Supporting Information

Acid and Base Switched Palladium-Catalyzed γ-C(sp^3)−H Alkylation and Alkenylation of Neopentylamine

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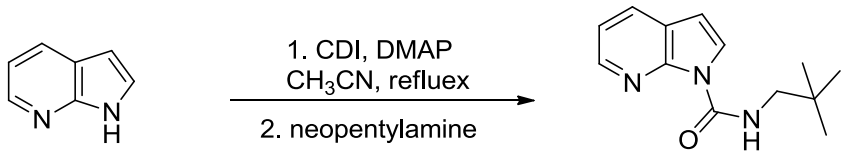
1. General Information

Catalytic reactions were carried out in Schlenk tubes using pre-dried glassware. *N*-neopentyl-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide (**1a**), *N*-neopentyl-1*H*-indole-1-carboxamide (**1b**) and acrylates (**2**) were synthesized according to previously described procedures[1,2]. Commercially available reagents were purchased from Energy Chemical, Bidepharm, Sigma Aldrich, Alfa Aesar, Acros or TCI, and used without purification unless otherwise noted. Column chromatography purification was performed using 200–300 mesh silica gel. NMR spectra were mostly recorded for ^{1}H NMR at 500 MHz and for ^{13}C NMR at 125 MHz. $CDCl_3$ was used as solvent. Chemical shifts were referenced relative to residual solvent signal ($CDCl_3$: ^{1}H NMR: δ 7.26 ppm, ^{13}C NMR: δ 77.16 ppm). The following abbreviations are used to describe peak patterns where appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (*J*) are reported in Hertz (Hz). HRMS was performed on Agilent Technologies 6224 TOF LC/MS apparatus (ESI).

2. Experimental Section

2.1 Substrates Preparation

2.1.1 Preparation of *N*-neopentyl-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide (1a)[1]

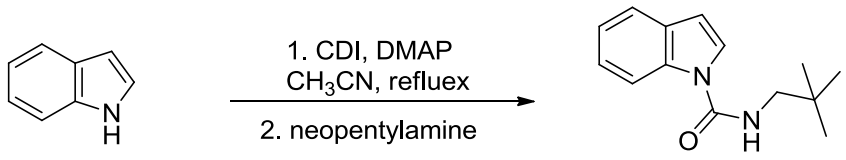


1a, 86%

A reaction tube (100 mL) with magnetic stir bar was charged with 7-azaindole (1.18 g, 10.0 mmol), 1,1'-carbonyldiimidazole (CDI, 2.43 g, 15.0 mmol) and 4-dimethylaminepyridine (DMAP, 61 mg, 0.5 mmol). Then 20 mL anhydrous acetonitrile was added to the reaction tube. The system was stirred at 85 ^{o}C in an oil bath for 10 h. After cooling to room temperature, neopentylamine (1.74 g, 20.0 mmol) was added and then the reaction was stirred at 85 ^{o}C in an oil bath for another 6 hours until most of 7-azaindole was consumed by TLC detection. Then the reaction was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (PET: EtOAc = 15:1) to afford **1a** as colorless oil (1.99 g) in 86% yield.

***N*-neopentyl-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide (1a):** ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.87 (s, 1H), 8.30 (dd, J = 5.0, 1.5 Hz, 1H), 8.01 (d, J = 4.0 Hz, 1H), 7.93 (dd, J = 7.5, 1.5 Hz, 1H), 7.18 (dd, J = 8.0, 5.0 Hz, 1H), 6.52 (d, J = 4.0 Hz, 1H), 3.33 (d, J = 6.0 Hz, 2H), 1.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.0, 146.8, 142.5, 129.9, 126.5, 123.6, 117.9, 102.7, 51.9, 32.2, 27.5 (3C); HRMS (ESI) *m/z* calcd for $C_{13}H_{18}N_3O$ $[M+H]^+$ 232.1444, found 232.1444.

2.1.2 Preparation of *N*-neopentyl-1*H*-indole-1-carboxamide (1b)[1]

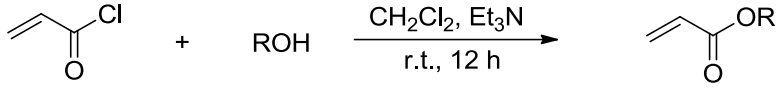


1b, 57%

A reaction tube (100 mL) with magnetic stir bar was charged with indole (1.17 g, 10.0 mmol), 1,1'-carbonyldiimidazole (CDI, 2.43 g, 15.0 mmol) and 4-dimethylaminepyridine (DMAP, 61 mg, 0.5 mmol). Then 20 mL anhydrous acetonitrile was added to reaction tube. The system was stirred at 85 ^{o}C in an oil bath for 10 h. After cooling to room temperature, neopentylamine (1.74 g, 20.0 mmol) was added and then the reaction was stirred at 85 ^{o}C in an oil bath for another 6 hours until most of indole was consumed by TLC detection. Then the reaction was cooled to room temperature and the solvent was removed under reduced pressure. Then the residue was purified by silica gel column chromatography (PET: EtOAc = 15:1) to afford **1b** as white solid (1.31 g) in 57% yield.

***N*-neopentyl-1*H*-indole-1-carboxamide (1b):** ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (dd, J = 8.5, 1.0 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 4.0 Hz, 1H), 7.34−7.31 (m, 1H), 7.25−7.21 (m, 1H), 6.62 (dd, J = 4.0, 1.0 Hz, 1H), 5.74 (s, 1H), 3.29 (d, J = 6.0 Hz, 2H), 1.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.5, 135.1, 130.4, 124.4, 124.2, 122.3, 121.4, 113.8, 106.9, 52.1, 32.2, 27.4 (3C); HRMS (ESI) *m/z* calcd. for $C_{14}H_{19}N_2O$ $[M+H]^+$ 231.1492, found 231.1494.

2.1.3 Preparation of acrylate (2)[2]

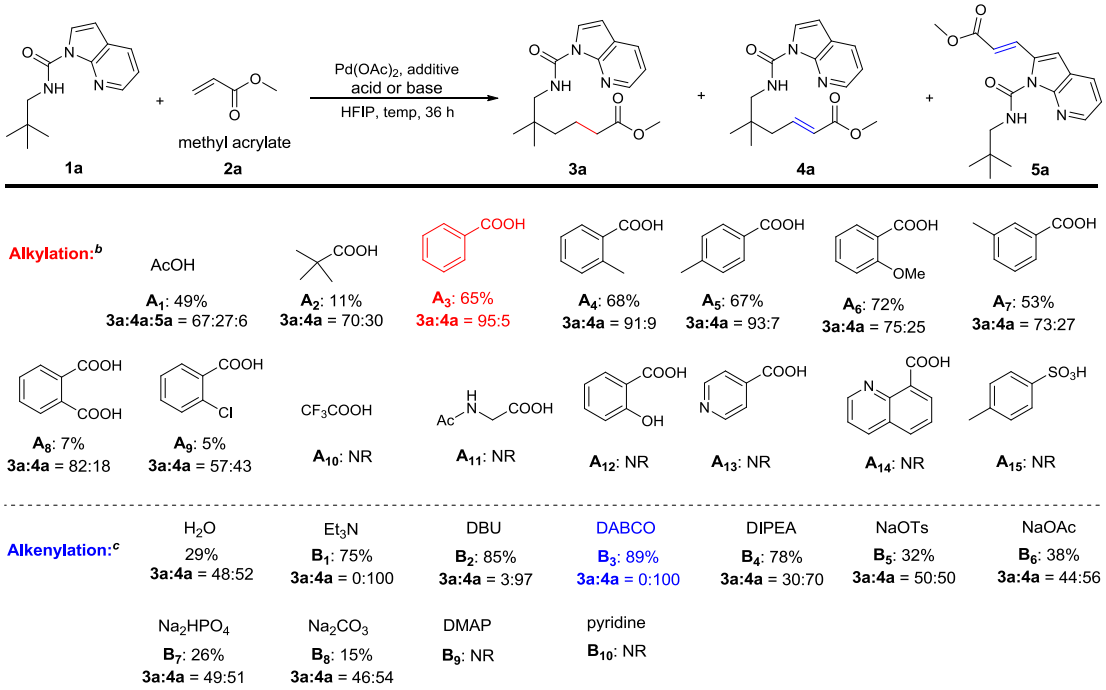


2, 80%-96%

Derivative of alcohol or phenol (3.0 mmol) was mixed with Et_3N (4.5 mmol) in dry CH_2Cl_2 (10 mL) and cooled to 0 ^{o}C in an ice-water bath. Then acryloyl chloride (3.6 mmol) was added dropwise. The mixture was warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (PET: EtOAc = 30:1) to get the desired product (80–96% yield).

2.2 Preliminary Optimization of Reaction Conditions

Table S1 Acid and Base Optimization for C(sp^3)−H Alkylation and Alkenylation

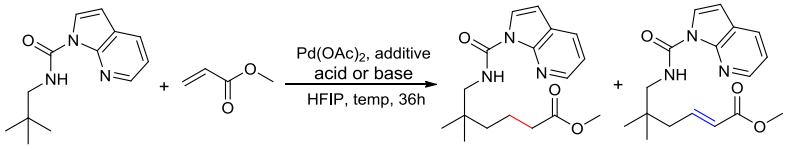


[a] Ratio of isolated **3a**, **4a** and **5a** was determined by crude ^{1}H NMR. [b] Conditions: 0.2 mmol of **1a**, 0.5 mmol of **2a**, 0.02 mmol of $Pd(OAc)_2$, 0.6 mmol of Ag_2CO_3, 0.6 mmol of acid, 1 mL of HFIP, 120 ℃ for 36 h. [c] Conditions: 0.2 mmol of **1a**, 0.5 mmol of **2a**, 0.02 mmol of $Pd(OAc)_2$, 0.6 mmol of Ag_2CO_3, 0.6 mmol of base, 1 mL of HFIP, 30 ℃ for 36 h.

We began our reaction investigations with *N*-neopentyl-1*H*-pyrrolo[2,3-b]pyridine-1-carboxamide (**1a**) and methyl acrylate (**2a**) at 120 ℃ under the $Pd(OAc)_2$ catalytic system with AgOAc as an additive in the presence of acetic acid (Table S1). The C(sp^2)−H alkenylation product **5a** was observed as the only outcome, with 33% yield. Interestingly, replacing AgOAc with Ag_2CO_3 resulted in the mixture of C(sp^3)−H alkylation (**3a**) and alkenylation (**4a**) products and **5a** at a ratio of 67:27:6, with 49% total yield (**A1**, Table S1). Encouraged by this finding, we screened out the suitable reaction conditions for the selective γ-C(sp^3)−H alkylation and alkenylation of **1a**. Various acids were first examined (**A$_2$**−**A$_{15}$**). Replacing acetic acid with trimethylacetic acid (**A$_2$**) dramatically decreased the total yield, and a trace amount of **5a** occurred, while this transformation could not proceed when trifluoroacetic acid and Ac-Gly-OH were used. Since these fatty acids were not preferred in this catalytic system, we tried using aromatic acids (**A$_3$**−**A$_9$**). Interestingly, benzoic acid (**A$_3$**) successfully initiated the reaction, with an excellent dominance of alkylation product (95%) and a total yield of 65%, with no detectable **5a**. We then systematically surveyed benzoic acids bearing different substituents to further optimize this selective transformation (**A$_4$**−**A$_9$**). When *o*-toluic acid (**A$_4$**), *p*-toluic acid (**A$_5$**), and *o*-anisic acid (**A$_6$**) were used, the total product yields were slightly higher than that when **A$_3$** was used, while the alkylation selectivity was lower. When *m*-toluic acid (**A$_7$**), phthalic acid (**A$_8$**), and 2-chlorobenzoic acid (**A$_9$**)

were used, both the yield and selectivity were lower than that for **A_3**. The other aromatic acids could not trigger these reactions. Interestingly, the ratio of alkenylation product increased to 52% when water was used instead of acid at a reduced temperature of 30 ℃, which prompted us to test bases to exclusively obtain the alkenylation products **4a** (Table S1). The first trial with triethylamine (Et_3N, **B_1**) showed that **4a** was formed as the only alkenylation product, with a yield of 75%. Other organic bases (**B_2**–**B_{10}**) were hence evaluated to improve the selective yield. Among these, *N*,*N*-diisopropylethylamine (DIPEA, **B_2**) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, **B_3**) slightly increased the **4a** yield to 78% and 85%, respectively, with decreased alkylation and alkenylation selectivities. Triethylenediamine (DABCO, **B_3**) was found to be the most favorable organic base, with an excellent isolated yield of 89% of the only alkenylation product. However, 4-dimethylaminopyridine and pyridine could not launch the reaction. Poor transformation rate and selectivity ratio were observed when inorganic bases were used (**B_5**–**B_8**), presumably due to their poor solubility in the reaction system.

Table S2. Optimization of Reaction Conditions[a,b,c]



1a 2a 3a 4a

Entry	Acid or base	Temp (℃)	Yield (%)	
			3a	**4a**
1	PhCOOH (3 equiv.)	120	62	3
2	DABCO (3 equiv.)	30	0	89
3	PhCOOH (3 equiv.)	100	78	2
4	PhCOOH (3 equiv.)	80	41	2
5	PhCOOH (3 equiv.)	140	58	6
6	PhCOOH (1 equiv.)	100	35	10
7	PhCOOH (5 equiv.)	100	77	2
8	DABCO (3 equiv.)	100	8	25
9	DABCO (3 equiv.)	60	3	72
10	DABCO (1 equiv.)	30	0	82
11	DABCO (5 equiv.)	30	0	87

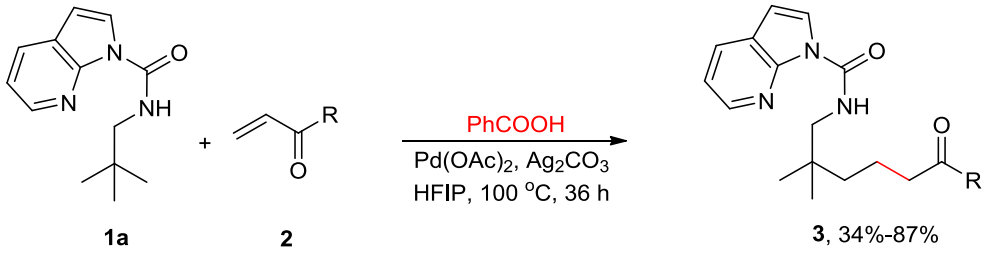
[a] Conditions: 0.2 mmol of **1a**, 0.5 mmol of **2a**, 0.02 mmol of $Pd(OAc)_2$, 0.6 mmol of additive, 1 mL of HFIP, 36 h reaction time. [b] The ratios of **3a** and **4a** were determined via crude ^1H NMR spectroscopy. [c] Isolated yields.

Having established the optimal acid (entry 1, Table S2) and base (entry 2), we continued to screen the reaction conditions by testing the amount of acid and the reaction temperature (Table S2). The results (entries 3–5) showed that 100 ℃ was most preferred for **3a** formation, with a yield of 78% and 2% production of **4a**. The amount of acid was also tested, and 1 equiv. of acid dramatically decreased the yield of **3a** to 35% (entry 6), while more equiv. of acid resulted in a similar outcome (entry 7). The effect of temperature on the yield of **3a** prompted the investigation of different

reaction temperatures of the C(sp^3)−H alkenylation. However, the increase in the temperature was not beneficial to either the yield or selectivity (entries 8, 9), and 30 ℃ was proved to be the most favorable reaction temperature (entry 2).

2.3 General Procedures for C(sp^3)−H Alkylation and Alkenylation

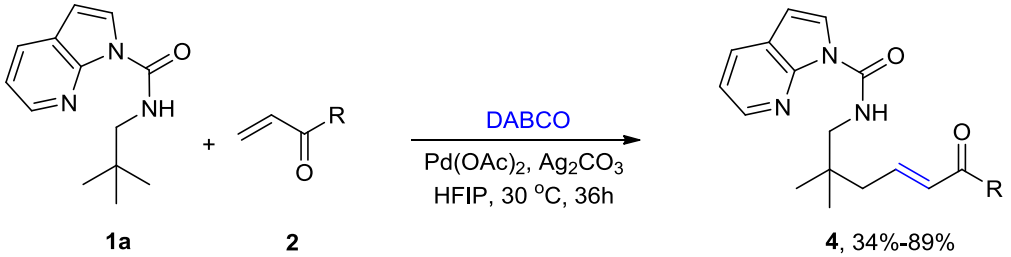
2.3.1 Preparation of Alkylation Products (Method A)



1a **2** **3**, 34%-87%

A reaction tube (10 mL) with magnetic stir bar was charged with *N*-neopentyl-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide **1a** (46 mg, 0.20 mmol), acrylate derivative **2** (0.50 mmol), $Pd(OAc)_2$ (5 mg, 0.020 mmol), Ag_2CO_3 (165 mg, 0.060 mmol), PhCOOH (73 mg, 0.060 mmol) and HFIP (1.0 mL). The reaction was allowed to stir at 100 ℃ in an oil bath for 36 hours. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET/EtOAc) to afford the desired product **3**.

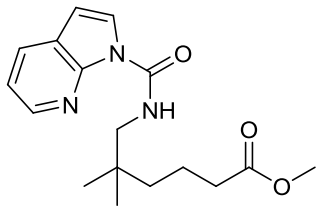
2.3.2 Preparation of Alkylation Products (Method B)



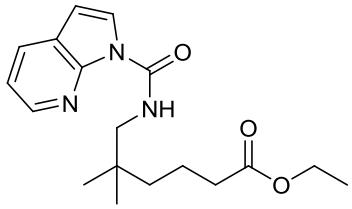
1a **2** **4**, 34%-89%

A reaction tube (10 mL) with magnetic stir bar was charged with *N*-neopentyl-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide **1a** (46 mg, 0.20 mmol), acrylate derivative **2** (0.50 mmol), $Pd(OAc)_2$ (5 mg, 0.020 mmol), Ag_2CO_3 (165 mg, 0.060 mmol), DABCO (67 mg, 0.060 mmol) and HFIP (1.0 mL). The reaction was allowed to stir at 30 ℃ in an oil bath for 36 hours. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET/EtOAc) to afford the desired product **4**.

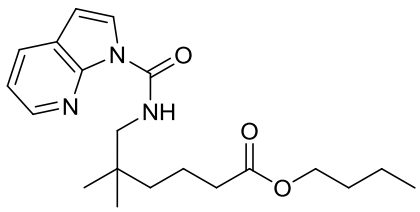
3. Characterization Data



Methyl 5,5-Dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3a): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (50 mg) in 78% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.87 (s, 1H), 8.30 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.00 (d, *J* = 4.0 Hz, 1H), 7.95 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.19 (dd, *J* = 8.0, 5.0 Hz, 1H), 6.53 (d, *J* = 4.0 Hz, 1H), 3.64 (s, 3H), 3.36 (d, *J* = 6.0 Hz, 2H), 2.33 (t, *J* = 7.5 Hz, 2H), 1.73−1.66 (m, 2H), 1.38−1.34 (m, 2H), 1.02 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.2, 152.0, 146.8, 142.5, 130.0, 126.5, 123.7, 118.0, 102.8, 51.7, 50.2, 39.5, 34.9, 34.6, 25.2 (2C), 19.8; HRMS (ESI) *m/z* calcd. for $C_{17}H_{24}N_3O_3$ $[M+H]^+$ 318.1812, found 318.1814.

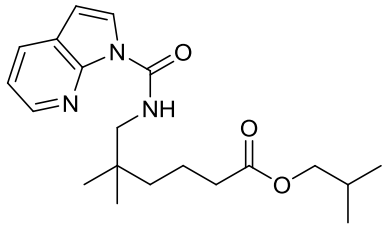


Ethyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3b): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (31 mg) in 46% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.87 (s, 1H), 8.31 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.01 (d, *J* = 4.0 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.19 (dd, *J* = 8.0, 5.0 Hz, 1H), 6.53 (d, *J* = 3.5 Hz, 1H), 4.11 (q, *J* = 7.0 Hz, 2H), 3.36 (d, *J* = 6.0 Hz, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.72−1.66 (m, 2H), 1.38−1.35 (m, 2H), 1.23 (t, *J* = 7.5 Hz, 3H), 1.03 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.8, 152.0, 146.8, 142.5, 130.0, 126.5, 123.7, 117.9, 102.8, 60.4, 50.3, 39.5, 35.2, 34.6, 25.2 (2C), 19.8, 14.4; HRMS (ESI) *m/z* calcd. for $C_{18}H_{26}N_3O_3$ $[M+H]^+$ 332.1969, found 332.1970.

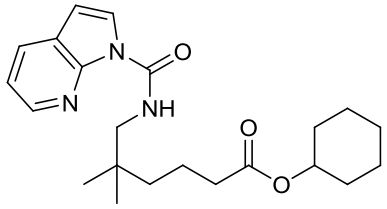


Butyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3c): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (41 mg) in 57% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.87 (s, 1H), 8.31 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.00 (d, *J* = 4.0 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.19 (dd, *J* = 8.0, 5.0 Hz, 1H), 6.53 (d, *J* = 4.0 Hz, 1H), 4.05 (t, *J* = 7.0 Hz, 2H), 3.36 (d, *J* = 6.0 Hz, 2H), 2.32 (t, *J*

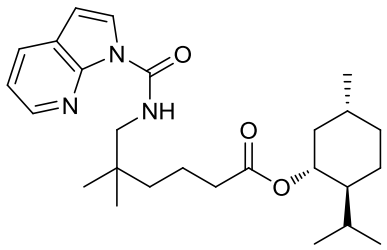
= 7.5 Hz, 2H), 1.72−1.66 (m, 2H), 1.59−1.55 (m, 2H), 1.39−1.33 (m, 4H), 1.03 (s, 6H), 0.91 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.9, 152.0, 146.8, 142.5, 130.0, 126.5, 123.7, 117.9, 102.8, 64.3, 50.3, 39.5, 35.2, 34.6, 30.8, 25.2 (2C), 19.9, 19.3, 13.9; HRMS (ESI) *m/z* calcd. for $C_{20}H_{30}N_3O_3$ $[M+H]^+$ 360.2282, found 360.2281.



Isobutyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3d): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (30 mg) in 41% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.87 (s, 1H), 8.30 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.00 (d, *J* = 4.0 Hz, 1H), 7.95 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.19 (dd, *J* = 8.0, 5.0 Hz, 1H), 6.53 (d, *J* = 4.0 Hz, 1H), 3.83 (d, *J* = 7.0 Hz, 2H), 3.36 (d, *J* = 5.5 Hz, 2H), 2.32 (t, *J* = 7.5 Hz, 2H), 1.93−1.85 (m, 1H), 1.73−1.67 (m, 2H), 1.39−1.36 (m, 2H), 1.03 (s, 6H), 0.90 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.8, 152.0, 146.8, 142.5, 130.0, 126.5, 123.7, 117.9, 102.8, 70.6, 50.3, 39.5, 35.2, 34.6, 27.8, 25.2 (2C), 19.9, 19.2 (2C); HRMS (ESI) *m/z* calcd. for $C_{20}H_{30}N_3O_3$ $[M+H]^+$ 360.2282, found 360.2282.

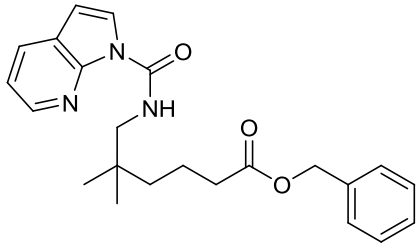


Cyclohexyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3e): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (26 mg) in 34% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.87 (s, 1H), 8.31 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.00 (d, *J* = 4.0 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.19 (dd, *J* = 8.0, 5.0 Hz, 1H), 6.53 (d, *J* = 4.0 Hz, 1H), 4.75−4.70 (m, 1H), 3.36 (d, *J* = 6.0 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.82−1.79 (m, 2H), 1.71−1.65 (m, 4H), 1.53−1.50 (m, 1H), 1.38−1.30 (m, 6H), 1.25−1.17 (m, 1H), 1.03 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.2, 152.0, 146.8, 142.5, 130.0, 126.5, 123.6, 117.9, 102.8, 72.6, 50.3, 39.4, 35.5, 34.6, 31.8 (2C), 25.5, 25.2 (2C), 23.9 (2C), 19.9; HRMS (ESI) *m/z* calcd. for $C_{22}H_{32}N_3O_3$ $[M+H]^+$ 386.2438, found 386.2436.

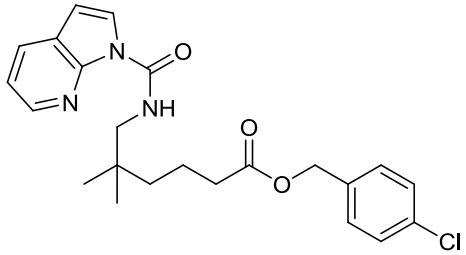


(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-

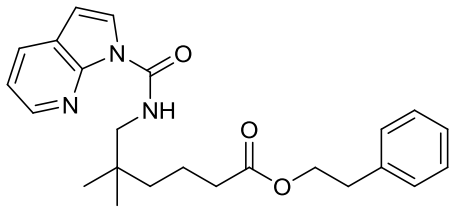
carboxamido)hexanoate (3f): The title compound was obtained by column chromatography (PET: EtOAc = 15:1) as a colorless oil (33 mg) in 37% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.87 (s, 1H), 8.31 (dd, J = 5.0, 1.5 Hz, 1H), 8.00 (d, J = 3.5 Hz, 1H), 7.95 (dd, J = 7.5, 1.5 Hz, 1H), 7.19 (dd, J = 8.0, 5.0 Hz, 1H), 6.53 (d, J = 4.0 Hz, 1H), 4.69−4.64 (m, 1H), 3.36 (d, J = 6.0 Hz, 2H), 2.30 (t, J = 7.5 Hz, 2H), 1.98−1.94 (m, 1H), 1.89−1.83 (m, 1H), 1.72−1.62 (m, 4H), 1.50−1.42 (m, 1H), 1.38−1.31 (m, 3H), 1.07−1.04 (m, 1H), 1.02 (s, 6H), 0.97−0.92 (m, 1H), 0.87 (dd, J = 7.0, 3.0 Hz, 1H), 0.84−0.79 (m, 1H), 0.73 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.3, 152.0, 146.8, 142.5, 130.0, 126.5, 123.7, 117.9, 102.8, 74.1, 50.3, 47.1, 41.1, 39.5, 35.5, 34.6, 34.4, 31.5, 26.4, 25.2, 25.1, 23.5, 22.1, 20.9, 19.9, 16.4; HRMS (ESI) *m/z* calcd. for $C_{26}H_{40}N_3O_3$ $[M+H]^+$ 442.3064, found 442.3066.



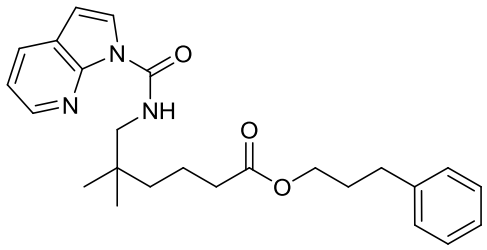
Benzyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3g): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (65 mg) in 82% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.86 (s, 1H), 8.29 (dd, J = 4.5, 1.5 Hz, 1H), 8.00 (d, J = 4.0 Hz, 1H), 7.95 (dd, J = 7.5, 1.5 Hz, 1H), 7.37−7.30 (m, 5H), 7.18 (dd, J = 8.0, 5.0 Hz, 1H), 6.53 (d, J = 4.0 Hz, 1H), 5.10 (s, 2H), 3.35 (d, J = 6.0 Hz, 2H), 2.38 (t, J = 7.5 Hz, 2H), 1.75−1.69 (m, 2H), 1.38−1.35 (m, 2H), 1.01 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.5, 152.0, 146.8, 142.5, 136.2, 130.0, 128.7 (2C), 128.4 (2C), 128.3, 126.5, 123.7, 117.9, 102.8, 66.3, 50.2, 39.5, 35.1, 34.6, 25.2 (2C), 19.8; HRMS (ESI) *m/z* calcd. for $C_{23}H_{28}N_3O_3$ $[M+H]^+$ 394.2125, found 394.2126.



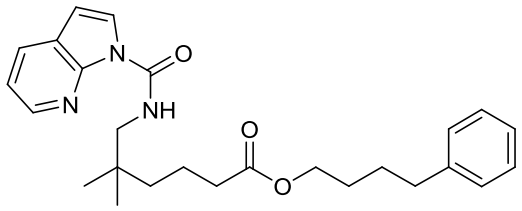
4-Chlorobenzyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3h): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (65 mg) in 76% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.87 (s, 1H), 8.29 (dd, J = 5.0, 1.5 Hz, 1H), 8.00 (d, J = 4.0 Hz, 1H), 7.95 (dd, J = 8.0, 1.5 Hz, 1H), 7.33−7.30 (m, 2H), 7.28−7.27 (m, 2H), 7.19 (dd, J = 8.0, 5.0 Hz, 1H), 6.54 (d, J = 4.0 Hz, 1H), 5.06 (s, 2H), 3.36 (d, J = 6.0 Hz, 2H), 2.37 (t, J = 7.5 Hz, 2H), 1.74−1.68 (m, 2H), 1.38−1.34 (m, 2H), 1.02 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.4, 152.0, 146.8, 142.5, 134.7, 134.2, 130.0, 129.7 (2C), 128.8 (2C), 126.5, 123.7, 117.9, 102.8, 65.4, 50.2, 39.4, 35.0, 34.6, 25.2 (2C), 19.8; HRMS (ESI) *m/z* calcd. for $C_{23}H_{27}ClN_3O_3$ $[M+H]^+$ 428.1735, found 428.1737.



Phenethyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3i): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (60 mg) in 73% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.86 (s, 1H), 8.29 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.01 (d, *J* = 4.0 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.30−7.27 (m, 2H), 7.23−7.17 (m, 4H), 6.53 (d, *J* = 4.0 Hz, 1H), 4.27 (t, *J* = 7.5 Hz, 2H), 3.35 (d, *J* = 6.0 Hz, 2H), 2.91 (t, *J* = 7.5 Hz, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.69−1.65 (m, 2H), 1.35−1.32 (m, 2H), 1.01 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.6, 152.0, 146.8, 142.5, 137.9, 130.0, 129.0 (2C), 128.6 (2C), 126.7, 126.5, 123.6, 117.9, 102.8, 64.9, 50.2, 39.4, 35.2, 35.1, 34.6, 25.2 (2C), 19.8; HRMS (ESI) *m/z* calcd. for $C_{24}H_{30}N_3O_3$ $[M+H]^+$ 408.2282, found 408.2285.

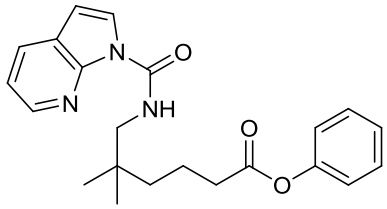


3-Phenylpropyl 5,5-dimethyl-6-(1H-pyrrolo[2,3-b]pyridine-1-carboxamido)hexanoate (3j): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (59 mg) in 70% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.88 (s, 1H), 8.30 (dd, *J* = 4.5, 1.5 Hz, 1H), 8.00 (d, *J* = 4.0 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.29−7.26 (m, 2H), 7.20−7.16 (m, 4H), 6.53 (d, *J* = 4.0 Hz, 1H), 4.08 (t, *J* = 6.5 Hz, 2H), 3.37 (d, *J* = 6.0 Hz, 2H), 2.67 (t, *J* = 7.5 Hz, 2H), 2.32 (t, *J* = 7.5 Hz, 2H), 1.97−1.91 (m, 2H), 1.73−1.67 (m, 2H), 1.39−1.36 (m, 2H), 1.03 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.8, 152.0, 146.8, 142.5, 141.3, 130.0, 128.6 (2C), 128.5 (2C), 126.5, 126.1, 123.7, 117.9, 102.8, 63.8, 50.2, 39.5, 35.1, 34.7, 32.3, 30.3, 25.2 (2C), 19.8; HRMS (ESI) *m/z* calcd. for $C_{25}H_{32}N_3O_3$ $[M+H]^+$ 422.2438, found 422.2439.

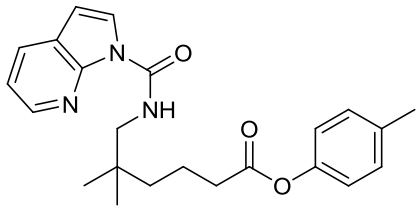


4-Phenylbutyl 5,5-dimethyl-6-(1H-pyrrolo[2,3-b]pyridine-1-carboxamido)hexanoate (3k): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (53 mg) in 61% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.87 (s, 1H), 8.30 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.00 (d, *J* = 3.5 Hz, 1H), 7.95 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.29−7.26 (m, 2H), 7.20−7.15 (m, 4H), 6.53 (d, *J* = 4.0 Hz, 1H), 4.07 (t, *J* = 6.5 Hz, 2H), 3.36 (d, *J* = 6.0 Hz, 2H), 2.62 (t, *J* = 7.5 Hz, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.72−1.65 (m, 6H), 1.38−1.35 (m, 2H), 1.02

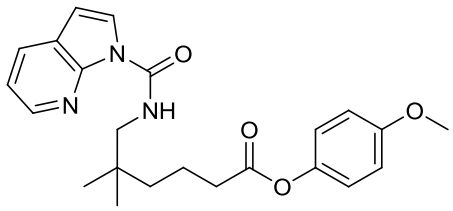
(s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.8, 152.0, 146.8, 142.5, 142.2, 130.0, 128.5 (2C), 128.5 (2C), 126.5, 125.9, 123.6, 117.9, 102.8, 64.3, 50.2, 39.5, 35.6, 35.1, 34.6, 28.4, 27.9, 25.2 (2C), 19.8; HRMS (ESI) *m/z* calcd. for $C_{26}H_{34}N_3O_3$ $[M+H]^+$ 436.2595, found 436.2596.



Phenyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3l): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (66 mg) in 87% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.91 (s, 1H), 8.28 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.00 (d, *J* = 4.0 Hz, 1H), 7.95 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.36−7.32 (m, 2H), 7.22−7.16 (m, 2H), 7.05−7.03 (m, 2H), 6.53 (d, *J* = 3.5 Hz, 1H), 3.40 (d, *J* = 6.0 Hz, 2H), 2.58 (t, *J* = 7.5 Hz, 2H), 1.86−1.80 (m, 2H), 1.49−1.45 (m, 2H), 1.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.2, 152.0, 150.8, 146.8, 142.5, 130.0, 129.5 (2C), 126.5, 125.8, 123.6, 121.7 (2C), 117.9, 102.8, 50.2, 39.3, 35.1, 34.7, 25.2 (2C), 19.8; HRMS (ESI) *m/z* calcd. for $C_{22}H_{26}N_3O_3$ $[M+H]^+$ 380.1969, found 380.1971.

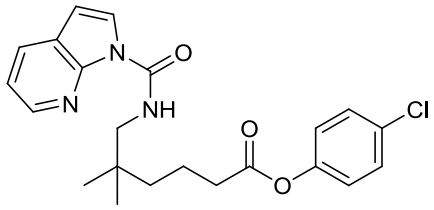


***p*-Tolyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3m):** The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (65 mg) in 83% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.90 (s, 1H), 8.28 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.00 (d, *J* = 4.0 Hz, 1H), 7.95 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.18 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.93−6.91 (m, 2H), 6.53 (d, *J* = 4.0 Hz, 1H), 3.39 (d, *J* = 6.0 Hz, 2H), 2.57 (t, *J* = 7.5 Hz, 2H), 2.33 (s, 3H), 1.85−1.79 (m, 2H), 1.48−1.45 (m, 2H), 1.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.4, 152.0, 148.6, 146.8, 142.5, 135.4, 130.0 (3C), 126.5, 123.7, 121.3 (2C), 117.9, 102.8, 50.2, 39.4, 35.1, 34.7, 25.2 (2C), 21.0, 19.9; HRMS (ESI) *m/z* calcd. for $C_{23}H_{28}N_3O_3$ $[M+H]^+$ 394.2125, found 394.2128.

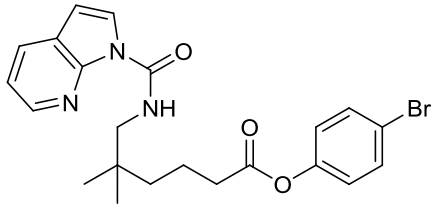


4-Methoxyphenyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3n): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless

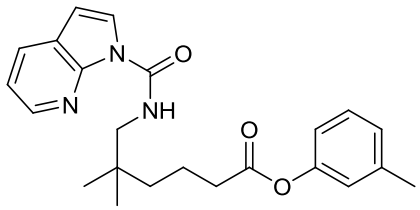
oil (70 mg) in 85% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.90 (s, 1H), 8.28 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.00 (d, *J* = 4.0 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.18 (dd, *J* = 8.0, 5.0 Hz, 1H), 6.97−6.94 (m, 2H), 6.85−6.82 (m, 2H), 6.53 (d, *J* = 4.0 Hz, 1H), 3.79 (s, 3H), 3.39 (d, *J* = 6.0 Hz, 2H), 2.56 (t, *J* = 7.5 Hz, 2H), 1.85−1.79 (m, 2H), 1.48−1.45 (m, 2H), 1.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.6, 157.3, 152.0, 146.8, 144.3, 142.5, 130.0, 126.5, 123.7, 122.4 (2C), 117.9, 114.5 (2C), 102.8, 55.7, 50.2, 39.4, 35.1, 34.7, 25.2 (2C), 19.9; HRMS (ESI) *m/z* calcd. for $C_{23}H_{28}N_3O_4$ $[M+H]^+$ 410.2074, found 410.2074.



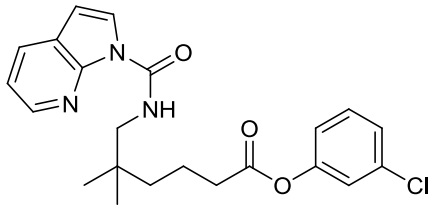
4-Chlorophenyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3o): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (61 mg) in 75% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.90 (s, 1H), 8.27 (dd, *J* = 4.5, 1.5 Hz, 1H), 7.99 (d, *J* = 4.0 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.29−7.26 (m, 2H), 7.18 (dd, *J* = 7.5, 5.0 Hz, 1H), 6.99−6.96 (m, 2H), 6.53 (d, *J* = 4.0 Hz, 1H), 3.39 (d, *J* = 5.5 Hz, 2H), 2.57 (t, *J* = 7.5 Hz, 2H), 1.85−1.78 (m, 2H), 1.47−1.44 (m, 2H), 1.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.9, 152.0, 149.3, 146.8, 142.5, 131.2, 130.0, 129.5 (2C), 126.5, 123.7, 123.0 (2C), 118.0, 102.9, 50.2, 39.3, 35.1, 34.7, 25.2 (2C), 19.8; HRMS (ESI) *m/z* calcd. for $C_{22}H_{25}ClN_3O_3$ $[M+H]^+$ 414.1579, found 414.1582.



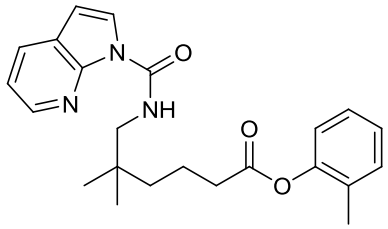
4-Bromophenyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3p): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (66 mg) in 72% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.89 (s, 1H), 8.27 (dd, *J* = 4.5, 1.5 Hz, 1H), 7.99 (d, *J* = 4.0 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.44−7.40 (m, 2H), 7.18 (dd, *J* = 7.5, 5.0 Hz, 1H), 6.94−6.90 (m, 2H), 6.53 (d, *J* = 4.0 Hz, 1H), 3.39 (d, *J* = 5.5 Hz, 2H), 2.57 (t, *J* = 7.5 Hz, 2H), 1.84−1.78 (m, 2H), 1.47−1.43 (m, 2H), 1.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.8, 152.0, 149.8, 146.8, 142.5, 132.5 (2C), 130.0, 126.5, 123.7, 123.5 (2C), 118.9, 118.0, 102.8, 50.2, 39.3, 35.1, 34.7, 25.2 (2C), 19.8; HRMS (ESI) *m/z* calcd. for $C_{22}H_{25}{}^{79}BrN_3O_3$ $[M+H]^+$ 458.1074, found 458.1079.



***m*-Tolyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3q):** The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (65 mg) in 82% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.90 (s, 1H), 8.28 (dd, *J* = 4.5, 1.5 Hz, 1H), 8.01 (d, *J* = 4.0 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.18 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.87−6.83 (m, 2H), 6.53 (d, *J* = 4.0 Hz, 1H), 3.40 (d, *J* = 6.0 Hz, 2H), 2.57 (t, *J* = 7.5 Hz, 2H), 2.33 (s, 3H), 1.86−1.79 (m, 2H), 1.49−1.45 (m, 2H), 1.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.3, 152.0, 150.8, 146.8, 142.5, 139.7, 130.0, 129.2, 126.7, 126.5, 123.7, 122.3, 118.6, 118.0, 102.8, 50.2, 39.4, 35.2, 34.7, 25.2 (2C), 21.4, 19.9; HRMS (ESI) *m/z* calcd. for $C_{23}H_{28}N_3O_3$ $[M+H]^+$ 394.2125, found 394.2126.

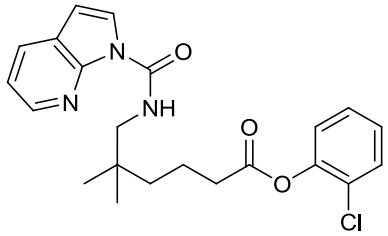


3-Chlorophenyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3r): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (59 mg) in 71% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.90 (s, 1H), 8.28 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.00 (d, *J* = 4.0 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.25 (t, *J* = 8.0 Hz, 1H), 7.20−7.17 (m, 2H), 7.09 (t, *J* = 2.0 Hz, 1H), 6.96−6.94 (m, 1H), 6.53 (d, *J* = 4.0 Hz, 1H), 3.40 (d, *J* = 6.0 Hz, 2H), 2.57 (t, *J* = 7.5 Hz, 2H), 1.85−1.79 (m, 2H), 1.48−1.44 (m, 2H), 1.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.7, 152.0, 151.3, 146.8, 142.5, 134.7, 130.2, 130.0, 126.5, 126.1, 123.7, 122.4, 120.1, 118.0, 102.8, 50.2, 39.3, 35.0, 34.7, 25.2 (2C), 19.7; HRMS (ESI) *m/z* calcd. for $C_{22}H_{25}ClN_3O_3$ $[M+H]^+$ 414.1579, found 414.1580.

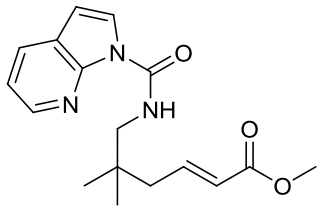


***o*-Tolyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3s):** The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (53 mg) in 67% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.91 (s, 1H), 8.28 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.01 (d, *J* = 4.0 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.21−7.11 (m, 4H), 6.96 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.53 (d, *J* = 4.0 Hz, 1H), 3.40 (d, *J* = 6.0 Hz, 2H), 2.61 (t, *J* = 7.5 Hz, 2H), 2.15 (s, 3H), 1.88−1.82 (m, 2H), 1.51−1.47 (m, 2H), 1.07 (s, 6H); ^{13}C NMR (125

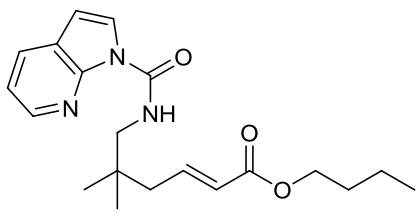
MHz, $CDCl_3$): δ 171.9, 152.0, 149.4, 146.8, 142.5, 131.2, 130.2, 130.0, 127.0, 126.5, 126.0, 123.6, 122.0, 117.9, 102.8, 50.3, 39.5, 35.0, 34.7, 25.2 (2C), 19.9, 16.3; HRMS (ESI) *m/z* calcd. for $C_{23}H_{28}N_3O_3$ $[M+H]^+$ 394.2125, found 394.2125.



2-Chlorophenyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3t): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (52 mg) in 63% yield according to the **Method A**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.91 (s, 1H), 8.29 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.01 (d, *J* = 4.0 Hz, 1H), 7.94 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.41 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.26−7.23 (m, 1H), 7.19−7.15 (m, 2H), 7.09 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.53 (d, *J* = 4.0 Hz, 1H), 3.40 (d, *J* = 6.0 Hz, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 1.89−1.83 (m, 2H), 1.52−1.48 (m, 2H), 1.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.2, 152.0, 147.1, 146.8, 142.5, 130.4, 130.0, 127.8, 127.1, 127.0, 126.5, 123.9, 123.6, 117.9, 102.8, 50.3, 39.4, 34.8, 34.7, 25.2 (2C), 19.8; HRMS (ESI) *m/z* calcd. for $C_{22}H_{25}ClN_3O_3$ $[M+H]^+$ 414.1579, found 414.1582.

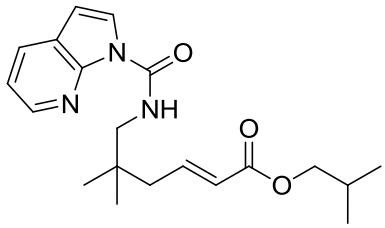


(*E*)-Methyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4a): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (56 mg) in 89% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.90 (s, 1H), 8.31 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.99 (d, *J* = 4.0 Hz, 1H), 7.95 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.19 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.04 (dt, *J* = 15.5, 8.0 Hz, 1H), 6.53 (d, *J* = 4.0 Hz, 1H), 5.94 (dt, *J* = 15.5, 1.0 Hz, 1H), 3.70 (s, 3H), 3.37 (d, *J* = 6.0 Hz, 2H), 2.26 (dd, *J* = 8.0, 1.0 Hz, 2H), 1.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.8, 152.0, 146.7, 145.7, 142.5, 130.1, 126.4, 123.8, 123.6, 118.0, 102.9, 51.6, 50.1, 42.7, 35.8, 25.3 (2C); HRMS (ESI) *m/z* calcd. for $C_{17}H_{22}N_3O_3$ $[M+H]^+$ 316.1656, found 316.1656.

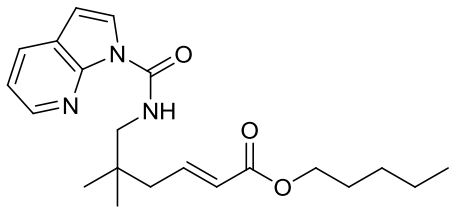


(*E*)-Butyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4b): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil

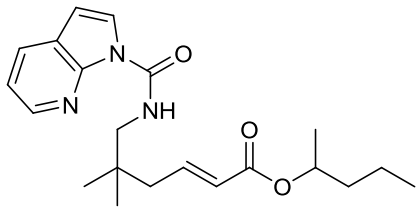
(56 mg) in 78% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.91 (s, 1H), 8.31 (dd, J = 4.5, 1.5 Hz, 1H), 7.99 (d, J = 4.0 Hz, 1H), 7.95 (dd, J = 7.5, 1.5 Hz, 1H), 7.20 (dd, J = 8.0, 5.0 Hz, 1H), 7.02 (dt, J = 15.5, 8.0 Hz, 1H), 6.53 (d, J = 4.0 Hz, 1H), 5.95 (dt, J = 15.5, 1.0 Hz, 1H), 4.11 (t, J = 6.5 Hz, 2H), 3.37 (d, J = 6.0 Hz, 2H), 2.26 (dd, J = 8.0, 1.5 Hz, 2H), 1.65−1.59 (m, 2H), 1.42−1.34 (m, 2H), 1.06 (s, 6H), 0.93 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.5, 152.0, 146.7, 145.3, 142.5, 130.1, 126.5, 124.3, 123.7, 118.0, 102.9, 64.3, 50.2, 42.8, 35.8, 30.8, 25.3 (2C), 19.3, 13.9; HRMS (ESI) *m/z* calcd. for $C_{20}H_{28}N_3O_3$ $[M+H]^+$ 358.2125, found 358.2126.



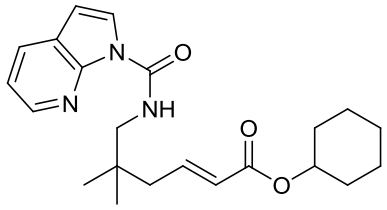
(*E*)-Isobutyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4c): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (55 mg) in 77% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.90 (s, 1H), 8.31 (dd, J = 5.0, 1.5 Hz, 1H), 7.99 (d, J = 4.0 Hz, 1H), 7.95 (dd, J = 8.0, 1.5 Hz, 1H), 7.19 (dd, J = 8.0, 5.0 Hz, 1H), 7.03 (dt, J = 15.5, 8.0 Hz, 1H), 6.53 (d, J = 4.0 Hz, 1H), 5.96 (dt, J = 15.5, 1.0 Hz, 1H), 3.89 (d, J = 6.5 Hz, 2H), 3.37 (d, J = 6.5 Hz, 2H), 2.26 (dd, J = 8.0, 1.0 Hz, 2H), 1.98−1.90 (m, 1H), 1.07 (s, 6H), 0.93 (d, J = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.5, 152.0, 146.7, 145.3, 142.5, 130.1, 126.5, 124.2, 123.6, 118.0, 102.9, 70.5, 50.2, 42.8, 35.8, 27.9, 25.3 (2C), 19.2 (2C); HRMS (ESI) *m/z* calcd. for $C_{20}H_{28}N_3O_3$ $[M+H]^+$ 358.2125, found 358.2128.



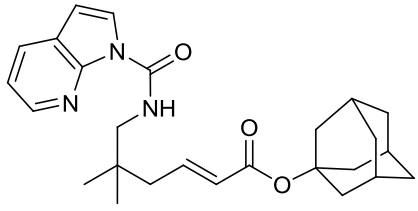
(*E*)-Pentyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4d): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (56 mg) in 75% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.90 (s, 1H), 8.31 (dd, J = 4.5, 1.5 Hz, 1H), 7.99 (d, J = 4.0 Hz, 1H), 7.94 (dd, J = 8.0, 1.5 Hz, 1H), 7.19 (dd, J = 8.0, 5.0 Hz, 1H), 7.02 (dt, J = 15.5, 8.0 Hz, 1H), 6.52 (d, J = 3.5 Hz, 1H), 5.95 (dt, J = 15.5, 1.5 Hz, 1H), 4.09 (t, J = 6.5 Hz, 2H), 3.37 (d, J = 6.0 Hz, 2H), 2.25 (dd, J = 8.0, 1.5 Hz, 2H), 1.66−1.61 (m, 2H), 1.34−1.31 (m, 4H), 1.06 (s, 6H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.5, 152.0, 146.7, 145.3, 142.5, 130.0, 126.4, 124.2, 123.6, 118.0, 102.9, 64.6, 50.1, 42.7, 35.8, 28.4, 28.2, 25.3 (2C), 22.4, 14.1; HRMS (ESI) *m/z* calcd. for $C_{21}H_{30}N_3O_3$ $[M+H]^+$ 372.2282, found 372.2284.



(*E*)-Pentan-2-yl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4e): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (54 mg) in 72% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.91 (s, 1H), 8.32 (dd, *J* = 4.5, 1.5 Hz, 1H), 7.99 (d, *J* = 4.0 Hz, 1H), 7.95 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.19 (dd, *J* = 7.5, 5.0 Hz, 1H), 7.01 (dt, *J* = 15.5, 8.0 Hz, 1H), 6.53 (d, *J* = 4.0 Hz, 1H), 5.93 (dt, *J* = 15.5, 1.0 Hz, 1H), 4.99−4.93 (m, 1H), 3.37 (d, *J* = 6.0 Hz, 2H), 2.25 (dd, *J* = 8.0, 1.5 Hz, 2H), 1.64−1.56 (m, 1H), 1.50−1.43 (m, 1H), 1.39−1.29 (m, 2H), 1.22 (d, *J* = 6.5 Hz, 3H), 1.07 (s, 6H), 0.90 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.1, 152.0, 146.7, 145.0, 142.5, 130.1, 126.5, 124.8, 123.7, 118.0, 102.9, 70.8, 50.2, 42.8, 38.3, 35.8, 25.3 (2C), 20.1, 18.8, 14.1; HRMS (ESI) *m/z* calcd. for $C_{21}H_{30}N_3O_3$ $[M+H]^+$ 372.2282, found 372.2282.

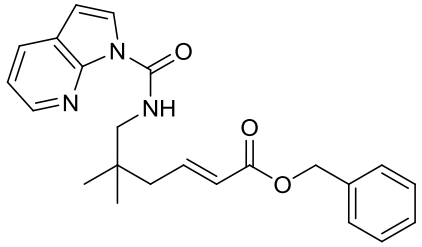


(*E*)-Cyclohexyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4f): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (51 mg) in 67% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.90 (s, 1H), 8.32 (dd, *J* = 4.5, 1.5 Hz, 1H), 7.99 (d, *J* = 4.0 Hz, 1H), 7.94 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.19 (dd, *J* = 7.5, 5.0 Hz, 1H), 7.01 (dt, *J* = 15.5, 8.0 Hz, 1H), 6.53 (d, *J* = 4.0 Hz, 1H), 5.94 (dt, *J* = 15.5, 1.5 Hz, 1H), 4.82−4.76 (m, 1H), 3.37 (d, *J* = 6.0 Hz, 2H), 2.25 (dd, *J* = 8.0, 1.5 Hz, 2H), 1.87−1.83 (m, 2H), 1.73−1.71 (m, 2H), 1.55−1.51 (m, 1H), 1.46−1.32 (m, 4H), 1.29−1.23 (m, 1H), 1.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.9, 152.0, 146.7, 144.9, 142.5, 130.0, 126.4, 124.8, 123.6, 118.0, 102.9, 72.6, 50.2, 42.8, 35.8, 31.8 (2C), 25.5, 25.3 (2C), 23.9 (2C); HRMS (ESI) *m/z* calcd. for $C_{22}H_{30}N_3O_3$ $[M+H]^+$ 384.2282, found 384.2283.

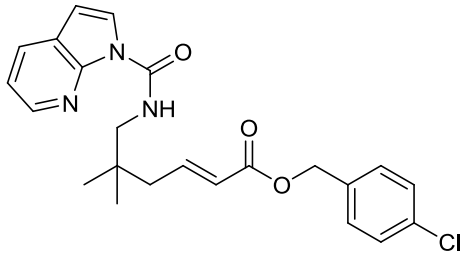


(*E*)-(3*s*,5*s*,7*s*)-Adamantan-1-yl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido) hex -2-enoate (4g): The title compound was obtained by column chromatography (PET: EtOAc = 12:1) as a colorless oil (41 mg) in 47% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.90 (s, 1H), 8.33 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.99 (d, *J* = 4.0 Hz, 1H), 7.95 (dd, *J* = 8.0,

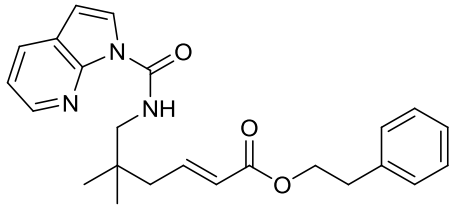
1.5 Hz, 1H), 7.20 (dd, *J* = 7.5, 5.0 Hz, 1H), 6.92 (dt, *J* = 15.5, 8.0 Hz, 1H), 6.53 (d, *J* = 3.5 Hz, 1H), 5.88 (dt, *J* = 15.5, 1.5 Hz, 1H), 3.37 (d, *J* = 6.0 Hz, 2H), 2.23 (dd, *J* = 8.0, 1.5 Hz, 2H), 2.16−2.13 (m, 9H), 1.69−1.63 (m, 6H), 1.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.5, 152.0, 146.7, 144.0, 142.5, 130.1, 126.5, 126.2, 123.7, 118.0, 102.9, 80.4, 50.2, 42.6, 41.5 (3C), 36.3 (3C), 35.8, 30.9 (3C), 25.3 (2C); HRMS (ESI) *m/z* calcd. for $C_{26}H_{34}N_3O_3$ $[M+H]^+$ 436.2595, found 436.2597.



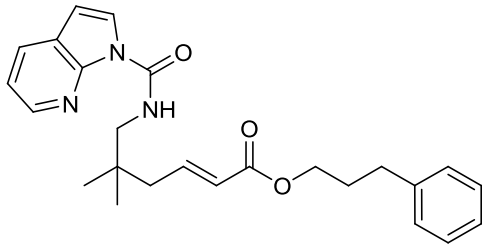
(*E*)-Benzyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4h): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (51 mg) in 65% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.91 (s, 1H), 8.30 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.00 (d, *J* = 3.5 Hz, 1H), 7.94 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.38−7.30 (m, 5H), 7.18 (dd, *J* = 7.5, 5.0 Hz, 1H), 7.10 (dt, *J* = 15.0, 8.0 Hz, 1H), 6.53 (d, *J* = 4.0 Hz, 1H), 6.01 (dt, *J* = 15.5, 1.5 Hz, 1H), 5.17 (s, 2H), 3.38 (d, *J* = 6.5 Hz, 2H), 2.27 (dd, *J* = 8.0, 1.5 Hz, 2H), 1.08 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.1, 152.0, 146.7, 146.1, 142.5, 136.1, 130.0, 128.6 (2C), 128.3 (2C), 128.3, 126.4, 123.9, 123.6, 118.0, 102.9, 66.2, 50.1, 42.8, 35.9, 25.3 (2C); HRMS (ESI) *m/z* calcd. for $C_{23}H_{26}N_3O_3$ $[M+H]^+$ 392.1969, found 392.1972.



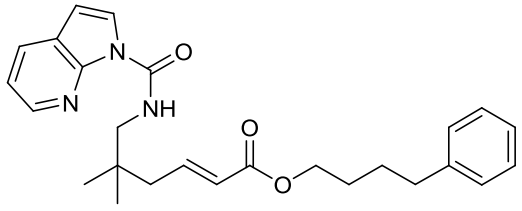
(*E*)-4-Chlorobenzyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4i): The title compound by column chromatography (PET: EtOAc = 10:1) was obtained as a colorless oil (53 mg) in 62% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.91 (s, 1H), 8.29 (dd, *J* = 4.5, 1.5 Hz, 1H), 7.99 (d, *J* = 3.5 Hz, 1H), 7.94 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.33−7.28 (m, 4H), 7.18 (dd, *J* = 7.5, 5.0 Hz, 1H), 7.09 (dt, *J* = 15.5, 8.0 Hz, 1H), 6.53 (d, *J* = 4.0 Hz, 1H), 5.99 (dt, *J* = 15.5, 1.5 Hz, 1H), 5.11 (s, 2H), 3.37 (d, *J* = 6.5 Hz, 2H), 2.27 (dd, *J* = 8.0, 1.5 Hz, 2H), 1.07 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.0, 152.0, 146.7, 146.4, 142.4, 134.7, 134.1, 130.1, 129.7 (2C), 128.8 (2C), 126.4, 123.6, 123.6, 118.0, 102.9, 65.3, 50.1, 42.8, 35.9, 25.3 (2C); HRMS (ESI) *m/z* calcd. for $C_{23}H_{25}ClN_3O_3$ $[M+H]^+$ 426.1579, found 426.1581.



(*E*)-Phenethyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4j): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (59 mg) in 73% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.91 (s, 1H), 8.31 (dd, *J* = 4.5, 1.5 Hz, 1H), 8.00 (d, *J* = 4.0 Hz, 1H), 7.96 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.31−7.28 (m, 2H), 7.24−7.19 (m, 4H), 7.03 (dt, *J* = 15.5, 8.0 Hz, 1H), 6.54 (d, *J* = 4.0 Hz, 1H), 5.94 (dt, *J* = 15.5, 1.5 Hz, 1H), 4.33 (t, *J* = 7.0 Hz, 2H), 3.38 (d, *J* = 6.0 Hz, 2H), 2.96 (t, *J* = 7.0 Hz, 2H), 2.27 (dd, *J* = 8.0, 1.5 Hz, 2H), 1.07 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.2, 152.0, 146.7, 145.7, 142.5, 138.0, 130.1, 129.1 (2C), 128.6 (2C), 126.6, 126.5, 124.0, 123.7, 118.0, 102.9, 64.9, 50.1, 42.8, 35.9, 35.3, 25.3 (2C); HRMS (ESI) *m/z* calcd. for $C_{24}H_{28}N_3O_3$ $[M+H]^+$ 406.2125, found 406.2128.

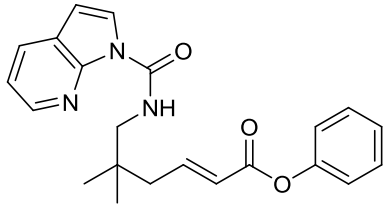


(*E*)-3-Phenylpropyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4k): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (65 mg) in 78% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.92 (s, 1H), 8.33 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.00 (d, *J* = 4.0 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.30−7.27 (m, 2H), 7.21−7.18 (m, 4H), 7.05 (dt, *J* = 15.5, 8.0 Hz, 1H), 6.54 (d, *J* = 4.0 Hz, 1H), 5.97 (dt, *J* = 15.5, 1.5 Hz, 1H), 4.14 (t, *J* = 7.0 Hz, 2H), 3.39 (d, *J* = 6.0 Hz, 2H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.28 (dd, *J* = 8.0, 1.5 Hz, 2H), 2.01−1.96 (m, 2H), 1.08 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.4, 152.0, 146.7, 145.6, 142.5, 141.3, 130.1, 128.5 (2C), 128.5 (2C), 126.5, 126.1, 124.1, 123.6, 118.0, 102.9, 63.7, 50.2, 42.8, 35.9, 32.3, 30.3, 25.3 (2C); HRMS (ESI) *m/z* calcd. for $C_{25}H_{30}N_3O_3$ $[M+H]^+$ 420.2282, found 420.2287.

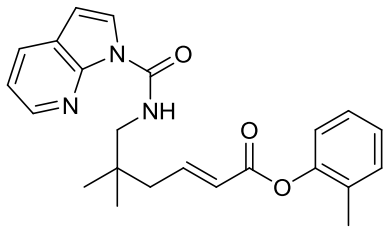


(*E*)-4-Phenylbutyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4l): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (64 mg) in 74% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.91 (s, 1H), 8.32 (dd, *J* = 4.5, 1.5 Hz, 1H), 8.00 (d, *J* = 4.0 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.5 Hz, 1H),

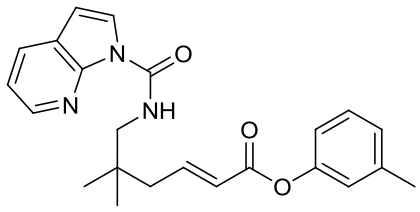
7.29−7.26 (m, 2H), 7.20−7.17 (m, 4H), 7.04 (dt, *J* = 15.5, 8.0 Hz, 1H), 6.54 (d, *J* = 4.0 Hz, 1H), 5.95 (dt, *J* = 15.5, 1.0 Hz, 1H), 4.14 (t, *J* = 6.5 Hz, 2H), 3.38 (d, *J* = 6.0 Hz, 2H), 2.65 (t, *J* = 7.0 Hz, 2H), 2.27 (dd, *J* = 8.0, 1.5 Hz, 2H), 1.72−1.69 (m, 4H), 1.08 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.4, 152.0, 146.7, 145.5, 142.5, 142.1, 130.1, 128.5 (2C), 128.4 (2C), 126.5, 125.9, 124.1, 123.6, 118.0, 102.9, 64.3, 50.1, 42.8, 35.8, 35.6, 28.3, 27.9, 25.3 (2C); HRMS (ESI) *m/z* calcd. for $C_{26}H_{32}N_3O_3$ $[M+H]^+$ 434.2438, found 434.2442.



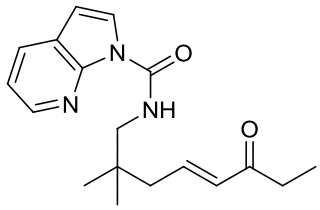
(*E*)-Phenyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4m): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (32 mg) in 43% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.93 (s, 1H), 8.32 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.99 (d, *J* = 4.0 Hz, 1H), 7.93 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.38−7.33 (m, 2H), 7.24−7.17 (m, 3H), 7.09−7.07 (m, 2H), 6.52 (d, *J* = 4.0 Hz, 1H), 6.14 (dt, *J* = 15.5, 1.5 Hz, 1H), 3.40 (d, *J* = 6.0 Hz, 2H), 2.34 (dd, *J* = 8.0, 1.5 Hz, 2H), 1.10 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.7, 152.0, 150.8, 147.9, 146.7, 142.5, 130.1, 129.5 (2C), 126.5, 125.8, 123.7, 123.5, 121.7 (2C), 118.1, 103.0, 50.2, 43.0, 36.0, 25.4 (2C); HRMS (ESI) *m/z* calcd. for $C_{22}H_{24}N_3O_3$ $[M+H]^+$ 378.1812, found 378.1812.



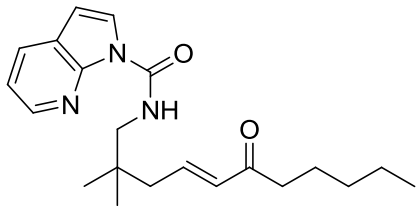
(*E*)-*o*-Tolyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4n): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (21 mg) in 27% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.96 (s, 1H), 8.34 (dd, *J* = 4.5, 1.5 Hz, 1H), 8.01 (d, *J* = 4.0 Hz, 1H), 7.96 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.30−7.19 (m, 4H), 7.14 (td, *J* = 7.5, 1.0 Hz, 1H), 7.02 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.55 (d, *J* = 4.0 Hz, 1H), 6.19 (dt, *J* = 15.5, 1.5 Hz, 1H), 3.43 (d, *J* = 6.0 Hz, 2H), 2.37 (dd, *J* = 8.0, 1.0 Hz, 2H), 2.17 (s, 3H), 1.10 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.4, 152.0, 149.4, 147.8, 146.8, 142.5, 131.2, 130.3, 130.1, 127.0, 126.5, 126.0, 123.7, 123.3, 122.0, 118.1, 103.0, 50.2, 43.0, 36.0, 25.4 (2C), 16.3; HRMS (ESI) *m/z* calcd. for $C_{23}H_{26}N_3O_3$ $[M+H]^+$ 392.1969, found 392.1974.



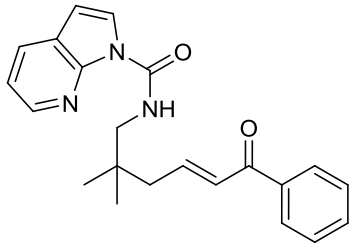
(*E*)-*m*-Tolyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4o): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (27 mg) in 35% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.95 (s, 1H), 8.34 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.01 (d, *J* = 4.0 Hz, 1H), 7.96 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.27−7.19 (m, 3H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.91−6.89 (m, 2H), 6.55 (d, *J* = 4.0 Hz, 1H), 6.19 (d, *J* = 15.5 Hz, 1H), 3.42 (d, *J* = 6.5 Hz, 2H), 2.36−2.34 (m, 5H), 1.12 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.8, 152.0, 150.7, 147.7, 146.7, 142.5, 139.6, 130.1, 129.2, 126.6, 126.5, 123.7, 123.6, 122.4, 118.7, 118.1, 103.0, 50.2, 43.0, 36.0, 25.4 (2C), 21.4; HRMS (ESI) *m/z* calcd. for $C_{23}H_{26}N_3O_3$ $[M+H]^+$ 392.1969, found 392.1970.



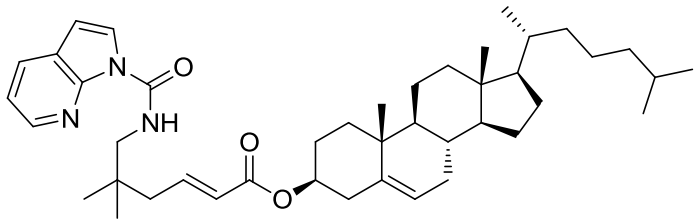
(*E*)-*N*-(2,2-Dimethyl-6-oxooct-4-en-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide (4p): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (30 mg) in 48% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.92 (s, 1H), 8.31 (dd, *J* = 4.5, 1.5 Hz, 1H), 7.99 (d, *J* = 4.0 Hz, 1H), 7.96 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.20 (dd, *J* = 8.0, 5.0 Hz, 1H), 6.91 (dt, *J* = 15.5, 8.0 Hz, 1H), 6.54 (d, *J* = 4.0 Hz, 1H), 6.19 (dt, *J* = 15.5, 1.5 Hz, 1H), 3.38 (d, *J* = 6.0 Hz, 2H), 2.54 (q, *J* = 7.5 Hz, 2H), 2.26 (dd, *J* = 8.0, 1.5 Hz, 2H), 1.08−1.05 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.0, 152.0, 146.7, 143.1, 142.5, 132.9, 130.1, 126.4, 123.7, 118.1, 103.0, 50.1, 43.0, 35.9, 33.4, 25.4 (2C), 8.2; HRMS (ESI) *m/z* calcd. for $C_{18}H_{24}N_3O_2$ $[M+H]^+$ 314.1863, found 314.1866.



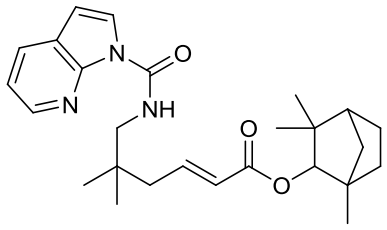
(*E*)-*N*-(2,2-Dimethyl-6-oxoundec-4-en-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide (4q): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (26 mg) in 36% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.91 (s, 1H), 8.31 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.99 (d, *J* = 4.0 Hz, 1H), 7.95 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.20 (dd, *J* = 8.0, 5.0 Hz, 1H), 6.89 (dt, *J* = 16.0, 7.5 Hz, 1H), 6.53 (d, *J* = 4.0 Hz, 1H), 6.18 (dt, *J* = 15.5, 1.5 Hz, 1H), 3.38 (d, *J* = 6.0 Hz, 2H), 2.49 (t, *J* = 7.5 Hz, 2H), 2.26 (dd, *J* = 8.0, 1.5 Hz, 2H), 1.60−1.54 (m, 2H), 1.32−1.23 (m, 4H), 1.07 (s, 6H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.7, 152.0, 146.7, 143.2, 142.5, 133.1, 130.1, 126.4, 123.7, 118.0, 103.0, 50.2, 43.0, 40.2, 35.9, 31.6, 25.4 (2C), 24.1, 22.6, 14.1; HRMS (ESI) *m/z* calcd. for $C_{21}H_{30}N_3O_2$ $[M+H]^+$ 356.2333, found 356.2335.



(*E*)-*N*-(2,2-dimethyl-6-oxo-6-phenylhex-4-en-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide (4r): The title compound was obtained by column chromatography (PET: EtOAc = 10:1) as a colorless oil (38 mg) in 52% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.95 (s, 1H), 8.30 (dd, *J* = 5.0, 1.5 Hz, 1H), 8.00 (d, *J* = 4.0 Hz, 1H), 7.96 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.94−7.91 (m, 2H), 7.57−7.53 (m, 1H), 7.47−7.44 (m, 2H), 7.20 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.14 (dt, *J* = 15.5, 8.0 Hz, 1H), 6.99 (d, *J* = 15.0 Hz, 1H), 6.54 (d, *J* = 4.0 Hz, 1H), 3.42 (d, *J* = 6.0 Hz, 2H), 2.39 (dd, *J* = 8.0, 1.5 Hz, 2H), 1.12 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ190.6, 152.0, 146.8, 145.9, 142.5, 138.0, 132.8, 130.1, 128.8, 128.7 (2C), 128.7 (2C), 126.1, 123.7, 118.1, 103.0, 50.4, 43.4, 36.2, 25.4 (2C); HRMS (ESI) *m/z* calcd. for $C_{22}H_{24}N_3O_2$ $[M+H]^+$ 362.1863, found 362.1864.

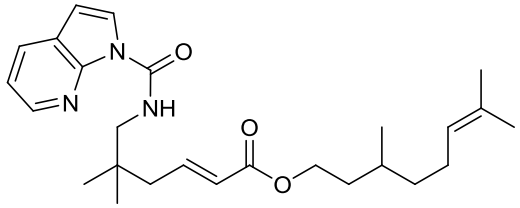


(*E*)-(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4s): The title compound was obtained by column chromatography (PET: EtOAc = 20:1) as a colorless oil (45 mg) in 34% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.91 (s, 1H), 8.32 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.99 (d, *J* = 4.0 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.20 (dd, *J* = 8.0, 5.0 Hz, 1H), 7.01 (dt, *J* = 15.5, 8.0 Hz, 1H), 6.53 (d, *J* = 4.0 Hz, 1H), 5.93 (d, *J* = 15.5 Hz, 1H), 5.37 (d, *J* = 5.0 Hz, 1H), 4.68−4.62 (m, 1H), 3.37 (d, *J* = 6.0 Hz, 2H), 2.33 (d, *J* = 7.0 Hz, 2H), 2.26 (dd, *J* = 8.0, 1.0 Hz, 2H), 2.02−1.94 (m, 2H), 1.89−1.79 (m, 3H), 1.65−1.09 (m, 18H), 1.07 (s, 6H), 1.02 (s, 3H), 1.00−0.93 (m, 3H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 7.0, 2.5 Hz, 6H), 0.67 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.8, 152.0, 146.7, 145.1, 142.5, 139.8, 130.1, 126.5, 124.7, 123.7, 122.7, 118.0, 102.9, 74.0, 56.8, 56.2, 50.2, 50.1, 42.8, 42.4, 39.9, 39.6, 38.3, 37.1, 36.7, 36.3, 35.9, 35.8, 32.0, 32.0, 28.4, 28.1, 27.9, 25.3 (2C), 24.4, 23.9, 23.0, 22.7, 21.2, 19.5, 18.8, 12.0; HRMS (ESI) *m/z* calcd. for $C_{43}H_{64}N_3O_3$ $[M+H]^+$ 670.4942, found 670.4948.

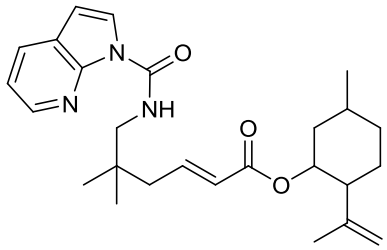


(*E*)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-

carboxamido)hex-2-enoate (4t): The title compound was obtained by column chromatography (PET: EtOAc = 20:1) as a colorless oil (49 mg) in 56% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.92 (s, 1H), 8.33 (dd, J = 4.5, 1.5 Hz, 1H), 8.00 (d, J = 4.0 Hz, 1H), 7.96 (dd, J = 8.0, 1.5 Hz, 1H), 7.20 (dd, J = 8.0, 5.0 Hz, 1H), 7.04 (dt, J = 15.5, 8.0 Hz, 1H), 6.54 (d, J = 4.0 Hz, 1H), 6.00 (dt, J = 15.5, 1.5 Hz, 1H), 4.42 (d, J = 2.0 Hz, 1H), 3.38 (dd, J = 6.0, 1.0 Hz, 2H), 2.28 (dd, J = 8.0, 1.0 Hz, 2H), 1.80−1.67 (m, 3H), 1.61−1.58 (m, 1H), 1.49−1.42 (m, 1H), 1.29−1.15 (m, 2H), 1.11 (s, 3H), 1.07 (s, 6H), 1.04 (s, 3H), 0.76 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.9, 152.0, 146.8, 145.1, 142.5, 130.1, 126.5, 124.4, 123.7, 118.0, 102.9, 86.1, 50.3, 48.5 (2C), 42.7, 41.6, 39.8, 35.8, 29.9, 26.8, 26.0, 25.3, 25.2, 20.3, 19.6; HRMS (ESI) *m/z* calcd. for $C_{26}H_{36}N_3O_3$ $[M+H]^+$ 438.2751, found 438.2753.

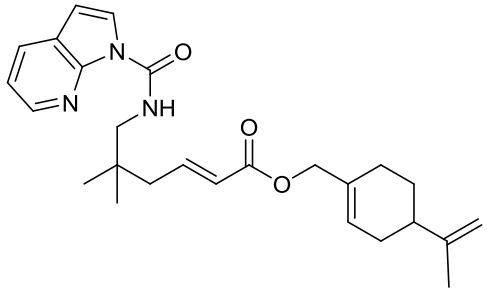


(*E*)-3,7-dimethyloct-6-en-1-yl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido) hex-2-enoate (4u): The title compound was obtained by column chromatography (PET: EtOAc = 20:1) as a colorless oil (36 mg) in 41% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.91 (s, 1H), 8.32 (dd, J = 5.0, 1.5 Hz, 1H), 8.00 (d, J = 4.0 Hz, 1H), 7.96 (dd, J = 8.0, 1.5 Hz, 1H), 7.20 (dd, J = 8.0, 5.0 Hz, 1H), 7.02 (dt, J = 15.5, 8.0 Hz, 1H), 6.54 (d, J = 4.0 Hz, 1H), 5.95 (dt, J = 15.5, 1.0 Hz, 1H), 5.10−5.06 (m, 1H), 4.19−4.11 (m, 2H), 3.38 (d, J = 6.5 Hz, 2H), 2.26 (dd, J = 8.0, 1.5 Hz, 2H), 2.03−1.92 (m, 2H), 1.73−1.66 (m, 4H), 1.59 (s, 3H), 1.58−1.53 (m, 1H), 1.49−1.42 (m, 1H), 1.39−1.32 (m, 1H), 1.22−1.16 (m, 1H), 1.07 (s, 6H), 0.92 (d, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.5, 152.0, 146.8, 145.4, 142.5, 131.5, 130.1, 126.5, 124.7, 124.3, 123.7, 118.0, 102.9, 63.0, 50.2, 42.8, 37.1, 35.9, 35.6, 29.7, 25.9, 25.5, 25.3 (2C), 19.6, 17.8; HRMS (ESI) *m/z* calcd. for $C_{26}H_{38}N_3O_3$ $[M+H]^+$ 440.2908, found 440.2913.

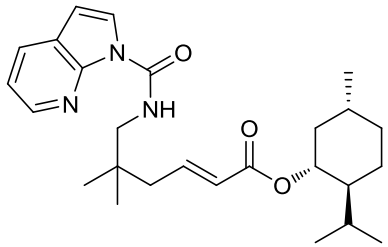


(*E*)-5-methyl-2-(prop-1-en-2-yl)cyclohexyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-b]pyridine-1-carboxamido)hex-2-enoate (4v): The title compound was obtained by column chromatography (PET: EtOAc = 20:1) as a colorless oil (45 mg) in 52% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.90 (s, 1H), 8.32 (dd, J = 5.0, 1.5 Hz, 1H), 8.00 (d, J = 4.0 Hz, 1H), 7.96 (dd, J = 8.0, 1.5 Hz, 1H), 7.20 (dd, J = 7.5, 5.0 Hz, 1H), 6.97 (dt, J = 15.5, 8.0 Hz, 1H), 6.54 (d, J = 4.0 Hz, 1H), 5.89 (dt, J = 15.5, 1.0 Hz, 1H), 4.85−4.80 (m, 1H), 4.71−4.71 (m, 2H), 3.40−3.32 (m, 2H), 2.24 (dd, J = 8.0, 1.0 Hz, 2H), 2.16−2.11 (m, 1H), 2.06−2.01 (m, 1H), 1.74−1.67 (m, 2H), 1.65 (s, 3H), 1.60−1.52 (m, 1H), 1.44−1.35 (m, 1H), 1.05 (d, J = 4.0 Hz, 6H), 1.04−0.94 (m, 2H),

0.92 (d, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.9, 152.0, 146.8, 146.4, 145.0, 142.5, 130.1, 126.5, 124.6, 123.7, 118.0, 111.8, 102.9, 73.7, 50.9, 50.2, 42.7, 40.6, 35.8, 34.3, 31.5, 30.6, 25.3, 25.2, 22.2, 19.7; HRMS (ESI) *m/z* calcd. for $C_{26}H_{36}N_3O_3$ $[M+H]^+$ 438.2751, found 438.2756.



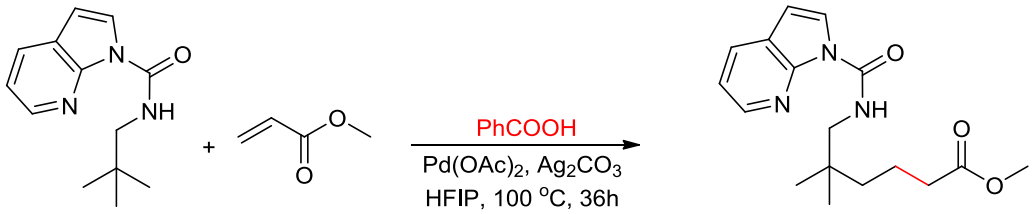
(*E*)-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4w): The title compound was obtained by column chromatography (PET: EtOAc = 20:1) as a colorless oil (41 mg) in 47% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.91 (s, 1H), 8.32 (dd, J = 5.0, 1.5 Hz, 1H), 8.00 (d, J = 4.0 Hz, 1H), 7.96 (dd, J = 7.5, 1.5 Hz, 1H), 7.20 (dd, J = 8.0, 5.0 Hz, 1H), 7.05 (dt, J = 15.0, 8.0 Hz, 1H), 6.54 (d, J = 3.5 Hz, 1H), 5.98 (dt, J = 15.5, 1.0 Hz, 1H), 5.77−5.76 (m, 1H), 4.73−4.71 (m, 2H), 4.51 (s, 2H), 3.38 (d, J = 6.5 Hz, 2H), 2.27 (dd, J = 8.0, 1.0 Hz, 2H), 2.18−2.13 (m, 2H), 2.10−2.08 (m, 2H), 2.00−1.94 (m, 1H), 1.86−1.83 (m, 1H), 1.73 (s, 3H), 1.53−1.45 (m, 1H), 1.07 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.3, 152.0, 149.8, 146.8, 145.7, 142.5, 132.8, 130.1, 126.5, 125.8, 124.1, 123.7, 118.0, 108.9, 102.9, 68.4, 50.2, 42.8, 41.0, 35.9, 30.6, 27.4, 26.6, 25.3 (2C), 20.9; HRMS (ESI) *m/z* calcd. for $C_{26}H_{34}N_3O_3$ $[M+H]^+$ 436.2595, found 436.2598.



(*E*)-(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4x): The title compound was obtained by column chromatography (PET: EtOAc = 20:1) as a colorless oil (55 mg) in 63% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.91 (s, 1H), 8.32 (dd, J = 5.0, 1.5 Hz, 1H), 8.00 (d, J = 4.0 Hz, 1H), 7.95 (dd, J = 8.0, 1.5 Hz, 1H), 7.20 (dd, J = 8.0, 5.0 Hz, 1H), 7.01 (dt, J = 15.5, 8.0 Hz, 1H), 6.53 (d, J = 4.0 Hz, 1H), 5.94 (dt, J = 15.5, 1.0 Hz, 1H), 4.76−4.71 (m, 1H), 3.38 (dd, J = 6.0, 1.5 Hz, 2H), 2.26 (dd, J = 8.0, 1.5 Hz, 2H), 2.02−1.98 (m, 1H), 1.89−1.83 (m, 1H), 1.70−1.64 (m, 2H), 1.53−1.45 (m, 1H), 1.42−1.37 (m, 1H), 1.07 (d, J = 2.0 Hz, 6H), 1.05−0.94 (m, 2H), 0.89 (t, J = 7.5 Hz, 6H), 0.86−0.83 (m, 1H), 0.76 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.0, 152.0, 146.7, 145.1, 142.5, 130.1, 126.5, 124.7, 123.7, 118.0, 102.9, 74.1, 50.2, 47.2, 42.8, 41.1, 35.8, 34.4, 31.5, 26.5, 25.3, 25.3, 23.8, 22.2, 20.8, 16.7; HRMS (ESI) *m/z* calcd. for $C_{26}H_{38}N_3O_3$ $[M+H]^+$ 440.2908, found 440.2912.

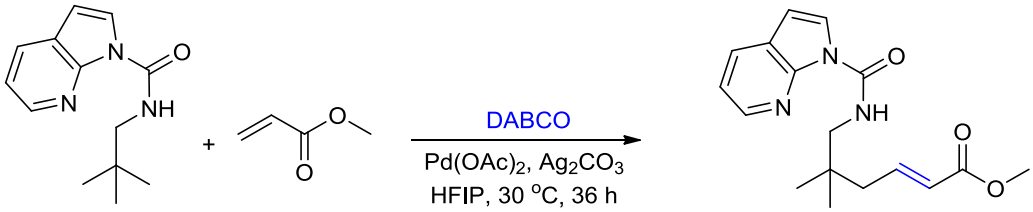
4. Synthetic Applications

4.1 Lager-Scale Preparation of 3a and 4a



1a **2a** **3a**

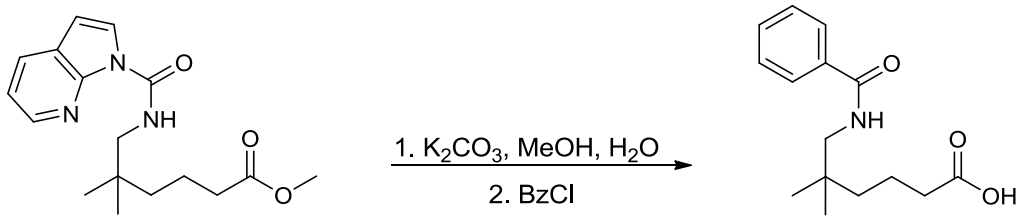
A reaction tube (50 mL) with magnetic stir bar was charged with *N*-neopentyl-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide **1a** (462 mg, 2.0 mmol), acrylate **2a** (430 mg, 5.0 mmol), $Pd(OAc)_2$ (45 mg, 0.20 mmol), Ag_2CO_3 (1.65 g, 6.0 mmol), PhCOOH (732 mg, 6.0 mmol) and HFIP (10 mL). The reaction was allowed to stir at 100 ℃ in an oil bath for 36 hours. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET: EtOAc = 10:1) to afford the desired product **3a** (348 mg) in 55% yield.



1a **2a** **4a**

A reaction tube (50 mL) with magnetic stir bar was charged with *N*-neopentyl-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide **1a** (462 mg, 2.0 mmol), acrylate **2a** (430 mg, 5.0 mmol), $Pd(OAc)_2$ (45 mg, 0.20 mmol), Ag_2CO_3 (1.65 g, 6.0 mmol), DABCO (672 mg, 6.0 mmol) and HFIP (10 mL). The reaction was allowed to stir at 30 ℃ in an oil bath for 36 hours. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET: EtOAc = 10:1) to afford the desired product **4a** (391 mg) in 62% yield.

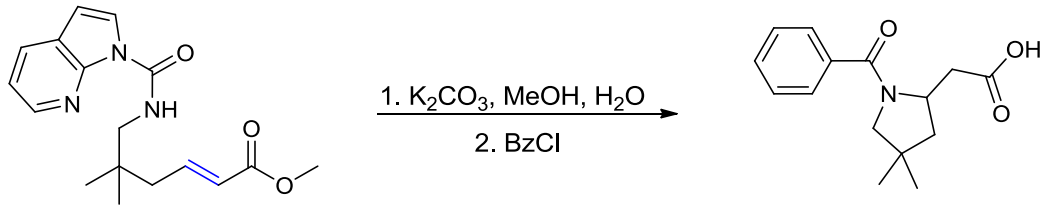
4.2 Directing Group Removal of 3a and 4a



3a **6**, 63%

A reaction tube (10 mL) with magnetic stir bar was charged with methyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate **3a** (159mg, 0.5 mmol), K_2CO_3 (41mg, 0.5 mmol), H_2O (1mL) and MeOH (3 mL). The reaction was allowed to stir at 100 ^oC in an oil bath for 12 hours until most of **3a** was consumed detected by TLC. After cooled to room temperature, the reaction mixture was evaporated to remove the solvent and dissolved in dichloromethane (5 mL), then benzoyl chloride (BzCl, 141mg, 1.0 mmol) was added and then the reaction was stirred at room temperature for another 12 hours. Upon completion, the reaction mixture was evaporated to remove the solvent and the residue was directly purified by flash column chromatography (PET: EtOAc = 3:1) to afford **6** as colorless oil (83 mg) in 63 % yield.

6-Benzamido-5,5-dimethylhexanoic acid (6): ^1H NMR (500 MHz, $CDCl_3$): δ 7.79−7.78 (m, 2H), 7.51−7.47 (m, 1H), 7.45−7.41 (m, 2H), 6.40 (s, 1H), 3.34 (d, J = 6.5 Hz, 2H), 2.39 (t, J = 7.0 Hz, 2H), 1.69−1.63 (m, 2H), 1.33−1.30 (m, 2H), 0.96 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 177.9, 167.9, 135.0, 131.5, 128.7 (2C), 127.0 (2C), 48.7, 38.9, 34.8, 33.9, 25.4 (2C), 19.1; HRMS (ESI) *m/z* calcd. for $C_{15}H_{22}NO_3$ $[M+H]^+$ 264.1594, found 264.1594.



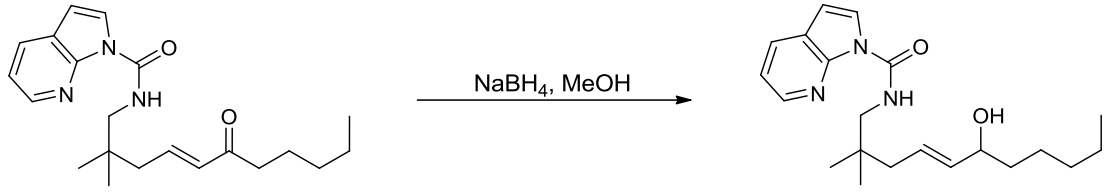
4a **7**, 51%

A reaction tube (10 mL) with magnetic stir bar was charged with (*E*)-Methyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate **4a** (160mg, 0.5 mmol), K_2CO_3 (41mg, 0.5 mmol), H_2O (1mL) and MeOH (3 mL). The reaction was allowed to stir at 100 ^oC in an oil bath for 12 hours when the most of **3a** was consumed by TLC detection. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and dissolved in dichloromethane (5 mL), benzoyl chloride (BzCl, 141mg, 1.0 mmol) was added and then the reaction was stirred at room temperature for another 12 hours. Upon completion, the reaction mixture was evaporated to remove the solvent and the residue was directly purified by flash column chromatography (PET: EtOAc = 3:1) to afford **7** as colorless oil (67 mg) in 51% yield.

2-(1-Benzoyl-4,4-dimethylpyrrolidin-2-yl)acetic acid (7): ^1H NMR (500 MHz, $CDCl_3$): δ 7.52−7.50 (m, 2H), 7.45−7.37 (m, 3H), 4.58−4.52 (m, 1H), 3.37−3.34 (m, 1H), 3.13−3.08 (m, 1H), 2.74 (dd, J = 16.0, 7.5 Hz, 2H), 2.07 (ddd, J = 12.5, 7.5, 1.0 Hz, 1H), 1.65 (dd, J = 12.5, 10.0 Hz, 1H), 1.06 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.7, 170.8, 136.3, 130.5, 128.41 (2C), 127.6 (2C), 63.2, 54.0, 45.1, 38.6, 38.3, 25.6, 25.5; HRMS (ESI) *m/z* calcd. for $C_{15}H_{20}NO_3$

$[M+H]^+$ 262.1438, found 262.1441.

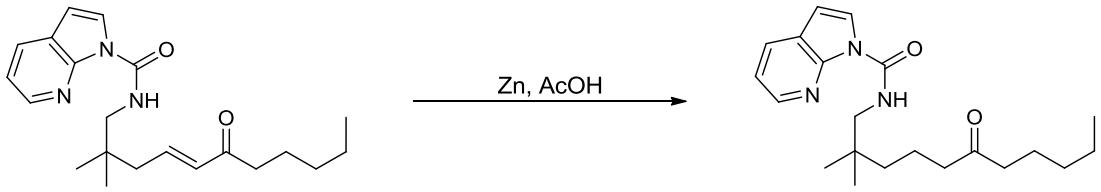
4.3 Further Derivatization of 4r



4r **8**, 52%

To a solution of **4r** (178 mg, 0.5 mmol) in MeOH (2 mL) was added $NaBH_4$ (19 mg, 0.5 mmol) at 0 ^oC in an ice-water bath. The mixture was stirred for 10 min before it was quenched with aqueous NH_4Cl. The aqueous layer was extracted with EtOAc for three times. The combined organic layers were dried with Na_2SO4, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (PET: EtOAc = 6:1) to give **8** as colorless oil (93 mg) in 52% yield.

(*E*)-*N*-(6-Hydroxy-2,2-dimethylundec-4-en-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide (8): ^1H NMR (500 MHz, $CDCl_3$): δ 9.86 (s, 1H), 8.29 (dd, J = 5.0, 1.5 Hz, 1H), 7.97 (d, J = 3.5 Hz, 1H), 7.92 (dd, J = 7.5, 1.5 Hz, 1H), 7.16 (dd, J = 8.0, 5.0 Hz, 1H), 6.50 (d, J = 4.0 Hz, 1H), 5.69 (dt, J = 15.5, 7.5 Hz, 1H), 5.54 (dd, J = 15.5, 7.0 Hz, 1H), 4.08−4.04 (m, 1H), 3.37 (dd, J = 13.0, 6.0 Hz, 1H), 3.27 (dd, J = 13.0, 6.0 Hz, 1H), 2.18 (s, 1H), 2.11−2.02 (m, 2H), 1.58−1.51 (m, 1H), 1.47−1.41 (m, 1H), 1.35−1.24 (m, 6H), 1.00 (d, J = 5.5 Hz, 6H), 0.84 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.9, 146.6, 142.4, 136.7, 130.0, 127.3, 126.4, 123.6, 117.9, 102.8, 73.0, 49.6, 42.7, 37.3, 35.1, 31.8, 25.5, 25.2, 25.2, 22.7, 14.1; HRMS (ESI) *m/z* calcd. for $C_{21}H_{32}N_3O_2$ $[M+H]^+$ 358.2489, found 358.2493.

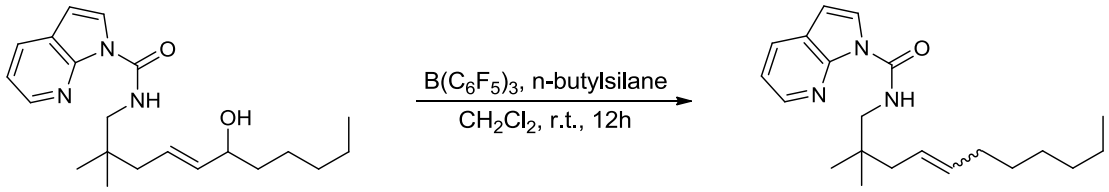


4r **9**, 43%

Zinc dust (327 mg, 5.0 mmol) was added to a solution of compound **4r** (178 mg, 0.5 mmol) in AcOH (1.5 mL) at room temperature. The resulting mixture was stirred at room temperature for 12 h, neutralised with saturated solution of $NaHCO_3$ (20 mL) until the pH is 7, and then extracted with ethyl acetate. The aqueous layer was further extracted with ethyl acetate (2 x 20 mL). The combined organic layers were washed with water (25 mL), brine (15 mL), dried with Na_2SO4, filtered and concentrated in vacuo. Purification by flash chromatography (PET: EtOAc = 10:1) furnished compound **9** as colorless oil (77 mg) in 43% yield.

***N*-(2,2-Dimethyl-6-oxoundecyl)-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide (9):** ^1H NMR (500 MHz, $CDCl_3$): δ 9.85 (s, 1H), 8.29 (dd, J = 4.5, 1.5 Hz, 1H), 7.99 (d, J = 4.0 Hz, 1H), 7.94 (dd, J = 8.0, 1.5 Hz, 1H), 7.18 (dd, J = 8.0, 5.0 Hz, 1H), 6.52 (d, J = 4.0 Hz, 1H), 3.35 (d, J = 5.5 Hz, 2H), 2.41−2.35 (m, 4H), 1.66−1.59 (m, 2H), 1.57−1.51 (m, 2H), 1.32−1.21 (m, 6H), 1.01 (s, 6H), 0.86 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 211.5, 151.9, 146.7, 142.5, 130.0, 126.5,

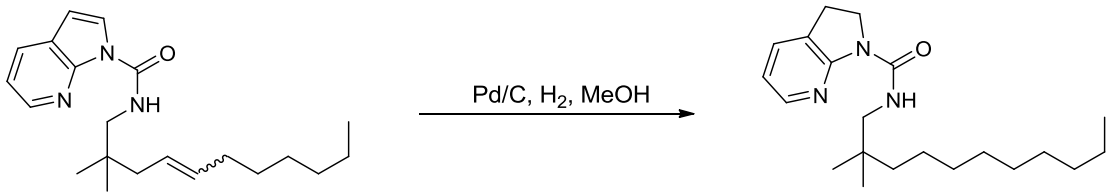
123.6, 117.9, 102.7, 50.2, 43.5, 42.9, 39.5, 34.6, 31.5, 25.1 (2C), 23.6, 22.6, 18.6, 14.0; HRMS (ESI) *m/z* calcd for $C_{21}H_{32}N_3O_2$ $[M+H]^+$ 358.2489, found 358.2492.



8 **10** (mixture of *E* and *Z*), 71%

A reaction tube (10 mL) with magnetic stir bar was charged with (*E*)-*N*-(6-hydroxy-2,2-dimethylundec-4-en-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide **8** (179mg, 0.5 mmol), $B(C_6F_5)_3$ (41mg, 0.1 mmol) and CH_2Cl_2 (3 mL). After stirring for 10 min, n-butylsilane (44mg, 0.5 mmol) was added and the reaction was stirred at room temperature for another 12 hours until most of **8** were consumed by TLC detection. Upon completion, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET: EtOAc = 10:1) to afford the desired product **10** (121 mg) in a mixture yield of 71%.

Mixture of (*E*)-*N*-(2,2-dimethylundec-4-en-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide and (*Z*)-*N*-(2,2-dimethylundec-4-en-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide (10): ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.87−9.84 (m, 1H), 8.31−8.29 (m, 1H), 8.01 (d, *J* = 4.0 Hz, 1H), 7.94 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.20−7.17 (m, 1H), 6.53 (d, *J* = 4.0 Hz, 1H), 5.57−5.34 (m, 2H), 3.37−3.33 (m, 2H), 2.16−1.94 (m, 3H), 1.43−1.24 (m, 9H), 1.02−1.00 (m, 6H), 0.89−0.85 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.9, 146.8, 142.4, 142.4, 134.1, 130.8, 130.5, 130.5, 130.1, 130.0, 126.6, 126.5, 125.8, 123.6, 117.9, 117.9, 102.7, 102.7, 50.3, 50.2, 49.9, 43.2, 40.2, 40.1, 39.7, 35.2, 34.6, 34.5, 33.5, 32.9, 32.7, 32.4, 32.0, 31.9, 31.8, 31.5, 30.7, 29.8, 29.7, 29.5, 29.4, 29.0, 27.4, 25.4, 25.4, 25.4, 25.3, 25.3, 24.2, 24.1, 22.8, 22.8, 22.7, 22.3, 14.2, 14.2, 14.2, 14.1, 13.9; HRMS (ESI) *m/z* calcd for $C_{21}H_{32}N_3O$ $[M+H]^+$ 342.2540, found 342.2546.



10 (mixture of *E* and *Z*) **11**, 94%

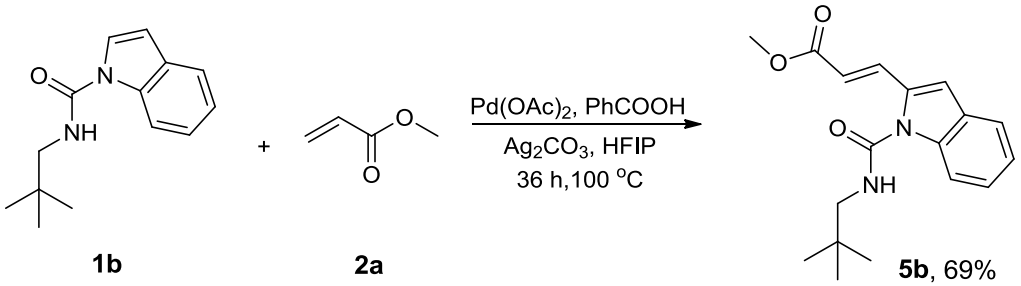
To the mixture of (*E*)-*N*-(2,2-dimethylundec-4-en-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide and (*Z*)-*N*-(2,2-dimethylundec-4-en-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide **10** (171 mg, 0.5 mmol) in MeOH (5 mL), Pd/C (18mg, 10% Pd) was added and the reaction flask was set under a H_2 atmosphere. The reaction mixture was stirred at room temperature for 12 h. Upon completion of the reaction by TLC detection, the reaction mixture was filtered over a silica gel pad then evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET: EtOAc = 15:1) to afford the desired product **11** as a colorless oil (162 mg) in 94% yield.

***N*-(2,2-dimethylundecyl)-2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide (11):** ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.19 (s, 1H), 7.94 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.39 (dd, *J* = 7.5, 1.5 Hz,

1H), 6.74 (dd, *J* = 7.5, 5.0 Hz, 1H), 4.11 (t, *J* = 9.0 Hz, 2H), 3.20 (d, *J* = 5.5 Hz, 2H), 3.05 (t, *J* = 9.0 Hz, 2H), 1.27−1.25 (m, 16H), 0.93 (s, 6H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 157.3, 155.3, 144.5, 133.0, 125.7, 116.0, 49.9, 45.3, 40.2, 34.4, 32.0, 30.7, 29.8 (2C), 29.5, 25.4 (2C), 24.3, 24.1, 22.8, 14.3; HRMS (ESI) *m/z* calcd for $C_{21}H_{36}N_3O$ $[M+H]^+$ 346.2853, found 346.2856.

5. Mechanism Study

5.1 Reaction of Indole Derivative 1b with 2a

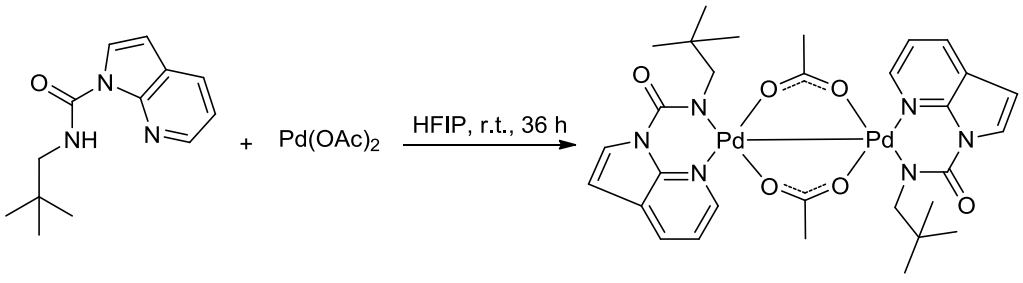


1b **2a** **5b**, 69%

A reaction tube (10 mL) with magnetic stir bar was charged with *N*-neopentyl-1*H*-indole-1-carboxamide **1b** (46 mg, 0.20 mmol), methyl acrylate **2a** (43 mg, 0.50 mmol), $Pd(OAc)_2$ (5 mg, 0.020 mmol), Ag_2CO_3 (165 mg, 0.060 mmol), PhCOOH (73 mg, 0.060 mmol) and HFIP (1.0 mL). The reaction was allowed to stir at 100 ℃ in an oil bath for 36 hours. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET: EtOAc = 12:1) to afford the desired product **5b** (43 mg) in 69% yield.

(*E*)-methyl 3-(1-(neopentylcarbamoyl)-1*H*-indol-2-yl)acrylate (5b): The title compound was obtained as a colorless oil in 89% yield according to the **Method B**. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 8.00 (d, *J* = 16.0 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.35−7.32 (m, 1H), 7.24−7.21 (m, 1H), 6.99 (s, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 5.57 (s, 1H), 3.80 (s, 3H), 3.34 (d, *J* = 6.0 Hz, 2H), 1.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 166.9, 152.0, 137.3, 134.4, 134.2, 128.4, 125.5, 122.8, 121.8, 119.6, 112.7, 108.9, 52.9, 51.9, 32.1, 27.5 (3C); HRMS (ESI) *m/z* calcd for $C_{18}H_{23}N_2O_3$ $[M+H]^+$ 315.1703, found 315.1706.

5.2 Preparation of the Six-Membered Palladacycle 12



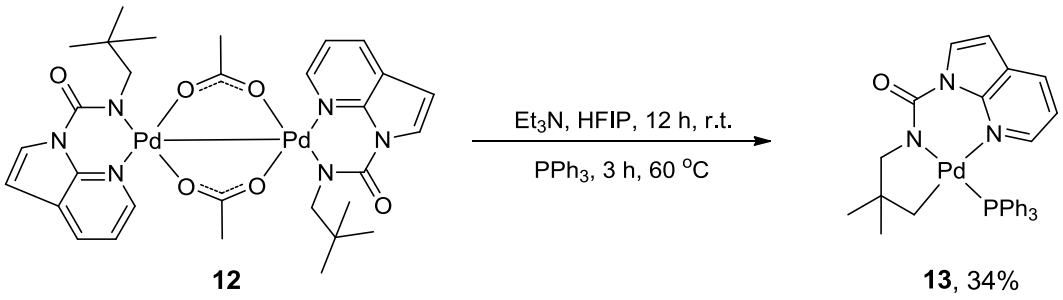
1a **12**, 92%

A reaction tube (10 mL) with magnetic stir bar was charged with *N*-neopentyl-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide **1a** (55 mg, 0.24 mmol), $Pd(OAc)_2$ (44 mg,

0.20 mmol) and HFIP (2 mL). The reaction was allowed to stir at room temperature for 36 hours. Upon completion, the reaction mixture was evaporated to remove the solvent and the solid obtained was washed with ether to remove excess **1a**. Analytically pure intermediate **12** was obtained as crystal (87 mg) in 92% yield by recrystallization using dichloromethane and ethyl acetate (DCM / EtOAc = 1:1) at room temperature. The crystal **12** was then used to perform NMR and X-ray analysis.

Six-membered palladacycle (12): ($C_{60}H_{76}N_{12}O_{12}Pd_4$) ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (dd, *J* = 8.0, 1.5 Hz, 3H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.84 (dd, *J* = 6.0, 1.0 Hz, 3H), 7.54−7.53 (m, 4H), 7.37 (dd, *J* = 6.0, 1.0 Hz, 1H), 7.14 (dd, *J* = 8.0, 6.0 Hz, 3H), 6.61 (dd, *J* = 8.0, 6.0 Hz, 1H), 6.45 (d, *J* = 4.0 Hz, 3H), 6.19 (d, *J* = 4.0 Hz, 1H), 3.53 (d, *J* = 13.5 Hz, 1H), 2.70 (d, *J* = 13.5 Hz, 3H), 2.44 (d, *J* = 14.0 Hz, 1H), 2.13−2.08 (m, 12H), 1.83 (d, *J* = 13.5 Hz, 3H), 1.13 (s, 9H), 0.98 (s, 27H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 184.7, 183.8 (3C), 148.9, 148.4 (3C), 142.9 (3C), 142.5, 140.1 (3C), 139.3, 132.3 (3C), 131.3, 130.7, 130.2 (3C), 126.0 (3C), 125.0, 117.3 (3C), 116.3, 103.3 (3C), 102.5, 56.1, 55.5 (3C), 33.6, 33.5 (3C), 28.4 (3C), 28.2 (9C), 24.3, 24.1 (3C); HRMS (ESI) *m/z* calcd for $C_{30}H_{39}N_6O_6Pd_2$ $[M+H]^+$ 791.0995, found 791.1331.

5.3 Preparation of the C−H Insertion Palladacycle 13

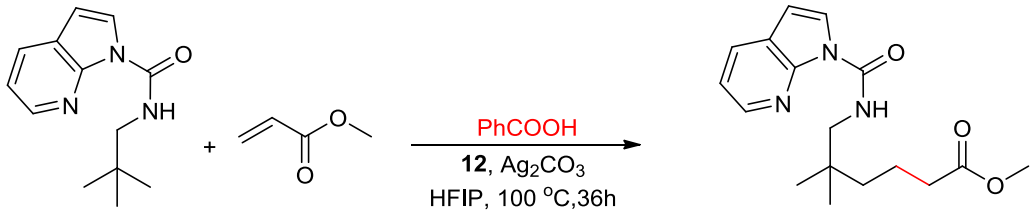


12 **13**, 34%

A reaction tube (10 mL) with magnetic stir bar was charged with **12** (158 mg, 0.20 mmol), Et_3N (61 mg, 0. 60 mmol) and HFIP (2 mL). The reaction was allowed to stir at room temperature for 12 hours. Then, triphenylphosphine (PPh_3, 79 mg, 0.30 mmol) was added and the reaction was stirred at 60 ℃ in an oil bath for another 12 hours. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and the residue was directly purified by flash column chromatography (PET: EtOAc = 4:1) to afford **13** as yellow solid (81 mg) in 34 % yield.

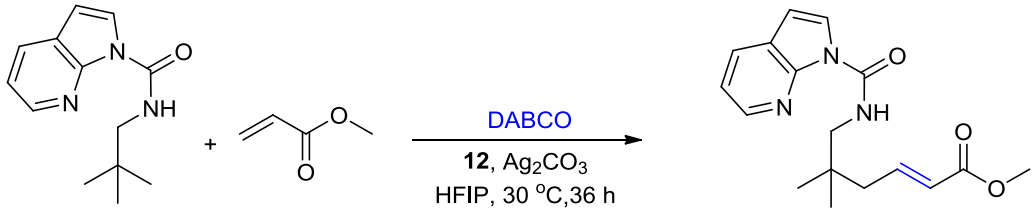
C−H Insertion Palladacycle (13): ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.40 (d, *J* = 4.0 Hz, 1H), 7.76 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.71−7.67 (m, 6H), 7.47−7.43 (m, 3H), 7.40−7.37 (m, 6H), 7.18 (d, *J* = 5.5 Hz, 1H), 6.46 (d, *J* = 4.0 Hz, 1H), 6.38 (dd, *J* = 7.5, 5.5 Hz, 1H), 3.49 (s, 2H), 1.52 (d, *J* = 6.5 Hz, 2H), 1.05 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.0, 145.2, 144.9 (d, *J* = 5.0 Hz, 1C), 134.8 (d, *J* = 12.4 Hz, 6C), 131.8 (d, *J* = 44.6 Hz, 3C), 130.6 (d, *J* = 2.4 Hz, 3C), 130.4, 130.1, 128.6 (d, *J* = 10.4 Hz, 6C), 126.0, 115.7, 101.2, 65.3, 50.7 (d, *J* = 5.3 Hz, 1C), 43.3 (d, *J* = 2.0 Hz, 1C), 28.2 (2C); HRMS (ESI) *m/z* calcd for $C_{31}H_{31}N_3OPPd$ $[M+H]^+$ 598.1234, found 598.1235.

5.4 Reaction of 1a with 2a Using 12 as Catalyst



1a **2a** **3a**, 71%

A reaction tube (10 mL) with magnetic stir bar was charged with *N*-neopentyl-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide **1a** (46 mg, 0.20 mmol), methyl acrylate **2a** (43 mg, 0.50 mmol), **12** (16 mg, 0.020 mmol), Ag_2CO_3 (165 mg, 0.60 mmol), PhCOOH (73 mg, 0.060 mmol) and HFIP (1 mL). The reaction was allowed to stir at 100 ℃ in an oil bath for 36 hours. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET: EtOAc = 10:1) to afford the desired product **3a** (45 mg) in 71% yield.



1a **2a** **4a**, 87%

A reaction tube (10 mL) with magnetic stir bar was charged with *N*-neopentyl-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide **1a** (46 mg, 0.2 mmol), methyl acrylate **2a** (43 mg, 0.50 mmol), **12** (16 mg, 0.020 mmol), Ag_2CO_3 (165 mg, 0.60 mmol), DABCO (67 mg, 0.060 mmol) and HFIP (1 mL). The reaction was allowed to stir at 30 ℃ in an oil bath for 36 hours. After cooling to room temperature, the reaction mixture was evaporated to remove the solvent and directly loaded onto silica gel for flash column chromatography (PET: EtOAc = 10:1) to afford the desired product **4a** (55 mg) in 87% yield.

6. X-ray crystallographic data of 12

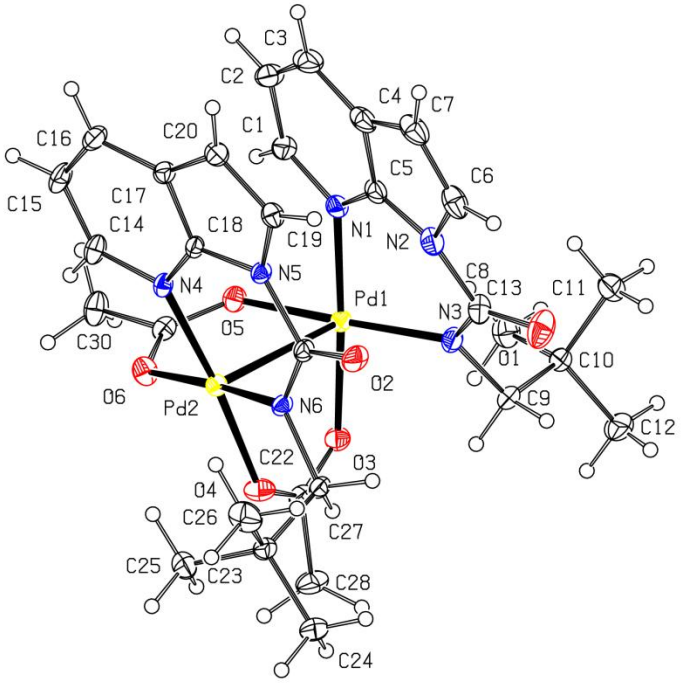


Table S3. Crystal data and structure refinement for 12

Empirical formula	$C_{30}H_{38}N_6O_6Pd_2$
Formula weight	791.46
Temperature/K	170(2)
Crystal system	triclinic
Space group	*P*-1
a/Å	9.369(2)
b/Å	10.227(3)
c/Å	17.134(4)
α/°	95.498(13)
β/°	92.123(10)
γ/°	101.964(11)
Volume/Å^3	1595.9(6)
Z	2
Wavelength/Å	0.71073
F(000)	800.0
Crystal size/mm^3	0.26×0.19×0.16
Radiation	MoKα (λ = 0.71073)
Θ_{min}/°	2.392
Θ_{max}/°	28.230
Index ranges	-12 ≤ h ≤ 11, -13 ≤ k ≤ 13, -22 ≤ l ≤ 22
Reflections collected	34619
Independent reflections	7880 [R_{int} = 0.0251]
Data/restraints/parameters	7880/0/405
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0196, wR_2 = 0.0472
Final R indexes [all data]	R_1 = 0.0212, wR_2 = 0.0483
Largest diff. peak/hole / e Å^{-3}	0.430/-0.765

7. References

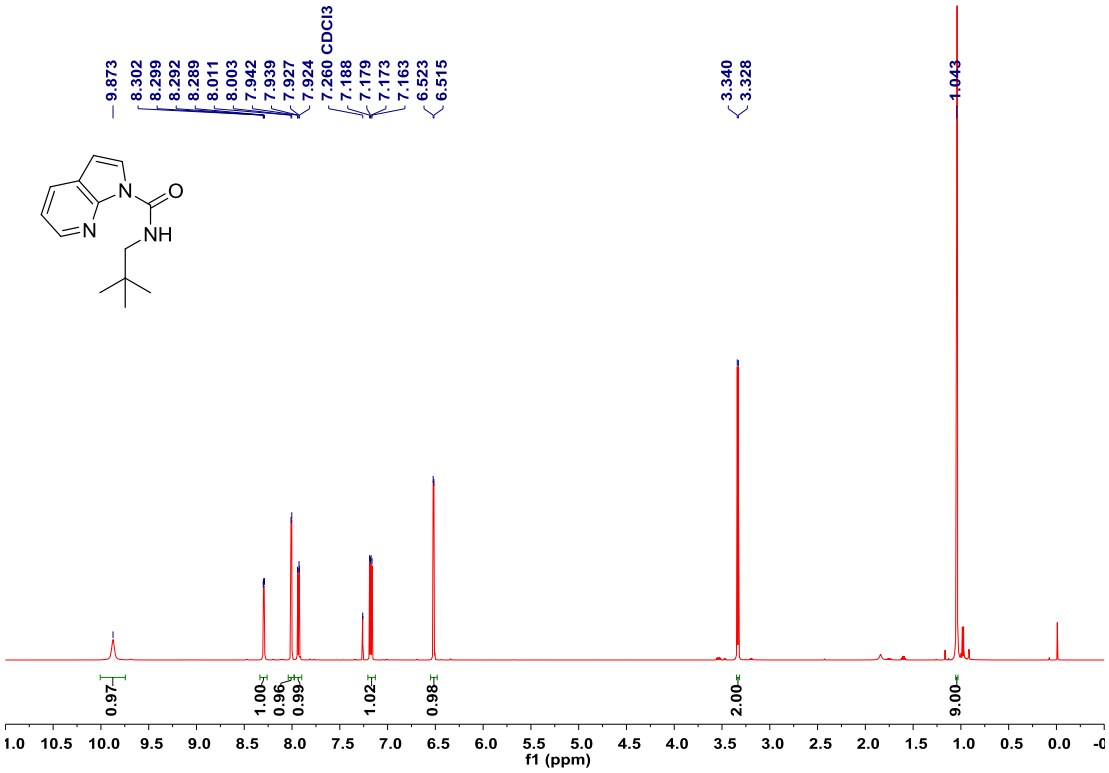
(1) (a) Kong, W.; Chen, X.; Wang, M.; Dai, H.; Yu, J. Rapid Syntheses of Heteroaryl-Substituted Imidazo[1,5-a]indole and Pyrrolo[1,2-c]imidazole via Aerobic C2–H Functionalizations. *Org. Lett.* **2018**, *20*, 284–287. (b) Zhang, W.; Wei, J.; Fu, S.; Lin, D.; Jiang, H.; Zeng, W. Highly Stereoselective Ruthenium(II)-Catalyzed Direct C2-syn-Alkenylation of Indoles with Alkynes. *Org. Lett.* **2015**, *17*, 1349–1352.

(2) Xiao, Q.; He, Q.; Li, J.; Wang, J. 1,4-Diazabicyclo[2.2.2]octane-Promoted Aminotrifluoromethylthiolation of α,β-Unsaturated Carbonyl Compounds: *N*-Trifluoromethylthio-4-nitrophthalimide Acts as Both the Nitrogen and SCF3 Sources. *Org. Lett.* **2015**, *17*, 6090–6093.

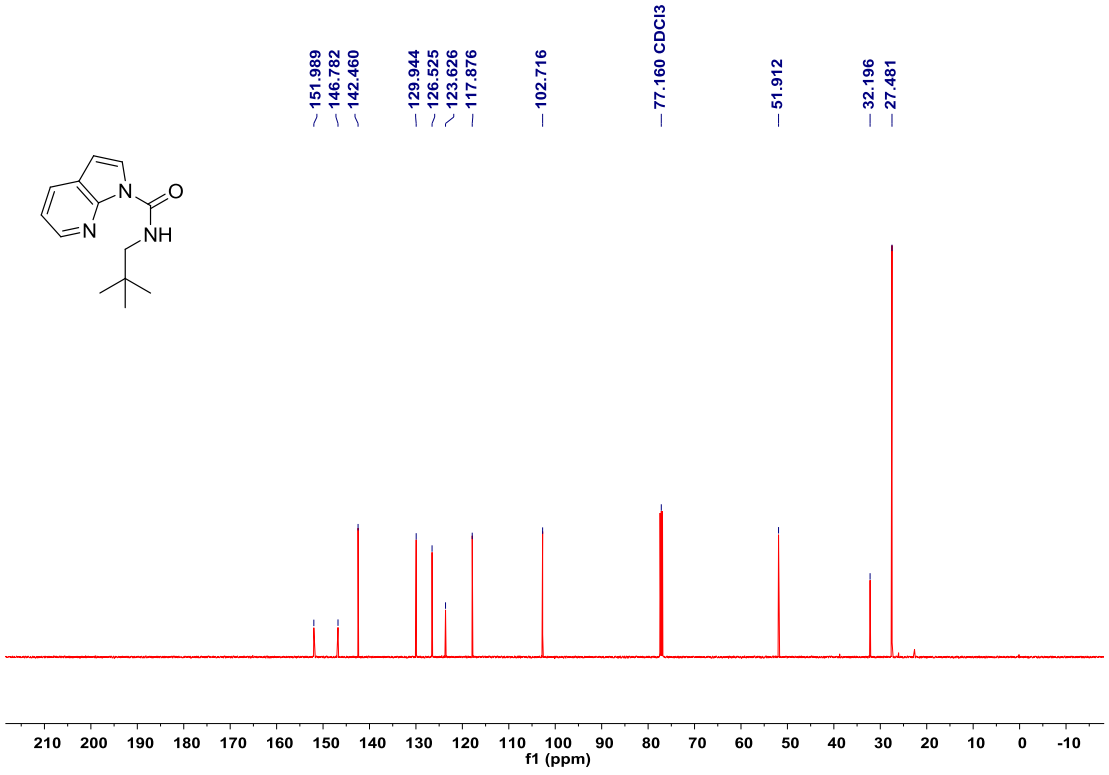
8. NMR Spectra

_N_-neopentyl-1_H_-pyrrolo[2,3-_b_]pyridine-1-carboxamide (1a)

^{1}H NMR, 500 MHz, $CDCl_3$

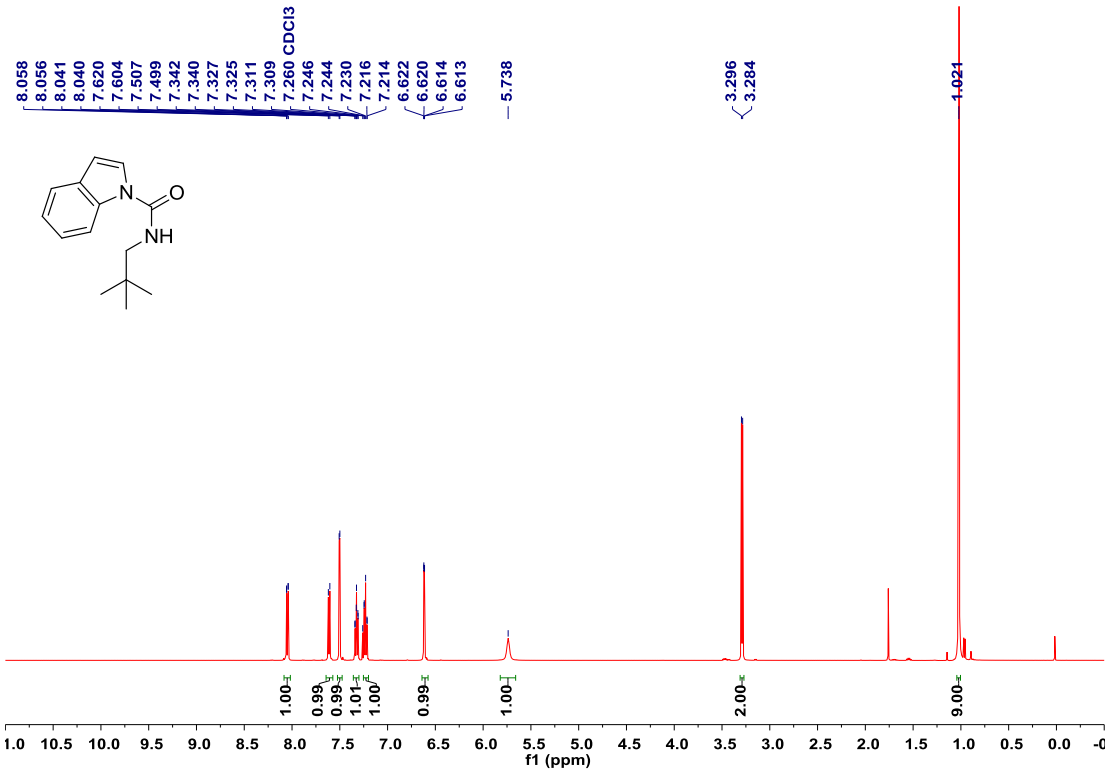


^{13}C NMR, 125 MHz, $CDCl_3$

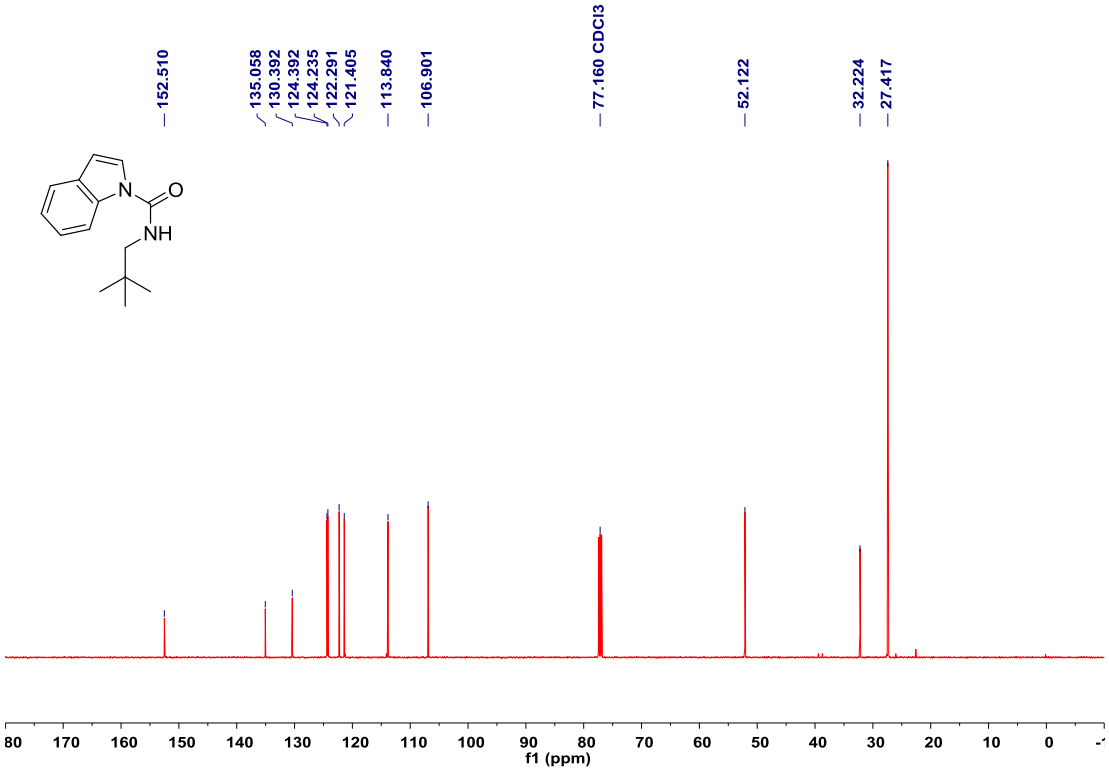


_N_-neopentyl-1_H_-indole-1-carboxamide (1b)

^{1}H NMR, 500 MHz, $CDCl_3$

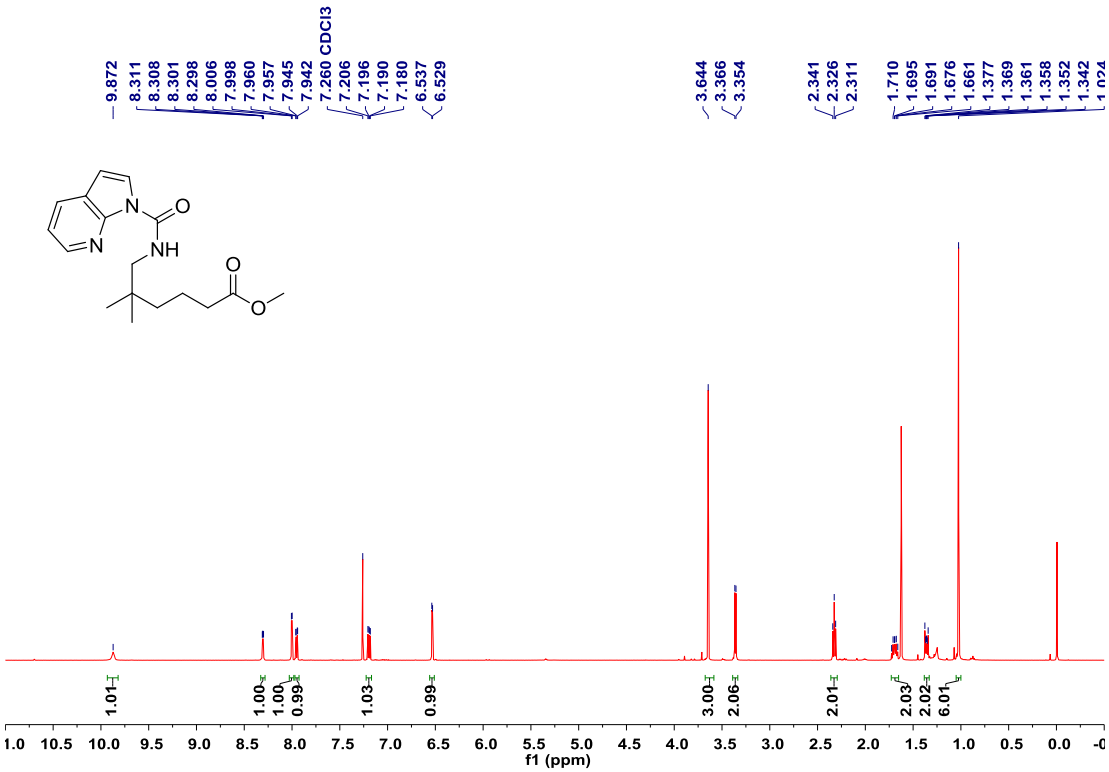


^{13}C NMR, 125 MHz, $CDCl_3$

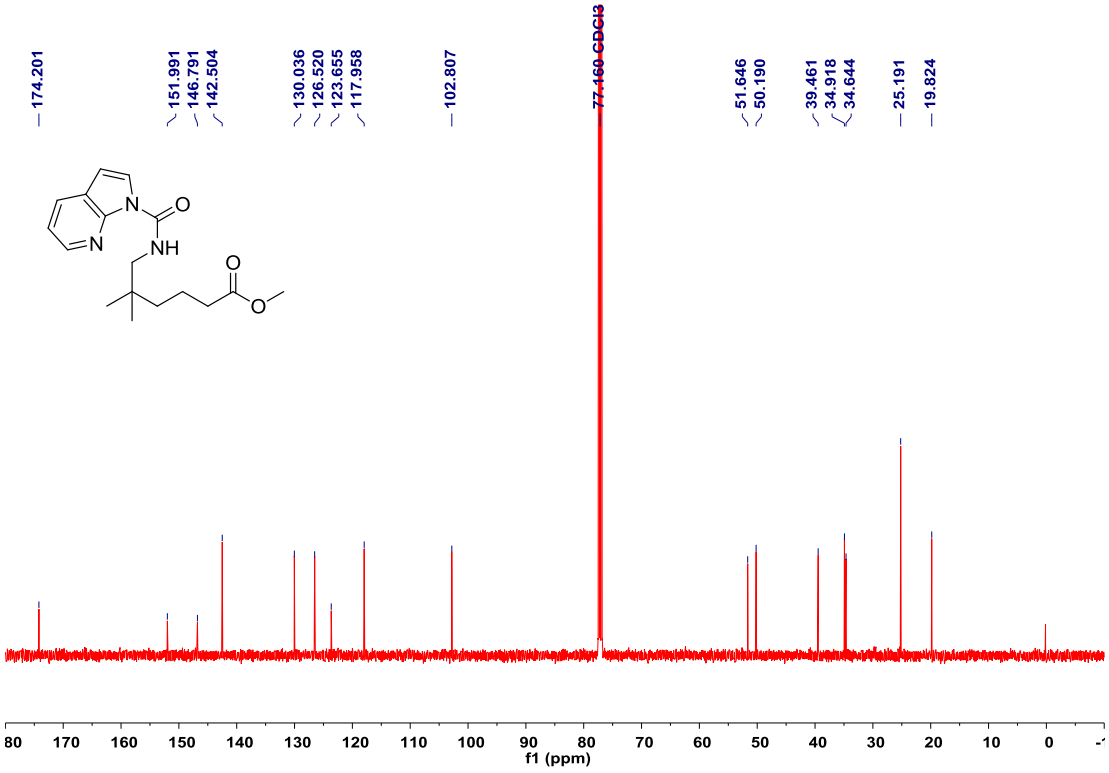


Methyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3a)

^{1}H NMR, 500 MHz, $CDCl_3$

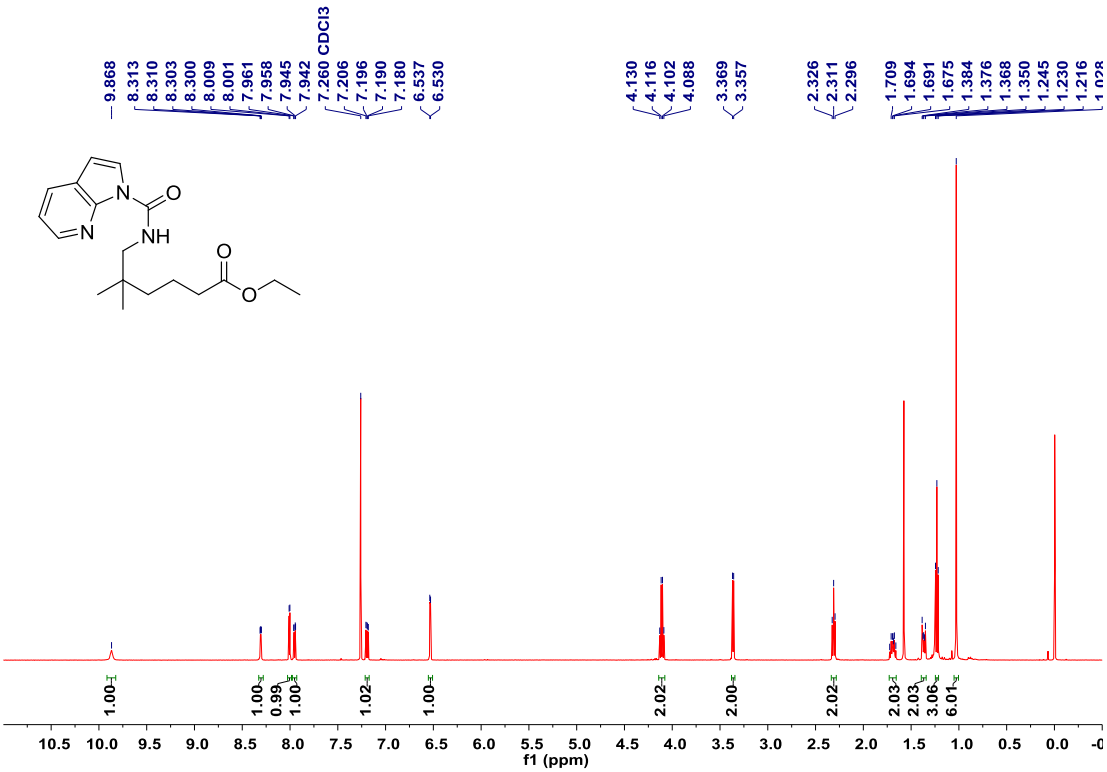


^{13}C NMR, 125 MHz, $CDCl_3$

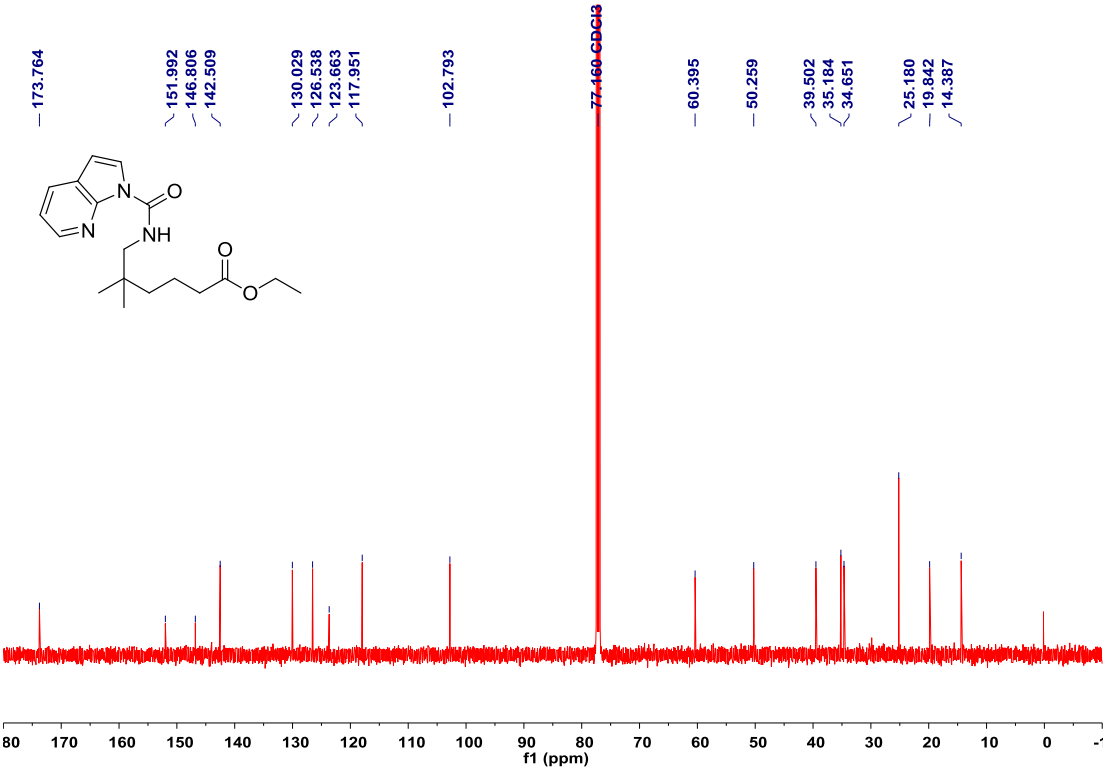


Ethyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3b)

^{1}H NMR, 500 MHz, $CDCl_3$

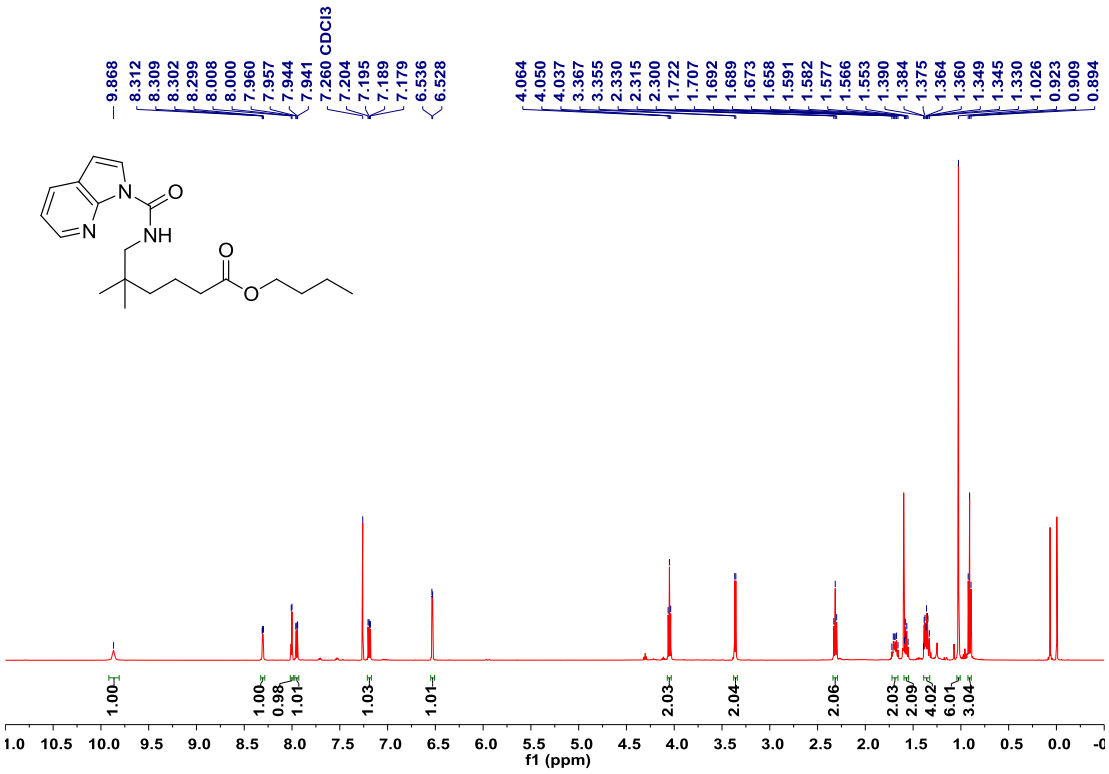


^{13}C NMR, 125 MHz, $CDCl_3$

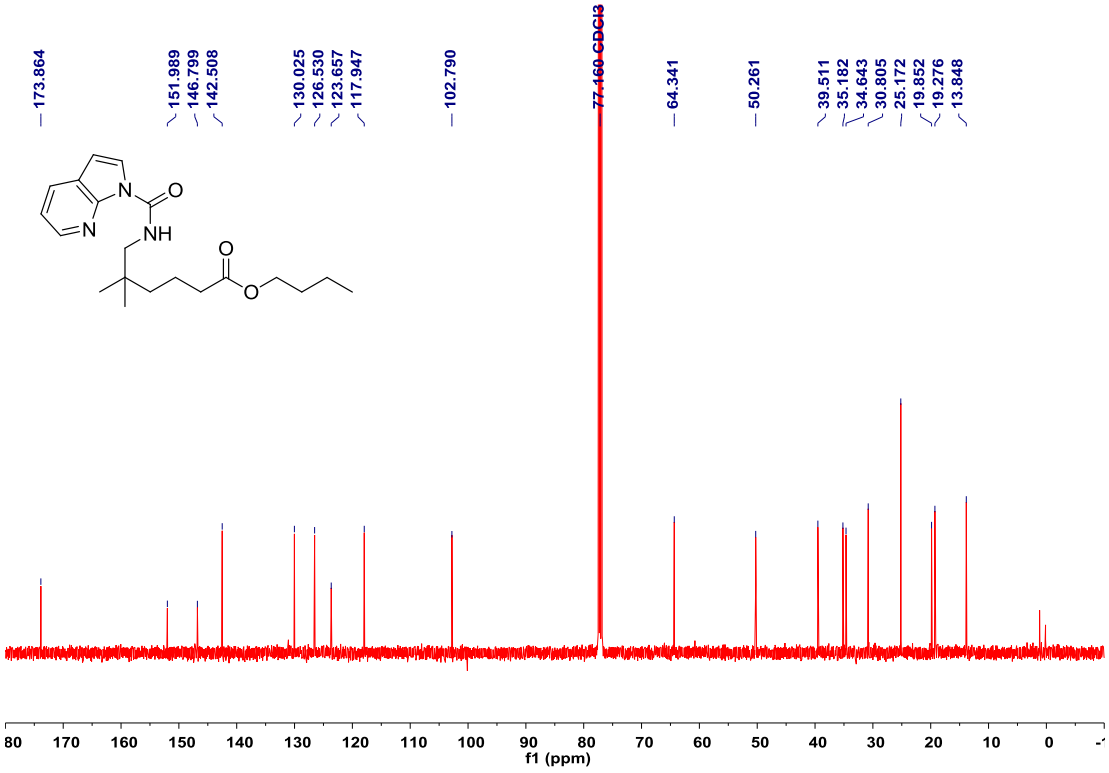


Butyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3c)

^{1}H NMR, 500 MHz, $CDCl_3$

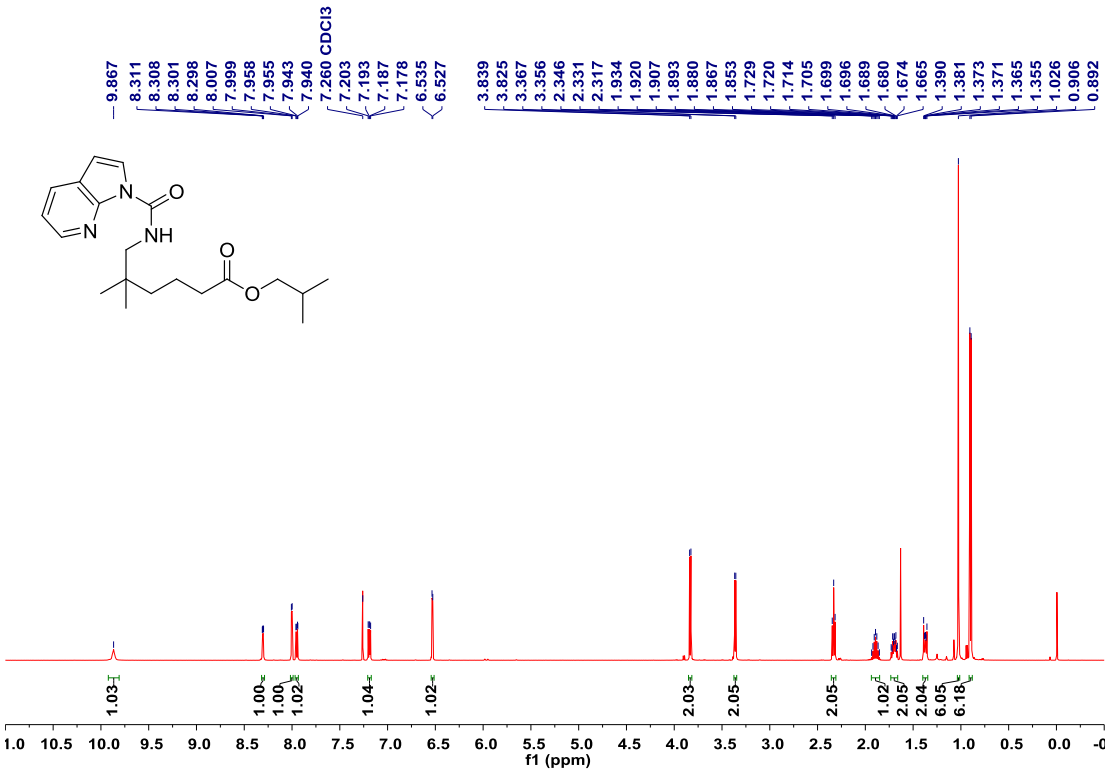


^{13}C NMR, 125 MHz, $CDCl_3$

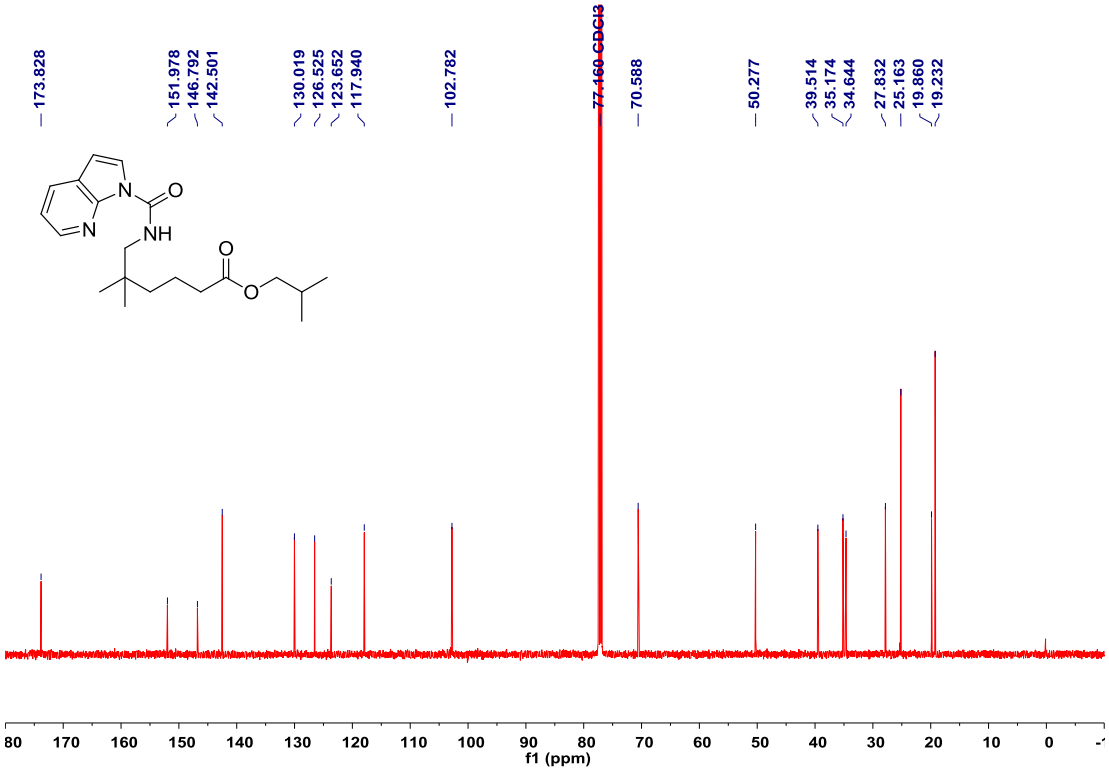


Isobutyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3d)

^{1}H NMR, 500 MHz, $CDCl_3$

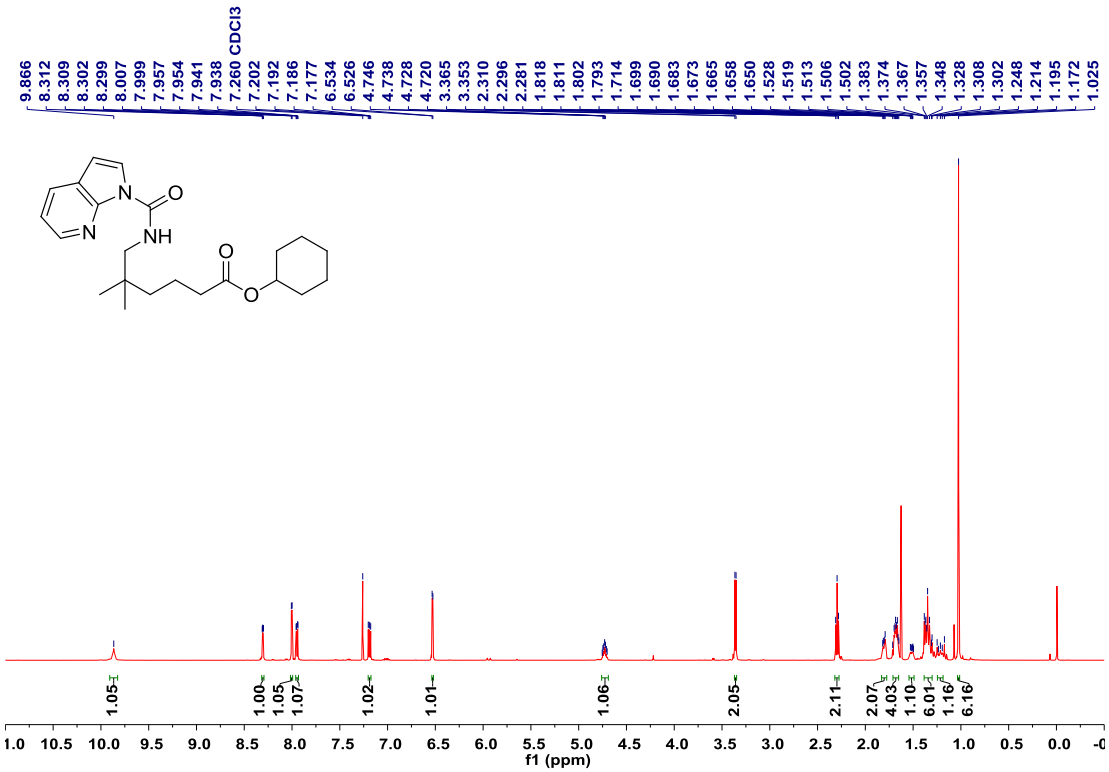


^{13}C NMR, 125 MHz, $CDCl_3$

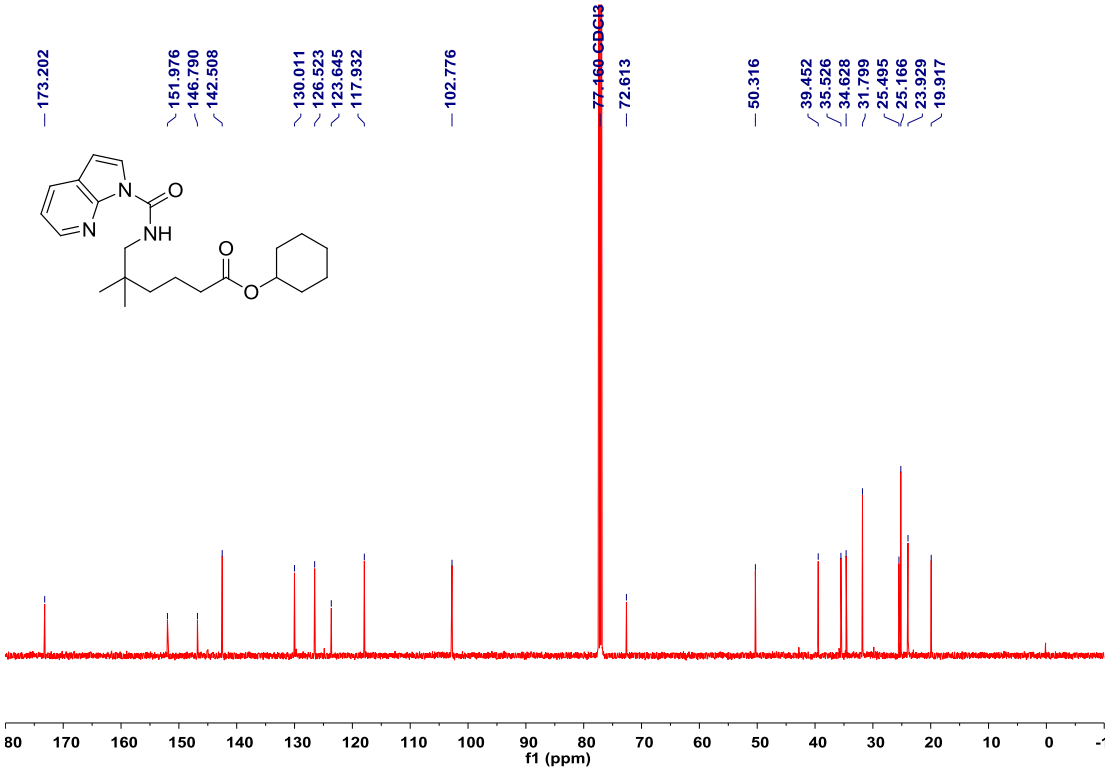


Cyclohexyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3e)

^{1}H NMR, 500 MHz, $CDCl_3$

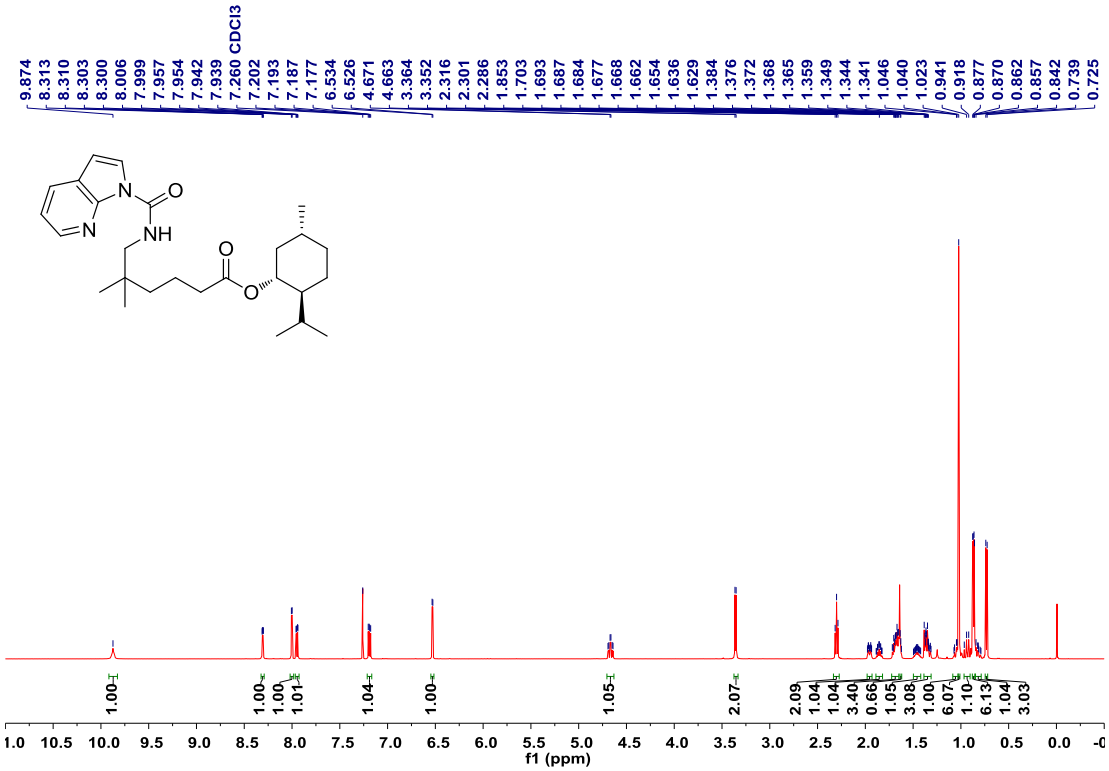


^{13}C NMR, 125 MHz, $CDCl_3$

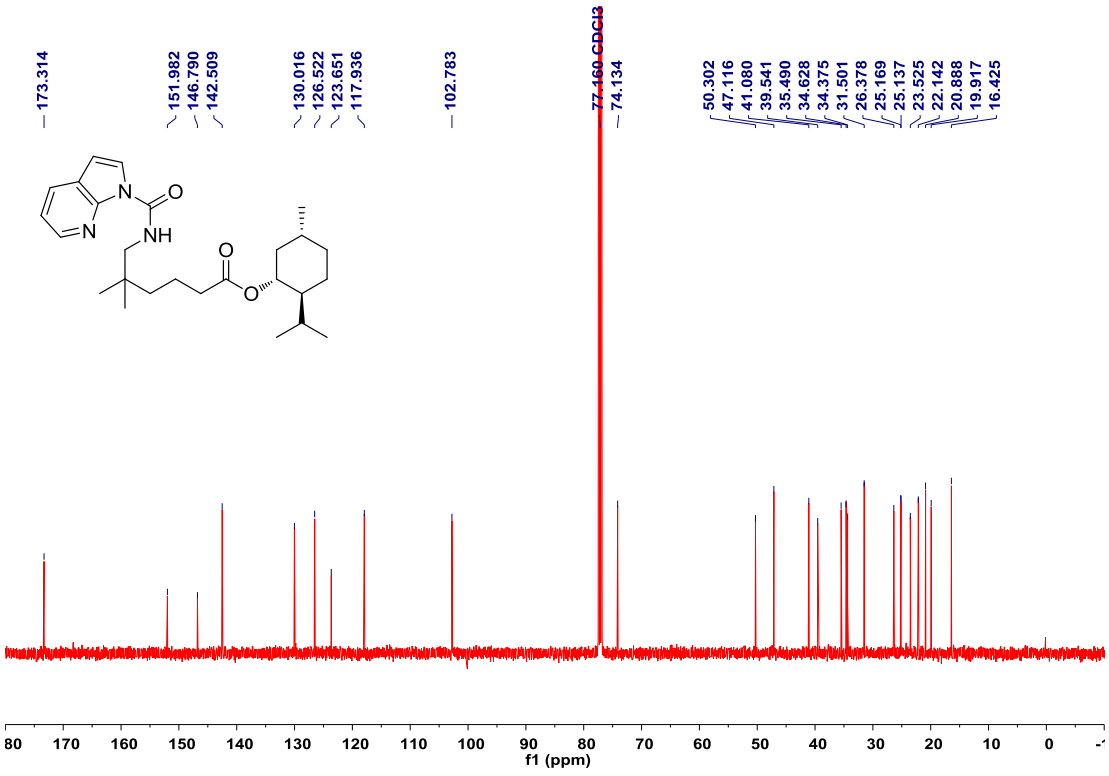


(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3f)

^{1}H NMR, 500 MHz, $CDCl_3$

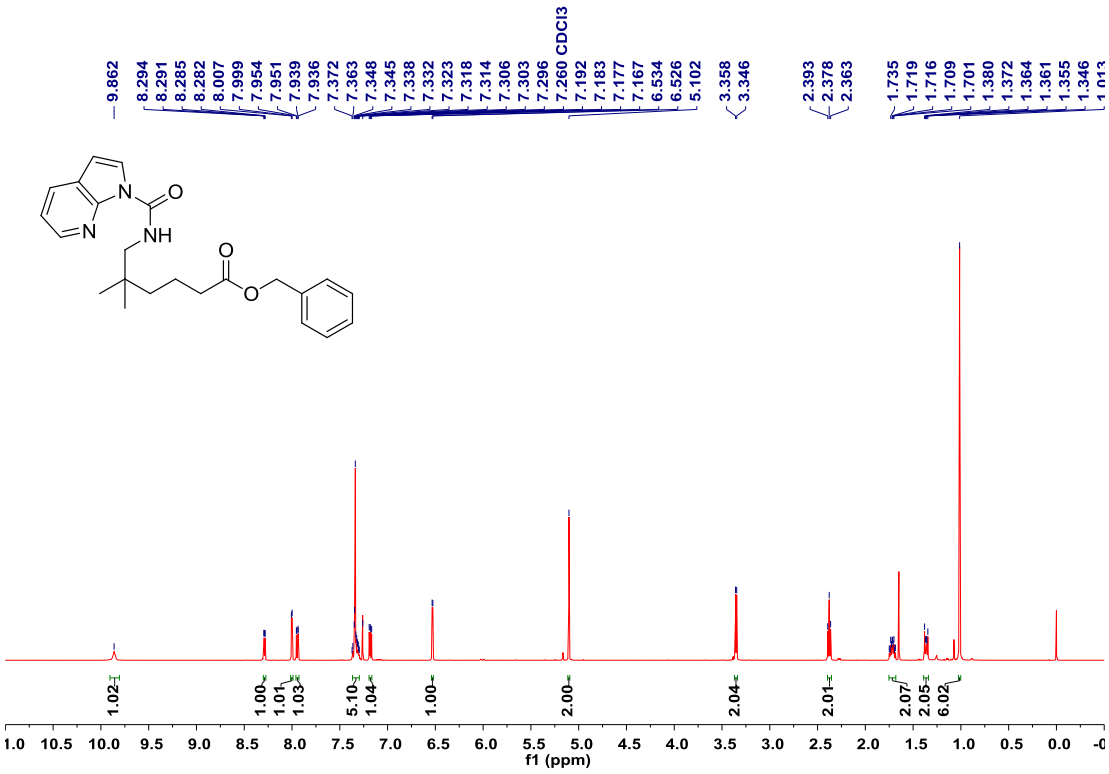


^{13}C NMR, 125 MHz, $CDCl_3$

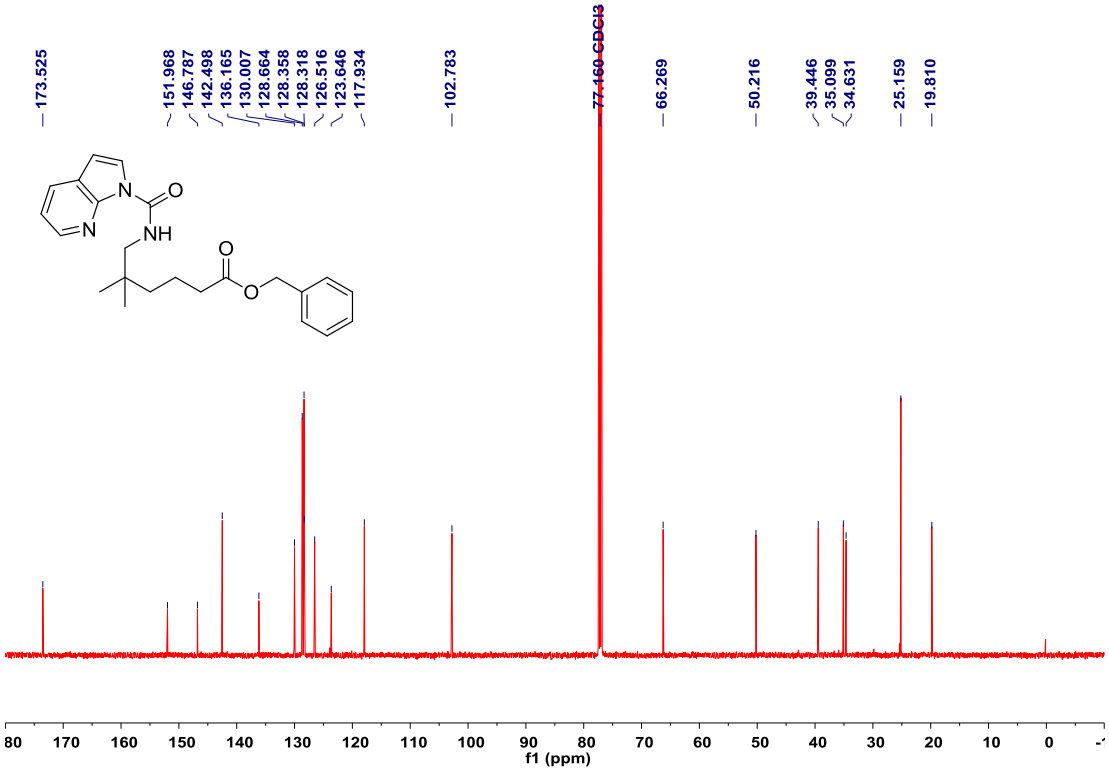


Benzyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3g)

^{1}H NMR, 500 MHz, $CDCl_3$

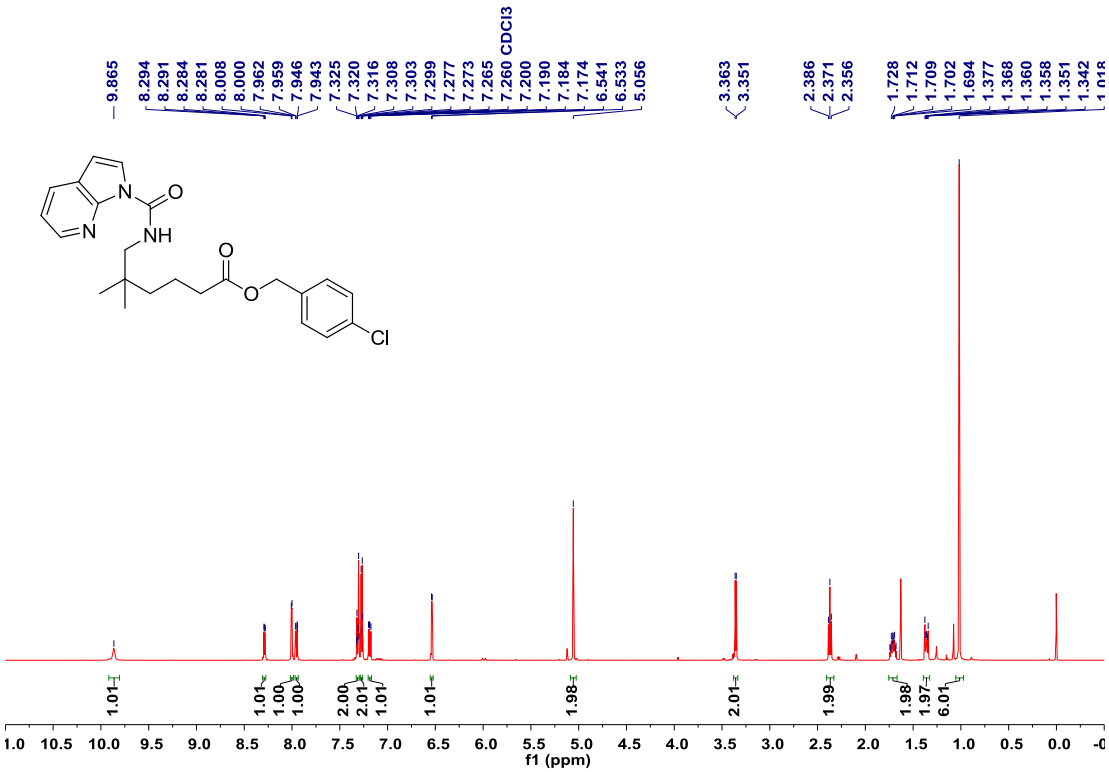


^{13}C NMR, 125 MHz, $CDCl_3$

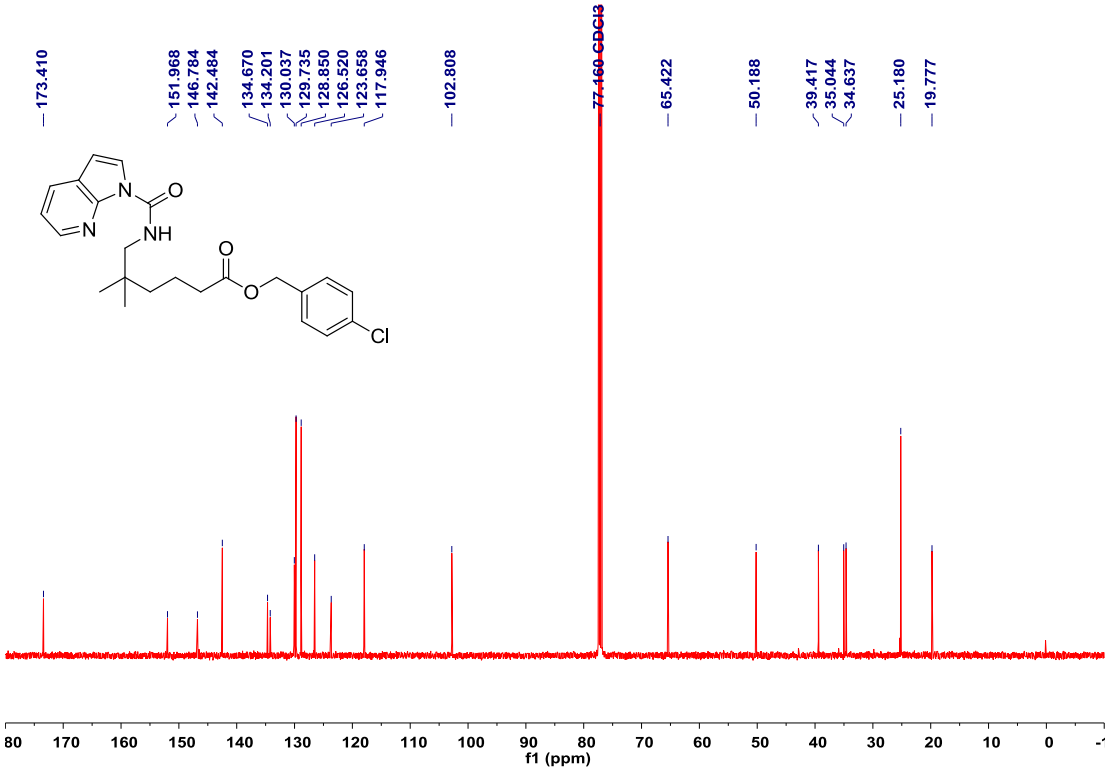


4-Chlorobenzyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3h)

^{1}H NMR, 500 MHz, $CDCl_3$

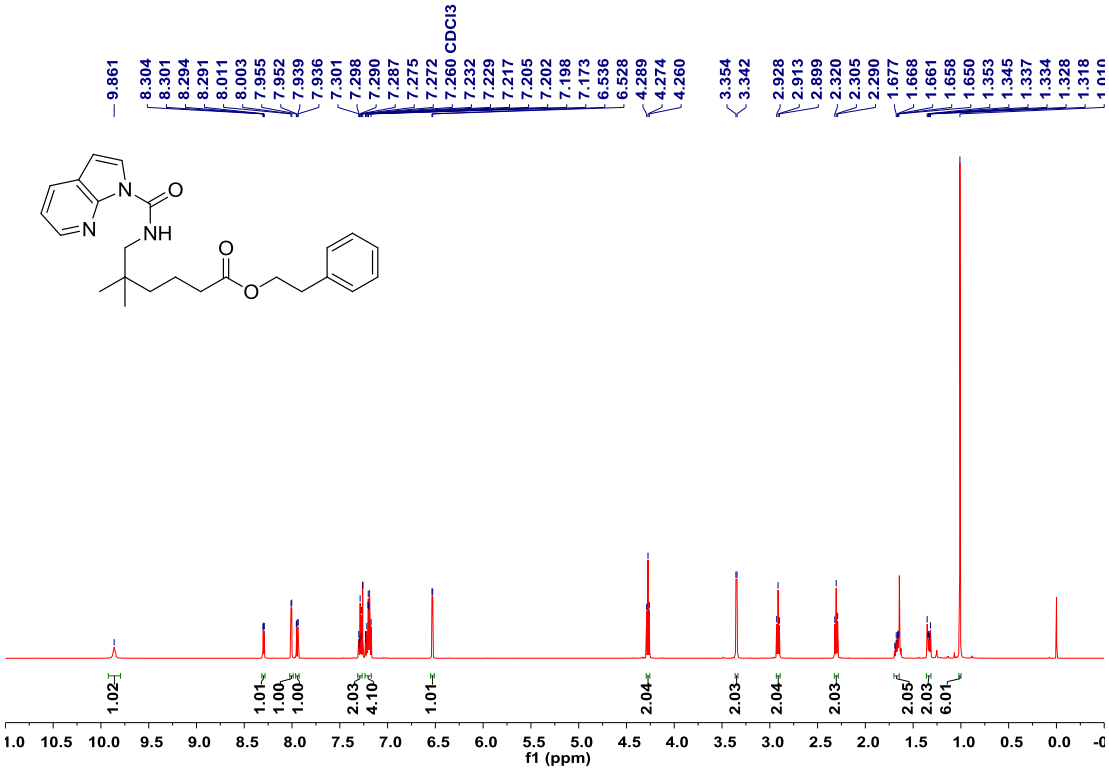


^{13}C NMR, 125 MHz, $CDCl_3$

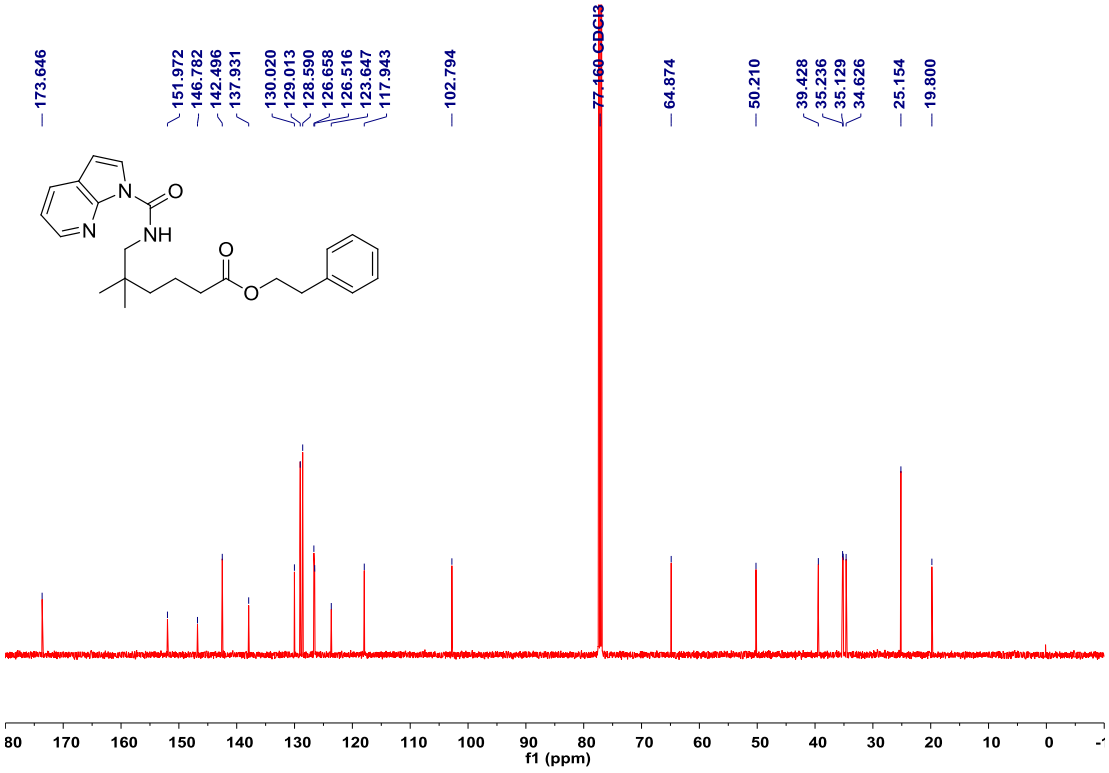


Phenethyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3i)

^{1}H NMR, 500 MHz, $CDCl_3$

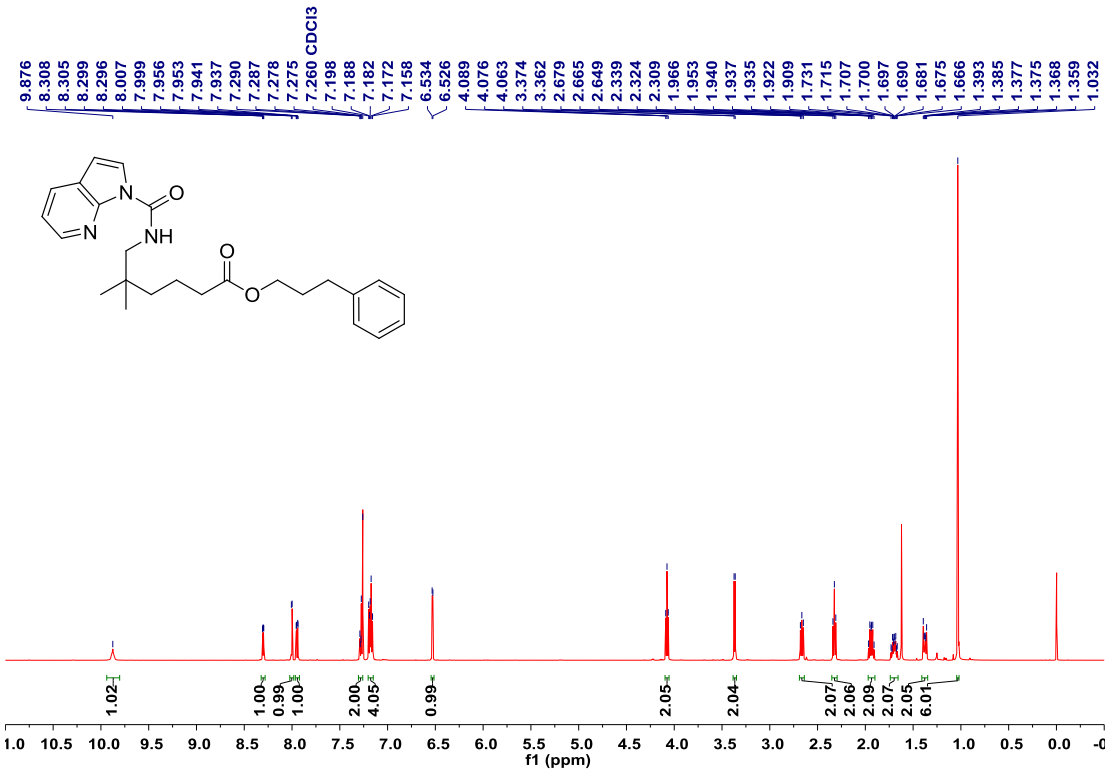


^{13}C NMR, 125 MHz, $CDCl_3$

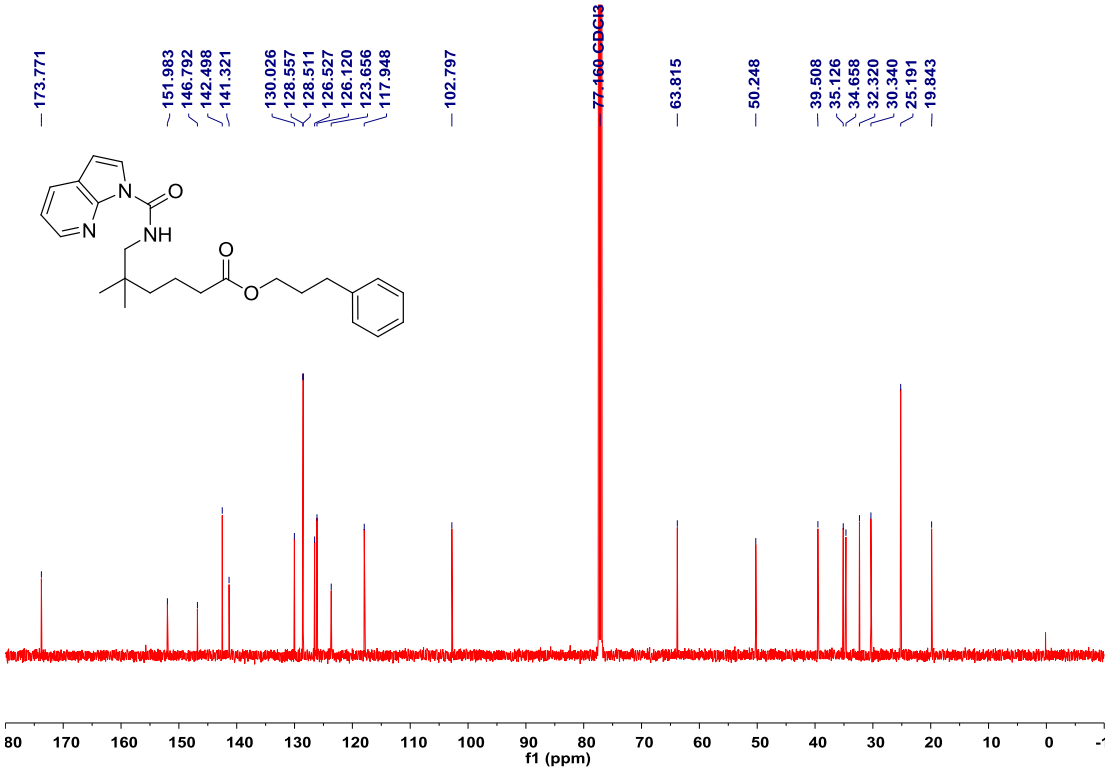


3-Phenylpropyl 5,5-dimethyl-6-(1H-pyrrolo[2,3-b]pyridine-1-carboxamido)hexanoate (3j)

^{1}H NMR, 500 MHz, $CDCl_3$

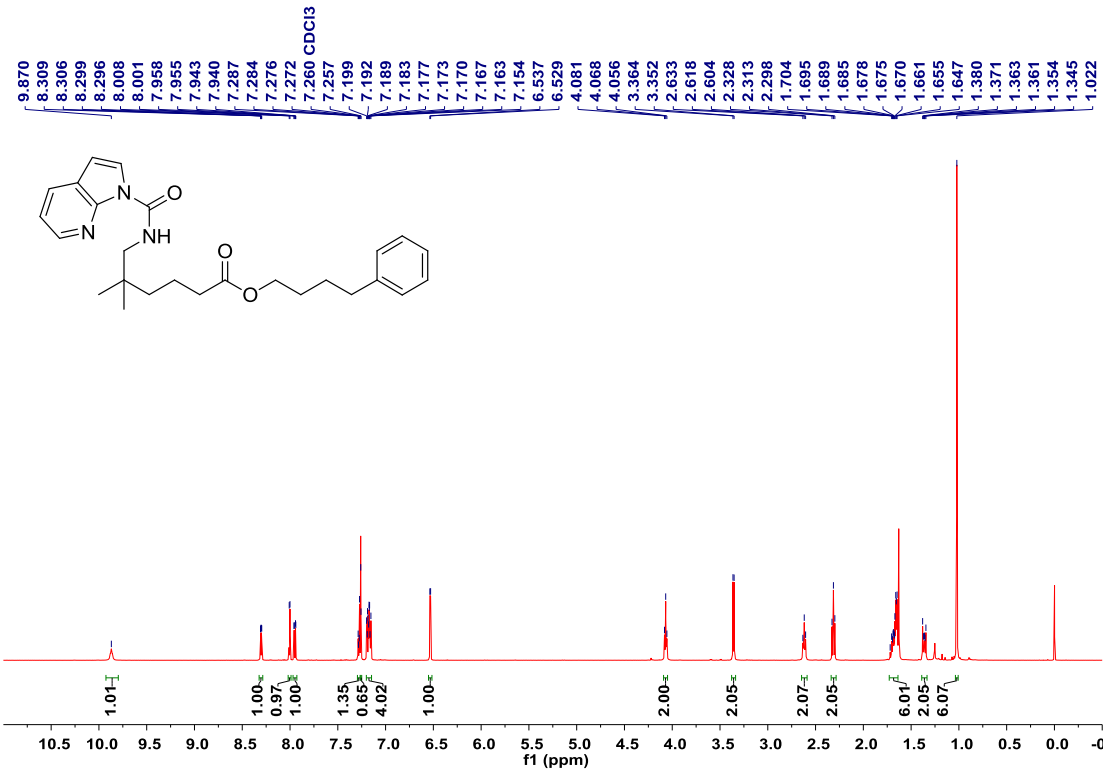


^{13}C NMR, 125 MHz, $CDCl_3$

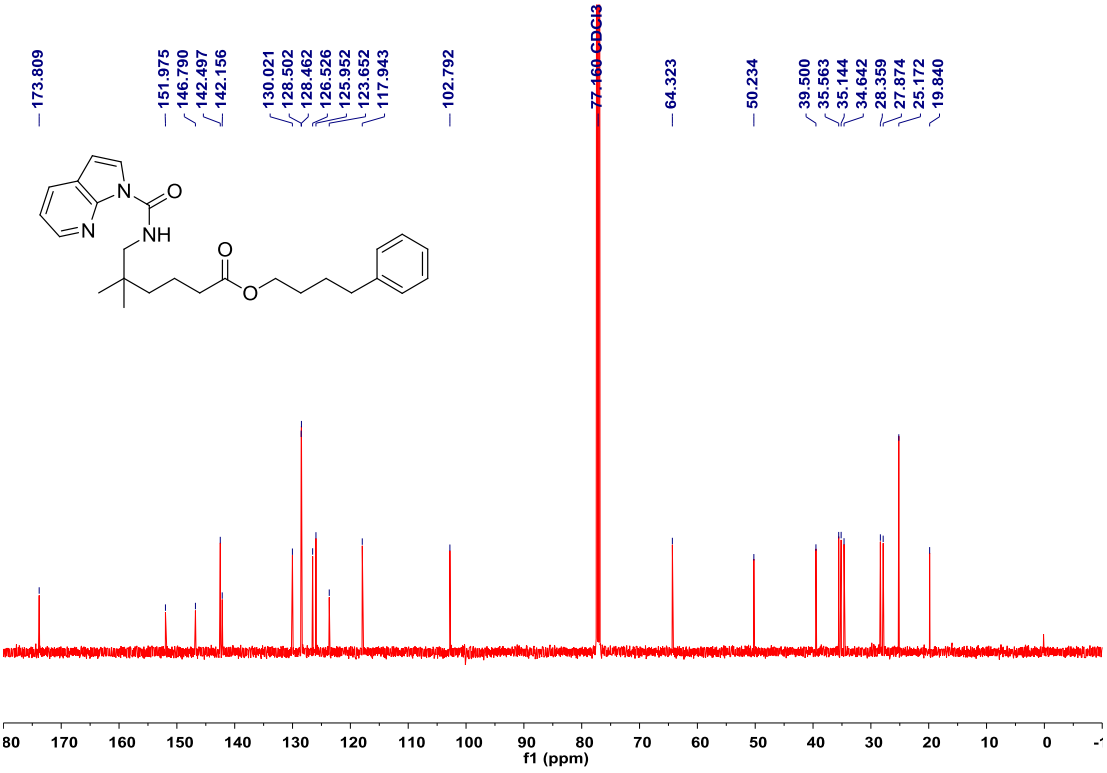


4-Phenylbutyl 5,5-dimethyl-6-(1H-pyrrolo[2,3-b]pyridine-1-carboxamido)hexanoate (3k)

^{1}H NMR, 500 MHz, $CDCl_3$

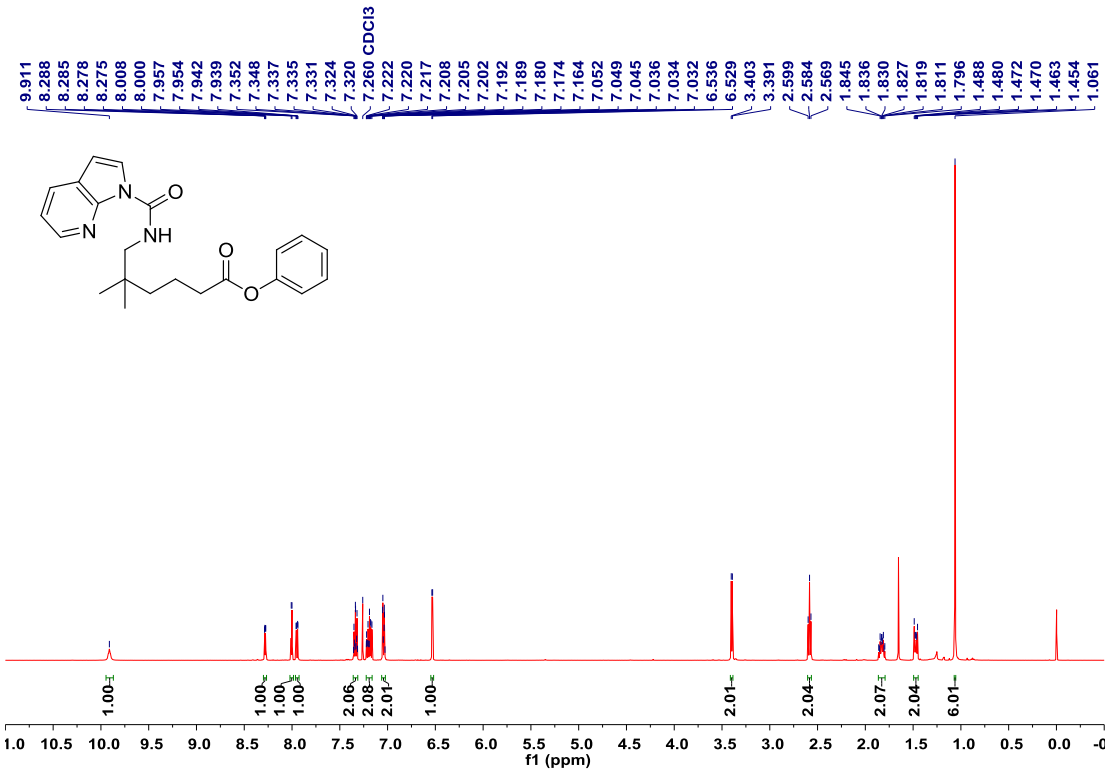


^{13}C NMR, 125 MHz, $CDCl_3$

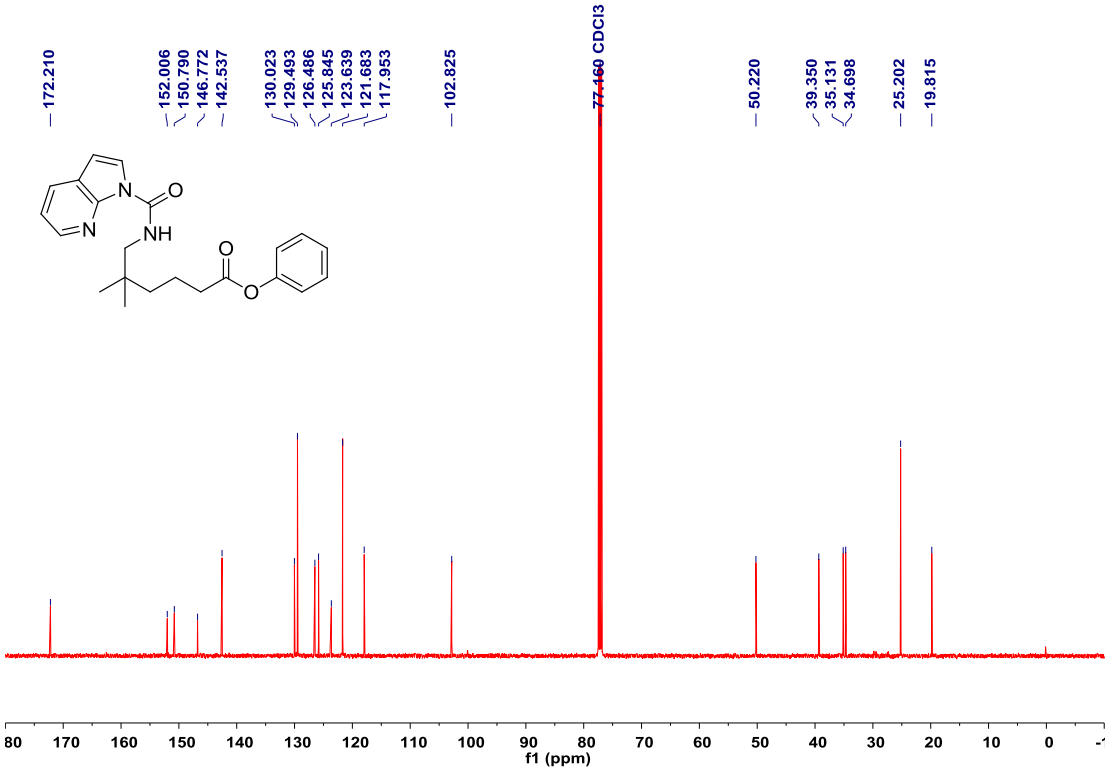


Phenyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3l)

^{1}H NMR, 500 MHz, $CDCl_3$

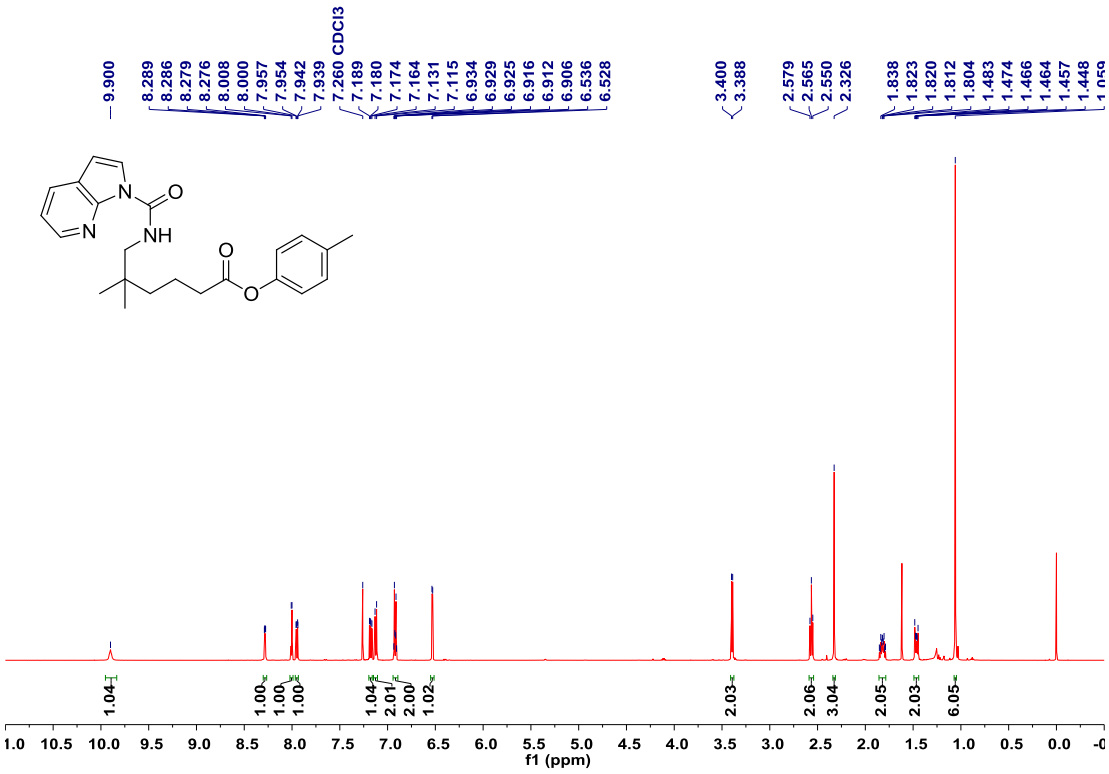


^{13}C NMR, 125 MHz, $CDCl_3$

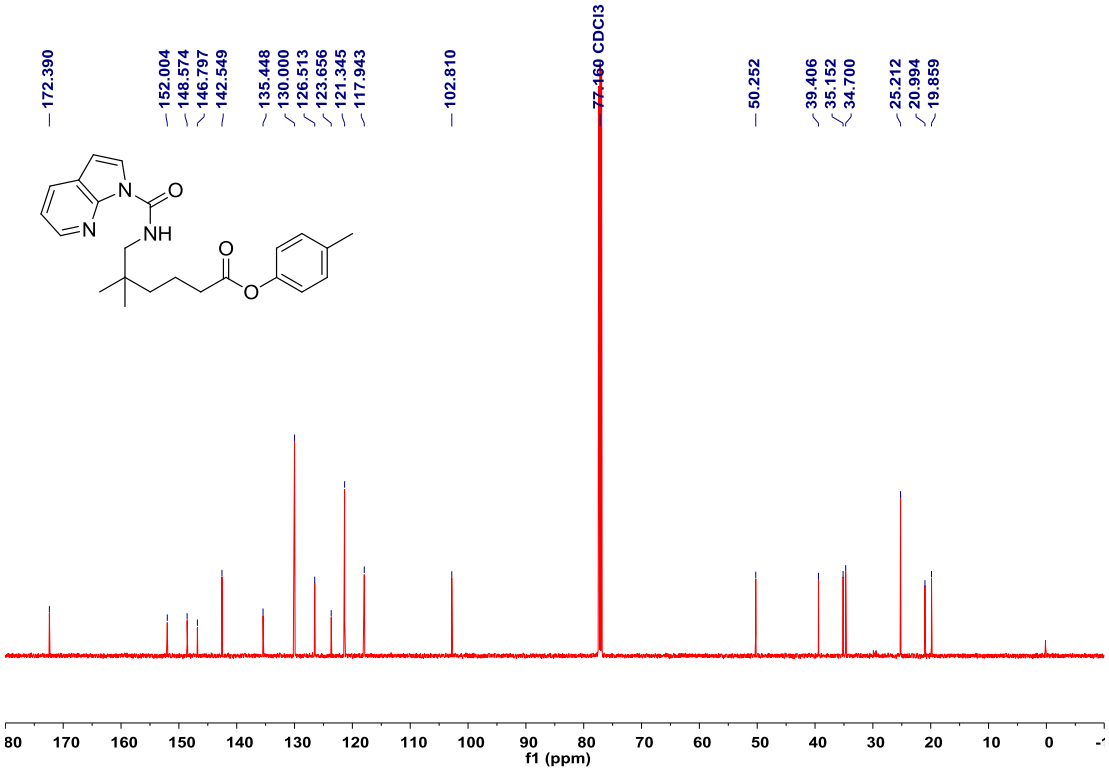


_p_-Tolyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3m)

^{1}H NMR, 500 MHz, $CDCl_3$

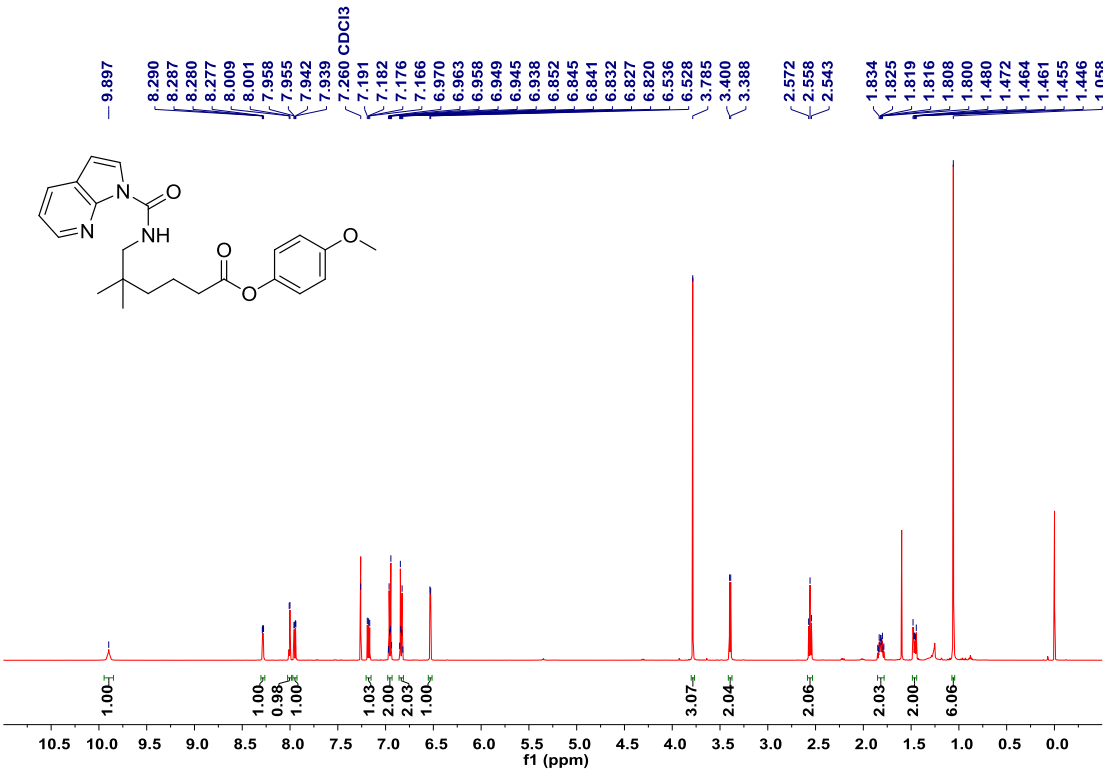


^{13}C NMR, 125 MHz, $CDCl_3$

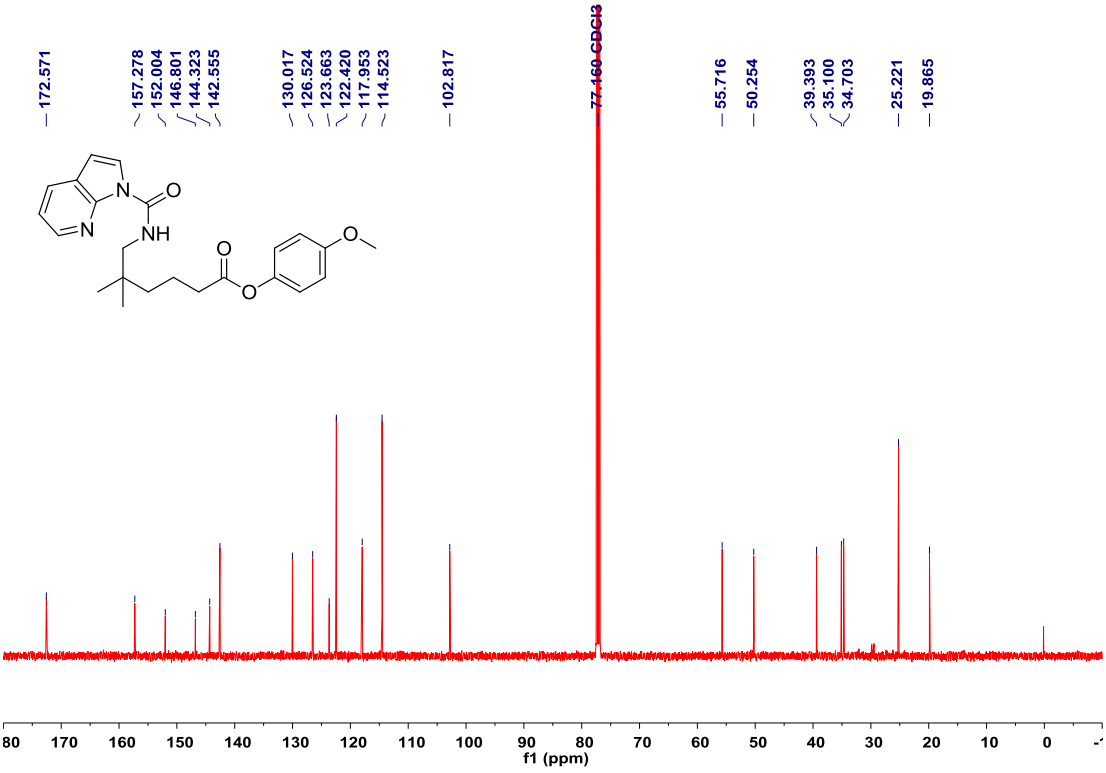


4-Methoxyphenyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3n)

^{1}H NMR, 500 MHz, $CDCl_3$

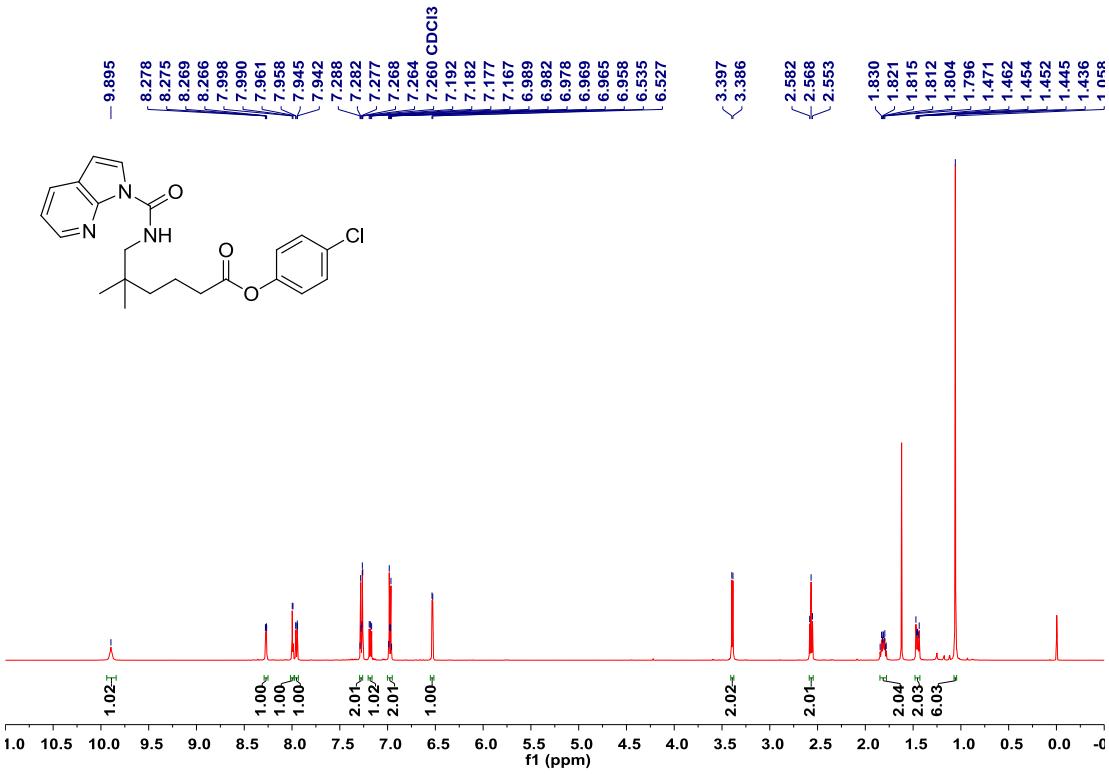


^{13}C NMR, 125 MHz, $CDCl_3$

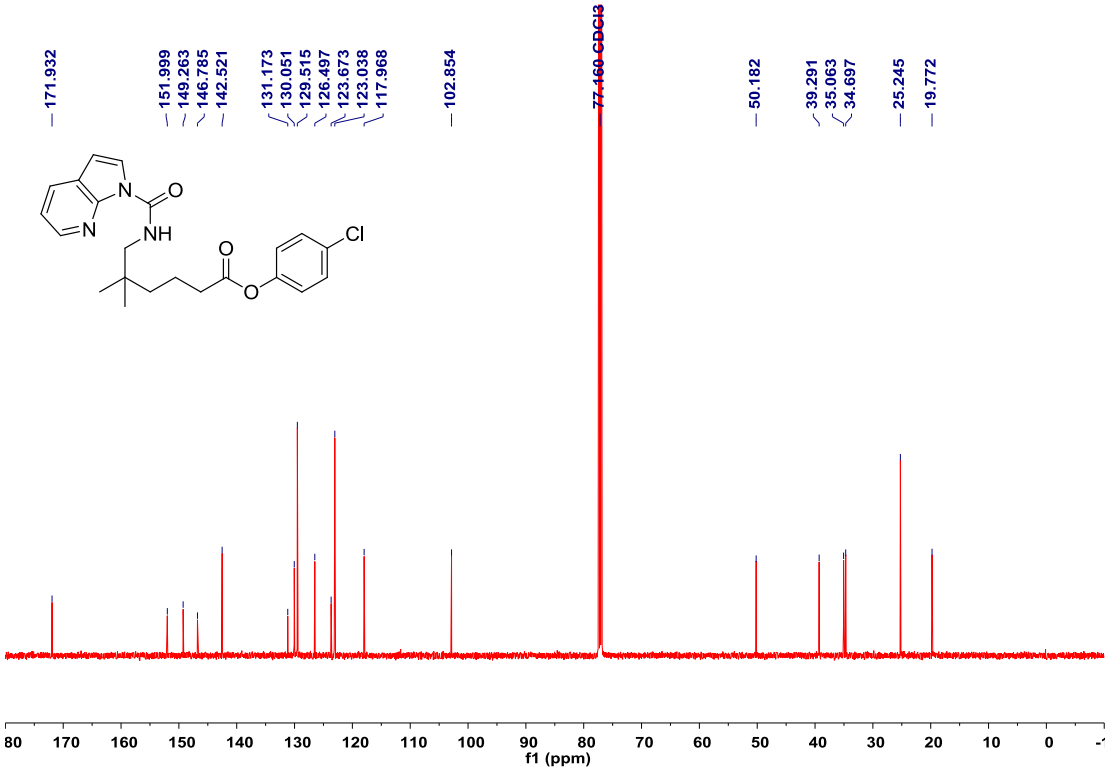


4-Chlorophenyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3o)

^{1}H NMR, 500 MHz, $CDCl_3$

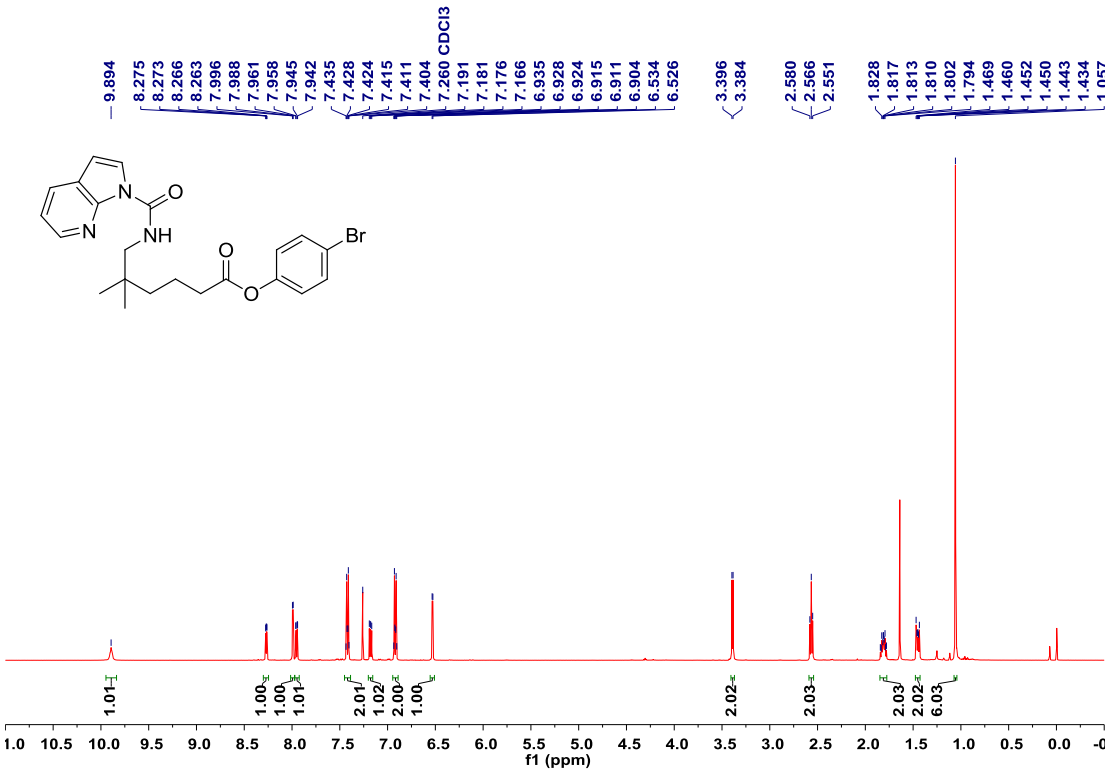


^{13}C NMR, 125 MHz, $CDCl_3$

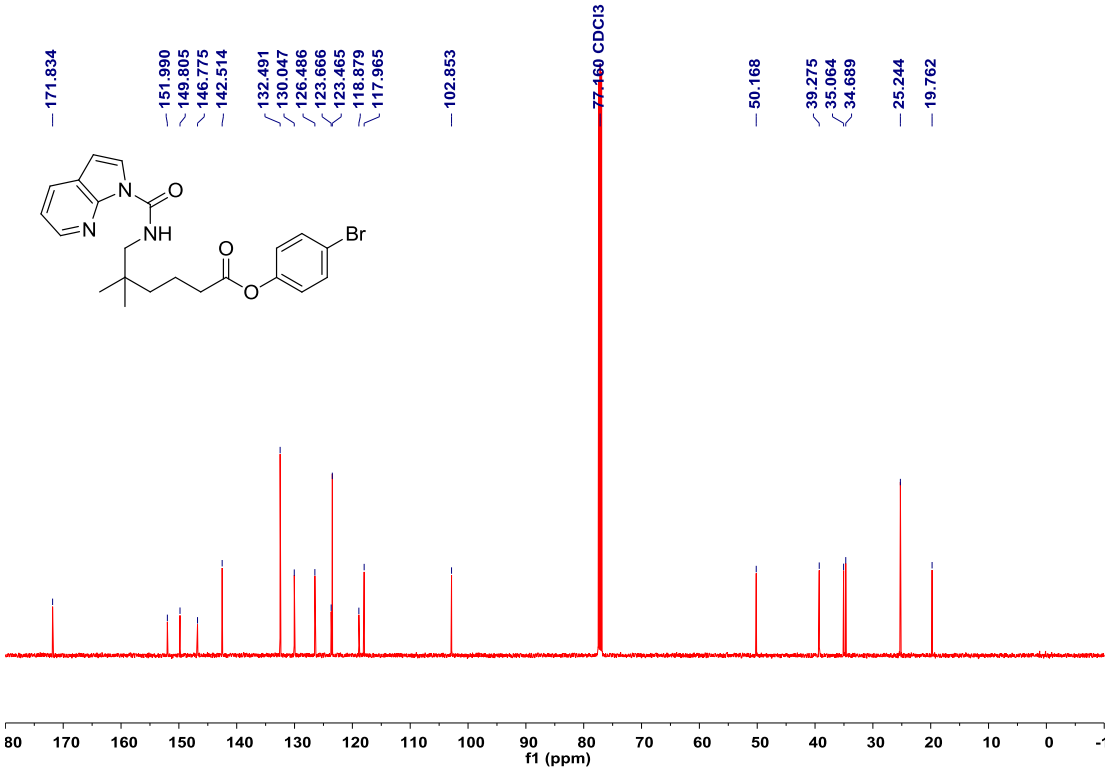


4-Bromophenyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3p)

^{1}H NMR, 500 MHz, $CDCl_3$

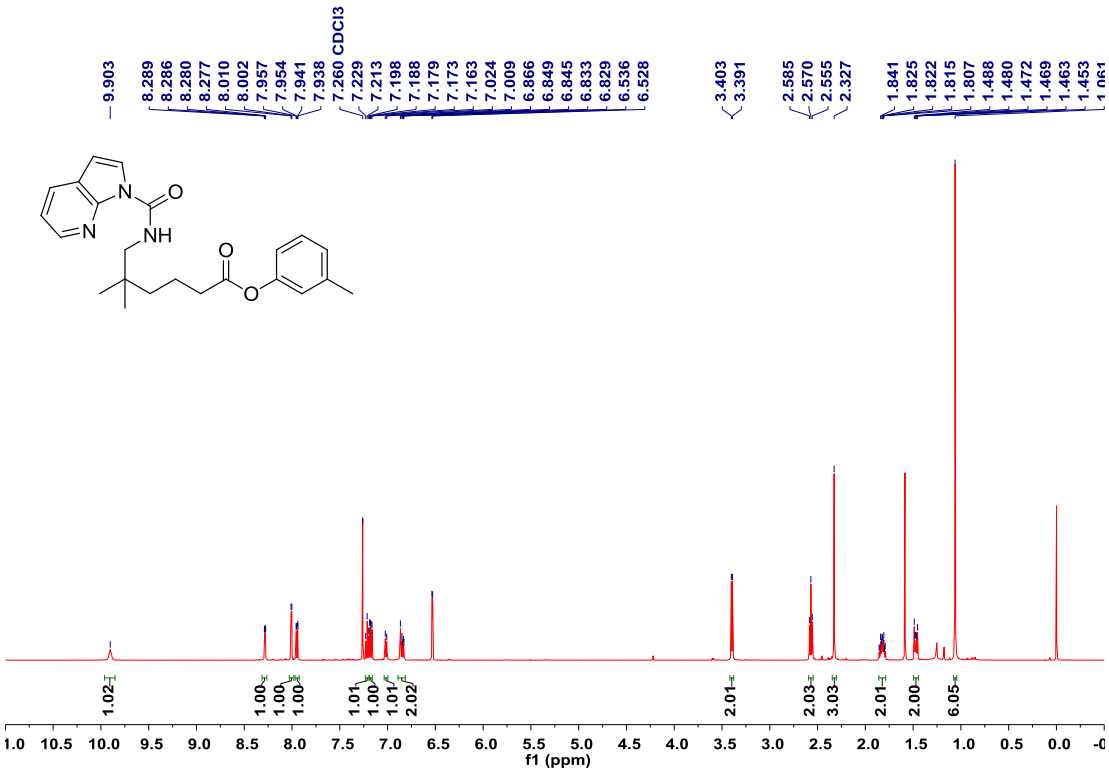


^{13}C NMR, 125 MHz, $CDCl_3$

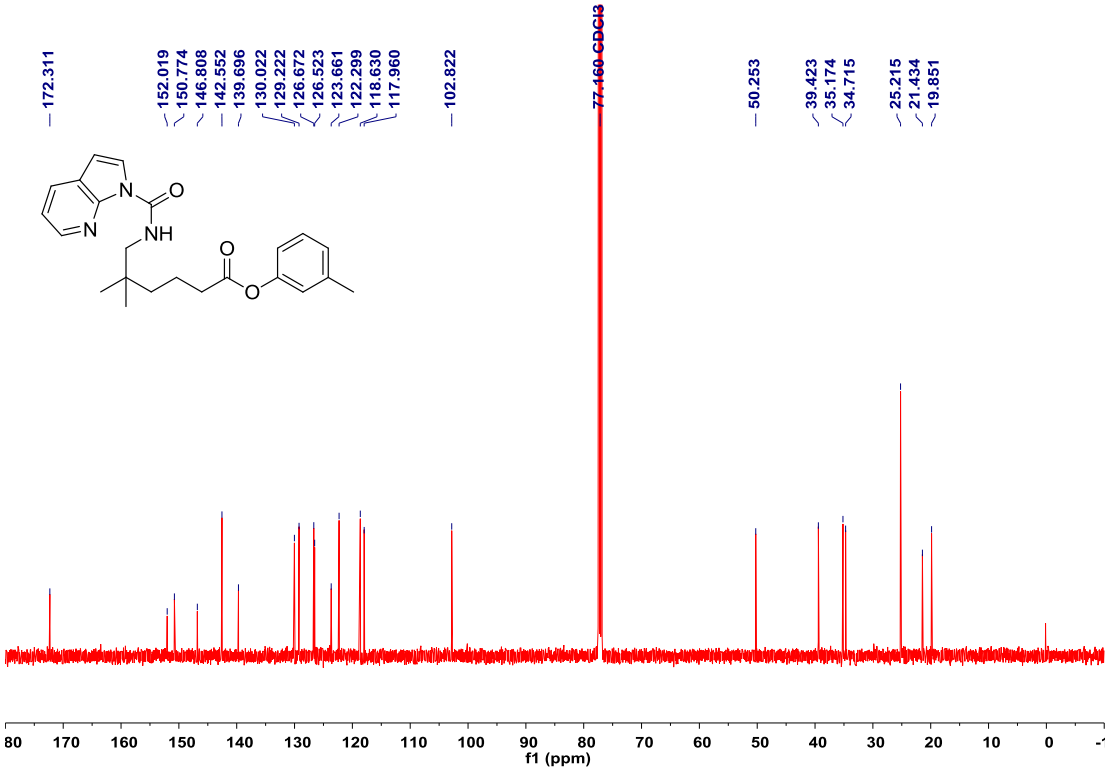


***m*-Tolyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3q)**

^{1}H NMR, 500 MHz, $CDCl_3$

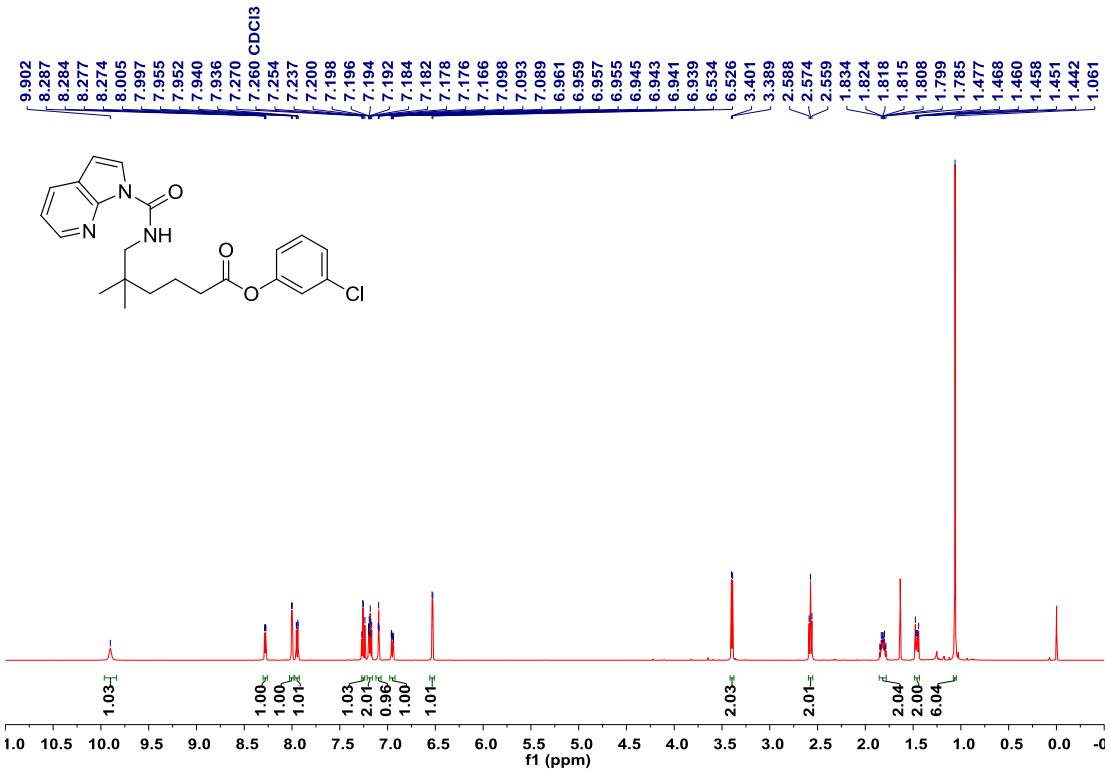


^{13}C NMR, 125 MHz, $CDCl_3$

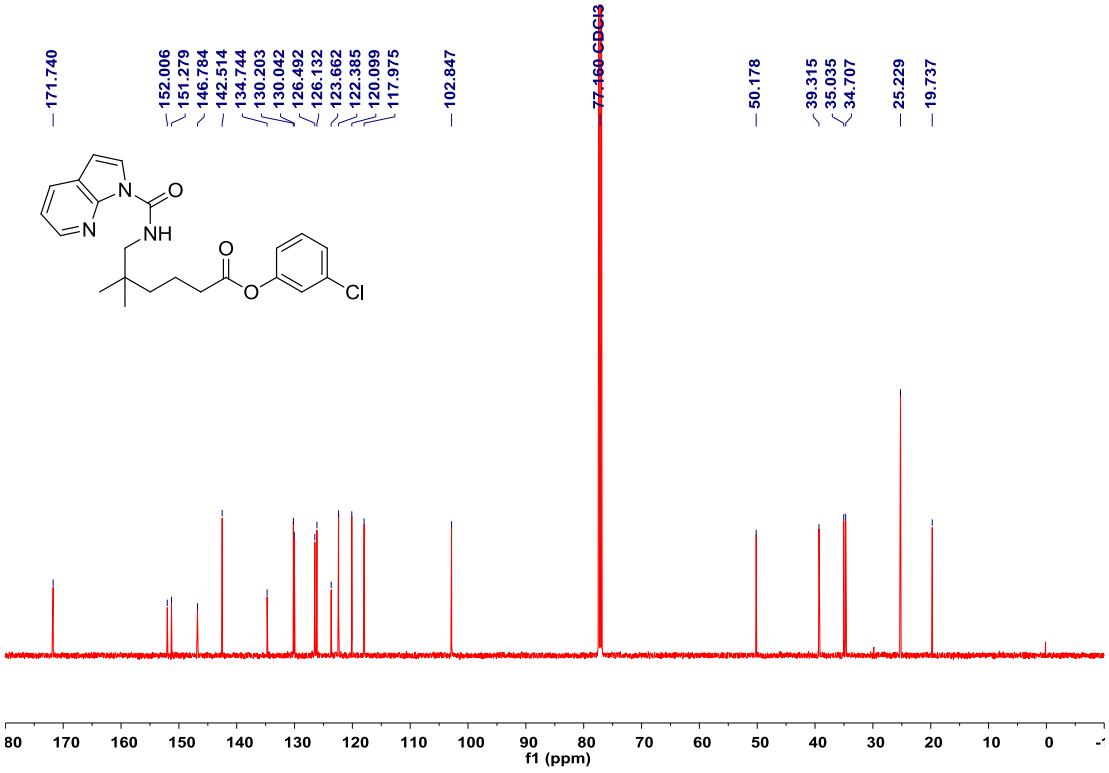


3-Chlorophenyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3r)

^{1}H NMR, 500 MHz, $CDCl_3$

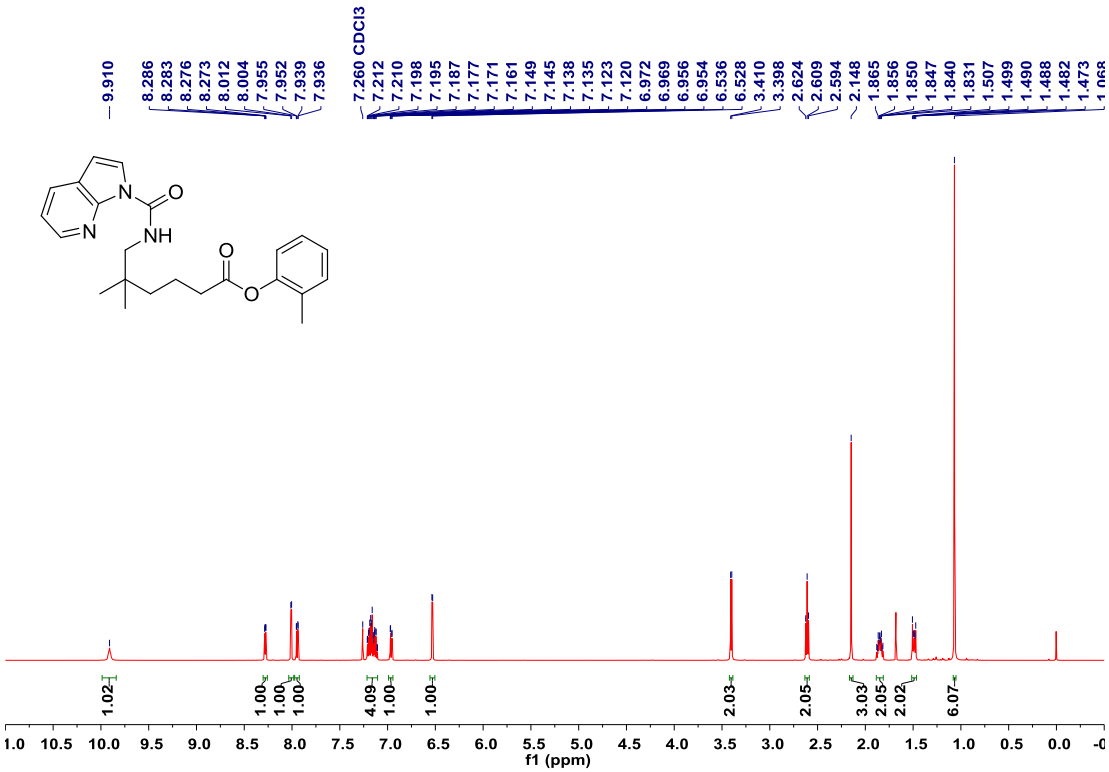


^{13}C NMR, 125 MHz, $CDCl_3$

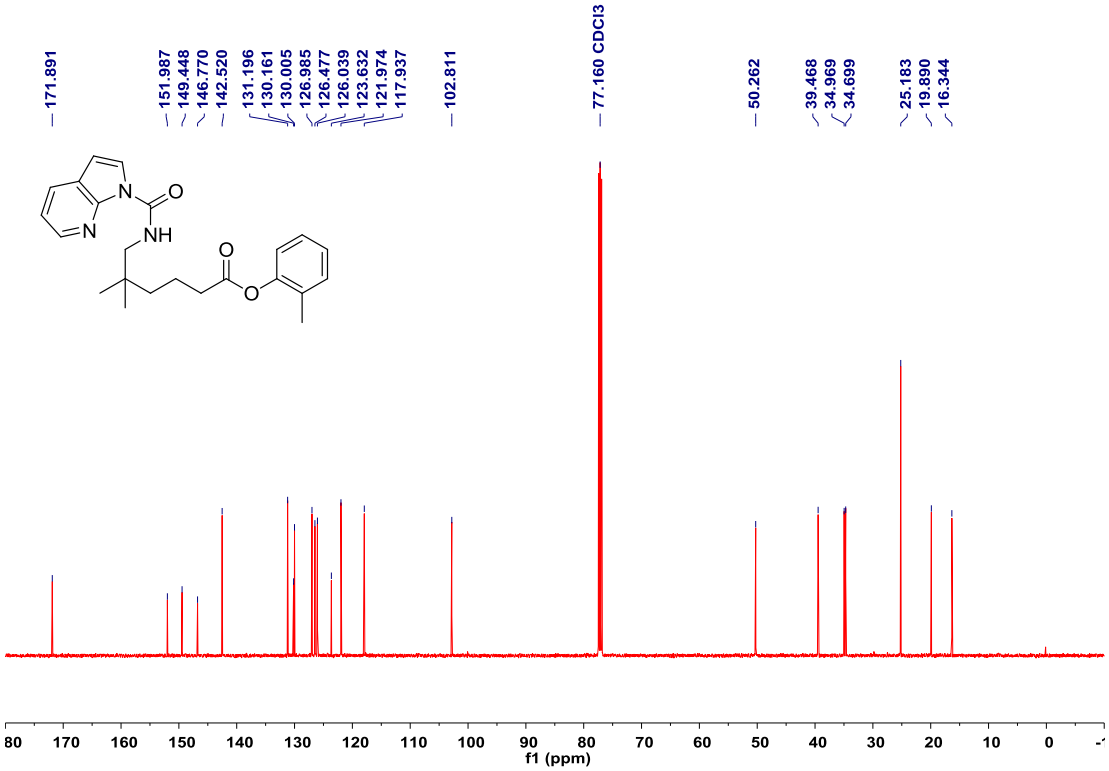


_o_-Tolyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3s)

^{1}H NMR, 500 MHz, $CDCl_3$

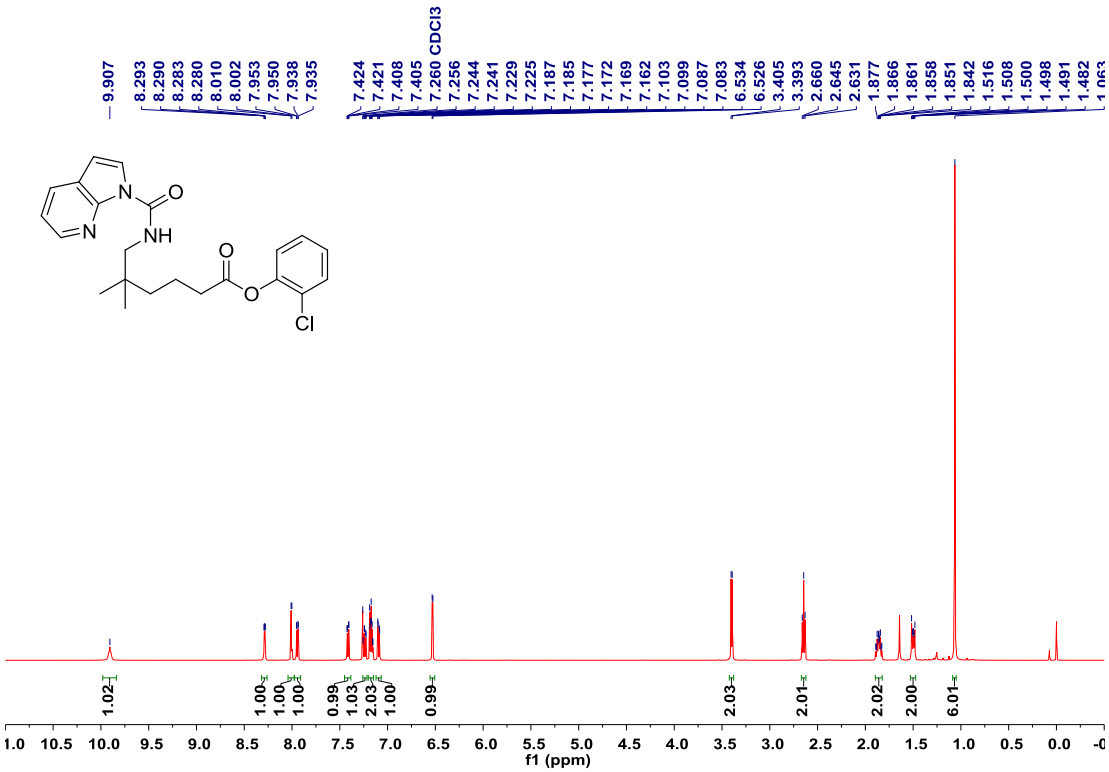


^{13}C NMR, 125 MHz, $CDCl_3$

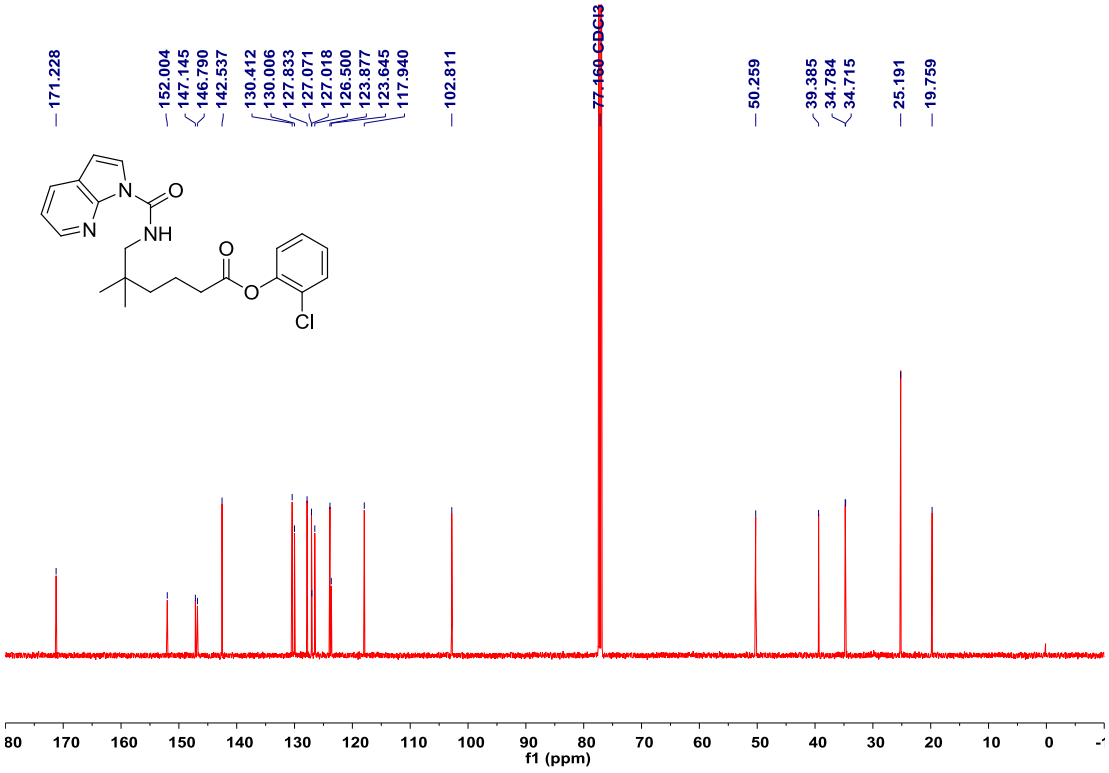


2-Chlorophenyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hexanoate (3t)

^{1}H NMR, 500 MHz, $CDCl_3$

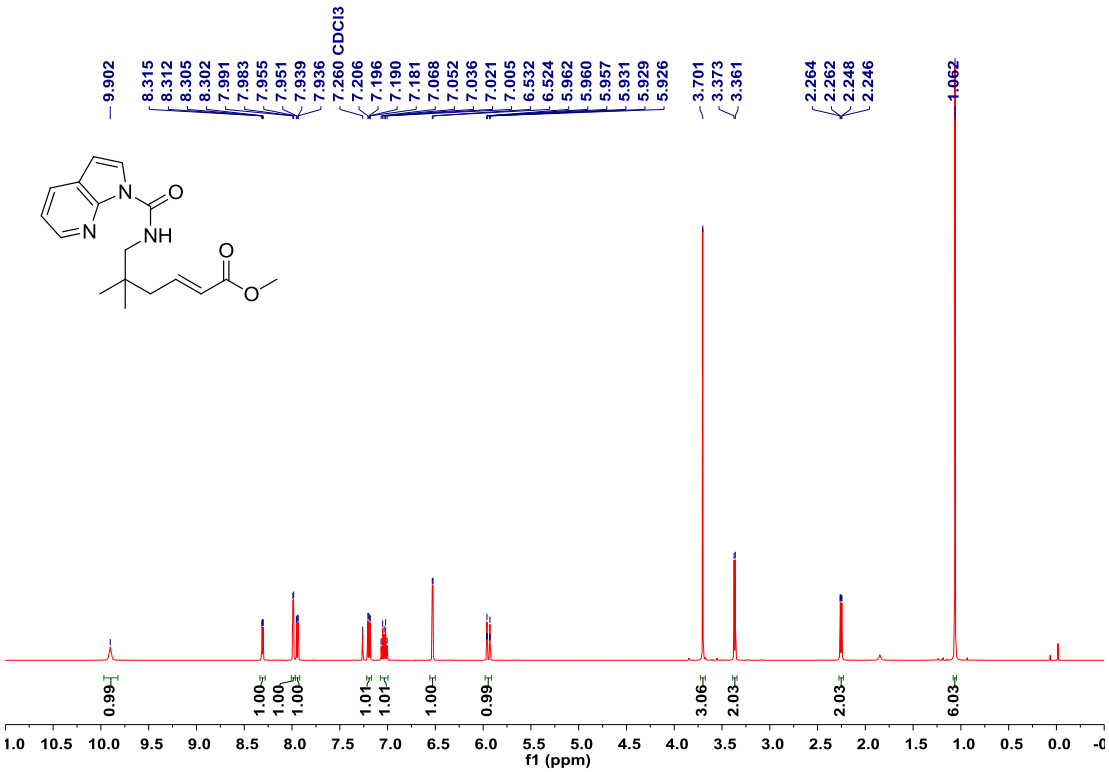


^{13}C NMR, 125 MHz, $CDCl_3$

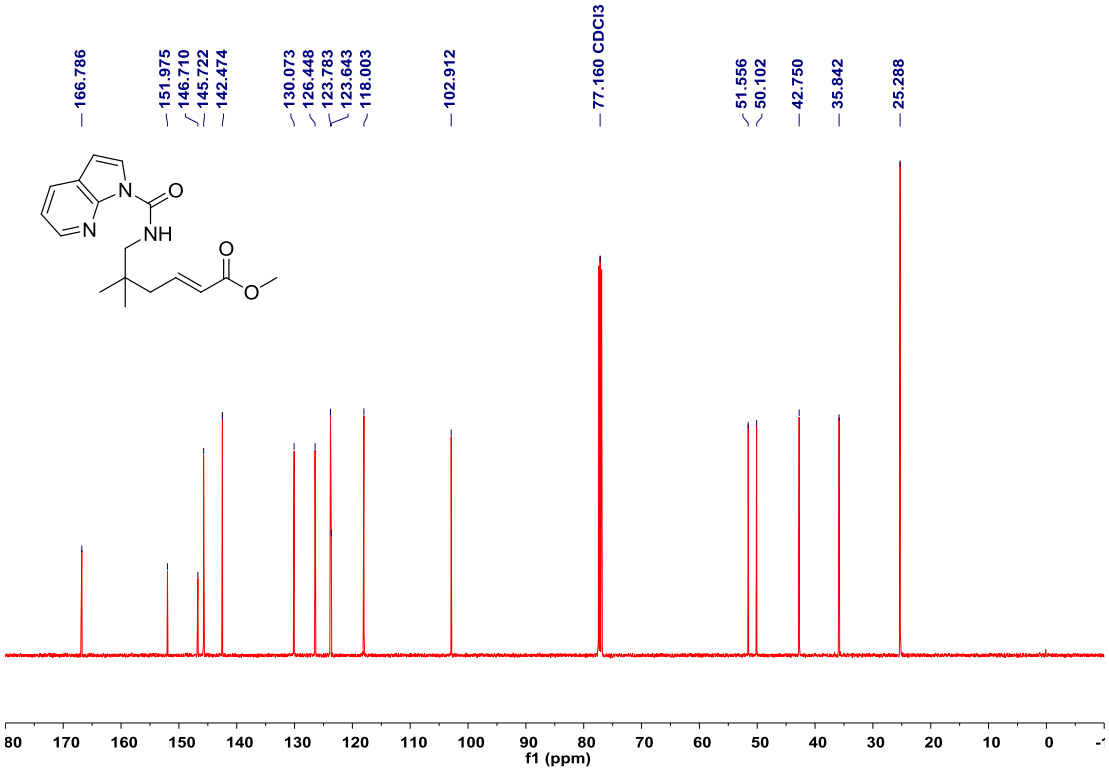


(*E*)-Methyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4a)

^{1}H NMR, 500 MHz, $CDCl_3$

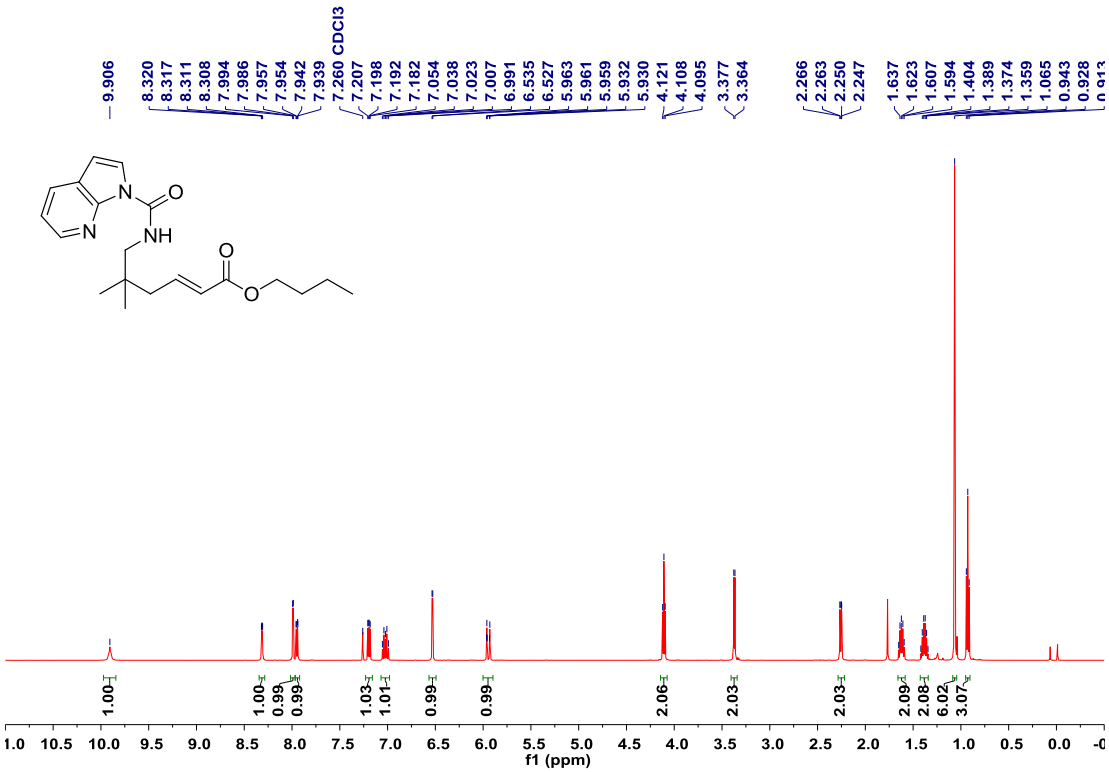


^{13}C NMR, 125 MHz, $CDCl_3$

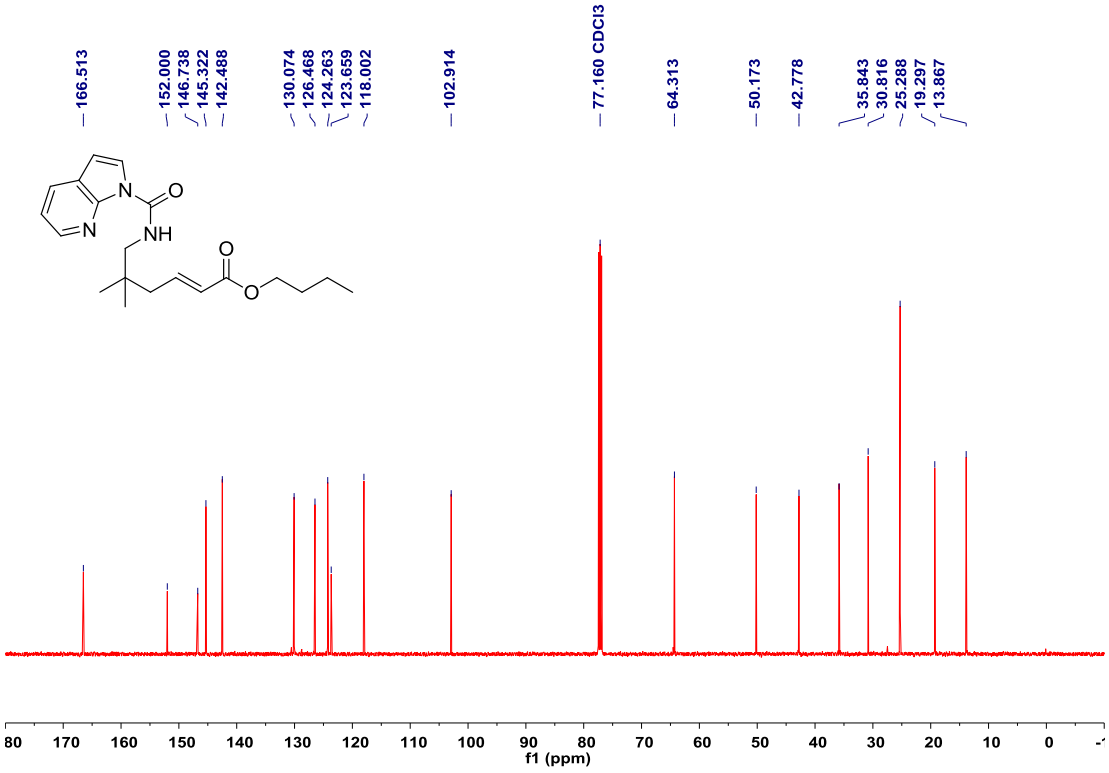


(*E*)-Butyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4b)

^{1}H NMR, 500 MHz, $CDCl_3$

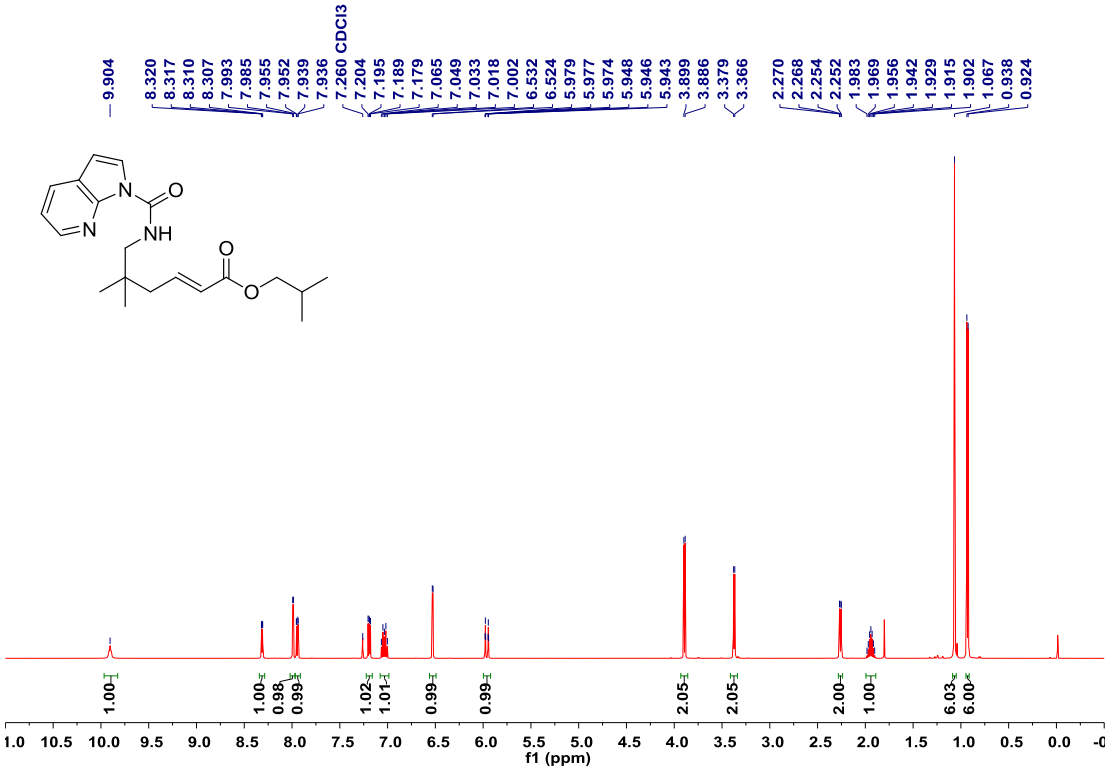


^{13}C NMR, 125 MHz, $CDCl_3$

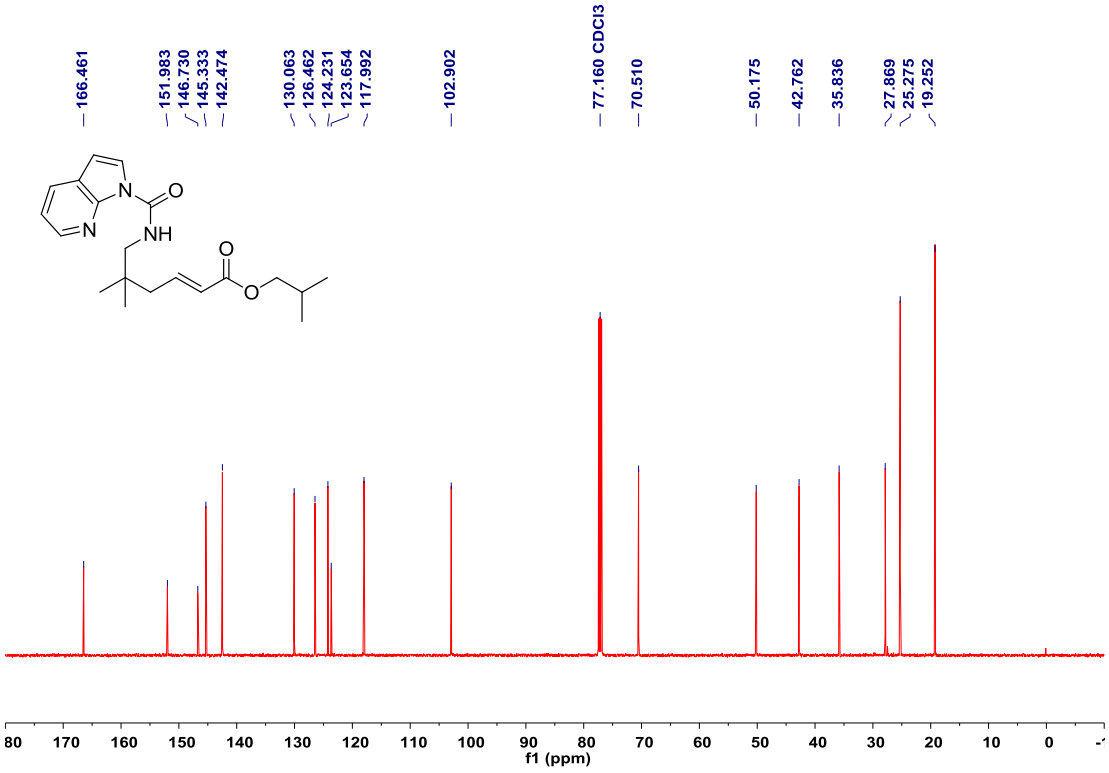


(*E*)-Isobutyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4c)

^{1}H NMR, 500 MHz, $CDCl_3$

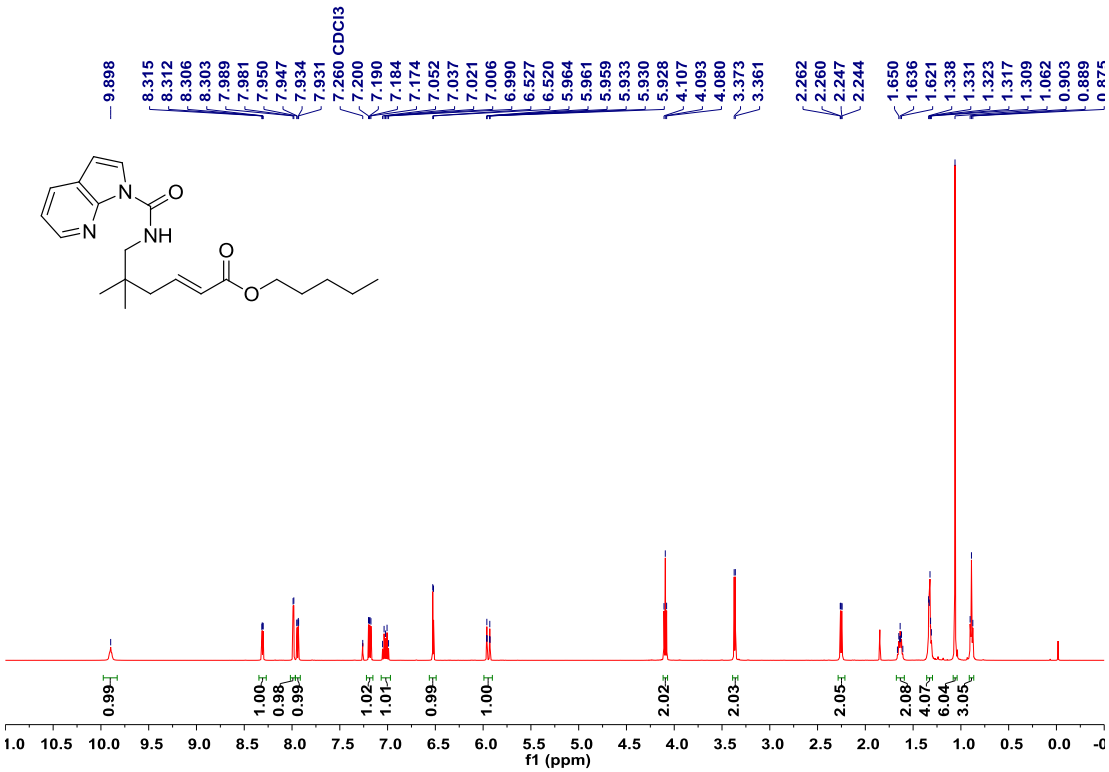


^{13}C NMR, 125 MHz, $CDCl_3$

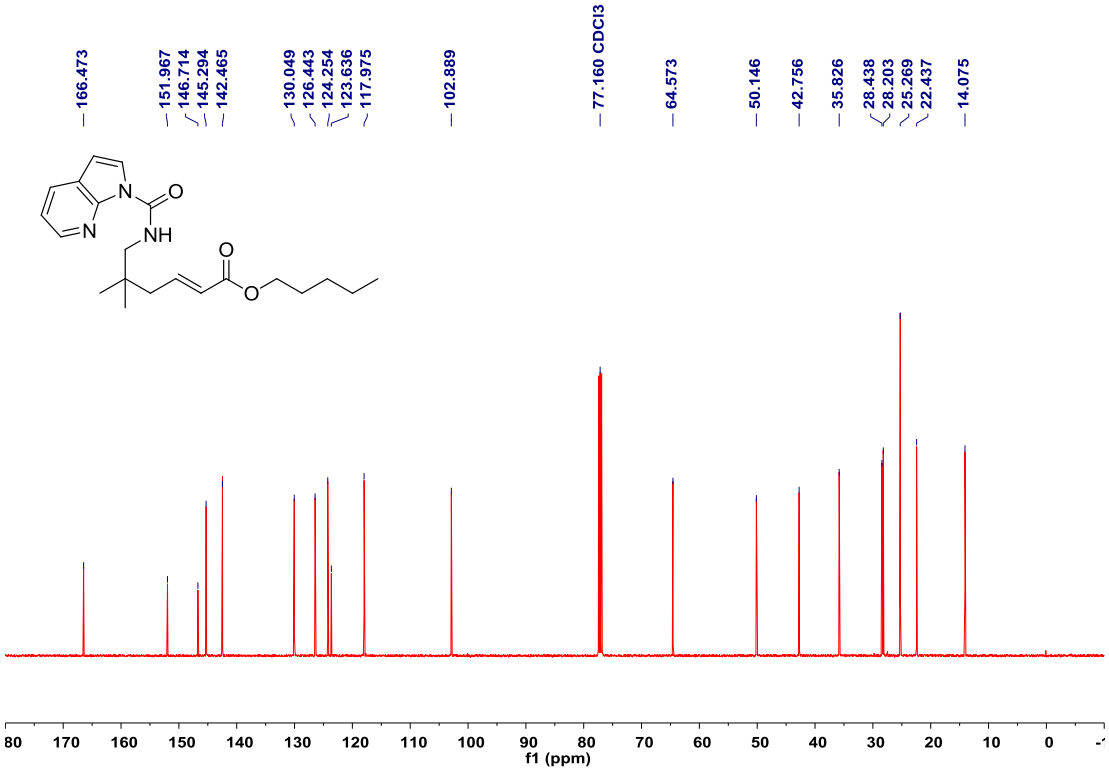


(*E*)-Pentyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4d)

^{1}H NMR, 500 MHz, $CDCl_3$

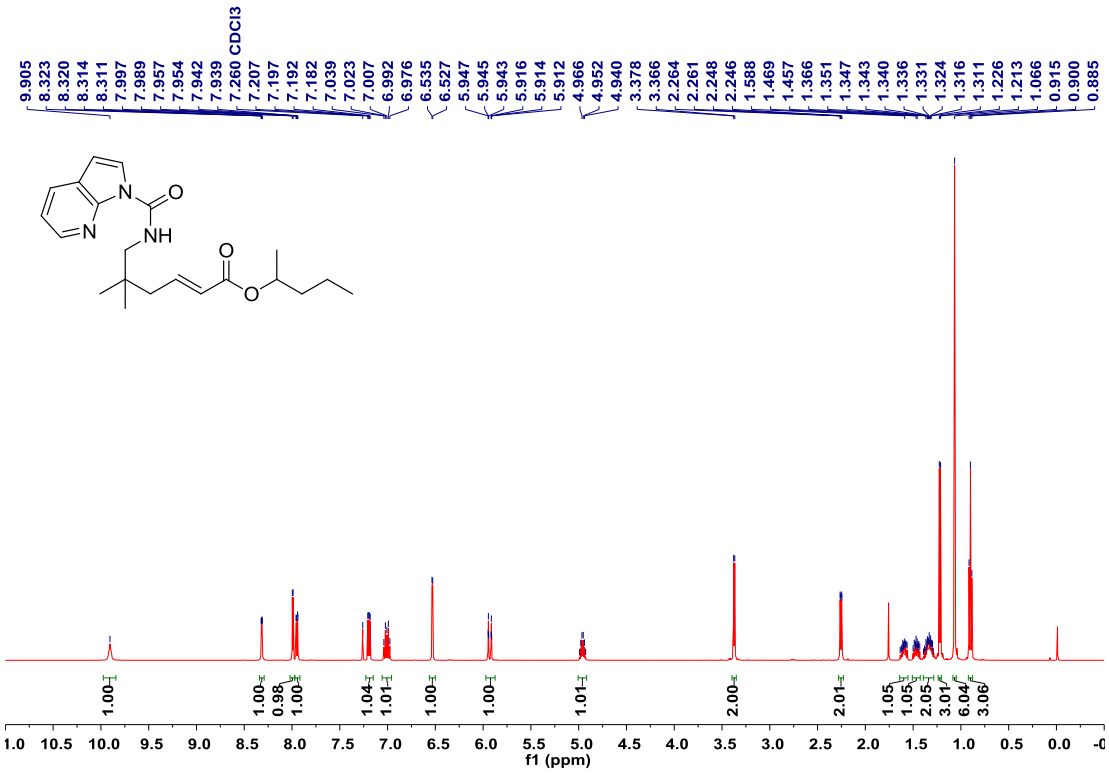


^{13}C NMR, 125 MHz, $CDCl_3$

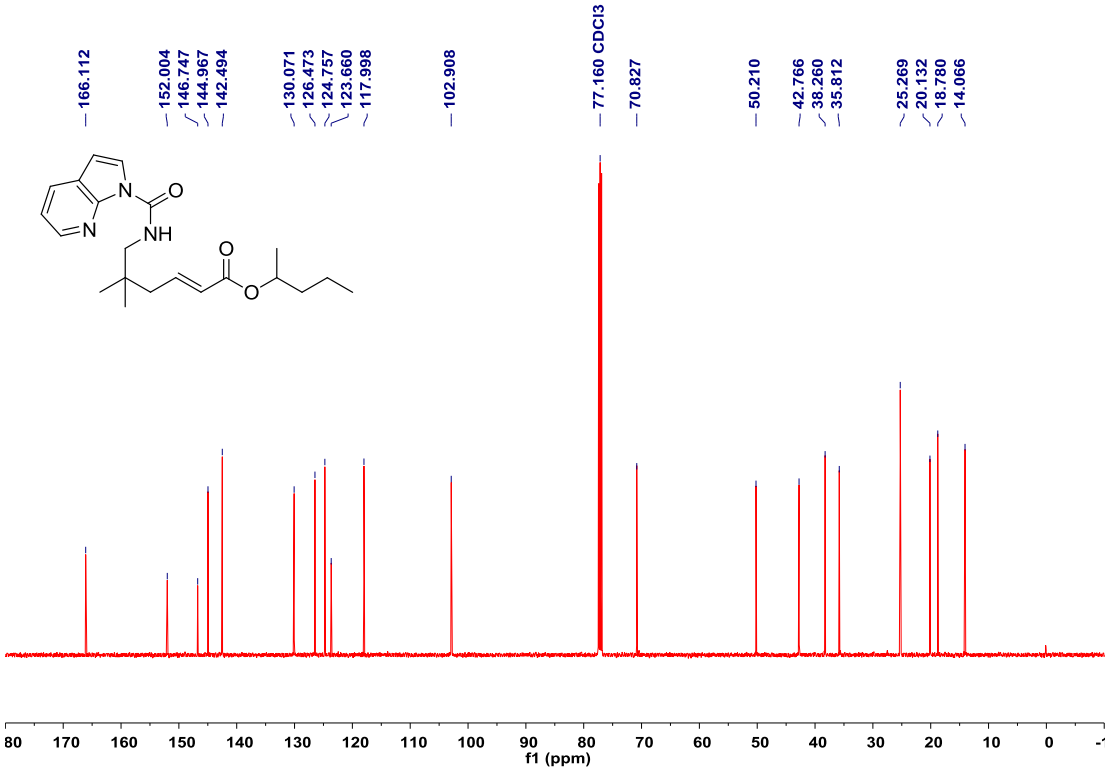


(*E*)-Pentan-2-yl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4e)

^{1}H NMR, 500 MHz, $CDCl_3$

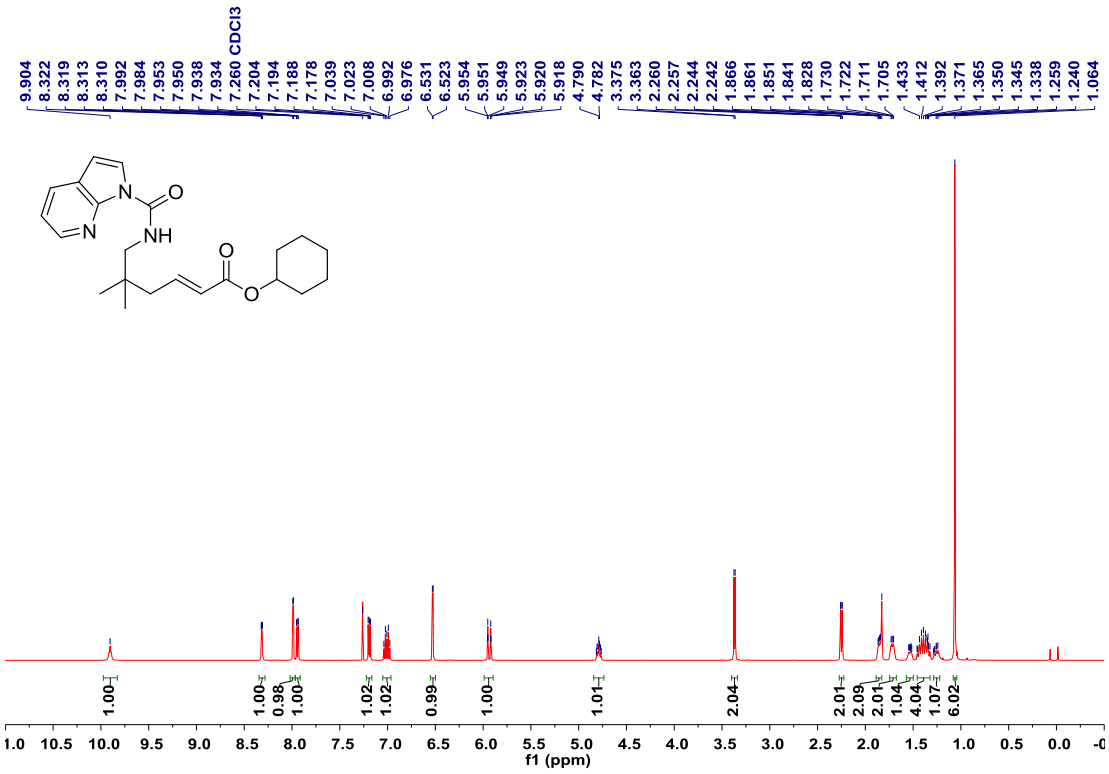


^{13}C NMR, 125 MHz, $CDCl_3$

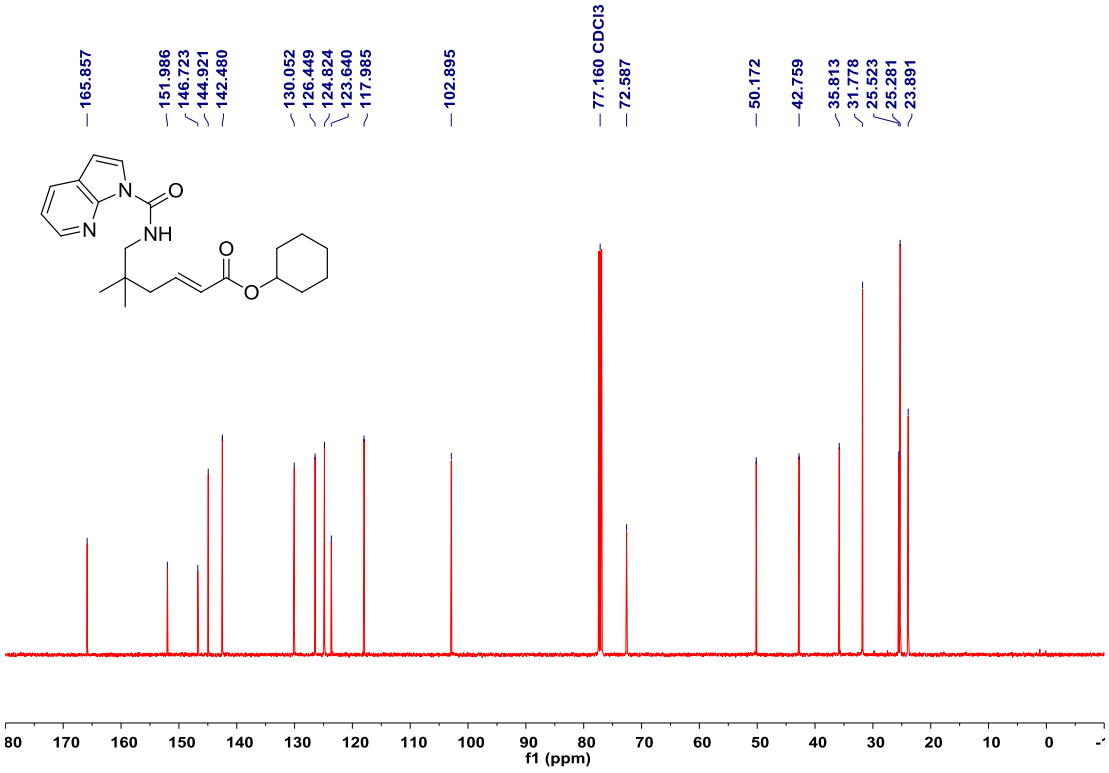


(*E*)-Cyclohexyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4f)

^{1}H NMR, 500 MHz, $CDCl_3$

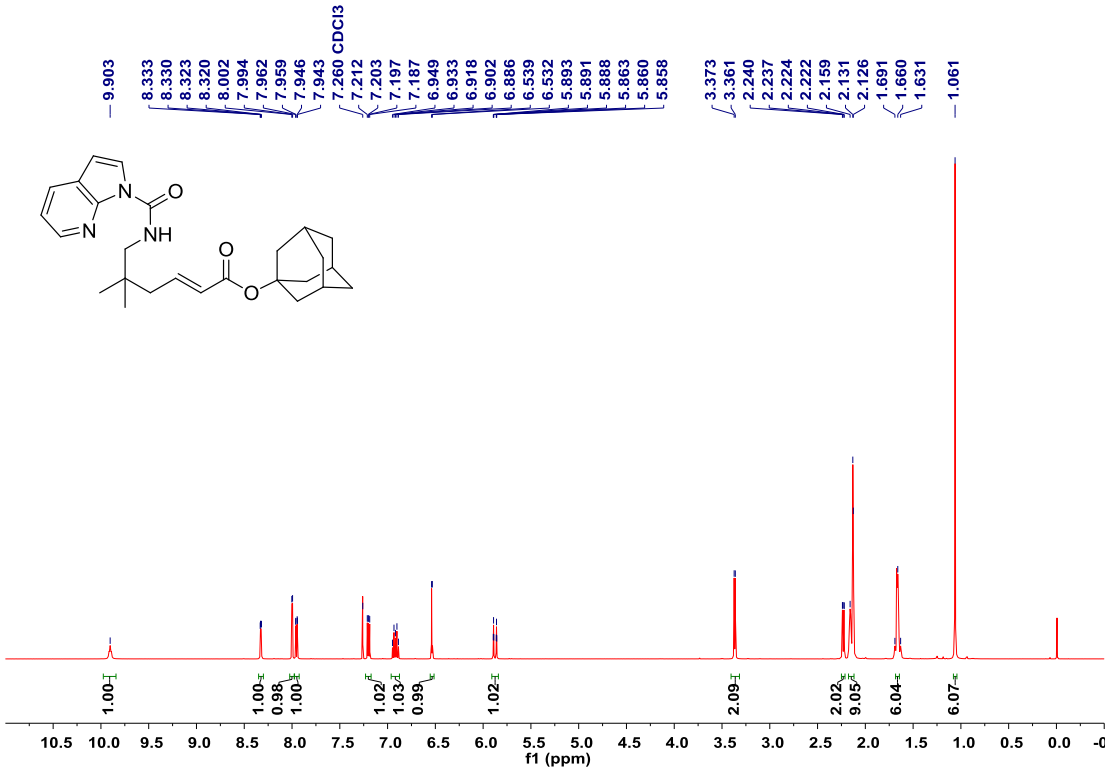


^{13}C NMR, 125 MHz, $CDCl_3$

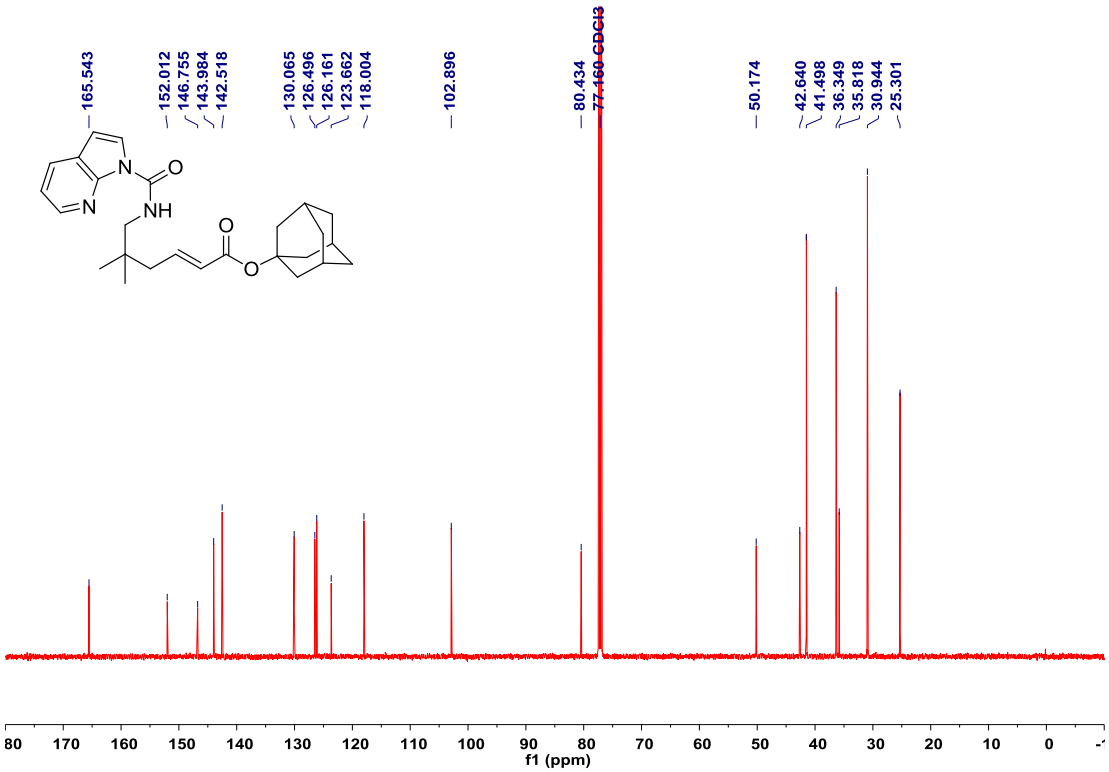


(*E*)-(3*s*,5*s*,7*s*)-Adamantan-1-yl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido) hex -2-enoate (4g)

^{1}H NMR, 500 MHz, $CDCl_3$

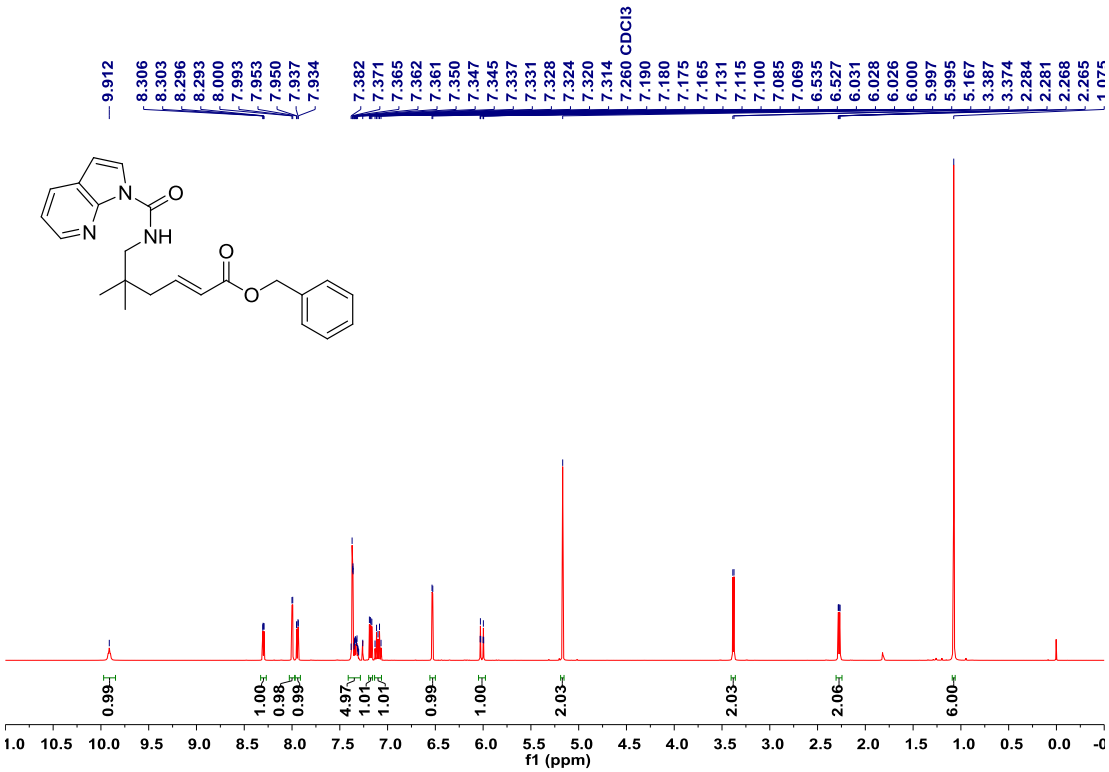


^{13}C NMR, 125 MHz, $CDCl_3$

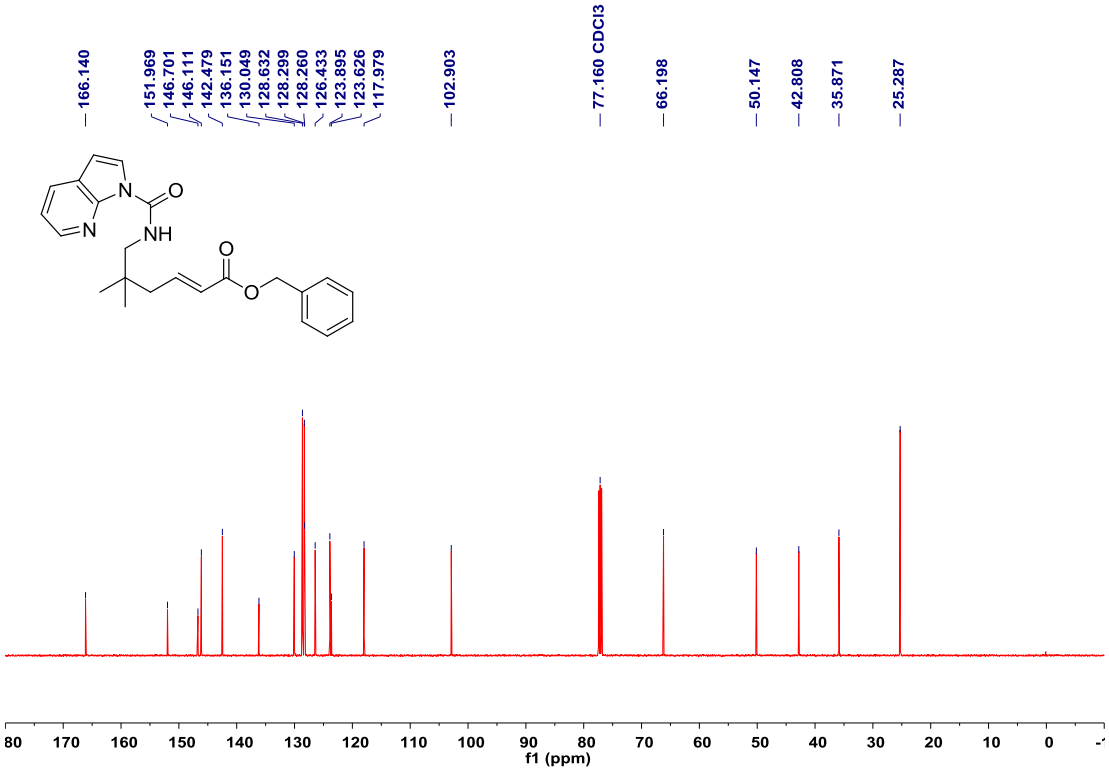


(*E*)-Benzyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4h)

^{1}H NMR, 500 MHz, $CDCl_3$

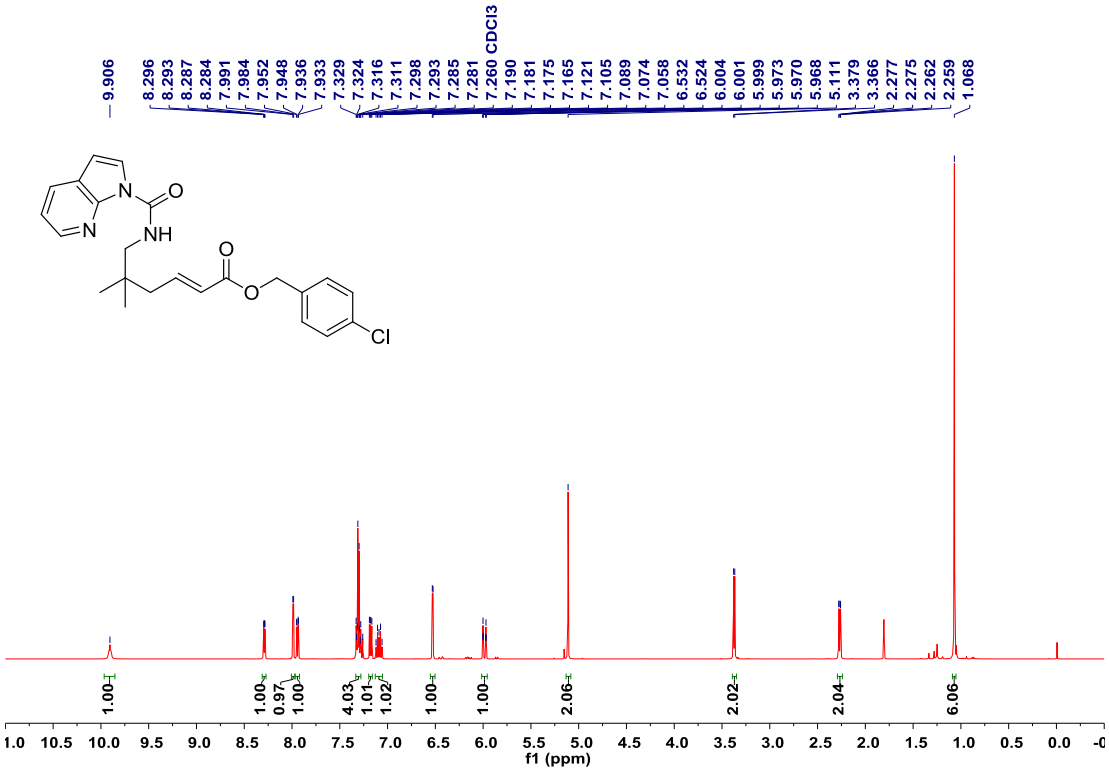


^{13}C NMR, 125 MHz, $CDCl_3$

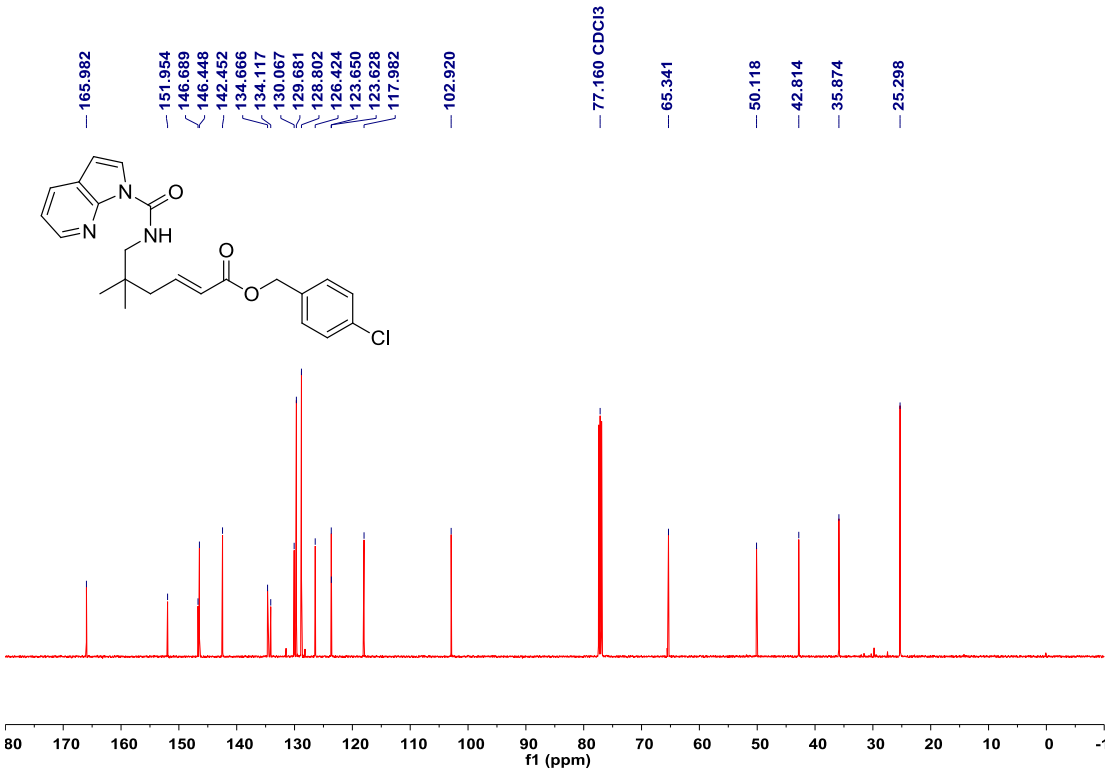


(*E*)-4-Chlorobenzyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4i)

^{1}H NMR, 500 MHz, $CDCl_3$

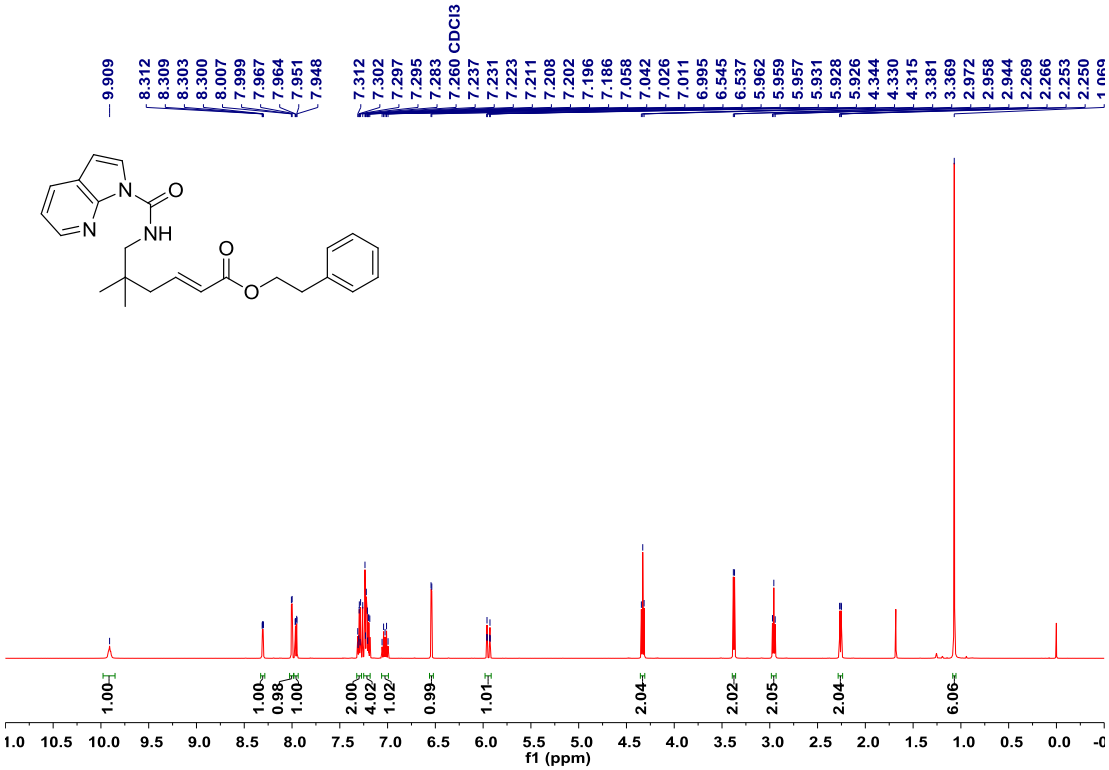


^{13}C NMR, 125 MHz, $CDCl_3$

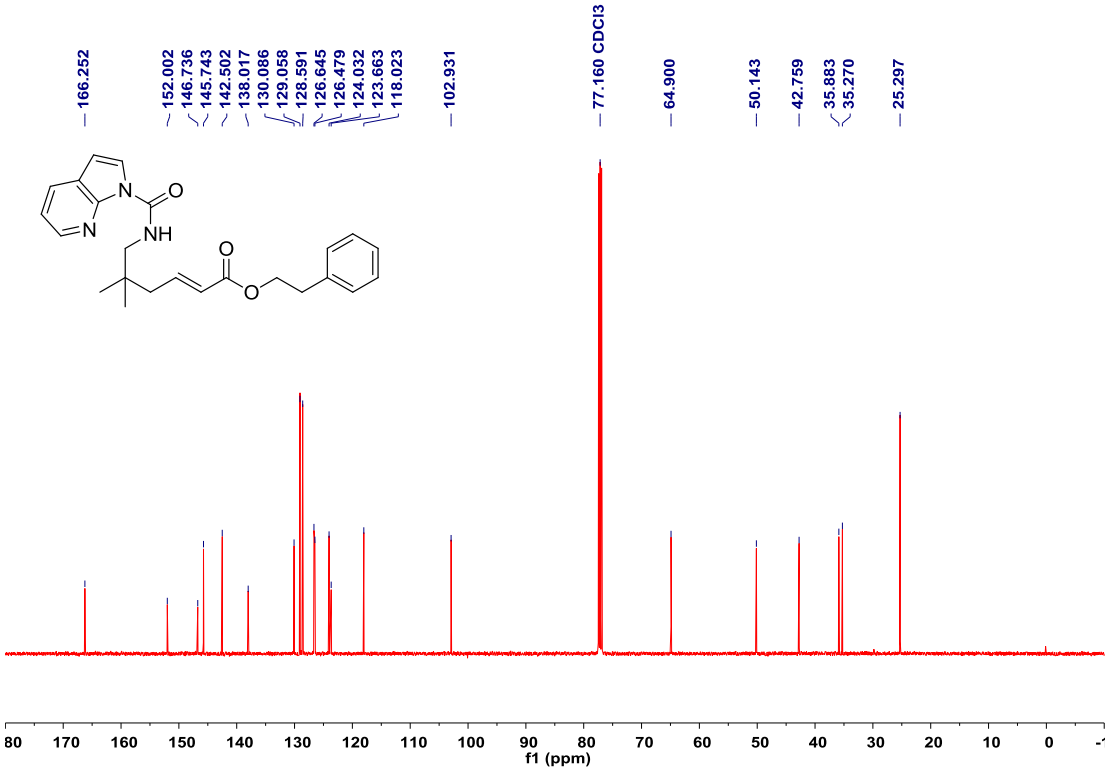


(*E*)-Phenethyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4j)

^{1}H NMR, 500 MHz, $CDCl_3$

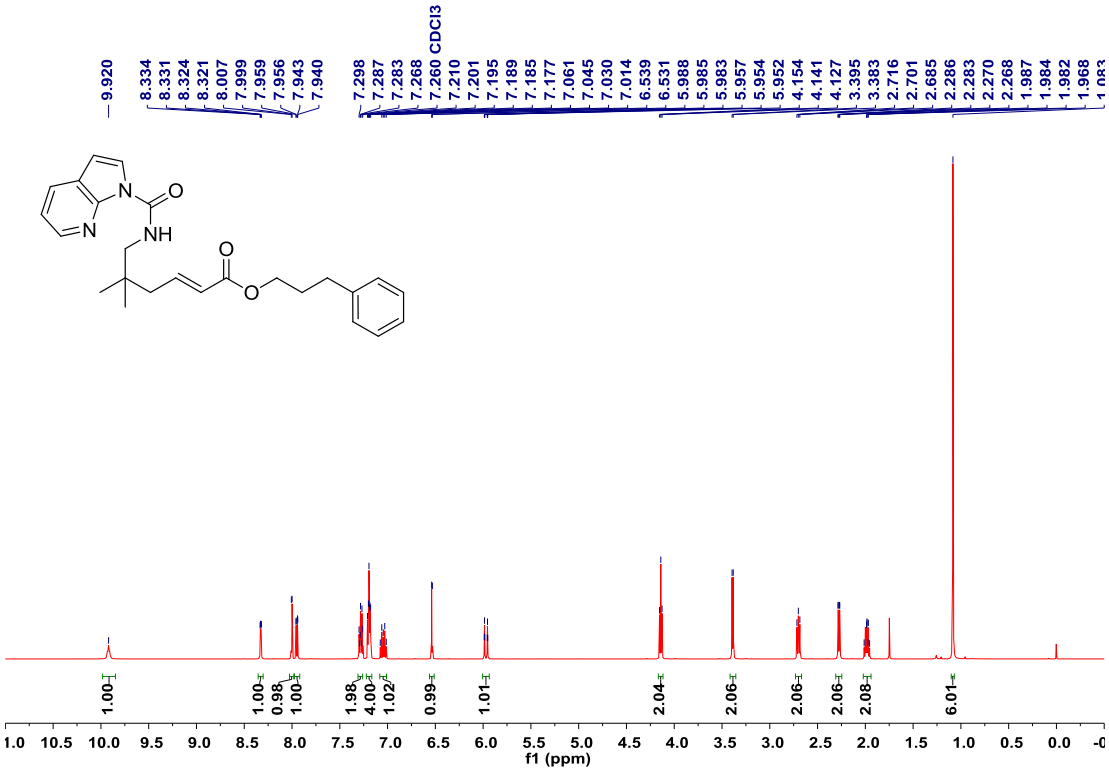


^{13}C NMR, 125 MHz, $CDCl_3$

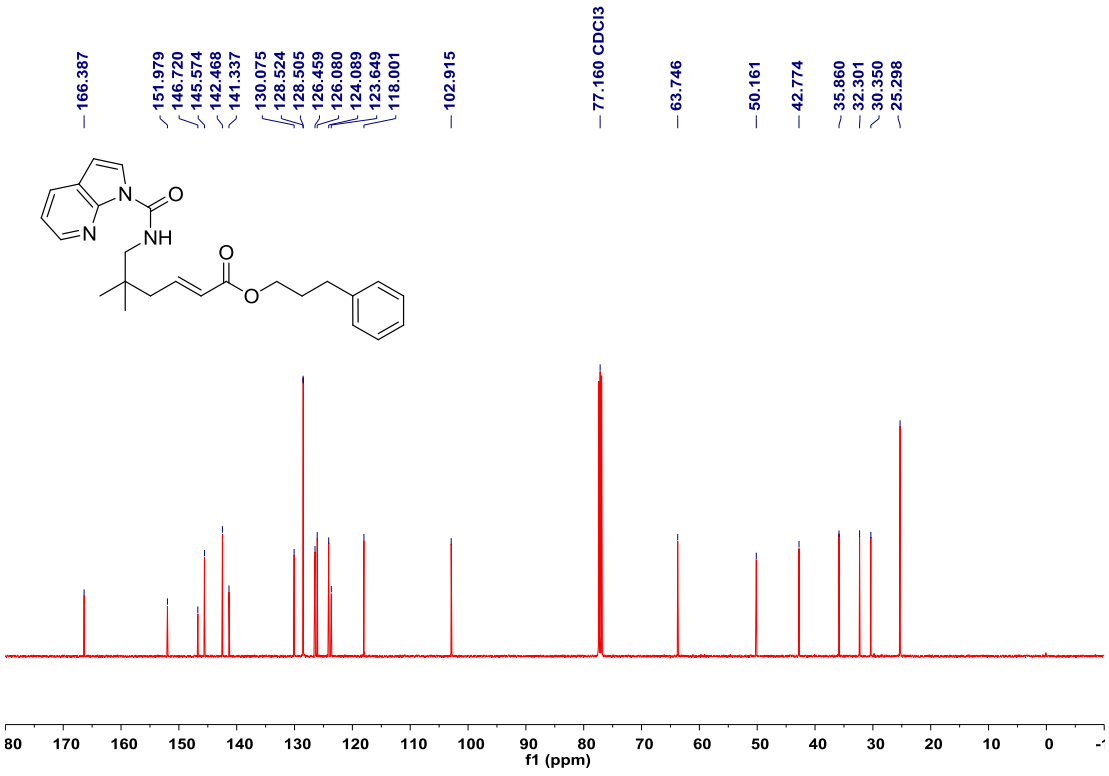


(*E*)-3-Phenylpropyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4k)

^{1}H NMR, 500 MHz, $CDCl_3$

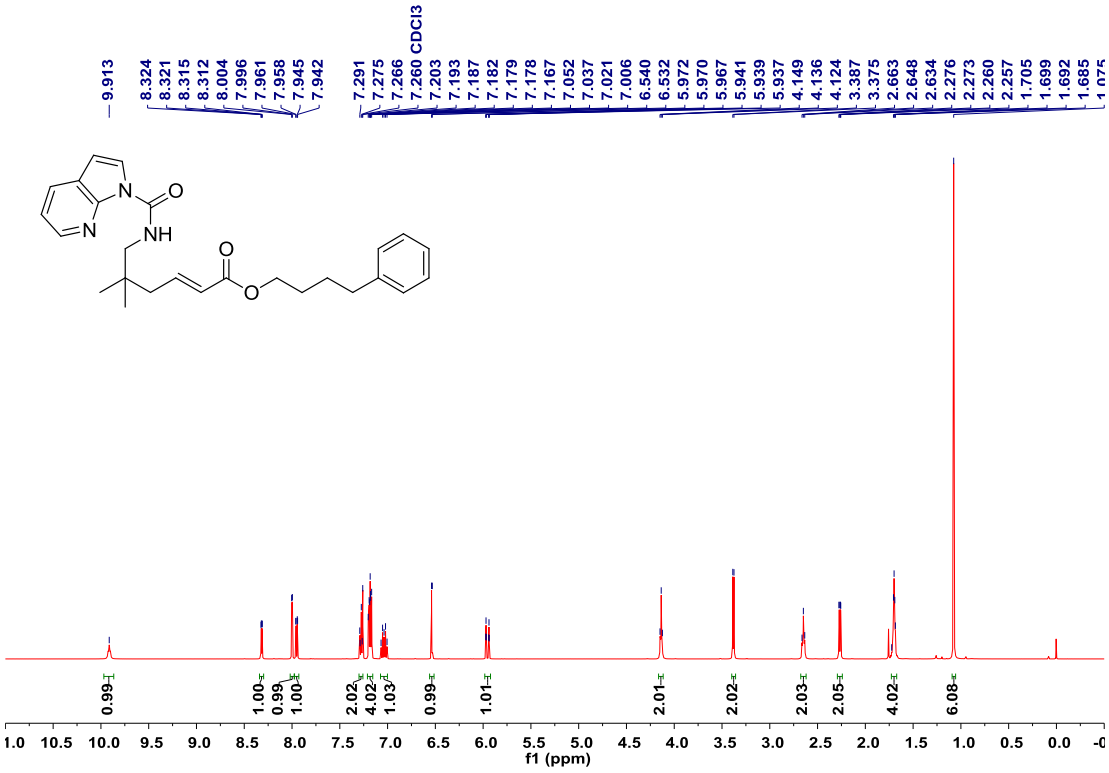


^{13}C NMR, 125 MHz, $CDCl_3$

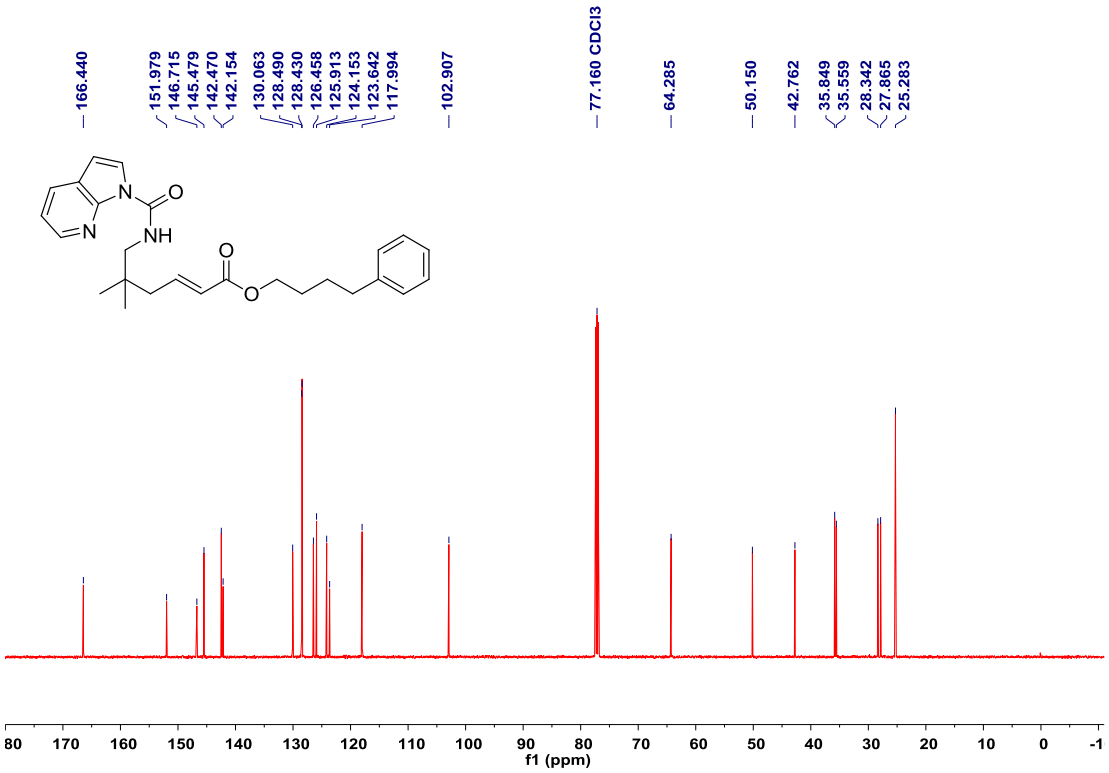


(*E*)-4-Phenylbutyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4l)

^{1}H NMR, 500 MHz, $CDCl_3$

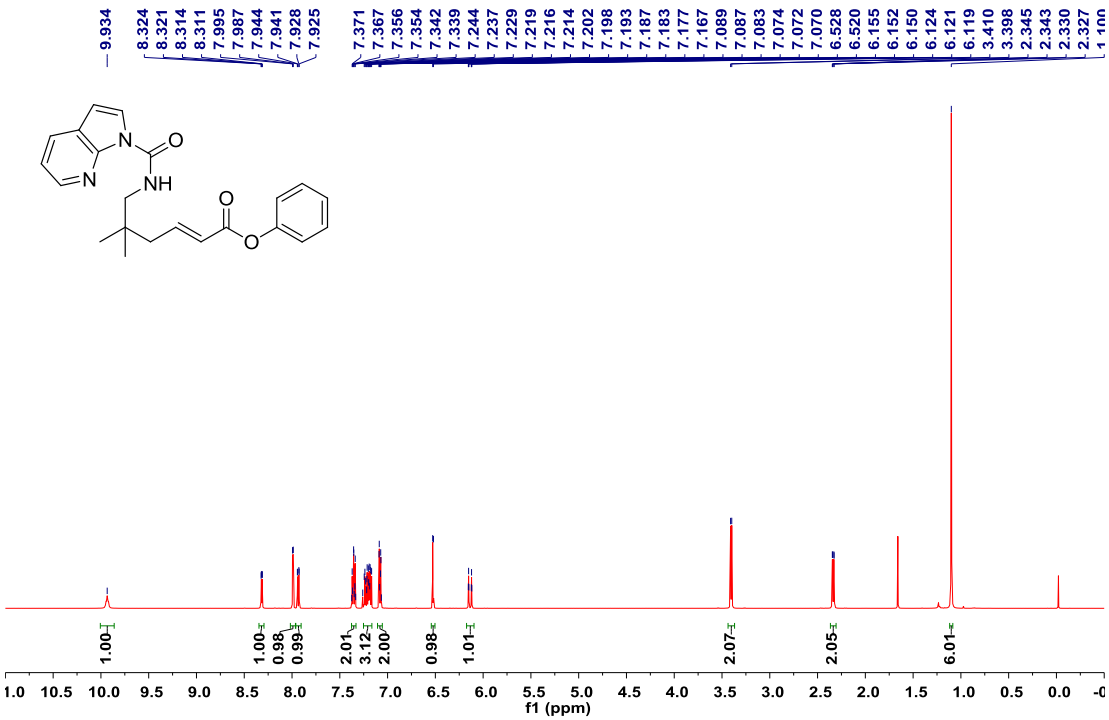


^{13}C NMR, 125 MHz, $CDCl_3$

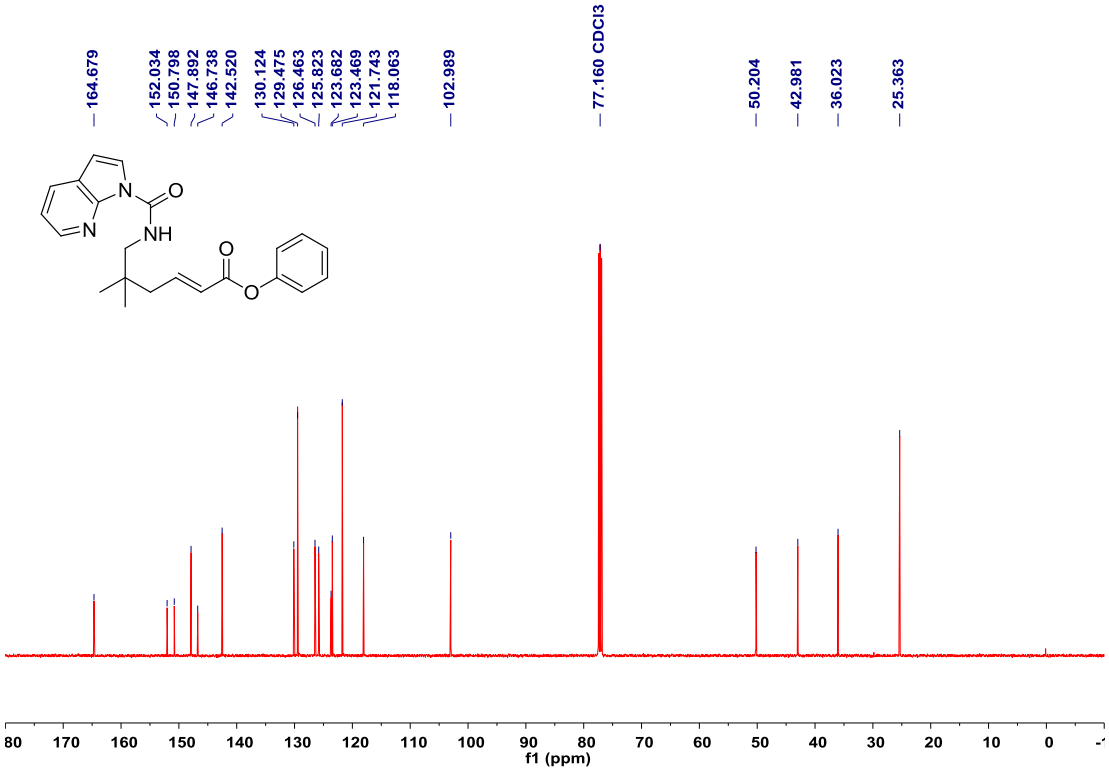


(*E*)-Phenyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4m)

^{1}H NMR, 500 MHz, $CDCl_3$

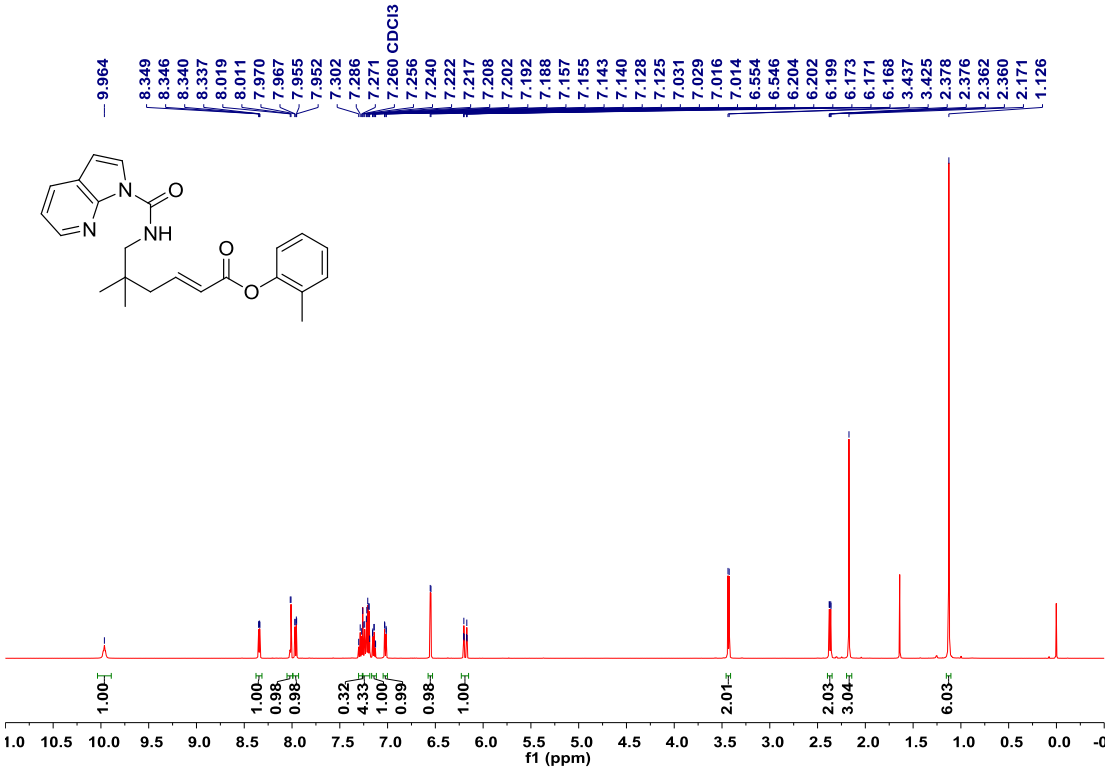


^{13}C NMR, 125 MHz, $CDCl_3$

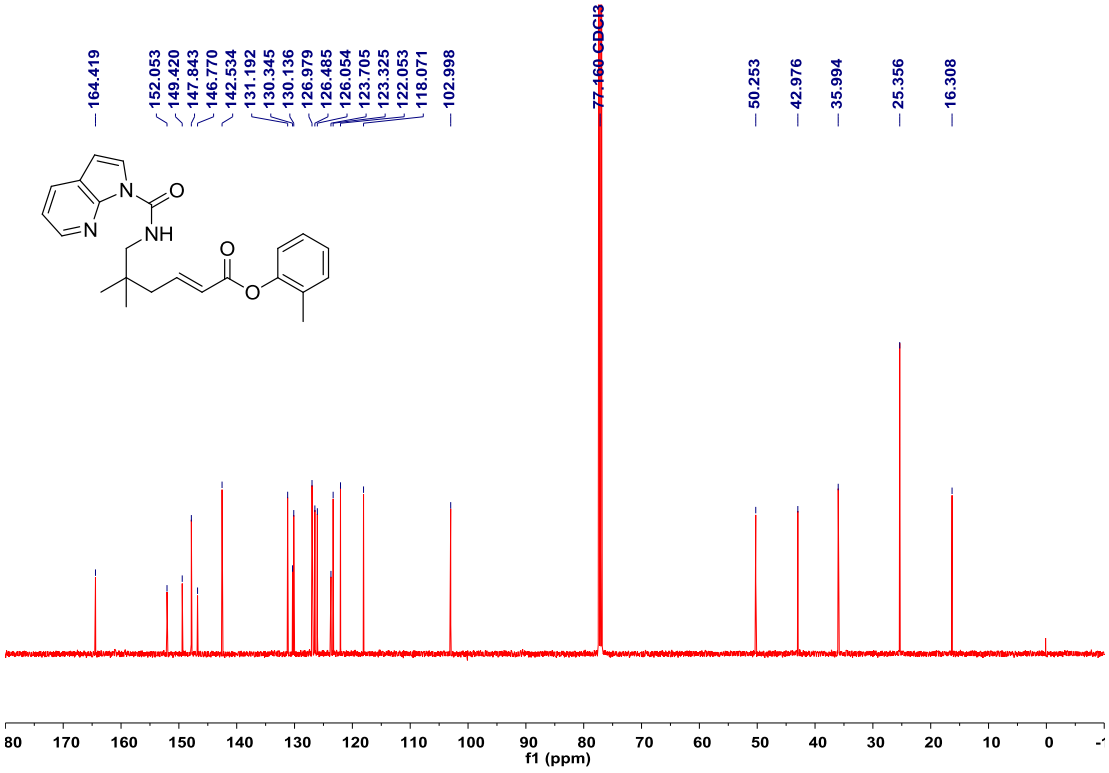


(*E*)-*o*-Tolyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4n)

^{1}H NMR, 500 MHz, $CDCl_3$

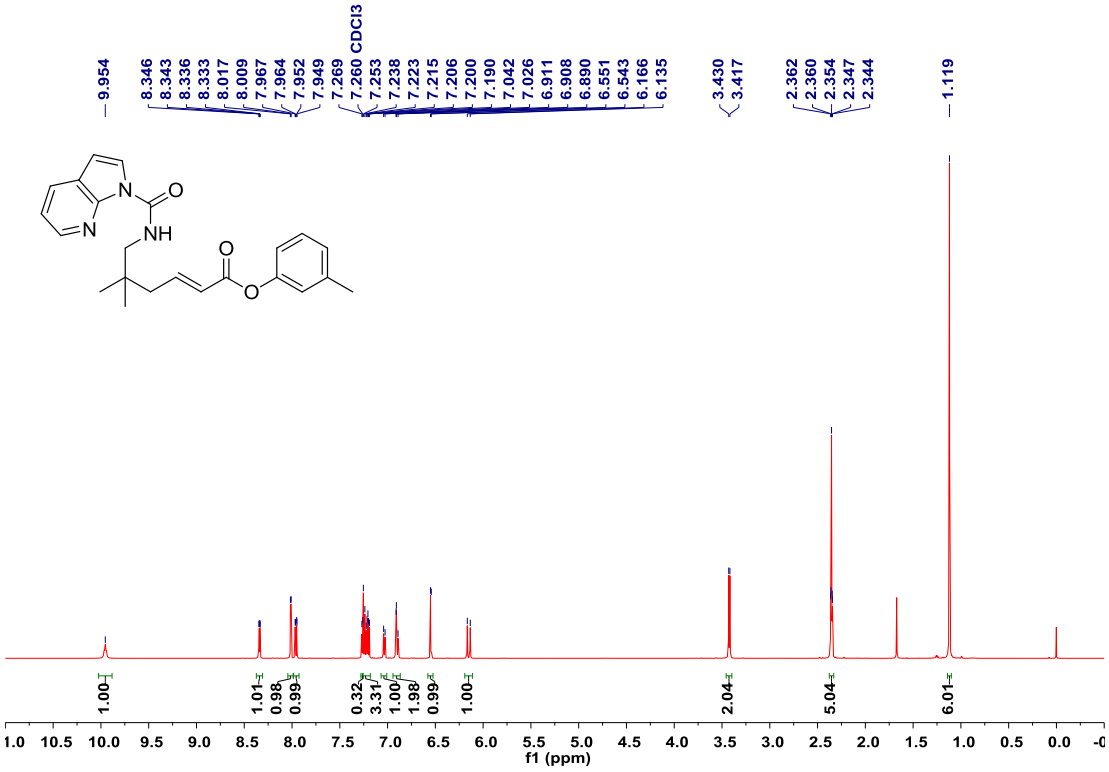


^{13}C NMR, 125 MHz, $CDCl_3$

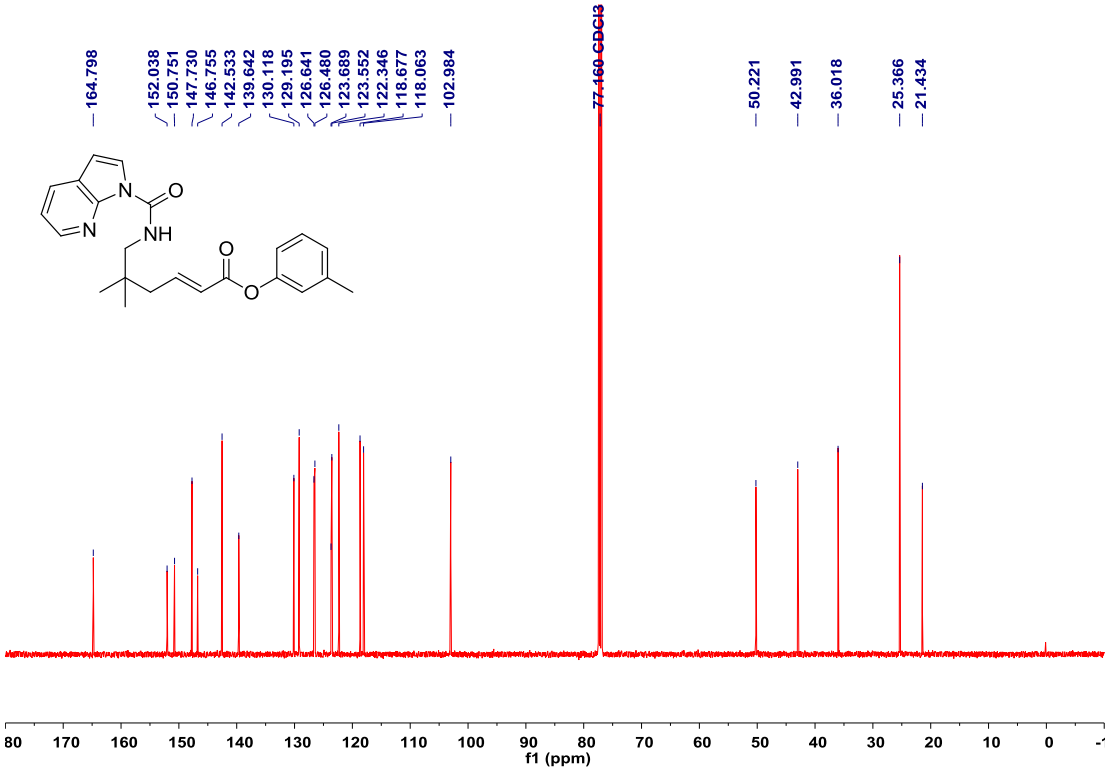


(*E*)-*m*-Tolyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4o)

^{1}H NMR, 500 MHz, $CDCl_3$

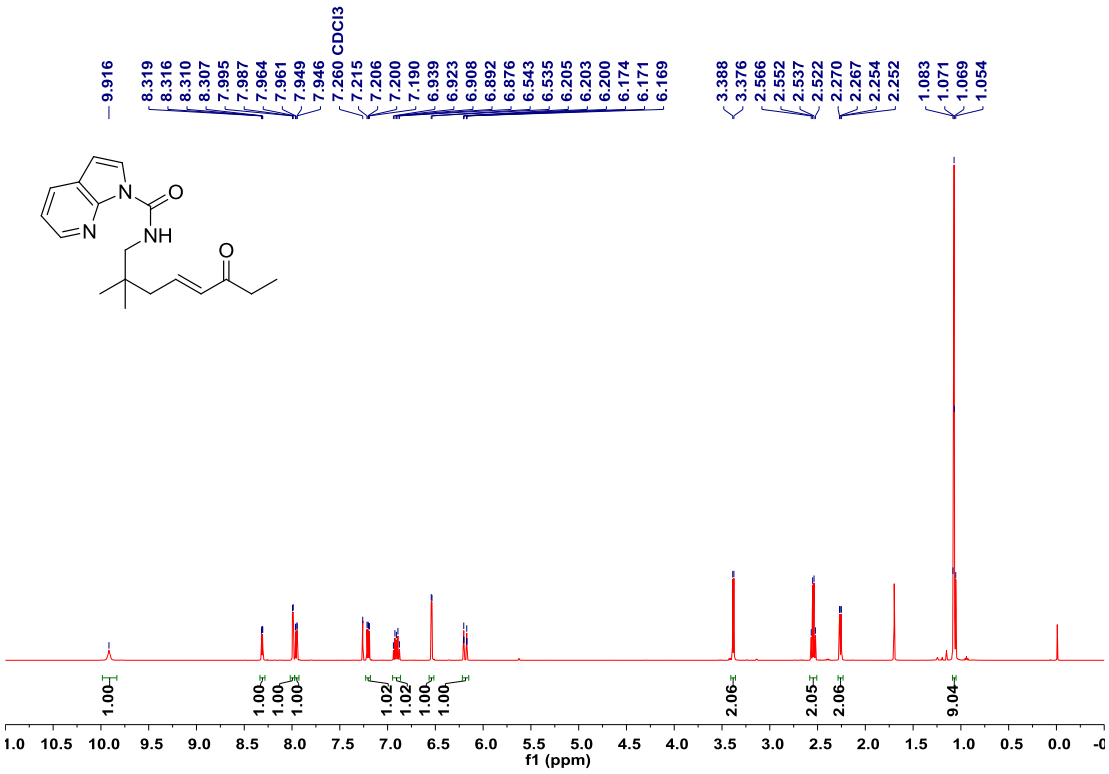


^{13}C NMR, 125 MHz, $CDCl_3$

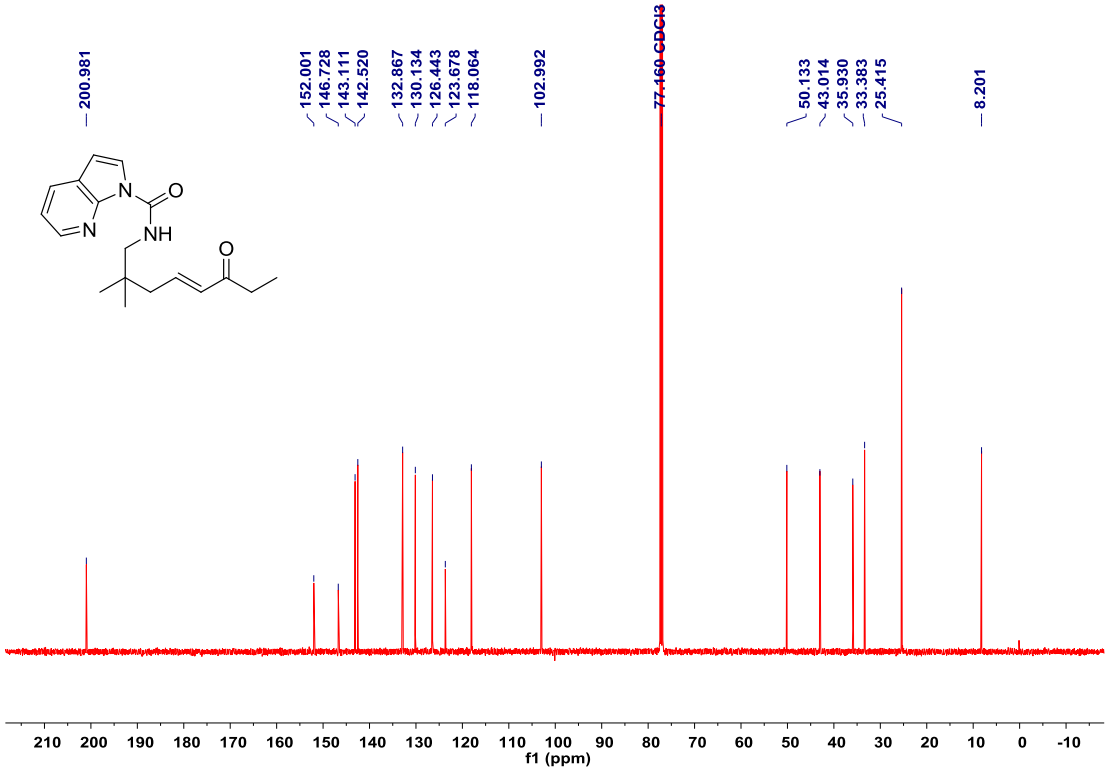


(*E*)-*N*-(2,2-Dimethyl-6-oxooct-4-en-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide (4p)

^{1}H NMR, 500 MHz, $CDCl_3$

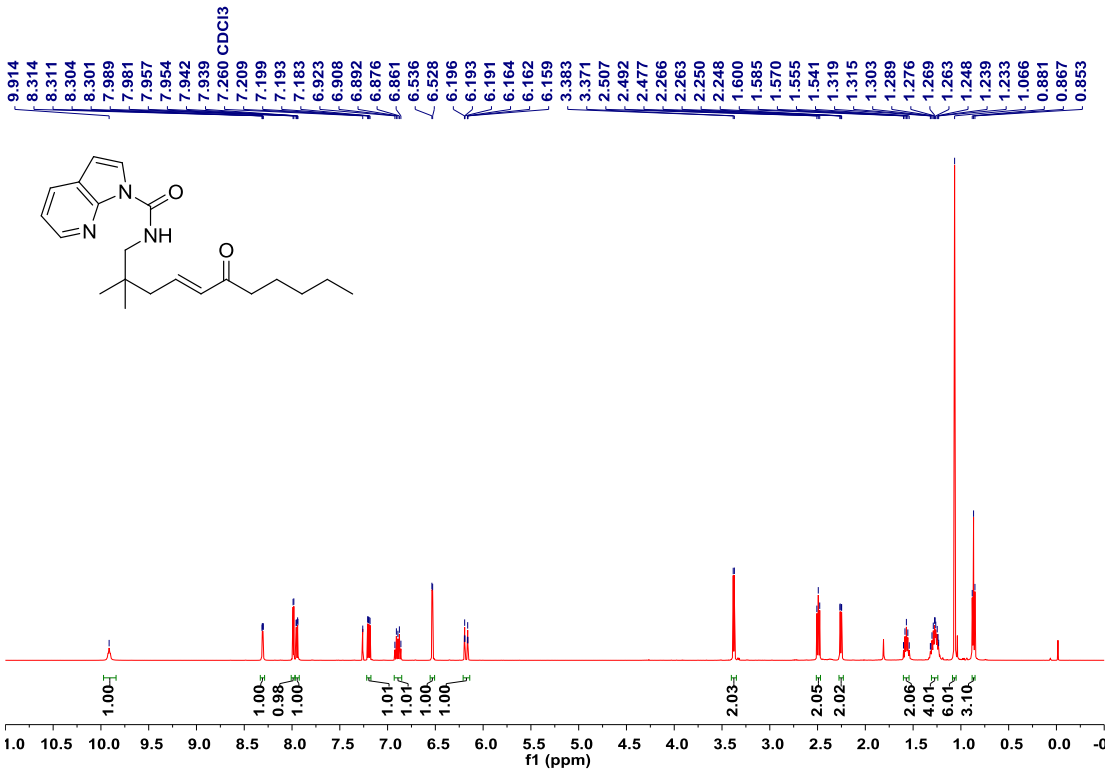


^{13}C NMR, 125 MHz, $CDCl_3$

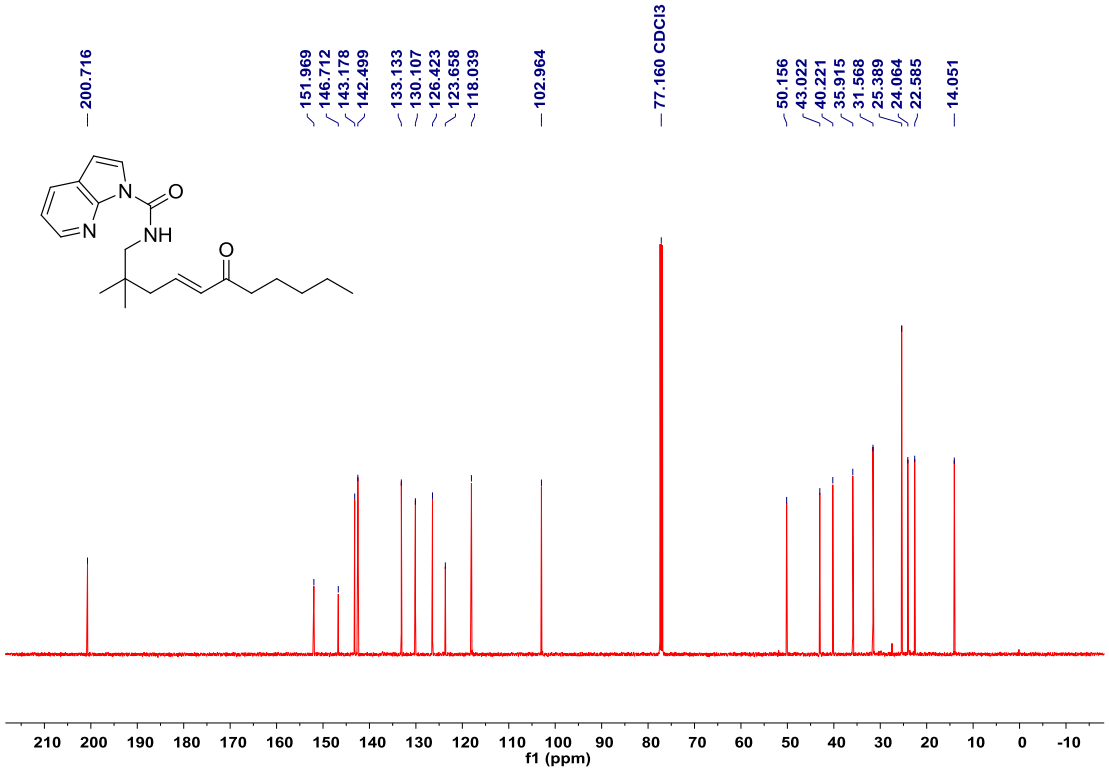


(*E*)-*N*-(2,2-Dimethyl-6-oxoundec-4-en-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide (4q)

^{1}H NMR, 500 MHz, $CDCl_3$

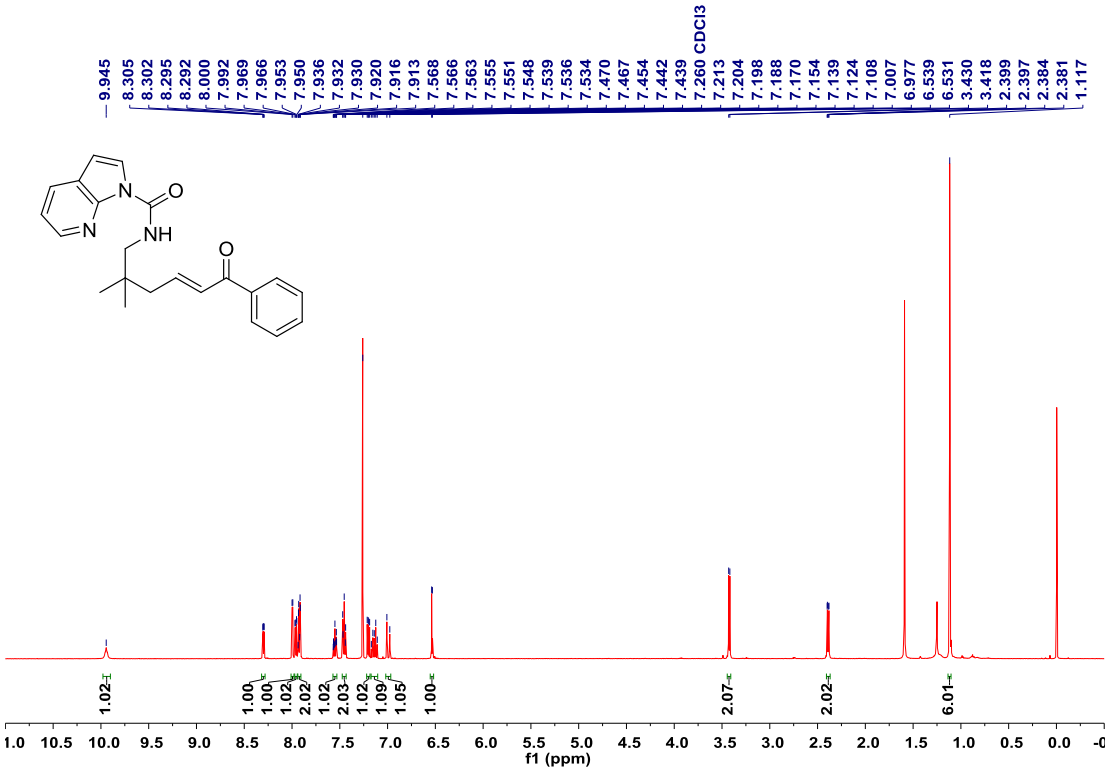


^{13}C NMR, 125 MHz, $CDCl_3$

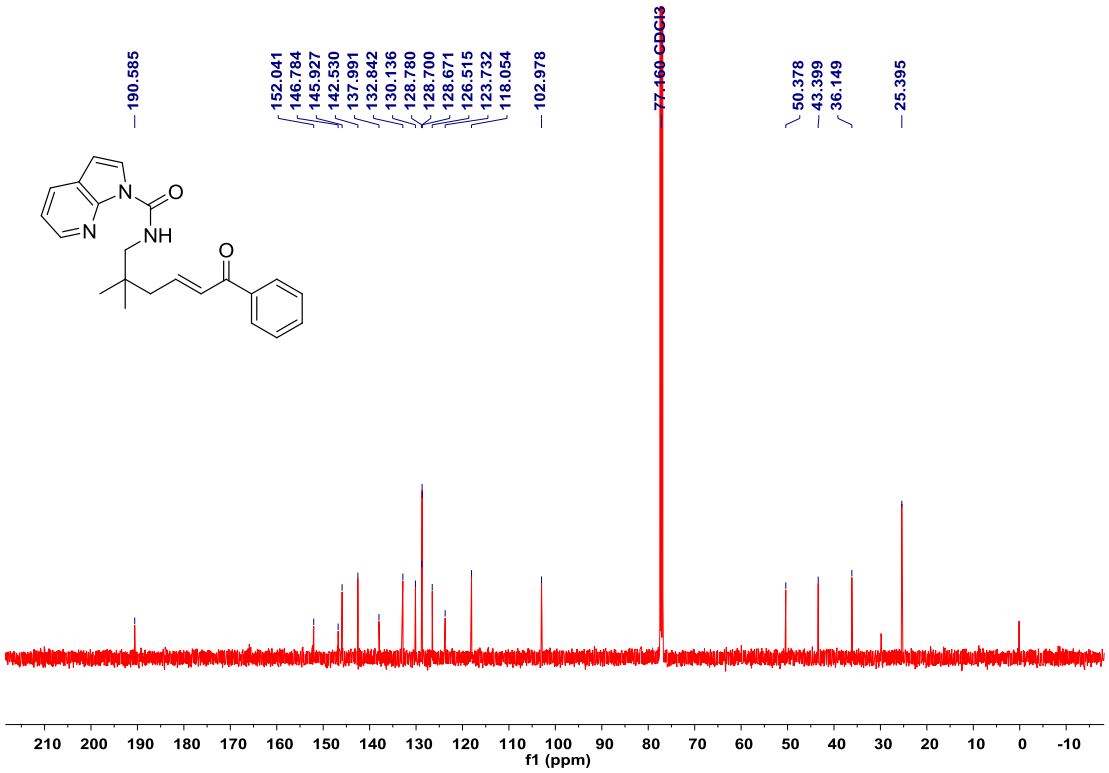


(*E*)-*N*-(2,2-Dimethyl-6-oxo-6-phenylhex-4-en-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide (4r)

^{1}H NMR, 500 MHz, $CDCl_3$

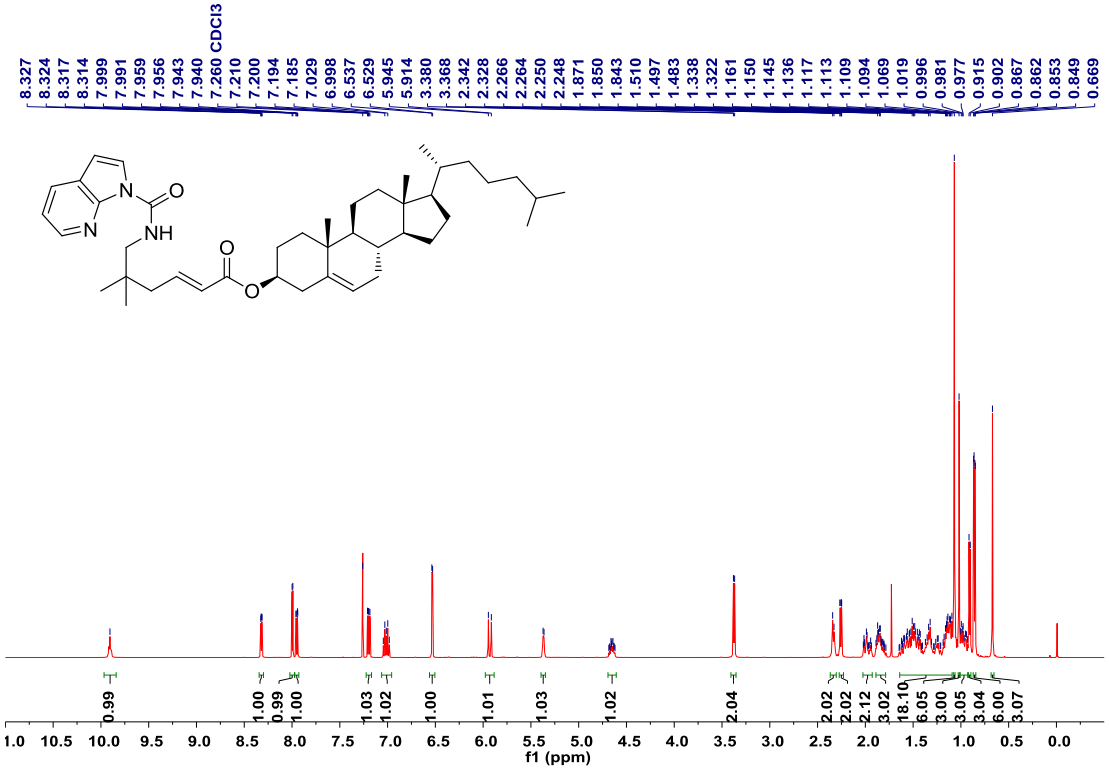


^{13}C NMR, 125 MHz, $CDCl_3$

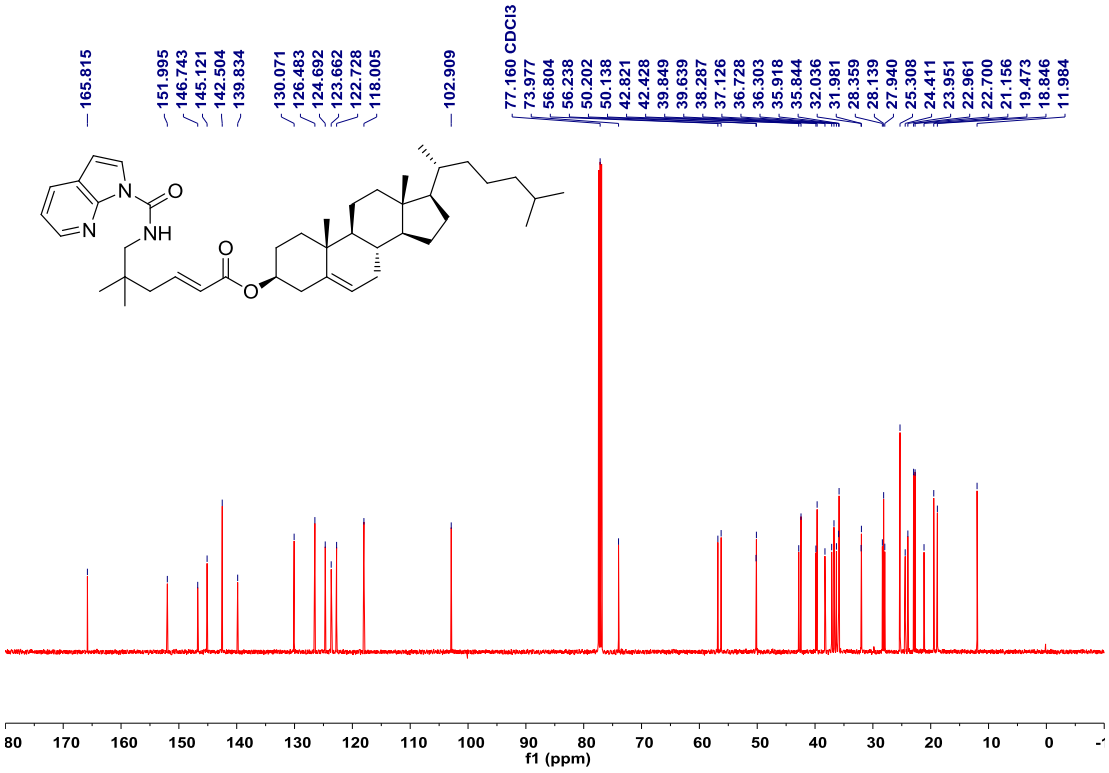


(*E*)-(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4s)

^{1}H NMR, 500 MHz, $CDCl_3$

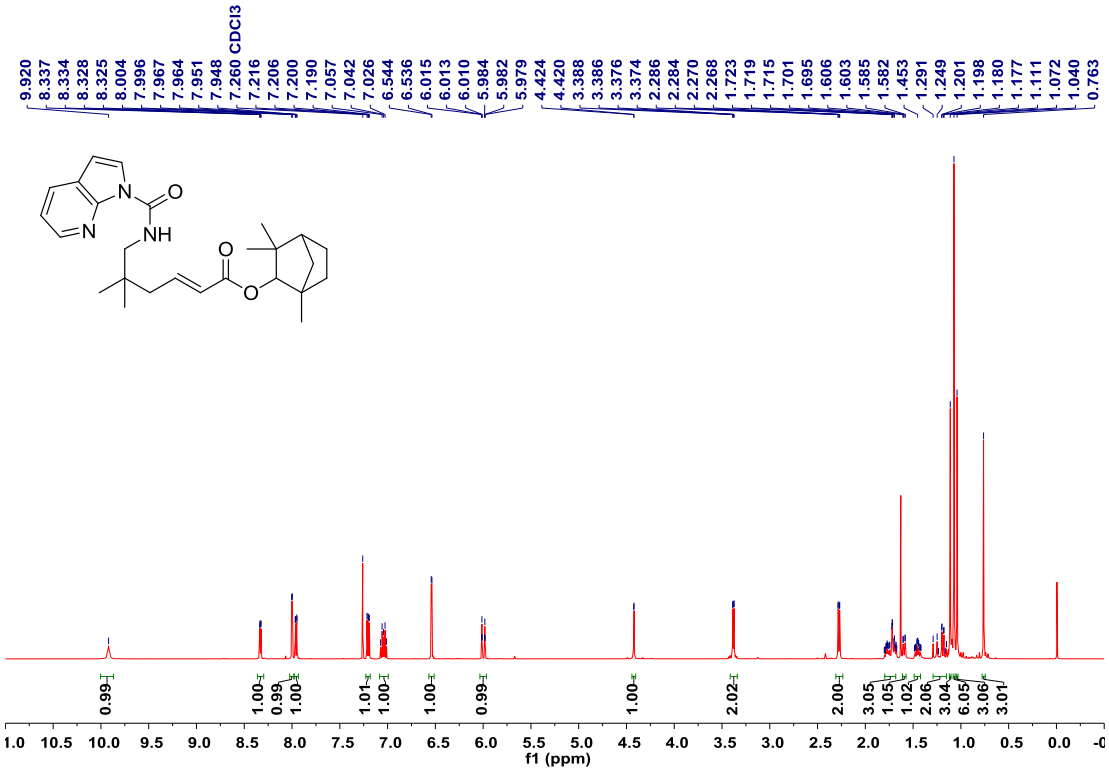


^{13}C NMR, 125 MHz, $CDCl_3$

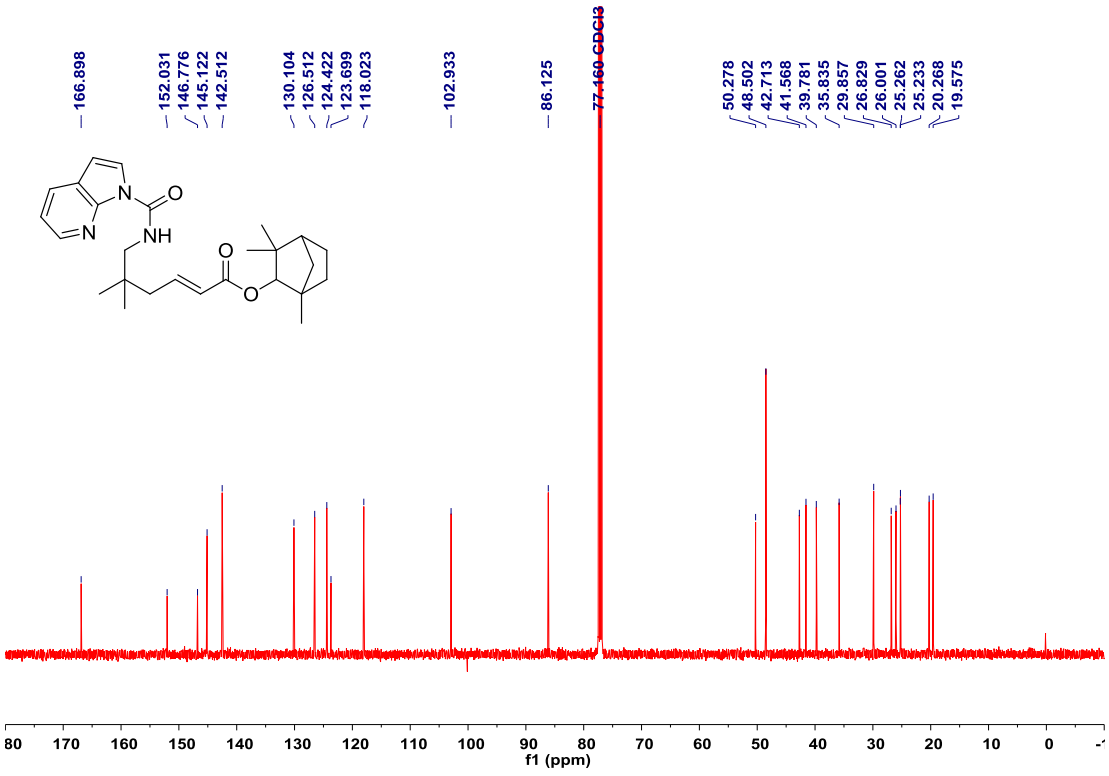


(*E*)-1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4t)

^{1}H NMR, 500 MHz, $CDCl_3$

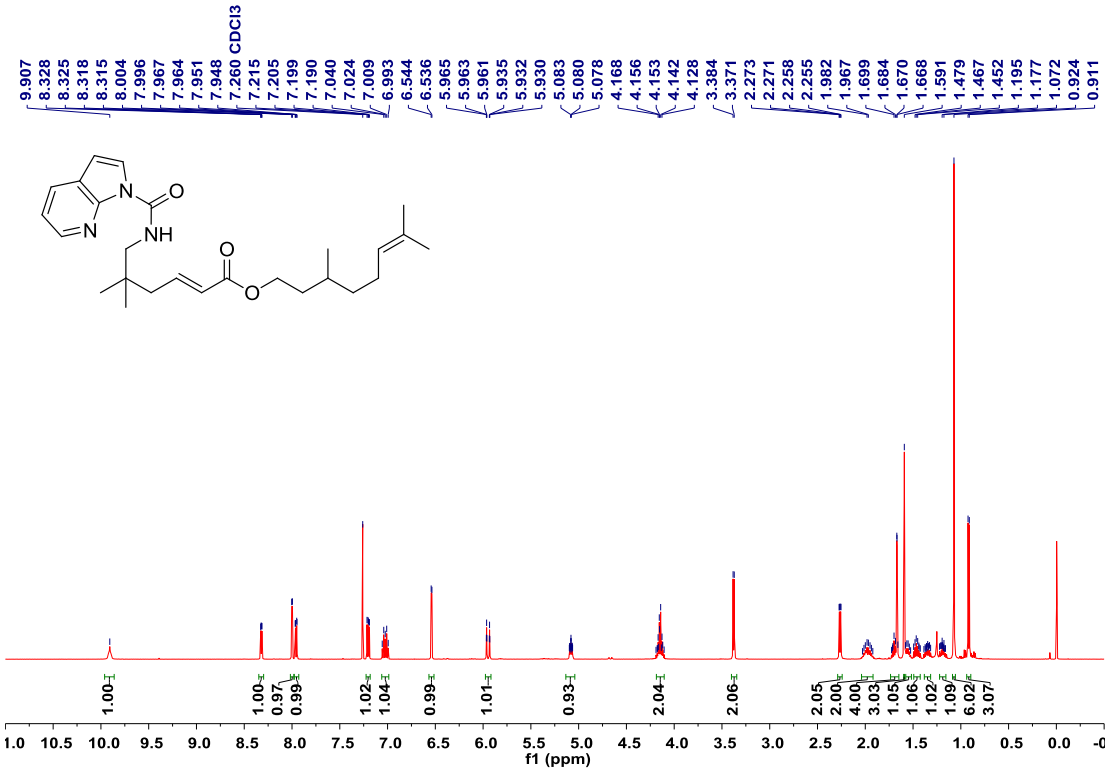


^{13}C NMR, 125 MHz, $CDCl_3$

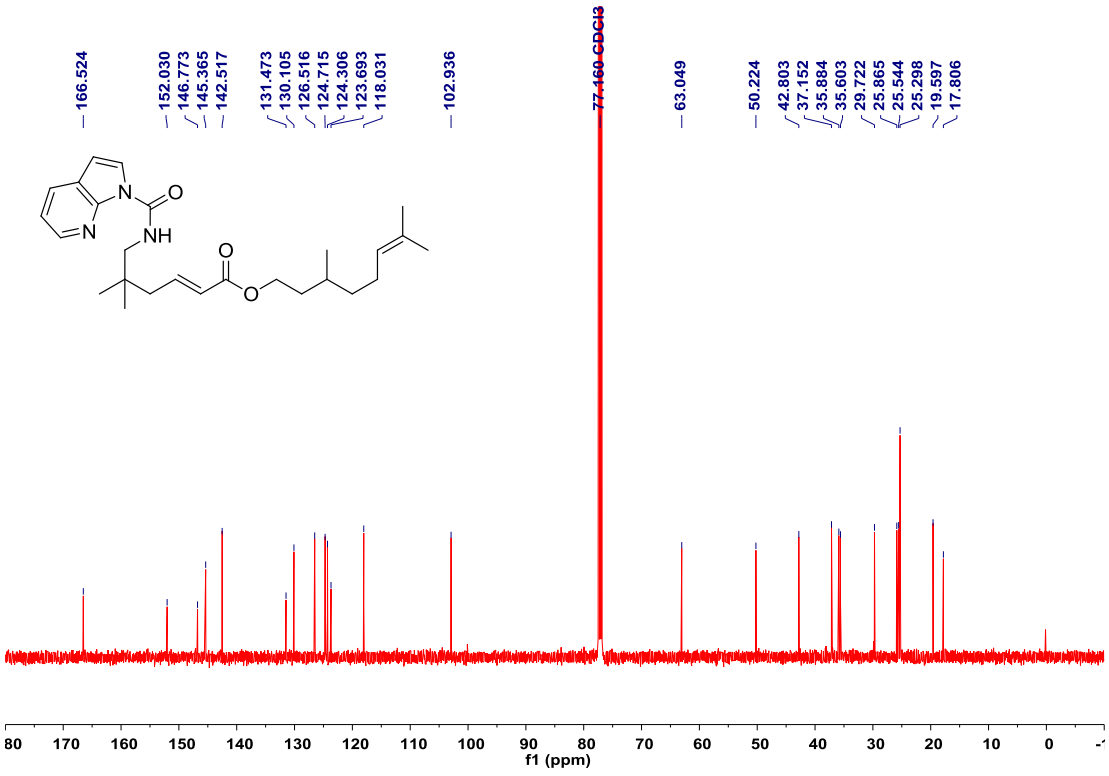


(*E*)-3,7-Dimethyloct-6-en-1-yl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido) hex-2-enoate (4u)

^{1}H NMR, 500 MHz, $CDCl_3$

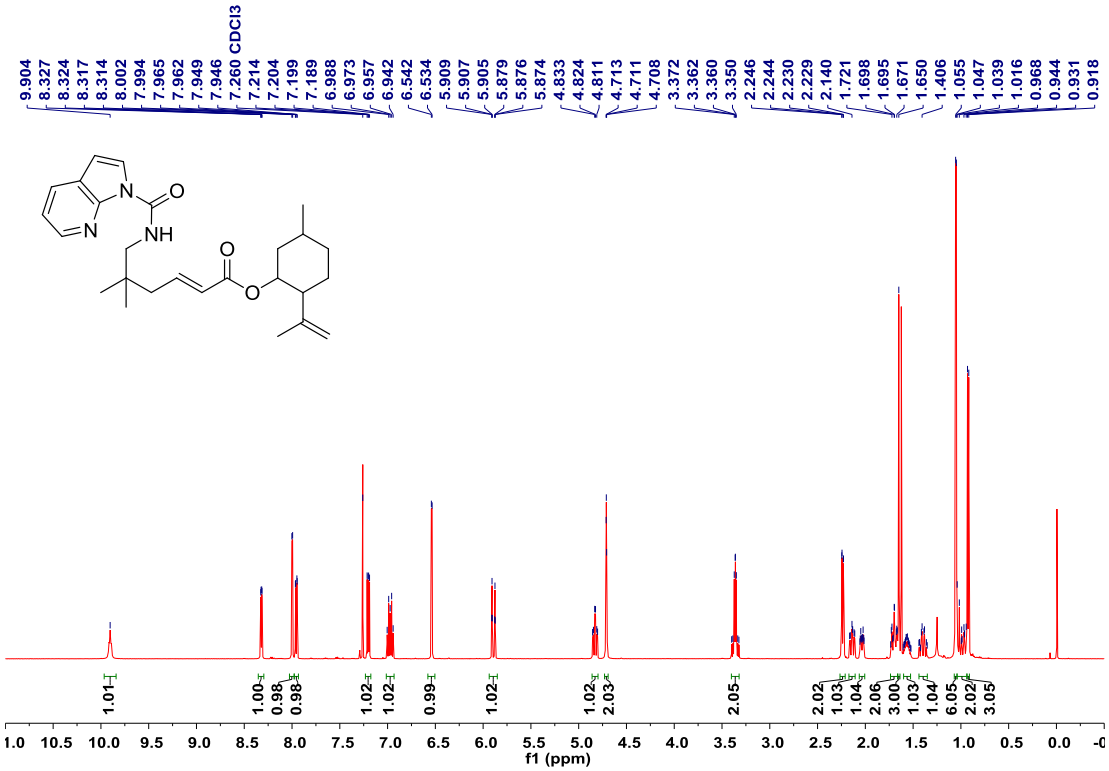


^{13}C NMR, 125 MHz, $CDCl_3$

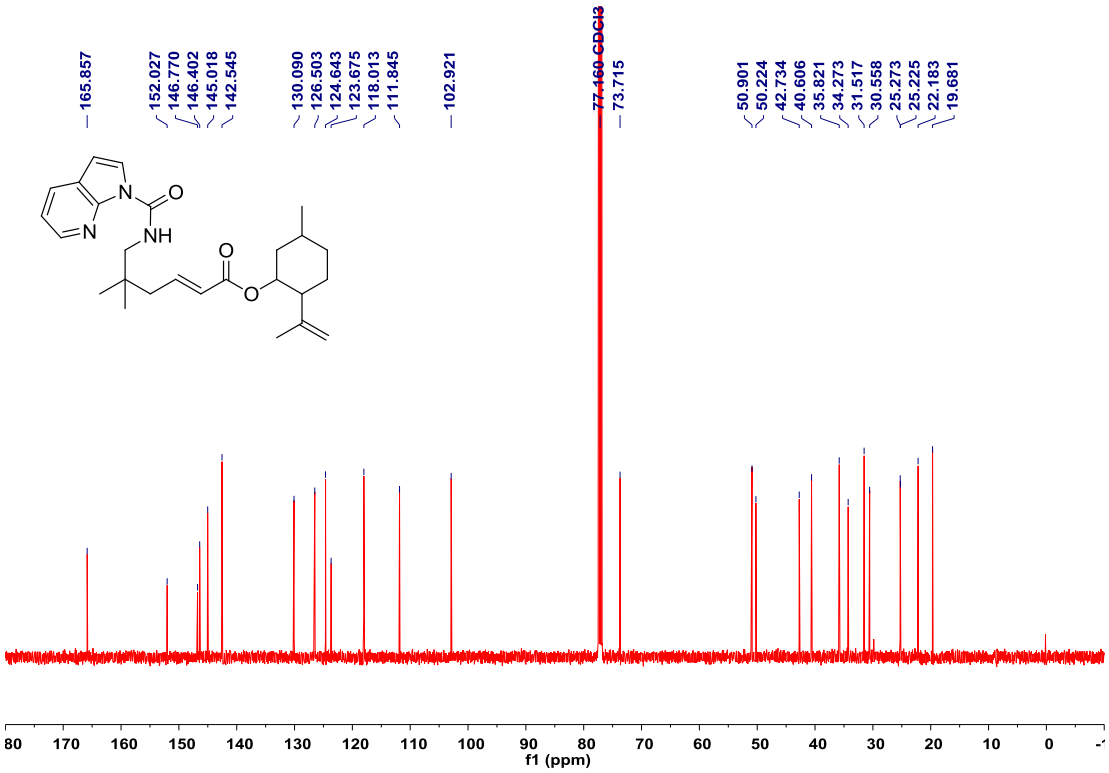


(*E*)-5-Methyl-2-(prop-1-en-2-yl)cyclohexyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-b]pyridine-1-carboxamido)hex-2-enoate (4v)

^{1}H NMR, 500 MHz, $CDCl_3$

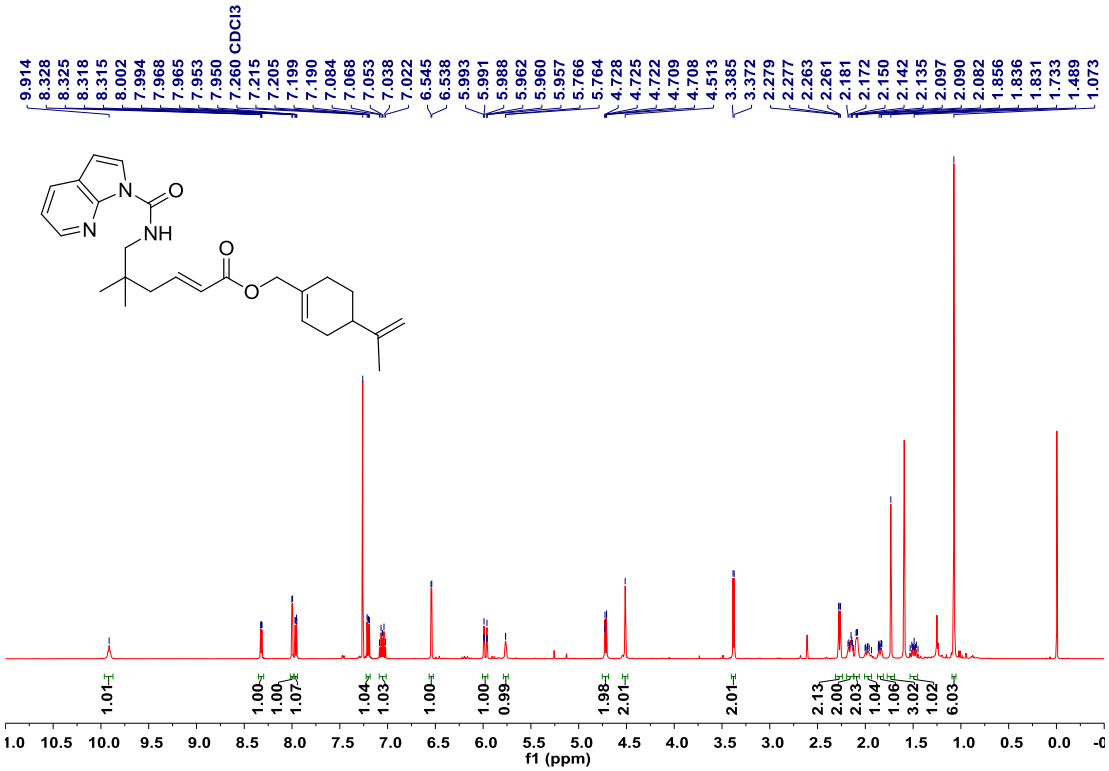


^{13}C NMR, 125 MHz, $CDCl_3$

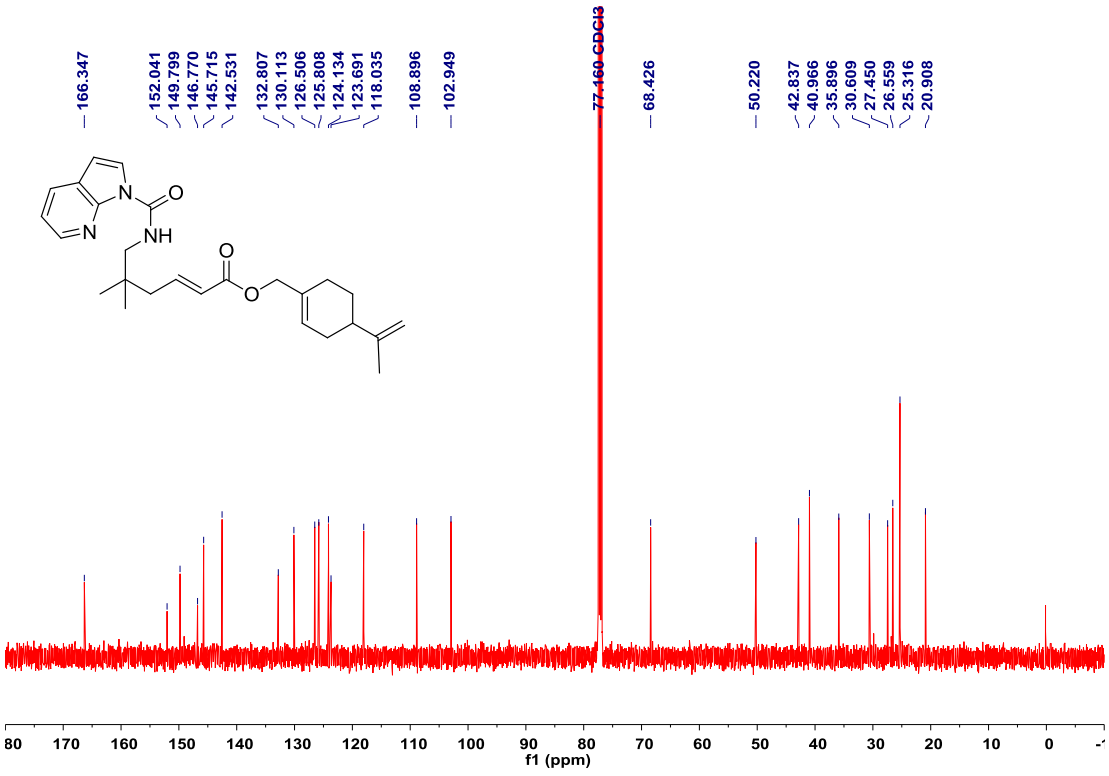


(*E*) -(4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine -1-carboxamido)hex-2-enoate (4w)

^{1}H NMR, 500 MHz, $CDCl_3$

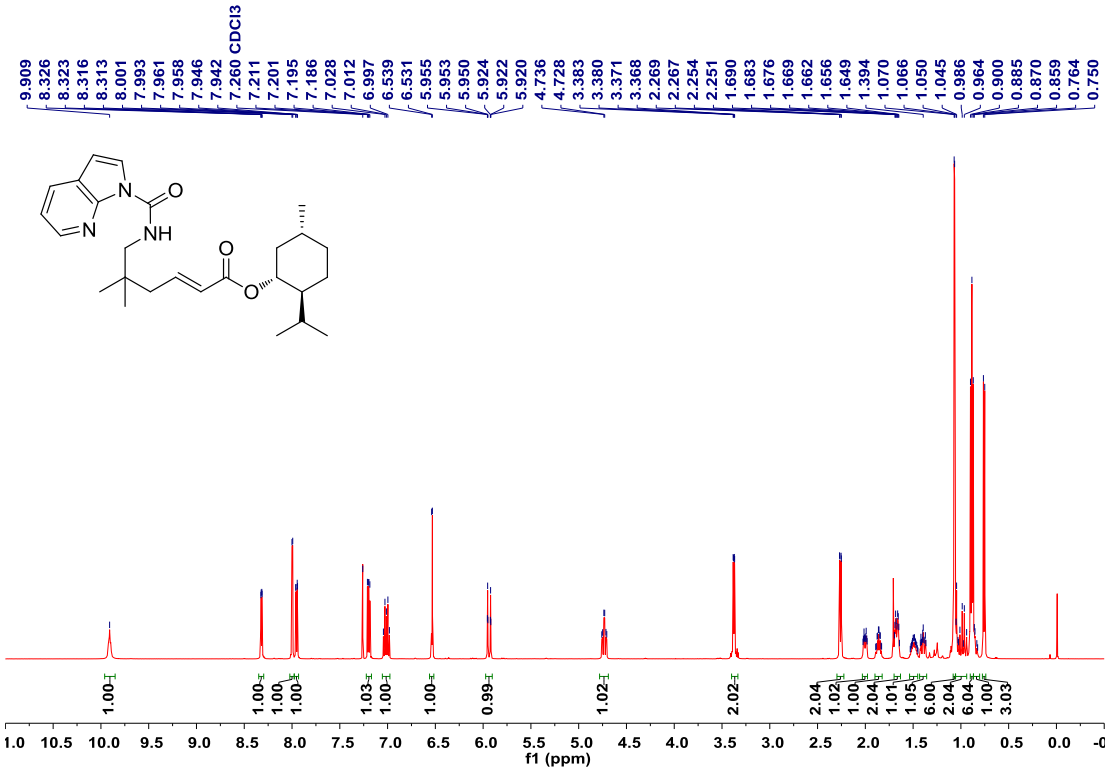


^{13}C NMR, 125 MHz, $CDCl_3$

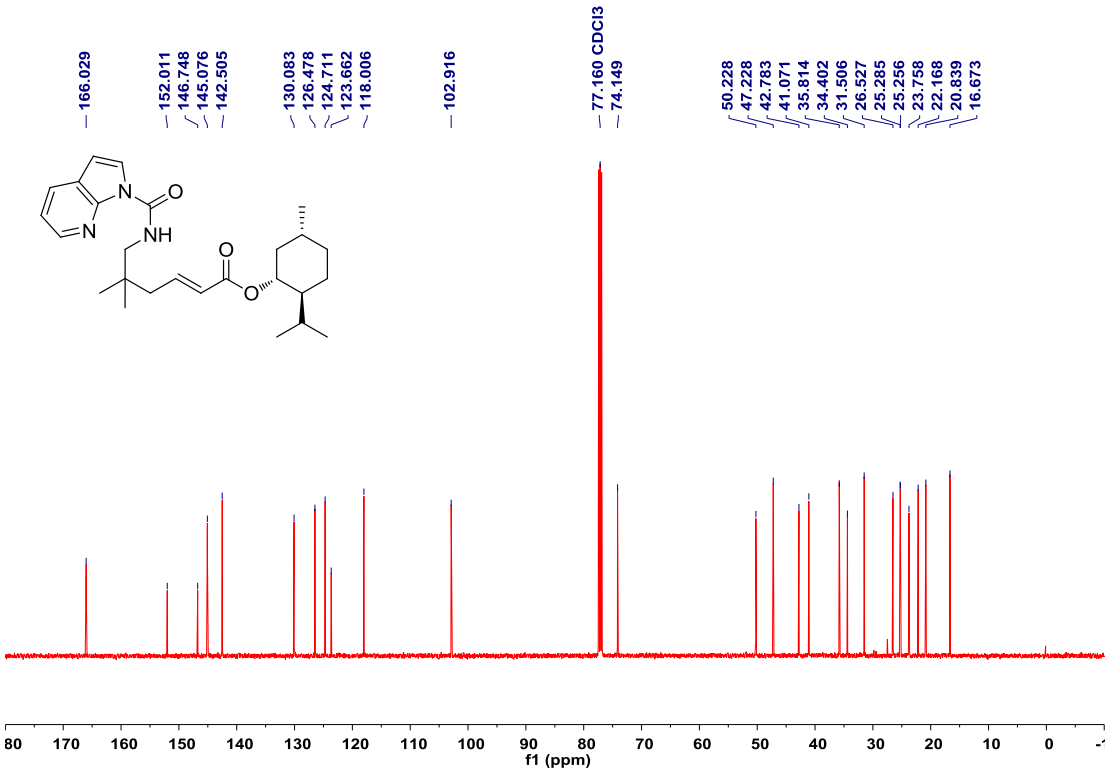


(*E*)-(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 5,5-dimethyl-6-(1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamido)hex-2-enoate (4x)

^{1}H NMR, 500 MHz, $CDCl_3$

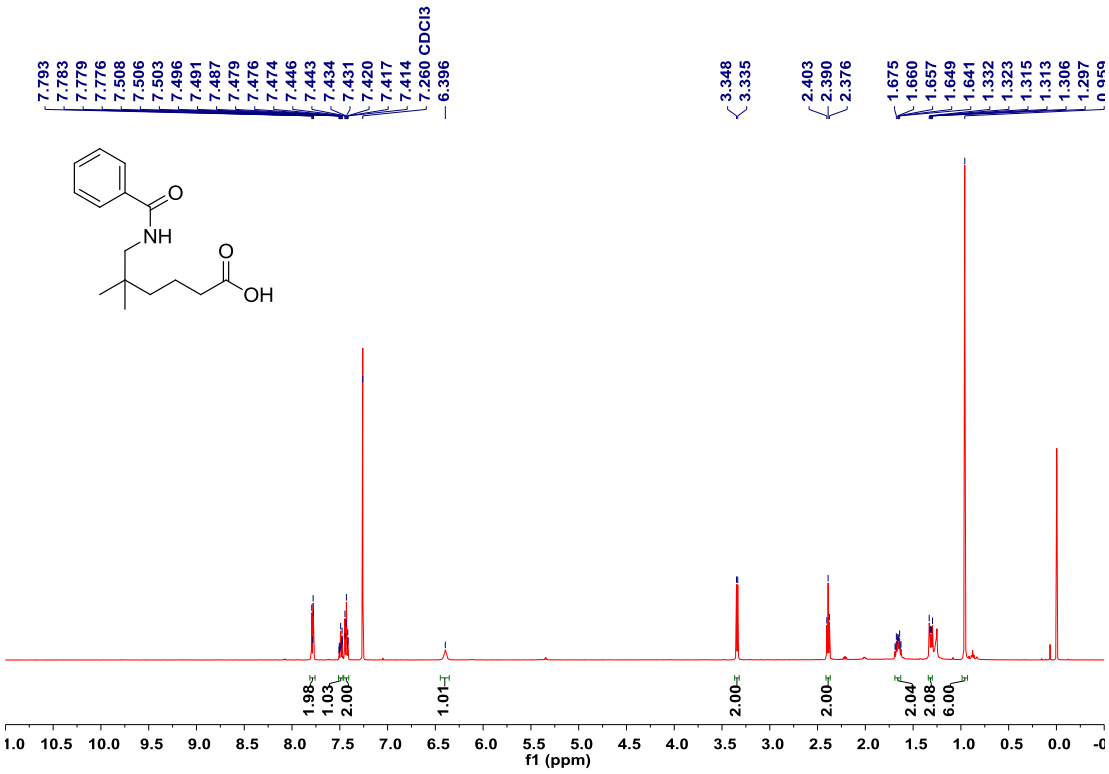


^{13}C NMR, 125 MHz, $CDCl_3$

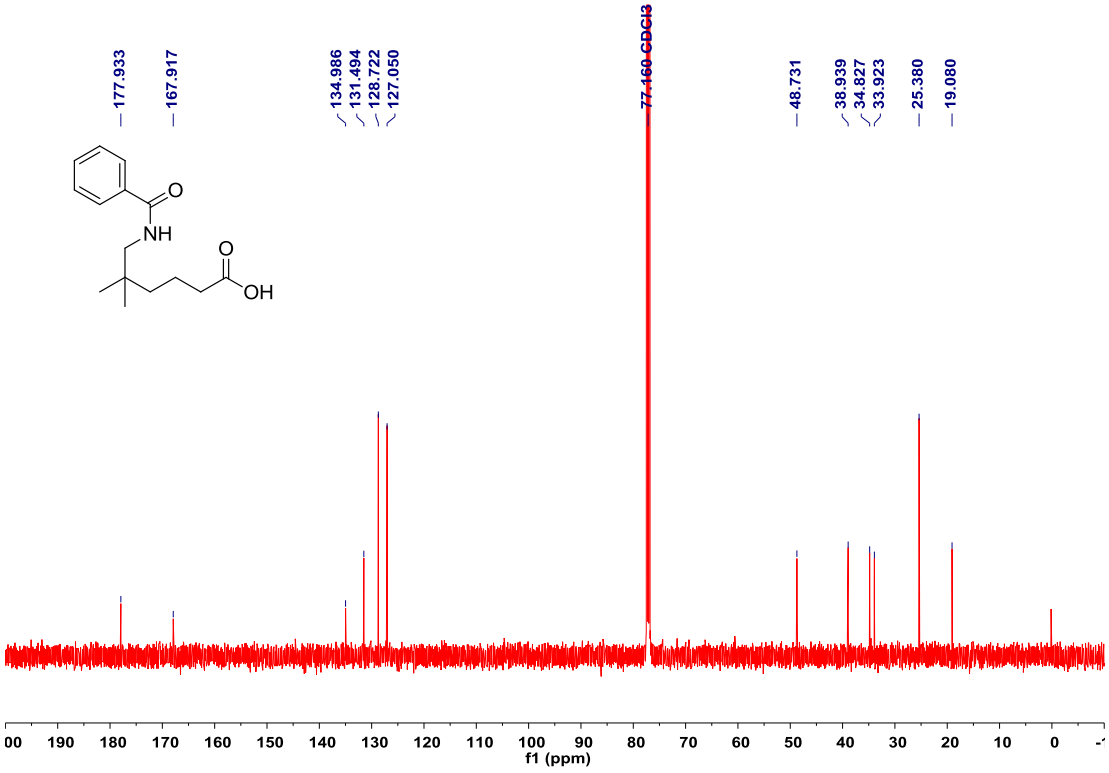


6-Benzamido-5,5-dimethylhexanoic acid (6)

^{1}H NMR, 500 MHz, $CDCl_3$

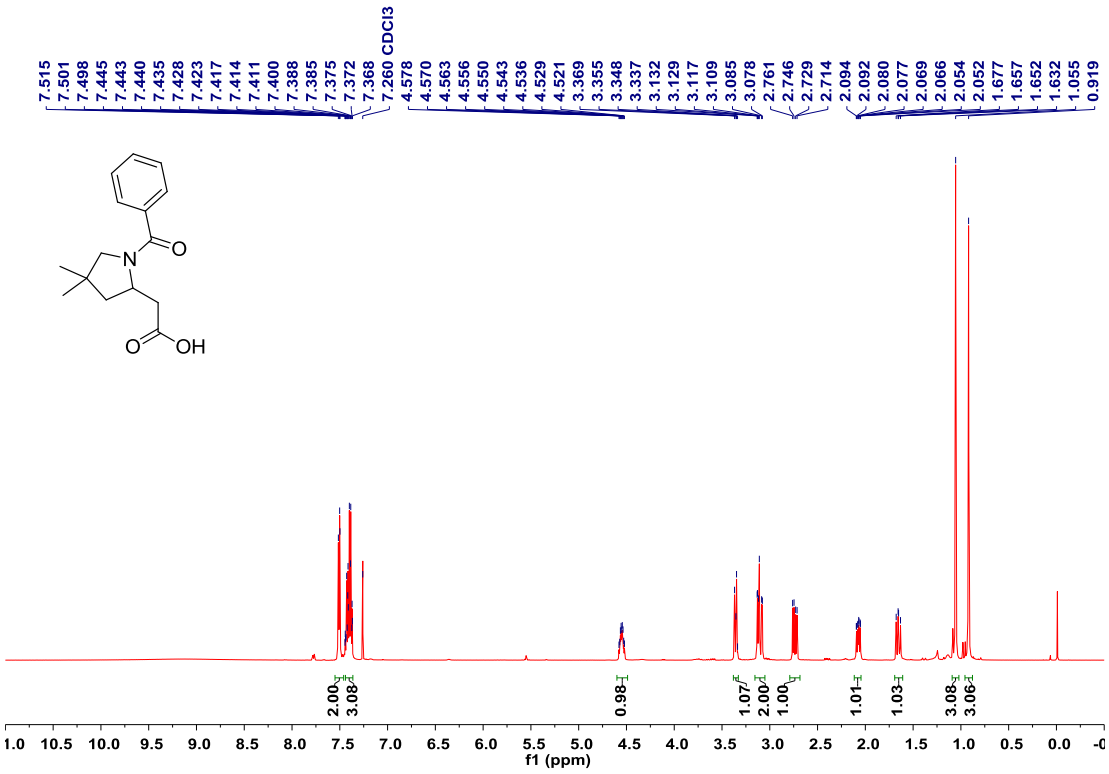


^{13}C NMR, 125 MHz, $CDCl_3$

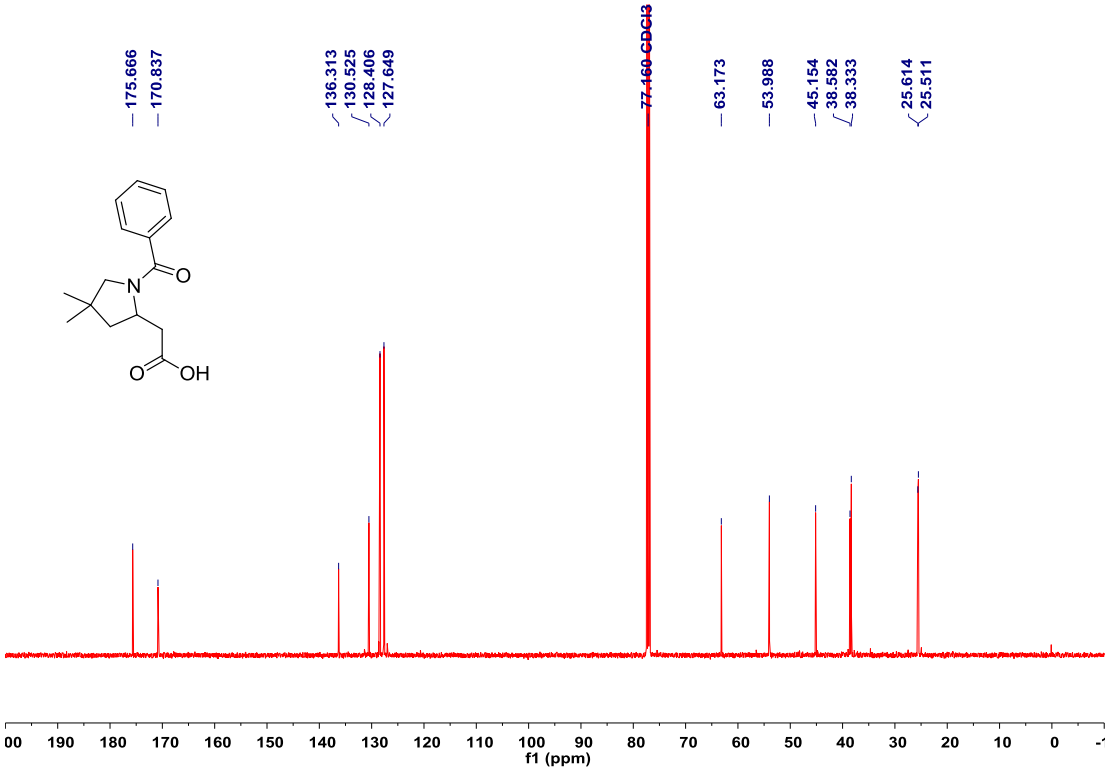


2-(1-Benzoyl-4,4-dimethylpyrrolidin-2-yl)acetic acid (7)

^{1}H NMR, 500 MHz, $CDCl_3$

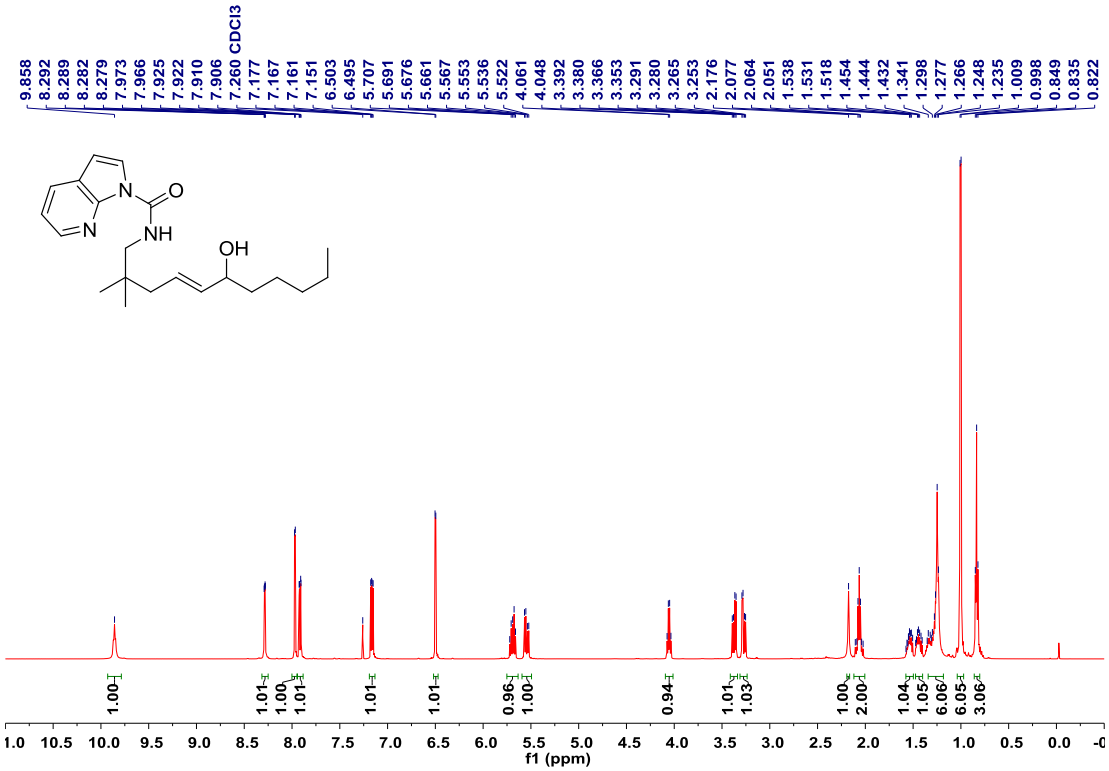


^{13}C NMR, 125 MHz, $CDCl_3$

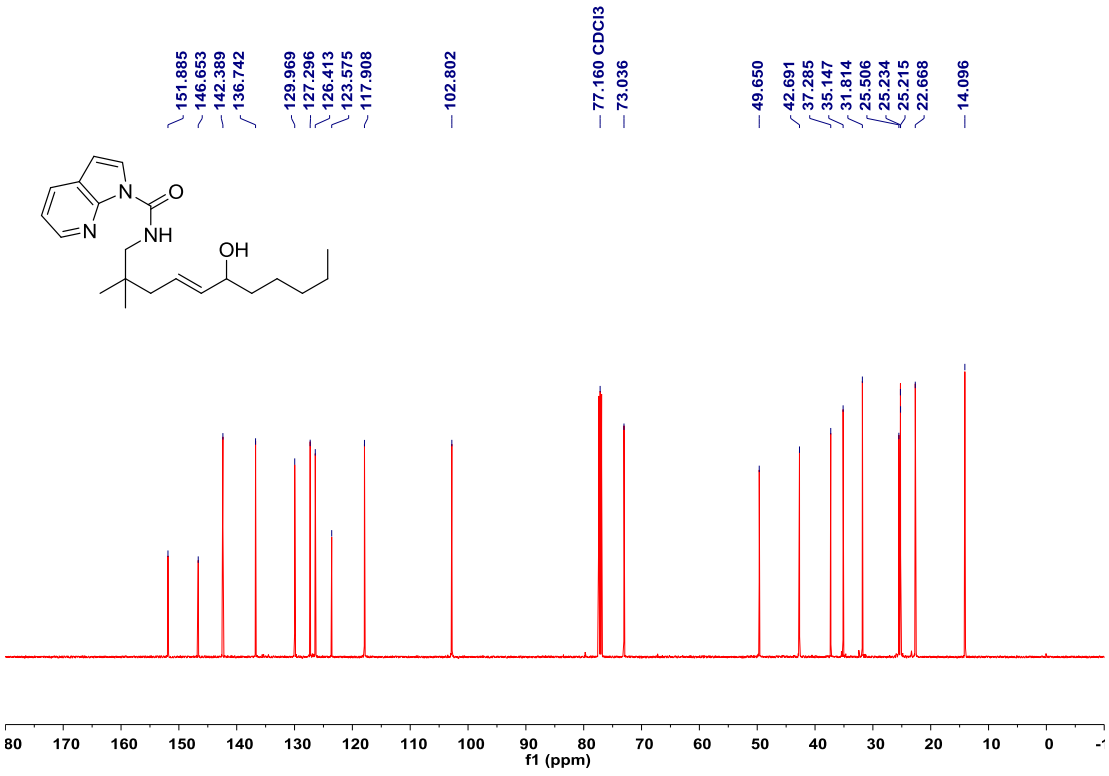


(*E*)-*N*-(6-hydroxy-2,2-dimethylundec-4-en-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide (8)

^{1}H NMR, 500 MHz, $CDCl_3$

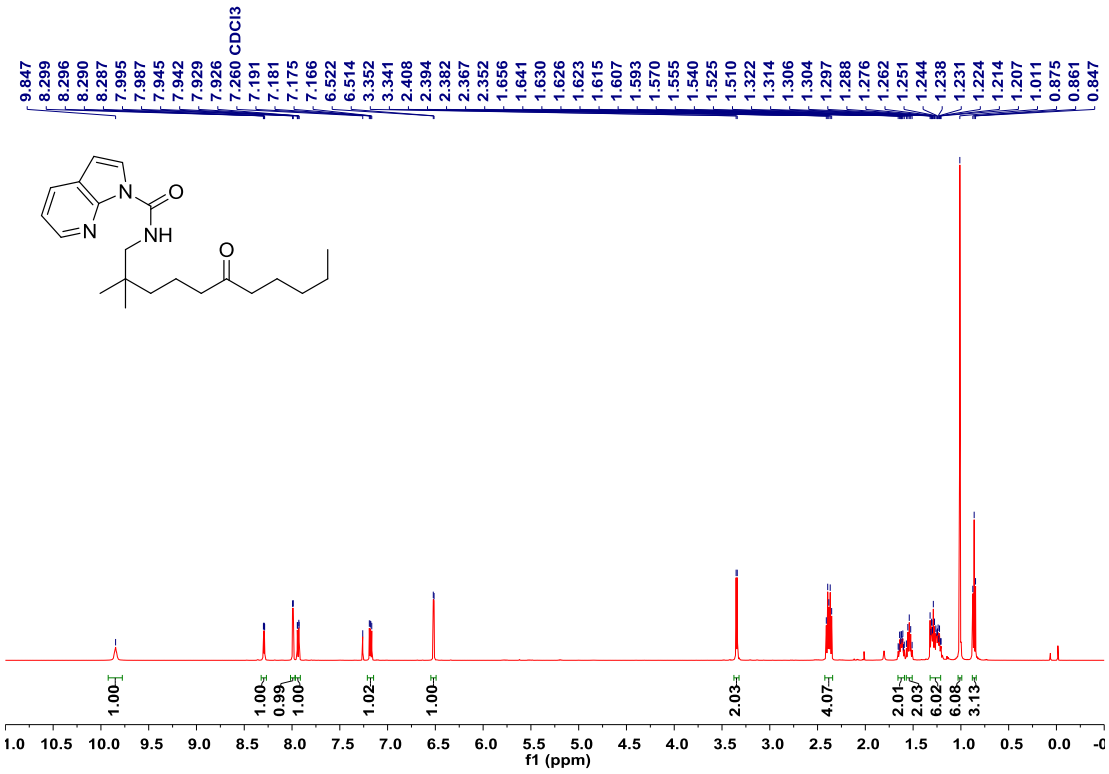


^{13}C NMR, 125 MHz, $CDCl_3$

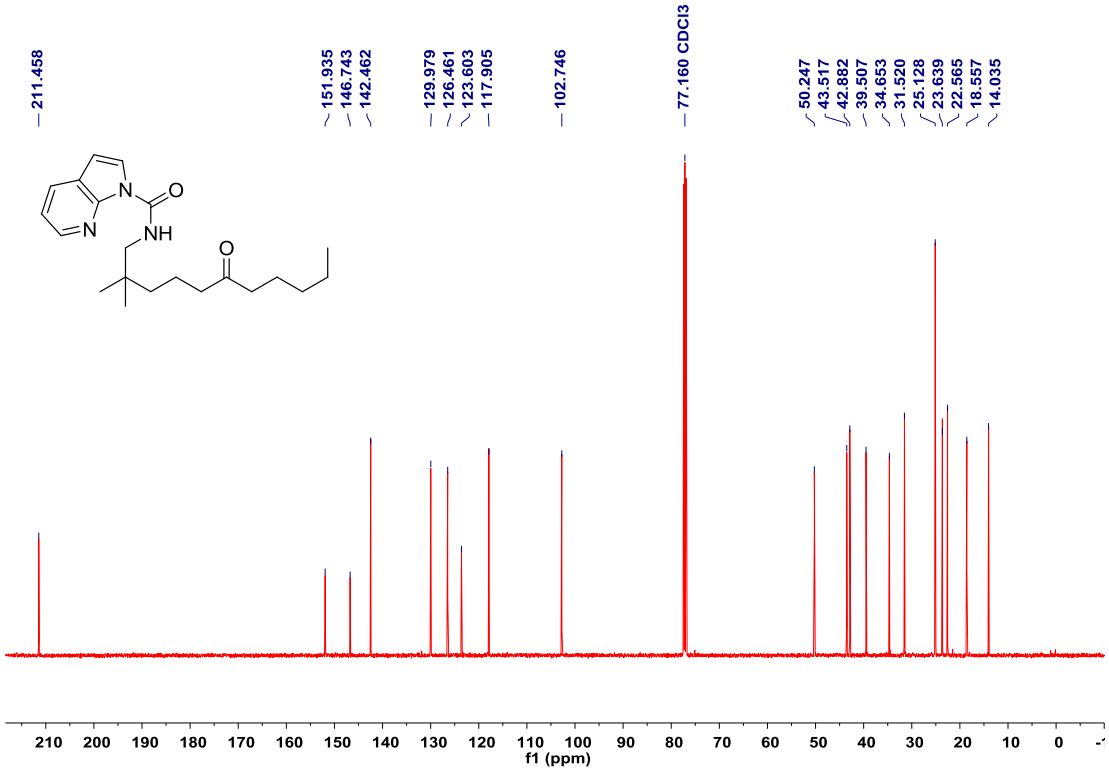


_N_-(2,2-Dimethyl-6-oxoundecyl)-1_H_-pyrrolo[2,3-_b_]pyridine-1-carboxamide (9)

^{1}H NMR, 500 MHz, $CDCl_3$

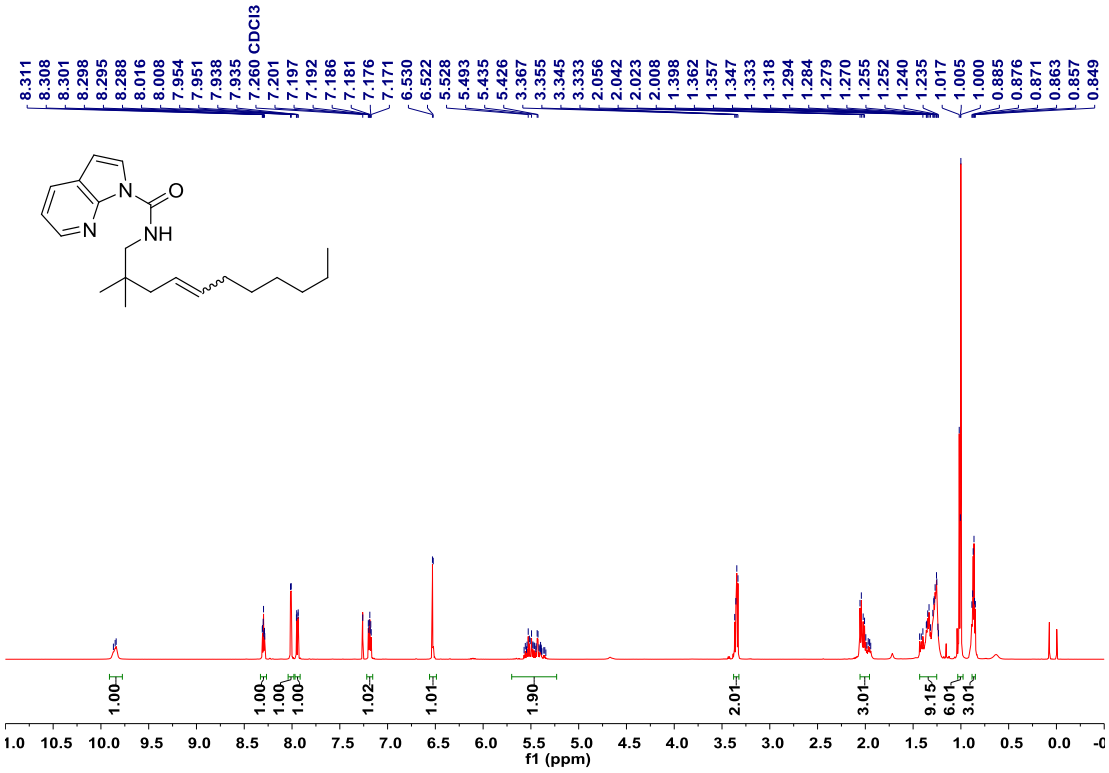


^{13}C NMR, 125 MHz, $CDCl_3$

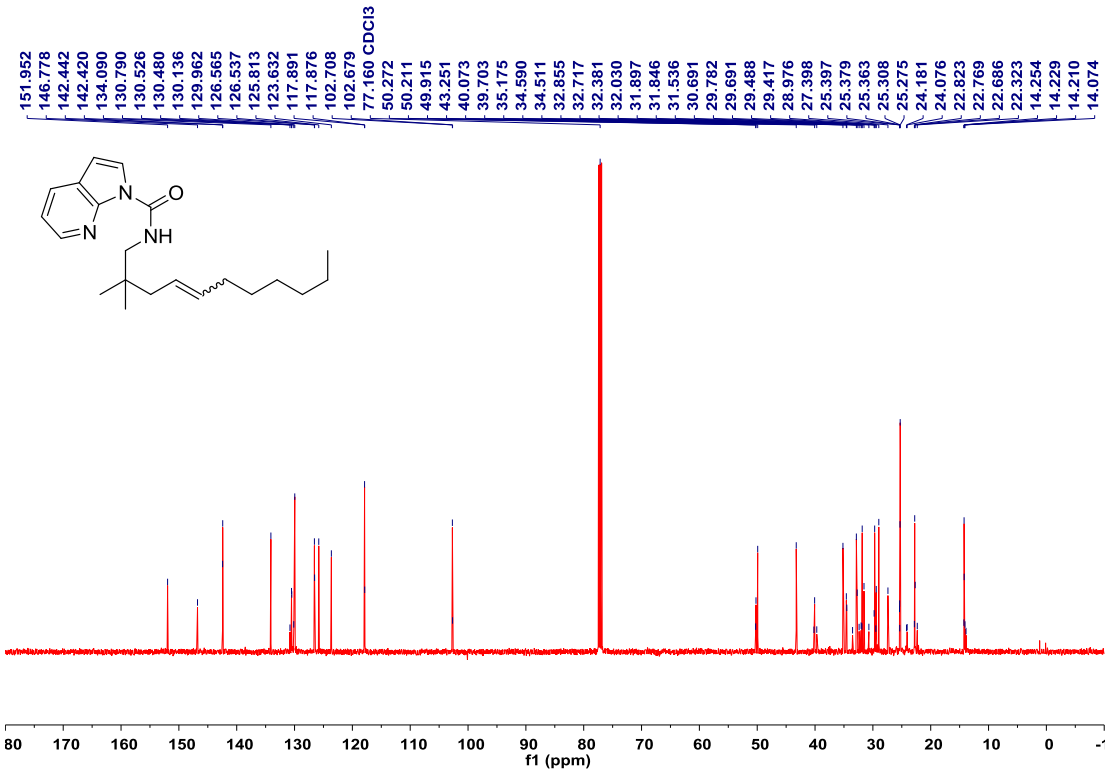


Mixture of (*E*)-*N*-(2,2-dimethylundec-4-en-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide and (*Z*)-*N*-(2,2-dimethylundec-4-en-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide (10)

^{1}H NMR, 500 MHz, $CDCl_3$

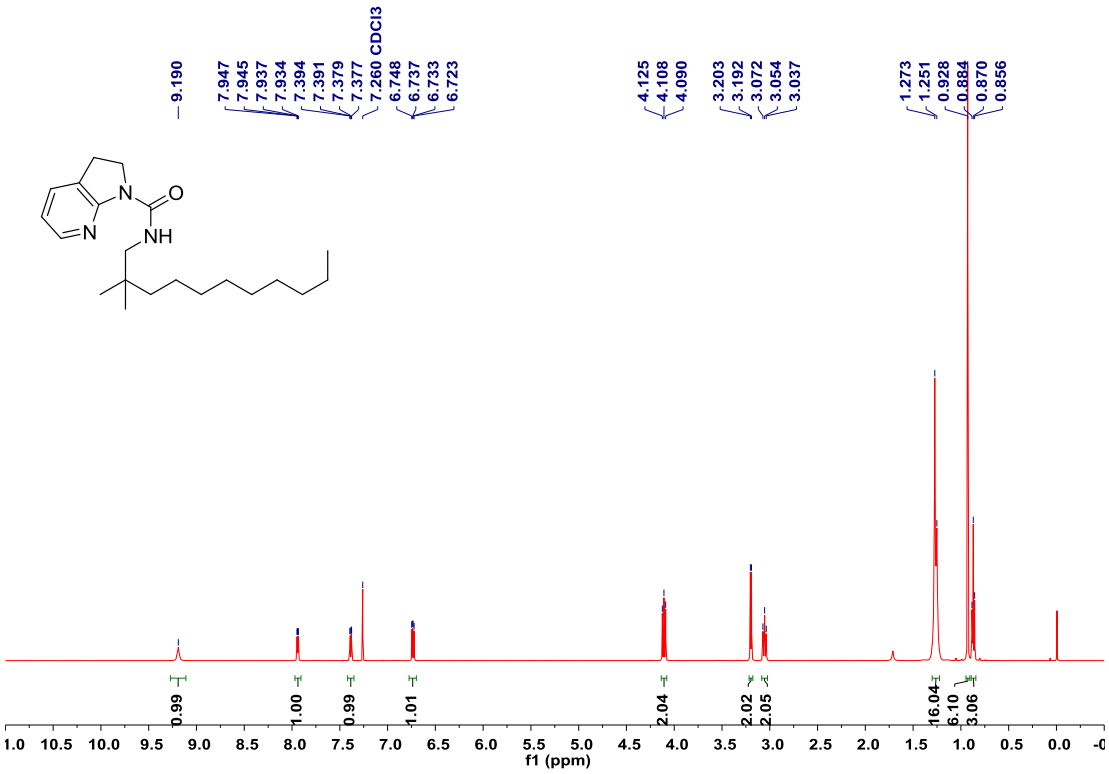


^{13}C NMR, 125 MHz, $CDCl_3$

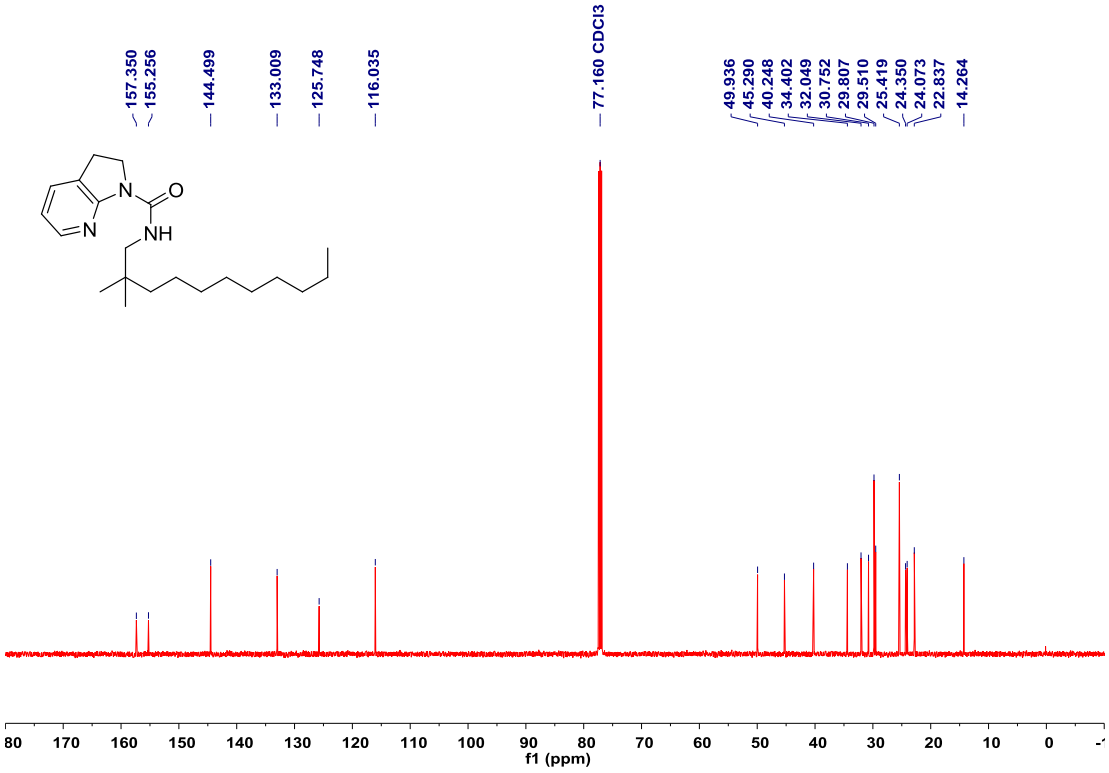


***N*-(2,2-dimethylundecyl)-2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxamide (11)**

^{1}H NMR, 500 MHz, $CDCl_3$

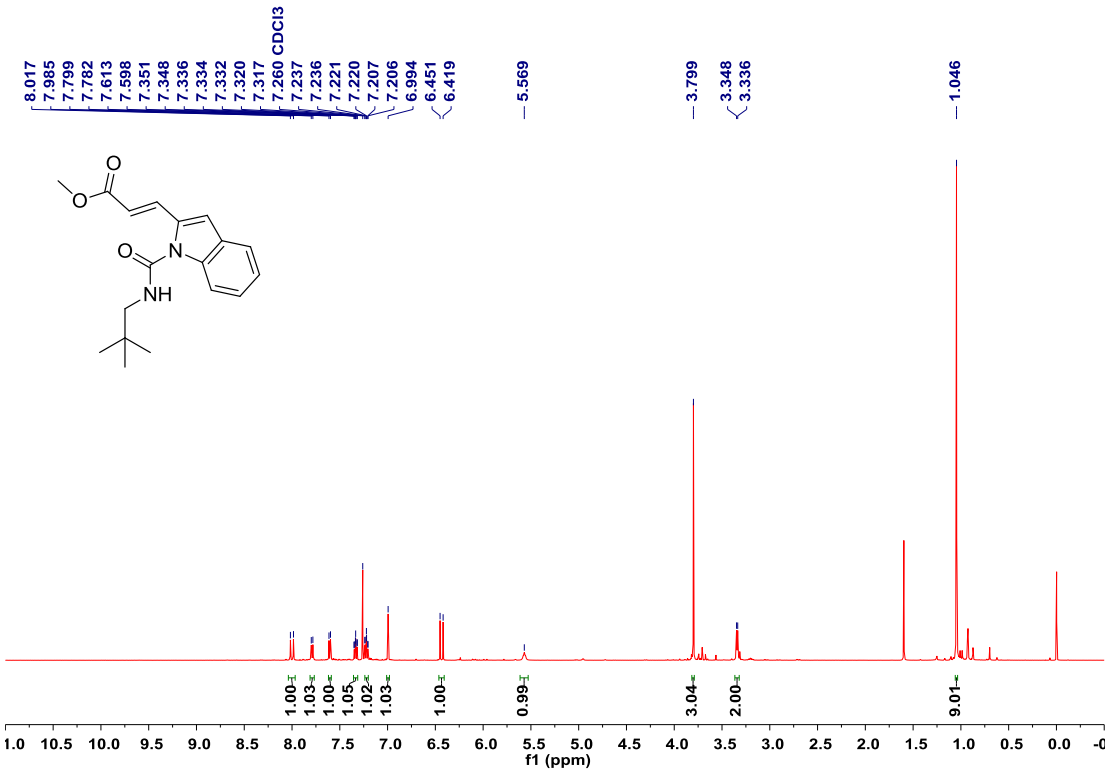


^{13}C NMR, 125 MHz, $CDCl_3$

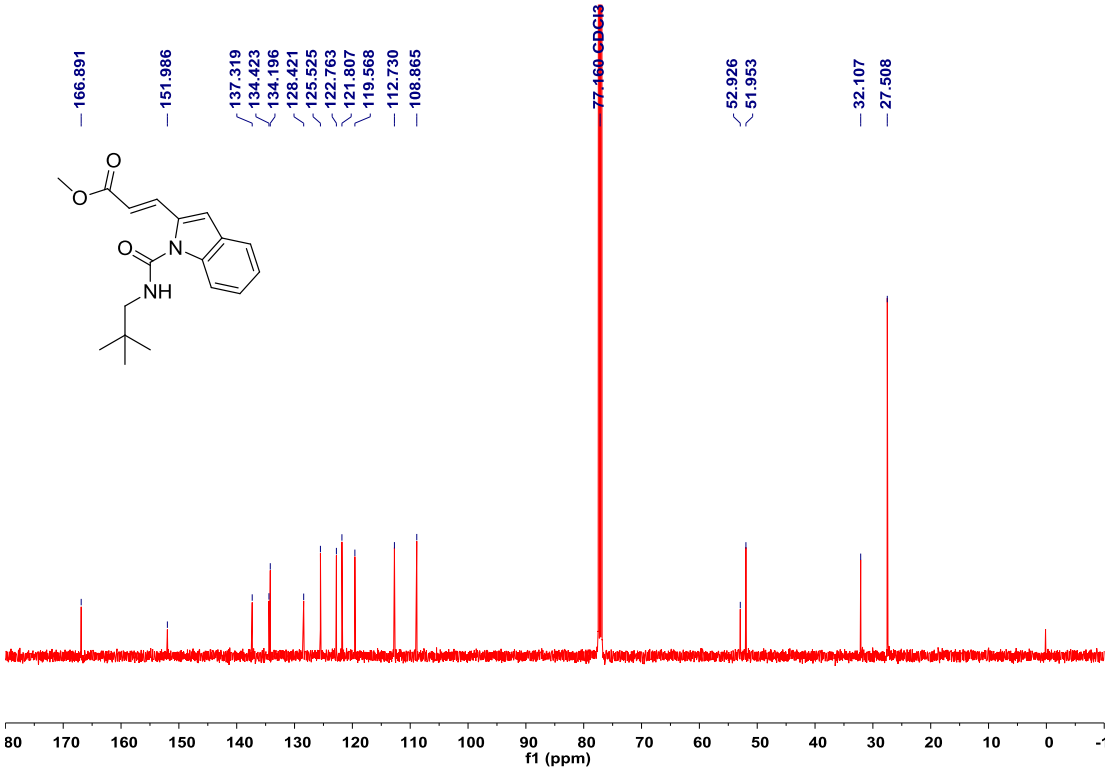


(*E*)-methyl 3-(1-(neopentylcarbamoyl)-1*H*-indol-2-yl)acrylate (5b)

^{1}H NMR, 500 MHz, $CDCl_3$

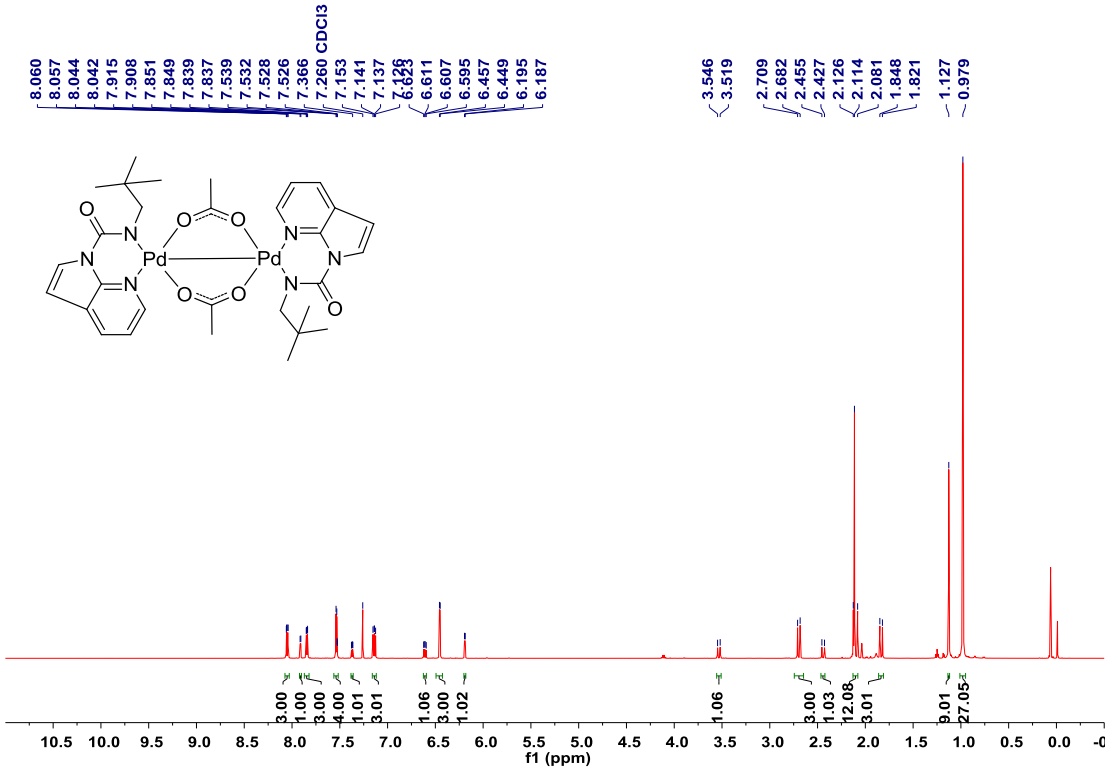


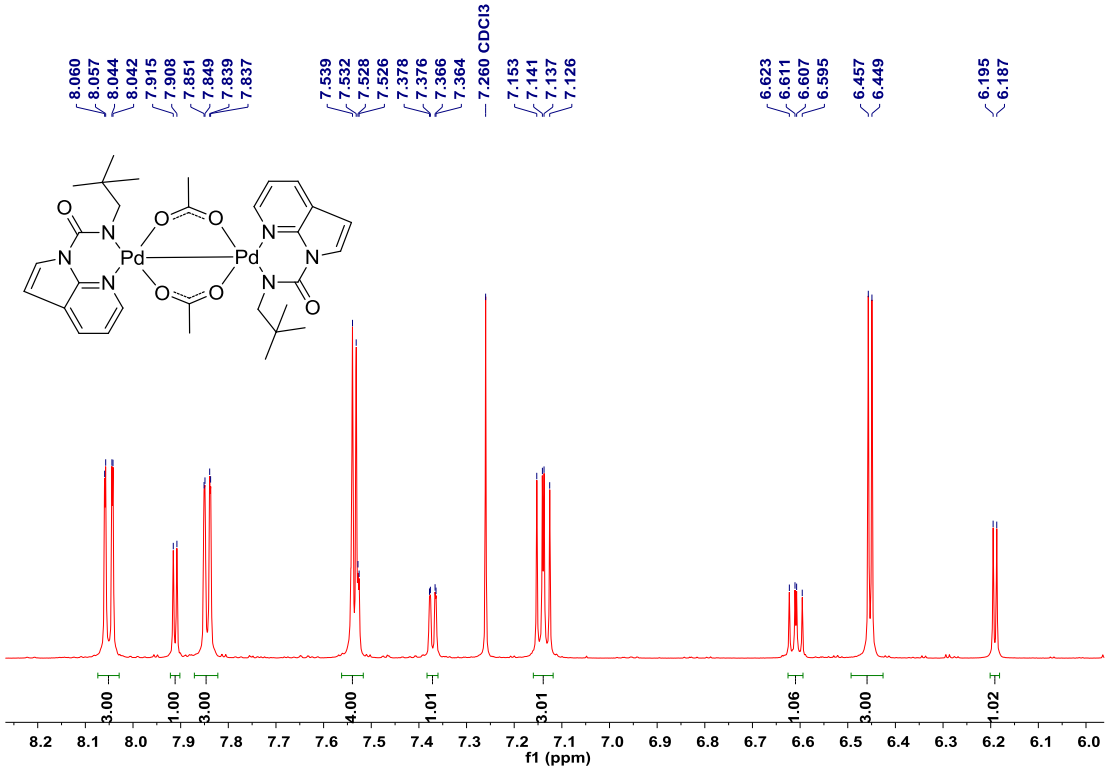
^{13}C NMR, 125 MHz, $CDCl_3$

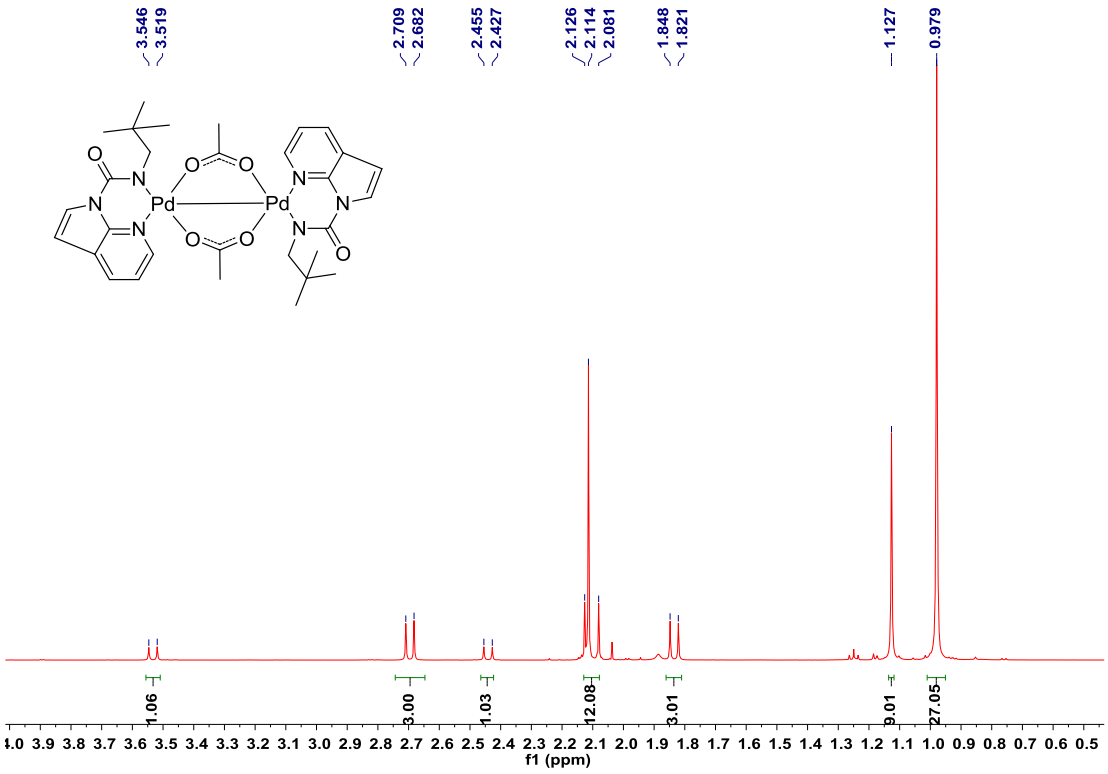


Six-membered palladacycle (12) ($C_{60}H_{76}N_{12}O_{12}Pd_4$):

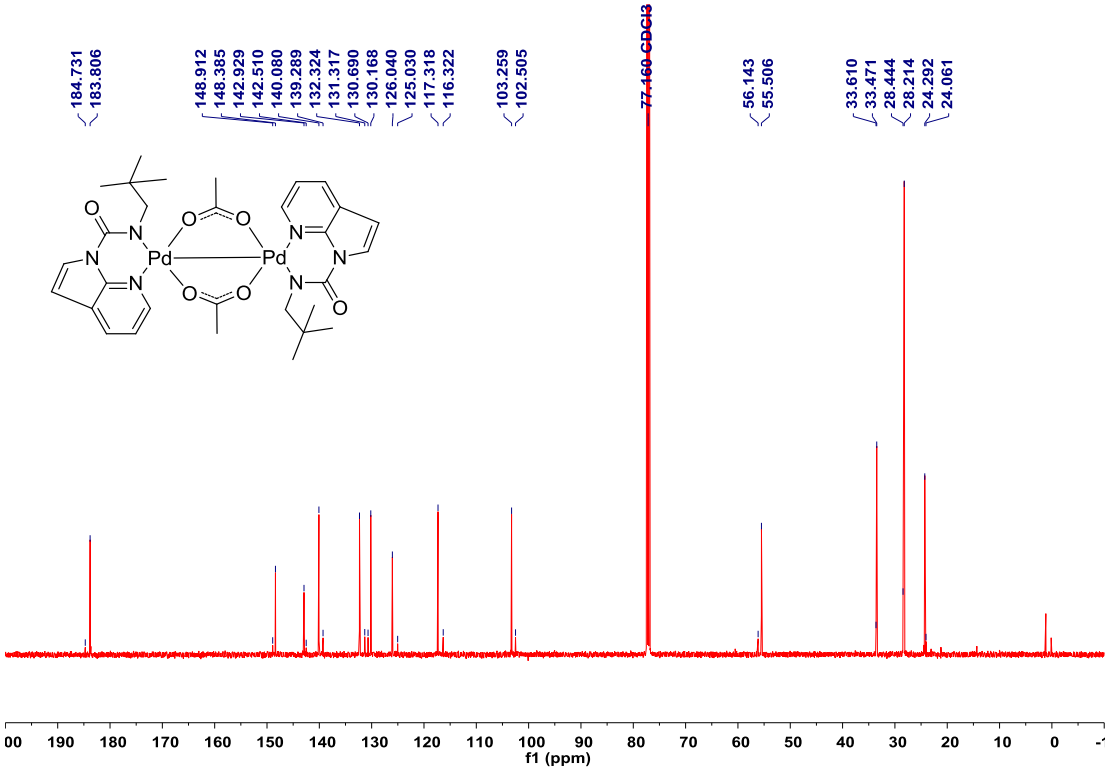
^{1}H NMR, 500 MHz, $CDCl_3$





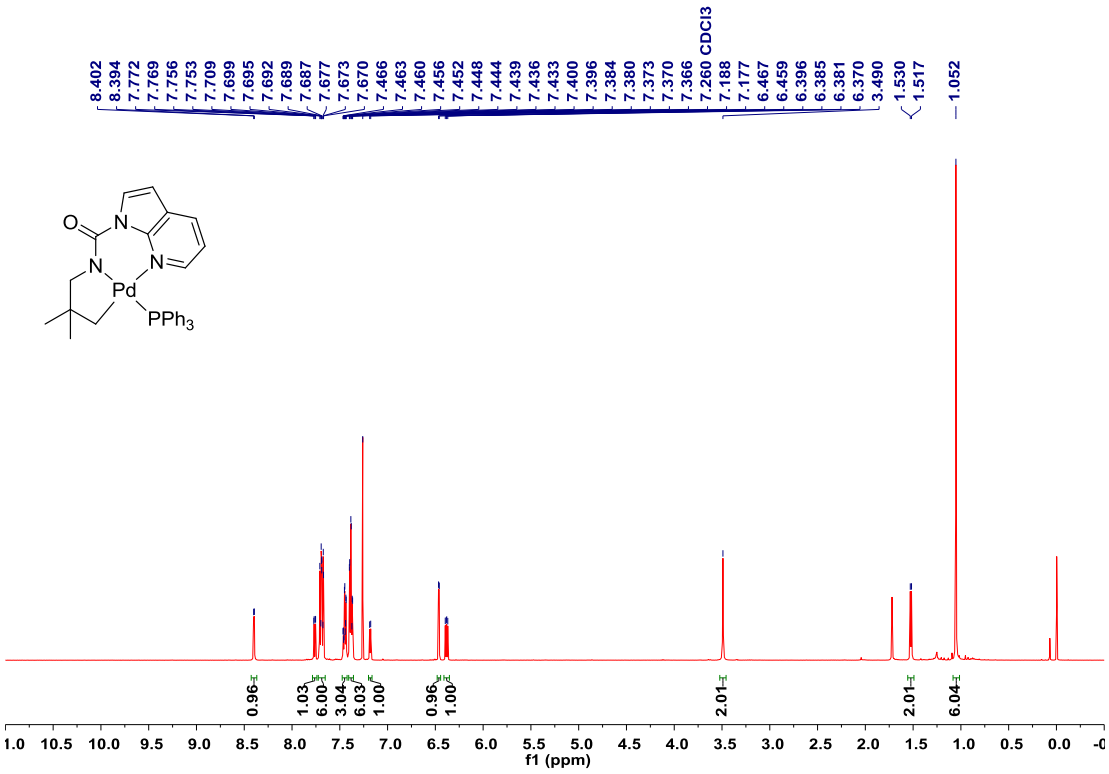


^{13}C NMR, 125 MHz, $CDCl_3$



C−H Insertion Palladacycle (13)

^{1}H NMR, 500 MHz, $CDCl_3$



^{13}C NMR, 125 MHz, $CDCl_3$