Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Rh(III)-Catalyzed 7-Azaindole Synthesis *via* C–H Activation/Annulative Coupling of Aminopyridines with Alkynes

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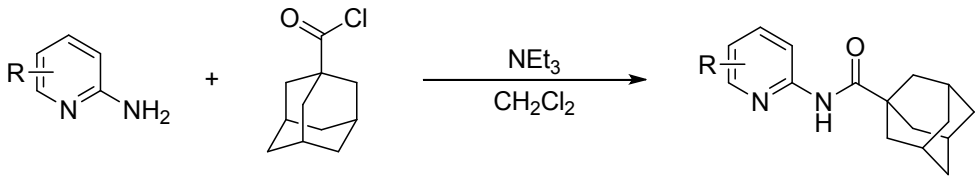
I. General Methods and Materials. Unless stated otherwise, reactions were performed in flame-dried glassware. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F_{254} plates and visualization on TLC was achieved by UV light (254 and 365nm). Flash column chromatography was undertaken on silica gel (400-630 mesh). ^{1}H NMR was recorded on 400 MHz or 300 MHz and chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet. Coupling constants, J, were reported in hertz unit (Hz). ^{13}C NMR was recorded on 100 MHz and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-*d*. Mass spectral data were obtained from the KAIST Basic Science Institute by using ESI method. Commercial grade reagents and solvents were used without further purification except as indicated below. Unless otherwise stated, all commercial reagents and solvents were used without additional purification.

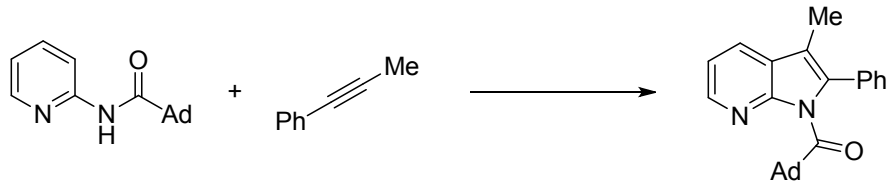
II. General Preparation of 2-Adamantamidopyridine Derivatives



Solution of 1-adamantanecarbonyl chloride (2.0 mmol) in dry dichloromethane (2.0 mL) was added dropwise to the magnetically stirred solution of 2-aminopyridine (2.0 mmol) and triethylamine (2.0 mmol) in dry dichloromethane (4.0 mL) at 0 ^{o}C under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 h. The resulting mixture was diluted with dichloromethane and then organic layer was extracted with aqueous NH_4Cl. The organic layer was dried over $MgSO_4$. After evaporation of solvent, the residue was purified by flash chromatography on silica gel (ethyl acetate/*n*-hexane) to give desired product.

III. Optimization Study

Table S1. Representative Optimization Studies[a]

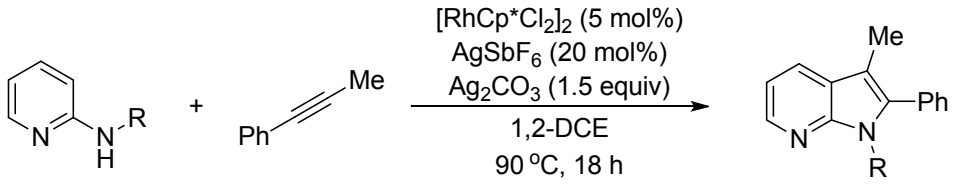


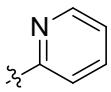
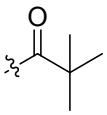
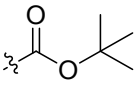
Entry	Catalyst system (mol %)	Oxidant (equiv.)	Temp. (°C)	Solvent	Yield[b] (%)
1	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	Ag_2CO_3 (1.5)	90	1,2-DCE	56
2	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	Ag_2CO_3 (1.5)	90	DMSO	n.r.
3	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	Ag_2CO_3 (1.5)	90	*t*-AmOH	< 5
4	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	Ag_2CO_3 (1.5)	90	MeCN	n.r.
5	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	Ag_2CO_3 (1.5)	90	Diglyme	n.r.
6	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	Ag_2CO_3 (1.5)	90	DMF	n.r.
7	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	Ag_2CO_3 (1.5)	90	1,4-dioxane	< 5
8	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	Ag_2CO_3 (1.5)	90	PhMe	n.r.
9	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	Ag_2CO_3 (1.5)	90	Xylene	< 5
10	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	Ag_2CO_3 (1.5)	90	Mesitylene	< 5
11	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	Ag_2CO_3 (1.5)	90	MeOH	n.r.
12	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	Ag_2CO_3 (1.5)	90	*t*-BuOH	n.r.
13	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	$Cu(OAc)_2$ (2.0)	90	1,2-DCE	n.r.
14	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	AgOAc (2.0)	90	1,2-DCE	n.r.
15	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	AgTFA (2.0)	90	1,2-DCE	n.r.
16	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	$AgBF_4$ (2.0)	90	1,2-DCE	< 5
17	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	Ag_2O (1.5)	90	1,2-DCE	7
18	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	AgF (2.0)	90	1,2-DCE	< 5
19	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	AgOTf (2.0)	90	1,2-DCE	n.r.
20	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	$AgPF_6$ (2.0)	90	1,2-DCE	n.r.
21	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	$AgNTf_2$ (2.0)	90	1,2-DCE	9
22	$[RhCp^*Cl_2]_2$ (5)	$AgSbF_6$ (2.0)	90	1,2-DCE	n.r.
23	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	AgOTs (2.0)	90	1,2-DCE	n.r.

24	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	$AgClO_4$ (2.0)	90	1,2-DCE	n.r.
25	$[RhCp^*Cl_2]_2$ (5) / $AgNTf_2$ (20)	Ag_2CO_3 (1.5)	90	1,2-DCE	47
26	$[RhCp^*Cl_2]_2$ (5) / $AgBF_4$ (20)	Ag_2CO_3 (1.5)	90	1,2-DCE	n.r.
27	$[RhCp^*Cl_2]_2$ (5) / $AgPF_6$ (20)	Ag_2CO_3 (1.5)	90	1,2-DCE	24
28	$[RhCp^*Cl_2]_2$ (5) / AgOAc (20)	Ag_2CO_3 (1.5)	90	1,2-DCE	n.r.
29	$[RhCp^*Cl_2]_2$ (5) / $Zn(OTf)_2$ (20)	Ag_2CO_3 (1.5)	90	1,2-DCE	n.r.
30	$[RhCp^*(MeCN)_3][SbF_6]$ (10)	Ag_2CO_3 (1.5)	90	1,2-DCE	39
31	$RhCp^*(OAc)_2$ (10)	Ag_2CO_3 (1.5)	90	1,2-DCE	26
32	$[Ru(p\text{-cymene})Cl_2]_2$ / $AgSbF_6$ (20)	Ag_2CO_3 (1.5)	90	1,2-DCE	n.r.
33	$[IrCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	Ag_2CO_3 (1.5)	90	1,2-DCE	n.r.
34	$Pd(OAc)_2$ (10)	Ag_2CO_3 (1.5)	90	1,2-DCE	n.r.
35	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	Ag_2CO_3 (1.5)	50	1,2-DCE	n.r.
36	$[RhCp^*Cl_2]_2$ (5) / $AgSbF_6$ (20)	Ag_2CO_3 (1.5)	120	1,2-DCE	34

[a] Reaction conditions: 2-adamantamidopyridine (0.10 mmol), 1-phenyl-1-propyne (0.15 mmol), catalyst, additive, oxidant, and solvent (1.2 mL) at an indicated temperature for 18 h. [b] Yields are reported after isolation and purification by flash silica gel chromatography. n.r. = no reaction.

Table S2. Directing group screening



Entry	R	Yield (%)	Entry	R	Yield (%)
1		-	4		-
2		42	5		-

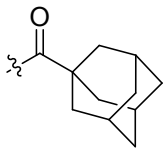
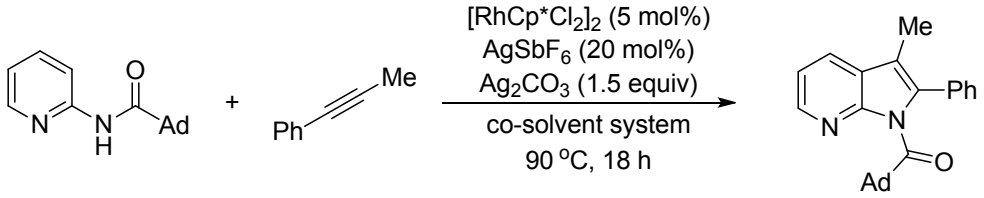
3		**56**

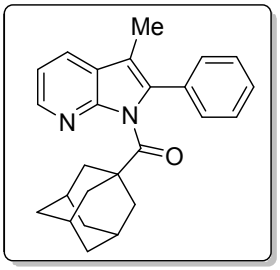
Table S3. Co-solvent system screening



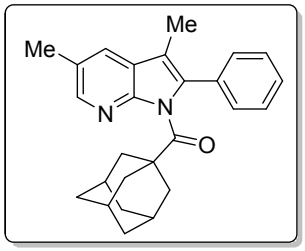
Entry	**Co-solvent system** (v/v)	**Yield** (%)
1	1,2-DCE / *t*-AmOH (5:1)	63
2	1,2-DCE / DMSO (5:1)	n.r.
3	**1,2-DCE / PhMe (5:1)**	**74**
4	1,2-DCE / Mesitylene (5:1)	62
5	1,2-DCE / PhCl (5:1)	64
6	1,2-DCE / Diglyme (5:1)	41
7	1,2-DCE / 1,4-dioxane (5:1)	43
8	1,2-DCE / MeCN (5:1)	20
9	1,2-DCE / DMF (5:1)	n.r.
10	1,2-DCE / PhMe (1:1)	40
11	1,2-DCE / PhMe (3:1)	65
12	1,2-DCE / PhMe (10:1)	67
13	1,2-DCE / PhMe (20:1)	59

IV. Experimental Procedures & Compound Characterizations

General procedure for 7-azaindole synthesis: 2-adamantamidopyridine derivative (0.1 mmol), internal alkyne (1.5 equiv), $[RhCp^*Cl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), and Ag_2CO_3 (1.5 equiv) were conbined in 1,2-DCE (1.0 mL) and PhMe (0.2 mL) under nitrogen atmosphere (balloon). The reaction mixture was heated to 90 °C with vigorous stirring. The mixture was monitored by TLC using diethyl ether and *n*-hexane = 1 : 10 as the mobile phase. When starting material disappeared, the mixture was diluted with dichloromethane and the residue was extracted with aqueous NH_4Cl. The organic layer was dried over $MgSO_4$. After evaporation of solvent, the residue was purified by flash chromatography on silica gel (diethyl ether/*n*-hexane) to give desired product.

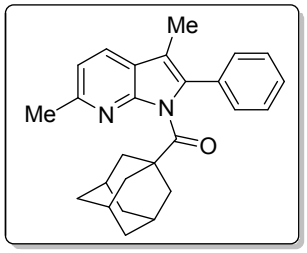


adamantan-1-yl(3-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3a). Yield 74%. mp 184-186 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.83 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.46 – 7.33 (m, 5H), 7.12 (dd, *J* = 7.8, 4.8 Hz, 1H), 2.28 (s, 3H), 1.97 – 1.91 (m, 9H), 1.63 (t, *J* = 2.8 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 185.1, 148.8, 143.6, 136.2, 132.2, 129.8, 128.4, 128.0, 126.9, 121.6, 116.8, 110.7, 46.0, 38.1, 36.3, 28.0, 9.1. HRMS (ESI$^+$) m/z calcd. $C_{25}H_{26}N_2NaO^+$ $[M+Na]^+$: 393.1937, found: 393.1935.

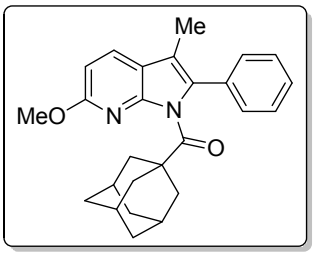


adamantan-1-yl(3,5-dimethyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3b). Yield 68%. mp 173-175 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (dd, *J* = 2.1, 0.8 Hz, 1H), 7.61 (dd, *J* = 2.0, 0.9 Hz, 1H), 7.45 – 7.33 (m, 5H), 2.43 (s, 3H), 2.25 (s, 3H), 1.99 (d, *J* = 3.0 Hz, 6H), 1.96 – 1.91 (m, 3H), 1.64 (t, *J* = 3.1 Hz,

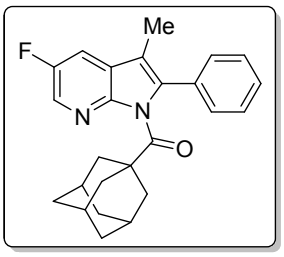
6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 184.9, 147.5, 144.4, 136.5, 132.4, 129.7, 128.4, 127.9, 127.0, 126.0, 121.6, 110.6, 45.9, 38.1, 36.3, 28.1, 18.5, 9.1. HRMS (ESI$^+$) m/z calcd. $C_{26}H_{28}N_2NaO^+$ [M+Na]$^+$: 407.2094, found: 407.2090.



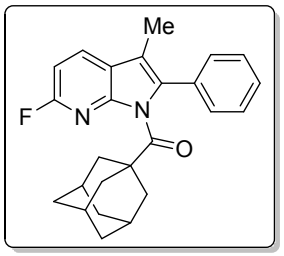
adamantan-1-yl(3,6-dimethyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3c). Yield 85%. mp 142-144 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 7.9 Hz, 1H), 7.48 – 7.38 (m, 2H), 7.41 – 7.30 (m, 3H), 6.99 (d, *J* = 7.9 Hz, 1H), 2.63 (s, 3H), 2.25 (s, 3H), 2.15 (d, *J* = 3.2 Hz, 6H), 2.05 – 1.96 (m, 3H), 1.75 – 1.68 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 184.6, 152.6, 148.6, 135.7, 132.5, 129.6, 128.3, 127.6, 127.0, 119.3, 116.8, 111.5, 45.7, 38.1, 36.4, 28.2, 24.4, 9.1. HRMS (ESI$^+$) m/z calcd. $C_{26}H_{28}N_2NaO^+$ [M+Na]$^+$: 407.2094, found: 407.2101.



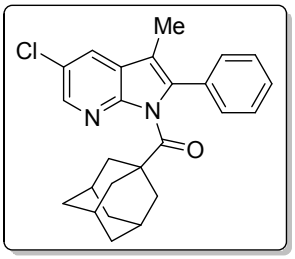
adamantan-1-yl(6-methoxy-3-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3d). Yield 76%. mp 150-153 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.4 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.37 – 7.30 (m, 3H), 6.64 (d, *J* = 8.4 Hz, 1H), 3.99 (s, 3H), 2.24 (s, 3H), 2.13 (d, *J* = 3.2 Hz, 6H), 2.03 – 1.98 (m, 3H), 1.71 (t, *J* = 3.2 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 184.9, 161.1, 146.1, 133.7, 132.5, 130.0, 129.7, 128.3, 127.4, 115.7, 111.6, 104.9, 54.1, 45.7, 38.2, 36.4, 28.1, 9.2. HRMS (ESI$^+$) m/z calcd. $C_{26}H_{28}N_2NaO_2^+$ [M+Na]$^+$: 423.2043, found: 423.2063.



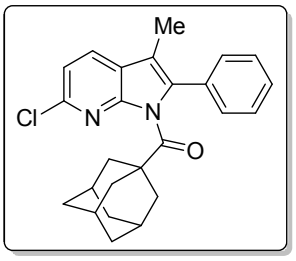
adamantan-1-yl(5-fluoro-3-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3e). Yield 80%. mp 167-170 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (dd, *J* = 2.7, 1.5 Hz, 1H), 7.50 (dd, *J* = 8.6, 2.7 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.41 – 7.35 (m, 3H), 2.24 (s, 3H), 1.93 (s, 9H), 1.68 – 1.58 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 184.6, 156.2 (d, J_{CF} = 244.3 Hz), 145.2, 138.6, 131.9 (d, J_{CF} = 5.8 Hz), 131.6, 129.7, 128.5, 128.3, 122.1 (d, J_{CF} = 6.5 Hz), 112. 7 (d, J_{CF} = 20.7 Hz), 110.6 (d, J_{CF} = 4.0 Hz), 46.0, 38.2, 36.2, 28.0, 9.1. HRMS (ESI^{+}) m/z calcd. $C_{25}H_{25}FN_2NaO^{+}$ [M+Na]$^{+}$: 411.1843, found: 411.1849.



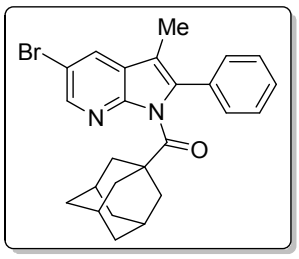
adamantan-1-yl(6-fluoro-3-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3f). Yield 69%. mp 193-195 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 8.3, 7.7 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.38 – 7.33 (m, 3H), 6.76 (dd, *J* = 8.3, 1.3 Hz, 1H), 2.26 (s, 3H), 1.99 – 1.93 (m, 9H), 1.65 (t, *J* = 2.6 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 184.0, 160.1 (d, J_{CF} = 237.3 Hz), 144.8 (d, J_{CF} = 17.9 Hz), 136.0 (d, J_{CF} = 4.6 Hz), 131.9, 131.4 (d, J_{CF} = 9.2 Hz), 129.6, 128.5, 128.1, 119.3 (d, J_{CF} = 3.1 Hz), 110.9, 102.4 (d, J_{CF} = 38.5 Hz), 45.9, 38.1, 36.2, 28.0, 9.2. HRMS (ESI^{+}) m/z calcd. $C_{25}H_{25}FN_2NaO^{+}$ [M+Na]$^{+}$: 411.1843, found: 411.1846.



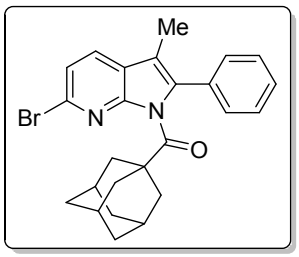
adamantan-1-yl(5-chloro-3-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3g). Yield 77%. mp 141-143 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 2.3 Hz, 1H), 7.79 (d, *J* = 2.3 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.40 – 7.35 (m, 3H), 2.24 (s, 3H), 1.94 – 1.89 (m, 9H), 1.66 – 1.59 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 184.5, 146.8, 142.0, 138.1, 131.7, 129.8, 128.5, 128.4, 126.2, 124.8, 122.5, 110.1, 46.0, 38.1, 36.2, 28.0, 9.0. HRMS (ESI$^+$) m/z calcd. $C_{25}H_{25}ClN_2NaO^+$ [M+Na]$^+$: 427.1548, found: 427.1561.



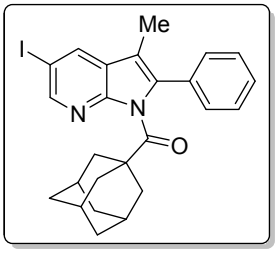
adamantan-1-yl(6-chloro-3-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3h). Yield 87%. mp 181-183 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.1 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.38 – 7.33 (m, 3H), 7.13 (d, *J* = 8.1 Hz, 1H), 2.24 (s, 3H), 2.05 (d, *J* = 3.1 Hz, 6H), 2.01 – 1.96 (m, 3H), 1.69 (t, *J* = 2.6 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 183.7, 147.2, 144.7, 137.0, 131.8, 129.7, 129.2, 128.4, 128.1, 120.3, 117.1, 111.3, 45.8, 38.1, 36.3, 28.1, 9.1. HRMS (ESI$^+$) m/z calcd. $C_{25}H_{25}ClN_2NaO^+$ [M+Na]$^+$: 427.1548, found: 427.1569.



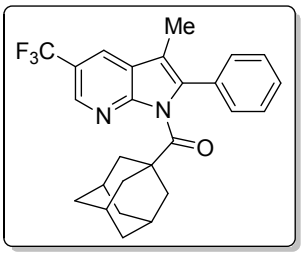
adamantan-1-yl(5-bromo-3-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3i). Yield 70%. mp 132-135 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 (d, *J* = 2.2 Hz, 1H), 7.94 (d, *J* = 2.2 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.40 – 7.35 (m, 3H), 2.24 (s, 3H), 1.94 – 1.89 (m, 9H), 1.66 – 1.58 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 184.4, 146.9, 144.0, 137.9, 131.6, 129.8, 129.1, 128.5, 128.4, 123.2, 112.8, 110.0, 46.1, 38.1, 36.2, 27.9, 9.0. HRMS (ESI$^+$) m/z calcd. $C_{25}H_{25}BrN_2NaO^+$ [M+Na]$^+$: 471.1042, found: 471.1065.



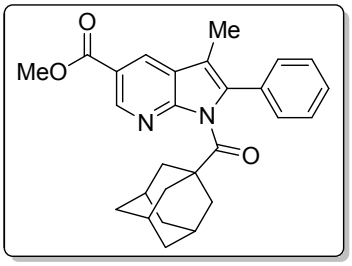
adamantan-1-yl(6-bromo-3-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3j). Yield 72%. mp 170-172 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.1 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.38 – 7.32 (m, 3H), 7.27 (d, *J* = 8.1 Hz, 1H), 2.24 (s, 3H), 2.09 (d, *J* = 3.0 Hz, 6H), 2.03 – 1.98 (m, 3H), 1.74 – 1.67 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 183.5, 147.5, 137.1, 134.6, 131.7, 129.6, 129.1, 128.4, 128.1, 120.6, 120.6, 111.5, 45.8, 38.1, 36.3, 28.1, 9.1. HRMS (ESI^{+}) m/z calcd. $C_{25}H_{25}BrN_2NaO^{+}$ [M+Na]$^{+}$: 471.1042, found: 471.1065.



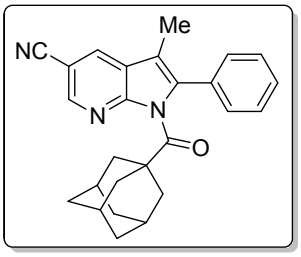
adamantan-1-yl(5-iodo-3-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3k). Yield 67%. mp 141-145 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 2.0 Hz, 1H), 8.13 (d, *J* = 2.0 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.39 – 7.34 (m, 3H), 2.23 (s, 3H), 1.94 – 1.89 (m, 9H), 1.65 – 1.59 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 184.4, 148.7, 147.1, 137.4, 134.9, 131.6, 129.8, 128.5, 128.3, 124.2, 109.9, 83.7, 46.0, 38.1, 36.2, 27.9, 9.0. HRMS (ESI^{+}) m/z calcd. $C_{25}H_{25}IN_2NaO^{+}$ [M+Na]$^{+}$: 519.0904, found: 519.0924.



adamantan-1-yl(3-methyl-2-phenyl-5-(trifluoromethyl)-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3l). Yield 70%. mp 129-131 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (dd, *J* = 2.2, 0.9 Hz, 1H), 8.08 (dd, *J* = 2.1, 0.6 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.43 – 7.38 (m, 3H), 2.31 (s, 3H), 1.95 – 1.91 (m, 3H), 1.89 (d, *J* = 2.9 Hz, 6H), 1.65 – 1.57 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 184.4, 149.6, 140.6 (q, J_{CF} = 4.0 Hz), 138.3, 131.3, 129.9, 128.6, 124.7 (q, J_{CF} = 272.8 Hz), 124.4 (q, J_{CF} = 3.8 Hz), 120.6, 120.0 (q, J_{CF} = 32.3 Hz), 110.8, 46.2, 38.2, 36.1, 27.9, 9.0. HRMS (ESI$^+$) m/z calcd. $C_{26}H_{25}F_3N_2NaO^+$ [M+Na]$^+$: 461.1811, found: 461.1835.

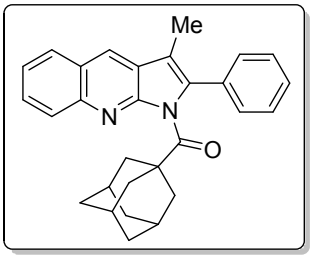


methyl 1-(adamantane-1-carbonyl)-3-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridine-5-carboxylate (3m). Yield 64%. mp 165-168 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.98 (d, *J* = 2.0 Hz, 1H), 8.50 (d, *J* = 2.0 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.41 – 7.36 (m, 3H), 3.95 (s, 3H), 2.30 (s, 3H), 1.93 – 1.89 (m, 3H), 1.87 (d, *J* = 3.4 Hz, 6H), 1.64 – 1.56 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 184.6, 166.9, 150.3, 145.7, 137.6, 131.5, 129.9, 129.0, 128.6, 128.5, 120.8, 119.4, 111.2, 52.1, 46.2, 38.1, 36.1, 27.9, 9.0. HRMS (ESI$^+$) m/z calcd. $C_{27}H_{28}N_2NaO_3^+$ [M+Na]$^+$: 451.1992, found: 451.2008.

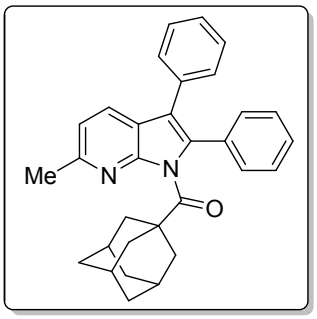


1-(adamantane-1-carbonyl)-3-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridine-5-carbonitrile (3n). Yield 58%. mp 161-163 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (d, *J* = 2.0 Hz, 1H), 8.12 (d, *J* = 2.0 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.43 – 7.38 (m, 3H), 2.29 (s, 3H), 1.93 – 1.87 (m, 3H), 1.80 (d, *J* = 2.9 Hz, 6H), 1.65 – 1.54 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 184.1, 148.8, 146.2, 138.6, 130.8, 130.8, 129.9, 128.9, 128.7, 120.8,

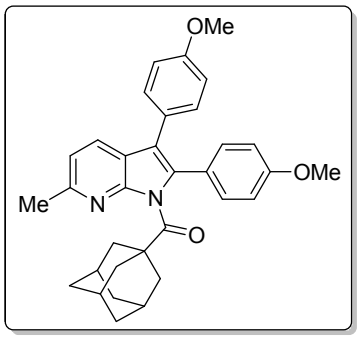
118.4, 110.3, 102.0, 46.2, 38.2, 36.0, 27.8, 9.0. HRMS (ESI$^+$) m/z calcd. $C_{26}H_{25}N_3NaO^+$ [M+Na]$^+$: 418.1890, found: 418.1898.



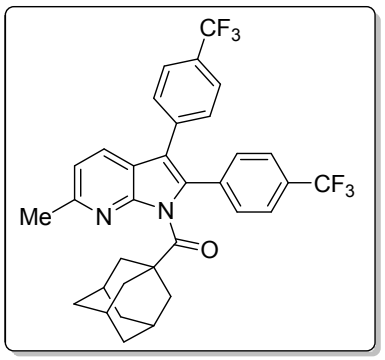
adamantan-1-yl(3-methyl-2-phenyl-1H-pyrrolo[2,3-b]quinolin-1-yl)methanone (3o). Yield 69%. mp 194-196 ^{o}C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (s, 1H), 8.11 (dt, *J* = 8.6, 1.0 Hz, 1H), 7.93 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.65 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.50 – 7.36 (m, 6H), 2.35 (d, *J* = 3.8 Hz, 9H), 2.10 – 2.05 (m, 3H), 1.86 – 1.73 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 184.2, 150.2, 145.1, 140.4, 132.3, 129.3, 128.4, 128.3, 128.0, 127.9, 127.9, 125.3, 125.1, 123.9, 123.9, 112.2, 45.6, 38.1, 36.6, 28.3, 9.3. HRMS (ESI$^+$) m/z calcd. $C_{29}H_{28}N_2NaO^+$ [M+Na]$^+$: 443.2094, found: 443.2109.



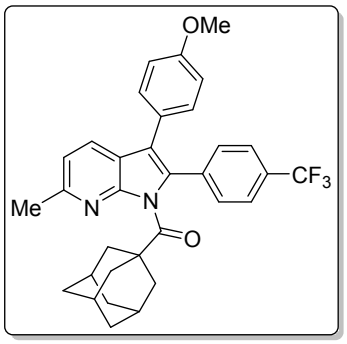
adamantan-1-yl(6-methyl-2,3-diphenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4a). Yield 94%. mp 145-147 ^{o}C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.31 – 7.19 (m, 10H), 7.01 (d, *J* = 8.0 Hz, 1H), 2.63 (s, 3H), 2.03 (d, *J* = 3.1 Hz, 6H), 1.99 – 1.94 (m, 3H), 1.66 (t, *J* = 3.0 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 185.3, 153.2, 148.6, 135.1, 133.6, 131.8, 130.5, 129.7, 128.4, 128.3, 128.1, 127.9, 126.4, 117.6, 117.4, 116.2, 46.1, 38.2, 36.3, 28.1, 24.5. HRMS (ESI$^+$) m/z calcd. $C_{31}H_{30}N_2NaO^+$ [M+Na]$^+$: 469.2250, found: 469.2266.



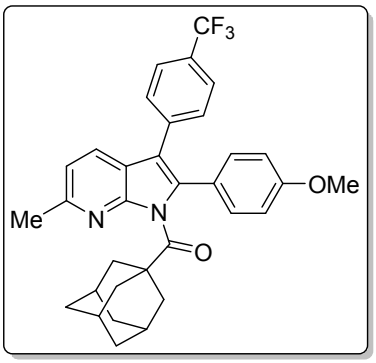
adamantan-1-yl(2,3-bis(4-methoxyphenyl)-6-methyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4b). Yield 86%. mp 91-94 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.16 (m, 4H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.86 – 6.81 (m, 4H), 3.80 (s, 3H), 3.79 (s, 3H), 2.61 (s, 3H), 2.05 – 2.00 (m, 6H), 1.98 – 1.94 (m, 3H), 1.66 (t, *J* = 3.1 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 185.6, 159.2, 158.1, 152.7, 148.5, 134.6, 131.7, 130.7, 127.6, 126.1, 124.2, 117.8, 117.2, 115.4, 113.9, 113.8, 55.2, 46.1, 38.2, 36.4, 28.1, 24.4. HRMS (ESI^{+}) m/z calcd. $C_{33}H_{34}N_2NaO_3^{+}$ [M+Na]$^{+}$: 529.2462, found: 529.2479.



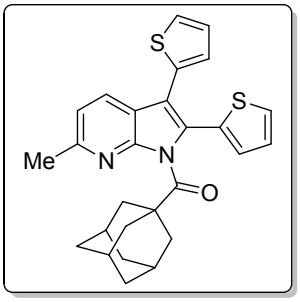
adamantan-1-yl(6-methyl-2,3-bis(4-(trifluoromethyl)phenyl)-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4c). Yield 64%. mp 242-244 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.64 – 7.58 (m, 4H), 7.43 – 7.33 (m, 4H), 7.11 (d, *J* = 8.1 Hz, 1H), 2.69 (s, 3H), 2.16 (d, *J* = 3.0 Hz, 6H), 2.09 – 2.03 (m, 3H), 1.75 (t, *J* = 3.1 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 184.5, 154.3, 148.7, 136.9, 135.2, 134.3, 130.6, 130.1 (q, J_{CF} = 32.3 Hz), 129.9, 129.0 (q, J_{CF} = 32.3 Hz), 128.0, 125.5 (dq, J_{CF} = 10.9, 3.8 Hz), 124.2 (q, J_{CF} = 270.3 Hz), 124.0 (q, J_{CF} = 270.9 Hz), 118.1, 117.3, 116.6, 46.0, 38.2, 36.4, 28.1, 24.5. HRMS (ESI^{+}) m/z calcd. $C_{33}H_{28}F_6N_2NaO^{+}$ [M+Na]$^{+}$: 605.1998, found: 605.2017.



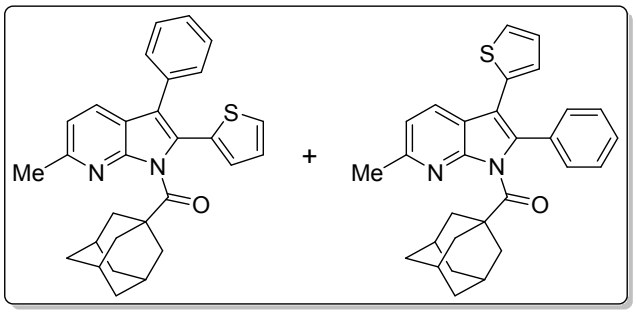
adamantan-1-yl(3-(4-methoxyphenyl)-6-methyl-2-(4-(trifluoromethyl)phenyl)-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4d) Yield 45%. mp 86-89 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.58 – 7.50 (m, 2H), 7.39 – 7.31 (m, 2H), 7.16 – 7.07 (m, 2H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.87 – 6.83 (m, 2H), 3.80 (s, 3H), 2.64 (s, 3H), 2.17 (d, *J* = 3.0 Hz, 6H), 2.05 – 1.99 (m, 3H), 1.72 (t, *J* = 3.2 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 184.6, 158.6, 153.7, 148.7, 135.9, 133.5, 130.8, 130.4, 129.6 (q, J_{CF} = 32.5 Hz), 128.2, 125.2 (q, J_{CF} = 3.6 Hz), 125.0, 124.1 (q, J_{CF} = 270.0 Hz), 118.2, 118.1, 117.7, 114.1, 55.2, 45.9, 38.2, 36.4, 28.2, 24.4. HRMS (ESI^{+}) m/z calcd. $C_{33}H_{31}F_3N_2NaO_2^{+}$ [M+Na]$^{+}$: 567.2230, found: 567.2234.



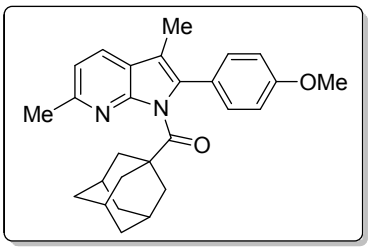
adamantan-1-yl(2-(4-methoxyphenyl)-6-methyl-3-(4-(trifluoromethyl)phenyl)-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4d') Yield 21%. mp 84-87 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.1 Hz, 1H), 7.64 – 7.49 (m, 2H), 7.44 – 7.31 (m, 2H), 7.23 – 7.18 (m, 2H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.88 – 6.83 (m, 2H), 3.81 (s, 3H), 2.62 (s, 3H), 2.01 – 1.92 (m, 9H), 1.69 – 1.60 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 185.5, 159.7, 153.3, 148.4, 137.9, 135.6, 131.9, 129.7, 128.1 (q, J_{CF} = 32.3 Hz), 127.4, 125.3 (q, J_{CF} = 3.8 Hz), 124.3 (q, J_{CF} = 270.1 Hz), 123.4, 117.6, 117.0, 114.1, 114.0, 55.2, 46.2, 38.2, 36.3, 28.0, 24.5. HRMS (ESI^{+}) m/z calcd. $C_{33}H_{31}F_3N_2NaO_2^{+}$ [M+Na]$^{+}$: 567.2230, found: 567.2237.



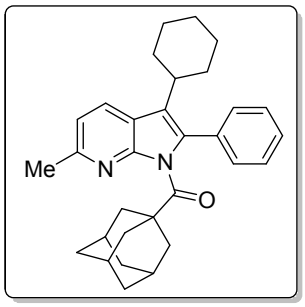
adamantan-1-yl(6-methyl-2,3-di(thiophen-2-yl)-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4e). Yield 86%. mp 165-167 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.42 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.25 (dd, *J* = 4.9, 1.4 Hz, 1H), 7.18 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.08 – 7.01 (m, 4H), 2.63 (s, 3H), 2.04 (d, *J* = 3.1 Hz, 6H), 2.01 – 1.96 (m, 3H), 1.68 (t, *J* = 2.8 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 184.9, 154.0, 148.1, 134.6, 131.4, 130.8, 128.4, 128.1, 127.8, 127.1, 127.0, 126.2, 124.9, 117.7, 116.9, 111.7, 46.1, 38.1, 36.3, 28.0, 24.5. HRMS (ESI^{+}) m/z calcd. $C_{27}H_{26}N_2NaOS_2^{+}$ [M+Na]$^{+}$: 481.1379, found: 481.1403.



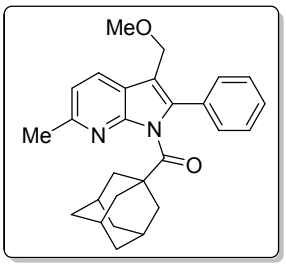
adamantan-1-yl(6-methyl-3-phenyl-2-(thiophen-2-yl)-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone & adamantan-1-yl(6-methyl-2-phenyl-3-(thiophen-2-yl)-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4f). Yield 75% (2.5:1 mixture). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.0 Hz, 0.4H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.30 (m, 8.2H), 7.23 (dd, *J* = 5.1, 1.2 Hz, 0.4H), 7.11 – 7.08 (m, 1.4H), 7.05 – 7.00 (m, 2.2H), 6.96 (dd, *J* = 3.5, 1.2 Hz, 0.4H), 2.68 (s, 1.2H), 2.67 (s, 3H), 2.08 (d, *J* = 3.0 Hz, 6H), 2.05 (d, *J* = 3.0 Hz, 2.4H), 2.03 – 2.00 (m, 4.2H), 1.71 (t, *J* = 3.2 Hz, 8.4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 185.4, 184.9, 153.8, 153.4, 148.4, 148.2, 135.5, 135.2, 133.3, 132.3, 131.5, 130.8, 130.4, 129.9, 129.8, 128.7, 128.3, 128.3, 128.3, 128.0, 127.6, 127.5, 127.1, 127.0, 126.8, 125.7, 124.4, 117.8, 117.6, 117.5, 117.3, 117.2, 46.3, 46.0, 38.9, 38.2, 38.2, 36.5, 36.3, 28.1, 28.0, 24.5, 24.4. HRMS (ESI^{+}) m/z calcd. $C_{29}H_{28}N_2NaOS^{+}$ [M+Na]$^{+}$: 475.1815, found: 475.1835.



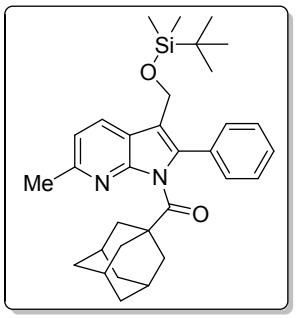
adamantan-1-yl(2-(4-methoxyphenyl)-3,6-dimethyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4g). Yield 56%. mp 175-177 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 7.9 Hz, 1H), 7.31 – 7.26 (m, 2H), 6.99 – 6.93 (m, 3H), 3.84 (s, 3H), 2.61 (s, 3H), 2.22 (s, 3H), 2.11 (d, *J* = 3.0 Hz, 6H), 2.01 – 1.96 (m, 3H), 1.70 (t, *J* = 3.2 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 185.0, 159.0, 152.3, 148.5, 135.5, 130.8, 126.8, 124.8, 119.3, 116.6, 113.8, 110.8, 55.2, 45.8, 38.1, 36.4, 28.2, 24.4, 9.1. HRMS (ESI^{+}) m/z calcd. $C_{27}H_{30}N_2NaO_2^{+}$ [M+Na]$^{+}$: 437.2199, found: 437.2206.



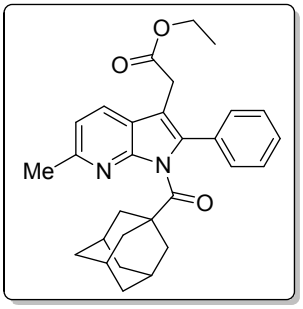
adamantan-1-yl(3-cyclohexyl-6-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4h). Yield 82%. mp 210-212 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.0 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.37 – 7.30 (m, 3H), 6.94 (d, *J* = 8.0 Hz, 1H), 2.75 – 2.63 (m, 1H), 2.59 (s, 3H), 2.06 (d, *J* = 3.0 Hz, 6H), 1.99 – 1.93 (m, 3H), 1.90 – 1.71 (m, 7H), 1.67 (t, *J* = 3.1 Hz, 6H), 1.32 – 1.21 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 185.1, 152.1, 148.9, 134.6, 132.6, 130.1, 128.9, 128.2, 127.8, 121.0, 117.0, 116.2, 45.7, 38.1, 36.4, 36.1, 33.1, 28.2, 26.8, 26.2, 24.3. HRMS (ESI^{+}) m/z calcd. $C_{31}H_{36}N_2NaO^{+}$ [M+Na]$^{+}$: 475.2720, found: 475.2730.



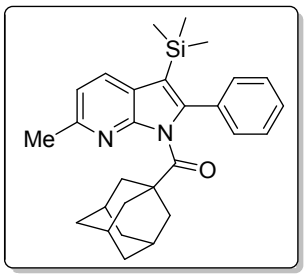
adamantan-1-yl(3-(methoxymethyl)-6-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4i). Yield 72%. mp 78-80 °C. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.96 (d, J = 8.0 Hz, 1H), 7.54 – 7.43 (m, 5H), 7.11 (dd, J = 8.0, 0.5 Hz, 1H), 4.54 (s, 2H), 3.37 (s, 3H), 2.68 (s, 3H), 2.10 (d, J = 3.1 Hz, 6H), 2.04 – 1.99 (m, 3H), 1.74 (t, J = 3.1 Hz, 6H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 184.9, 153.2, 148.5, 137.9, 131.6, 129.9, 128.4, 128.3, 127.9, 118.1, 117.2, 112.4, 65.2, 57.6, 45.9, 38.1, 36.3, 28.3, 24.2. HRMS (ESI$^+$) m/z calcd. $C_{27}H_{30}N_2NaO_2^+$ [M+Na]$^+$: 437.2199, found: 437.2210.



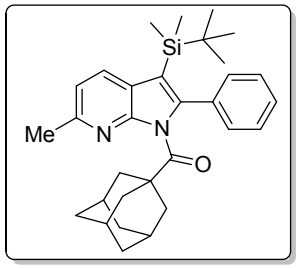
adamantan-1-yl(3-(((tert-butyldimethylsilyl)oxy)methyl)-6-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4j). Yield 65%. mp 55-57 °C. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.98 (d, J = 8.0 Hz, 1H), 7.53 – 7.42 (m, 5H), 7.10 (d, J = 8.0 Hz, 1H), 4.82 (s, 2H), 2.68 (s, 3H), 2.15 (d, J = 3.0 Hz, 6H), 2.07 – 2.00 (m, 3H), 1.76 (t, J = 3.0 Hz, 6H), 0.93 (s, 9H), 0.06 (s, 6H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 185.6, 153.9, 149.5, 137.5, 132.6, 130.7, 129.1, 129.0, 129.0, 118.9, 117.9, 116.2, 57.4, 46.7, 39.0, 37.2, 29.2, 26.5, 25.0, 19.0, -4.8. HRMS (ESI$^+$) m/z calcd. $C_{32}H_{42}N_2NaO_2Si^+$ [M+Na]$^+$: 537.2908, found: 537.2920.



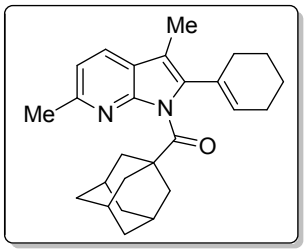
ethyl 2-(1-(adamantane-1-carbonyl)-6-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (4k). Yield 67%. mp 117-119 °C. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.88 (d, J = 8.0 Hz, 1H), 7.55 – 7.44 (m, 5H), 7.10 (d, J = 8.0 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 3.68 (s, 2H), 2.68 (s, 3H), 2.14 (d, J = 3.2 Hz, 6H), 2.06 – 2.01 (m, 3H), 1.81 – 1.72 (m, 6H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Methylene Chloride-d_2) δ 185.4, 171.9, 154.0, 149.2, 138.1, 132.4, 130.7, 129.2, 129.1, 128.6, 119.0, 117.9, 109.5, 61.7, 46.6, 38.9, 37.2, 31.6, 29.2, 25.0, 14.8. HRMS (ESI$^+$) m/z calcd. $C_{29}H_{32}N_2NaO_3^+$ [M+Na]$^+$: 479.2305, found: 479.2322.



adamantan-1-yl(6-methyl-2-phenyl-3-(trimethylsilyl)-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4l). Yield 64%. mp 151-153 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, J = 8.0 Hz, 1H), 7.42 – 7.34 (m, 5H), 6.96 (d, J = 8.2 Hz, 1H), 2.60 (s, 3H), 1.99 – 1.90 (m, 9H), 1.64 (t, J = 2.7 Hz, 6H), 0.09 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 185.5, 152.1, 149.8, 144.8, 133.9, 131.0, 129.7, 128.6, 127.6, 122.2, 116.6, 109.9, 45.7, 38.1, 36.4, 28.1, 24.3, 0.8. HRMS (ESI$^+$) m/z calcd. $C_{28}H_{34}N_2NaOSi^+$ [M+Na]$^+$: 465.2333, found: 465.2333.

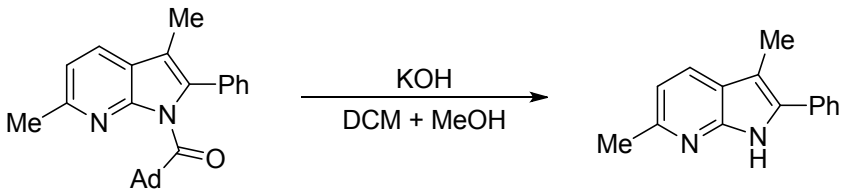


adamantan-1-yl(3-(tert-butyldimethylsilyl)-6-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4m). Yield 56%. mp 162-164 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.45 – 7.31 (m, 5H), 6.96 (d, *J* = 8.1 Hz, 1H), 2.59 (s, 3H), 2.00 – 1.90 (m, 9H), 1.69 – 1.59 (m, 6H), 0.92 (s, 9H), -0.06 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 185.6, 152.1, 149.7, 145.2, 133.8, 131.5, 130.8, 128.6, 127.3, 122.6, 116.6, 107.7, 45.7, 38.1, 36.4, 28.1, 27.3, 24.3, 18.2, -3.8. HRMS (ESI^{+}) m/z calcd. $C_{31}H_{40}N_2NaOSi^{+}$ [M+Na]$^{+}$: 507.2802, found: 507.2822.



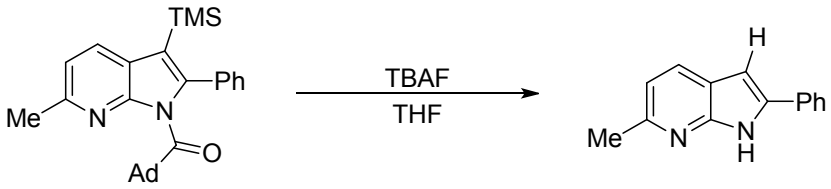
adamantan-1-yl(2-(cyclohex-1-en-1-yl)-3,6-dimethyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4n). Yield 46%. mp 114-116 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.9 Hz, 1H), 6.92 (dd, *J* = 7.8, 0.5 Hz, 1H), 5.79 (dq, *J* = 3.8, 1.8 Hz, 1H), 2.58 (s, 3H), 2.29 (d, *J* = 2.9 Hz, 6H), 2.23 – 2.18 (m, 2H), 2.17 – 2.12 (m, 5H), 2.07 – 2.00 (m, 3H), 1.80 – 1.65 (m, 10H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 184.3, 151.7, 148.0, 138.8, 130.2, 130.1, 126.5, 119.5, 116.5, 110.2, 45.5, 38.1, 36.6, 29.4, 28.4, 25.5, 24.3, 22.7, 22.0, 9.2. HRMS (ESI^{+}) m/z calcd. $C_{26}H_{32}N_2NaO^{+}$ [M+Na]$^{+}$: 411.2407, found: 411.2426.

General procedure for deacylation of N-adamantanecarbonyl-7-azaindole:



Adamantan-1-yl(3,6-dimethyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (0.1 mmol, 38.5 mg) was weighed into a 25ml round-bottomed flask and dissolved in dichloromethane (1.0 mL) and methanol (0.5 mL). Potassium hydroxide (0.3 mmol, 28.1 mg) was added to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was diluted with dichloromethane and then organic layer was extracted with aqueous NH_4Cl. The organic layer was dried over $MgSO_4$. After evaporation of solvent, the residue was purified by flash chromatography on silica gel (diethyl ether/*n*-hexane = 1.5 : 1) to give desired product. Yield 98% (21.8 mg). mp 124-127 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.50 (s, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.48 – 7.41 (m, 2H), 7.38 – 7.31 (m, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 2.43 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.7, 148.5, 133.8, 133.0, 128.7, 128.0, 127.5, 127.4, 120.3, 115.5, 106.7, 23.9, 9.6. HRMS (ESI$^+$) m/z calcd. $C_{15}H_{15}N_2^+$ $[M+H]^+$: 223.1230, found: 223.1248.

General procedure for desilylation of 3-trimethylsilyl-7-azaindole:



Adamantan-1-yl(6-methyl-2-phenyl-3-(trimethylsilyl)-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (0.1 mmol, 44.3 mg) was weighed into a 25ml round-bottomed flask and dissolved in THF (1.0 mL). Tetrabutylammonium fluoride (1.0 M in THF, 0.3 mmol, 0.3 mL) was added to the reaction mixture and stirred at room temperature for 30 h. The resulting mixture was diluted with diethyl ether and then organic layer was extracted with aqueous NH_4Cl. The organic layer was dried over $MgSO_4$. After evaporation of solvent, the residue was purified by flash chromatography on silica gel (diethyl ether/*n*-hexane = 1 : 1) to give desired product. Yield 83% (17.3 mg). mp 123-125 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.80 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.59 (m, 1H), 7.41 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.34 – 7.28 (m, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.73 (s, 1H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.8, 149.4, 138.0, 132.1, 129.1, 129.0, 128.0, 125.5, 119.6, 116.5, 97.7, 24.2. HRMS (ESI$^+$) m/z calcd. $C_{14}H_{13}N_2^+$ $[M+H]^+$: 209.1073, found: 209.1081.

NOE studies of 4d and 4f:

Figure S1.

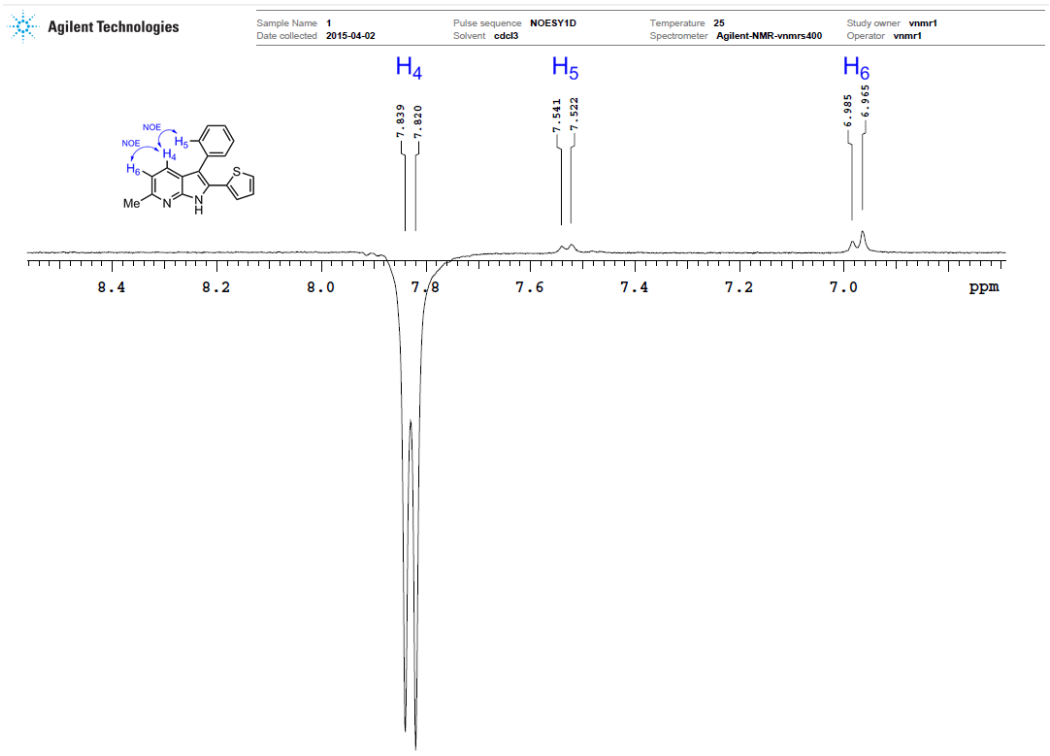


Figure S2.

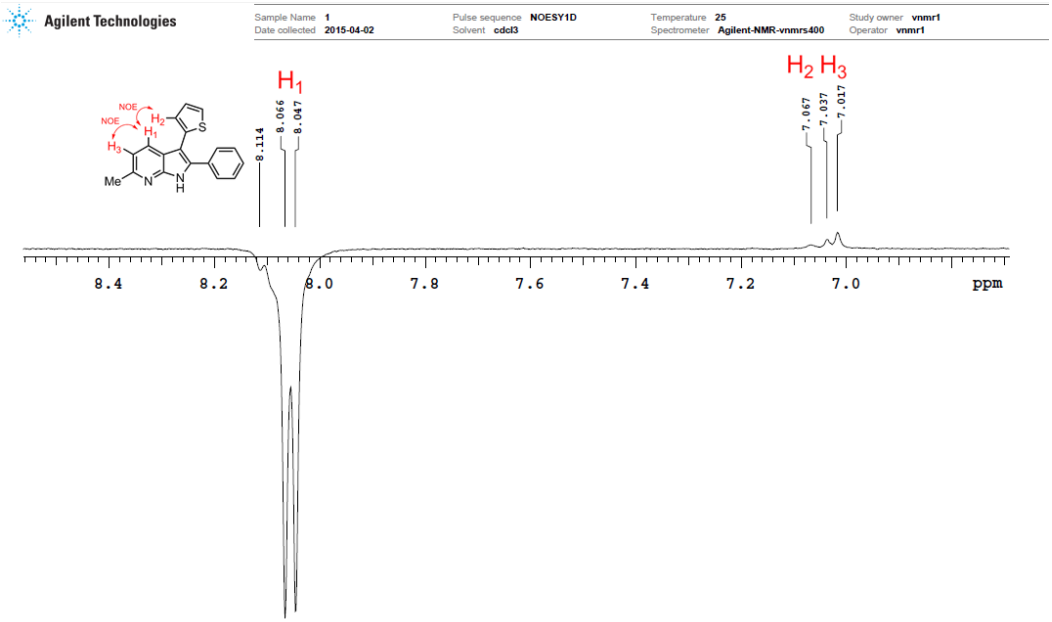


Figure S3.

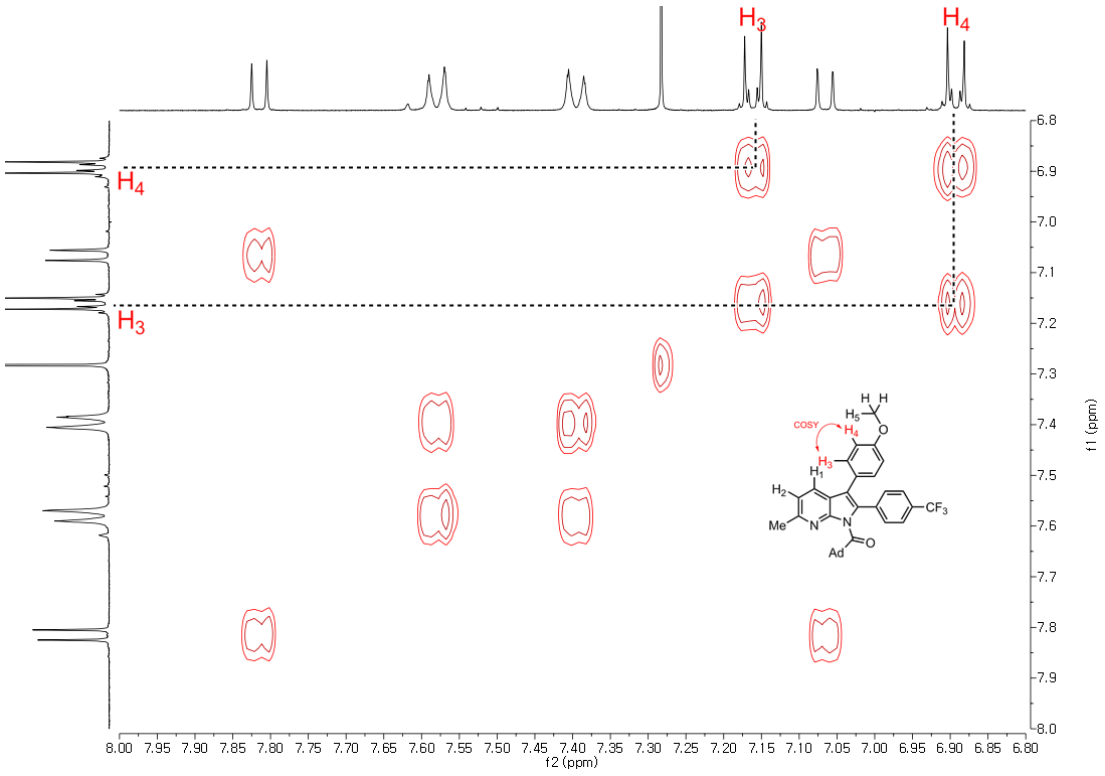


Figure S4.

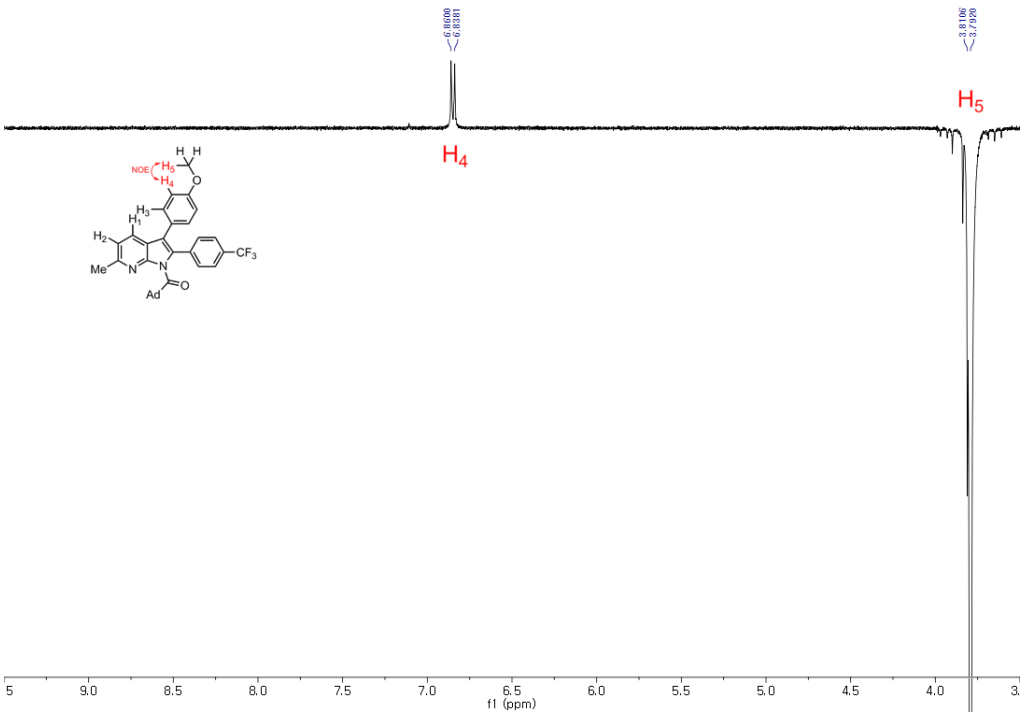
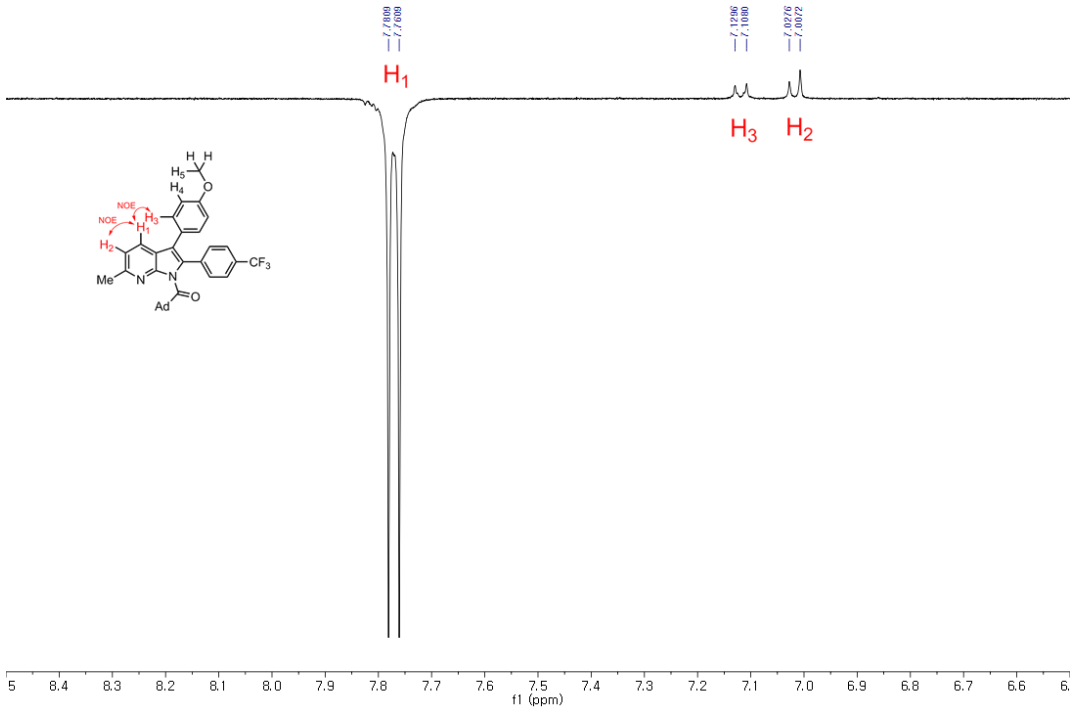


Figure S5.

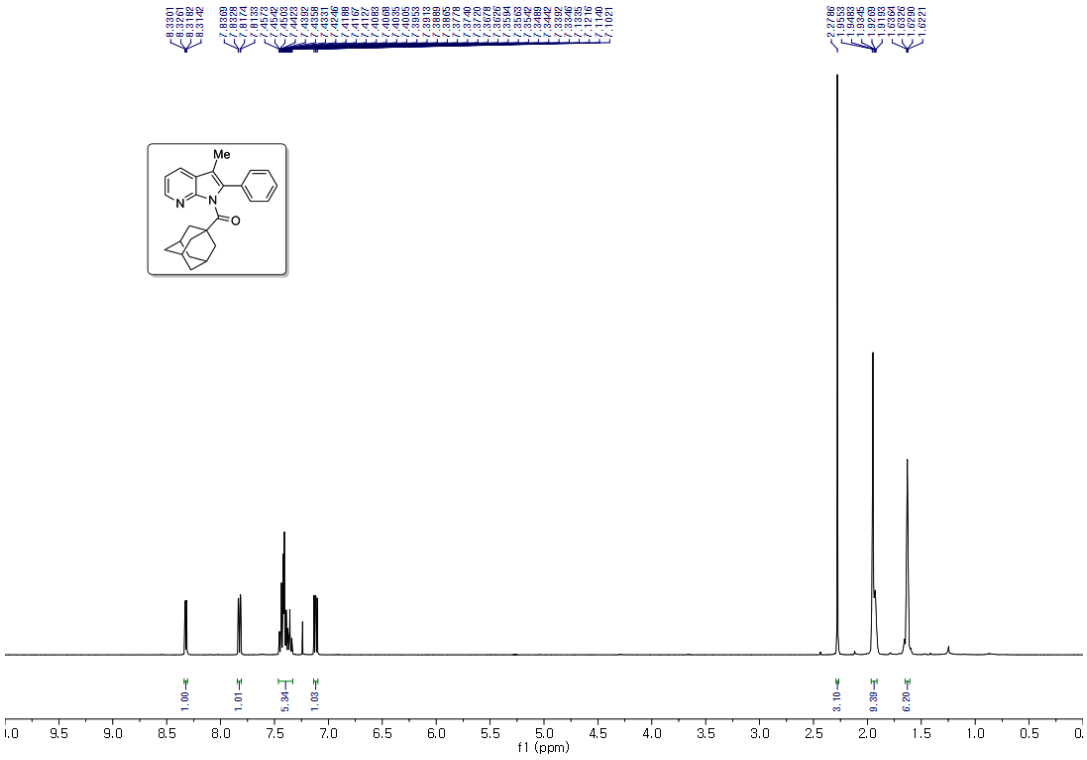

7.7809
7.7699
7.1296
7.1080
7.0276
7.0072
H1
H3
H2
NOE
NOE
H5
H4
H3
H1
H2
Me
N
N
O
Ad
CF3
5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
f1 (ppm)

Appendix I

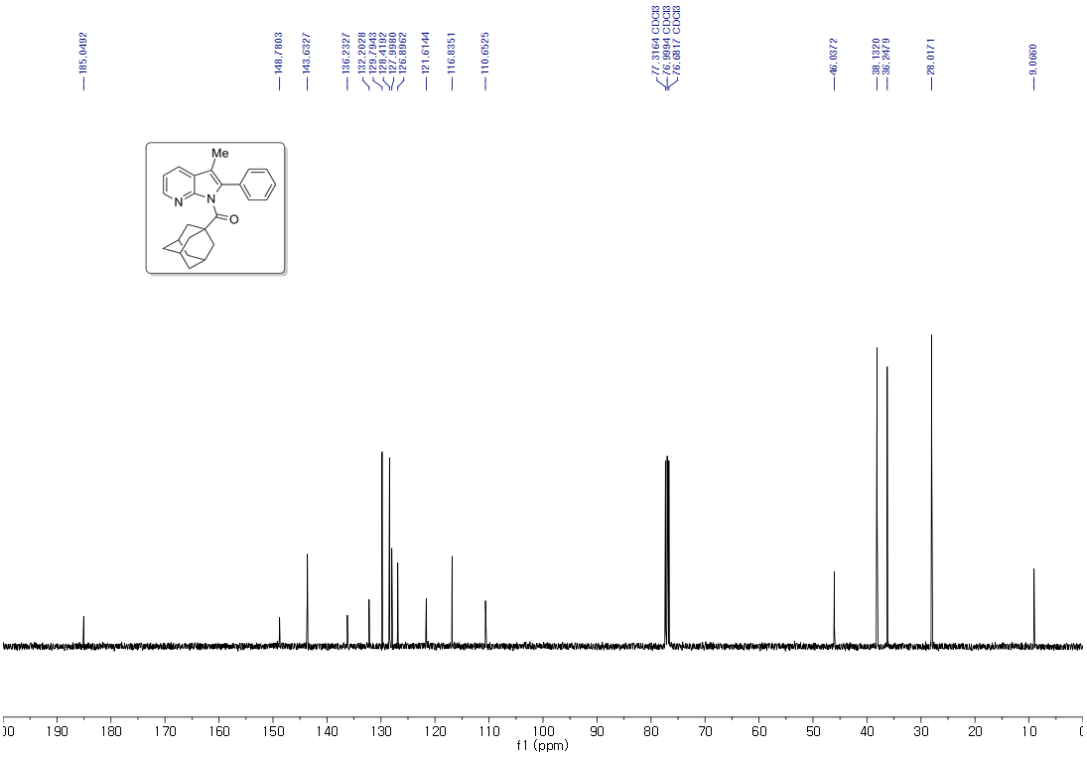
Spectral Copies of ^{1}H- and ^{13}C-NMR Data

Obtained in This Study

adamantan-1-yl(3-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3a).

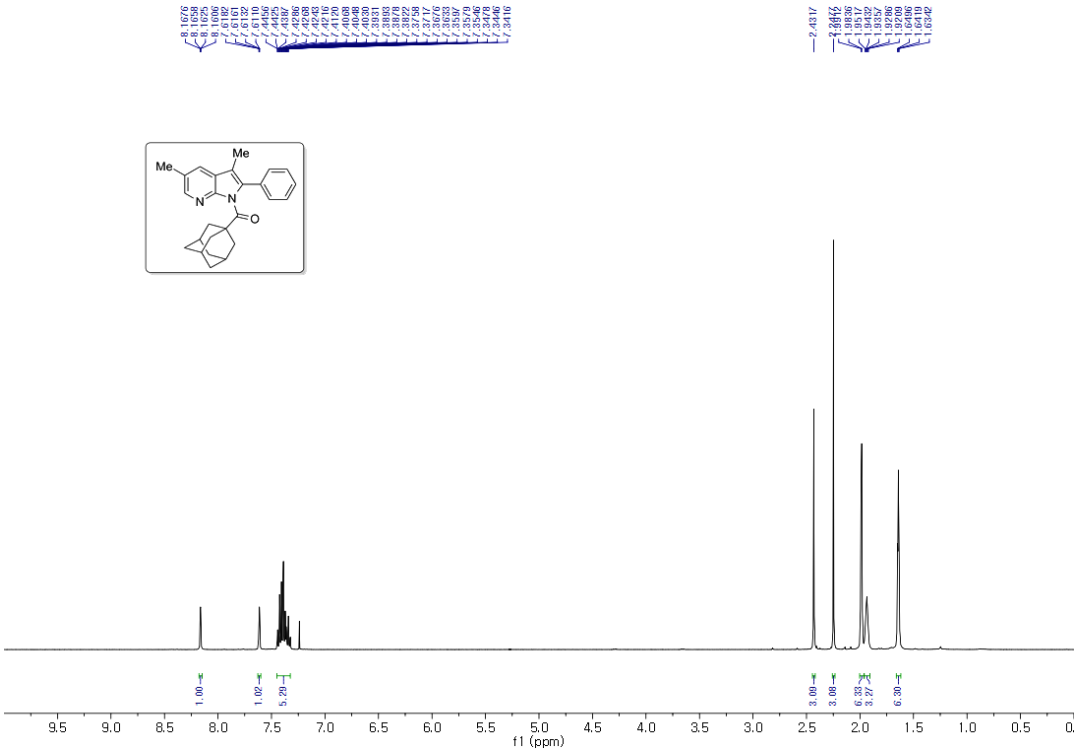


400 MHz, ^{1}H NMR in $CDCl_3$

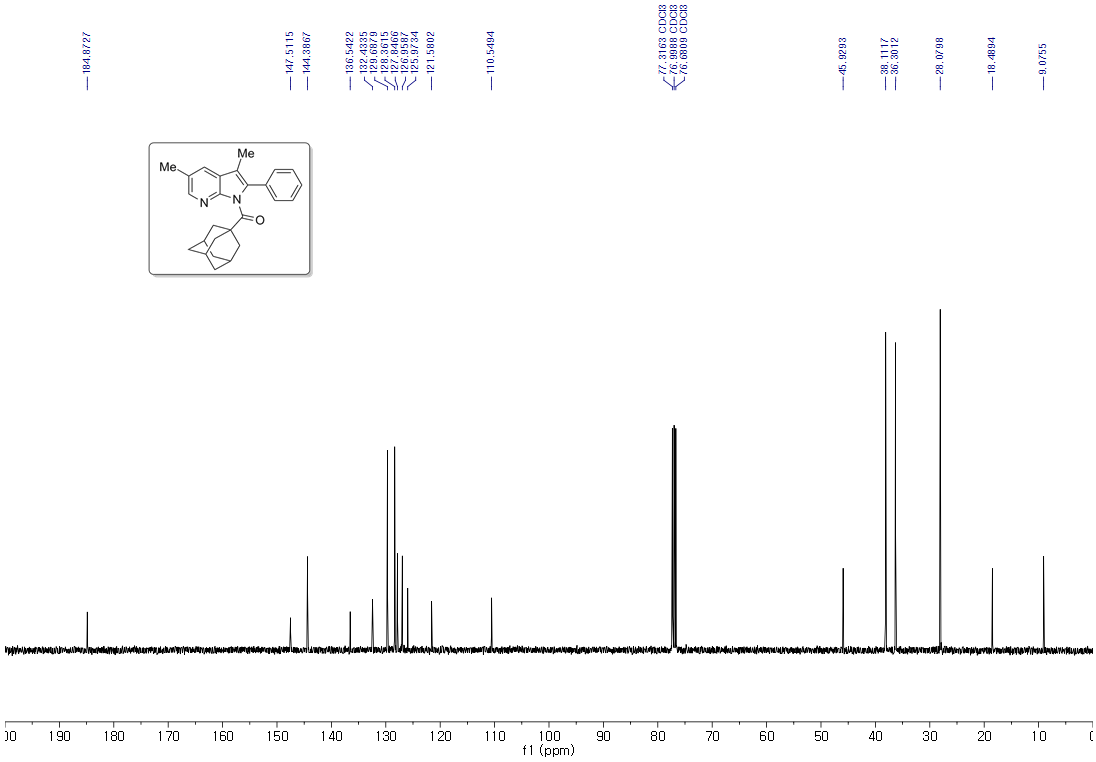


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(3,5-dimethyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3b).

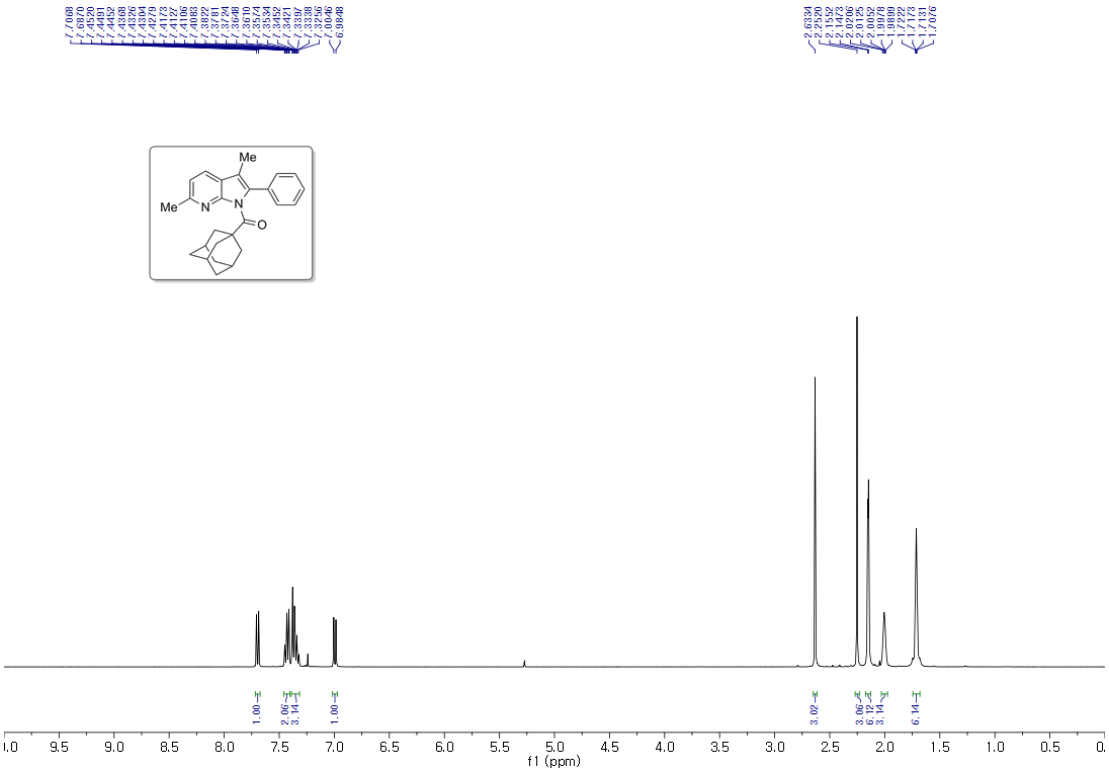


400 MHz, ^{1}H NMR in $CDCl_3$

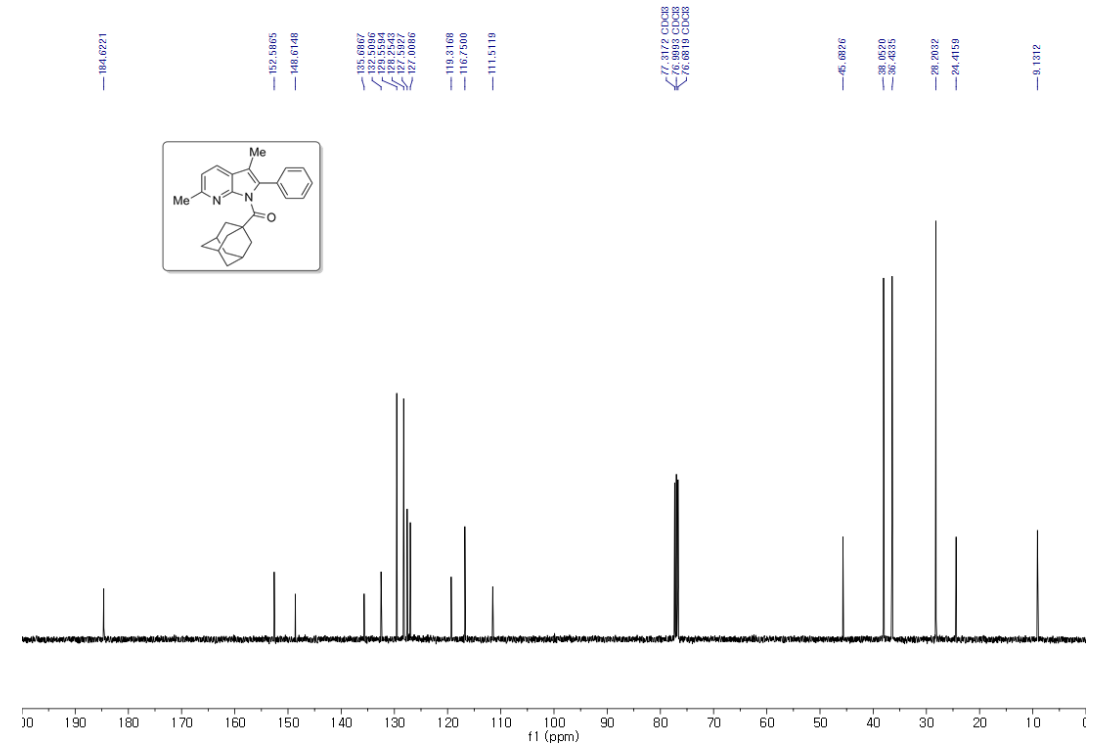


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(3,6-dimethyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3c).

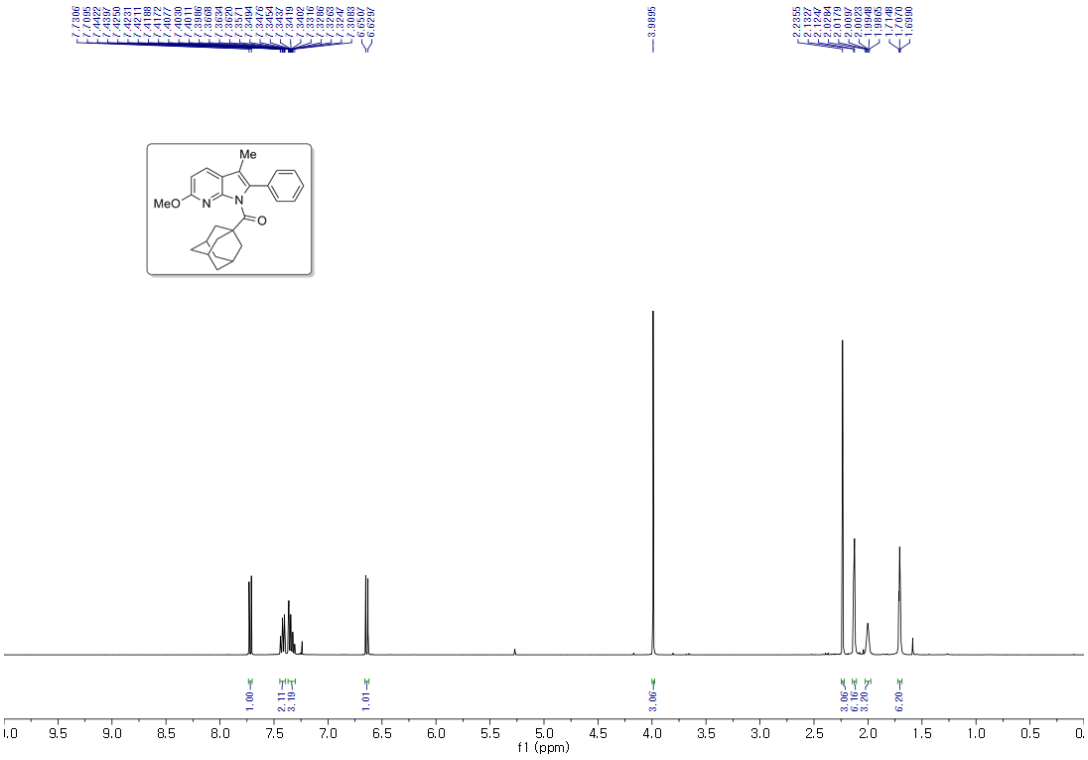


400 MHz, ^{1}H NMR in $CDCl_3$

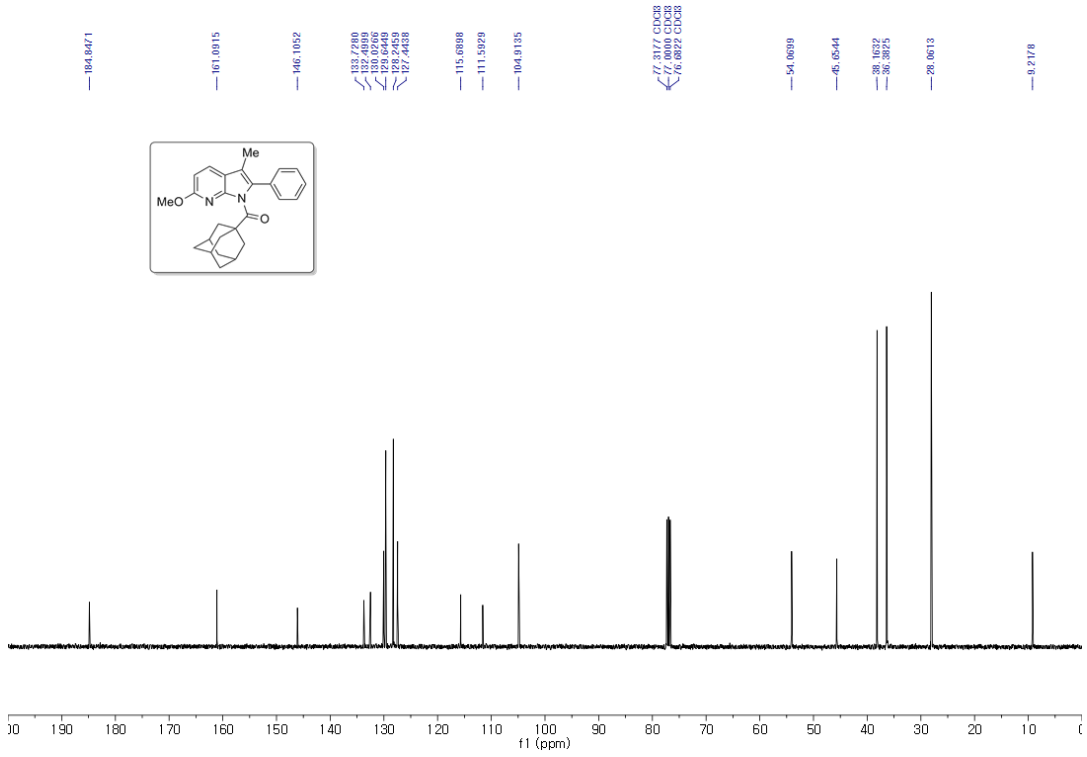


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(6-methoxy-3-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3d).

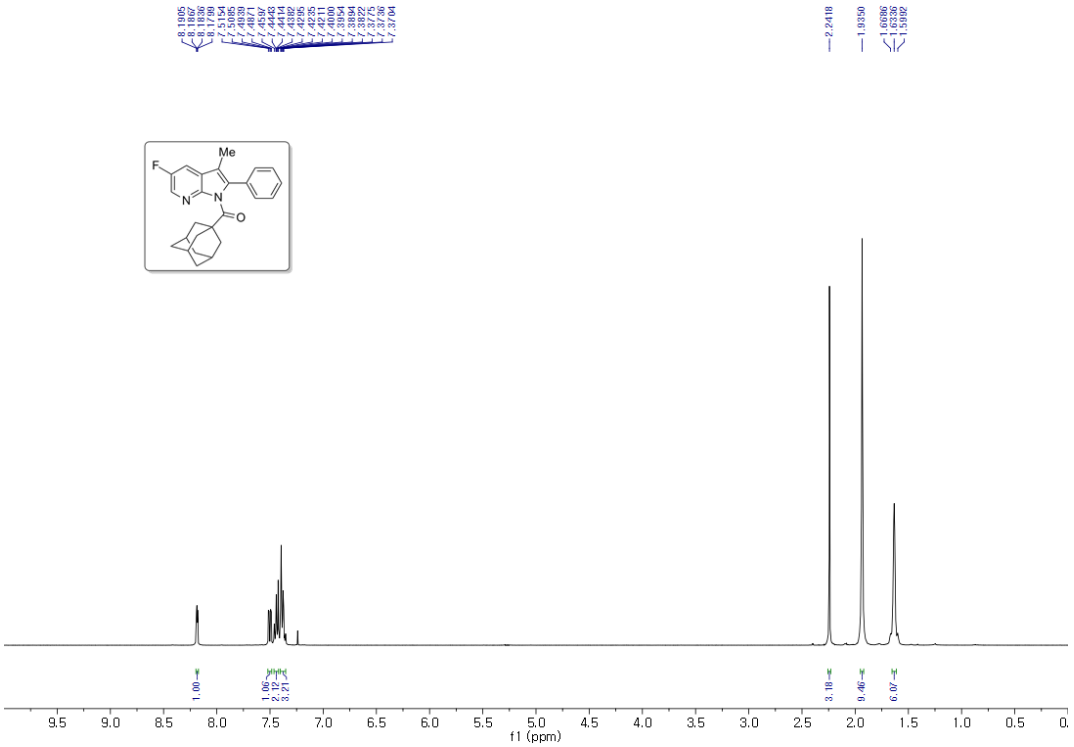


400 MHz, ^{1}H NMR in $CDCl_3$

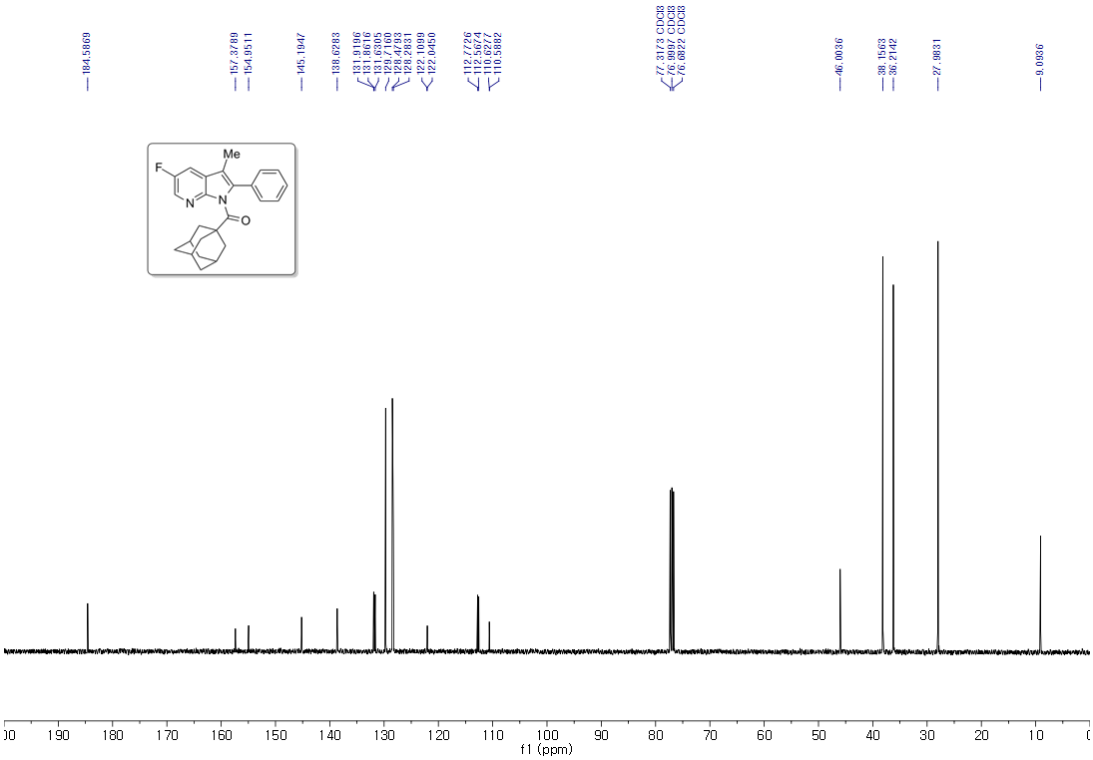


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(5-fluoro-3-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3e).

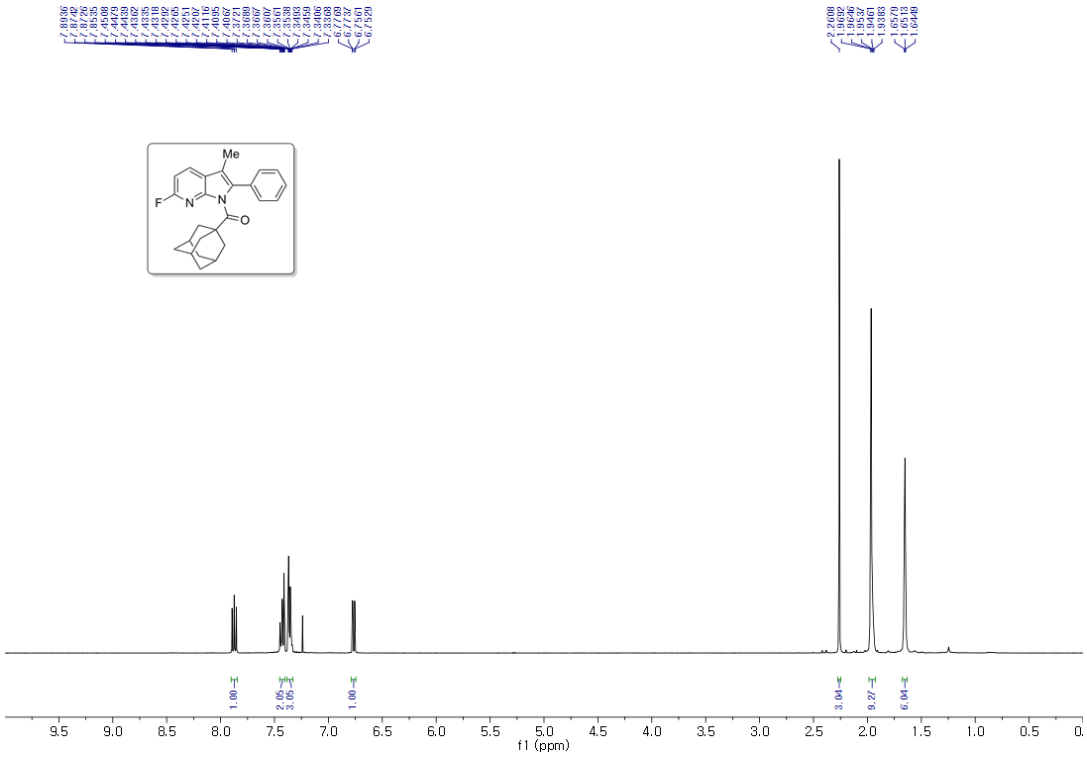


400 MHz, ^{1}H NMR in $CDCl_3$

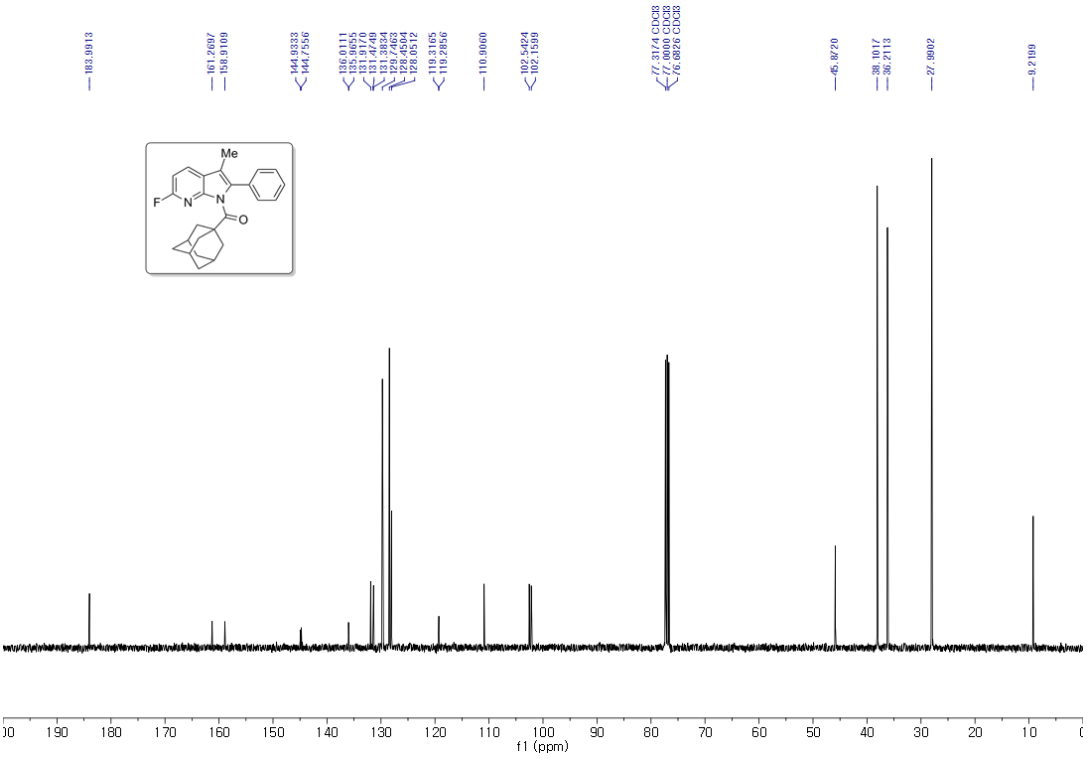


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(6-fluoro-3-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3f).

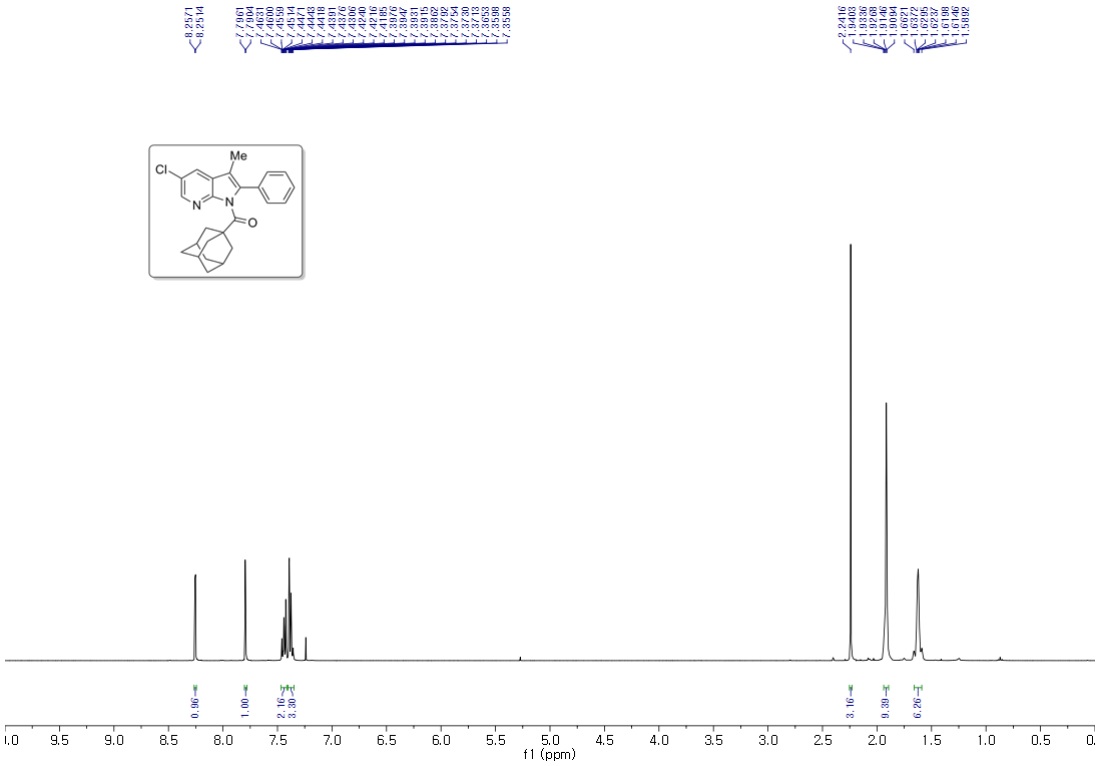


400 MHz, ^{1}H NMR in $CDCl_3$

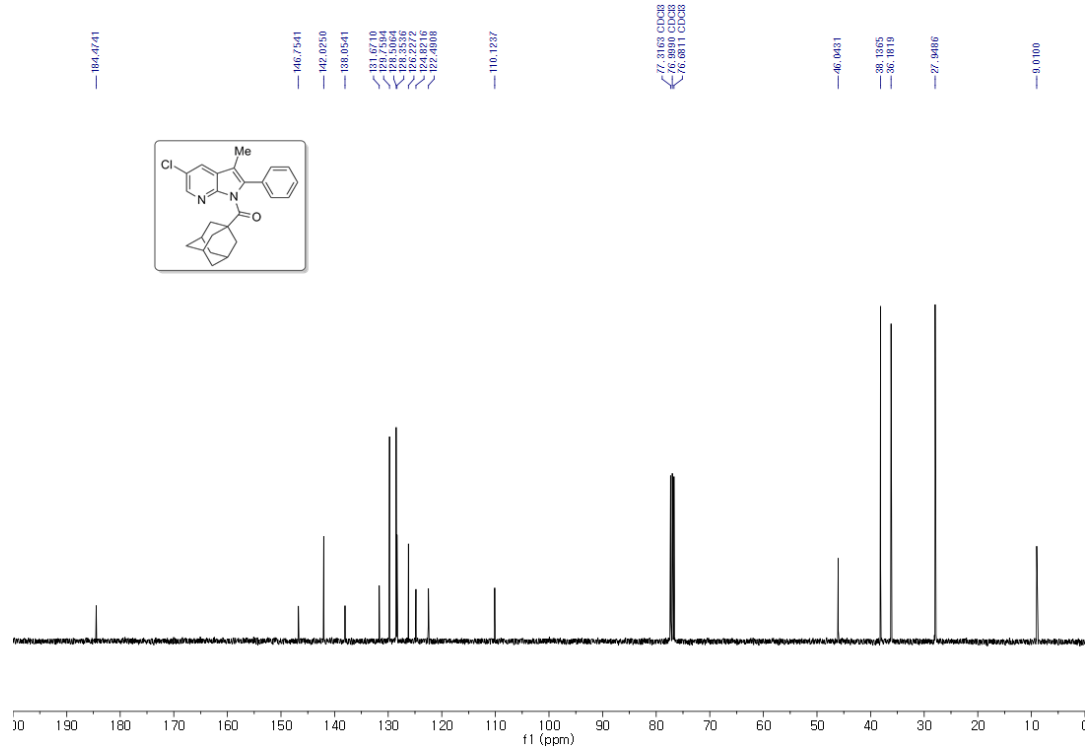


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(5-chloro-3-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3g).

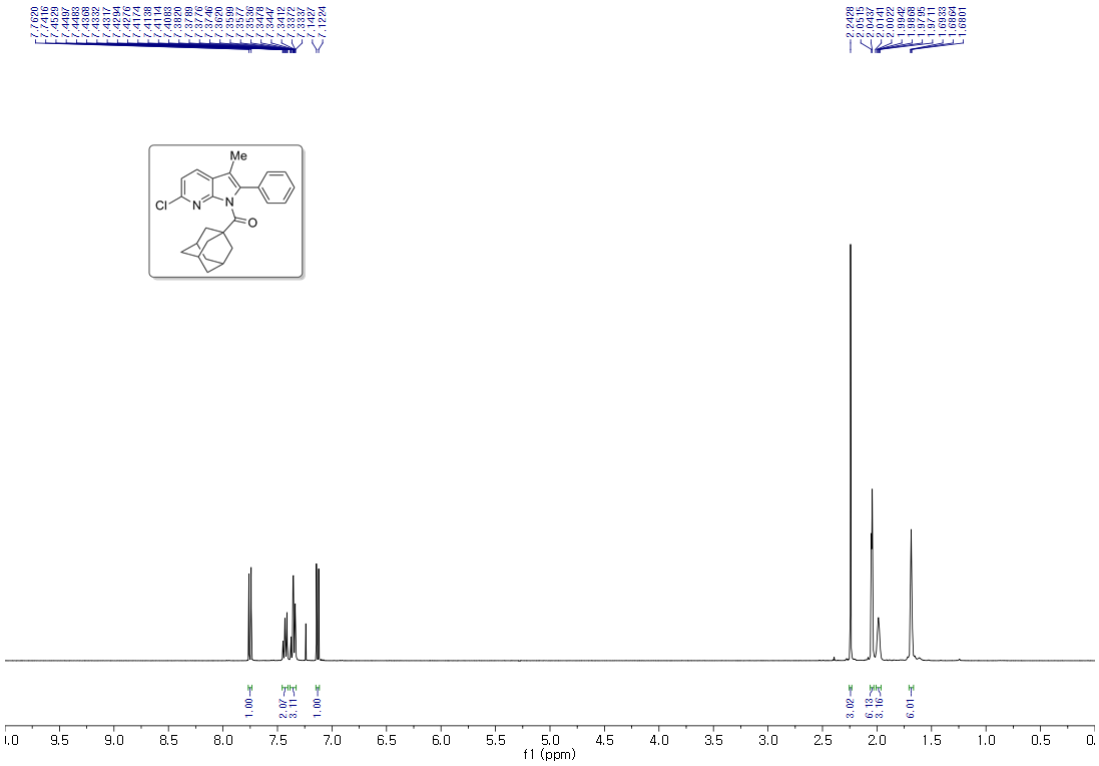


400 MHz, ^{1}H NMR in $CDCl_3$

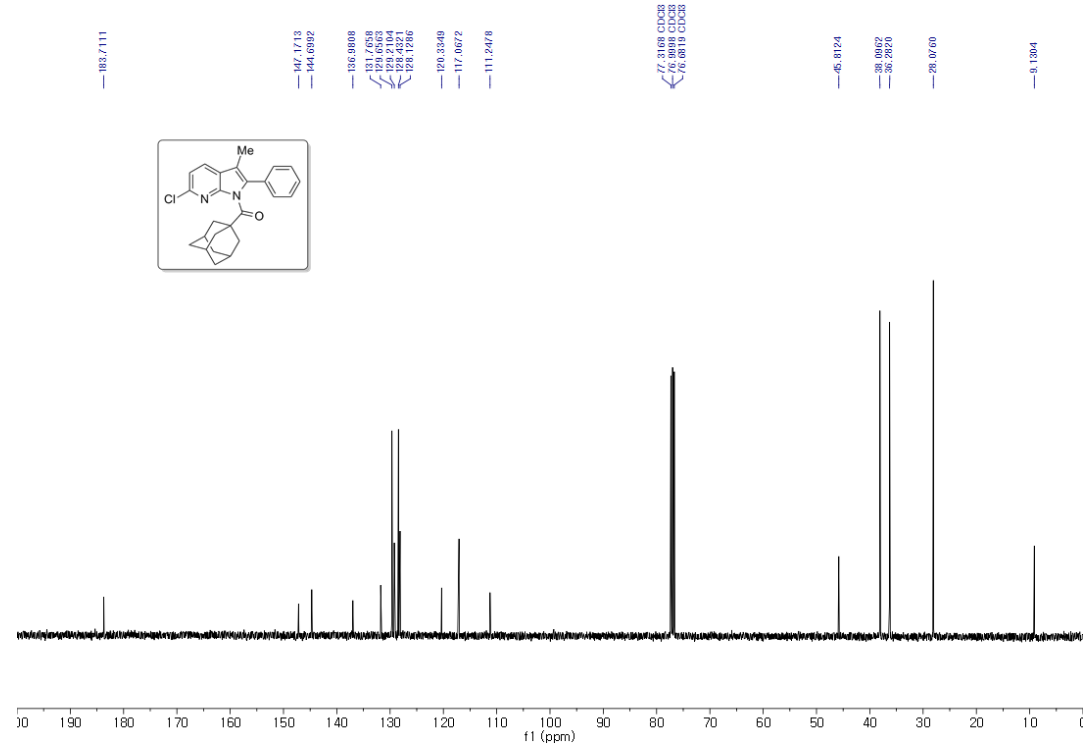


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(6-chloro-3-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3h).

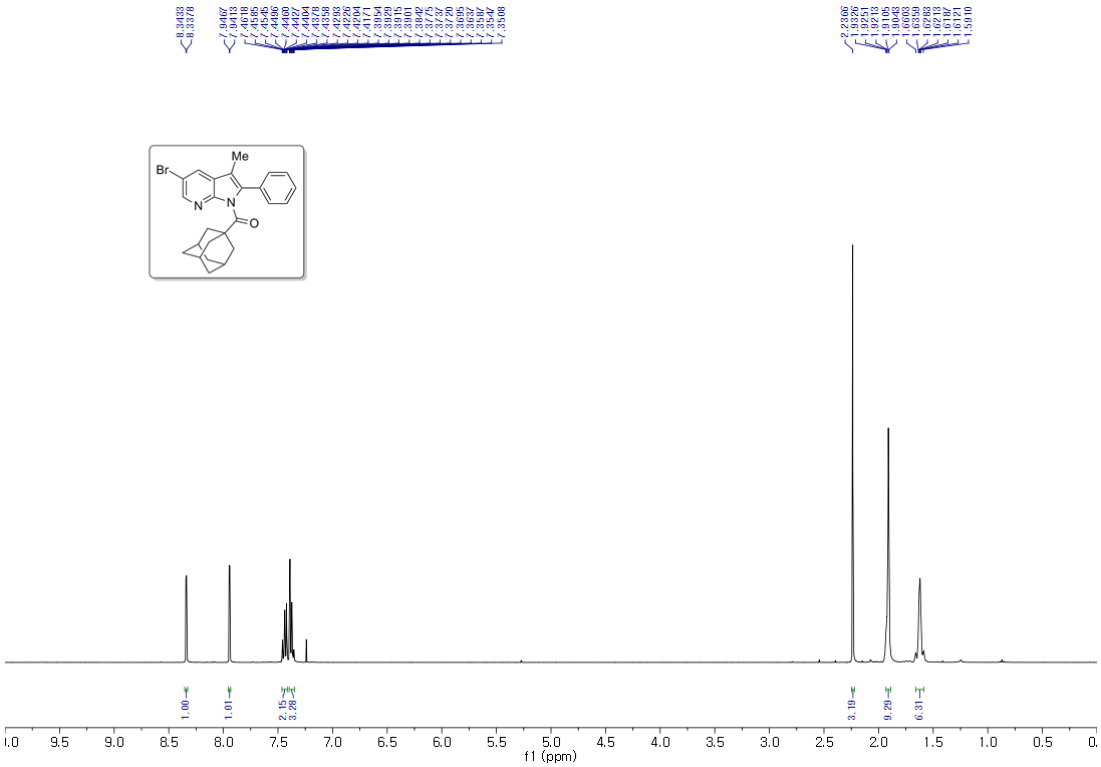


400 MHz, ^{1}H NMR in $CDCl_3$

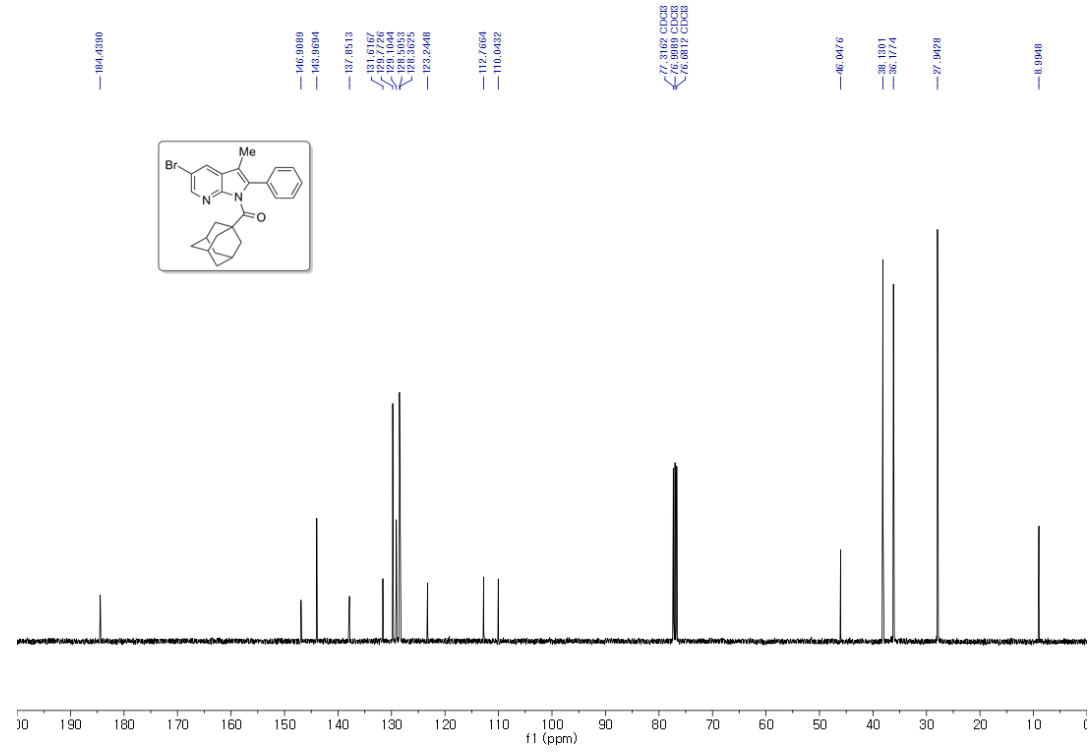


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(5-bromo-3-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3i).

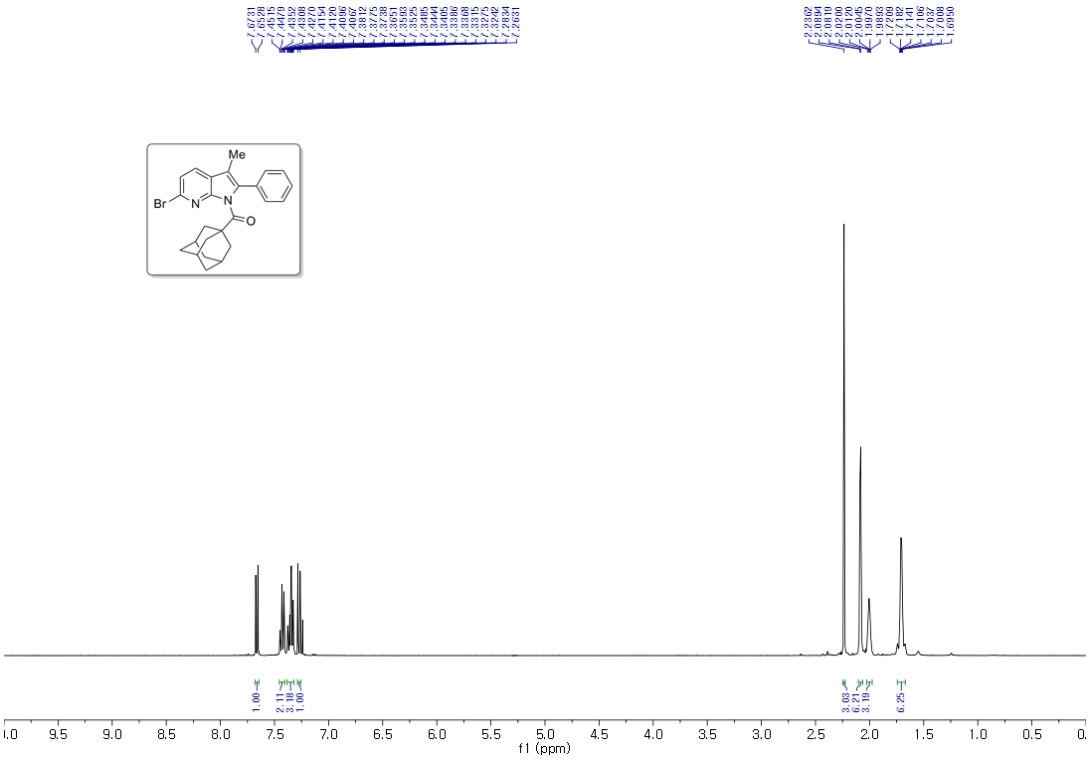


400 MHz, ^{1}H NMR in $CDCl_3$

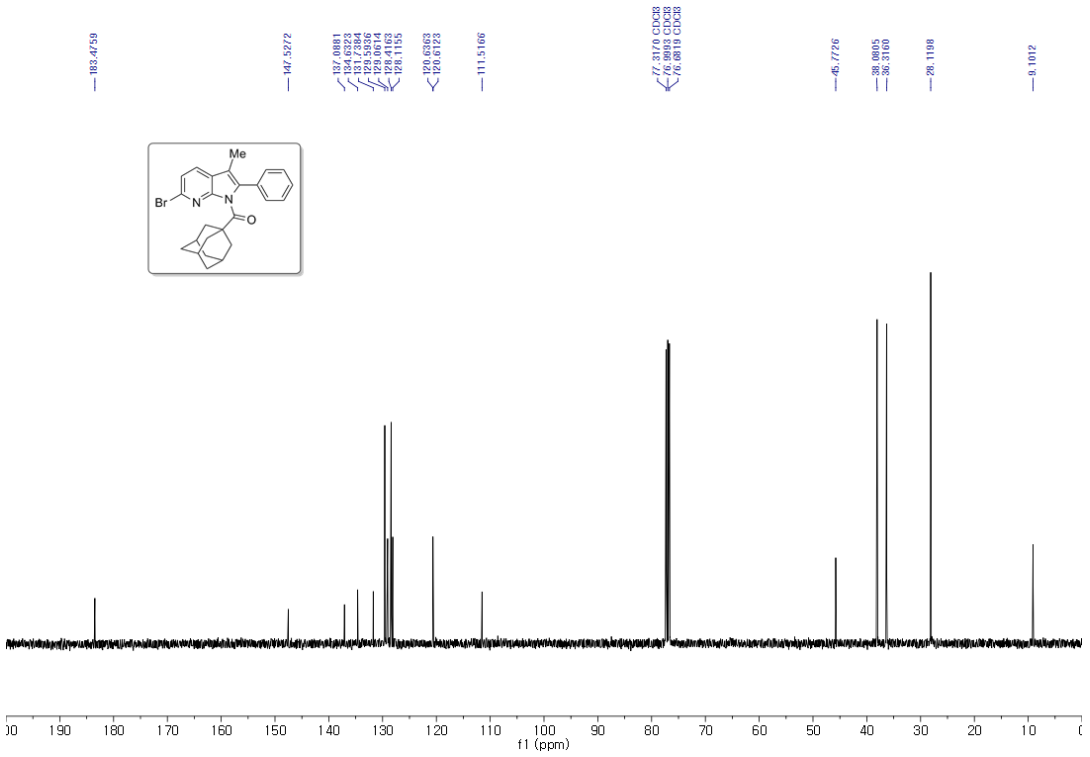


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(6-bromo-3-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3j).

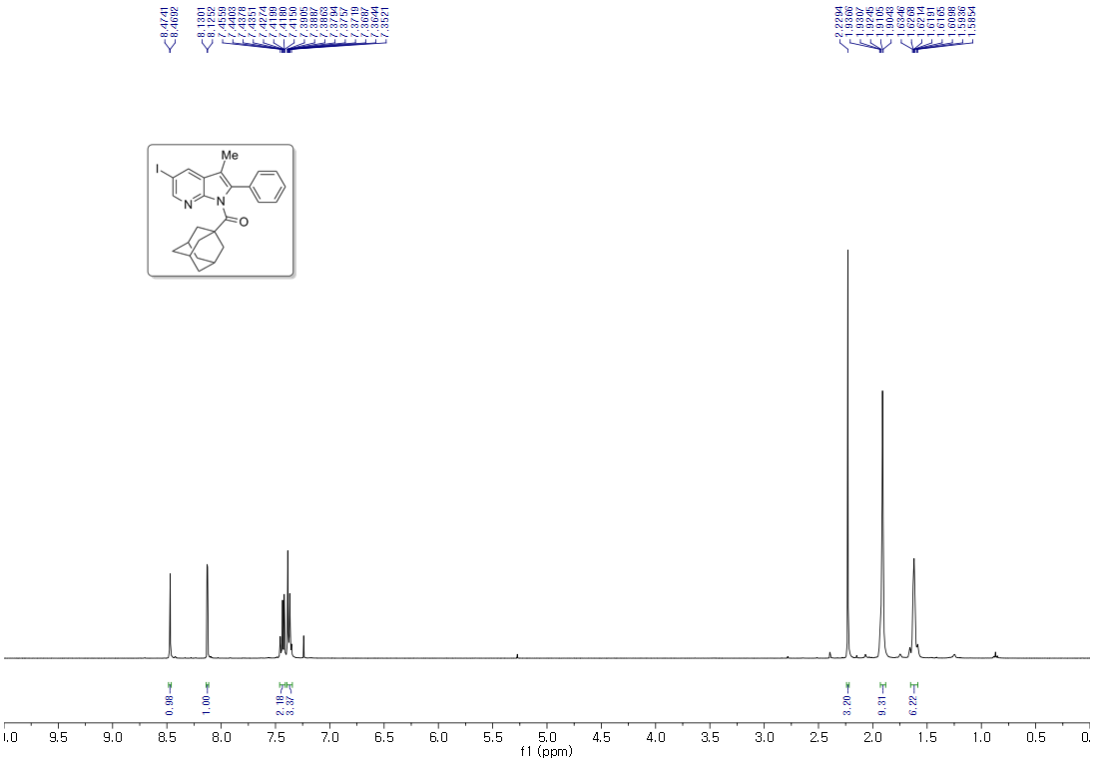


400 MHz, ^{1}H NMR in $CDCl_3$

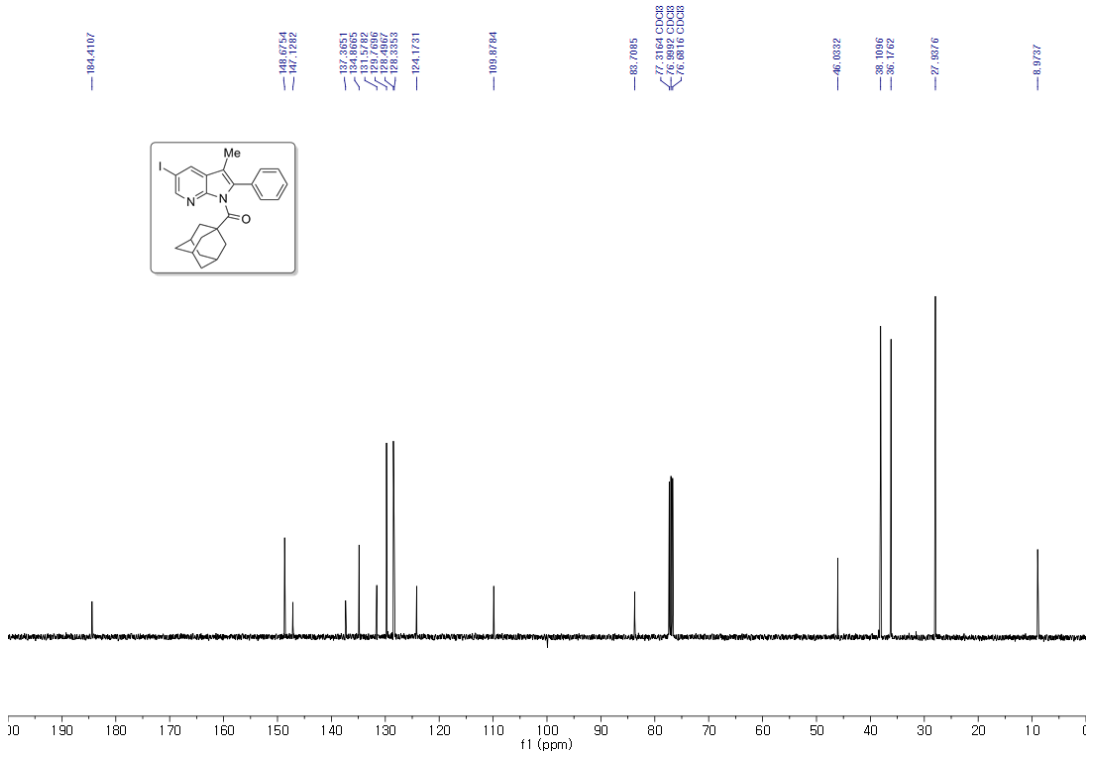


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(5-iodo-3-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3k).

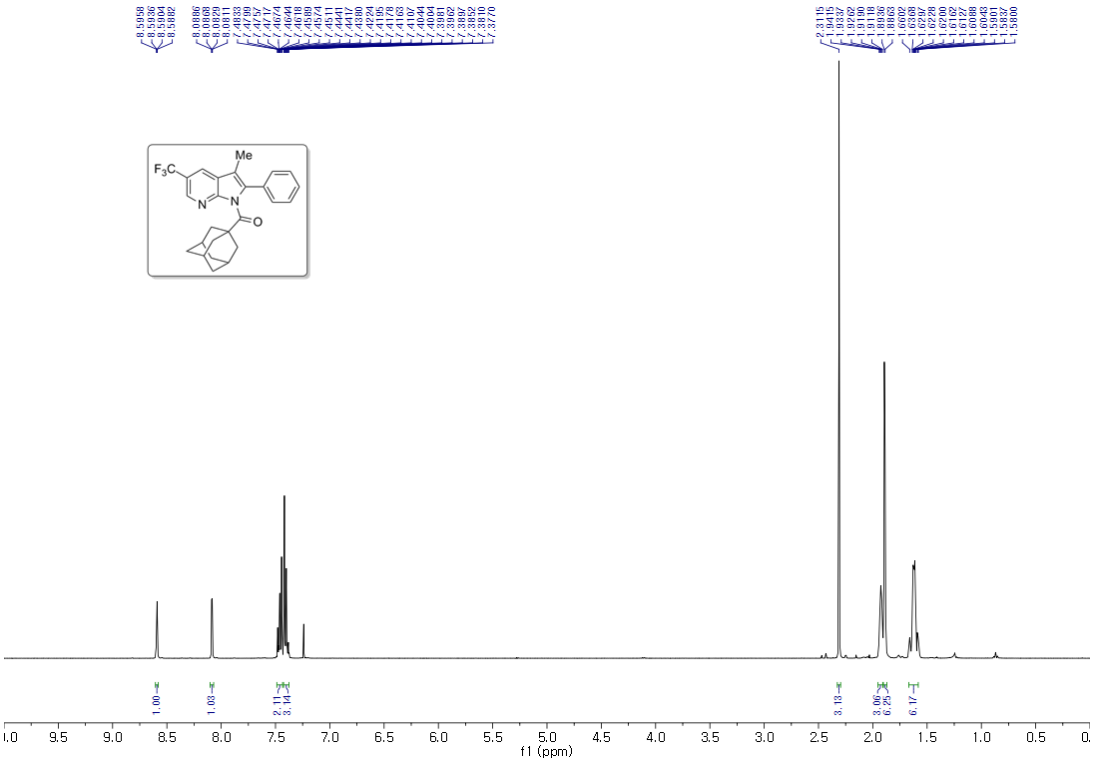


400 MHz, ^{1}H NMR in $CDCl_3$

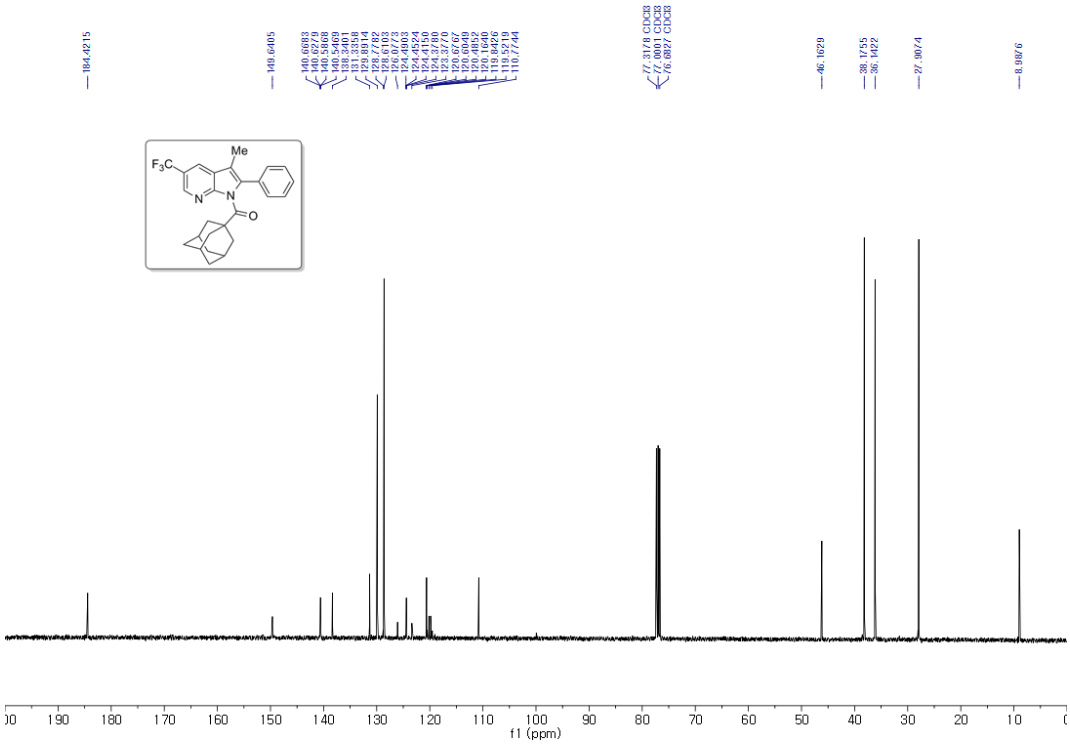


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(3-methyl-2-phenyl-5-(trifluoromethyl)-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (3l).

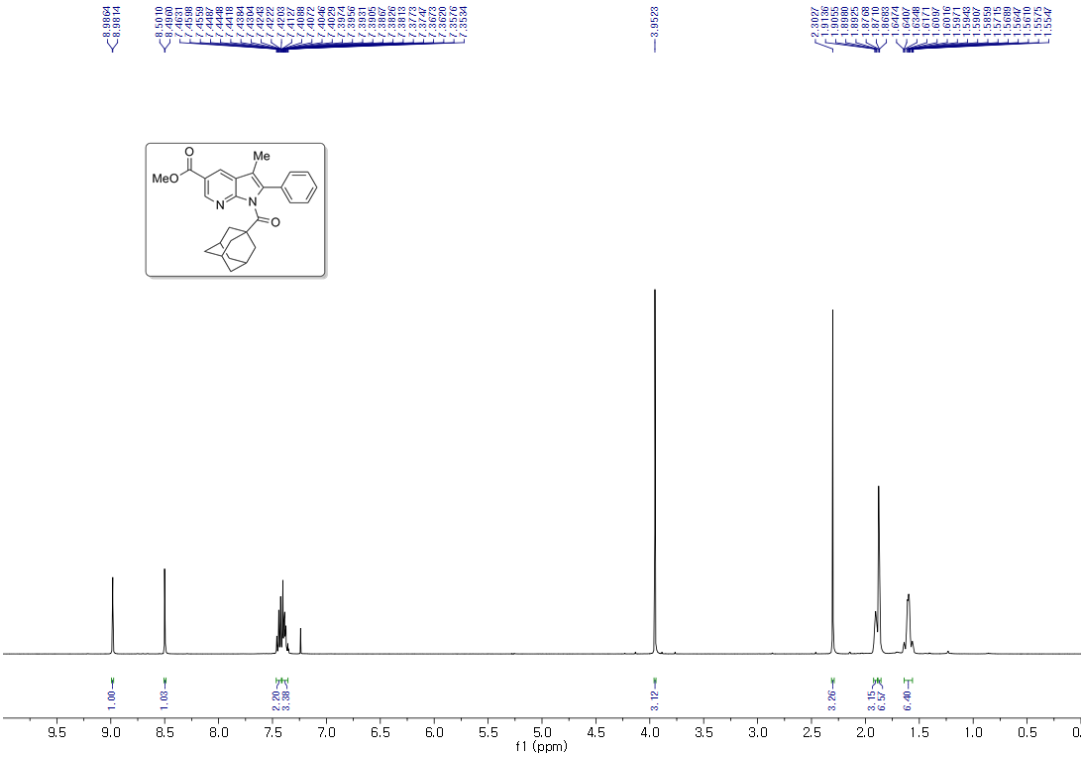


400 MHz, ^{1}H NMR in $CDCl_3$

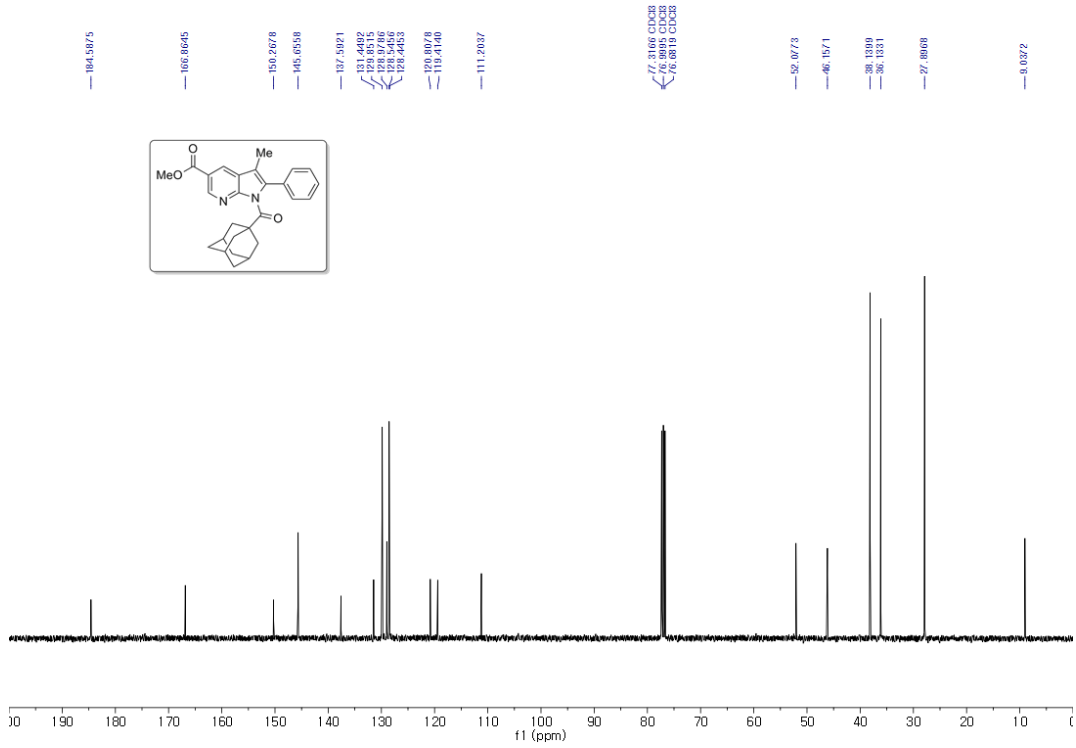


100 MHz, ^{13}C NMR in $CDCl_3$

methyl 1-(adamantane-1-carbonyl)-3-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridine-5-carboxylate (3m).

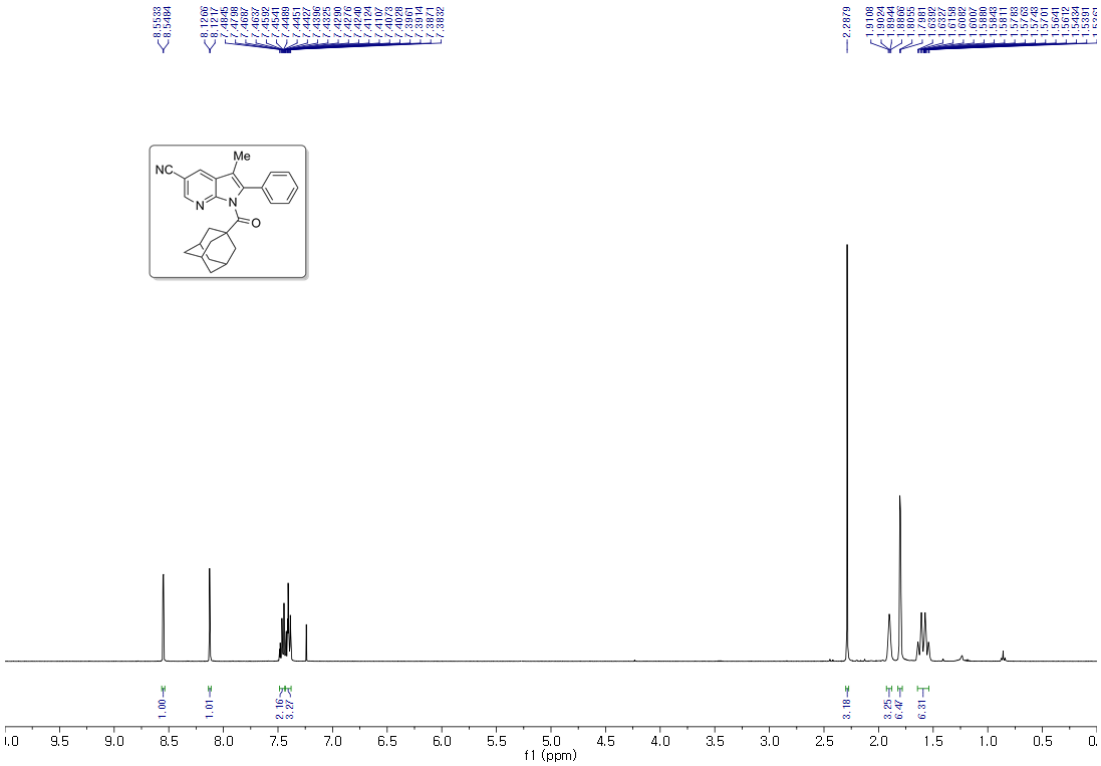


400 MHz, ^{1}H NMR in $CDCl_3$

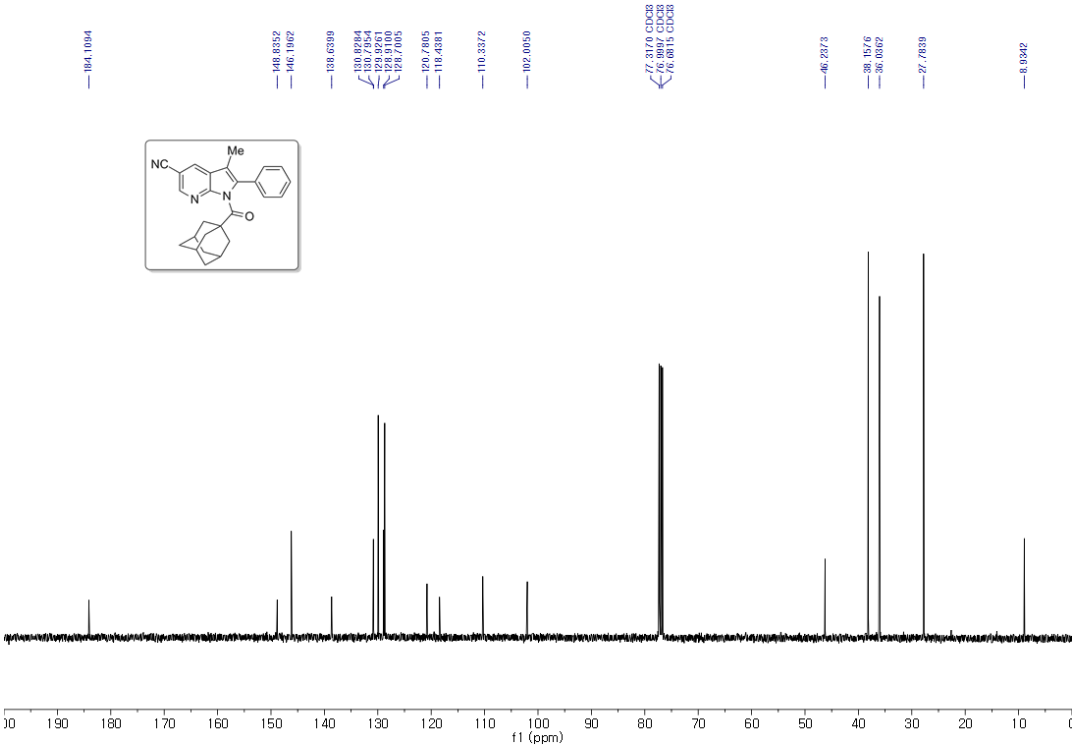


100 MHz, ^{13}C NMR in $CDCl_3$

1-(adamantane-1-carbonyl)-3-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridine-5-carbonitrile (3n).

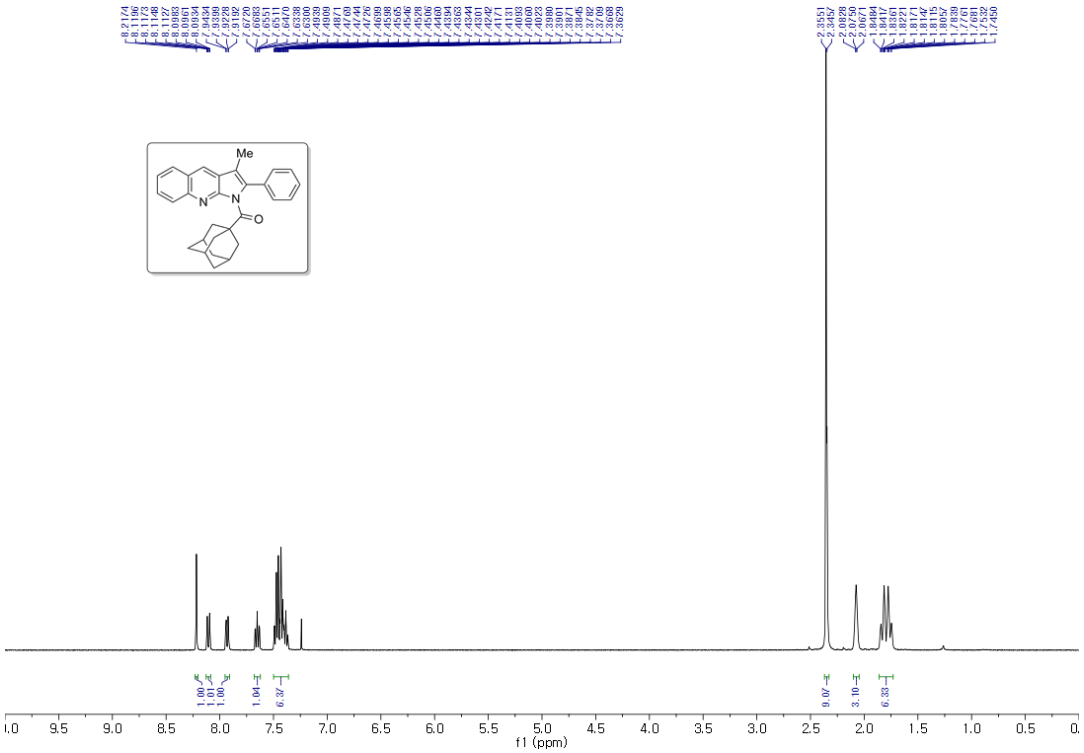


400 MHz, ^{1}H NMR in $CDCl_3$

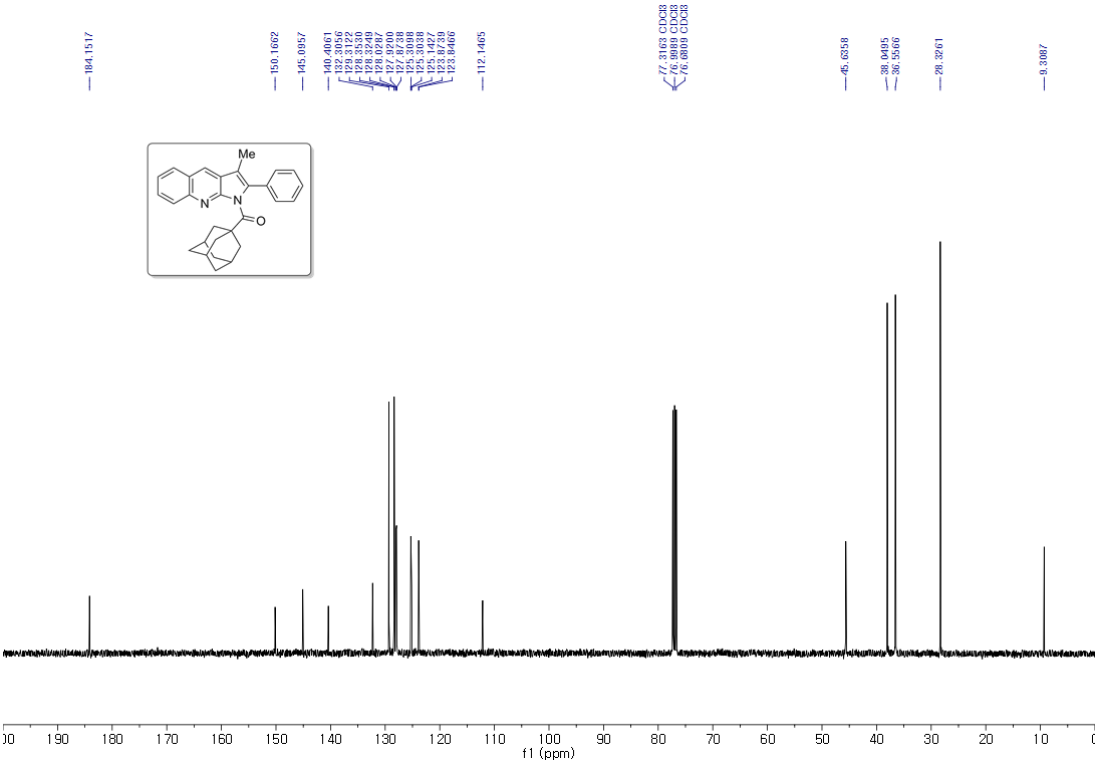


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(3-methyl-2-phenyl-1H-pyrrolo[2,3-b]quinolin-1-yl)methanone (3o).

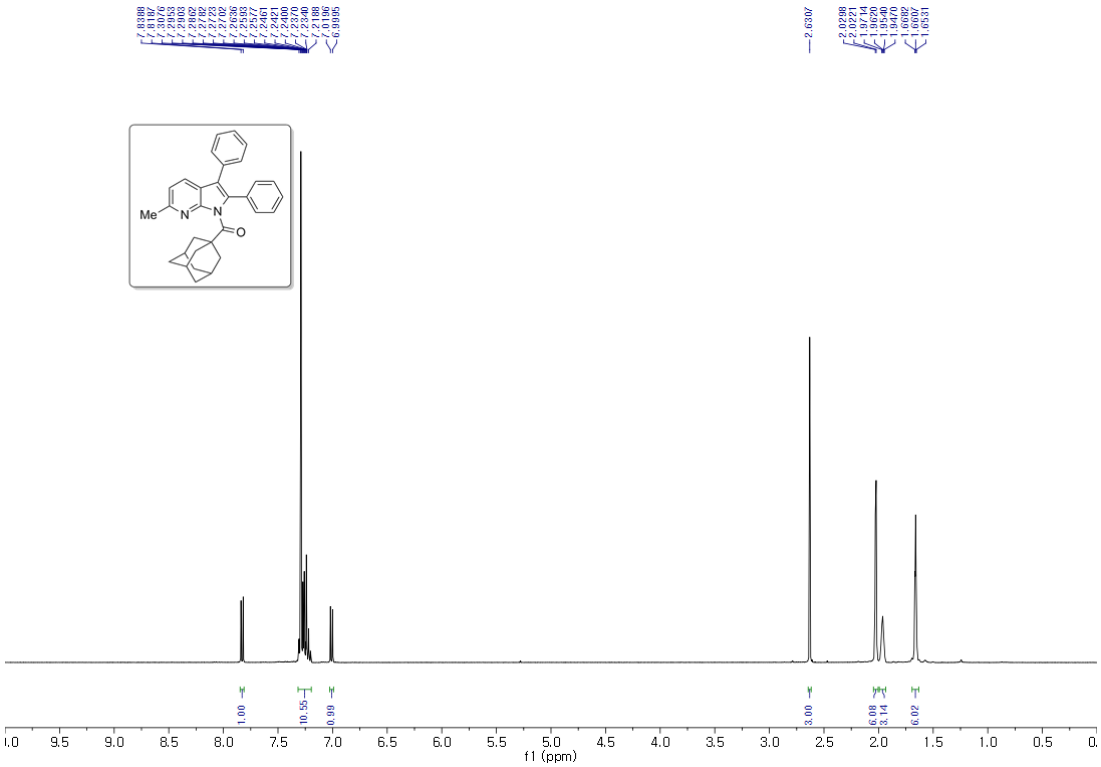


400 MHz, ^{1}H NMR in $CDCl_3$

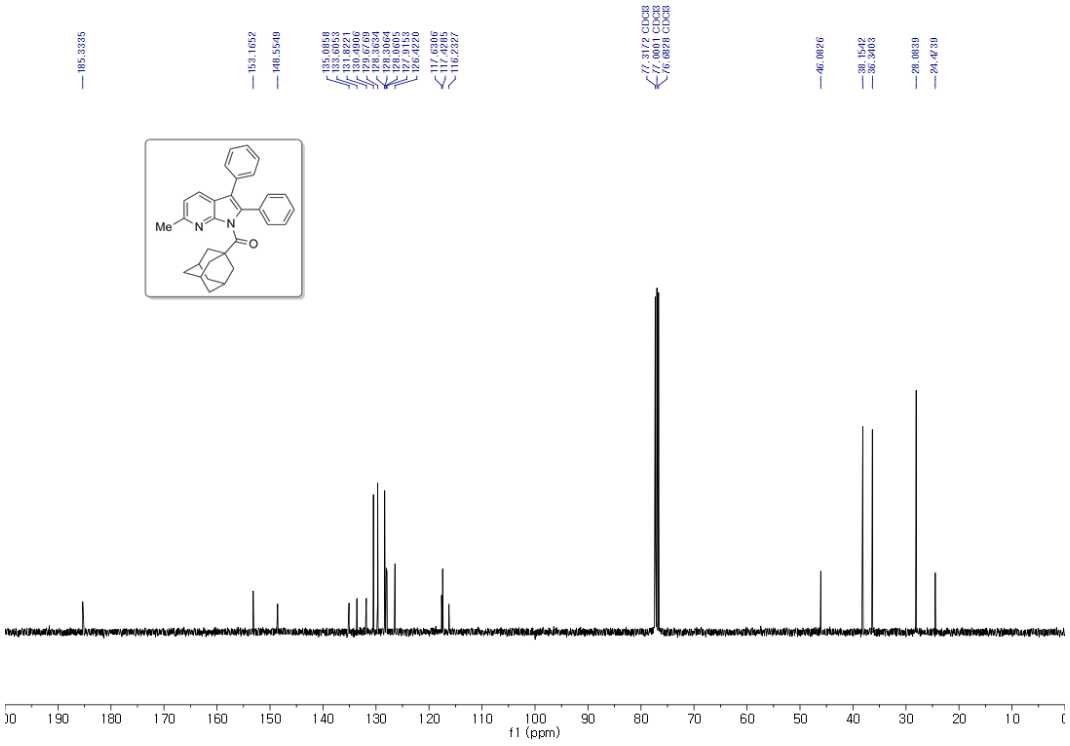


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(6-methyl-2,3-diphenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4a).

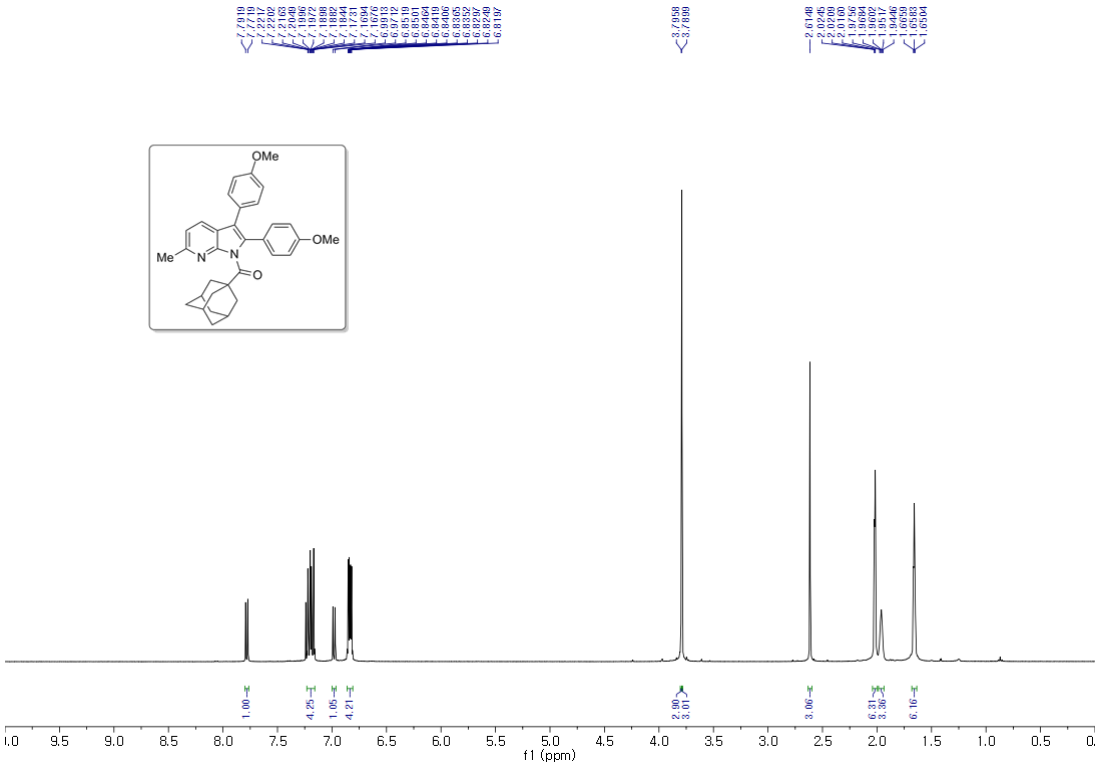


400 MHz, ^{1}H NMR in $CDCl_3$

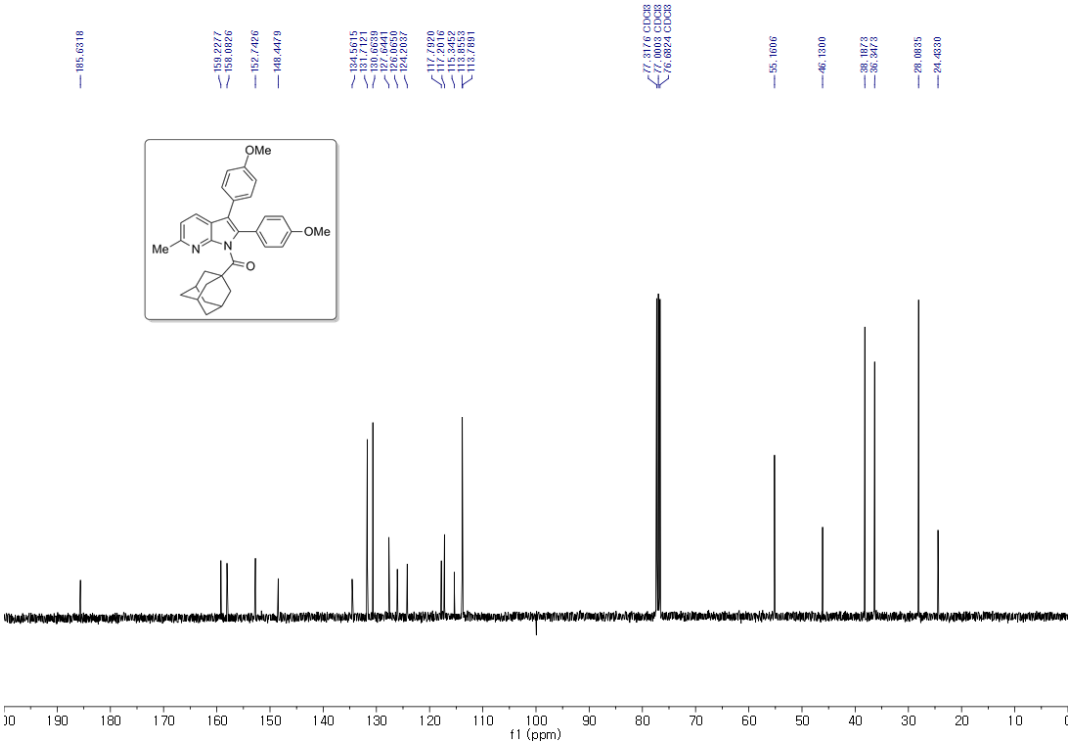


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(2,3-bis(4-methoxyphenyl)-6-methyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4b).

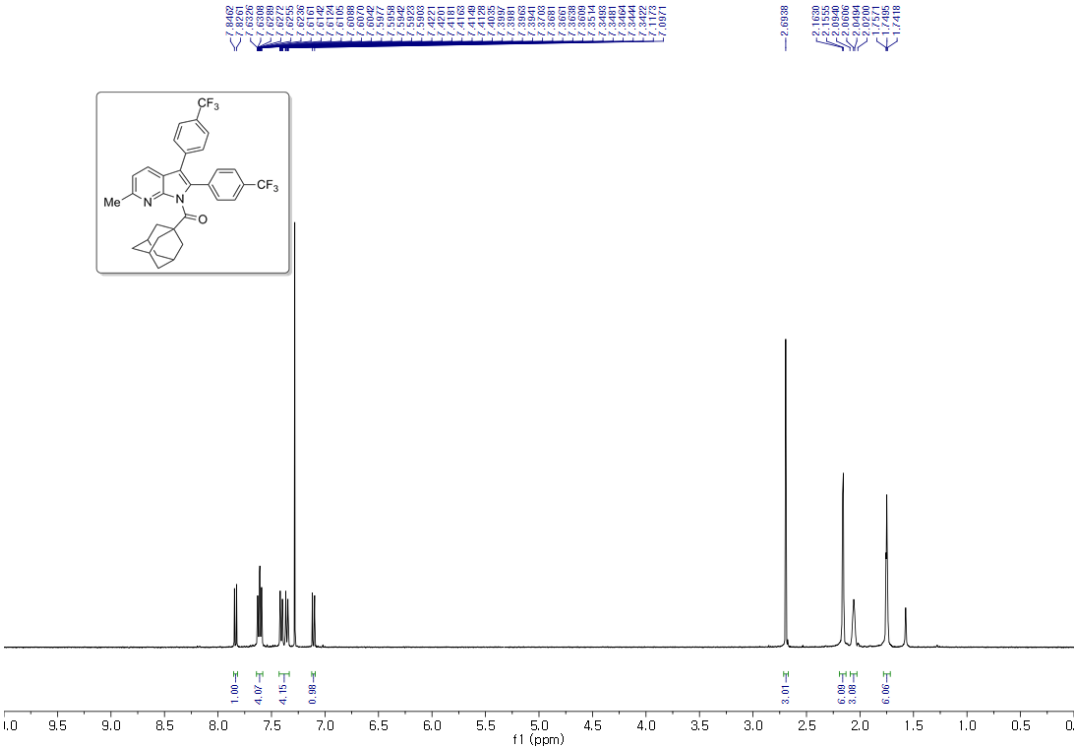


400 MHz, ^{1}H NMR in $CDCl_3$

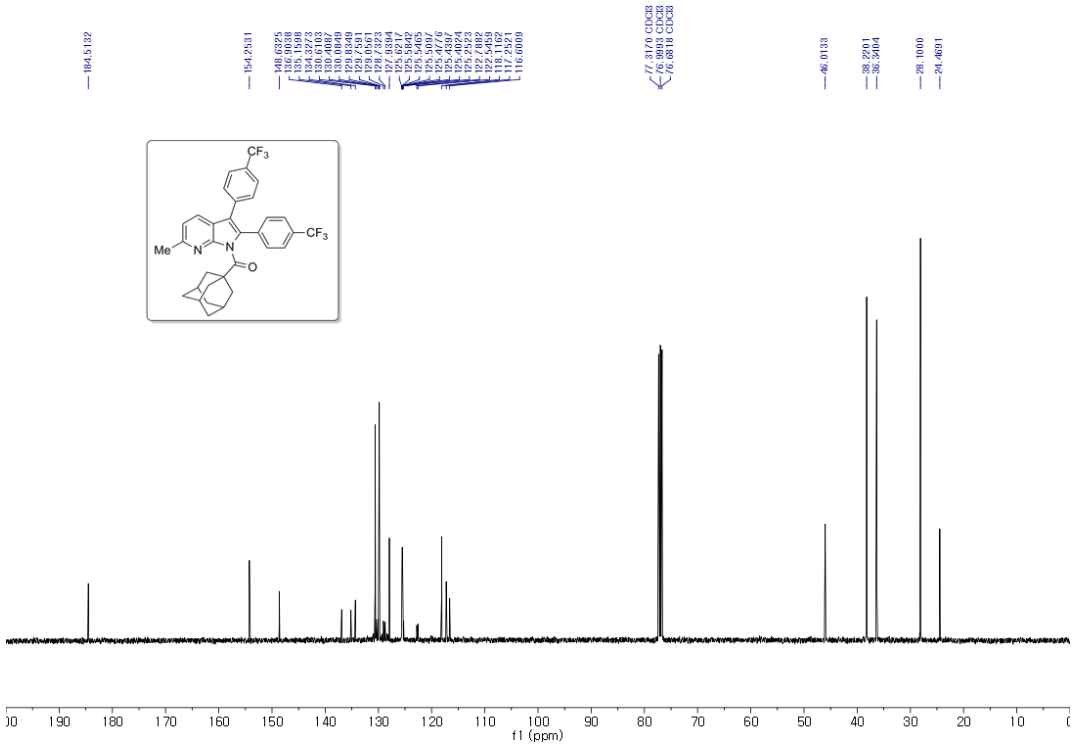


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(6-methyl-2,3-bis(4-(trifluoromethyl)phenyl)-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4c).

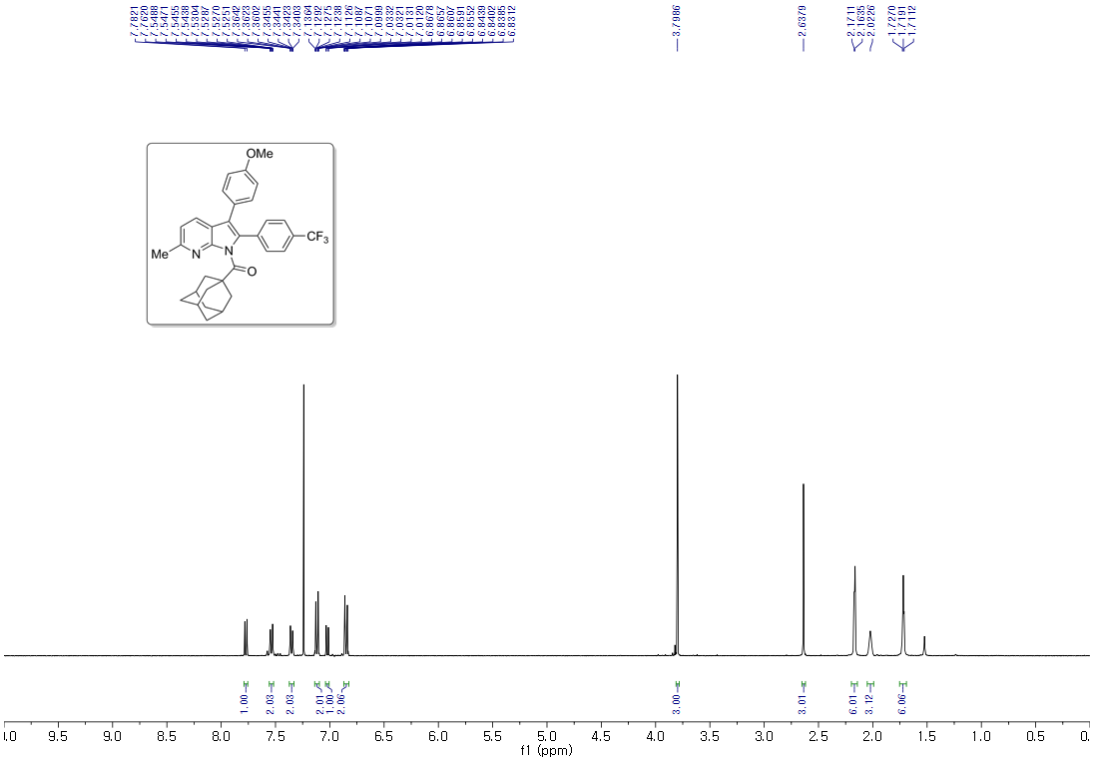


400 MHz, ^{1}H NMR in $CDCl_3$

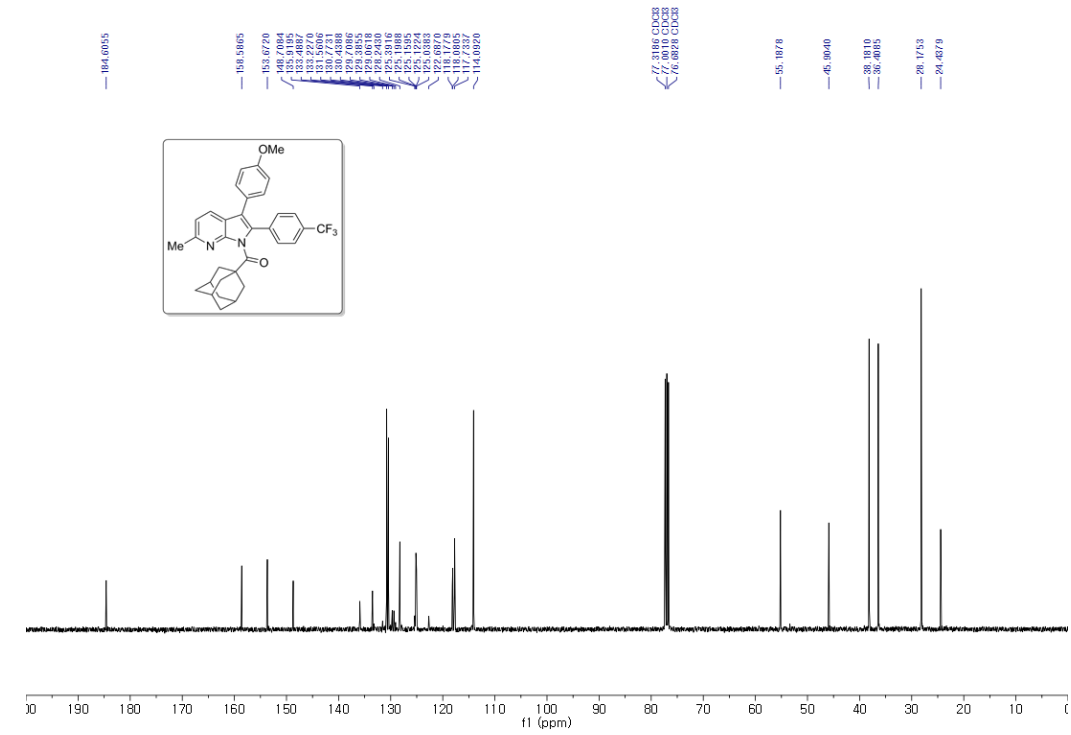


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(3-(4-methoxyphenyl)-6-methyl-2-(4-(trifluoromethyl)phenyl)-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4d)

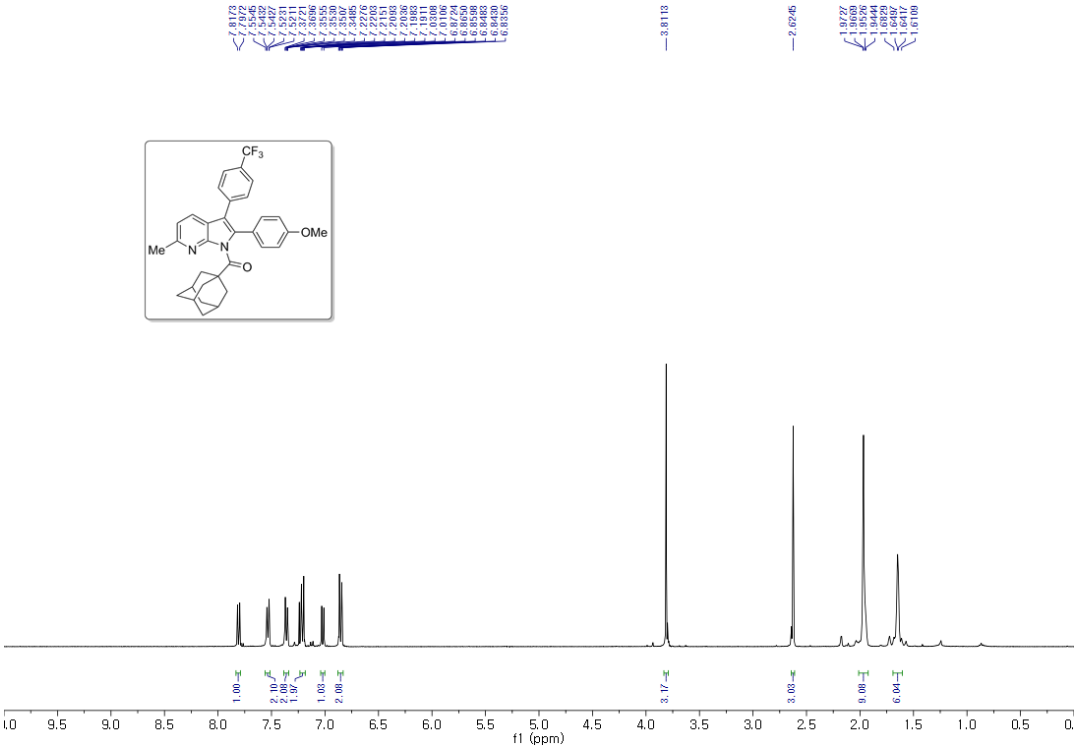


400 MHz, ^{1}H NMR in $CDCl_3$

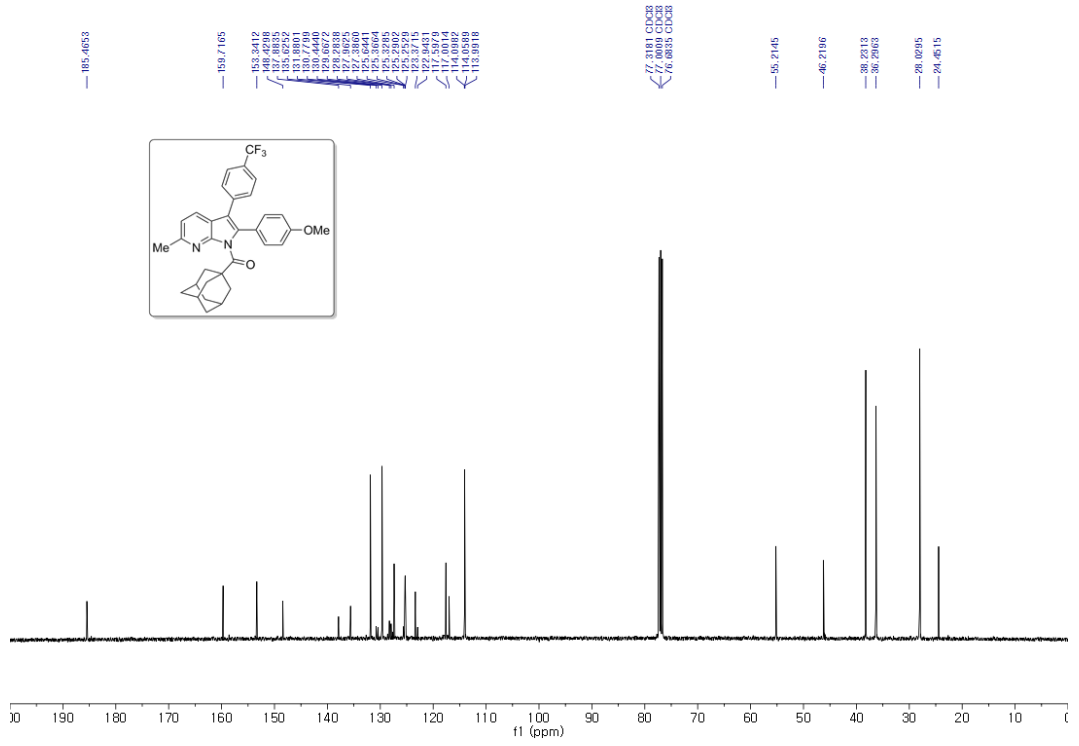


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(2-(4-methoxyphenyl)-6-methyl-3-(4-(trifluoromethyl)phenyl)-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4d')

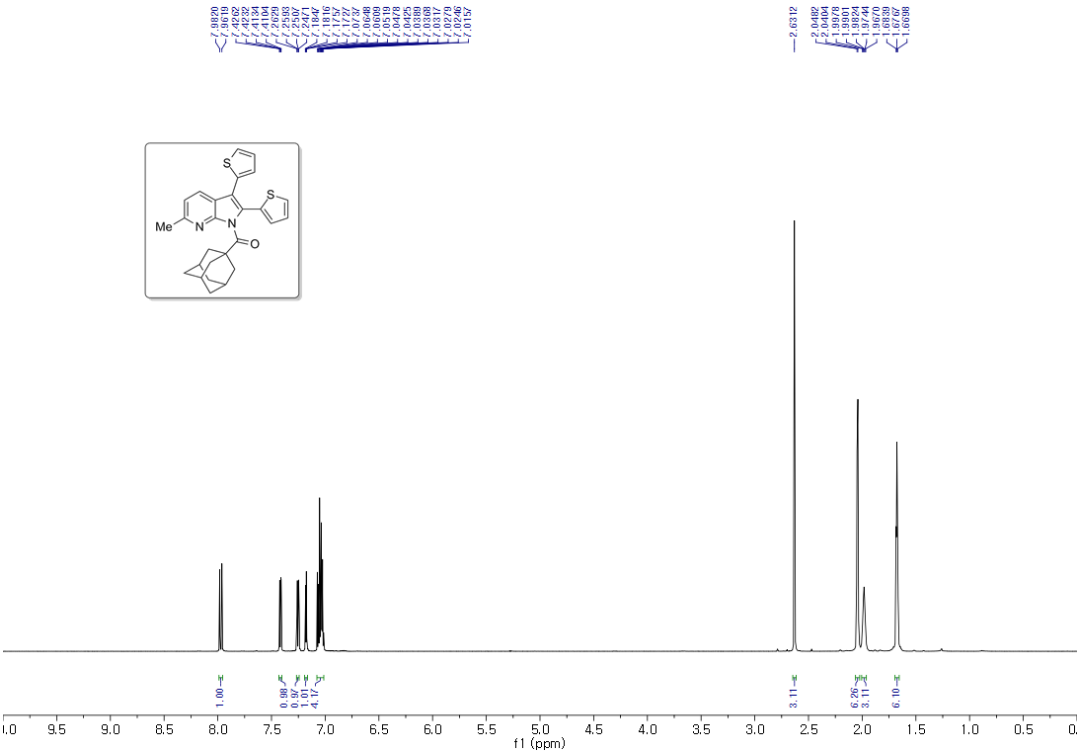


400 MHz, ^{1}H NMR in $CDCl_3$

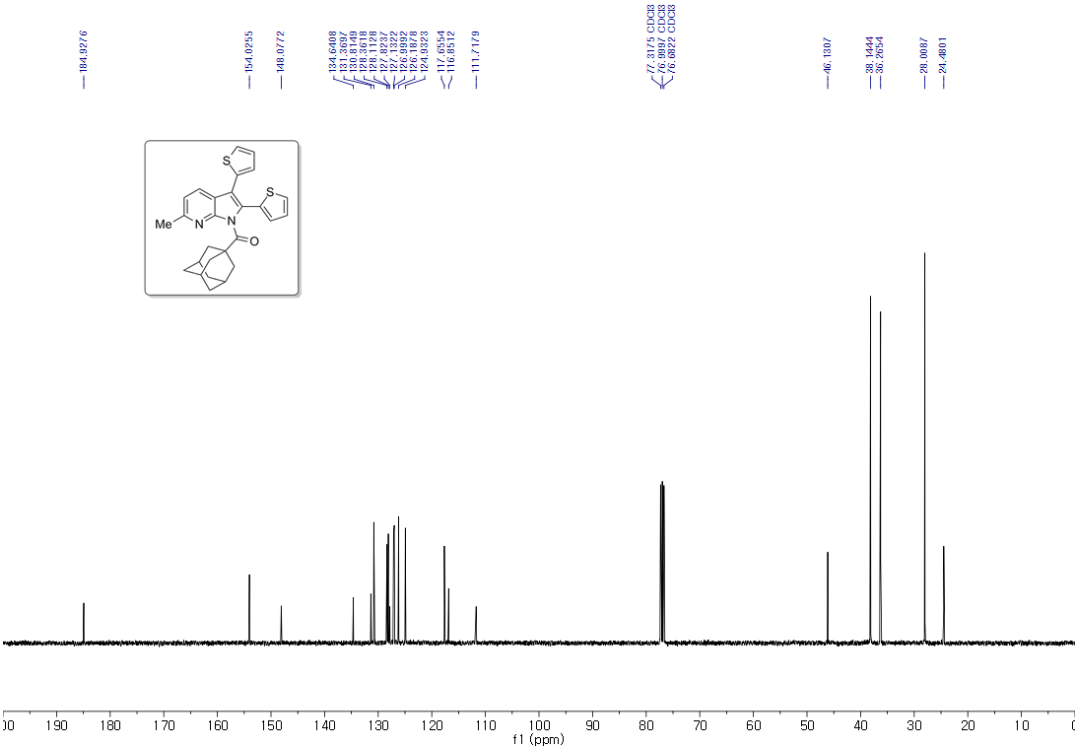


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(6-methyl-2,3-di(thiophen-2-yl)-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4e).

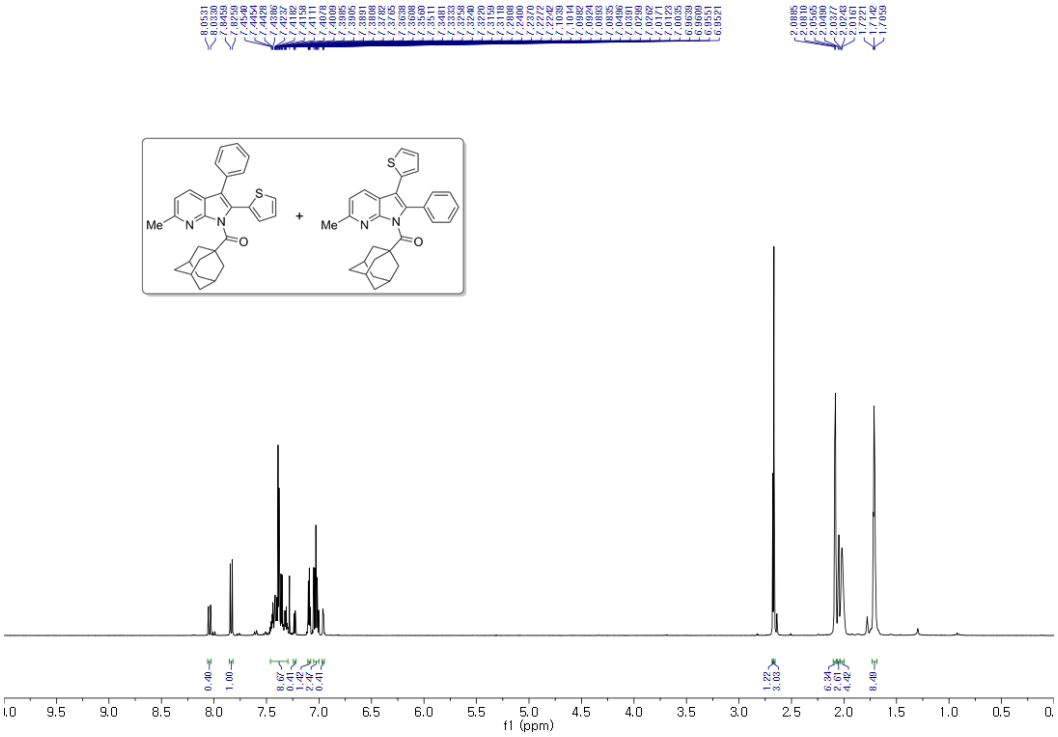


400 MHz, ^{1}H NMR in $CDCl_3$

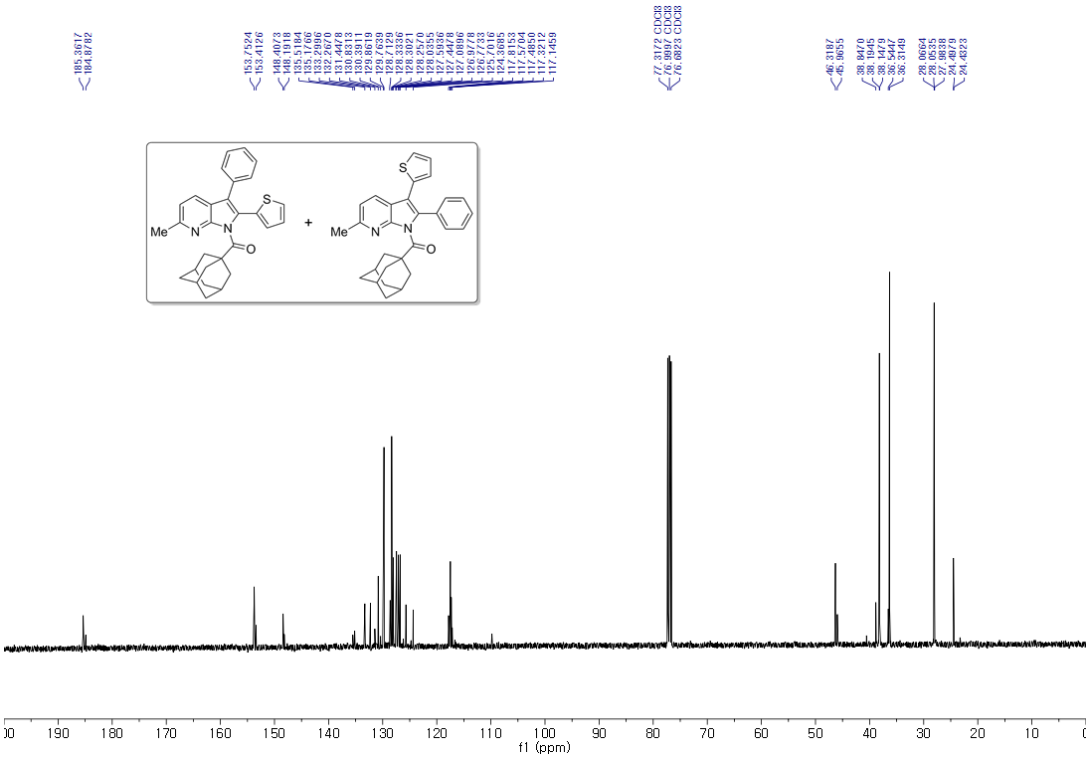


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(6-methyl-3-phenyl-2-(thiophen-2-yl)-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone & adamantan-1-yl(6-methyl-2-phenyl-3-(thiophen-2-yl)-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4f)

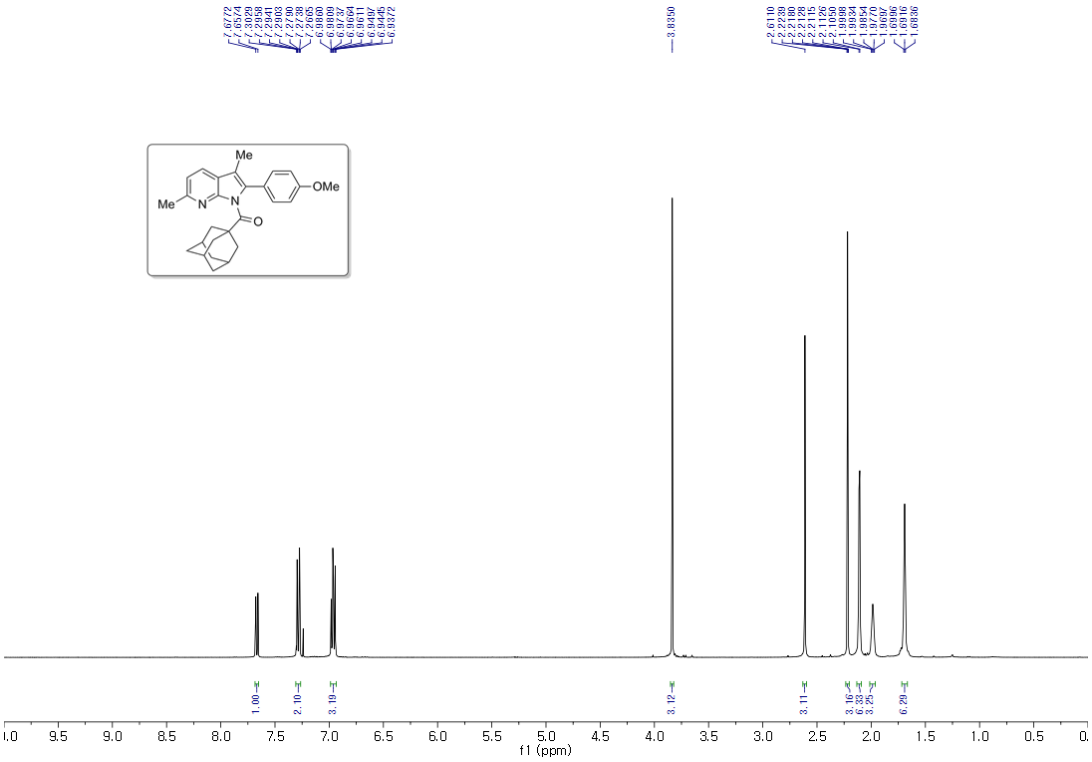


400 MHz, ^{1}H NMR in $CDCl_3$

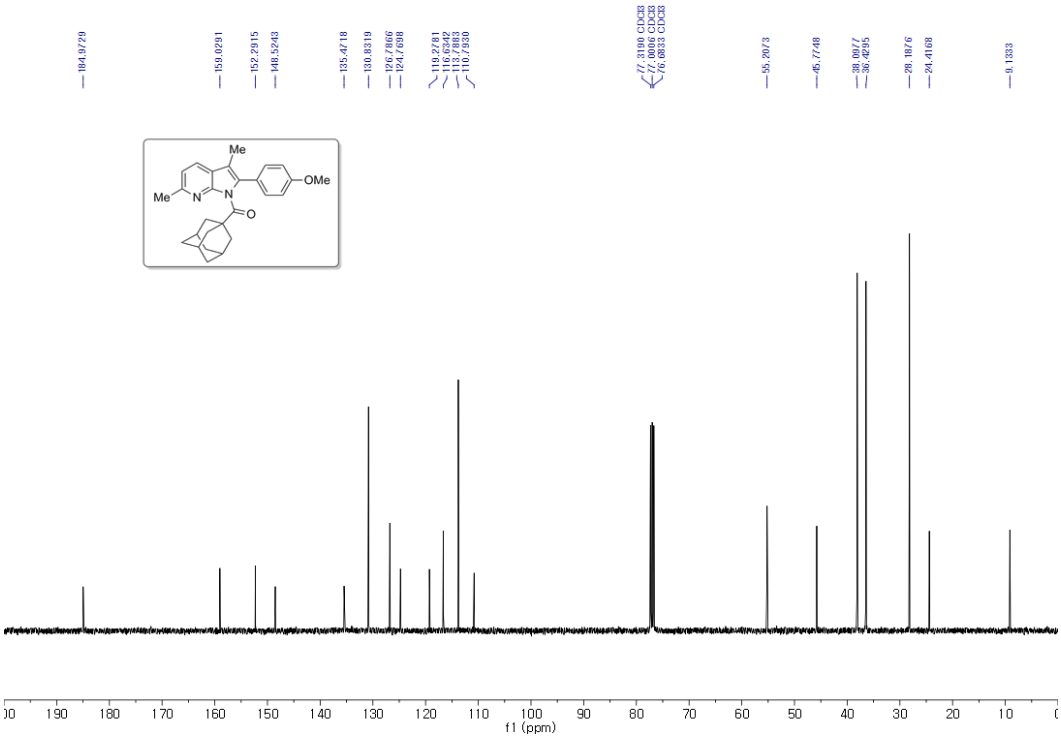


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(2-(4-methoxyphenyl)-3,6-dimethyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4g).

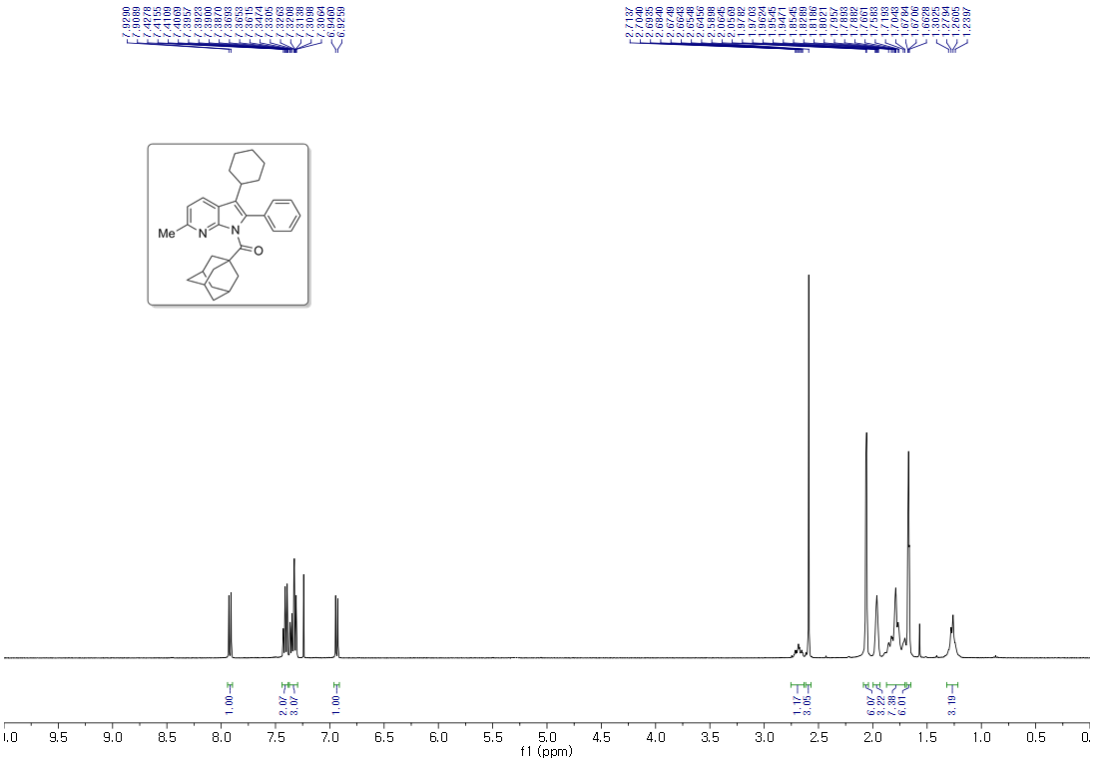


400 MHz, ^{1}H NMR in $CDCl_3$

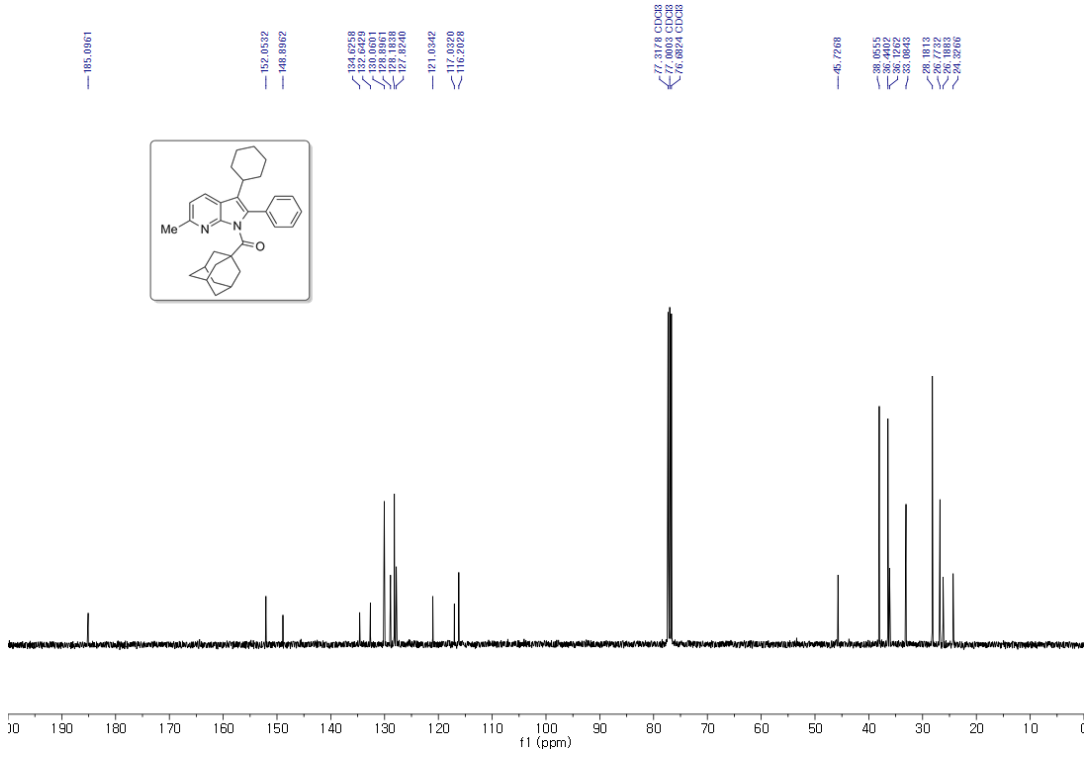


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(3-cyclohexyl-6-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4h).

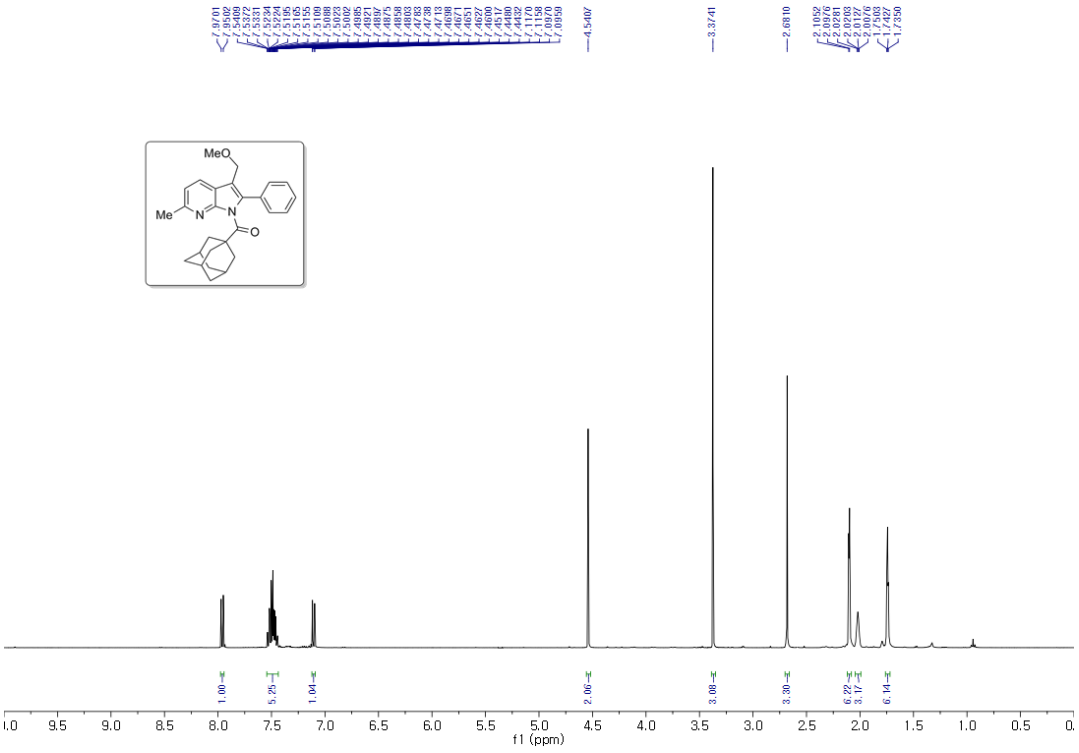


400 MHz, ^{1}H NMR in $CDCl_3$

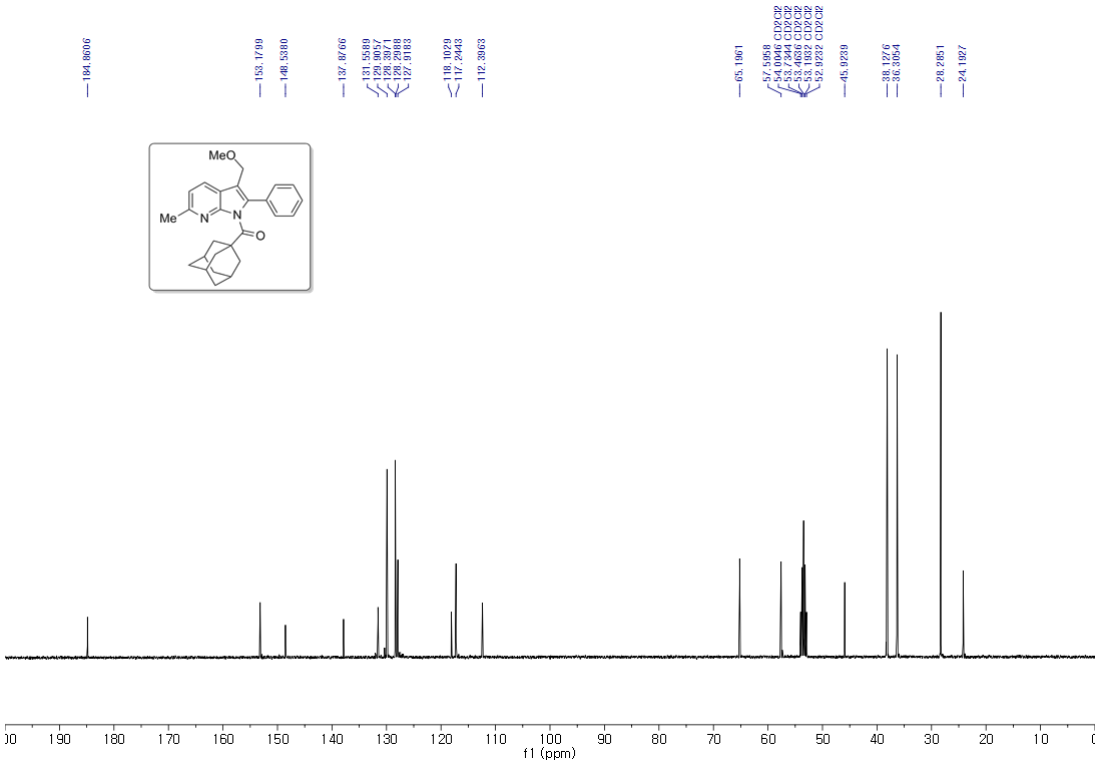


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(3-(methoxymethyl)-6-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4i).

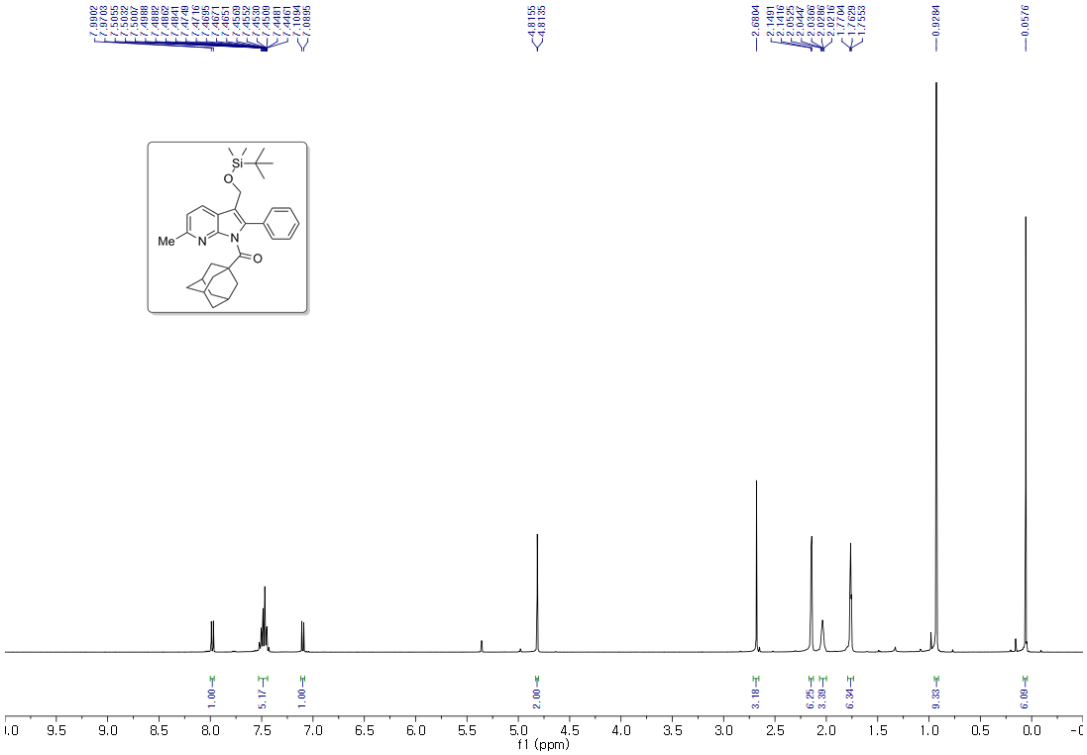


400 MHz, ^{1}H NMR in CD_2Cl_2

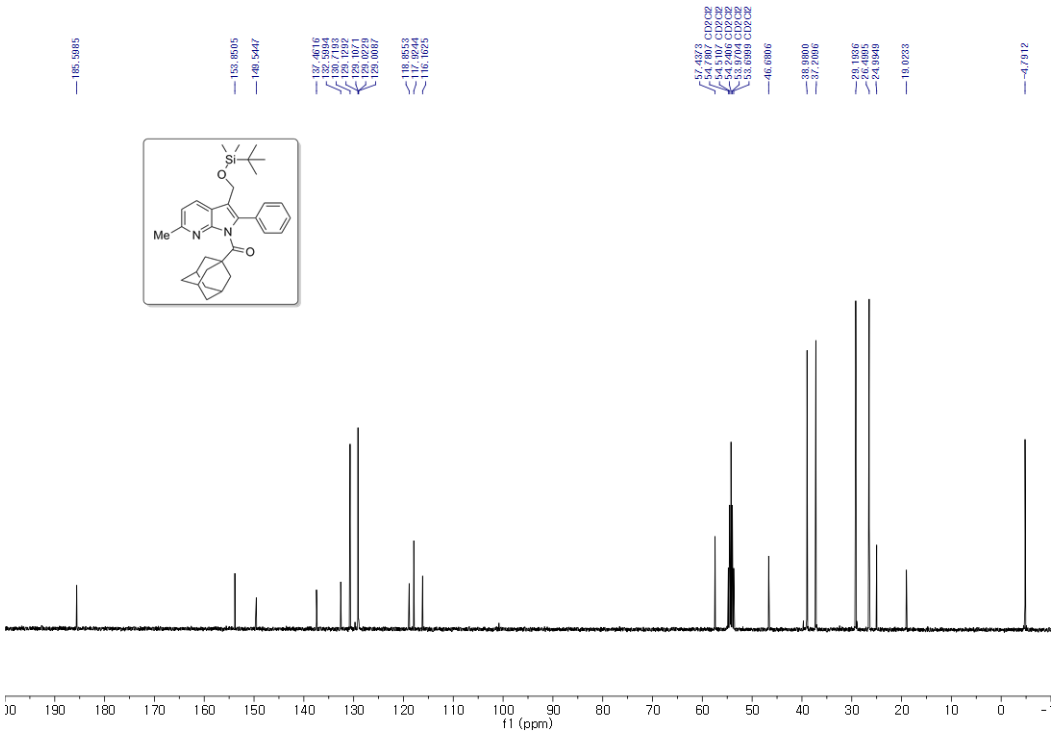


100 MHz, ^{13}C NMR in CD_2Cl_2

adamantan-1-yl(3-(((tert-butyldimethylsilyl)oxy)methyl)-6-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4j).

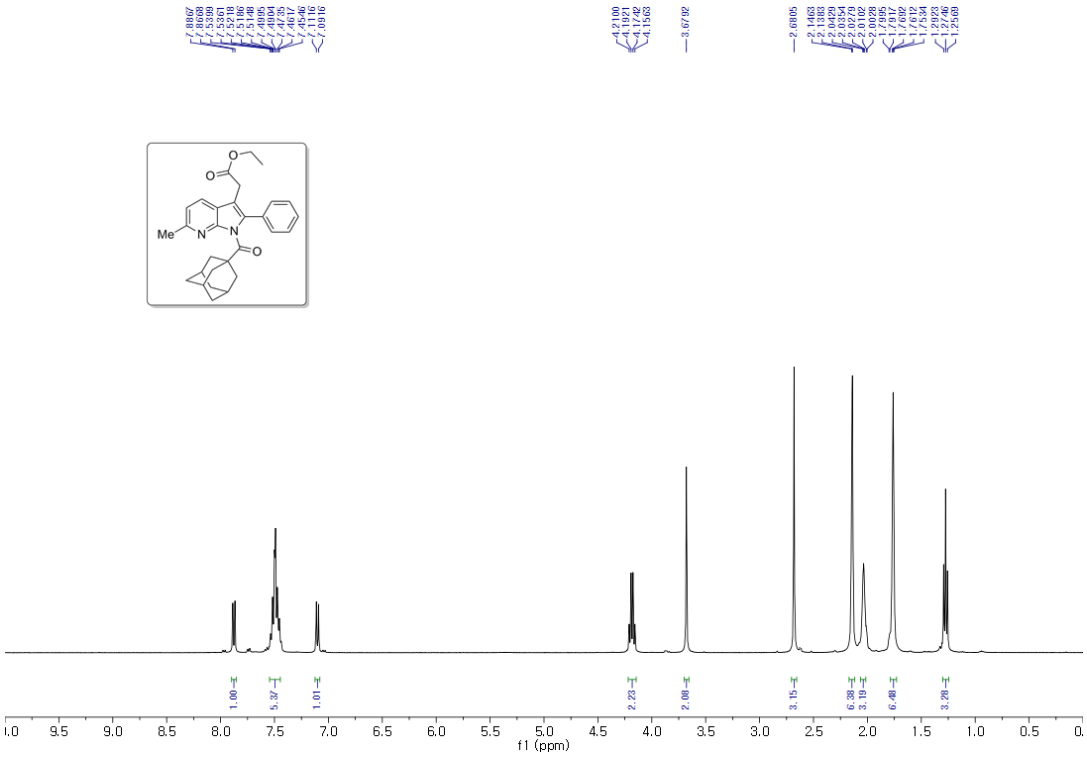


400 MHz, ^{1}H NMR in CD_2Cl_2

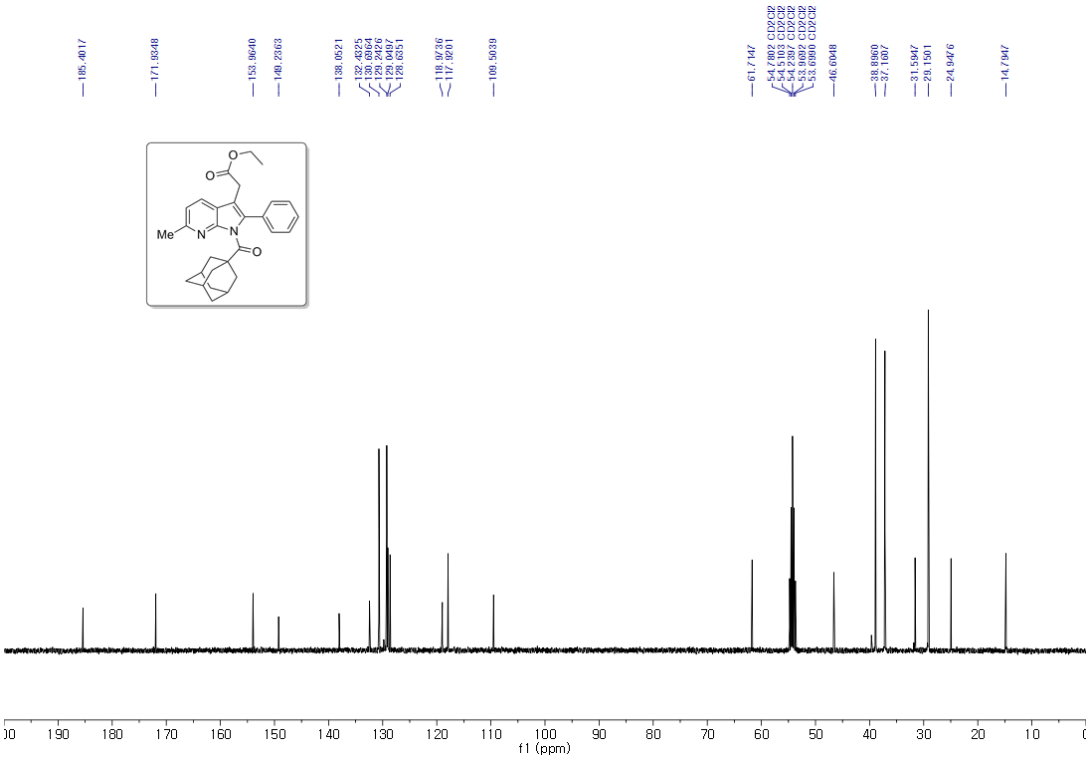


100 MHz, ^{13}C NMR in CD_2Cl_2

ethyl 2-(1-(adamantane-1-carbonyl)-6-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (4k).

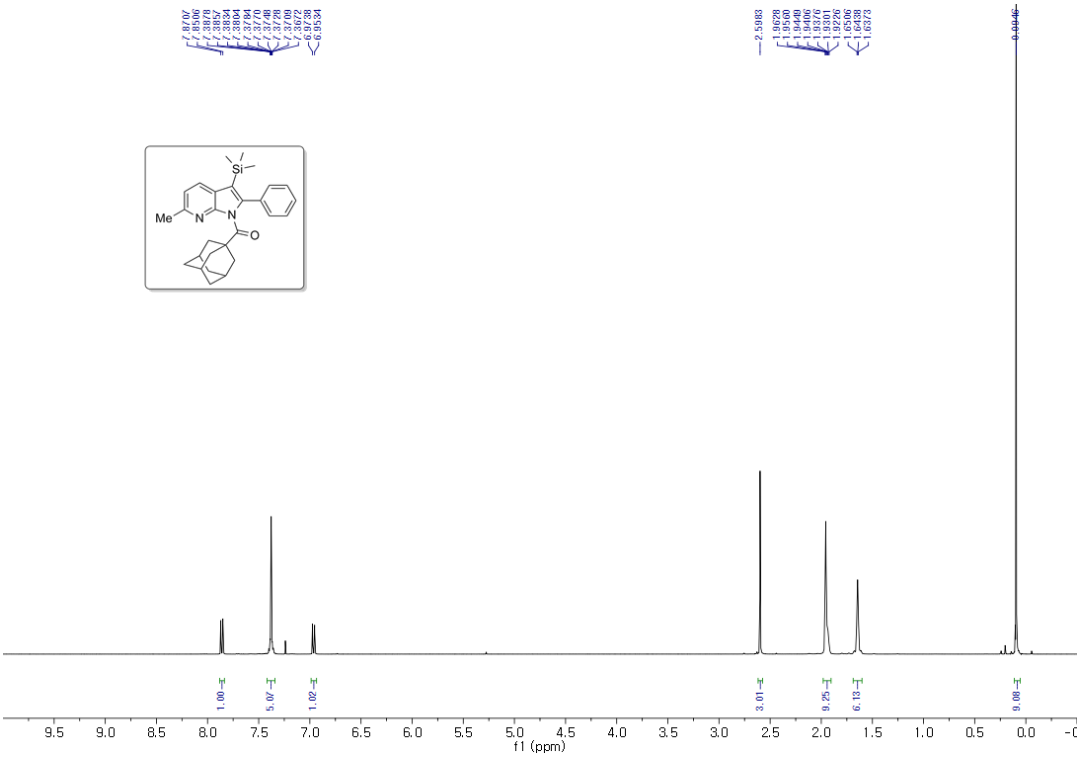


400 MHz, ^{1}H NMR in CD_2Cl_2

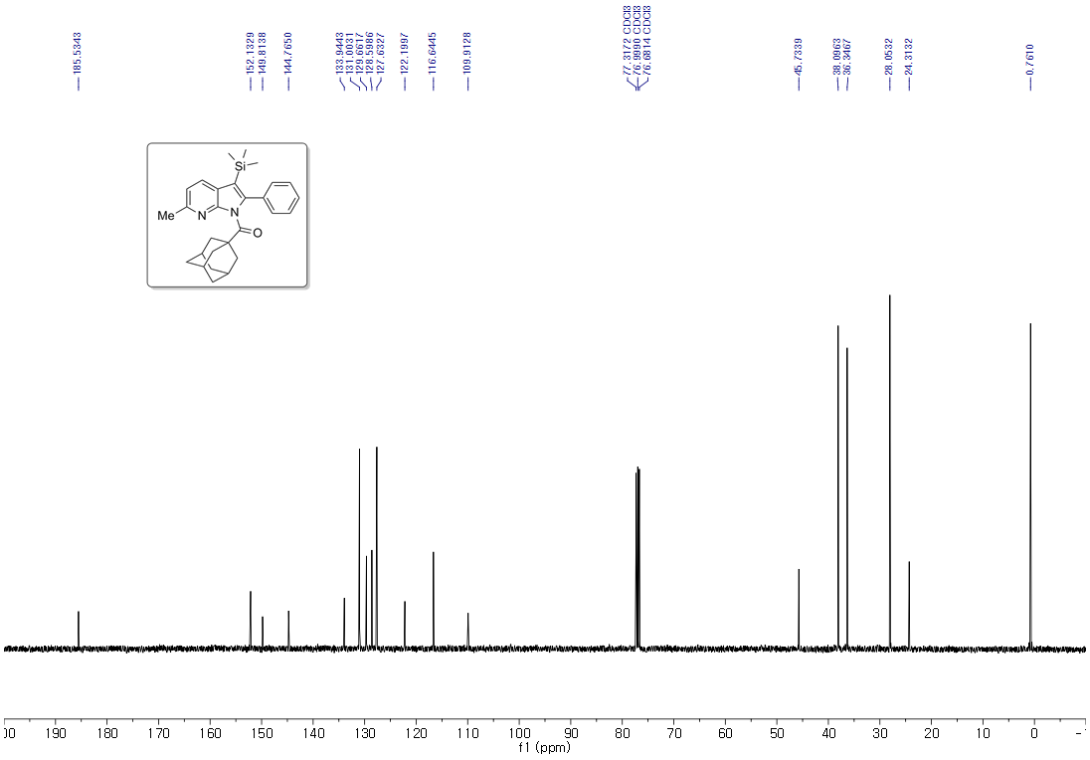


100 MHz, ^{13}C NMR in CD_2Cl_2

adamantan-1-yl(6-methyl-2-phenyl-3-(trimethylsilyl)-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4l).

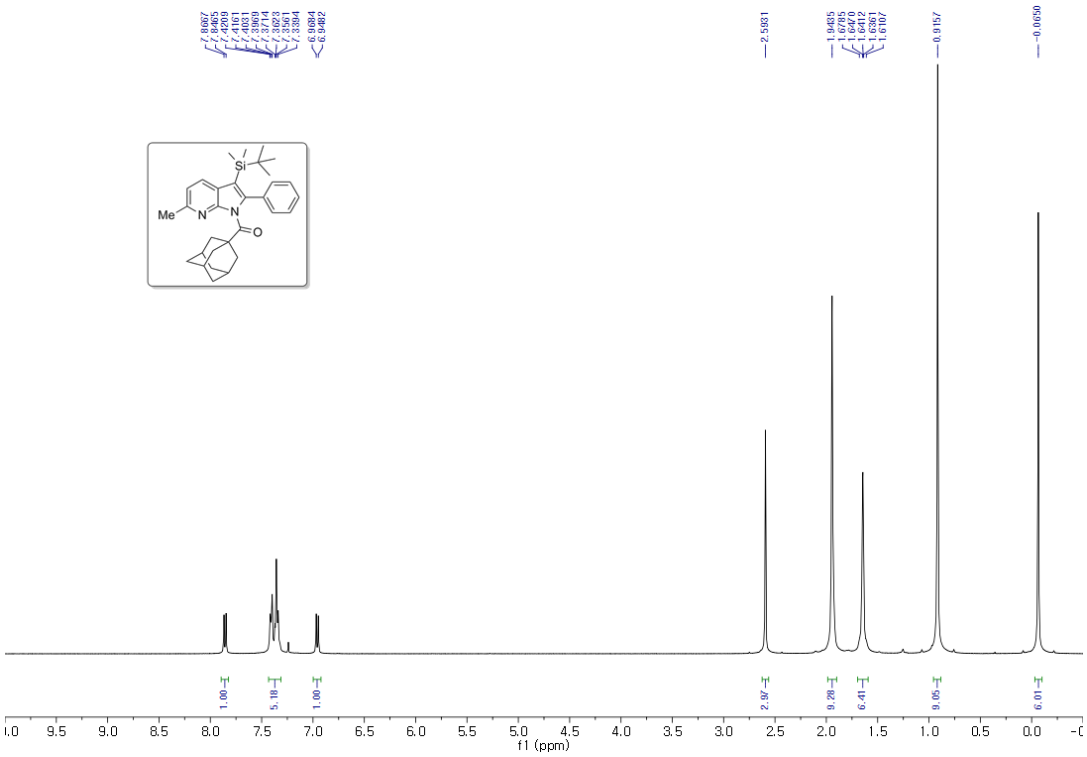


400 MHz, ^{1}H NMR in $CDCl_3$

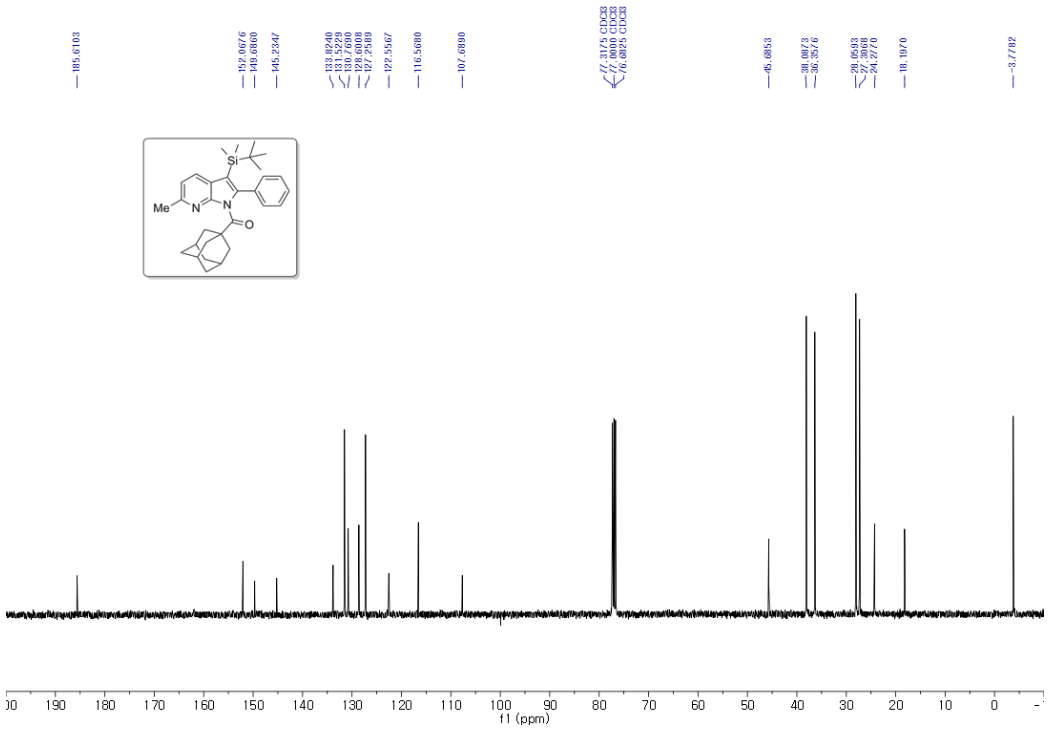


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(3-(tert-butyldimethylsilyl)-6-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4m).

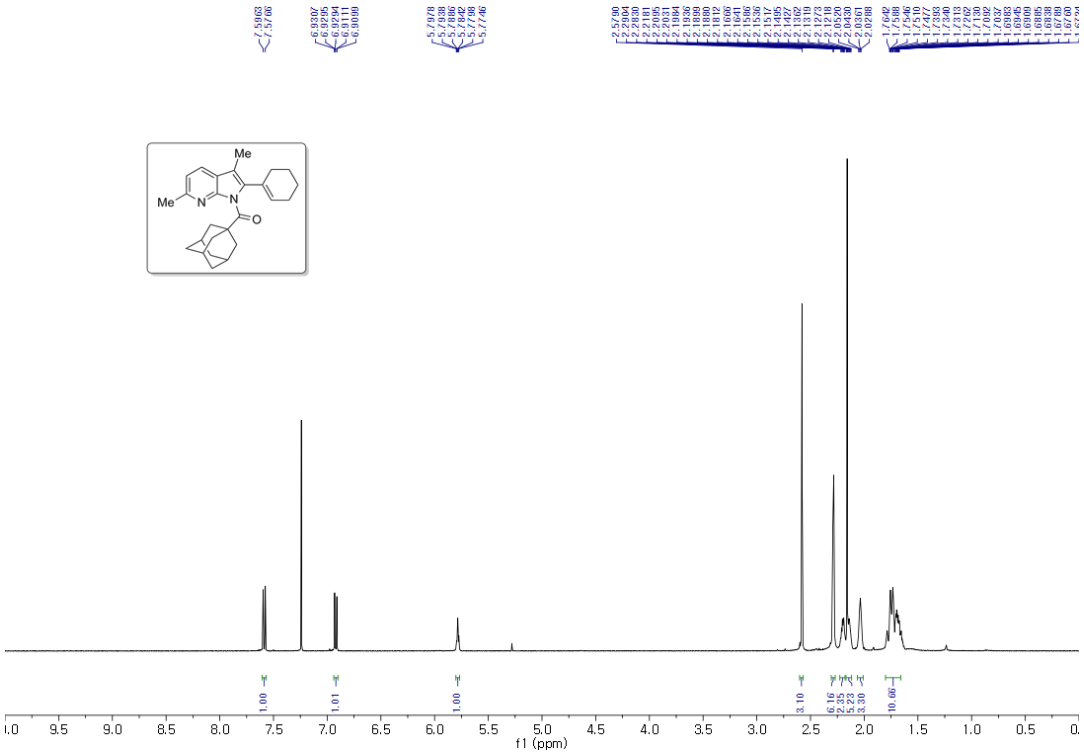


400 MHz, ^{1}H NMR in $CDCl_3$

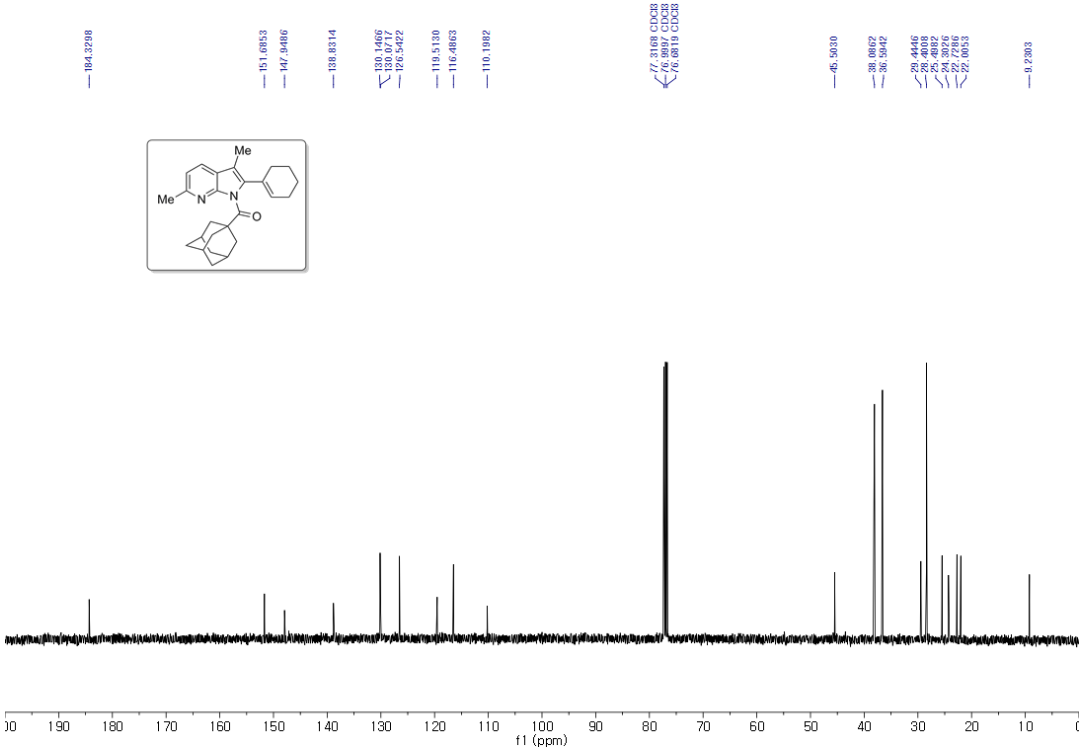


100 MHz, ^{13}C NMR in $CDCl_3$

adamantan-1-yl(2-(cyclohex-1-en-1-yl)-3,6-dimethyl-1H-pyrrolo[2,3-b]pyridin-1-yl)methanone (4n).

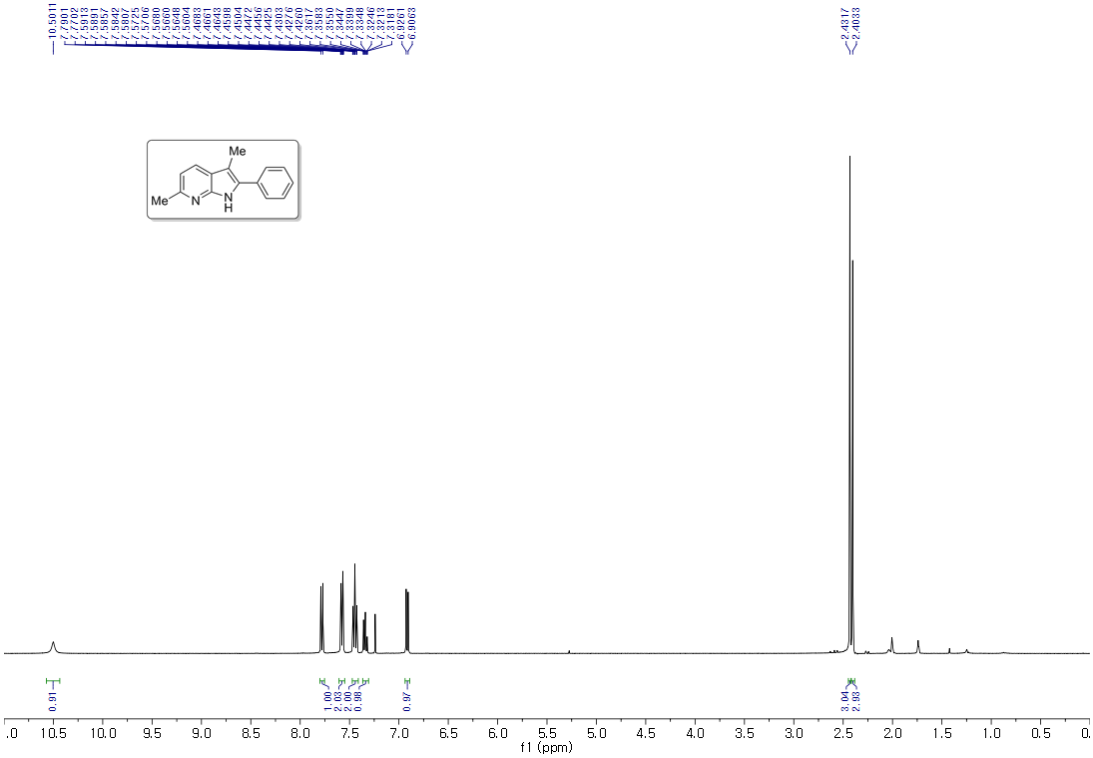


400 MHz, ^{1}H NMR in $CDCl_3$

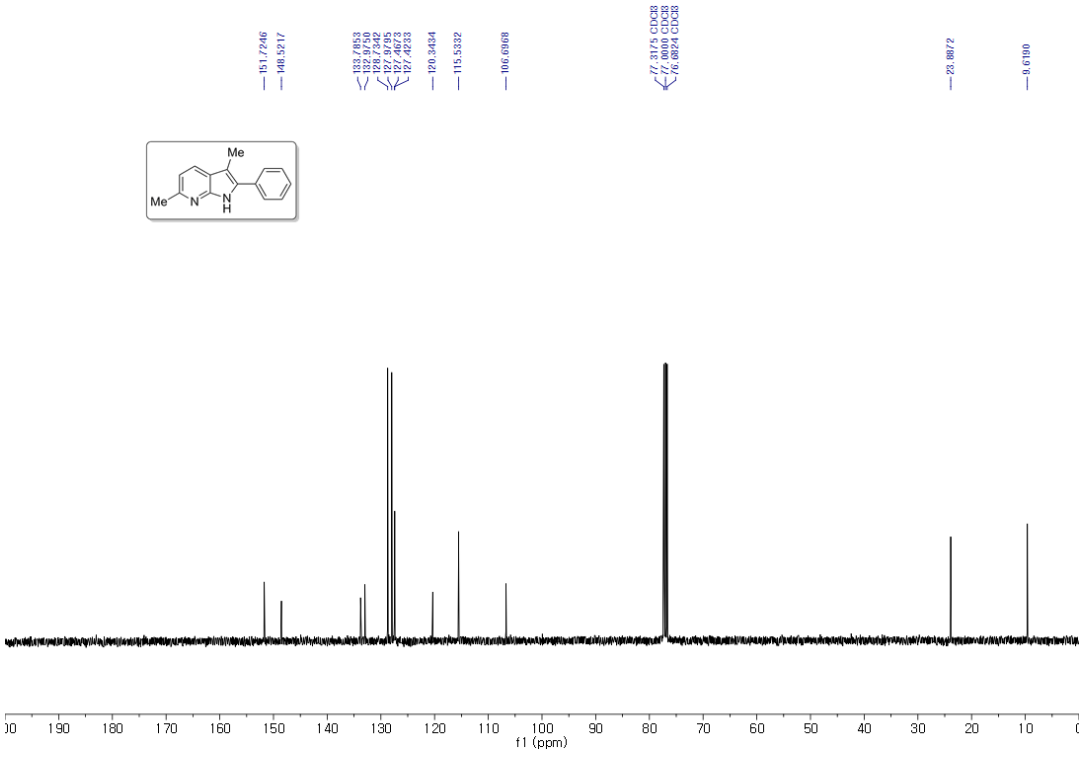


100 MHz, ^{13}C NMR in $CDCl_3$

3,6-dimethyl-2-phenyl-1H-pyrrolo[2,3-b]pyridine

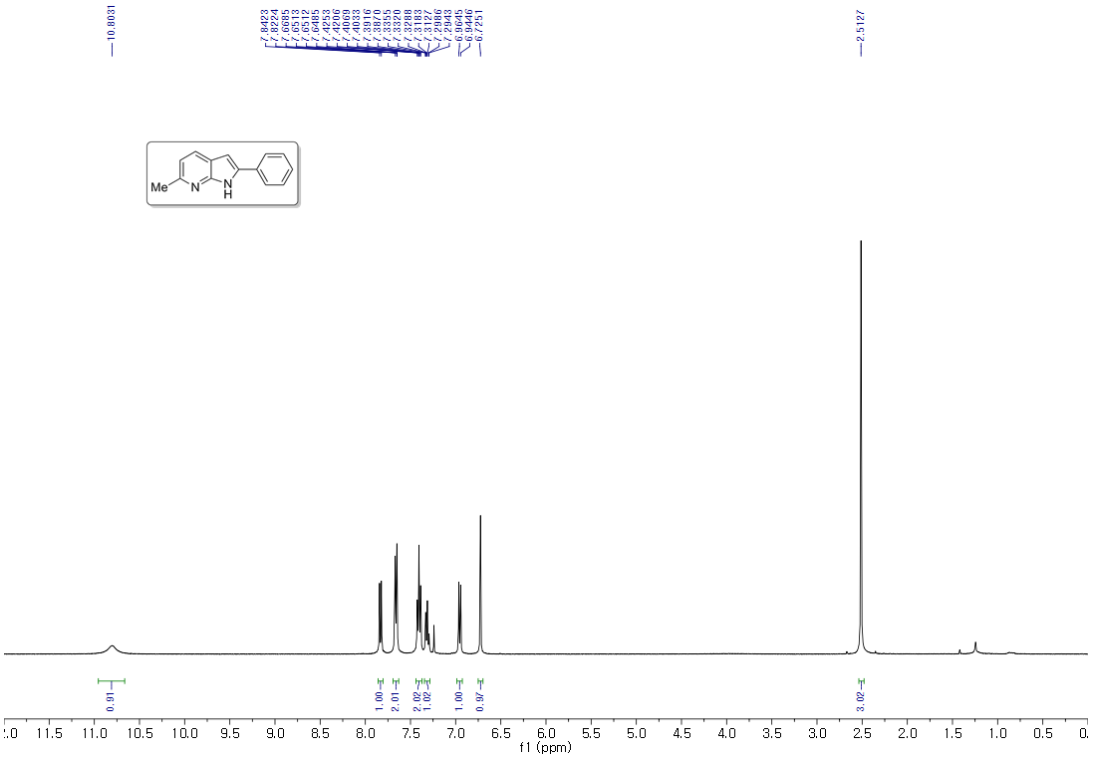


400 MHz, ^{1}H NMR in $CDCl_3$

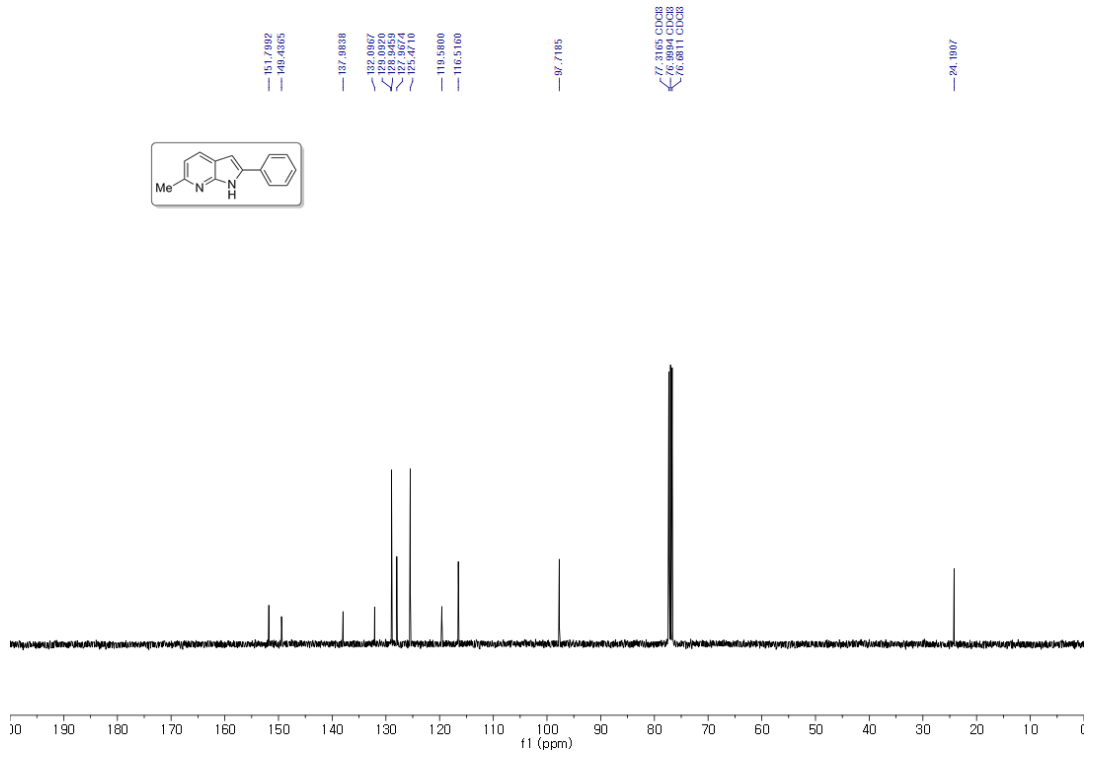


100 MHz, ^{13}C NMR in $CDCl_3$

6-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridine



400 MHz, ^{1}H NMR in $CDCl_3$



100 MHz, ^{13}C NMR in $CDCl_3$