Supporting information

Molecular Oxygen Promoted Sustainable Synthesis of Functionalized Quinolines Using Catalytic Glucose Derived Ionic Liquid and Copper

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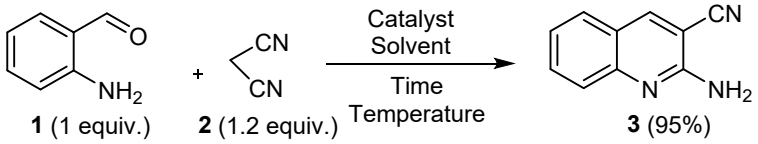
1. General materials & methods

All the reactions were carried out in an oven dried glassware. Solvents for the key step synthesis of the catalyst are dried and distilled out. All key step reactions involved in the synthesis of catalyst were conducted under nitrogen atmosphere unless otherwise indicated. Organic solutions were concentrated under reduced pressure on rotary evaporator using water bath. Analytical thin layer chromatography (TLC) was performed using Merck TLC Silica gel 60 F254 precoated plate and spots were visualized by UV light. All the products were purified by column chromatography using silica gel (100−200 mesh).

The data were characterized on the basis of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS spectroscopy. NMR spectra were obtained on a Bruker Advance-400 MHz instrument at ambient temperature unless otherwise stated. All chemical shifts are reported in ppm. $CDCl_3$ was calibrated as 7.26 ppm (^{1}H) and 77.00 ppm (^{13}C). DMSO-d_6 was calibrated as 2.49 ppm (^{1}H) and 39.50 (^{13}C). D_2O was calibrated as 4.80 (^{1}H). All the ^{13}C spectra are proton-decoupled. All multiplets are designated by the following abbreviations: s = singlet, br s = broad singlet, d = doublet, dt = doublet triplet, td = triplet doublet, ddd = doublet of doublets of doublets, q = quartet, br q = broad quartet, m = multiplet. All coupling constants (J) are reported in Hertz (Hz). GC-MS results were recorded using a GC-MS on a PerkinElmer. The HRMS electrospray ionization (ESI) was performed on a Waters(R) Micromass(R) Q-TOF MicroTM mass spectrometer. The resources were obtained from commercial sources (Alfa Aesar, Aldrich, SRL) and were used as received without further purification. All reactions in this work were conducted using an oil bath as a heat source. Yields refers to the quantities obtained after purification through column chromatography.

2. Optimization of reaction conditions

Table S1. Optimization of Reaction Conditions for annulation from *o*-aminobenzaldehydes [a]

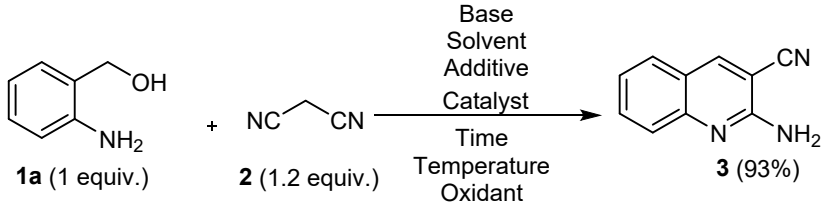


1 (1 equiv.) **2** (1.2 equiv.) **3** (95%)

Entry	Cat. (mol%)	Solvent (mL)	Time (h)	Temp. (℃)	Yield (%)
1.	-	EtOH: H_2O	10	70	traces
2.	GSIL I (1)	EtOH: H_2O	3.5	70	43
3.	GSIL I (5)	EtOH: H_2O	3	70	56
4.	GSIL I (5)	MeCN:H_2O	3	70	65
5.	GSIL II (1)	EtOH: H_2O	2	70	68
6.	GSIL II (5)	EtOH: H_2O	0.25	70	93
7.	GSIL II (1)	MeCN:H_2O	2	70	70
8.	**GSIL II (5)**	**MeCN:H_2O**	**0.25**	**70**	**95**
9.	GSIL II (15)	MeCN:H_2O	0.25	70	95

[a] Reaction conditions: **1** (0.25 mmol), **2** (0.3 mmol) and GSIL II (5 mol%) in 3 mL of solvent (1.5 mL of H_2O and 1.5 mL of MeCN under stirring at 70℃ for 0.25 h. [b] isolated yields are shown.

Table S2. Optimization of Reaction Conditions for one-pot annulation from *o*-aminobenzyl alcohols [a]



1a (1 equiv.) **2** (1.2 equiv.) **3** (93%)

Entry	CuI (mol%)	GSIL II (mol%)	DMAP (mol%)	TEMPO (mol%)	Oxidant	Temp. (℃)	Solvent [a] (mL)	Time (h)	Yield [b] (%)
1.[c]	10	-	10	1	O_2	70	MeCN:H_2O	8	42
2.	10	5	-	1	air	70	MeCN:H_2O	6	65
3.	10	5	10	1	air	70	MeCN:H_2O	3	94
4.	10	5	5	1	air	70	MeCN:H_2O	3	94
5.	**10**	**5**	**0.1**	**1**	**air**	**70**	**MeCN:H_2O**	**3**	**93**
6.[c]	10	5	0.1	1	O_2	70	MeCN:H_2O	3	92

[a] Reaction conditions: **1** (0.5 mmol) **2** (0.6 mmol) CuI (10 mol%) DMAP (0.1 mol%) TEMPO (1 mol%) GSIL II (5 mol%) in 3 mL of solvent (1.5 mL of H_2O and 1.5 mL of MeCN under stirring at 70℃ for 3 h, under atmospheric oxygen/air (atm. O_2). [b] isolated yields are shown. [c] Reaction was carried out in presence of O_2 balloon.

3. Representative synthesis of catalysts GSIL I & GSIL II (C3 and C4)

i) Synthesis of Methyl 6-Iodo-α-D-Glucopyranoside (C2)

The desired product **C2** was synthesized via Appel reaction by using Methyl-D-α-glucopyranoside **C1** (1.01 g; 5.2 mmol), triphenylphosphine (2.05 g; 7.8 mmol; 1.5 eq.), imidazole (0.71 g; 10.4 mmol; 2.0 eq.) and iodine (1.98 g; 7.8 mmol; 1.5 eq.). The reaction mixture was refluxed in THF (30 mL) for 4 hours. After the completion of the reaction, the solid was filtered off and the solvent was removed via rotary evaporator and purified by silica-gel column chromatography using chloroform/methanol in 90:10. Finally, the purified compound was recrystallized in ethanol solution to obtain as a white solid. The desired product was fully characterized by ^{1}H NMR, ^{13}C NMR and HRMS spectroscopy.

ii) Synthesis of 1-(Methyl-α-D-glucopyranosid-6-yl)-1,4-diazabicyclo[2.2.2]octan-1-ium iodide (C3, GSIL I)

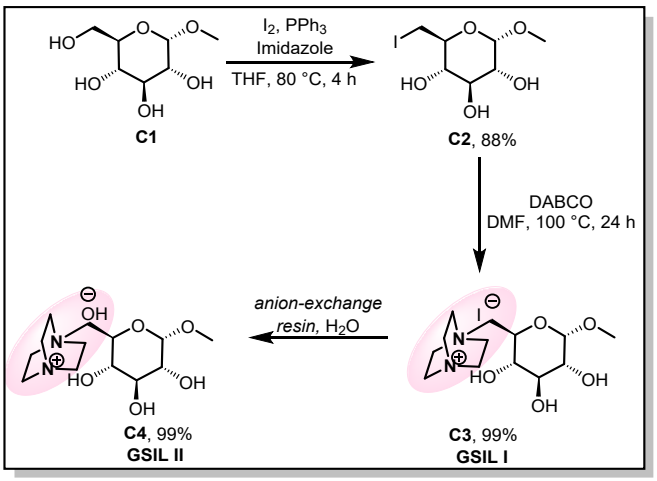
The synthesized product **C2** (3.649 g, 12.0 mmol) and 1,4-diazabicyclo[2.2.2]octane **(**1.346 g, 12.0 mmol) was dissolved in DMF (20 mL) and stirred at 100 °C for 24 hours. After cooling the solution to room temperature, ethyl acetate (160 mL) was added and the flask was refrigerated for over 6 h. Later, the solvent was decanted and the precipitated solid was washed with ethyl acetate (3×40 mL) and dried under high vacuum to isolate the product as a pale brown solid (4.574 g, 99%).

iii) Synthesis of hydroxide form of Amberlite anion exchange resin

Initially**,** 30 g of Amberlite® IRA-400 chloride resin was treated with 300 mL of 1 N NaOH in a round bottom flask and agitated for 12 hours. Then the resin was washed with double-distilled water until it reached neutral pH of 7. Finally, the resin was filtered and air dried.

1-(Methyl-α-D-glucopyranosid-6-yl)-1,4-diazabicyclo[2.2.2]octan-1-ium hydroxide (C4, GSIL II)

Amberlite® IRA-400 ion exchange gel was set up like a column chromatography and **C3** (2.05 g; 5.3 mmol) was eluted with water. All test tubes were tested with pH 0–14 test strips and all alkaline test tubes were collected. The product **C4** was obtained as a yellow-coloured viscous semisolid (1.46 g; >99%) after the removal of water via rotary evaporator. [1a]



[a] Reaction performed on a closed Schlenk type tube: Step I: **C1** (5.2 mmol) Triphenyl phosphine (7.8 mmol) Imidazole (10.4 mmol) Iodine (7.8 mmol) in 30 mL of THF stirred under 80 ℃ for 4 h, under N_2. Step II: **C2** (1 mmol), DABCO (1.2 mmol) in 5 mL of DMF stirred under 100 ℃ for 24 h. Step III: anion exchange chromatography was performed using Amberlite™ IRA-400 hydroxy form of resin from **C3** to **C4**. [b] isolated yields are shown.

Figure S1. Image of synthesized GSIL I (**C3**) and GSIL II (**C4**) from left to right

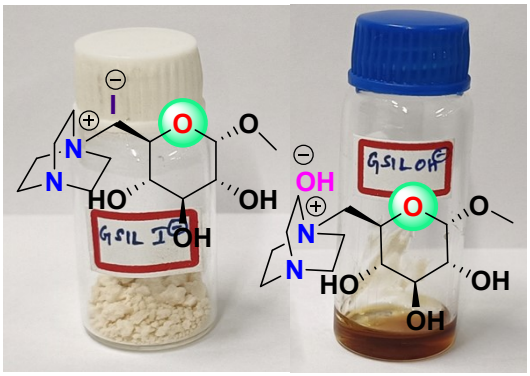


Figure S2. Various alcohol derivatives used in the study (synthesized following known method in the literature)[1b]

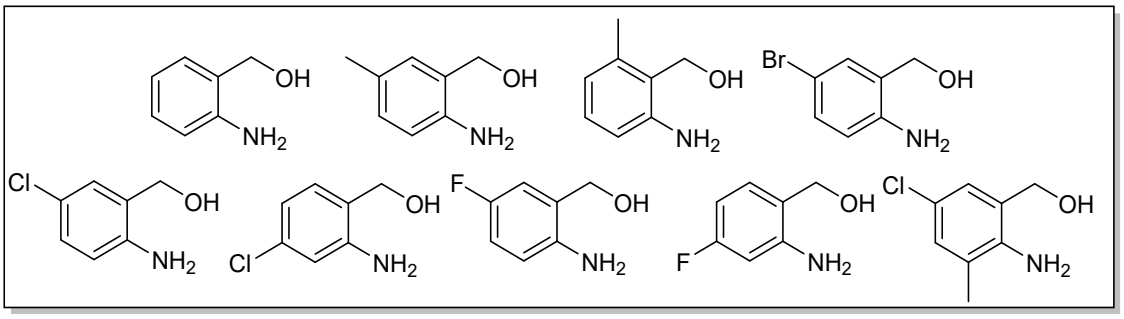
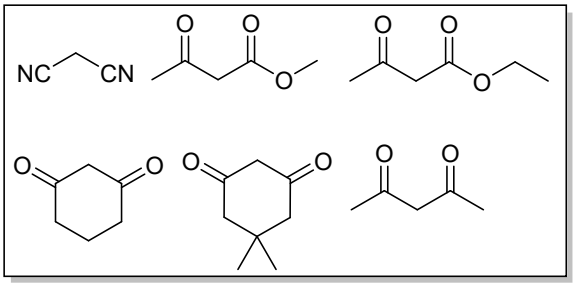
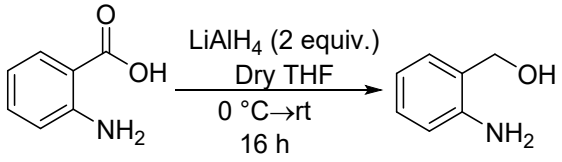


Figure S3. Various 1,3-dicarbonyl compounds or nitriles used in the study (Commercially available)



4. Representative synthesis of *o*-aminobenzyl alcohols



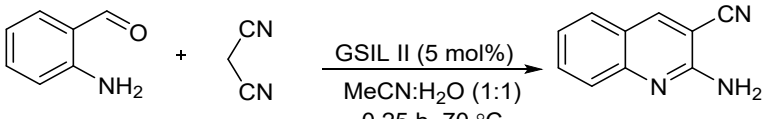
S1 **S2**

1 equiv.

2-aminobenzyl alcohols were prepared according to the reported literatures. [1b]

S1 to **S2**: To an oven-dried Schlenk tube, added anthranilic acid **S1** (5.07 mmol, 1.231g) in dry THF (25 mL) was added portion wise the powder of $LiAlH_4$ (5 mmol, 1.237g) while the temperature was maintained at -0 °C with stirring. The resulting mixture was allowed to warm to room temperature and stirred in the same temperature for additional 12 h. Until the end of the reaction, the resulting mixture was then hydrolyzed by addition of water (1 mL) and 5% NaOH (1.5 mL). The resulting suspension was filtered, and the precipitate was washed with dichloromethane. The combined organic layer was evaporated. The residue was recrystallized from dichloromethane, affording the corresponding alcohols **S2** quantitatively as a off-white solid.

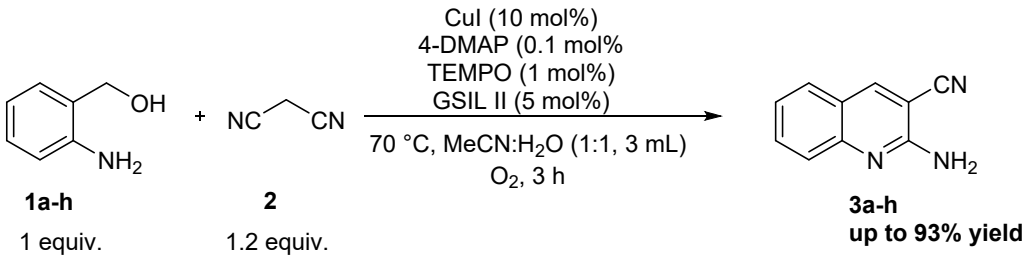
5. Representative synthesis for the direct conversion of *o*-aminobenzaldehyde (1a) into quinolines (3) by GSIL II



1 (1 equiv.) **2** (1.2 equiv.) **3** (95%)

o-aminobenzaldehyde (0.25 mmol) was dissolved in 1.5 mL of acetonitrile and was stirred for 5 minutes. Later malononitrile (0.3 mmol) was added to the reaction medium, followed by the addition of 5 mol% of GSIL II dissolved in water. The reaction was stirred at 70℃ for 0.25 h until the completion as monitored by TLC. After the completion, the resulting mixture was cooled to room temperature, and was diluted with ethyl acetate (3 x 5 mL), washed with saturated brine solution (5 mL), and dried over anhydrous Na_2SO_4. The organic layer was concentrated under vacuo. The crude product was purified by column chromatography on silica gel to obtain the desired product **3** in 95% yield.

6. Representative strategy for the one-pot formation of 2,3-substituted quinolines



Into a 30 mL reaction tube, 2-aminobenzylalcohols (0.5 mmol), malononitrile (0.6 mmol), CuI (10 mol%), TEMPO (1 mol%), 0.1 mol% of DMAP were stirred in 1.5 mL of acetonitrile. Later 5 mol% of GSIL II dissolved in 1.5 mL of water were added in the same tube. The reaction mixture was then stirred at 70℃ for 3 h under atmospheric oxygen. After the reaction was complete as monitored by TLC, the reaction mixture was cooled to room temperature and filtered through celite, and the filtrate was diluted with ethyl acetate (5 mL), washed with aqueous saturated brine solution (5 mL), and dried over anhydrous Na_2SO_4. The organic layer was concentrated under vacuo. The crude product was purified by column chromatography on silica gel to obtain the desired product **3** in 93% yield.

7. Representative strategy for the synthesis of quinolines using 1,3-dicarbonyl compounds

Into a 30 mL reaction tube, 2-aminobenzylalcohols (0.5 mmol), 1,3-dicarbonyl compounds (1.5 mmol), CuI (10 mol%), TEMPO (1 mol%), 0.1 mol% of DMAP were stirred in 1.5 mL of acetonitrile. Later 5 mol% of GSIL II dissolved in 1.5 mL of water were added in the same tube. The reaction mixture was then stirred at 70℃ for 3 h under atmospheric oxygen. After the reaction was complete as monitored by TLC, the reaction mixture was cooled to room temperature and filtered through Celite, and the filtrate was diluted with ethyl acetate (5 mL), washed with aqueous saturated brine solution (5 mL), and dried over anhydrous Na_2SO_4. The organic layer was concentrated under vacuo. The crude product was purified by flash chromatography on silica gel to obtain the desired product in good yields.

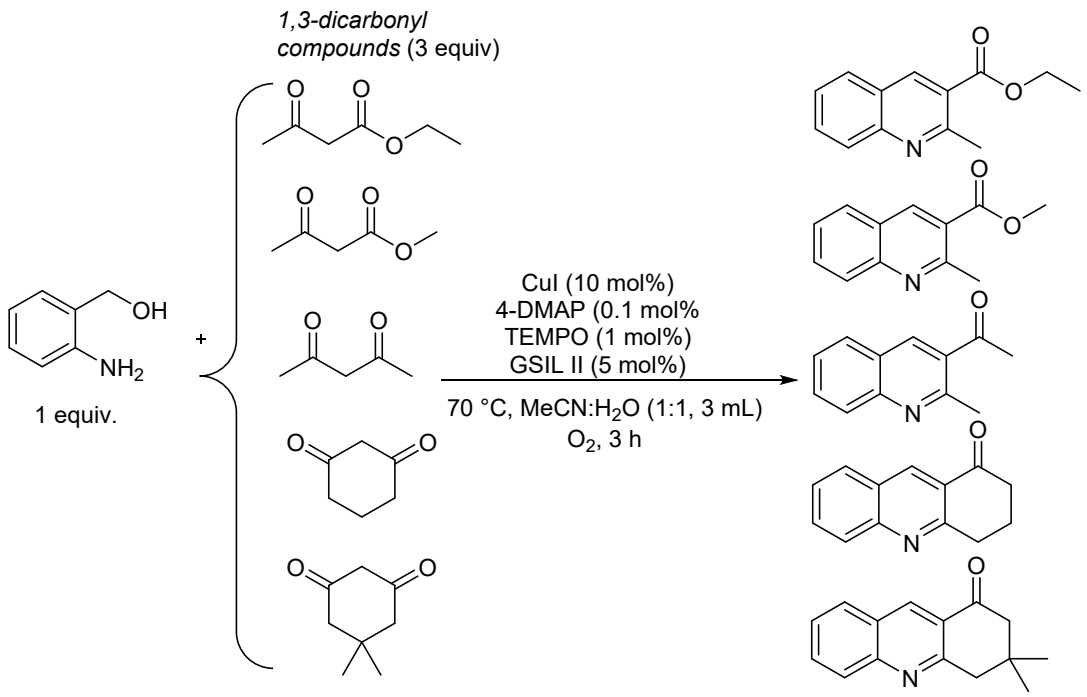
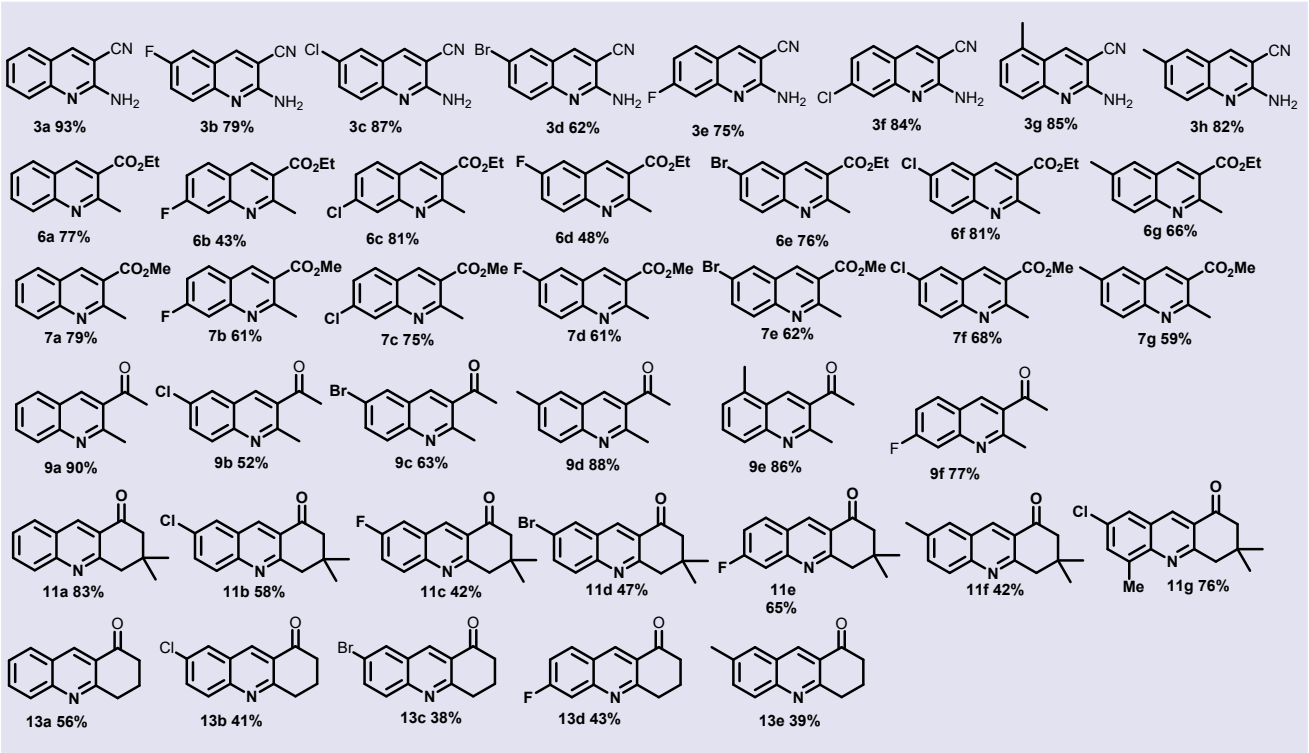
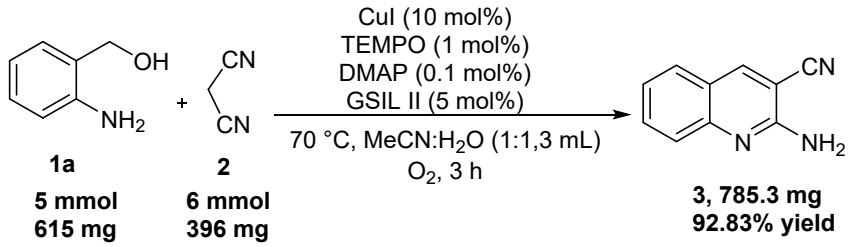


Figure S4. Substrate scope developed in this study



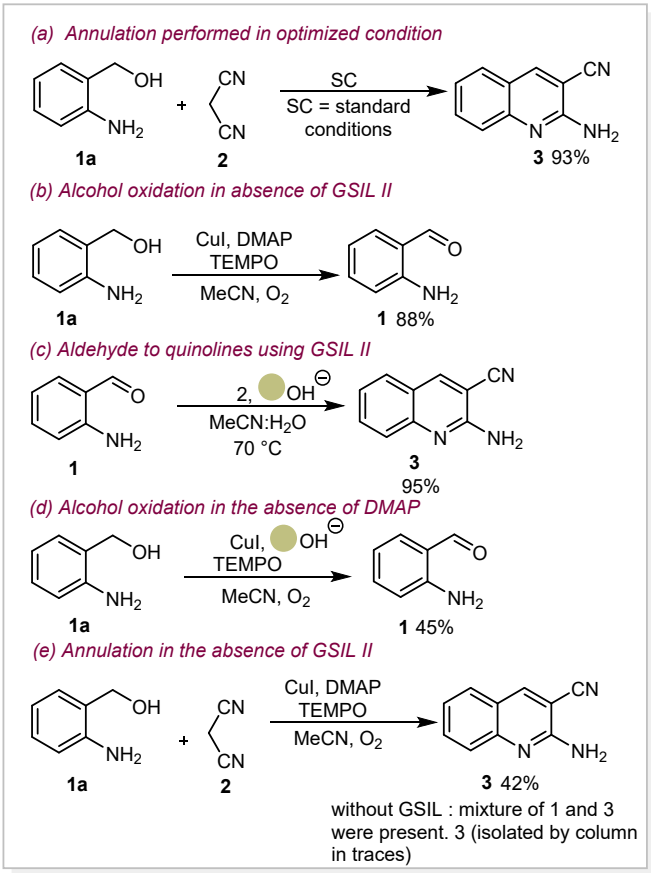
8. Scale-Up synthesis of 2,3-substituted quinolines



In a 100 mL pressure tube, 2-aminobenzyl alcohol (5 mmol), nitriles (6 mmol), CuI (10 mol%), TEMPO (1 mol%), 0.1 mol% of DMAP with 5 mol% of GSIL II in acetonitrile-water (1:1 ratio) was stirred at 70 ℃ for 3 h under atmospheric oxygen and monitored the completion of reaction by TLC. After the reaction was complete, the reaction mixture was cooled to room temperature and filtered through Celite, and the filtrate was diluted with ethyl acetate, washed with aqueous saturated buffer solution and dried over anhydrous Na_2SO_4. The organic layer was concentrated in vacuo. The crude product was purified by flash chromatography on silica gel to afford the desired product in 92% yield.

Control Experiments

In order to further understand the reaction mechanism of this catalytic system, control experiments were carried out (a-e). The reaction of *o*-aminobenzyl alcohol **1a** with **2** in standard conditions gave **3** in 93% yield (a). Meanwhile, when *o*-aminobenzyl alcohols were treated with CuI, DMAP and TEMPO in the absence of GSIL II, *o*-aminobenzaldehyde **1** was obtained in 88% yield in 3-6 hours (b). While *o*-aminobenzaldehyde **1** and malononitrile **2** only were the coupling partners, compound **3** was formed in 95% yield (c). The above observations indicated that 2-aminobenzaldehyde might be the intermediate. 2-aminobenzaldehyde **1** was formed in 45% when *o*-aminobenzyl alcohol **1a** went through this reaction in the absence of malononitrile and DMAP (d). Therefore, it shows the necessity of DMAP in the first step of reaction. Later, treating 2-aminobenzyl alcohol with malononitrile in the absence of GSIL II enabled the quinoline skeletons in only 42% yield (e). The above two investigations suggested that when alcohol oxidation was conducted in absence of DMAP, it led to a decrease in the yield of aldehyde and when annulation was performed in the absence of GSIL II, this led to the production of annulated products in lesser yield. Therefore, it is evident from the above performed experiments that both DMAP and GSIL II were crucial in facilitating the intermediate and annulated product respectively. Also, GSIL along with copper is essential in producing a synergistic effect in the reaction as well as the developed GSIL II enhances the hydrogen bonding with the substrates leading to faster rate of reaction and thereby reducing the reaction time of annulation itself to 3 hours.



Green Chemistry parameter calculation for compound 3

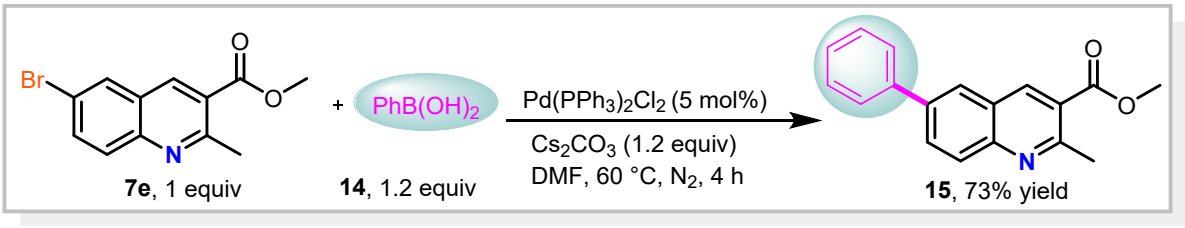
The green chemistry parameters for the reported reactions were calculated using the literature reports.[1c]

Table S3. Evaluation of green chemistry standards for compound **3**

Entry	Parameters	Formula	Ideal Value (%)	Calculated value for compound **3** (%)
1.	Environmental factor	[(Total mass of raw materials-the total mass of product)/ mass of product]	0	3.94
2.	Atom Economy	[MW of product/ (MW of stoichiometric reactants)] *100	100	89.35
3.	Carbon Efficiency	[Amount of carbon in product/Total carbon present in reactants] *100	100	100
4.	Percentage Yield	[Actual mass of product/theoretical mass of product] *100	100	93.23
5.	Atom Efficiency	[Product yield*Atom economy]/100	100	83.39
6.	Reaction Mass Efficiency	[Mass of desired products/Mass of all reactants] *100	100	61.90

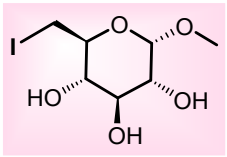
9. Synthetic transformation of product 7e

The synthetic transformation of quinoline is demonstrated. Quinoline **7e** (1 equiv, 0.053 mmol), phenyl boronic acid **14** (1.2 equiv, 0.064 mmol) can be employed as a cross-coupling partner as demonstrated for the conversion to **15** using a Suzuki reaction in the presence of 5 mol% of $Pd(PPh_3)_2Cl_2$, 1.2 equiv. of Cs_2CO_3 under N_2 atmosphere in DMF (2 mL) at 60 ℃ providing the product in 73% yield.[10] Into an oven dried Schlenk tube, N_2 is bubbled for about 15 minutes and degassed it. Further, **7e** was weighed into it under inert atmosphere followed by the addition of palladium catalyst and base. The reaction was stirred at room temperature for 5-10 minutes. Added phenyl boronic acid to the reaction mixture under the inert atmosphere and degas it finally. The reaction was kept at 60℃ for 4-6 hours until the completion of starting materials as monitored by TLC. Cooled the reaction to room temperature. The resultant solution was filtered using celite and the filtrate was diluted with ethyl acetate (3x5 mL), washed with aqueous saturated buffer solution and dried over anhydrous Na_2SO_4. The organic layer was concentrated in vacuo. The crude product was purified by flash chromatography on silica gel to afford the desired product in 73% yield.



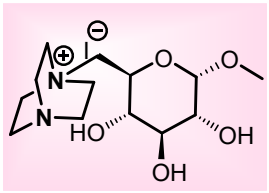
10. Spectral and Analytical data of the catalyst

Methyl 6-Iodo-α-D-Glucopyranoside **(C2)**



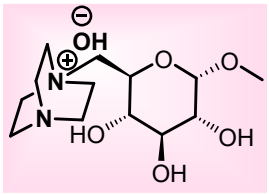
Purified by column chromatography using (chloroform/methanol) as white solid. Mp**:**146-149 °C (lit:147-148 °C). **$[\alpha]_D^{20}$**=+94.8 (C=1.0, H_2O) ^{1}H NMR (400 MHz, DMSO-d_6) δ= 5.19 (d, *J* = 5.7 Hz, 1H), 4.88 (d, *J* = 3.5 Hz, 1H), 4.80 (d, *J* = 5.8 Hz, 1H), 4.55 (d, *J* = 3.6 Hz, 1H), 3.60 – 3.51 (m, 1H), 3.40 – 3.35 (m, 1H), 3.32 (s, 3H), 3.28 – 3.17 (m, 3H), 2.93 (dt, *J* = 14.3, 7.2 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 100.29, 74.52, 73.16, 72.32, 71.34, 55.11, 39.89, 10.00.

1-(Methyl-α-D-glucopyranosid-6-yl)-1,4-diazabicyclo[2.2.2]octan-1-ium iodide **(C3)**



The product was obtained as pale brown solid. Mp:225-230 °C (lit:147-148 °C). **$[\alpha]_D$** ^{20}=+72.5 (C=1.0, H_2O). ^{1}H NMR (400 MHz, D_2O) δ 4.79 (d, *J* = 3.8 Hz, 1H), 4.20 (t, *J* = 9.0 Hz, 1H), 3.65 (dd, *J* = 12.1, 6.6 Hz, 2H), 3.52 (ddd, *J* = 19.2, 13.7, 8.0 Hz, 8H), 3.45 (s, 3H), 3.26 – 3.14 (m, 7H). ^{13}C{^{1}H} NMR (100 MHz, D_2O) δ 100.10(C-1), 72.34, 70.94, 70.56, 65.83,65.62, 57.03, 53.36, 44.16. HRMS (ESI+): Calculated for $C_{13}H_{25}N_2O_5^+$ (M+H) m/z: 289.1758, found: 289.1761. Calculated for I^-, 126.9050; found 126.8978.

1-(Methyl-α-D-glucopyranosid-6-yl)-1,4-diazabicyclo[2.2.2]octan-1-ium hydroxide **(C4)**



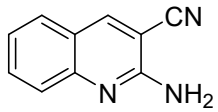
The product was obtained as yellow viscous semisolid. **$[\alpha]_D^{25}$**=+75 (C=1.0, H_2O). ^{1}H NMR (400 MHz, D_2O) δ 4.82 (d, *J* = 3.7 Hz, 1H), 4.24 (t, *J* = 9.0 Hz, 1H), 3.72 – 3.65 (m, 2H), 3.63 – 3.51 (m, 8H), 3.49 (s, 3H), 3.33 – 3.17 (m, 7H). ^{13}C{^{1}H} NMR (100 MHz, D_2O) δ 100.10(C-1), 72.34, 70.94, 70.56, 65.83,65.62, 57.03, 53.36, 44.16. HRMS (ESI+): Calculated for $C_{13}H_{25}N_2O_5^+$ (M+H) m/z: 289.1758, found: 289.1761.

11. Spectral and Analytical data of the developed products

Spectral data matched with previously reported

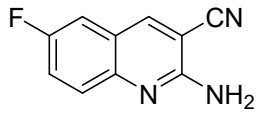
^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectral data of 2-amino-6-chloroquinoline-3-carbonitrile **3c**, 2-amino-6-bromoquinoline-3-carbonitrile **3d**, 2-amino-7-fluoroquinoline-3-carbonitrile **3e**, 2-amino-5-methylquinoline-3-carbonitrile **3g** matches with those previously reported. [1b, 2]

2-aminoquinoline-3-carbonitrile **(3a)**



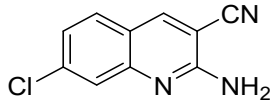
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:2) as an orange solid (79 mg, 93%). Mp: 204.2−209.1 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.68 (s, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 1H), 6.96 (s, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 156.25, 149.55, 145.74, 133.26, 128.95, 125.94, 123.22, 121.46, 116.99, 95.10. HRMS (ESI+): for $C_{10}H_7N_3$ (M+H) m/z:170.0718. Found: 170.0713.

2-amino-6-fluoroquinoline-3-carbonitrile **(3b)**



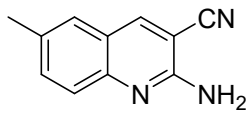
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:2) as a brown solid (74 mg, 79%).^{1}H NMR (400 MHz, DMSO-d_6) δ 8.66 (s, 1H), 7.57 (dd, *J* = 8.1, 2.6 Hz, 3H), 6.98 (s, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 158.91, 156.52, 155.95, 146.70, 145.17, 145.12, 128.42, 128.33, 123.00, 122.75, 121.38, 121.28, 116.75, 112.07, 111.86, 96.03. ^{19}F NMR (376 MHz, DMSO-d_6) δ -114.18 (dd, *J* = 14.6, 7.1 Hz). Spectral data matched with previously reported.[2]

2-amino-7-chloroquinoline-3-carbonitrile **(3f)**



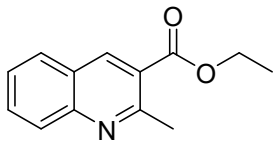
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:2) as a brown solid (85 mg, 84%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.72 (s, 1H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.52 (d, *J* = 1.5 Hz, 1H), 7.30 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.19 (s, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 156.90, 150.16, 145.79, 137.94, 130.84, 124.58, 123.67, 120.02, 116.69, 95.41. Spectral data matched with previously reported.[2]

2-amino-6-methylquinoline-3-carbonitrile **(3h)**



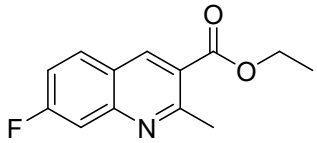
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:2) as a brown solid (75 mg, 82%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.58 (s, 1H), 7.47 (dd, *J* = 27.6, 8.1 Hz, 3H), 6.84 (s, 2H), 2.39 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 155.87, 148.03, 145.04, 135.36, 132.37, 127.59, 125.84, 121.41, 117.14, 94.85, 21.05. Spectral data matched with previously reported.[2]

Ethyl 2-methylquinoline-3-carboxylate **(6a)**



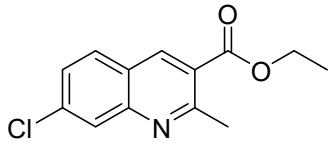
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) as a white solid (83 mg, 77%). Mp: 69-70℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.84 (t, *J* = 11.5 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 2.99 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.48, 158.41, 148.55, 139.84, 131.60, 128.47, 128.43, 126.47, 125.73, 123.91, 61.35, 25.64, 14.30. Spectral data matched with previously reported.[3]

Ethyl 7-fluoro-2-methylquinoline-3-carboxylate **(6b)**



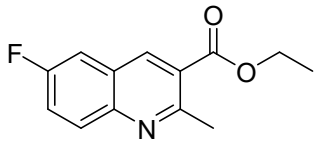
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) as a yellow solid (51 mg, 43%). Mp: 55-57℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.85 (dd, *J* = 8.9, 6.1 Hz, 1H), 7.66 (dd, *J* = 10.1, 2.3 Hz, 1H), 7.32 (td, *J* = 8.6, 2.5 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 2.97 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.21, 164.72, 162.21, 158.76, 148.72, 148.58, 138.67, 129.67, 129.57, 122.31, 122.28, 121.74, 116.25, 116.00, 111.46, 111.25, 60.43, 24.63, 13.28. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.69 (dd, *J* = 15.6, 8.5 Hz). GCMS for $C_{12}H_9FNO_3$, Calculated: 234.2064 Found: 234.2890.

Ethyl 7-chloro-2-methylquinoline-3-carboxylate **(6c)**



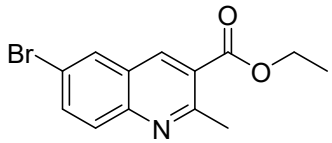
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) as a Yellow crystalline solid (101 mg, 81%). Mp: 77-79℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.10 (s, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.50 (dd, *J* = 8.7, 1.3 Hz, 1H), 4.56-4.38 (q, 2H), 3.00 (s, 3H), 1.45 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.20, 159.77, 148.87, 139.52, 137.63, 129.59, 127.71, 127.64, 124.10, 61.53, 25.72, 14.31. The spectral data matches with the previously reported.[5]

Ethyl 6-fluoro-2-methylquinoline-3-carboxylate **(6d)**



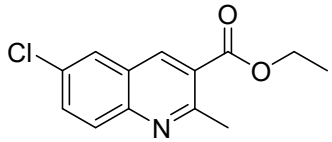
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) as a viscous brown solid (56 mg, 48%). Mp: 70-71 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.16 (s, 1H), 7.57 (td, *J* = 8.8, 2.7 Hz, 1H), 7.50 (dd, *J* = 8.4, 2.7 Hz, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 3.01 (s, 3H), 1.46 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.11, 160.55, 158.08, 156.70, 156.67, 144.24, 138.34, 138.29, 129.78, 129.70, 125.36, 125.26, 123.74, 121.05, 120.80, 110.39, 110.17, 60.60, 24.22, 13.27. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.28 – -113.39 (m). GCMS for $C_{12}H_9FNO_3$, Calculated: 234.2064 Found: 234.5671.

Ethyl 6-bromo-2-methylquinoline-3-carboxylate **(6e)**



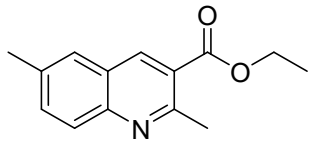
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) as an off-white solid (112 mg, 76%). Mp: 80-83 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.02 (d, *J* = 1.5 Hz, 1H), 7.94 (d, *J* = 8.9 Hz, 1H), 7.83 (dd, *J* = 9.0, 1.8 Hz, 1H), 4.45-4.40 (q, 2H), 2.98 (s, 3H), 1.45 (q, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.96, 157.90, 145.73, 137.89, 134.07, 129.28, 129.00, 125.87, 123.79, 119.36, 60.62, 24.43, 13.27. The spectral data matches with the previously reported.[4]

Ethyl 6-chloro-2-methylquinoline-3-carboxylate **(6f)**



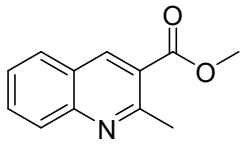
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) as a crystalline yellow solid (102 mg, 81%). Mp: 75-76 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.04 (d, *J* = 9.0 Hz, 1H), 7.84 (d, *J* = 1.8 Hz, 1H), 7.71 (dd, *J* = 9.0, 2.1 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 2.99 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.22, 158.80, 146.94, 139.78, 132.45, 132.20, 126.94, 126.37, 124.85, 61.61, 25.63, 14.31. The spectral data matches with the previously reported.[6]

Ethyl 2,6-dimethylquinoline-3-carboxylate **(6g)**



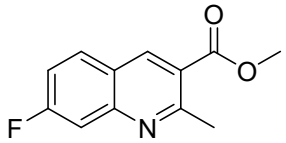
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) as a yellow solid (76 mg, 66%). Mp: 60-62 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 7.64 (d, *J* = 6.7 Hz, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 3.03 (s, 3H), 2.55 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.31, 157.42, 146.32, 139.95, 136.85, 134.43, 127.51, 127.25, 125.85, 123.93, 61.47, 25.06, 21.49, 14.31. The spectral data matches with the previously reported.[7]

Methyl 2-methyl quinoline-3-carboxylate **(7a)**



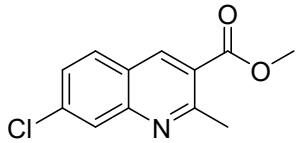
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) as a brown solid (79 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 3.97 (s, 3H), 2.99 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.82, 158.47, 148.52, 140.09, 131.77, 128.47, 128.39, 126.56, 125.69, 123.48, 52.34, 25.56. The spectral data matches with the previously reported.[3]

Methyl 7-fluoro-2-methyl quinoline-3-carboxylate **(7b)**



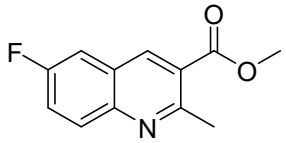
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) as a cream solid (67 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.86 (dd, *J* = 8.9, 6.1 Hz, 1H), 7.67 (dd, *J* = 10.1, 2.2 Hz, 1H), 7.33 (td, *J* = 8.7, 4.4 Hz, 1H), 3.98 (s, 3H), 2.98 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.56, 165.94, 163.42, 159.86, 149.43, 140.15, 130.80, 130.69, 122.98, 122.81, 117.54, 117.29, 112.39, 112.19, 52.46, 25.50. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.02. GCMS for $C_{12}H_{10}FNO_2$, calculated: 219.2154, Found: 219.2159.

Methyl 7-chloro-2-methylquinoline-3-carboxylate **(7c)**



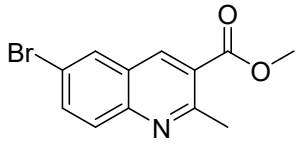
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) as a white solid (88 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.20 (s, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 3.99 (s, 3H), 3.05 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.52, 159.82, 148.75, 139.86, 137.91, 129.63, 127.81, 127.61, 124.10, 123.72, 52.48, 25.58. GCMS for $C_{12}H_{10}ClNO_2$, Calculated: 235.6670, Found: 236.8432.

Methyl 6-fluoro-2-methyl quinoline-3-carboxylate **(7d)**



Purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) as a white solid (67 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.02 (dd, *J* = 9.1, 5.2 Hz, 1H), 7.52 (td, *J* = 9.1, 2.6 Hz, 1H), 7.44 (dd, *J* = 8.4, 2.3 Hz, 1H), 3.97 (s, 3H), 2.95 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.52, 161.52, 159.05, 157.71, 145.46, 139.33, 130.92, 130.83, 126.27, 126.17, 124.27, 122.03, 121.78, 111.37, 111.16, 52.46, 25.30. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.22 (dd, *J* = 13.6, 8.2 Hz). GCMS for $C_{12}H_{10}FNO_2$, Calculated: 219.2154, Found: 219.2138.

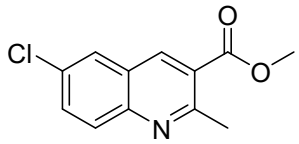
Methyl 6-bromo-2-methylquinoline-3-carboxylate **(7e)**



Purified by column chromatography on silica gel (hexane/ethyl acetate10:1) as a white solid (86 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.01 (d, *J* = 2.1 Hz, 1H), 7.91 (t, *J* = 8.7 Hz, 1H), 7.84 (dd, *J* = 9.0, 2.1 Hz, 1H), 3.99 (d, *J* = 5.3 Hz, 3H), 2.97 (s, 3H). ^{13}C{^{1}H}

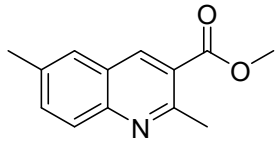
NMR (100 MHz, $CDCl_3$) δ 166.56, 159.00, 147.21, 138.84, 135.07, 130.33, 126.88, 124.41, 120.29, 52.53, 25.65. GCMS for $C_{12}H_{10}BrNO_2$, Calculated: 280.1210, Found: 280.1308.

Methyl 6-chloro-2-methylquinoline-3-carboxylate **(7f)**



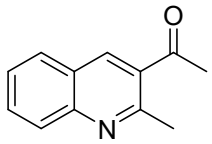
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) as a pink solid (80 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 7.86 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 3.99 (s, 3H), 3.02 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.48, 158.84, 146.70, 139.19, 132.72, 132.43, 130.00, 126.97, 126.37, 124.49, 52.56, 25.43. GCMS for $C_{12}H_{10}ClNO_2$, Calculated: 235.6670, Found: 235.6824.

Methyl 2,6-dimethylquinoline-3-carboxylate **(7g)**



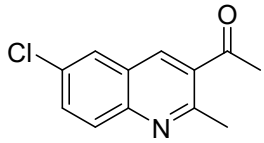
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) as a yellow solid (64 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.25 (d, *J* = 7.9 Hz, 1H), 7.76-7.64 (m, 2H), 4.00 (s, 3H), 3.11 (s, 3H), 2.57 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.95, 157.50, 147.00, 139.64, 136.59, 134.23, 127.98, 127.24, 125.78, 123.48, 52.34, 25.39, 21.49. GCMS for $C_{13}H_{13}NO_2$, Calculated: 215.2520, Found: 215.2663.

1-(2-methylquinolin-3-yl)ethan-1-one **(9a)**



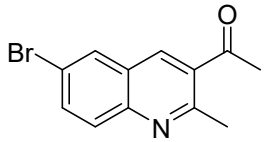
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) as a brown crystalline solid (83 mg, 90%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.81-7.75 (m, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 2.92 (s, 3H), 2.71 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.82, 157.55, 148.12, 138.24, 131.72, 131.02, 128.44, 128.34, 126.66, 125.57, 29.18, 25.58. The spectral data matches with the previously reported.[3]

1-(6-chloro-2-methylquinolin-3-yl)ethan-1-one **(9b)**



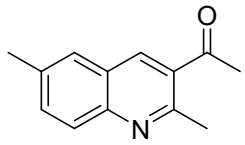
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) as an off-white solid (57 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.98 (d, *J* = 9.0 Hz, 1H), 7.85 (d, *J* = 2.2 Hz, 1H), 7.72 (dd, *J* = 9.0, 2.3 Hz, 1H), 2.89 (s, 3H), 2.71 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.72, 157.85, 146.57, 136.85, 132.46, 132.38, 131.99, 130.22, 126.83, 126.27, 29.31, 25.48. The spectral data matches with the previously reported.[6]

1-(6-bromo-2-methylquinolin-3-yl)ethan-1-one **(9c)**



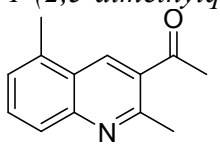
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) as a off-white solid (84 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.03 (d, *J* = 2.0 Hz, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.84 (dd, *J* = 9.0, 2.1 Hz, 1H), 2.89 (s, 3H), 2.71 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.70, 158.03, 146.78, 136.77, 135.01, 131.96, 130.32, 130.20, 126.81, 120.41, 29.32, 25.53. GCMS for $C_{12}H_{10}BrNO$, Calculated: 264.1220. Found: 264.2200.

1-(2,6-dimethylquinolin-3-yl)ethan-1-one **(9d)** ***new***



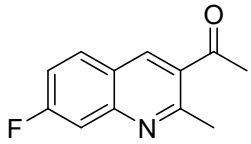
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) as a brown solid (88 mg, 88%). Mp: 85-87 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.97-7.88 (m, 1H), 7.68-7.57 (m, 2H), 2.90 (s, 3H), 2.71 (s, 3H), 2.55 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.03, 156.60, 146.77, 137.71, 136.63, 134.07, 131.08, 128.10, 127.15, 125.66, 29.21, 25.43, 21.48. HRMS (ESI+): Calculated for $C_{13}H_{13}NO$ (M+H) m/z: 200.1075. Found: 200.1083.

1-(2,5-dimethylquinolin-3-yl)ethan-1-one **(9e)** ***new***



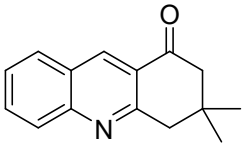
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) as a yellow solid (86 mg, 86%). Mp: 93-94 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.66 (dd, *J* = 8.3, 7.2 Hz, 1H), 7.37 (d, *J* = 7.0 Hz, 1H), 2.91 (s, 3H), 2.73 (d, *J* = 4.3 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.25, 156.93, 148.61, 135.38, 134.49, 131.49, 130.80, 127.24, 126.78, 125.00, 29.34, 25.43, 18.49. HRMS (ESI+): Calculated for $C_{13}H_{13}NO$ (M+H) m/z: 200.1075. Found: 200.1083.

1-(7-fluoro-2-methylquinolin-3-yl)ethan-1-one **(9f)** ***new***



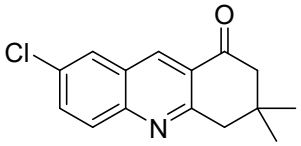
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:2) as a cream solid (78 mg, 77%). Mp: 80-82 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.87 (dd, *J* = 8.9, 6.0 Hz, 1H), 7.67 (dd, *J* = 10.1, 2.2 Hz, 1H), 7.35 (td, *J* = 8.6, 2.4 Hz, 1H), 2.91 (s, 3H), 2.71 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.52, 164.80, 162.28, 157.97, 148.48, 148.35, 136.96, 129.54, 129.48, 129.44, 121.59, 116.38, 116.12, 111.68, 111.48, 28.13, 24.68. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.69 (dd, *J* = 16.0, 8.4 Hz). HRMS (ESI+): Calculated for $C_{12}H_{10}FNO$ (M+H) m/z: 204.0824. Found: 204.0828.

3,3-dimethyl-3,4-dihydroacridin-1(2H)-one **(11a)**



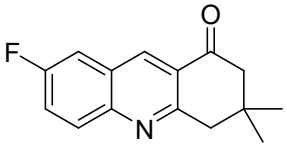
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:2) as a yellow solid (51mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.86-7.76 (m, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 3.21 (s, 2H), 2.65 (s, 2H), 1.15 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.94, 160.81, 149.94, 136.59, 132.26, 129.77 ,128.55, 126.77, 126.73, 125.30, 52.49, 47.17, 32.78, 28.39. The spectral data matches with the previously reported.[3]

7-chloro-3,3-dimethyl-3,4-dihydroacridin-1(2H)-one **(11b)**



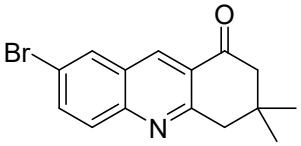
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:2) as a yellow solid (75 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.99 (d, *J* = 9.0 Hz, 1H), 7.91 (d, *J* = 2.2 Hz, 1H), 7.73 (dd, *J* = 9.0, 2.3 Hz, 1H), 3.18 (s, 2H), 2.66 (s, 2H), 1.15 (d, *J* = 2.8 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.61, 161.10, 148.30, 135.49, 133.01, 130.20, 128.05, 127.35, 125.87, 52.42, 47.08, 32.74, 28.37. The spectral data matches with the previously reported.[6]

7-fluoro-3,3-dimethyl-3,4-dihydroacridin-1(2H)-one **(11c)**



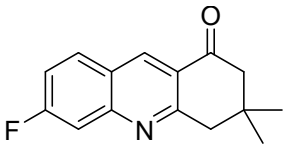
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:2) as a cream solid (51 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.05 (dd, *J* = 9.1, 5.2 Hz, 1H), 7.61-7.51 (m, 2H), 3.18 (s, 2H), 2.66 (s, 2H), 1.15 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.77, 161.56, 160.13, 160.10, 159.08, 147.14, 135.84, 135.78, 131.14, 131.05, 127.39, 127.29, 125.75, 122.62, 122.37, 112.44, 112.23, 52.47, 47.03, 32.79, 28.38. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.84 (dd, *J* = 13.5, 8.1 Hz). The spectral data matches with the previously reported.[8]

7-bromo-3,3-dimethyl-3,4-dihydroacridin-1(2H)-one **(11d)**



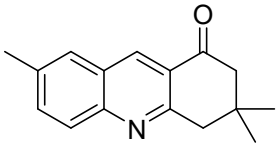
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:2) as a yellow solid (70 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.09 (d, *J* = 2.1 Hz, 1H), 7.92 (d, *J* = 9.1 Hz, 1H), 7.85 (dd, *J* = 9.0, 2.1 Hz, 1H), 3.17 (d, *J* = 12.1 Hz, 2H), 2.66 (s, 2H), 1.15 (d, *J* = 2.3 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.60, 161.26, 148.53, 135.53, 135.40, 131.46, 130.32, 127.91, 125.85, 120.47, 52.44, 47.15, 32.75, 28.38. GCMS for $C_{15}H_{14}BrNO$, Calculated: 304.1870. Found: 303.2639.

6-fluoro-3,3-dimethyl-3,4-dihydroacridin-1(2H)-one **(11e)** ***new***



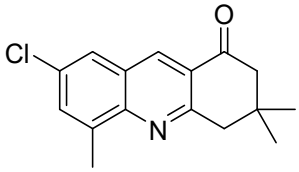
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:2) as yellow crystalline solid (79 mg, 65%). Mp: 105-107 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.93 (dd, *J* = 8.9, 6.2 Hz, 1H), 7.66 (dd, *J* = 10.1, 1.8 Hz, 1H), 7.33 (td, *J* = 8.7, 2.2 Hz, 1H), 3.17 (s, 2H), 2.64 (s, 2H), 1.14 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.62, 166.05, 163.52, 162.03, 151.25, 151.11, 136.29, 132.05, 131.94, 124.82, 124.79, 123.82, 117.62, 117.36, 112.60, 112.39, 52.36, 47.12, 32.73, 28.35. ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.30 (dd, *J* = 15.5, 8.5 Hz). HRMS (ESI+): Calculated for $C_{15}H_{14}FNO$ (M+H) m/z: 244.1137. Found: 244.1131.

3,3,7-trimethyl-3,4-dihydroacridin-1(2H)-one **(11f)**



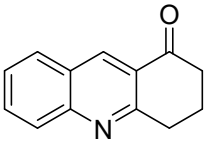
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:2) as a yellow solid (50 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.95 (d, *J* = 8.6 Hz, 1H), 7.73-7.59 (m, 2H), 3.18 (s, 2H), 2.65 (s, 2H), 2.55 (s, 3H), 1.15 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.16, 159.90 (s), 148.65, 136.66, 135.86, 134.66, 128.40, 126.82, 125.29, 52.54, 47.11, 32.81, 28.40, 21.48. GCMS for $C_{14}H_{13}NO$, Calculated: 211.2640. Found: 211.3149.

7-chloro-3,3,5-trimethyl-3,4-dihydroacridin-1(2H)-one **(11g)*[new]***



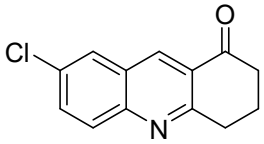
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) as a yellow solid (103.2 mg, 76%). Purified by hexane/AcOEt = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.73 (d, *J* = 2.2 Hz, 1H), 7.58 (d, *J* = 1.2 Hz, 1H), 3.20 (s, 2H), 2.78 (s, 3H), 2.64 (s, 2H), 1.15 (d, *J* = 3.0 Hz, 6H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 198.04, 159.90, 147.61, 139.03, 135.51, 132.64, 131.80, 127.70, 127.32, 125.81, 125.59, 52.54, 47.30, 32.79, 28.39, 17.82. HRMS (ESI+): Calculated for $C_{16}H_{16}ClNO$ (M+H) m/z: 274.0998. Found: 274.0993.

3,4-dihydroacridin-1(2H)-one **(13a)**



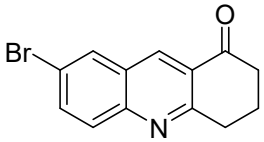
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:2.5) as an orange crystalline solid (56 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.81 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.59-7.51 (m, 1H), 3.36-3.28 (m, 2H), 2.83-2.75 (m, 2H), 2.33 – 2.23 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.88, 161.93, 149.64, 137.09, 132.32, 129.71, 128.55, 126.81, 126.67, 126.31, 39.06, 33.42, 21.75. The spectral data matches with the previously reported.[3]

7-chloro-3,4-dihydroacridin-1(2H)-one **(13b)**



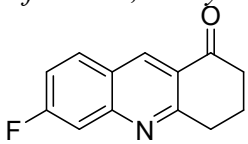
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:2.5) as a green solid (41 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.98 (d, *J* = 9.0 Hz, 1H), 7.90 (d, *J* = 2.1 Hz, 1H), 7.73 (dd, *J* = 9.0, 2.3 Hz, 1H), 3.33-3.28 (m, 2H), 2.84-2.77 (m, 2H), 2.31-2.24 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.53 (s), 162.22 (s), 147.95, 136.06, 133.14, 132.42, 130.18, 128.01, 127.38, 126.88, 39.01, 33.33, 21.61. The spectral data matches with the previously reported.[9]

7-bromo-3,4-dihydroacridin-1(2H)-one **(13c)**



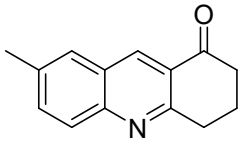
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:2.5) as a brown solid (53 mg, 38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.07 (d, *J* = 2.0 Hz, 1H), 7.91 (d, *J* = 8.9 Hz, 1H), 7.85 (dd, *J* = 9.0, 2.1 Hz, 1H), 3.30 (dd, *J* = 12.8, 6.5 Hz, 2H), 2.83-2.77 (m, 2H), 2.32-2.23 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.50, 162.38, 148.14, 135.97, 135.65, 131.41, 130.26, 127.92, 126.86, 120.47, 39.01, 33.36, 21.59 (d, *J* = 16.2 Hz). GCMS for $C_{13}H_{10}BrNO$ Calculated: 276.1330. Found: 276.1267.

6-fluoro-3,4-dihydroacridin-1(2H)-one **(13d)**



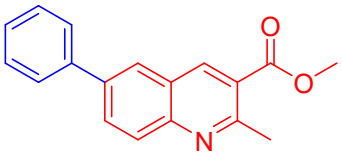
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:2.5) as a white solid (46 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 7.94 (dd, *J* = 9.0, 6.1 Hz, 1H), 7.67 (dd, *J* = 10.1, 2.3 Hz, 1H), 7.34 (td, *J* = 8.6, 2.5 Hz, 1H), 3.30 (t, *J* = 6.3 Hz, 2H), 2.83-2.76 (m, 2H), 2.31-2.24 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.58, 166.21, 163.68, 163.15, 150.81, 150.68, 137.02, 132.07, 131.97, 125.85, 125.83, 123.91, 117.74, 117.48, 112.49, 112.29, 38.95, 33.31, 21.63. ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.14 (dd, *J* = 16.2, 8.3 Hz). GCMS for $C_{13}H_{10}FNO$, Calculated: 215.2274. Found: 215.2126.

7-methyl-3,4-dihydroacridin-1(2H)-one **(13e)**



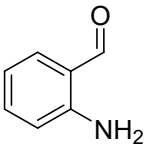
Purified by column chromatography on silica gel (hexane/ethyl acetate 10:2.5) as a brown solid (41 mg, 39%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.94 (d, *J* = 8.6 Hz, 1H), 7.69-7.62 (m, 2H), 3.34-3.26 (m, 2H), 2.82-2.76 (m, 2H), 2.54 (s, 3H), 2.26 (dd, *J* = 12.8, 6.2 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.09, 161.02, 148.23, 136.65, 136.43, 134.81, 128.35, 128.12, 126.85, 126.28, 39.09, 33.28, 21.80, 21.49. GCMS for $C_{14}H_{13}NO$, Calculated: 211.2640. Found: 211.2348.

*Methyl 2-methyl-6-phenylquinoline-3-carboxylate (**15**)*



Purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) as cream solid (10.73 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.11 (d, J = 8.5 Hz, 1H), 8.07 – 8.00 (m, 2H), 7.70 (d, J = 7.4 Hz, 2H), 7.50 (t, J = 7.6 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 3.99 (d, J = 4.8 Hz, 3H), 3.00 (d, J = 5.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 166.92, 158.52, 147.97, 140.29, 139.93, 139.40, 131.56, 129.63, 129.05, 127.91, 127.38, 126.04, 123.94, 115.47, 52.44, 25.64. HRMS (ESI+): Calculated for $C_{18}H_{15}NO_2$ (M+H) m/z: 278.1180. Found: 278.1176.

2-aminobenzaldehyde **(1)**



Obtained as yellow liquid (53 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.33 (t, J = 6.9 Hz, 1H), 6.76 (t, J = 7.2 Hz, 1H), 6.67 (d, J = 7.8 Hz, 1H), 6.14 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 193.37, 149.24, 135.02, 134.51, 118.14, 115.64, 115.47.

12. References

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^{1}H, $^{13}C\{^{1}H\}$ NMR and HRMS spectra of the developed catalysts (Glu-I, GSIL-I and GSIL-II).

Figure S5. ^{1}H NMR spectrum of **C2** (DMSO-d_6, 400 MHz)

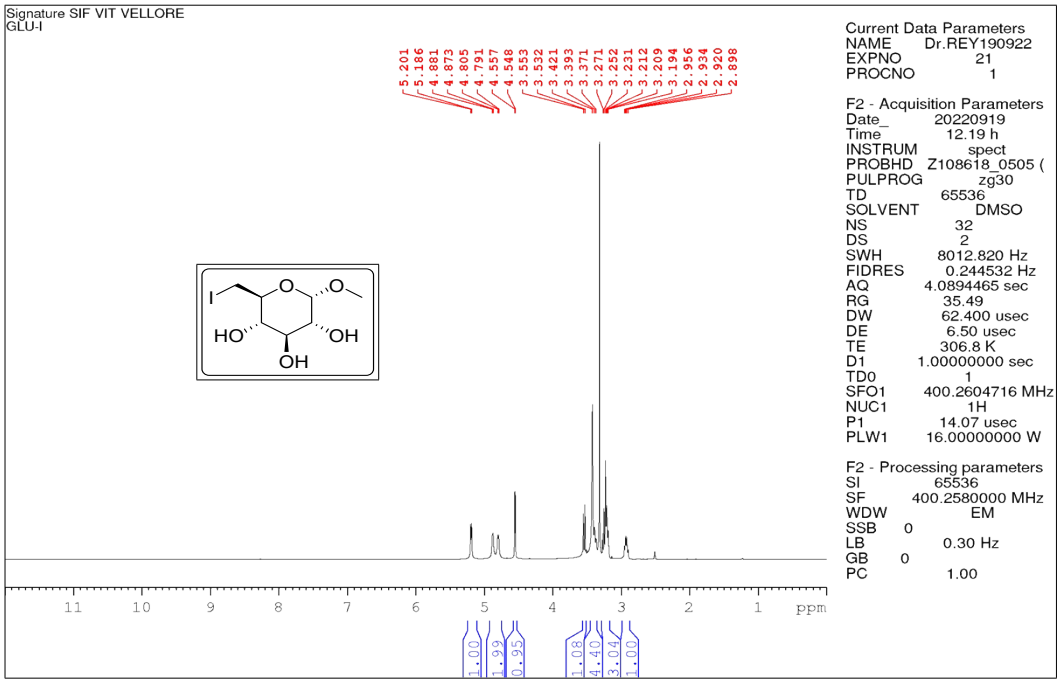


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **C2** (DMSO-d_6, 100 MHz)

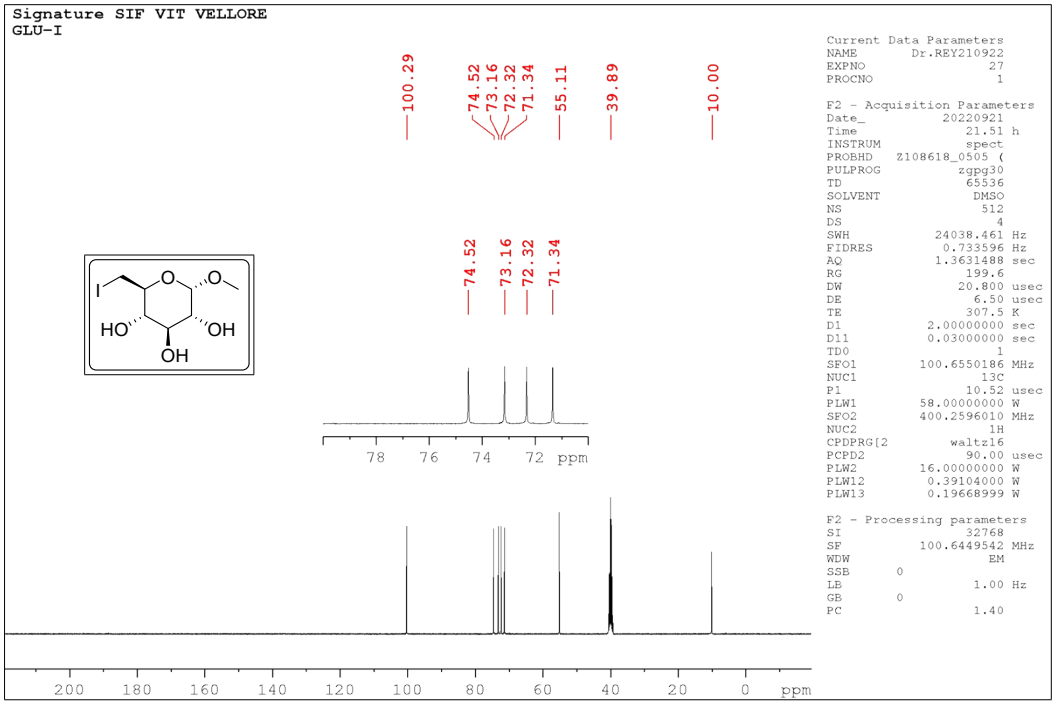


Figure S7. ^{1}H NMR spectrum of **GSIL I** (I^- form, **C3**) (D_2O, 400 MHz)

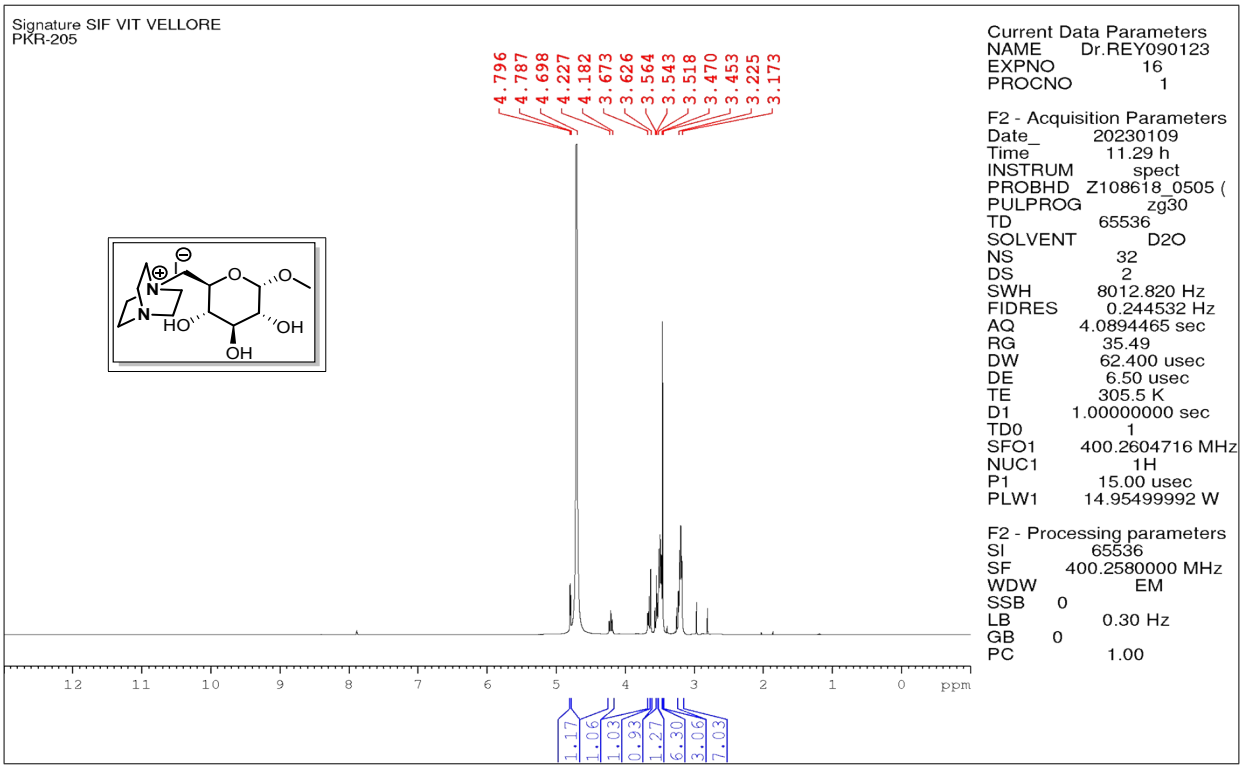


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **GSIL I** (I^- form, **C3**) (D_2O, 100 MHz)

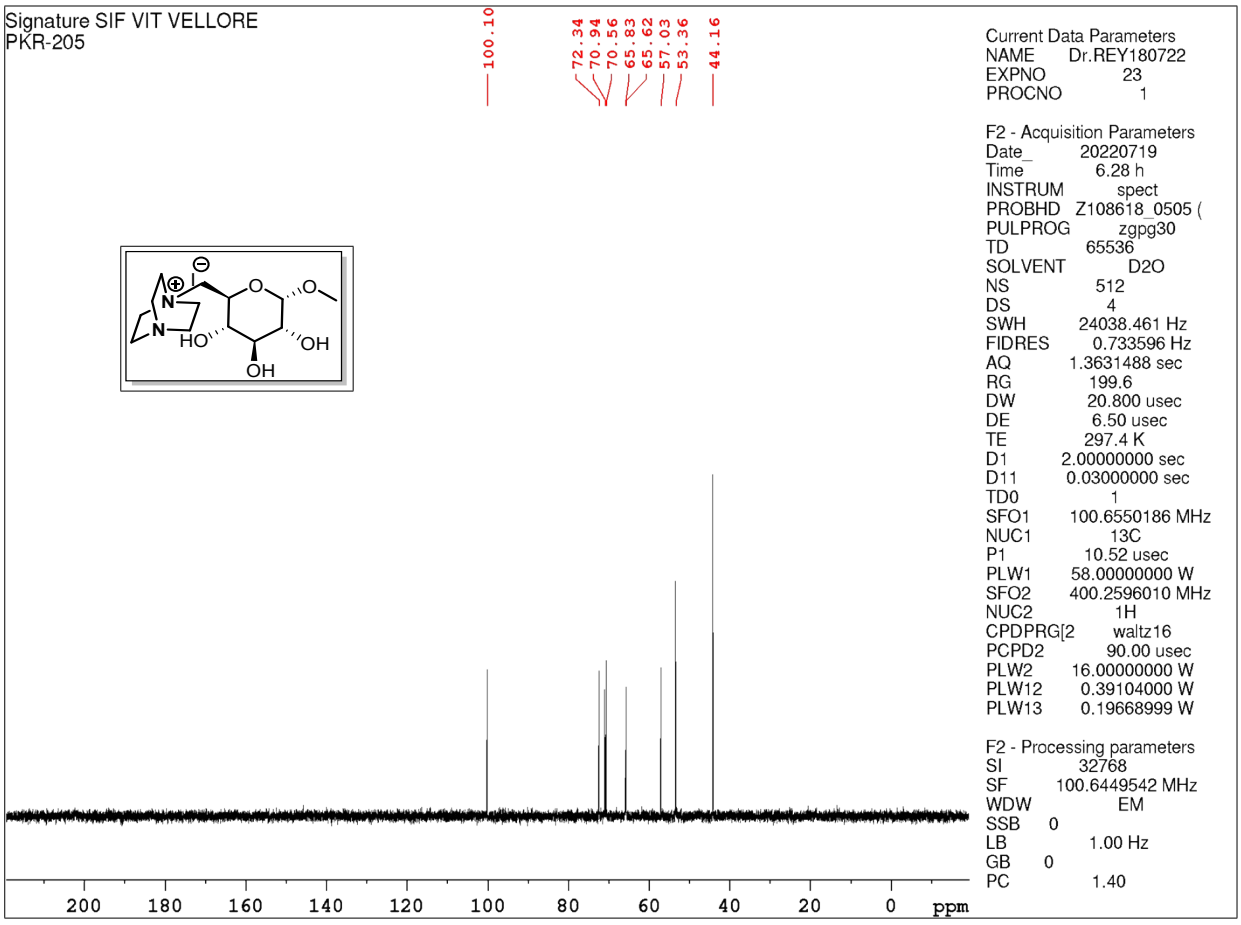
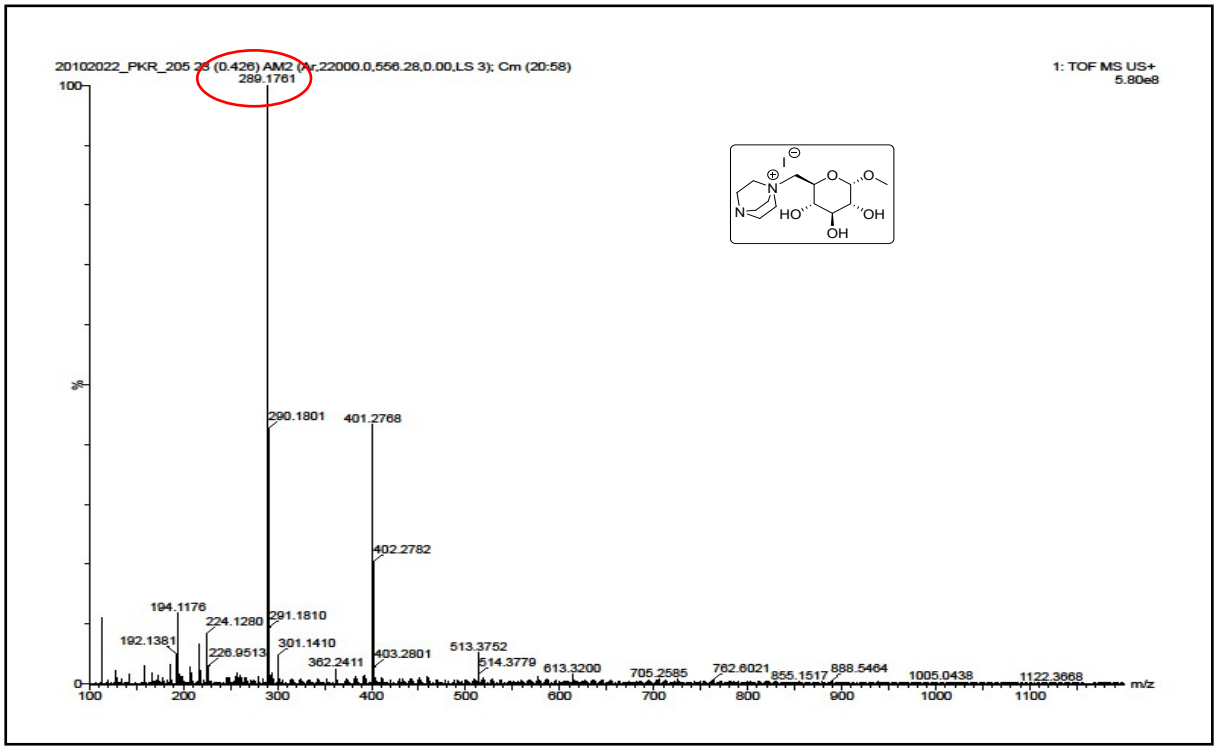


Figure S9. HRMS Spectra of GSIL I (I^- form, **C3**)



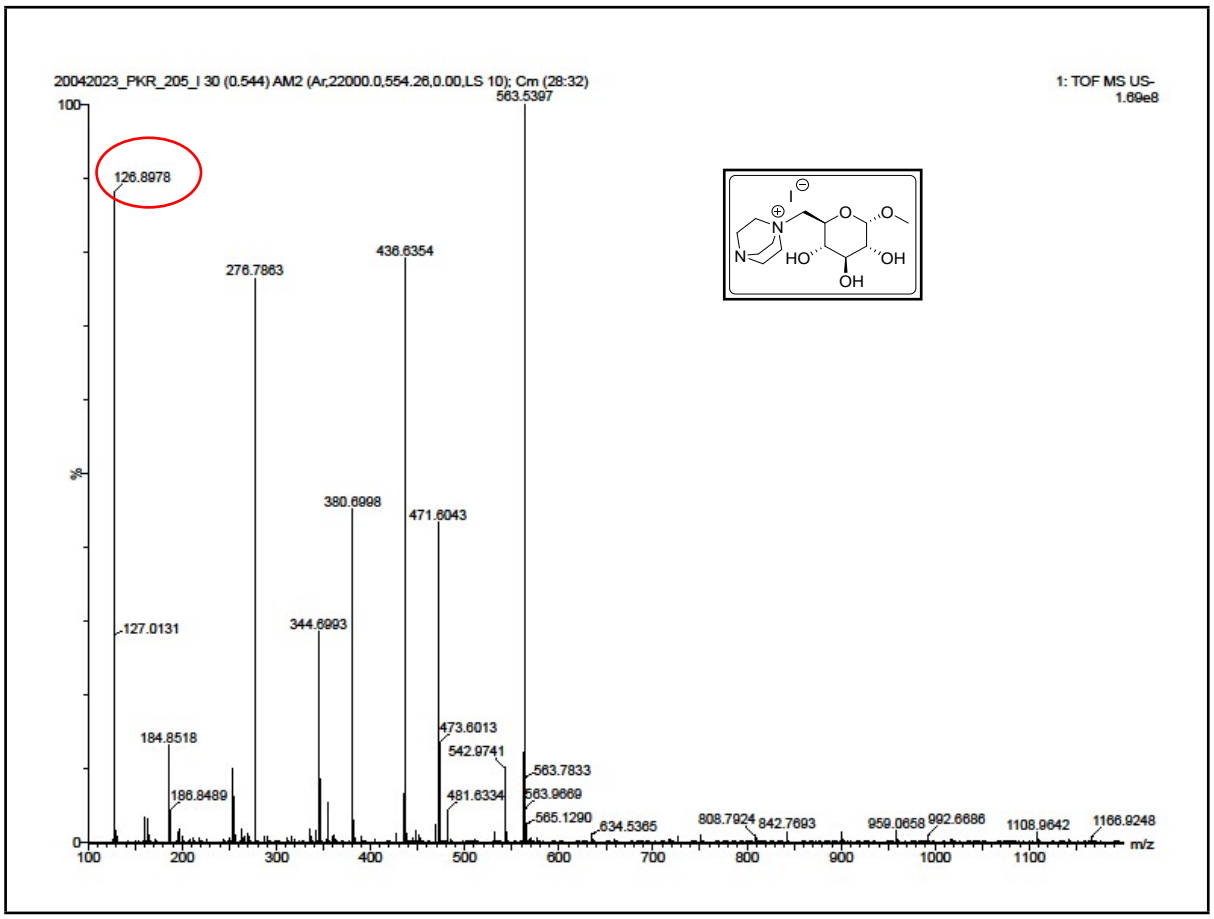


Figure S10. ^{1}H NMR spectrum of **GSIL II** (OH^- form, **C4**) (D_2O, 400 MHz)

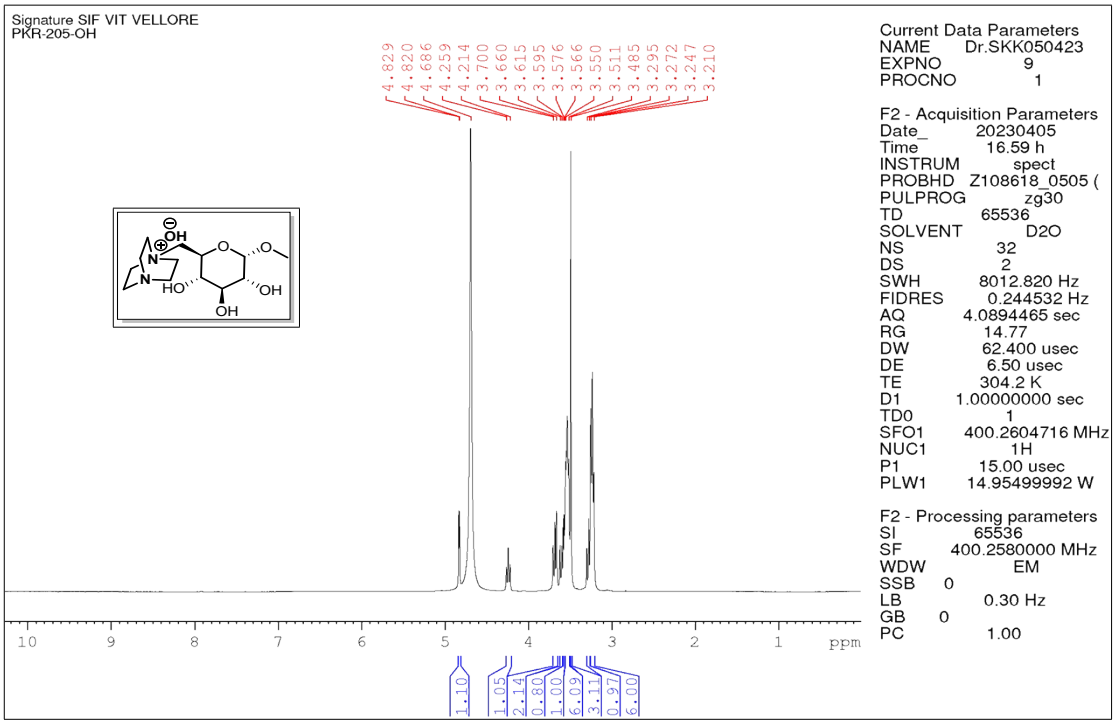
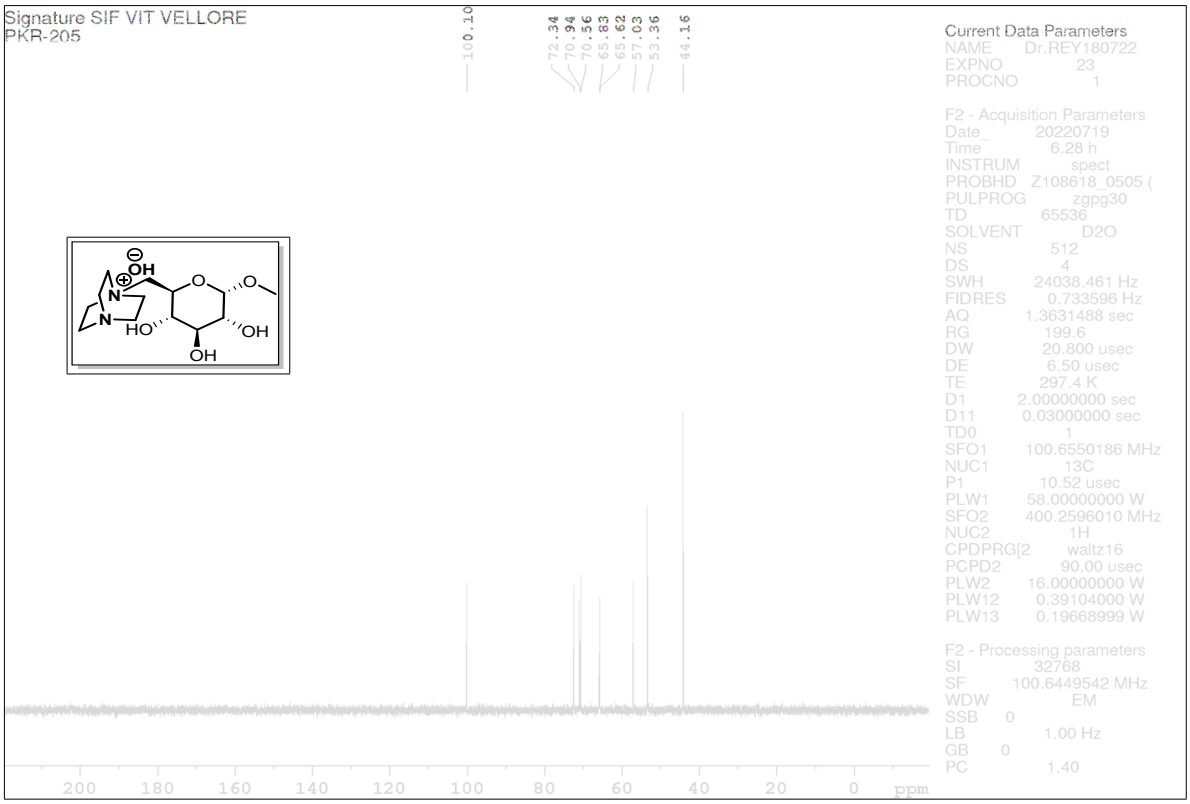


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **GSIL II** (OH^- form, **C4**) (D_2O, 100 MHz)



Copies of ^{1}H NMR, $^{13}C\{^{1}H\}$ NMR, and ^{19}F NMR Spectra of developed products

Figure S12. ^{1}H NMR spectrum of **3a** (DMSO-d_6, 400 MHz)

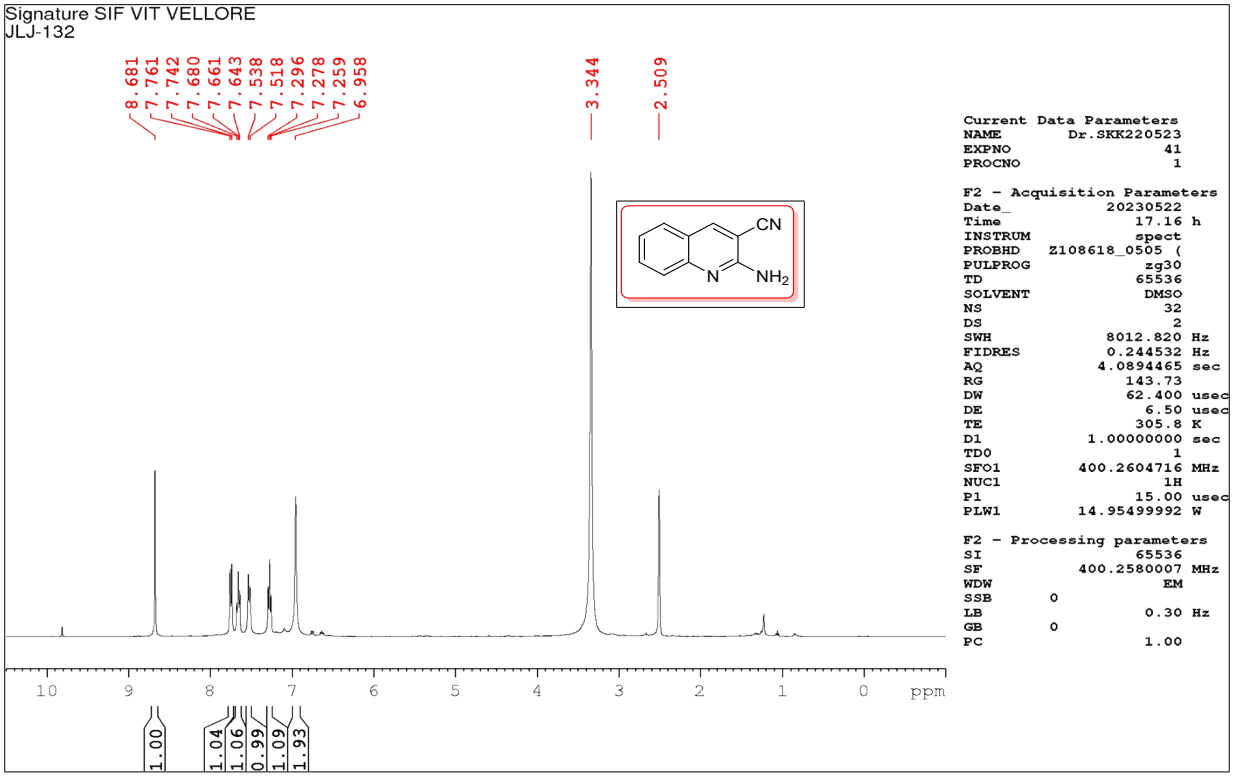


Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of **3a** (DMSO-d_6, 100 MHz)

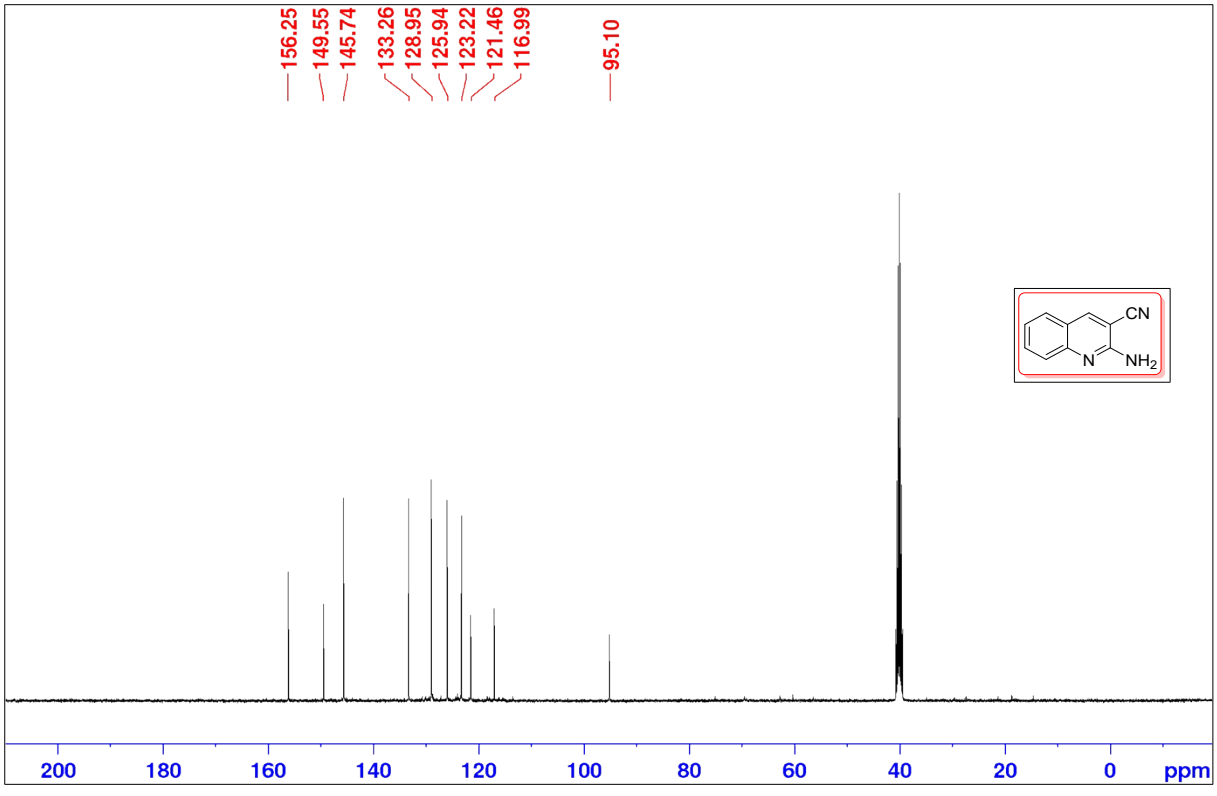


Figure S14. ^{1}H NMR spectrum of **3b** (DMSO-d_6, 400 MHz)

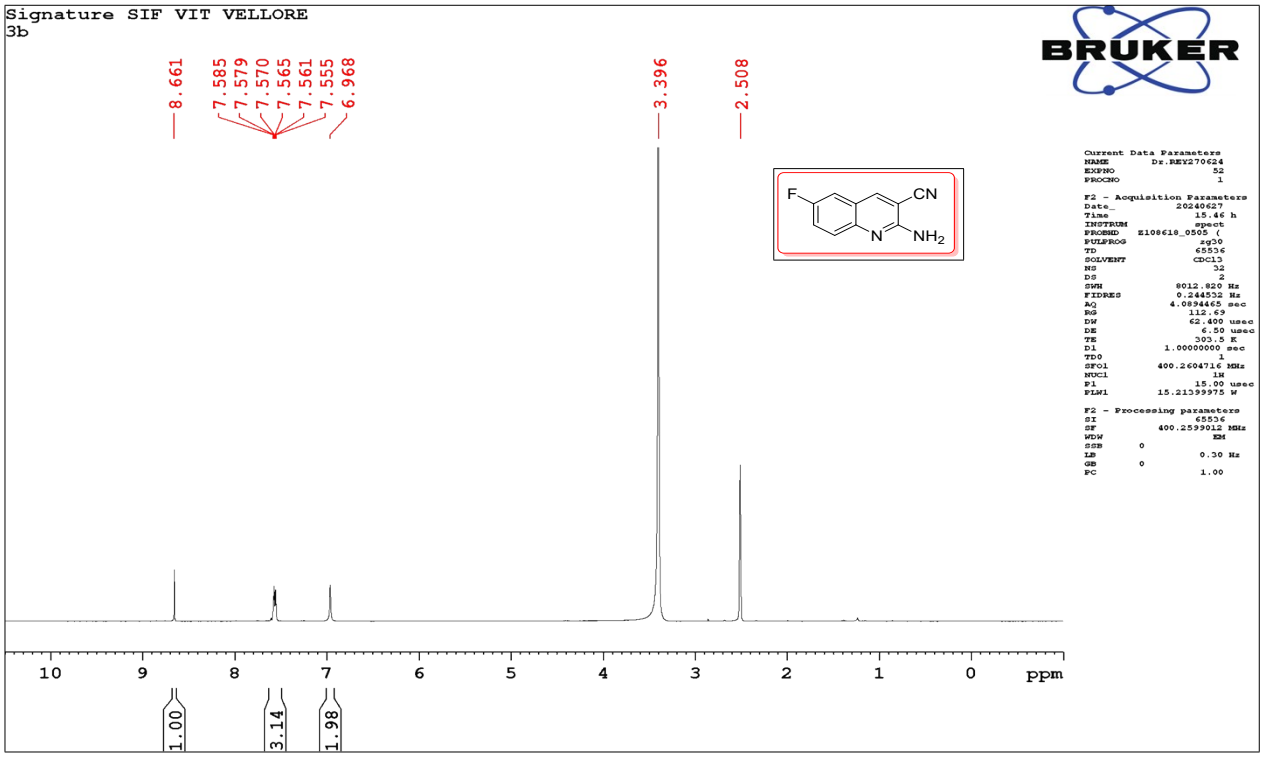


Figure S15. ^{13}C{^{1}H} NMR spectrum of **3b** (DMSO-d_6, 100 MHz)

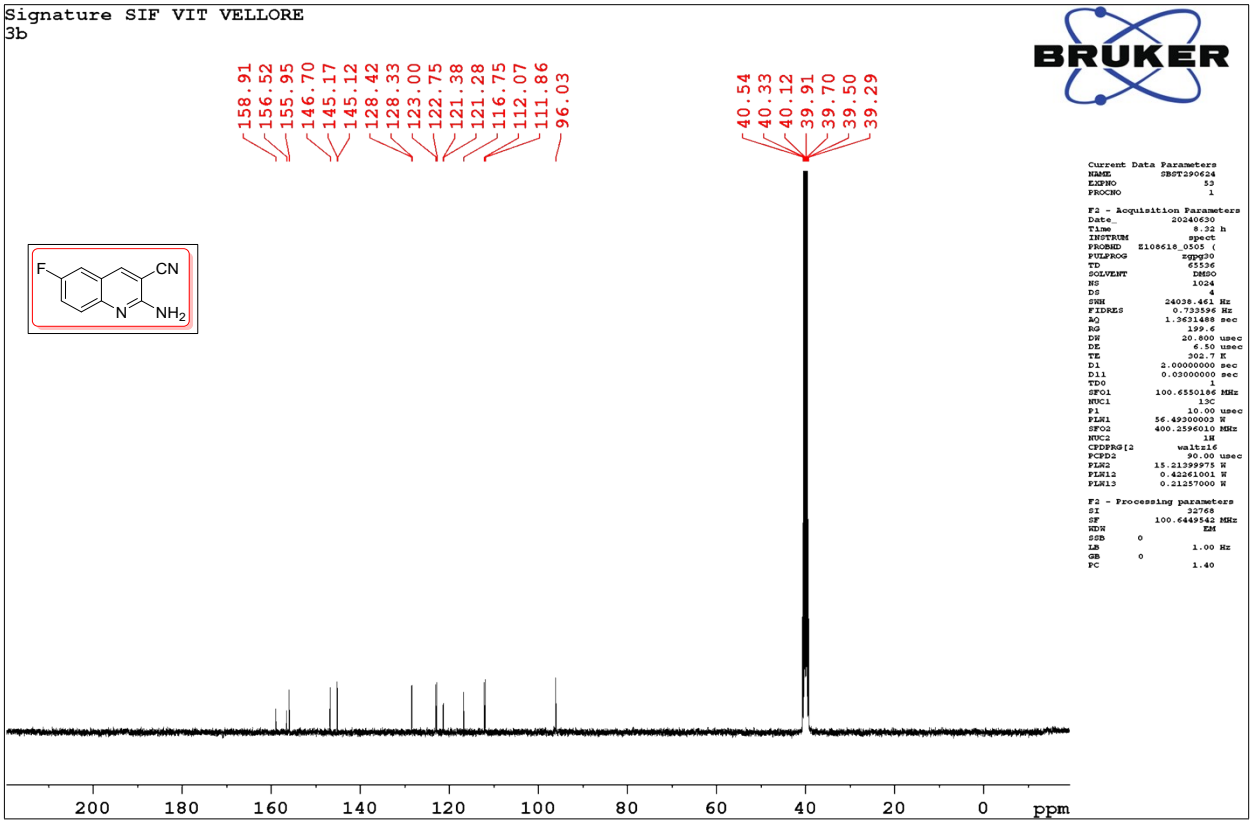


Figure S16. ^{19}F NMR spectrum of **3b** (DMSO-d_6, 376 MHz)

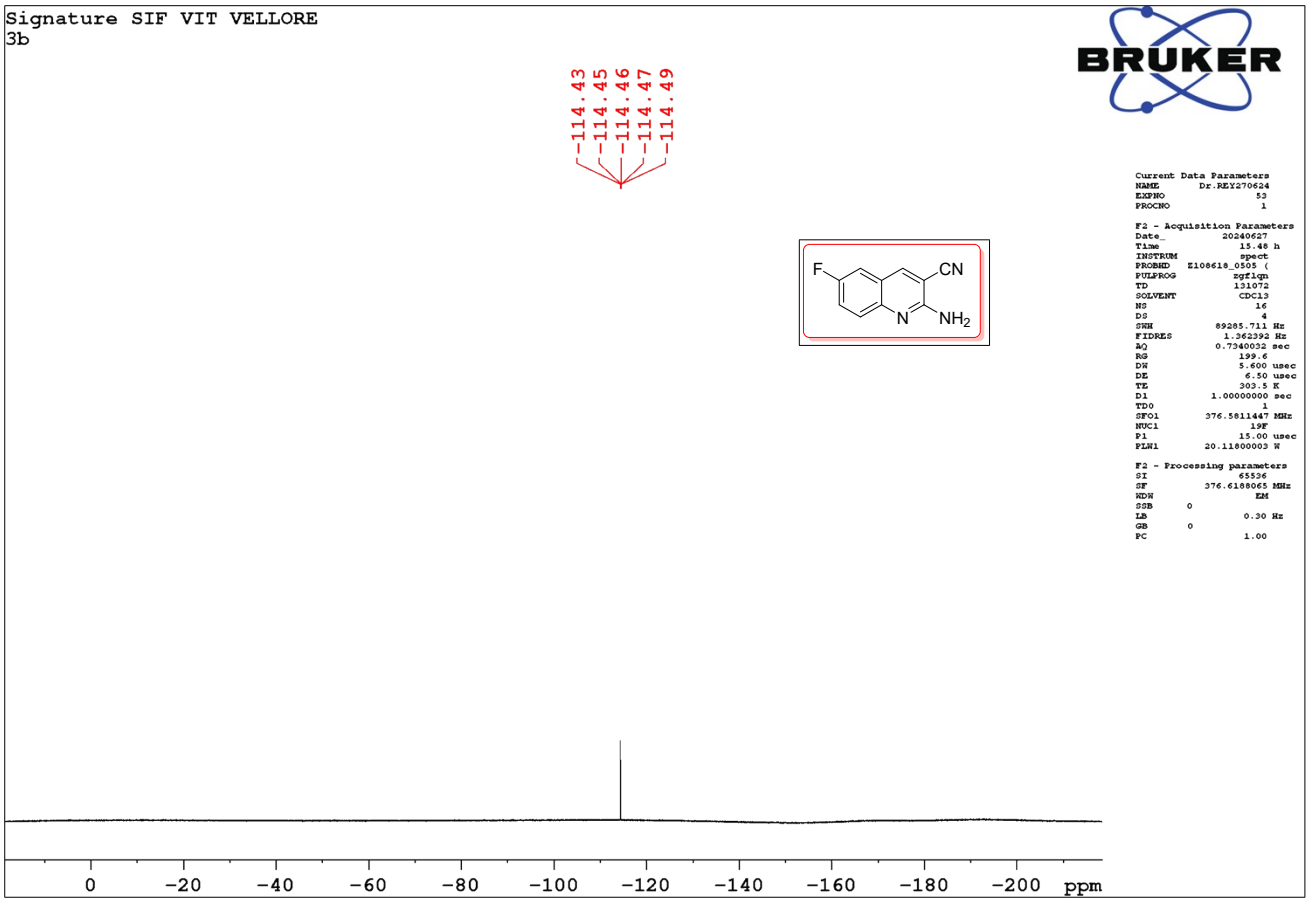


Figure S17. ^{1}H NMR spectrum of **3f** (DMSO-d_6, 400 MHz)

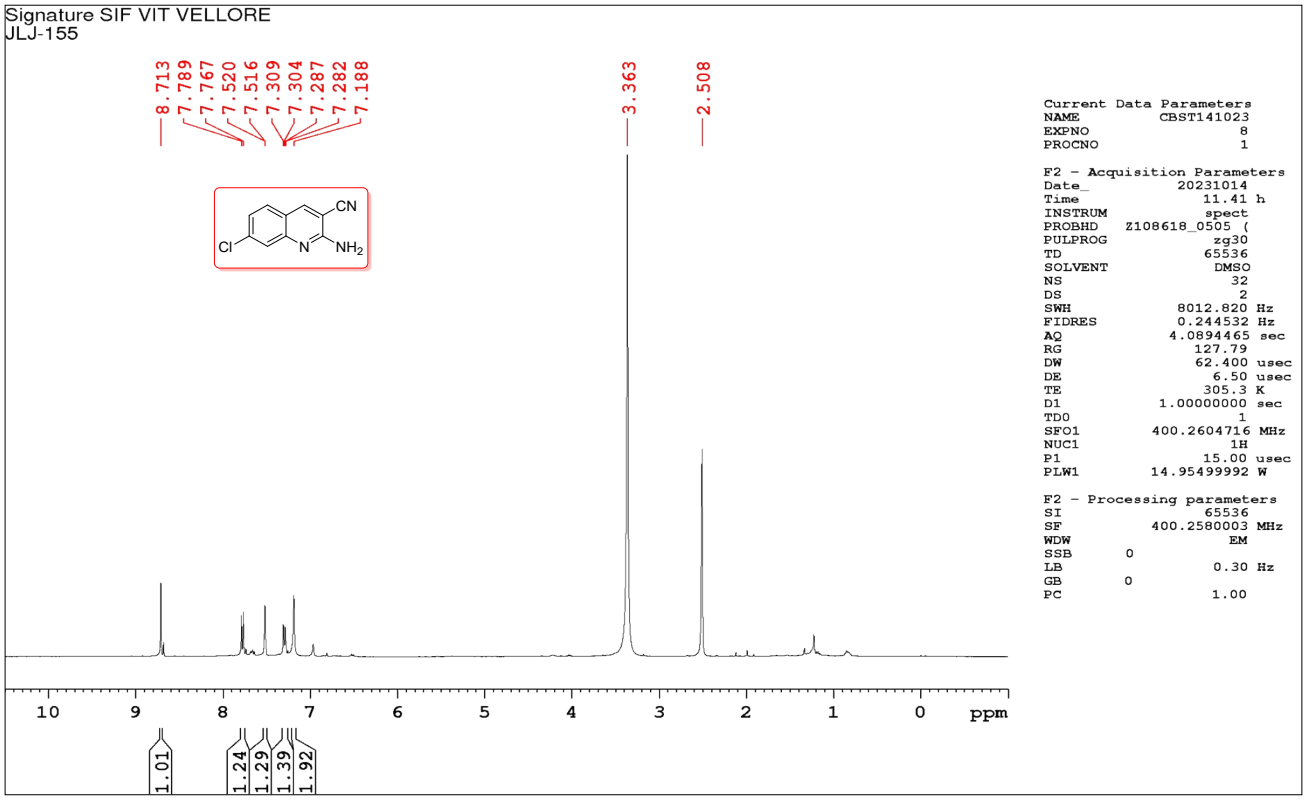


Figure S18. $^{13}C\{^{1}H\}$ NMR of compound **3f** (DMSO-d_6, 100 MHz)

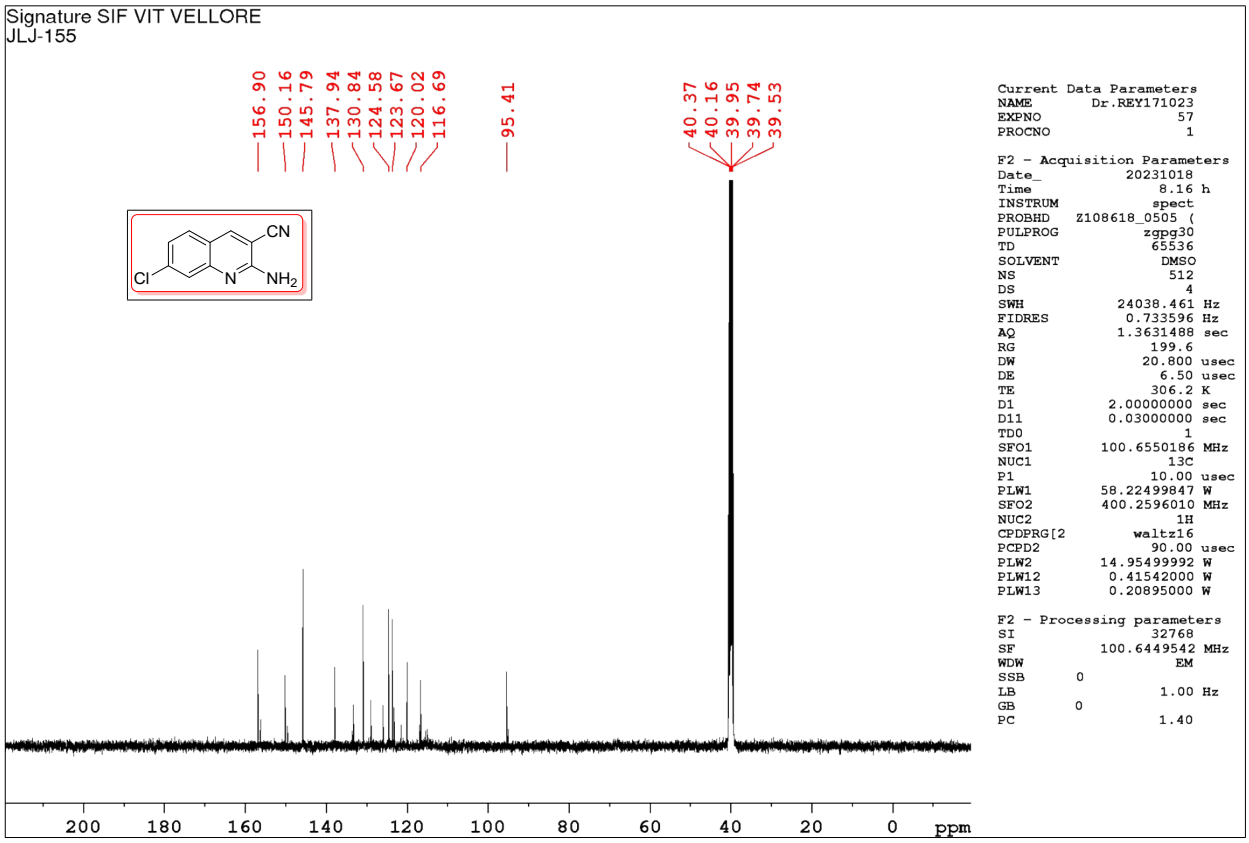


Figure S19. ^{1}H NMR compound of **3h** (DMSO-d_6, 400 MHz)

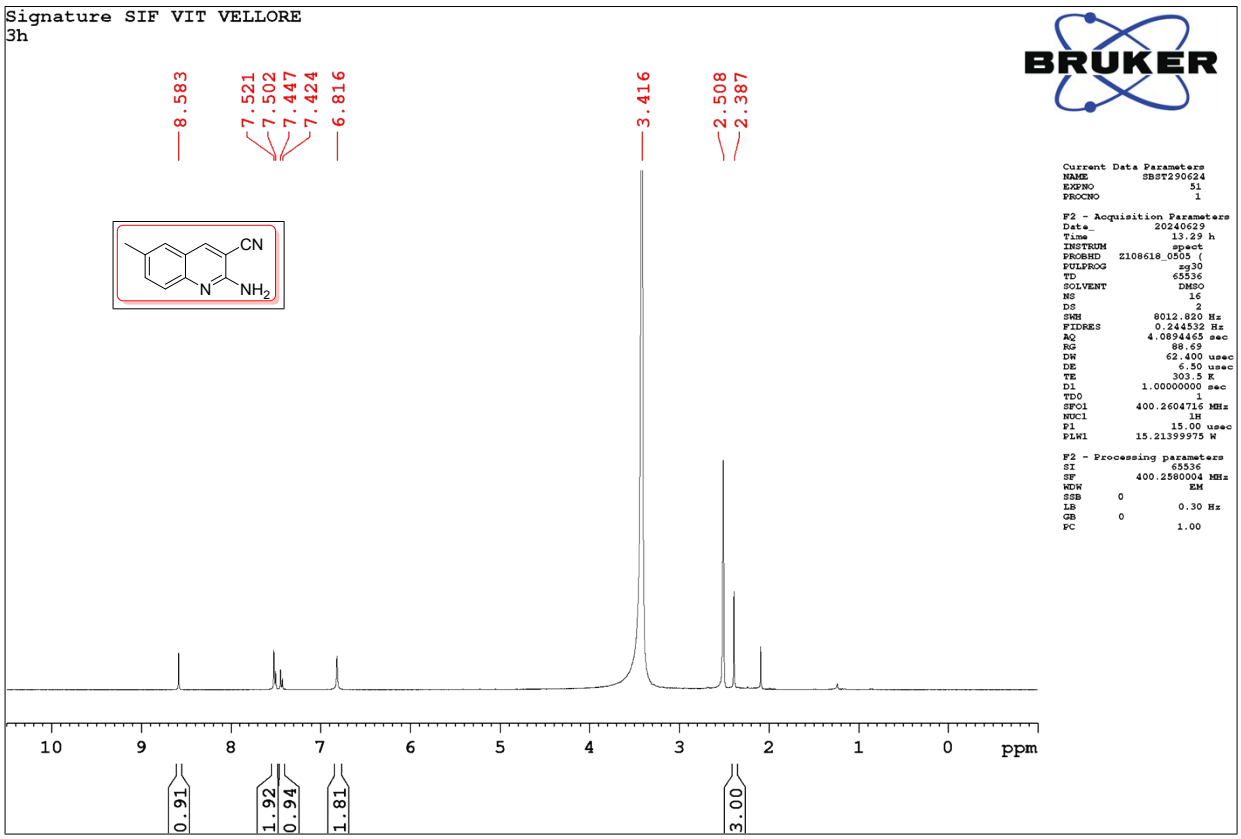


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of **3h** (DMSO-d_6, 100 MHz)

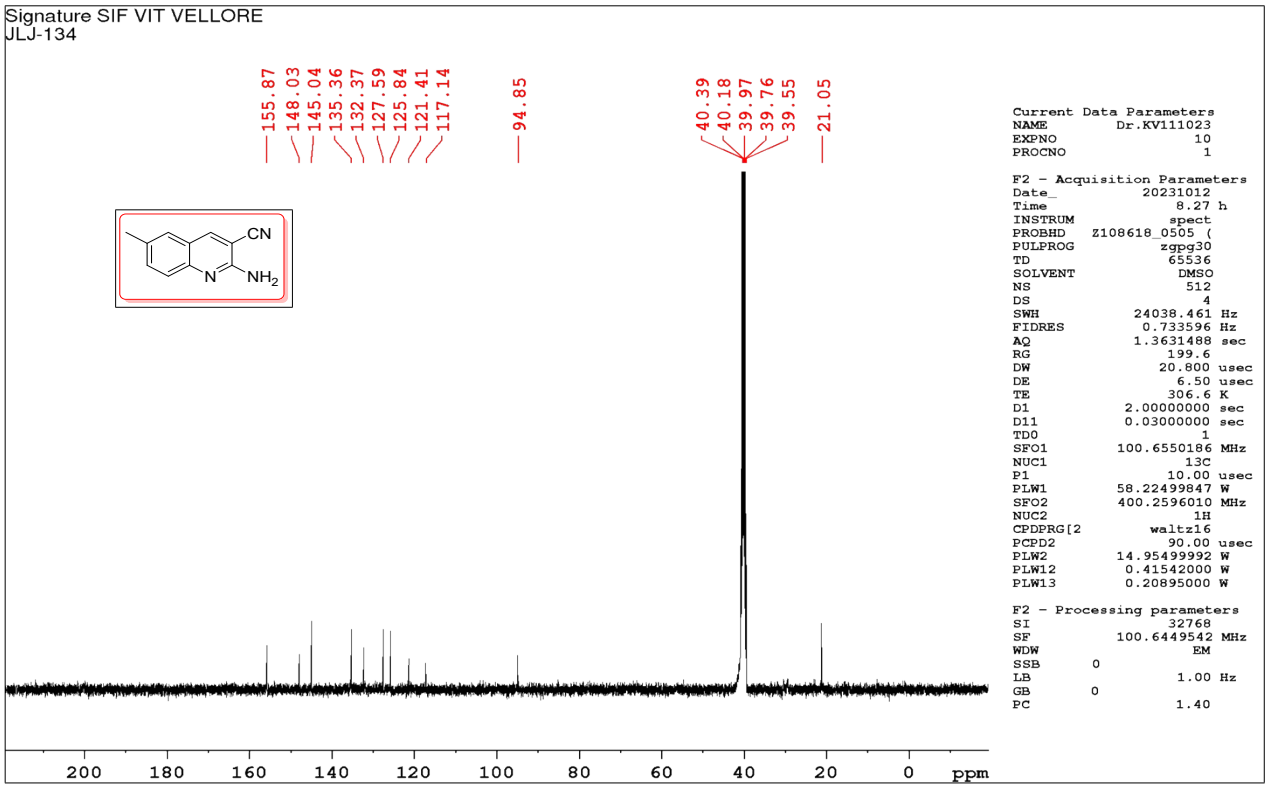


Figure S21. ^{1}H NMR spectrum of **6a** ($CDCl_3$, 400 MHz)

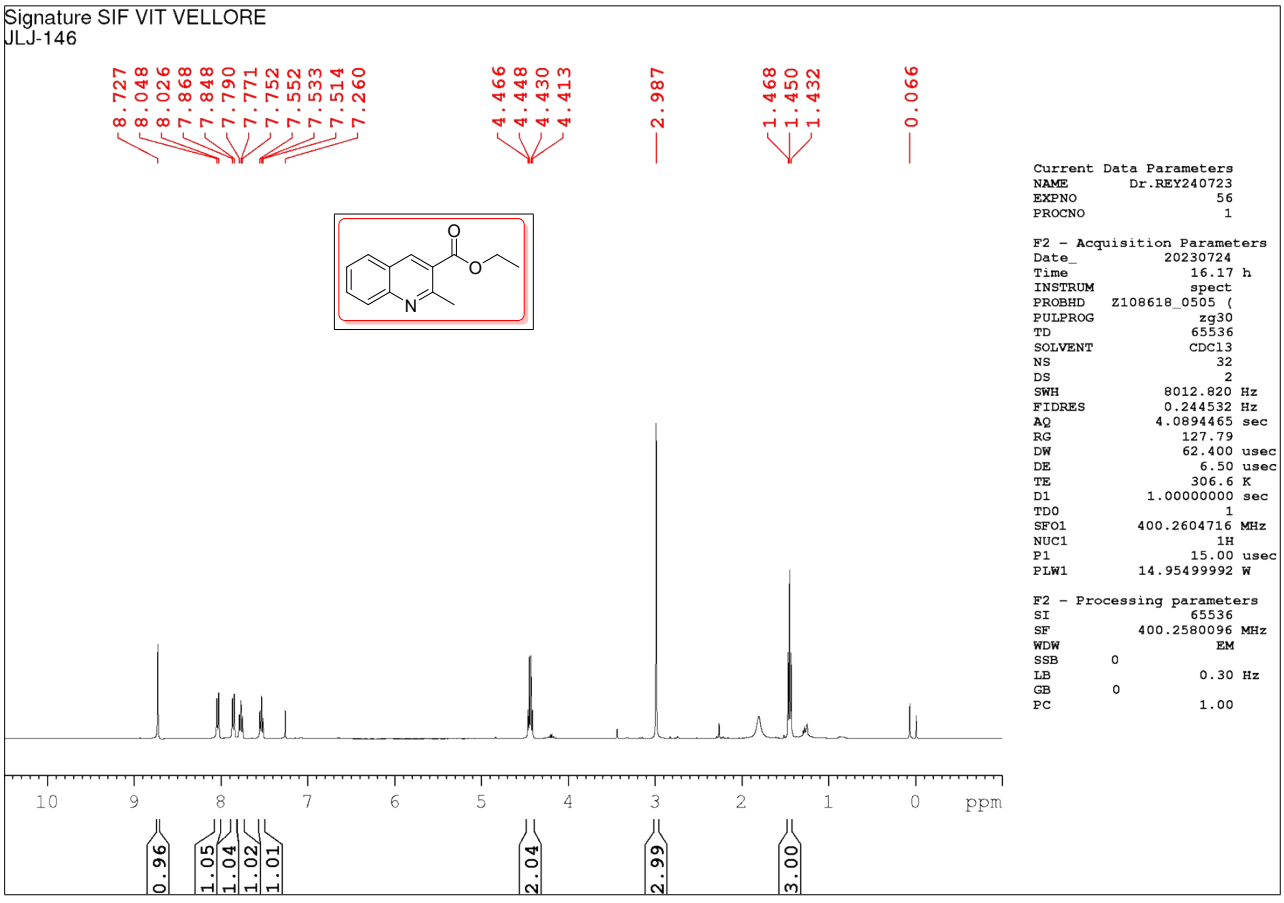


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of **6a** ($CDCl_3$, 100 MHz)

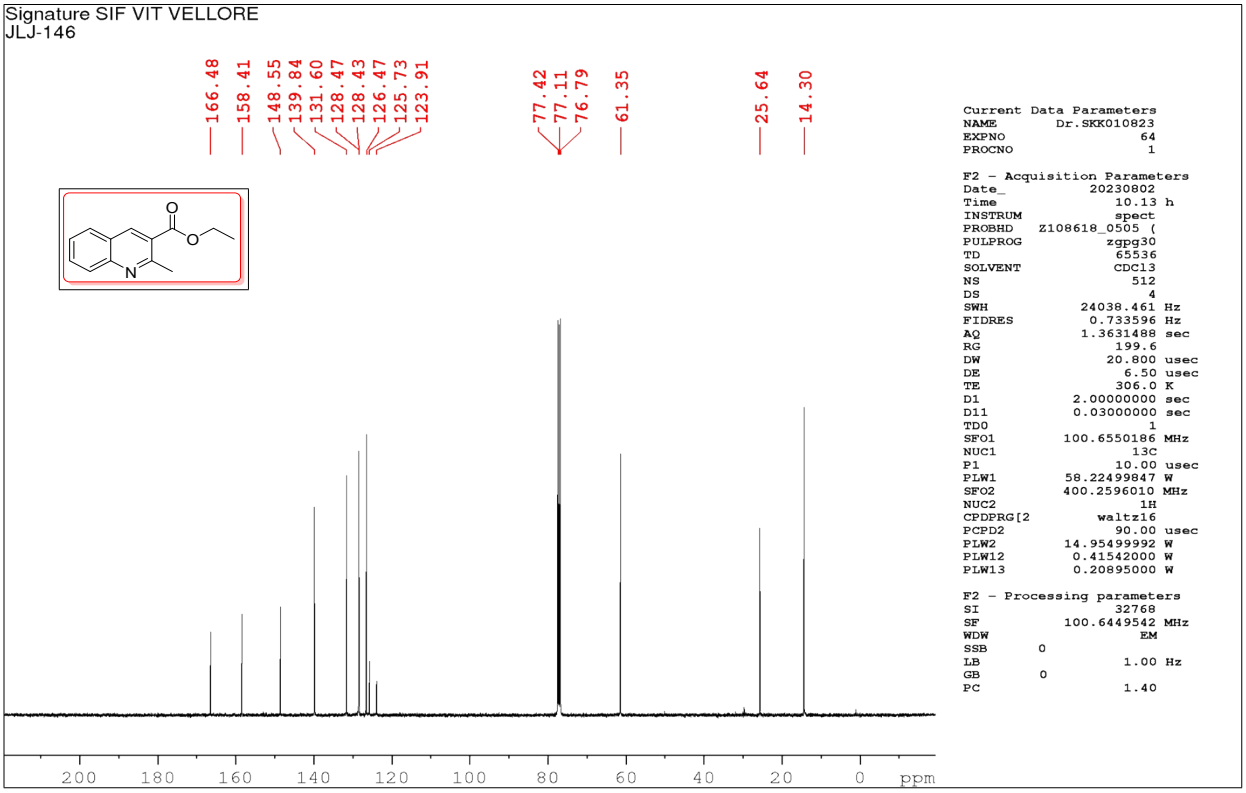


Figure S23. ^{1}H NMR spectrum of **6b** ($CDCl_3$, 400 MHz)

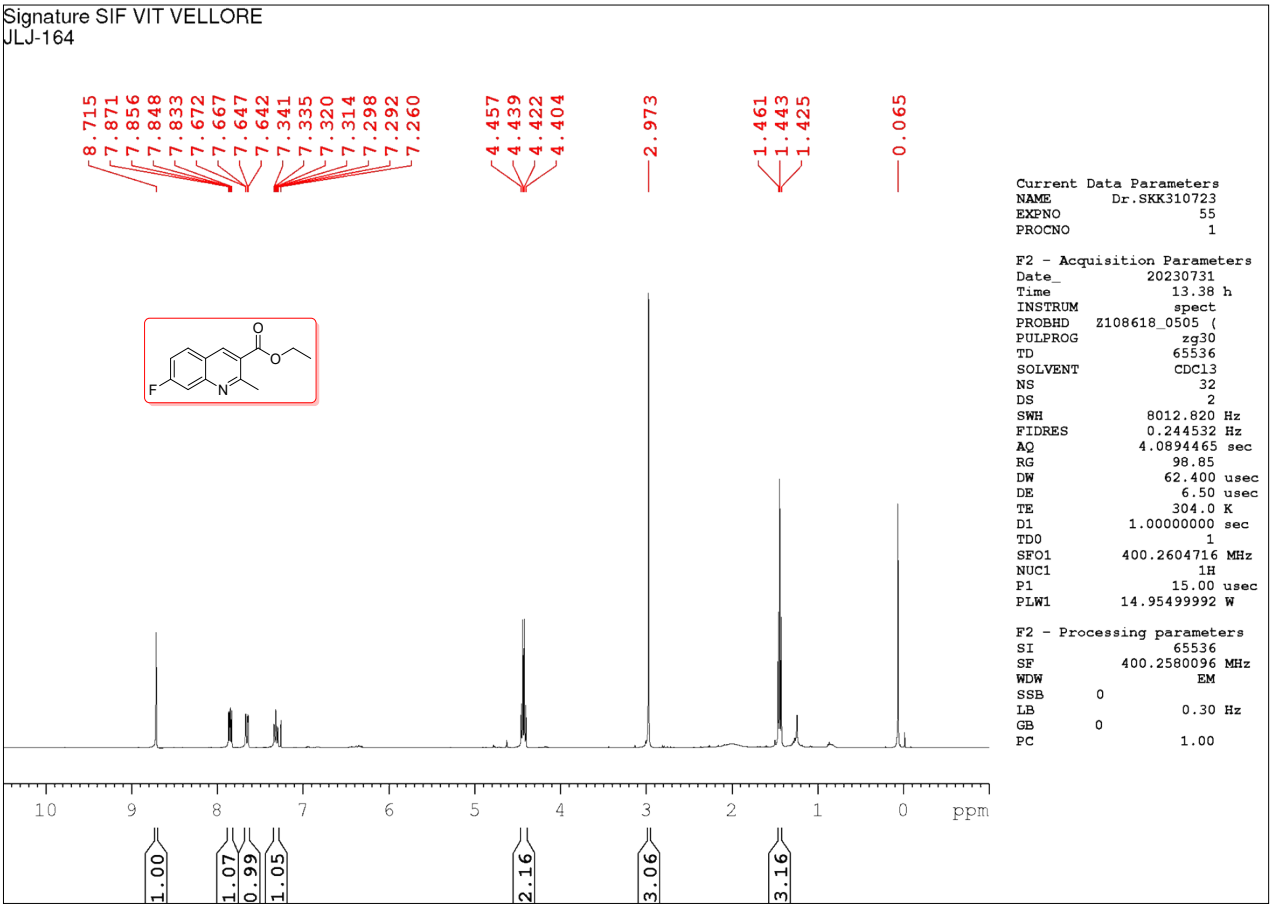


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of **6b** ($CDCl_3$, 100 MHz)

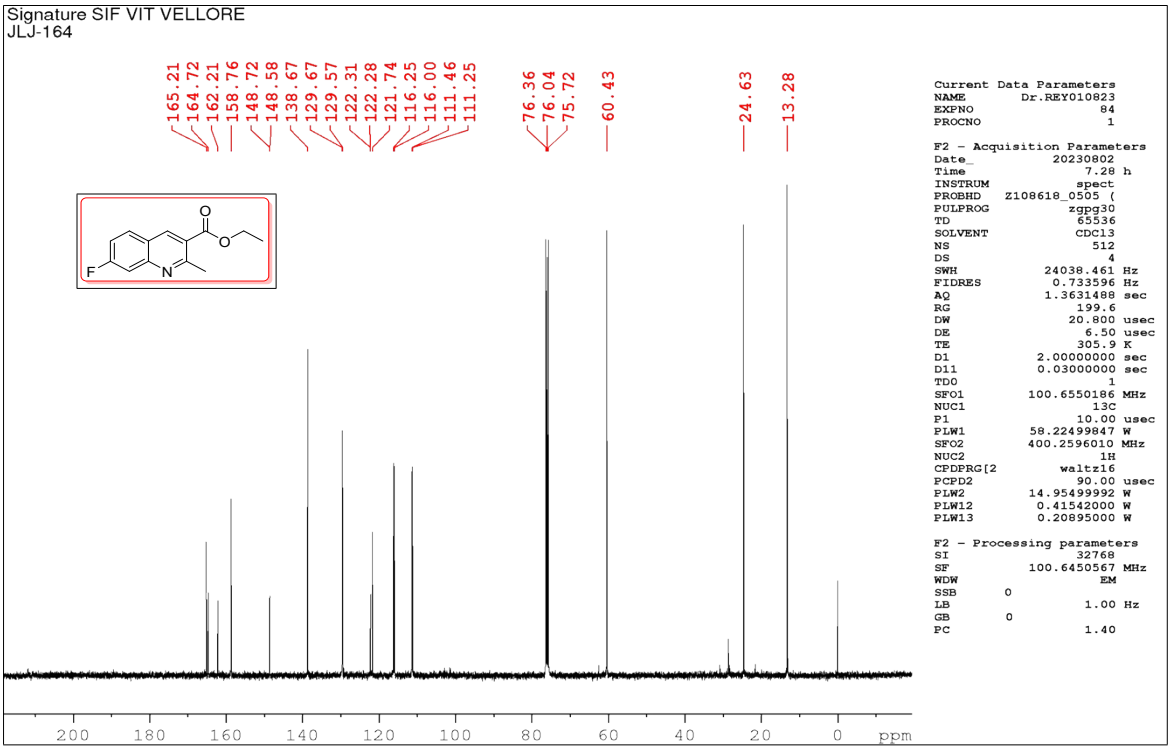


Figure S25. ^{19}F NMR spectrum of **6b** ($CDCl_3$, 376 MHz)

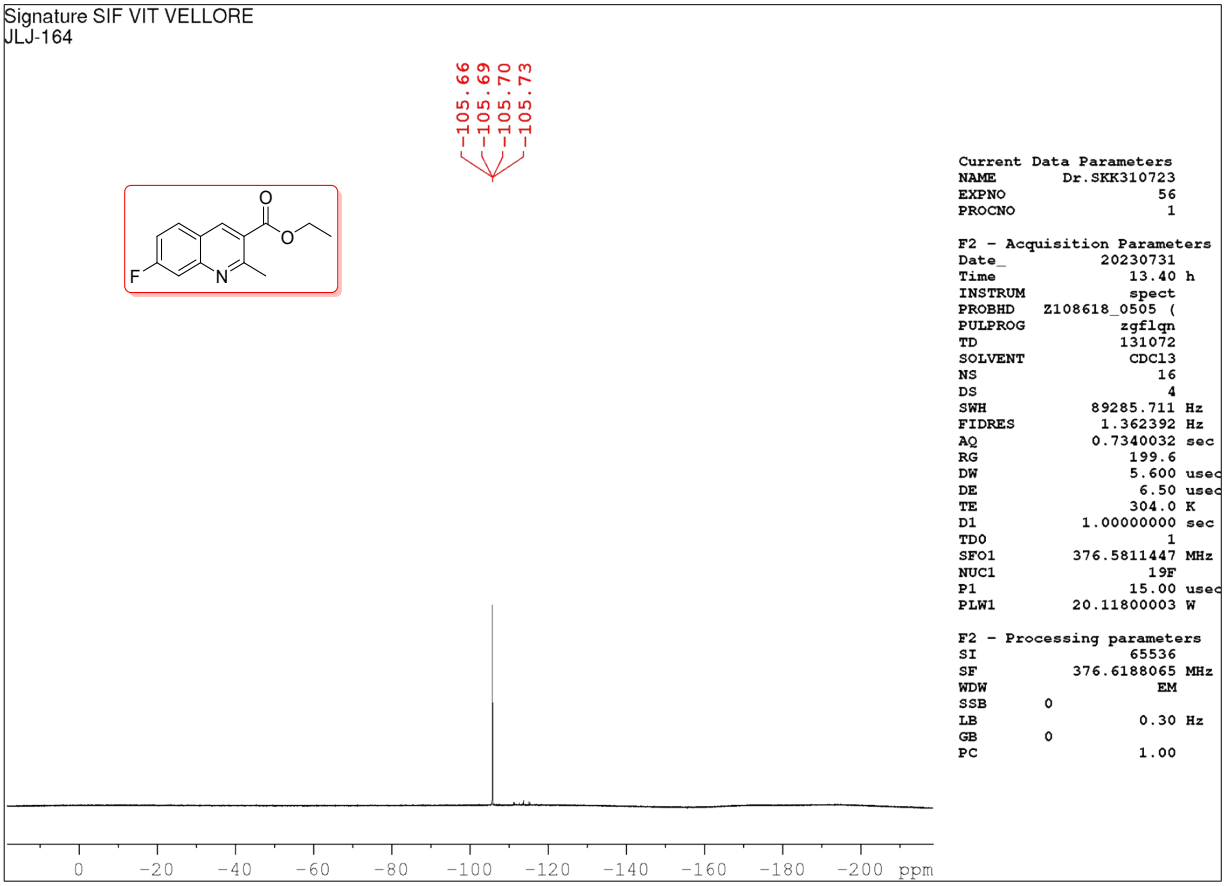


Figure S26. ^{1}H NMR spectrum of **6c** ($CDCl_3$, 400 MHz)

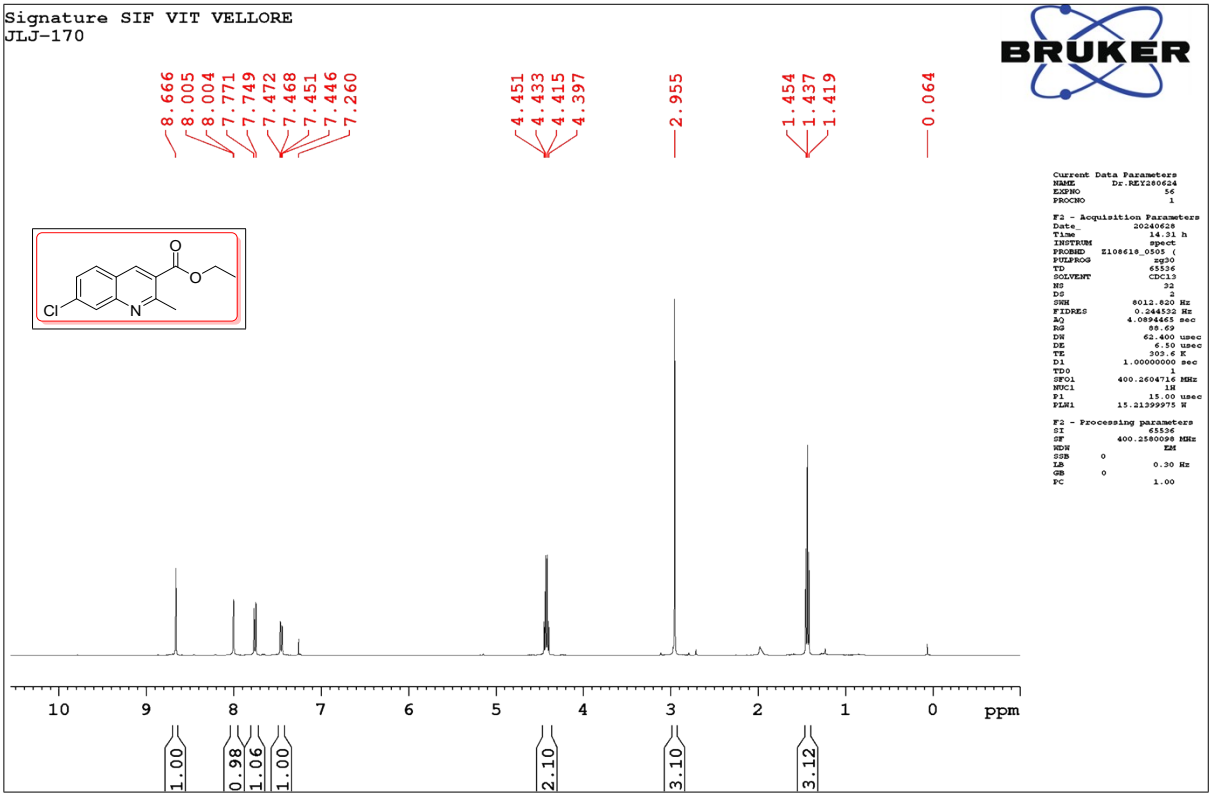


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of **6c** ($CDCl_3$, 100 MHz)

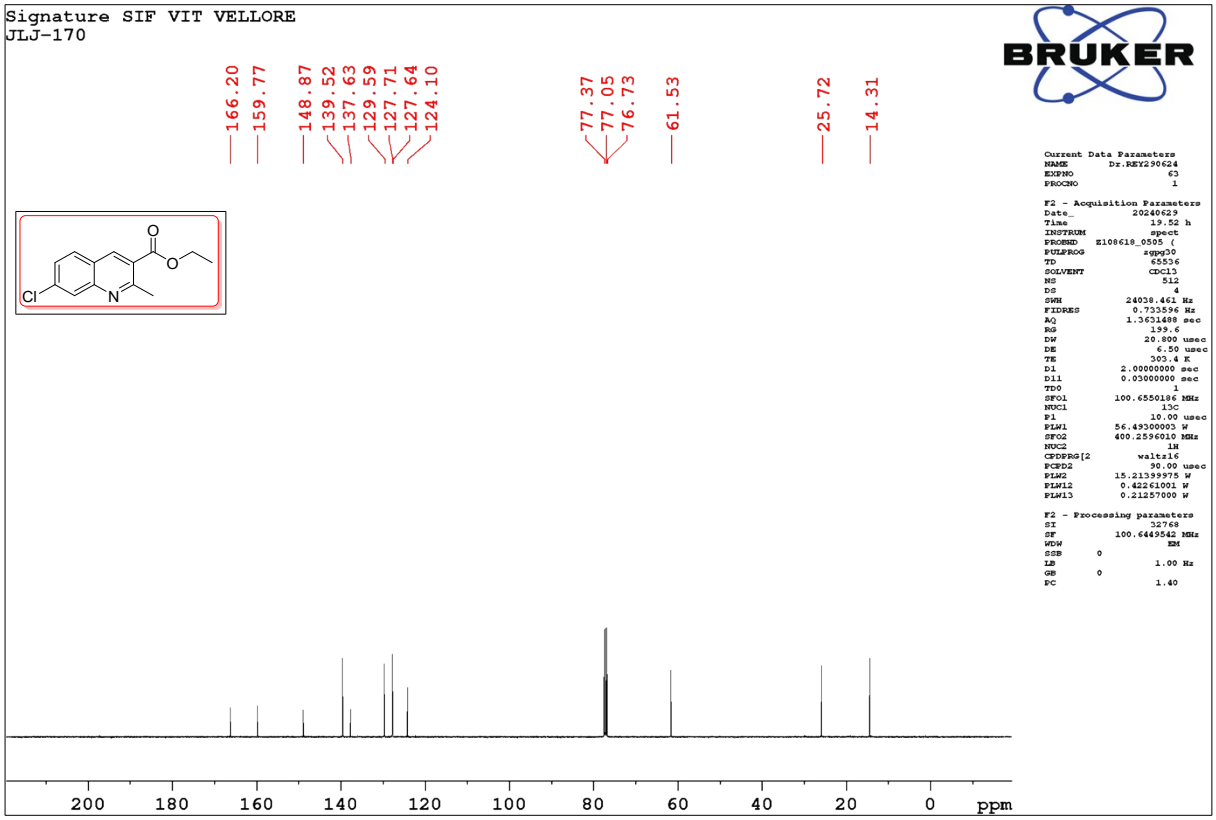


Figure S28. ^{1}H NMR spectrum of **6d** ($CDCl_3$, 400 MHz)

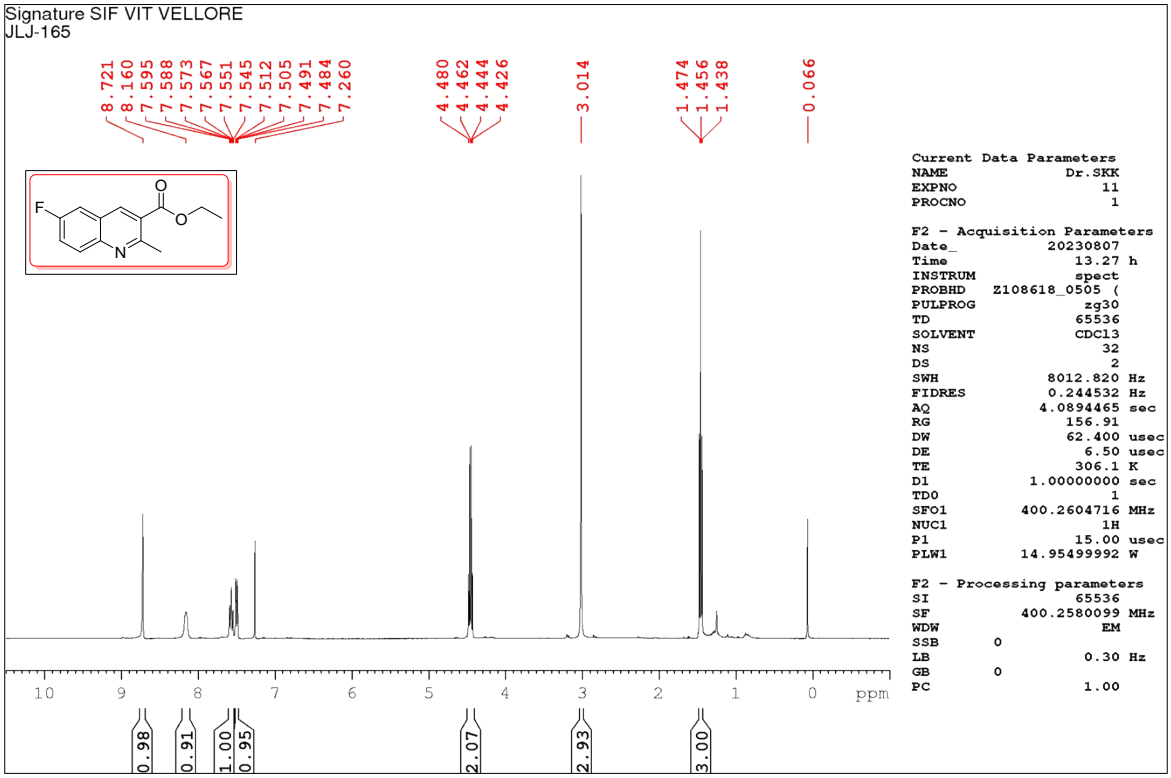


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of **6d** ($CDCl_3$, 100 MHz)

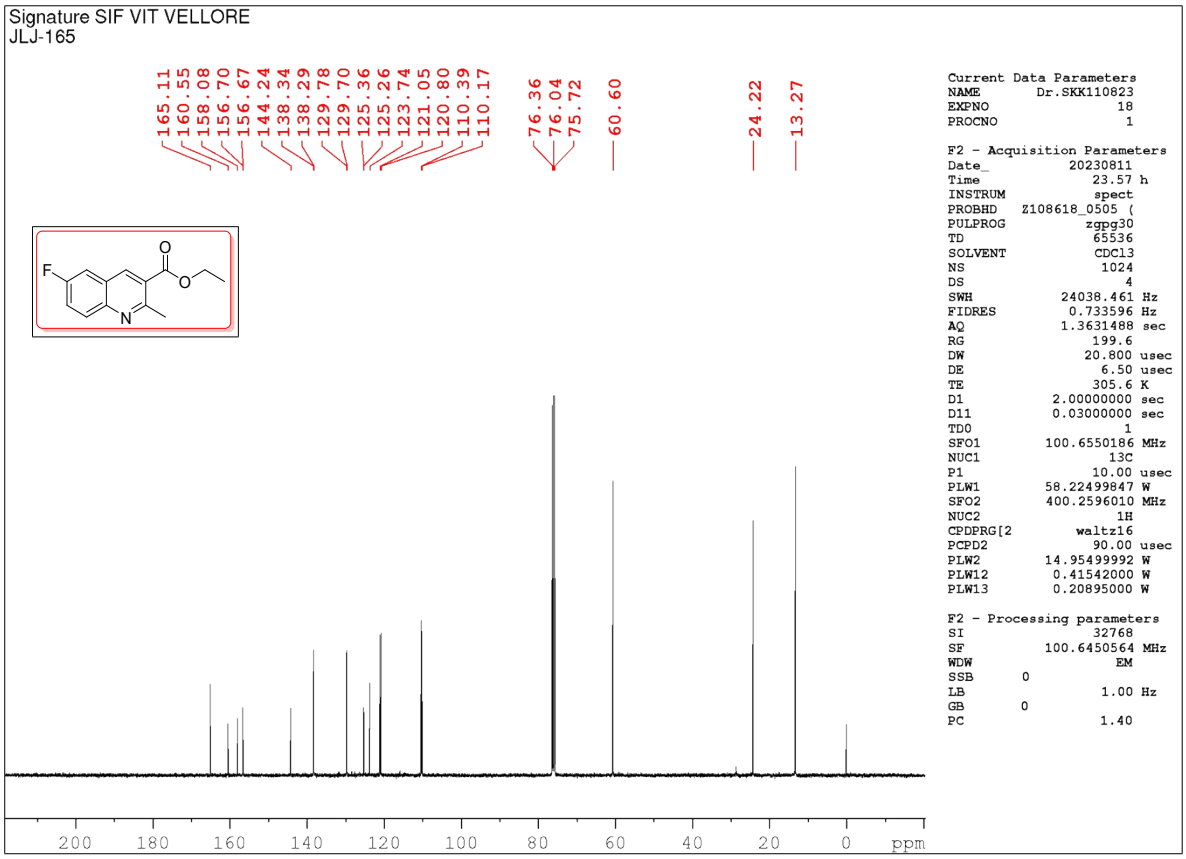


Figure S30. ^{19}F NMR spectrum of **6d** ($CDCl_3$, 376 MHz)

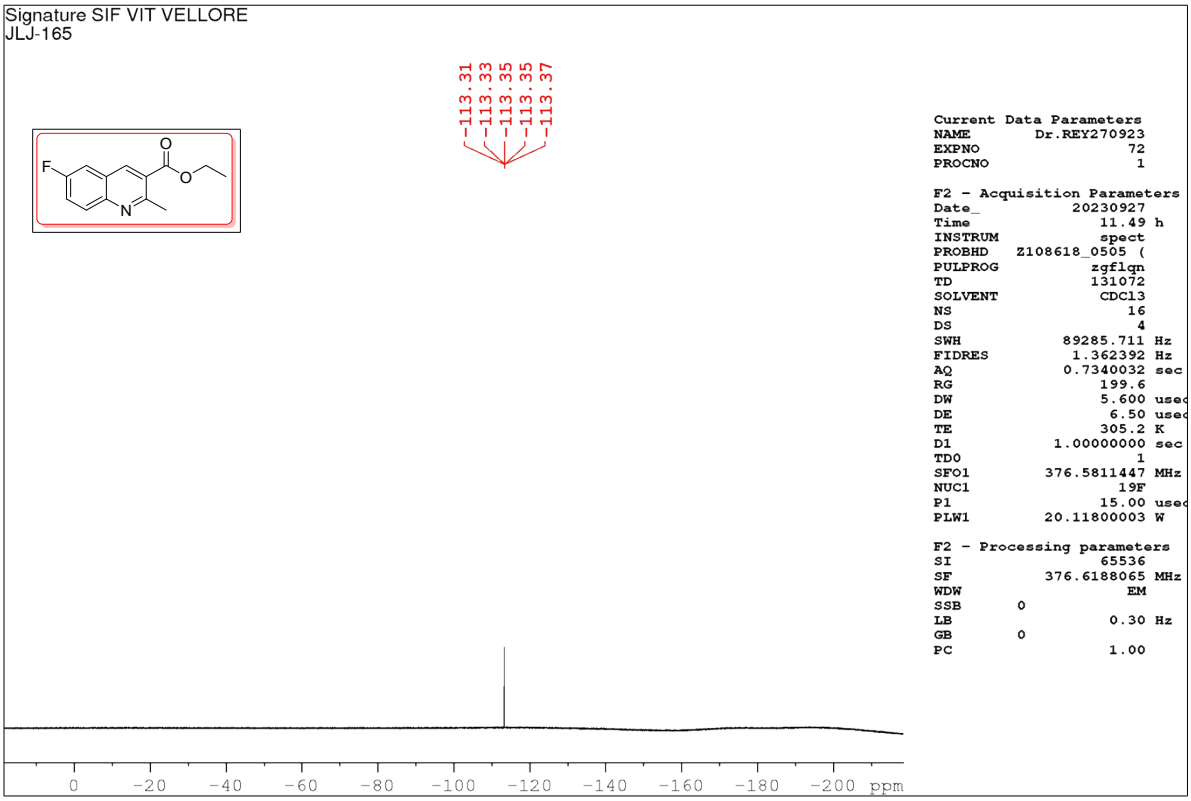


Figure S31.^{1}H NMR spectrum of **6e** ($CDCl_3$, 400 MHz)

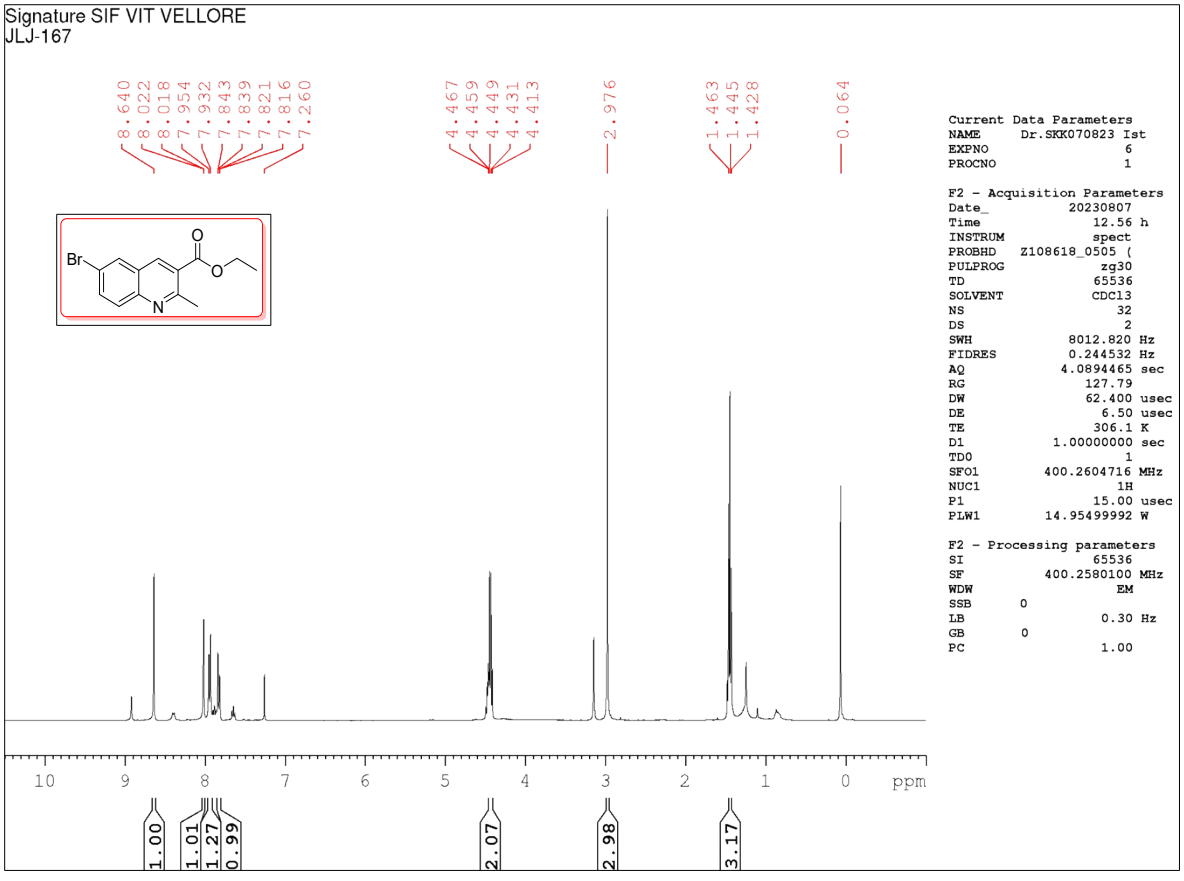


Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum of **6e** ($CDCl_3$, 100 MHz)

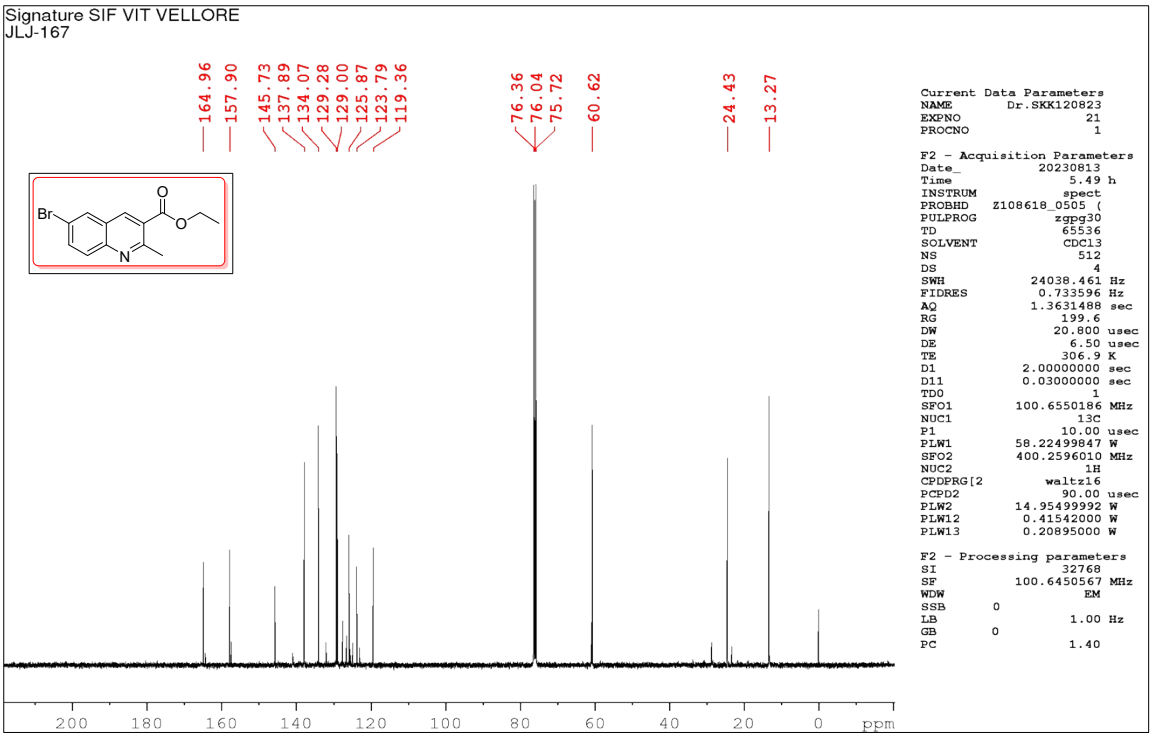


Figure S33. ^{1}H NMR spectrum of **6f** ($CDCl_3$, 400 MHz)

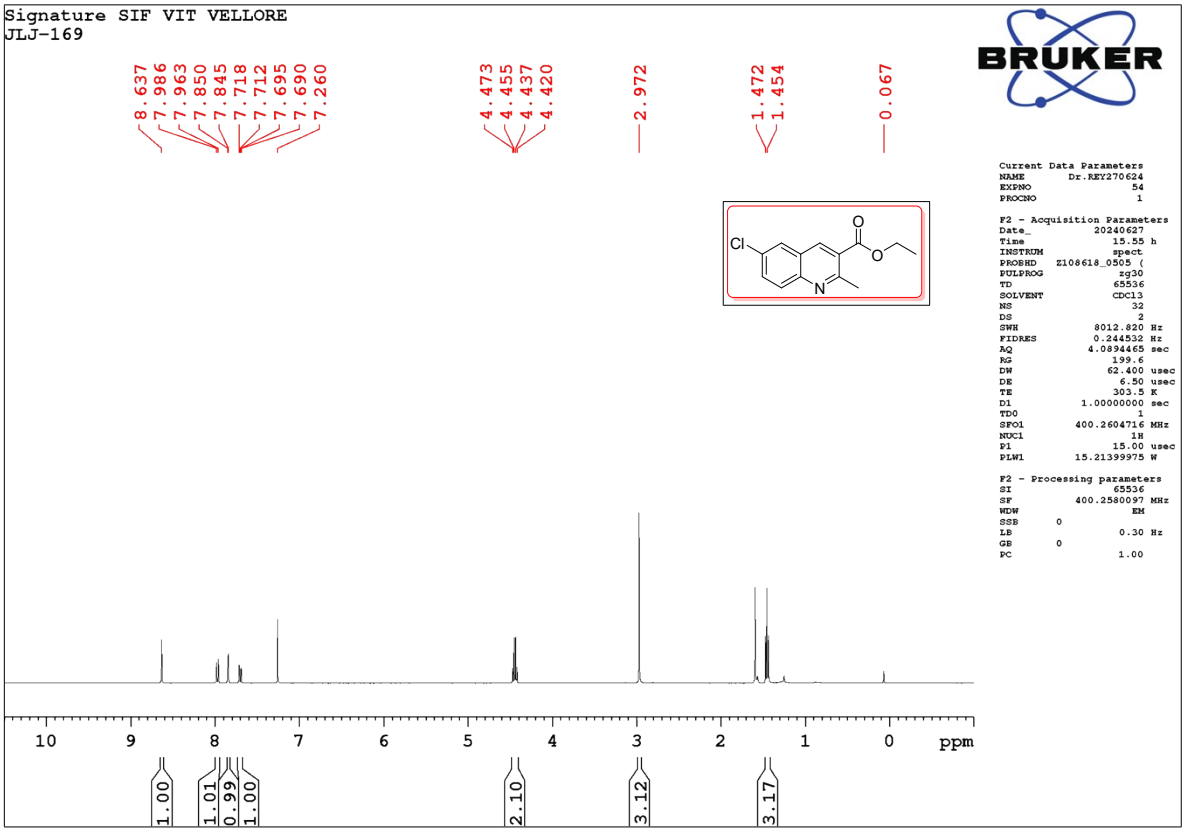


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of **6f** ($CDCl_3$, 100 MHz)

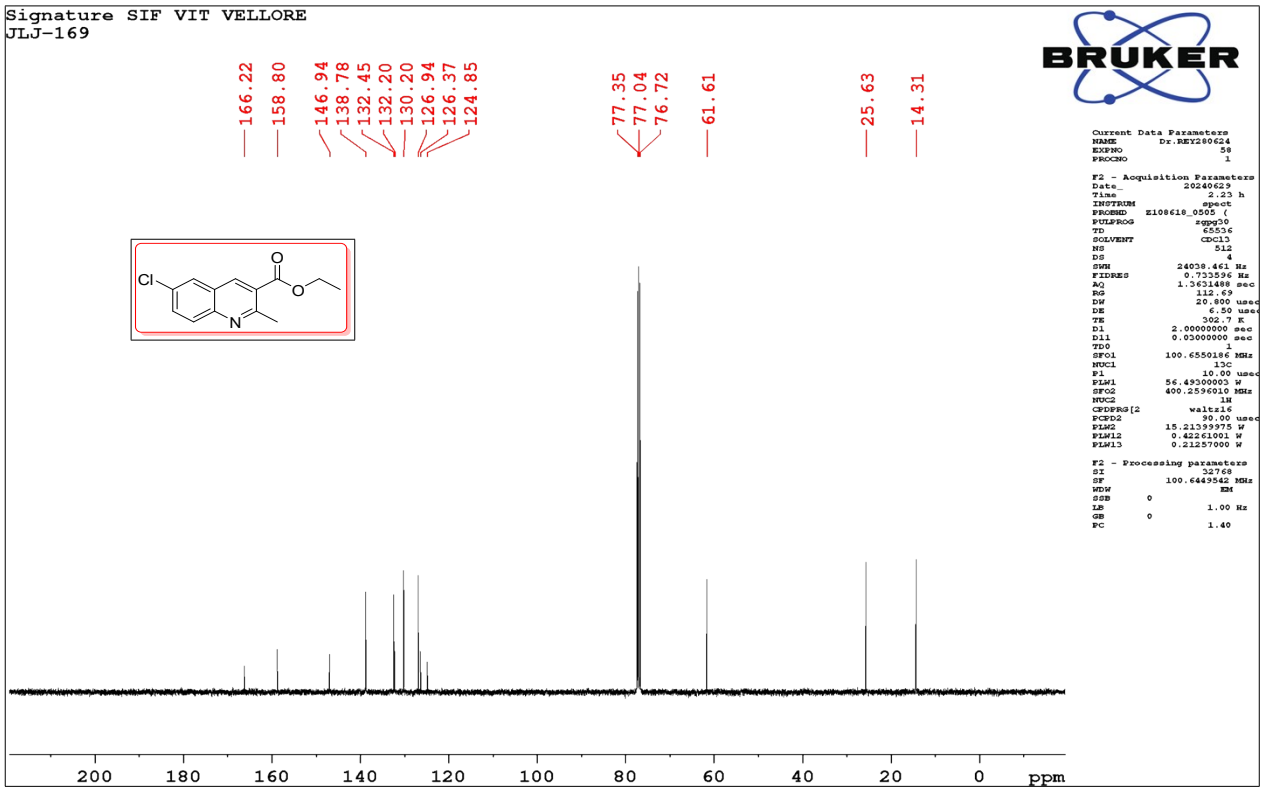


Figure S35. ^{1}H NMR spectrum of **6g** ($CDCl_3$, 400 MHz)

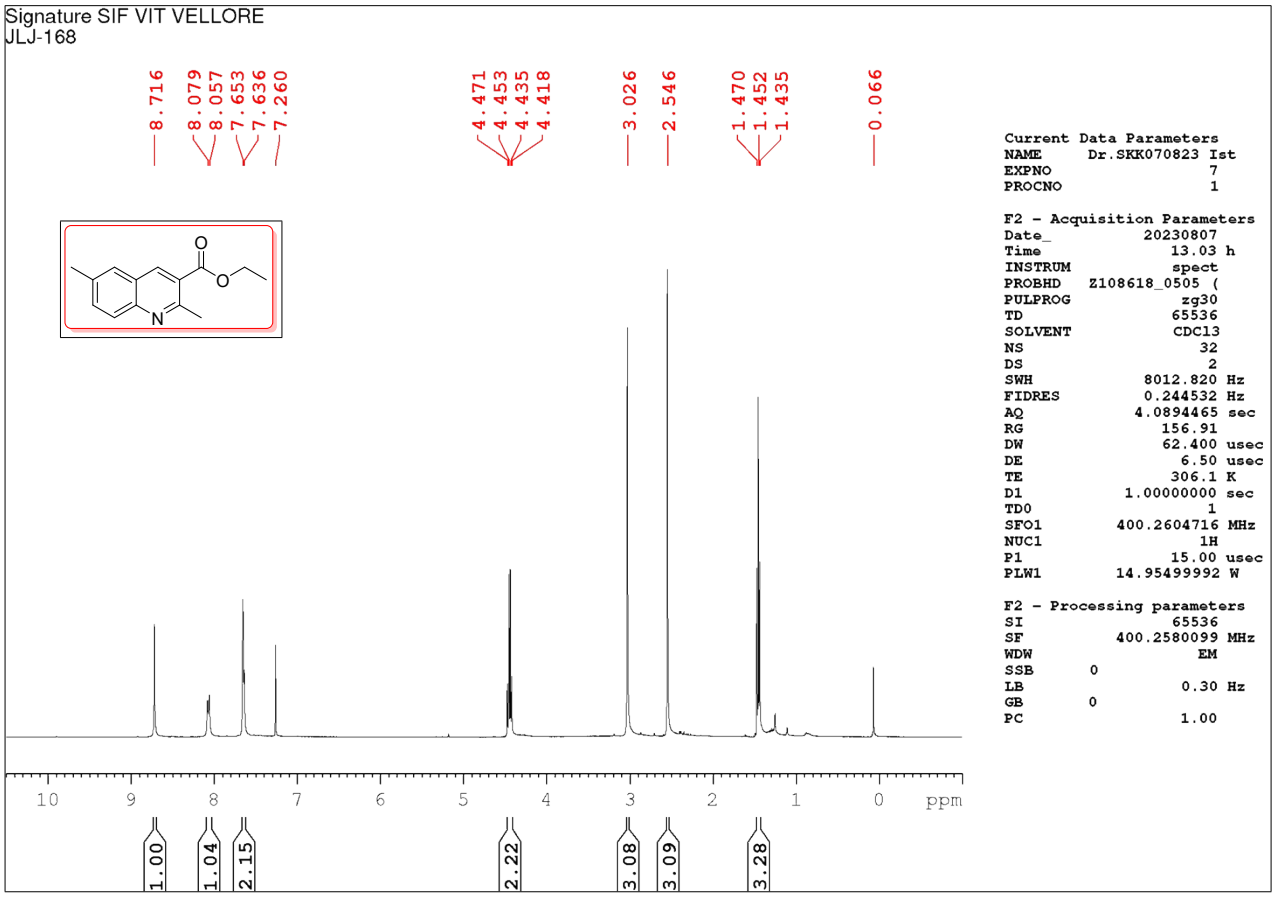


Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum of **6g** ($CDCl_3$, 100 MHz)

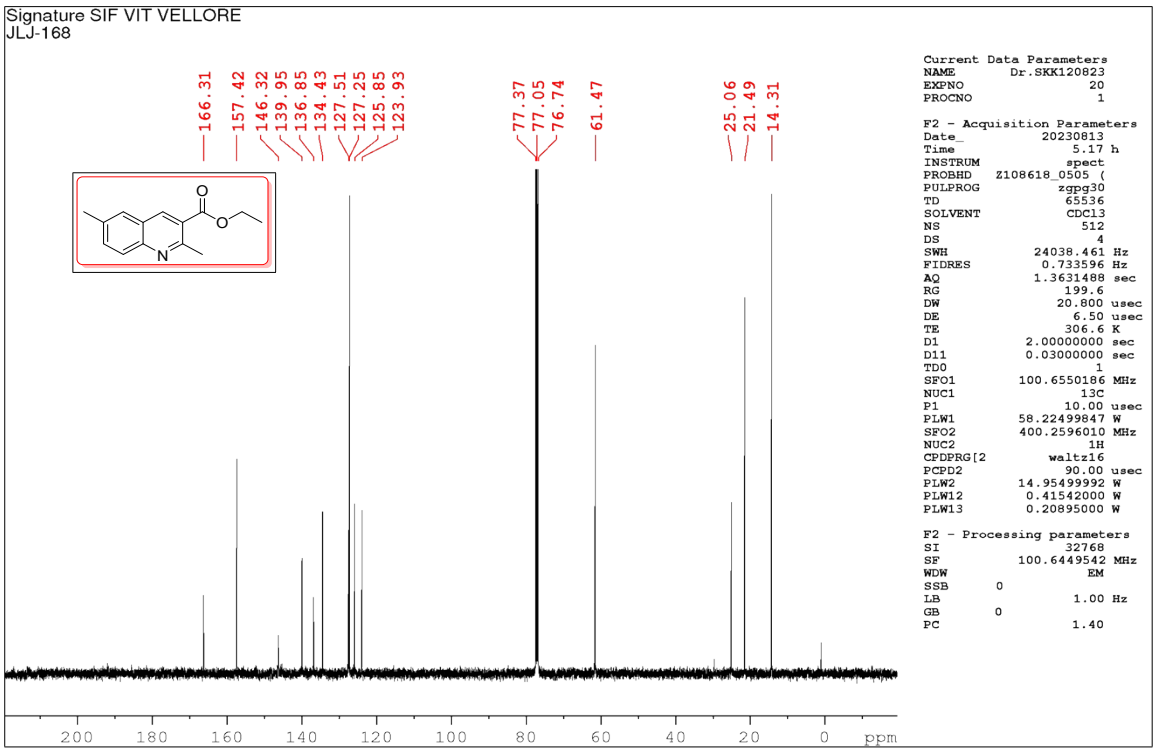


Figure S37. ^{1}H NMR spectrum of **7a** ($CDCl_3$, 400 MHz)

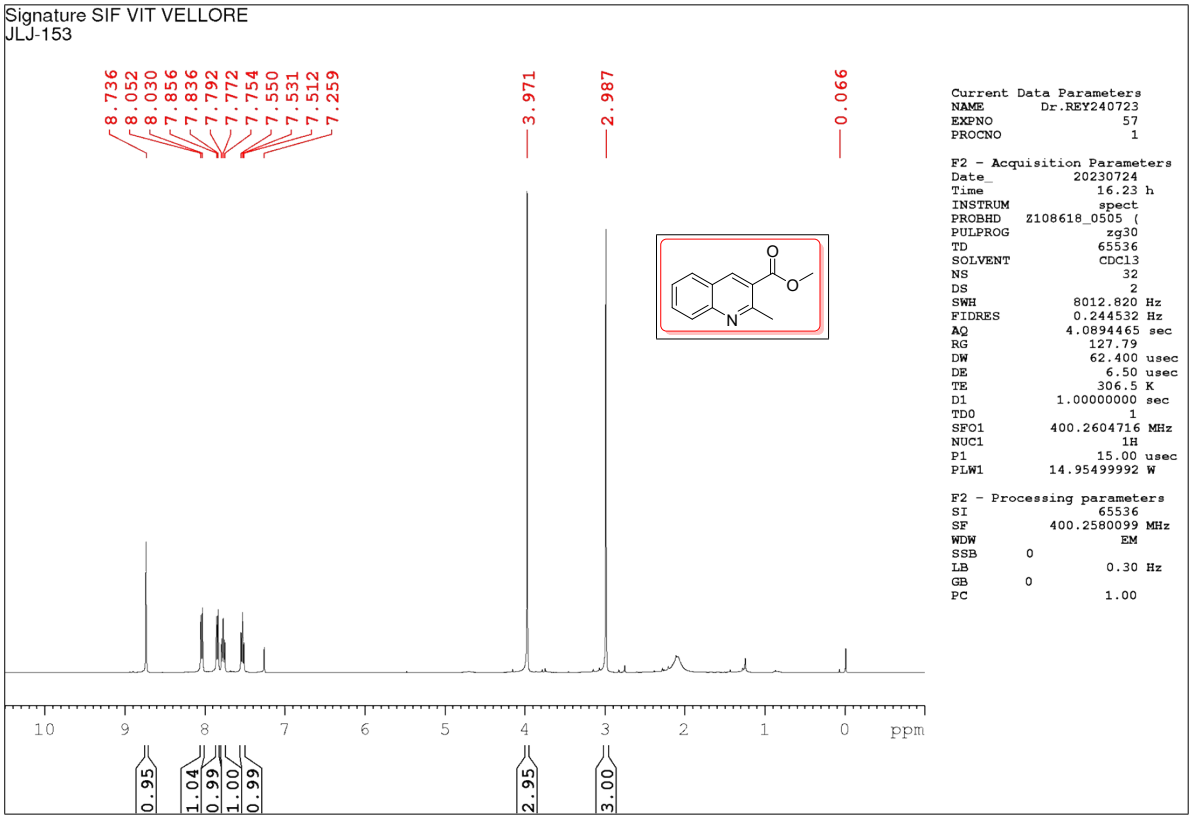


Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum of **7a** ($CDCl_3$, 100 MHz)

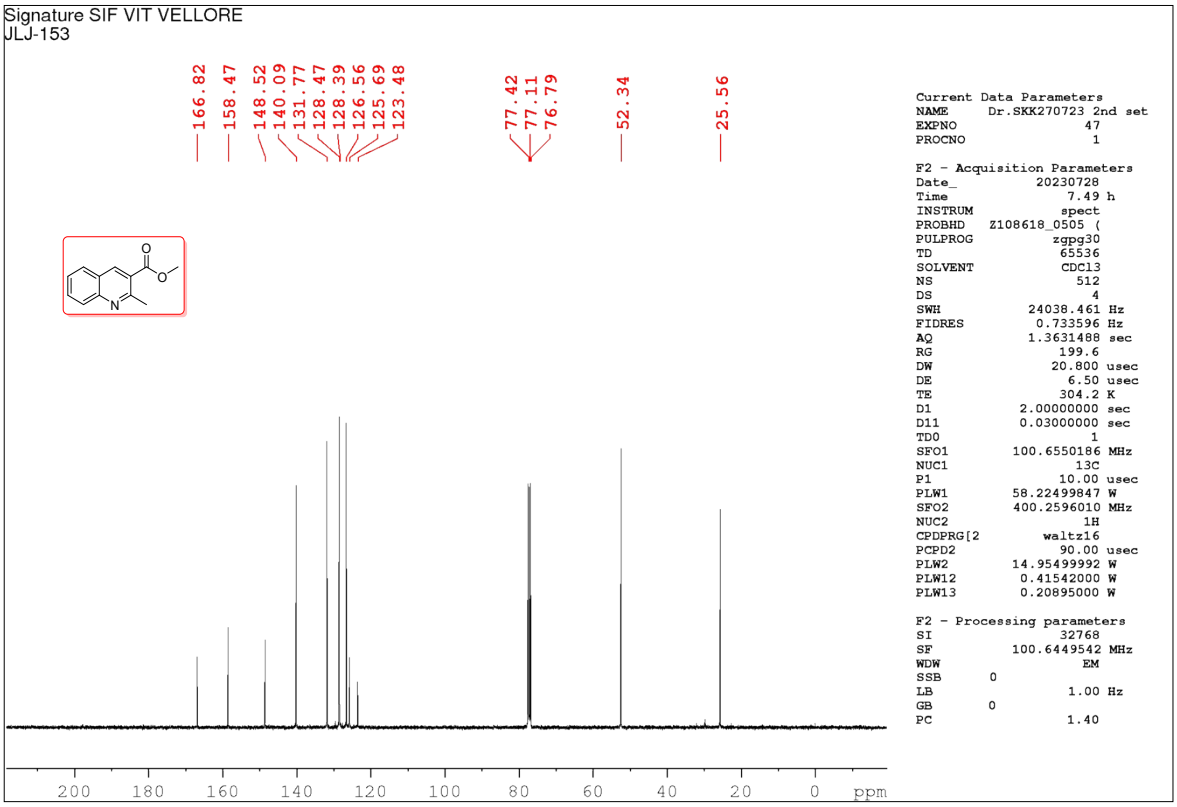


Figure S39. ^{1}H NMR spectrum of **7b** ($CDCl_3$, 400 MHz)

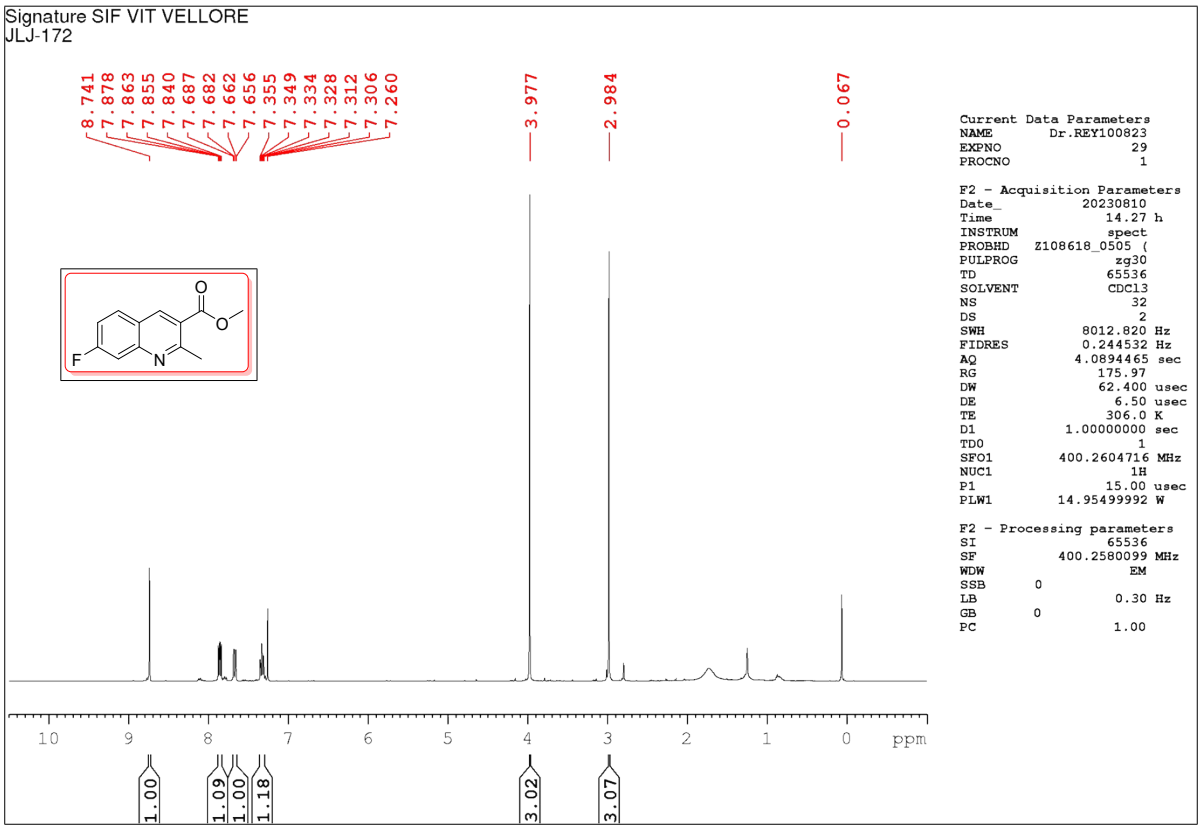


Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum of **7b** ($CDCl_3$, 100MHz)

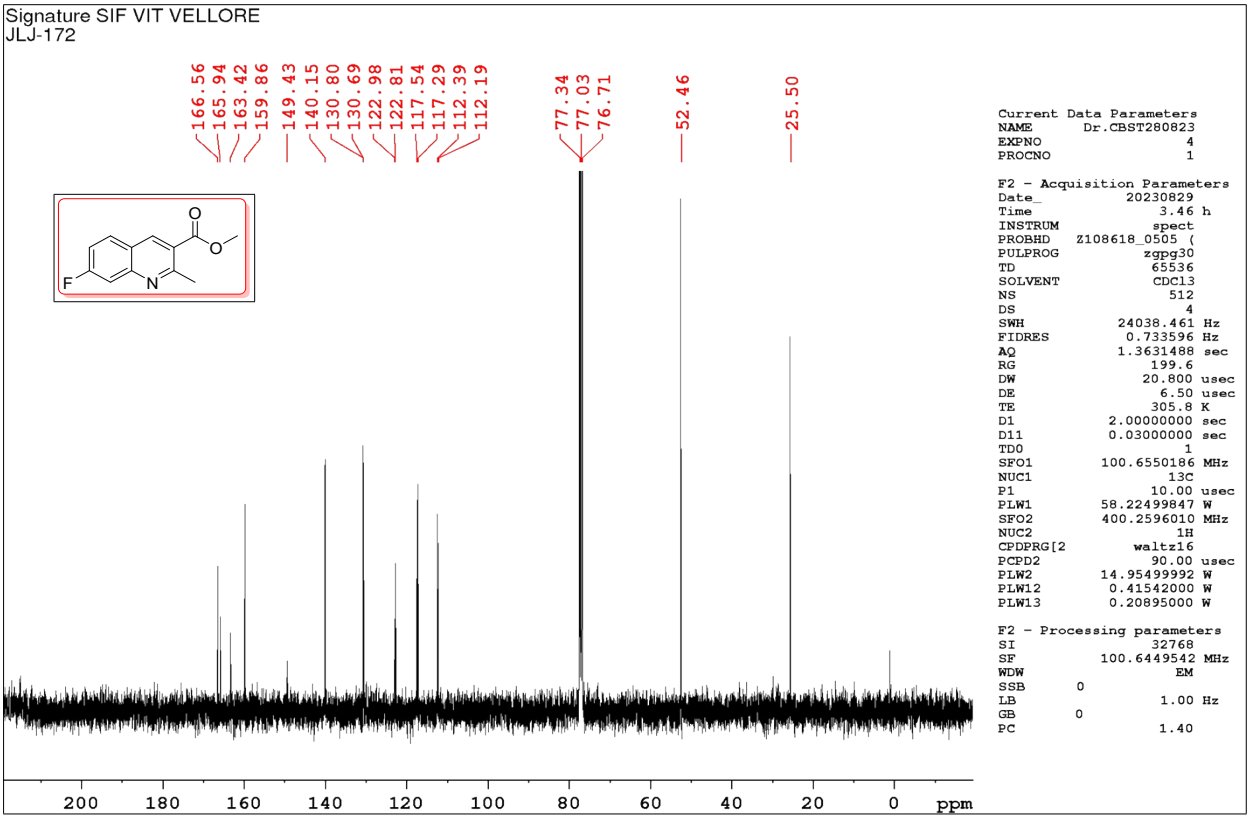


Figure S41. ^{19}F NMR spectrum of **7b** ($CDCl_3$, 376 MHz)

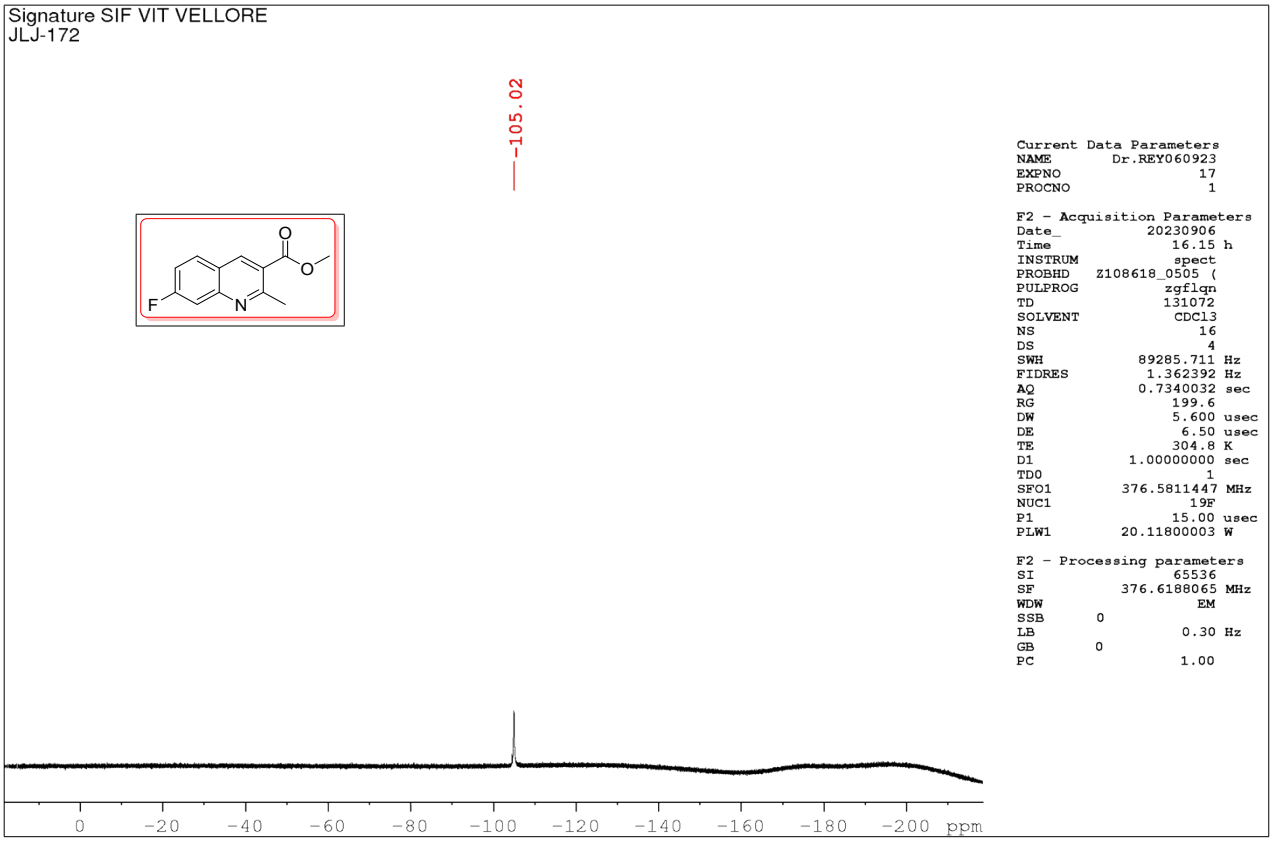


Figure S42. ^{1}H NMR spectrum of **7c** ($CDCl_3$, 400 MHz)

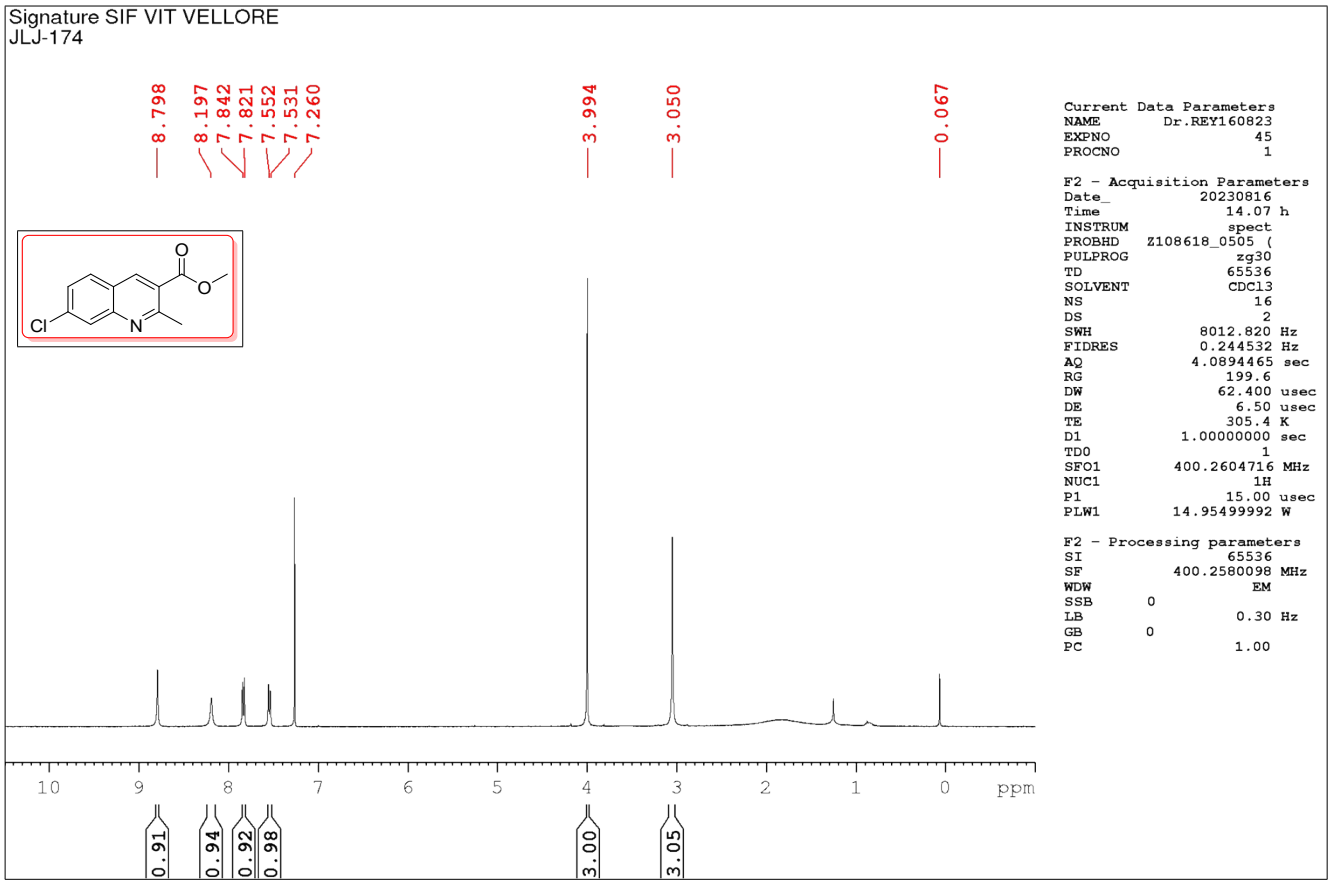


Figure S43. $^{13}C\{^{1}H\}$ NMR spectrum of **7c** ($CDCl_3$, 100 MHz)

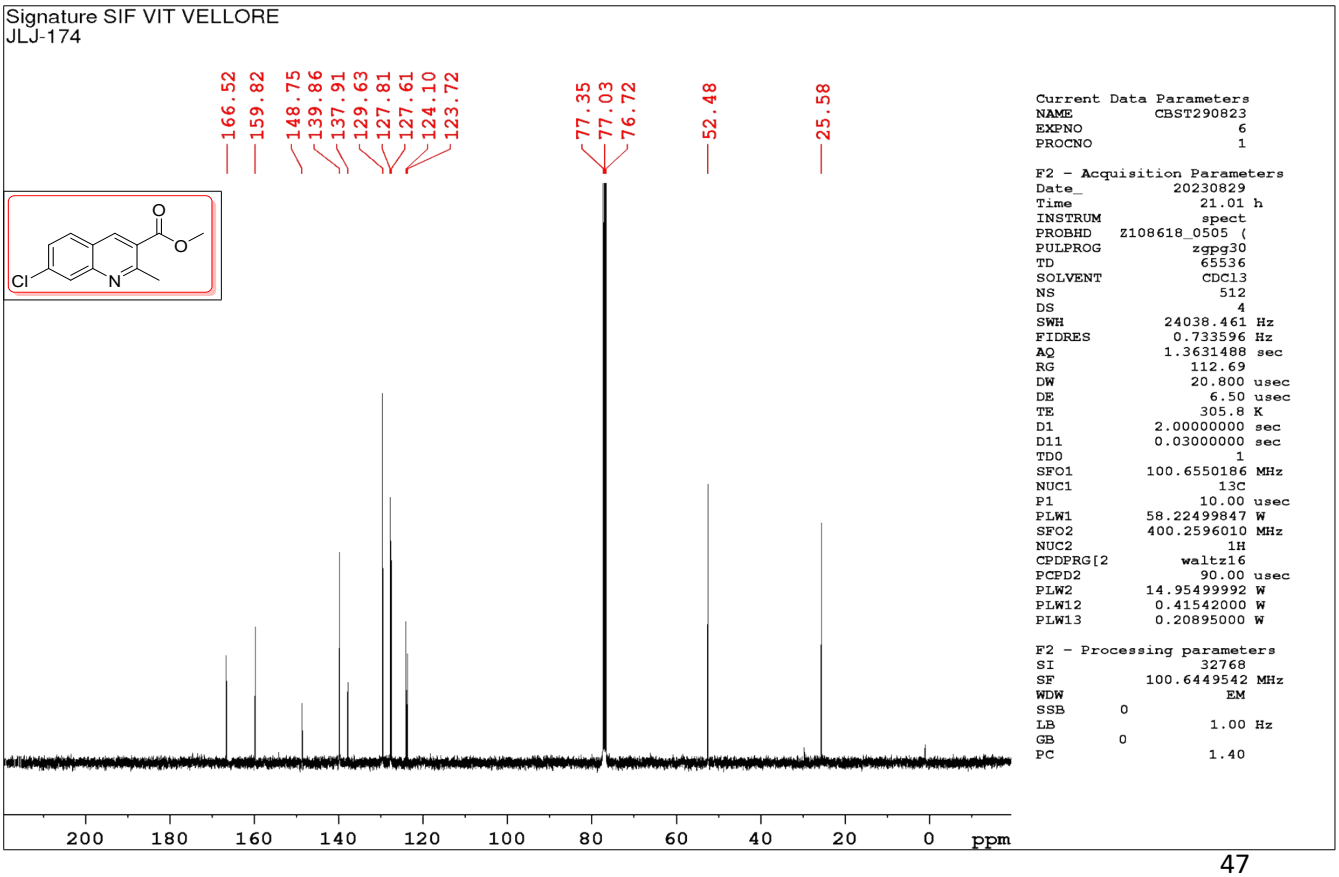


Figure S44. ^{1}H NMR spectrum of **7d** ($CDCl_3$, 400 MHz)

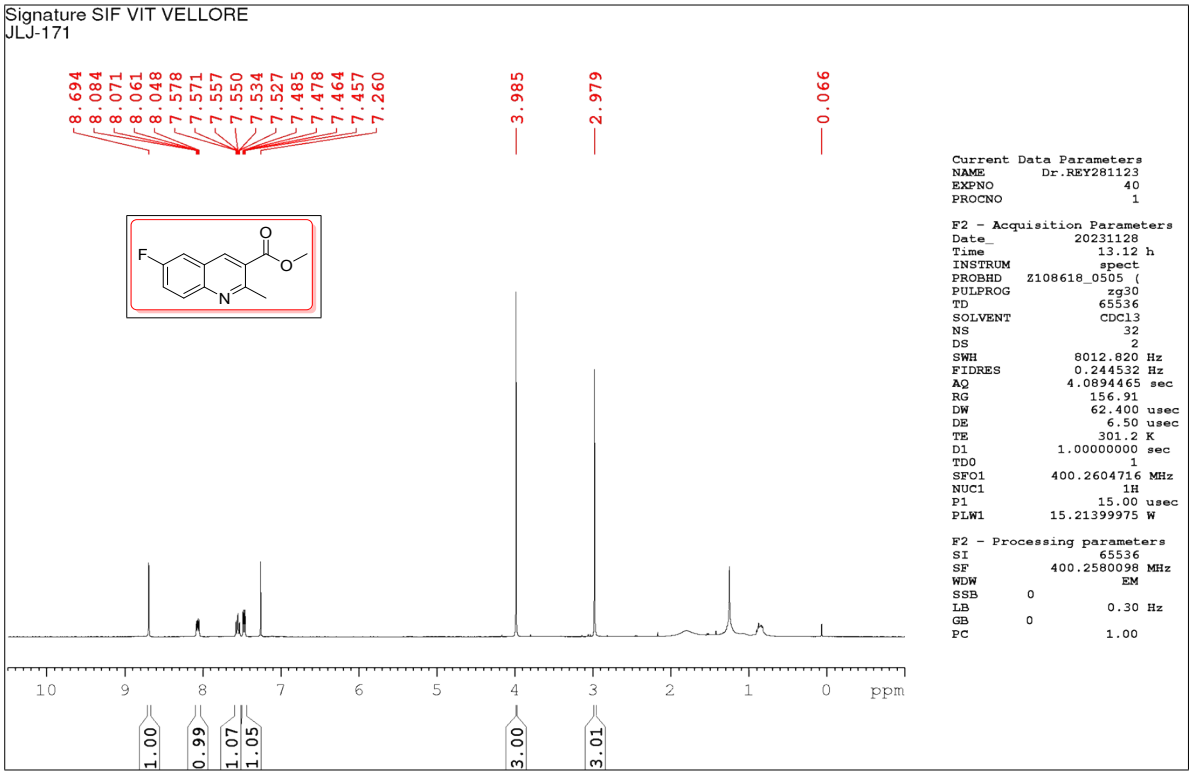


Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum of **7d** ($CDCl_3$, 100 MHz)

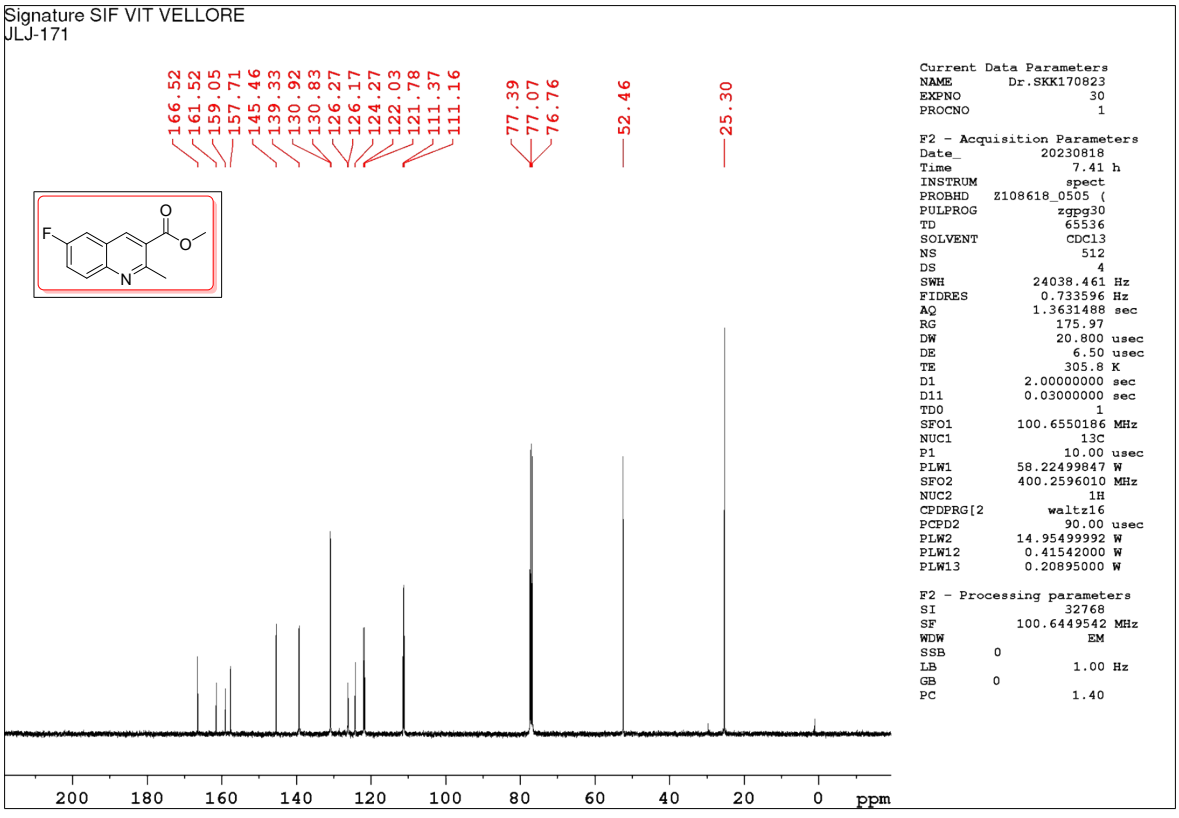


Figure S46. ^{19}F NMR spectrum of **7d** ($CDCl_3$, 376 MHz)

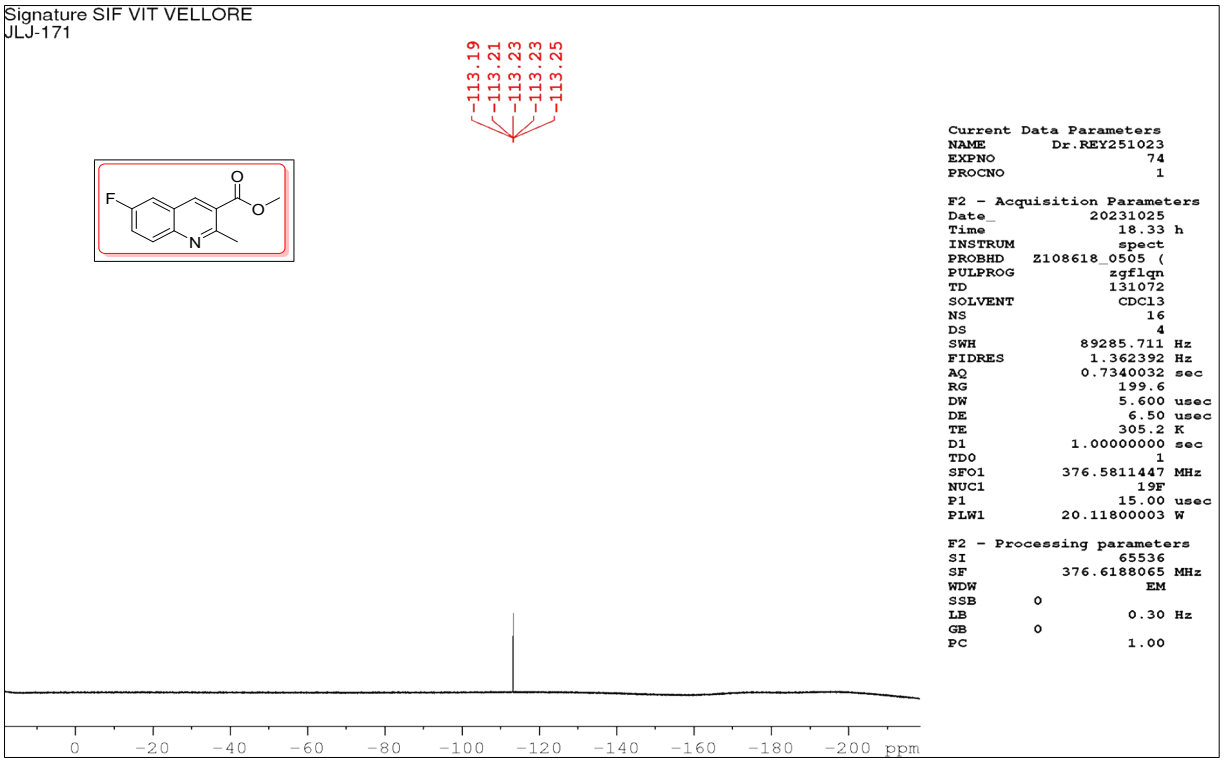


Figure S47. ^{1}H NMR spectrum of **7e** ($CDCl_3$, 400 MHz)

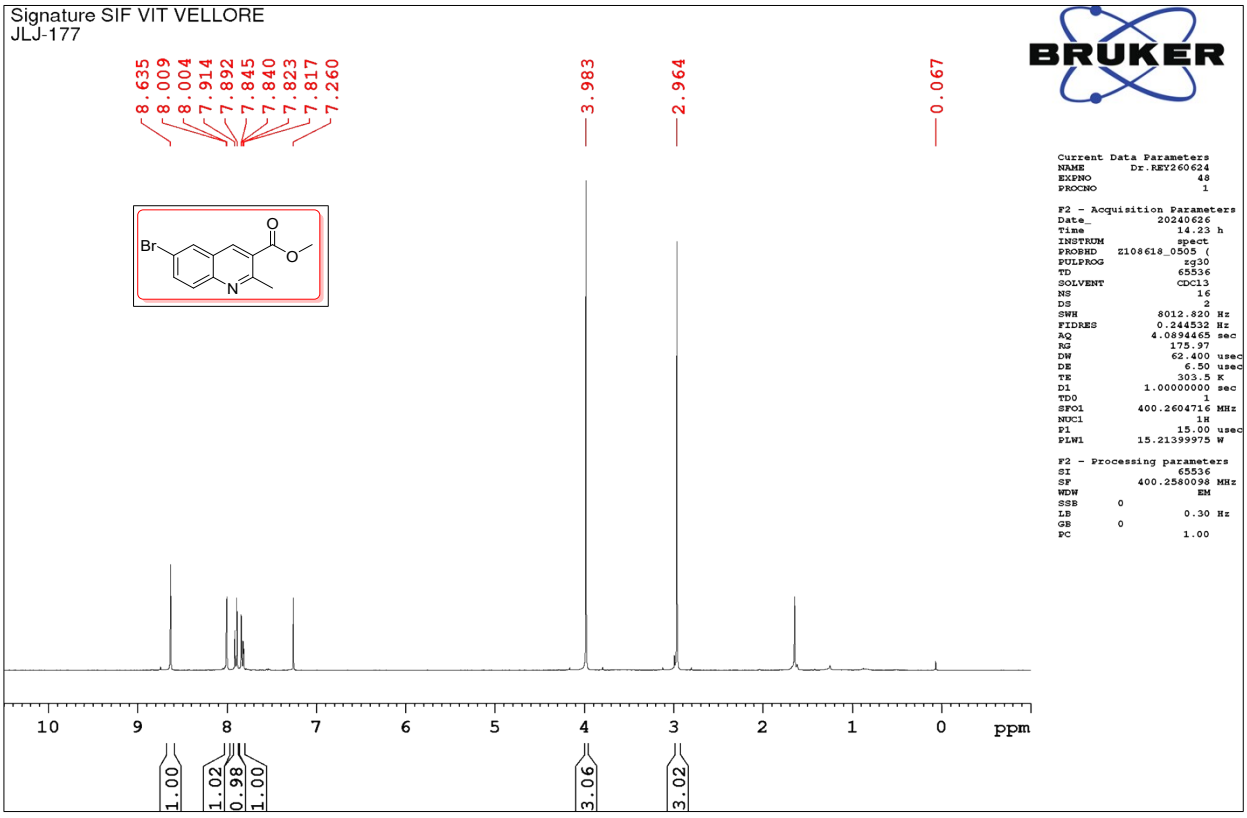


Figure S48. $^{13}C\{^{1}H\}$ NMR spectrum of **7e** ($CDCl_3$, 100 MHz)

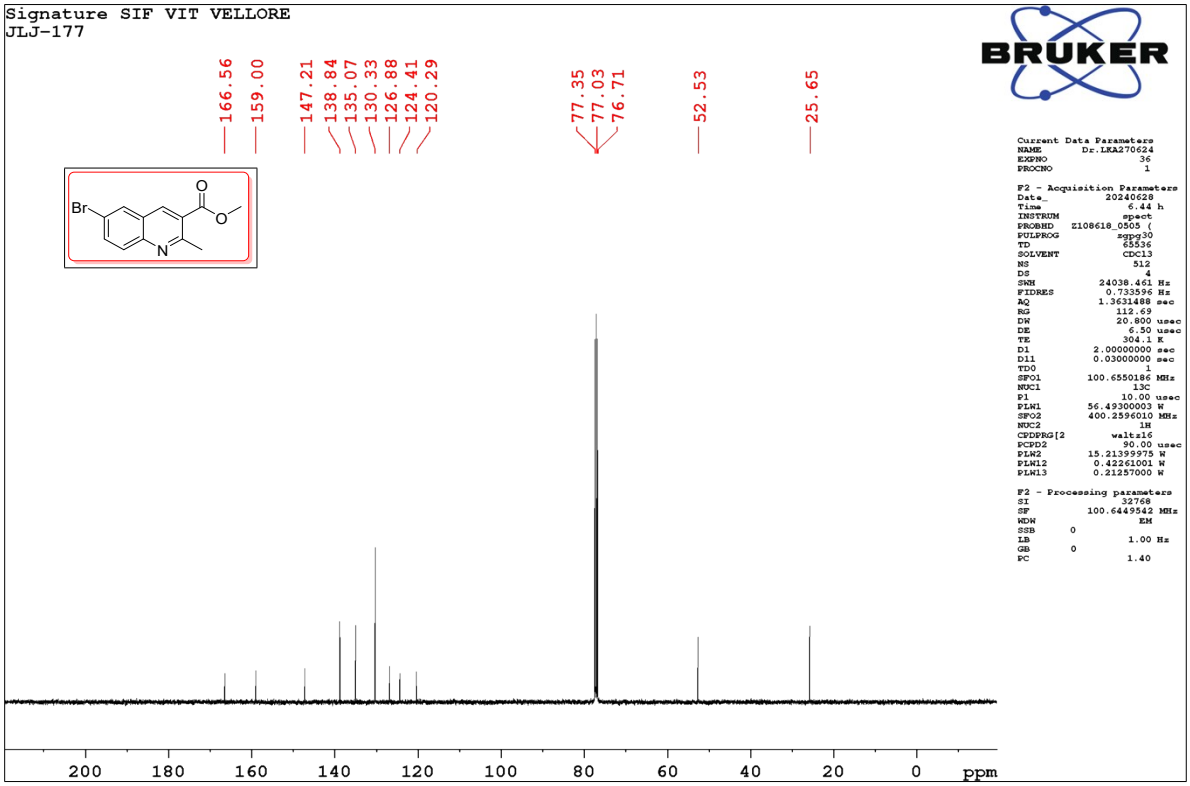


Figure S49. ^{1}H NMR spectrum of **7f** ($CDCl_3$, 400 MHz)

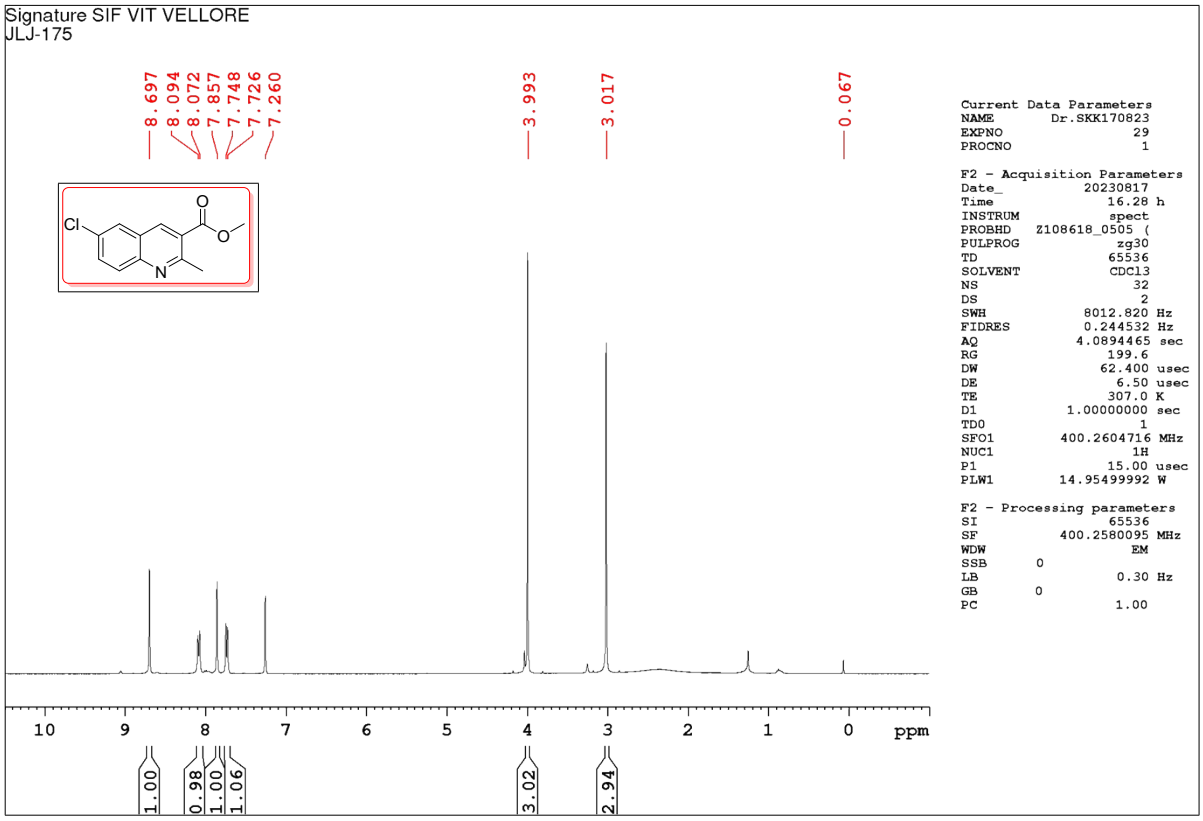


Figure S50. $^{13}C\{^{1}H\}$ NMR spectrum of **7f** ($CDCl_3$, 100 MHz)

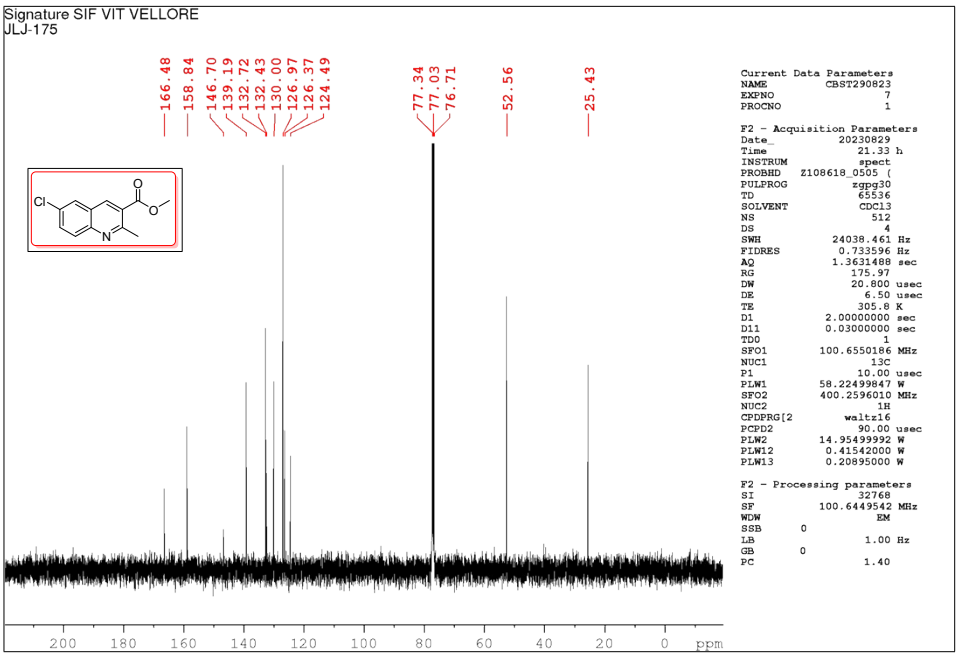


Figure S51. ^{1}H NMR spectrum of **7g** ($CDCl_3$, 400 MHz)

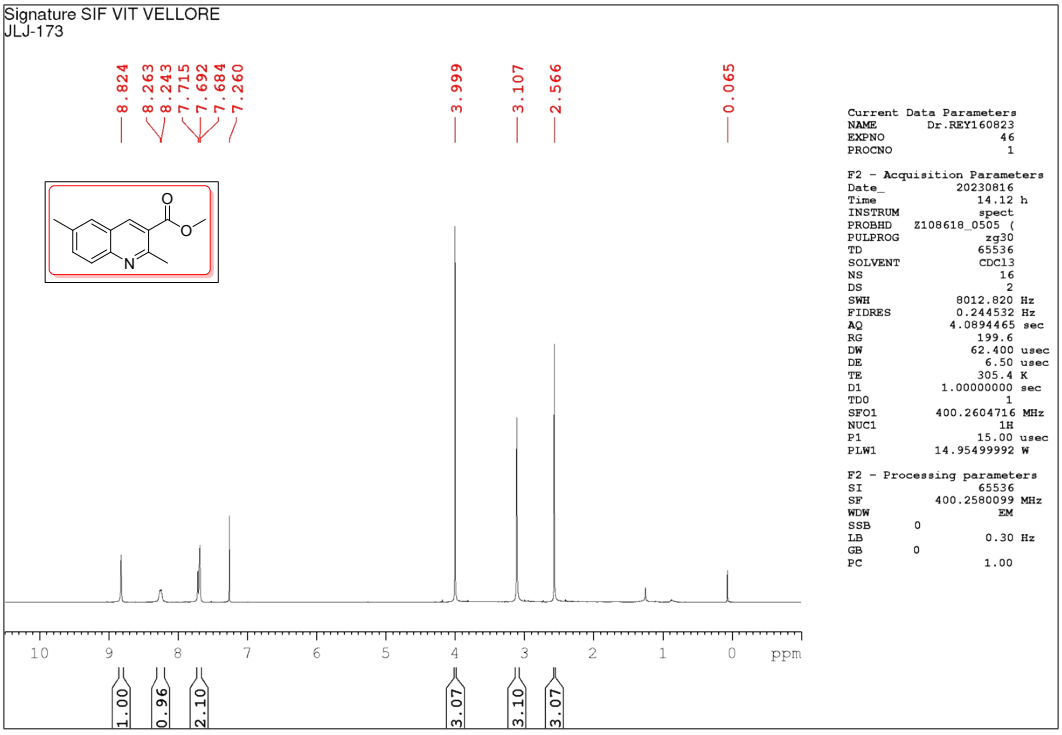


Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum of **7g** ($CDCl_3$, 100 MHz)

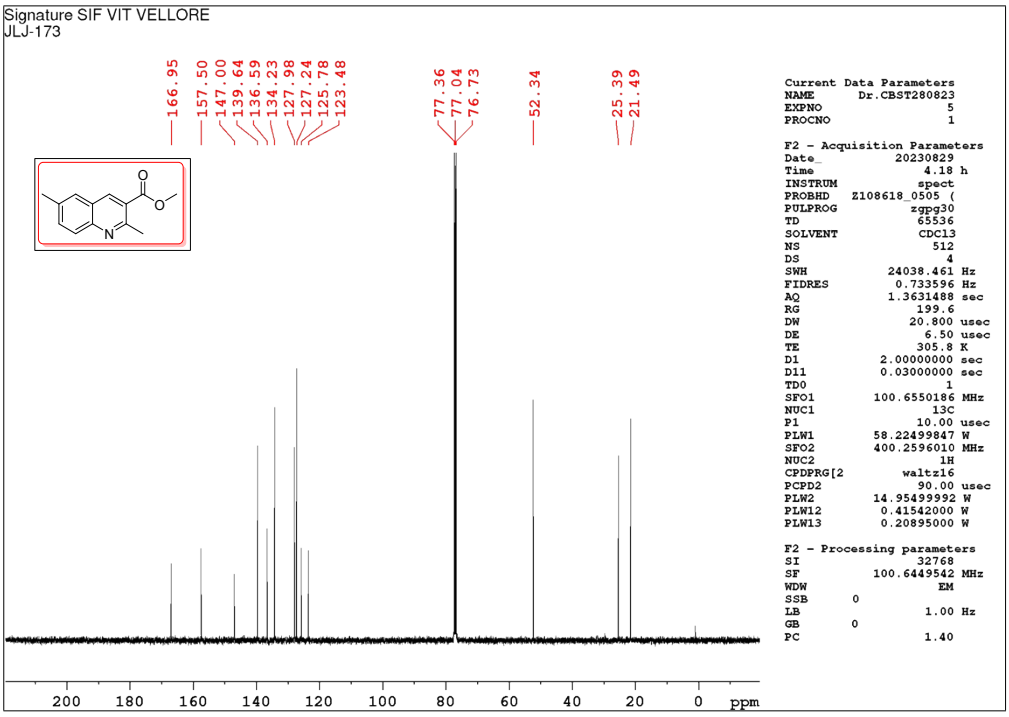


Figure S53. ^{1}H NMR spectrum of **9a** ($CDCl_3$, 400 MHz)

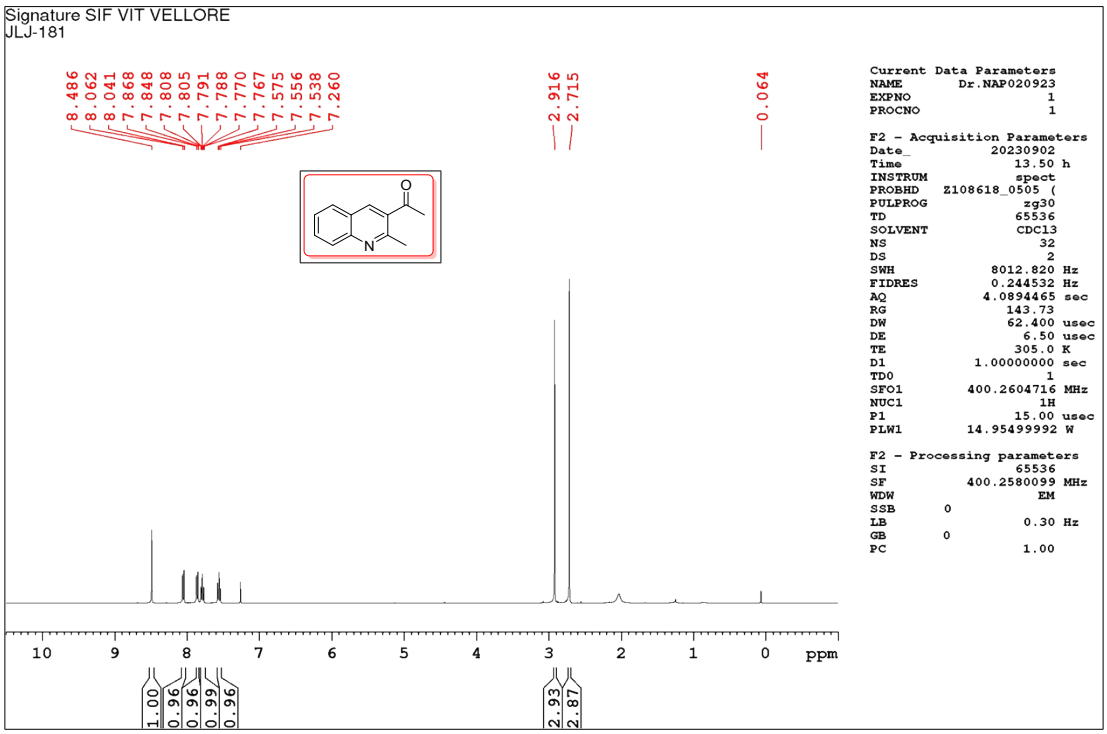


Figure S54. $^{13}C\{^{1}H\}$ NMR spectrum of **9a** ($CDCl_3$, 100 MHz)

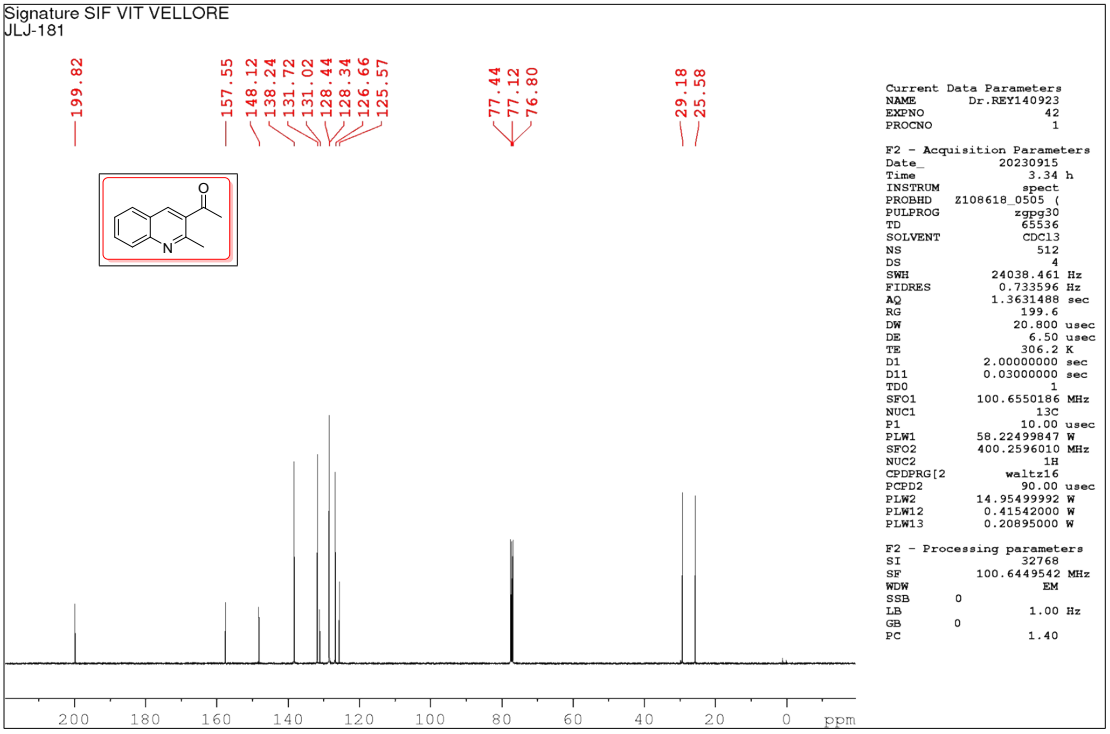


Figure S55. ^{1}H NMR spectrum of **9b** ($CDCl_3$, 400 MHz)

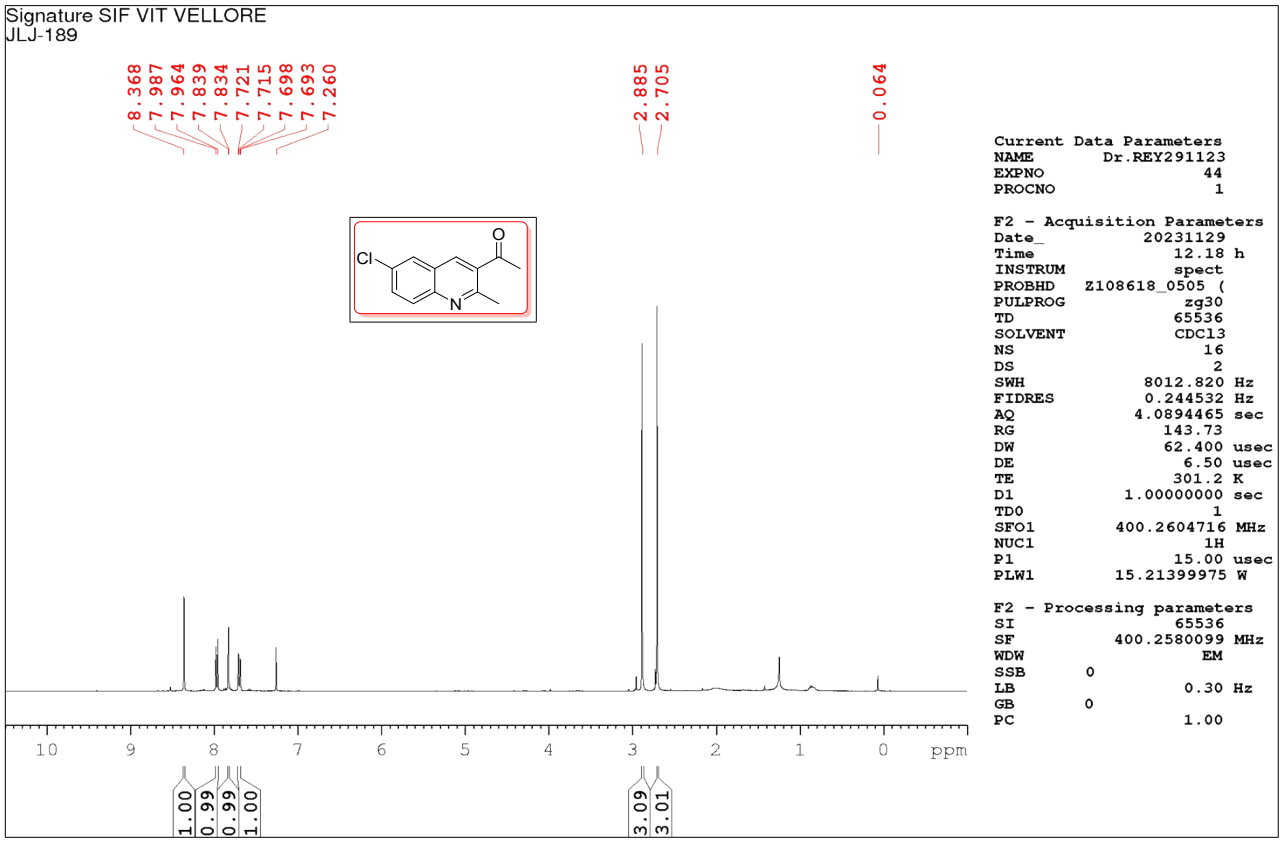


Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum of **9b** ($CDCl_3$, 100 MHz)

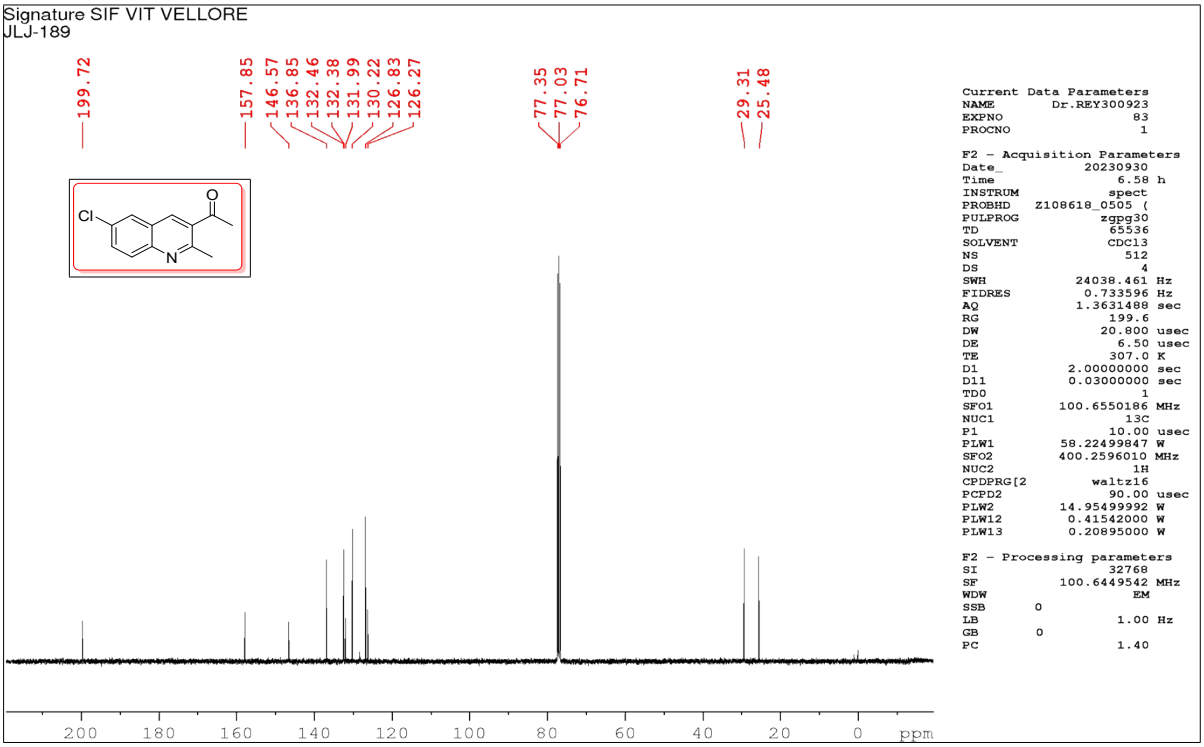


Figure S57. ^{1}H NMR spectrum of **9c** ($CDCl_3$, 400 MHz)

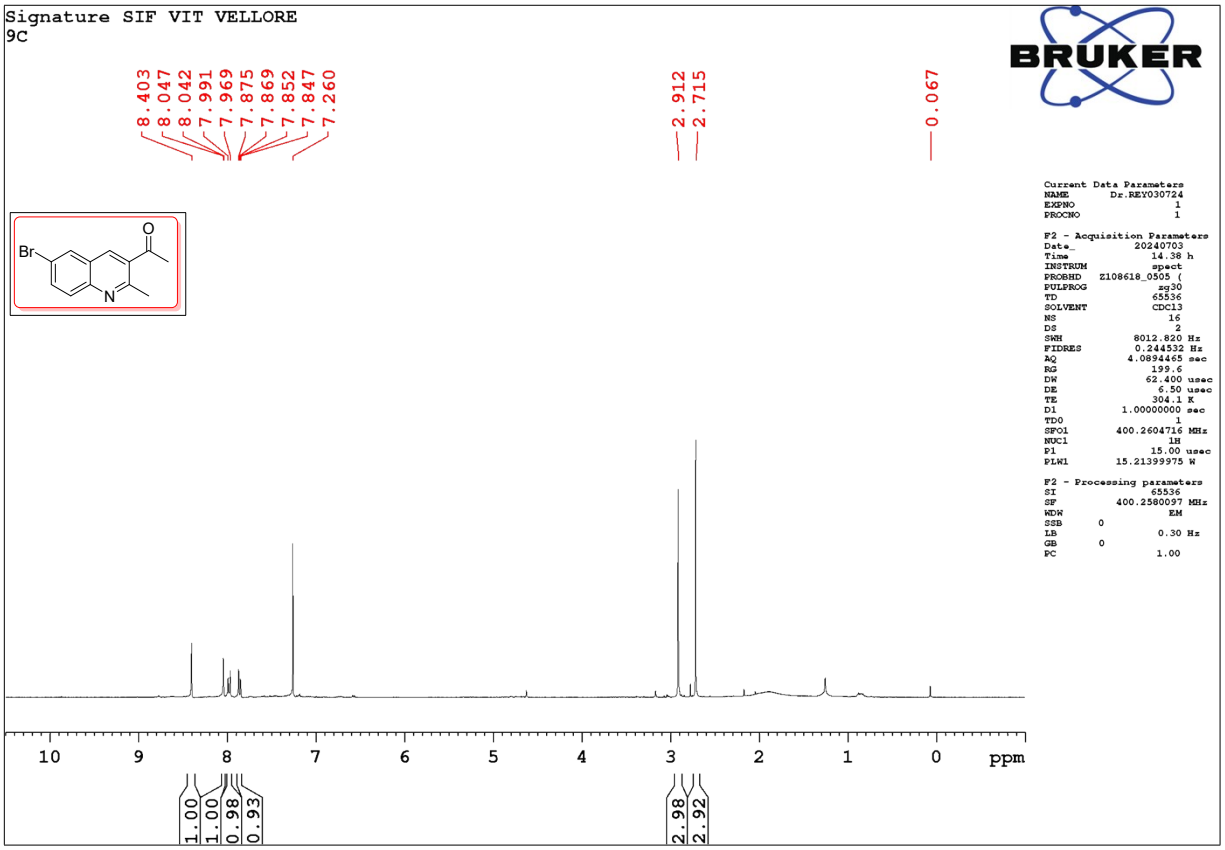


Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum of **9c** ($CDCl_3$, 100 MHz)

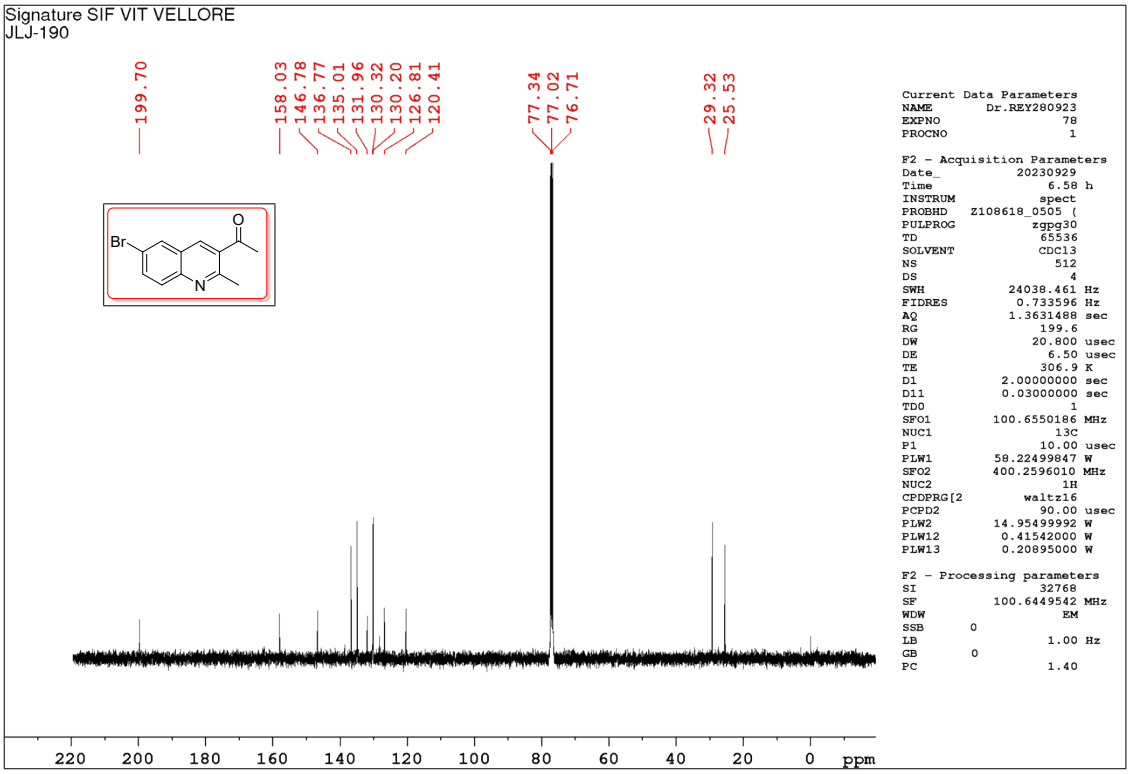


Figure S59. ^{1}H NMR spectrum of **9d** ($CDCl_3$, 400 MHz)

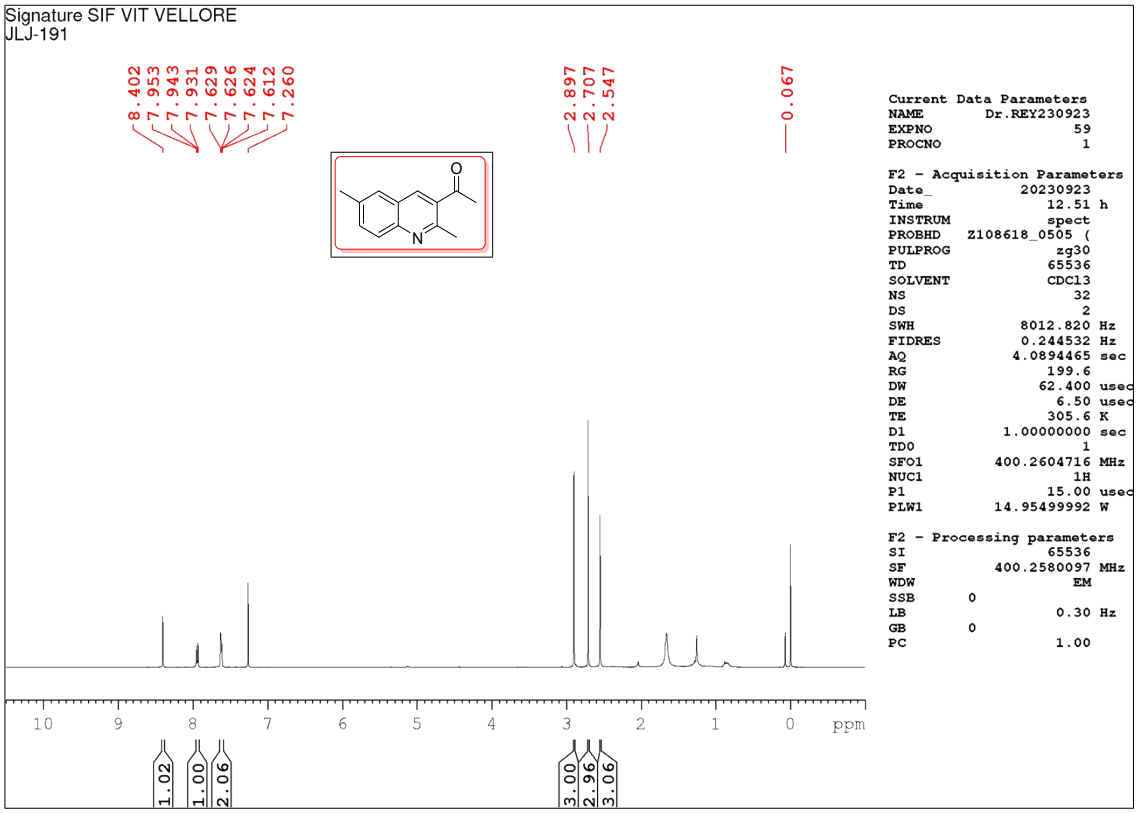


Figure S60. $^{13}C\{^{1}H\}$ NMR spectrum of **9d** ($CDCl_3$, 100 MHz)

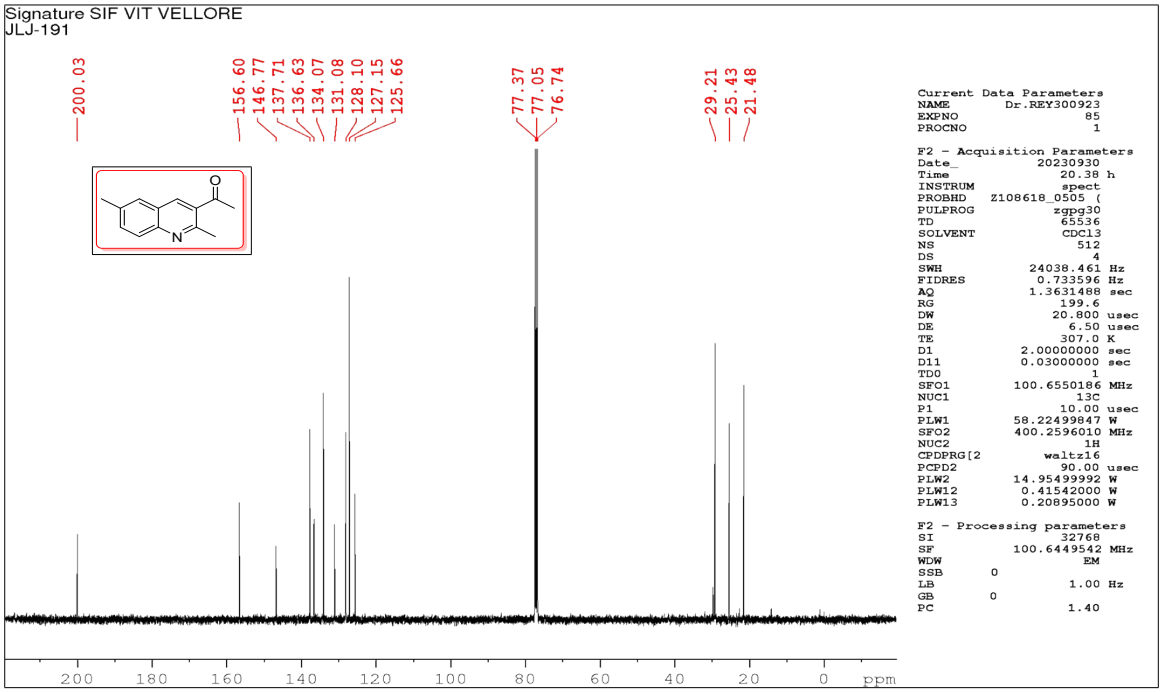


Figure S61. HRMS Spectrum of compound **9d**

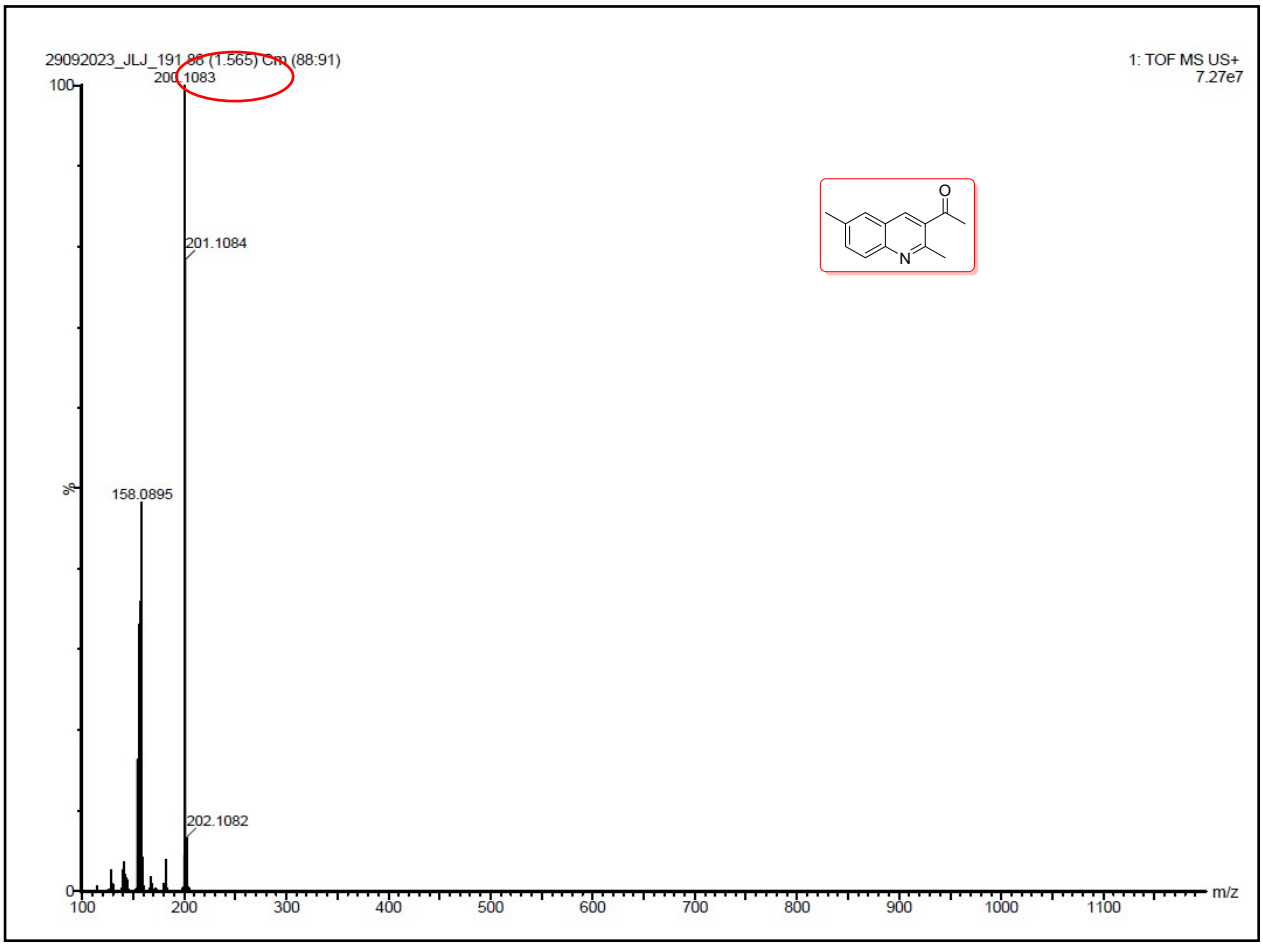


Figure S62. ^{1}H NMR spectrum of **9e** ($CDCl_3$, 400 MHz)

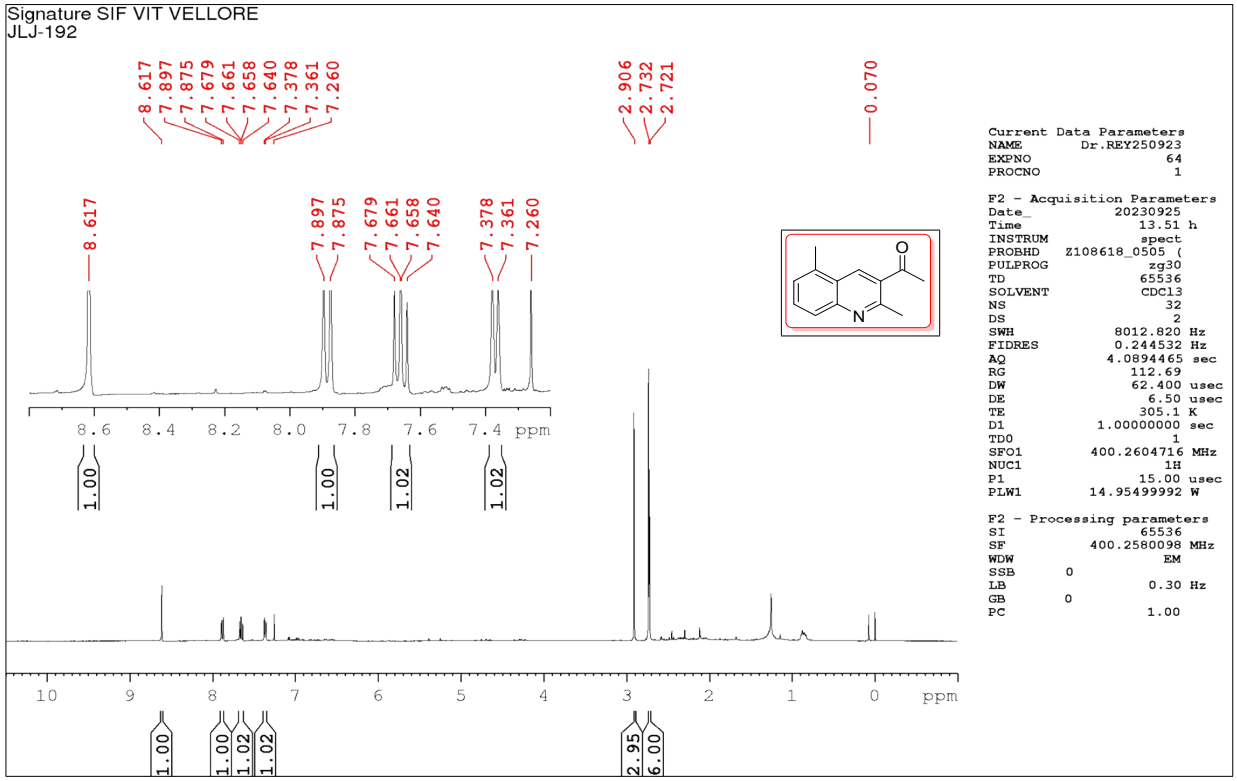


Figure S63. $^{13}C\{^{1}H\}$ NMR spectrum of **9e** ($CDCl_3$, 100 MHz)

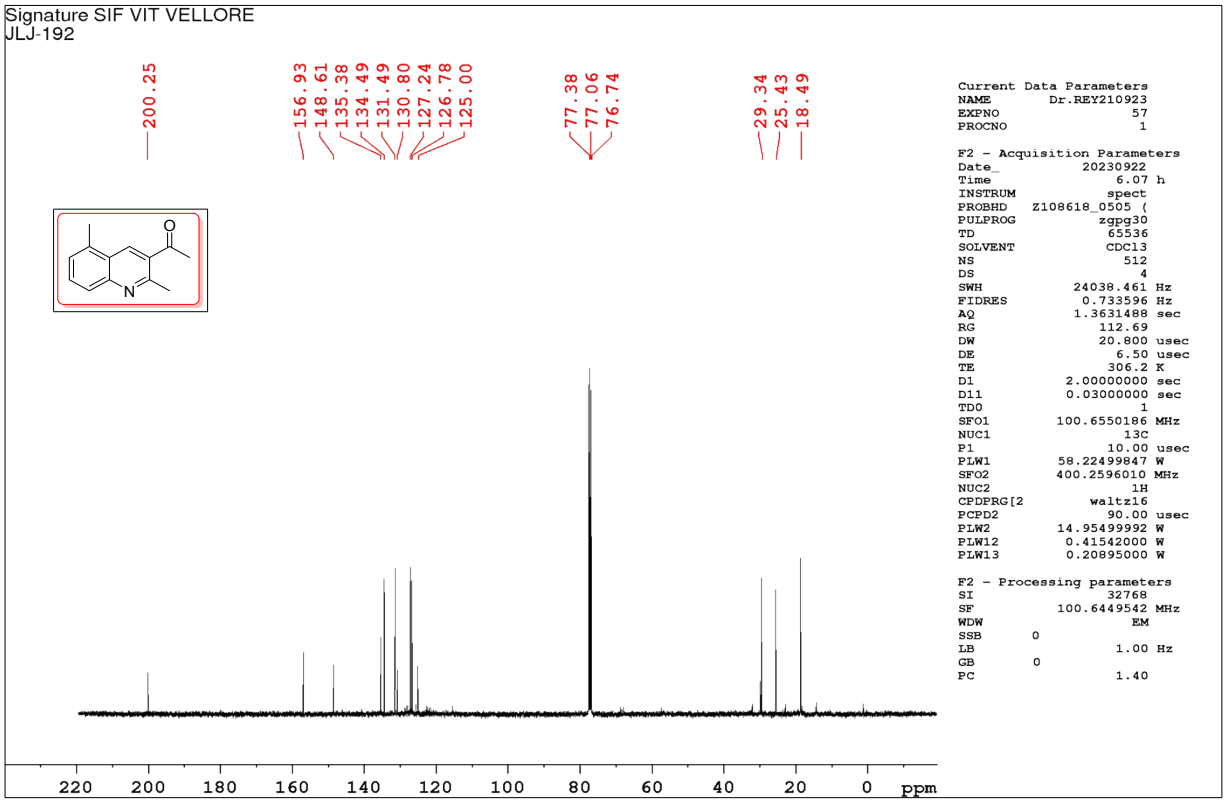


Figure S64. HRMS Spectrum of compound **9e**

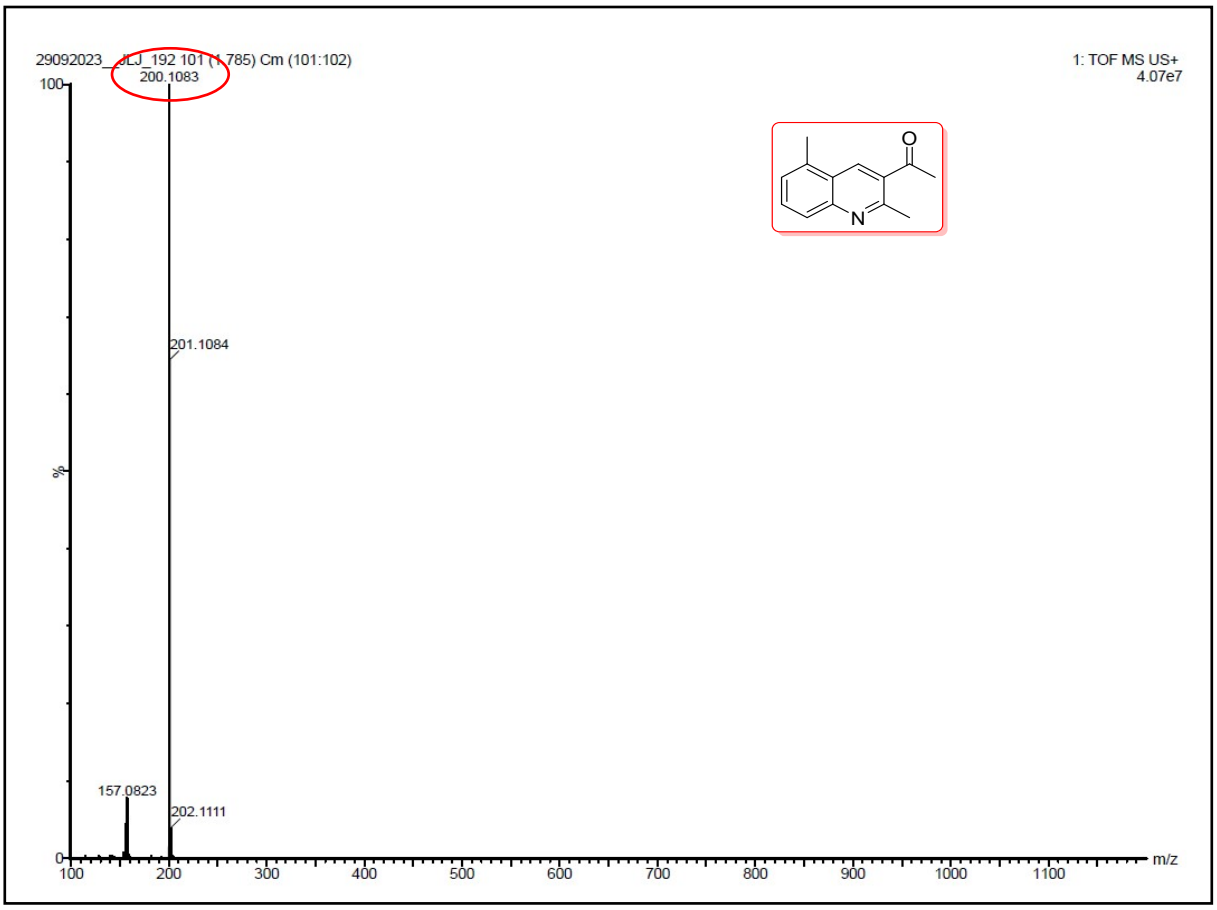


Figure S65. ^{1}H NMR spectrum of **9f** ($CDCl_3$, 400 MHz)

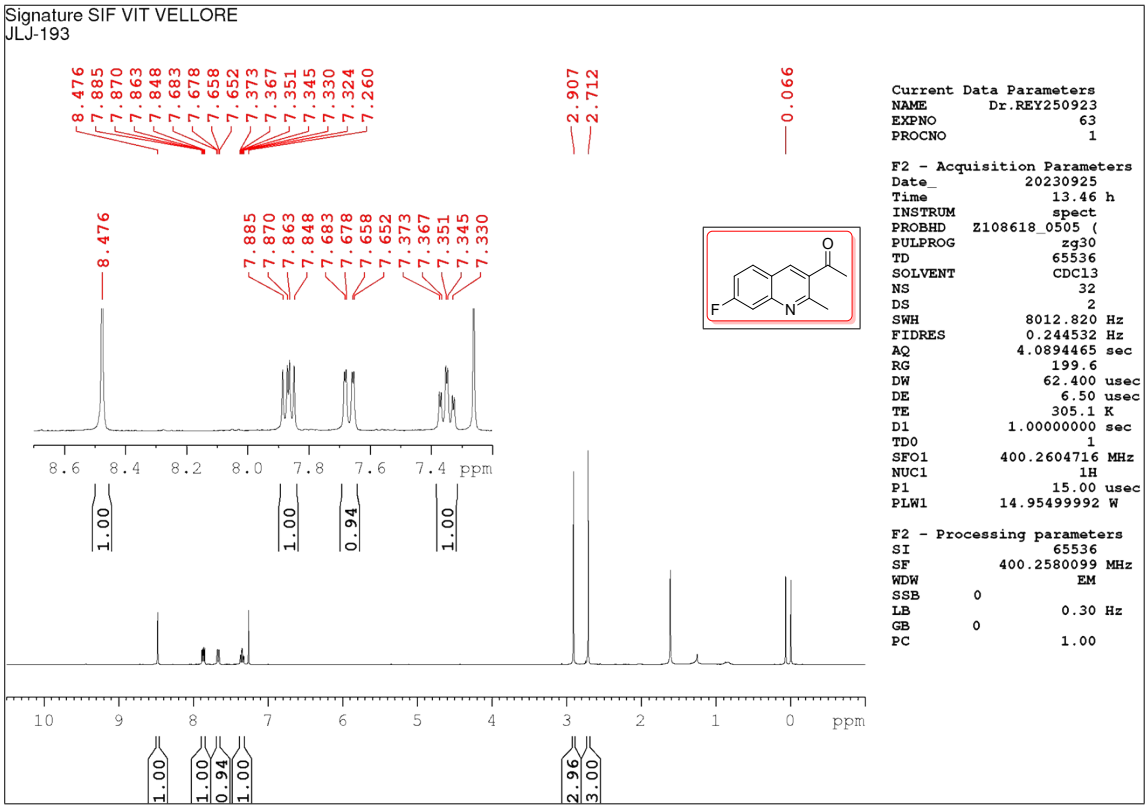


Figure S66. $^{13}C\{^{1}H\}$ NMR spectrum of **9f** ($CDCl_3$, 100 MHz)

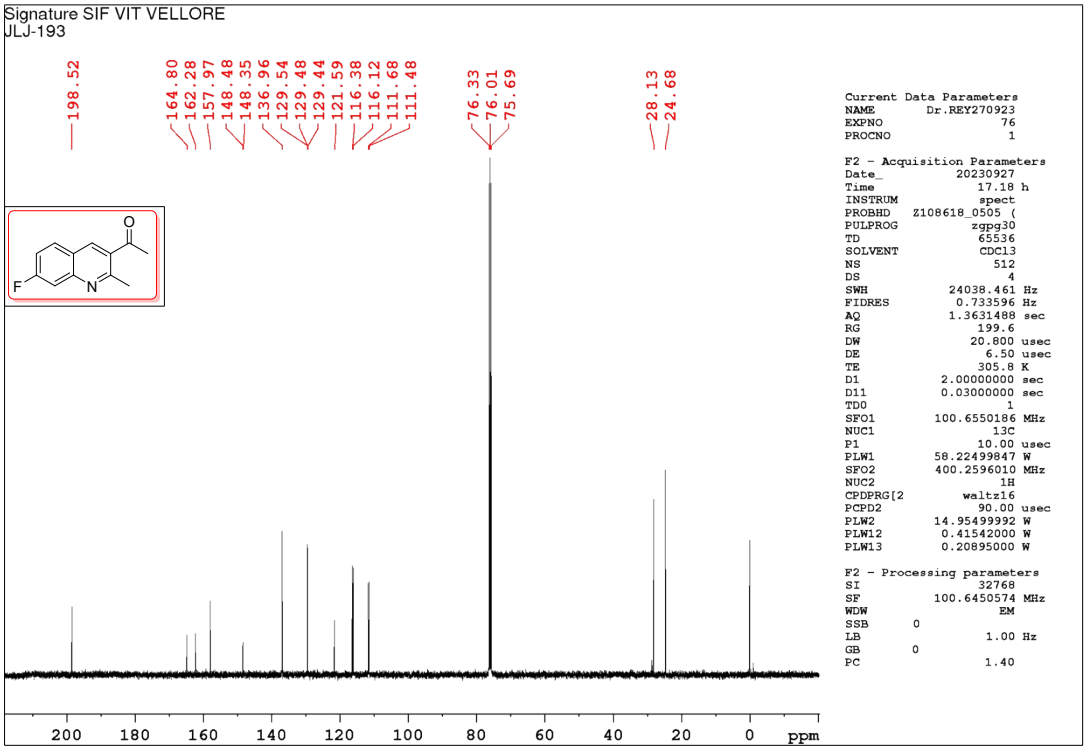


Figure S67. ^{19}F NMR spectrum of **9f** ($CDCl_3$, 376 MHz)

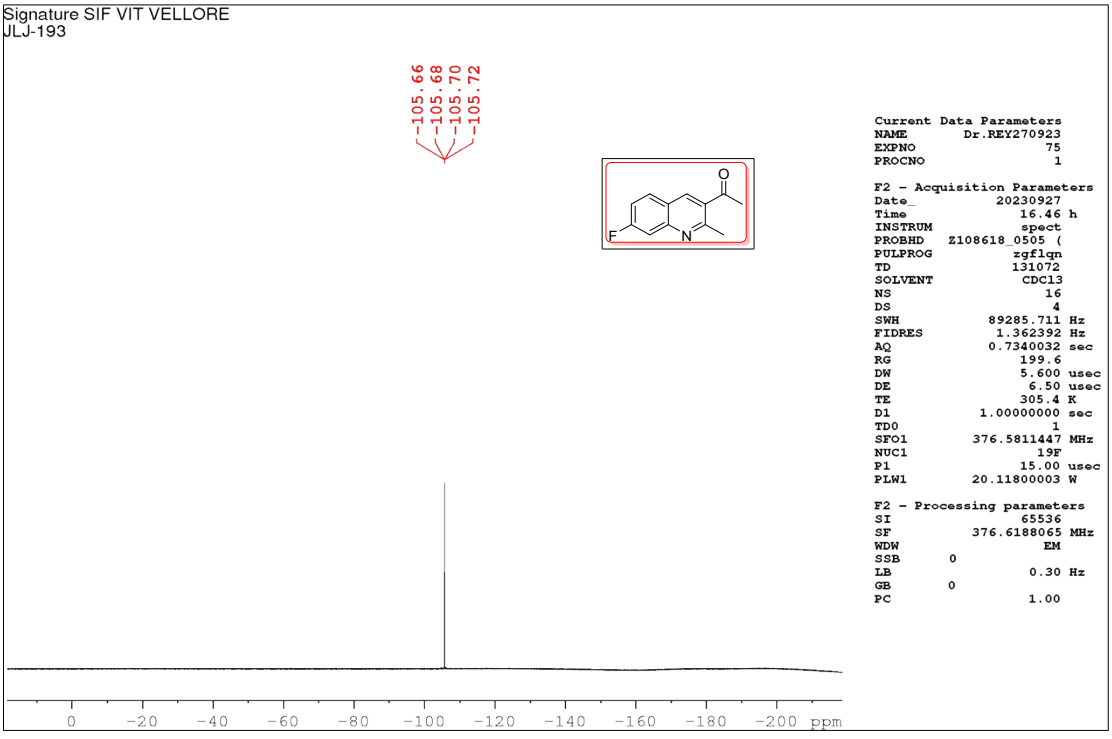


Figure S68. HRMS Spectrum of compound **9f**

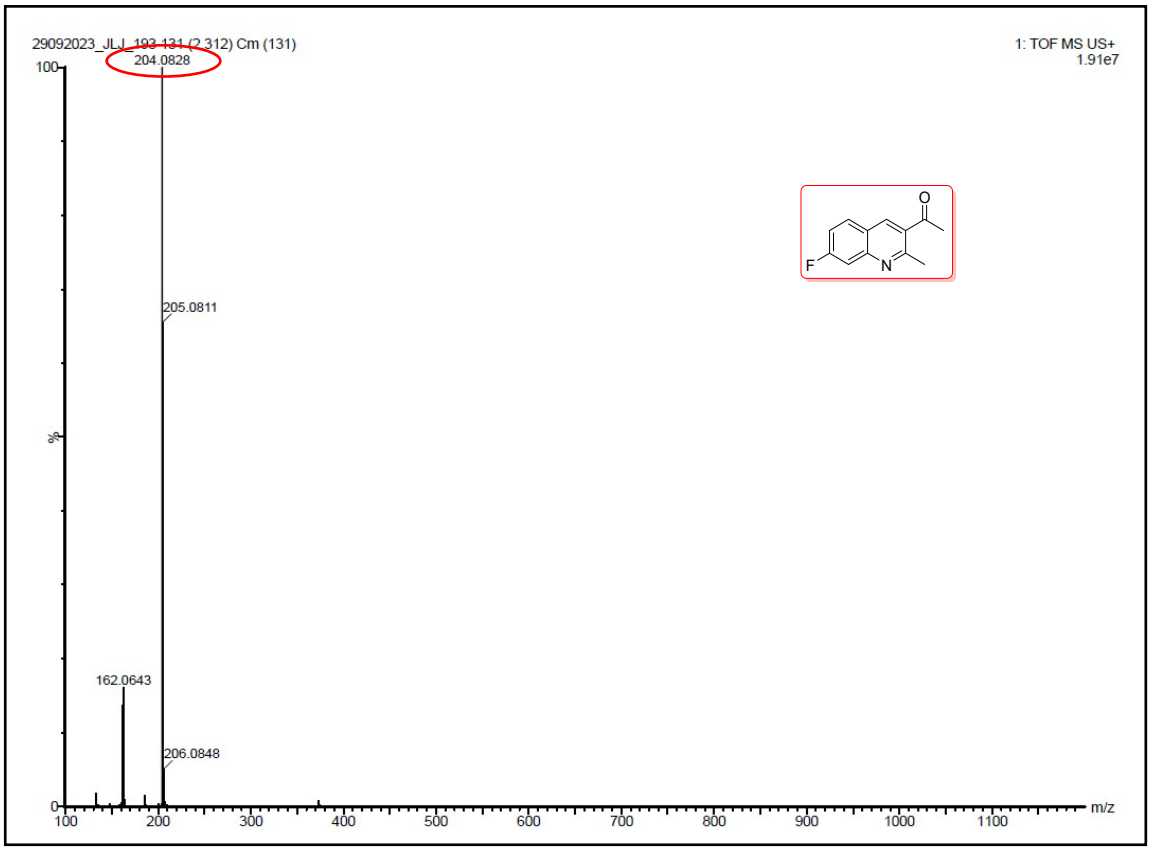


Figure S69. ^{1}H NMR spectrum of **11a** ($CDCl_3$, 400 MHz)

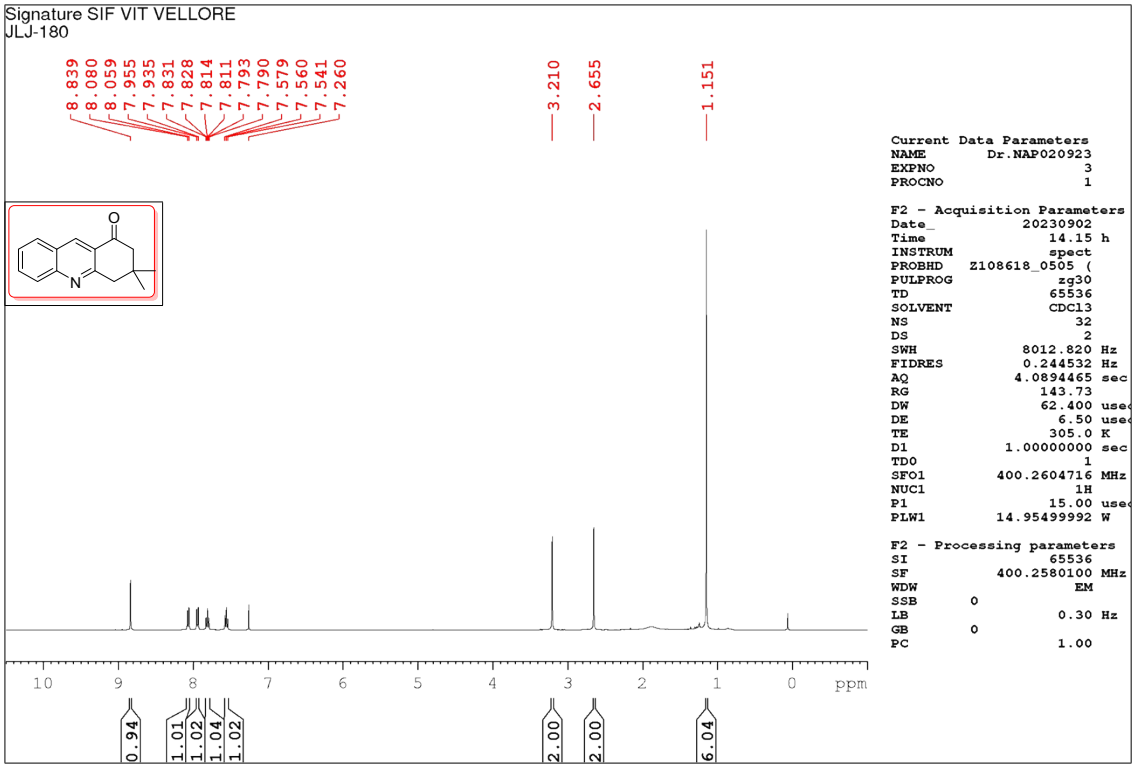


Figure S70. $^{13}C\{^{1}H\}$ NMR spectrum of **11a** ($CDCl_3$, 400 MHz)

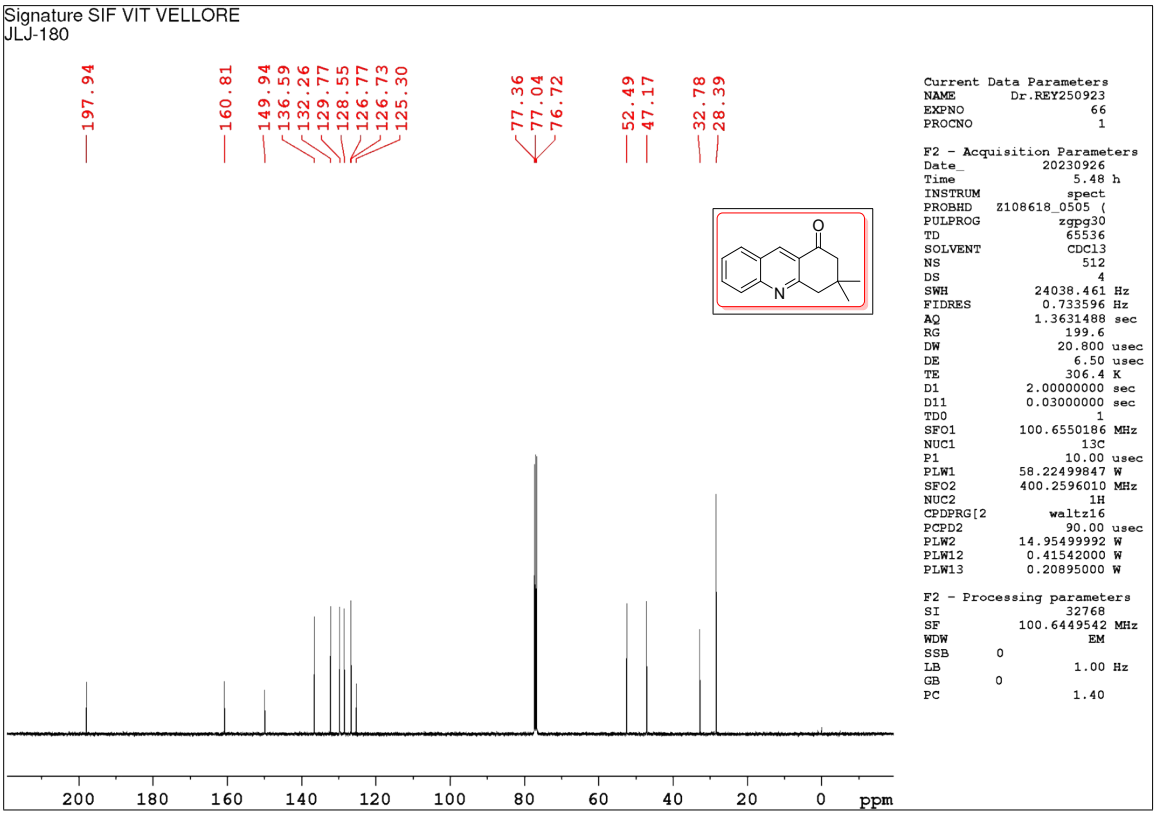


Figure S71. ^{1}H NMR spectrum of **11b** ($CDCl_3$, 400 MHz)

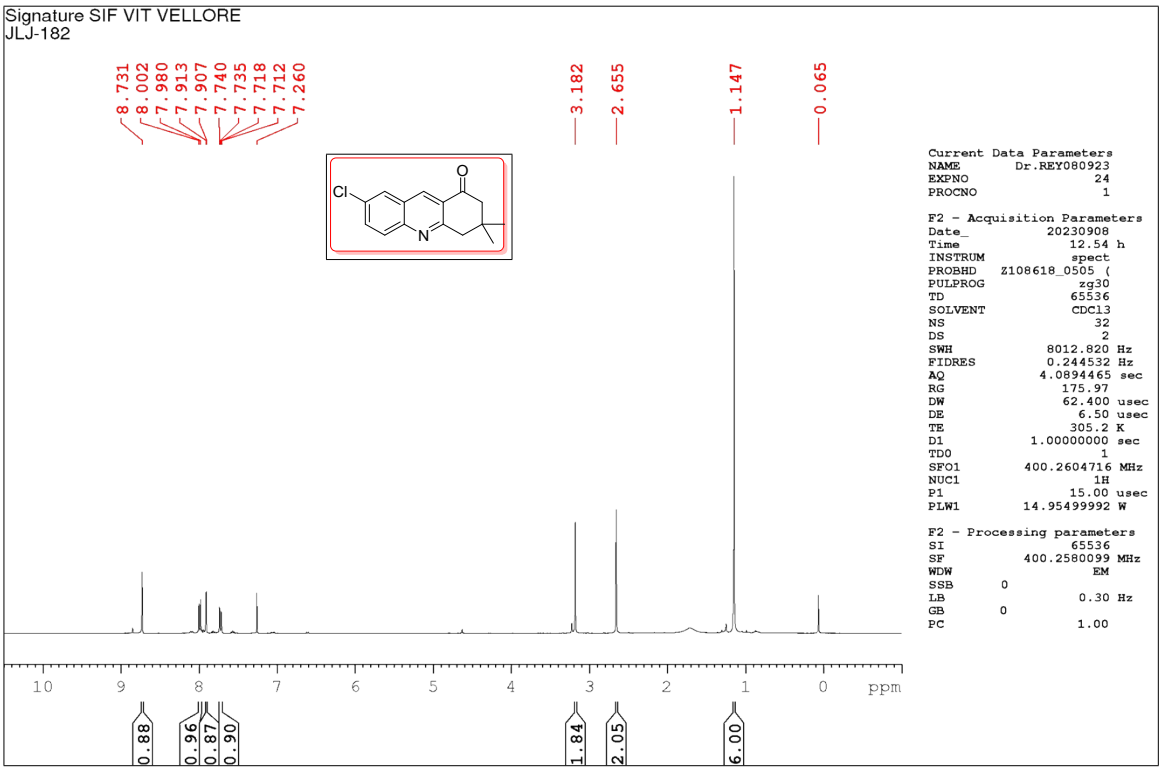


Figure S72. $^{13}C\{^{1}H\}$ NMR spectrum of **11b** ($CDCl_3$, 100 MHz)

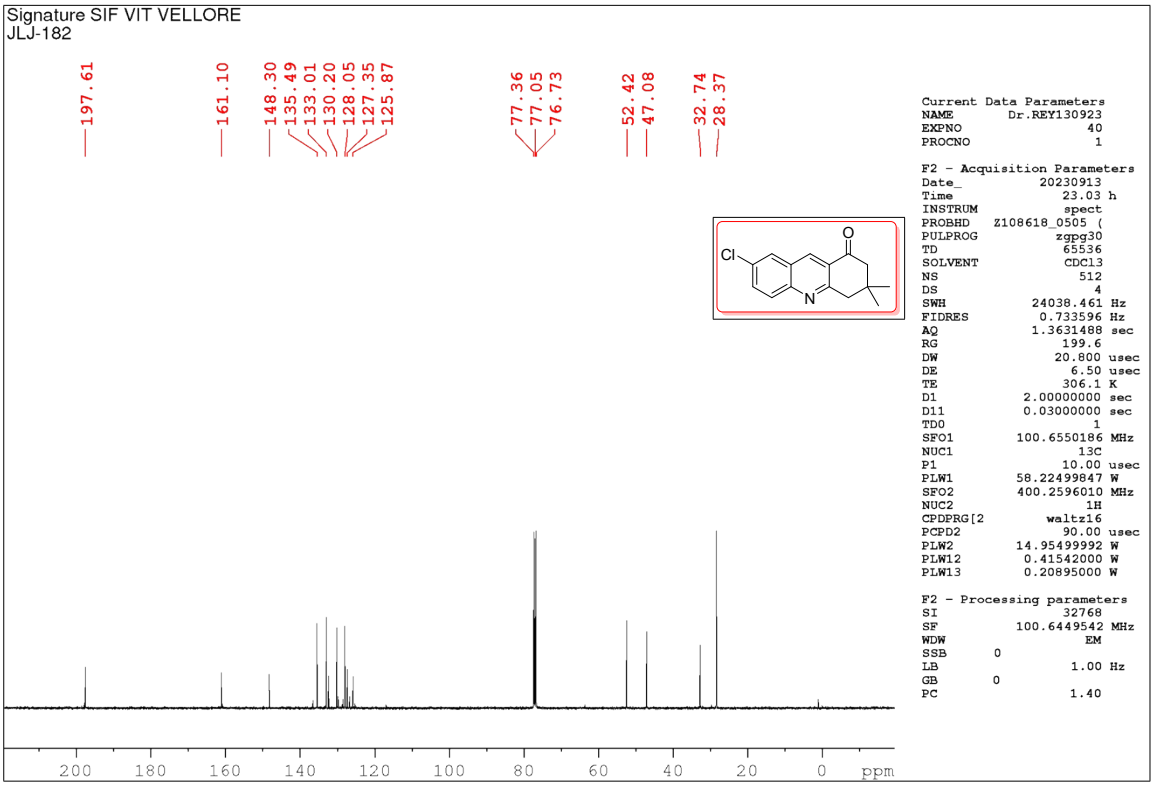


Figure S73. ^{1}H NMR spectrum of **11c** ($CDCl_3$, 400 MHz)

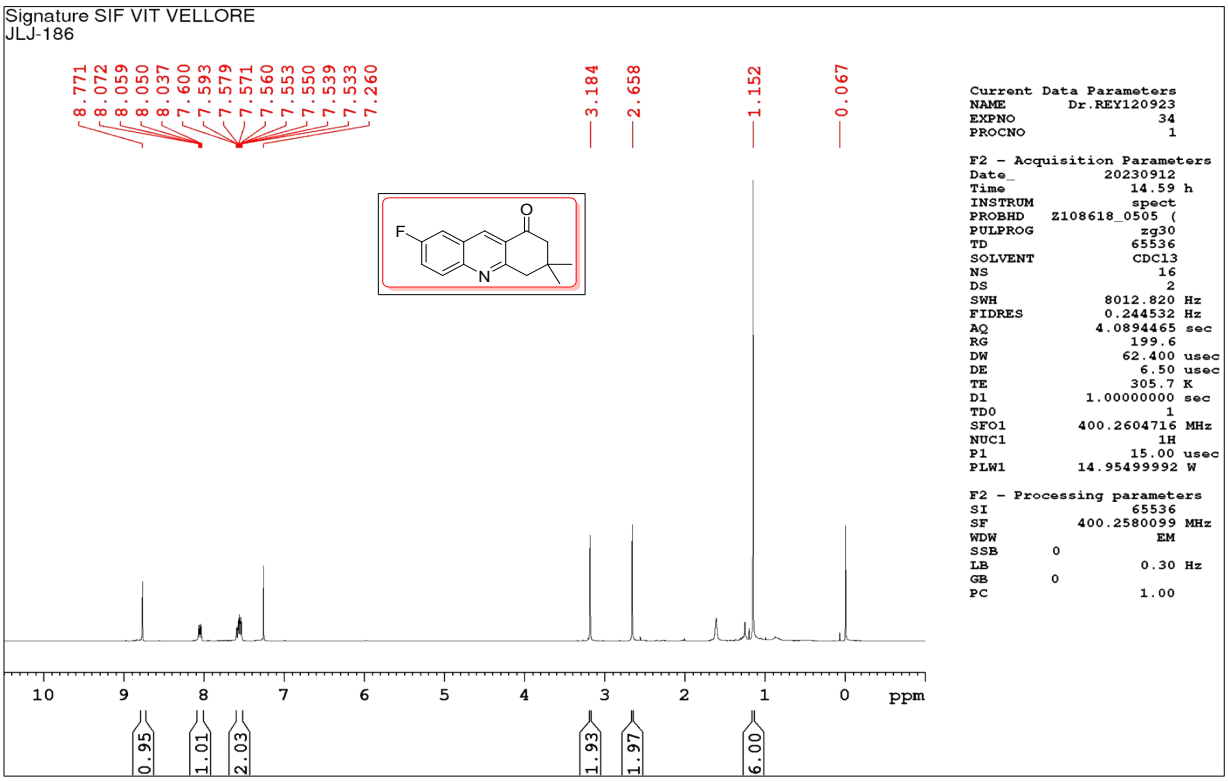


Figure S74. $^{13}C\{^{1}H\}$ NMR spectrum of **11c** ($CDCl_3$, 100 MHz)

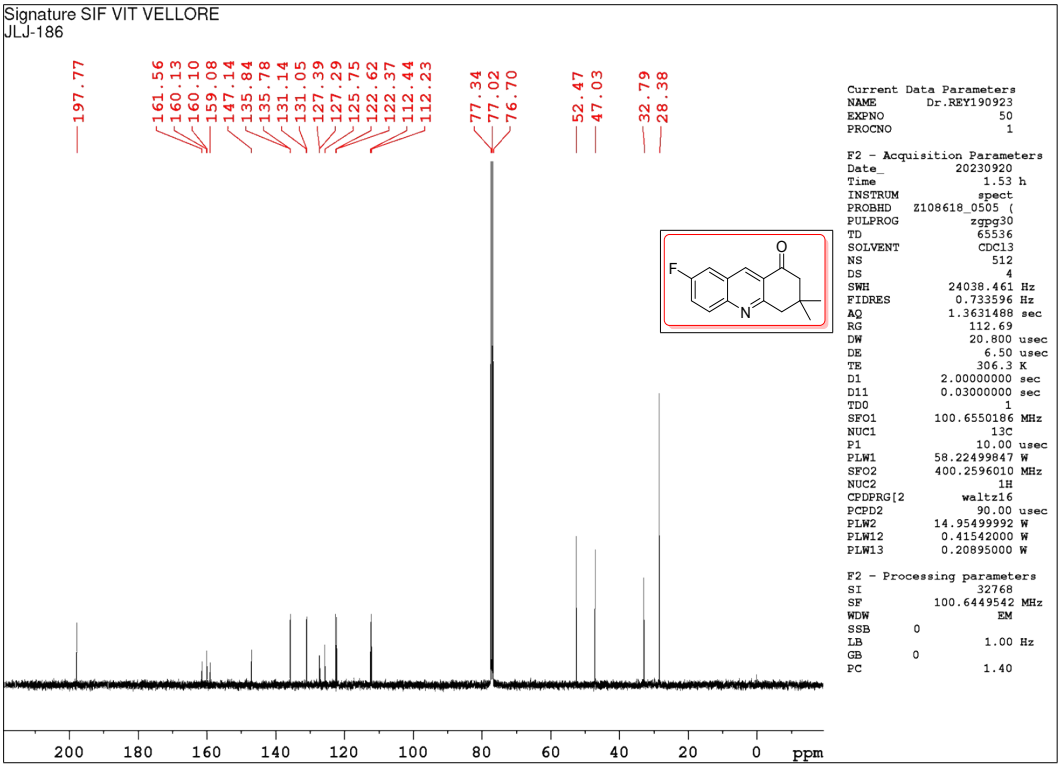


Figure S75. ^{19}F NMR spectrum of **11c** ($CDCl_3$, 376 MHz)

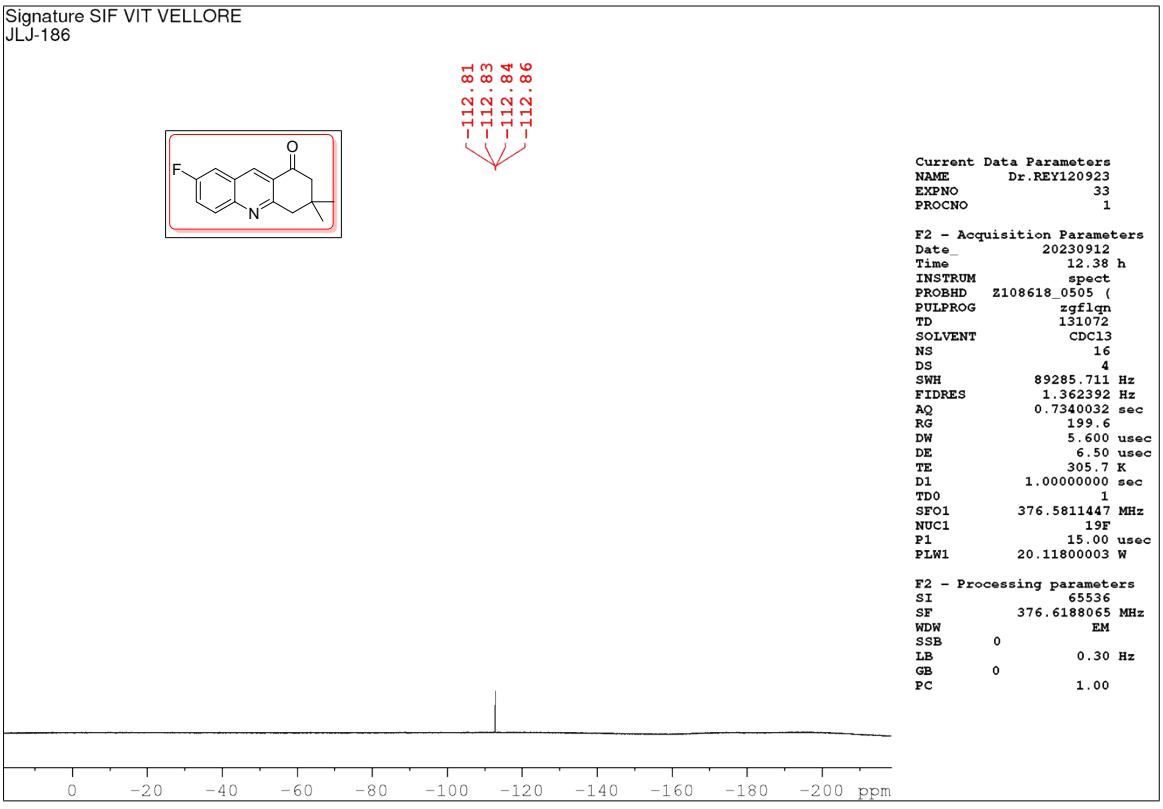


Figure S76. ^{1}H NMR spectrum of **11d** ($CDCl_3$, 400 MHz)

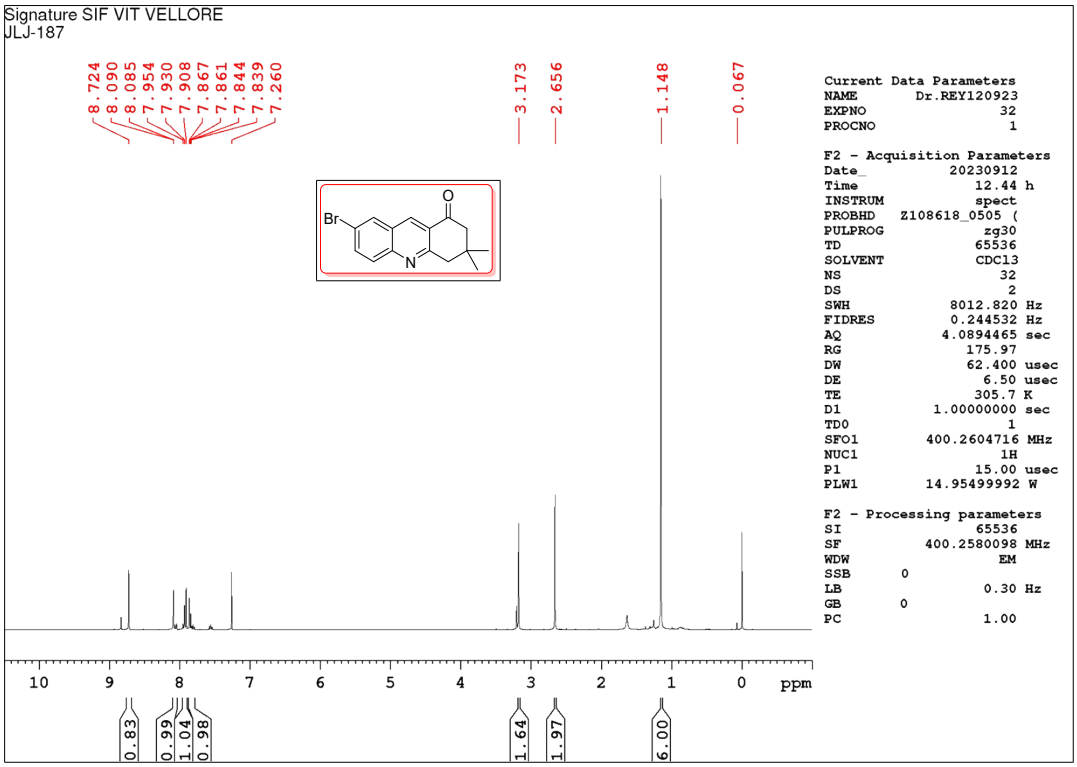


Figure S77. $^{13}C\{^{1}H\}$ NMR spectrum of **11d** ($CDCl_3$, 100 MHz)

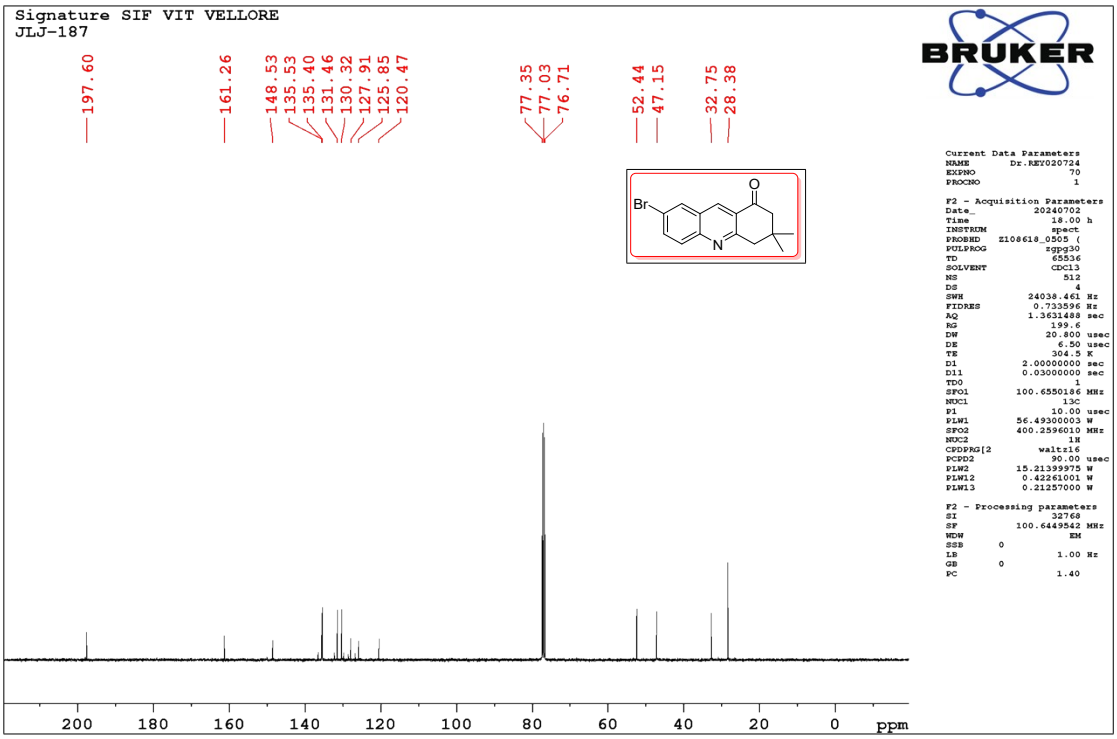


Figure S78. ^{1}H NMR spectrum of **11e** ($CDCl_3$, 400 MHz)

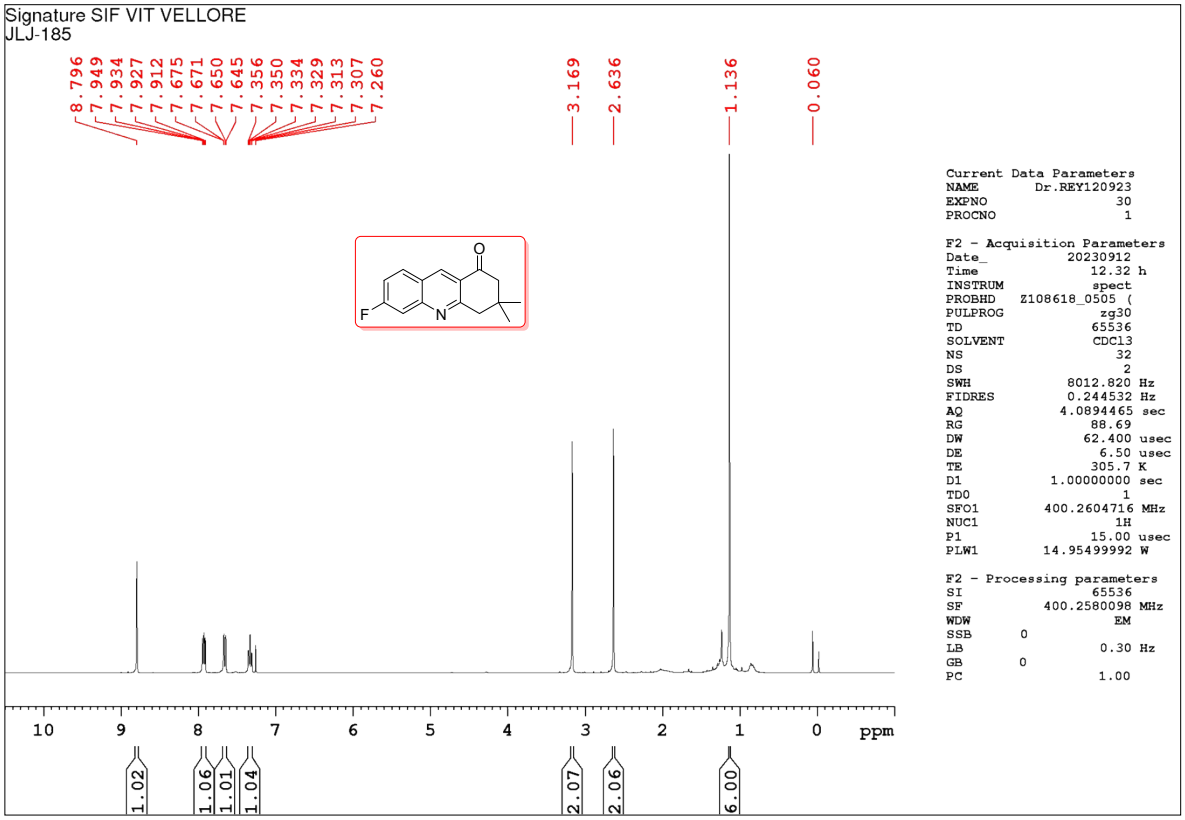


Figure S79. $^{13}C\{^{1}H\}$ NMR spectrum of **11e** ($CDCl_3$, 100 MHz)

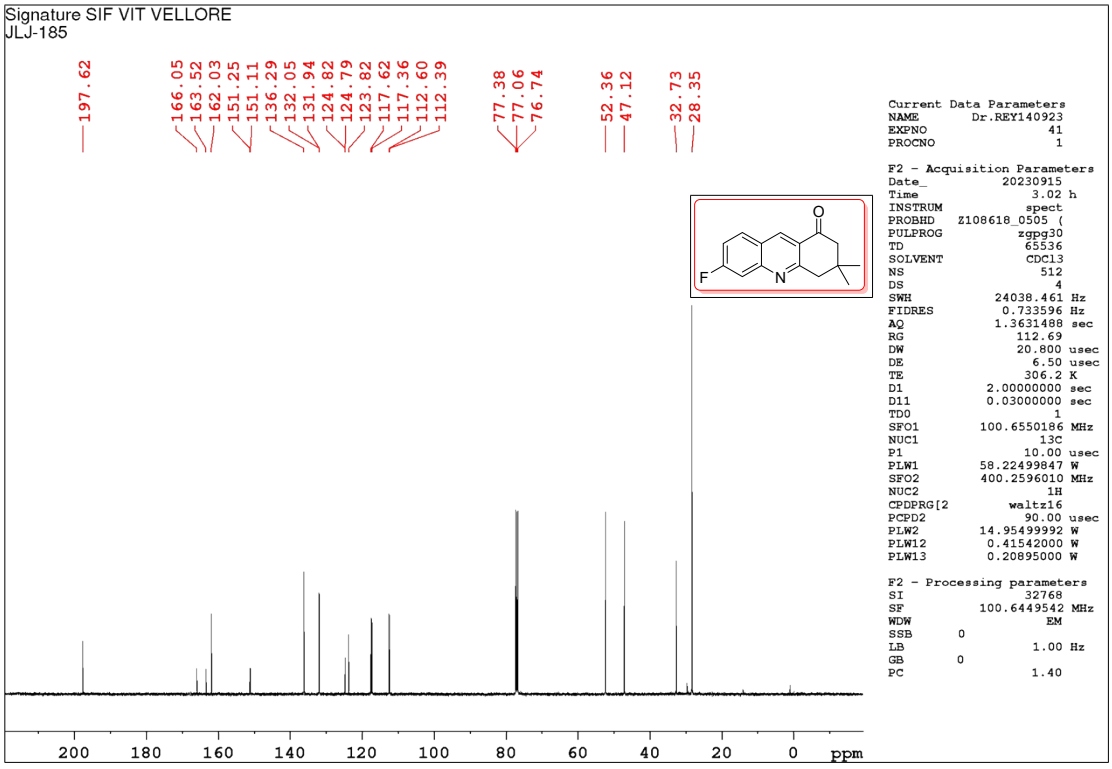


Figure S80. ^{19}F NMR spectrum of **11e** ($CDCl_3$, 376 MHz)

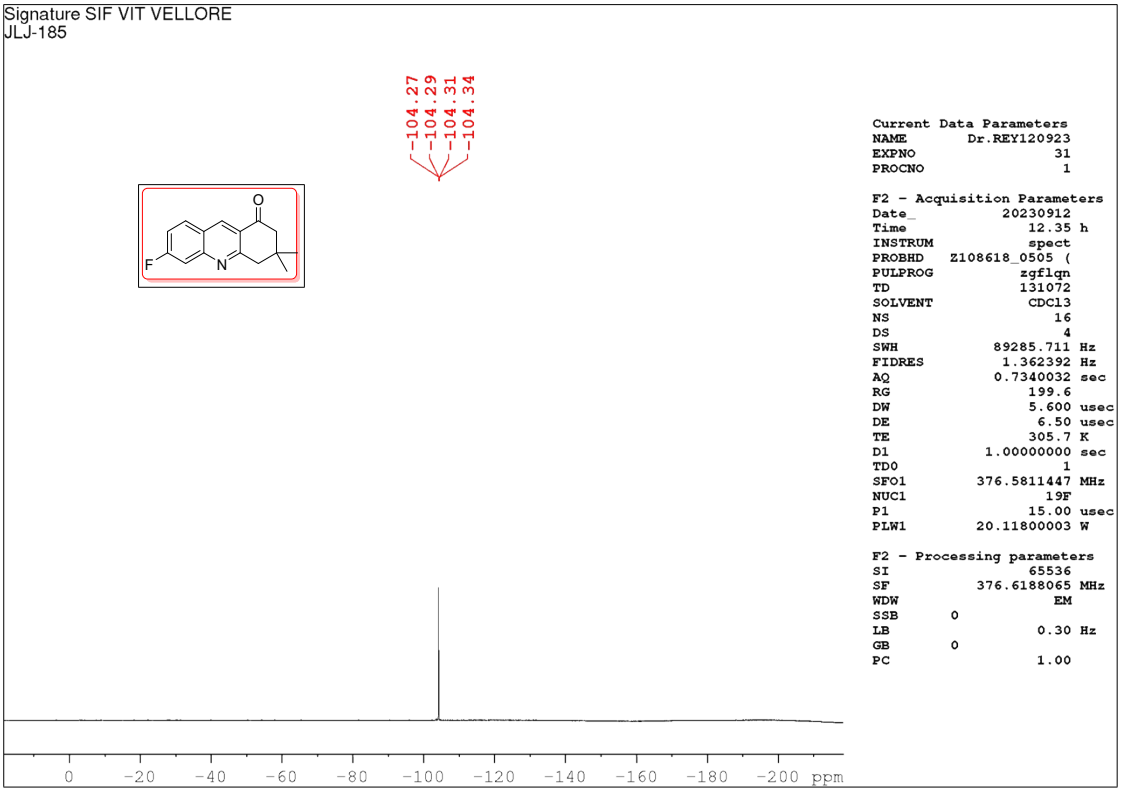


Figure S81. HRMS Spectrum of compound **11e**

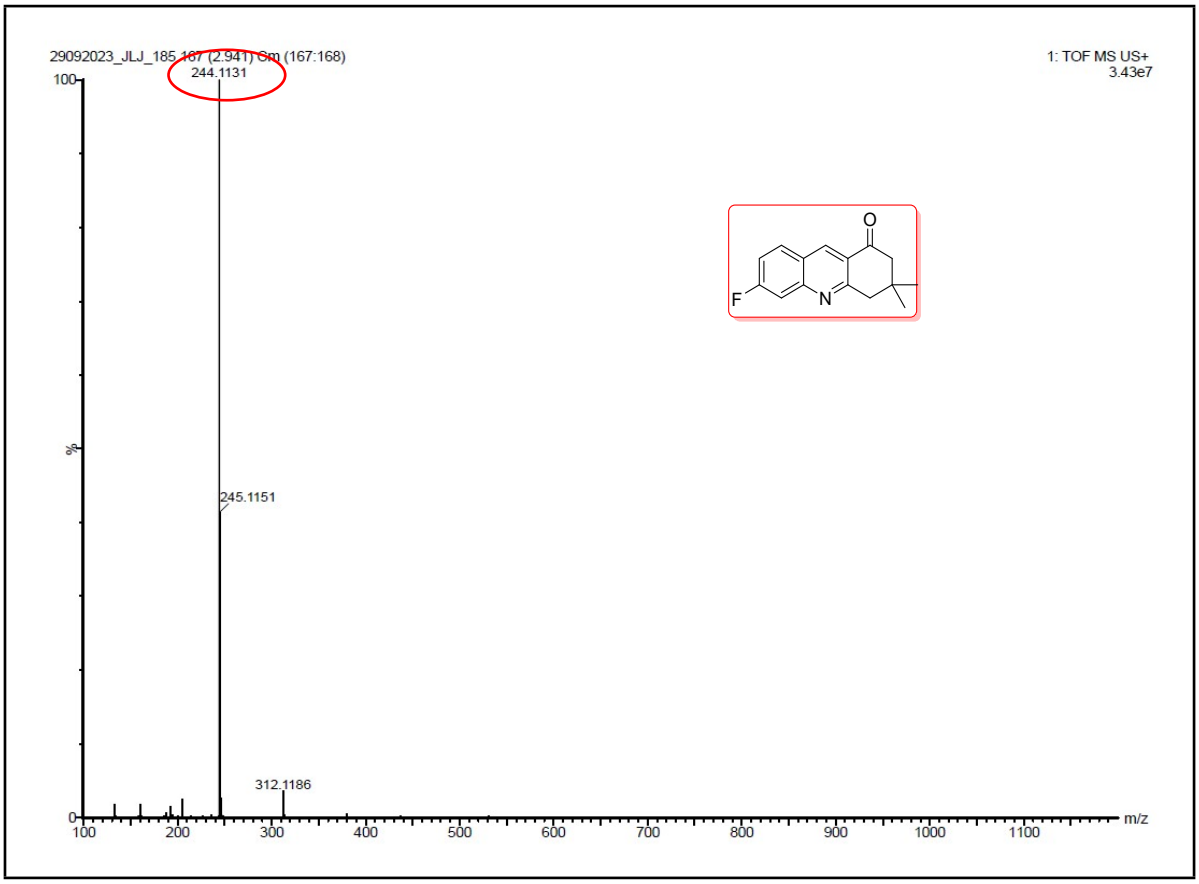


Figure S82. ^{1}H NMR spectrum of **11f** ($CDCl_3$, 400 MHz)

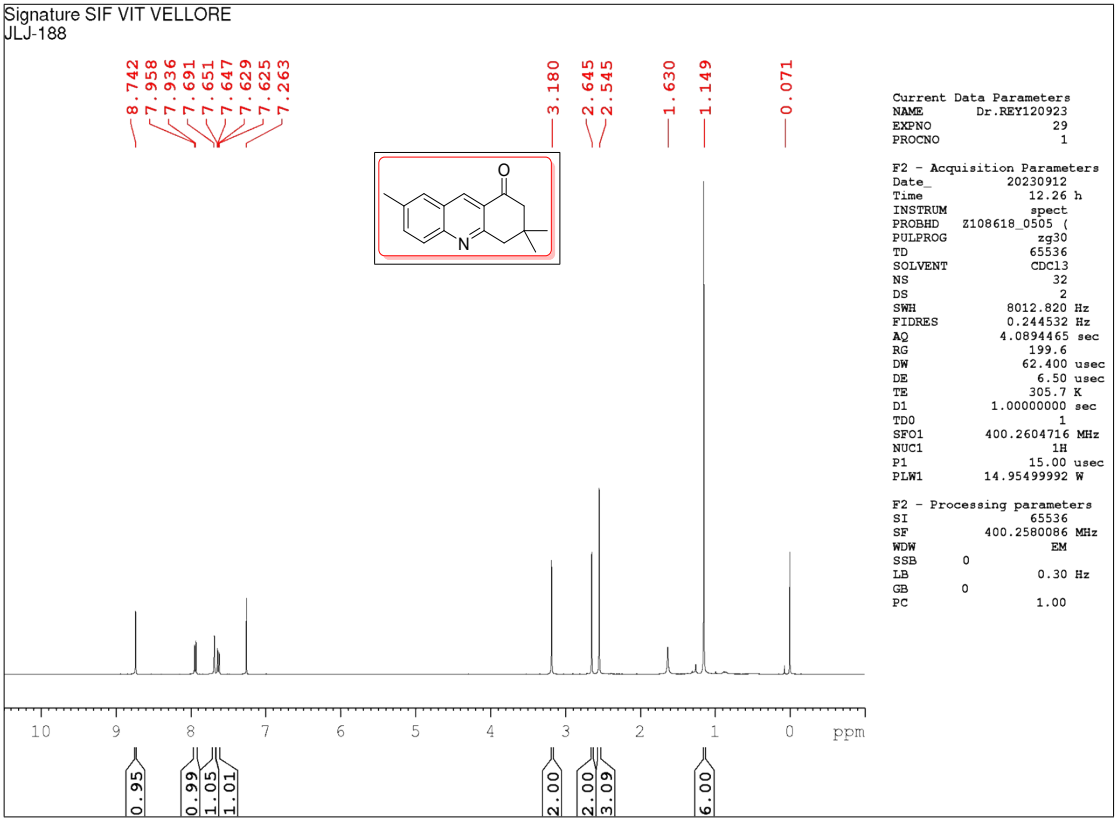


Figure S83. $^{13}C\{^{1}H\}$ NMR spectrum of **11f** ($CDCl_3$, 100 MHz)

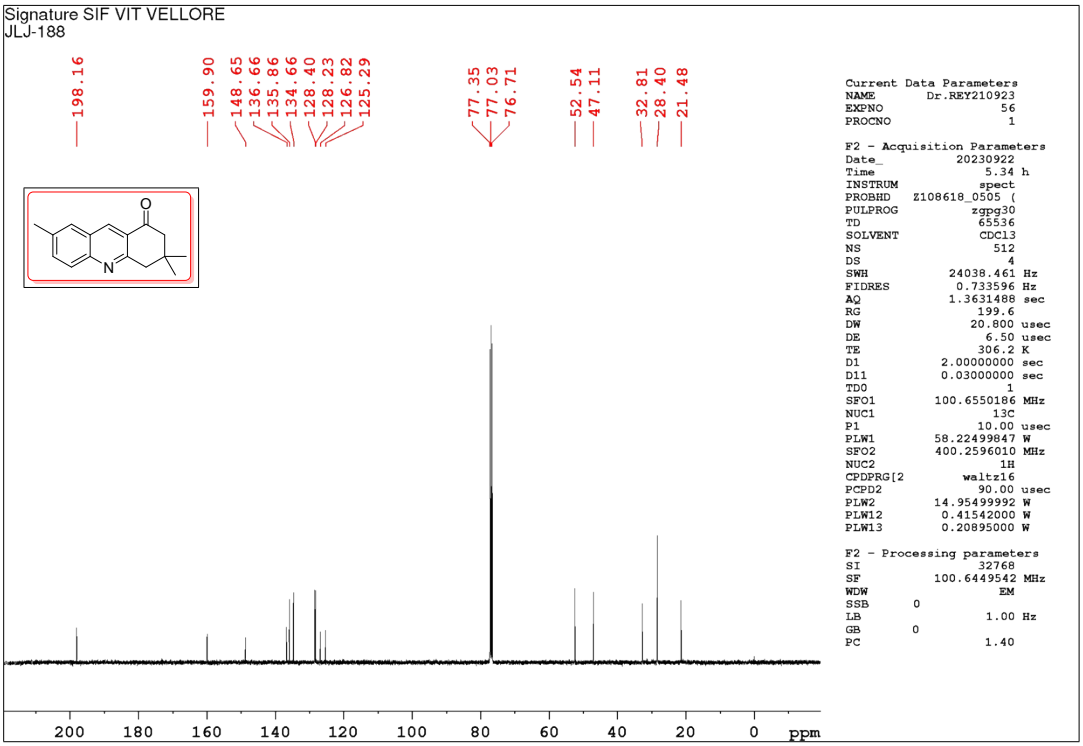


Figure S84. ^{1}H NMR spectrum of **11g** ($CDCl_3$, 400 MHz)

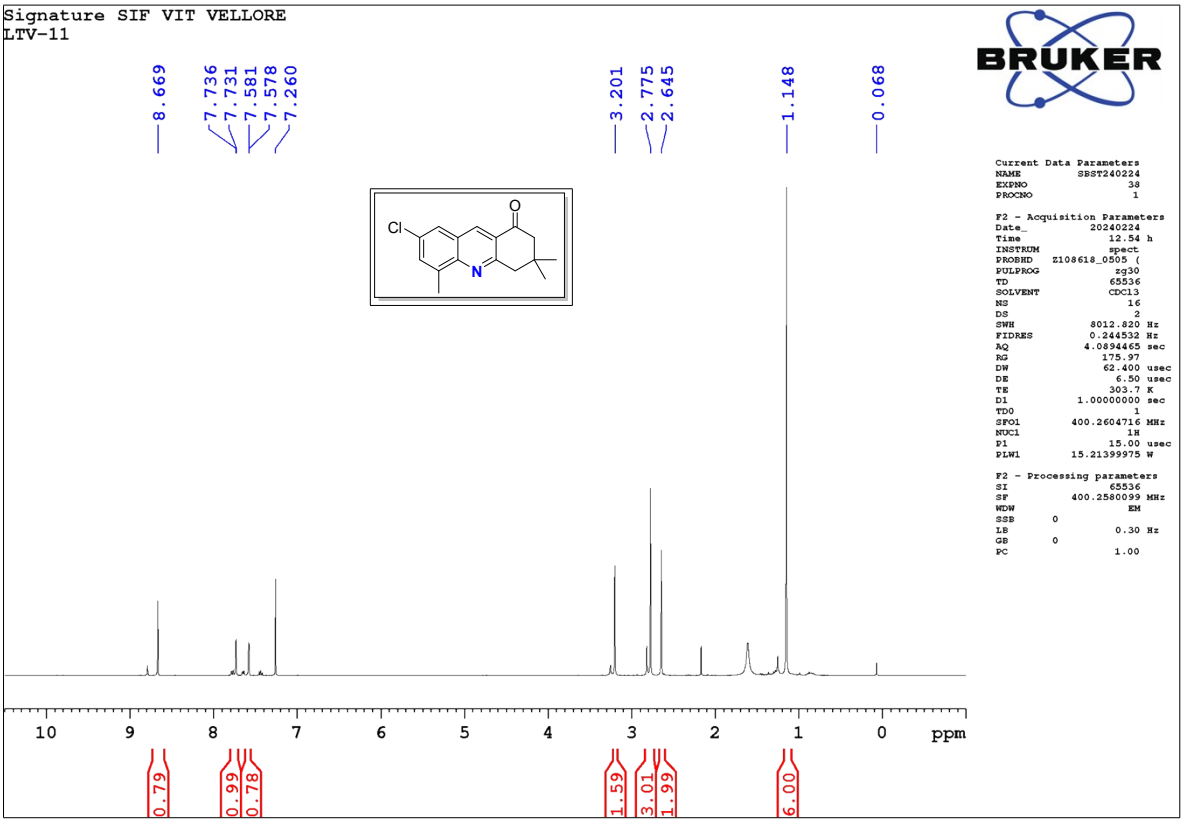


Figure S85. $^{13}C\{^{1}H\}$ NMR spectrum of **11g** ($CDCl_3$, 100 MHz)

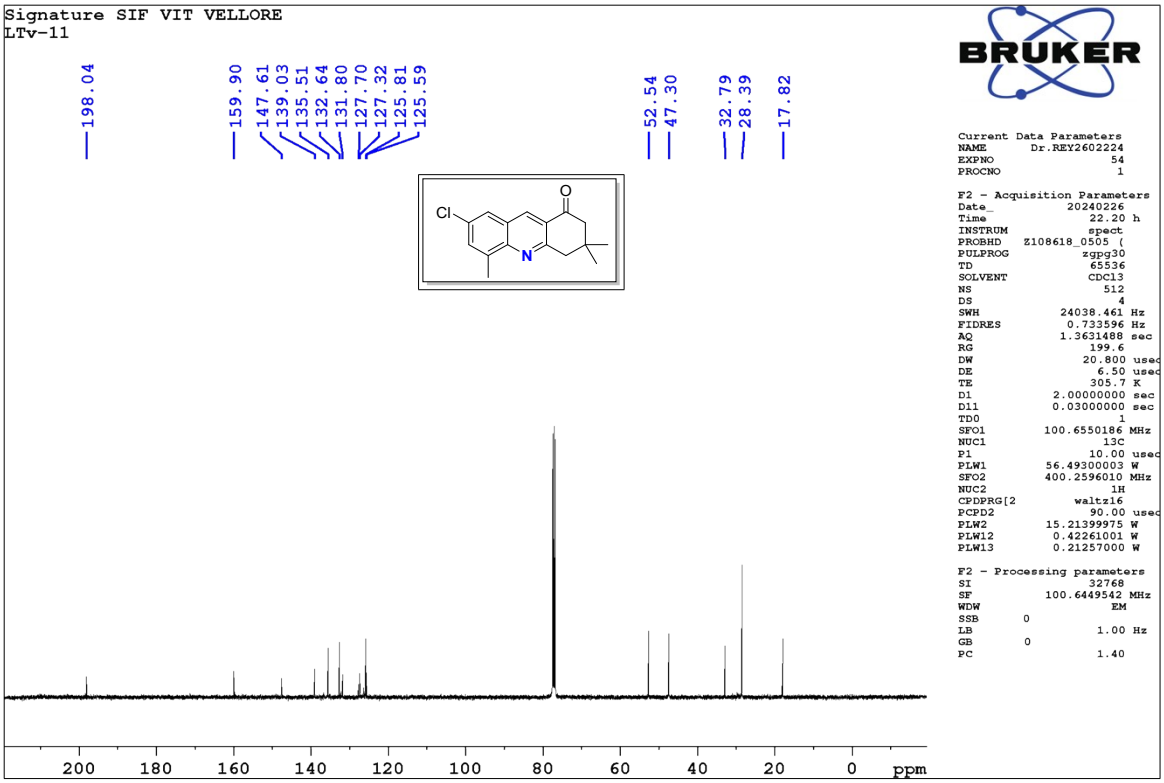


Figure S86. ^{1}H NMR spectrum of **13a** ($CDCl_3$, 400 MHz)

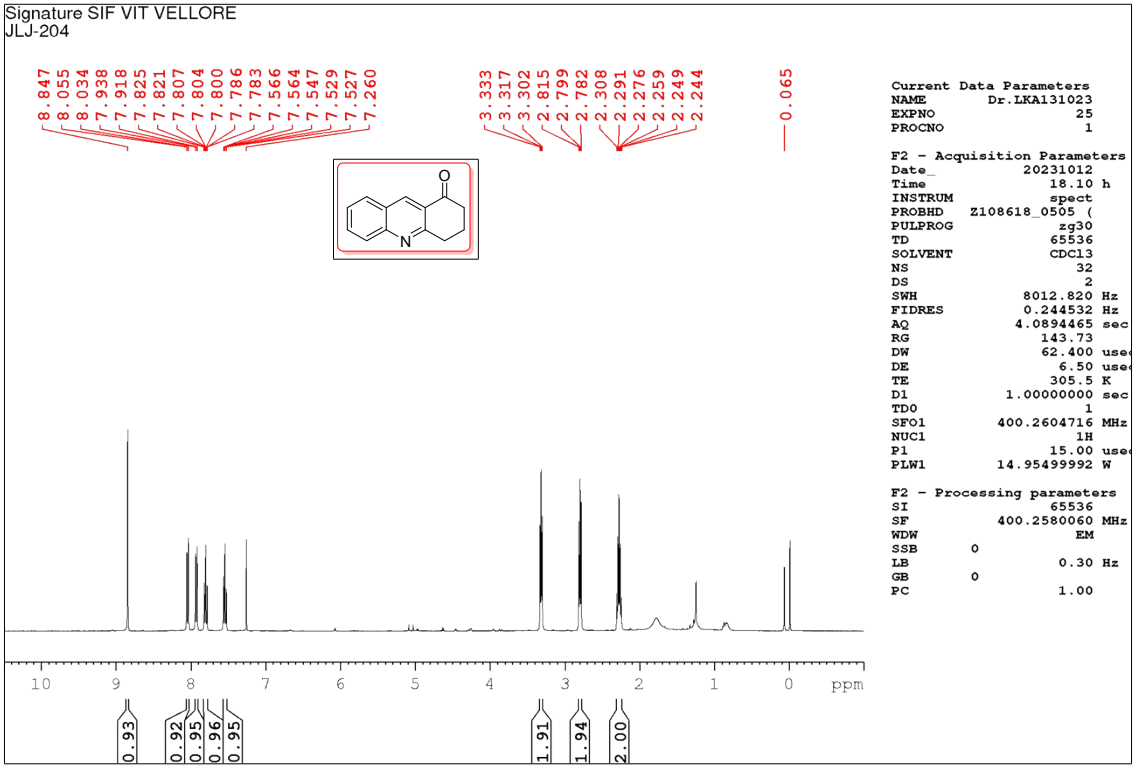


Figure S87. $^{13}C\{^{1}H\}$ NMR spectrum of **13a** ($CDCl_3$, 100 MHz)

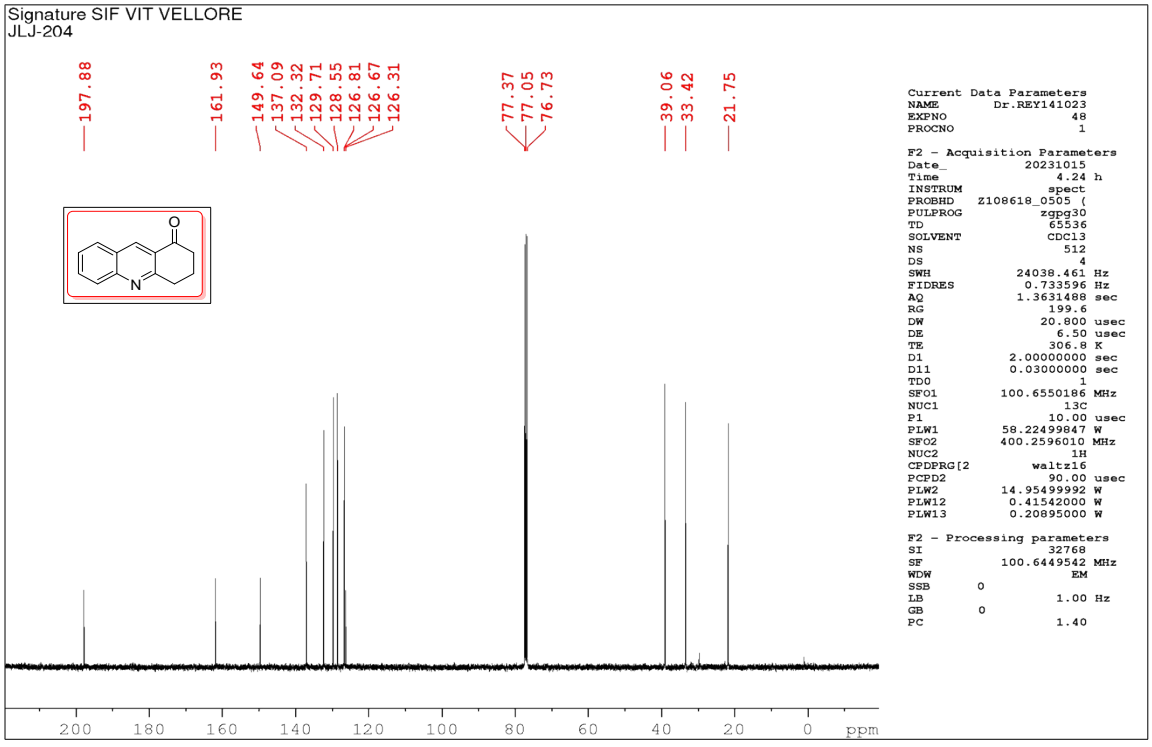


Figure S88. ^{1}H NMR spectrum of **13b** ($CDCl_3$, 400 MHz)

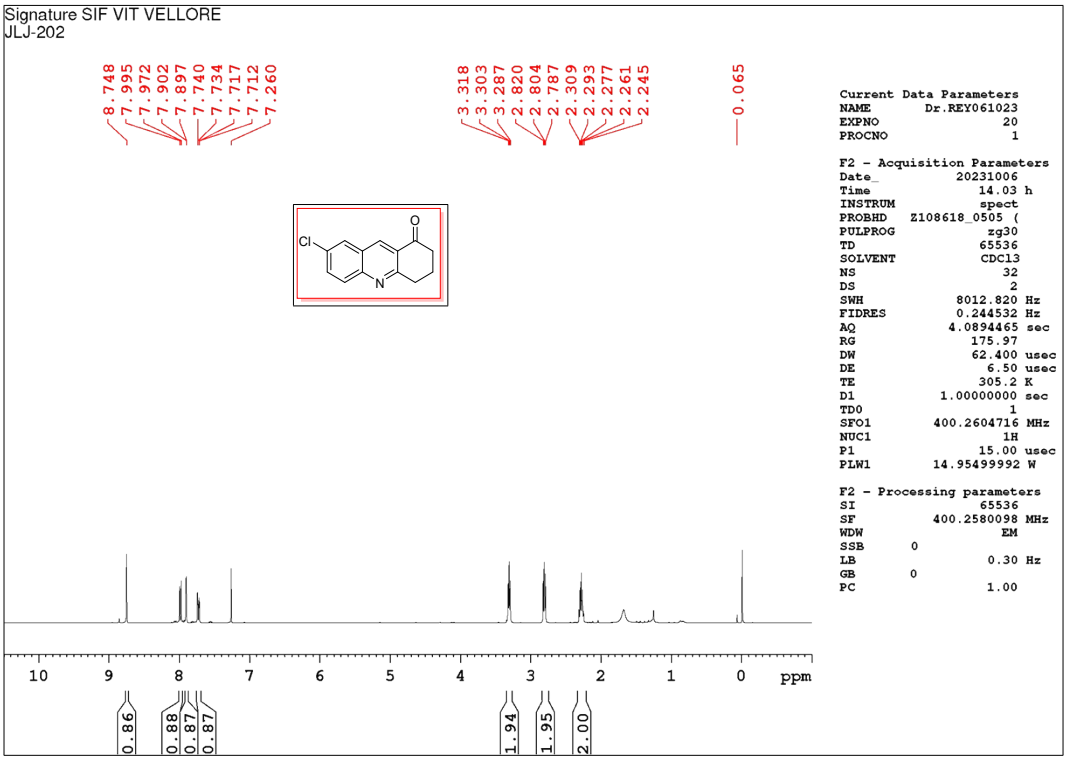


Figure S89. $^{13}C\{^{1}H\}$ NMR spectrum of **13b** ($CDCl_3$, 100 MHz)

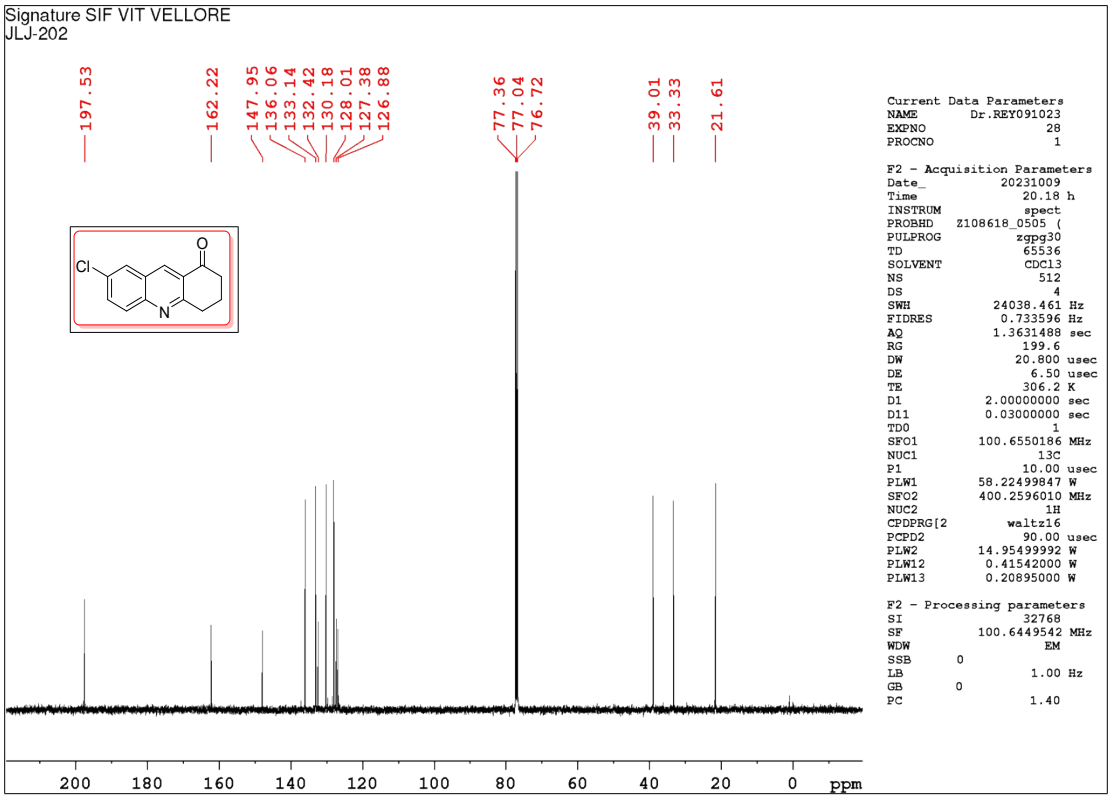


Figure S90. ^{1}H NMR spectrum of **13c** ($CDCl_3$, 400 MHz)

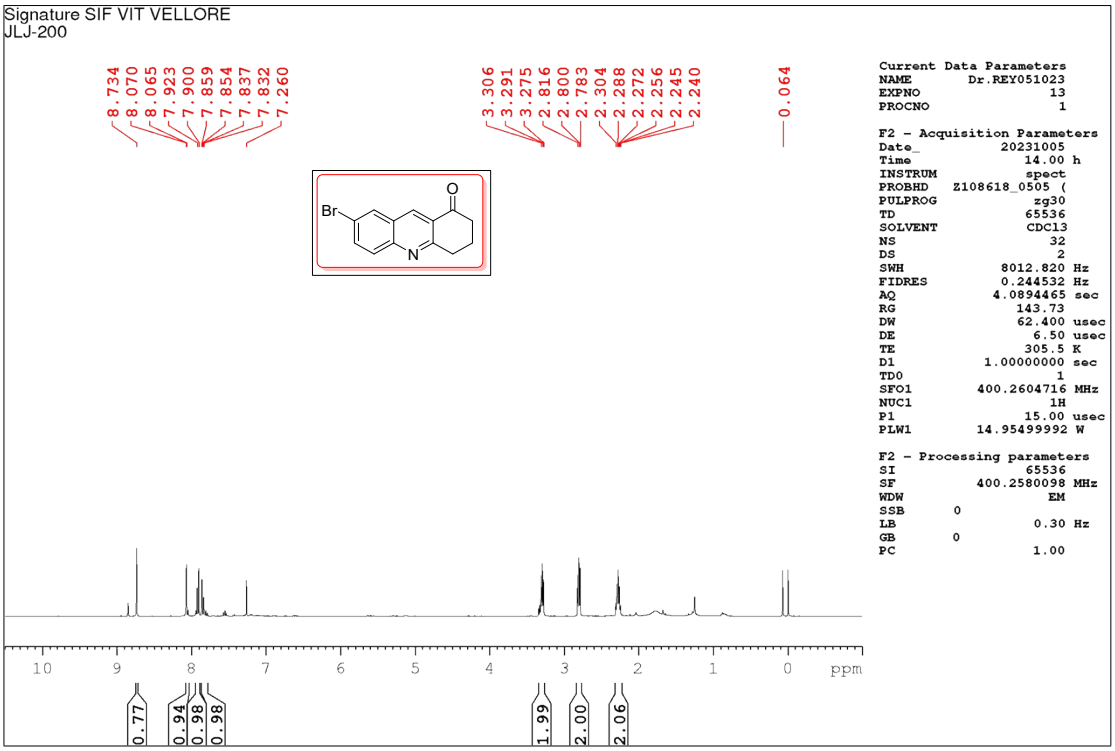


Figure S91. $^{13}C\{^{1}H\}$ NMR spectrum of **13c** ($CDCl_3$, 100 MHz)

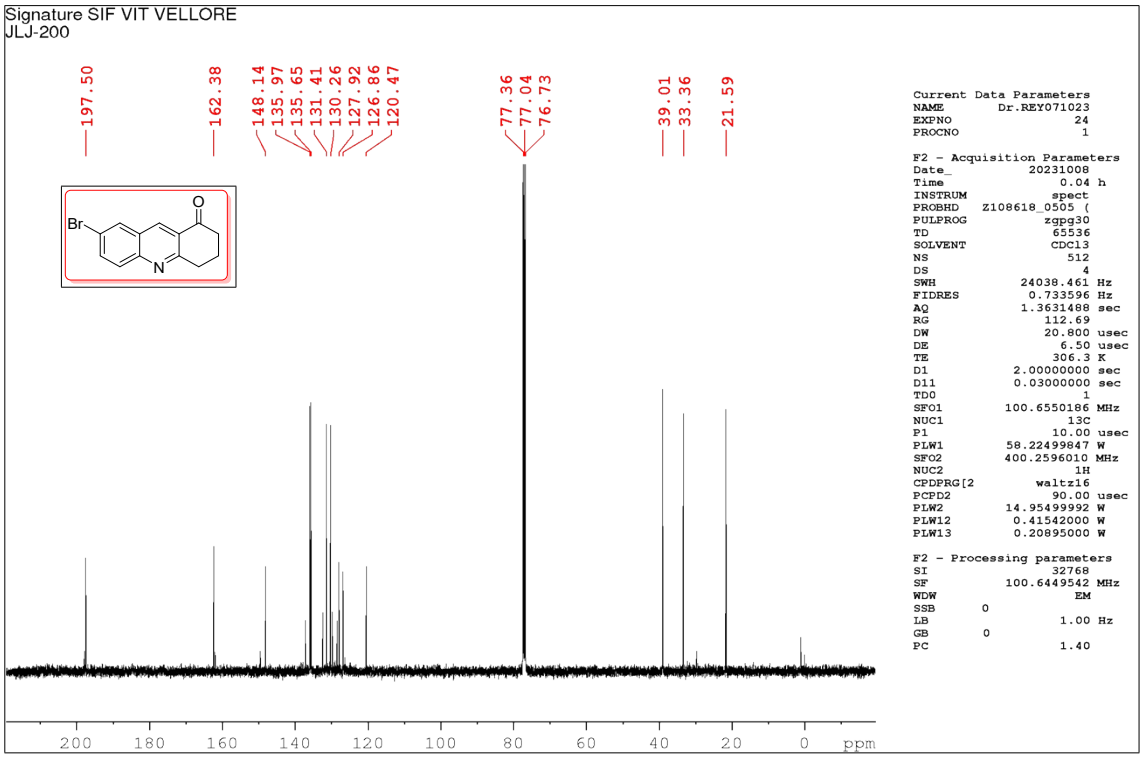


Figure S92. ^{1}H NMR spectrum of **13d** ($CDCl_3$, 400 MHz)

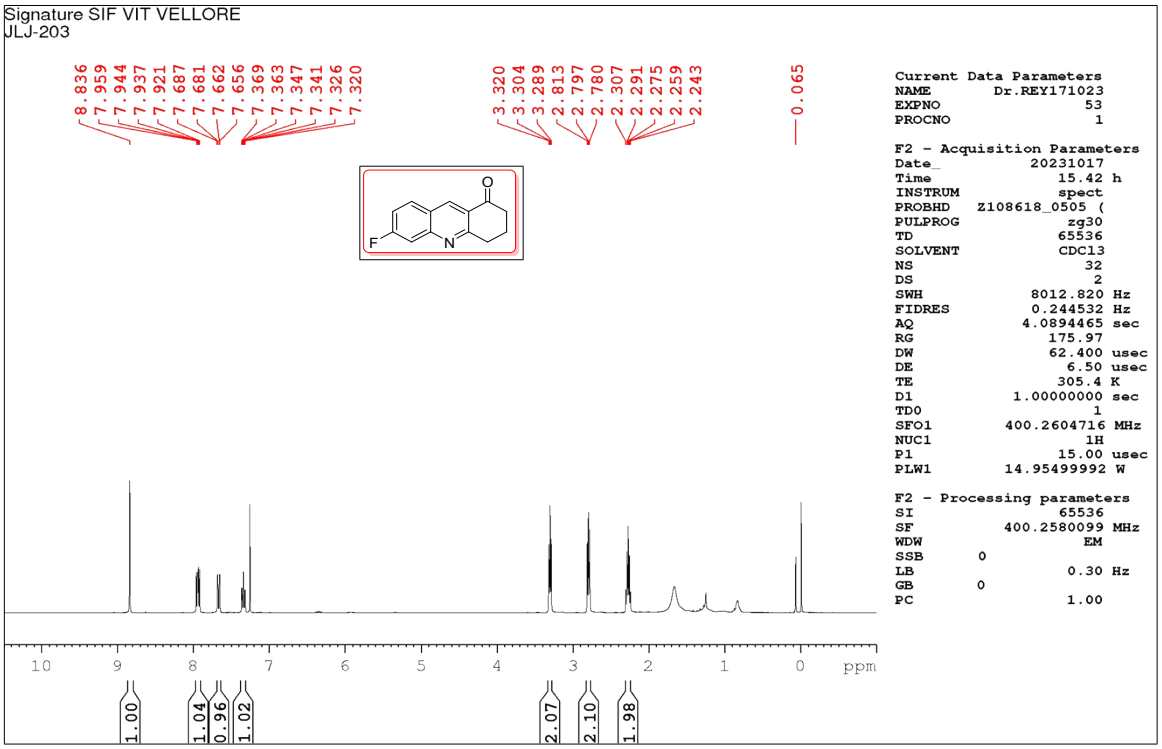


Figure S93. $^{13}C\{^{1}H\}$ NMR spectrum of **13d** ($CDCl_3$, 400 MHz)

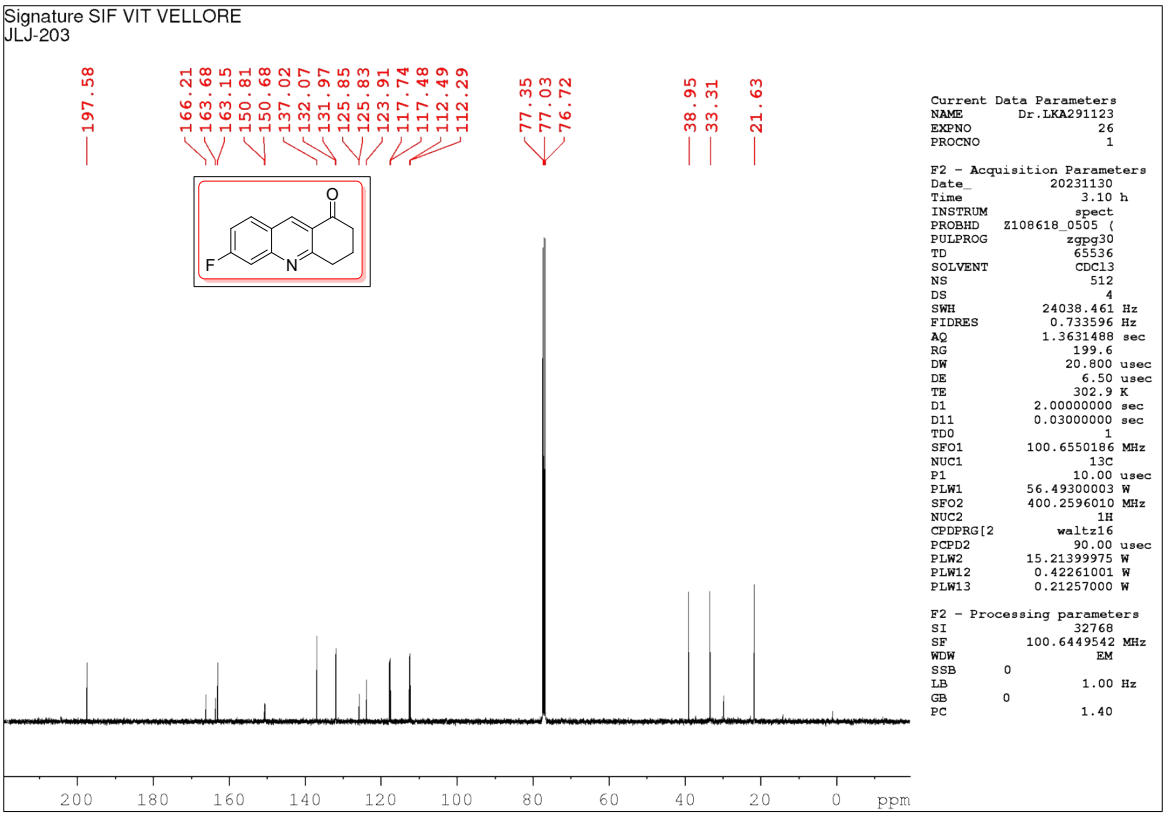


Figure S94. ^{19}F NMR spectrum of **13d** ($CDCl_3$, 376 MHz)

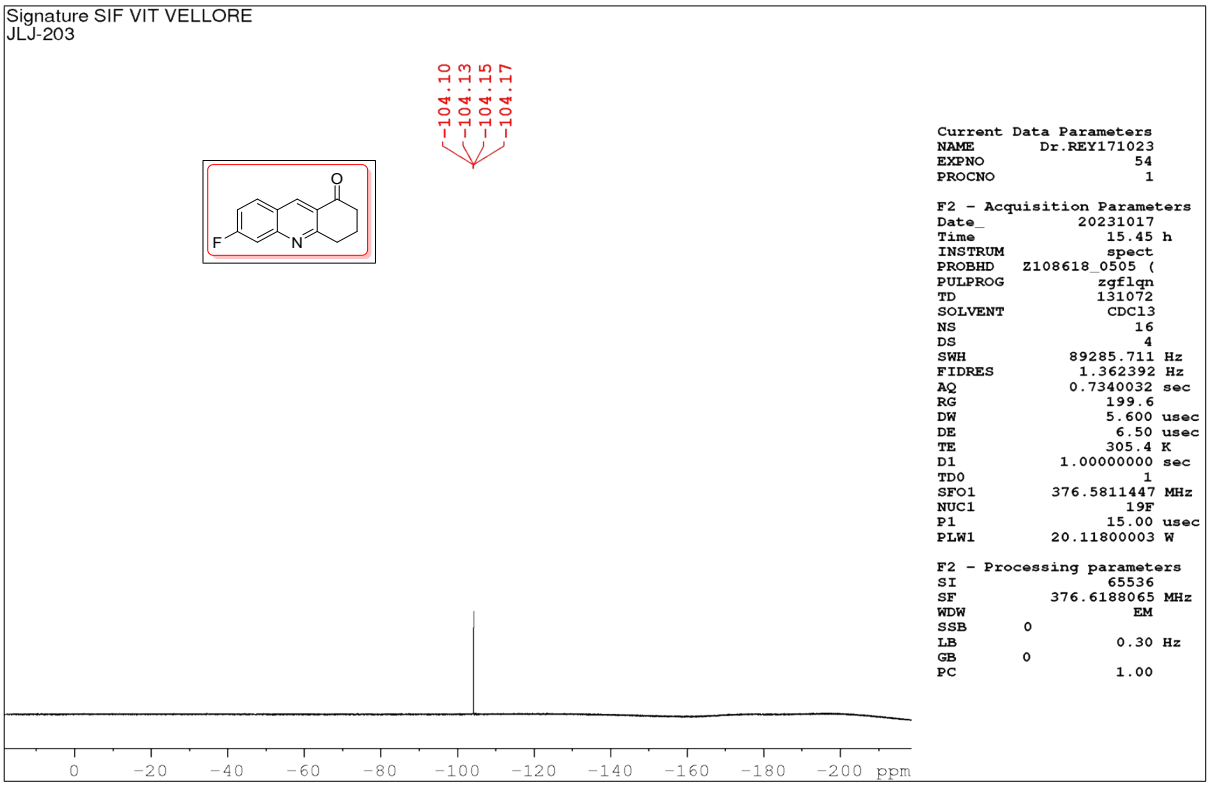


Figure S95. ^{1}H NMR spectrum of **13e** ($CDCl_3$, 400 MHz)

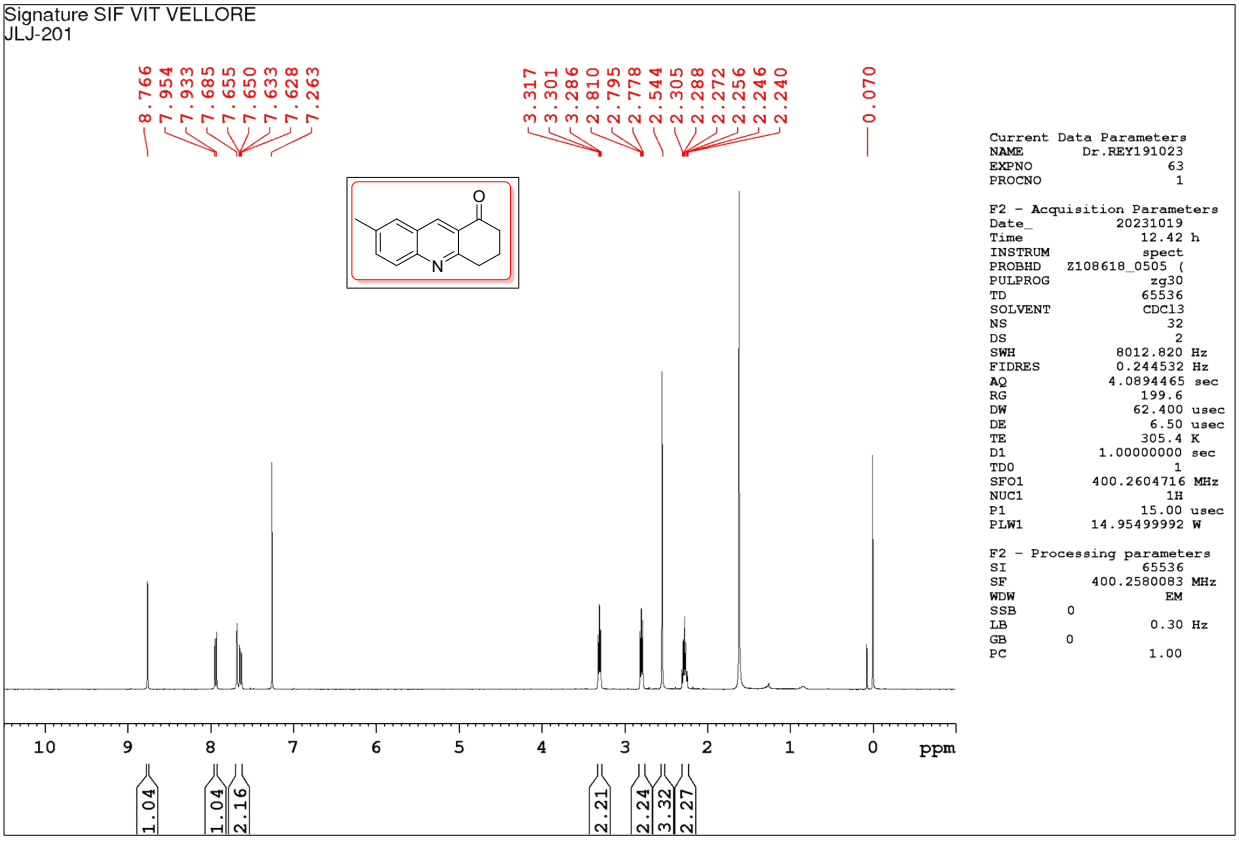


Figure S96. $^{13}C\{^{1}H\}$ NMR spectrum of **13e** ($CDCl_3$, 100 MHz)

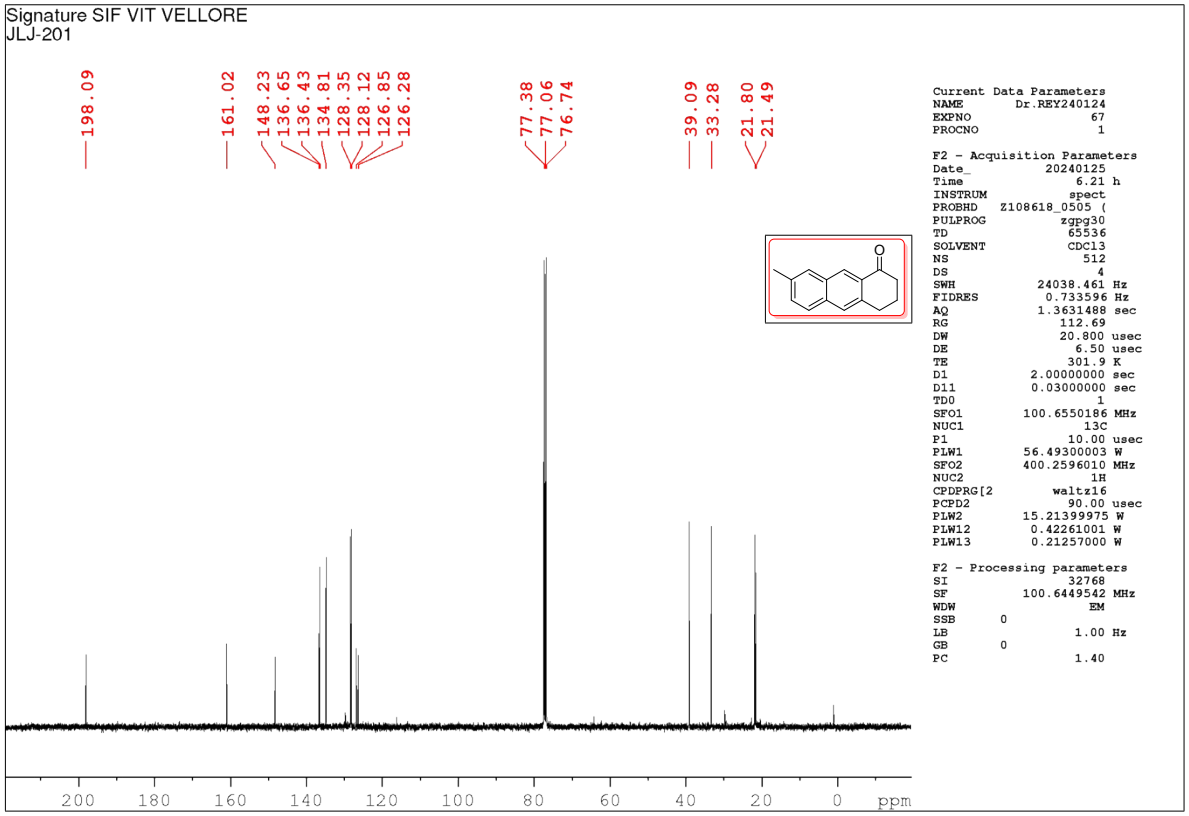


Figure S97. ^{1}H NMR spectrum of **15** ($CDCl_3$, 400 MHz)

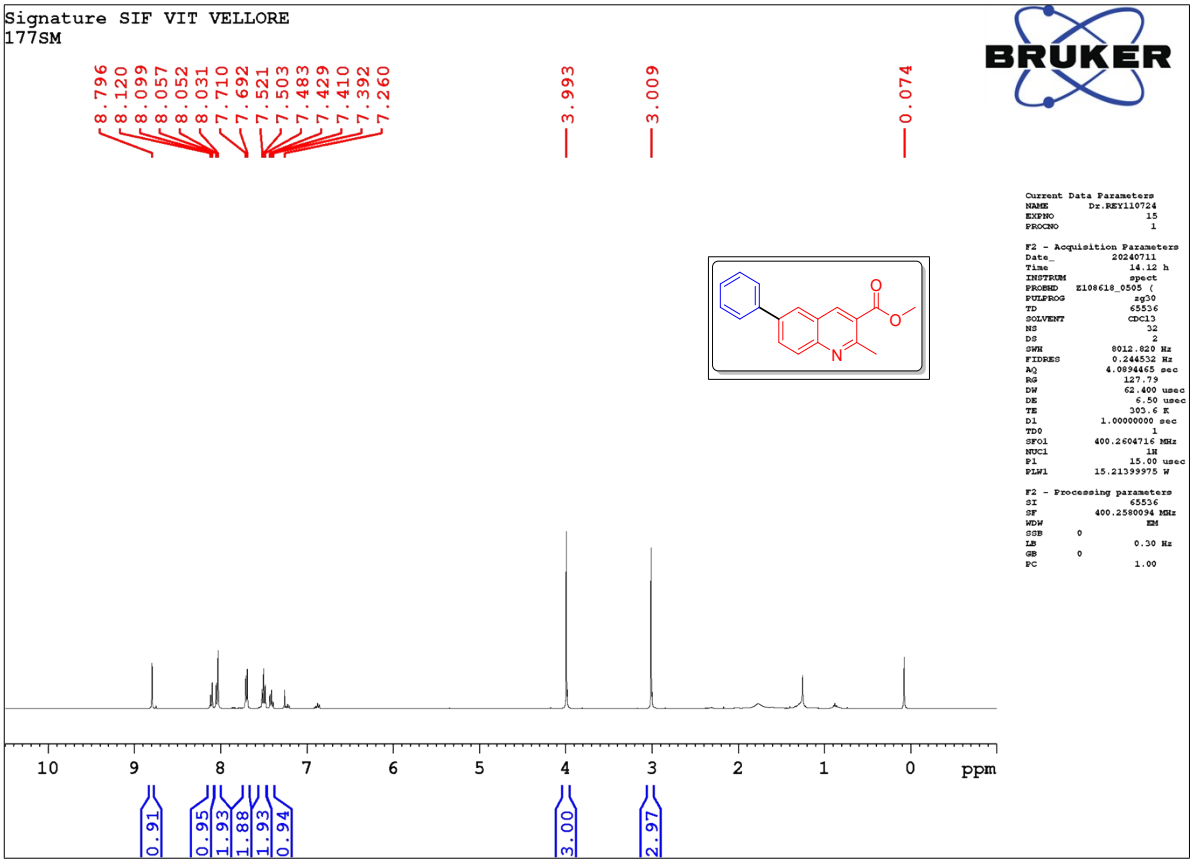


Figure S98. $^{13}C\{^{1}H\}$ NMR spectrum of **15** ($CDCl_3$, 100 MHz)

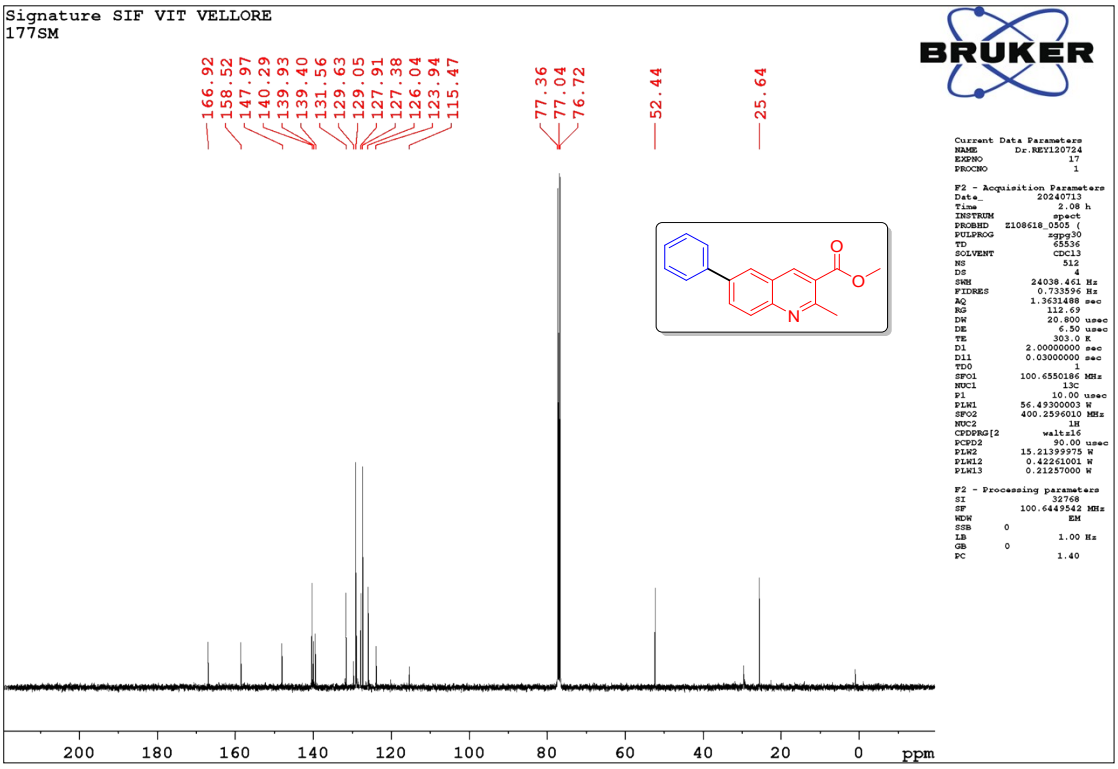


Figure S99. Crude ^{1}H NMR spectrum of isolated 2-aminobenzaldehyde ($CDCl_3$, 400 MHz)

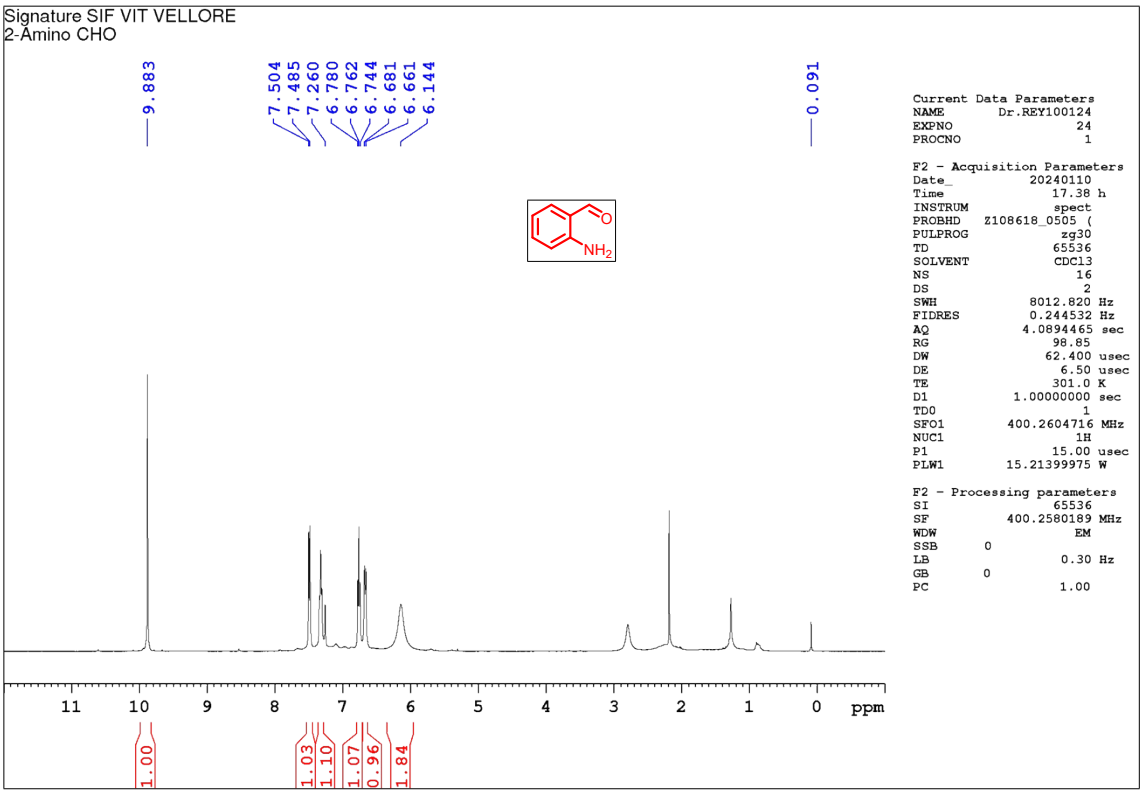


Figure S100. Crude $^{13}C\{^{1}H\}$ NMR spectrum of isolated 2-aminobenzaldehyde ($CDCl_3$, 100 MHz)

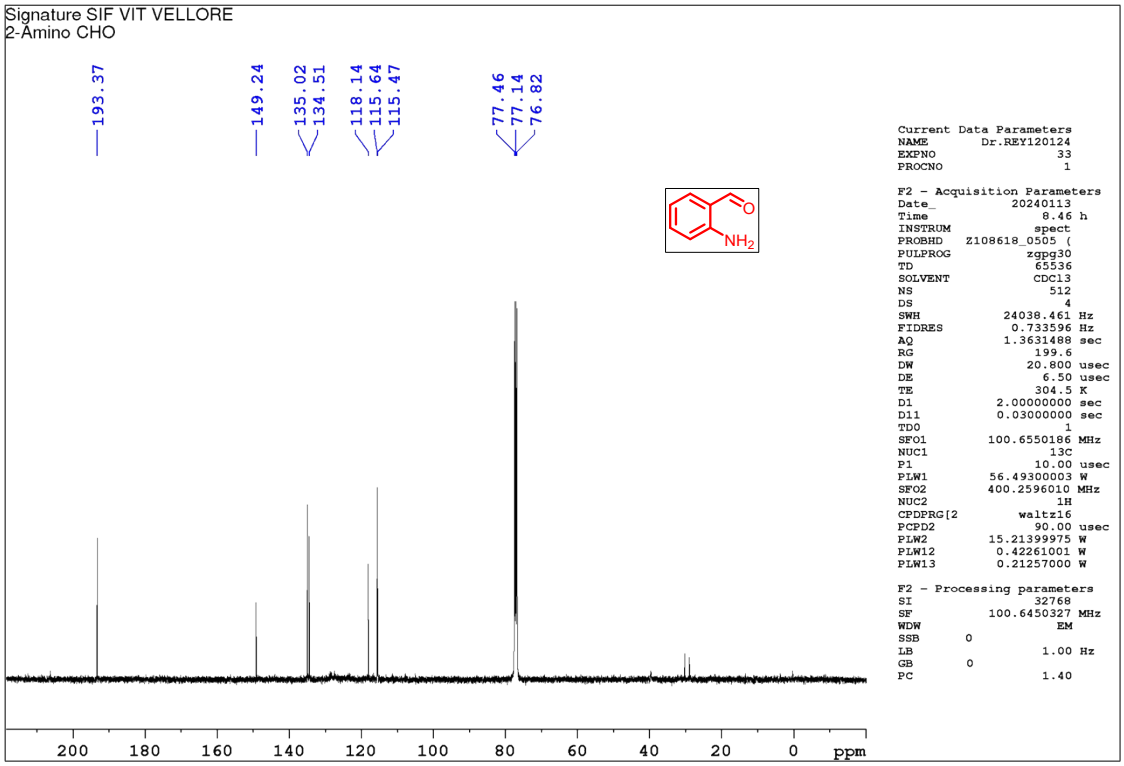
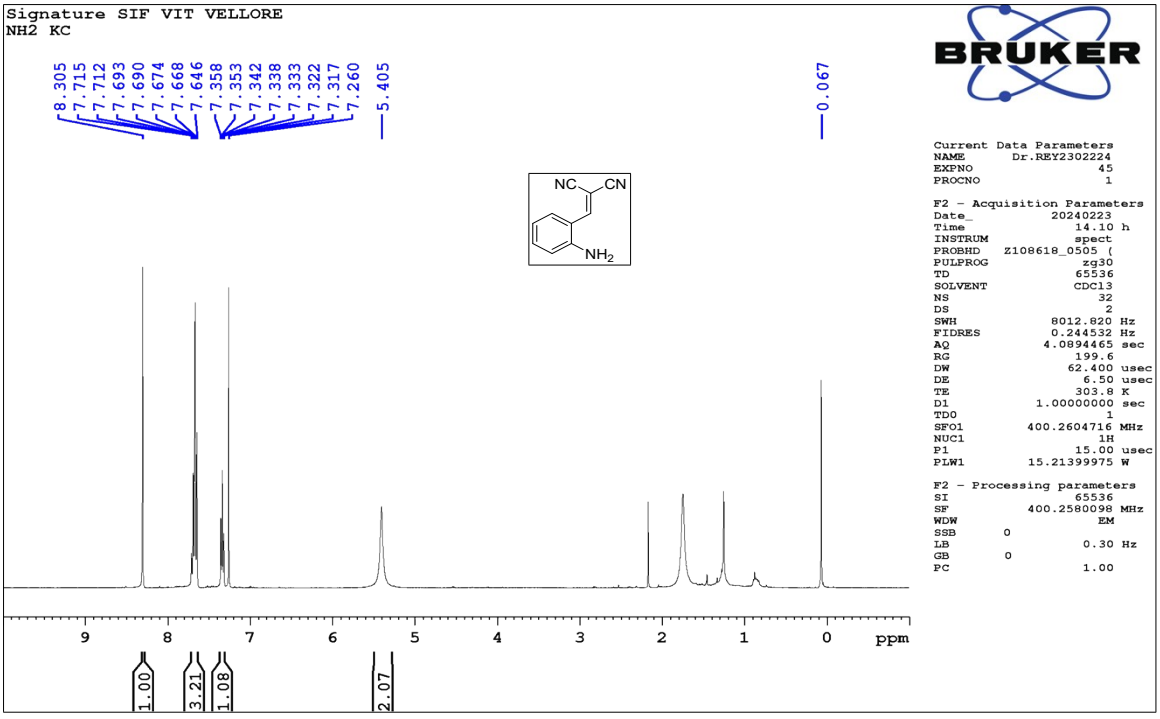


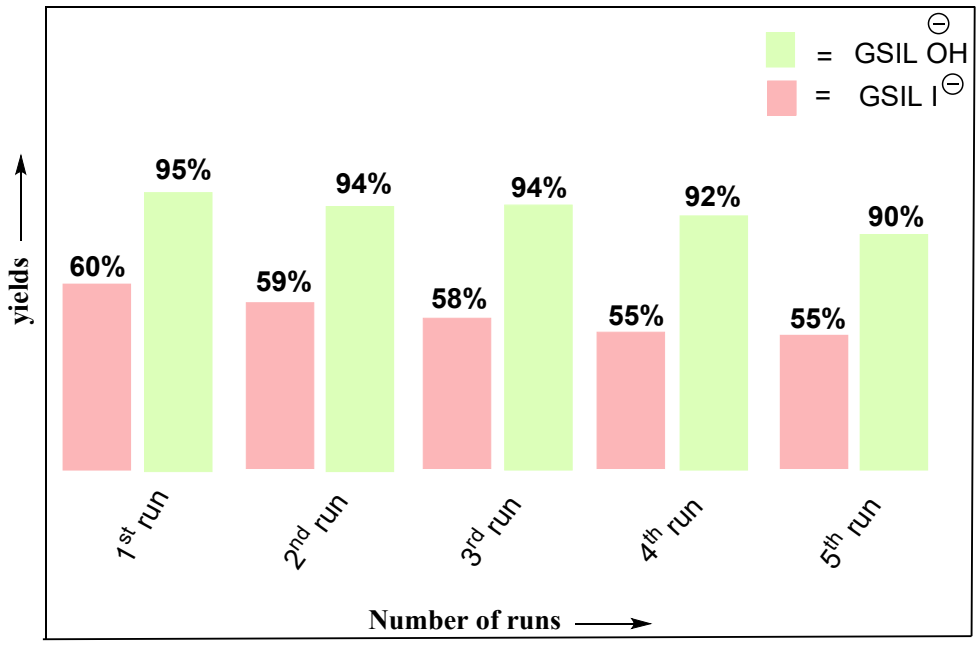
Figure S101. Crude ^{1}H NMR spectrum of Knoevenagel condensation product in presence of IL ($CDCl_3$, 400 MHz)



13. Recyclability studies of the catalyst

Recyclability of ionic liquid was carried out for two ionic liquids: GSIL I and GSIL II in the annulation of quinolines. Recyclability was performed using aqueous biphasic system method as this involves two immiscible phases, an aqueous phase and organic phase. After the completion of the reaction, aqueous acetonitrile solution is distilled out. Further, ethyl acetate or diethyl ether was added to the reaction mixture to make it aqueous two phasic system. Then, organic layer and water layer gets separated. The product as well as unreacted starting materials are soluble in organic solvents and ionic liquid becomes soluble in water. The ionic liquid is collected from the aqueous layer and then dried under reduced pressure to further utilize for the next reaction. The recovered IL was reused for up to five cycles and showed a minimal loss in catalytic activity in the context of decreasing product yield in the same reaction time. The NMR spectrum of the IL reused for the fifth time is shown below. The NMR spectra of the used catalyst match with the NMR spectra of fresh catalyst.

Figure S102. Recyclability study of GSIL I and GSIL II



^{1}H NMR of Catalysts of fresh catalyst and after fifth run

Figure S103. ^{1}H NMR Spectrum of GSIL I (**C3**) after fifth run (D_2O, 400 MHz)

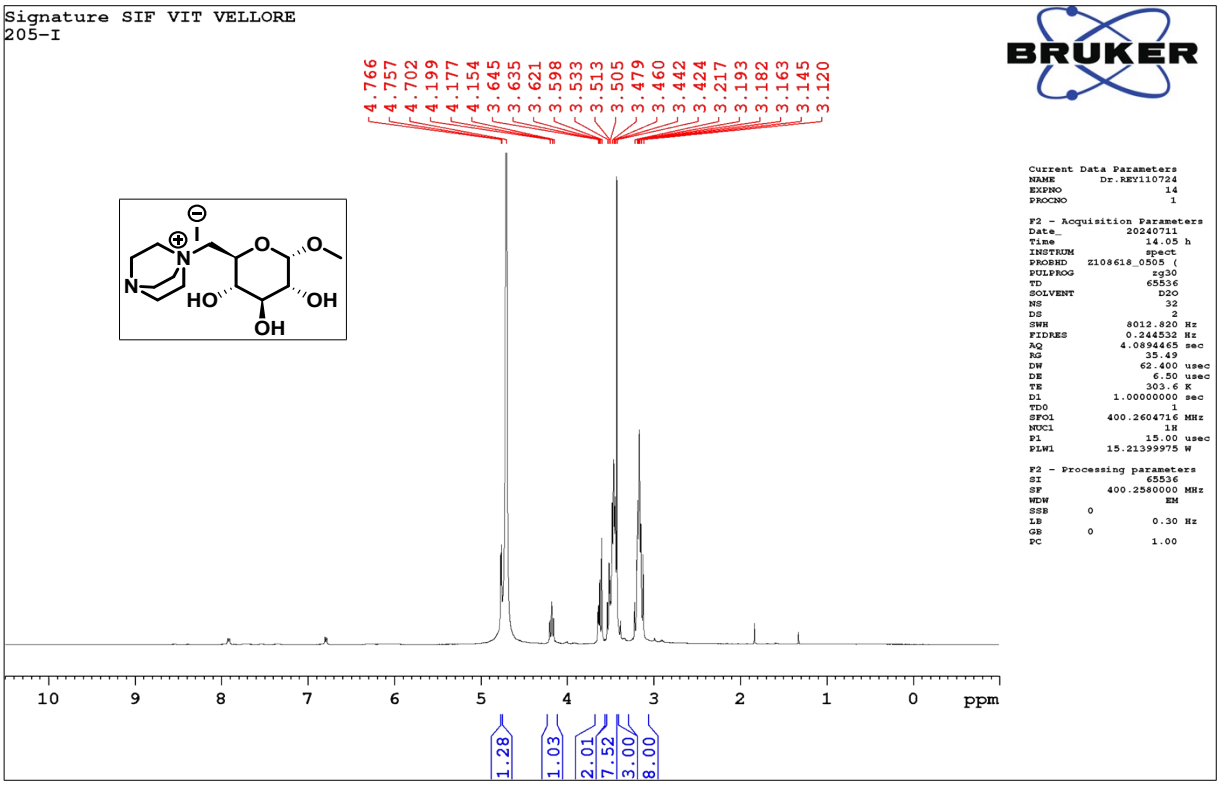
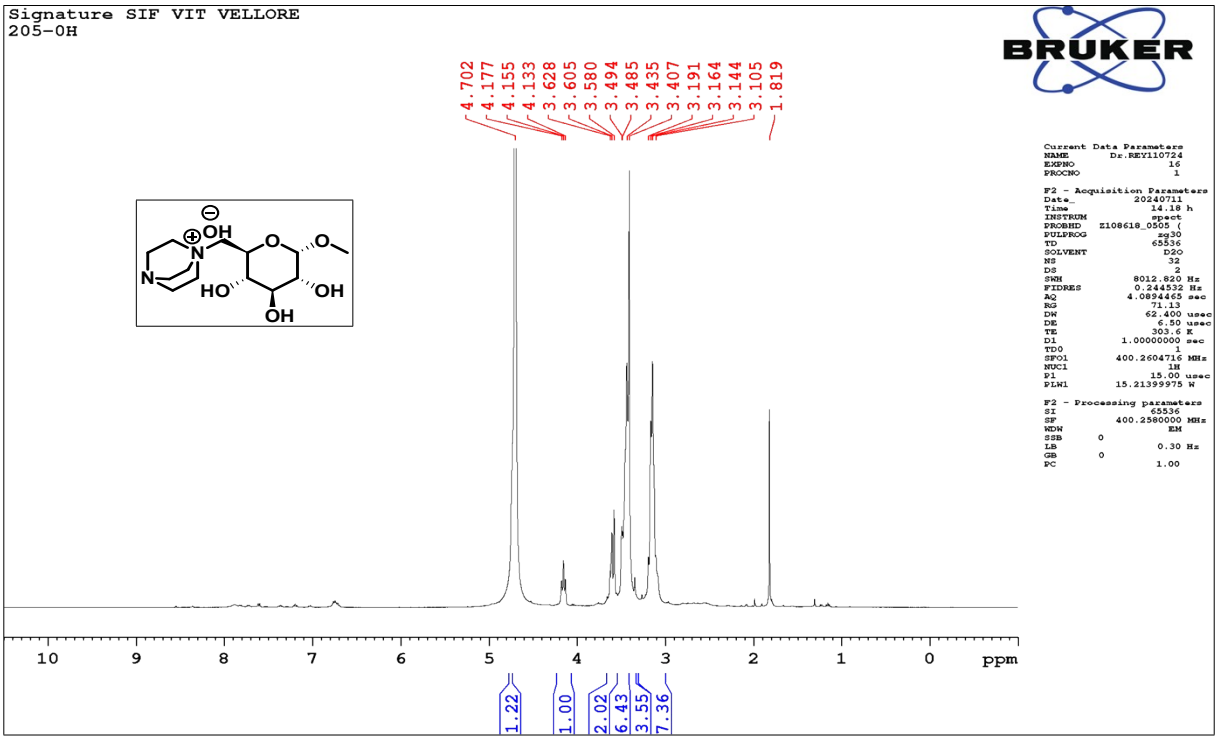
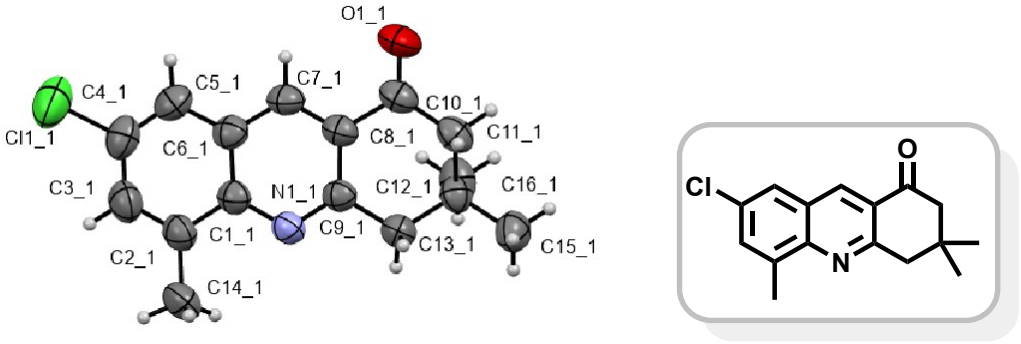


Figure S104. ^{1}H NMR Spectrum of GSIL II (**C4**) after fifth run (D_2O, 400 MHz)



14. Basic Crystallographic data for compound

Crystal structure report for compound 11g



ORTEP diagram of compound **11g (CCDC No. 2374048)**

A specimen of $C_{16}H_{16}ClNO$, approximate dimensions 0.054 mm x 0.072 mmx 0.350 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å).

The integration of the data using a triclinic unit cell yielded a total of 27989 reflections to a maximum θ angle of 28.28° (0.75 Å resolution), of which 3416 were independent (average redundancy 8.194, completeness = 99.8%, R_{int} = 5.28%, R_{sig} = 3.65%) and 2067 (60.51%) were greater than $2\sigma(F^2)$. The final cell constants of a = 5.6237(3) Å, b = 7.7655(5) Å, c = 16.0712(10) Å, α = 83.991(3), β = 84.029(3)°, γ = 82.486(3)°, volume = 689.08(7) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9120 and 0.9860.

The final anisotropic full-matrix least-squares refinement on F^2 with 175 variables converged at R1 = 5.94%, for the observed data and wR2 = 18.84% for all data. The goodness-of-fit was 1.033. The largest peak in the final difference electron density synthesis was 0.217 $e^-/Å^3$ and the largest hole was -0.370 $e^-/Å^3$ with an RMS deviation of 0.044 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.319 g/cm^3 and F(000), 288 e^-.

Table S4. Sample and crystal data for 11g

Identification code	**11g**	
Chemical formula	$C_{16}H_{16}ClNO$	
Formula weight	273.75 g/mol	
Temperature	300(2) K	
Wavelength	0.71073 Å	
Crystal size	0.054 x 0.072 x 0.350 mm	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 5.6237(3) Å	α = 83.991(3)°
	b = 7.7655(5) Å	β = 84.029(3)°
	c = 16.0712(10) Å	γ = 82.486(3)°

Volume	689.08(7) $Å^3$	
Z	2	
Density (calculated)	1.319 g/cm^3	
Absorption coefficient	0.268 mm^{-1}	
F(000)	288	

Table S5. Data collection and structure refinement for 11g

Theta range for data collection	2.56 to 28.28°	
Index ranges	-7<=h<=7, -10<=k<=10, -21<=l<=21	
Reflections collected	27989	
Independent reflections	3416 [R(int) = 0.0528]	
Max. and min. transmission	0.9860 and 0.9120	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3416 / 0 / 175	
Goodness-of-fit on F^2	1.033	
Δ/σ_{max}	0.001	
Final R indices	2067 data; I>2σ(I)	R1 = 0.0594, wR2 = 0.1545
	all data	R1 = 0.1069, wR2 = 0.1884
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0762P)^2+0.3295P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.217 and -0.370 $eÅ^{-3}$	
R.M.S. deviation from mean	0.044 $eÅ^{-3}$	

Table S6. Atomic coordinates and equivalent isotropic atomic displacement parameters (A^2) for 11g

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Cl1_1	0.57212(15)	0.82827(12)	0.90564(6)	0.0903(4)
O1_1	0.7473(4)	0.6986(2)	0.60691(13)	0.0764(6)
N1_1	0.3484(3)	0.2941(2)	0.79695(11)	0.0460(5)
C1_1	0.1777(4)	0.4228(3)	0.82395(13)	0.0442(5)
C2_1	0.9913(5)	0.3756(3)	0.88559(14)	0.0516(6)
C3_1	0.8132(5)	0.5032(4)	0.90908(16)	0.0612(7)
C4_1	0.8103(5)	0.6758(4)	0.87444(17)	0.0592(7)
C5_1	0.9879(5)	0.7262(3)	0.81726(16)	0.0561(6)
C6_1	0.1766(4)	0.5998(3)	0.79050(14)	0.0477(6)
C7_1	0.3657(4)	0.6392(3)	0.72977(15)	0.0496(6)
C8_1	0.5382(4)	0.5107(3)	0.70427(13)	0.0443(5)
C9_1	0.5219(4)	0.3366(3)	0.73910(13)	0.0427(5)
C10_1	0.7401(4)	0.5516(3)	0.64032(15)	0.0509(6)
C11_1	0.9313(4)	0.4043(3)	0.62119(15)	0.0503(6)
C12_1	0.8350(4)	0.2280(3)	0.62361(14)	0.0459(5)
C13_1	0.7060(4)	0.1910(3)	0.71110(14)	0.0501(6)
C14_1	0.9929(6)	0.1904(4)	0.92358(17)	0.0705(8)
C15_1	0.0459(5)	0.0856(4)	0.60940(18)	0.0617(7)
C16_1	0.6642(5)	0.2339(4)	0.55551(16)	0.0602(7)

Table S7. Bond lengths (°) for 11g

Cl1_1-C4_1	1.737(3)	O1_1-C10_1	1.213(3)
N1_1-C9_1	1.325(3)	N1_1-C1_1	1.364(3)
C1_1-C6_1	1.422(3)	C1_1-C2_1	1.422(3)
C2_1-C3_1	1.367(3)	C2_1-C14_1	1.502(3)
C3_1-C4_1	1.395(4)	C4_1-C5_1	1.353(4)

C5_1-C6_1	1.413(3)	C6_1-C7_1	1.409(3)
C7_1-C8_1	1.361(3)	C8_1-C9_1	1.419(3)
C8_1-C10_1	1.493(3)	C9_1-C13_1	1.502(3)
C10_1-C11_1	1.497(3)	C11_1-C12_1	1.533(3)
C12_1-C16_1	1.523(3)	C12_1-C15_1	1.528(3)
C12_1-C13_1	1.531(3)		

Table S8. Bond angles (A°) for 11g

C9_1-N1_1-C1_1	118.74(18)	N1_1-C1_1-C6_1	122.1(2)
N1_1-C1_1-C2_1	118.3(2)	C6_1-C1_1-C2_1	119.5(2)
C3_1-C2_1-C1_1	118.1(2)	C3_1-C2_1-C14_1	121.5(2)
C1_1-C2_1-C14_1	120.4(2)	C2_1-C3_1-C4_1	122.0(2)
C5_1-C4_1-C3_1	121.5(2)	C5_1-C4_1-Cl1_1	119.6(2)
C3_1-C4_1-Cl1_1	118.9(2)	C4_1-C5_1-C6_1	119.0(2)
C7_1-C6_1-C5_1	123.1(2)	C7_1-C6_1-C1_1	117.1(2)
C5_1-C6_1-C1_1	119.8(2)	C8_1-C7_1-C6_1	120.4(2)
C7_1-C8_1-C9_1	118.8(2)	C7_1-C8_1-C10_1	120.7(2)
C9_1-C8_1-C10_1	120.4(2)	N1_1-C9_1-C8_1	122.7(2)
N1_1-C9_1-C13_1	117.00(19)	C8_1-C9_1-C13_1	120.3(2)
O1_1-C10_1-C8_1	120.6(2)	O1_1-C10_1-C11_1	122.5(2)
C8_1-C10_1-C11_1	116.85(19)	C10_1-C11_1-C12_1	113.70(18)
C16_1-C12_1-C15_1	109.6(2)	C16_1-C12_1-C13_1	111.17(19)
C15_1-C12_1-C13_1	109.2(2)	C16_1-C12_1-C11_1	110.0(2)
C15_1-C12_1-C11_1	109.32(19)	C13_1-C12_1-C11_1	107.51(19)
C9_1-C13_1-C12_1	114.62(19)		

Table S9. Anisotropic atomic displacement parameters (Å²) for 11g

The anisotropic atomic displacement factor exponent takes the form: -2π2 [h2 a *2 U11 + ... + 2 h k a * b * U12]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1_1	0.0707(5)	0.0850(6)	0.1131(7)	-0.0347(5)	0.0075(5)	0.0064(4)

O1_1	0.0802(14)	0.0534(11)	0.0893(14)	0.0149(10)	0.0129(11)	-0.0184(10)
N1_1	0.0551(11)	0.0433(10)	0.0383(10)	-0.0004(8)	-0.0001(8)	-0.0075(9)
C1_1	0.0524(13)	0.0452(13)	0.0359(11)	-0.0053(9)	-0.0036(10)	-0.0080(10)
C2_1	0.0604(15)	0.0549(14)	0.0390(12)	-0.0052(10)	0.0031(11)	-0.0105(12)
C3_1	0.0612(16)	0.0703(18)	0.0510(15)	-0.0127(13)	0.0093(12)	-0.0100(13)
C4_1	0.0556(15)	0.0623(17)	0.0612(16)	-0.0231(13)	-0.0032(12)	-0.0008(12)
C5_1	0.0626(16)	0.0441(13)	0.0621(16)	-0.0120(11)	-0.0056(13)	-0.0031(11)
C6_1	0.0558(14)	0.0423(13)	0.0468(13)	-0.0085(10)	-0.0059(11)	-0.0080(10)
C7_1	0.0587(14)	0.0374(12)	0.0531(14)	0.0002(10)	-0.0056(11)	-0.0108(11)
C8_1	0.0509(13)	0.0421(12)	0.0414(12)	-0.0001(9)	-0.0067(10)	-0.0127(10)
C9_1	0.0489(12)	0.0416(12)	0.0380(11)	-0.0019(9)	-0.0058(10)	-0.0065(10)
C10_1	0.0547(14)	0.0507(14)	0.0497(13)	0.0015(11)	-0.0060(11)	-0.0192(11)
C11_1	0.0437(12)	0.0605(15)	0.0484(13)	0.0001(11)	-0.0047(10)	-0.0166(11)
C12_1	0.0384(11)	0.0516(13)	0.0488(13)	-0.0066(10)	-0.0018(10)	-0.0096(10)
C13_1	0.0527(13)	0.0445(13)	0.0505(13)	0.0007(10)	0.0026(11)	-0.0064(11)
C14_1	0.085(2)	0.0639(17)	0.0561(16)	0.0059(13)	0.0167(14)	-0.0142(15)
C15_1	0.0482(14)	0.0626(16)	0.0734(17)	-0.0116(13)	0.0050(12)	-0.0078(12)
C16_1	0.0490(14)	0.0823(18)	0.0535(15)	-0.0196(13)	-0.0030(11)	-0.0147(13)

Table S10. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for 11g

	x/a	**y/b**	**z/c**	**U(eq)**
H3_1	-0.3096	0.4742	0.9494	0.073000
H5_1	-0.0143	0.8424	0.7959	0.067000

H7_1	0.3729	0.7537	0.7069	0.060000
H11A_1	1.0503	0.3950	0.6615	0.060000
H11B_1	1.0116	0.4311	0.5658	0.060000
H13A_1	0.6270	0.0870	0.7116	0.060000
H13B_1	0.8255	0.1665	0.7515	0.060000
H14A_1	0.0215	0.1131	0.8797	0.106000
H14B_1	-0.1599	0.1761	0.9544	0.106000
H14C_1	0.1181	0.1636	0.9608	0.106000
H15A_1	1.1293	0.1095	0.5550	0.093000
H15B_1	0.9864	-0.0255	0.6124	0.093000
H15C_1	1.1546	0.0833	0.6519	0.093000
H16A_1	0.7493	0.2577	0.5014	0.090000
H16B_1	0.5327	0.3242	0.5642	0.090000
H16C_1	0.6030	0.1236	0.5580	0.090000