Supporting Information

Photoinduced N-Heterocyclic Nitreium-Catalyzed Single Electron Reduction of α-Chloro Esters for Phenanthridine Synthesis

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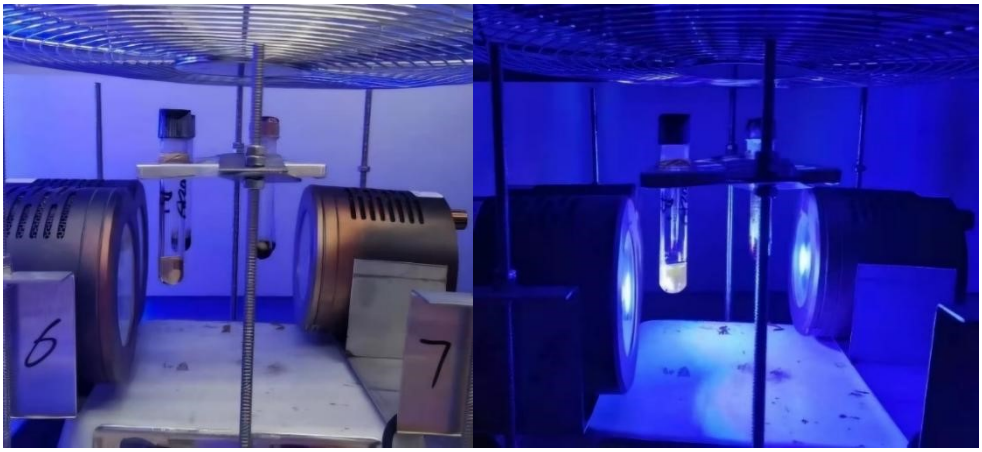
Contents

1. General Experimental Details.

- Chemicals were purchased from Heowns, Innochem and Bidepharm. They were used without further purification unless otherwise noted. The starting materials were readily prepared according to the related literatures.[1-3] Solvents were purified using a solvent-purification system (VSPS-8, Vigor) that contained activated alumina and molecular sieves.
- Chromatographic purification of the products was performed on Mietek 200-300 mesh silica gel.
- HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource. The mass analysis mode of the HRMS was orbitrap.
- ^{1}H, ^{19}F and ^{13}C- NMR spectra were recorded at ambient temperature on a JEOL JNM-LA400 Spectrometer and JEOL JNM-ECZ500R Spectrometer. The chemical shifts are reported in ppm downfield of tetramethylsilane (TMS) and referenced to residual solvent peaks resonance as the internal standard. The order of citation in parentheses is a) multiplicity (s = singlet, d = doublet, t = triplet, dd= doublet of doublet, td = triplet of doublet, m = multiplet), b) coupling constants, c) number of protons. Coupling constants (*J*) are reported in Hertz (Hz).
- Photochemical experiments were performed magnetically stirred in 10 mL glass tubes, sealed with a rubber septum. The tubes were irradiated with blue light (450 nm,) using a LED lamp with a power output of 100 W. The distance from the light source to the irradiation vessel is 2 cm, and a fan was used to keep the reaction temperature at 45±5 °C. （The purchase link for LED lamp is https://item.jd.com/52714507033.html）



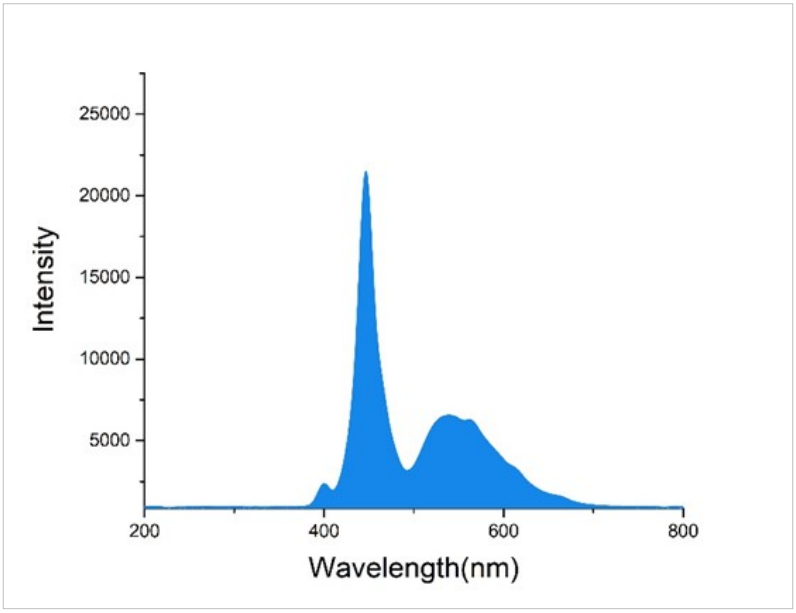
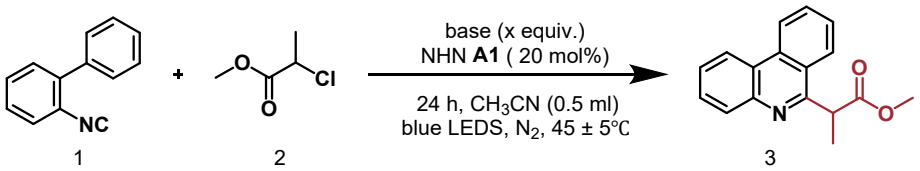


Fig. S1 The spectrum of blue LEDs employed in the reaction

2. Detailed Optimization of Reaction Conditions.

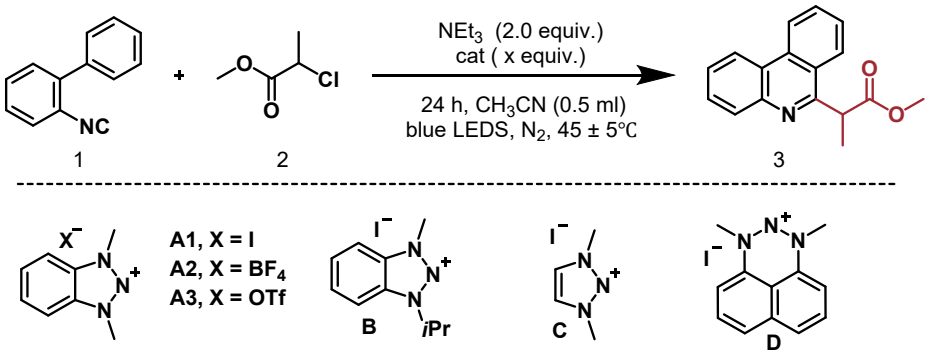
Scheme S1 The screen of the Base.



Entry[a]	base	x	Yield(%)[b]
1	NEt_3	2.0	87(75)
2	DIPEA	2.0	60
3	TMEDA	2.0	20
4	DBU	2.0	55
5	DABCO	2.0	ND
6	NaOAc	2.0	17
7	TPA	2.0	ND
8	$NaHCO_3$	2.0	trace
9	KH_2PO_4	2.0	trace
10	Cs_2CO_3	2.0	19
11	NEt_3	1.0	70
12	NEt_3	0.2	15
13[c]	/	/	ND

[a]**1** (36 mg, 0.2 mmol), **2** (49 mg, 0.4 mmol) and addition (20 mol%) in solvent (0.5 mL) under irradiation with blue LED (100 W); [b]isolated yields. Yields were determined by ^1H NMR analysis using sym-tetrachloroethane as an external standard. The value within parentheses refers to yield of isolated product. [c]No base, reaction temperature is 45 °C.

Scheme S2 The screen of the Cat.

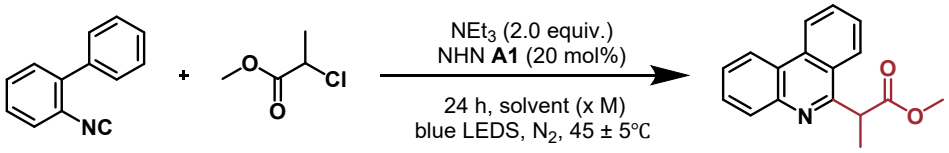


Entry[a]	Cat	X	Yield(%)[b]
1	**A1**	0.2	87(75)
2	**A2**	0.2	trace
3	**A3**	0.2	trace
4	**B**	0.2	45
5	**C**	0.2	47
6	**D**	0.2	10
7	**A1**	0.1	51
8	**A1**	0.05	47

9	**A1**	0.02	43
10[c]	/	/	trace

[a]**1** (36 mg, 0.2 mmol), **2** (49 mg, 0.4 mmol) and addition (20 mol%) in solvent (0.5 mL) under irradiation with blue LED (100 W); [b]isolated yields. Yields were determined by ^{1}H NMR analysis using sym-tetrachloroethane as an external standard. The value within parentheses refers to yield of isolated product. [c]No cat, reaction temperature is 45 °C.

Scheme S3 The screen of the Solvent.

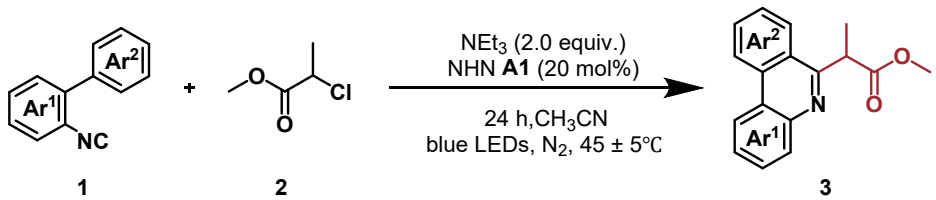


Entry[a]	Solvent	X	Yield/%[b]
1	CH_3CN	0.4	87(75)
2	Toluene	0.4	10
3	DCM	0.4	12
4	Et_2O	0.4	trace
5	THF	0.4	21
6	DMF	0.4	70
7	DMA	0.4	68
8	DMSO	0.4	65
9	CH_3CN	0.2	54
10	CH_3CN	0.1	35

[a]**1** (36 mg, 0.2 mmol), **2** (49 mg, 0.4 mmol) and addition (20 mol%) in solvent (0.5 mL) under irradiation with blue LED (100 W); [b]isolated yields. Yields were determined by ^{1}H NMR analysis using sym-tetrachloroethane as an external standard. The value within parentheses refers to yield of isolated product.

3. General Procedures and Spectral Data of Products.

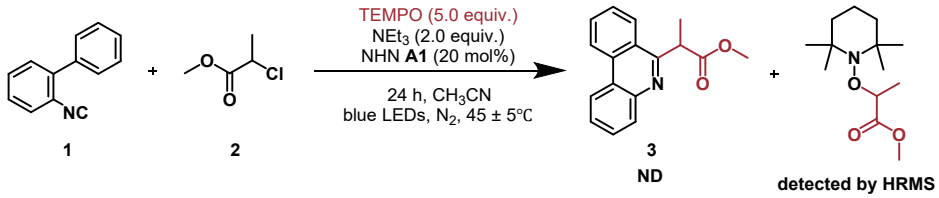
3.1 General Procedure A for the Synthesis of **3-23**.



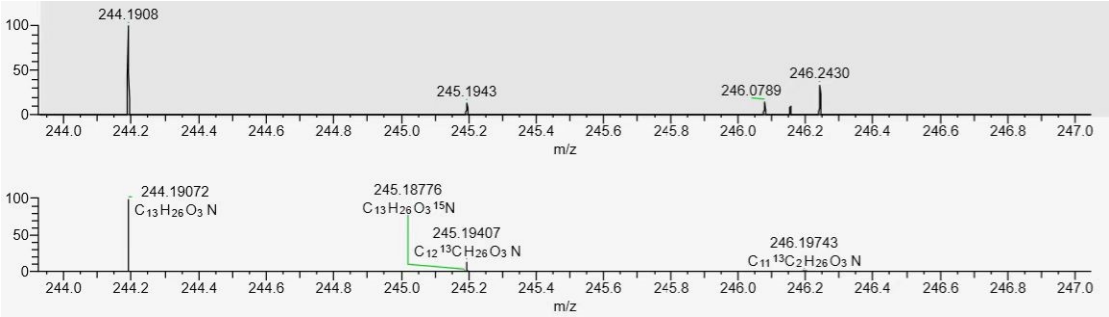
In a nitrogen-filled glovebox, a dry tube equipped with a magnetic stirring bar was charged sequentially with 1-biphenyl,2-isocyano (0.20 mmol), **2** (0.40 mmol), NHN **A1** (0.04 mmol), Triethylamine (0.40 mmol) and acetonitrile (0.5 mL). The tube was closed and removed from the glovebox. The resulting mixture was allowed to stir at 45±5 °C under blue LED (100 W) irradiation for 24 hours. Upon completion, the solvent was removed under vacuum and the residue was subjected to silica gel chromatography using petroleum ether and ethyl acetate as eluent to afford the desired products **3-23**.

4. The Mechanism Studies.

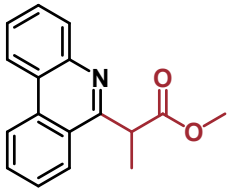
4.1 TEMPO Trapping Experiment.



In a nitrogen-filled glovebox, a dry tube equipped with a magnetic stirring bar was charged sequentially with **1** (0.20 mmol), **2** (0.40 mmol), NHN **A1** (0.02 mmol), TEMPO (1.0 mmol) and acetone (0.5 mL). The tube was closed and removed from the glovebox. The resulting mixture was allowed to stir at 45±5 °C under blue LED (100 W) irradiation for 24 hours. The adduct of TEMPO and alkyl radical was detected by HRMS. **HRMS** (ESI): *m/z* $[M+H]^+$ calcd for $C_{13}H_{26}N_2O^+$: 245.1943; found: 245.1877, unfortunately, we could not isolate it.

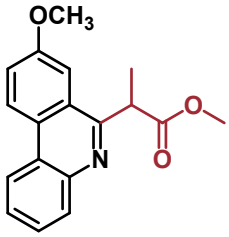


5. Compound Characterization Data.

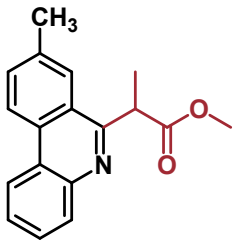


Methyl 2-(phenanthridin-6-yl) propanoate (3): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 50:1) as a white solid (40 mg, 0.150 mmol, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.60 (m, 1H), 8.49 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.20 – 8.16 (m, 1H), 8.14 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.79 (m, 1H), 7.71 – 7.67 (m, 1H), 7.67 – 7.63 (m, 1H), 7.60 (m, 1H), 4.75 (q, *J* = 7.1 Hz, 1H), 3.67 (s, 3H), 1.78 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 159.4, 143.6, 133.3, 130.4, 130.3, 128.7, 127.5, 125.5, 124.7, 123.8, 122.8, 121.9, 52.3, 45.5, 16.5.

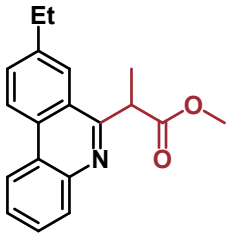
These data are in agreement with those reported previously in the literature.[4]



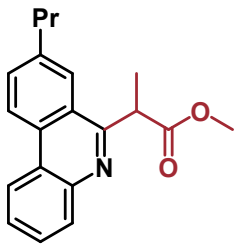
Methyl 2-(8-methoxyphenanthridin-6-yl) propanoate (4): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 50:1 – 30:1) as a white solid (47.8 mg, 0.162 mmol, 81%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 9.1 Hz, 1H), 8.44 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.12 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.64 (m, 1H), 7.60 (m, 1H), 7.54 (d, *J* = 2.5 Hz, 1H), 7.45 (dd, *J* = 9.0, 2.6 Hz, 1H), 4.69 (q, *J* = 7.1 Hz, 1H), 3.96 (s, 3H), 3.69 (s, 3H), 1.80 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.4, 158.9, 158.4, 142.8, 130.3, 127.7, 127.1, 126.1, 124.5, 124.0, 121.5, 121.0, 105.9, 55.7, 52.4, 46.0, 16.3.



Methyl 2-(8-methylphenanthridin-6-yl) propanoate (5): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 50:1) as a white solid (46.4 mg, 0.166 mmol, 83%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.4 Hz, 1H), 8.49 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.12 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.97 (s, 1H), 7.67 (m 2H), 7.61 (m, 1H), 4.76 (q, *J* = 7.1 Hz, 1H), 3.69 (s, 3H), 2.60 (s, 3H), 1.77 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.4, 159.2, 143.3, 137.6, 132.3, 131.3, 130.3, 128.3, 126.9, 125.1, 124.9, 123.9, 122.7, 121.8, 52.3, 45.4, 22.0, 16.6.

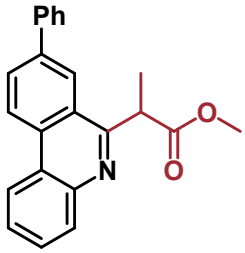


Methyl 2-(8-ethylphenanthridin-6-yl) propanoate (6): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 50:1) as a white solid (44 mg, 0.150 mmol, 75%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.4 Hz, 1H), 8.52 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.13 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.99 (s, 1H), 7.72 – 7.66 (m, 2H), 7.62 (m, 1H), 4.77 (q, *J* = 7.1 Hz, 1H), 3.70 (s, 3H), 2.90 (q, *J* = 7.6 Hz, 2H), 1.79 (d, *J* = 7.1 Hz, 3H), 1.37 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.5, 159.3, 143.8, 143.3, 131.5, 131.2, 130.3, 128.3, 126.9, 125.0, 124.0, 123.9, 122.9, 121.8, 52.4, 45.6, 29.3, 16.6, 15.8.

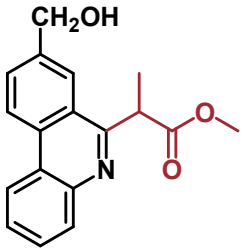


Methyl 2-(8-propylphenanthridin-6-yl) propanoate (7): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 50:1) as a white solid (50.4 mg, 0.164

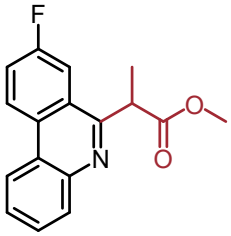
mmol, 82%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.4 Hz, 1H), 8.49 (d, *J* = 7.5 Hz, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 7.96 (s, 1H), 7.69 – 7.64 (m, 2H), 7.60 (m, 1H), 4.76 (q, *J* = 7.1 Hz, 1H), 3.68 (s, 3H), 2.82 (t, *J* = 7.6 Hz, 2H), 1.77 (m, 5H), 0.99 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.4, 159.3, 143.3, 142.2, 131.6, 131.5, 130.2, 128.3, 126.9, 124.9, 124.6, 124.0, 122.8, 121.8, 52.3, 45.6, 38.3, 24.7, 16.6, 13.8.



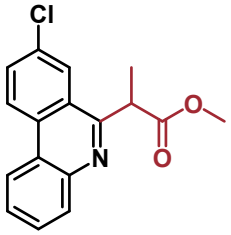
Methyl 2-(8-phenylphenanthridin-6-yl) propanoate (8): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 50:1) as a white solid (49.2 mg, 0.144 mmol, 72%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.6 Hz, 1H), 8.53 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.41 (d, *J* = 1.8 Hz, 1H), 8.16 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.06 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.74 – 7.69 (m, 3H), 7.64 (m, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.45 – 7.41 (m, 1H), 4.84 (q, *J* = 7.1 Hz, 1H), 3.70 (s, 3H), 1.82 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.3, 159.5, 143.6, 140.4, 132.4, 130.4, 129.7, 129.3, 128.7, 128.1, 127.5, 127.1, 125.1, 123.7, 123.4, 122.0, 77.4, 76.9, 52.4, 45.6, 16.6.



Methyl 2-(8-(hydroxymethyl) phenanthridin-6-yl) propanoate (9): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 50:1 – 35:1) as a white solid (40.1 mg, 0.136 mmol, 68%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 9.0 Hz, 1H), 8.46 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.15 – 8.11 (m, 1H), 7.63 (m, 2H), 7.54 (d, *J* = 2.6 Hz, 1H), 7.47 (dd, *J* = 9.0, 2.6 Hz, 1H), 4.69 (q, *J* = 7.1 Hz, 1H), 3.97 (s, 3H), 3.69 (s, 3H), 1.80 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.2, 158.6, 158.2, 142.6, 130.1, 127.5, 126.8, 125.8, 124.2, 123.7, 121.2, 120.8, 105.6, 55.4, 52.2, 45.8, 29.6, 16.1.

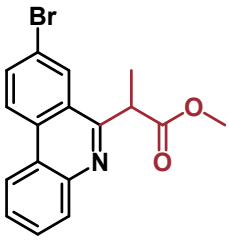


Methyl 2-(8-fluorophenanthridin-6-yl) propanoate (10): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 50:1) as a white solid (48.7 mg, 0.172 mmol, 86%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.64 (dd, *J* = 9.1, 5.4 Hz, 1H), 8.47 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.18 – 8.12 (m, 1H), 7.84 (dd, *J* = 9.9, 2.6 Hz, 1H), 7.71 (m, 1H), 7.64 (m, 1H), 7.58 (m, 1H), 4.66 (q, *J* = 7.1 Hz, 1H), 3.71 (s, 3H), 1.78 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.9, 162.6, 160.6, 158.5 (d, *J* = 3.8 Hz), 143.3, 130.5, 130.1, 128.6, 127.4, 126.1 (d, *J* = 7.7 Hz), 125.4 (d, *J* = 8.5 Hz), 123.4, 121.7, 119.8, 119.6, 110.4, 110.3, 52.5, 45.4, 16.4. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -111.4.

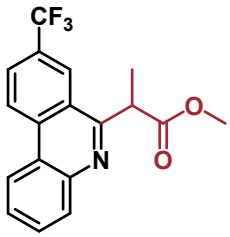


Methyl 2-(8-chlorophenanthridin-6-yl) propanoate (11): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 50:1) as a white solid (52.2 mg, 0.174 mmol, 87%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.9 Hz, 1H), 8.45 (d, *J* = 8.2 Hz, 1H), 8.17 (d, *J* = 2.1 Hz, 1H), 8.14 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.77 – 7.69 (m, 2H), 7.63 (m, 1H), 4.69 (q, *J* = 7.1 Hz, 1H), 3.71 (s, 3H), 1.77 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.9, 158.3, 143.5, 133.6, 131.8, 131.0, 130.5, 129.1, 127.4,

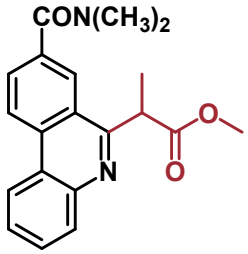
125.7, 125.0, 124.6, 123.2, 121.8, 52.5, 45.1, 16.5.



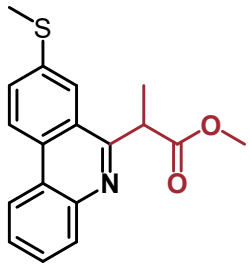
Methyl 2-(8-bromophenanthridin-6-yl) propanoate (12): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 50:1) as a white solid (55.7 mg, 0.162 mmol, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.8 Hz, 2H), 8.47 (d, *J* = 1.4 Hz, 1H), 8.35 (d, *J* = 2.0 Hz, 1H), 8.14 (m, 1H), 7.91 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.73 (m, 1H), 7.65 (m, 1H), 4.70 (q, *J* = 7.1 Hz, 1H), 3.71 (s, 3H), 1.77 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 158.3, 143.6, 133.7, 132.1, 130.6, 129.2, 128.2, 127.5, 126.1, 124.7, 123.3, 121.8, 121.7, 52.5, 45.0, 16.6.



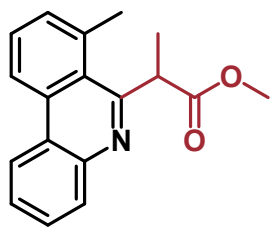
Methyl 2-(8-(trifluoromethyl) phenanthridin-6-yl) propanoate (13): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 50:1) as a white solid (44.7 mg, 0.134 mmol, 67%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.77 (d, *J* = 8.7 Hz, 1H), 8.55 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.51 (s, 1H), 8.19 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.03 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.79 (m, 1H), 7.70 (m, 1H), 4.80 (q, *J* = 7.1 Hz, 1H), 3.72 (s, 3H), 1.81 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.8, 159.2, 144.3, 135.6, 130.6, 130.0, 127.7, 126.4, 126.4, 124.2, 124.0, 123.2, 123.1, 122.9, 122.4, 76.9, 52.5, 45.1, 16.6. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.1.



Methyl 2-(8-(dimethyl carbamoyl) phenanthridin-6-yl) propanoate (14): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 40:1) as a white solid (53.8 mg, 0.160 mmol, 80%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.5 Hz, 1H), 8.55 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.30 (d, *J* = 1.6 Hz, 1H), 8.16 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.92 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.75 (m, 1H), 7.67 (m, 1H), 4.77 (q, *J* = 7.1 Hz, 1H), 3.69 (s, 3H), 3.14 (d, *J* = 53.2 Hz, 6H), 1.79 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.0, 170.9, 159.3, 144.0, 135.1, 134.1, 130.5, 129.4, 129.2, 127.4, 124.7, 124.2, 123.3, 123.2, 122.2, 52.4, 45.3, 39.8, 35.7, 16.6.

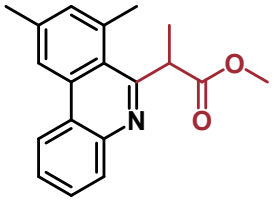


Methyl 2-(8-(methylthio)phenanthridin-6-yl) propanoate （15）: Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 50:1) as a white solid (48.6 mg, 0.156 mmol, 78%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.7 Hz, 1H), 8.47 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.13 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.96 (d, *J* = 1.9 Hz, 1H), 7.73 – 7.66 (m, 2H), 7.62 (m, 1H), 4.71 (q, *J* = 7.1 Hz, 1H), 3.69 (s, 3H), 2.63 (s, 3H), 1.79 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.3, 158.4, 143.3, 138.9, 130.7, 130.4, 129.4, 128.5, 127.2, 125.3, 123.7, 123.2, 121.7, 121.4, 52.4, 45.8, 16.4, 15.8.

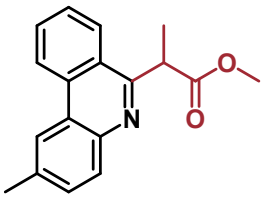


Methyl 2-(7-methylphenanthridin-6-yl) propanoate (16): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 40:1) as a white solid (43.6 mg,

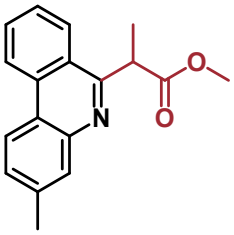
0.156 mmol, 78%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.4 Hz, 1H), 8.52 (d, *J* = 8.3 Hz, 1H), 8.05 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.70 – 7.65 (m, 2H), 7.60 (m, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 5.06 (q, *J* = 6.9 Hz, 1H), 3.71 (s, 3H), 3.01 (s, 3H), 1.66 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.4, 160.5, 142.9, 135.3, 135.1, 132.2, 129.9, 129.8, 128.6, 126.9, 125.0, 123.9, 122.3, 121.4, 52.2, 47.8, 25.7, 18.0.



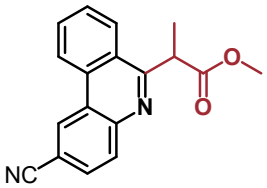
Methyl 2-(7,9-dimethylphenanthridin-6-yl) propanoate (17): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 50:1) as a white solid (46.4 mg, 0.158 mmol, 79%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.36 (s, 1H), 8.03 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.67 – 7.62 (m, 1H), 7.59 – 7.54 (m, 1H), 7.34 (s, 1H), 5.02 (q, *J* = 6.9 Hz, 1H), 3.71 (s, 3H), 2.96 (s, 3H), 2.56 (s, 3H), 1.64 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.5, 160.3, 143.1, 139.9, 135.3, 135.1, 134.0, 129.8, 128.4, 126.6, 123.7, 123.1, 122.3, 121.1, 52.1, 47.7, 25.6, 21.9, 18.0.



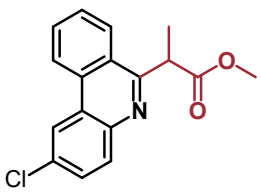
Methyl 2-(2-methylphenanthridin-6-yl) propanoate (18): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 50:1) as a white solid (43.0 mg, 0.154 mmol, 77%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.2 Hz, 1H), 8.33 (s, 1H), 8.18 (d, *J* = 8.3 Hz, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.82 (m, 1H), 7.68 (m, 1H), 7.54 (dd, *J* = 8.3, 1.9 Hz, 1H), 4.74 (q, *J* = 7.1 Hz, 1H), 3.69 (s, 3H), 2.62 (s, 3H), 1.78 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.5, 158.5, 142.0, 136.9, 133.2, 130.5, 130.3, 130.1, 127.4, 125.6, 124.8, 123.7, 122.8, 121.6, 52.4, 45.6, 22.1, 16.6.



Methyl 2-(3-methylphenanthridin-6-yl) propanoate (19): Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 50:1) as a white solid (44.2 mg, 0.158 mmol, 75%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.59 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.39 (d, *J* = 8.3 Hz, 1H), 8.17 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.95 (s, 1H), 7.78 (m, 1H), 7.64 (m, 1H), 7.44 (dd, *J* = 8.4, 1.9 Hz, 1H), 4.74 (q, *J* = 7.1 Hz, 1H), 3.68 (s, 3H), 2.56 (s, 3H), 1.77 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.3, 159.4, 143.7, 138.9, 133.4, 130.4, 129.9, 128.7, 127.1, 125.6, 124.4, 122.6, 121.7, 121.5, 52.3, 45.5, 21.5, 16.6.

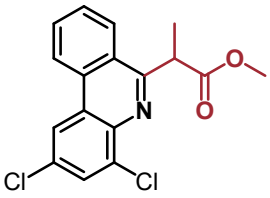


Methyl 2-(2-cyanophenanthridin-6-yl) propanoate （20）： Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 30:1) as a white solid (34.8 mg, 0.120 mmol, 60%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.88 (d, *J* = 1.7 Hz, 1H), 8.62 (dd, *J* = 8.3, 1.1 Hz, 1H), 8.30 – 8.26 (m, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.94 (m, 1H), 7.89 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.81 (m, 1H), 4.80 (q, *J* = 7.1 Hz, 1H), 3.71 (s, 3H), 1.79 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.7, 162.8, 145.3, 132.3, 131.6, 131.6, 130.3, 129.0, 127.8, 126.0, 125.2, 124.1, 122.8, 119.2, 110.4, 52.5, 45.5, 16.5.

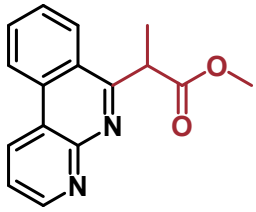


Methyl 2-(2-chlorophenanthridin-6-yl) propanoate （21）： Following the general procedure A, the title product was obtained after purification

by column chromatography (PE/EA = 50:1) as a white solid (51.0 mg, 0.170 mmol, 85%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.57 (dd, *J* = 8.3, 1.3 Hz, 1H), 8.49 (d, *J* = 2.3 Hz, 1H), 8.21 (d, *J* = 8.2 Hz, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 7.85 (m, 1H), 7.73 (m, 1H), 7.65 (dd, *J* = 8.7, 2.3 Hz, 1H), 4.75 (q, *J* = 7.1 Hz, 1H), 3.70 (s, 3H), 1.78 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.1, 159.7, 142.1, 132.9, 132.4, 131.9, 130.8, 129.3, 128.3, 125.7, 125.0, 125.0, 122.9, 121.7, 52.4, 45.5, 16.5.



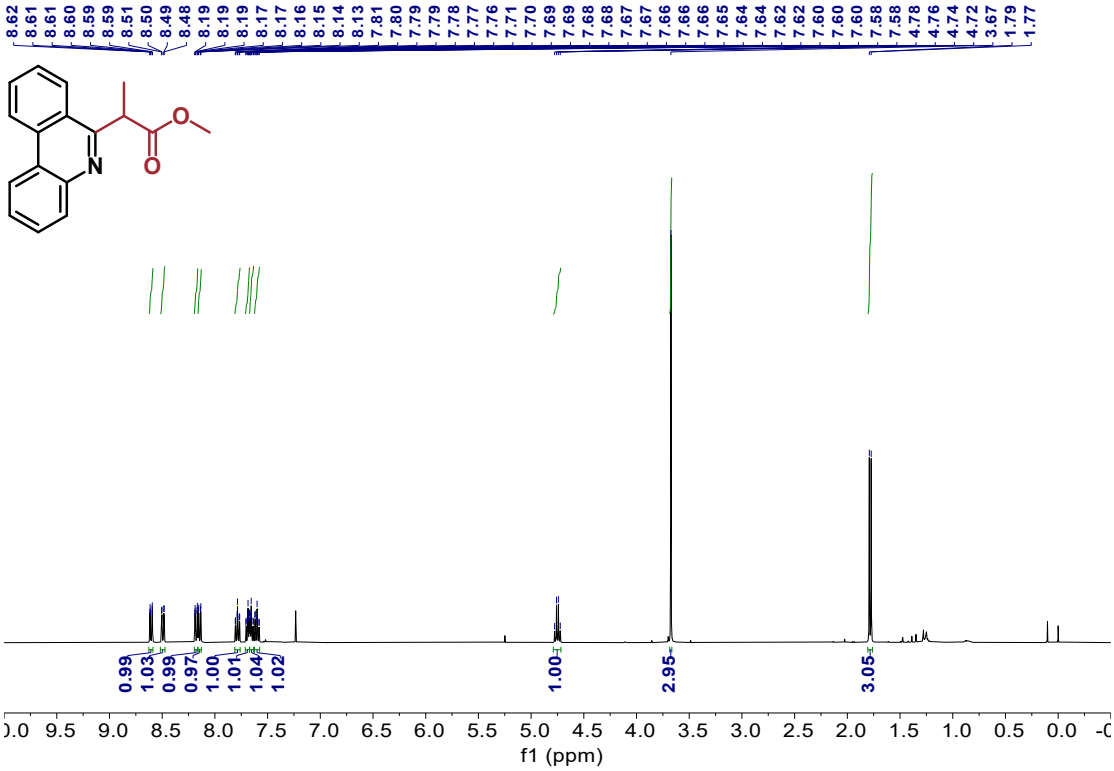
Methyl 2-(2,4-dichlorophenanthridin-6-yl) propanoate （22）： Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 50:1) as a white solid (54.8 mg, 0.164 mmol, 82%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.2 Hz, 1H), 8.40 (d, *J* = 2.2 Hz, 1H), 8.22 (d, *J* = 8.2 Hz, 1H), 7.87 (m, 1H), 7.79 (d, *J* = 2.2 Hz, 1H), 7.76 (m, 1H), 4.77 (q, *J* = 7.1 Hz, 1H), 3.73 (s, 3H), 1.81 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.9, 160.2, 138.4, 135.9, 132.3, 132.2, 131.1, 129.3, 128.9, 126.1, 125.9, 125.1, 123.2, 120.6, 52.5, 45.8, 16.5.



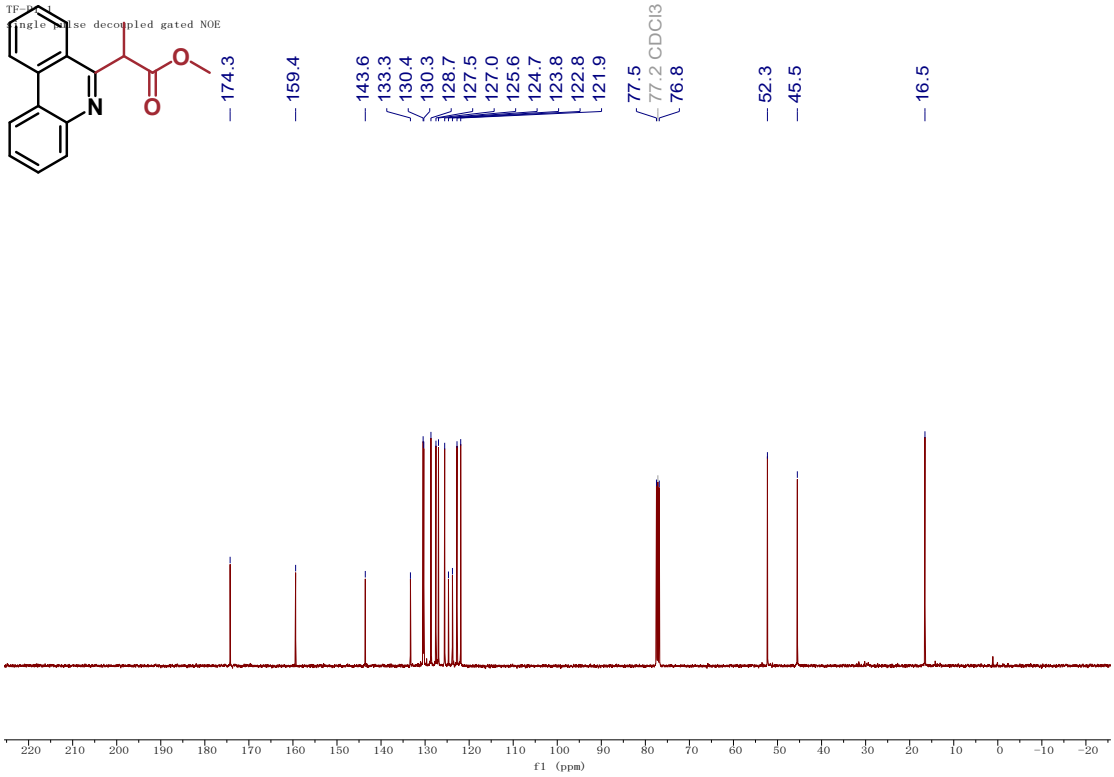
Methyl 2-(benzo[c][1,8]naphthyridin-6-yl) propanoate （23）： Following the general procedure A, the title product was obtained after purification by column chromatography (PE/EA = 30:1) as a white solid (32 mg, 0.120 mmol, 60%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.57 (dt, *J* = 8.5, 1.9 Hz, 1H), 8.50 (d, *J* = 2.3 Hz, 1H), 8.22 (dd, *J* = 8.3, 1.3 Hz, 1H), 8.07 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.86 (m, 1H), 7.74 (m, 1H), 7.65 (dd, *J* = 8.7, 2.3 Hz, 1H), 4.75 (q, *J* = 7.1 Hz, 1H), 3.70 (s, 3H), 1.78 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.7, 163.4, 152.9, 151.5, 133.4, 131.5, 131.2, 128.5, 126.0, 125.2, 122.9, 122.4, 118.8, 52.5, 45.7, 16.4.

6. NMR Spectra.

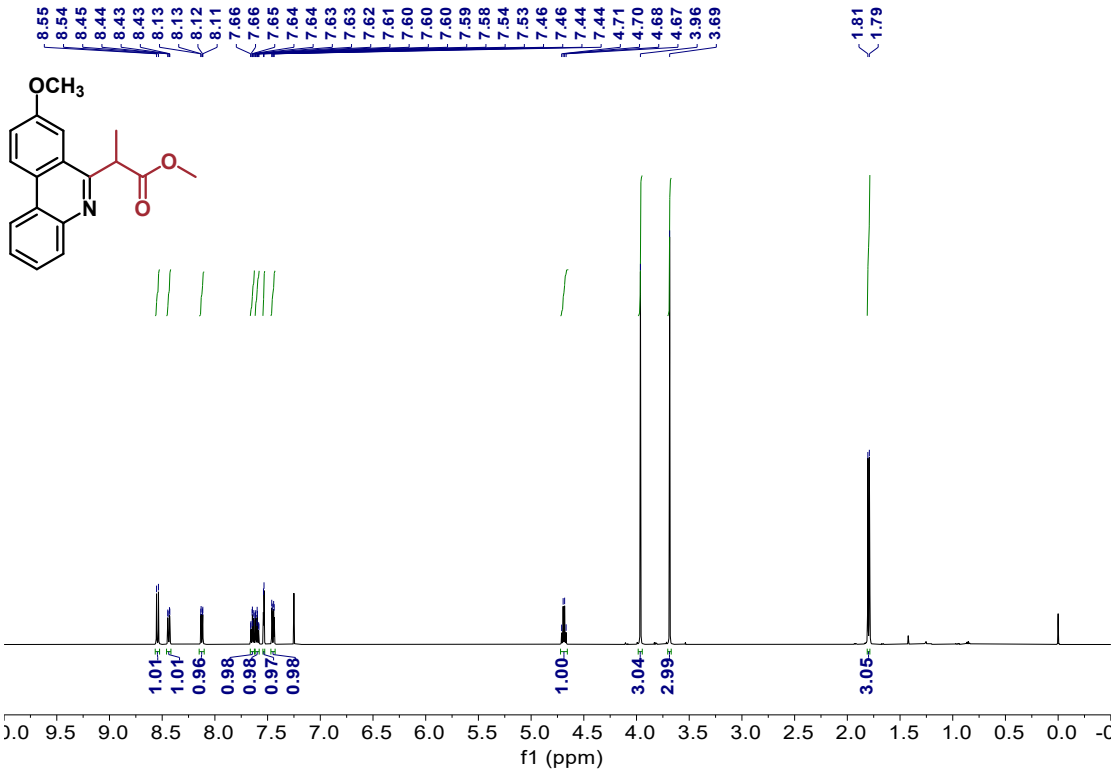
^{1}H NMR of compound **3** (400 MHz in $CDCl_3$)



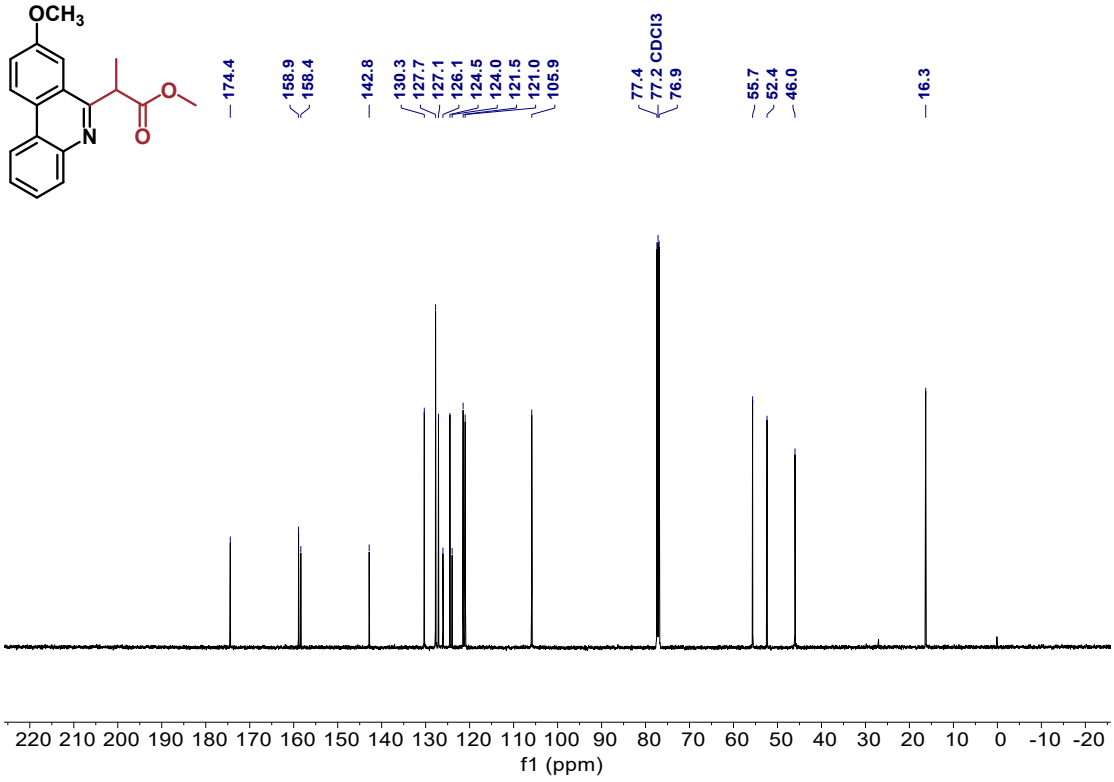
^{13}C NMR of compound **3** (101 MHz in $CDCl_3$)



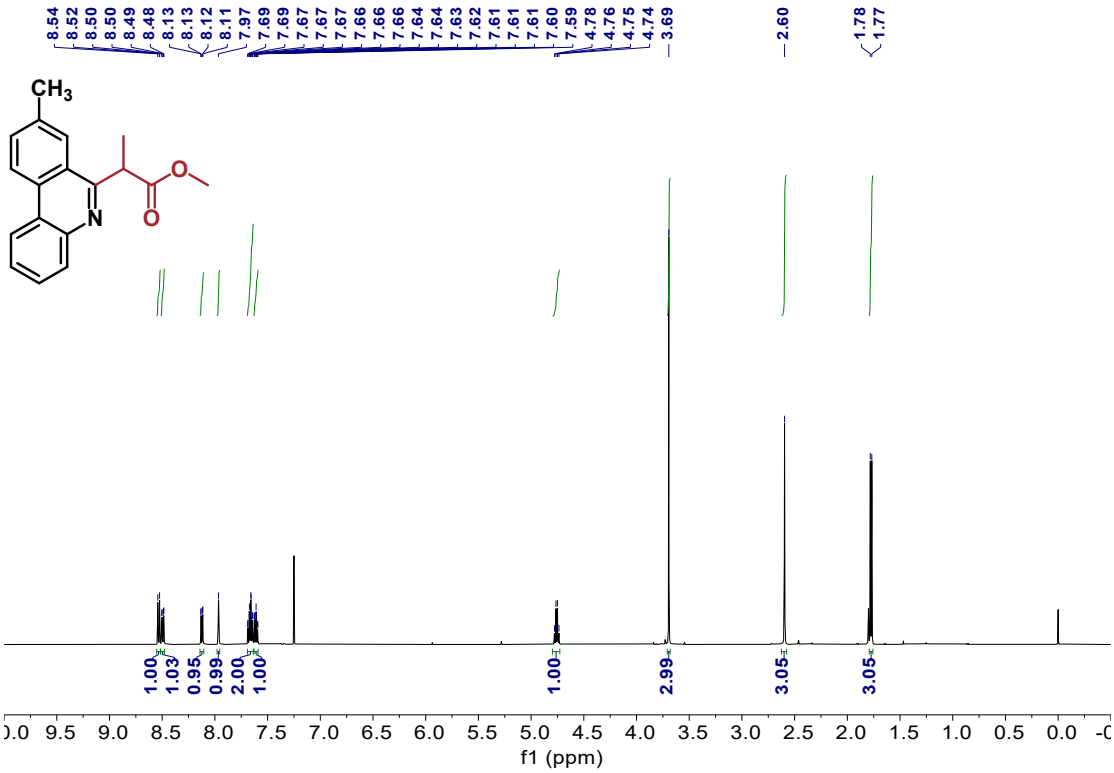
^{1}H NMR of compound **4** (500 MHz in $CDCl_3$)



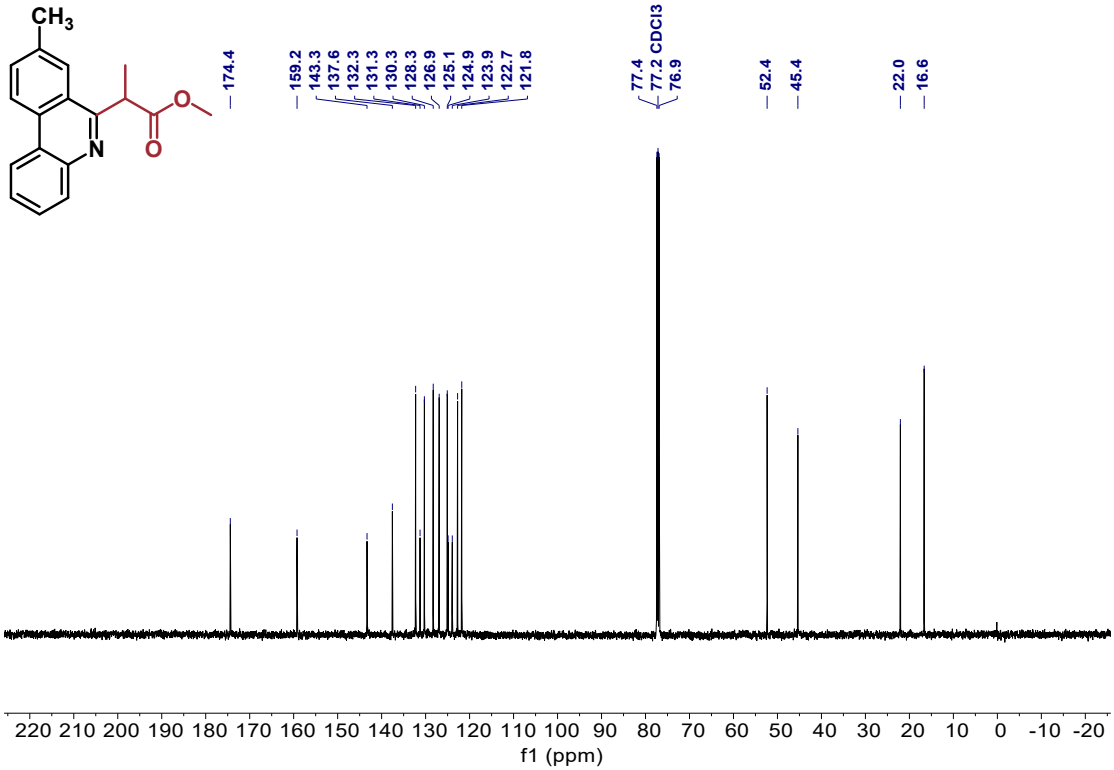
^{13}C NMR of compound **4** (126 MHz in $CDCl_3$)



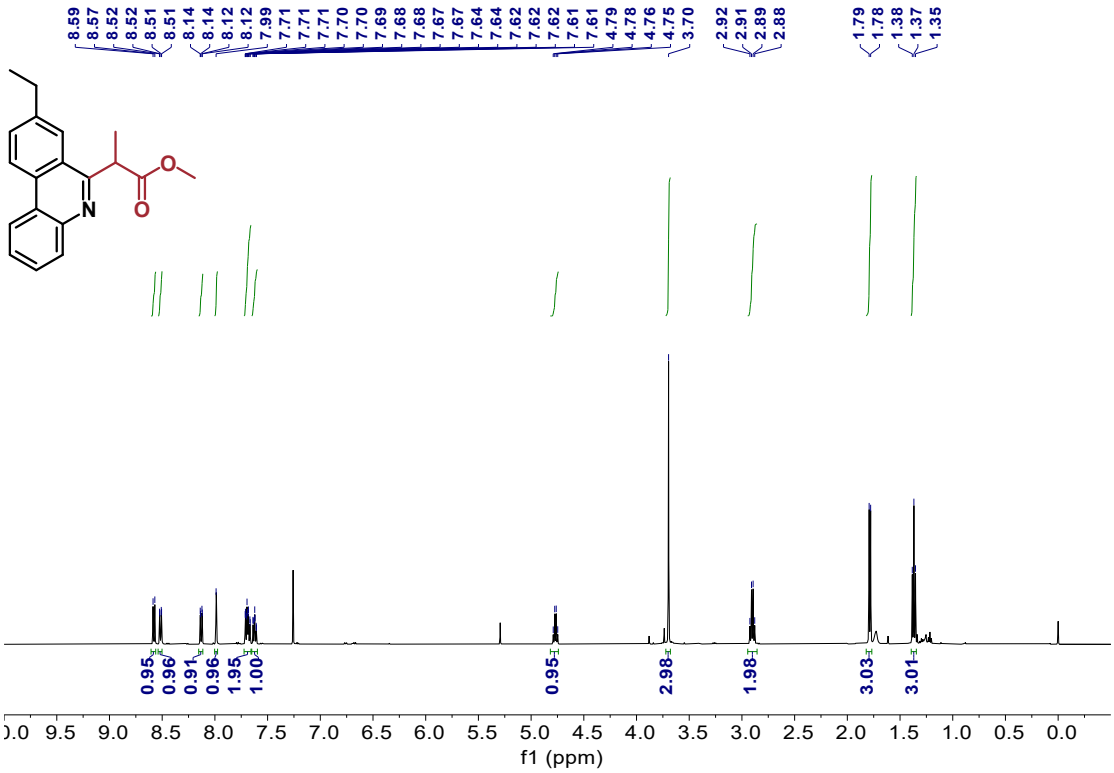
^{1}H NMR of compound **5** (500 MHz in $CDCl_3$)



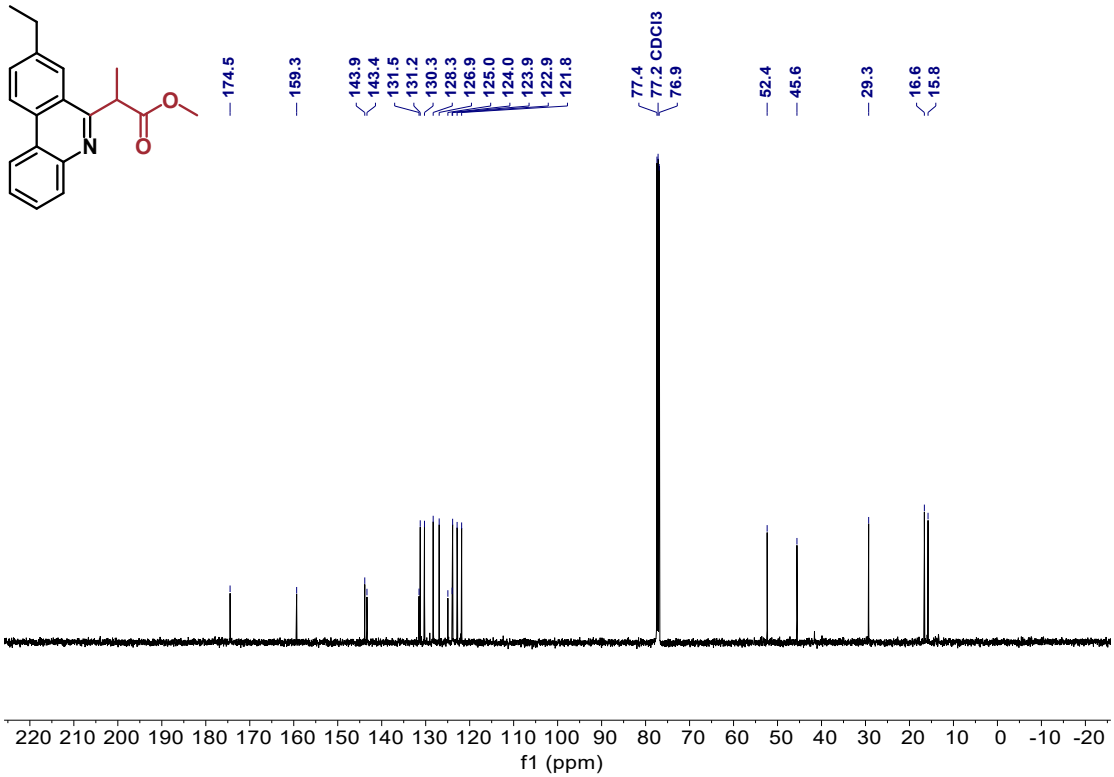
^{13}C NMR of compound **5** (126 MHz in $CDCl_3$)



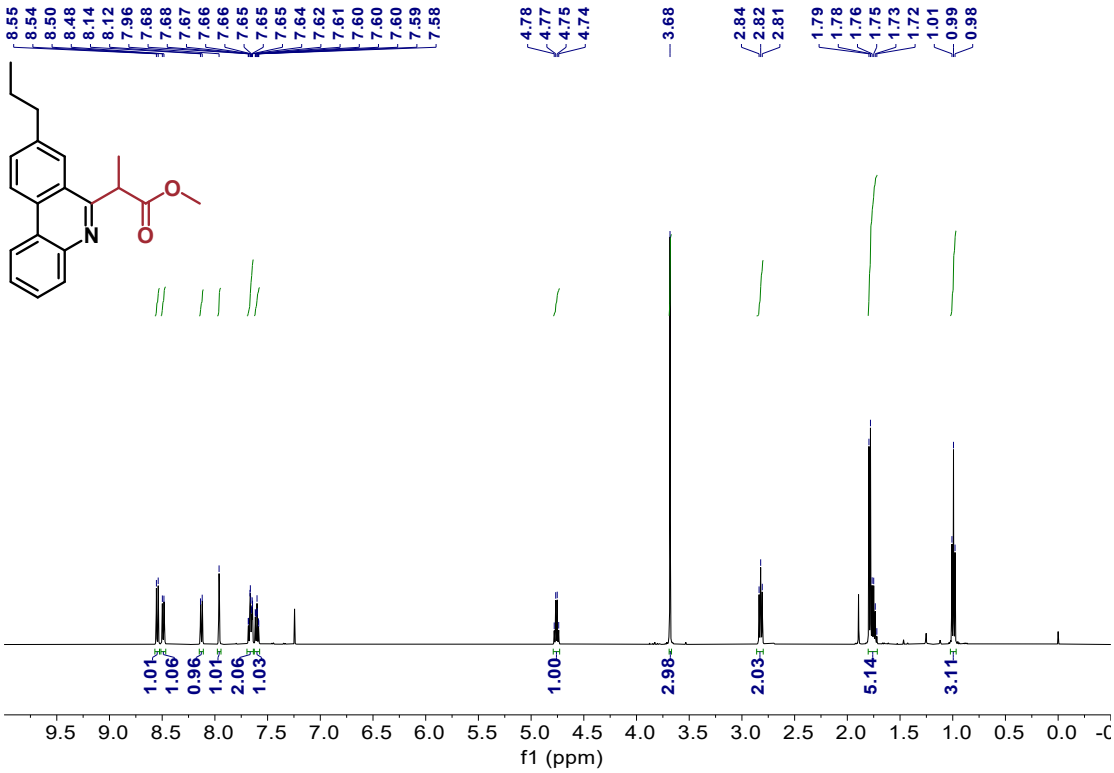
^{1}H NMR of compound **6** (500 MHz in $CDCl_3$)



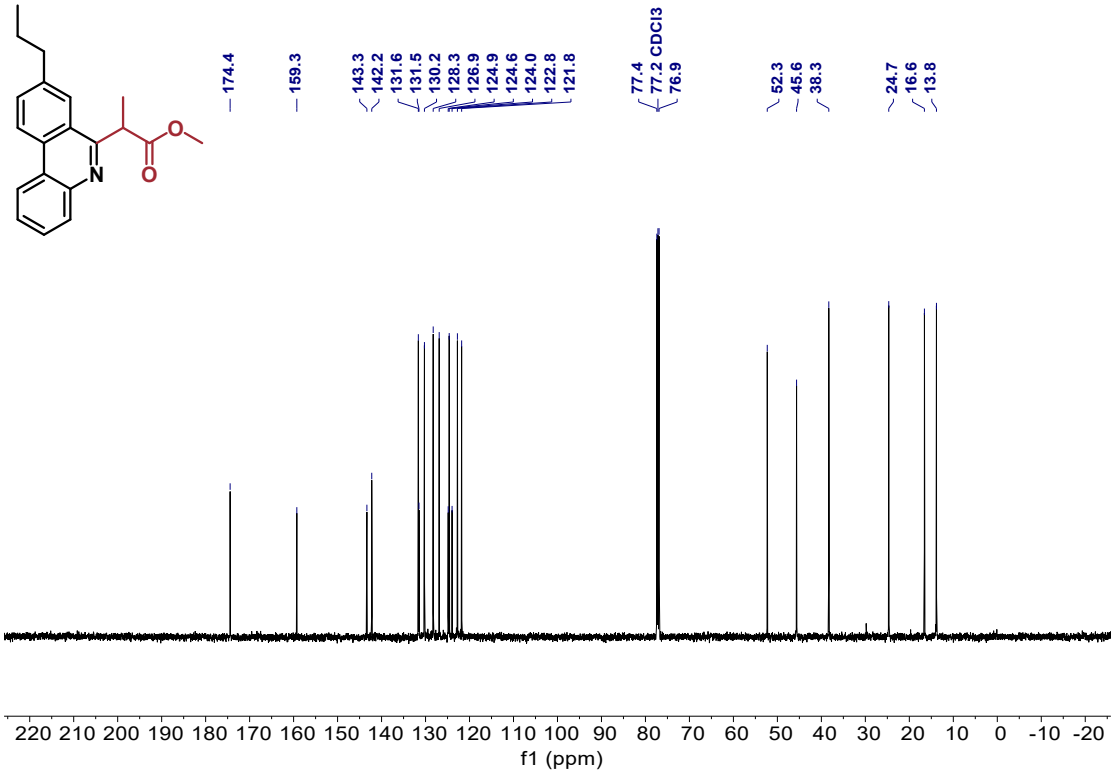
^{13}C NMR of compound **6** (126 MHz in $CDCl_3$)



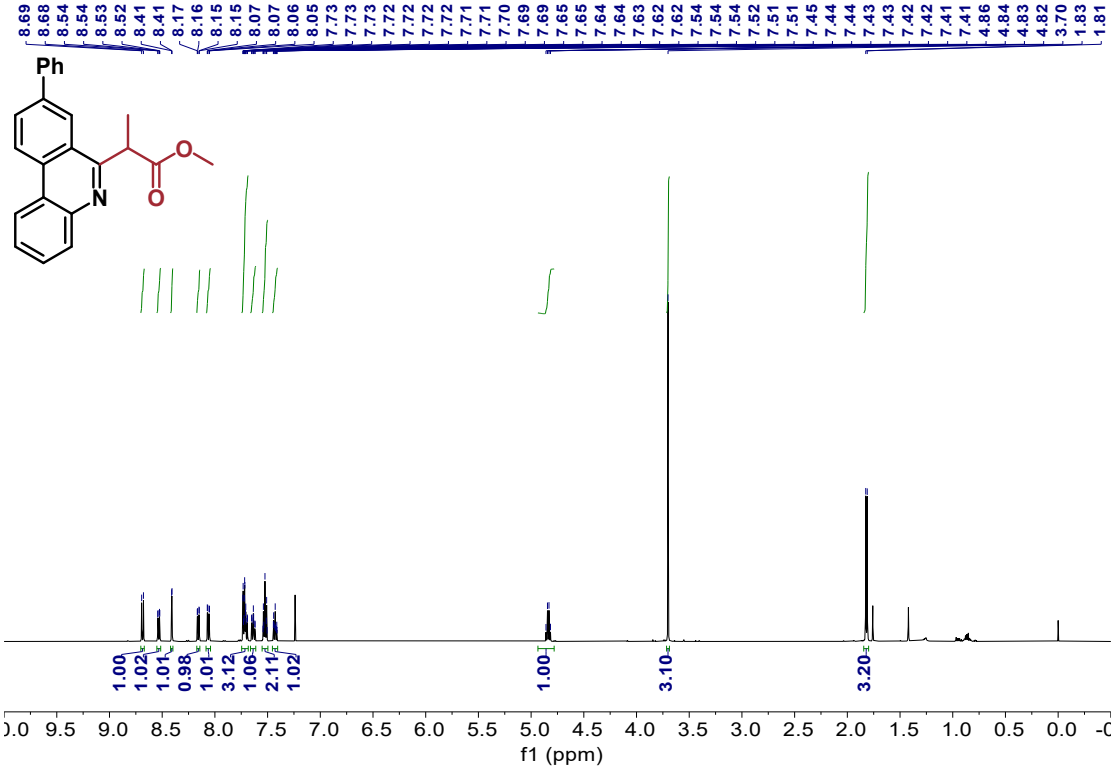
^{1}H NMR of compound **7** (500 MHz in $CDCl_3$)



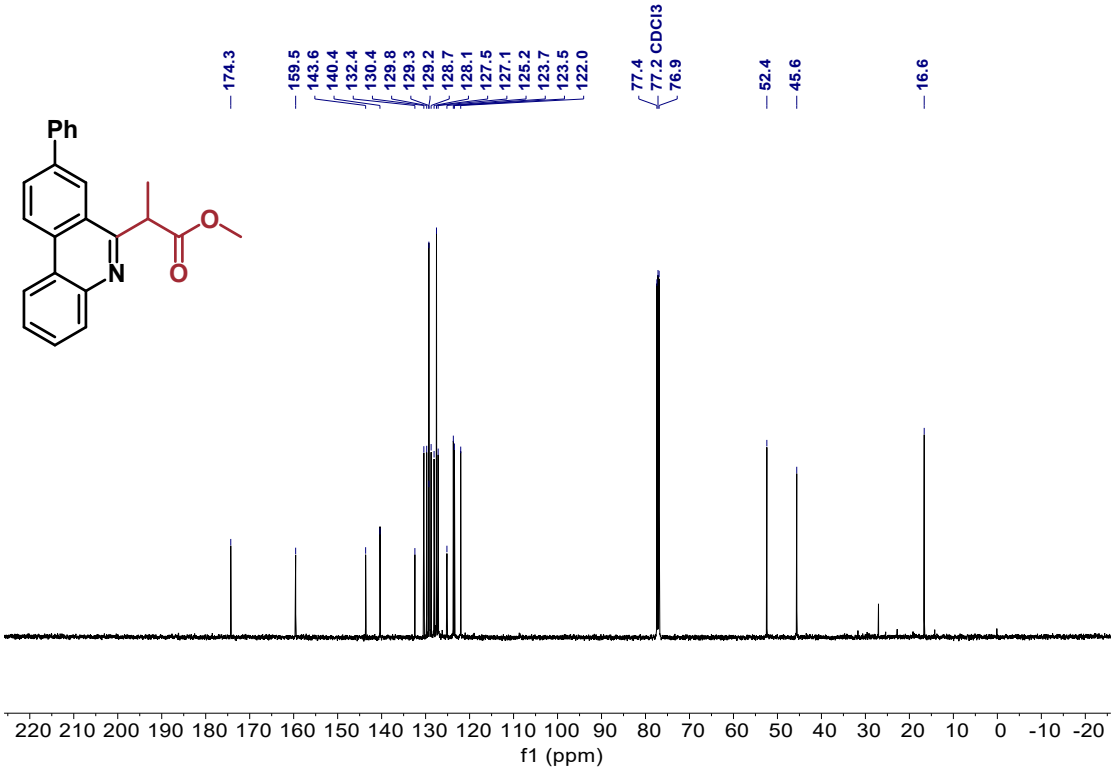
^{13}C NMR of compound **7** (126 MHz in $CDCl_3$)



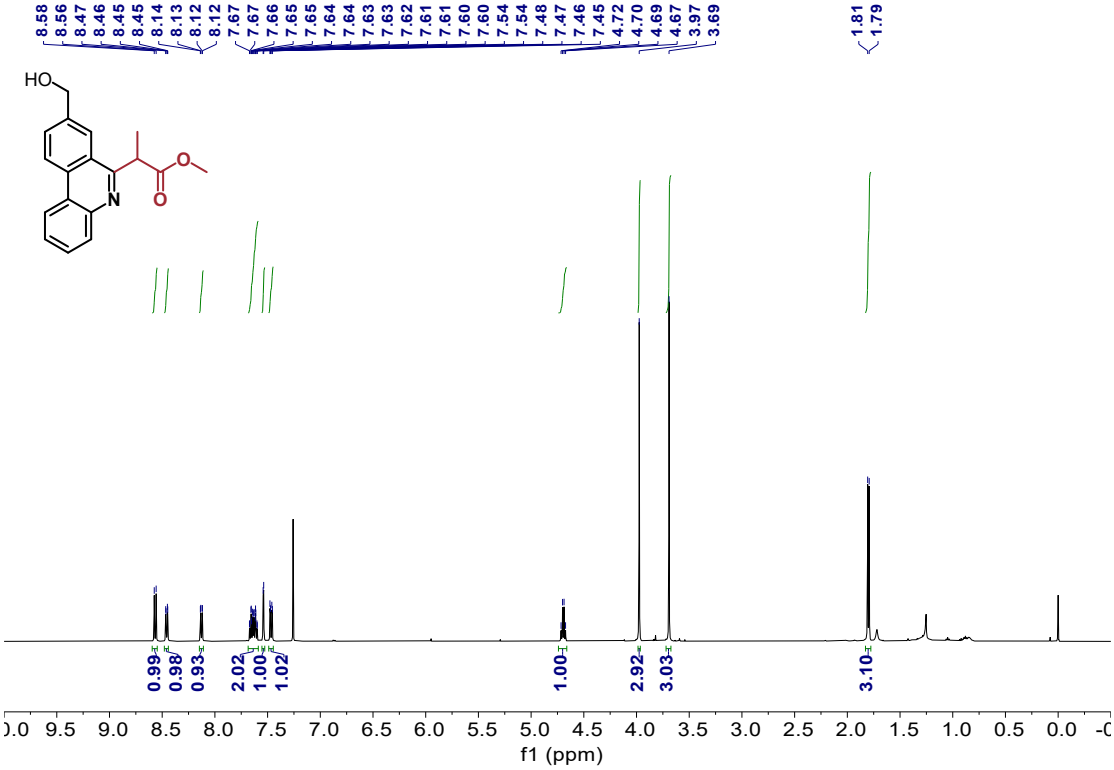
^{1}H NMR of compound **8** (500 MHz in $CDCl_3$)



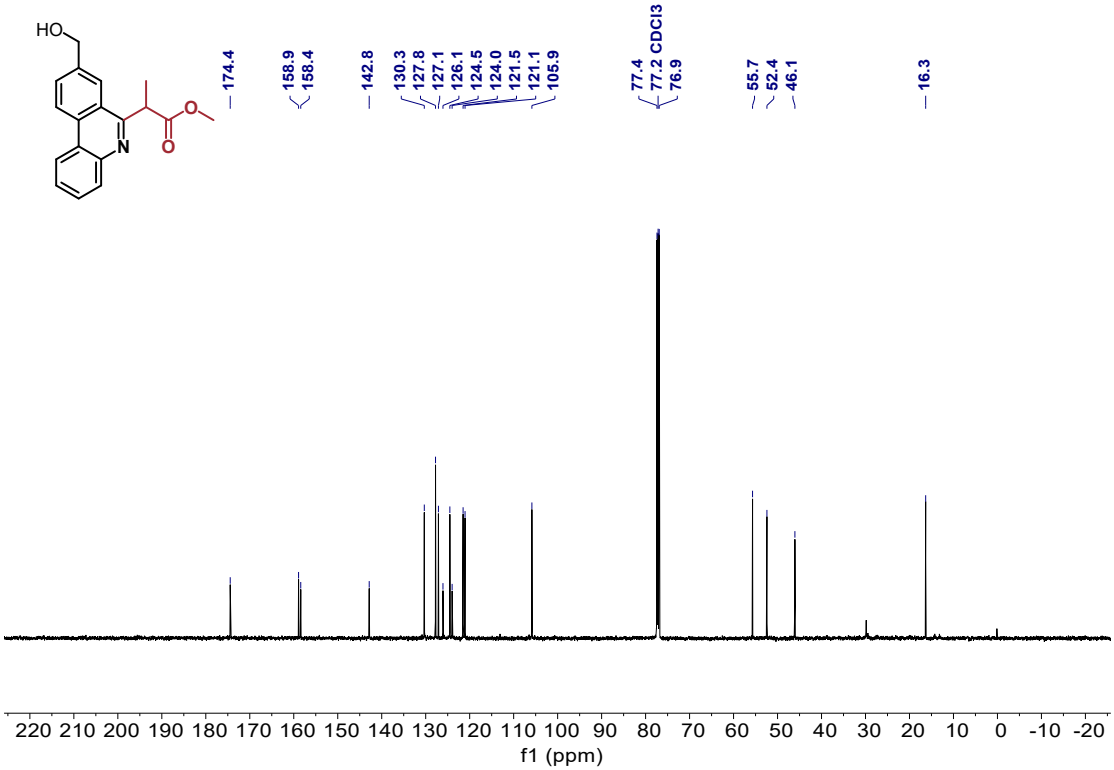
^{13}C NMR of compound **8** (126 MHz in $CDCl_3$)



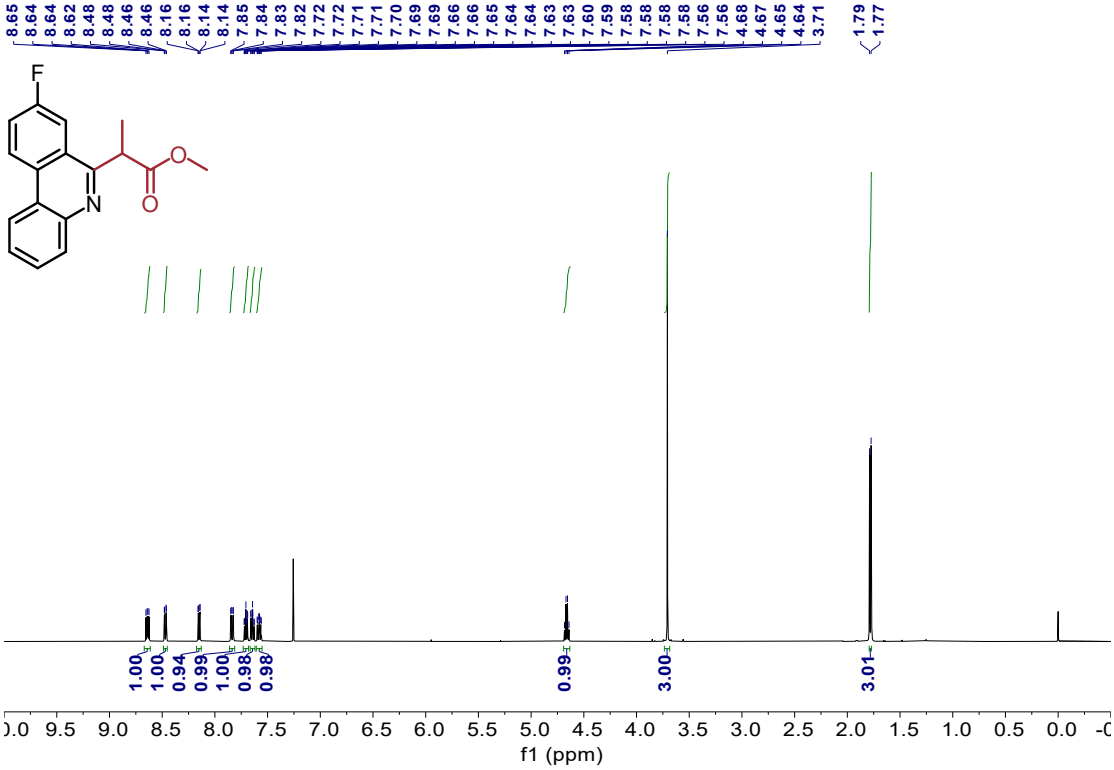
^{1}H NMR of compound **9** (500 MHz in $CDCl_3$)



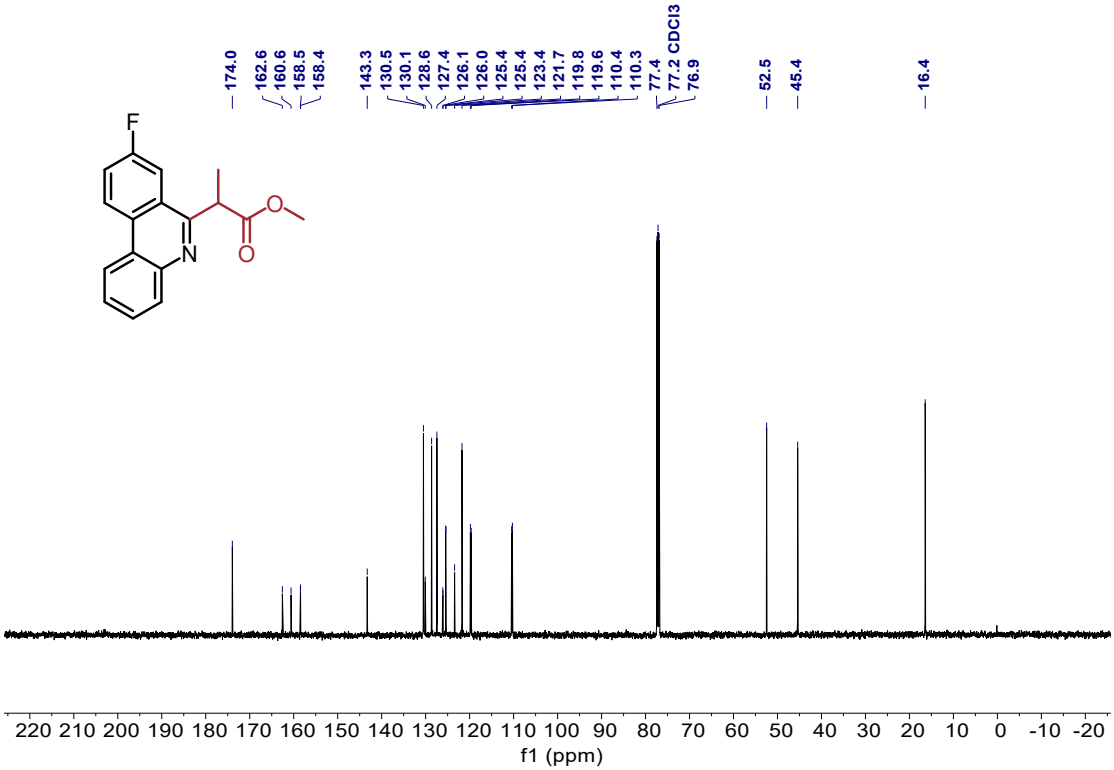
^{13}C NMR of compound **9** (126 MHz in $CDCl_3$)



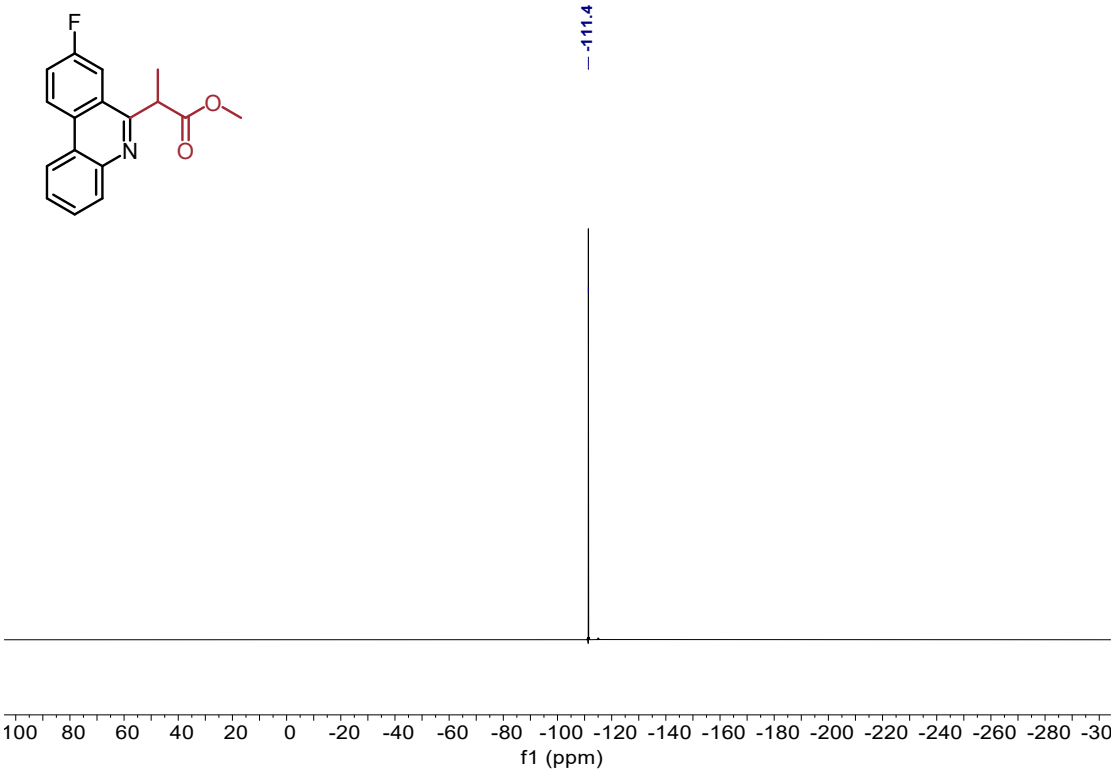
^{1}H NMR of compound **10** (500 MHz in $CDCl_3$)



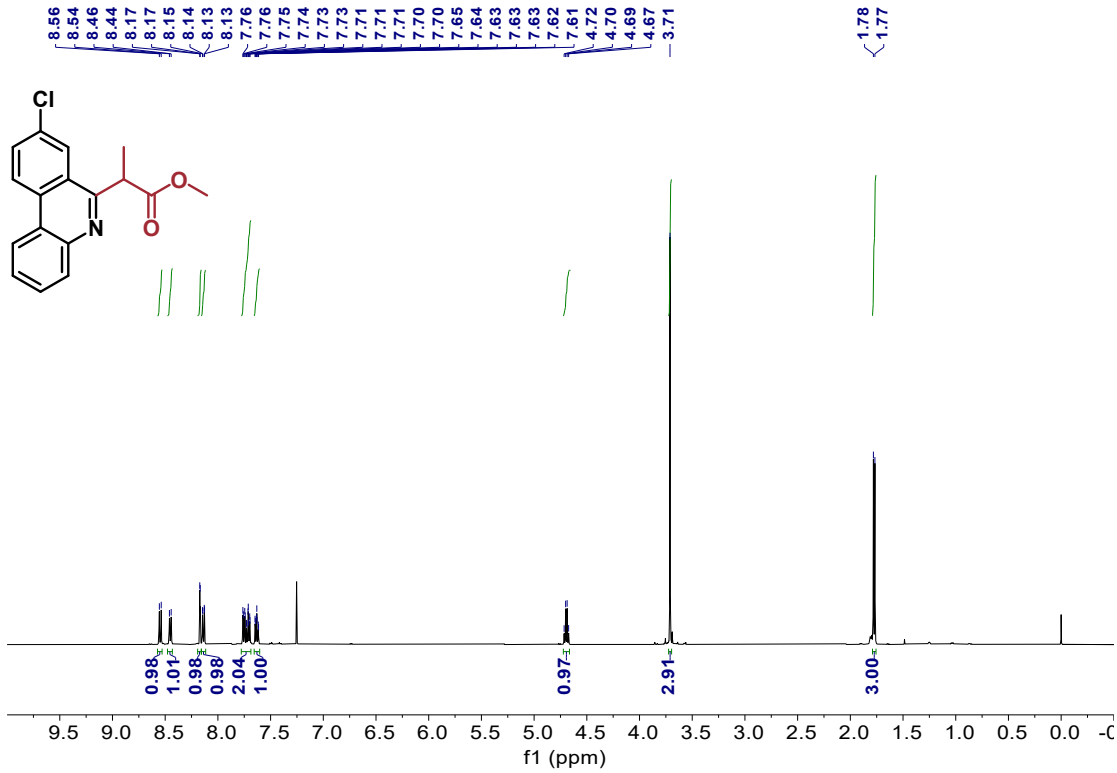
^{13}C NMR of compound **10** (126 MHz in $CDCl_3$)



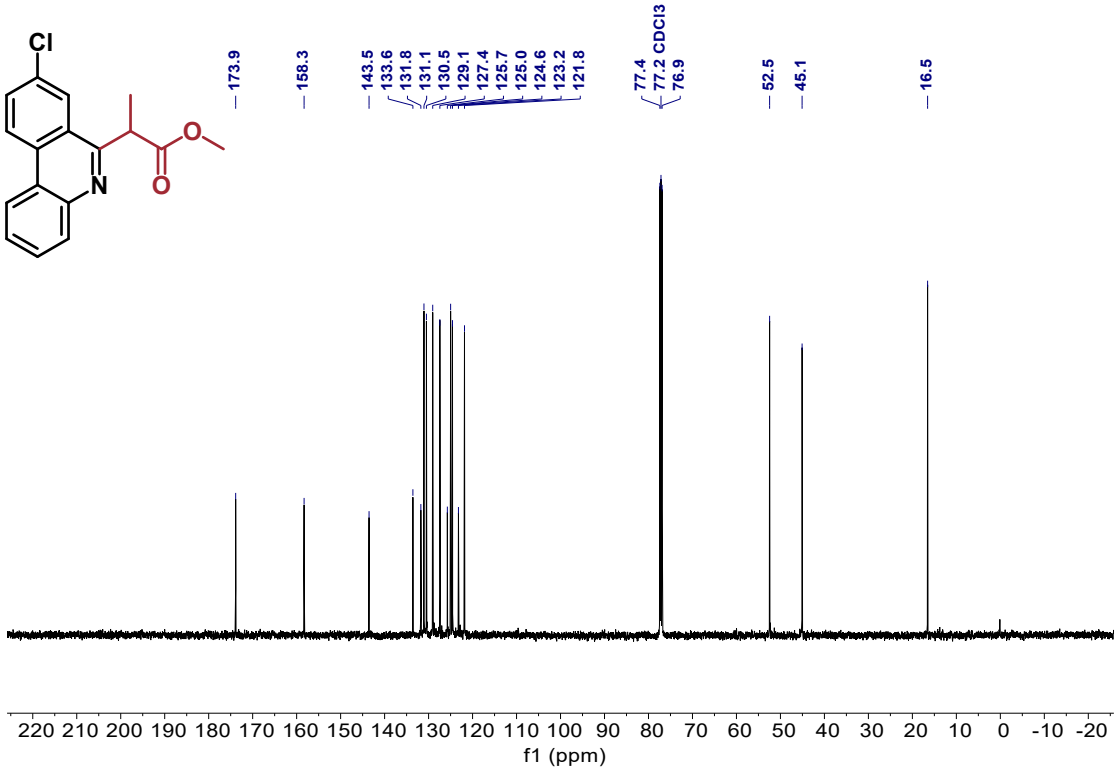
^{19}F NMR of compound **10** (471 MHz in $CDCl_3$)



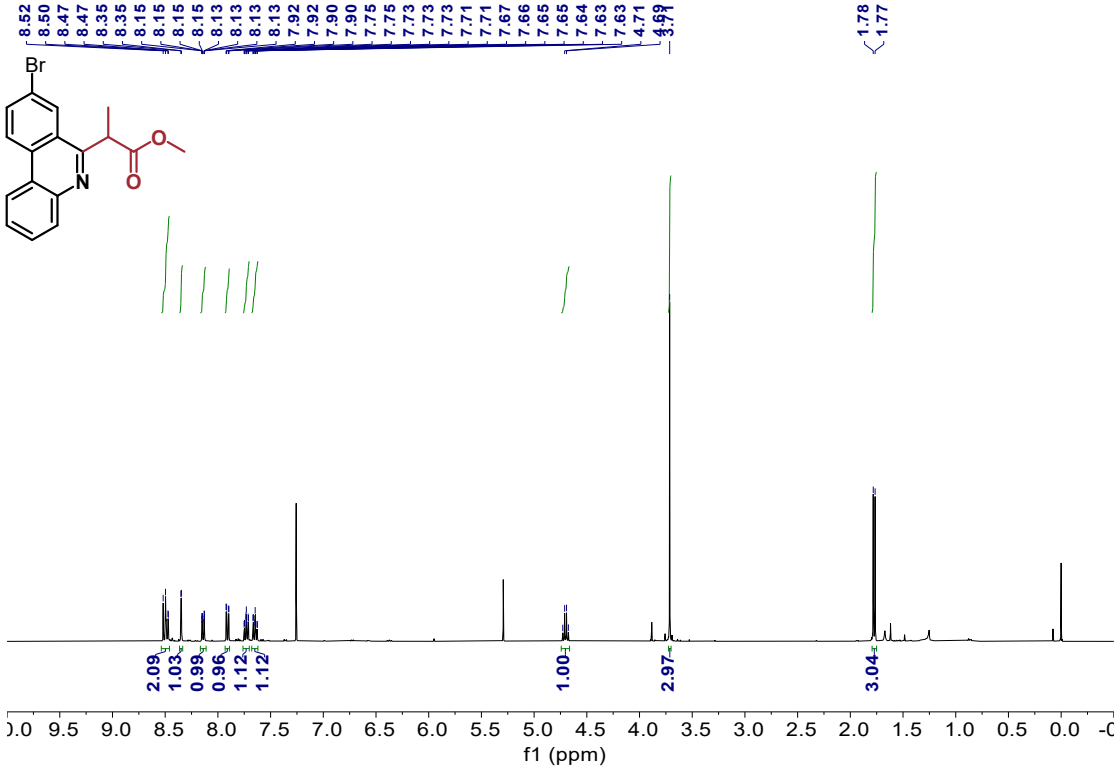
^{1}H NMR of compound **11** (500 MHz in $CDCl_3$)



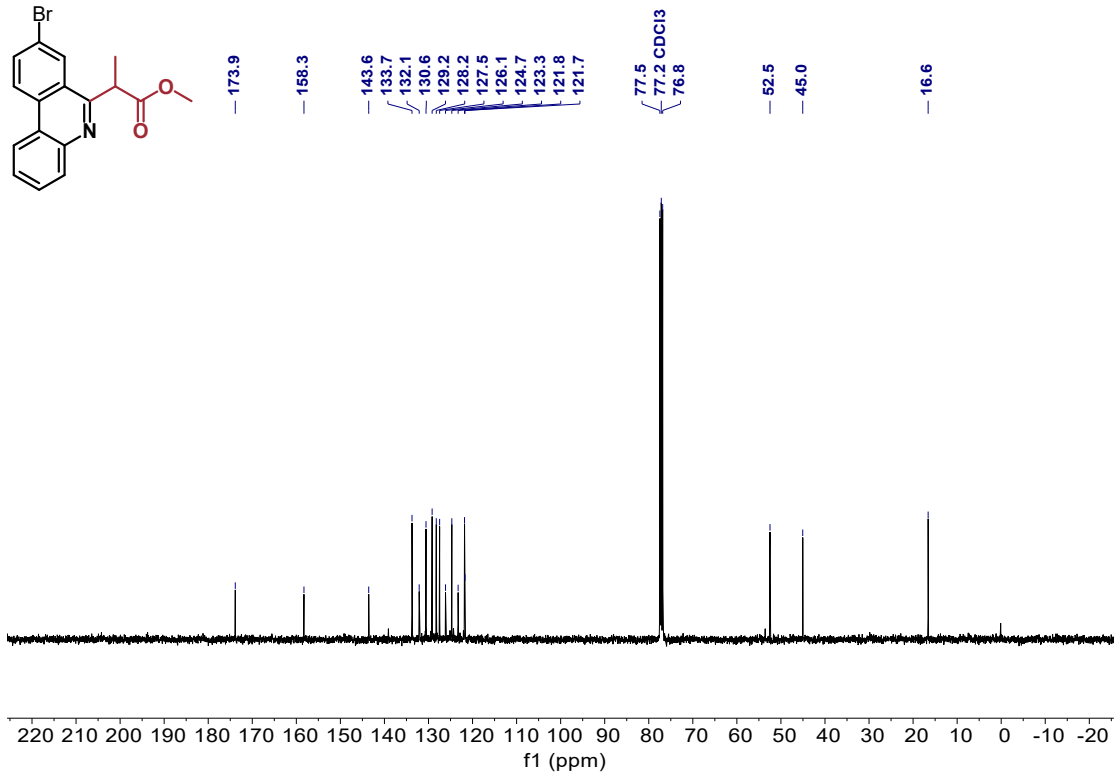
^{13}C NMR of compound **11** (126 MHz in $CDCl_3$)



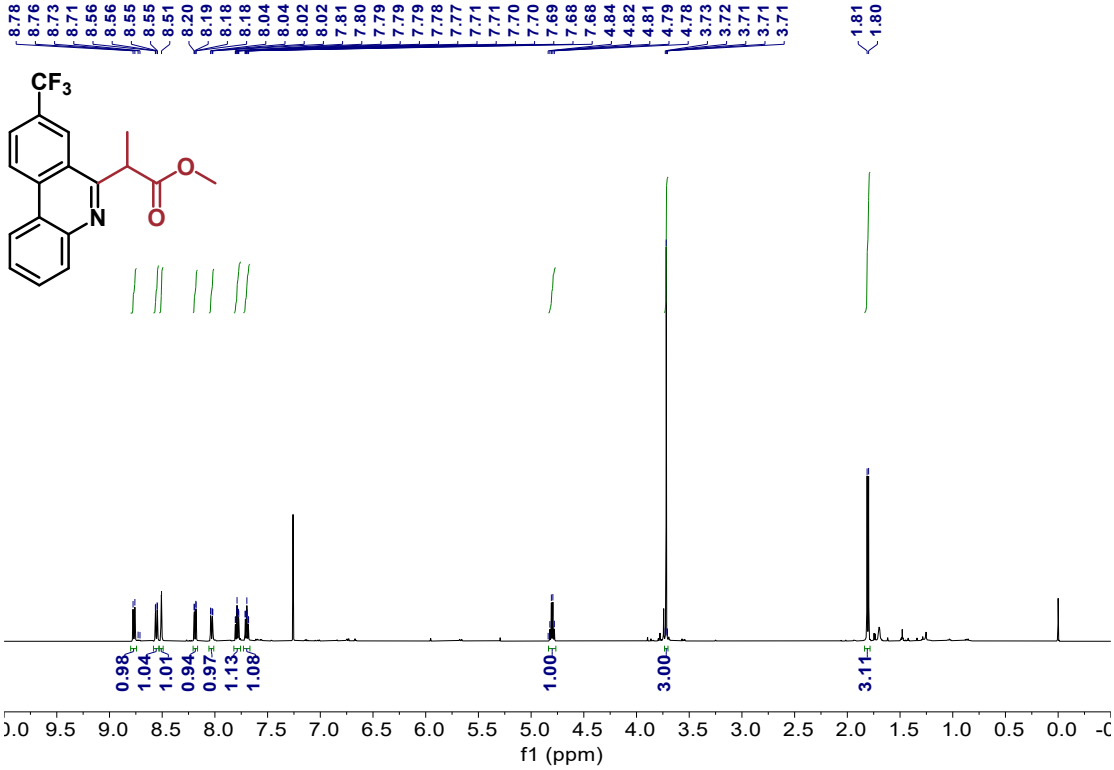
^{1}H NMR of compound **12** (400 MHz in $CDCl_3$)



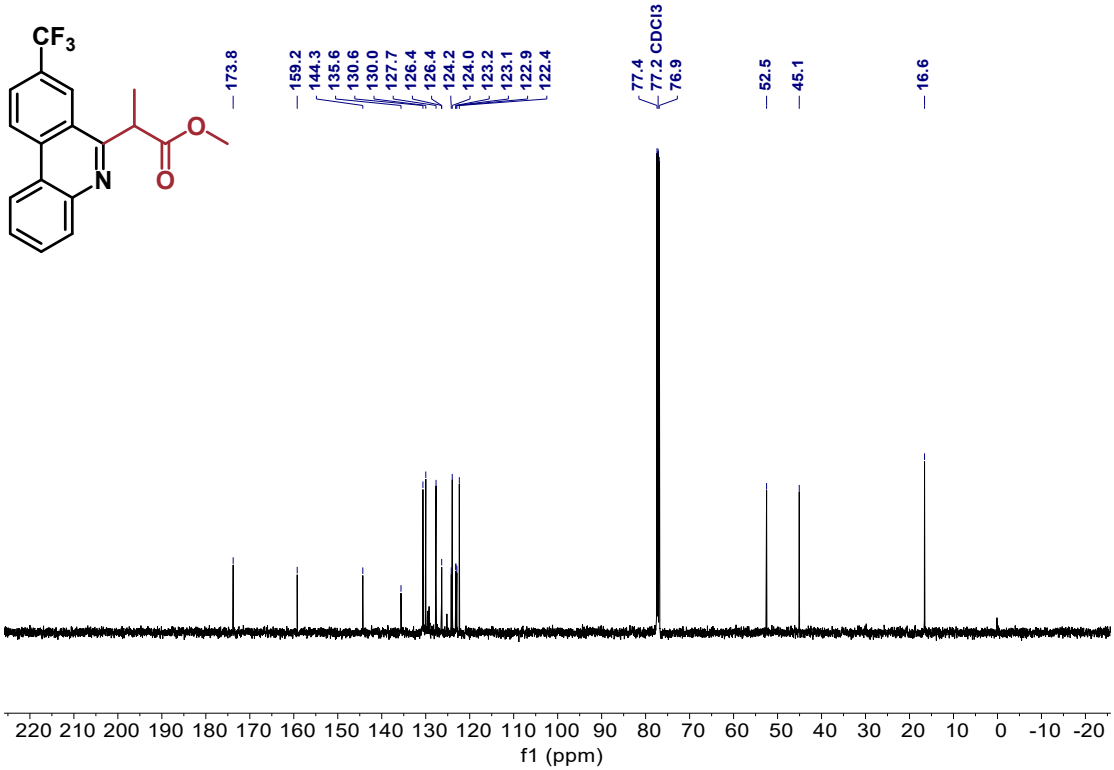
^{13}C NMR of compound **12** (101 MHz in $CDCl_3$)



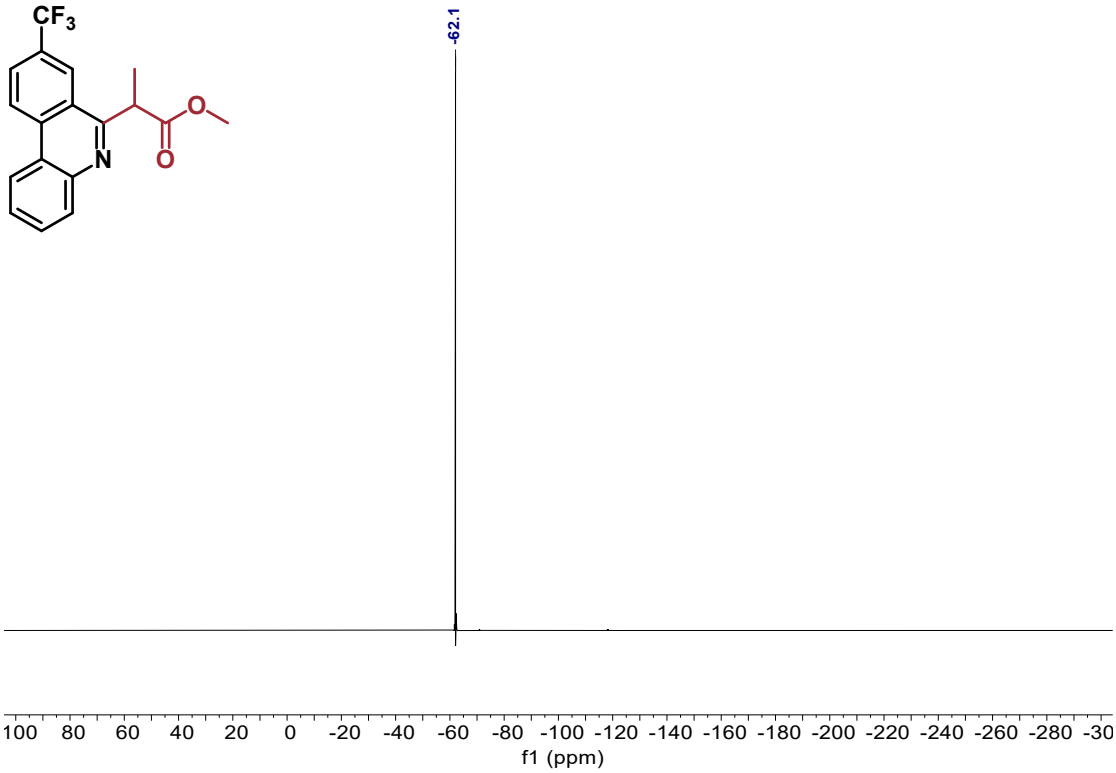
^{1}H NMR of compound **13** (500 MHz in $CDCl_3$)



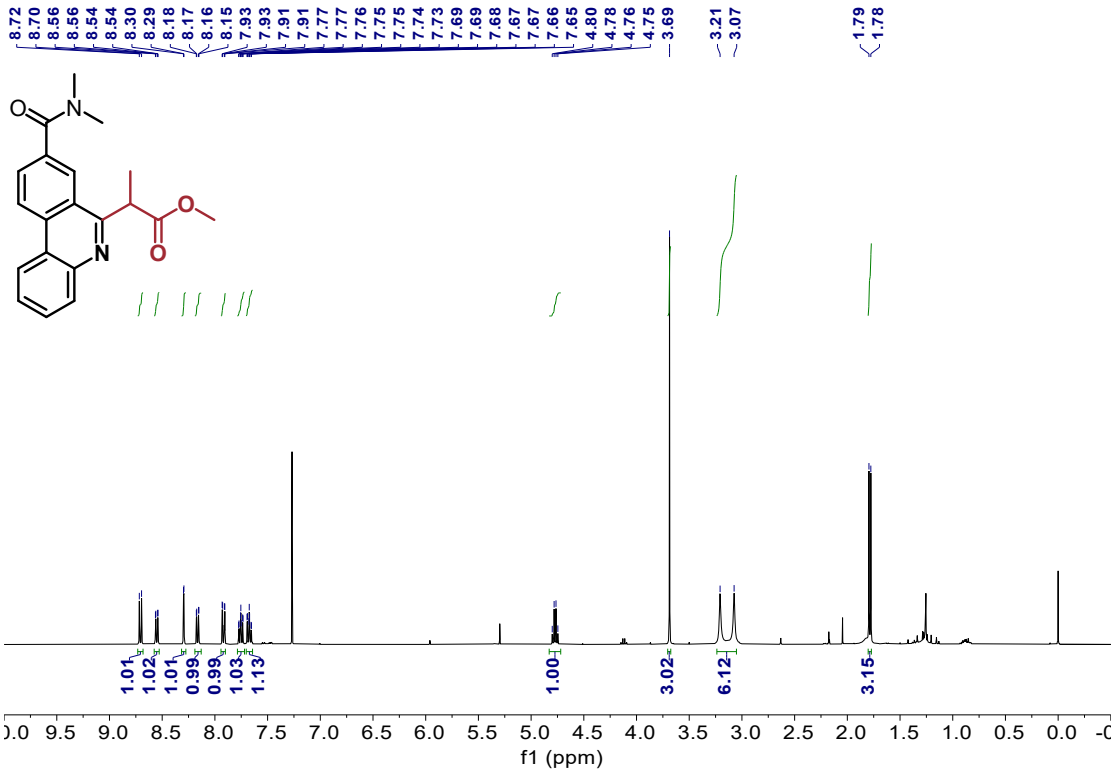
^{13}C NMR of compound **13** (126 MHz in $CDCl_3$)



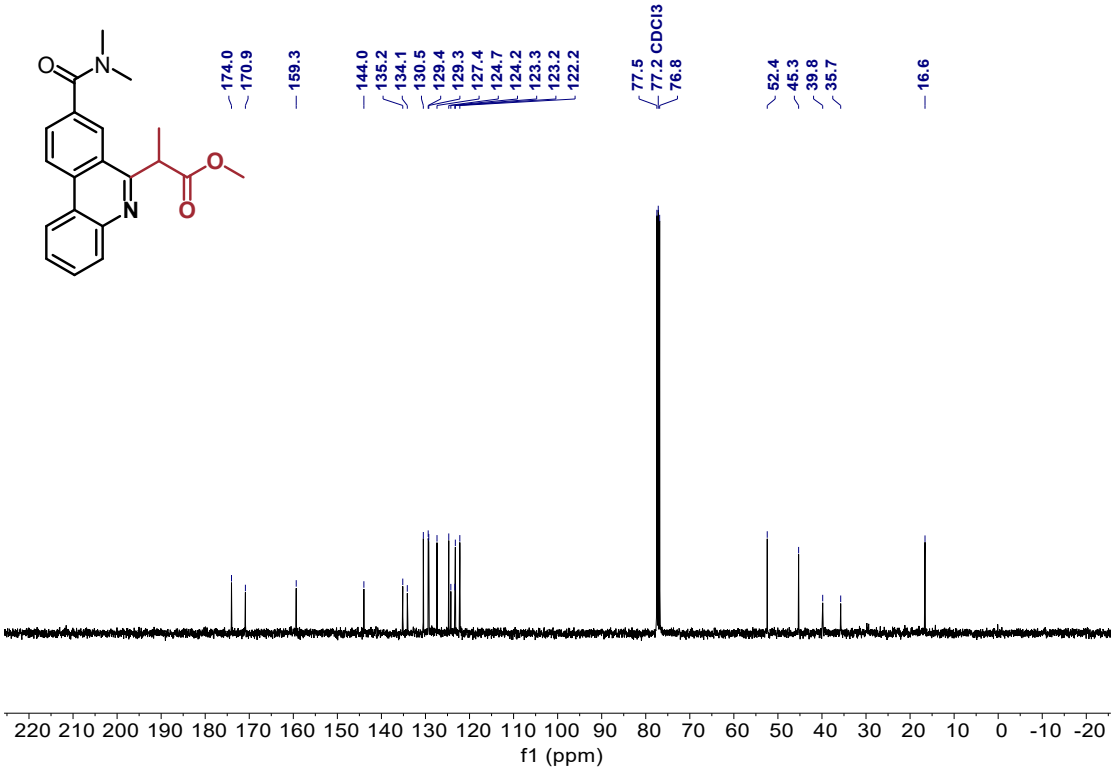
^{19}F NMR of compound **13** (471 MHz in $CDCl_3$)



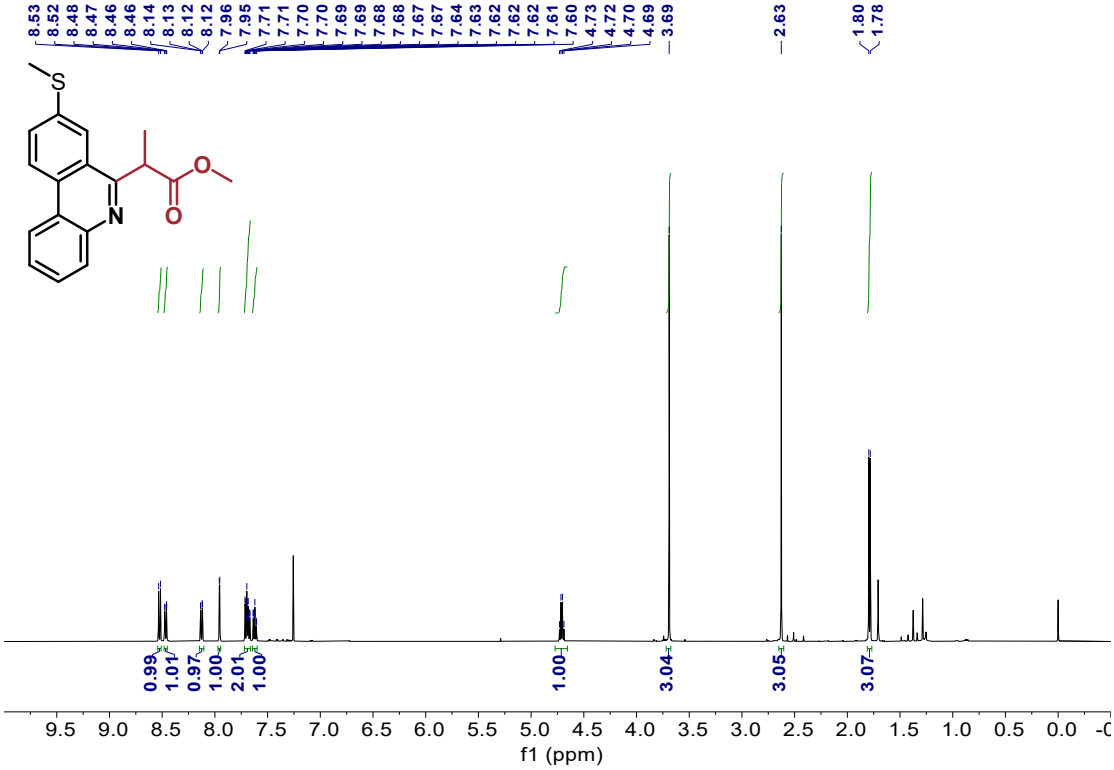
^{1}H NMR of compound **14** (400 MHz in $CDCl_3$)



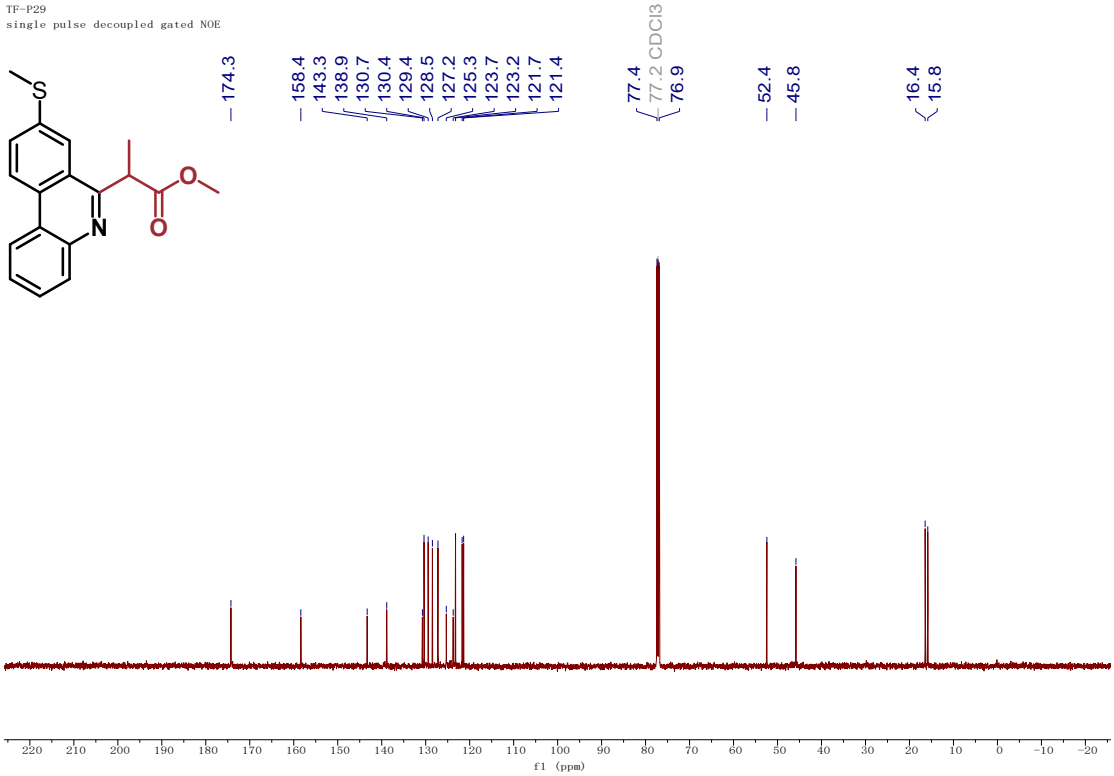
^{13}C NMR of compound **14** (101 MHz in $CDCl_3$)



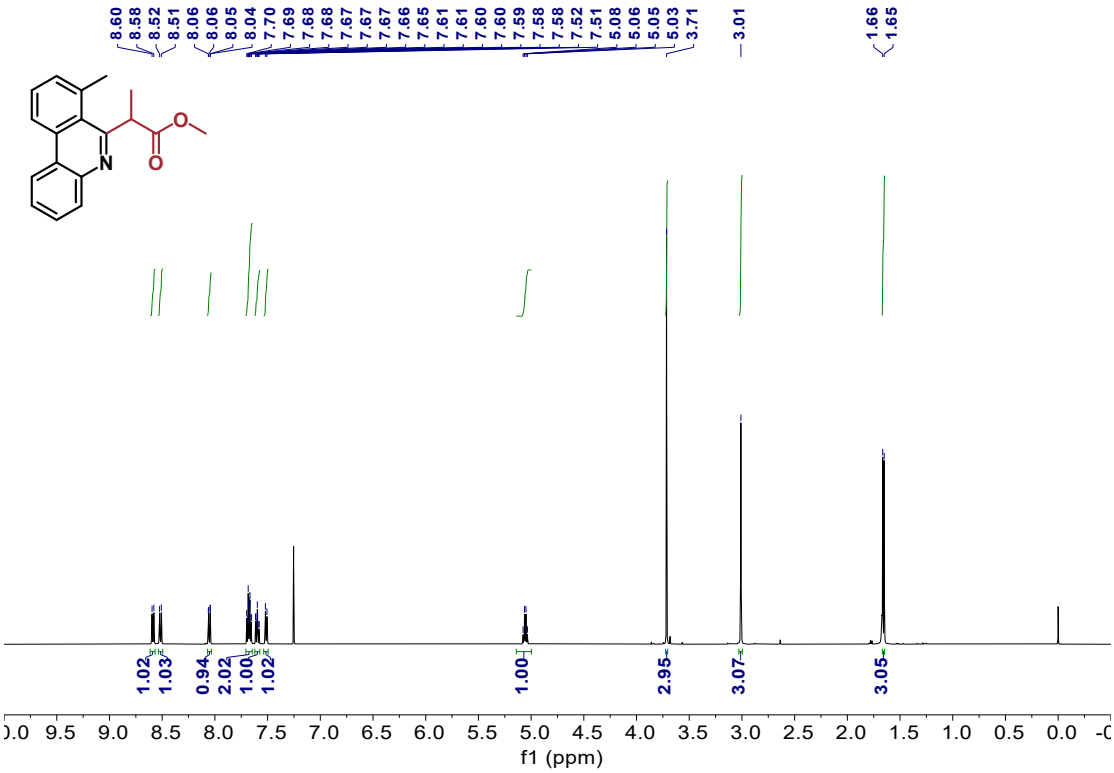
^{1}H NMR of compound **15** (500 MHz in $CDCl_3$)



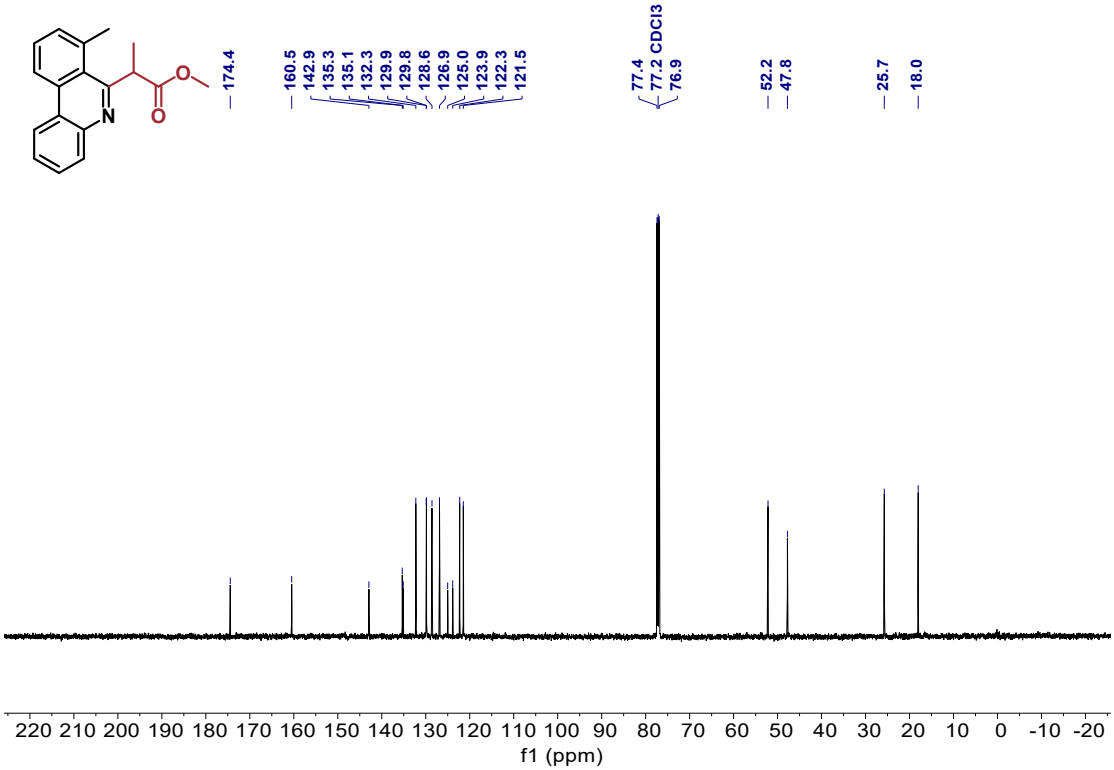
^{13}C NMR of compound **15** (126 MHz in $CDCl_3$)



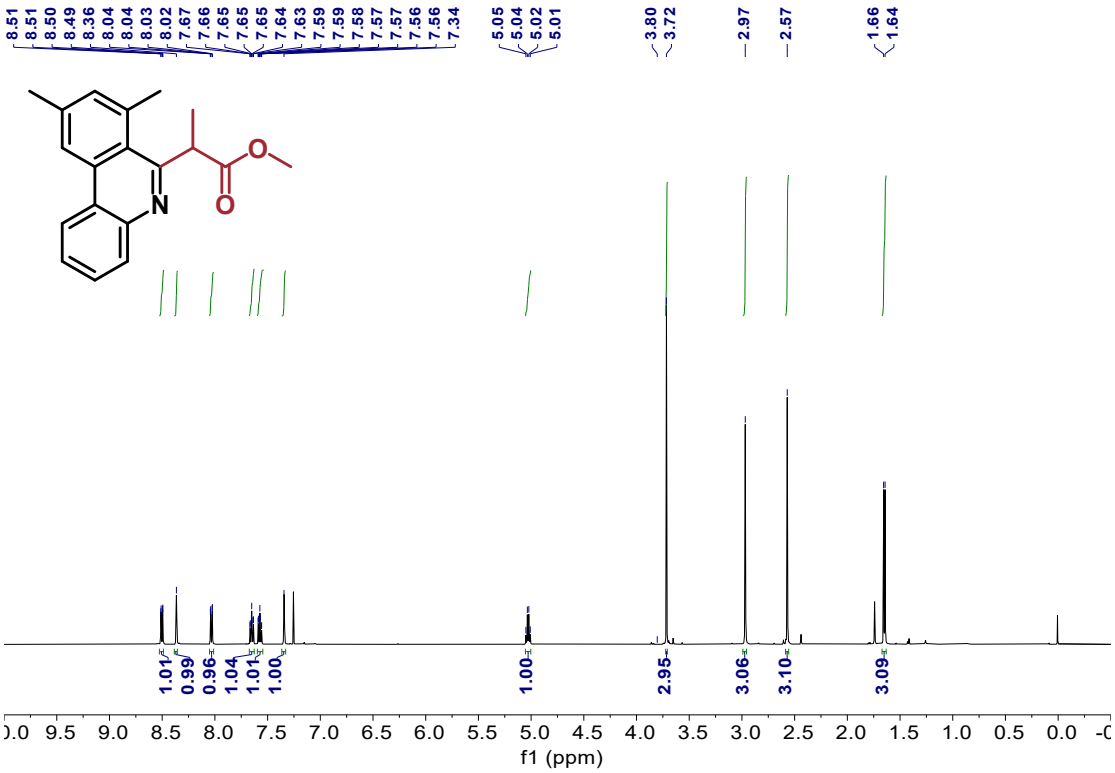
^{1}H NMR of compound **16** (500 MHz in $CDCl_3$)



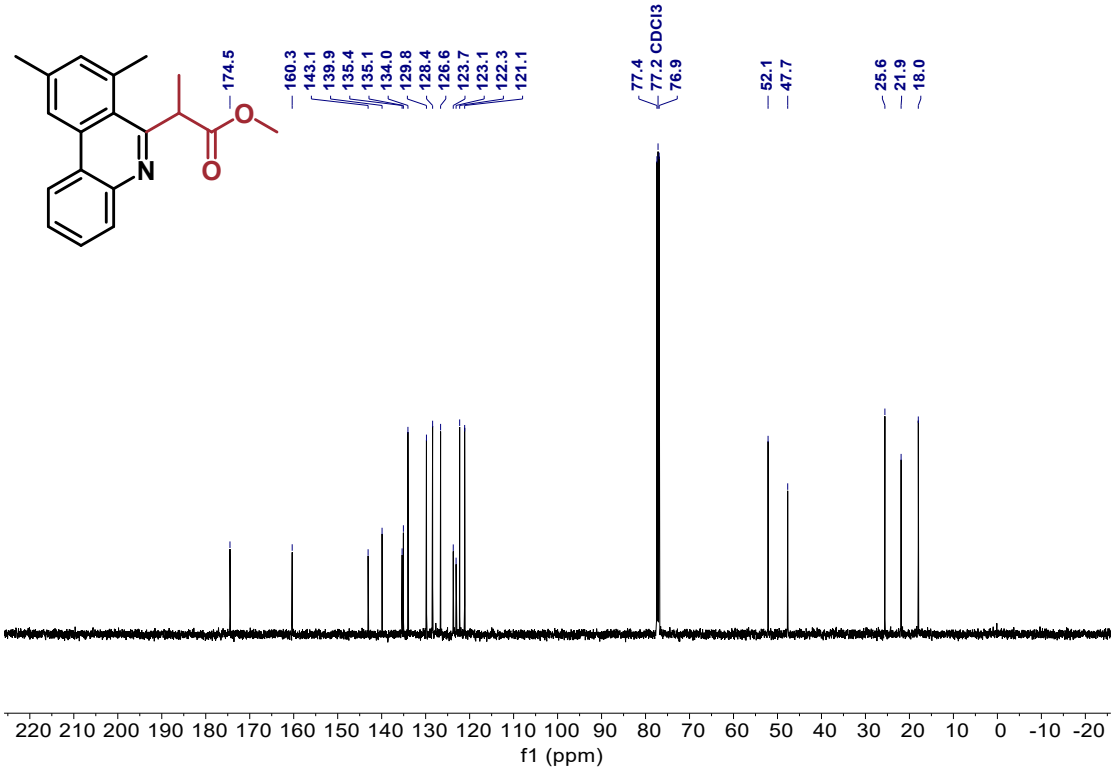
^{13}C NMR of compound **16** (126 MHz in $CDCl_3$)



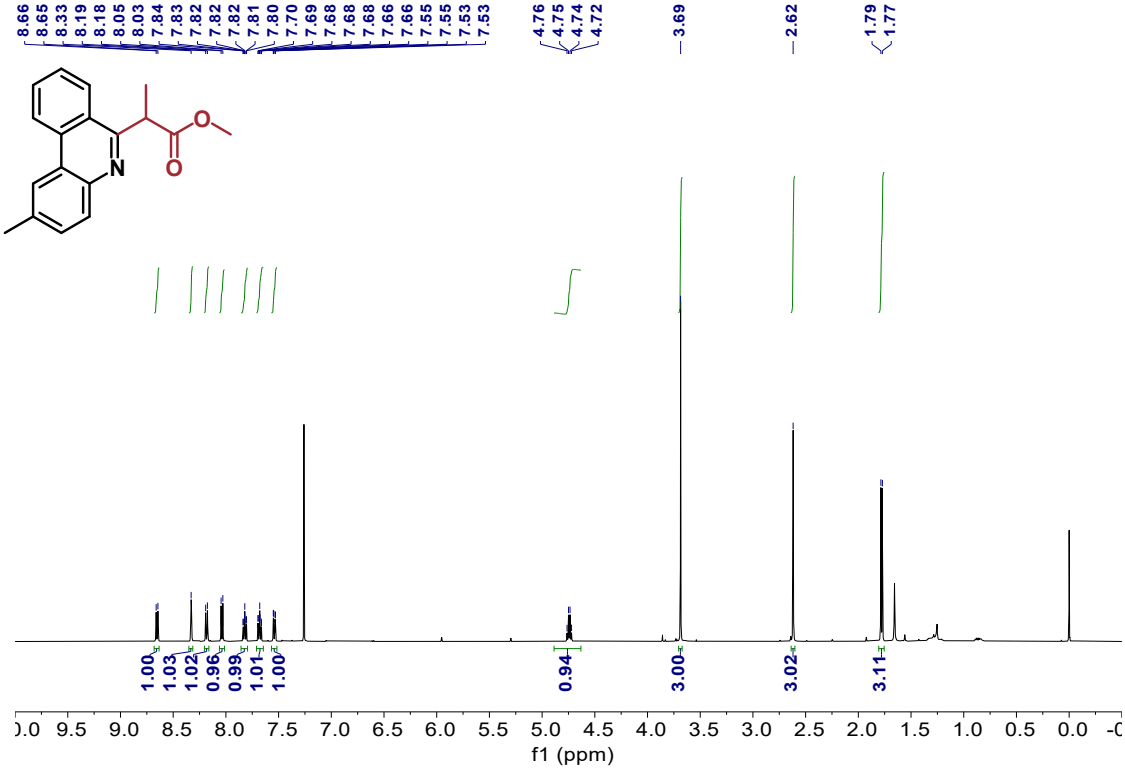
^{1}H NMR of compound **17** (500 MHz in $CDCl_3$)



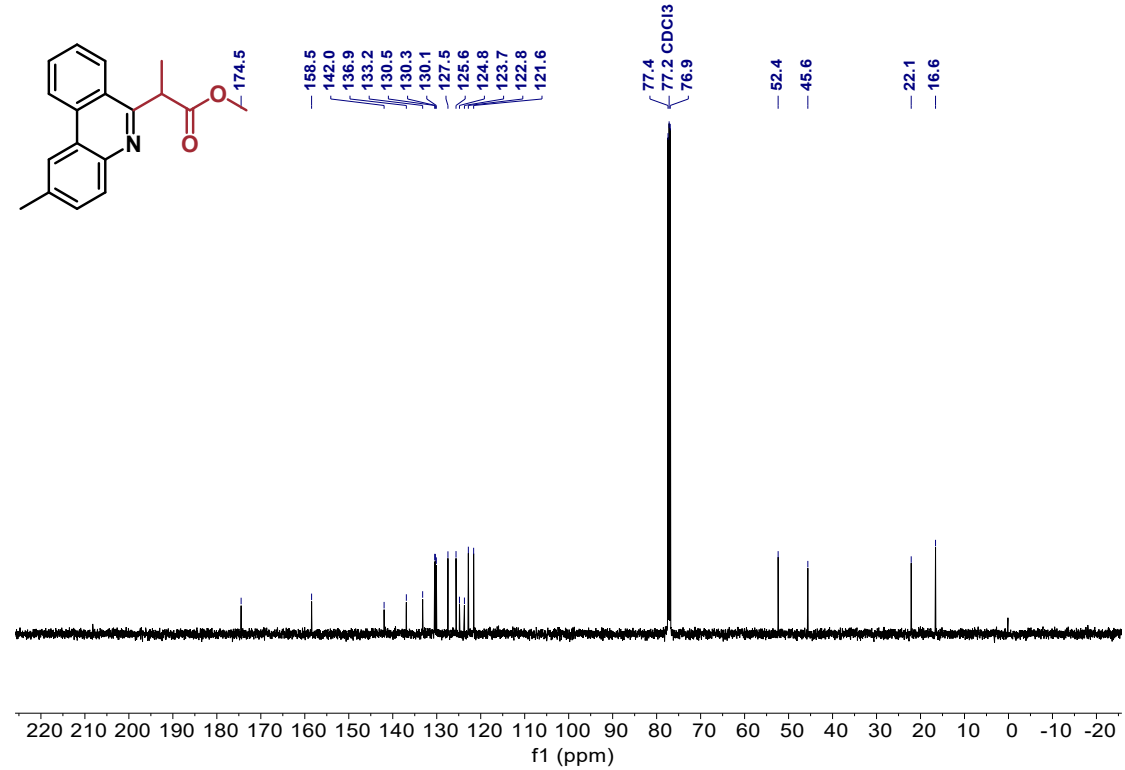
^{13}C NMR of compound **17** (126 MHz in $CDCl_3$)



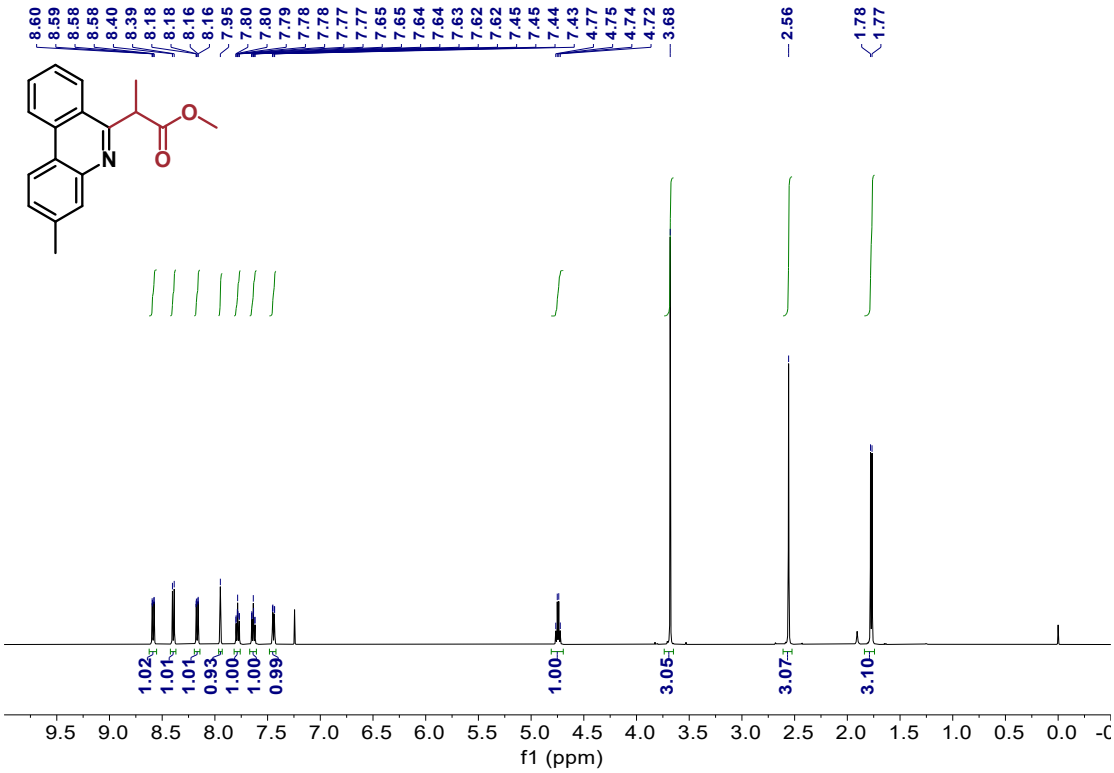
^{1}H NMR of compound **18** (500 MHz in $CDCl_3$)



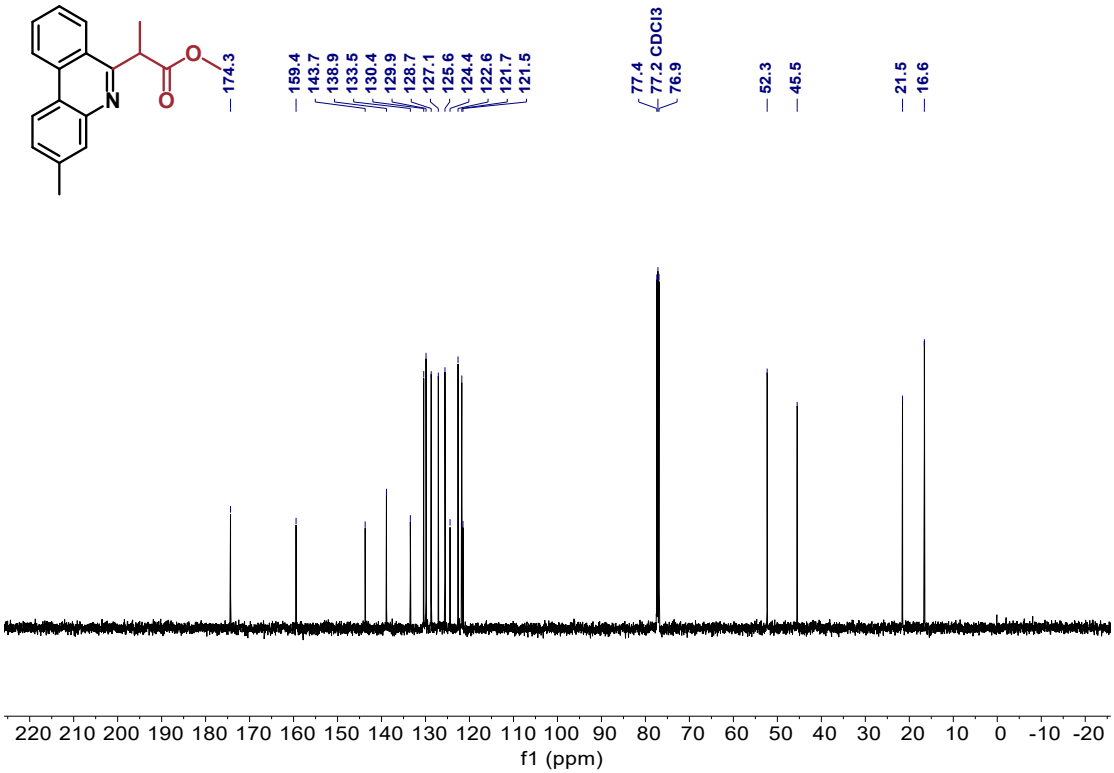
^{13}C NMR of compound **18** (126 MHz in $CDCl_3$)



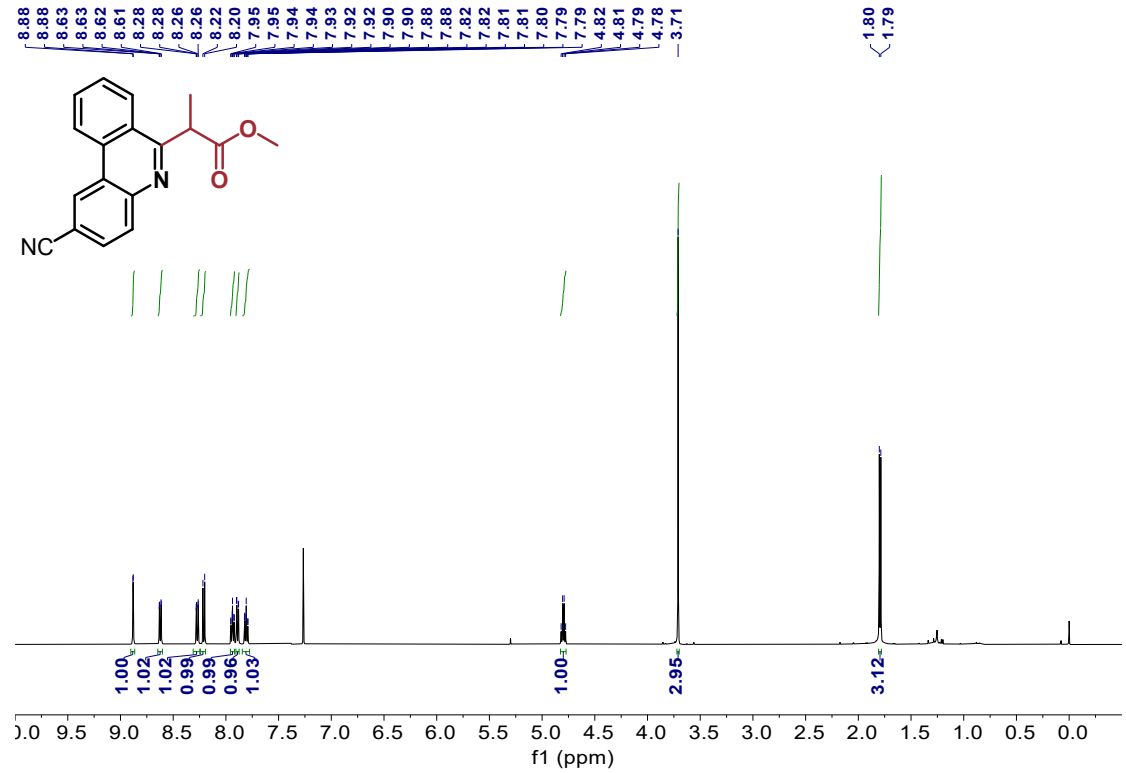
^{1}H NMR of compound **19** (500 MHz in $CDCl_3$)



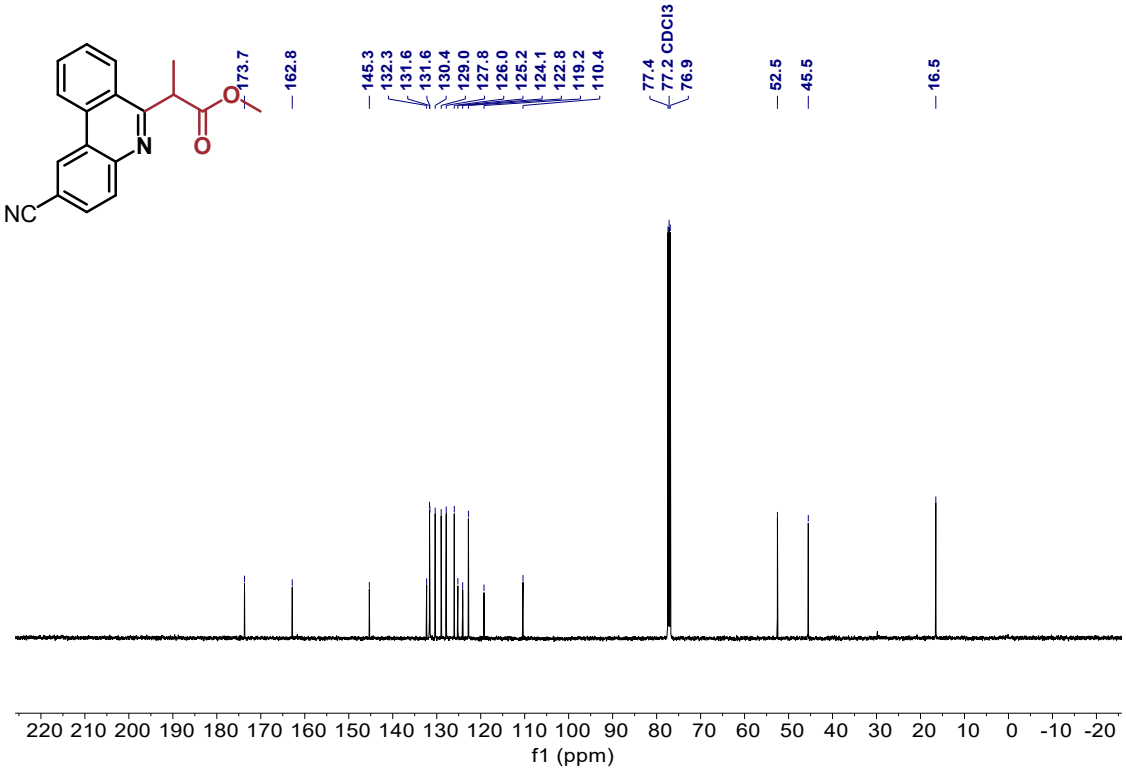
^{13}C NMR of compound **19**(126 MHz in $CDCl_3$)



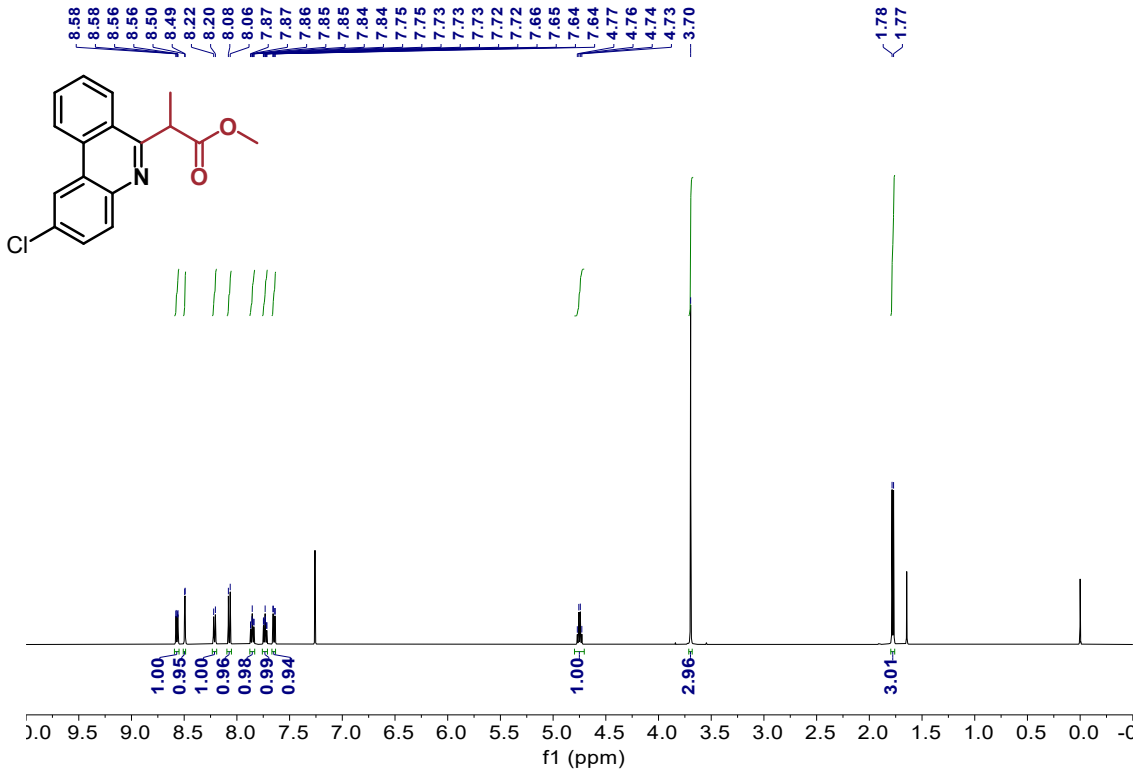
^{1}H NMR of compound **20** (500 MHz in $CDCl_3$)



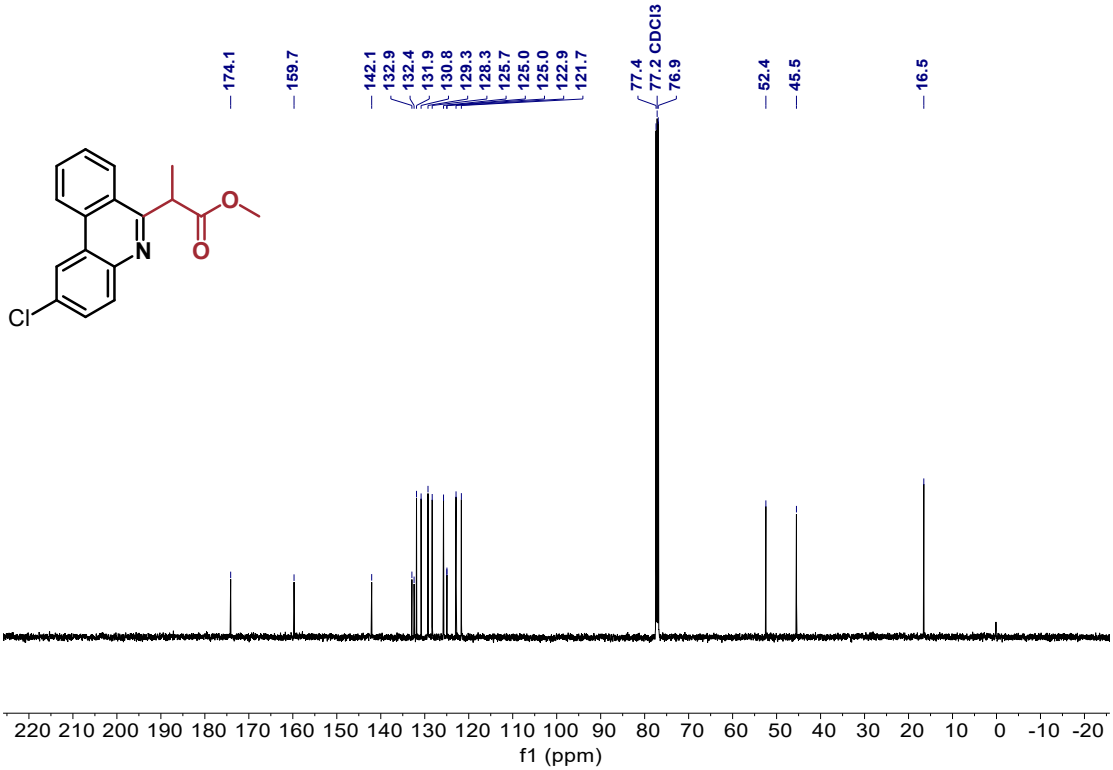
^{13}C NMR of compound **20** (126 MHz in $CDCl_3$)



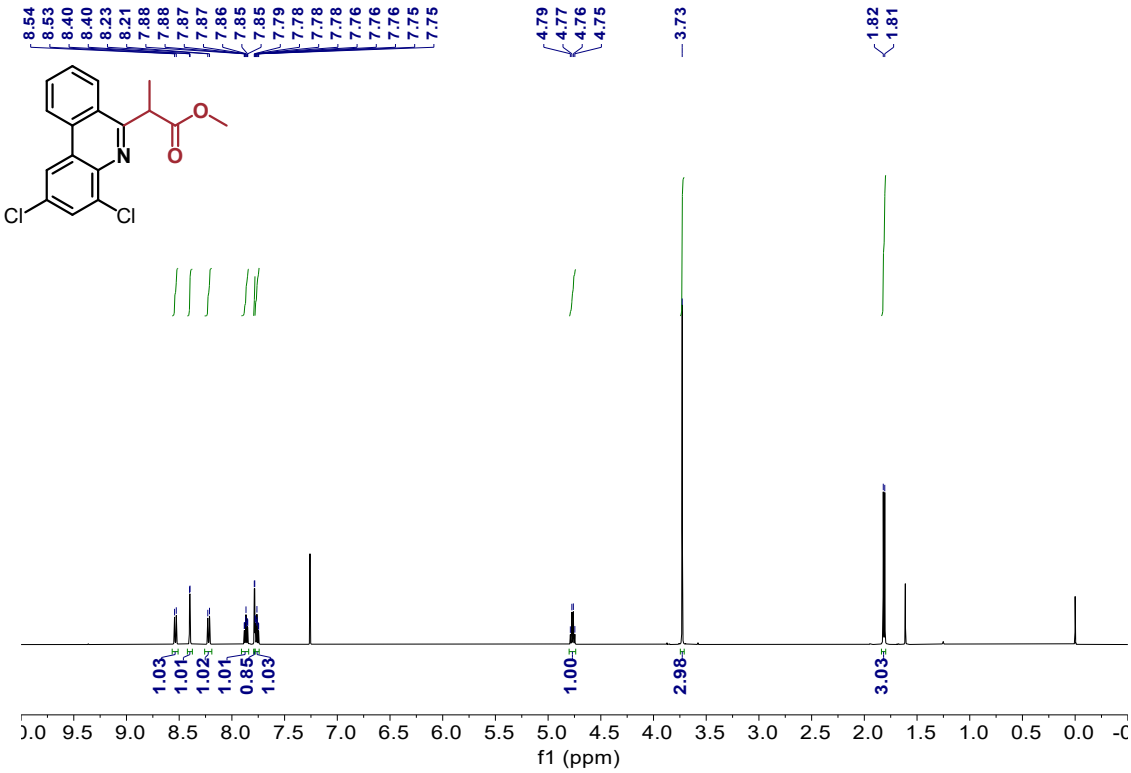
^{1}H NMR of compound **21** (500 MHz in $CDCl_3$)



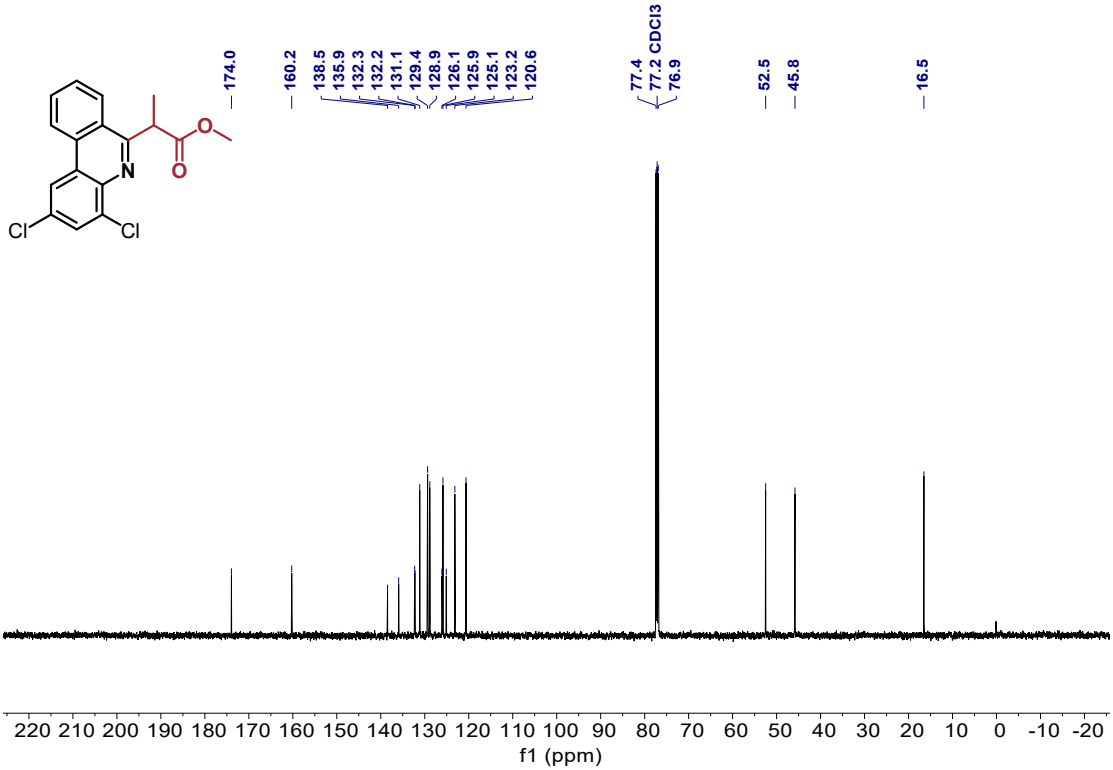
^{13}C NMR of compound **21** (126 MHz in $CDCl_3$)



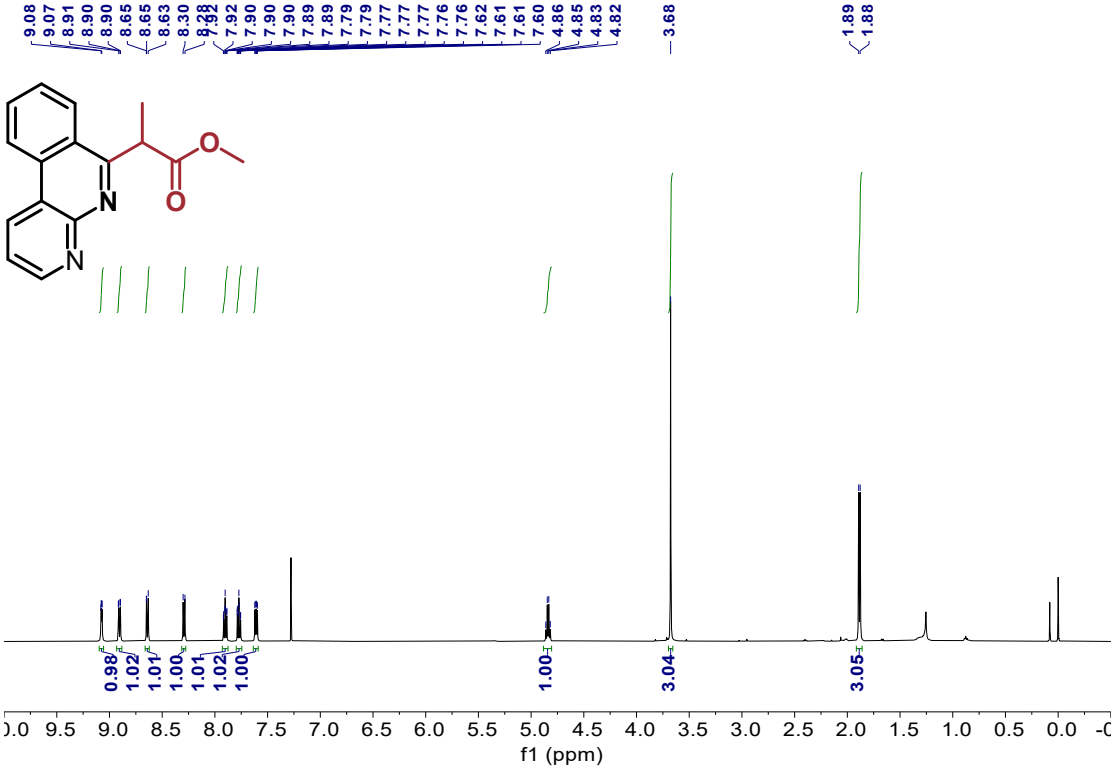
^{1}H NMR of compound **22**(500 MHz in $CDCl_3$)



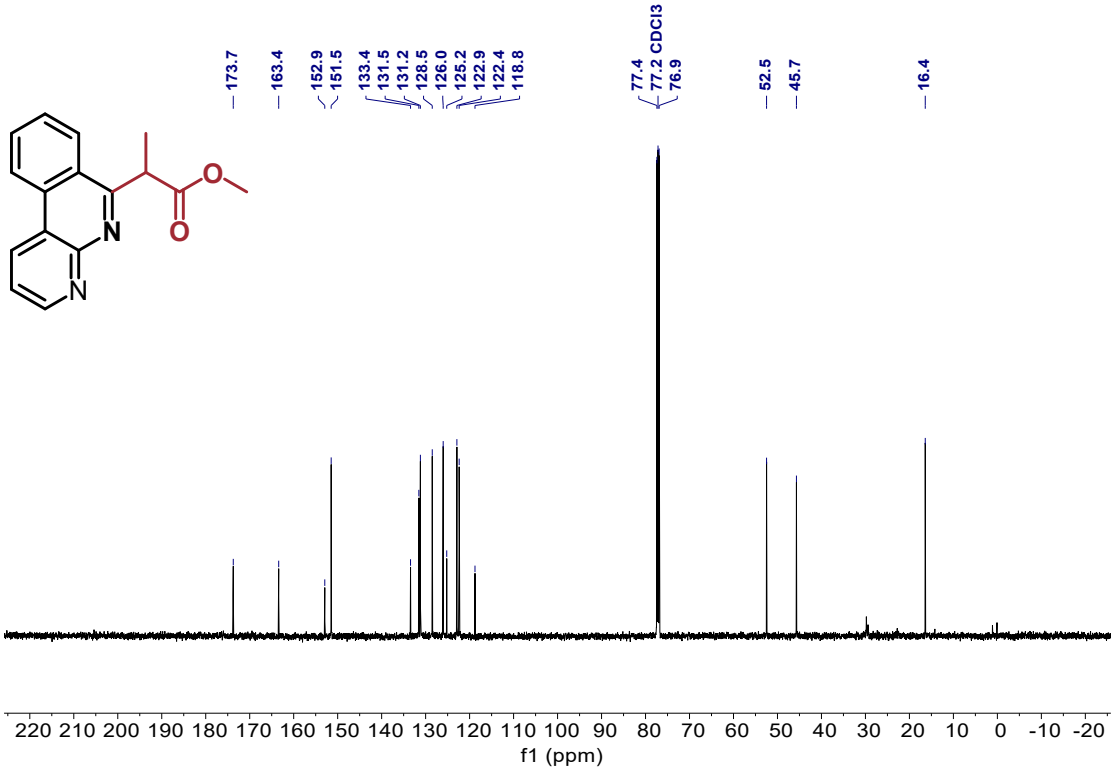
^{13}C NMR of compound **22**(126 MHz in $CDCl_3$)



^{1}H NMR of compound **23** (500 MHz in $CDCl_3$)



^{13}C NMR of compound **23** (126 MHz in $CDCl_3$)



7. Reference.

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(2) Tran, C. C.; Kawaguchi, S.; Kobiki, Y.; Matsubara, H.; Tran, D. P.; Kodama, S.; Nomoto, A.;Ogawa, A., Palladium-Catalyzed Diarylation of Isocyanides with Tetraarylleads for the Selective Synthesis of Imines and α-Diimines*. J. Org. Chem.* **2019***, 84,* 11741−11751.

(3) Wu, X. T.; Chen, P.; Gan, M. G.; Ji, X. C.;Deng, G.-J., Redox-Neutral Cyclization of 2-Isocyanobiaryls Through Photoredox/PPh3 Dual Catalysis. *Org. Lett.* **2023**, *25, 51*, 9186–919.

(4) Zhu, Z.-F.; Zhang, M.-M.; Liu, F, Radical alkylation of isocyanides with amino acid-/peptide-derived Katritzky salts via photoredox catalysis.*Org. Biomol. Chem.***2019**, *17*, 3640-3640.