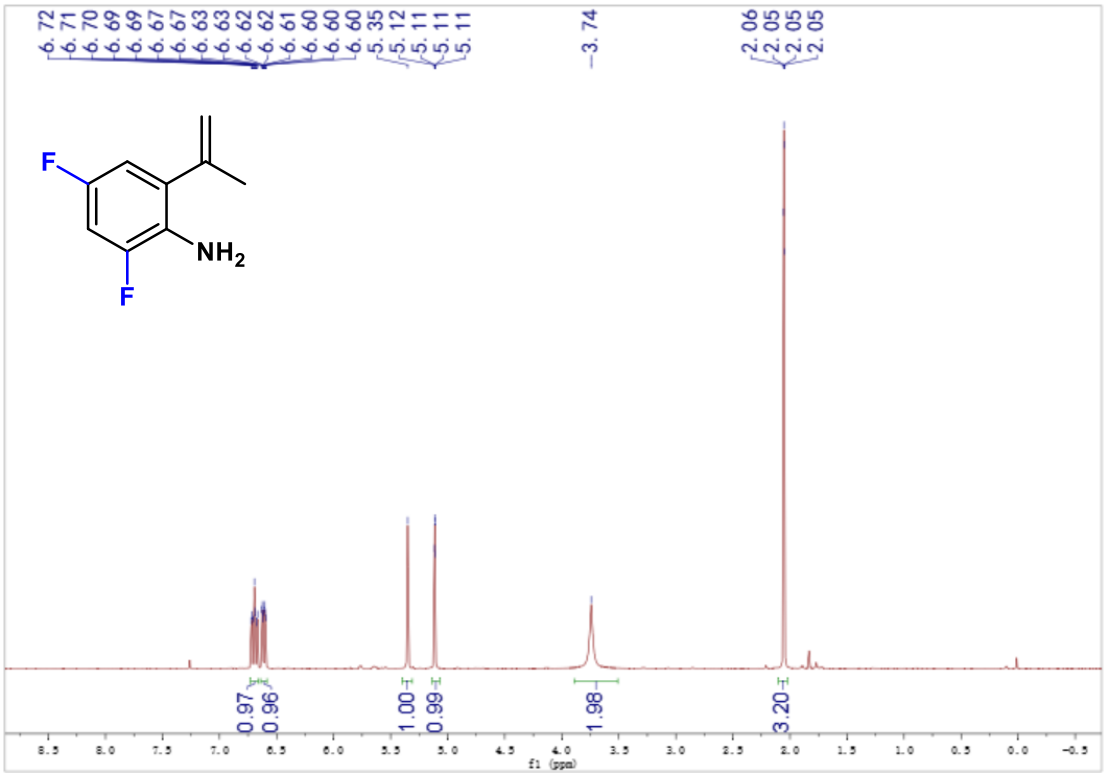


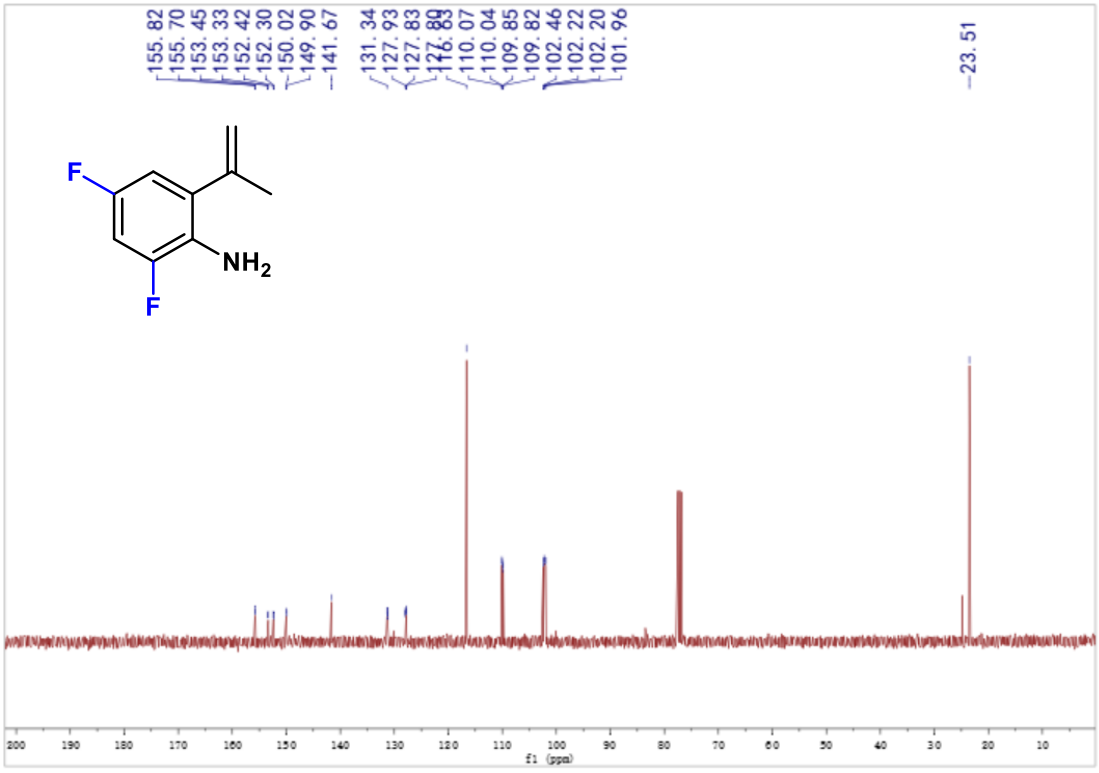
^{1}H NMR of **1u**



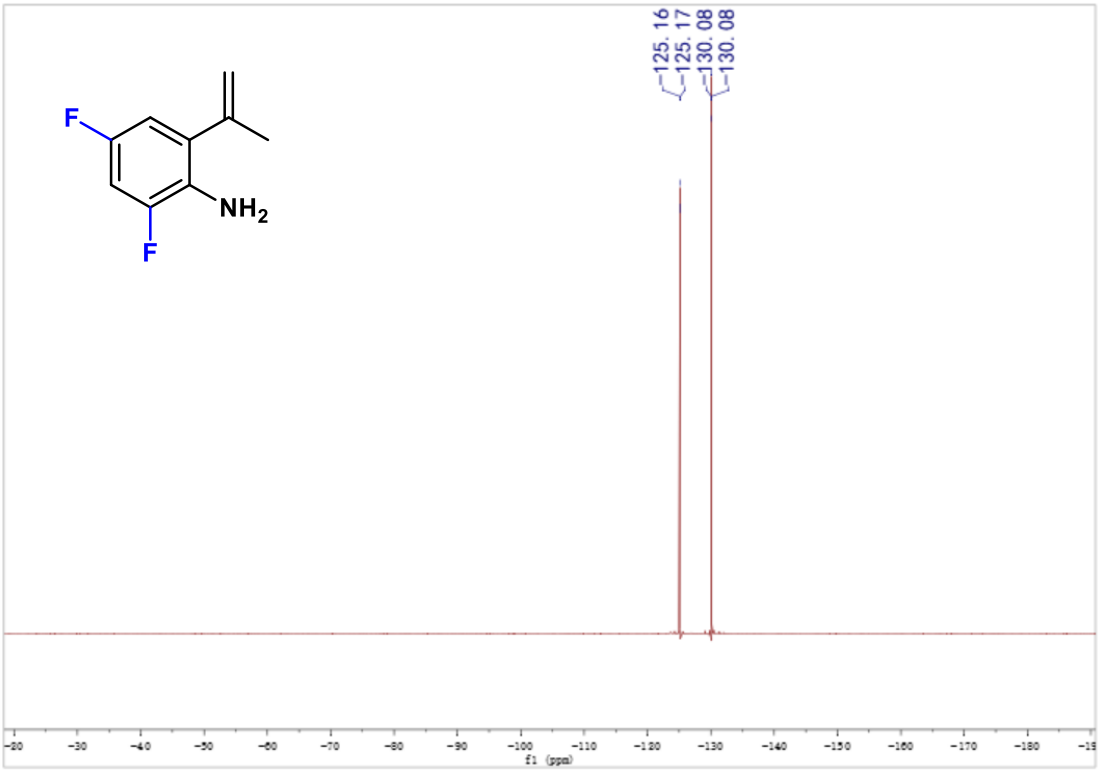
^{1}H NMR of **1v**



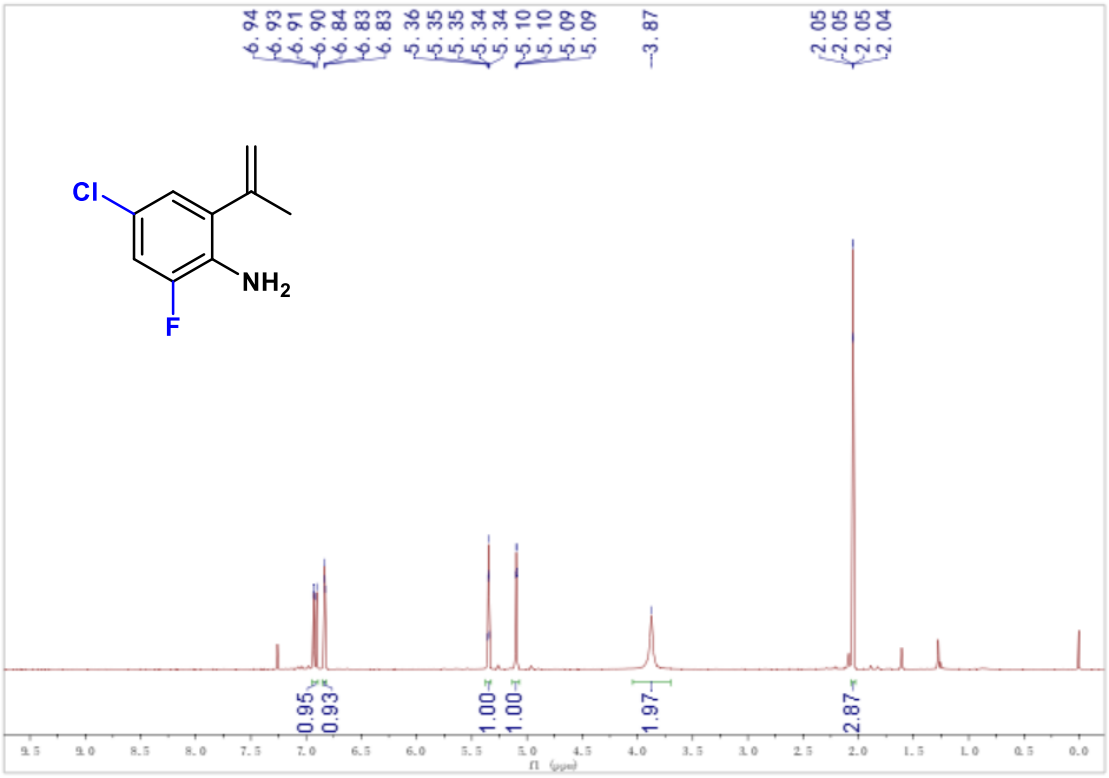
^{1}H NMR of **1w**



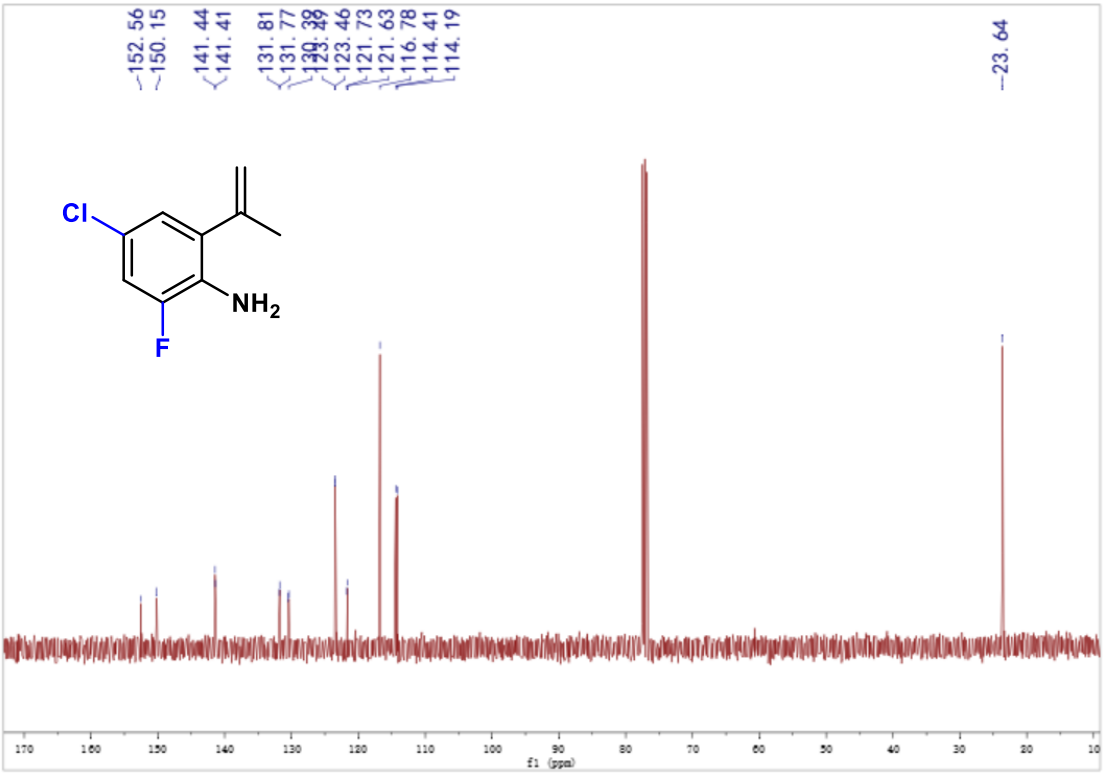
^{13}C NMR of **1w**



^{19}F NMR of **1w**



^{1}H NMR of **1x**



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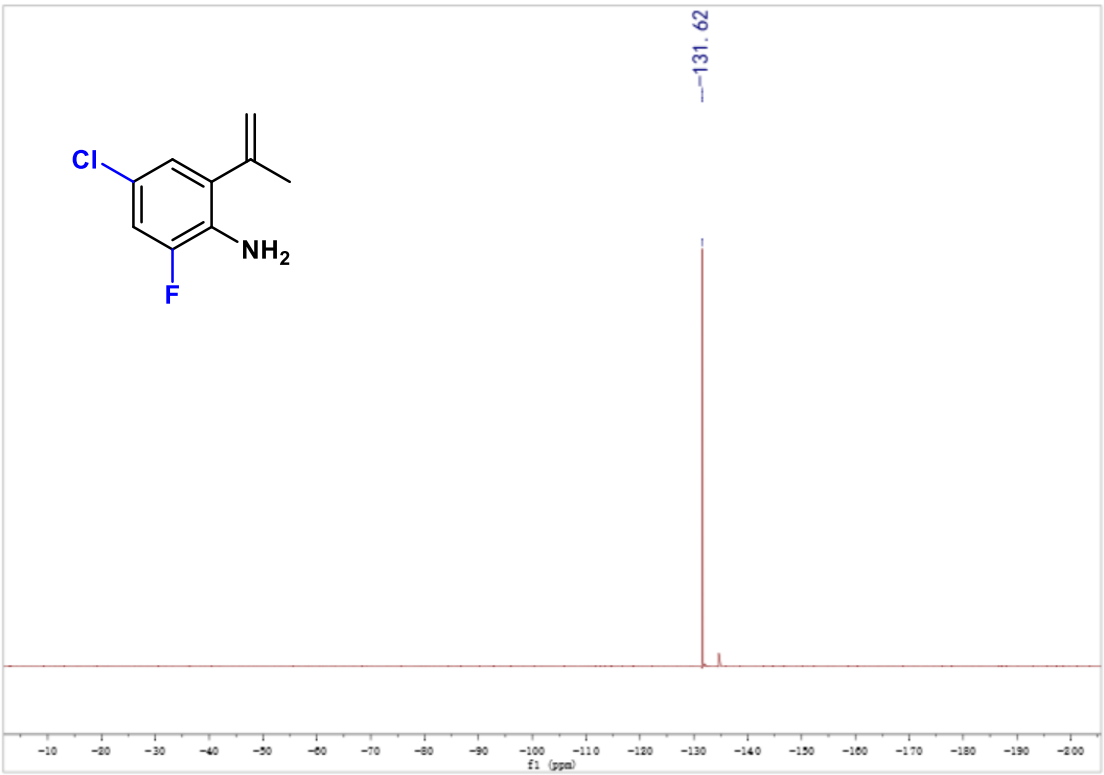
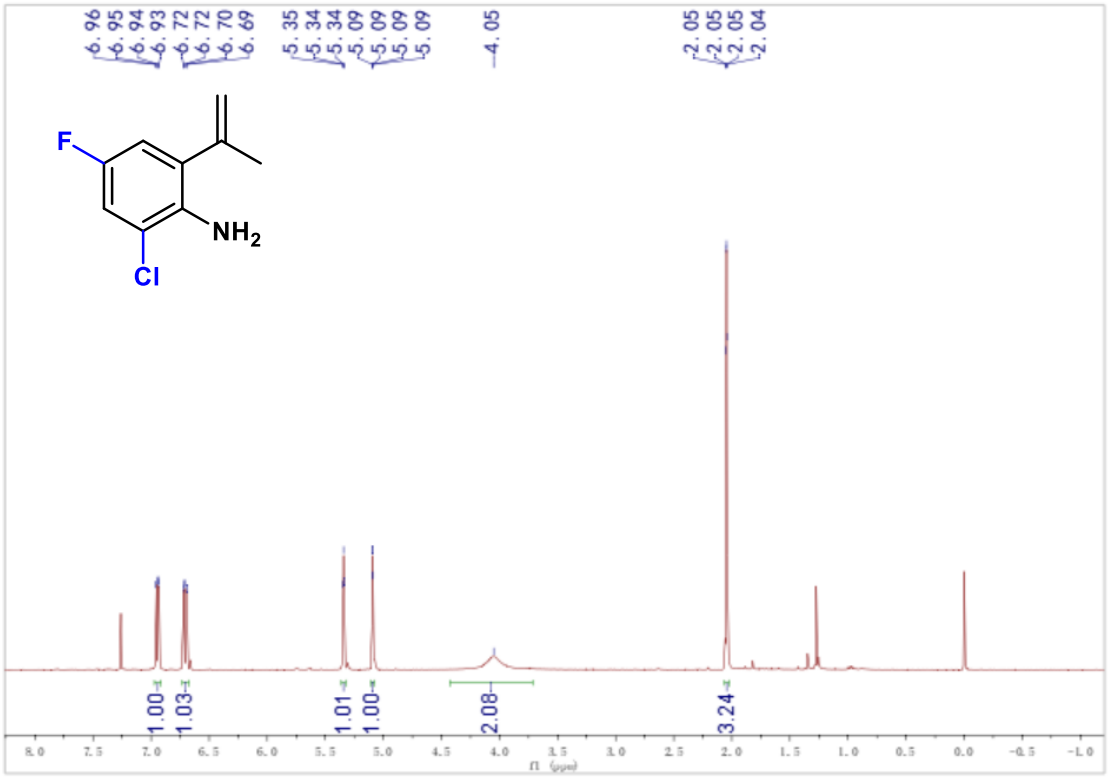
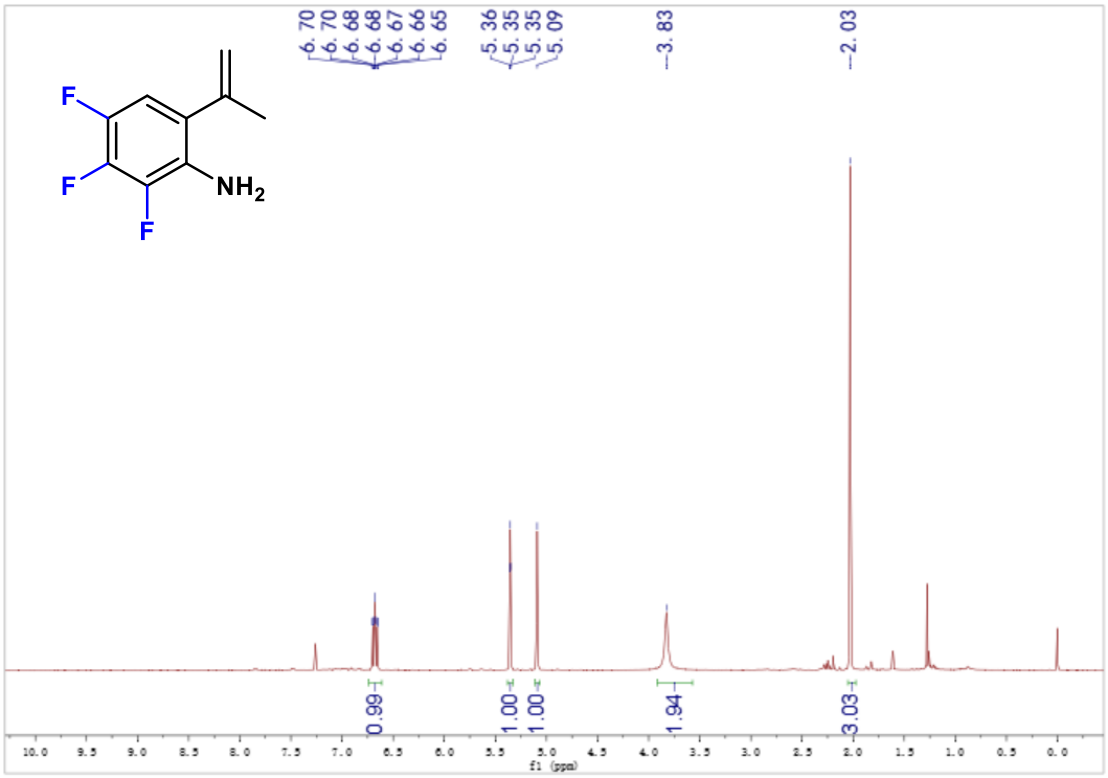


^{19}F NMR of **1x**



^{1}H NMR of **1y**



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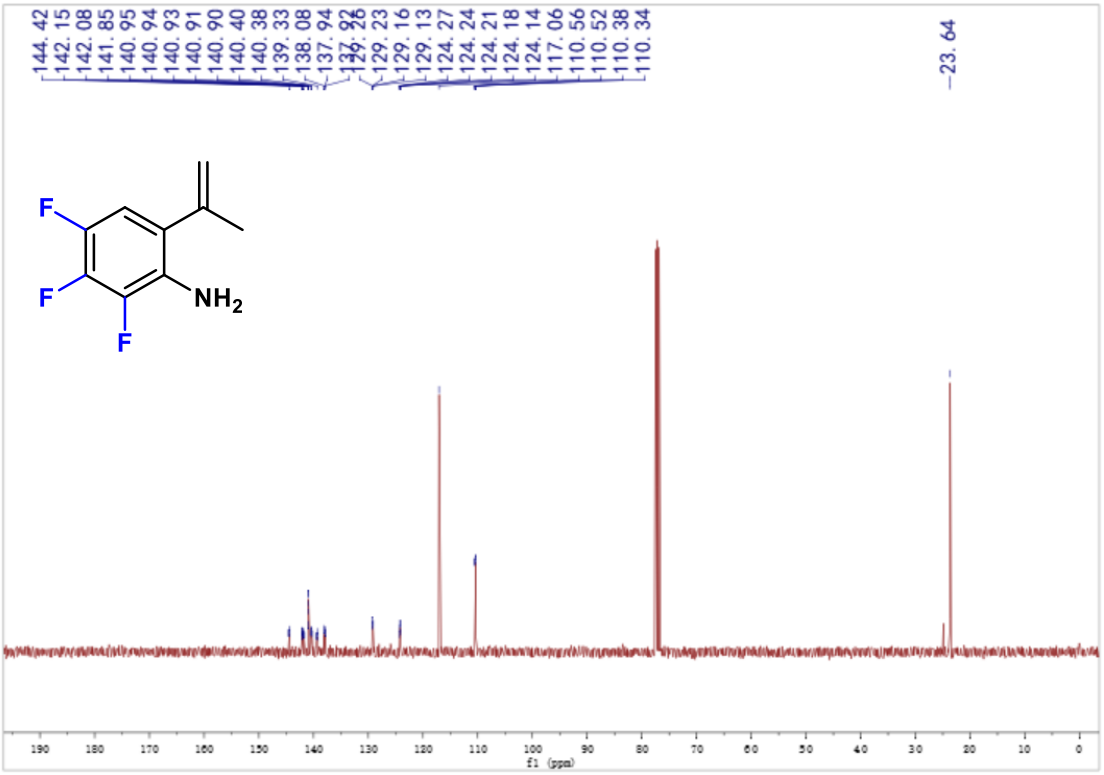
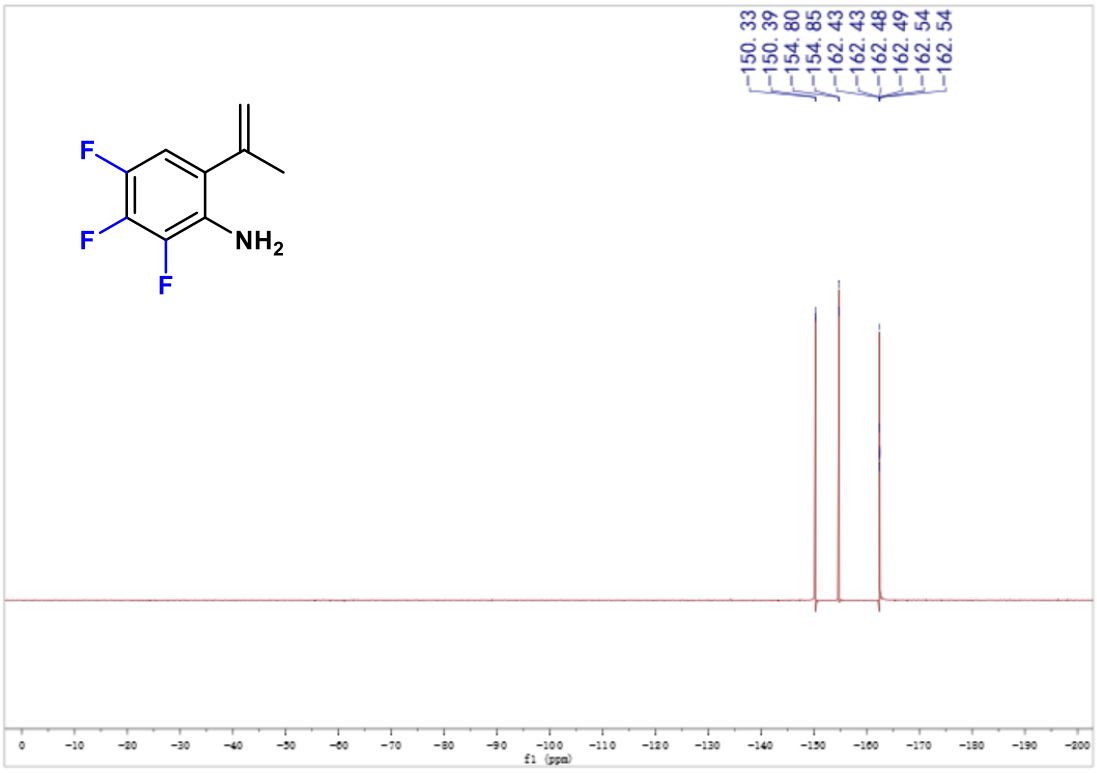
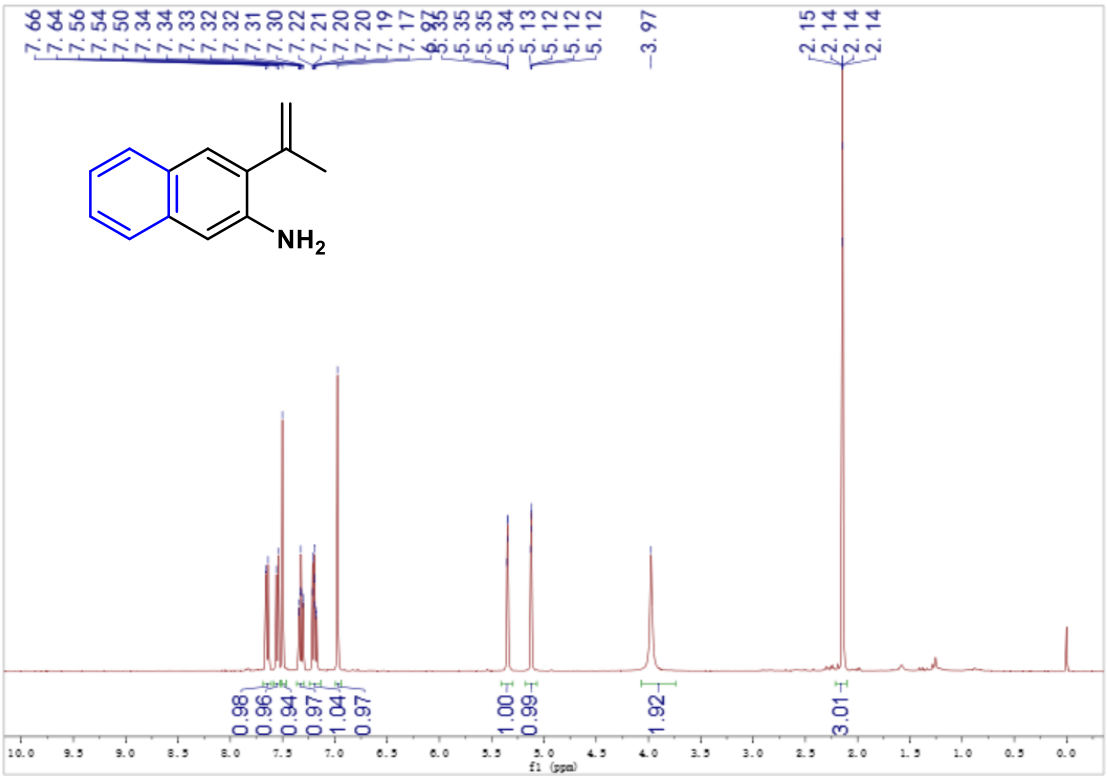


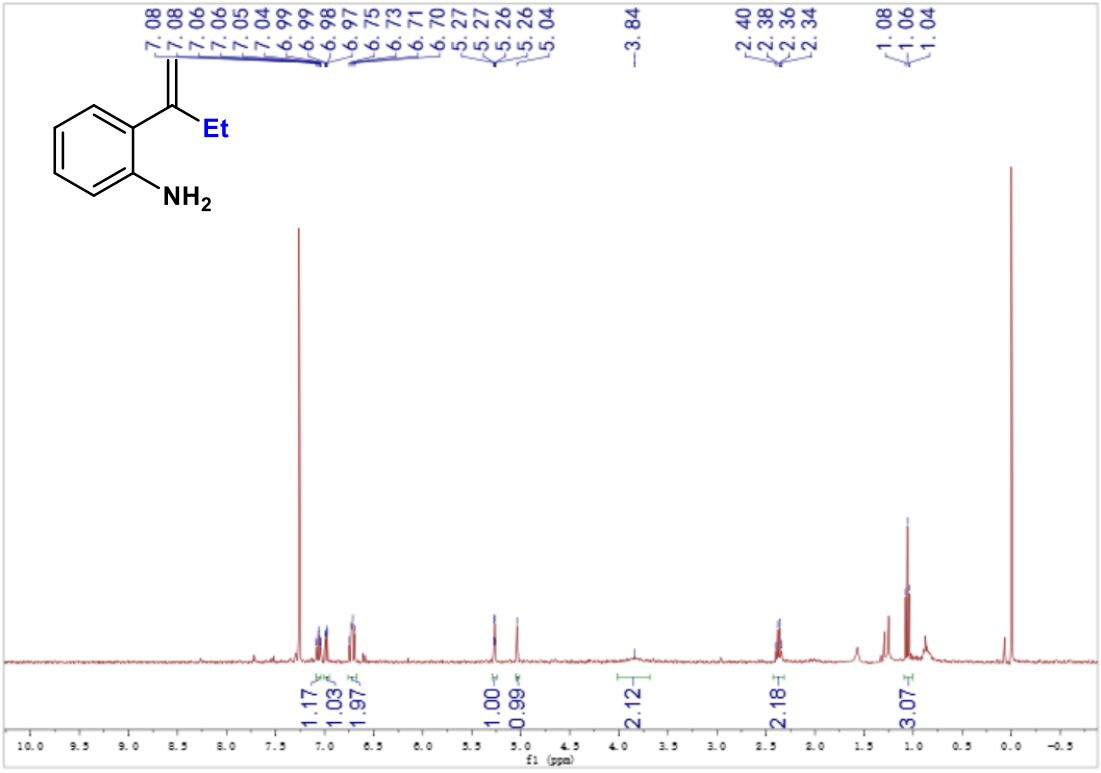
^{13}C NMR of **1z**



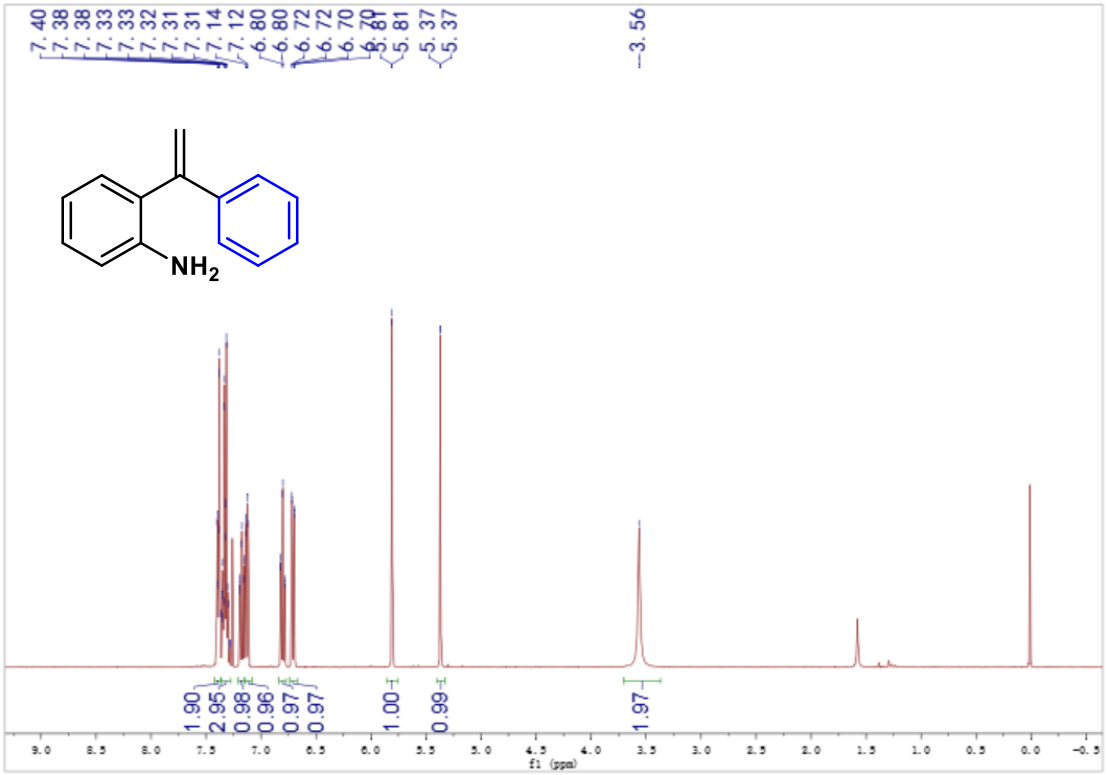
^{19}F NMR of **1z**



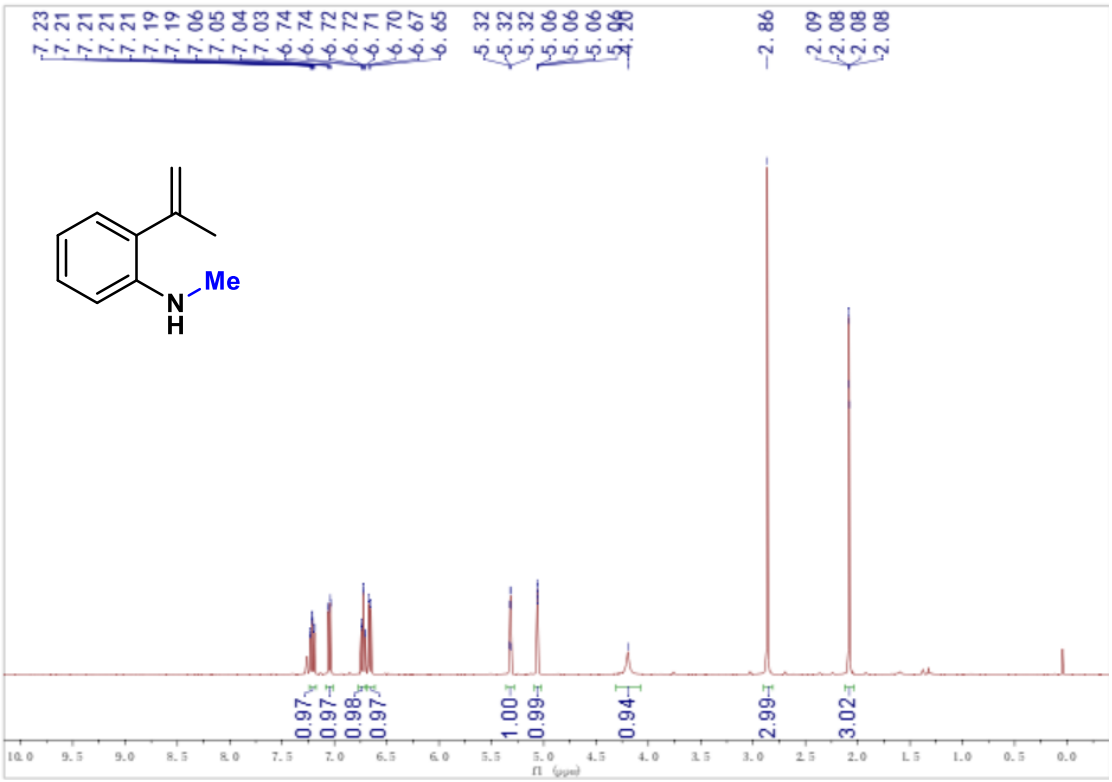
^{1}H NMR of **1aa**



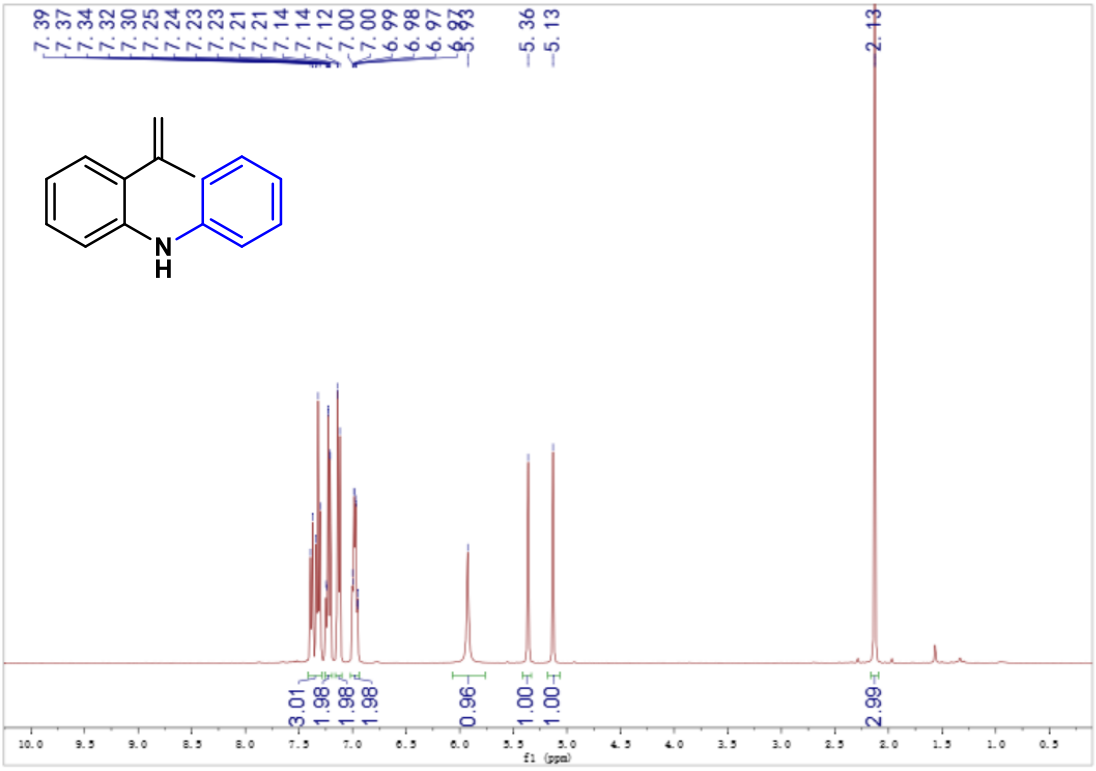
^{1}H NMR of **1ab**



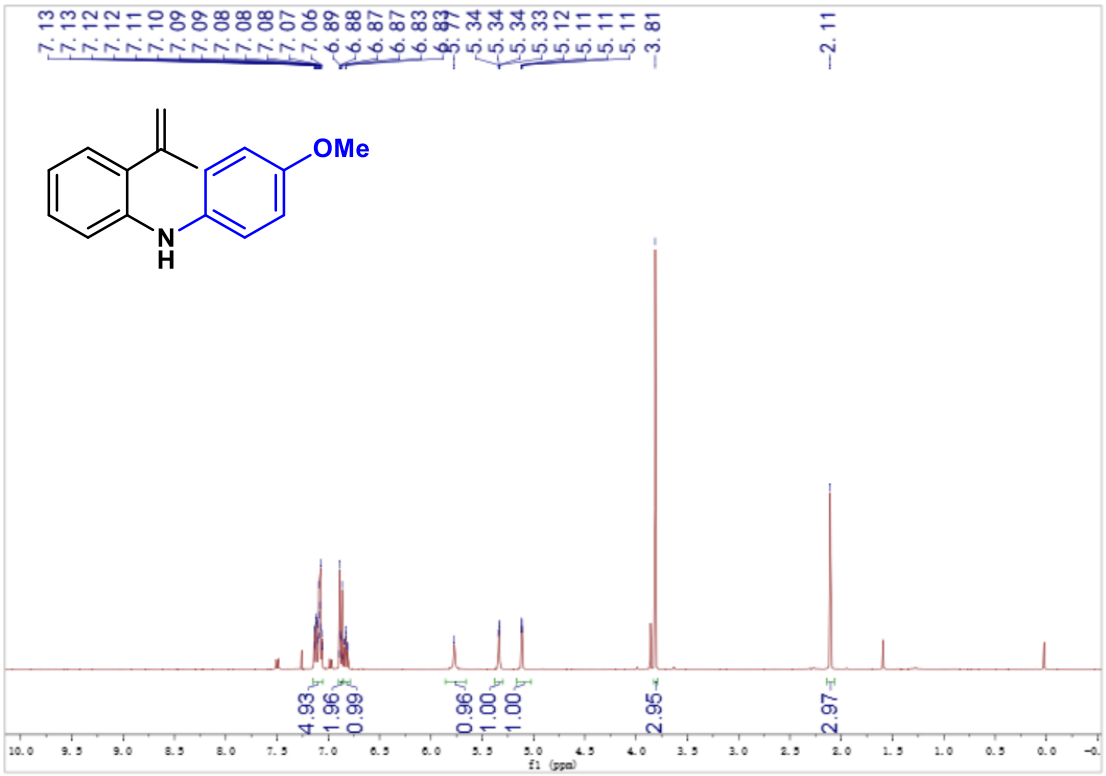
^{1}H NMR of **1ac**



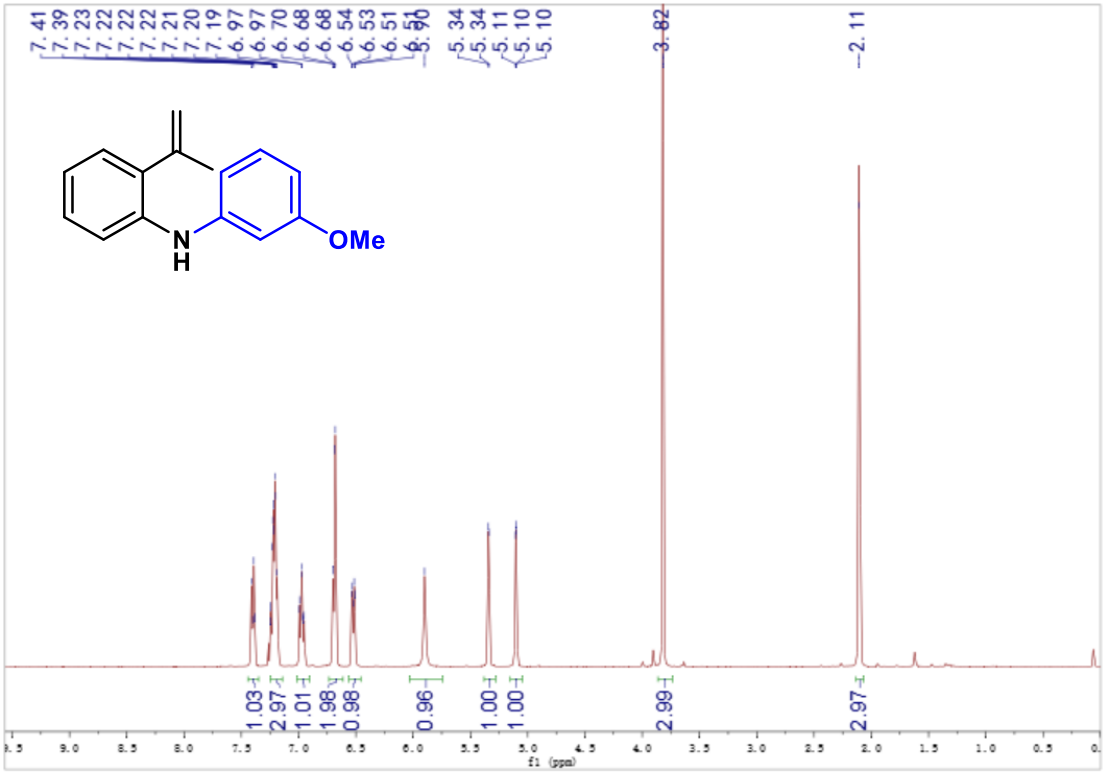
^{1}H NMR of **1ad**



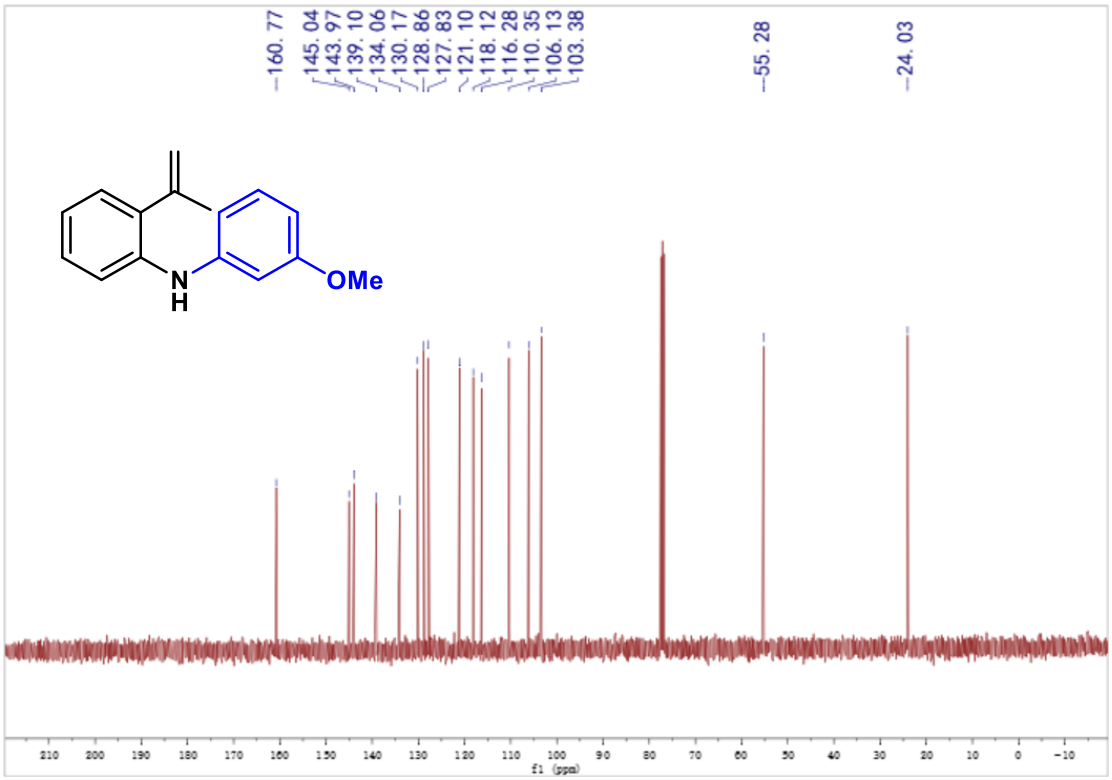
^{1}H NMR of **1ae**



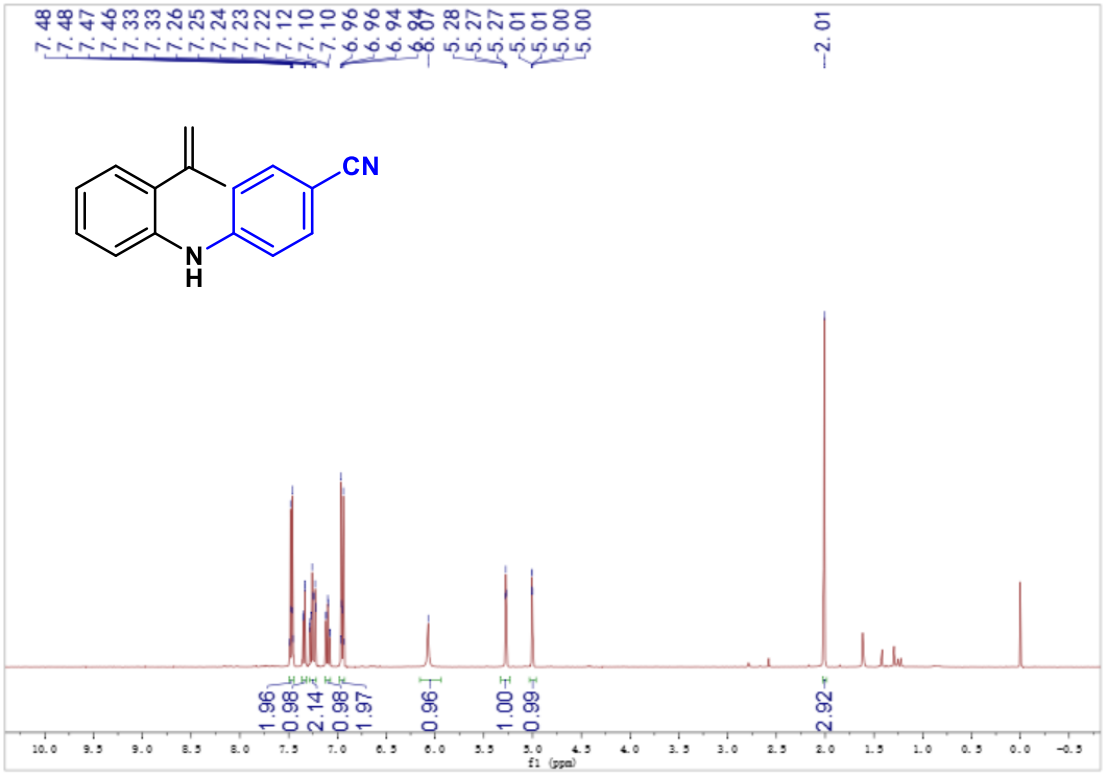
^{1}H NMR of **1af**



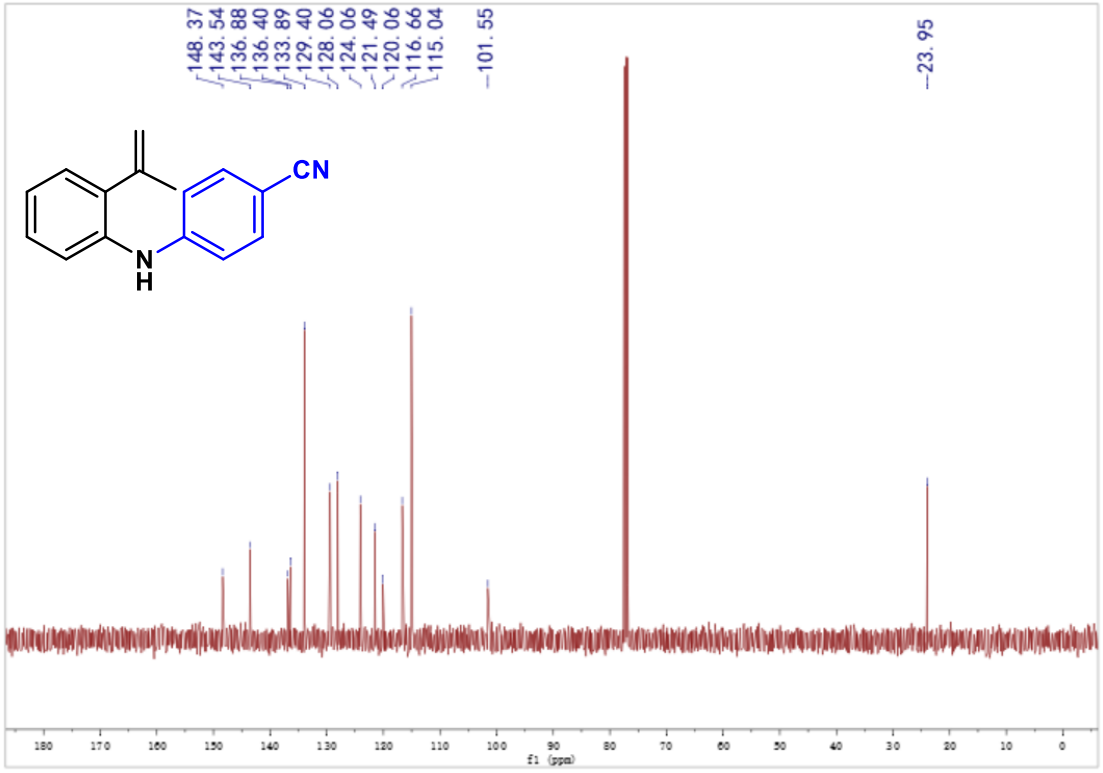
^{1}H NMR of **1ag**



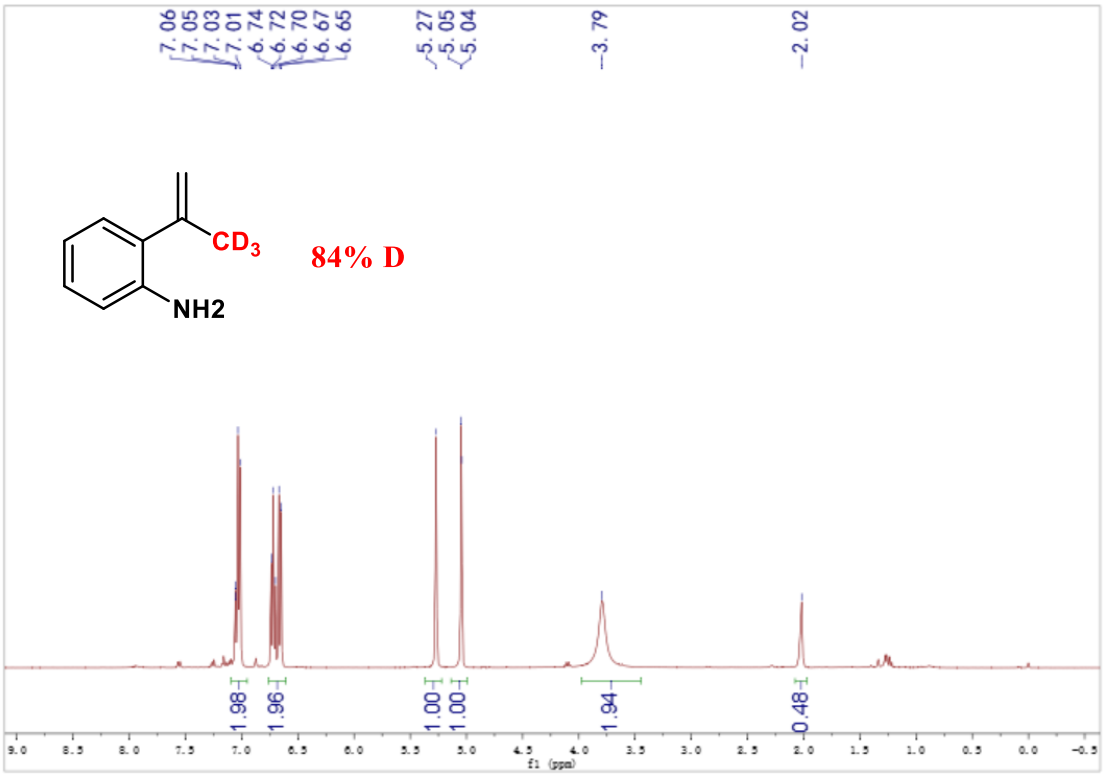
^{13}C NMR of **1ag**



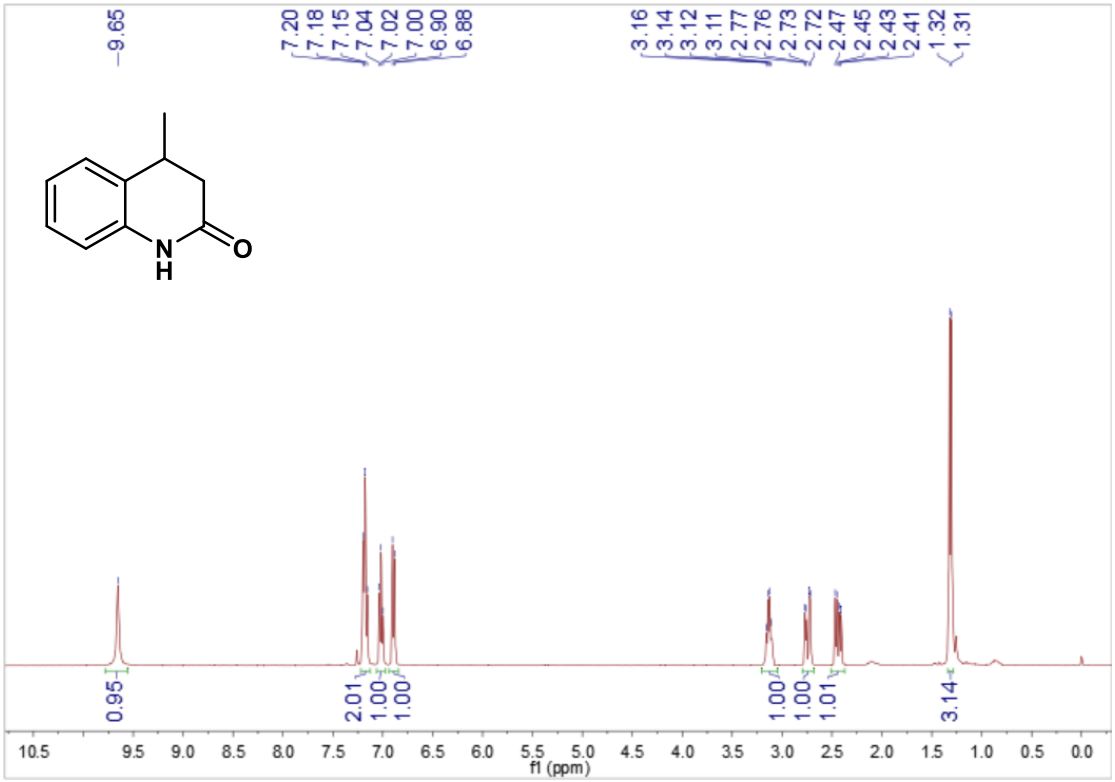
^{1}H NMR of **1ah**



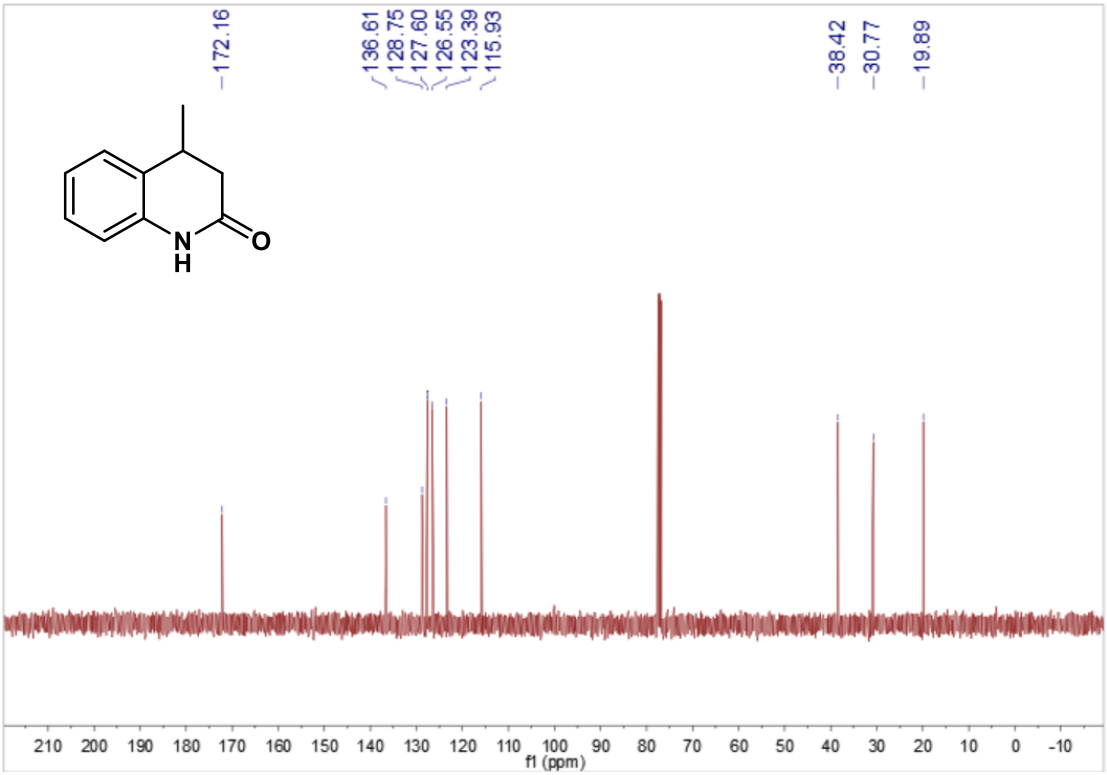
^{13}C NMR of **1ah**



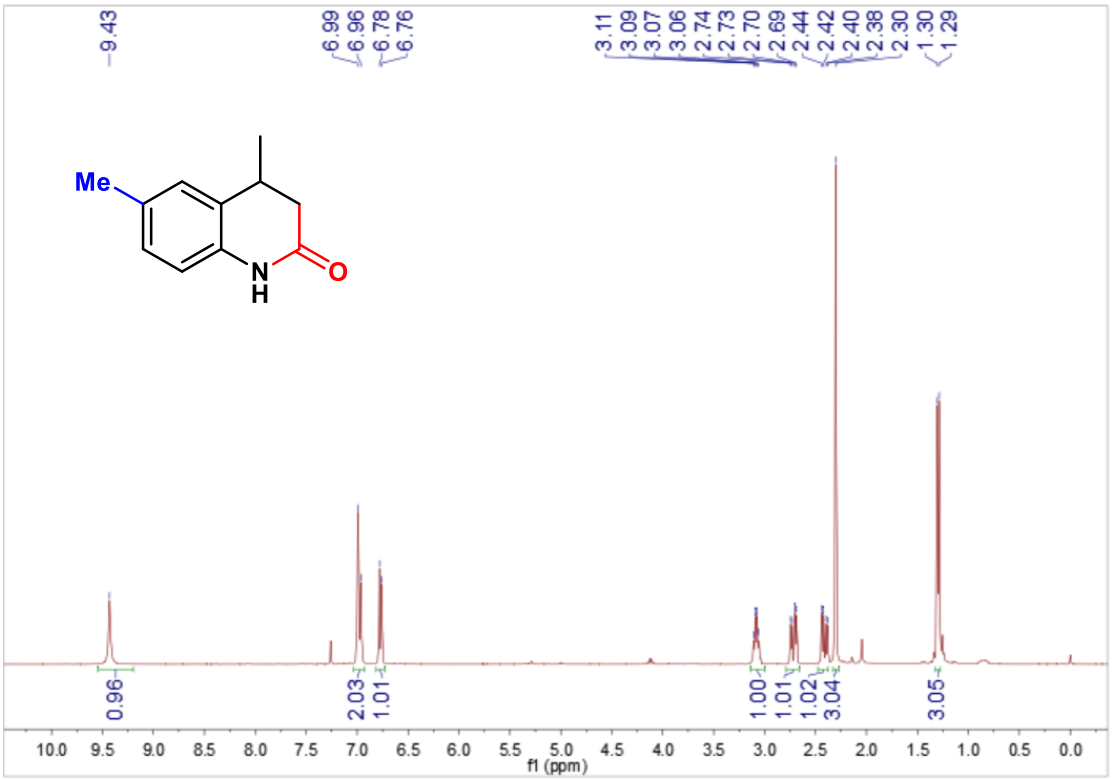
^{1}H NMR of **1a-CD$_3$**



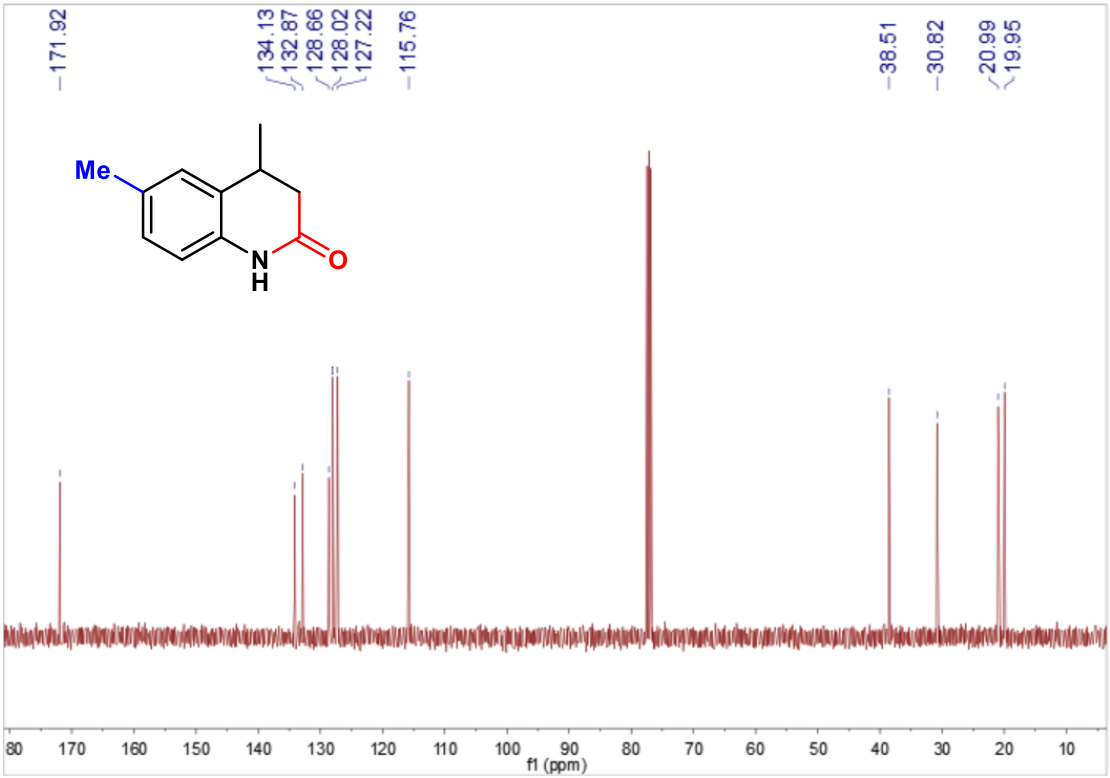
^{1}H NMR of **2a**



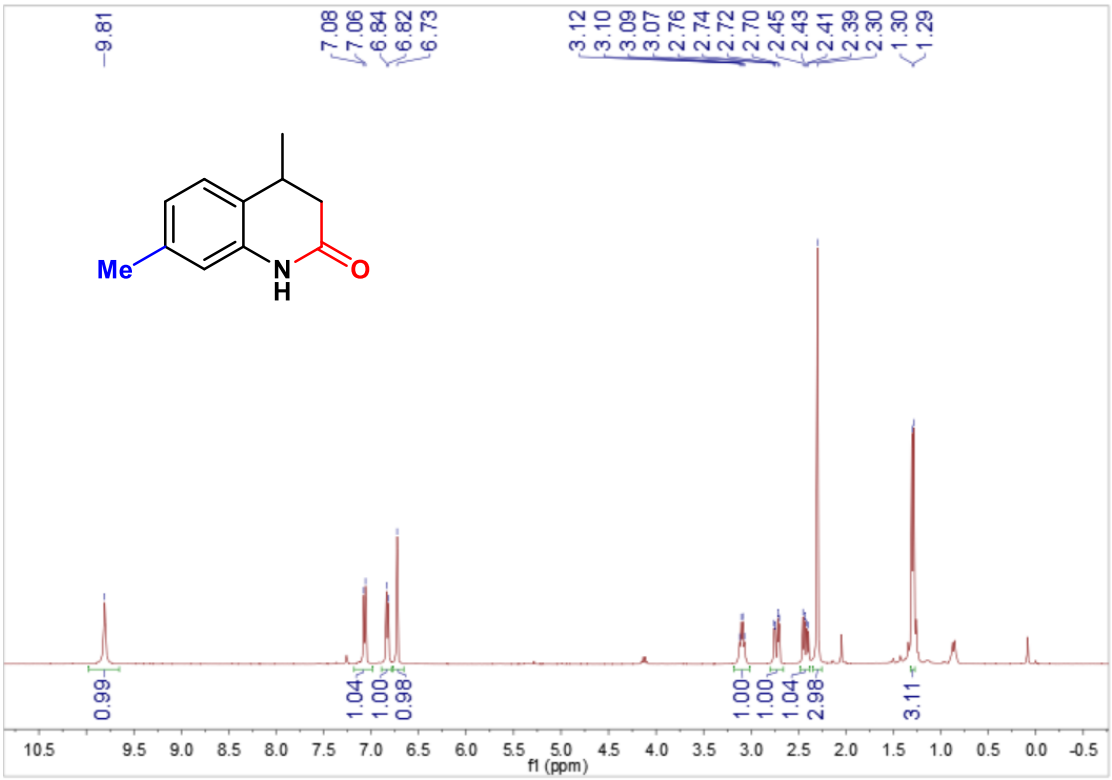
^{13}C NMR of **2a**



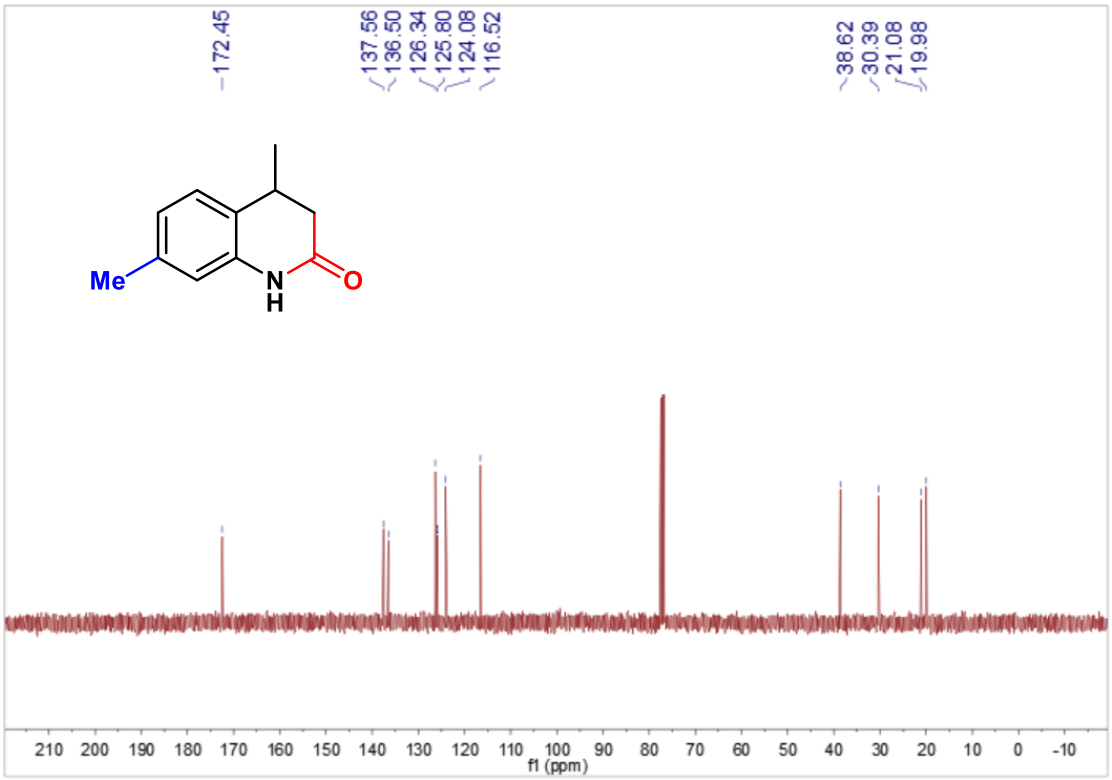
^{1}H NMR of **2b**



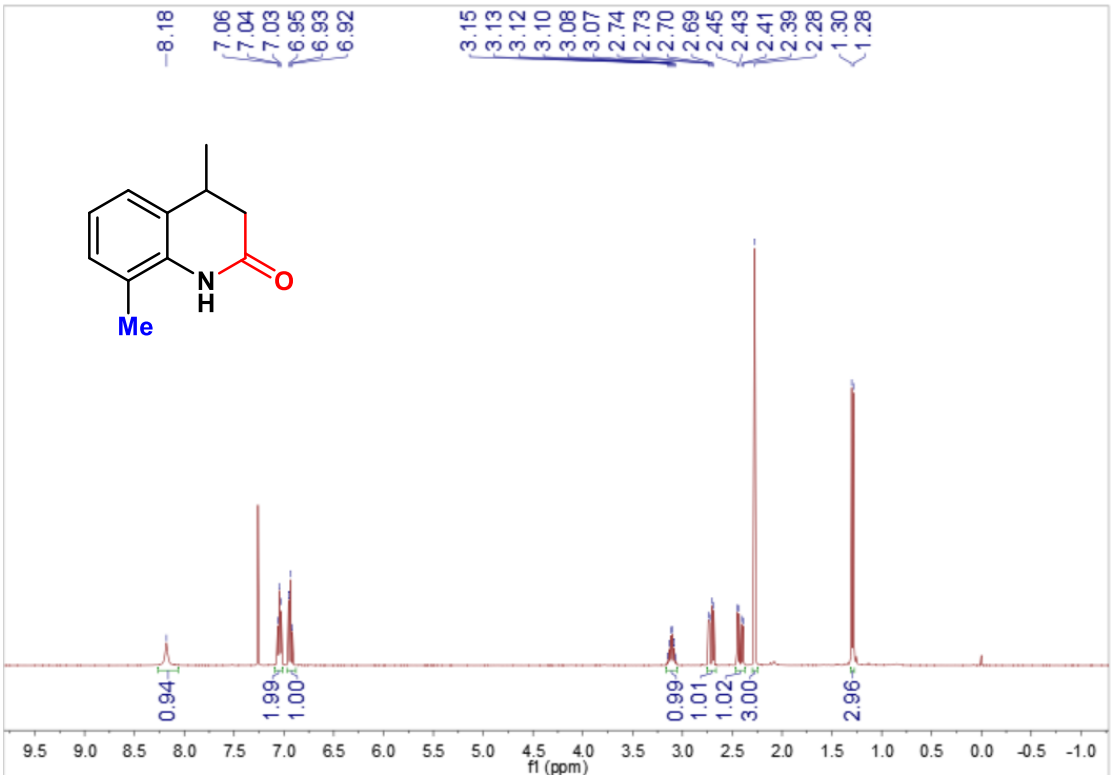
^{13}C NMR of **2b**



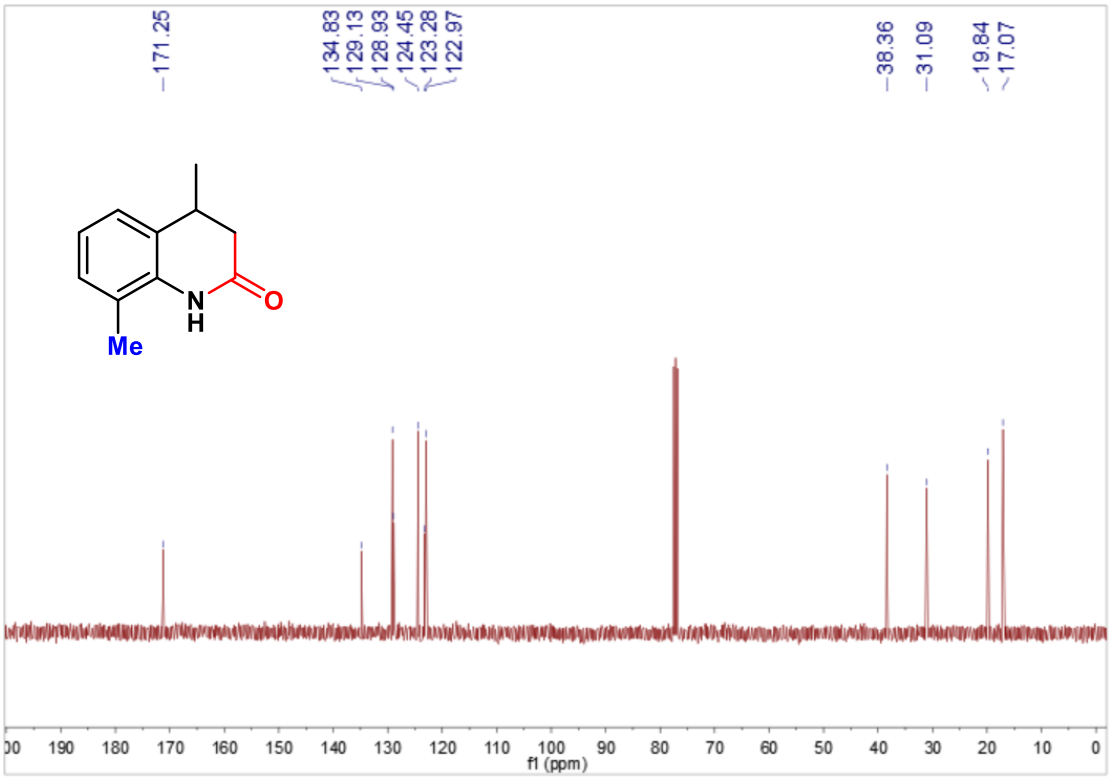
^{1}H NMR of **2c**



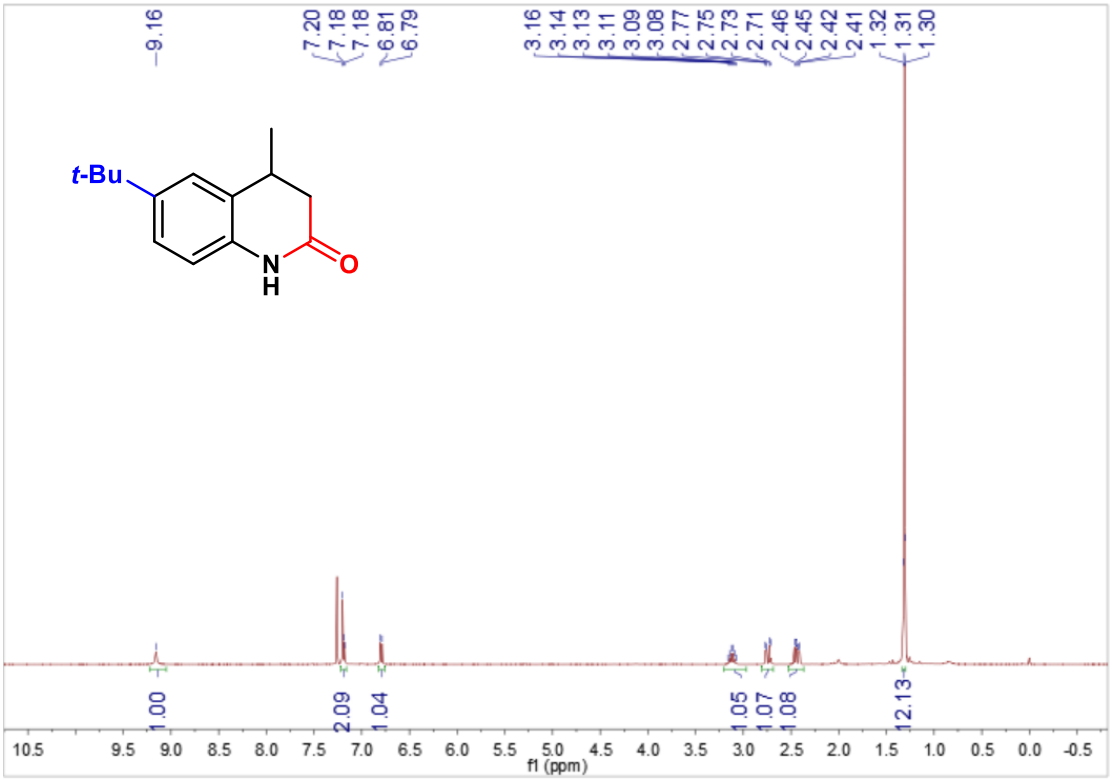
^{13}C NMR of **2c**



^{1}H NMR of **2d**



^{13}C NMR of **2d**



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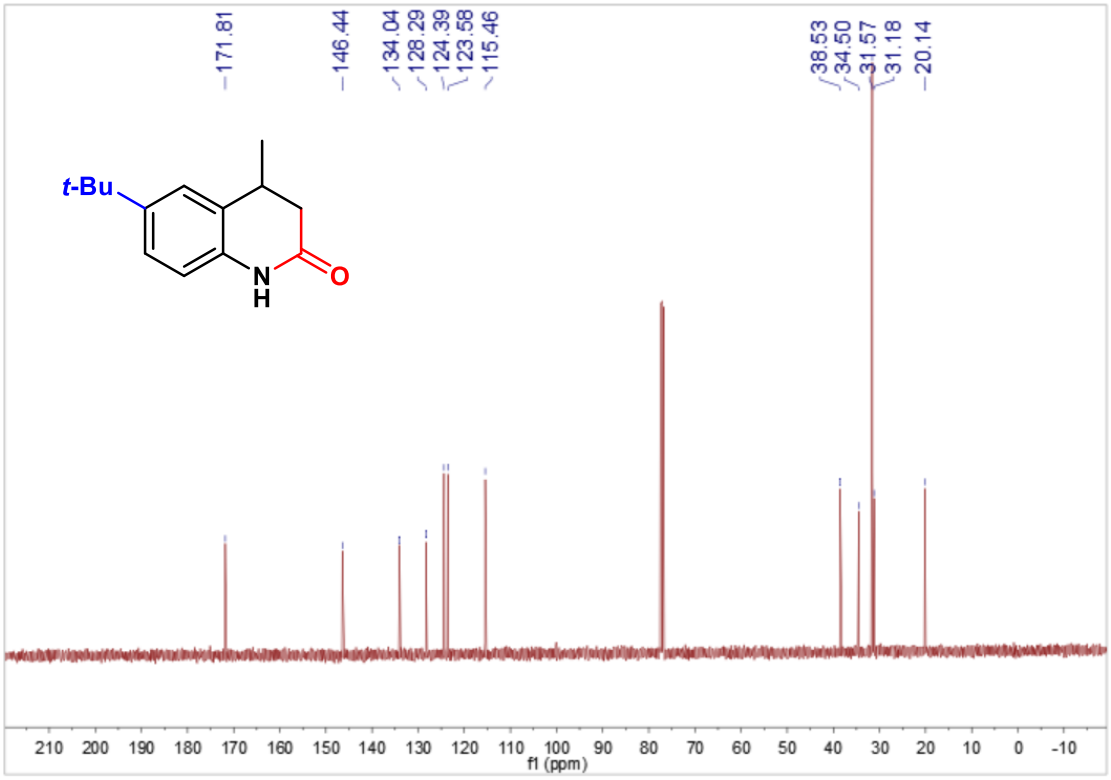
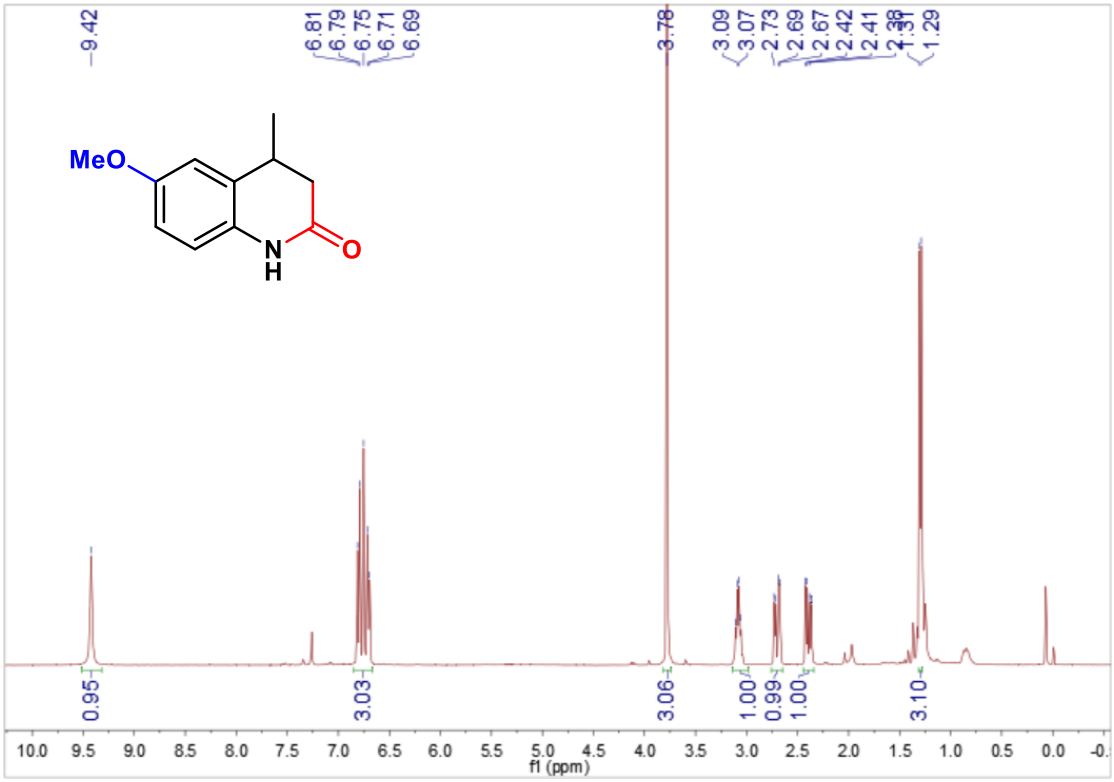
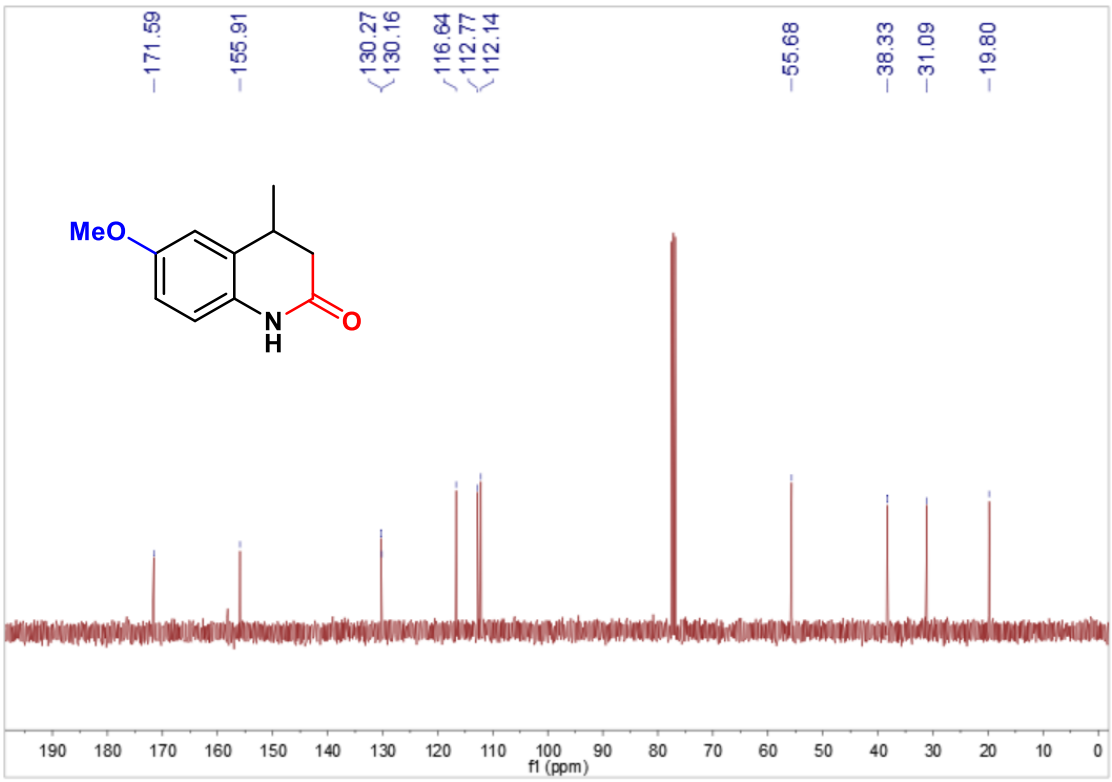


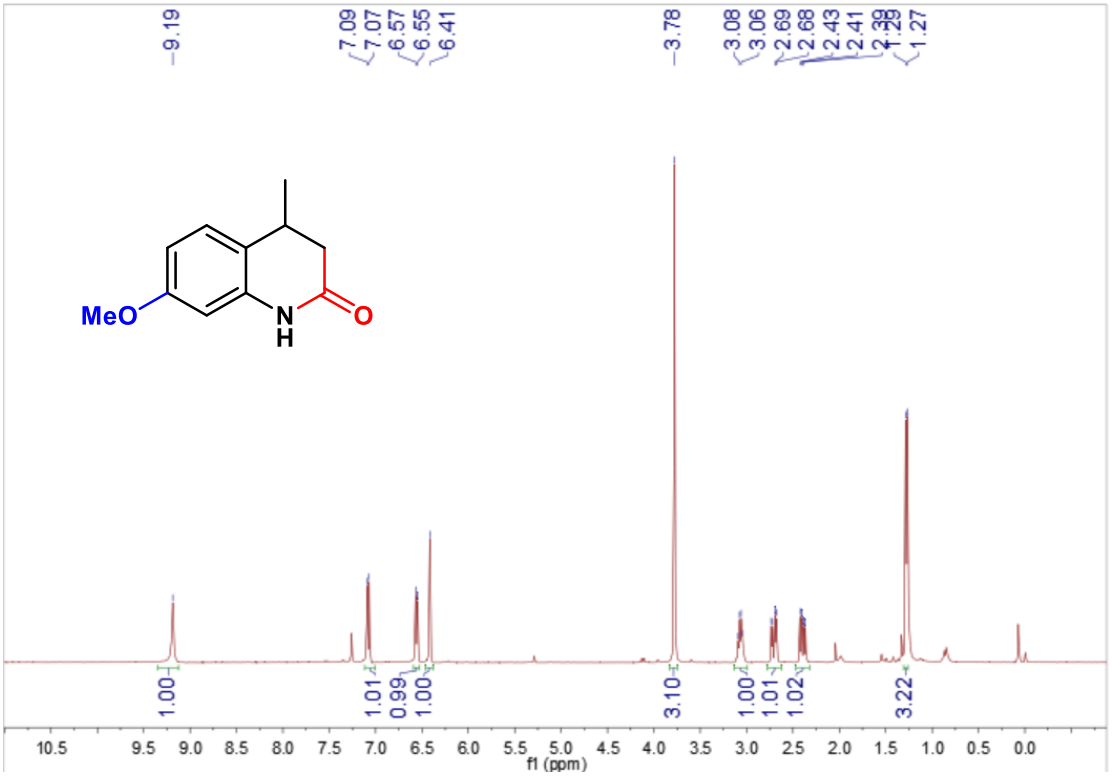
^{13}C NMR of **2e**



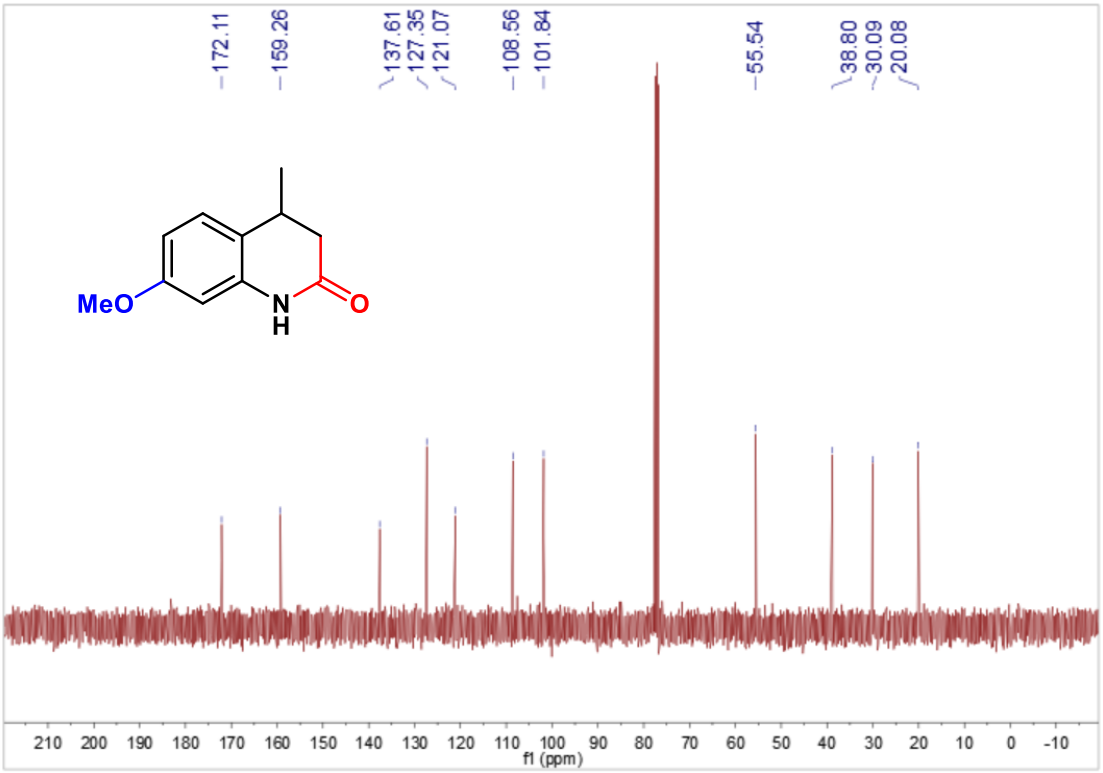
^{1}H NMR of **2f**



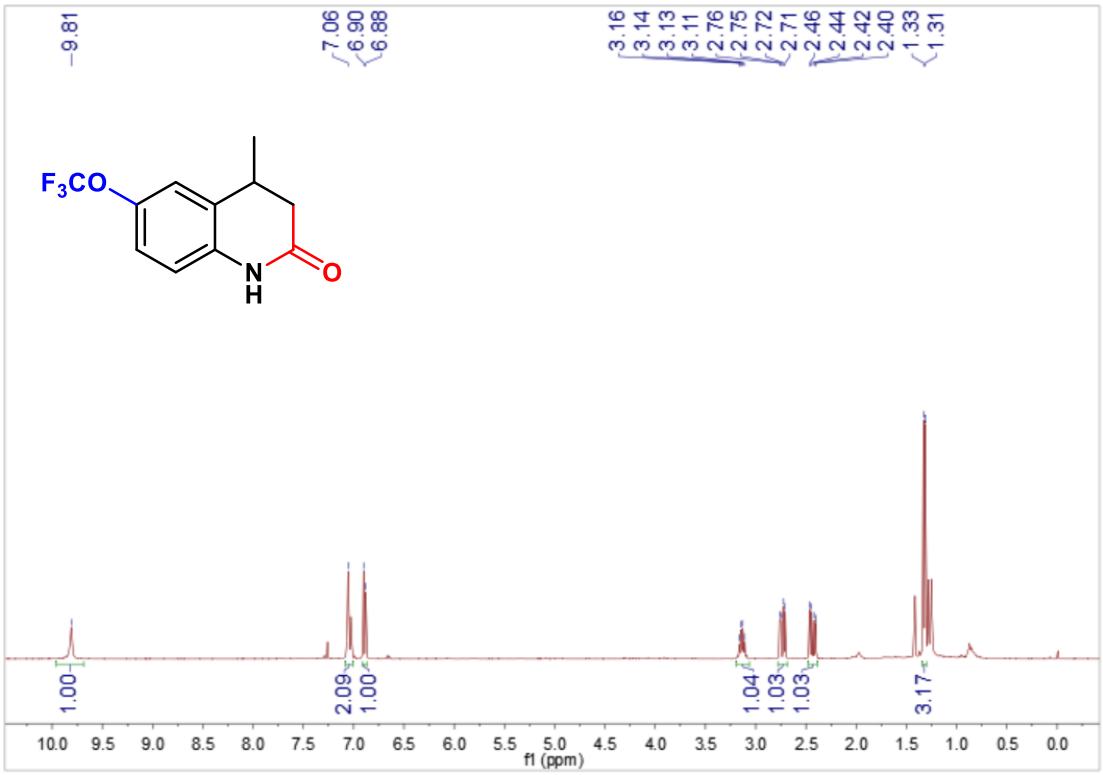
^{13}C NMR of **2f**



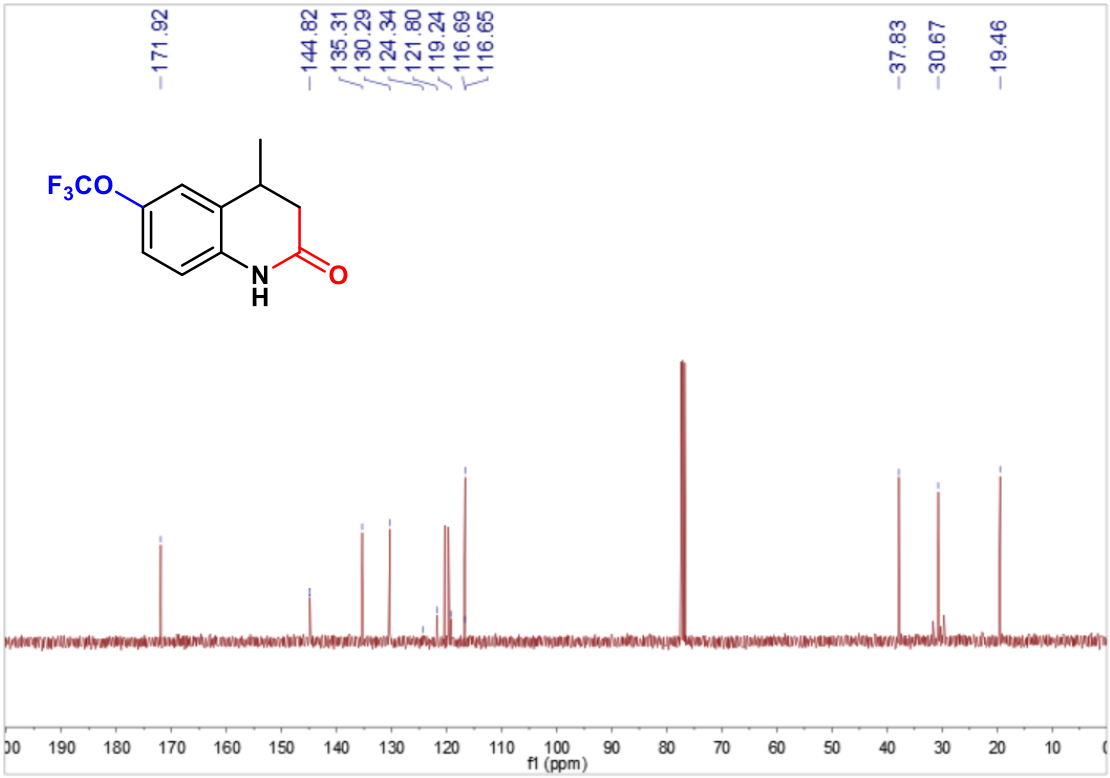
^{1}H NMR of **2g**



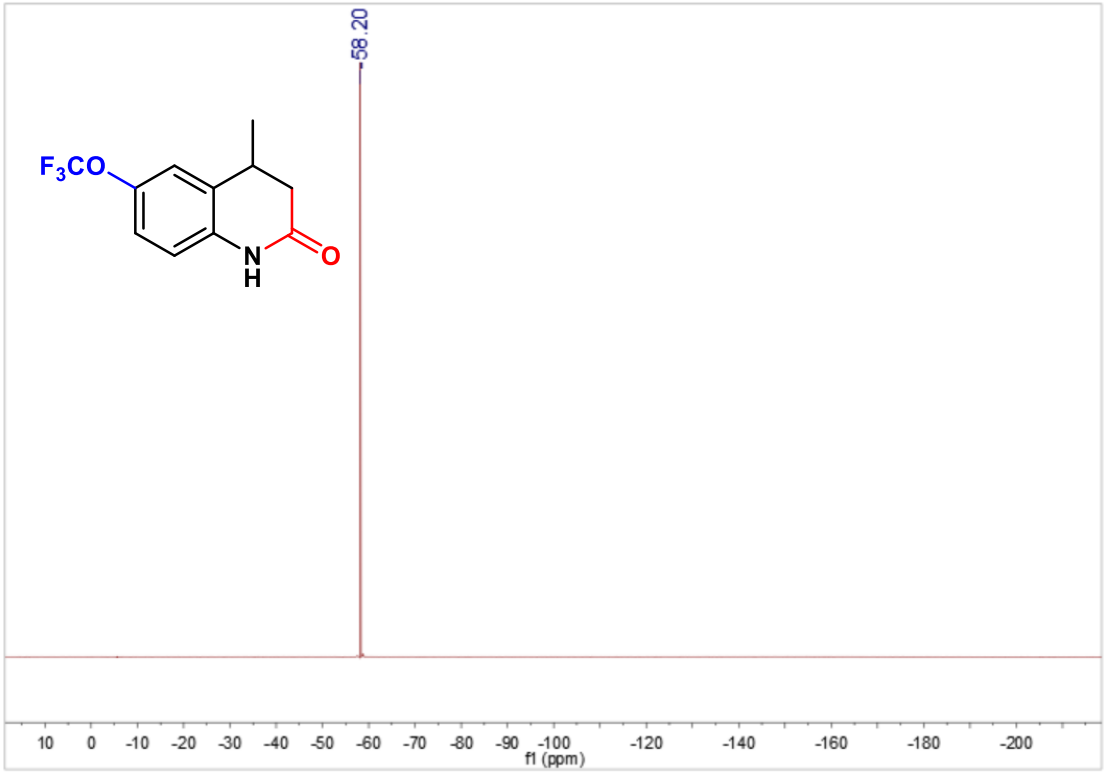
^{13}C NMR of **2g**



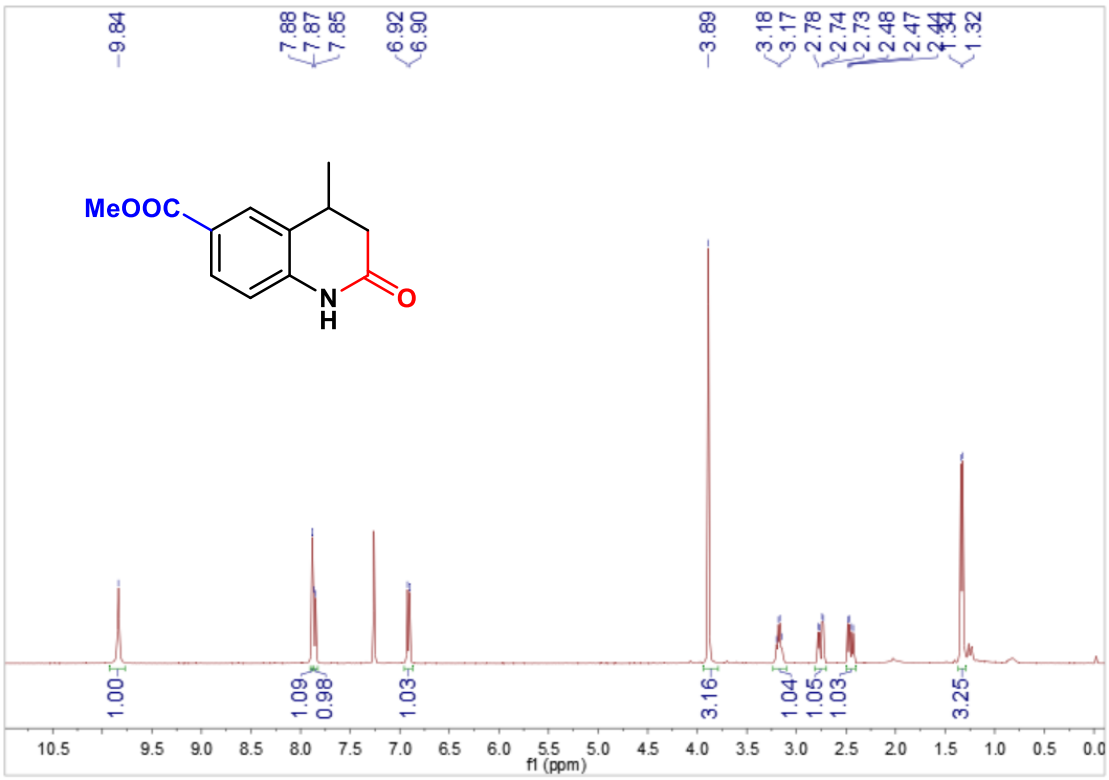
^{1}H NMR of **2h**



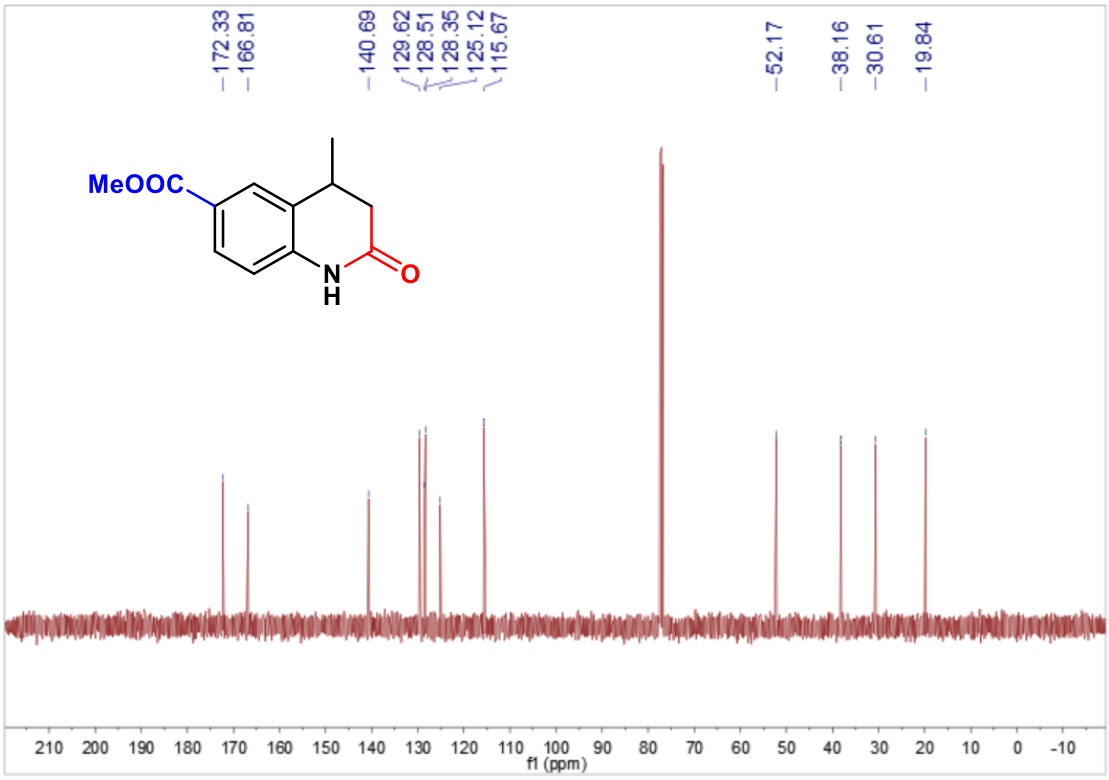
^{13}C NMR of **2h**



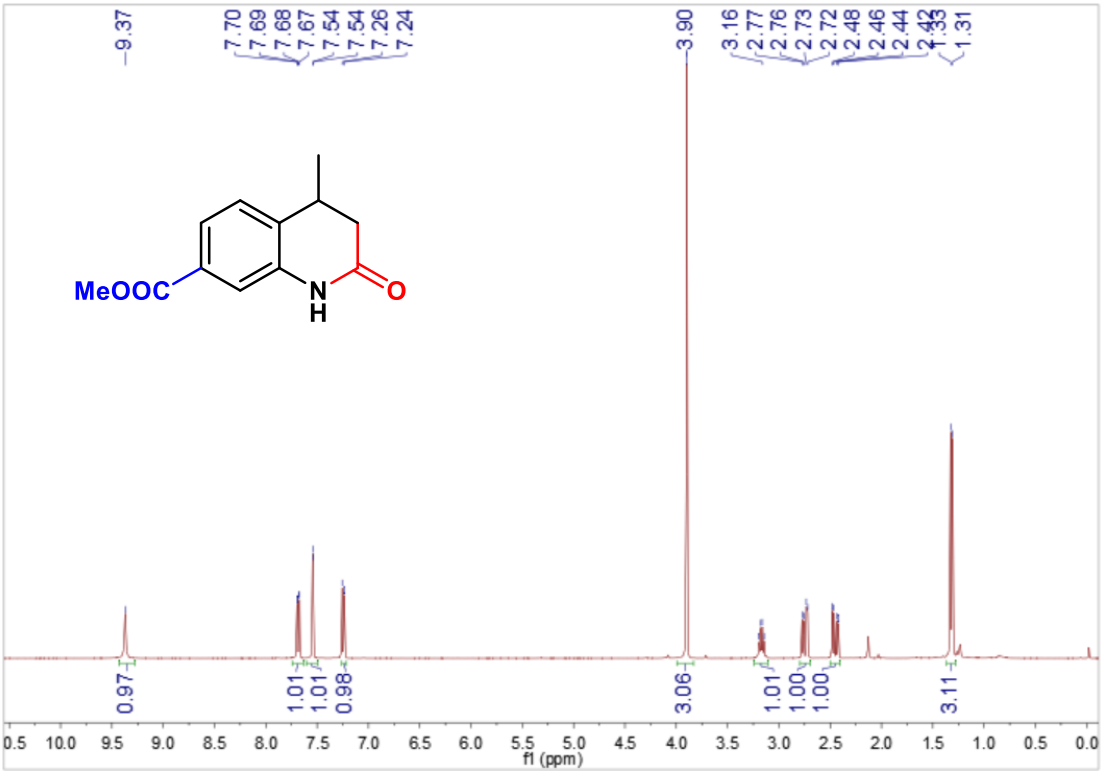
^{19}F NMR of **2h**



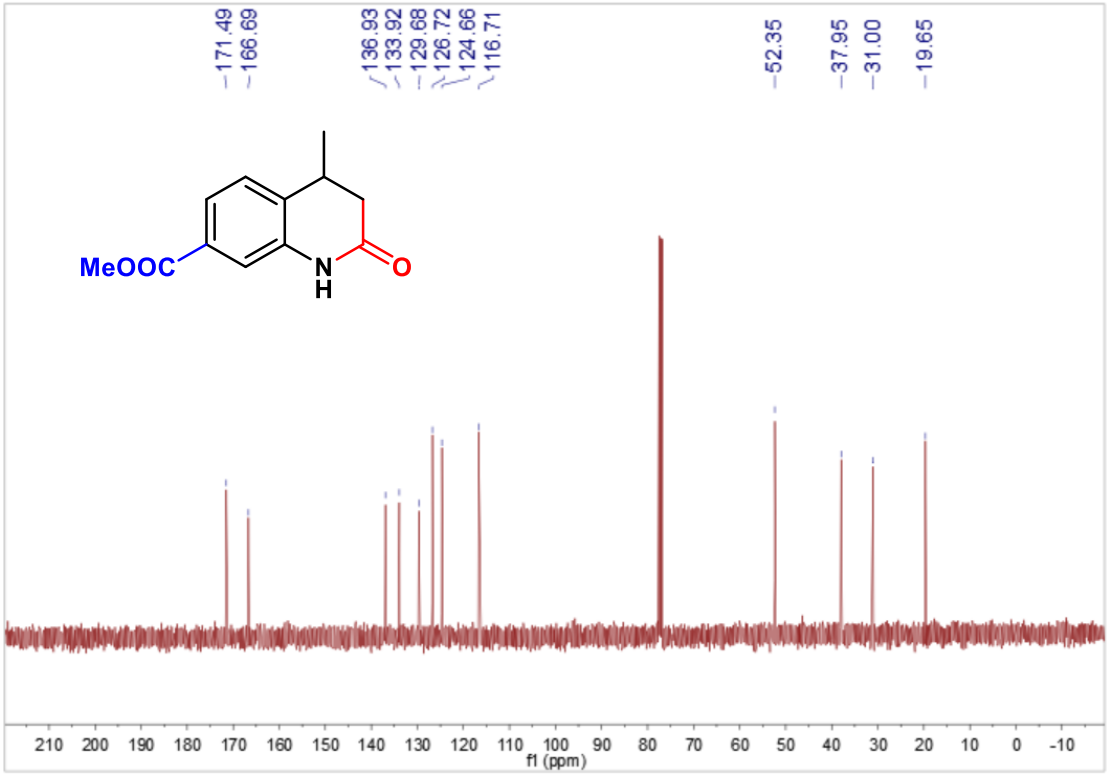
^{1}H NMR of **2i**



^{13}C NMR of **2i**



^{1}H NMR of **2j**



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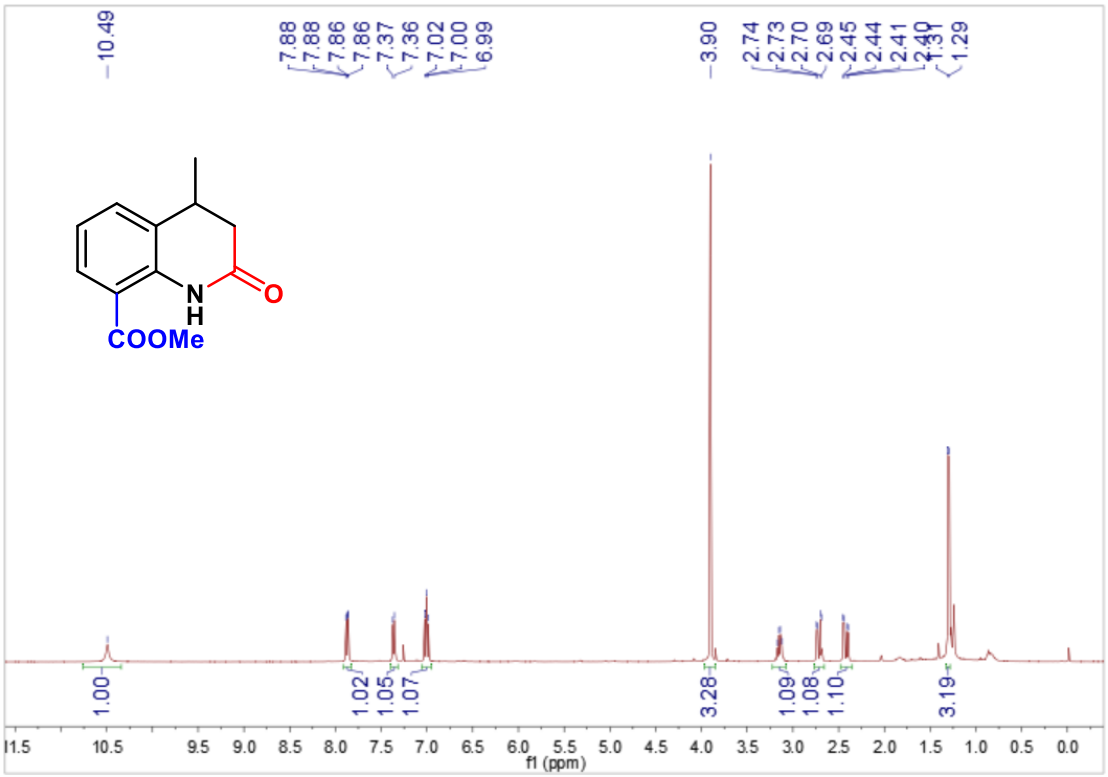
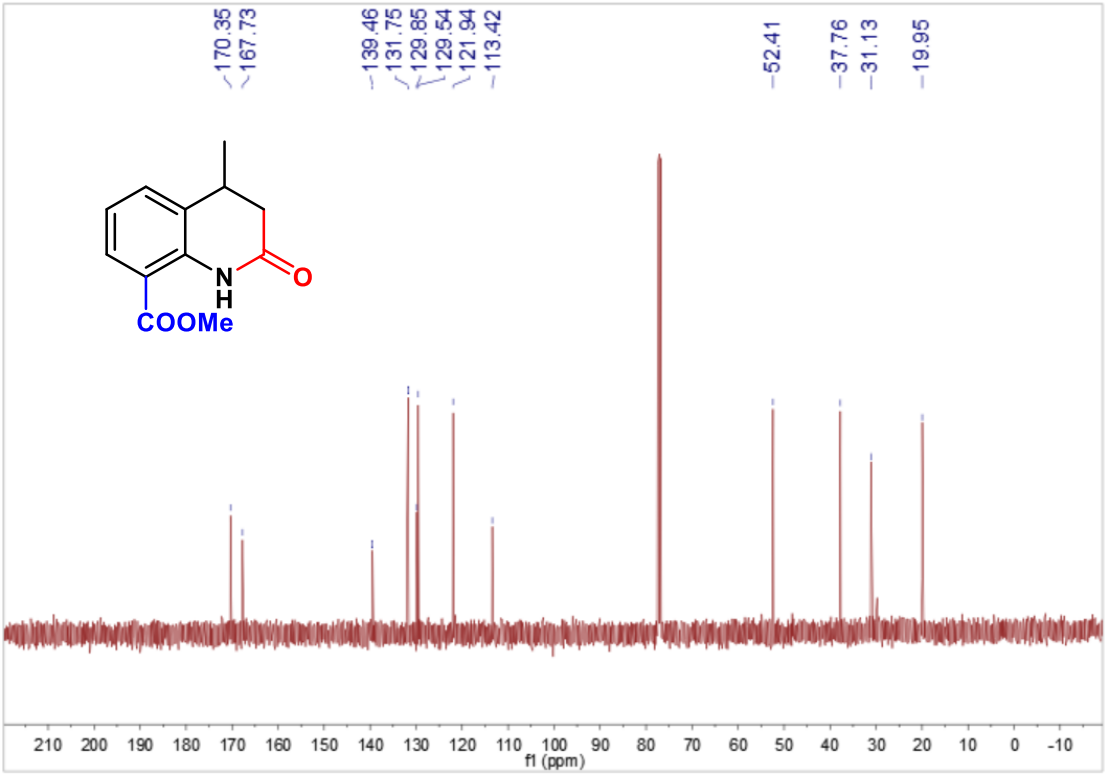


^{1}H NMR of **2k**



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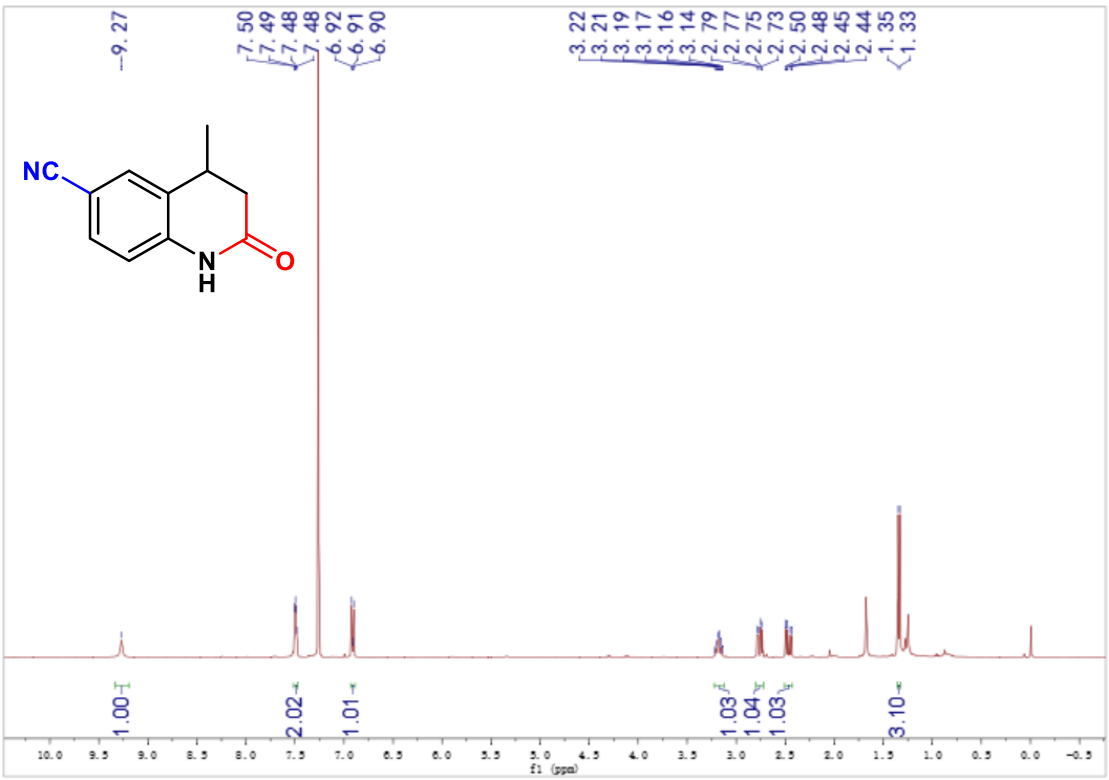
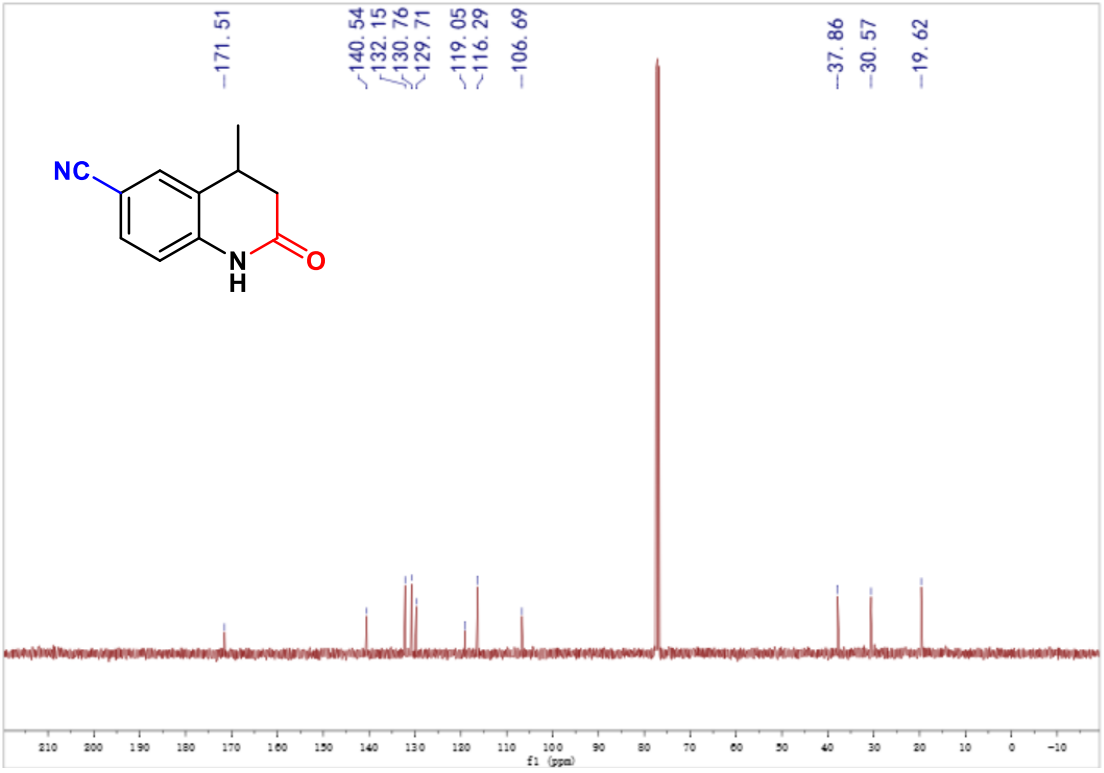


^{1}H NMR of **2l**



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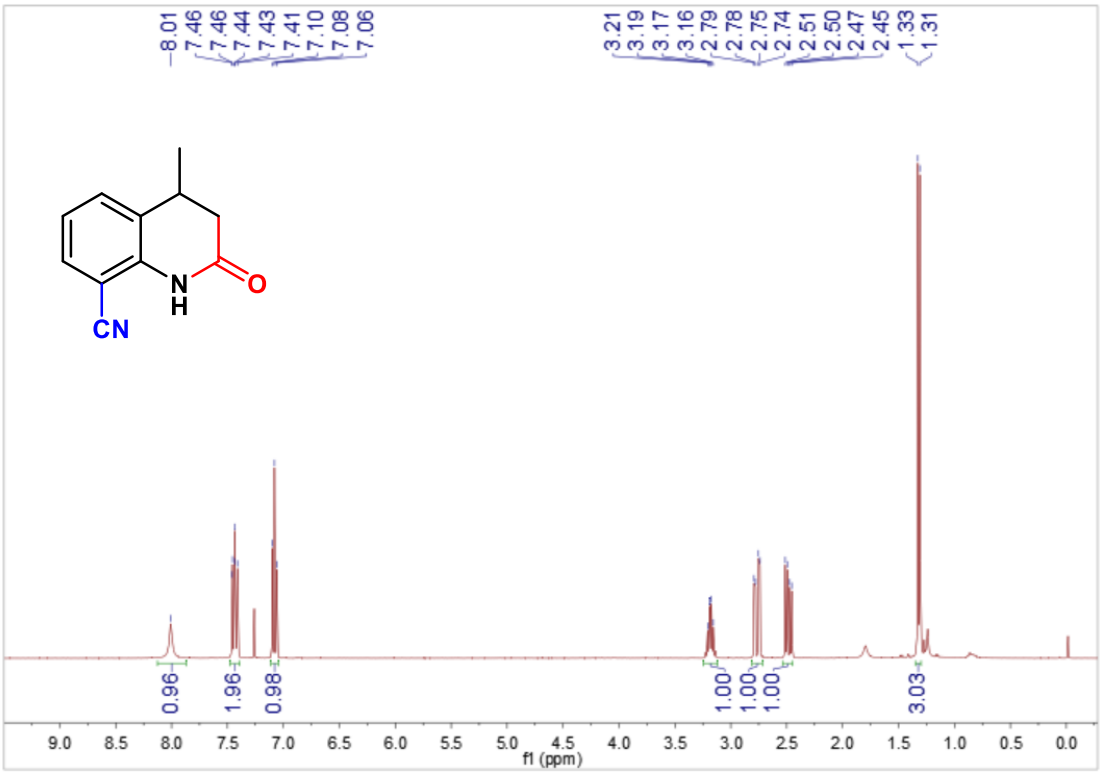
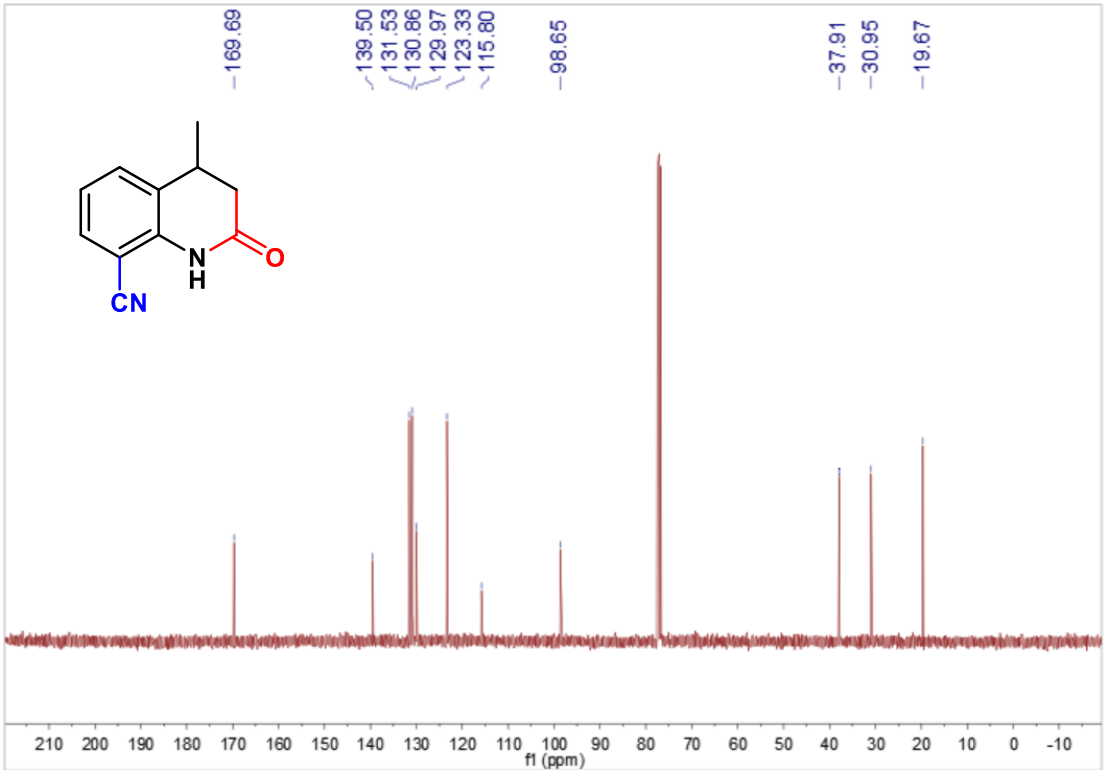
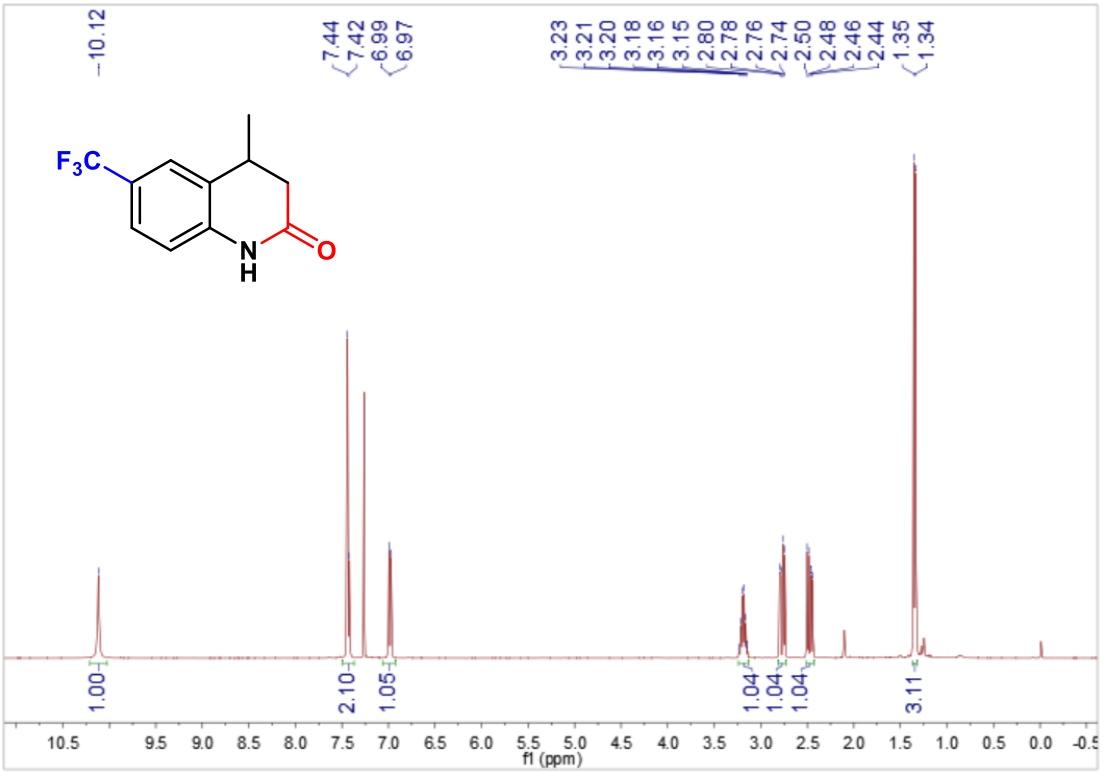


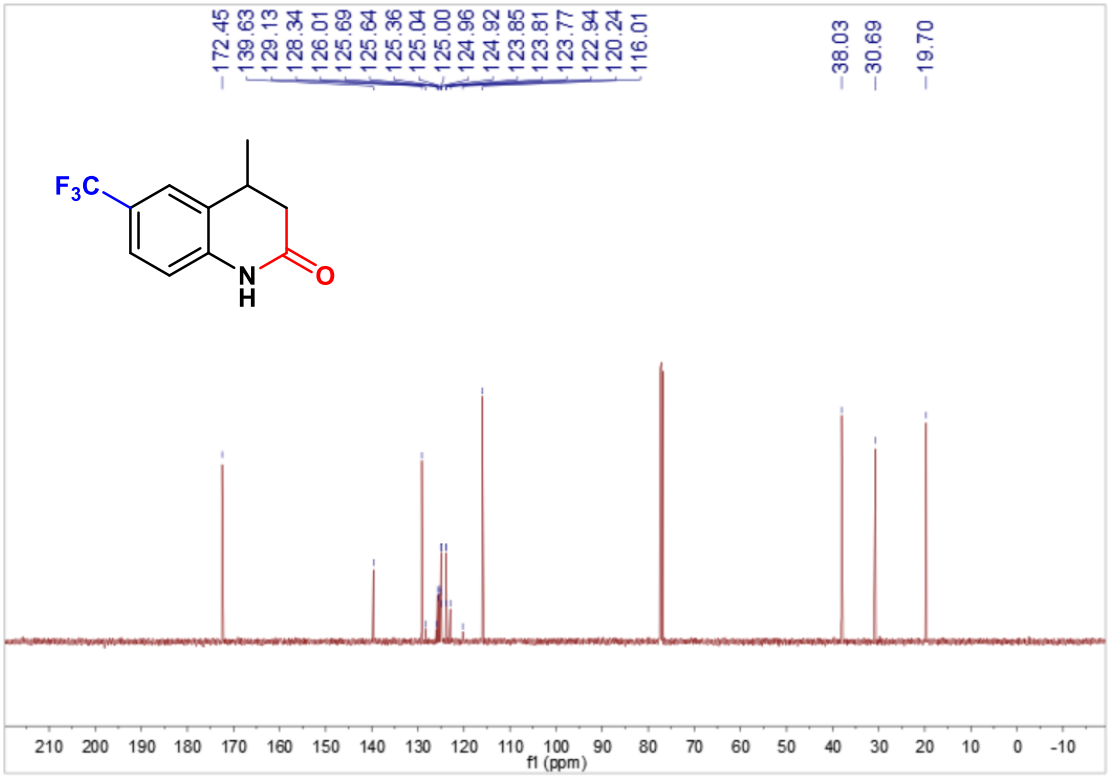
^{1}H NMR of **2m**



^{13}C NMR of **2m**



^{1}H NMR of **2n**



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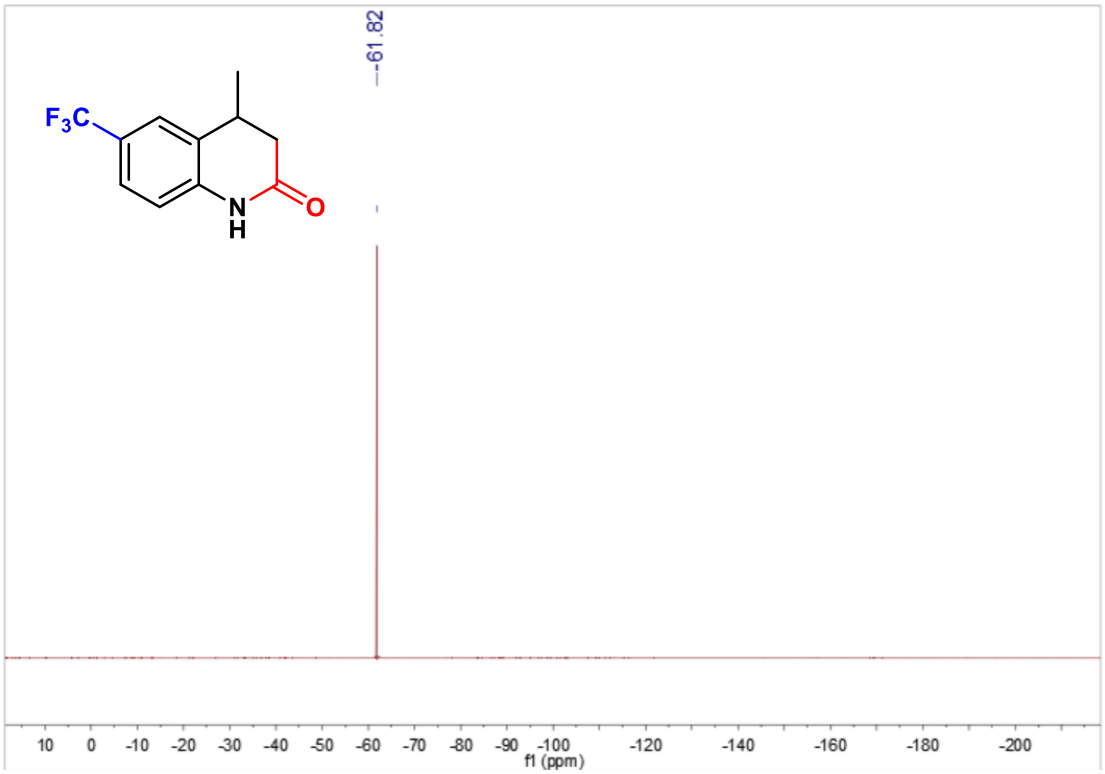

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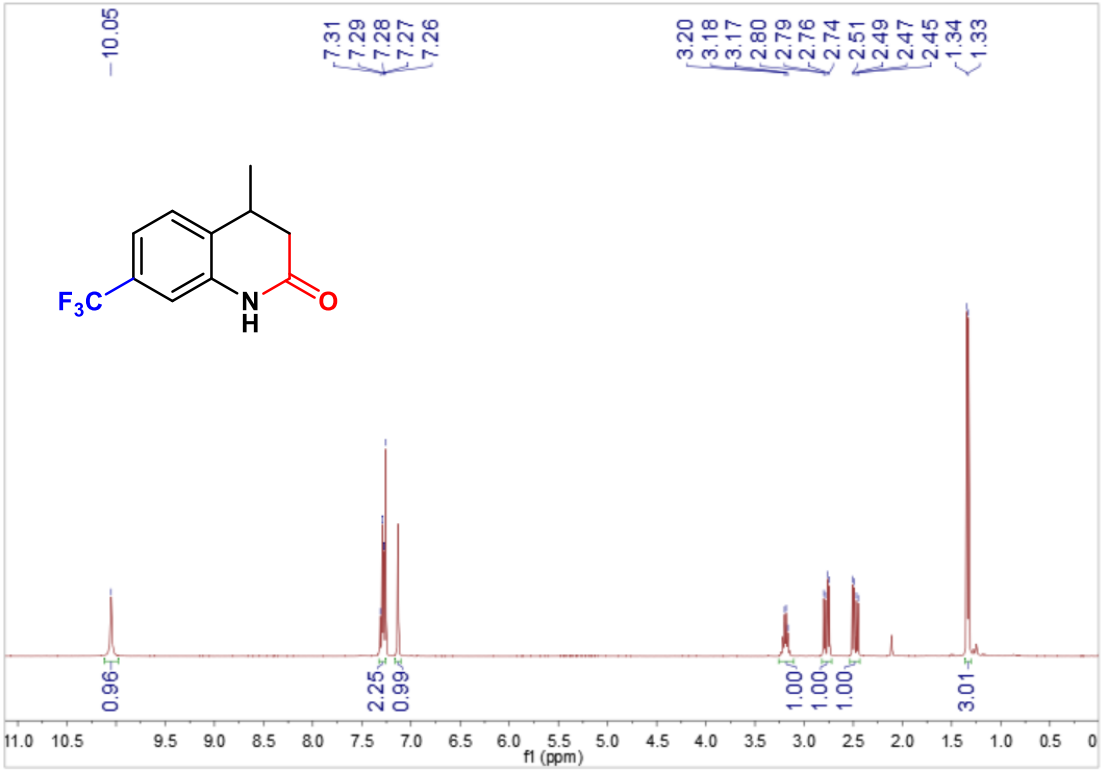
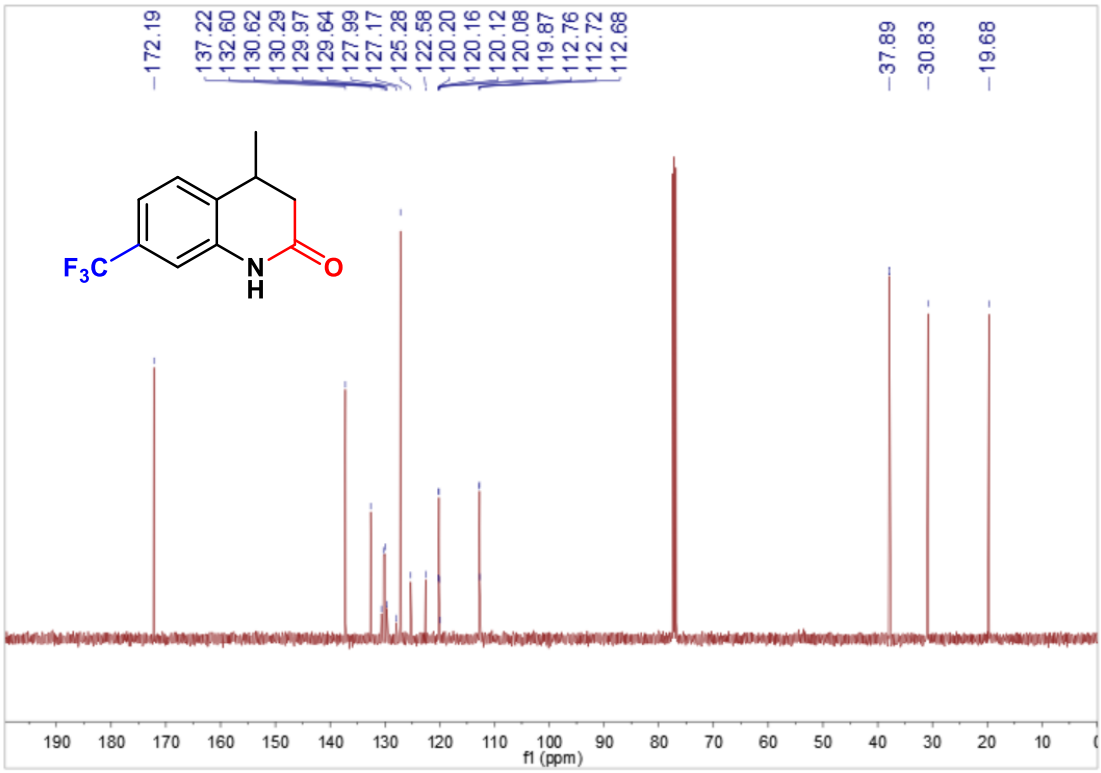


^{1}H NMR of **2o**



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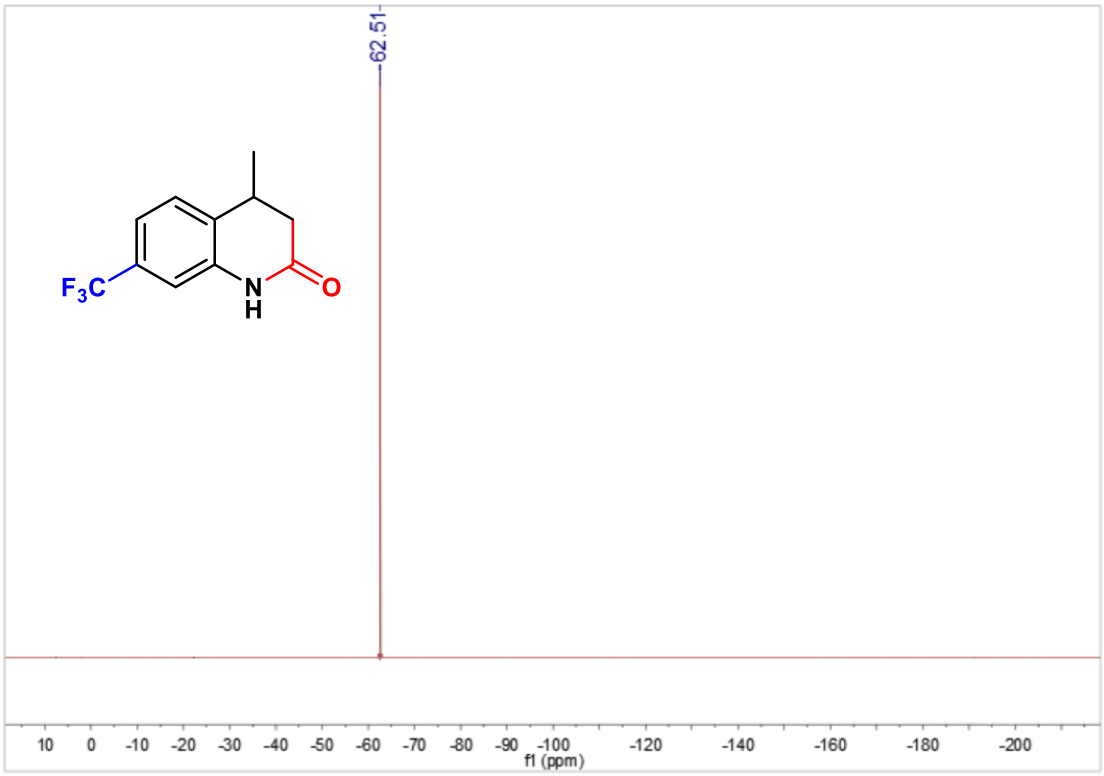
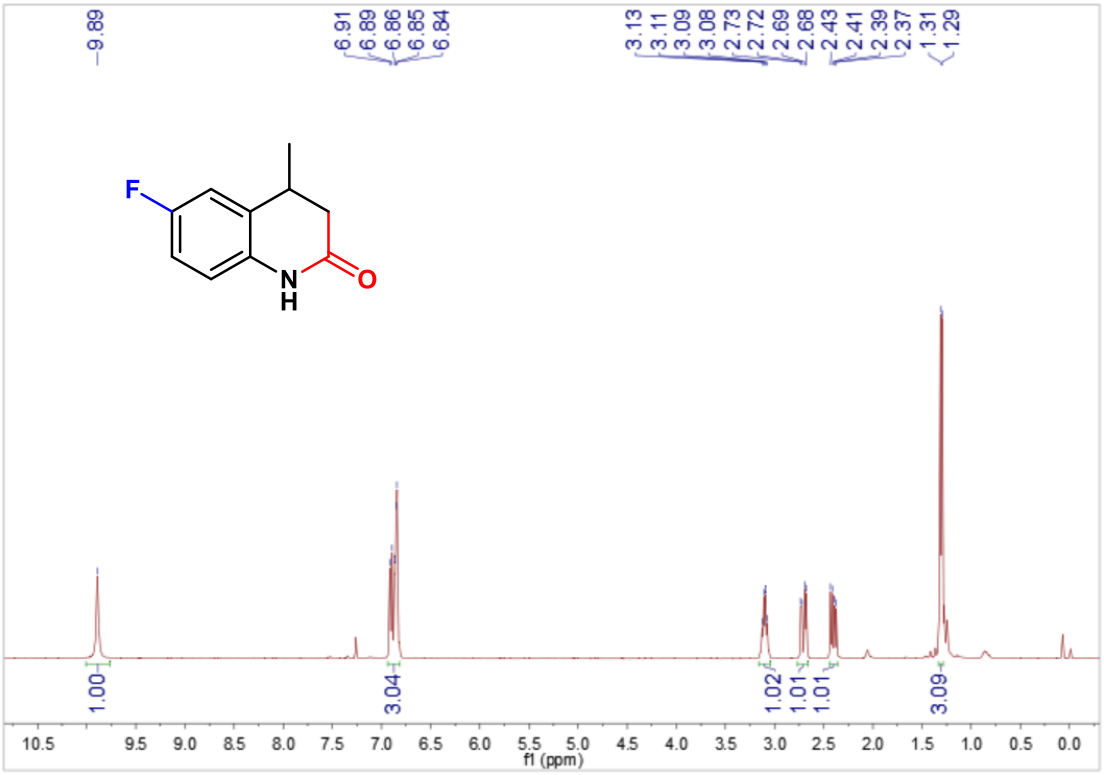
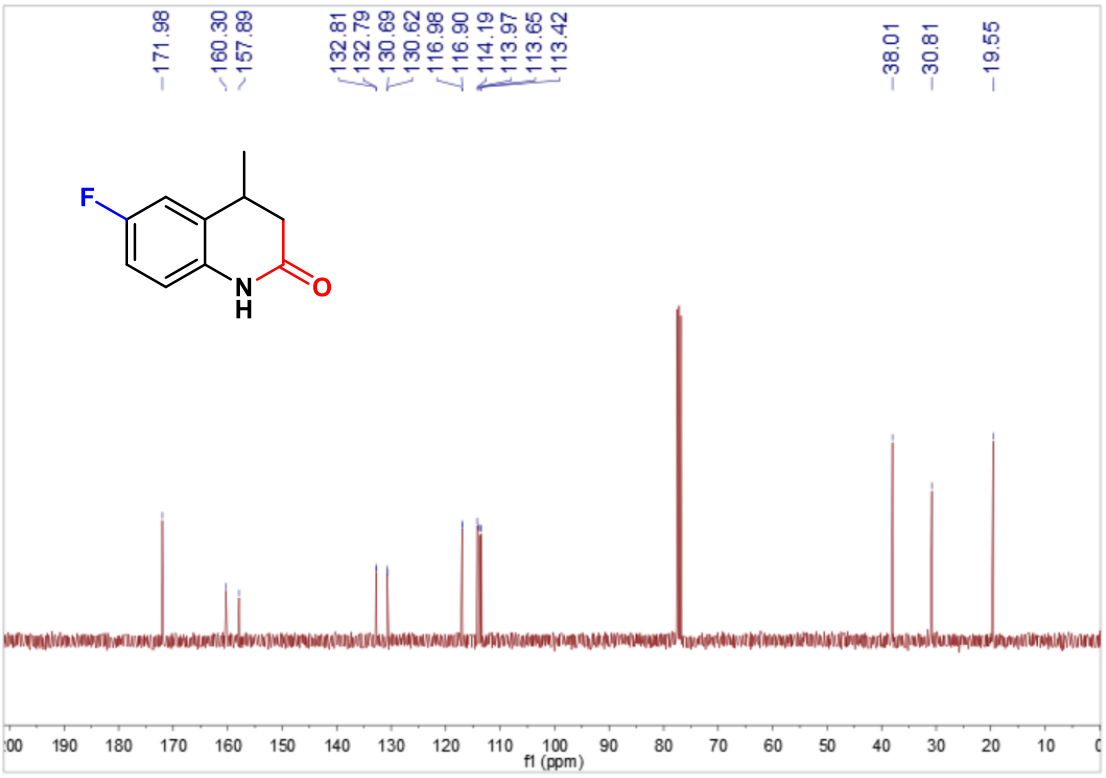


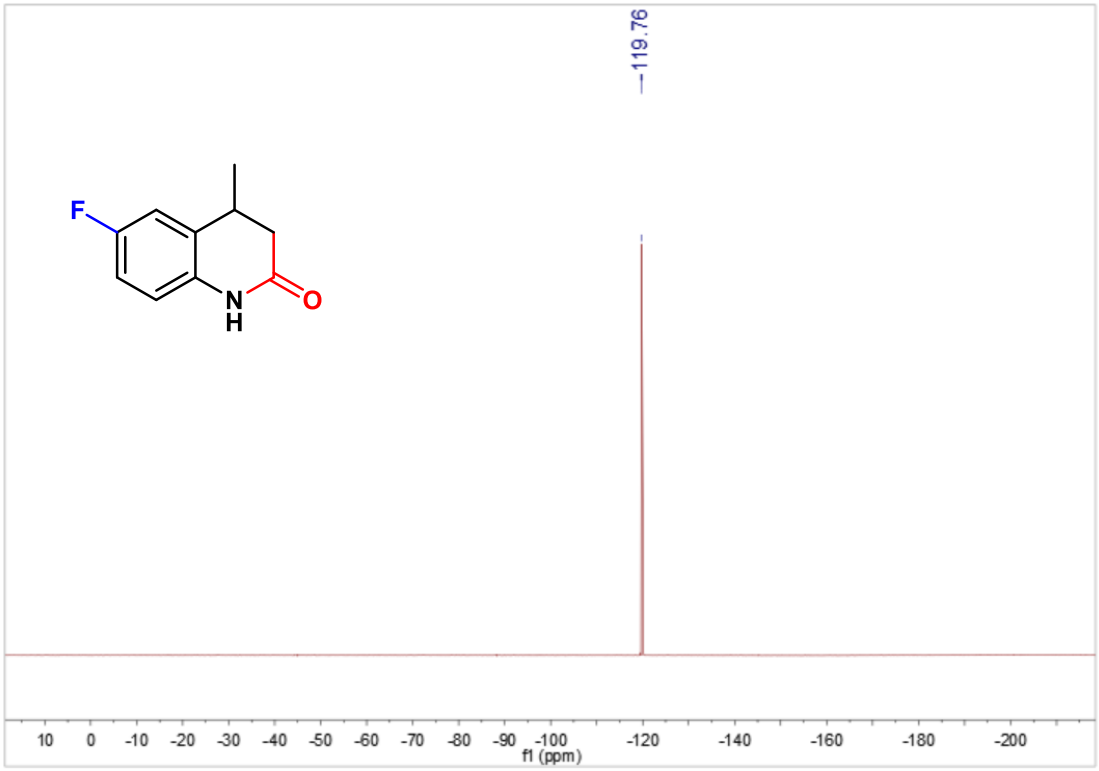
^{19}F NMR of **2o**



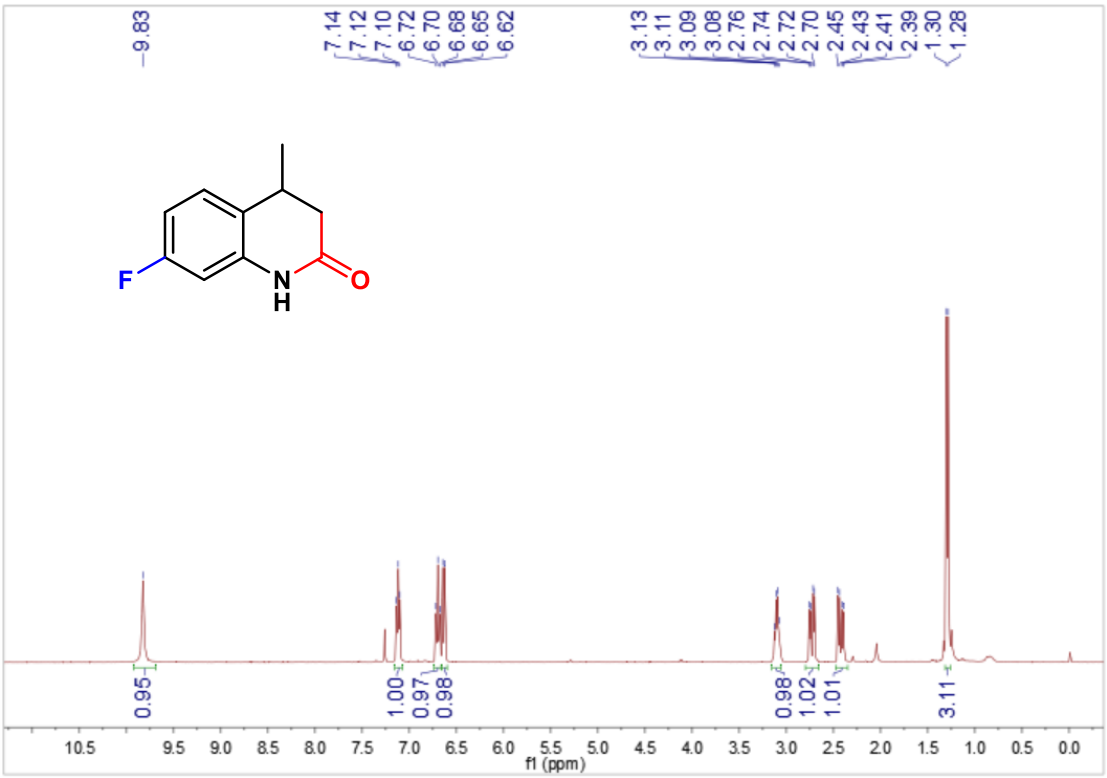
^{1}H NMR of **2p**



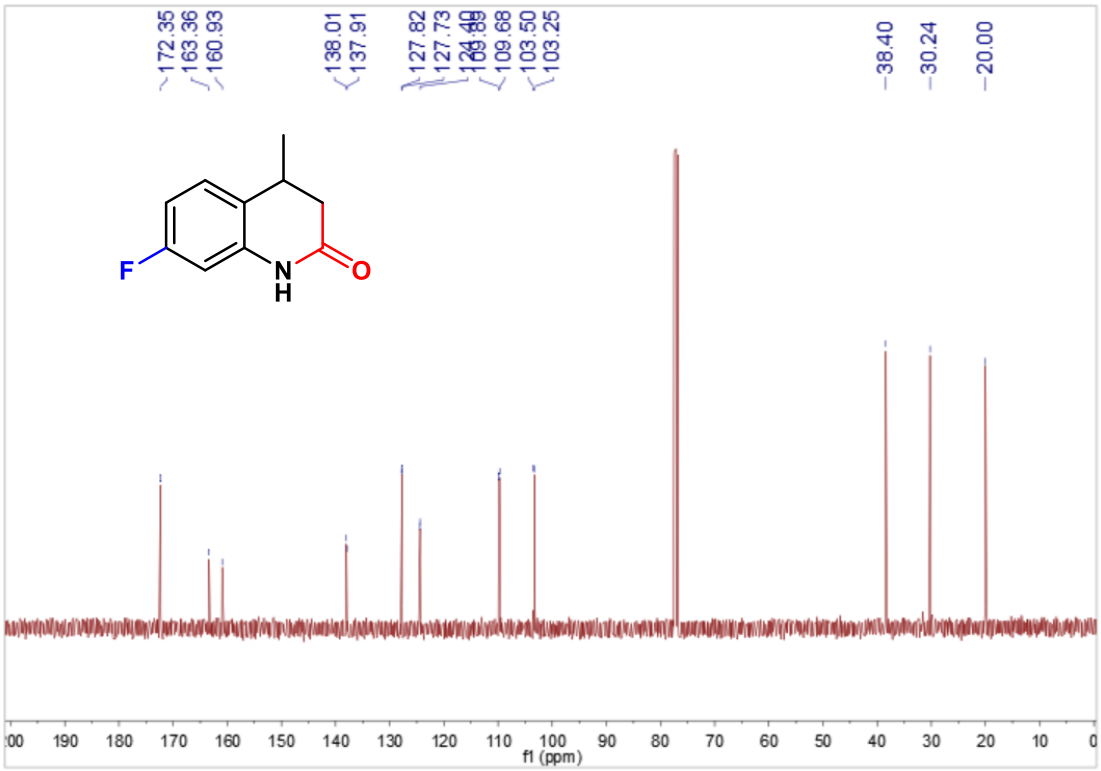
^{13}C NMR of **2p**



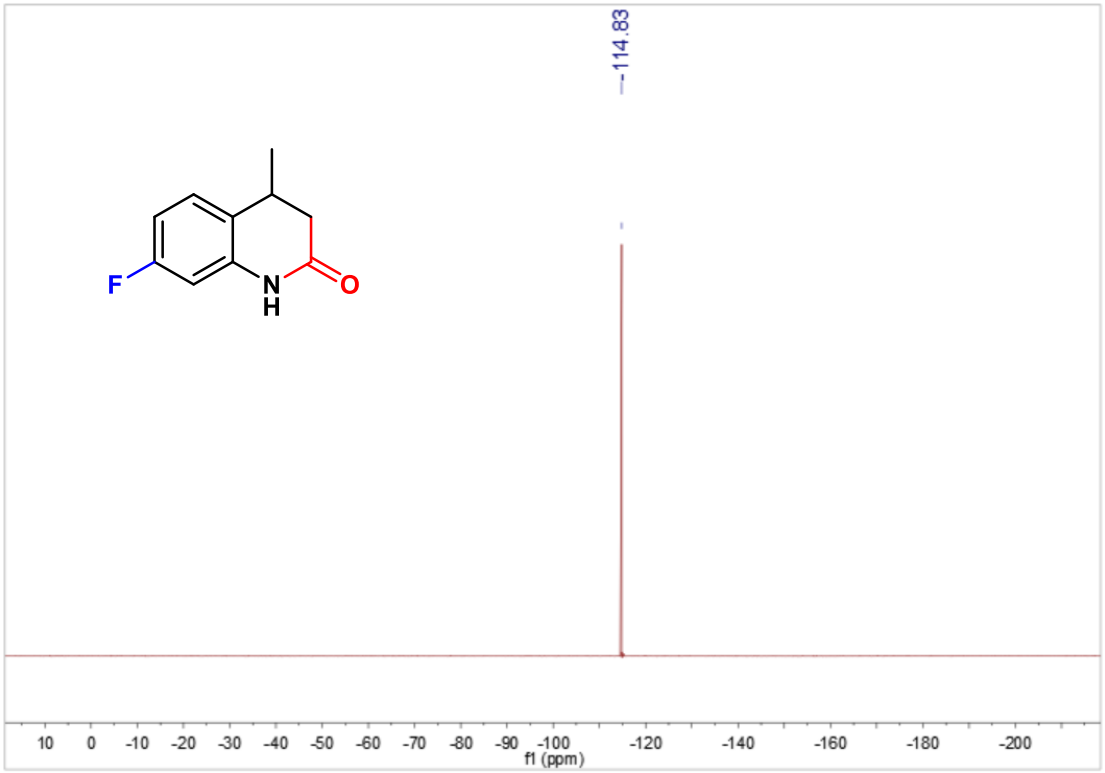
^{19}F NMR of **2p**



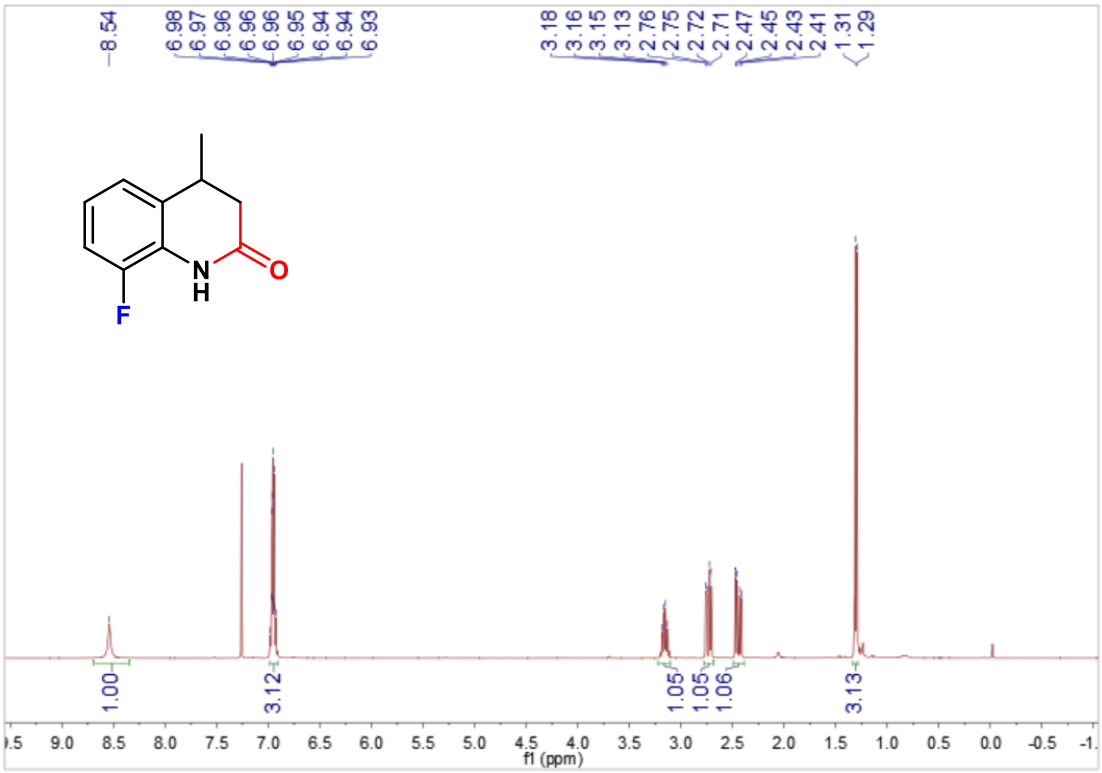
^{1}H NMR of **2q**



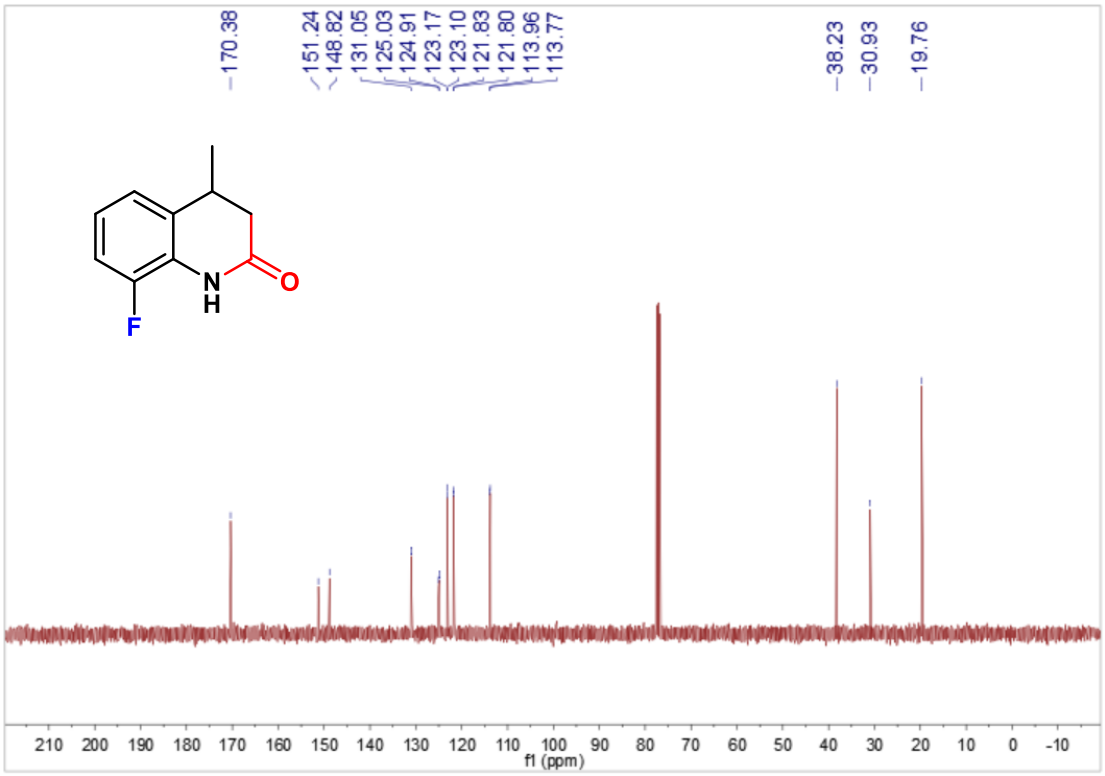
^{13}C NMR of **2q**



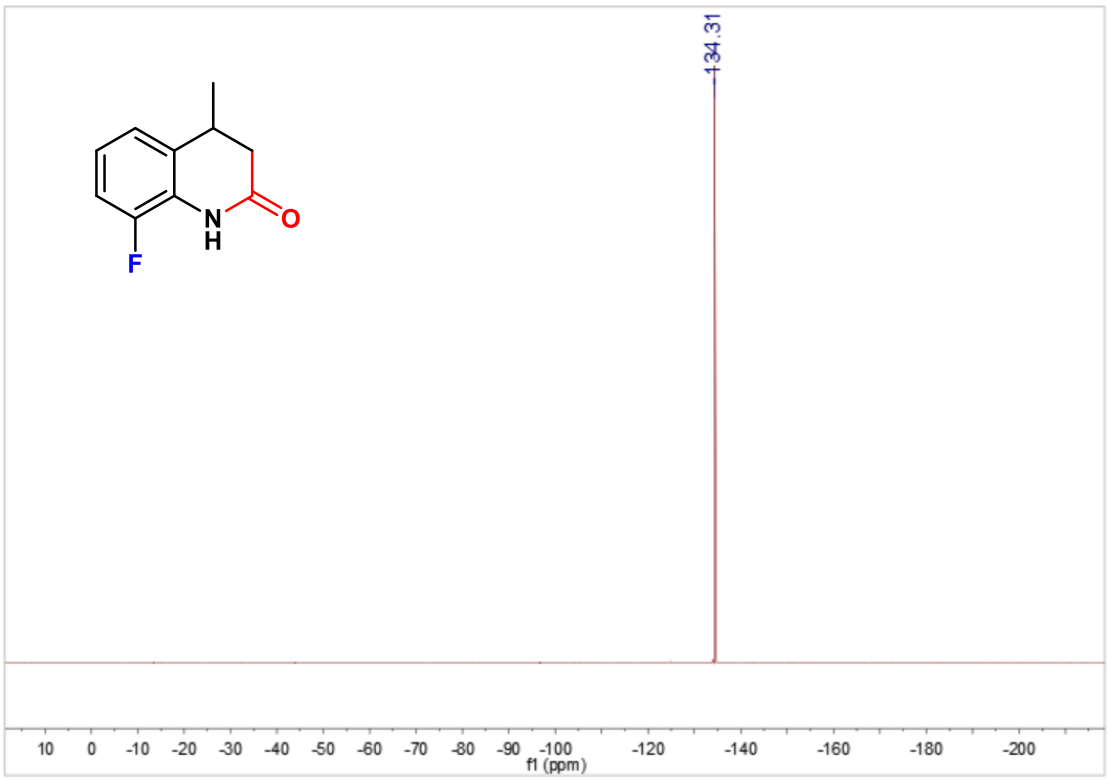
^{19}F NMR of **2q**



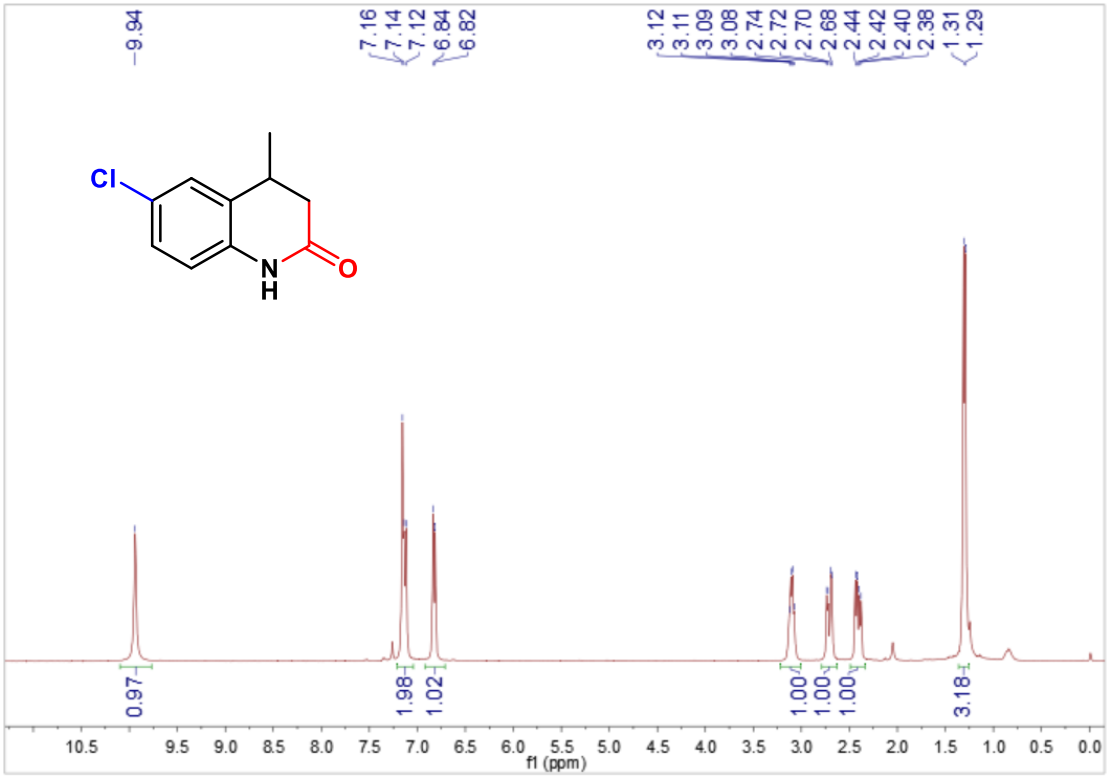
^{1}H NMR of **2r**



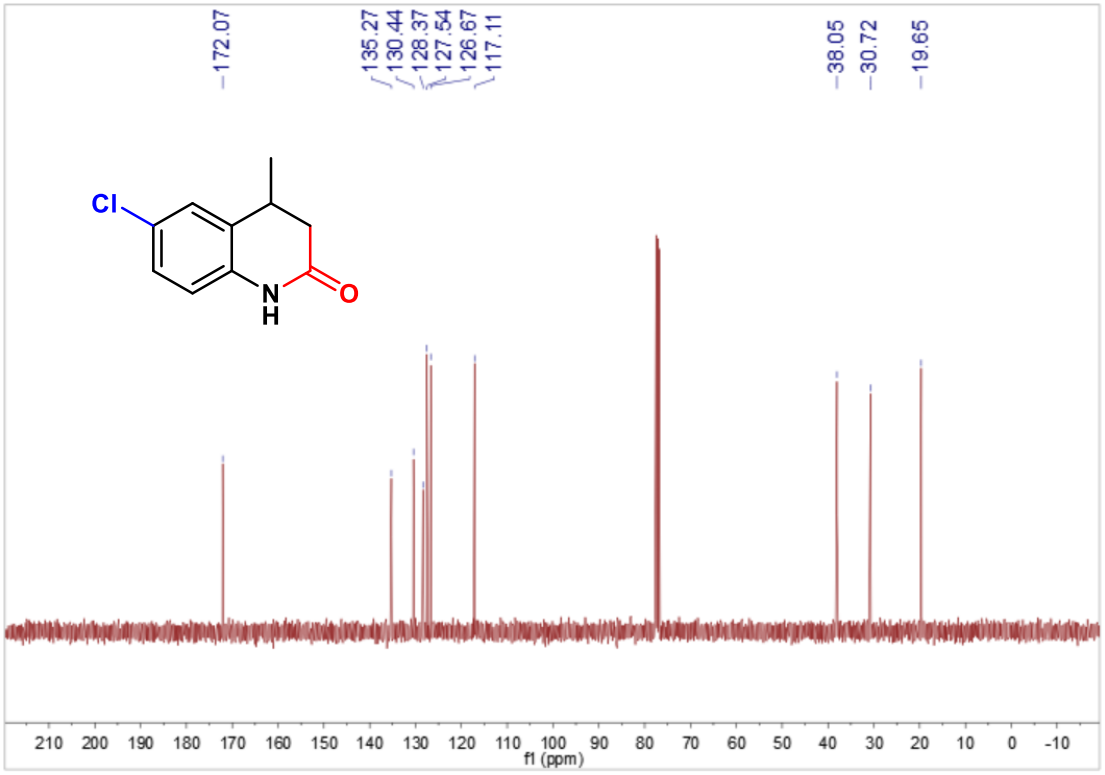
^{13}C NMR of **2r**



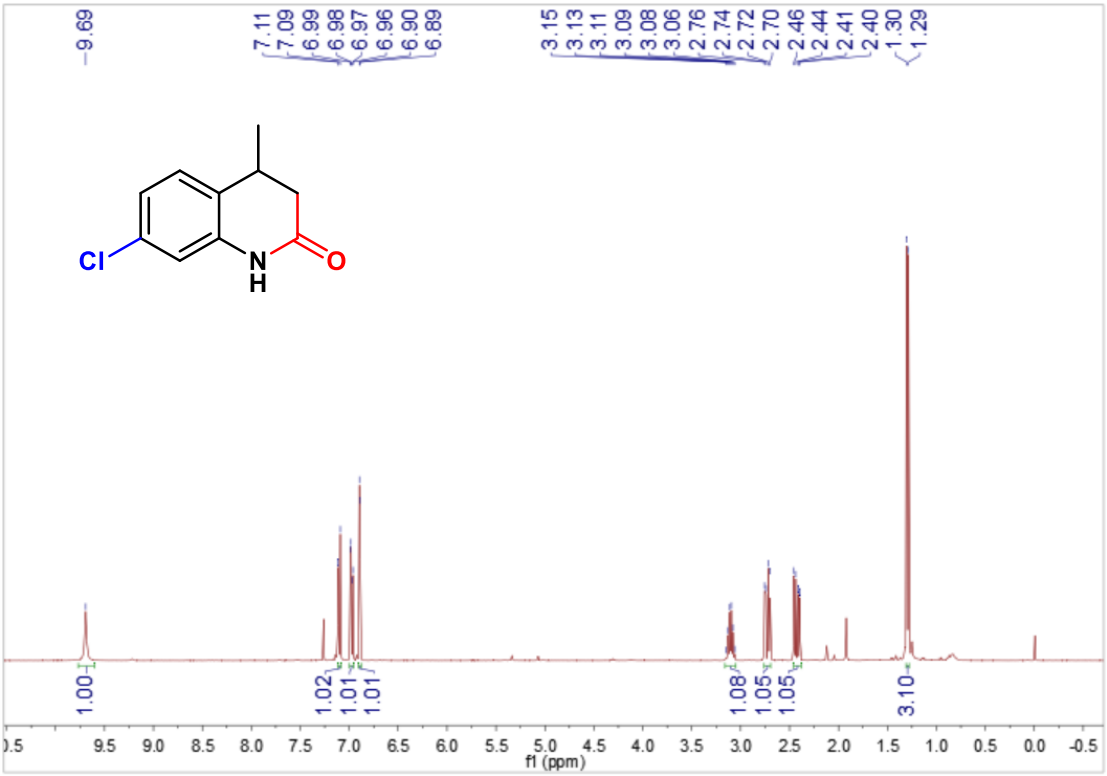
^{19}F NMR of **2r**



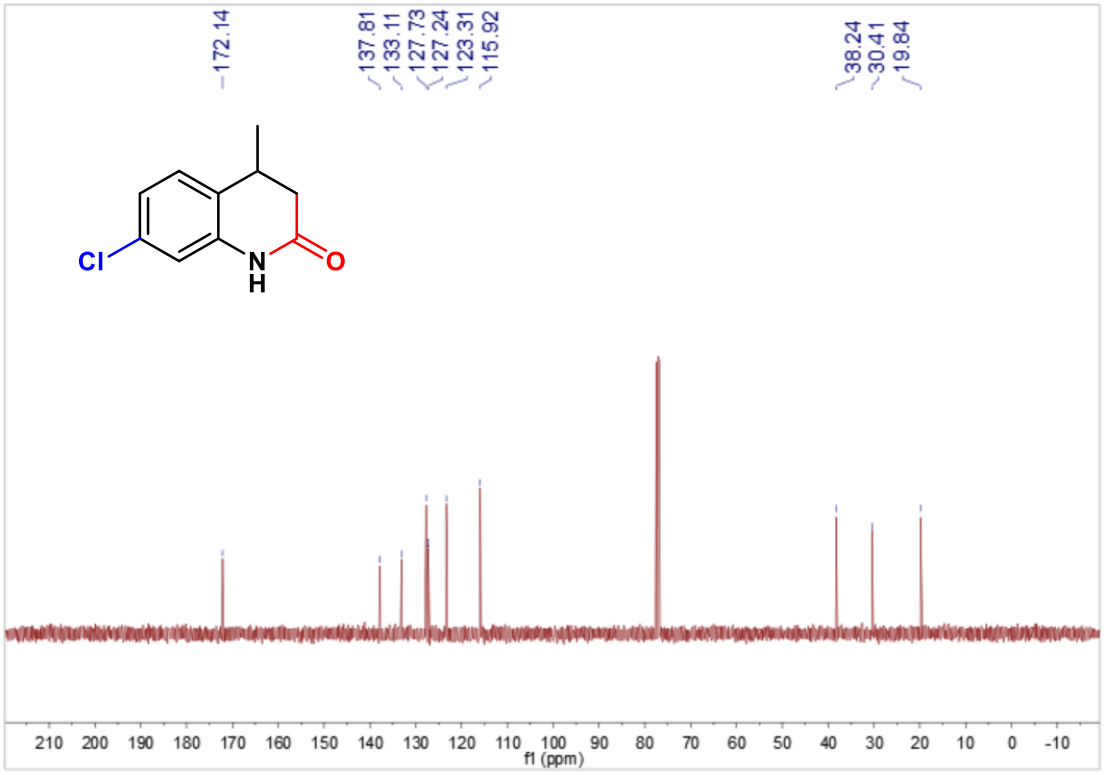
^{1}H NMR of **2s**



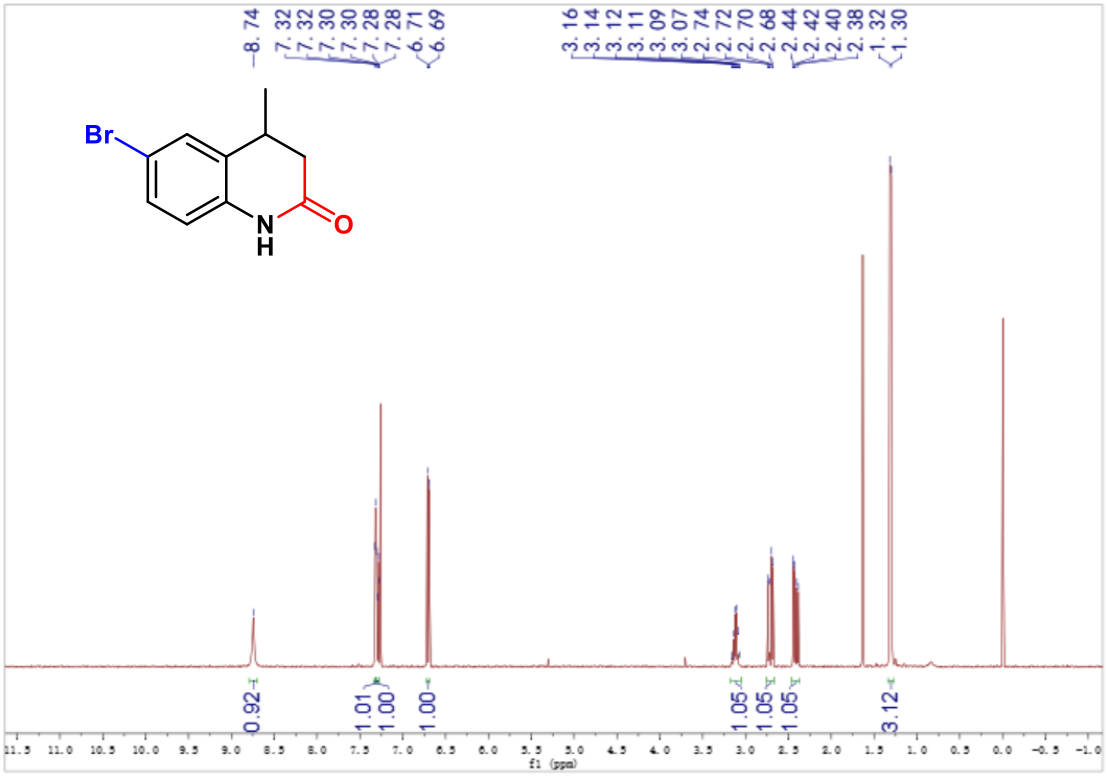
^{13}C NMR of **2s**



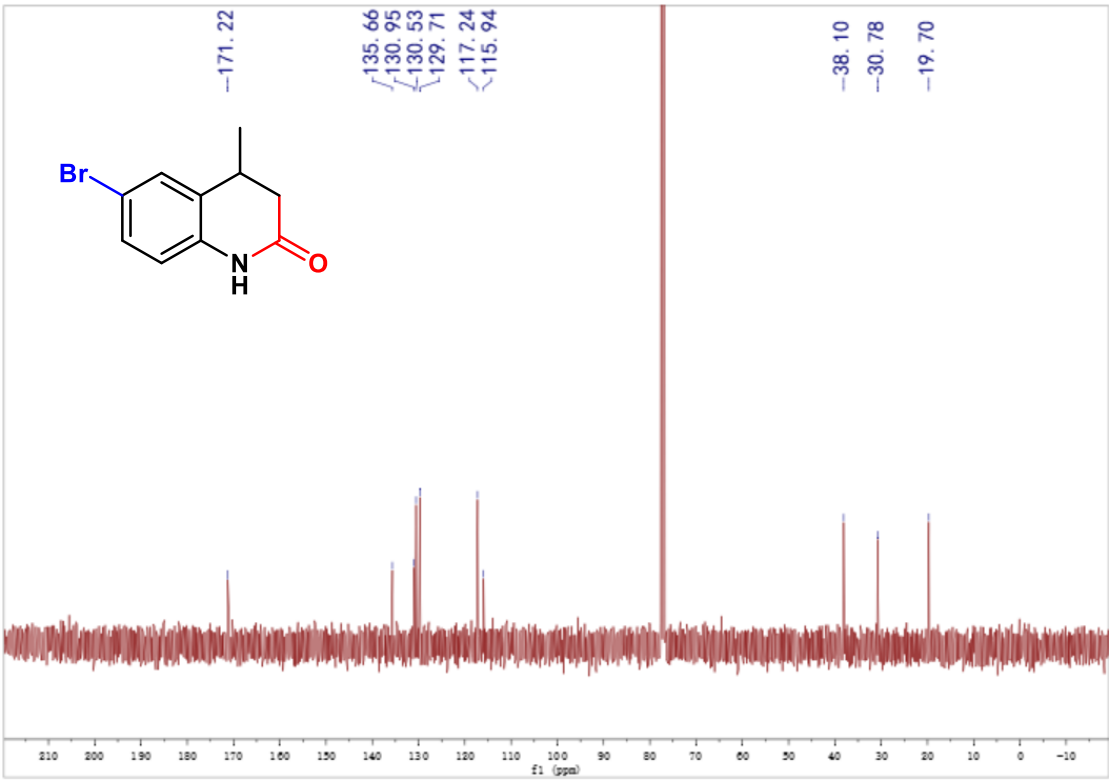
1H NMR of **2t**



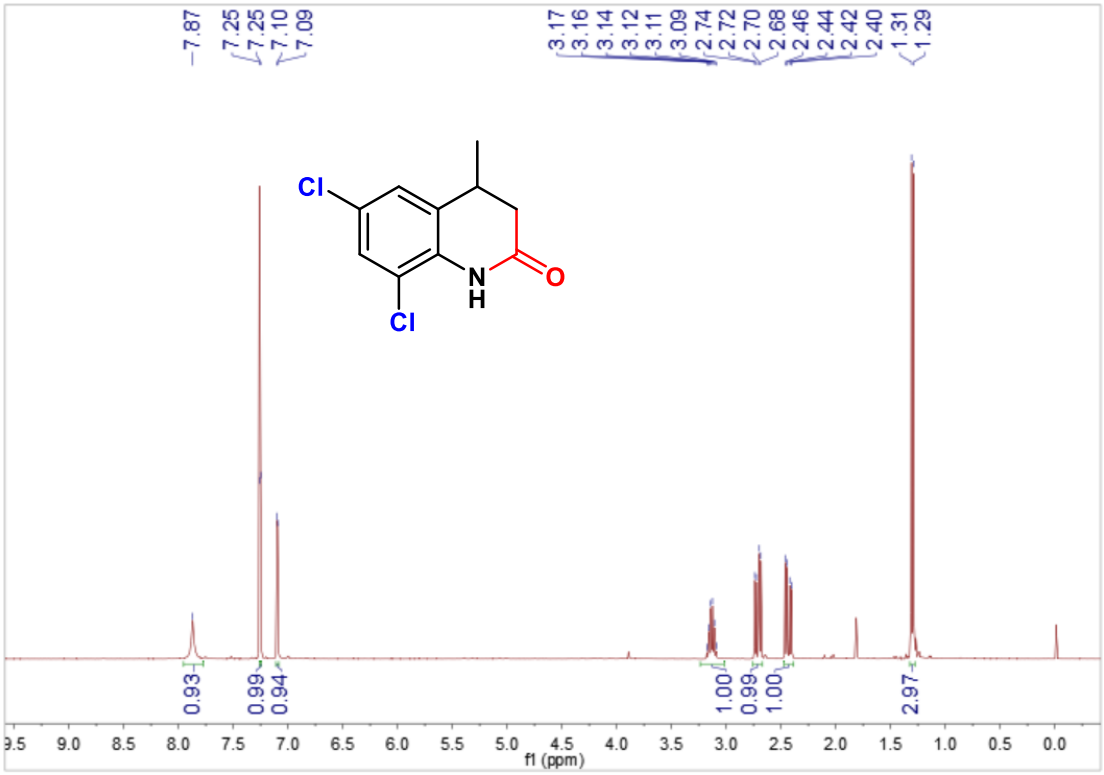
^{13}C NMR of **2t**



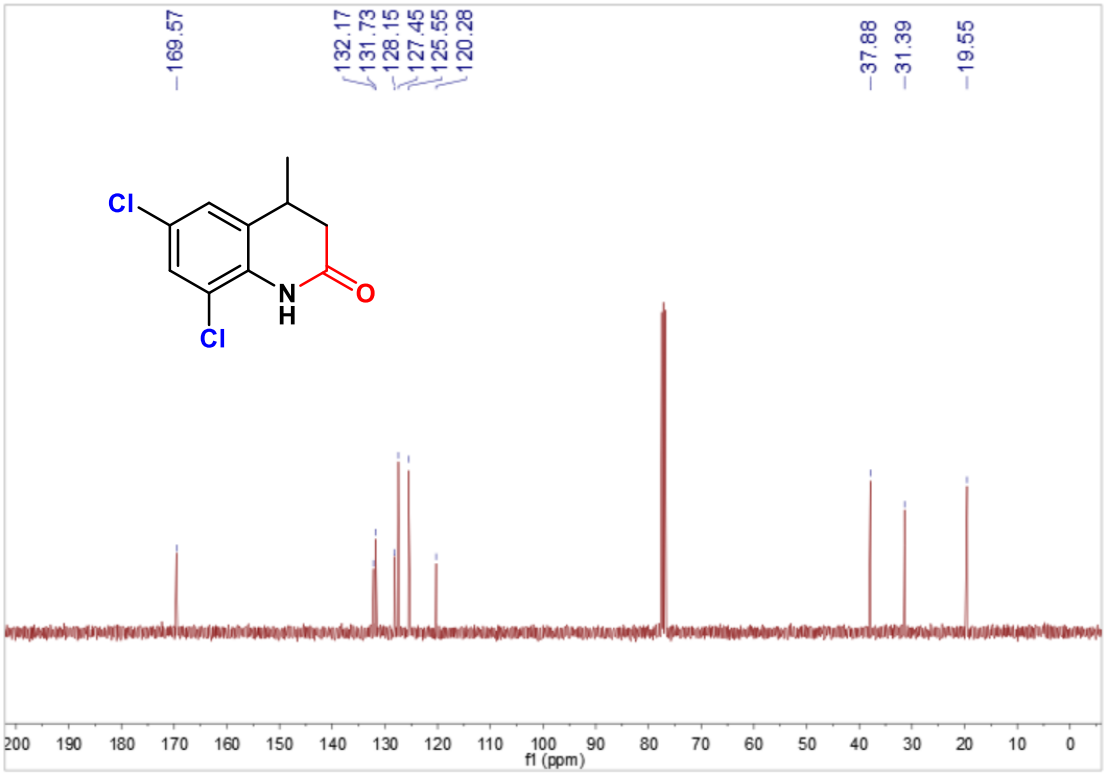
^{1}H NMR of **2u**



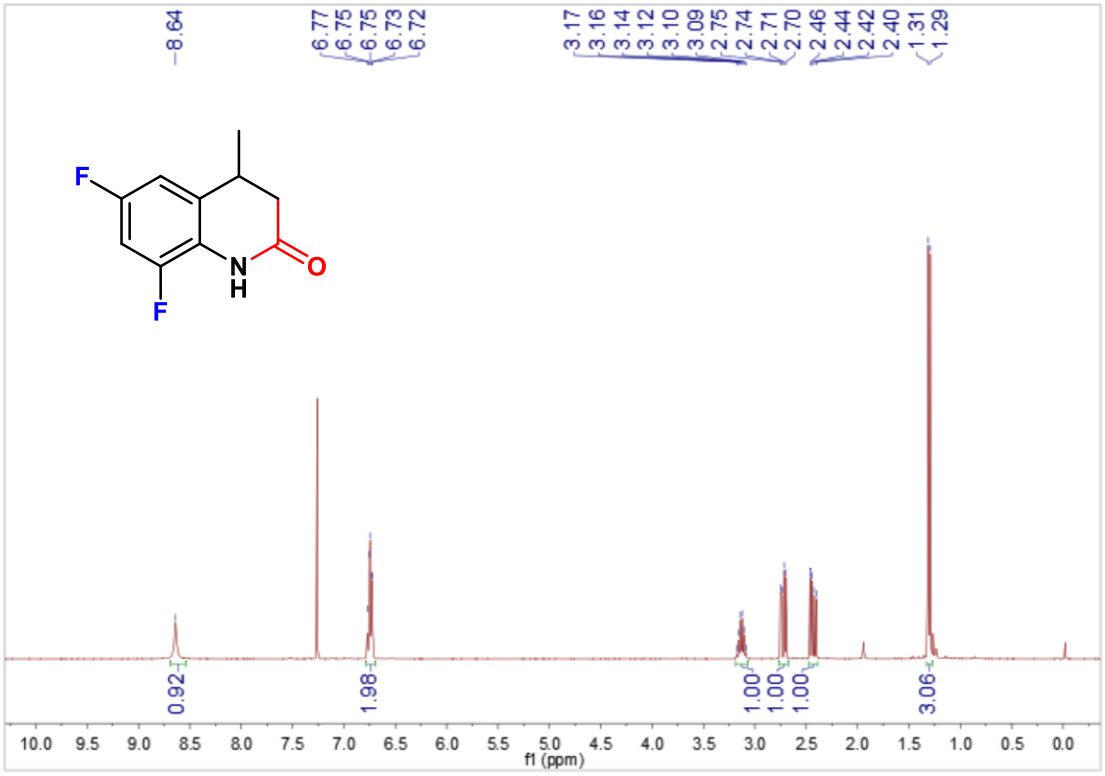
^{13}C NMR of **2u**



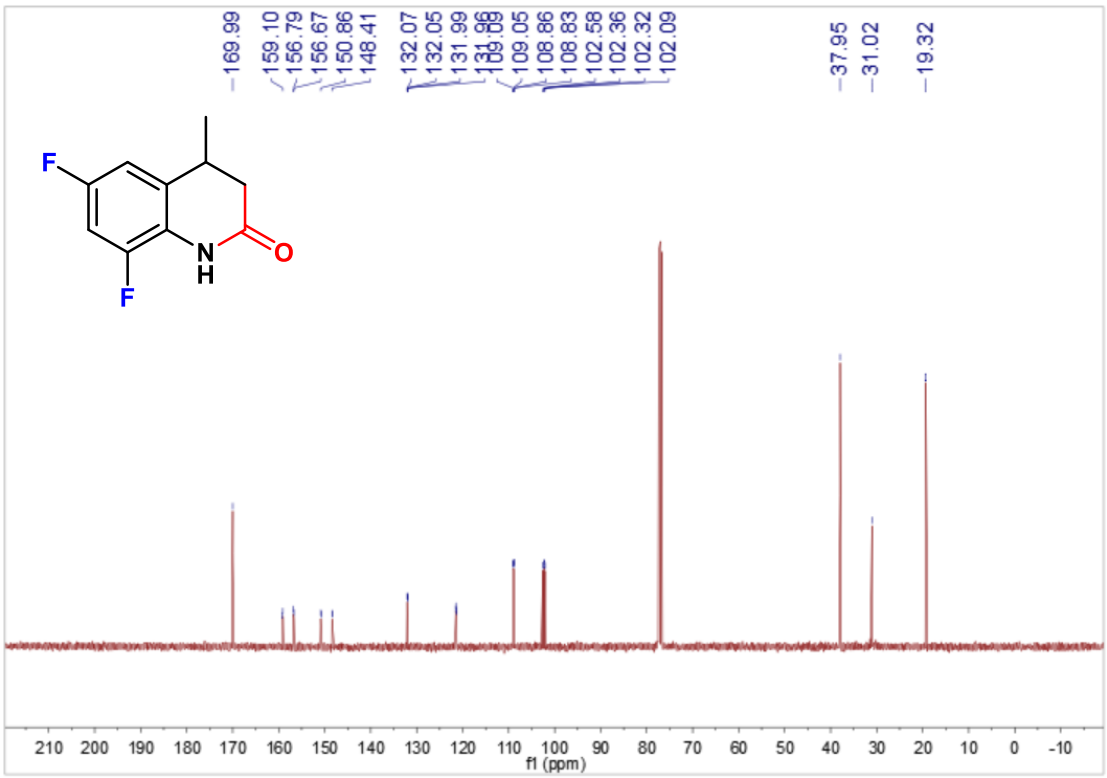
^{1}H NMR of **2v**



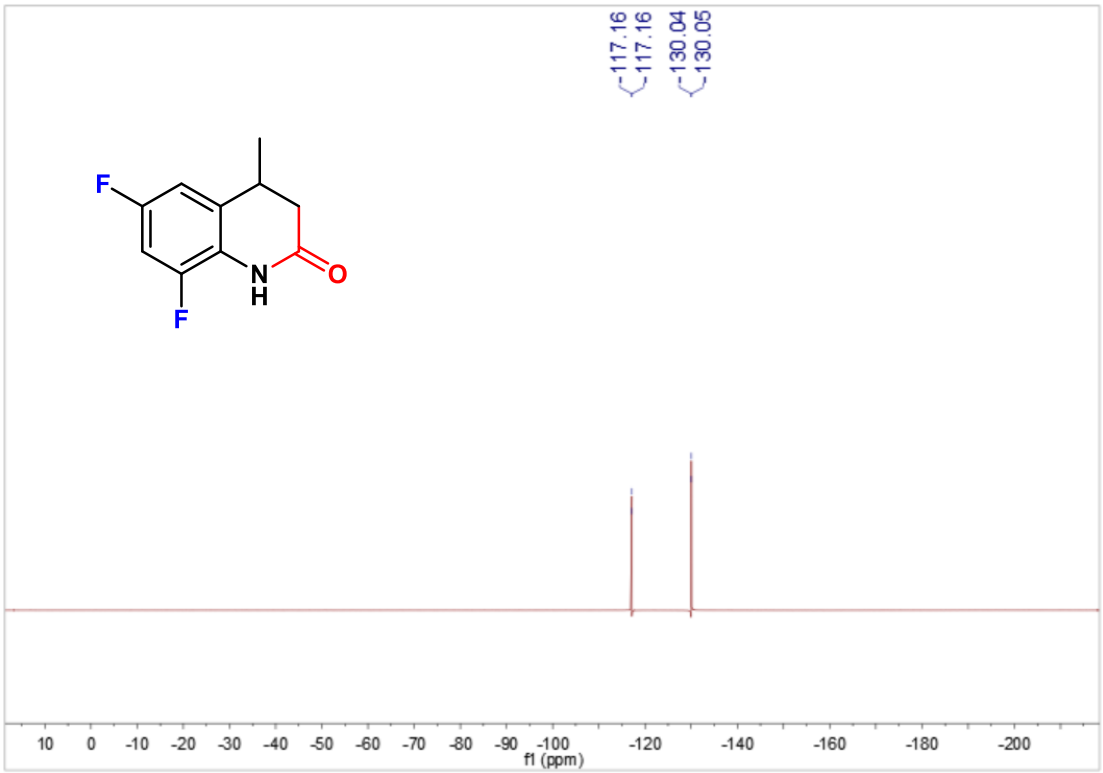
^{13}C NMR of **2v**



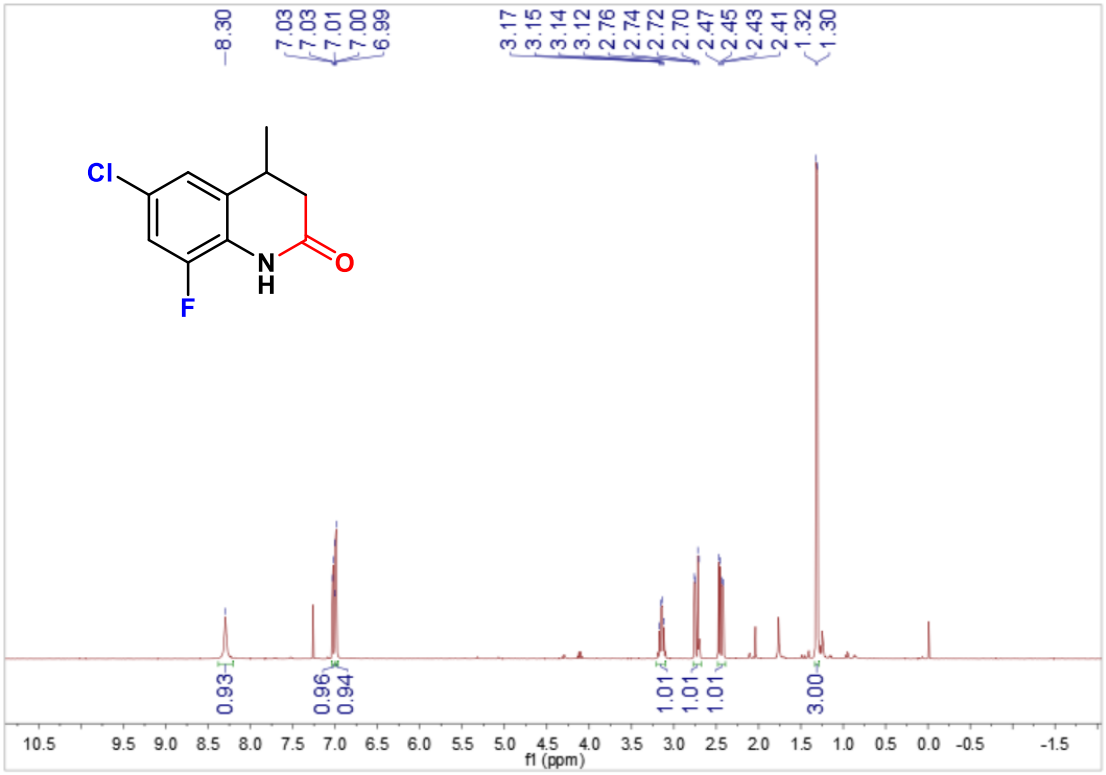
^{1}H NMR of **2w**



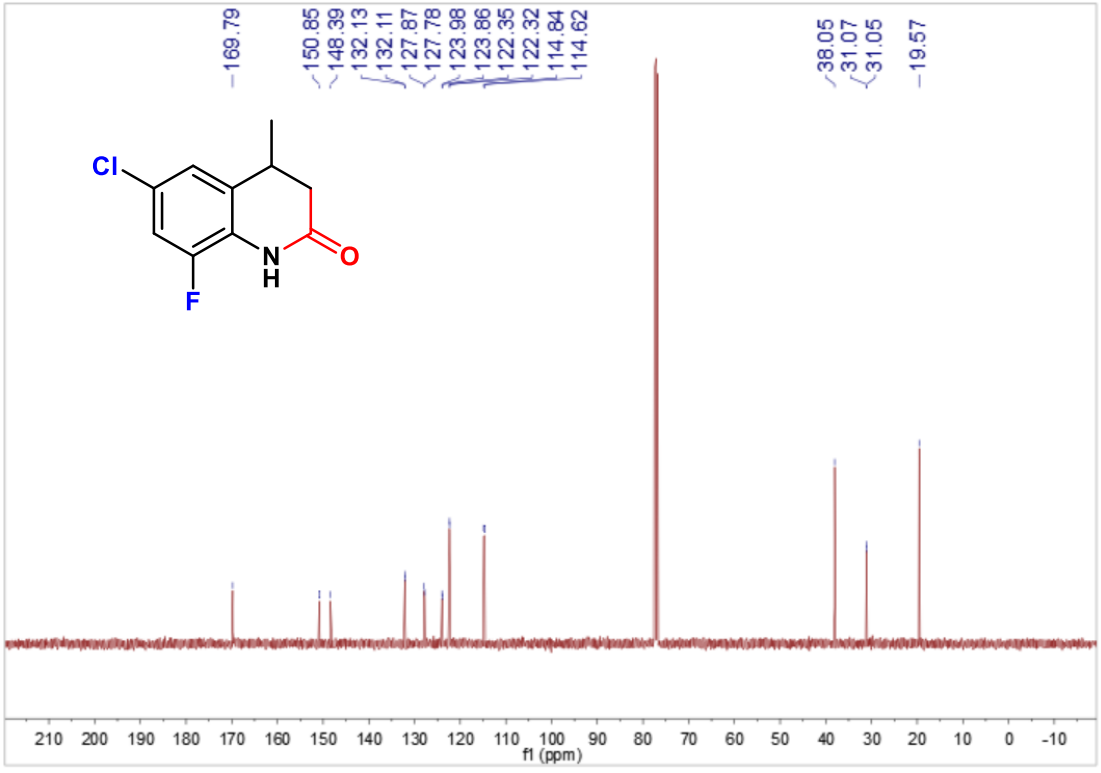
^{13}C NMR of **2w**



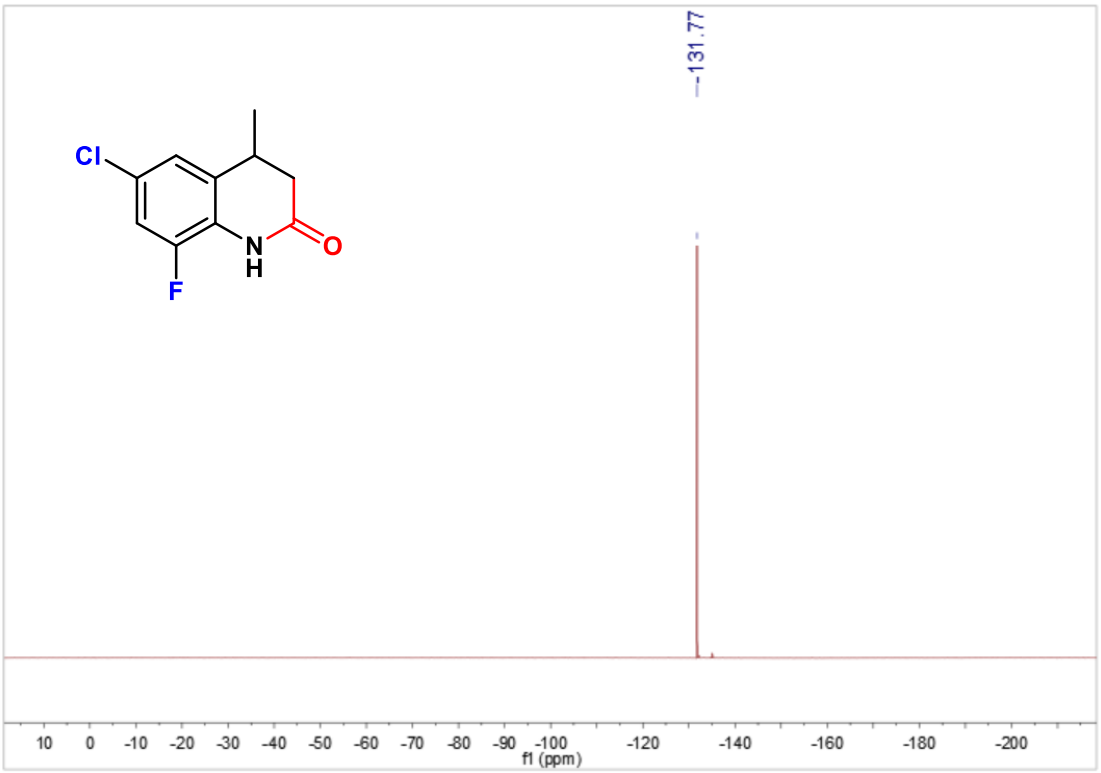
^{19}F NMR of **2w**



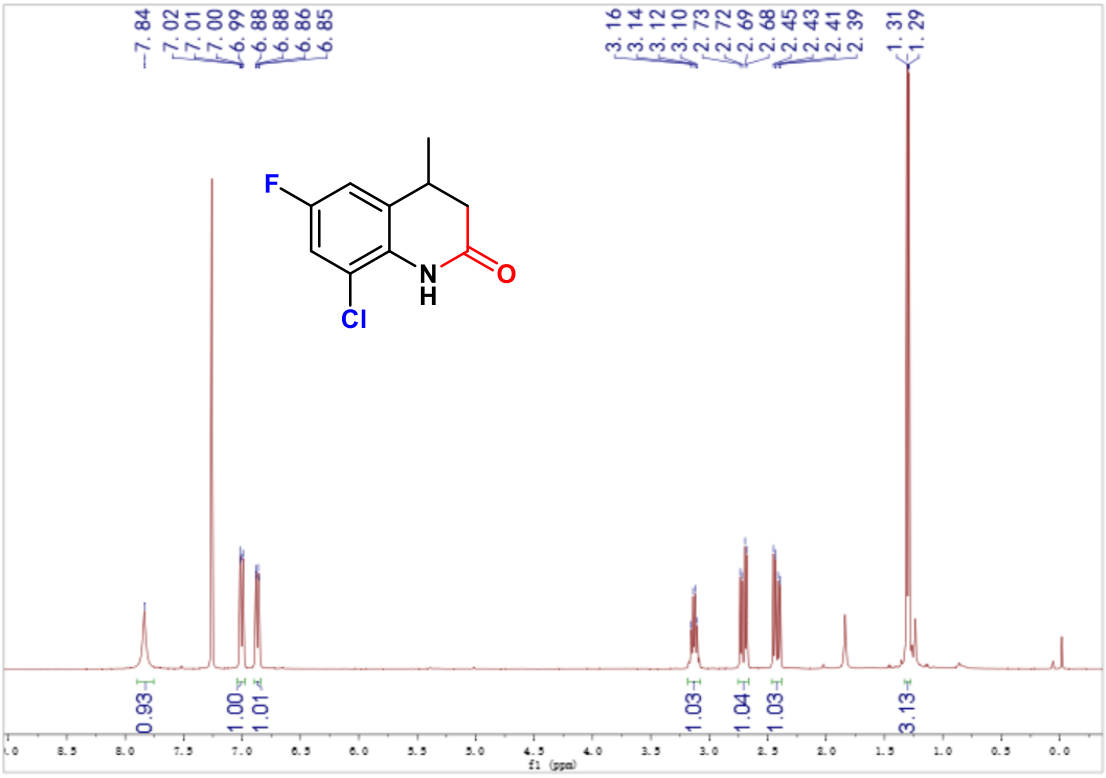
^{1}H NMR of **2x**



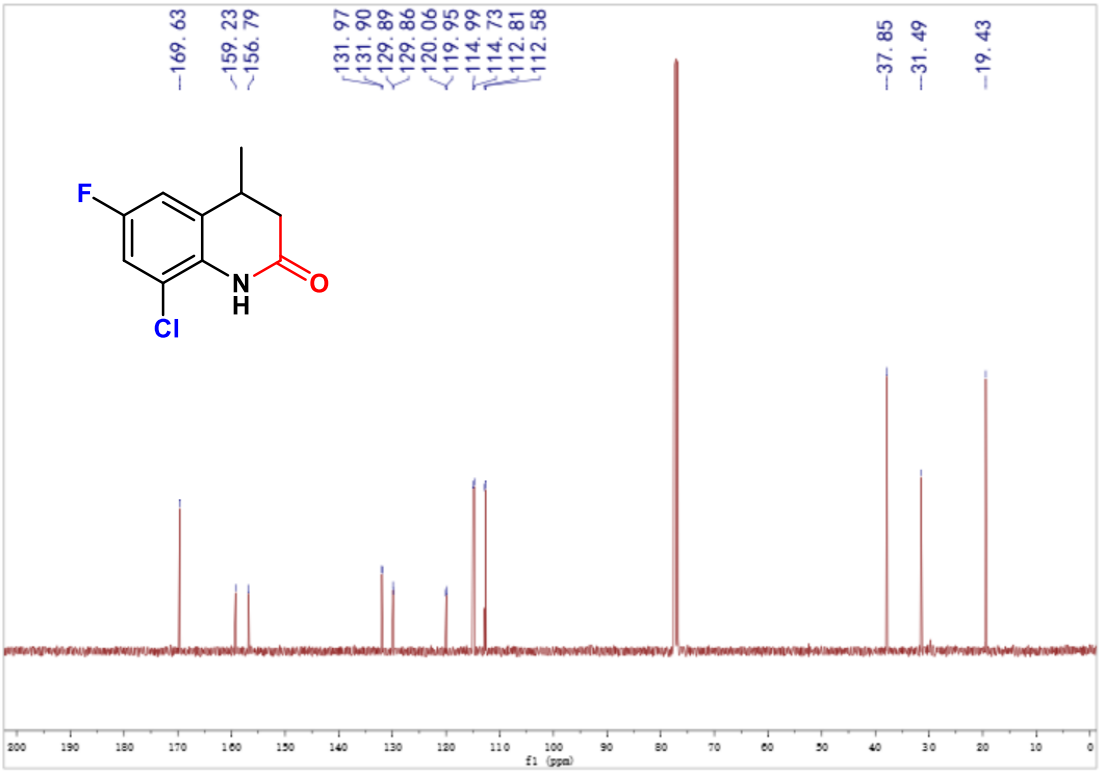
^{13}C NMR of **2x**



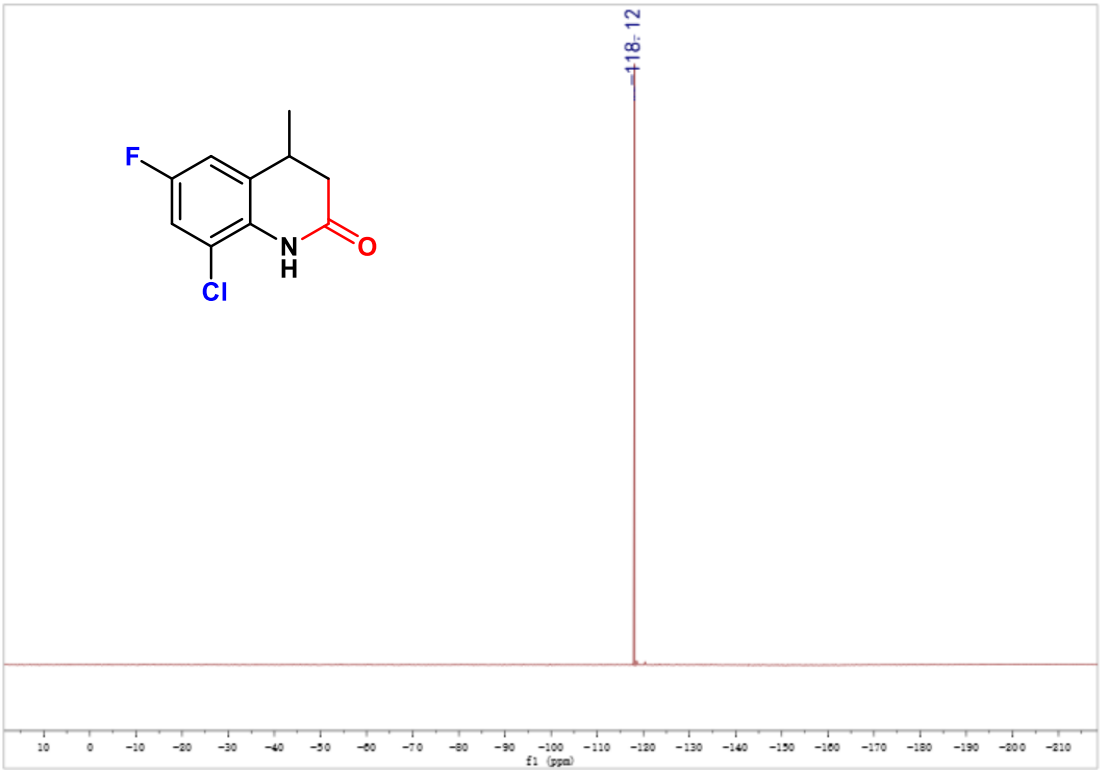
^{19}F NMR of **2x**



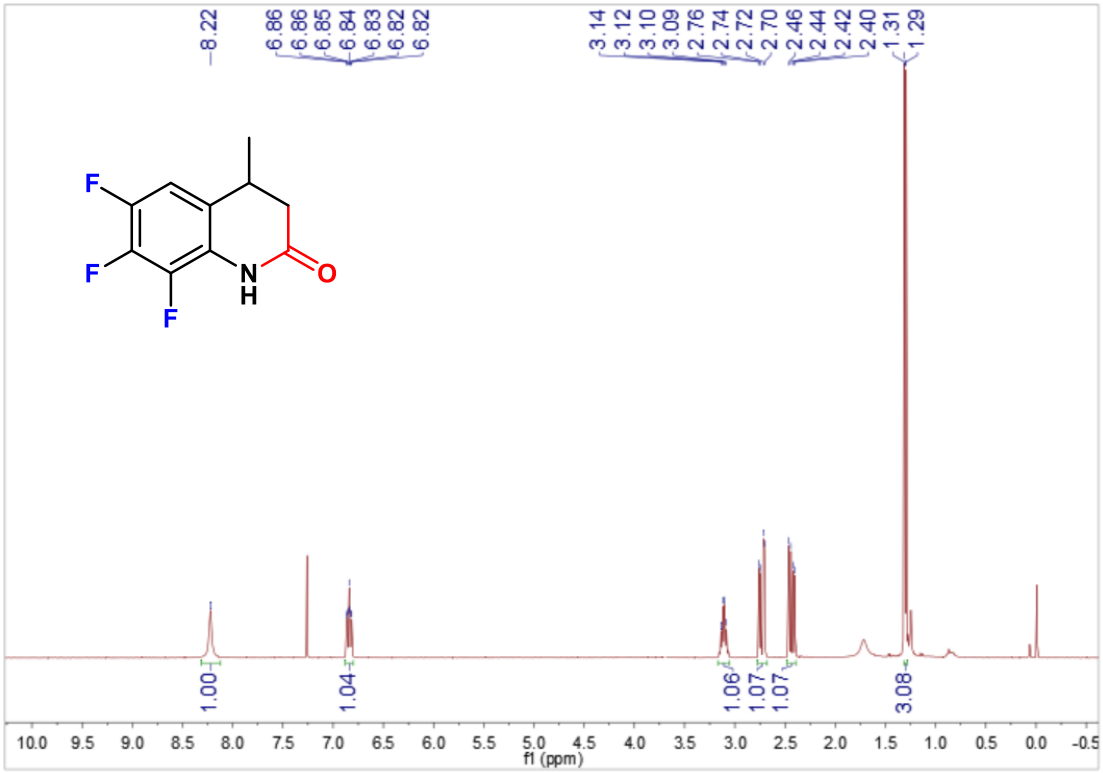
^{1}H NMR of **2y**



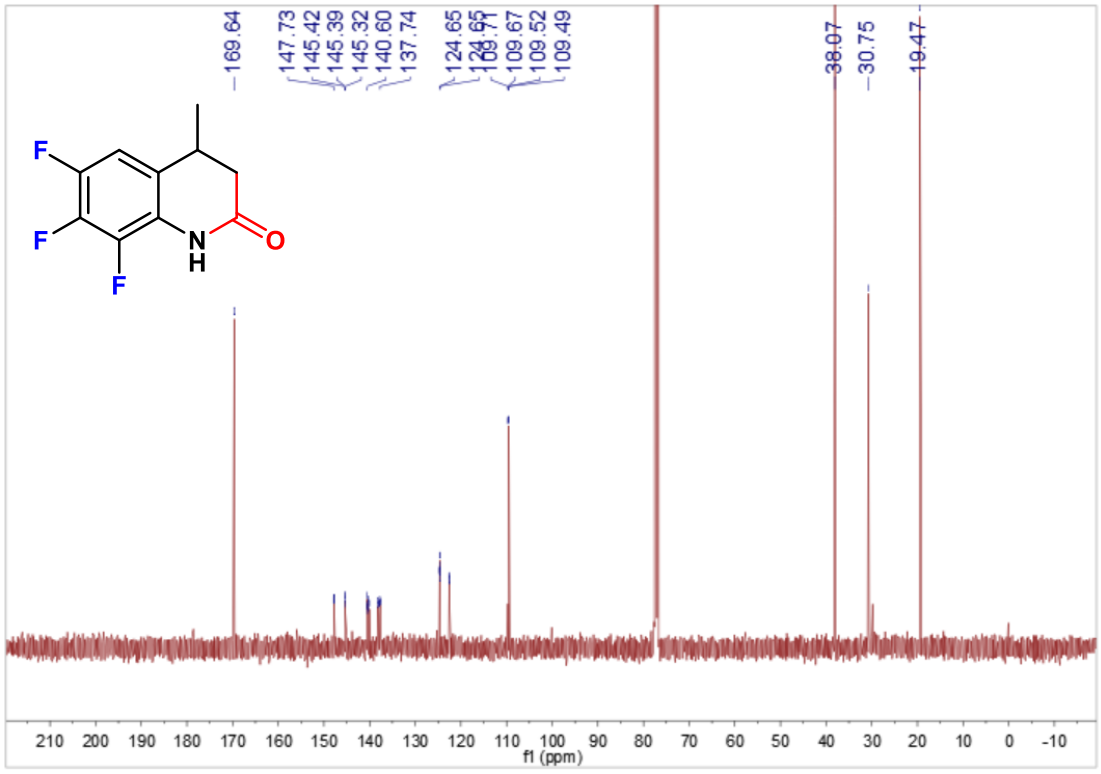
^{13}C NMR of **2y**



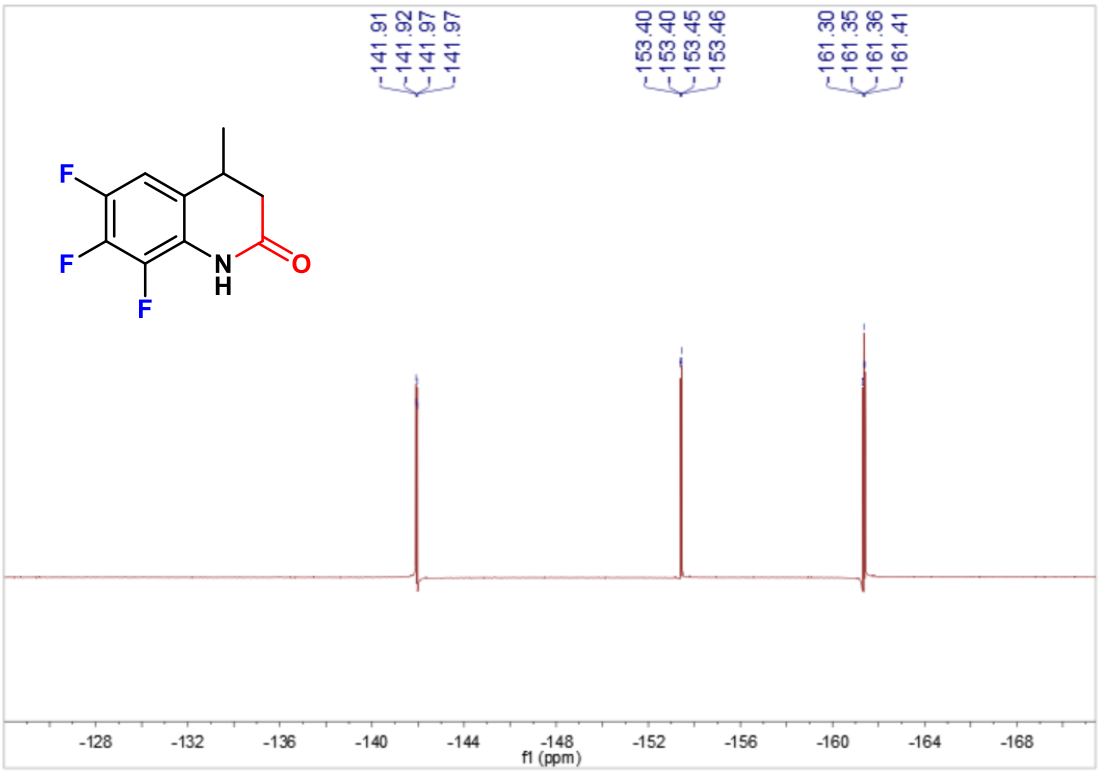
^{19}F NMR of **2y**



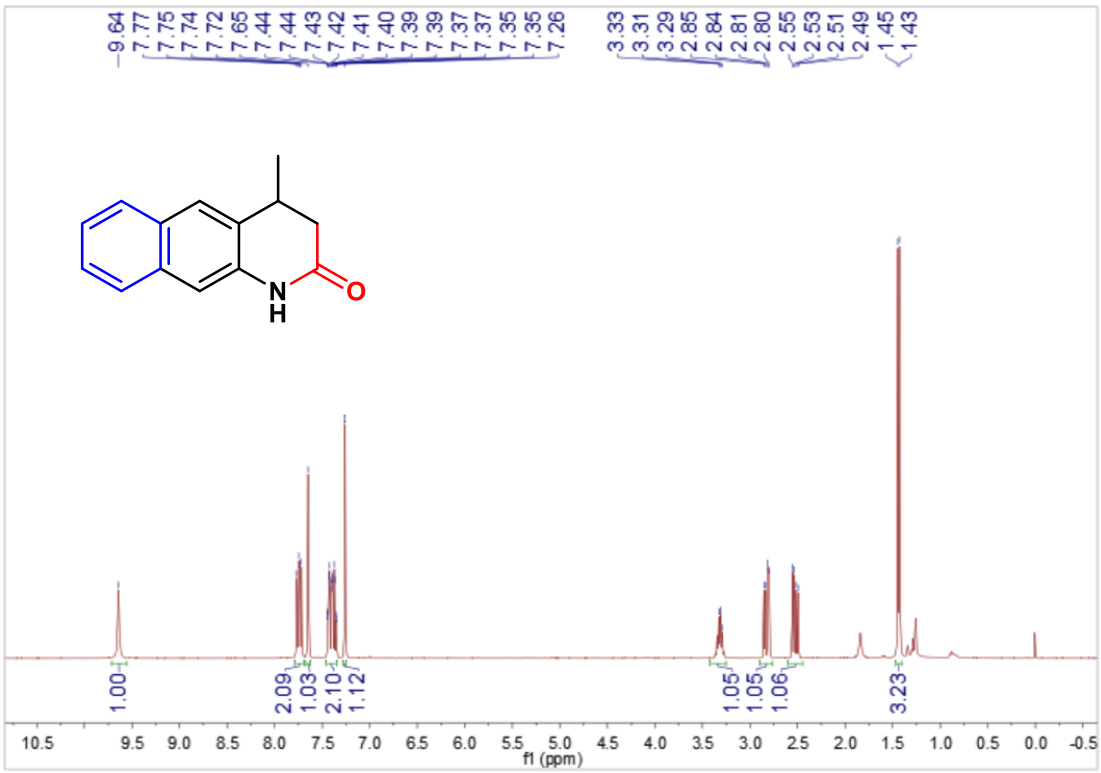
^{1}H NMR of **2z**



^{13}C NMR of **2z**



^{19}F NMR of **2z**



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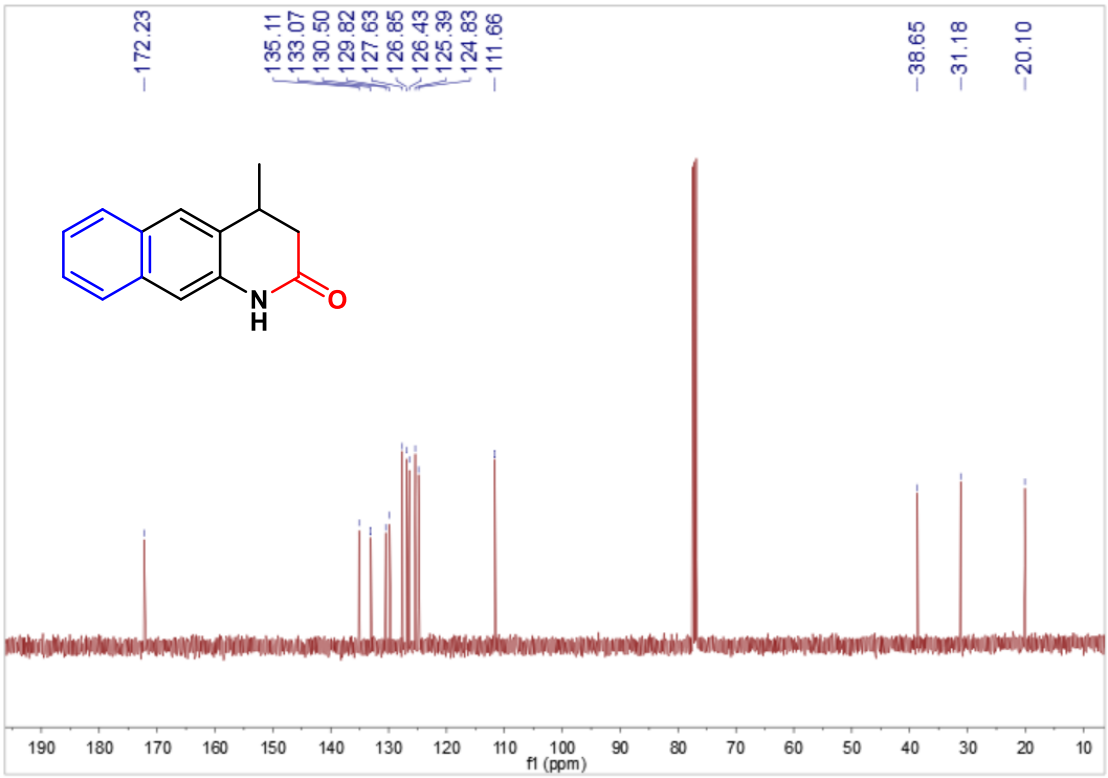
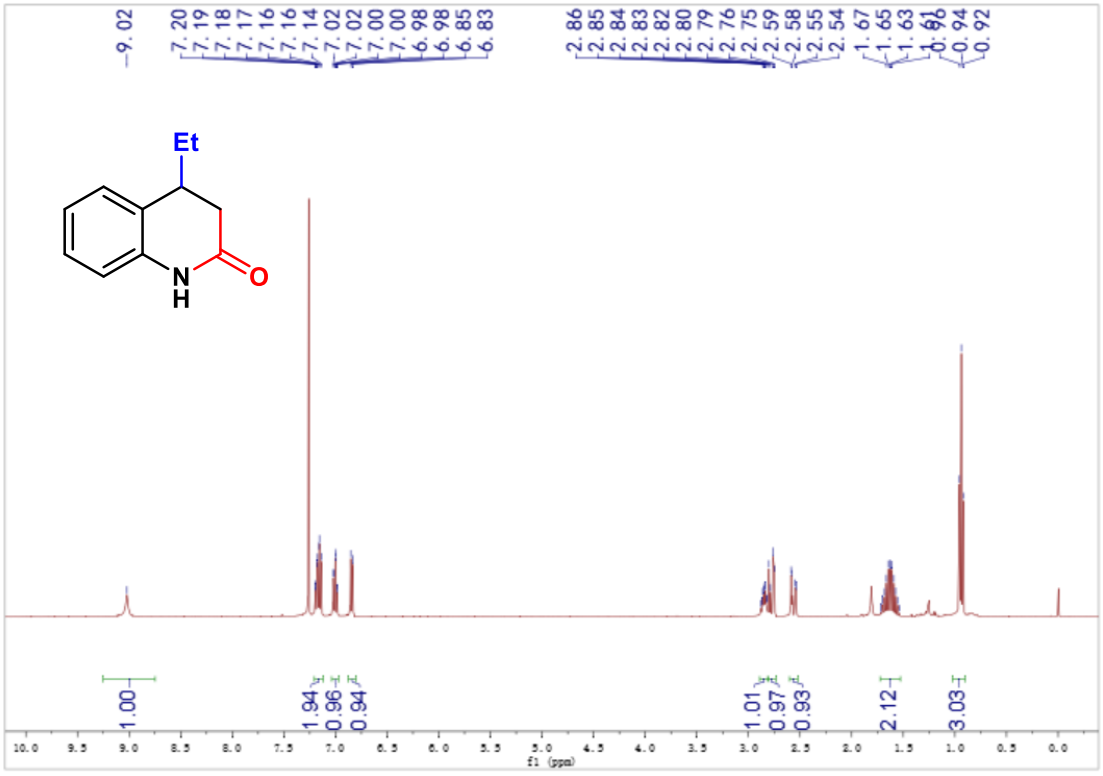
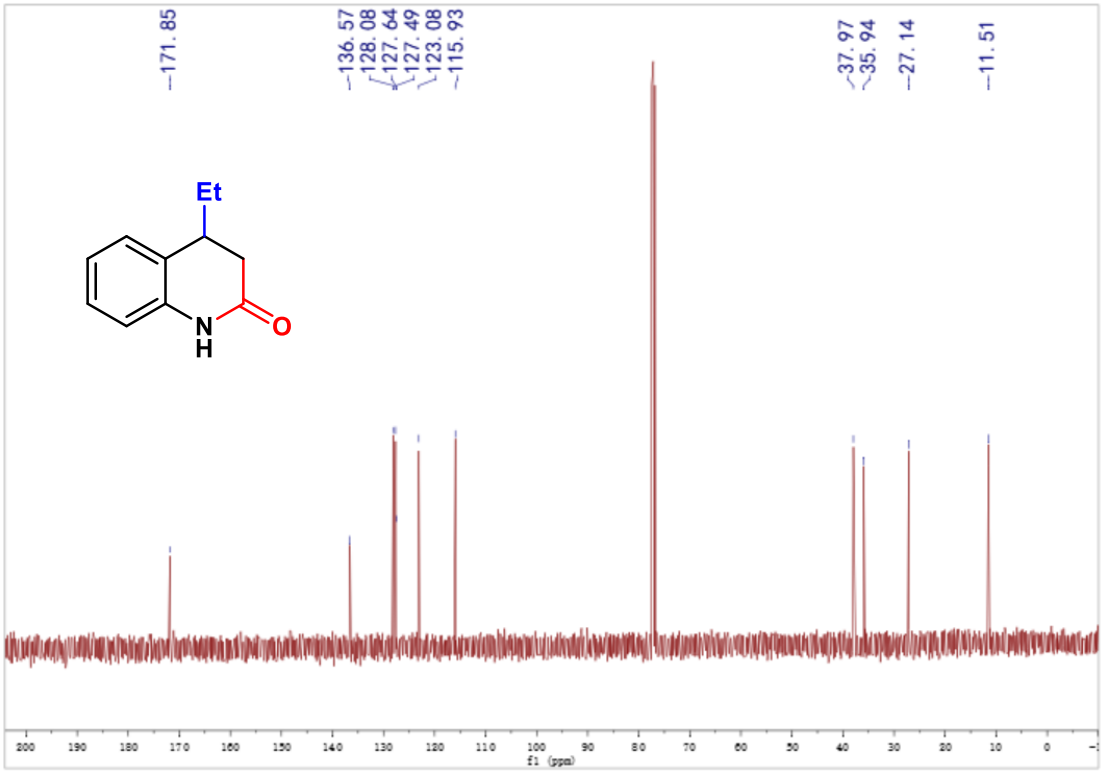


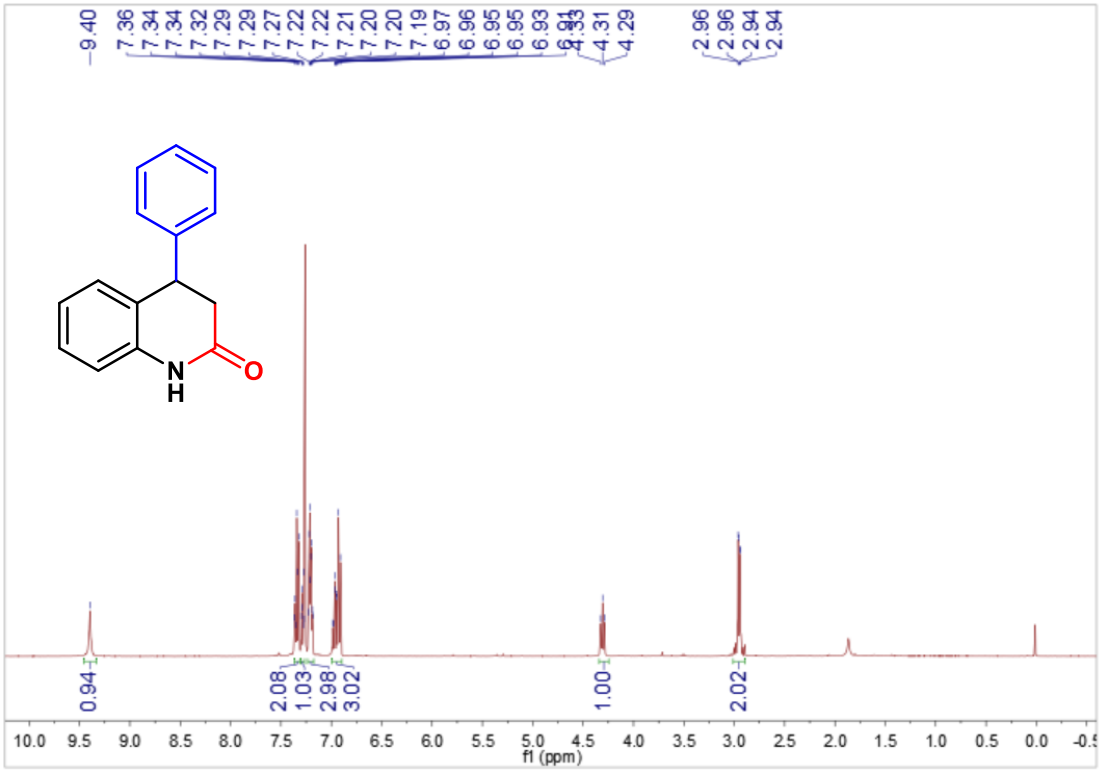
^{13}C NMR of **2aa**



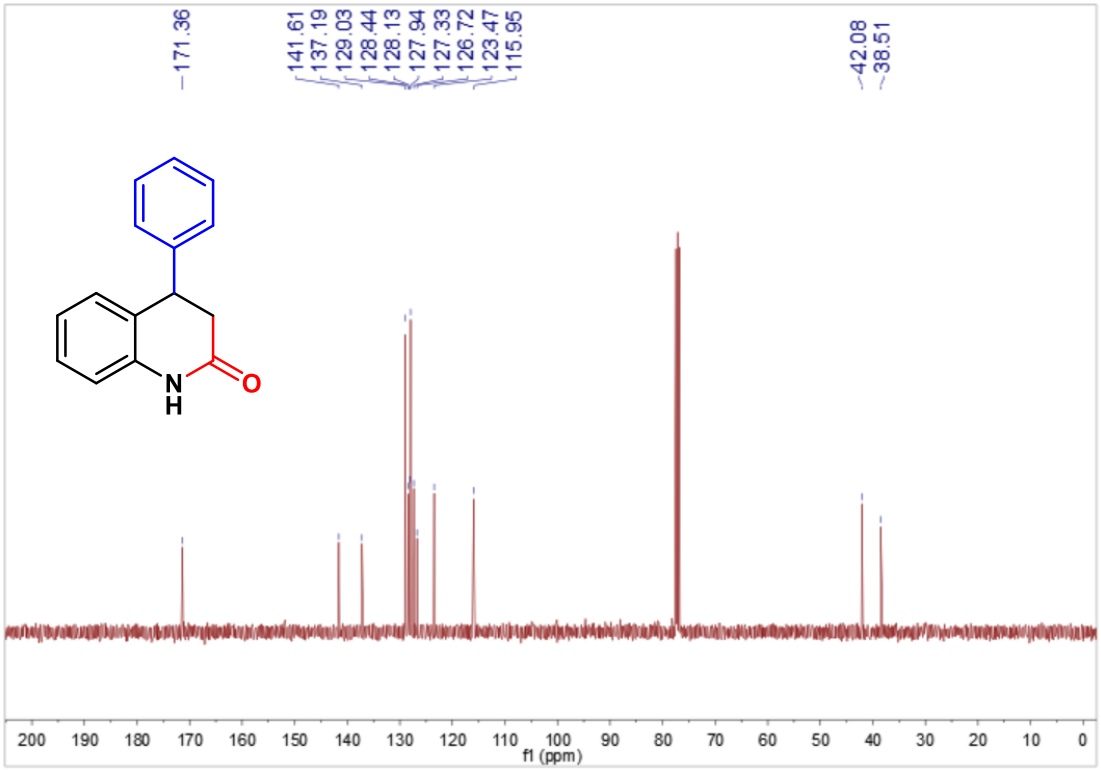
^{1}H NMR of **2ab**



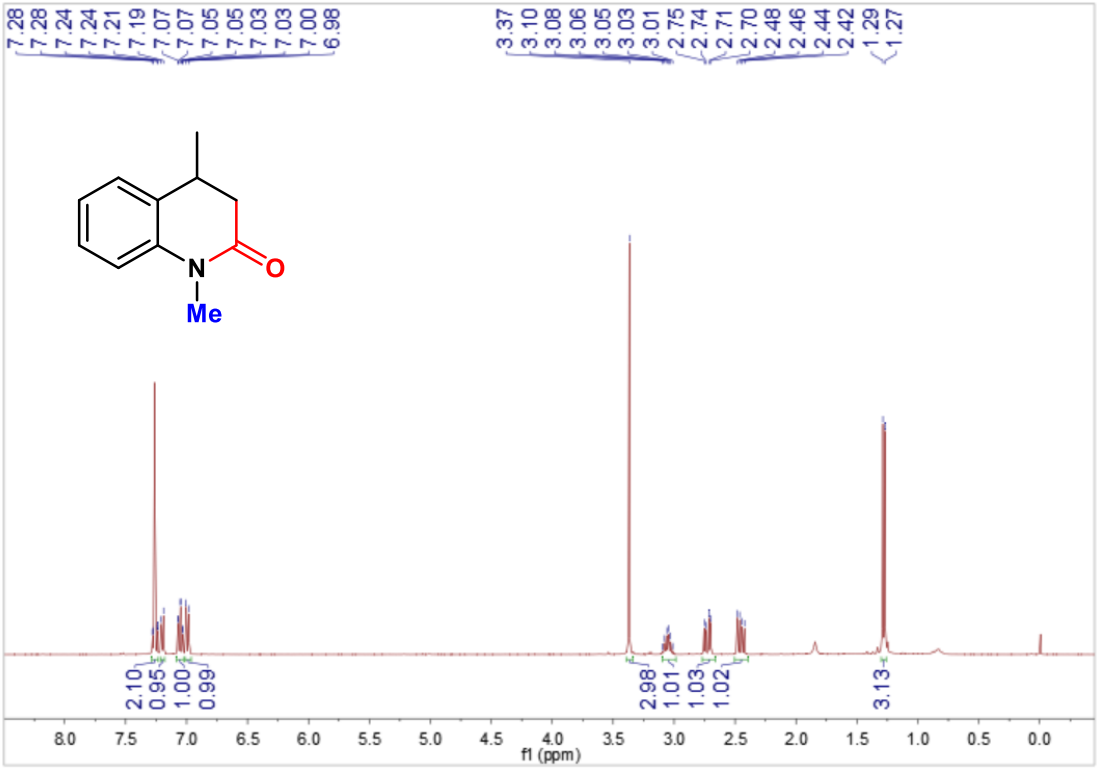
^{13}C NMR of **2ab**



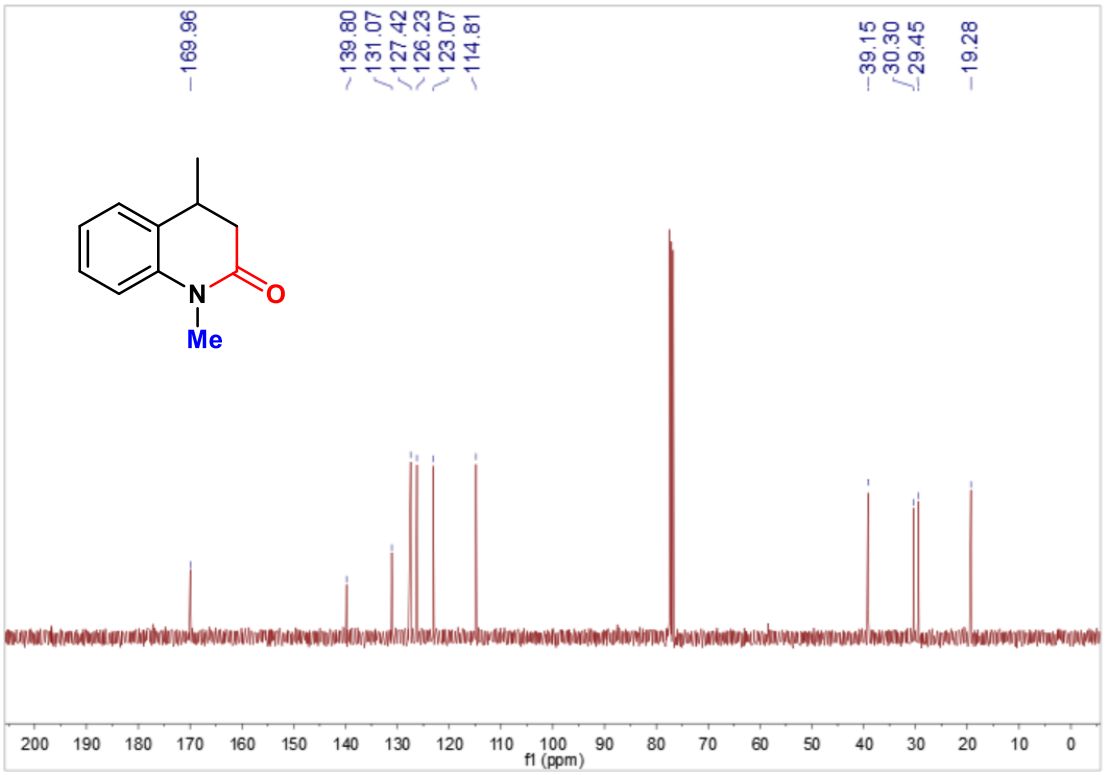
^{1}H NMR of **2ac**



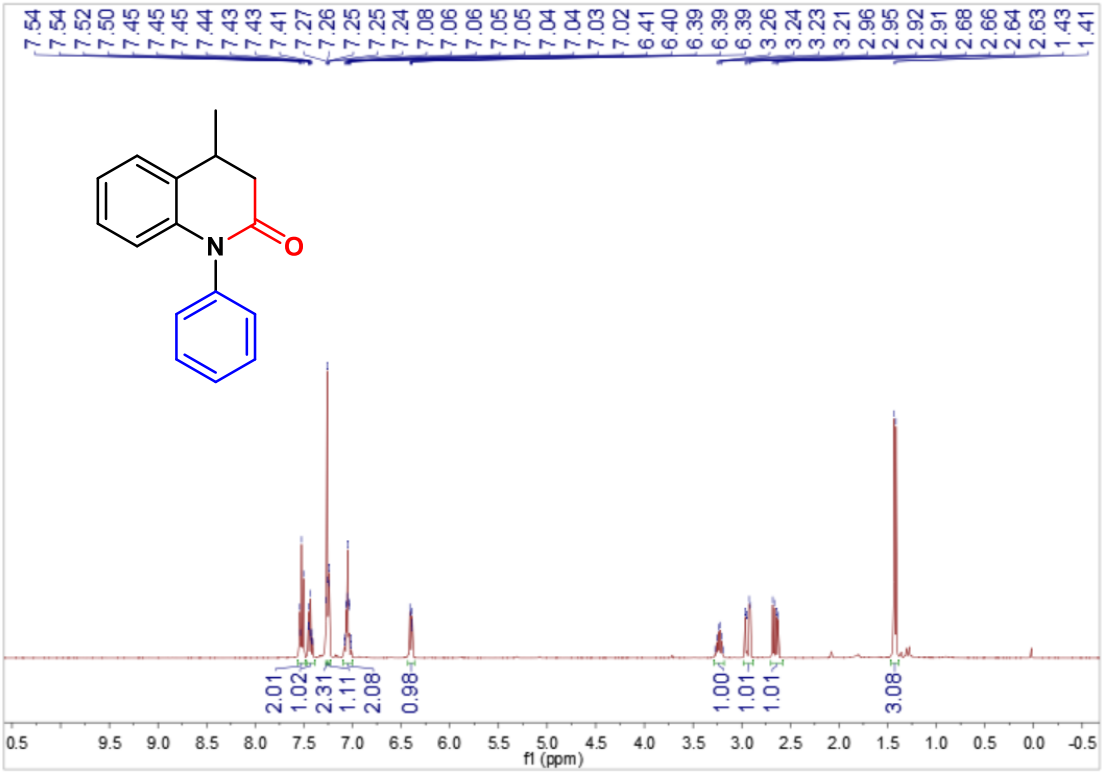
^{13}C NMR of **2ac**



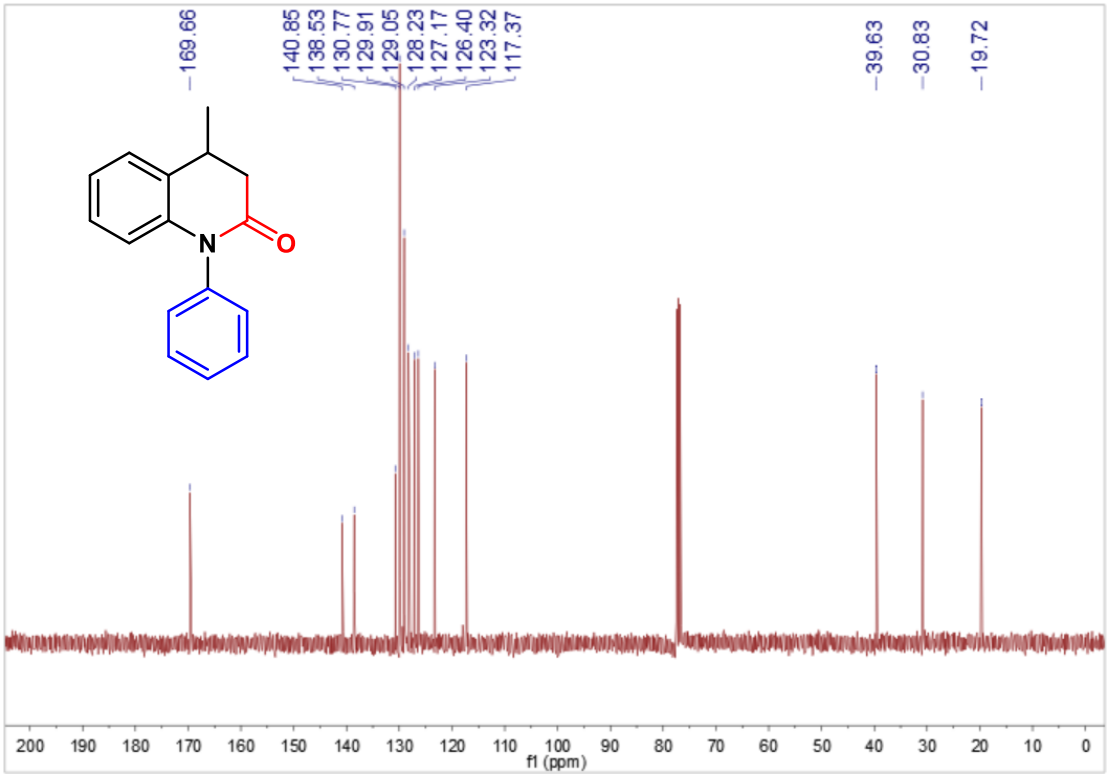
^{1}H NMR of **2ad**



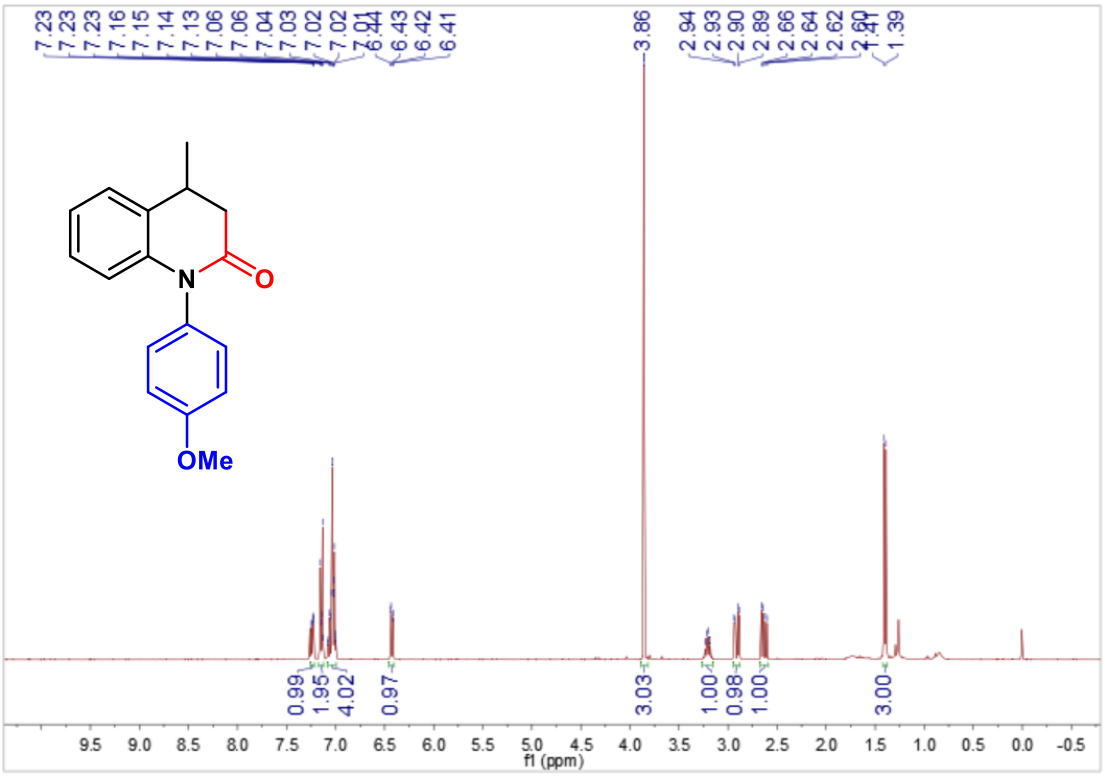
^{13}C NMR of **2ad**



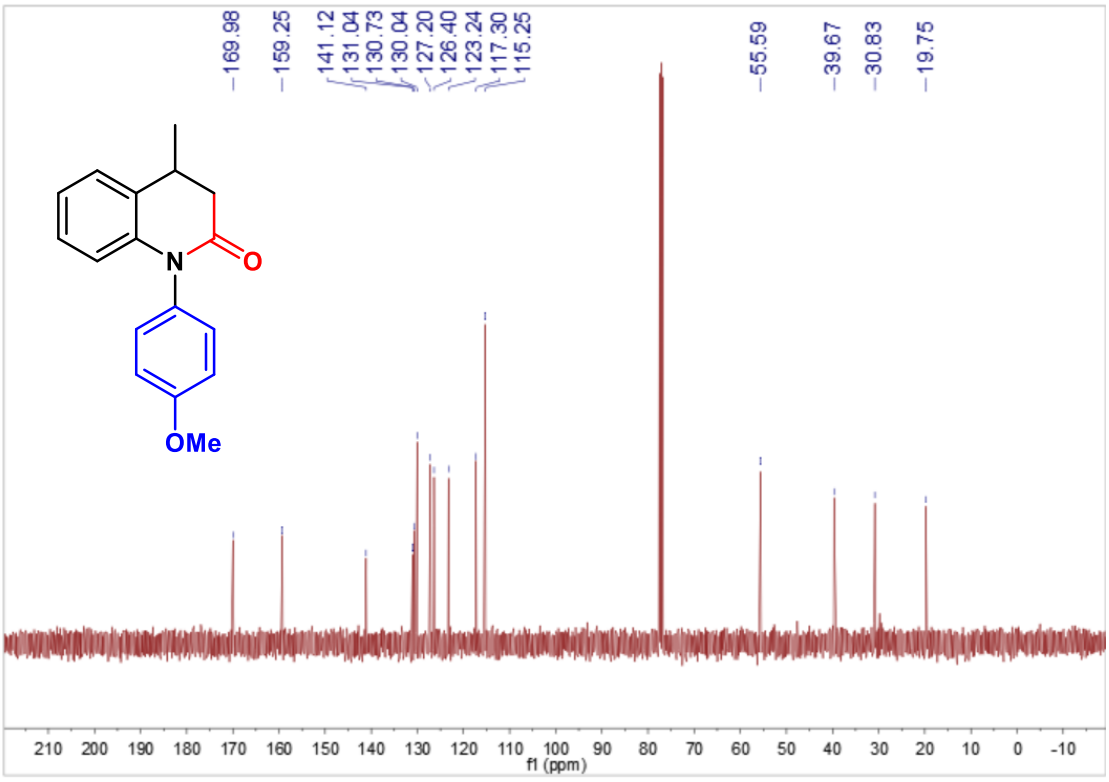
^{1}H NMR of **2ae**



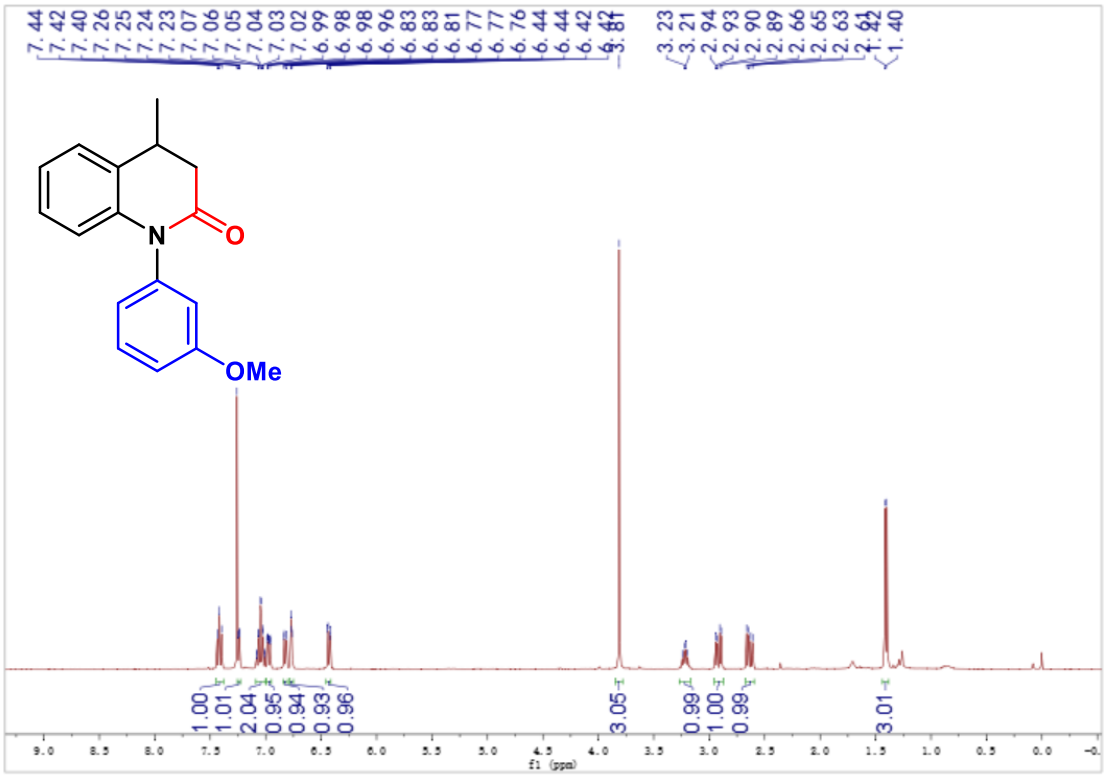
^{13}C NMR of **2ae**



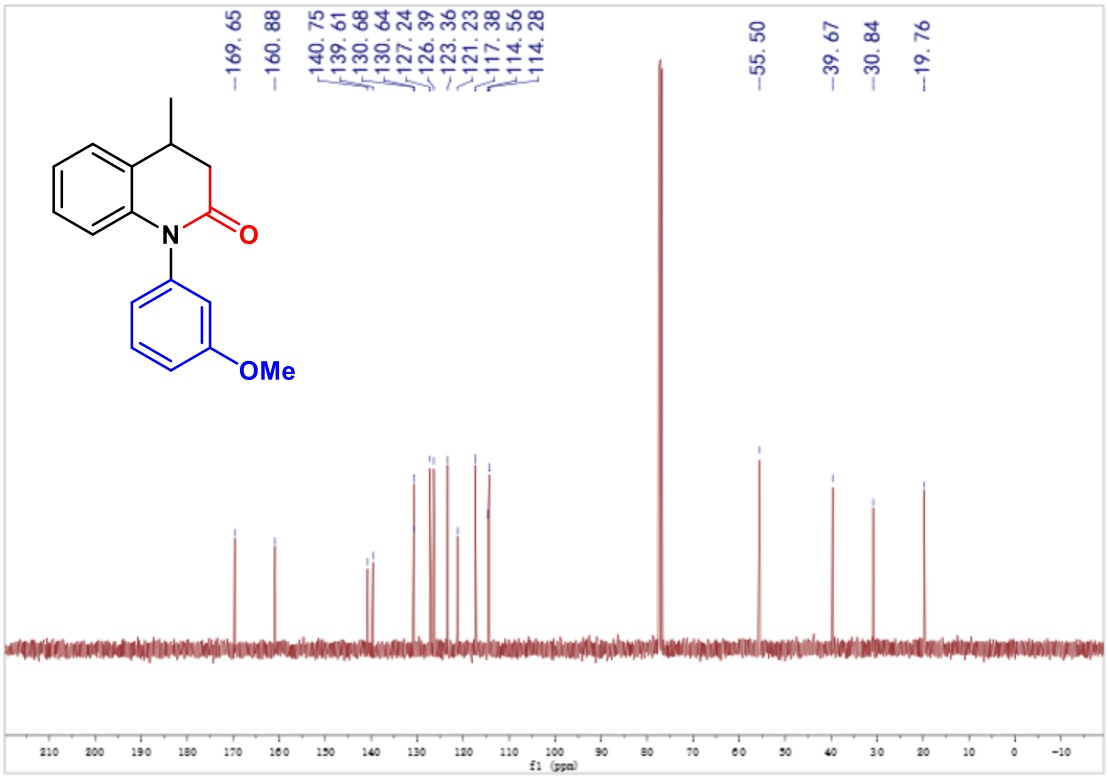
^{1}H NMR of **2af**



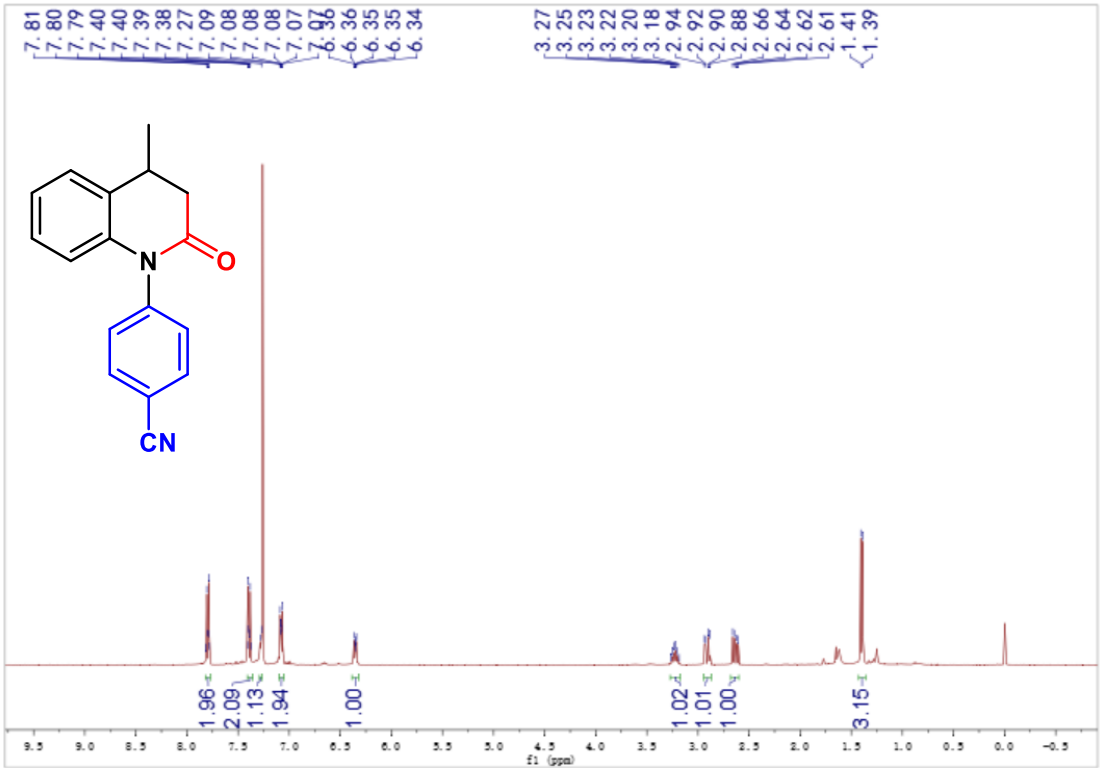
^{13}C NMR of **2af**



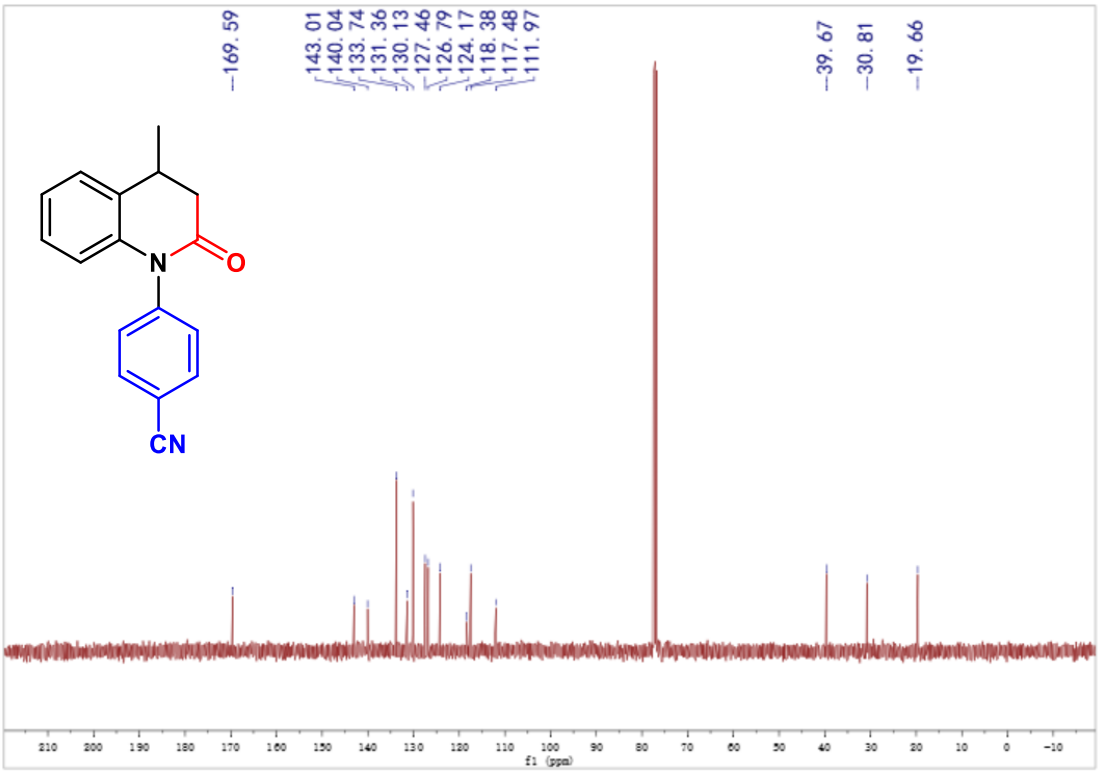
^{1}H NMR of **2ag**



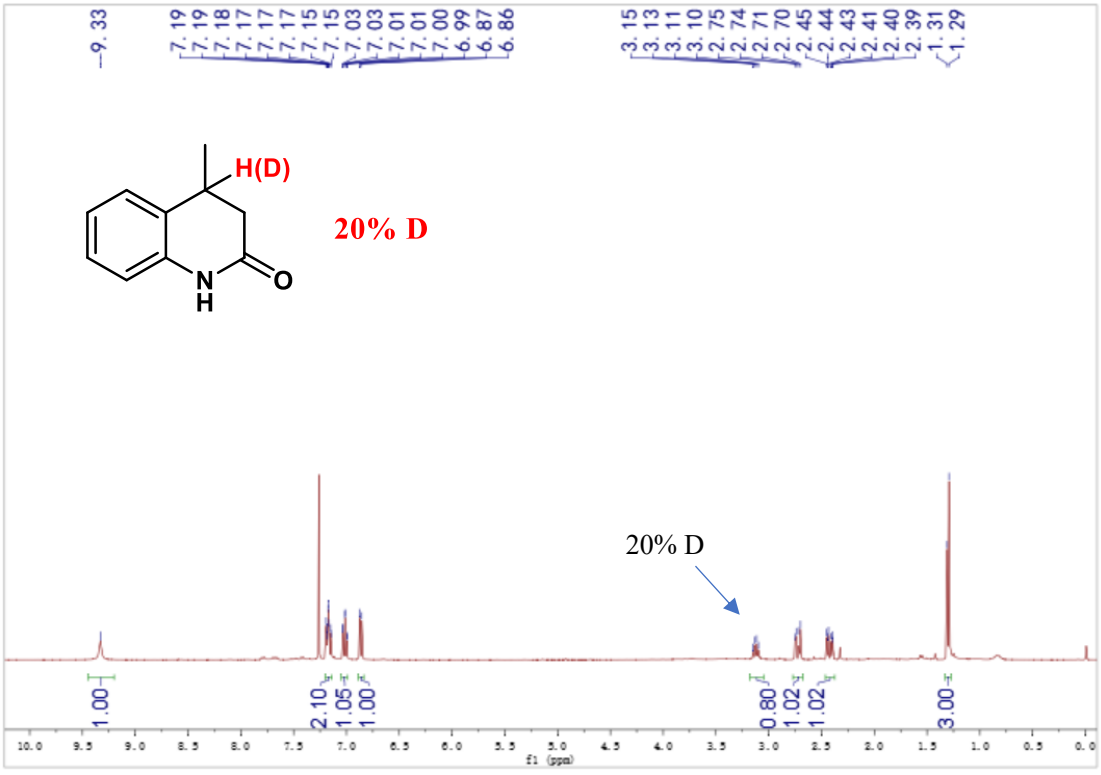
^{13}C NMR of **2ag**



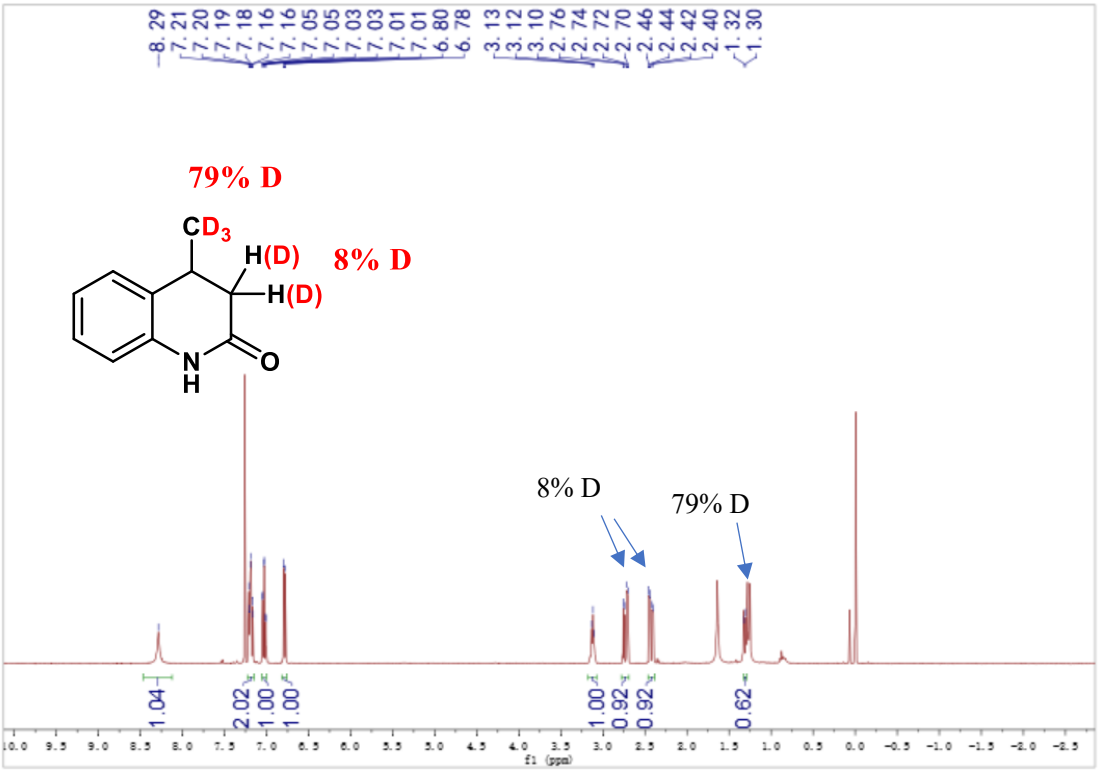
^{1}H NMR of **2ah**



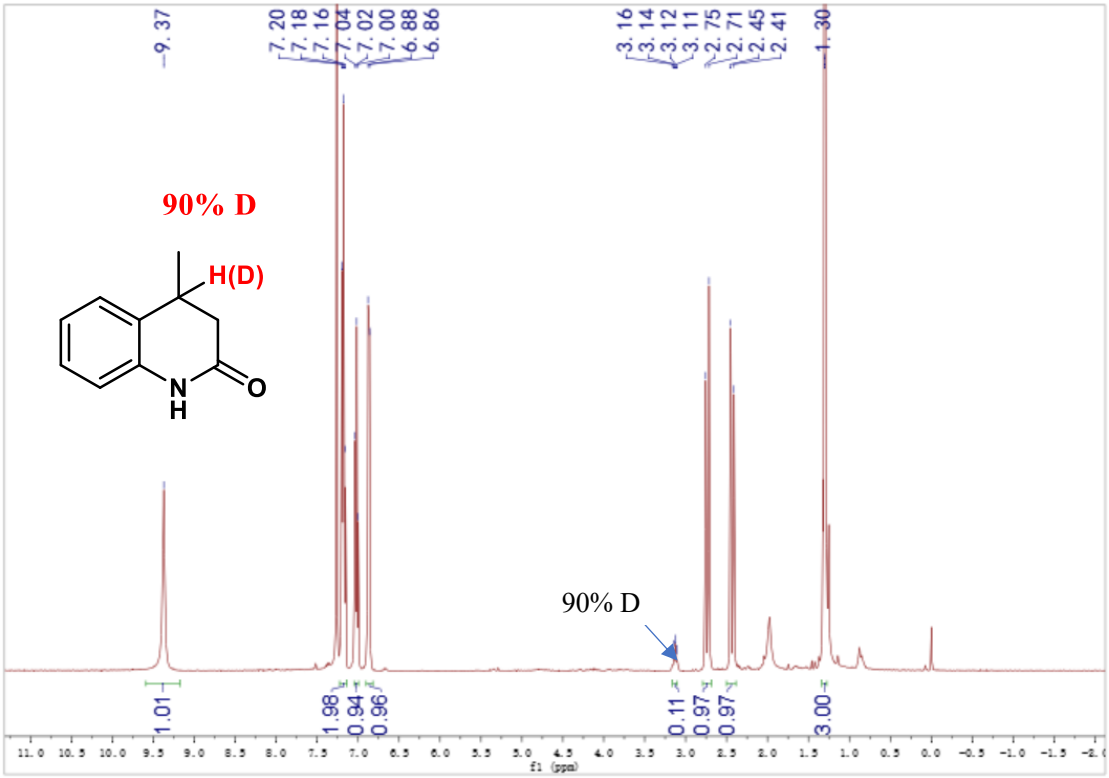
^{13}C NMR of **2ah**



^{1}H NMR of **3a** (Product of hydroaminocarbonlyation reactions performed with additional 0.125 ml D_2O and 0.125 ml H_2O)



^{1}H NMR of **4a** (Product of hydroaminocarbonlyation reactions of **1a-CD$_3$**)



^{1}H NMR of **5a** (Product of hydroaminocarbonlyation reactions performed with additional 0.25 ml D_2O)