Supporting Information

Coordinating Activation Strategy Enables 1,2-Alkylamidation of Alkynes

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I. General remarks

NMR spectra were obtained on a Bruker AV II-400 MHz or a Varian Inova 400 MHz spectrometer. The aluminum block [9-hole inner diameter 26-27 mm, H200927 (Syhtnwre)] was used as heat source. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$, Acetone-d_6 or TMS as the internal reference ($CDCl_3$: δ = 7.26 ppm, Acetone-d_6: δ = 2.05 ppm, TMS: δ = 0.00 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ or Acetone-d_6 as the internal standard ($CDCl_3$: δ = 77.16 ppm, Acetone-d_6: δ = 29.84, 206.26 ppm). Chemical shifts δ are reported in ppm relative to residual solvent. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, bs = broad singlet, m = multiplet), coupling constants (Hz), integration. High-resolution mass spectra (HRMS) were obtained with a high-resolution quadrupole-orbitrap tandem mass spectrometer (Q-Exactive plus; Thermo Fisher Scientific, Waltham, MA, USA) with electrospray ionization (ESI). X-Ray single-crystal diffraction data were collected on a Bruker D8 VENTURE single crystal diffraction.

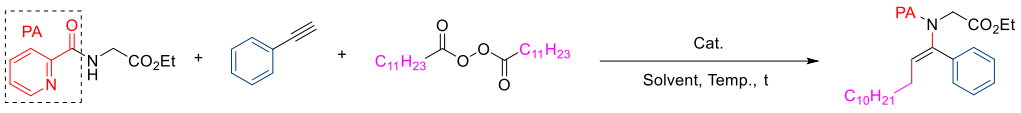
Unless otherwise noted, all reagents and solvents were obtained from commercially available sources and used without further purification. Reactions were monitored by Thin Layer Chromatography (TLC) using UV light (254/365 nm) for detection. Products were purified by column chromatography, which was carried out on 200-300 mesh of silica gel purchased from Qing Dao Hai Yang Chemical Industry Co. 2-Picolinamide derivatives **1** were prepared according to the literature procedure.[1] Alkyl peroxide derivatives **3** were prepared according to the literature procedure.[2]

II. Optimization of the 1,2-difunctional alkylamidation of ethyl picolinoylglycinate 1a with phenylacetylene 2a and lauroyl peroxide 3a

An oven-dried Schlenk tube with a magnetic stir bar was charged with ethyl picolinoylglycinate **1a** (20.8 mg, 0.10 mmol, 1.0 equiv.), phenylacetylene **2a** (22.0 μl, 0.20 mmol, 2.0 equiv.), LPO, catalyst, and solvent under N_2. The tube was sealed with a teflon-coated cap and the reaction solution was heated at indicated temperature for indicated time. After being cooled to ambient temperature, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1/10, v/v) to provide the desired product **4a**.

Table S1: Optimization of the 1,2-difunctional alkylamidation of ethyl picolinoylglycinate (**1a**) with phenylacetylene (**2a**)

and lauroyl peroxide (**3a**, LPO)[a]



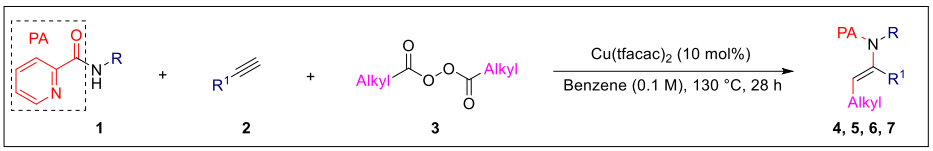
1a **2a** **3a** (LPO) **4a**

Entry	Cat. (equiv.)	LPO (equiv.)	Solvent	Temp. (°C)	t (h)	Yield (%)[b]
1	$Cu(acac)_2$ (0.2)	2.0	benzene	120	12	23
2	$Cu(acac)_2$ (0.2)	3.0	benzene	120	20	36
3	$Cu(acac)_2$ (0.2)	3.0	benzene	130	20	45
4	$Cu(hmacac)_2$ (0.2)	3.0	benzene	130	20	51
5	$Cu(tfacac)_2$ (0.2)	3.0	benzene	130	20	65
6	$Cu(hfacac)_2$ (0.2)	3.0	benzene	130	20	53
7	$Ni(acac)_2$ (0.2)	3.0	benzene	130	20	n.d.
8	$Co(acac)_2$ (0.2)	3.0	benzene	130	20	n.d.
9	$Mn(acac)_2$ (0.2)	3.0	benzene	130	20	n.d.
10	$Fe(acac)_2$ (0.2)	3.0	benzene	130	20	n.d.
11	CuCl (0.2)	3.0	benzene	130	20	trace
12	CuBr (0.2)	3.0	benzene	130	20	trace
13	CuI (0.2)	3.0	benzene	130	20	trace
14	$Cu(OAc)_2$ (0.2)	3.0	benzene	130	20	trace
15[c]	$Cu(OAc)_2$ (0.2)	3.0	benzene	130	20	44
16	$CuBr_2$ (0.2)	3.0	benzene	130	20	trace
17	$Cu(tfacac)_2$ (0.1)	3.0	benzene	130	24	74
18	$Cu(tfacac)_2$ (0.1)	3.0	benzene	130	26	80
19	**$Cu(tfacac)_2$ (0.1)**	**3.0**	**benzene**	**130**	**28**	**81**
20	$Cu(tfacac)_2$ (0.1)	3.0	benzene	130	32	72
21	$Cu(tfacac)_2$ (0.1)	3.0	benzene	140	24	72
22[d]	$Cu(tfacac)_2$ (0.1)	3.0	benzene	130	28	59
23	$Cu(tfacac)_2$ (0.1)	3.0	cyclohexane	130	28	43
24	$Cu(tfacac)_2$ (0.1)	3.0	toluene	130	28	67
25	$Cu(tfacac)_2$ (0.1)	3.0	$PhCF_3$	130	28	75
26	$Cu(tfacac)_2$ (0.1)	3.0	PhCl	130	28	73
27	$Cu(tfacac)_2$ (0.1)	3.0	MeOH	130	28	48
28	$Cu(tfacac)_2$ (0.1)	3.0	HOAc	130	28	n.d.
29	$Cu(tfacac)_2$ (0.1)	3.0	CH_3CN	130	28	45
30	$Cu(tfacac)_2$ (0.1)	3.0	^{t}AmyOH	130	28	n.d.
31	--	3.0	benzene	130	28	n.d.
32	$Cu(acac)_2$ (0.1)	--	benzene	130	28	n.d.

[a]Reaction conditions: **1a** (20.8 mg, 0.10 mmol, 1.0 equiv.), **2a** (22.0 μl, 0.20 mmol, 2.0 equiv.), LPO, cat. and solvent (1.0 mL) at indicated temperature under N_2 atmosphere. [b]Isolated yield after chromatographic purification. [c]2,2,6,6-tetramethylheptane-3,5-dione (20 mol%)

was added. [d]The reaction under an air atmosphere. $Cu(acac)_2$ = Cupric acetylacetonate. $Cu(hmacac)_2$ = Copper(II) bis(2,2,6,6-tetramethyl-3,5-heptanedionate). $Cu(tfacac)_2$ = Copper(II) trifluoroacetylacetonate. $Cu(hfacac)_2$ = Copper(II) hexafluor-2,4-pentanedionate. n.d. = no product detected. PA = 2-Pyridylacyl.

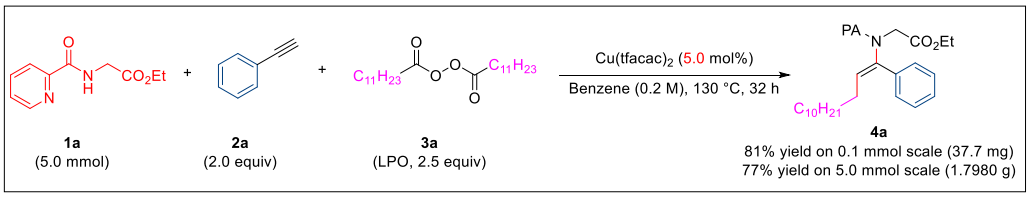
III. General procedure for the 1,2-difunctional alkylamidation of alkynes



An oven-dried Schlenk tube with a magnetic stir bar was charged with 2-picolinamide derivative **1** (0.1 mmol, 1.0 equiv.), alkyne **2** (0.20 mmol or 0.15 mmol, 2.0 equiv. or 1.5 equiv.), alkyl peroxides (0.30 mmol or 0.40 mmol, 3.0 equiv. or 4.0 equiv.), $Cu(tfacac)_2$ (3.7 mg, 0.01 mmol, 0.1 equiv.) and benzene (1.0 mL). Then the tube was sealed with a teflon-coated cap under N_2 atmosphere and the reaction mixture was stirred at room temperature for several minutes. Then the mixture was stirred at 130 °C for 28 h. After being cooled to ambient temperature, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel to provide the desired products.

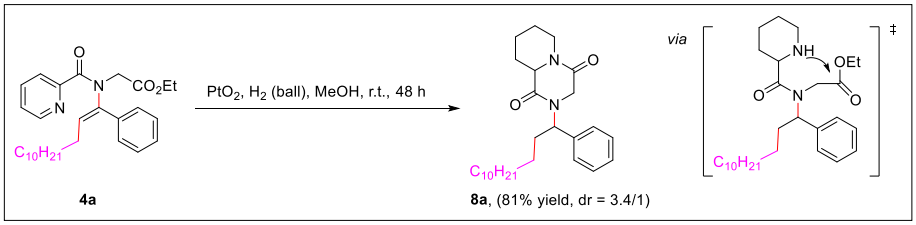
IV. Synthetic manipulation

a) Gram-scale synthesis of 4a



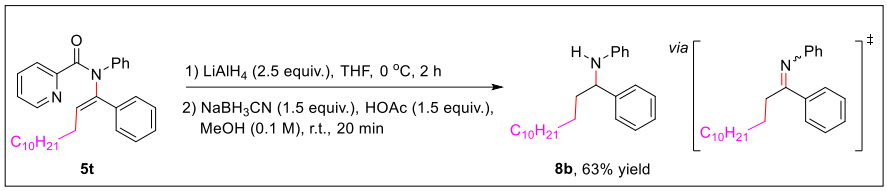
Ethyl picolinoylglycinate **1a** (5.0 mmol, 1.0 equiv., 1.04 g), ethynylbenzene **2a** (10.0 mmol, 2.0 equiv., 1.02 g/1.10 ml), LPO (**3a**, 4.98 g, 12.5 mmol, 2.5 equiv.), and $Cu(tfacac)_2$ (92.4 mg, 0.25 mmol, 0.05 equiv.) were added sequentially into a Schlenk tube under nitrogen, then the tube was capped with a rubber stopper. Benzene (25.0 mL) was then added by syringe. Then the tube was sealed with a teflon-coated cap under N_2 atmosphere and the reaction mixture was stirred at room temperature for several minutes. Then the mixture was stirred at 130 °C for 32 h. After being cooled to ambient temperature, the reaction mixture was quenched with 1 M sodium thiosulfate solution and the aqueous phase was extracted with EtOAc. The combined organic phases were washed with aqueous $NaHCO_3$ and brine, dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel to to afford product **4a** (1.80 g, 77% yield).

b) Procedure for the hydrogenation of 4a



The product **4a** (46.5 mg, 0.1 mmol) and PtO_2 (20%, w/w) were added sequentially into a flask Schlenk tube under nitrogen, then the tube was capped by a rubber stopper. The nitrogen in the tube was then evacuated and backfilled with hydrogen by using a hydrogen balloon. MeOH (1.0 mL) was then added by syringe. The resulting mixture was stirred at room tempeature for 48 hours as monitored by TLC. Upon completion, solvent was removed under vacuum and the residue was purified by flash silica gel column chromatography using eluent petroleum ether/ethyl acetate as eluent to afford product **8a** as colourless oil (34.6 mg, 81% yield, dr = 3.4/1).

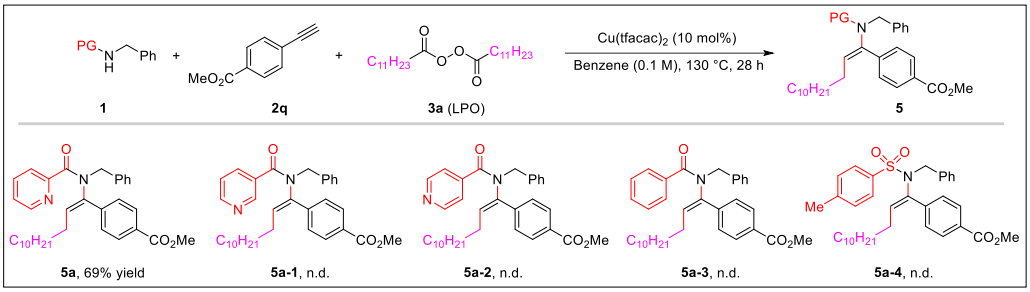
c) The procedure for the removal of PA group



Compound enamide **5t** (48.5 mg, 0.1 mmol, 1.0 equiv.) was dissolved in anhydrous THF (1.0 mL) in an ovendried 25 mL vial at 0 °C, and $LiAlH_4$ (9.9 mg, 0.25 mmol, 2.5 equiv.) was added. The mixture was stirred at same temperature for 2 hours, then aqueous $NaHCO_3$ (sat.) was added. The mixture was extracted with ethyl acetate, the combined organic layers were dried with anhydrous Na_2SO_4 and concentrated in vacuo. Then the resulting residue was redissolved in MeOH (1.0 mL), and $NaBH_3CN$ (9.4 mg, 0.15 mmol, 1.5 equiv.), AcOH (9.0 mg, 0.15 mmol, 1.5 equiv.) were added at room temperature. After stirring for 20 min, the reaction system was quenched with $NaHCO_3$, and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, filtered and evaporated in vacuo. The residue was purified by flash column chromatography on silica gel to give **8b** as pale yellow oil (22.2 mg, 63% yield).

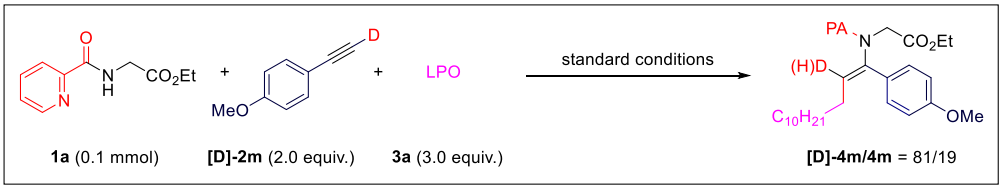
V. Investigation of the reaction mechanism

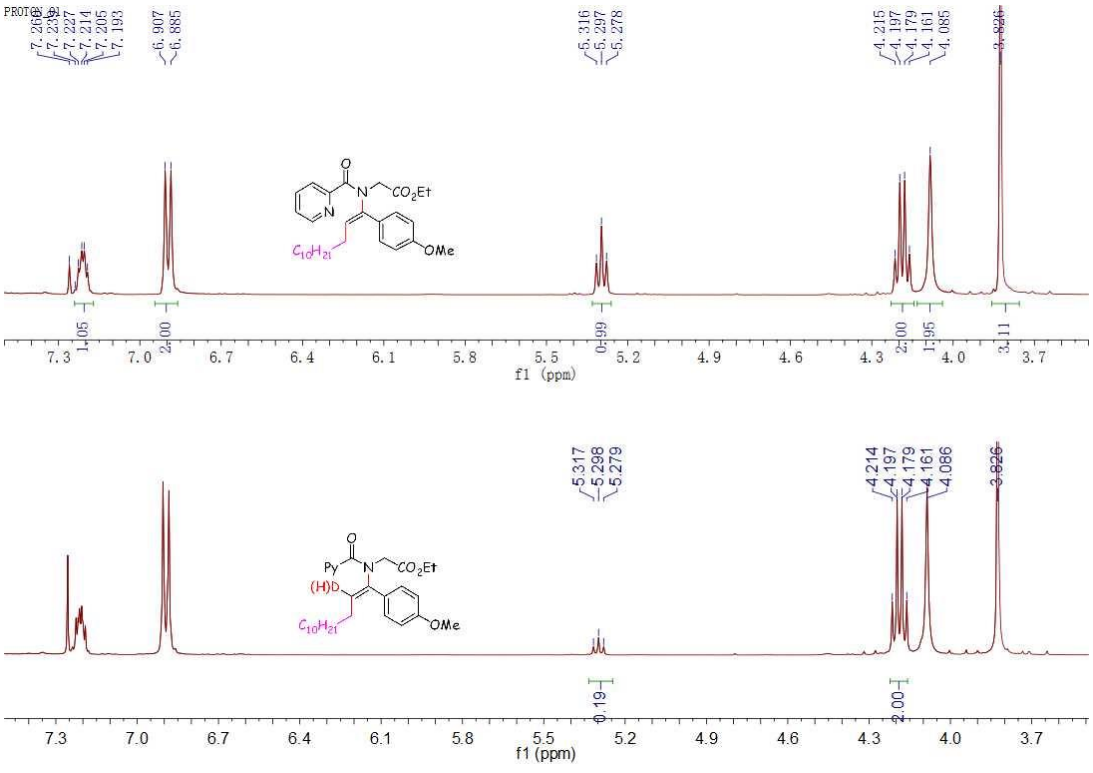
a) The effect of N-protecting groups



In a 25 mL Schlenk tube equipped with a stir bar was charged with **1** (0.10 mmol, 1.0 equiv.), **2q** (32.0 mg, 0.2 mmol, 2.0 equiv.), LPO (159.4 mg, 0.40 mmol, 4.0 equiv.) and $Cu(tfacac)_2$ (3.7 mg, 0.01 mmol, 0.1 equiv.) in benzene (1.0 mL). The reaction was stirred at 130 °C for 28 h under N_2 atmosphere. After being cooled to ambient temperature, the crude mixture was analyzed by TLC. Then the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography using petroleum ether and ethyl acetate as eluents to obtain the products **5** (if necessary).

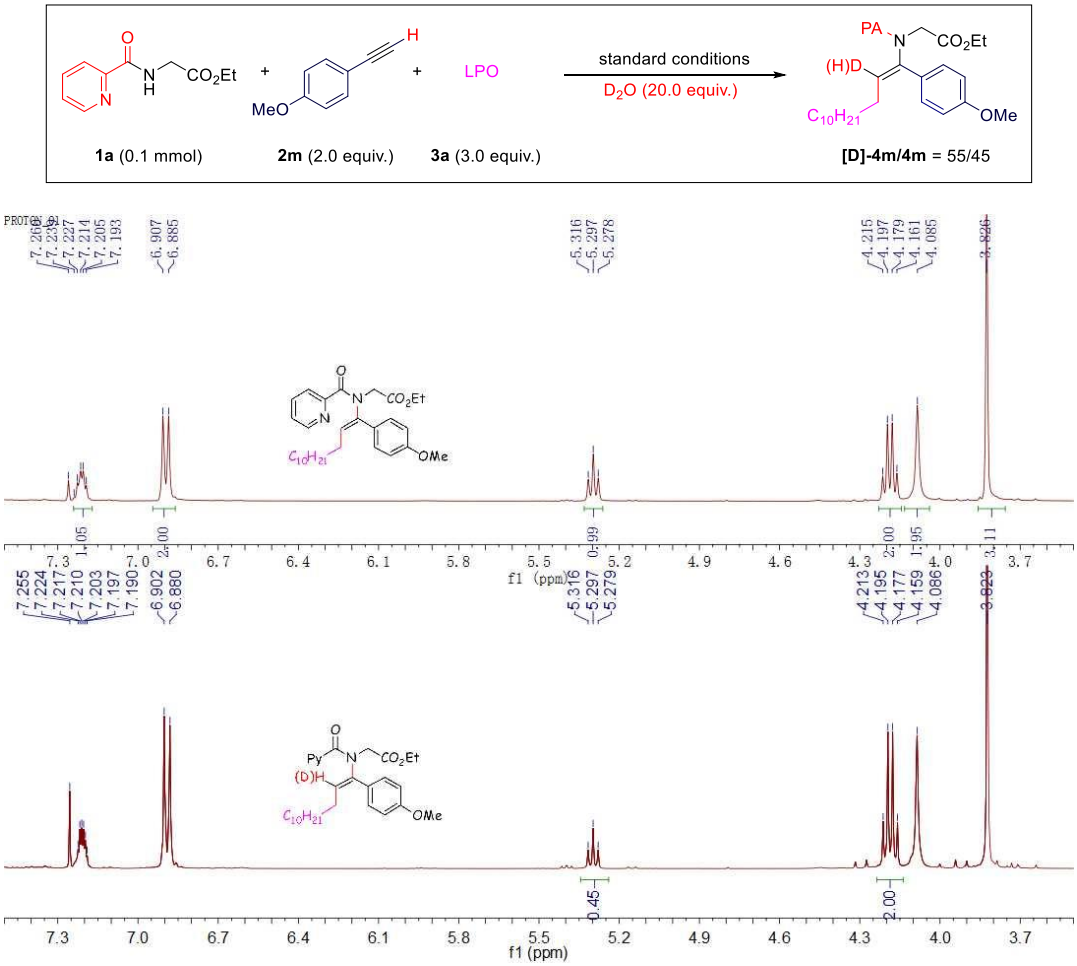
b) Deuterium-labeling experiments





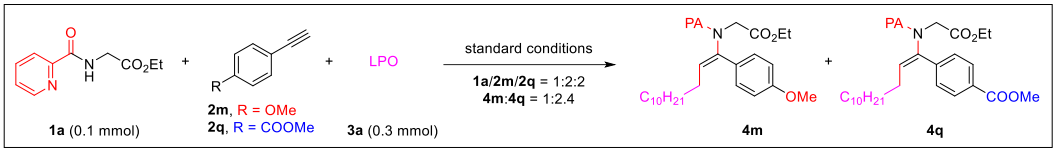
In a 25 mL Schlenk tube equipped with a stir bar was charged with **1a** (20.8 mg, 0.10 mmol, 1.0 equiv.),

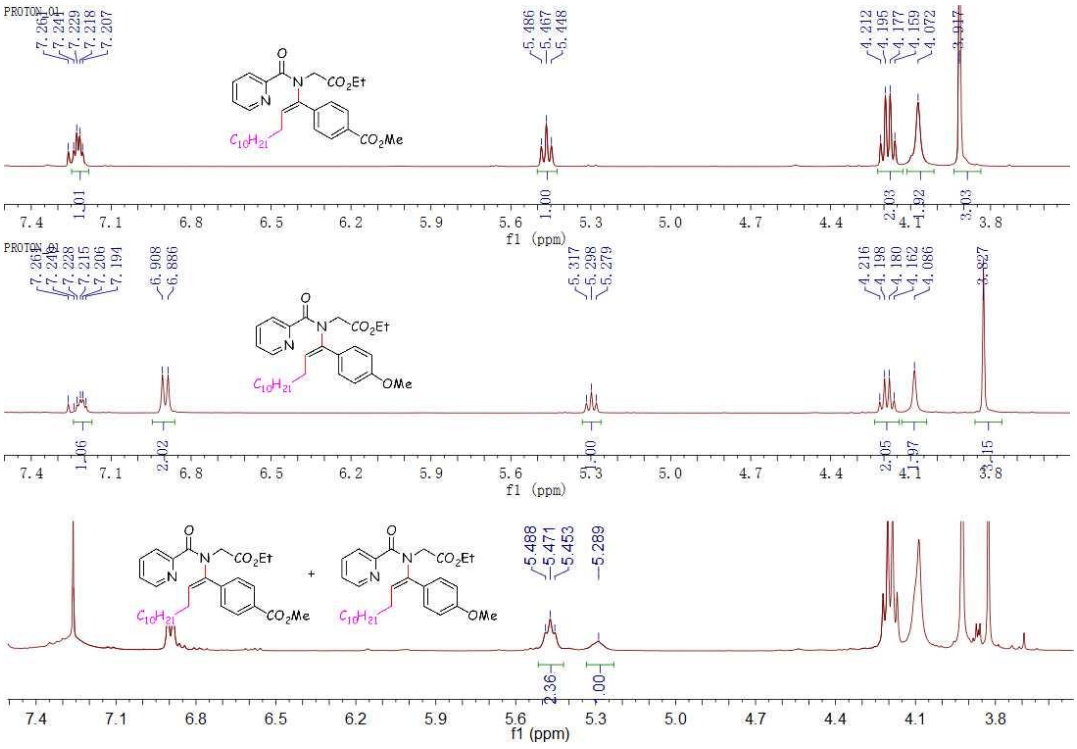
1-(ethynyl-*d*)-4-methoxybenzene ([**D**]-**2m**, 26.6 mg, 0.2 mmol, 2.0 equiv), LPO (119.6 mg, 0.30 mmol, 3.0 equiv.) and Cu(tfacac)$_2$ (3.7 mg, 0.01 mmol, 0.1 equiv.) in benzene (1.0 mL). The reaction was stirred at 130 °C for 28 h under N_2 atmosphere. After being cooled to ambient temperature, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography using petroleum ether and ethyl acetate as eluents to obtain the products **4m** and [**D**]-**4m** as the mixture. Then the mixture was detected by ^{1}H NMR to obtain the ratio.



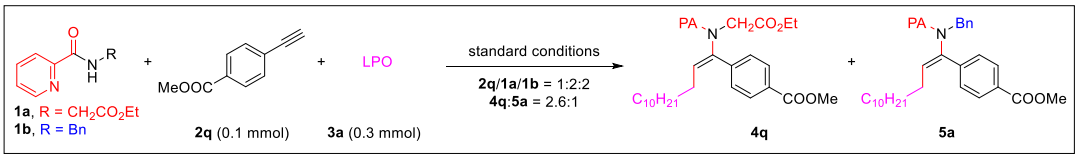
In a 25 mL Schlenk tube equipped with a stir bar was charged with **1a** (20.8 mg, 0.10 mmol, 1.0 equiv.), 1-ethynyl-4-methoxybenzene (**2m**, 26.4 mg, 0.2 mmol, 2.0 equiv), LPO (119.6 mg, 0.30 mmol, 3.0 equiv.), D2O (40.0 ul, 2.0 mmol, 20.0 equiv.) and Cu(tfacac)$_2$ (3.7 mg, 0.01 mmol, 0.1 equiv.) in benzene (1.0 mL). The reaction was stirred at 130 °C for 28 h under N_2 atmosphere. After being cooled to ambient temperature, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography using petroleum ether and ethyl acetate as eluents to obtain the products **4m** and [**D**]-**4m** as the mixture. Then the mixture was detected by ^{1}H NMR to obtain the ratio.

c) Intermolecular competition experiments



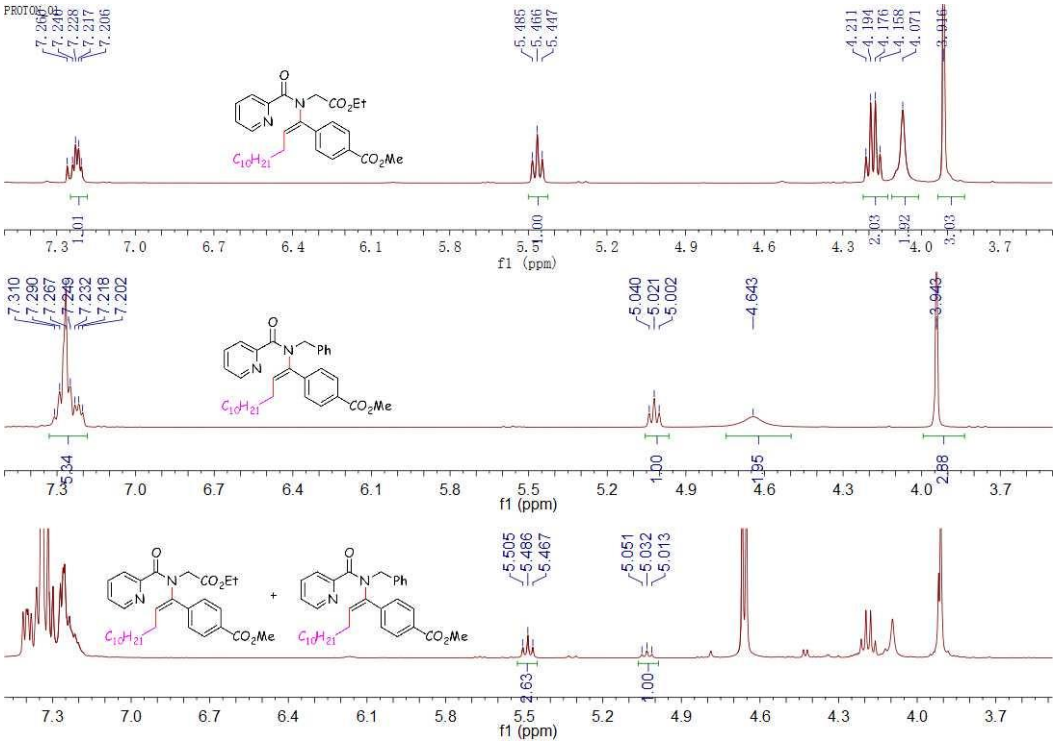


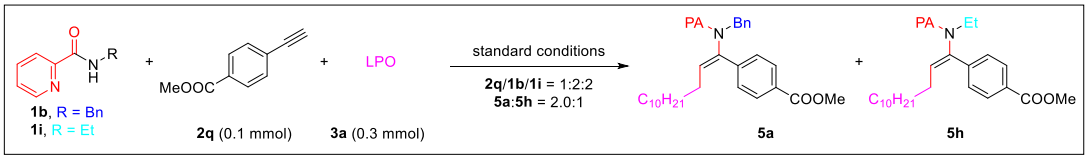
In a 25 mL Schlenk tube equipped with a stir bar was charged with **1a** (20.8 mg, 0.10 mmol, 1.0 equiv.), 1-ethynyl-4-methoxybenzene (**2m**, 26.4 mg, 0.2 mmol, 2.0 equiv), methyl 4-ethynylbenzoate (**2q**, 32.0 mg, 0.2 mmol, 2.0 equiv), LPO (119.6 mg, 0.30 mmol, 3.0 equiv.) and $Cu(tfacac)_2$ (3.7 mg, 0.01 mmol, 0.1 equiv.) in benzene (1.0 mL). The reaction was stirred at 130 °C for 28 h under N_2 atmosphere. After being cooled to ambient temperature, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography using petroleum ether and ethyl acetate as eluents to obtain the products **4m** and **4q** as the mixture. Then the mixture was detected by ^1H NMR to obtain the ratio.



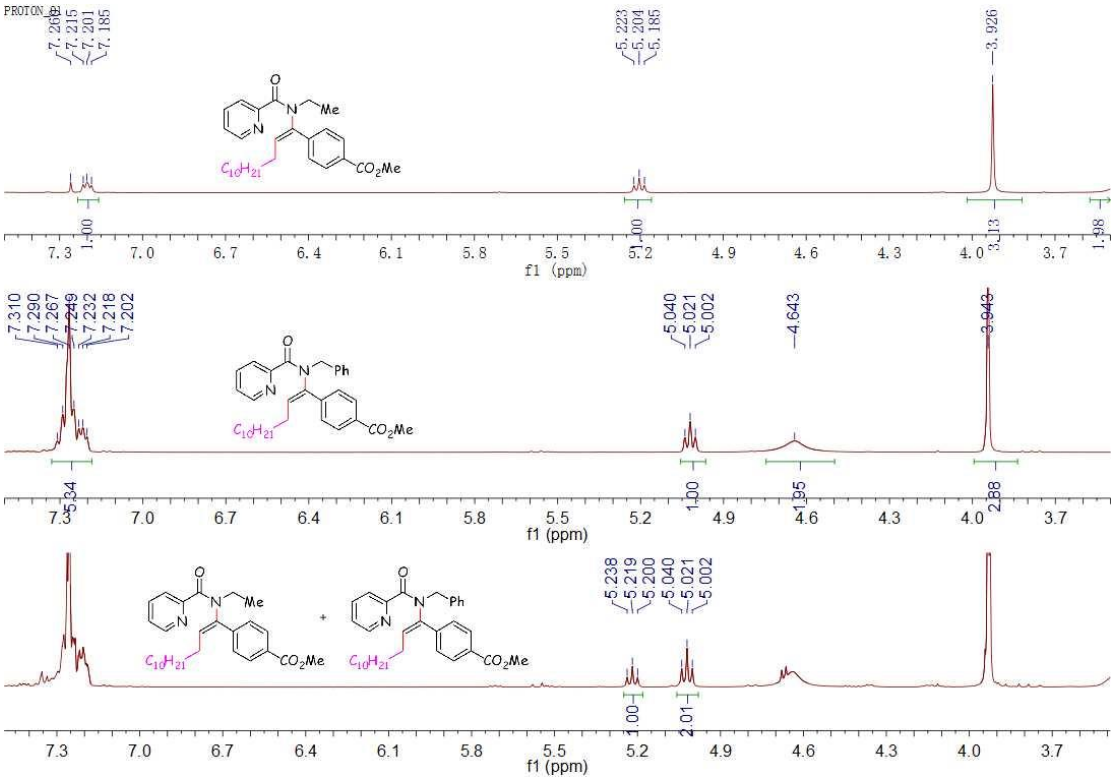
In a 25 mL Schlenk tube equipped with a stir bar was charged with **1a** (41.6 mg, 0.20 mmol, 2.0 equiv.), **1b** (42.4 mg, 0.20 mmol, 2.0 equiv.), methyl 4-ethynylbenzoate (**2q**, 16.0 mg, 0.1 mmol, 1.0 equiv), LPO (119.6 mg, 0.30 mmol, 3.0 equiv.) and $Cu(tfacac)_2$ (3.7 mg, 0.01 mmol, 0.1 equiv.) in benzene (1.0 mL). The

reaction was stirred at 130 °C for 28 h under N_2 atmosphere. After being cooled to ambient temperature, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography using petroleum ether and ethyl acetate as eluents to obtain the products **4q** and **5a** as the mixture. Then the mixture was detected by ^{1}H NMR to obtain the ratio.





In a 25 mL Schlenk tube equipped with a stir bar was charged with **1b** (42.4 mg, 0.20 mmol, 2.0 equiv.), **1i** (30.0 mg, 0.20 mmol, 2.0 equiv.), methyl 4-ethynylbenzoate (**2q**, 16.0 mg, 0.1 mmol, 1.0 equiv), LPO (119.6 mg, 0.30 mmol, 3.0 equiv.) and $Cu(tfacac)_2$ (3.7 mg, 0.01 mmol, 0.1 equiv.) in benzene (1.0 mL). The reaction was stirred at 130 °C for 28 h under N_2 atmosphere. After being cooled to ambient temperature, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography using petroleum ether and ethyl acetate as eluents to obtain the products **5a** and **5h** as the mixture. Then the mixture was detected by ^{1}H NMR to obtain the ratio.



Computational Methods. Calculations were conducted using Gaussian 16 program package.[3] CBS-QB3 model was used for gas-phase calculations.[4] The complete basis set methods (CBS) are a model chemistry that makes use of a complete basis set extrapolation of the correlation energy, which is performed at the MP2 level of theory and then corrected to the CCSD(T) level via additivity corrections. CBS-QB3 has been proved to predict extremely accurate gas-phase deprotonation reactions with less than 1 kcal/mol error.[5] All the structures were fully optimized and characterized as true minima by the absence of imaginary frequencies. Solvation energies were calculated using M06-2X[6]/6-311+G(d,p)[7] level of theory with the SMD[8] continuum model (benzene as the solvent).

Theoretical calculation of pK_a. Continuum solvent pK_a calculations using direct method utilize a thermodynamic cycle (Fig. S1).

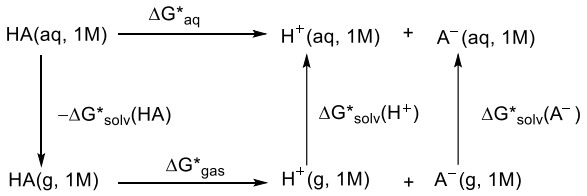


Figure S1. Thermodynamic cycle used in pK_a calculations with direct method.

The dissociation of an acid can be represented as follows:

$$HA(aq) \longrightarrow H^+(aq) + A^-(aq) \qquad (1)$$

$$K_a = \frac{[A^-][H^+]}{[HA]} \qquad (2)$$

$$pK_a = -log_{10}K_a \qquad (3)$$

The directly calculated pK_as may be obtained through Eq. (4).

$$pKa = \frac{\Delta G^*_{aq}}{2.303RT} \qquad (4)$$

ΔG^*_{aq} is defined as the difference in the free energies in solution between the acid (HA) and the conjugate base (A^-) and the free proton (H^+). For computational efficiency, ΔG^*_{aq} can be obtained through the thermodynamic cycle defined in Fig. S1 using Eqs. (5)-(8)

$$\Delta G^*_{aq} = \Delta G^*_{gas} + \delta\, \Delta G^*_{solv} \qquad (5)$$

Where $\Delta G^*_{(gas)}$ and $\delta\, \Delta G^*_{(solv)}$ are

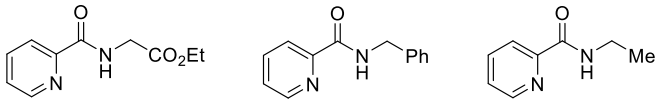
$$\Delta G^*_{gas} = G^*_{gas}(H^+) + G^*_{gas}(A^-) - G^*_{gas}(HA) \qquad (6)$$

$$\delta\, \Delta G^*_{solv} = \Delta G^*_{solv}(H^+) + \Delta G^*_{solv}(A^-) - \Delta G^*_{solv}(HA) \qquad (7)$$

In this work, gas-phase Gibbs free energies and solvation energies of HA and its anion A^-, have been calculated. We have used the most recent experimental–theoretical values of 6.28 kcal/mol[9] and 265.9 kcal/mol[10] for the gas-phase Gibbs free energy of H^+, $G^*_{gas}(H^+)$, and solvation energy of H^+ in water, $\Delta G^*_{solv}(H^+)$, respectively. Calculation of the gas-phase energies are for a standard state of 1 atm but solvation energies use a standard state of 1 mol/L, therefore, the value of 1.89 kcal/ mol which corresponds to $RT\ln(24.46)$ has been considered and added to gas-phase energies.[11] Therefore, ΔG^*_{aq} value is obtained as:

$$\Delta G^*_{aq} = G^*_{gas}(A^-) - G^*_{gas}(HA) + \Delta G^*_{solv}(A^-) - \Delta G^*_{solv}(HA) - 270.29 \qquad (8)$$

Table S2 shows the gas-phase energies of **1a**, **1b**, **1h** and its anions calculated at different levels of theory. Using the energies presented in Table S2, theoretically calculated pK_a's are derived and shown in Figure S2.



1a pK_a = 44.4 **1b** pK_a = 45.3 **1h** pK_a = 45.8

Figure S2. Computed pK_a values.

Table S2. Gas-phase and solvation energies of **1a**, **1b**, **1h** and its anion calculated at different levels of theory

Geometry	G^*_{gas} [a]	E_{gas} [b]	E_{solv} [c]	ΔG^*_{solv} [d]
1a	-722.396115	-723.409237	-723.425936	-0.016699
1a-anion	-721.828601	-722.826869	-722.883767	-0.056898
1b	-686.208809	-687.253757	-687.272758	-0.019001
1-anion	-685.640672	-686.67485	-686.732776	-0.057926
1h	-455.58118	-456.241255	-456.252822	-0.011567
1h-anion	-455.00682	-455.652345	-455.707951	-0.055606

[a]The free energy calculated by CBS-QB3. [b]The electronic energy calculated by M06-2X in gas-phase. [c]The electronic energy calculated by M06-2X in benzene. [d]$\Delta G^*_{solv} = E_{solv} - E_{gas}$.

Geometries for all the optimized compounds

1a

C	-2.39234200	0.27961800	0.00027400
C	-3.59504600	0.98454400	-0.00223100
C	-4.78241100	0.26162600	-0.00313100
C	-4.72127300	-1.12928600	-0.00153600
C	-3.46871000	-1.74091500	0.00090200
H	-3.56603500	2.06606600	-0.00341900
H	-5.73862700	0.77252800	-0.00505400
H	-5.62127600	-1.73238700	-0.00217200
H	-3.38096500	-2.82342200	0.00216300
N	-2.32352500	-1.05717100	0.00181900
C	-1.09240400	1.05126600	0.00116100
O	-1.06911000	2.27553700	-0.00089100
N	0.01411500	0.27578700	0.00461100
H	-0.09031700	-0.73197200	0.00418400
C	1.33655100	0.84675800	0.00381700
H	1.50102500	1.48562600	0.87874300
H	1.49850700	1.48816500	-0.86968000
C	2.37045600	-0.26049200	0.00099900
O	2.11678500	-1.43956600	-0.00047900
O	3.60952000	0.25208000	0.00051800
C	4.70346700	-0.70301200	-0.00212500
H	4.60742200	-1.33820400	-0.88542000
H	4.60975700	-1.34041100	0.87982100
C	5.99448200	0.08809100	-0.00284400
H	6.84711500	-0.59579000	-0.00467700

H	6.06144600	0.72395700	-0.88809400
H	6.06362700	0.72193900	0.88368600

1a-anion

C	-2.37831300	0.26928200	-0.03533000
C	-2.47935500	-1.12020400	-0.23323600
C	-3.72784200	-1.72089200	-0.24993100
C	-4.86116100	-0.92319300	-0.07350700
C	-4.66497400	0.44083500	0.11203300
H	-1.55349800	-1.66400700	-0.36519800
H	-3.82336400	-2.79359900	-0.39603000
H	-5.86240000	-1.34284200	-0.07852200
H	-5.52308400	1.09890100	0.25184600
N	-3.46791600	1.03503300	0.13551700
C	-1.00288600	0.94721700	-0.00280600
O	-0.93814700	2.15857200	0.30011100
N	-0.02789600	0.09980000	-0.31410000
C	1.27228700	0.70217300	-0.27790000
H	1.30110900	1.58440600	0.39058500
H	1.60443700	1.08811000	-1.25695000
C	2.34980700	-0.24146300	0.20262200
O	2.24610200	-1.21081900	0.90944800
O	3.58747500	0.17554200	-0.25360500
C	4.70617900	-0.58477900	0.20954500
H	4.58517900	-1.63288900	-0.08209500
H	4.74125500	-0.56059600	1.30384100
C	5.95633000	0.02390000	-0.40100300
H	6.84694500	-0.52266000	-0.07463400
H	5.90847500	-0.01175100	-1.49231000
H	6.06176600	1.06948800	-0.10101400

1b

C	-2.30414000	0.23706000	-0.01364200
C	-3.46854700	0.66655100	0.62117000
C	-4.59179900	-0.15027400	0.56205100
C	-4.50843900	-1.35795200	-0.12565300
C	-3.29885400	-1.69869400	-0.72819100
H	-3.46069700	1.61740400	1.13711800
H	-5.51620100	0.14865300	1.04312800
H	-5.35892000	-2.02517400	-0.19725800
H	-3.19568100	-2.63234200	-1.27333100
N	-2.21517600	-0.92227400	-0.67770400
C	-1.07290400	1.11717300	0.04232000
O	-1.08611300	2.18952300	0.63099600

N	-0.00039700	0.59906400	-0.60397500
H	-0.13930500	-0.29860600	-1.04995200
C	1.28171300	1.27755900	-0.68939100
H	1.19474400	2.16634400	-0.05931800
H	1.45669300	1.62319500	-1.71437300
C	2.44504700	0.41221800	-0.24438100
C	3.58604600	0.29605900	-1.04070400
C	2.40837600	-0.26358800	0.98032500
C	4.67282700	-0.47155900	-0.62373900
H	3.62538100	0.81041500	-1.99589000
C	3.48995600	-1.03260700	1.39783600
H	1.52570200	-0.18562700	1.60556500
C	4.62715400	-1.13846900	0.59701300
H	5.55065200	-0.55138800	-1.25535400
H	3.44761300	-1.54895000	2.35052800
H	5.46931900	-1.73851300	0.92284400

1b-anion

C	2.36066500	-0.27171400	-0.00796200
C	2.33770700	1.04232900	-0.51102100
C	3.50036500	1.79652900	-0.51803300
C	4.67285900	1.23001000	-0.01315900
C	4.60139400	-0.07353300	0.46652400
H	1.39128800	1.41430100	-0.87950200
H	3.49943900	2.81046700	-0.90931900
H	5.61032300	1.77691500	0.00610900
H	5.49329800	-0.55265400	0.87121900
N	3.49135300	-0.81703400	0.47018400
C	1.09135700	-1.13224700	-0.01605300
O	1.20214300	-2.36297400	0.16809300
N	-0.00363000	-0.41200600	-0.23368700
C	-1.20751700	-1.19984600	-0.24366400
H	-1.19432000	-1.96914600	0.55074000
H	-1.30778700	-1.79151600	-1.17463600
C	-2.46692900	-0.36723000	-0.08743900
C	-3.73015400	-0.92780900	-0.31893500
C	-2.40768200	0.97121500	0.31256300
C	-4.89526800	-0.18322400	-0.15226200
H	-3.79518400	-1.96555300	-0.63682900
C	-3.57098000	1.72147200	0.48169700
H	-1.42233900	1.38916200	0.47936800
C	-4.82175800	1.15086400	0.25081600
H	-5.86227600	-0.64184900	-0.33927900
H	-3.50062600	2.75997200	0.79374600

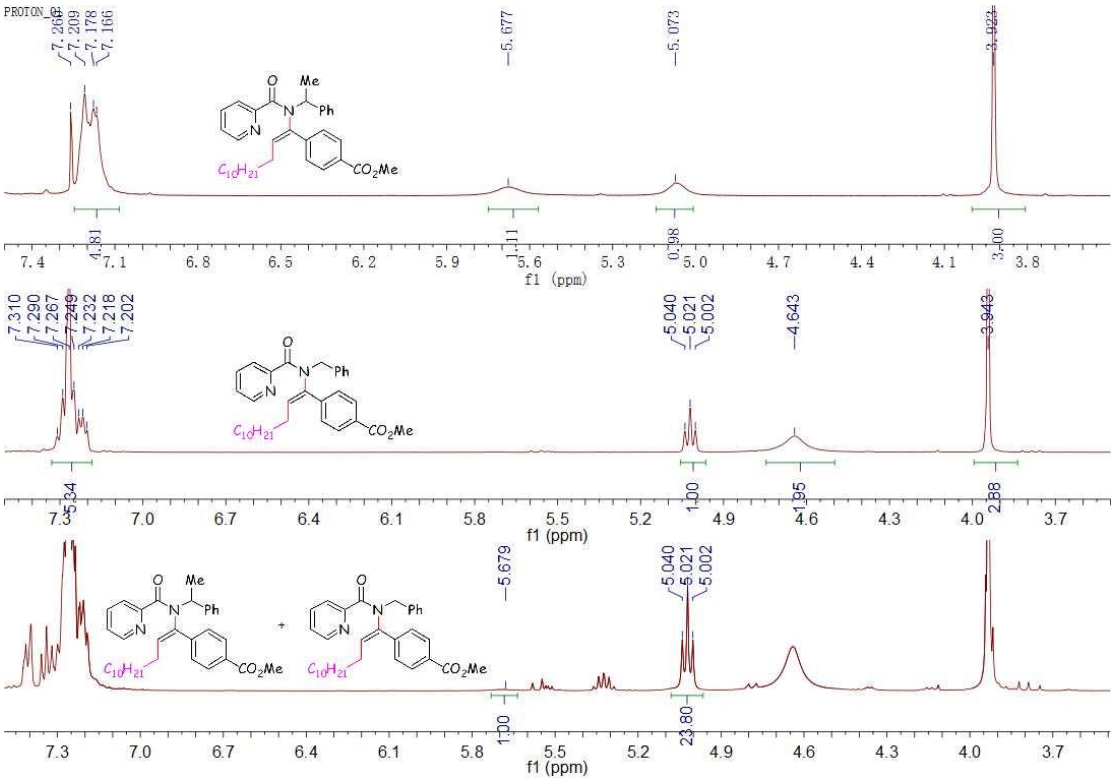
H	-5.72737800	1.73607100	0.37973600

1h

C	0.26757600	0.15325500	0.00007800
C	1.16858700	1.21691100	-0.00014100
C	2.52867400	0.93010500	-0.00030100
C	2.93420300	-0.40184400	-0.00022800
C	1.95654400	-1.39483200	0.00001400
H	0.78120400	2.22701300	-0.00017300
H	3.26034200	1.73012600	-0.00047900
H	3.98350500	-0.67129300	-0.00034800
H	2.23446200	-2.44478700	0.00008100
N	0.64874700	-1.13066700	0.00015900
C	-1.21744900	0.45197500	0.00031800
O	-1.63197100	1.60323000	0.00007900
N	-1.99493400	-0.65545800	0.00006100
H	-1.50214300	-1.53824600	0.00013600
C	-3.44297100	-0.60375800	0.00002000
H	-3.85511800	-1.09028700	0.88930100
H	-3.85507900	-1.09073700	-0.88902700
H	-3.73908100	0.44437300	-0.00023100

1h-anion

C	0.22258400	0.13945200	-0.00000500
C	0.75112300	-1.16650900	0.00008300
C	2.12312800	-1.35498100	0.00006500
C	2.95726800	-0.23285300	-0.00003300
C	2.34901800	1.01715400	-0.00009300
H	0.03527500	-1.97778900	0.00014900
H	2.54441800	-2.35728900	0.00012400
H	4.03930600	-0.32320300	-0.00005200
H	2.96316300	1.91869800	-0.00016800
N	1.02693900	1.21643100	-0.00007000
C	-1.29639700	0.36232300	0.00006400
O	-1.73085200	1.53648100	0.00017100
N	-1.96485400	-0.78256200	-0.00002600
C	-3.39851000	-0.59383100	-0.00015300
H	-3.75786100	-0.02019400	-0.87457700
H	-3.75852200	-0.02389200	0.87646500
H	-3.90284100	-1.56978900	-0.00221700

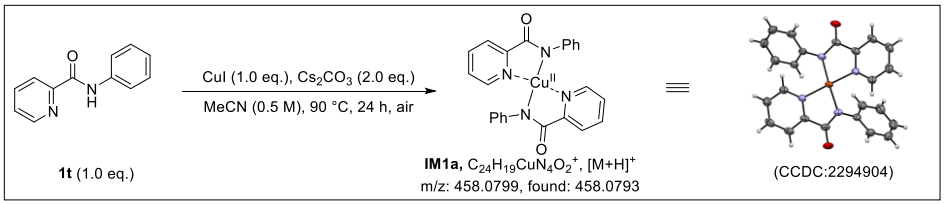


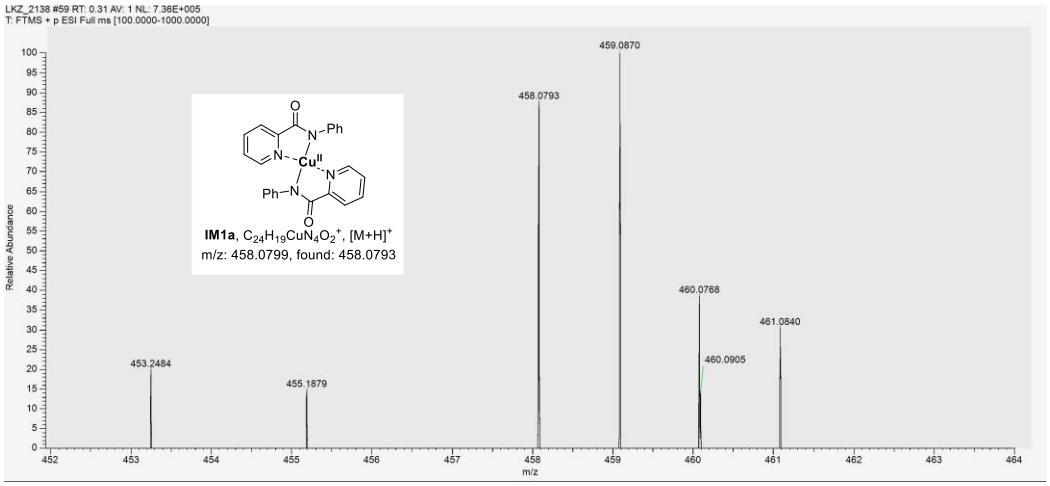
In a 25 mL Schlenk tube equipped with a stir bar was charged with **1b** (42.4 mg, 0.20 mmol, 2.0 equiv.), **1x** (45.2 mg, 0.20 mmol, 2.0 equiv.), methyl 4-ethynylbenzoate (**2q**, 16.0 mg, 0.1 mmol, 1.0 equiv), LPO (159.4 mg, 0.40 mmol, 4.0 equiv.) and $Cu(tfacac)_2$ (3.7 mg, 0.01 mmol, 0.1 equiv.) in benzene (1.0 mL). The reaction was stirred at 130 °C for 28 h under N_2 atmosphere. After being cooled to ambient temperature, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography using petroleum ether and ethyl acetate as eluents to obtain the mixture. Then the mixture was detected by ^1H NMR to obtain the ratio.

d) Preparation and reactivity of intermediate IM1a

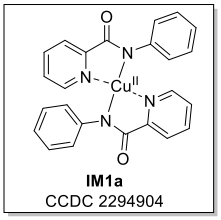
Preparation of intermediate IM1a.[12] An oven-dried Schlenk tube with a magnetic stir bar was charged with *N*-phenylpicolinamide **1t** (0.50 mmol), CuI (0.50 mmol), Cs_2CO_3 (1.00 mmol), and MeCN (1.0 mL) under an air atmosphere. The reaction solution was stirred at room temperature for several minutes the tube was sealed with a teflon-coated cap and the mixture was stirred at 90 °C for 24 h. After being cooled to ambient temperature, the crude mixture was firstly analyzed by HRMS, and the solution was diluted with 20 mL of

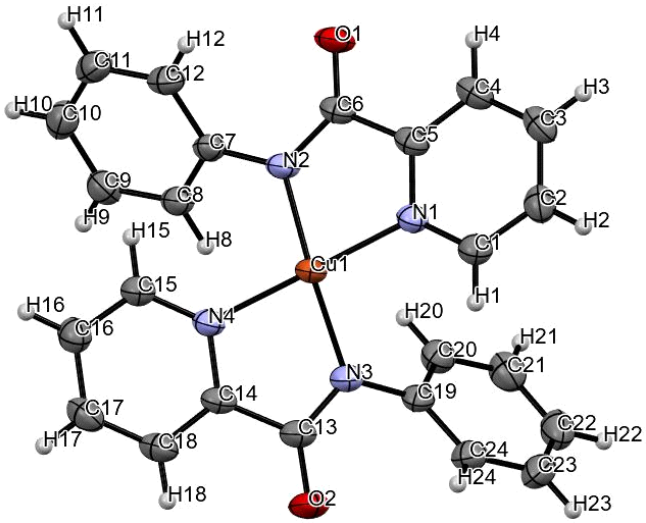
CH_2Cl_2, filtered through a celite pad, and washed with 10-20 mL of CH_2Cl_2. The combined organic phases were concentrated and Cu(II) complexe with *N*-phenylpicolinamide ligand was obtained as powder and, following recrystallisation, led to single crystals of **IM1a** (evaporation of DCM solution).





The X-Ray Diffraction Data of IM1a

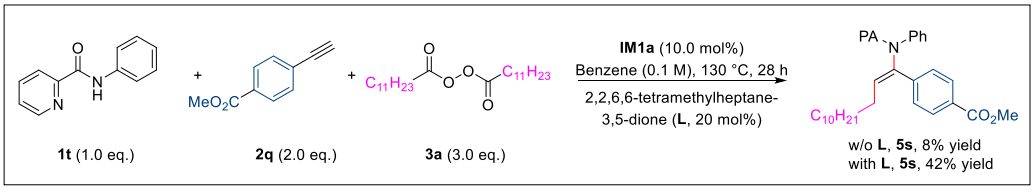




X-ray crystal structures of **IM1a** (The X-ray crystallographic structures are ORTEP representation with 50% probability thermal ellipsoids)

Table S3. Crystal data and structure refinement for **IM1a**

Identification code	**IM1a**
Empirical formula	$C_{24}H_{18}CuN_4O_2$
Formula weight	457.96
Temperature/K	286.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.225(2)
b/Å	18.985(4)
c/Å	10.7936(18)
α/°	90
β/°	104.967(6)
γ/°	90
Volume/Å^3	2024.2(6)
Z	4
ρ_{calc}g/cm^3	1.503
μ/mm^{-1}	1.109
F(000)	940.0
Crystal size/mm^3	0.26 × 0.19 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.29 to 55.206
Index ranges	-13 ≤ h ≤ 13, -24 ≤ k ≤ 24, -12 ≤ l ≤ 14
Reflections collected	44281
Independent reflections	4675 [R_{int} = 0.0547, R_{sigma} = 0.0278]
Data/restraints/parameters	4675/0/280
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0298, wR_2 = 0.0770
Final R indexes [all data]	R_1 = 0.0370, wR_2 = 0.0817
Largest diff. peak/hole / e Å^{-3}	0.39/-0.23

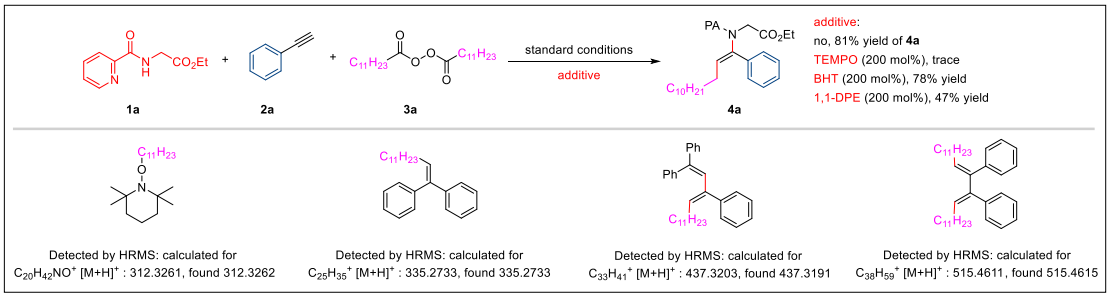


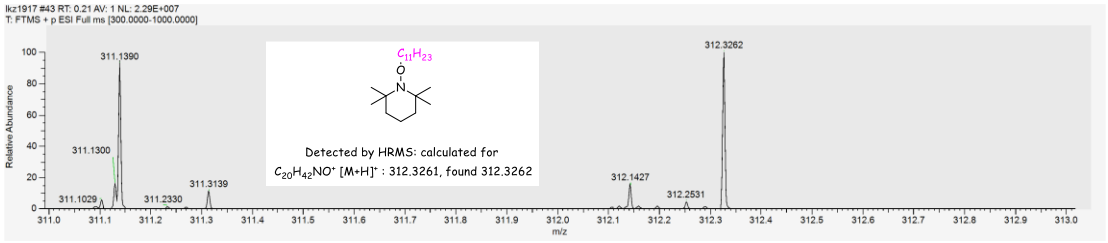
Reactivity of intermediate IM1a. In a 25 mL Schlenk tube equipped with a stir bar was charged with **1t** (19.8 mg, 0.10 mmol, 1.0 equiv.), methyl 4-ethynylbenzoate (**2q**, 32.0 mg, 0.2 mmol, 2.0 equiv), LPO (119.6 mg, 0.30 mmol, 3.0 equiv.), **IM1a** (4.6 mg, 0.01 mmol, 0.1 equiv.) and 2,2,6,6-tetramethylheptane-3,5-dione (3.7

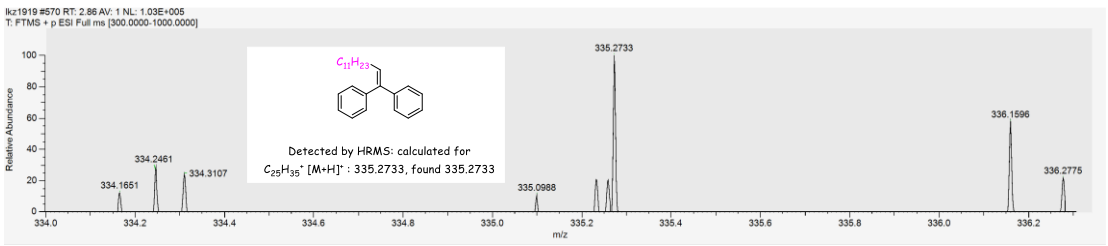
mg, 0.02 mmol, 0.2 equiv., if necessary) in benzene (1.0 mL). The reaction was stirred at 130 °C for 28 h under N_2 atmosphere. After being cooled to ambient temperature, the crude mixture was analyzed by TLC. Then the solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel to afford product **5s** to determine the yield.

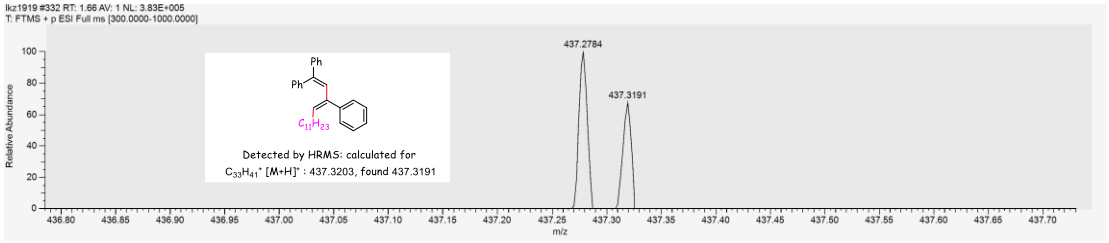
e) Radical scavenger experiments

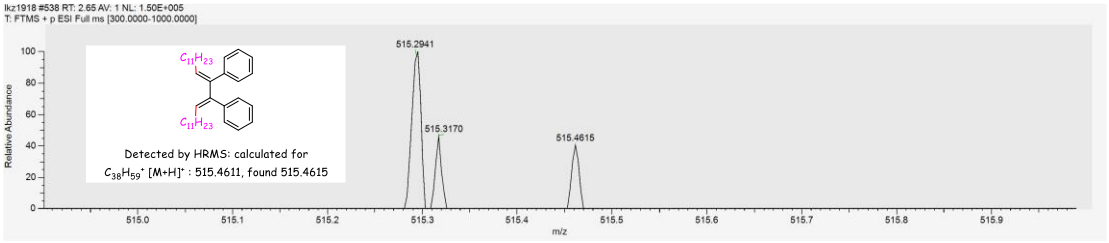
These reactions were conducted with general procedure with minor modification. In a 25 mL Schlenk tube equipped with a stir bar was charged with **1a** (20.8 mg, 0.10 mmol, 1.0 equiv.), ethynylbenzene (**2a**, 22.0 ul, 0.2 mmol, 2.0 equiv), LPO (119.6 mg, 0.30 mmol, 3.0 equiv.), $Cu(tfacac)_2$ (3.7 mg, 0.01 mmol, 0.1 equiv.) and additive (0.2 mmol, 2.0 equiv.) in benzene (1.0 mL). The reaction was stirred at 130 °C for 28 h under N_2 atmosphere. After being cooled to ambient temperature, the crude mixture was firstly analyzed by HRMS (High Resolution Mass Spectrometry). Then the solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel to afford product **4a** to determine the yield (if necessary).



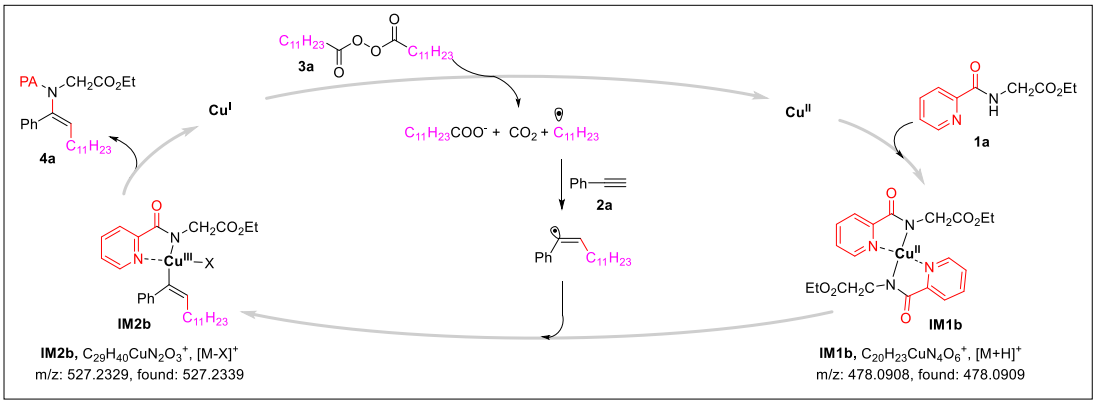


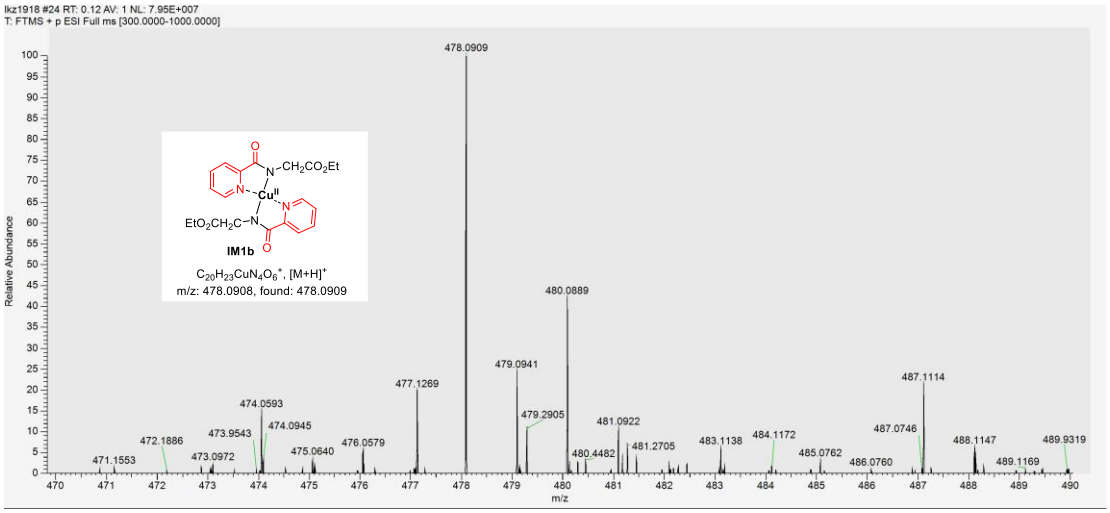


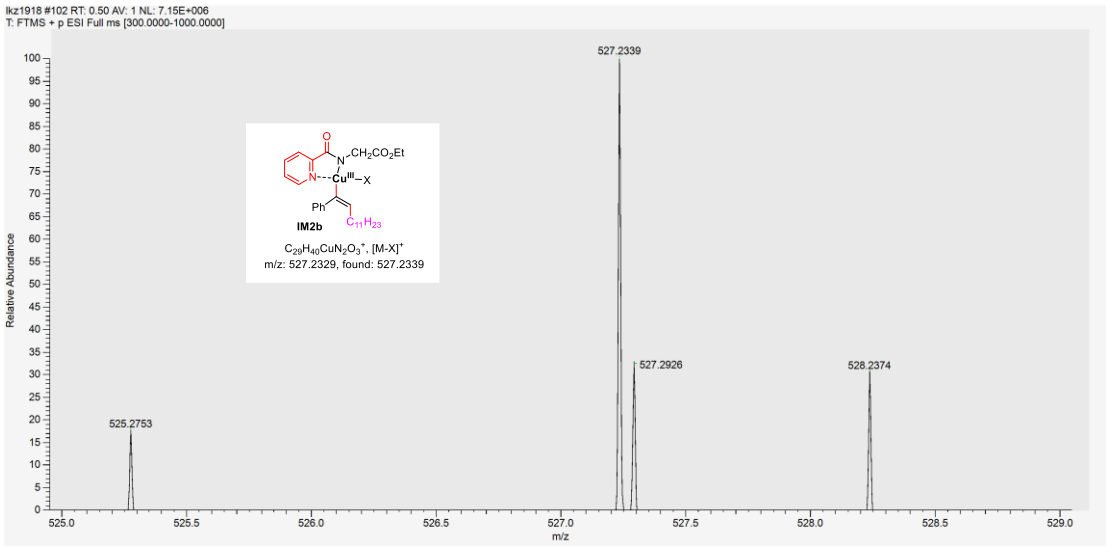




f) Proposed catalytic cycle

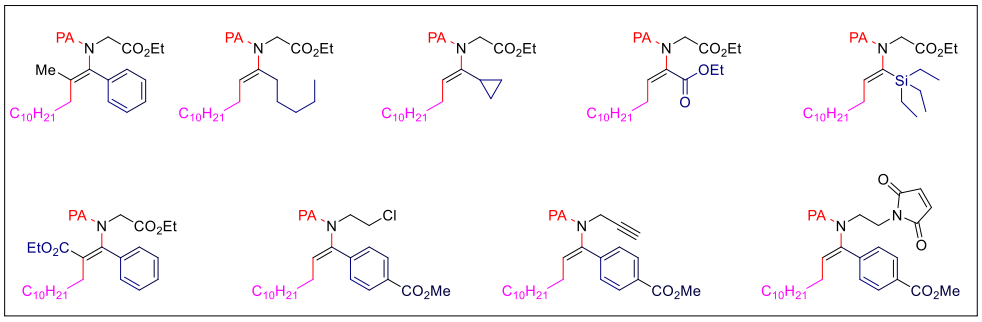




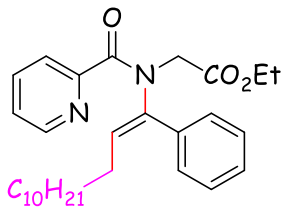


Based on the experimental results and literature precedence, a plausible reaction mechanism is proposed. Initially, alkyl radical is generated from diacyl peroxides with the aid of copper catalyst and/or thermal decomposition, which subsequently undergoes regioselective addition to the alkyne to furnish the alkylated vinyl radical. Meanwhile, the 2-picolinamide acts as a ligand to coordinate with copper(II) to yield the intermediate **IM1**, and then the alkylated vinyl radical is trapped by this coordinated species to form a copper(III) intermediate **IM2**, followed by reductive elimination to furnish the difunctionalization product. Finally, the release of the low-valent metal cataylst Cu(I) is reoxidized by diacyl peroxides and fulfills a catalytic cycle. The intermediate **IM1b** and **IM2b** could be detected by HRMS (High Resolution Mass Spectrum).

VI. Unsuccessful substrates (The products shown below were not obtained)



VII. Experimental data for the described substances



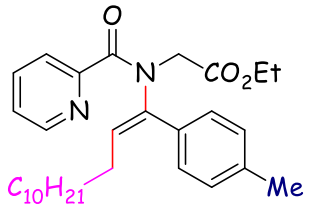
ethyl (*E*)-*N*-(1-phenyltridec-1-en-1-yl)-*N*-picolinoylglycinate (4a)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/9, v/v) afforded **4a** as pale yellow oil (37.7 mg, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, J = 4.7 Hz, 1H), 7.68 (d, J = 4.2 Hz, 2H), 7.62 (d, J = 7.4 Hz, 2H), 7.39 – 7.30 (m, 3H), 7.22 (dd, J = 9.0, 4.5 Hz, 1H), 5.38 (t, J = 7.5 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.09 (s, 2H), 1.93 (dd, J = 14.8, 7.4 Hz, 2H), 1.35 – 0.96 (m, 17H), 0.93 – 0.81 (m, 5H), 0.75 (dt, J = 14.7, 7.3 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.95, 168.88, 154.48, 148.31, 139.32, 136.43, 134.99, 131.74, 130.14, 128.46, 128.28, 124.26, 123.72, 61.15, 48.45, 32.02, 29.72, 29.51, 29.48, 29.44, 29.21, 28.98, 28.58, 22.80, 14.27, 14.25 ppm.

HRMS (ESI^+): calcd for $C_{29}H_{41}N_2O_3^+$ $[M+H]^+$ 465.3112, found 465.3112.



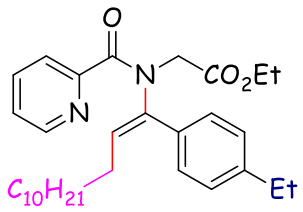
ethyl (*E*)-*N*-picolinoyl-*N*-(1-(*p*-tolyl)tridec-1-en-1-yl)glycinate (4b)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/9, v/v) afforded **4b** as pale yellow oil (31.3 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (d, J = 4.5 Hz, 1H), 7.68 (d, J = 4.1 Hz, 2H), 7.50 (d, J = 7.8 Hz, 2H), 7.24 – 7.11 (m, 3H), 5.34 (t, J = 7.5 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.08 (s, 2H), 2.37 (s, 3H), 1.93 (dd, J = 14.8, 7.4 Hz, 2H), 1.37 – 0.94 (m, 17H), 0.87 (t, J = 6.7 Hz, 3H), 0.84 – 0.69 (m, 4H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.97, 168.91, 154.52, 148.35, 139.17, 138.40, 136.40, 131.94, 131.43, 130.01, 129.02, 124.22, 123.62, 61.14, 48.38, 32.02, 29.73, 29.52, 29.49, 29.46, 29.23, 28.99, 28.64, 22.81, 21.44, 14.26 ppm.

HRMS (ESI$^+$): calcd for $C_{30}H_{43}N_2O_3^+$ $[M+H]^+$ 479.3268, found 479.3268.



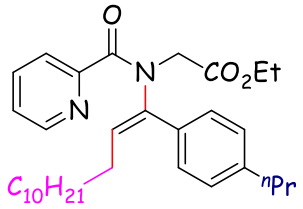
ethyl (*E*)-*N*-(1-(4-ethylphenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (4c)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/9, v/v) afforded **4c** as pale yellow oil (35.3 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, J = 4.7 Hz, 1H), 7.67 (d, J = 4.1 Hz, 2H), 7.52 (d, J = 7.7 Hz, 2H), 7.23 – 7.19 (m, 3H), 5.34 (t, J = 7.5 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.09 (s, 2H), 2.67 (q, J = 7.5 Hz, 2H), 1.94 (dd, J = 14.8, 7.4 Hz, 2H), 1.37 – 0.94 (m, 20H), 0.90 – 0.85 (m, 5H), 0.77 – 0.71 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.00, 168.96, 154.64, 148.40, 144.67, 139.26, 136.39, 132.24, 131.42, 130.09, 127.82, 124.20, 123.63, 61.14, 48.45, 32.04, 29.84, 29.75, 29.54, 29.52, 29.47, 29.28, 29.02, 28.78, 28.65, 22.82, 15.50, 14.29, 14.25 ppm.

HRMS (ESI$^+$): calcd for $C_{31}H_{45}N_2O_3^+$ $[M+H]^+$ 493.3425, found 493.3425.



ethyl (*E*)-*N*-picolinoyl-*N*-(1-(4-propylphenyl)tridec-1-en-1-yl)glycinate (4d)

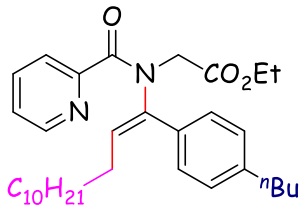
Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/9, v/v) afforded **4d** as pale yellow oil (35.0 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, J = 4.7 Hz, 1H), 7.68 – 7.66 (m, 2H), 7.50 (d, J = 8.1 Hz, 2H), 7.24 – 7.19 (m, 1H), 7.17 (d, J = 8.1 Hz, 2H), 5.35 (t, J = 7.5 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.10 (s, 2H), 2.64 – 2.54 (m, 2H), 1.94 (dd, J = 14.8, 7.5 Hz, 2H), 1.66 (dq, J = 14.8, 7.4 Hz, 2H), 1.34 – 1.00 (m, 17H), 0.96 (t, J = 7.2 Hz, 3H), 0.90 – 0.83 (m, 5H), 0.79 – 0.72 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.01, 168.98, 154.67, 148.42, 143.18, 139.33, 136.39, 132.29, 131.32,

129.99, 128.41, 124.19, 123.64, 61.16, 48.53, 38.01, 32.05, 29.85, 29.76, 29.56, 29.53, 29.48, 29.30, 29.03, 28.65, 24.56, 22.83, 14.30, 14.27, 14.07 ppm.

HRMS (ESI$^+$): calcd for $C_{32}H_{47}N_2O_3^+$ $[M+H]^+$ 507.3581, found 507.3582.



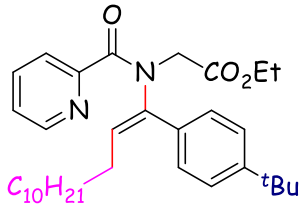
ethyl (*E*)-*N*-(1-(4-butylphenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (4e)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/10, v/v) afforded **4e** as pale yellow oil (36.5 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, J = 4.5 Hz, 1H), 7.66 (m, 2H), 7.49 (d, J = 7.8 Hz, 2H), 7.23 – 7.10 (m, 3H), 5.35 (t, J = 7.5 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.09 (s, 2H), 2.62 (t, J = 7.7 Hz, 2H), 1.94 (dd, J = 14.8, 7.4 Hz, 2H), 1.61 (dt, J = 15.2, 7.7 Hz, 2H), 1.44 – 0.66 (m, 29H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.99, 168.97, 154.67, 148.41, 143.39, 139.33, 136.38, 132.24, 131.31, 129.99, 128.35, 124.18, 123.62, 61.14, 48.52, 35.60, 33.63, 32.04, 29.84, 29.75, 29.54, 29.52, 29.47, 29.29, 29.02, 28.64, 22.82, 22.58, 14.29, 14.25, 14.10 ppm.

HRMS (ESI$^+$): calcd for $C_{33}H_{49}N_2O_3^+$ $[M+H]^+$ 521.3738, found 521.3740.



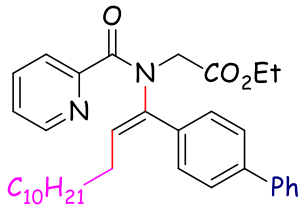
ethyl (*E*)-*N*-(1-(4-(*tert*-butyl)phenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (4f)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/10, v/v) afforded **4f** as pale yellow oil (38.7 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, J = 4.8 Hz, 1H), 7.72 – 7.60 (m, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.22 – 7.15 (m, 1H), 5.36 (t, J = 7.5 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.10 (s, 2H), 1.95 (dd, J = 14.8, 7.5 Hz, 2H), 1.41 – 0.95 (m, 26H), 0.95 – 0.68 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.00, 168.97, 154.68, 151.49, 148.44, 139.22, 136.34, 132.00, 131.45, 129.77, 125.24, 124.14, 123.59, 61.13, 48.52, 34.80, 32.04, 31.44, 29.84, 29.75, 29.55, 29.46, 29.33, 29.04, 28.65, 22.82, 14.30, 14.23 ppm.

HRMS (ESI^+): calcd for $C_{33}H_{49}N_2O_3^+$ $[M+H]^+$ 521.3738, found 521.3740.



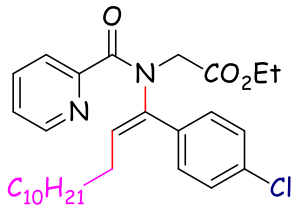
ethyl (*E*)-*N*-(1-([1,1'-biphenyl]-4-yl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (4g)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/9, v/v) afforded **4g** as brown oil (43.8 mg, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (d, J = 4.7 Hz, 1H), 7.70 (d, J = 8.1 Hz, 4H), 7.61 (t, J = 6.6 Hz, 4H), 7.46 (t, J = 7.5 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 7.27 – 7.19 (m, 1H), 5.43 (t, J = 7.5 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 4.15 (s, 2H), 2.00 (dd, J = 14.6, 7.4 Hz, 2H), 1.37 – 0.97 (m, 17H), 0.94 – 0.73 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.00, 168.90, 154.48, 148.35, 141.21, 140.68, 139.11, 136.46, 133.96, 131.98, 130.57, 128.95, 127.62, 127.16, 126.97, 124.30, 123.76, 61.18, 48.56, 32.01, 29.81, 29.73, 29.52, 29.50, 29.44, 29.25, 29.01, 28.69, 22.80, 14.28, 14.23 ppm.

HRMS (ESI^+): calcd for $C_{35}H_{45}N_2O_3^+$ $[M+H]^+$ 541.3425, found 541.3430.



ethyl (*E*)-*N*-(1-(4-chlorophenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (4h)

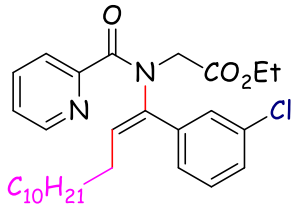
Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/8, v/v) afforded **4h** as pale yellow oil (34.9 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, J = 4.6 Hz, 1H), 7.70 (d, J = 4.6 Hz, 2H), 7.59 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.23 (dd, J = 8.8, 4.6 Hz, 1H), 5.38 (t, J = 7.5 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.07 (s,

2H), 1.90 (dd, *J* = 14.7, 7.4 Hz, 2H), 1.36 – 0.94 (m, 17H), 0.91 – 0.80 (m, 5H), 0.74 (dt, *J* = 14.2, 7.2 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.86, 168.75, 154.17, 148.17, 138.51, 136.58, 134.31, 133.52, 132.15, 131.59, 128.49, 124.46, 123.93, 61.23, 48.42, 32.01, 29.72, 29.71, 29.49, 29.44, 29.10, 28.94, 28.55, 22.80, 14.26, 14.24 ppm.

HRMS (ESI$^+$): calcd for $C_{29}H_{40}{}^{35}ClN_2O_3^+$ $[M+H]^+$ 499.2722, found 499.2728; $C_{29}H_{40}{}^{37}ClN_2O_3^+$ $[M+H]^+$ 501.2692, found 501.2695.



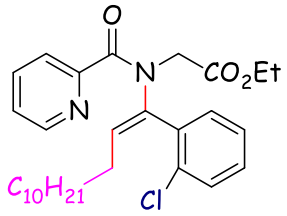
ethyl (*E*)-*N*-(1-(3-chlorophenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (4i)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/8, v/v) afforded **4i** as pale yellow oil (40.0 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, *J* = 4.7 Hz, 1H), 7.75 – 7.68 (m, 2H), 7.66 (s, 1H), 7.57 – 7.51 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.23 (m, 1H), 5.42 (t, *J* = 7.5 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.09 (s, 2H), 1.93 (dd, *J* = 14.6, 7.3 Hz, 2H), 1.36 – 0.96 (m, 17H), 0.92 – 0.82 (m, 5H), 0.77 (dt, *J* = 14.3, 7.2 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.83, 168.76, 154.05, 148.22, 138.34, 137.06, 136.59, 134.17, 132.59, 130.19, 129.55, 128.59, 128.43, 124.49, 123.95, 61.28, 48.49, 32.02, 29.72, 29.50, 29.45, 29.09, 28.93, 28.52, 22.81, 14.27, 14.26 ppm.

HRMS (ESI$^+$): calcd for $C_{29}H_{40}{}^{35}ClN_2O_3^+$ $[M+H]^+$ 499.2722, found 499.2728; $C_{29}H_{40}{}^{37}ClN_2O_3^+$ $[M+H]^+$ 501.2692, found 501.2698.



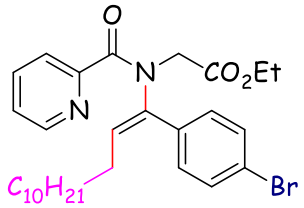
ethyl (*E*)-*N*-(1-(2-chlorophenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (4j)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/8, v/v) afforded **4j** as pale yellow oil (38.1 mg, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (d, J = 4.2 Hz, 1H), 8.29 (d, J = 7.4 Hz, 1H), 7.77 – 7.74 (m, 2H), 7.37 (d, J = 7.8 Hz, 1H), 7.33 – 7.27 (m, 3H), 5.45 (t, J = 7.7 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 4.11 (brs, 2H), 1.65 (brs, 2H), 1.35 – 0.92 (m, 17H), 0.88 (t, J = 6.7 Hz, 3H), 0.83 – 0.65 (m, 4H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.44, 168.79, 154.54, 148.07, 136.72, 134.68, 134.43, 134.01, 133.97, 132.78, 129.84, 129.32, 127.06, 124.41, 124.20, 61.20, 47.57, 32.04, 29.74, 29.52, 29.47, 29.43, 28.94, 28.45, 28.30, 22.83, 14.32, 14.28 ppm.

HRMS (ESI$^+$): calcd for $C_{29}H_{40}{}^{35}ClN_2O_3^+$ $[M+H]^+$ 499.2722, found 499.2727; $C_{29}H_{40}{}^{37}ClN_2O_3^+$ $[M+H]^+$ 501.2692, found 501.2699.



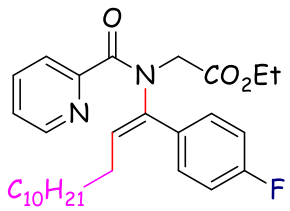
ethyl (*E*)-*N*-(1-(4-bromophenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (4k)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/8, v/v) afforded **4k** as pale yellow oil (40.2 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, J = 4.6 Hz, 1H), 7.70 (d, J = 4.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 7.23 (dd, J = 8.9, 4.5 Hz, 1H), 5.38 (t, J = 7.5 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.06 (s, 2H), 1.89 (dd, J = 14.6, 7.3 Hz, 2H), 1.35 – 0.95 (m, 17H), 0.93 – 0.79 (m, 5H), 0.77 – 0.70 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.84, 168.73, 154.14, 148.15, 138.55, 136.58, 133.98, 132.23, 131.89, 131.45, 124.47, 123.94, 122.60, 61.22, 48.41, 32.00, 29.71, 29.70, 29.48, 29.43, 29.08, 28.93, 28.55, 22.80, 14.25, 14.24 ppm.

HRMS (ESI$^+$): calcd for $C_{29}H_{40}{}^{79}BrN_2O_3^+$ $[M+H]^+$ 543.2217, found 543.2223; $C_{29}H_{40}{}^{81}BrN_2O_3^+$ $[M+H]^+$ 545.2196, found 545.2202.



ethyl (*E*)-*N*-(1-(4-fluorophenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (4l)

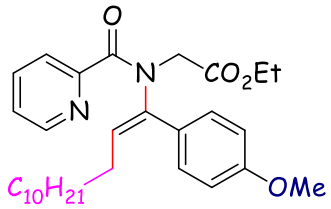
Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/8, v/v) afforded **4l** as pale yellow oil (30.4 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, J = 3.7 Hz, 1H), 7.72 – 7.61 (m, 2H), 7.66 – 7.59 (m, 2H), 7.25 – 7.19 (m, 1H), 7.05 (t, J = 8.3 Hz, 2H), 5.36 (t, J = 7.4 Hz, 1H), 4.19 (q, J = 6.9 Hz, 2H), 4.07 (s, 2H), 1.89 (dd, J = 14.5, 7.3 Hz, 2H), 1.35 – 0.92 (m, 17H), 0.88 – 0.85 (m, 5H), 0.78 – 0.71 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.86, 168.81, 162.70 (d, J = 248.2 Hz), 154.31, 148.18, 138.56, 136.56, 132.06 (d, J = 8.2 Hz), 131.56, 131.03 (d, J = 3.1 Hz), 124.41, 123.89, 115.23 (d, J = 21.5 Hz), 61.22, 48.40, 32.02, 29.72, 29.50, 29.46, 29.44, 29.13, 28.95, 28.52, 22.81, 14.27, 14.24 ppm.

^{19}F NMR (376 MHz, CDCl3): δ = -112.92 ppm.

HRMS (ESI^+): calcd for $C_{29}H_{40}FN_2O_3^+$ $[M+H]^+$ 483.3017, found 483.3018.



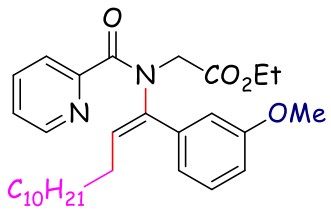
ethyl (*E*)-*N*-(1-(4-methoxyphenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (4m)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/5, v/v) afforded **4m** as yellow oil (31.7 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (d, J = 4.6 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.55 (d, J = 8.5 Hz, 2H), 7.24 – 7.17 (m, 1H), 6.90 (d, J = 8.6 Hz, 2H), 5.30 (t, J = 7.5 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.08 (s, 2H), 3.83 (s, 3H), 1.91 (dd, J = 14.7, 7.4 Hz, 2H), 1.35 – 0.95 (m, 17H), 0.89 – 0.82 (m, 5H), 0.77 – 0.69 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.95, 168.92, 159.67, 154.59, 148.31, 138.98, 136.39, 131.45, 130.71, 127.25, 124.21, 123.63, 113.63, 61.12, 55.38, 48.39, 32.02, 29.73, 29.51, 29.49, 29.45, 29.24, 28.99, 28.60, 22.80, 14.27, 14.24 ppm.

HRMS (ESI$^+$): calcd for $C_{30}H_{43}N_2O_4^+$ $[M+H]^+$ 495.3217, found 495.3218.



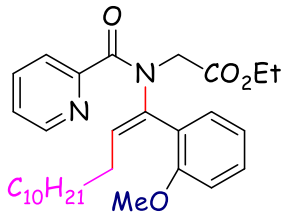
ethyl (*E*)-*N*-(1-(3-methoxyphenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (4n)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/5, v/v) afforded **4n** as yellow oil (36.1 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, J = 4.5 Hz, 1H), 7.68 – 7.67 (m, 2H), 7.28 (s, 1H), 7.27 – 7.18 (m, 2H), 7.13 (d, J = 7.5 Hz, 1H), 6.86 (d, J = 8.1 Hz, 1H), 5.37 (t, J = 7.5 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 4.09 (s, 2H), 3.81 (s, 3H), 1.93 (dd, J = 14.7, 7.3 Hz, 2H), 1.36 – 0.92 (m, 17H), 0.91 – 0.80 (m, 5H), 0.77 – 0.70 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.92, 168.90, 159.61, 154.53, 148.32, 139.24, 136.49, 136.45, 131.94, 129.19, 124.27, 123.77, 122.68, 115.47, 114.34, 61.16, 55.42, 48.46, 32.03, 29.83, 29.73, 29.53, 29.51, 29.45, 29.22, 29.01, 28.62, 22.81, 14.28, 14.24 ppm.

HRMS (ESI$^+$): calcd for $C_{30}H_{43}N_2O_4^+$ $[M+H]^+$ 495.3217, found 495.3218.



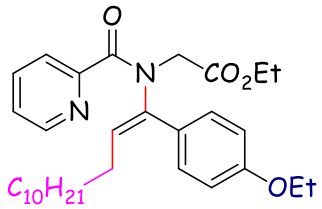
ethyl (*E*)-*N*-(1-(2-methoxyphenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (4o)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/5, v/v) afforded **4o** as yellow oil (35.2 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (d, J = 4.6 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.25 (d, J = 6.9 Hz, 1H), 7.23 – 7.18 (m, 1H), 6.86 (t, J = 7.6 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 5.49 (t, J = 7.5 Hz, 1H), 4.27 – 4.14 (m, 4H), 3.75 (s, 3H), 1.65 (d, J = 6.7 Hz, 2H), 1.36 – 0.93 (m, 18H), 0.88 – 0.84 (m, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.40, 169.18, 157.27, 154.89, 148.37, 136.23, 134.98, 132.28, 131.95, 129.78, 124.07, 123.95, 123.53, 120.43, 110.51, 61.05, 55.27, 49.09, 32.00, 29.72, 29.56, 29.47, 29.43, 29.02, 28.73, 28.51, 22.79, 14.31, 14.24 ppm.

HRMS (ESI^+): calcd for $C_{30}H_{43}N_2O_4^+$ $[M+H]^+$ 495.3217, found 495.3217.



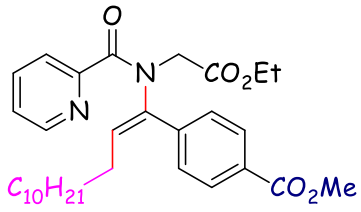
ethyl (*E*)-*N*-(1-(4-ethoxyphenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (4p)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/5, v/v) afforded **4p** as yellow oil (32.2 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (d, J = 4.4 Hz, 1H), 7.71 – 7.63 (m, 2H), 7.52 (d, J = 8.3 Hz, 2H), 7.21 (t, J = 5.6 Hz, 1H), 6.88 (d, J = 8.4 Hz, 2H), 5.29 (t, J = 7.4 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.09 (s, 2H), 4.05 (q, J = 7.1 Hz, 2H), 1.91 (dd, J = 14.7, 7.4 Hz, 2H), 1.42 (t, J = 6.9 Hz, 3H), 1.33 – 0.94 (m, 17H), 0.88 – 0.82 (m, 5H), 0.76 – 0.69 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.98, 168.96, 159.11, 154.67, 148.35, 139.07, 136.40, 131.44, 130.64, 127.12, 124.20, 123.63, 114.17, 63.57, 61.13, 48.44, 32.03, 29.83, 29.74, 29.53, 29.51, 29.46, 29.27, 29.01, 28.61, 22.82, 14.97, 14.28, 14.25 ppm.

HRMS (ESI^+): calcd for $C_{31}H_{45}N_2O_4^+$ $[M+H]^+$ 509.3374, found 509.3375.



methyl (*E*)-4-(1-(*N*-(2-ethoxy-2-oxoethyl)picolinamido)tridec-1-en-1-yl)benzoate (4q)

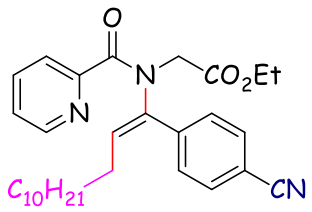
Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/6, v/v) afforded **4q** as yellow oil (41.9 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, J = 4.7 Hz, 1H), 8.02 (d, J = 7.9 Hz, 2H), 7.72 – 7.70 (m, 4H), 7.22

(dd, J = 8.9, 4.4 Hz, 1H), 5.47 (t, J = 7.6 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 4.07 (s, 2H), 3.92 (s, 3H), 1.93 (dd, J = 14.5, 7.3 Hz, 2H), 1.35 – 0.92 (m, 17H), 0.87 – 0.84 (m, 5H), 0.81 – 0.74 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.85, 168.71, 166.87, 154.00, 148.18, 139.78, 138.76, 136.59, 133.17, 130.15, 129.90, 129.49, 124.51, 123.95, 61.25, 52.31, 48.59, 31.99, 29.70, 29.68, 29.46, 29.42, 29.08, 28.92, 28.61, 22.78, 14.23 ppm.

HRMS (ESI$^+$): calcd for $C_{31}H_{43}N_2O_5^+$ $[M+H]^+$ 523.3166, found 523.3170.



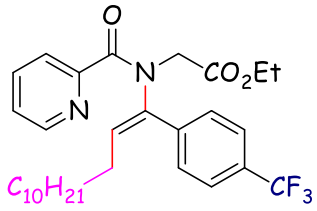
ethyl (*E*)-*N*-(1-(4-cyanophenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (4r)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/6, v/v) afforded **4r** as yellow oil (41.0 mg, 84% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, J = 4.7 Hz, 1H), 7.79 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 3.8 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H), 7.24 (dd, J = 8.6, 4.9 Hz, 1H), 5.50 (t, J = 7.6 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.05 (s, 2H), 1.92 (dd, J = 14.5, 7.3 Hz, 2H), 1.33 – 0.94 (m, 17H), 0.88 – 0.75 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.75, 168.58, 153.70, 148.08, 140.00, 138.31, 136.75, 133.93, 132.03, 130.92, 124.72, 124.20, 118.83, 111.96, 61.34, 48.63, 32.00, 29.70, 29.68, 29.46, 29.42, 29.02, 28.90, 28.61, 22.79, 14.25, 14.23 ppm.

HRMS (ESI$^+$): calcd for $C_{30}H_{40}N_3O_3^+$ $[M+H]^+$ 490.3064, found 490.3064.



ethyl (*E*)-*N*-picolinoyl-*N*-(1-(4-(trifluoromethyl)phenyl)tridec-1-en-1-yl)glycinate (4s)

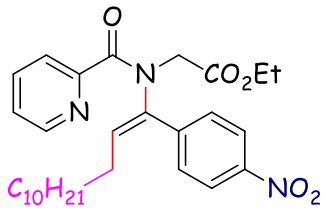
Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/8, v/v) afforded **4s** as yellow oil (37.3 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, *J* = 4.4 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 3.7 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.24 (dd, *J* = 8.4, 4.5 Hz, 1H), 5.48 (t, *J* = 7.6 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.07 (s, 2H), 1.93 (dd, *J* = 14.6, 7.3 Hz, 2H), 1.37 – 0.94 (m, 17H), 0.92 – 0.68 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.88, 168.74, 154.05, 148.19, 138.88, 138.51, 136.69, 133.27, 130.64, 130.35 (q, *J* = 32.5 Hz), 125.24 (q, *J* = 3.7 Hz), 124.61, 124.12, 124.21 (d, *J* = 271.8 Hz), 61.31, 48.52, 32.04, 29.85, 29.74, 29.73, 29.51, 29.46, 29.11, 28.97, 28.60, 22.83, 14.28, 14.25 ppm.

^{19}F NMR (376 MHz, CDCl3): δ = -62.66 ppm.

HRMS (ESI^+): calcd for $C_{30}H_{40}F_3N_2O_3^+$ $[M+H]^+$ 533.2986, found 533.2990.



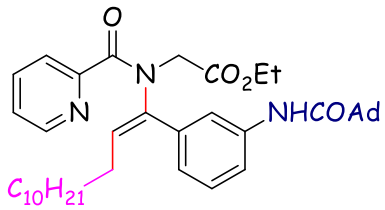
ethyl (*E*)-*N*-(1-(4-nitrophenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (4t)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/6, v/v) afforded **4t** as brown oil (30.0 mg, 59% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (d, *J* = 4.6 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.78 – 7.69 (m, 2H), 7.27 – 7.24 (m, 1H), 5.55 (t, *J* = 7.6 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.07 (s, 2H), 1.95 (dd, *J* = 14.3, 7.1 Hz, 2H), 1.36 – 0.95 (m, 17H), 0.88 – 0.79 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.74, 168.59, 153.69, 148.11, 147.66, 142.00, 138.16, 136.82, 134.47, 131.21, 124.82, 124.32, 123.51, 61.40, 48.71, 32.03, 29.84, 29.73, 29.71, 29.49, 29.44, 29.03, 28.95, 28.72, 22.81, 14.28, 14.24ppm.

HRMS (ESI^+): calcd for $C_{29}H_{40}N_3O_5^+$ $[M+H]^+$ 510.2962, found 510.2964.



ethyl *N*-((*E*)-1-(3-((3*s*)-adamantane-1-carboxamido)phenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate

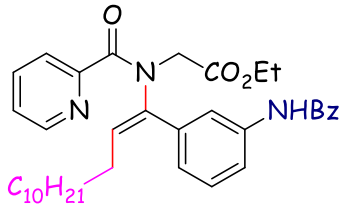
(**4u**)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/4, v/v) afforded **4u** as pale yellow oil (40.4 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, *J* = 4.5 Hz, 1H), 7.73 (d, *J* = 5.3 Hz, 1H), 7.71 – 7.62 (m, 3H), 7.43 (s, 1H), 7.30 (d, *J* = 4.5 Hz, 2H), 7.22 (dd, *J* = 8.8, 4.3 Hz, 1H), 5.37 (t, *J* = 7.5 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.06 (s, 2H), 2.09 (s, 3H), 2.01 – 1.87 (m, 8H), 1.83 – 1.65 (m, 6H), 1.35 – 0.93 (m, 17H), 0.91 – 0.66 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.33, 169.90, 168.80, 154.36, 148.33, 138.74, 138.21, 136.53, 135.62, 132.38, 128.86, 126.00, 124.32, 123.76, 121.25, 120.37, 61.18, 48.36, 41.61, 39.33, 36.50, 32.01, 29.73, 29.71, 29.51, 29.44, 29.14, 28.94, 28.56, 28.21, 22.80, 14.25 ppm.

HRMS (ESI^+): calcd for $C_{40}H_{56}N_3O_4^+$ $[M+H]^+$ 642.4265, found 642.4265.



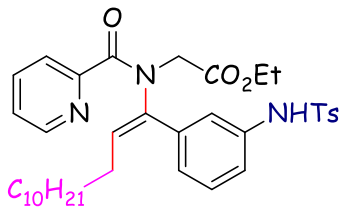
ethyl (*E*)-*N*-(1-(3-benzamidophenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (**4v**)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/3, v/v) afforded **4v** as yellow oil (40.3 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (d, *J* = 8.1 Hz, 1H), 8.43 (d, *J* = 4.6 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 3H), 7.84 (s, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.23 – 7.16 (m, 1H), 5.38 (t, *J* = 7.5 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.05 (s, 2H), 1.96 (dd, *J* = 14.7, 7.4 Hz, 2H), 1.33 – 0.94 (m, 17H), 0.91 – 0.65 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.94, 168.79, 166.10, 154.20, 148.36, 138.64, 138.47, 136.48, 135.55, 134.92, 132.60, 131.91, 128.88, 128.78, 127.35, 126.24, 124.32, 123.60, 121.46, 120.62, 61.20, 48.35, 31.99, 29.70, 29.69, 29.48, 29.42, 29.13, 28.93, 28.58, 22.78, 14.23, 14.22 ppm.

HRMS (ESI^+): calcd for $C_{36}H_{46}N_3O_4^+$ $[M+H]^+$ 584.3483, found 584.3484.



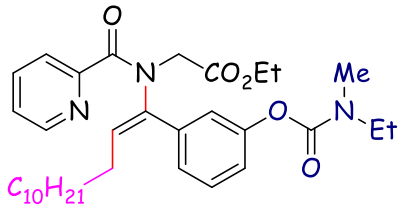
ethyl (*E*)-*N*-(1-(3-((4-methylphenyl)sulfonamido)phenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (4w)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/4, v/v) afforded **4w** as pale yellow oil (33.6 mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (d, *J* = 4.6 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 3H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 3.9 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 3H), 7.24 (d, *J* = 4.5 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 1H), 5.39 (t, *J* = 7.5 Hz, 1H), 4.20 (q, *J* = 7.0 Hz, 2H), 3.95 (s, 2H), 2.43 (s, 4H), 1.83 (dd, *J* = 14.4, 7.2 Hz, 2H), 1.34 – 0.94 (m, 17H), 0.92 – 0.65 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.78, 168.72, 153.86, 148.16, 145.18, 138.06, 136.73, 136.60, 136.30, 134.39, 133.50, 133.16, 131.85, 131.42, 129.72, 129.01, 128.64, 124.57, 123.93, 61.28, 48.26, 32.02, 29.74, 29.55, 29.52, 29.46, 29.06, 28.89, 28.46, 22.81, 21.82, 14.28, 14.26 ppm.

HRMS (ESI^+): calcd for $C_{36}H_{48}N_3O_5S^+$ $[M+H]^+$ 634.3309, found 634.3304.



ethyl (*E*)-*N*-(1-(3-((ethyl(methyl)carbamoyl)oxy)phenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (4x)

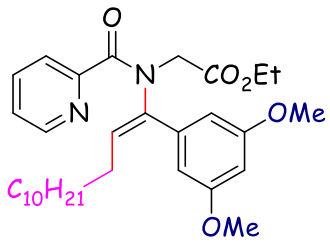
Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/4, v/v) afforded **4x** as yellow oil (40.9 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 4.7 Hz, 1H), 7.68 (d, *J* = 3.8 Hz, 2H), 7.44 – 7.36 (m, 2H), 7.35 – 7.30 (m, 1H), 7.21 (dd, *J* = 9.0, 4.5 Hz, 1H), 7.09 (d, *J* = 7.9 Hz, 1H), 5.39 (t, *J* = 7.5 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.09 (s, 2H), 3.43 (dq, *J* = 20.7, 6.6 Hz, 3H), 3.02 (d, *J* = 32.9 Hz, 3H), 1.94 (dd, *J* = 14.7, 7.4 Hz, 2H), 1.35 – 0.94 (m, 20H), 0.91 – 0.66 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.90, 168.81, 154.41 (d, *J* = 18.3 Hz), 154.28, 151.49, 148.30, 138.60, 136.43, 132.42, 128.91, 126.90, 124.28, 123.69, 123.24, 121.98, 61.09, 48.41, 44.18, 34.12 (d, *J* = 41.1 Hz),

31.97, 29.68, 29.46, 29.39, 29.13, 28.90, 28.52, 22.75, 14.20, 14.18, 12.93 (d, J = 78.7 Hz) ppm.

HRMS (ESI$^+$): calcd for $C_{33}H_{48}N_3O_5^+$ $[M+H]^+$ 566.3588, found 566.3588.



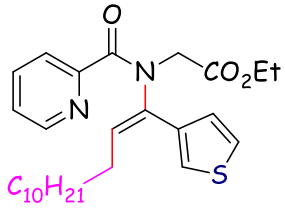
ethyl (*E*)-*N*-(1-(3,5-dimethoxyphenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (4y)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/5, v/v) afforded **4y** as pale yellow oil (35.4 mg, 67% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, J = 4.6 Hz, 1H), 7.69 (d, J = 3.5 Hz, 2H), 7.22 (dd, J = 8.8, 4.6 Hz, 1H), 6.84 (s, 2H), 6.43 (s, 1H), 5.35 (t, J = 7.5 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.09 (s, 2H), 3.80 (s, 6H), 1.94 (dd, J = 14.7, 7.4 Hz, 2H), 1.36 – 0.94 (m, 17H), 0.92 – 0.68 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.88, 168.88, 160.54, 154.38, 148.28, 139.12, 136.99, 136.45, 132.04, 124.28, 123.73, 108.16, 100.63, 61.16, 55.51, 48.33, 32.01, 29.71, 29.51, 29.44, 29.19, 28.98, 28.63, 22.80, 14.26, 14.24 ppm.

HRMS (ESI$^+$): calcd for $C_{31}H_{45}N_2O_5^+$ $[M+H]^+$ 525.3323, found 525.3326.



ethyl (*E*)-*N*-picolinoyl-*N*-(1-(thiophen-3-yl)tridec-1-en-1-yl)glycinate (4z)

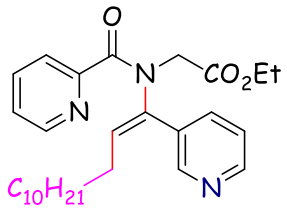
Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/8, v/v) afforded **4z** as pale yellow oil (30.7 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (d, J = 4.6 Hz, 1H), 7.69 – 7.62 (m, 2H), 7.49 (d, J = 1.1 Hz, 1H), 7.31 (d, J = 5.0 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.24 – 7.17 (m, 1H), 5.38 (t, J = 7.4 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 4.15 (s, 2H), 1.97 (dd, J = 13.7, 6.8 Hz, 2H), 1.35 – 0.95 (m, 17H), 0.88 – 0.85 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.77, 168.91, 154.28, 148.39, 136.66, 136.39, 134.97, 131.85, 128.93,

126.16, 125.19, 124.28, 123.47, 61.22, 48.75, 32.02, 29.73, 29.52, 29.50, 29.45, 29.12, 28.98, 28.50, 22.81, 14.27, 14.26 ppm.

HRMS (ESI$^+$): calcd for $C_{27}H_{39}N_2O_3S^+$ $[M+H]^+$ 471.2676, found 471.2676.



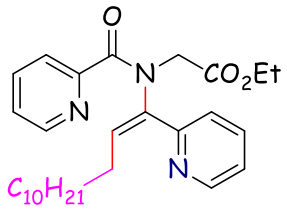
ethyl (*E*)-*N*-picolinoyl-*N*-(1-(pyridin-3-yl)tridec-1-en-1-yl)glycinate (4aa)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/3, v/v) afforded **4aa** as brown oil (28.1 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.71 (s, 1H), 8.54 (d, J = 4.5 Hz, 1H), 8.42 (d, J = 4.7 Hz, 1H), 8.17 (d, J = 7.9 Hz, 1H), 7.76 – 7.67 (m, 2H), 7.33 (dd, J = 7.6, 5.1 Hz, 1H), 7.26 – 7.20 (m, 1H), 5.48 (t, J = 7.6 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 4.07 (s, 2H), 1.92 (dd, J = 14.3, 7.2 Hz, 2H), 1.36 – 0.93 (m, 17H), 0.89 – 0.70 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.78, 168.61, 153.79, 151.23, 149.44, 148.09, 137.69, 136.73, 136.68, 133.36, 131.14, 124.64, 124.12, 123.43, 61.30, 48.44, 31.98, 29.68, 29.67, 29.45, 29.41, 29.04, 28.88, 28.48, 22.78, 14.23 ppm.

HRMS (ESI$^+$): calcd for $C_{28}H_{40}N_3O_3^+$ $[M+H]^+$ 466.3064, found 466.3064.



ethyl (*E*)-*N*-picolinoyl-*N*-(1-(pyridin-2-yl)tridec-1-en-1-yl)glycinate (4ab)

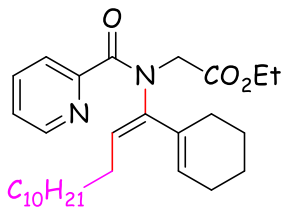
Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/3, v/v) afforded **4ab** as brown oil (18.8mg, 40% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.61 (d, J = 4.8 Hz, 1H), 8.44 (d, J = 4.7 Hz, 1H), 7.82 – 7.63 (m, 4H), 7.24 – 7.17 (m, 2H), 5.67 (t, J = 7.6 Hz, 1H), 4.25 – 4.15 (m, 4H), 2.15 (dd, J = 14.4, 7.2 Hz, 2H), 1.34 – 0.95 (m,

17H), 0.92 – 0.73 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.89, 168.67, 154.44, 154.17, 149.14, 148.42, 138.43, 136.44, 136.43, 136.41, 124.90, 124.37, 123.64, 122.76, 61.22, 49.00, 32.01, 29.72, 29.50, 29.45, 29.44, 28.97, 28.24, 22.80, 14.25 ppm.

HRMS (ESI^+): calcd for $C_{28}H_{40}N_3O_3^+$ $[M+H]^+$ 466.3064, found 466.3064.



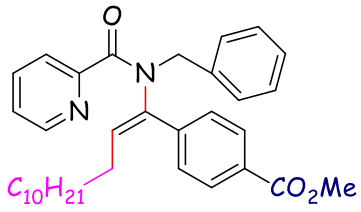
ethyl (*E*)-*N*-(1-(cyclohex-1-en-1-yl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (4ac)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/8, v/v) afforded **4ac** as pale yellow oil (24.9 mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (d, J = 4.3 Hz, 1H), 7.68 (t, J = 7.7 Hz, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.24 – 7.19 (m, 1H), 5.65 (brs, 1H), 5.08 (t, J = 7.5 Hz, 1H), 4.24 – 4.19 (m, 4H), 2.21 (brs, 2H), 2.05 (brs, 2H), 1.86 (dd, J = 14.5, 7.2 Hz, 2H), 1.68 – 1.51 (m, 4H), 1.36 – 0.98 (m, 17H), 0.94 – 0.75 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.87, 169.02, 154.88, 148.41, 141.67, 136.22, 132.22, 132.03, 129.98, 123.95, 123.55, 61.18, 48.25, 32.04, 29.80, 29.77, 29.60, 29.53, 29.48, 29.43, 29.07, 28.46, 27.05, 25.65, 22.83, 22.79, 22.18, 14.32, 14.27 ppm.

HRMS (ESI^+): calcd for $C_{29}H_{45}N_2O_3^+$ $[M+H]^+$ 469.3425, found 469.3426.



methyl (*E*)-4-(1-(*N*-benzylpicolinamido)tridec-1-en-1-yl)benzoate (5a)

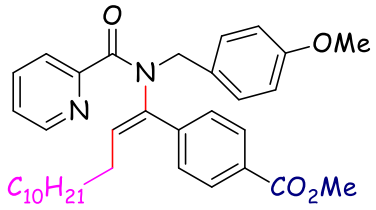
Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/8, v/v) afforded **5a** as pale yellow oil (36.5 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, J = 4.5 Hz, 1H), 8.04 (d, J = 7.7 Hz, 2H), 7.70 – 7.65 (m, 2H), 7.61

(d, J = 8.1 Hz, 2H), 7.33 – 7.18 (m, 6H), 5.02 (t, J = 7.6 Hz, 1H), 4.64 (brs, 2H), 3.94 (s, 3H), 1.80 (dd, J = 14.7, 7.4 Hz, 2H), 1.37 – 0.92 (m, 14H), 0.88 (t, J = 6.6 Hz, 3H), 0.80 (dt, J = 14.2, 7.1 Hz, 2H), 0.68 (dt, J = 14.2, 7.1 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.63, 166.95, 155.03, 148.26, 140.17, 138.11, 137.06, 136.51, 133.64, 130.09, 129.80, 129.52, 129.16, 128.41, 127.45, 124.19, 123.64, 52.33, 49.77, 32.01, 29.72, 29.69, 29.48, 29.44, 29.42, 29.05, 28.91, 28.44, 22.81, 14.25 ppm.

HRMS (ESI$^+$): calcd for $C_{34}H_{43}N_2O_3^+$ $[M+H]^+$ 527.3268, found 527.3273.



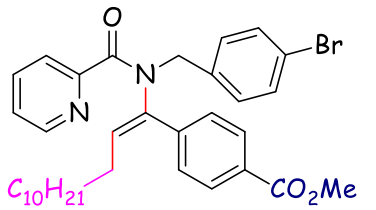
methyl (*E*)-4-(1-(*N*-(4-methoxybenzyl)picolinamido)tridec-1-en-1-yl)benzoate (5b)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/6, v/v) afforded **5b** as yellow oil (34.2 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (d, J = 4.6 Hz, 1H), 8.03 (d, J = 8.1 Hz, 2H), 7.66 (t, J = 7.6 Hz, 1H), 7.63 – 7.53 (m, 3H), 7.21 – 7.17 (m, 3H), 6.81 (d, J = 8.4 Hz, 2H), 4.99 (t, J = 7.6 Hz, 1H), 4.57 (brs, 2H), 3.93 (s, 3H), 3.78 (s, 3H), 1.81 (dd, J = 14.7, 7.4 Hz, 2H), 1.37 – 0.91 (m, 14H), 0.86 (t, J = 6.8 Hz, 3H), 0.79 (dt, J = 14.1, 7.0 Hz, 2H), 0.68 (dt, J = 14.7, 7.4 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.54, 166.93, 158.90, 155.08, 148.23, 140.22, 138.01, 136.47, 133.67, 130.53, 130.07, 129.74, 129.49, 129.22, 124.14, 123.57, 113.69, 55.29, 52.32, 49.10, 32.00, 29.70, 29.47, 29.42, 29.39, 29.05, 28.91, 28.45, 22.79, 14.24 ppm.

HRMS (ESI$^+$): calcd for $C_{35}H_{45}N_2O_4^+$ $[M+H]^+$ 557.3374, found 557.3374.



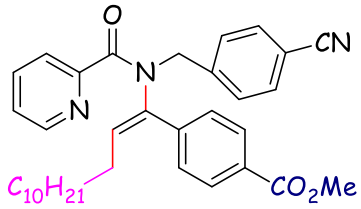
methyl (*E*)-4-(1-(*N*-(4-bromobenzyl)picolinamido)tridec-1-en-1-yl)benzoate (5c)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/8, v/v) afforded **5c** as pale yellow oil (44.9 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (d, *J* = 4.4 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 2H), 7.73 – 7.58 (m, 4H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.25 – 7.19 (m, 1H), 7.13 (d, *J* = 8.1 Hz, 2H), 4.97 (t, *J* = 7.6 Hz, 1H), 4.55 (brs, 2H), 3.94 (s, 3H), 1.81 (dd, *J* = 14.7, 7.4 Hz, 2H), 1.31 – 0.91 (m, 14H), 0.87 (t, *J* = 6.7 Hz, 3H), 0.79 (dt, *J* = 14.2, 7.1 Hz, 2H), 0.66 (dt, *J* = 14.1, 7.2 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.68, 166.89, 154.73, 148.29, 139.90, 138.03, 136.57, 136.08, 133.75, 131.54, 130.93, 130.10, 129.97, 129.61, 124.34, 123.70, 121.50, 52.37, 49.08, 32.01, 29.71, 29.49, 29.44, 29.04, 28.92, 28.44, 22.81, 14.26 ppm.

HRMS (ESI$^+$): calcd for $C_{34}H_{42}{}^{79}BrN_2O_3^+$ $[M+H]^+$ 605.2373, found 605.2378; $C_{34}H_{42}{}^{81}BrN_2O_3^+$ $[M+H]^+$ 607.2353, found 607.2360.



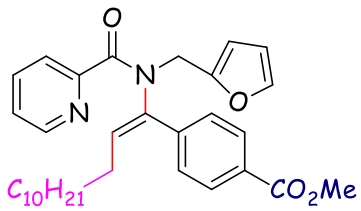
methyl (*E*)-4-(1-(*N*-(4-cyanobenzyl)picolinamido)tridec-1-en-1-yl)benzoate (5d)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/5, v/v) afforded **5d** as pale yellow oil (37.0 mg, 67% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, *J* = 4.4 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 2H), 7.74 – 7.61 (m, 4H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.28 – 7.20 (m, 1H), 4.98 (t, *J* = 7.6 Hz, 1H), 4.63 (brs, 2H), 3.93 (s, 3H), 1.80 (dd, *J* = 14.6, 7.3 Hz, 2H), 1.34 – 0.91 (m, 14H), 0.85 (t, *J* = 6.7 Hz, 3H), 0.78 (dt, *J* = 13.9, 7.0 Hz, 2H), 0.66 (dt, *J* = 14.3, 7.3 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.78, 166.76, 154.30, 148.30, 142.48, 139.58, 138.22, 136.65, 133.57, 132.26, 130.11, 130.05, 129.65, 129.59, 124.53, 123.76, 118.87, 111.30, 52.37, 49.49, 31.96, 29.66, 29.64, 29.44, 29.39, 29.35, 28.96, 28.86, 28.41, 22.76, 14.22 ppm.

HRMS (ESI$^+$): calcd for $C_{35}H_{42}N_3O_3^+$ $[M+H]^+$ 552.3221, found 552.3226.



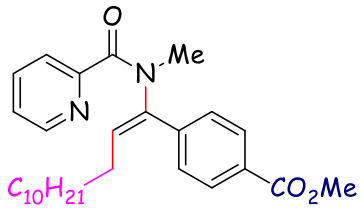
methyl (*E*)-4-(1-(*N*-(furan-2-ylmethyl)picolinamido)tridec-1-en-1-yl)benzoate (5e)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/6, v/v) afforded **5e** as yellow oil (31.6 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, J = 4.4 Hz, 1H), 8.01 (d, J = 7.9 Hz, 2H), 7.69 – 7.53 (m, 4H), 7.33 (s, 1H), 7.21 – 7.19 (m, 1H), 6.27 (d, J = 1.6 Hz, 1H), 6.18 (s, 1H), 5.14 (t, J = 7.6 Hz, 1H), 4.66 (brs, 2H), 3.92 (s, 3H), 1.85 (dd, J = 14.4, 7.2 Hz, 2H), 1.35 – 0.93 (m, 14H), 0.88 – 0.74 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.36, 166.94, 154.69, 150.68, 148.16, 142.23, 140.20, 138.32, 136.52, 132.94, 129.99, 129.70, 129.42, 124.28, 123.78, 110.34, 109.25, 52.31, 42.80, 32.00, 29.71, 29.69, 29.50, 29.43, 29.09, 28.92, 28.44, 22.80, 14.25 ppm.

HRMS (ESI^+): calcd for $C_{32}H_{41}N_2O_4^+$ $[M+H]^+$ 517.3061, found 517.3065.



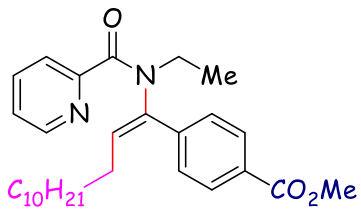
methyl (*E*)-4-(1-(*N*-methylpicolinamido)tridec-1-en-1-yl)benzoate (5f)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/6, v/v) afforded **5f** as pale yellow oil (29.4 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, J = 4.3 Hz, 1H), 8.02 (d, J = 8.4 Hz, 2H), 7.69 – 7.53 (m, 4H), 7.23 – 7.15 (m, 1H), 5.28 (t, J = 7.5 Hz, 1H), 3.92 (s, 3H), 3.06 (s, 3H), 1.91 (dd, J = 14.4, 7.2 Hz, 2H), 1.36 – 0.96 (m, 14H), 0.88 – 0.78 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.78, 166.90, 154.92, 148.25, 140.38, 140.30, 136.50, 131.32, 129.76, 129.72, 129.52, 124.15, 123.45, 52.32, 35.27, 32.01, 29.72, 29.70, 29.51, 29.44, 29.20, 28.98, 28.45, 22.80, 14.25 ppm.

HRMS (ESI^+): calcd for $C_{28}H_{39}N_2O_3^+$ $[M+H]^+$ 451.2955, found 451.2956.



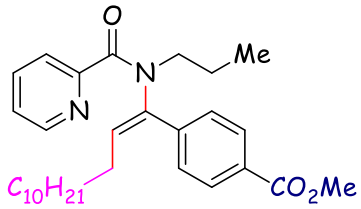
methyl (*E*)-4-(1-(*N*-ethylpicolinamido)tridec-1-en-1-yl)benzoate (5g)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/6, v/v) afforded **5g** as pale yellow oil (30.7 mg, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, J = 4.6 Hz, 1H), 8.03 (d, J = 8.2 Hz, 2H), 7.72 – 7.57 (m, 4H), 7.23 – 7.16 (m, 1H), 5.20 (t, J = 7.6 Hz, 1H), 3.93 (s, 3H), 3.47 (brs, 2H), 1.91 (dd, J = 14.7, 7.4 Hz, 2H), 1.36 – 0.95 (m, 17H), 0.93 – 0.67 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.29, 166.96, 155.37, 148.27, 140.42, 138.53, 136.47, 132.74, 130.04, 129.88, 129.50, 124.07, 123.49, 52.30, 41.13, 32.03, 29.83, 29.73, 29.72, 29.51, 29.45, 29.21, 29.00, 28.59, 22.81, 14.23, 12.49 ppm.

HRMS (ESI^+): calcd for $C_{29}H_{41}N_2O_3^+$ $[M+H]^+$ 465.3112, found 465.3113.



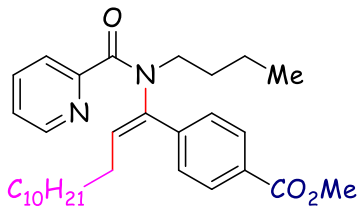
methyl (*E*)-4-(1-(*N*-propylpicolinamido)tridec-1-en-1-yl)benzoate (5h)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/7, v/v) afforded **5h** as pale yellow oil (29.7 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, J = 2.4 Hz, 1H), 8.04 (d, J = 8.0 Hz, 2H), 7.73 – 7.56 (m, 4H), 7.23 – 7.16 (m, 1H), 5.20 (t, J = 7.6 Hz, 1H), 3.93 (s, 3H), 3.35 (brs, 2H), 1.89 (dd, J = 14.7, 7.4 Hz, 2H), 1.58 (dq, J = 14.8, 7.3 Hz, 2H), 1.33 – 0.95 (m, 15H), 0.87 (t, J = 6.2 Hz, 7H), 0.75 (dd, J = 14.4, 7.4 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.49, 166.96, 155.43, 148.24, 140.27, 138.69, 136.46, 132.63, 130.01, 129.82, 129.49, 124.01, 123.45, 52.33, 47.61, 32.03, 29.73, 29.71, 29.51, 29.45, 29.19, 29.00, 28.56, 22.82, 20.70, 14.26, 11.45 ppm.

HRMS (ESI$^+$): calcd for $C_{30}H_{43}N_2O_3^+$ $[M+H]^+$ 479.3268, found 479.3269.



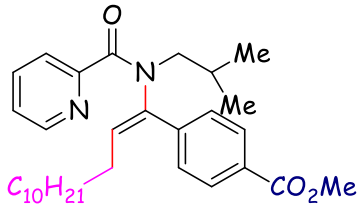
methyl (*E*)-4-(1-(*N*-butylpicolinamido)tridec-1-en-1-yl)benzoate (5i)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/8, v/v) afforded **5i** as pale yellow oil (29.1 mg, 59% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, J = 3.0 Hz, 1H), 8.04 (d, J = 8.1 Hz, 2H), 7.72 – 7.56 (m, 4H), 7.23 – 7.16 (m, 1H), 5.19 (t, J = 7.5 Hz, 1H), 3.93 (s, 3H), 3.38 (brs, 2H), 1.90 (dd, J = 14.7, 7.4 Hz, 2H), 1.54 (dt, J = 15.2, 7.7 Hz, 2H), 1.37 – 0.95 (m, 17H), 0.89 – 0.85 (m, 7H), 0.78 – 0.73 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.45, 166.97, 155.43, 148.24, 140.30, 138.70, 136.47, 132.64, 130.01, 129.81, 129.49, 124.02, 123.44, 52.33, 45.83, 32.03, 29.74, 29.72, 29.52, 29.50, 29.46, 29.19, 29.01, 28.56, 22.82, 20.22, 14.26, 13.99 ppm.

HRMS (ESI$^+$): calcd for $C_{31}H_{45}N_2O_3^+$ $[M+H]^+$ 493.3425, found 493.3427.



methyl (*E*)-4-(1-(*N*-isobutylpicolinamido)tridec-1-en-1-yl)benzoate (5j)

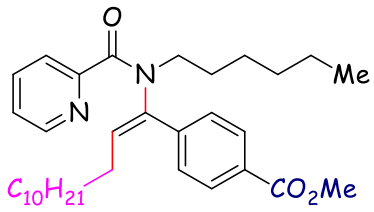
Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/9, v/v) afforded **5j** as pale yellow oil (29.6 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (d, J = 4.6 Hz, 1H), 8.05 (d, J = 8.1 Hz, 2H), 7.69 – 7.67 (m, 3H), 7.61 (d, J = 7.7 Hz, 1H), 7.23 – 7.17 (m, 1H), 5.22 (t, J = 7.6 Hz, 1H), 3.93 (s, 3H), 3.25 (brs, 2H), 1.98 – 1.79 (m, 3H), 1.38 – 0.96 (m, 15H), 0.92 – 0.79 (m, 10H), 0.70 (dt, J = 14.7, 7.5 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.86, 166.98, 155.76, 148.27, 140.08, 138.85, 136.46, 132.71, 130.06, 129.90, 129.53, 123.90, 123.40, 52.31, 52.25, 32.02, 29.83, 29.72, 29.70, 29.50, 29.44, 29.14, 29.04, 28.52,

27.29, 22.81, 20.31, 14.24 ppm.

HRMS (ESI$^+$): calcd for $C_{31}H_{45}N_2O_3^+$ $[M+H]^+$ 493.3425, found 493.3427.



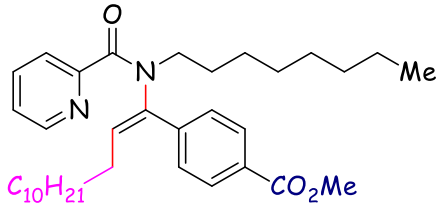
methyl (*E*)-4-(1-(*N*-hexylpicolinamido)tridec-1-en-1-yl)benzoate (5k)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/10, v/v) afforded **5k** as pale yellow oil (29.7 mg, 57% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (brs, 1H), 8.04 (d, J = 7.8 Hz, 2H), 7.69 – 7.62 (m, 4H), 7.20 (brs, 1H), 5.19 (t, J = 7.5 Hz, 1H), 3.93 (s, 3H), 3.38 (brs, 2H), 1.90 (dd, J = 14.4, 7.2 Hz, 2H), 1.55 – 1.54 (m, 2H), 1.35 – 0.95 (m, 21H), 0.89 – 0.73 (m, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.42, 166.96, 155.38, 148.23, 140.28, 138.65, 136.49, 132.64, 129.98, 129.79, 129.48, 124.02, 123.43, 52.33, 46.09, 32.02, 31.62, 29.73, 29.71, 29.51, 29.45, 29.40, 29.18, 29.00, 28.55, 27.28, 26.61, 22.81, 22.65, 14.26, 14.15 ppm.

HRMS (ESI$^+$): calcd for $C_{33}H_{49}N_2O_3^+$ $[M+H]^+$ 521.3738, found 521.3740.



methyl (*E*)-4-(1-(*N*-octylpicolinamido)tridec-1-en-1-yl)benzoate (5l)

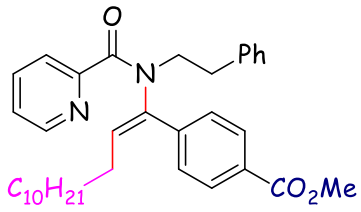
Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/10, v/v) afforded **5l** as pale yellow oil (29.7 mg, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, J = 4.5 Hz, 1H), 8.04 (d, J = 8.4 Hz, 2H), 7.69 – 7.65 (m, 3H), 7.61 (d, J = 7.7 Hz, 1H), 7.23 – 7.16 (m, 1H), 5.20 (t, J = 7.6 Hz, 1H), 3.93 (s, 3H), 3.38 (brs, 2H), 1.90 (q, J = 7.5 Hz, 2H), 1.59 – 1.49 (m, 2H), 1.36 – 0.94 (m, 24H), 0.95 – 0.68 (m, 10H)ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.44, 166.99, 155.50, 148.26, 140.36, 138.78, 136.48, 132.60, 130.04,

129.85, 129.51, 124.02, 123.48, 52.33, 46.11, 32.04, 31.93, 29.85, 29.75, 29.74, 29.54, 29.47, 29.40, 29.31, 29.21, 29.03, 28.57, 27.35, 26.96, 22.83, 22.78, 14.26, 14.24 ppm.

HRMS (ESI$^+$): calcd for $C_{35}H_{53}N_2O_3^+$ $[M+H]^+$ 549.4051, found 549.4049.



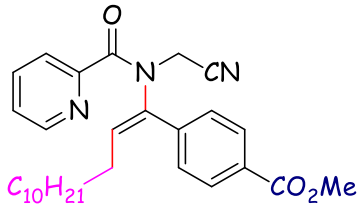
methyl (*E*)-4-(1-(*N*-phenethylpicolinamido)tridec-1-en-1-yl)benzoate (5m)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/8, v/v) afforded **5m** as pale yellow oil (38.1 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (brs, 1H), 8.11 – 7.98 (m, 2H), 7.69 – 7.66 (m, 4H), 7.43 – 7.01 (m, 6H), 5.15 (t, J = 7.3 Hz, 1H), 3.94 (s, 3H), 3.63 (brs, 2H), 2.94 (t, J = 7.2 Hz, 2H), 1.88 (d, J = 6.8 Hz, 2H), 1.43 – 0.67 (m, 21H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.42, 166.85, 155.03, 148.21, 140.15, 138.94, 138.65, 136.49, 132.78, 129.93, 129.84, 129.50, 128.93, 128.44, 126.33, 124.12, 123.46, 52.26, 47.83, 33.72, 31.97, 29.67, 29.53, 29.45, 29.39, 29.09, 28.92, 28.47, 22.76, 14.20 ppm.

HRMS (ESI$^+$): calcd for $C_{35}H_{45}N_2O_3^+$ $[M+H]^+$ 541.3425, found 541.3431.



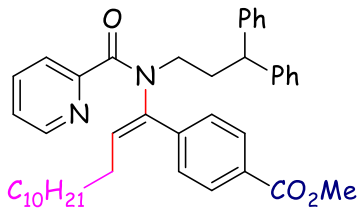
methyl (*E*)-4-(1-(*N*-(cyanomethyl)picolinamido)tridec-1-en-1-yl)benzoate (5n)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/6, v/v) afforded **5n** as pale yellow oil (31.5 mg, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (d, J = 4.2 Hz, 1H), 8.07 (d, J = 8.0 Hz, 2H), 7.82 – 7.70 (m, 4H), 7.30 (m, 1H), 5.38 (t, J = 7.5 Hz, 1H), 4.29 (brs, 2H), 3.93 (s, 3H), 1.99 (d, J = 6.4 Hz, 2H), 1.37 – 0.92 (m, 14H), 0.88 – 0.83 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.32, 166.74, 152.64, 148.32, 138.64, 137.68, 136.94, 134.22, 130.57, 130.09, 129.86, 125.26, 124.43, 114.99, 52.41, 35.01, 32.02, 29.83, 29.71, 29.70, 29.47, 29.44, 29.40, 28.98, 28.88, 28.59, 22.81, 14.24 ppm.

HRMS (ESI^+): calcd for $C_{29}H_{38}N_3O_3^+$ $[M+H]^+$ 476.2908, found 476.2910.



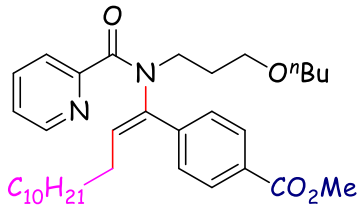
methyl (*E*)-4-(1-(*N*-(3,3-diphenylpropyl)picolinamido)tridec-1-en-1-yl)benzoate (5o)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/8, v/v) afforded **5o** as yellow oil (34.9 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (d, J = 4.5 Hz, 1H), 8.02 (d, J = 8.3 Hz, 2H), 7.70 – 7.60 (m, 4H), 7.31 – 7.06 (m, 10H), 5.17 (t, J = 7.6 Hz, 1H), 3.94 (s, 3H), 3.89 (t, J = 7.8 Hz, 1H), 3.37 (brs, 2H), 2.40 (dd, J = 15.7, 7.9 Hz, 2H), 1.88 (dd, J = 14.7, 7.4 Hz, 2H), 1.30 – 0.95 (m, 14H), 0.93 – 0.80 (m, 5H), 0.74 (dt, J = 14.3, 7.2 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.37, 166.88, 155.05, 148.18, 144.17, 140.10, 138.90, 136.47, 132.34, 130.01, 129.41, 128.52, 127.76, 126.30, 124.10, 123.44, 52.28, 49.03, 45.66, 32.73, 31.98, 29.68, 29.46, 29.40, 29.08, 28.92, 28.46, 22.77, 14.22 ppm.

HRMS (ESI^+): calcd for $C_{42}H_{51}N_2O_3^+$ $[M+H]^+$ 631.3894, found 631.3895.



methyl (*E*)-4-(1-(*N*-(3-butoxypropyl)picolinamido)tridec-1-en-1-yl)benzoate (5p)

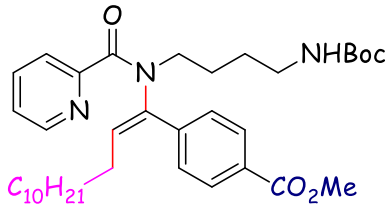
Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/6, v/v) afforded **5p** as brown oil (28.1 mg, 51% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, J = 4.4 Hz, 1H), 8.02 (d, J = 8.2 Hz, 2H), 7.73 – 7.54 (m, 4H), 7.24

– 7.15 (m, 1H), 5.20 (t, *J* = 7.6 Hz, 1H), 3.91 (s, 3H), 3.47 (brs, 2H), 3.40 (t, *J* = 6.4 Hz, 2H), 3.32 (t, *J* = 6.6 Hz, 2H), 1.96 – 1.79 (m, 4H), 1.51 – 1.40 (m, 2H), 1.31 – 0.94 (m, 17H), 0.87 – 0.84 (m, 7H), 0.73 (dt, *J* = 13.9, 7.0 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.50, 166.90, 155.18, 148.22, 140.15, 138.69, 136.47, 132.71, 129.98, 129.81, 129.47, 124.07, 123.41, 70.71, 68.43, 52.27, 43.60, 31.98, 31.88, 29.69, 29.46, 29.41, 29.13, 28.95, 28.53, 27.67, 22.78, 19.41, 14.22, 14.02 ppm.

HRMS (ESI$^+$): calcd for $C_{34}H_{51}N_2O_4^+$ $[M+H]^+$ 551.3843, found 551.3849.



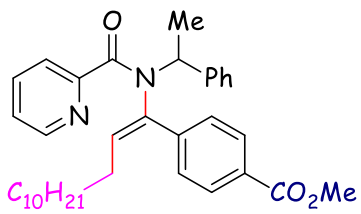
methyl (*E*)-4-(1-(*N*-(4-((*tert*-butoxycarbonyl)amino)butyl)picolinamido)tridec-1-en-1-yl)benzoate (5q)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/3, v/v) afforded **5q** as brown oil (30.6 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, *J* = 4.4 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 2H), 7.69 – 7.60 (m, 4H), 7.24 – 7.17 (m, 1H), 5.18 (t, *J* = 7.5 Hz, 1H), 4.62 (brs, 1H), 3.92 (s, 3H), 3.38 (brs, 2H), 3.09 (d, *J* = 5.9 Hz, 2H), 1.89 (dd, *J* = 14.7, 7.3 Hz, 2H), 1.58 (dt, *J* = 14.6, 7.2 Hz, 2H), 1.46 – 1.42 (m, 2H), 1.42 (s, 9H), 1.28 – 0.95 (m, 14H), 0.92 – 0.78 (m, 5H), 0.79 – 0.63 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.54, 166.88, 156.06, 155.17, 148.25, 140.04, 138.56, 136.51, 132.81, 129.99, 129.93, 129.54, 124.12, 123.45, 79.17, 52.31, 45.57, 40.33, 32.01, 29.70, 29.48, 29.43, 29.13, 28.98, 28.55, 28.53, 27.37, 24.69, 22.80, 14.24 ppm.

HRMS (ESI$^+$): calcd for $C_{36}H_{54}N_3O_5^+$ $[M+H]^+$ 608.4058, found 608.4067.



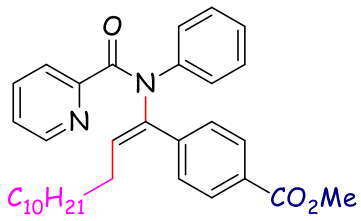
methyl (*E*)-4-(1-(*N*-(1-phenylethyl)picolinamido)tridec-1-en-1-yl)benzoate (5r)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/8, v/v) afforded **5r** as pale yellow oil (11.2 mg, 21% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, J = 3.4 Hz, 1H), 7.89 (brs, 2H), 7.70 – 7.59 (m, 2H), 7.55 (d, J = 7.8 Hz, 2H), 7.25 – 7.08 (m, 6H), 5.68 (brs, 1H), 5.07 (brs, 1H), 3.92 (s, 3H), 1.76 (brs, 2H), 1.52 (brs, 2H), 1.27 – 0.95 (m, 15H), 0.92 – 0.61 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.71, 167.07, 155.90, 148.09, 140.43, 136.45, 135.32, 130.62, 129.41, 128.93, 128.24, 127.98, 127.25, 123.97, 123.58, 121.75, 54.81, 52.27, 32.03, 29.84, 29.73, 29.72, 29.50, 29.45, 29.03, 29.01, 28.65, 22.82, 17.25, 14.25 ppm.

HRMS (ESI$^+$): calcd for $C_{35}H_{45}N_2O_3^+$ $[M+H]^+$ 541.3425, found 541.3433.



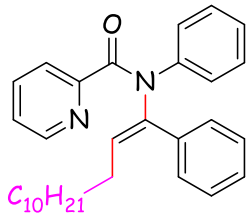
methyl (*E*)-4-(1-(*N*-phenylpicolinamido)tridec-1-en-1-yl)benzoate (5s)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/4, v/v) afforded **5s** as yellow oil (32.4 mg, 63% yield).

^{1}H NMR (400 MHz, acetone-d_6): δ = 8.51 (brs, 1H), 7.93 – 7.77 (m, 6H), 7.40 (brs, 1H), 7.30 (brs, 2H), 7.24 (t, J = 7.4 Hz, 2H), 7.07 (t, J = 7.3 Hz, 1H), 5.59 (brs, 1H), 3.84 (s, 3H), 2.08 (brs, 2H), 1.35 – 0.71 (m, 21H) ppm.

^{13}C NMR (100 MHz, acetone-d_6): δ = 167.60, 167.26, 156.80, 149.43, 140.46, 138.07, 134.73, 131.54, 130.70, 130.01, 129.73, 127.70, 127.10, 125.83, 125.23, 52.72, 33.03, 30.74, 30.73, 30.51, 30.42, 29.96, 29.57, 23.74, 14.79 ppm.

HRMS (ESI$^+$): calcd for $C_{33}H_{41}N_2O_3^+$ $[M+H]^+$ 513.3112, found 513.3113.



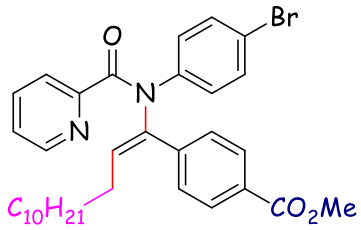
(*E*)-*N*-phenyl-*N*-(1-phenyltridec-1-en-1-yl)picolinamide (5t)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/4, v/v) afforded **5t** as yellow oil (20.7mg, 45% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (brs, 1H), 7.66 (brs, 2H), 7.55 (d, J = 7.7 Hz, 2H), 7.41 – 6.91 (m, 9H), 5.42 (brs, 1H), 2.03 (brs, 2H), 1.32 – 0.78 (m, 21H) ppm.

^{13}C NMR (100 MHz, acetone-d_6): δ = 174.68, 149.07, 137.57, 130.98, 129.74, 129.54, 129.26, 128.71, 128.60, 127.67, 127.39, 126.59, 125.25, 124.70, 120.57, 34.23, 32.67, 30.51, 30.37, 30.32, 30.17, 29.23, 25.71, 23.37, 14.40 ppm.

HRMS (ESI^+): calcd for $C_{31}H_{39}N_2O^+$ $[M+H]^+$ 455.3057, found 455.3048.



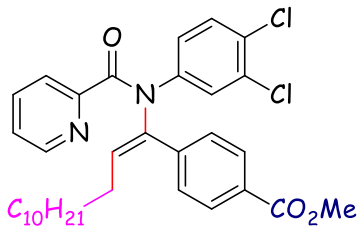
methyl (*E*)-4-(1-(*N*-(4-bromophenyl)picolinamido)tridec-1-en-1-yl)benzoate (5u)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/5, v/v) afforded **5u** as brown oil (42.9 mg, 72% yield).

^{1}H NMR (400 MHz, acetone-d_6): δ = 8.52 (brs, 1H), 8.05 – 7.67 (m, 6H), 7.42 (d, J = 7.8 Hz, 3H), 7.29 (d, J = 6.3 Hz, 2H), 5.62 (brs, 1H), 3.85 (s, 3H), 2.17 – 2.06 (m, 2H), 1.31 – 0.82 (m, 21H) ppm.

^{13}C NMR (100 MHz, acetone-d_6): δ = 170.16, 167.18, 156.34, 149.44, 141.44, 140.12, 138.16, 135.17, 132.76, 131.50, 130.81, 130.09, 129.51, 126.03, 125.33, 119.85, 52.73, 34.61, 33.01, 30.72, 30.48, 30.40, 29.93, 29.58, 26.05, 23.72, 14.78 ppm.

HRMS (ESI^+): calcd for $C_{33}H_{40}{}^{79}BrN_2O_3^+$ $[M+H]^+$ 591.2217, found 591.2217; $C_{33}H_{40}{}^{81}BrN_2O_3^+$ $[M+H]^+$ 593.2196, found 593.2191.



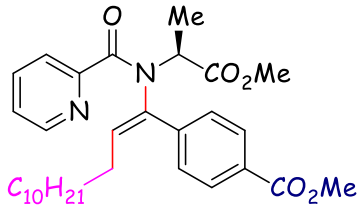
methyl (*E*)-4-(1-(*N*-(3,4-dichlorophenyl)picolinamido)tridec-1-en-1-yl)benzoate (5v)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/5, v/v) afforded **5v** as brown oil (45.1 mg, 77% yield).

^{1}H NMR (400 MHz, acetone-d_6): δ = 8.53 (d, J = 3.1 Hz, 1H), 7.99 – 7.75 (m, 6H), 7.56 (s, 1H), 7.45 (d, J = 9.2 Hz, 2H), 7.32 (d, J = 8.3 Hz, 1H), 5.66 (t, J = 7.4 Hz, 1H), 3.85 (s, 3H), 2.12 (d, J = 6.2 Hz, 2H), 1.29 – 1.05 (m, 14H), 0.94 – 0.86 (m, 7H) ppm.

^{13}C NMR (100 MHz, acetone-d_6): δ = 170.21, 167.17, 155.90, 149.50, 141.17, 139.78, 138.27, 135.80, 132.82, 131.54, 130.97, 130.65, 130.20, 130.01, 129.29, 127.97, 127.50, 126.26, 125.46, 52.76, 34.61, 33.03, 30.73, 30.49, 30.42, 30.01, 29.94, 29.62, 26.07, 23.74, 14.80 ppm.

HRMS (ESI$^+$): calcd for $C_{33}H_{39}{}^{35}Cl^{35}Cl\,N_2O_3^+$ $[M+H]^+$ 581.2332, found 581.2337; $C_{33}H_{39}{}^{35}Cl^{37}Cl\,N_2O_3^+$ $[M+H]^+$ 583.2303, found 583.2308; $C_{33}H_{39}{}^{37}Cl^{37}ClN_2O_3^+$ $[M+H]^+$ 585.2273, found 585.2263.



methyl (*S*,*E*)-4-(1-(*N*-(1-methoxy-1-oxopropan-2-yl)picolinamido)tridec-1-en-1-yl)benzoate (5w)

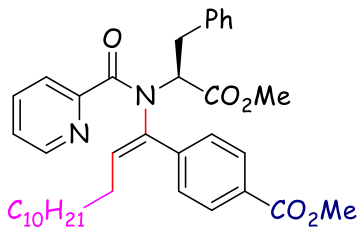
Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/6, v/v) afforded **5w** as pale yellow oil (19.6 mg, 37% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 – 8.39 (m, 1H), 8.04 (d, J = 8.2 Hz, 2H), 7.80 (d, J = 8.3 Hz, 2H), 7.70 – 7.67 (m, 2H), 7.26 – 7.20 (m, 1H), 5.34 (t, J = 7.6 Hz, 1H), 4.05 (dd, J = 13.5, 6.6 Hz, 1H), 3.91 (s, 3H), 3.69 (s, 3H), 1.94 (d, J = 6.9 Hz, 2H), 1.46 (d, J = 7.0 Hz, 3H), 1.30 – 0.95 (m, 14H), 0.93 – 0.79 (m, 5H), 0.76 – 0.74 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.47, 169.07, 166.89, 154.33, 148.21, 140.04, 136.55, 133.65, 130.49, 129.91, 129.32, 124.45, 123.74, 56.29, 52.35, 52.29, 31.98, 29.68, 29.44, 29.41, 29.07, 28.93, 28.71, 22.77,

14.21 ppm.

HRMS (ESI$^+$): calcd for $C_{31}H_{43}N_2O_5^+$ $[M+H]^+$ 523.3166, found 523.3152.



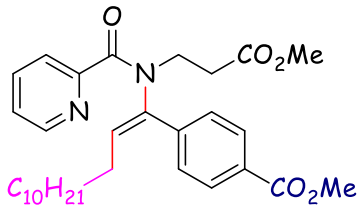
methyl (*S*,*E*)-4-(1-(*N*-(1-methoxy-1-oxo-3-phenylpropan-2-yl)picolinamido)tridec-1-en-1-yl)benzoate (5x)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/6, v/v) afforded **5x** as pale yellow oil (20.6 mg, 34% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, J = 3.4 Hz, 1H), 7.95 (d, J = 7.5 Hz, 2H), 7.74 – 7.63 (m, 2H), 7.57 (d, J = 7.5 Hz, 2H), 7.26 – 7.19 (m, 4H), 7.10 (m, 2H), 4.85 (brs, 1H), 4.19 (brs, 1H), 3.92 (s, 3H), 3.69 (s, 3H), 3.49 (dd, J = 13.8, 5.9 Hz, 1H), 3.44 – 3.33 (m, 1H), 1.65 (d, J = 6.1 Hz, 2H), 1.32 – 0.94 (m, 14H), 0.87 (t, J = 6.0 Hz, 3H), 0.80 – 0.70 (m, 2H), 0.61 – 0.60 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.39, 169.55, 166.93, 154.42, 148.32, 139.42, 138.91, 138.29, 136.51, 133.69, 130.56, 129.75, 129.59, 129.22, 128.41, 126.61, 124.37, 123.55, 61.77, 52.41, 52.28, 35.43, 31.99, 29.69, 29.44, 29.41, 29.36, 28.90, 28.86, 28.53, 22.78, 14.22 ppm.

HRMS (ESI$^+$): calcd for $C_{37}H_{47}N_2O_5^+$ $[M+H]^+$ 599.3479, found 599.3482.



methyl (*E*)-4-(1-(*N*-(3-methoxy-3-oxopropyl)picolinamido)tridec-1-en-1-yl)benzoate (5y)

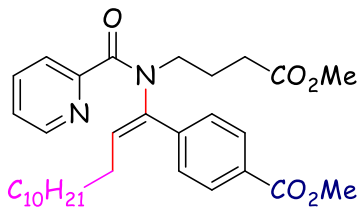
Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/5, v/v) afforded **5y** as pale yellow oil (33.6 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, J = 3.7 Hz, 1H), 8.13 – 7.96 (m, 2H), 7.84 – 7.57 (m, 4H), 7.23 – 7.15 (m, 1H), 5.17 (t, J = 7.5 Hz, 1H), 3.90 (s, 3H), 3.65 (brs, 2H), 3.61 (s, 3H), 2.62 (t, J = 7.2 Hz, 2H), 1.88

(dd, J = 14.3, 7.1 Hz, 2H), 1.37 – 0.90 (m, 14H), 0.86 – 0.82 (m, 5H), 0.73 – 0.71 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.02, 169.49, 166.80, 154.58, 148.19, 139.74, 138.42, 136.50, 133.07, 130.00, 129.96, 129.51, 124.26, 123.55, 52.25, 51.76, 42.18, 32.05, 31.93, 29.63, 29.40, 29.36, 29.34, 29.03, 28.87, 28.54, 22.73, 14.17 ppm.

HRMS (ESI$^+$): calcd for $C_{31}H_{43}N_2O_5^+$ $[M+H]^+$ 523.3166, found 523.3171.



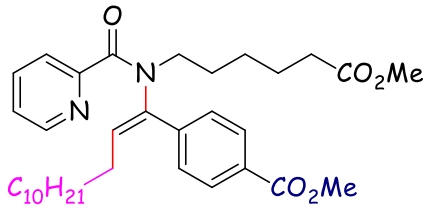
methyl (*E*)-4-(1-(*N*-(4-methoxy-4-oxobutyl)picolinamido)tridec-1-en-1-yl)benzoate (5z)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/5, v/v) afforded **5z** as pale yellow oil (33.7 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (d, J = 4.3 Hz, 1H), 8.03 (d, J = 8.4 Hz, 2H), 7.79 – 7.58 (m, 4H), 7.23 – 7.12 (m, 1H), 5.18 (t, J = 7.6 Hz, 1H), 3.90 (s, 3H), 3.60 (s, 3H), 3.41 (brs, 2H), 2.31 (t, J = 7.6 Hz, 2H), 1.97 – 1.78 (m, 4H), 1.29 – 0.92 (m, 14H), 0.91 – 0.75 (m, 5H), 0.74 – 0.69 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.46, 169.54, 166.82, 155.00, 148.18, 139.93, 138.45, 136.47, 132.83, 129.99, 129.88, 129.47, 124.12, 123.50, 52.24, 51.64, 45.02, 31.94, 31.39, 29.64, 29.41, 29.36, 29.04, 28.89, 28.48, 22.73, 22.66, 14.18 ppm.

HRMS (ESI$^+$): calcd for $C_{32}H_{45}N_2O_5^+$ $[M+H]^+$ 537.3323, found 537.3330.



methyl (*E*)-4-(1-(*N*-(6-methoxy-6-oxohexyl)picolinamido)tridec-1-en-1-yl)benzoate (5aa)

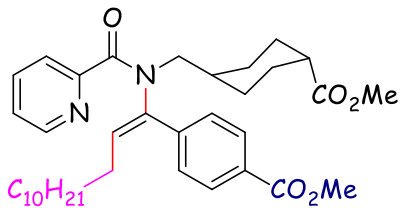
Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/5, v/v) afforded **5aa** as pale yellow oil (31.8 mg, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (s, 1H), 8.06 – 7.96 (m, 2H), 7.67 – 7.58 (m, 4H), 7.17 (m, 1H), 5.16 (t,

J = 7.4 Hz, 1H), 3.90 (s, 3H), 3.61 (s, 3H), 3.35 (brs, 2H), 2.24 (t, J = 7.3 Hz, 2H), 1.87 (d, J = 6.9 Hz, 2H), 1.58 – 1.53 (m, 4H), 1.28 – 0.95 (m, 16H), 0.84 – 0.82 (m, 5H), 0.73 – 0.71 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.07, 169.38, 166.82, 155.22, 148.16, 140.08, 138.57, 136.41, 132.62, 129.92, 129.80, 129.43, 123.99, 123.38, 52.22, 51.51, 45.67, 33.92, 31.93, 29.63, 29.41, 29.35, 29.07, 28.90, 28.46, 26.92, 26.35, 24.65, 22.72, 14.17 ppm.

HRMS (ESI$^+$): calcd for $C_{34}H_{49}N_2O_5^+$ $[M+H]^+$ 565.3636, found 565.3637.



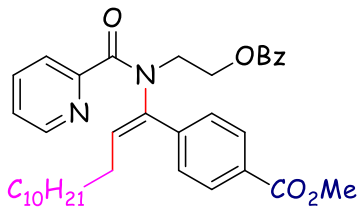
methyl 4-((*E*)-1-(*N*-(((1*r*,4*r*)-4-(methoxycarbonyl)cyclohexyl)methyl)picolinamido)tridec-1-en-1-yl)benzoate (**5ab**)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/5, v/v) afforded **5ab** as yellow oil (31.7 mg, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, J = 4.4 Hz, 1H), 8.05 (d, J = 8.3 Hz, 2H), 7.69 – 7.67 (m, 3H), 7.61 (d, J = 7.7 Hz, 1H), 7.23 – 7.13 (m, 1H), 5.20 (t, J = 7.6 Hz, 1H), 3.93 (s, 3H), 3.64 (s, 3H), 3.27 (brs, 2H), 2.21 (ddd, J = 12.2, 8.8, 3.4 Hz, 1H), 1.96 (d, J = 11.2 Hz, 2H), 1.86 (dd, J = 14.8, 7.4 Hz, 2H), 1.74 (d, J = 11.8 Hz, 2H), 1.60 (ddd, J = 11.2, 9.6, 5.5 Hz, 1H), 1.39 – 0.99 (m, 18H), 0.92 – 0.80 (m, 5H), 0.78 – 0.64 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.58, 169.93, 166.91, 155.51, 148.28, 139.95, 138.94, 136.49, 132.72, 130.01, 129.98, 129.57, 124.00, 123.41, 52.31, 51.63, 50.98, 43.20, 36.03, 32.00, 29.87, 29.70, 29.69, 29.49, 29.42, 29.10, 29.03, 28.64, 28.51, 22.79, 14.22 ppm.

HRMS (ESI$^+$): calcd for $C_{36}H_{51}N_2O_5^+$ $[M+H]^+$ 591.3792, found 591.3795.



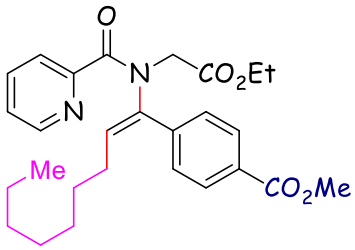
methyl (*E*)-4-(1-(*N*-(2-(benzoyloxy)ethyl)picolinamido)tridec-1-en-1-yl)benzoate (5ac)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/5, v/v) afforded **5ac** as yellow oil (28.1mg, 48% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, J = 4.5 Hz, 1H), 8.01 (d, J = 8.0 Hz, 4H), 7.71 – 7.62 (m, 4H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.25 – 7.19 (m, 1H), 5.24 (t, J = 7.6 Hz, 1H), 4.56 (t, J = 5.4 Hz, 2H), 3.92 (s, 3H), 3.82 (brs, 2H), 1.78 (dd, J = 14.9, 7.5 Hz, 2H), 1.25 – 0.91 (m, 14H), 0.88 (t, J = 7.2 Hz, 3H), 0.78 (dt, J = 14.6, 7.3 Hz, 2H), 0.64 (dt, J = 14.6, 7.5 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.96, 166.89, 166.46, 154.83, 148.30, 139.87, 138.82, 136.60, 133.18, 133.02, 130.17, 130.07, 130.04, 129.85, 129.63, 128.50, 124.31, 123.68, 62.39, 52.32, 44.95, 32.04, 29.85, 29.74, 29.48, 29.47, 29.41, 29.04, 28.97, 28.56, 22.83, 14.26 ppm.

HRMS (ESI^+): calcd for $C_{36}H_{45}N_2O_5^+$ $[M+H]^+$ 585.3323, found 585.3323.



methyl (*E*)-4-(1-(*N*-(2-ethoxy-2-oxoethyl)picolinamido)non-1-en-1-yl)benzoate (6a)

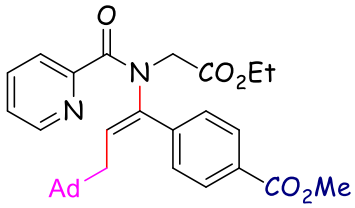
Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/5, v/v) afforded **6a** as pale yellow oil (32.9 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, J = 4.5 Hz, 1H), 8.03 (d, J = 8.3 Hz, 2H), 7.72 – 7.69 (m, 4H), 7.23 (dd, J = 8.8, 4.6 Hz, 1H), 5.47 (t, J = 7.6 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.07 (brs, 2H), 3.92 (s, 3H), 1.93 (dd, J = 14.7, 7.4 Hz, 2H), 1.27 (t, J = 7.2 Hz, 3H), 1.18 (dt, J = 13.7, 7.0 Hz, 2H), 1.13 – 0.97 (m, 4H), 0.90 – 0.73 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.85, 168.73, 166.90, 154.09, 148.21, 139.84, 138.85, 136.59, 133.15, 130.19, 129.98, 129.51, 124.51, 123.99, 61.25, 52.31, 48.63, 31.68, 29.10, 29.07, 28.90, 28.62, 22.67, 14.26,

14.16 ppm.

HRMS (ESI$^+$): calcd for $C_{27}H_{35}N_2O_5^+$ $[M+H]^+$ 467.2540, found 467.2543.



methyl

4-((*E*)-3-((3*s*)-adamantan-1-yl)-1-(*N*-(2-ethoxy-2-oxoethyl)picolinamido)prop-1-en-1-yl)benzoate

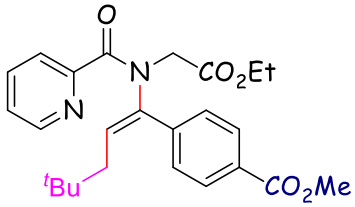
(6b)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/5, v/v) afforded **6b** as pale yellow oil (38.4 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.48 (d, J = 4.6 Hz, 1H), 8.04 (d, J = 8.3 Hz, 2H), 7.79 – 7.77 (m, 3H), 7.74 – 7.70 (m, 1H), 7.27 – 7.19 (m, 1H), 5.68 (t, J = 7.5 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 4.08 (s, 2H), 3.94 (s, 3H), 1.79 (d, J = 7.5 Hz, 2H), 1.72 (brs, 3H), 1.55 (d, J = 12.1 Hz, 3H), 1.37 (d, J = 11.8 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H), 0.96 (s, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.80, 168.74, 166.94, 154.05, 148.53, 140.03, 139.92, 136.74, 130.49, 129.88, 129.43, 129.03, 124.55, 124.22, 61.23, 52.30, 48.84, 42.92, 41.87, 36.76, 33.27, 28.55, 14.28 ppm.

HRMS (ESI$^+$): calcd for $C_{31}H_{37}N_2O_5^+$ $[M+H]^+$ 517.2697, found 517.2702.



methyl (*E*)-4-(1-(*N*-(2-ethoxy-2-oxoethyl)picolinamido)-4,4-dimethylpent-1-en-1-yl)benzoate (6c)

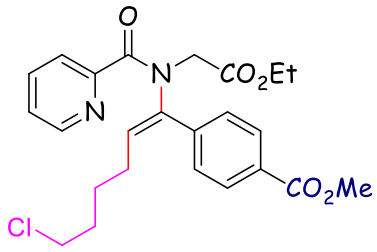
Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/5, v/v) afforded **6c** as pale yellow oil (29.8 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (d, J = 4.6 Hz, 1H), 8.01 (d, J = 8.3 Hz, 2H), 7.76 – 7.67 (m, 4H), 7.24 – 7.14 (m, 1H), 5.64 (t, J = 7.5 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.09 (s, 2H), 3.92 (s, 3H), 1.90 (d, J = 7.5 Hz,

2H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.48 (s, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.69, 168.72, 166.89, 153.88, 148.45, 140.12, 140.02, 136.84, 130.38, 129.87, 129.77, 129.43, 124.70, 124.17, 61.22, 52.28, 48.94, 42.34, 31.10, 29.00, 14.25 ppm.

HRMS (ESI^+): calcd for $C_{25}H_{31}N_2O_5^+$ $[M+H]^+$ 439.2227, found 439.2226.



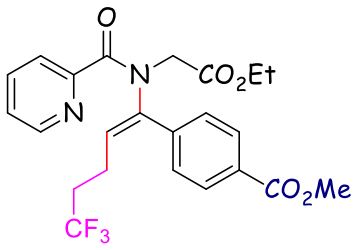
methyl (*E*)-4-(6-chloro-1-(*N*-(2-ethoxy-2-oxoethyl)picolinamido)hex-1-en-1-yl)benzoate (6d)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/4, v/v) afforded **6d** as yellow oil (24.6 mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, *J* = 4.7 Hz, 1H), 8.03 (d, *J* = 8.3 Hz, 2H), 7.72 (dd, *J* = 6.4, 1.4 Hz, 4H), 7.28 – 7.19 (m, 1H), 5.44 (t, *J* = 7.6 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.06 (brs, 2H), 3.92 (s, 3H), 3.23 (t, *J* = 6.6 Hz, 2H), 1.99 (q, *J* = 7.5 Hz, 2H), 1.28 – 1.18 (m, 5H), 1.01 – 0.89 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.75, 168.67, 166.81, 153.93, 148.22, 139.56, 136.75, 131.91, 130.20, 130.17, 129.57, 124.70, 124.10, 61.27, 52.32, 48.51, 44.56, 31.53, 27.73, 26.28, 14.24 ppm.

HRMS (ESI^+): calcd for $C_{24}H_{28}{}^{35}ClN_2O_5^+$ $[M+H]^+$ 459.1681, found 459.1684; $C_{24}H_{28}{}^{35}ClN_2O_5^+$ $[M+H]^+$ 561.1652, found 561.1657.



methyl (*E*)-4-(1-(*N*-(2-ethoxy-2-oxoethyl)picolinamido)-5,5,5-trifluoropent-1-en-1-yl)benzoate (6e)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/4, v/v) afforded **6e** as yellow oil (21.3 mg, 46% yield).

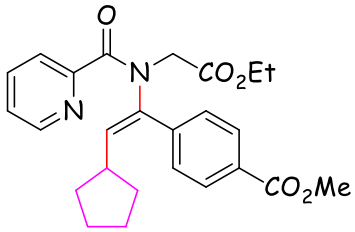
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (d, *J* = 4.6 Hz, 1H), 8.09 – 8.02 (m, 2H), 7.75 – 7.70 (m, 4H), 7.31 –

7.25 (m, 1H), 5.38 (t, J = 7.6 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.08 (brs, 2H), 3.93 (s, 3H), 2.20 (dd, J = 15.7, 7.7 Hz, 2H), 1.58 – 1.44 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.56, 168.63, 166.73, 153.68, 148.06, 141.23, 138.97, 136.88, 130.64, 130.17, 129.80, 127.95, 124.84, 124.37, 61.38, 52.40, 48.45, 32.99 (q, J = 28.8 Hz), 21.29, 14.24 ppm.

^{19}F NMR (376 MHz, CDCl3): δ = -66.64 ppm.

HRMS (ESI^+): calcd for $C_{23}H_{24}F_3N_2O_5^+$ $[M+H]^+$ 465.1632, found 465.1633.



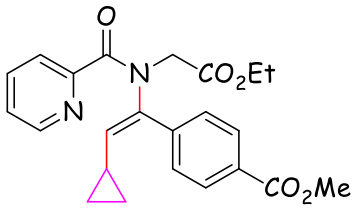
methyl (*E*)-4-(2-cyclopentyl-1-(*N*-(2-ethoxy-2-oxoethyl)picolinamido)vinyl)benzoate (6f)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/7, v/v) afforded **6f** as yellow oil (23.6 mg, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (d, J = 4.7 Hz, 1H), 8.05 (d, J = 8.2 Hz, 2H), 7.74 – 7.71 (m, 4H), 7.28 – 7.19 (m, 1H), 5.27 (d, J = 10.7 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.04 (brs, 2H), 3.93 (s, 3H), 2.44 – 2.24 (m, 1H), 1.46 – 1.35 (m, 6H), 1.26 (t, J = 7.1 Hz, 3H), 0.77 (brs, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.93, 168.63, 166.93, 154.31, 148.26, 139.93, 138.22, 137.61, 136.57, 130.16, 130.09, 129.61, 124.45, 123.88, 61.23, 52.33, 48.36, 39.19, 33.37, 25.36, 14.29 ppm.

HRMS (ESI^+): calcd for $C_{25}H_{29}N_2O_5^+$ $[M+H]^+$ 437.2071, found 437.2064.



methyl (*E*)-4-(2-cyclopropyl-1-(*N*-(2-ethoxy-2-oxoethyl)picolinamido)vinyl)benzoate (6g)

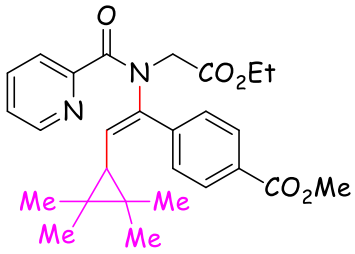
Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/6, v/v) afforded **6g** as yellow oil (13.3 mg, 33% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (d, J = 4.7 Hz, 1H), 8.07 – 8.02 (m, 2H), 7.82 (d, J = 8.4 Hz, 2H), 7.71

– 7.67 (m, 1H), 7.66 – 7.62 (m, 1H), 7.25 – 7.22 (m, 1H), 4.85 (d, *J* = 10.0 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 4.09 (brs, 2H), 3.93 (s, 3H), 1.44 – 1.35 (m, 1H), 1.26 – 1.24 (m, 3H), 0.91 – 0.81 (m, 1H), 0.54 (d, *J* = 7.6 Hz, 2H), 0.00 (m, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.88, 168.74, 166.94, 154.14, 148.36, 140.08, 137.54, 137.47, 136.47, 130.00, 129.84, 129.65, 124.36, 123.66, 61.28, 52.33, 48.71, 14.28, 10.93, 7.74 ppm.

HRMS (ESI$^+$): calcd for $C_{23}H_{25}N_2O_5^+$ $[M+H]^+$ 409.1758, found 409.1751.



methyl

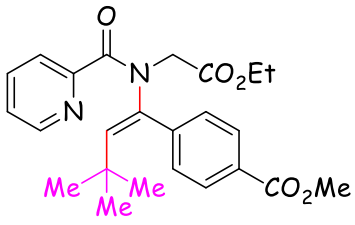
(*E*)-4-(1-(*N*-(2-ethoxy-2-oxoethyl)picolinamido)-2-(2,2,3,3-tetramethylcyclopropyl)vinyl)benzoate (6h)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/6, v/v) afforded **6h** as yellow oil (14.0 mg, 30% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (dt, *J* = 4.8, 1.3 Hz, 1H), 8.07 – 8.01 (m, 2H), 7.76 – 7.71 (m, 2H), 7.70 – 7.64 (m, 2H), 7.23 (dd, *J* = 9.0, 4.6 Hz, 1H), 5.32 (d, *J* = 9.7 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.11 (brs, 2H), 3.93 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.93 (s, 6H), 0.81 (d, *J* = 9.8 Hz, 1H), 0.74 (s, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.92, 168.68, 166.99, 154.05, 148.36, 140.27, 139.12, 136.44, 131.97, 130.02, 129.66, 129.49, 124.32, 123.85, 61.24, 52.32, 49.05, 34.63, 27.12, 22.98, 17.67, 14.30 ppm.

HRMS (ESI$^+$): calcd for $C_{27}H_{33}N_2O_5^+$ $[M+H]^+$ 465.2384, found 465.2378.



methyl (*E*)-4-(1-(*N*-(2-ethoxy-2-oxoethyl)picolinamido)-3,3-dimethylbut-1-en-1-yl)benzoate (6i)

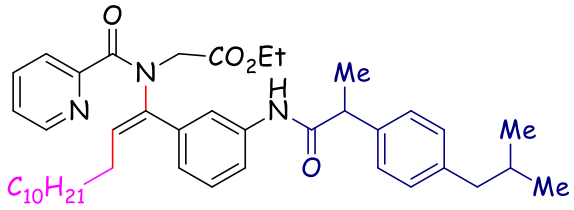
Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/7, v/v) afforded **6i** as

yellow oil (9.8 mg, 23% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (d, J = 4.7 Hz, 1H), 8.04 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.3 Hz, 2H), 7.80 – 7.76 (m, 2H), 7.33 – 7.28 (m, 1H), 5.33 (s, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.99 (brs, 2H), 3.94 (s, 3H), 0.88 – 0.86 (m, 3H), 0.53 (s, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.62, 168.71, 166.99, 154.57, 148.03, 142.49, 140.95, 136.82, 136.35, 131.45, 130.47, 129.21, 124.50, 61.22, 52.37, 47.46, 30.38, 29.85, 14.31, 14.27 ppm.

HRMS (ESI$^+$): calcd for $C_{24}H_{29}N_2O_5^+$ $[M+H]^+$ 425.2071, found 425.2066.



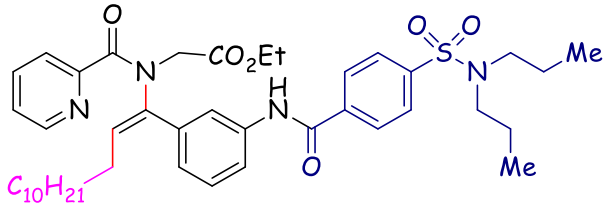
ethyl (*E*)-*N*-(1-(3-(2-(4-isobutylphenyl)propanamido)phenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (7a)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/4, v/v) afforded **7a** as yellow oil (37.0 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (brs, 1H), 7.66 – 7.64 (m, 3H), 7.58 (s, 1H), 7.43 (brs, 1H), 7.30 – 7.14 (m, 7H), 5.37 (t, J = 7.5 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 4.04 (brs, 2H), 3.72 (q, J = 7.0 Hz, 1H), 2.46 (d, J = 7.2 Hz, 2H), 1.92 – 1.84 (m, 3H), 1.58 (d, J = 7.1 Hz, 3H), 1.28 – 0.96 (m, 17H), 0.91 – 0.80 (m, 11H), 0.73 (dt, J = 14.5, 7.2 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.82, 169.89, 168.79, 154.35, 148.29, 141.10, 138.75, 138.28, 138.24, 136.49, 135.61, 132.39, 129.90, 128.82, 127.52, 125.94, 124.29, 123.70, 120.99, 120.00, 77.36, 61.18, 48.43, 47.81, 45.14, 32.02, 30.29, 29.72, 29.51, 29.44, 29.14, 28.95, 28.54, 22.80, 22.49, 18.74, 14.23 ppm.

HRMS (ESI$^+$): calcd for $C_{42}H_{58}N_3O_4^+$ $[M+H]^+$ 668.4422, found 668.4422.



ethyl

(*E*)-*N*-(1-(3-(4-(*N*,*N*-dipropylsulfamoyl)benzamido)phenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate

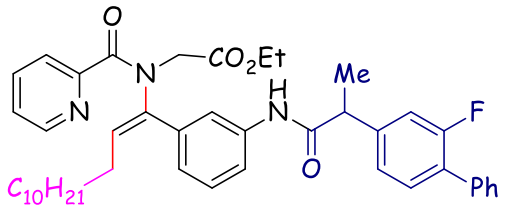
(7b)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/3, v/v) afforded **7b** as yellow oil (47.3 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.00 (brs, 1H), 8.43 (brs, 1H), 8.02 (d, J = 8.4 Hz, 2H), 7.95 (d, J = 8.2 Hz, 1H), 7.89 (s, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.59 (m, 1H), 7.36 (t, J = 7.9 Hz, 1H), 7.27 (d, J = 10.8 Hz, 1H), 7.20 (brs, 1H), 5.38 (t, J = 7.5 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 4.05 (brs, 2H), 3.14 – 3.03 (m, 4H), 1.95 (dd, J = 14.7, 7.4 Hz, 2H), 1.58 – 1.46 (m, 4H), 1.27 – 0.97 (m, 17H), 0.84 (dt, J = 16.9, 7.3 Hz, 11H), 0.72 (dt, J = 14.6, 7.3 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.98, 168.71, 164.98, 154.10, 148.42, 142.93, 138.68, 138.64, 138.44, 136.50, 135.57, 132.79, 128.91, 128.33, 127.33, 126.61, 124.40, 123.52, 121.51, 120.79, 77.36, 61.24, 50.05, 48.49, 31.99, 29.70, 29.48, 29.42, 29.14, 28.99, 28.62, 22.77, 22.01, 14.24, 14.21, 11.26 ppm.

HRMS (ESI^+): calcd for $C_{42}H_{59}N_4O_6S^+$ $[M+H]^+$ 747.4150, found 747.4152.



ethyl

(*E*)-*N*-(1-(3-(2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanamido)phenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (7c)

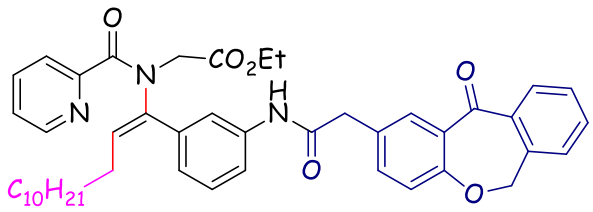
Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/4, v/v) afforded **7c** as yellow oil (36.0 mg, 51% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, J = 4.6 Hz, 1H), 8.10 (brs, 1H), 7.81 (d, J = 7.7 Hz, 1H), 7.65 – 7.60 (m, 3H), 7.55 – 7.49 (m, 2H), 7.46 – 7.39 (m, 3H), 7.39 – 7.33 (m, 1H), 7.31 – 7.25 (m, 2H), 7.25 – 7.15 (m, 3H), 5.39 (t, J = 7.5 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 4.04 (brs, 2H), 3.82 (q, J = 6.9 Hz, 1H), 1.93 (dd, J = 14.8, 7.4 Hz, 2H), 1.62 (d, J = 7.0 Hz, 3H), 1.25 – 0.97 (m, 17H), 0.89 – 0.79 (m, 5H), 0.77 – 0.66 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.09, 169.98, 168.72, 159.92 (d, J = 248.9 Hz), 154.16, 148.42, 142.79, 138.62, 138.51, 136.50, 135.54, 135.42, 132.68, 131.18 (d, J = 3.6 Hz), 129.02 (d, J = 2.8 Hz), 128.83, 128.57, 127.81, 126.05, 124.38, 123.74 (d, J = 3.1 Hz), 123.51, 120.81, 120.16, 115.52 (d, J = 23.4 Hz), 61.23, 48.50, 47.46, 32.00, 29.71, 29.49, 29.43, 29.14, 28.98, 28.60, 22.79, 18.86, 14.22 ppm.

^{19}F NMR (376 MHz, CDCl3): δ = -117.13 ppm.

HRMS (ESI^+): calcd for $C_{44}H_{53}FN_3O_4^+$ $[M+H]^+$ 706.4015, found 706.4014.



ethyl

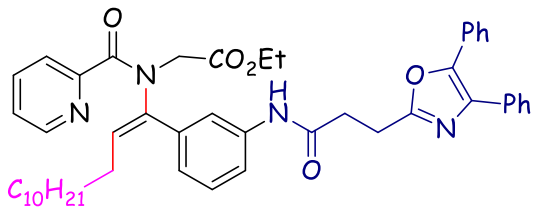
(*E*)-*N*-(1-(3-(2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetamido)phenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (7d)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/2, v/v) afforded **7d** as yellow oil (35.7 mg, 49% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, J = 4.7 Hz, 1H), 8.17 (d, J = 2.1 Hz, 1H), 8.10 (brs, 1H), 7.87 (d, J = 7.7 Hz, 1H), 7.74 – 7.62 (m, 4H), 7.56 – 7.51 (m, 2H), 7.48 – 7.44 (m, 1H), 7.36 (d, J = 7.4 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.19 (dd, J = 8.9, 4.7 Hz, 1H), 7.05 (d, J = 8.4 Hz, 1H), 5.39 (t, J = 7.5 Hz, 1H), 5.18 (s, 2H), 4.16 (q, J = 7.1 Hz, 2H), 4.06 (brs, 2H), 3.73 (s, 2H), 1.92 (dd, J = 14.7, 7.4 Hz, 2H), 1.24 – 0.95 (m, 17H), 0.87 (t, J = 6.9 Hz, 3H), 0.84 – 0.78 (m, 2H), 0.72 (dt, J = 14.4, 7.2 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.01, 169.97, 169.25, 168.74, 160.73, 154.25, 148.41, 140.45, 138.69, 138.27, 136.59, 136.48, 135.65, 135.51, 132.96, 132.57, 129.55, 129.38, 128.81, 128.67, 128.65, 127.96, 126.08, 125.35, 124.33, 123.57, 121.54, 121.09, 120.21, 73.72, 61.19, 48.48, 43.51, 31.99, 29.69, 29.48, 29.41, 29.12, 28.93, 28.56, 22.77, 14.22 ppm.

HRMS (ESI^+): calcd for $C_{45}H_{52}N_3O_6^+$ $[M+H]^+$ 730.3851, found 730.3848.



ethyl

(*E*)-*N*-(1-(3-(3-(4,5-diphenyloxazol-2-yl)propanamido)phenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate

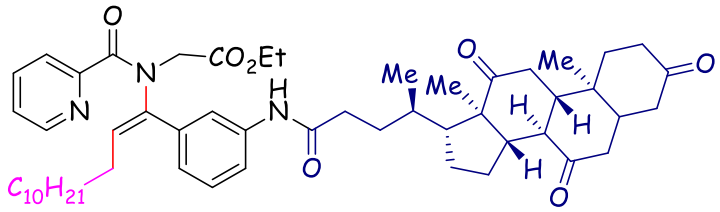
(**7e**)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/2, v/v) afforded **7e** as yellow oil (35.4 mg, 47% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (brs, 1H), 8.40 (d, J = 4.3 Hz, 1H), 7.72 – 7.58 (m, 6H), 7.58 – 7.51 (m, 2H), 7.38 – 7.27 (m, 8H), 7.19 – 7.13 (m, 1H), 5.36 (t, J = 7.5 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 4.05 (brs, 2H), 3.28 (t, J = 7.0 Hz, 2H), 2.96 (t, J = 7.0 Hz, 2H), 1.89 (dd, J = 14.7, 7.4 Hz, 2H), 1.27 – 0.94 (m, 17H), 0.87 (t, J = 6.9 Hz, 3H), 0.85 – 0.77 (m, 2H), 0.76 – 0.63 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.99, 168.77, 162.58, 154.33, 148.37, 145.73, 138.79, 138.34, 136.45, 135.63, 134.98, 132.42, 132.36, 129.65, 128.89, 128.84, 128.76, 128.74, 128.67, 128.32, 127.97, 126.56, 125.90, 124.28, 123.63, 121.07, 120.06, 61.17, 48.44, 34.09, 32.00, 29.71, 29.49, 29.43, 29.14, 28.92, 28.51, 24.06, 22.78, 14.22 ppm.

HRMS (ESI^+): calcd for $C_{47}H_{55}N_4O_5^+$ $[M+H]^+$ 755.4167, found 755.4161.



ethyl

***N*-((*E*)-1-(3-((4*R*)-4-((8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanamido)phenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate** (**7f**)

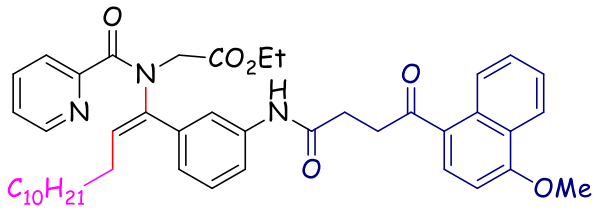
Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/1, v/v) afforded **7f** as yellow oil (33.7 mg, 39% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (d, J = 4.3 Hz, 1H), 7.80 (brs, 1H), 7.76 (d, J = 7.9 Hz, 1H), 7.71 – 7.65

(m, 3H), 7.34 – 7.27 (m, 1H), 7.23 (d, *J* = 7.6 Hz, 2H), 5.36 (t, *J* = 7.5 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 4.05 (brs, 2H), 2.92 – 2.79 (m, 4H), 2.49 – 2.26 (m, 8H), 2.22 – 2.07 (m, 4H), 2.05 – 1.90 (m, 8H), 1.64 – 1.52 (m, 2H), 1.23 – 1.01 (m, 20H), 0.88 – 0.67 (m, 13H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.21, 209.35, 209.10, 171.97, 169.87, 168.76, 154.35, 148.33, 138.75, 138.48, 136.52, 135.55, 132.39, 128.84, 125.84, 124.33, 123.69, 120.86, 120.09, 61.18, 57.02, 51.88, 49.08, 48.42, 46.91, 45.59, 45.50, 45.09, 42.88, 38.76, 36.56, 36.09, 35.52, 35.36, 34.46, 31.99, 31.52, 30.93, 30.28, 29.70, 29.48, 29.41, 29.14, 28.95, 28.56, 27.74, 25.25, 22.77, 21.95, 18.88, 14.24, 14.22, 11.97 ppm.

HRMS (ESI$^+$): calcd for $C_{53}H_{74}N_3O_7^+$ $[M+H]^+$ 864.5521, found 864.5518.



ethyl

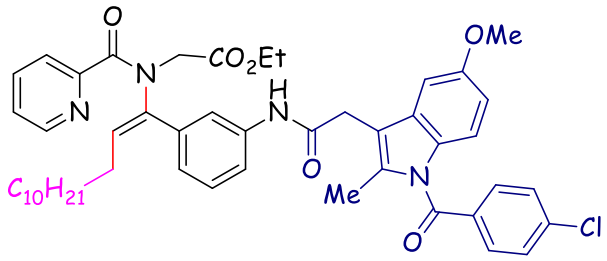
(*E*)-*N*-(1-(3-(4-(4-methoxynaphthalen-1-yl)-4-oxobutanamido)phenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (**7g**)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/2, v/v) afforded **7g** as brown oil (21.0 mg, 29% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.94 (d, *J* = 8.5 Hz, 1H), 8.47 (d, *J* = 4.7 Hz, 1H), 8.31 (dd, *J* = 8.4, 0.9 Hz, 1H), 8.13 – 8.10 (m, 2H), 7.77 – 7.63 (m, 4H), 7.59 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 7.51 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.31 – 7.29 (m, 2H), 7.19 (ddd, *J* = 6.8, 4.9, 2.1 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 5.39 (t, *J* = 7.5 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.09 (brs, 2H), 4.06 (s, 3H), 3.51 (t, *J* = 6.4 Hz, 2H), 2.86 (t, *J* = 6.4 Hz, 2H), 1.94 (dd, *J* = 14.7, 7.4 Hz, 2H), 1.26 – 0.96 (m, 17H), 0.87 (t, *J* = 7.0 Hz, 3H), 0.85 – 0.79 (m, 2H), 0.77 – 0.71 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.08, 170.99, 169.97, 168.84, 159.52, 154.42, 148.42, 138.84, 138.35, 136.50, 135.67, 132.38, 132.13, 131.56, 128.87, 126.86, 126.08, 125.95, 125.92, 125.89, 124.31, 123.69, 122.29, 121.12, 120.09, 102.28, 61.19, 55.95, 48.45, 36.29, 32.21, 32.03, 29.73, 29.52, 29.45, 29.18, 28.97, 28.59, 22.81, 14.25 ppm.

HRMS (ESI$^+$): calcd for $C_{44}H_{54}N_3O_6^+$ $[M+H]^+$ 720.4007, found 720.4007.



ethyl

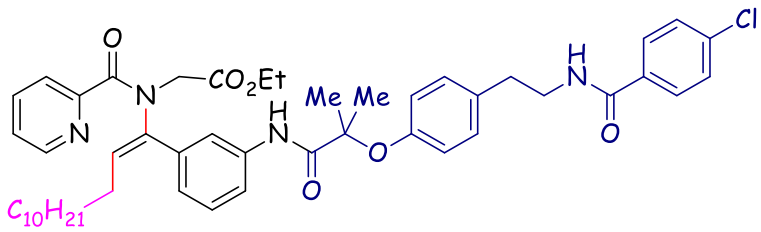
(*E*)-*N*-(1-(3-(2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetamido)phenyl)tridec-1-en-1-yl)-*N*-picolinoylglycinate (7h)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/2, v/v) afforded **7h** as pale yellow oil (26.2 mg, 32% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (d, J = 4.3 Hz, 1H), 7.70 – 7.65 (m, 5H), 7.61 – 7.55 (m, 2H), 7.45 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 4.8 Hz, 2H), 7.21 – 7.18 (m, 1H), 6.98 (d, J = 2.3 Hz, 1H), 6.86 (d, J = 9.0 Hz, 1H), 6.69 (dd, J = 9.0, 2.4 Hz, 1H), 5.37 (t, J = 7.5 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 4.03 (brs, 2H), 3.81 (s, 2H), 3.79 (s, 3H), 2.46 (s, 3H), 1.90 (dd, J = 14.6, 7.4 Hz, 2H), 1.28 – 0.95 (m, 17H), 0.87 (t, J = 7.0 Hz, 3H), 0.84 – 0.77 (m, 2H), 0.77 – 0.64 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.88, 168.76, 168.45, 166.93, 156.46, 154.31, 148.27, 139.70, 138.68, 137.69, 136.79, 136.54, 135.78, 133.65, 132.51, 131.33, 131.10, 130.37, 129.34, 128.84, 126.44, 124.38, 123.75, 121.62, 120.43, 115.33, 112.54, 112.38, 101.04, 61.18, 55.87, 48.41, 33.43, 32.01, 29.72, 29.51, 29.44, 29.14, 28.95, 28.54, 22.80, 14.23, 13.48 ppm.

HRMS (ESI$^+$): calcd for $C_{48}H_{56}{}^{35}ClN_4O_6^+$ $[M+H]^+$ 819.3883, found 819.3883; $C_{48}H_{56}{}^{37}ClN_4O_6^+$ $[M+H]^+$ 821.3853, found 821.3861.



ethyl

(*E*)-*N*-(1-(3-(2-(4-(2-(4-chlorobenzamido)ethyl)phenoxy)-2-methylpropanamido)phenyl)tridec-1-en-

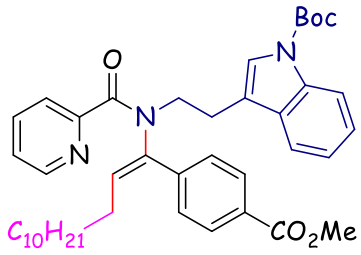
1-yl)-*N*-picolinoylglycinate (7i)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/2, v/v) afforded **7i** as pale yellow oil (47.2 mg, 57% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.66 (brs, 1H), 8.43 (d, J = 4.7 Hz, 1H), 7.75 (s, 1H), 7.69 – 7.62 (m, 5H), 7.41 – 7.28 (m, 4H), 7.22 – 7.19 (m, 1H), 7.14 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 6.45 – 6.44 (m, 1H), 5.39 (t, J = 7.5 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 4.07 (brs, 2H), 3.64 (dd, J = 13.2, 6.7 Hz, 2H), 2.87 (t, J = 7.0 Hz, 2H), 1.95 (dd, J = 14.6, 7.4 Hz, 2H), 1.57 (s, 6H), 1.28 – 0.98 (m, 17H), 0.89 – 0.70 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.13, 169.90, 168.76, 166.54, 154.29, 152.58, 148.30, 138.73, 137.68, 137.56, 136.49, 135.90, 134.53, 133.03, 132.48, 129.78, 128.98, 128.83, 128.41, 126.37, 124.33, 123.70, 122.28, 121.41, 120.17, 82.07, 77.48, 77.16, 76.84, 61.17, 48.45, 41.39, 34.98, 31.98, 29.69, 29.48, 29.40, 29.12, 28.92, 28.55, 25.06, 22.76, 14.23, 14.20 ppm.

HRMS (ESI$^+$): calcd for $C_{48}H_{60}{}^{35}ClN_4O_6^+$ $[M+H]^+$ 823.4196, found 823.4194; $C_{48}H_{60}{}^{37}ClN_4O_6^+$ $[M+H]^+$ 825.4166, found 825.4188.



***tert*-butyl**

(*E*)-3-(2-(*N*-(1-(4-(methoxycarbonyl)phenyl)tridec-1-en-1-yl)picolinamido)ethyl)-1*H*-indole-1-carboxylate (7j)

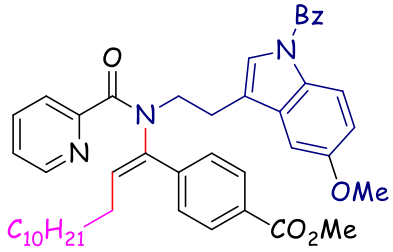
Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/8, v/v) afforded **7j** as yellow oil (37.4 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (d, J = 3.2 Hz, 1H), 8.06 – 8.01 (m, 3H), 7.73 – 7.63 (m, 4H), 7.39 (d, J = 7.5 Hz, 1H), 7.33 (s, 1H), 7.28 – 7.17 (m, 2H), 7.17 – 7.10 (m, 1H), 5.16 – 5.09 (m, 1H), 3.91 (s, 3H), 3.68 (brs, 2H), 3.02 (t, J = 7.1 Hz, 2H), 1.83 (d, J = 6.6 Hz, 2H), 1.63 (s, 9H), 1.30 – 0.93 (m, 17H), 0.89 – 0.76 (m, 5H), 0.71 – 070 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.61, 166.84, 154.98, 149.75, 148.26, 140.04, 138.84, 136.54, 132.71, 130.52, 130.02, 129.91, 129.50, 127.28, 124.39, 124.22, 123.50, 123.26, 122.49, 119.10, 117.69, 115.26, 83.47,

52.29, 46.45, 31.99, 29.69, 29.46, 29.42, 29.39, 29.08, 28.94, 28.52, 28.29, 23.14, 22.78, 14.22 ppm.

HRMS (ESI$^+$): calcd for $C_{42}H_{54}N_3O_5^+$ $[M+H]^+$ 680.4058, found 680.4057.



methyl

(*E*)-4-(1-(*N*-(2-(1-benzoyl-5-methoxy-1*H*-indol-3-yl)ethyl)picolinamido)tridec-1-en-1-yl)benzoate

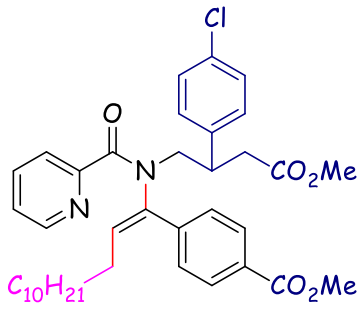
(**7k**)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/4, v/v) afforded **7k** as yellow oil (43.1 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (d, J = 4.4 Hz, 1H), 8.27 (d, J = 8.9 Hz, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.76 – 7.61 (m, 6H), 7.58 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.4 Hz, 2H), 7.23 (ddd, J = 7.3, 4.8, 1.0 Hz, 1H), 7.04 (s, 1H), 6.95 (dd, J = 8.9, 2.4 Hz, 1H), 6.91 (d, J = 2.3 Hz, 1H), 5.12 (t, J = 7.6 Hz, 1H), 3.93 (s, 3H), 3.82 (s, 3H), 3.67 (brs, 2H), 2.97 (t, J = 7.7 Hz, 2H), 1.84 (dd, J = 14.8, 7.4 Hz, 2H), 1.30 – 0.95 (m, 17H), 0.87 (t, J = 6.8 Hz, 3H), 0.86 – 0.82 (m, 2H), 0.73 – 0.67 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.69, 168.13, 166.77, 156.81, 154.96, 148.34, 139.93, 138.86, 136.55, 134.80, 132.86, 131.97, 131.73, 131.01, 129.97, 129.53, 129.06, 128.66, 125.58, 124.27, 123.45, 119.06, 117.55, 113.60, 101.85, 55.80, 52.29, 46.15, 31.99, 29.69, 29.46, 29.42, 29.39, 29.09, 28.93, 28.54, 23.24, 22.78, 14.22 ppm.

HRMS (ESI$^+$): calcd for $C_{45}H_{52}N_3O_5^+$ $[M+H]^+$ 714.3901, found 714.3903.



methyl

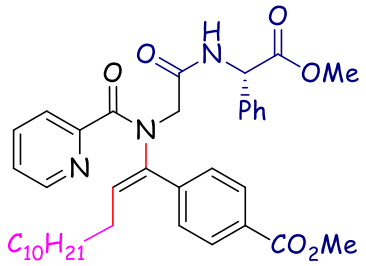
(*E*)-4-(1-(*N*-(2-(4-chlorophenyl)-4-methoxy-4-oxobutyl)picolinamido)tridec-1-en-1-yl)benzoate (7l)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/5, v/v) afforded **7l** as pale yellow oil (42.7 mg, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, J = 4.3 Hz, 1H), 8.04 (d, J = 8.0 Hz, 2H), 7.67 (t, J = 7.7 Hz, 1H), 7.61 (d, J = 7.9 Hz, 2H), 7.53 (d, J = 7.7 Hz, 1H), 7.23 – 7.18 (m, 3H), 7.10 (d, J = 8.0 Hz, 2H), 4.81 (t, J = 7.6 Hz, 1H), 3.93 (s, 3H), 3.90 – 3.63 (m, 2H), 3.54 (m, 1H), 3.51 (s, 3H), 2.70 (dd, J = 15.6, 4.7 Hz, 1H), 2.59 (dd, J = 15.7, 9.8 Hz, 1H), 1.79 – 1.67 (m, 2H), 1.31 – 0.96 (m, 17H), 0.89 – 0.79 (m, 5H), 0.65 – 0.63 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.03, 169.85, 166.86, 154.89, 148.25, 139.75, 139.49, 137.93, 136.52, 133.61, 132.85, 130.02, 129.95, 129.61, 129.48, 128.64, 124.15, 123.40, 52.35, 51.74, 40.24, 38.63, 32.01, 29.72, 29.57, 29.50, 29.45, 29.39, 29.22, 29.00, 28.46, 22.81, 14.25 ppm.

HRMS (ESI^+): calcd for $C_{38}H_{48}{}^{35}ClN_2O_5^+$ $[M+H]^+$ 647.3246, found 647.3247; $C_{38}H_{48}{}^{37}ClN_2O_5^+$ $[M+H]^+$ 649.3217, found 649.3220.



methyl

(*S*,*E*)-4-(1-(*N*-(2-((2-methoxy-2-oxo-1-phenylethyl)amino)-2-oxoethyl)picolinamido)tridec-1-en-1-yl) benzoate (7m)

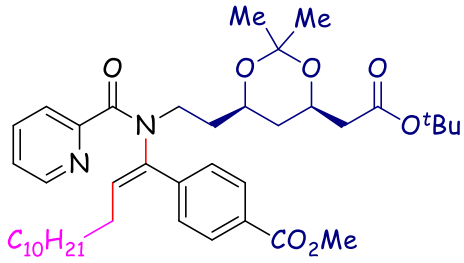
Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/2, v/v) afforded **7m** as pale yellow oil (34.1 mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (brs, 1H), 7.99 (d, J = 8.0 Hz, 2H), 7.84 – 7.51 (m, 5H), 7.44 – 7.26 (m, 5H), 5.59 (d, J = 7.2 Hz, 1H), 5.33 (brs, 1H), 4.08 (brs, 2H), 3.92 (s, 3H), 3.72 (s, 3H), 1.87 (brs, 2H), 1.29 – 0.96 (m, 14H), 0.88 – 0.85 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.24, 170.10, 167.80, 166.84, 153.65, 148.19, 139.57, 136.52, 132.92, 130.07, 129.96, 129.59, 129.05, 128.61, 127.38, 124.91, 124.23, 56.44, 52.90, 52.30, 32.01, 29.72, 29.50, 29.44,

29.05, 28.94, 28.51, 22.80, 14.24 ppm.

HRMS (ESI$^+$): calcd for $C_{38}H_{48}N_3O_6^+$ $[M+H]^+$ 642.3538, found 642.3539.



methyl

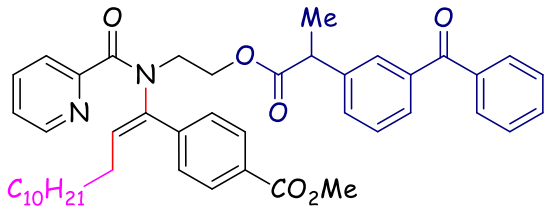
4-((*E*)-1-(*N*-(2-((4*R*,6*R*)-6-(2-(*tert*-butoxy)-2-oxoethyl)-2,2-dimethyl-1,3-dioxan-4-yl)ethyl)picolinamido)tridec-1-en-1-yl)benzoate (**7n**)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/5, v/v) afforded **7n** as pale yellow oil (29.8 mg, 43% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, J = 4.3 Hz, 1H), 8.03 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 7.8 Hz, 3H), 7.59 (d, J = 7.7 Hz, 1H), 7.23 – 7.17 (m, 1H), 5.19 (t, J = 7.5 Hz, 1H), 4.25 – 4.15 (m, 1H), 3.93 (s, 3H), 3.91 – 3.82 (m, 1H), 3.46 (brs, 2H), 2.39 (dd, J = 15.1, 7.1 Hz, 1H), 2.26 (dd, J = 15.1, 5.9 Hz, 1H), 1.88 (dd, J = 14.6, 7.2 Hz, 2H), 1.74 (dd, J = 13.7, 6.7 Hz, 2H), 1.42 (s, 9H), 1.39 (s, 3H), 1.31 – 0.97 (m, 19H), 0.88 – 0.85 (m, 5H), 0.76 – 0.71 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.39, 169.46, 166.95, 155.17, 148.25, 140.19, 138.58, 136.51, 132.90, 130.02, 129.86, 129.49, 124.11, 123.43, 98.77, 80.72, 67.09, 66.22, 52.33, 42.81, 42.62, 36.45, 34.00, 32.02, 30.14, 29.73, 29.72, 29.50, 29.45, 29.43, 29.15, 28.97, 28.56, 28.21, 22.81, 19.81, 14.26 ppm.

HRMS (ESI$^+$): calcd for $C_{41}H_{61}N_2O_7^+$ $[M+H]^+$ 693.4473, found 693.4471.



methyl

(*E*)-4-(1-(*N*-(2-((2-(3-benzoylphenyl)propanoyl)oxy)ethyl)picolinamido)tridec-1-en-1-yl)benzoate

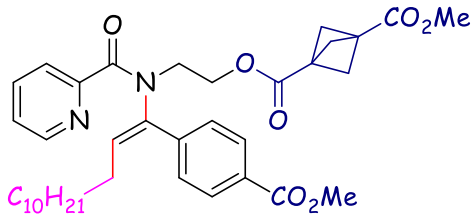
(**7o**)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/4, v/v) afforded **7o** as pale yellow oil (32.8 mg, 46% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, J = 4.4 Hz, 1H), 8.03 (d, J = 8.4 Hz, 2H), 7.82 – 7.76 (m, 2H), 7.75 (s, 1H), 7.71 – 7.62 (m, 4H), 7.62 – 7.53 (m, 3H), 7.51 – 7.45 (m, 2H), 7.43 (t, J = 7.8 Hz, 1H), 7.21 (dd, J = 6.6, 4.9 Hz, 1H), 5.14 (t, J = 7.6 Hz, 1H), 4.32 (dt, J = 11.2, 5.6 Hz, 1H), 4.21 (dt, J = 11.5, 5.7 Hz, 1H), 3.93 (s, 3H), 3.82 – 3.70 (m, 2H), 3.61 (brs, 1H), 1.84 (dd, J = 15.0, 7.5 Hz, 2H), 1.54 (d, J = 7.2 Hz, 3H), 1.25 – 0.96 (m, 14H), 0.88 (t, J = 6.9 Hz, 3H), 0.85 – 0.79 (m, 2H), 0.71 – 0.65 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.45, 173.93, 169.80, 166.82, 154.68, 148.21, 140.89, 139.75, 138.46, 138.00, 137.56, 136.57, 132.98, 132.61, 131.72, 130.16, 130.00, 129.58, 129.33, 129.16, 128.65, 128.41, 124.29, 123.66, 61.95, 52.30, 45.47, 44.51, 31.99, 29.70, 29.47, 29.42, 29.41, 29.07, 28.99, 28.56, 22.78, 18.69, 14.22 ppm.

HRMS (ESI$^+$): calcd for $C_{45}H_{53}N_2O_6^+$ $[M+H]^+$ 717.3898, found 717.3896.



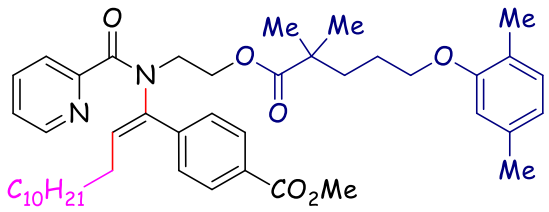
(*E*)-1-(2-(*N*-(1-(4-(methoxycarbonyl)phenyl)tridec-1-en-1-yl)picolinamido)ethyl) 3-methyl bicyclo[1.1.1]pentane-1,3-dicarboxylate (**7p**)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/4, v/v) afforded **7p** as pale yellow oil (26.0 mg, 41% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, J = 4.5 Hz, 1H), 8.04 (d, J = 7.6 Hz, 2H), 7.71 – 7.67 (t, J = 9.4 Hz, 3H), 7.60 (d, J = 7.8 Hz, 1H), 7.25 – 7.18 (m, 1H), 5.23 (t, J = 7.5 Hz, 1H), 4.28 (t, J = 5.6 Hz, 2H), 3.93 (s, 3H), 3.69 (s, 3H), 3.68 (brs, 2H), 2.31 (s, 6H), 1.91 (dd, J = 14.7, 7.4 Hz, 2H), 1.27 – 0.95 (m, 14H), 0.88 – 0.82 (m, 5H), 0.75 – 0.69 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.86, 169.07, 166.84, 154.65, 148.26, 139.81, 138.67, 136.63, 132.69, 130.05, 130.00, 129.62, 124.36, 123.66, 61.79, 52.97, 52.37, 52.00, 44.62, 37.75, 32.02, 29.72, 29.71, 29.49, 29.45, 29.43, 29.15, 28.99, 28.64, 22.81, 14.26 ppm.

HRMS (ESI$^+$): calcd for $C_{37}H_{49}N_2O_7^+$ $[M+H]^+$ 633.3534, found 633.3533.



methyl

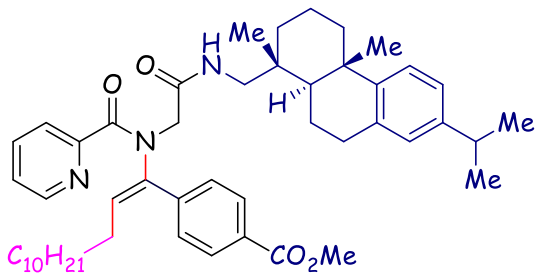
(*E*)-4-(1-(*N*-(2-((5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoyl)oxy)ethyl)picolinamido)tridec-1-en-1-yl)benzoate (**7q**)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/8, v/v) afforded **7q** as pale yellow oil (37.6 mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, J = 4.5 Hz, 1H), 8.05 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H), 7.67 – 7.62 (m, 1H), 7.61 (t, J = 7.2 Hz, 1H), 7.24 – 7.18 (m, 1H), 6.99 (d, J = 7.5 Hz, 1H), 6.65 (d, J = 7.5 Hz, 1H), 6.60 (s, 1H), 5.26 (t, J = 7.6 Hz, 1H), 4.25 (t, J = 5.8 Hz, 2H), 3.93 (s, 3H), 3.90 (t, J = 4.8 Hz, 2H), 3.71 (brs, 2H), 2.30 (s, 3H), 2.15 (s, 3H), 1.91 (dd, J = 14.9, 7.5 Hz, 2H), 1.72 – 1.71 (m, 4H), 1.26 – 0.98 (m, 20H), 0.90 – 0.81 (m, 5H), 0.78 – 0.64 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.67, 169.73, 166.83, 157.03, 154.83, 148.22, 139.82, 138.46, 136.53, 133.00, 130.37, 130.04, 129.98, 129.61, 124.24, 123.62, 123.59, 120.79, 112.03, 68.01, 61.46, 52.29, 44.51, 42.16, 37.10, 32.00, 29.70, 29.69, 29.47, 29.42, 29.40, 29.12, 28.98, 28.59, 25.23, 22.78, 21.50, 15.88, 14.22 ppm.

HRMS (ESI$^+$): calcd for $C_{44}H_{61}N_2O_6^+$ $[M+H]^+$ 713.4524, found 713.4509.



methyl

4-((*E*)-1-(*N*-(2-((((1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthre

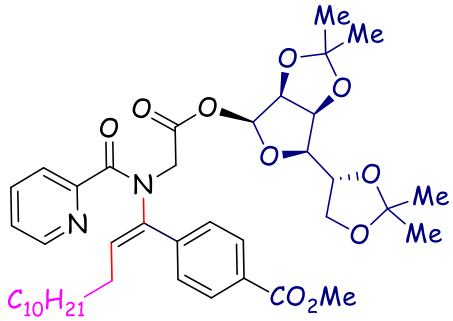
n-1-yl)methyl)amino)-2-oxoethyl)picolinamido)tridec-1-en-1-yl)benzoate (**7r**)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/4, v/v) afforded **7r** as pale yellow oil (41.2 mg, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (d, J = 4.3 Hz, 1H), 8.00 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 8.1 Hz, 2H), 7.46 (brs, 1H), 7.23 – 7.11 (m, 3H), 7.00 (dd, J = 8.1, 1.7 Hz, 2H), 6.91 (d, J = 1.3 Hz, 1H), 5.16 (brs, 1H), 4.14 (d, J = 14.4 Hz, 1H), 3.92 (s, 3H), 3.88 (d, J = 12.5 Hz, 1H), 3.24 (dd, J = 13.6, 5.4 Hz, 1H), 3.12 (dd, J = 13.7, 7.1 Hz, 1H), 2.97 – 2.88 (m, 2H), 2.84 (dt, J = 13.8, 6.9 Hz, 1H), 2.34 – 2.22 (m, 1H), 1.92 – 1.88 (m, 1H), 1.80 – 1.74 (m, 2H), 1.68 – 1.57 (m, 2H), 1.32 – 1.02 (m, 26H), 0.95 (m, 5H), 0.90 – 0.59 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.69, 168.78, 166.81, 153.55, 148.17, 147.22, 145.68, 139.31, 138.87, 136.85, 135.03, 132.52, 130.11, 130.09, 129.60, 127.07, 124.70, 124.40, 124.04, 123.95, 52.29, 49.36, 44.94, 38.71, 37.61, 37.58, 35.96, 33.57, 32.01, 30.39, 29.72, 29.48, 29.44, 29.41, 28.99, 28.81, 28.19, 25.47, 24.17, 24.12, 22.80, 19.18, 19.02, 18.79, 14.23 ppm.

HRMS (ESI$^+$): calcd for $C_{49}H_{68}N_3O_4^+$ $[M+H]^+$ 762.5204, found 762.5190.



methyl

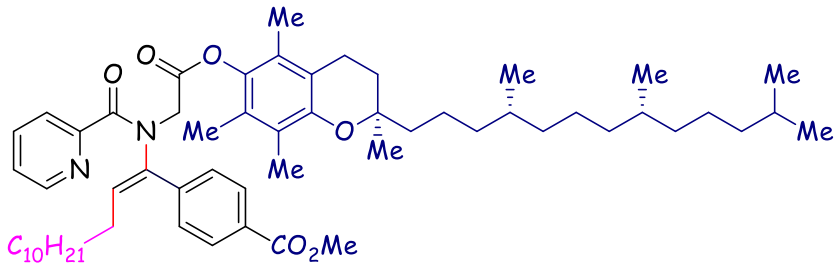
4-((*E*)-1-(*N*-(2-(((3a*S*,4*R*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)oxy)-2-oxoethyl)picolinamido)tridec-1-en-1-yl)benzoate (**7s**)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/4, v/v) afforded **7s** as pale yellow oil (24.3 mg, 33% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, J = 4.7 Hz, 1H), 8.04 (d, J = 8.4 Hz, 2H), 7.78 – 7.66 (m, 4H), 7.25 – 7.21 (m, 1H), 6.15 (s, 1H), 5.44 (t, J = 7.6 Hz, 1H), 4.81 (dd, J = 5.8, 3.6 Hz, 1H), 4.72 (d, J = 5.9 Hz, 1H), 4.38 (ddd, J = 7.9, 6.1, 4.4 Hz, 1H), 4.16 – 4.06 (m, 2H), 4.04 – 3.98 (m, 2H), 3.95 – 3.93 (m, 1H), 3.93 (s, 3H), 1.97 – 1.91 (m, 2H), 1.47 (s, 3H), 1.42 (s, 3H), 1.37 (s, 3H), 1.33 (s, 3H), 1.25 – 0.96 (m, 14H), 0.90 – 0.70 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.87, 167.26, 166.86, 153.83, 148.30, 139.63, 138.72, 136.67, 133.31, 130.18, 130.12, 129.61, 124.64, 123.98, 113.42, 109.48, 101.96, 85.20, 82.77, 79.23, 77.36, 72.92, 66.98, 52.32, 48.73, 32.01, 31.55, 30.31, 29.71, 29.48, 29.44, 29.10, 28.96, 28.63, 27.07, 26.05, 25.27, 24.78, 22.80, 14.23 ppm.

HRMS (ESI^+): calcd for $C_{41}H_{57}N_2O_{10}^+$ $[M+H]^+$ 737.4008, found 737.4008.



methyl

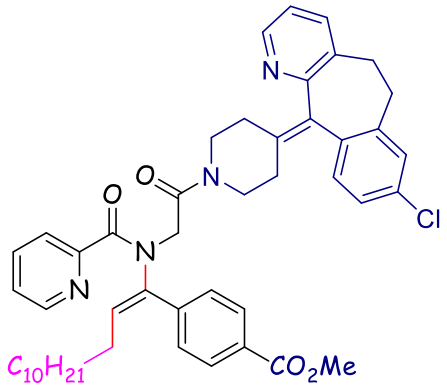
4-((*E*)-1-(*N*-(2-oxo-2-(((*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)ethyl)picolinamido)tridec-1-en-1-yl)benzoate (7t)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/10, v/v) afforded **7t** as pale yellow oil (50.0 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, J = 4.7 Hz, 1H), 8.07 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 3.5 Hz, 2H), 7.25 – 7.20 (m, 1H), 5.52 (t, J = 7.6 Hz, 1H), 4.39 (brs, 2H), 3.95 (s, 3H), 2.59 (t, J = 6.5 Hz, 2H), 2.34 (t, J = 7.5 Hz, 2H), 2.09 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.94 (dd, J = 14.5, 7.3 Hz, 2H), 1.80 – 1.71 (m, 2H), 1.66 – 1.59 (m, 2H), 1.57 – 1.47 (m, 2H), 1.24 – 0.98 (m, 25H), 0.89 – 0.74 (m, 21H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.92, 167.80, 166.91, 153.98, 149.66, 148.25, 140.41, 139.86, 138.71, 136.64, 133.46, 130.18, 130.09, 129.67, 126.88, 125.20, 124.58, 124.01, 123.23, 117.58, 75.20, 52.34, 48.37, 39.50, 37.57, 37.41, 34.14, 32.92, 32.84, 32.03, 29.72, 29.56, 29.48, 29.45, 29.44, 29.37, 29.20, 29.10, 28.97, 28.67, 28.10, 24.93, 24.84, 24.57, 22.84, 22.80, 22.75, 21.16, 20.72, 19.88, 19.78, 14.23, 13.12, 12.28, 11.92 ppm.

HRMS (ESI^+): calcd for $C_{58}H_{87}N_2O_6^+$ $[M+H]^+$ 907.6559, found 907.6551.



methyl

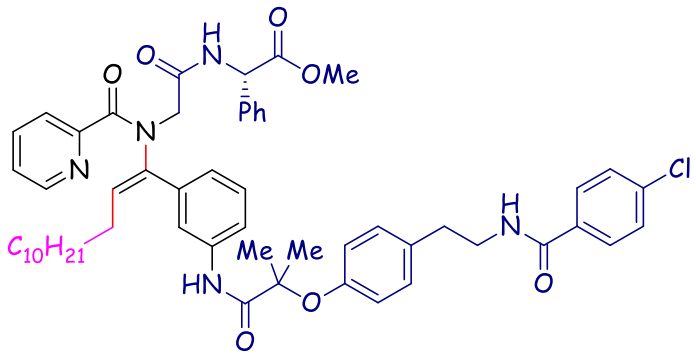
(*E*)-4-(1-(*N*-(2-(4-(8-chloro-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidin-1-yl)-2-oxoethyl)picolinamido)tridec-1-en-1-yl)benzoate (7u)

Purification via column chromatography on silica gel (ethyl acetate/MeOH = 50/1, v/v) afforded **7u** as yellow oil (31.4 mg, 40% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 – 8.36 (m, 2H), 8.03 (d, J = 8.3 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.72 – 7.62 (m, 2H), 7.44 (dd, J = 7.0, 3.5 Hz, 1H), 7.25 – 7.00 (m, 5H), 5.61 (t, J = 7.6 Hz, 1H), 4.29 – 4.15 (m, 1H), 4.10 – 3.96 (m, 2H), 3.92 (s, 3H), 3.57 – 3.51 (m, 1H), 3.42 – 3.14 (m, 4H), 2.88 – 2.73 (m, 2H), 2.57 – 2.23 (m, 4H), 2.00 – 1.86 (m, 2H), 1.28 – 0.94 (m, 14H), 0.87 (t, J = 6.9 Hz, 3H), 0.84 – 0.78 (m, 2H), 0.74 – 0.60 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.02, 166.96, 165.88, 156.78, 154.52, 148.12, 146.53, 140.19, 139.56, 138.60, 137.92, 137.48, 136.87, 136.57, 134.47, 134.10, 133.63, 133.20, 130.59, 130.28, 129.87, 129.50, 129.15, 126.41, 124.31, 124.05, 122.58, 52.30, 47.91, 45.60, 43.22, 32.00, 31.74, 31.54, 31.03, 30.83, 30.43, 30.19, 29.71, 29.47, 29.43, 29.03, 28.96, 28.70, 22.79, 14.23 ppm.

HRMS (ESI$^+$): calcd for $C_{48}H_{56}{}^{35}ClN_4O_4^+$ $[M+H]^+$ 787.3985, found 787.3983; $C_{48}H_{56}{}^{37}ClN_4O_4^+$ $[M+H]^+$ 789.3955, found 789.3969.



methyl

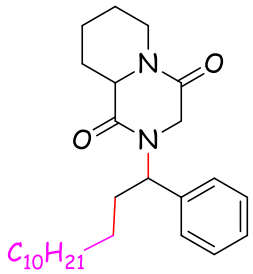
(*S*,*E*)-2-(2-(*N*-(1-(3-(2-(4-(2-(4-chlorobenzamido)ethyl)phenoxy)-2-methylpropanamido)phenyl)tridec-1-en-1-yl)picolinamido)acetamido)-2-phenylacetate (7v)

Purification via column chromatography on silica gel (ethyl acetate/petroleum ether = 1/1, v/v) afforded **7v** as pale yellow oil (28.8 mg, 30% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.68 (brs, 1H), 8.47 (d, J = 4.6 Hz, 1H), 7.73 – 7.71 (m, 4H), 7.64 – 7.56 (m, 2H), 7.36 – 7.26 (m, 11H), 7.13 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 8.5 Hz, 2H), 6.38 (d, J = 5.5 Hz, 1H), 5.60 – 5.48 (m, 1H), 5.25 (brs, 1H), 4.08 (brs, 2H), 3.69 (s, 3H), 3.64 (dd, J = 13.1, 6.6 Hz, 2H), 2.88 (t, J = 7.0 Hz, 2H), 1.89 (d, J = 5.5 Hz, 2H), 1.56 (d, J = 3.6 Hz, 6H), 1.28 – 0.98 (m, 14H), 0.88 – 0.74 (m, 7H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.14, 171.26, 170.52, 167.98, 166.56, 152.68, 148.27, 137.70, 136.52, 135.63, 134.44, 133.04, 129.80, 129.14, 129.02, 128.87, 128.57, 128.41, 127.32, 126.32, 124.03, 122.19, 121.41, 120.35, 82.03, 56.48, 52.88, 41.40, 34.98, 32.01, 31.53, 30.29, 29.73, 29.52, 29.51, 29.44, 29.10, 28.94, 28.47, 25.08, 22.79, 14.23 ppm.

HRMS (ESI$^+$): calcd for $C_{55}H_{65}{}^{35}ClN_5O_7^+$ $[M+H]^+$ 942.4567, found 942.4557; $C_{55}H_{65}{}^{37}ClN_5O_7^+$ $[M+H]^+$ 944.4538, found 944.4552.

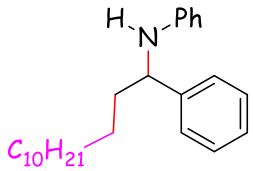


2-(1-phenyltridecyl)hexahydro-4*H*-pyrido[1,2-*a*]pyrazine-1,4(6*H*)-dione (8a)

^{1}H NMR (400 MHz, $CDCl_3$, major isomer): δ = 7.41 – 7.25 (m, 5H), 5.88 (t, J = 7.8 Hz, 1H), 4.62 (d, J = 13.3 Hz, 1H), 3.91 (d, J = 12.1 Hz, 1H), 3.79 (d, J = 17.8 Hz, 1H), 3.45 (d, J = 17.8 Hz, 1H), 2.52 (t, J = 12.9 Hz, 1H), 2.41 (d, J = 13.1 Hz, 1H), 2.03 – 1.90 (m, 3H), 1.74 – 1.53 (m, 2H), 1.48 – 1.19 (m, 22H), 0.88 (t, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, major isomer): δ = 165.51, 162.25, 138.01, 128.93, 128.21, 128.05, 59.53, 54.62, 43.64, 42.60, 32.05, 31.37, 29.77, 29.75, 29.71, 29.62, 29.56, 29.49, 28.38, 26.32, 24.56, 24.50, 22.83, 14.26 ppm.

HRMS (ESI$^+$): calcd for $C_{27}H_{43}N_2O_2^+$ $[M+H]^+$ 427.3319, found 427.3322.



***N*-(1-phenyltridecyl)aniline (8b)**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 – 7.27 (m, 4H), 7.21 (ddd, *J* = 8.5, 3.6, 1.8 Hz, 1H), 7.07 (dd, *J* = 8.4, 7.4 Hz, 2H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 2H), 4.28 (t, *J* = 6.8 Hz, 1H), 1.84 – 1.72 (m, 2H), 1.25 (d, *J* = 6.7 Hz, 20H), 0.88 (t, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.61, 144.49, 129.22, 128.65, 126.97, 126.52, 117.25, 113.38, 58.43, 39.13, 32.07, 29.85, 29.79, 29.77, 29.72, 29.66, 29.65, 29.50, 26.50, 22.84, 14.27 ppm.

HRMS (ESI^+): calcd for $C_{25}H_{38}N^+$ $[M+H]^+$ 352.2999, found 352.2990.

VIII. References

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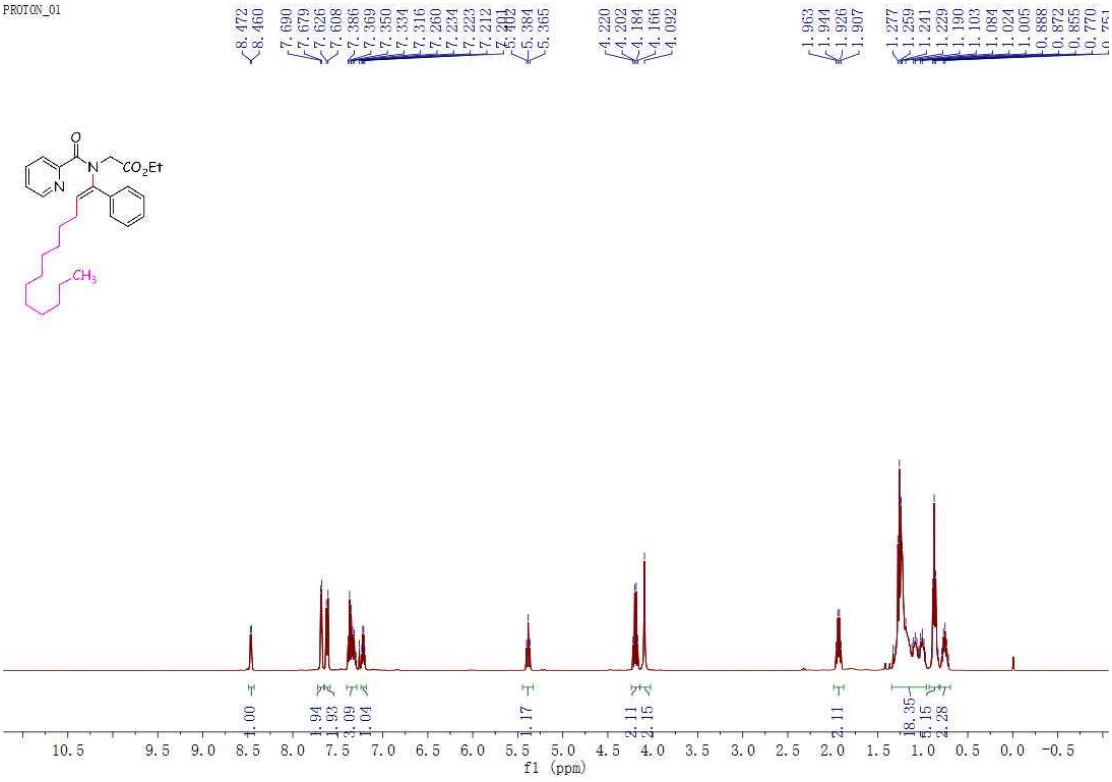
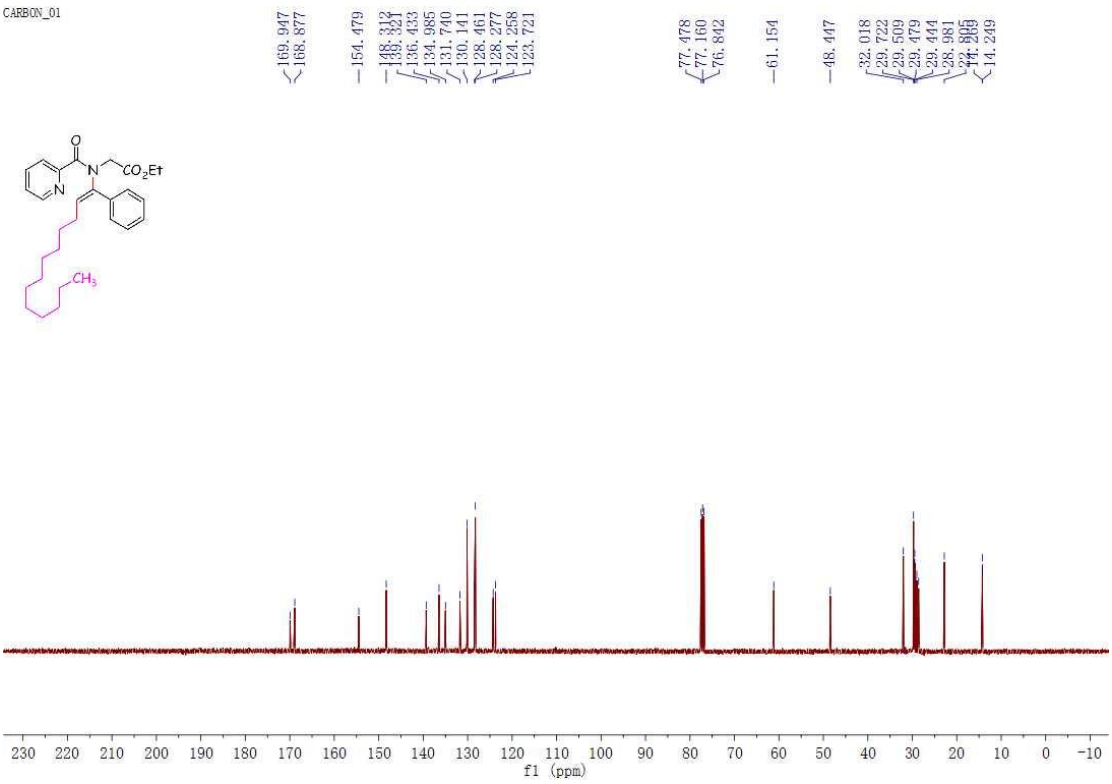
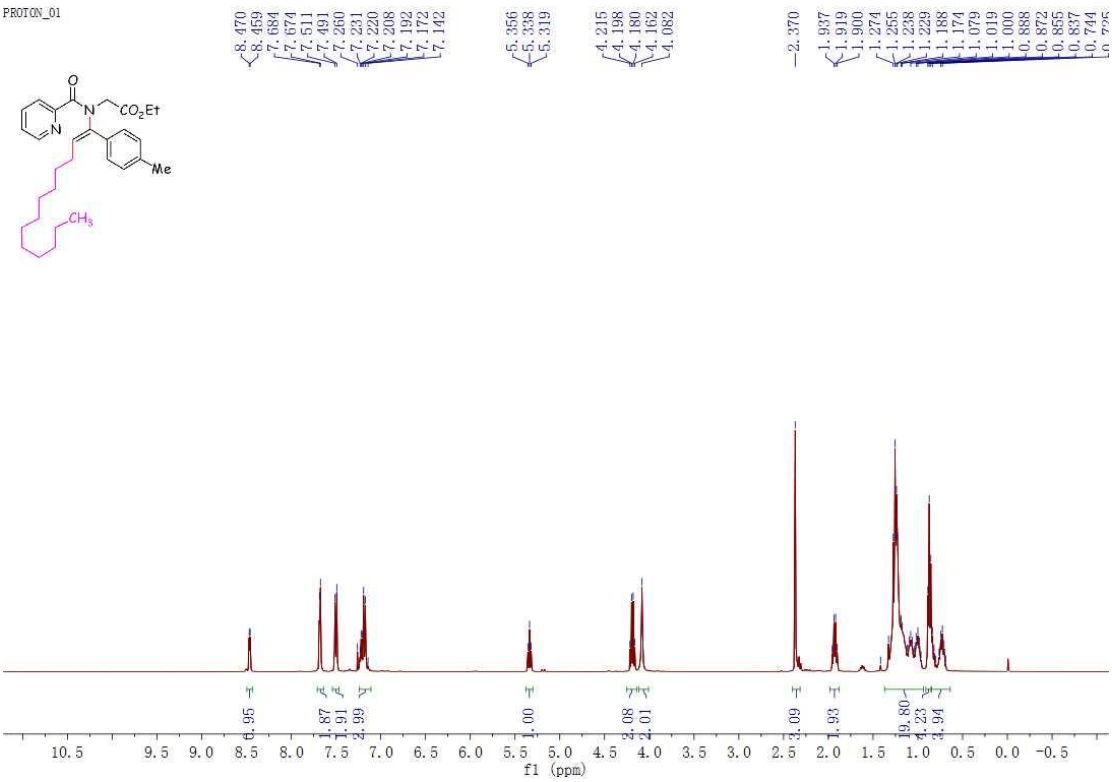
IX. Copies of NMR spectra



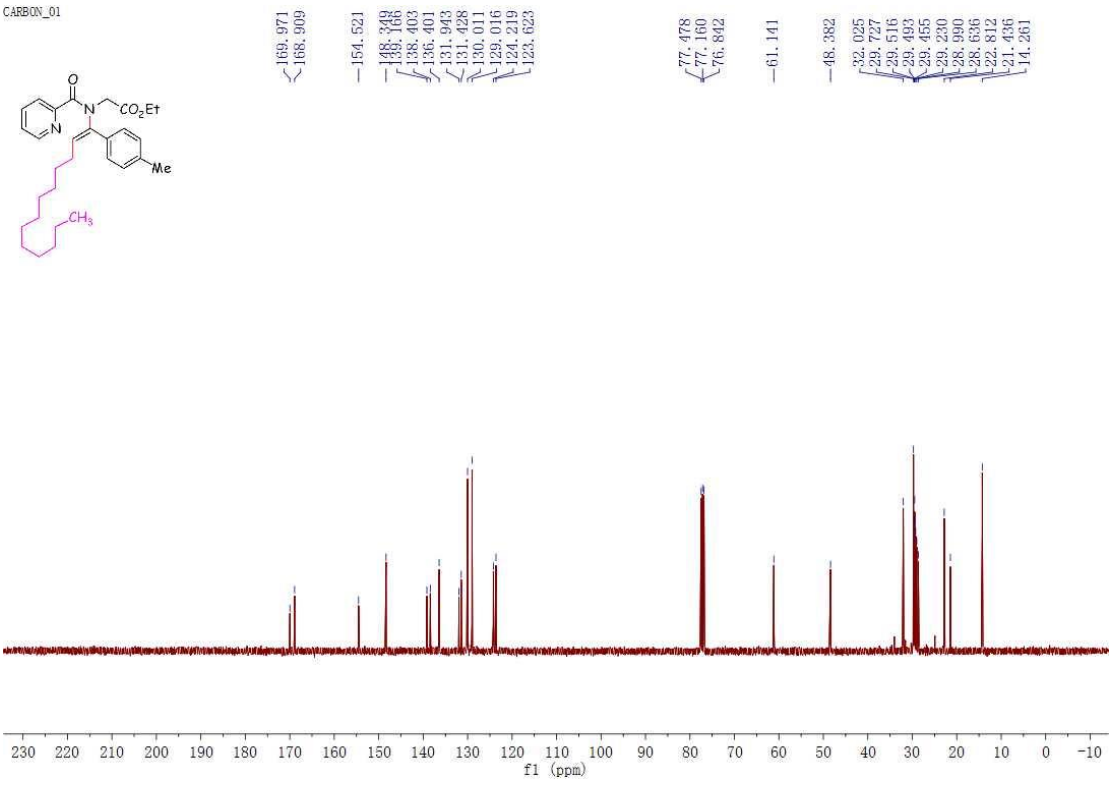
^{1}H NMR spectra for compound **4a** (400 MHz, $CDCl_3$)



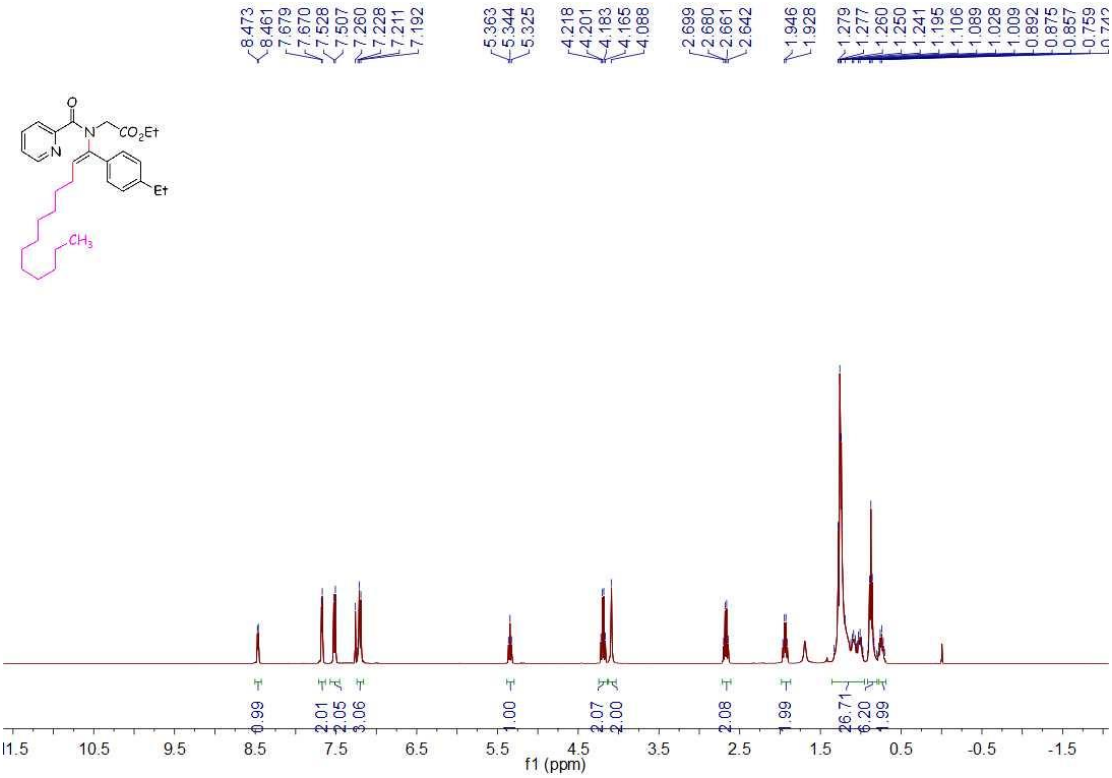
^{13}C NMR spectra for compound **4a** (100 MHz, $CDCl_3$)



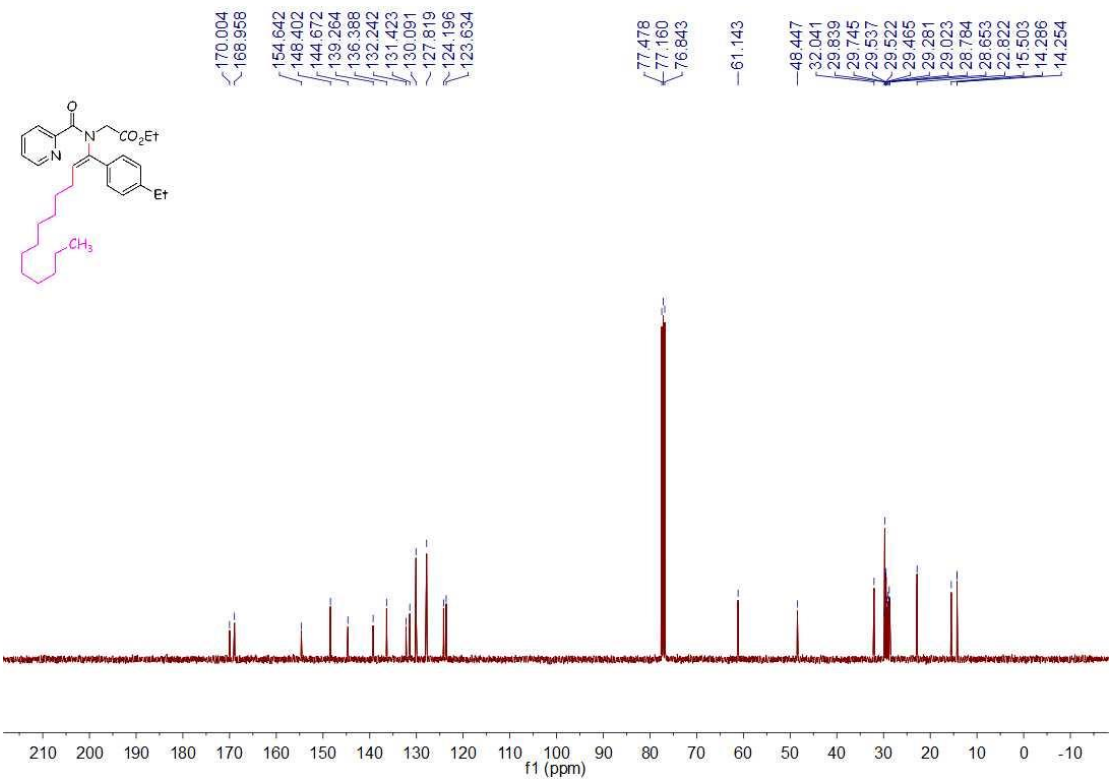
^{1}H NMR spectra for compound **4b** (400 MHz, $CDCl_3$)



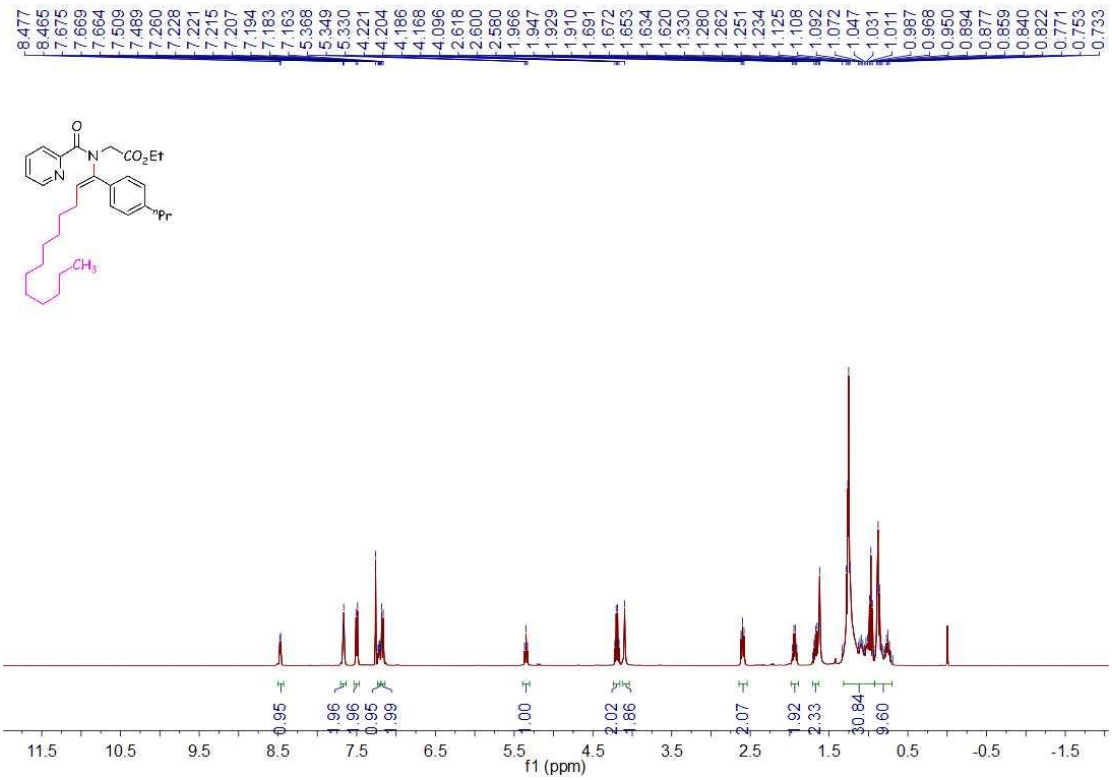
^{13}C NMR spectra for compound **4b** (100 MHz, $CDCl_3$)



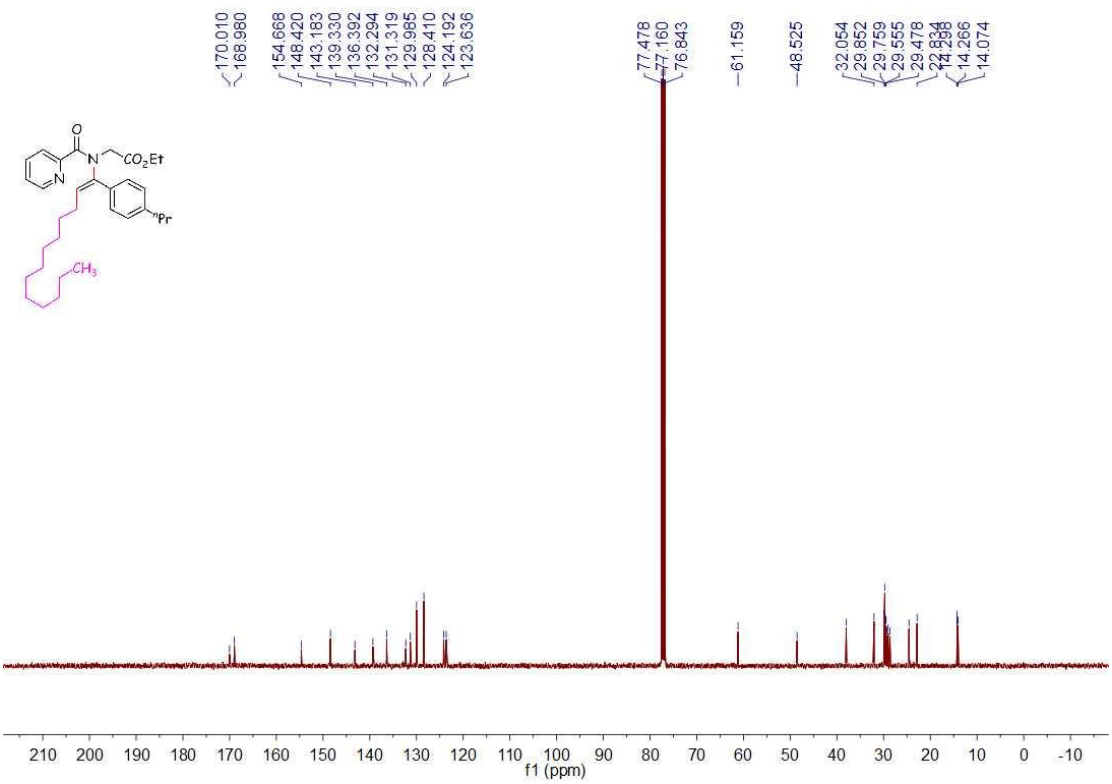
^{1}H NMR spectra for compound **4c** (400 MHz, $CDCl_3$)



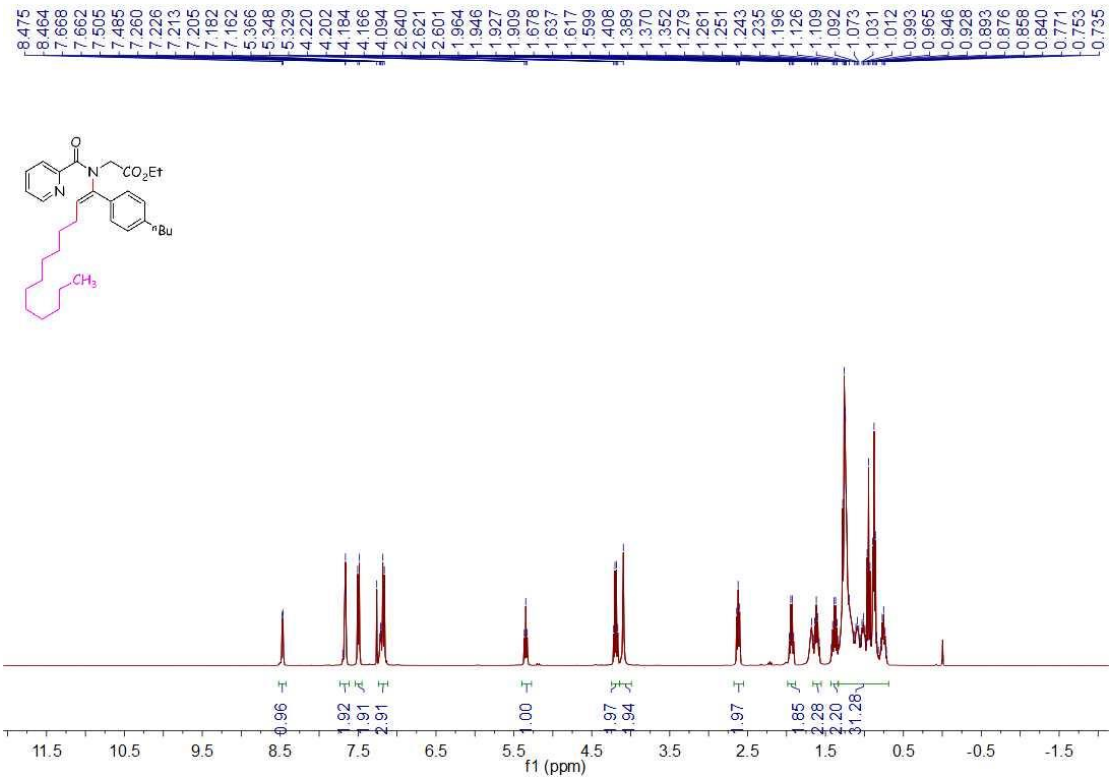
^{13}C NMR spectra for compound **4c** (100 MHz, $CDCl_3$)



^{1}H NMR spectra for compound **4d** (400 MHz, $CDCl_3$)



^{13}C NMR spectra for compound **4d** (100 MHz, $CDCl_3$)



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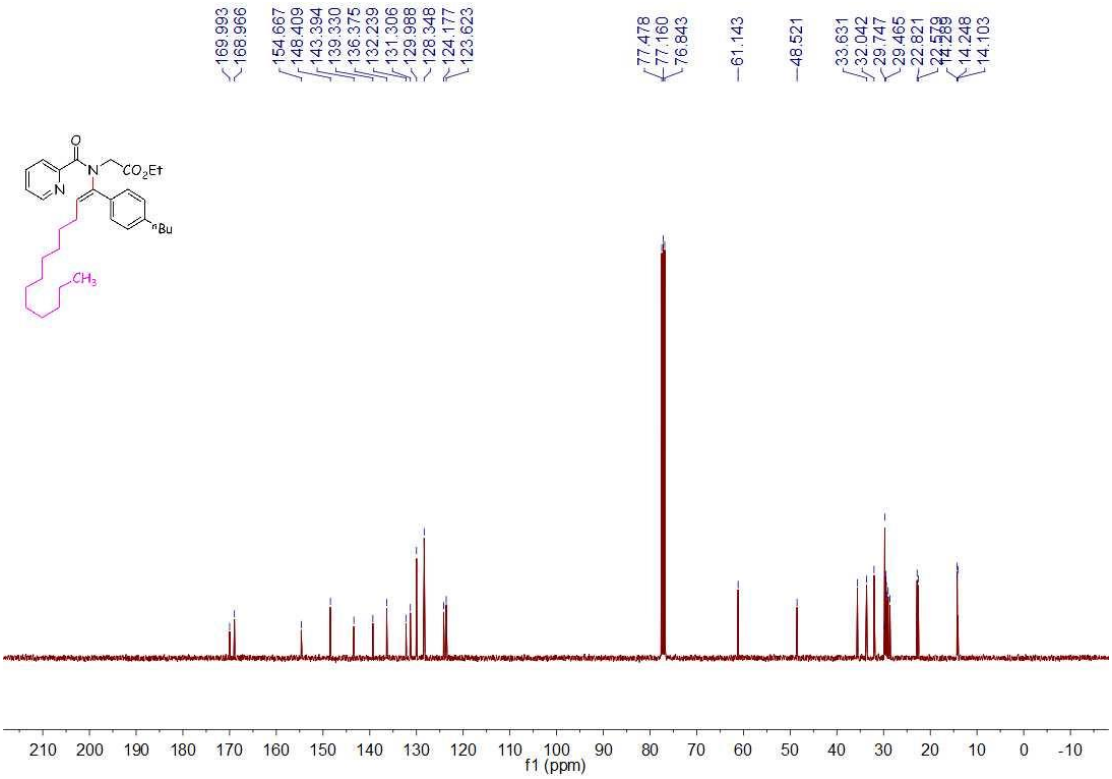

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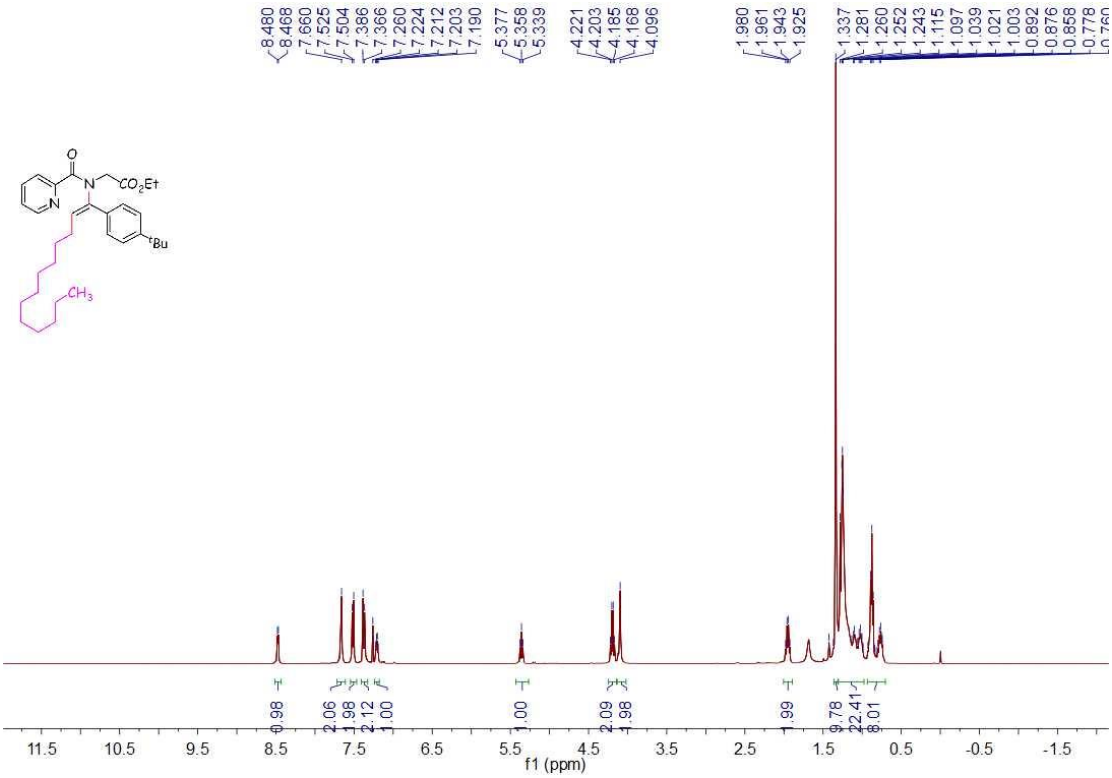
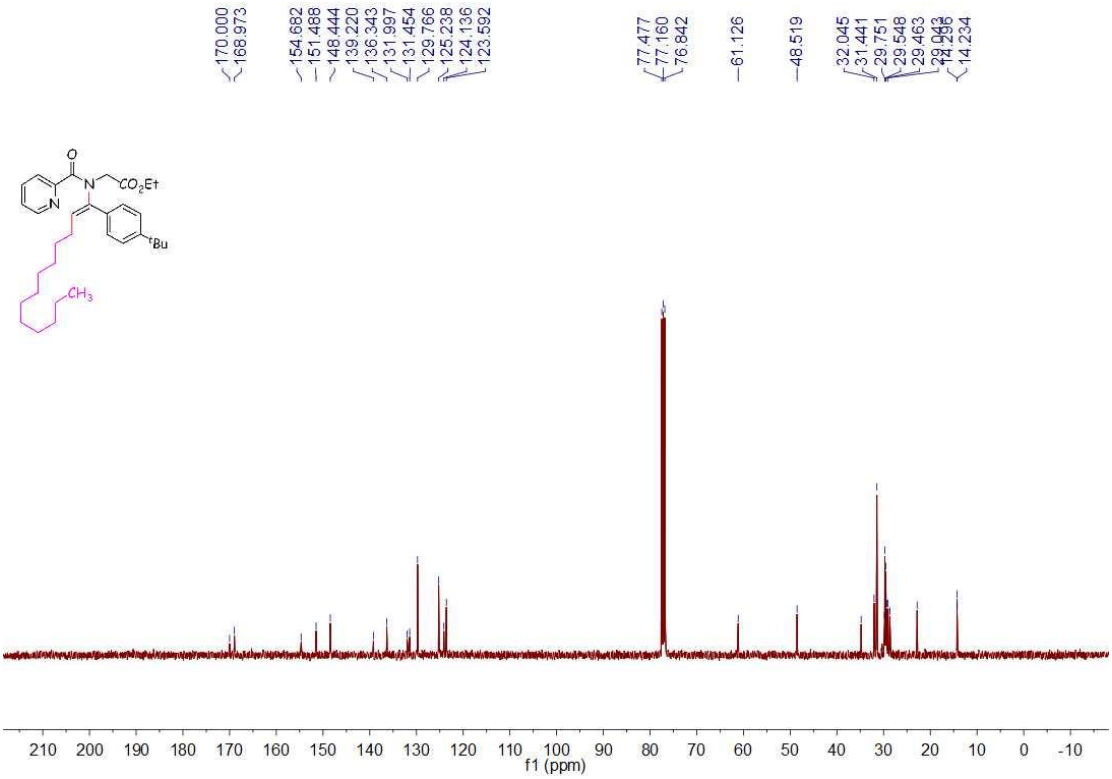
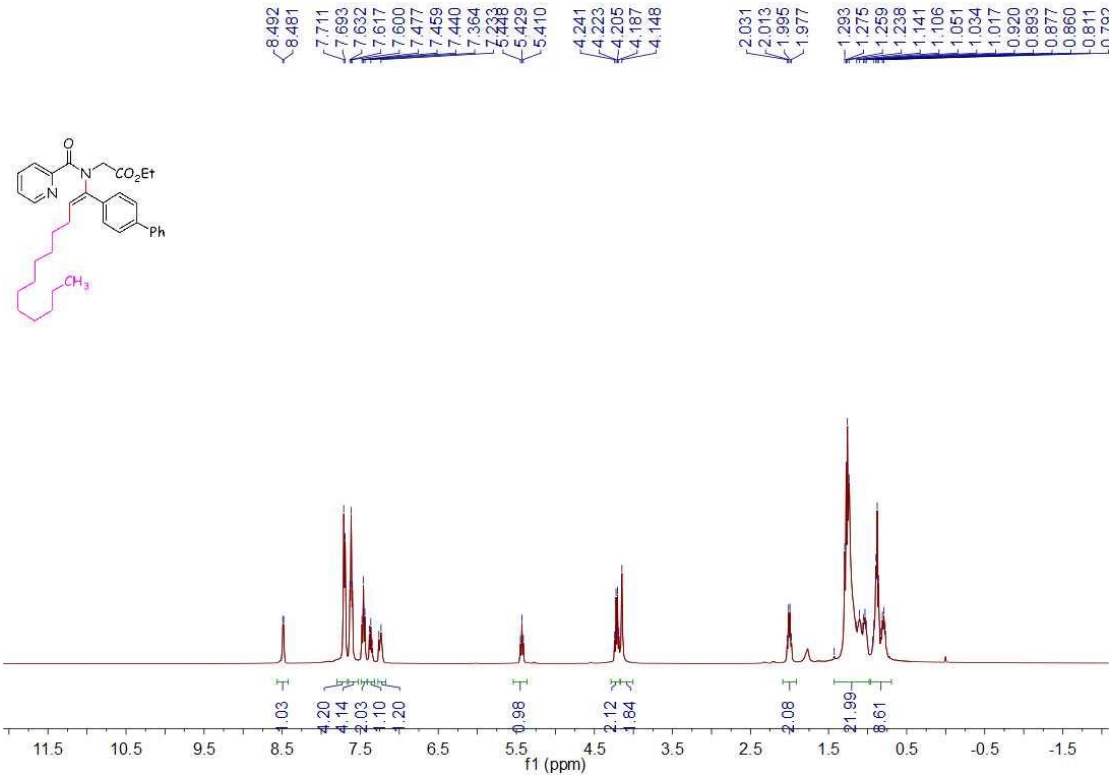


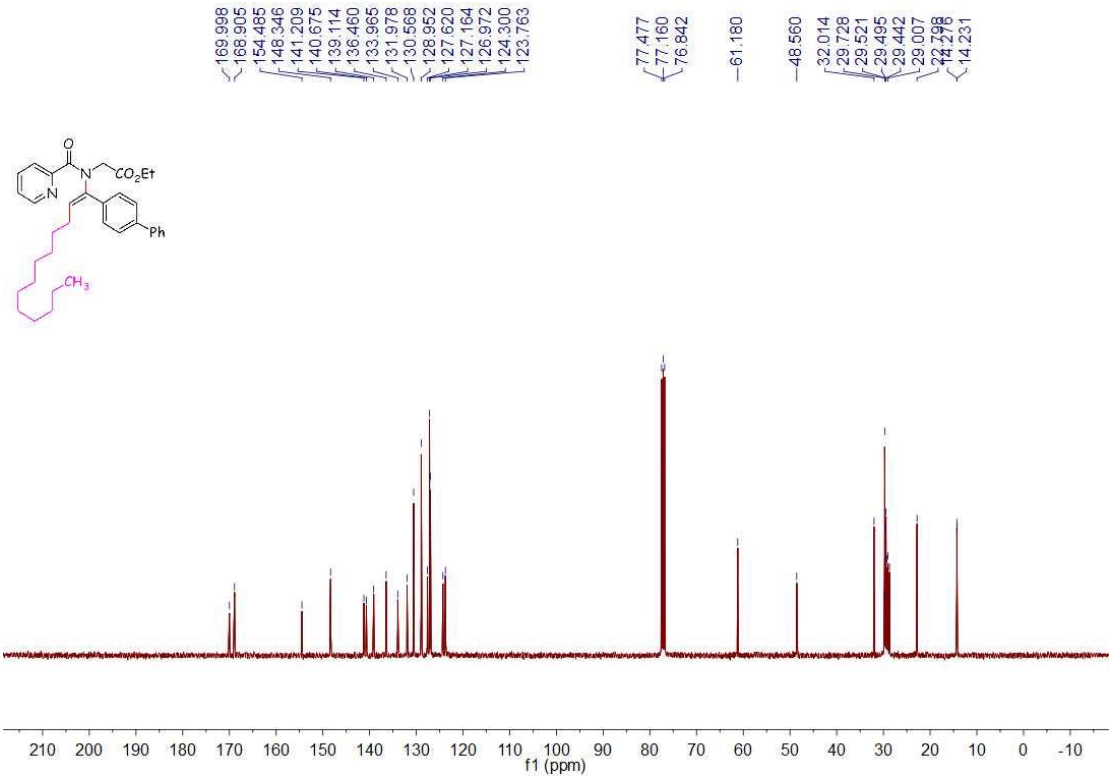
^{1}H NMR spectra for compound **4f** (400 MHz, $CDCl_3$)



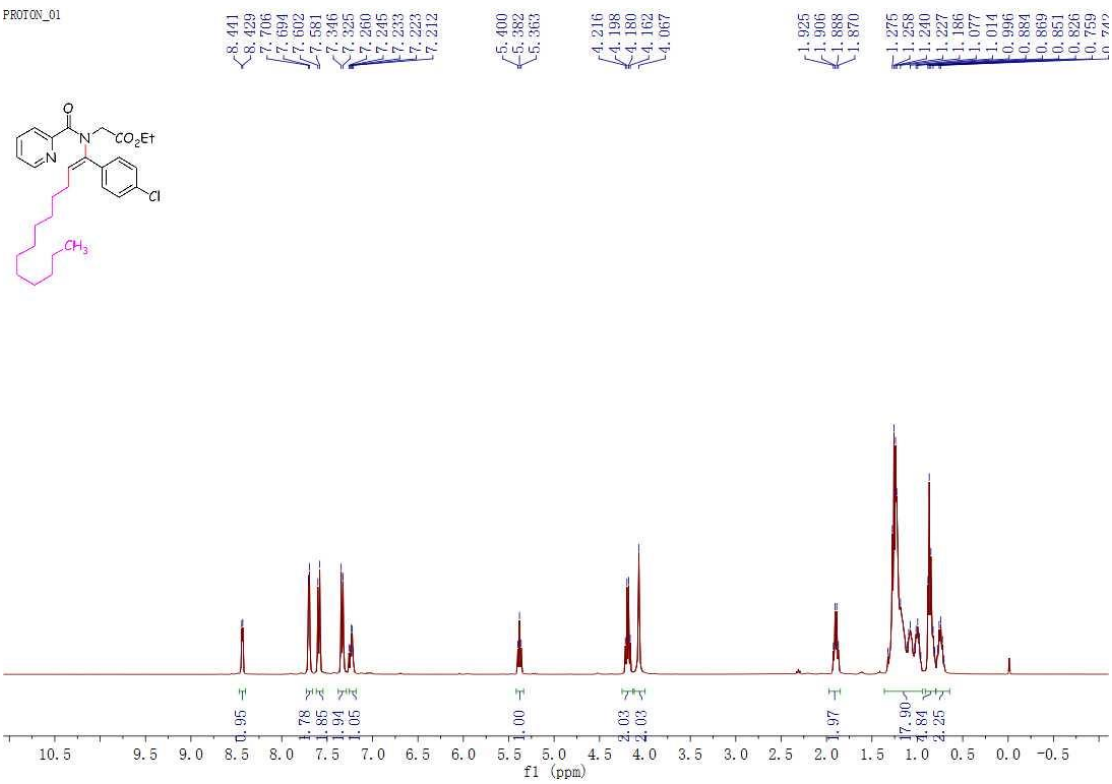
^{13}C NMR spectra for compound **4f** (100 MHz, $CDCl_3$)



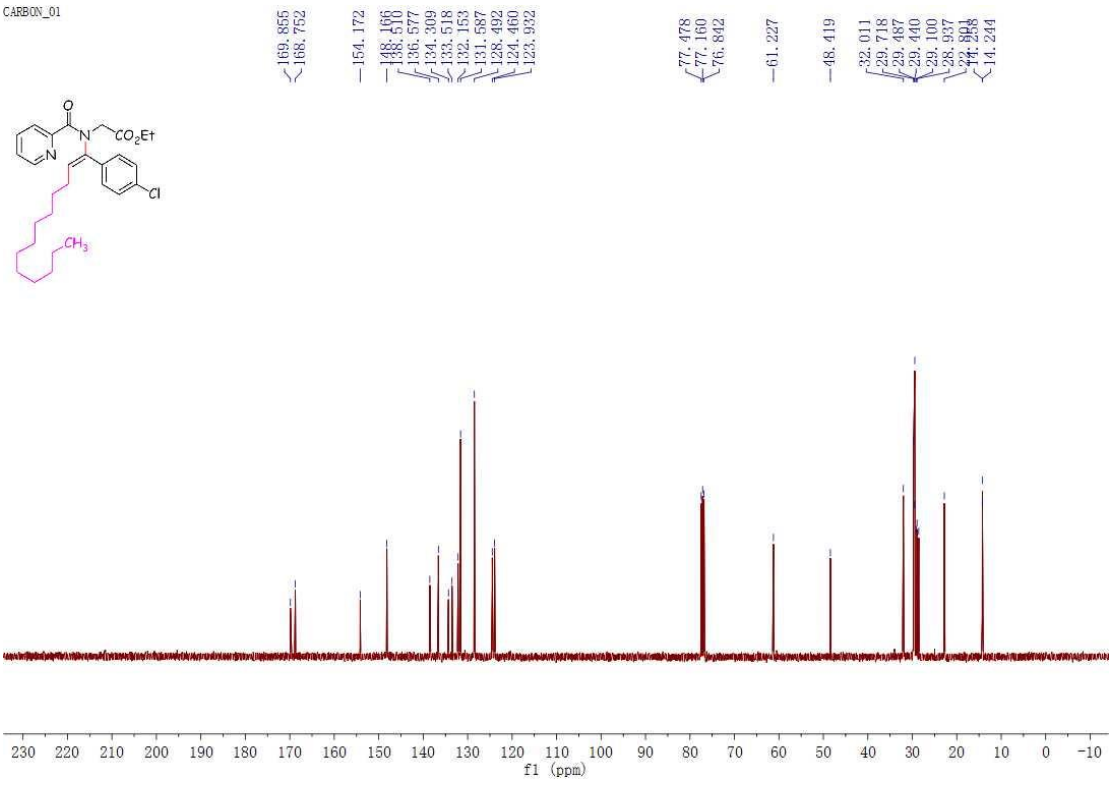
^{1}H NMR spectra for compound **4g** (400 MHz, $CDCl_3$)



^{13}C NMR spectra for compound **4g** (100 MHz, $CDCl_3$)



^{1}H NMR spectra for compound **4h** (400 MHz, $CDCl_3$)



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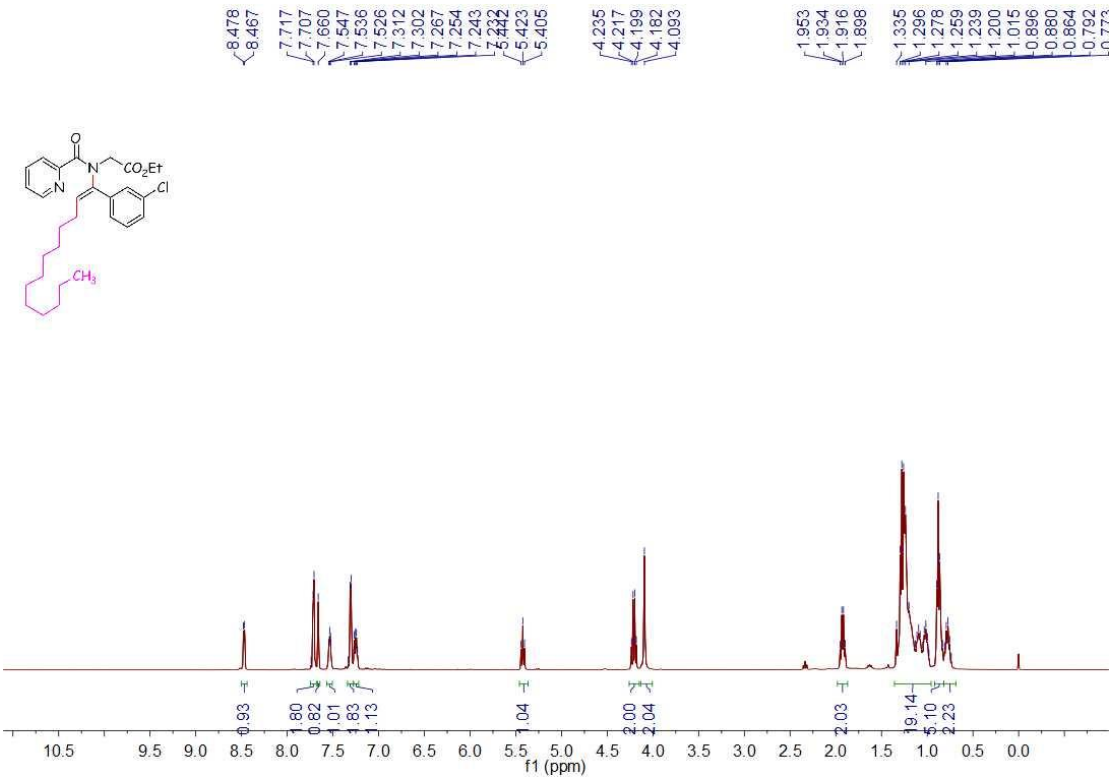
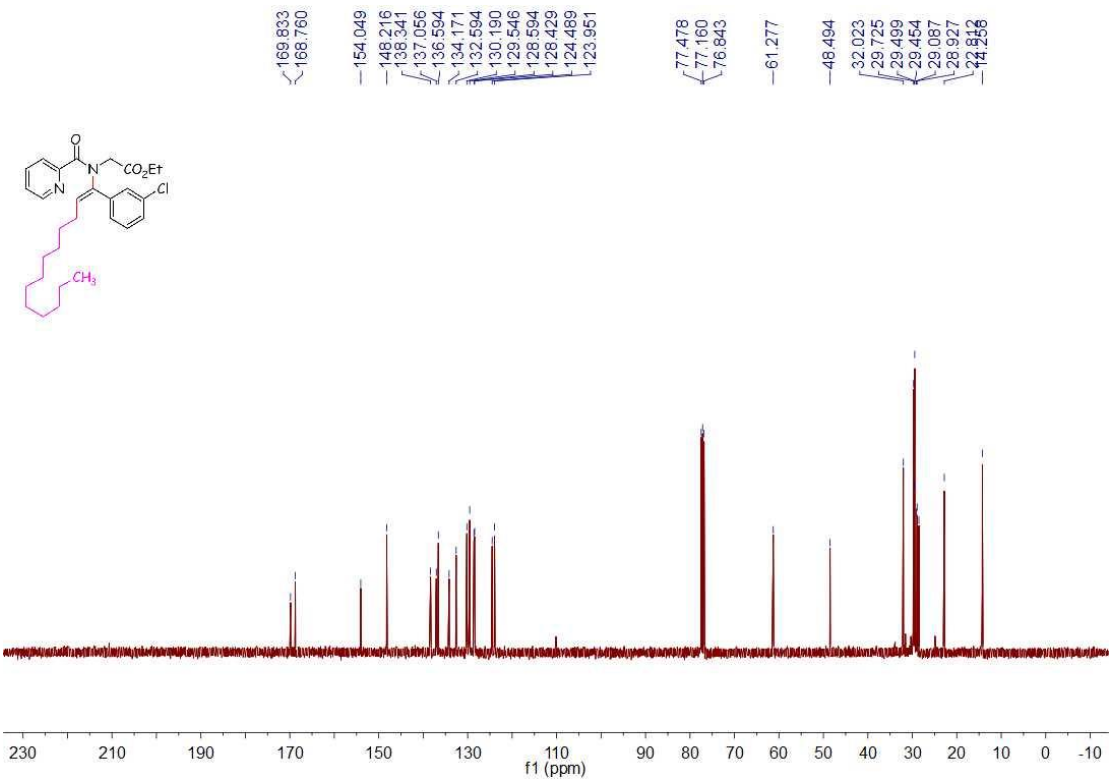
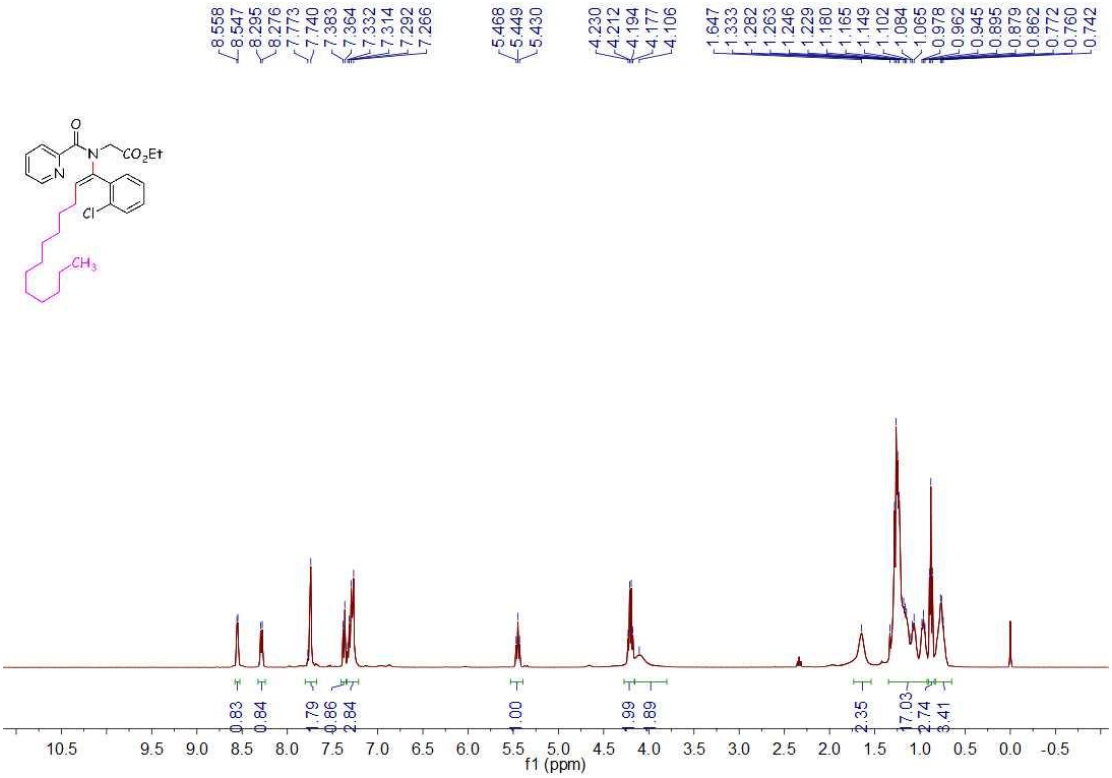


^{1}H NMR spectra for compound **4i** (400 MHz, $CDCl_3$)



^{13}C NMR spectra for compound **4i** (100 MHz, $CDCl_3$)



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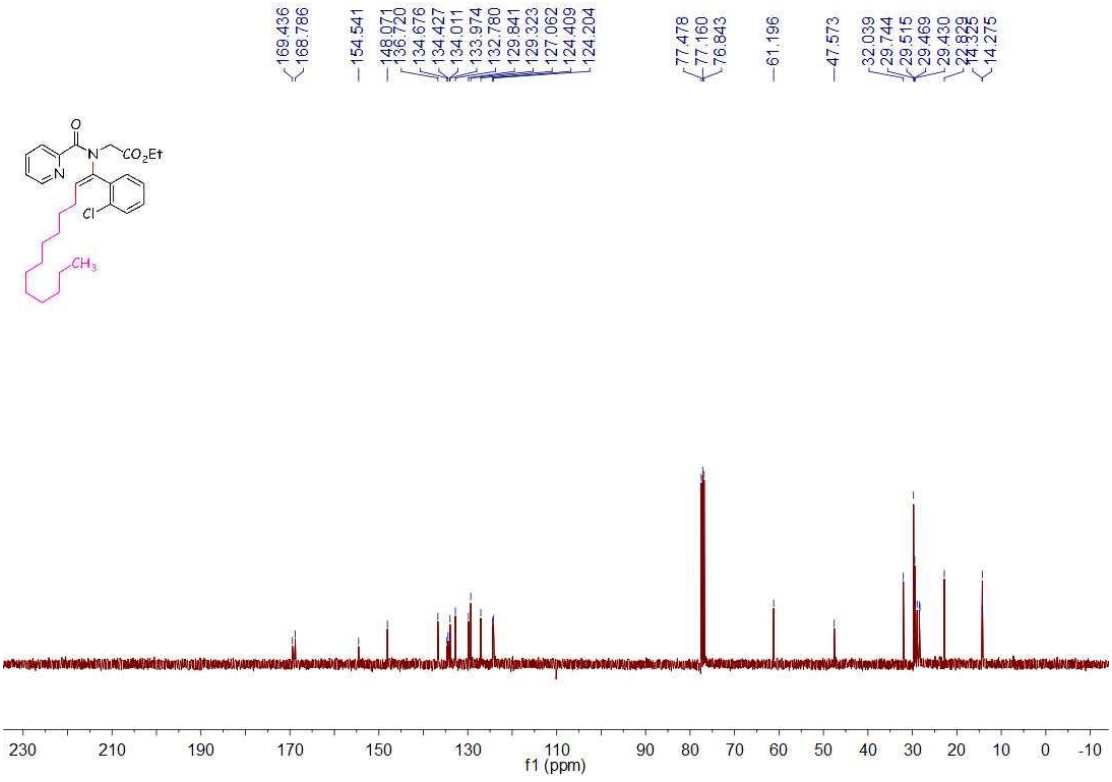

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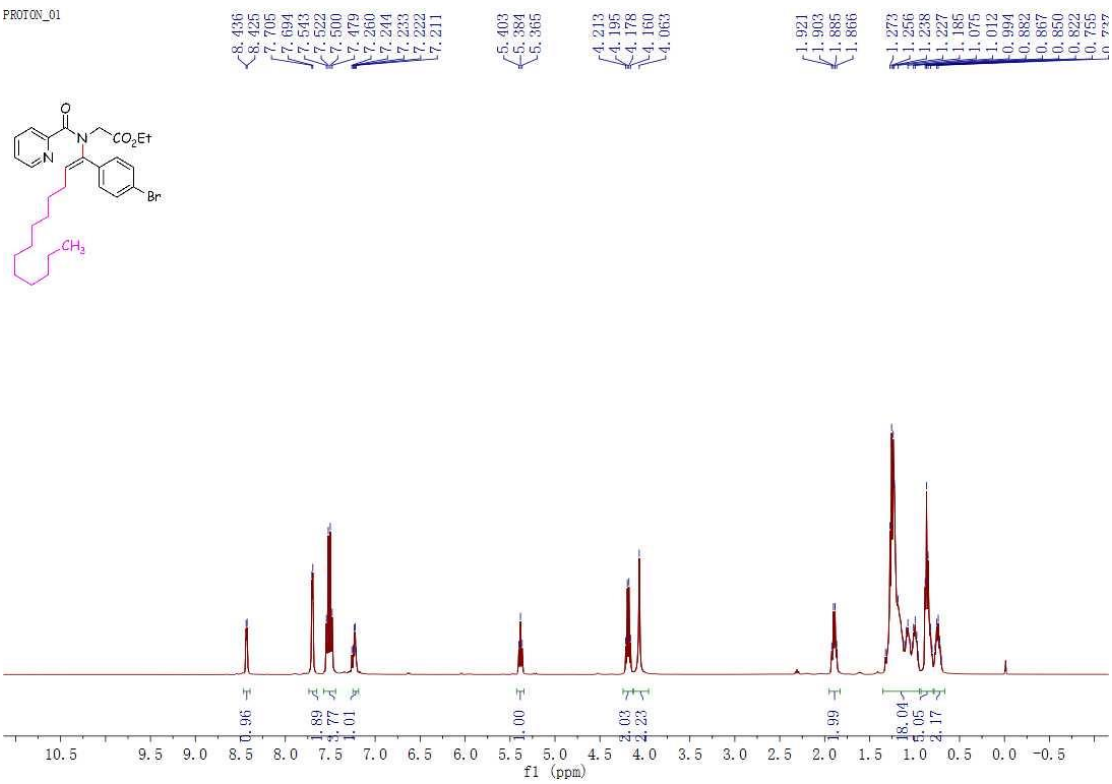
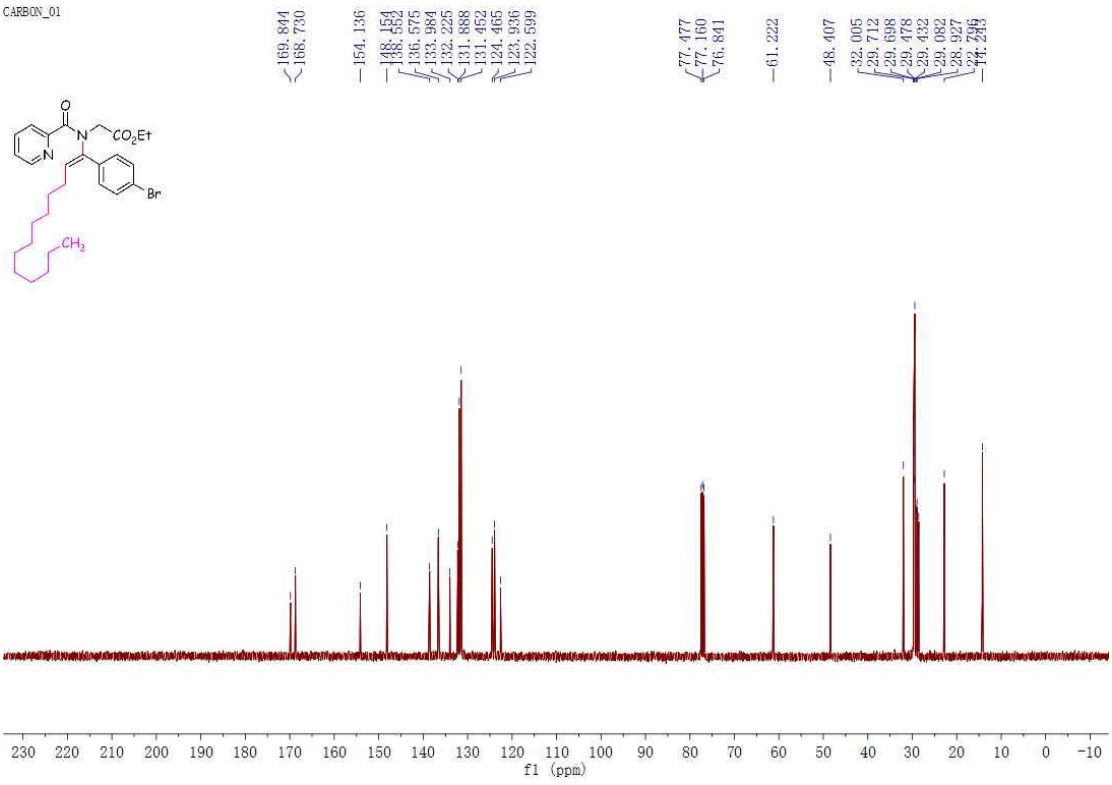
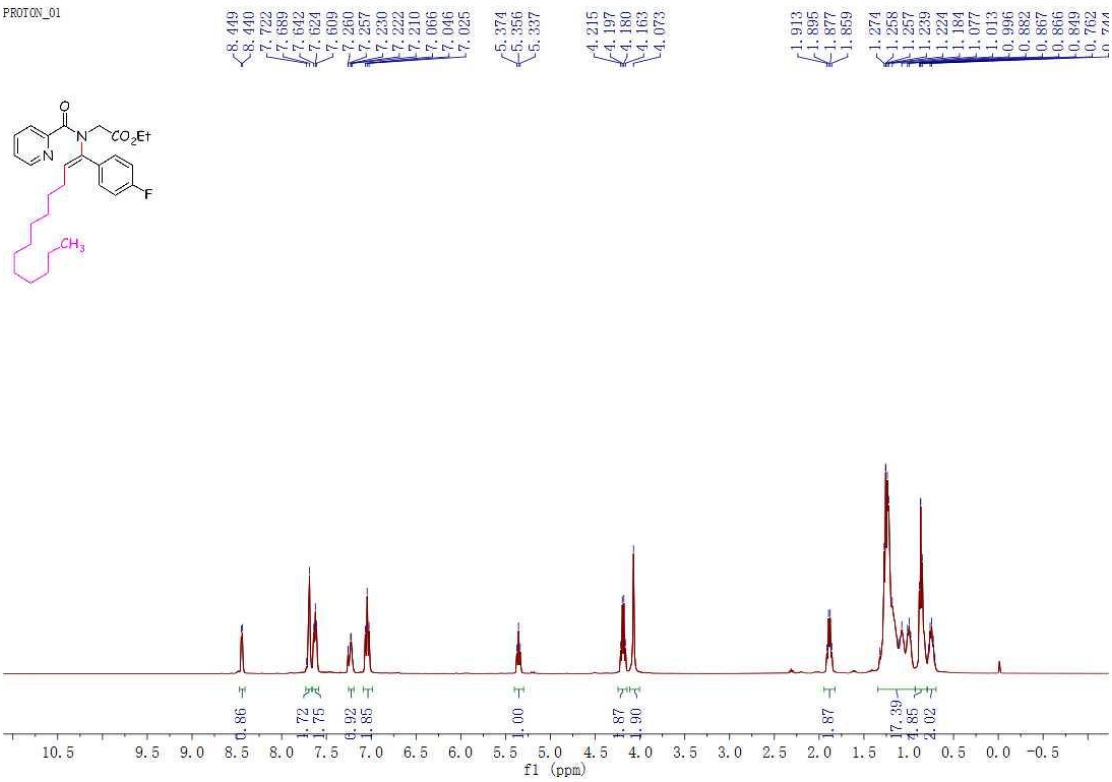


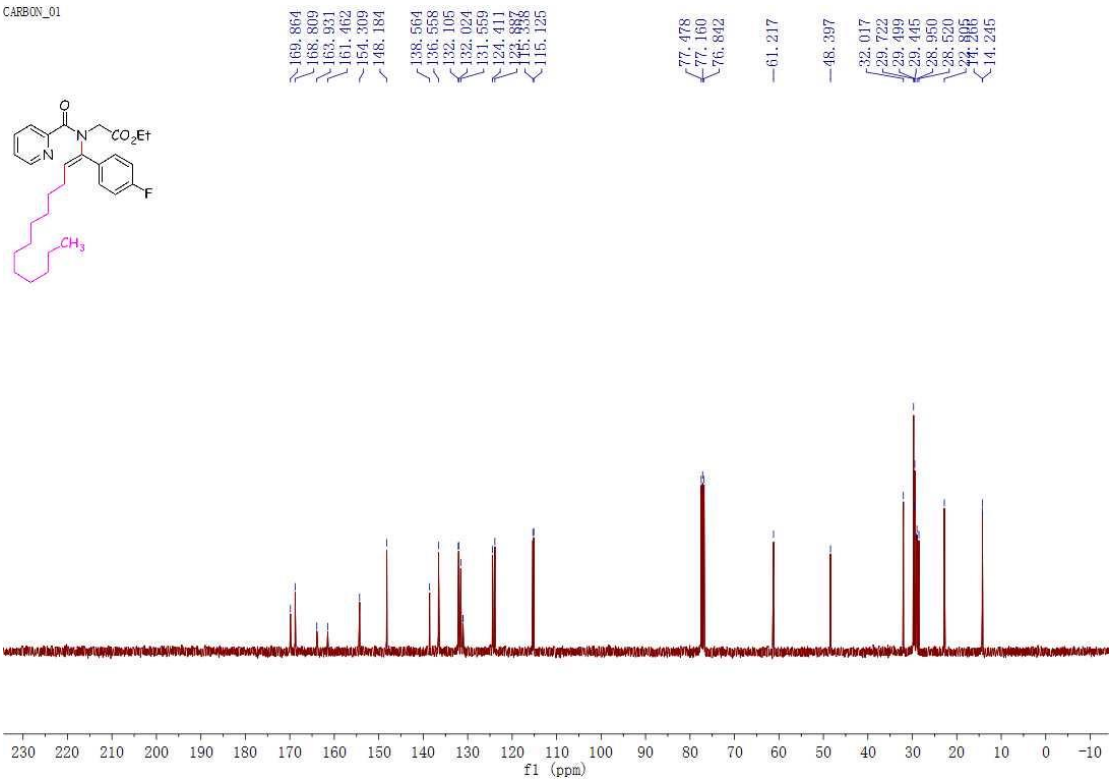
^{1}H NMR spectra for compound **4k** (400 MHz, $CDCl_3$)



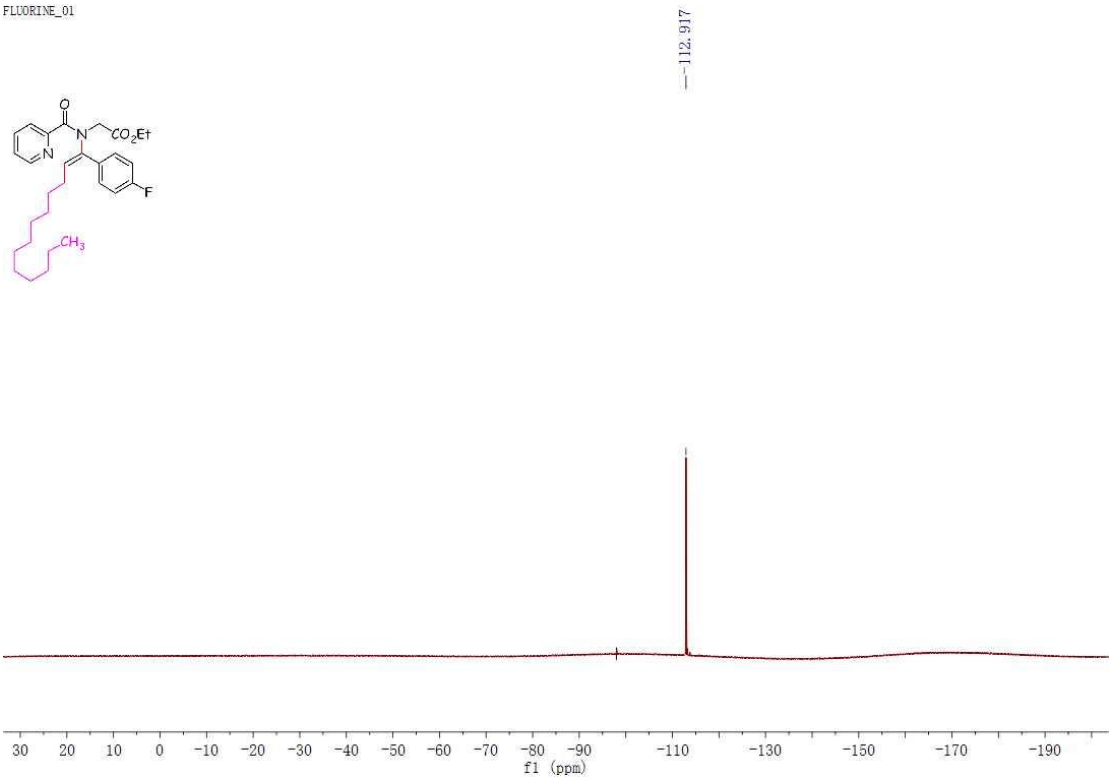
^{13}C NMR spectra for compound **4k** (100 MHz, $CDCl_3$)



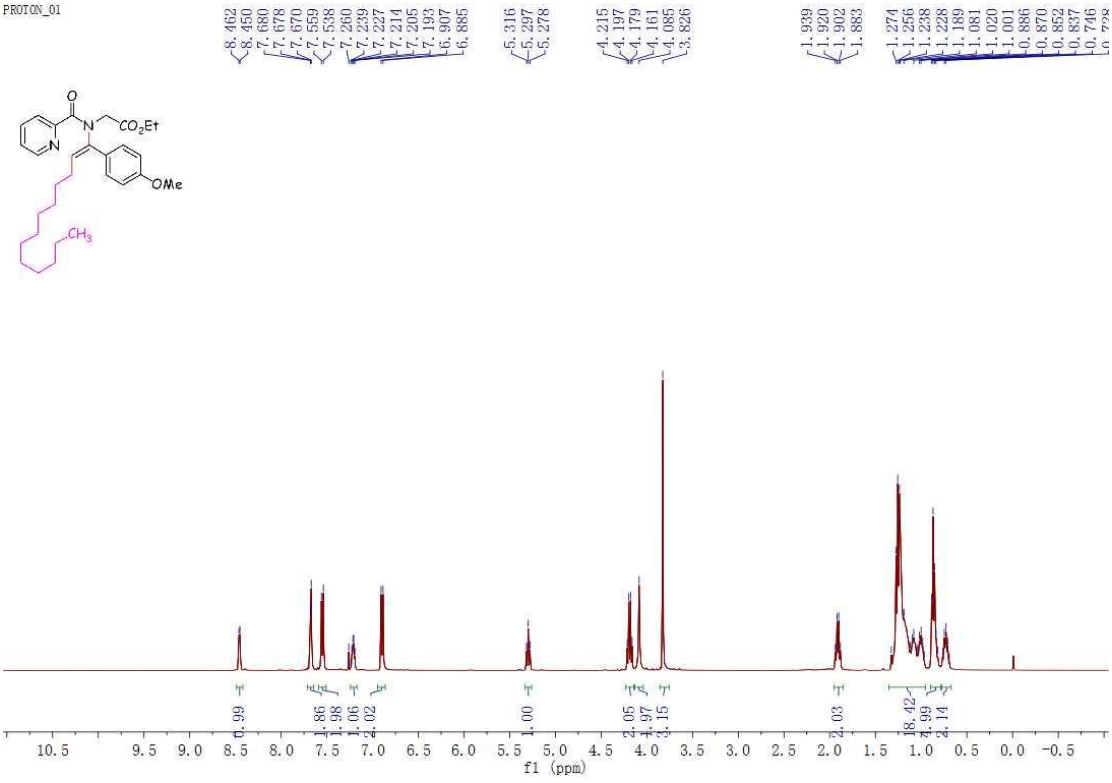
^{1}H NMR spectra for compound **4l** (400 MHz, $CDCl_3$)



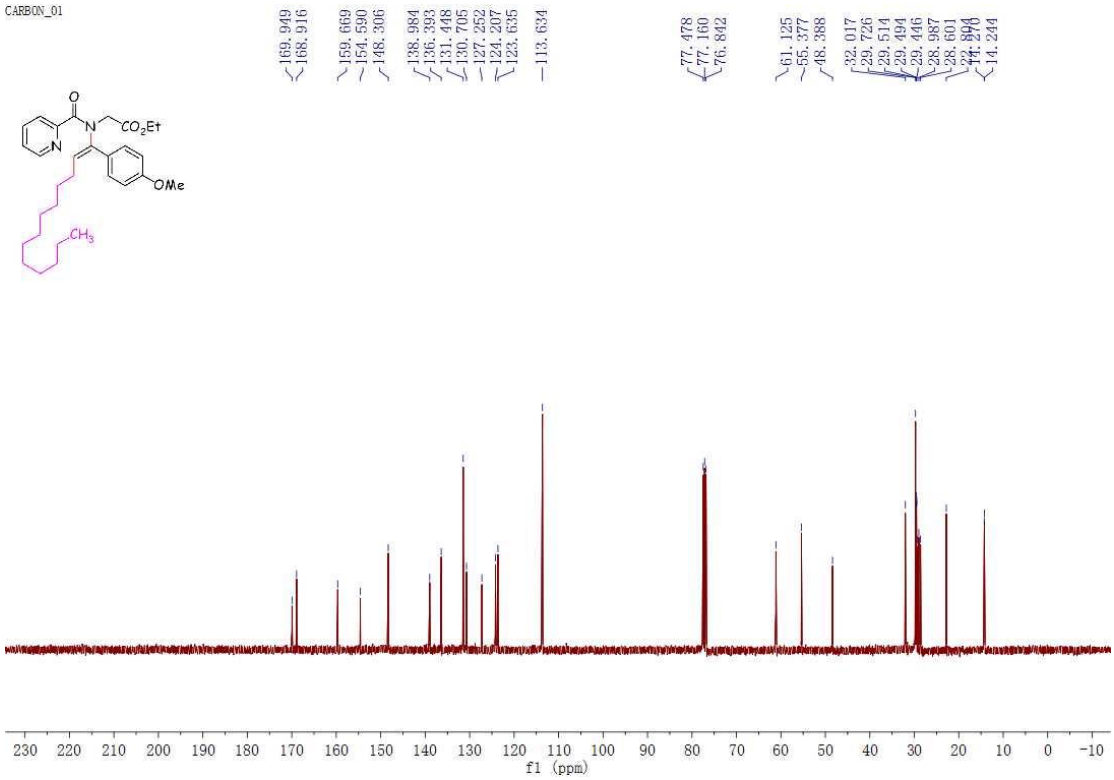
^{13}C NMR spectra for compound **4l** (100 MHz, $CDCl_3$)



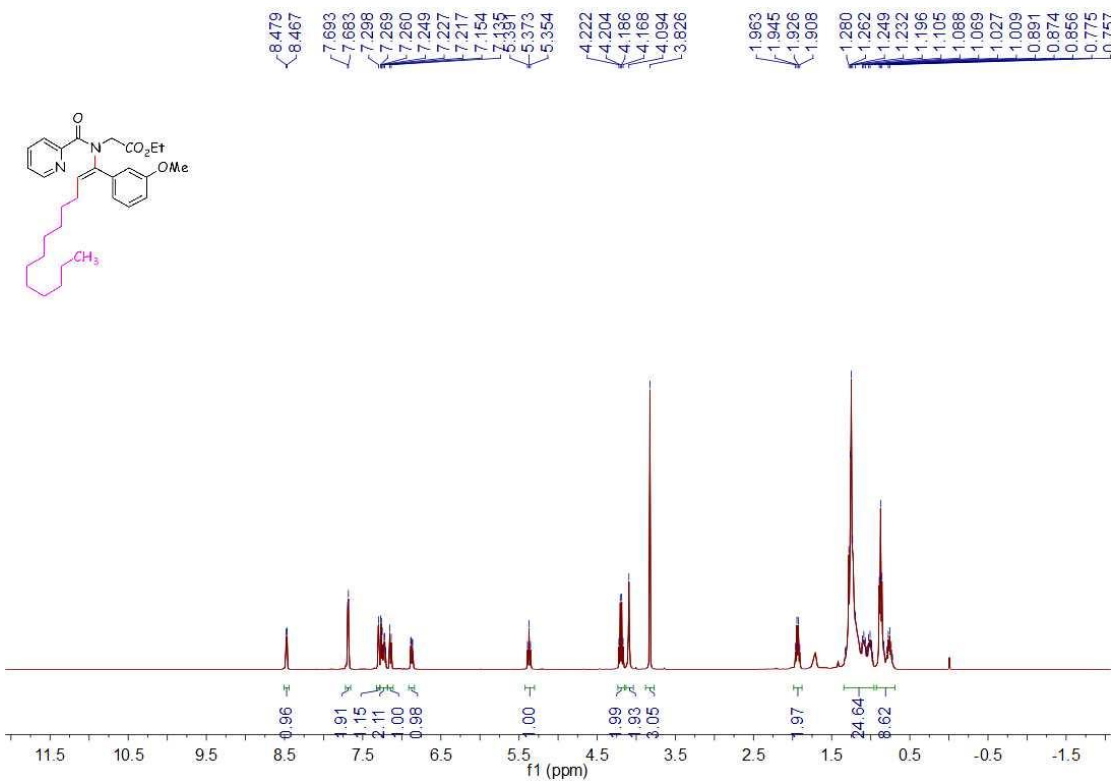
^{19}F NMR spectra for compound **4l** (376 MHz, $CDCl_3$)



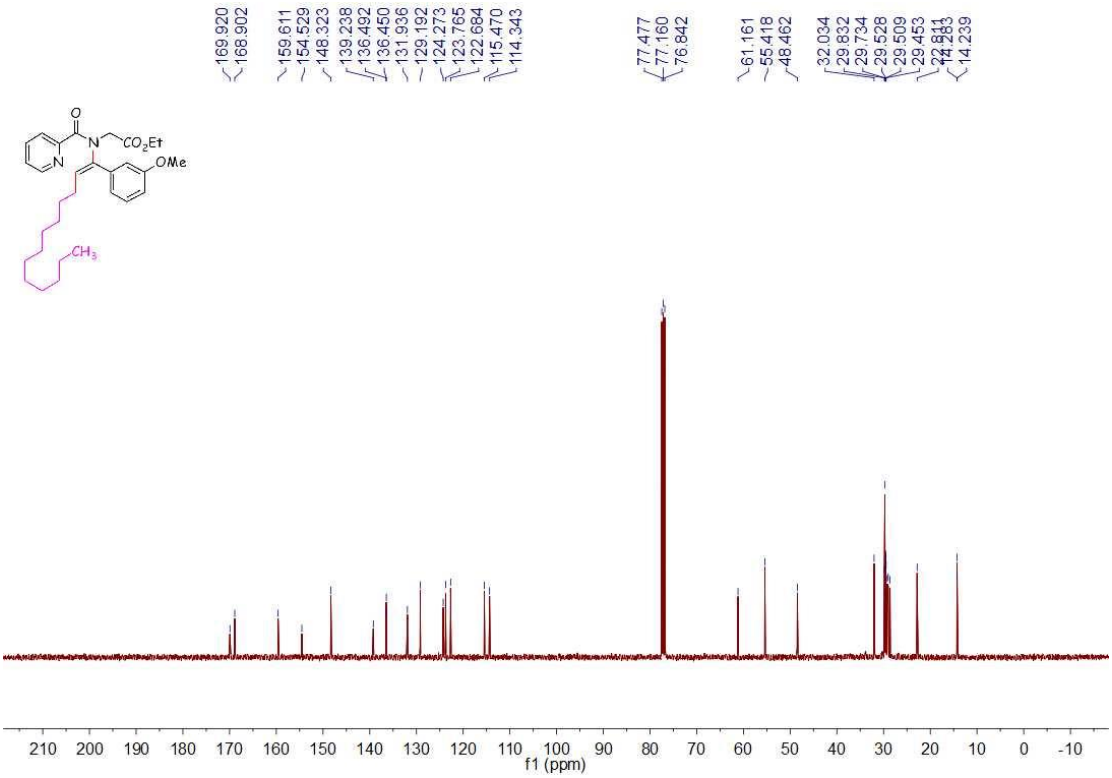
^{1}H NMR spectra for compound **4m** (400 MHz, $CDCl_3$)



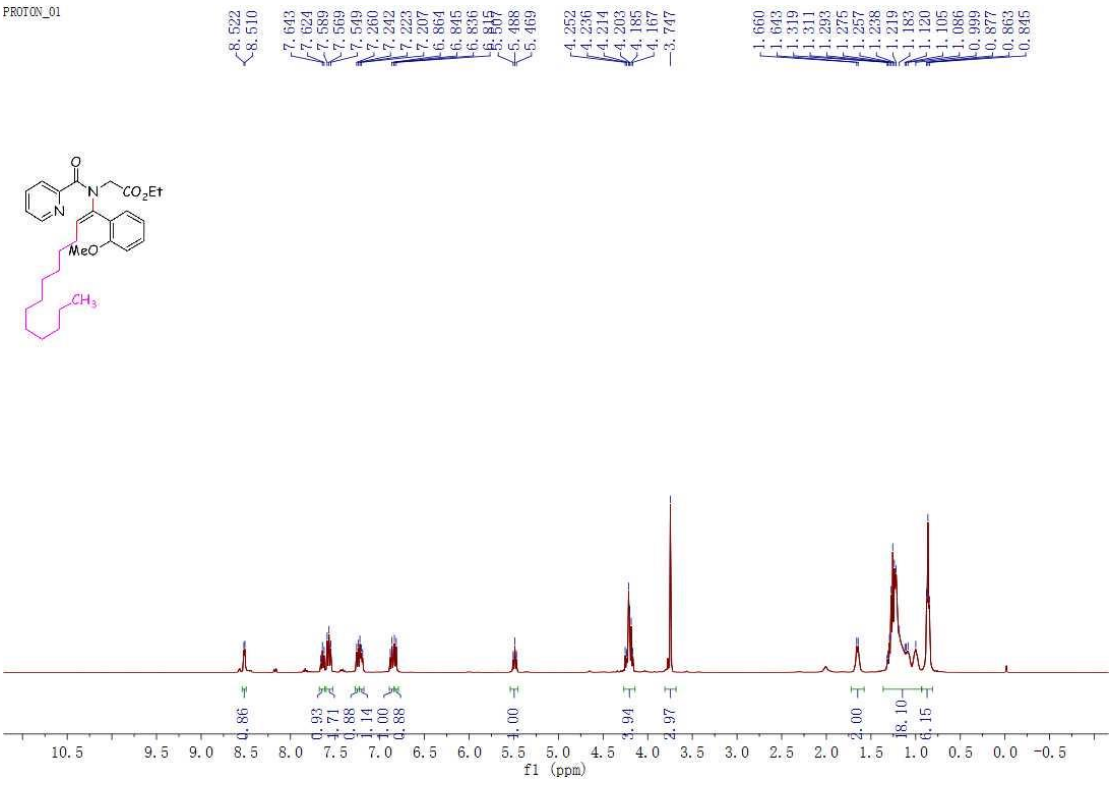
^{13}C NMR spectra for compound **4m** (100 MHz, $CDCl_3$)



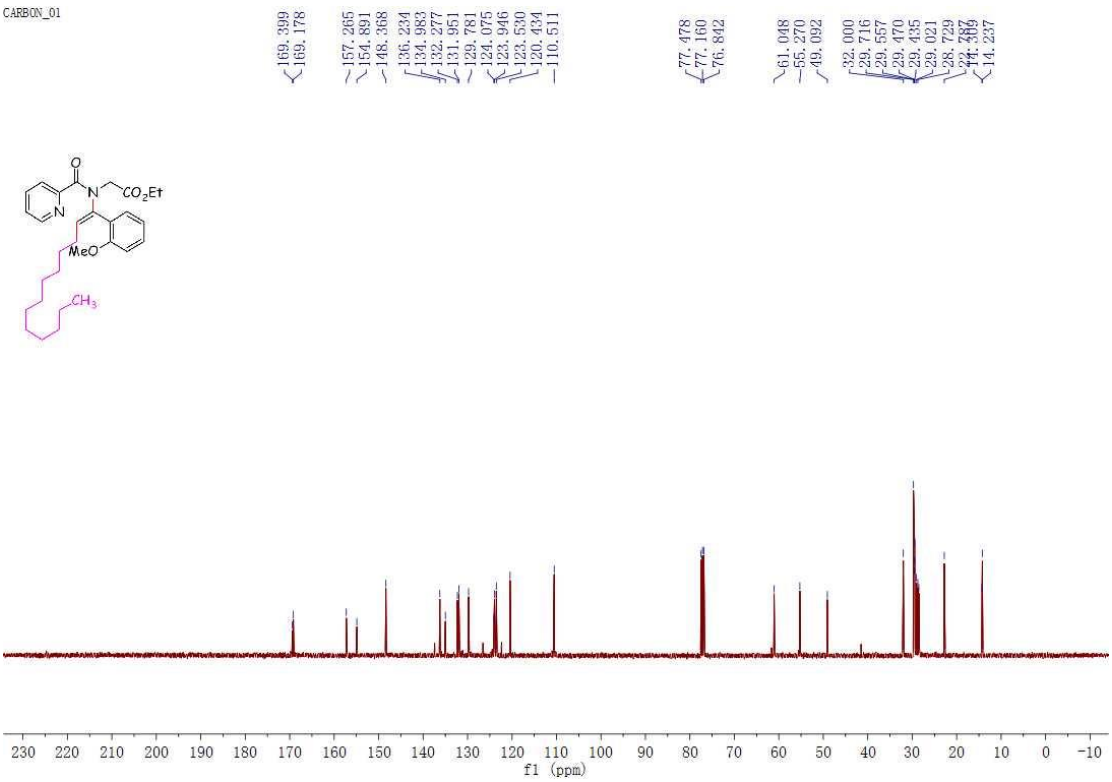
^{1}H NMR spectra for compound **4n** (400 MHz, $CDCl_3$)



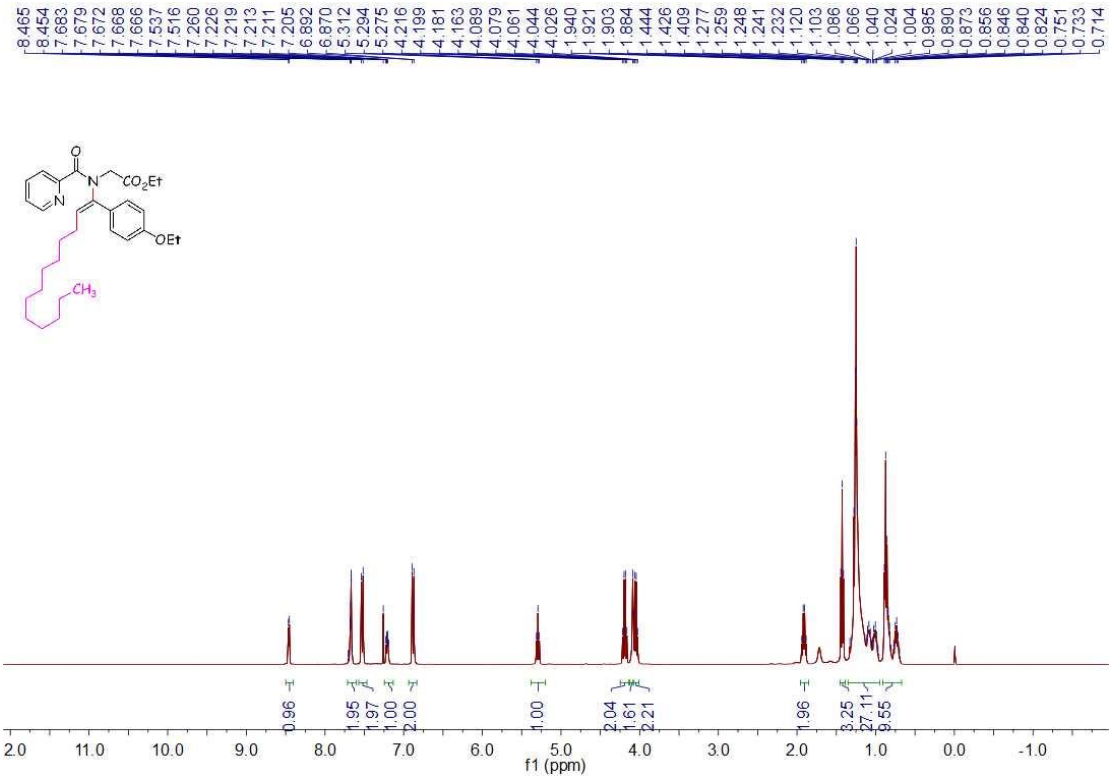
^{13}C NMR spectra for compound **4n** (100 MHz, $CDCl_3$)



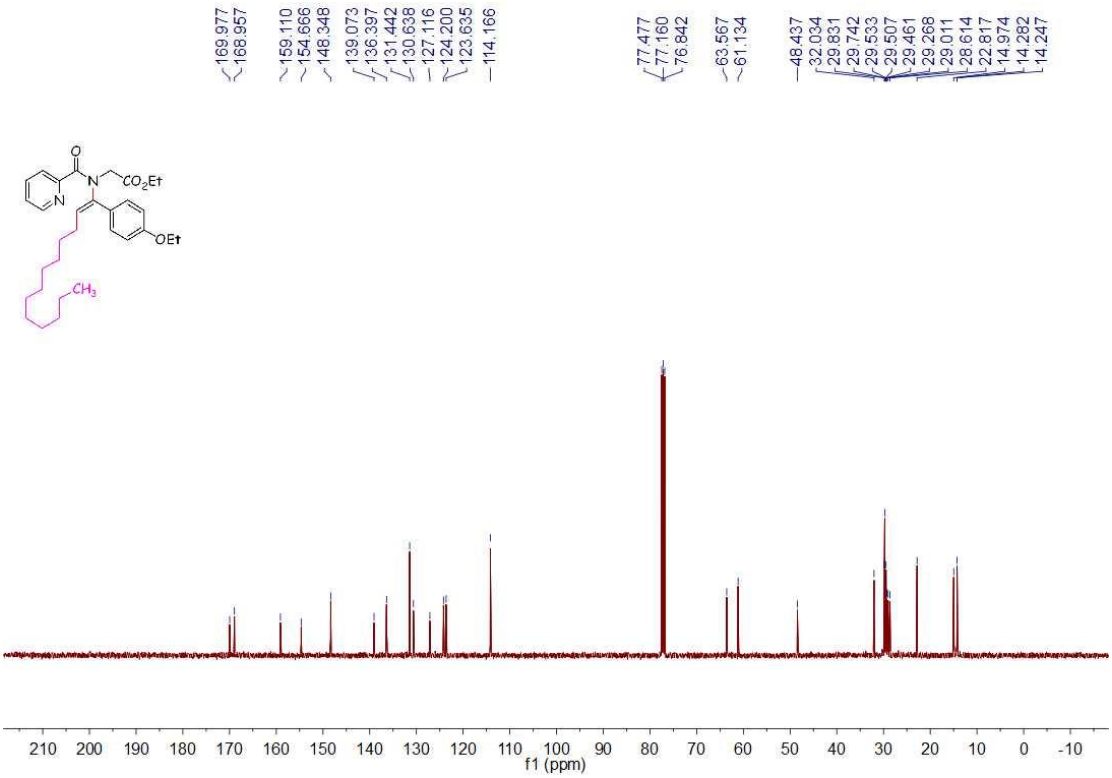
^{1}H NMR spectra for compound **4o** (400 MHz, $CDCl_3$)



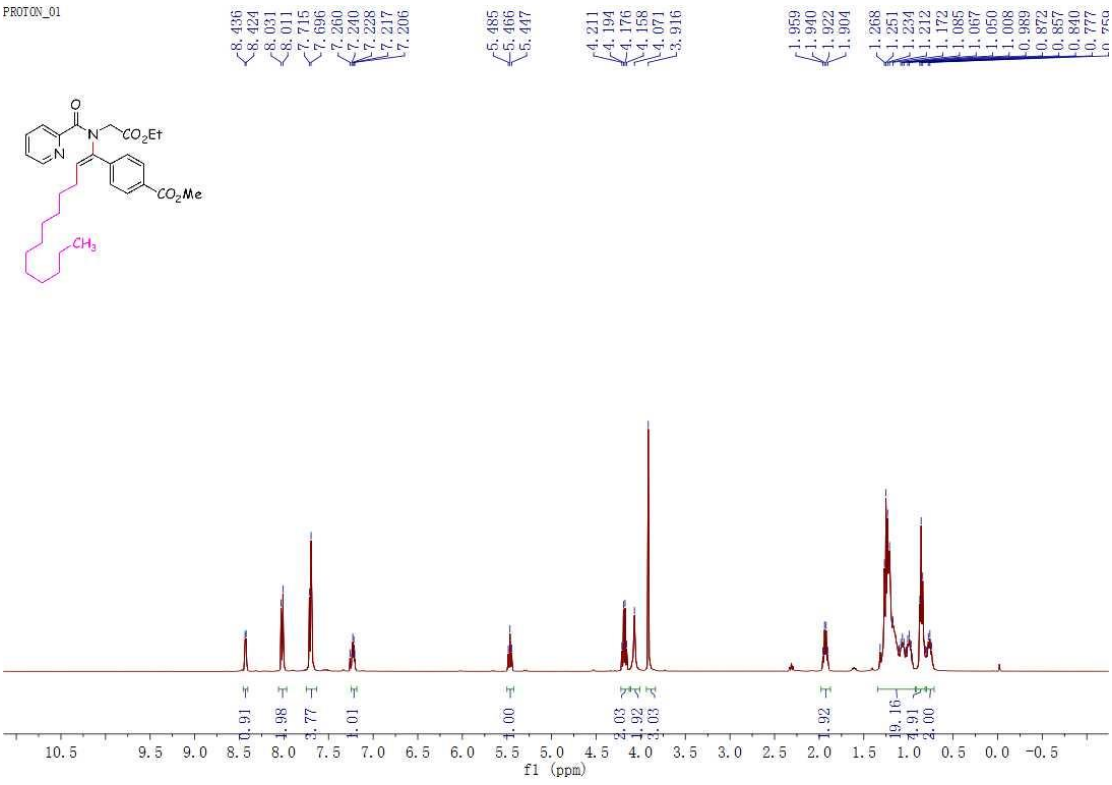
^{13}C NMR spectra for compound **4o** (100 MHz, $CDCl_3$)



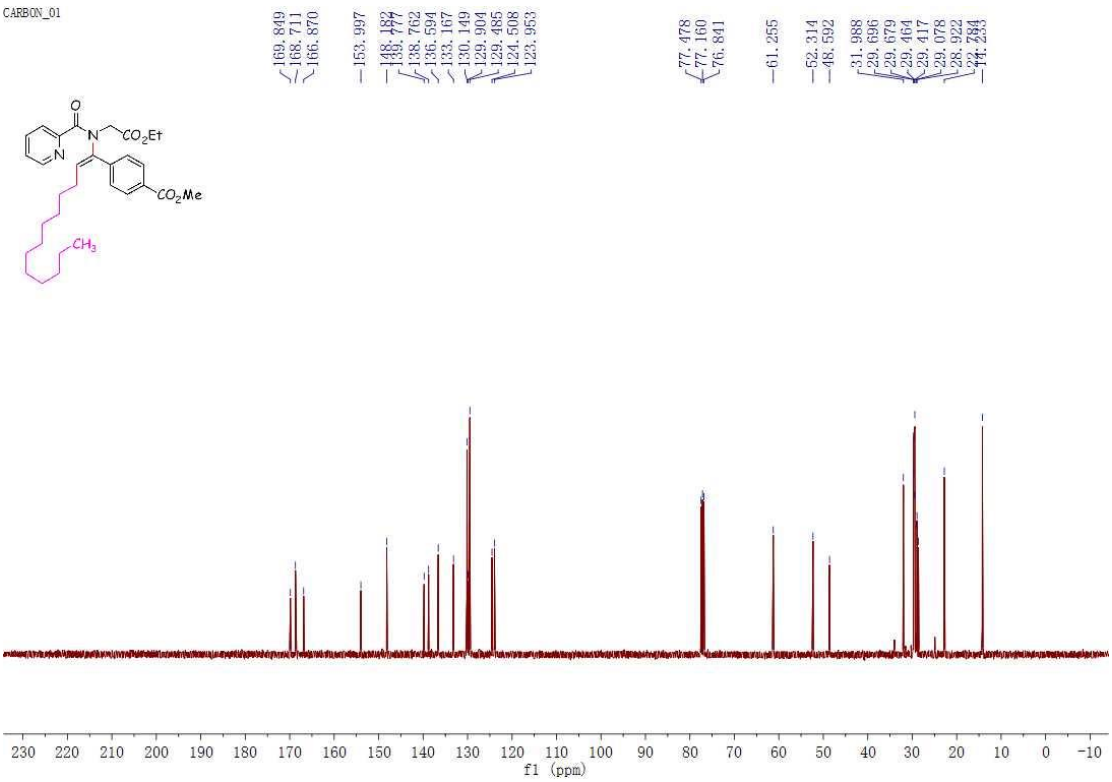
^{1}H NMR spectra for compound **4p** (400 MHz, $CDCl_3$)



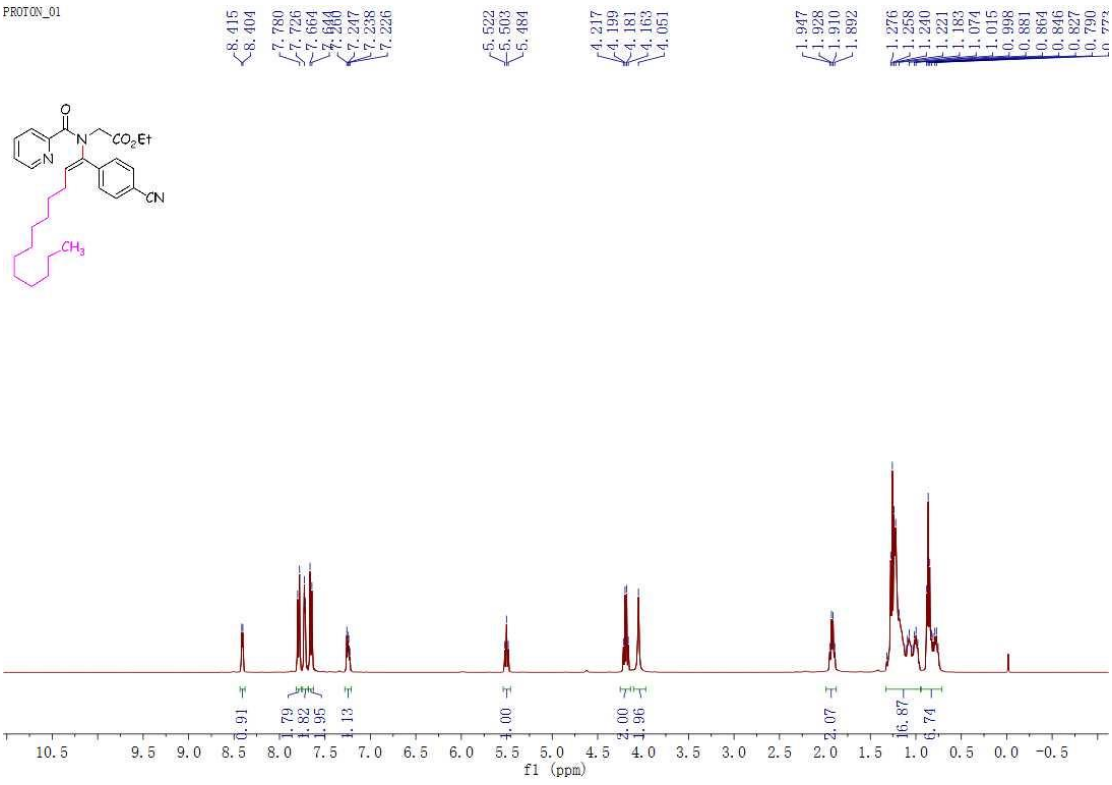
^{13}C NMR spectra for compound **4p** (100 MHz, $CDCl_3$)



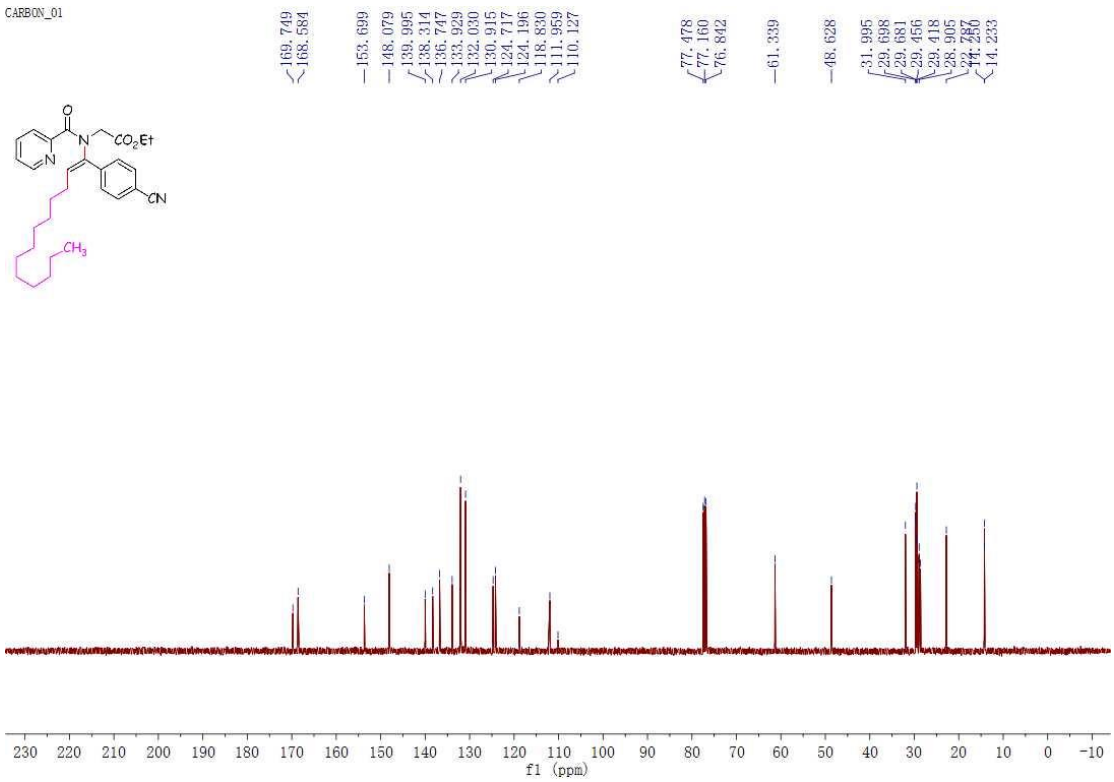
^{1}H NMR spectra for compound **4q** (400 MHz, $CDCl_3$)



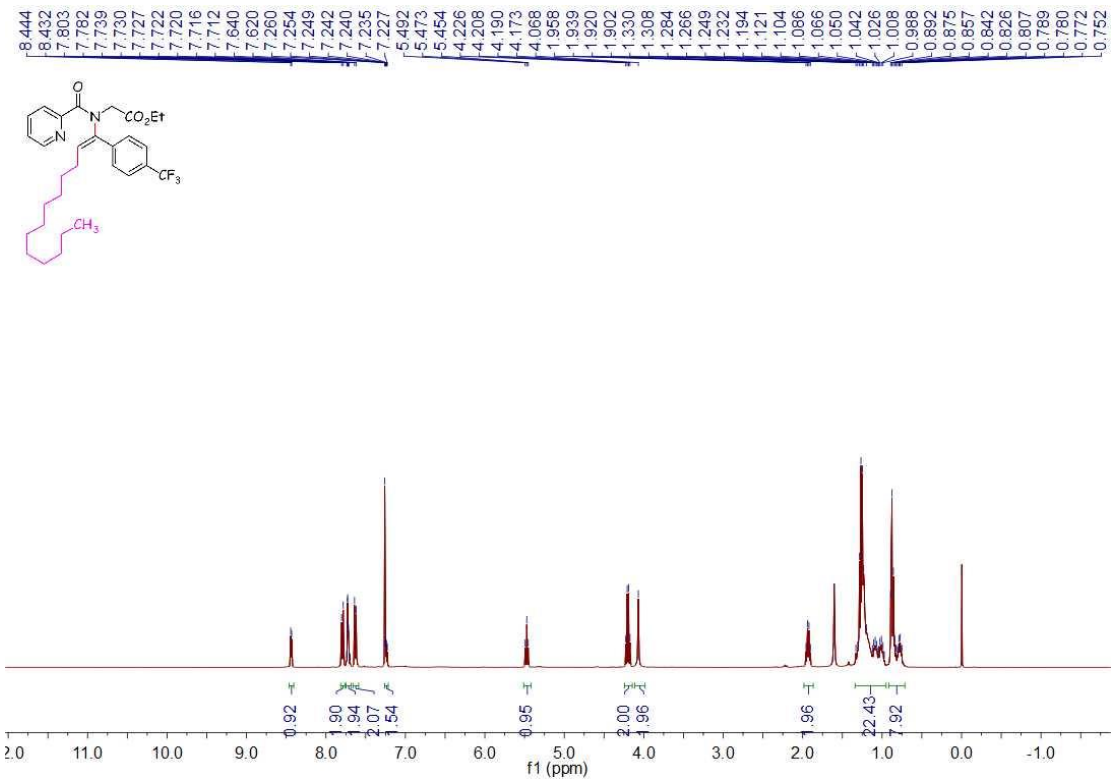
^{13}C NMR spectra for compound **4q** (100 MHz, $CDCl_3$)



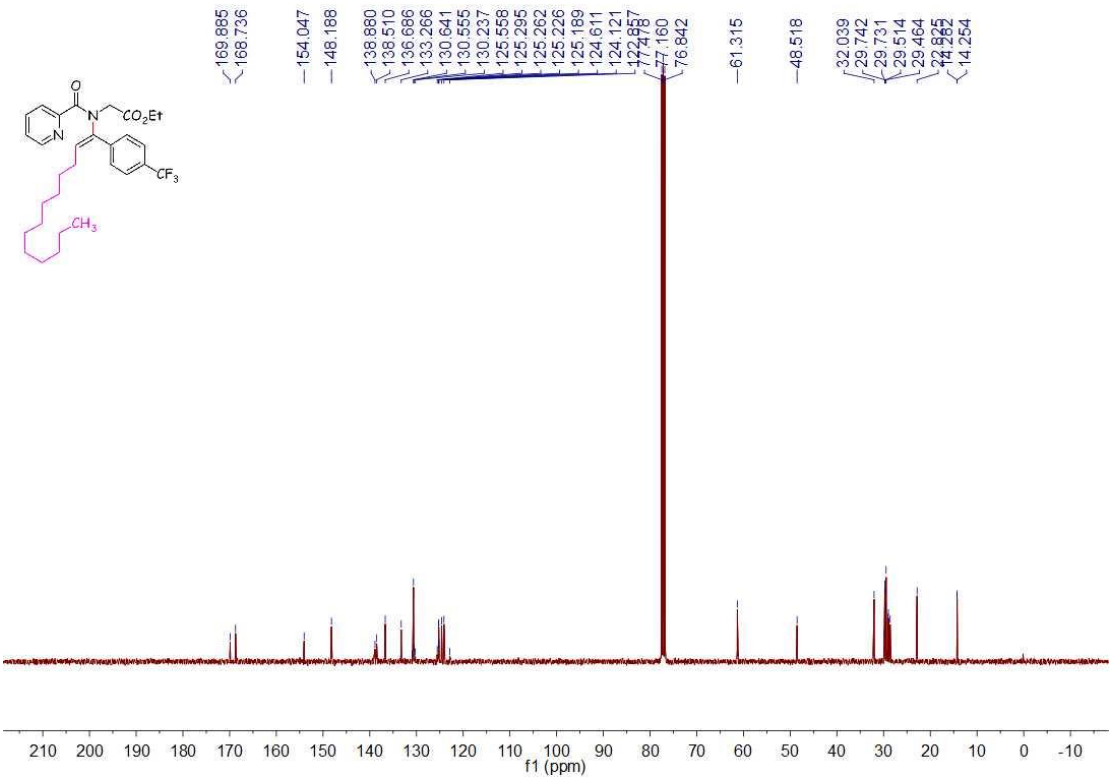
^{1}H NMR spectra for compound **4r** (400 MHz, $CDCl_3$)



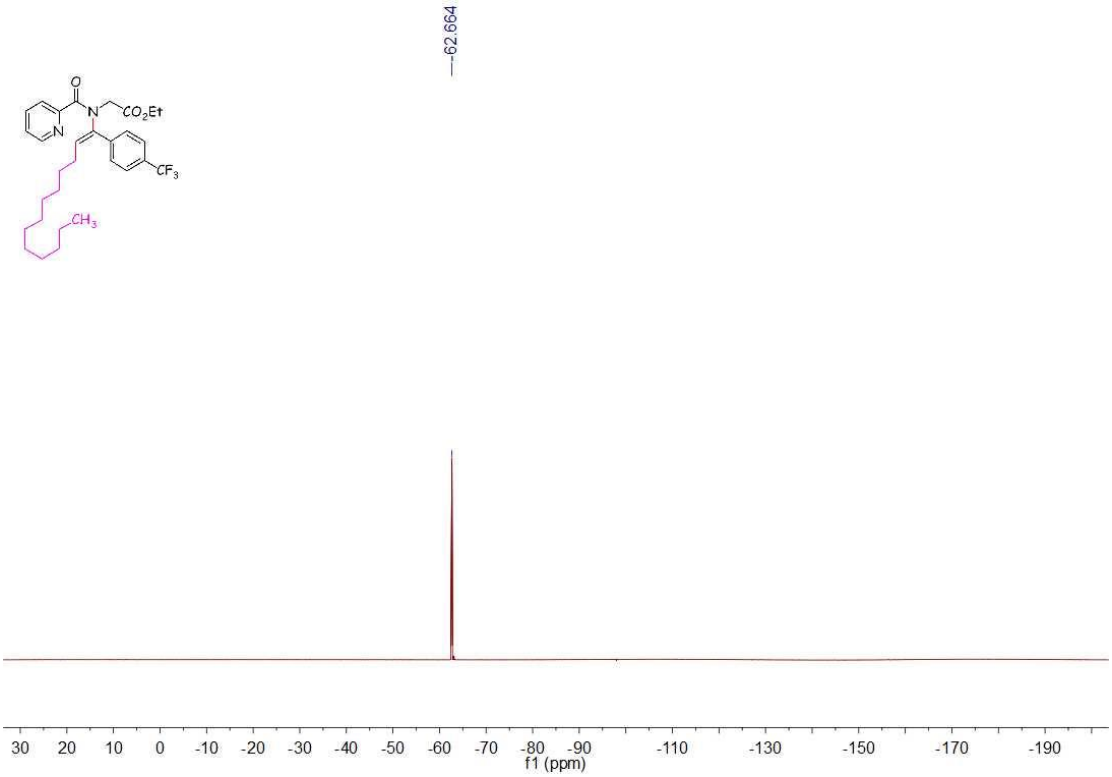
^{13}C NMR spectra for compound **4r** (100 MHz, $CDCl_3$)



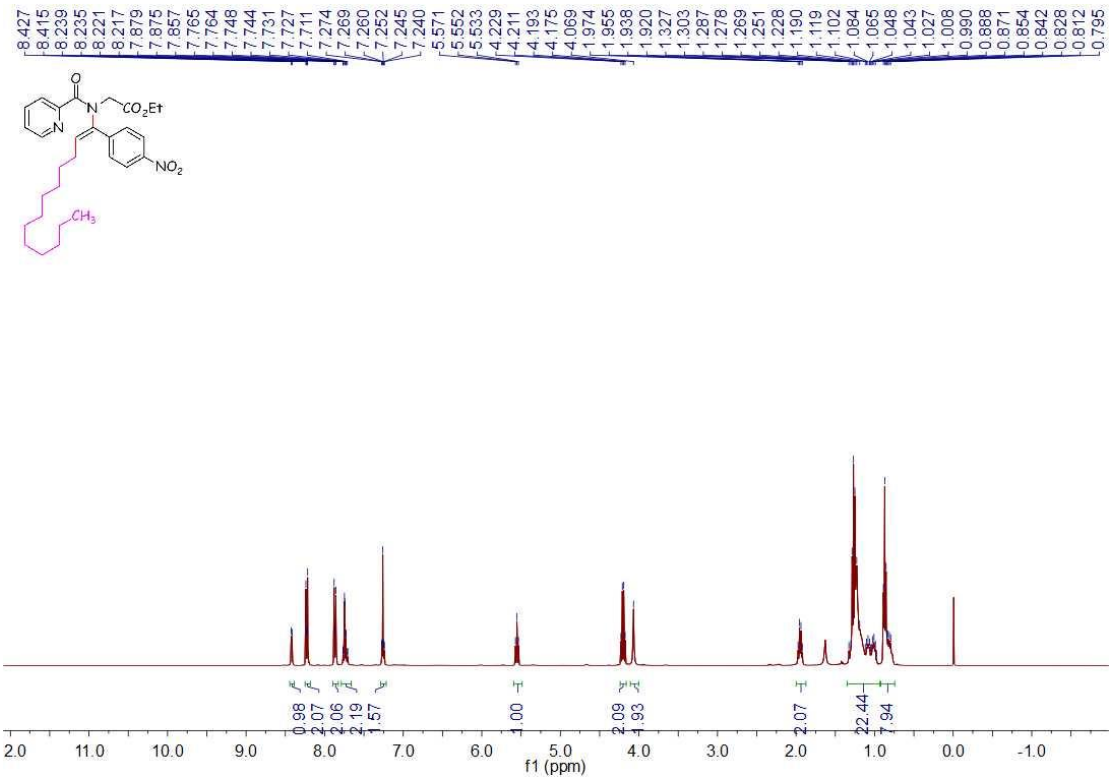
^{1}H NMR spectra for compound **4s** (400 MHz, $CDCl_3$)



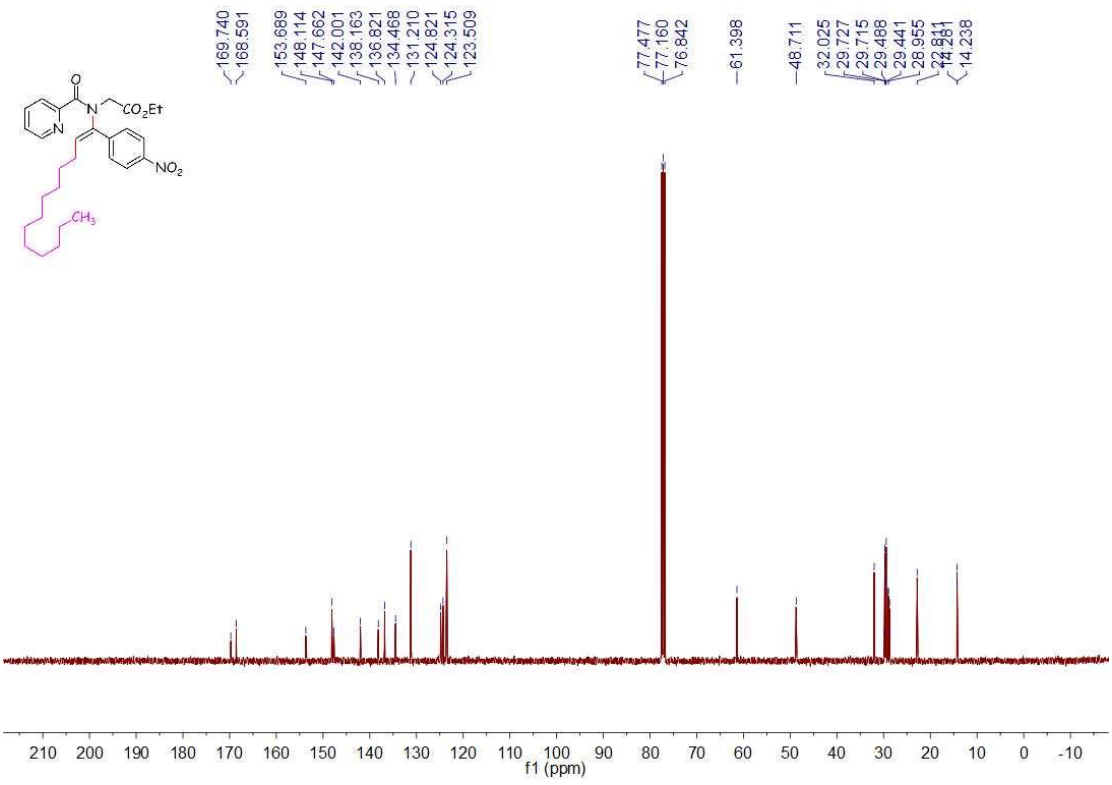
^{13}C NMR spectra for compound **4s** (100 MHz, $CDCl_3$)



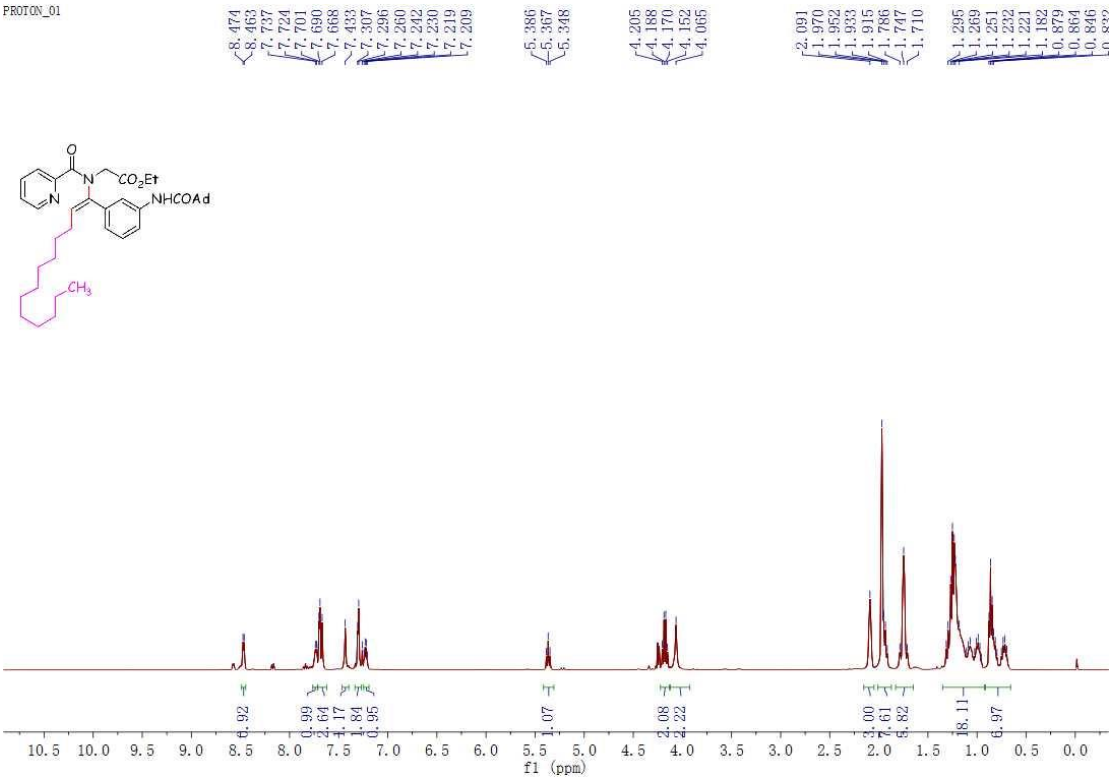
^{19}F NMR spectra for compound **4s** (376 MHz, $CDCl_3$)



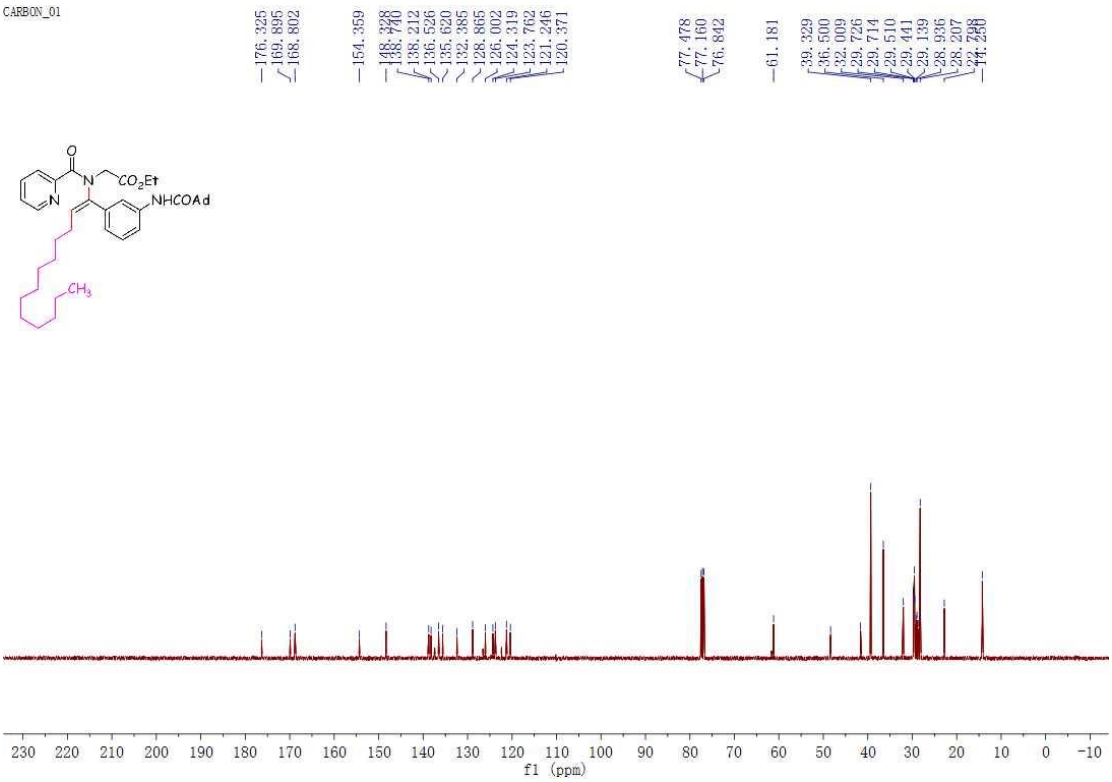
^{1}H NMR spectra for compound **4t** (400 MHz, $CDCl_3$)



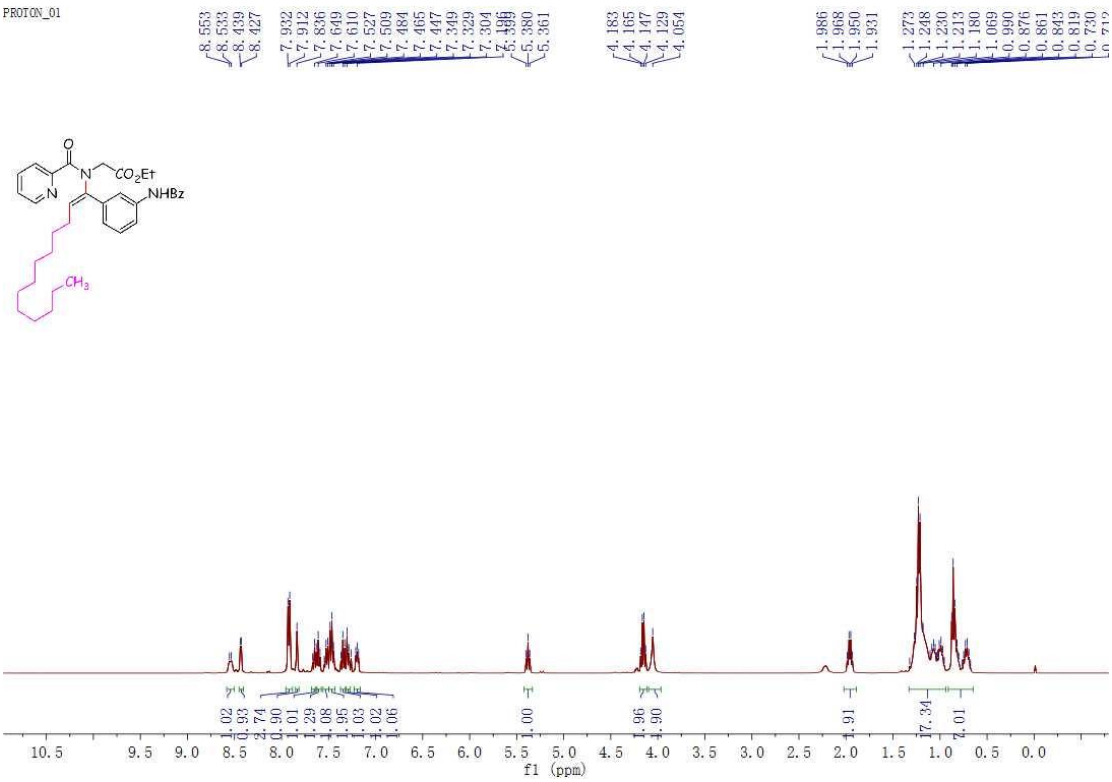
^{13}C NMR spectra for compound **4t** (100 MHz, $CDCl_3$)



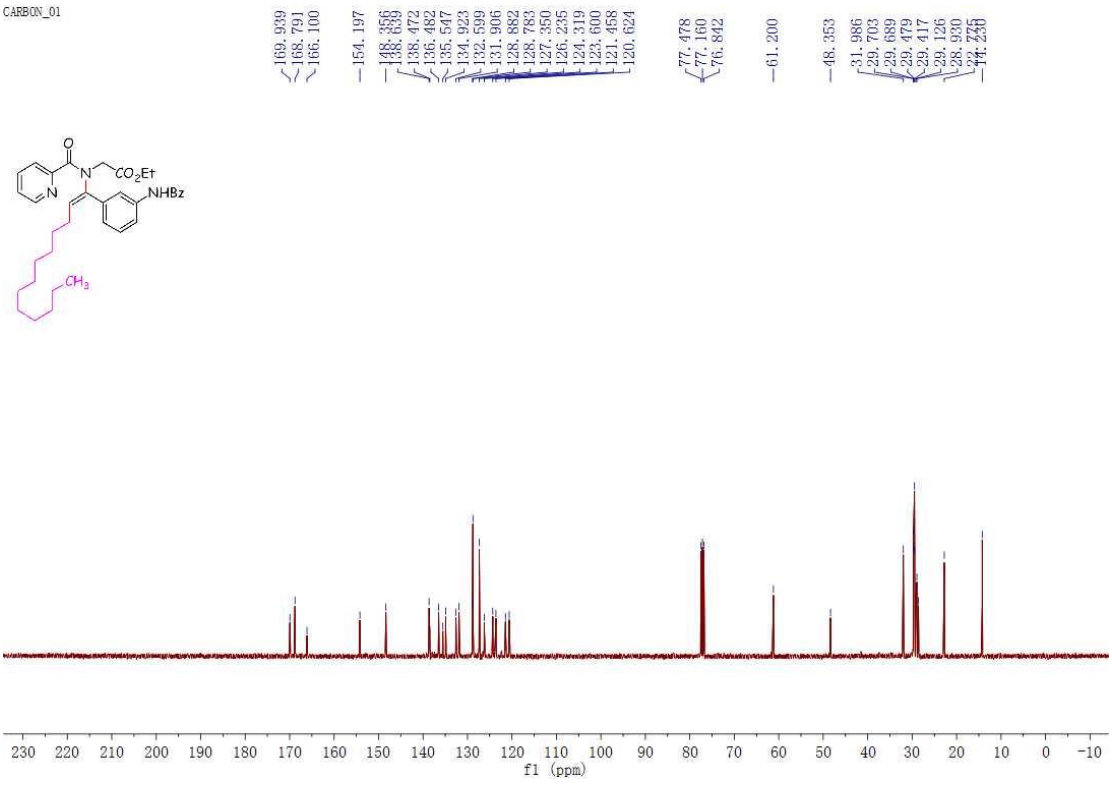
^{1}H NMR spectra for compound **4u** (400 MHz, $CDCl_3$)



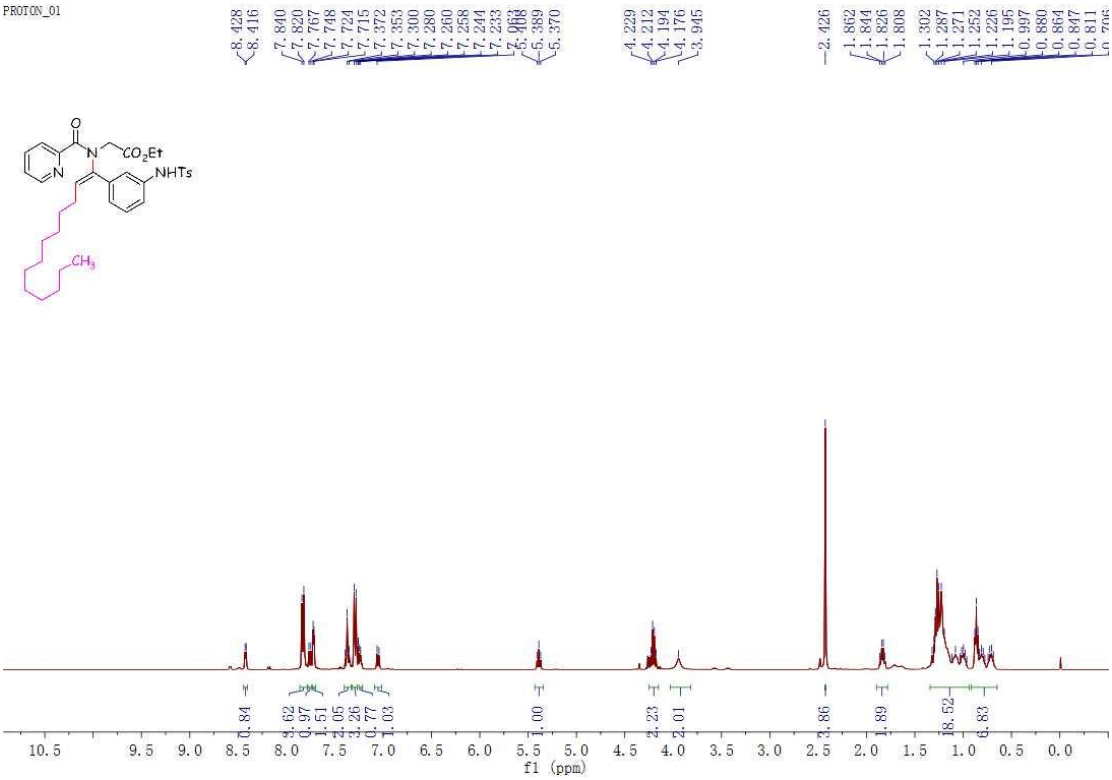
^{13}C NMR spectra for compound **4u** (100 MHz, $CDCl_3$)



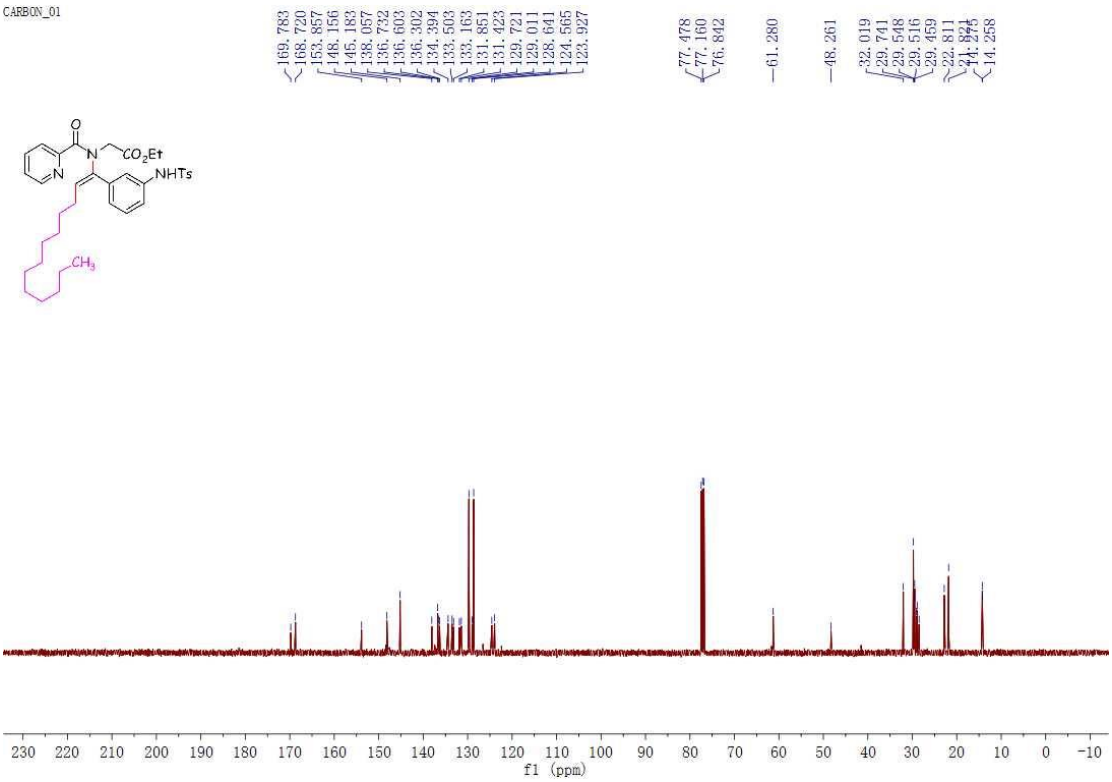
^{1}H NMR spectra for compound **4v** (400 MHz, $CDCl_3$)



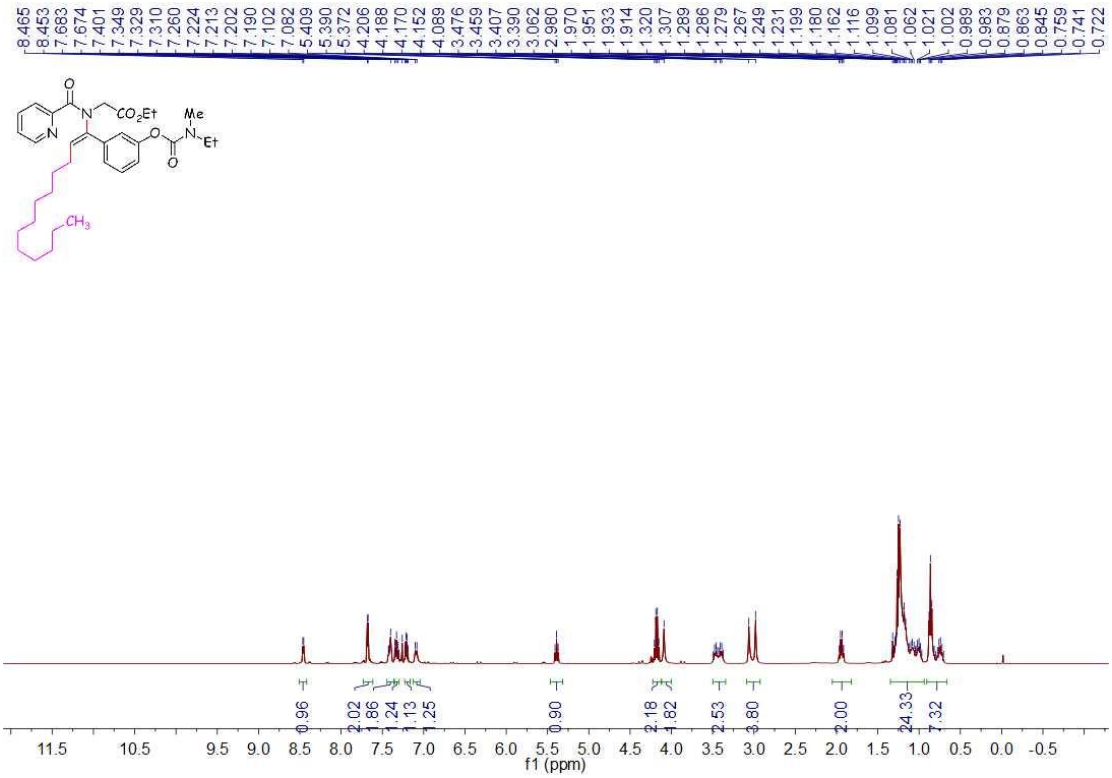
^{13}C NMR spectra for compound **4v** (100 MHz, $CDCl_3$)



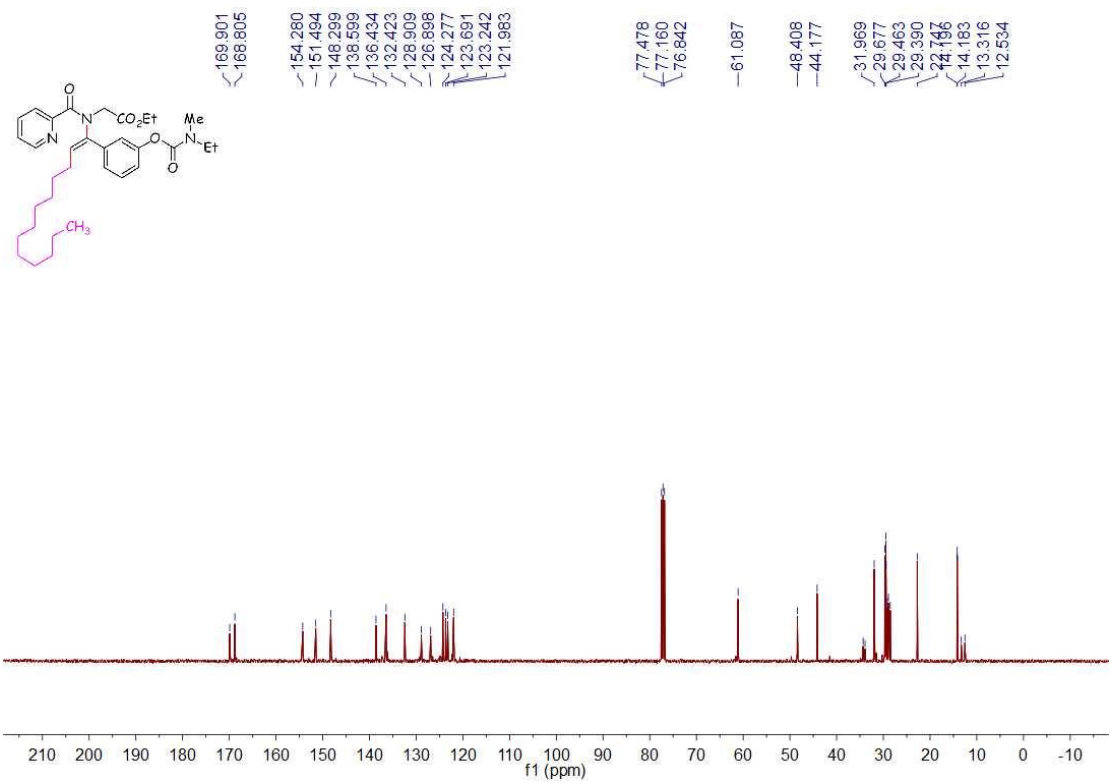
^{1}H NMR spectra for compound **4w** (400 MHz, $CDCl_3$)



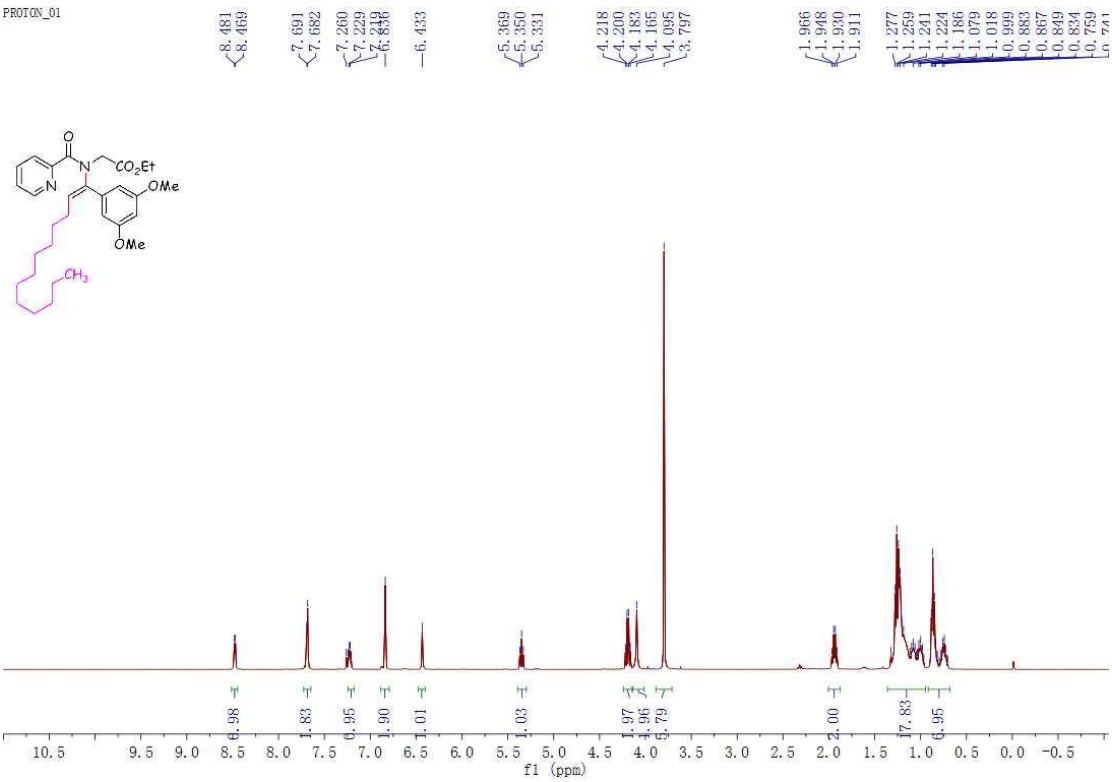
^{13}C NMR spectra for compound **4w** (100 MHz, $CDCl_3$)



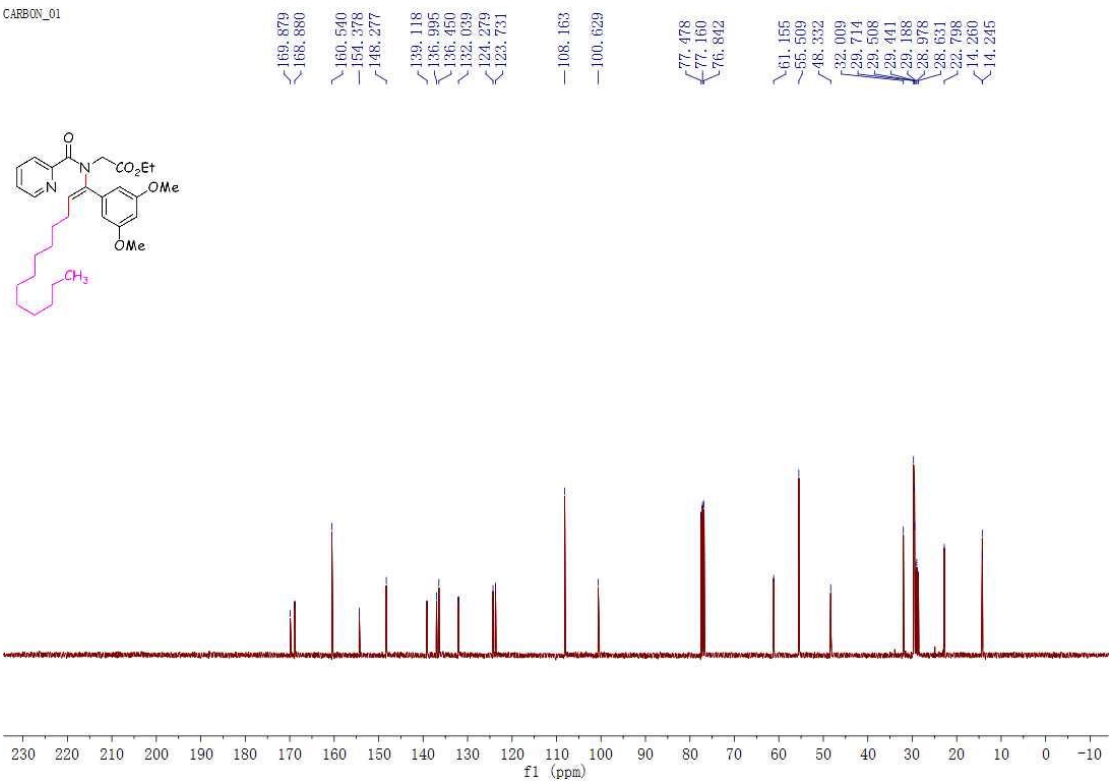
^{1}H NMR spectra for compound **4x** (400 MHz, $CDCl_3$)



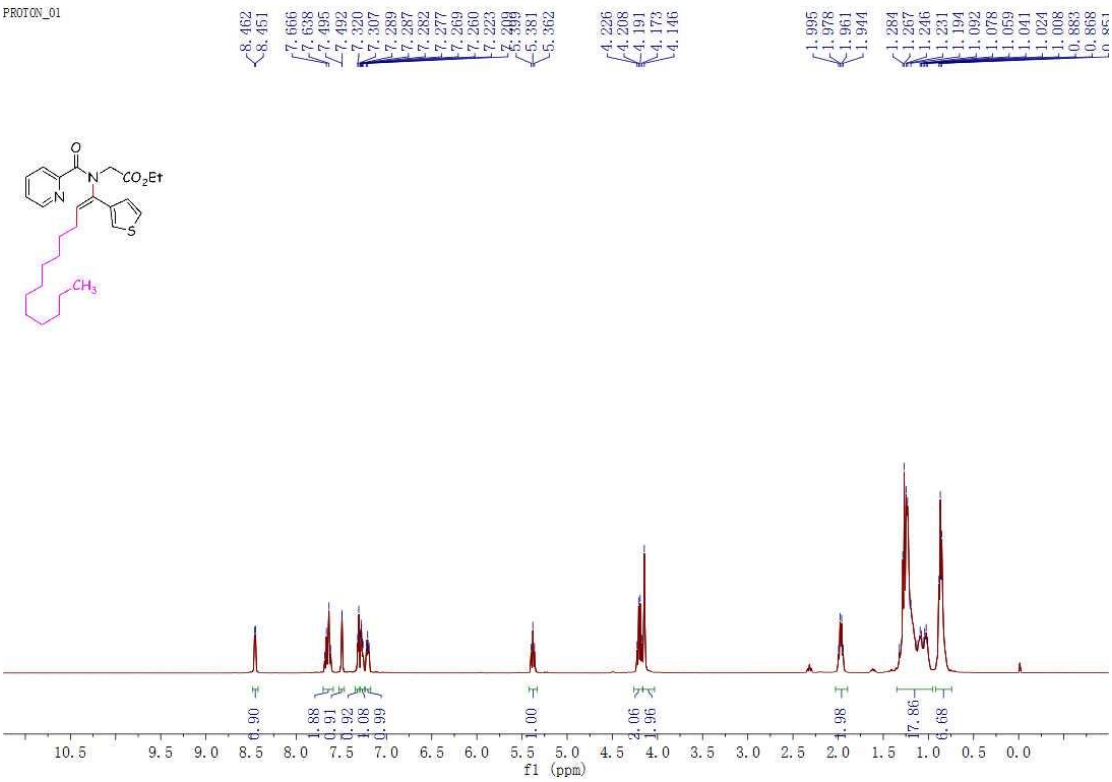
^{13}C NMR spectra for compound **4x** (100 MHz, $CDCl_3$)



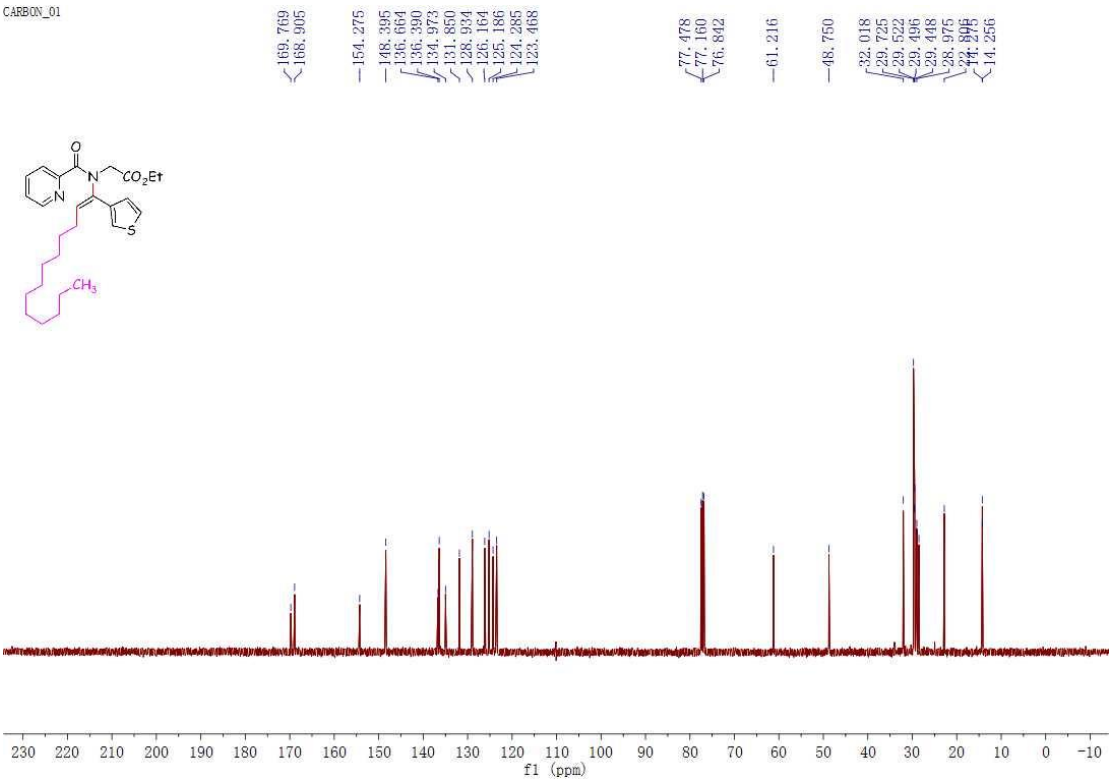
^{1}H NMR spectra for compound **4y** (400 MHz, $CDCl_3$)



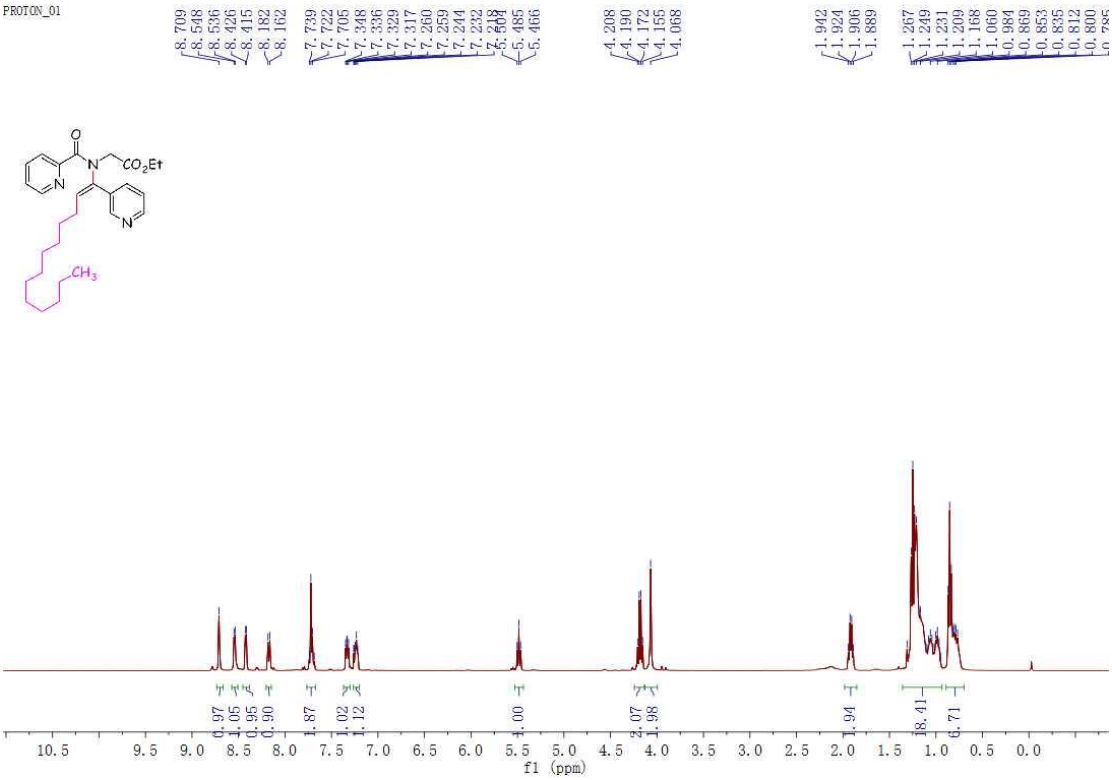
^{13}C NMR spectra for compound **4y** (100 MHz, $CDCl_3$)



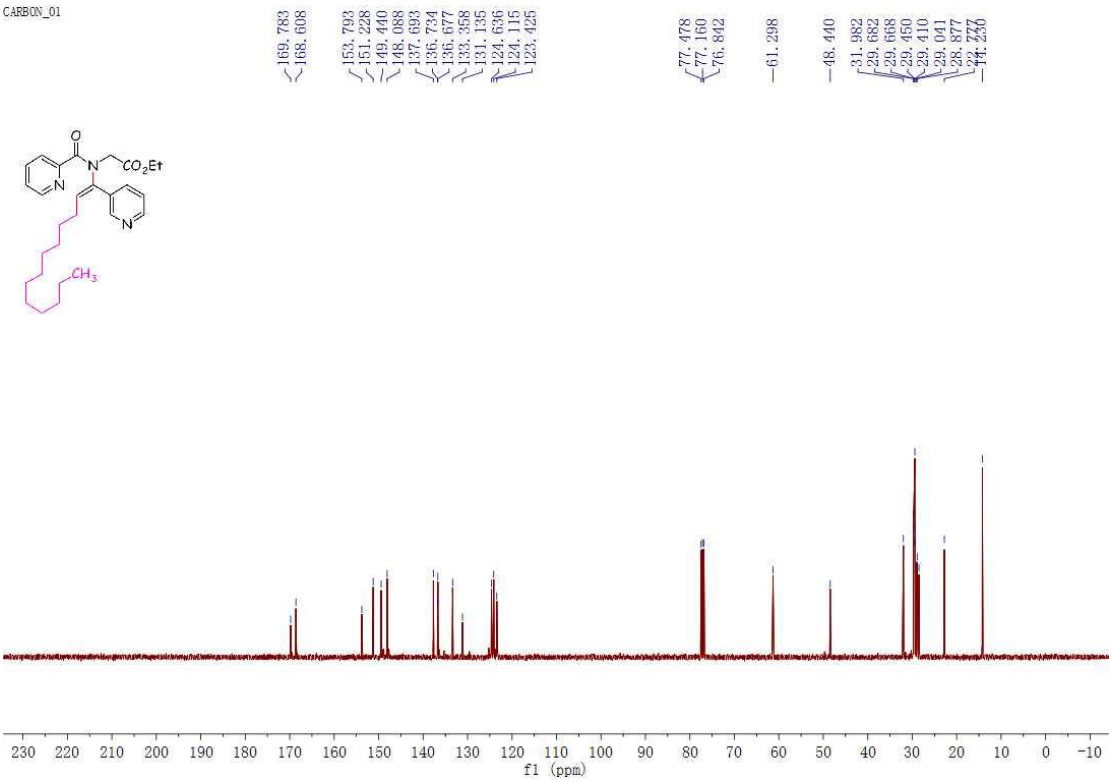
^{1}H NMR spectra for compound **4z** (400 MHz, $CDCl_3$)



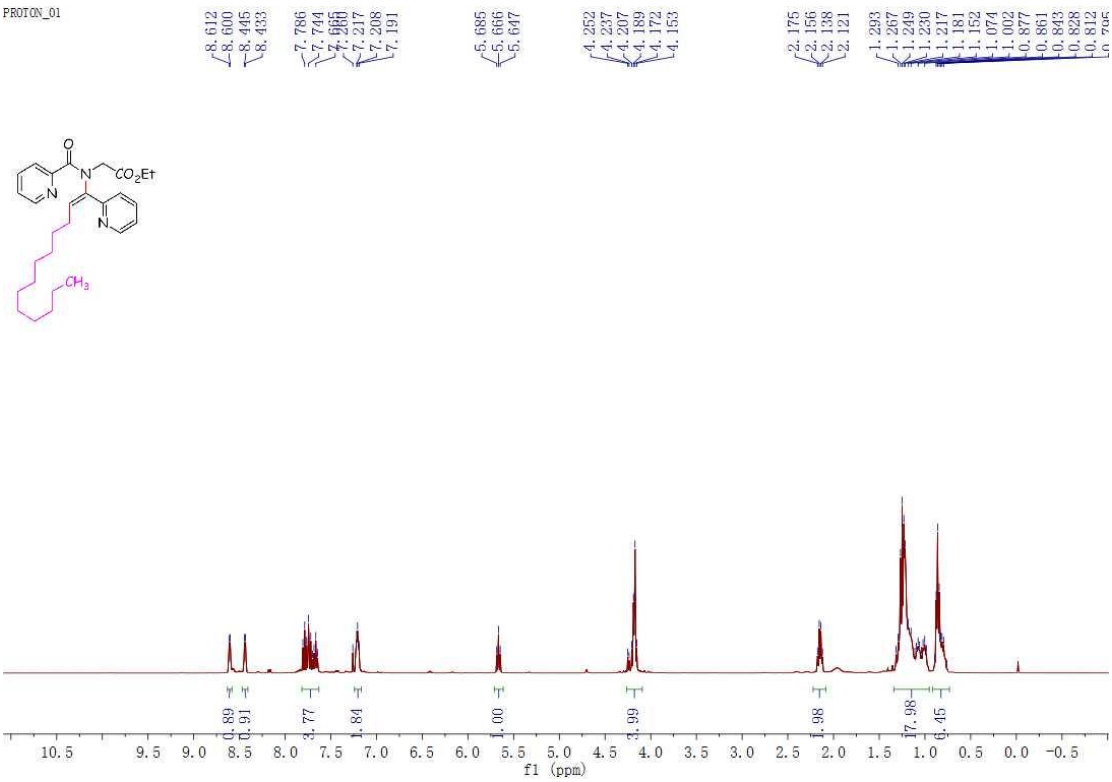
^{13}C NMR spectra for compound **4z** (100 MHz, $CDCl_3$)



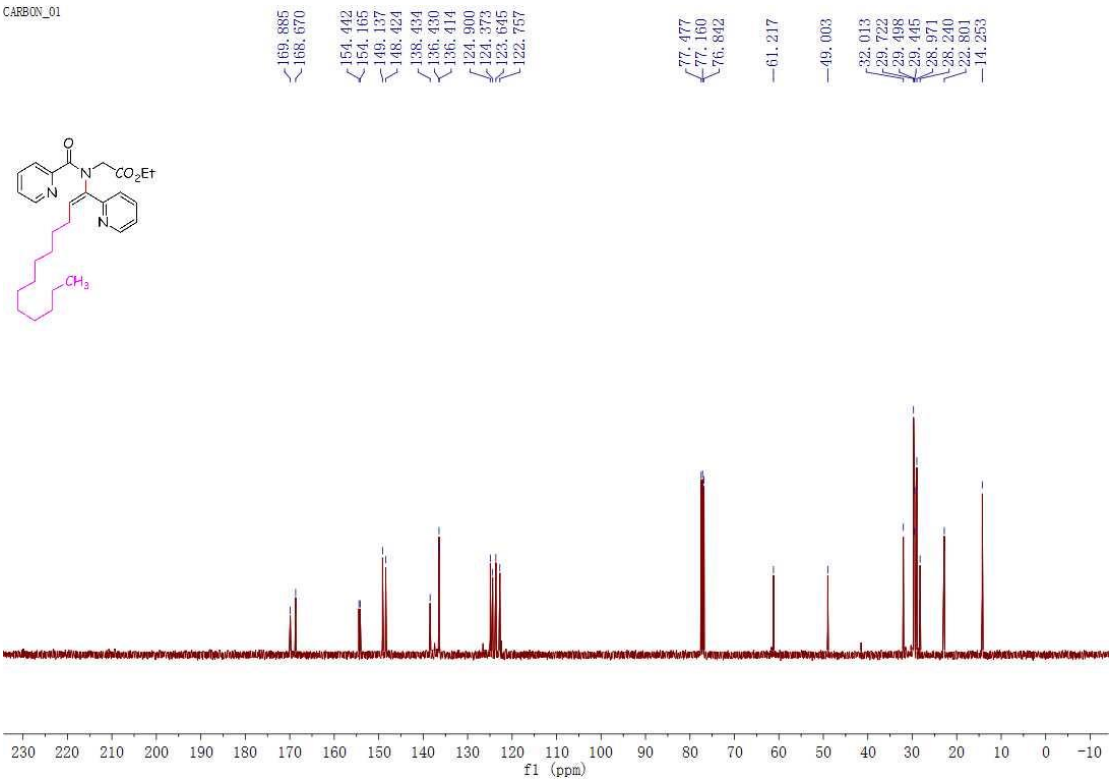
^{1}H NMR spectra for compound **4aa** (400 MHz, $CDCl_3$)



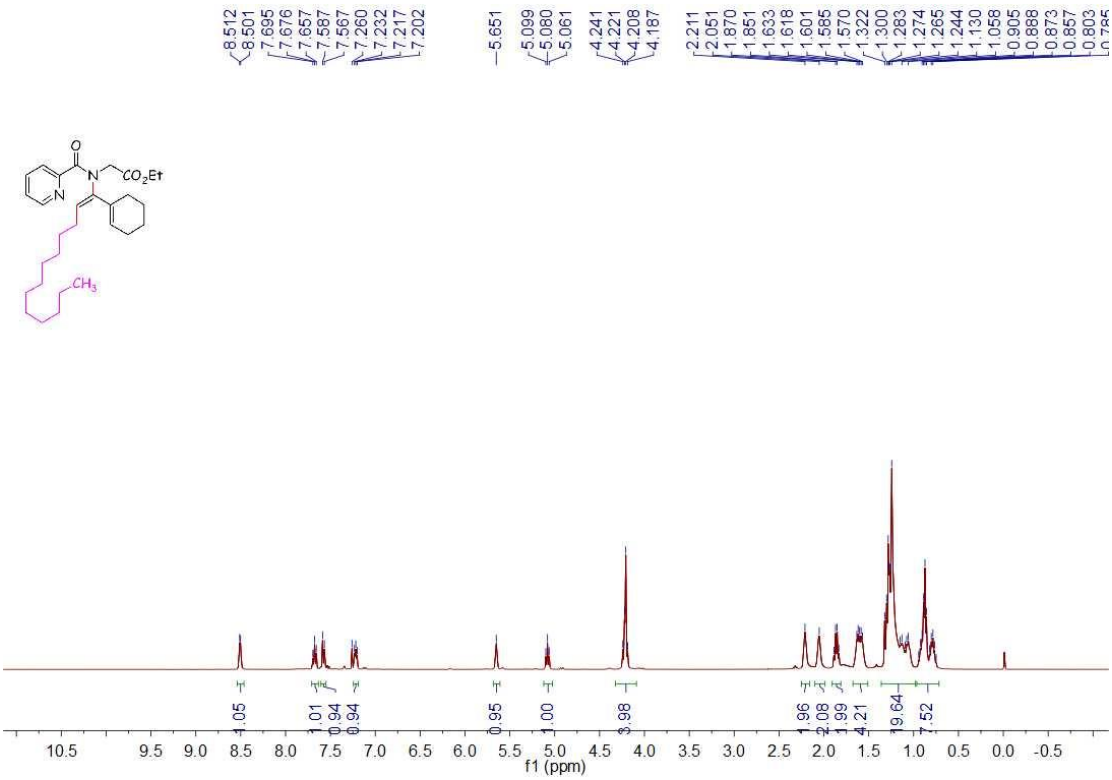
^{13}C NMR spectra for compound **4aa** (100 MHz, $CDCl_3$)



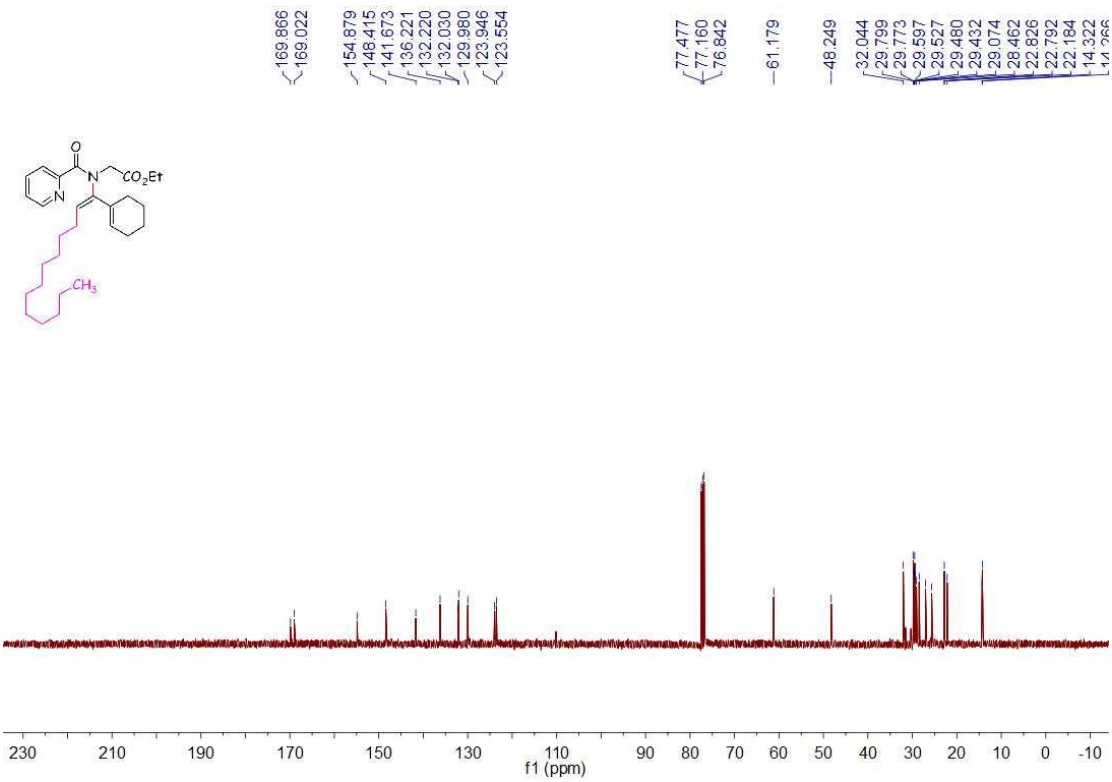
^{1}H NMR spectra for compound **4ab** (400 MHz, $CDCl_3$)



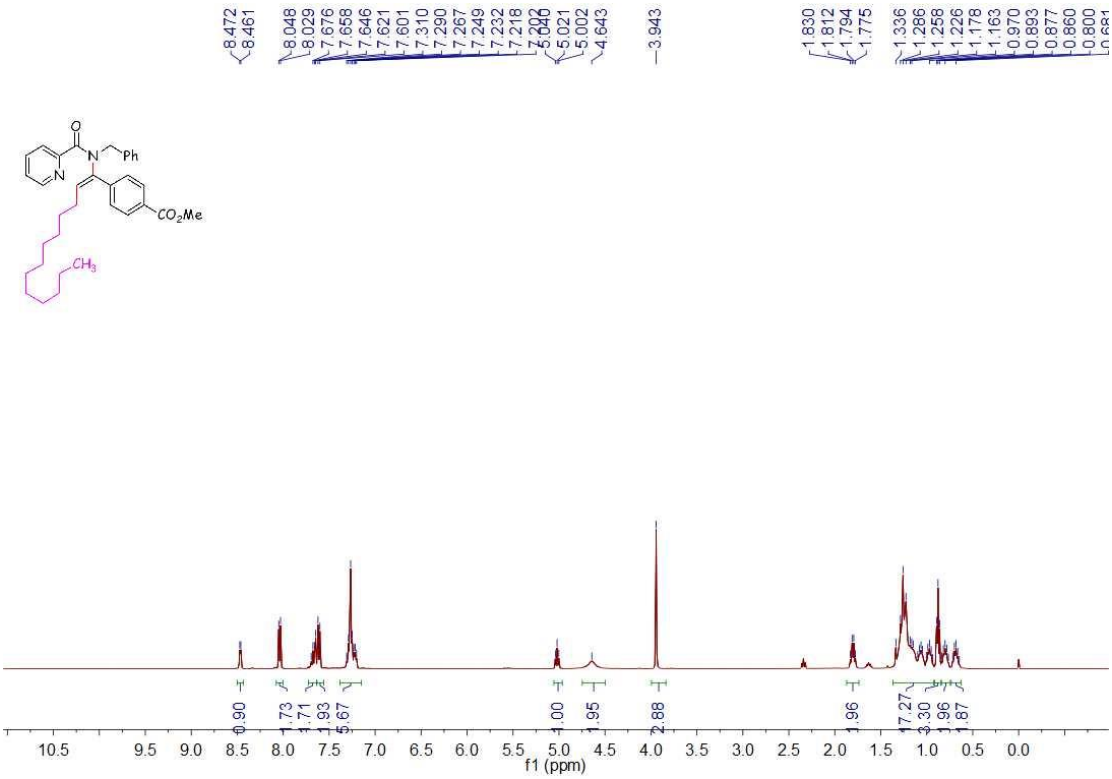
^{13}C NMR spectra for compound **4ab** (100 MHz, $CDCl_3$)



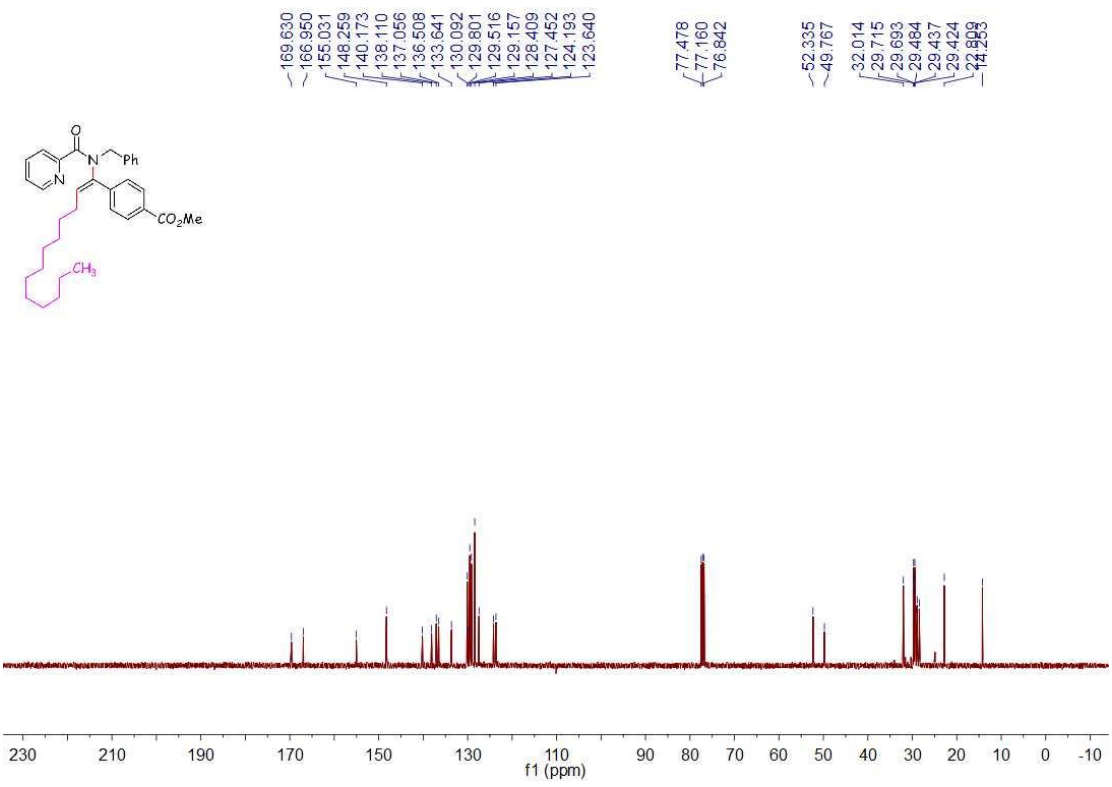
^{1}H NMR spectra for compound **4ac** (400 MHz, $CDCl_3$)



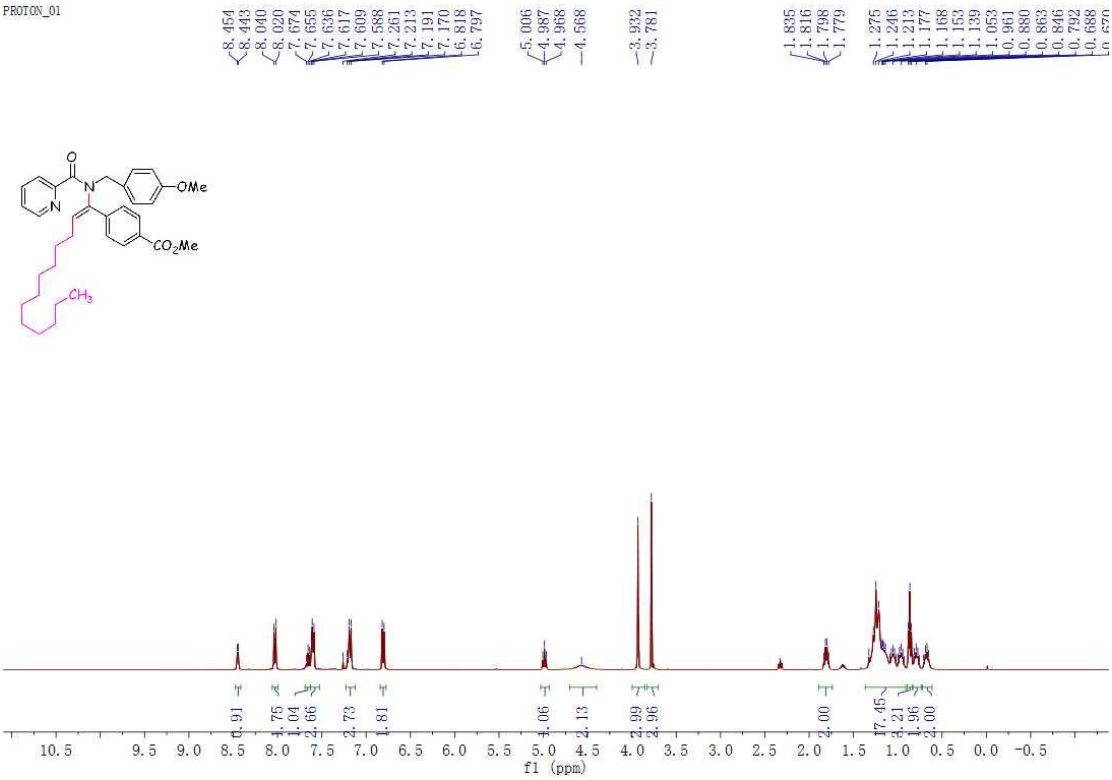
^{13}C NMR spectra for compound **4ac** (100 MHz, $CDCl_3$)



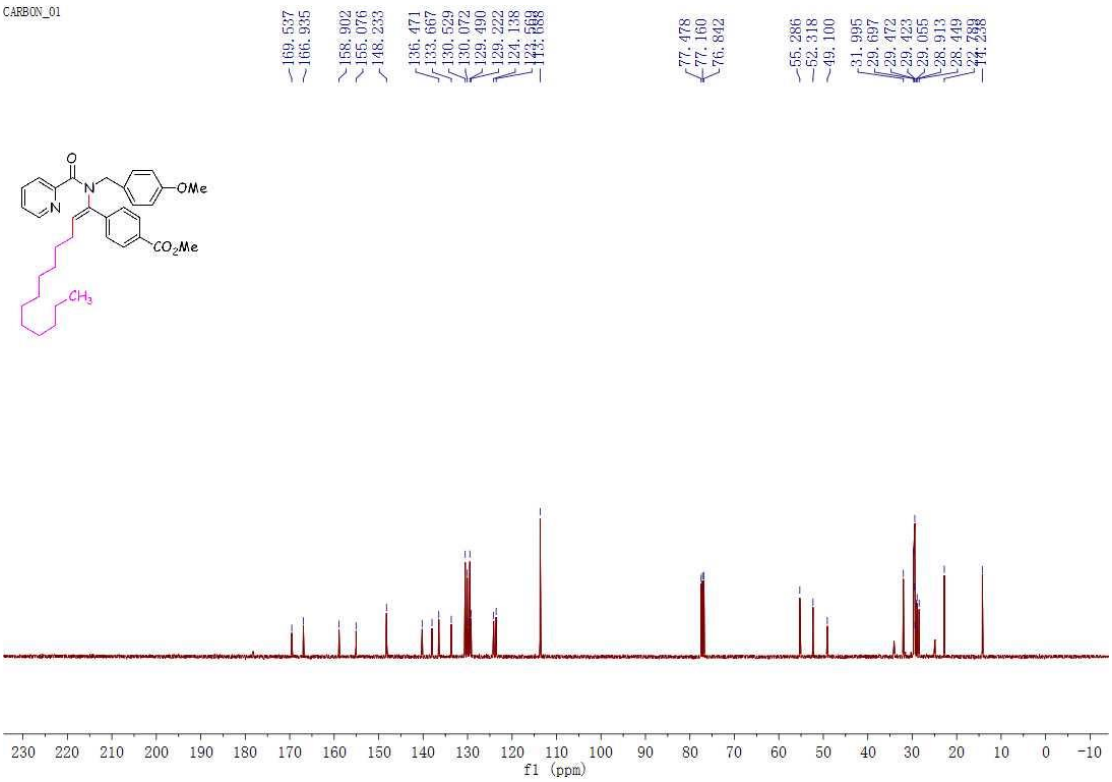
^{1}H NMR spectra for compound **5a** (400 MHz, $CDCl_3$)



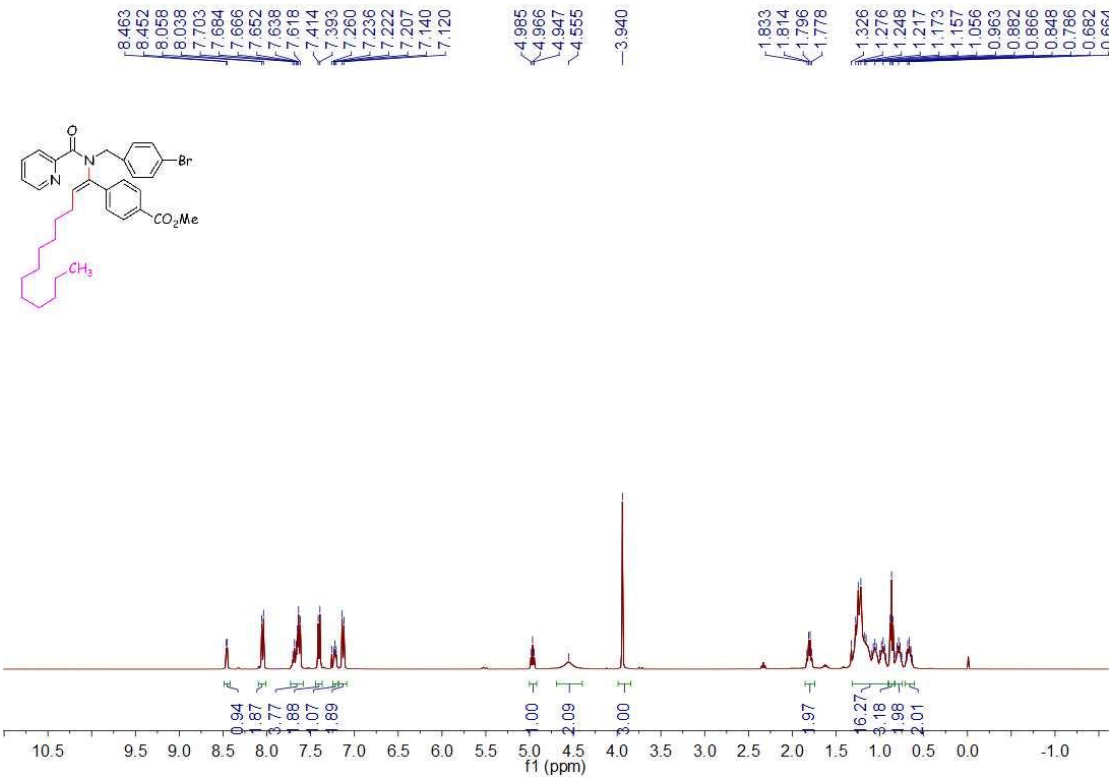
^{13}C NMR spectra for compound **5a** (100 MHz, $CDCl_3$)



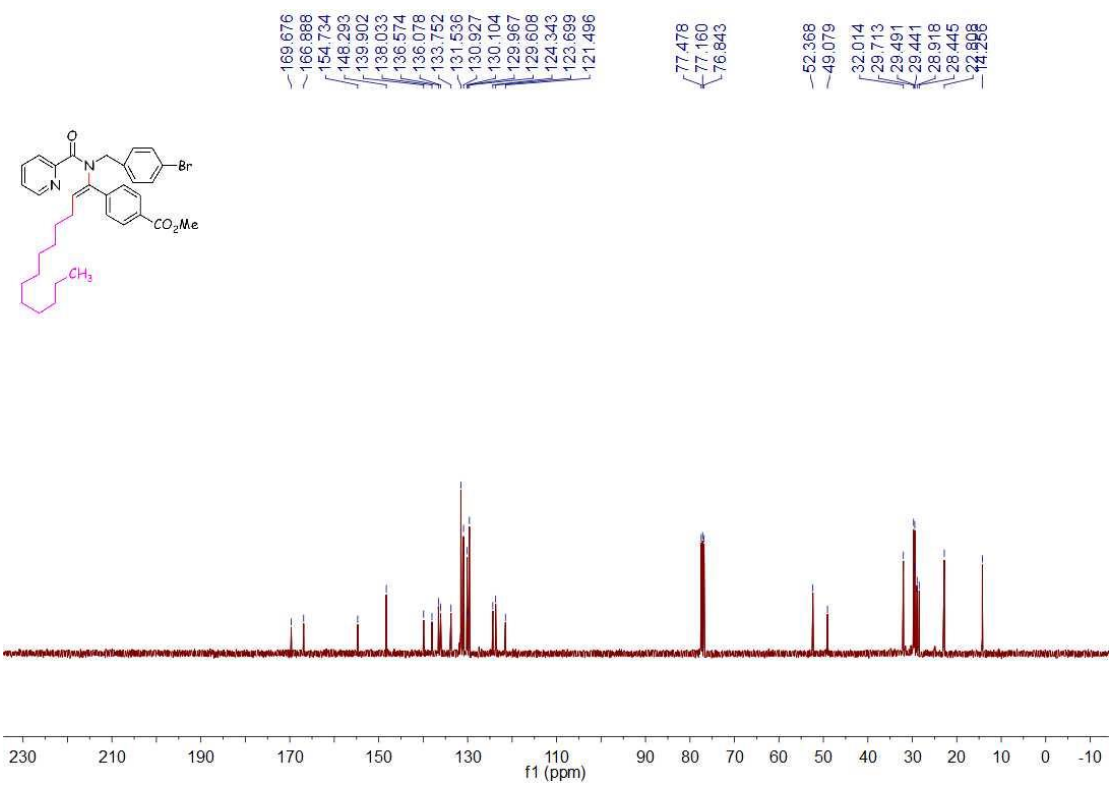
^{1}H NMR spectra for compound **5b** (400 MHz, $CDCl_3$)



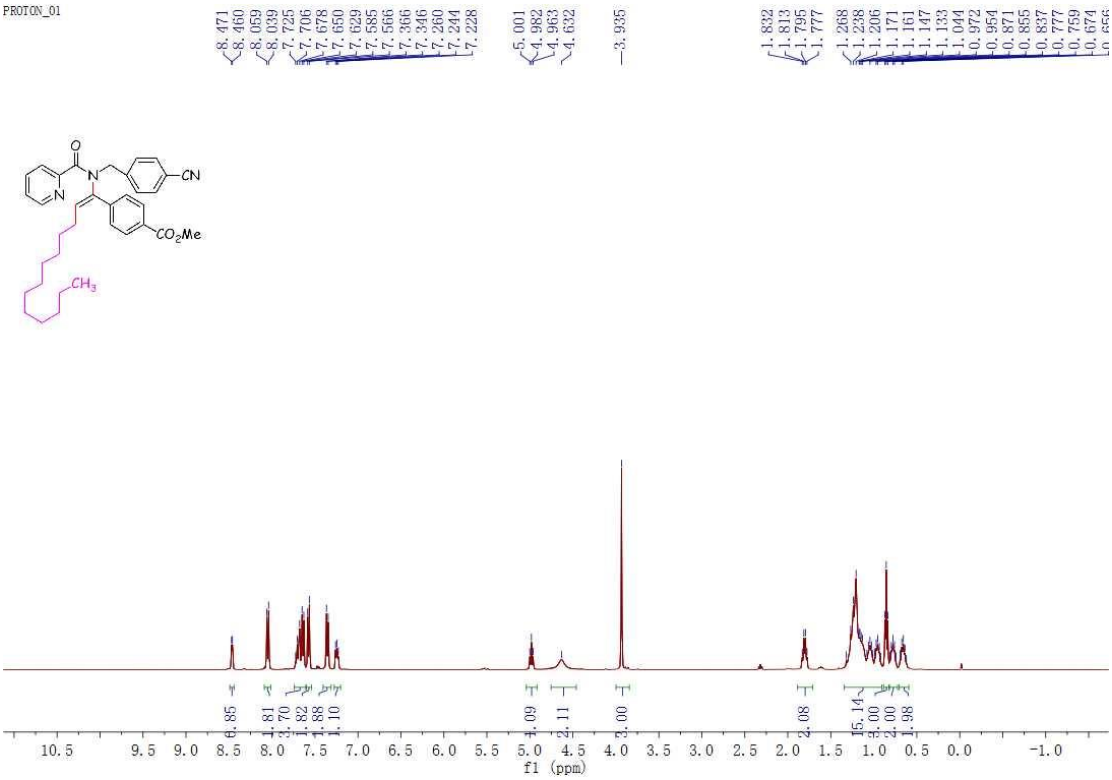
^{13}C NMR spectra for compound **5b** (100 MHz, $CDCl_3$)



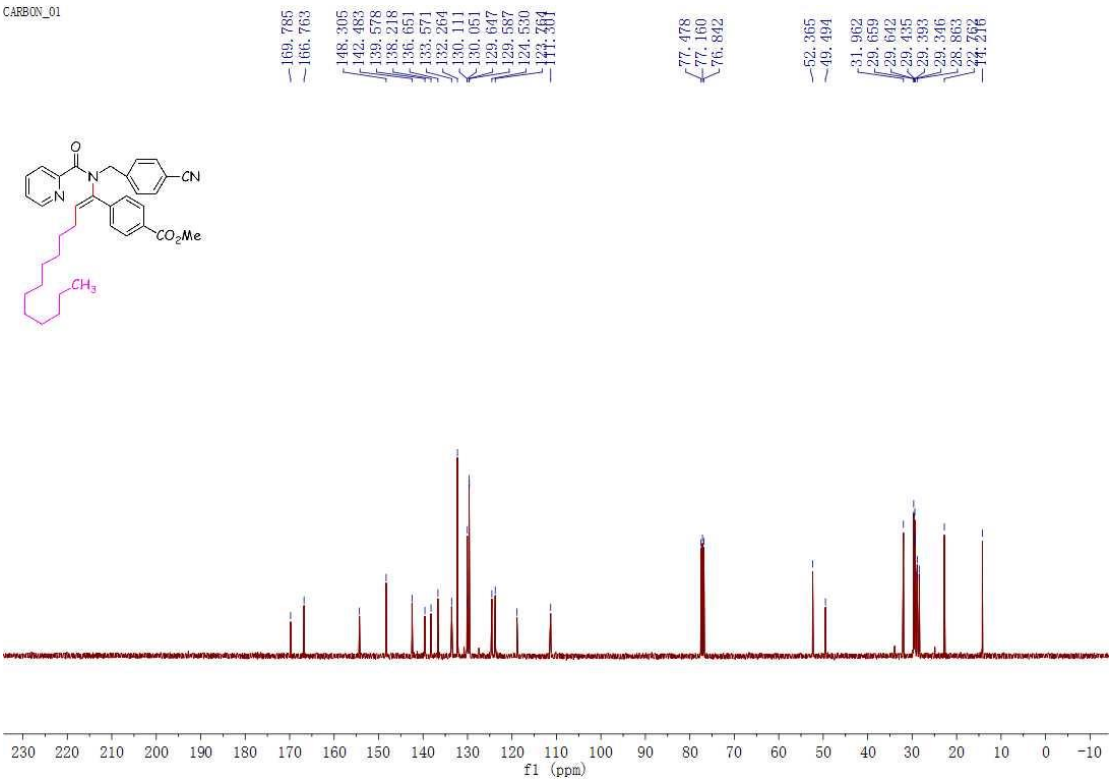
^{1}H NMR spectra for compound **5c** (400 MHz, $CDCl_3$)



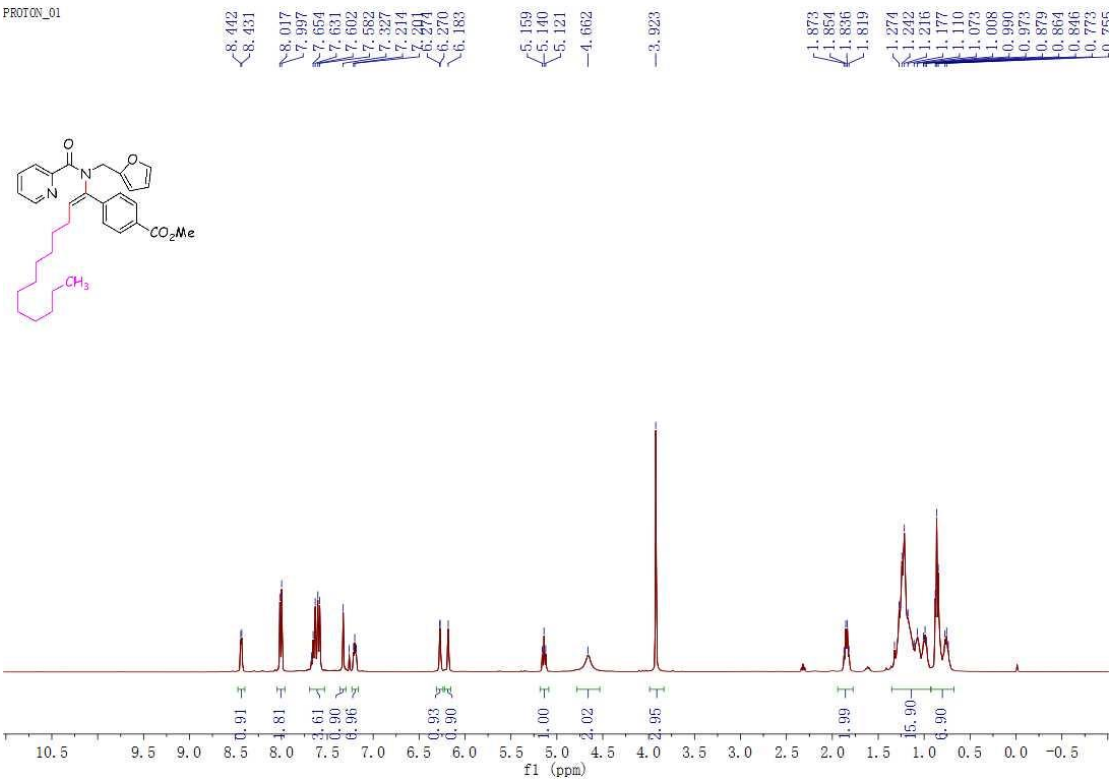
^{13}C NMR spectra for compound **5c** (100 MHz, $CDCl_3$)



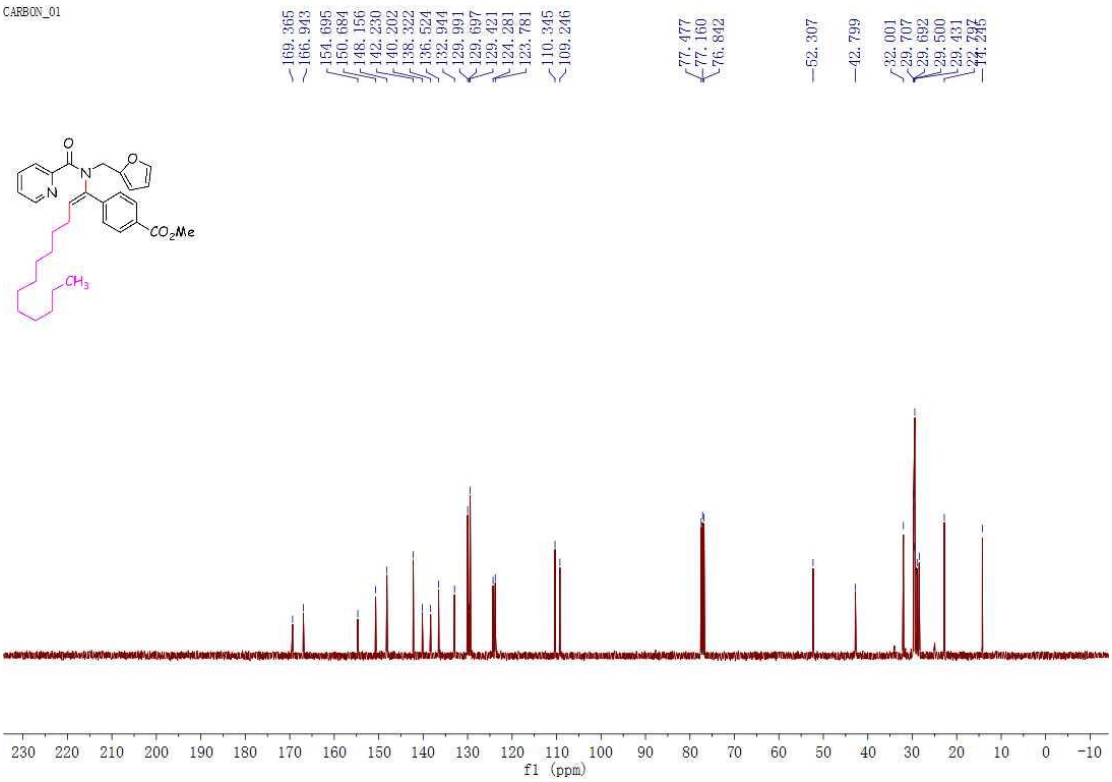
^{1}H NMR spectra for compound **5d** (400 MHz, $CDCl_3$)



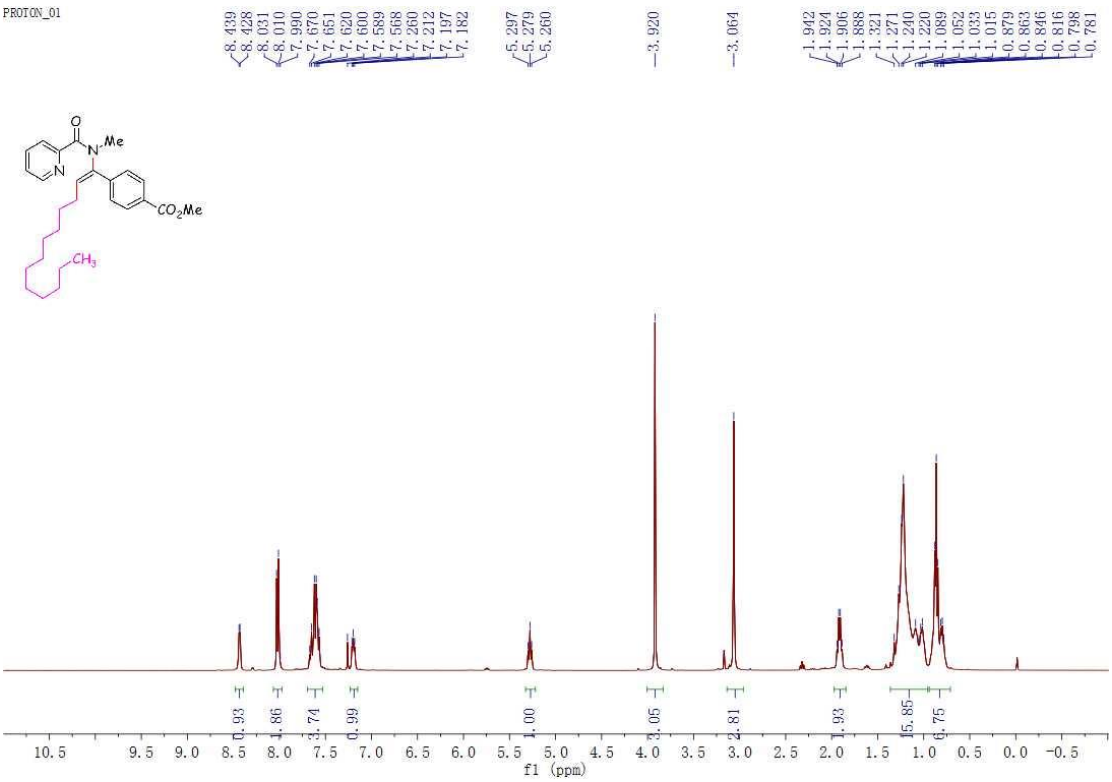
^{13}C NMR spectra for compound **5d** (100 MHz, $CDCl_3$)



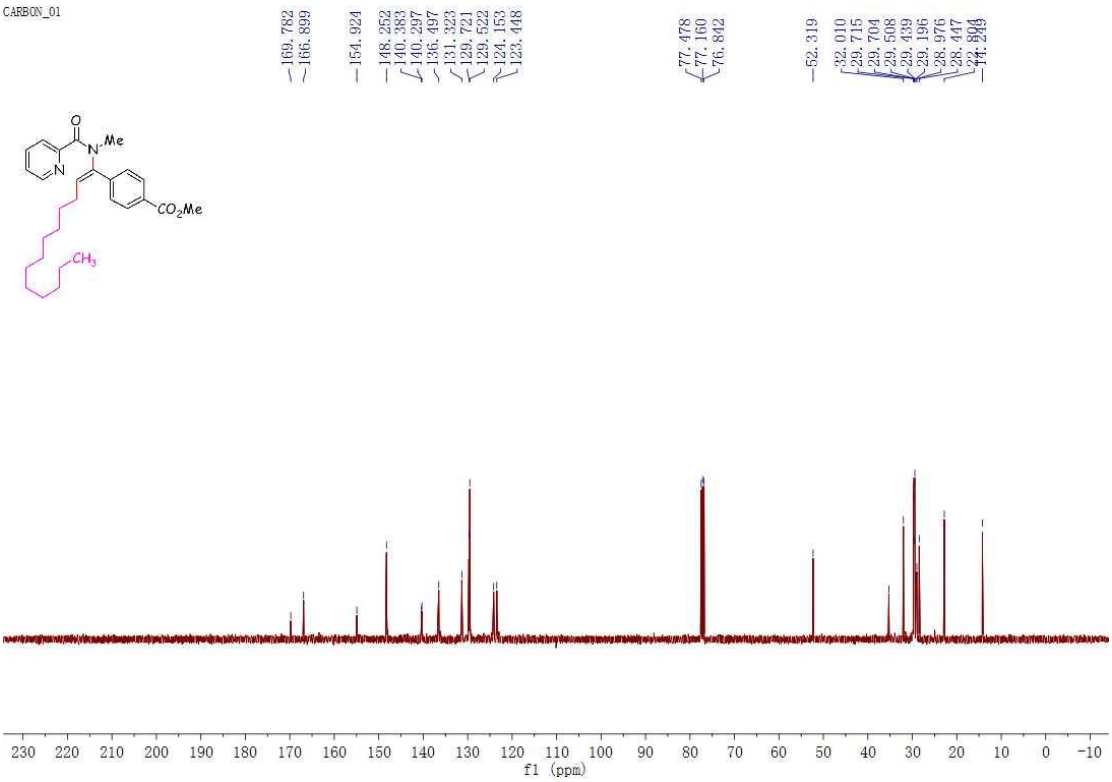
^{1}H NMR spectra for compound **5e** (400 MHz, $CDCl_3$)



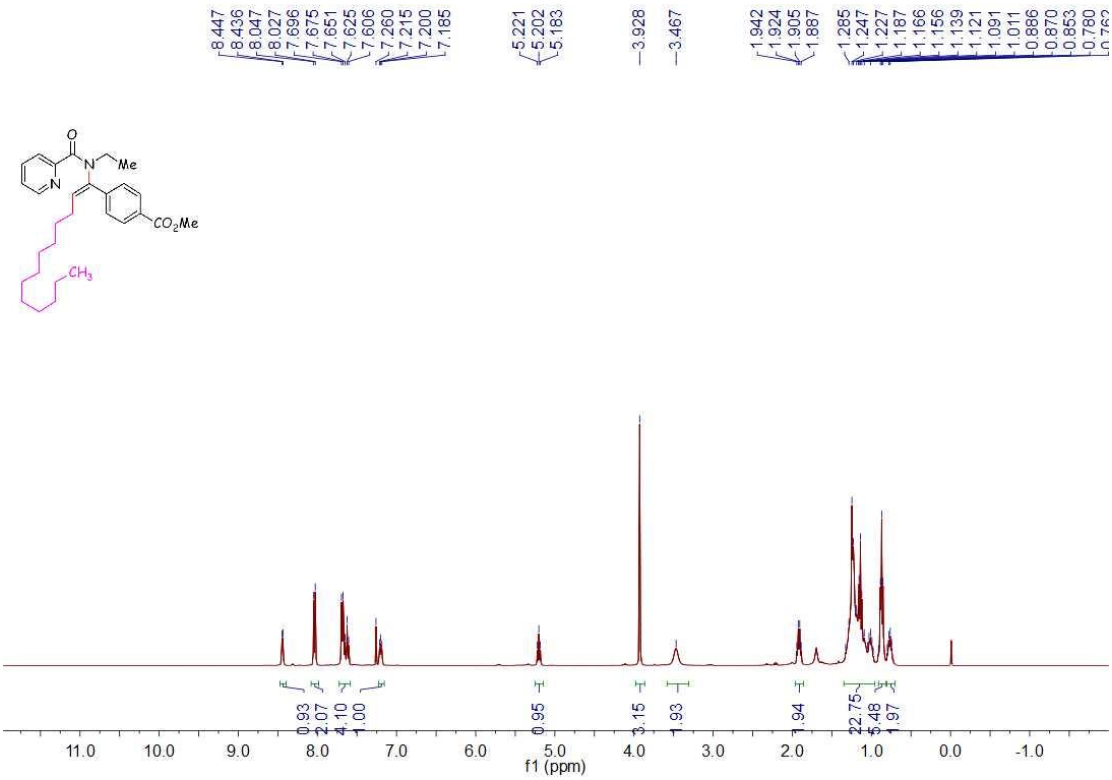
^{13}C NMR spectra for compound **5e** (100 MHz, $CDCl_3$)



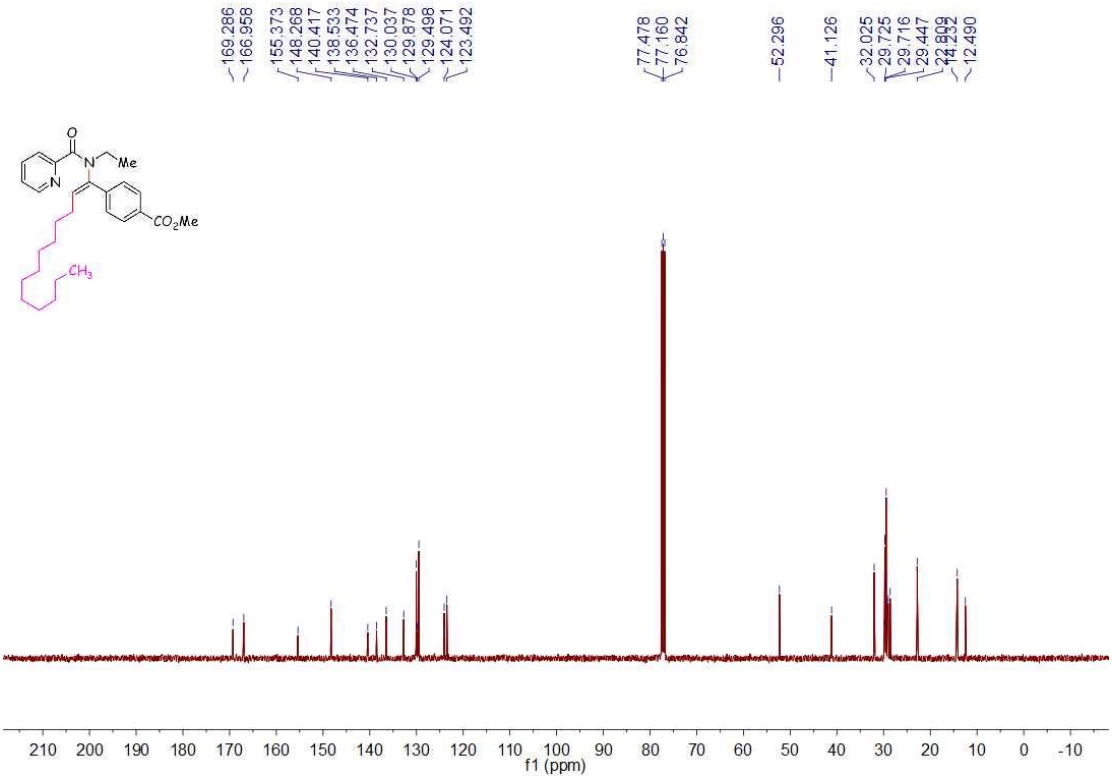
^{1}H NMR spectra for compound **5f** (400 MHz, $CDCl_3$)



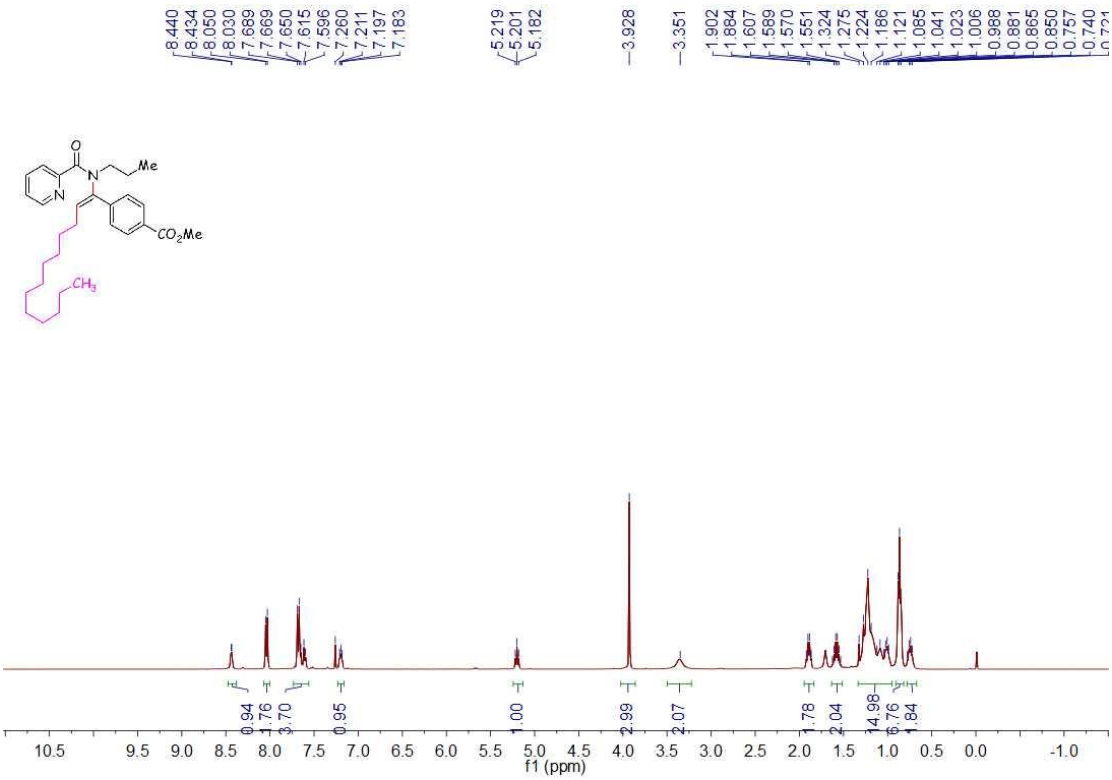
^{13}C NMR spectra for compound **5f** (100 MHz, $CDCl_3$)



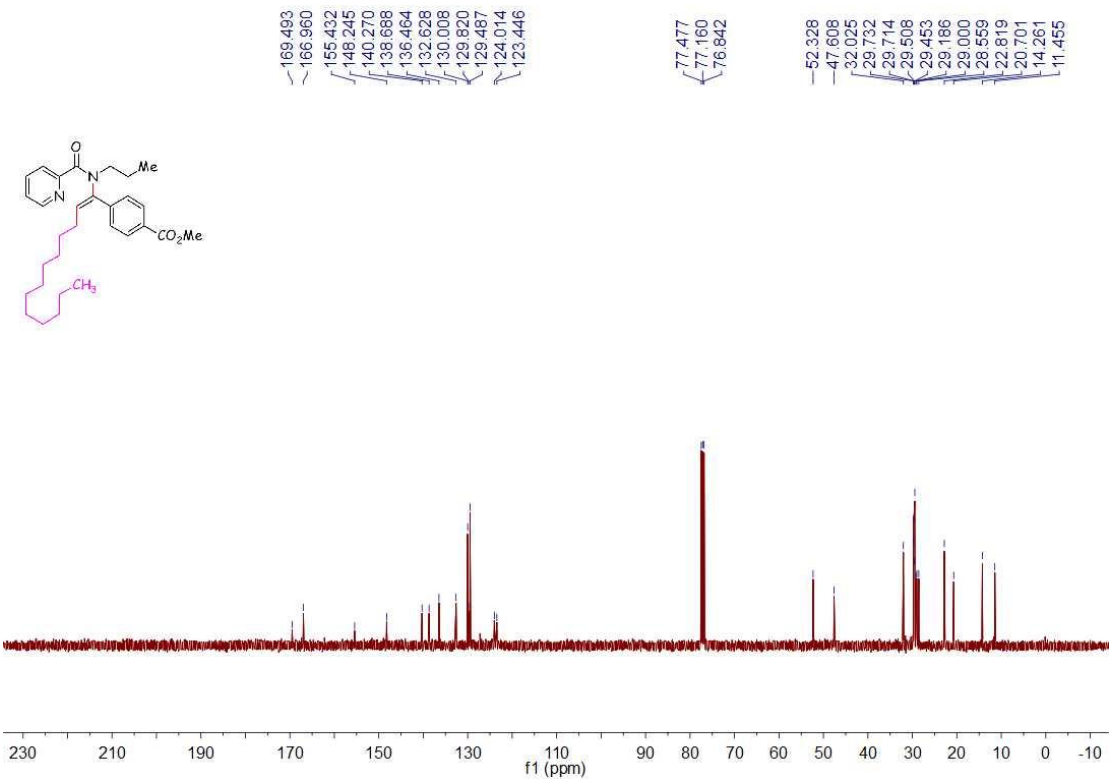
^{1}H NMR spectra for compound **5g** (400 MHz, $CDCl_3$)



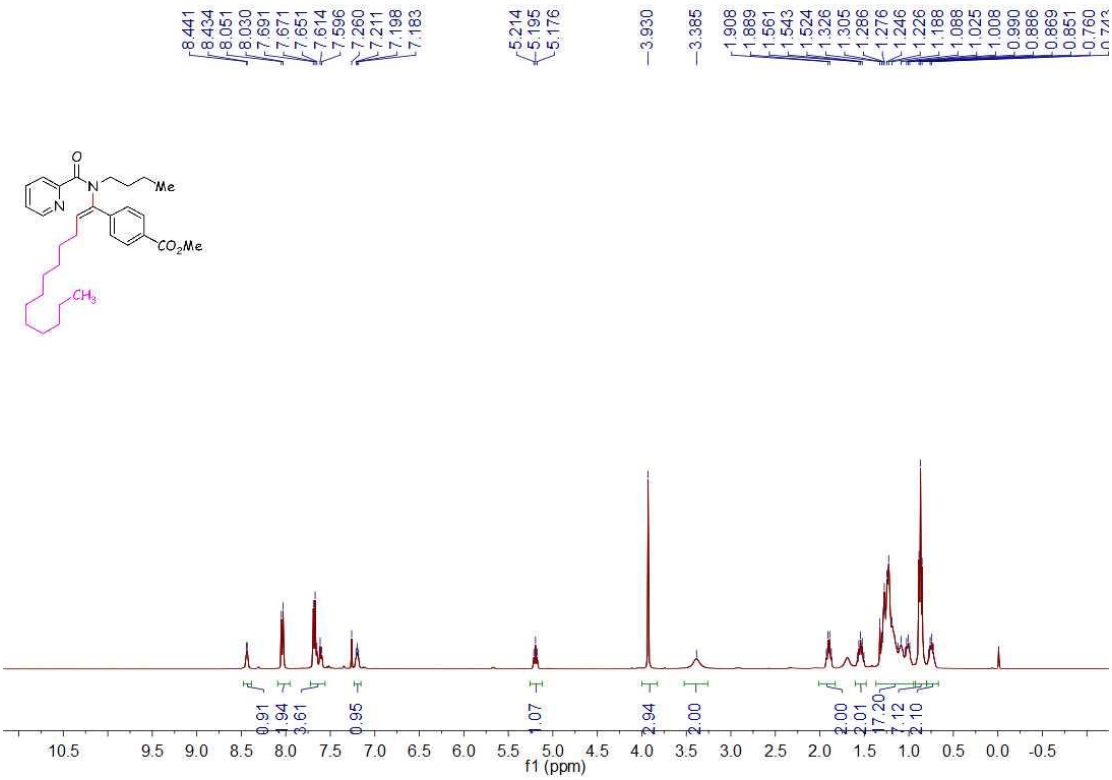
^{13}C NMR spectra for compound **5g** (100 MHz, $CDCl_3$)



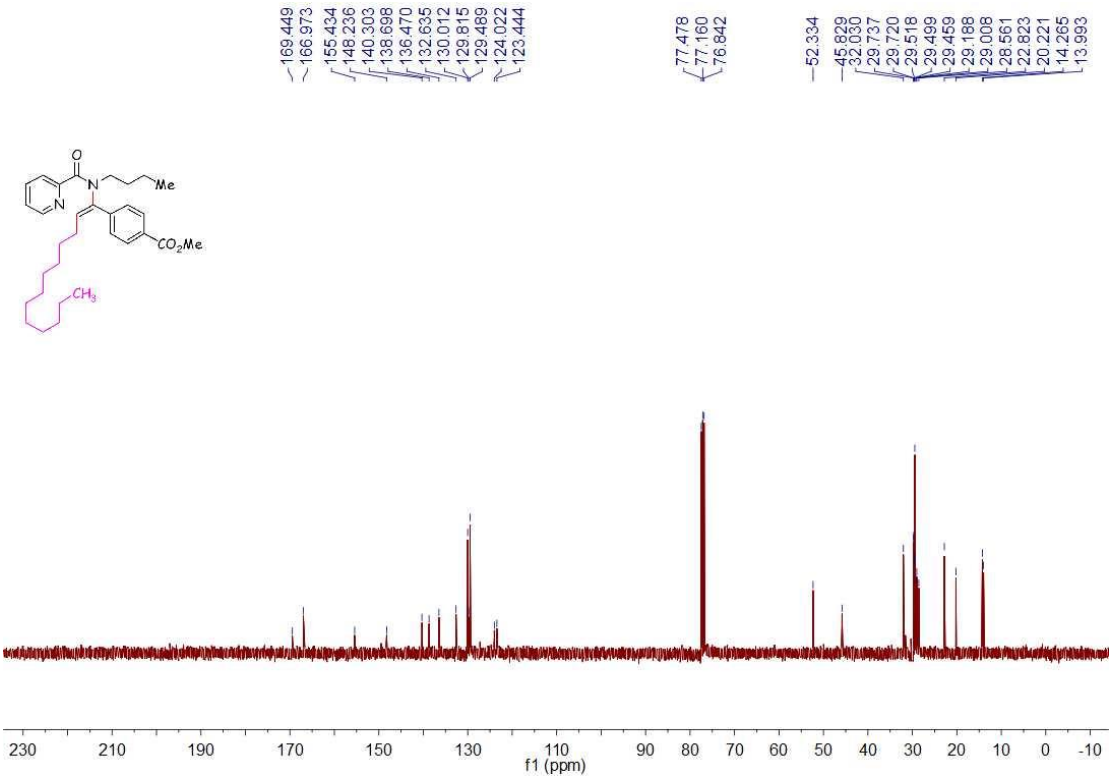
^{1}H NMR spectra for compound **5h** (400 MHz, $CDCl_3$)



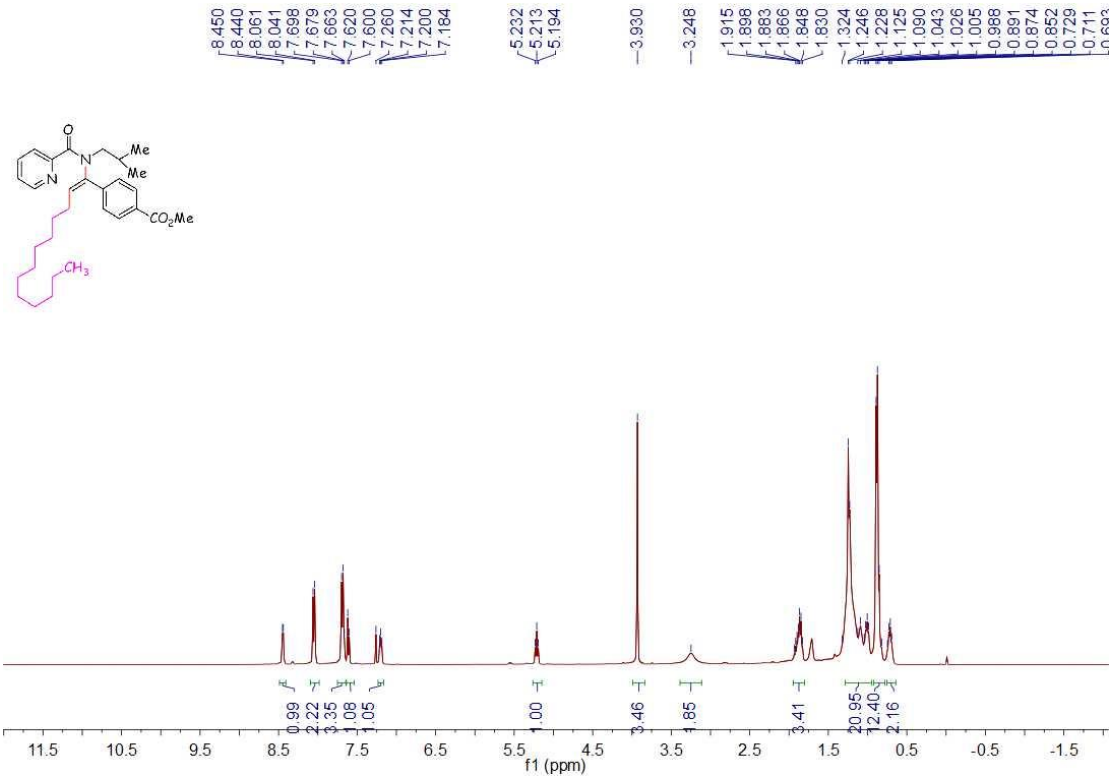
^{13}C NMR spectra for compound **5h** (100 MHz, $CDCl_3$)



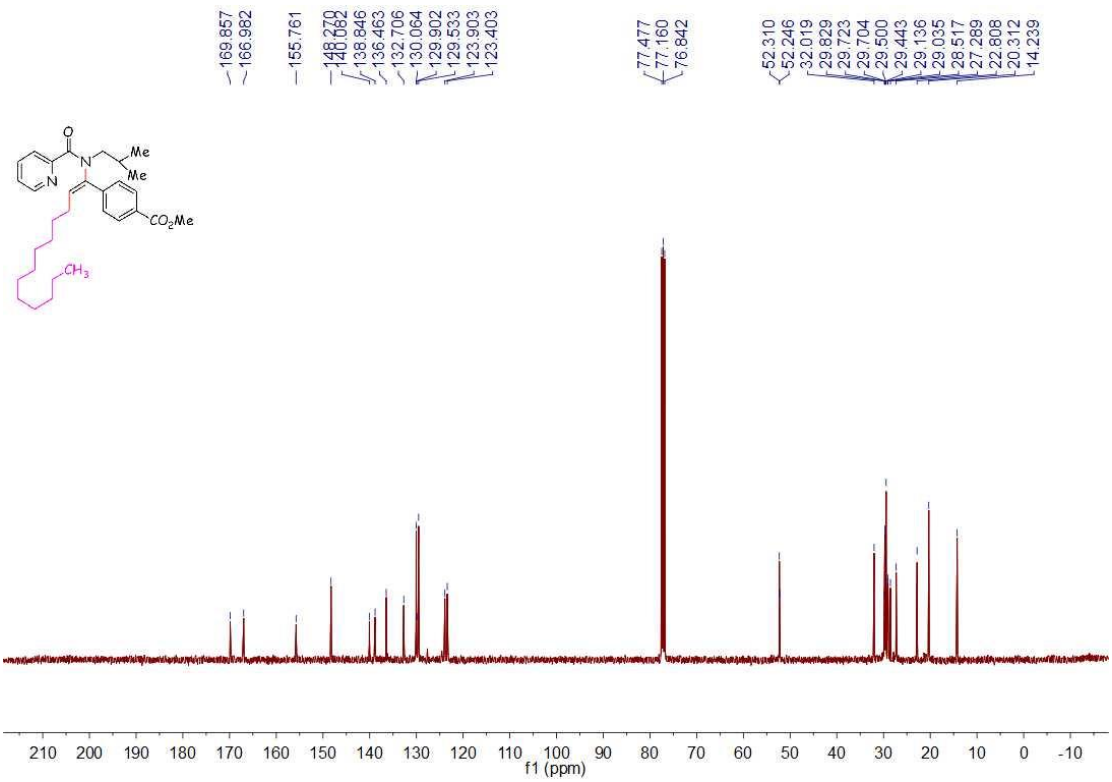
^{1}H NMR spectra for compound **5i** (400 MHz, $CDCl_3$)



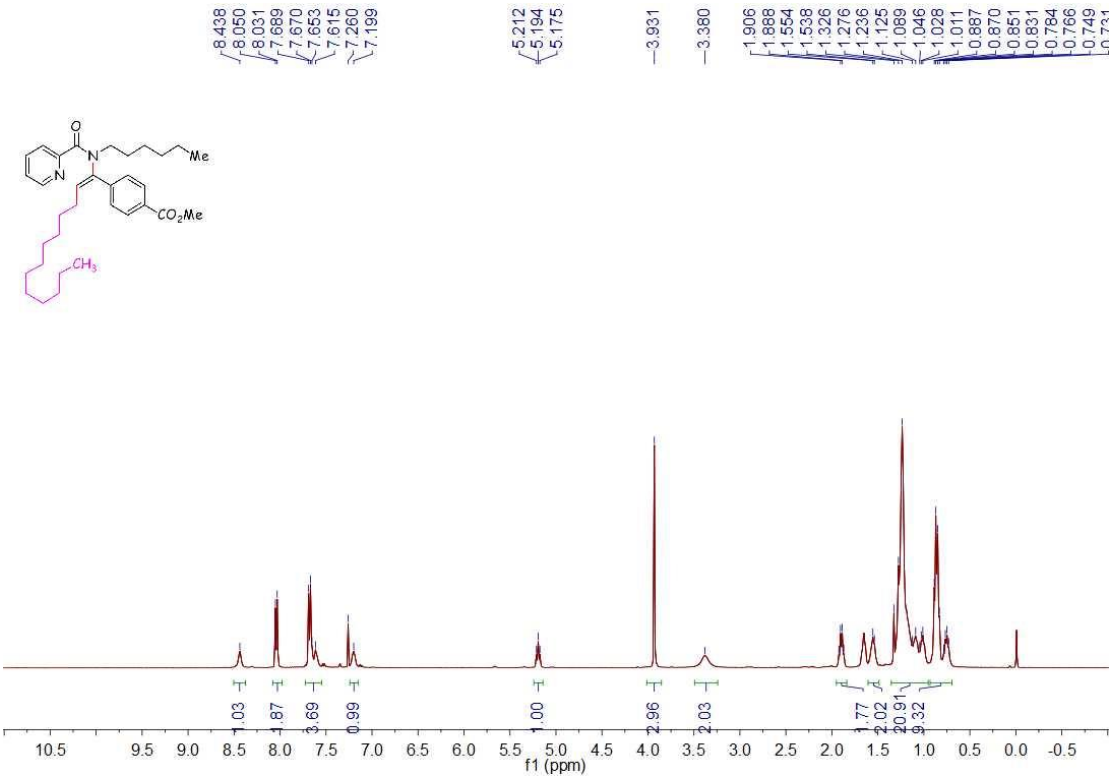
^{13}C NMR spectra for compound **5i** (100 MHz, $CDCl_3$)



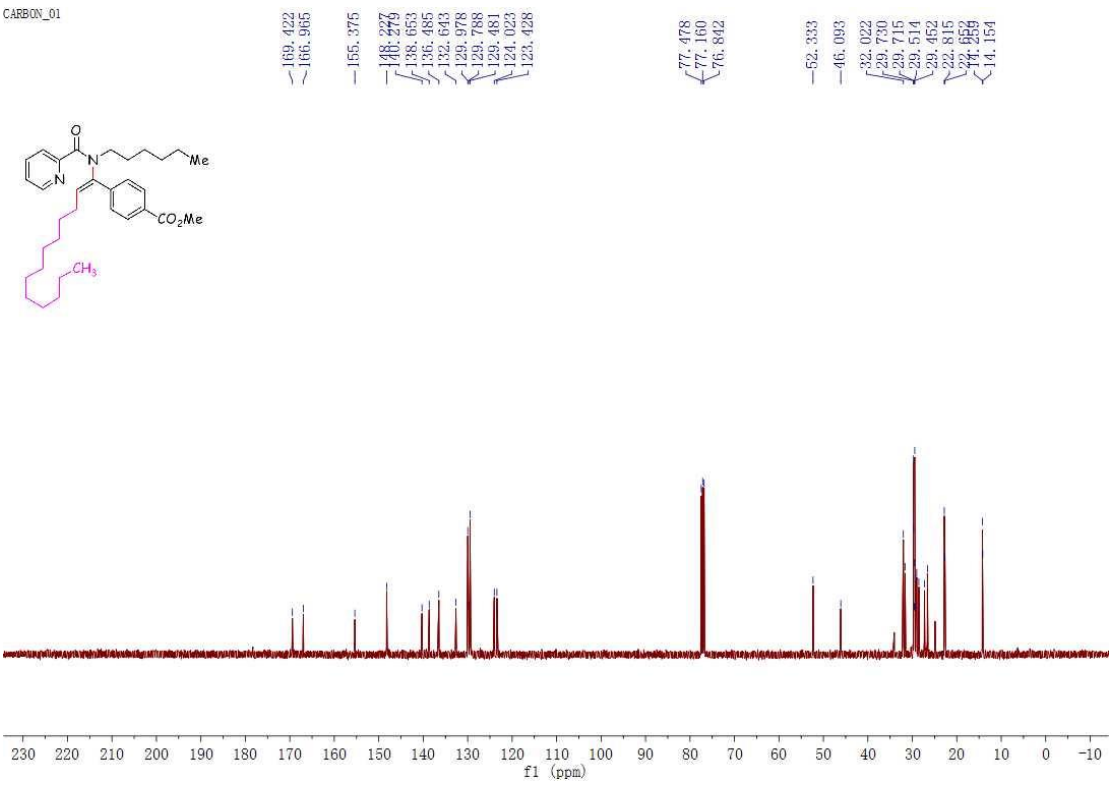
^{1}H NMR spectra for compound **5j** (400 MHz, $CDCl_3$)



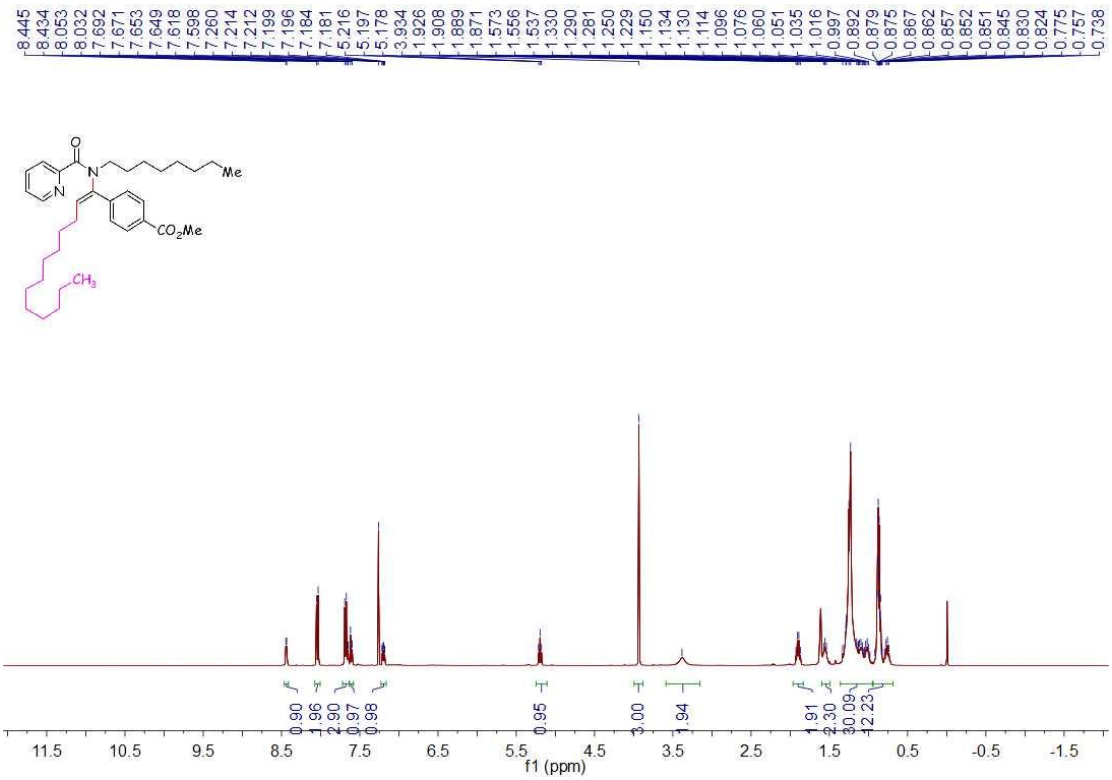
^{13}C NMR spectra for compound **5j** (100 MHz, $CDCl_3$)



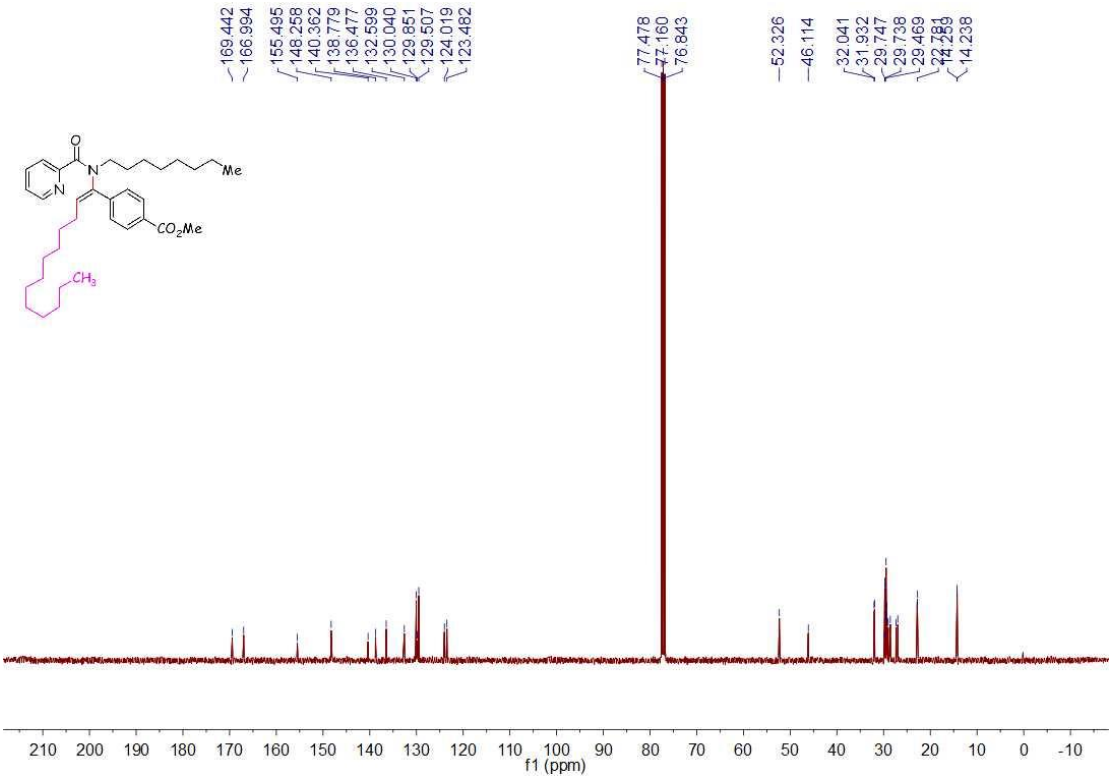
^{1}H NMR spectra for compound **5k** (400 MHz, $CDCl_3$)



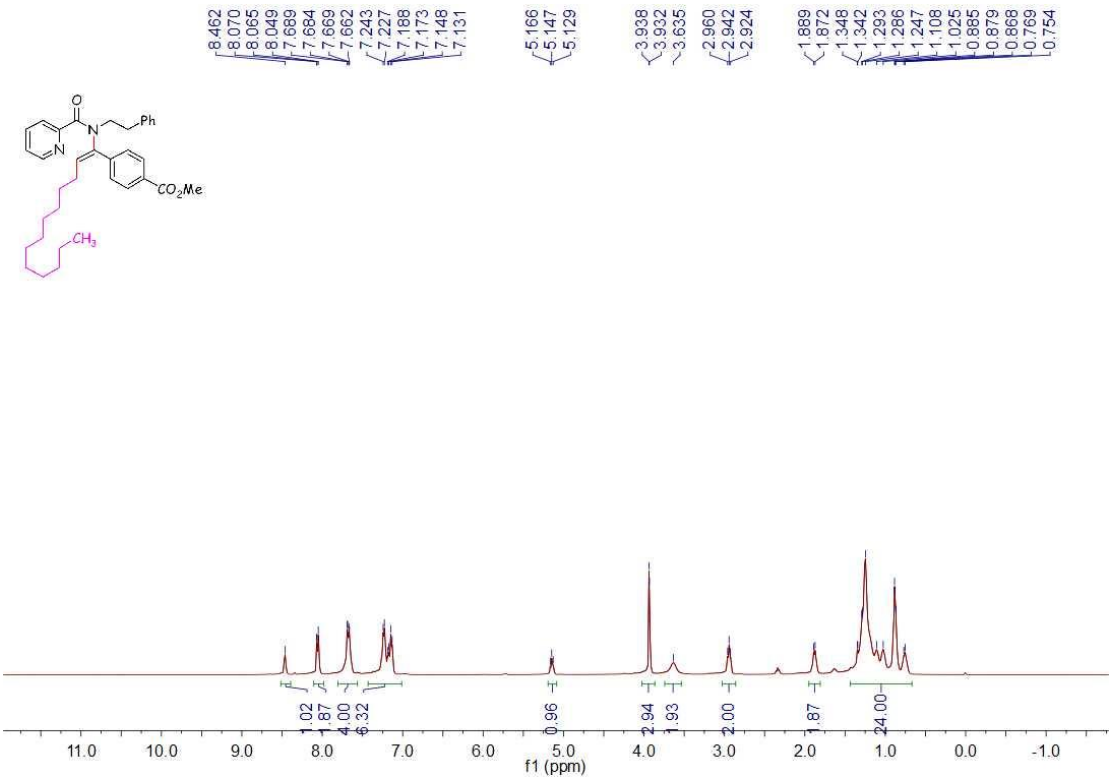
^{13}C NMR spectra for compound **5k** (100 MHz, $CDCl_3$)



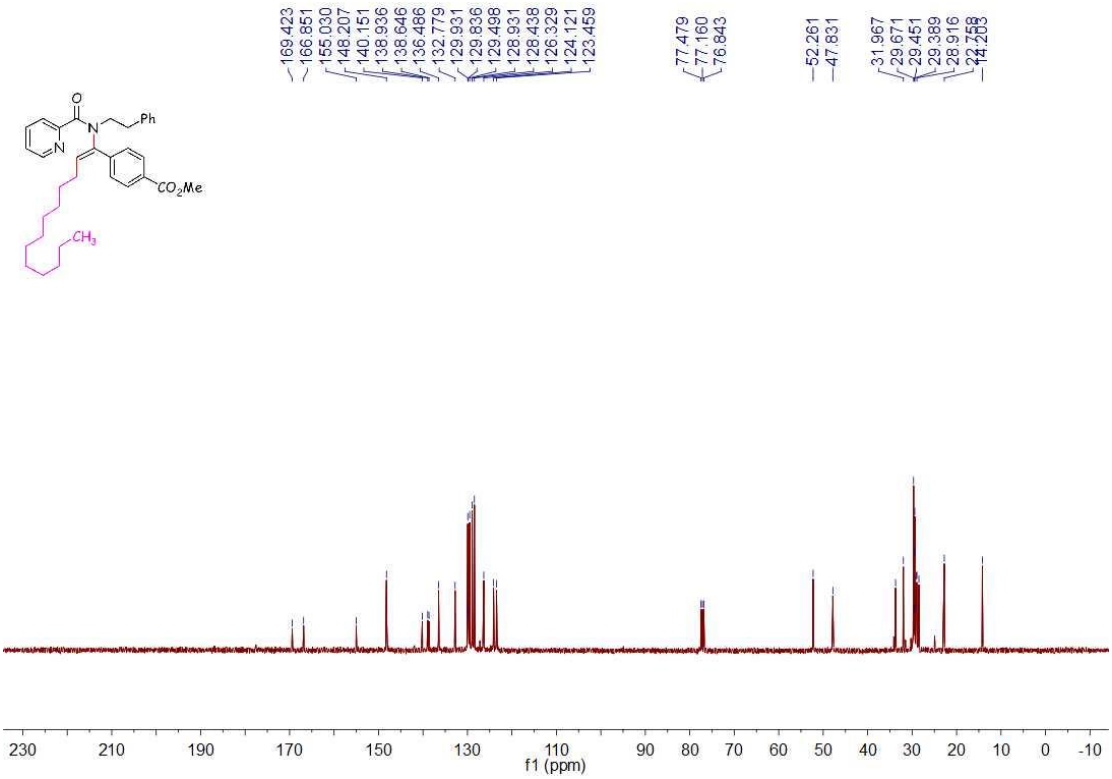
^{1}H NMR spectra for compound **5l** (400 MHz, $CDCl_3$)



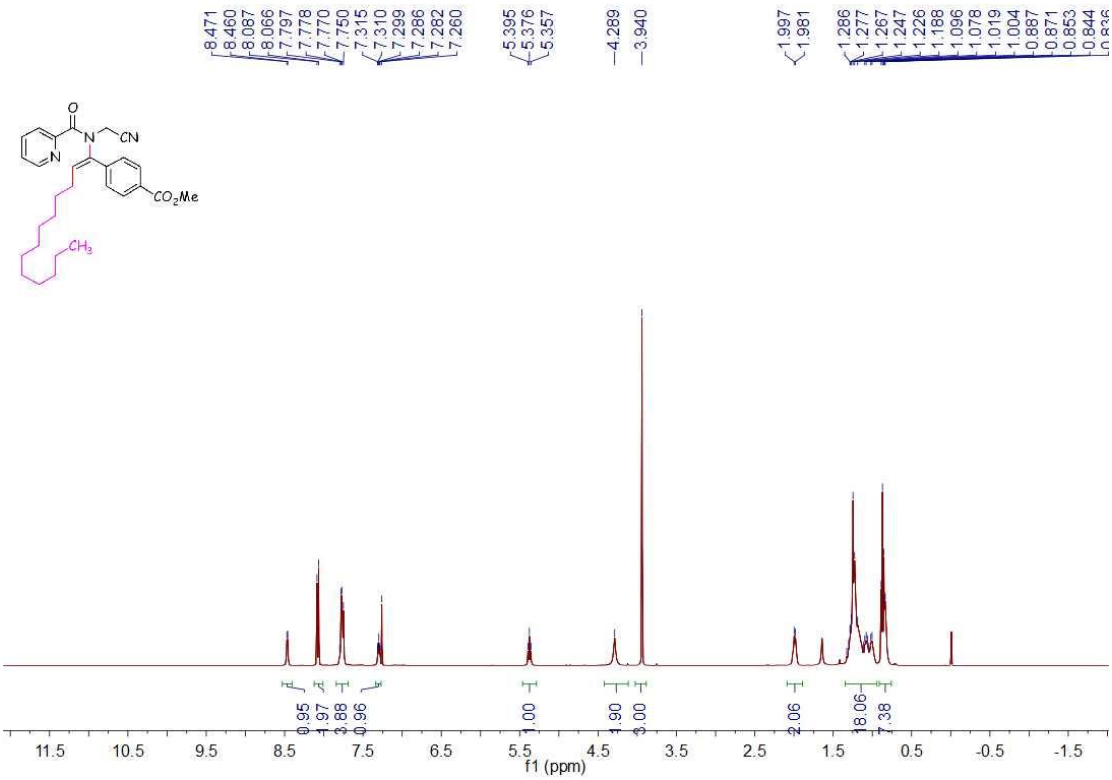
^{13}C NMR spectra for compound **5l** (100 MHz, $CDCl_3$)



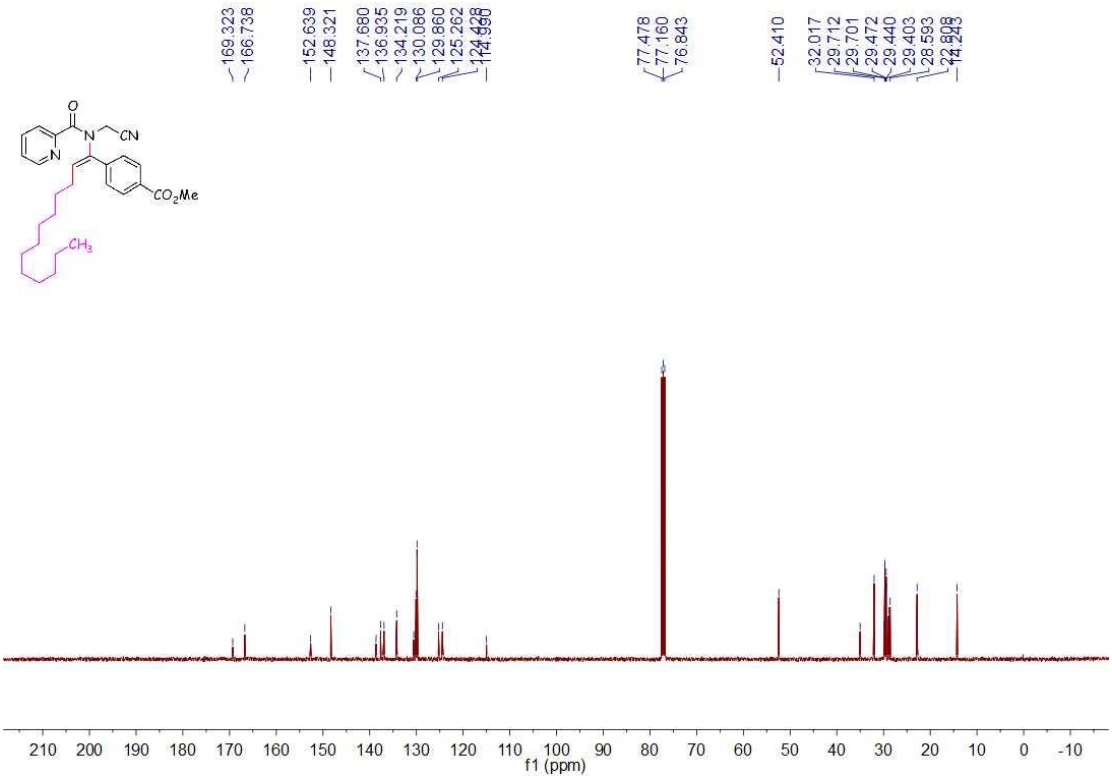
^{1}H NMR spectra for compound **5m** (400 MHz, $CDCl_3$)



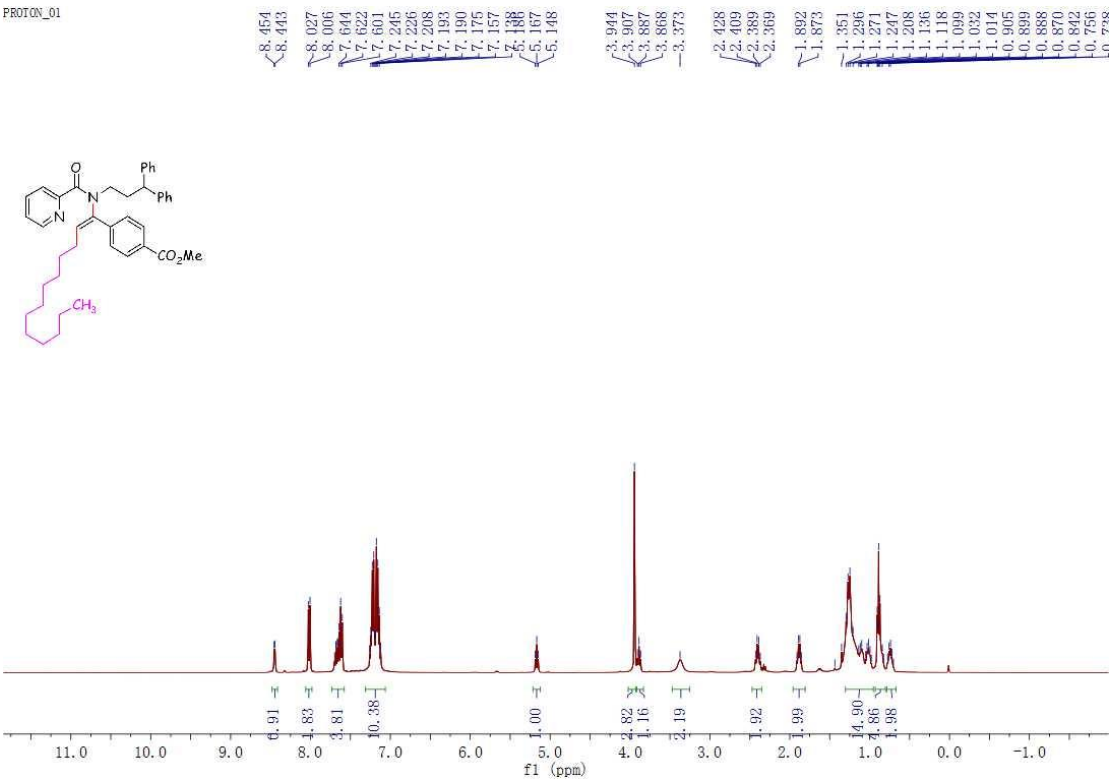
^{13}C NMR spectra for compound **5m** (100 MHz, $CDCl_3$)



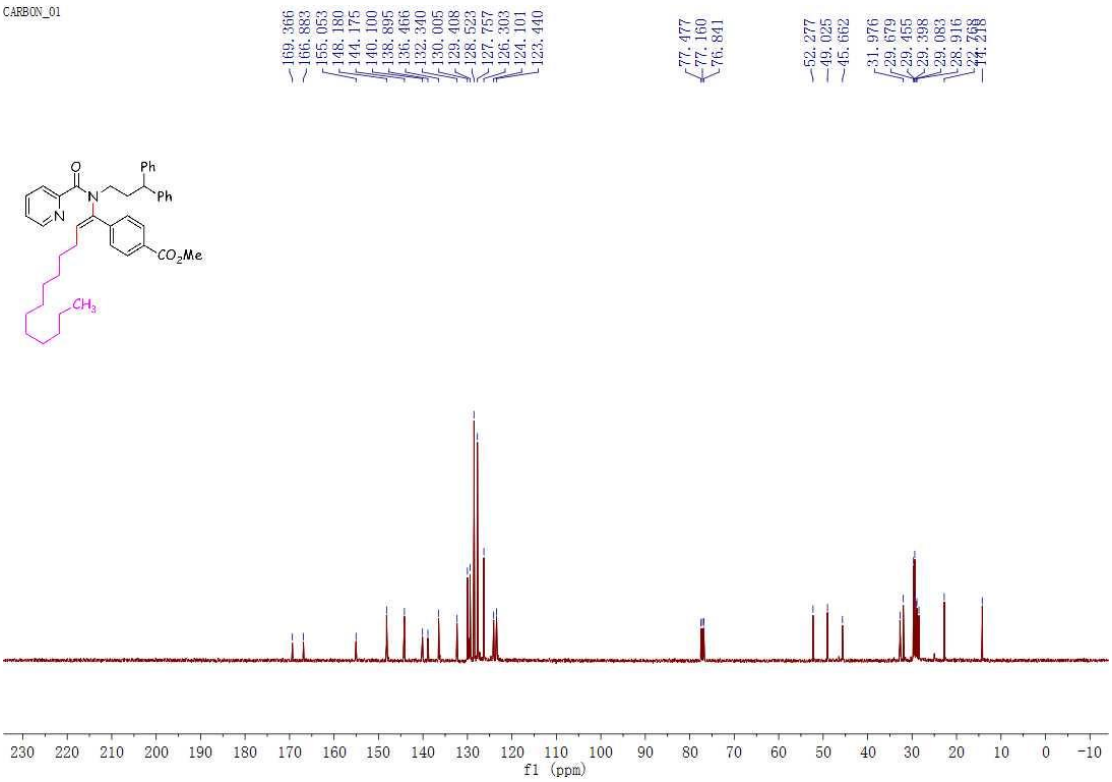
^{1}H NMR spectra for compound **5n** (400 MHz, $CDCl_3$)



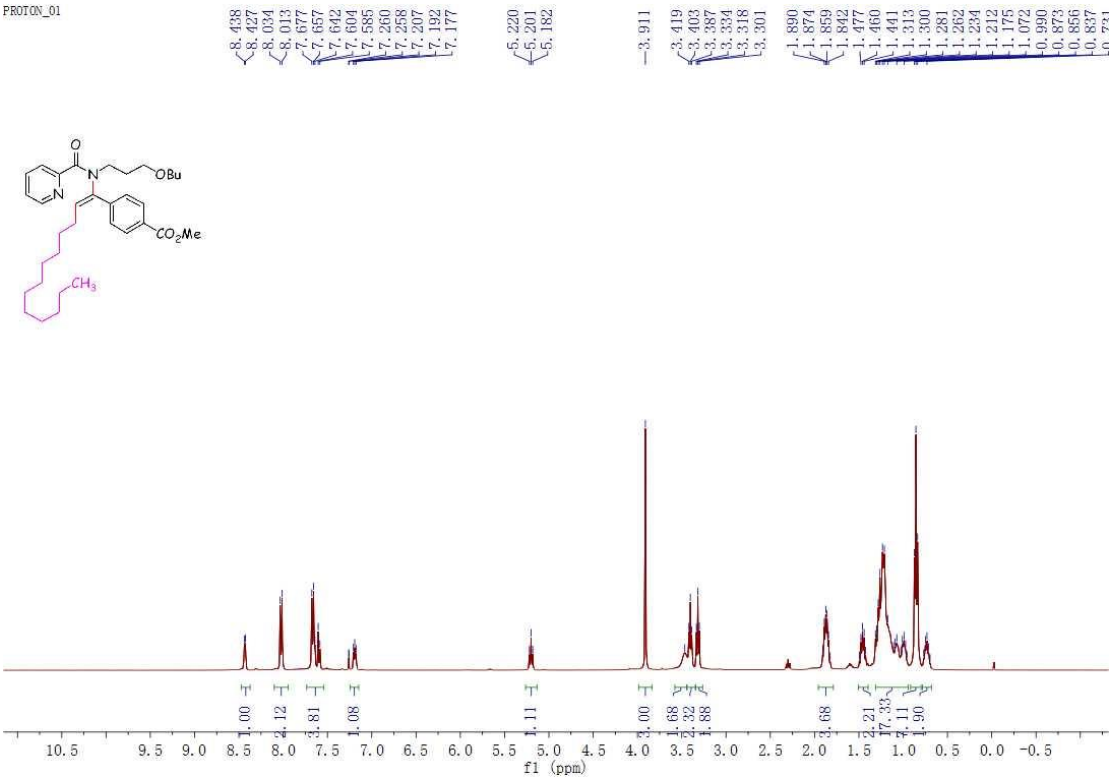
^{13}C NMR spectra for compound **5n** (100 MHz, $CDCl_3$)



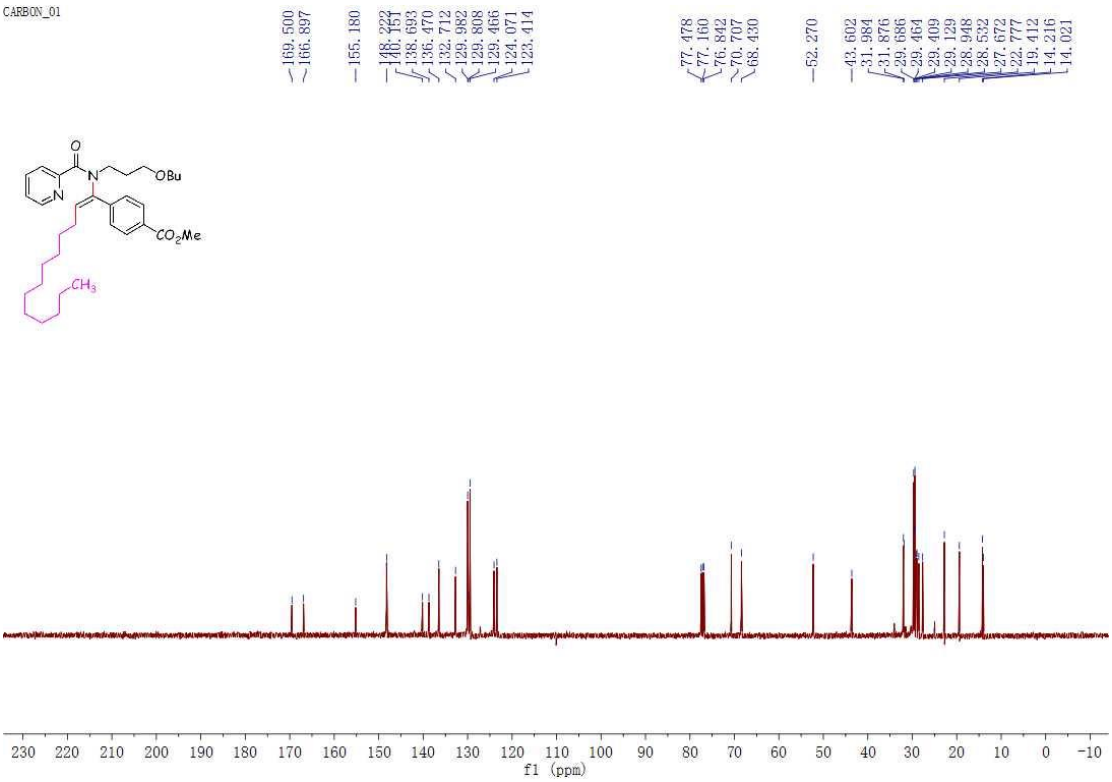
^{1}H NMR spectra for compound **5o** (400 MHz, $CDCl_3$)



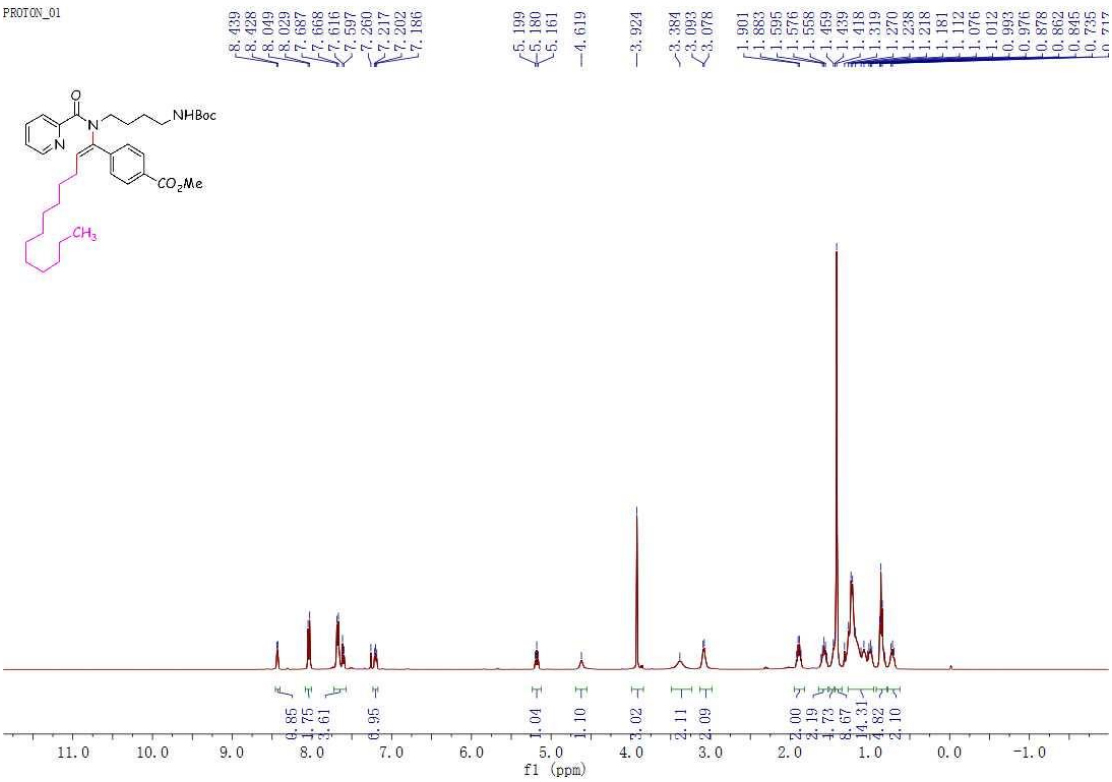
^{13}C NMR spectra for compound **5o** (100 MHz, $CDCl_3$)



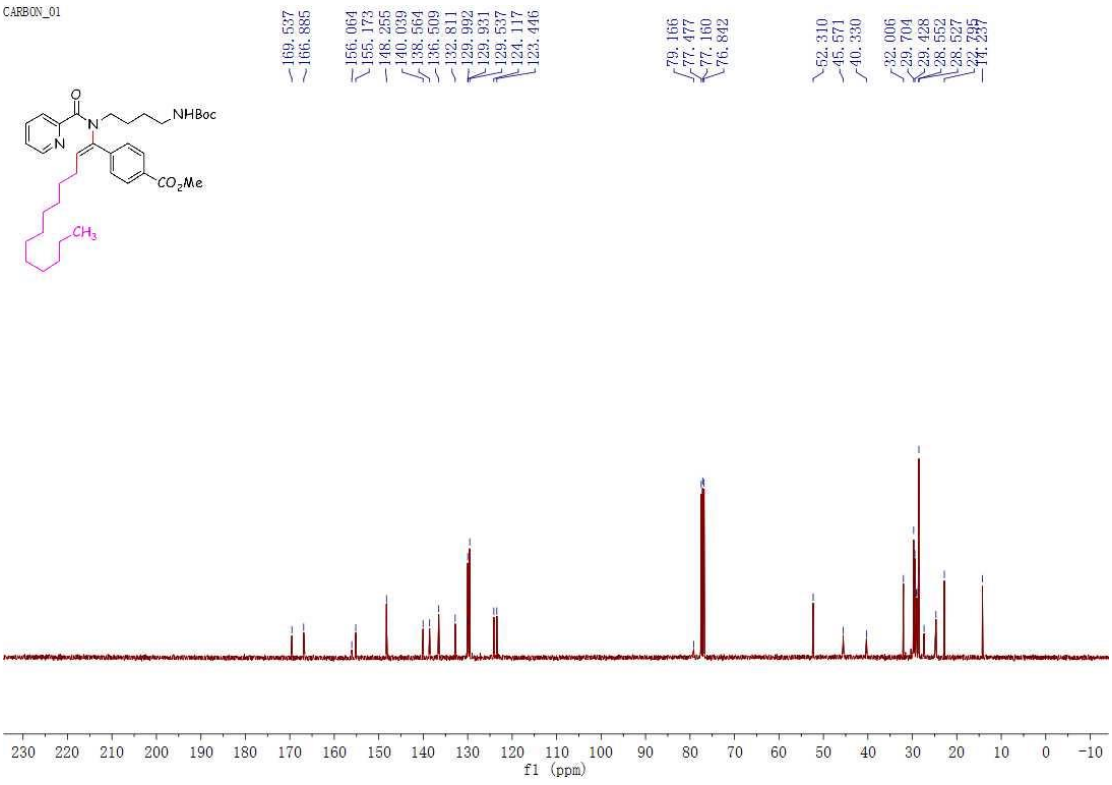
^{1}H NMR spectra for compound **5p** (400 MHz, $CDCl_3$)



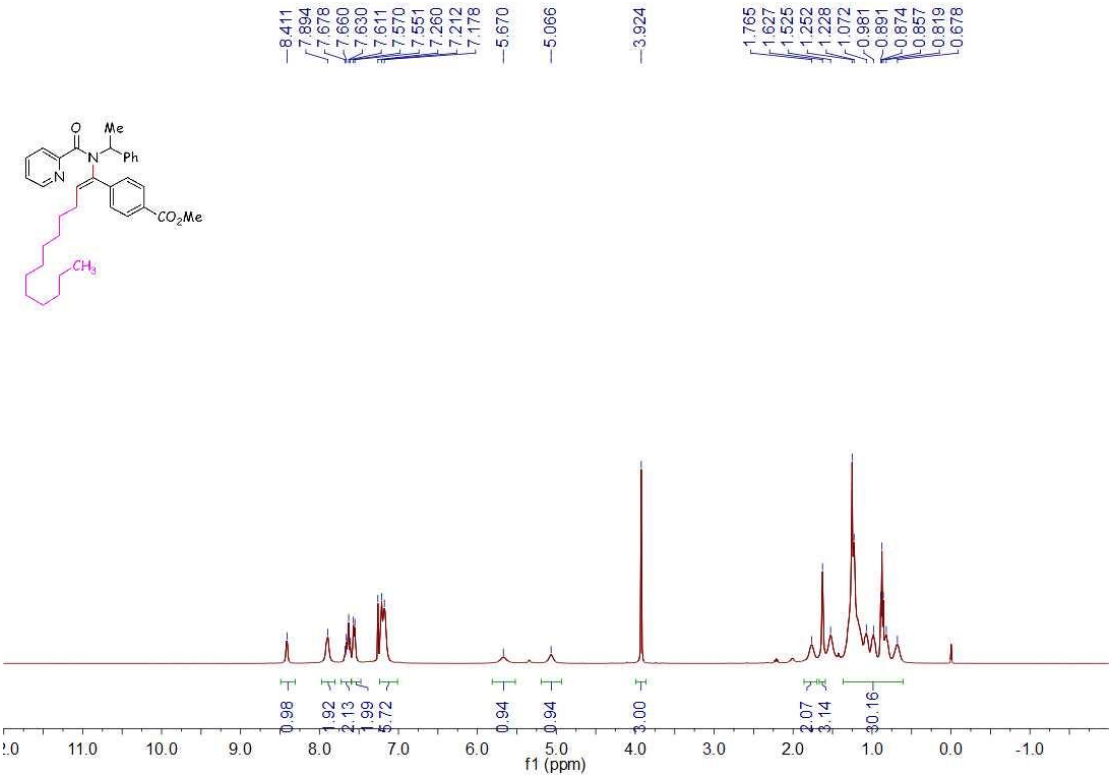
^{13}C NMR spectra for compound **5p** (100 MHz, $CDCl_3$)



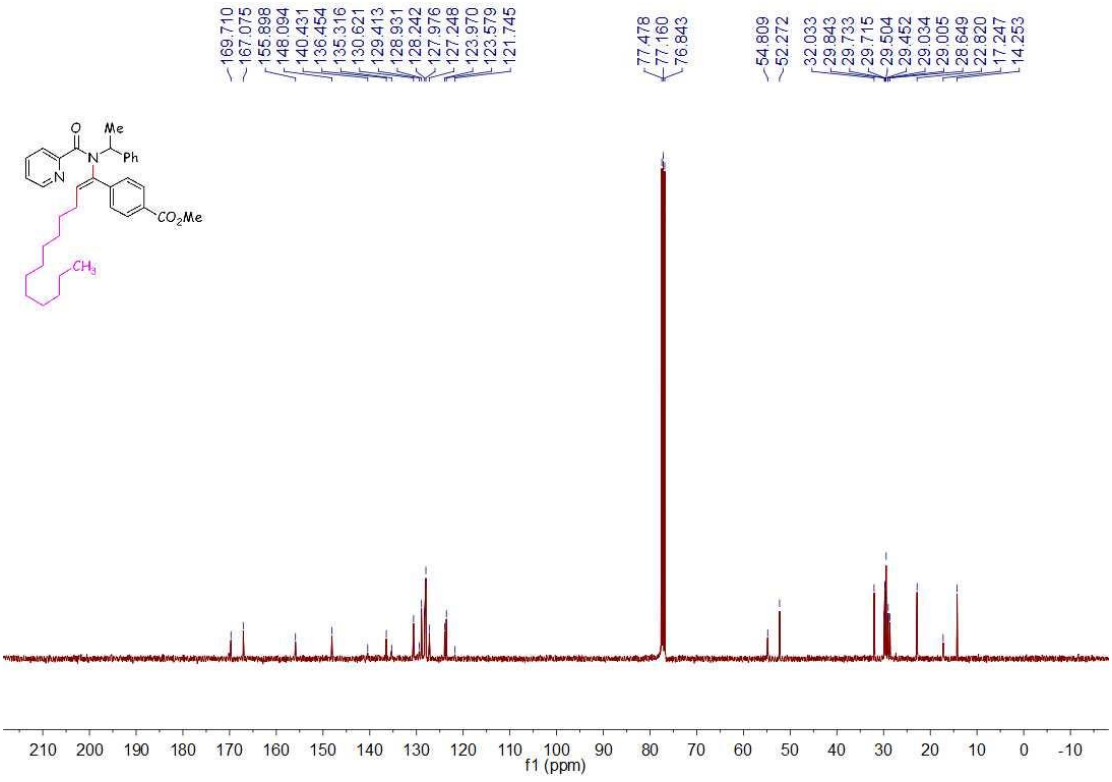
^{1}H NMR spectra for compound **5q** (400 MHz, $CDCl_3$)



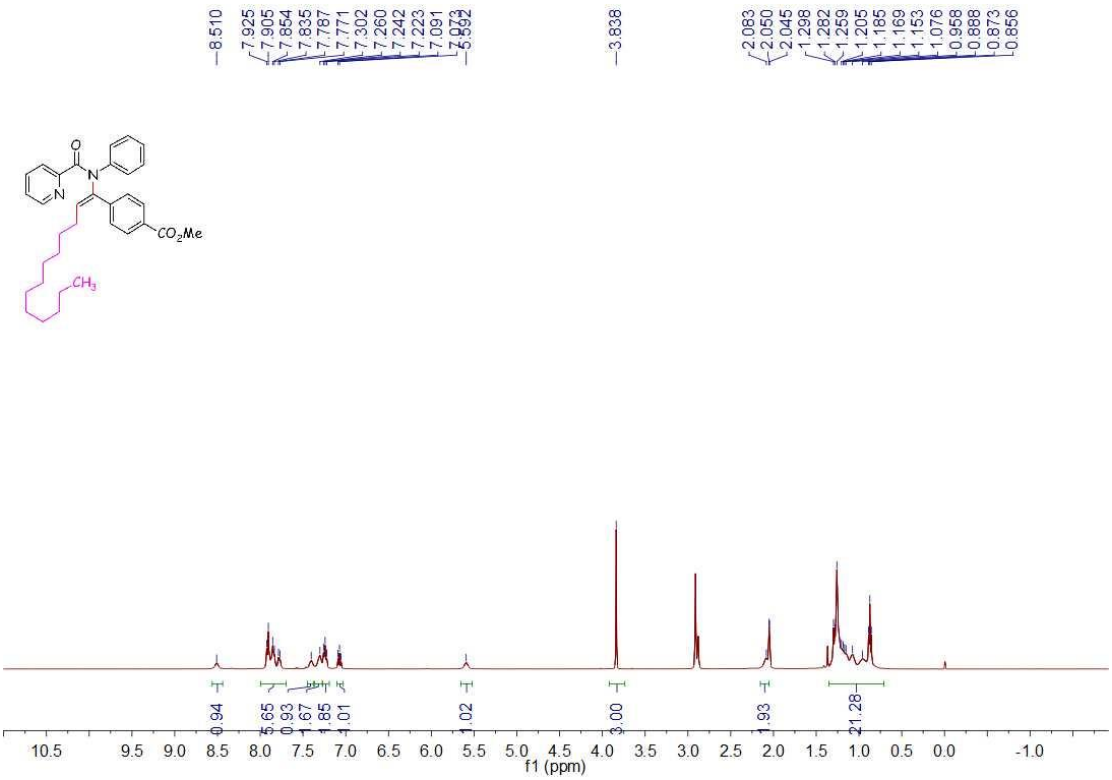
^{13}C NMR spectra for compound **5q** (100 MHz, $CDCl_3$)



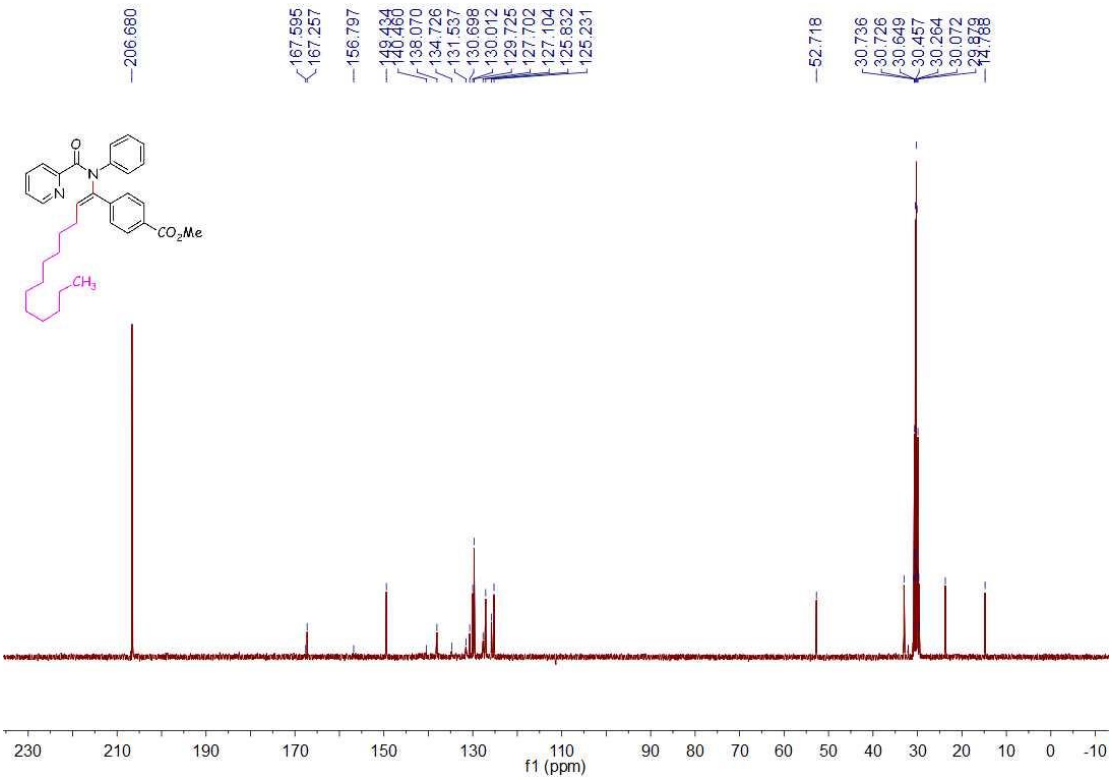
^{1}H NMR spectra for compound **5r** (400 MHz, $CDCl_3$)



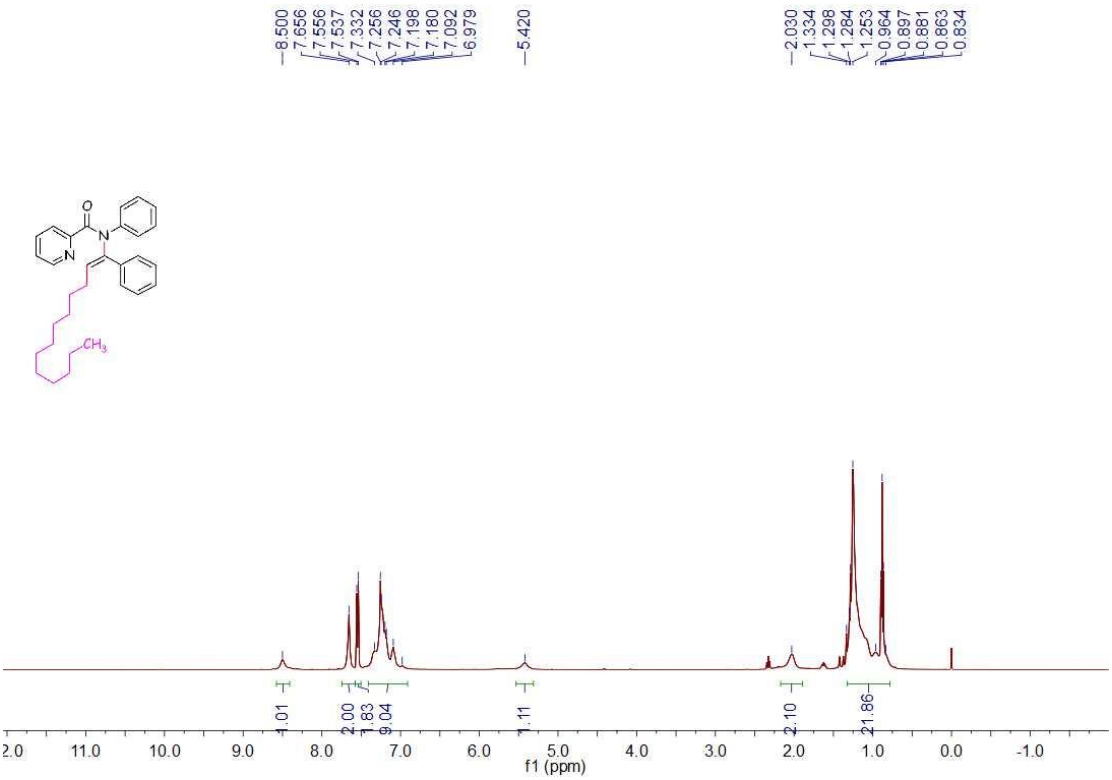
^{13}C NMR spectra for compound **5r** (100 MHz, $CDCl_3$)



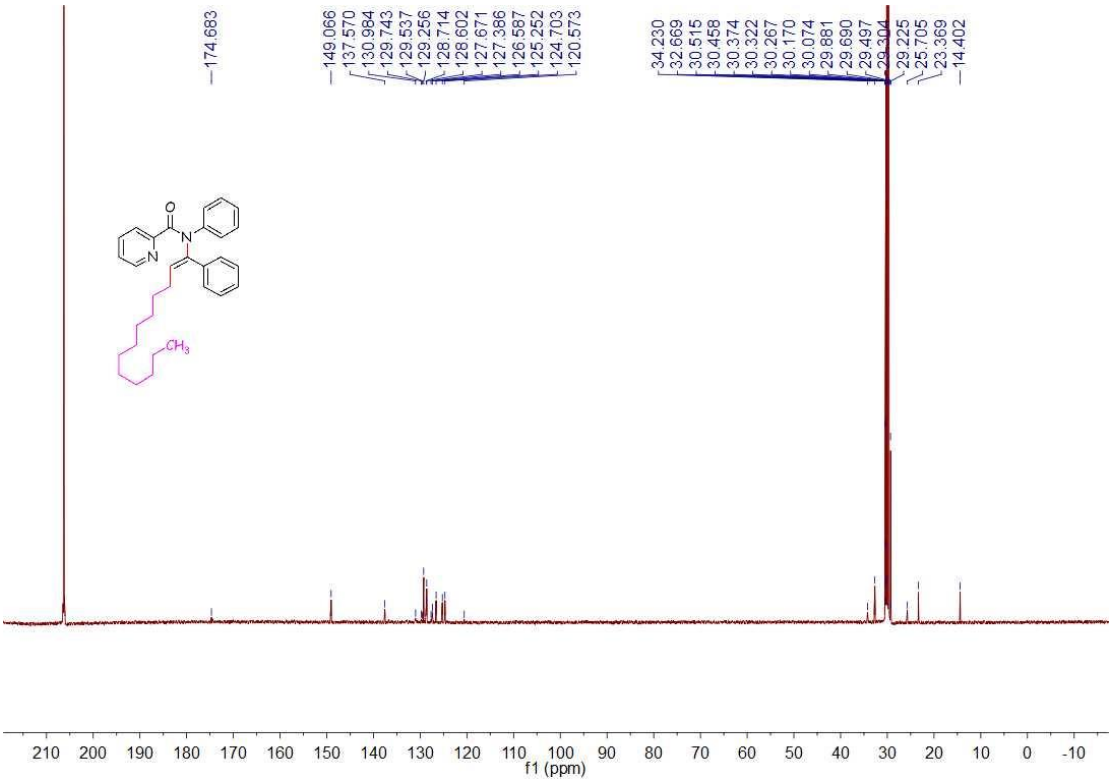
^{1}H NMR spectra for compound **5s** (400 MHz, Acetone-d_6)



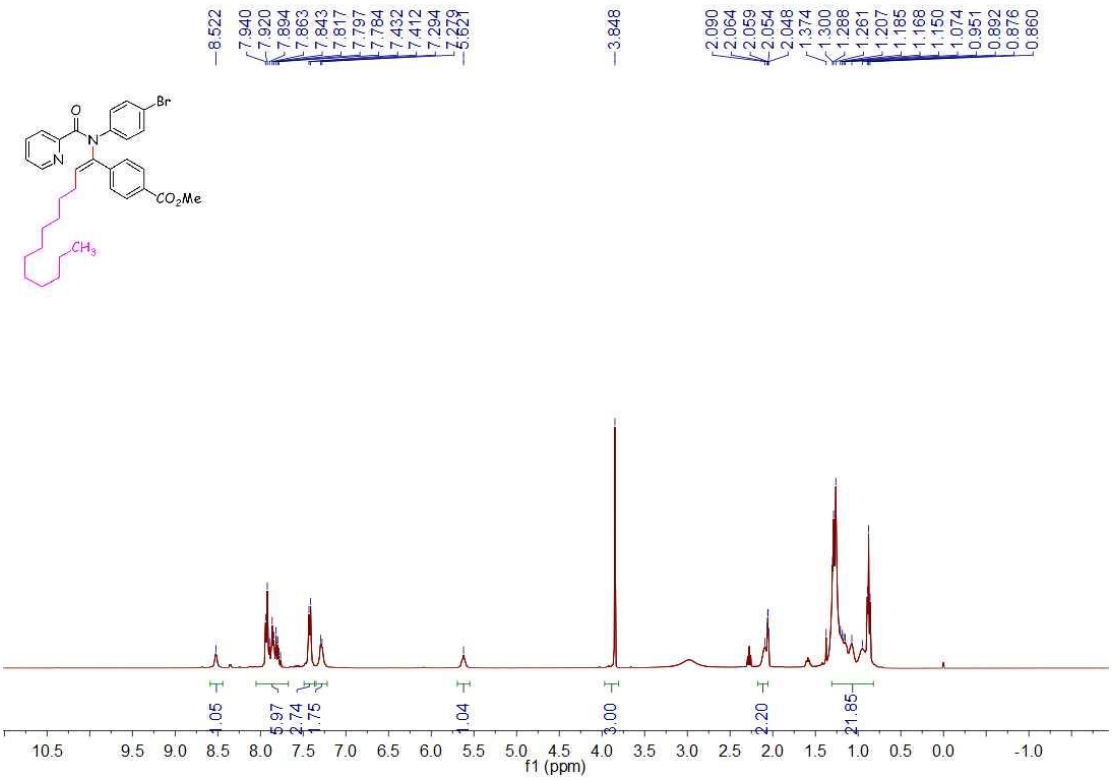
^{13}C NMR spectra for compound **5s** (100 MHz, Acetone-d_6)



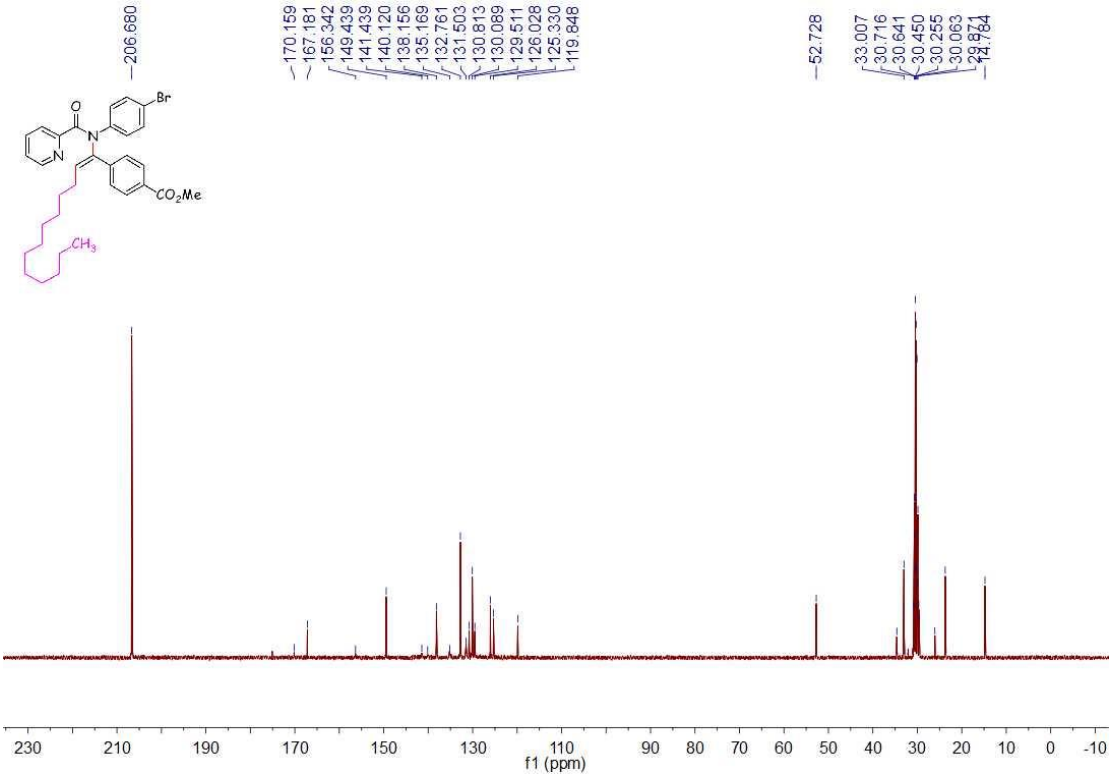
^{1}H NMR spectra for compound **5t** (400 MHz, $CDCl_3$)



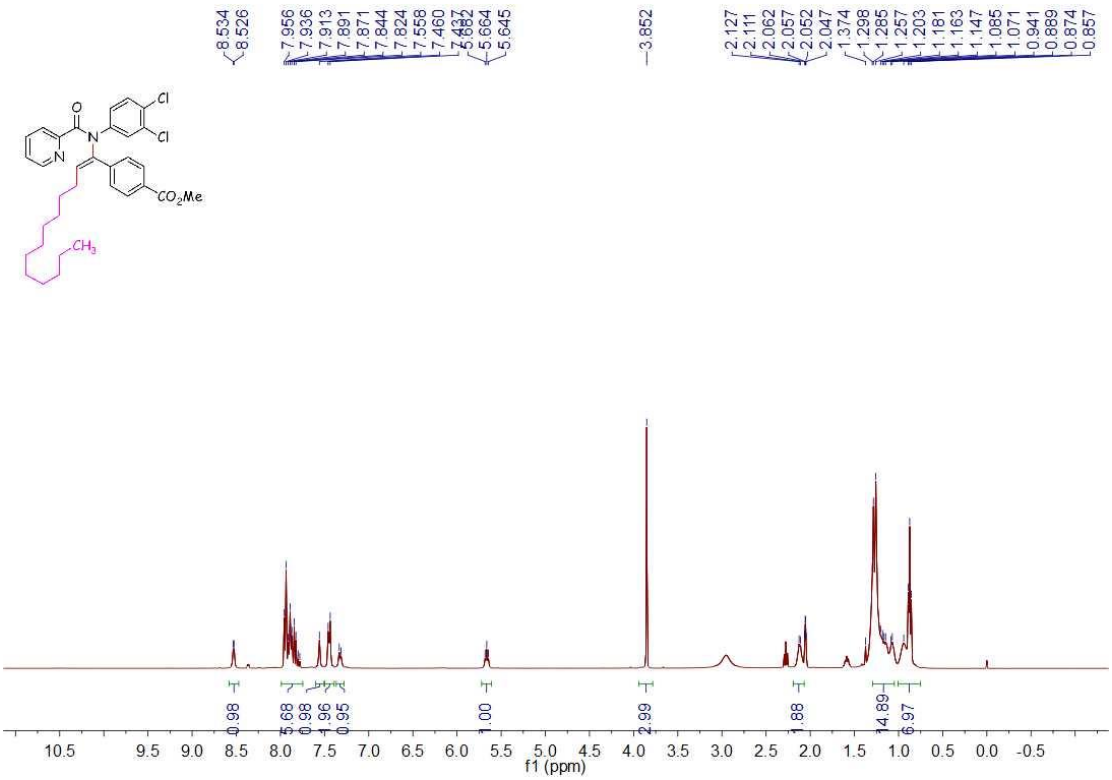
^{13}C NMR spectra for compound **5t** (100 MHz, Acetone-d_6)



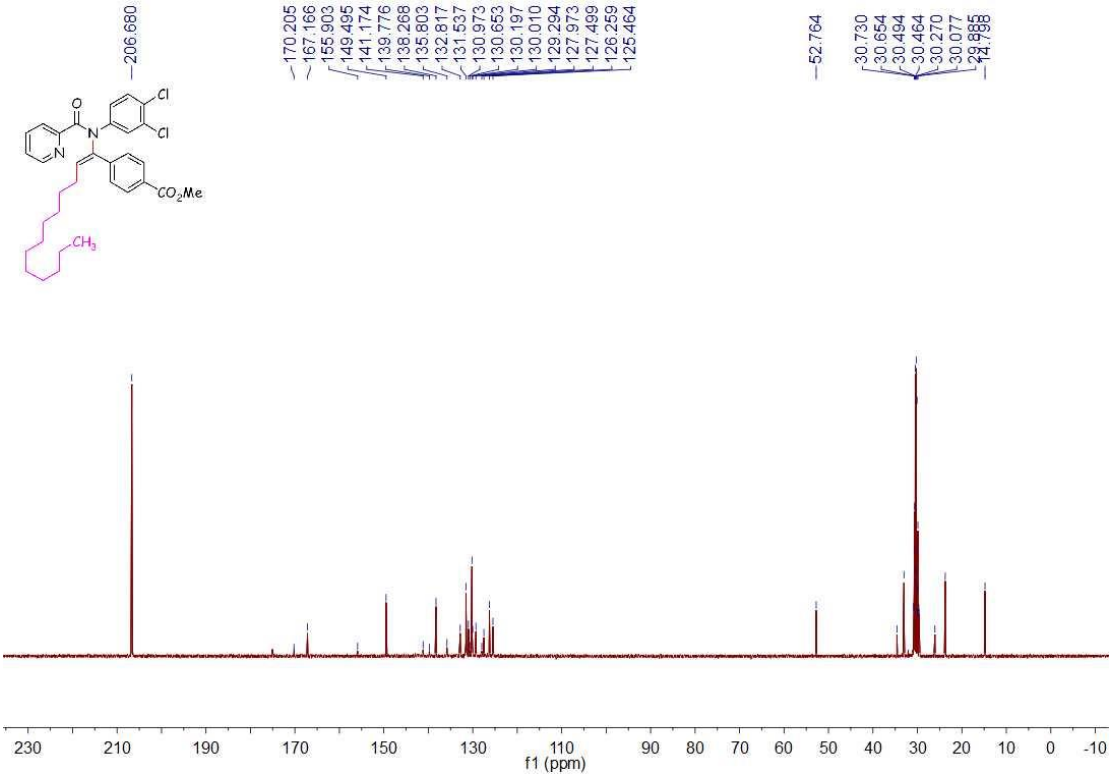
^{1}H NMR spectra for compound **5u** (400 MHz, Acetone-d_6)



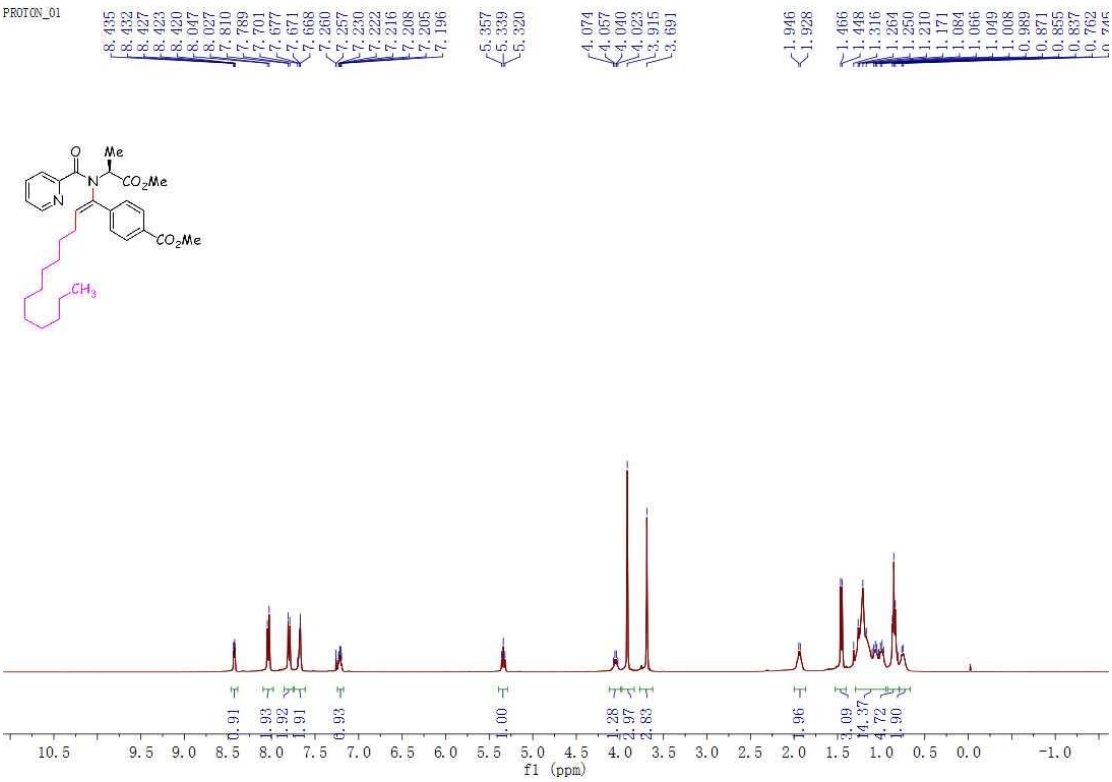
^{13}C NMR spectra for compound **5u** (100 MHz, Acetone-d_6)



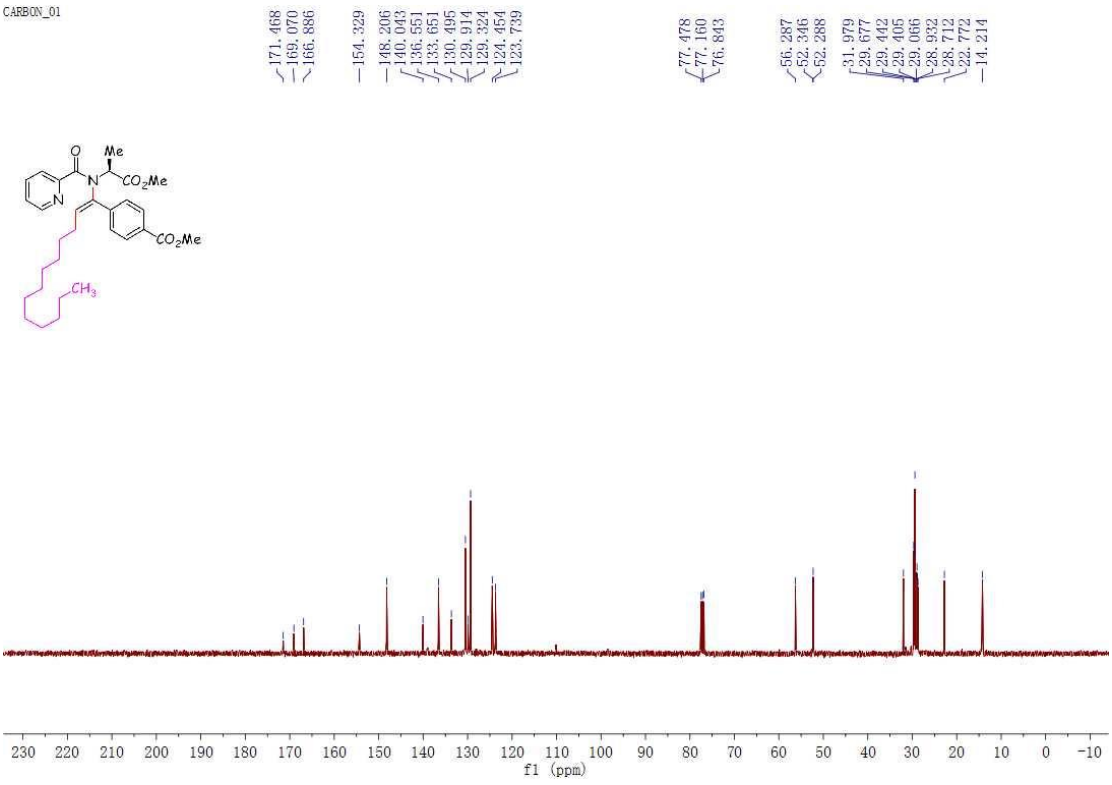
^{1}H NMR spectra for compound **5v** (400 MHz, Acetone-d_6)



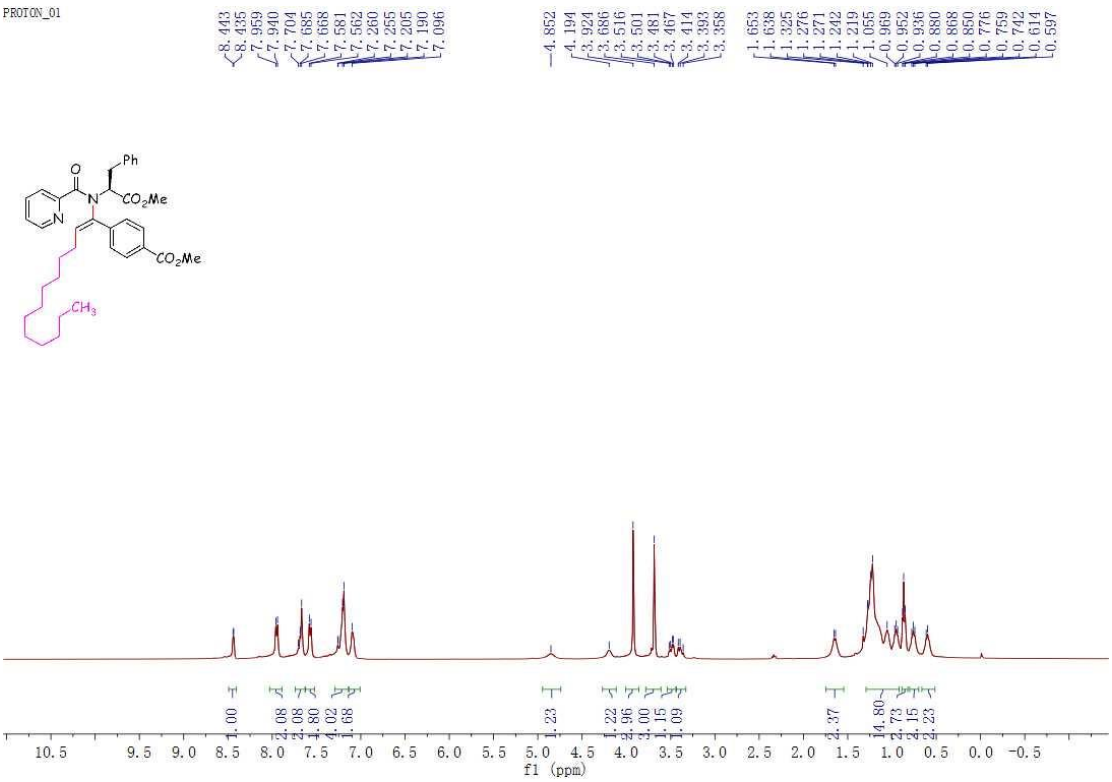
^{13}C NMR spectra for compound **5v** (100 MHz, Acetone-d_6)



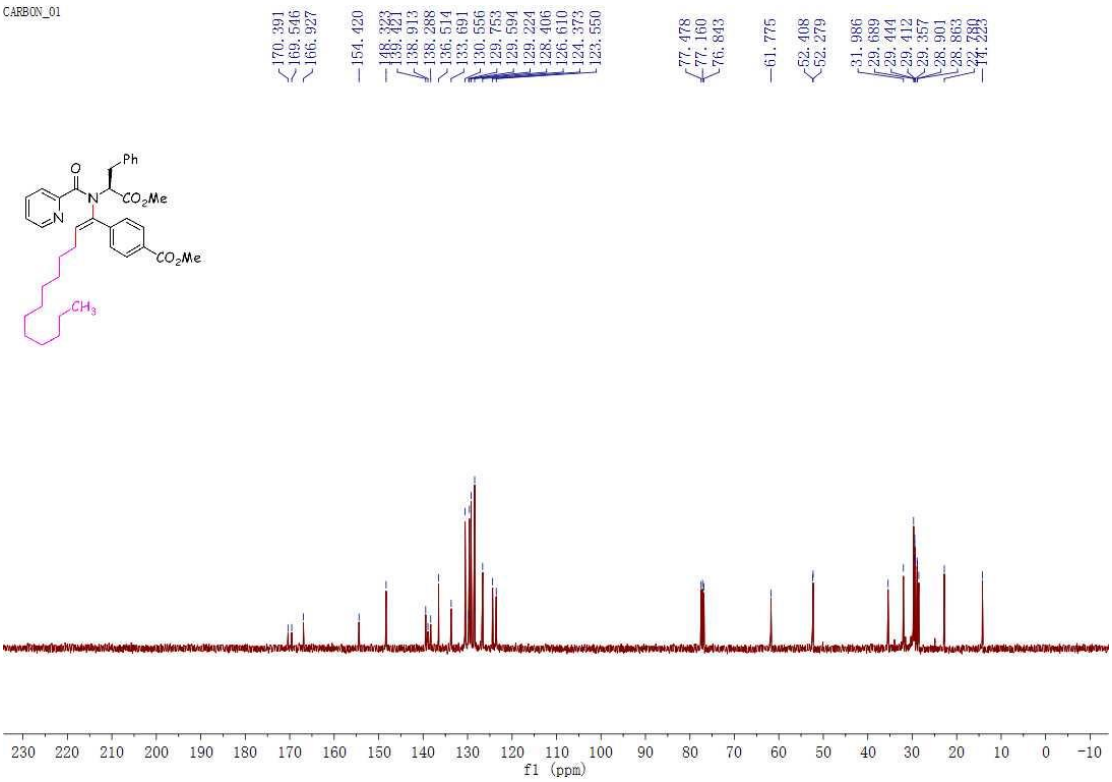
^{1}H NMR spectra for compound **5w** (400 MHz, $CDCl_3$)



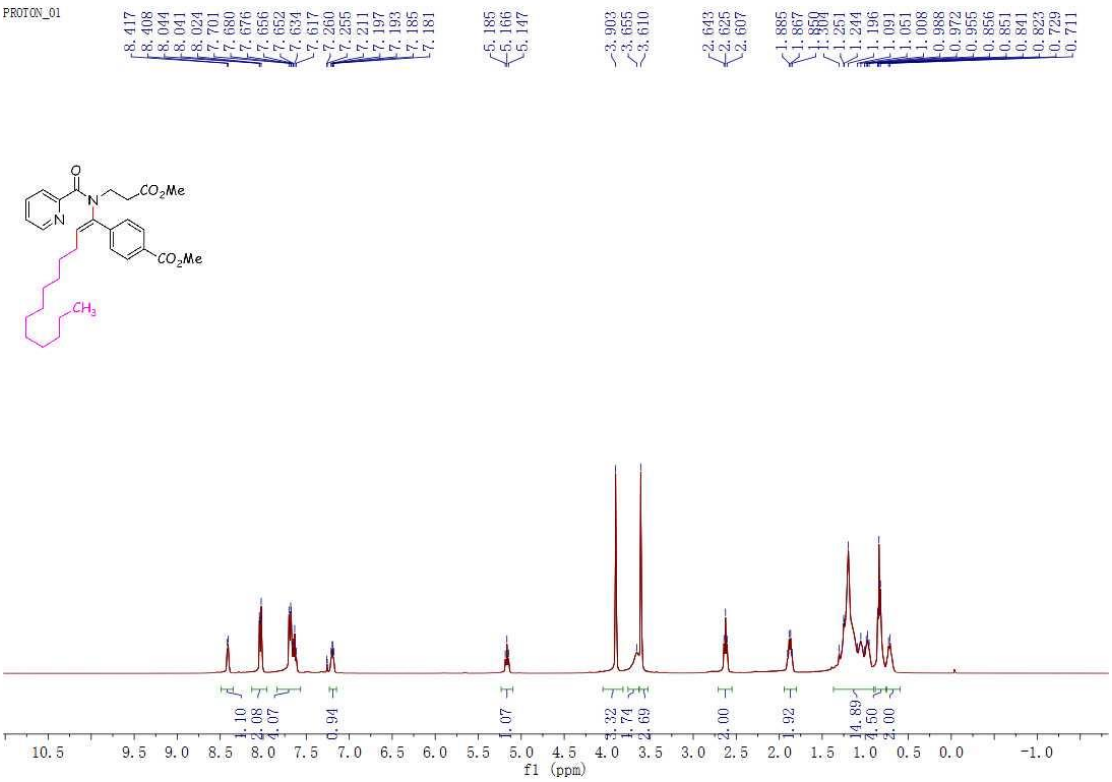
^{13}C NMR spectra for compound **5w** (100 MHz, $CDCl_3$)



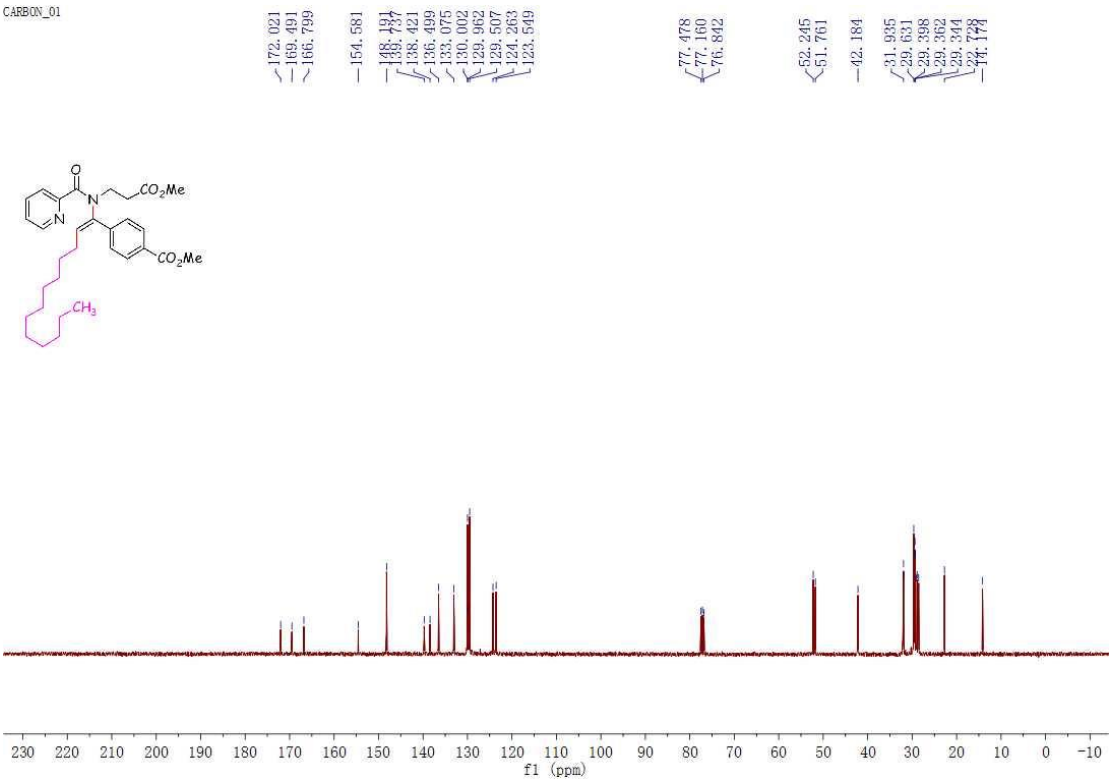
^{1}H NMR spectra for compound **5x** (400 MHz, $CDCl_3$)



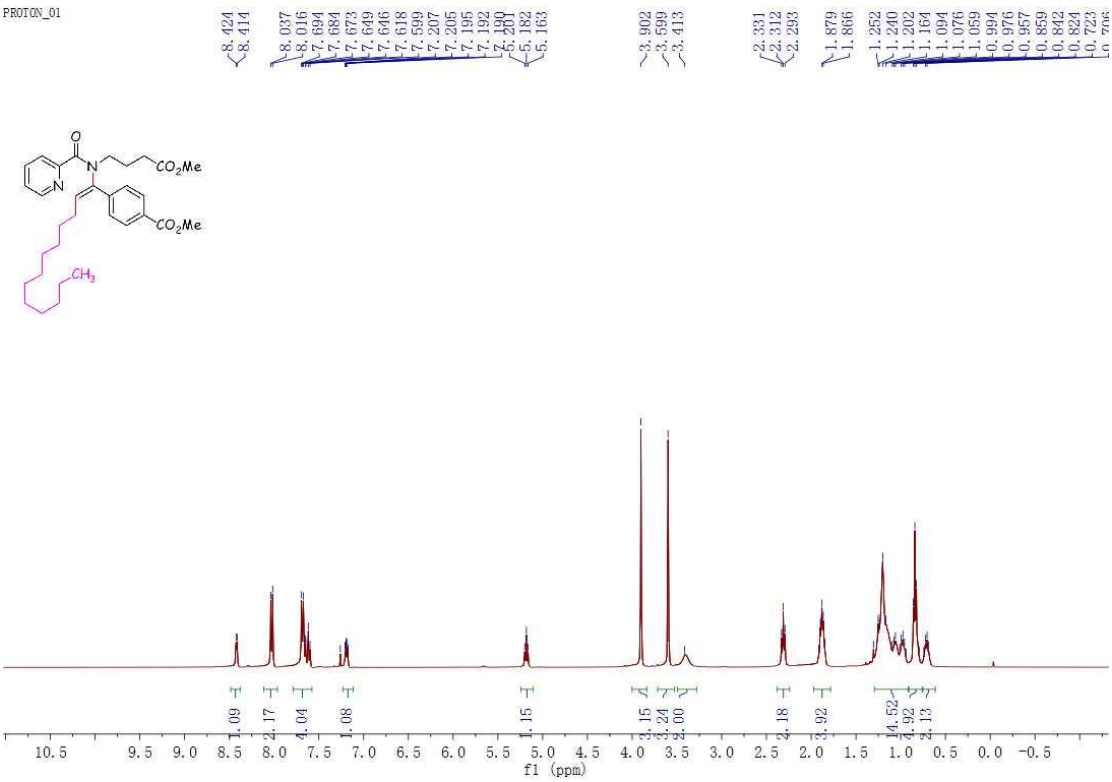
^{13}C NMR spectra for compound **5x** (100 MHz, $CDCl_3$)



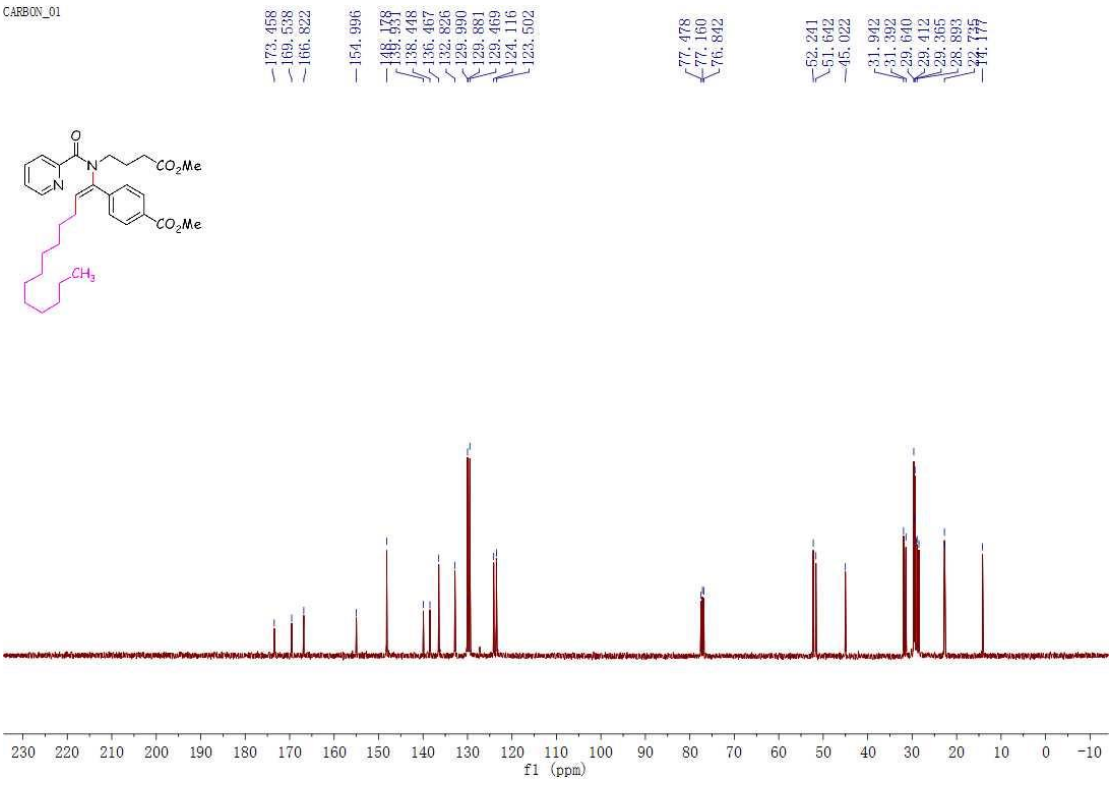
^{1}H NMR spectra for compound **5y** (400 MHz, $CDCl_3$)



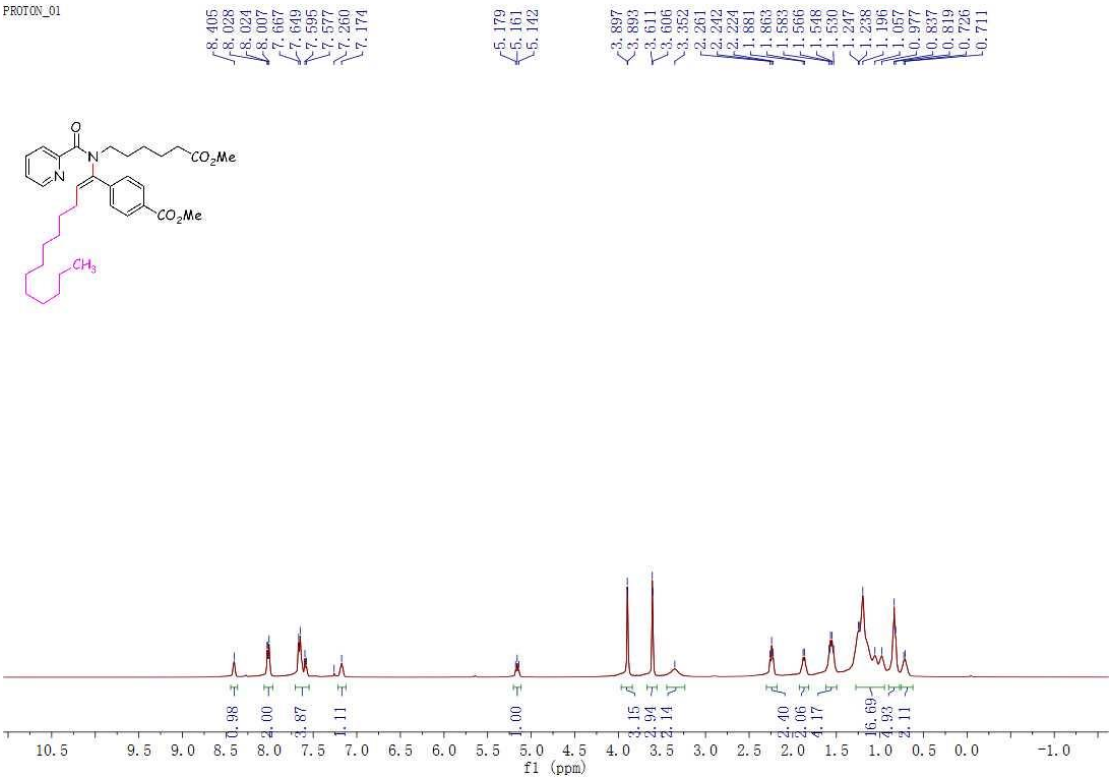
^{13}C NMR spectra for compound **5y** (100 MHz, $CDCl_3$)



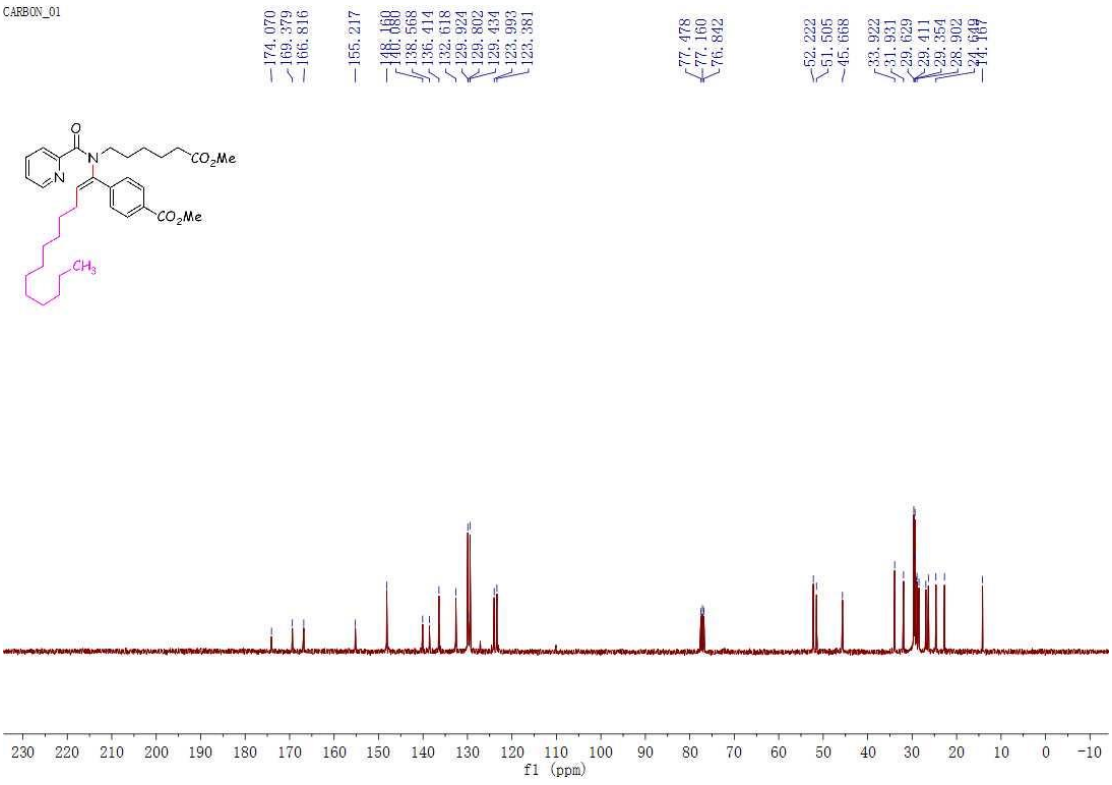
^{1}H NMR spectra for compound **5z** (400 MHz, $CDCl_3$)



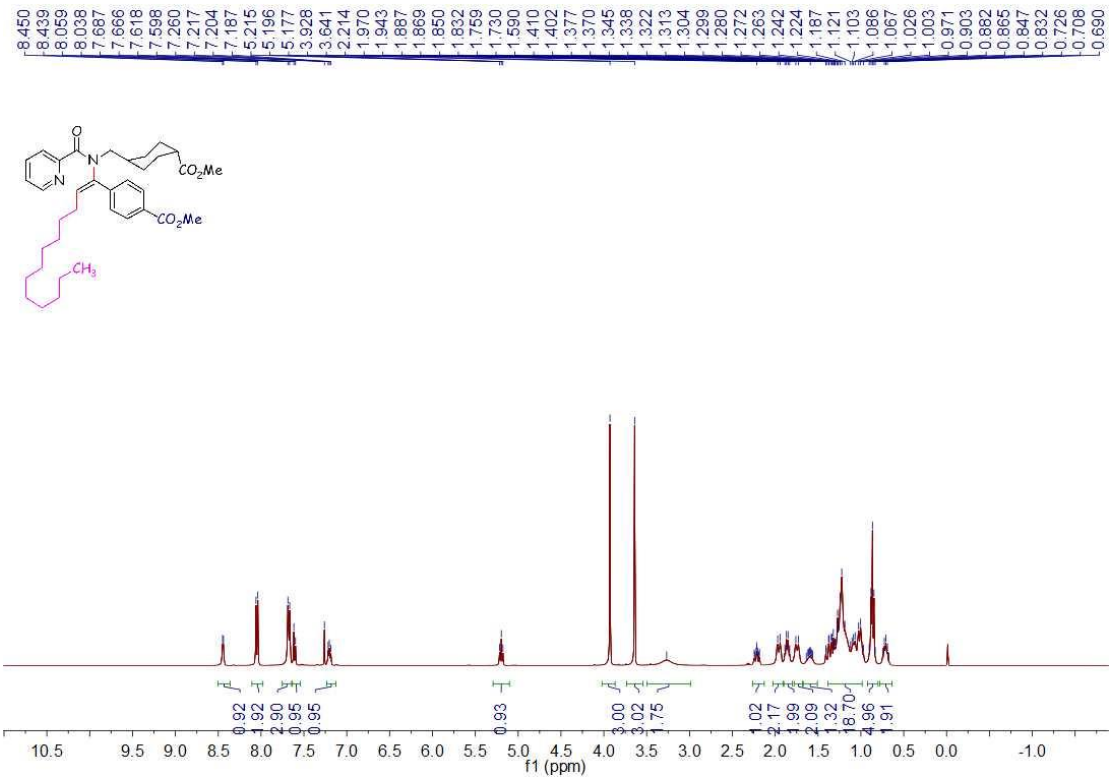
^{13}C NMR spectra for compound **5z** (100 MHz, $CDCl_3$)



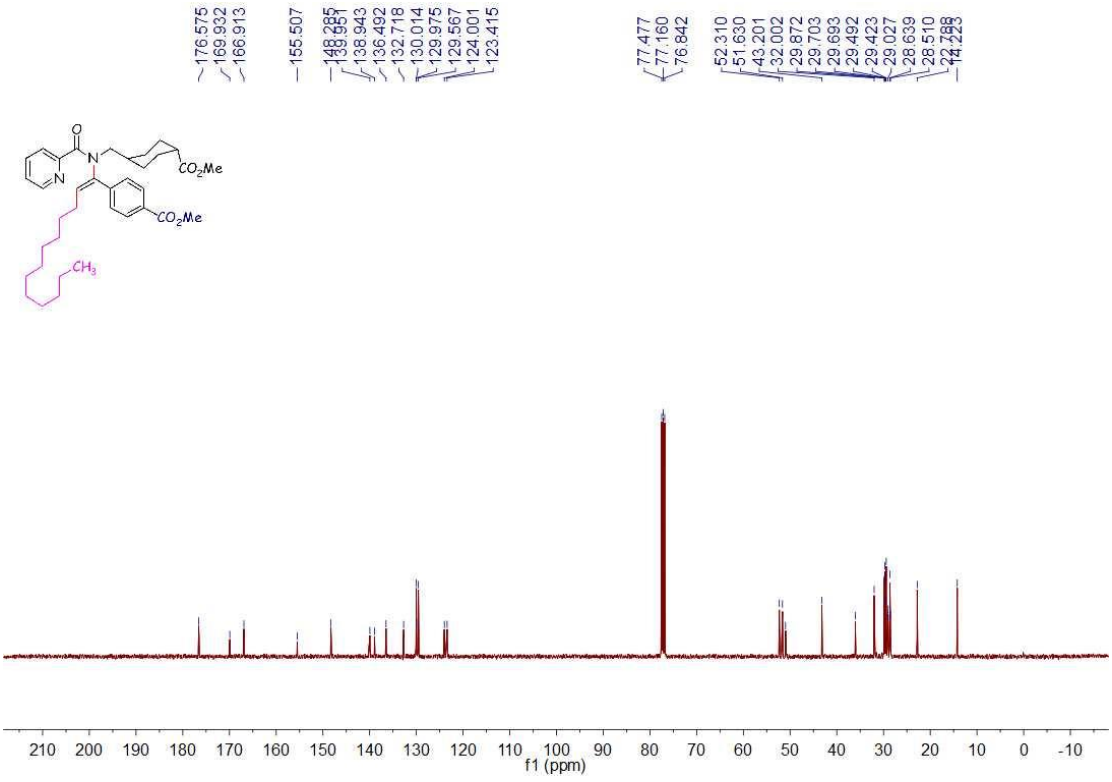
^{1}H NMR spectra for compound **5aa** (400 MHz, $CDCl_3$)



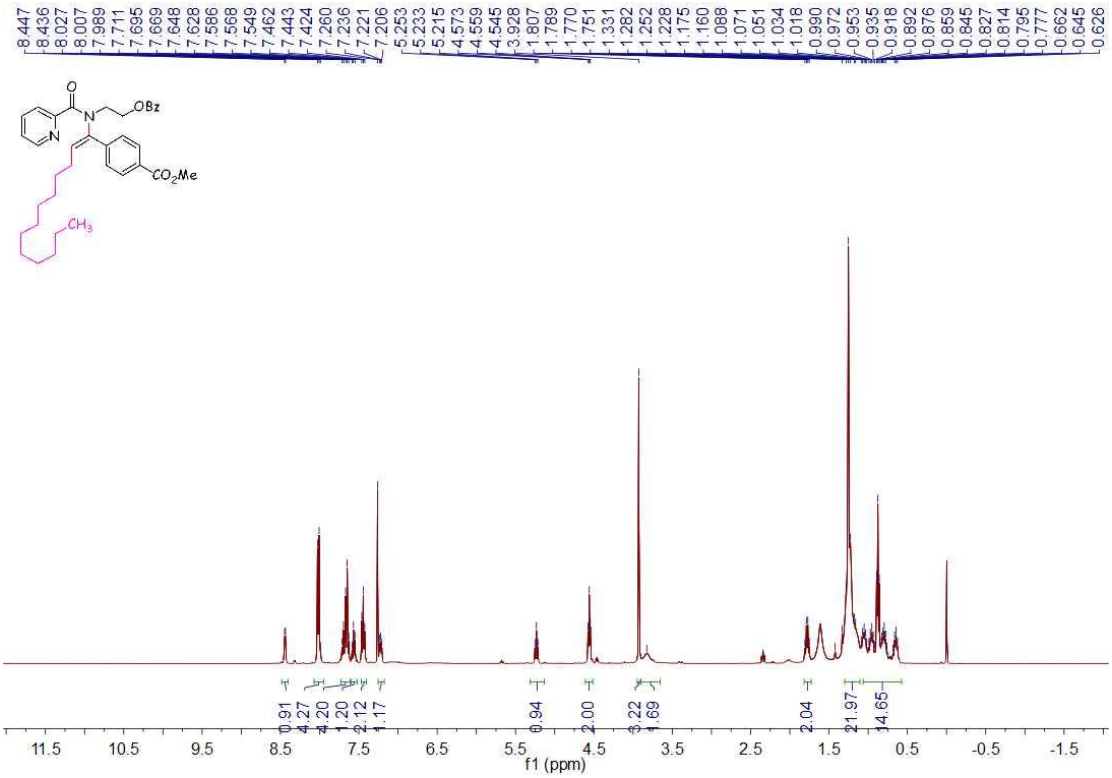
^{13}C NMR spectra for compound **5aa** (100 MHz, $CDCl_3$)



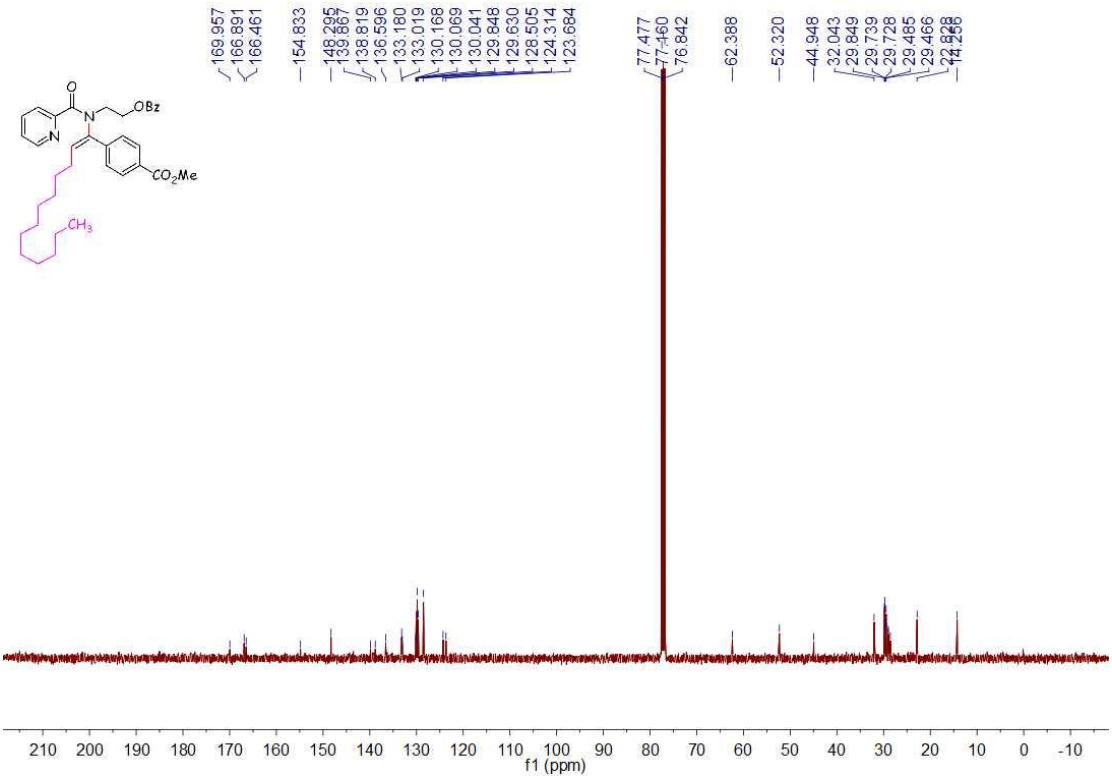
^{1}H NMR spectra for compound **5ab** (400 MHz, $CDCl_3$)



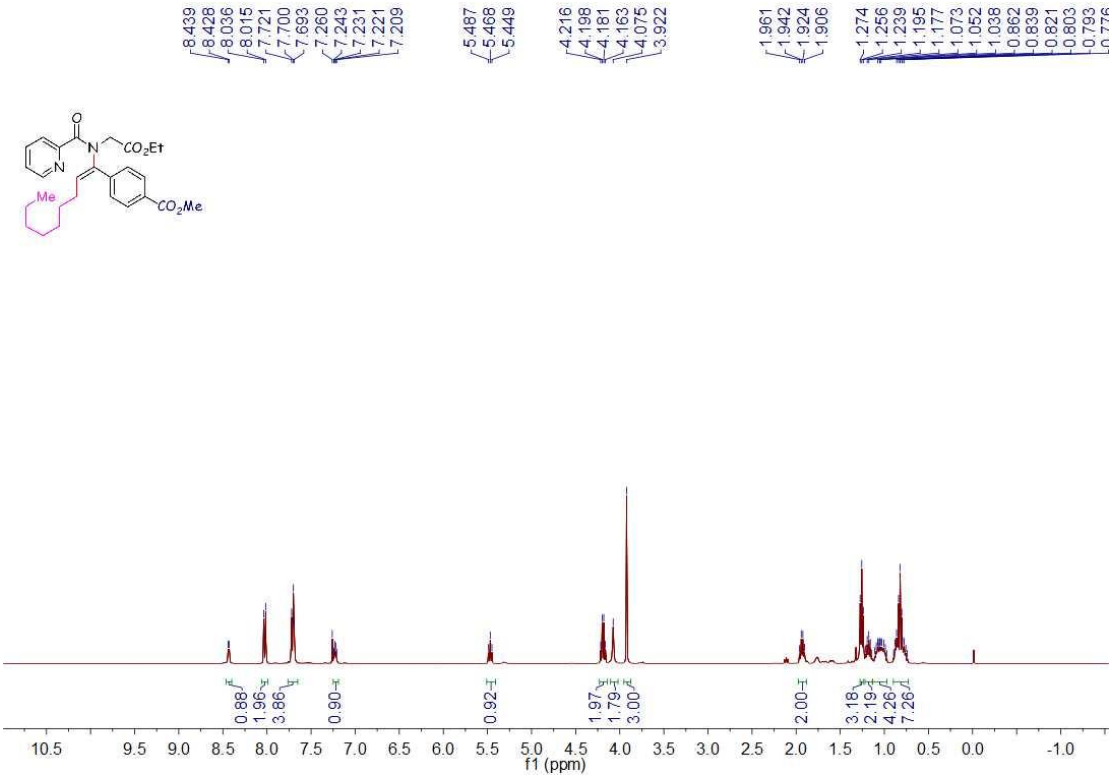
^{13}C NMR spectra for compound **5ab** (100 MHz, $CDCl_3$)



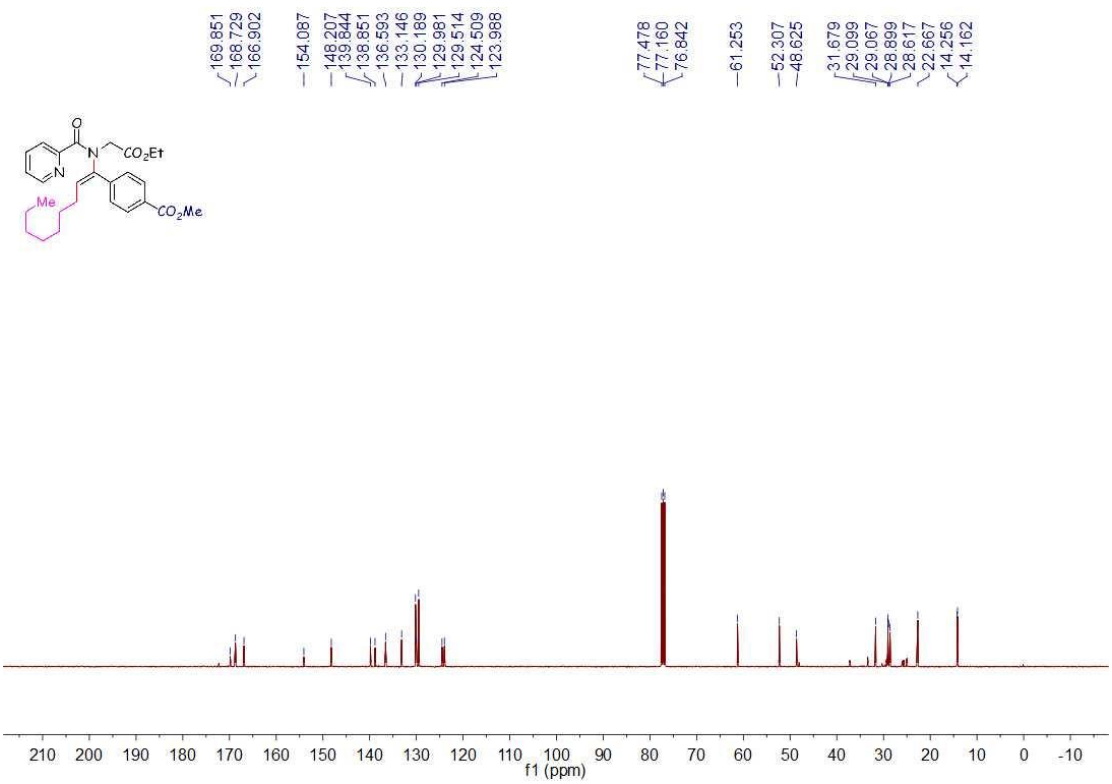
^{1}H NMR spectra for compound **5ac** (400 MHz, $CDCl_3$)



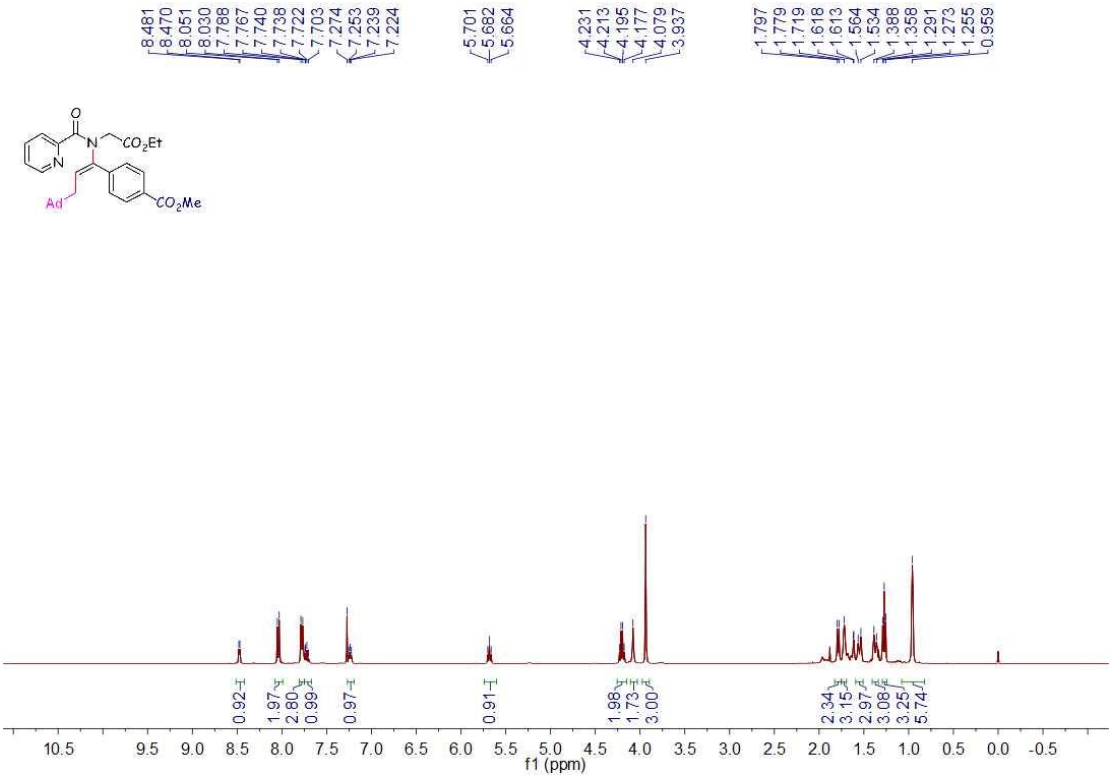
^{13}C NMR spectra for compound **5ac** (100 MHz, $CDCl_3$)



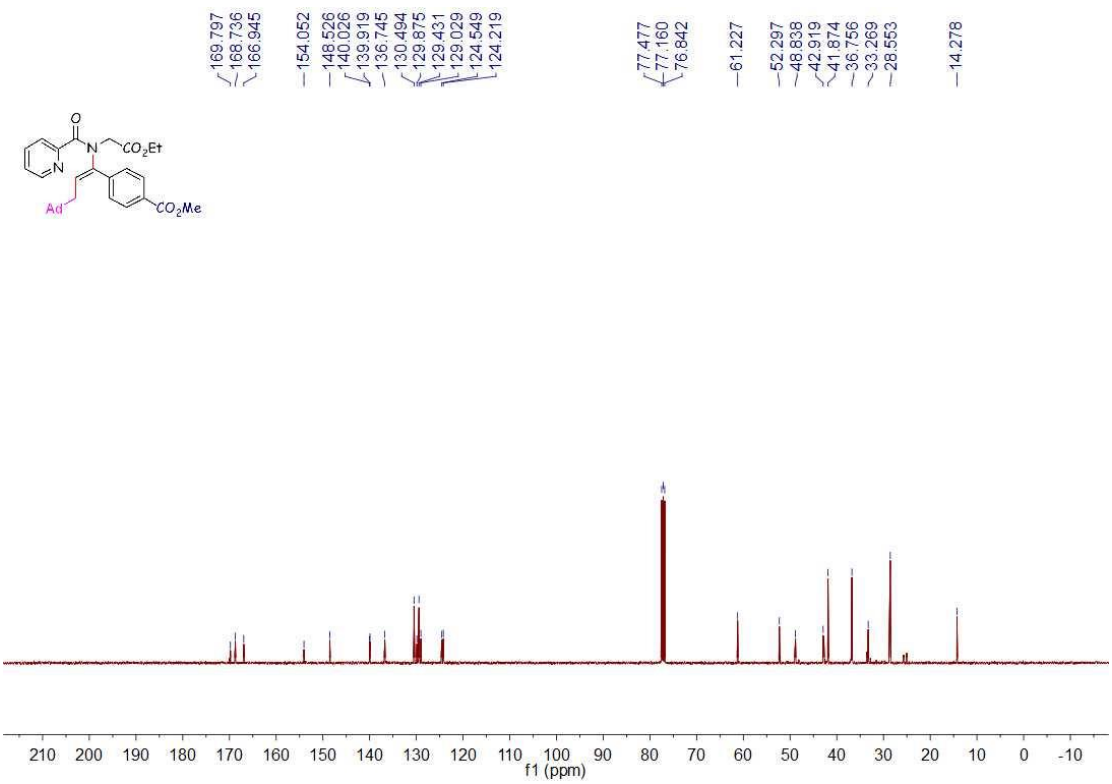
^{1}H NMR spectra for compound **6a** (400 MHz, $CDCl_3$)



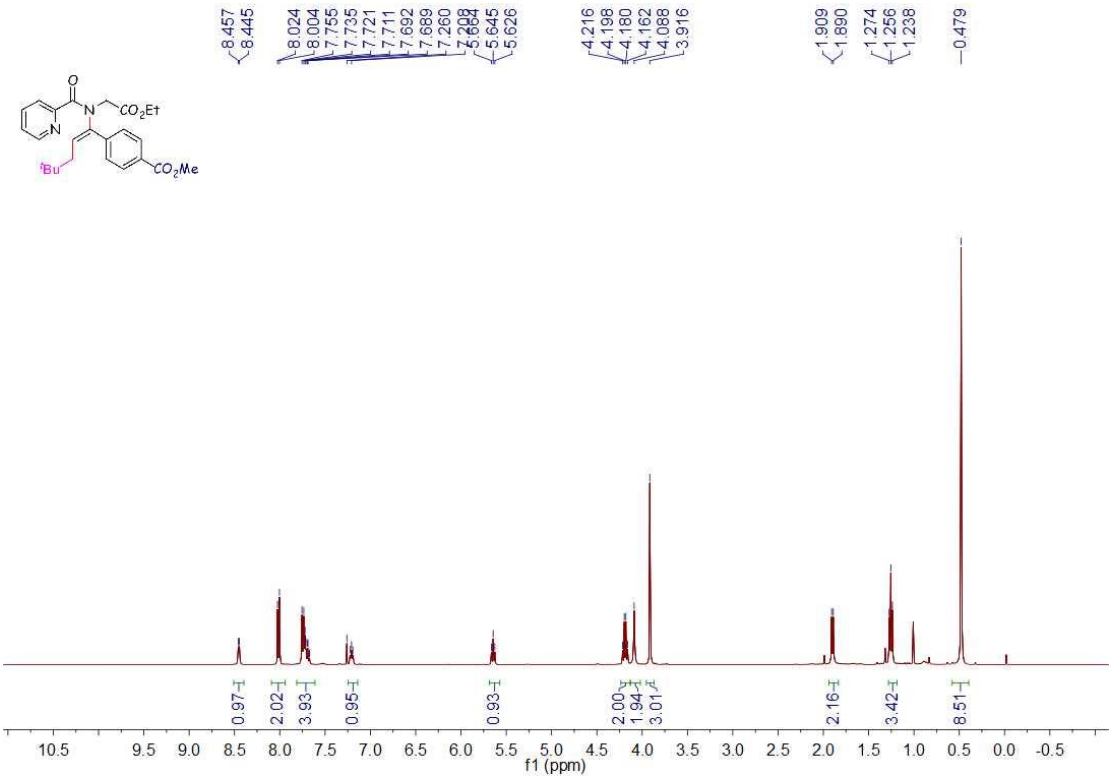
^{13}C NMR spectra for compound **6a** (100 MHz, $CDCl_3$)



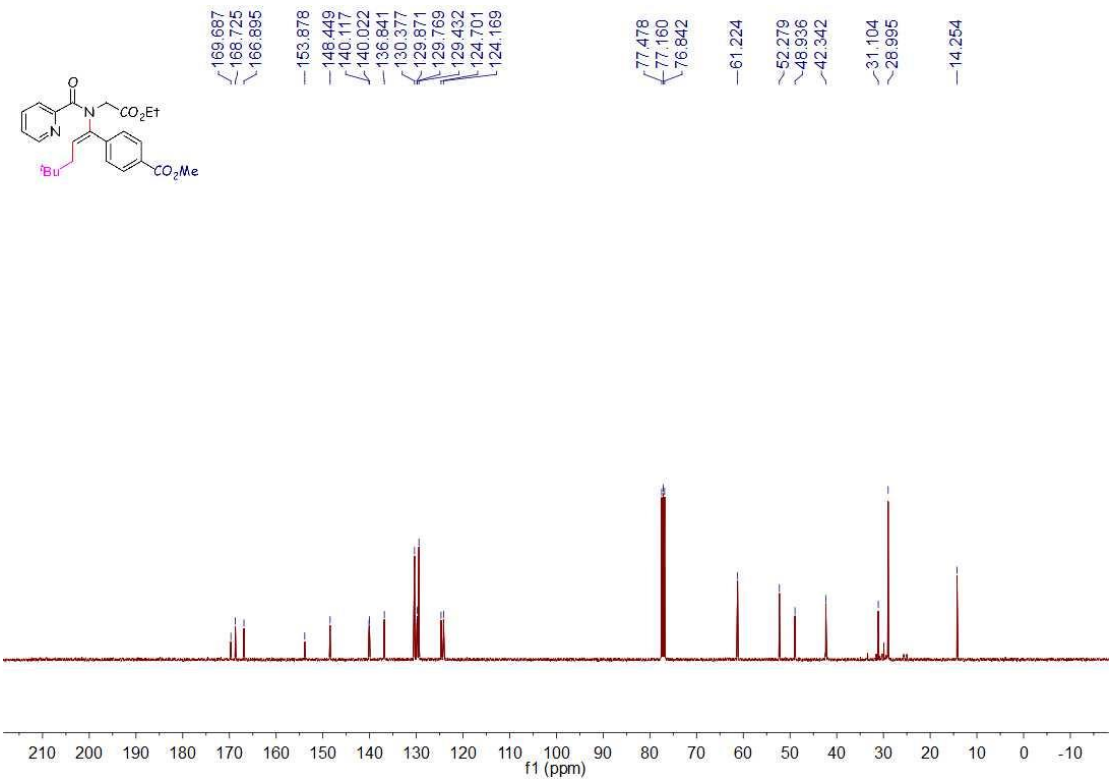
^{1}H NMR spectra for compound **6b** (400 MHz, $CDCl_3$)



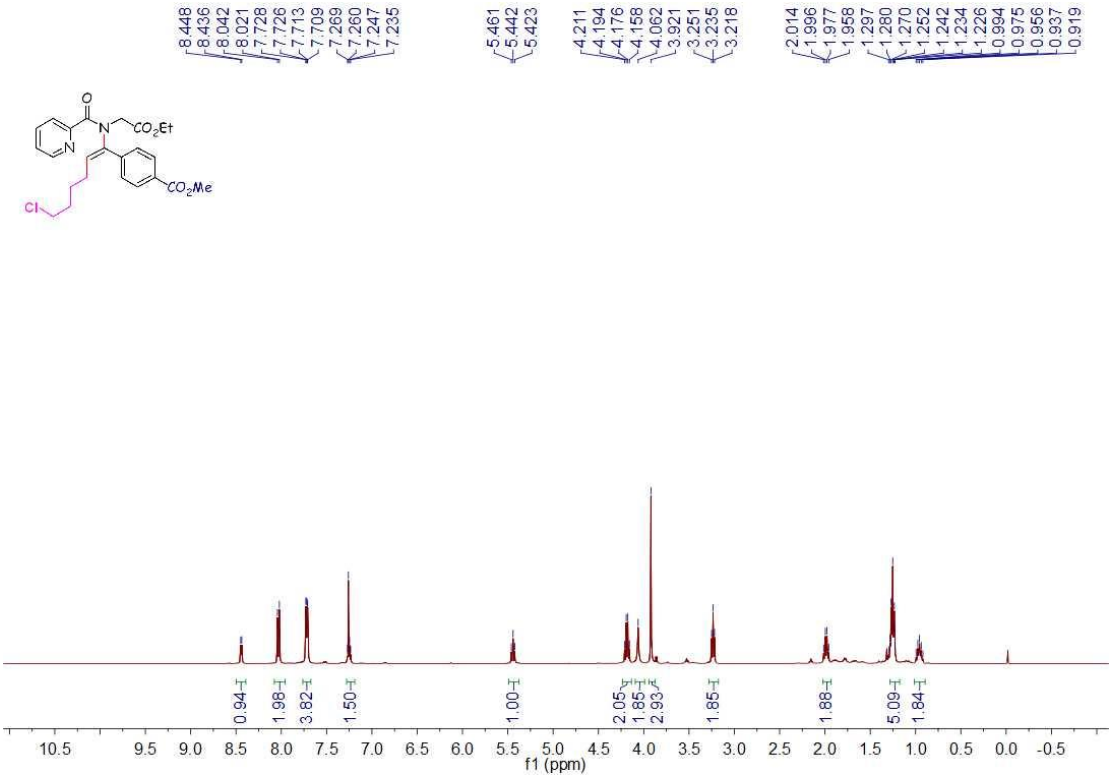
^{13}C NMR spectra for compound **6b** (100 MHz, $CDCl_3$)



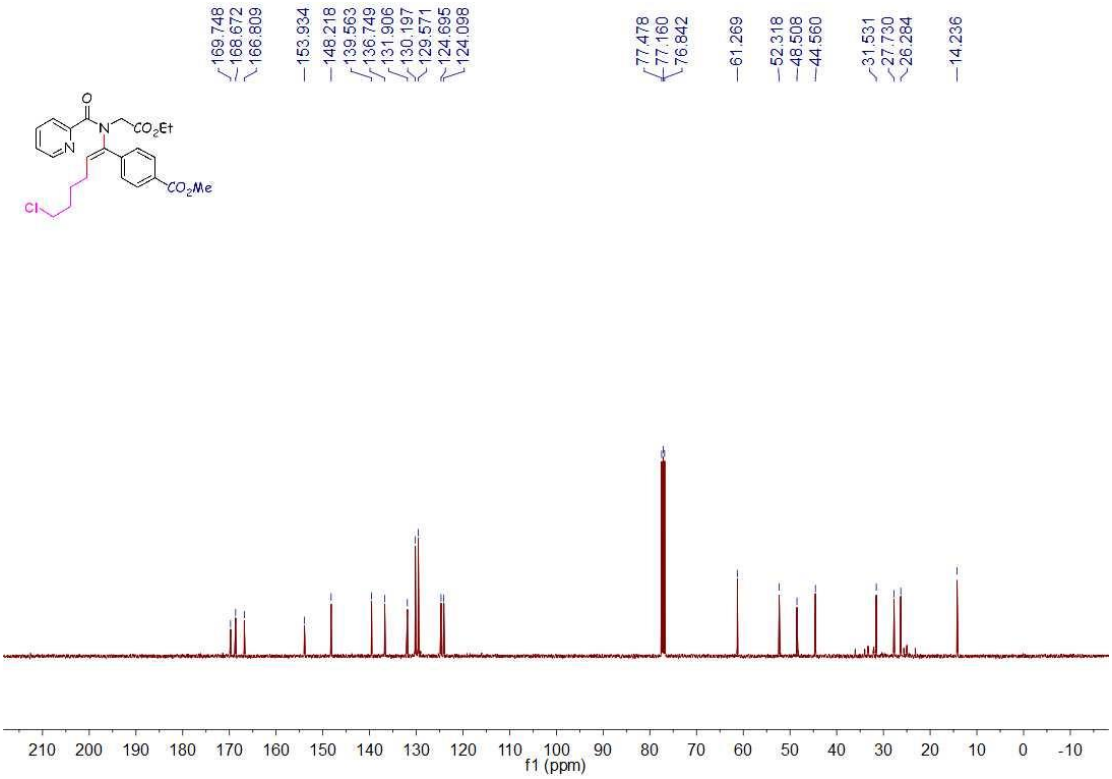
^{1}H NMR spectra for compound **6c** (400 MHz, $CDCl_3$)



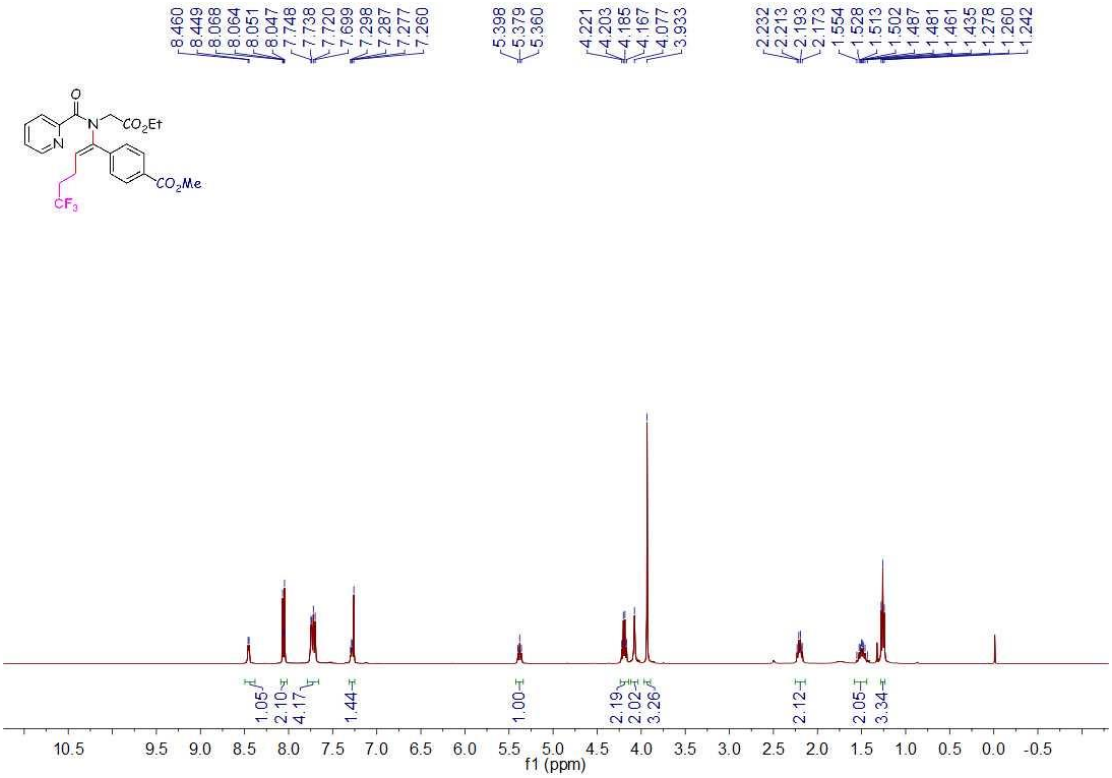
^{13}C NMR spectra for compound **6c** (100 MHz, $CDCl_3$)



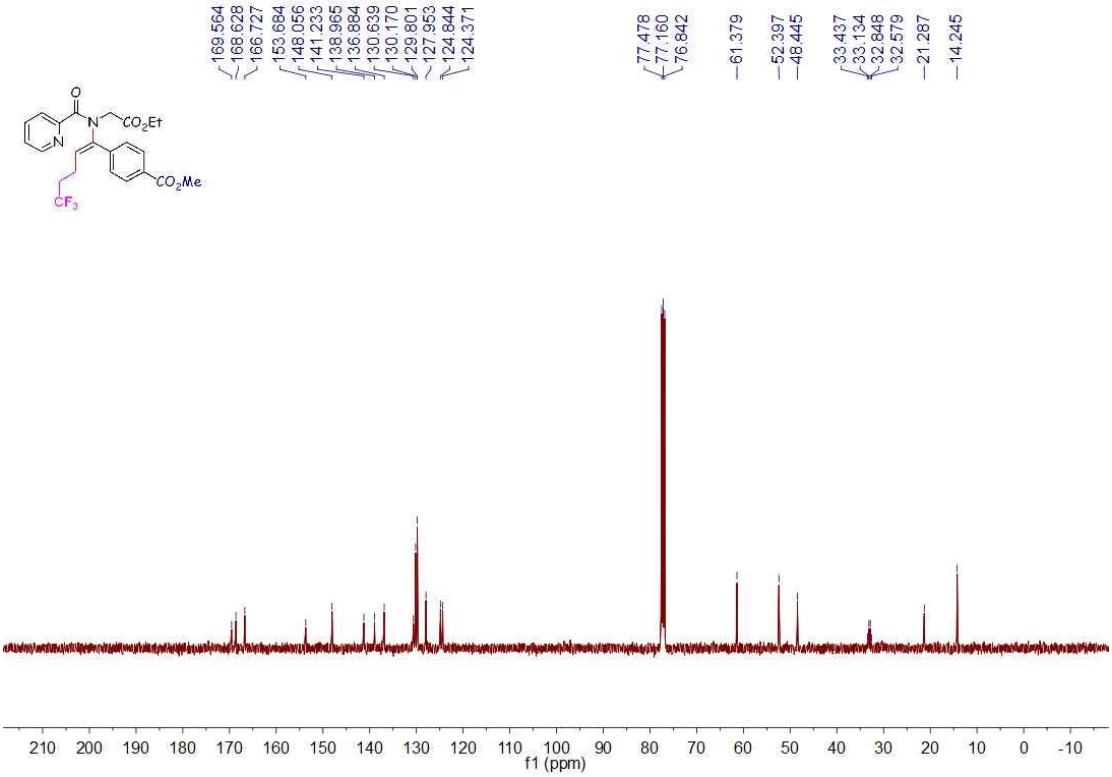
^{1}H NMR spectra for compound **6d** (400 MHz, $CDCl_3$)



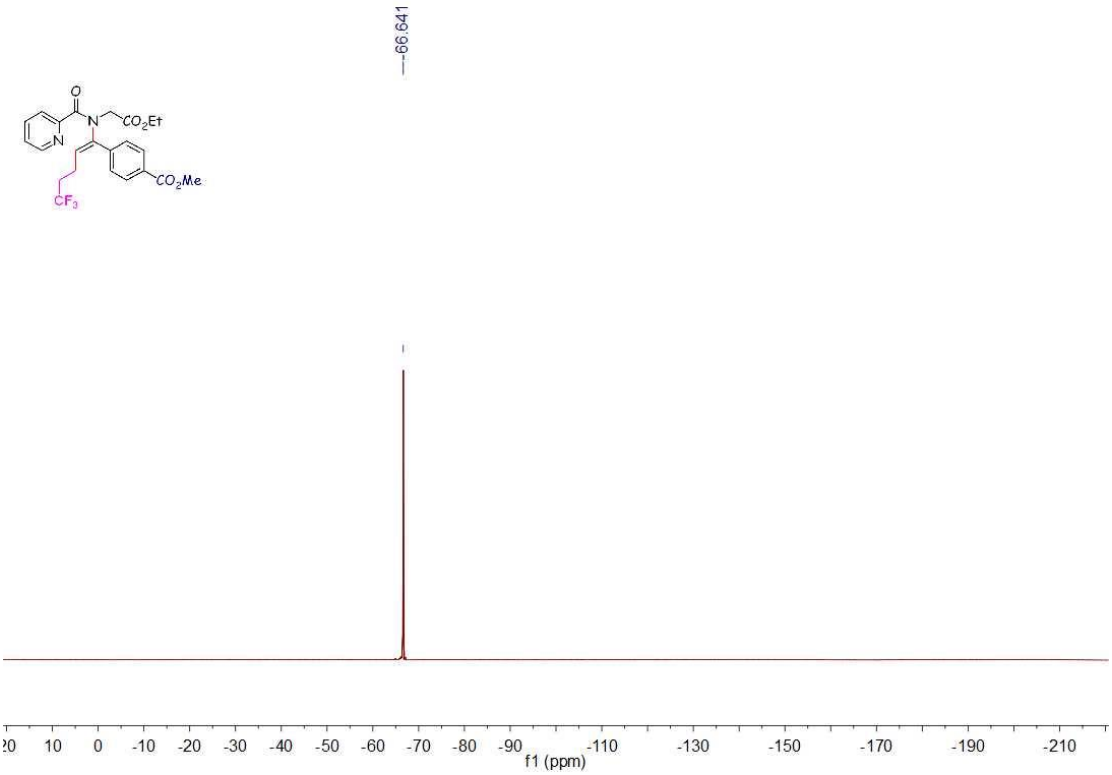
^{13}C NMR spectra for compound **6d** (100 MHz, $CDCl_3$)



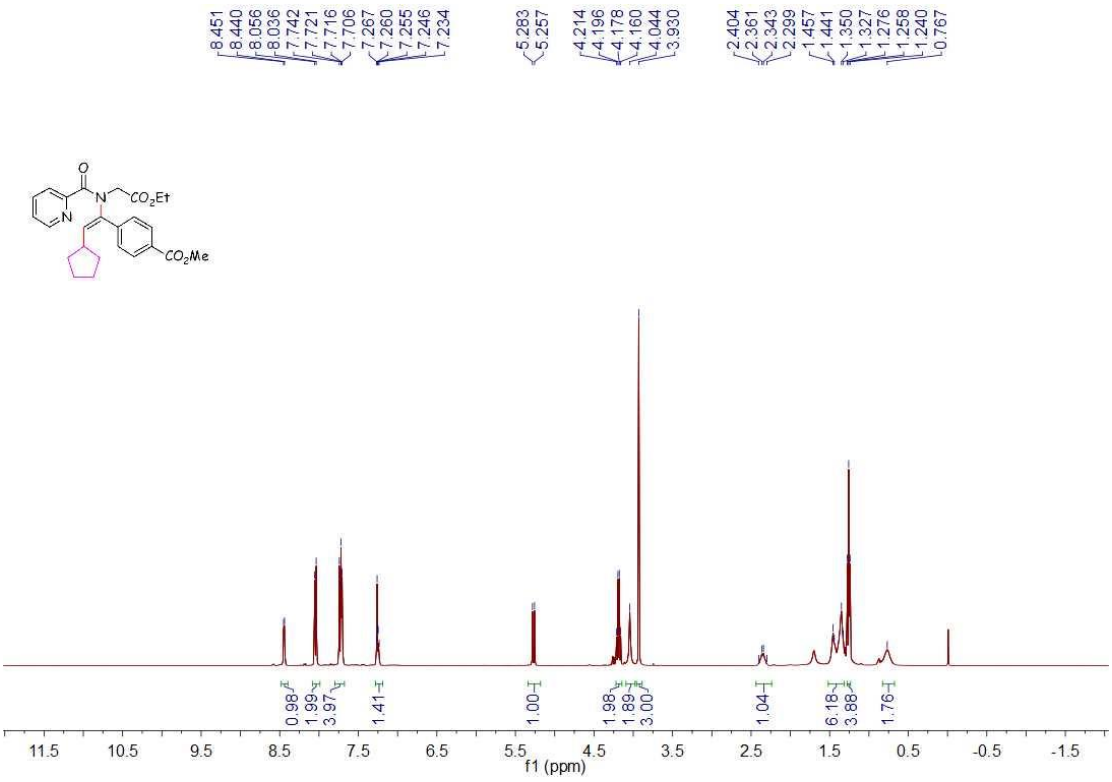
^{1}H NMR spectra for compound **6e** (400 MHz, $CDCl_3$)



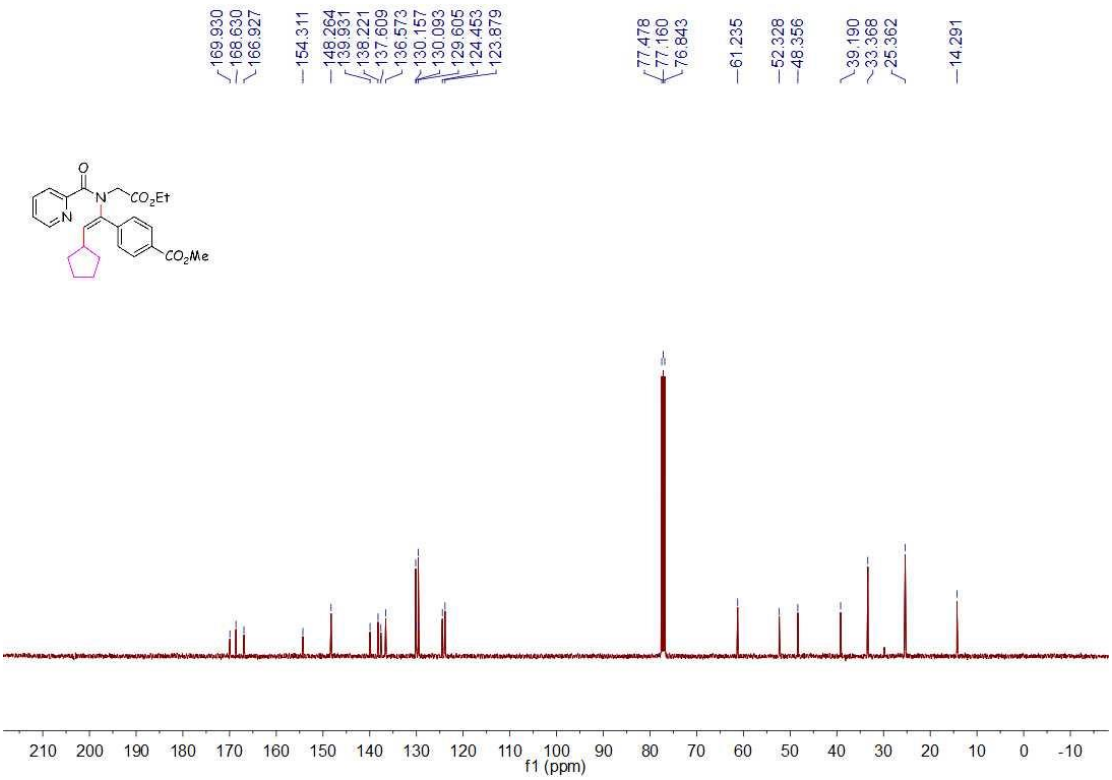
^{13}C NMR spectra for compound **6e** (100 MHz, $CDCl_3$)



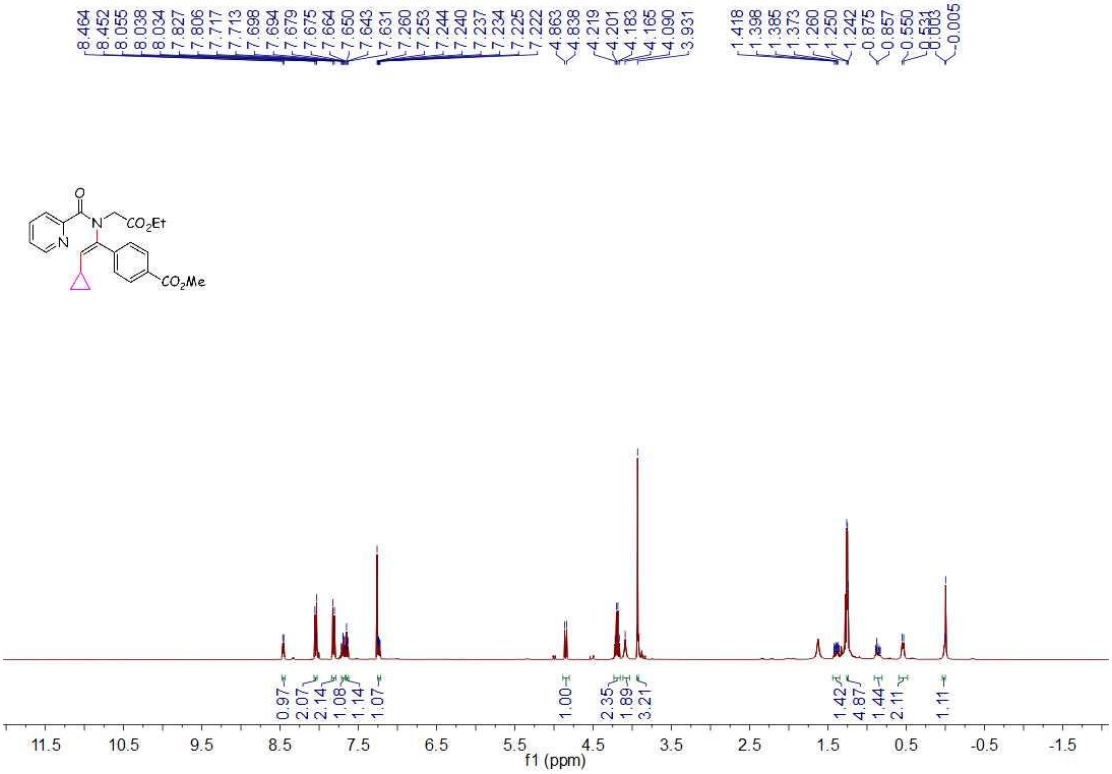
^{19}F NMR spectra for compound **6e** (376 MHz, $CDCl_3$)



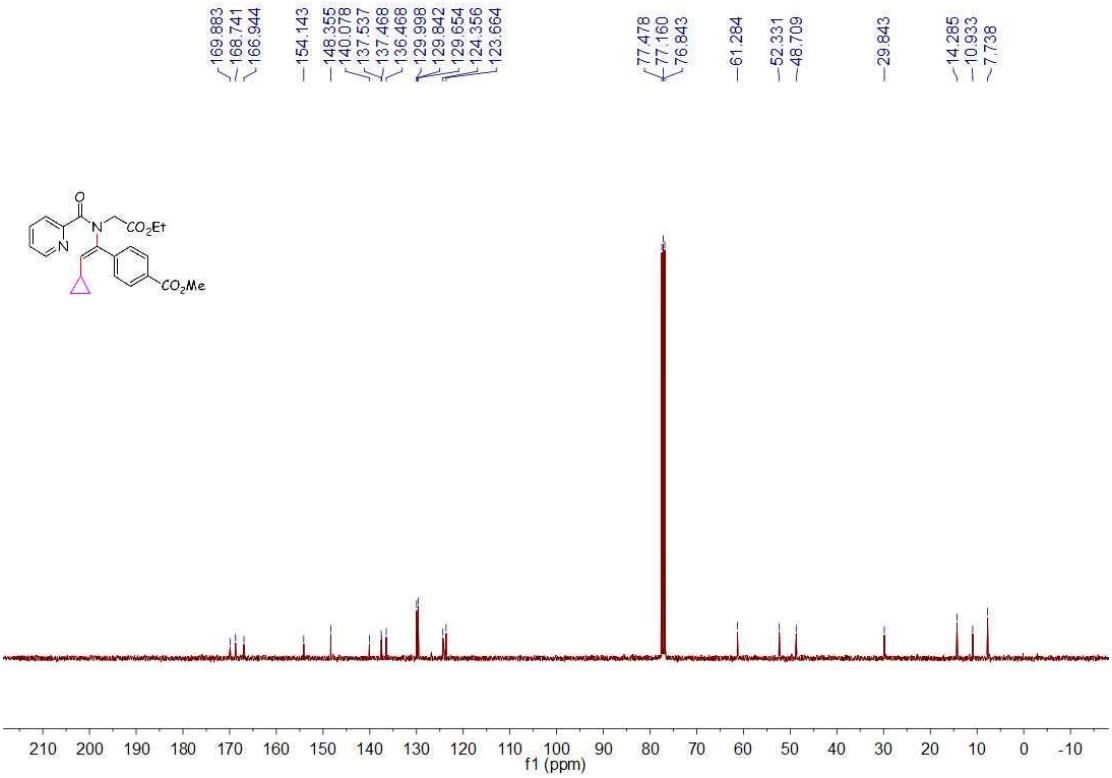
^{1}H NMR spectra for compound **6f** (400 MHz, $CDCl_3$)



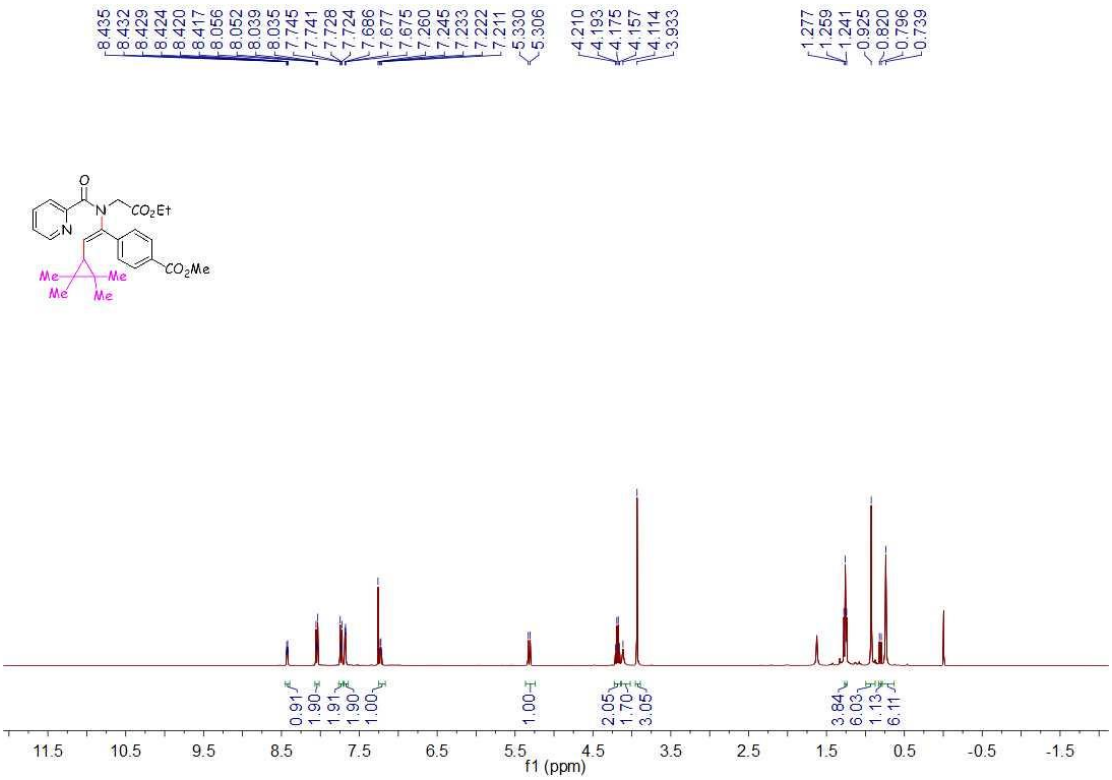
^{13}C NMR spectra for compound **6f** (100 MHz, $CDCl_3$)



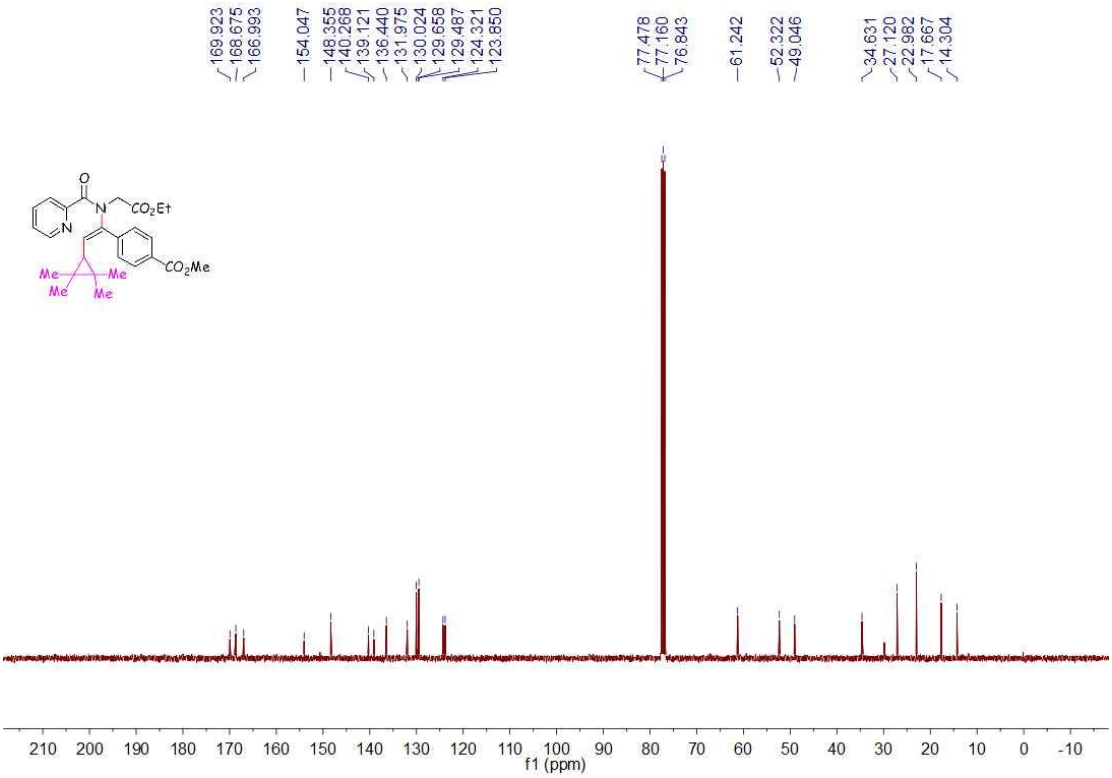
^{1}H NMR spectra for compound **6g** (400 MHz, $CDCl_3$)



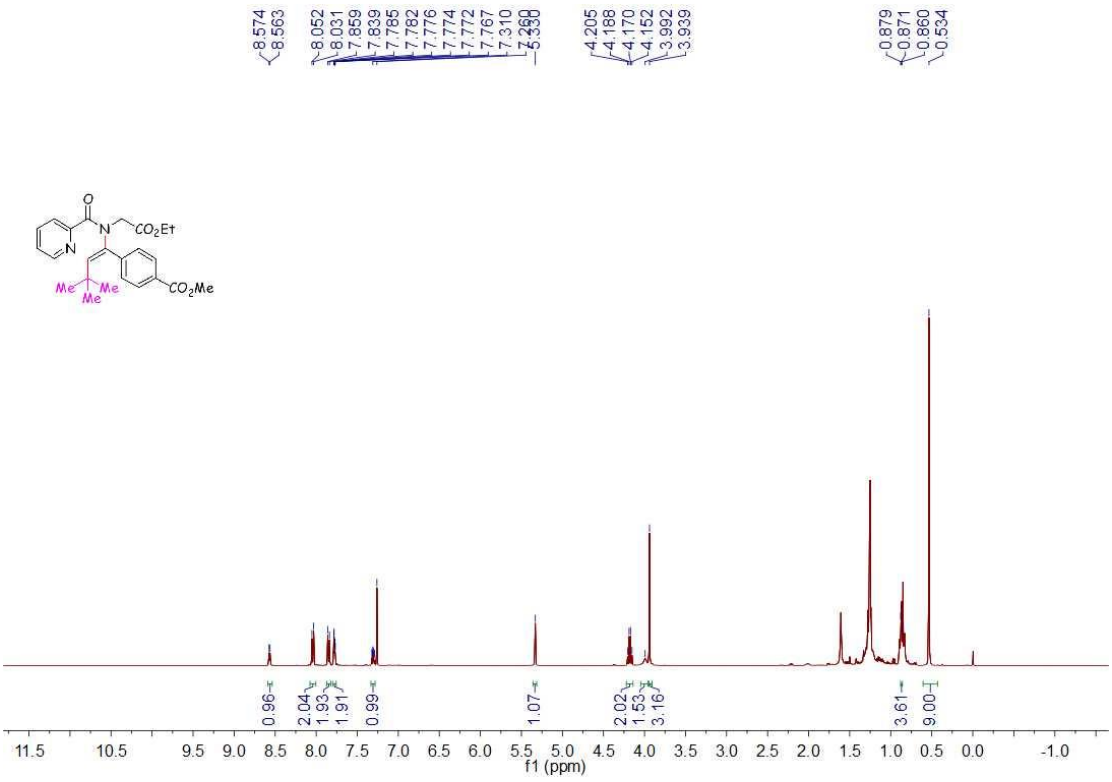
^{13}C NMR spectra for compound **6g** (100 MHz, $CDCl_3$)



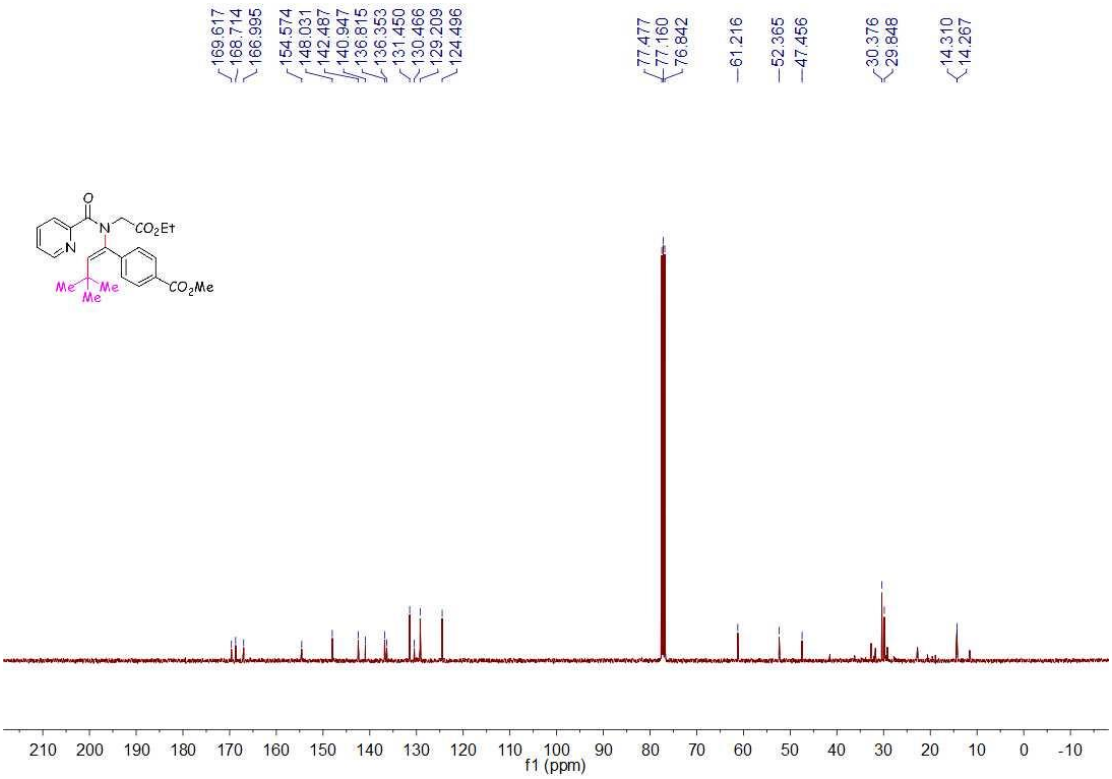
^{1}H NMR spectra for compound **6h** (400 MHz, $CDCl_3$)



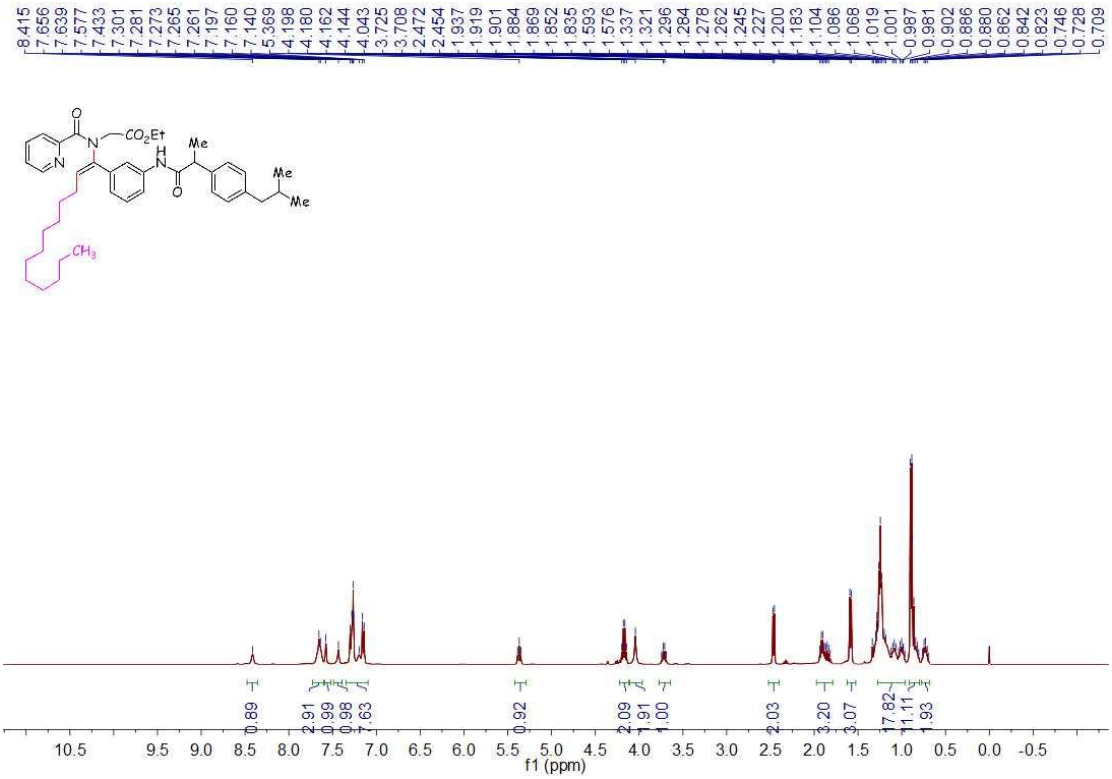
^{13}C NMR spectra for compound **6h** (100 MHz, $CDCl_3$)



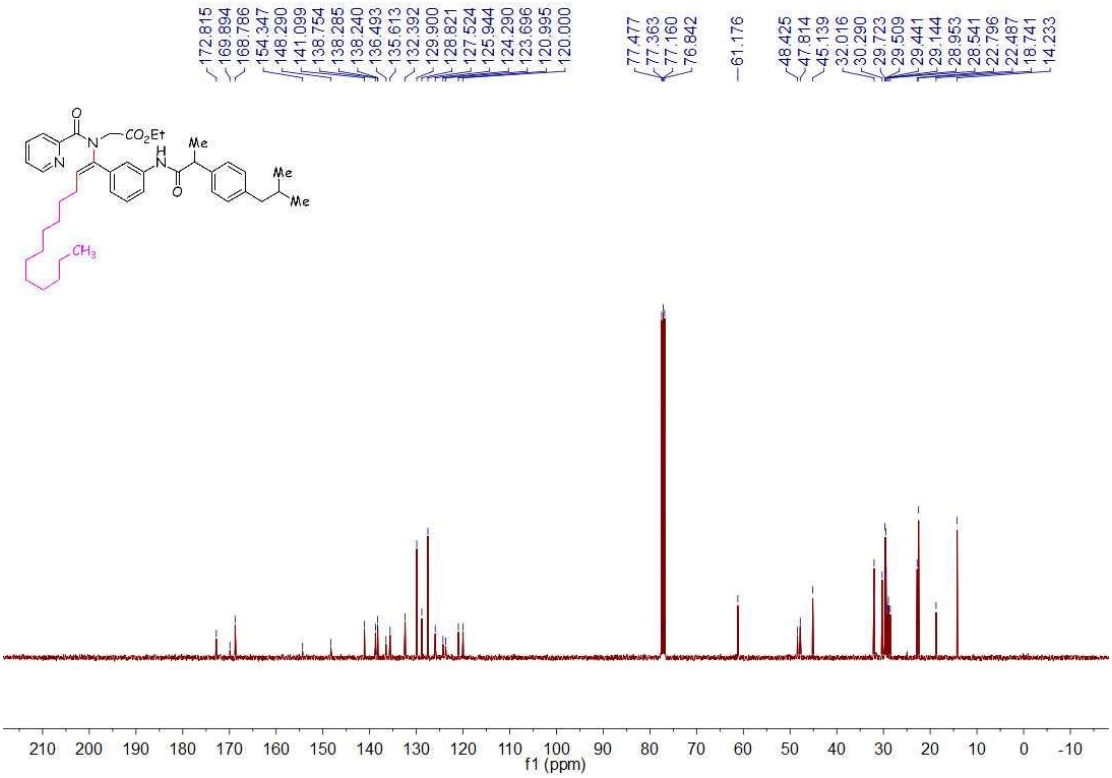
^{1}H NMR spectra for compound **6i** (400 MHz, $CDCl_3$)



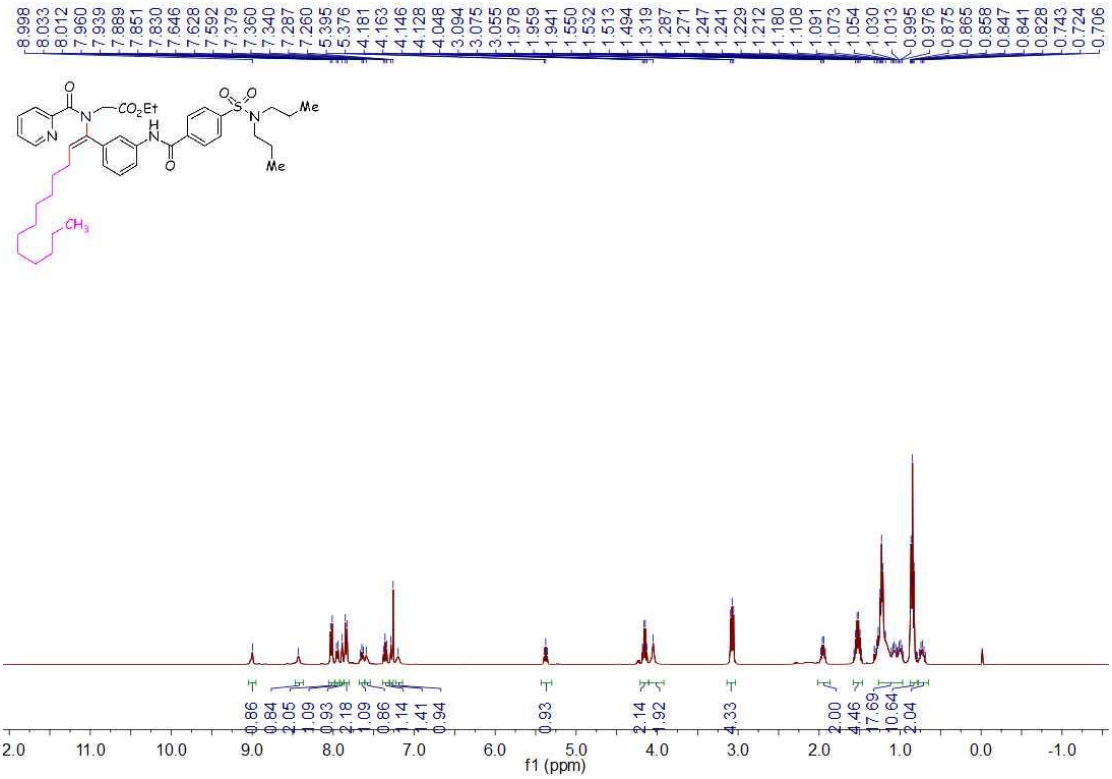
^{13}C NMR spectra for compound **6j** (100 MHz, $CDCl_3$)



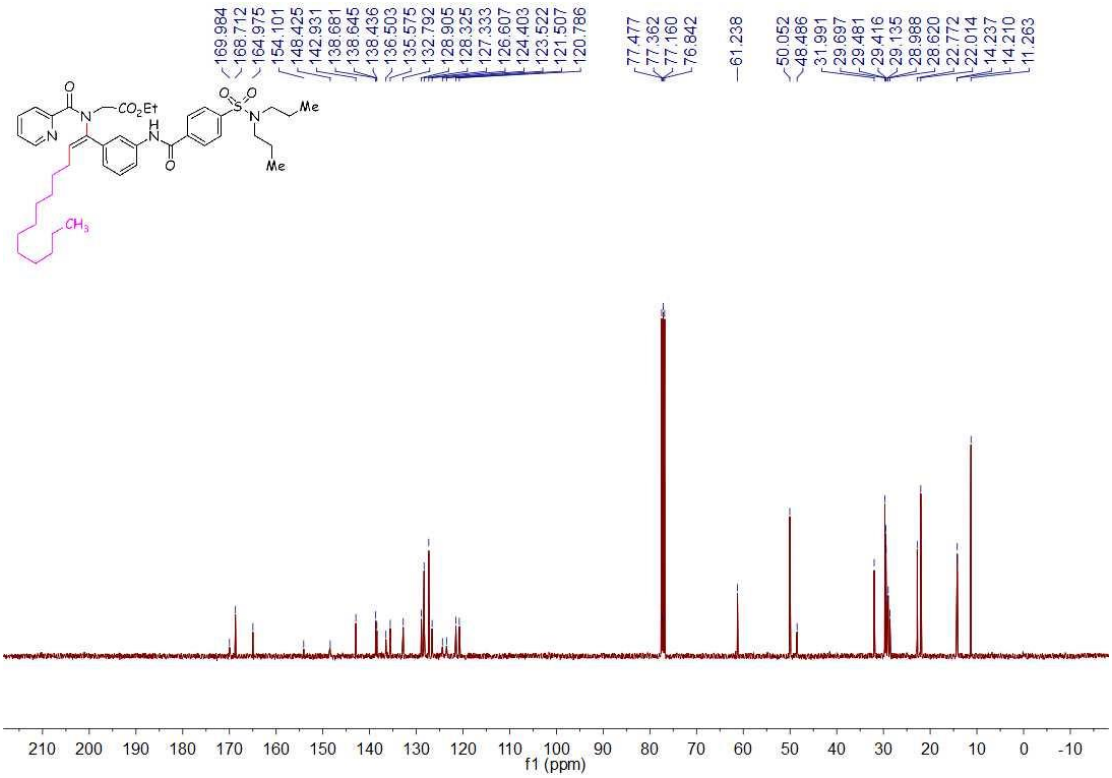
^{1}H NMR spectra for compound **7a** (400 MHz, $CDCl_3$)



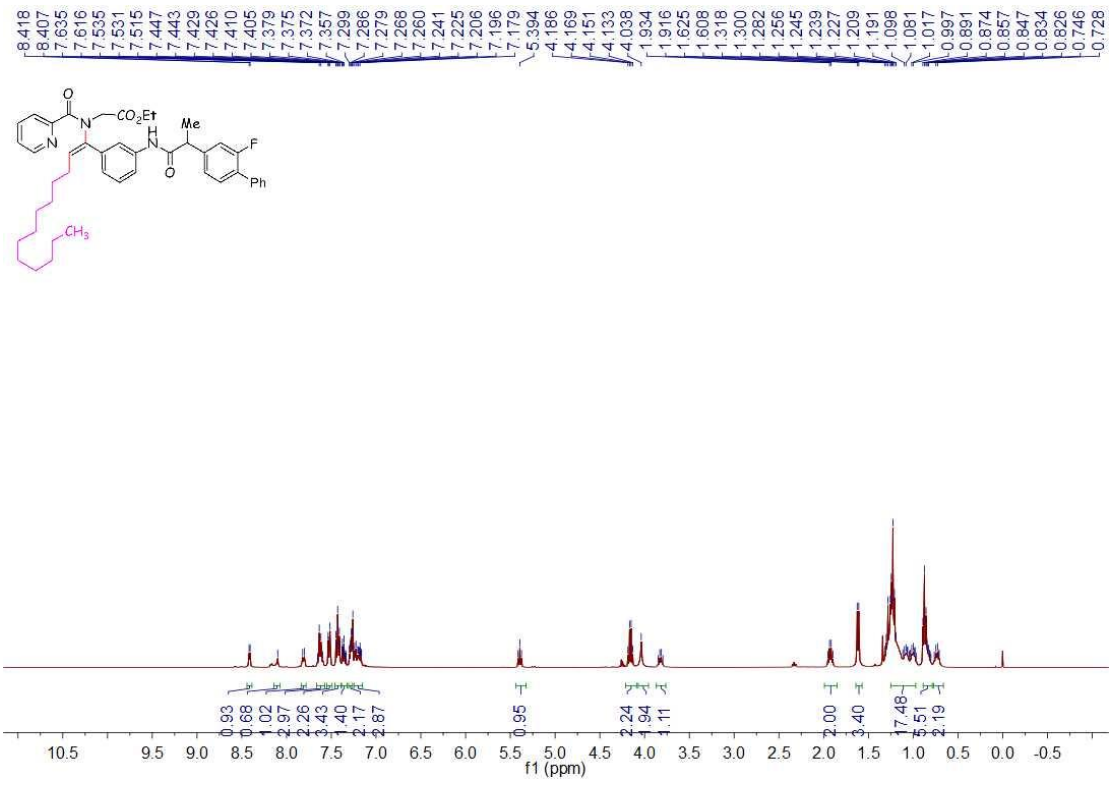
^{13}C NMR spectra for compound **7a** (100 MHz, $CDCl_3$)



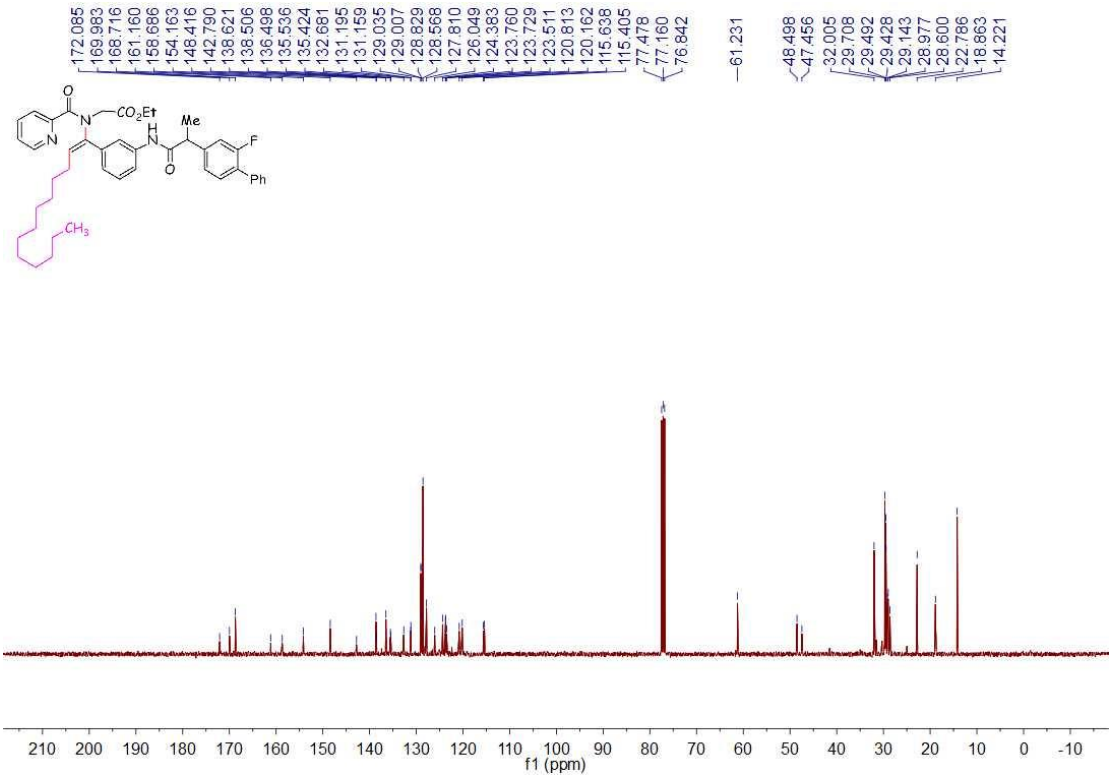
^{1}H NMR spectra for compound **7b** (400 MHz, $CDCl_3$)



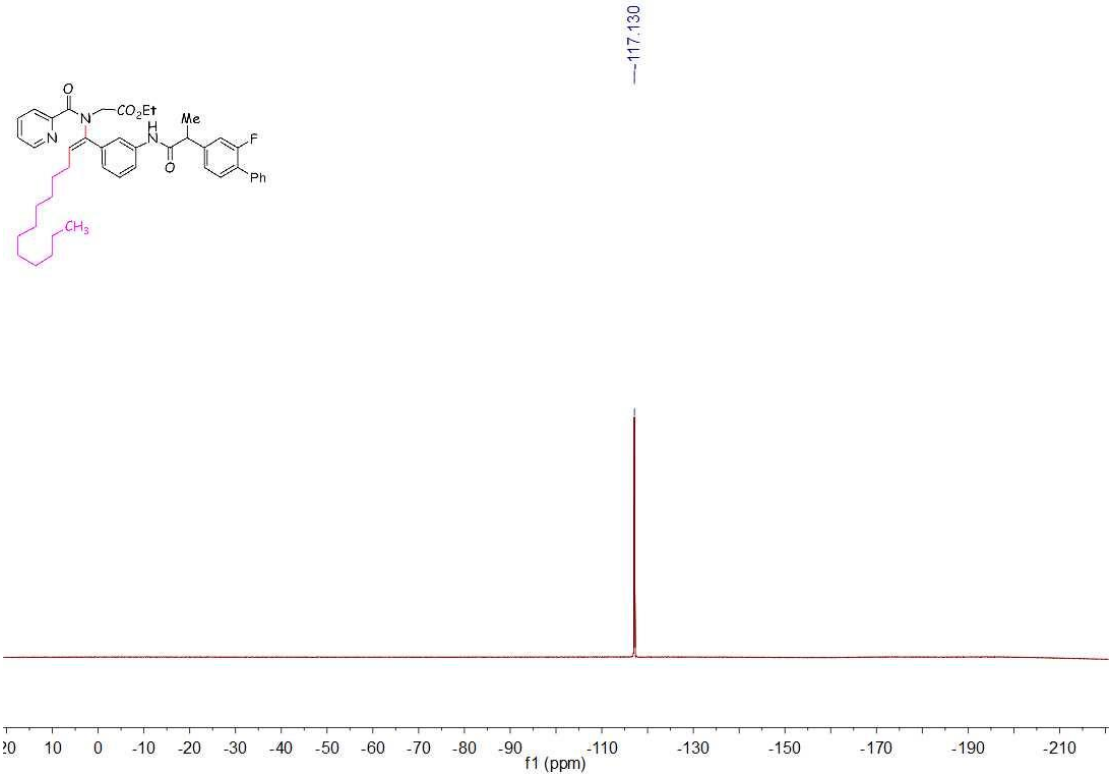
^{13}C NMR spectra for compound **7b** (100 MHz, $CDCl_3$)



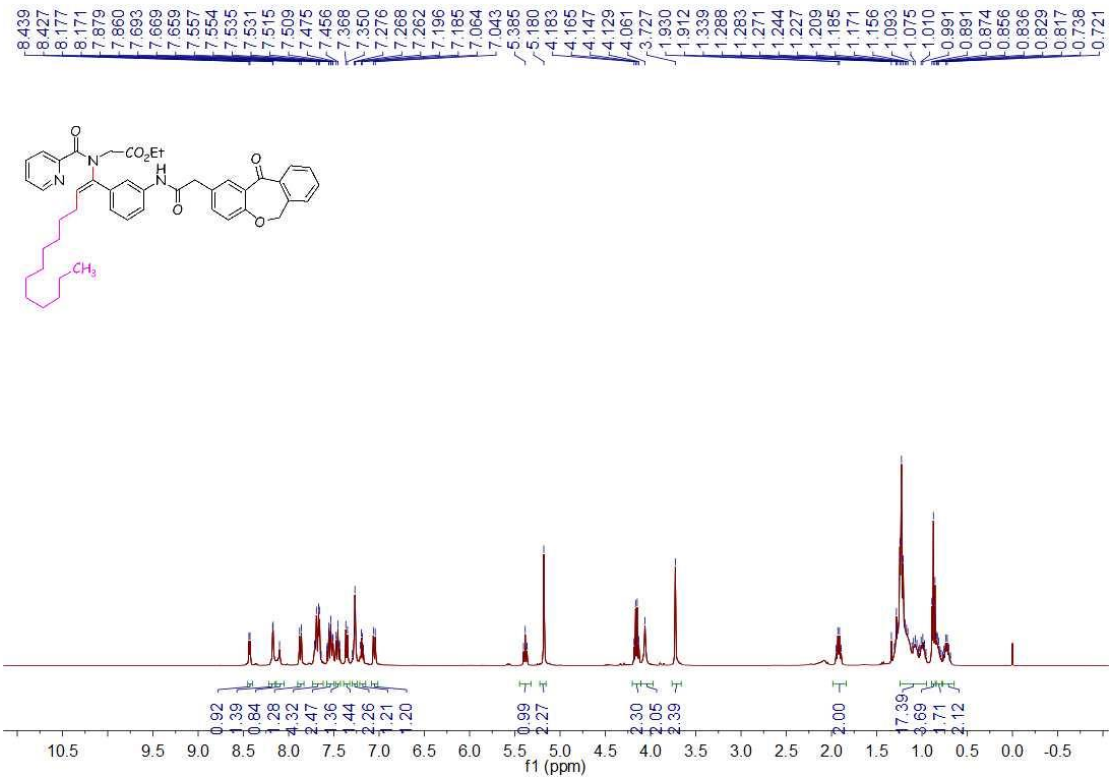
^{1}H NMR spectra for compound **7c** (400 MHz, $CDCl_3$)



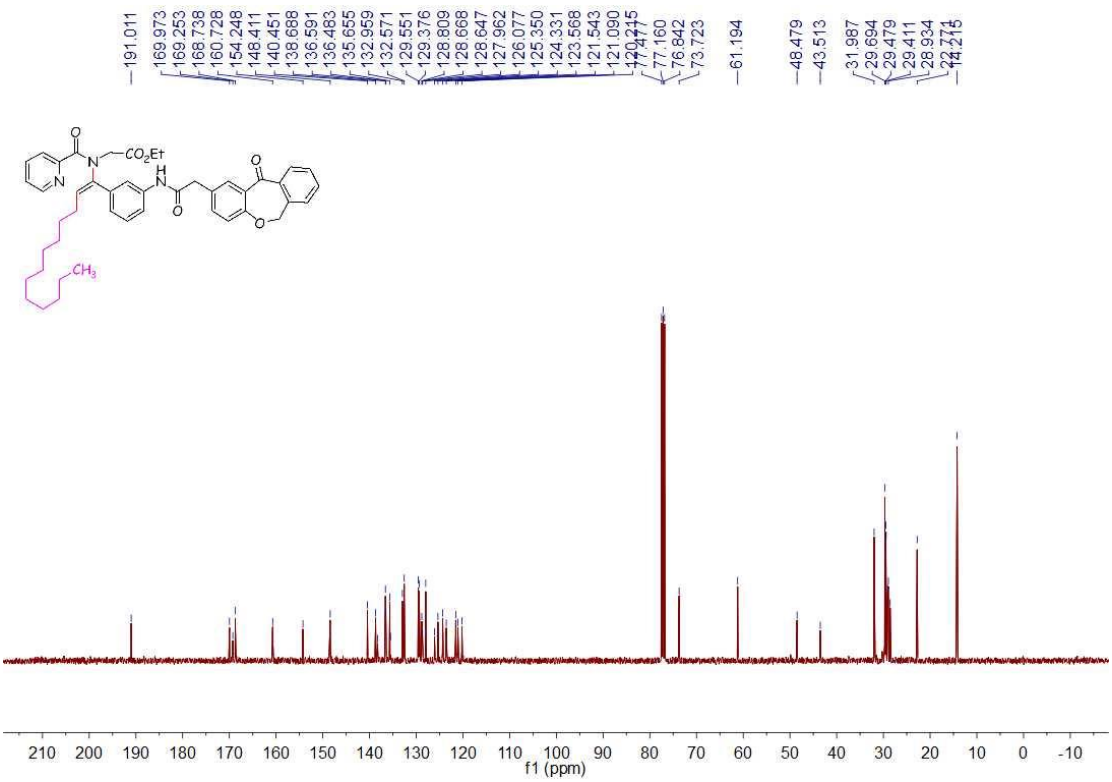
^{13}C NMR spectra for compound **7c** (100 MHz, $CDCl_3$)



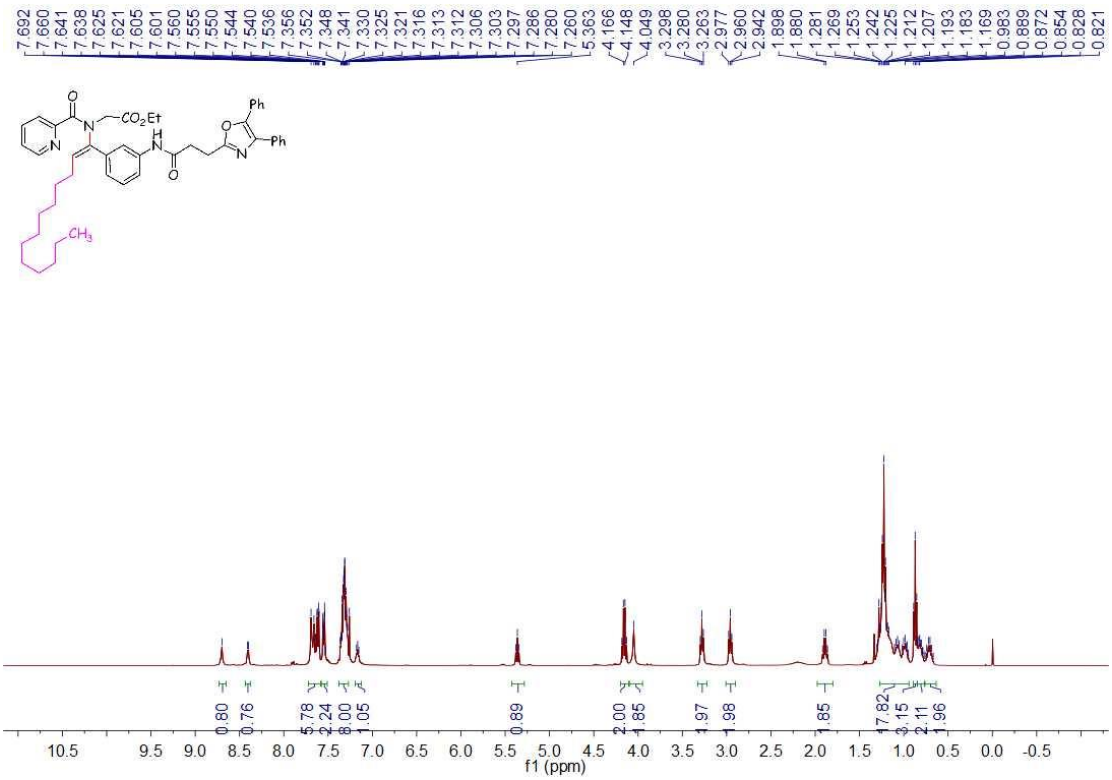
^{19}F NMR spectra for compound **7c** (376 MHz, $CDCl_3$)



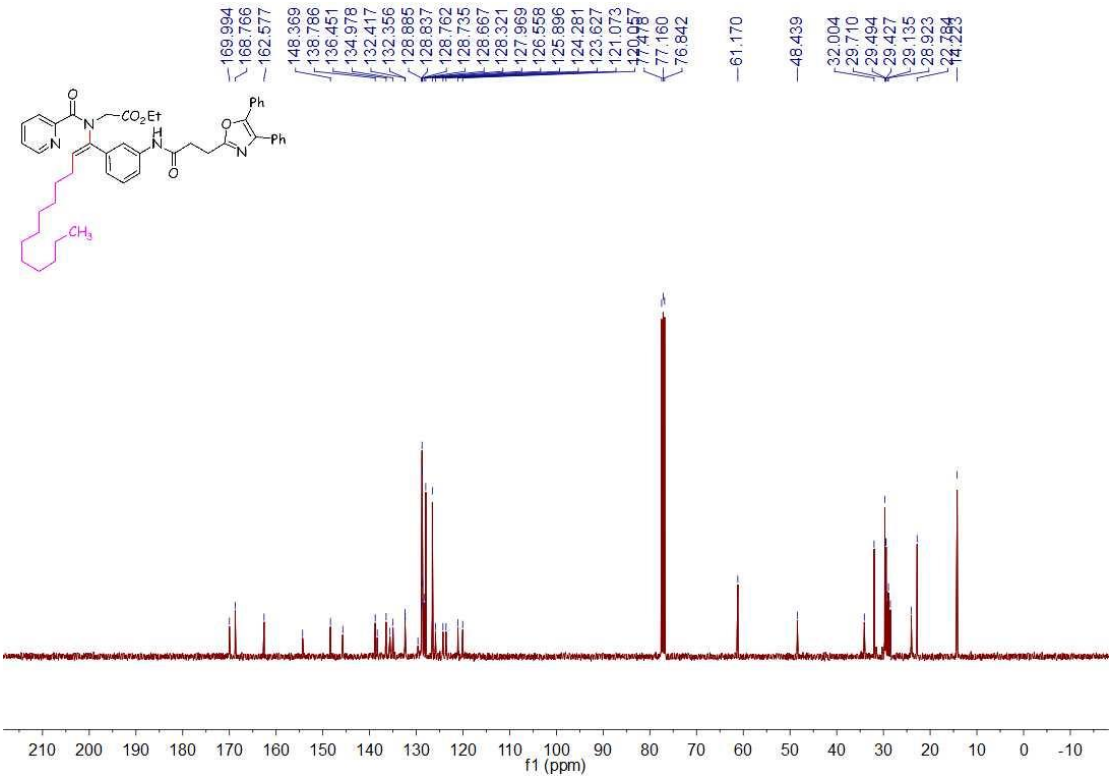
^{1}H NMR spectra for compound **7d** (400 MHz, $CDCl_3$)



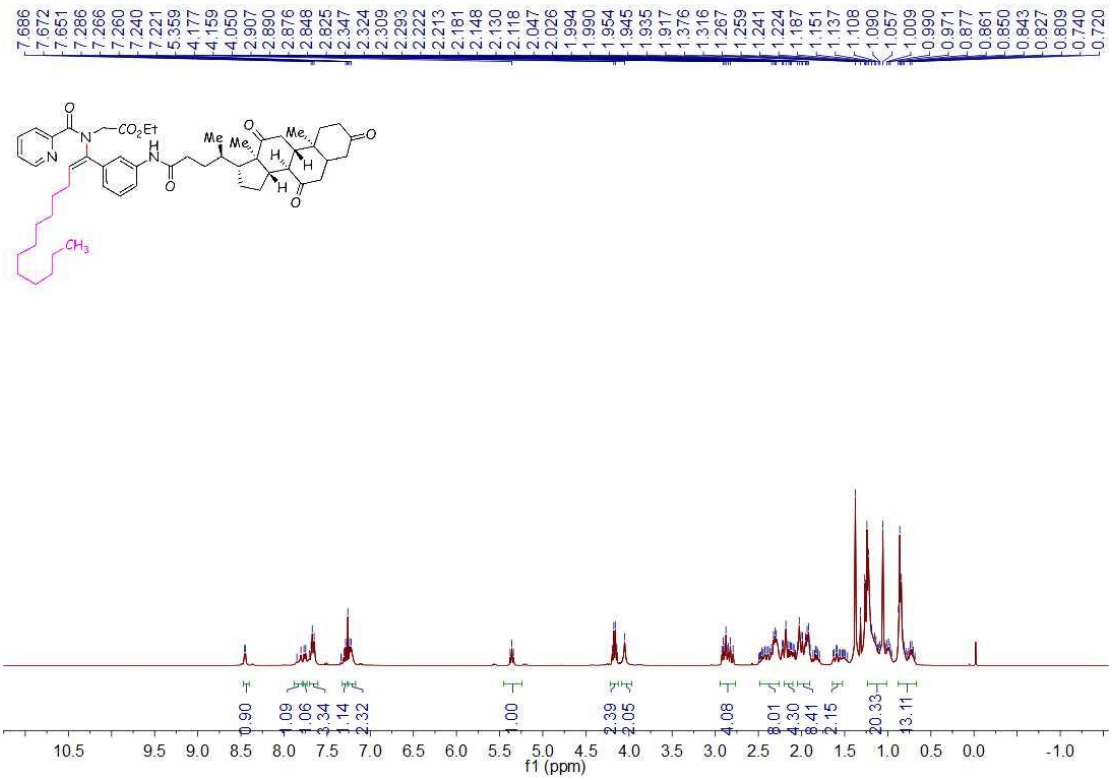
^{13}C NMR spectra for compound **7d** (100 MHz, $CDCl_3$)



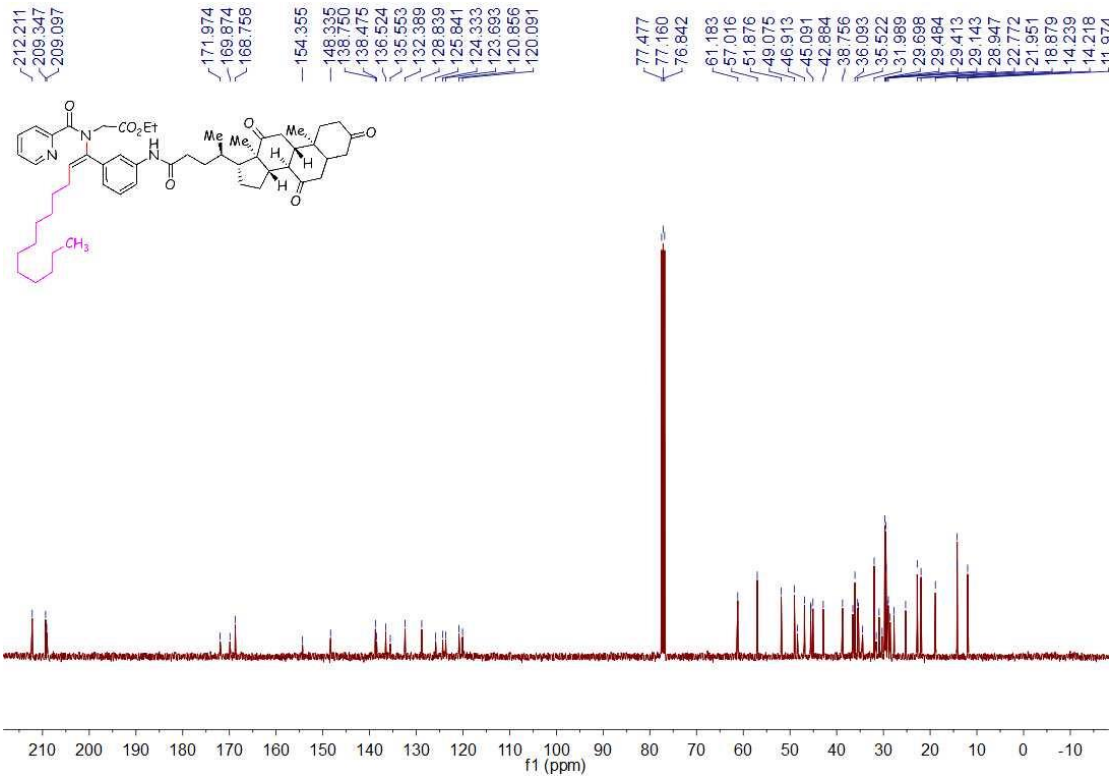
^{1}H NMR spectra for compound **7e** (400 MHz, $CDCl_3$)



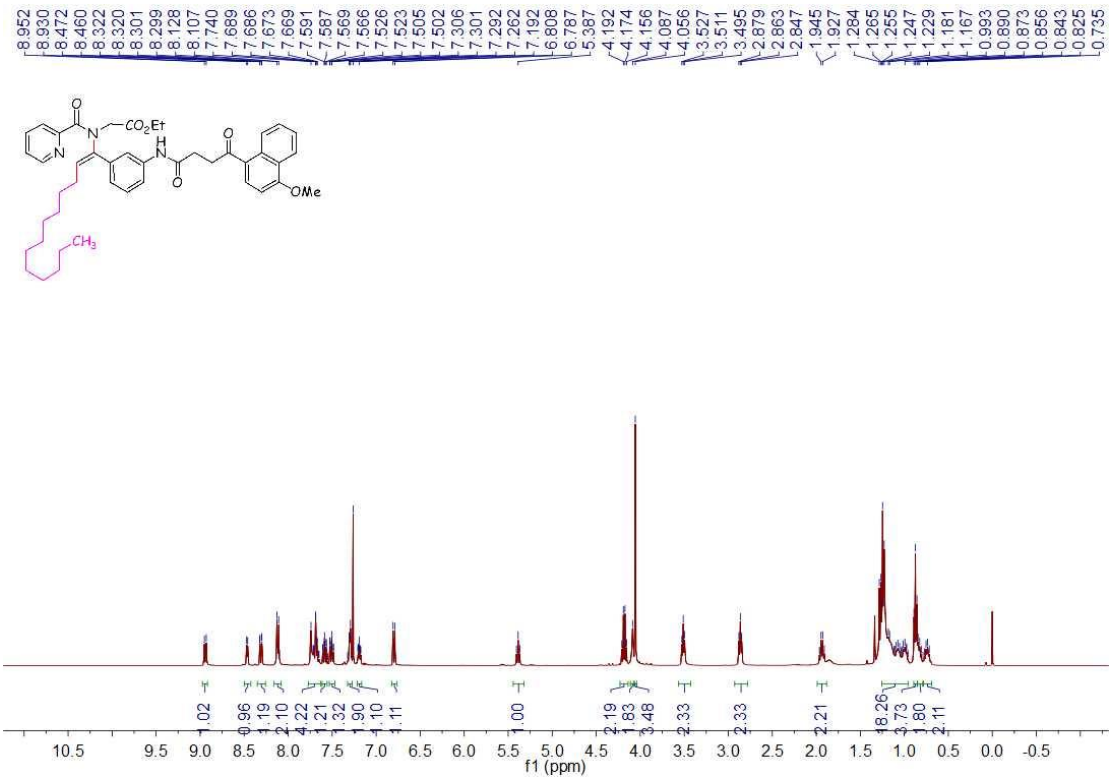
^{13}C NMR spectra for compound **7e** (100 MHz, $CDCl_3$)



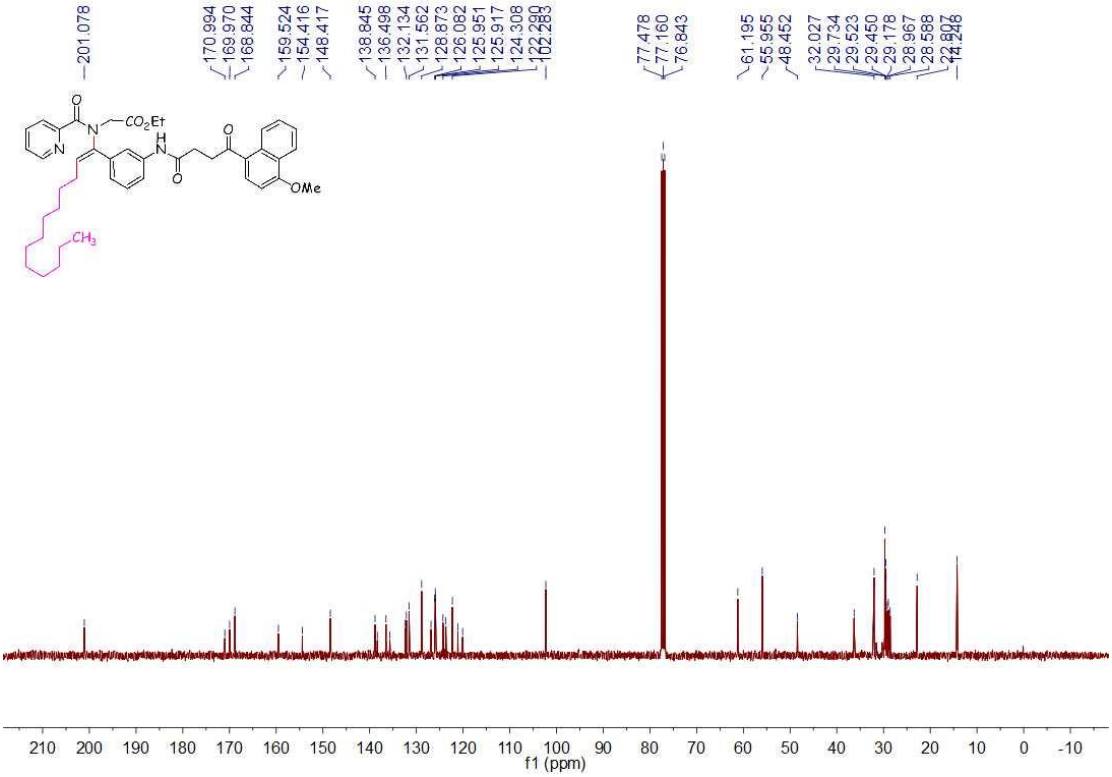
^{1}H NMR spectra for compound **7f** (400 MHz, $CDCl_3$)



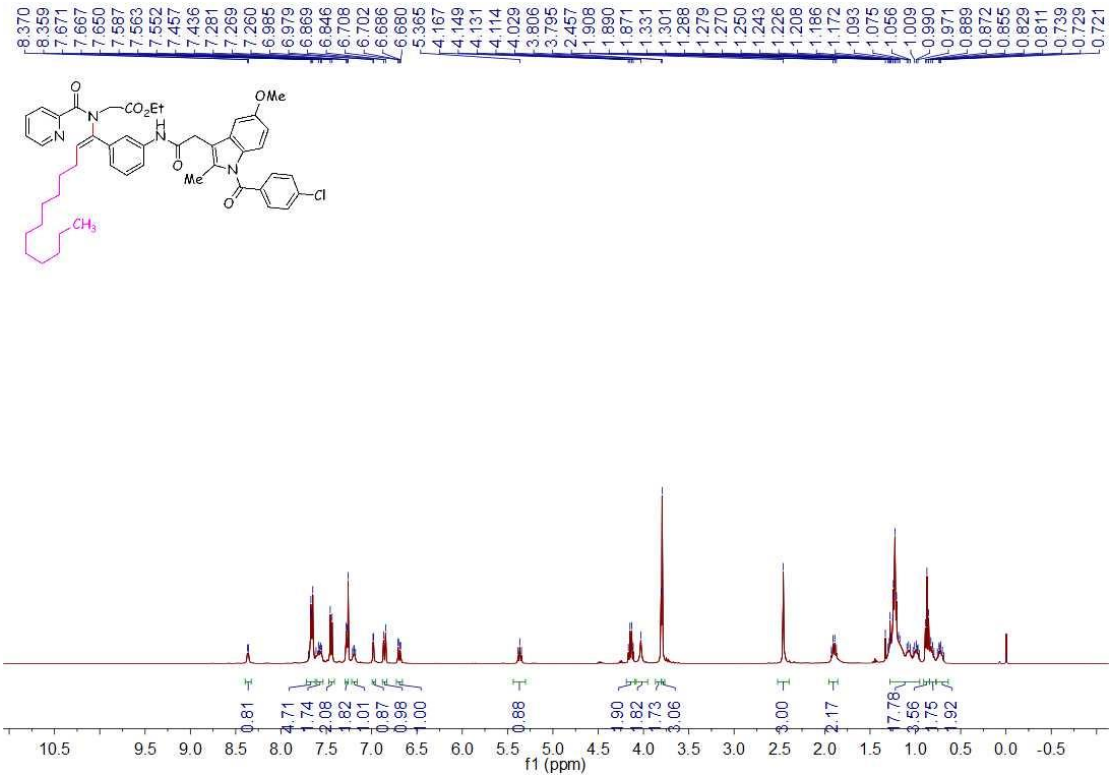
^{13}C NMR spectra for compound **7f** (100 MHz, $CDCl_3$)



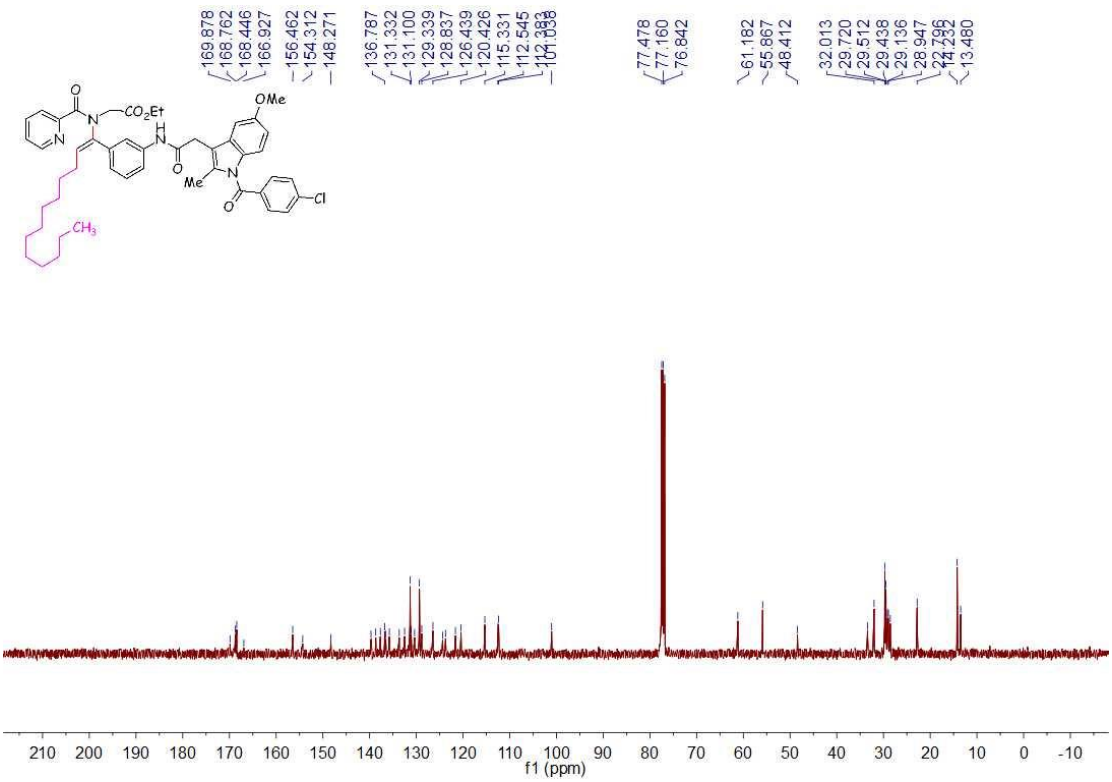
^{1}H NMR spectra for compound **7g** (400 MHz, $CDCl_3$)



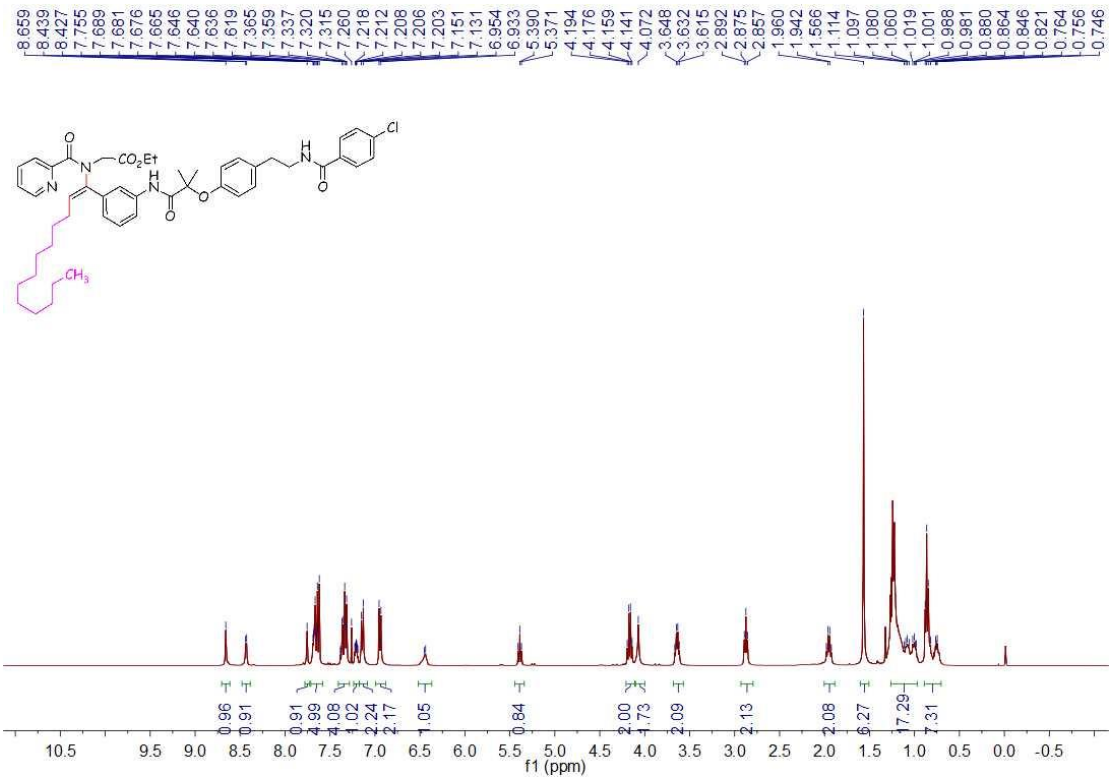
^{13}C NMR spectra for compound **7g** (100 MHz, $CDCl_3$)



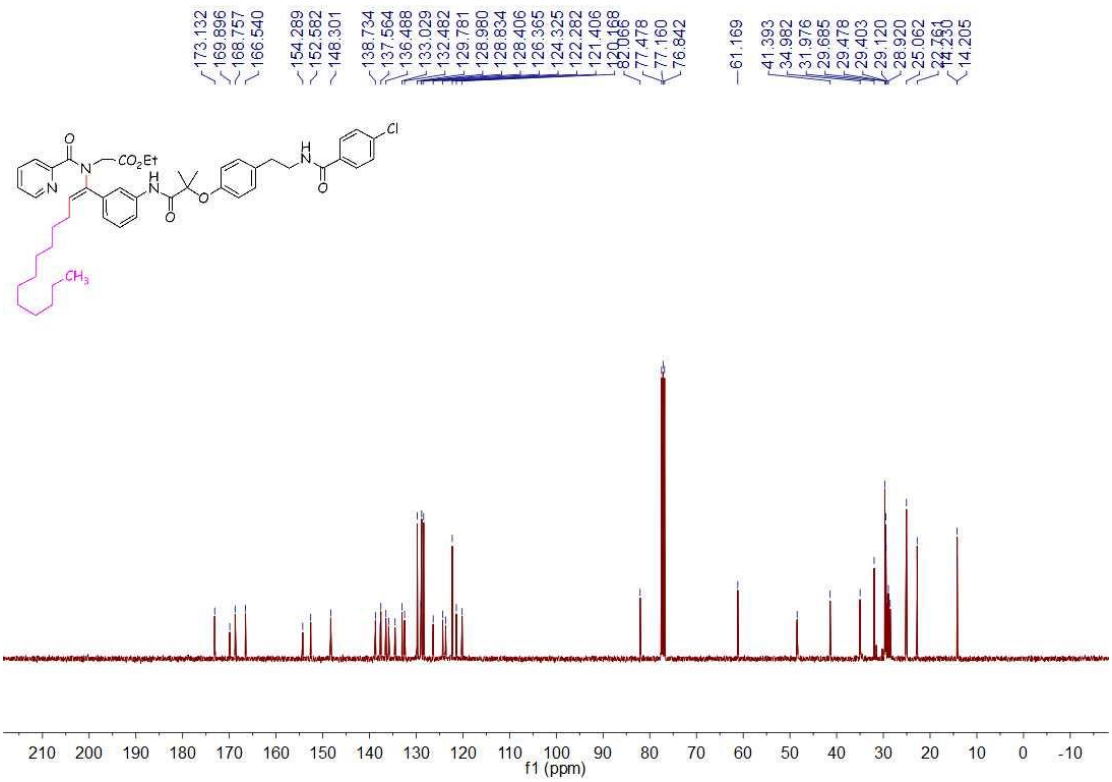
^{1}H NMR spectra for compound **7h** (400 MHz, $CDCl_3$)



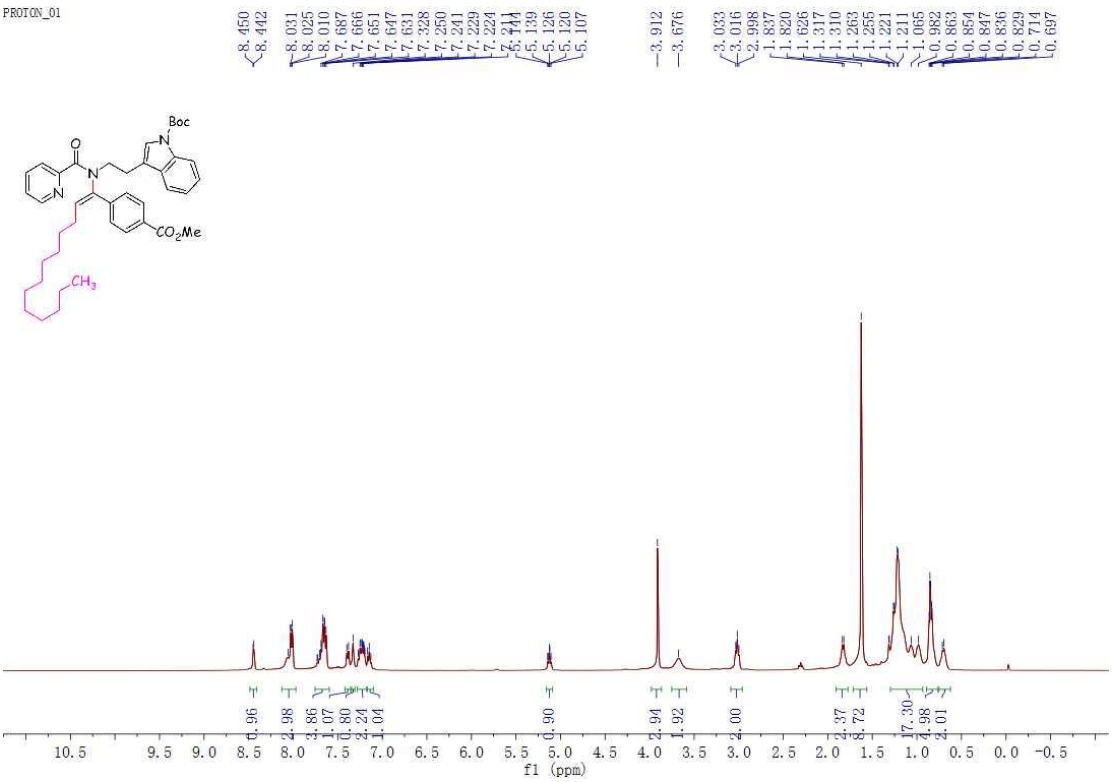
^{13}C NMR spectra for compound **7h** (100 MHz, $CDCl_3$)



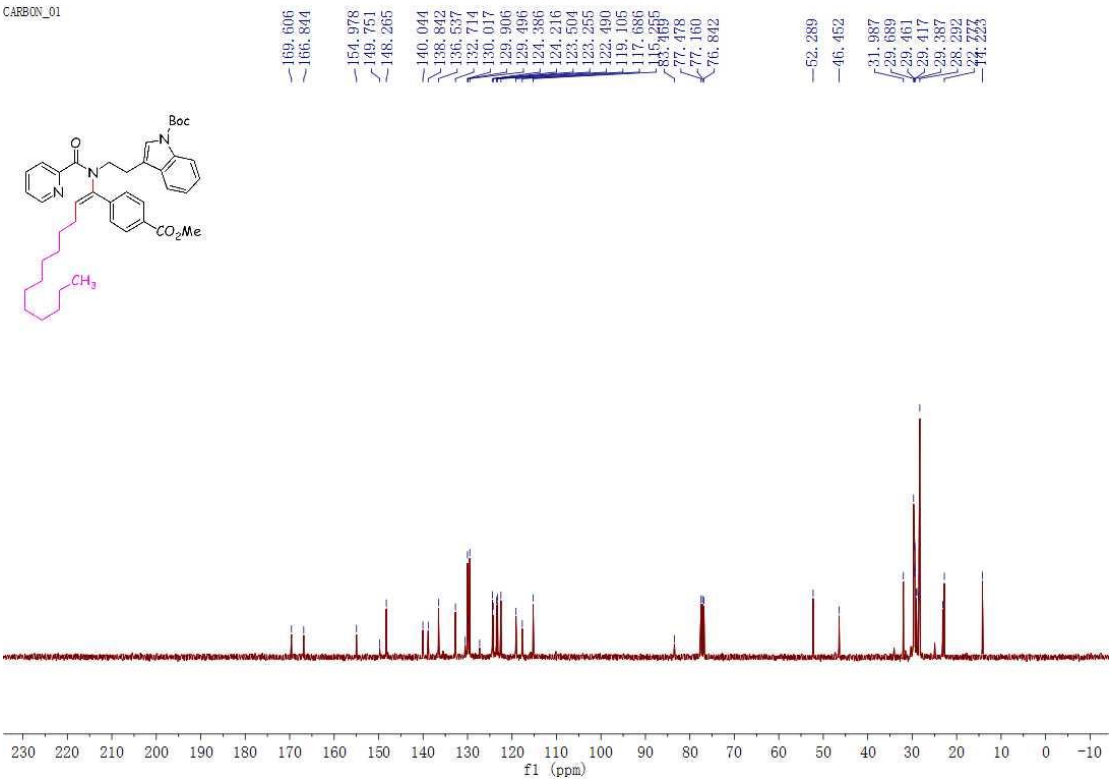
^{1}H NMR spectra for compound **7i** (400 MHz, $CDCl_3$)



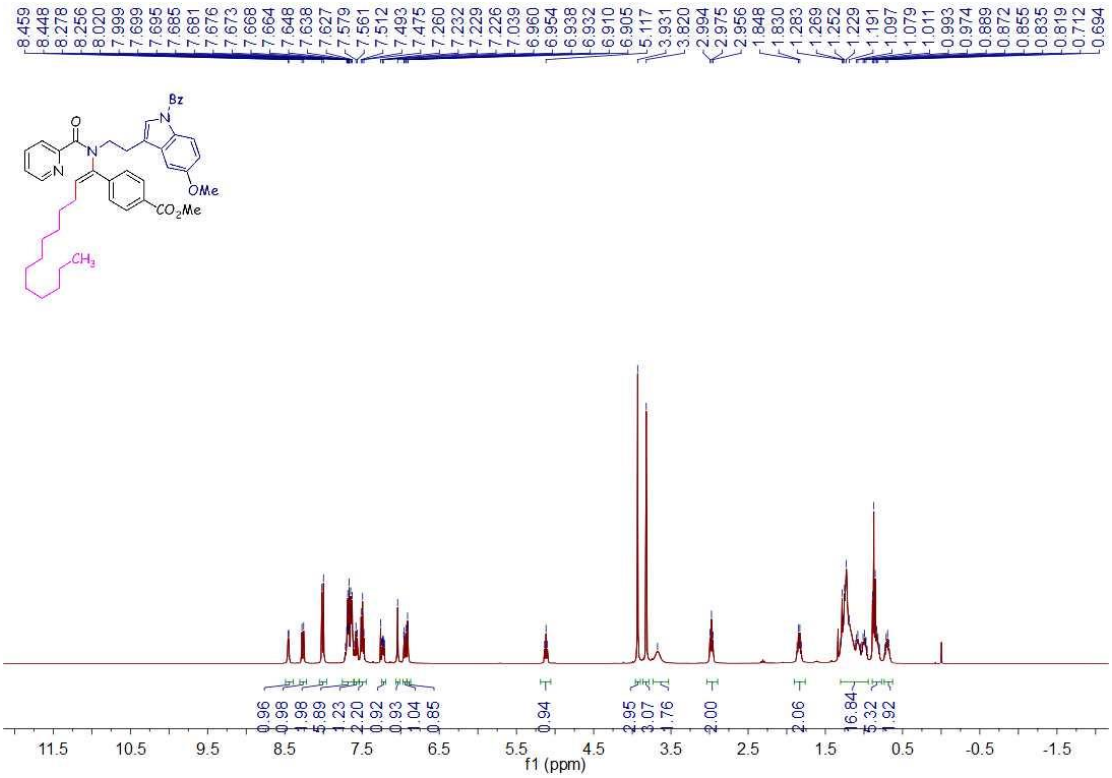
^{13}C NMR spectra for compound **7i** (100 MHz, $CDCl_3$)



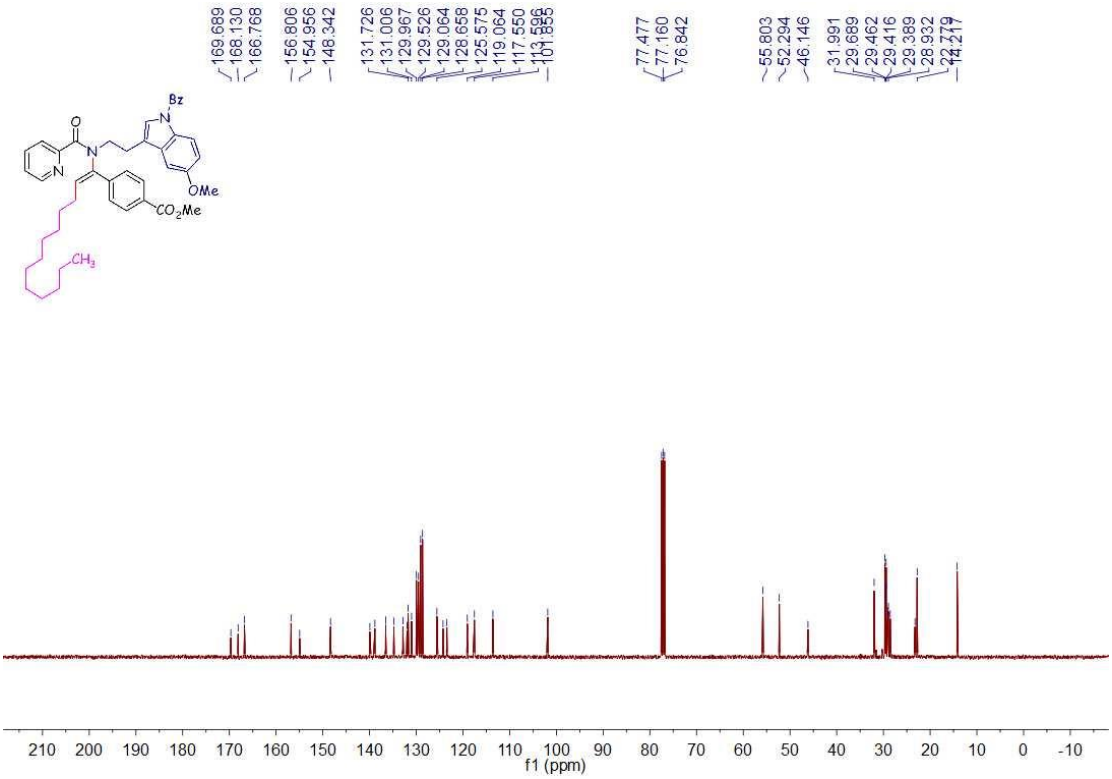
^{1}H NMR spectra for compound **7j** (400 MHz, $CDCl_3$)



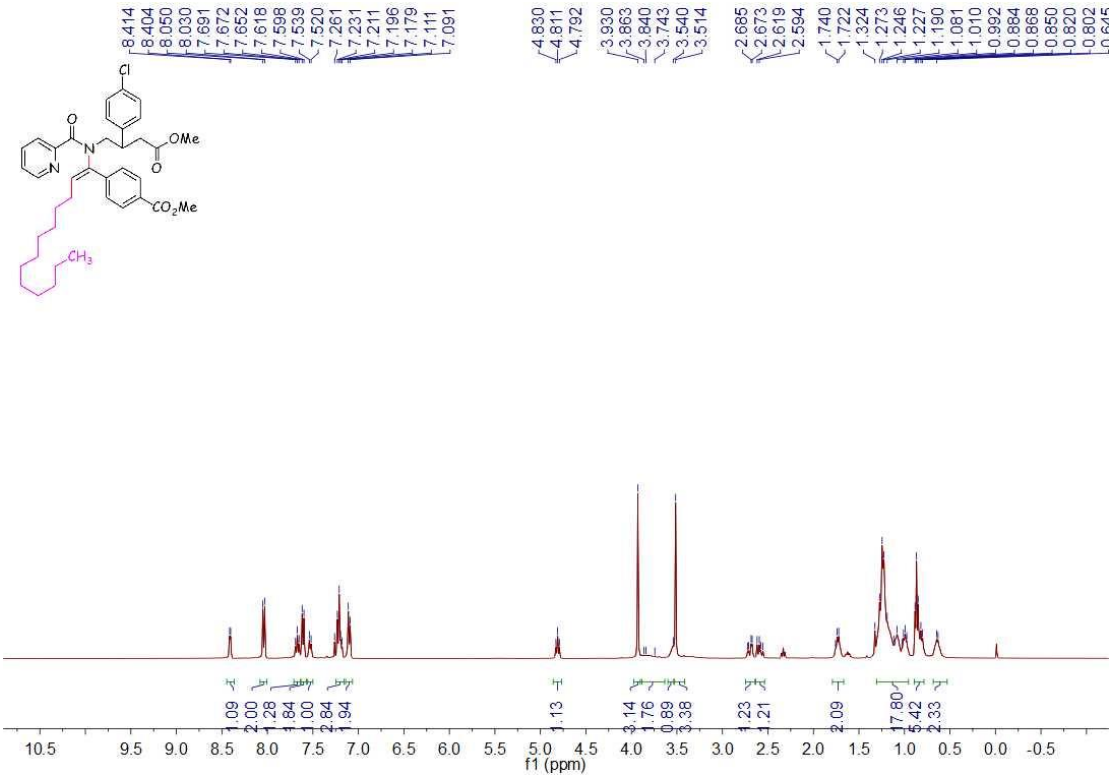
^{13}C NMR spectra for compound **7j** (100 MHz, $CDCl_3$)



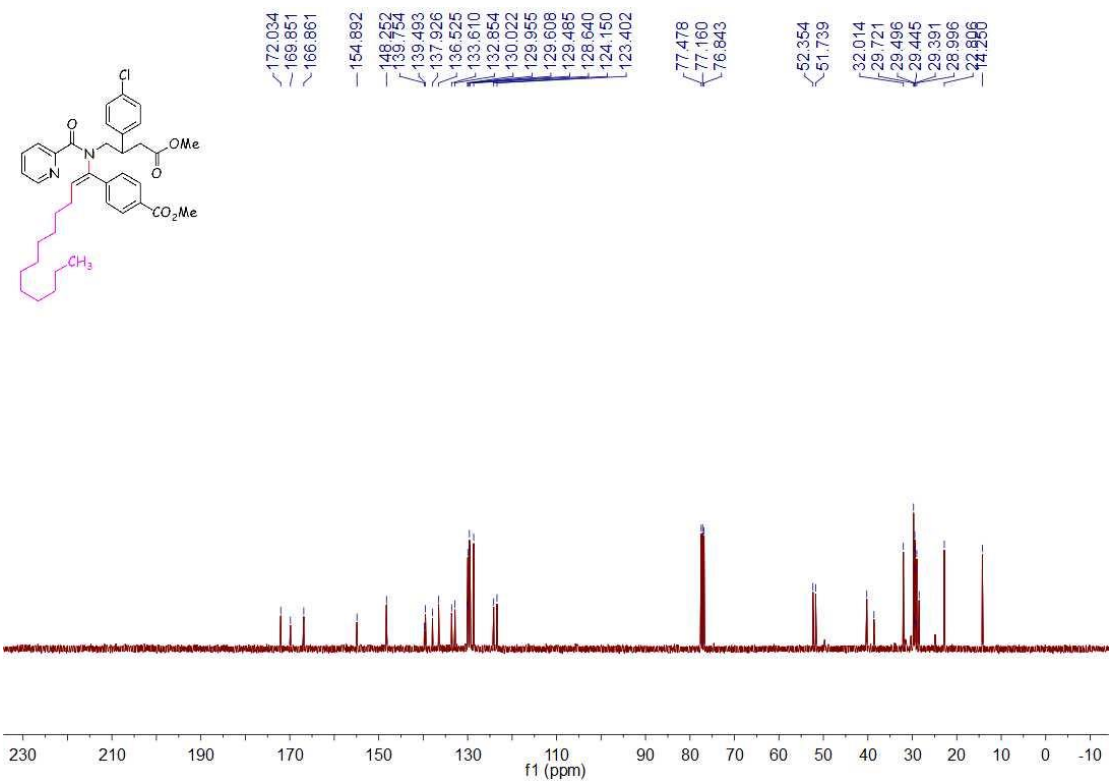
^{1}H NMR spectra for compound **7k** (400 MHz, $CDCl_3$)



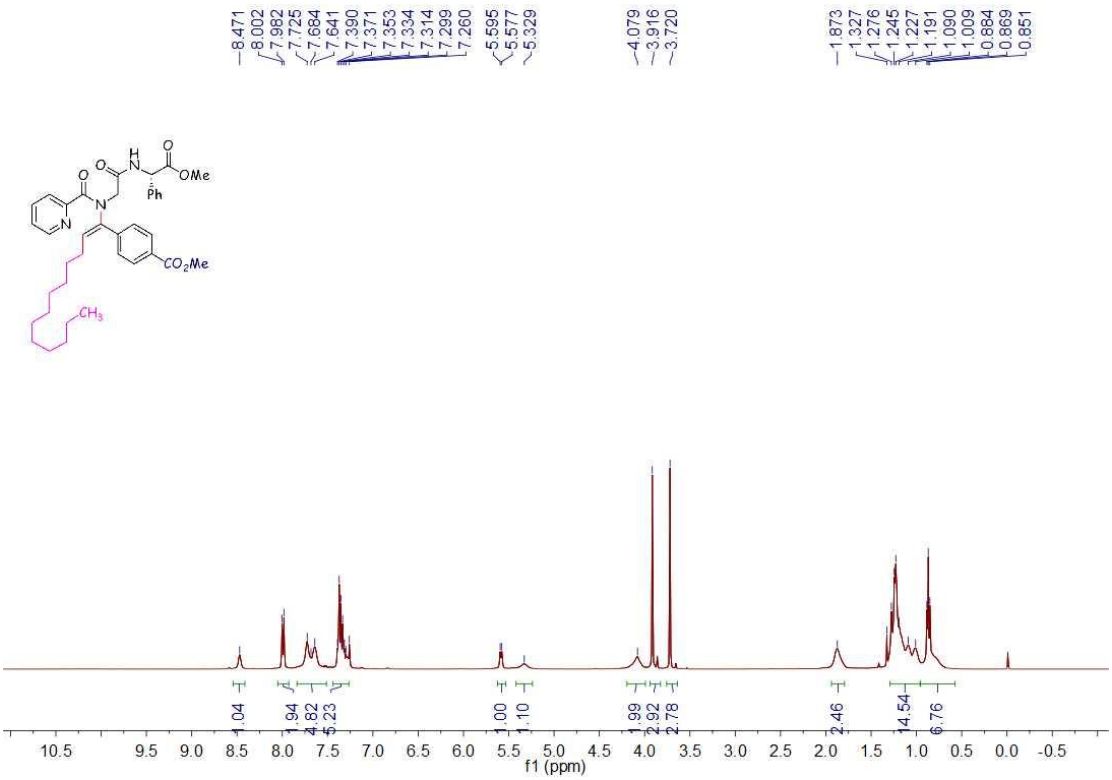
^{13}C NMR spectra for compound **7k** (100 MHz, $CDCl_3$)



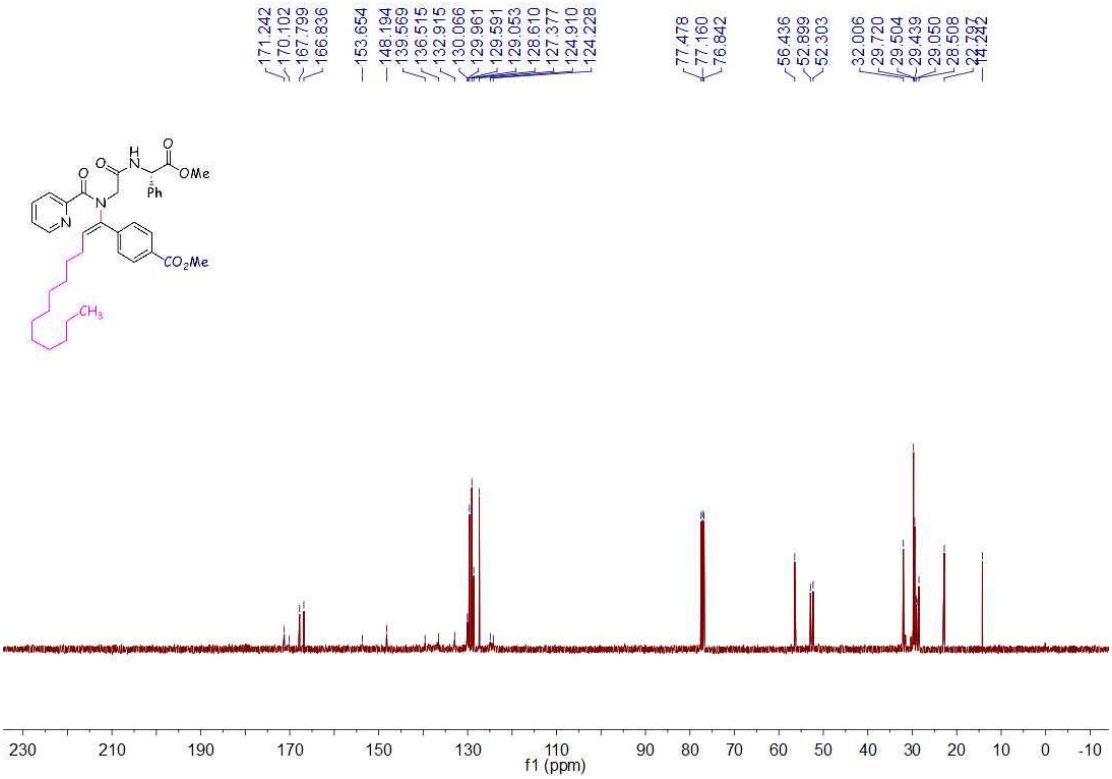
^{1}H NMR spectra for compound **7l** (400 MHz, $CDCl_3$)



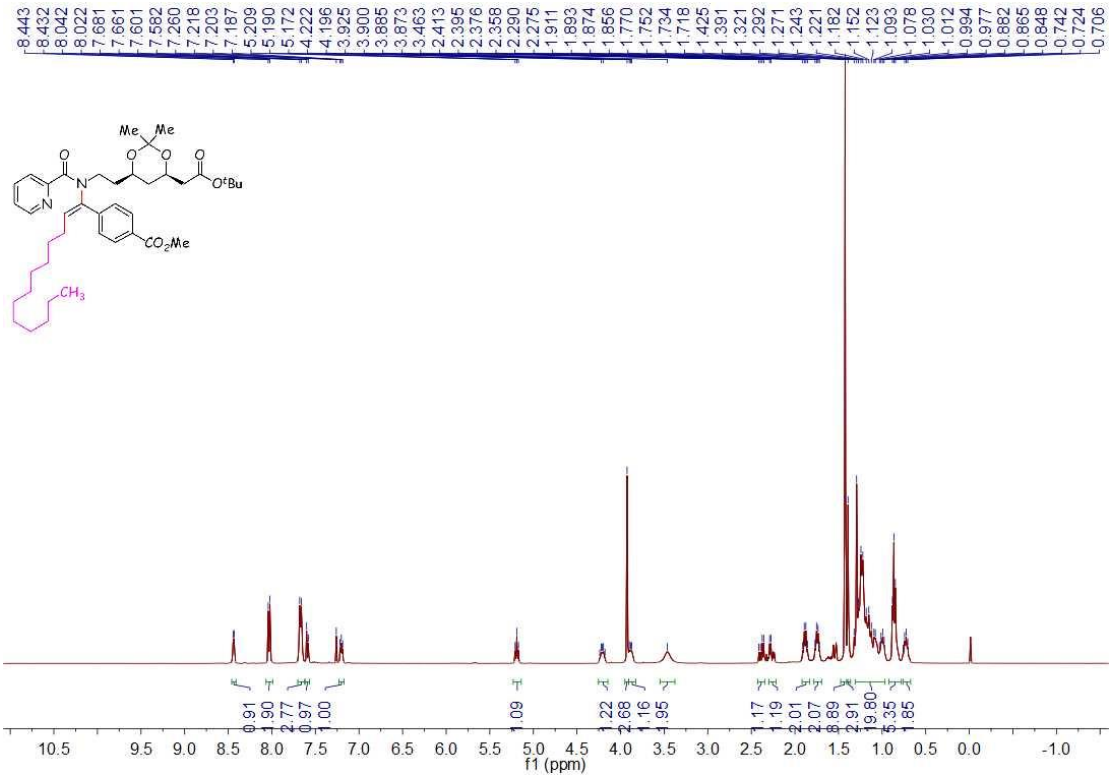
^{13}C NMR spectra for compound **7l** (100 MHz, $CDCl_3$)



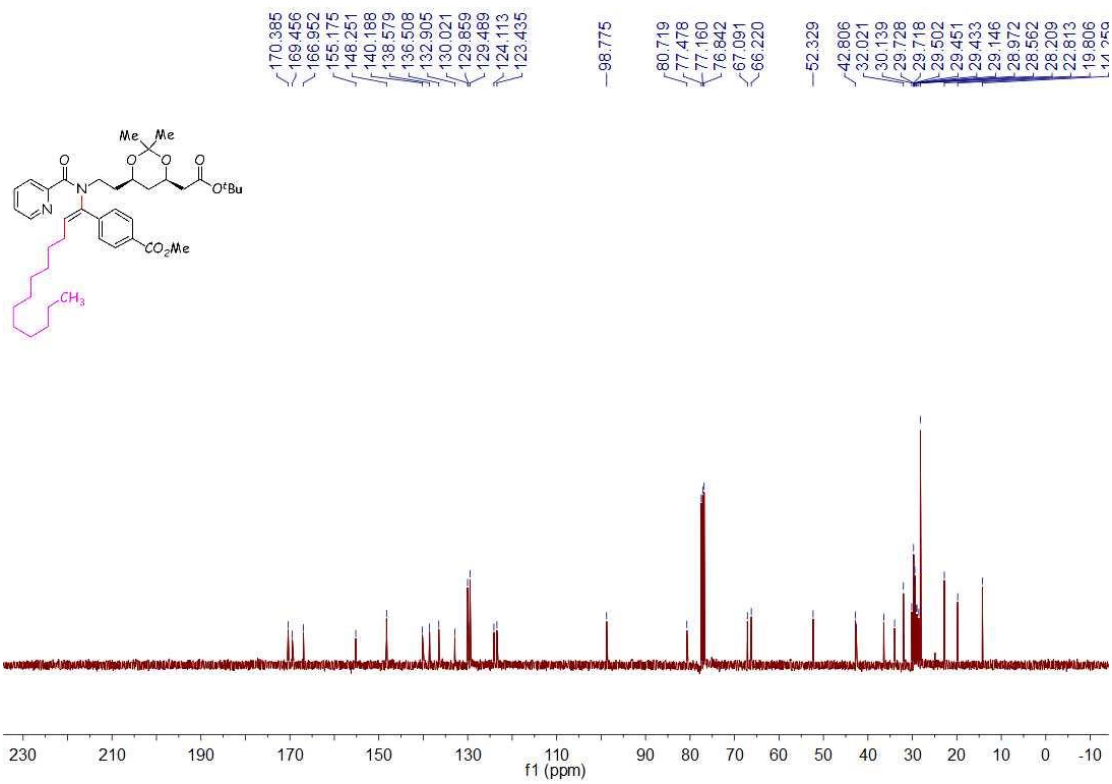
^{1}H NMR spectra for compound **7m** (400 MHz, $CDCl_3$)



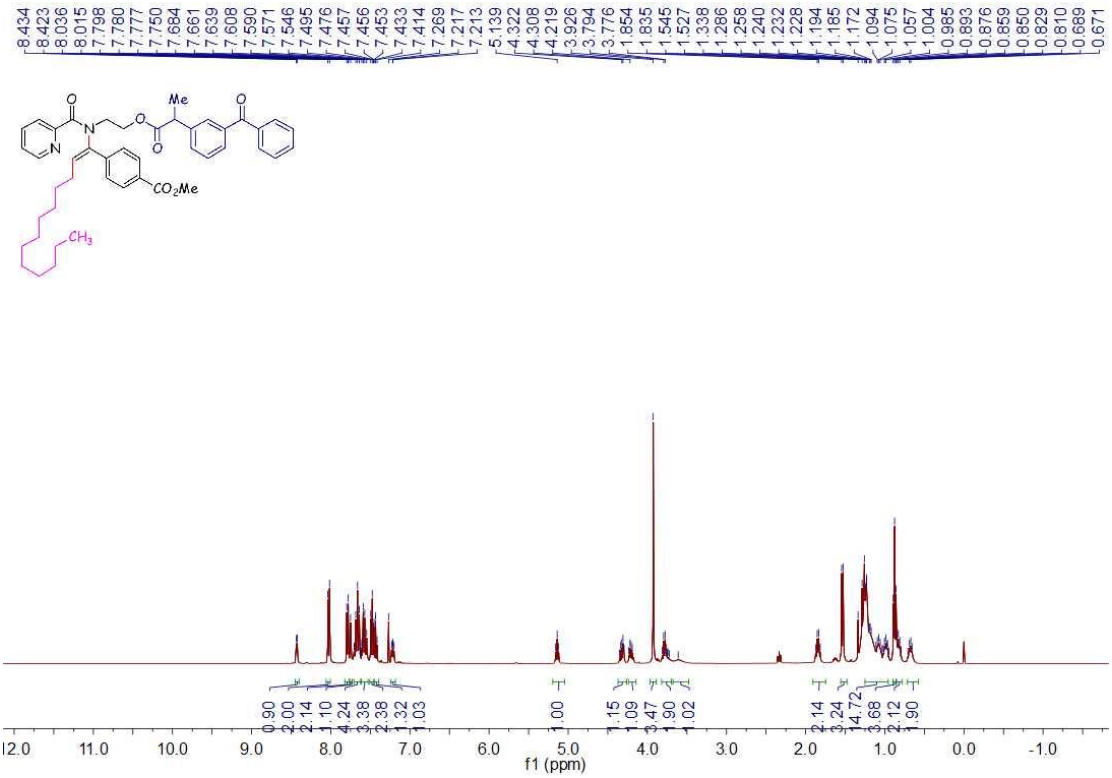
^{13}C NMR spectra for compound **7m** (100 MHz, $CDCl_3$)



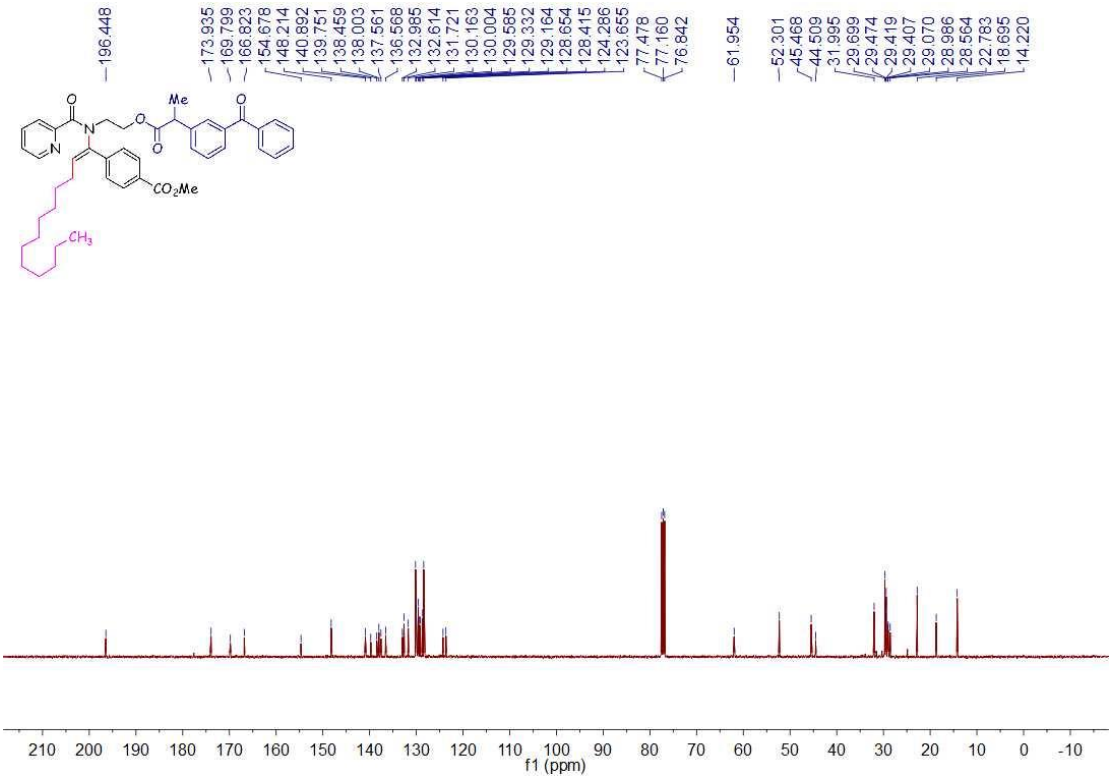
^{1}H NMR spectra for compound **7n** (400 MHz, $CDCl_3$)



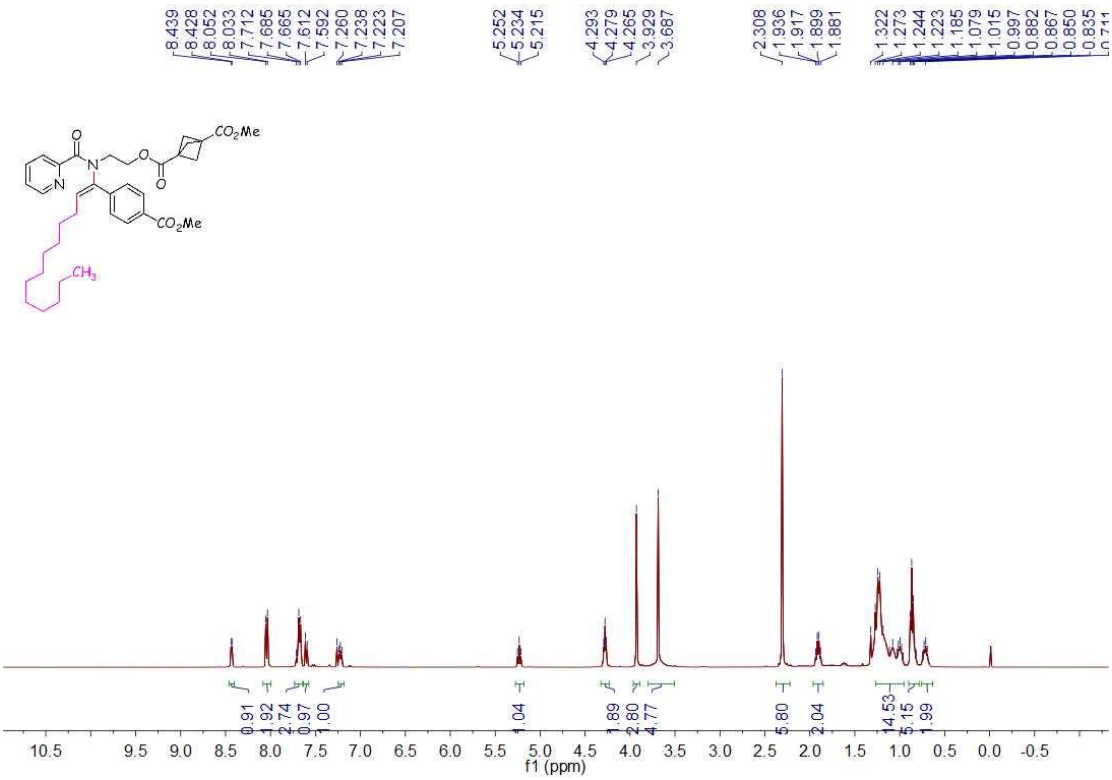
^{13}C NMR spectra for compound **7n** (100 MHz, $CDCl_3$)



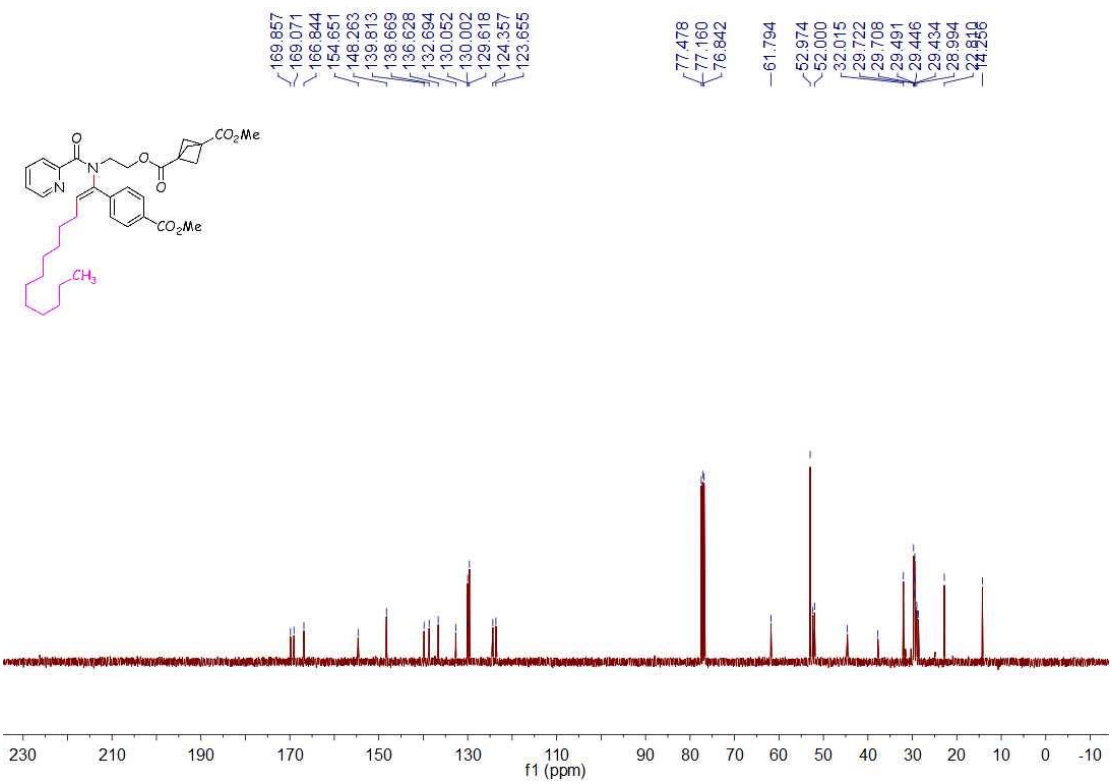
^{1}H NMR spectra for compound **7o** (400 MHz, $CDCl_3$)



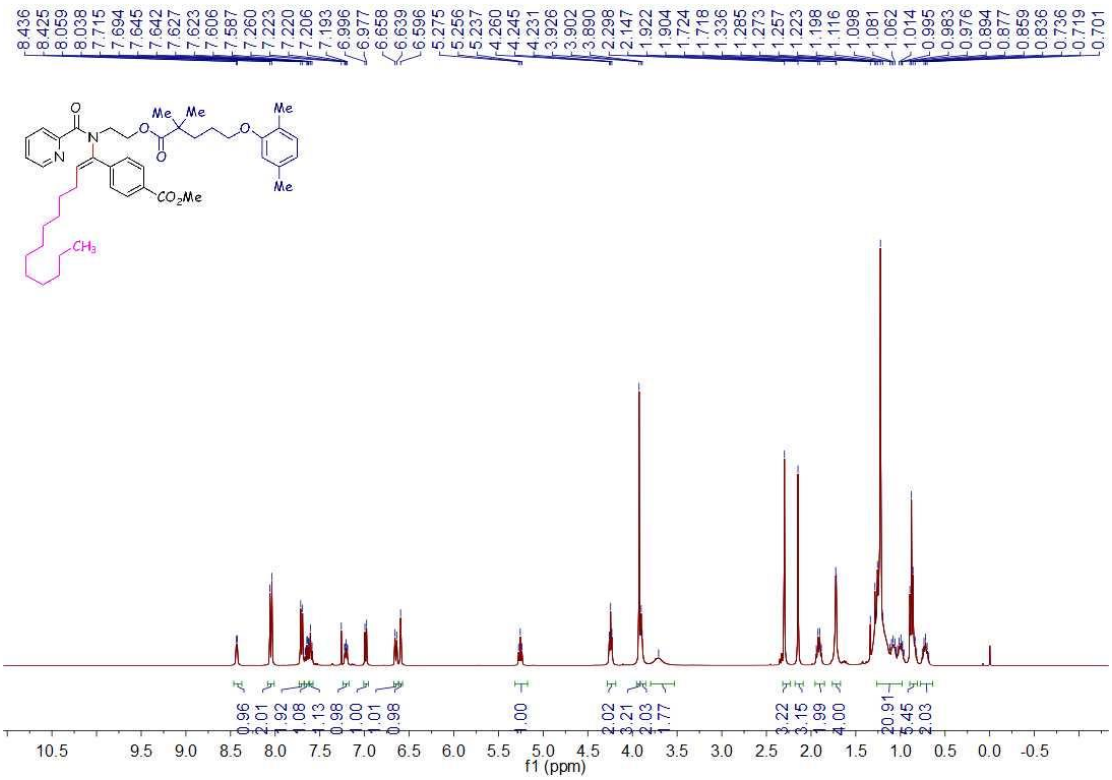
^{13}C NMR spectra for compound **7o** (100 MHz, $CDCl_3$)



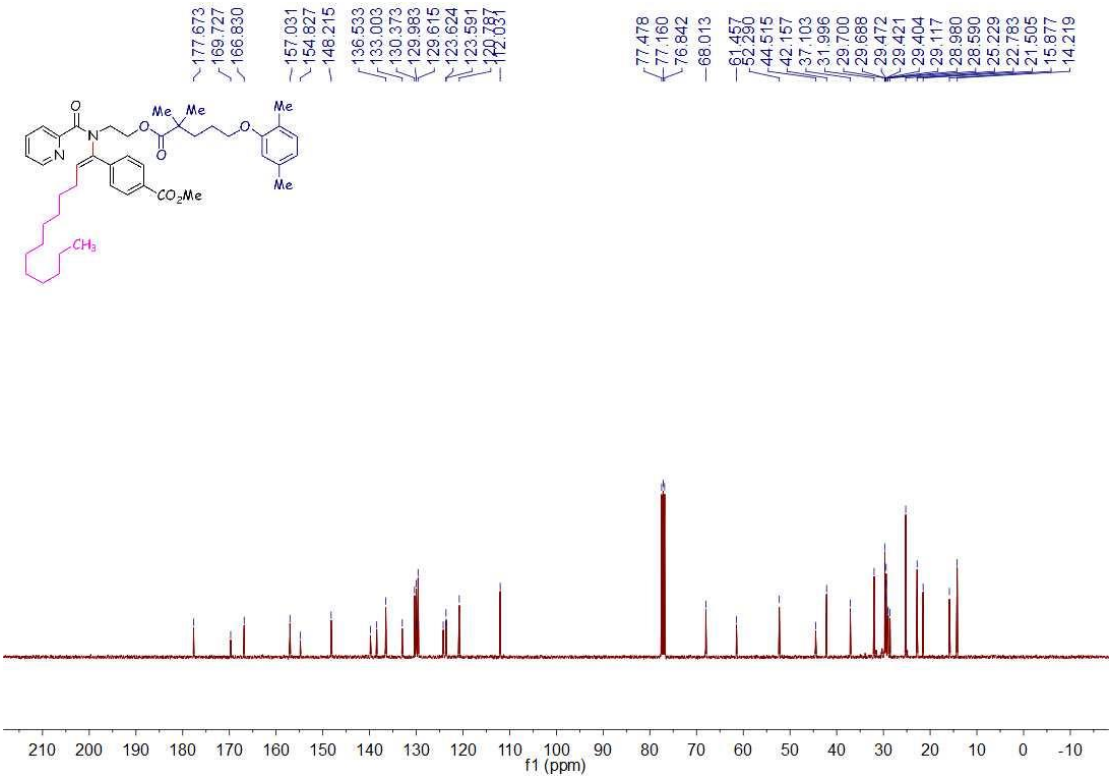
^{1}H NMR spectra for compound **7p** (400 MHz, $CDCl_3$)



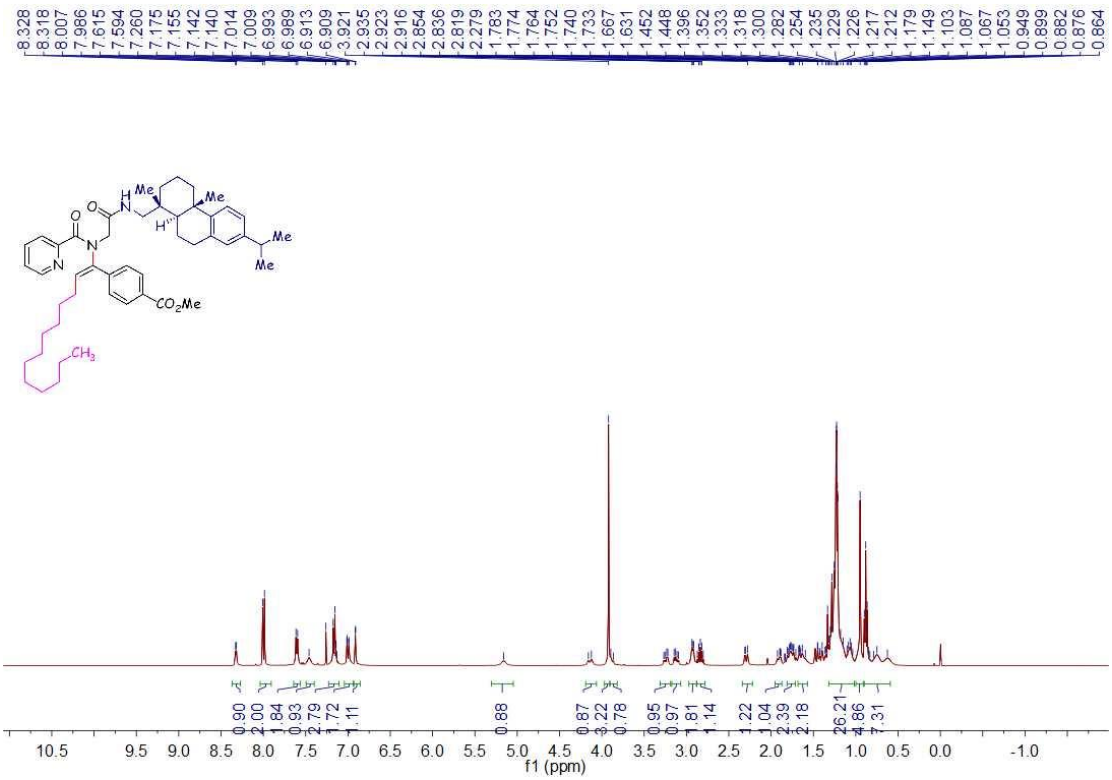
^{13}C NMR spectra for compound **7p** (100 MHz, $CDCl_3$)



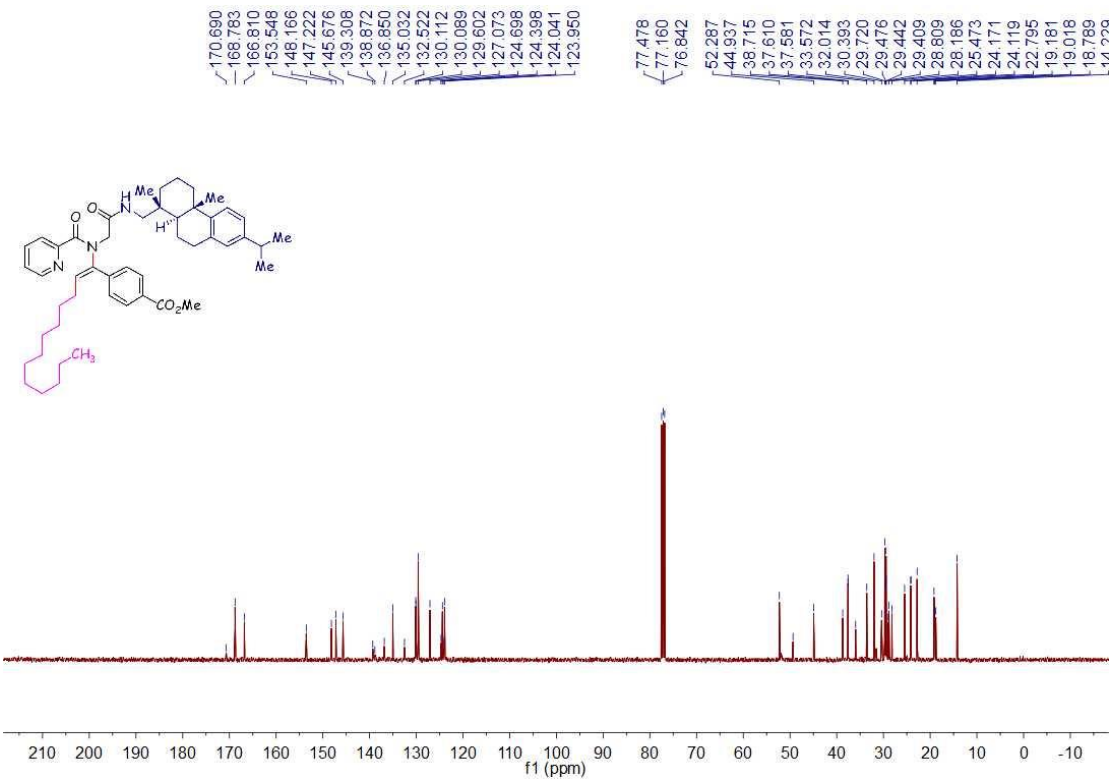
^{1}H NMR spectra for compound **7q** (400 MHz, $CDCl_3$)



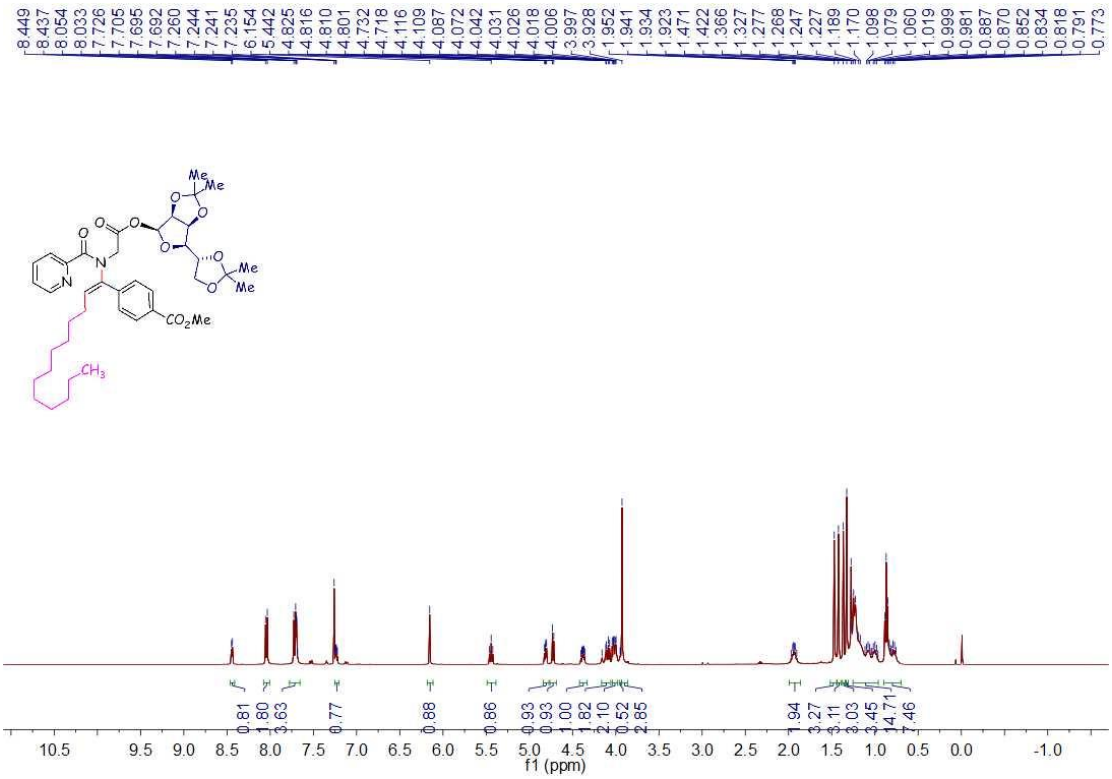
^{13}C NMR spectra for compound **7q** (100 MHz, $CDCl_3$)



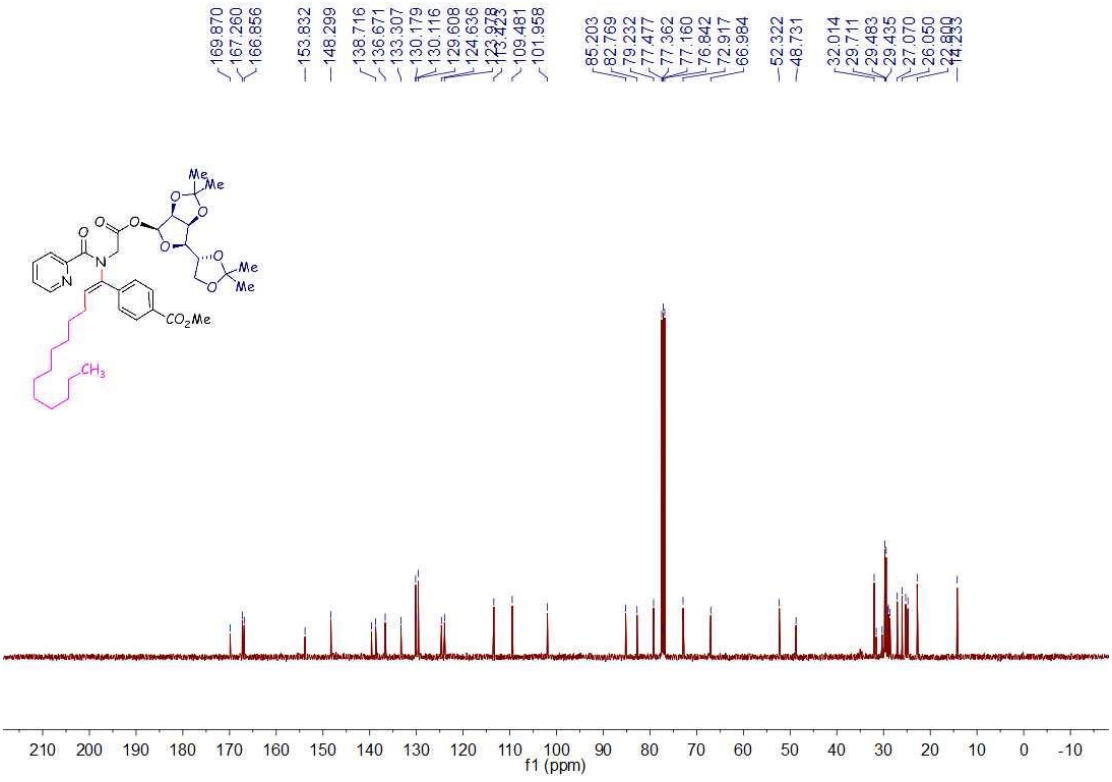
^{1}H NMR spectra for compound **7r** (400 MHz, $CDCl_3$)



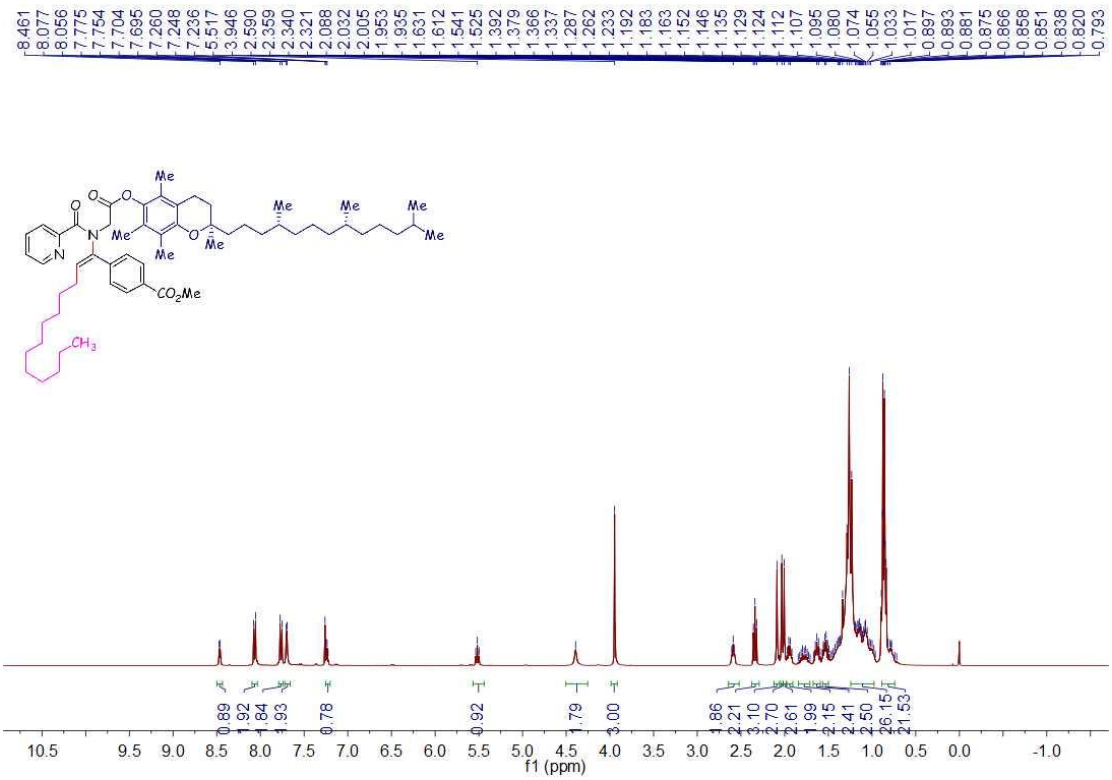
^{13}C NMR spectra for compound **7r** (100 MHz, $CDCl_3$)



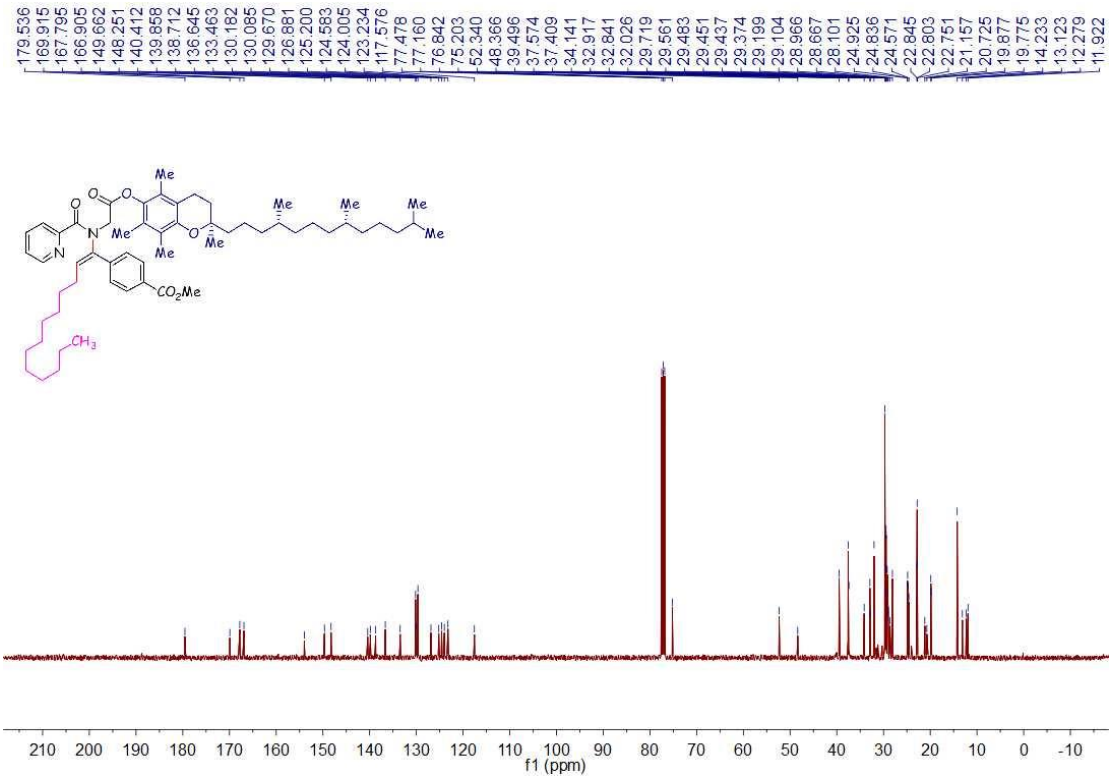
^{1}H NMR spectra for compound **7s** (400 MHz, $CDCl_3$)



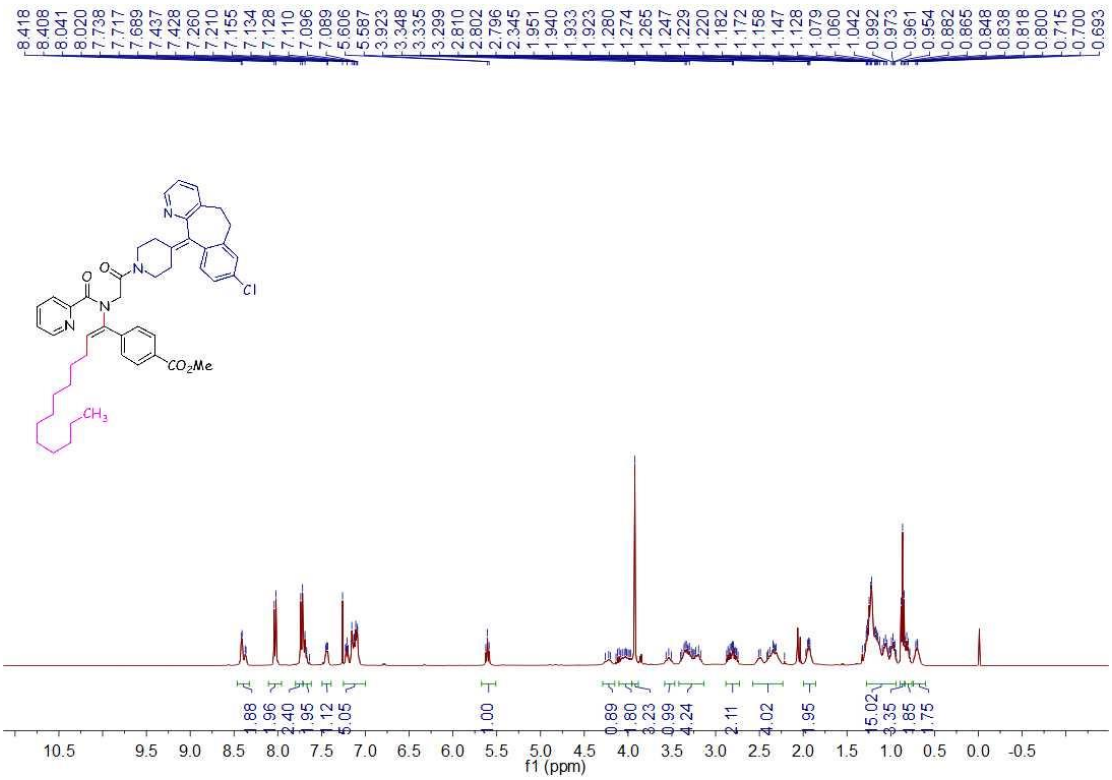
^{13}C NMR spectra for compound **7s** (100 MHz, $CDCl_3$)



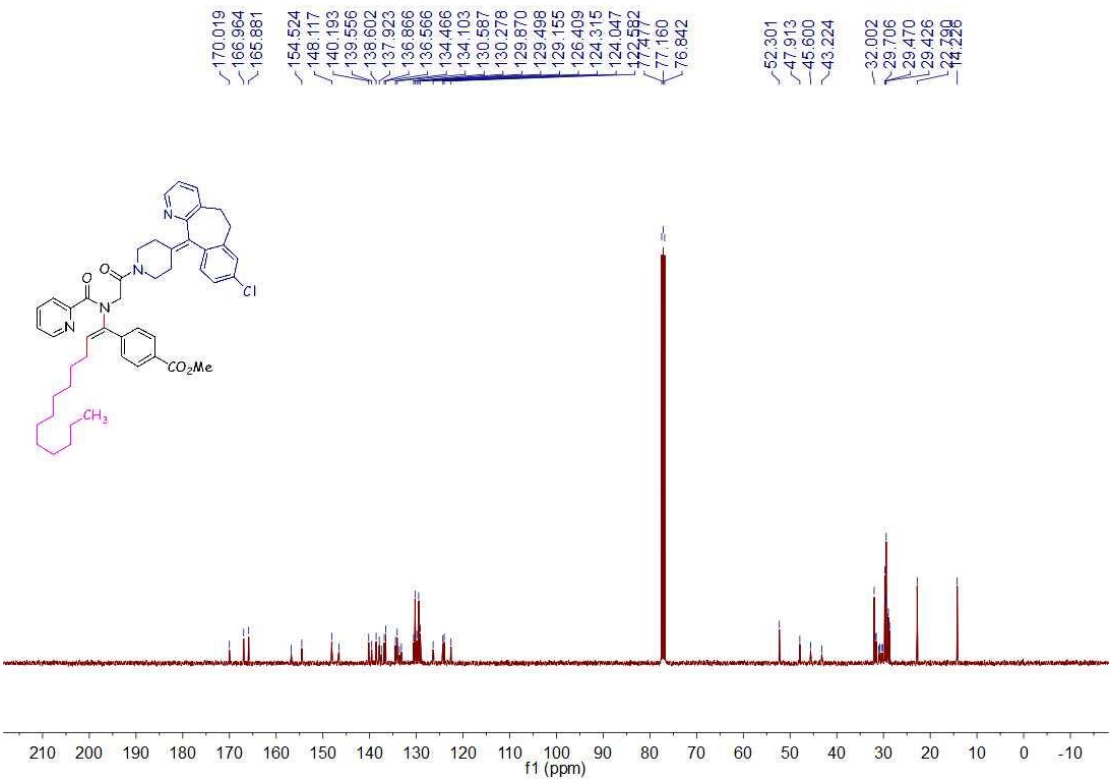
^{1}H NMR spectra for compound **7t** (400 MHz, $CDCl_3$)



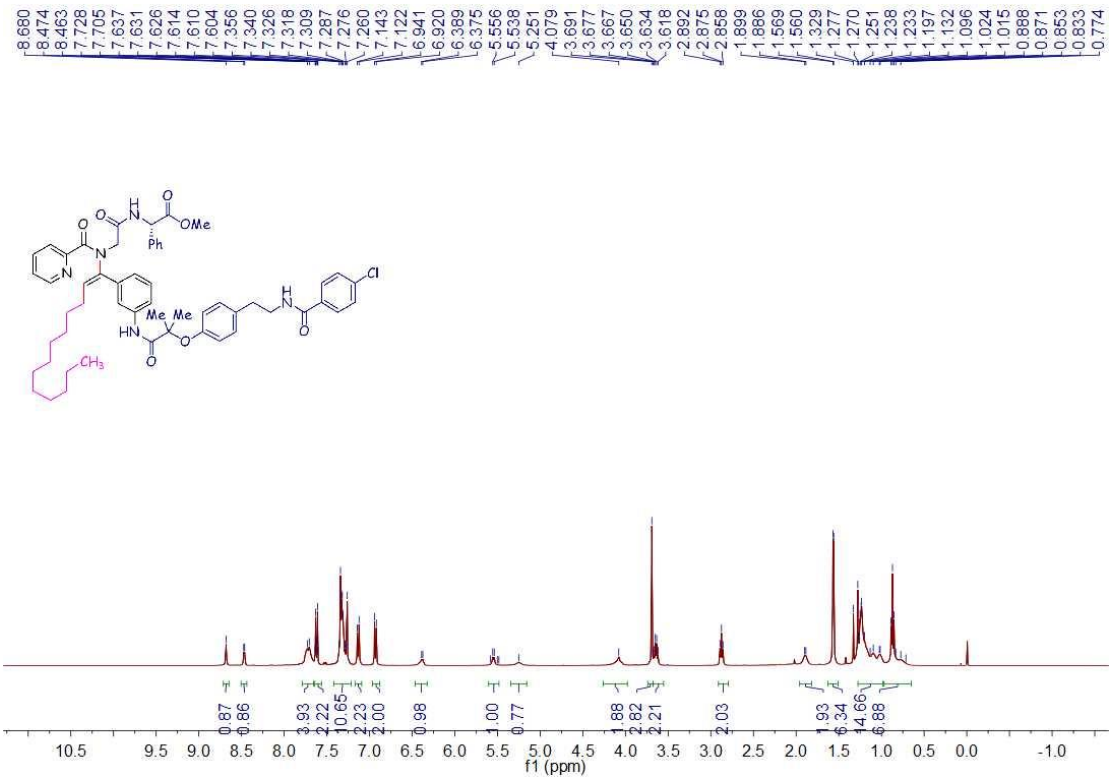
^{13}C NMR spectra for compound **7t** (100 MHz, $CDCl_3$)



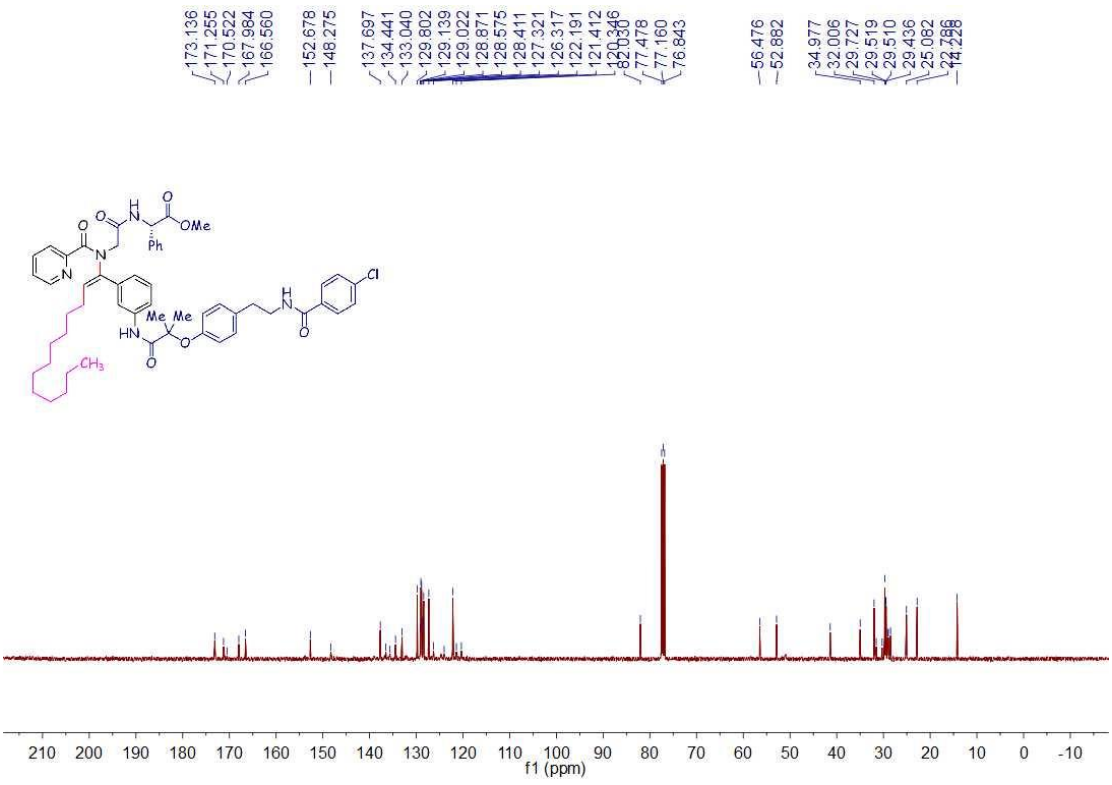
^{1}H NMR spectra for compound **7u** (400 MHz, $CDCl_3$)



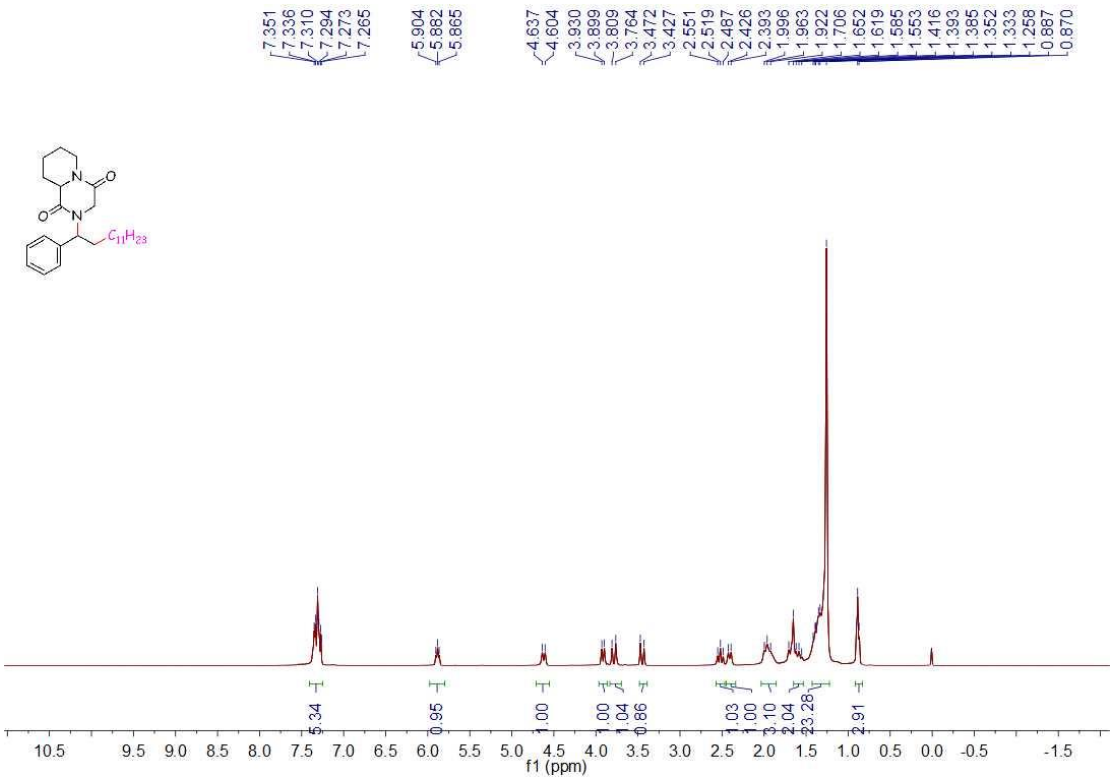
^{13}C NMR spectra for compound **7u** (100 MHz, $CDCl_3$)



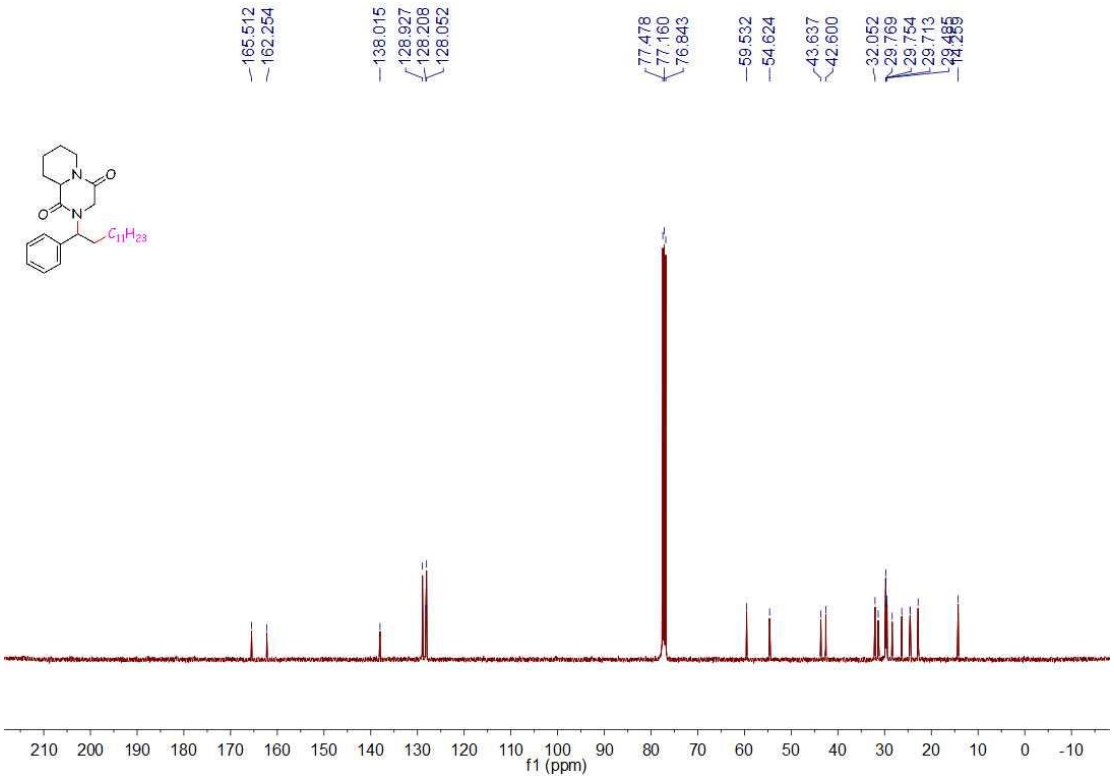
^{1}H NMR spectra for compound **7v** (400 MHz, $CDCl_3$)



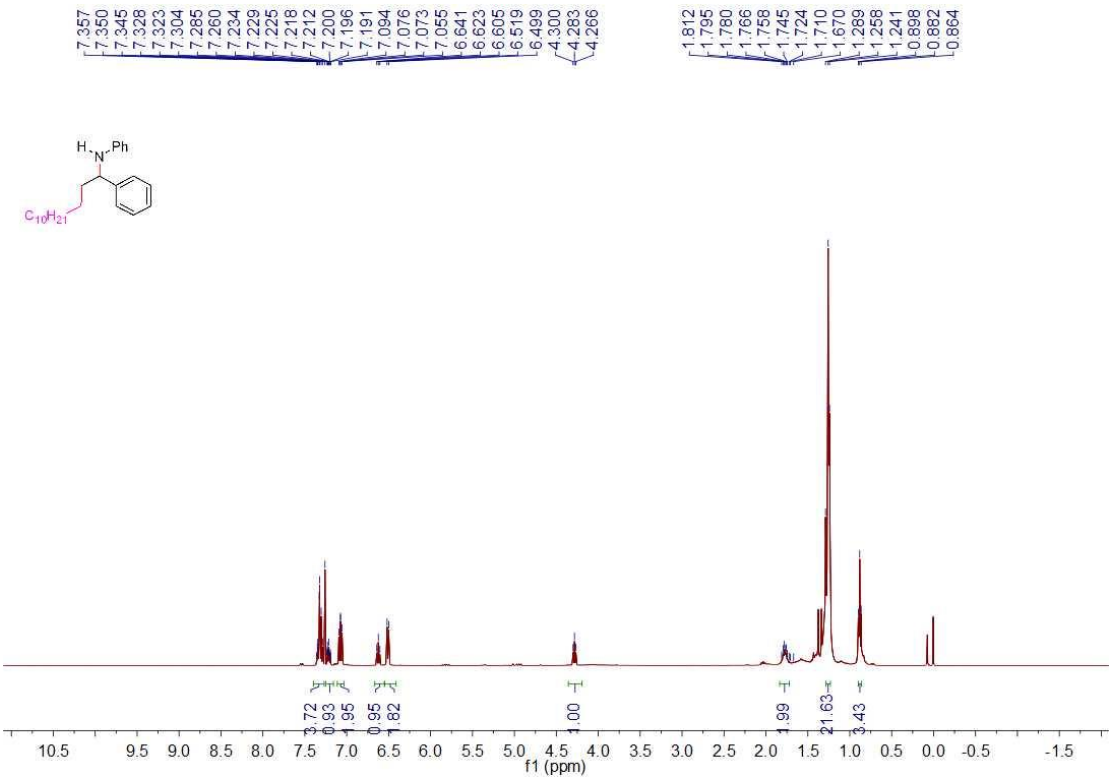
^{13}C NMR spectra for compound **7v** (100 MHz, $CDCl_3$)



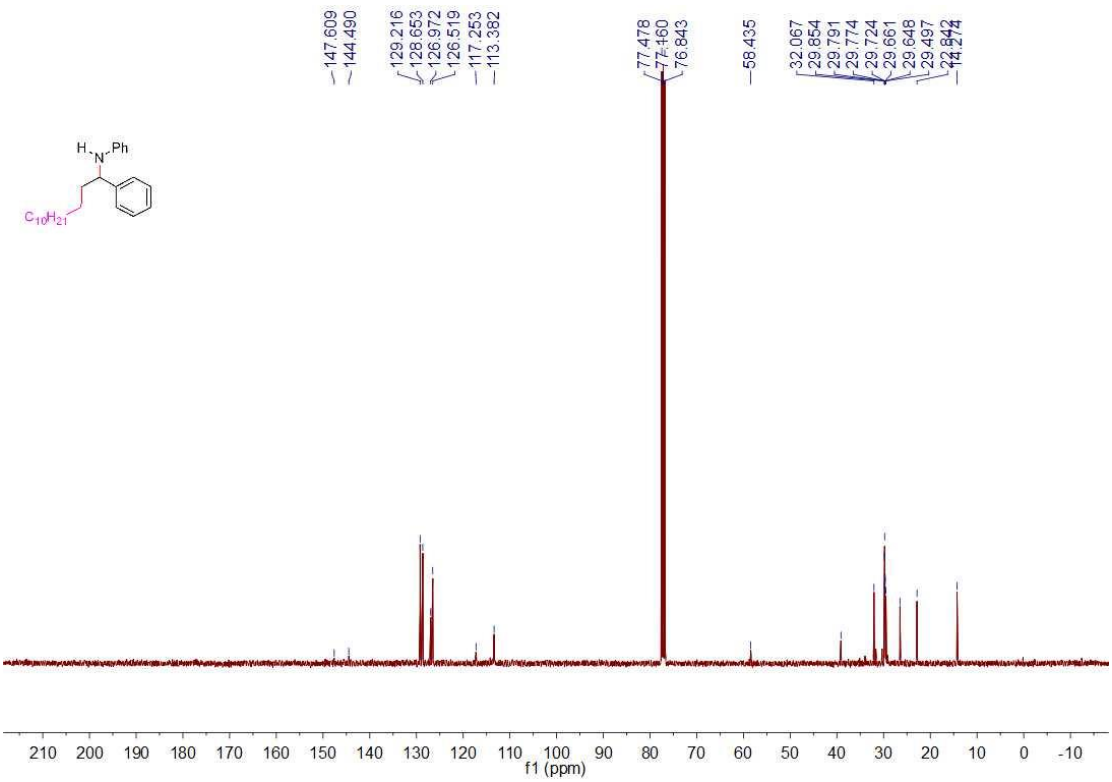
^{1}H NMR spectra for compound **8a** (400 MHz, $CDCl_3$)



^{13}C NMR spectra for compound **8a** (100 MHz, $CDCl_3$)



^{1}H NMR spectra for compound **8b** (400 MHz, $CDCl_3$)



^{13}C NMR spectra for compound **8b** (100 MHz, $CDCl_3$)