Supporting Information

Solvent-controlled Catalytic Divergent C–H Alkylation of Quinolones Driven by Unusual DMSO-promoted 1,3-Heteroarene Migration

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1. General Information

Unless otherwise noted, all reactions were carried out under an argon atmosphere in oven-dried Schlenk tubes. All reactions requiring heating were conducted in a pre-heated heating mantle, and reaction temperatures are reported as the temperature of the heat transfer medium surrounding the vessel. Dry solvents (<50 ppm H_2O) were purchased from Acros Organics, Sigma-Aldrich, or TCI and stored over molecular sieves under argon atmosphere.

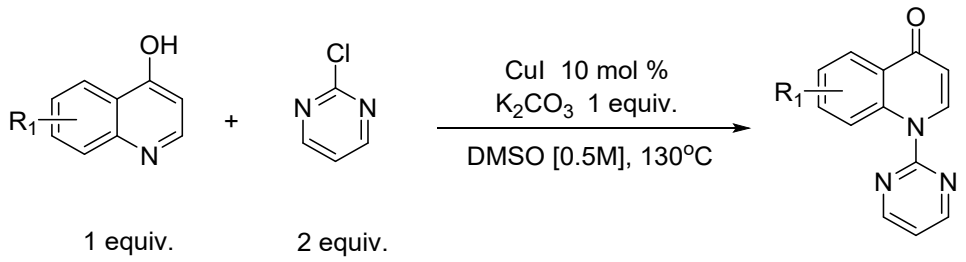
Commercially available chemicals were purchased from Acros Organics, Aldrich Chemical Co., Alfa Aesar, and TCI. Flash chromatography was performed using Merck silica gel (40–63 mesh).

The ^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX-300 and Bruker DRX-500, and the chemical shifts (δ) in ^{1}H and ^{13}C NMR spectra are given in ppm relative to TMS. ($CDCl_3$: δ ^{1}H = 7.26 ppm, δ ^{13}C = 77.16 ppm, DSMO-d_6: δ ^{1}H = 2.50 ppm, δ ^{13}C = 39.51 ppm).

The high-resolution mass spectra were measured by electron ionization from JEOL (JMS-700).

2. Synthesis of Starting materials

2.1 General procedure for the preparation of Substitued 1-(2-Pyrimidinyl)-4(1*H*)-quinolinone (1)



Substituted 2-hydroxypyridine (5 mmol), copper(I) iodide (10 mol %), and potassium carbonate (5 mmol) were taken in DMSO (10 mL), and 2-chloropyridine (10 mmol) was added to the resulting mixture. The mixture was stirred at 130 °C for 12 h under nitrogen atmosphere. The resulting mixture was allowed to cool to room temperature and then quenched with water. Extraction with ethyl acetate, concentrated under reduced pressure, and silica gel column purification with acetone : dichoromethane (DCM) afforded 1-(2-Pyrimidinyl)-4(1*H*)-quinolinone derivatives in 34−81% yields.

The following 1-(2-Pyrimidinyl)-4(1*H*)-quinolinone are known compounds and displayed spectroscopic properties in accord with published data.

1-(2-Pyrimidinyl)-4(1*H*)-quinolinone (**1a**) (CAS : 1687724-48-6)

6-Methyl-1-(2-pyrimidinyl)-4(1*H*)-quinolinone (**1b**) (CAS : 1687724-49-7)

6-Methoxy-1-(2-pyrimidinyl)-4(1*H*)-quinolinone (**1c**) (CAS : 1802551-21-8)

6-Chloro-1-(2-pyrimidinyl)-4(1*H*)-quinolinone (**1d**) (CAS :1687724-51-1)

6-Nitro-1-(2-pyrimidinyl)-4(1*H*)-quinolinone (**1f**) (CAS : 1687724-54-4)

7-Methoxy-1-(2-pyrimidinyl)-4(1*H*)-quinolinone (**1g**) (CAS : 1687724-59-9)

7-Chloro-1-(2-pyrimidinyl)-4(1*H*)-quinolinone (**1h**) (CAS : 1687724-56-6)

7-Bromo-1-(2-pyrimidinyl)-4(1*H*)-quinolinone (**1i**) (CAS : 1687724-57-7)

1-(2-Pyrimidinyl)-4(1*H*)-pyridinone (**1l**) (CAS : 29049-26-1)

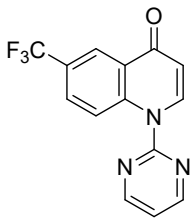
1-(2-Pyrimidinyl)-2(1*H*)-pyridinone (**1m**) (CAS : 1862952-04-2)

2-(2-Pyrimidinyl)-1(2*H*)-isoquinolinone (**1n**) (CAS : 1687724-73-7)

1-(2-Pyridinyl)-4(1*H*)-quinolinone (**1s**) (CAS : 4547-00-6)

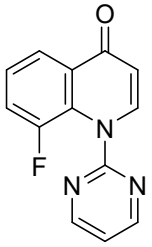
Characterization data of compounds 1

1-(pyrimidin-2-yl)-6-(trifluoromethyl)quinolin-4(1*H*)-one (1e):



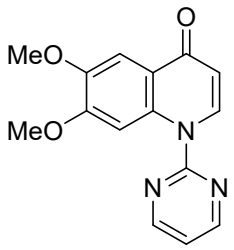
Slightly yellow solid (1.22 g, yield: 81%); mp 138–140 °C; purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R_f}$ = 0.36); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.89 (d, *J* = 4.9 Hz, 2H), 8.74 – 8.65 (m, 1H), 8.45 (d, *J* = 8.2 Hz, 1H), 8.31 – 8.21 (m, 1H), 7.75 (dd, *J* = 9.2, 2.3 Hz, 1H), 7.43 (t, *J* = 4.8 Hz, 1H), 6.43 (d, *J* = 8.3 Hz, 1H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 177.9, 159.3, 159.1, 141.8, 140.7, 128.0 (q, *J* = 3.4 Hz), 126.8 (q, *J* = 33.5 Hz), 126.3, 124.6 (q, *J* = 4.1 Hz), 123.9 (q, *J* = 270.8 Hz), 120.1, 119.5, 112.4, 77.6, 77.2, 76.7; **^{19}F NMR** (471 MHz, Chloroform-d) δ -62.3; **HRMS** (EI-MS) *m/z* calcd for $C_{14}H_8F_3N_3O$ $[M]^+$ 291.0619, found 291.0617.

8-fluoro-1-(pyrimidin-2-yl)quinolin-4(1*H*)-one (1j):



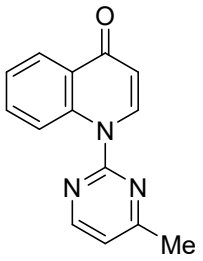
Slightly yellow solid (0.70 g, yield: 48%); mp 111–113 °C; purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R_f}$ = 0.43); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.99 (d, *J* = 4.9 Hz, 1H), 8.63 (d, *J* = 4.8 Hz, 2H), 7.92 – 7.85 (m, 1H), 7.54 – 7.41 (m, 2H), 7.38 (d, *J* = 5.0 Hz, 1H), 7.18 (t, *J* = 4.8 Hz, 1H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 164.4, 160.1, 159.1, 158.4 (q, *J* = 261.8 Hz), 157.1, 156.6, 151.2, 140.5 (q, *J* = 12.6 Hz), 126.7 (q, *J* = 8.1 Hz), 124.6, 124.5, 117.7 (q, *J* = 4.9 Hz), 117.6, 114.3 (q, *J* = 18.8 Hz), 112.9, 77.4, 77.2, 76.9; **^{19}F NMR** (471 MHz, Chloroform-d) δ -124.2; **HRMS** (EI-MS) *m/z* calcd for $C_{13}H_8FN_3O$ $[M]^+$ 241.0651, found 241.0649.

6,7-dimethoxy-1-(pyrimidin-2-yl)quinolin-4(1*H*)-one (1k):



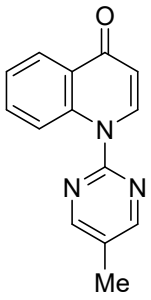
White solid (0.57 g, yield: 40%); mp 210–212 °C; purification by silica gel chromatography (Acetone:DCM= 1:3, $\mathbf{R}_f$ = 0.2); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.89 (d, *J* = 4.8 Hz, 2H), 8.42 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 3.1 Hz, 2H), 7.38 (t, *J* = 4.8 Hz, 1H), 6.39 (d, *J* = 8.2 Hz, 1H), 4.01 (s, 3H), 3.90 (s, 3H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 177.7, 159.5, 158.9, 152.8, 147.5, 140.1, 134.3, 121.1, 119.5, 111.1, 105.8, 100.4, 56.2, 56.1; **HRMS** (EI-MS) *m/z* calcd for $C_{15}H_{13}N_3O_3$ $[M]^+$ 283.0957, found 283.0954.

1-(4-methylpyrimidin-2-yl)quinolin-4(1*H*)-one (1t):



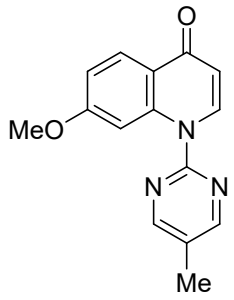
Slightly yellow solid (0.40 g, yield: 35%); mp 156–158 °C; purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R}_f$ = 0.20); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.71 (d, *J* = 5.1 Hz, 1H), 8.45 (dd, *J* = 8.1, 1.7 Hz, 1H), 8.38 (d, *J* = 8.2 Hz, 1H), 8.07 (dd, *J* = 8.7, 0.9 Hz, 1H), 7.59 (ddd, *J* = 8.8, 7.0, 1.7 Hz, 1H), 7.45 – 7.38 (m, 1H), 7.23 (d, *J* = 5.1 Hz, 1H), 6.42 (d, *J* = 8.2 Hz, 1H), 2.65 (s, 3H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 178.9, 170.4, 159.3, 158.5, 141.4, 139.1, 131.9, 126.7, 126.7, 124.8, 119.4, 118.2, 111.5, 24.4; **HRMS** (EI-MS) *m/z* calcd for $C_{14}H_{11}N_3O$ $[M]^+$ 237.0902, found 237.0899.

1-(5-methylpyrimidin-2-yl)quinolin-4(1*H*)-one (1u):



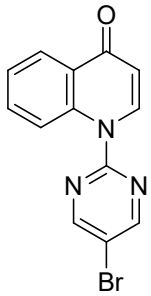
Slightly yellow solid (0.93 g, yield: 79%); mp 184–186 °C; purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R}_f$ = 0.23); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.69 (d, *J* = 0.8 Hz, 2H), 8.44 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.30 (d, *J* = 8.2 Hz, 1H), 7.99 (dd, *J* = 8.8, 1.0 Hz, 1H), 7.57 (ddd, *J* = 8.8, 7.0, 1.7 Hz, 1H), 7.40 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 1H), 6.41 (d, *J* = 8.1 Hz, 1H), 2.43 (s, 3H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 178.8, 159.1, 157.6, 141.3, 139.1, 131.9, 129.7, 126.7, 124.7, 118.0, 111.4, 15.4; **HRMS** (EI-MS) *m/z* calcd for $C_{14}H_{11}N_3O$ $[M]^+$ 237.0902, found 237.0904.

7-methoxy-1-(5-methylpyrimidin-2-yl)quinolin-4(1H)-one (1v):



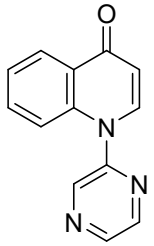
Slightly yellow solid (0.83 g, yield: 40%); mp 155–157 °C; purification by silica gel chromatography (Acetone:DCM= 1:3, $\mathbf{R}_f$ = 0.5); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.70 – 8.65 (m, 2H), 8.36 (d, *J* = 9.0 Hz, 1H), 8.24 (d, *J* = 8.2 Hz, 1H), 7.51 (d, *J* = 2.3 Hz, 1H), 6.99 (dd, *J* = 9.0, 2.3 Hz, 1H), 6.32 (d, *J* = 8.2 Hz, 1H), 3.82 (s, 3H), 2.42 (s, 3H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 178.3, 162.5, 159.0, 157.6, 141.1, 140.6, 129.6, 128.4, 120.9, 113.0, 111.2, 101.1, 55.5, 15.3; **HRMS** (EI-MS) *m/z* calcd for $C_{14}H_{11}N_3O$ $[M]^+$ 267.1008, found 267.1008.

1-(5-bromopyrimidin-2-yl)quinolin-4(1*H*)-one (1w):



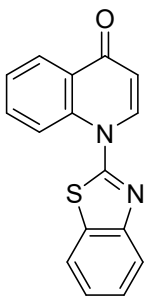
White solid (1.03 g, yield: 68%); mp 166–168 °C; purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R}_f$ = 0.38); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.90 (s, 2H), 8.44 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.37 (d, *J* = 8.3 Hz, 1H), 8.10 (d, *J* = 8.7 Hz, 1H), 7.60 (ddd, *J* = 8.7, 7.0, 1.7 Hz, 1H), 7.49 – 7.35 (m, 1H), 6.42 (d, *J* = 8.2 Hz, 1H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 178.8, 159.6, 157.7, 140.9, 138.7, 132.1, 126.8, 126.7, 125.1, 118.2, 117.7, 112.1; **HRMS** (EI-MS) *m/z* calcd for $C_{13}H_8BrN_3O$ $[M]^+$ 300.9851, found 300.9849.

1-(pyrazin-2-yl)quinolin-4(1*H*)-one (1x):



White solid (0.38 g, yield: 34%); mp 175–177 °C; purification by silica gel chromatography (Acetone:DCM= 1:3, $\mathbf{R}_f$ = 0.25); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.85 (d, *J* = 1.4 Hz, 1H), 8.74 (d, *J* = 2.5 Hz, 1H), 8.69 (dd, *J* = 2.5, 1.4 Hz, 1H), 8.45 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.55 (ddd, *J* = 8.6, 7.0, 1.7 Hz, 1H), 7.41 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H), 7.24 (d, *J* = 8.6 Hz, 1H), 6.42 (d, *J* = 8.0 Hz, 1H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 178.4, 150.1, 144.6, 144.4, 142.9, 141.1, 139.8, 132.4, 127.2, 126.6, 124.9, 116.1, 111.8; **HRMS** (EI-MS) *m/z* calcd for $C_{23}H_{19}N_3O_2$ $[M]^+$ 223.0746, found 223.0748.

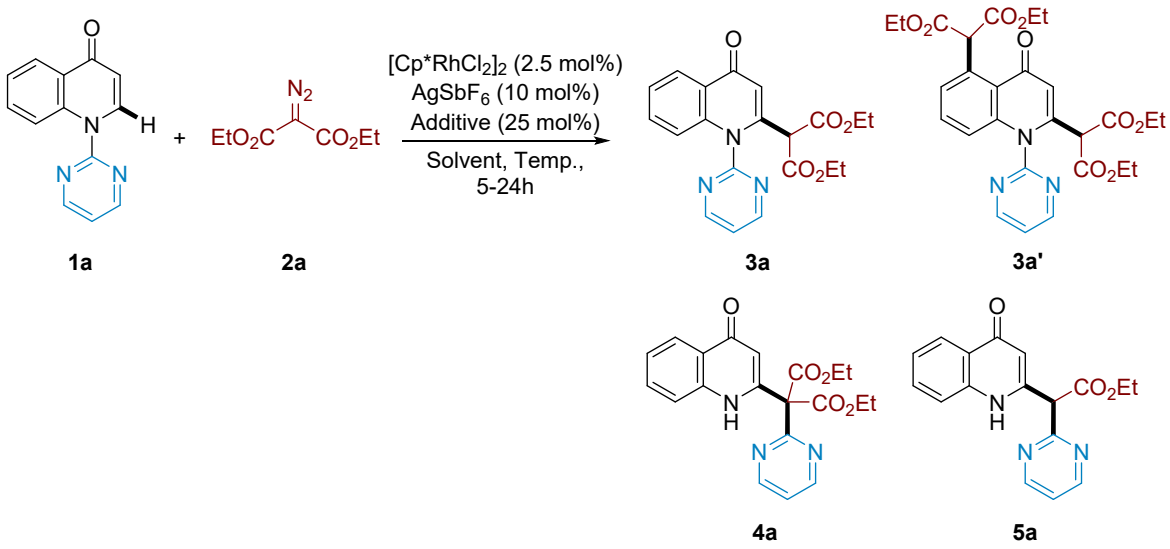
1-(benzo[d]thiazol-2-yl)quinolin-4(1*H*)-one (1y):



White solid (1.36 g, yield: 81%); mp 129–131 °C; purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R}_f$ = 0.5); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.45 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.13 – 8.07 (m, 1H), 7.94 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.88 – 7.82 (m, 1H), 7.62 (ddt, *J* = 8.2, 7.3, 1.6 Hz, 2H), 7.54 (ddd, *J* = 8.6, 7.3, 1.3 Hz, 1H), 7.45 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 1H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 178.3, 160.0, 150.0, 141.4, 140.0, 134.7, 132.9, 127.5, 126.9, 126.8, 126.4, 125.3, 124.1, 121.9, 117.1, 112.1; **HRMS** (EI-MS) *m/z* calcd for $C_{16}H_{10}N_2OS$ $[M]^+$ 278.0514, found 278.0510.

3. Reaction Optimization

Table S1. Optimization of reaction conditions[a]



Entry	Additives	Solvent	Temp. (°C)	Yield (%)[f]			
				3a	3a'	4a	5a
1	-	DCE	80	-	-	-	-
2	PivOH	DCE	80	34	19	-	-
3	PivOH	DCM	30	**79**	17	-	-
4	PivOH	DCM (0.05M)	30	78	18	-	-
5	PivOH	DCM (0.2M)	30	75	18	-	-
6	PivOH	DCM	r.t	70	19	-	-
7	1-AdCO$_2$H	DCM	30	71	20	-	-
8[b]	PivOH /NaOMe	DCM	30 to 40	(78)[g]	(16)[g]	-	-

9[b]	PivOH /KO^{t}Bu	DCM	30 to 40	(78)[g]	(13)[g]	-	-
10[c]	1-AdCO_2H	MeCN	60	46	6	29	-
11[c]	1-AdCO_2H	MeOH	60	trace	0	39	39
12[c]	AcOH	MeOH	60	trace	0	20	6
13[c]	1-AdCO_2H	EtOH	60	trace	0	50	14
14[d]	PivOH	DMSO	60	0	0	29	0
15[d]	PivOH	EtOH/DMSO = 3/1	60	trace	0	60	0
16[d]	PivOH	EtOH/DMSO = 9/1	60	trace	0	74	0
17[d,e]	PivOH (1 equiv.)	EtOH/DMSO = 9/1	60	trace	0	63	0
18[d]	PivOH	EtOH/DMSO =9/1	70	0	0	**77**	0
19[d]	PivOH	EtOH/DMSO =9/1 (0.05M)	70	0	0	70	0

[a]Reaction conditions A: **1a** (0.1 mmol), **2a** (0.12 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), and acid (25 mol%) in solvent (1.0 mL). [b]After proceeding to entry3 (check by TLC), add base (0.1 mmol). [c]Reaction conditions B: **1a** (0.1 mmol), **2a** (0.14 mmol), $[Cp^*RhCl_2]_2$ (5.0 mol%), $AgSbF_6$ (20 mol%), and acid (50 mol%). [d]**2a** (0.16 mmol) was used for reaction conditions B. [e]Acid (0.1 mmol). [f]Isolated yield after column chromatography. [g]NMR yield: Determined using CH_2Br_2(2H, 4.93 ppm).

4. General Procedure

4.1 Procedure for the syntesis of 3 via Cp*Rh-catalyzed C–H bond alkylation

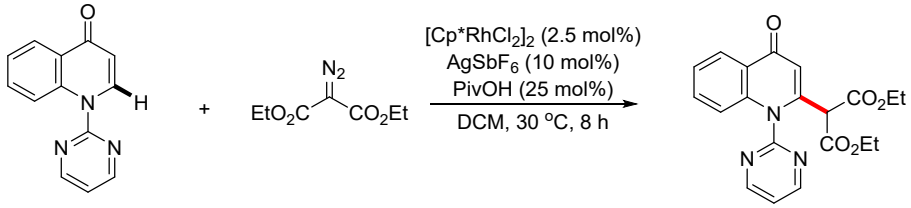
An oven-dried Schlenk tube was evacuated and flushed with argon three times. Then, it was evacuated and transferred to the glovebox. $AgSbF_6$ (6.9 mg, 0.02 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) were added, and the Schlenk tube was transferred to the fume hood. 1-(2-Pyrimidinyl)-4(1*H*)-quinolinone **1** (0.2 mmol), diethyl 2-diazomalonate **2** (0.24 mmol), PivOH (5.1mg, 0.05 mmol) and DCM (2.0 mL) were added under Ar. The reaction mixture was stirred at 30 ℃ for 5–12 h. The reaction was quenched with saturated $NaHCO_3$ solution, and the mixture was extracted three times with DCM. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and the solvents evaporated to dryness. The crude product was purified by column chromatography on silica gel using Acetone:DCM mixture as the eluent.

4.2 Procedure for the syntesis of 4 via Cp*Rh-catalyzed C–H alkylation/[1,3]-heteroareme migration cascade

An oven-dried Schlenk tube was evacuated and flushed with argon three times. Then, it was evacuated and transferred to the glovebox. $AgSbF_6$ (13.7 mg, 0.04 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol) were added, and the Schlenk tube was transferred to the fume hood. 1-(2-Pyrimidinyl)-4(1*H*)-quinolinone **1** (0.2 mmol), diethyl 2-diazomalonate **2** (0.32 mmol), PivOH (10.2mg, 0.1 mmol), EtOH (1.8 mL) and DMSO (0.2 mL) were added under Ar. The reaction mixture was stirred at 70 ℃ for 24 h. The reaction was quenched with saturated $NaHCO_3$ solution, and the mixture was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and the solvents evaporated to dryness. The crude product was purified by column chromatography

on silica gel using Acetone:DCM mixture as the eluent.

4.3 Procedure of scale-up (4 mmol) reaction for the synthesis of 3a



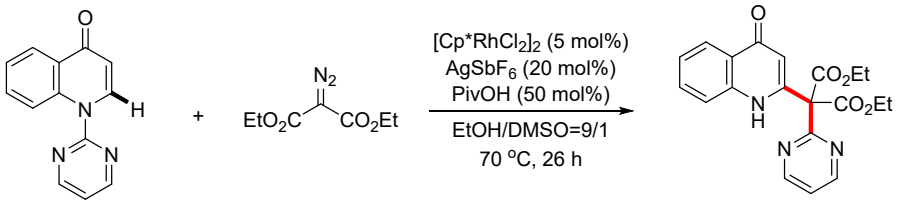
1a
1 equiv
4mmol

2a
1.2 equiv.

3a, 72%
1.098g

A two-neck round bottom flask was evacuated and flushed with argon three times. Then, it was evacuated and transferred to the glovebox. $AgSbF_6$ (137.4 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (61.8 mg, 0.1 mmol) were added, and the Schlenk tube was transferred to the fume hood. 1-(2-Pyrimidinyl)-4(1*H*)-quinolinone **1** (4.0 mmol), diethyl 2-diazomalonate **2** (4.8 mmol), PivOH (102.1 mg, 1.0 mmol) and DCM (40 mL) were added under Ar. The reaction mixture was stirred at 30 ℃ for 8 h. The reaction was quenched with saturated $NaHCO_3$ solution, and the mixture was extracted three times with DCM. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and the solvents evaporated to dryness. The crude product was purified by column chromatography on silica gel using Acetone:DCM = 1:5 as the eluent. The product **3a** was isolated in 72% yield (1.098 g).

4.4 Procedure of scale-up (4 mmol) reaction for the synthesis of 4a



1a
1 equiv
4mmol

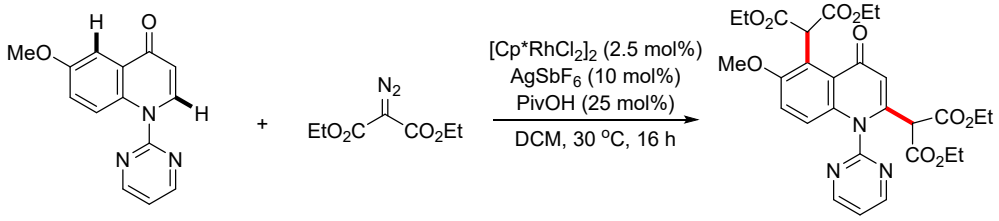
2a
1.6 equiv.

4a, 71%
1.083g

A two-neck round bottom flask was evacuated and flushed with argon three times. Then, it was evacuated and transferred to the glovebox. $AgSbF_6$ (274.9 mg, 0.8 mmol), $[Cp^*RhCl_2]_2$ (123.6 mg, 0.2 mmol) were added, and the Schlenk tube was transferred to the fume hood. 1-(2-Pyrimidinyl)-4(1*H*)-quinolinone **1** (4 mmol), diethyl 2-diazomalonate **2** (6.4 mmol), PivOH (204.3 mg, 2.0 mmol), EtOH (36 mL) and DMSO (4 mL) were added under Ar. The reaction mixture was stirred at 70 ℃ for 26 h. The reaction was quenched with saturated $NaHCO_3$ solution, and the mixture was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and the solvents evaporated to dryness. The crude product was purified by column chromatography on silica gel using Acetone:DCM = 1:5 as the eluent. The product **4a** was isolated in 71% yield (1.083 g).

4.5 Procedure for application toward the synthesis of distomadine analog

4.5.1 Procedure for the syntesis of 3y via dialkylation



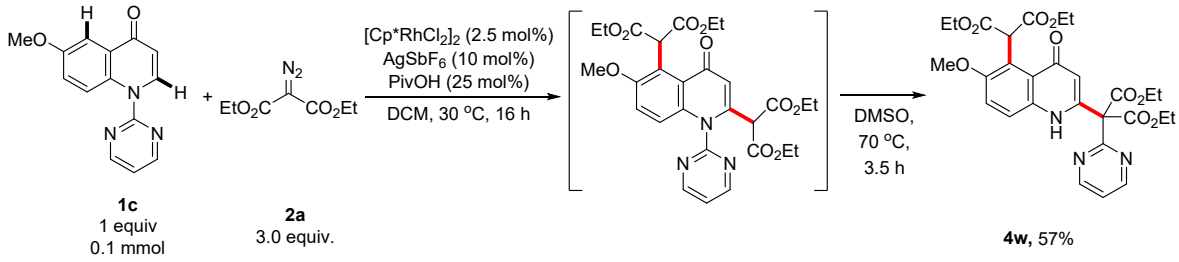
1c
1 equiv
0.2 mmol

2a
3 equiv.

3y, 82%

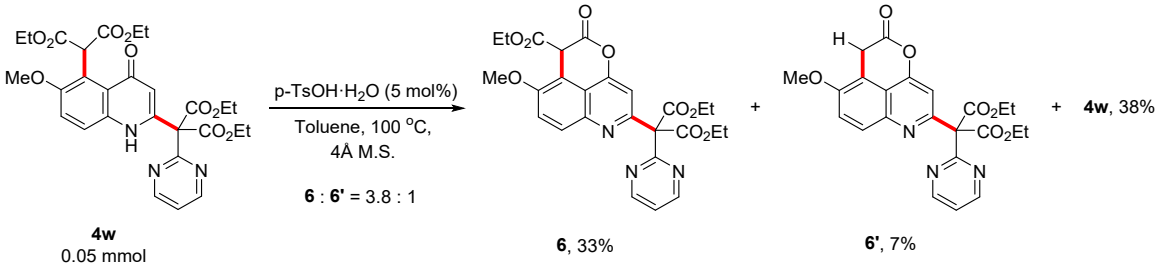
An oven-dried Schlenk tube was evacuated and flushed with argon three times. Then, it was evacuated and transferred to the glovebox. $AgSbF_6$ (6.9 mg, 0.02 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) were added, and the Schlenk tube was transferred to the fume hood. 1-(2-Pyrimidinyl)-4(1*H*)-quinolinone **1** (0.2 mmol), diethyl 2-diazomalonate **2** (0.24 mmol), PivOH (5.1mg, 0.05 mmol) and DCM (2.0 mL) were added under Ar. The reaction mixture was stirred at 30 ℃ for 16 h. The reaction was quenched with saturated $NaHCO_3$ solution, and the mixture was extracted three times with DCM. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and the solvents evaporated to dryness. The crude product was purified by column chromatography on silica gel using Acetone:DCM = 1:5 as the eluent.

4.5.2 Procedure for the syntesis of 4 via directing group migration



An oven-dried Schlenk tube was evacuated and flushed with argon three times. Then, it was evacuated and transferred to the glovebox. $AgSbF_6$ (3.5 mg, 0.01 mmol), $[Cp^*RhCl_2]_2$ (1.6 mg, 0.0025 mmol) were added, and the Schlenk tube was transferred to the fume hood. 1-(2-Pyrimidinyl)-4(1*H*)-quinolinone **1c** (0.2 mmol), diethyl 2-diazomalonate **2a** (0.24 mmol), PivOH (2.6mg, 0.025 mmol) and DCM (1.0 mL) were added under Ar. The reaction mixture was stirred at 30 ℃ for 16 h. And then, The reaction solvents evaporated and DMSO (1.0 mL) added. The reaction mixture was stirred at 70 ℃ for 3.5 h. The reaction was quenched with saturated $NaHCO_3$ solution, and the mixture was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and the solvents evaporated to dryness. The crude product was purified by column chromatography on silica gel using Acetone:DCM = 1:5 as the eluent.

4.5.3 Procedure for the syntesis of 6 via acid-catalyzed lactonization



An oven-dried Schlenk tube was evacuated and flushed with argon three times. Then, **4w** (28.5 mg, 0.05 mmol), p-TsOH·H_2O (1.0 mg, 0.0025 mmol), 4Å M.S. and toluene (0.38 mL) were added under Ar. The reaction mixture was stirred at 100 ℃ for 16 h. Afterward, The crude product was purified by flash column chromatography on silica gel, mixture of **6** in 40% yield as yellow oil. Purification by silica gel chromatography (Acetone:DCM = 1:5, **6** + **6'** R_f = 0.6); ^{1}H NMR (500 MHz, $CDCl_3$, major product **6**) δ 8.74 (d, *J* = 4.9 Hz, 2H), 8.05 (dd, *J* = 9.3, 0.8 Hz, 1H), 7.48 – 7.38 (m, 2H), 7.23 (t, *J* = 4.9 Hz, 1H), 5.18 (s, 1H), 4.48 – 4.35 (m, 5H), 4.27 – 4.16 (m, 2H), 3.97 (s, 4H), 1.32 (td, *J* = 7.1, 1.6 Hz, 7H), 1.22 (d, *J* = 7.1 Hz, 3H); **HRMS** (EI-MS) *m/z* calcd for $C_{26}H_{25}N_3O_9$ $[M]^+$ 523.1591, found 523.1592; minor product **6'**: HRMS (FAB) *m/z* calcd for $C_{23}H_{22}N_3O_7$ $[M + H]^+$ 452.1458, found 452.1582.

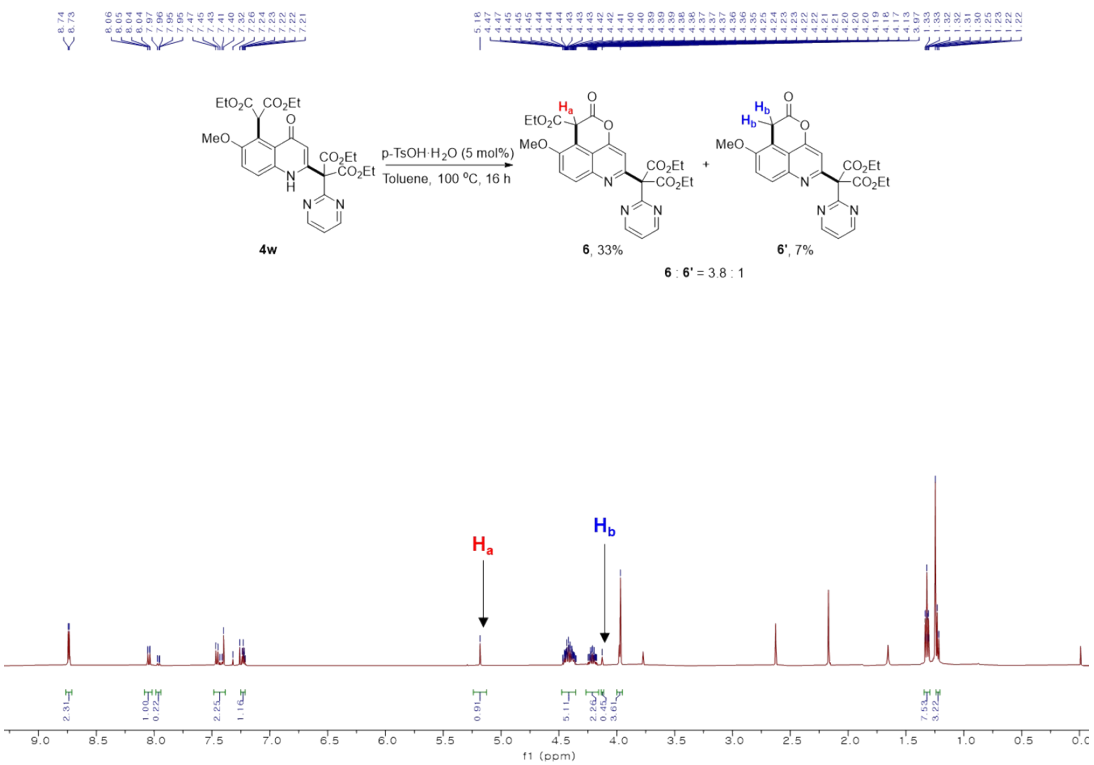


Figure S1. ^{1}H in Chloroform-*d* spectrum of products **6** + **6'**

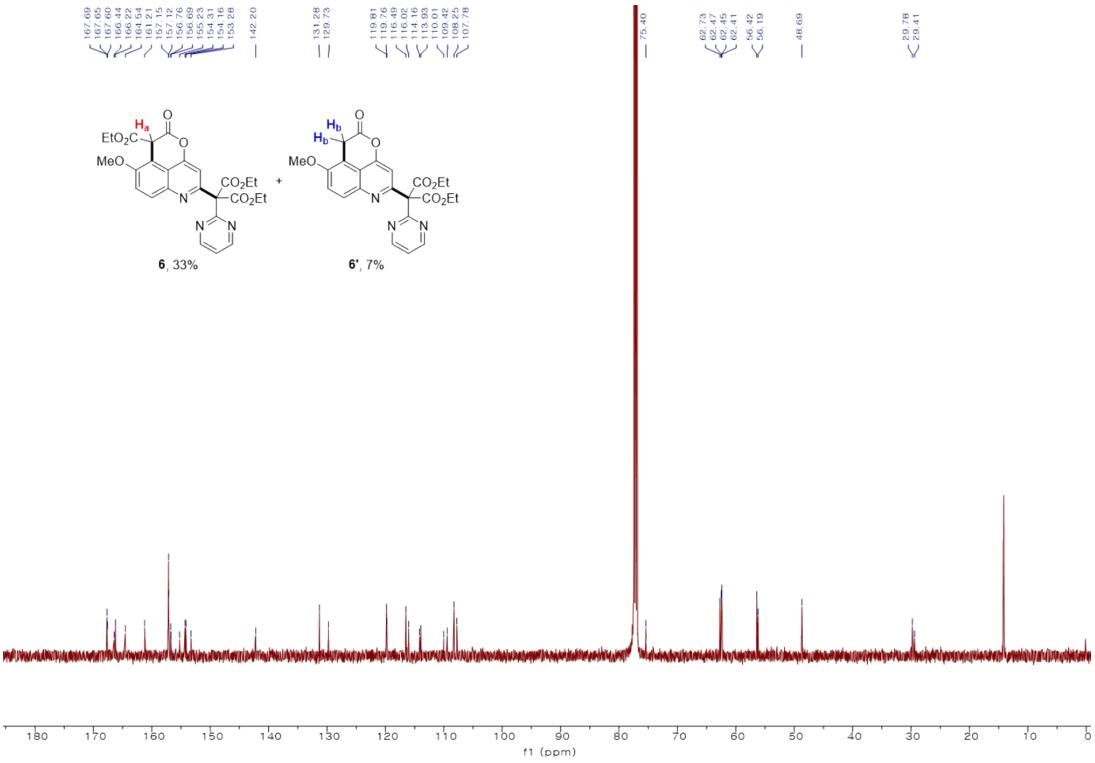
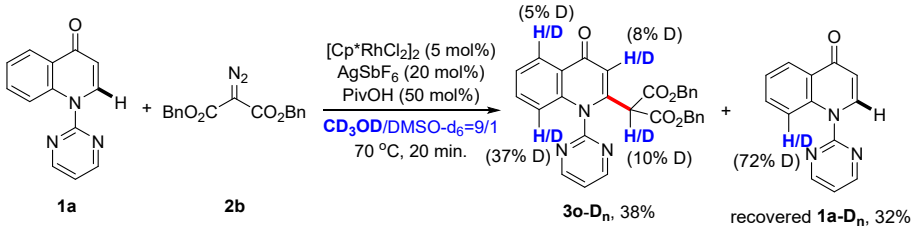


Figure S2. ^{13}C NMR in Chloroform-*d* spectrum of products **6** + **6'**

5. Mechanistic Study

5.1 Deuterium-labeling expriment



An oven-dried Schlenk tube was evacuated and flushed with argon three times. Then, it was evacuated and transferred to the glovebox. $AgSbF_6$ (6.9 mg, 0.02 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) were added, and the Schlenk tube was transferred to the fume hood. 1-(2-Pyrimidinyl)-4(1*H*)-quinolinone **1a** (0.1 mmol), dimethyl 2-diazomalonate **2b** (0.16 mmol), PivOH (5.1mg, 0.05 mmol), CD_3OD (0.9 mL) and DMSO-d_6 (0.1 mL) were added under Ar. The reaction mwixture was stirred at 70 ℃ for 20 min. The reaction was quenched with saturated $NaHCO_3$ solution, and the mixture was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and the solvents evaporated to dryness. The crude product was purified by column chromatography on silica gel using Acetone:DCM = 1:5 as the eluent. Due to the shortened reaction time, the alkylation product was predominantly obtained, with the migration product yielding less than 10%. The D-incorporation of **3o-D_n** were estimated by ^{1}H NMR analysis as shown in Figure S3.

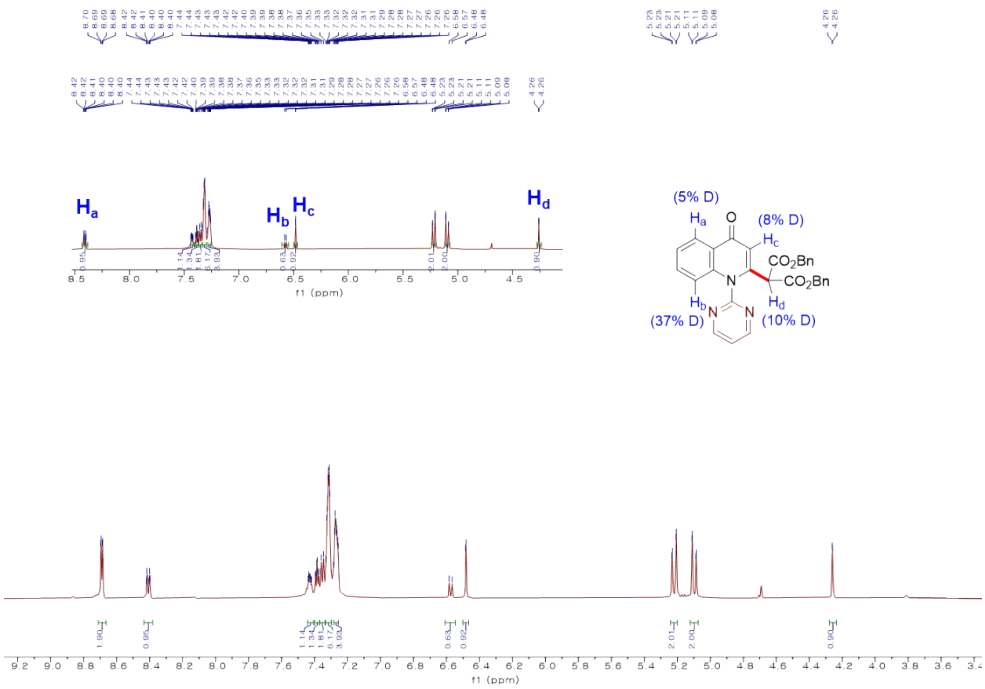


Figure S3. ^{1}H NMR in Chloroform-*d* spectrum of the reaction of **1a** and **2b** in CD_3OD/DMSO-d_6 (300 MHz)

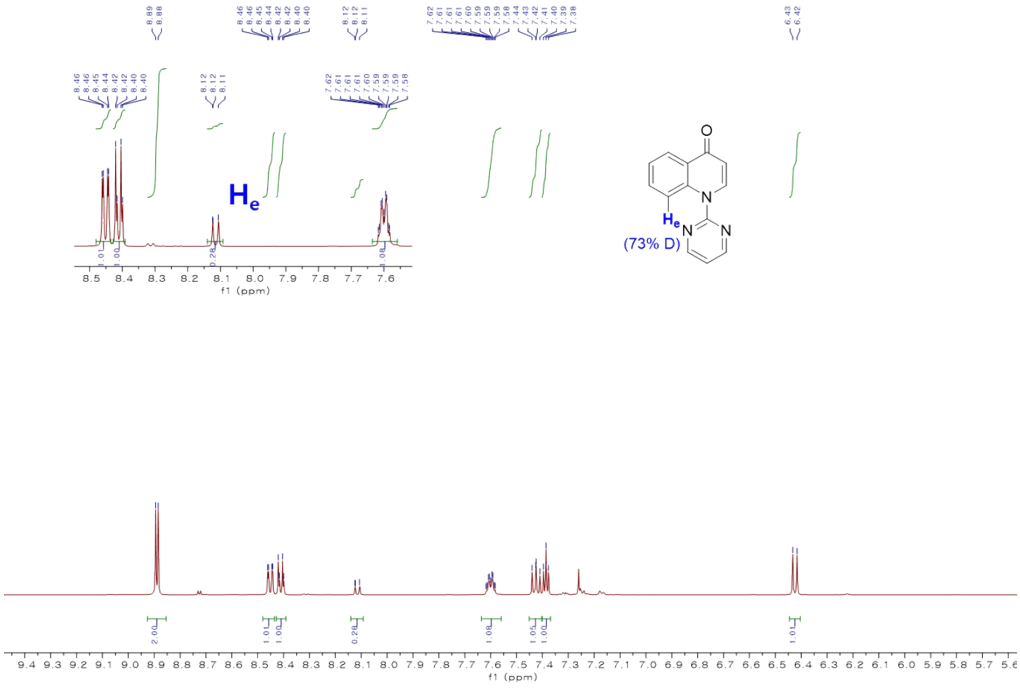
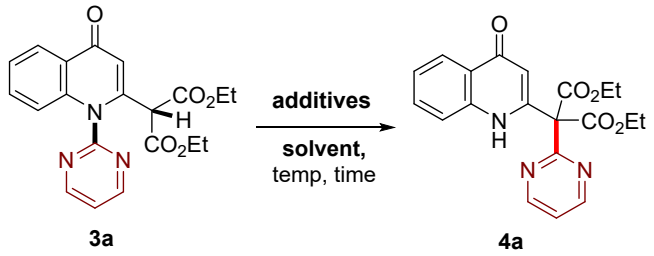


Figure S3. ^{1}H NMR in Chloroform-*d* spectrum of the recovered **1a** in CD_3OD/DMSO-d_6 (300 MHz)

5.2 Heteroarene migration test using C2-alkylated compound 3a



3a 4a

Table S2. Heteroarene migration test using C2-alkylated product 3a

Entry	Additives	Solvent	Temp (°C)	Time (h)	Yield (%) 4a
1	NaO*t*Bu (1 equiv.)	DMSO	70	4	76
2	NaOMe (1 equiv.)	DMSO	70	4	49
3	HCl (1 equiv.)	DMSO	70	4	65
4	PivOH (50 mol%)	DMSO	70	1	56
5	H_2O (1 equiv.)	DMSO	70	5	68
6	-	DMSO	70	4	90
7	-	DMSO	30	48	39
8	-	EtOH/DMSO (v/v = 9/1)	70	4	65
9	-	EtOH	70	4	60
10	-	MeCN	70	4	10
11	-	DCE	70	4	2

Procedure for the experimental entries 1–5 of Table S2

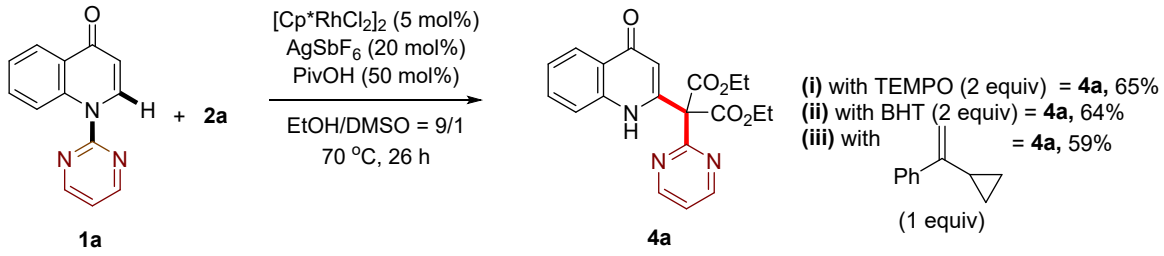
An oven-dried Schlenk tube was evacuated and flushed with argon three times. Then, diethyl 2-(4-oxo-1-(pyrimidin-2-yl)-1,4-dihydroquinolin-2-yl)malonate **3a** (0.1 mmol), the corresponding base or acid (1 equiv.) and DMSO (1 mL) were added unver Ar. The reaction

mixture was stirred at 70 ℃. The reaction was quenched with saturated $NaHCO_3$ solution, and the mixture was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and the solvents evaporated to dryness. The crude product was purified by flash column chromatography on silica gel.

Procedure for the experimental entries 6–11 of Table S2

An oven-dried Schlenk tube was evacuated and flushed with argon three times. Then, diethyl 2-(4-oxo-1-(pyrimidin-2-yl)-1,4-dihydroquinolin-2-yl) malonate **3a** (0.1 mmol) and the corresponding solvent (1 mL) were added unver Ar. The reaction mixture was stirred at corresponding temperature. The reaction was quenched with saturated $NaHCO_3$ solution, and the mixture was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and the solvents evaporated to dryness. The crude product was purified by flash column chromatography on silica gel.

5.3 Radical trapping experiments



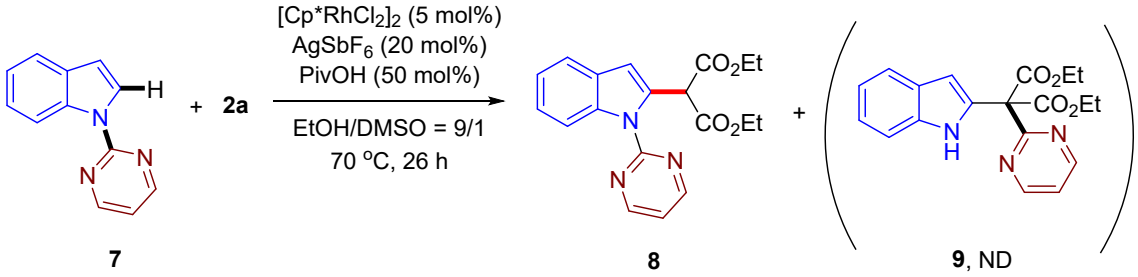
Procedure for the experiments (i)–(ii)

An oven-dried Schlenk tube was evacuated and flushed with argon three times. Then, it was evacuated and transferred to the glovebox. $AgSbF_6$ (13.7 mg, 0.04 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol) were added, and the Schlenk tube was transferred to the fume hood. 1-(2-Pyrimidinyl)-4(1*H*)-quinolinone **1** (0.2 mmol), diethyl 2-diazomalonate **2** (0.32 mmol), PivOH (10.2mg, 0.1 mmol), TEMPO or BHT (2 equiv.), EtOH (1.8 mL) and DMSO (0.2 mL) were added under Ar. The reaction mixture was stirred at 70 °C for 24 h. The reaction was quenched with saturated $NaHCO_3$ solution, and the mixture was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and the solvents evaporated to dryness. The crude product was purified by flash column chromatography on silica gel, affording the product **4a** as a white solid.

Procedure for the experiment (iii)

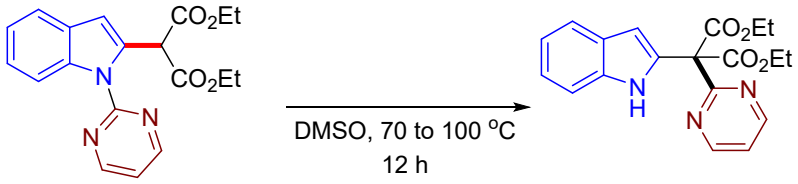
An oven-dried Schlenk tube was evacuated and flushed with argon three times. Then, it was evacuated and transferred to the glovebox. $AgSbF_6$ (13.7 mg, 0.04 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol) were added, and the Schlenk tube was transferred to the fume hood. 1-(2-Pyrimidinyl)-4(1*H*)-quinolinone **1** (0.2 mmol), diethyl 2-diazomalonate **2** (0.32 mmol), PivOH (10.2mg, 0.1 mmol), (1-cyclopropylvinyl)benzene (1 equiv.), EtOH (1.8 mL) and DMSO (0.2 mL) were added under Ar. The reaction mixture was stirred at 70 ℃ for 24 h. The reaction was quenched with saturated $NaHCO_3$ solution, and the mixture was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and the solvents evaporated to dryness. The crude product was purified by flash column chromatography on silica gel, affording the product **4a** as a white solid.

5.4 Attempted Cp*Rh(III) catalysis using N-pyrimidyl indole 6



An oven-dried Schlenk tube was evacuated and flushed with argon three times. Then, it was evacuated and transferred to the glovebox. $AgSbF_6$ (13.7 mg, 0.04 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol) were added, and the Schlenk tube was transferred to the fume hood. 1-(pyrimidin-2-yl)-1*H*-indole **7** (0.2 mmol), diethyl 2-diazomalonate **2a** (0.32 mmol), PivOH (10.2mg, 0.1 mmol), EtOH (1.8 mL) and DMSO (0.2 mL) were added under Ar. The reaction mixture was stirred at 70 ℃ for 24 h. The reaction was quenched with saturated $NaHCO_3$ solution, and the mixture was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and the solvents evaporated to dryness. The crude product was purified by flash column chromatography on silica gel. Alkylated product, diethyl 2-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)malonate, **8** was isolated in 31% yield (22 mg), but C-H alkylation/[1,3]-pyrimidine migration product **9** was not detected.

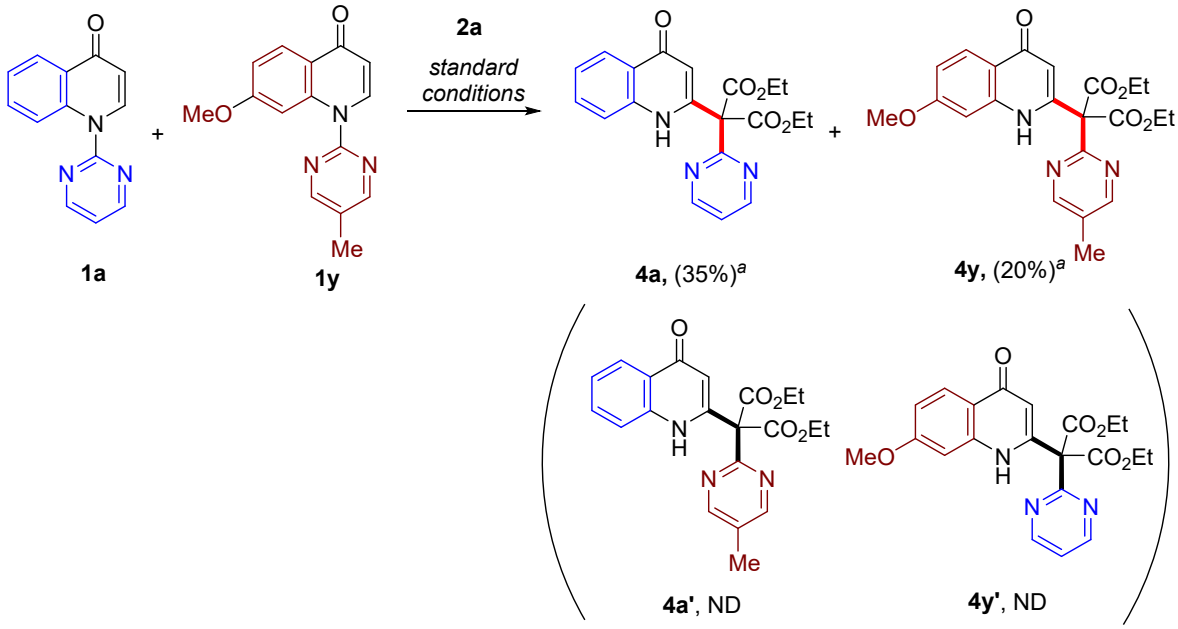
5.5 Rearrangement test using alkylated indole compound 7



8 **9**, NR

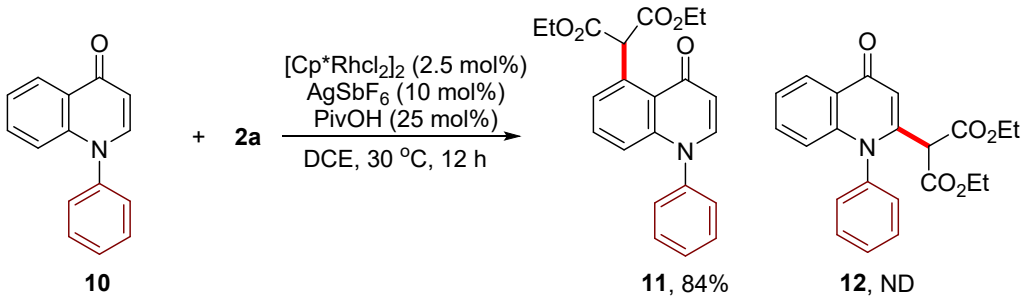
An oven-dried Schlenk tube was evacuated and flushed with argon three times. Then, diethyl 2-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)malonate **8** (0.1 mmol) and DMSO (1 mL) were added unver Ar. The reaction mixture was stirred at 70 °C. After checking TLC after 4 h, the reaction temperature was increased to 100°C and stirred for 12h. The reaction was quenched with saturated $NaHCO_3$ solution, and the mixture was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and the solvents evaporated to dryness. The crude mixture was checked by NMR, but the desired product **9** was not obtained.

5.6 Cross-over experiments



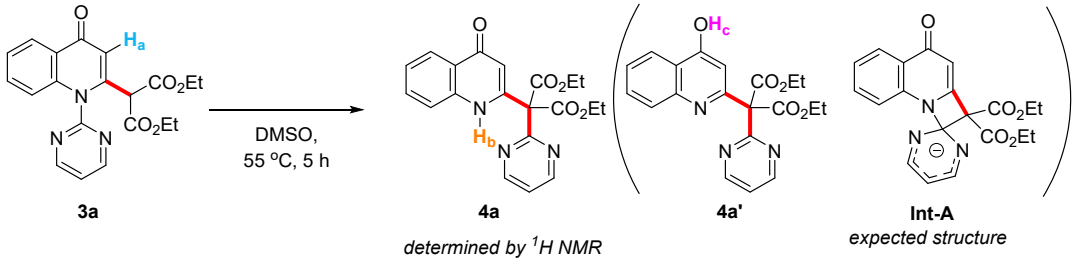
An oven-dried Schlenk tube was evacuated and flushed with argon three times. Then, it was evacuated and transferred to the glovebox. $AgSbF_6$ (6.9 mg, 0.02 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol) were added, and the Schlenk tube was transferred to the fume hood. 1-(pyrimidin-2-yl)quinolin-4(1*H*)-one **1a** (0.1 mmol), 7-methoxy-1-(5-methylpyrimidin-2-yl)quinolin-4(1*H*)-one **1y** (0.1 mmol), diethyl 2-diazomalonate **2a** (0.32 mmol), PivOH (5.1 mg, 0.05 mmol), EtOH (1.8 mL) and DMSO (0.2 mL) were added under Ar. The reaction mixture was stirred at 70 ℃ for 24 h. The reaction was quenched with saturated $NaHCO_3$ solution, and the mixture was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and the solvents evaporated to dryness. Only the intramolecular heteroarene migration products **4a** and **4y** were obtained in 35% and 20% respectively, without forming intermolecularly heteroarene transferred products **4a′** and **4y′**. The yields of **4a** and **4y** were determined by ^1H NMR analysis using dibromomethane as an internal standard.

5.7 Directing group ability test using *N*-phenyl substituted quinolone 9



An oven-dried Schlenk tube was evacuated and flushed with argon three times. Then, it was evacuated and transferred to the glovebox. $AgSbF_6$ (3.4 mg, 0.01 mmol), $[Cp^*RhCl_2]_2$ (1.5 mg, 0.0025 mmol) were added, and the Schlenk tube was transferred to the fume hood. 1-phenylquinolin-4(1*H*)-one **9** (0.1 mmol), diethyl 2-diazomalonate **2a** (0.12 mmol), PivOH (2.6 mg, 0.025 mmol) and dichloroethane (DCE) (1.0 mL) were added under Ar. The reaction mixture was stirred at 30 ℃ for 12 h. The reaction was quenched with saturated $NaHCO_3$ solution, and the mixture was extracted three times with DCM. The combined organic layers were washed with brine, dried with anhydrous $MgSO_4$, and the solvents evaporated to dryness. The crude product was purified by flash column chromatography on silica gel, affording the product **11** (84%, 31.9 mg) as a slightly yellow solid. Eluent for silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R_f}$ = 0.48); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.6 – 7.5 (m, 3H), 7.5 (d, *J* = 7.7 Hz, 1H), 7.4 (dd, *J* = 8.7, 7.5 Hz, 1H), 7.4 – 7.3 (m, 2H), 7.2 (dd, *J* = 7.5, 1.1 Hz, 1H), 6.9 (dd, *J* = 8.7, 1.1 Hz, 1H), 6.6 (s, 1H), 6.3 (d, *J* = 7.7 Hz, 1H), 4.3 (qd, *J* = 7.1, 1.6 Hz, 4H), 1.3 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 179.9, 169.4, 143.1, 141.8, 141.7, 135.0, 131.1, 130.5, 129.7, 127.7, 125.0, 124.2, 118.1, 111.9, 77.6, 77.2, 76.7, 61.5, 56.1, 14.2; **HRMS** (EI-MS) *m/z* calcd for $C_{22}H_{21}NO_5$ $[M]^+$ 379.1420, found 379.1420.

5.8 NMR experiments



To find out the Int-A, the migration reaction of **3a** and DMSO-d_6 was conducted and analyzed by ^{1}H NMR. To NMR tube, **3a** (0.05 mmol, 1 equiv) were dissolved in DMSO-d_6. The ^{1}H NMR were measured immediately, every 30 min. at 55 °C. The results are shown in Figure S4. However, in ^{1}H NMR spectra, we couldn't detect any reaction intermediates in time-dependent NMR experiments.

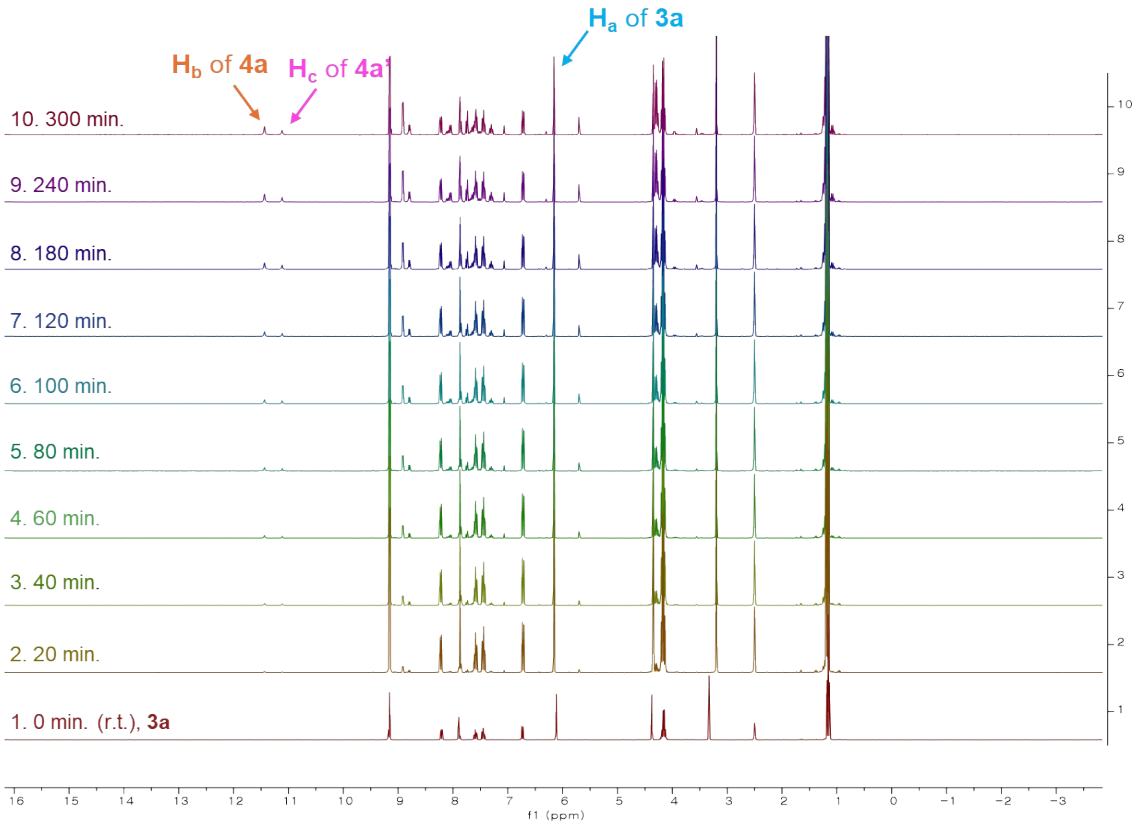
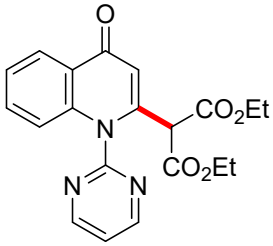


Figure S4. ^{1}H NMR spectra of migration reaction of **3a** in DMSO-d_6.

6. Characterization Data of All Compounds

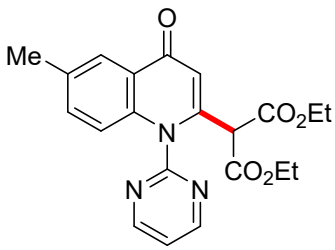
Characterization of products 3

Diethyl 2-(4-oxo-1-(pyrimidin-2-yl)-1,4-dihydroquinolin-2-yl)malonate (3a):



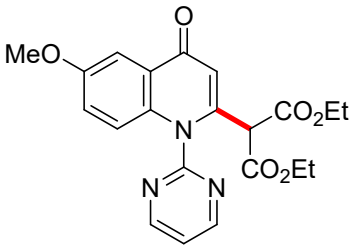
White solid (60.3 mg, yield: 79%); mp 131–133 °C; purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R}_f$ = 0.38); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 9.00 (d, *J* = 4.9 Hz, 2H), 8.42 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.58 (t, *J* = 4.9 Hz, 1H), 7.45 (ddd, *J* = 8.7, 7.1, 1.8 Hz, 1H), 7.35 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 6.62 – 6.55 (m, 1H), 6.46 (s, 1H), 4.28 – 4.13 (m, 5H), 1.23 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 178.3, 165.3, 160.4, 158.3, 144.0, 141.4, 132.3, 126.4, 125.6, 124.4, 121.9, 117.1, 112.6, 62.8, 56.5, 14.0; **HRMS** (EI-MS) *m/z* calcd for $C_{20}H_{19}N_3O_5$ $[M]^+$ 381.1325, found 381.1327.

Diethyl 2-(6-methyl-4-oxo-1-(pyrimidin-2-yl)-1,4-dihydroquinolin-2-yl)malonate (3b):



Slightly yellow solid (69.6 mg, yield: 88%); mp 127–129 °C; purification by silica gel chromatography (Acetone:DCM= 1:10, $\mathbf{R}_f$ = 0.25); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.97 (d, *J* = 4.9 Hz, 2H), 8.21 – 8.13 (m, 1H), 7.58 (t, *J* = 4.9 Hz, 1H), 7.29 – 7.23 (m, 1H), 6.50 (d, *J* = 8.7 Hz, 1H), 6.45 (s, 1H), 4.22 – 4.11 (m, 5H), 2.38 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 178.1, 165.3, 160.2, 158.1, 143.7, 139.4, 134.4, 133.7, 125.5, 125.3, 121.9, 117.0, 112.0, 62.7, 56.3, 20.8, 13.9; **HRMS** (EI-MS) *m/z* calcd for $C_{21}H_{21}N_3O_5$ $[M]^+$ 395.1481, found 395.1485.

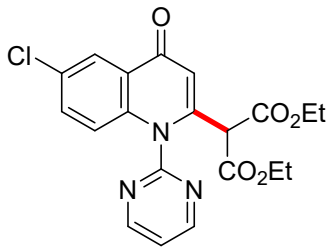
Diethyl 2-(6-methoxy-4-oxo-1-(pyrimidin-2-yl)-1,4-dihydroquinolin-2-yl)malona te (3c):



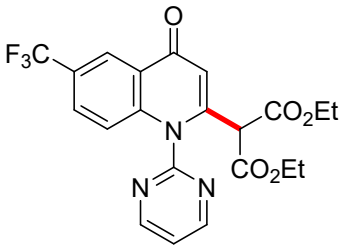
White solid (58.4 mg, yield: 71%); mp 155–157 °C;

purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R_f}$ = 0.38); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.99 (d, *J* = 4.9 Hz, 2H), 7.81 (d, *J* = 3.1 Hz, 1H), 7.56 (t, *J* = 4.9 Hz, 1H), 7.07 (dd, *J* = 9.3, 3.1 Hz, 1H), 6.57 (d, *J* = 9.3 Hz, 1H), 6.45 (s, 1H), 4.21 (ddp, *J* = 10.3, 7.1, 3.5 Hz, 5H), 3.90 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 177.8, 165.4, 160.3, 158.3, 156.8, 143.2, 136.0, 126.9, 123.0, 121.8, 118.9, 111.6, 105.3, 62.8, 56.4, 55.9, 14.0; **HRMS** (EI-MS) *m/z* calcd for $C_{21}H_{21}N_3O_6$ $[M]^+$ 411.1430, found 411.1430.

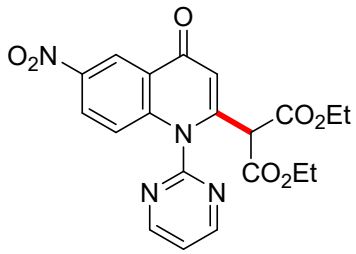
Diethyl 2-(6-chloro-4-oxo-1-(pyrimidin-2-yl)-1,4-dihydroquinolin-2-yl)malonate (3d):



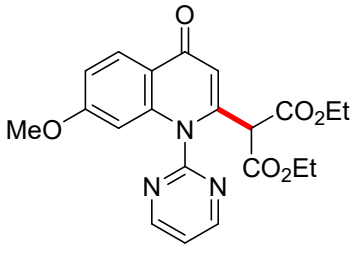
Slightly yellow solid (54.9 mg, yield: 66%); mp 110–112 °C; purification by silica gel chromatography (Acetone:DCM= 1:10, $\mathbf{R_f}$ = 0.38); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.98 (dd, *J* = 5.0, 1.0 Hz, 2H), 8.33 (d, *J* = 2.6 Hz, 1H), 7.60 (td, *J* = 4.9, 1.0 Hz, 1H), 7.40 – 7.31 (m, 1H), 6.56 (d, *J* = 9.1 Hz, 1H), 6.42 (d, *J* = 0.9 Hz, 1H), 4.22 – 4.11 (m, 5H), 1.19 (td, *J* = 7.1, 1.0 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 176.8, 165.0, 160.4, 157.7, 144.4, 139.7, 132.4, 130.6, 126.5, 125.5, 122.1, 119.0, 112.5, 62.8, 56.1, 13.9; **HRMS** (EI-MS) *m/z* calcd for $C_{20}H_{18}ClN_3O_5$ $[M]^+$ 415.0935, found 415.0937.

Diethyl 2-(4-oxo-1-(pyrimidin-2-yl)-6-(trifluoromethyl)-1,4-dihydroquinolin-2 yl)malonate (3e): 

Slightly yellow sticky solid (83.6 mg, yield: 93%); purification by silica gel chromatography (Acetone:DCM= 1:10, $\mathbf{R_f}$ = 0.5); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 9.02 (d, *J* = 4.9 Hz, 2H), 8.71 (d, *J* = 2.2 Hz, 1H), 7.67 – 7.60 (m, 2H), 6.72 (d, *J* = 9.0 Hz, 1H), 6.51 (s, 1H), 4.27 – 4.13 (m, 5H), 1.23 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 177.4, 165.0, 160.6, 157.9, 144.9, 143.1, 128.4 (q, *J* = 3.4 Hz), 126.6 (q, *J* = 33.5 Hz), 125.2, 124.5 (q, *J* = 4.2 Hz), 123.8 (q, *J* = 270.8 Hz), 122.3, 118.2, 113.5, 77.6, 77.2, 76.7, 63.0, 56.4, 14.0; **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -62.3; **HRMS** (EI-MS) *m/z* calcd for $C_{21}H_{18}F_3N_3O_5$ $[M]^+$ 449.1199, found 449.1201.

Diethyl 2-(6-nitro-4-oxo-1-(pyrimidin-2-yl)-1,4-dihydroquinolin-2-yl)malonate (3f): 

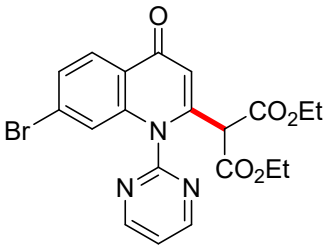
Slightly yellow solid (51.2 mg, yield: 60%); mp 127–130 °C; purification by silica gel chromatography (Acetone:DCM= 1:10, $\mathbf{R_f}$ = 0.45); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 9.25 (d, *J* = 2.7 Hz, 1H), 9.05 (d, *J* = 4.9 Hz, 2H), 8.23 (dd, *J* = 9.4, 2.7 Hz, 1H), 7.68 (t, *J* = 4.9 Hz, 1H), 6.73 (d, *J* = 9.4 Hz, 1H), 6.52 (s, 1H), 4.27 – 4.16 (m, 5H), 1.24 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 177.0, 164.9, 160.7, 157.6, 145.3, 144.6, 144.0, 126.3, 125.4, 123.2, 122.5, 118.7, 113.9, 63.1, 56.3, 14.0; **HRMS** (EI-MS) *m/z* calcd for $C_{20}H_{18}N_4O_7$ $[M]^+$ 426.1175, found 426.1173.

Diethyl 2-(7-methoxy-4-oxo-1-(pyrimidin-2-yl)-1,4-dihydroquinolin-2-yl)malona te (3g): 

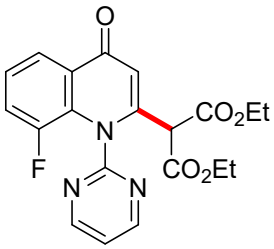
Slightly yellow solid (66.0 mg, yield: 68%); mp 93–95 °C; purification by silica gel

chromatography (Acetone:DCM= 1:5, $\mathbf{R}_f$ = 0.38); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.95 (dd, *J* = 4.9, 1.0 Hz, 2H), 8.28 (d, *J* = 9.0 Hz, 1H), 7.56 (td, *J* = 4.9, 1.1 Hz, 1H), 6.89 (dt, *J* = 9.0, 1.6 Hz, 1H), 6.34 (d, *J* = 1.0 Hz, 1H), 5.92 (d, *J* = 2.2 Hz, 1H), 4.14 (ddd, *J* = 15.1, 7.5, 1.4 Hz, 5H), 3.62 (d, *J* = 1.0 Hz, 3H), 1.17 (td, *J* = 7.1, 1.0 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 177.5, 165.2, 162.7, 160.3, 158.0, 143.8, 142.9, 128.2, 121.9, 119.8, 112.5, 112.2, 100.4, 62.6, 56.2, 55.4, 13.9; **HRMS** (EI-MS) *m/z* calcd for $C_{21}H_{21}N_3O_6$ $[M]^+$ 411.1430, found 411.1428.

Diethyl 2-(7-bromo-4-oxo-1-(pyrimidin-2-yl)-1,4-dihydroquinolin-2-yl)malonate (3h):

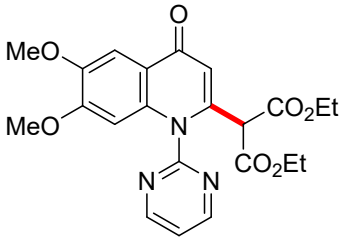


White solid (62.6 mg, yield: 68%); mp 169–171 °C; purification by silica gel chromatography (Acetone:DCM= 1:10, $\mathbf{R}_f$ = 0.38); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.99 (d, *J* = 4.9 Hz, 2H), 8.24 (d, *J* = 8.6 Hz, 1H), 7.60 (t, *J* = 4.9 Hz, 1H), 7.42 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.75 (d, *J* = 1.6 Hz, 1H), 6.42 (s, 1H), 4.22 – 4.10 (m, 5H), 1.20 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 177.5, 165.0, 160.5, 157.6, 144.4, 141.9, 128.0, 127.9, 127.1, 124.3, 122.2, 119.8, 113.0, 62.8, 56.3, 13.9; **HRMS** (EI-MS) *m/z* calcd for $C_{20}H_{18}BrN_3O_5$ $[M]^+$ 459.0430, found 459.0432.

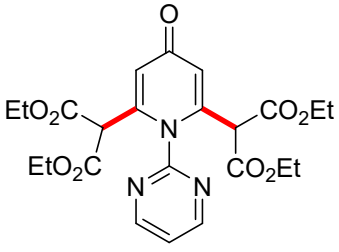


Diethyl 2-(8-fluoro-4-oxo-1-(pyrimidin-2-yl)-1,4-dihydroquinolin-2-yl)malonate (3i): White solid (59.1 mg, yield: 74%); mp 97–99 °C; purification by silica gel chromatography (Acetone:DCM= 1:10, $\mathbf{R}_f$ = 0.55); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 9.19 (s, 1H), 8.50 (d, *J* = 4.8 Hz, 2H), 7.63 – 7.52 (m, 1H), 7.46 – 7.34 (m, 2H), 7.10 (t, *J* = 4.8 Hz, 1H), 5.04 (s, 1H), 4.15 (qd, *J* = 7.1, 3.2 Hz, 4H), 1.18 (t,

J = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) 166.8, 164.7, 160.2, 158.3 (d, J = 257.5 Hz), 154.0, 154.0, 152.8, 139.7 (d, J = 12.6 Hz), 127.3, 127.2 (d, J = 8.2 Hz), 124.6, 124.6, 119.8, 118.0 (d, J = 5.0 Hz), 117.9, 117.4, 114.4 (d, J = 18.8 Hz), 77.6, 77.2, 76.7, 62.4, 50.2, 14.0; **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -124.1; **HRMS** (EI-MS) *m/z* calcd for $C_{20}H_{18}FN_3O_5$ $[M]^+$ 399.1230, found 399.1232.



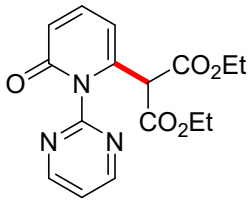
Diethyl 2-(6,7-dimethoxy-4-oxo-1-(pyrimidin-2-yl)-1,4-dihydroquinolin-2-yl)mal onate (3j): Slightly yellow solid (35.3 mg, yield: 40%); mp 65–67 °C; purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R}_f$ = 0.25); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 9.01 (d, J = 4.8 Hz, 2H), 7.76 (s, 1H), 7.60 (t, J = 4.8 Hz, 1H), 6.48 (s, 1H), 6.01 (s, 1H), 4.18 (dtd, J = 13.3, 6.6, 3.7 Hz, 5H), 3.96 (s, 3H), 3.64 (s, 3H), 1.22 (t, J = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 176.8, 165.4, 160.3, 158.3, 153.5, 147.7, 143.0, 137.0, 122.0, 119.9, 111.9, 105.4, 98.8, 62.8, 56.5, 56.4, 56.0, 14.0; **HRMS** (EI-MS) *m/z* calcd for $C_{22}H_{23}N_3O_7$ $[M]^+$ 441.1536, found 441.1535.



Tetraethyl 2,2'-(4-oxo-1-(pyrimidin-2-yl)-1,4-dihydropyridine-2,6-diyl)dimalona te (3k): Slightly yellow solid (64.6 mg, yield: 66%); mp 129–131 °C; purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R}_f$ = 0.18); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.86 (d, J = 4.9 Hz, 2H), 7.52 (t, J = 4.9 Hz, 1H), 6.50 (s, 2H), 4.15 (dt, J = 14.5, 7.3 Hz, 10H), 1.22 (t, J = 7.1 Hz, 12H);

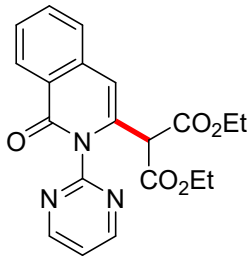
^{13}C NMR (75 MHz, Chloroform-*d*) δ 178.7, 165.2, 159.8, 157.2, 143.6, 122.0, 119.6, 62.8, 56.3, 14.0; **HRMS** (EI-MS) *m/z* calcd for $C_{23}H_{27}N_3O_9$ $[M]^+$ 489.1747, found 489.1745.

Diethyl 2-(6-oxo-1-(pyrimidin-2-yl)-1,6-dihydropyridin-2-yl)malonate (3l):



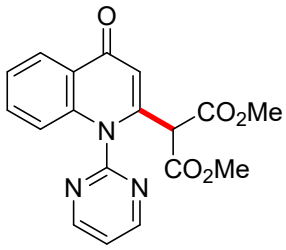
Slightly yellow solid (61.6 mg, yield: 93%); mp 115–117 °C; purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R_f}$ = 0.20); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.87 (d, *J* = 4.9 Hz, 2H), 7.48 – 7.33 (m, 2H), 6.61 (dd, *J* = 9.3, 1.1 Hz, 1H), 6.32 (dd, *J* = 7.0, 1.1 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 4H), 4.03 (s, 1H), 1.19 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 165.3, 163.0, 159.8, 157.9, 139.9, 139.3, 121.4, 121.4, 106.8, 62.6, 55.3, 13.9; **HRMS** (EI-MS) *m/z* calcd for $C_{16}H_{17}N_3O_5$ $[M]^+$ 331.1168, found 331.1169.

Diethyl 2-(1-oxo-2-(pyrimidin-2-yl)-1,2-dihydroisoquinolin-3-yl)malonate (3m):



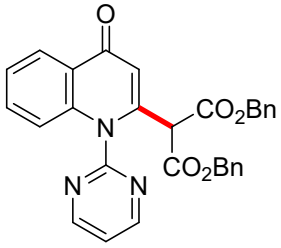
White solid (75.5 mg, yield: 99%); mp 167–169 °C; purification by silica gel chromatography (Acetone:DCM= 1:10, $\mathbf{R}_f$ = 0.28); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.92 (d, *J* = 4.9 Hz, 2H), 8.42 – 8.34 (m, 1H), 7.68 (ddd, *J* = 8.2, 7.1, 1.4 Hz, 1H), 7.58 – 7.41 (m, 3H), 6.69 (s, 1H), 4.26 – 4.15 (m, 5H), 1.24 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 165.9, 163.1, 159.6, 158.4, 136.3, 133.2, 132.9, 128.0, 127.6, 126.6, 125.7, 121.1, 107.6, 77.5, 77.1, 76.7, 62.5, 55.4, 13.9; **HRMS** (EI-MS) *m/z* calcd for $C_{20}H_{19}N_3O_5$ $[M]^+$ 381.1325, found 381.1327.

Dimethyl 2-(4-oxo-1-(pyrimidin-2-yl)-1,4-dihydroquinolin-2-yl)malonate (3n):



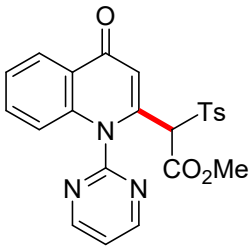
White solid (44.5 mg, yield: 63%); mp 156–158 °C; purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R}_f$ = 0.30); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.99 (d, *J* = 4.8 Hz, 2H), 8.39 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.58 (t, *J* = 4.9 Hz, 1H), 7.44 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.33 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 6.63 – 6.53 (m, 1H), 6.41 (s, 1H), 4.22 (s, 1H), 3.72 (s, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 178.2, 165.7, 160.4, 158.1, 143.9, 141.4, 132.5, 126.4, 125.5, 124.6, 122.1, 117.1, 112.4, 56.1, 53.6; **HRMS** (EI-MS) *m/z* calcd for $C_{18}H_{15}N_3O_5$ $[M]^+$ 353.1012, found 353.1014.

Dibenzyl 2-(4-oxo-1-(pyrimidin-2-yl)-1,4-dihydroquinolin-2-yl)malonate (3o):

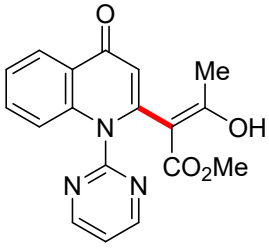


Slightly yellow solid (72.8 mg, yield: 72%); mp 69–72 °C; purification by silica gel chromatography (Acetone:DCM= 1:10, $\mathbf{R}_f$

= 0.38); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.68 (d, *J* = 4.9 Hz, 2H), 8.39 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.42 (ddd, *J* = 8.7, 7.0, 1.7 Hz, 1H), 7.38 (t, *J* = 4.9 Hz, 1H), 7.34 – 7.28 (m, 7H), 7.28 – 7.23 (m, 4H), 6.57 (d, *J* = 8.6 Hz, 1H), 6.50 (s, 1H), 5.21 (d, *J* = 12.2 Hz, 2H), 5.09 (d, *J* = 12.2 Hz, 2H), 4.28 (s, 1H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 178.0, 165.0, 160.1, 157.9, 143.6, 141.3, 134.6, 132.3, 128.6, 128.6, 128.6, 126.2, 125.5, 124.4, 121.7, 117.1, 112.6, 68.3, 56.2; **HRMS** (EI-MS) *m/z* calcd for $C_{30}H_{23}N_3O_5$ $[M]^+$ 505.1638, found 505.1635.

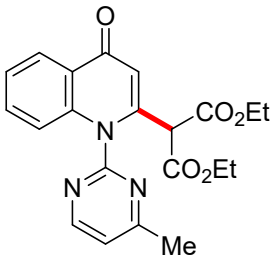


Methyl (*R*)-2-(4-oxo-1-(pyrimidin-2-yl)-1,4-dihydroquinolin-2-yl)-2-tosylacetate (3p): White solid (66.5 mg, yield: 74%); mp 75–77 °C; purification by silica gel chromatography (Acetone:DCM= 1:10, $\mathbf{R}_f$ = 0.20); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.99 (d, *J* = 4.9 Hz, 2H), 8.33 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.65 – 7.54 (m, 3H), 7.43 (ddd, *J* = 8.7, 7.0, 1.8 Hz, 1H), 7.32 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.26 – 7.21 (m, 2H), 6.67 – 6.59 (m, 1H), 6.53 (s, 1H), 5.16 (s, 1H), 3.74 (s, 3H), 2.38 (s, 3H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 177.4, 163.2, 160.2, 158.0, 146.5, 141.7, 139.3, 132.4, 132.3, 130.4, 129.6, 126.2, 125.7, 124.7, 121.9, 117.8, 114.3, 69.9, 53.9, 21.8; **HRMS** (EI-MS) *m/z* calcd for $C_{23}H_{19}N_3O_5S$ $[M]^+$ 449.1045, found 449.1043.



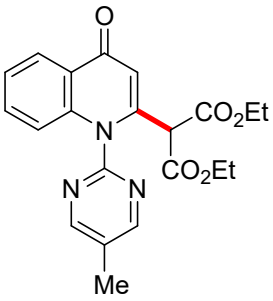
Methyl (*Z*)-3-hydroxy-2-(4-oxo-1-(pyrimidin-2-yl)-1,4-dihydroquinolin-2-yl)but-2-enoate (3q): Slightly yellow solid (29.7 mg, yield: 44%); mp 67–69 °C; purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R}_f$ = 0.28); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 12.68 (s, 1H), 8.90 (d, *J* = 4.9 Hz, 2H), 8.45

(dd, J = 8.0, 1.7 Hz, 1H), 7.51 – 7.42 (m, 2H), 7.36 (t, J = 7.5 Hz, 1H), 6.63 (d, J = 8.5 Hz, 1H), 6.32 (s, 1H), 3.66 (s, 3H), 1.97 (s, 3H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 178.8, 177.4, 171.0, 159.7, 159.0, 145.9, 141.3, 132.2, 126.5, 125.6, 124.2, 121.4, 117.0, 114.7, 99.4, 52.1, 20.4; **HRMS** (EI-MS) *m/z* calcd for $C_{18}H_{15}N_3O_4$ $[M]^+$ 337.1063, found 337.1063.



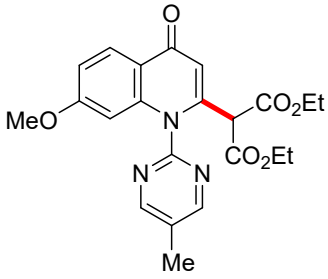
Diethyl 2-(1-(4-methylpyrimidin-2-yl)-4-oxo-1,4-dihydroquinolin-2-yl)malonate (3s): Slightly yellow solid (61.7 mg, yield: 78%); mp 103–105 °C; purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R}_f$ = 0.40); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.79 (d, J = 5.1 Hz, 1H), 8.37 (dd, J = 8.0, 1.6 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.31 (ddd, J = 8.1, 7.0, 1.0 Hz, 1H), 6.65 – 6.58 (m, 1H), 6.43 (s, 1H), 4.17 (qd, J = 7.1, 1.1 Hz, 4H), 4.10 (s, 1H), 2.61 (s, 3H), 1.20 (t, J = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 178.1, 171.8, 165.3, 159.6, 157.6, 144.0, 141.2, 132.2, 126.2, 125.5, 124.3, 121.5, 117.1, 112.3, 62.7, 56.5, 24.1, 13.9; **HRMS** (EI-MS) *m/z* calcd for $C_{21}H_{21}N_3O_5$ $[M]^+$ 395.1481, found 395.1483.

Diethyl 2-(1-(5-methylpyrimidin-2-yl)-4-oxo-1,4-dihydroquinolin-2-yl)malonate (3t):



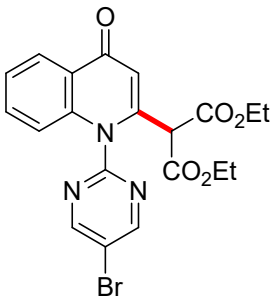
Slightly yellow sticky solid (58.5 mg, yield: 74%); purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R}_f$ = 0.43); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.77 (s, 2H), 8.37 (dd, J = 8.0, 1.7 Hz, 1H), 7.41 (ddd, J = 8.7, 7.0, 1.8 Hz, 1H), 7.31 (ddd, J = 8.0, 7.1, 1.1 Hz, 1H), 6.54 (d, J = 8.6 Hz, 1H), 6.44 (s, 1H), 4.17 (qd, J = 7.1, 3.0 Hz, 5H), 2.46 (s, 3H), 1.20 (t, J = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 178.2,

165.3, 160.2, 155.9, 144.1, 141.4, 132.2, 132.2, 126.2, 125.5, 124.2, 117.1, 112.2, 62.7, 56.3, 15.5, 13.9; **HRMS** (EI-MS) *m/z* calcd for $C_{21}H_{21}N_3O_5$ $[M]^+$ 395.1481, found 395.1479.

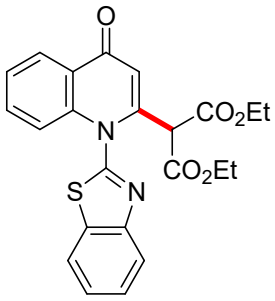


Diethyl 2-(7-methoxy-1-(5-methylpyrimidin-2-yl)-4-oxo-1,4-dihydroquinolin-2-yl)malonate (3u): Slightly yellow solid (61.3 mg, yield: 72%); mp 111–113 °C; purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R}_f$ = 0.40); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.77 (s, 2H), 8.33 (d, *J* = 8.9 Hz, 1H), 6.93 (dd, *J* = 9.0, 2.3 Hz, 1H), 6.36 (s, 1H), 5.93 (d, *J* = 2.3 Hz, 1H), 4.18 (qq, *J* = 6.9, 3.7 Hz, 4H), 4.10 (s, 1H), 3.68 (s, 3H), 2.47 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 177.8, 165.4, 162.7, 160.3, 156.0, 144.0, 143.1, 132.1, 128.4, 120.1, 112.3, 112.2, 100.7, 62.7, 56.4, 55.5, 15.6, 14.0; HRMS (EI-MS) *m/z* calcd for $C_{22}H_{23}N_3O_6$ $[M]^+$ 425.1587, found 425.1590.

Diethyl 2-(1-(5-bromopyrimidin-2-yl)-4-oxo-1,4-dihydroquinolin-2-yl)malonate (3v):

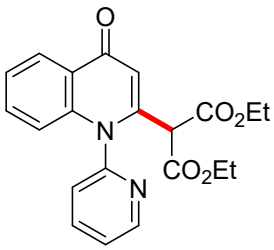


Yellow solid (28.5 mg, yield: 31%); purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R}_f$ = 0.55); For the major **3u**, **^{1}H NMR** (300 MHz, Chloroform-*d*) δ δ 9.0 (s, 2H), 8.4 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.5 (ddd, *J* = 8.7, 7.1, 1.8 Hz, 1H), 7.4 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 6.6 (d, *J* = 8.5 Hz, 1H), 6.5 (s, 1H), 4.3 – 4.1 (m, 5H), 1.3 (dt, *J* = 12.9, 7.1 Hz, 6H); For the mixture of major **3u** and C5-alkylated product **3u'**, **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 180.3, 178.2, 169.2, 165.2, 161.0, 159.9, 158.1, 143.7, 141.3, 140.5, 139.8, 135.0, 132.4, 131.1, 126.6, 126.3, 125.7, 124.6, 124.4, 121.2, 118.5, 118.1, 117.0, 113.4, 113.0, 77.6, 77.2, 76.7, 62.9, 61.6, 56.5, 56.2, 14.2, 14.0; **HRMS** (EI-MS) *m/z* calcd for $C_{20}H_{18}BrN_3O_5$ $[M]^+$ 459.0430, found 459.0426.



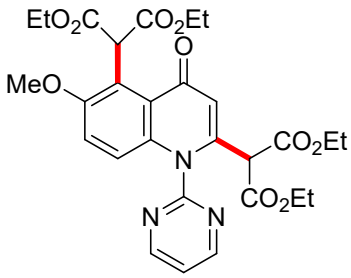
Diethyl 2-(1-(benzo[d]thiazol-2-yl)-4-oxo-1,4-dihydroquinolin-2-yl)malonate (3w): Slightly yellow sticky solid (39.3 mg, yield: 45%); purification by silica gel chromatography (Acetone:DCM= 1:20, $\mathbf{R}_f$ = 0.5); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.41 – 8.35 (m, 1H), 8.17 – 8.11 (m, 1H), 8.02 – 7.95 (m, 1H), 7.70 – 7.56 (m, 2H), 7.48 (ddd, *J* = 8.7, 7.1, 1.8 Hz, 1H), 7.37 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 6.89 (dt, *J* = 8.5, 0.8 Hz, 1H), 6.51 (s, 1H), 4.52 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 4H), 1.19 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 178.3, 165.2, 157.4, 149.8, 144.7, 142.2, 136.6, 132.8, 127.7, 127.6, 126.5, 125.6, 125.0, 124.9, 122.3, 117.4, 113.3, 63.0, 55.8, 14.0; **HRMS** (EI-MS) *m/z* calcd for $C_{23}H_{20}N_2O_5S$ $[M]^+$ 436.1093, found 436.1096.

Diethyl 2-(4-oxo-1-(pyridin-2-yl)-1,4-dihydroquinolin-2-yl)malonate (3x):



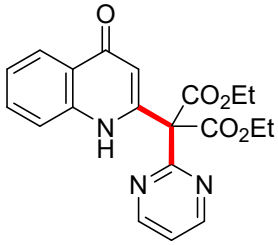
White solid (61.6 mg, yield: 81%); mp 137–139 °C; purification by silica gel chromatography (Acetone:DCM= 1:10, $\mathbf{R_f}$ = 0.21); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.71 (ddd, *J* = 4.9, 2.0, 0.8 Hz, 1H), 8.35 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.98 (td, *J* = 7.7, 2.0 Hz, 1H), 7.55 (ddd, *J* = 7.6, 4.9, 1.0 Hz, 1H), 7.43 – 7.23 (m, 3H), 6.55 – 6.46 (m, 1H), 6.43 (s, 1H), 4.24 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 4H), 1.16 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 178.0, 165.4, 151.2, 151.0, 144.8, 142.1, 139.8, 132.2, 126.2, 125.6, 125.5, 125.1, 124.1, 117.3, 111.8, 62.6, 55.8, 13.9; **HRMS** (EI-MS) *m/z* calcd for $C_{21}H_{20}N_2O_5$ $[M]^+$ 380.1372, found 380.1374.

tetraethyl 2,2'-(6-methoxy-4-oxo-1-(pyrimidin-2-yl)-1,4-dihydroquinoline-2,5-diyl)dimalonate (3y):



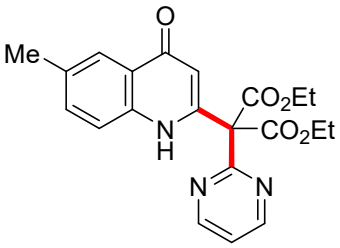
Sticky yellow solid (46.7 mg, yield: 82%); purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R_f}$ = 0.5); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.97, 8.96, 7.56, 7.55, 7.54, 7.13, 7.11, 6.97, 6.54, 6.52, 6.29, 4.21, 4.19, 4.19, 4.18, 4.17, 4.16, 4.16, 4.15, 4.14, 4.14, 4.13, 4.09, 3.76, 1.24, 1.22, 1.22, 1.21, 1.20, 1.19; ^{13}C NMR (126 MHz, $CDCl_3$) δ 180.0, 168.8, 165.2, 160.4, 158.4, 154.7, 142.5, 137.6, 124.2, 122.9, 121.9, 118.7, 117.8, 112.7, 62.8, 61.1, 57.0, 56.1, 49.9, 14.2, 14.0; **HRMS** (EI-MS) *m/z* calcd for $C_{28}H_{31}N_3O_{10}$ $[M]^+$ 569.2009, found 569.2013.

Characterization of products 4

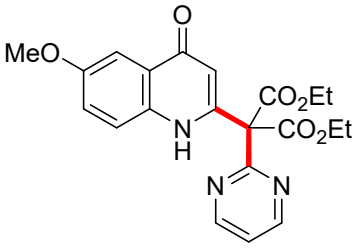


Diethyl 2-(4-oxo-1,4-dihydroquinolin-2-yl)-2-(pyrimidin-2-yl)malonate (4a):

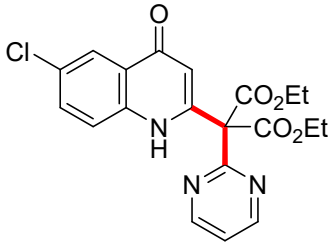
White solid (58.7 mg, yield: 77%); mp 175–177 °C; purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R_f}$ = 0.15); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 11.53 (s, 1H), 8.74 (d, *J* = 4.9 Hz, 2H), 8.32 – 8.24 (m, 1H), 7.54 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1H), 7.36 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.33 – 7.24 (m, 2H), 6.15 (d, *J* = 1.9 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 4H), 1.22 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 178.5, 167.1, 165.1, 157.2, 146.2, 139.3, 132.1, 125.9, 125.3, 123.9, 120.5, 118.2, 113.0, 69.7, 63.5, 13.7; **HRMS** (EI-MS) *m/z* calcd for $C_{20}H_{19}N_3O_5$ $[M]^+$ 381.1325, found 381.1327.



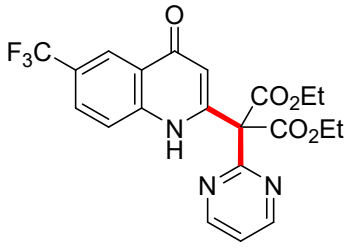
Diethyl 2-(6-methyl-4-oxo-1,4-dihydroquinolin-2-yl)-2-(pyrimidin-2-yl)malonate (4b): Slightly yellow solid (69.6 mg, yield: 88%); mp 185–187 °C; purification by silica gel chromatography (Acetone:DCM= 1:3, $\mathbf{R_f}$ = 0.25); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 11.43 (s, 1H), 8.78 (d, *J* = 4.9 Hz, 2H), 8.12 (d, *J* = 2.0 Hz, 1H), 7.41 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.38 – 7.27 (m, 2H), 6.14 (d, *J* = 1.9 Hz, 1H), 4.42 – 4.28 (m, 4H), 2.44 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 178.5, 167.3, 165.3, 157.3, 145.9, 137.4, 134.0, 133.7, 125.4, 125.3, 120.5, 118.1, 112.9, 69.7, 63.6, 21.2, 13.8; **HRMS** (EI-MS) *m/z* calcd for $C_{21}H_{21}N_3O_5$ $[M]^+$ 395.1481, found 395.1479.



Diethyl 2-(6-methoxy-4-oxo-1,4-dihydroquinolin-2-yl)-2-(pyrimidin-2-yl)malona te (4c): Slightly yellow solid (46.1 mg, yield: 56%); mp 183–185 °C; purification by silica gel chromatography (Acetone:DCM= 1:3 R_f = 0.25); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 11.55 (s, 1H), 8.78 (d, *J* = 4.9 Hz, 2H), 7.70 (d, *J* = 2.9 Hz, 1H), 7.37 – 7.29 (m, 2H), 7.22 (dd, *J* = 9.0, 2.9 Hz, 1H), 6.16 (d, *J* = 1.9 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 4H), 3.89 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 178.0, 167.3, 165.3, 157.3, 156.7, 145.3, 134.0, 126.5, 123.5, 120.5, 119.8, 112.1, 104.6, 69.6, 63.6, 55.9, 13.8; HRMS (EI-MS) *m/z* calcd for $C_{21}H_{21}N_3O_6$ $[M]^+$ 411.1430, found 411.1427.

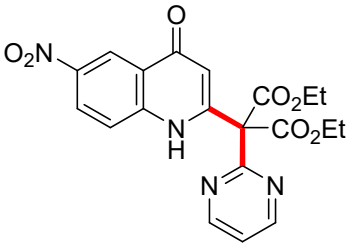


Diethyl 2-(6-chloro-4-oxo-1,4-dihydroquinolin-2-yl)-2-(pyrimidin-2-yl)malonate (4d): White solid (48.2 mg, yield: 58%); mp 185–187 °C; purification by silica gel chromatography (Acetone:DCM= 1:7 R_f = 0.5); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 11.60 (s, 1H), 8.78 (d, *J* = 4.9 Hz, 2H), 8.30 (d, *J* = 2.4 Hz, 1H), 7.53 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.39 – 7.31 (m, 2H), 6.17 (d, *J* = 1.7 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 4H), 1.26 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 177.4, 167.2, 165.1, 157.3, 146.6, 137.7, 132.6, 130.0, 126.4, 125.5, 120.6, 119.9, 113.3, 69.6, 63.7, 13.8; HRMS (EI-MS) *m/z* calcd for $C_{20}H_{18}ClN_3O_5$ $[M]^+$ 415.0935, found 415.0937.



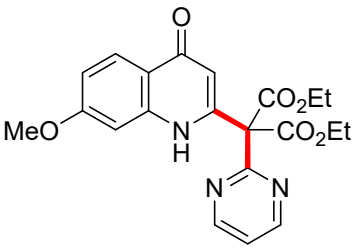
Diethyl 2-(4-oxo-6-(trifluoromethyl)-1,4-dihydroquinolin-2-yl)-2-(pyrimidin-2-yl)malonate (4e): White solid (69.2 mg, yield: 77%); mp 199–201 °C; purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R_f}$ = 0.38); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 11.80 (s, 1H), 8.75 (d, *J* = 4.9 Hz, 2H), 8.62 – 8.55 (m, 1H), 7.73 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.51 (d, *J* = 8.7 Hz, 1H), 7.32 (t, *J* = 4.9 Hz, 1H), 6.20 (d, *J* = 1.9 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 4H), 1.23 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 177.9, 166.9, 164.9, 157.3, 147.3, 141.1, 128.3 (q, *J* = 3.3 Hz), 127.6 (q, *J* = 270.8 Hz), 125.9 (q, *J* = 33.0 Hz), 124.7, 124.2 (q, *J* = 4.2 Hz), 122.2, 120.7, 119.3, 118.6, 114.0, 77.6, 77.2, 76.7, 69.7, 63.7, 13.7; **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -62.0; **HRMS** (EI-MS) *m/z* calcd for $C_{21}H_{18}F_3N_3O_5$ $[M]^+$ 449.1199, found 449.1195.

Diethyl 2-(6-nitro-4-oxo-1,4-dihydroquinolin-2-yl)-2-(pyrimidin-2-yl)malonate (4f):

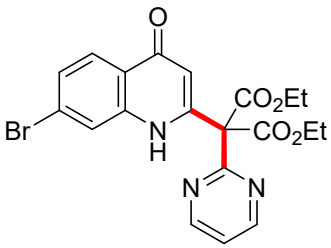


White solid (36.7 mg, yield: 43%); mp 207–209 °C; purification by silica gel chromatography (Acetone:DCM= 1:7, $\mathbf{R_f}$ = 0.63); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 11.92 (s, 1H), 9.16 (d, *J* = 2.6 Hz, 1H), 8.80 (d, *J* = 4.9 Hz, 2H), 8.37 (dd, *J* = 9.1, 2.6 Hz, 1H), 7.52 (d, *J* = 9.1 Hz, 1H), 7.38 (t, *J* = 4.9 Hz, 1H), 6.22 (d, *J* = 1.8 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 4H), 1.25 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 177.7, 166.8, 164.8, 157.4, 147.5, 143.8, 142.8, 126.4, 124.7, 123.2, 120.8, 119.6, 114.5, 69.6, 63.9, 13.8; **HRMS** (EI-MS) *m/z* calcd for $C_{20}H_{18}N_4O_7$ $[M]^+$ 426.1175, found 426.1174.

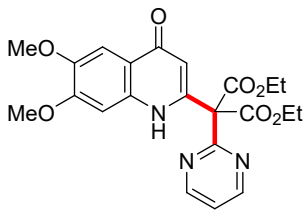
Diethyl 2-(7-methoxy-4-oxo-1,4-dihydroquinolin-2-yl)-2-(pyrimidin-2-yl)malon ate (4g): Slightly yellow solid (60.9



mg, yield: 74%); mp 179–181 °C; purification by silica gel chromatography (Acetone:DCM= 1:7, $\mathbf{R_f}$ = 0.26); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 11.61 (s, 1H), 8.72 (d, *J* = 4.9 Hz, 2H), 8.16 (d, *J* = 9.0 Hz, 1H), 7.31 – 7.23 (m, 1H), 6.93 – 6.83 (m, 1H), 6.79 (d, *J* = 2.3 Hz, 1H), 6.10 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 4H), 3.82 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 167.1, 165.0, 163.0, 157.2, 146.3, 141.3, 127.5, 120.5, 119.4, 114.6, 112.5, 99.2, 69.9, 63.5, 55.7, 13.8; **HRMS** (EI-MS) *m/z* calcd for $C_{21}H_{21}N_3O_6$ $[M]^+$ 411.1430, found 411.1428.



Diethyl 2-(7-bromo-4-oxo-1,4-dihydroquinolin-2-yl)-2-(pyrimidin-2-yl)malona te (4h): White solid (52.5 mg, yield: 57%); mp 201–203 °C; purification by silica gel chromatography (Acetone:DCM= 1:7, $\mathbf{R_f}$ = 0.25); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 11.51 (s, 1H), 8.80 (d, *J* = 4.9 Hz, 2H), 8.18 (d, *J* = 8.6 Hz, 1H), 7.58 (d, *J* = 1.7 Hz, 1H), 7.41 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.36 (t, *J* = 4.9 Hz, 1H), 6.17 (d, *J* = 1.9 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 4H), 1.26 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 178.1, 167.1, 165.1, 157.3, 146.6, 140.1, 127.9, 127.5, 126.7, 124.2, 120.8, 120.7, 113.7, 69.6, 63.7, 13.9; **HRMS** (EI-MS) *m/z* calcd for $C_{20}H_{18}BrN_3O_5$ $[M]^+$ 459.0430, found 459.0430.



Diethyl 2-(6,7-dimethoxy-4-oxo-1,4-dihydroquinolin-2-yl)-2-(pyrimidin-2-yl)malonate (4j): White solid (32.7 mg, yield: 37%); mp 207–209 °C; purification by silica gel chromatography (Acetone:DCM= 1:1, $\mathbf{R_f}$ = 0.20); **^{1}H NMR** (300 MHz,

Chloroform-*d*) δ 11.37 (s, 1H), 8.78 (d, *J* = 4.9 Hz, 2H), 7.67 (s, 1H), 7.33 (t, *J* = 4.9 Hz, 1H), 6.74 (s, 1H), 6.10 (d, *J* = 1.7 Hz, 1H), 4.35 (qd, *J* = 7.1, 1.0 Hz, 4H), 3.97 (s, 6H), 1.26 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 177.5, 167.5, 165.4, 157.3, 153.9, 147.6, 144.8, 135.1, 120.5, 119.7, 112.4, 105.0, 99.0, 69.6, 63.6, 56.4, 56.4, 13.9; **HRMS** (EI-MS) *m/z* calcd for $C_{22}H_{23}N_3O_7$ $[M]^+$ 441.1536, found 441.1536.

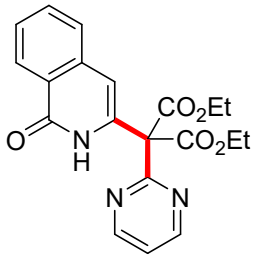
Diethyl 2-(6-(1,3-diethoxy-1,3-dioxopropan-2-yl)-4-oxo-1,4-dihydropyridin-2-yl)-2-(pyrimidin-2-yl)malonate (4k): White solid (73.4 mg, yield: 75%); mp 120–122 °C; purification by silica gel chromatography (Acetone:DCM= 1:3, $\mathbf{R}_f$ = 0.25); **^{1}H NMR** (300 MHz, DMSO-d_6) δ 10.7 (s, 1H), 8.8 (d, *J* = 4.9 Hz, 2H), 7.4 (t, *J* = 4.9 Hz, 1H), 7.0 (d, *J* = 2.1 Hz, 1H), 6.7 (d, *J* = 2.1 Hz, 1H), 4.8 (s, 1H), 4.1 (m, *J* = 16.4, 14.2, 8.4, 5.3 Hz, 8H), 1.1 (q, *J* = 7.0 Hz, 13H); **^{13}C NMR** (75 MHz, DMSO-d_6) δ 167.2, 167.0, 166.0, 164.1, 157.1, 156.6, 152.4, 120.2, 111.4, 110.4, 74.1, 61.4, 59.5, 40.4, 40.1, 39.8, 39.7, 39.5, 39.4, 39.2, 39.0, 38.7, 13.9, 13.7; **HRMS** (EI-MS) *m/z* calcd for $C_{23}H_{27}N_3O_9$ $[M]^+$ 489.1747 found 489.1747.

Diethyl 2-(6-oxo-1,6-dihydropyridin-2-yl)-2-(pyrimidin-2-yl)malonate (4l):

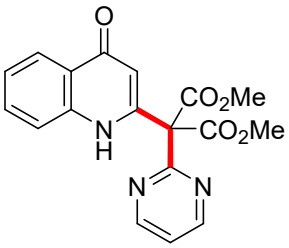
Slightly brown solid (25.8 mg, yield: 39%); mp 155–157 °C; purification by silica gel chromatography (Acetone:DCM= 1:1, $\mathbf{R}_f$ = 0.25); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 11.25 (s, 1H), 8.77 (d, *J* = 4.9 Hz, 2H), 7.41 – 7.30 (m, 2H), 6.50 (dd, *J* = 9.2, 0.9 Hz, 1H), 6.21 (dd, *J* = 7.1, 0.9 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 4H), 1.24 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 166.6, 164.8, 163.0,

157.3, 141.6, 140.5, 120.6, 120.5, 108.0, 69.6, 63.4, 13.8; **HRMS** (EI-MS) *m/z* calcd for $C_{16}H_{17}N_3O_5$ $[M]^+$ 331.1168, found 331.1171.

Diethyl 2-(1-oxo-1,2-dihydroisoquinolin-3-yl)-2-(pyrimidin-2-yl)malonate (4m):

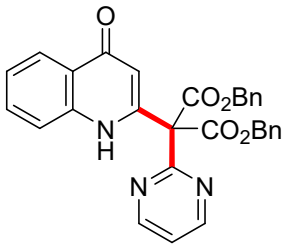


Slightly yellow solid (68.7 mg, yield: 90%); mp 157–159 °C; purification by silica gel chromatography (Acetone:DCM= 1:7, $\mathbf{R_f}$ = 0.50); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 10.61 (s, 1H), 8.79 (d, *J* = 5.0 Hz, 2H), 8.42 – 8.32 (m, 1H), 7.62 (ddd, *J* = 8.2, 7.0, 1.4 Hz, 1H), 7.54 – 7.43 (m, 2H), 7.33 (t, *J* = 4.9 Hz, 1H), 6.62 (d, *J* = 1.9 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 4H), 1.27 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 166.9, 165.2, 162.7, 157.3, 137.4, 134.8, 132.6, 127.4, 127.3, 127.0, 125.6, 120.5, 108.3, 70.0, 63.3, 13.9; **HRMS** (EI-MS) *m/z* calcd for $C_{20}H_{19}N_3O_5$ $[M]^+$ 381.1325, found 381.1328.



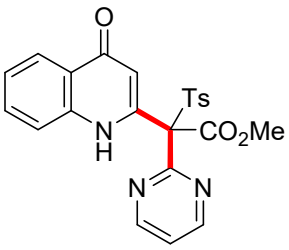
Dimethyl 2-(4-oxo-1,4-dihydroquinolin-2-yl)-2-(pyrimidin-2-yl)malonate (4n):

White solid (49.5 mg, yield: 70%); mp 207–209 °C; purification by silica gel chromatography (Acetone:DCM= 1:7, $\mathbf{R_f}$ = 0.25); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 11.45 (s, 1H), 8.80 (d, *J* = 5.0 Hz, 2H), 8.36 – 8.30 (m, 1H), 7.60 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1H), 7.42 – 7.30 (m, 3H), 6.14 (d, *J* = 2.0 Hz, 1H), 3.88 (s, 6H) ; **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 178.6, 167.6, 164.9, 157.3, 146.0, 139.4, 132.2, 125.9, 125.3, 124.0, 120.6, 118.3, 113.0, 69.9, 54.2; **HRMS** (EI-MS) *m/z* calcd for $C_{18}H_{15}N_3O_5$ $[M]^+$ 353.1012, found 353.1008.



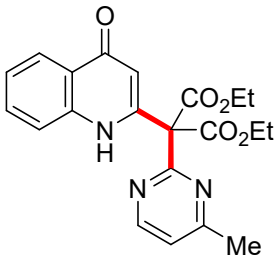
Dibenzyl 2-(4-oxo-1,4-dihydroquinolin-2-yl)-2-(pyrimidin-2-yl)malonate (4o):

Slightly yellow solid (68.8 mg, yield: 68%); mp 165–167 °C; purification by silica gel chromatography (Acetone:DCM= 1:7, $\mathbf{R_f}$ = 0.45); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 11.35 (s, 1H), 8.70 (d, *J* = 4.9 Hz, 2H), 8.31 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.62 – 7.54 (m, 1H), 7.38 – 7.28 (m, 4H), 7.26 – 7.13 (m, 9H), 6.23 (s, 1H), 5.32 – 5.20 (m, 4H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 178.5, 166.8, 164.8, 157.2, 146.0, 139.4, 134.4, 132.2, 128.5, 128.4, 128.3, 128.2, 125.9, 125.2, 124.0, 120.6, 118.3, 112.9, 70.0, 68.9; **HRMS** (EI-MS) *m/z* calcd for $C_{30}H_{23}N_3O_5$ $[M]^+$ 505.1638, found 505.1635.

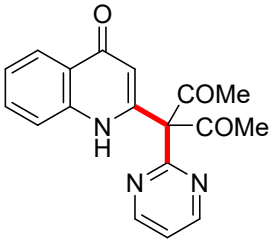


Methyl 2-(4-oxo-1,4-dihydroquinolin-2-yl)-2-(pyrimidin-2-yl)-2-tosylacetate (4p): Slightly yellow solid (53.9 mg, yield: 60%); mp 198–200 °C; purification by silica gel chromatography

(Acetone:DCM= 1:7, $\mathbf{R}_f$ = 0.38); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 12.38 (s, 1H), 8.93 (d, *J* = 5.0 Hz, 2H), 8.32 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.71 – 7.60 (m, 3H), 7.58 – 7.47 (m, 2H), 7.38 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.17 (d, *J* = 8.2 Hz, 2H), 5.68 (d, *J* = 1.8 Hz, 1H), 3.81 (s, 3H), 2.38 (s, 3H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 177.7, 165.4, 161.2, 157.1, 146.6, 141.8, 139.4, 132.5, 132.0, 131.5, 129.0, 125.9, 125.4, 124.3, 121.5, 118.6, 114.1, 84.0, 53.9, 21.8; **HRMS** (EI-MS) *m/z* calcd for $C_{23}H_{19}N_3O_5S$ $[M]^+$ 449.1045, found 449.1043.



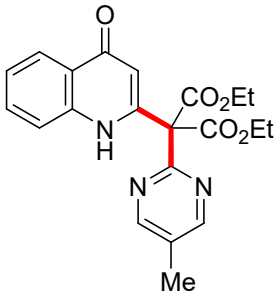
Diethyl 2-(4-methylpyrimidin-2-yl)-2-(4-oxo-1,4-dihydroquinolin-2-yl)malonate (4q): Slightly yellow solid (55.4 mg, yield: 70%); mp 161–163 °C; purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R}_f$ = 0.18); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 11.79 (s, 1H), 8.59 (d, *J* = 5.1 Hz, 1H), 8.29 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.55 (s, 1H), 7.38 – 7.24 (m, 2H), 7.16 (d, *J* = 5.2 Hz, 1H), 6.18 (d, *J* = 1.8 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 4H), 2.53 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 178.6, 167.8, 167.1, 164.5, 156.6, 146.3, 139.3, 132.1, 125.9, 125.3, 123.8, 120.1, 118.1, 113.0, 69.5, 63.4, 24.2, 13.8; **HRMS** (EI-MS) *m/z* calcd for $C_{21}H_{21}N_3O_5$ $[M]^+$ 395.1481, found 395.1478.



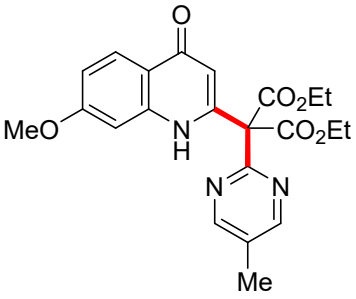
3-(4-oxo-1,4-dihydroquinolin-2-yl)-3-(pyrimidin-2-yl)pentane-2,4-dione (4r): Slightly yellow solid (37.9 mg, yield: 59%); mp 80–82 °C; purification by silica gel chromatography (MeOH: DCM = 1:30, $\mathbf{R}_f$ = 0.2); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.91 (d, *J* = 4.9 Hz, 2H), 8.49 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.55 – 7.44 (m, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 6.60 (d, *J* = 8.5 Hz, 1H), 6.38 (s, 1H), 2.12 (s, 6H); **^{13}C NMR** (75 MHz,

Chloroform-*d*) δ 192.0, 178.8, 159.9, 159.1, 147.5, 141.4, 132.5, 126.6, 125.6, 124.5, 121.6, 117.1, 114.5, 109.7, 24.4; **HRMS** (EI-MS) *m/z* calcd for $C_{18}H_{16}N_3O_3$ $[M+H]^+$ 322.1192, found 322.1190.

Diethyl 2-(5-methylpyrimidin-2-yl)-2-(4-oxo-1,4-dihydroquinolin-2-yl)malonate (4s):

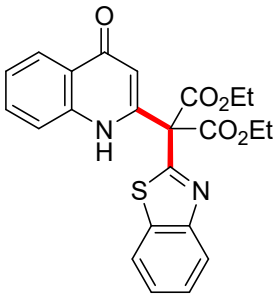


Slightly yellow solid (36.4 mg, yield: 46%); mp 75–78 °C; purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R}_f$ = 0.20); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 11.62 (s, 1H), 8.59 (d, *J* = 0.8 Hz, 2H), 8.30 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.57 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.30 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 6.17 (s, 1H), 4.39 – 4.27 (m, 4H), 2.39 – 2.29 (m, 3H), 1.24 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 178.5, 167.3, 162.4, 157.3, 146.5, 139.3, 132.1, 130.3, 125.9, 125.3, 124.0, 118.2, 112.9, 69.3, 63.5, 15.6, 13.8; **HRMS** (EI-MS) *m/z* calcd for $C_{21}H_{21}N_3O_5$ $[M]^+$ 395.1481, found 395.1482.



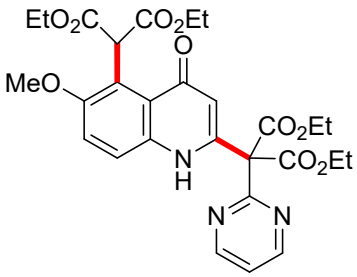
Diethyl 2-(7-methoxy-4-oxo-1,4-dihydroquinolin-2-yl)-2-(5-methylpyrimidin-2-yl)malonate (4t): White solid (59.6 mg, yield: 70%); mp 180–182 °C; purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R}_f$ = 0.25); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 11.37 (s, 1H), 8.58 (d, *J* = 0.8 Hz, 2H), 8.20 (d, *J* = 9.0 Hz, 1H), 6.89 (dd, *J* = 9.0, 2.3 Hz, 1H), 6.70 (d, *J* = 2.3 Hz, 1H), 6.06 (d, *J* = 1.9 Hz, 1H), 4.32 (qd, *J* = 7.1, 0.8 Hz, 4H), 3.85 (s, 3H), 2.33 (t, *J* = 0.7 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 178.1, 167.4, 162.9, 162.5, 157.3, 146.0,

141.1, 130.2, 127.7, 119.8, 114.1, 113.0, 99.1, 69.3, 63.5, 55.7, 15.6, 13.8; **HRMS** (EI-MS) *m/z* calcd for $C_{22}H_{23}N_3O_6$ $[M]^+$ 425.1587, found 425.1587.



Diethyl 2-(benzo[d]thiazol-2-yl)-2-(4-oxo-1,4-dihydroquinolin-2-yl)malonate (4u): Slightly orange solid (24.4 mg, yield: 28%); mp 272–274 °C; purification by silica gel chromatography (Acetone:DCM= 1:20, $\mathbf{R}_f$ = 0.25); **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 10.92 (s, 1H), 8.27 (dd, *J* = 8.2, 1.5 Hz, 1H), 8.04 – 7.96 (m, 1H), 7.89 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.58 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.51 – 7.36 (m, 3H), 7.36 – 7.25 (m, 1H), 6.19 (d, *J* = 1.8 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 4H), 1.30 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 178.2, 165.9, 164.2, 151.2, 145.1, 138.9, 135.2, 132.0, 126.1, 125.7, 125.6, 124.9, 123.9, 123.1, 121.3, 117.9, 109.6, 64.0, 63.6, 13.5; **HRMS** (EI-MS) *m/z* calcd for $C_{23}H_{20}N_2O_5S$ $[M]^+$ 436.1093, found 436.1095.

diethyl 2-(5-(1,3-diethoxy-1,3-dioxopropan-2-yl)-6-methoxy-4-oxo-1,4-dihydroquinolin-2-yl)-2-(pyrimidin-2-yl)malonate (4x):



Slightly yellow solid (46.7 mg, yield: 57%); mp 60–62 °C; purification by silica gel chromatography (Acetone:DCM= 1:5, $\mathbf{R}_f$ = 0.3); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 11.38, 8.77, 8.76, 7.39, 7.37, 7.33, 7.33, 7.32, 7.31, 7.21, 6.05, 6.05, 4.37, 4.36, 4.36, 4.35, 4.35, 4.34, 4.33, 4.33, 4.32, 4.32, 4.23, 4.23, 4.22, 4.21, 4.21, 4.20, 4.19, 4.18, 4.18, 4.17, 3.82, 1.28, 1.26, 1.26, 1.25, 1.24, 1.24, 1.23; ^{13}C NMR (126 MHz, Chloroform-*d*) δ 211.0, 180.2, 169.2, 167.2, 165.2, 157.3, 154.7, 144.7, 135.5, 123.7, 122.6,

120.5, 119.8, 118.8, 113.3, 69.6, 69.1, 63.6, 61.1, 57.4, 53.9, 49.8, 31.9, 29.8, 29.4, 14.3, 13.9; **HRMS** (EI-MS) *m/z* calcd for $C_{28}H_{31}N_3O_{10}$ $[M]^+$ 569.2009, found 569.2010.

7. Single crystal X-ray diffraction data

Single-crystal X-ray dirffraction data were collected using an Bruker SMART APEX2 ULTRA and a APEX II CCD area detector with a multilayer-monochromated Mo Kα radiation (λ = 0.71073 Å) generated by a rotating anode. Data collection, data reduction, and semiempirical absorption correction were carried out using the software package APEX2.* All of the calculations for the structure determination were carried out using the SHELXTL package.** All non-H atoms were refined anisotropically. All hydrogen atoms were included in calculated positions with isotropic thermal parameters 1.2 times those of attached atoms. The ellipsoids are drawn at the 50% probability level.

* APEX2 (Version 2009.1−0) Data Collection and Processing Software; Bruker AXS Inc.: Madison, Wisconsin, U.S.A., 2008.

** SHELXTL-PC (Version 6.22) Program for Solution and Refinement of Crystal Structures; Bruker AXS Inc.: Madison, Wisconsin, U.S.A., 2001.

X-ray crystallographic data of 4a (CCDC No. 2295767)

Single-crystal sample (**4a**) was prepared in DMSO. The ethyl group residue shows a disorder (Figure S5).

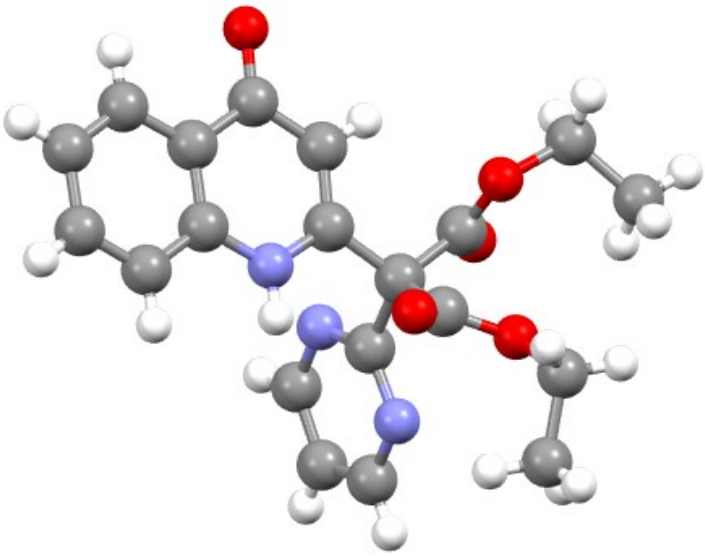


Figure S5. X-ray crystal structure of **4a**. The main residue disorder is 50%.

Table S3. Crystal data and structure refinement for **4a**.

Identification code	4a	
Empirical formula	C20 H19 N3 O5	
Formula weight	381.38	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.7958(3) Å	α= 84.9440(10)°.
	b = 13.0685(4) Å	β= 84.5000(10)°.
	c = 16.1565(5) Å	γ = 86.6780(10)°.
Volume	1839.12(10) Å^3	

Z	4
Density (calculated)	1.377 Mg/m^3
Absorption coefficient	0.101 mm^{-1}
F(000)	800
Crystal size	0.502 x 0.483 x 0.475 mm^3
Theta range for data collection	1.566 to 27.495°.
Index ranges	-11<=h<=11, -16<=k<=16, -20<=l<=20
Reflections collected	49692
Independent reflections	8390 [R(int) = 0.0307]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7455 and 0.7226
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8390 / 0 / 523
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0470, wR2 = 0.1236
R indices (all data)	R1 = 0.0510, wR2 = 0.1270
Extinction coefficient	n/a
Largest diff. peak and hole	0.571 and -0.360 $e.Å^{-3}$

8. Computational Details

All calculations were conducted using the Gaussian 09[1] software package in the framework of the density functional theory (DFT).[2] Geometry optimizations were performed using the B3LYP functional[3] with Grimme's D3 correction,[4] and the 6-31G(d,p) basis set.[5] Vibrational frequency calculations were carried out at the same level of theory as that used for geometry optimizations, wherein thermochemistry correction energy (G – E) was acquired. Transition states were located by the presence of one imaginary frequency and confirmed by intrinsic reaction coordinate (IRC) calculations.[6,7] The single-point calculations of the optimized geometries were performed with B3LYP functional with Grimme's D3 correction.[4] For all calculations, the solvation environment was considered with PCM[8] solvation model with DMSO (ε = 46.826) as the solvent. Finally, to increase the accuracy of the integration grid, we used the int = ultrafine option for all types of calculations. Figures of three-dimensional molecular structures were prepared using CYLview.[9]

Final solution phase Gibbs free energies were calculated as follows:

$$G_{sol} = E_{sol} + (G - E) \quad (1)$$

$$\Delta G(sol) = \Sigma G(sol) \text{ for products } - \Sigma G(sol) \text{ for reactants} \quad (2)$$

Table S3. Calculated electronic energies at the B3LYP/6-31G(d,p)/PCM level of theory.

Structure	Electronic energies (Hatree/Particle)	Total Gibbs free energies (Hatree/Particle)
3a_I	-1235.713230	-1235.455069
3a_II	-1235.715730	-1235.458292
3a_III	-1235.726713	-1235.469812
3a_IV	-1235.714441	-1235.457292
Indole_I	-1122.364858	-1122.115135
Indole_II	-1122.340011	-1122.087335
Indole_III	-1122.352327	-1122.102334
Indole_IV	-1122.342953	-1122.092905
Int A	-1235.079911	-1234.837614
TS1	-1235.04095	-1234.801510
Int B	-1235.041865	-1234.800026
TS2	-1235.033091	-1234.792529
Int C	-1235.084848	-1234.842534

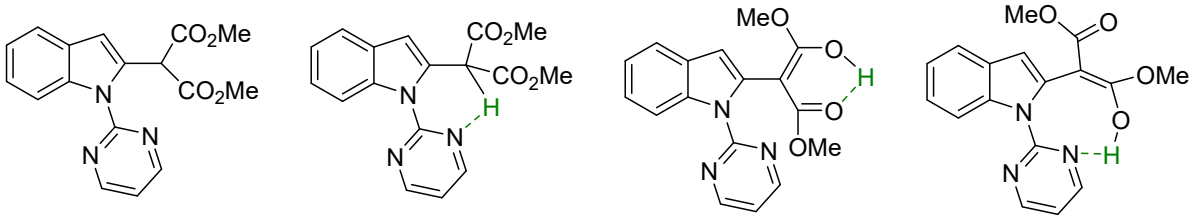


Figure S6. Calculated relative Gibbs free energies for tautomers of alkylated indole

Cartesian coordinates of the optimized structures

3a_I

Charge=0, Multiplicity=1

C	-4.13363011	3.88516363	1.56432415
C	-3.53103912	2.73970614	1.02026871
C	-4.29780479	1.70895427	0.49988553
C	-5.70326268	1.80448670	0.51564398
C	-6.31579942	2.95212551	1.06127135
C	-5.51434904	3.98117803	1.58079397
N	-6.49668162	0.77244773	-0.00849801
C	-7.87484016	0.85479266	0.02907863
C	-8.50199563	1.94843707	0.54432637
C	-7.78886997	3.09062221	1.08774343
O	-8.35830914	4.09075632	1.53295668
C	-5.83558641	-0.29094708	-0.71512404
N	-5.63672287	-0.06540282	-2.01536937
C	-5.07734626	-1.07184670	-2.69934034
C	-4.71501104	-2.26781160	-2.08613775
C	-4.93001344	-2.35553794	-0.71183610
N	-5.48428987	-1.35947693	-0.01030120
C	-8.72631016	-0.31709733	-0.44535827
H	-9.72743118	0.10108198	-0.59057291
C	-8.36603253	-0.99610371	-1.78472257
O	-8.06568804	-2.16771325	-1.84726177
O	-8.49390578	-0.29135040	-2.92125314
C	-8.59034405	1.14462011	-2.94283760

C	-8.81929237	-1.38173524	0.67652434
O	-8.03697816	-1.42033005	1.58882600
O	-9.86483232	-2.23794751	0.66256762
C	-10.80766176	-2.33960034	-0.41054044
H	-3.52028077	4.68399073	1.96878243
H	-2.44885400	2.65053258	1.00652057
H	-3.81244258	0.82916964	0.09600857
H	-6.02918924	4.84421773	1.98975474
H	-9.58477224	1.98601195	0.57758337
H	-4.92747847	-0.90884203	-3.76343538
H	-4.28045729	-3.08634797	-2.64799873
H	-4.65357746	-3.24401046	-0.14962565
H	-8.80945920	1.39824978	-3.98006940
H	-9.39339952	1.51572687	-2.30113235
H	-7.63582789	1.58273090	-2.64417268
H	-11.59986926	-2.98896095	-0.03687858
H	-11.24950703	-1.37045567	-0.66959590
H	-10.34657782	-2.78888339	-1.29199963

3a_II

Charge=0, Multiplicity=1

C	-4.14757074	4.05685705	1.23063735
C	-3.47832425	2.85768959	0.94014523
C	-4.17964453	1.72245083	0.56576351
C	-5.58377837	1.76285131	0.46228981
C	-6.26137110	2.95588388	0.77984257
C	-5.52855608	4.09368698	1.15541196
N	-6.31415336	0.60496324	0.11184647

C	-7.71027730	0.61560793	0.18679900
C	-8.39160047	1.75003573	0.48765204
C	-7.73929479	3.02231493	0.75801407
O	-8.36374543	4.05787239	0.99260205
C	-5.63874036	-0.43274870	-0.60644306
N	-4.96871139	-0.05114307	-1.69533804
C	-4.38280831	-1.02272643	-2.39590880
C	-4.46813518	-2.36685659	-2.02685237
C	-5.17283615	-2.63978715	-0.86098433
N	-5.74886850	-1.67509671	-0.12777782
C	-8.44096879	-0.70136721	-0.03321446
H	-7.87550819	-1.48087963	0.48257061
C	-9.86168784	-0.65471177	0.54201832
O	-10.83992522	-0.54890418	-0.15891816
O	-10.01254892	-0.76836281	1.87798169
C	-8.89523735	-0.88290928	2.77281981
C	-8.46683064	-1.07818848	-1.52835498
O	-8.07110475	-0.33110777	-2.38733324
O	-8.84350689	-2.33072124	-1.86549279
C	-9.43284746	-3.25297082	-0.94035386
H	-3.58644272	4.93941187	1.52065449
H	-2.39610824	2.80775359	1.01493754
H	-3.64058212	0.80700525	0.35717697
H	-6.09693541	4.98857348	1.38593702
H	-9.47394654	1.74048879	0.52492514
H	-3.83871760	-0.71402521	-3.28554457
H	-4.00636630	-3.15205857	-2.61354815

H	-5.27687163	-3.65493320	-0.48521080
H	-9.33089443	-0.92698350	3.77083581
H	-8.32492282	-1.79981875	2.58967662
H	-8.23668405	-0.01444427	2.69826570
H	-9.43451273	-4.21574612	-1.45239108
H	-8.84635677	-3.34736629	-0.01933570
H	-10.45679650	-2.95878897	-0.70230124

3a_III

Charge=0, Multiplicity=1

C	-9.26218357	2.30599645	0.44477972
C	-9.18858030	0.94998460	0.09107617
C	-7.96546525	0.32548704	-0.09767280
C	-6.76941005	1.05536544	0.05924829
C	-6.83666673	2.41635153	0.43113215
C	-8.09024303	3.02226524	0.61337185
N	-5.51076778	0.45266802	-0.10196091
C	-4.33723401	1.18610468	0.07951169
C	-4.37316152	2.49704961	0.43547971
C	-5.61088987	3.22119570	0.65389481
O	-5.65241790	4.41081775	0.98233618
C	-5.40849317	-0.94036618	-0.39689254
N	-5.85759966	-1.33577070	-1.59075630
C	-5.72071960	-2.63948110	-1.86476070
C	-5.12545755	-3.53140952	-0.97593255
C	-4.70992417	-3.00026743	0.24433902

N	-4.85979179	-1.70756045	0.55039364
C	-3.06058919	0.47965491	-0.17846405
C	-2.18394796	0.05572783	0.88331917
C	-2.69480437	0.10963787	-1.46260549
O	-1.61074291	-0.57899964	-1.74233006
O	-1.13569052	-0.60163389	0.69527667
O	-3.47881320	0.44376544	-2.48008438
C	-3.17844970	-0.10423077	-3.77472125
O	-2.57421762	0.40793301	2.11171779
C	-1.74032267	-0.04205620	3.19200227
H	-10.22692359	2.78231084	0.58844923
H	-10.09922328	0.37204993	-0.03763776
H	-7.93873778	-0.71906681	-0.37727537
H	-8.08826364	4.06951827	0.89717807
H	-3.44234464	3.03945909	0.54284035
H	-6.09442373	-2.96925158	-2.83190802
H	-5.00195812	-4.58135053	-1.21494111
H	-4.25037069	-3.62566975	1.00649166
H	-3.95398683	0.28557863	-4.43208591
H	-2.18987435	0.21446088	-4.11272036
H	-3.21857723	-1.19649391	-3.74636760
H	-2.21060938	0.34091278	4.09693985
H	-1.69602151	-1.13399578	3.21381044
H	-0.72621103	0.35171031	3.08787486
H	-1.17230431	-0.74130125	-0.82634697

3a_IV

Charge=0, Multiplicity=1

C	-9.53624288	1.86131059	0.80542718
C	-9.35155367	0.51576627	0.45659014
C	-8.08240496	-0.00272814	0.24456412
C	-6.95143962	0.82715811	0.37589055
C	-7.13083271	2.18133971	0.73352789
C	-8.42751610	2.67849376	0.93971222
N	-5.63748954	0.33965639	0.19630878
C	-4.53363591	1.20102948	0.26388893
C	-4.68723715	2.50529296	0.60851114
C	-5.97808755	3.09733367	0.91381093
O	-6.11670256	4.27193666	1.26391946
C	-5.37758096	-1.05239766	0.19760380
N	-5.89000282	-1.79712330	-0.78130522
C	-5.61471301	-3.10619862	-0.73734765
C	-4.81943578	-3.67459661	0.25549819
C	-4.33597999	-2.80547230	1.22922809
N	-4.62747478	-1.50062958	1.21909505
C	-3.20448396	0.67794466	-0.16530993
C	-2.26757797	0.35884949	0.78779429
O	-2.58310751	0.12393636	2.06678465
H	-3.48667630	-0.27990312	2.06846287
C	-2.91155922	0.58640210	-1.60111628
O	-1.87963474	0.20808821	-2.12375906
O	-4.01068015	0.94914905	-2.32592271
C	-3.85967170	0.84406647	-3.74565461
O	-0.97691510	0.25667624	0.49992756

C	-0.10379347	-0.34011386	1.47234743
H	-10.53532450	2.25367713	0.96662109
H	-10.21084518	-0.13870329	0.34222637
H	-7.97113385	-1.03629861	-0.05055561
H	-8.51038082	3.72516205	1.21320458
H	-3.82105202	3.15498986	0.60881858
H	-6.03854822	-3.71153737	-1.53529456
H	-4.58992551	-4.73323956	0.27011594
H	-3.70633478	-3.15249207	2.04470440
H	-4.81214529	1.16608247	-4.16733155
H	-3.04703850	1.48451139	-4.09985496
H	-3.64038909	-0.18677620	-4.03925000
H	0.86395138	-0.40724152	0.97649296
H	-0.02977869	0.28250644	2.36725867
H	-0.45293912	-1.33680726	1.75636641

Indole_I

Charge=0, Multiplicity=1

C	-6.36131062	5.01746576	-0.60794264
C	-5.27595690	4.22993430	-1.02813850
C	-5.30146310	2.83931820	-0.94822981
C	-6.45448535	2.23933565	-0.42958150
C	-7.55234409	3.02356434	0.00206458
C	-7.50386505	4.42060000	-0.09103070
N	-6.78504793	0.88329387	-0.19398283
C	-8.08345379	0.84610175	0.36402738
C	-8.55365079	2.11850565	0.48222075

C	-5.93034359	-0.20396263	-0.37140634
N	-6.24503683	-1.33951020	0.26795702
C	-5.39117447	-2.35488185	0.14462531
C	-4.22747343	-2.27005292	-0.61517199
C	-4.01385514	-1.05117368	-1.25436831
N	-4.85119800	-0.01903226	-1.14353590
C	-8.90879101	-0.37525382	0.65994859
H	-9.81713371	0.03668322	1.11018123
C	-9.31748063	-1.07850542	-0.63915323
O	-8.61027853	-1.14035408	-1.61517495
O	-10.55326869	-1.64420485	-0.69651458
C	-11.47279761	-1.59085296	0.40350926
C	-8.34850147	-1.21591416	1.84513394
O	-7.94567365	-0.63407369	2.81837364
O	-8.51295928	-2.56178821	1.91234932
C	-8.57667455	-3.45726633	0.78997292
H	-6.30406444	6.09873202	-0.68969788
H	-4.39179331	4.71306865	-1.43331403
H	-4.47093881	2.24097195	-1.28881083
H	-8.34766236	5.01832800	0.24075516
H	-9.53007770	2.38374245	0.86367363
H	-5.65266979	-3.26463425	0.68058007
H	-3.53620516	-3.09893838	-0.70537826
H	-3.14059193	-0.89083850	-1.88361278
H	-12.31019811	-2.22539414	0.11153347
H	-11.03202434	-1.97995736	1.32665929
H	-11.84079001	-0.57233421	0.56660238

H	-8.12380392	-4.38875010	1.13575529
H	-9.61145209	-3.65202054	0.50069810
H	-8.02233080	-3.07795111	-0.06627624

Indole_II

Charge=0, Multiplicity=1

C	-9.29257803	1.89609206	-0.71866238
C	-9.47376837	0.52585850	-0.46602163
C	-8.39561666	-0.35294468	-0.37842125
C	-7.11270808	0.17673423	-0.55004357
C	-6.91551218	1.55684297	-0.79882456
C	-8.01611641	2.41915743	-0.88614195
N	-5.83415821	-0.42574703	-0.49548248
C	-4.86431079	0.58633787	-0.72805028
C	-5.50214161	1.77485582	-0.91012518
C	-5.56874164	-1.75402911	-0.15803655
N	-6.57230613	-2.63761225	-0.26896155
C	-6.28686464	-3.89794383	0.06545672
C	-5.02142167	-4.30615190	0.48393953
C	-4.05557046	-3.30441389	0.55437690
N	-4.32395850	-2.03471231	0.25327916
C	-3.38884013	0.31051992	-0.84097853
H	-3.21229743	-0.59064151	-1.42755338
C	-2.69099977	1.42669934	-1.62387323
O	-2.37239637	1.35132028	-2.78646108
O	-2.47312752	2.50987531	-0.84768649
C	-1.80015607	3.60313281	-1.50087315

C	-2.65727381	0.08327110	0.48729950
O	-1.57109126	-0.44639093	0.56045252
O	-3.33212535	0.58512855	1.53366851
C	-2.70063979	0.39267755	2.80863280
H	-10.15801493	2.54870467	-0.78451962
H	-10.47898003	0.13429923	-0.34129633
H	-8.54097049	-1.40777094	-0.20180104
H	-7.86525448	3.47723185	-1.07868028
H	-5.01081652	2.71536467	-1.10707123
H	-7.10709970	-4.60854461	-0.01605965
H	-4.80427717	-5.33618179	0.73930190
H	-3.03434473	-3.50976936	0.86872406
H	-1.69867326	4.37947819	-0.74332943
H	-0.81974396	3.28435033	-1.86292962
H	-2.38940421	3.96322499	-2.34811352
H	-3.35850576	0.86507961	3.53772756
H	-2.59387161	-0.67460311	3.02195431
H	-1.71073624	0.85582041	2.82278406

Indole_III

Charge=0, Multiplicity=1

C	-4.51901590	4.10899327	-1.94005935
C	-3.46318538	3.27775642	-1.52645831
C	-3.69826233	2.04322531	-0.92461372
C	-5.02799938	1.65076378	-0.74686722
C	-6.10394463	2.47456586	-1.16527330
C	-5.83989836	3.71492639	-1.76343933

N	-5.58431776	0.46856394	-0.22232195
C	-6.99941345	0.58129617	-0.27654181
C	-7.31668654	1.78370969	-0.84146264
C	-4.86142330	-0.64884550	0.20346078
N	-5.44188521	-1.84956229	0.04631637
C	-4.76285683	-2.89891037	0.50971652
C	-3.49851927	-2.78601807	1.08715471
C	-2.97445358	-1.49657372	1.14575558
N	-3.64566246	-0.42265940	0.72431226
C	-7.92425796	-0.42162457	0.26095153
C	-8.95108915	-0.94911158	-0.50956314
C	-7.81118151	-0.95174556	1.59586690
O	-9.79597842	-1.85769471	-0.06933608
O	-8.54747455	-1.84290568	2.07269311
H	-9.47997382	-2.06412774	0.88409137
O	-9.12919418	-0.53826811	-1.76192137
C	-10.17523637	-1.16143556	-2.52675916
O	-6.82362209	-0.41090526	2.32949291
C	-6.61365498	-0.98598557	3.62756362
H	-4.29756309	5.06748893	-2.40036325
H	-2.43764476	3.60493383	-1.67057831
H	-2.88479716	1.41735676	-0.58672306
H	-6.66020464	4.35049921	-2.08434117
H	-8.32540326	2.14255224	-0.98410689
H	-5.24580521	-3.86806849	0.39665958
H	-2.95150356	-3.64768209	1.45098952
H	-1.98346307	-1.30969252	1.55567979

H	-10.12795618	-0.68860626	-3.50713756
H	-10.00529580	-2.23754757	-2.61439998
H	-11.15121617	-0.98848733	-2.06626991
H	-5.78406455	-0.42640881	4.05883195
H	-7.50906983	-0.88916947	4.24619201
H	-6.35654305	-2.04519559	3.53940893

Indole_IV

Charge=0, Multiplicity=1

C	-9.39936668	2.15772953	-1.01813720
C	-9.60392581	0.92324351	-0.37696673
C	-8.53531385	0.11317748	0.00227122
C	-7.24739998	0.57628682	-0.27430204
C	-7.02145458	1.81129786	-0.92956780
C	-8.11425968	2.60771413	-1.29890567
N	-5.98718183	-0.01511229	-0.05821613
C	-4.97738041	0.87101123	-0.54452594
C	-5.60078496	1.96276907	-1.07245616
C	-5.78252644	-1.32435652	0.34078719
N	-6.60349457	-1.84060051	1.26739022
C	-6.36731160	-3.09970802	1.63614085
C	-5.30889354	-3.85623109	1.12887060
C	-4.53349140	-3.23846037	0.15519828
N	-4.77798623	-1.99186909	-0.26137174
C	-3.52790925	0.74638923	-0.26744789
C	-2.71049008	0.06765740	-1.14504746
C	-2.96742642	1.45552056	0.89223321

O	-3.17554046	-0.81243640	-2.03021803
O	-1.79584158	1.53986176	1.21471519
H	-3.93224601	-1.28099744	-1.56428062
O	-1.39389431	0.25103140	-1.16387809
C	-0.59400445	-0.66288387	-1.92779503
O	-3.96570933	2.00941327	1.64760554
C	-3.51618827	2.69304804	2.82077568
H	-10.25628563	2.76498065	-1.29420963
H	-10.61616209	0.59432436	-0.16146088
H	-8.69267206	-0.82463235	0.51744458
H	-7.95224773	3.55818429	-1.79862602
H	-5.08039297	2.82678986	-1.46013483
H	-7.04709565	-3.51512086	2.37733367
H	-5.11605036	-4.86972359	1.45811541
H	-3.70579060	-3.75005927	-0.33003595
H	0.43671059	-0.37890079	-1.71657899
H	-0.77109662	-1.69715026	-1.61917017
H	-0.80116695	-0.57018259	-2.99703877
H	-4.41689453	3.07660540	3.30187896
H	-2.98423690	2.01283889	3.49299650
H	-2.84151092	3.51465090	2.56241462

Int A

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C	-1.30323619	2.73784896	-1.11699979
C	-2.18889512	1.67139113	-1.05365675

C	-3.30820015	1.72820954	-0.19905878
C	-3.49753592	2.88740742	0.58908443
C	-2.58772822	3.95322781	0.49945646
N	-4.22488454	0.65131706	-0.07126554
C	-5.35305000	0.78783057	0.75460914
C	-5.54624520	1.88785542	1.53736859
C	-4.62729230	3.01282186	1.53577759
O	-4.79006746	4.00079172	2.25532145
C	-3.95900039	-0.65005884	-0.57686644
N	-3.50714035	-0.78279348	-1.82571550
C	-3.34482292	-2.03716649	-2.26183130
C	-3.66576677	-3.15167036	-1.49044183
C	-4.12447816	-2.89072558	-0.20019401
N	-4.24440841	-1.64785865	0.26888646
C	-6.38926801	-0.24978707	0.69689158
C	-7.03209454	-0.68769066	-0.55215492
O	-7.95642638	-1.47925031	-0.61553000
C	-6.91129671	-0.81455002	1.97491154
O	-7.25290951	-0.14600180	2.93018720
O	-6.93872804	-2.15589278	1.94803340
C	-7.48747918	-2.77540664	3.12672246
O	-6.49837875	-0.07684897	-1.63711780
C	-7.05966975	-0.46575191	-2.89976963
H	-0.79416359	4.71826579	-0.40706569
H	-0.45287614	2.66866825	-1.78924944
H	-2.03489618	0.81122684	-1.68558529
H	-2.78412765	4.81543343	1.12783795

H	-6.43001614	1.94824069	2.15709659
H	-2.96263620	-2.14383756	-3.27472252
H	-3.55854907	-4.16119608	-1.86881771
H	-4.39691785	-3.68892208	0.48574592
H	-7.44993781	-3.84733607	2.93584936
H	-6.89438870	-2.51654004	4.00755727
H	-8.51811871	-2.44823423	3.28404618
H	-6.49654631	0.08824388	-3.64981639
H	-6.95018700	-1.54306535	-3.05204535
H	-8.12166345	-0.21105749	-2.94370491

TS1

Charge=0, Multiplicity=2

C	-2.23174323	3.72800360	0.34255917
C	-2.80186707	2.60187986	0.95638706
C	-2.13397895	1.38889859	0.96622454
C	-0.87840439	1.29934142	0.34987318
C	-0.28751431	2.41878578	-0.28005845
C	-0.99075395	3.63178184	-0.26554256
C	1.05469833	0.01234456	-0.30248467
C	1.68307594	1.02000517	-0.94250579
C	1.04249170	2.33241932	-0.96171710
O	1.54813427	3.31200078	-1.50765706
C	1.25972854	-1.45107690	-0.02194846
C	-0.46099729	-1.25040814	0.64367629
N	-0.46822507	-1.56030437	2.00779402
C	-1.03256526	-2.70055344	2.33005584
C	-1.71515733	-3.50527717	1.39515785

C	-1.88480300	-2.97091011	0.10181712
N	-1.34070354	-1.83769832	-0.27067441
C	1.34544231	-2.44336039	-1.15926249
O	0.88956025	-3.55536665	-1.12828781
O	2.01935464	-1.91320654	-2.18876127
C	2.18156544	-2.76800627	-3.34267876
C	2.15926617	-1.83449131	1.13649168
O	2.38388138	-2.97214946	1.46482950
O	2.63514037	-0.74838313	1.75225860
C	3.41354150	-0.99067160	2.94214912
H	-2.76515442	4.67126540	0.34479905
H	-3.77381642	2.67903422	1.43050354
H	-2.56302209	0.51674099	1.44474176
H	-0.52761912	4.48315680	-0.74978029
H	2.63307855	0.88525284	-1.43775718
H	-0.98477439	-2.99081889	3.37635426
H	-2.15541509	-4.45179378	1.67903973
H	-2.51388508	-3.47499632	-0.62667583
H	1.20489322	-3.03676662	-3.74723252
H	2.74796369	-2.17828492	-4.05905922
H	2.72281021	-3.67405498	-3.06699515
H	3.72222691	-0.00721978	3.28765063
H	2.79783674	-1.48996146	3.69179848
H	4.27947256	-1.61179458	2.70926246
N	-0.14436184	0.13284248	0.32775580

Int B

Charge=0, Multiplicity=2

C	-9.54828584	1.57180315	-1.94534451
C	-9.70932242	0.43901746	-1.12975059
C	-8.61782417	-0.14141058	-0.49983606
C	-7.34875833	0.42649352	-0.68380893
C	-7.16308125	1.57251989	-1.49406308
C	-8.28846309	2.12652193	-2.12209093
N	-6.20620358	-0.09734753	-0.11797507
C	-4.97857145	0.49429077	-0.21144161
C	-4.71060144	1.59637391	-0.94288493
C	-5.81873317	2.21235474	-1.67792035
O	-5.67654293	3.20816717	-2.39093811
C	-5.90858535	-0.98301525	1.01539384
N	-6.05356352	-2.37432305	0.70122277
C	-6.31721068	-3.16633633	1.70535522
C	-6.59027837	-2.69612960	3.01762677
C	-6.69764483	-1.29167651	3.18533589
N	-6.43116900	-0.43853100	2.23393467
C	-4.34464892	-0.46560130	0.77362059
C	-3.63144185	0.08511163	1.99921056
O	-3.71423848	-0.36689302	3.11461257
O	-2.84629688	1.11257092	1.63567397
C	-2.06002552	1.69007434	2.69856343
C	-3.49573651	-1.59788146	0.18423217
O	-2.86175272	-2.37247321	0.86366187
O	-3.57240679	-1.62258173	-1.14941163
C	-2.89398957	-2.72521154	-1.78178104

H	-10.41158973	2.01163874	-2.43484373
H	-10.69654665	0.00816938	-0.99087199
H	-8.72718341	-1.02208543	0.12471177
H	-8.12914703	3.00281265	-2.74181915
H	-3.72595501	2.04094958	-0.98663616
H	-6.36175428	-4.23356295	1.49010088
H	-6.78840640	-3.38142079	3.83313696
H	-7.04545716	-0.87928886	4.13154354
H	-1.48776820	2.49212132	2.23472494
H	-2.71396973	2.08271231	3.48072015
H	-1.39723955	0.93663563	3.13082738
H	-3.03821086	-2.57957335	-2.85125842
H	-1.83177162	-2.71724845	-1.52638292
H	-3.33503958	-3.67024778	-1.45544984

TS2

Charge=0, Multiplicity=2

C	-2.44644668	3.22743807	0.37661747
C	-2.71560111	2.12553871	1.20323143
C	-1.83787016	1.05651021	1.25610787
C	-0.68670264	1.07317596	0.44911020
C	-0.41354350	2.17067510	-0.40443826
C	-1.30203463	3.24983697	-0.40993233
C	1.26519501	-0.01687187	-0.39447963
C	1.62722136	0.97944874	-1.23272667
C	0.80621991	2.18667720	-1.26917247
O	1.06920280	3.14817793	-1.98900685

C	1.56451548	-1.48340061	-0.18682727
C	0.14151497	-1.66631883	0.48661273
N	0.13039590	-2.20121467	1.77488100
C	-1.00465278	-2.71840975	2.17425878
C	-2.14900709	-2.79911937	1.35096087
C	-1.98865533	-2.40498006	0.01295397
N	-0.86670064	-1.90027006	-0.45040929
C	1.79061161	-2.36240420	-1.41204700
O	1.30421575	-3.44505990	-1.58144213
O	2.65833581	-1.76403827	-2.24400749
C	3.03036904	-2.52536148	-3.41368045
C	2.69231009	-1.78181365	0.82019744
O	3.28876491	-2.82551247	0.85758200
O	2.90806086	-0.74315401	1.62958044
C	3.86462971	-0.96175790	2.68737038
H	-3.13274914	4.06592480	0.35735489
H	-3.61065711	2.11583930	1.81462915
H	-2.02093259	0.20674280	1.90209254
H	-1.06852097	4.09456573	-1.04703830
H	2.46970925	0.89061472	-1.90283491
H	-1.02809506	-3.11918676	3.18525183
H	-3.07939903	-3.21489449	1.71414661
H	-2.79475661	-2.53486625	-0.70454171
H	2.14741838	-2.74335496	-4.01582623
H	3.72535443	-1.89319438	-3.96115405
H	3.50670873	-3.45987739	-3.11438264
H	3.90869495	-0.02261809	3.23352121

H	3.52279964	-1.77187146	3.33296415
H	4.83992320	-1.21517407	2.26966473
N	0.23501786	0.05598162	0.50221968

Int C

Charge=0, Multiplicity=2

C	-0.95994759	3.84628898	-0.50517995
C	-0.74899594	2.82267484	-1.44598734
C	-1.56863027	1.70538013	-1.46004692
C	-2.62383341	1.58706968	-0.52590772
C	-2.83048004	2.62851854	0.42017091
C	-1.99514906	3.74825728	0.42064860
N	-3.40352985	0.46172900	-0.58045324
C	-4.40325134	0.32194532	0.29030523
C	-4.72179180	1.27494995	1.26195020
C	-3.94122531	2.48935928	1.37821170
O	-4.20596589	3.35939279	2.22980733
C	-6.64468953	-0.49325154	-0.42892158
N	-7.72925767	-0.96215132	0.19395820
C	-8.91170646	-0.57346869	-0.30114536
C	-9.01345031	0.26743856	-1.40452993
C	-7.81141895	0.70955569	-1.95827980
N	-6.62358822	0.34234586	-1.47296228
C	-5.27503579	-0.92910275	0.10982166
C	-4.60304284	-1.87671479	-0.91218423
O	-5.02407719	-2.13262392	-2.01292097
O	-3.48254870	-2.39383260	-0.37913801

C	-2.72312750	-3.23538680	-1.26121109
C	-5.48701021	-1.69227095	1.43689465
O	-5.39068344	-1.21517304	2.54380452
O	-5.82108949	-2.96695176	1.19082191
C	-6.16792428	-3.74487741	2.34970073
H	-0.31239446	4.71786577	-0.50247786
H	0.05996752	2.90974169	-2.16490830
H	-1.43048886	0.90171033	-2.17549405
H	-2.17943441	4.52574817	1.15486242
H	-5.54661129	1.13263950	1.94710091
H	-9.79635535	-0.94904736	0.20870395
H	-9.97372112	0.57419172	-1.80334863
H	-7.79822667	1.38441545	-2.81176992
H	-1.86545442	-3.57295190	-0.67998093
H	-3.32425800	-4.08540481	-1.59396902
H	-2.39639260	-2.66565502	-2.13506755
H	-6.39981435	-4.74091937	1.97432323
H	-5.33207548	-3.77972517	3.05255033
H	-7.03700281	-3.30670959	2.84664795

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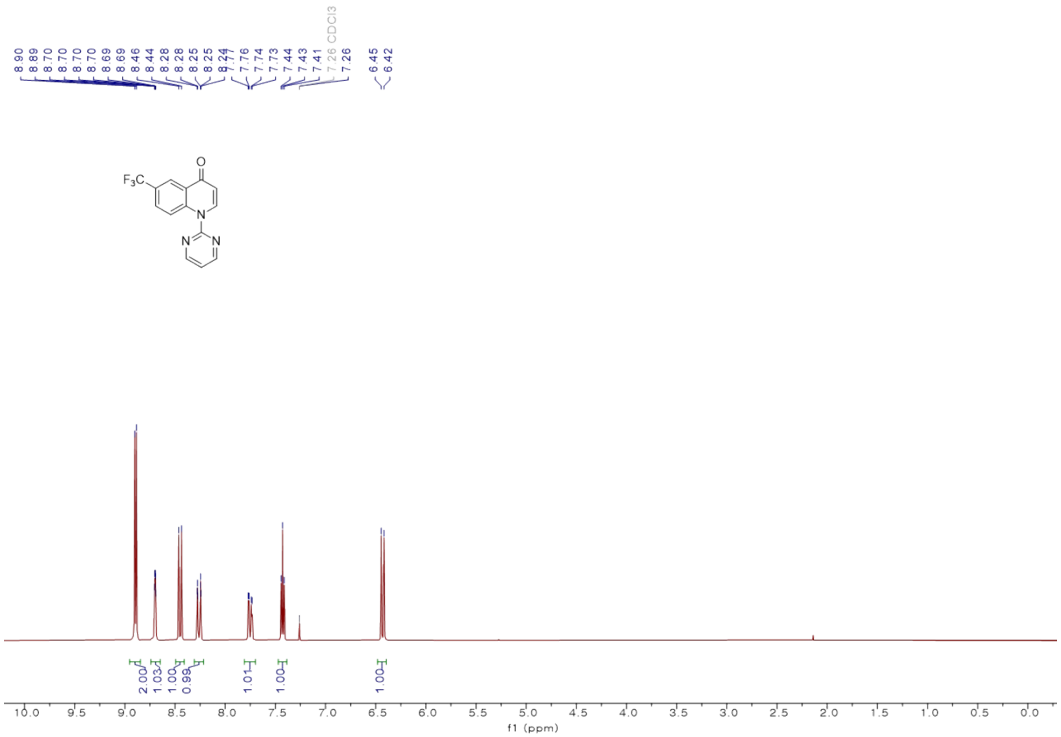
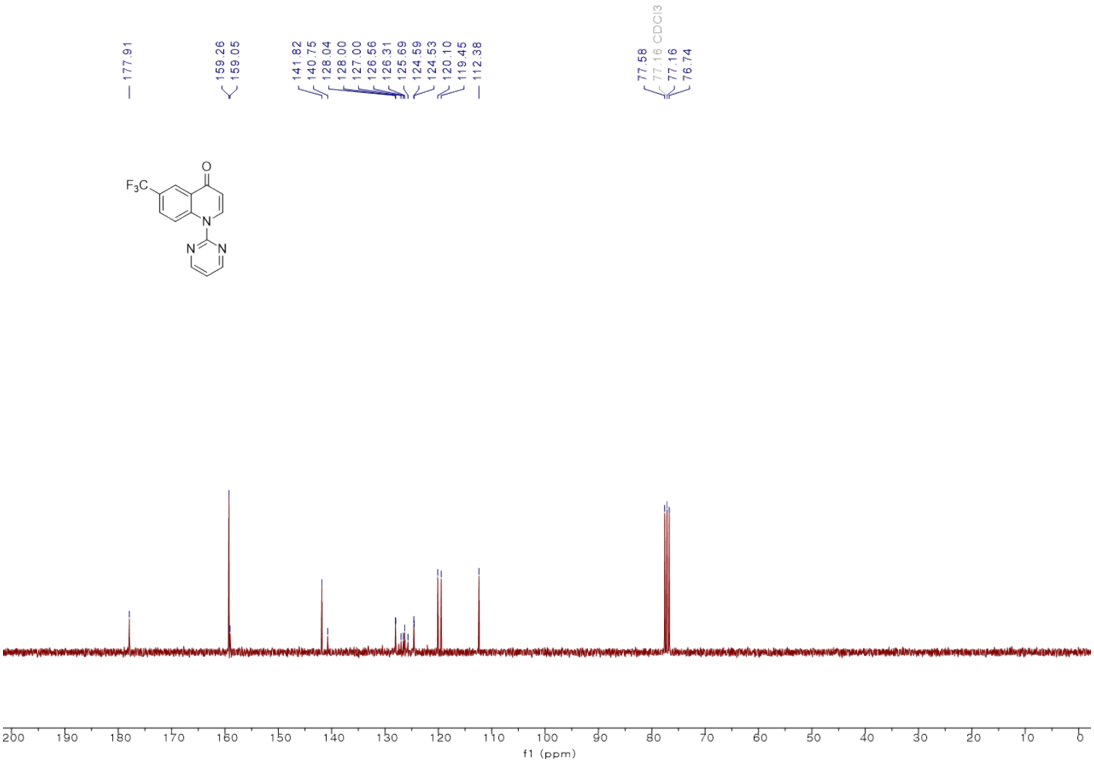
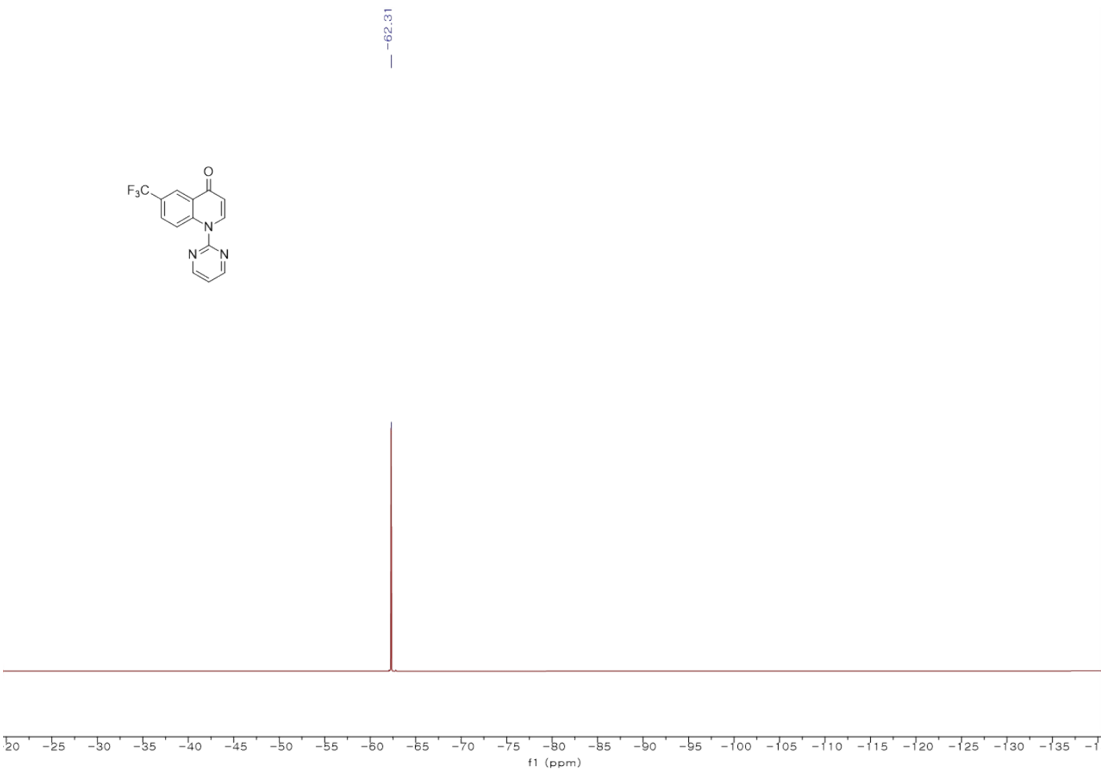
10. Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra



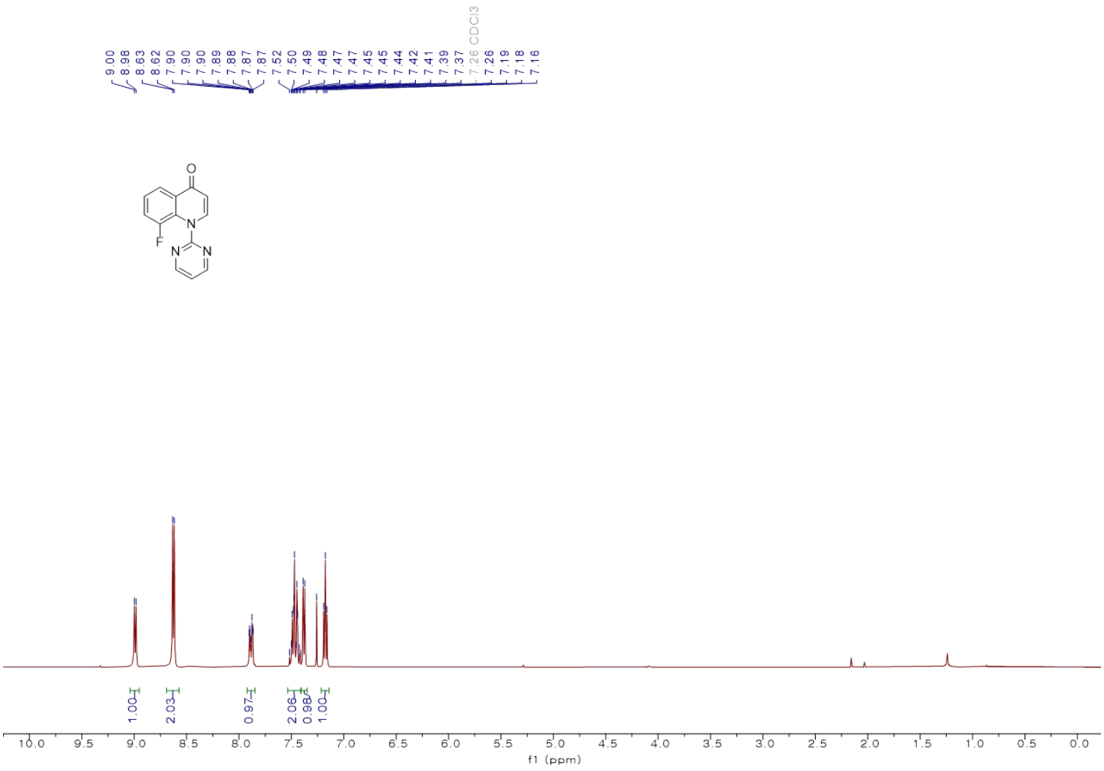
^{1}H NMR spectrum of **1e** (300 MHz, Chloroform-*d*)



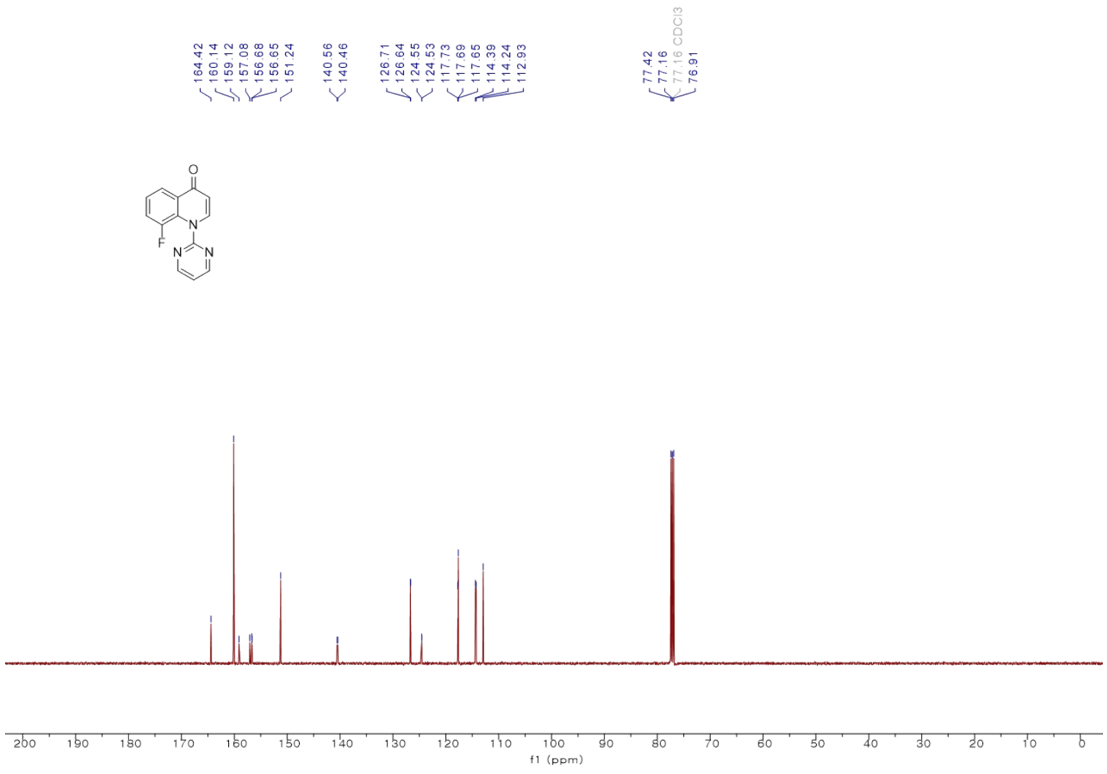
^{13}C NMR spectrum of **1e** (75 MHz, Chloroform-*d*)



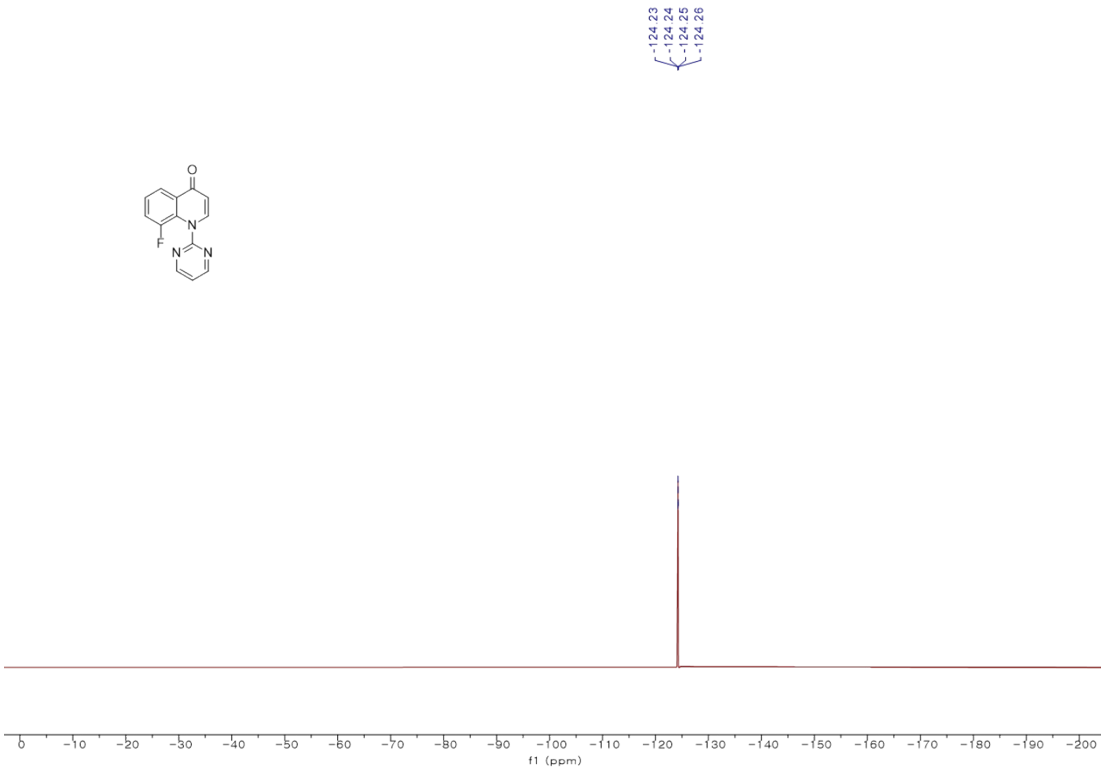
^{19}F NMR spectrum of **1e** (471 MHz, Chloroform-*d*)



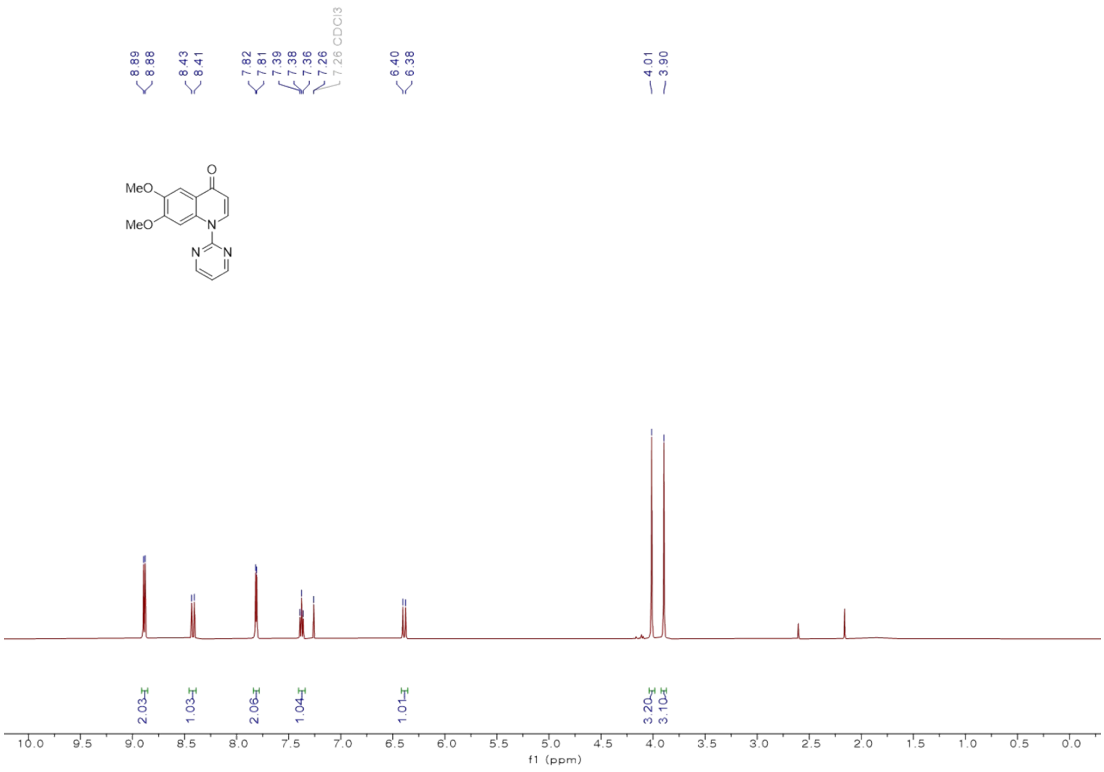
^{1}H NMR spectrum of **1i** (300 MHz, Chloroform-*d*)



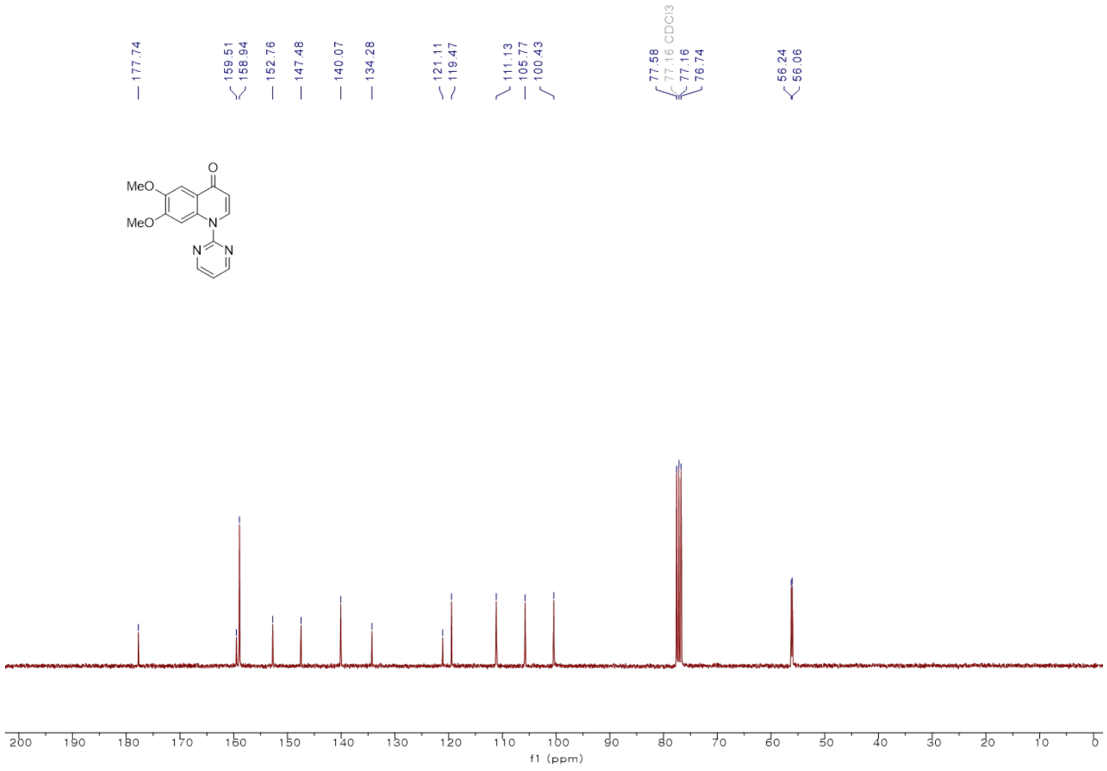
^{13}C NMR spectrum of **1i** (75 MHz, Chloroform-*d*)



^{19}F NMR spectrum of **1i** (471 MHz, Chloroform-*d*)



^{1}H NMR spectrum of **1j** (300 MHz, Chloroform-*d*)



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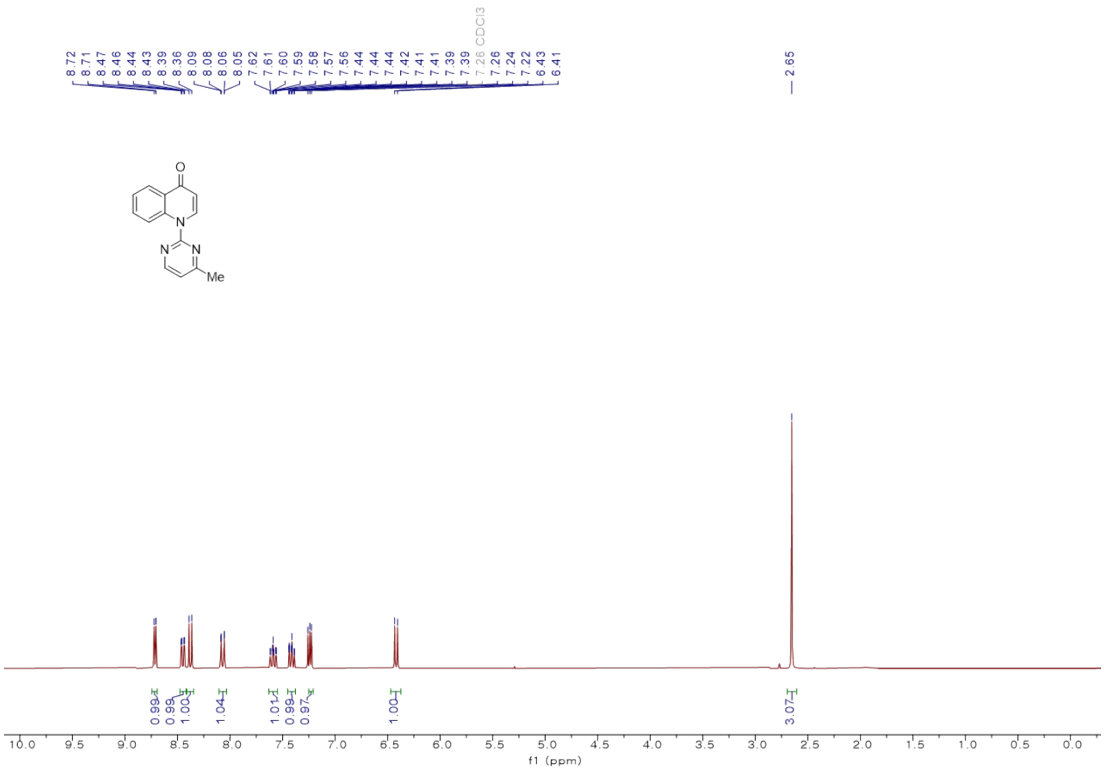

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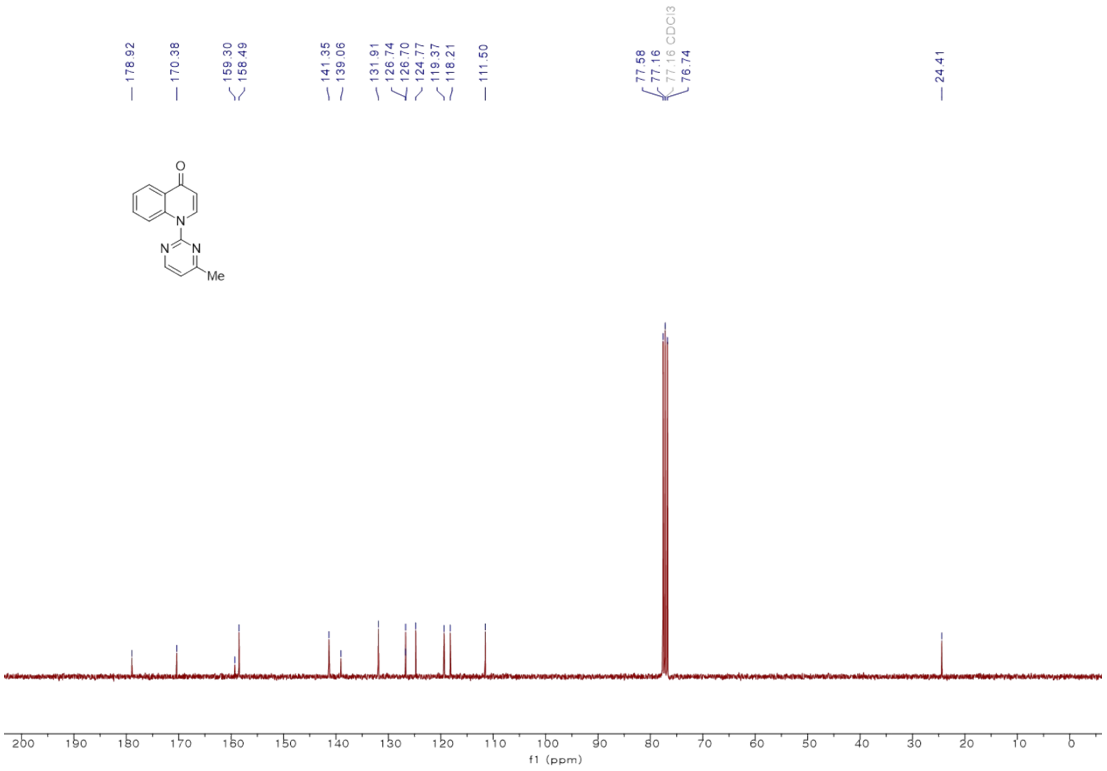
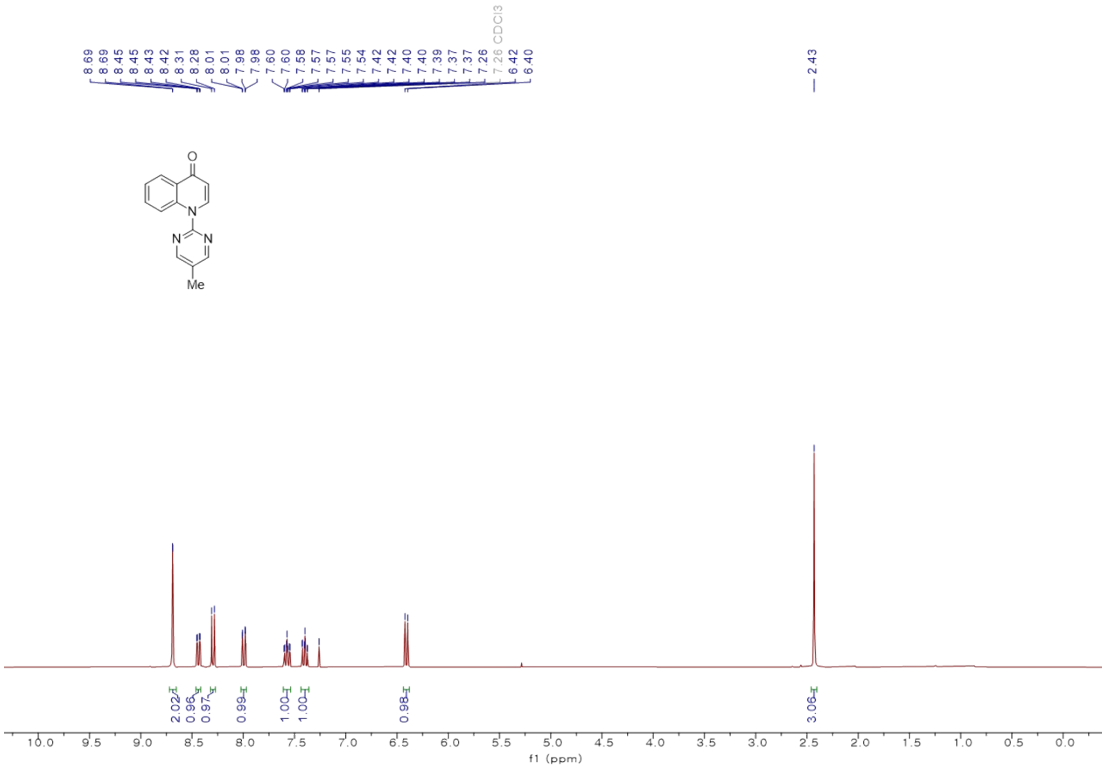
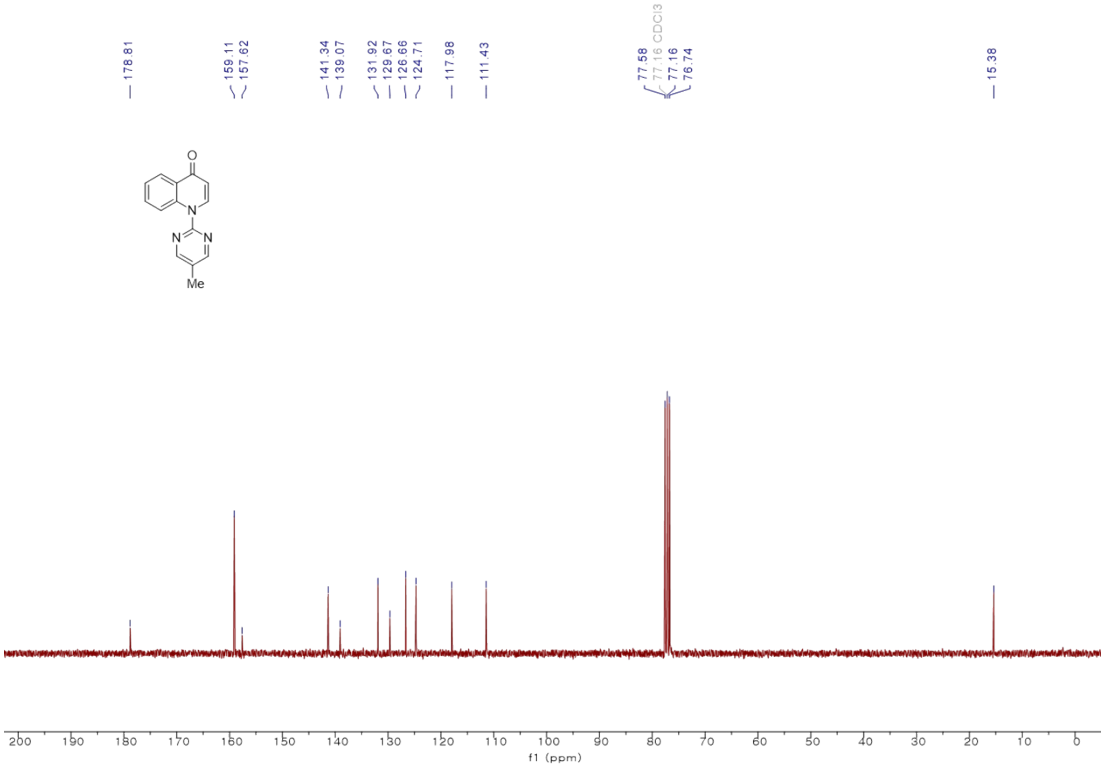


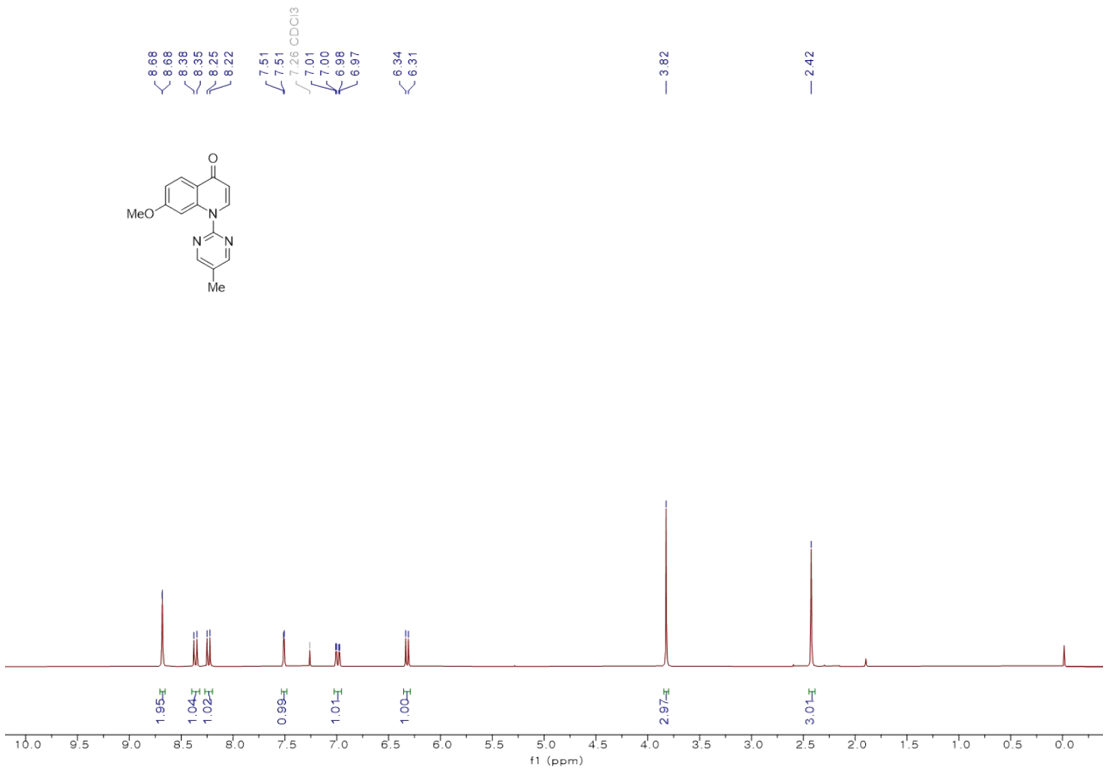
^{13}C NMR spectrum of **1r** (75 MHz, Chloroform-*d*)



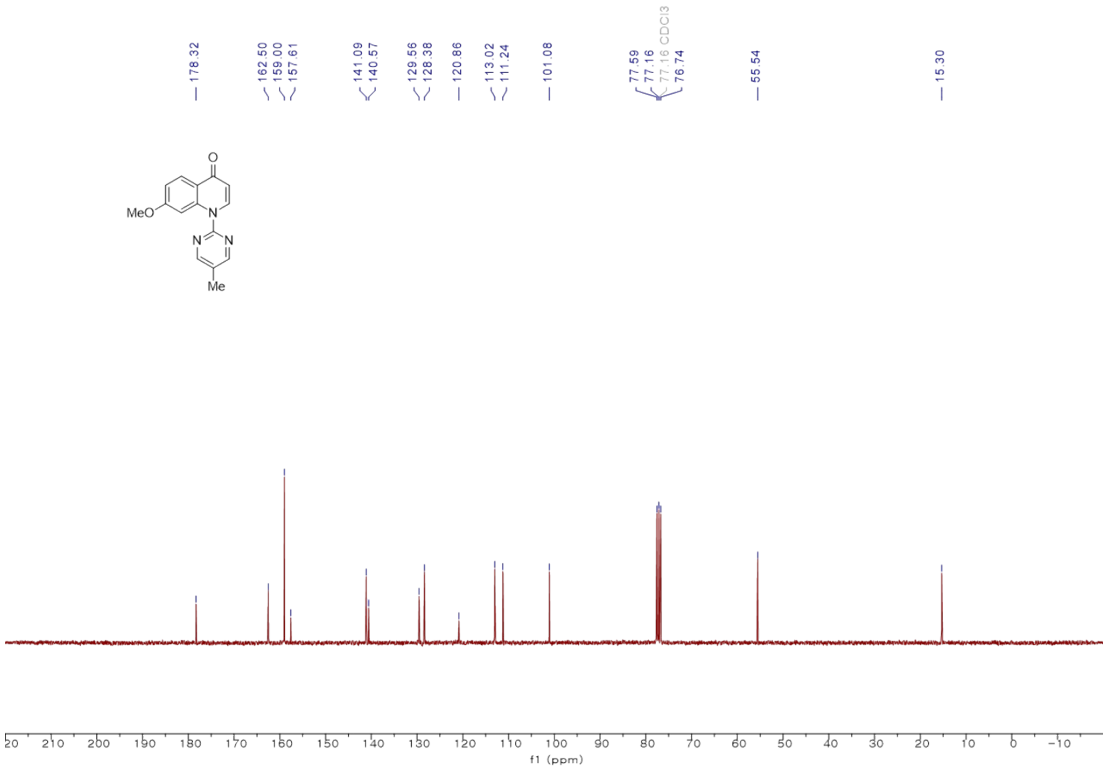
^{1}H NMR spectrum of **1s** (300 MHz, Chloroform-*d*)



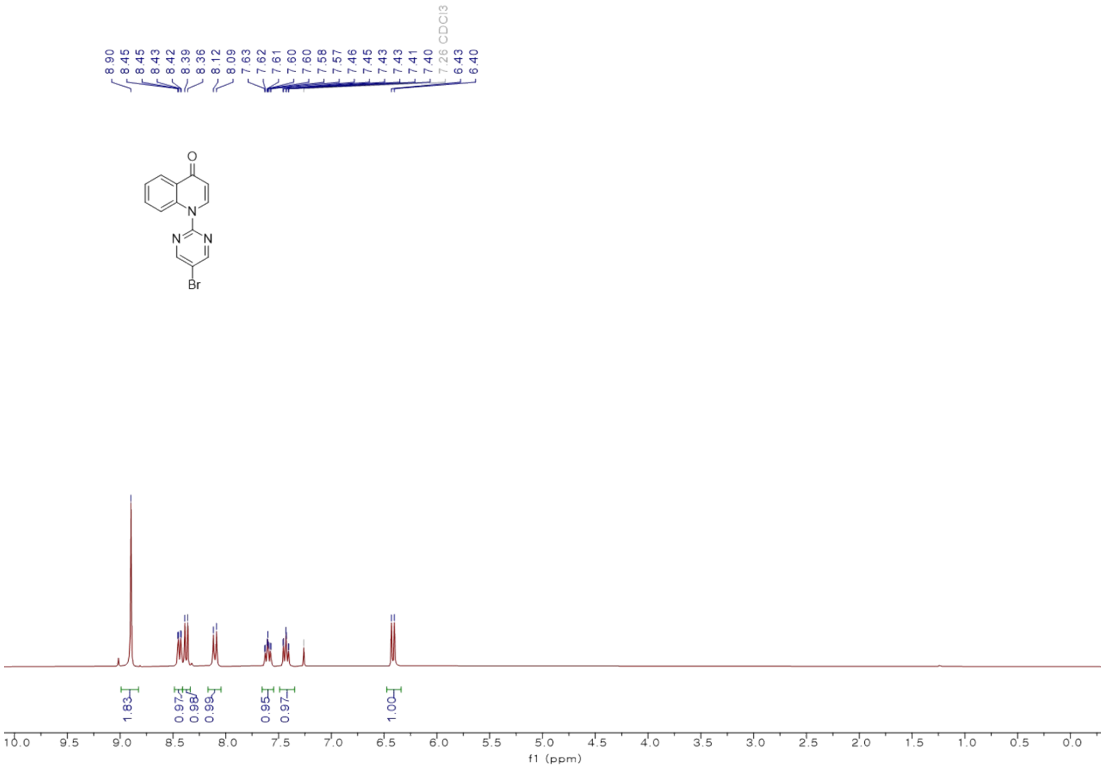
^{13}C NMR spectrum of **1s** (75 MHz, Chloroform-*d*)



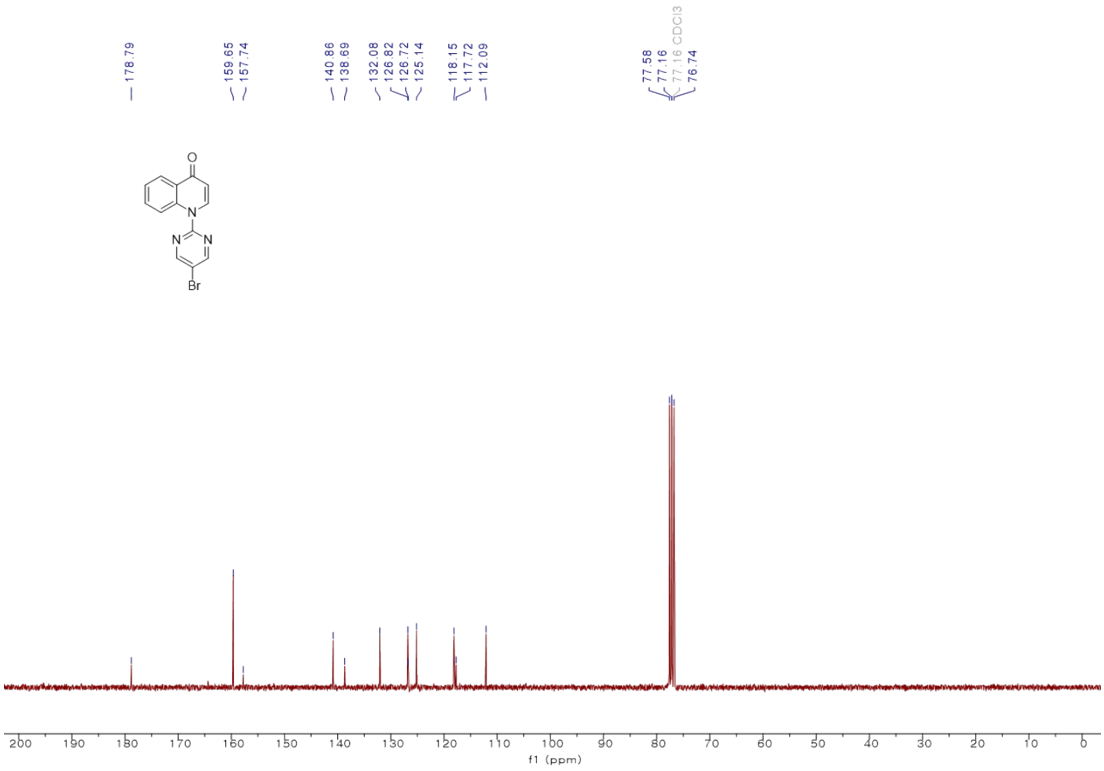
^{1}H NMR spectrum of **1t** (300 MHz, Chloroform-*d*)



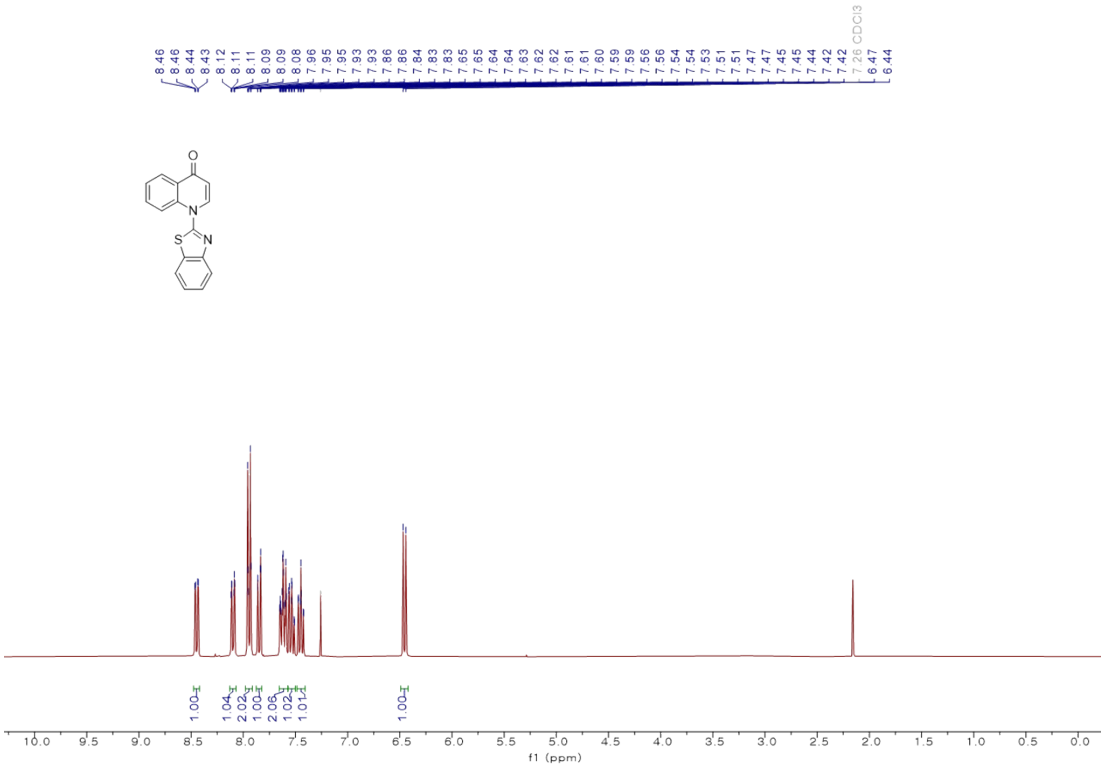
^{13}C NMR spectrum of **1t** (75 MHz, Chloroform-*d*)



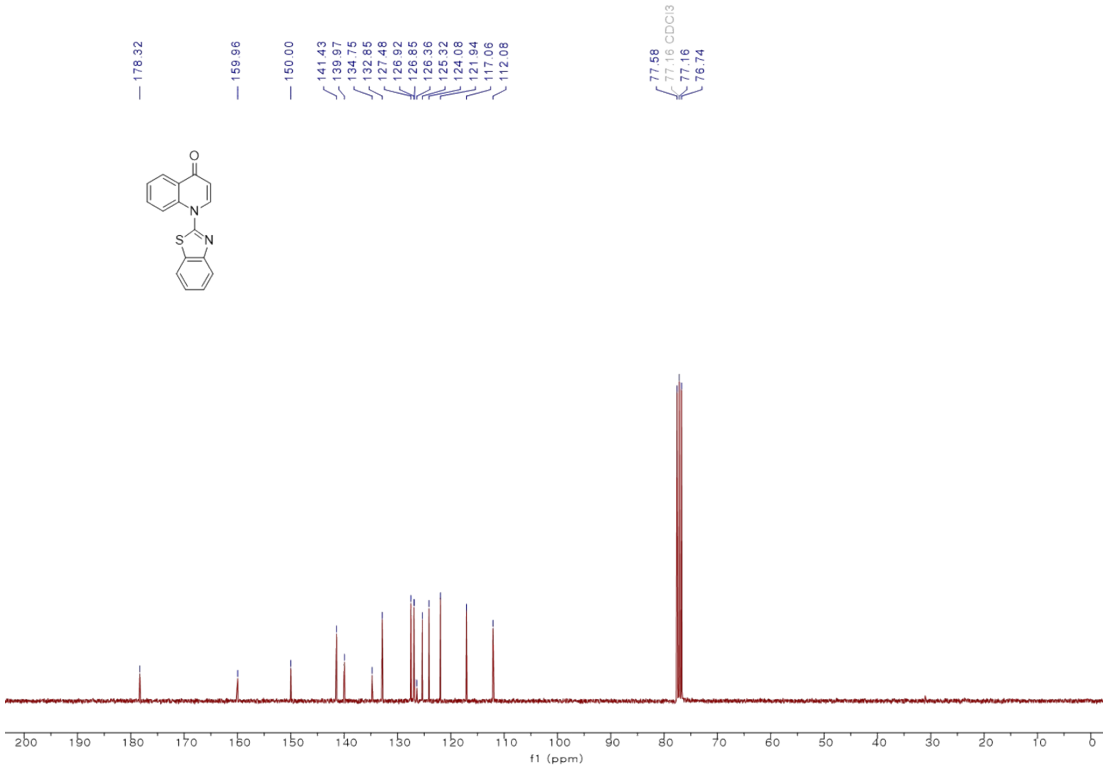
^{1}H NMR spectrum of **1u** (300 MHz, Chloroform-*d*)



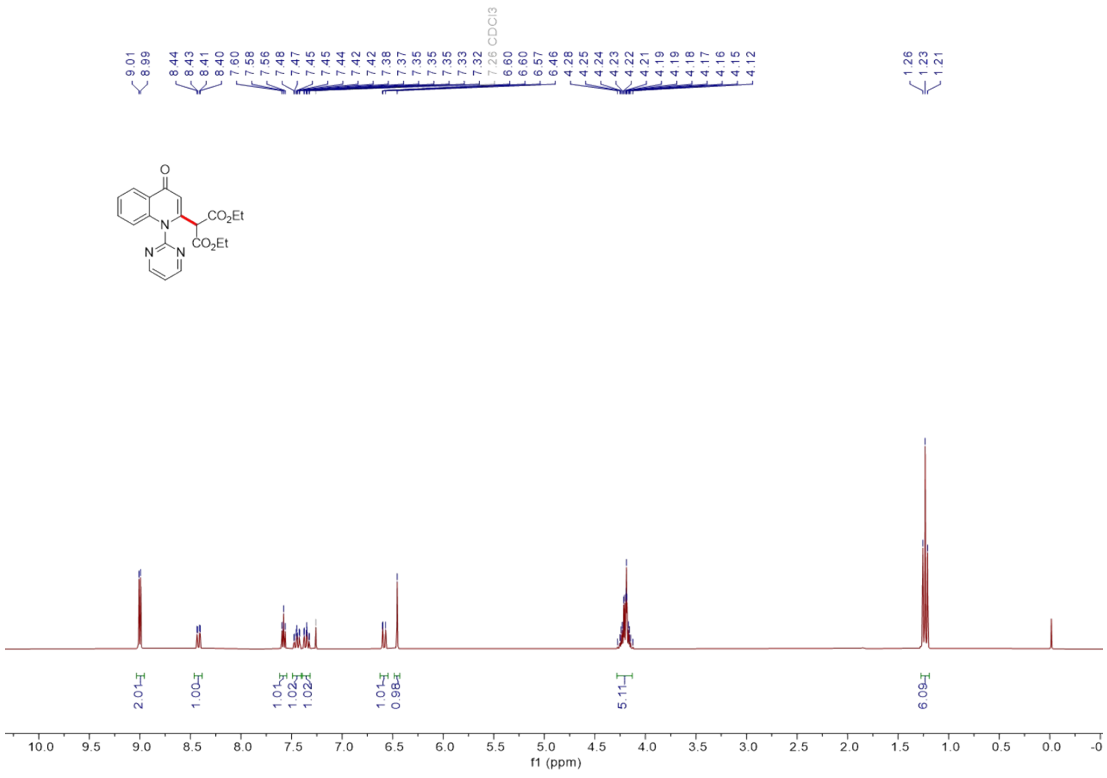
^{13}C NMR spectrum of **1u** (75 MHz, Chloroform-*d*)



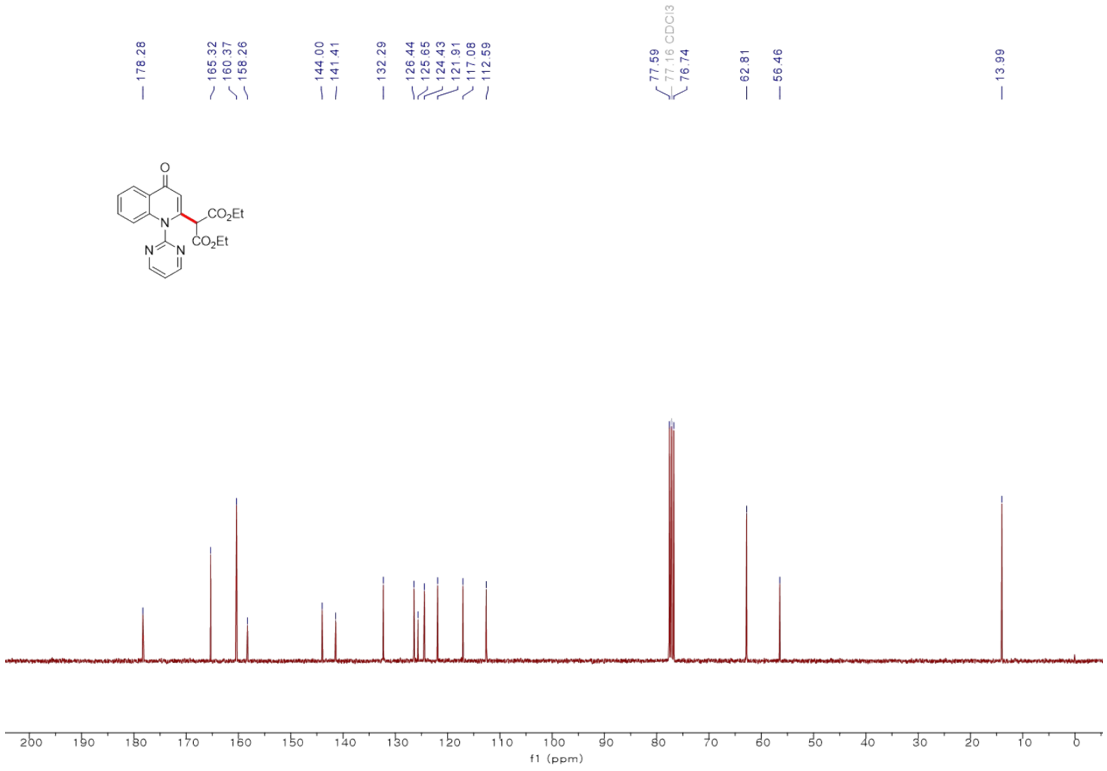
^{1}H NMR spectrum of **1v** (300 MHz, Chloroform-*d*)



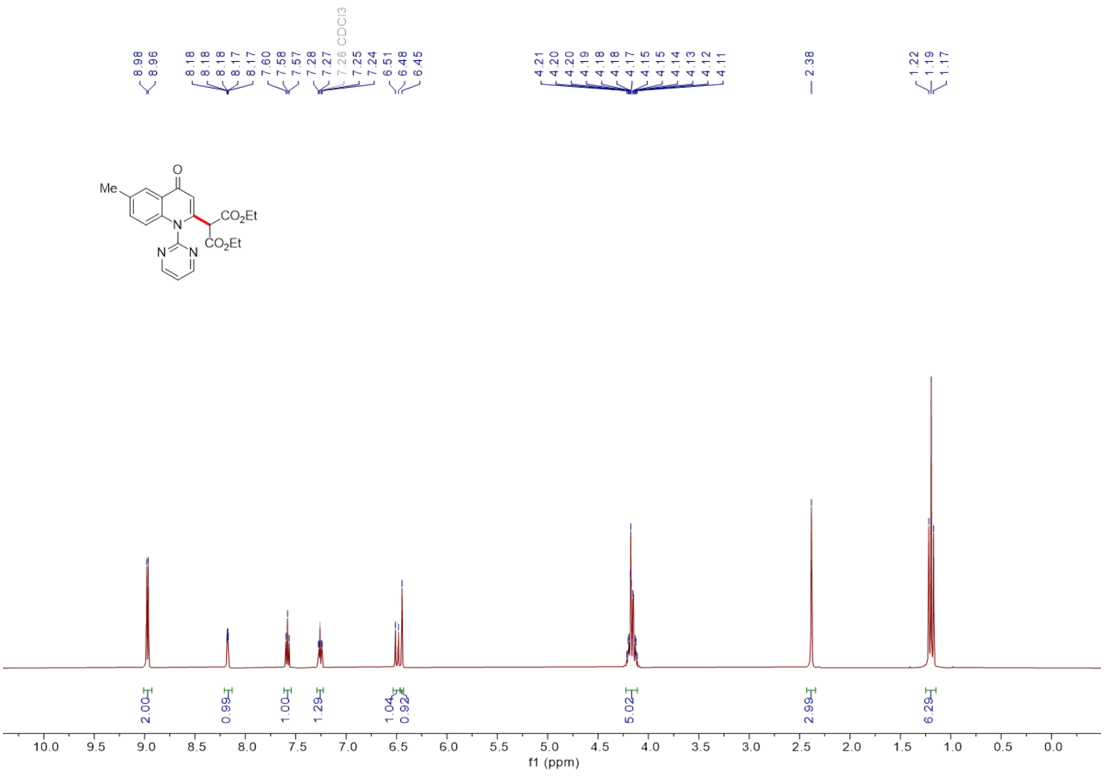
^{13}C NMR spectrum of **1v** (75 MHz, Chloroform-*d*)



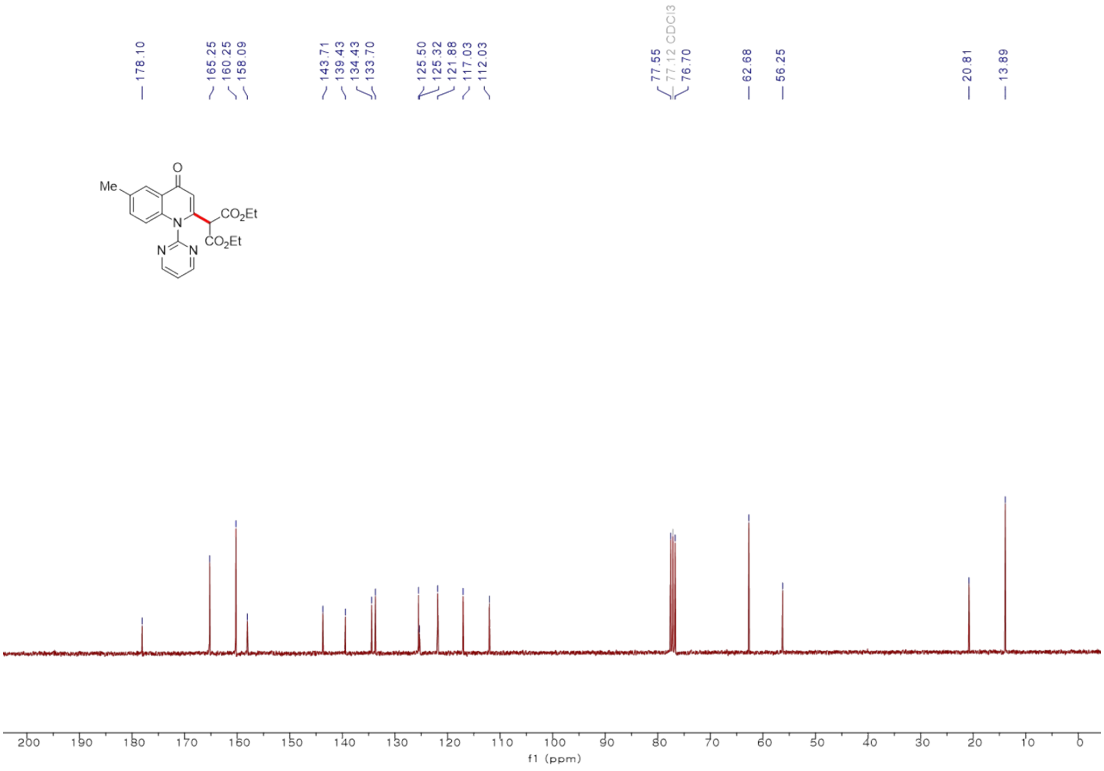
^{1}H NMR of **3a** (300 MHz, Chloroform-*d*)



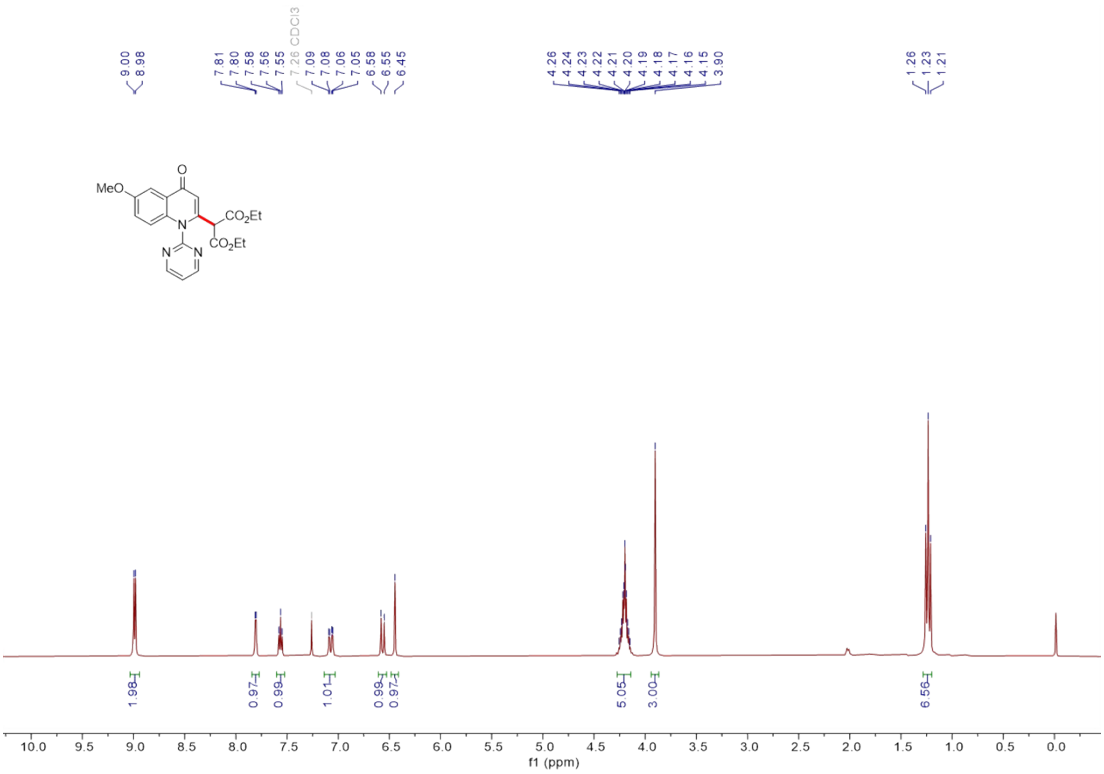
^{13}C NMR of **3a** (75 MHz, Chloroform-*d*)



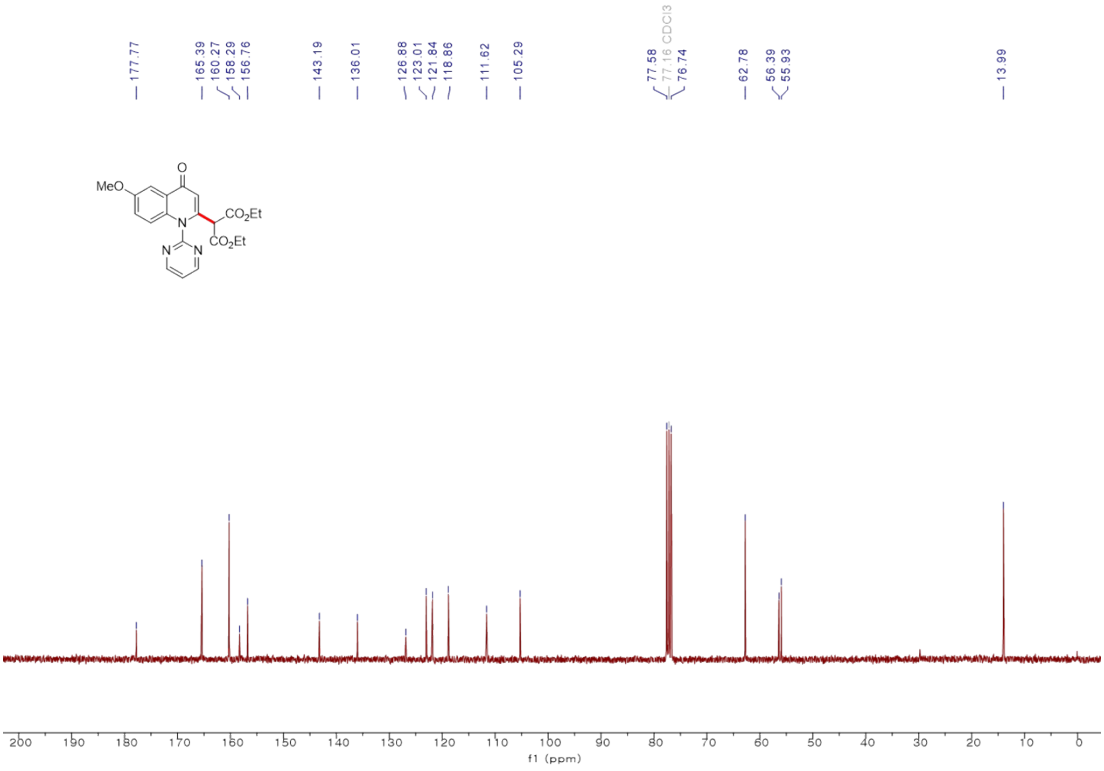
^{1}H NMR of **3b** (300 MHz, Chloroform-*d*)



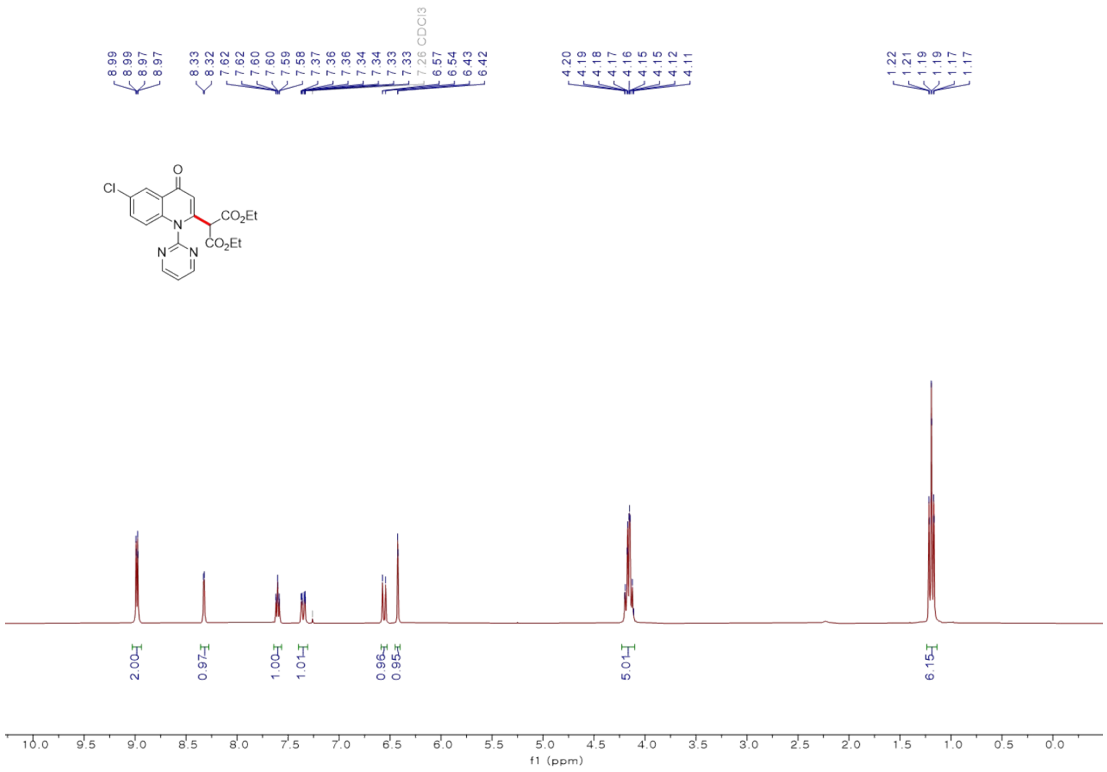
^{13}C NMR of **3b** (75 MHz, Chloroform-*d*)



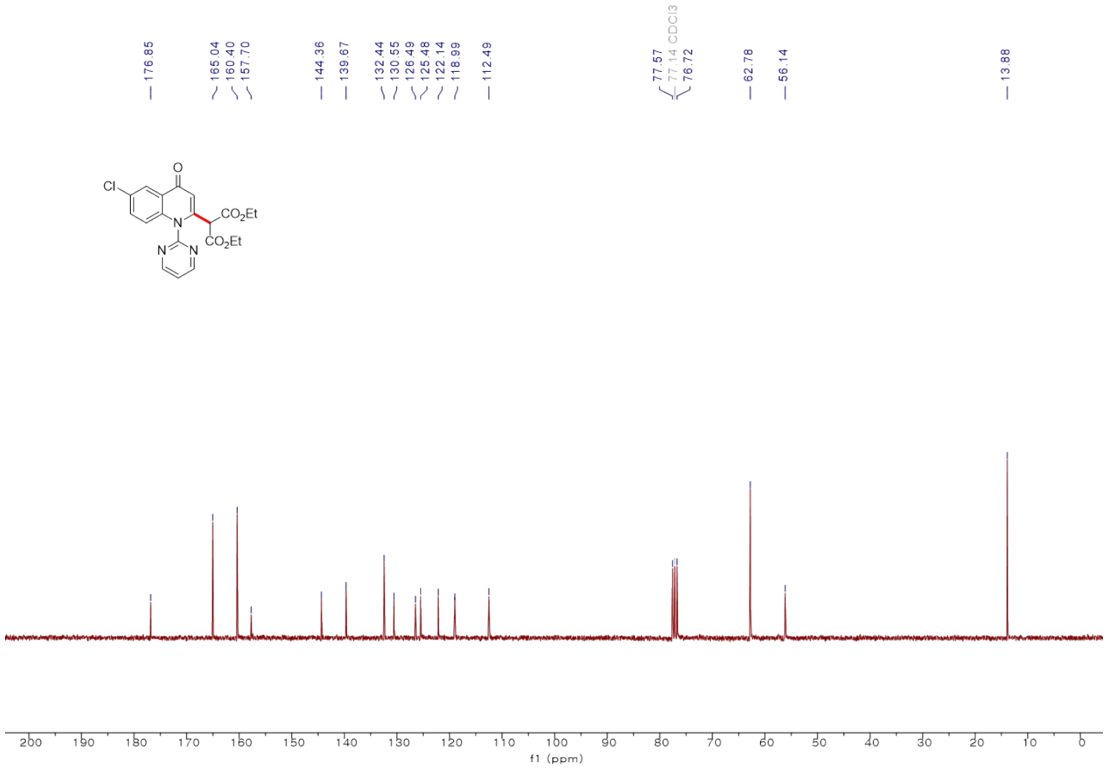
^{1}H NMR of **3c** (300 MHz, Chloroform-*d*)



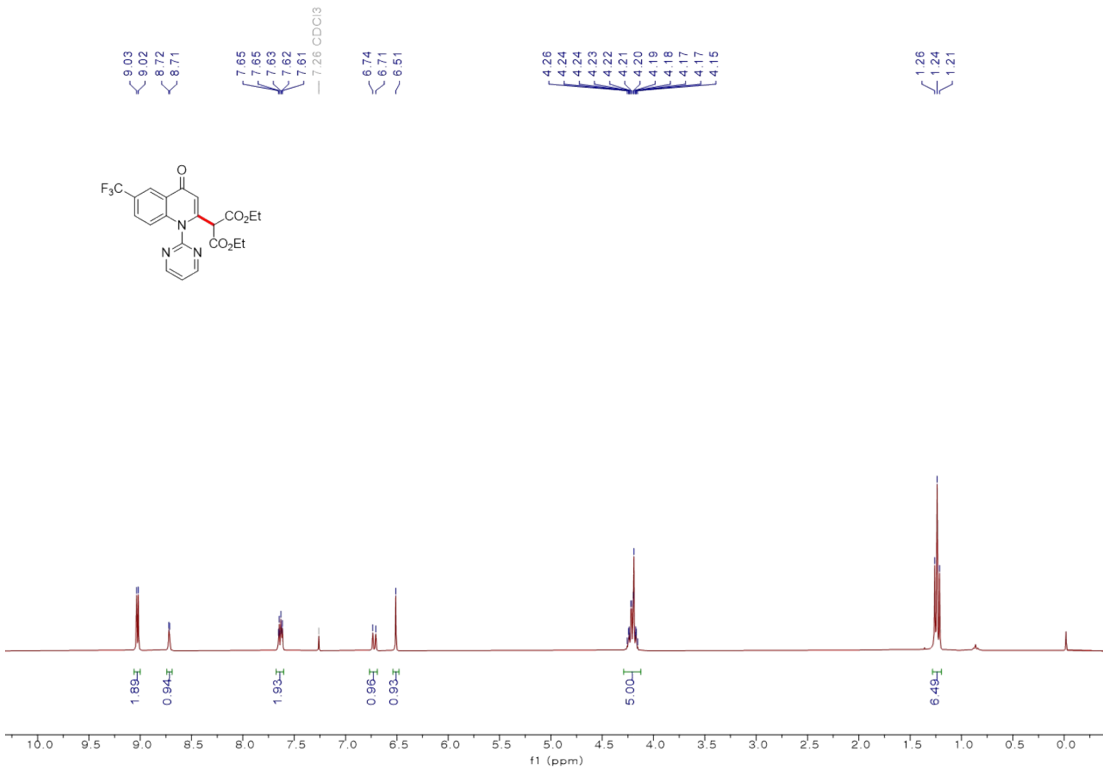
^{13}C NMR of **3c** (75 MHz, Chloroform-*d*)



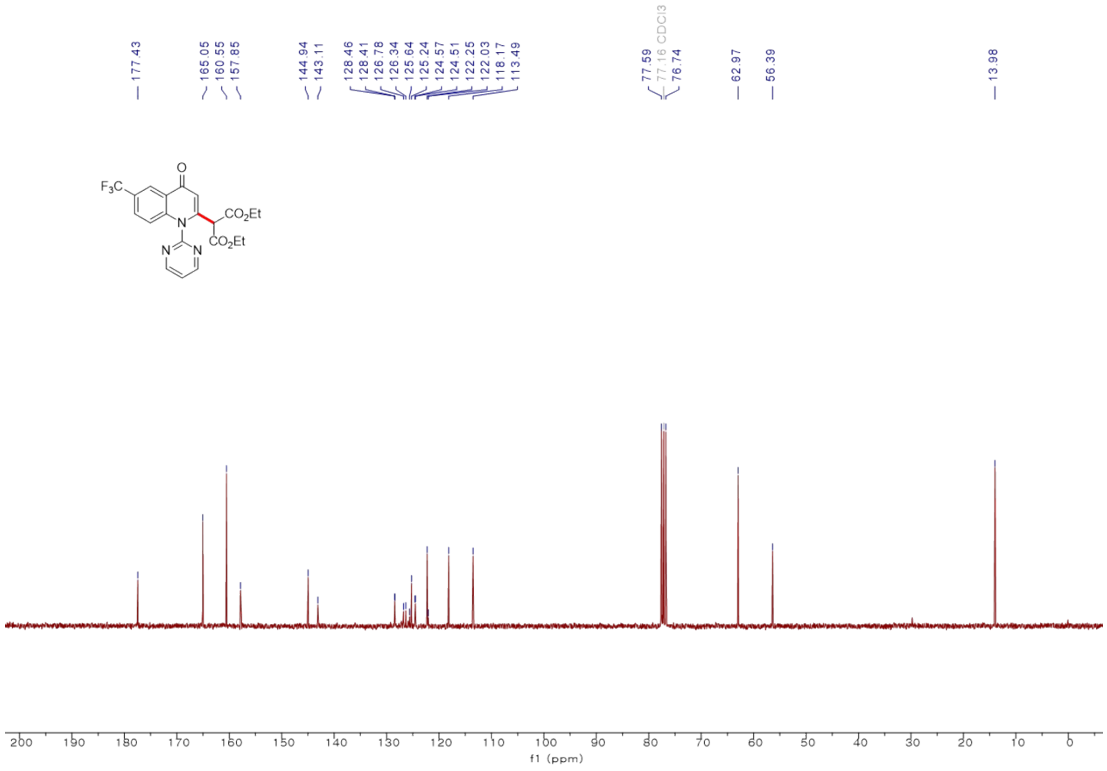
^{1}H NMR of **3d** (300 MHz, Chloroform-*d*)



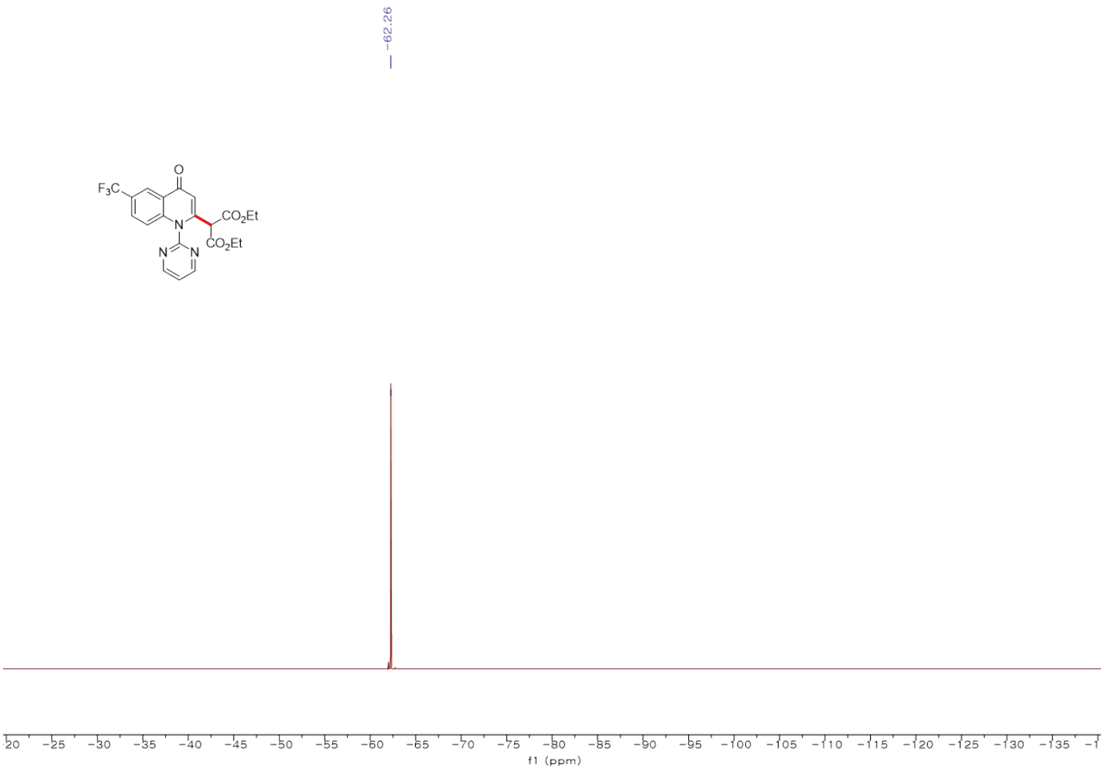
^{13}C NMR of **3d** (75 MHz, Chloroform-*d*)



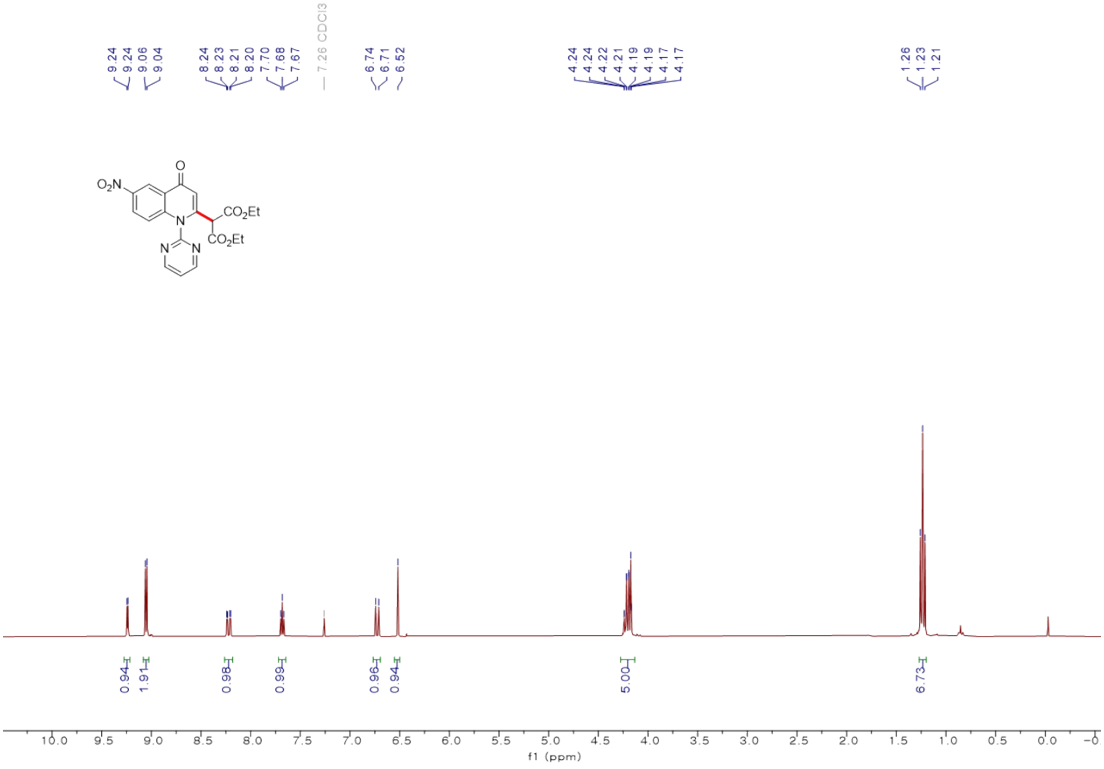
^{1}H NMR of **3e** (300 MHz, Chloroform-*d*)



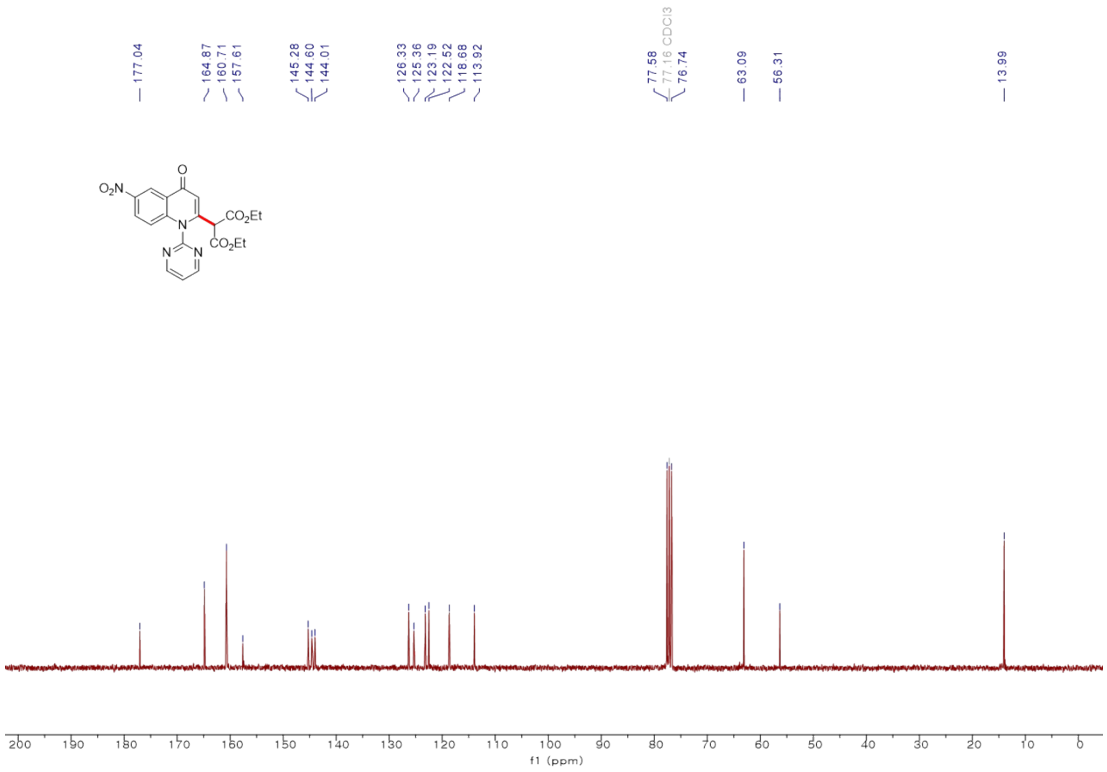
^{13}C NMR of **3e** (75 MHz, Chloroform-*d*)



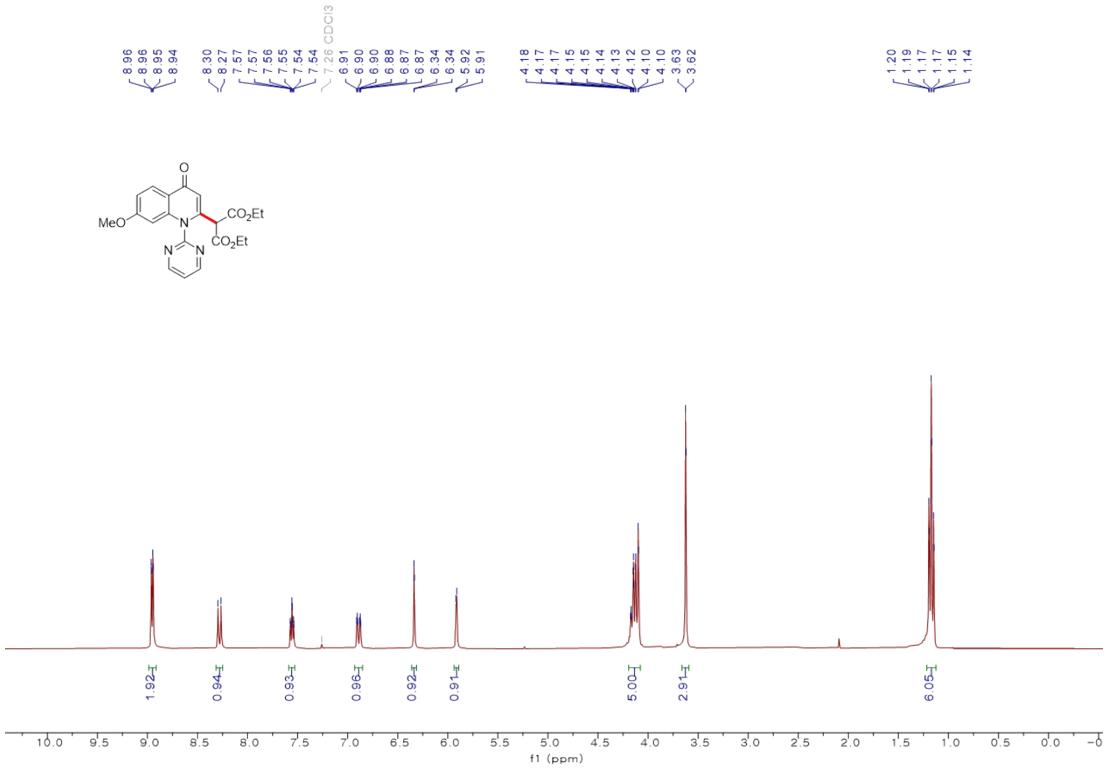
^{19}F NMR of **3e** (471MHz, Chloroform-*d*)



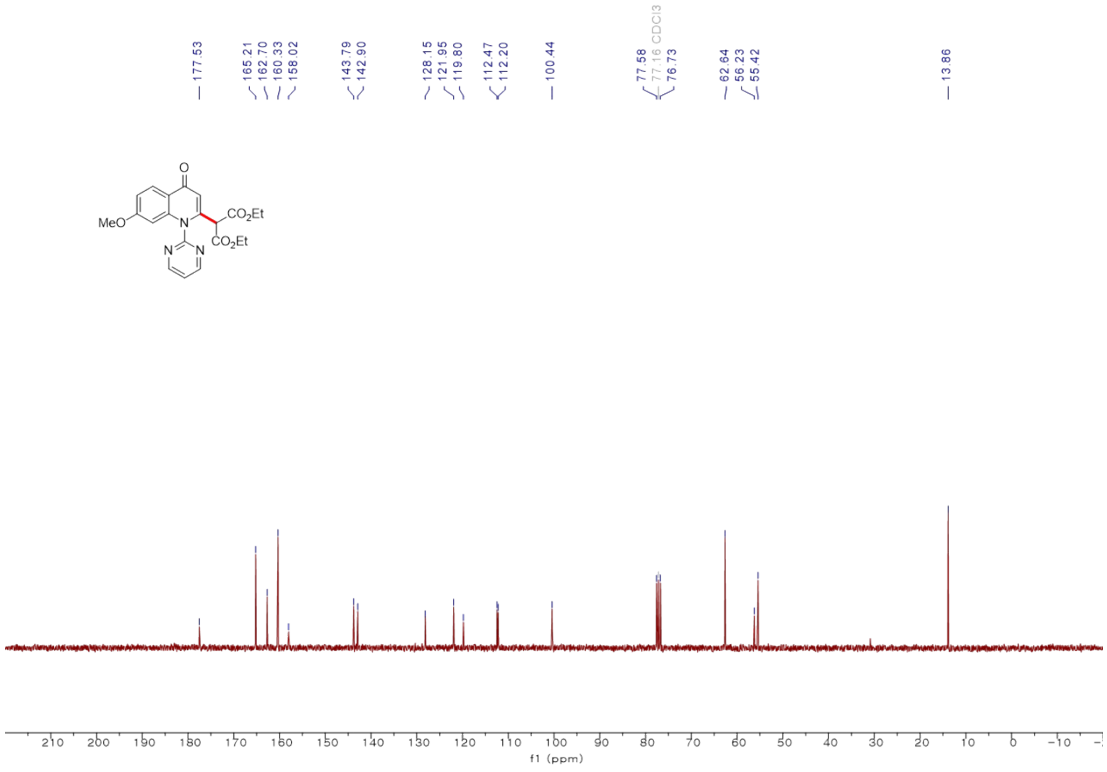
^{1}H NMR of **3f** (300 MHz, Chloroform-*d*)



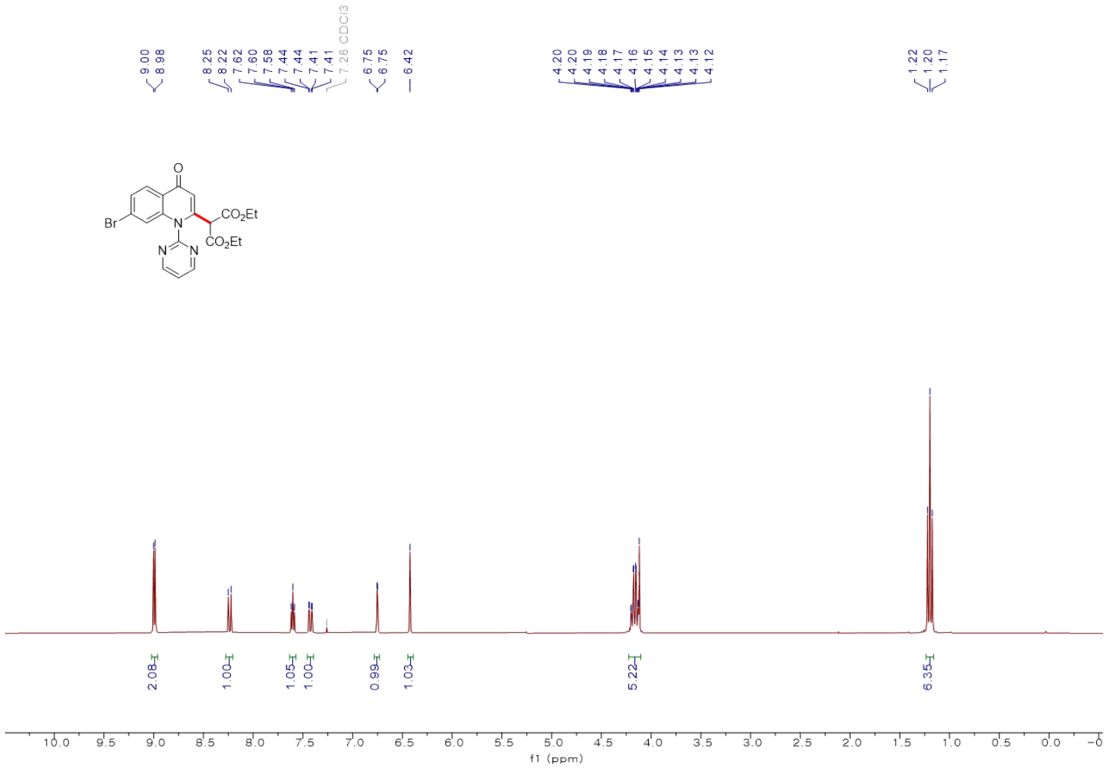
^{13}C NMR of **3f** (75 MHz, Chloroform-*d*)



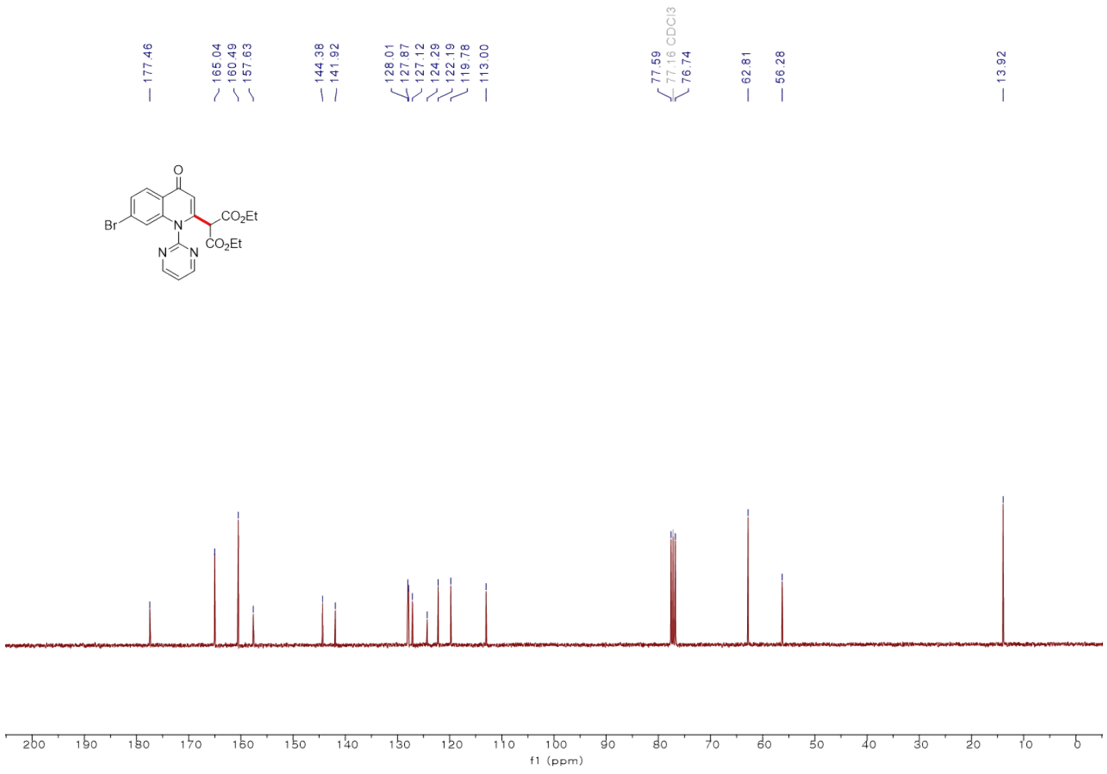
^{1}H NMR of **3g** (300 MHz, Chloroform-*d*)



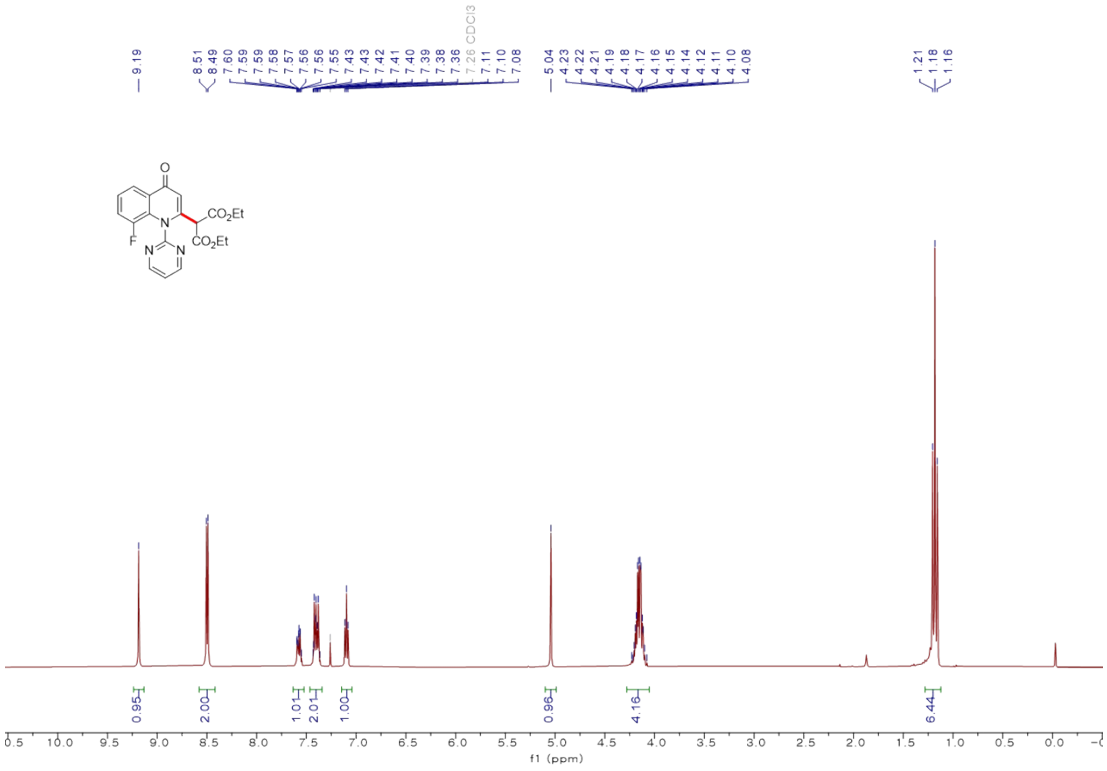
^{13}C NMR of **3g** (75 MHz, Chloroform-*d*)



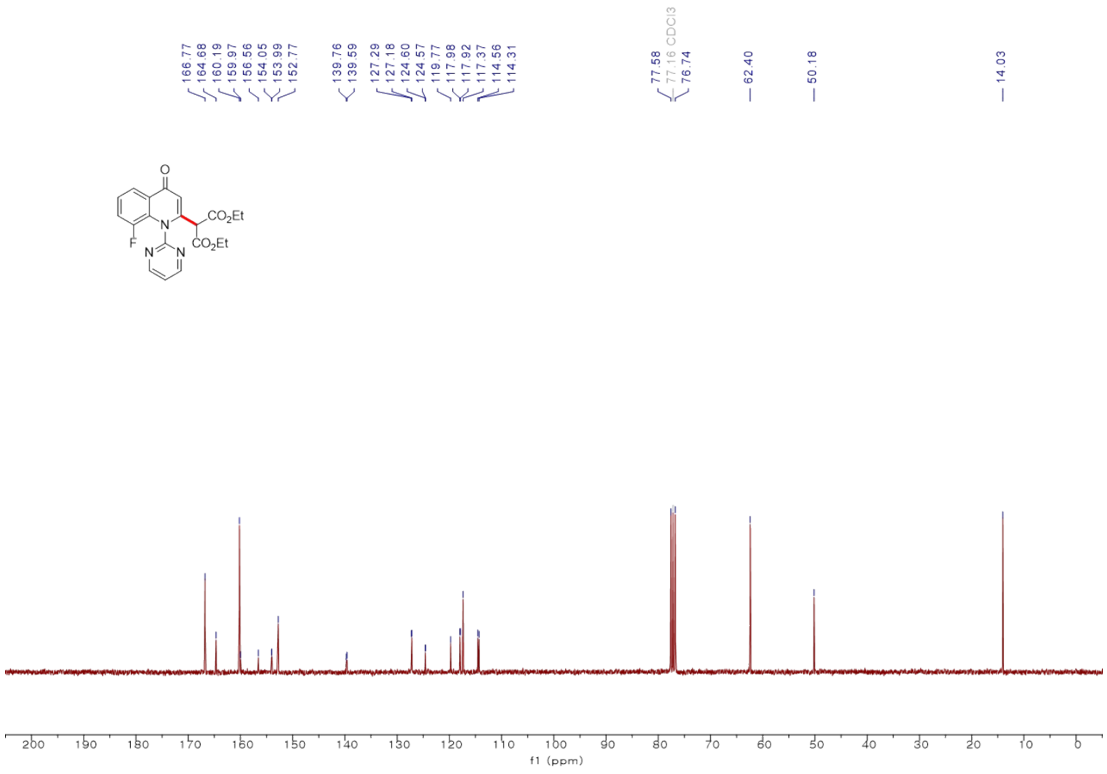
^{1}H NMR of **3h** (300 MHz, Chloroform-*d*)



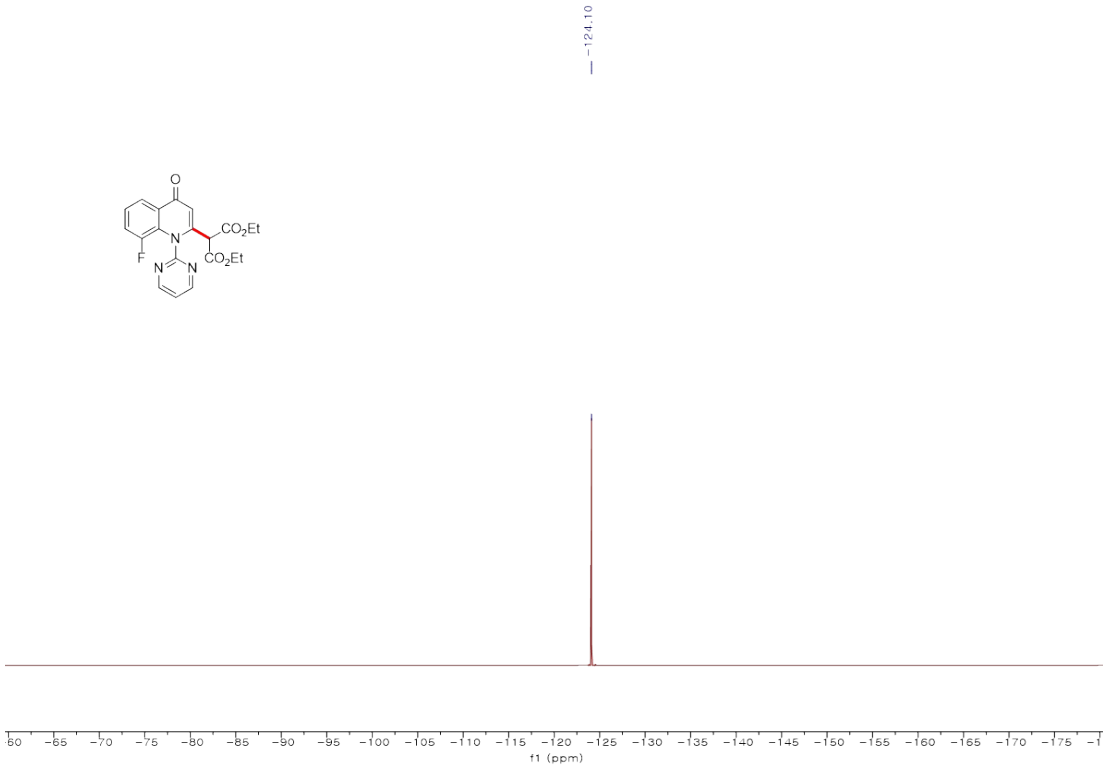
^{13}C NMR of **3h** (75 MHz, Chloroform-*d*)



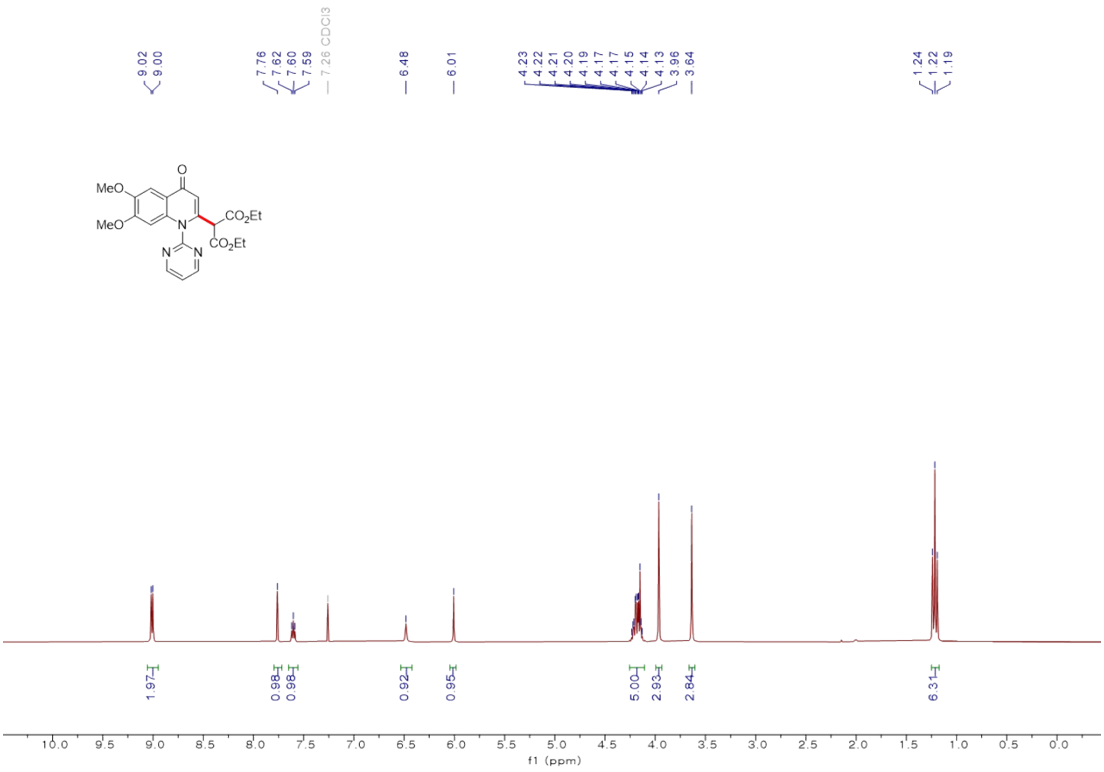
^{1}H NMR of **3i** (300 MHz, Chloroform-*d*)



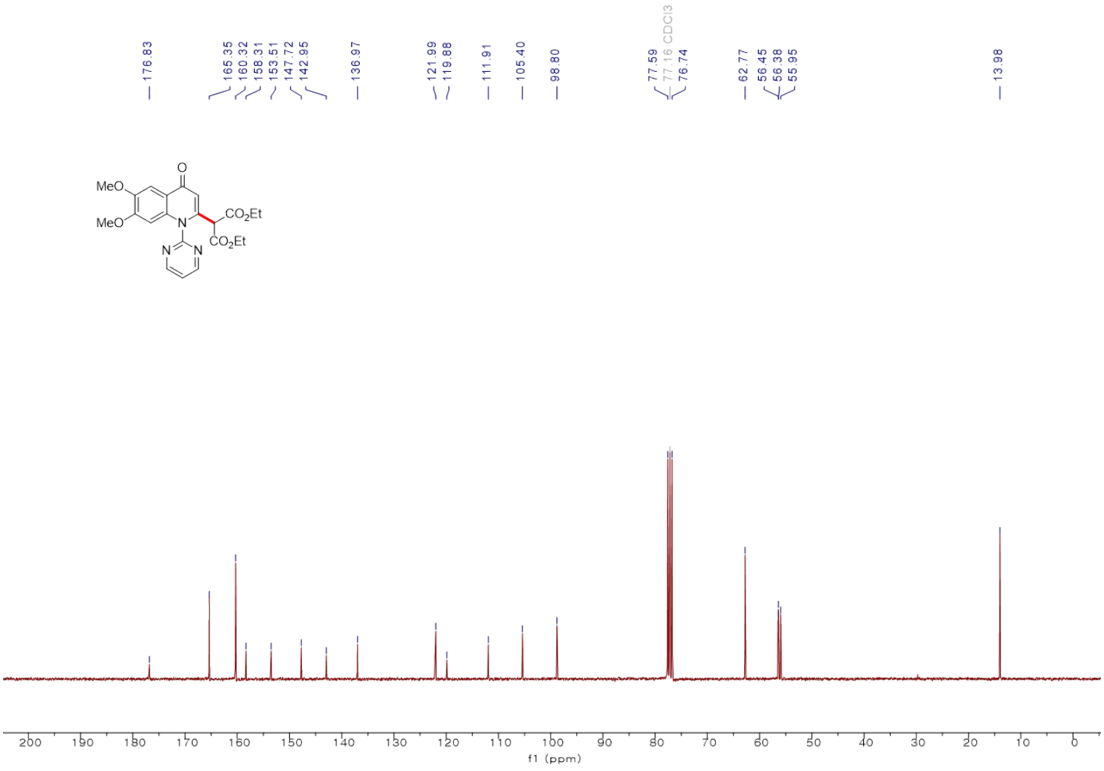
^{13}C NMR of **3i** (75 MHz, Chloroform-*d*)



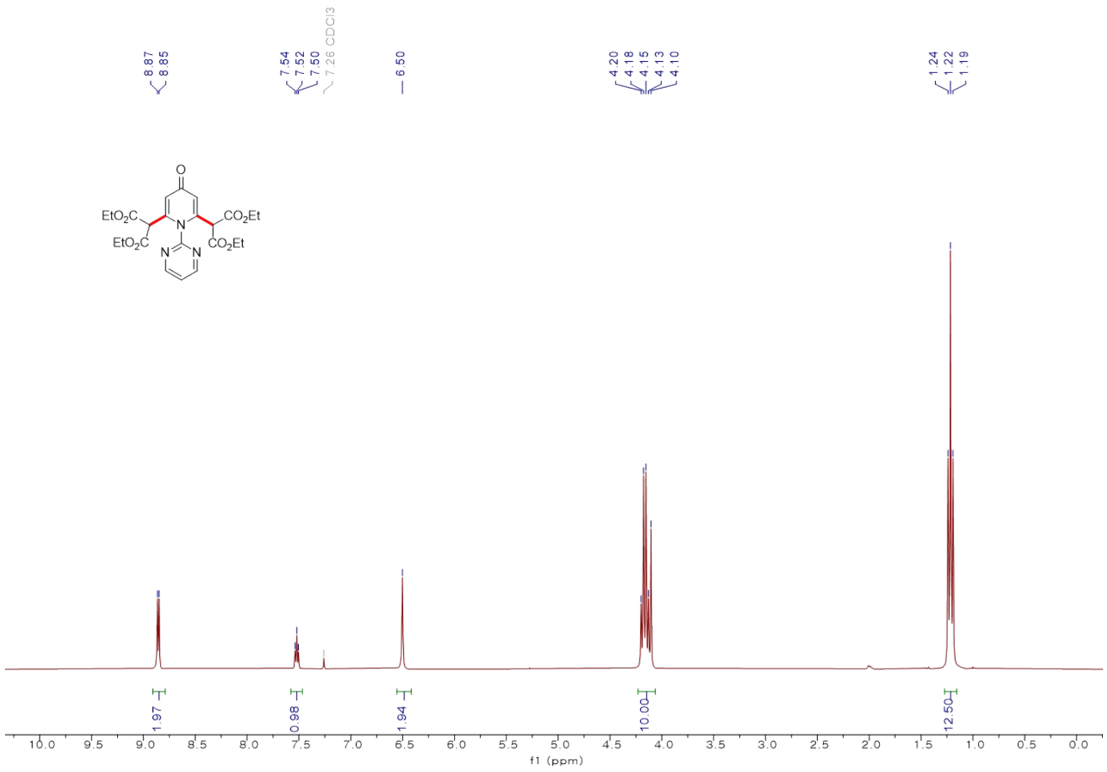
^{19}F NMR of **3i** (471MHz, Chloroform-*d*)



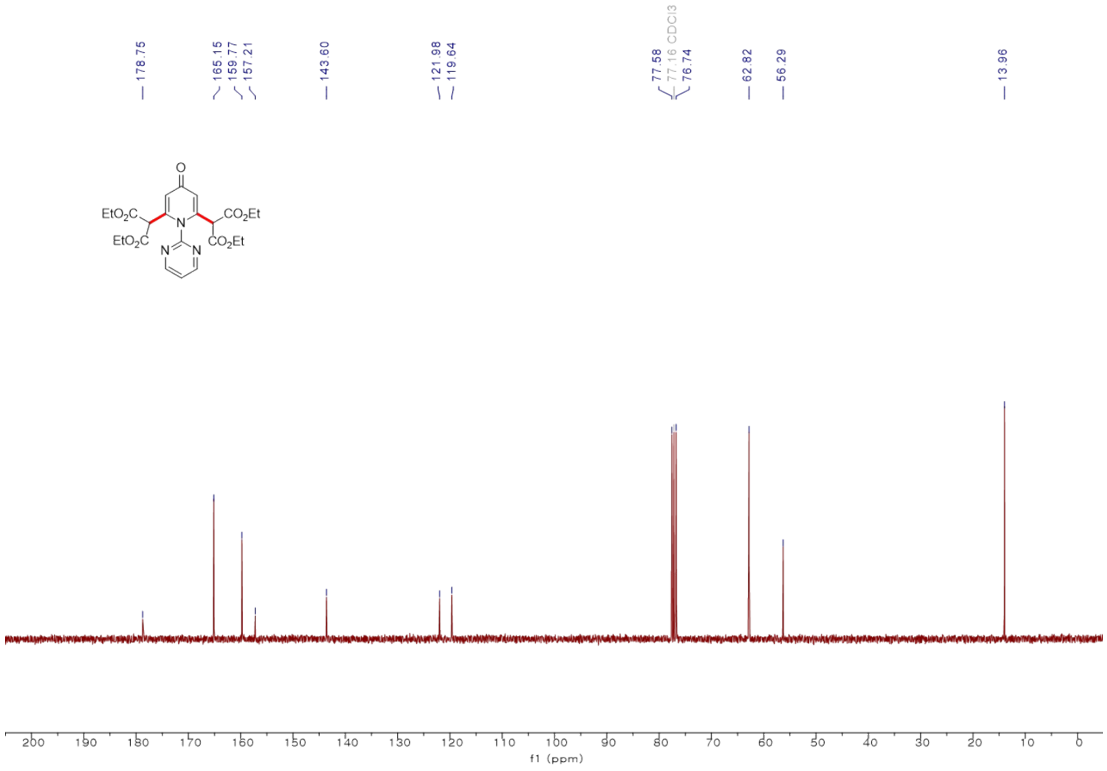
^{1}H NMR of **3j** (300 MHz, Chloroform-*d*)



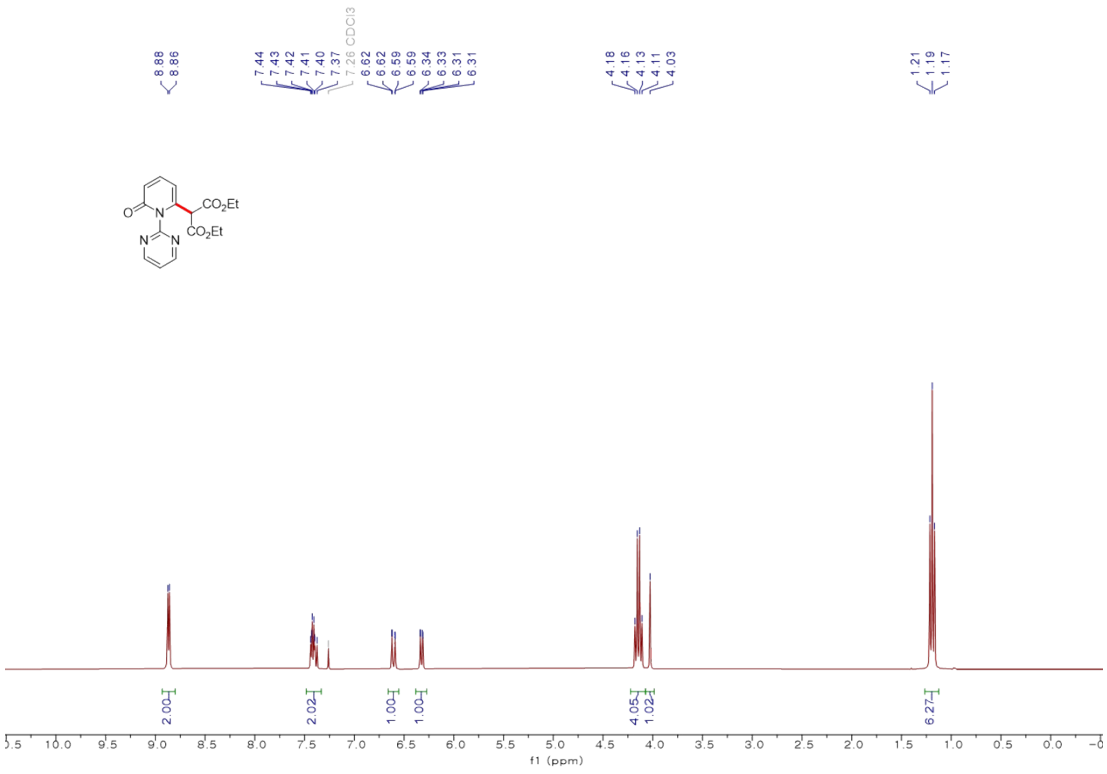
^{13}C NMR of **3j** (75 MHz, Chloroform-*d*)



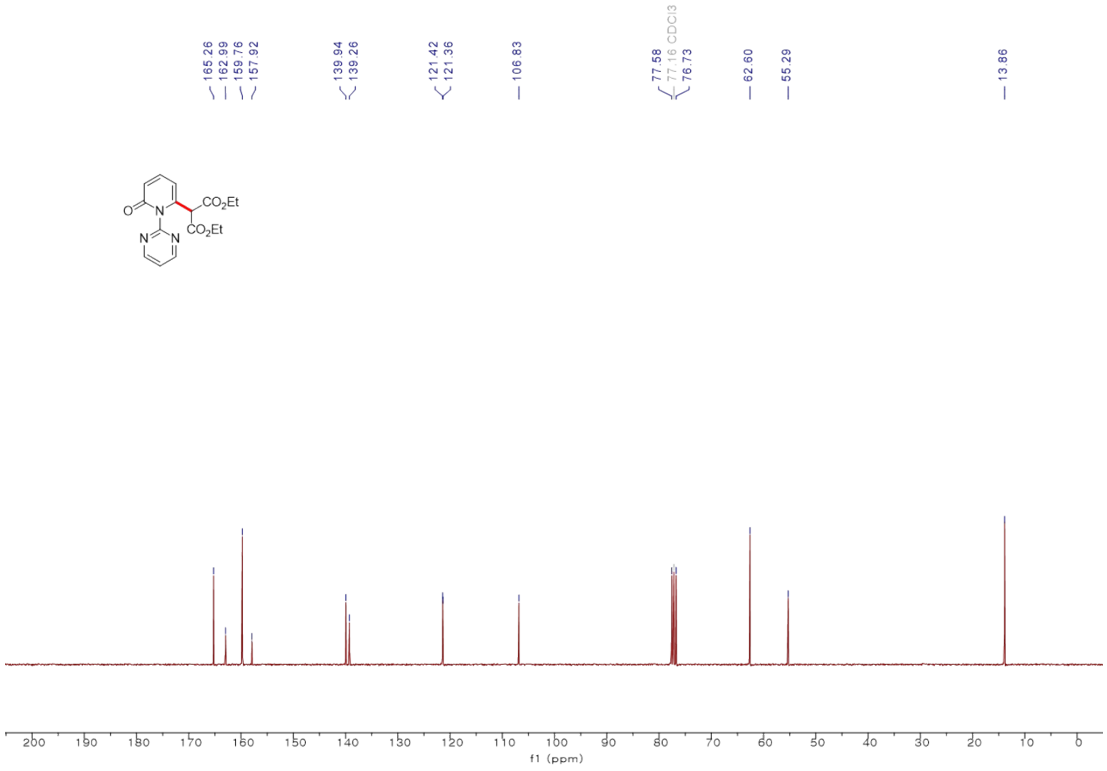
^{1}H NMR of **3k** (300 MHz, Chloroform-*d*)



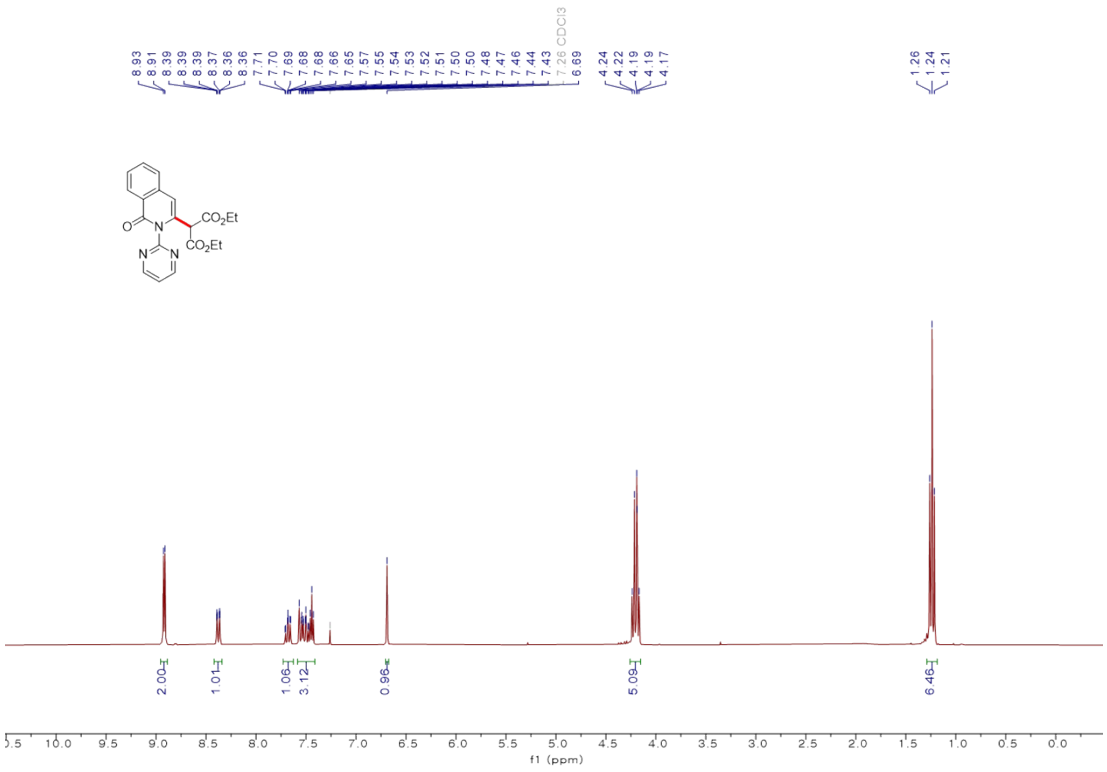
^{13}C NMR of **3k** (75 MHz, Chloroform-*d*)



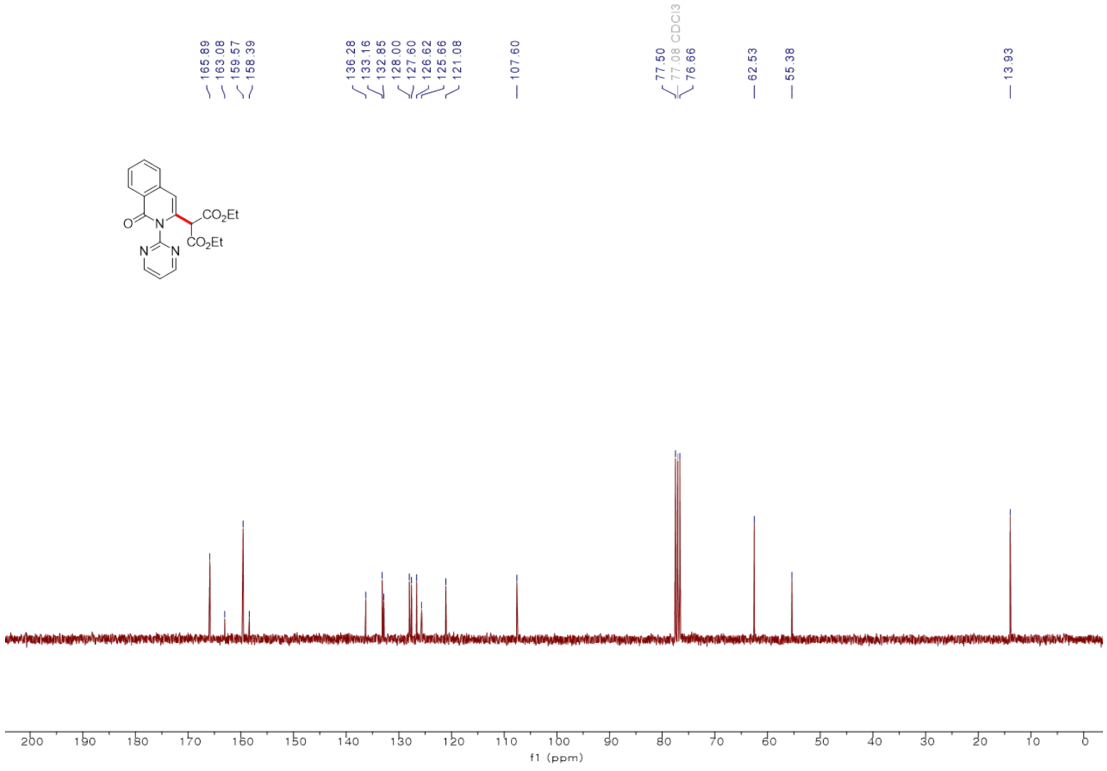
^{1}H NMR of **3l** (300 MHz, Chloroform-*d*)



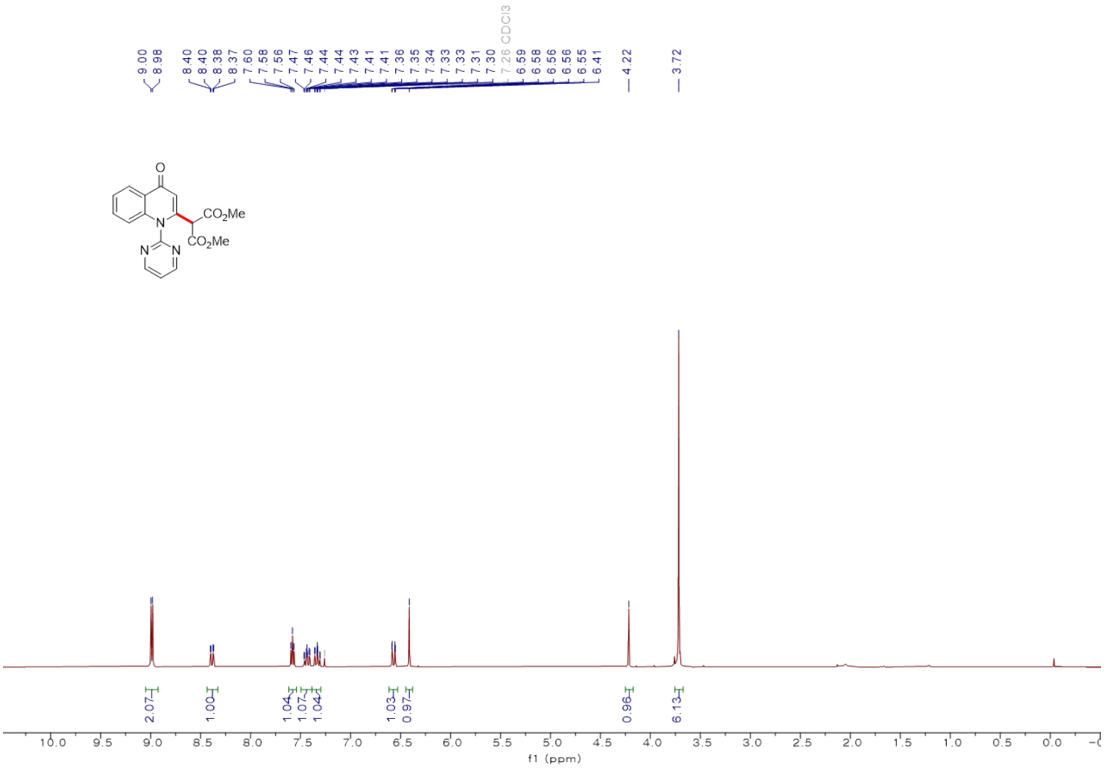
^{13}C NMR of **3l** (75 MHz, Chloroform-*d*)



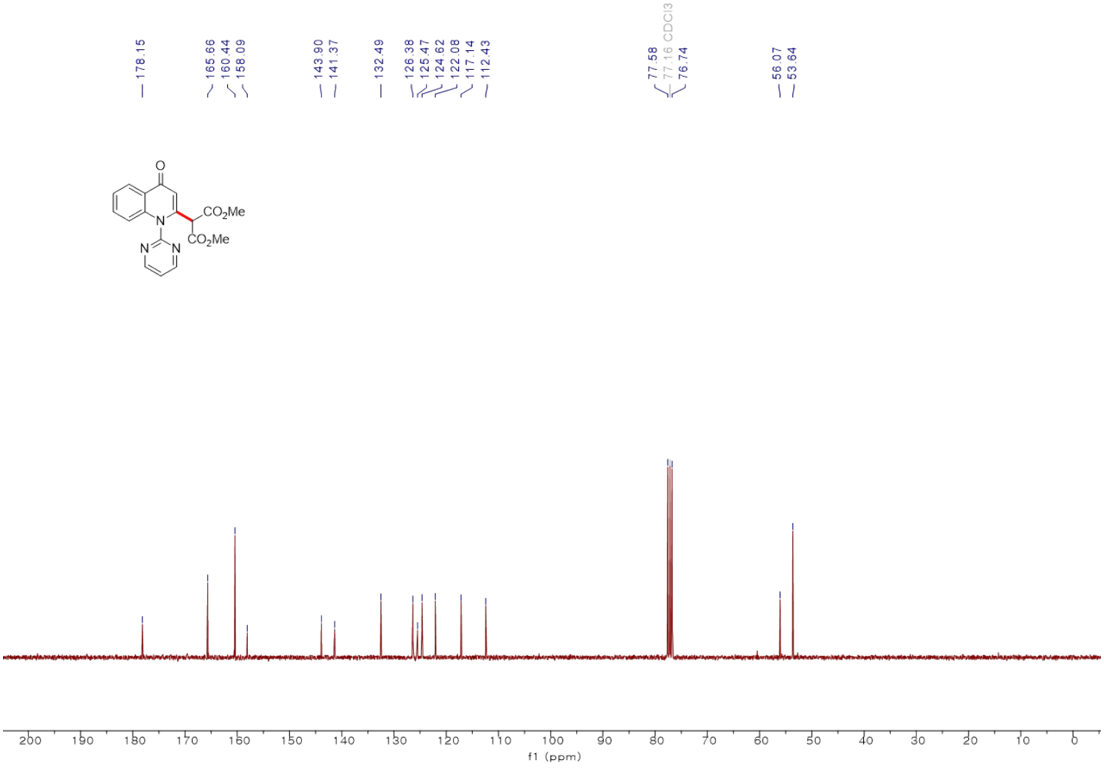
^{1}H NMR of **3m** (300 MHz, Chloroform-*d*)



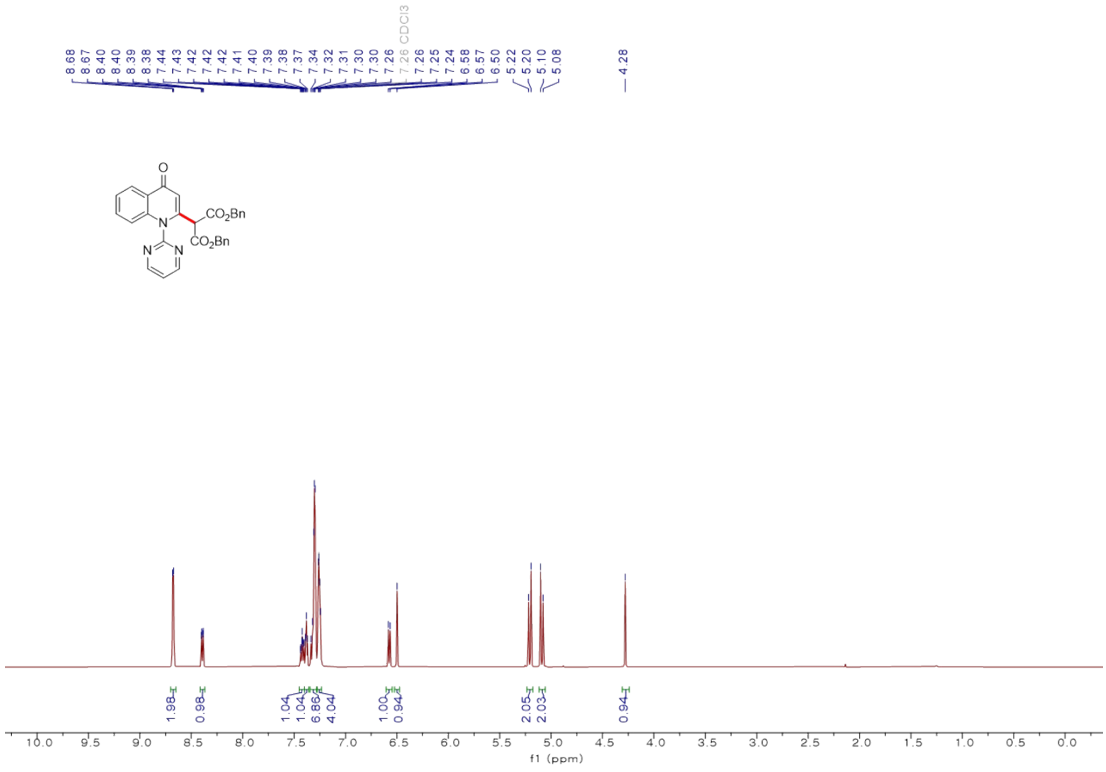
^{13}C NMR of **3m** (75 MHz, Chloroform-*d*)



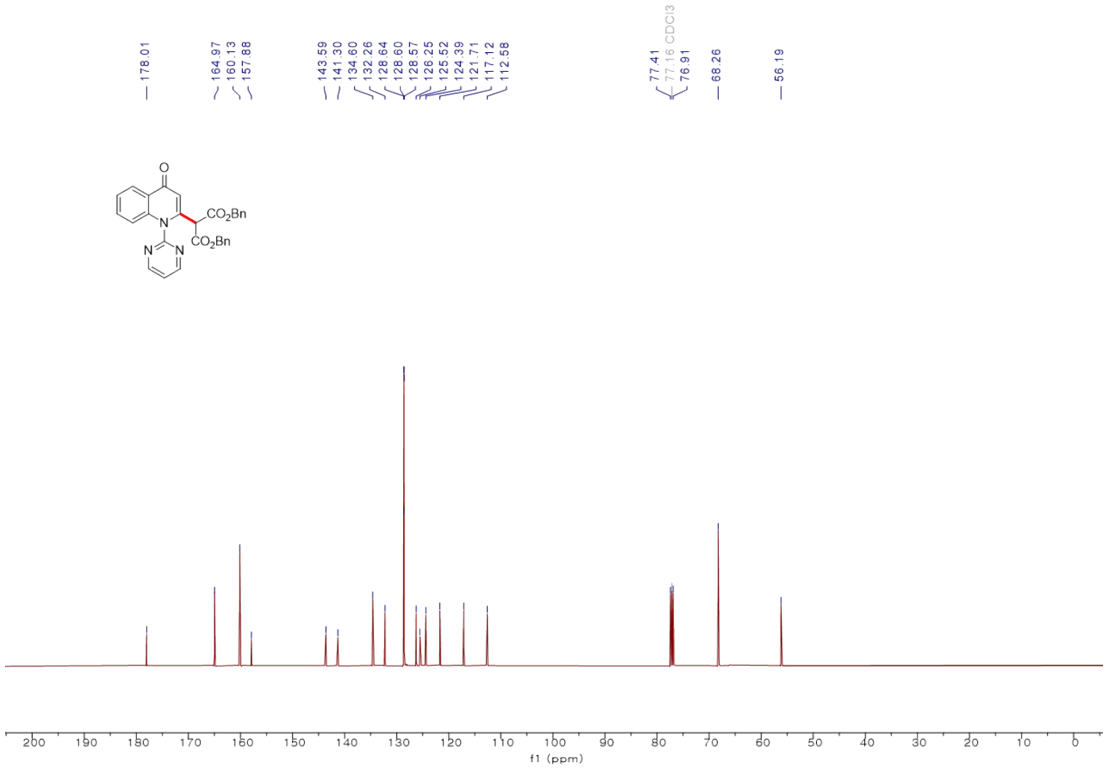
^{1}H NMR of **3n** (300 MHz, Chloroform-*d*)



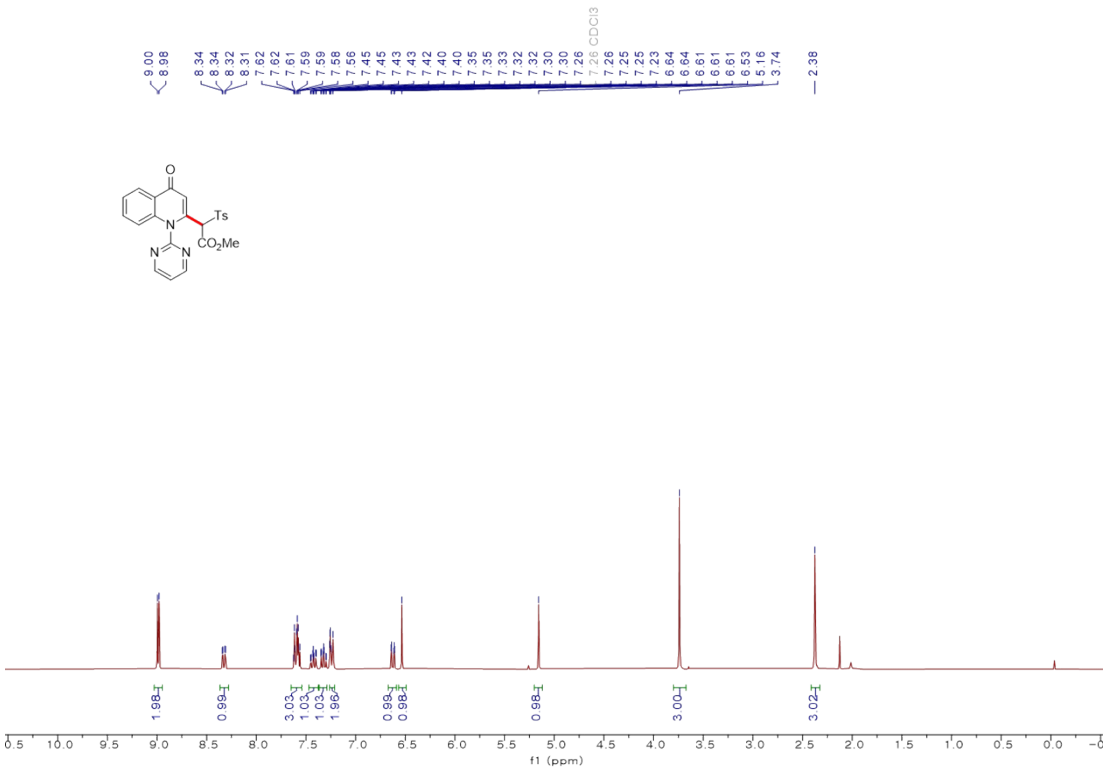
^{13}C NMR of **3n** (75 MHz, Chloroform-*d*)



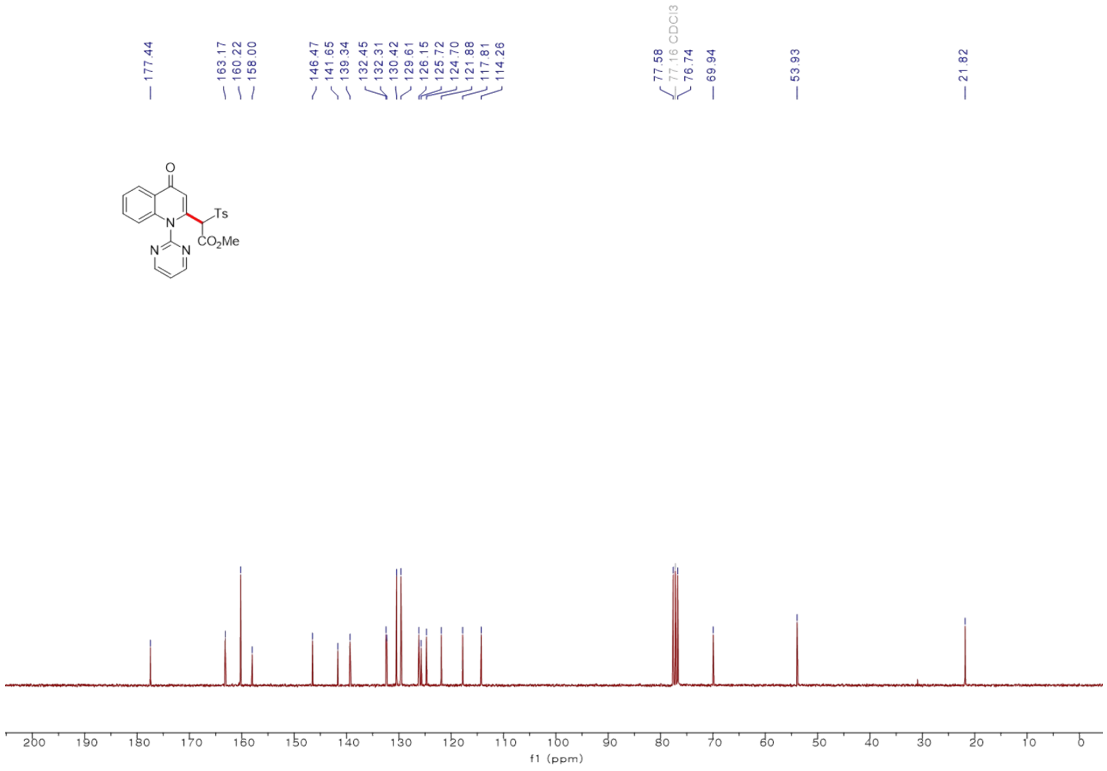
^{1}H NMR of **3o** (300 MHz, Chloroform-*d*)



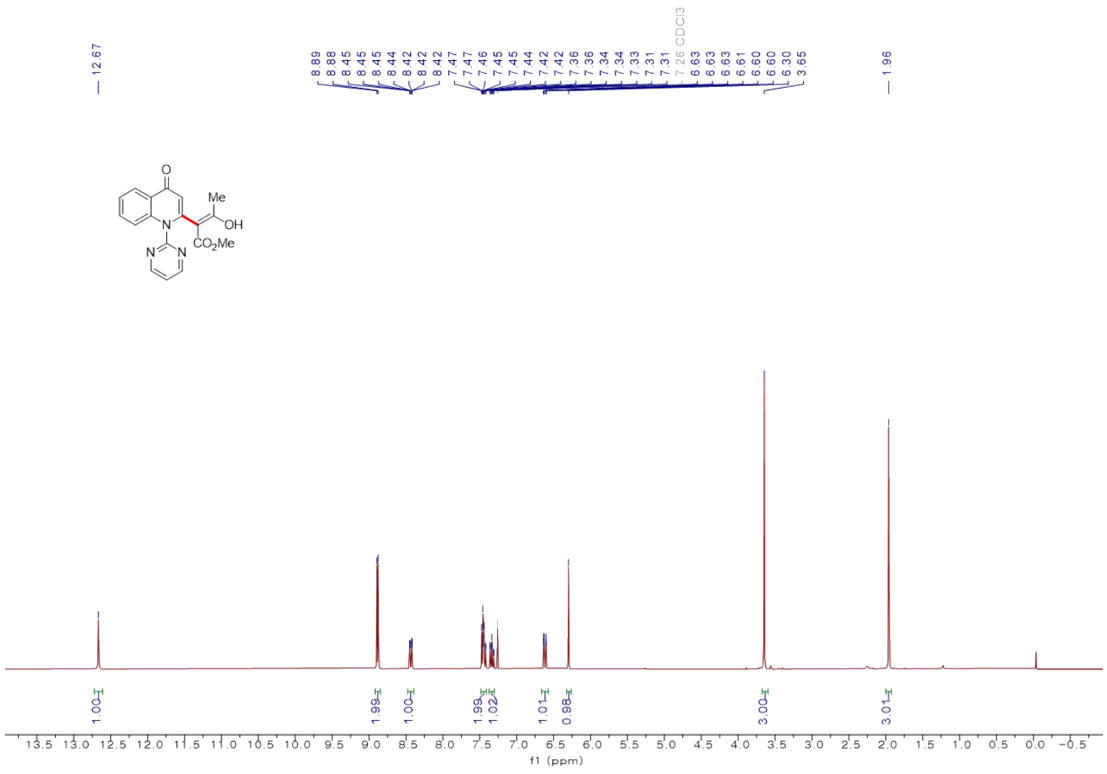
^{13}C NMR of **3o** (75 MHz, Chloroform-*d*)



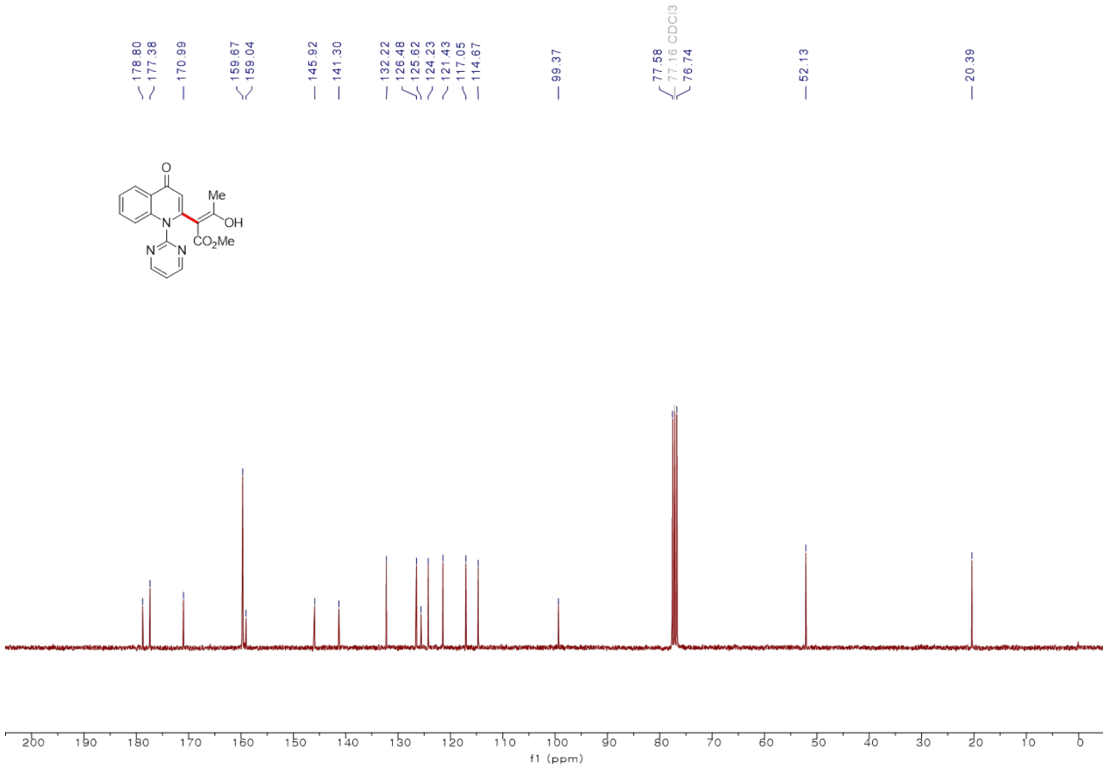
^{1}H NMR of **3p** (300 MHz, Chloroform-*d*)



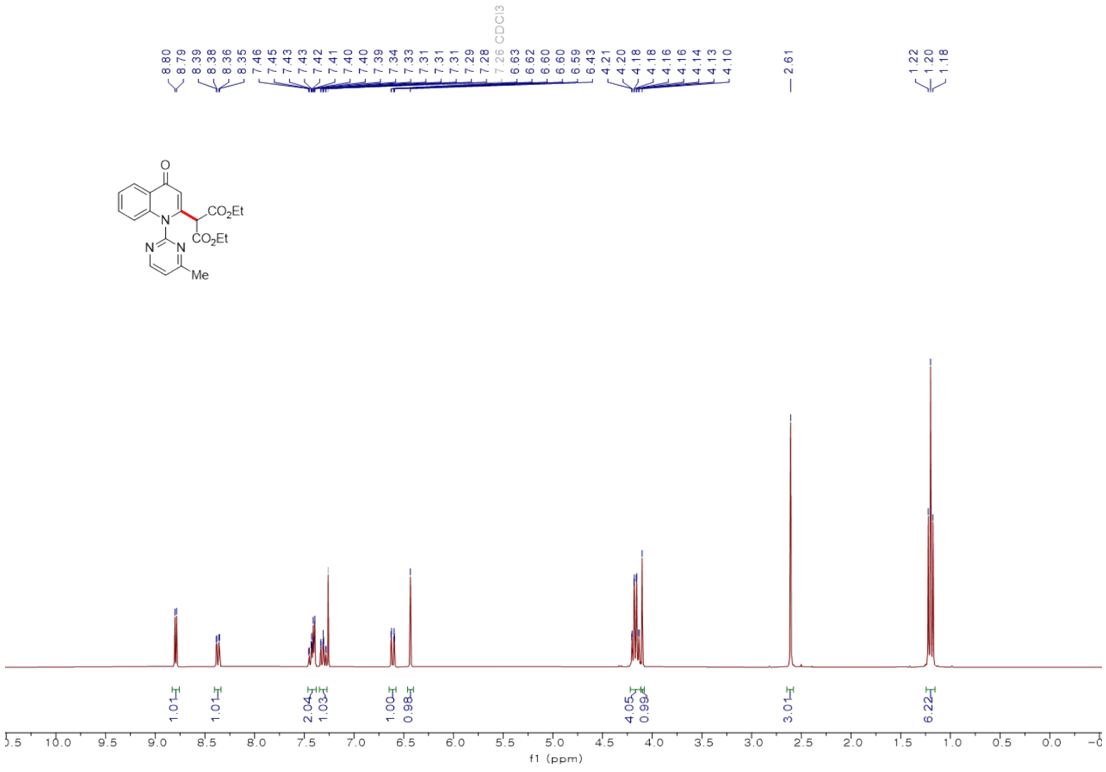
^{13}C NMR of **3p** (75 MHz, Chloroform-*d*)



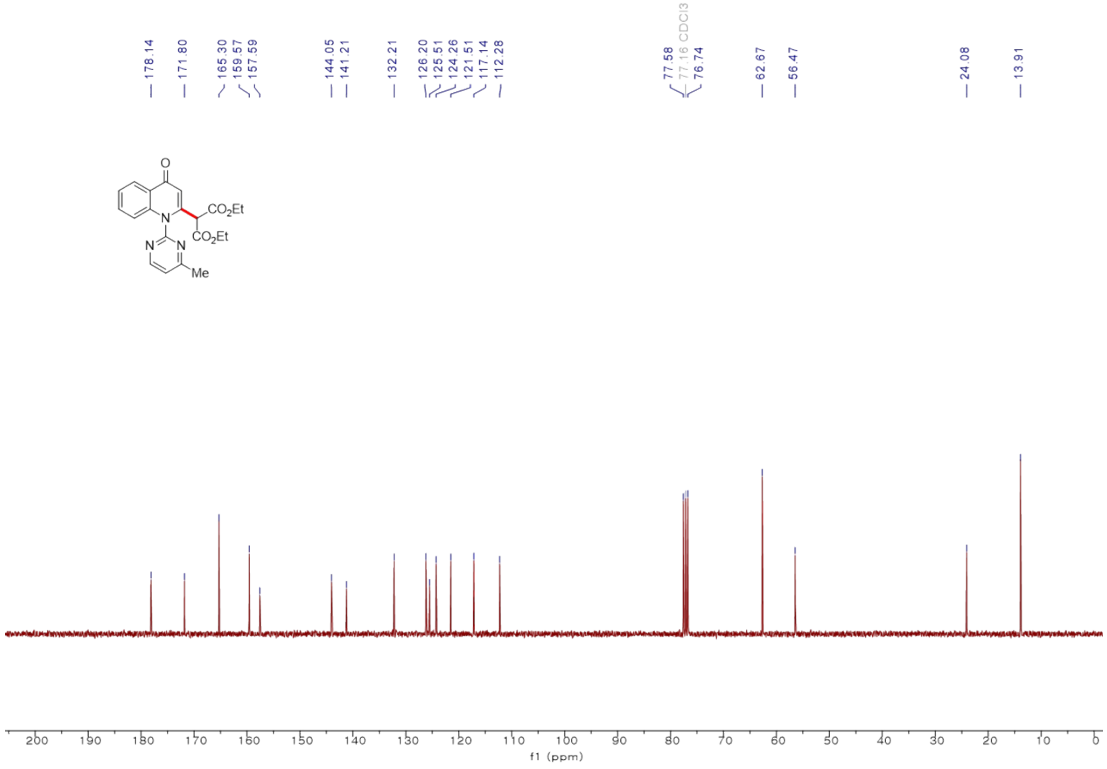
^{1}H NMR of **3q** (300 MHz, Chloroform-*d*)



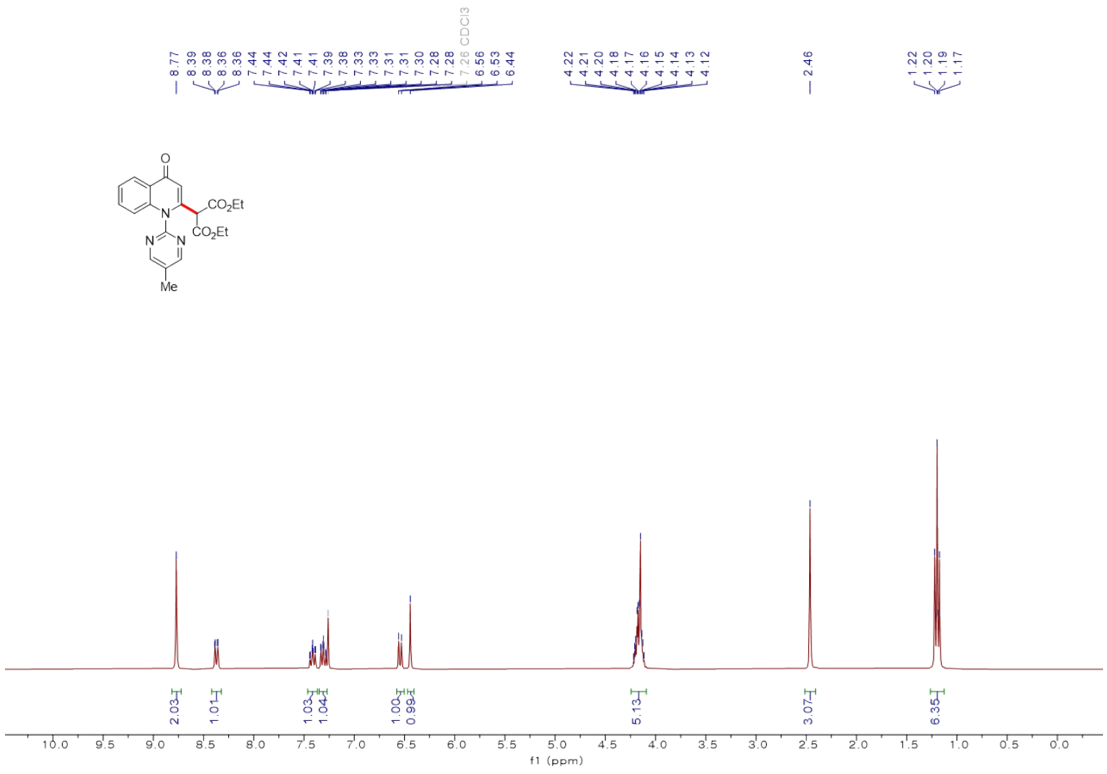
^{13}C NMR of **3q** (75 MHz, Chloroform-*d*)



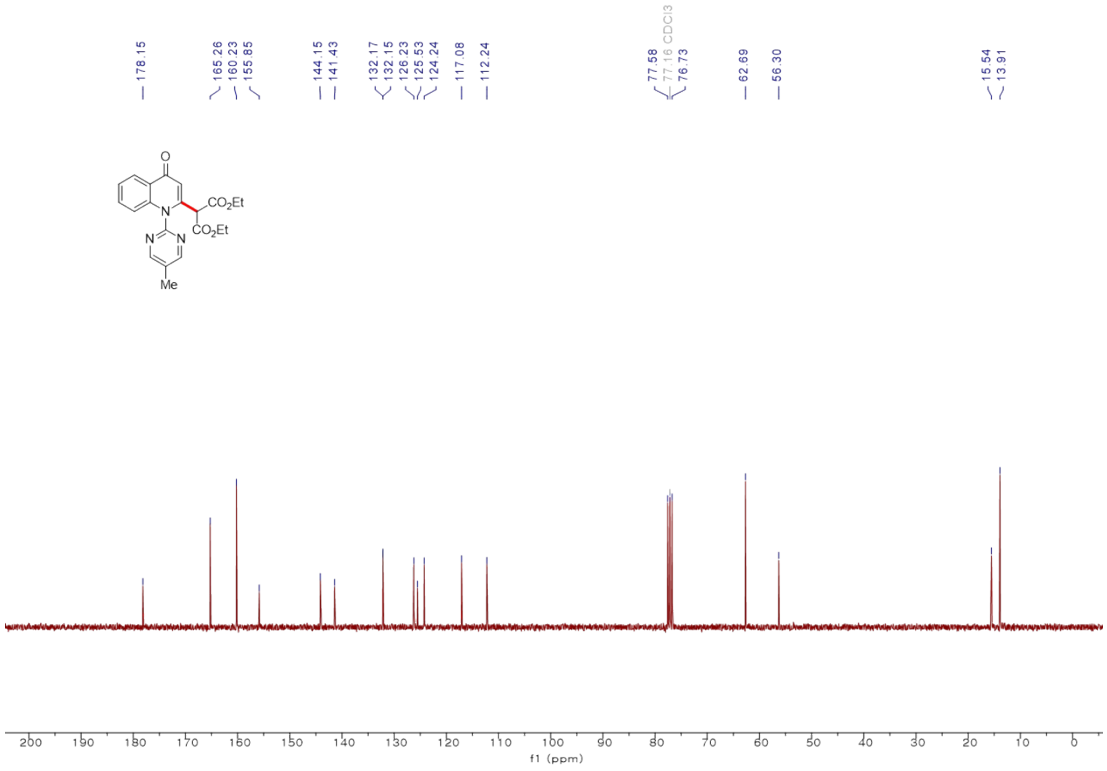
^{1}H NMR of **3s** (300 MHz, Chloroform-*d*)



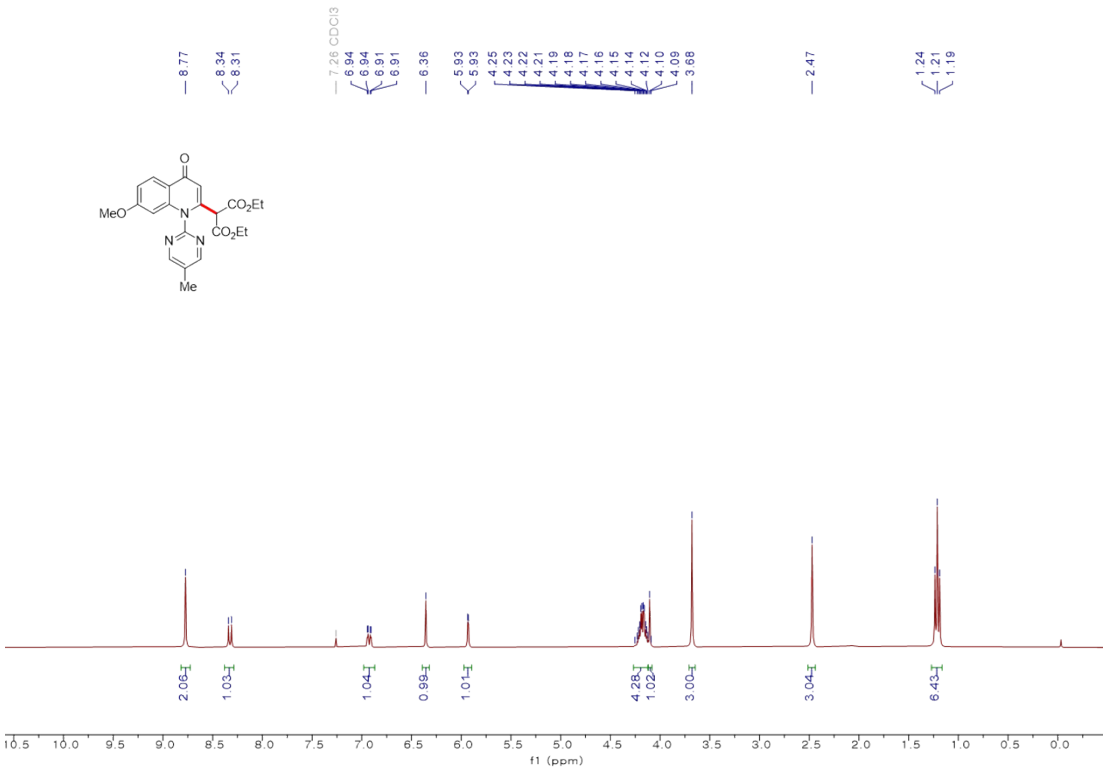
^{13}C NMR of **3s** (75 MHz, Chloroform-*d*)



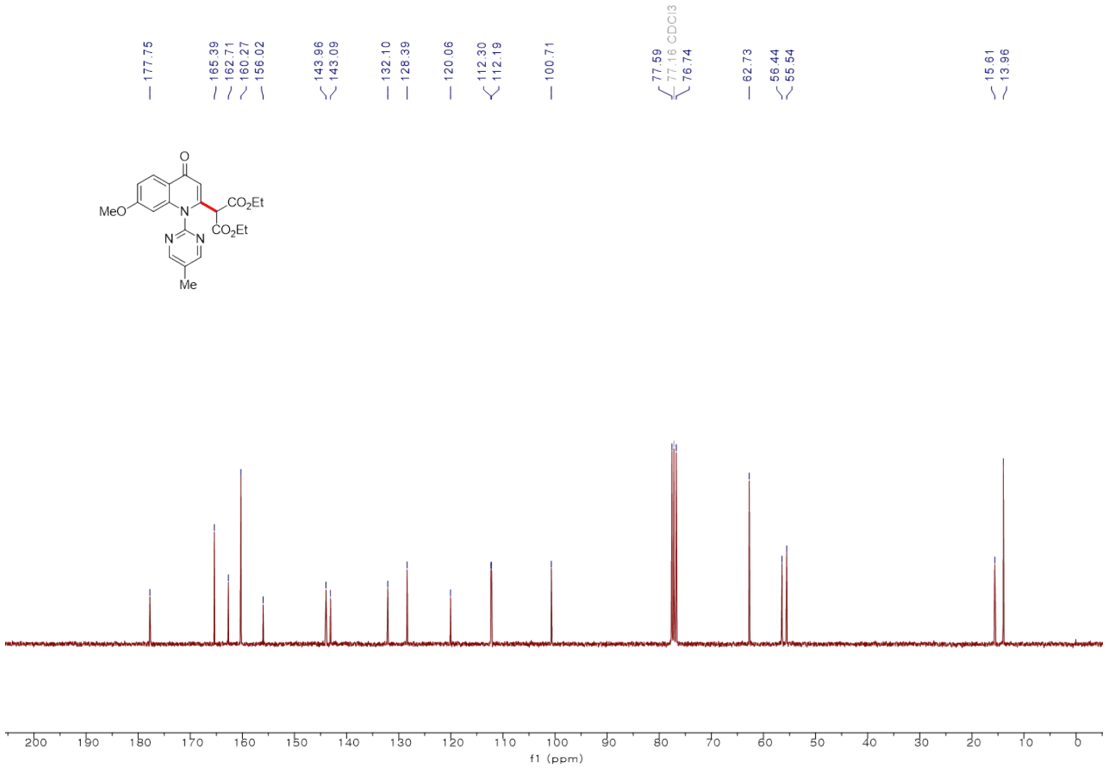
^{1}H NMR of **3t** (300 MHz, Chloroform-*d*)



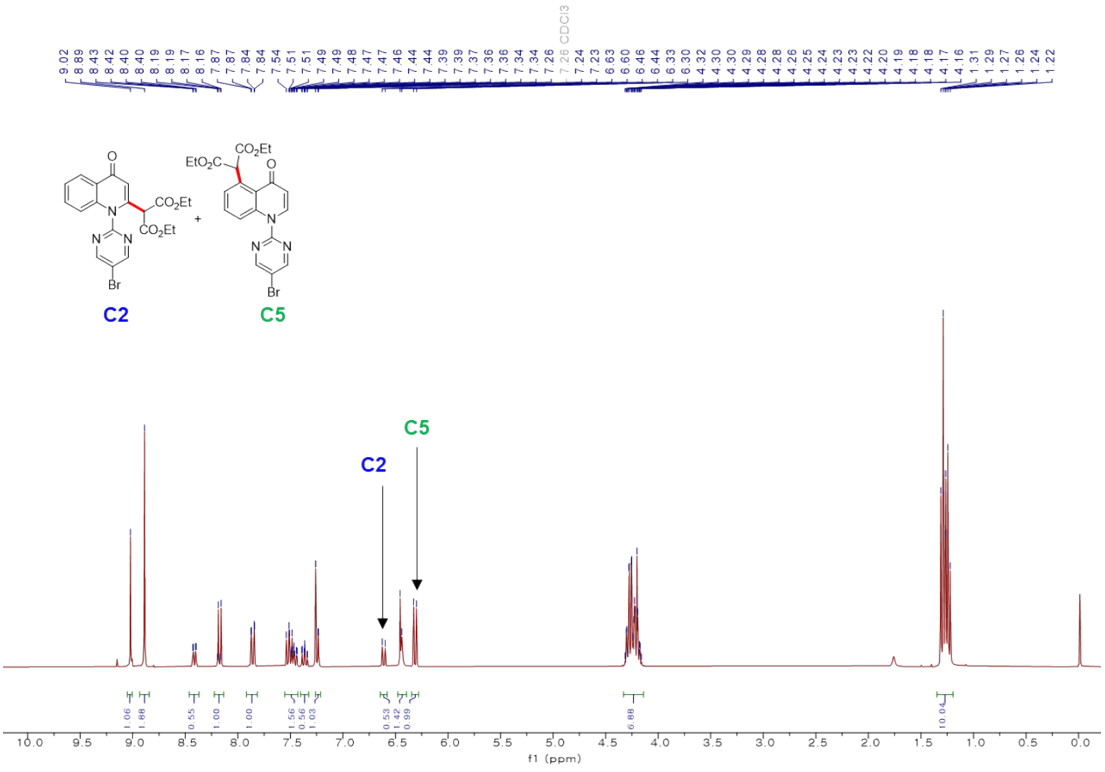
^{13}C NMR of **3t** (75 MHz, Chloroform-*d*)



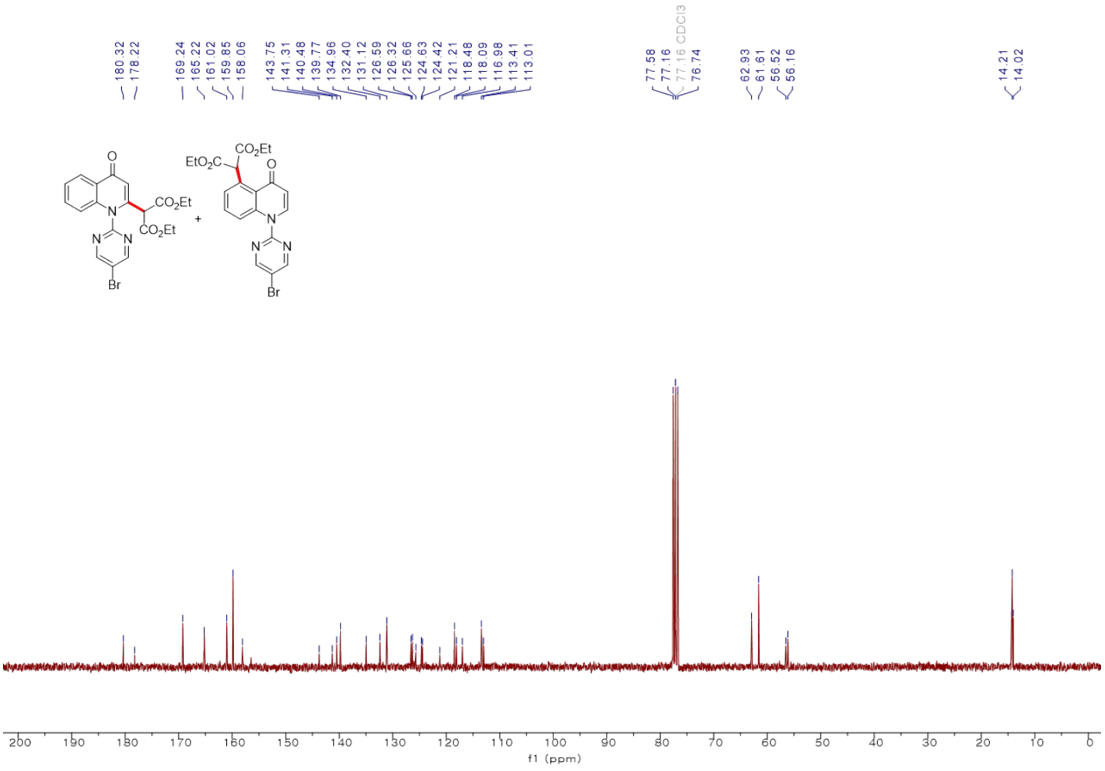
^{1}H NMR of **3u** (300 MHz, Chloroform-*d*)



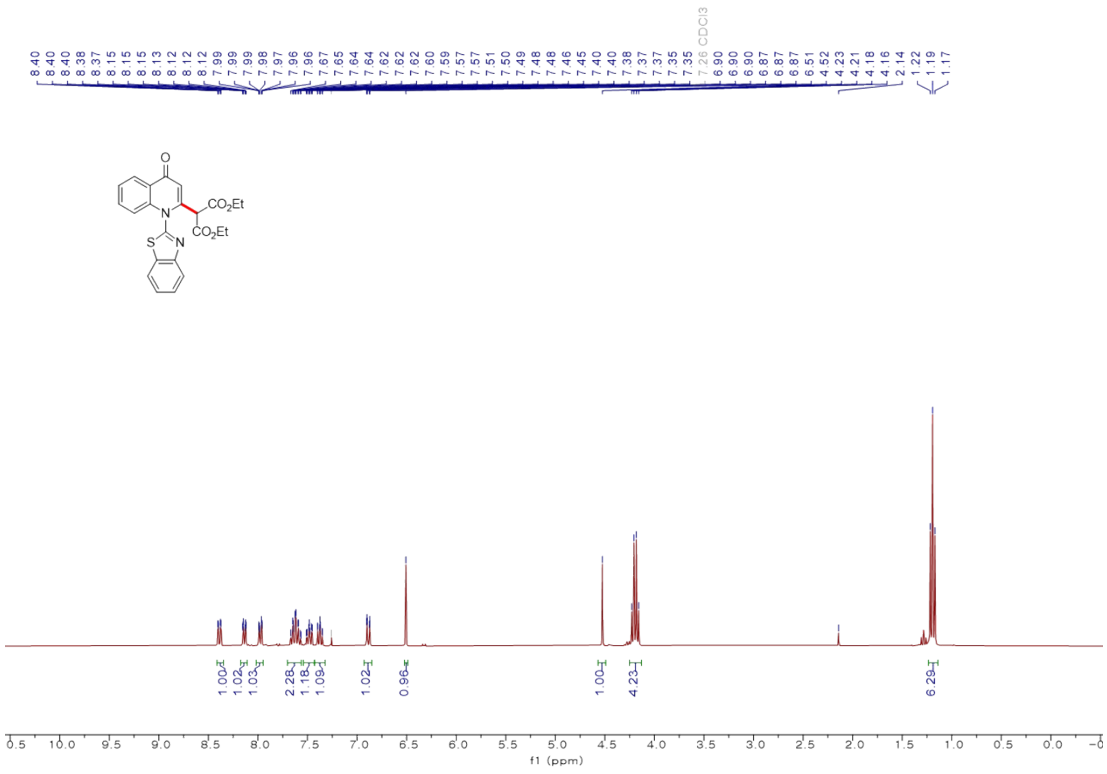
^{13}C NMR of **3u** (75 MHz, Chloroform-*d*)



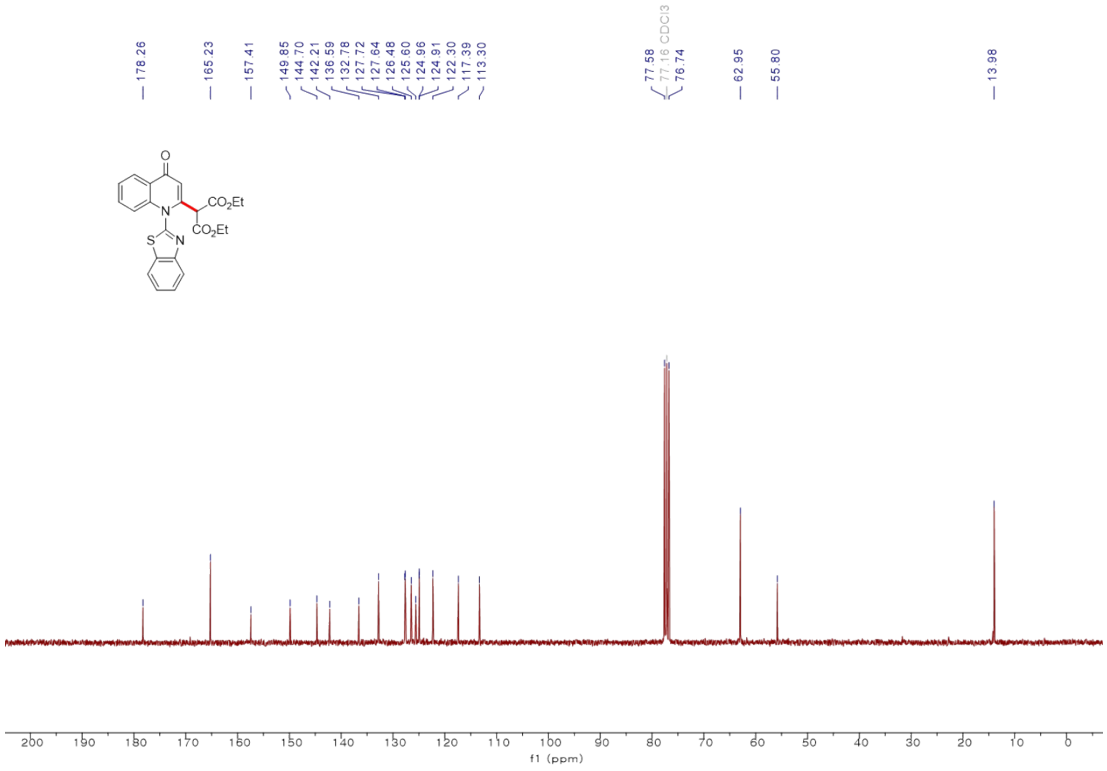
^{1}H NMR of mixture of **3v** and **3v'** (300 MHz, Chloroform-*d*)



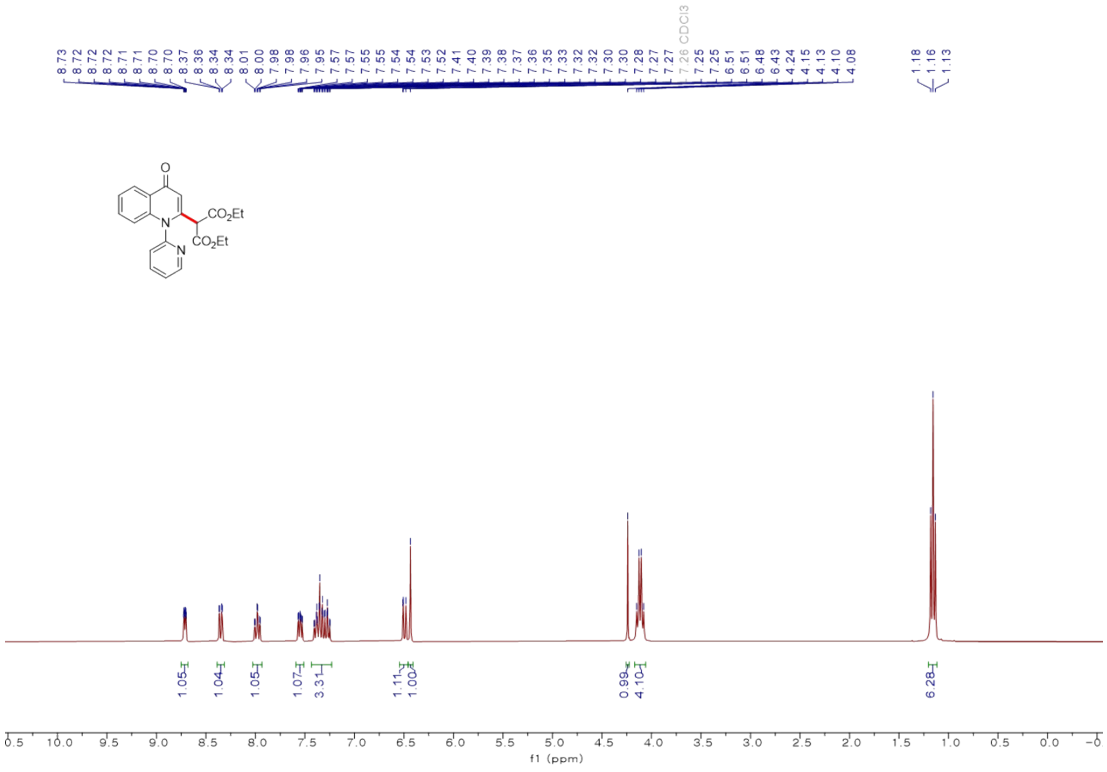
^{13}C NMR of mixture of **3v** and **3v'** (75 MHz, Chloroform-*d*)



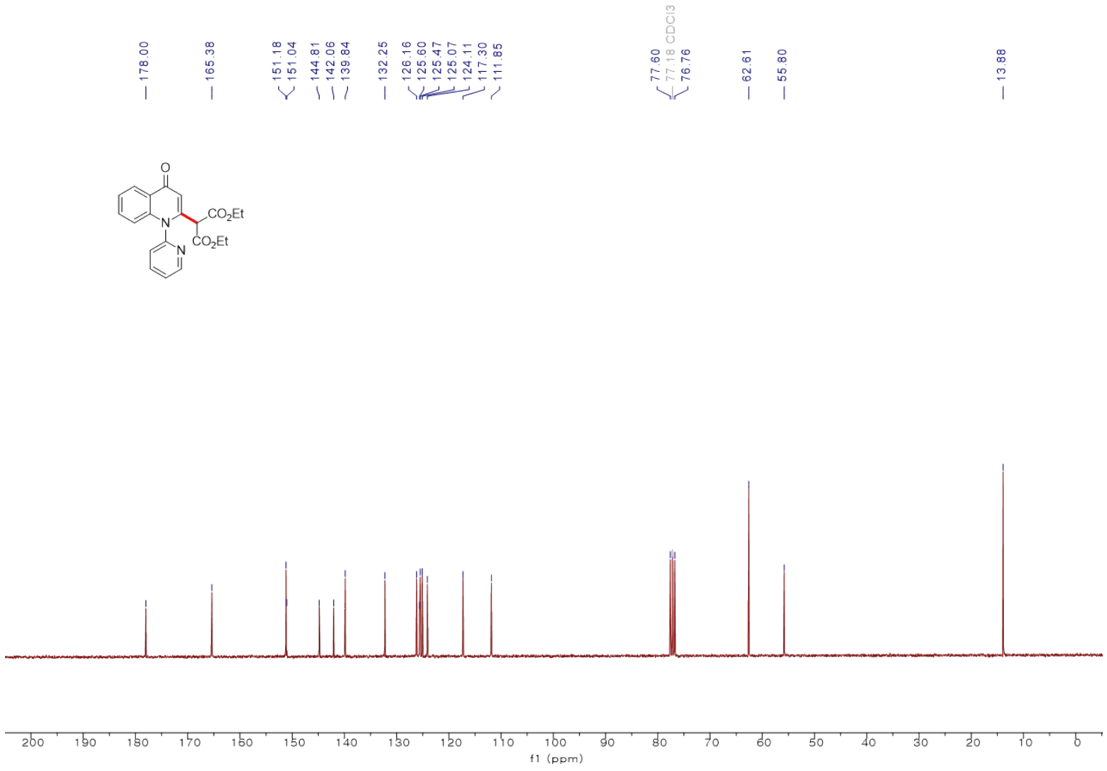
^{1}H NMR of **3w** (300 MHz, Chloroform-*d*)



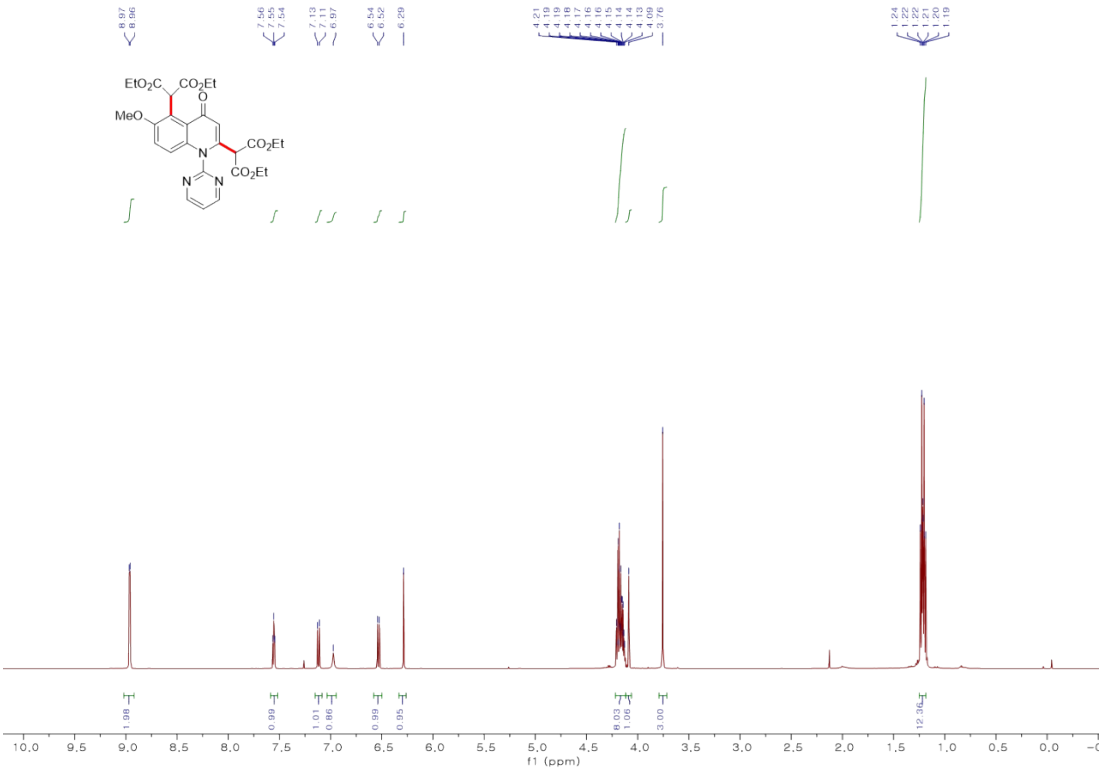
^{13}C NMR of **3w** (75 MHz, Chloroform-*d*)



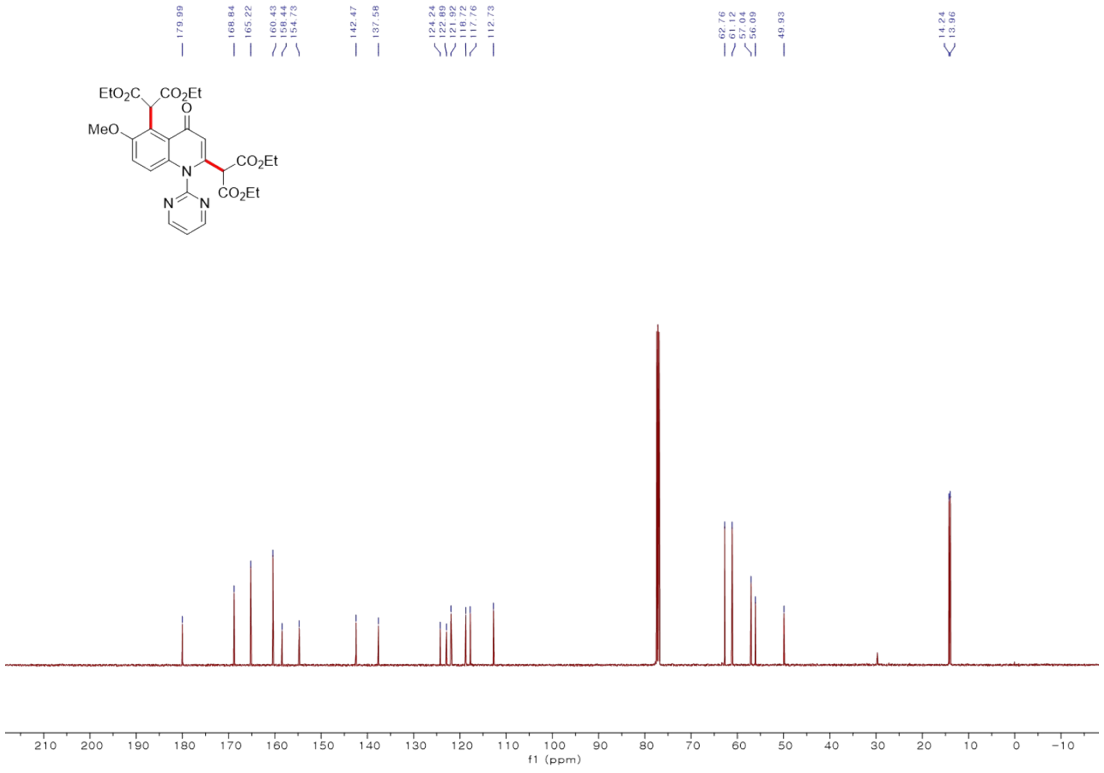
^{1}H NMR of **3x** (300 MHz, Chloroform-*d*)



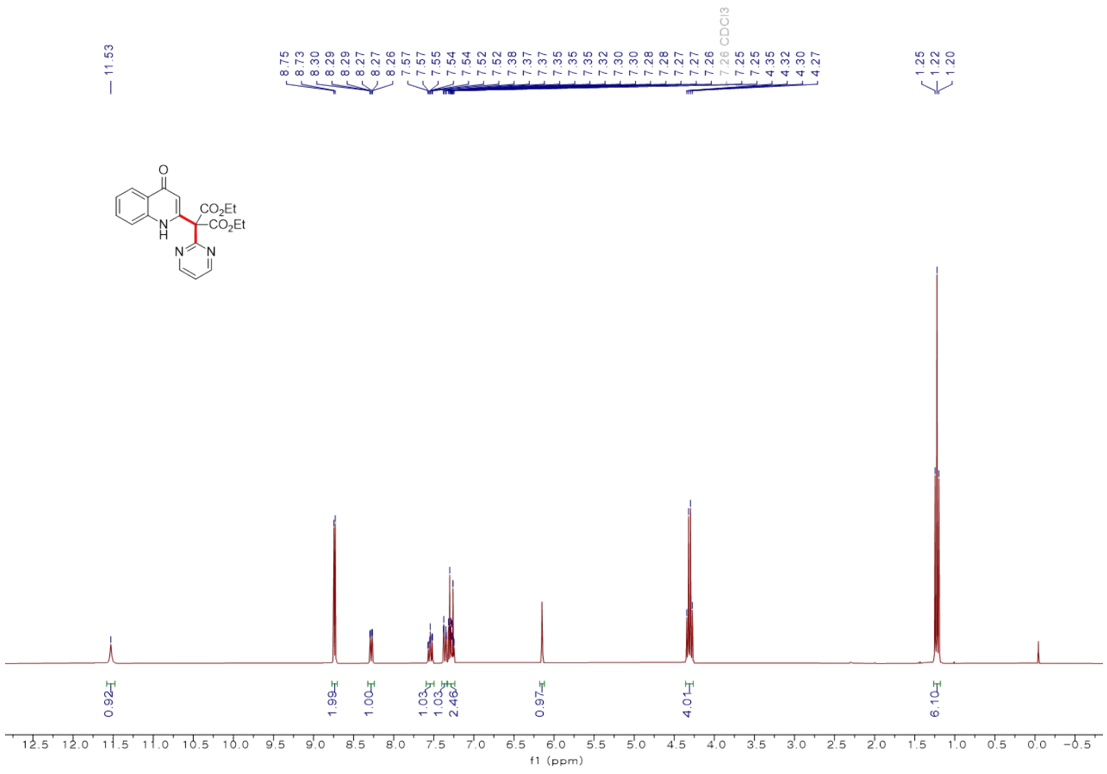
^{13}C NMR of **3x** (75 MHz, Chloroform-*d*)



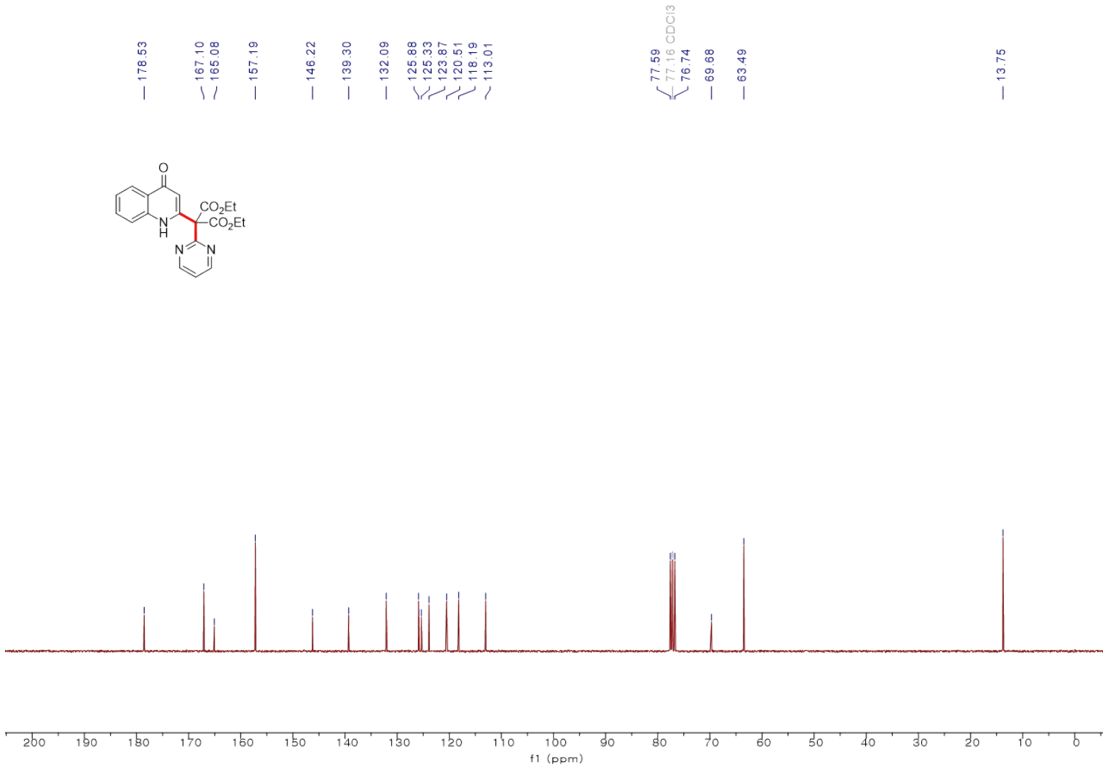
^{1}H NMR of **3y** (500 MHz, Chloroform-*d*)



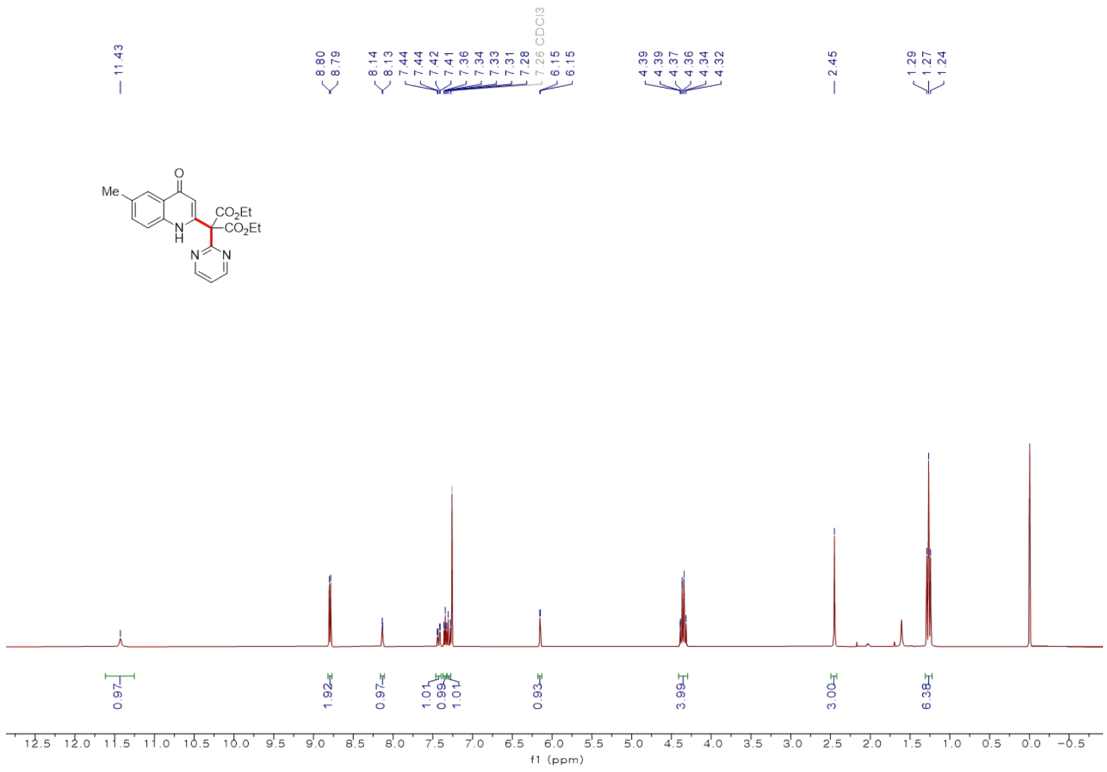
^{13}C NMR of **3y** (126 MHz, Chloroform-*d*)



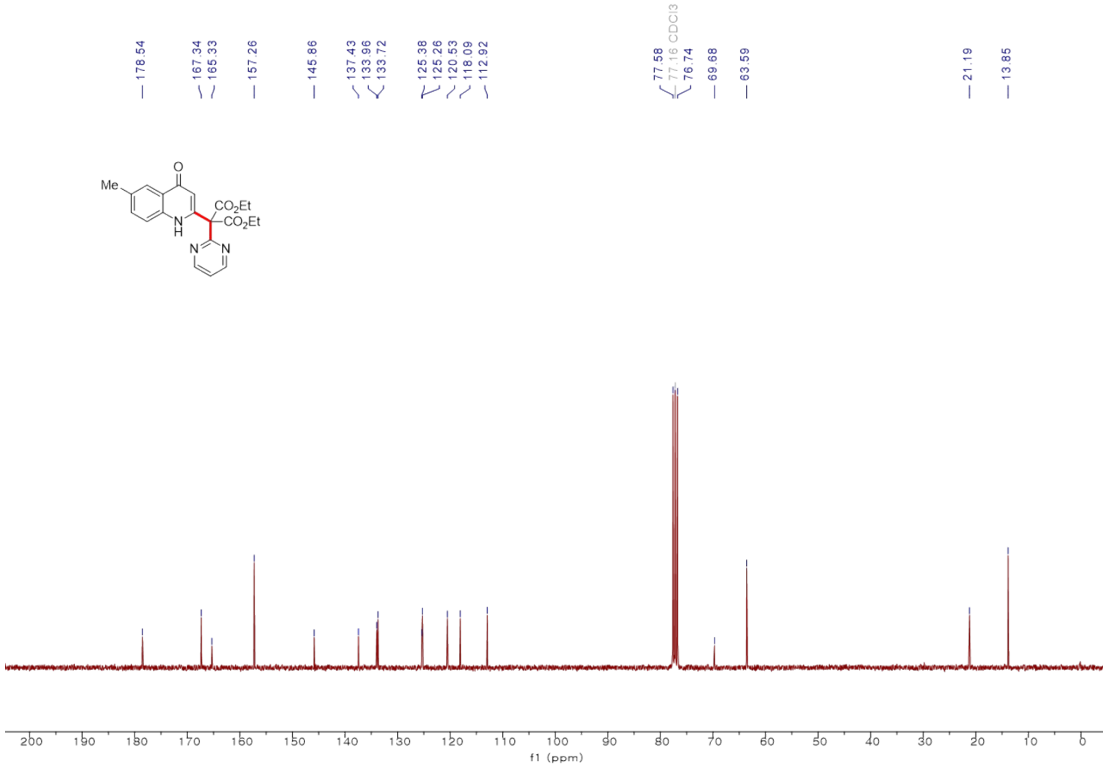
^{1}H NMR of **4a** (300 MHz, Chloroform-*d*)



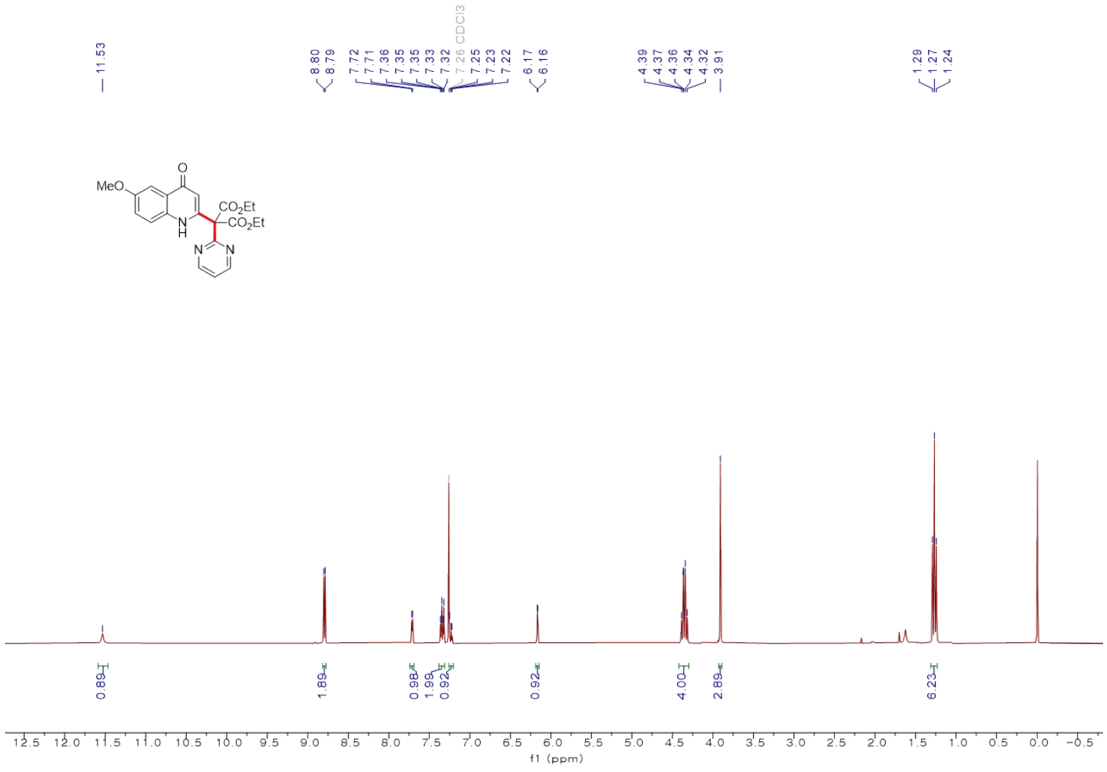
^{13}C NMR of **4a** (75 MHz, Chloroform-*d*)



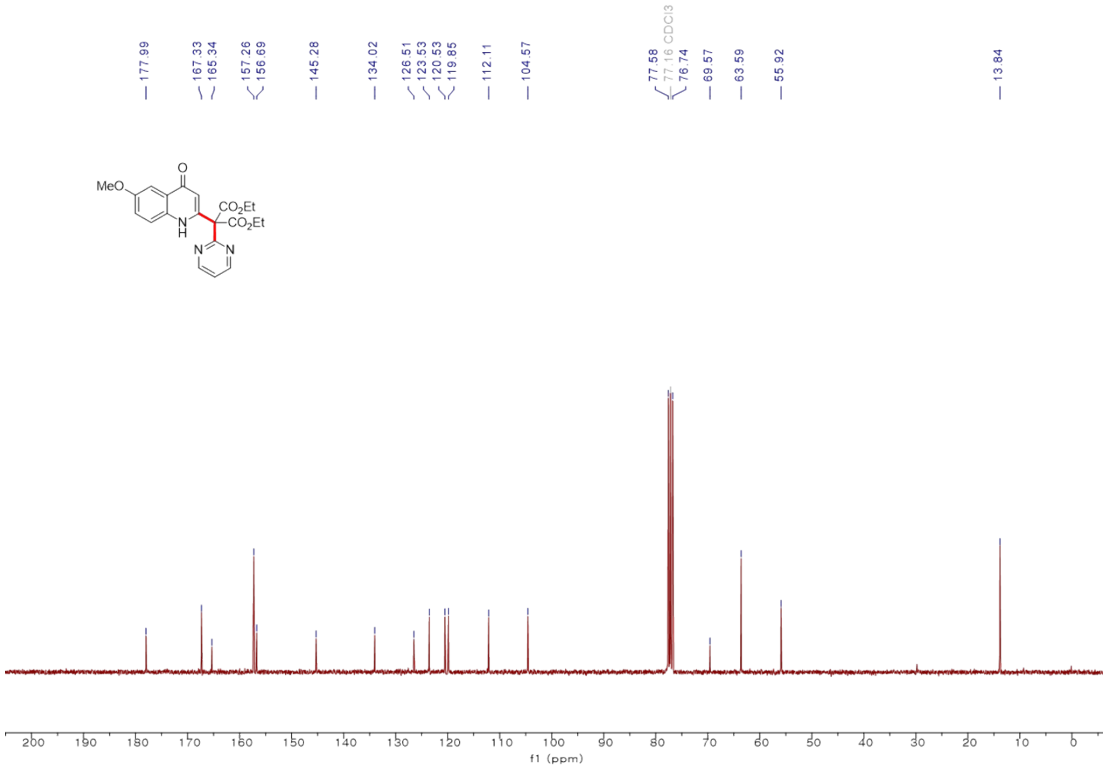
^{1}H NMR of **4b** (300 MHz, Chloroform-*d*)



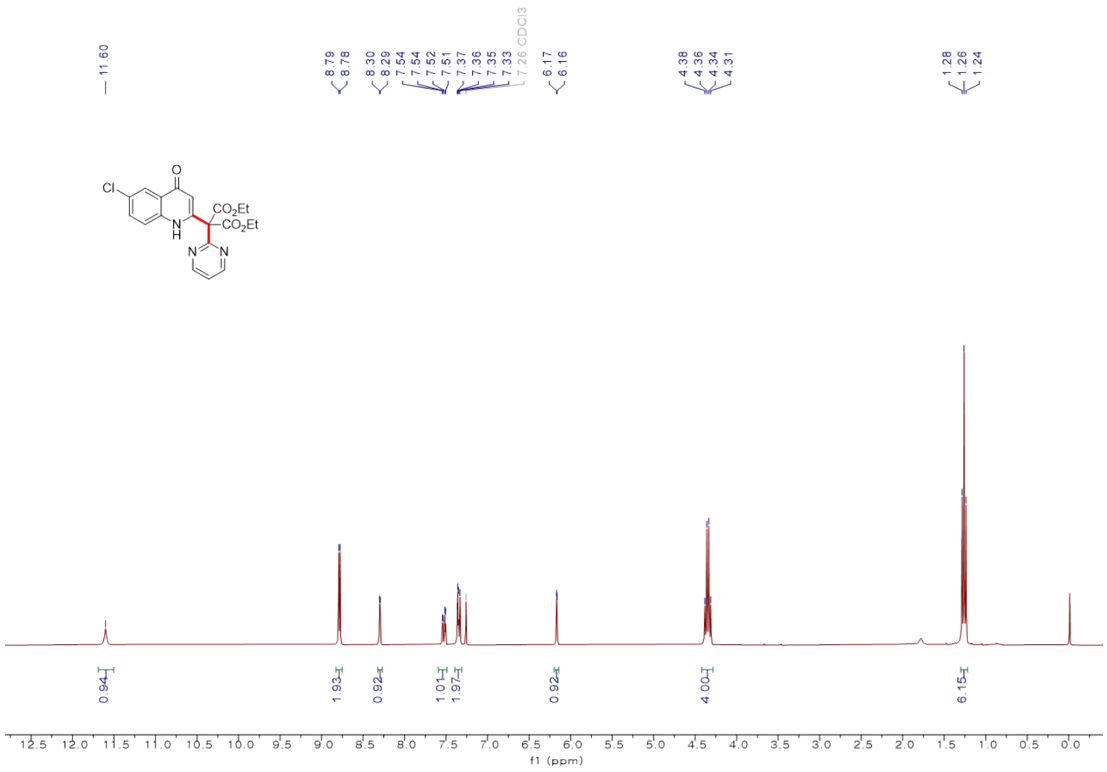
^{13}C NMR of **4b** (75 MHz, Chloroform-*d*)



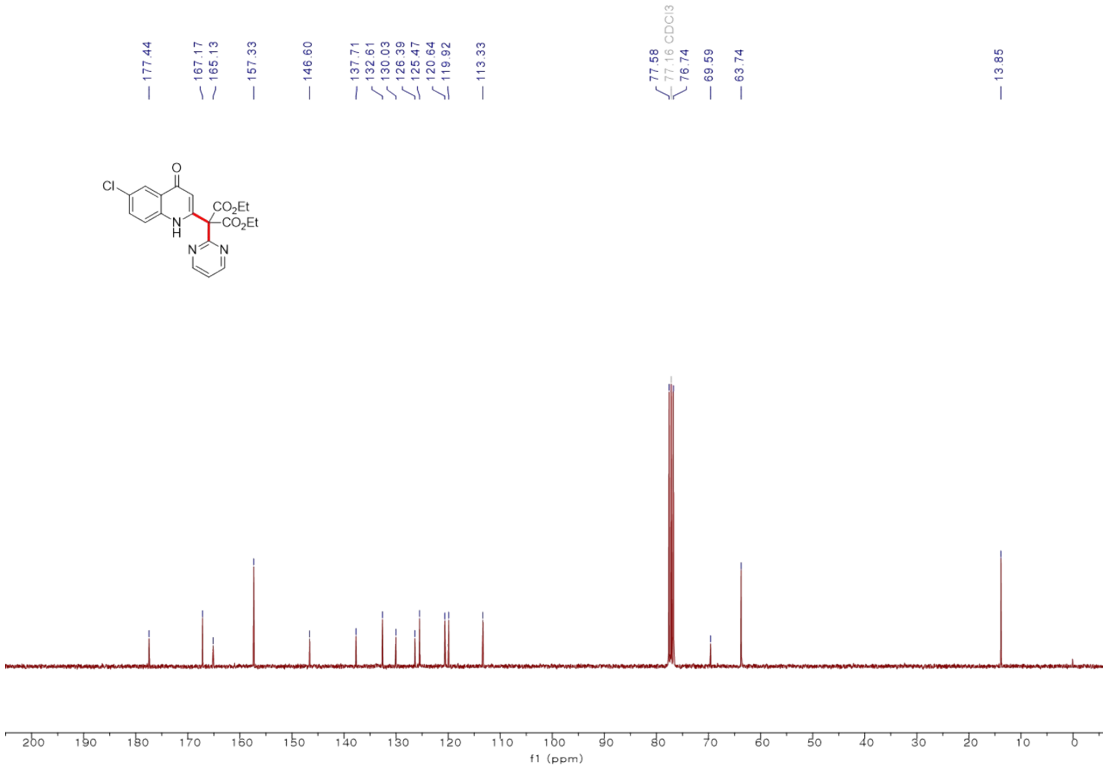
^{1}H NMR of **4c** (300 MHz, Chloroform-*d*)



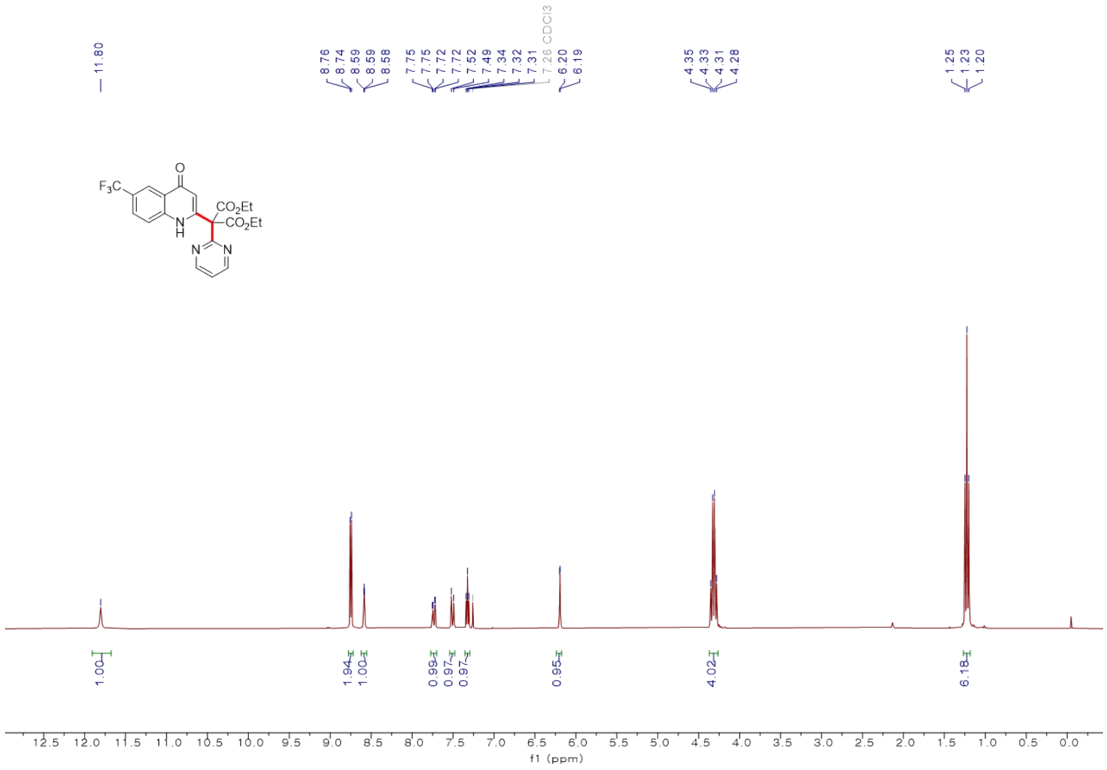
^{13}C NMR of **4c** (75 MHz, Chloroform-*d*)



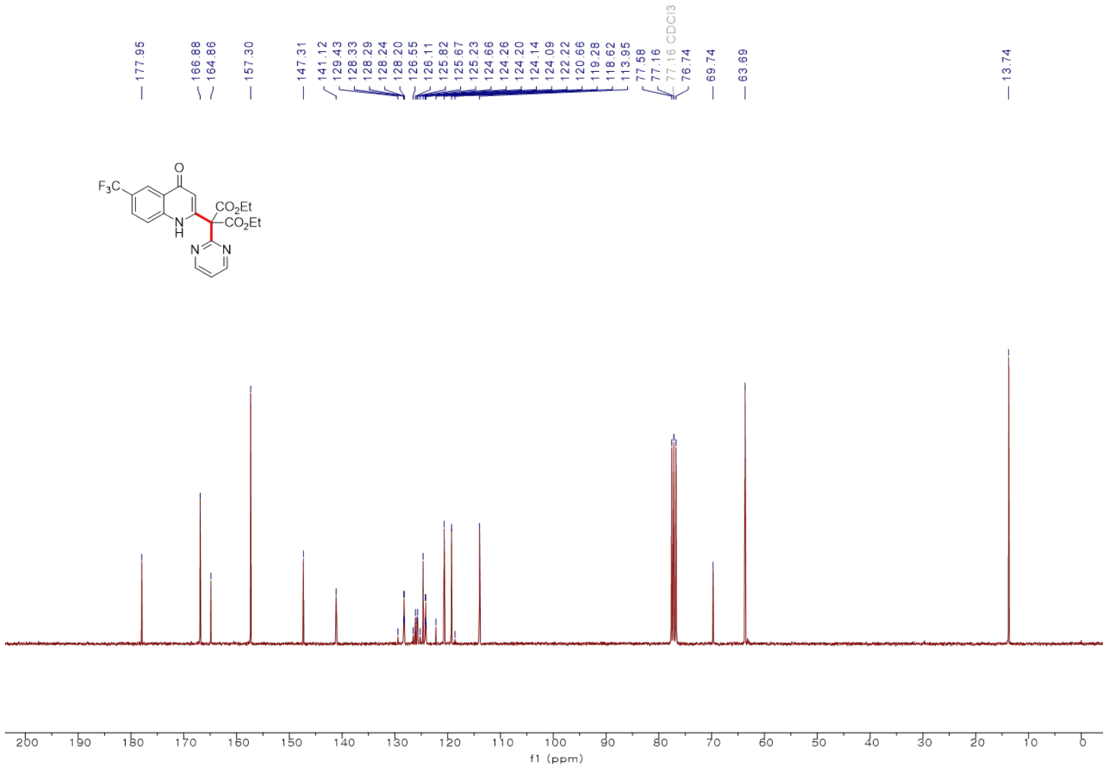
^{1}H NMR of **4d** (300 MHz, Chloroform-*d*)



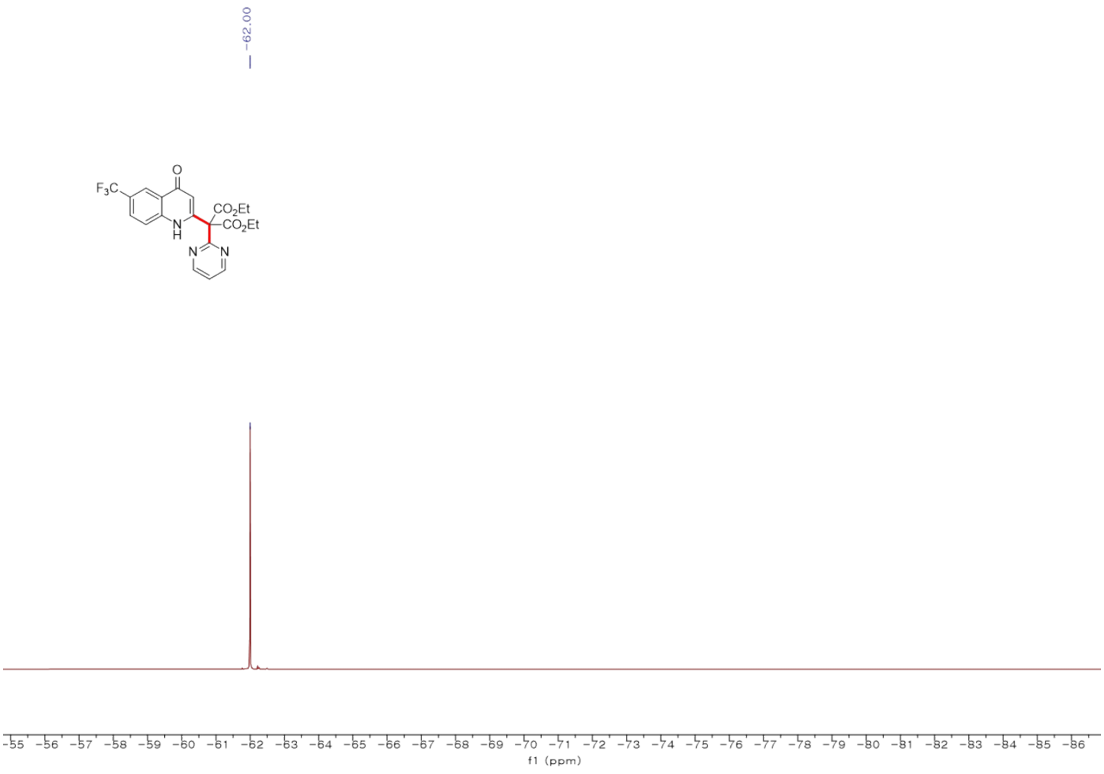
^{13}C NMR of **4d** (75 MHz, Chloroform-*d*)



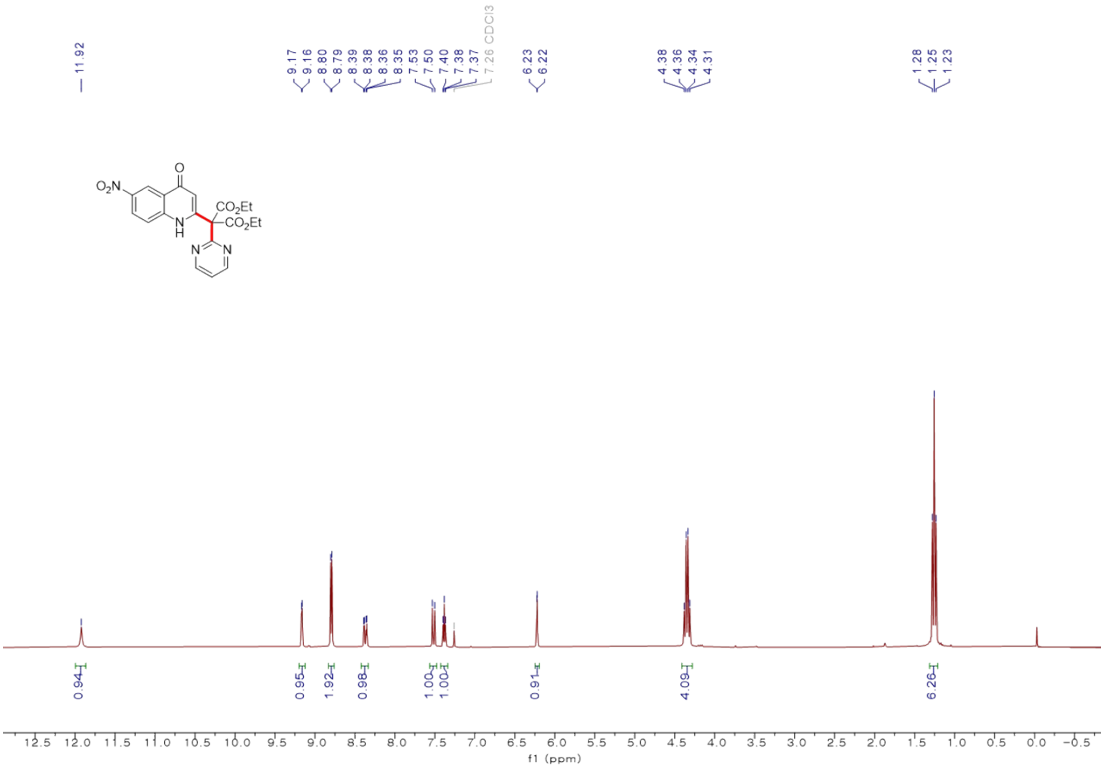
^{1}H NMR of **4e** (300 MHz, Chloroform-*d*)



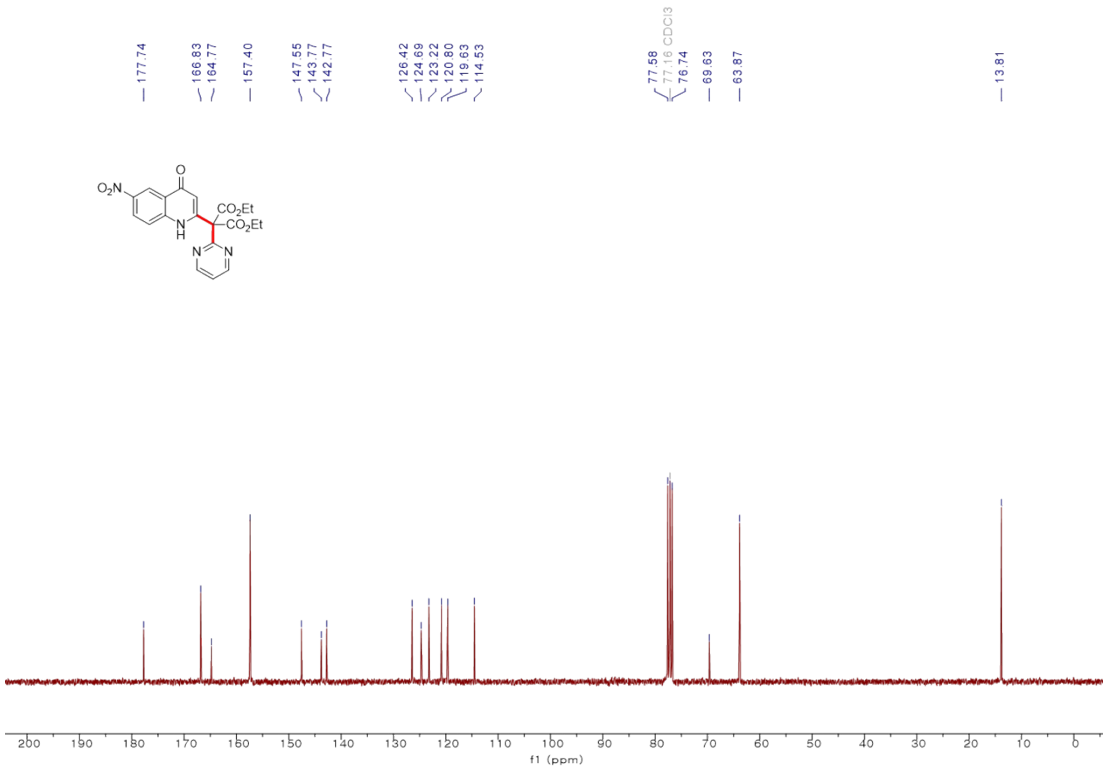
^{13}C NMR of **4e** (75 MHz, Chloroform-*d*)



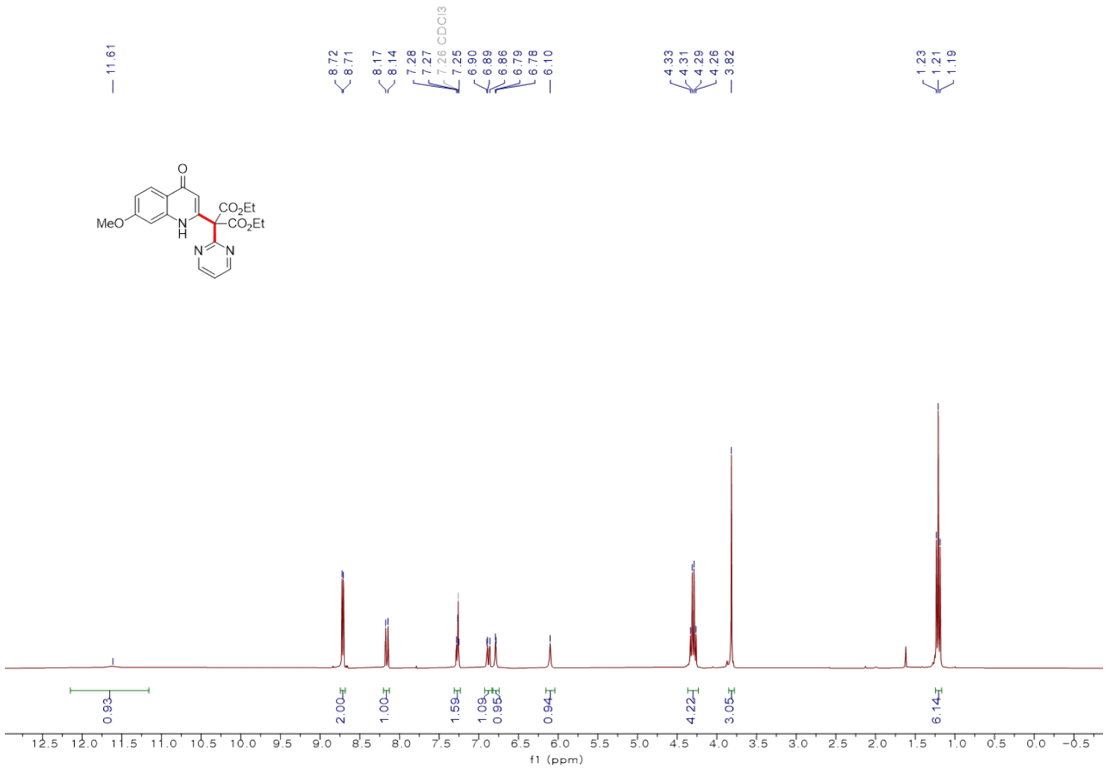
^{19}F NMR of **4e** (471MHz, Chloroform-*d*)



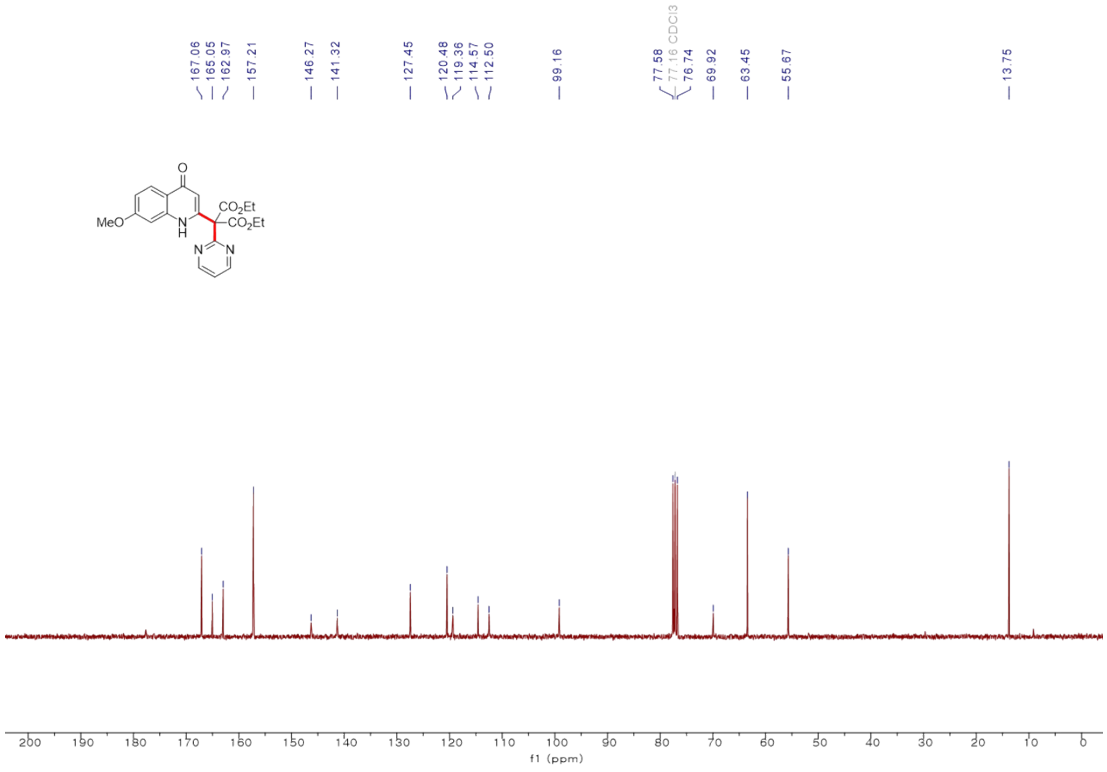
^{1}H NMR of **4f** (300 MHz, Chloroform-*d*)



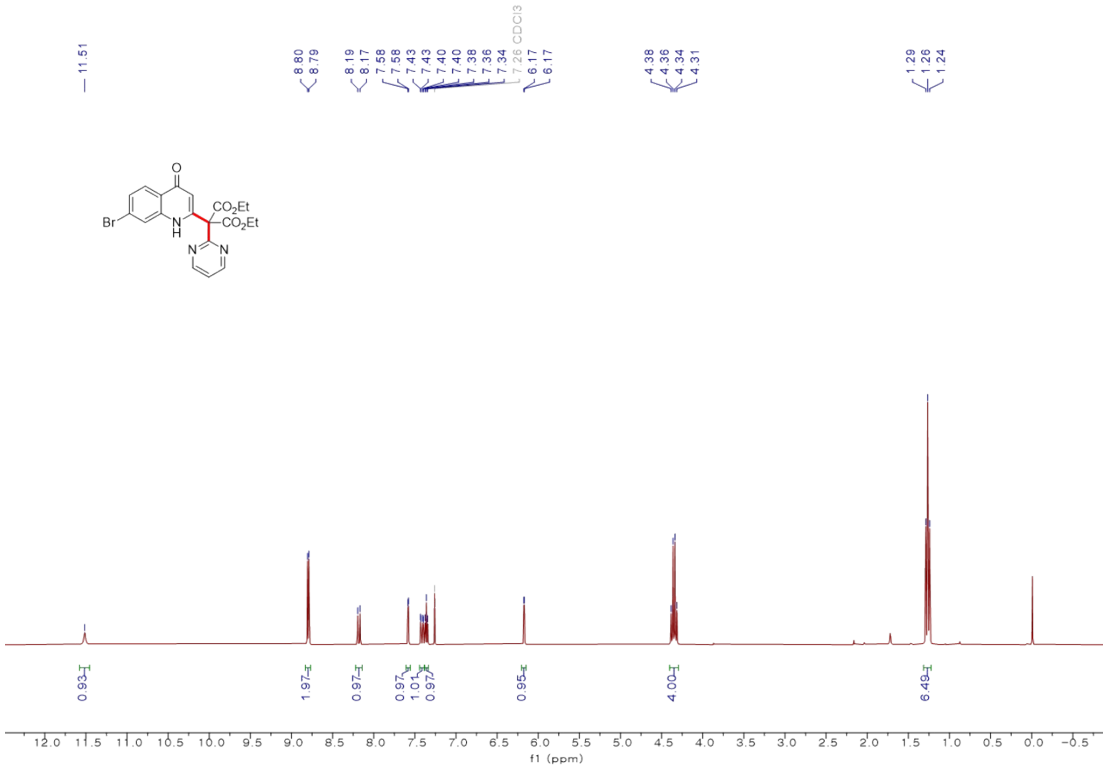
^{13}C NMR of **4f** (75 MHz, Chloroform-*d*)



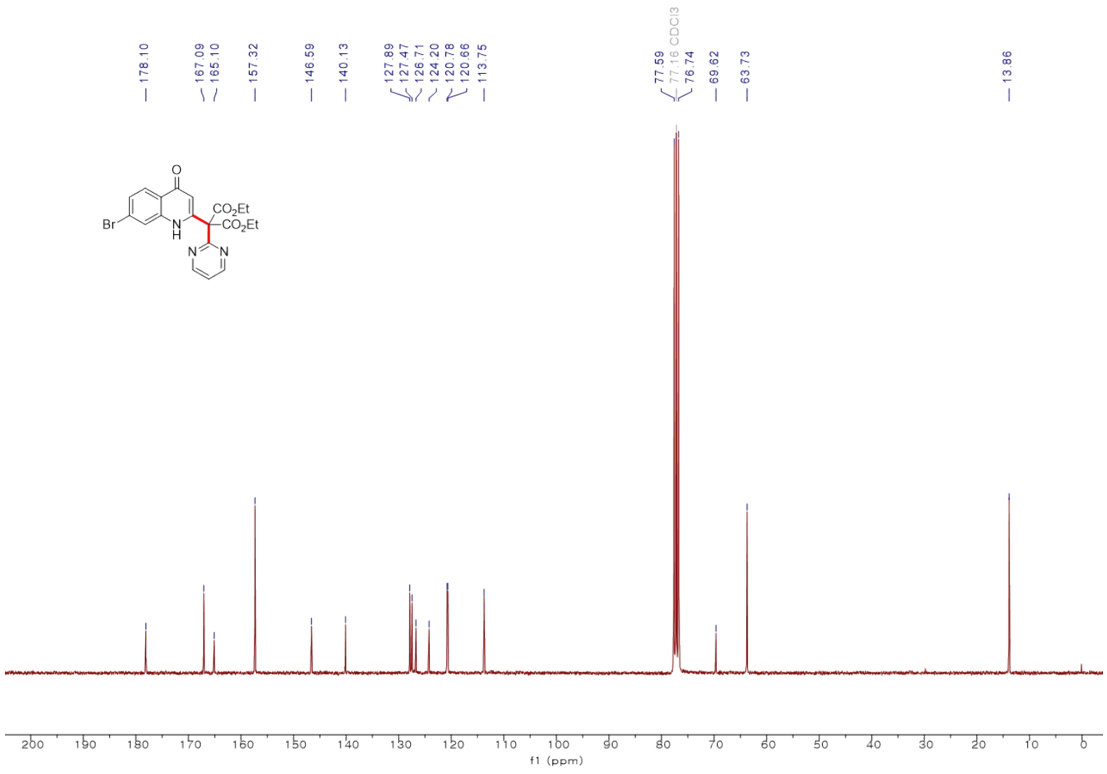
^{1}H NMR of **4g** (300 MHz, Chloroform-*d*)



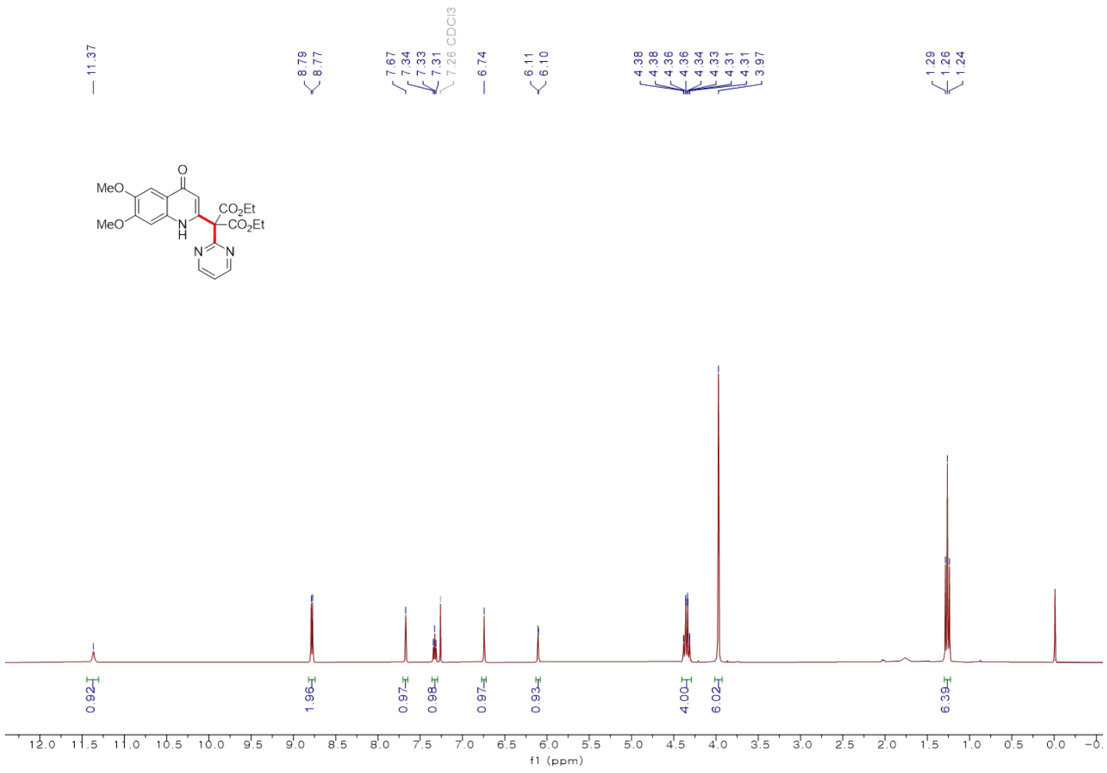
^{13}C NMR of **4g** (75 MHz, Chloroform-*d*)



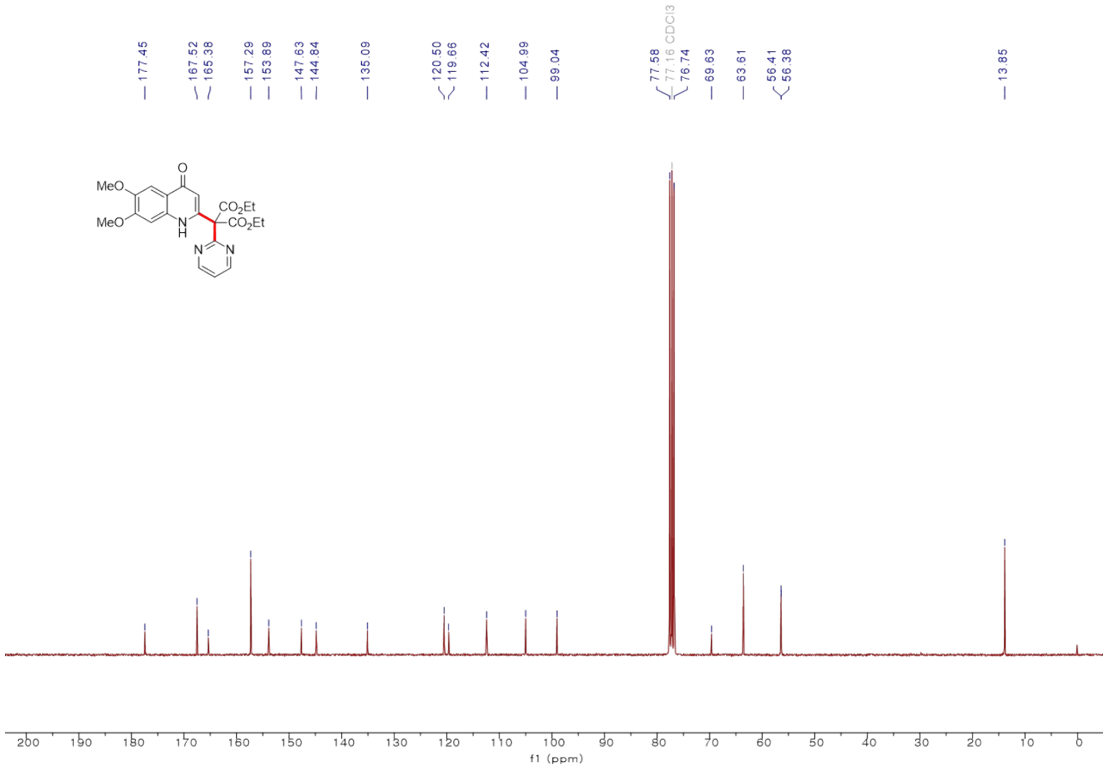
^{1}H NMR of **4h** (300 MHz, Chloroform-*d*)



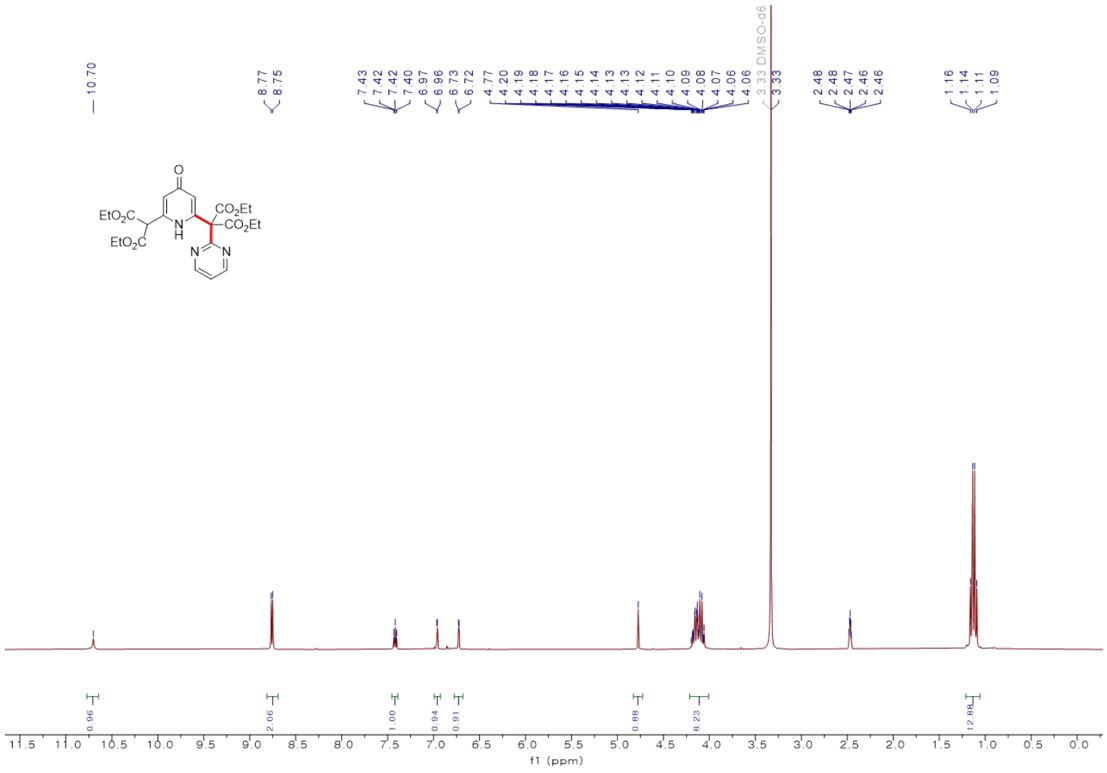
^{13}C NMR of **4h** (75 MHz, Chloroform-*d*)



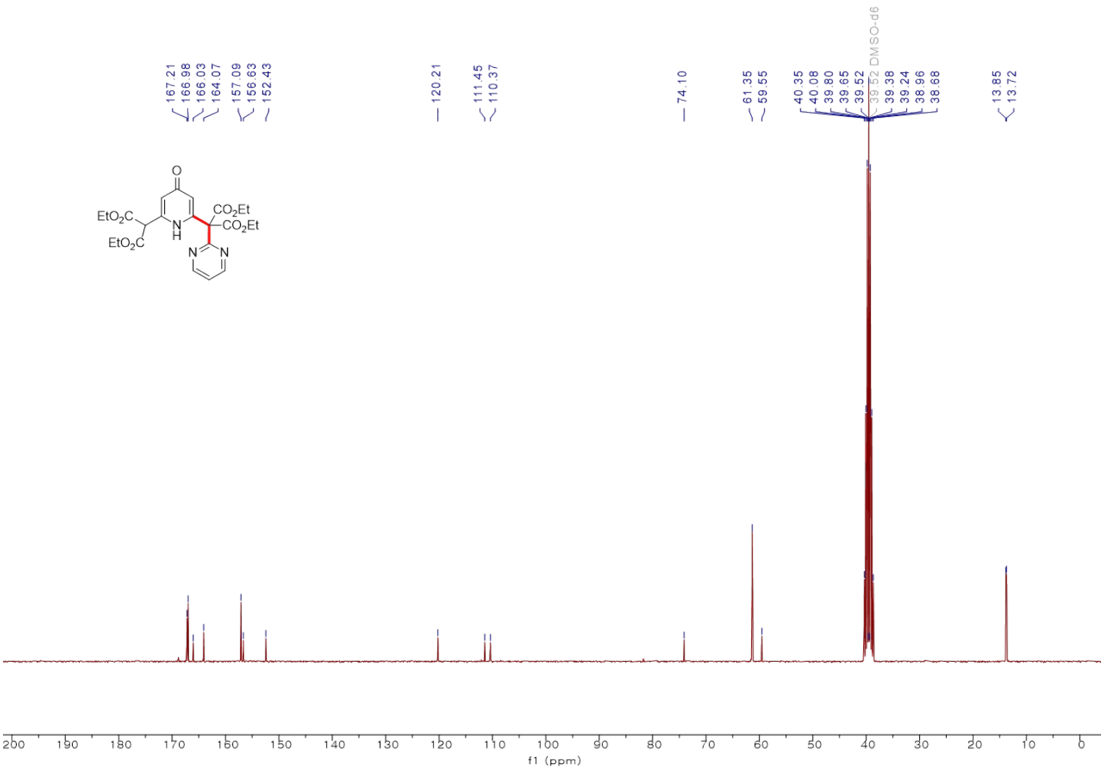
^{1}H NMR of **4j** (300 MHz, Chloroform-*d*)



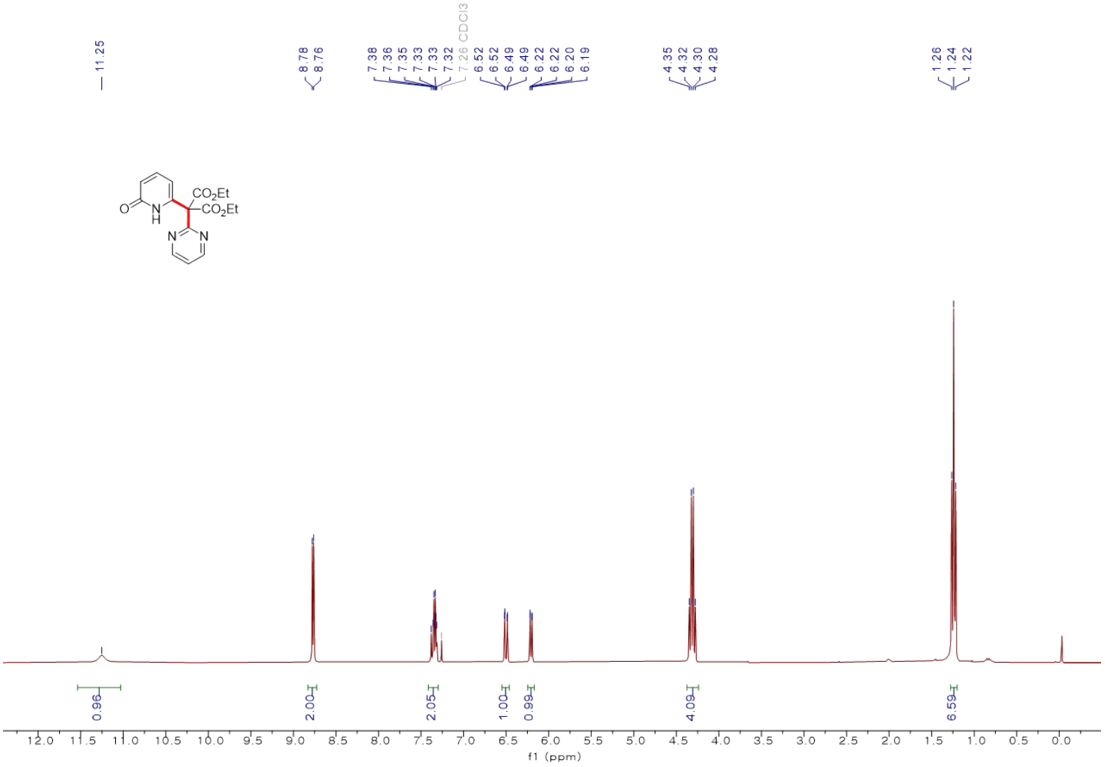
^{13}C NMR of **4j** (75 MHz, Chloroform-*d*)



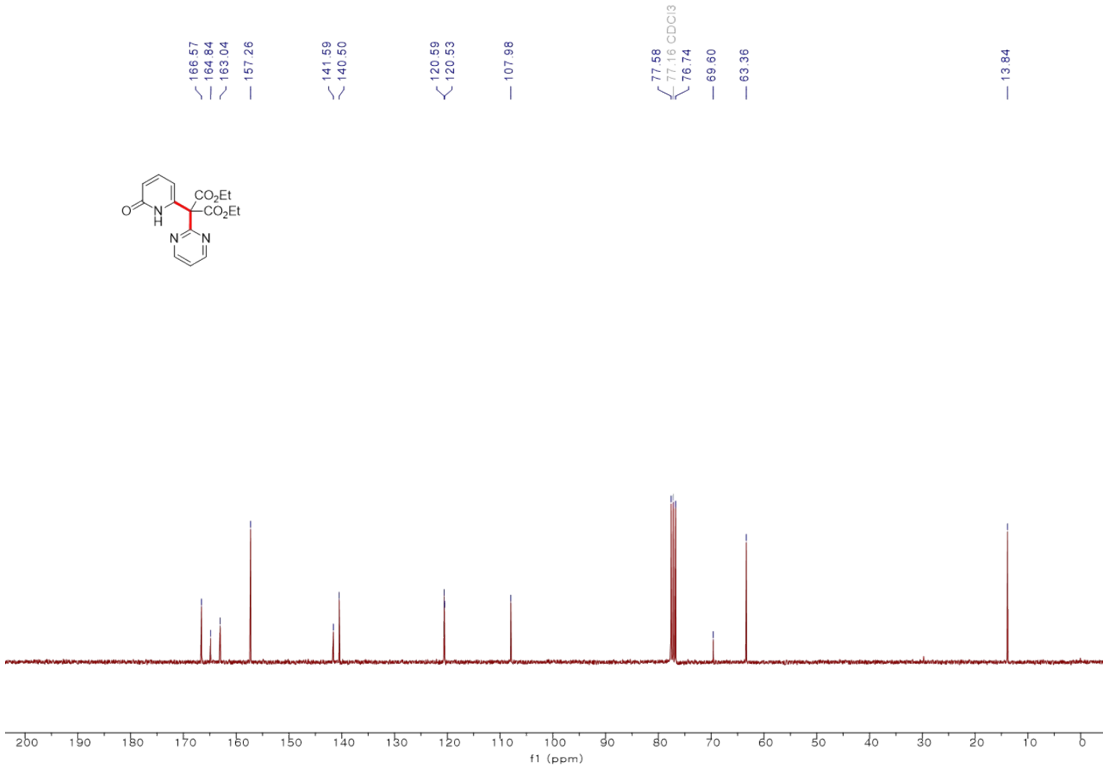
^{1}H NMR of **4k** (300 MHz, DMSO-d_6)



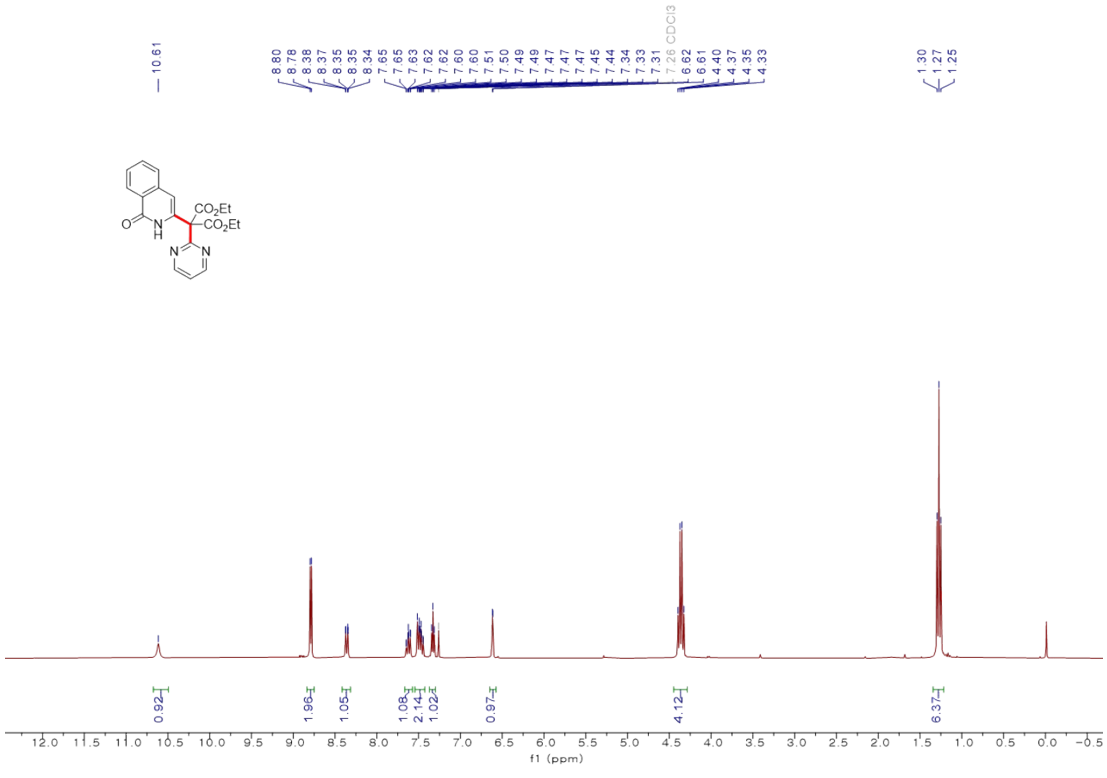
^{13}C NMR of **4k** (75 MHz, DMSO-d_6)



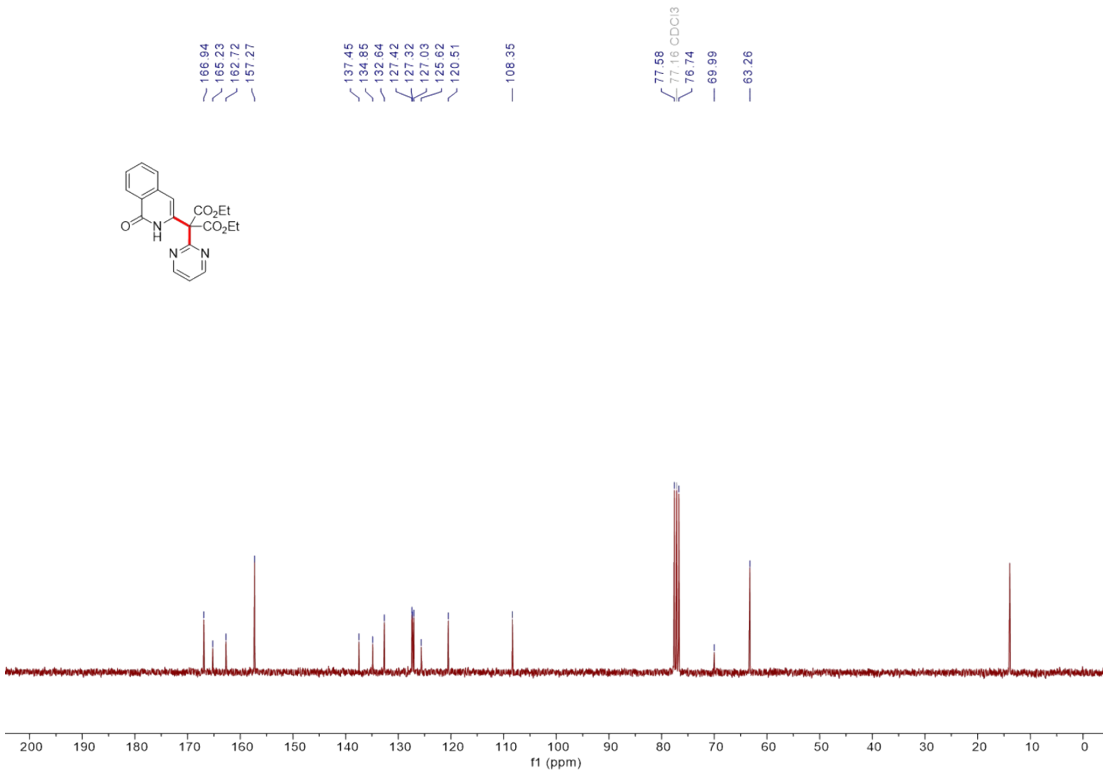
^{1}H NMR of **4l** (300 MHz, Chloroform-*d*)



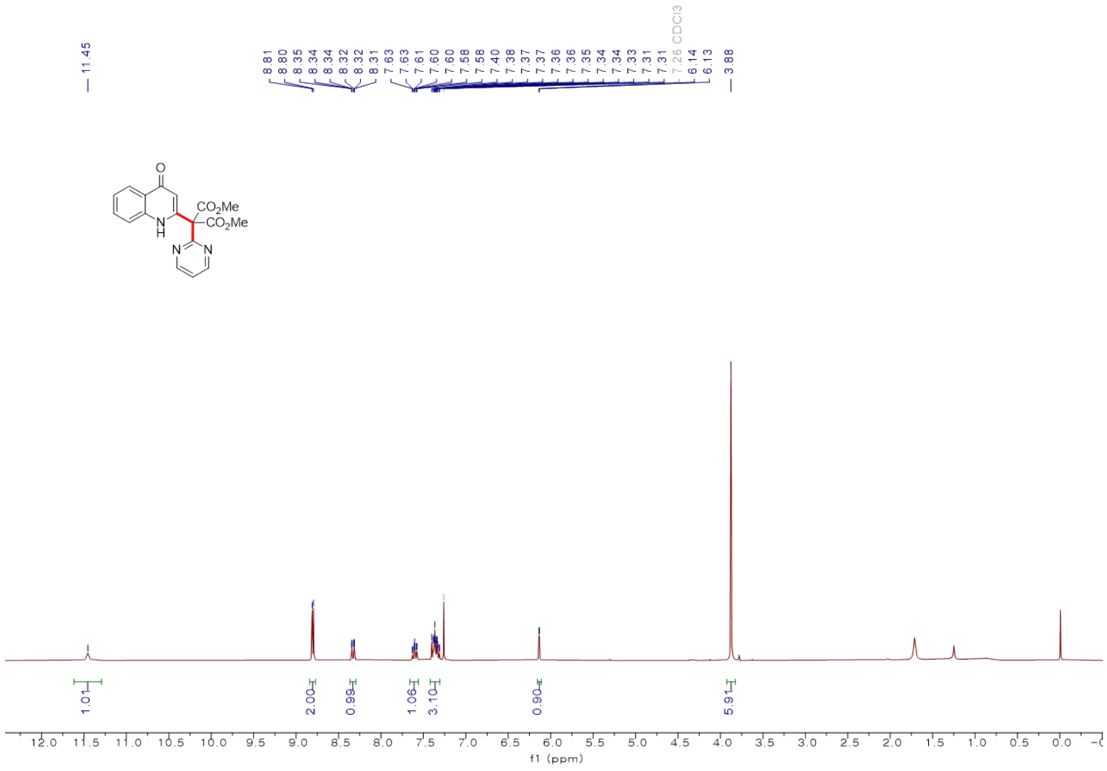
^{13}C NMR of **4l** (75 MHz, Chloroform-*d*)



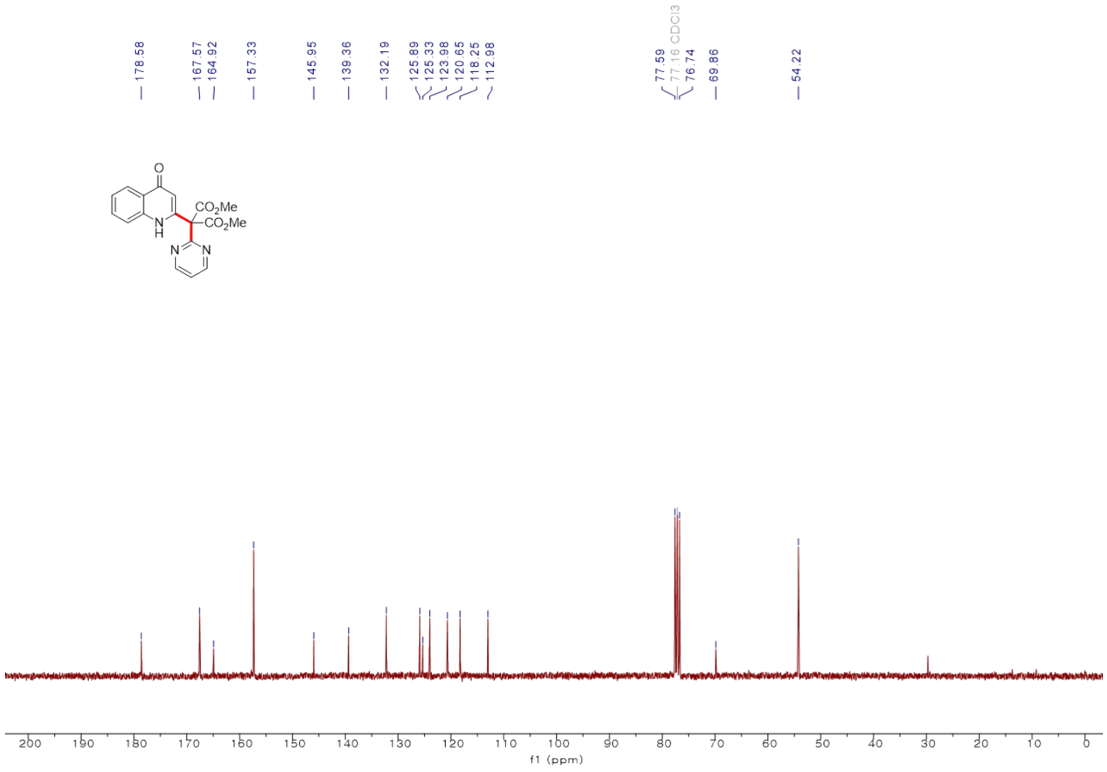
^{1}H NMR of **4m** (300 MHz, Chloroform-*d*)



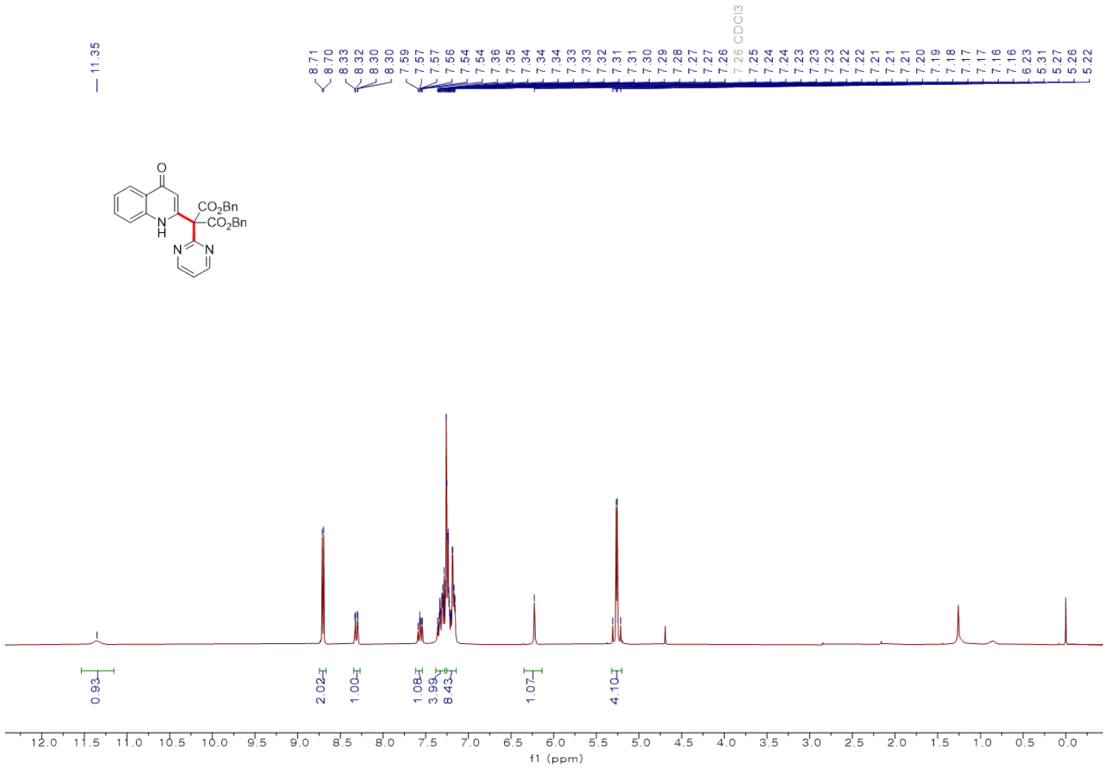
^{13}C NMR of **4m** (75 MHz, Chloroform-*d*)



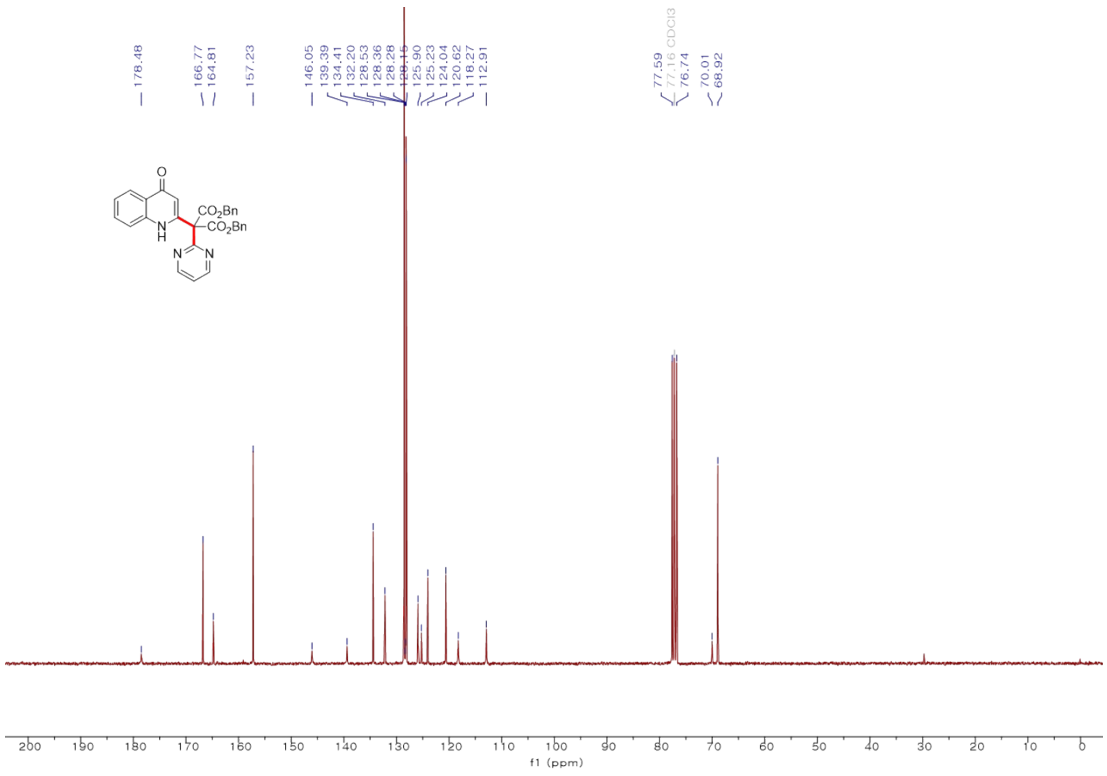
^{1}H NMR of **4n** (300 MHz, Chloroform-*d*)



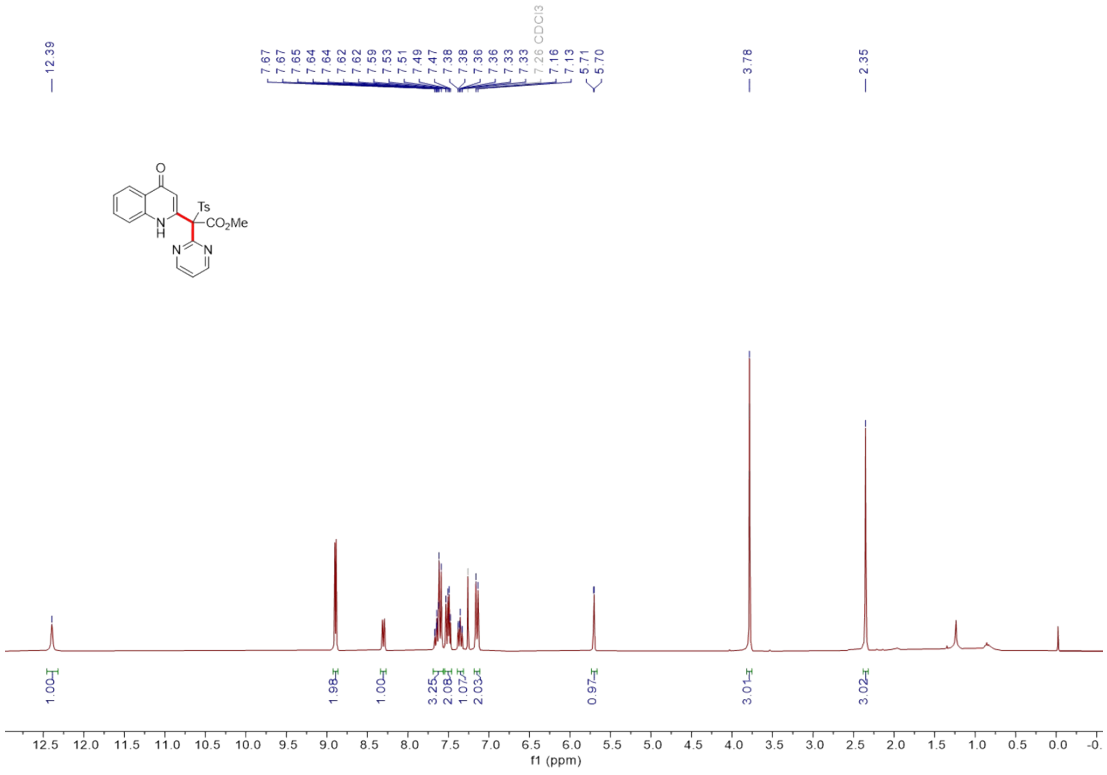
^{13}C NMR of **4n** (75 MHz, Chloroform-*d*)



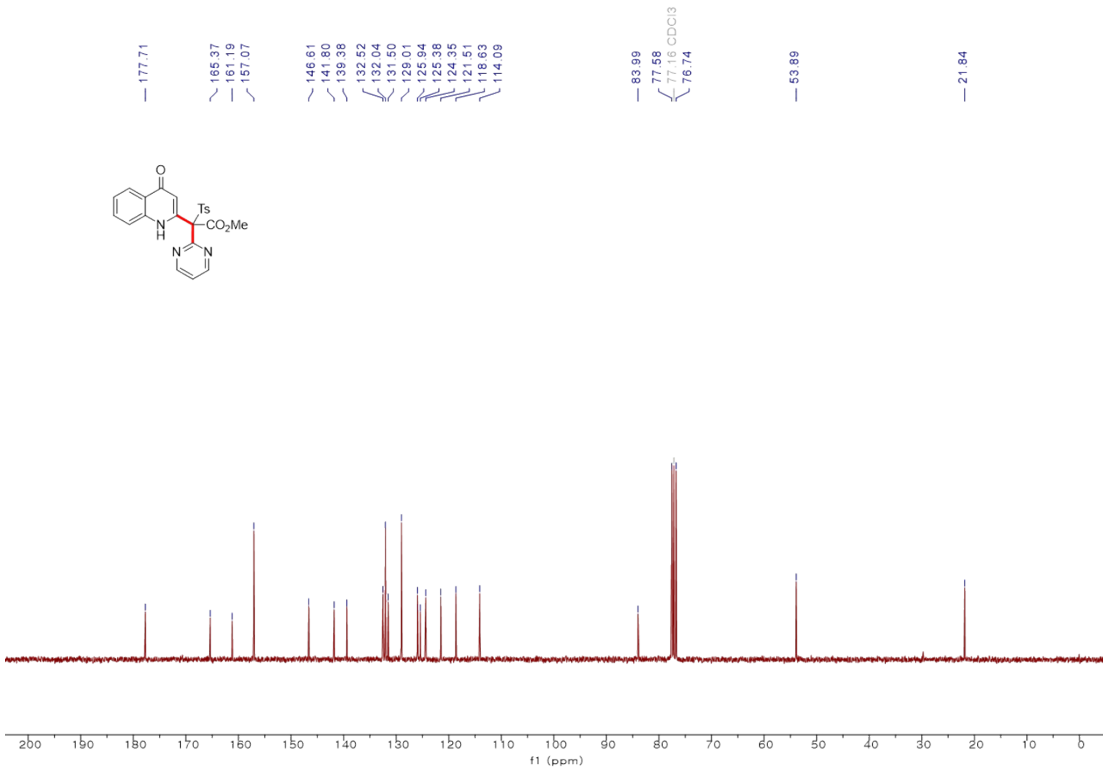
^{1}H NMR of **4o** (300 MHz, Chloroform-*d*)



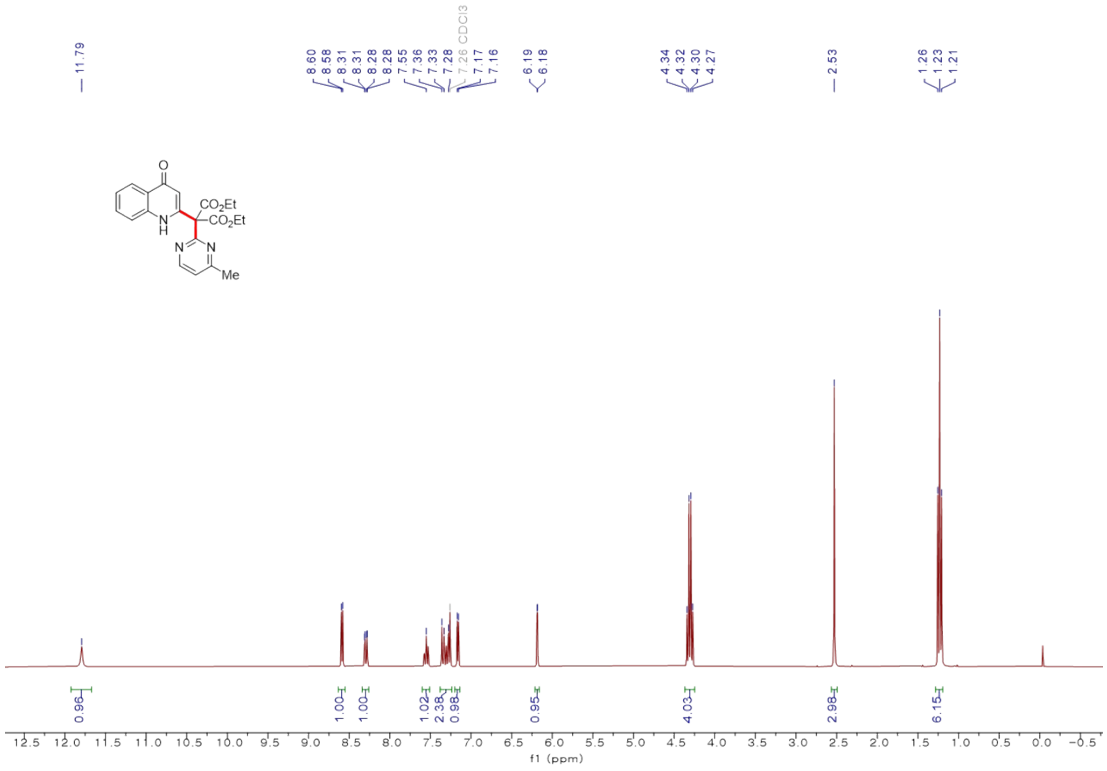
^{13}C NMR of **4o** (75 MHz, Chloroform-*d*)



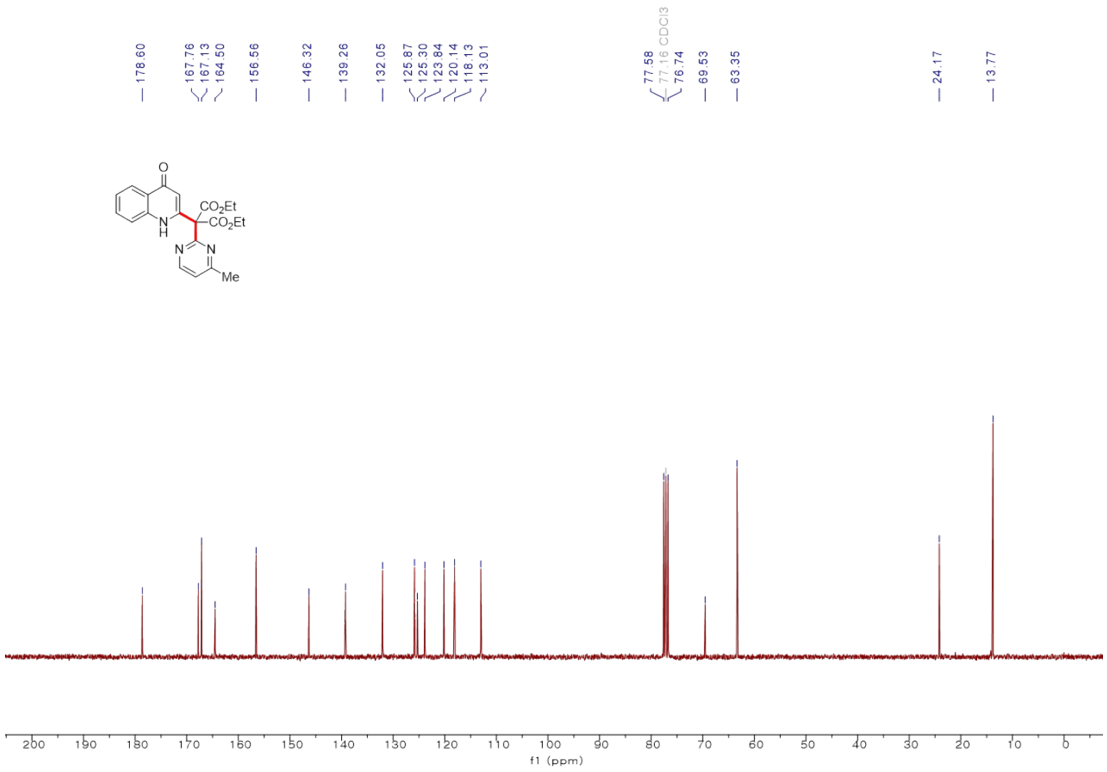
^{1}H NMR of **4p** (300 MHz, Chloroform-*d*)



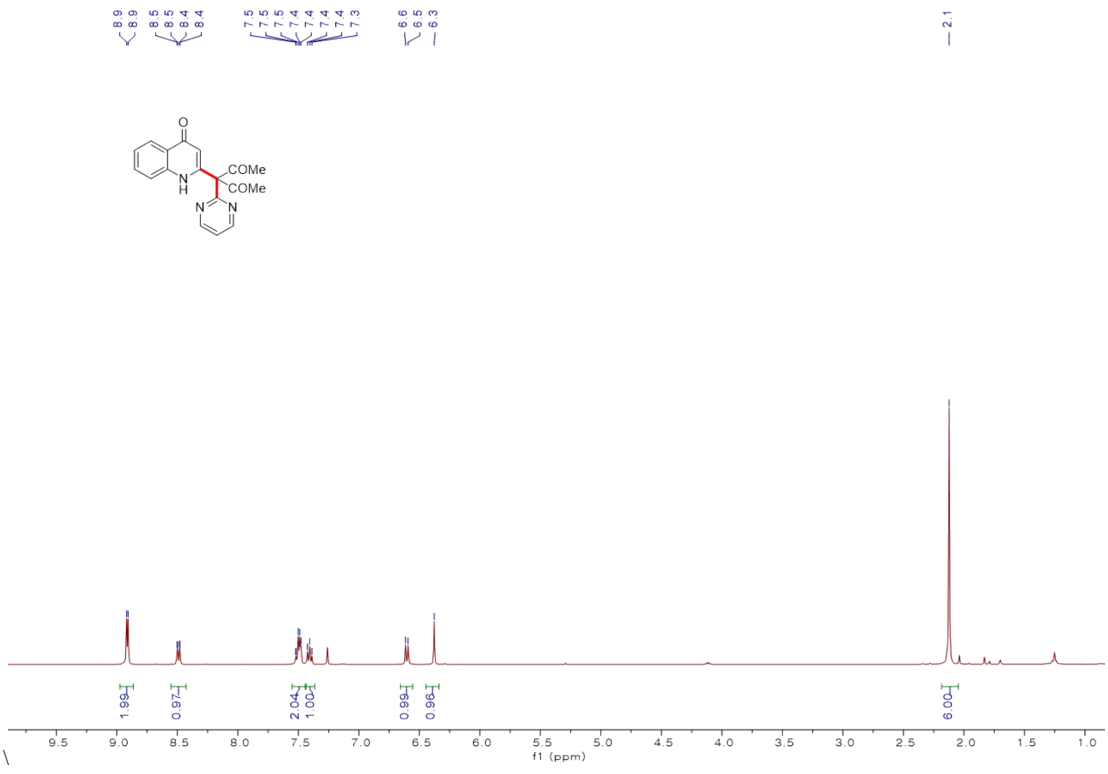
^{13}C NMR of **4p** (75 MHz, Chloroform-*d*)



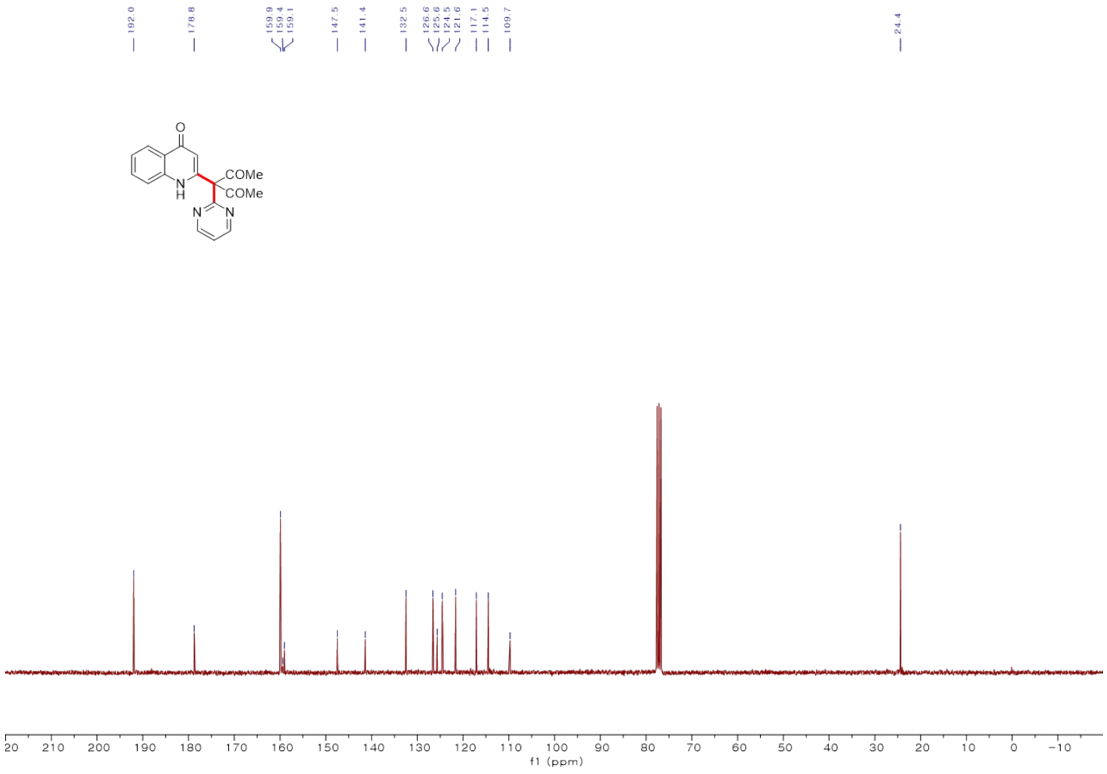
^{1}H NMR of **4q** (300 MHz, Chloroform-*d*)



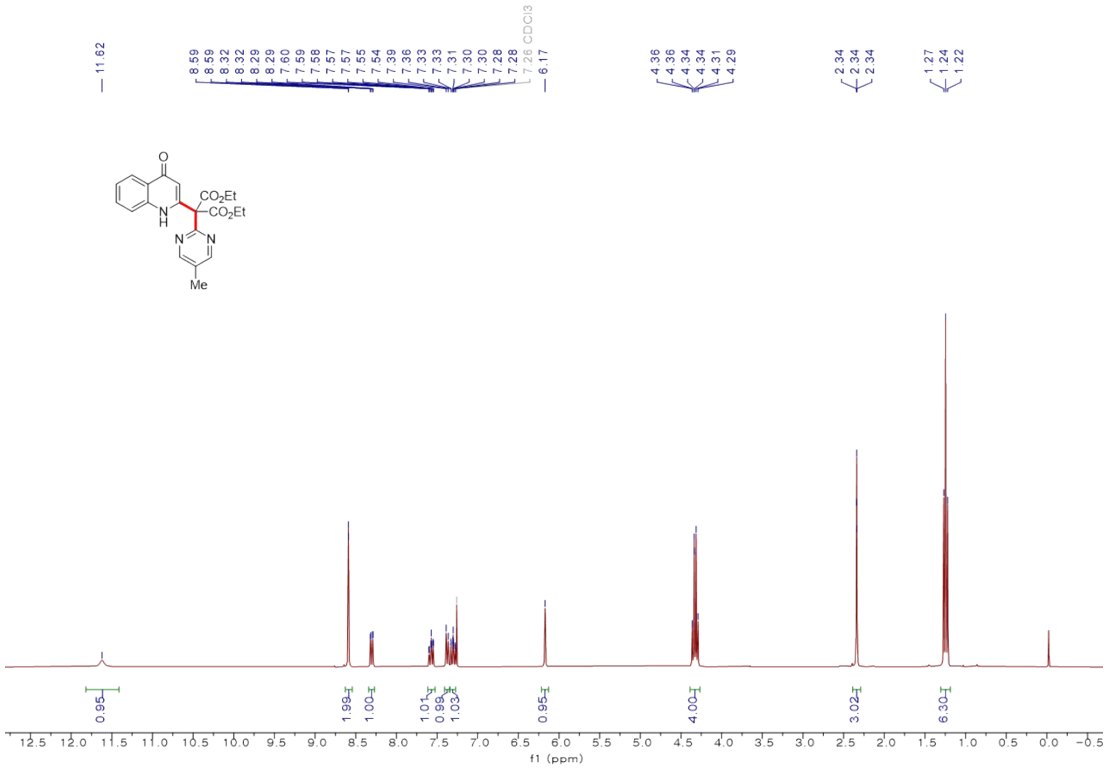
^{13}C NMR of **4q** (75 MHz, Chloroform-*d*)



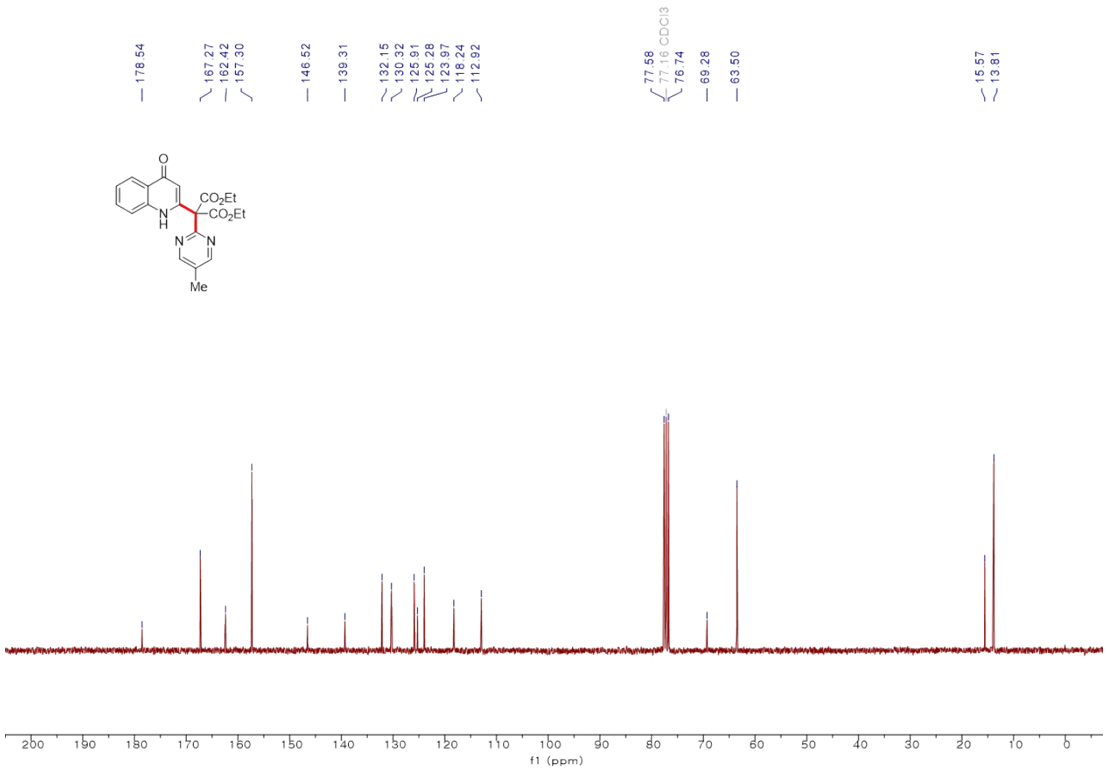
^{1}H NMR of **4r** (400 MHz, Chloroform-*d*)



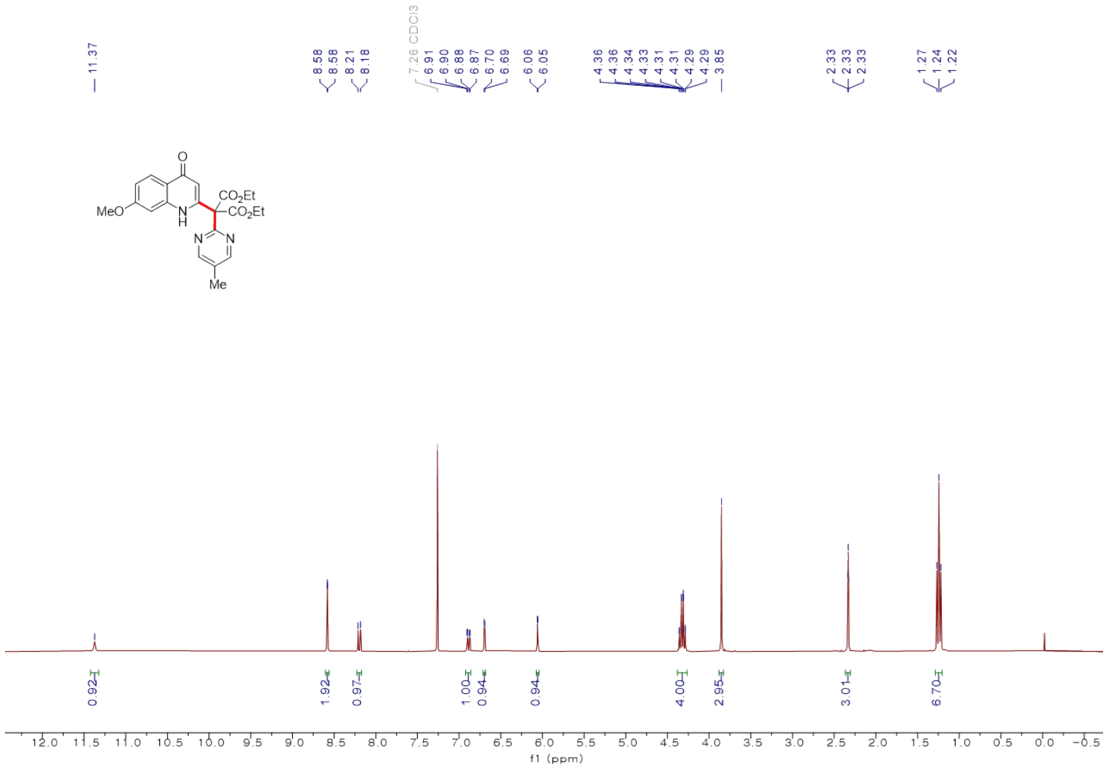
^{13}C NMR of **4r** (75 MHz, Chloroform-*d*)



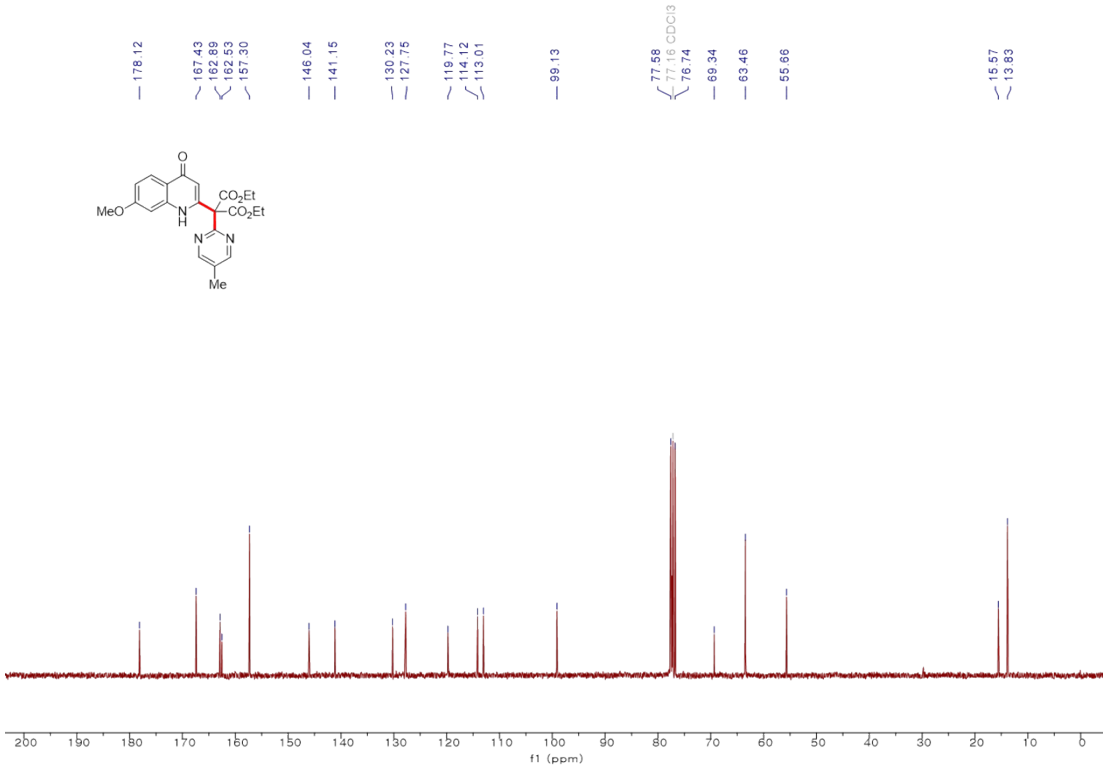
^{1}H NMR of **4s** (300 MHz, Chloroform-*d*)



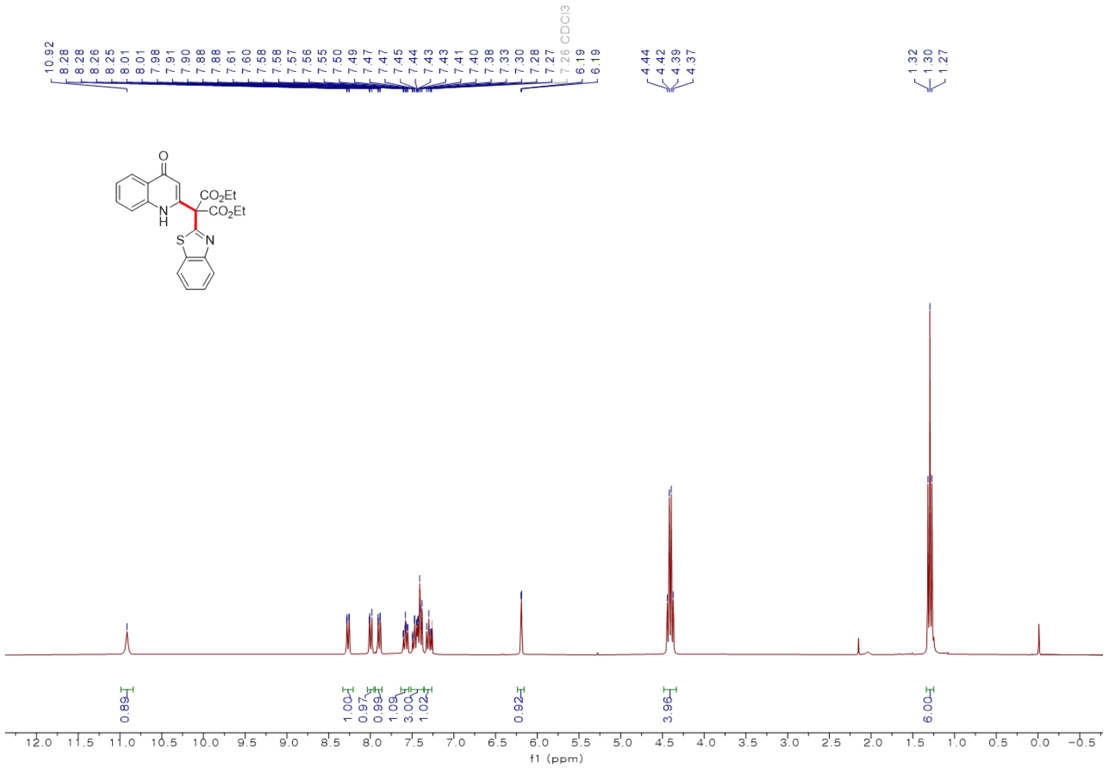
^{13}C NMR of **4s** (75 MHz, Chloroform-*d*)



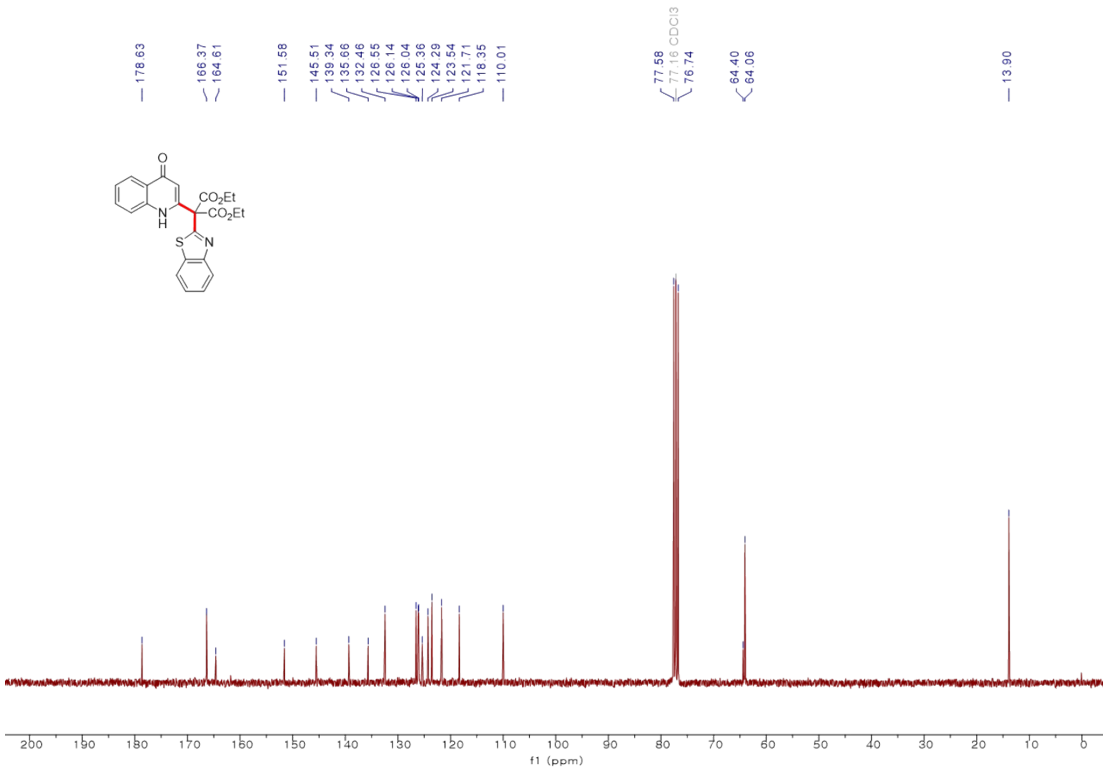
^{1}H NMR of **4t** (300 MHz, Chloroform-*d*)



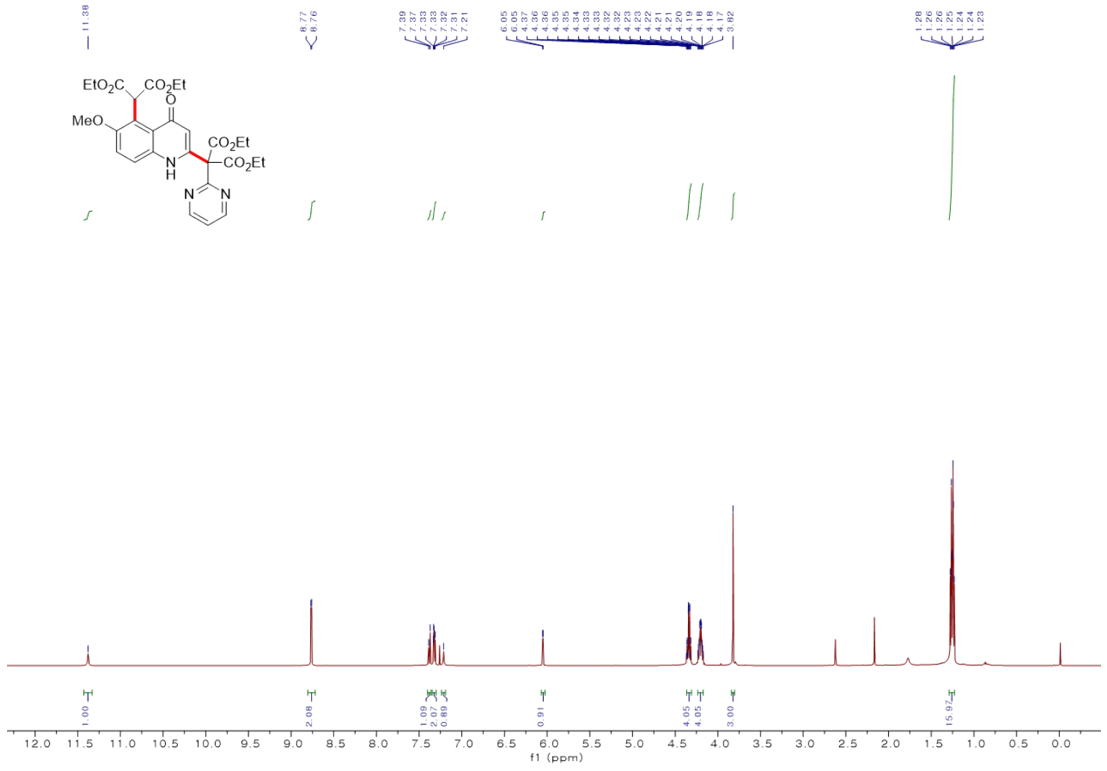
^{13}C NMR of **4t** (75 MHz, Chloroform-*d*)



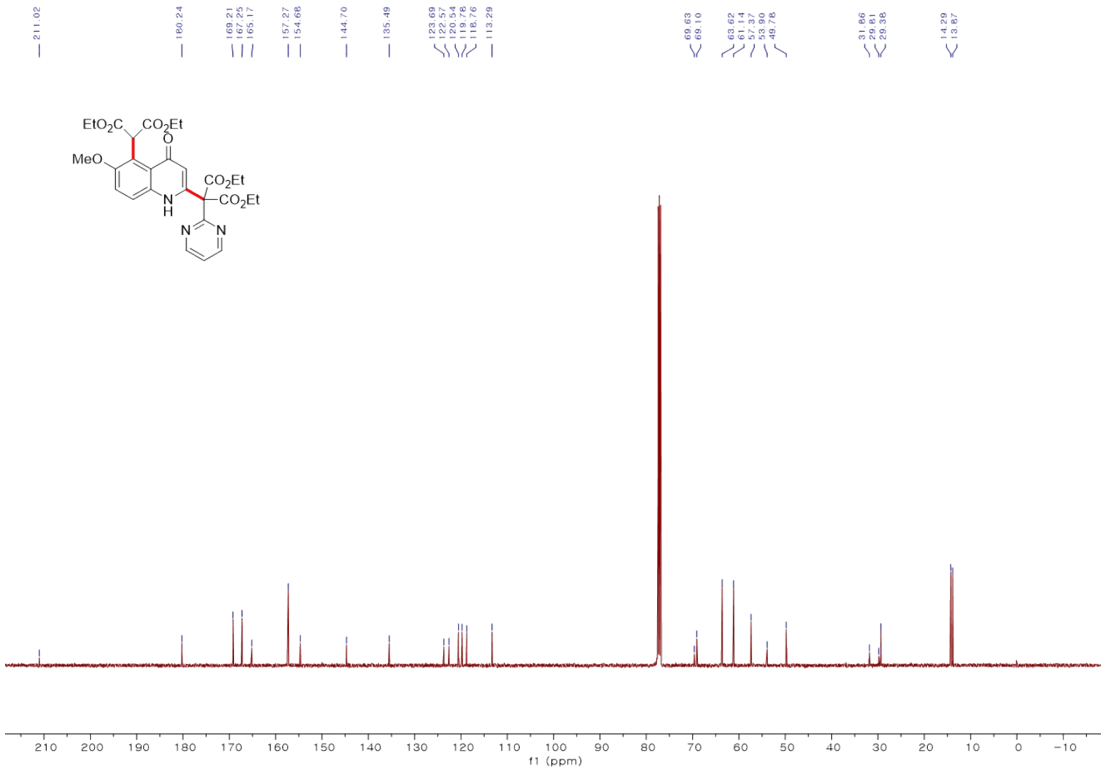
^{1}H NMR of **4u** (300 MHz, Chloroform-*d*)



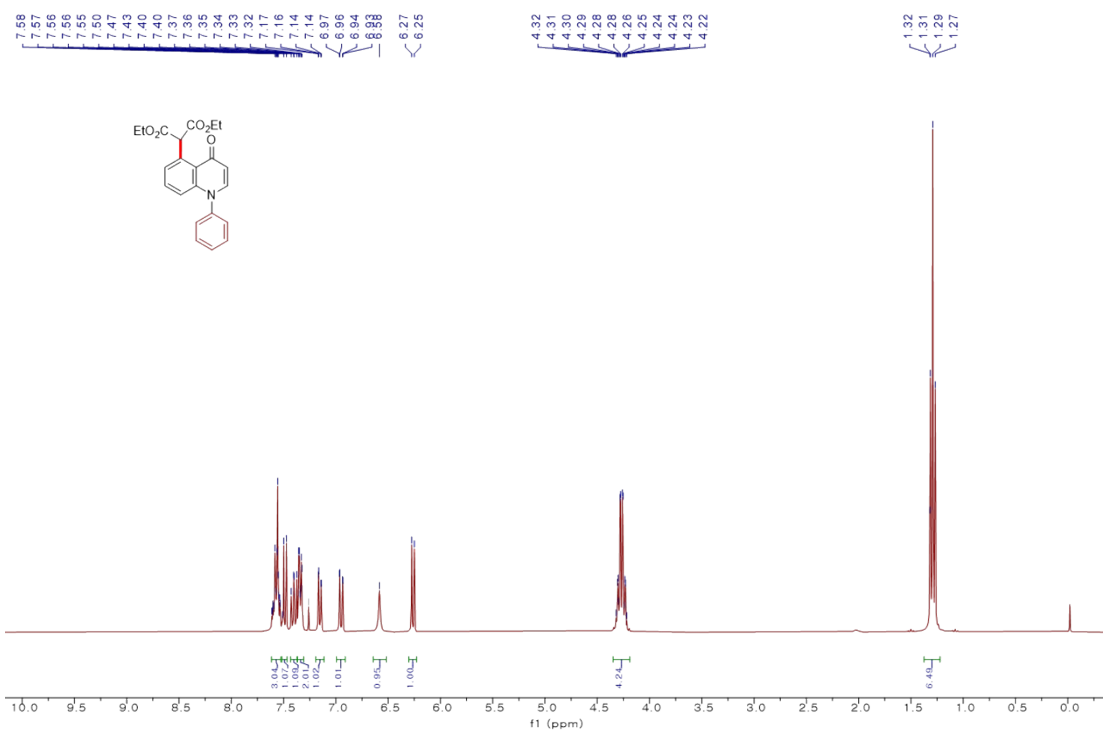
^{13}C NMR of **4u** (75 MHz, Chloroform-*d*)



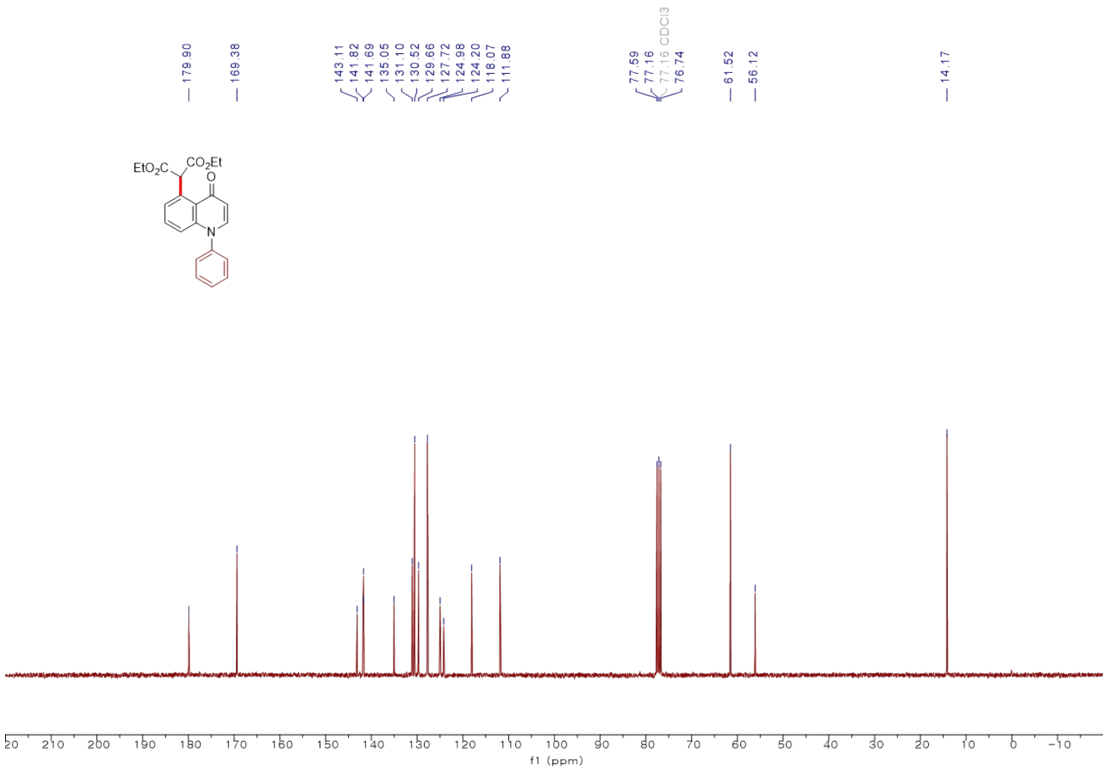
^{1}H NMR of **4x** (500 MHz, Chloroform-*d*)



^{13}C NMR of **4x** (126 MHz, Chloroform-*d*)

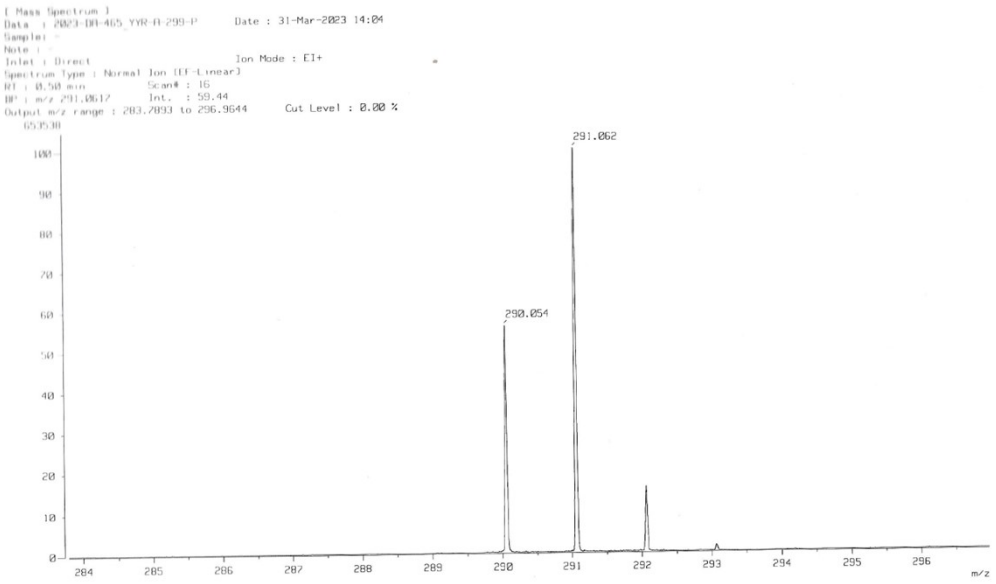


^{1}H NMR of **11** (300 MHz, Chloroform-*d*)

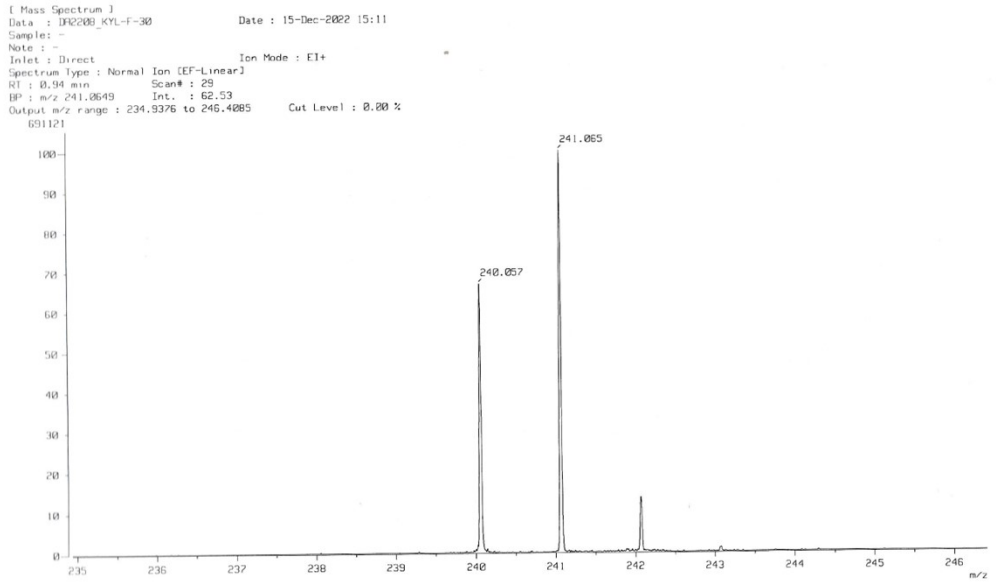


^{13}C NMR of **11** (75 MHz, Chloroform-*d*)

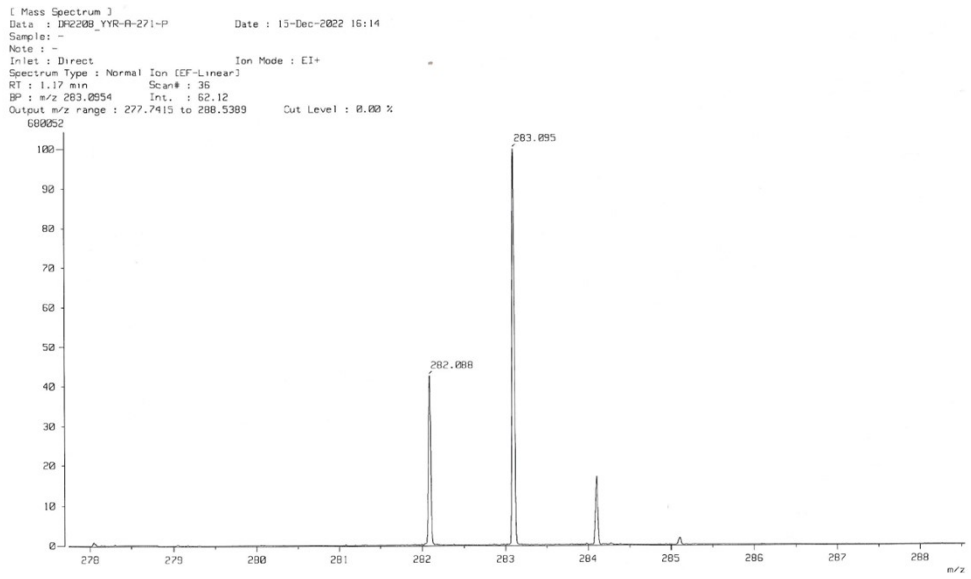
11. Copies of HRMS Spectra



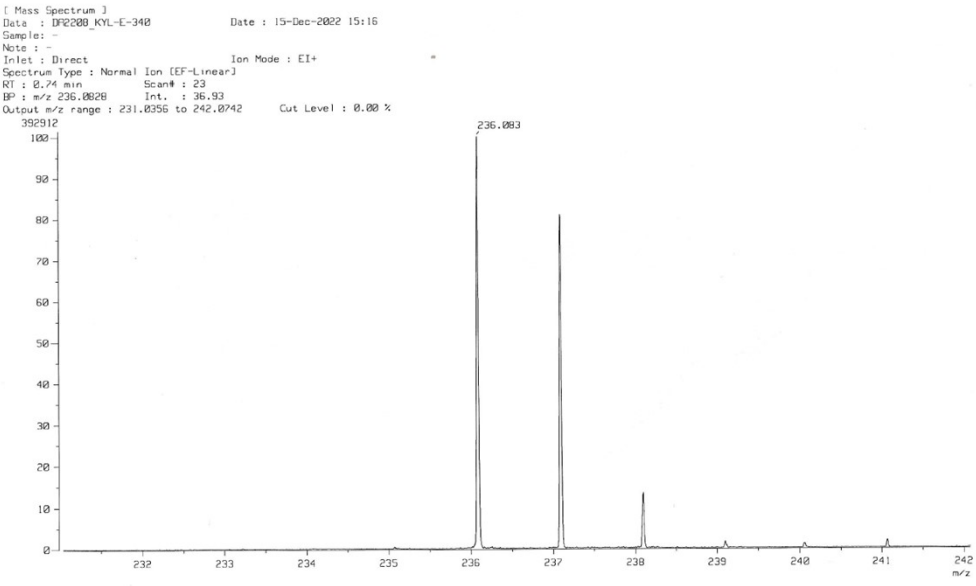
HRMS spectra of **1e**



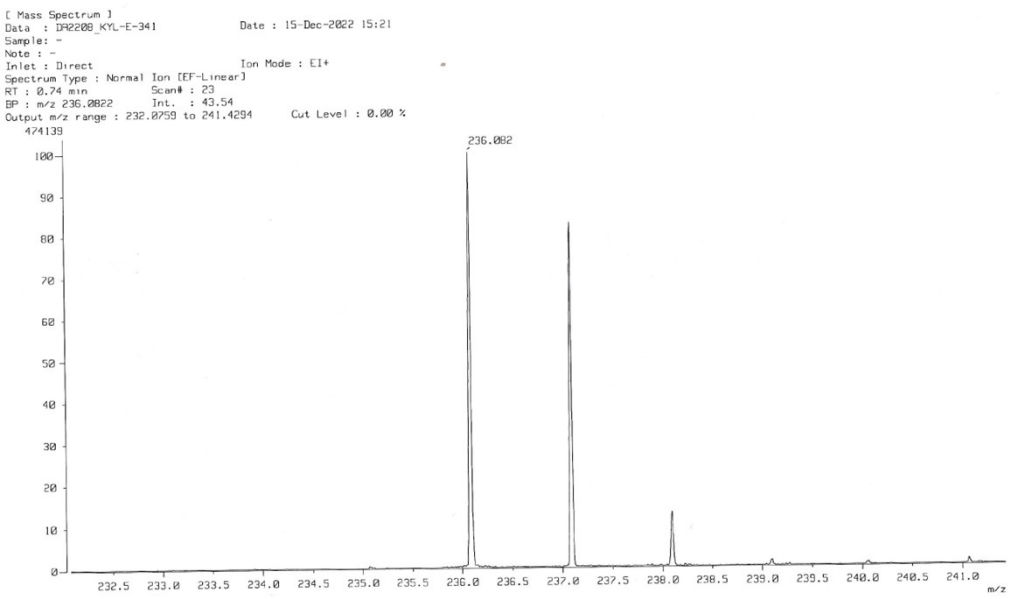
HRMS spectra of **1j**



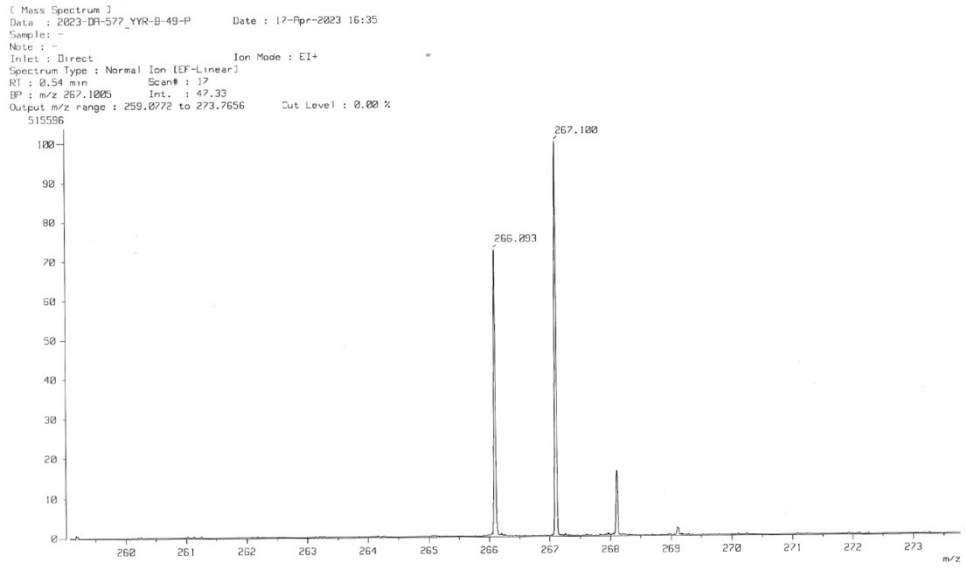
HRMS spectra of **1k**



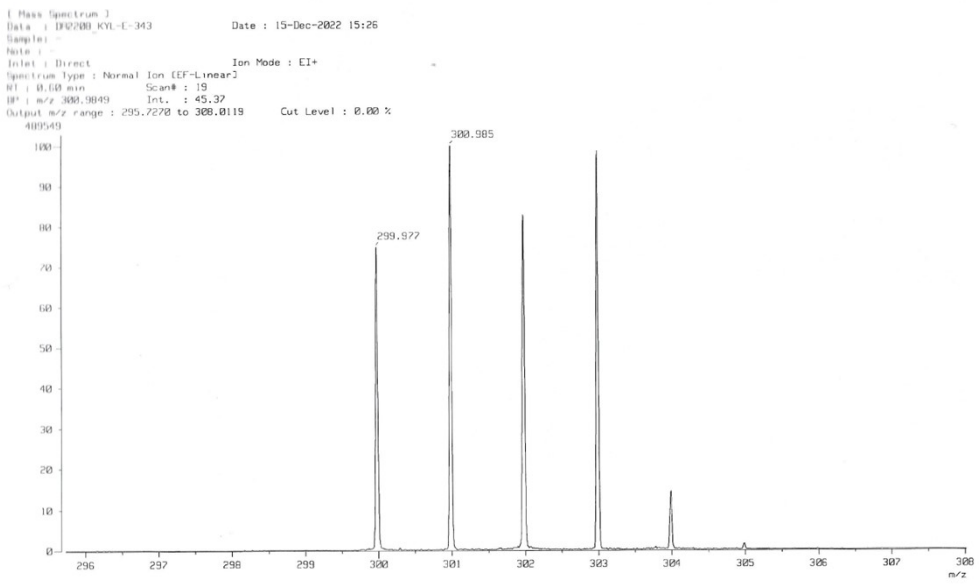
HRMS spectra of **1t**



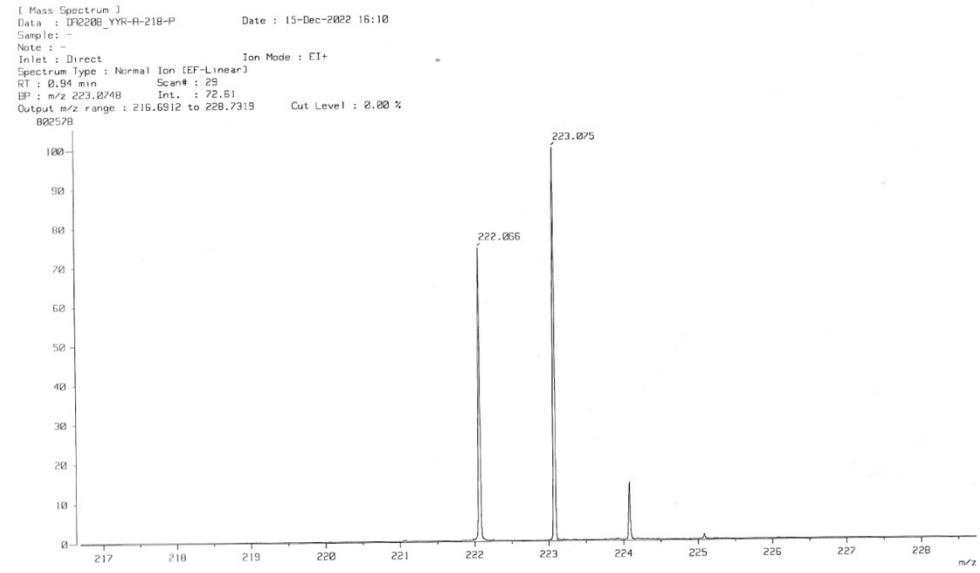
HRMS spectra of **1u**



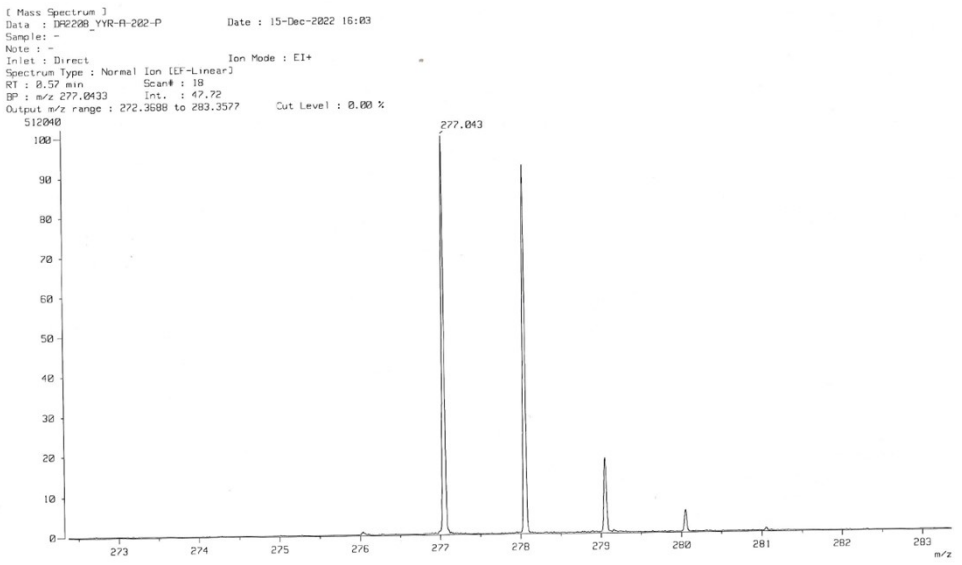
HRMS spectra of **1v**



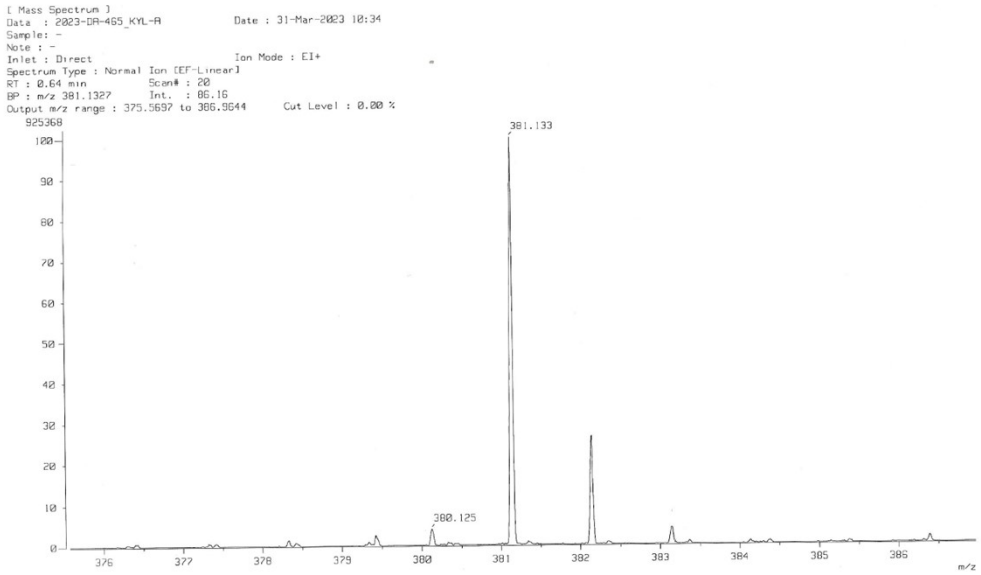
HRMS spectra of **1w**



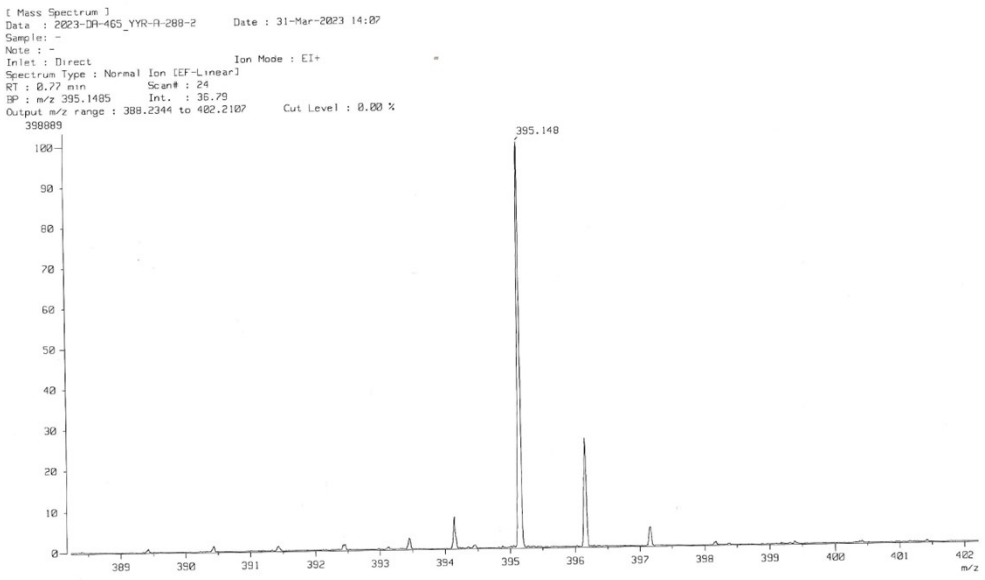
HRMS spectra of **1x**



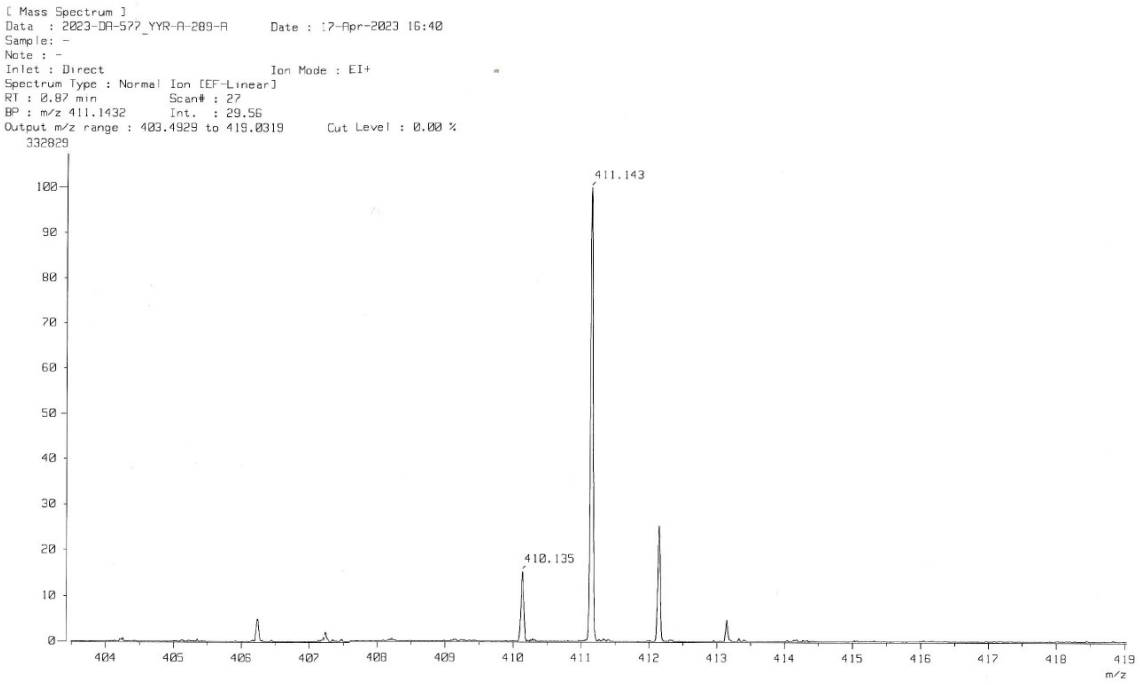
HRMS spectra of **1y**



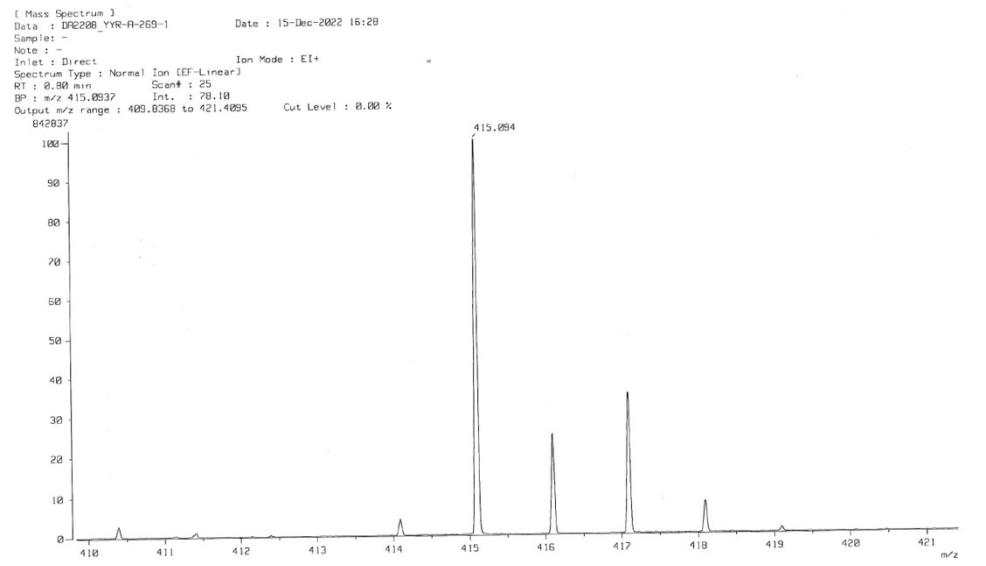
HRMS spectra of **3a**



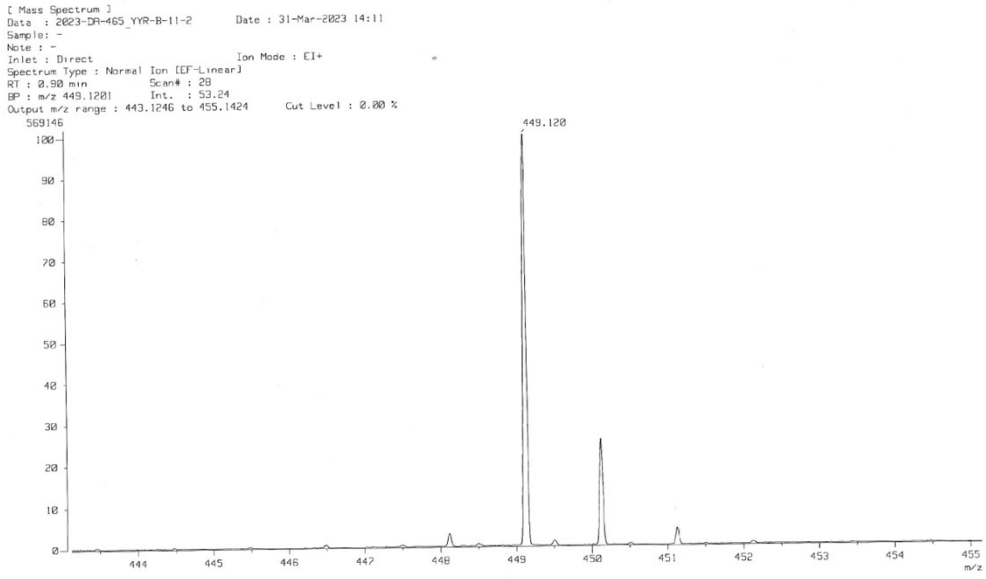
HRMS spectra of **3b**



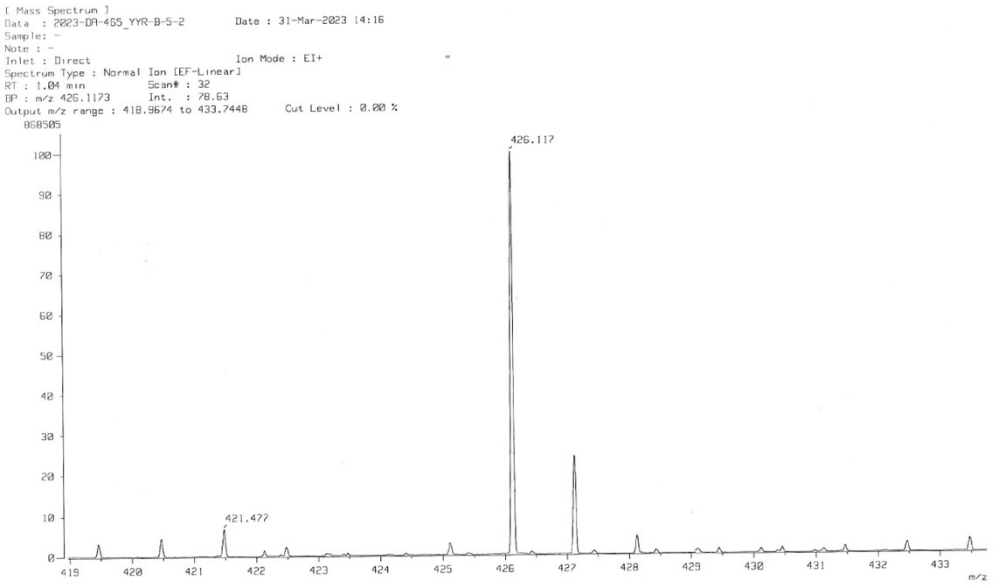
HRMS spectra of **3c**



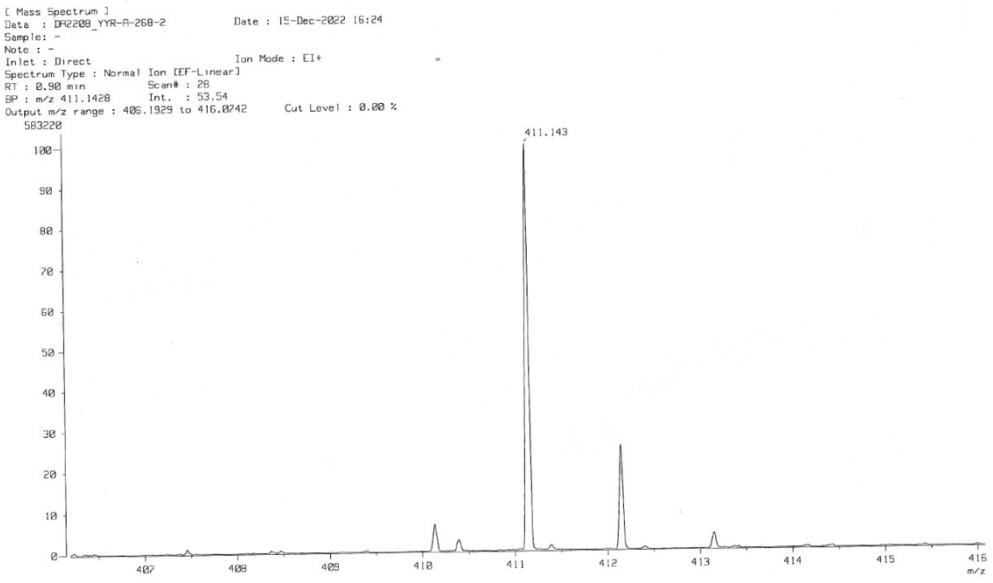
HRMS spectra of **3d**



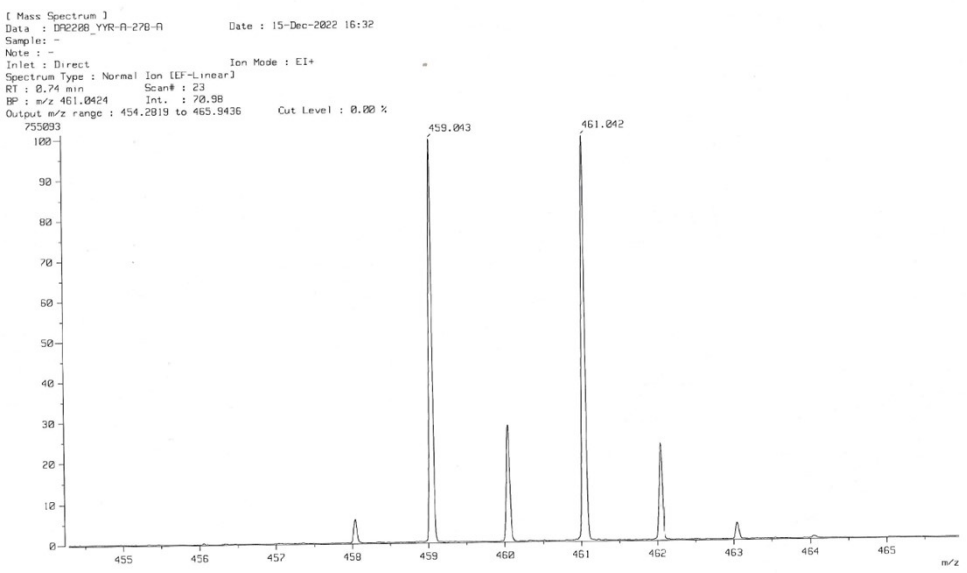
HRMS spectra of **3e**



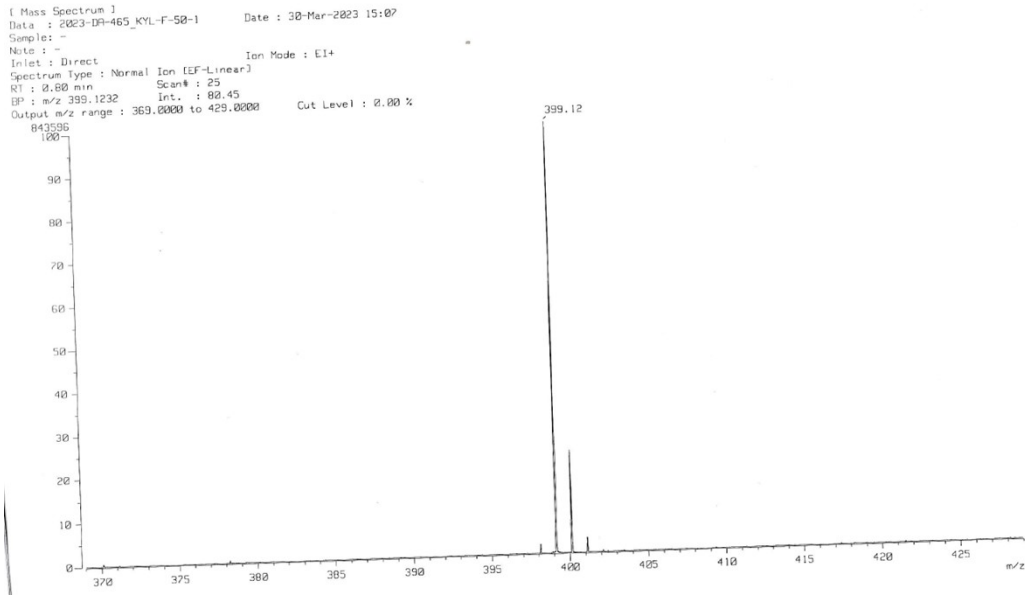
HRMS spectra of **3f**



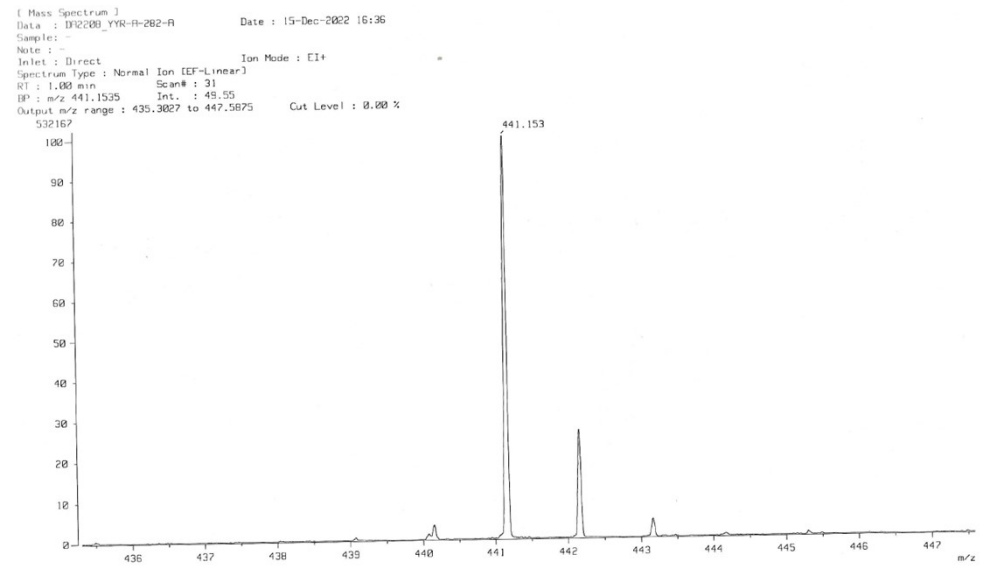
HRMS spectra of **3g**



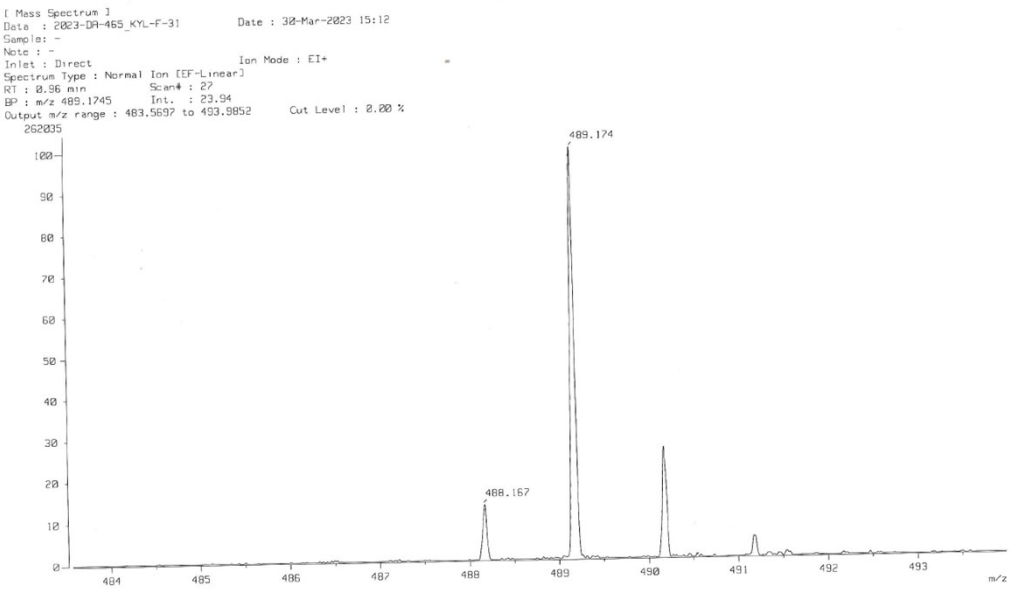
HRMS spectra of **3h**



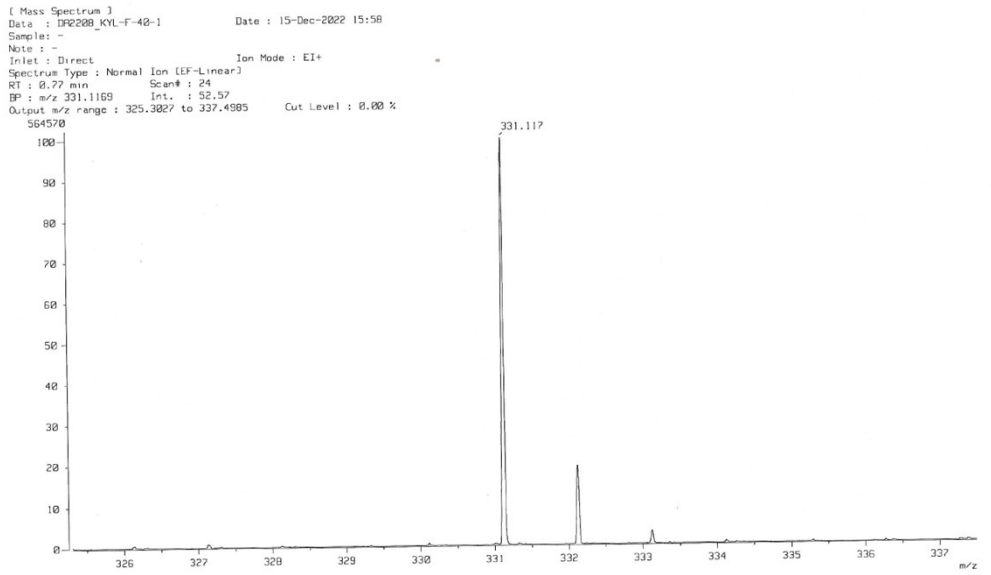
HRMS spectra of **3i**



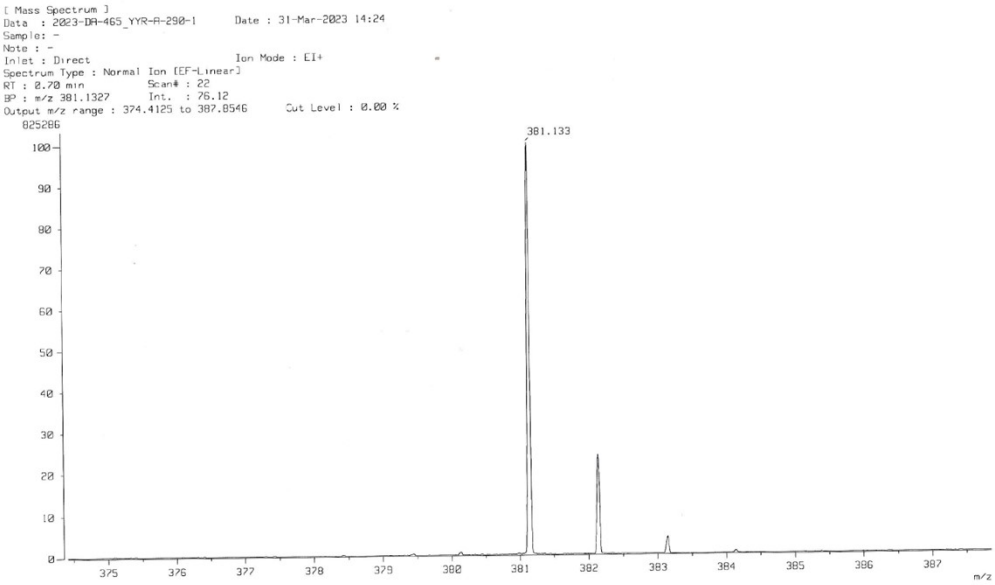
HRMS spectra of **3j**



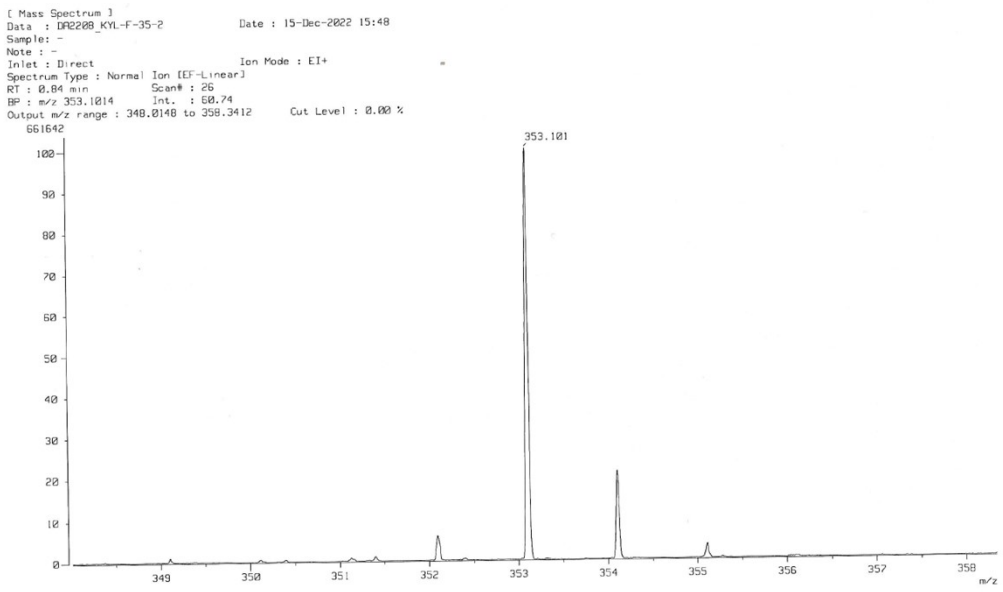
HRMS spectra of **3k**



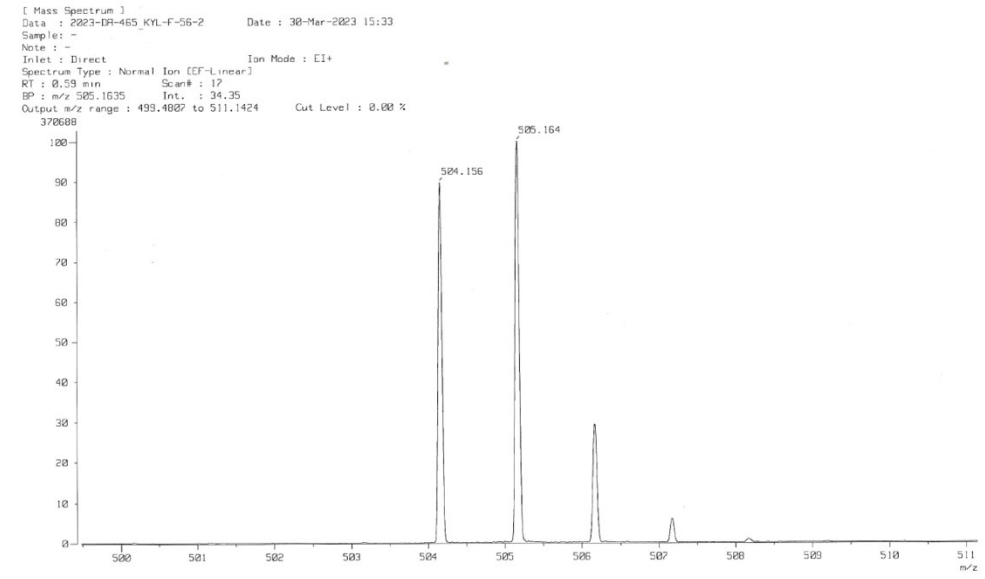
HRMS spectra of **3l**



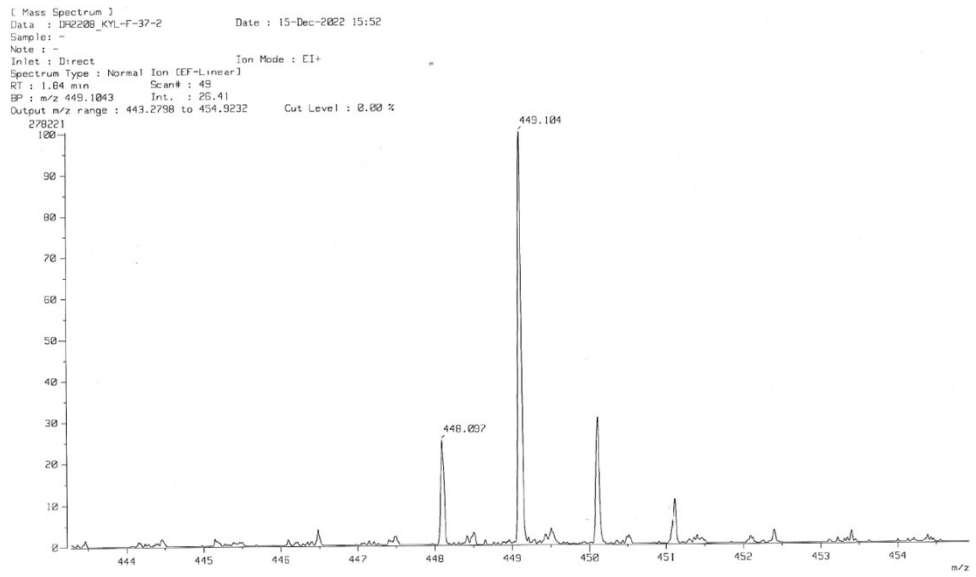
HRMS spectra of **3m**



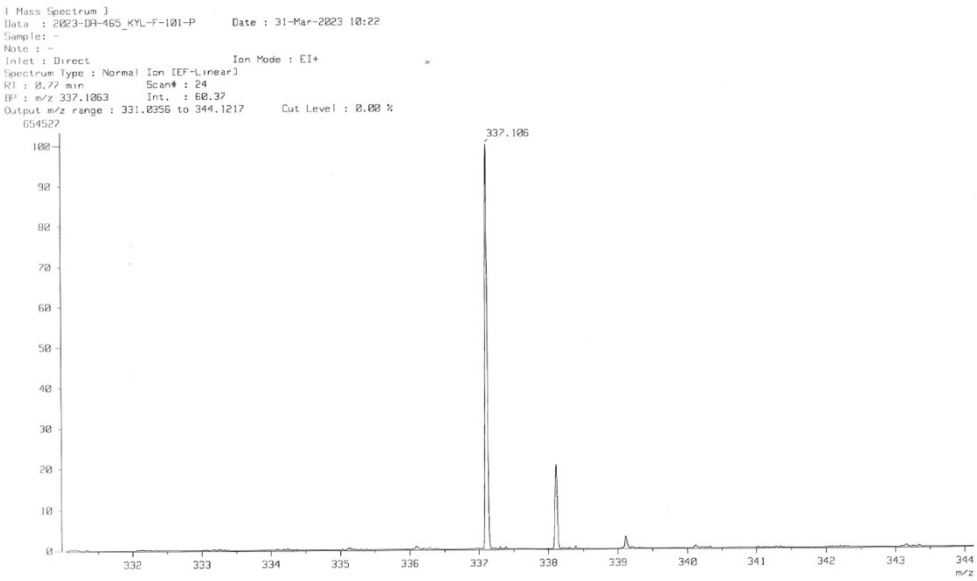
HRMS spectra of **3n**



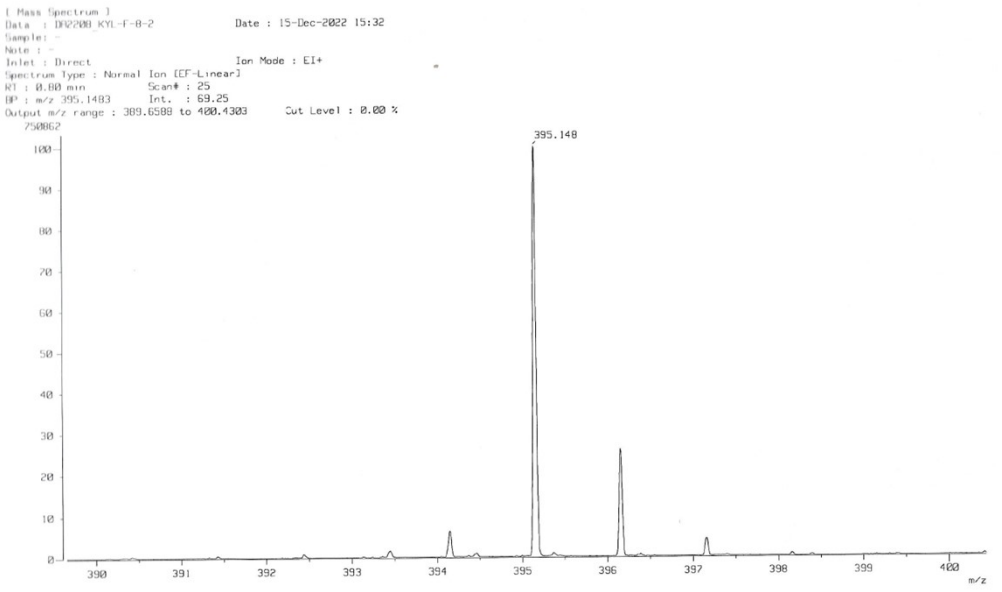
HRMS spectra of **3o**



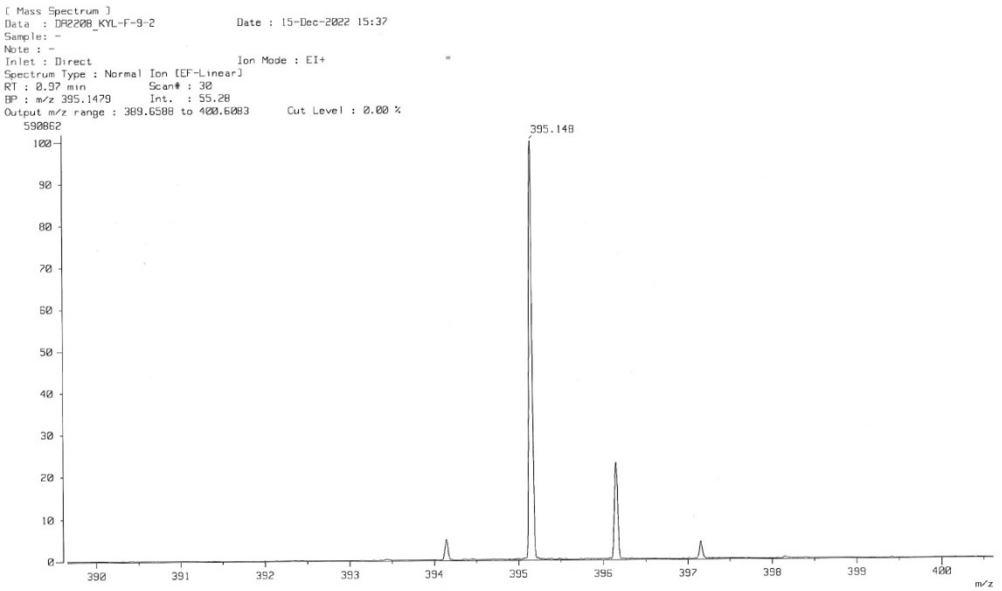
HRMS spectra of **3p**



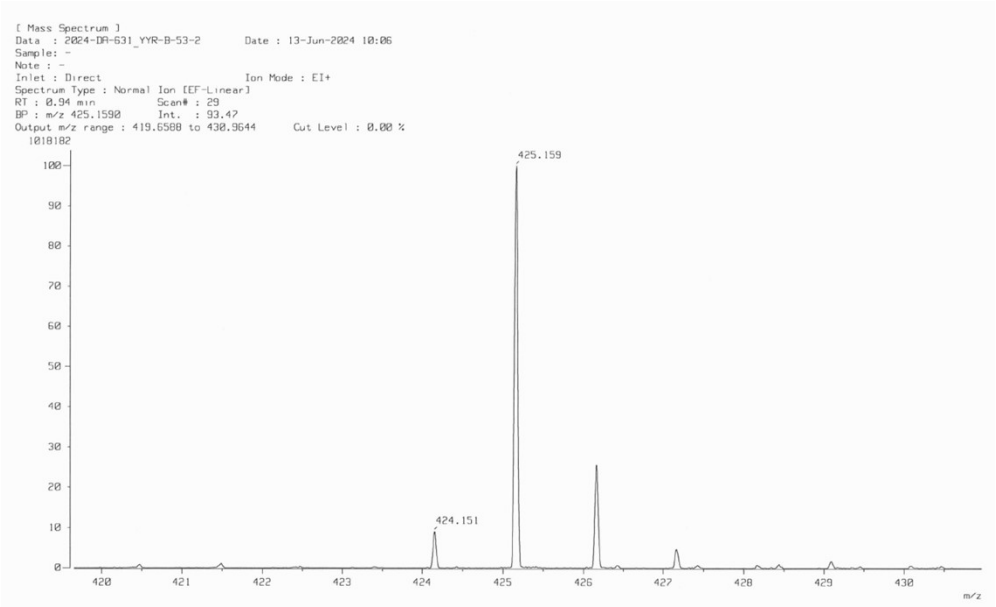
HRMS spectra of **3q**



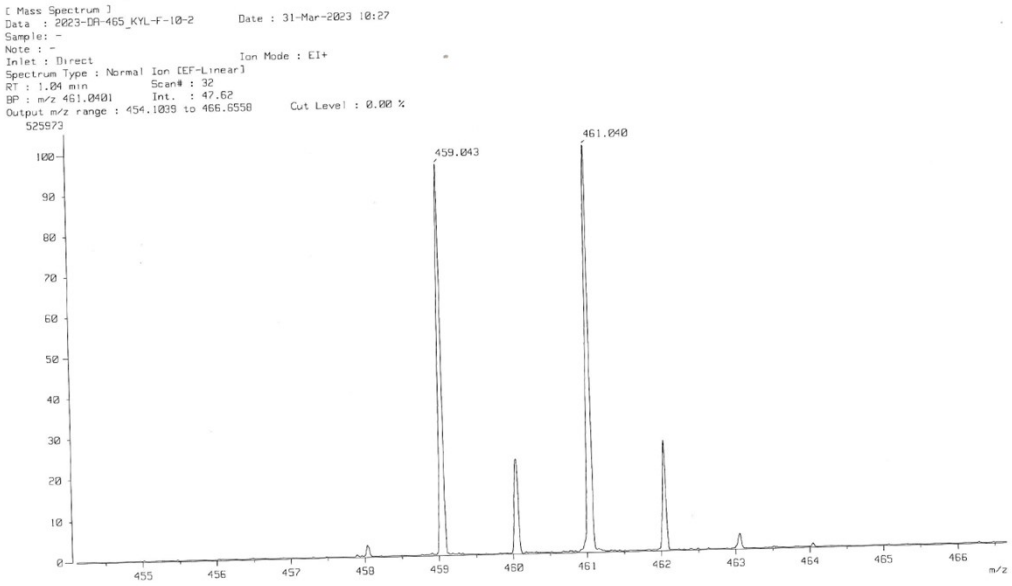
HRMS spectra of **3s**



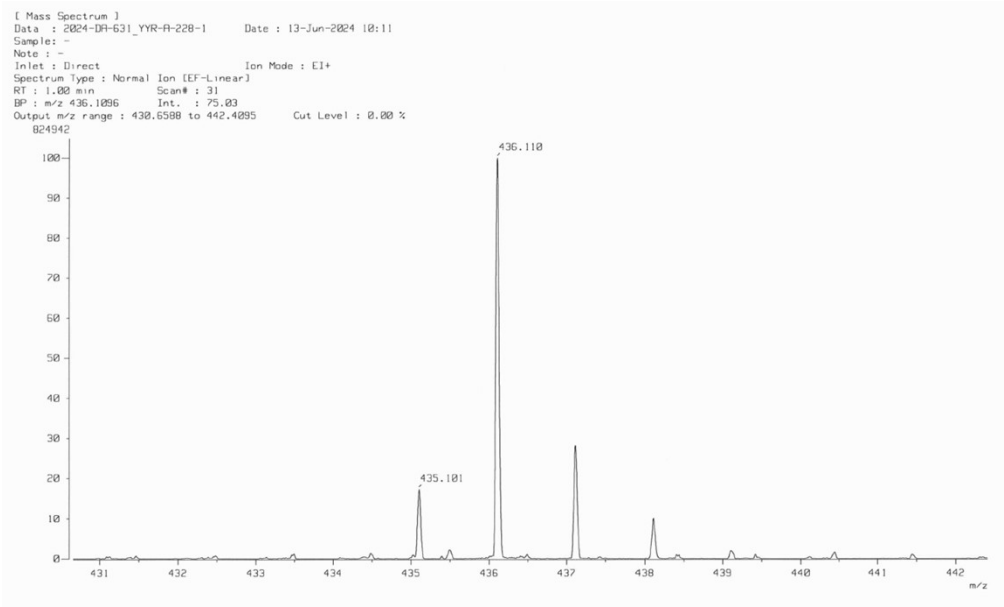
HRMS spectra of **3t**



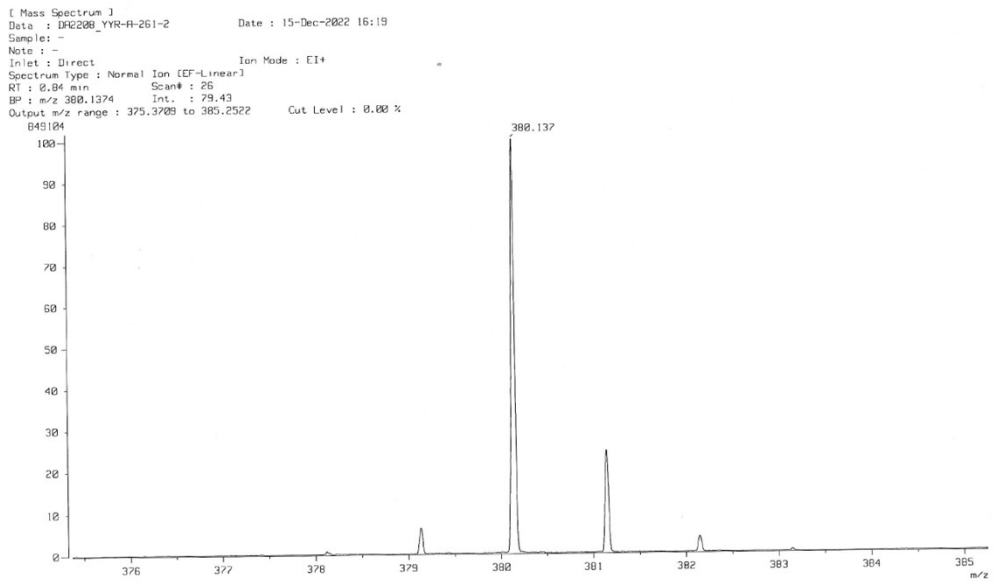
HRMS spectra of **3u**



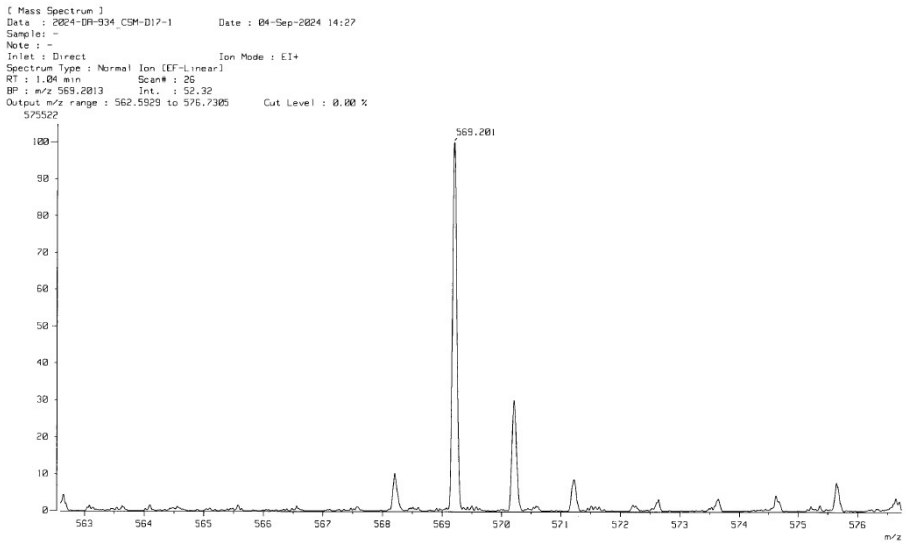
HRMS spectra of **3v**



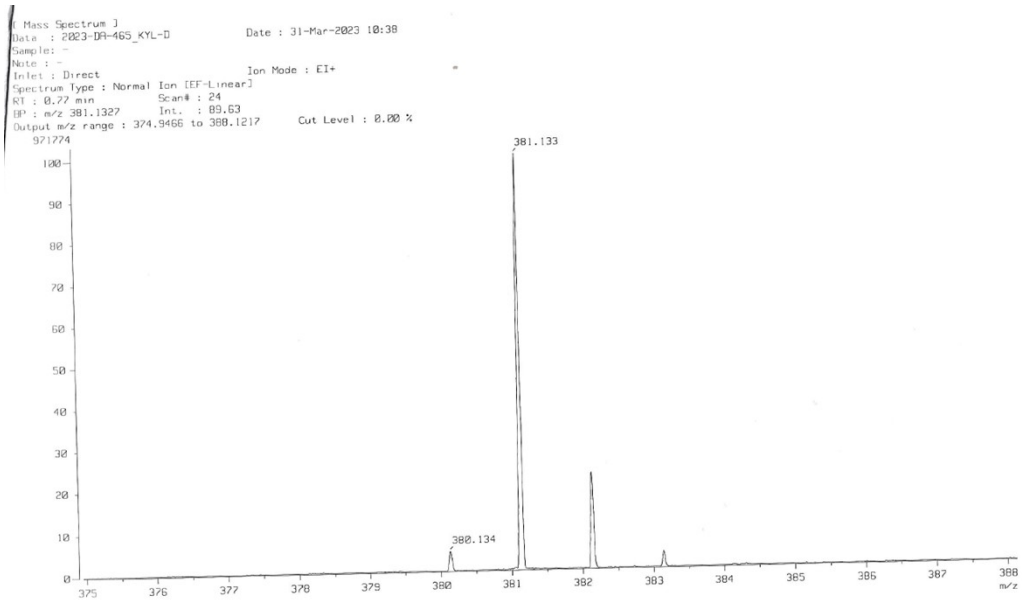
HRMS spectra of **3w**



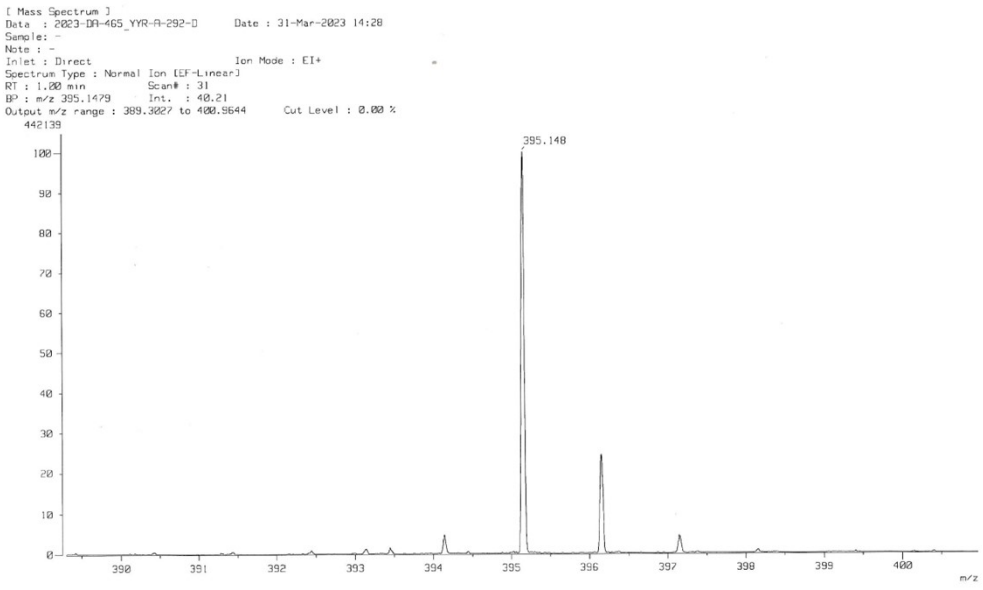
HRMS spectra of **3x**



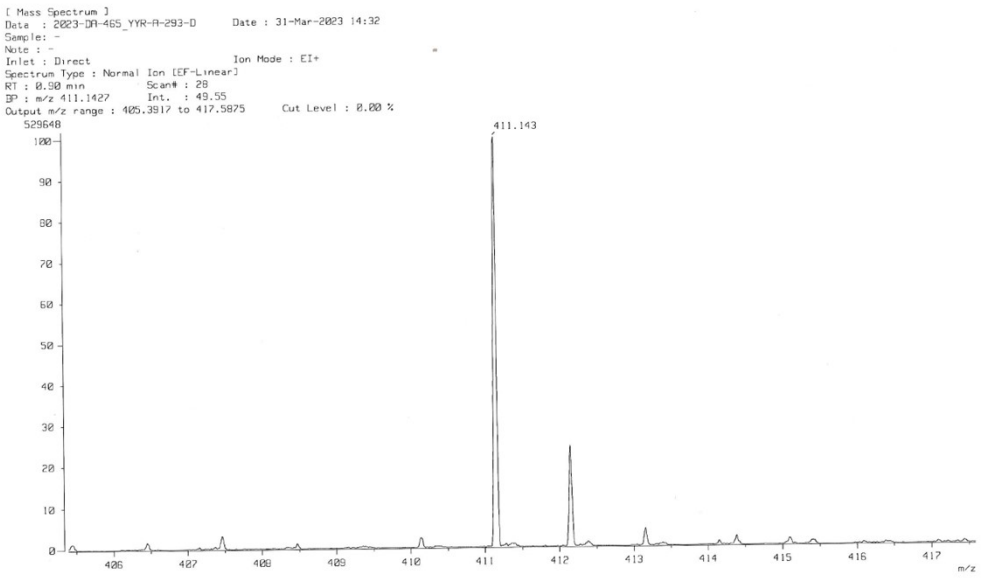
HRMS spectra of **3y**



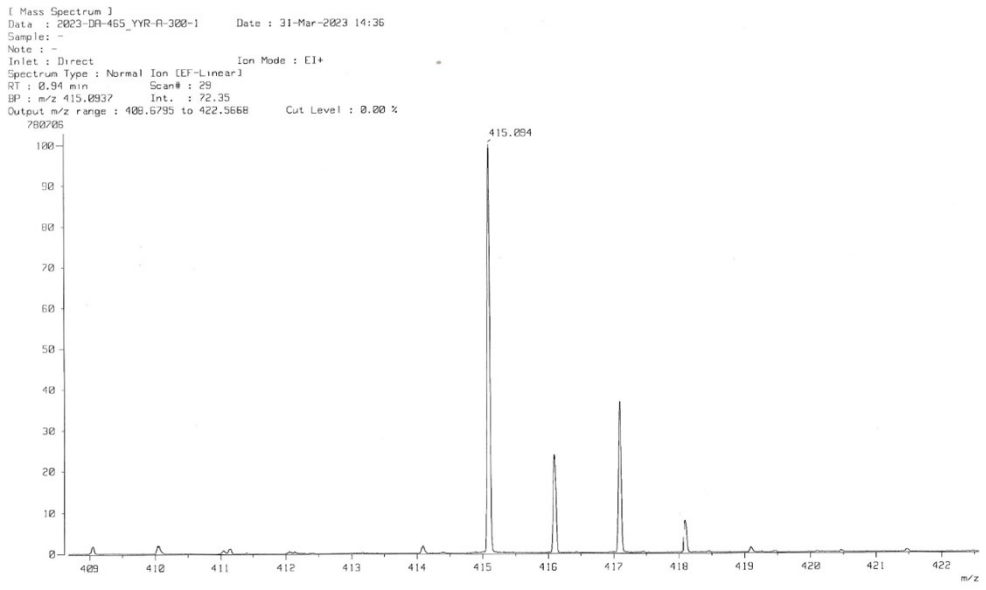
HRMS spectra of **4a**



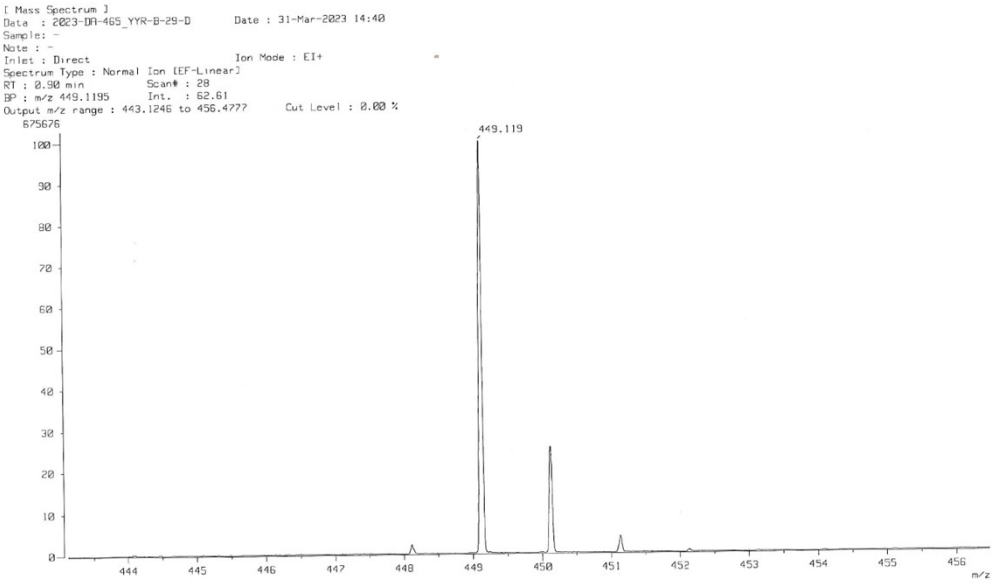
HRMS spectra of **4b**



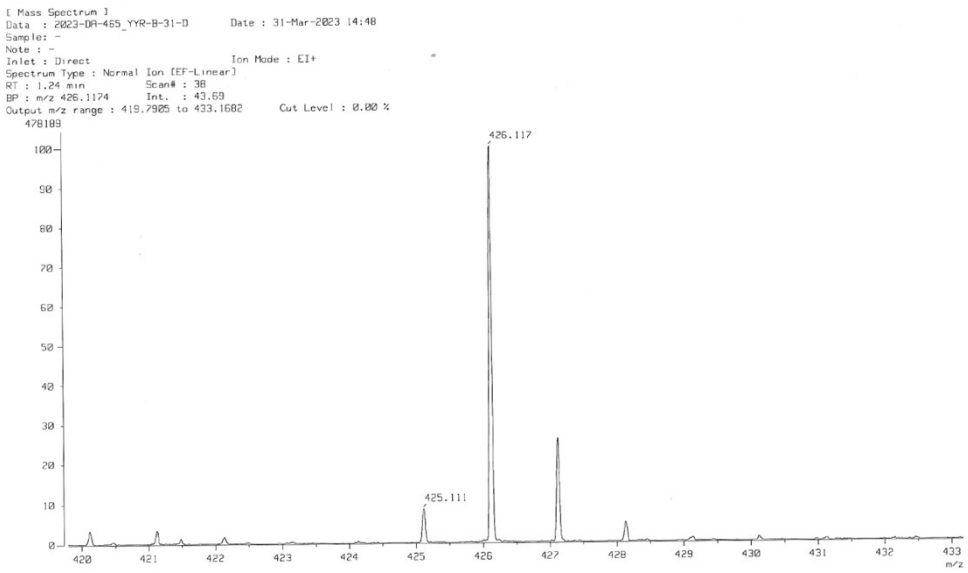
HRMS spectra of **4c**



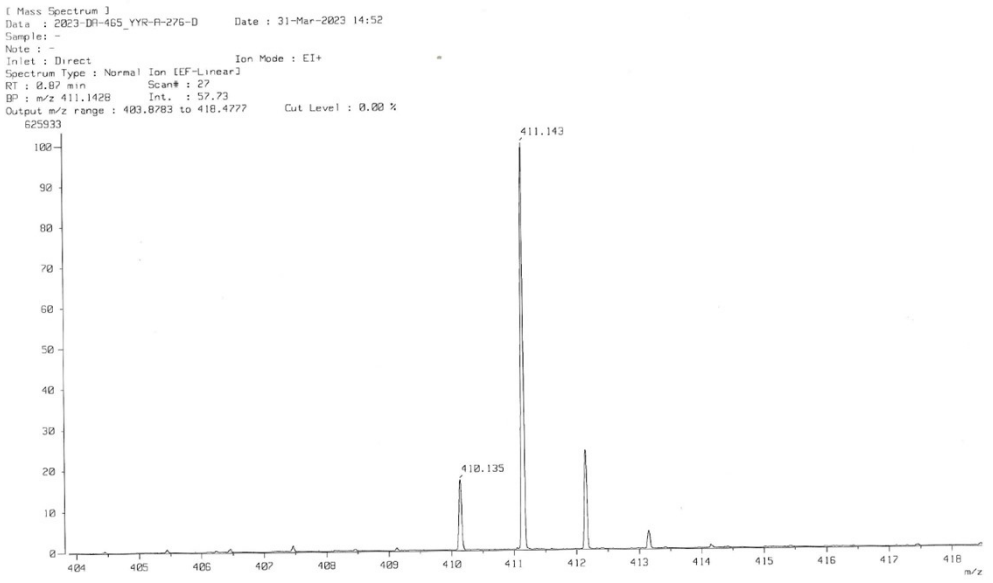
HRMS spectra of **4d**



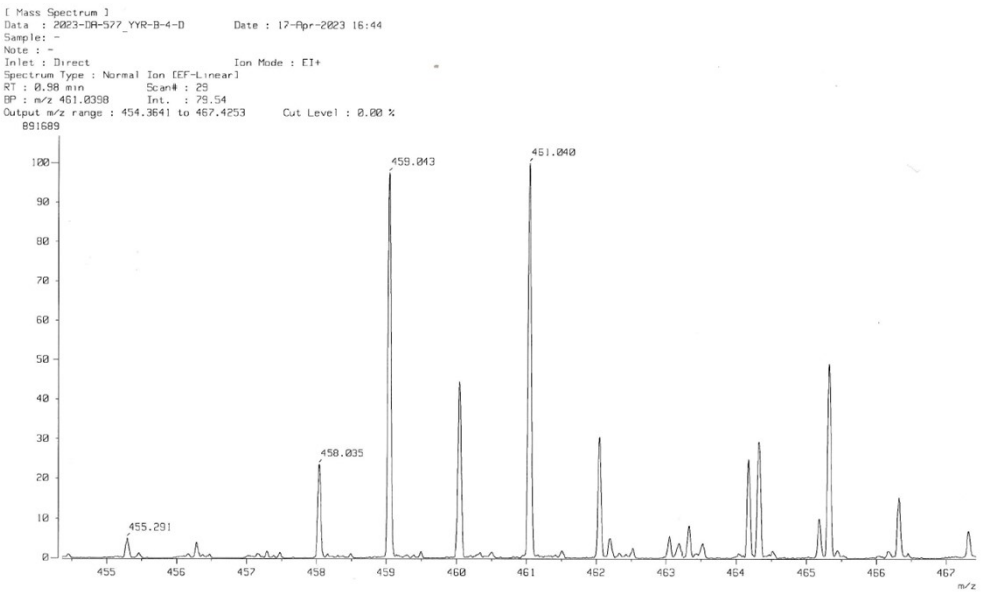
HRMS spectra of **4e**



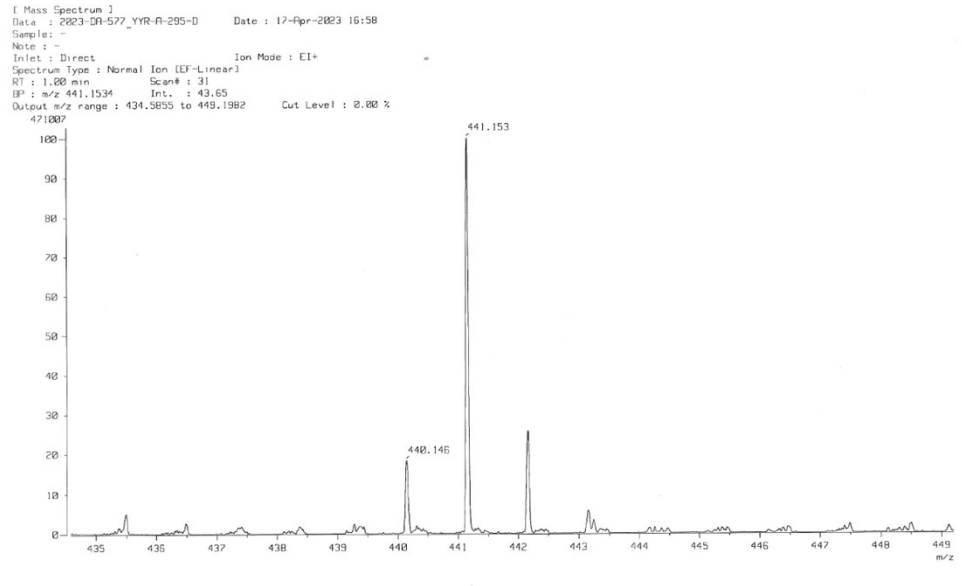
HRMS spectra of **4f**



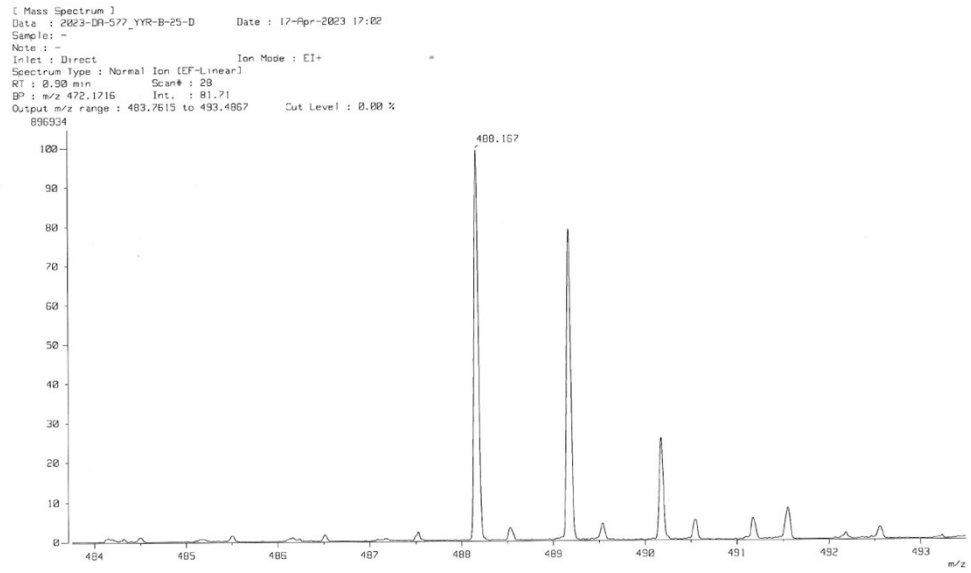
HRMS spectra of **4g**



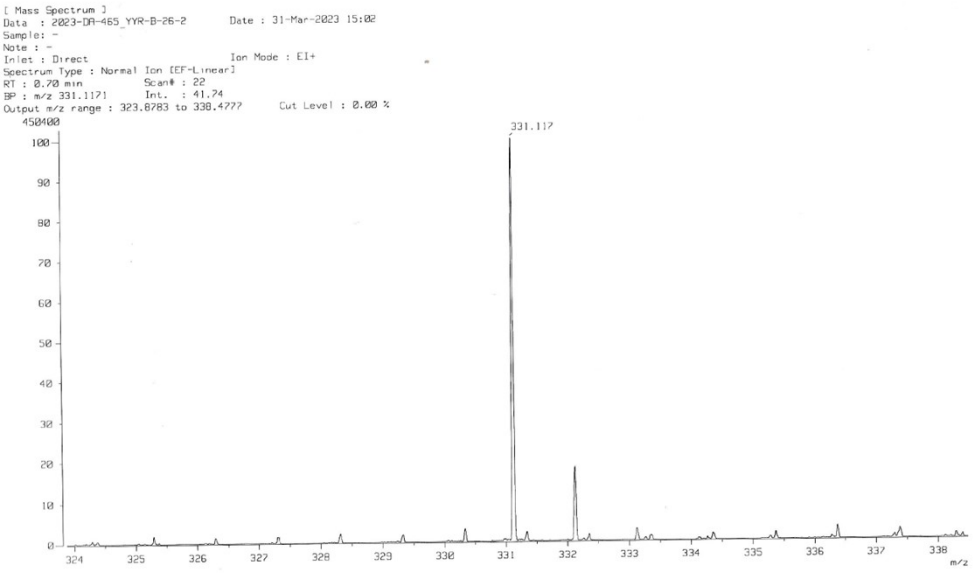
HRMS spectra of **4h**



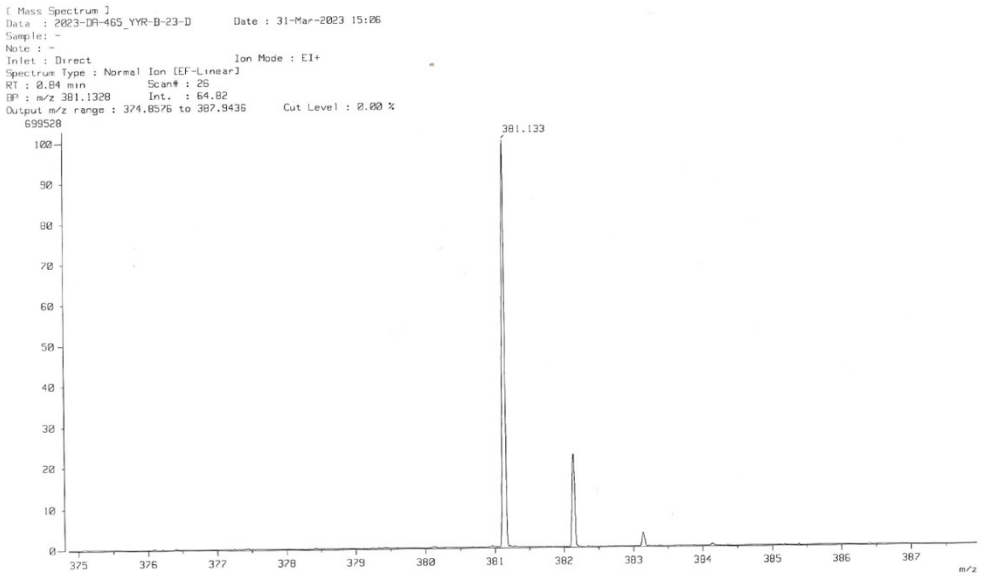
HRMS spectra of **4j**



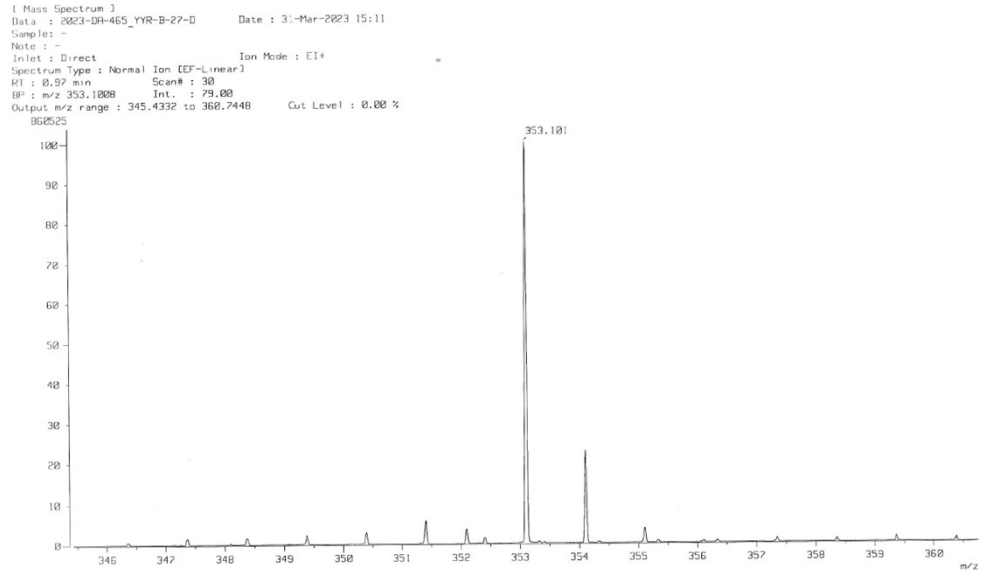
HRMS spectra of **4k**



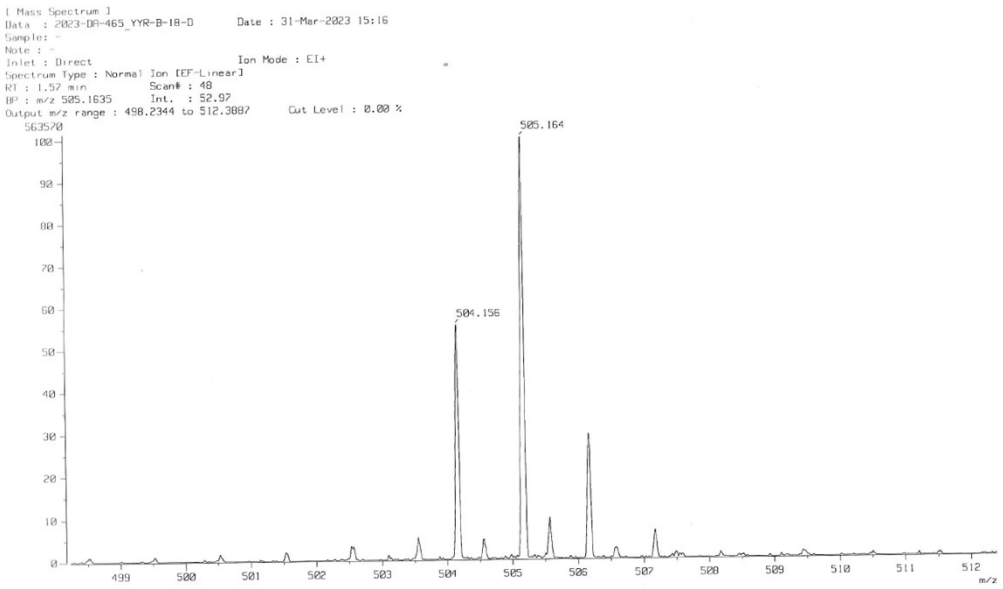
HRMS spectra of **4l**



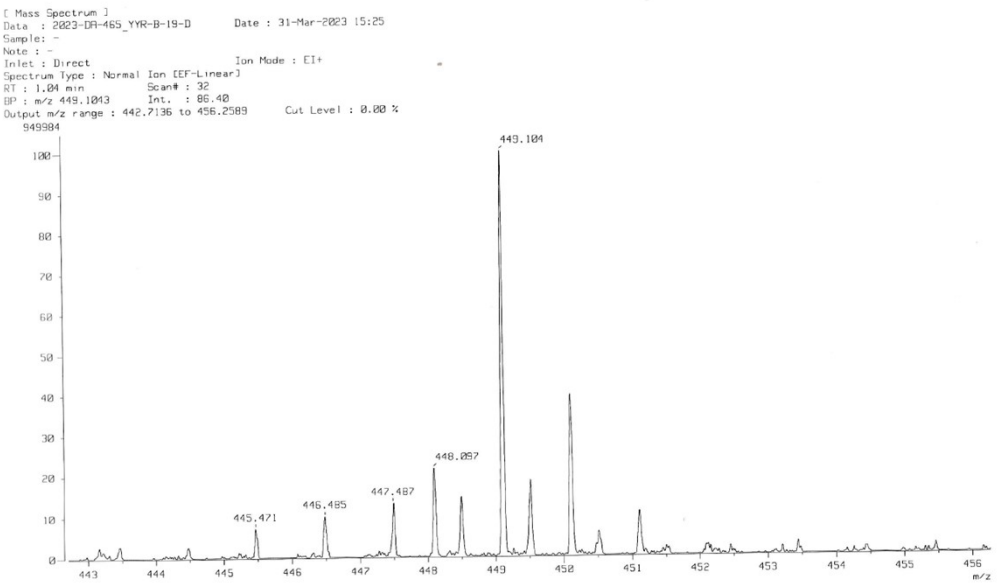
HRMS spectra of **4m**



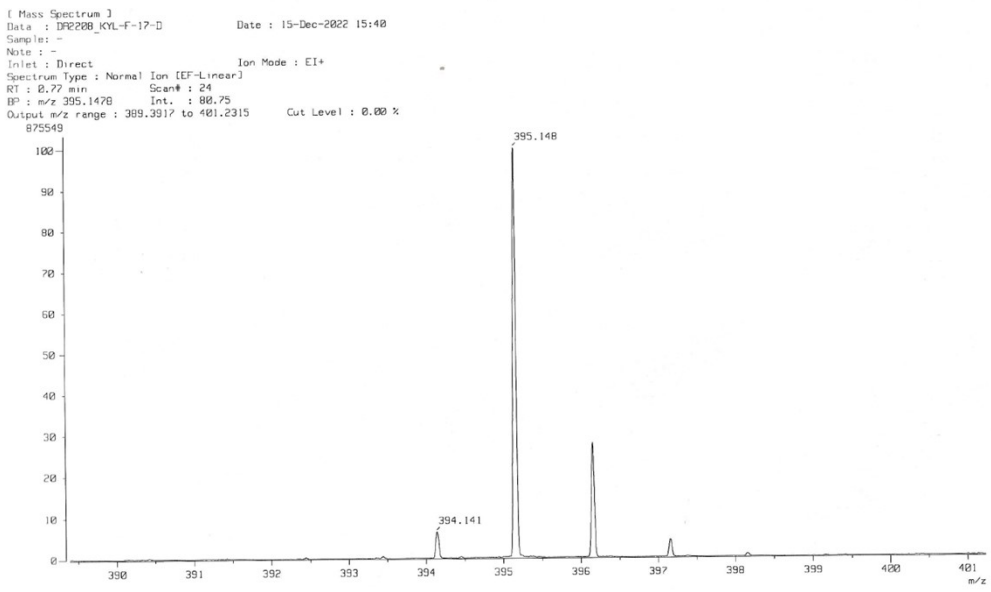
HRMS spectra of **4n**



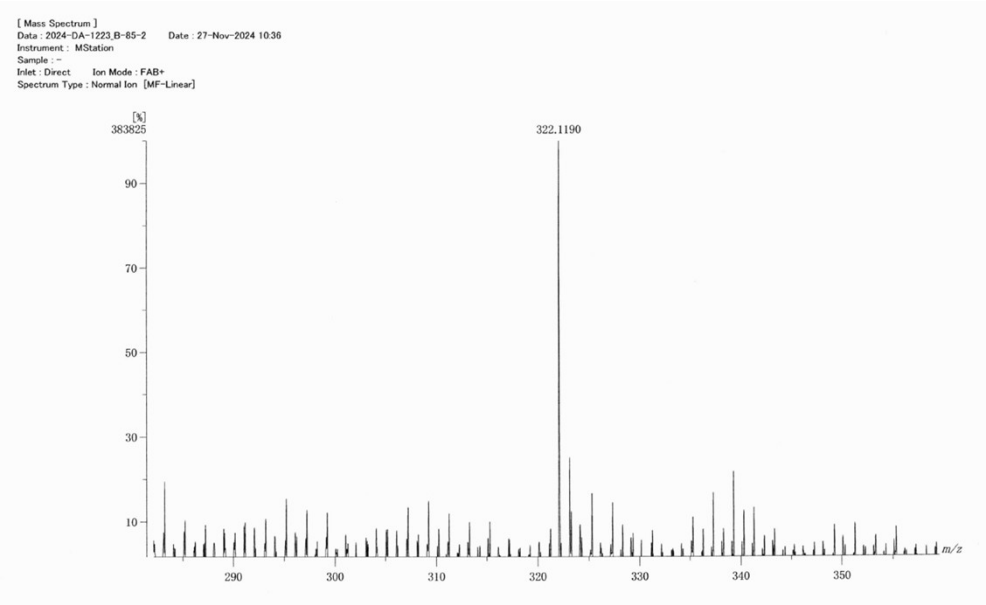
HRMS spectra of **4o**



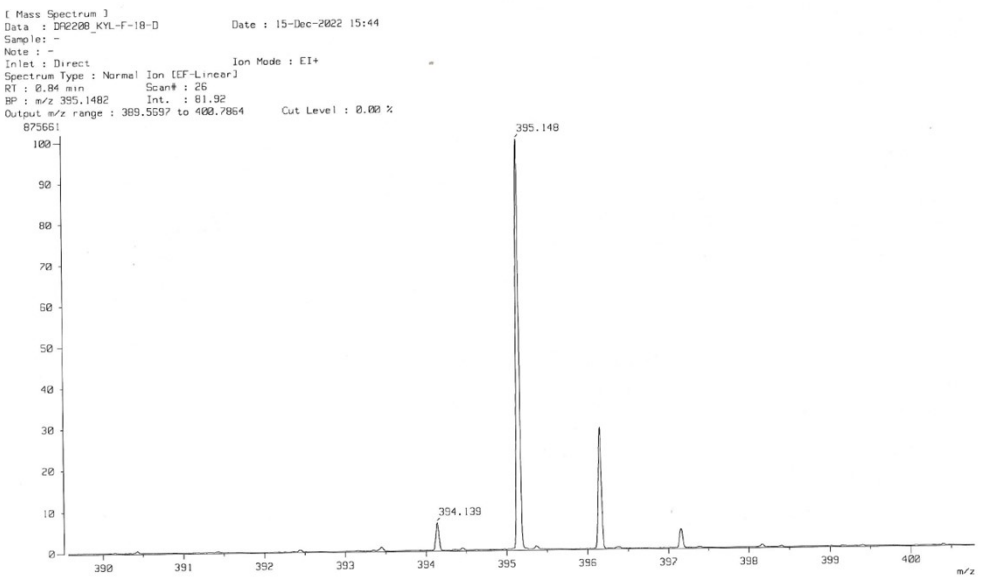
HRMS spectra of **4p**



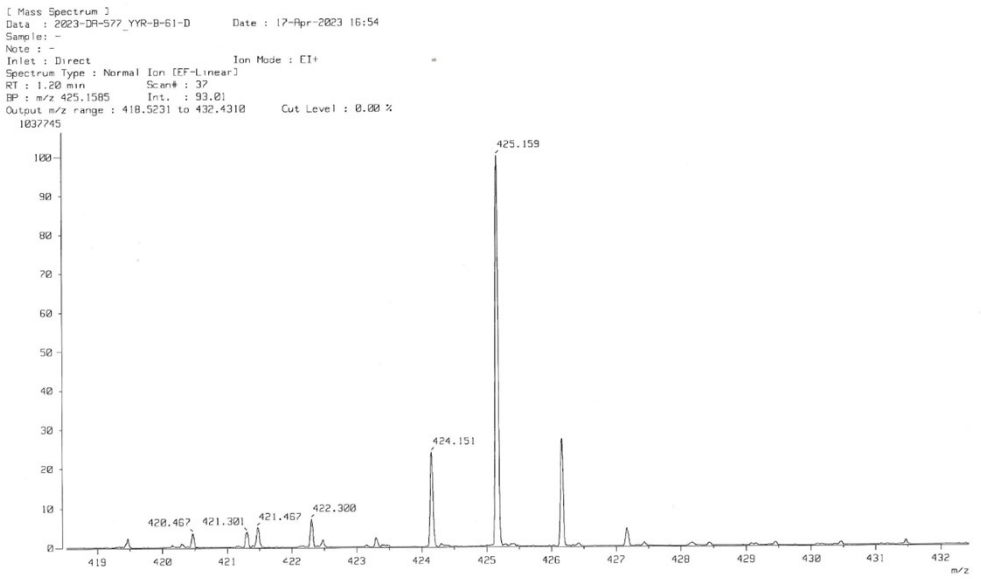
HRMS spectra of **4q**



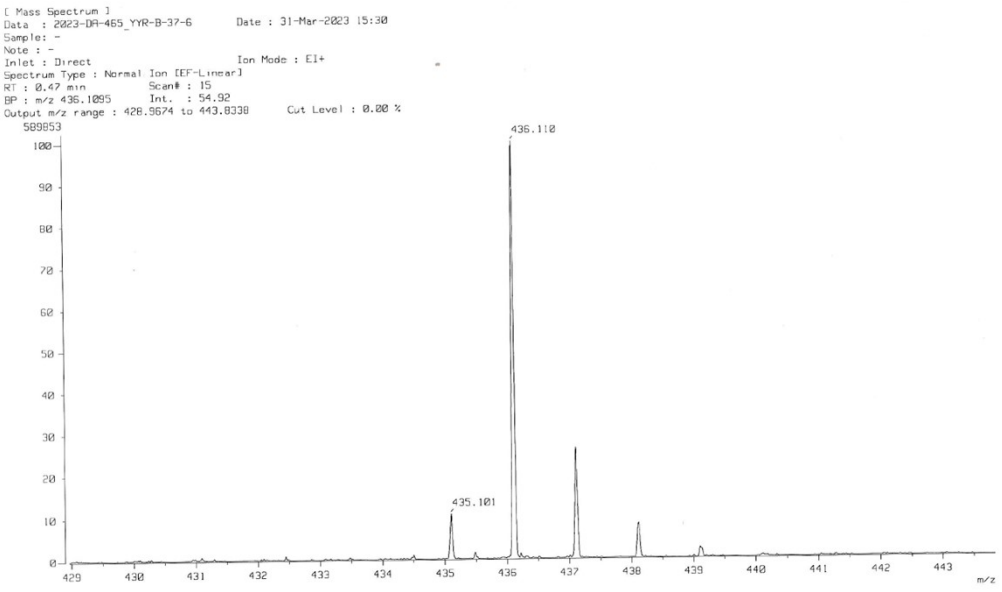
HRMS spectra of **4r**



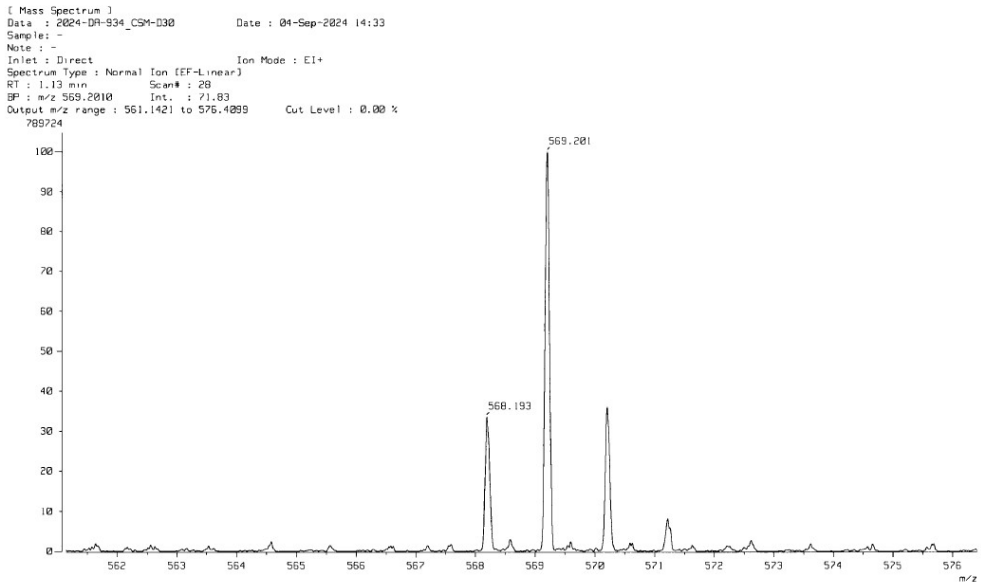
HRMS spectra of **4s**



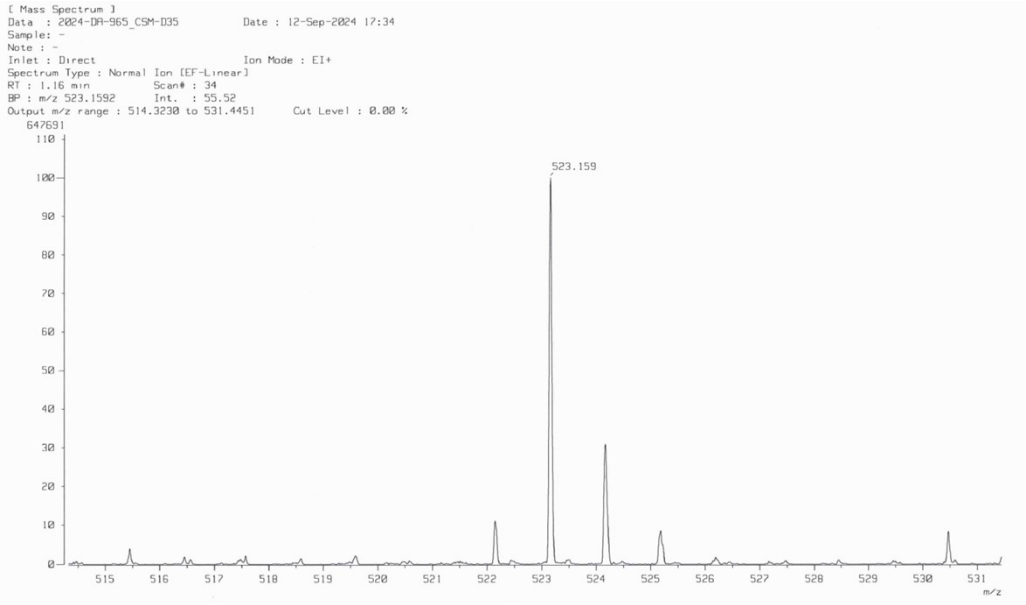
HRMS spectra of **4t**



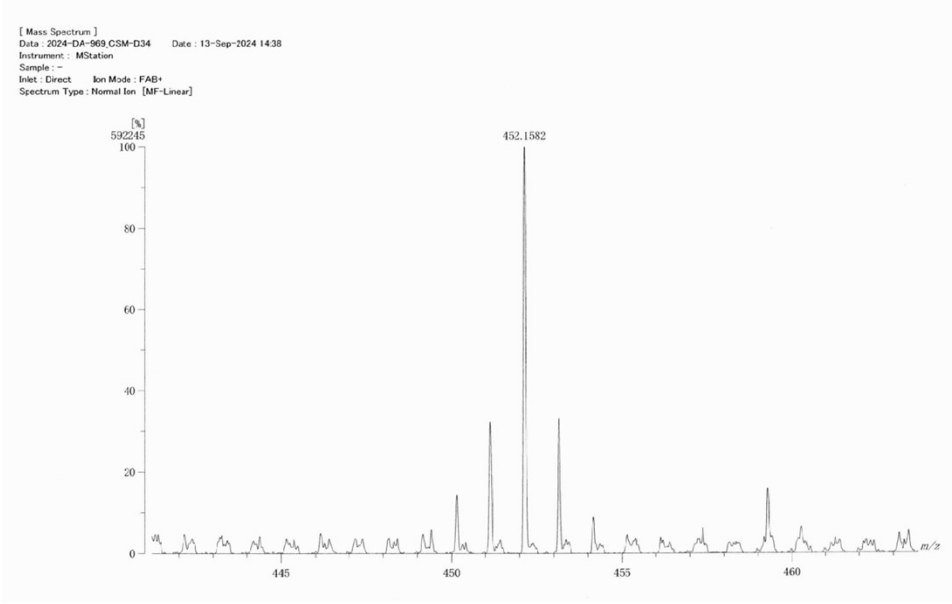
HRMS spectra of **4u**



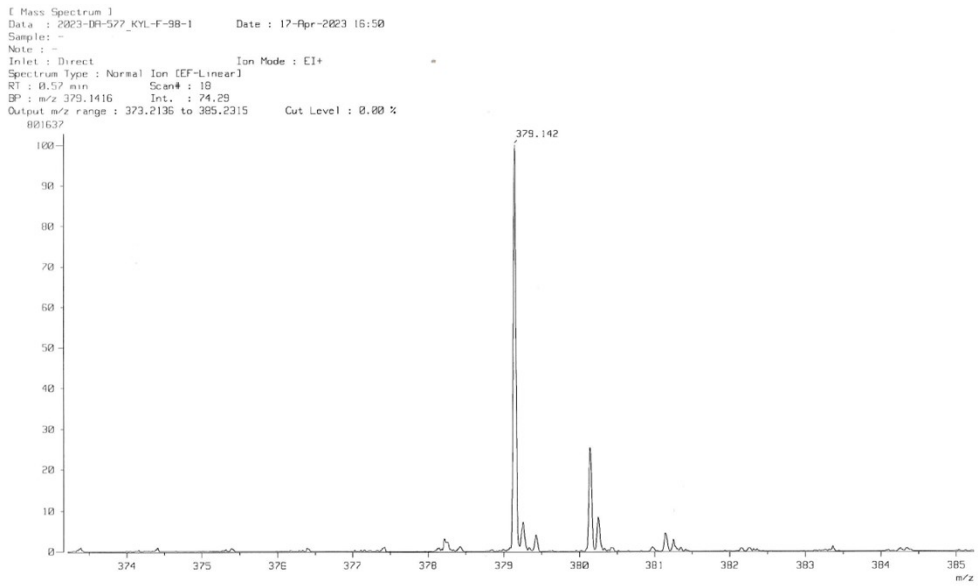
HRMS spectra of **4x**



HRMS spectra of **6**



HRMS spectra of **6'**



HRMS spectra of **11**