Supporting Information

Pd-Catalyzed Solvent-controlled Direct Site-selective Arene C−H Monoacyloxylation of Pyrrolo[2,3-*d*]pyrimidine Derivatives

Zhengtong Mao, Min Liu, Hongjie Qian, Yunfeng Jiang, Xingxian Zhang*

College of Pharmaceutical Science, Zhejiang University of Technology, Hangzhou 310014, P. R. China

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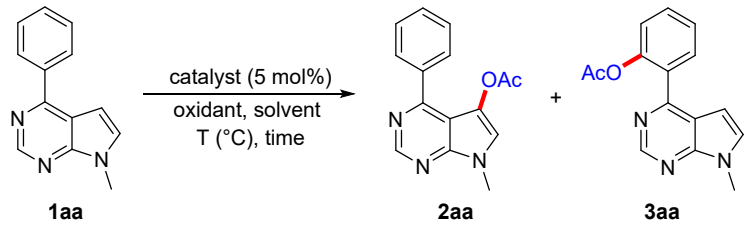
1. General Information

All reagents were obtained from commercial suppliers and used without further purification. A series of substrates **1** were prepared according to the literature procedure.[1]4-Chloro-7-methyl-7H-pyrrolo[2,3-*d*]pyrimidine is commercially available from Aladdin. Yields for all products were determined by the silica gel (200-300 mesh) column chromatography (eluent: petroleum ether 40-60/EtOAc), and the reactions were monitored by thin layer chromatography (TLC) on a glass pate coated with silica gel with fluorescent indicator (GF254) using UV light. The ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ADNANCE 400 at 400 MHz, Bruker ADNANCE 500 at 500 MHz and Bruker ADNANCE 600 at 600 MHz using $CDCl_3$ as solvent with TMS as internal standard. ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 at 101 MHz, Bruker AVANCE 500 at 126 MHz and Bruker AVANCE 600 at 151 MHz. Chemical shifts are given in ppm (δ) referenced to $CDCl_3$ with 7.26 for ^{1}H and 77.16 for ^{13}C, and to DMSO-d6 with 2.50 for ^{1}H and 39.52 for ^{13}C. Signals are abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and coupling constants are expressed in hertz. Melting points were measured on a BUCHI B-540 and uncorrected. HRMS (ESI) was recorded using Agilent 6520 accurate-Mass Q-TOF LC/MS system (1200-6520/Agilent).

2. Condition Optimization

1. Mao, Z.; Liu, M.; Zhu, G.; Zhou, J.; Zhang, X., Transition-metal-free highly regioselective C–H acetoxylation of pyrrolo[2,3-d]pyrimidine derivatives. *Organic Chemistry Frontiers* 2020, **7**, 2696-2702.

Table S1. Condition optimization[a]

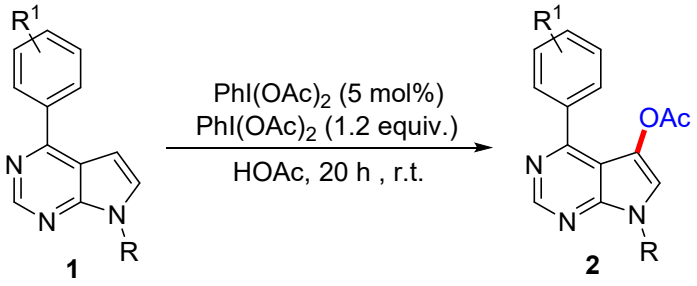


Entry	Catalyst	Additive	Solvent	T	t(h)	2aa(%)[b]	3aa (%)[b]
1	$Pd(OAc)_2$	PIDA	Ac_2O:HOAc = 1:1	r.t.	20	30	20
2	$Pd(OAc)_2$	PIDA	HOAc	r.t.	20	85	-
3	/	PIDA	HOAc	r.t.	20	16	-
4	$PdCl_2$	PIDA	HOAc	r.t.	20	70	
5	$Pd(PPh_3)_2Cl_2$	PIDA	HOAc	r.t.	20	50	-
6	$Pd(MeCN)_2Cl_2$	PIDA	HOAc	r.t.	20	56	-
7	$Pd(PPh_3)_4$	PIDA	HOAc	r.t.	20	53	-
8	$Pd(OAc)_2$	PIDA	HOAc	50 ℃	6	20	56
9	$Pd(OAc)_2$	PIDA	HOAc	60 ℃	6	11	50
10	$Pd(OAc)_2$	PIDA	Ac_2O	50 ℃	6	-	90
11	/	PIDA	Ac_2O	50 ℃	6	-	30
12	$Pd(PPh_3)_2Cl_2$	PIDA	Ac_2O	50 ℃	6	-	52
13	$Pd(MeCN)_2Cl_2$	PIDA	Ac_2O	50 ℃	6	-	56
14	$Pd(PPh_3)_4$	PIDA	Ac_2O	50 ℃	6	-	48
15	$PdCl_2$	PIDA	Ac_2O	50 ℃	6	38	23
16	$Cu(OAc)_2$	PIDA	Ac_2O	50 ℃	6	-	20
17	$Co(OAc)_2$	PIDA	Ac_2O	50 ℃	6	-	21
18	$Pd(OAc)_2$	$Cu(OAc)_2$	Ac_2O	50 ℃	6	-	-
19	$Pd(OAc)_2$	O_2 (1 atm)	Ac_2O	50 ℃	6	-	-
20	$Pd(OAc)_2$	AgOAc (200 mol%)	Ac_2O	50 ℃	6	-	-
21	$Pd(OAc)_2$	$K_2S_2O_8$ (300 mol%)	Ac_2O	50 ℃	6	-	-
22	$Pd(OAc)_2$	$PhI(OCOCF_3)_2$ (PIFA)	Ac_2O	50 ℃	6	-	-
23[c]	$Pd(OAc)_2$	PIDA	HOAc	r.t.	20	80	
24[c]	$Pd(OAc)_2$	PIDA	Ac_2O	50 ℃	6		86

[a] Unless otherwise noted the reactions were performed on a 0.4 mmol scale of **1aa** using 1.2 equiv. of PIDA and 5 mol% of catalyst in solvent (4.0 mL) under air atmosphere. [b] Isolated yields. [c] 5 mmol gram scale.

2. General Procedures for the acetoxylation

(1) General Procedures for the synthesis of **2**



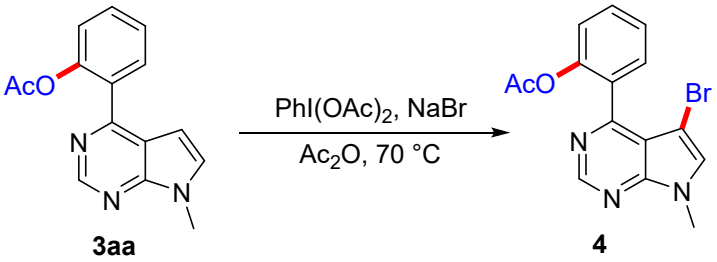
The reaction of 7-methyl-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate **2aa** was exemplified here. Diacetoxyiodobenzene (155 mg, 0.48 mmol), HOAc (4 mL), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and 7-methyl-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine **1aa** (84 mg, 0.4 mmol) were added in a pressure vessel. The reaction mixture was stirred at room temperature for 20 h. After completion, the reaction was quenched with water (10 mL) and extracted with EA (3×20 mL). The organic layer was washed with saturated sodium bicarbonate (20 mL), brine (20 mL) and dried over anhydrous Na_2SO_4. After concentration in vacuo, the residue was purified by flash column chromatography (PE/EtOAc v/v 2:1) on silica gel to provide the desired product 7-methyl-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate **2aa** (91 mg, 85% yield).

(2) General Procedures for the synthesis of **3**:

The reaction of 2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate **3aa** was exemplified here. Diacetoxyiodobenzene (155 mg, 0.48 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), Ac_2O (4 mL) and 7-methyl-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine **1aa** (84 mg, 0.4 mmol) were added in a pressure vessel. The reaction mixture was stirred at 50 °C for 6 h. After completion, it was then cooled to room temperature, the reaction was quenched with water (10 mL) and extracted with EA (3×20 mL). The organic layer

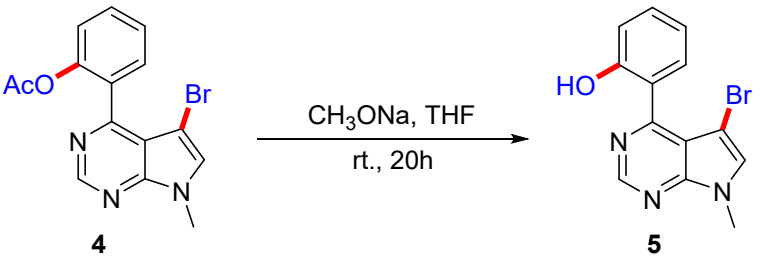
was washed with saturated sodium bicarbonate (20 mL), brine (20 mL) and dried over anhydrous Na_2SO_4. After concentration in vacuo, the residue was purified by flash column chromatography (PE/EtOAc v/v 2:1) on silica gel to provide the desired product 2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl) phenyl acetate **3aa** (96 mg, 90% yield).

(3) Preparation of compound **4**



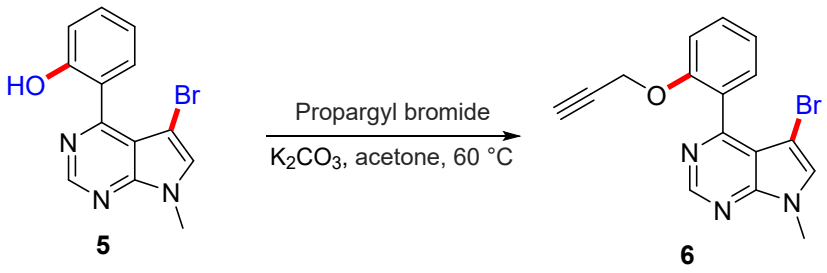
The reaction of 2-(5-bromo-7-methyl-7H-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate **4** was exemplified here. $PhI(OAc)_2$ (934 mg, 2.9 mmol), NaBr (391 mg, 3.8 mmol), MeCN (20 mL) and **3aa** (507 mg, 1.9 mmol) were added in a 50 mL round-bottomed flask. The reaction mixture was stirred at 70 °C for 6 h. After completion, it was then cooled to room temperature, the reaction was quenched with water (10 mL) and extracted with EA (3×20 mL). The organic layer was washed with saturated sodium bicarbonate (20 mL), brine (20 mL) and dried over anhydrous Na_2SO_4. After concentration in vacuo, the residue was purified by flash silica gel chromatography using PE/EA (4:1) as eluents to afford the title compound **4** (427 mg, 65% yield).

(4) Preparation of compound **5**



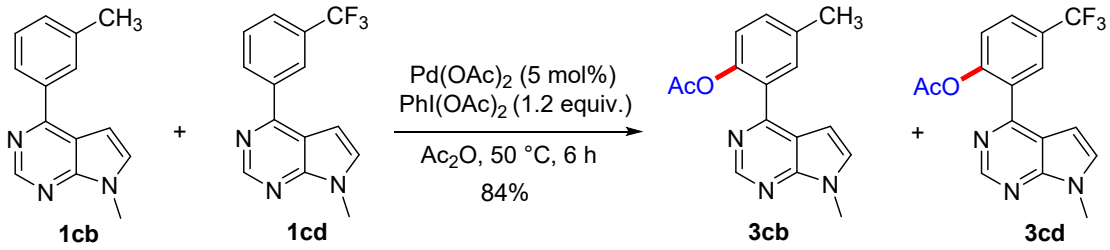
Compound **4** (170 mg, 0.5 mmol), CH_3ONa (33 mg, 0.6 mmol) and THF (5 mL) were added in a pressure vessel. The reaction mixture was stirred at room temperature for 20 h. After completion, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA (4:1) as eluents to afford the title compound **5** (110 mg, 73% yield).

(5) Preparation of compound **6**



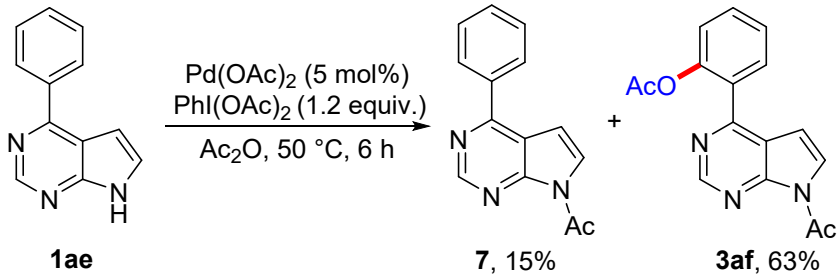
Compound **5** (80 mg, 0.26 mmol), K_2CO_3 (43 mg, 0.3 mmol) and acetone (2 mL) were added in a pressure vessel. Propargyl bromide (47 mg, 0.4 mmol) was added and stirred at 60 °C for 6 h. After completion, the mixture was quenched by water (10 mL) and extracted with EtOAc (20 mL). The organic layer was washed with brine (10 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (PE/EtOAc v/v 4:1) on silica gel to provide the desired product **6** (70 mg, 78% yield).

(6) The competitive experiment 2



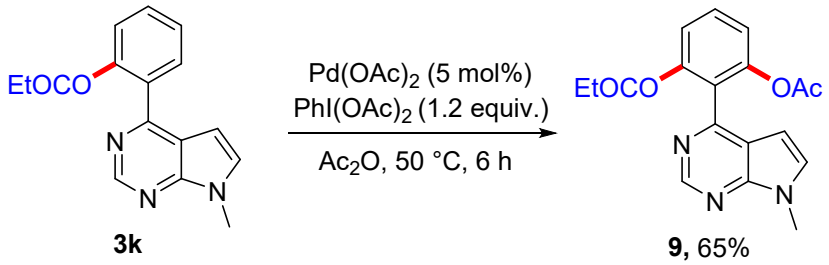
Compound **1cb** (89 mg, 0.4 mmol), compound **1cd** (111 mg, 0.4 mmol), $PhI(OAc)_2$ (155 mg, 0.48 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and Ac_2O (4 mL) were added in a pressure vessel. The reaction mixture was stirred at 50 °C for 6 h. After completion, it was then cooled to room temperature, the reaction was quenched with water (10 mL) and extracted with EA (3×20 mL). The organic layer was washed with saturated sodium bicarbonate (20 mL), brine (20 mL) and dried over anhydrous Na_2SO_4. After concentration in vacuo, the residue was purified by flash column chromatography (PE/EtOAc v/v 4:1) on silica gel. Only product **3cb** (93mg, 84% yield) was obtained.

(7) Control experiment 3



The reaction of control experiment was exemplified here. $PhI(OAc)_2$ (419 mg, 1.3 mmol), $Pd(OAc)_2$ (14 mg, 0.06 mmol), Ac_2O (10 mL) and compound **1ae** (210 mg, 1.1 mmol) were added in a 25 mL round-bottomed flask. The reaction mixture was stirred at 50 °C for 6 h. After completion, it was then cooled to room temperature, the reaction was quenched with water (10 mL) and extracted with EA (3×20 mL). The organic layer was washed with saturated sodium bicarbonate (20 mL), brine (20 mL) and dried over anhydrous Na_2SO_4. After concentration in vacuo, the residue was purified by flash column chromatography (PE/EtOAc v/v 2:1) on silica gel to provide the product **7** (40 mg, 15% yield) and compound **3af** (205 mg, 63% yield).

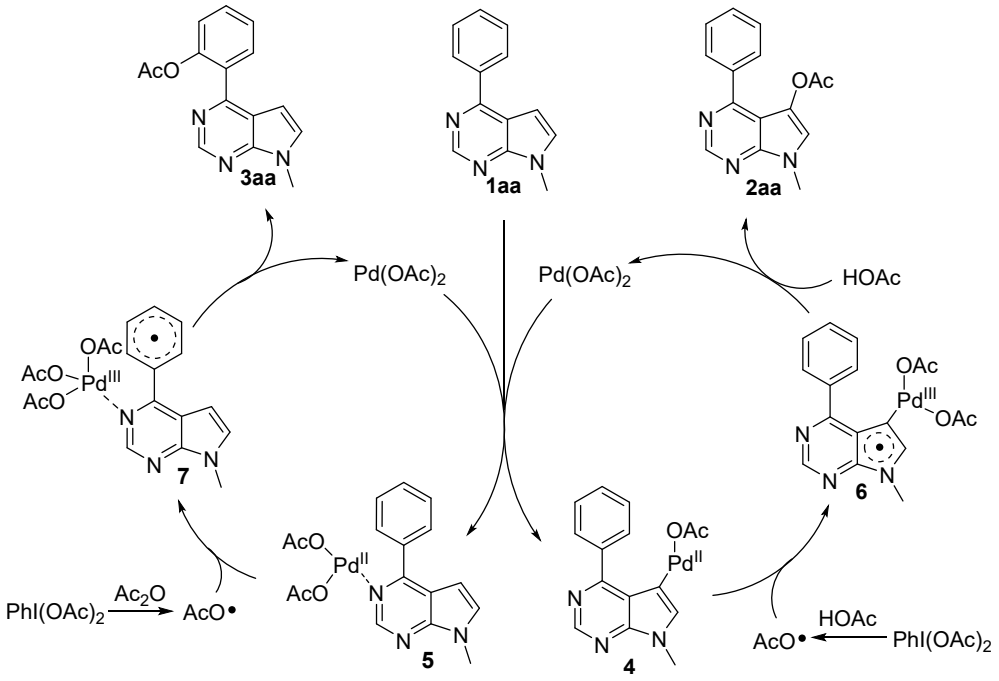
(8) Control experiment 4



The reaction of compound **9** was exemplified here. $PhI(OAc)_2$ (139 mg, 0.43 mmol), $Pd(OAc)_2$ (4 mg, 0.02 mmol), Ac_2O (4 mL) and compound **3k** (101 mg, 0.36 mmol) were added in a pressure vessel. The reaction mixture was stirred at 50 °C for 6 h. After completion, it was then cooled to room temperature, the reaction was quenched with water (10 mL) and extracted with EA (3×20 mL). The organic layer was washed with saturated sodium bicarbonate (20 mL), brine (20 mL) and dried over anhydrous Na_2SO_4. After concentration in vacuo, the residue was purified by flash column chromatography (PE/EtOAc v/v 2:1) on silica gel to provide the desired product **9** (79 mg, 65% yield).

4. **The supposed reaction mechanism**

Based on the control experiments and the reported literatures[1-3], we supposed a plausible pathway to explain this acetoxylation. The Pd(II)-complex **4/5** was formed by coordination **1aa** with $Pd(OAc)_2$, followed by an oxidative addition of acetoxy radical in the presence of PIDA with HOAc or Ac_2O to generate Pd (III) complex. Finally, the intramolecular acetoxy group transfer of Pd (III)-complex **6/7** produced the desired acetoxylated product **2aa/3aa**. However, the mechanism remains unclear. The investigations on the detailed mechanistic pathway are under way in our laboratory.



Reference :

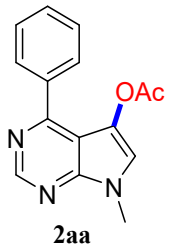
1. Liu, Q.; Li, G.; Yi, H.; Wu, P.; Liu, J.; Lei, A. Pd-Catalyzed Direct and Selective C-H Functionalization: C3-Acetoxylation of Indoles. *Chem. Eur. J.* **2011**, *17*, 2353-2357.

2. K. K. Yu, Y. Guo, Y. H. Hu, Z. Xu, H. W. Liu, D. H. Liao, Y. F. Ji, Palladium-Catalyzed Diverse mono-Acyloxylation of 5-Alkyl-4-aryl-thiazole-2-carboxylates, *Asian. J.Org. Chem*., 2016, **5**, 1219-1224.

3. S. K. Santra, A. Banerjee, N. Khatun, B. K. Patel, Ceric Ammonium Nitrate (CAN) Promoted PdII-Catalyzed Substrate-Directed o-Benzoxylation and Decarboxylative o-Aroylation, *Eur. J. Org. Chem.* 2015, **2015**, 350-356.

4. Characterization of the products

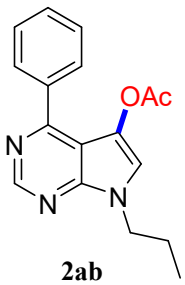
7-methyl-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2aa)



2aa

Yellow solid (90 mg, 84% yield) Mp: 128-131 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.89-7.82 (m, 2H), 7.52 (dd, *J* = 5.2, 2.0 Hz, 3H), 7.26 (s, 1H), 3.92 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.70, 158.54, 151.74, 148.28, 139.88, 134.88, 129.41, 128.82, 126.93, 119.15, 108.47, 31.07, 20.65. HRMS-ESI calculated for $C_{15}H_{14}N_3O_2$ $[M+H]^+$ 268.1086, found 268.1082.

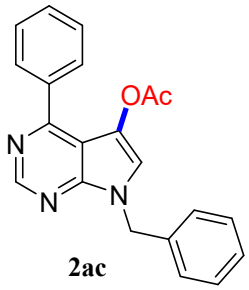
4-phenyl-7-propyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2ab)



2ab

Yellow viscous oil (99 mg, 84% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.87 -7.82 (m, 2H), 7.50 (p, *J* = 3.0, 2.4 Hz, 3H), 7.30 (s, 1H), 4.27 (t, *J* = 7.2 Hz, 2H), 2.02 (s, 3H), 1.92 (dt, *J* = 14.7, 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.56, 158.45, 151.59, 147.98, 137.71, 129.62, 129.41, 128.05, 126.89, 118.26, 108.59, 46.18, 23.47, 20.54, 11.27. HRMS-ESI calculated for $C_{17}H_{18}N_3O_2$ $[M+H]^+$ 296.1394, found 296.1394.

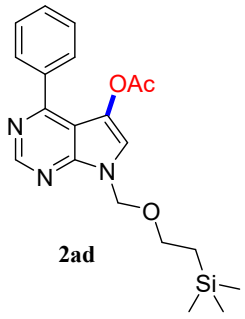
7-benzyl-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2ac)



2ac

White solid (104 mg, 76% yield). Mp: 97-100 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.88-7.85 (m, 2H), 7.54-7.50 (m, 3H), 7.38-7.32 (m, 2H), 7.32-7.27 (m, 3H), 7.25 (s, 1H), 5.50 (s, 2H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.46, 158.64, 151.94, 148.30, 137.64, 136.35, 129.69, 129.42, 128.91, 128.11, 128.08, 127.79, 127.40, 118.09, 108.68, 47.87, 20.51. HRMS-ESI calculated for $C_{21}H_{18}N_3O_2$ $[M+H]^+$ 344.1394, found 344.1394.

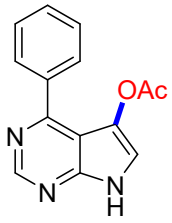
4-phenyl-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2ad)



2ad

White solid (132 mg, 87% yield). Mp: 63-66 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.88-7.82 (m, 2H), 7.52 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.43 (s, 1H), 5.70 (s, 2H), 3.64-3.58 (m, 2H), 2.02 (s, 3H), 1.00-0.90 (m, 2H), -0.02 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.35, 158.77, 152.13, 149.06, 137.51, 129.77, 129.44, 128.11, 128.03, 117.93, 108.90, 72.80, 66.73, 20.53, 17.75, -1.45. HRMS-ESI calculated for $C_{20}H_{26}N_3O_3Si$ $[M+H]^+$ 384.1738, found 384.1737.

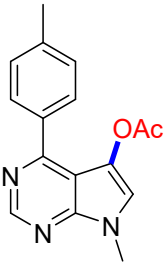
4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2ae)



2ae

White solid (88 mg, 87% yield). Mp: 99-101 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.44 (s, 1H), 9.02 (s, 1H), 7.91-7.86 (m, 1H), 7.71 (dd, *J* = 11.5, 7.6 Hz, 1H), 7.54 (d, *J* = 3.4 Hz, 2H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.41 (s, 1H), 2.04 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.41, 152.74, 152.36, 151.42, 132.35, 130.88, 130.00, 128.85, 127.88, 118.91, 104.92, 26.01. $C_{14}H_{11}N_3O_2Na$ $[M+Na]^+$ 276.0743, found 276.0643.

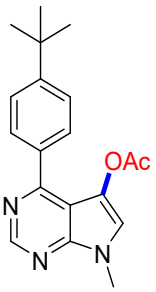
7-methyl-4-(p-tolyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2ba)



2ba

Yellow solid (99 mg, 88% yield). Mp: 155-157 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.80-7.73 (m, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.25 (s, 1H), 3.90 (s, 3H), 2.45 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.70, 158.54, 151.74, 148.28, 139.88, 134.88, 129.41, 128.82, 126.93, 119.15, 108.47, 31.07, 21.44, 20.65. HRMS-ESI calculated for $C_{16}H_{16}N_3O_2$ $[M+H]^+$ 282.1242, found 282.1243.

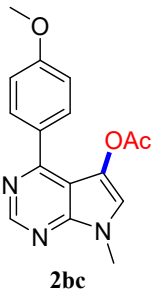
4-(4-(tert-butyl)phenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2bb)



2bb

Yellow solid (107 mg, 83% yield). Mp: 110-112 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.85 (s, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.14 (s, 1H), 3.80 (s, 3H), 1.92 (s, 3H), 1.29 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.75, 158.53, 153.07, 151.64, 148.25, 134.58, 129.18, 127.00, 125.12, 119.31, 108.62, 34.81, 31.29, 31.12, 20.52. HRMS-ESI calculated for $C_{19}H_{22}N_3O_2$ $[M+H]^+$ 324.1707, found 324.1717.

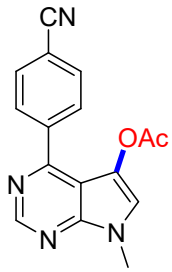
4-(4-methoxyphenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2bc)



2bc

Yellow solid (108 mg, 91% yield). Mp: 138-141 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.93 (s, 1H), 7.90-7.83 (m, 2H), 7.25 (s, 1H), 7.08-6.99 (m, 2H), 3.90 (s, 6H), 2.10 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.70, 161.12, 158.14, 151.74, 148.29, 131.07, 130.25, 126.96, 119.03, 113.60, 108.24, 55.42, 31.11, 20.74. HRMS-ESI calculated for $C_{16}H_{16}N_3O_3$ $[M+H]^+$ 298.1191, found 298.1192.

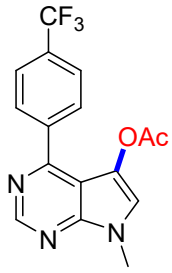
4-(4-cyanophenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2bd)



2bd

Yellow solid (77 mg, 66% yield). Mp:182-185 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.00 – 7.98 (m, 2H), 7.83 – 7.81 (m, 2H), 7.38 (s, 1H), 3.93 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.26, 163.57, 155.95, 151.78, 142.10, 132.33, 131.81, 130.40, 130.25, 126.56, 120.14, 113.34, 31.23, 20.64. HRMS-ESI calculated for $C_{16}H_{13}N_4O_2$ $[M+H]^+$ 293.1038, found 293.1035.

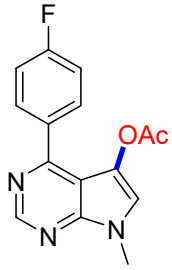
7-methyl-4-(4-(trifluoromethyl)phenyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2be)



2be

Yellow solid (103 mg, 77% yield). Mp:123-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.95 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.1 Hz, 2H), 7.30 (s, 1H), 3.88 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.38, 156.57, 151.69, 148.26, 141.13, 131.49 ($J_{C\text{-}F}$ = 64.64 Hz), 129.88, 126.60, 124.94 ($J_{C\text{-}F}$ = 4.04 Hz), 124.04 ($J_{C\text{-}F}$ = 272.7 Hz), 119.88, 108.63, 31.08, 20.45. HRMS-ESI calculated for $C_{16}H_{13}F_3N_3O_2$ $[M+H]^+$ 36.0960, found 336.0950.

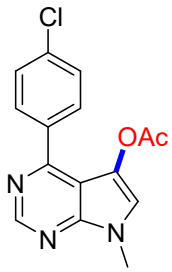
4-(4-fluorophenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2bf)



2bf

Yellow solid (93 mg, 81% yield). Mp:126-129 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (s, 1H), 7.86 – 7.81 (m, 2H), 7.24 (s, 1H), 7.16 (t, J = 8.7 Hz, 2H), 3.84 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ168.53, 164.91, 162.93, 157.28, 151.75, 148.29, 131.52 ($J_{C\text{-}F}$ = 8.82 Hz), 126.80, 119.43, 115.19 ($J_{C\text{-}F}$ = 21.4 Hz), 108.44, 31.14, 20.64. HRMS-ESI calculated for $C_{15}H_{13}FN_3O_2$ $[M+H]^+$ 286.0992, found 286.0983.

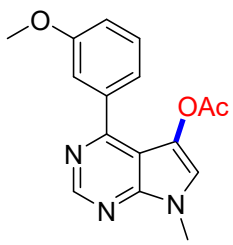
4-(4-chlorophenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2bg)



2bg

Yellow solid (110 mg, 90% yield). Mp:162-165 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (s, 1H), 7.79 – 7.74 (m, 2H), 7.46 – 7.42 (m, 2H), 7.26 (s, 1H), 3.83 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.52, 157.07, 151.75, 148.31, 136.18, 136.06, 130.87, 128.35, 126.74, 119.56, 108.46, 31.15, 20.68. HRMS-ESI calculated for $C_{15}H_{13}ClN_3O_2$ $[M+H]^+$ 302.0691, found 302.0680.

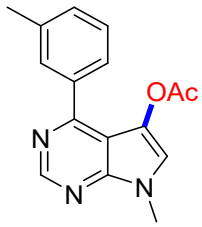
4-(3-methoxyphenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2ca)



2ca

White solid (98 mg, 82% yield). Mp: 156-159 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.45-7.39 (m, 3H), 7.24 (s, 1H), 7.07-7.03 (m, 1H), 3.90 (s, 6H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.87, 159.43, 158.29, 151.69, 148.36, 138.92, 129.15, 126.83, 121.91, 119.52, 115.72, 114.57, 108.66, 55.39, 31.13, 20.49. HRMS-ESI calculated for $C_{16}H_{16}N_3O_3$ $[M+H]^+$ 298.1186, found 298.1181.

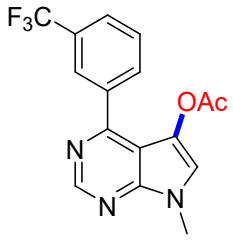
7-methyl-4-(m-tolyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2cb)



2cb

Yellow solid (90 mg, 80% yield). Mp:99-102 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.88 (s, 1H), 7.59 (d, J = 2.1 Hz, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 7.5 Hz, 1H), 7.16 (s, 1H), 3.83-3.81 (m, 3H), 2.38 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.73, 158.69, 151.76, 148.30, 137.80, 137.59, 130.52, 130.01, 127.97, 126.92, 126.64, 119.28, 108.61, 31.11, 21.46, 20.50. HRMS-ESI calculated for $C_{16}H_{16}N_3O_2$ $[M+H]^+$ 282.1237, found 282.1241.

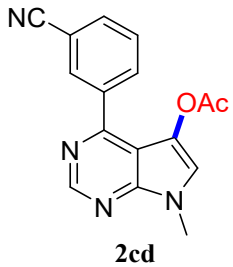
7-methyl-4-(3-(trifluoromethyl)phenyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2cc)



2cc

Yellow solid (99 mg, 74% yield). Mp:123-125 °C. ^{1}H NMR (500 MHz, CDCl3) δ 8.98 (s, 1H), 8.18-8.10 (m, 2H), 7.78 (d, J = 7.8 Hz, 1H), 7.67 (t, J = 7.8 Hz, 1H), 7.39 (s, 1H), 3.92 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.43, 156.55, 151.74, 148.23, 138.48, 132.84, 130.45 ($J_{C\text{-}F}$ = 32.76 Hz), 128.84, 126.72, 126.56 ($J_{C\text{-}F}$ =7.53 Hz), 126.40($J_{C\text{-}F}$ = 7.56 Hz), 124.08($J_{C\text{-}F}$ = 136.71 Hz), 119.77, 108.42, 31.17, 20.39. HRMS-ESI calculated for $C_{16}H_{13}F_3N_3O_2$ $[M+H]^+$ 336.0960, found 336.0947.

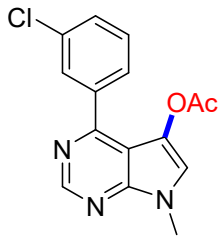
4-(3-cyanophenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2cd)



2cd

Yellow solid (98 mg, 84% yield). Mp:120-122 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.21 (t, J = 1.4 Hz, 1H), 8.17 (dt, J = 7.9, 1.3 Hz, 1H), 7.80 (dt, J = 7.7, 1.4 Hz, 1H), 7.66 (t, J = 7.8 Hz, 1H), 7.42 (s, 1H), 3.93 (s, 3H), 2.14 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 168.17, 155.49, 151.68, 148.21, 138.77, 133.84, 133.34, 133.01, 129.15, 126.55, 120.08, 118.41, 112.32, 108.38, 31.24, 20.63. HRMS-ESI calculated for $C_{16}H_{13}N_4O_2$ $[M+H]^+$ 293.1038, found 293.1036.

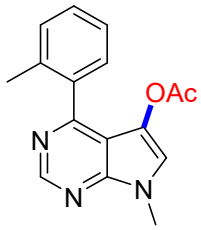
4-(3-chlorophenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2ce)



2ce

White solid (95 mg, 79% yield). Mp: 117-119 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.87 (d, *J* = 1.9 Hz, 1H), 7.80 (dt, *J* = 7.0, 1.7 Hz, 1H), 7.50-7.43 (m, 2H), 7.32 (s, 1H), 3.90 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.49, 156.64, 151.67, 148.26, 139.37, 133.87, 129.71, 129.53, 127.62, 126.66, 119.65, 108.41, 31.11, 20.52 (one sp^2 signal were not observed because of overlapping). HRMS-ESI calculated for $C_{15}H_{13}ClN_3O_2$ $[M+H]^+$ 302.0691, found 302.0689.

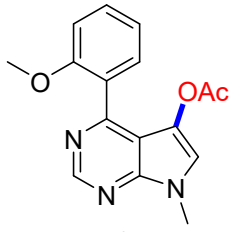
7-methyl-4-(o-tolyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2da)



2da

Yellow viscous oil (90 mg, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.32-7.30 (m, 1H), 7.30-7.28 (m, 3H), 7.14 (s, 1H), 3.91 (s, 3H), 2.24 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.02, 159.31, 151.77, 148.00, 136.82, 136.47, 130.27, 129.36, 128.89, 127.15, 125.26, 119.24, 110.15, 31.03, 19.79, 19.57. HRMS-ESI calculated for $C_{16}H_{16}N_3O_2$ $[M+H]^+$ 282.1242, found 282.1032.

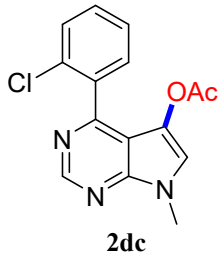
4-(2-methoxyphenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2db)



2db

Yellow viscous oil (97 mg, 82% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.49-7.41 (m, 2H), 7.16 (s, 1H), 7.09 (td, *J* = 7.5, 1.0 Hz, 1H), 7.02 (dd, *J* = 8.2, 1.0 Hz, 1H), 3.89 (s, 3H), 3.76 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.76, 157.14, 156.28, 151.91, 147.61, 130.79, 130.63, 127.35, 127.00, 120.56, 119.13, 110.79, 110.65, 55.60, 31.00, 20.09. HRMS-ESI calculated for $C_{16}H_{16}N_3O_3$ $[M+H]^+$ 298.1191, found 298.1189.

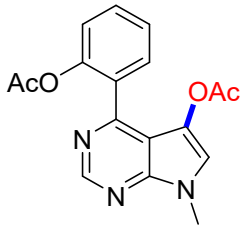
4-(2-chlorophenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2dc)



2dc

Yellow viscous oil (85 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.47 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.37– 7.40 (m, 2H), 7.22 (s, 1H), 3.84 (s, 3H), 1.79 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 168.52, 156.03, 151.79, 147.58, 136.56, 133.08, 130.99, 130.20, 129.43, 126.97, 126.58, 119.56, 110.13, 31.06, 20.06. HRMS-ESI calculated for $C_{15}H_{13}ClN_3O_2$ $[M+H]^+$ 302.0696, found 302.0685.

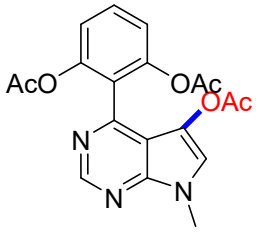
2-(5-acetoxy-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (2dd)



2dd

Yellow viscous oil (114 mg, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.59-7.57 (m, 1H), 7.54-7.49 (m, 1H), 7.39-7.37 (m, 1H), 7.34-7.32 (m, 1H), 7.26 (s, 1H), 3.91 (s, 3H), 1.99 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.77, 168.70, 155.06, 151.70, 148.40, 147.78, 131.17, 130.30, 130.28, 126.84, 125.46, 122.69, 119.58, 109.74, 31.06, 20.75, 20.29. HRMS-ESI calculated for $C_{17}H_{16}N_3O_4$ $[M+H]^+$ 326.1141, found 326.1135.

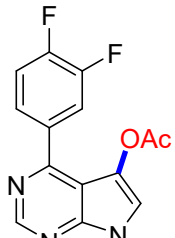
2-(5-acetoxy-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)-1,3-phenylene diacetate (2de)



2de

Yellow oil (123 mg, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.52 (t, J = 8.3 Hz, 1H), 7.30 (s, 1H), 7.27 (d, J = 3.3 Hz, 2H), 3.91 (s, 3H), 1.92 (s, 3H), 1.91 (s, 6H). 13C NMR (126 MHz, CDCl3) δ 168.63, 168.26, 151.70, 151.07, 149.15, 147.35, 129.79, 126.70, 123.63, 119.92, 119.69, 110.56, 31.08, 20.67, 20.23. HRMS-ESI calculated for $C_{19}H_{18}N_3O_6$ $[M+H]^+$ 384.1190, found 384.1189.

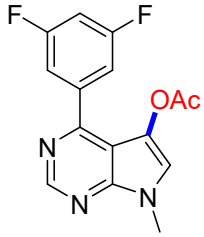
4-(3,4-difluorophenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2e)



2e

Yellow solid (97 mg, 80% yield). Mp:145-148 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.80-7.76 (m, 1H), 7.72-7.65 (m, 1H), 7.35 (s, 1H), 7.33-7.29 (m, 1H), 3.92 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.41, 155.86, 151.78 ($J_{C\text{-}F}$ = 146.16 Hz), 151.67, 149.79 ($J_{C\text{-}F}$ = 180.18 Hz) , 148.35, 134.69, 126.59, 125.98($J_{C\text{-}F}$ = 6.3Hz), 119.78, 118.84 ($J_{C\text{-}F}$ = 18.90 Hz), 117.10 ($J_{C\text{-}F}$ = 8.82 Hz), 108.28, 31.18, 20.60; HRMS-ESI calculated for $C_{15}H_{12}F_2N_3O_2$ $[M+H]^+$ 304.0897, found 304.0889.

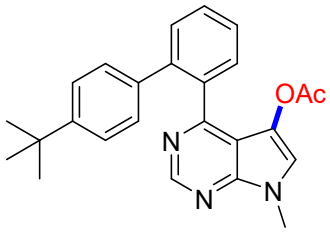
4-(3,5-difluorophenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2f)



2f

Yellow solid (91 mg, 75% yield). Mp:146-148 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.52-7.44 (m, 2H), 7.36 (s, 1H), 7.01-6.93 (m, 1H), 3.93 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.49, 162.73($J_{C\text{-}F}$ = 236.88 Hz) , 155.57, 151.66, 148.47, 140.88, 126.51, 120.09, 112.63 ($J_{C\text{-}F}$=26.8 Hz), 108.37, 105.01($J_{C\text{-}F}$ = 25.2 Hz), 31.22, 20.47. HRMS-ESI calculated for $C_{15}H_{12}F_2N_3O_2$ $[M+H]^+$ 304.0897, found 304.0893.

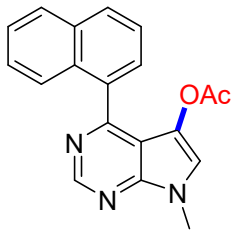
4-(4'-(tert-butyl)-[1,1'-biphenyl]-2-yl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2g)



2g

White amorphous solid (140 mg, 88% yield). Mp: 133-136 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.54-7.50 (m, 2H), 7.49-7.43 (m, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 6.6 Hz, 2H), 7.03 (s, 1H), 3.83 (s, 3H), 1.81 (s, 3H), 1.23 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.89, 159.59, 151.55, 149.40, 147.65, 141.30, 137.37, 135.96, 130.21, 130.17, 129.09, 128.77, 126.97, 126.44, 124.73, 118.91, 110.42, 34.32, 31.22, 30.90, 19.99. HRMS-ESI calculated for $C_{25}H_{25}N_3O_2$ $[M+H]^+$ 400.2020, found 400.2022.

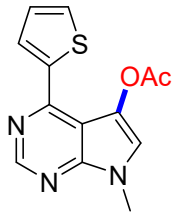
7-methyl-4-(naphthalen-1-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2h)



2h

Yellow viscous solid (109 mg, 86% yield). Mp: 148-150 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.07 (s, 1H), 7.98 (d, *J* = 7.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.64-7.59 (m, 2H), 7.54-7.49 (m, 1H), 7.44-7.42 (m, 1H), 7.21 (s, 1H), 3.93 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.41, 157.97, 151.92, 147.76, 134.99, 133.40, 131.30, 129.48, 128.06, 127.81, 126.91, 126.52, 126.02, 125.60, 124.92, 119.48, 110.70, 31.04, 19.52. HRMS-ESI calculated for $C_{19}H_{16}N_3O_2$ $[M+H]^+$ 318.1242, found 318.1241.

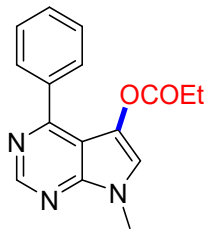
7-methyl-4-(thiophen-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2i)



2i

Yellow soild (85 mg, 78% yield). Mp: 144-146 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (s, 1H), 8.02 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.55 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.34 (s, 1H), 7.17 (dd, *J* = 5.0, 3.8 Hz, 1H), 3.83 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.27, 151.25, 148.34, 135.82, 130.13, 129.85, 129.17, 127.79, 126.72, 119.99, 119.45, 31.15, 21.05. HRMS-ESI calculated for $C_{13}H_{12}N_3O_2S$ $[M+H]^+$ 274.0645, found 274.0645.

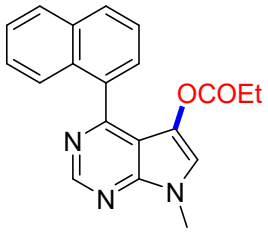
7-methyl-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl propionate (2j)



2j

White solid (68mg, 60% yield). Mp: 93-96 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.82 (dd, *J* = 6.3, 3.0 Hz, 2H), 7.47 (dd, *J* = 4.7, 1.9 Hz, 3H), 7.24 (s, 1H), 3.86 (s, 3H), 2.30 (q, *J* = 7.5 Hz, 2H), 0.99 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.07, 158.36, 151.58, 148.14, 137.66, 129.54, 129.35, 127.97, 126.88, 119.20, 108.59, 30.97, 27.14, 8.51. HRMS-ESI calculated for $C_{16}H_{16}N_3O_2$ $[M+H]^+$ 282.1237, found 282.1238.

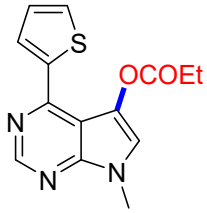
7-methyl-4-(naphthalen-1-yl)-7H-pyrrolo[2,3-d]pyrimidin-5-yl propionate (2k)



2k

White amorphous solid (80 mg, 60% yield). Mp: 130-133 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.06 (s, 1H), 7.95 (dd, *J* = 26.7, 7.9 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.64-7.56 (m, 2H), 7.55-7.47 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.24 (s, 1H), 3.94 (s, 3H), 1.60 (q, *J* = 7.5 Hz, 2H), 0.62 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.86, 158.01, 151.95, 147.75, 135.23, 133.43, 131.33, 129.43, 128.07, 127.75, 127.06, 126.50, 126.00, 125.63, 124.96, 119.41, 110.86, 31.11, 26.42, 8.13. HRMS-ESI calculated for $C_{20}H_{18}N_3O_2$ $[M+H]^+$ 332.1394, found 332.1398.

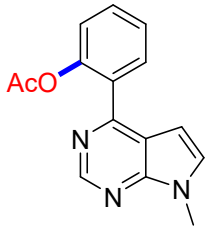
7-methyl-4-(thiophen-2-yl)-7H-pyrrolo[2,3-d]pyrimidin-5-yl propionate (2l)



2l

White solid (69 mg, 60% yield). Mp: 139-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.03 (dt, *J* = 3.0, 1.0 Hz, 1H), 7.73 (dt, *J* = 5.0, 1.0 Hz, 1H), 7.43-7.41 (m, 1H), 7.31 (s, 1H), 3.89 (s, 3H), 2.52 (q, *J* = 7.5 Hz, 2H), 1.16 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.10, 153.17, 151.59, 148.33, 139.68, 128.57, 127.75, 126.92, 125.36, 119.28, 108.03, 31.08, 27.53, 8.77. HRMS-ESI calculated for $C_{14}H_{14}N_3O_2S$ $[M+H]^+$ 288.0801, found 288.0802.

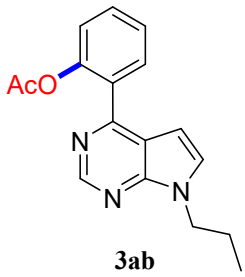
2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3aa)



3aa

Yellow oil (95 mg, 89% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.79-7.78 (m, 1H), 7.63-7.53 (m, 1H), 7.42 (t, *J* = 1.2 Hz, 1H), 7.28 (t, *J* = 4.9 Hz, 1H), 7.22 (d, *J* = 3.6 Hz, 1H), 6.57 (d, *J* = 3.6 Hz, 1H), 3.93 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.30, 155.67, 151.50, 151.26, 148.38, 131.24, 130.54, 129.89, 126.15, 123.45, 117.16, 100.26, 31.22, 20.94 (one sp^2 signal were not observed because of overlapping). HRMS-ESI calculated for $C_{15}H_{14}N_3O_2$ $[M+H]^+$ 268.1086, found 268.1085.

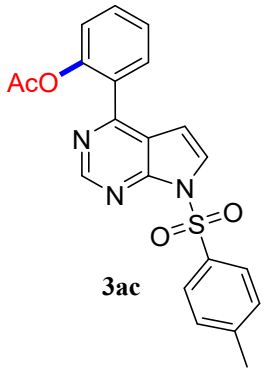
2-(7-propyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3ab)



3ab

Yellow oil (98 mg, 83% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.27 (t, *J* = 8.7 Hz, 1H), 7.24 (d, *J* = 3.5 Hz, 1H), 6.55 (d, *J* = 3.5 Hz, 1H), 4.28-4.24 (m, 2H), 2.05 (s, 3H), 1.92 (h, *J* = 7.3 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.31, 155.54, 151.17, 151.06, 148.35, 131.23, 130.86, 130.49, 128.99, 126.14, 123.44, 117.17, 100.10, 46.32, 23.55, 20.92, 11.30. HRMS-ESI calculated for $C_{17}H_{18}N_3O_2$ $[M+H]^+$ 296.1394, found 296.1393.

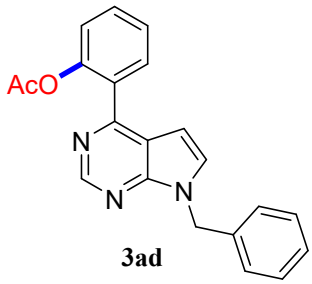
2-(7-tosyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3ac)



3ac

Yellow oil (142 mg, 87% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 4.0 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 2.3 Hz, 1H), 6.59 (d, *J* = 4.0 Hz, 1H), 2.33 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.09, 156.92, 153.01, 151.59, 148.23, 146.04, 134.74, 131.22, 131.12, 129.96, 129.75, 128.39, 126.78, 126.35, 123.62, 119.13, 104.42, 21.73, 20.86. HRMS-ESI calculated for $C_{21}H_{18}N_3O_4S$ $[M+H]^+$ 408.1013, found 408.1011.

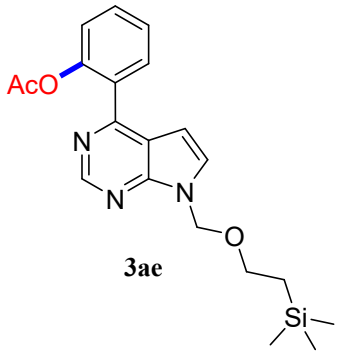
2-(7-benzyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3ad)



3ad

Yellow oil (115 mg, 84% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.81 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.53 (td, *J* = 7.9, 1.6 Hz, 1H), 7.42 (td, *J* = 7.6, 1.0 Hz, 1H), 7.38-7.31 (m, 3H), 7.31-7.28 (m, 1H), 7.28-7.27 (m, 1H), 7.26 (s, 1H), 7.22 (d, *J* = 3.6 Hz, 1H), 6.60 (d, *J* = 3.6 Hz, 1H), 5.51 (s, 2H), 2.08 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 169.36, 155.76, 151.46, 148.37, 136.76, 131.26, 130.77, 130.61, 128.97, 128.92, 128.82, 128.05, 127.66, 126.20, 123.50, 117.10, 100.90, 48.02, 20.96. HRMS-ESI calculated for $C_{21}H_{18}N_3O_2$ $[M+H]^+$ 344.1394, found 344.1397.

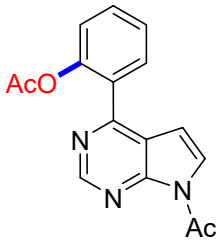
2-(7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3ae)



3ae

Yellow oil (121 mg, 79% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.79 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.54 (td, *J* = 7.8, 1.6 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.39 (d, *J* = 3.7 Hz, 1H), 7.30-7.27 (m, 1H), 6.63 (d, *J* = 3.7 Hz, 1H), 5.70 (s, 2H), 3.61-3.57 (m, 2H), 2.06 (s, 3H), 0.96-0.92 (m, 2H), -0.04 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.21, 155.85, 152.02, 151.60, 148.33, 131.23, 130.69, 130.57, 128.77, 126.20, 123.45, 117.23, 101.65, 72.90, 66.64, 20.90, 17.73, -1.44. HRMS-ESI calculated for $C_{20}H_{26}N_3O_3Si$ $[M+H]^+$ 384.1738, found 384.1744.

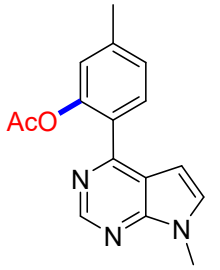
2-(7-acetyl-7H-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3af)



3af

Yellow oil (91 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.03 (d, *J* = 4.1 Hz, 1H), 7.75 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.58 (td, *J* = 7.9, 1.6 Hz, 1H), 7.45 (td, *J* = 7.6, 1.0 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 6.72 (d, *J* = 4.1 Hz, 1H), 3.12 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.15, 168.65, 156.64, 152.58, 152.27, 148.22, 131.17, 131.16, 129.92, 126.41, 125.99, 123.56, 119.94, 105.04, 26.00, 20.95. HRMS-ESI calculated for $C_{16}H_{14}N_3O_3Na$ $[M+H]^+$ 296.1030, found 296.1022.

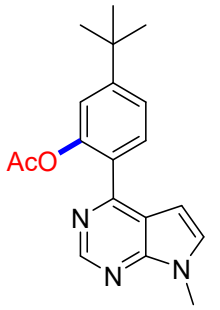
5-methyl-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3ba)



3ba

Yellow oil (99 mg, 88% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.23-7.20 (m, 1H), 7.19 (d, *J* = 3.5 Hz, 1H), 7.08 (s, 1H), 6.56 (d, *J* = 3.6 Hz, 1H), 3.90 (s, 3H), 2.45 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.36, 155.71, 151.41, 151.16, 148.21, 141.13, 130.98, 129.68, 127.88, 126.95, 123.91, 117.02, 100.28, 31.13, 21.26, 20.90. HRMS-ESI calculated for $C_{16}H_{16}N_3O_2$ $[M+H]^+$ 282.1242, found 282.1249.

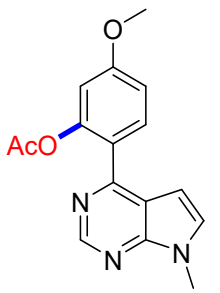
5-(tert-butyl)-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3bb)



3bb

Yellow oil (97 mg, 75% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.43 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.25 (d, *J* = 1.9 Hz, 1H), 7.20 (d, *J* = 3.6 Hz, 1H), 6.60 (dd, *J* = 3.5, 0.7 Hz, 1H), 3.91 (d, *J* = 0.9 Hz, 3H), 2.07 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.31, 155.78, 154.46, 151.45, 151.18, 148.16, 130.77, 129.63, 128.81, 127.84, 123.23, 120.39, 116.90, 100.36, 34.90, 31.14, 20.96. HRMS-ESI calculated for $C_{19}H_{22}N_3O_2$ $[M+H]^+$ 324.1707, found 324.1712.

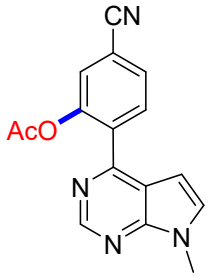
5-methoxy-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3bc)



3bc

Yellow oil (107 mg, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.20 (d, *J* = 3.5 Hz, 1H), 6.97-6.95 (m, 1H), 6.81 (d, *J* = 2.5 Hz, 1H), 6.59 (d, *J* = 3.5 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.43, 155.62, 151.23, 149.55, 132.11, 130.89, 129.58, 128.83, 123.34, 116.88, 112.17, 109.08, 100.38, 55.64, 29.71, 20.98. HRMS-ESI calculated for $C_{16}H_{16}N_3O_3$ $[M+H]^+$ 298.1191, found 298.1188.

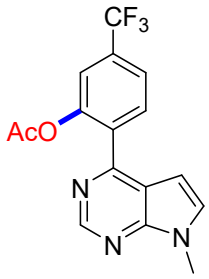
5-cyano-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3bd)



3bd

Yellow oil (79 mg, 68% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.71 (dd, J = 8.0, 1.5 Hz, 1H), 7.60 (d, J = 1.5 Hz, 1H), 7.31-7.26 (m, 1H), 6.52 (d, J = 3.6 Hz, 1H), 3.95 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.63, 153.46, 151.62, 151.23, 148.53, 135.66, 132.22, 130.83, 129.71, 127.41, 117.62, 117.04, 114.05, 99.71, 31.35, 20.80. HRMS-ESI calculated for $C_{16}H_{13}N_4O_2$ $[M+H]^+$ 293.1033, found 293.1042.

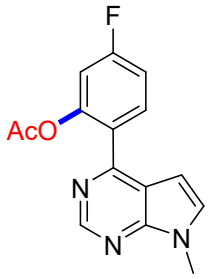
2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)-5-(trifluoromethyl)phenyl acetate (3be)



3be

Yellow oil (88 mg, 66% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.67 (dd, J = 8.1 Hz, 1H), 7.56 (s, 1H), 7.26 (d, J = 3.6 Hz, 1H), 6.54 (d, J = 3.6 Hz, 1H), 3.94 (s, 3H), 2.08 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 168.75, 154.12, 151.61, 151.26, 148.51, 134.41, 132.55 ($J_{C\text{-}F}$ = 34.0 Hz), 131.89, 130.48, 124.48, 122.92 ($J_{C\text{-}F}$ = 3.8 Hz), 120.93 ($J_{C\text{-}F}$ = 3.8 Hz), 117.10, 99.86, 31.26, 20.78. HRMS-ESI calculated for $C_{16}H_{13}F_3N_3O_2$ $[M+H]^+$ 336.0960, found 336.0966.

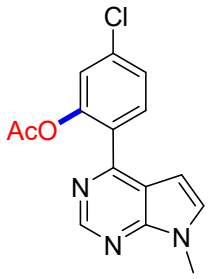
5-fluoro-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3bf)



3bf

Yellow oil (89 mg, 78% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.76 (dd, J = 8.6, 6.3 Hz, 1H), 7.21 (d, J = 3.6 Hz, 1H), 7.13-7.09 (m, 1H), 7.03 (dd, J = 9.1, 2.5 Hz, 1H), 6.52 (d, J = 3.5 Hz, 1H), 3.90 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.79, 163.36 ($J_{C\text{-}F}$ = 252 Hz), 154.79, 151.24, 149.38 ($J_{C\text{-}F}$ = 11.34 Hz), 132.42 ($J_{C\text{-}F}$ = 8.8 Hz), 130.04, 127.16, 119.66, 117.06, 113.41 ($J_{C\text{-}F}$ = 21.4 Hz), 111.36 ($J_{C\text{-}F}$ = 25.2 Hz), 100.06, 31.24, 20.85. HRMS-ESI calculated for $C_{15}H_{13}FN_3O_2$ $[M+H]^+$ 286.0992, found 286.0993.

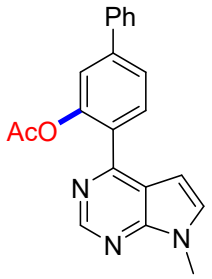
5-chloro-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3bg)



3bg

Yellow oil (81 mg, 67% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.08 (d, J = 2.0 Hz, 1H), 7.78 (dd, J = 8.5 Hz, 1H), 7.41 (d, J = 8.5 Hz, 1H), 7.26 (d, J = 3.6 Hz, 1H), 6.54 (d, J = 3.6 Hz, 1H), 3.93 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.68, 153.97, 151.56, 151.24, 150.84, 131.58, 130.51, 128.65, 128.42, 127.43, 124.18, 117.06, 99.79, 31.24, 20.83. HRMS-ESI calculated for $C_{15}H_{13}ClN_3O_2$ $[M+H]^+$ 302.0691, found 302.0680.

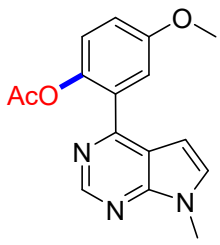
4-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)-[1,1'-biphenyl]-3-yl acetate (3bh)



3bh

Yellow oil (87 mg, 63% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.69-7.65 (m, 3H), 7.52-7.47 (m, 3H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 3.5 Hz, 1H), 6.64 (d, *J* = 3.5 Hz, 1H), 3.94 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.32, 155.39, 151.51, 151.24, 148.75, 143.82, 139.55, 131.65, 129.96, 129.52, 128.93, 128.08, 127.22, 124.78, 122.06, 117.07, 100.32, 31.24, 21.00. HRMS-ESI calculated for $C_{21}H_{18}N_3O_2$ $[M+H]^+$ 344.1394, found 344.1389.

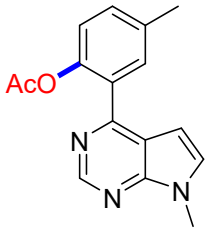
4-methoxy-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3ca)



3ca

Yellow oil (101 mg, 85% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.29 (d, *J* = 3.1 Hz, 1H), 7.21 (d, *J* = 3.6 Hz, 1H), 7.18 (d, *J* = 8.9 Hz, 1H), 7.06-7.03 (m, 1H), 6.58 (d, *J* = 3.5 Hz, 1H), 3.91 (s, 3H), 3.86 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 169.63, 157.31, 155.45, 151.46, 151.21, 141.82, 131.45, 129.92, 124.23, 117.07, 116.16, 115.75, 100.27, 55.76, 31.19, 20.84. ESI calculated for $C_{16}H_{16}N_3O_3$ $[M+H]^+$ 298.1191, found 298.1191.

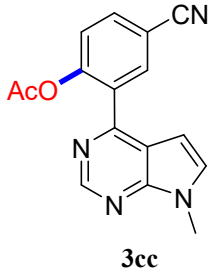
4-methyl-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3cb)



3cb

Yellow oil (96 mg, 85% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.59 (d, *J* = 1.8 Hz, 1H), 7.33 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.22 (d, *J* = 3.5 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 6.57 (d, *J* = 3.5 Hz, 1H), 3.92 (s, 3H), 2.44 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.48, 155.63, 151.37, 151.17, 146.08, 135.93, 131.59, 131.22, 130.29, 129.89, 123.06, 117.13, 100.40, 31.23, 20.94, 20.92. HRMS-ESI calculated for $C_{16}H_{16}N_3O_2$ $[M+H]^+$ 282.1237, found 282.1233.

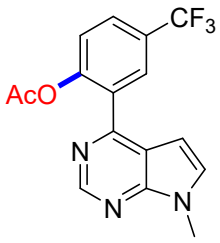
4-cyano-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3cc)



3cc

Yellow oil (76 mg, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.11 (d, *J* = 2.0 Hz, 1H), 7.82 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 3.6 Hz, 1H), 6.53 (d, *J* = 3.5 Hz, 1H), 3.95 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.39, 153.12, 151.67, 151.64, 151.27, 135.38, 134.00, 132.44, 130.77, 124.86, 117.89, 117.00, 110.39, 99.62, 31.32, 20.85. HRMS-ESI calculated for $C_{16}H_{13}N_4O_2$ $[M+H]^+$ 293.1038, found 293.1032.

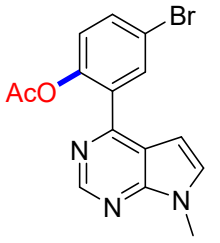
2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)-4-(trifluoromethyl)phenyl acetate (3cd)



3cd

Yellow oil (102 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.09 (d, J = 2.3 Hz, 1H), 7.79 (dd, J = 8.5, 2.3 Hz, 1H), 7.42 (d, J = 8.5 Hz, 1H), 7.27 (d, J = 3.6 Hz, 1H), 6.55 (d, J = 3.5 Hz, 1H), 3.94 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.72, 153.99, 151.59, 151.27, 150.86 ($J_{C\text{-}F}$ = 1.01 Hz), 131.61, 130.51, 128.65 ($J_{C\text{-}F}$ = 8.08 Hz), 128.41, 127.44 ($J_{C\text{-}F}$ = 7.07 Hz), 124.21, 123.71 ($J_{C\text{-}F}$ = 273.71 Hz), 117.06, 99.80, 31.27, 20.87. HRMS-ESI calculated for $C_{16}H_{13}F_3N_3O_2$ $[M+H]^+$ 336.0960, found 336.0956.

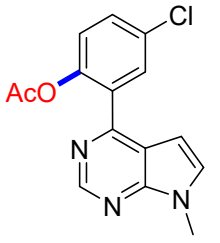
4-bromo-2-(7-methyl-7H-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3ce)



3ce

Yellow oil (116 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.92 (d, J = 2.5 Hz, 1H), 7.64 (dd, J = 8.6, 2.5 Hz, 1H), 7.25 (d, J = 3.6 Hz, 1H), 7.17 (d, J = 8.6 Hz, 1H), 6.56 (d, J = 3.5 Hz, 1H), 3.93 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.93, 153.99, 151.54, 151.22, 147.40, 133.93, 133.36, 132.70, 130.33, 125.18, 119.19, 117.02, 99.97, 31.26, 20.85. HRMS-ESI calculated for $C_{15}H_{13}BrN_3O_2$ $[M+H]^+$ 346.0186, found 346.0179.

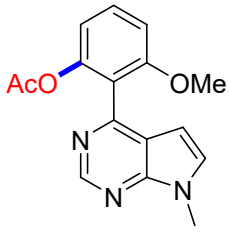
4-chloro-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3cf)



3cf

Yellow oil (99 mg, 82% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.77 (d, J = 2.6 Hz, 1H), 7.48 (dd, J = 8.7, 2.6 Hz, 1H), 7.25 (d, J = 3.6 Hz, 1H), 7.22 (d, J = 8.7 Hz, 1H), 6.57 (d, J = 3.6 Hz, 1H), 3.93 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.04, 154.10, 151.55, 151.22, 146.83, 132.32, 131.57, 131.01, 130.38, 130.32, 124.85, 117.00, 99.96, 31.26, 20.86. HRMS-ESI calculated for $C_{15}H_{13}ClN_3O_2$ $[M+H]^+$ 302.0691, found 302.0677.

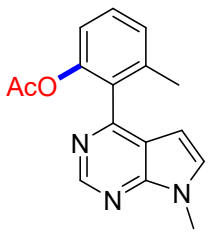
3-methoxy-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3da)



3da

Yellow oil (74 mg, 62% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.45 (t, J = 8.3 Hz, 1H), 7.15 (d, J = 3.5 Hz, 1H), 6.95 (d, J = 8.5 Hz, 1H), 6.88 (dd, J = 8.2, 0.8 Hz, 1H), 6.32 (d, J = 3.5 Hz, 1H), 3.91 (s, 3H), 3.75 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.06, 158.19, 153.35, 151.04, 151.01, 149.41, 130.36, 129.63, 120.23, 118.99, 115.51, 108.87, 100.36, 56.03, 31.11, 20.65. HRMS-ESI calculated for $C_{16}H_{16}N_3O_3$ $[M+H]^+$ 298.1186, found 298.1197.

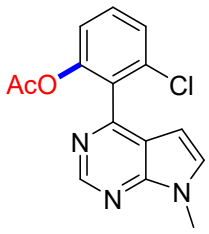
3-methyl-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3db)



3db

Yellow oil (64 mg, 57% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.91 (s, 1H), 7.38 – 7.32 (m, 1H), 7.30 – 7.26 (m, 3H), 7.14 (s, 1H), 3.89 (s, 3H), 2.22 (s, 3H), 1.70 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.94, 159.03, 151.46, 147.94, 136.53, 136.45, 130.27, 129.35, 128.97, 127.18, 125.28, 119.47, 110.13, 31.05, 19.75, 19.55. HRMS-ESI calculated for $C_{16}H_{16}N_3O_2$ $[M+H]^+$ 282.1237, found 282.1243.

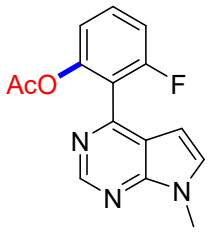
3-chloro-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3dc)



3dc

Yellow oil (52 mg, 43% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.46 (s, 1H), 7.45 (s, 1H), 7.23-7.18 (m, 2H), 6.34 (d, J = 3.6 Hz, 1H), 3.94 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.82, 153.36, 151.20, 151.11, 149.44, 133.95, 130.36, 130.28, 130.21, 127.45, 121.83, 118.36, 99.95, 31.21, 20.56. HRMS-ESI calculated for $C_{15}H_{13}ClN_3O_2$ $[M+H]^+$ 302.0691, found 302.0685.

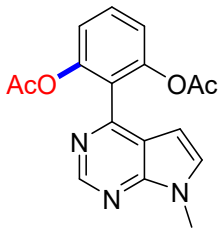
3-fluoro-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3dd)



3dd

Yellow oil (64 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.48 (q, J = 7.9 Hz, 1H), 7.21 (d, J = 3.1 Hz, 1H), 7.15 (t, J = 8.8 Hz, 1H), 7.09 (d, J = 8.2 Hz, 1H), 6.42 (s, 1H), 3.90 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.93, 161.70, 159.20, 150.96, 150.85 ($J_{C\text{-}F}$ = 1.01 Hz), 149.47 ($J_{C\text{-}F}$ = 6.06 Hz), 130.71 ($J_{C\text{-}F}$ = 10.1 Hz), 130.37, 119.64 ($J_{C\text{-}F}$ = 17.17 Hz), 119.27 ($J_{C\text{-}F}$ = 3.03 Hz), 118.70, 113.64 ($J_{C\text{-}F}$ = 22.22 Hz), 100.04 ($J_{C\text{-}F}$ = 4.04 Hz), 31.18, 20.67. HRMS-ESI calculated for $C_{15}H_{13}FN_3O_2$ $[M+H]^+$ 286.0986, found 286.0983.

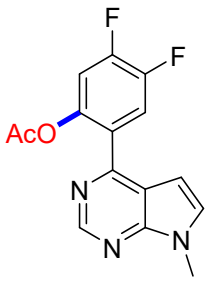
2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)-1,3-phenylene diacetate (3df)



3df

Yellow oil (88 mg, 68% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.51 (t, J = 8.3 Hz, 1H), 7.19 (d, J = 2.9 Hz, 2H), 7.17 (s, 1H), 6.36 (d, J = 3.5 Hz, 1H), 3.90 (s, 3H), 1.90 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.71, 152.01, 151.07, 150.93, 149.15, 130.29, 130.04, 124.21, 120.68, 118.47, 99.93, 31.17, 20.65. HRMS-ESI calculated for $C_{17}H_{16}N_3O_4$ $[M+H]^+$ 326.1135, found 326.1143.

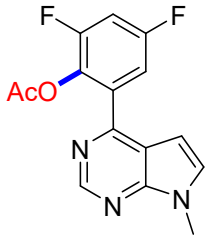
4,5-difluoro-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3e)



3e

Yellow oil (88 mg, 73% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.31 – 7.28 (m, 1H), 7.26 (d, J = 3.6 Hz, 1H), 7.10 – 7.05 (m, 1H), 6.56 (d, J = 3.6 Hz, 1H), 3.93 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.06, 159.72 (J_{C-F} = 248.22 Hz), 155.13(J_{C-F} = 253.26 Hz), 153.16 (J_{C-F} = 3.78 Hz), 151.63, 151.14, 133.85 (J_{C-F} = 8.82 Hz), 132.93 (J_{C-F} = 13.86 Hz), 130.58, 117.05, 112.90 (J_{C-F} = 23.94 Hz), 105.80 (J_{C-F} = 26.46 Hz), 99.79, 31.25, 20.27. HRMS-ESI calculated for $C_{15}H_{12}F_2N_3O_2$ [M+H] $^{+}$304.0897, found 304.0893.

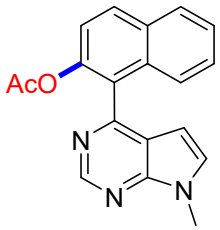
2,4-difluoro-6-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3f)



3f

Yellow oil (85 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.62 (dd, J = 10.5, 8.6 Hz, 1H), 7.25 (t, J = 3.6 Hz, 1H), 7.14 (dd, J = 10.4, 6.9 Hz, 1H), 6.54 (d, J = 3.6 Hz, 1H), 3.92 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.41, 151.62, 151.57, 151.22, 147.99 (J_{C-F} = 54.18 Hz), 130.41, 126.58, 119.95, 119.68 (J_{C-F} = 84.42 Hz), 113.58 (J_{C-F} = 75.60 Hz), 112.47, 109.48, 99.82, 31.13, 20.64. HRMS-ESI calculated for $C_{15}H_{11}F_2N_3O_2$ [M+H] $^{+}$ 304.0897, found 304.0893.

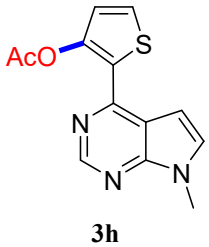
1-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)naphthalen-2-yl acetate (3g)



3g

Yellow oil (94 mg, 74% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.02 (d, J = 8.9 Hz, 1H), 7.93 (d, J = 8.8 Hz, 1H), 7.49 (dd, J = 7.8, 6.3 Hz, 2H), 7.40 (d, J = 8.9 Hz, 2H), 7.17 (d, J = 3.6 Hz, 1H), 6.22 (d, J = 3.6 Hz, 1H), 3.97 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.36, 154.78, 151.37, 151.14, 146.18, 132.16, 131.77, 130.53, 130.13, 128.16, 126.96, 125.85, 125.83, 125.65, 121.80, 119.29, 100.21, 31.23, 20.77. HRMS-ESI calculated for $C_{19}H_{16}N_3O_2$ $[M+H]^{+}$ 318.1237, found 318.1248.

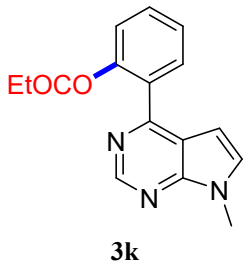
2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)thiophen-3-yl acetate (3h)



3h

Yellow oil (84 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 7.50 (d, J = 5.4 Hz, 1H), 7.23 (d, J = 3.6 Hz, 1H), 7.06 (d, J = 5.4 Hz, 1H), 6.84 (d, J = 3.6 Hz, 1H), 3.90 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.56, 151.84, 151.02, 149.91, 145.79, 129.65, 127.19, 123.73, 120.37, 114.97, 100.61, 31.22, 21.05. HRMS-ESI calculated for $C_{13}H_{12}N_3O_2S$ $[M+H]^{+}$ 274.0645, found 274.0647.

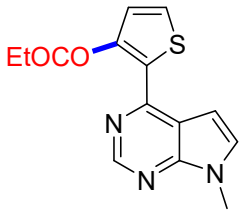
2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl propionate (3k)



3k

Yellow oil (88 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.80-7.66 (m, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.18 (d, *J* = 3.5 Hz, 1H), 6.53 (d, *J* = 3.5 Hz, 1H), 3.88 (s, 3H), 2.33 (q, *J* = 7.6 Hz, 2H), 1.02 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.66, 155.64, 151.35, 151.11, 148.40, 131.14, 130.75, 130.48, 129.97, 126.00, 123.44, 117.16, 100.25, 31.18, 27.53, 8.76. HRMS-ESI calculated for $C_{16}H_{16}N_3O_2$ $[M+H]^+$ 282.1237, found 282.1240.

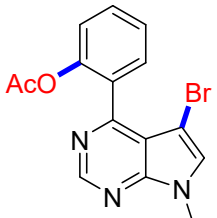
2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)thiophen-3-yl propionate (3l)



3l

Yellow oil (80 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (s, 1H), 7.49 (d, *J* = 5.4 Hz, 1H), 7.21 (d, *J* = 3.6 Hz, 1H), 7.05 (d, *J* = 5.4 Hz, 1H), 6.82 (d, *J* = 3.6 Hz, 1H), 3.88 (s, 3H), 2.60 (q, *J* = 7.5 Hz, 2H), 1.19 (d, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.03, 151.76, 150.87, 149.87, 145.99, 129.70, 127.18, 123.77, 115.00, 100.72, 31.23, 27.64, 8.82. HRMS-ESI calculated for $C_{14}H_{14}N_3O_2S$ $[M+H]^+$ 288.0801, found 282.0798.

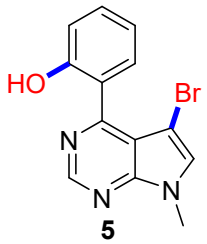
2-(5-bromo-7-methyl-7H-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (4).



4

Colorless liquid (427 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.53 (td, *J* = 7.7, 1.5 Hz, 2H), 7.38 (td, *J* = 7.4, 1.2 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.27 (s, 1H), 3.91 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.84, 156.57, 151.39, 150.59, 148.57, 132.10, 130.52, 129.95, 129.13, 125.26, 122.59, 115.36, 87.80, 31.33, 20.77. HRMS-ESI calculated for $C_{15}H_{12}BrN_3O_2$ $[M+H]^+$ 345.0113, found 346.0186.

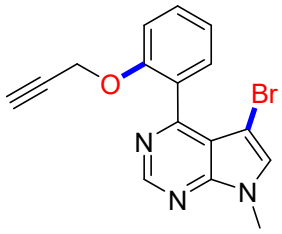
2-(5-bromo-7-methyl-7H-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenol (5).



5

White solid (110 mg, 73% yield). Mp: 122−125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 7.91 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.48 – 7.40 (m, 1H), 7.38 (s, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 7.03 (td, *J* = 7.5, 1.3 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.29, 158.25, 151.47, 149.21, 134.43, 132.48, 131.25, 118.62, 118.44, 117.41, 113.16, 87.67, 31.47. HRMS-ESI calculated for $C_{13}H_{10}BrN_3O$ $[M+H]^+$ 304.0080, found 304.0076.

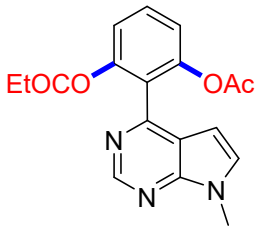
5-bromo-7-methyl-4-(2-(prop-2-yn-1-yloxy)phenyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (6)



6

White solid (70 mg, 78% yield). Mp: 103−105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.51-7.49 (m, 1H), 7.44 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.22 (s, 1H), 7.20-7.13 (m, 2H), 4.65 (d, *J* = 2.4 Hz, 2H), 3.91 (s, 3H), 2.45 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.39, 155.63, 151.76, 150.14, 131.01, 130.59, 129.18, 126.60, 121.26, 116.14, 112.34, 88.55, 78.53, 75.58, 56.33,31.21. HRMS-ESI calculated for $C_{16}H_{13}BrN_3O$ $[M+Na]^+$ 364.0056, found 364.0064.

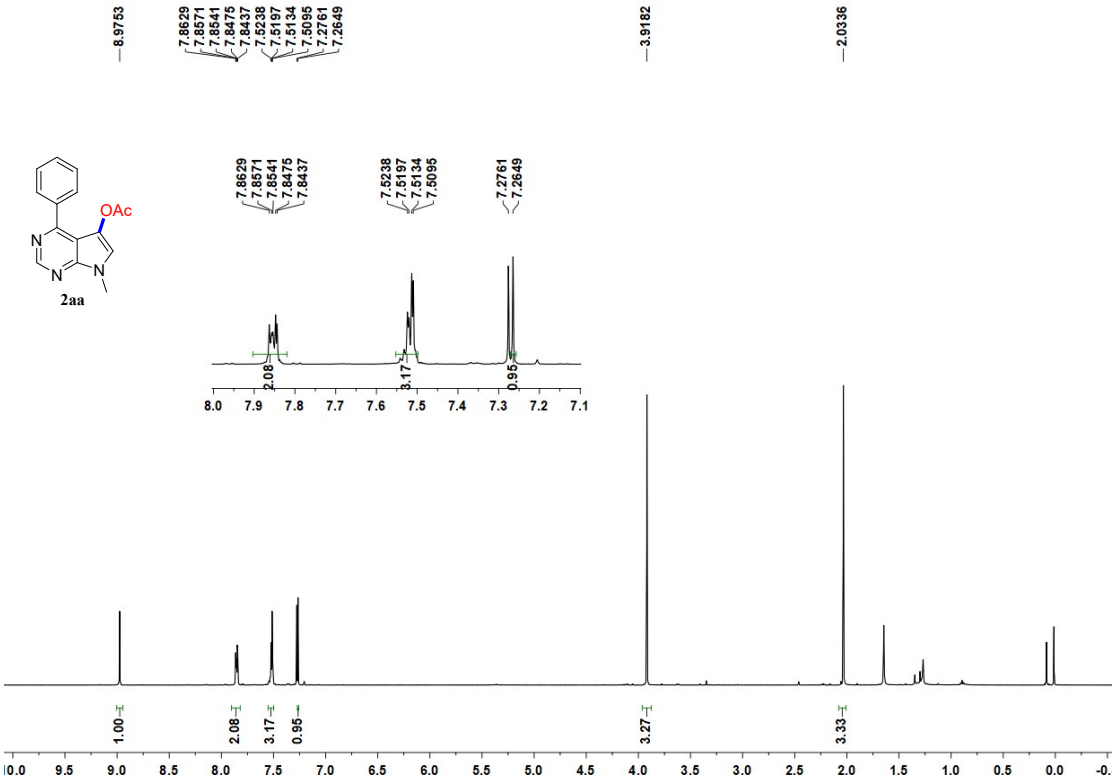
3-acetoxy-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl propionate (9)

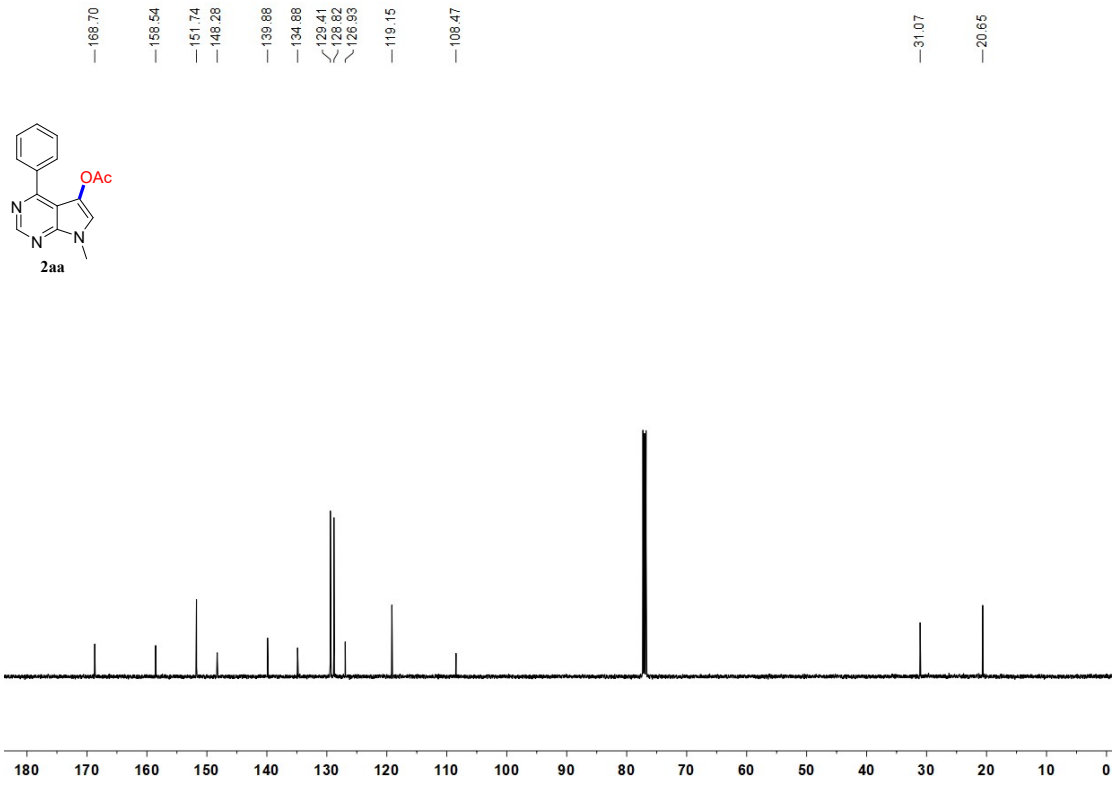


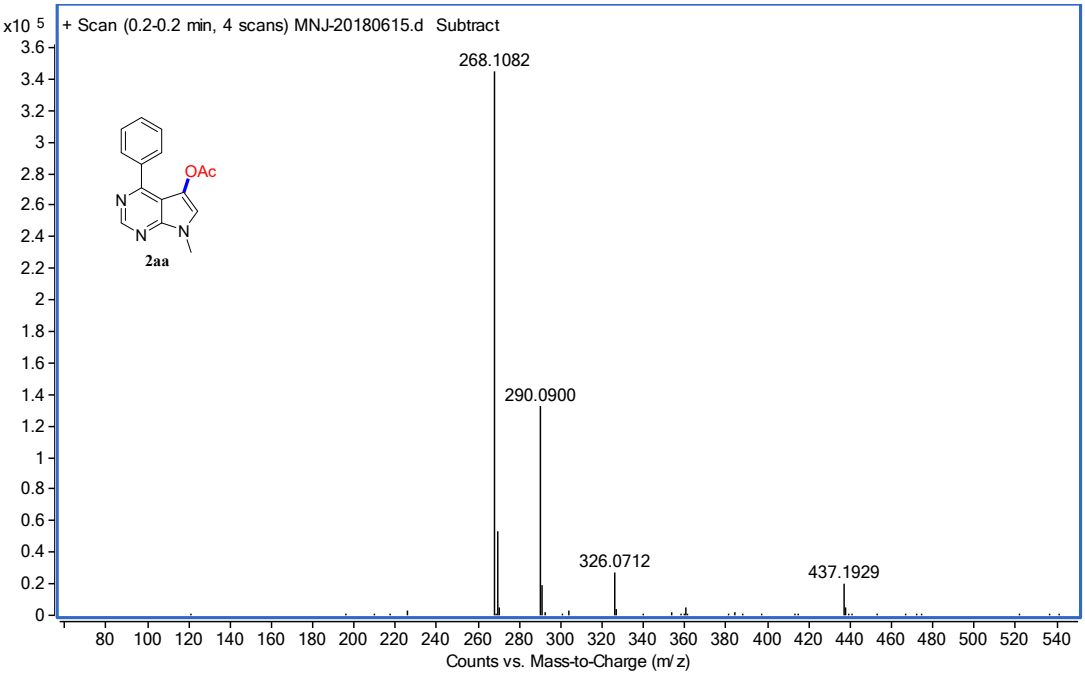
9

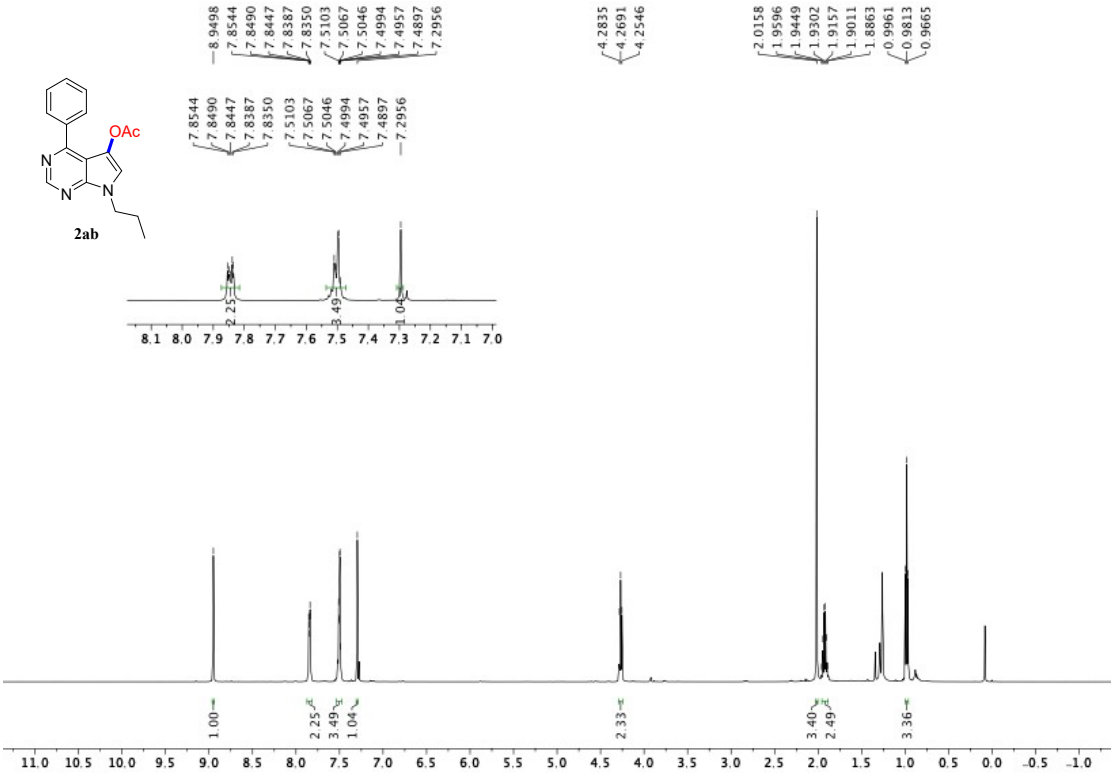
Yellow oil (79 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.50 (t, *J* = 8.2 Hz, 1H), 7.20-7.17 (m, 2H), 7.16-7.12 (m, 1H), 6.34 (d, *J* = 3.6 Hz, 1H), 3.89 (s, 3H), 2.15 (qd, *J* = 7.6, 4.0 Hz, 2H), 1.89 (s, 3H), 0.87 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.20, 168.82, 152.00, 150.97, 150.87, 149.18, 149.10, 130.38, 130.08, 124.16, 120.73, 120.59, 118.51, 99.98, 31.22, 27.39, 20.69, 8.65. HRMS-ESI calculated for $C_{18}H_{18}N_3O_4$ $[M+H]^+$ 340.1292, found 340.1295.

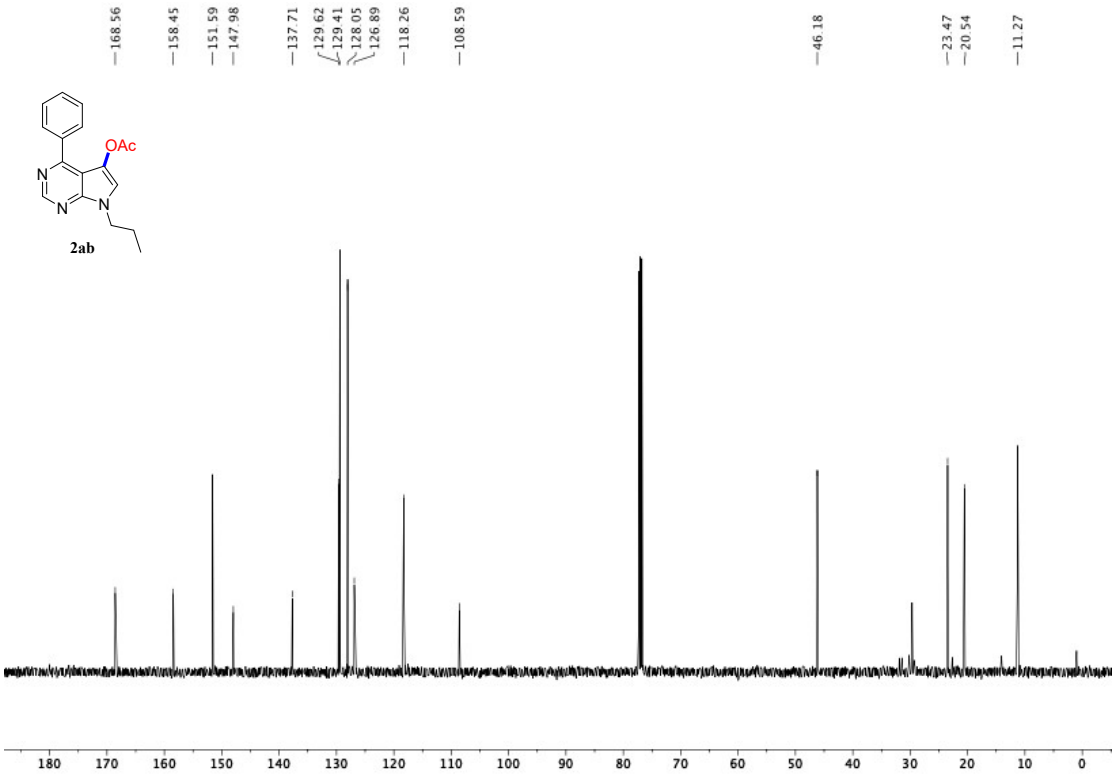
5. NMR Spectra of Compounds

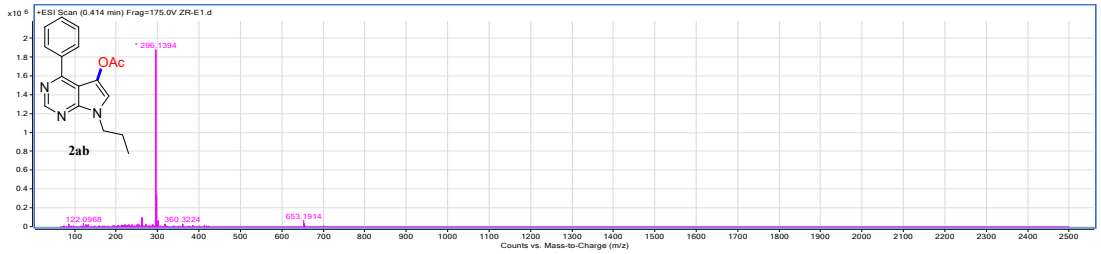


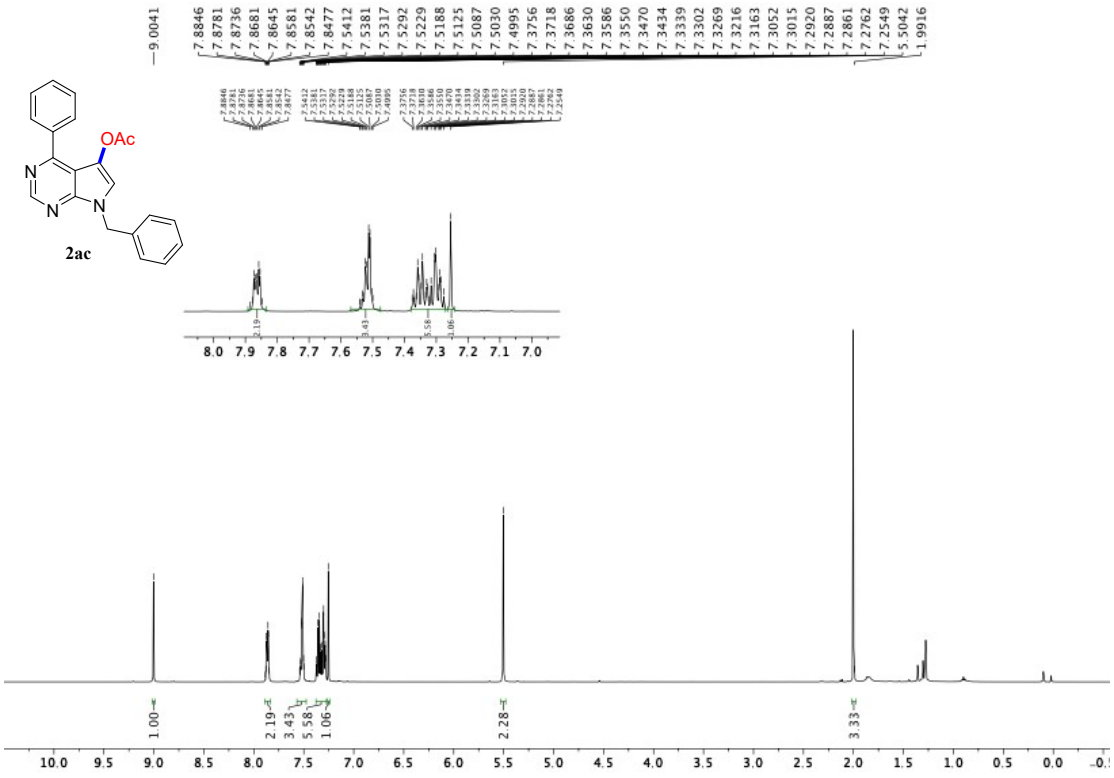


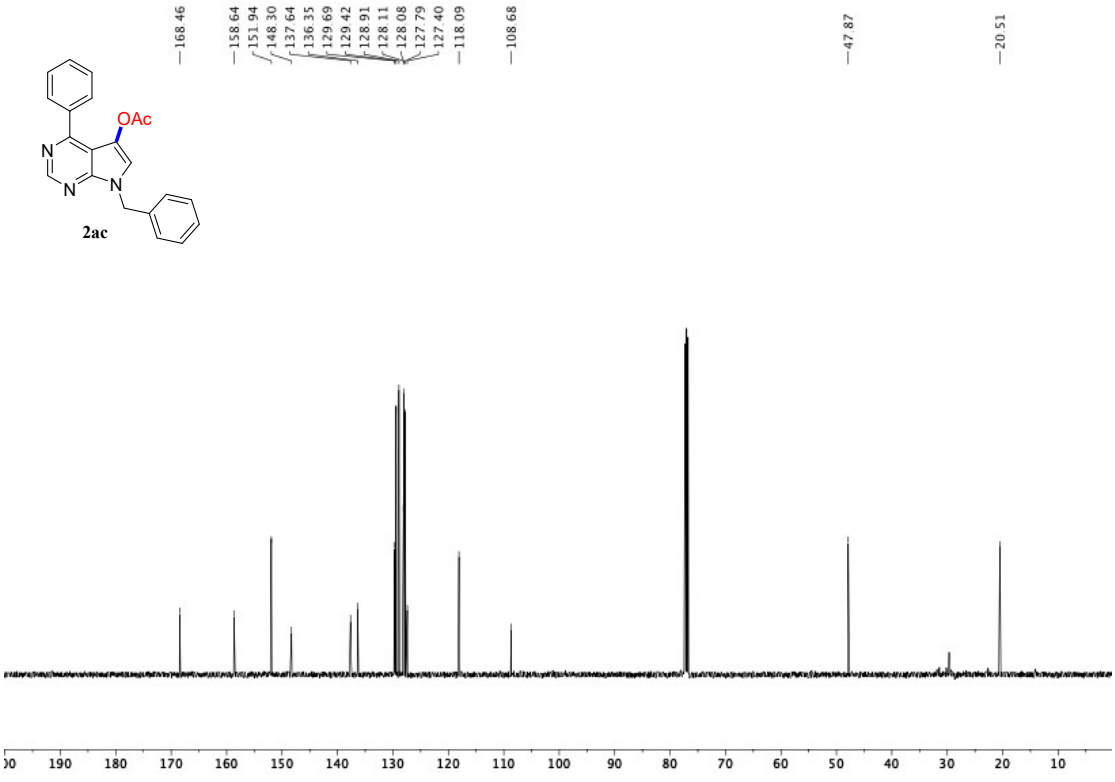

x10 5
+ Scan (0.2-0.2 min, 4 scans) MNJ-20180615.d Subtract
268.1082
290.0900
326.0712
437.1929
OAc
2aa
Counts vs. Mass-to-Charge (m/z)

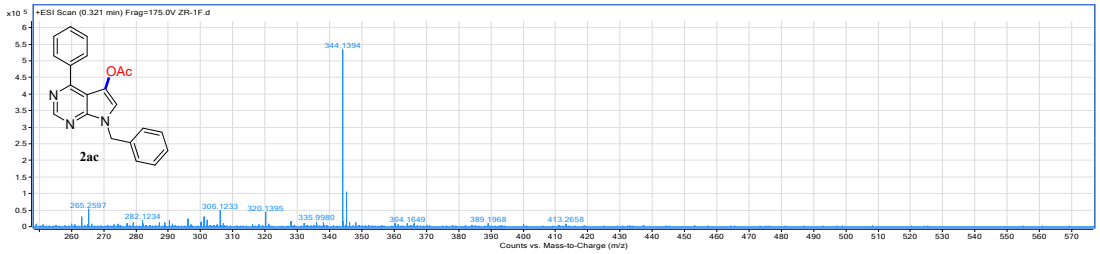

OAc
2ab


168.56
158.45
151.59
147.98
137.71
129.62
129.41
128.05
126.89
118.26
108.59
46.18
23.47
20.54
11.27
OAc
N
N
N
2ab
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


x10 6
+ESI Scan (0.414 min) Frag=175.0V ZR-E1.d
* 296.1394
122.0968
360.3224
653.1914
OAc
N
N
N
2ab
Counts vs. Mass-to-Charge (m/z)


OAc
N
N
N
2ac
9.0041
7.8846
7.8781
7.8736
7.8681
7.8645
7.8581
7.8542
7.8477
7.5412
7.5381
7.5317
7.5292
7.5229
7.5188
7.5125
7.5087
7.5030
7.4995
7.3756
7.3718
7.3686
7.3630
7.3586
7.3550
7.3470
7.3434
7.3339
7.3302
7.3269
7.3216
7.3163
7.3052
7.3015
7.2920
7.2887
7.2861
7.2762
7.2549
5.5042
1.9916
1.00
2.19
3.43
5.58
1.06
2.28
3.33


OAc
N
N
N
2ac
168.46
158.64
151.94
148.30
137.64
136.35
129.69
129.42
128.91
128.11
128.08
127.79
127.40
118.09
108.68
47.87
20.51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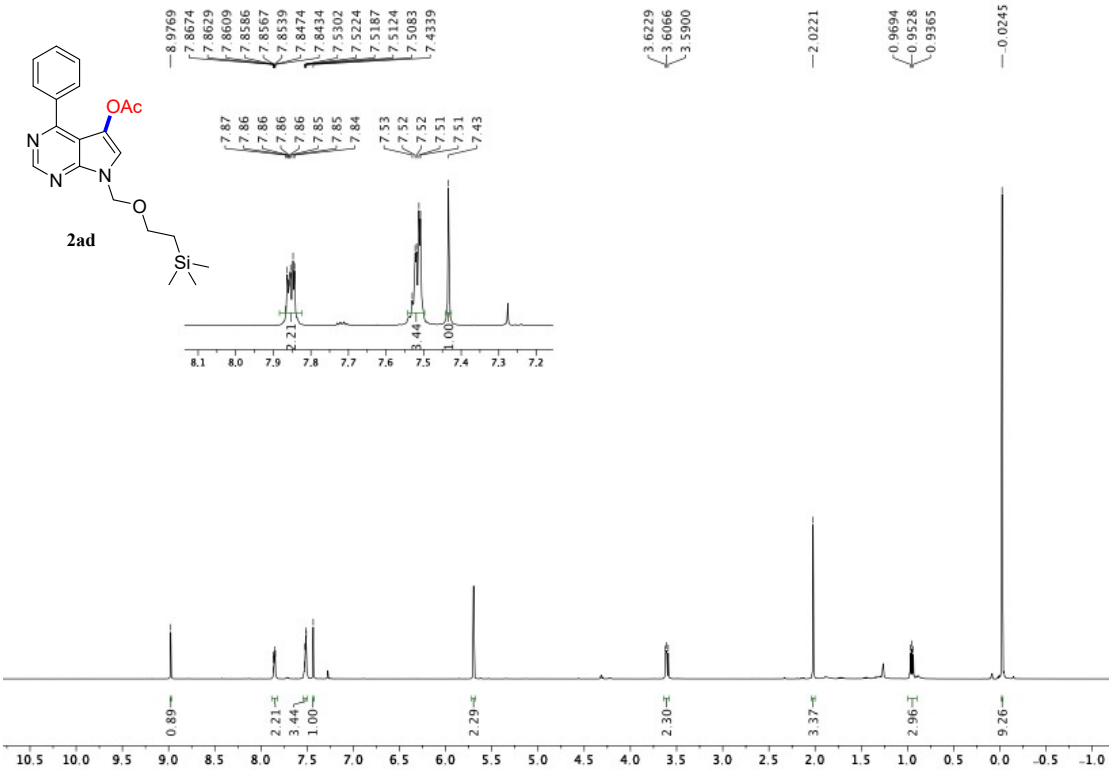
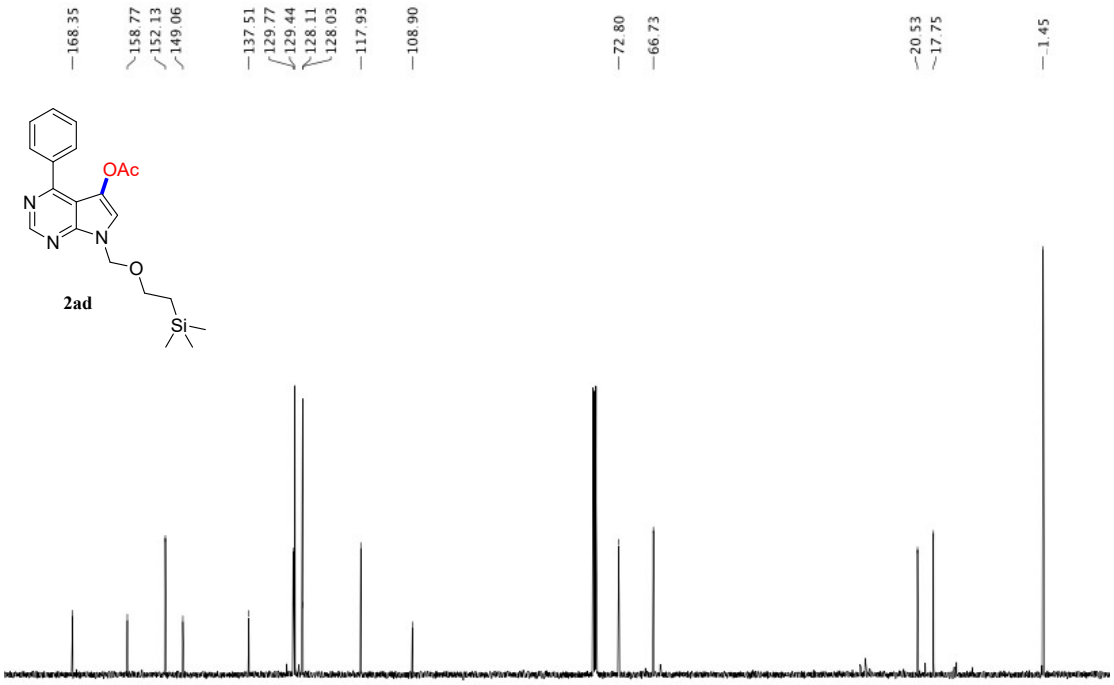
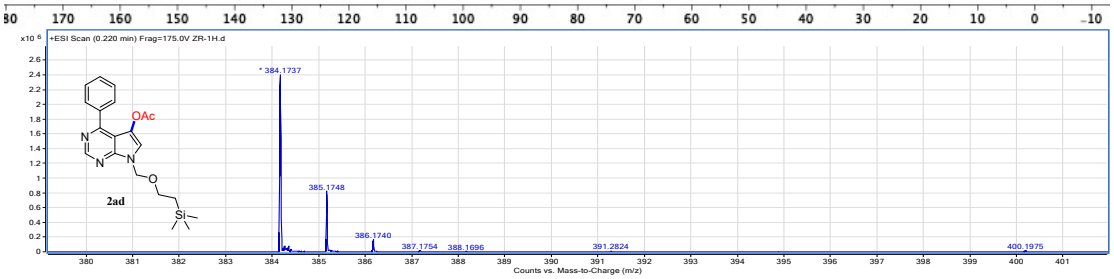
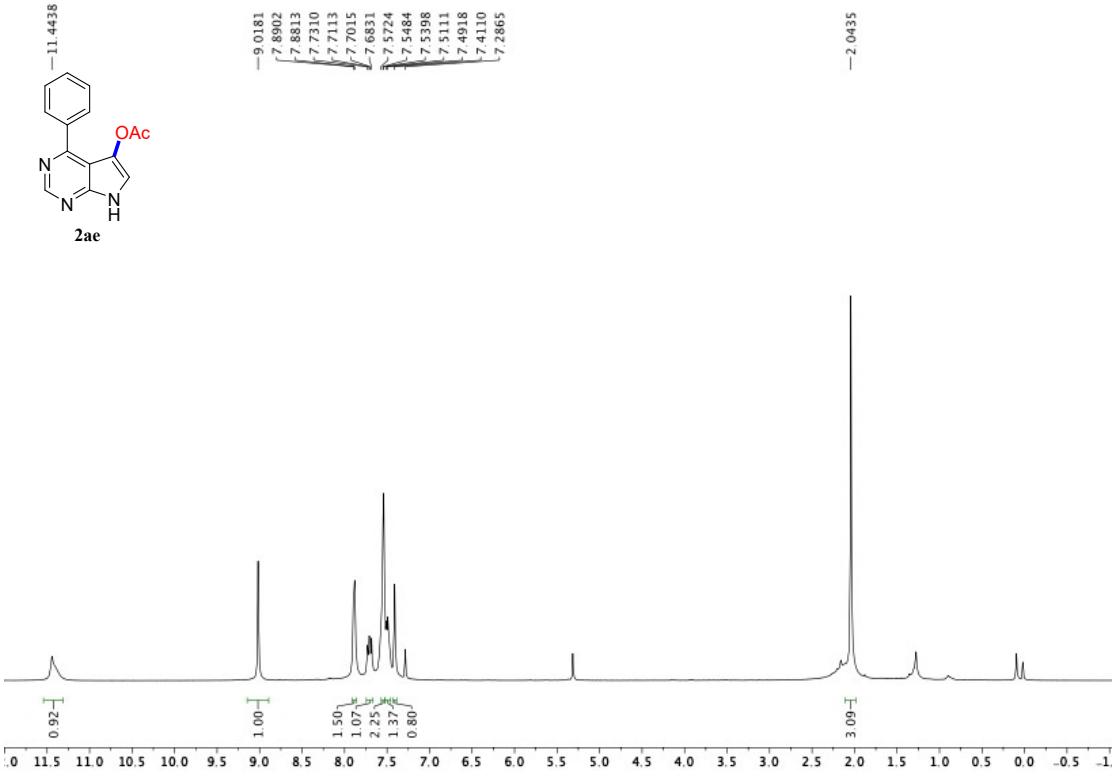
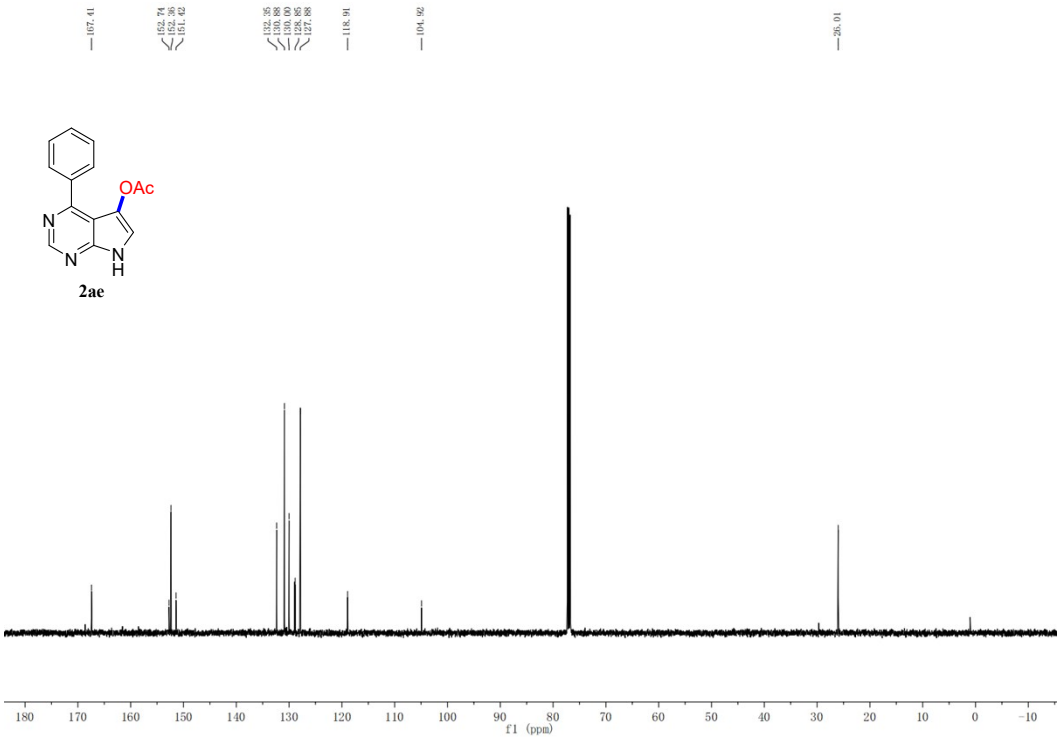
OAc
2ac
344.1394
265.2597
282.1234
306.1233
320.1395
335.9980
364.1649
389.1968
413.2658
Counts vs. Mass-to-Charge (m/z)

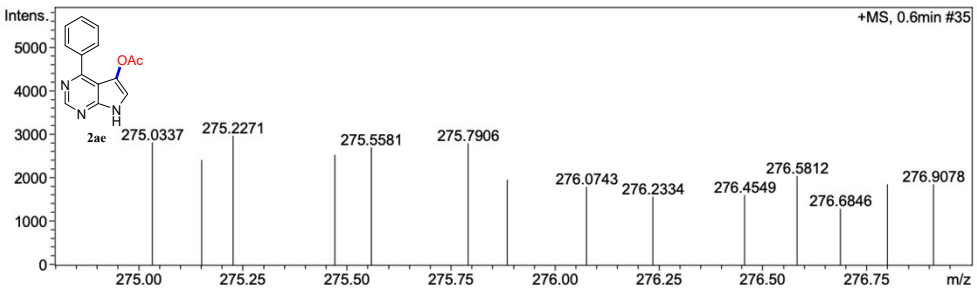

OAc
2ad
Si
8.9769
7.8674
7.8629
7.8609
7.8586
7.8567
7.8539
7.8474
7.8434
7.5302
7.5224
7.5187
7.5124
7.5083
7.4339
3.6229
3.6066
3.5900
2.0221
0.9694
0.9528
0.9365
0.0245
0.89
2.21
3.44
1.00
2.29
2.30
3.37
2.96
9.26

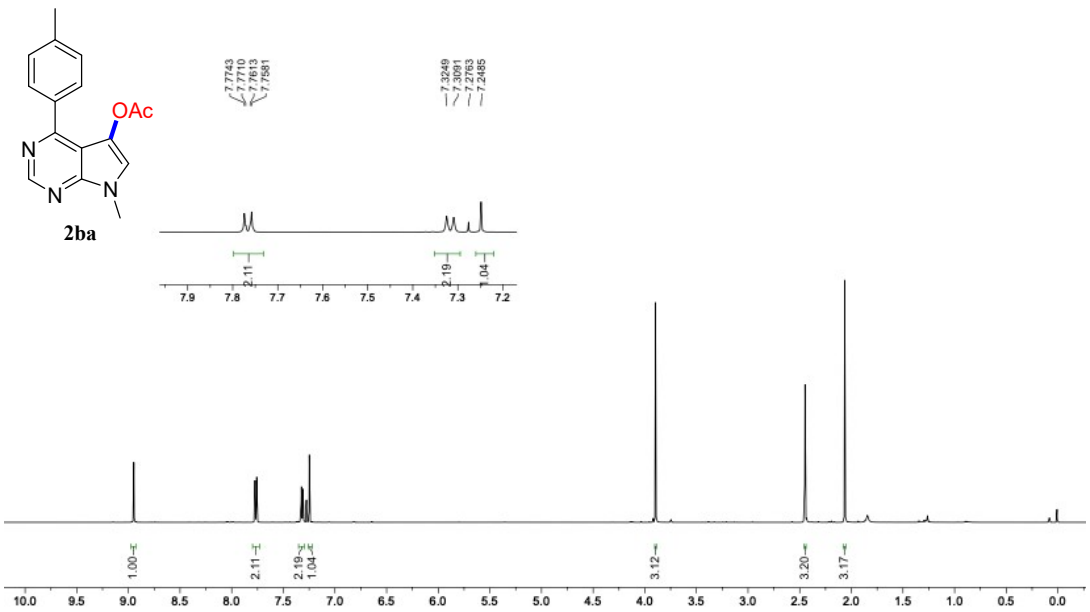

168.35
158.77
152.13
149.06
137.51
129.77
129.44
128.11
128.03
117.93
108.90
72.80
66.73
20.53
17.75
1.45
OAc
N
N
N
O
Si
2ad

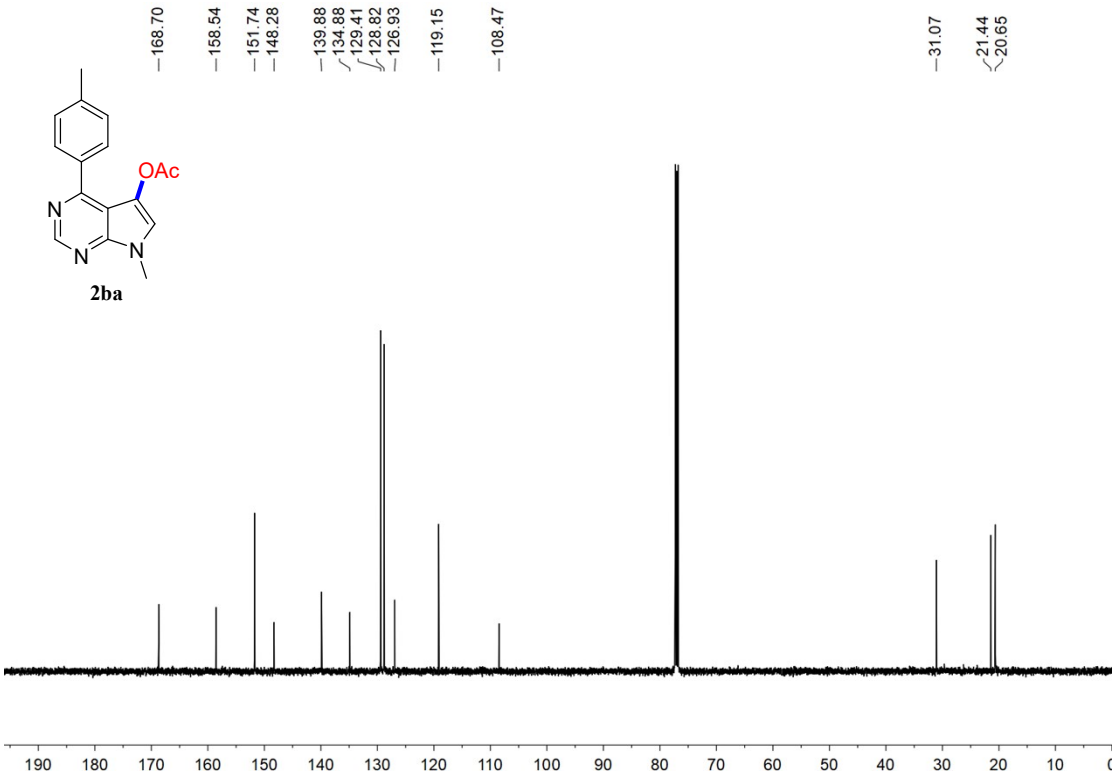

+ESI Scan (0.220 min) Frag=175.0V ZR-1H.d
* 384.1737
385.1748
386.1740
387.1754
388.1696
391.2824
400.1975
OAc
2ad
Counts vs. Mass-to-Charge (m/z)

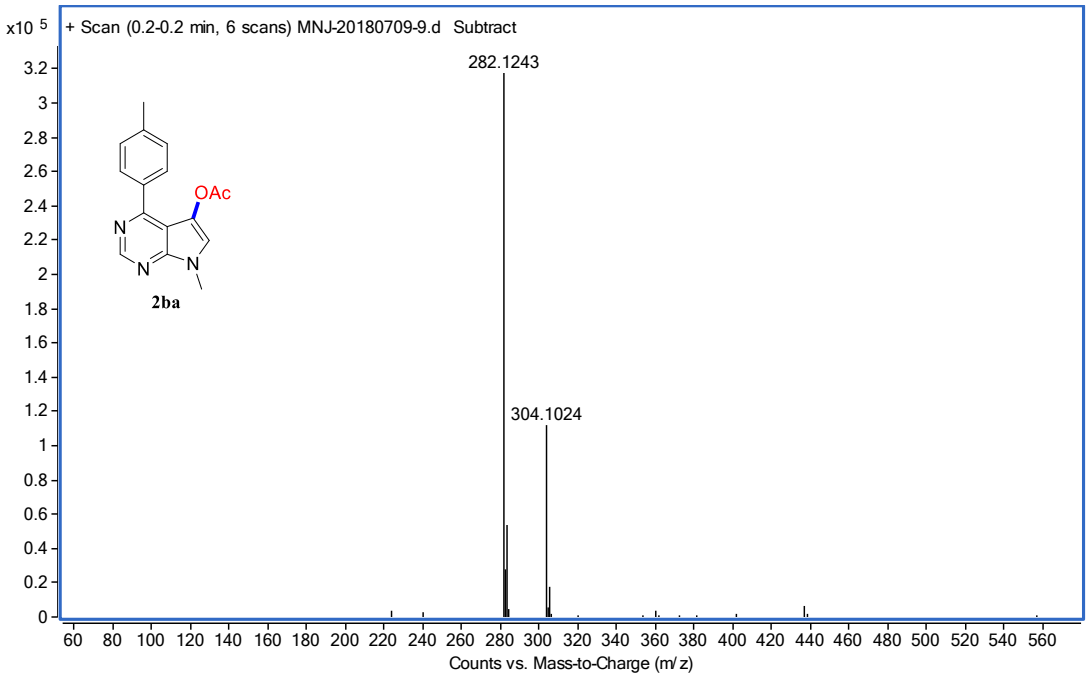

11.4438
9.0181
7.8902
7.8813
7.7310
7.7113
7.7015
7.6831
7.5724
7.5484
7.5398
7.5111
7.4918
7.4110
7.2865
2.0435
OAc
N
N
N
H
2ae
0.92
1.00
1.50
1.07
2.25
1.37
0.80
3.09

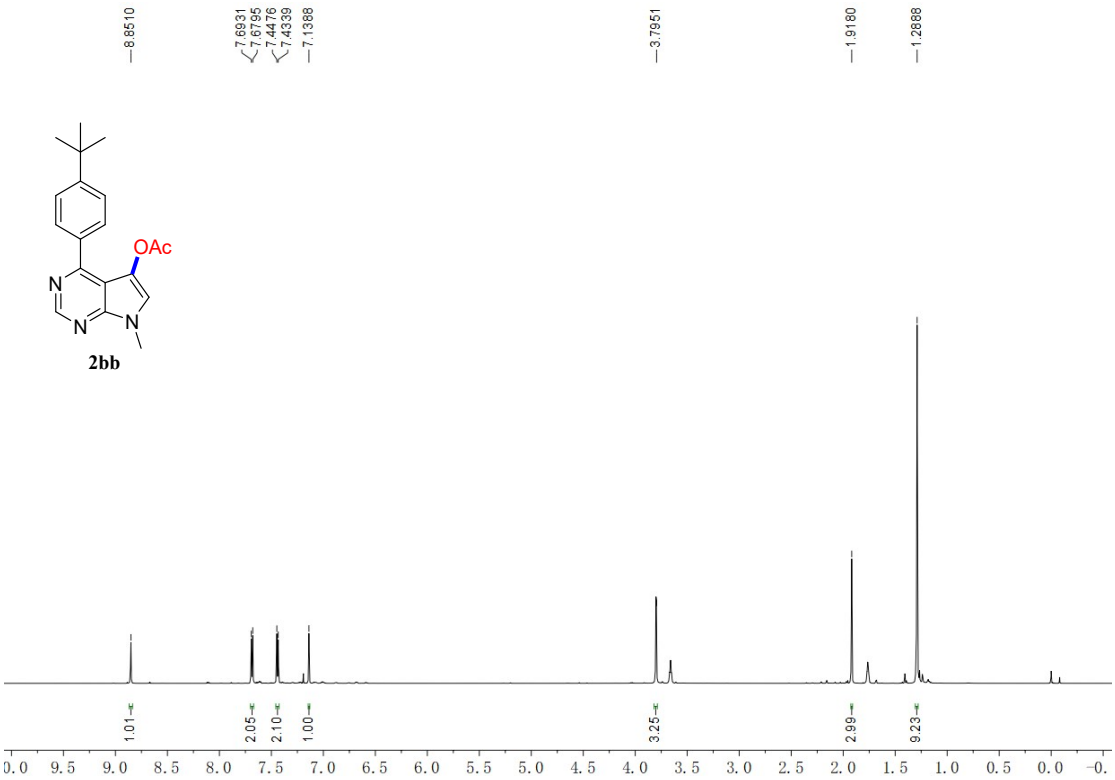

OAc
N
N
N
H
2ae
f1 (ppm)

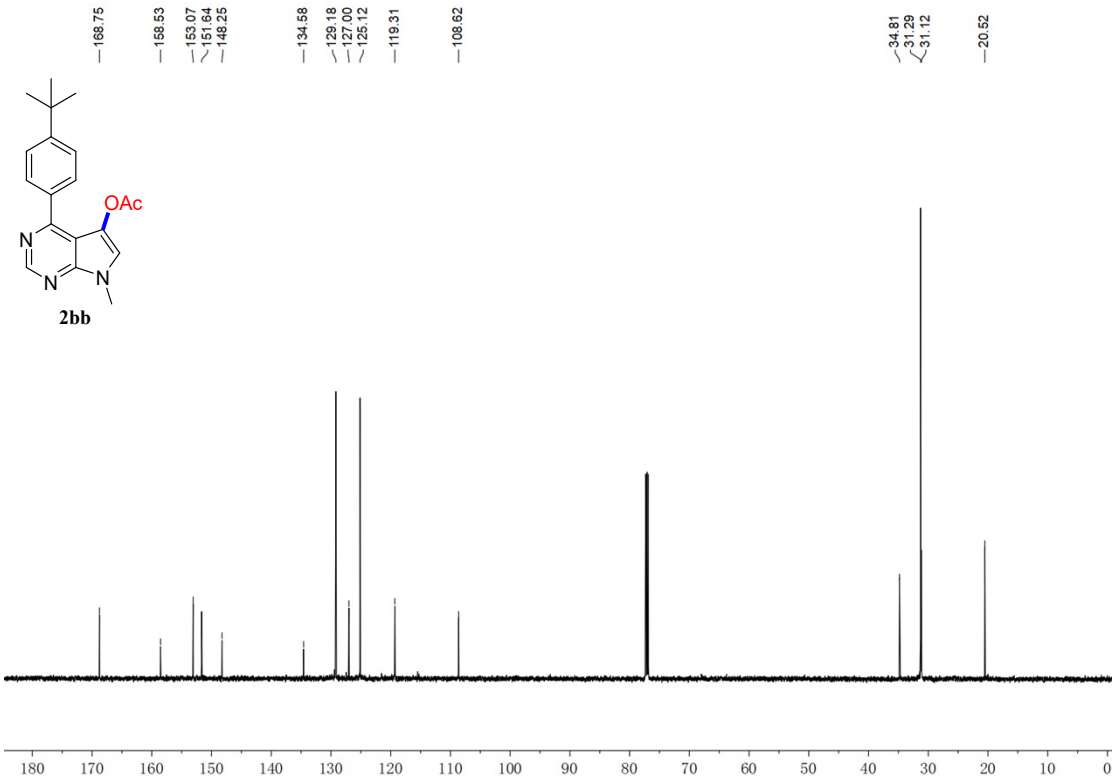

Intens.
+MS, 0.6min #35
OAc
2ae
275.0337
275.2271
275.5581
275.7906
276.0743
276.2334
276.4549
276.5812
276.6846
276.9078
m/z

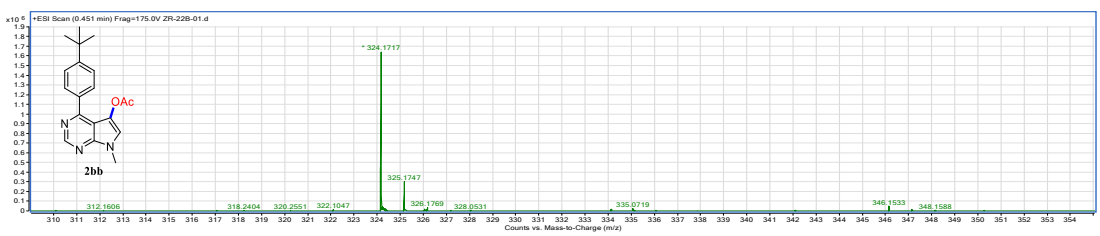

OAc
N
N
N
2ba
f1 (ppm)


168.70
158.54
151.74
148.28
139.88
134.88
129.41
128.82
126.93
119.15
108.47
31.07
21.44
20.65
OAc
N
N
N
2ba
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

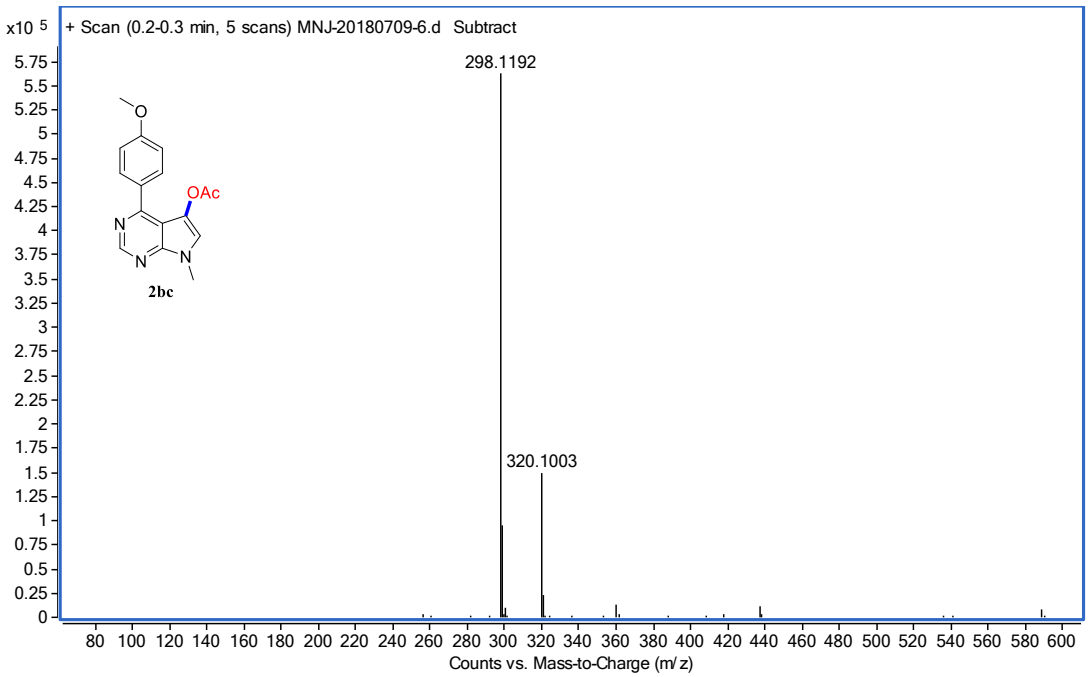

x10 5
+ Scan (0.2-0.2 min, 6 scans) MNJ-20180709-9.d Subtract
282.1243
304.1024
OAc
N
N
N
2ba
3.2 3 2.8 2.6 2.4 2.2 2 1.8 1.6 1.4 1.2 1 0.8 0.6 0.4 0.2 0
60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560
Counts vs. Mass-to-Charge (m/z)

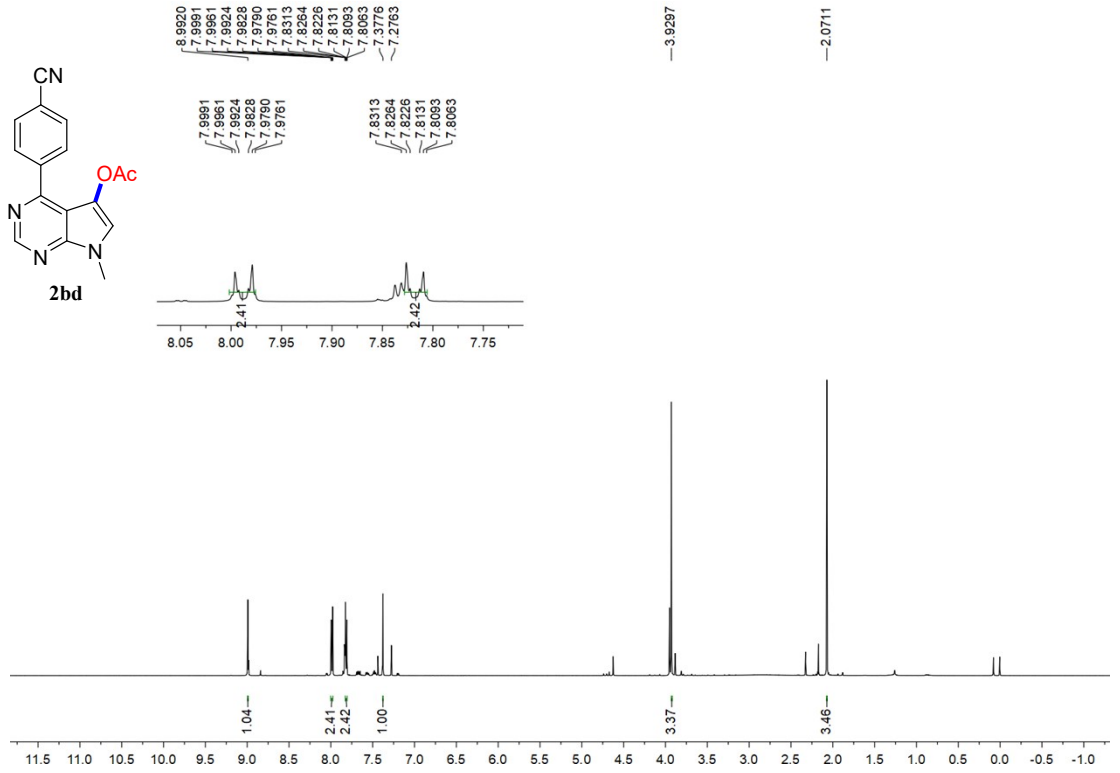

8.8510
7.6931
7.6795
7.4476
7.4339
7.1388
3.7951
1.9180
1.2888
OAc
N
N
N
2bb
1.01
2.05
2.10
1.00
3.25
2.99
9.23


168.75
158.53
153.07
151.64
148.25
134.58
129.18
127.00
125.12
119.31
108.62
34.81
31.29
31.12
20.52
OAc
N
N
N
2bb


+ESI Scan (0.451 min) Frag=175.0V ZR-22B-01.d
OAc
N
N
N
2bb
324.1717
325.1747
326.1769
312.1606
318.2404
320.2551
322.1047
328.0531
335.0719
346.1533
348.1588
Counts vs. Mass-to-Charge (m/z)


8.9272
7.8717
7.8660
7.8618
7.8525
7.8493
7.8426
7.2519
7.0527
7.0470
7.0428
7.0334
7.0292
7.0235
3.8973
2.1020
OAc
N
N
N
O
2bc
1.00
2.19
1.01
2.29
6.31
3.41
168.70
161.12
158.14
151.74
148.29
131.07
130.26
126.96
119.03
113.60
108.24
55.42
31.11
20.75
OAc
N
N
N
O
2bc


x10 5
+ Scan (0.2-0.3 min, 5 scans) MNJ-20180709-6.d Subtract
298.1192
320.1003
OAc
2bc
Counts vs. Mass-to-Charge (m/z)


CN
OAc
2bd
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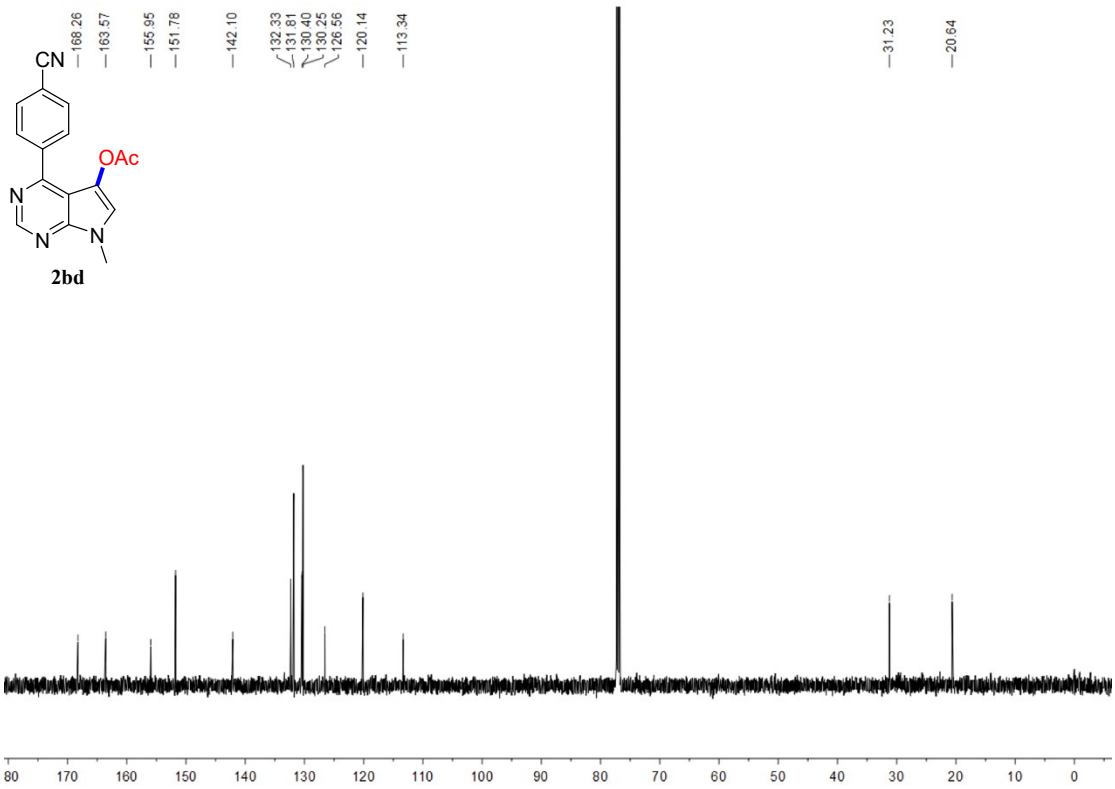
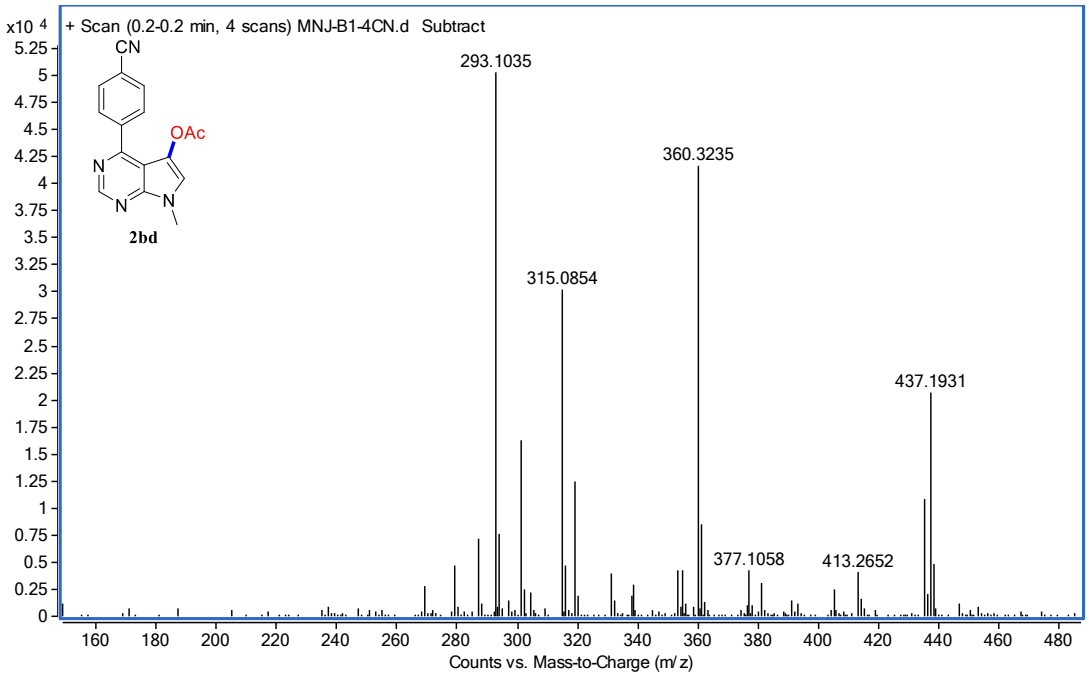
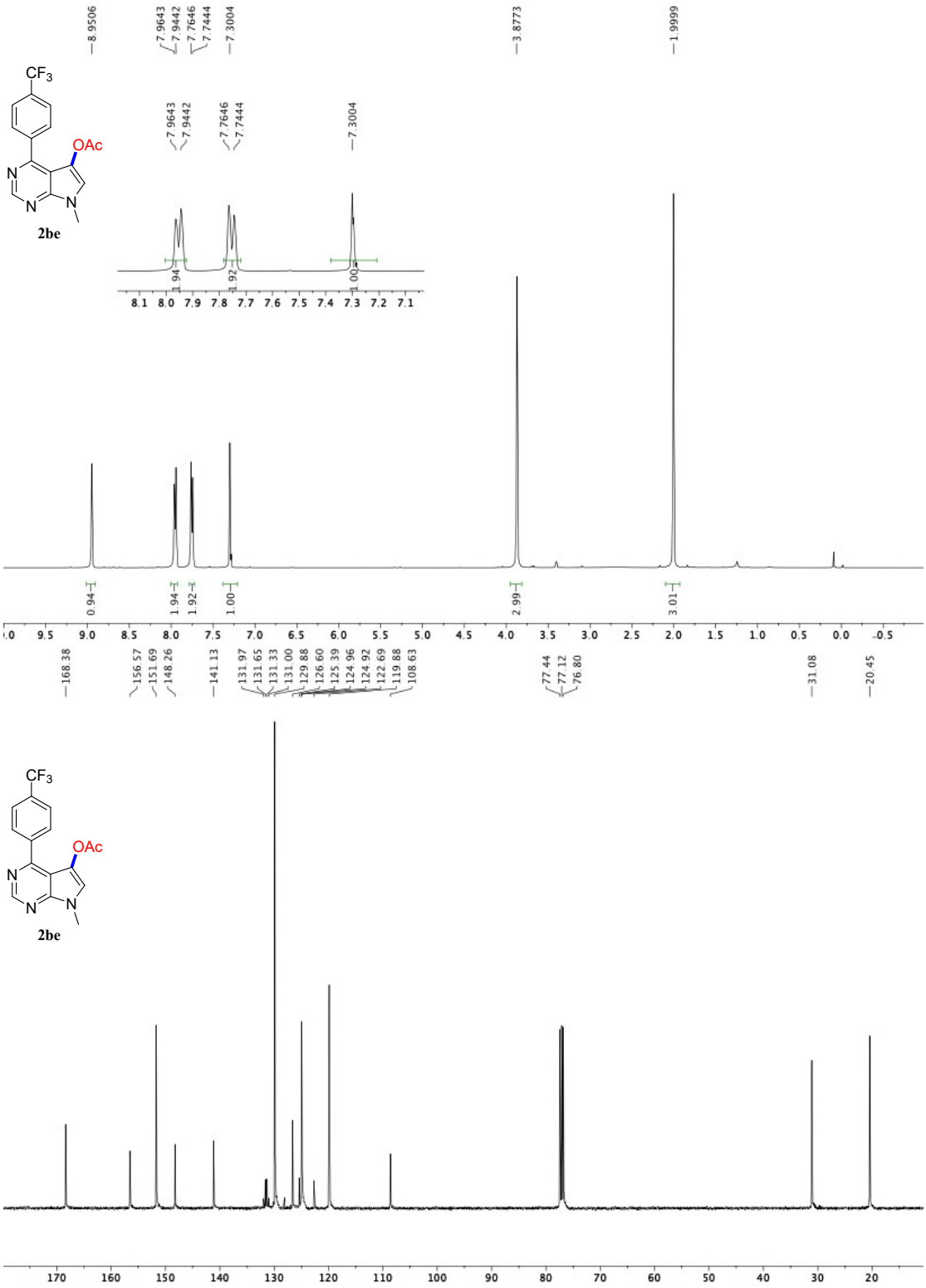
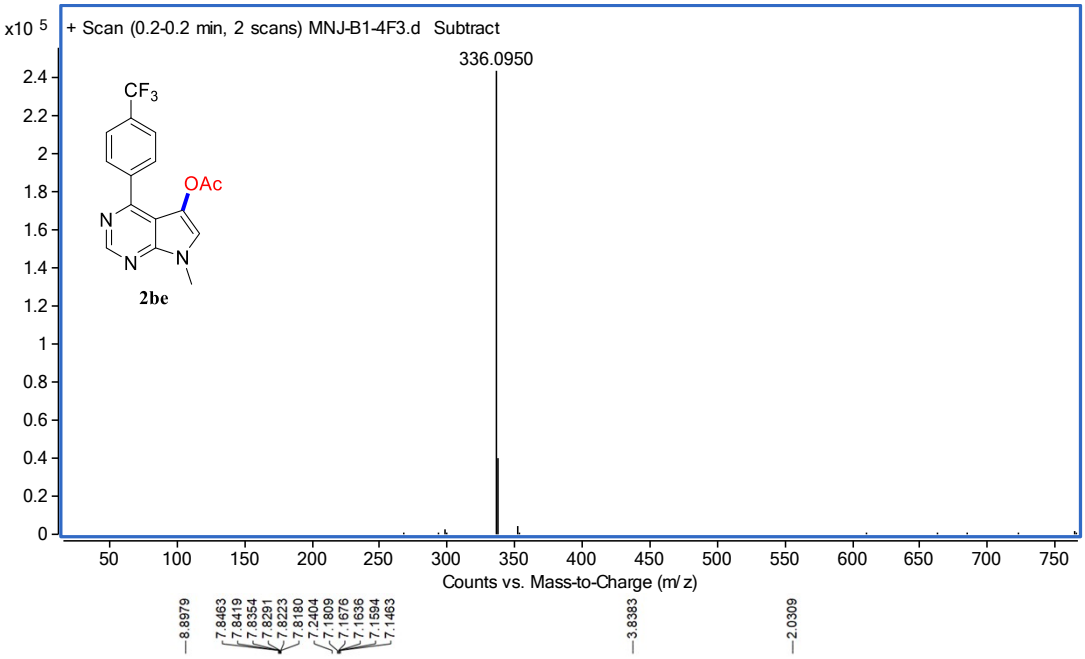
7.9991
7.9961
7.9924
7.9828
7.9790
7.9761
7.8313
7.8264
7.8226
7.8131
7.8093
7.8063
7.3776
7.2763
3.9297
2.0711
2.41
2.42

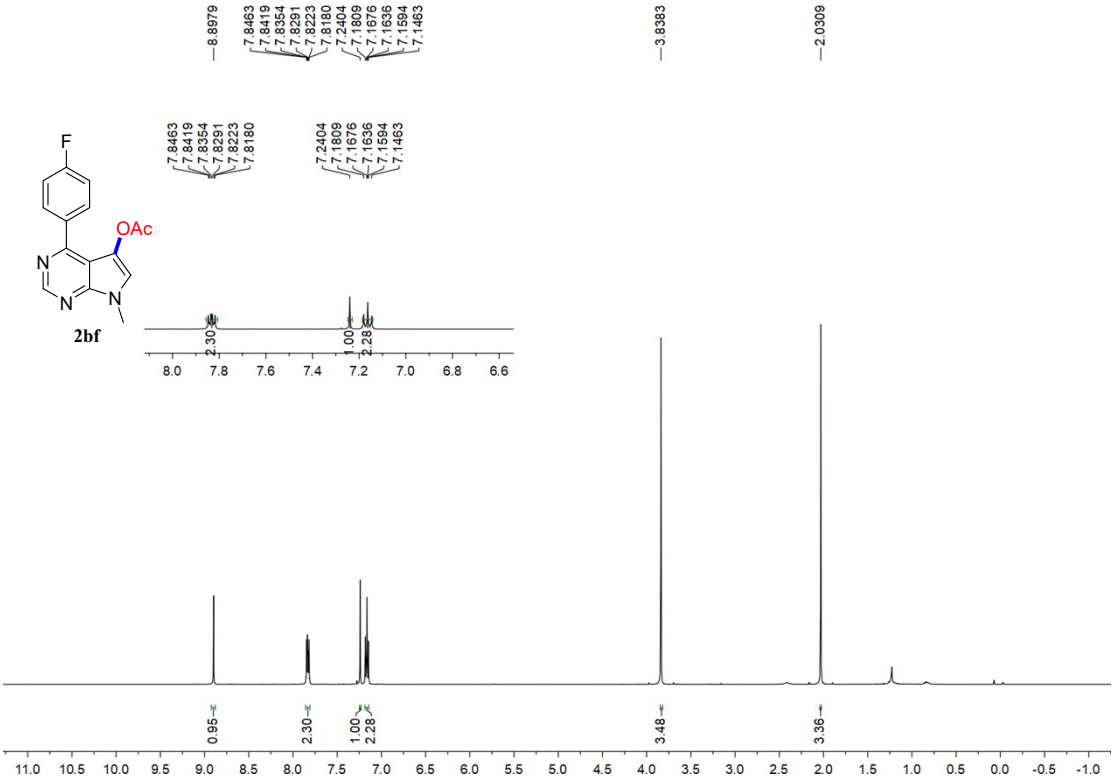
1.04
2.41
2.42
1.00
3.37
3.46

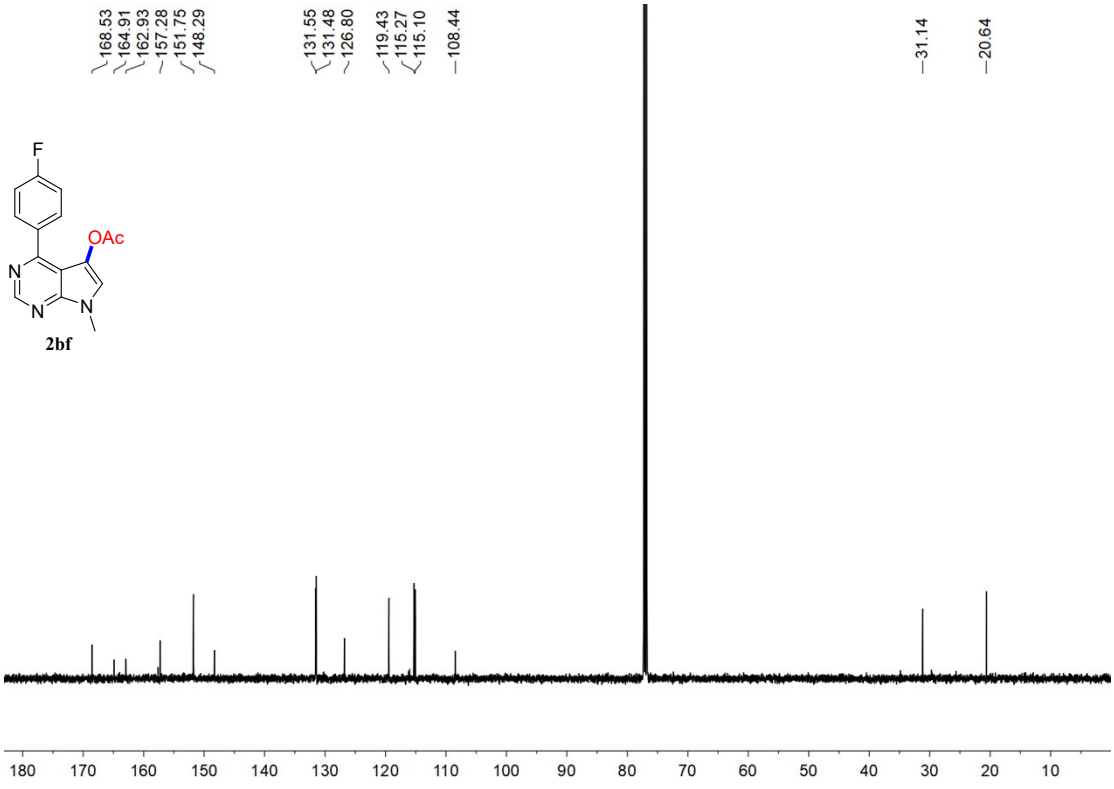

CN
OAc
N
N
N
2bd
168.26
163.57
155.95
151.78
142.10
132.33
131.81
130.40
130.25
126.56
120.14
113.34
31.23
20.64
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

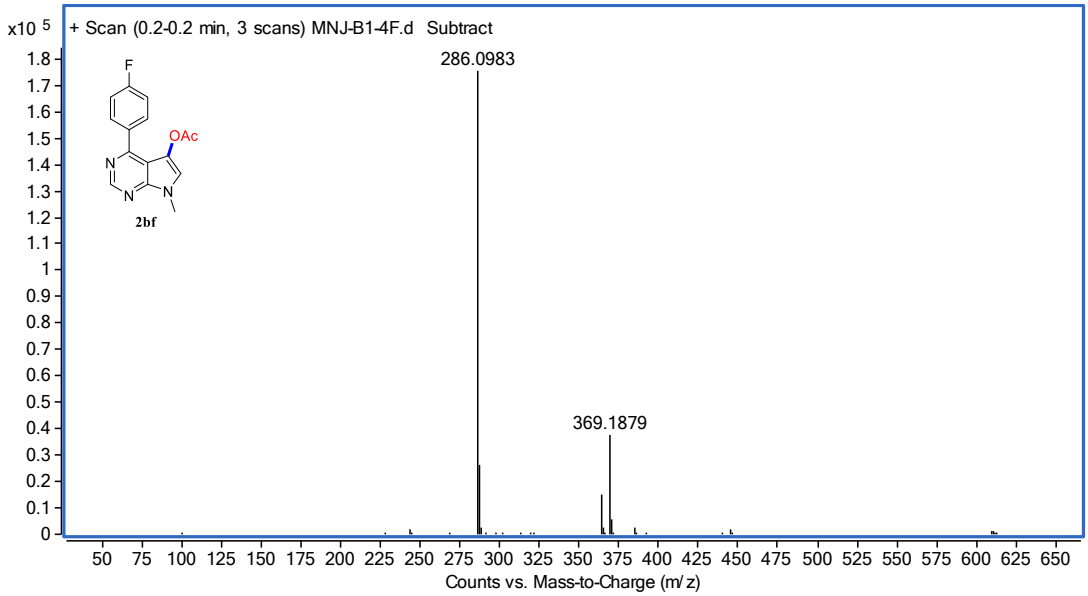

x10 4
+ Scan (0.2-0.2 min, 4 scans) MNJ-B1-4CN.d Subtract
CN
OAc
N
N
N
2bd
293.1035
360.3235
315.0854
437.1931
377.1058
413.2652
5.25
5
4.75
4.5
4.25
4
3.75
3.5
3.25
3
2.75
2.5
2.25
2
1.75
1.5
1.25
1
0.75
0.5
0.25
0
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
460
480
Counts vs. Mass-to-Charge (m/z)

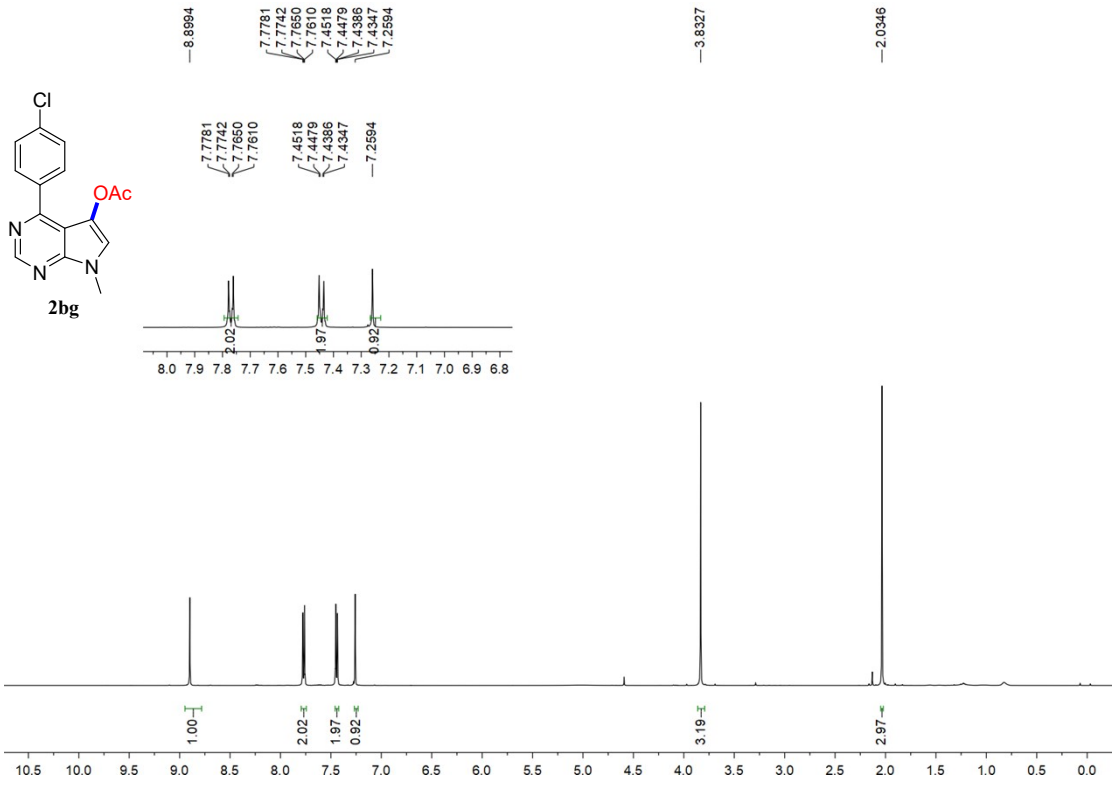

8.9506
7.9643
7.9442
7.7646
7.7444
7.3004
3.8773
1.9999
CF3
OAc
N
N
N
2be
0.94
1.94
1.92
1.00
2.99
3.01
168.38
156.57
151.69
148.26
141.13
131.97
131.65
131.33
131.00
129.88
126.60
125.39
124.96
124.92
122.69
119.88
108.63
77.44
77.12
76.80
31.08
20.45

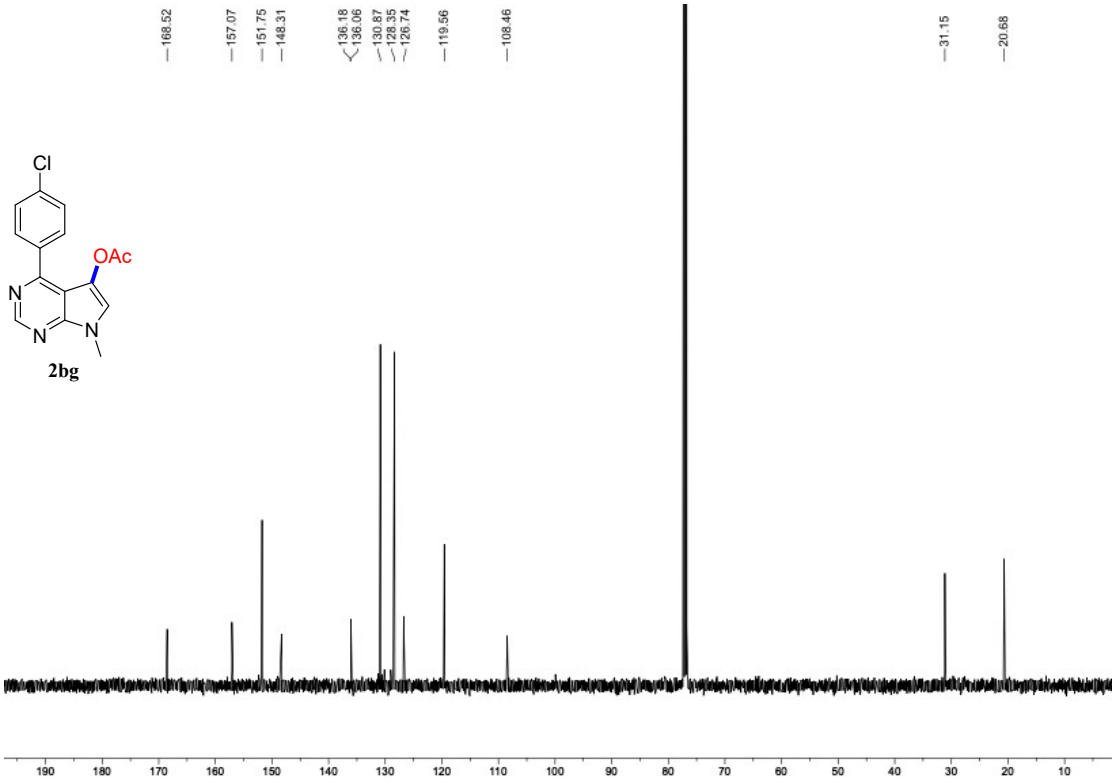

x10 5
+ Scan (0.2-0.2 min, 2 scans) MNJ-B1-4F3.d Subtract
336.0950
CF3
OAc
N
N
N
2be
Counts vs. Mass-to-Charge (m/z)

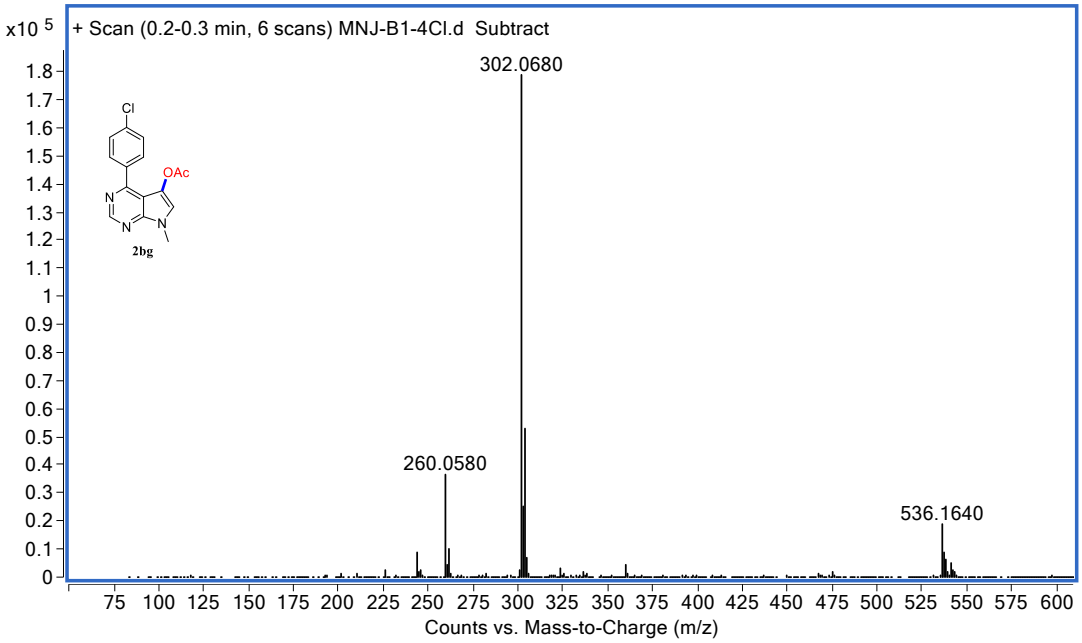

8.8979
7.8463
7.8419
7.8354
7.8291
7.8223
7.8180
7.2404
7.1809
7.1676
7.1636
7.1594
7.1463
3.8383
2.0309
F
OAc
N
N
N
2bf
2.30
1.00
2.28
0.95
2.30
1.00
2.28
3.48
3.36

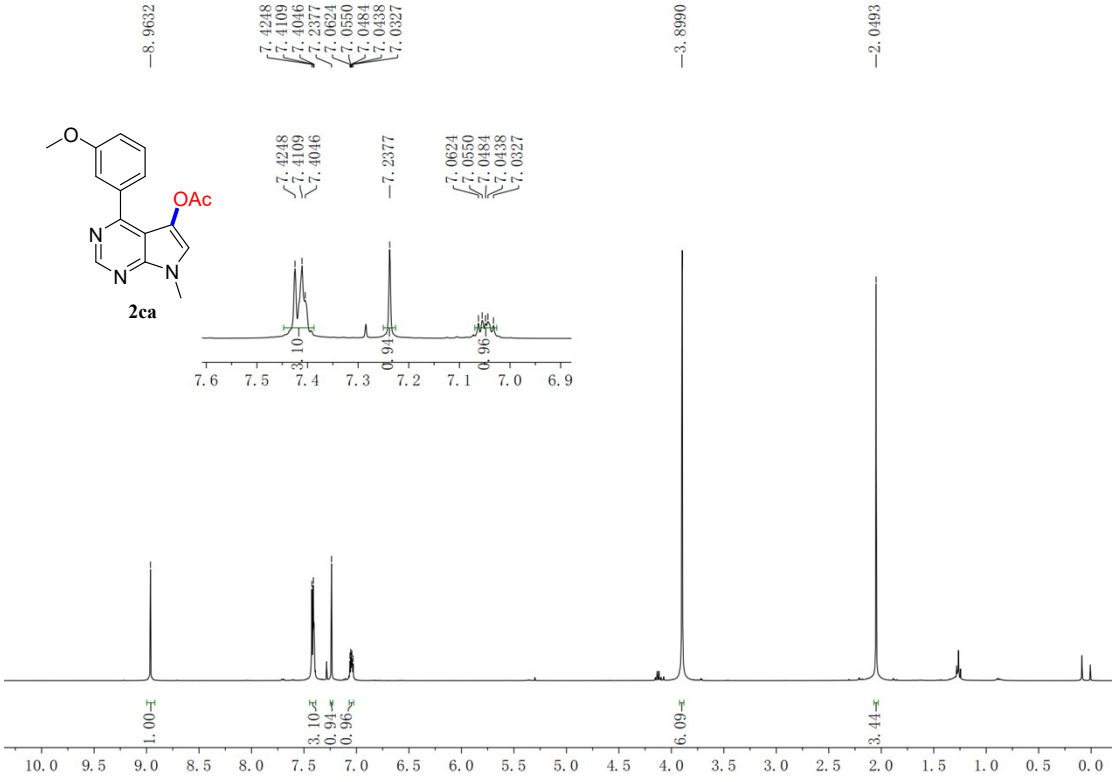

168.53
164.91
162.93
157.28
151.75
148.29
131.55
131.48
126.80
119.43
115.27
115.10
108.44
31.14
20.64
F
OAc
N
N
N
2bf
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

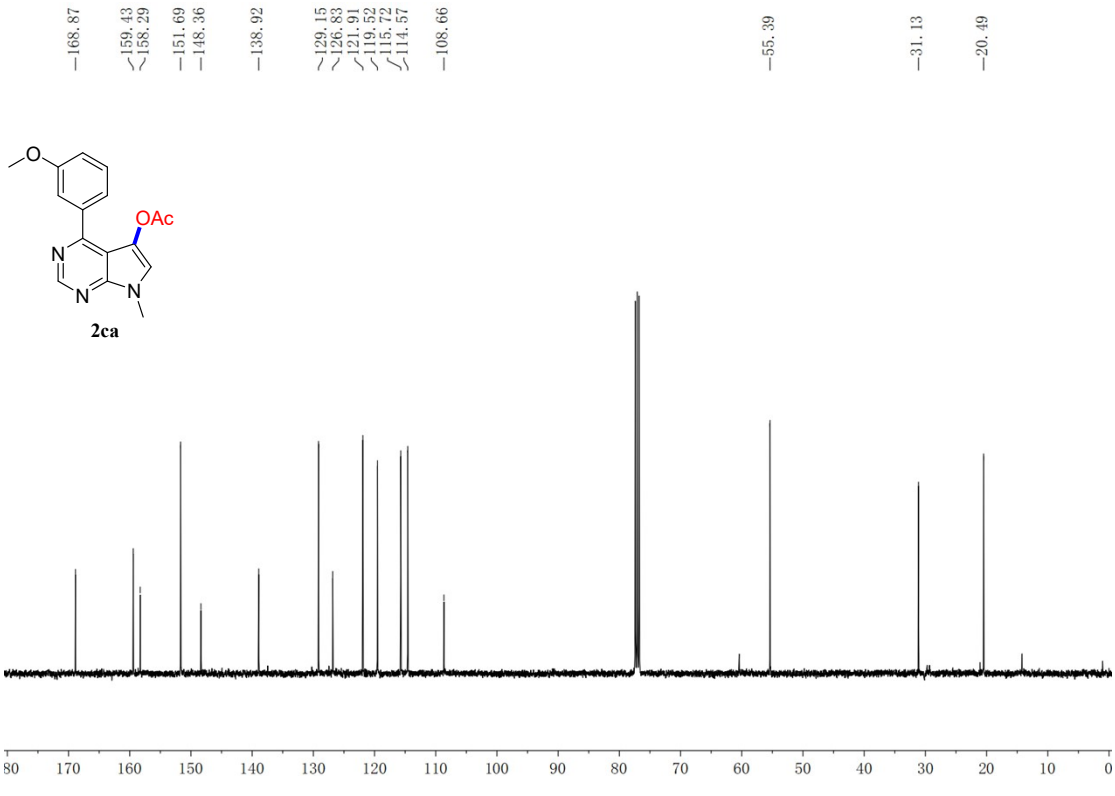

x10 5
+ Scan (0.2-0.2 min, 3 scans) MNJ-B1-4F.d Subtract
286.0983
369.1879
F
OAc
N
N
N
2bf
1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0
50 75 100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 625 650
Counts vs. Mass-to-Charge (m/z)

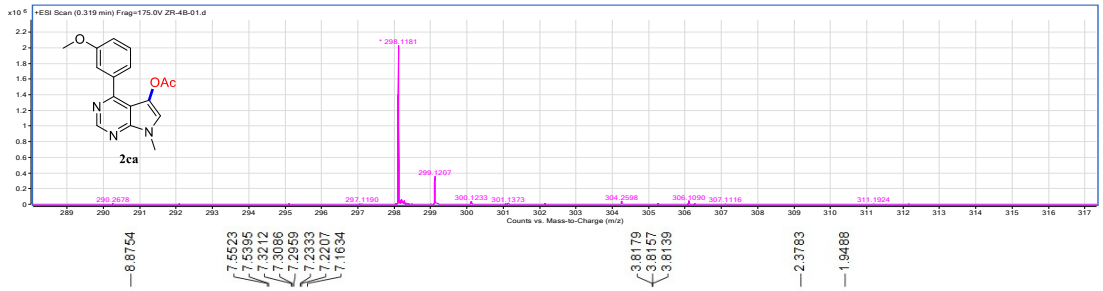

8.8994
7.7781
7.7742
7.7650
7.7610
7.4518
7.4479
7.4386
7.4347
7.2594
3.8327
2.0346
Cl
OAc
N
N
N
2bg
2.02
1.97
0.92
1.00
3.19
2.97

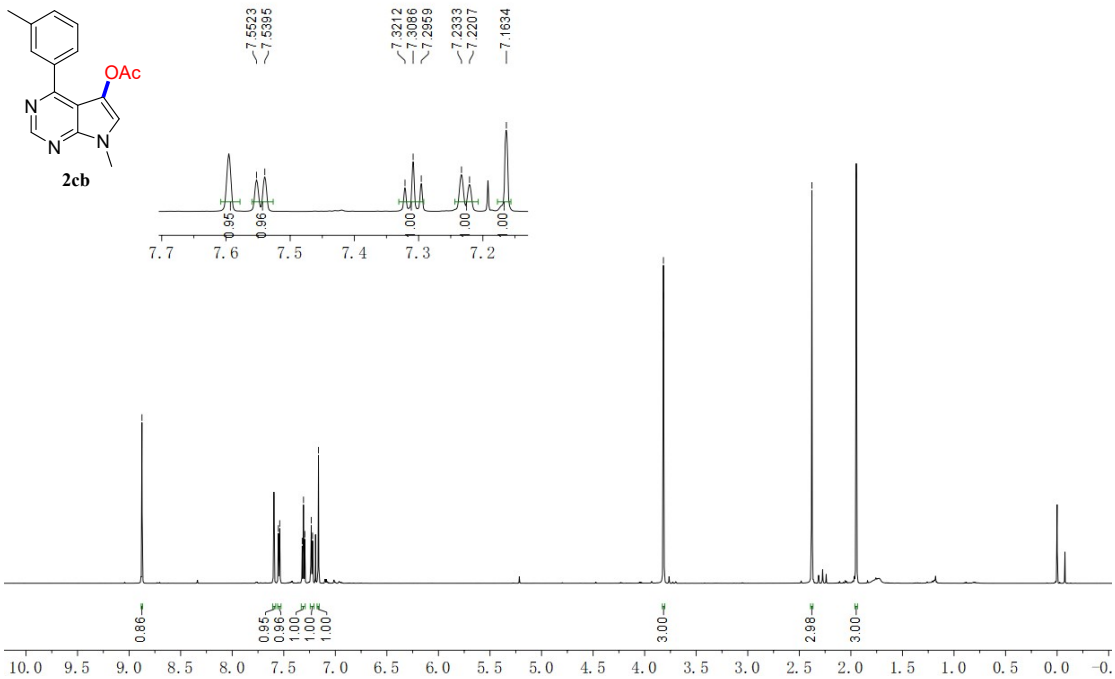

168.52
157.07
151.75
148.31
136.18
136.06
130.87
128.35
126.74
119.56
108.46
31.15
20.68
Cl
OAc
N
N
N
2bg

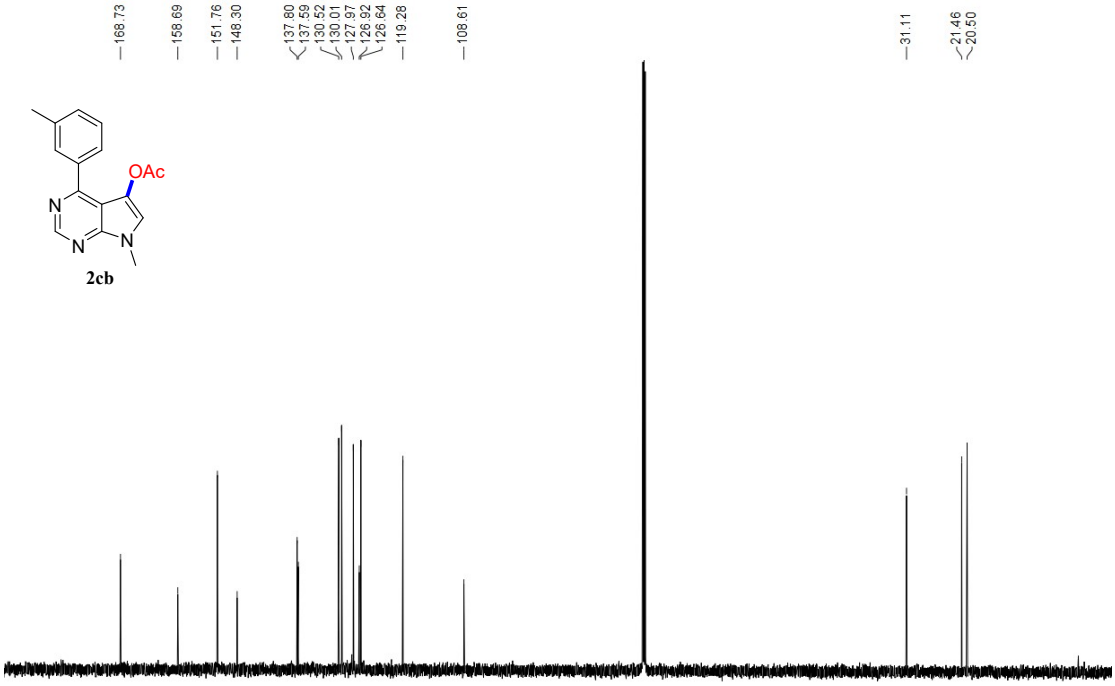

x10 5
+ Scan (0.2-0.3 min, 6 scans) MNJ-B1-4Cl.d Subtract
302.0680
260.0580
536.1640
Cl
OAc
N
N
N
2bg
Counts vs. Mass-to-Charge (m/z)


8.9632
7.4248
7.4109
7.4046
7.2377
7.0624
7.0550
7.0484
7.0438
7.0327
3.8990
2.0493
O
OAc
N
N
N
2ca
1.00
3.10
0.94
0.96
6.09
3.44

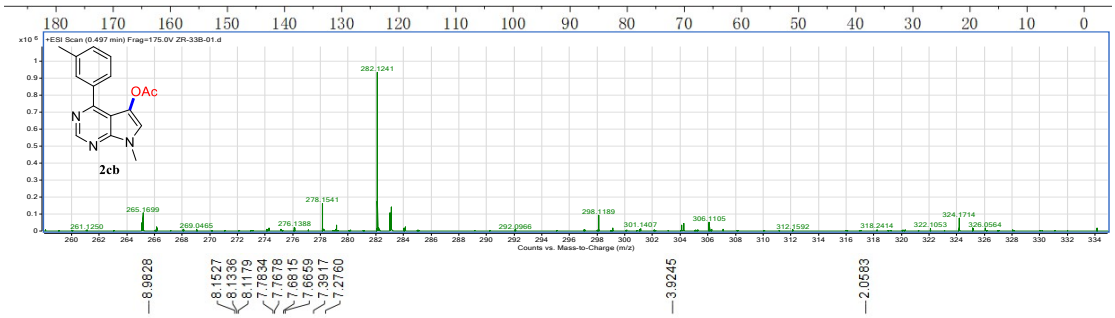

168.87
159.43
158.29
151.69
148.36
138.92
129.15
126.83
121.91
119.52
115.72
114.57
108.66
55.39
31.13
20.49
OAc
2ca


+ESI Scan (0.319 min) Frag=175.0V ZR-4B-01.d
298.1181
299.1207
OAc
2ca
Counts vs. Mass-to-Charge (m/z)

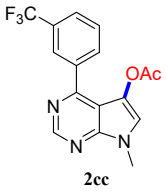

8.8754
7.5523
7.5395
7.3212
7.3086
7.2959
7.2333
7.2207
7.1634
3.8179
3.8157
3.8139
2.3783
1.9488
OAc
2cb
0.86
0.95
0.96
1.00
1.00
1.00
3.00
2.98
3.00


168.73
158.69
151.76
148.30
137.80
137.59
130.52
130.01
127.97
126.92
126.64
119.28
108.61
31.11
21.46
20.50
OAc
N
N
N

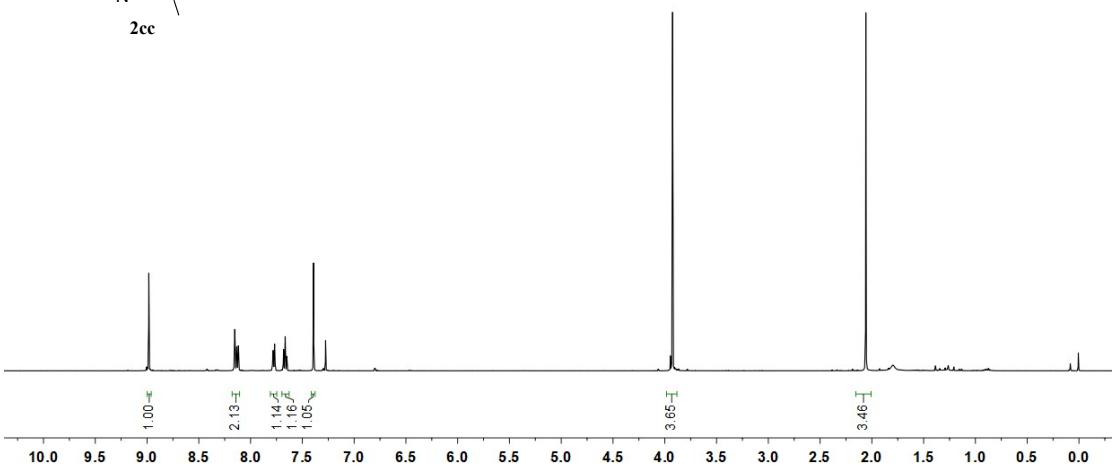
2cb

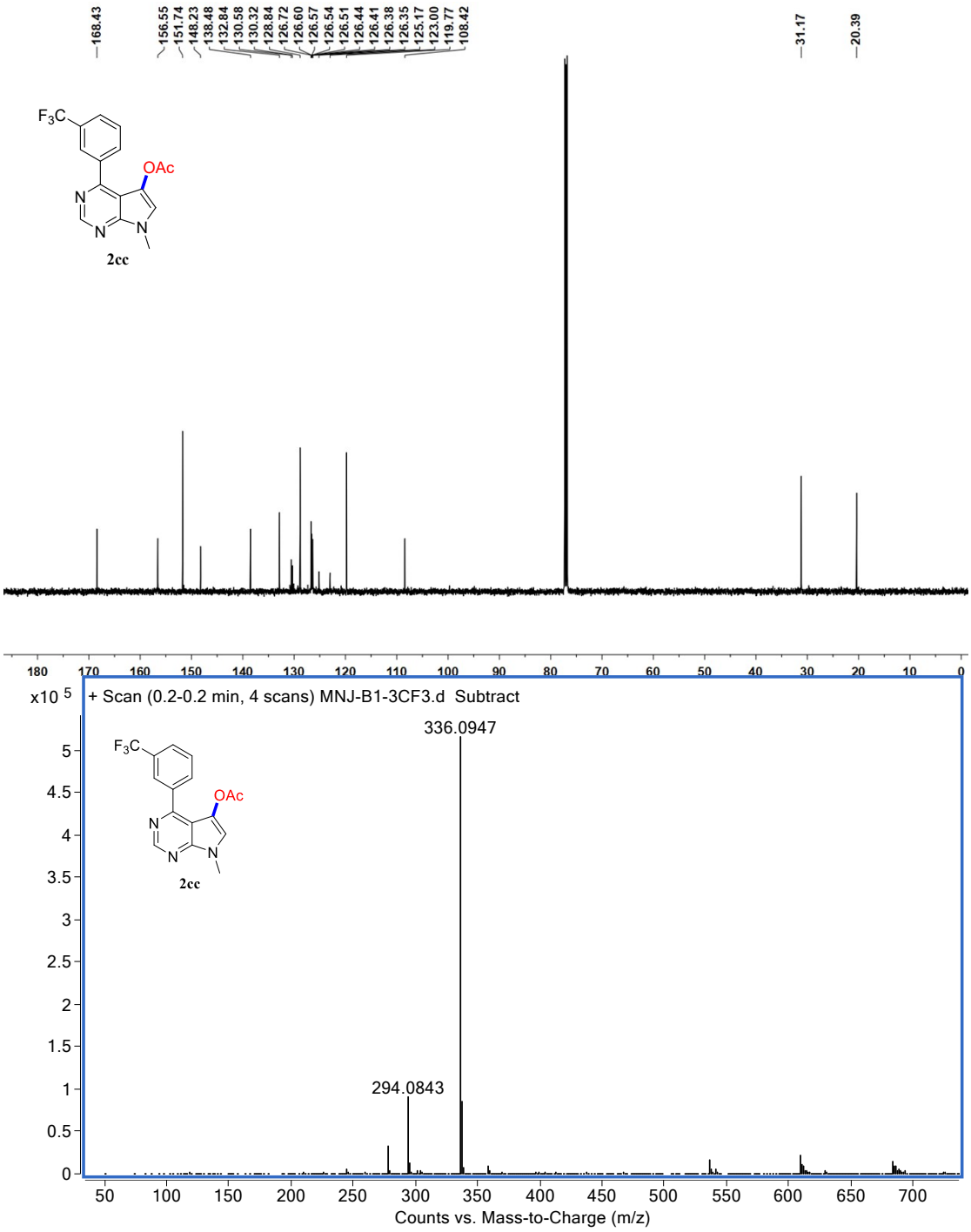

+ESI Scan (0.497 min) Frag=175.0V ZR-33B-01.d
OAc
282.1241
278.1541
265.1699
276.1388
269.0465
261.1250
298.1189
301.1407
306.1105
312.1592
318.2414
322.1053
324.1714
326.0564
Counts vs. Mass-to-Charge (m/z)

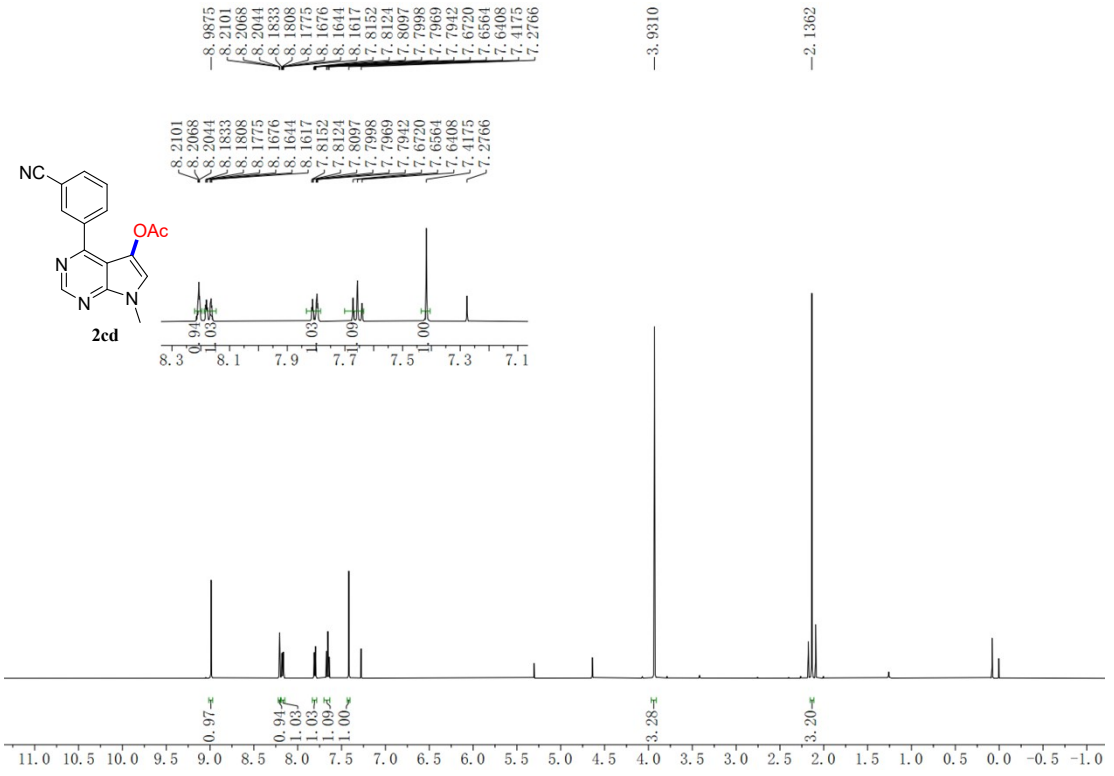
8.9828
8.1527
8.1336
8.1179
7.7834
7.7678
7.6815
7.6659
7.3917
7.2760
3.9245
2.0583

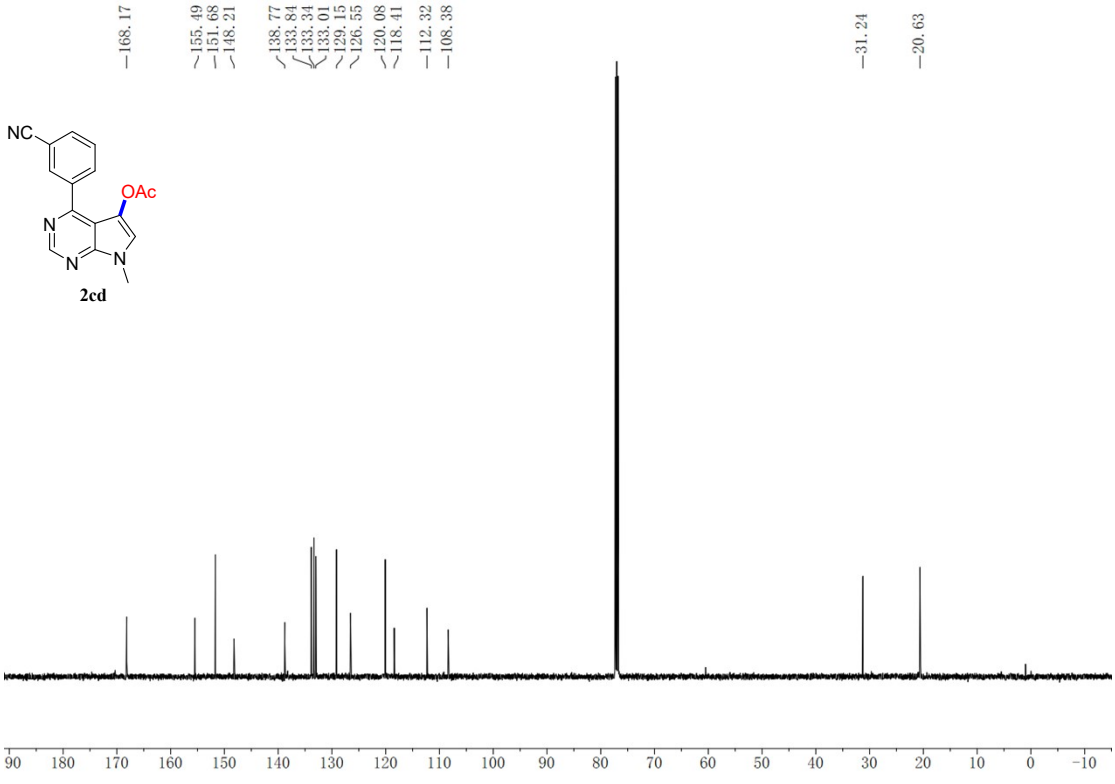

F3C
OAc
N
N
N

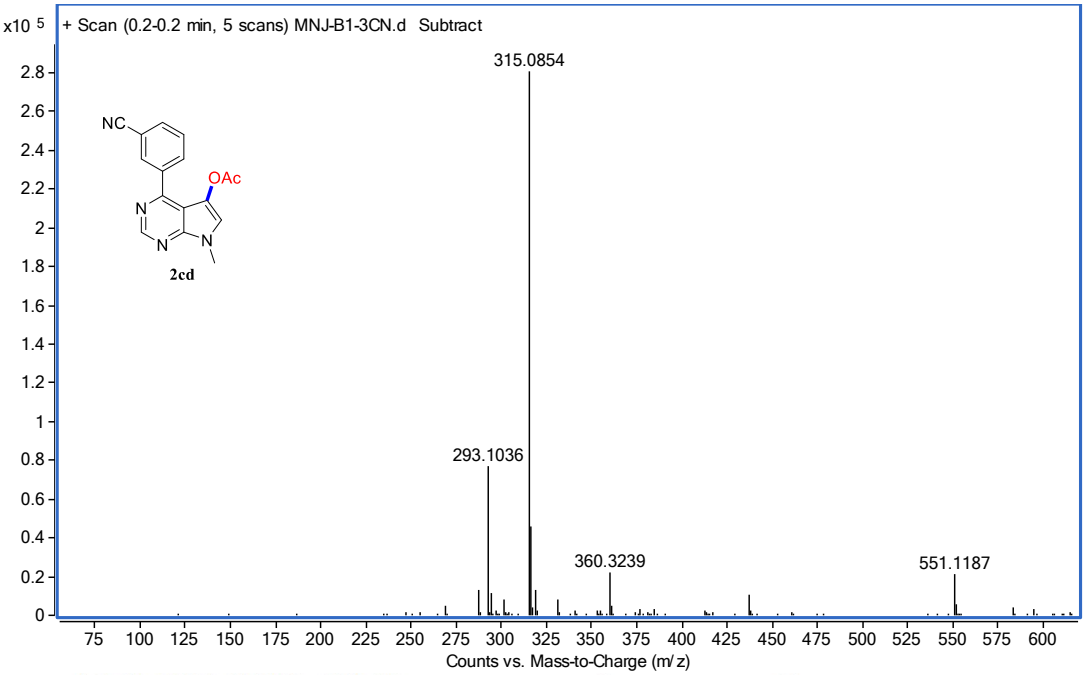
2cc

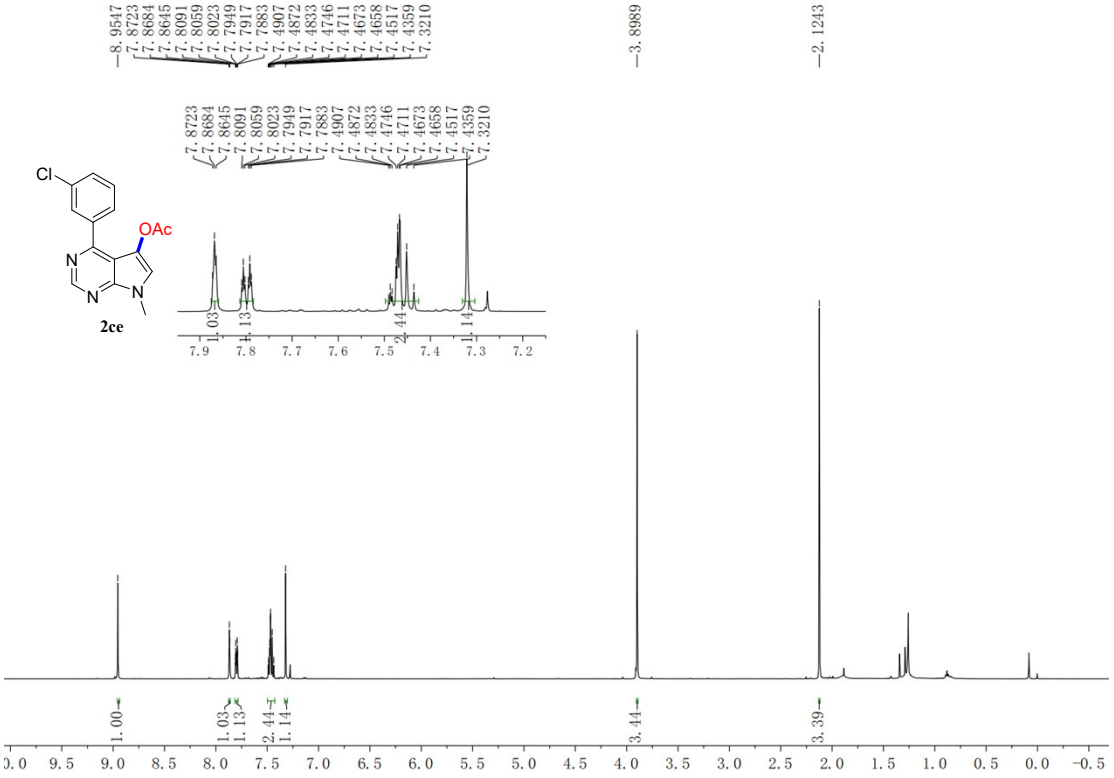

1.00
2.13
1.14
1.16
1.05
3.65
3.46
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

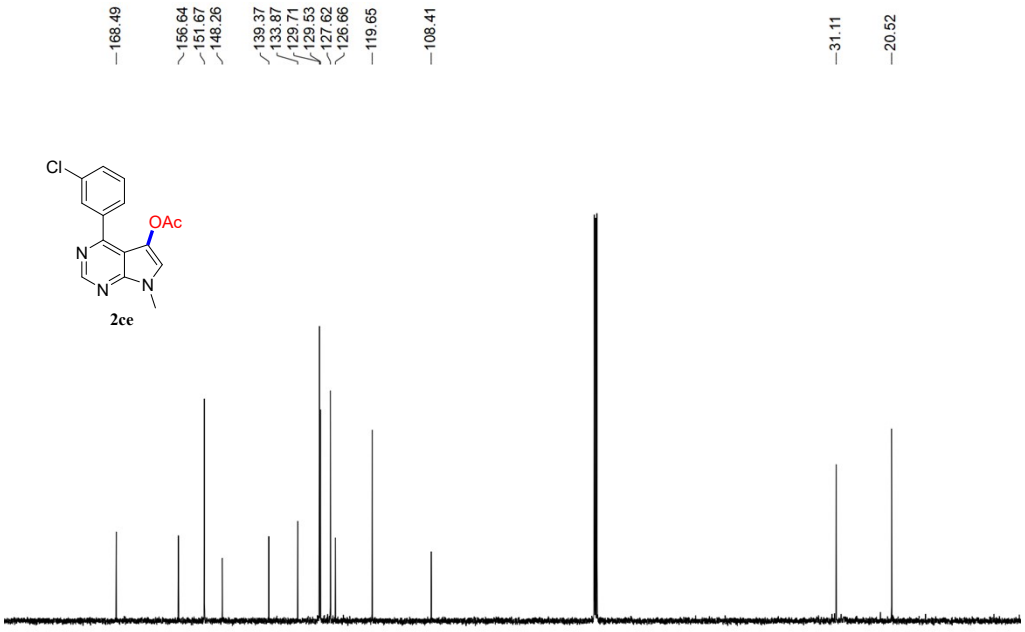

168.43
156.55
151.74
148.23
138.48
132.84
130.58
130.32
128.84
126.72
126.60
126.57
126.54
126.51
126.44
126.41
126.38
126.35
125.17
123.00
119.77
108.42
31.17
20.39
F3C
OAc
N
N
N
2cc
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
x10 5
+ Scan (0.2-0.2 min, 4 scans) MNJ-B1-3CF3.d Subtract
336.0947
294.0843
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
50 100 150 200 250 300 350 400 450 500 550 600 650 700
Counts vs. Mass-to-Charge (m/z)

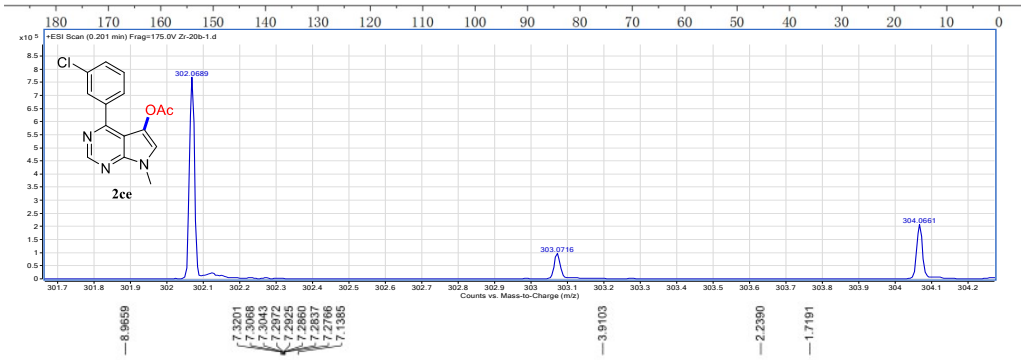

8.9875
8.2101
8.2068
8.2044
8.1833
8.1808
8.1775
8.1676
8.1644
8.1617
7.8152
7.8124
7.8097
7.7998
7.7969
7.7942
7.6720
7.6564
7.6408
7.4175
7.2766
3.9310
2.1362
NC
OAc
N
N
N
2cd
0.97
0.94
1.03
1.03
1.09
1.00
3.28
3.20


168.17
155.49
151.68
148.21
138.77
133.84
133.34
133.01
129.15
126.55
120.08
118.41
112.32
108.38
31.24
20.63
NC
OAc
N
N
N
2cd

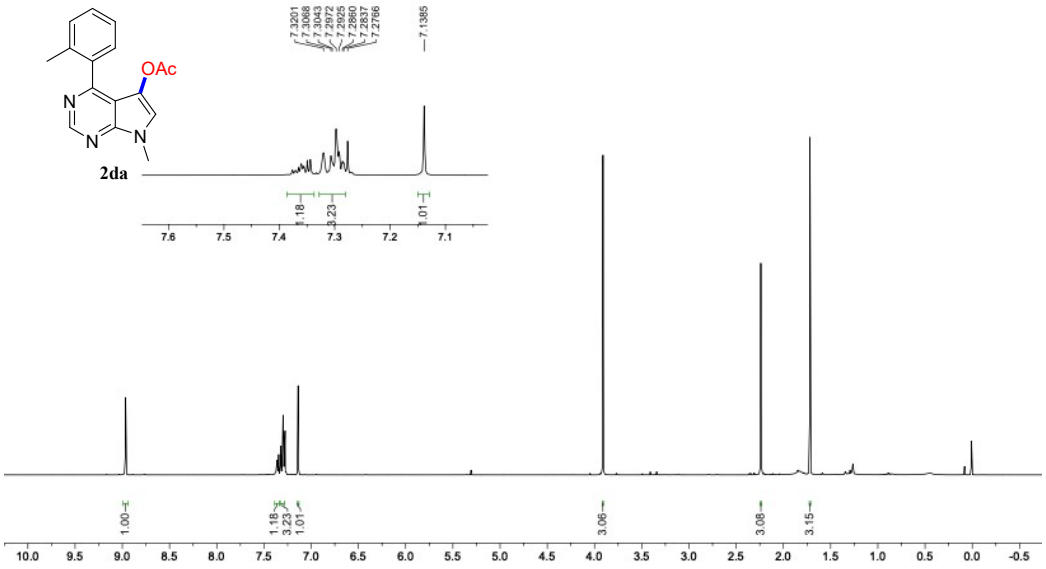

x10 5
+ Scan (0.2-0.2 min, 5 scans) MNJ-B1-3CN.d Subtract
315.0854
293.1036
360.3239
551.1187
NC
OAc
N
N
N
2cd
Counts vs. Mass-to-Charge (m/z)

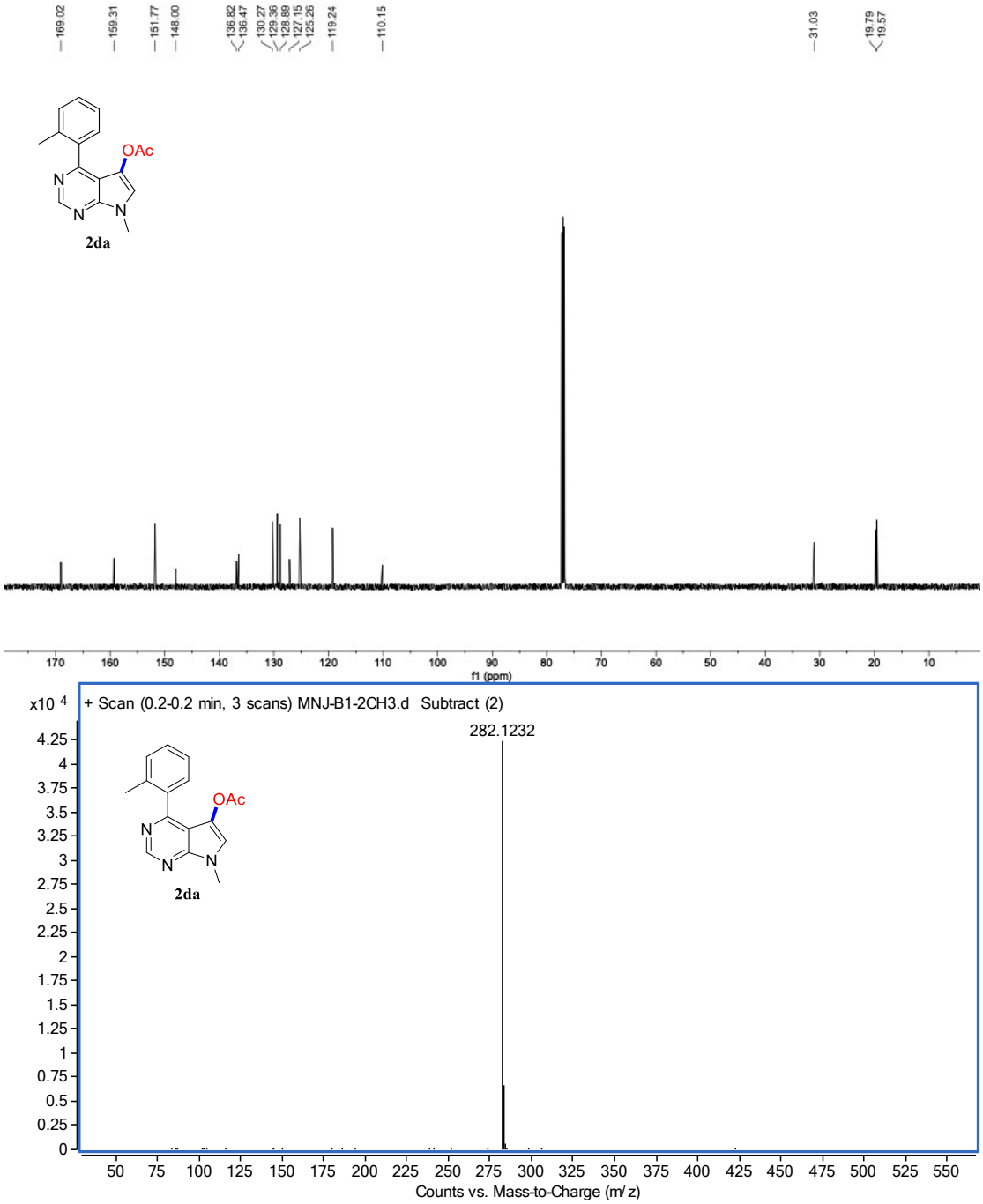

Cl
OAc
N
N
N
2ce

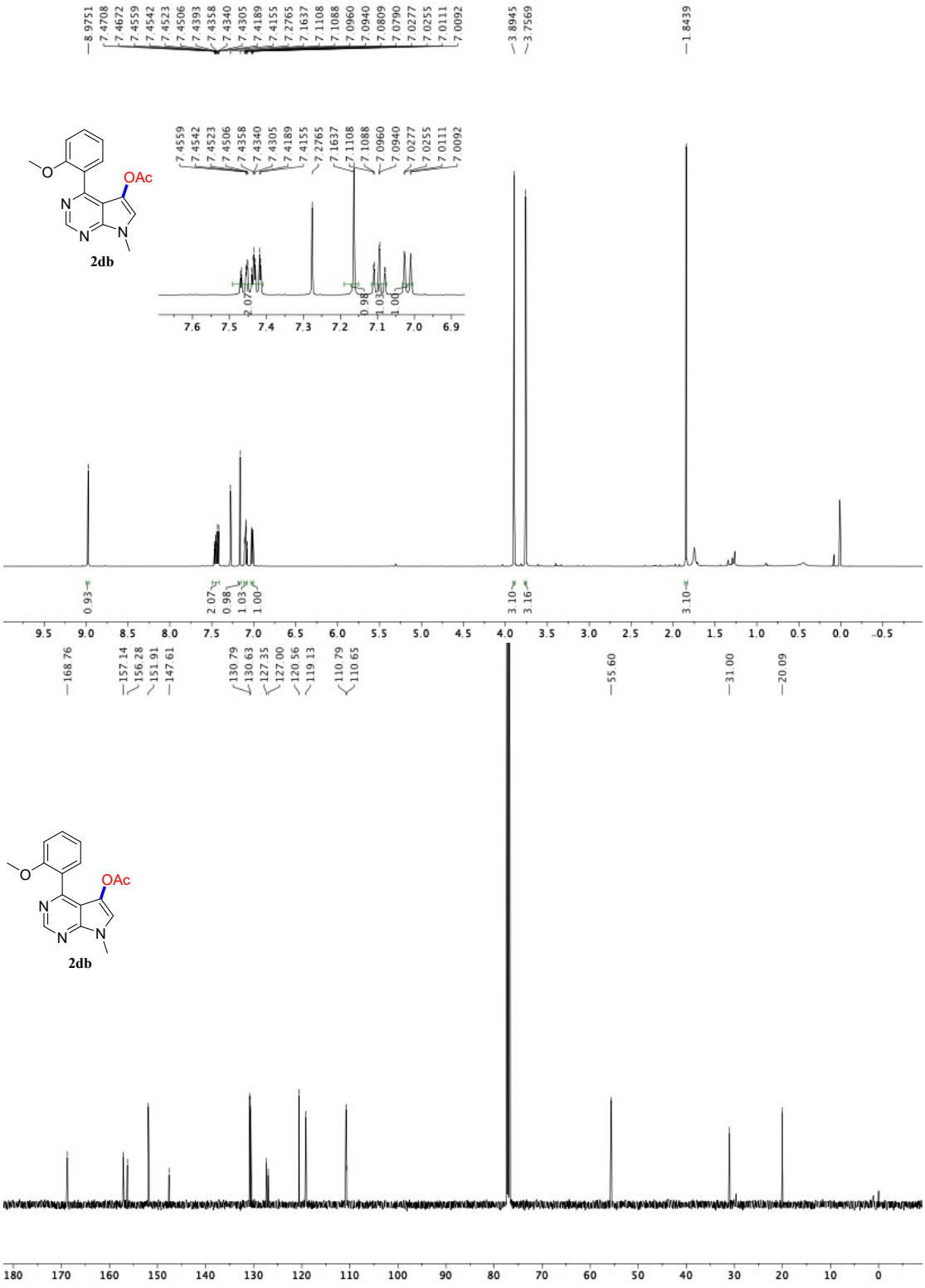

168.49
156.64
151.67
148.26
139.37
133.87
129.71
129.53
127.62
126.66
119.65
108.41
31.11
20.52
Cl
OAc
N
N
N
2ce

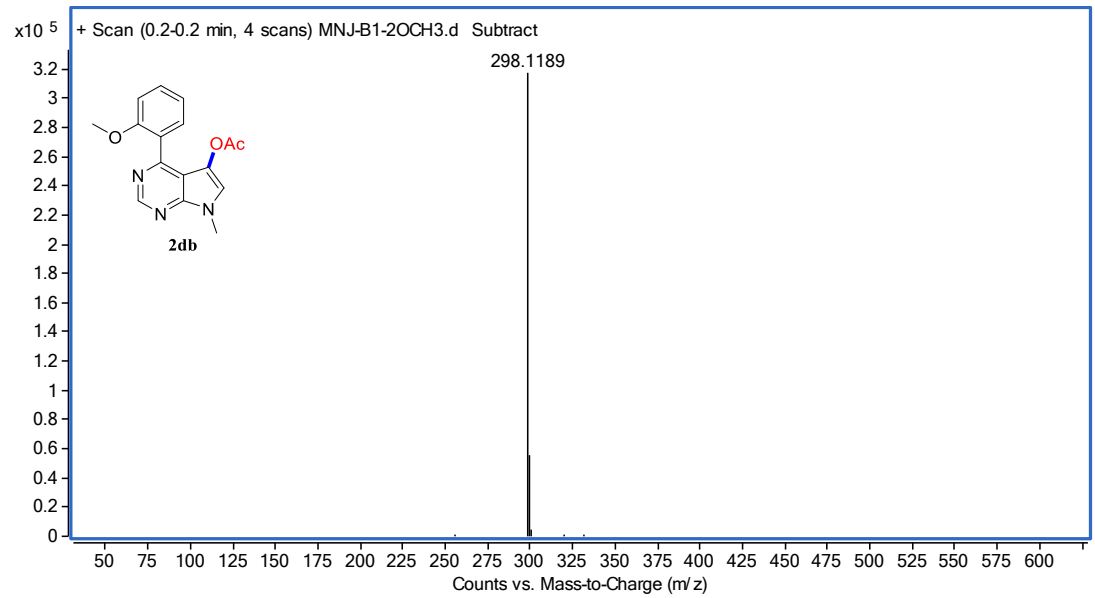

+ESI Scan (0.201 min) Frag=175.0V Zr-20b-1.d
Cl
OAc
2ce
302.0689
303.0716
304.0661
Counts vs. Mass-to-Charge (m/z)

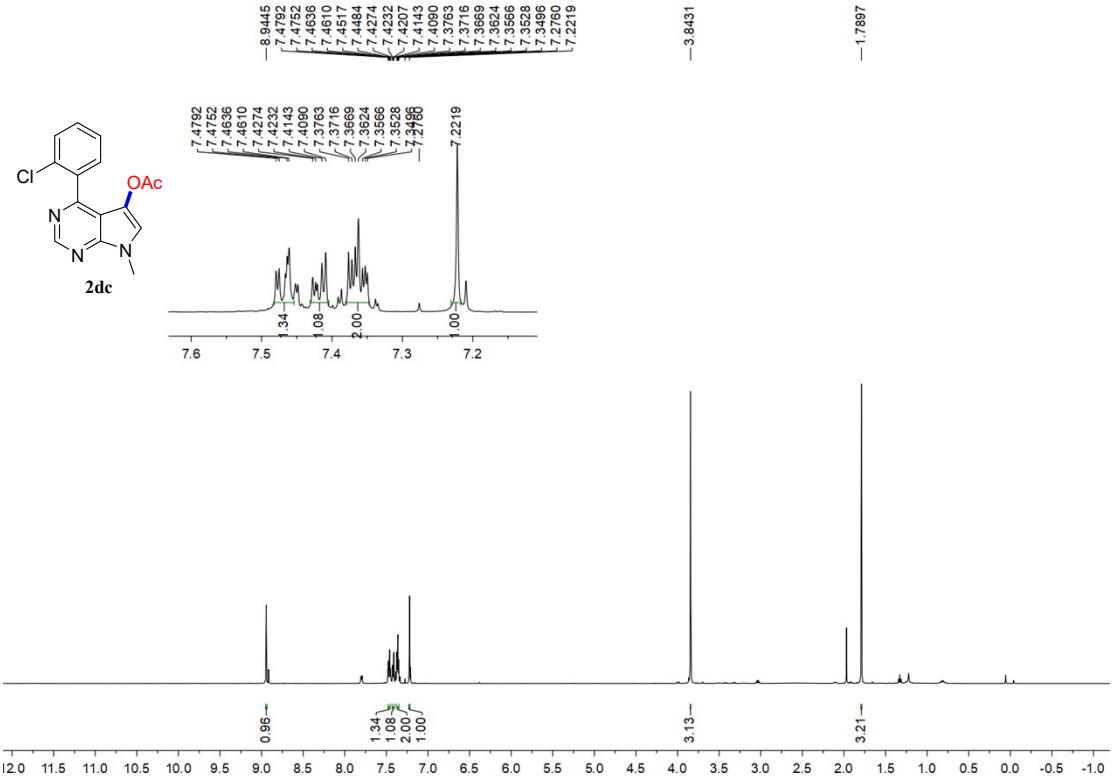
8.9659
7.3201
7.3068
7.3043
7.2972
7.2925
7.2860
7.2837
7.2766
7.1385
3.9103
2.2390
1.7191

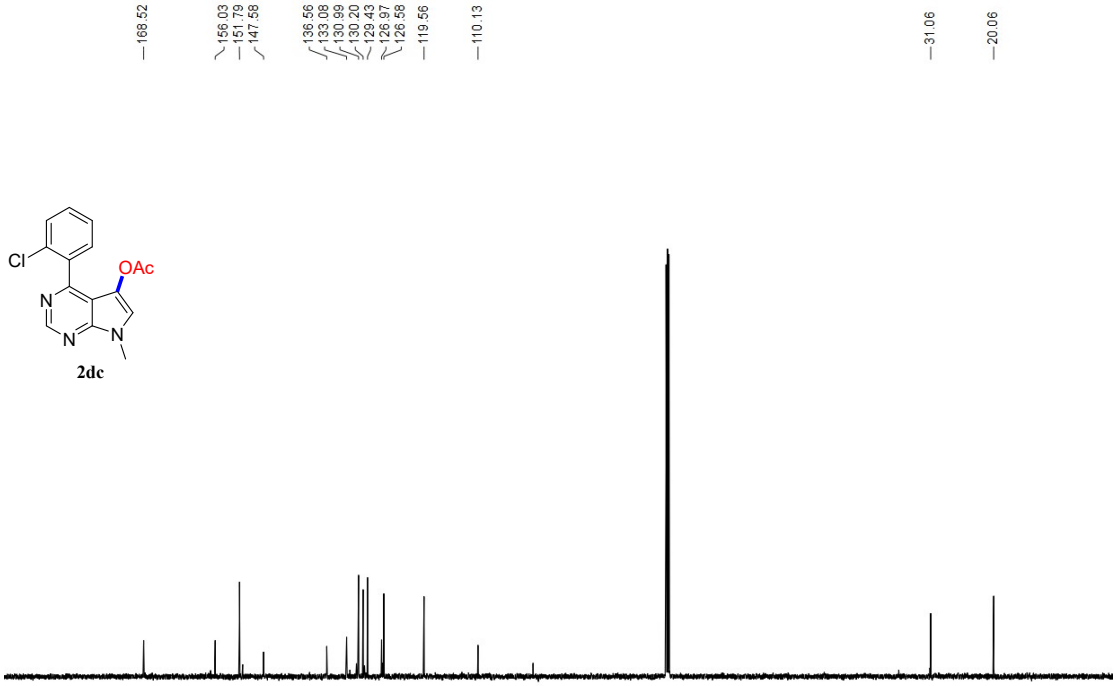

OAc
N
N
N
2da
7.3201
7.3068
7.3043
7.2972
7.2925
7.2860
7.2837
7.2766
7.1385
1.18
3.23
1.01
1.00
1.18
3.23
1.01
3.06
3.08
3.15

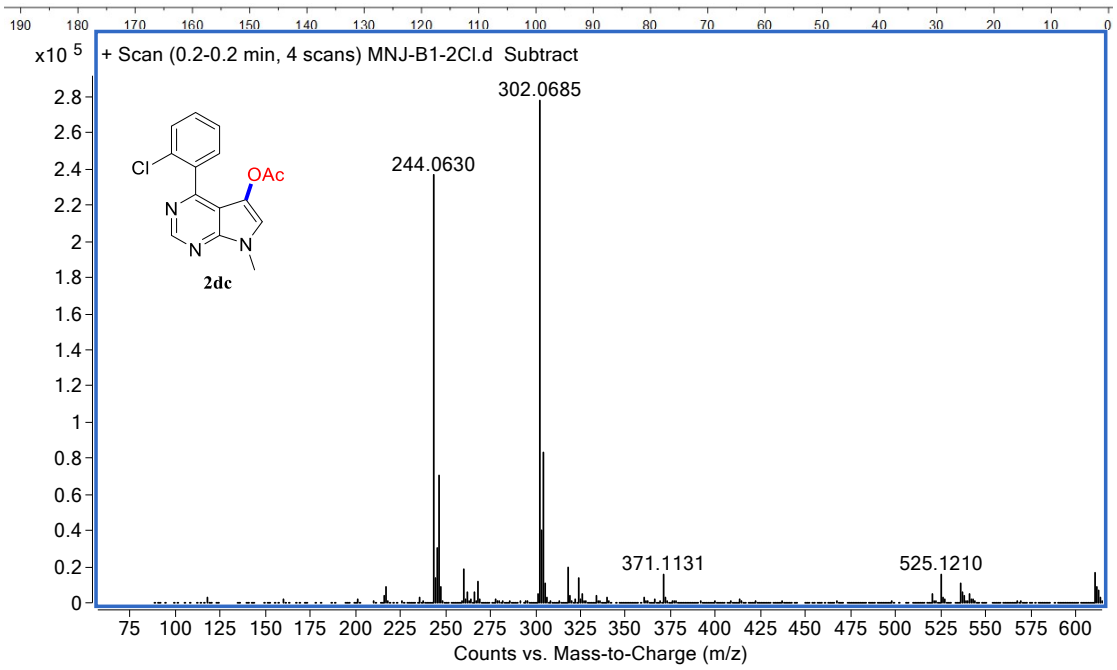

169.02
159.31
151.77
148.00
136.82
136.47
130.27
129.36
128.89
127.15
125.26
119.24
110.15
31.03
19.79
19.57
OAc
N
N
N
2da
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
x10 4
+ Scan (0.2-0.2 min, 3 scans) MNJ-B1-2CH3.d Subtract (2)
282.1232
OAc
N
N
N
2da
4.25
4
3.75
3.5
3.25
3
2.75
2.5
2.25
2
1.75
1.5
1.25
1
0.75
0.5
0.25
0
50
75
100
125
150
175
200
225
250
275
300
325
350
375
400
425
450
475
500
525
550
Counts vs. Mass-to-Charge (m/z)

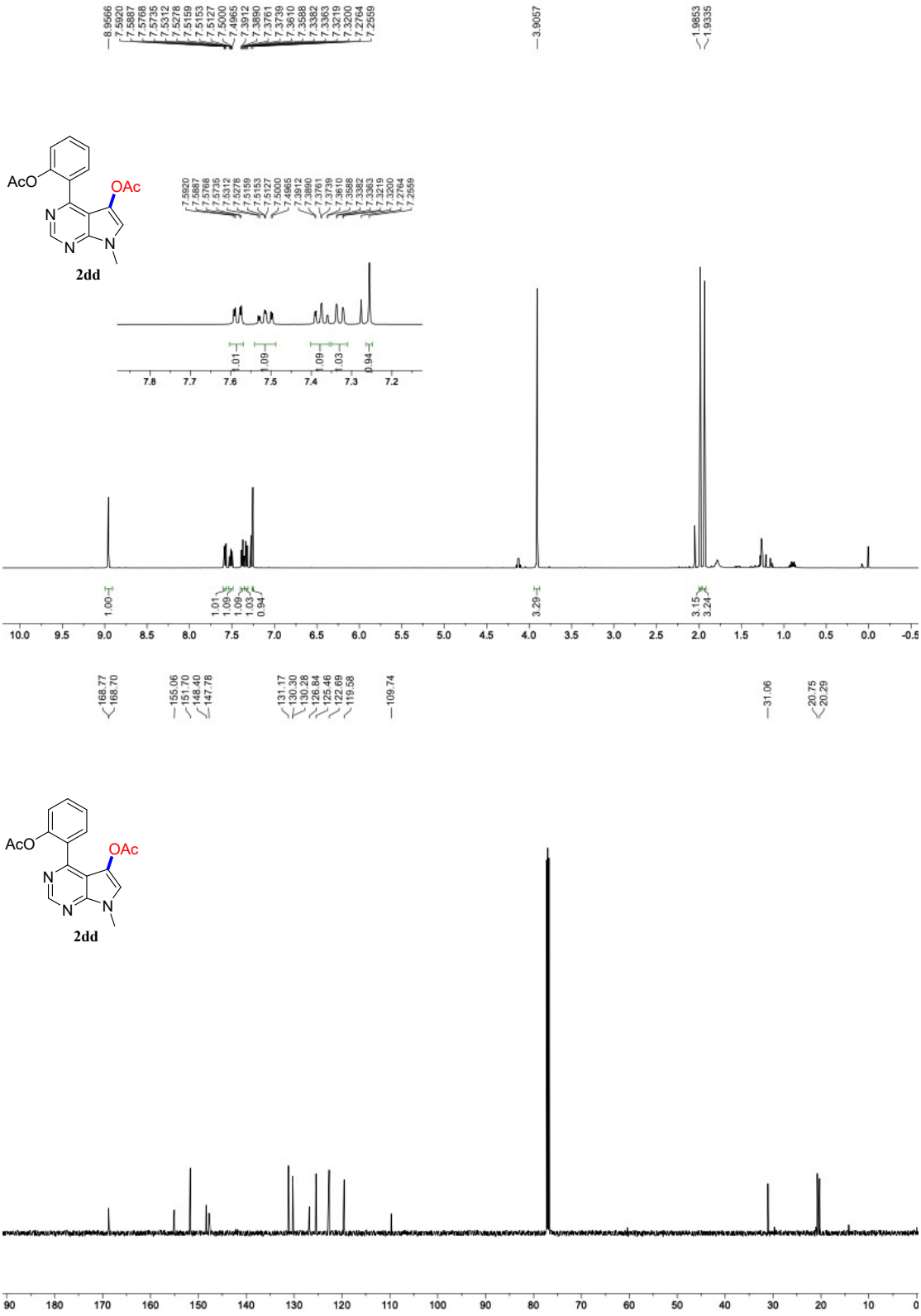

8.9751
7.4708
7.4672
7.4559
7.4542
7.4523
7.4506
7.4393
7.4358
7.4340
7.4305
7.4189
7.4155
7.2765
7.1637
7.1108
7.1088
7.0960
7.0940
7.0809
7.0790
7.0277
7.0255
7.0111
7.0092
3.8945
3.7569
1.8439
OAc
N
O
N
N
2db
0.93
2.07
0.98
1.03
1.00
3.10
3.16
3.10
168.76
157.14
156.28
151.91
147.61
130.79
130.63
127.35
127.00
120.56
119.13
110.79
110.65
55.60
31.00
20.09

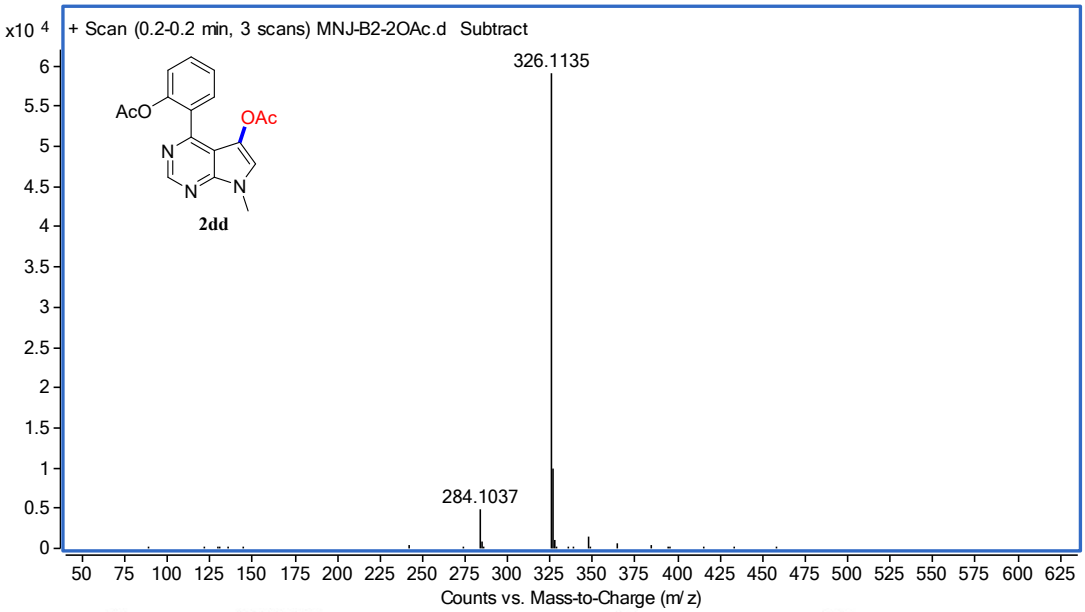

x10 5
+ Scan (0.2-0.2 min, 4 scans) MNJ-B1-2OCH3.d Subtract
298.1189
OAc
2db
Counts vs. Mass-to-Charge (m/z)

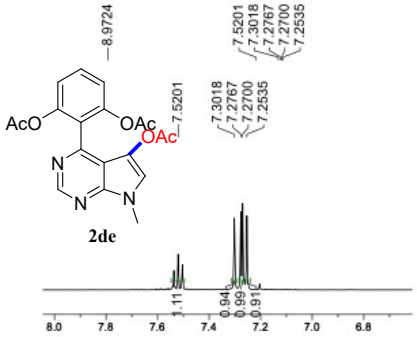

8.9445
7.4792
7.4752
7.4636
7.4610
7.4517
7.4484
7.4274
7.4232
7.4207
7.4143
7.4090
7.3763
7.3716
7.3669
7.3624
7.3566
7.3528
7.3486
7.3460
7.2760
7.2219
3.8431
1.7897
OAc
Cl
2dc
1.34
1.08
2.00
1.00
0.96
3.13
3.21

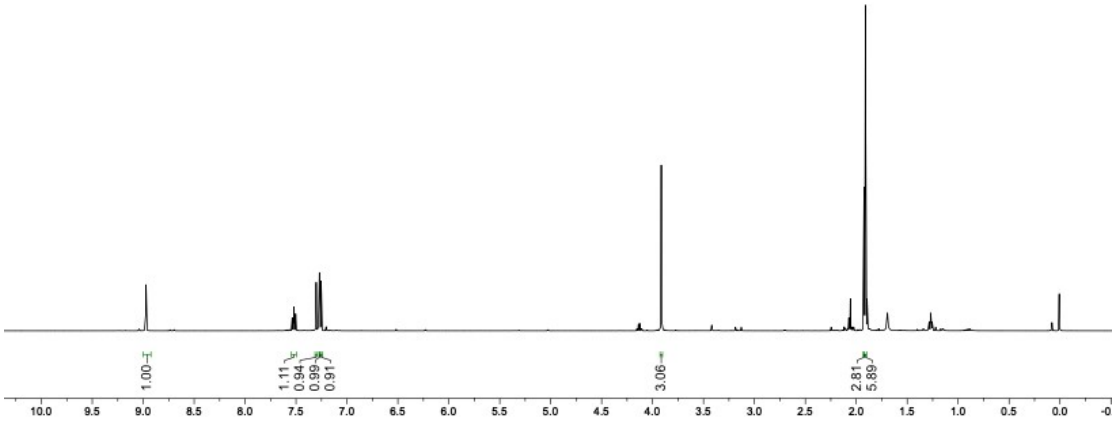

168.52
156.03
151.79
147.58
136.56
133.08
130.99
130.20
129.43
126.97
126.58
119.56
110.13
31.06
20.06
Cl
OAc
N
N
N
2dc

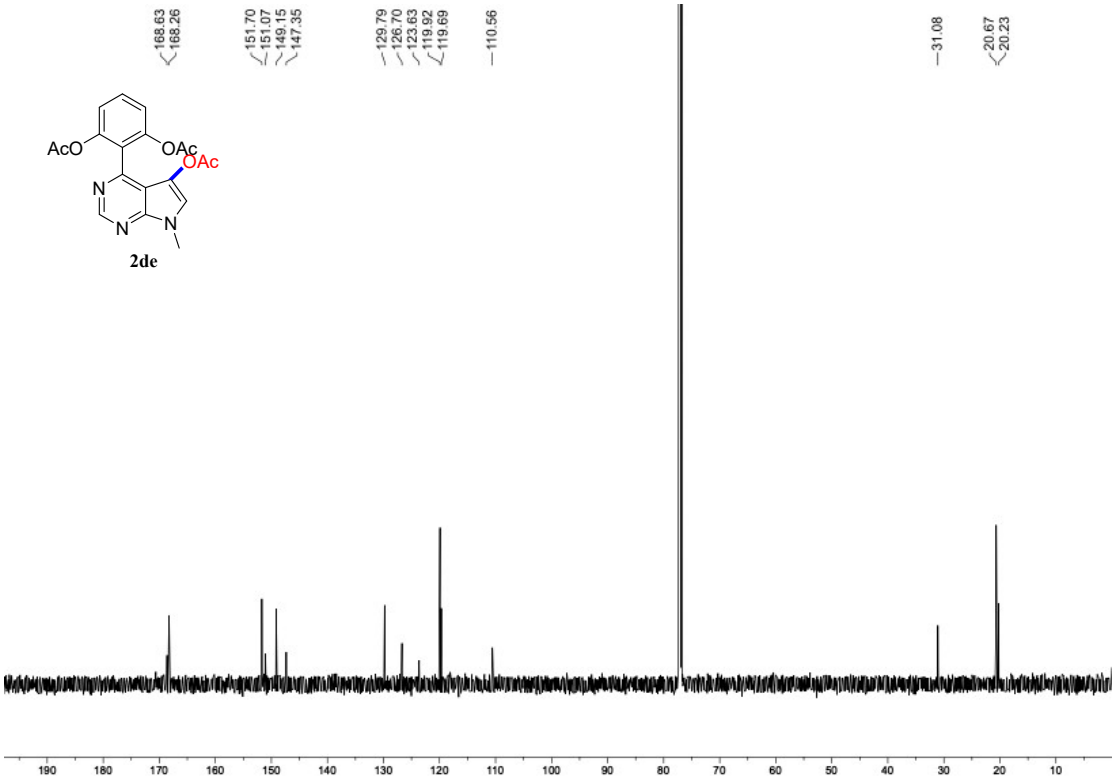

+ Scan (0.2-0.2 min, 4 scans) MNJ-B1-2Cl.d Subtract
x10 5
302.0685
244.0630
371.1131
525.1210
Cl
OAc
N
N
N
2dc
Counts vs. Mass-to-Charge (m/z)

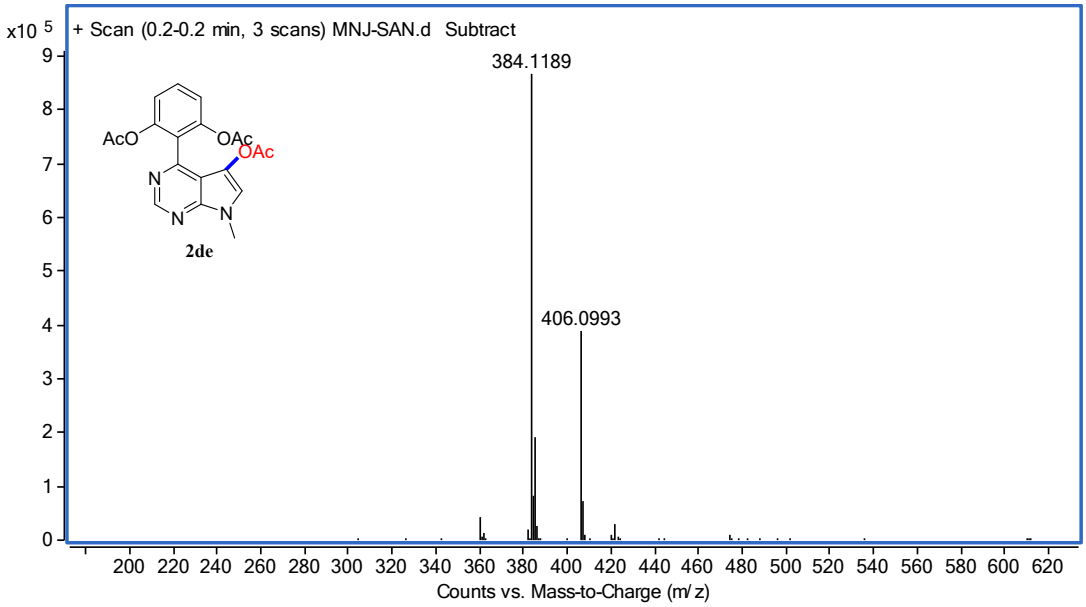

AcO
OAc
N
N
N
2dd
8.9566
7.5920
7.5887
7.5768
7.5735
7.5312
7.5278
7.5159
7.5153
7.5127
7.5000
7.4965
7.3912
7.3890
7.3761
7.3739
7.3610
7.3588
7.3382
7.3363
7.3219
7.3200
7.2764
7.2559
3.9057
1.9853
1.9335
1.01
1.09
1.09
1.03
0.94
1.00
3.29
3.15
3.24
168.77
168.70
155.06
151.70
148.40
147.78
131.17
130.30
130.28
126.84
125.46
122.69
119.58
109.74
31.06
20.75
20.29

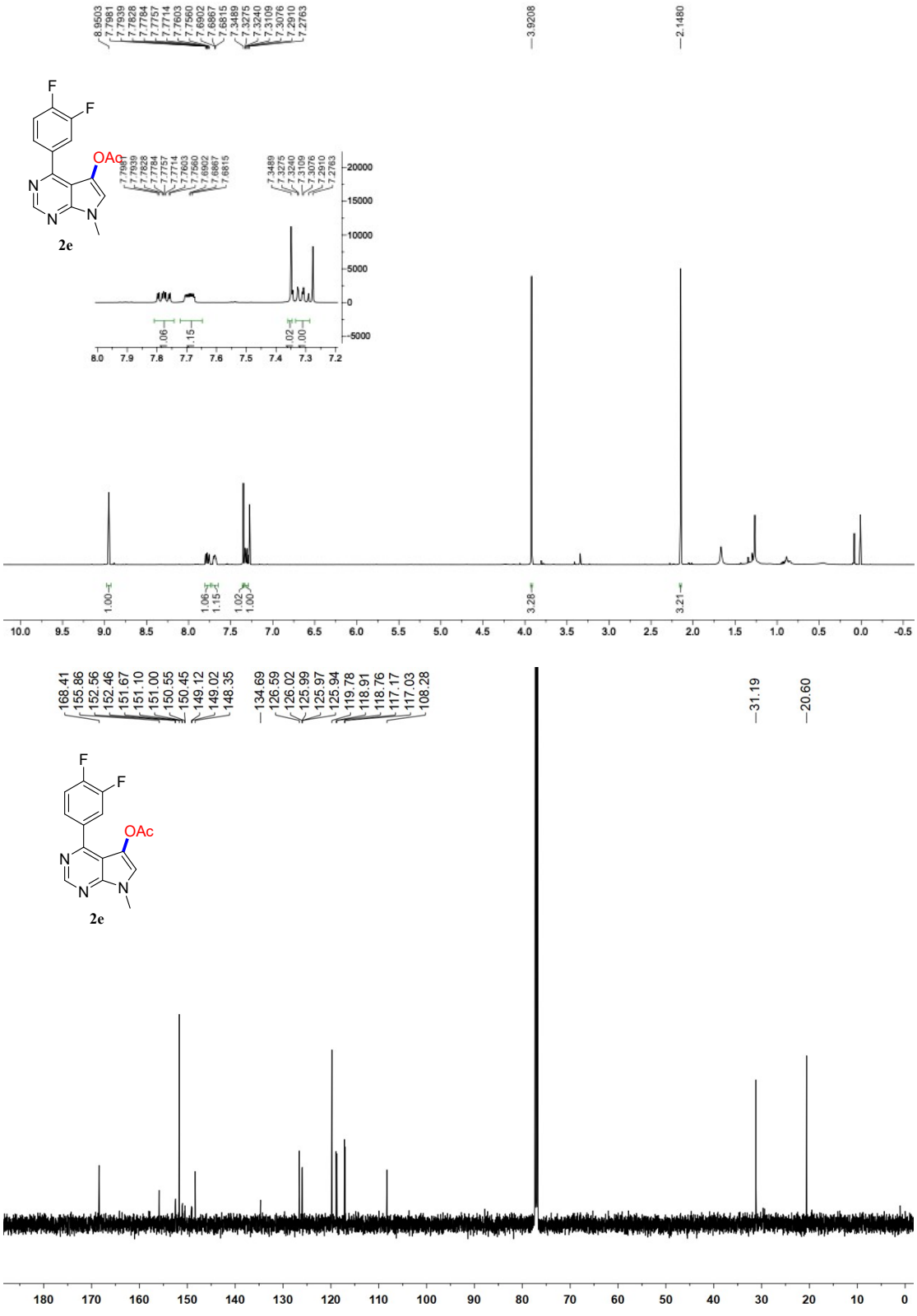

x10 4
+ Scan (0.2-0.2 min, 3 scans) MNJ-B2-2OAc.d Subtract
326.1135
284.1037
AcO
OAc
N
N
N
2dd
Counts vs. Mass-to-Charge (m/z)

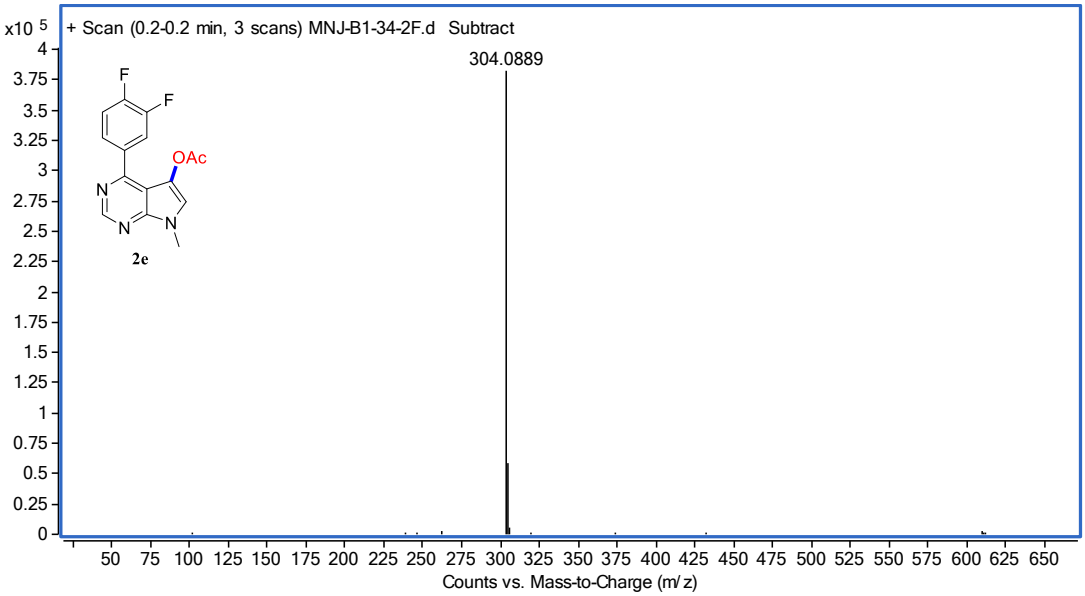

8.9724
7.5201
7.3018
7.2767
7.2700
7.2535
3.9144
1.9227
1.9101
AcO
OAc
OAc
N
N
N
2de
1.11
0.94
0.99
0.91

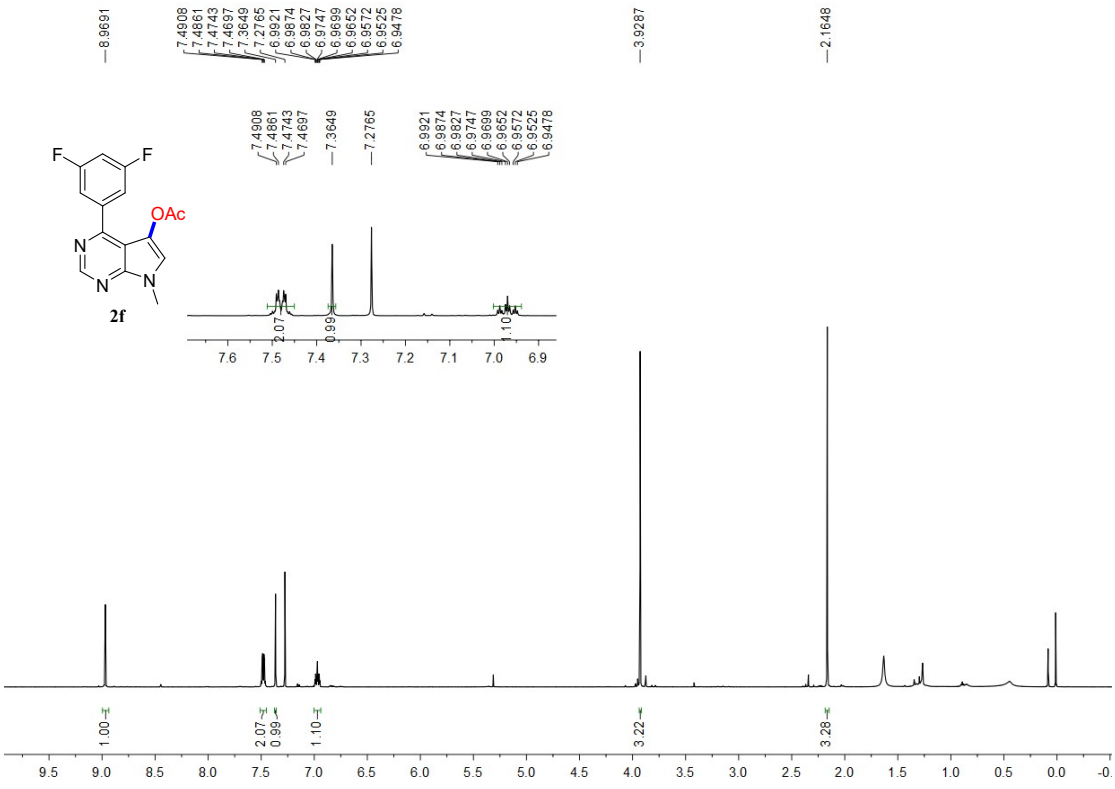

1.00
1.11
0.94
0.99
0.91
3.06
2.81
5.89

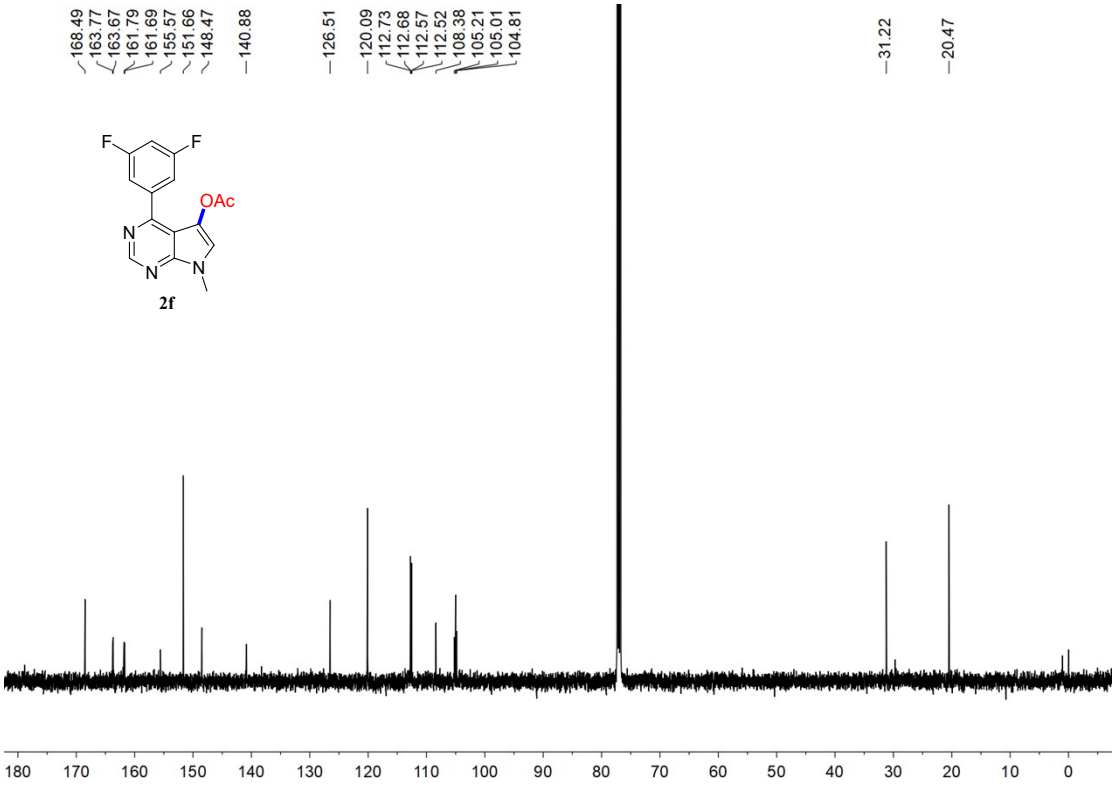

168.63
168.26
151.70
151.07
149.15
147.35
129.79
126.70
123.63
119.92
119.69
110.56
31.08
20.67
20.23
AcO
OAc
OAc
N
N
N
2de
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

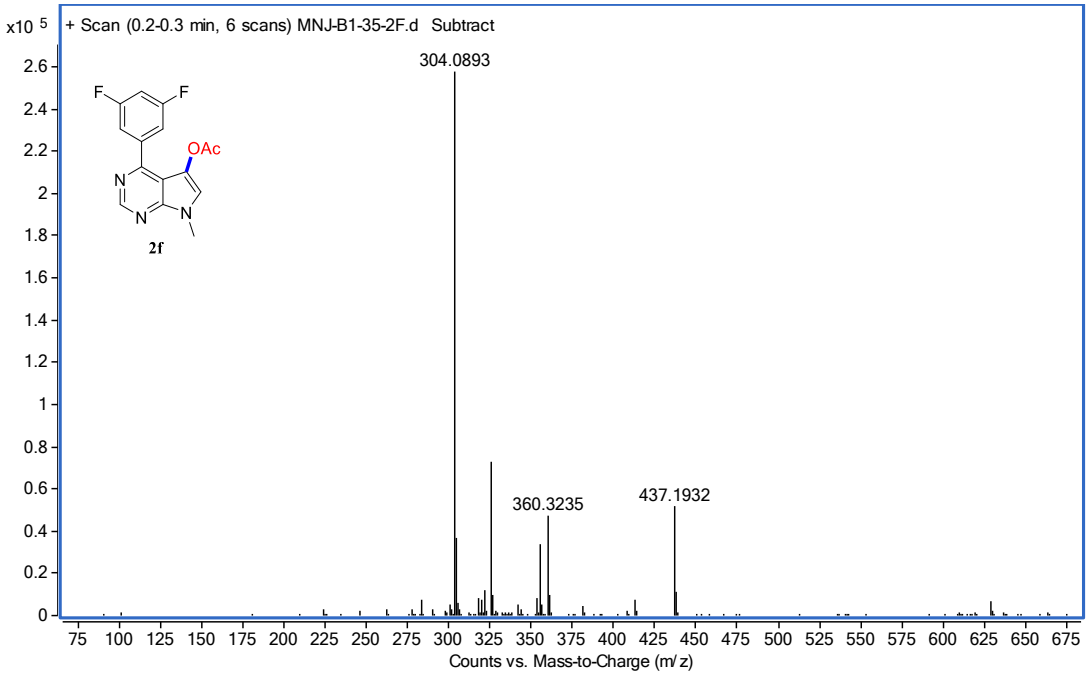

x10 5
+ Scan (0.2-0.2 min, 3 scans) MNJ-SAN.d Subtract
384.1189
406.0993
AcO
OAc
OAc
N
N
N
2de
9
8
7
6
5
4
3
2
1
0
200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560 580 600 620
Counts vs. Mass-to-Charge (m/z)

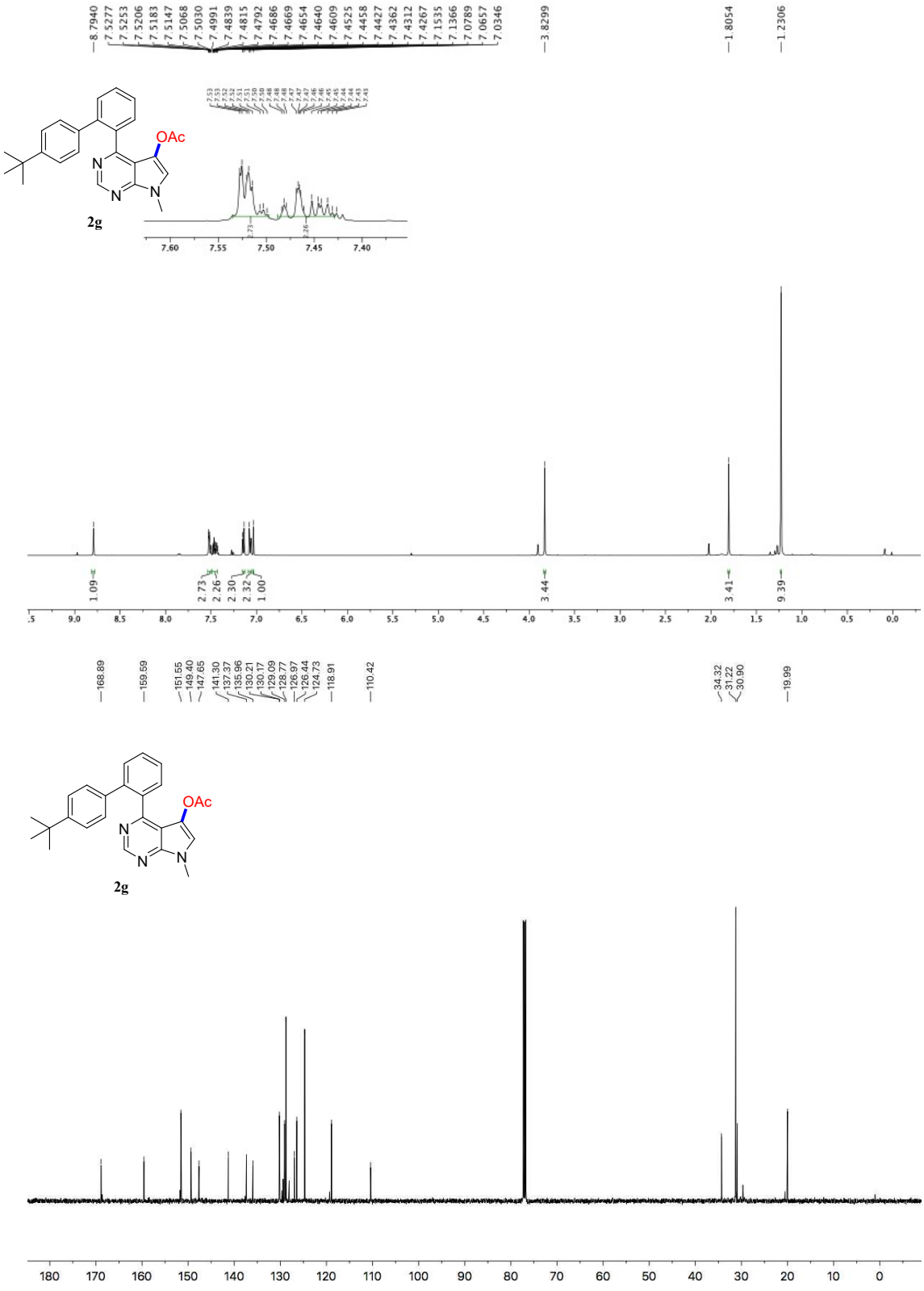

8.9503
7.7981
7.7939
7.7828
7.7784
7.7757
7.7714
7.7603
7.7560
7.6902
7.6867
7.6815
7.3489
7.3275
7.3240
7.3109
7.3076
7.2910
7.2763
3.9208
2.1480
F
F
OAc
N
N
N
2e
1.00
1.06
1.15
1.02
1.00
3.28
3.21
168.41
155.86
152.56
152.46
151.67
151.10
151.00
150.55
150.45
149.12
149.02
148.35
134.69
126.59
126.02
125.99
125.97
125.94
119.78
118.91
118.76
117.17
117.03
108.28
31.19
20.60

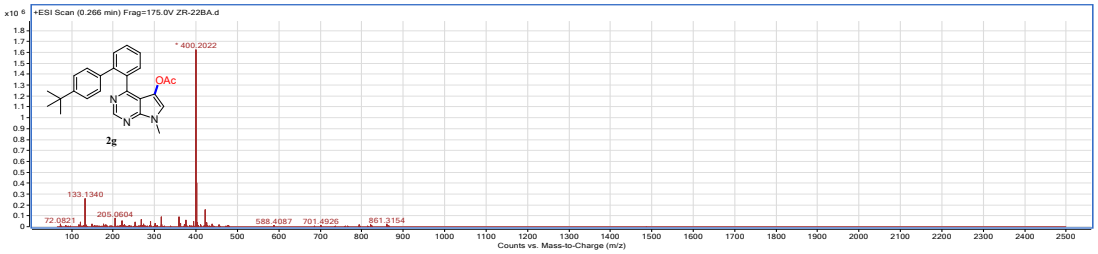

+ Scan (0.2-0.2 min, 3 scans) MNJ-B1-34-2F.d Subtract
304.0889
x10 5
Counts vs. Mass-to-Charge (m/z)
2e

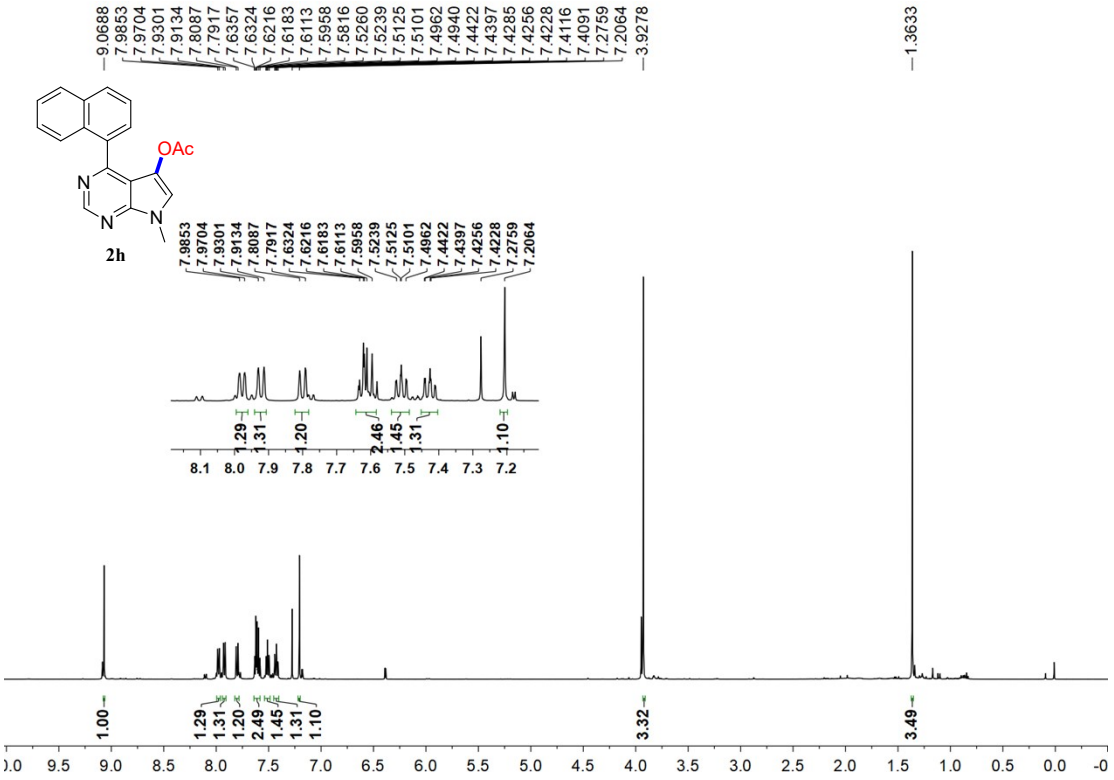

8.9691
7.4908
7.4861
7.4743
7.4697
7.3649
7.2765
6.9921
6.9874
6.9827
6.9747
6.9699
6.9652
6.9572
6.9525
6.9478
3.9287
2.1648
2f

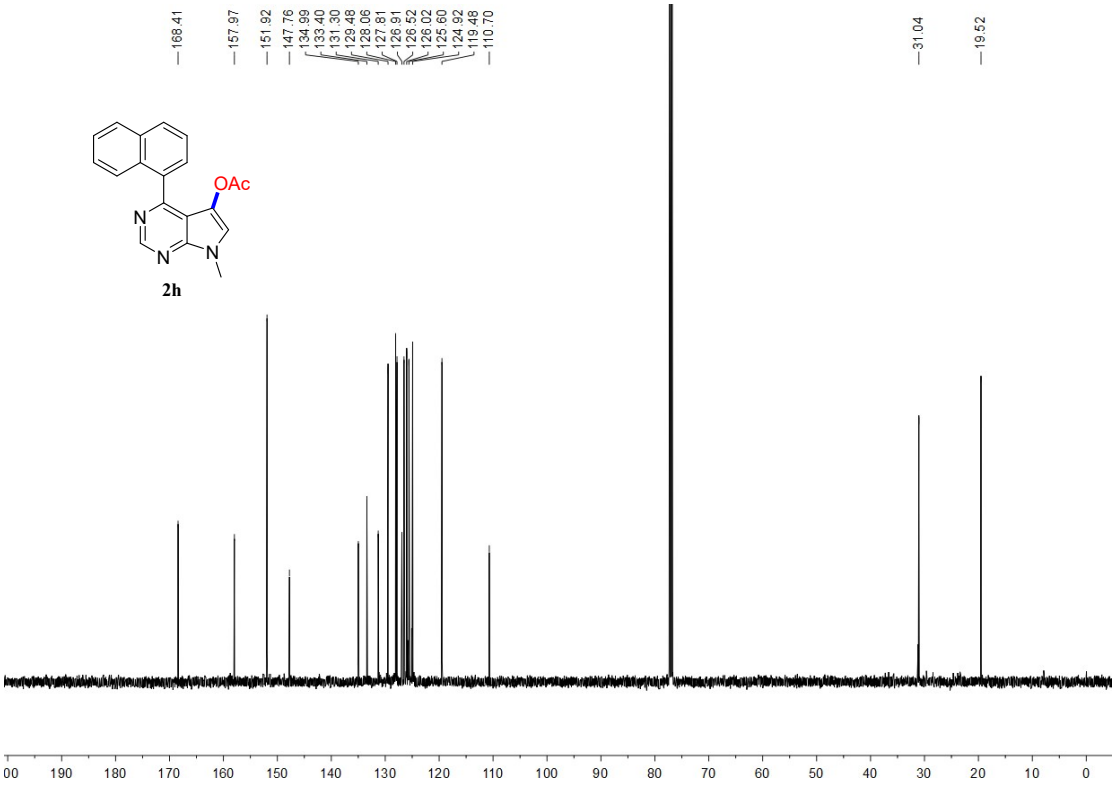

168.49
163.77
163.67
161.79
161.69
155.57
151.66
148.47
140.88
126.51
120.09
112.73
112.68
112.57
112.52
108.38
105.21
105.01
104.81
31.22
20.47
F
F
OAc
N
N
N
2f
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

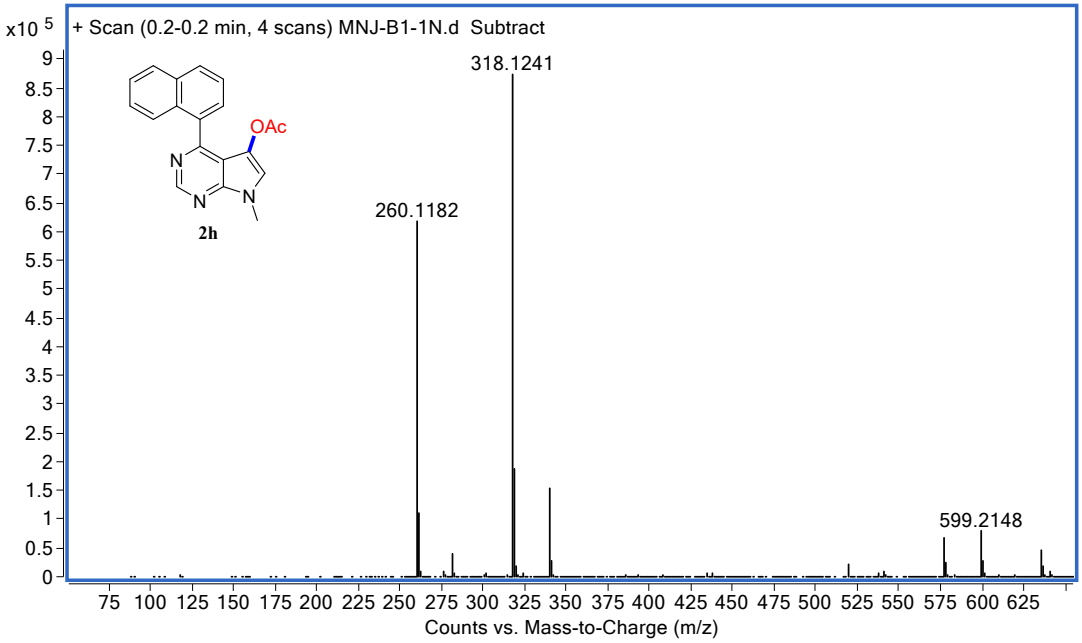

x10 5
+ Scan (0.2-0.3 min, 6 scans) MNJ-B1-35-2F.d Subtract
304.0893
360.3235
437.1932
F
F
OAc
N
N
N
2f
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
75 100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 625 650 675
Counts vs. Mass-to-Charge (m/z)

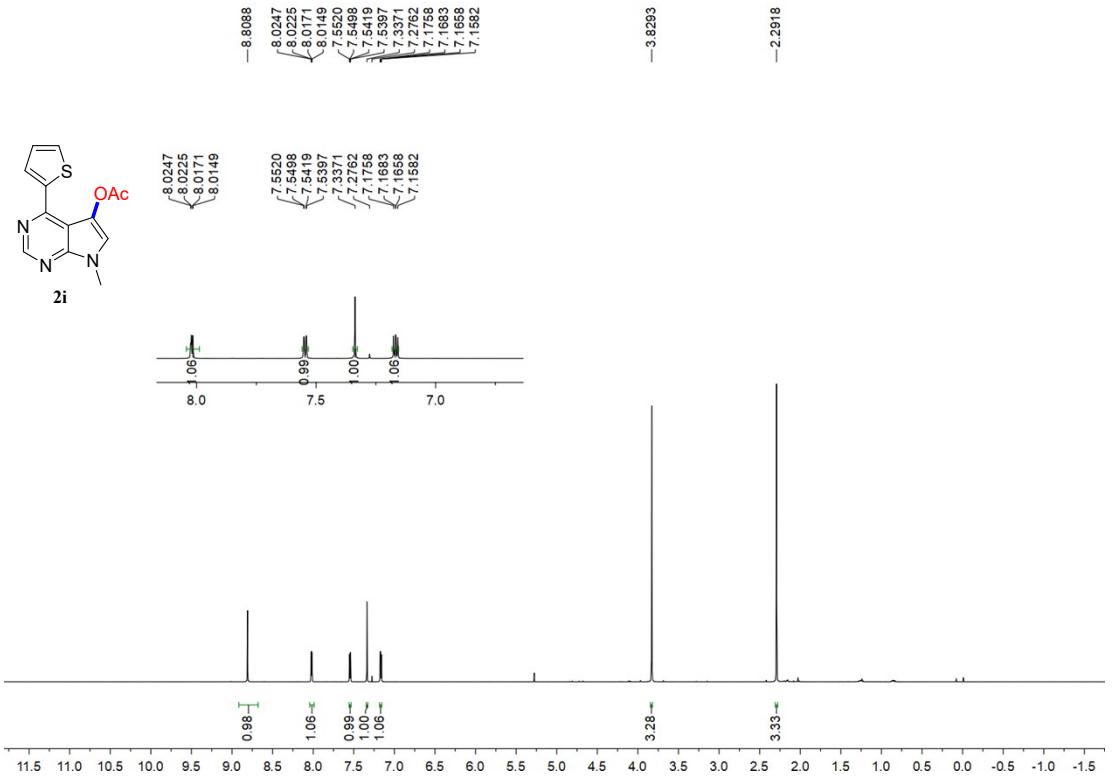

8.7940
7.5277
7.5253
7.5206
7.5183
7.5147
7.5068
7.5030
7.4991
7.4839
7.4815
7.4792
7.4686
7.4669
7.4654
7.4640
7.4609
7.4525
7.4458
7.4427
7.4362
7.4312
7.4267
7.1535
7.1366
7.0789
7.0657
7.0346
3.8299
1.8054
1.2306
OAc
N
N
N
2g
7.60
7.55
7.50
7.45
7.40
1.09
2.73
2.26
2.30
2.32
1.00
3.44
3.41
9.39
168.89
159.59
151.55
149.40
147.65
141.30
137.37
135.96
130.21
130.17
129.09
128.77
126.97
126.44
124.73
118.91
110.42
34.32
31.22
30.90
19.99
OAc
N
N
N
2g
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

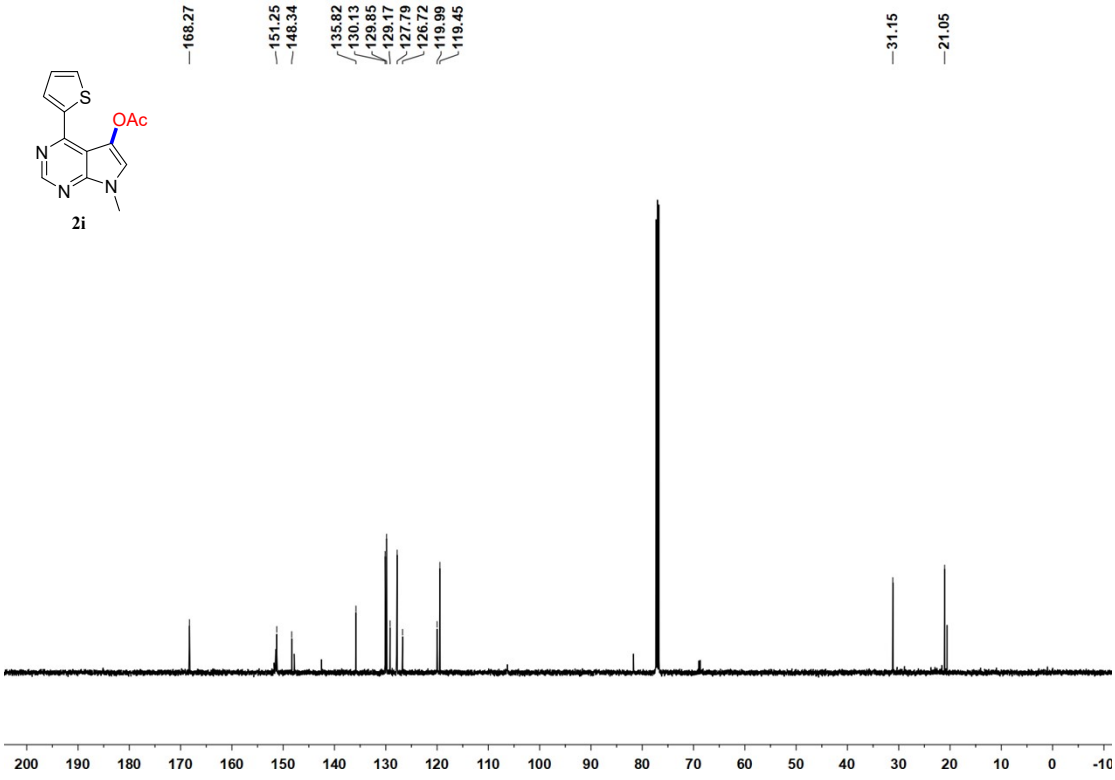

+ESI Scan (0.266 min) Frag=175.0V ZR-22BA.d
400.2022
OAc
2g
133.1340
205.0604
72.0821
588.4087
701.4926
861.3154
Counts vs. Mass-to-Charge (m/z)

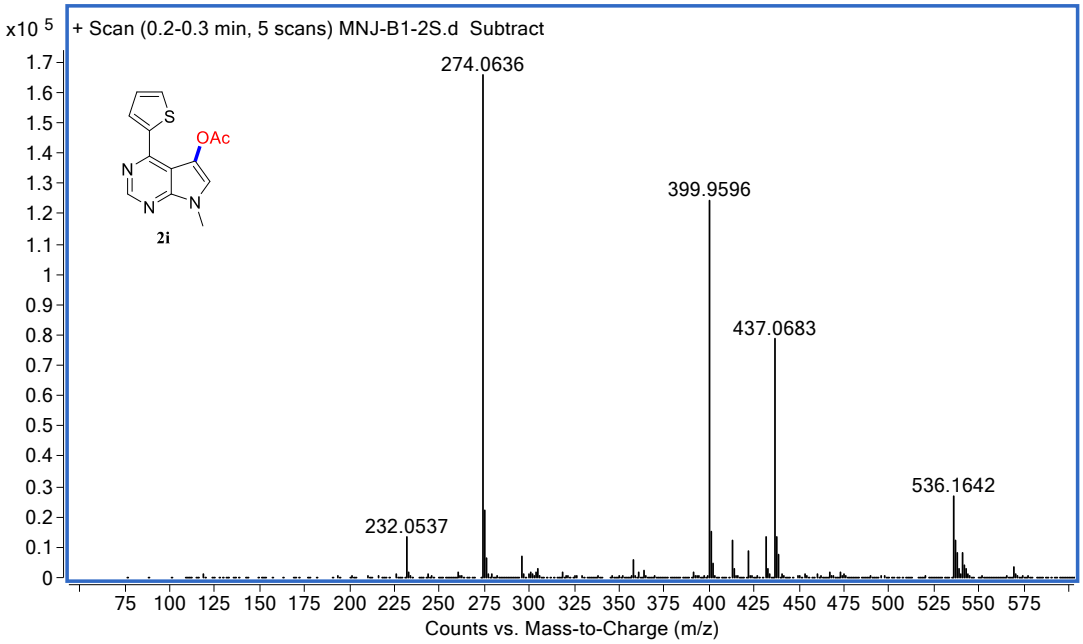

9.0688
7.9853
7.9704
7.9301
7.9134
7.8087
7.7917
7.6357
7.6324
7.6216
7.6183
7.6113
7.5958
7.5816
7.5260
7.5239
7.5125
7.5101
7.4962
7.4940
7.4422
7.4397
7.4285
7.4256
7.4228
7.4116
7.4091
7.2759
7.2064
3.9278
1.3633
OAc
2h
1.29
1.31
1.20
2.46
1.45
1.31
1.10
1.00
3.32
3.49

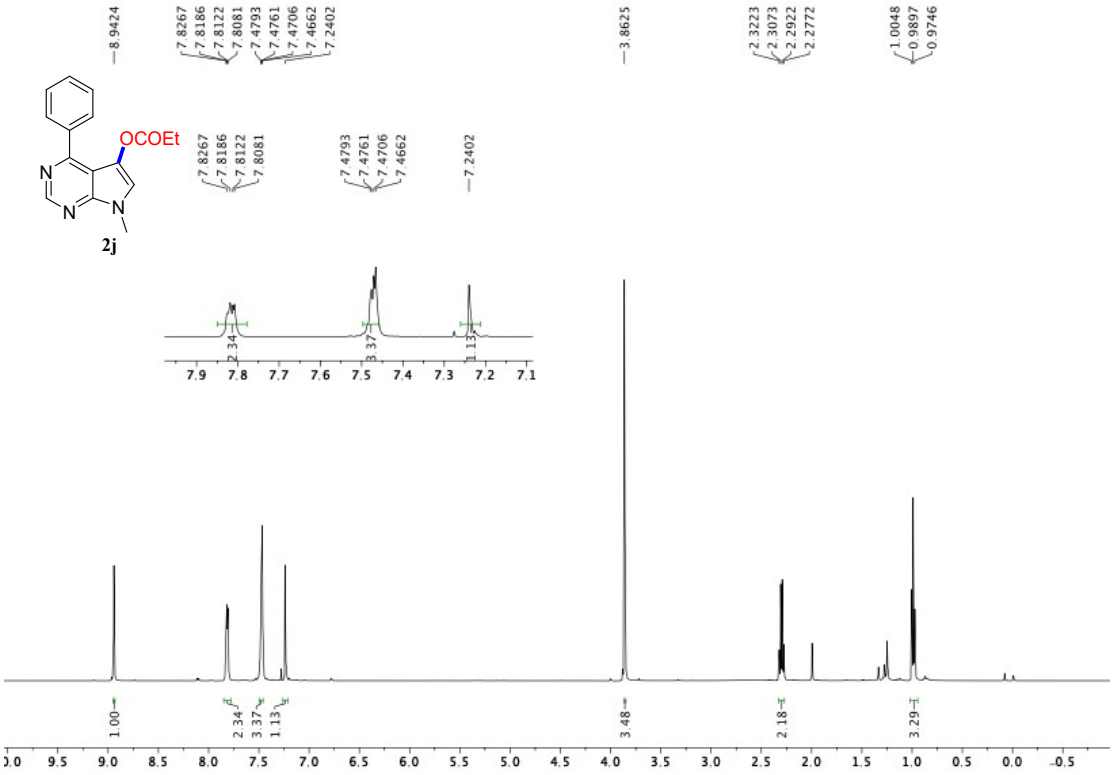

168.41
157.97
151.92
147.76
134.99
133.40
131.30
129.48
128.06
127.81
126.91
126.52
126.02
125.60
124.92
119.48
110.70
31.04
19.52
OAc
N
N
N
2h
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

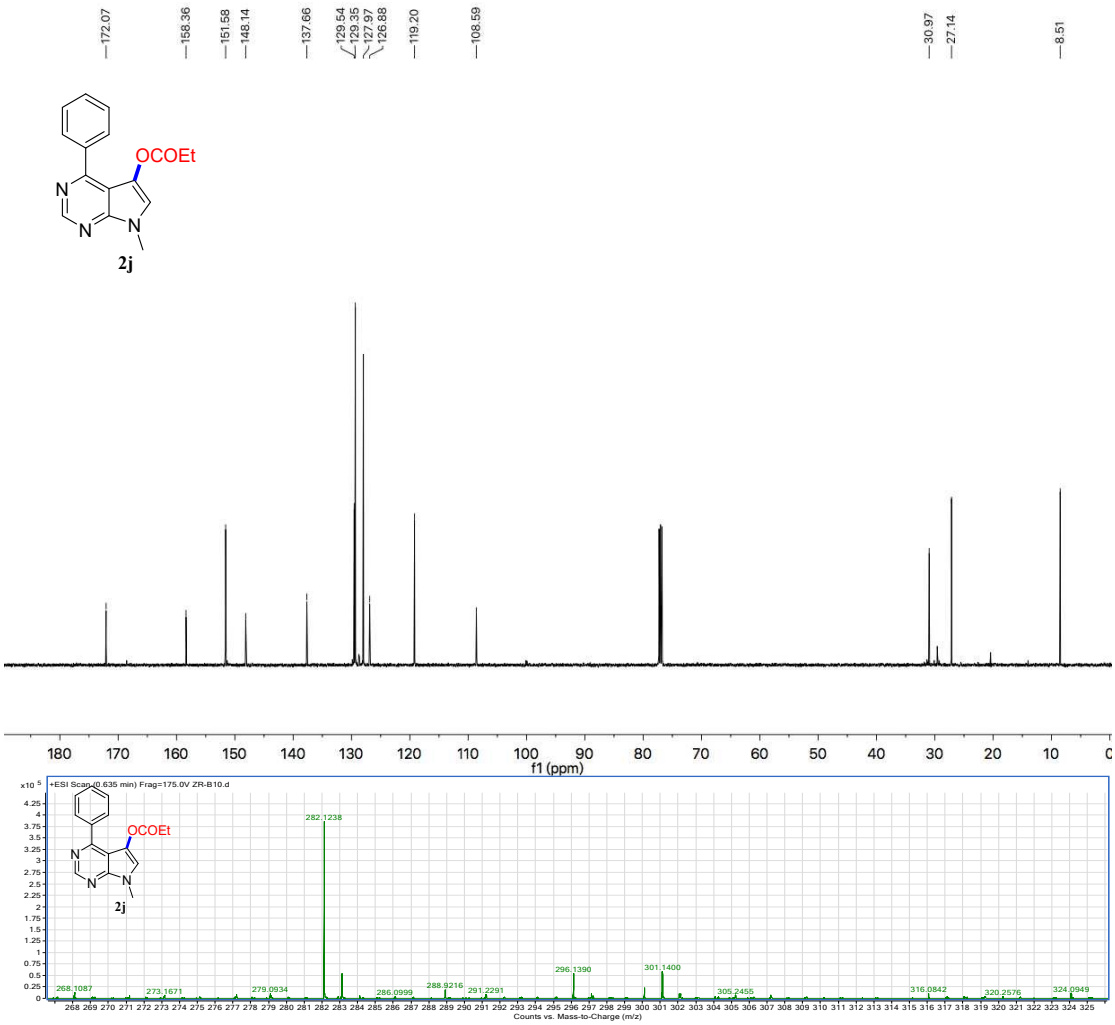

x10 5
+ Scan (0.2-0.2 min, 4 scans) MNJ-B1-1N.d Subtract
318.1241
260.1182
599.2148
OAc
N
N
N
2h
9
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
75 100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 625
Counts vs. Mass-to-Charge (m/z)

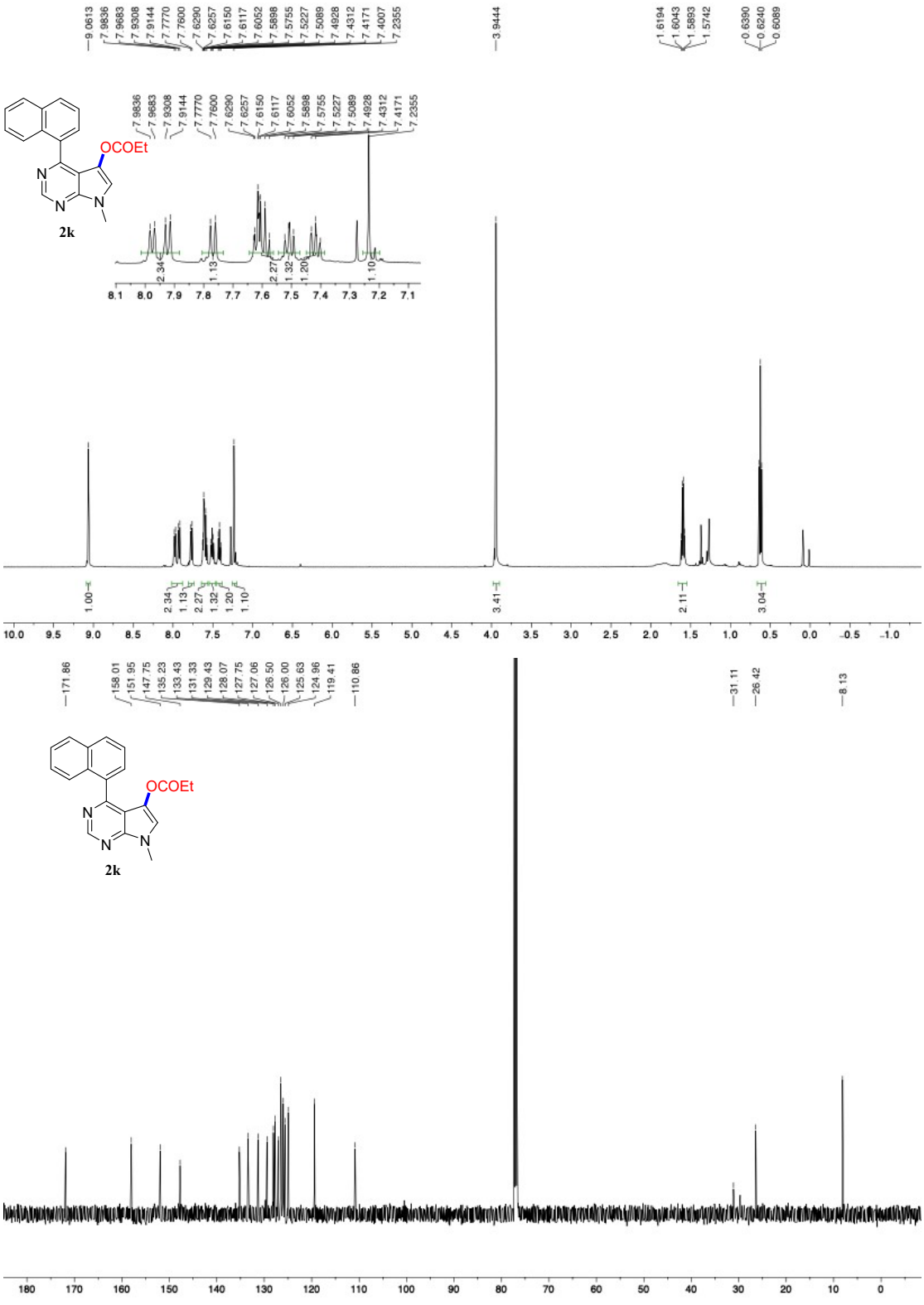

8.8088
8.0247
8.0225
8.0171
8.0149
7.5520
7.5498
7.5419
7.5397
7.3371
7.2762
7.1758
7.1683
7.1658
7.1582
3.8293
2.2918
OAc
N
N
S
N
2i
1.06
0.99
1.00
1.06
8.0
7.5
7.0
0.98
1.06
0.99
1.00
1.06
3.28
3.33

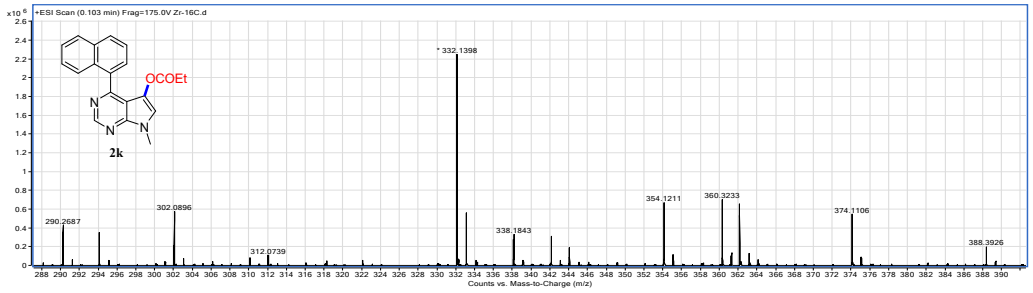

168.27
151.25
148.34
135.82
130.13
129.85
129.17
127.79
126.72
119.99
119.45
31.15
21.05
OAc
N
N
S
N
2i

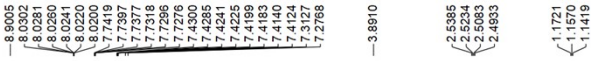

x10 5
+ Scan (0.2-0.3 min, 5 scans) MNJ-B1-2S.d Subtract
274.0636
399.9596
437.0683
536.1642
232.0537
OAc
2i
Counts vs. Mass-to-Charge (m/z)

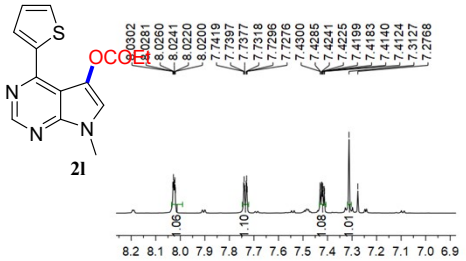

OCOEt
2j

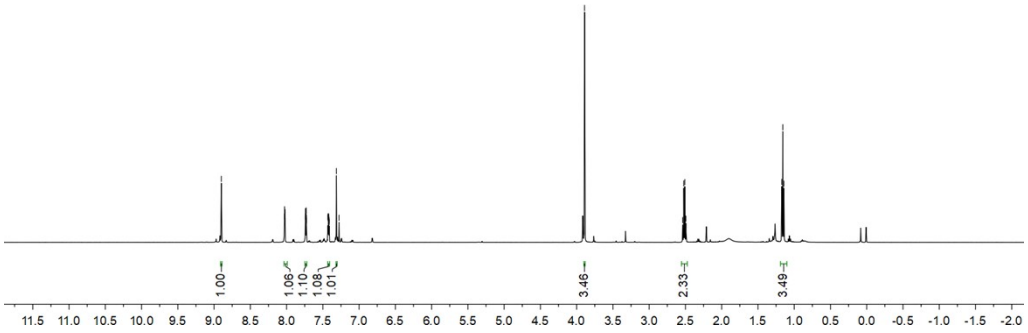

172.07
158.36
151.58
148.14
137.66
129.54
129.35
127.97
126.88
119.20
108.59
30.97
27.14
8.51
OCOEt
N
N
N
2j
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
+ESI Scan (0.635 min) Frag=175.0V ZR-B10.d
x10 5
OCOEt
2j
282.1238
296.1390
301.1400
268.1087
273.1671
279.0934
286.0999
288.9216
291.2291
305.2455
316.0842
320.2576
324.0949
Counts vs. Mass-to-Charge (m/z)

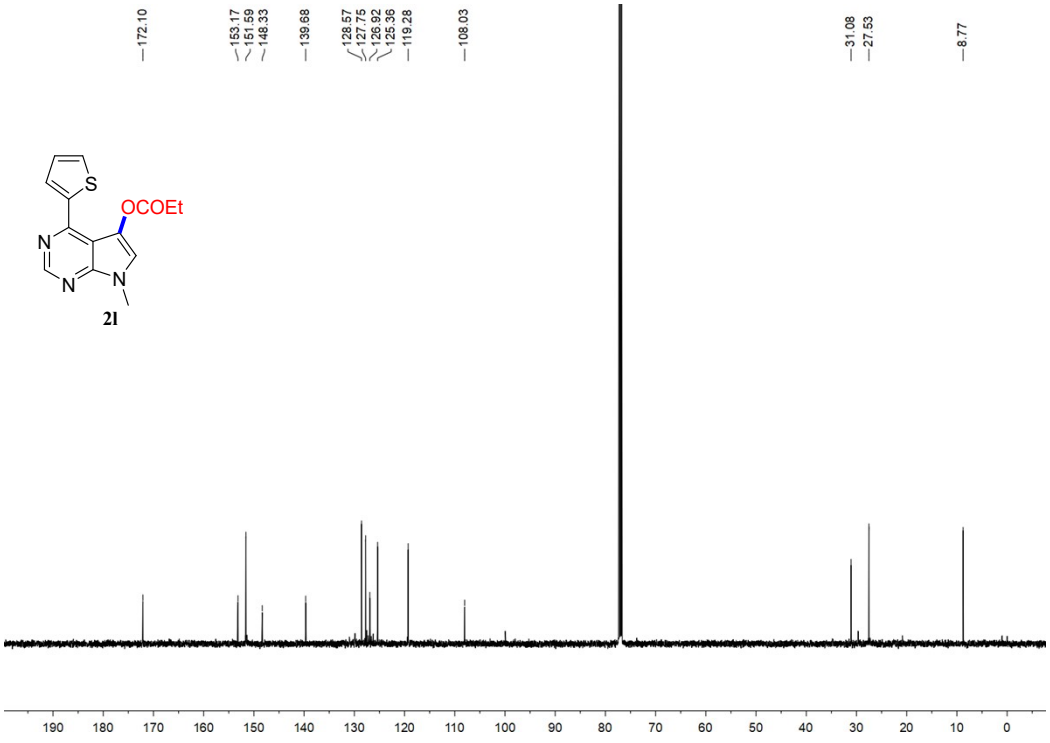

OCOEt
2k
OCOEt
2k

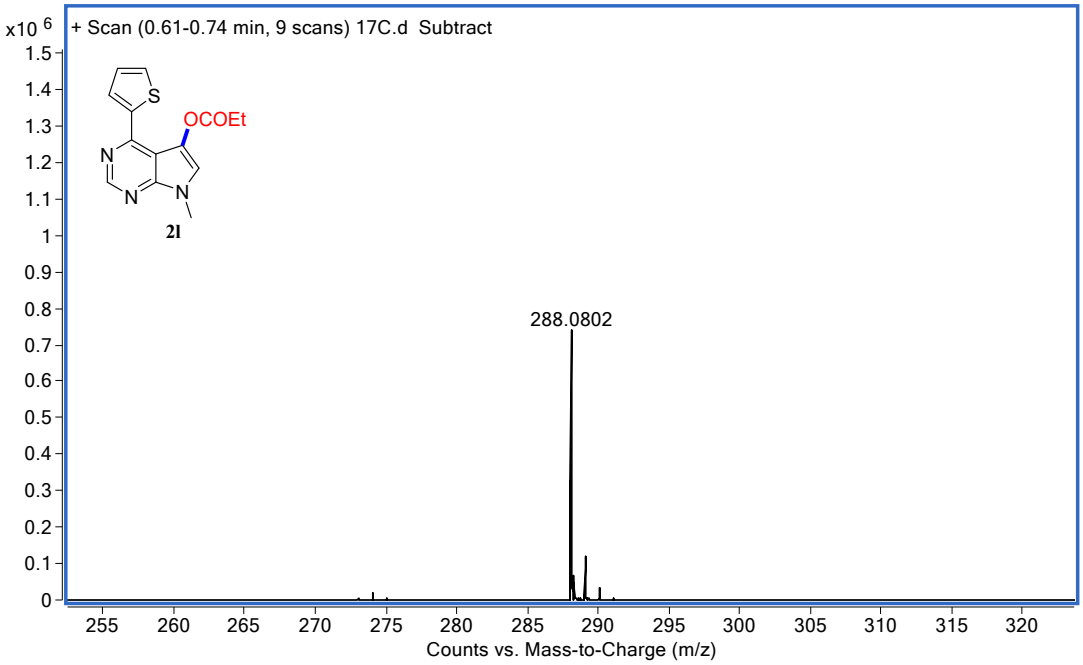

+ESI Scan (0.103 min) Frag=175.0V Zr-16C.d
OCOEt
2k
332.1398
354.1211
360.3233
374.1106
388.3926
290.2687
302.0896
312.0739
338.1843
Counts vs. Mass-to-Charge (m/z)

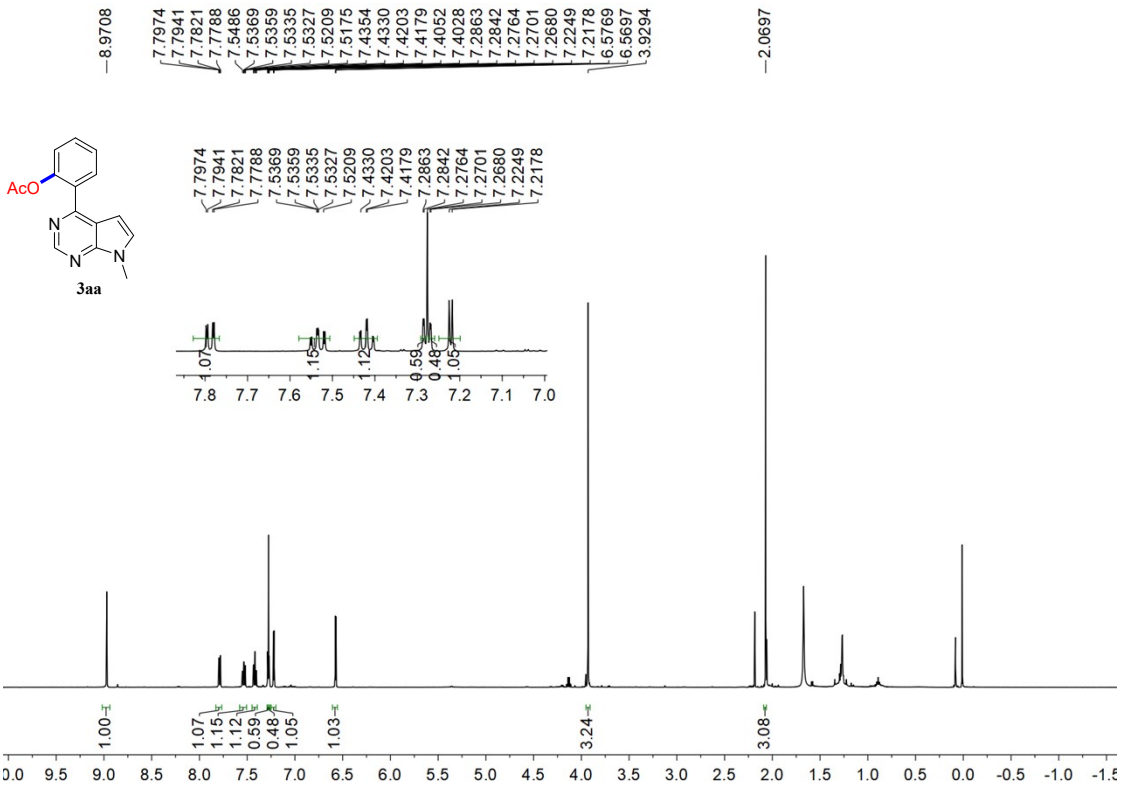

8.9005
8.0302
8.0281
8.0260
8.0241
8.0220
8.0200
7.7419
7.7397
7.7377
7.7318
7.7296
7.7276
7.4300
7.4285
7.4241
7.4225
7.4199
7.4183
7.4140
7.4124
7.3127
7.2768
3.8910
2.5385
2.5234
2.5083
2.4933
1.1721
1.1570
1.1419

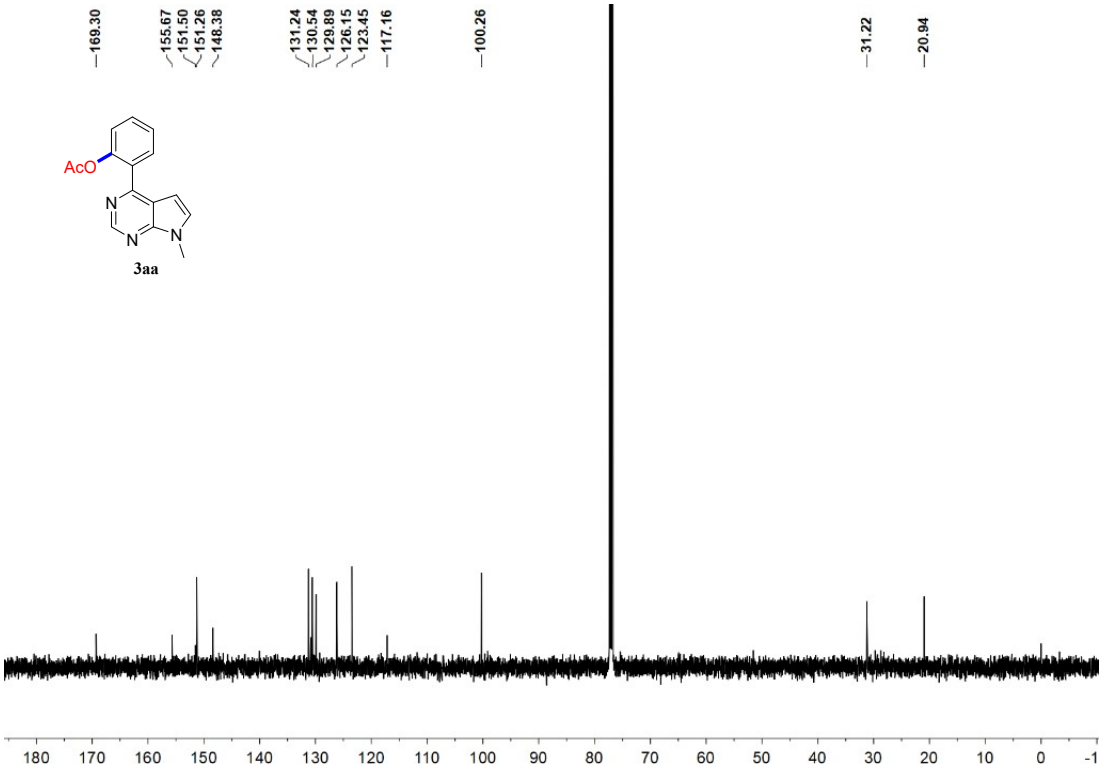

OCOEt
2l
1.06
1.10
1.08
1.01

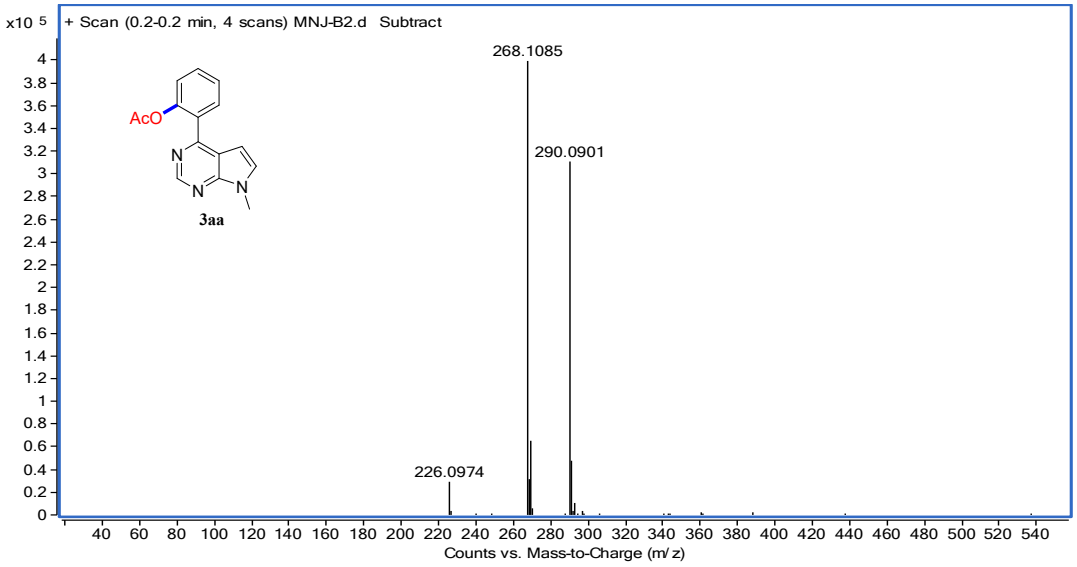

1.00
1.06
1.10
1.08
1.01
3.46
2.33
3.49

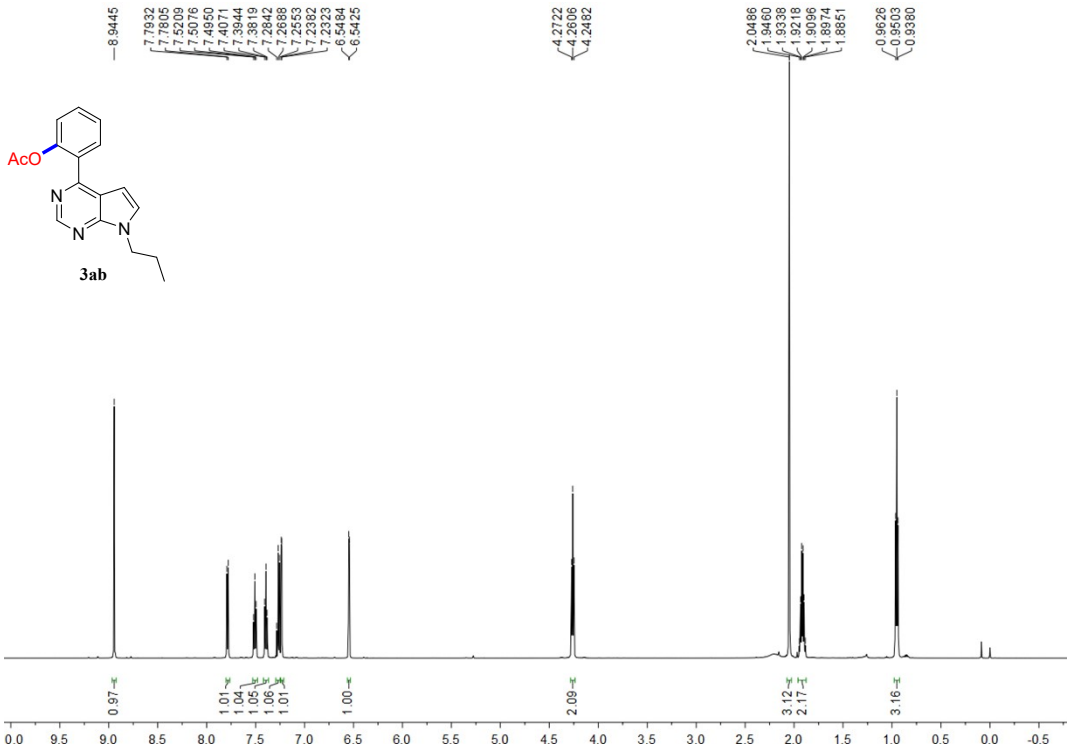

172.10
153.17
151.59
148.33
139.68
128.57
127.75
126.92
125.36
119.28
108.03
31.08
27.53
8.77
OCOEt
2l

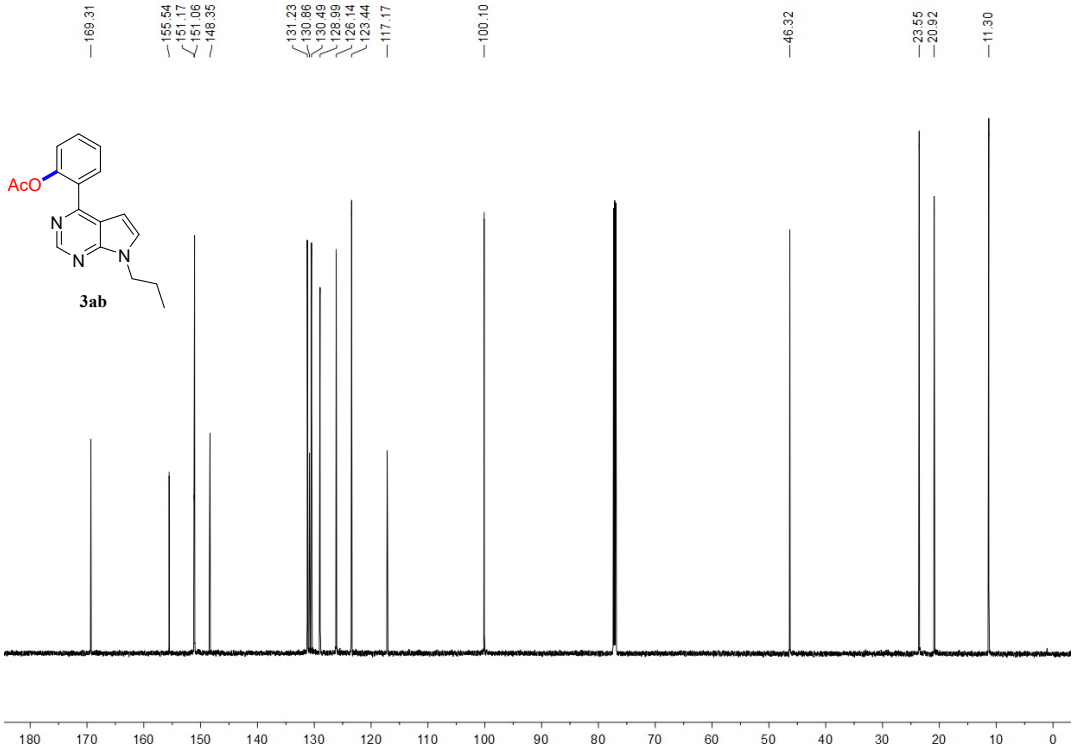

x10 6
+ Scan (0.61-0.74 min, 9 scans) 17C.d Subtract
OCOEt
2l
288.0802
Counts vs. Mass-to-Charge (m/z)

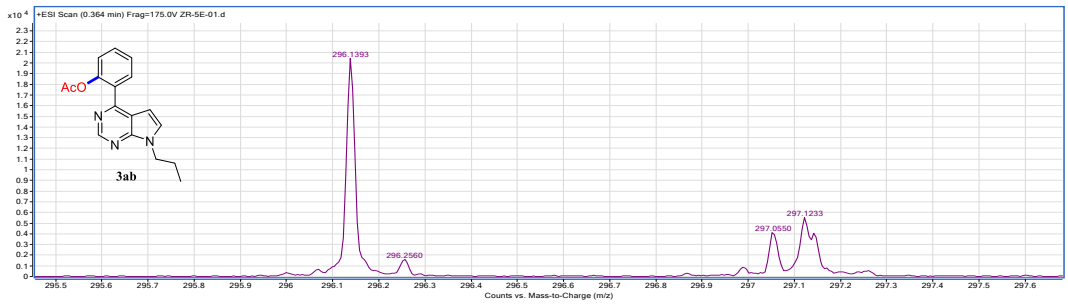

8.9708
7.7974
7.7941
7.7821
7.7788
7.5486
7.5369
7.5359
7.5335
7.5327
7.5209
7.5175
7.4354
7.4330
7.4203
7.4179
7.4052
7.4028
7.2863
7.2842
7.2764
7.2701
7.2680
7.2249
7.2178
6.5769
6.5697
3.9294
2.0697
AcO
3aa
1.00
1.07
1.15
1.12
0.59
0.48
1.05
1.03
3.24
3.08

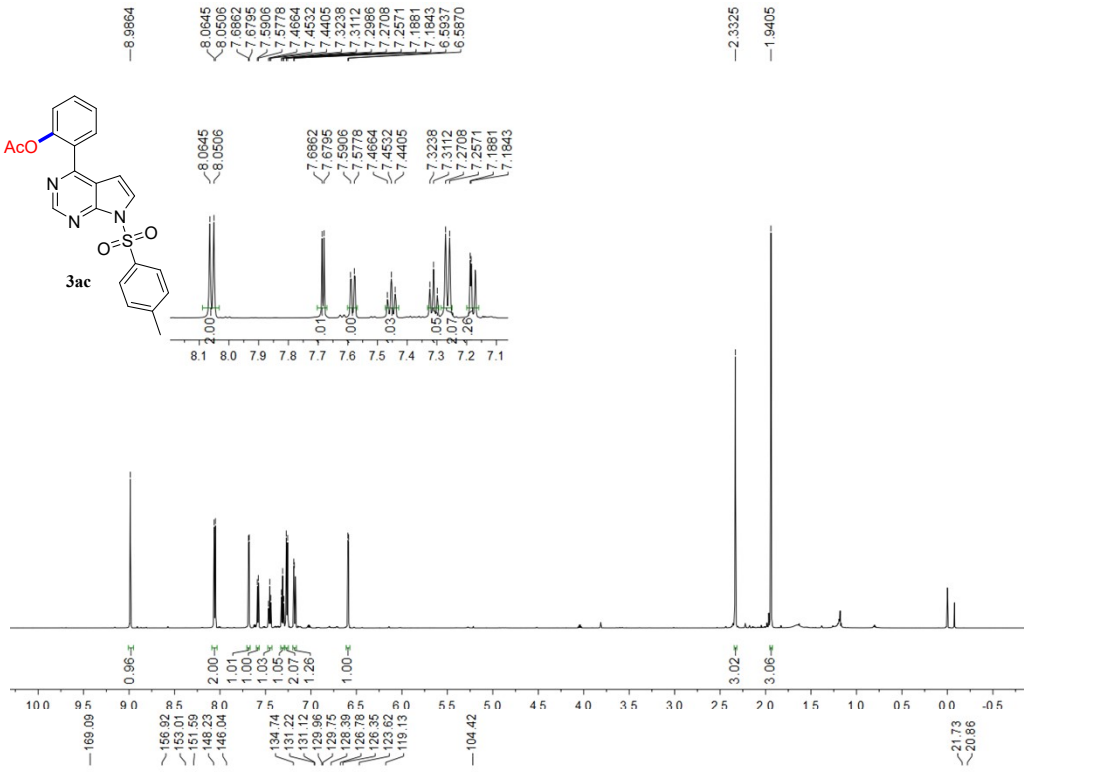

169.30
155.67
151.50
151.26
148.38
131.24
130.54
129.89
126.15
123.45
117.16
100.26
31.22
20.94
AcO
N
N
N
3aa
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

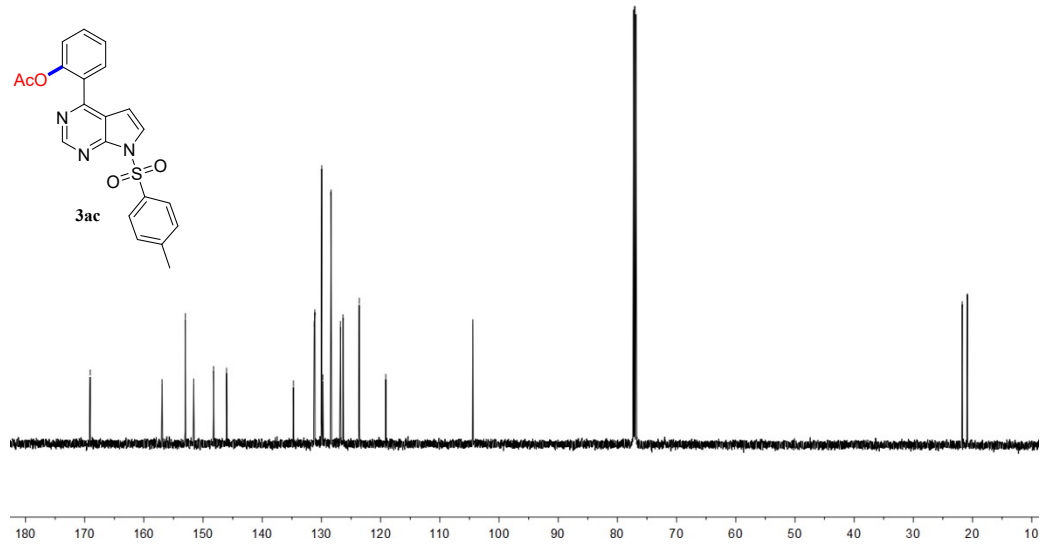

x10 5
+ Scan (0.2-0.2 min, 4 scans) MNJ-B2.d Subtract
268.1085
290.0901
226.0974
AcO
N
N
N
3aa
4 3.8 3.6 3.4 3.2 3 2.8 2.6 2.4 2.2 2 1.8 1.6 1.4 1.2 1 0.8 0.6 0.4 0.2 0
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540
Counts vs. Mass-to-Charge (m/z)

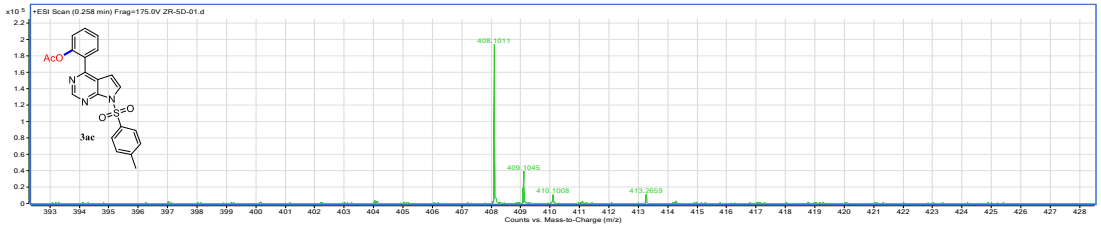

8.9445
7.7932
7.7805
7.5209
7.5076
7.4950
7.4071
7.3944
7.3819
7.2842
7.2688
7.2553
7.2382
7.2323
6.5484
6.5425
4.2722
4.2606
4.2482
2.0486
1.9460
1.9338
1.9218
1.9096
1.8974
1.8851
0.9626
0.9503
0.9380
AcO
N
N
N
3ab
0.97
1.01
1.04
1.05
1.06
1.01
1.00
2.09
3.12
2.17
3.16

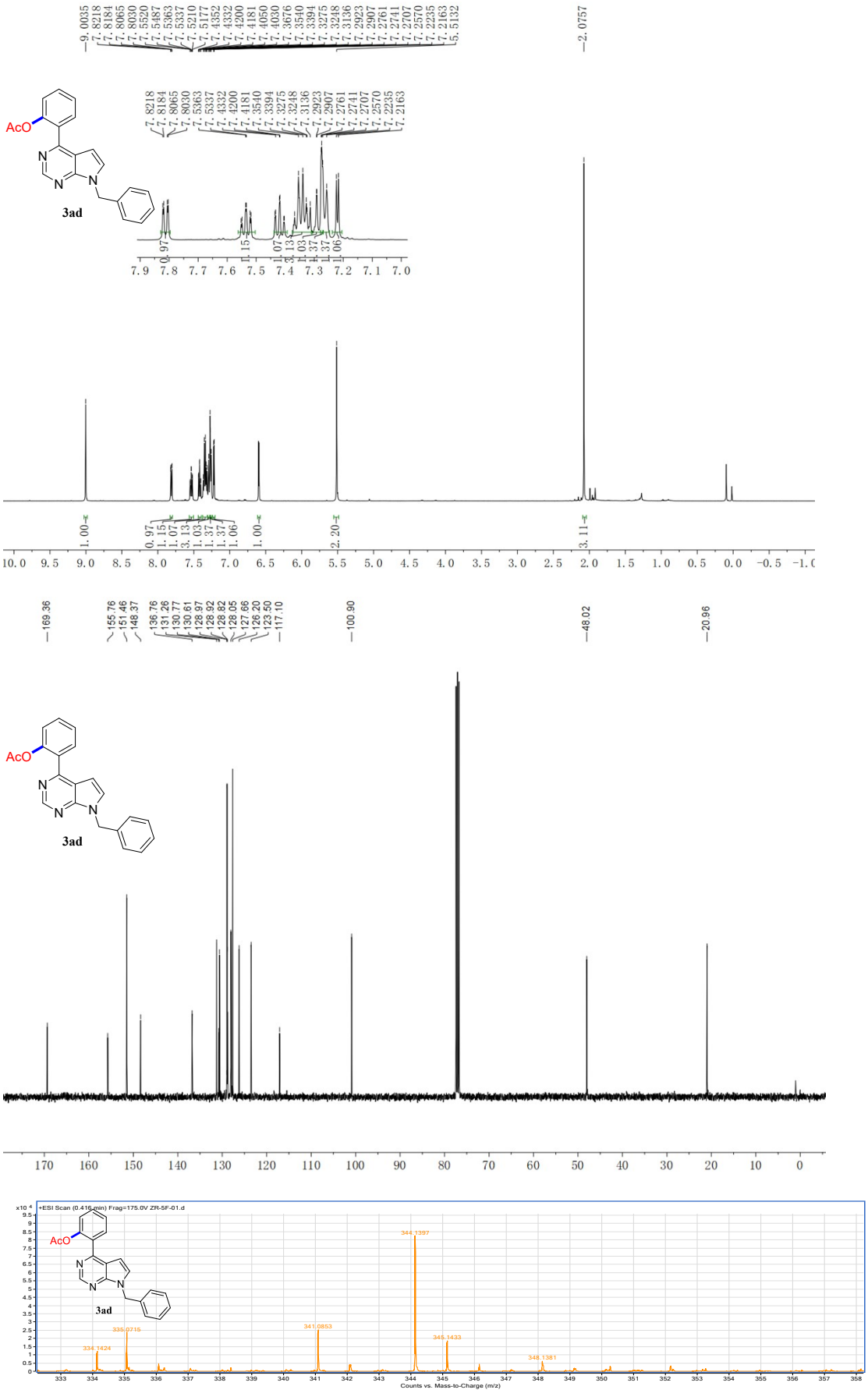

169.31
155.54
151.17
151.06
148.35
131.23
130.86
130.49
128.99
126.14
123.44
117.17
100.10
46.32
23.55
20.92
11.30
AcO
N
N
N
3ab


+ESI Scan (0.364 min) Frag=175.0V ZR-5E-01.d
296.1393
296.2560
297.0550
297.1233
AcO
N
N
N
3ab
Counts vs. Mass-to-Charge (m/z)

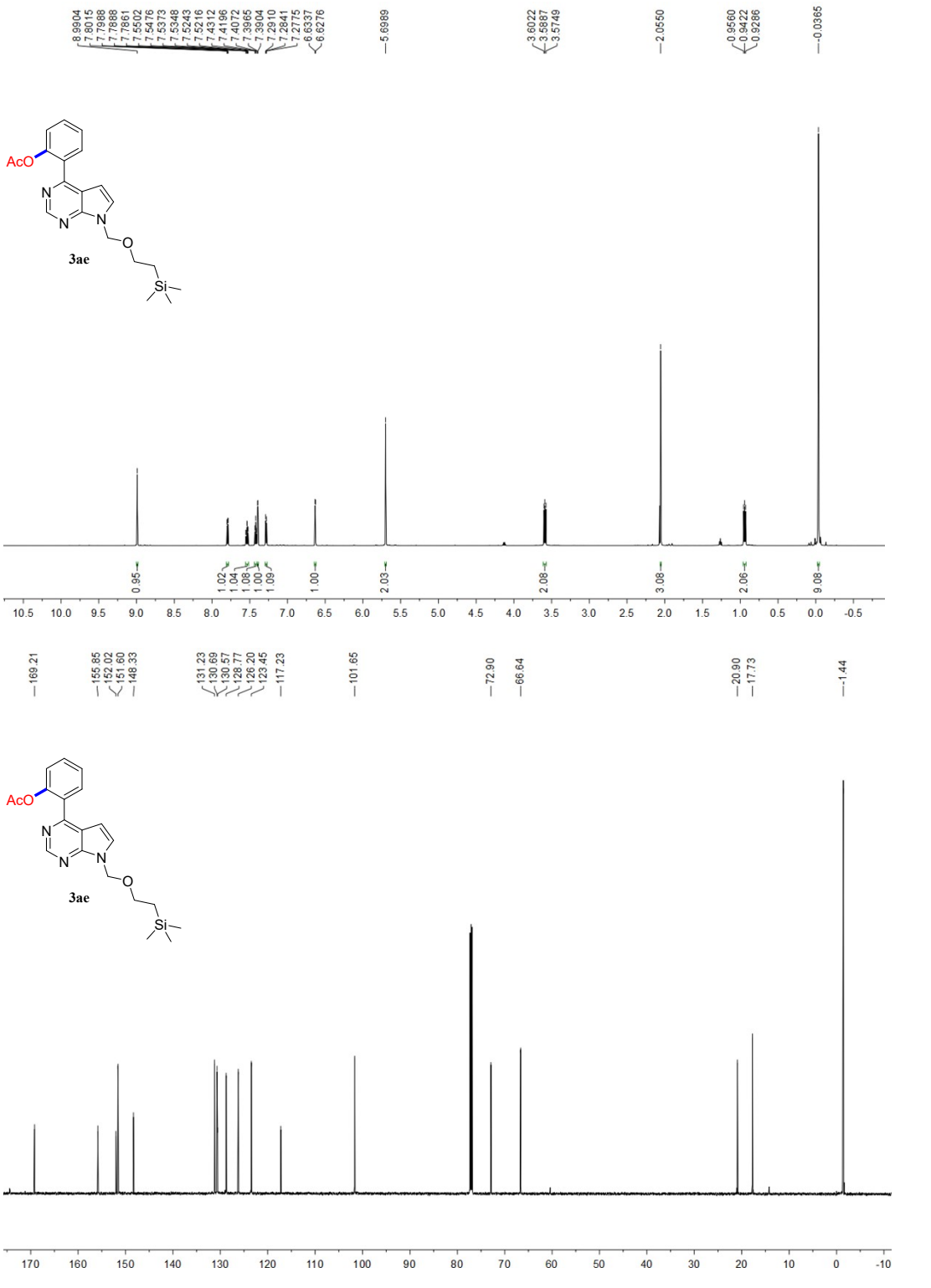

AcO
3ac

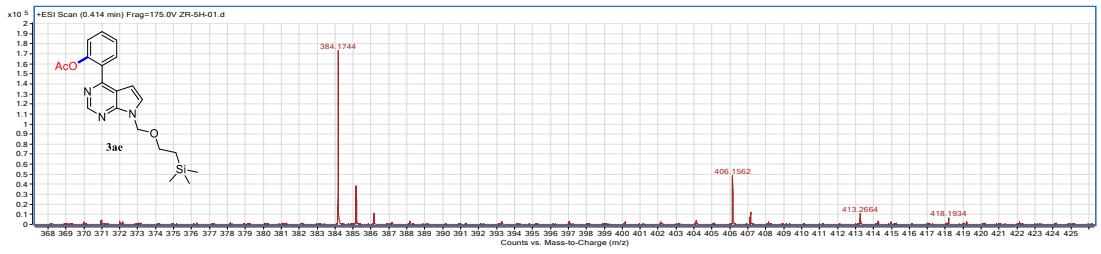

AcO
3ac

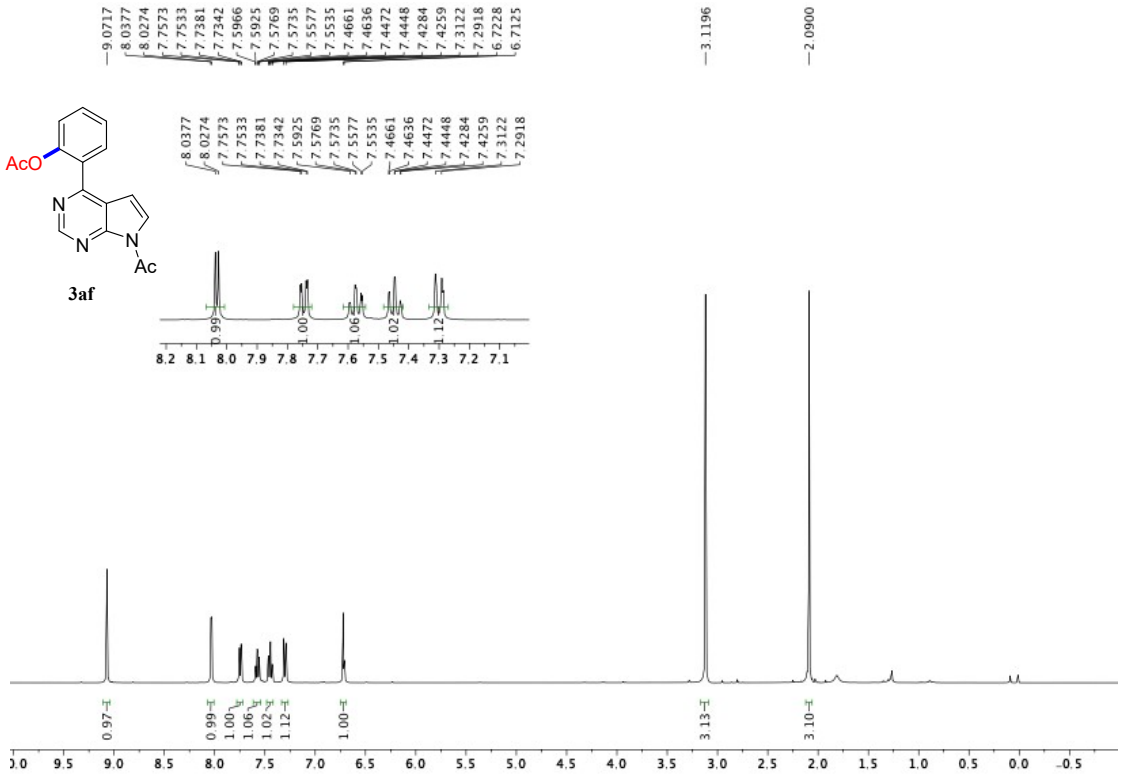

+ESI Scan (0.258 min) Frag=175.0V ZR-5D-01.d
AcO
3ac
408.1011
409.1045
410.1008
413.2659
Counts vs. Mass-to-Charge (m/z)

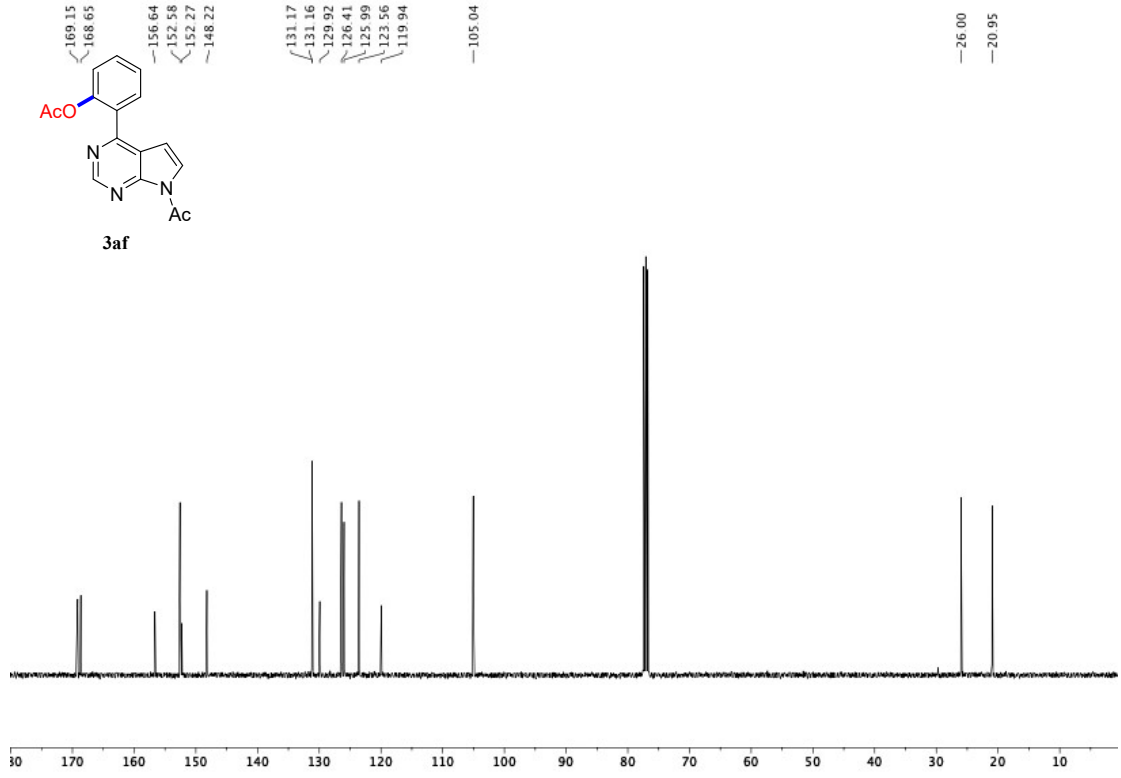

AcO
N
N
3ad

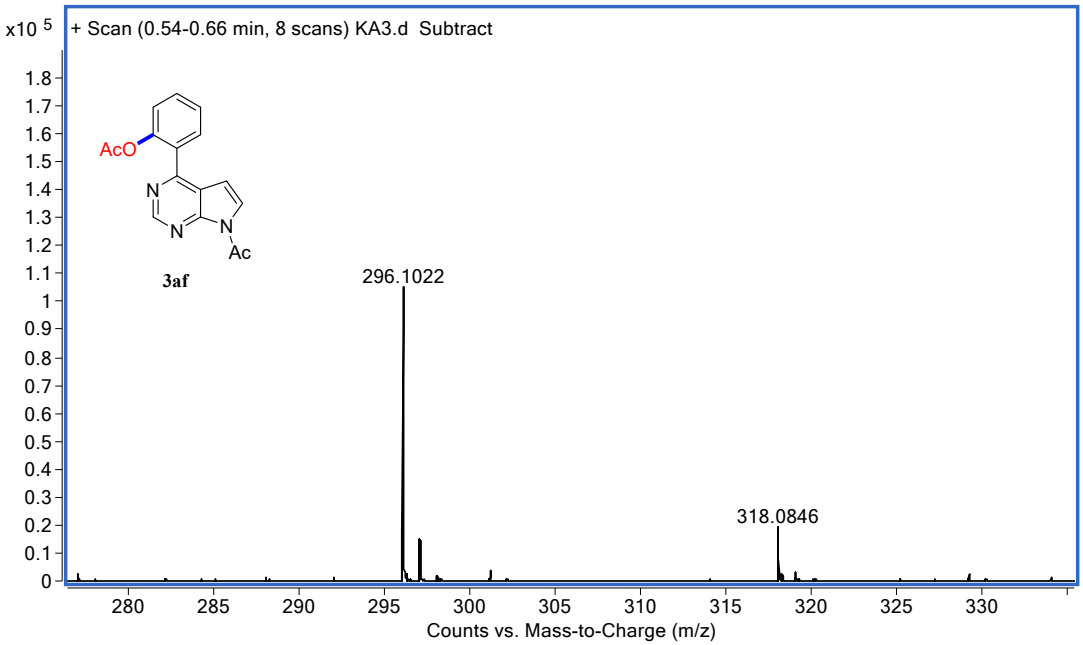
+ESI Scan (0.416 min) Frag=175.0V ZR-5F-01.d
AcO
N
N
3ad
334.1424
335.0715
341.0853
344.1397
345.1433
348.1381
Counts vs. Mass-to-Charge (m/z)

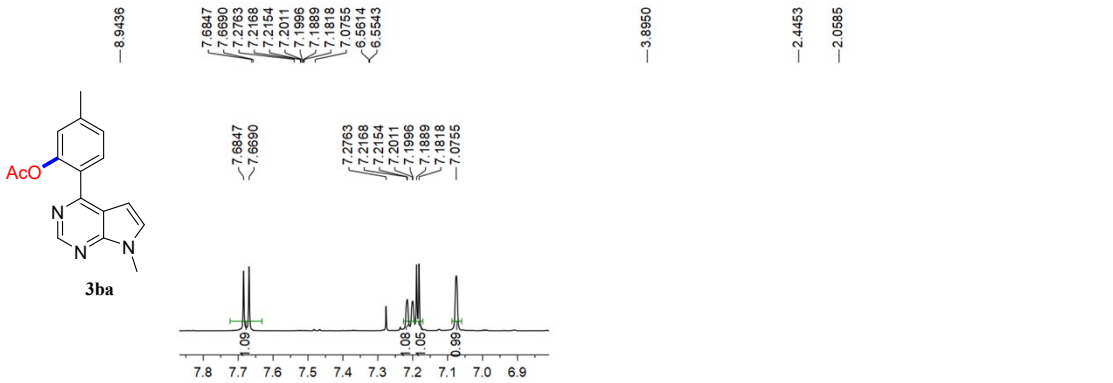

8.9904
7.8015
7.7988
7.7888
7.7861
7.5502
7.5476
7.5373
7.5348
7.5243
7.5216
7.4312
7.4196
7.4072
7.3965
7.3904
7.2810
7.2641
7.2775
6.6337
6.6276
5.6989
3.6022
3.5887
3.5749
2.0550
0.9560
0.9422
0.9286
-0.0365
AcO
N
N
N
O
Si
3ae
0.95
1.02
1.04
1.08
1.00
1.09
1.00
2.03
2.08
3.08
2.06
9.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
169.21
155.85
152.02
151.60
148.33
131.23
130.69
130.57
128.77
126.20
123.45
117.23
101.65
72.90
66.64
20.90
17.73
-1.44
AcO
N
N
N
O
Si
3ae
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

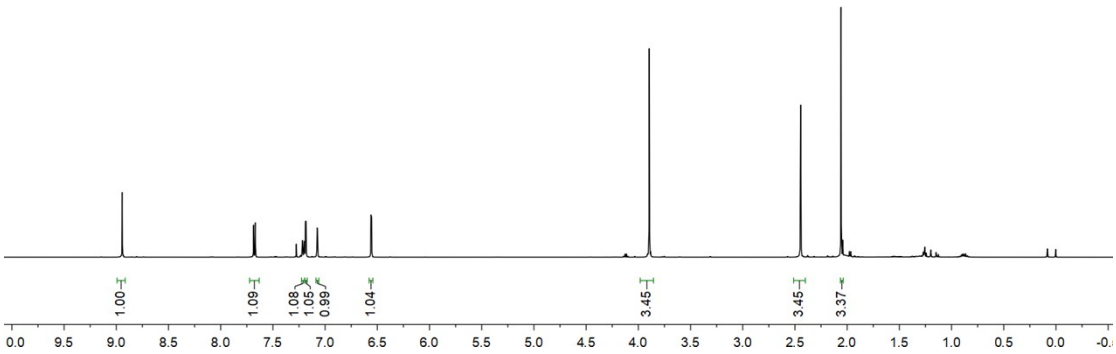

+ESI Scan (0.414 min) Frag=175.0V ZR-5H-01.d
384.1744
406.1562
413.2664
418.1934
AcO
3ae
Counts vs. Mass-to-Charge (m/z)

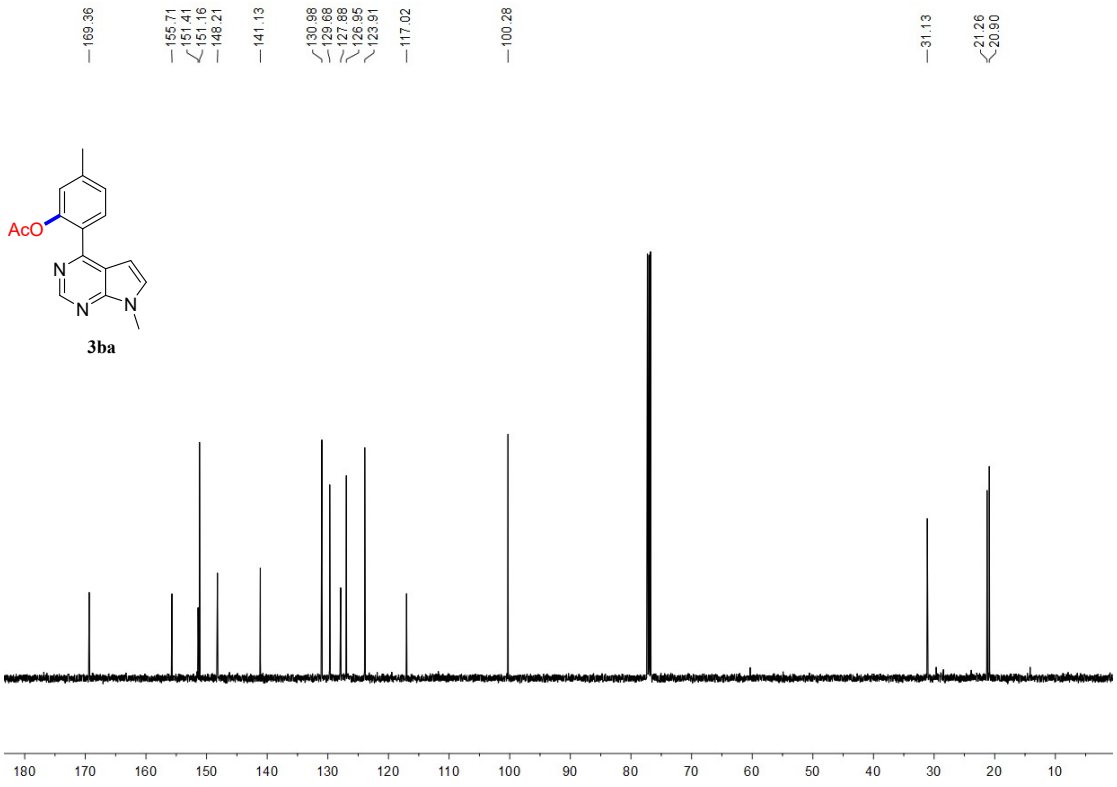

9.0717
8.0377
8.0274
7.7573
7.7533
7.7381
7.7342
7.5966
7.5925
7.5769
7.5735
7.5577
7.5535
7.4661
7.4636
7.4472
7.4448
7.4284
7.4259
7.3122
7.2918
6.7228
6.7125
3.1196
2.0900
AcO
N
N
N
Ac
3af
0.99
1.00
1.06
1.02
1.12
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
0.97
0.99
1.00
1.06
1.02
1.12
1.00
3.13
3.10
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

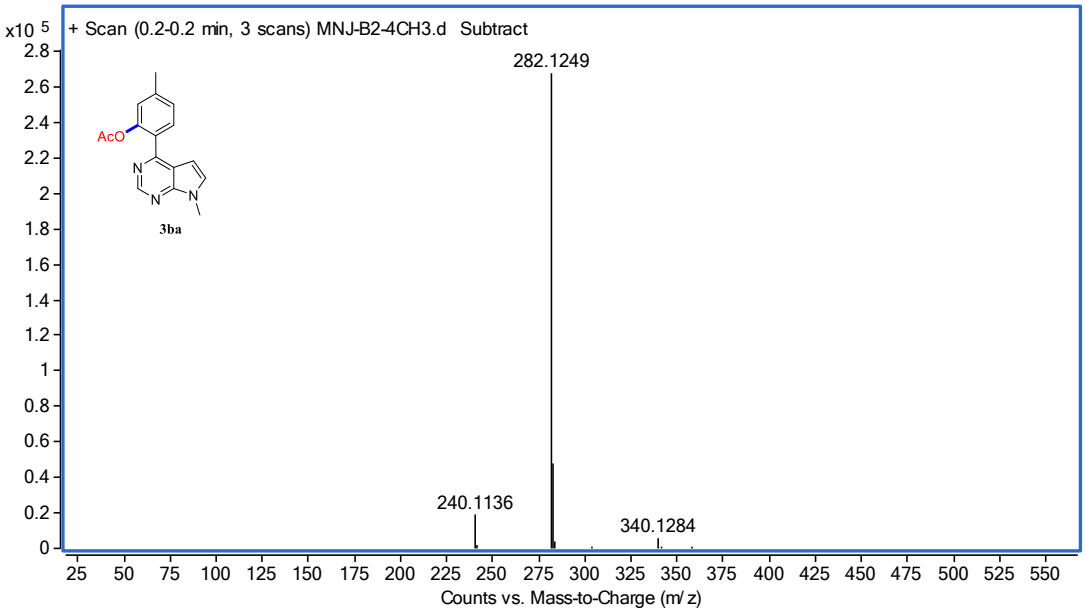

169.15
168.65
156.64
152.58
152.27
148.22
131.17
131.16
129.92
126.41
125.99
123.56
119.94
105.04
26.00
20.95
AcO
N
N
N
Ac
3af
30 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

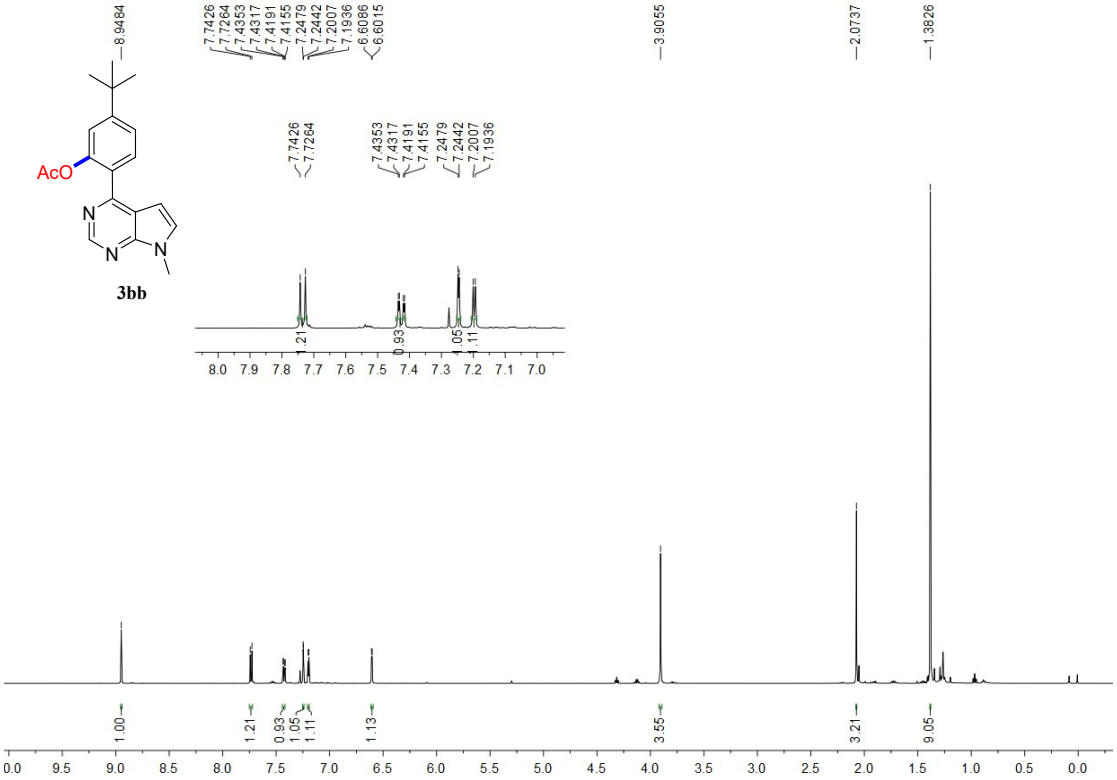

x10 5
+ Scan (0.54-0.66 min, 8 scans) KA3.d Subtract
AcO
N
N
N
Ac
3af
296.1022
318.0846
Counts vs. Mass-to-Charge (m/z)

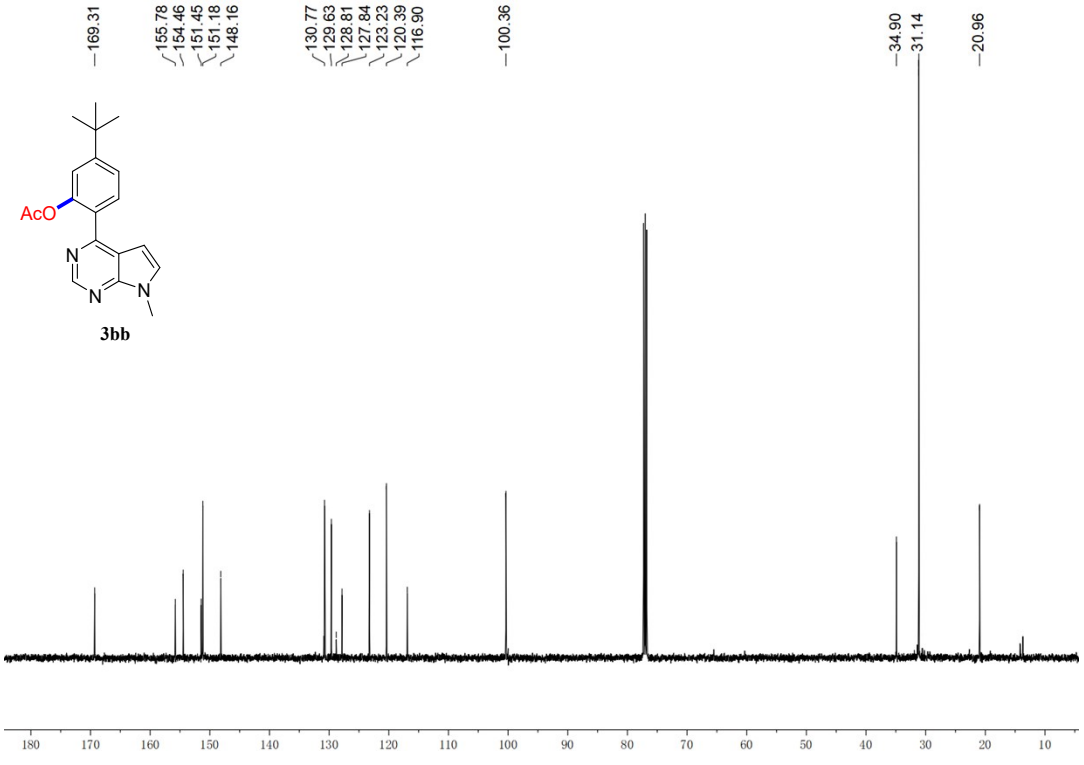

8.9436
7.6847
7.6690
7.2763
7.2168
7.2154
7.2011
7.1996
7.1889
7.1818
7.0755
6.5614
6.5543
3.8950
2.4453
2.0585
AcO
N
N
N
3ba

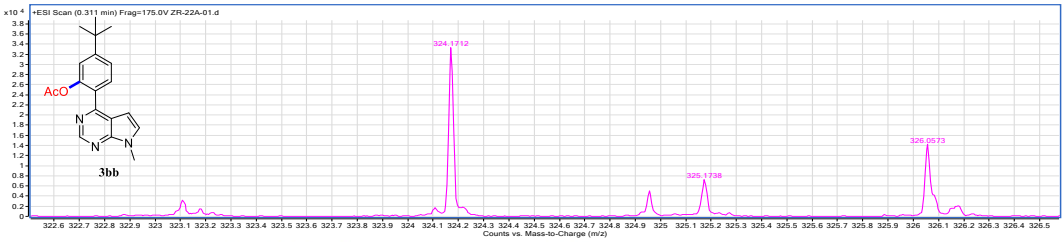

1.00
1.09
1.08
1.05
0.99
1.04
3.45
3.45
3.37

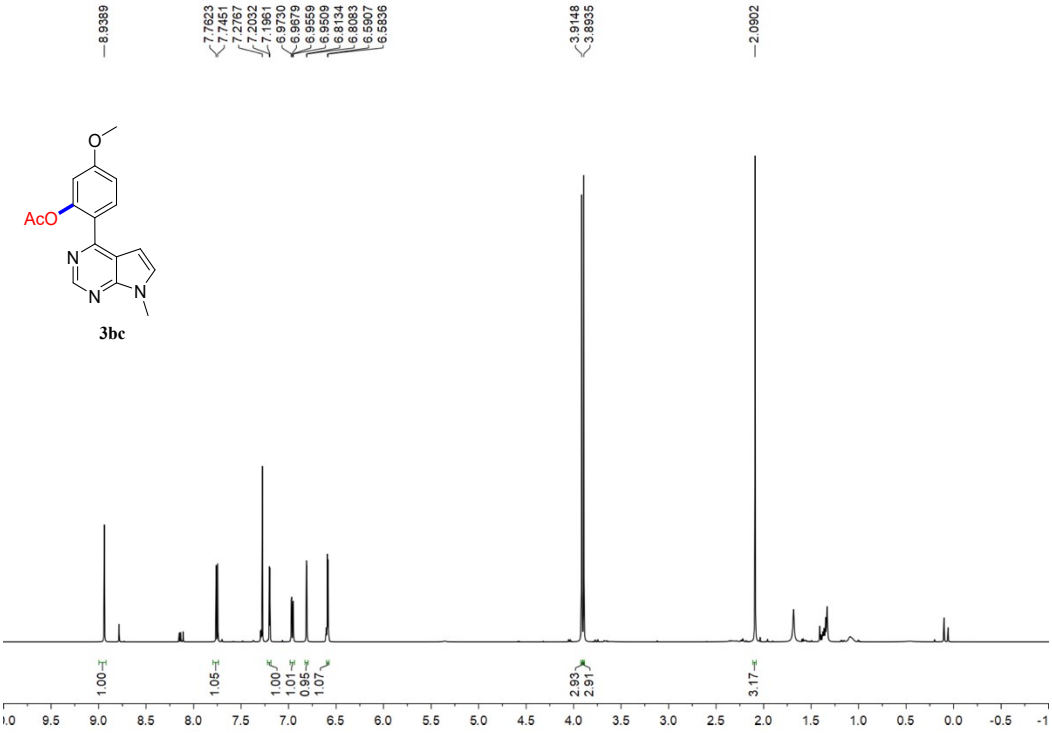

169.36
155.71
151.41
151.16
148.21
141.13
130.98
129.68
127.88
126.95
123.91
117.02
100.28
31.13
21.26
20.90
AcO
N
N
N
3ba
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

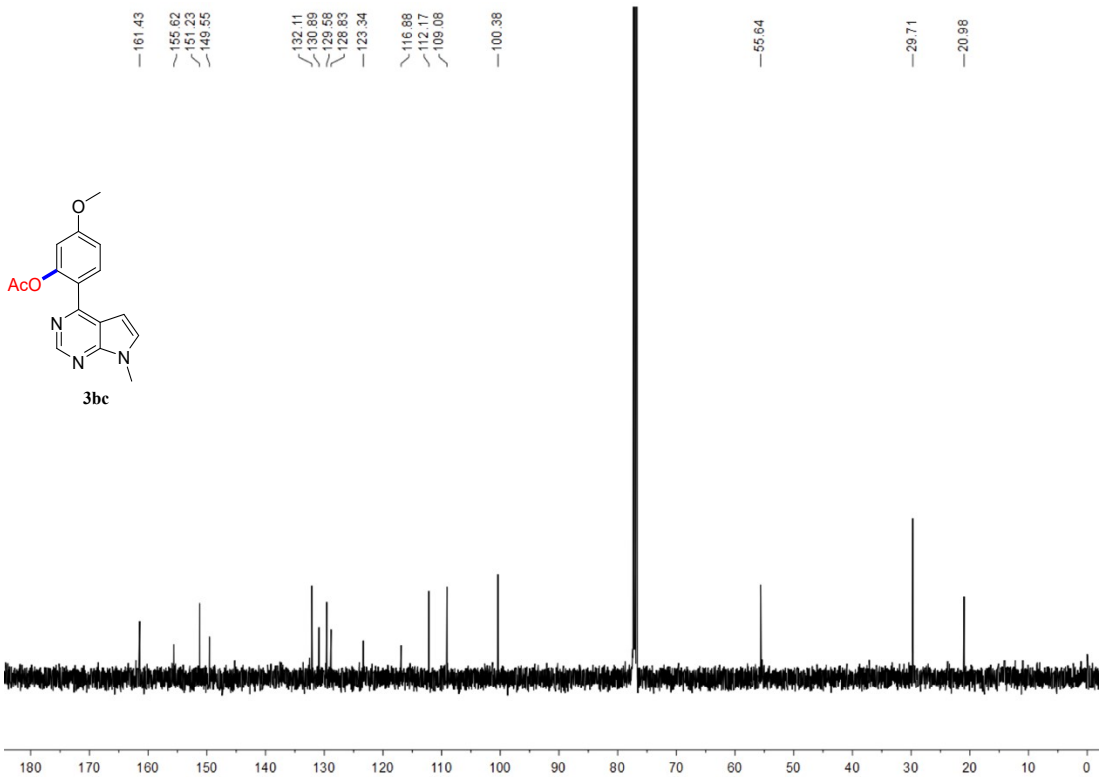

x10 5
+ Scan (0.2-0.2 min, 3 scans) MNJ-B2-4CH3.d Subtract
282.1249
240.1136
340.1284
AcO
N
N
N
3ba
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
25 50 75 100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550
Counts vs. Mass-to-Charge (m/z)

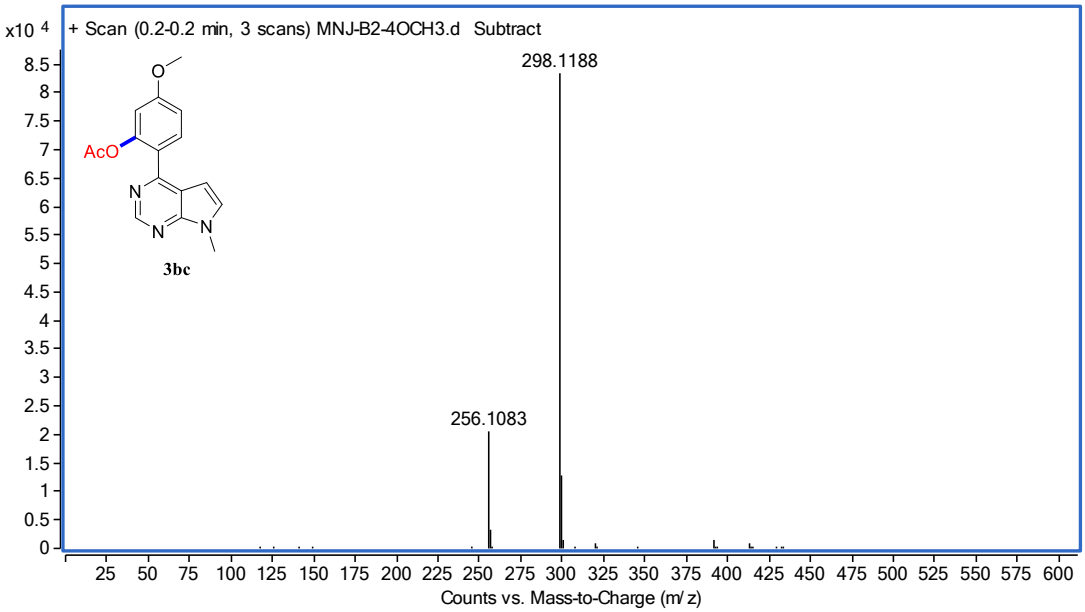

8.9484
7.7426
7.7264
7.4353
7.4317
7.4191
7.4155
7.2479
7.2442
7.2007
7.1936
6.6086
6.6015
3.9055
2.0737
1.3826
AcO
N
N
N
3bb
1.21
0.93
1.05
1.11
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
1.00
1.21
0.93
1.05
1.11
1.13
3.55
3.21
9.05
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

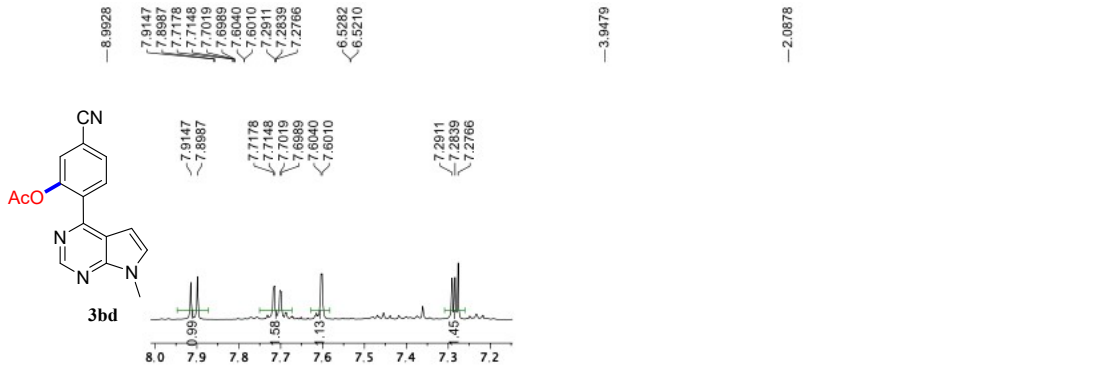

169.31
155.78
154.46
151.45
151.18
148.16
130.77
129.63
128.81
127.84
123.23
120.39
116.90
100.36
34.90
31.14
20.96
AcO
N
N
N
3bb
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

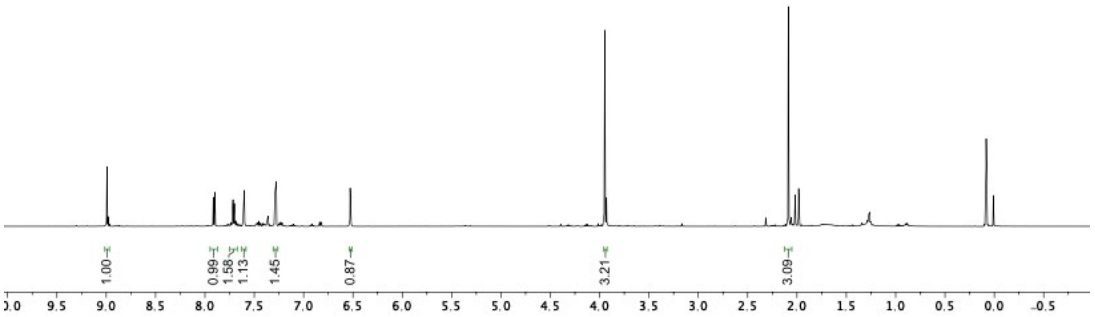

+ESI Scan (0.311 min) Frag=175.0V ZR-22A-01.d
AcO
3bb
324.1712
325.1738
326.0573
Counts vs. Mass-to-Charge (m/z)

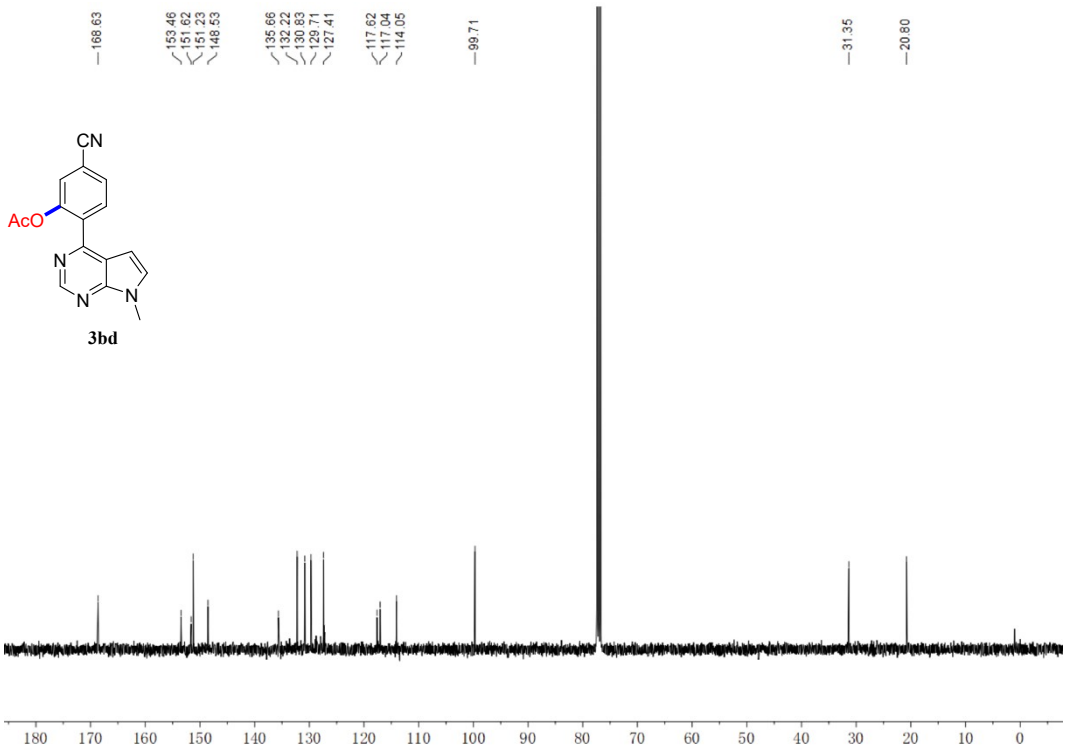

8.9389
7.7623
7.7451
7.2767
7.2032
7.1961
6.9730
6.9679
6.9559
6.9509
6.8134
6.8083
6.5907
6.5836
3.9148
3.8935
2.0902
AcO
3bc
1.00
1.05
1.00
1.01
0.95
1.07
2.93
2.91
3.17

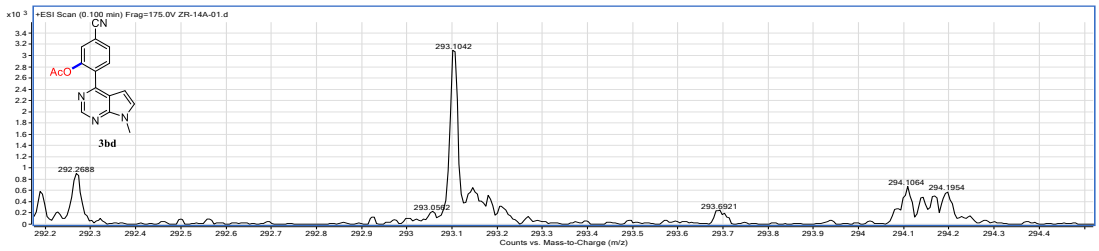

161.43
155.62
151.23
149.55
132.11
130.89
129.58
128.83
123.34
116.88
112.17
109.08
100.38
55.64
29.71
20.98
AcO
N
N
N
O
3bc
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

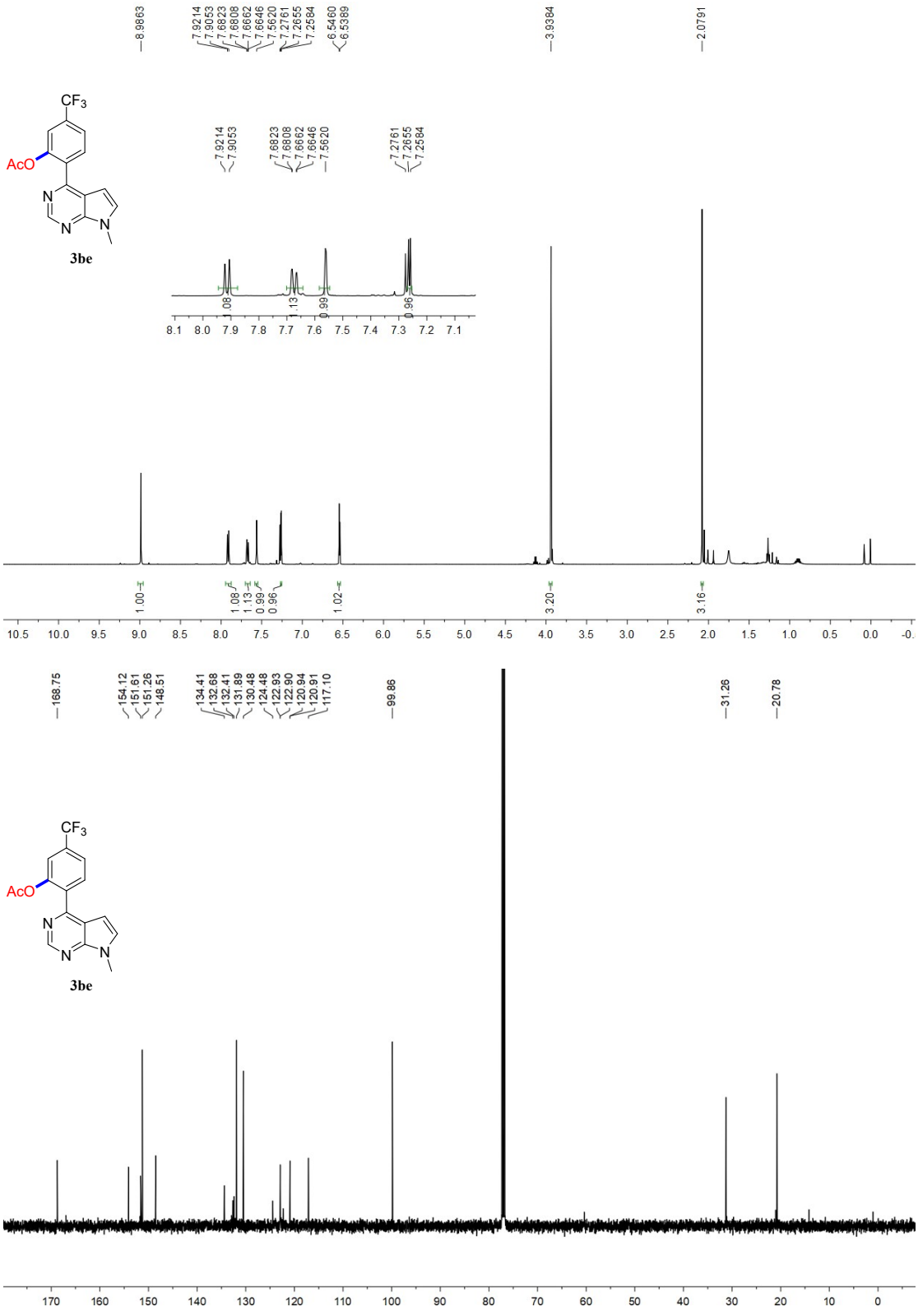

x10 4
+ Scan (0.2-0.2 min, 3 scans) MNJ-B2-4OCH3.d Subtract
298.1188
256.1083
AcO
N
N
N
O
3bc
8.5 8 7.5 7 6.5 6 5.5 5 4.5 4 3.5 3 2.5 2 1.5 1 0.5 0
25 50 75 100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600
Counts vs. Mass-to-Charge (m/z)

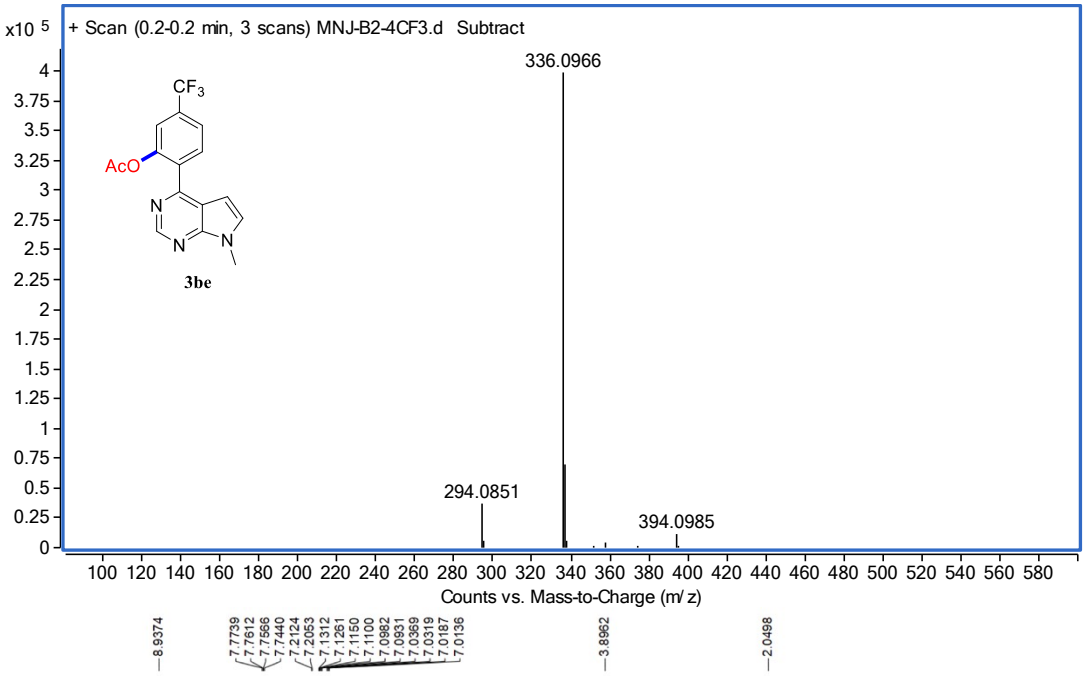

8.9928
7.9147
7.8987
7.7178
7.7148
7.7019
7.6989
7.6040
7.6010
7.2911
7.2839
7.2766
6.5282
6.5210
3.9479
2.0878
CN
AcO
N
N
N
3bd
0.99
1.58
1.13
1.45
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2

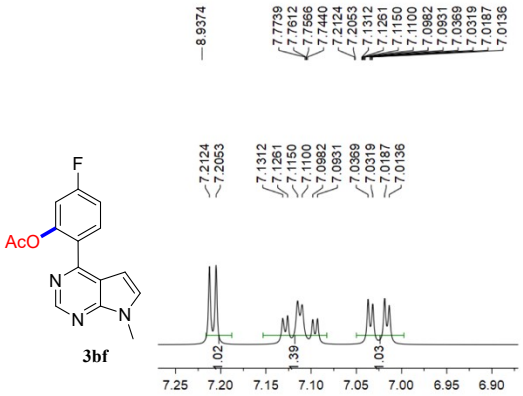

1.00
0.99
1.58
1.13
1.45
0.87
3.21
3.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

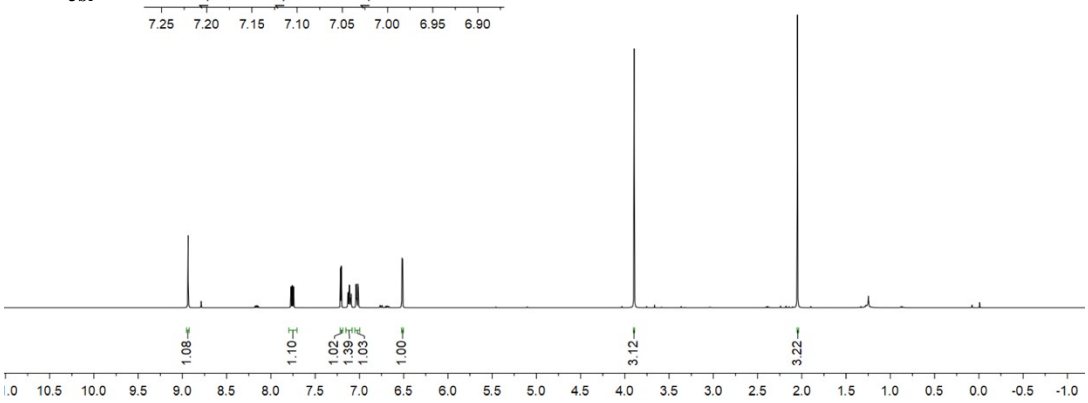

168.63
153.46
151.62
151.23
148.53
135.66
132.22
130.83
129.71
127.41
117.62
117.04
114.05
99.71
31.35
20.80
CN
AcO
N
N
N
3bd
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

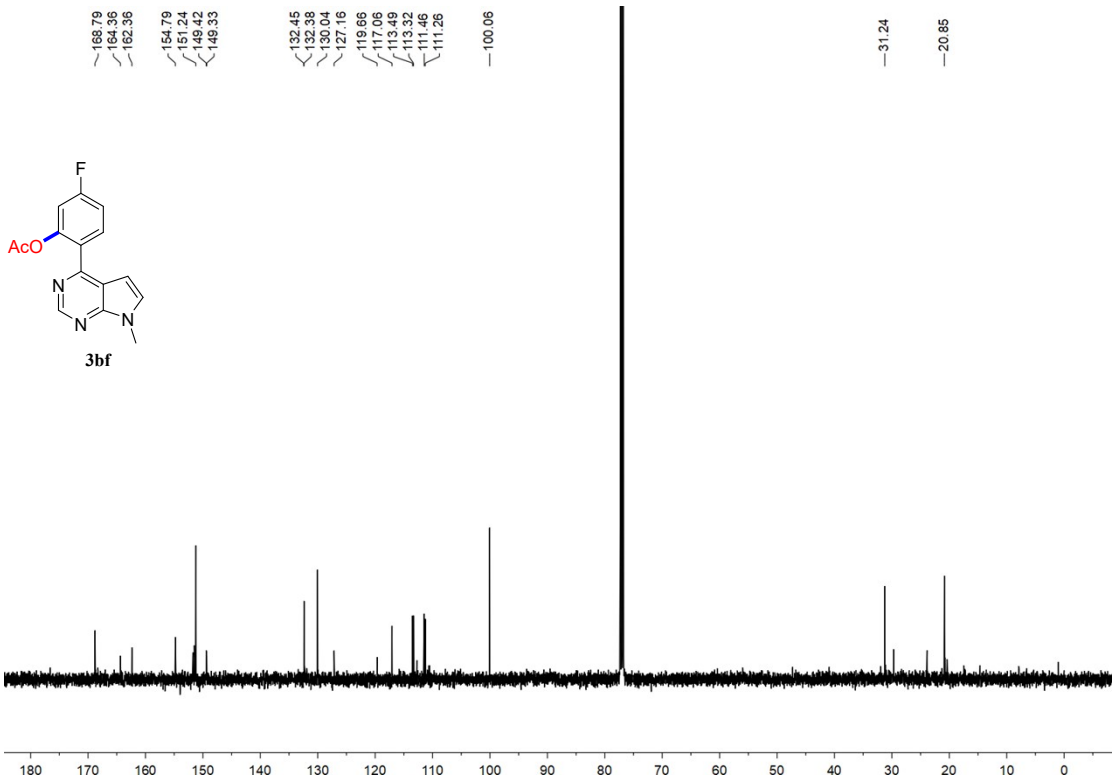

+ESI Scan (0.100 min) Frag=175.0V ZR-14A-01.d
CN
AcO
N
N
N
3bd
293.1042
292.2688
293.0562
293.6921
294.1064
294.1954
Counts vs. Mass-to-Charge (m/z)

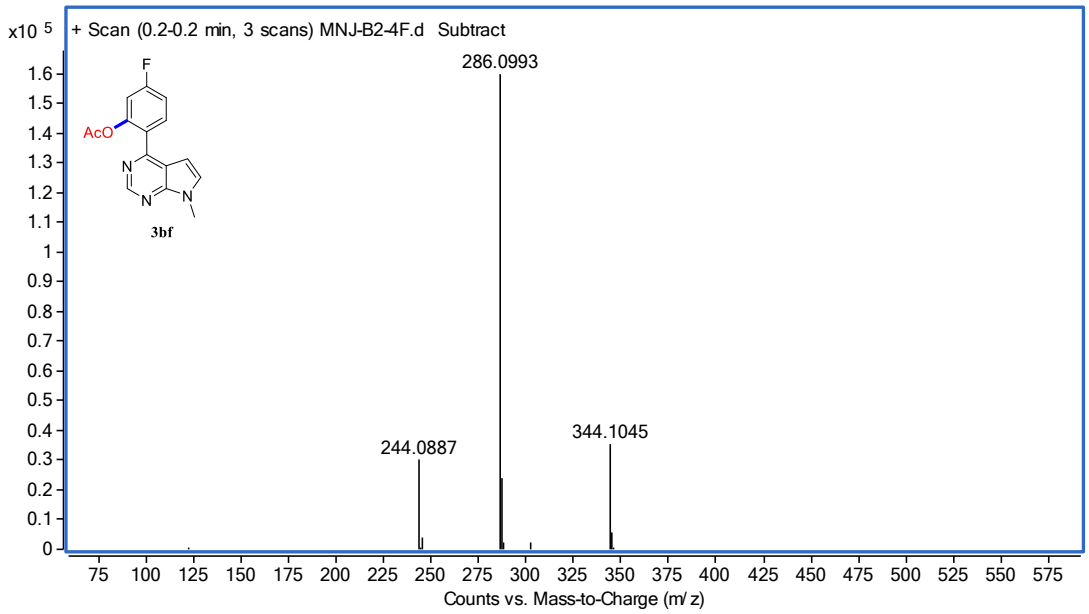

8.9863
7.9214
7.9053
7.6823
7.6808
7.6662
7.6646
7.5620
7.2761
7.2655
7.2584
6.5460
6.5389
3.9384
2.0791
CF3
AcO
N
N
N
3be
1.00
1.08
1.13
0.99
0.96
1.02
3.20
3.16
168.75
154.12
151.61
151.26
148.51
134.41
132.68
132.41
131.89
130.48
124.48
122.93
122.90
120.94
120.91
117.10
99.86
31.26
20.78

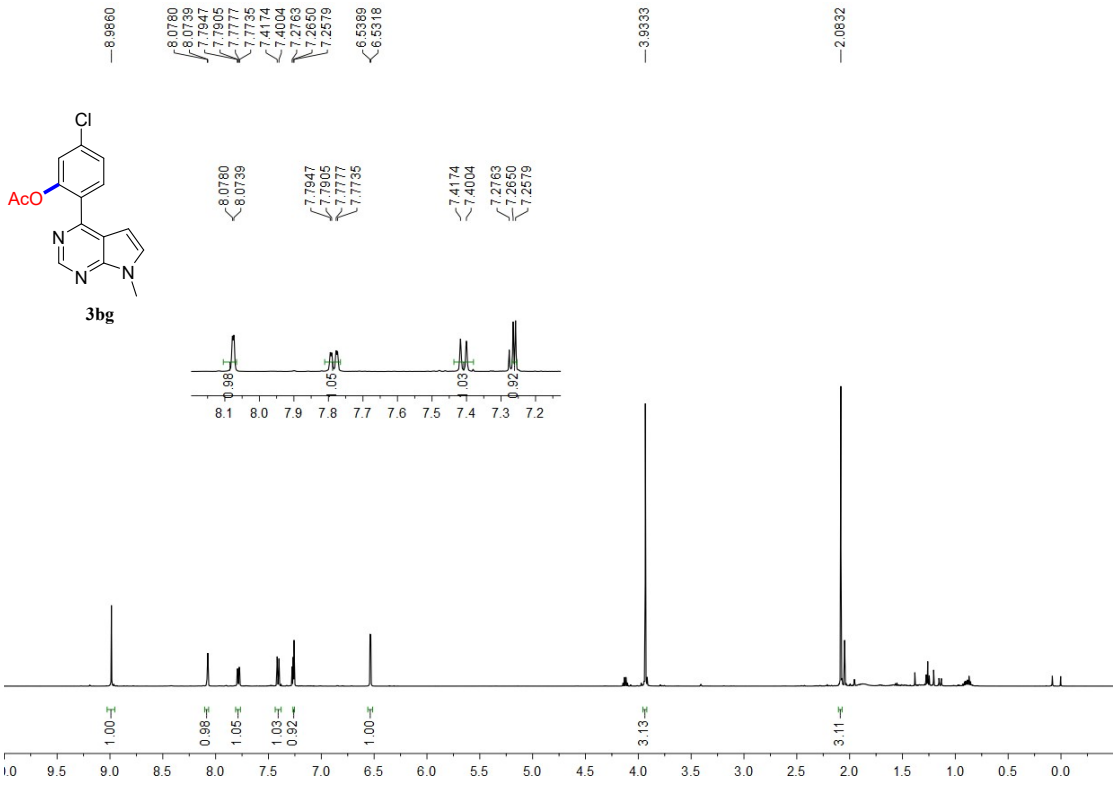

x10 5
+ Scan (0.2-0.2 min, 3 scans) MNJ-B2-4CF3.d Subtract
336.0966
294.0851
394.0985
CF3
AcO
N
N
N
3be
Counts vs. Mass-to-Charge (m/z)

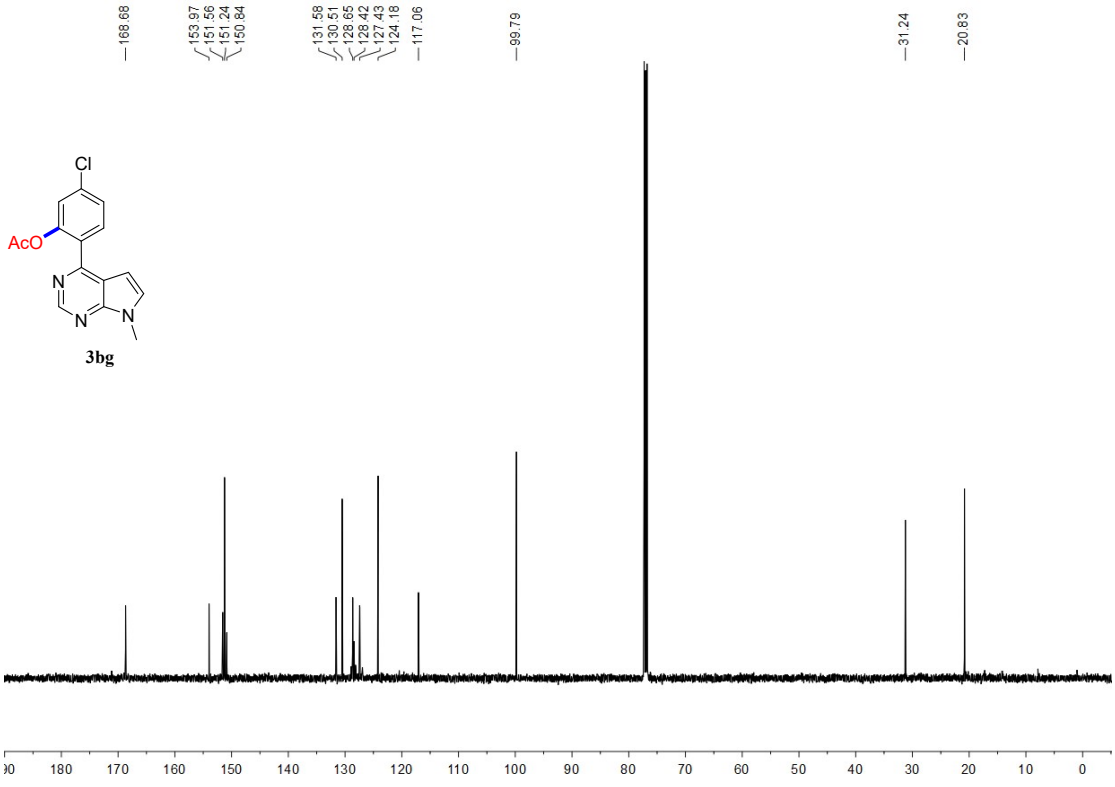

8.9374
7.7739
7.7612
7.7566
7.7440
7.2124
7.2053
7.1312
7.1261
7.1150
7.1100
7.0982
7.0931
7.0369
7.0319
7.0187
7.0136
3.8962
2.0498
F
AcO
N
N
N
3bf
1.02
1.39
1.03
7.25
7.20
7.15
7.10
7.05
7.00
6.95
6.90

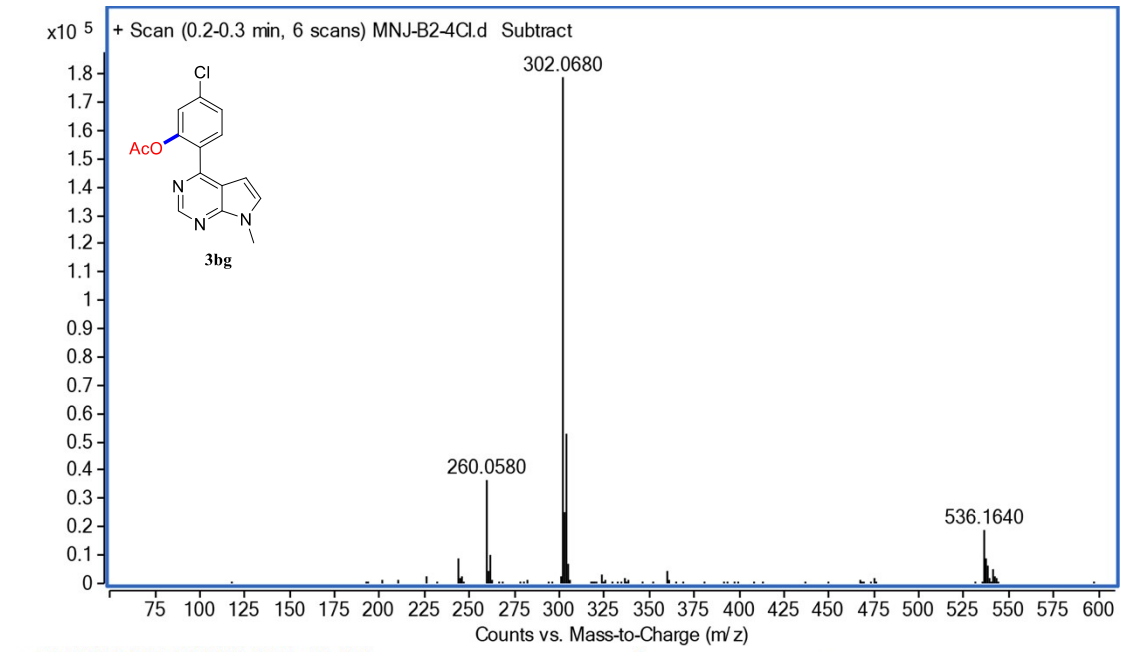

1.08
1.10
1.02
1.39
1.03
1.00
3.12
3.22
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

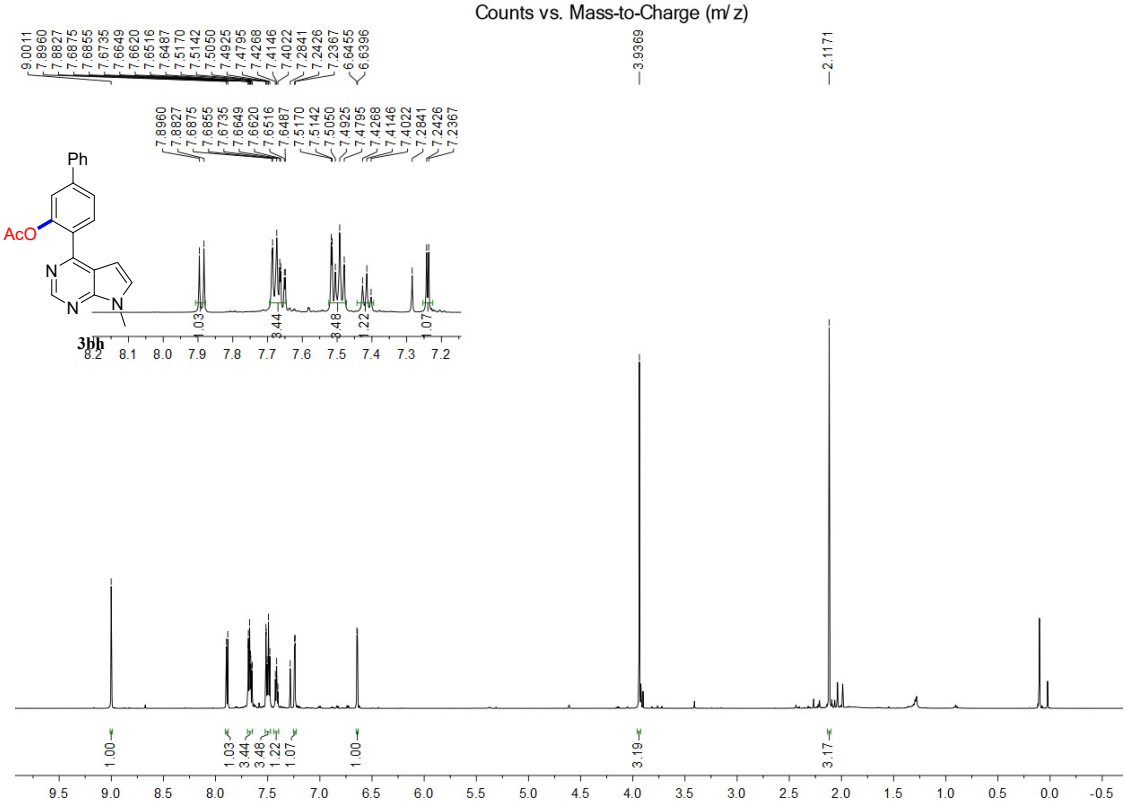

168.79
164.36
162.36
154.79
151.24
149.42
149.33
132.45
132.38
130.04
127.16
119.66
117.06
113.49
113.32
111.46
111.26
100.06
31.24
20.85
F
AcO
N
N
N
3bf
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

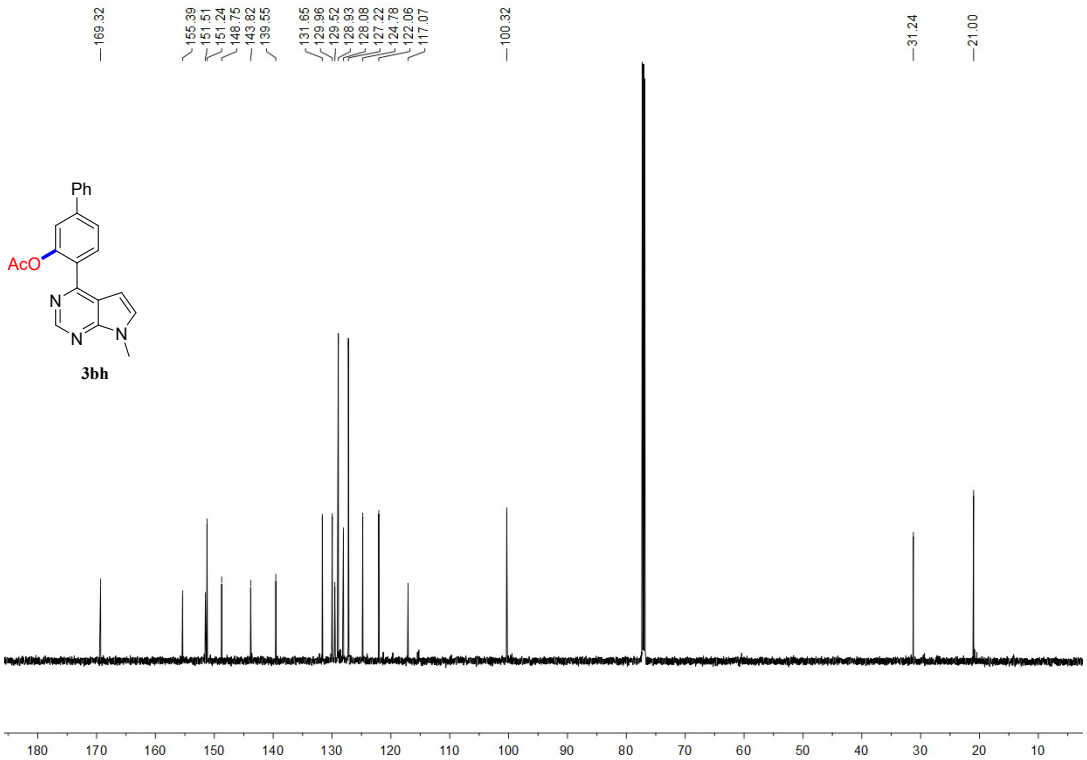

x10 5
+ Scan (0.2-0.2 min, 3 scans) MNJ-B2-4F.d Subtract
286.0993
344.1045
244.0887
F
AcO
N
N
N
3bf
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
75
100
125
150
175
200
225
250
275
300
325
350
375
400
425
450
475
500
525
550
575
Counts vs. Mass-to-Charge (m/z)

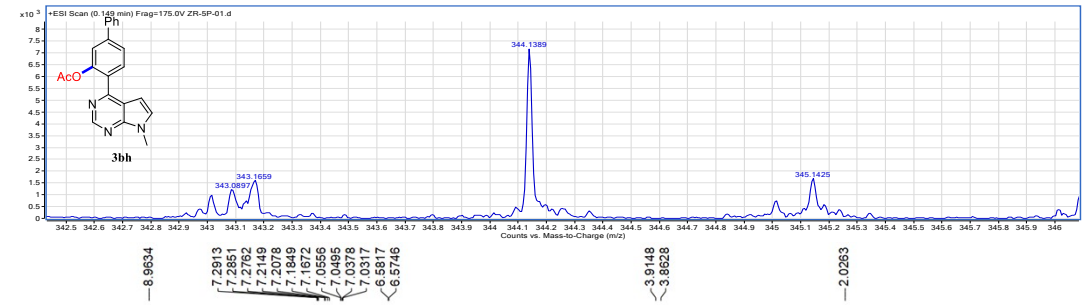

8.9860
8.0780
8.0739
7.7947
7.7905
7.7777
7.7735
7.4174
7.4004
7.2763
7.2650
7.2579
6.5389
6.5318
3.9333
2.0832
Cl
AcO
N
N
N
3bg
1.00
0.98
1.05
1.03
0.92
1.00
3.13
3.11

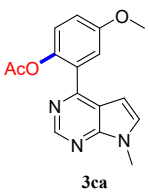

168.68
153.97
151.56
151.24
150.64
131.58
130.51
128.65
128.42
127.43
124.18
117.06
99.79
31.24
20.83
Cl
AcO
N
N
N
3bg

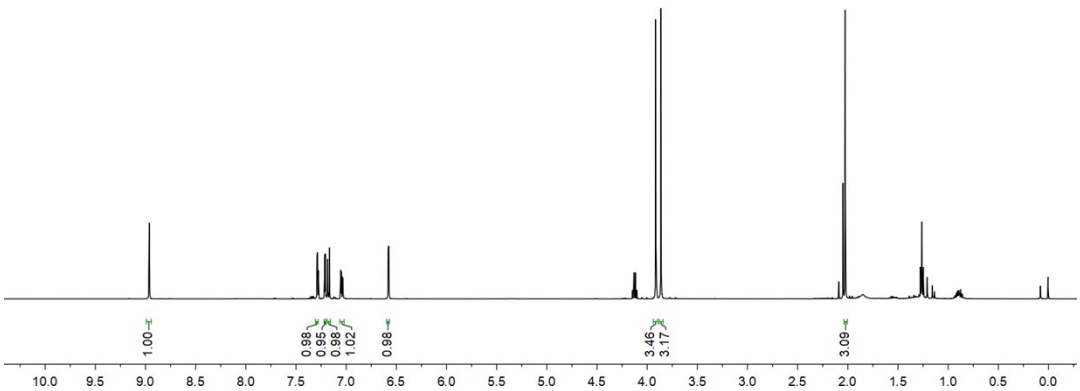

x10 5
+ Scan (0.2-0.3 min, 6 scans) MNJ-B2-4Cl.d Subtract
302.0680
260.0580
536.1640
Cl
AcO
N
N
N
3bg
Counts vs. Mass-to-Charge (m/z)

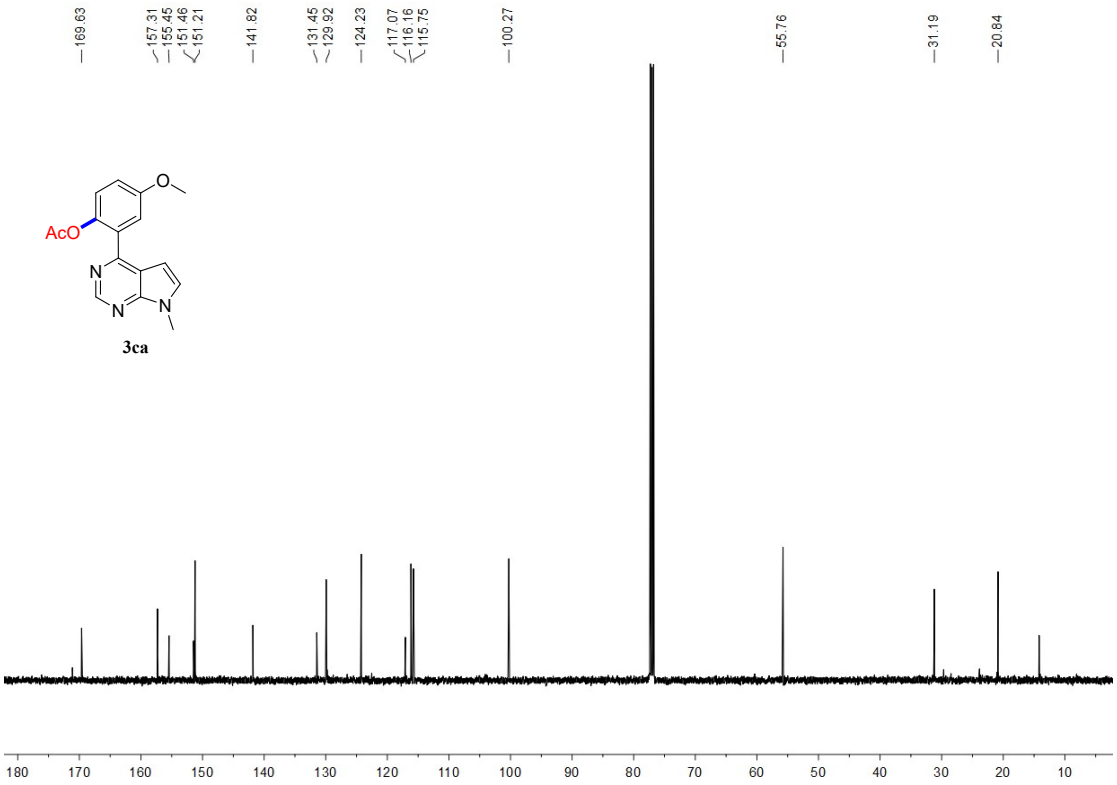

Ph
AcO
N
N
N
3bh
3.9369
2.1171
1.03
3.44
3.48
1.22
1.07
1.00
3.19
3.17

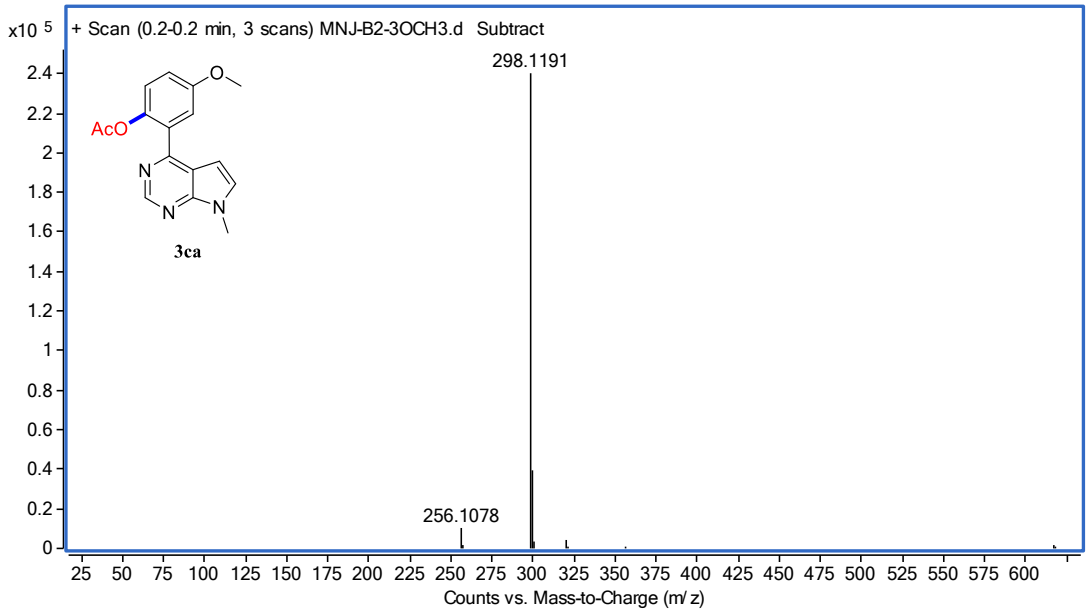

169.32
155.39
151.51
151.24
148.75
143.82
139.55
131.65
129.96
129.52
128.93
128.08
127.22
124.78
122.06
117.07
100.32
31.24
21.00
Ph
AcO
N
N
N
3bh

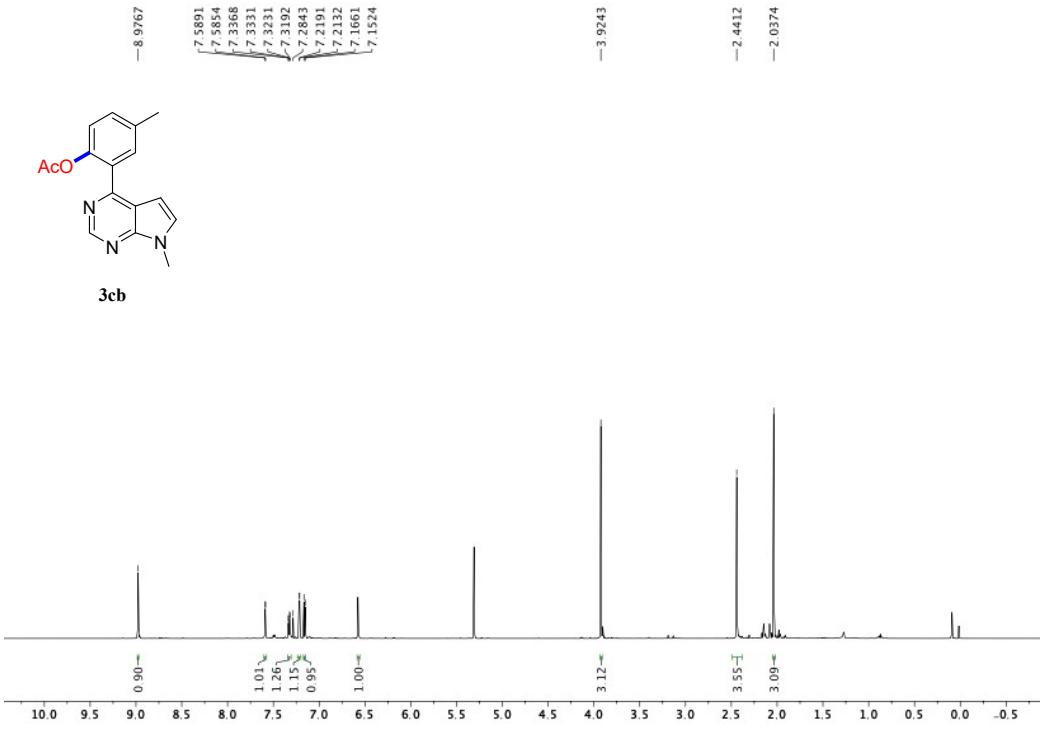

+ESI Scan (0.149 min) Frag=175.0V ZR-5P-01.d
Ph
AcO
3bh
344.1389
343.1659
343.0897
345.1425
Counts vs. Mass-to-Charge (m/z)
8.9634
7.2913
7.2851
7.2762
7.2149
7.2078
7.1849
7.1672
7.0556
7.0495
7.0378
7.0317
6.5817
6.5746
3.9148
3.8628
2.0263

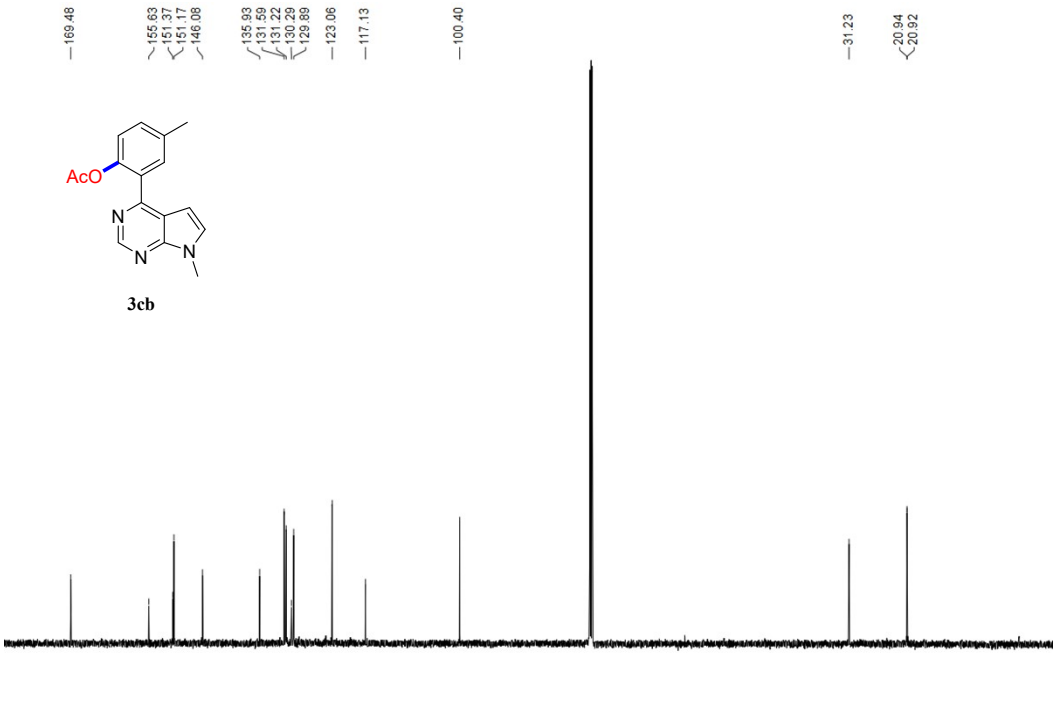

O
AcO
N
N
N
3ca

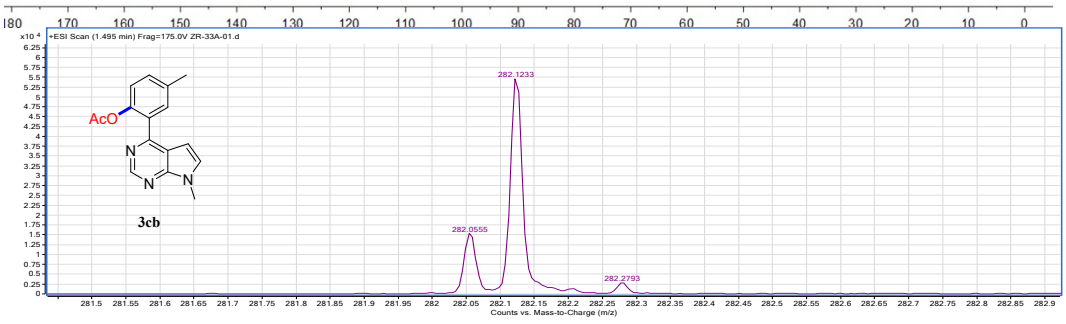

1.00
0.98
0.95
0.98
1.02
0.98
3.46
3.17
3.09


169.63
157.31
155.45
151.46
151.21
141.82
131.45
129.92
124.23
117.07
116.16
115.75
100.27
55.76
31.19
20.84
AcO
O
N
N
N
3ca
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

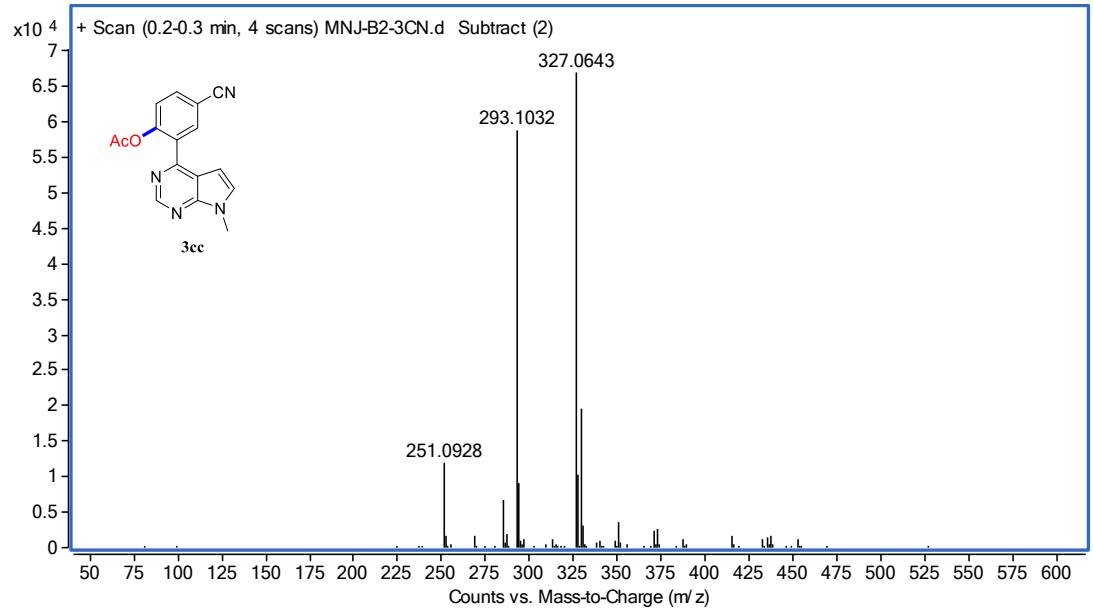

x10 5
+ Scan (0.2-0.2 min, 3 scans) MNJ-B2-3OCH3.d Subtract
298.1191
256.1078
AcO
O
N
N
N
3ca
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
25 50 75 100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600
Counts vs. Mass-to-Charge (m/z)

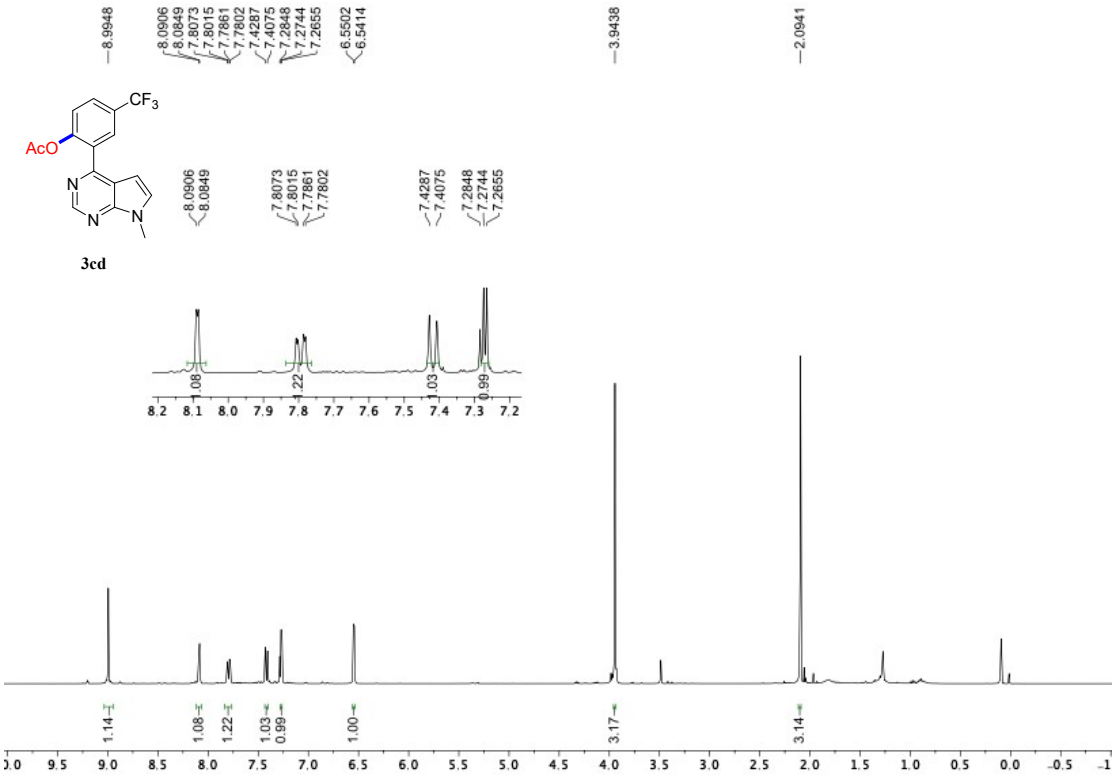

8.9767
7.5891
7.5854
7.3368
7.3331
7.3231
7.3192
7.2843
7.2191
7.2132
7.1661
7.1524
3.9243
2.4412
2.0374
AcO
N
N
N
3cb
0.90
1.01
1.26
1.15
0.95
1.00
3.12
3.55
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

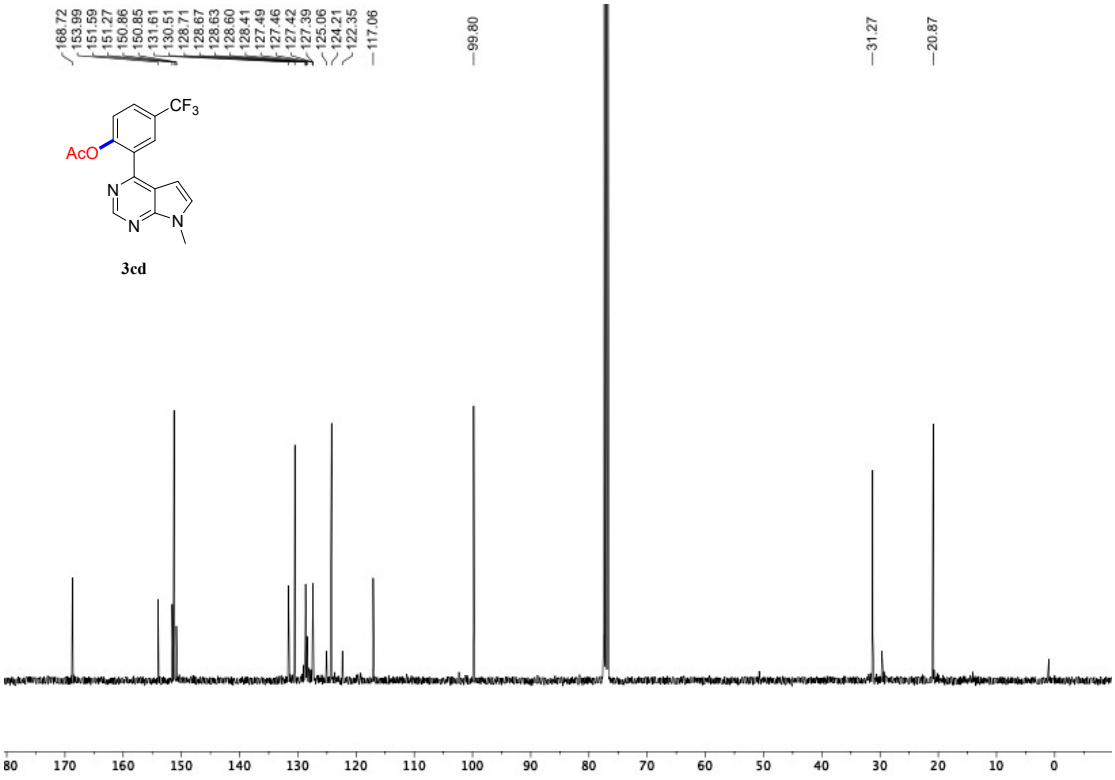

169.48
155.63
151.37
151.17
146.08
135.93
131.59
131.22
130.29
129.89
123.06
117.13
100.40
31.23
20.94
20.92
AcO
N
N
N
3cb

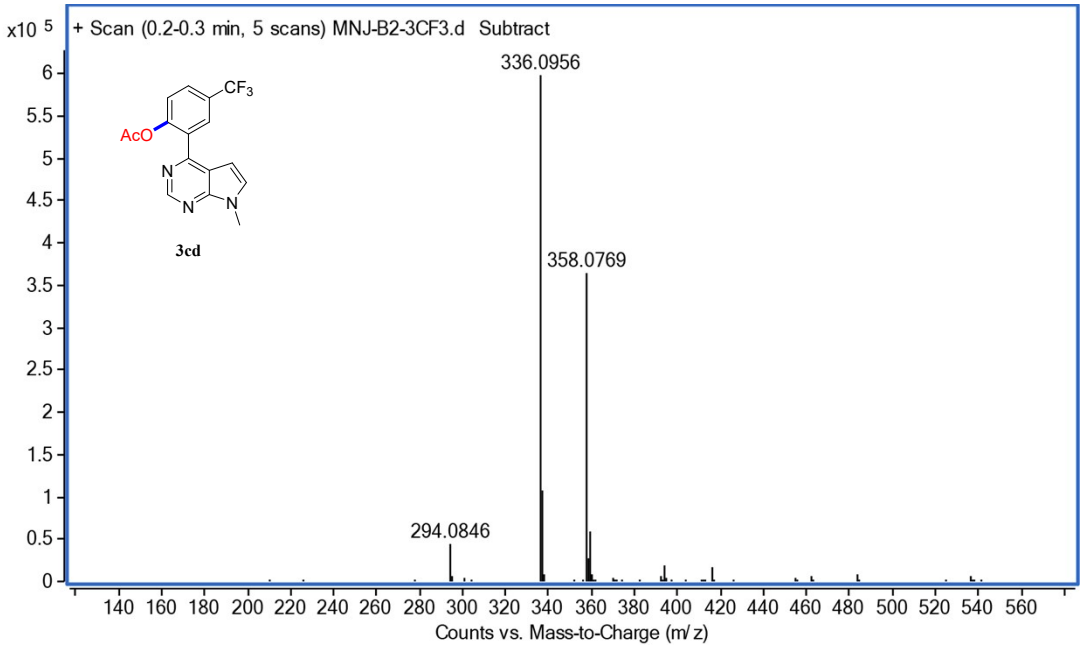

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
+ESI Scan (1.495 min) Frag=175.0V ZR-33A-01.d
282.1233
282.0555
282.2793
AcO
N
N
N
3cb
281.5 281.55 281.6 281.65 281.7 281.75 281.8 281.85 281.9 281.95 282 282.05 282.1 282.15 282.2 282.25 282.3 282.35 282.4 282.45 282.5 282.55 282.6 282.65 282.7 282.75 282.8 282.85 282.9
Counts vs. Mass-to-Charge (m/z)

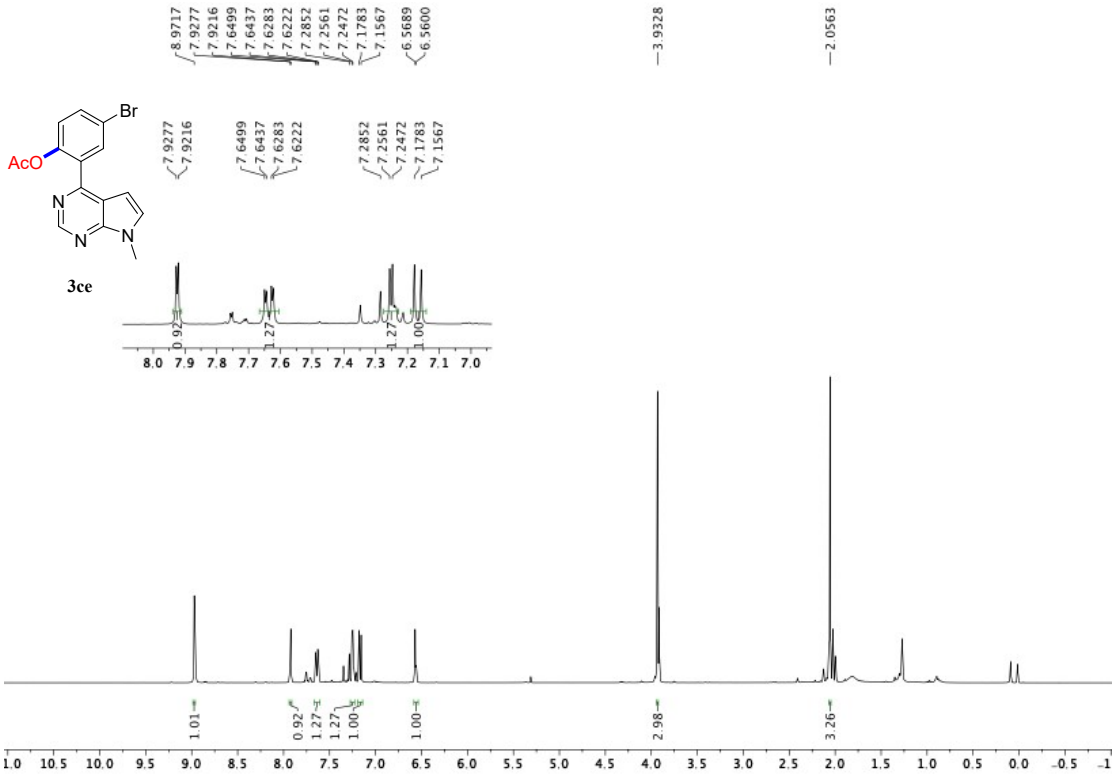

8.9837
8.1155
8.1115
7.8298
7.8257
7.8130
7.8088
7.4283
7.4114
7.2951
7.2879
7.2769
3.9506
2.0943
CN
AcO
N
N
N
3cc
0.95
1.28
1.03
1.01
0.91
1.00
3.43
3.05
168.39
153.12
151.67
151.64
151.27
135.38
134.00
132.44
130.77
124.86
117.89
117.00
110.39
99.62
31.32
20.85

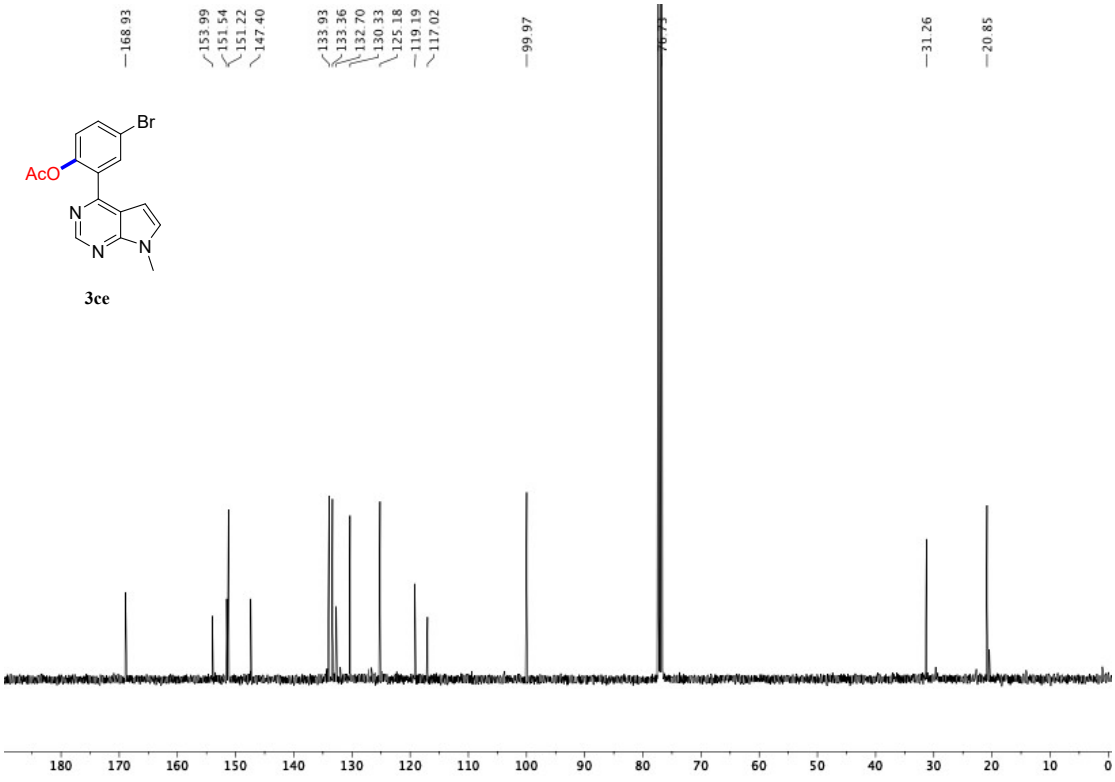

+ Scan (0.2-0.3 min, 4 scans) MNJ-B2-3CN.d Subtract (2)
x10 4
327.0643
293.1032
251.0928
CN
AcO
3cc
Counts vs. Mass-to-Charge (m/z)

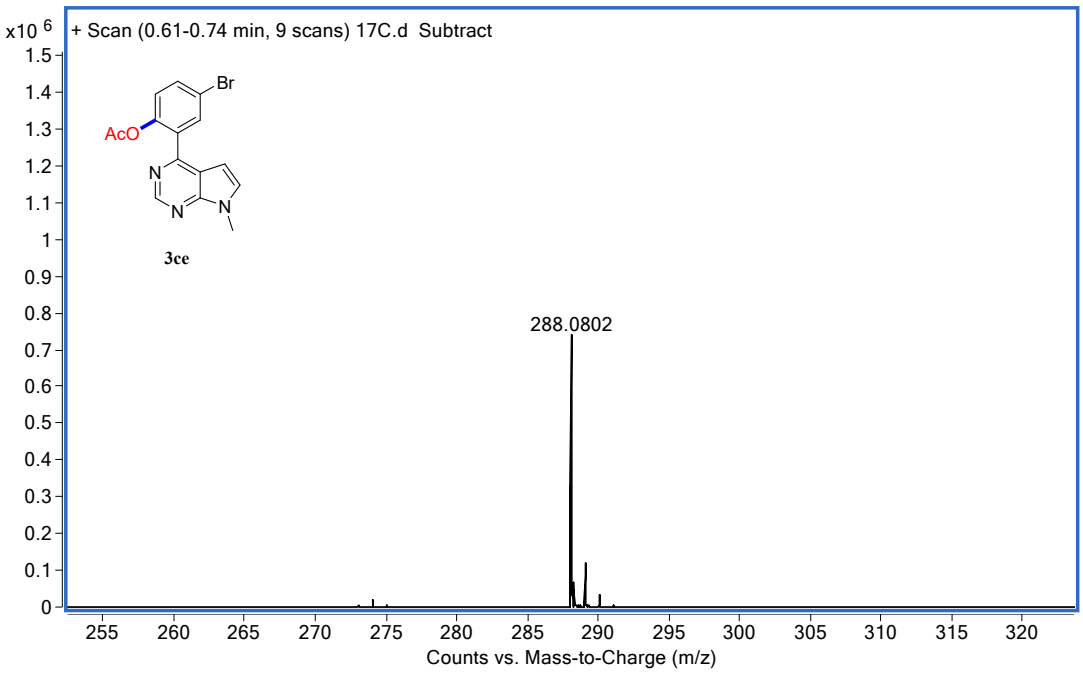

8.9948
8.0906
8.0849
7.8073
7.8015
7.7861
7.7802
7.4287
7.4075
7.2848
7.2744
7.2655
6.5502
6.5414
3.9438
2.0941
CF3
AcO
3cd
1.14
1.08
1.22
1.03
0.99
1.00
3.17
3.14

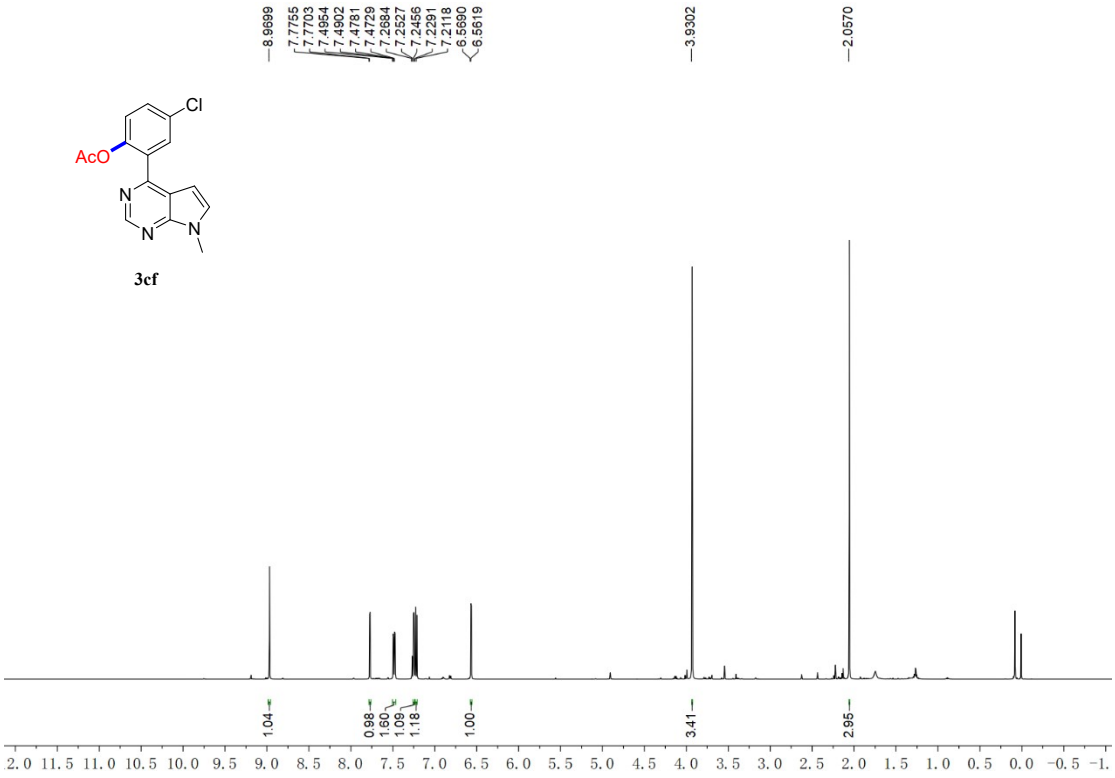

168.72
153.99
151.59
151.27
150.86
150.85
131.61
130.51
128.71
128.67
128.63
128.60
128.41
127.49
127.46
127.42
127.39
125.06
124.21
122.35
117.06
99.80
31.27
20.87
CF3
AcO
N
N
N
3cd
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

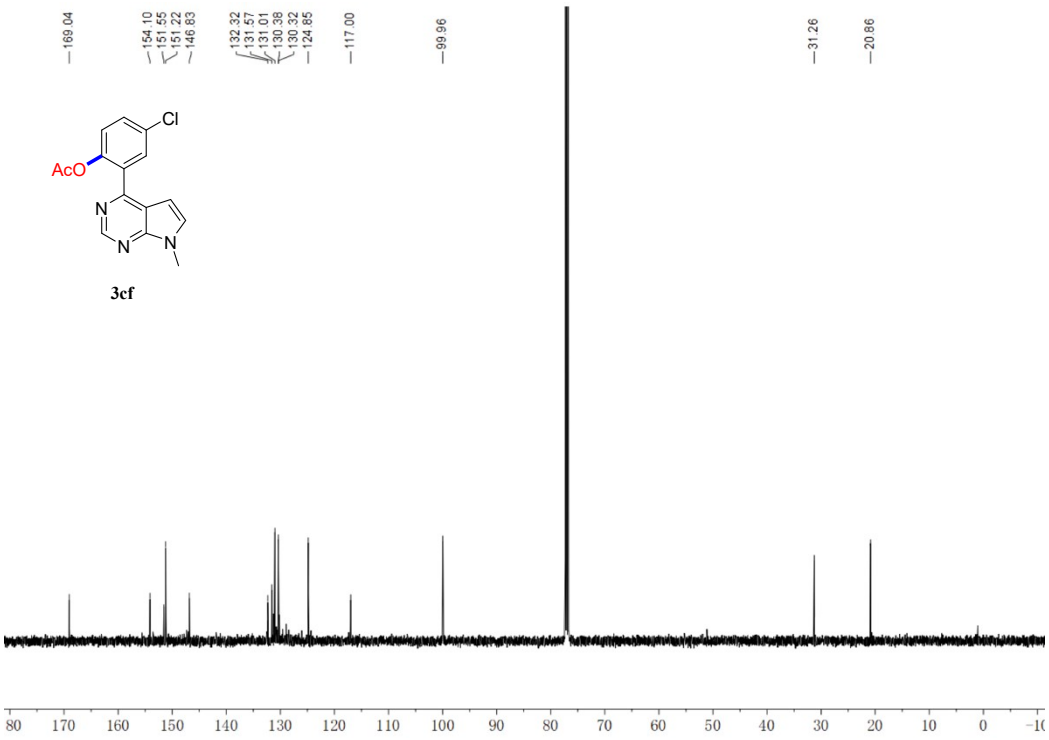

x10 5
+ Scan (0.2-0.3 min, 5 scans) MNJ-B2-3CF3.d Subtract
336.0956
358.0769
294.0846
CF3
AcO
N
N
N
3cd
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560
Counts vs. Mass-to-Charge (m/z)


8.9717
7.9277
7.9216
7.6499
7.6437
7.6283
7.6222
7.2852
7.2561
7.2472
7.1783
7.1567
6.5689
6.5600
3.9328
2.0563
Br
AcO
N
N
N
3ce
1.01
0.92
1.27
1.27
1.00
1.00
2.98
3.26

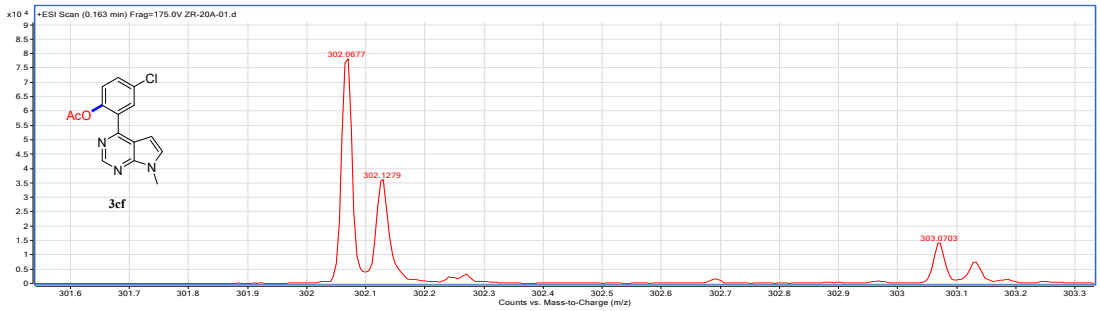

168.93
153.99
151.54
151.22
147.40
133.93
133.36
132.70
130.33
125.18
119.19
117.02
99.97
76.73
31.26
20.85
Br
AcO
N
N
N
3ce


x10 6
+ Scan (0.61-0.74 min, 9 scans) 17C.d Subtract
Br
AcO
N
N
N
3ce
288.0802
Counts vs. Mass-to-Charge (m/z)

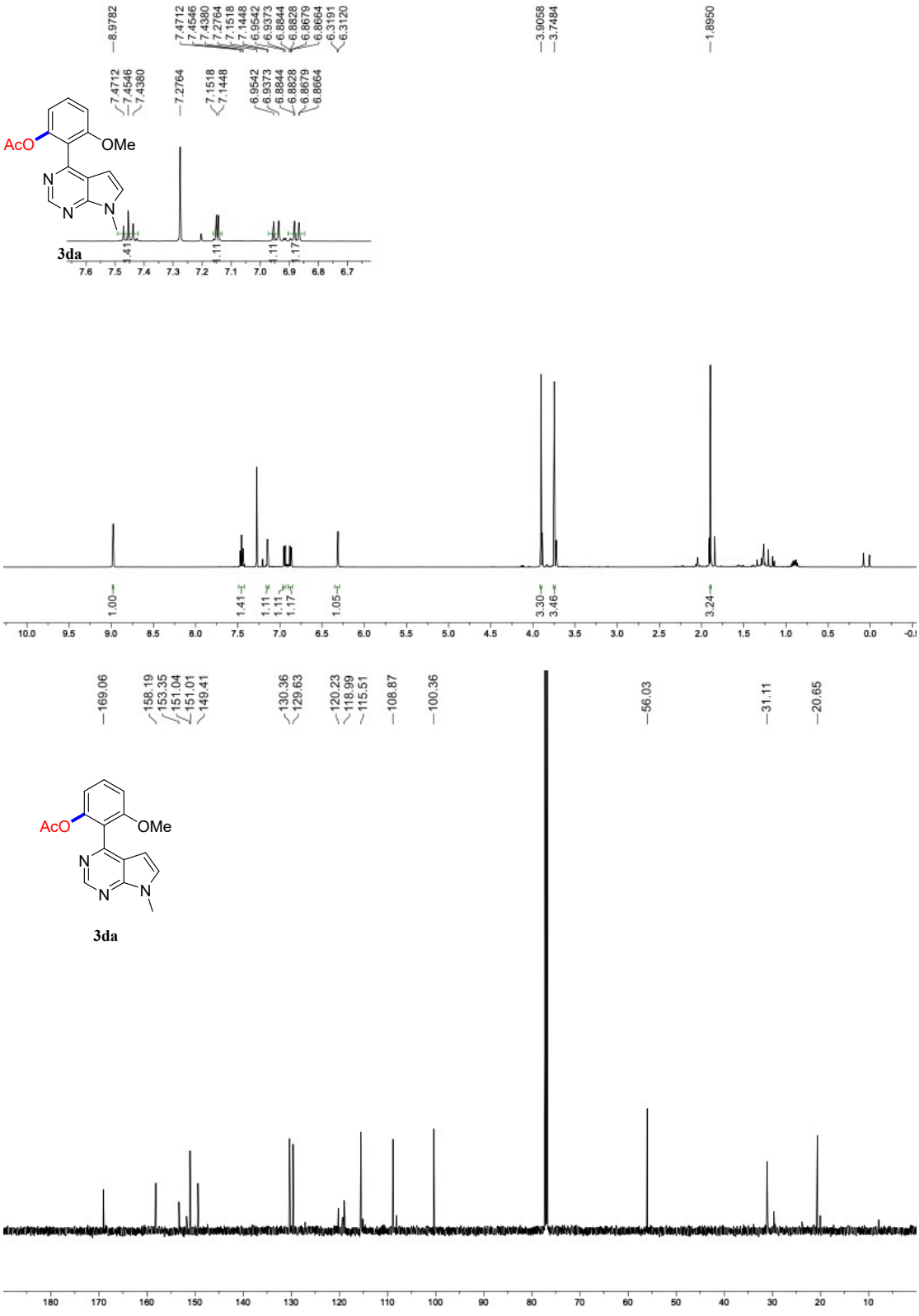

8.9699
7.7755
7.7703
7.4954
7.4902
7.4781
7.4729
7.2684
7.2527
7.2456
7.2291
7.2118
6.5690
6.5619
3.9302
2.0570
Cl
AcO
N
N
N
3cf
1.04
0.98
1.60
1.09
1.18
1.00
3.41
2.95

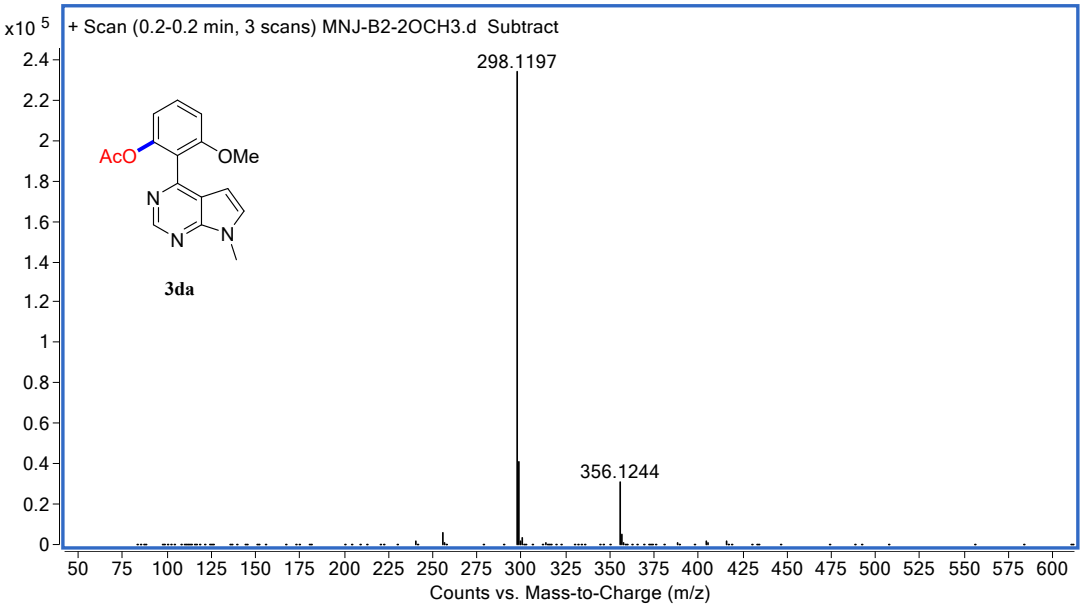

169.04
154.10
151.55
151.22
146.83
132.32
131.57
131.01
130.38
130.32
124.85
117.00
99.96
31.26
20.86
Cl
AcO
N
N
N
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

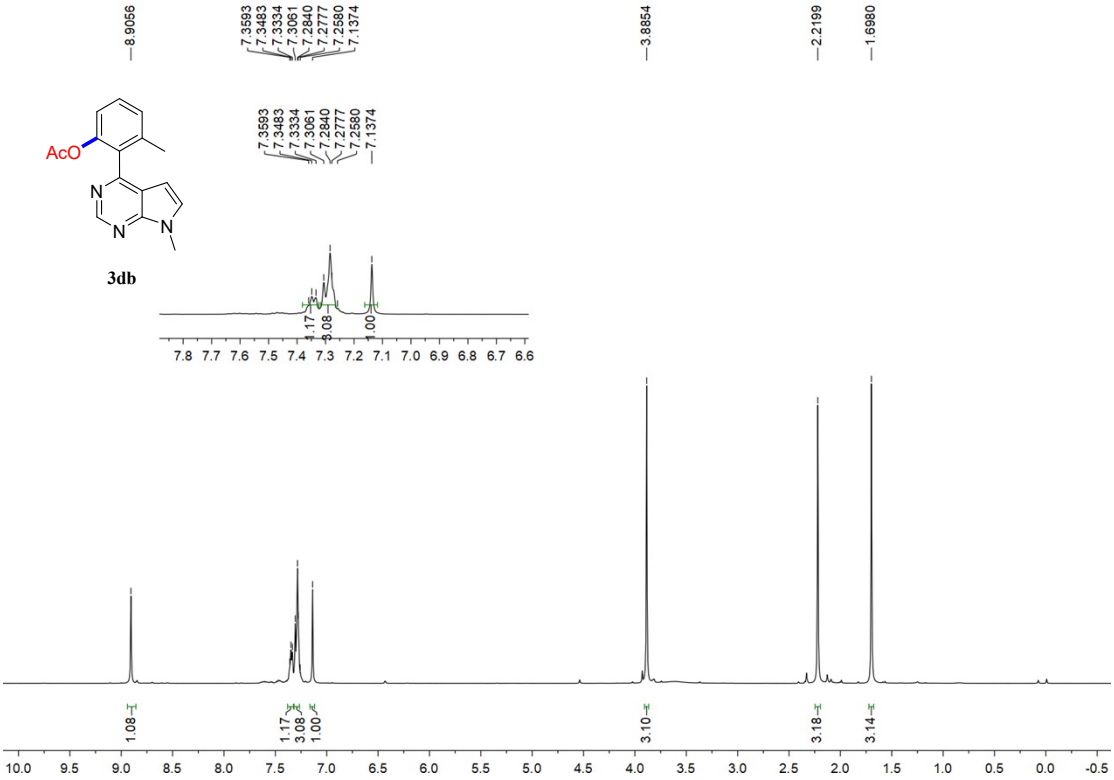
3cf

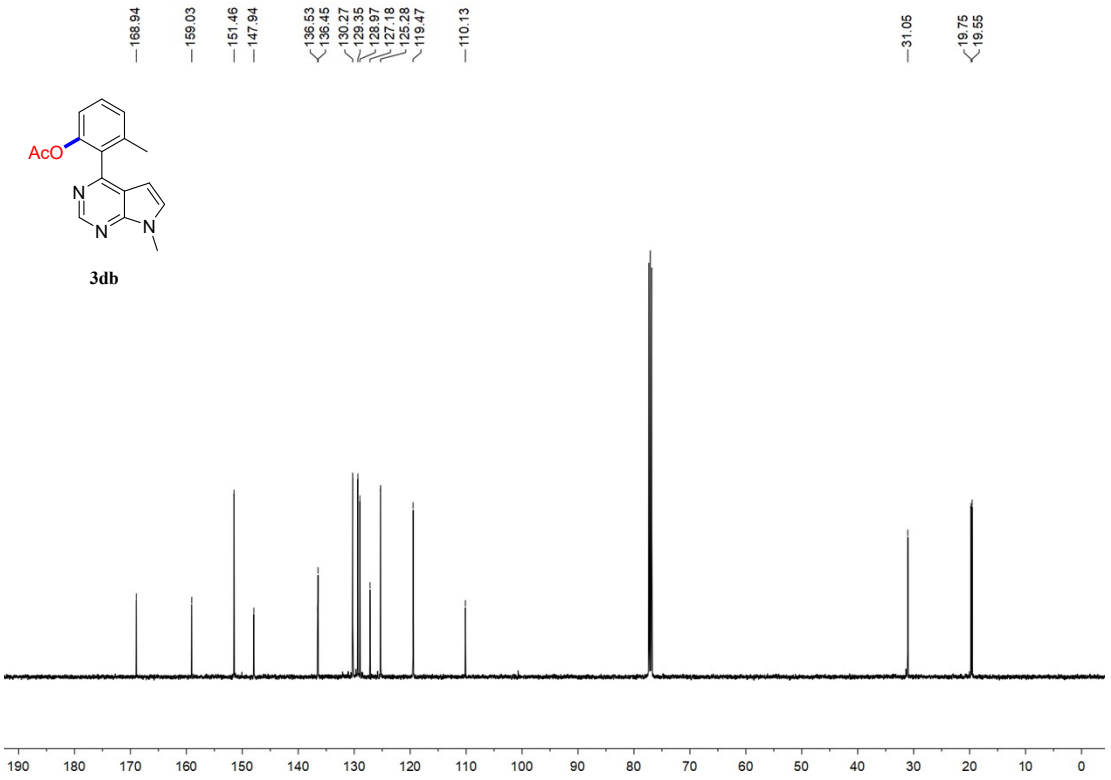

+ESI Scan (0.163 min) Frag=175.0V ZR-20A-01.d
302.0677
302.1279
303.0703
Cl
AcO
N
N
N
Counts vs. Mass-to-Charge (m/z)

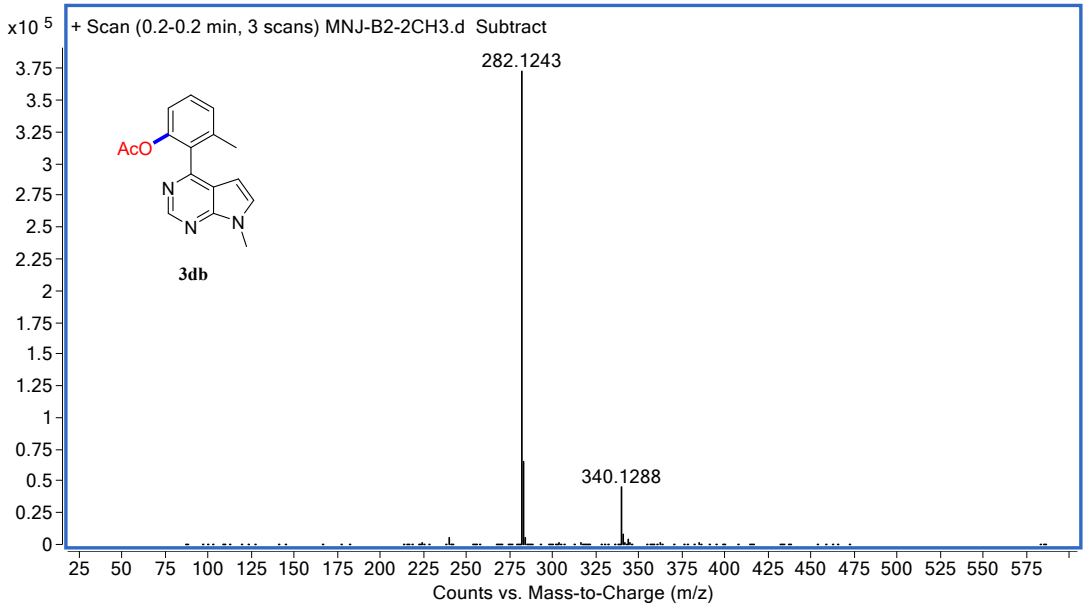
3cf

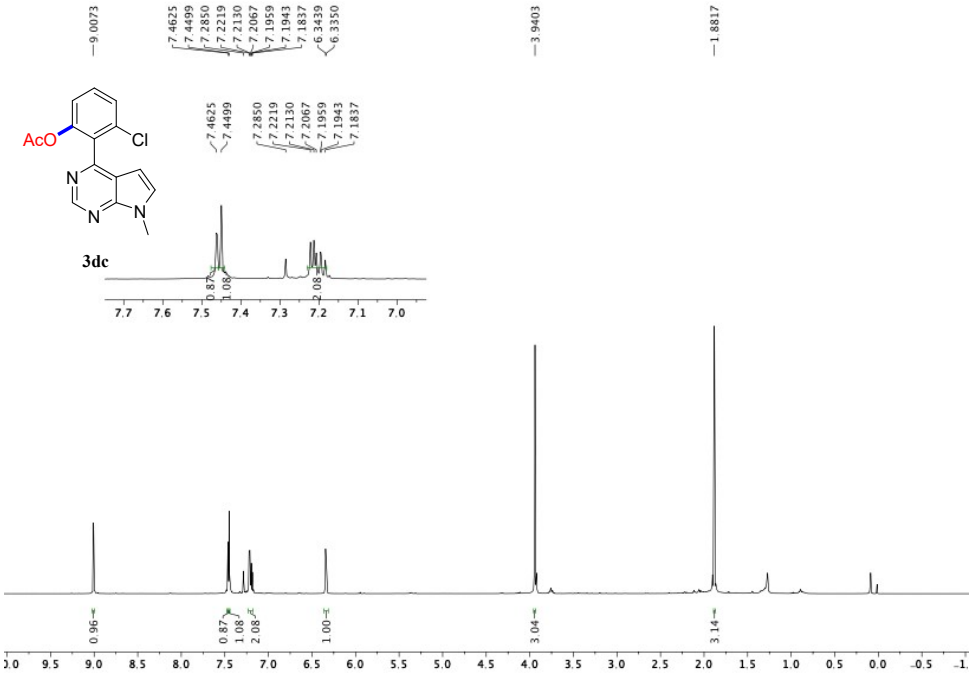

8.9782
7.4712
7.4546
7.4380
7.2764
7.1518
7.1448
6.9542
6.9373
6.8844
6.8828
6.8679
6.8664
6.3191
6.3120
3.9058
3.7484
1.8950
AcO
OMe
N
N
N
3da
1.00
1.41
1.11
1.11
1.17
1.05
3.30
3.46
3.24
169.06
158.19
153.35
151.04
151.01
149.41
130.36
129.63
120.23
118.99
115.51
108.87
100.36
56.03
31.11
20.65

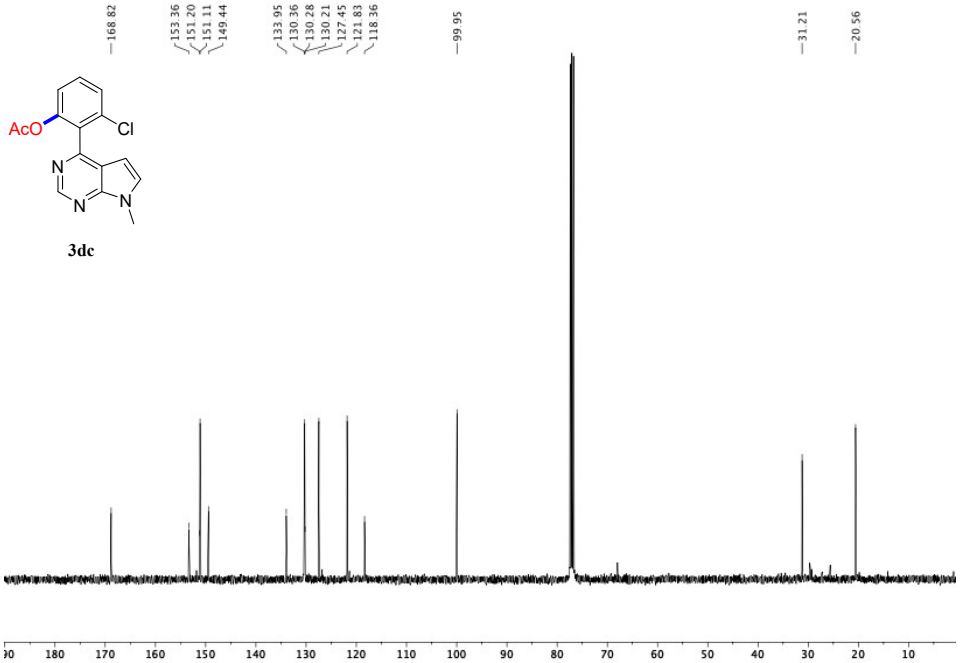

x10 5
+ Scan (0.2-0.2 min, 3 scans) MNJ-B2-2OCH3.d Subtract
298.1197
356.1244
AcO
OMe
N
N
N
3da
Counts vs. Mass-to-Charge (m/z)

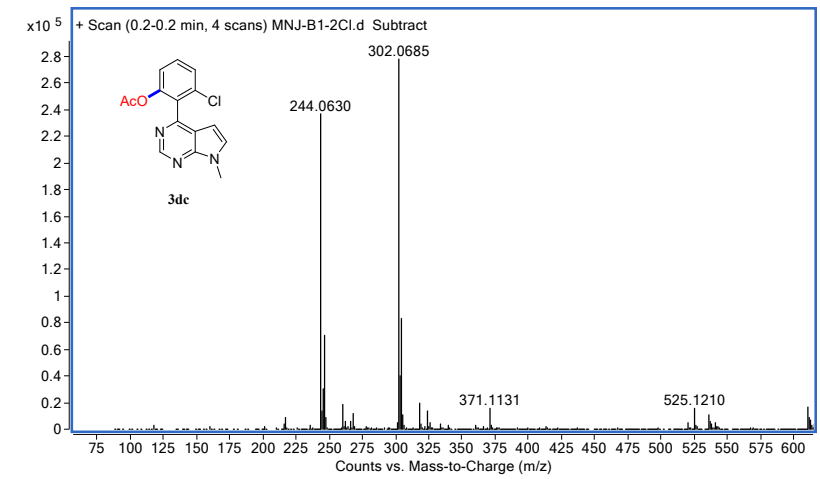

8.9056
7.3593
7.3483
7.3334
7.3061
7.2840
7.2777
7.2580
7.1374
3.8854
2.2199
1.6980
AcO
N
N
N
3db
1.17
3.08
1.00
1.08
3.10
3.18
3.14


168.94
159.03
151.46
147.94
136.53
136.45
130.27
129.35
128.97
127.18
125.28
119.47
110.13
31.05
19.75
19.55
AcO
N
N
N
3db
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


x10 5
+ Scan (0.2-0.2 min, 3 scans) MNJ-B2-2CH3.d Subtract
282.1243
340.1288
AcO
N
N
N
3db
3.75
3.5
3.25
3
2.75
2.5
2.25
2
1.75
1.5
1.25
1
0.75
0.5
0.25
0
25 50 75 100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575
Counts vs. Mass-to-Charge (m/z)

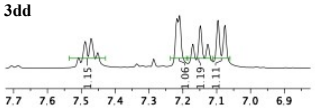

9.0073
7.4625
7.4499
7.2850
7.2219
7.2130
7.2067
7.1959
7.1943
7.1837
6.3439
6.3350
3.9403
1.8817
AcO
Cl
N
N
N
3dc
0.87
1.08
2.08
0.96
1.00
3.04
3.14

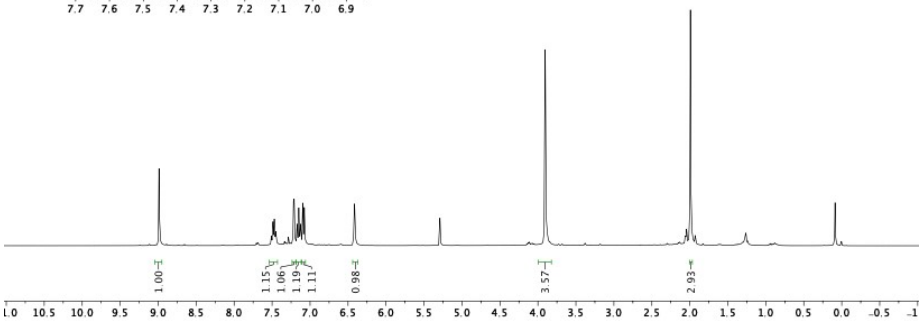

168.82
153.36
151.20
151.11
149.44
133.95
130.36
130.28
130.21
127.45
121.83
118.36
99.95
31.21
20.56
AcO
Cl
N
N
N
3dc


x10 5
+ Scan (0.2-0.2 min, 4 scans) MNJ-B1-2Cl.d Subtract
302.0685
244.0630
371.1131
525.1210
AcO
Cl
N
N
N
3dc
Counts vs. Mass-to-Charge (m/z)

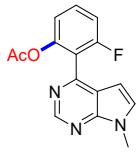

8.9890
7.5079
7.4879
7.4709
7.4512
7.2175
7.2098
7.1705
7.1485
7.1263
7.0962
7.0758
6.4151
3.9045
1.9925
AcO
F
N
N
N

3dd

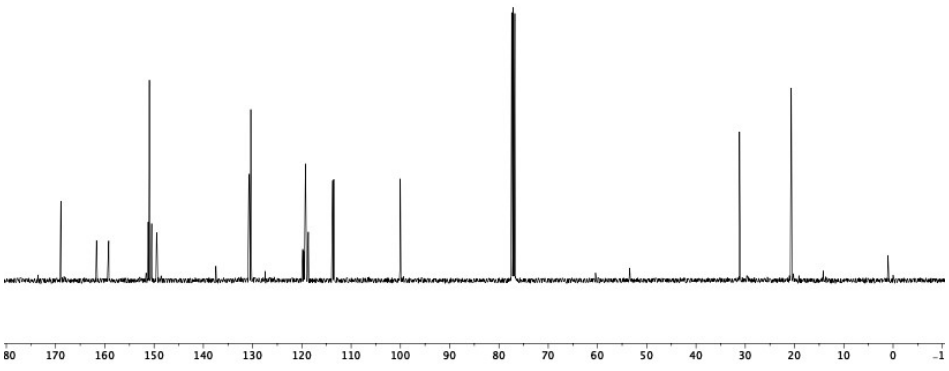

1.15
1.06
1.19
1.11
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9

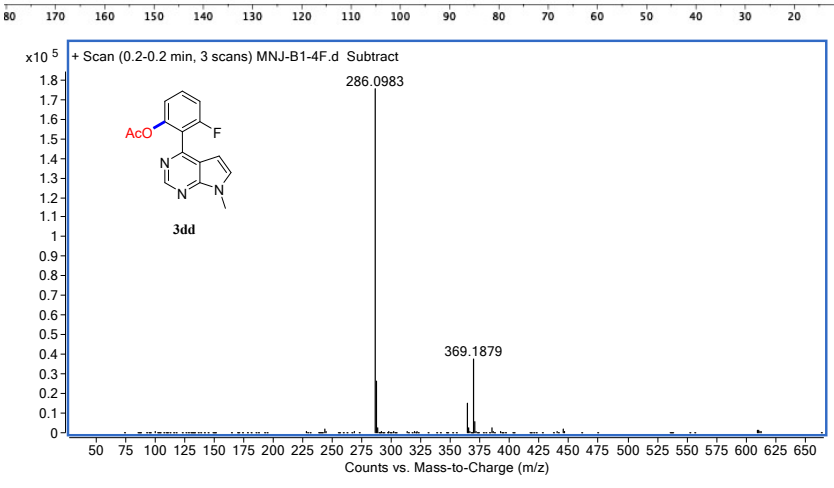

1.00
1.15
1.06
1.19
1.11
0.98
3.57
2.93

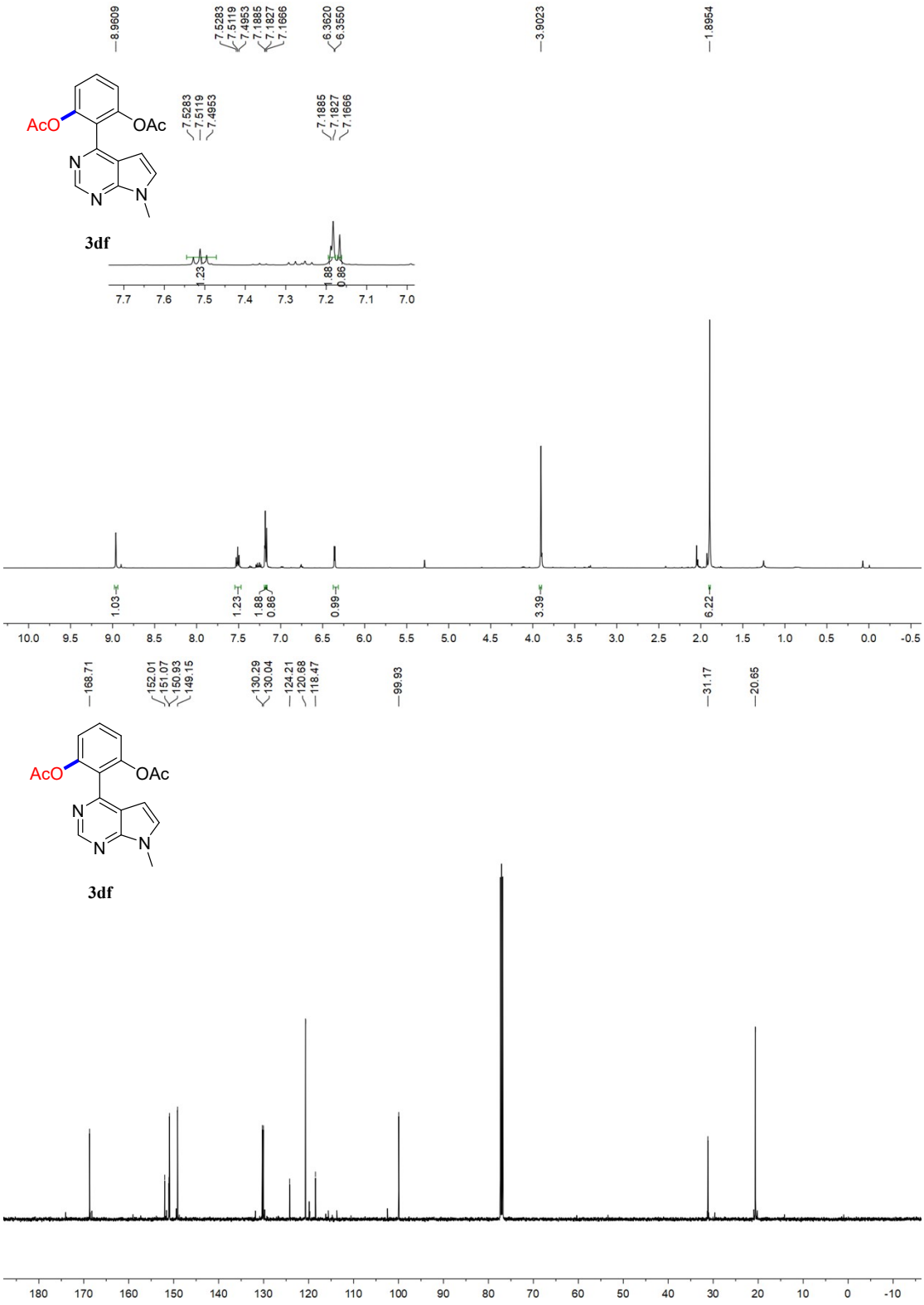

168.93
161.70
159.20
151.20
150.96
150.49
149.50
149.44
130.76
130.66
130.37
119.82
119.65
119.28
119.25
118.70
113.75
113.53
100.06
100.02
31.18
20.67

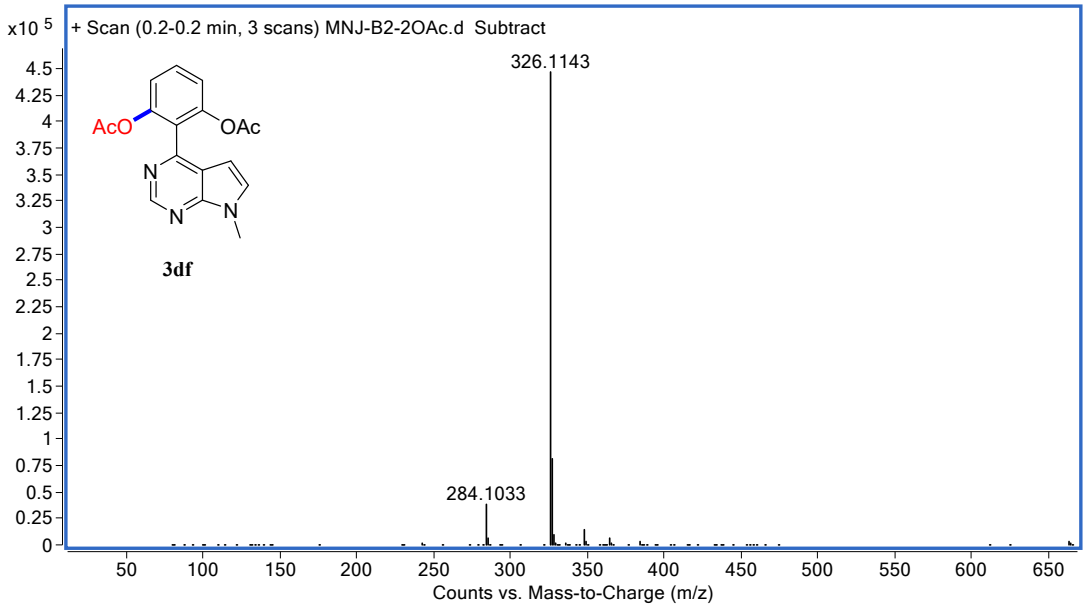

AcO
F
N
N
N

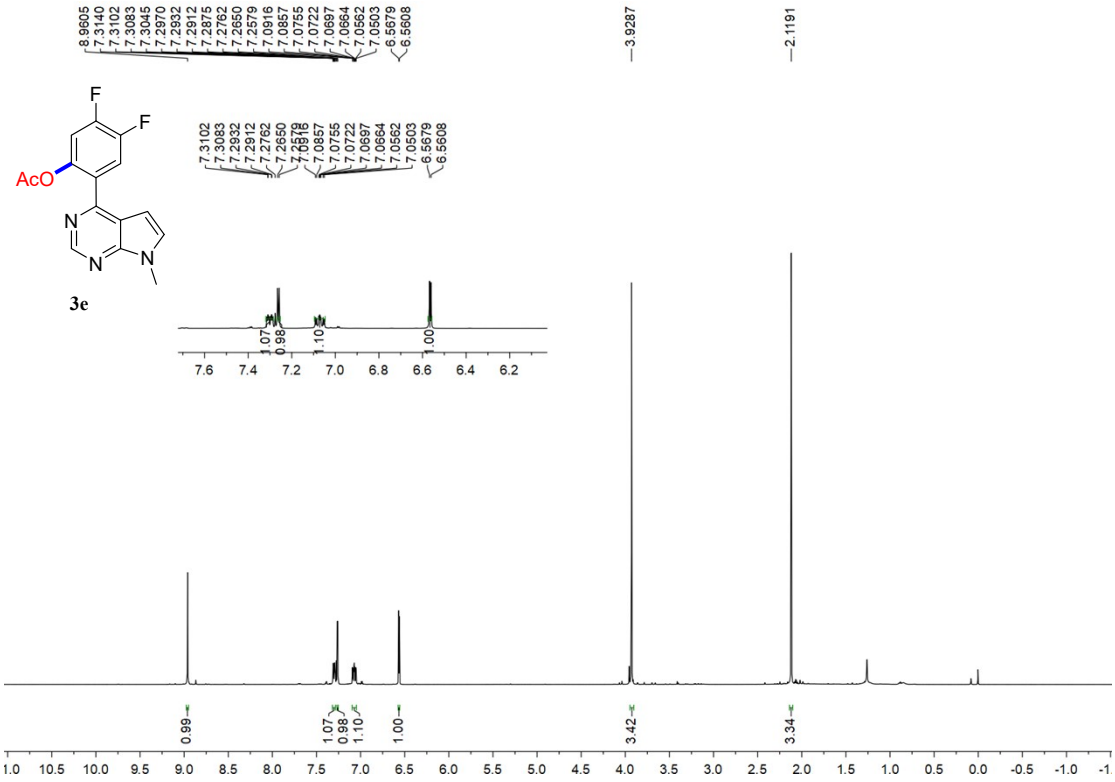
3dd

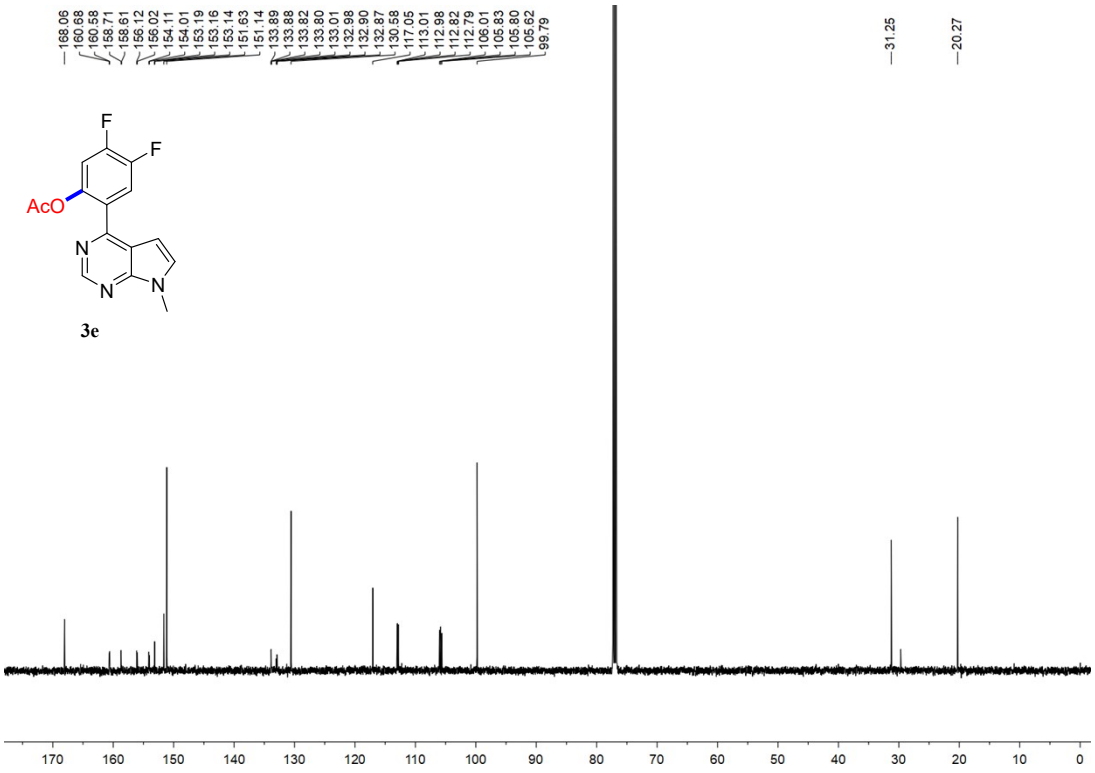


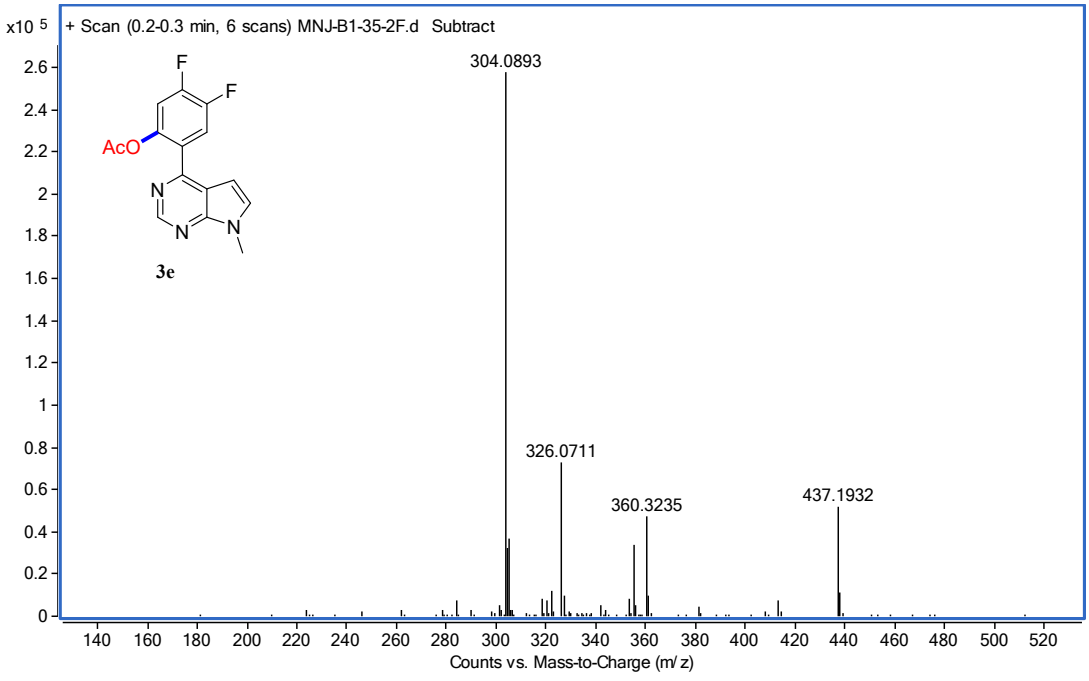

+ Scan (0.2-0.2 min, 3 scans) MNJ-B1-4F.d Subtract
286.0983
369.1879
AcO
F
N
N
N
3dd
Counts vs. Mass-to-Charge (m/z)

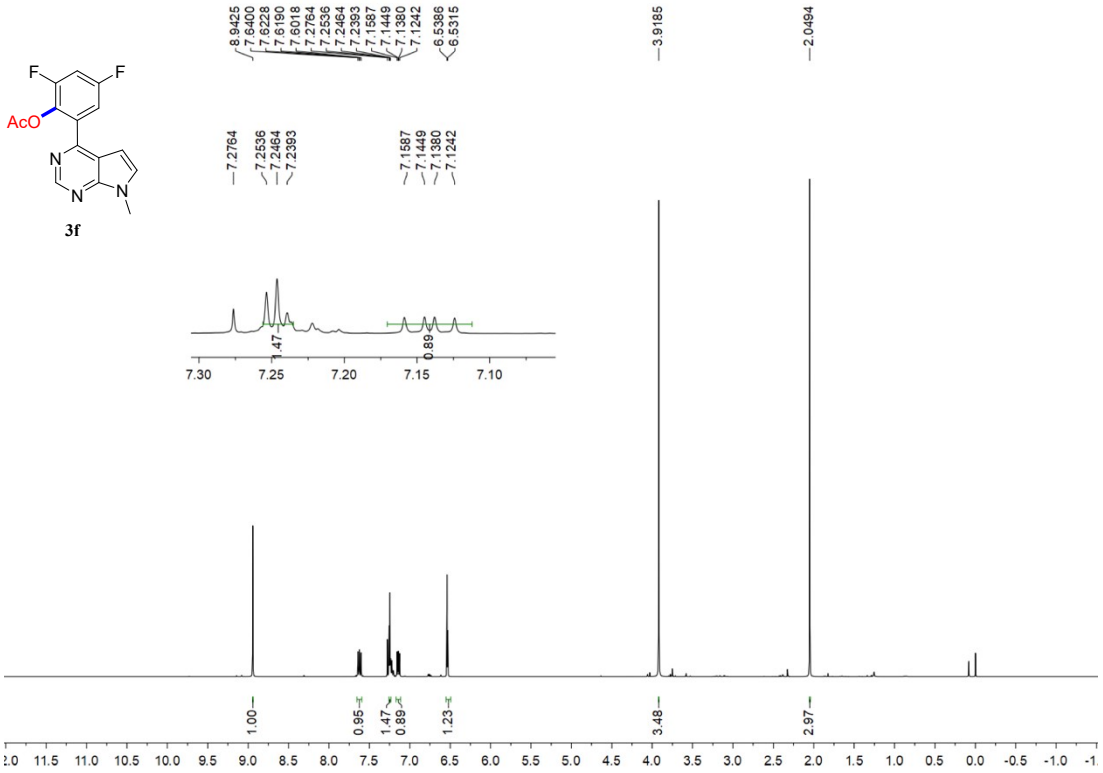

8.9609
7.5283
7.5119
7.4953
7.1885
7.1827
7.1666
6.3620
6.3550
3.9023
1.8954
AcO
OAc
N
N
N
3df
1.23
1.88
0.86
1.03
0.99
3.39
6.22
168.71
152.01
151.07
150.93
149.15
130.29
130.04
124.21
120.68
118.47
99.93
31.17
20.65

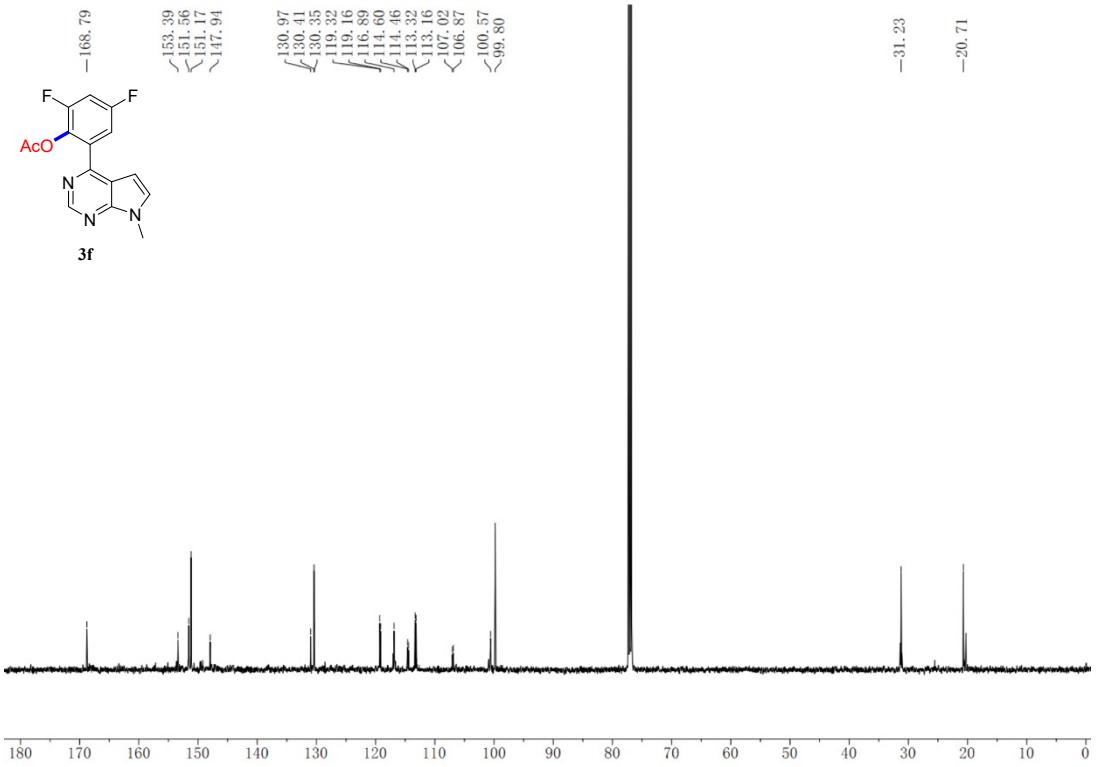

x10 5
+ Scan (0.2-0.2 min, 3 scans) MNJ-B2-2OAc.d Subtract
326.1143
284.1033
AcO
OAc
N
N
N
3df
Counts vs. Mass-to-Charge (m/z)

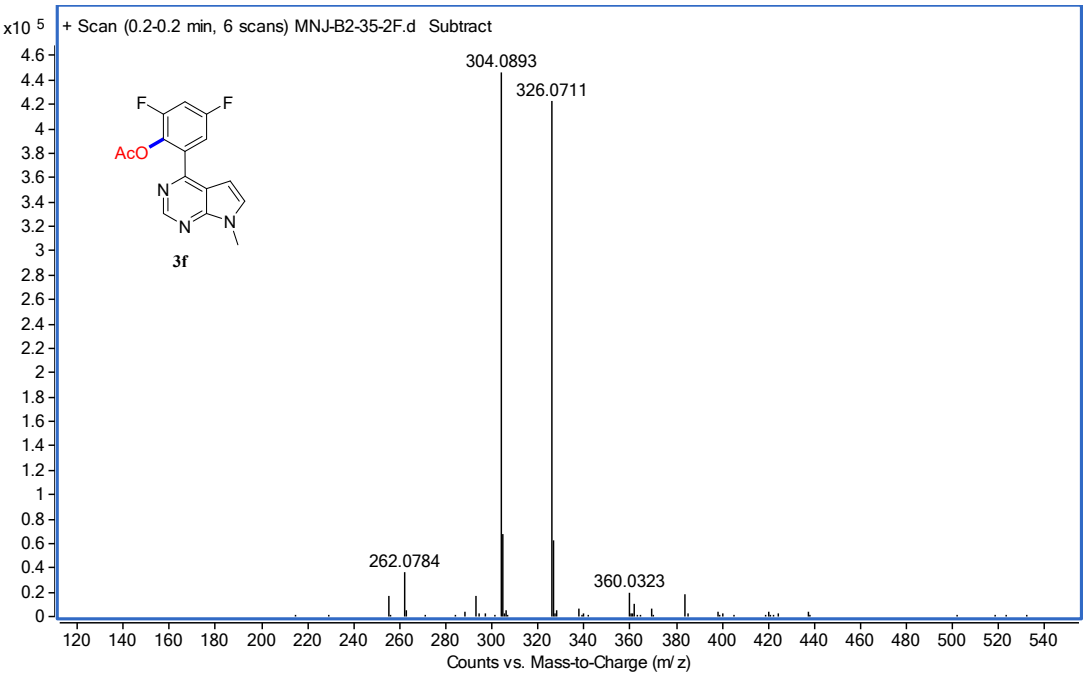

8.9605
7.3140
7.3102
7.3083
7.3045
7.2970
7.2932
7.2912
7.2875
7.2762
7.2650
7.2579
7.0916
7.0857
7.0755
7.0722
7.0697
7.0664
7.0562
7.0503
6.5679
6.5608
3.9287
2.1191
F
F
AcO
N
N
N
3e
1.07
0.98
1.10
1.00
0.99
3.42
3.34

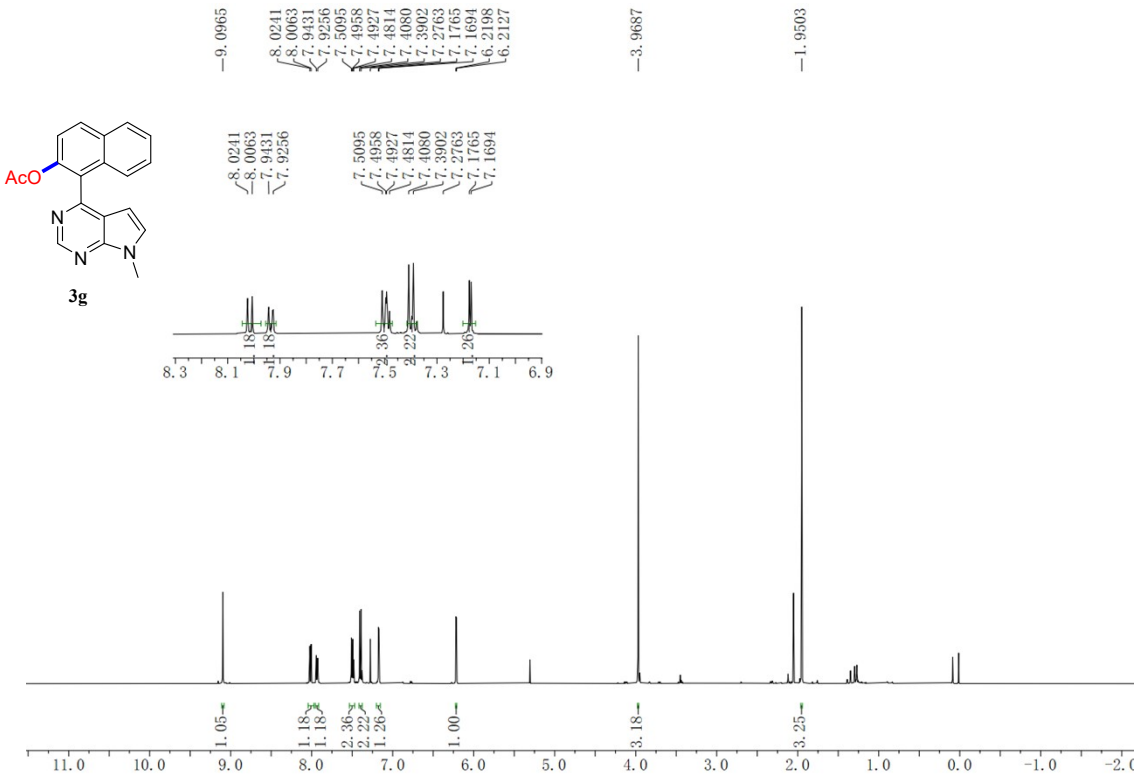

168.06
160.68
160.58
158.71
158.61
156.12
156.02
154.11
154.01
153.19
153.16
153.14
151.63
151.14
133.89
133.88
133.82
133.80
133.01
132.98
132.90
132.87
130.58
117.05
113.01
112.98
112.82
112.79
106.01
105.83
105.80
105.62
99.79
31.25
20.27
F
F
AcO
N
N
N
3e
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

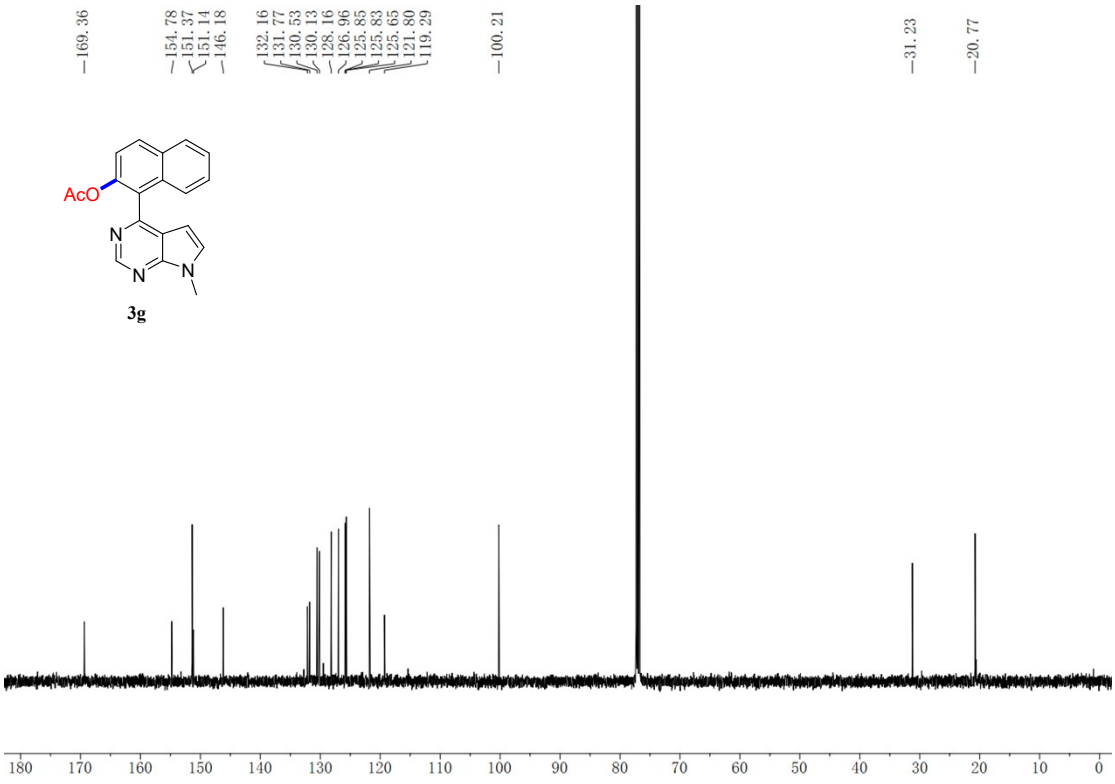

x10 5
+ Scan (0.2-0.3 min, 6 scans) MNJ-B1-35-2F.d Subtract
304.0893
326.0711
360.3235
437.1932
F
F
AcO
N
N
N
3e
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
460
480
500
520
Counts vs. Mass-to-Charge (m/z)

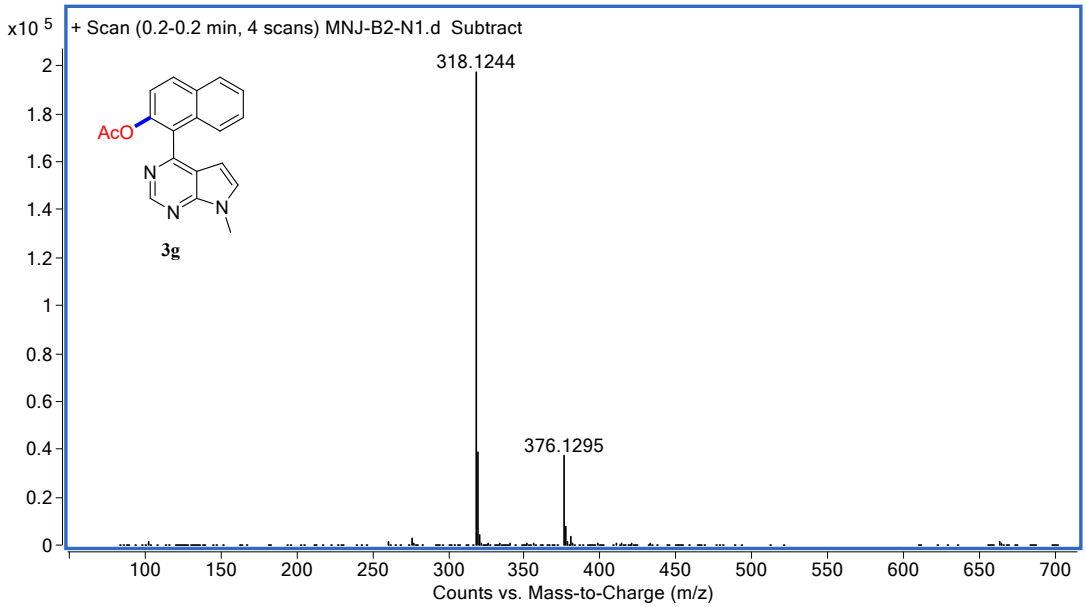

F
F
AcO
N
N
N
3f
8.9425
7.6400
7.6228
7.6190
7.6018
7.2764
7.2536
7.2464
7.2393
7.1587
7.1449
7.1380
7.1242
6.5386
6.5315
3.9185
2.0494
1.47
0.89
7.30
7.25
7.20
7.15
7.10
1.00
0.95
1.47
0.89
1.23
3.48
2.97

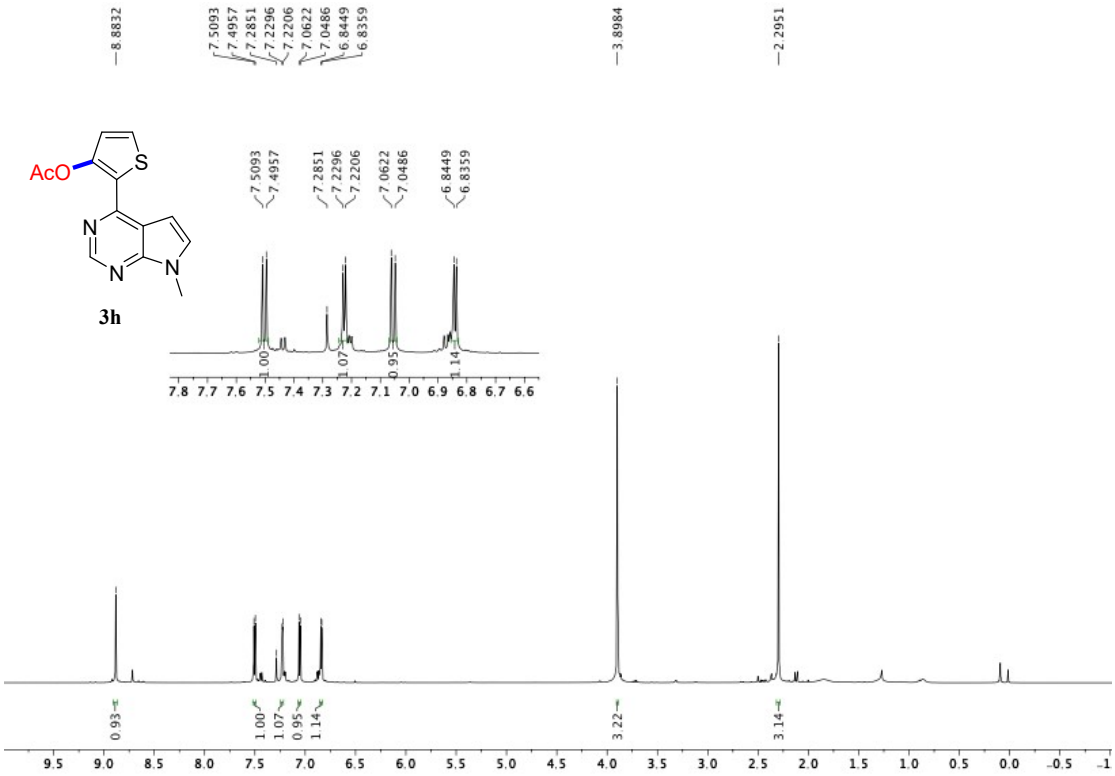

F
F
AcO
N
N
N
3f
168.79
153.39
151.56
151.17
147.94
130.97
130.41
130.35
119.32
119.16
116.89
114.60
114.46
113.32
113.16
107.02
106.87
100.57
99.80
31.23
20.71

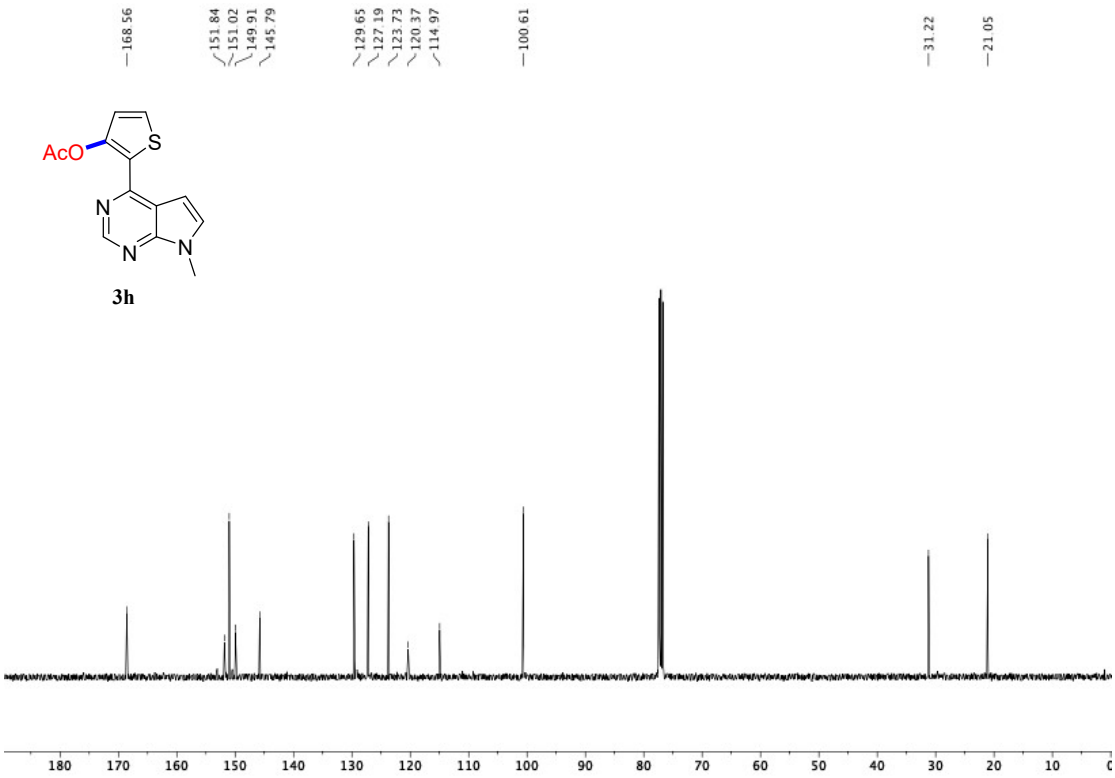

x10 5
+ Scan (0.2-0.2 min, 6 scans) MNJ-B2-35-2F.d Subtract
304.0893
326.0711
262.0784
360.0323
F
F
AcO
N
N
N
3f
Counts vs. Mass-to-Charge (m/z)

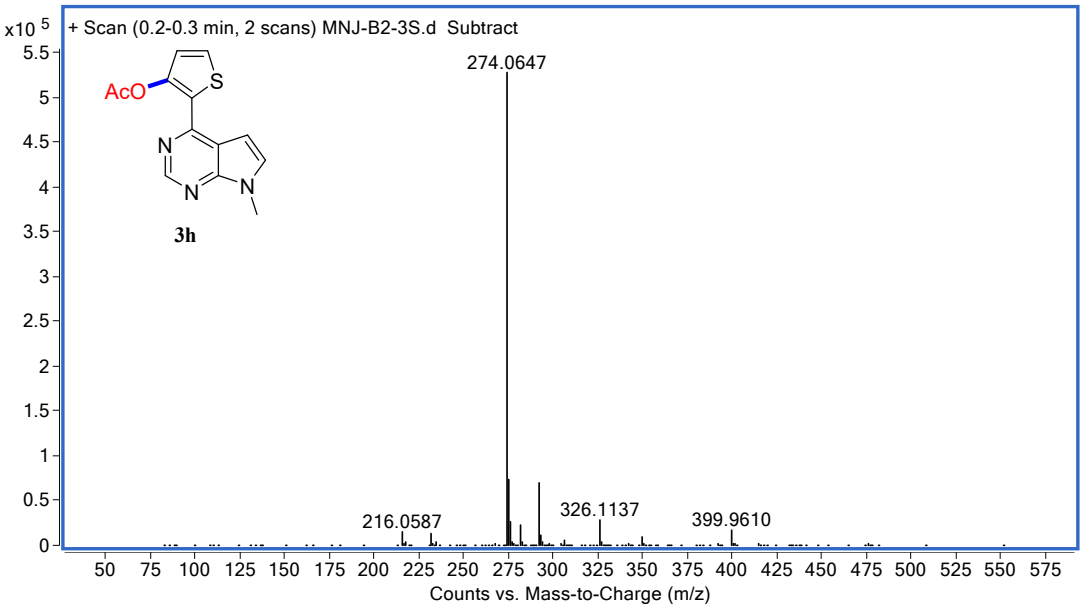

AcO
N
N
N
3g

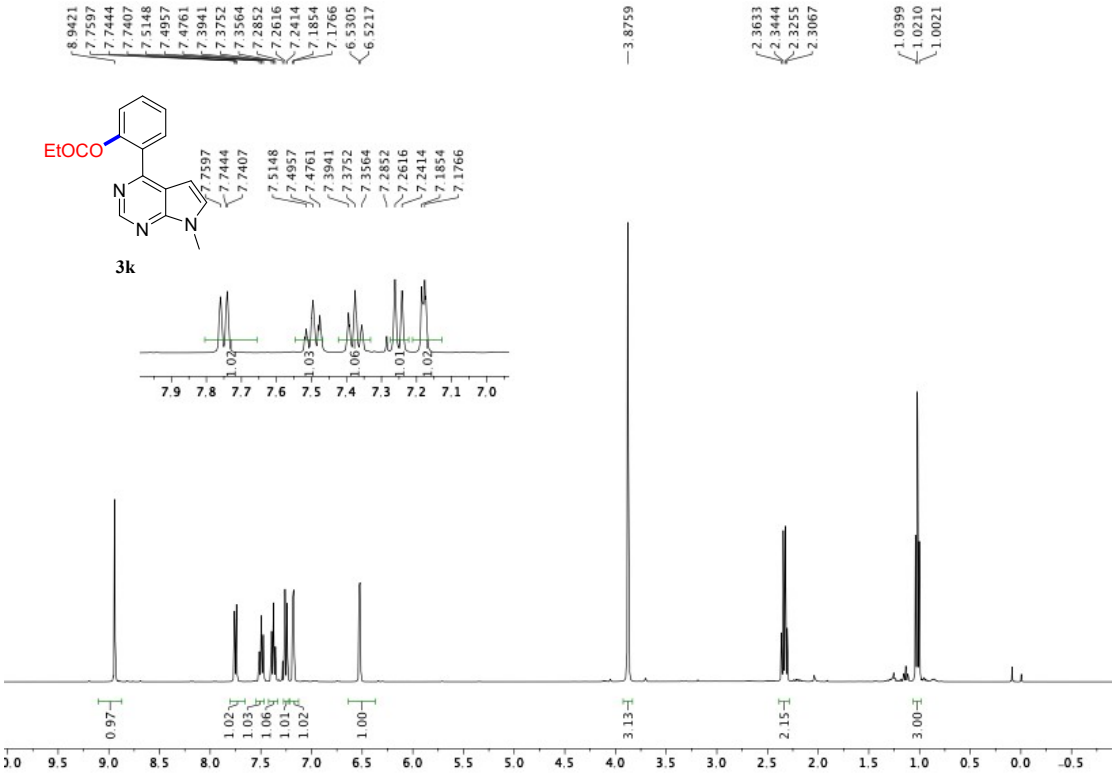

169.36
154.78
151.37
151.14
146.18
132.16
131.77
130.53
130.13
128.16
126.96
125.85
125.83
125.65
121.80
119.29
100.21
31.23
20.77
AcO
N
N
N
3g
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

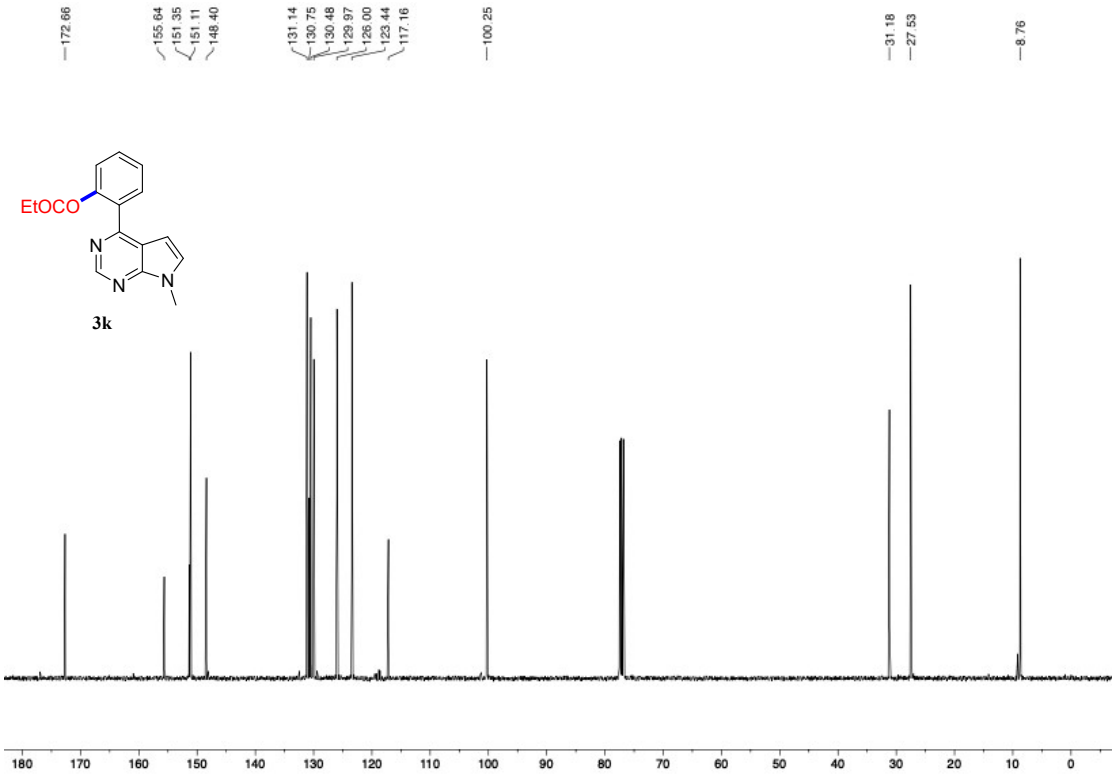

x10 5
+ Scan (0.2-0.2 min, 4 scans) MNJ-B2-N1.d Subtract
318.1244
376.1295
AcO
N
N
N
3g
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
100
150
200
250
300
350
400
450
500
550
600
650
700
Counts vs. Mass-to-Charge (m/z)


8.8832
7.5093
7.4957
7.2851
7.2296
7.2206
7.0622
7.0486
6.8449
6.8359
3.8984
2.2951
AcO
S
N
N
N
3h
0.93
1.00
1.07
0.95
1.14
3.22
3.14

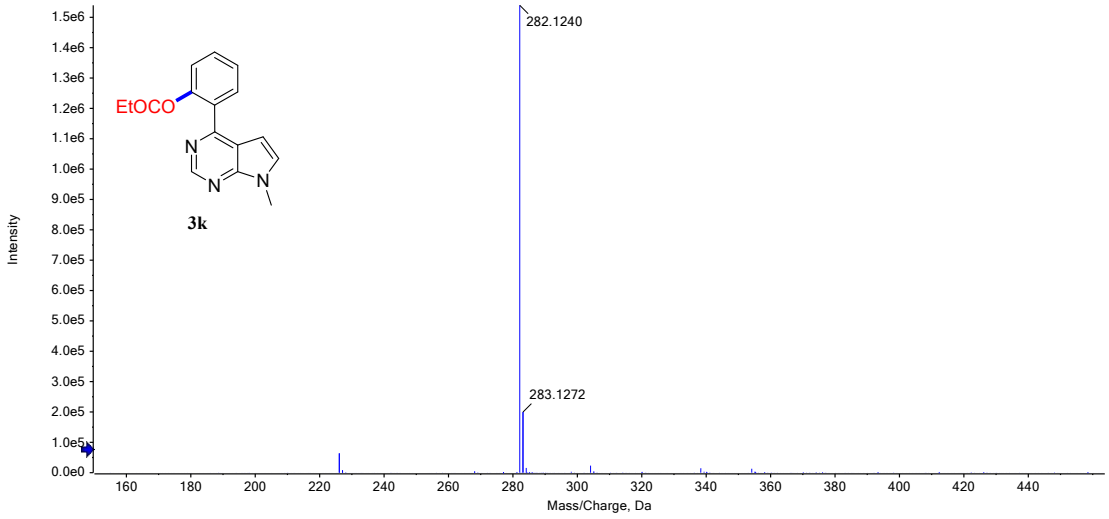

168.56
151.84
151.02
149.91
145.79
129.65
127.19
123.73
120.37
114.97
100.61
31.22
21.05
AcO
S
N
N
N
3h

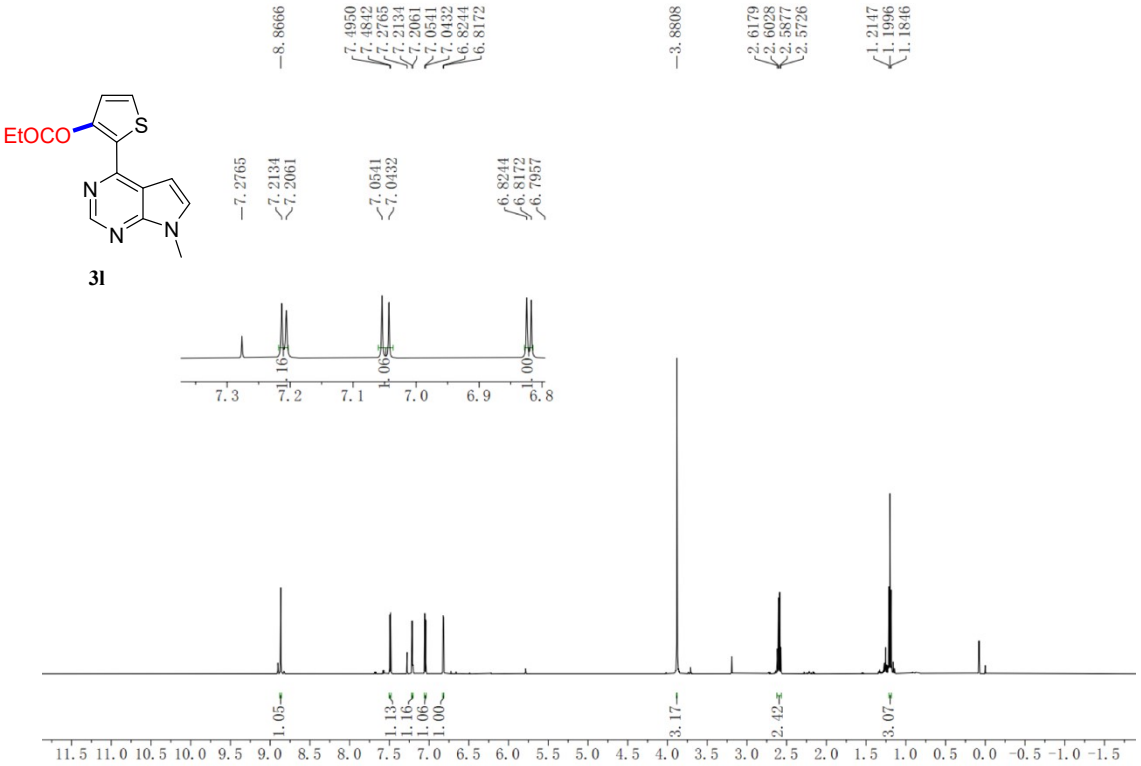

x10 5
+ Scan (0.2-0.3 min, 2 scans) MNJ-B2-3S.d Subtract
AcO
S
N
N
N
3h
274.0647
216.0587
326.1137
399.9610
Counts vs. Mass-to-Charge (m/z)


EtOCO
N
N
N
3k



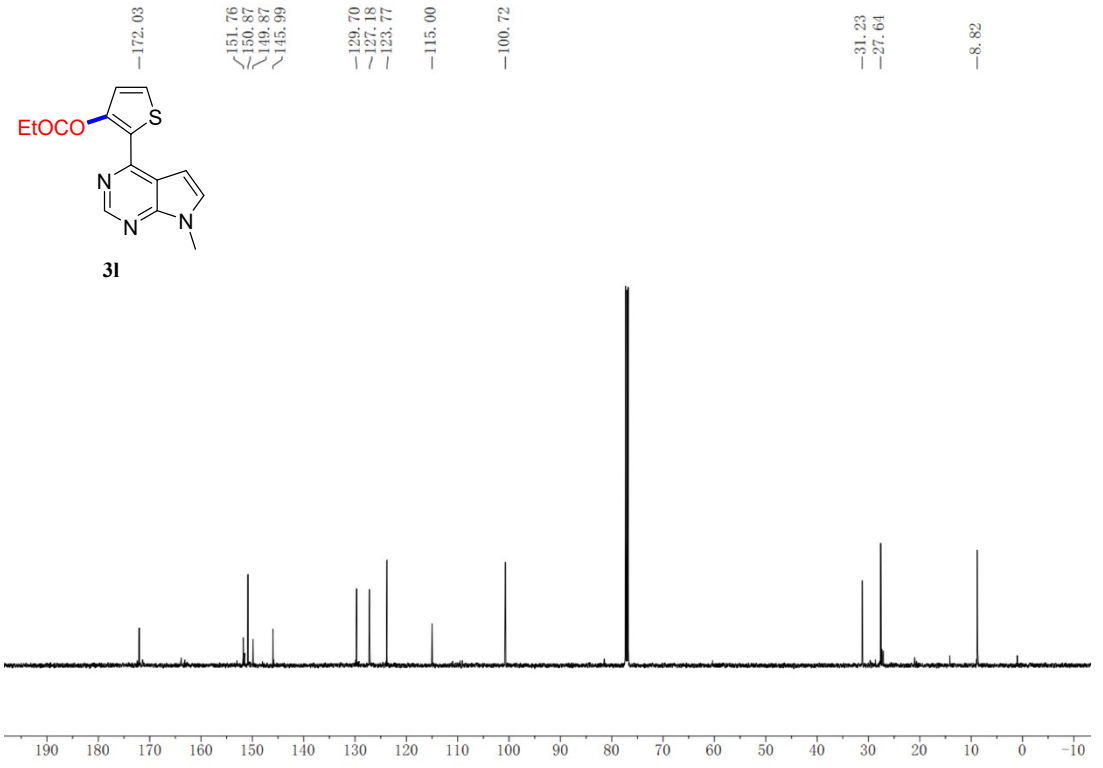
Spectrum from 0115.wiff (sample 39) - B38, +TOF MS (100 - 1000) from 0.219 to 0.265 min,...pectrum from 0115.wiff (sample 39) - B38, +TOF MS (100 - 1000) from 0.321 to 0.386 min)

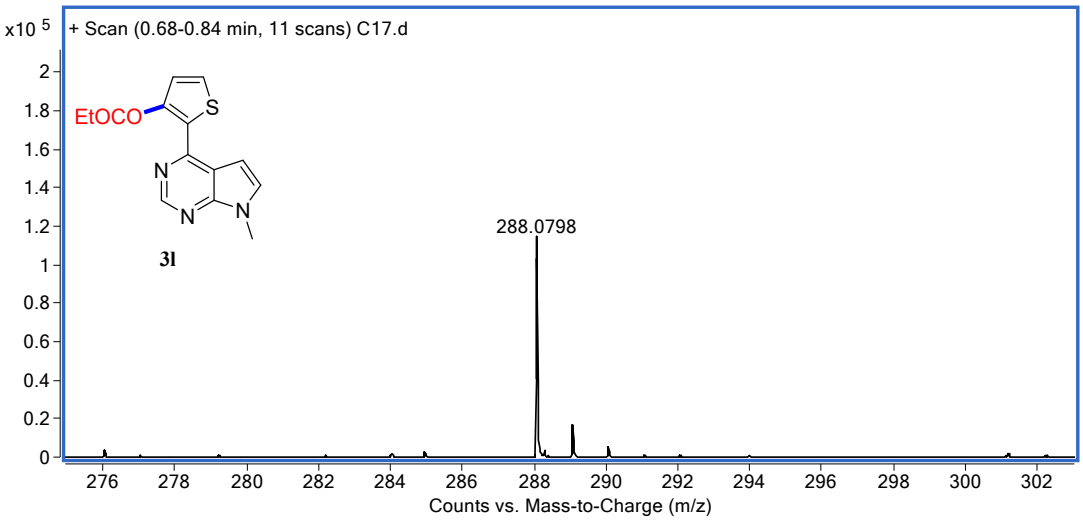


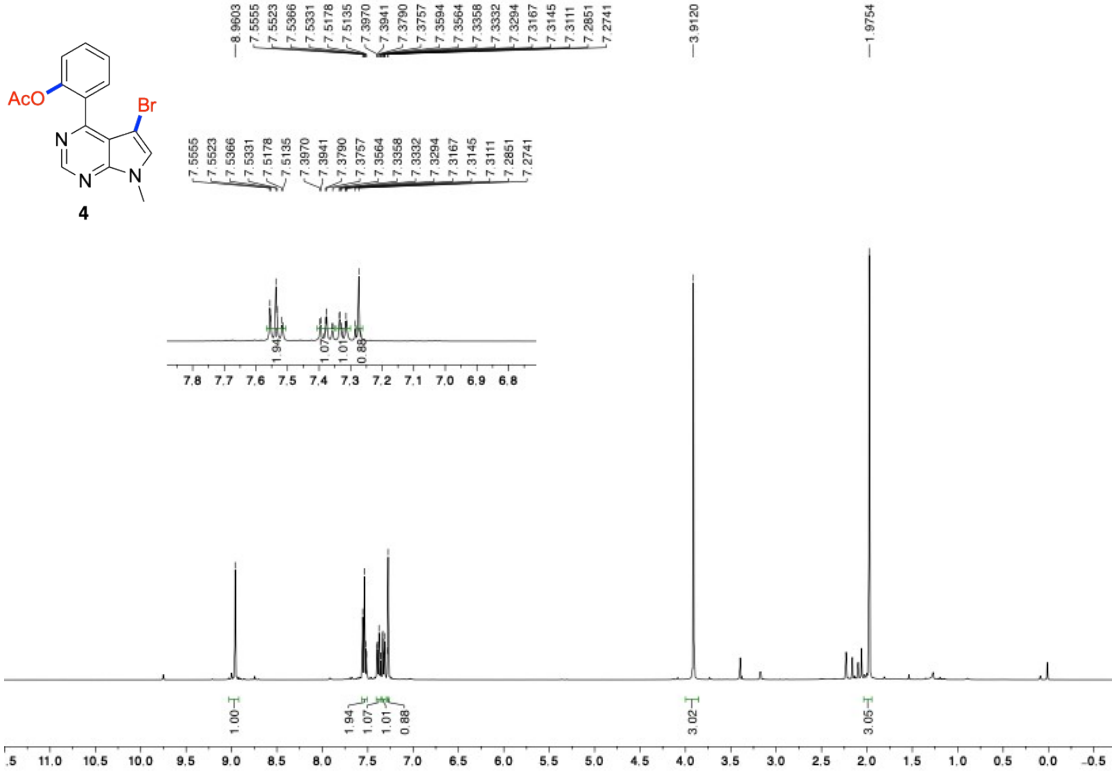

EtOCO
S
N
N
N
3l

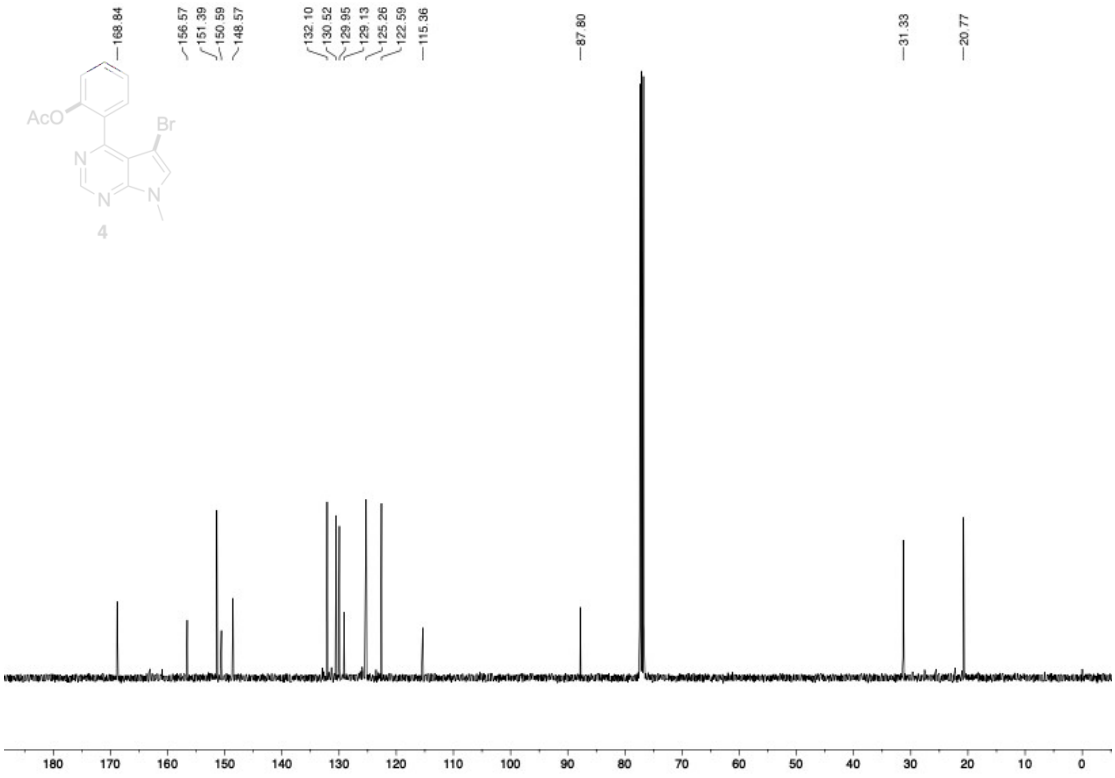
8.8666
7.4950
7.4842
7.2765
7.2134
7.2061
7.0541
7.0432
6.8244
6.8172
3.8808
2.6179
2.6028
2.5877
2.5726
1.2147
1.1996
1.1846
1.05
1.13
1.16
1.06
1.00
3.17
2.42
3.07

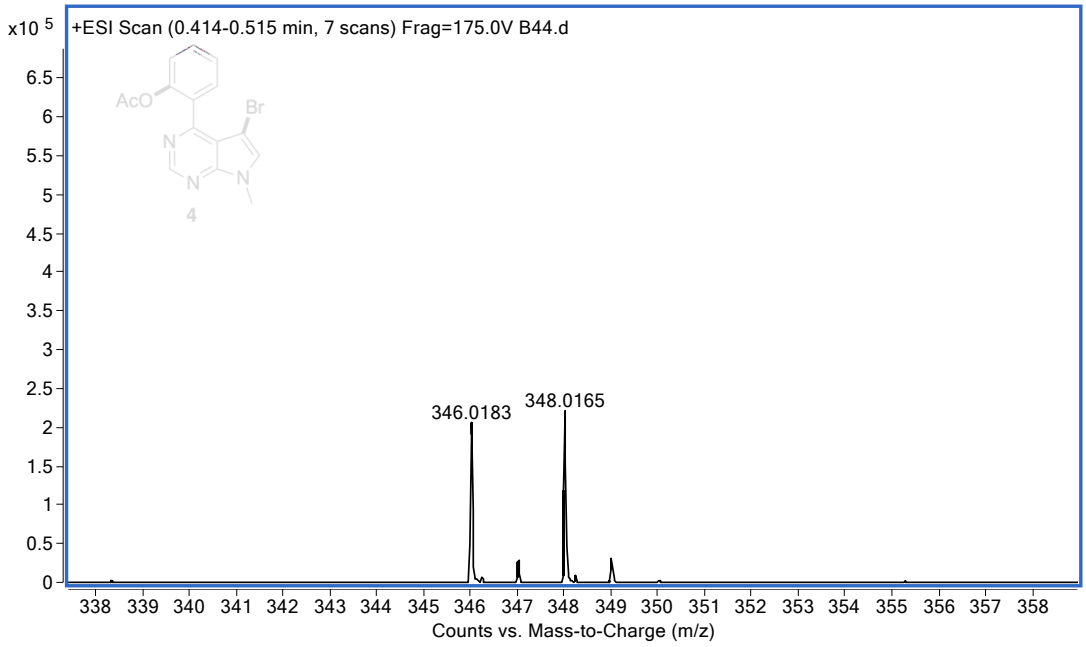
EtOCO
S
N
N
N
3l

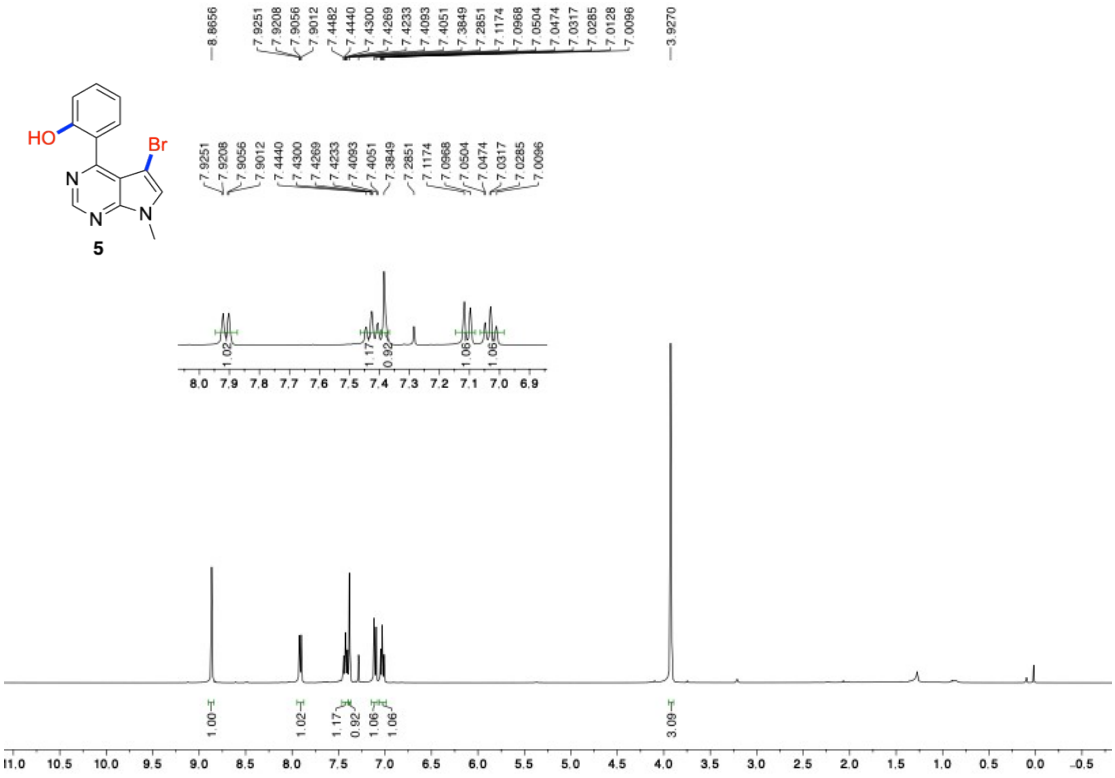

172.03
151.76
150.87
149.87
145.99
129.70
127.18
123.77
115.00
100.72
31.23
27.64
8.82

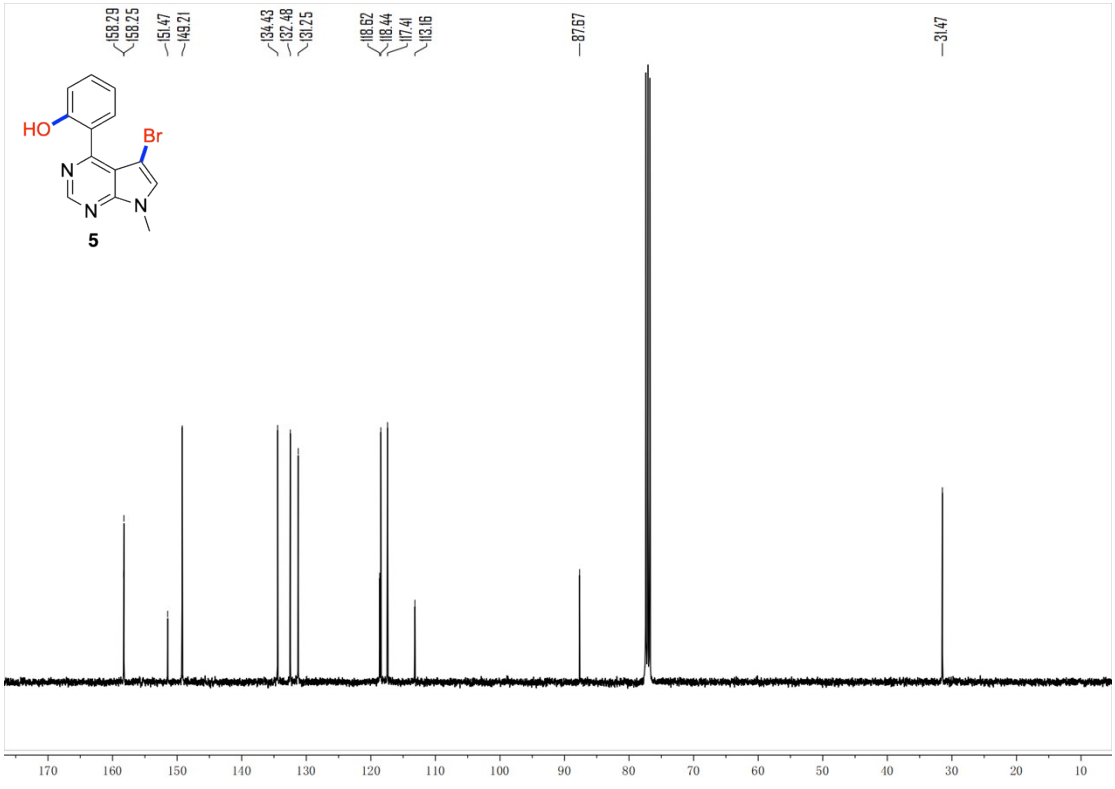

x10 5
+ Scan (0.68-0.84 min, 11 scans) C17.d
EtOCO
S
N
N
N
3l
288.0798
Counts vs. Mass-to-Charge (m/z)

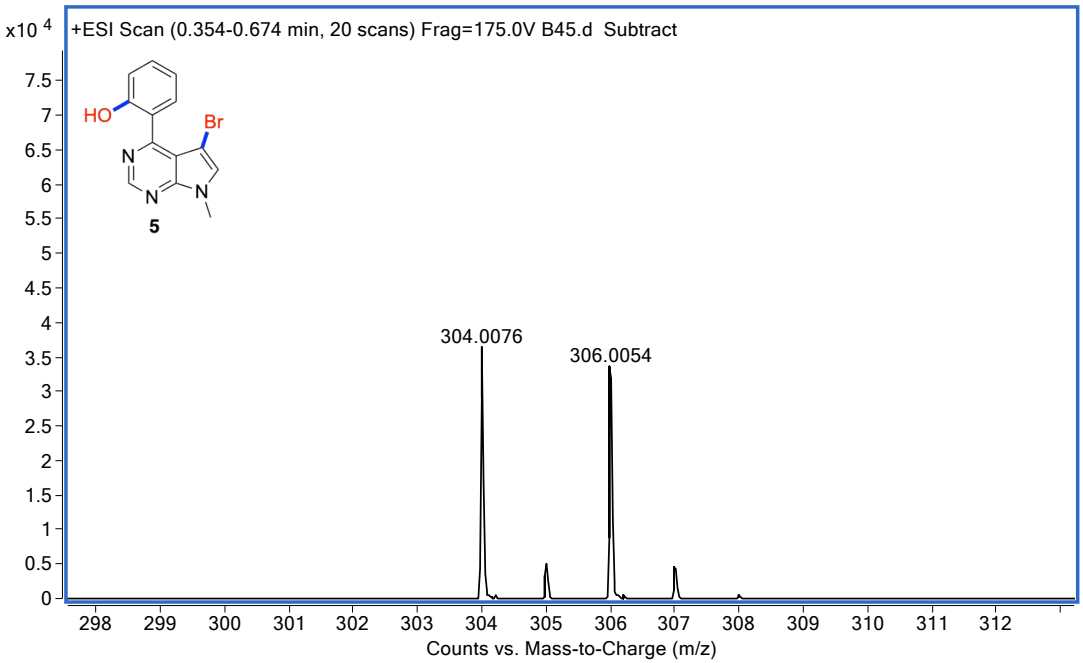

AcO
Br
N
N
N
4
8.9603
7.5555
7.5523
7.5366
7.5331
7.5178
7.5135
7.3970
7.3941
7.3790
7.3757
7.3594
7.3564
7.3358
7.3332
7.3294
7.3167
7.3145
7.3111
7.2851
7.2741
3.9120
1.9754


168.84
156.57
151.39
150.59
148.57
132.10
130.52
129.95
129.13
125.26
122.59
115.36
87.80
31.33
20.77
AcO
Br
N
N
4
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

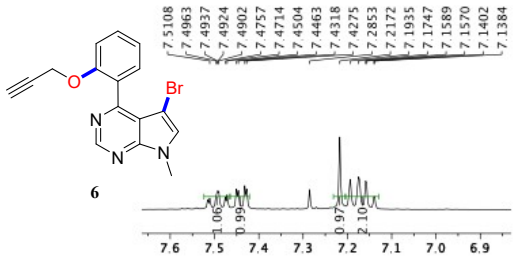

x10 5
+ESI Scan (0.414-0.515 min, 7 scans) Frag=175.0V B44.d
AcO
Br
N
N
4
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
346.0183
348.0165
338 339 340 341 342 343 344 345 346 347 348 349 350 351 352 353 354 355 356 357 358
Counts vs. Mass-to-Charge (m/z)

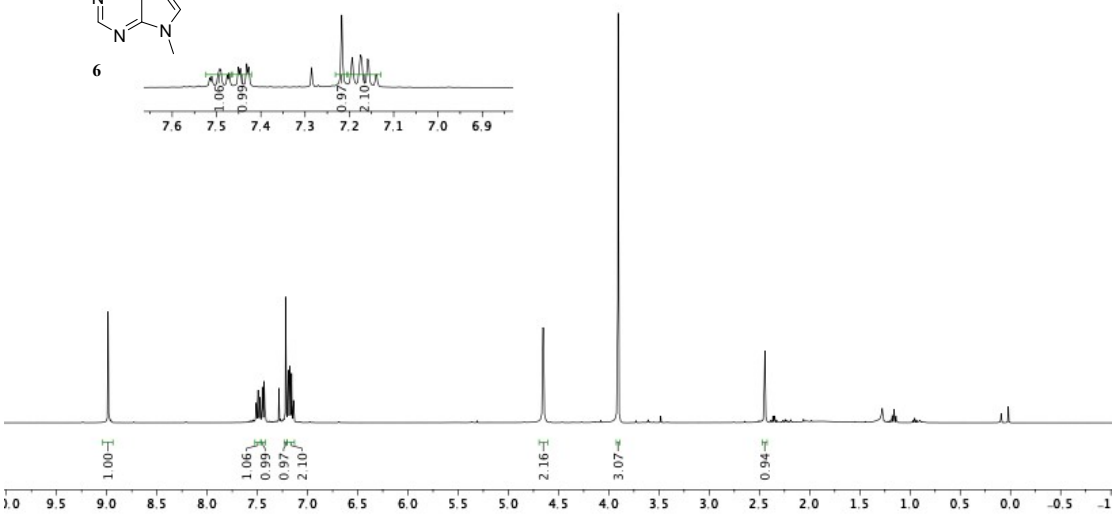

HO
Br
N
N
N
5
8.6556
7.9251
7.9208
7.9056
7.9012
7.4482
7.4440
7.4300
7.4269
7.4233
7.4093
7.4051
7.3849
7.2851
7.1174
7.0968
7.0504
7.0474
7.0317
7.0285
7.0128
7.0096
3.9270
1.00
1.02
1.17
0.92
1.06
1.06
3.09

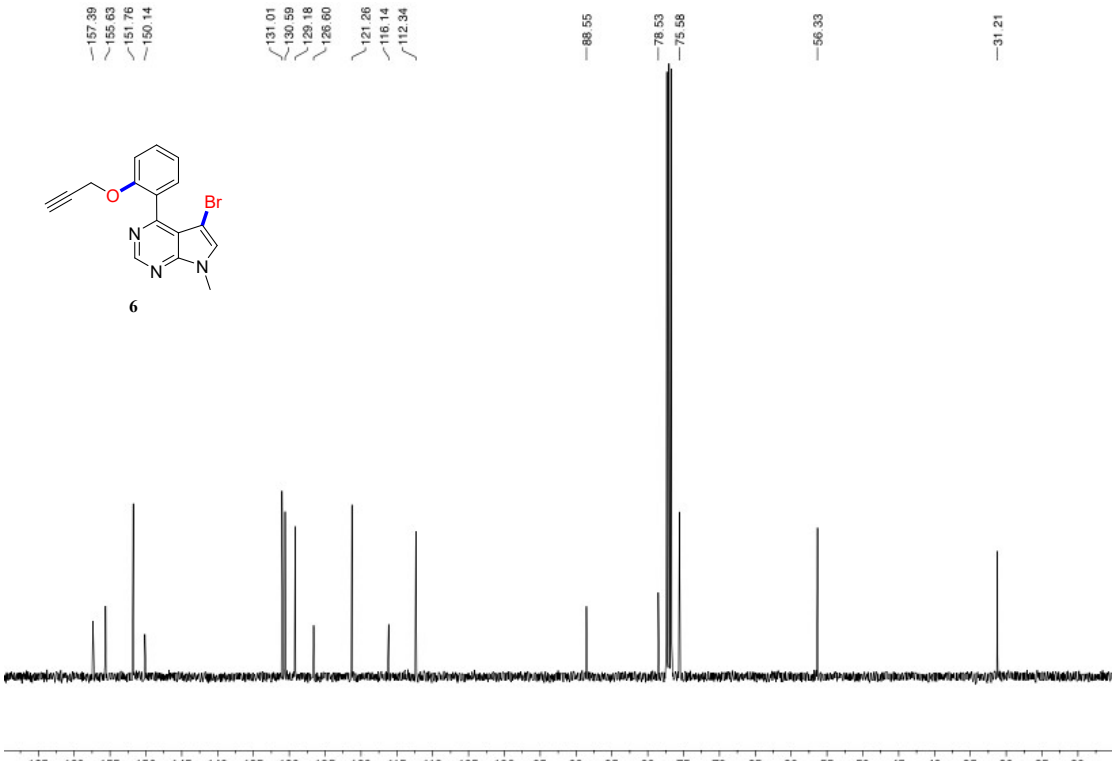

HO
Br
N
N
N
5
158.29
158.25
151.47
149.21
134.43
132.48
131.25
118.62
118.44
117.41
113.16
87.67
31.47

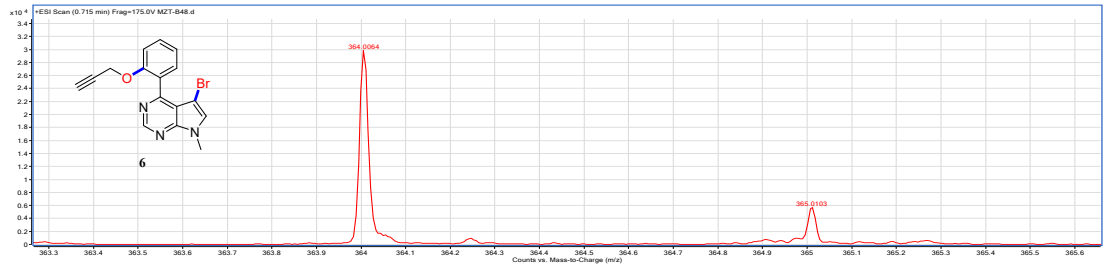

x10 4
+ESI Scan (0.354-0.674 min, 20 scans) Frag=175.0V B45.d Subtract
HO
Br
N
N
N
5
304.0076
306.0054
Counts vs. Mass-to-Charge (m/z)

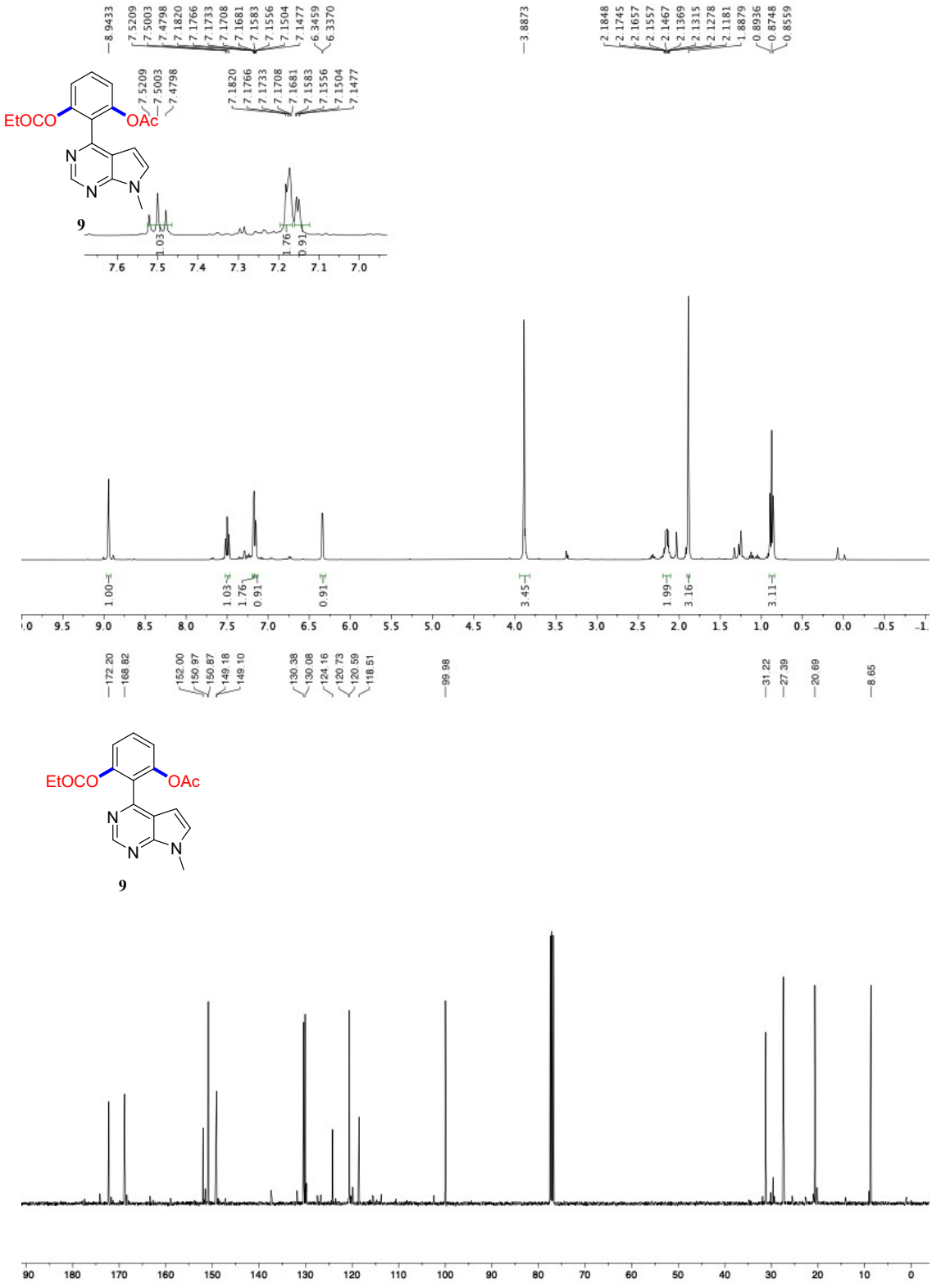

8.9859
7.5152
7.5108
7.4963
7.4937
7.4924
7.4902
7.4757
7.4714
7.4504
7.4463
7.4318
7.4275
7.2853
7.2172
7.1935
7.1747
7.1589
7.1570
7.1402
7.1384
4.6561
4.6500
3.9073
2.4514
2.4455
2.4395

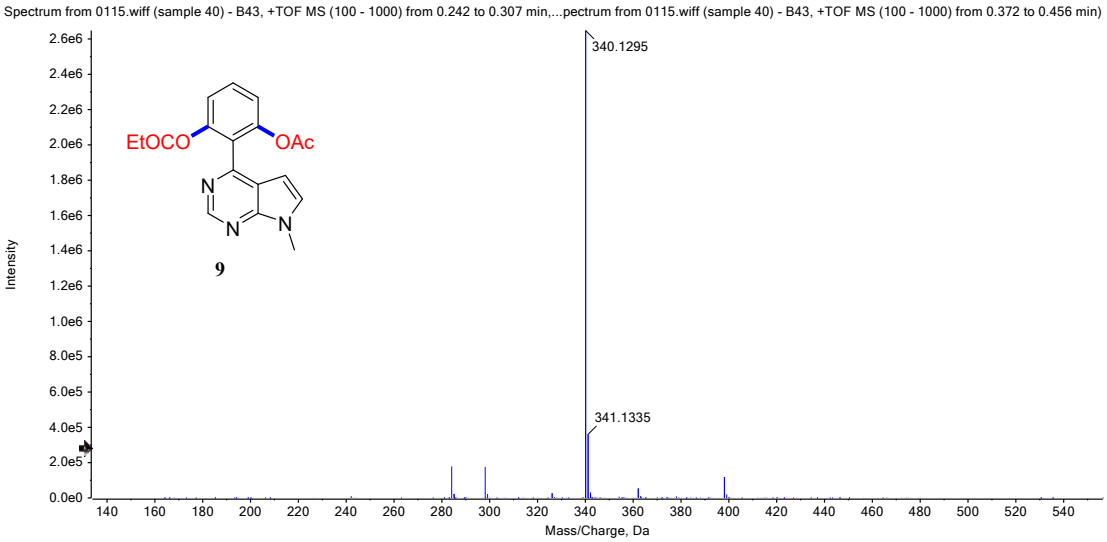

O
Br
N
N
N
6
7.5108
7.4963
7.4937
7.4924
7.4902
7.4757
7.4714
7.4504
7.4463
7.4318
7.4275
7.2853
7.2172
7.1935
7.1747
7.1589
7.1570
7.1402
7.1384
1.06
0.99
0.97
2.10
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9


1.00
1.06
0.99
0.97
2.10
2.16
3.07
0.94


157.39
155.63
151.76
150.14
131.01
130.59
129.18
126.60
121.26
116.14
112.34
88.55
78.53
75.58
56.33
31.21
O
Br
N
N
N
6
165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20

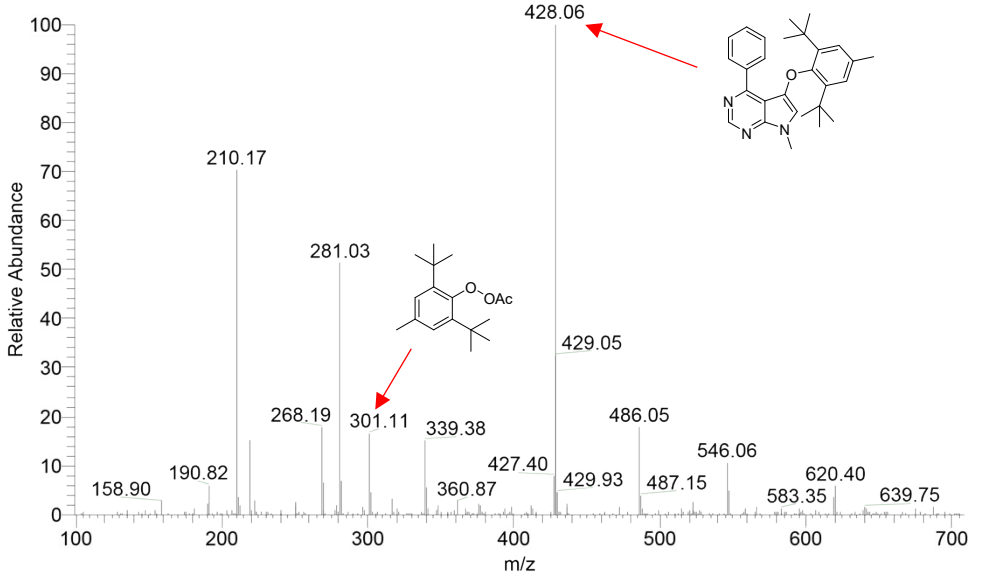

+ESI Scan (0.715 min) Frag=175.0V MZT-B48.d
364.0064
365.0103
O
Br
N
N
N
6
Counts vs. Mass-to-Charge (m/z)


EtOCO
OAc
N
N
N
9
EtOCO
OAc
N
N
N
9


Spectrum from 0115.wiff (sample 40) - B43, +TOF MS (100 - 1000) from 0.242 to 0.307 min,...pectrum from 0115.wiff (sample 40) - B43, +TOF MS (100 - 1000) from 0.372 to 0.456 min)
Intensity
Mass/Charge, Da
340.1295
341.1335
EtOCO
OAc
N
N
N
9

6. ESI-MS spectra for radical trapping experiment with BHT

MZT-BHT1 #81 RT: 0.44 AV: 1 SB: 86 0.05-0.28 , 0.69-1.40 NL: 3.20E5 F:ITMS + c ESI Full ms [50.00-1200.00]



MZT-BHT2 #89 RT: 0.48 AV: 1 NL: 2.13E4
F: ITMS + c ESI Full ms [50.00-1200.00]