Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Transition-metal-free highly regioselective C-H acetoxylation of pyrrolo[2,3-*d*]pyrimidine derivatives

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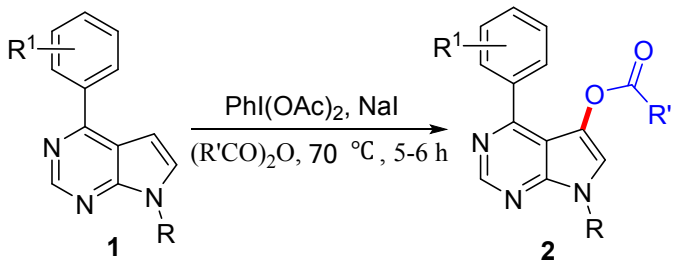
1. General Information

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 **4a** is commercially available from Aladdin. 4-Methoxy-7-methyl-7H-pyrrolo[2,3-d] pyrimidine **4b** was prepared according to the literature. [2] *N,N*-Diethyl-7-methyl-7H-pyrrolo[2,3-d] pyrimidin-4-amine **4c** was prepared according to the method provided by Flanagan.[3] 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 and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ADNANCE III 500 MHz using $CDCl_3$ as solvent with TMS as internal standard. 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).

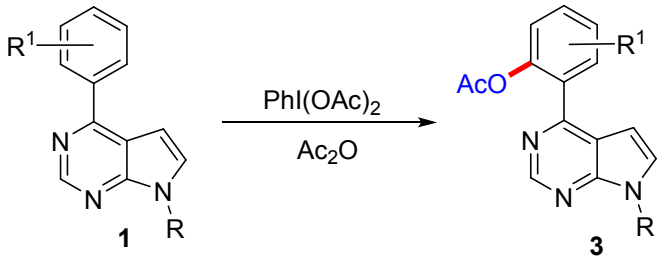
2. General Procedures for the acetoxylation

(1) General Procedures for NaI-promoted acyloxylation



The reaction of 7-methyl-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate **2aa** was exemplified here. Diacetoxyiodobenzene (193 mg, 0.6 mmol), Ac_2O (1mL), sodium iodide (60 mg, 0.4 mmol) and 7-methyl-4-phenyl-7*H*-pyrrolo [2,3-*d*]pyrimidine **1aa** (42 mg, 0.2 mmol) were added in a pressure vessel. The reaction mixture was stirred at 70 °C for 6 h. After completion of the reaction, it was then cooled to room temperature, extracted with EA (3×20 mL) and washed with water (20 mL), saturated sodium bicarbonate (20 mL) and brine (20 mL) before the organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by 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** (47.6 mg, 89% yield).

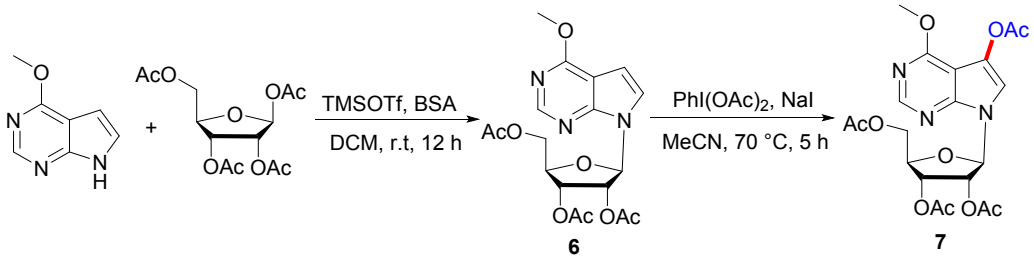
(2) General Procedures for the acetoxylation without NaI as an additive



The reaction of 2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate **3aa** was exemplified here. Diacetoxyiodobenzene (193 mg, 0.6 mmol), Ac_2O (1 mL) and 7-methyl-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine **1aa** (42 mg, 0.2 mmol) were added in a pressure vessel. The reaction mixture was stirred at 70 °C for 12 h. After completion of the reaction, it was then cooled to room temperature, extracted with EA (3×20 mL) and washed with water (20 mL), saturated sodium bicarbonate (20 mL) and brine (20 mL) before the organic phase was dried over anhydrous Na_2SO_4 and concentrated in

vacuo. The residue was purified by 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** (35.8 mg, 69% yield).

(3) Synthesis of acetoxylated compound **7**



4-Methoxy-7*H*-pyrrolo[2,3-d]pyrimidine **4b** (164 mg, 1.1 mmol), 1,2,3,5-tetra- *O*-acetyl-D-ribose (318 mg, 1.0 mmol), *N,O*-bis(trimethylsilyl) acetamide (0.05 mL), TMSOTf (0.05 mL) and DCM (10 mL) were added in a round-bottomed flask. The reaction mixture was stirred at room temperature for 12 h. After completion of the reaction, extracted with EA (3×20 mL) and washed with water (20 mL), saturated sodium bicarbonate (20 mL) and brine (20 mL) before the organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc V/V 4:1) on silica gel to provide the desired product 2-(acetoxymethyl)-5-(4-methoxy-7*H*-pyrrolo[2,3-d] pyrimidin-7-yl) tetrahydrofuran-3,4-diyl diacetate **6** (257 mg, 64% yield).

Diacetoxyiodobenzene (193 mg, 0.6 mmol), MeCN (1.0 mL) and **6** (86 mg, 0.2 mmol) were added in a pressure vessel. The reaction mixture was stirred at 70 °C for 5 h. After completion of the reaction, it was then cooled to room temperature, extracted with EA (3×20 mL) and washed with water (20 mL), saturated sodium bicarbonate (20 mL) and brine (20 mL) before the organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc v/v 4:1) on silica gel to provide the desired product 2-(5-acetoxy-4-methoxy-7H-pyrrolo[2,3-d] pyrimidin-7-yl)-5-(acetoxymethyl) tetrahydrofuran-3,4-diyl diacetate **7** (59 mg, 63% yield).

Reference:

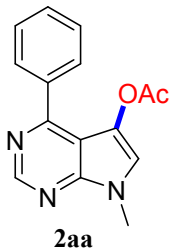
1. M. Klečka, R. Pohl, B. Klepetářov and M. Hocek, *Org Biomol Chem,* 2009, **7**,

866−868.

2. A. Thiyagarajan, M. Toyama, M. Baba, A. Sharon and C. Bal, Nucleosides *Nucleotides Nucleic Acids*, 2016, **35**, 305-314.
3. M. E. Flanagan, T. A. Blumenkopf, W. H. Brissette, M. F. Brown, J. M. Casavant, C. Shang-Poa, J. L. Doty, *J Med Chem,* 2010, **53**, 8468-8484.

4. Characterization of the products

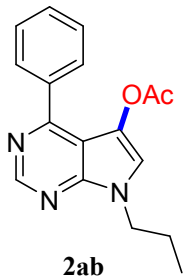
7-methyl-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2aa)



2aa

Yellow solid (89% 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 $C_{15}H_{13}N_3O_2$ $[M+H]^+$ 268.1086, found 268.1082.

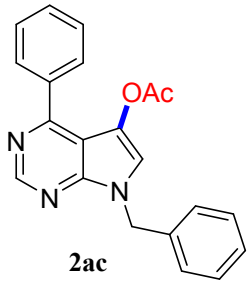
4-phenyl-7-propyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2ab)



2ab

Yellow viscous oil (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 $C_{17}H_{17}N_3O_2$ $[M+H]^+$ 296.1394, found 296.1394.

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

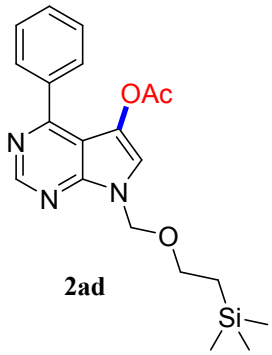


2ac

White solid (92% 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 $C_{21}H_{17}N_3O_2$ $[M+H]^+$ 344.1394, found 344.1394.

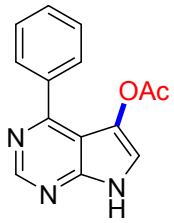
4-phenyl-7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2ad)



2ad

White solid (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 $C_{20}H_{25}N_3O_3Si$ $[M+H]^+$ 384.1738, found 384.1737.

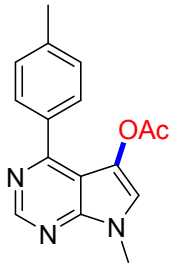
4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2ae)



2ae

White solid (84% yield). Mp: 99−101 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.21 (s, 1H), 7.67 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.58 – 7.54 (m, 3H), 7.53 (s, 1H), 3.08 (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. $C_{14}H_{11}N_3O_2$ $[M+Na]^+$ 276.0743, found 276.0643.

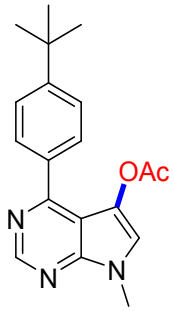
7-methyl-4-(p-tolyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2ba)



2ba

Yellow solid (78% 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 $C_{16}H_{15}N_3O_2$ $[M+H]^+$ 282.1242, found 282.1243.

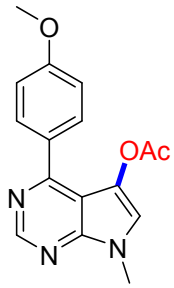
4-(4-(tert-butyl)phenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2bb)



2bb

Yellow solid (84% 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 $C_{19}H_{21}N_3O_2$ $[M+H]^+$ 324.1707, found 324.1717.

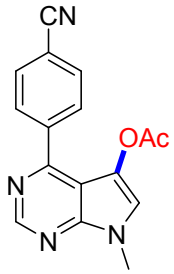
4-(4-methoxyphenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2bc)



2bc

Yellow solid (92% 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 $C_{16}H_{15}N_3O_3$ $[M+H]^+$ 298.1191, found 298.1192.

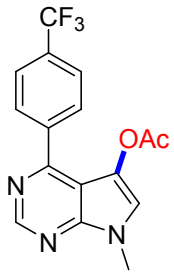
4-(4-cyanophenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2bd)



2bd

Yellow solid (68% yield). Mp:182-185 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.02 – 7.99 (m, 2H), 7.84 – 7.81 (m, 2H), 7.38 (s, 1H), 3.94 (s, 3H), 2.08 (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 $C_{16}H_{12}N_4O_2$ $[M+H]^+$ 293.1038, found 293.1035.

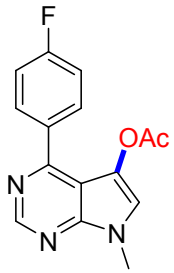
7-methyl-4-(4-(trifluoromethyl)phenyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2be)



2be

Yellow solid (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 ($J_{C\text{-}F}$ = 64.64Hz), 129.88, 126.60, 124.94 ($J_{C\text{-}F}$ = 4.04Hz), 124.04 ($J_{C\text{-}F}$ = 272.7Hz), 119.88, 108.63, 31.08, 20.45. HRMS-ESI calculated for $C_{16}H_{12}F_3N_3O_2$ $[M+H]^+$ 36.0960, found 336.0950.

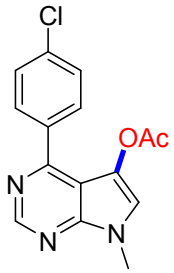
4-(4-fluorophenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2bf)



2bf

Yellow solid (79% yield). Mp:126-129 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.88 (dd, J = 8.8, 5.4 Hz, 2H), 7.29 (s, 1H), 7.21 (t, J = 8.7 Hz, 2H), 3.91 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ168.53, 164.91, 162.93, 157.28, 151.75, 148.29, 131.52 ($J_{C\text{-}F}$ = 8.82Hz), 126.80, 119.43, 115.19 ($J_{C\text{-}F}$ = 21.4Hz), 108.44, 31.14, 20.64. HRMS-ESI calculated for $C_{15}H_{12}FN_3O_2$ $[M+H]^+$ 286.0992, found 286.0983.

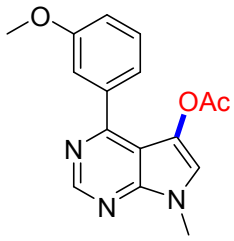
4-(4-chlorophenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2bg)



2bg

Yellow solid (93% yield). Mp:162-165 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.87 – 7.79 (m, 2H), 7.52 – 7.48 (m, 2H), 7.31 (s, 1H), 3.91 (s, 3H), 2.09 (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 $C_{15}H_{12}ClN_3O_2$ $[M+H]^+$ 302.0691, found 302.0680.

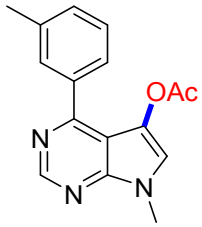
4-(3-methoxyphenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2ca)



2ca

White solid (92% 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 $C_{16}H_{15}N_3O_3$ $[M+H]^+$ 298.1186, found 298.1181.

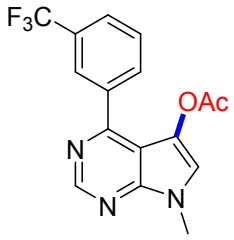
7-methyl-4-(m-tolyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2cb)



2cb

Yellow solid (90% 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 $C_{16}H_{15}N_3O_2$ $[M+H]^+$ 282.1237, found 282.1241.

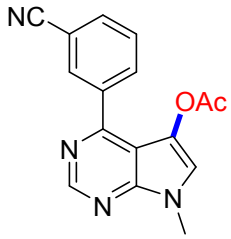
7-methyl-4-(3-(trifluoromethyl)phenyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2cc)



2cc

Yellow solid (77% 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 ($J_{C\text{-}F}$ = 32.76Hz), 128.84, 126.72, 126.56 ($J_{C\text{-}F}$ =7.53Hz), 126.40($J_{C\text{-}F}$ = 7.56Hz), 124.08($J_{C\text{-}F}$ = 136.71Hz), 119.77, 108.42, 31.17, 20.39. HRMS-ESI calculated for $C_{16}H_{12}F_3N_3O_2$ $[M+H]^+$ 336.0960, found 336.0947.

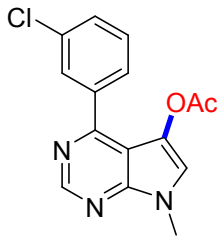
4-(3-cyanophenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2cd)



2cd

Yellow solid (85% yield). Mp:120-122 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.23 (t, *J* = 1.4 Hz, 1H), 8.21 – 8.17 (m, 1H), 7.82 – 7.80 (m, 1H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.42 (s, 1H), 3.94 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.19, 163.54, 155.50, 151.74, 138.89, 133.93, 133.83, 133.44, 133.34, 132.98, 129.14, 126.52, 120.04, 112.31, 31.22, 20.63. HRMS-ESI calculated for $C_{16}H_{12}N_4O_2$ $[M+H]^+$ 293.1038, found 293.1036.

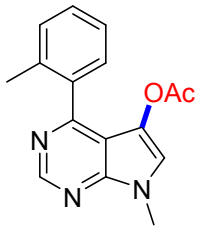
4-(3-chlorophenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2ce)



2ce

White solid (89% 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 $C_{15}H_{12}ClN_3O_2$ $[M+H]^+$ 302.0691, found 302.0689.

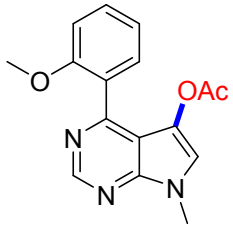
7-methyl-4-(o-tolyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2da)



2da

Yellow viscous oil (82% 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 $C_{16}H_{15}N_3O_2$ $[M+H]^+$ 282.1242, found 282.1032.

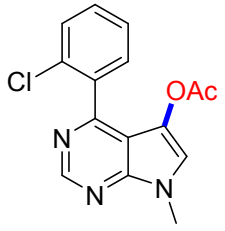
4-(2-methoxyphenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2db)



2db

Yellow viscous oil (85% 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 $C_{16}H_{15}N_3O_3$ $[M+H]^+$ 298.1191, found 298.1189.

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

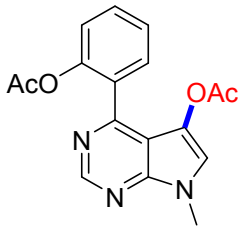


2dc

Yellow viscous oil (73% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.52 (dd,

J = 7.5, 1.6 Hz, 1H), 7.46 (dd, *J* = 6.9, 2.3 Hz, 1H), 7.42 (td, *J* = 6.5, 5.9, 1.8 Hz, 2H), 7.27 (s, 1H), 3.91 (s, 3H), 1.84 (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 $C_{15}H_{12}ClN_3O_2$ $[M+H]^+$ 302.0696, found 302.0685.

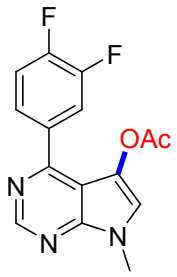
2-(5-acetoxy-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (2dd)



2dd

Yellow viscous oil (86% 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 $C_{17}H_{15}N_3O_4$ $[M+H]^+$ 326.1141, found 326.1135.

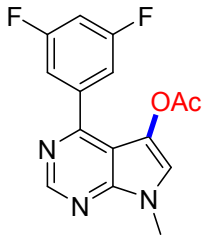
4-(3,4-difluorophenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2e)



2e

Yellow solid (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 $C_{15}H_{11}F_2N_3O_2$ $[M+H]^+$ 304.0897, found 304.0889.

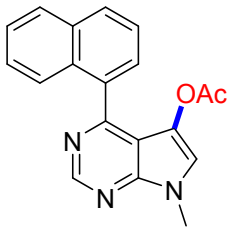
4-(3,5-difluorophenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2f)



2f

Yellow solid (77% 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 $C_{15}H_{11}F_2N_3O_2$ $[M+H]^+$ 304.0897, found 304.0893.

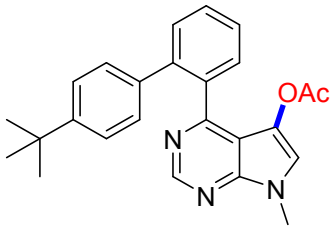
7-methyl-4-(naphthalen-1-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2g)



2g

Yellow viscous solid (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), 7.43 (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 $C_{19}H_{15}N_3O_2$ $[M+H]^+$ 318.1242, found 318.1241.

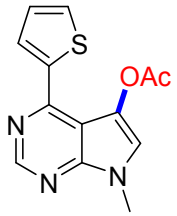
4-(4'-(tert-butyl)-[1,1'-biphenyl]-2-yl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2h)



2h

White solid (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 400.2012.

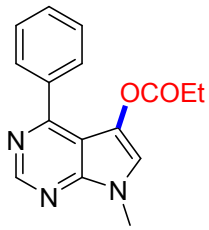
7-methyl-4-(thiophen-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (2i)



2i

Yellow soild (93% yield). Mp: 144−146 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.97 (m, 1H), 7.49 (m, 1H), 7.29 (s, 1H), 7.13 – 7.10 (m, 1H), 3.79 (s, 3H), 2.24 (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 $C_{13}H_{11}N_3O_2S$ $[M+H]^+$ 274.0645, found 274.0645.

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

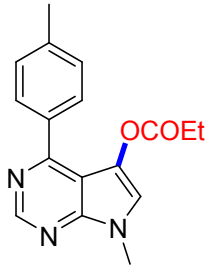


2ja

White solid (84% 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 $C_{16}H_{15}N_3O_2$ $[M+H]^+$ 282.1237, found 282.1238.

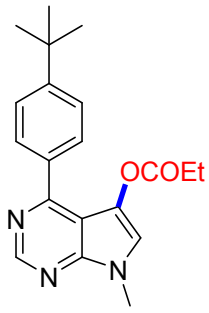
7-methyl-4-(p-tolyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl propionate (2jb)



2jb

White solid (85% yield). Mp: 113−115 °C. ^{1}H NMR (500 MHz, $CDCl_3$ δ 8.94 (s, 1H), 7.75 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 7.27 (d, J = 7.8 Hz, 1H), 3.89 (s, 3H), 2.44 (s, 3H), 2.36 (q, J = 7.5 Hz, 2H), 1.04 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.20, 158.55, 151.67, 148.24, 139.82, 134.95, 129.42, 128.77, 127.05, 119.08, 108.54, 31.07, 27.32, 21.42, 8.59. HRMS-ESI calculated for $C_{17}H_{17}N_3O_2$ $[M+H]^+$ 296.1394, found 296.1392.

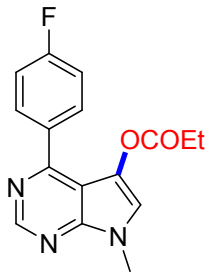
4-(4-(tert-butyl)phenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl propionate (2jc)



2jc

White solid (85% yield). Mp: 105−108 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.77 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 8.3 Hz, 2H), 7.23 (s, 1H), 3.91 (s, 3H), 2.33 (q, J = 7.5 Hz, 2H), 1.38 (s, 9H), 0.99 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.26, 158.66, 152.92, 151.76, 148.32, 134.94, 129.15, 127.11, 125.07, 119.09, 108.74, 34.81, 31.30, 31.09, 27.25, 8.60. HRMS-ESI calculated for $C_{20}H_{23}N_3O_2$ $[M+H]^+$ 338.1863, found 338.1864.

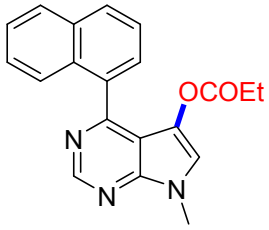
4-(4-fluorophenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl propionate (2jd)



2jd

White solid (91% yield). Mp: 69−73 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.90 – 7.82 (m, 2H), 7.29 (d, *J* = 16.3 Hz, 1H), 7.25 – 7.16 (m, 2H), 3.91 (s, 3H), 2.37 (q, *J* = 7.6 Hz, 2H), 1.07 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.07, 163.89 ($J_{C\text{-}F}$ = 249.48 Hz), 157.29, 151.69, 148.24, 133.96 ($J_{C\text{-}F}$ = 3.78 Hz), 131.53 ($J_{C\text{-}F}$ = 8.82 Hz), 126.89, 119.36, 115.13 ($J_{C\text{-}F}$ = 21.42 Hz), 108.50, 31.14, 27.35, 8.69. HRMS-ESI calculated for $C_{16}H_{14}FN_3O_2$ $[M+H]^+$ 300.1143, found 300.1142.

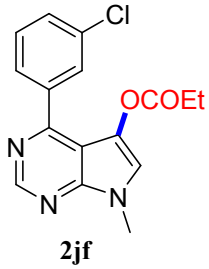
7-methyl-4-(naphthalen-1-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl propionate (2je)



2je

White solid (89% 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 $C_{20}H_{17}N_3O_2$ $[M+H]^+$ 332.1394, found 332.1398.

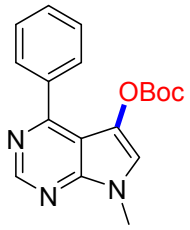
4-(3-chlorophenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl propionate (2jf)



2jf

White solid (89% yield). Mp: 73−76°C. ^{1}H NMR (500 MHz, $CDCl_3$ δ 8.96 (s, 1H), 7.89 – 7.77 (m, 2H), 7.50 – 7.42 (m, 2H), 7.34 (s, 1H), 3.91 (s, 3H), 2.43 (q, *J* = 7.5 Hz, 2H), 1.07 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.10, 156.70, 151.63, 148.27, 139.47, 133.90, 129.73, 129.68, 129.54, 127.67, 126.82, 119.63, 108.53, 31.15, 27.25, 8.66. HRMS-ESI calculated for $C_{16}H_{14}ClN_3O_2$ $[M+H]^+$ 316.0847, found 316.0844.

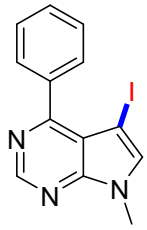
tert-butyl (7-methyl-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl) carbonate (2k)



2k

Brown viscous oil (27% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.95 – 7.91 (m, 2H), 7.49 (q, *J* = 7.5 Hz, 3H), 7.29 (s, 1H), 3.14 (s, 3H), 0.09 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 164.68, 164.18, 163.45, 158.23, 139.67, 130.85, 129.96, 129.17, 128.68, 126.57, 109.91, 50.85, 29.70, 1.02. HRMS-ESI calculated for $C_{18}H_{19}N_3O_3$ $[M-H]^+$ 324.1354, found 324.1321.

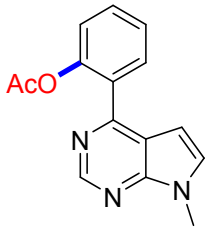
5-iodo-7-methyl-4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (2l)



2l

White solid (73% yield). MP:142-144 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.72 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.52 (dd, *J* = 4.7, 1.9 Hz, 3H), 7.36 (d, *J* = 1.2 Hz, 1H), 3.90 (d, *J* = 1.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.35, 151.20, 135.78, 135.56, 130.87, 129.53, 127.70, 116.57, 51.33, 31.34. HRMS-ESI calculated for $C_{13}H_{10}IN_3$ $[M+H]^+$ 335.9992, found 335.9992.

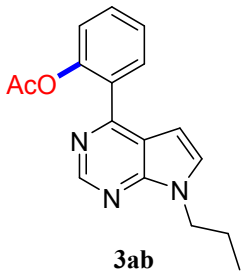
2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3aa)



3aa

Yellow oil (69% 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 $C_{15}H_{13}N_3O_2$ $[M+H]^+$ 268.1086, found 268.1085.

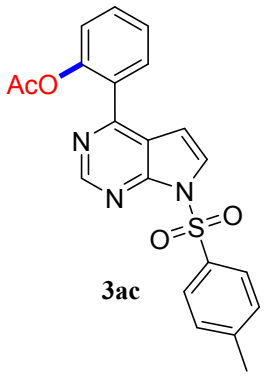
2-(7-propyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3ab)



3ab

Yellow oil (65% 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 $C_{17}H_{17}N_3O_2$ $[M+H]^+$ 296.1394, found 296.1393.

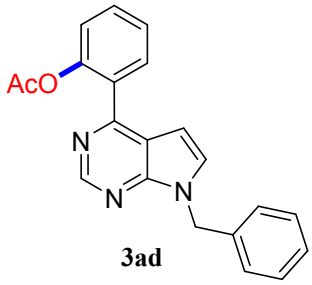
2-(7-tosyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3ac)



3ac

Yellow oil (73% 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 $C_{21}H_{17}N_3O_4S$ $[M+H]^+$ 408.1013, found 408.1011.

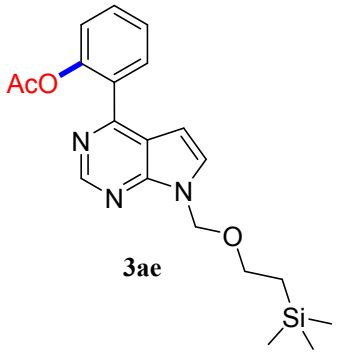
2-(7-benzyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3ad)



3ad

Yellow oil (73% 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 $C_{21}H_{17}N_3O_2$ $[M+H]^+$ 344.1394, found 344.1397.

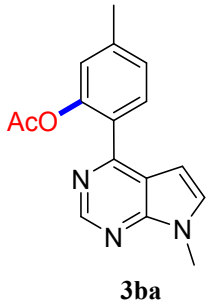
2-(7-((2-(trimethylsilyl)ethoxy)methyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3ae)



3ae

Yellow oil (61% 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 $C_{20}H_{25}N_3O_3Si$ $[M+H]^+$ 384.1738, found 384.1744.

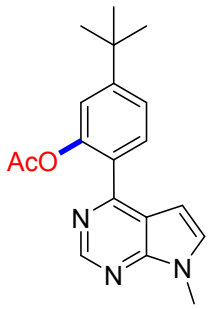
5-methyl-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3ba)



3ba

Yellow oil (69% 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 $C_{16}H_{15}N_3O_2$ $[M+H]^+$ 282.1242, found 282.1249.

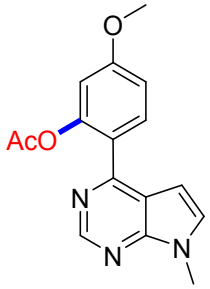
5-(tert-butyl)-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3bb)



3bb

Yellow oil (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 $C_{19}H_{21}N_3O_2$ $[M+H]^+$ 324.1707, found 324.1712.

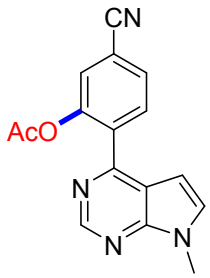
5-methoxy-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3bc)



3bc

Yellow oil (43% 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 $C_{16}H_{15}N_3O_3$ $[M+H]^+$ 298.1191, found 298.1188.

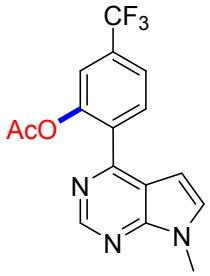
5-cyano-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3bd)



3bd

Yellow oil (69% 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 $C_{16}H_{12}N_4O_2$ $[M+H]^+$ 293.1033, found 293.1042.

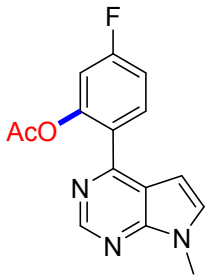
2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)-5-(trifluoromethyl)phenyl acetate (3be)



3be

Yellow oil (74% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.67 (m, 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 $C_{16}H_{12}F_3N_3O_2$ $[M+H]^+$ 336.0960, found 336.0966.

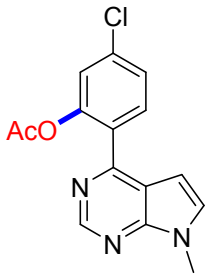
5-fluoro-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3bf)



3bf

Yellow oil (79% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.79 – 7.76 (m, 1H), 7.23 (d, J = 3.6 Hz, 1H), 7.15 – 7.13 (m, 1H), 7.04 (m, 1H), 6.54 (d, J = 3.6 Hz, 1H), 3.93 (s, 3H), 2.07 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 168.79, 162.36, 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 $C_{15}H_{12}FN_3O_2$ $[M+H]^+$ 286.0992, found 286.0993.

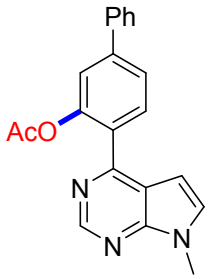
5-chloro-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3bg)



3bg

Yellow oil (67% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.08 (d, J = 2.0 Hz, 1H), 7.78 (m, 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 $C_{15}H_{12}ClN_3O_2$ $[M+H]^+$ 302.0691, found 302.0680.

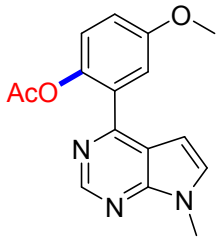
4-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)-[1,1'-biphenyl]-3-yl acetate (3bh)



3bh

Yellow oil (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 $C_{21}H_{17}N_3O_2$ $[M+H]^+$ 344.1394, found 344.1389.

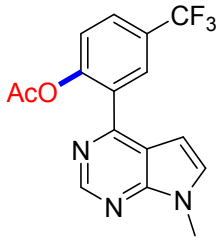
4-methoxy-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3ca)



3ca

Yellow oil (63% 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), 7.04 (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 $C_{16}H_{15}N_3O_3$ $[M+H]^+$ 298.1191, found 298.1191.

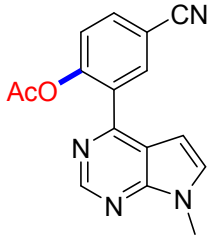
2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)-4-(trifluoromethyl)phenyl acetate (3cb)



3cb

Yellow oil (25% 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, CDCl3) 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. ESI calculated for $C_{16}H_{12}F_3N_3O_2$ $[M+H]^+$ 336.0960, found 336.0956.

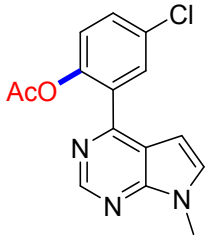
4-cyano-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3cc)



3cc

Yellow oil (35% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.11 (d, *J* = 2.0 Hz, 1H), 7.84 – 7.81 (m, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 3.6 Hz, 1H), 6.53 (d, *J* = 3.6 Hz, 1H), 3.95 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (126 MHz, CDCl3) 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 $C_{16}H_{12}N_4O_2$ $[M+H]^+$ 293.1038, found 293.1032.

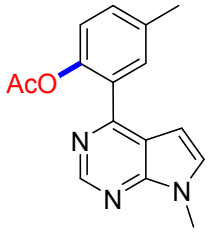
4-chloro-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3cd)



3cd

Yellow oil (83% 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 $C_{15}H_{12}ClN_3O_2$ $[M+H]^+$ 302.0691, found 302.0677.

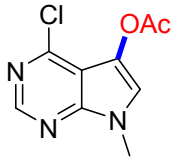
4-methyl-2-(7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4-yl)phenyl acetate (3ce)



3ce

Yellow oil (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 $C_{16}H_{15}N_3O_2$ $[M+H]^+$ 282.1237, found 282.1233.

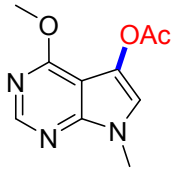
4-chloro-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (5a)



5a

White solid (83% yield). Mp: 148−151 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.26 (s, 1H), 3.85 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (500 MHz, $CDCl_3$)δ 169.03, 151.07, 150.58, 147.88, 126.44, 119.88, 109.49, 31.36, 20.75. HRMS-ESI calculated for $C_9H_8ClN_3O_2$ $[M+H]^+$ 226.0378, found 226.0380.

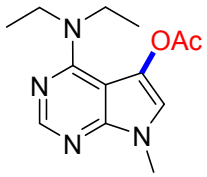
4-methoxy-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (5b)



5b

White solid (93% yield). Mp: 102−105 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.01 (s, 1H), 4.09 (s, 3H), 3.80 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.23, 162.48, 151.36, 148.45, 127.14, 116.02, 98.54, 53.81, 31.23, 20.75. HRMS-ESI calculated for $C_{10}H_{11}N_3O_2$ $[M+H]^+$ 222.0873, found 222.0872.

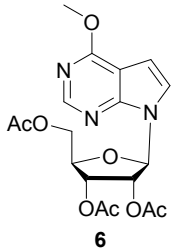
4-(diethylamino)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl acetate (5c)



5c

Brown viscous oil (55% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.07 (s, 1H), 3.72 (dd, J = 13.4, 6.3 Hz, 7H), 2.31 (s, 3H), 1.24 (t, J = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.42, 158.29, 156.47, 150.91, 147.81, 126.36, 114.66, 43.58, 31.25, 21.34, 13.48. HRMS-ESI calculated for $C_{13}H_{18}N_4O_2$ $[M+H]^+$ 263.1503, found 263.1502.

2-(acetoxymethyl)-5-(4-methoxy-7H-pyrrolo[2,3-d]pyrimidin-7-yl)tetrahydrofuran-3,4-diyl diacetate (6)

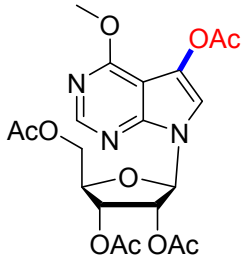


6

Colorless oil (64%, yield), ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.59 (s, 1H), 6.77 (d, J = 3.7 Hz, 1H), 6.69 (d, J = 2.6 Hz, 1H), 5.85 – 5.81 (m, 1H), 5.57 (t, J = 5.7 Hz, 1H), 4.60 – 4.56 (m, 1H), 4.50 (dd, J = 7.7, 3.3 Hz, 2H), 4.21 (s, 3H), 2.20 (s, 3H), 2.12 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.26, 169.52, 169.36, 161.78, 148.40,

141.68, 137.13, 108.85, 99.85, 90.45, 80.43, 74.28, 69.80, 62.58, 54.92, 29.69, 20.81, 20.48.

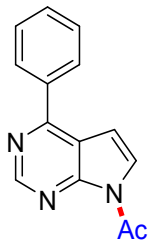
2-(5-acetoxy-4-methoxy-7*H*-pyrrolo[2,3-*d*]pyrimidin-7-yl)-5-(acetoxymethyl)tetrahydrofuran-3,4-diyl diacetate (7)



7

Colorless oil (63% yield). ^{1}H NMR (500 MHz, $CDCl_3$) 8.58 (s, 1H), 7.58 (s, 1H), 6.71 (s, 1H), 5.76 (dd, J = 5.4, 3.8 Hz, 1H), 5.53 (q, J = 5.9 Hz, 1H), 4.60 (dt, J = 6.3, 3.2 Hz, 1H), 4.51 – 4.47 (m, 2H), 4.24 (s, 3H), 2.20 (s, 3H), 2.13 (d, J = 2.3 Hz, 6H), 2.10 (d, J = 2.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.21, 169.55, 169.49, 162.61, 138.33, 109.75, 90.51, 80.58, 74.22, 69.59, 62.44, 60.45, 60.41, 55.15, 21.05, 20.82, 20.50, 20.48, 14.20, 1.02. HRMS-ESI calculated for $C_{20}H_{23}N_3O_{10}$ $[M+Na]^+$ 488.1276, found 488.1283.

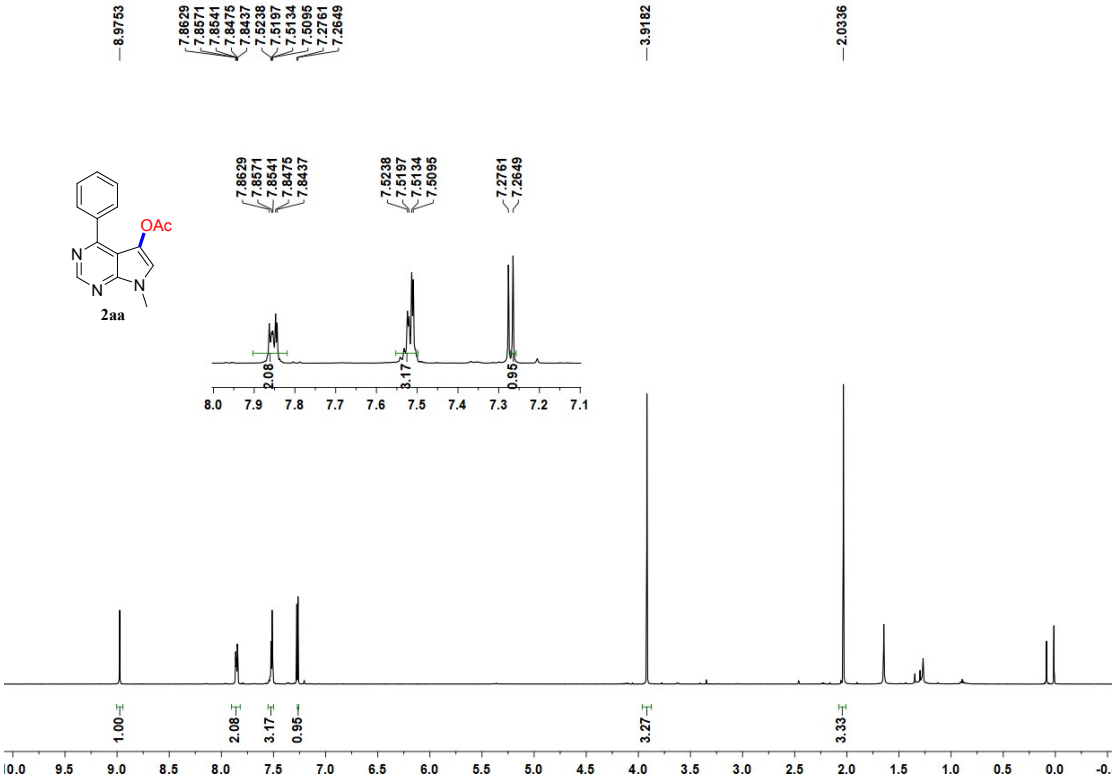
1-(4-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-7-yl)ethan-1-one (1gg)

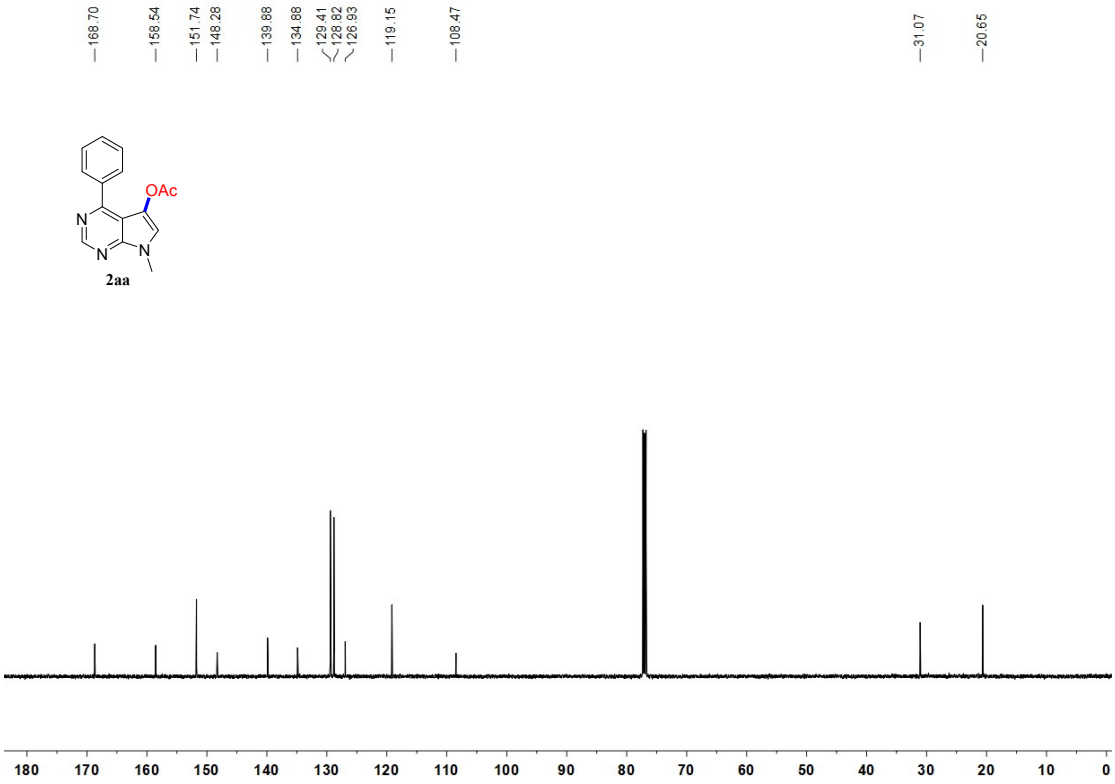


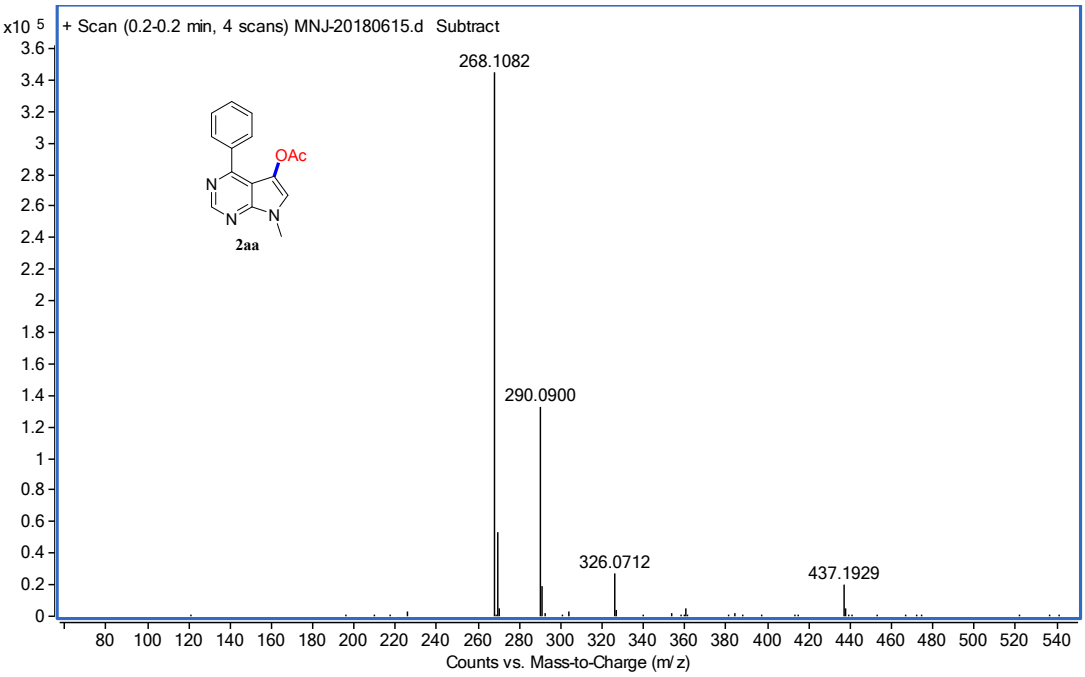
1gg

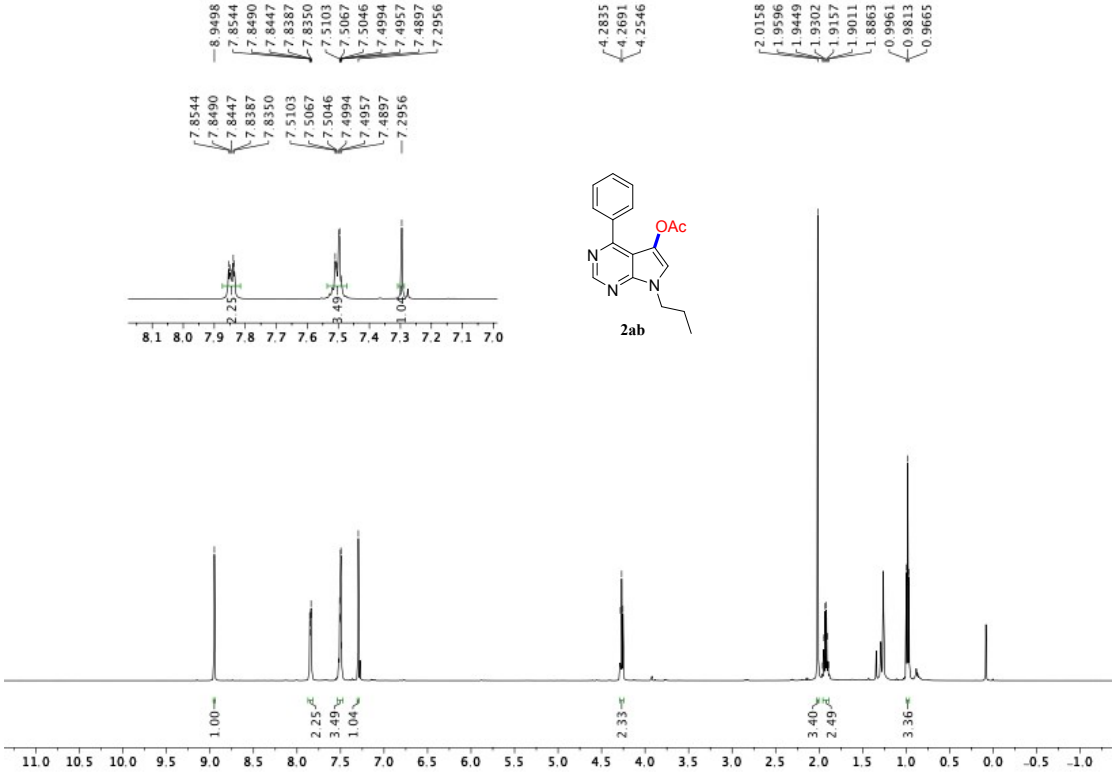
White solid (85% yield). MP: 146-148℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.05 (dd, *J* = 5.6, 2.9 Hz, 3H), 7.56 (ddt, *J* = 7.0, 5.2, 3.6 Hz, 3H), 6.95 (d, *J* = 4.1 Hz, 1H), 3.11 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.62, 158.51, 152.68, 152.68, 137.30, 130.44, 128.92, 128.83, 125.96, 118.47, 104.90, 25.93. HRMS-ESI calculated for $C_{14}H_{11}N_3O$ $[M+H]^+$ 238.0975, found 238.0975.

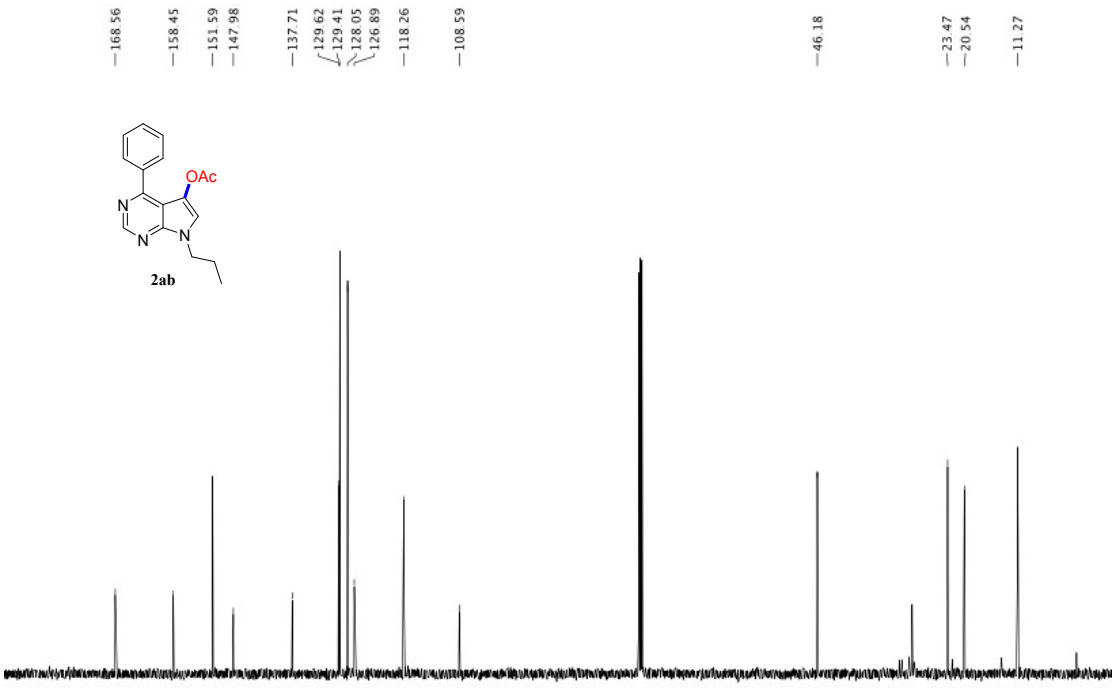
5. NMR Spectra of Compounds

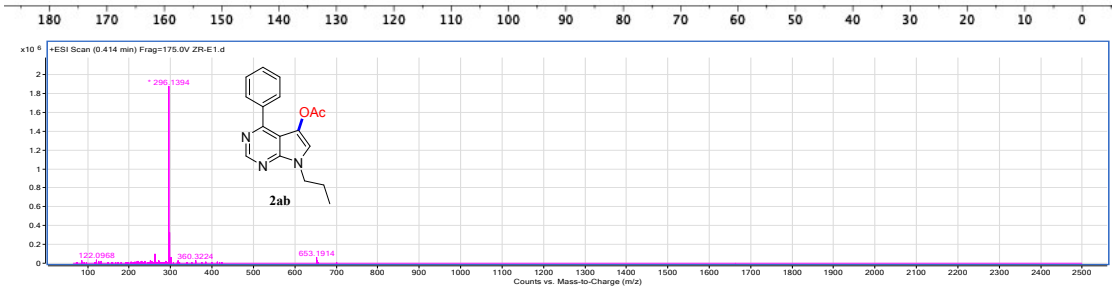


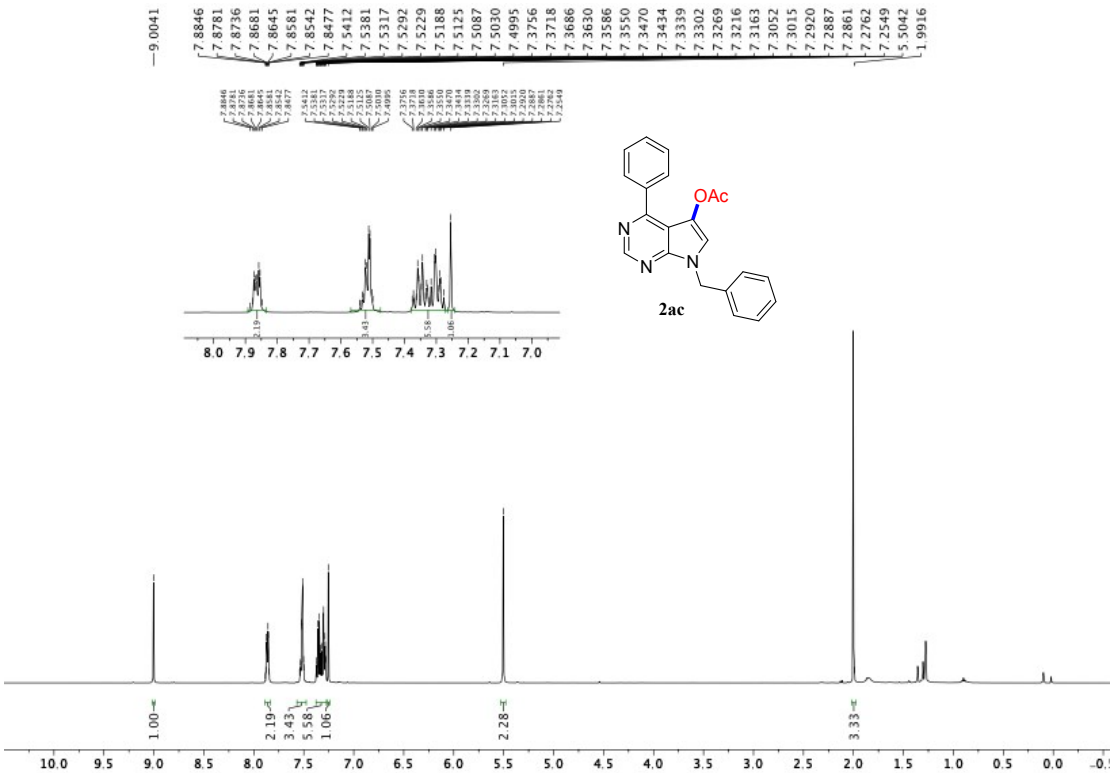


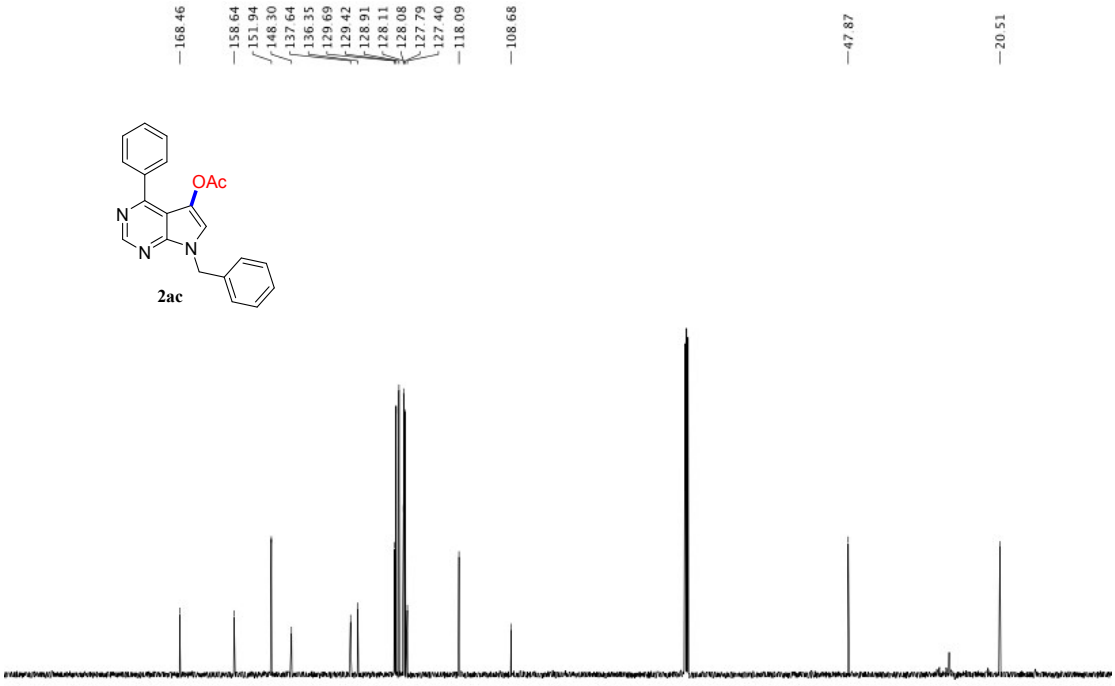

x10 5
+ Scan (0.2-0.2 min, 4 scans) MNJ-20180615.d Subtract
268.1082
290.0900
326.0712
437.1929
OAc
N
N
N
2aa
Counts vs. Mass-to-Charge (m/z)

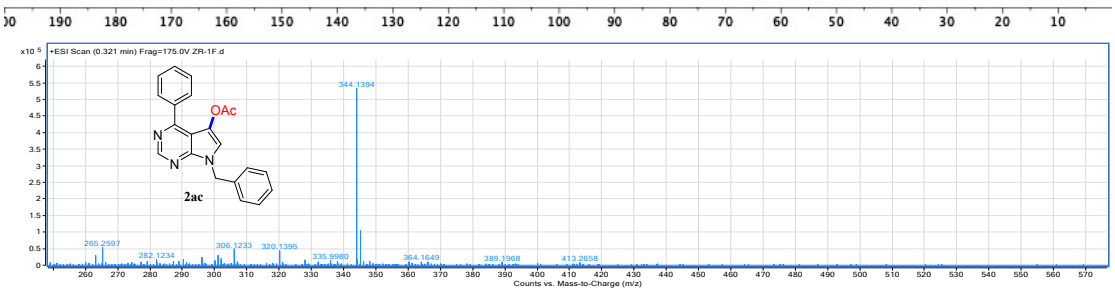

OAc
N
N
N
2ab

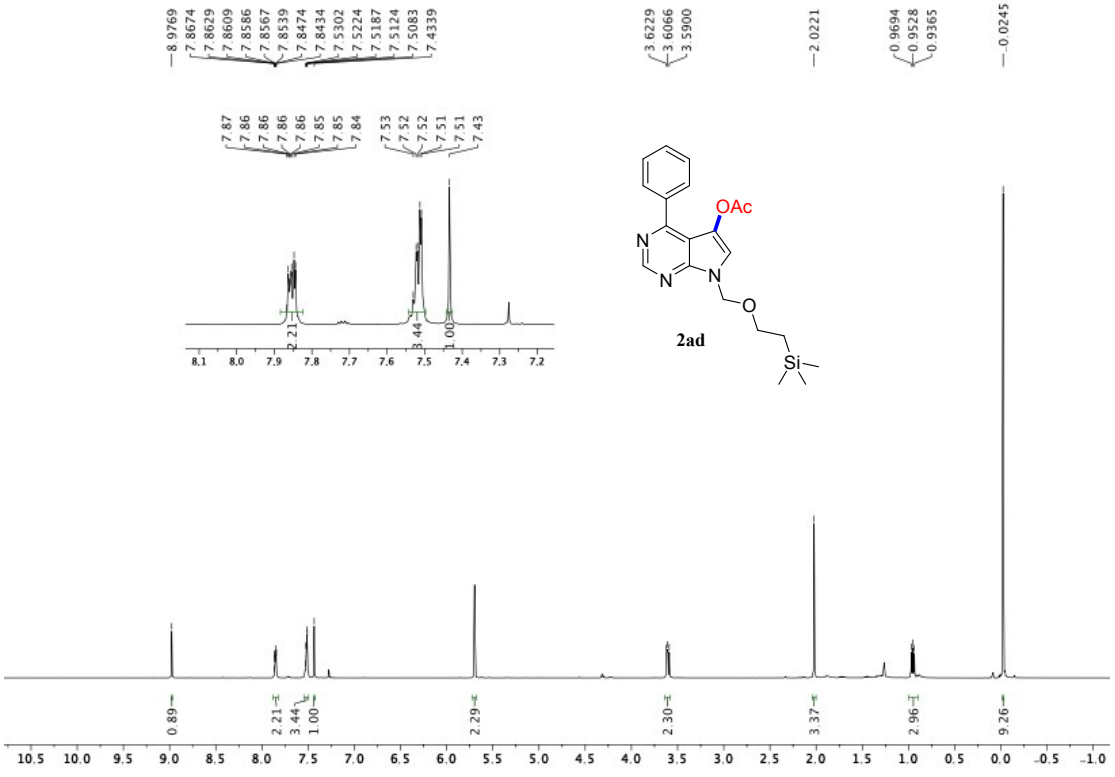

168.56
158.45
151.59
147.98
137.71
129.62
129.41
128.05
126.89
118.26
108.59
46.18
23.47
20.54
11.27
OAc
N
N
N
2ab

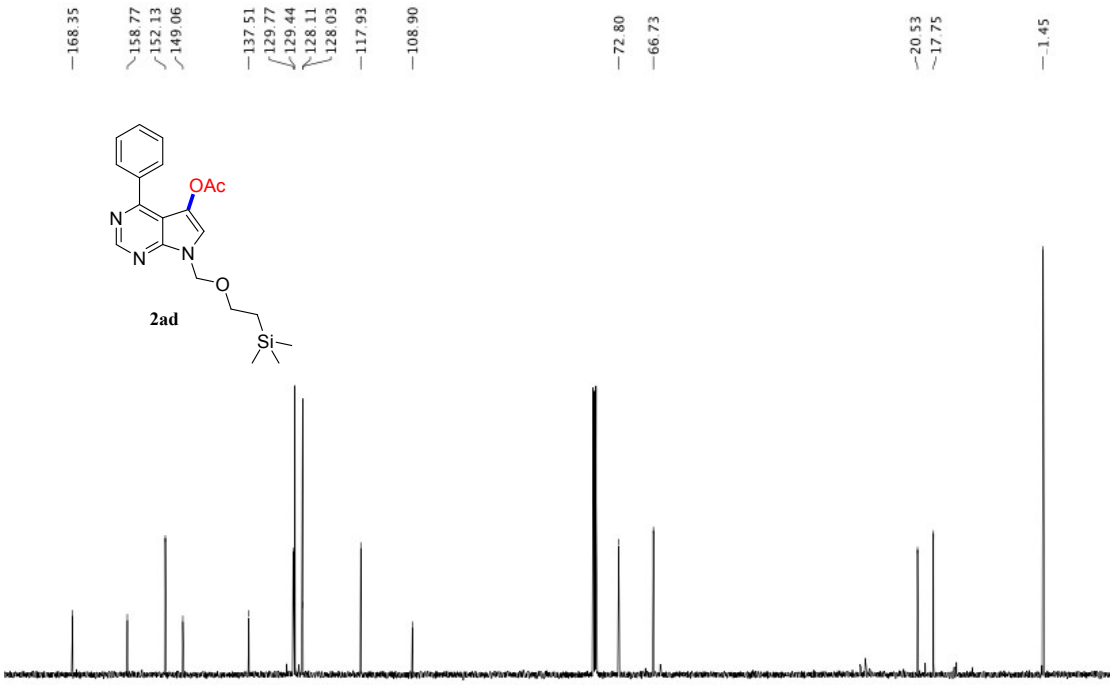

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
+ESI Scan (0.414 min) Frag=175.0V ZR-E1.d
296.1394
122.0968
360.3224
653.1914
OAc
2ab
Counts vs. Mass-to-Charge (m/z)

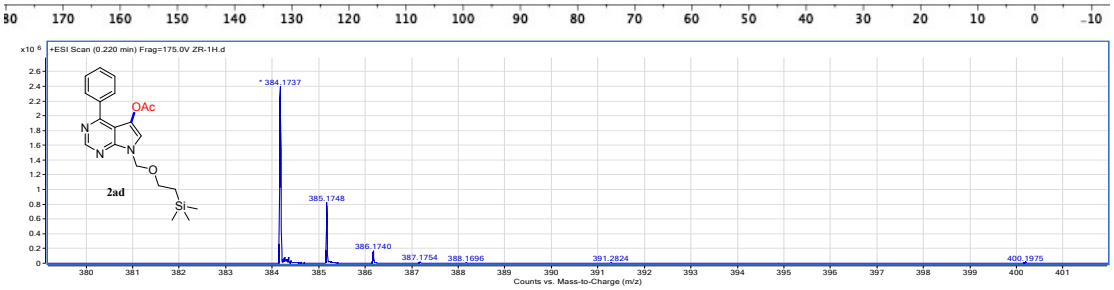

9.0041
7.8846
7.8781
7.8736
7.8681
7.8645
7.8581
7.8542
7.8477
7.5412
7.5381
7.5317
7.5292
7.5229
7.5188
7.5125
7.5087
7.5030
7.4995
7.3756
7.3718
7.3686
7.3630
7.3586
7.3550
7.3470
7.3434
7.3339
7.3302
7.3269
7.3216
7.3163
7.3052
7.3015
7.2920
7.2887
7.2861
7.2762
7.2549
5.5042
1.9916
OAc
N
N
N
2ac
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
1.00
2.19
3.43
5.58
1.06
2.28
3.33
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

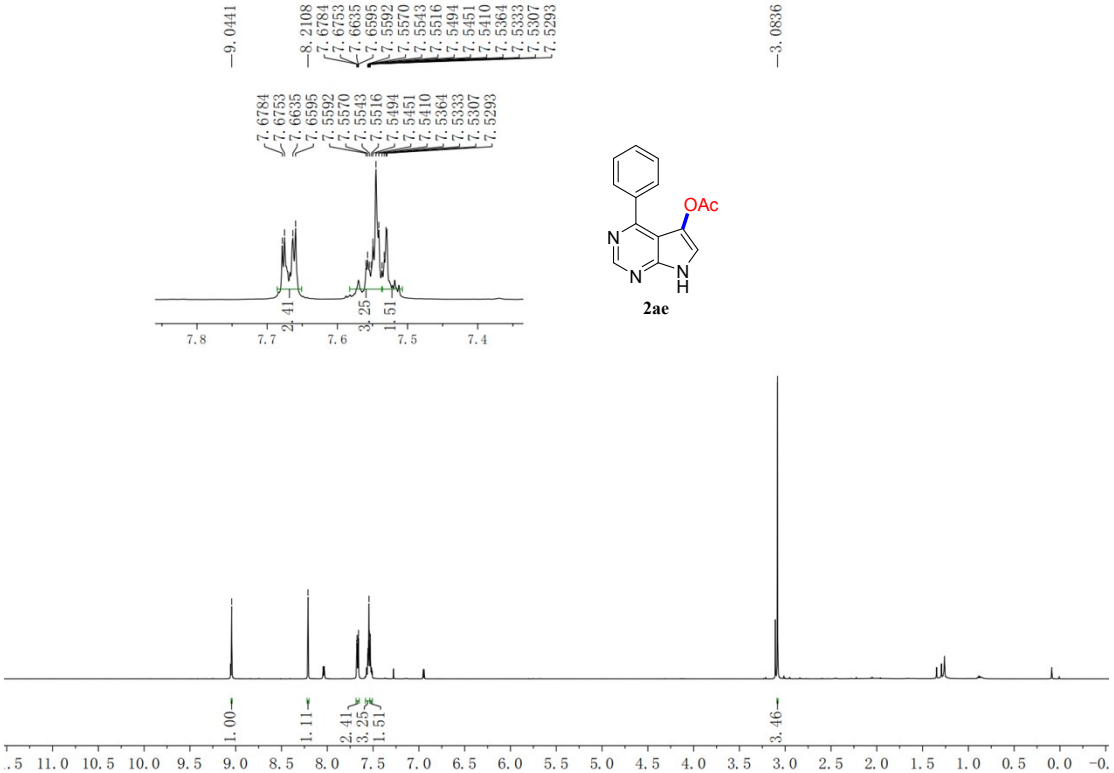

168.46
158.64
151.94
148.30
137.64
136.35
129.69
129.42
128.91
128.11
128.08
127.79
127.40
118.09
108.68
47.87
20.51
OAc
N
N
N
2ac

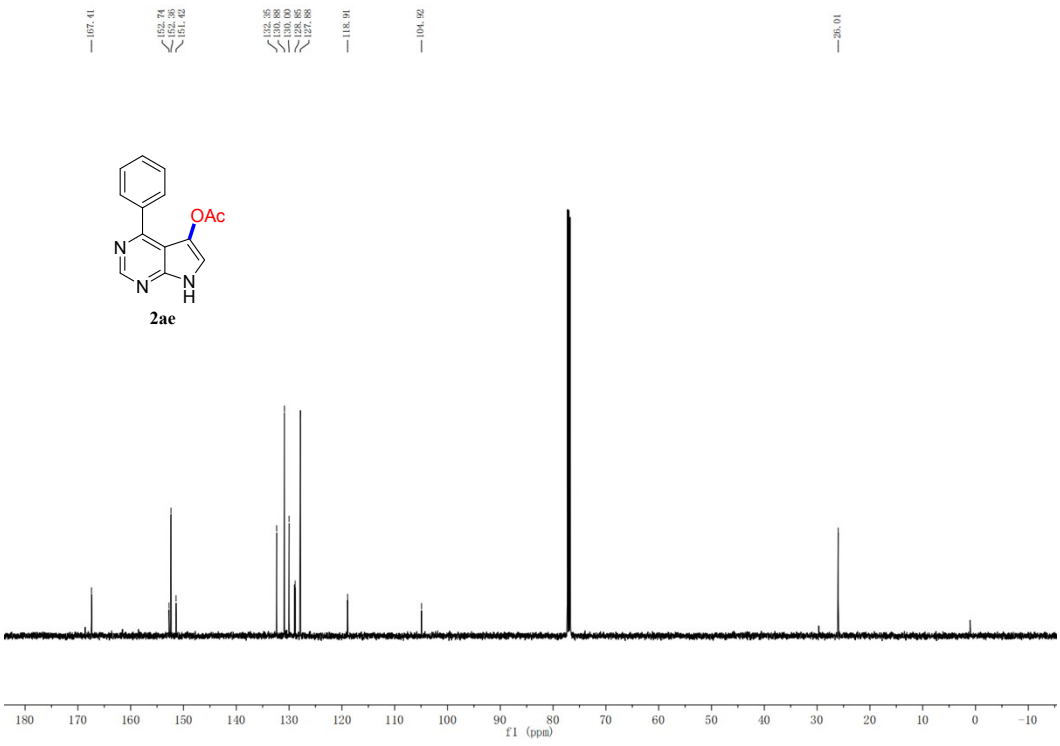

+ESI Scan (0.321 min) Frag=175.0V ZR-1F.d
OAc
2ac
344.1394
265.2597
282.1234
306.1233
320.1395
335.9980
364.1649
389.1968
413.2658
Counts vs. Mass-to-Charge (m/z)

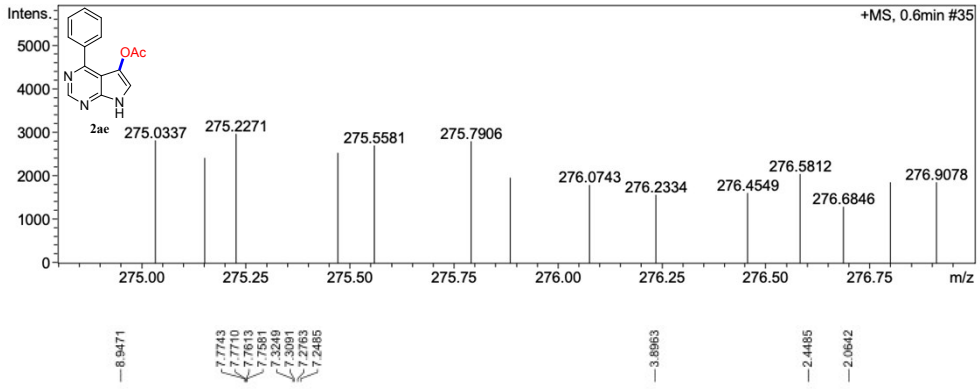

8.9769
7.8674
7.8629
7.8609
7.8586
7.8567
7.8539
7.8474
7.8434
7.5302
7.5224
7.5187
7.5124
7.5083
7.4339
3.6229
3.6066
3.5900
2.0221
0.9694
0.9528
0.9365
0.0245
7.87
7.86
7.86
7.86
7.86
7.85
7.85
7.84
7.53
7.52
7.52
7.51
7.51
7.43
OAc
N
N
N
O
Si
2ad

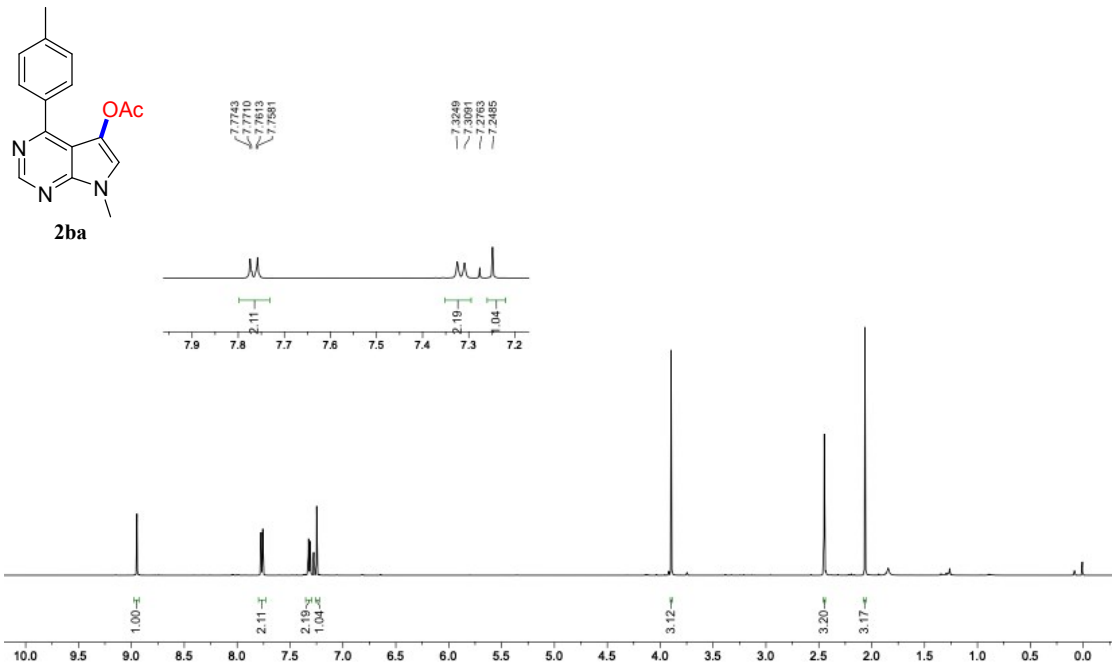

168.35
158.77
152.13
149.06
137.51
129.77
129.44
128.11
128.03
117.93
108.90
72.80
66.73
20.53
17.75
1.45
OAc
N
N
N
O
Si
2ad

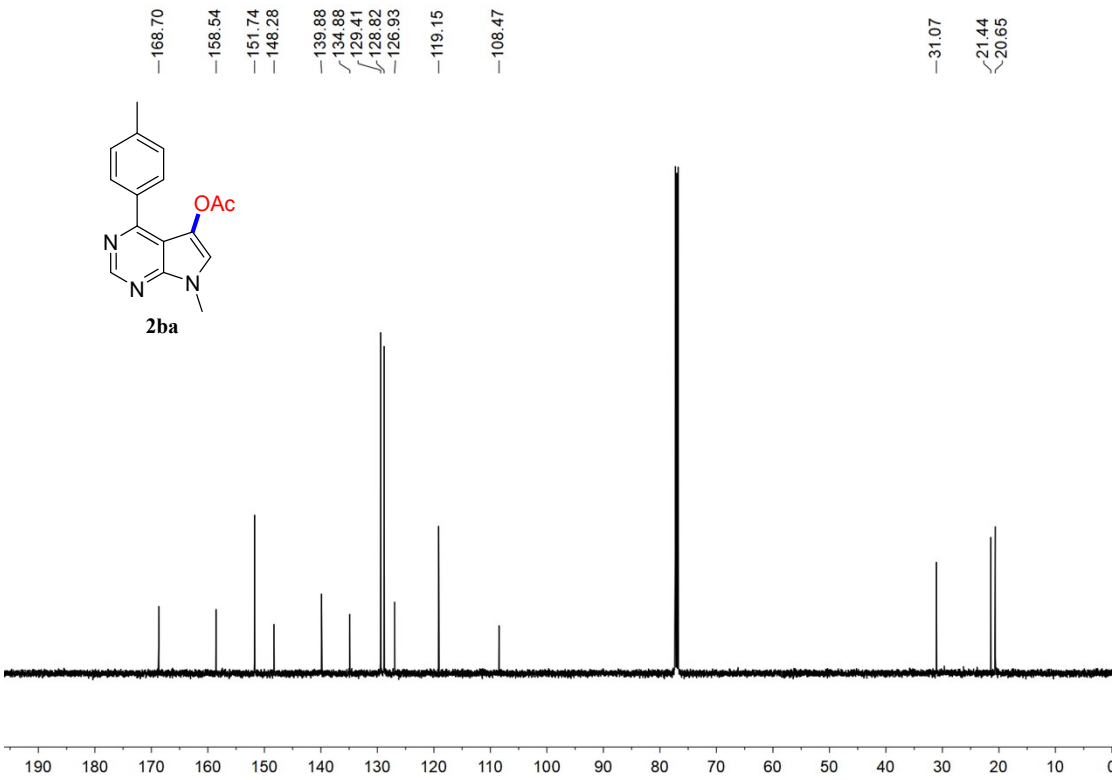

+ESI Scan (0.220 min) Frag=175.0V ZR-1H.d
OAc
2ad
384.1737
385.1748
386.1740
387.1754
388.1696
391.2824
400.1975
Counts vs. Mass-to-Charge (m/z)

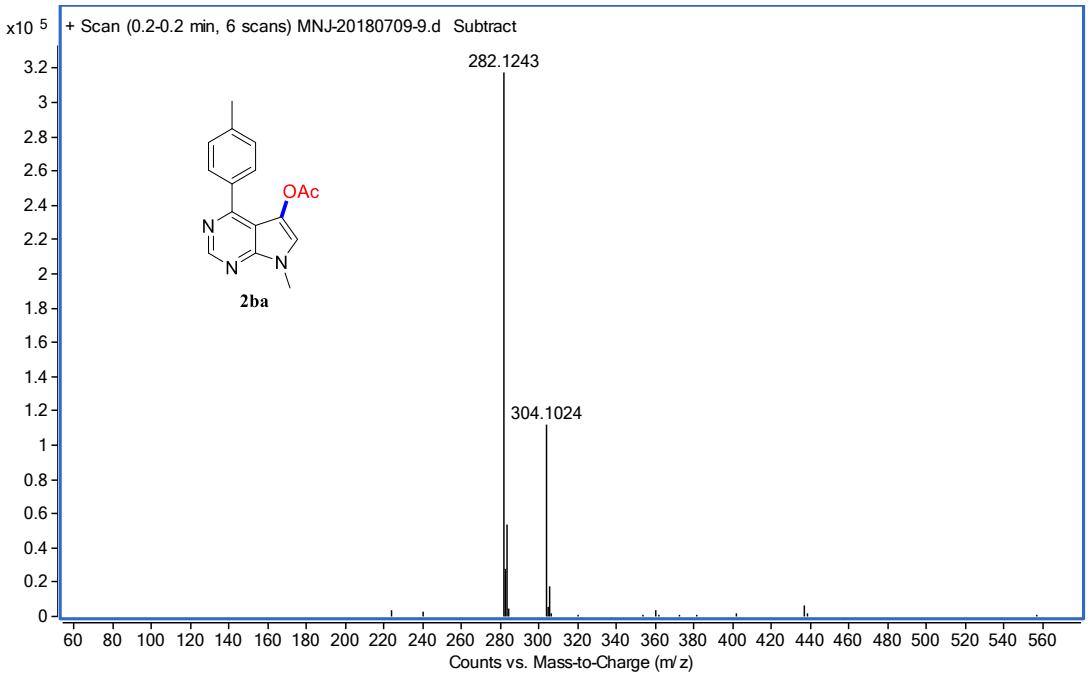

9.0441
8.2108
7.6784
7.6753
7.6635
7.6595
7.5592
7.5570
7.5543
7.5516
7.5494
7.5451
7.5410
7.5364
7.5333
7.5307
7.5293
3.0836
OAc
N
N
N
H
2ae
2.41
3.25
1.51
1.00
1.11
2.41
3.25
1.51
3.46

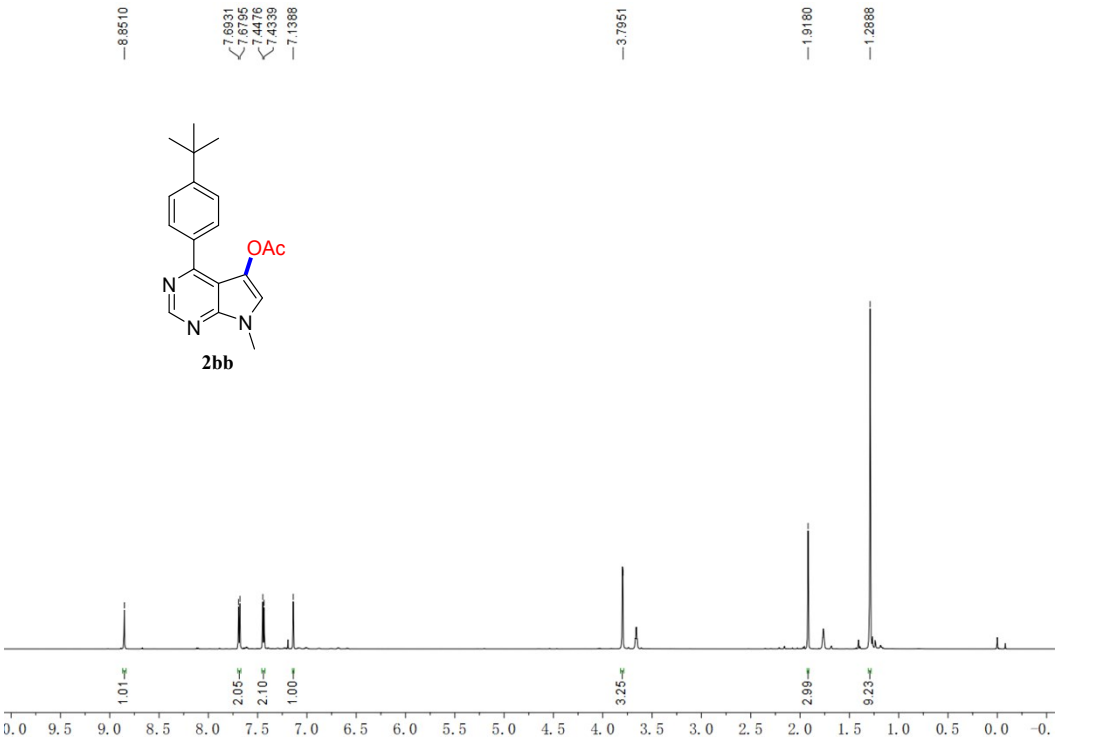

167.41
152.74
152.35
151.62
132.35
130.88
130.00
128.65
128.08
127.88
118.91
104.92
26.01
OAc
N
N
N
H
2ae
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

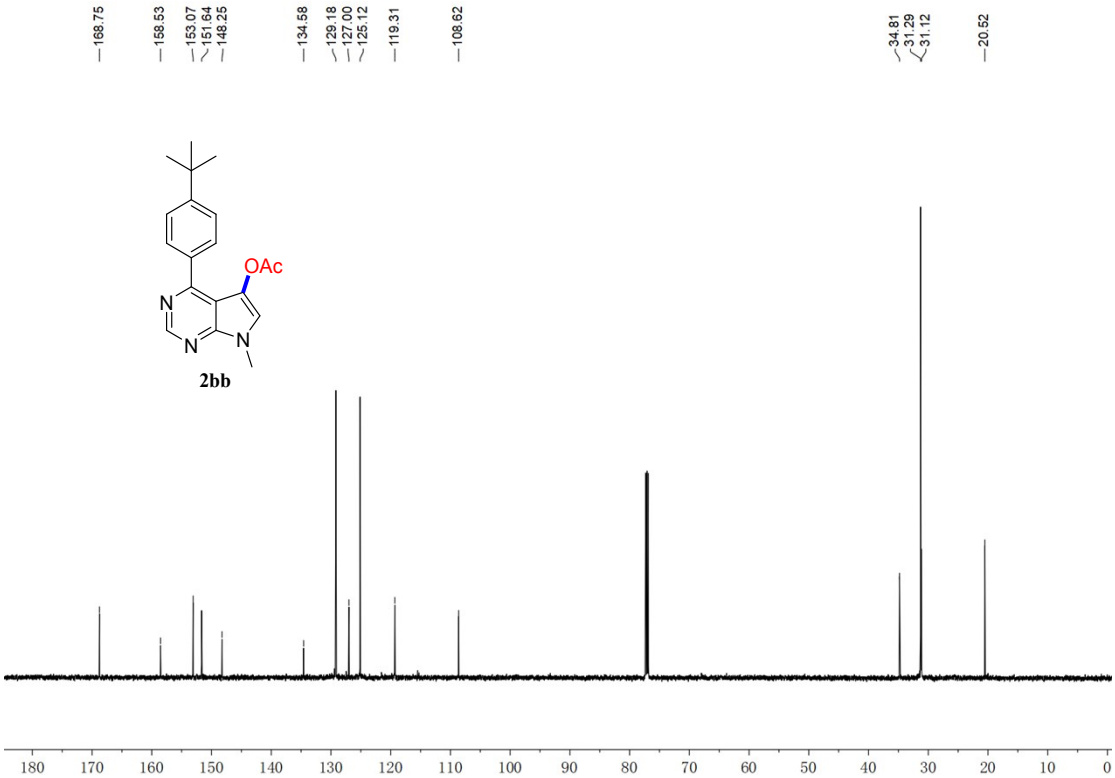

Intens.
+MS, 0.6min #35
5000
4000
3000
2000
1000
0
OAc
2ae
275.0337
275.2271
275.5581
275.7906
276.0743
276.2334
276.4549
276.5812
276.6846
276.9078
275.00 275.25 275.50 275.75 276.00 276.25 276.50 276.75 m/z

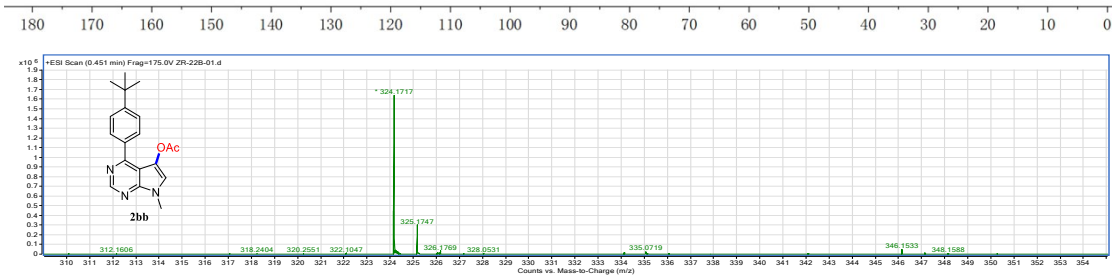

8.9471
7.7743
7.7710
7.7613
7.7581
7.3249
7.3091
7.2763
7.2485
3.8963
2.4485
2.0642
OAc
N
N
N
2ba
2.11
2.19
1.04
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
1.00
2.11
2.19
1.04
3.12
3.20
3.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


168.70
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

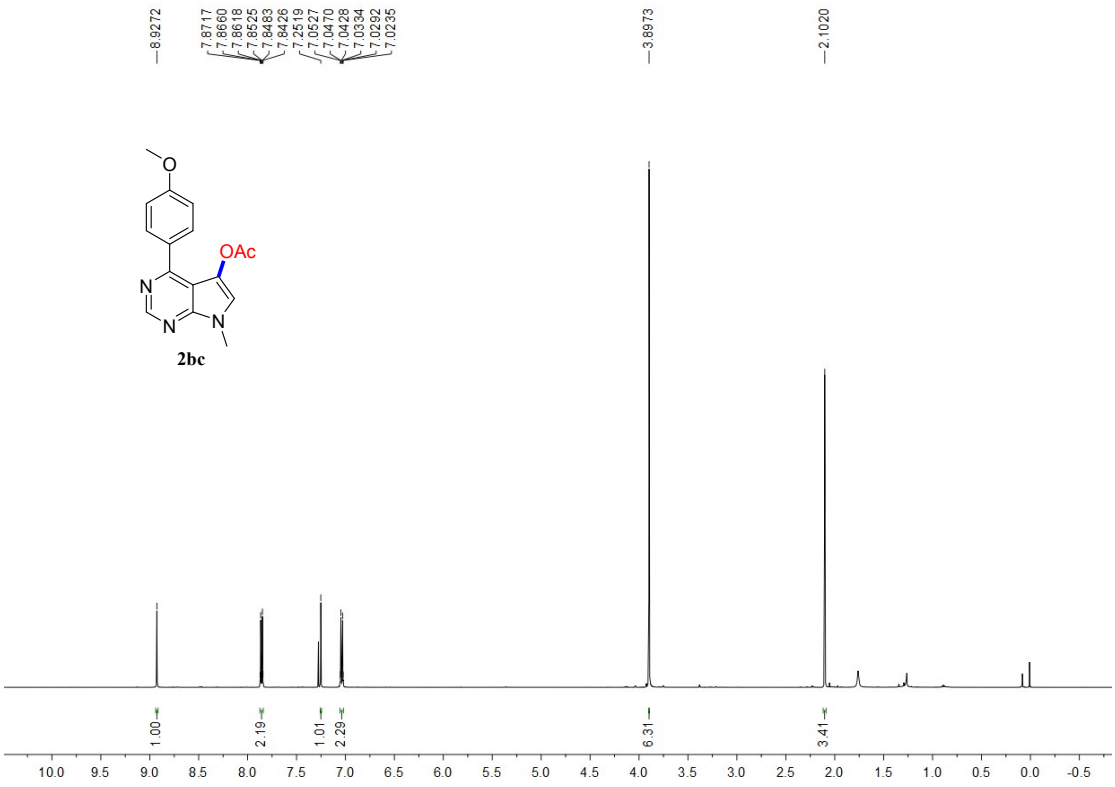

x10 5
+ Scan (0.2-0.2 min, 6 scans) MNJ-20180709-9.d Subtract
282.1243
304.1024
OAc
N
N
N
2ba
3.2 3 2.8 2.6 2.4 2.2 2 1.8 1.6 1.4 1.2 1 0.8 0.6 0.4 0.2 0
60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560
Counts vs. Mass-to-Charge (m/z)

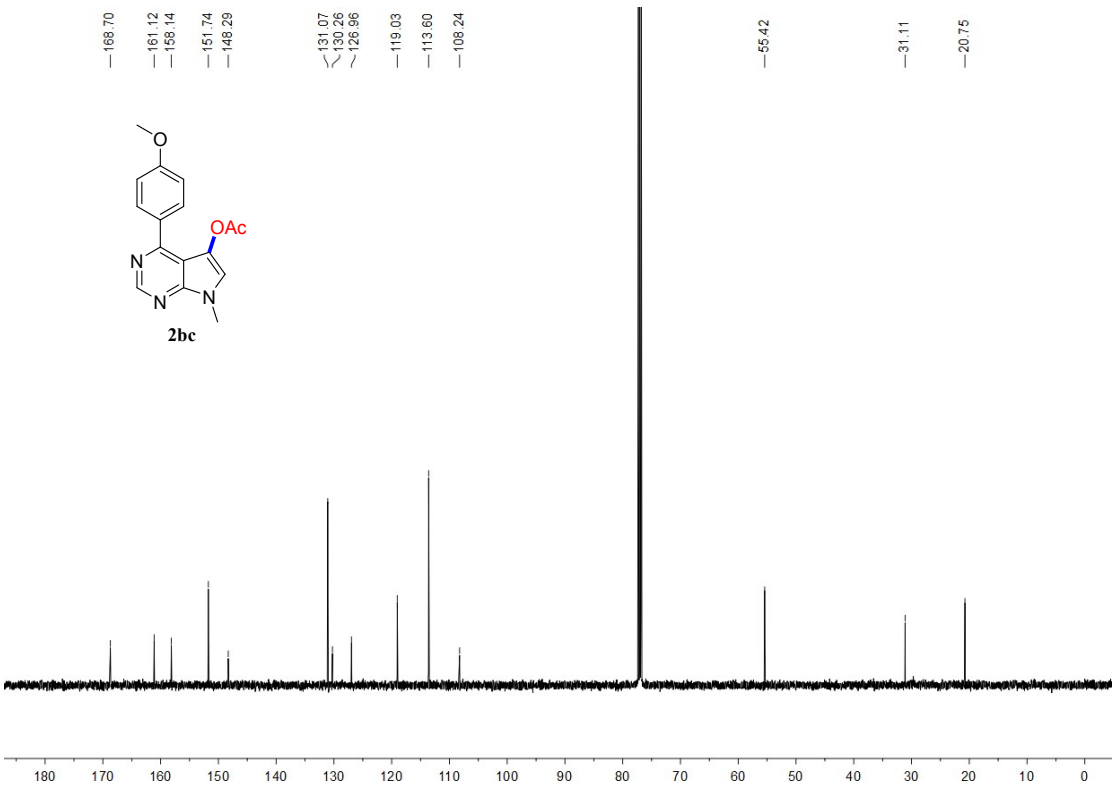

8.8510
7.6931
7.6795
7.4476
7.4339
7.1388
3.7951
1.9180
1.2888
OAc
N
N
N
2bb
1.01
2.05
2.10
1.00
3.25
2.99
9.23

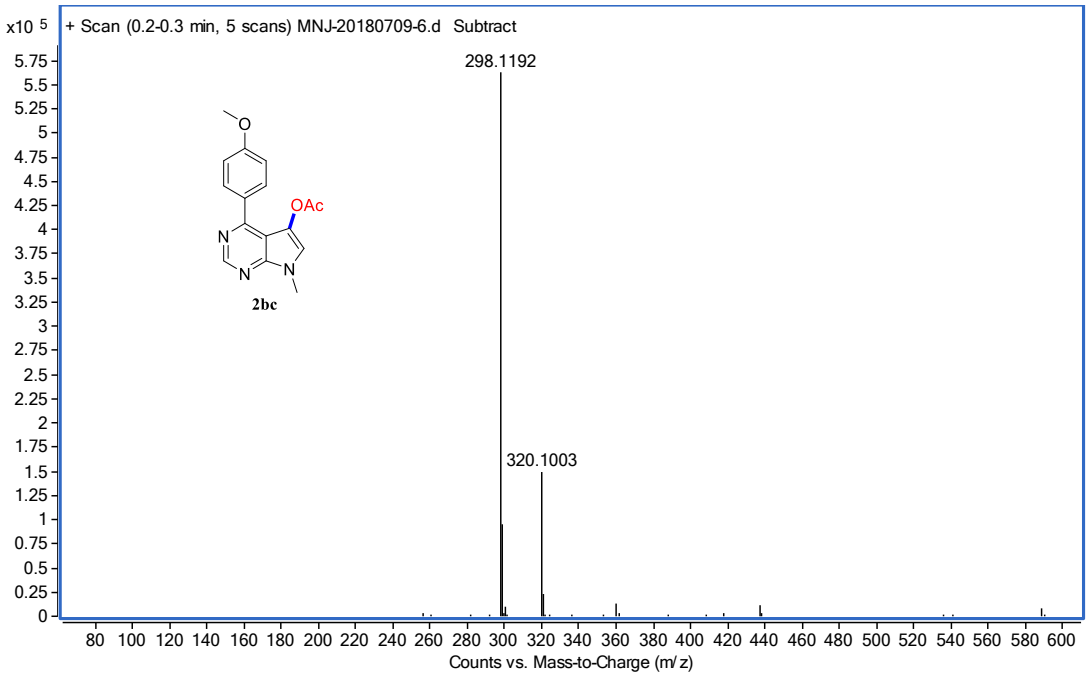

168.75
158.53
153.07
151.64
148.25
134.58
129.18
127.00
125.12
119.31
108.62
34.81
31.29
31.12
20.52
OAc
N
N
N
2bb

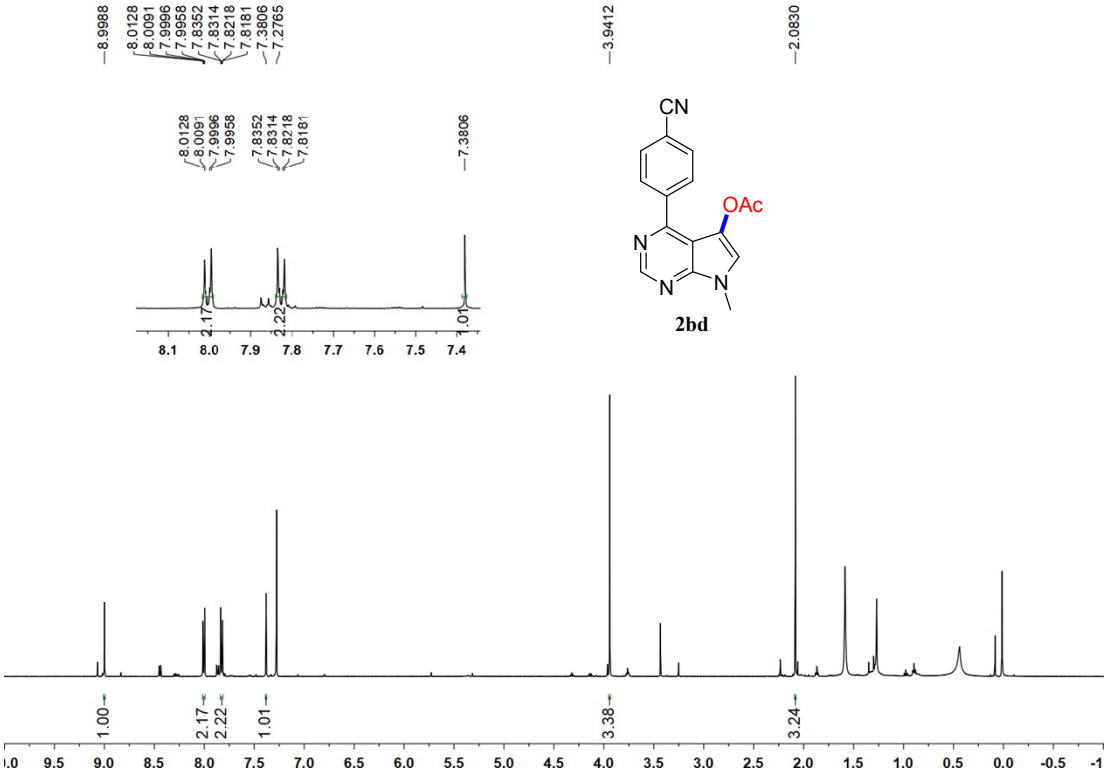


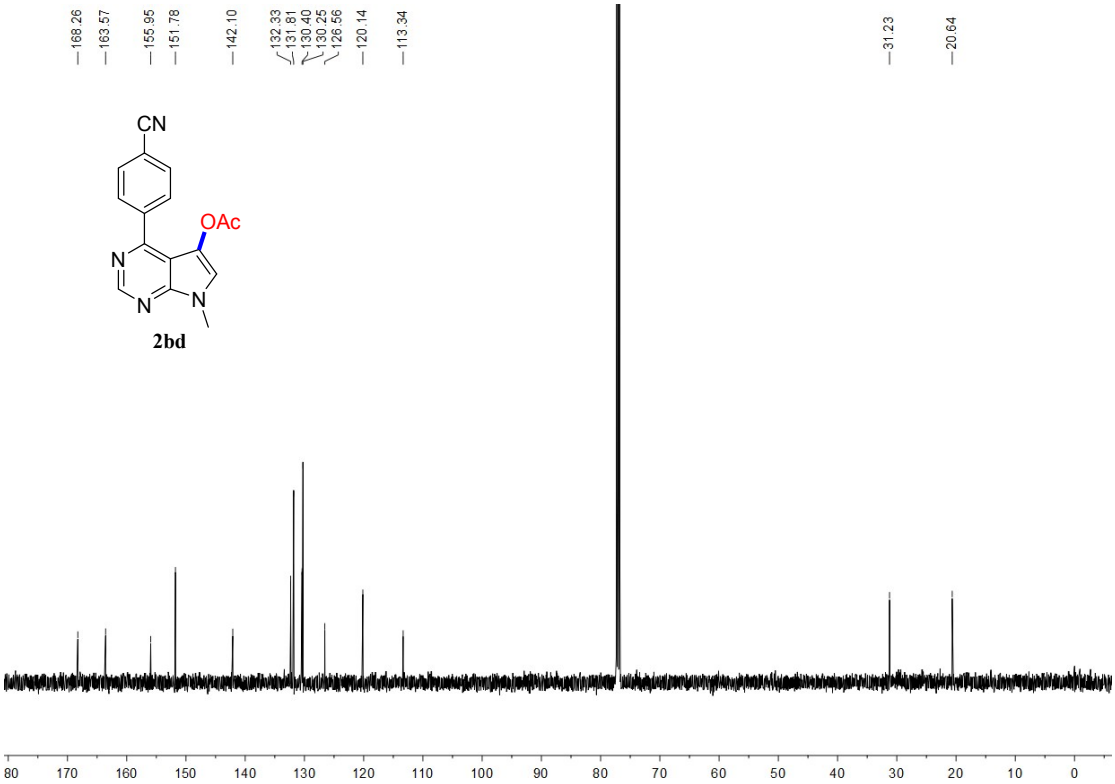
+ESI Scan (0.451 min) Frag=175.0V ZR-22B-01.d
OAc
N
N
N
2bb
324.1717
325.1747
326.1769
312.1606
318.2404
320.2551
322.1047
328.0531
335.0719
346.1533
348.1588
Counts vs. Mass-to-Charge (m/z)

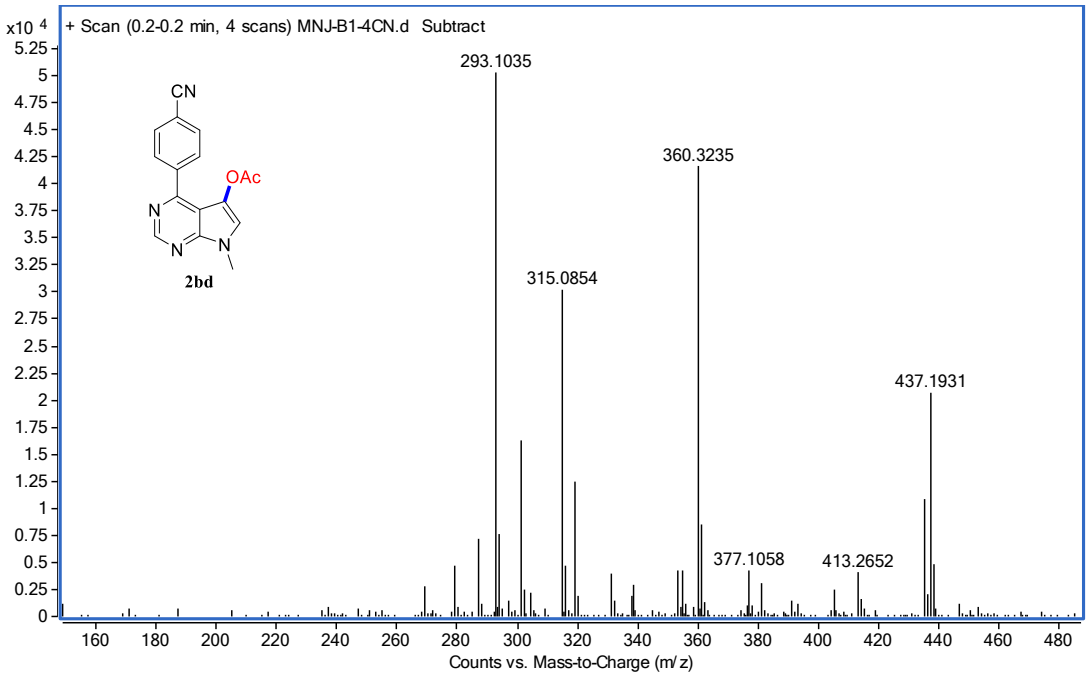

8.9272
7.8717
7.8660
7.8618
7.8525
7.8483
7.8426
7.2519
7.0527
7.0470
7.0428
7.0334
7.0292
7.0235
3.8973
2.1020
O
OAc
N
N
N
2bc
1.00
2.19
1.01
2.29
6.31
3.41
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

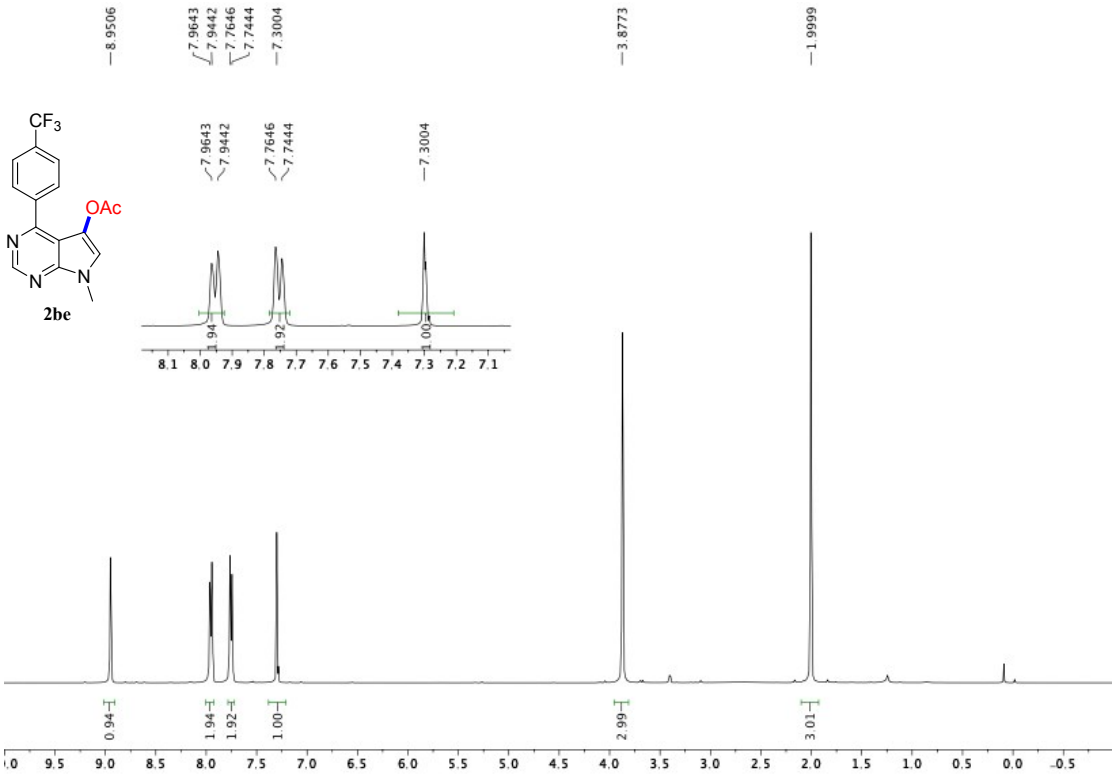

168.70
161.12
158.14
151.74
148.29
131.07
130.26
126.96
119.03
113.60
108.24
55.42
31.11
20.75
O
OAc
N
N
N
2bc
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

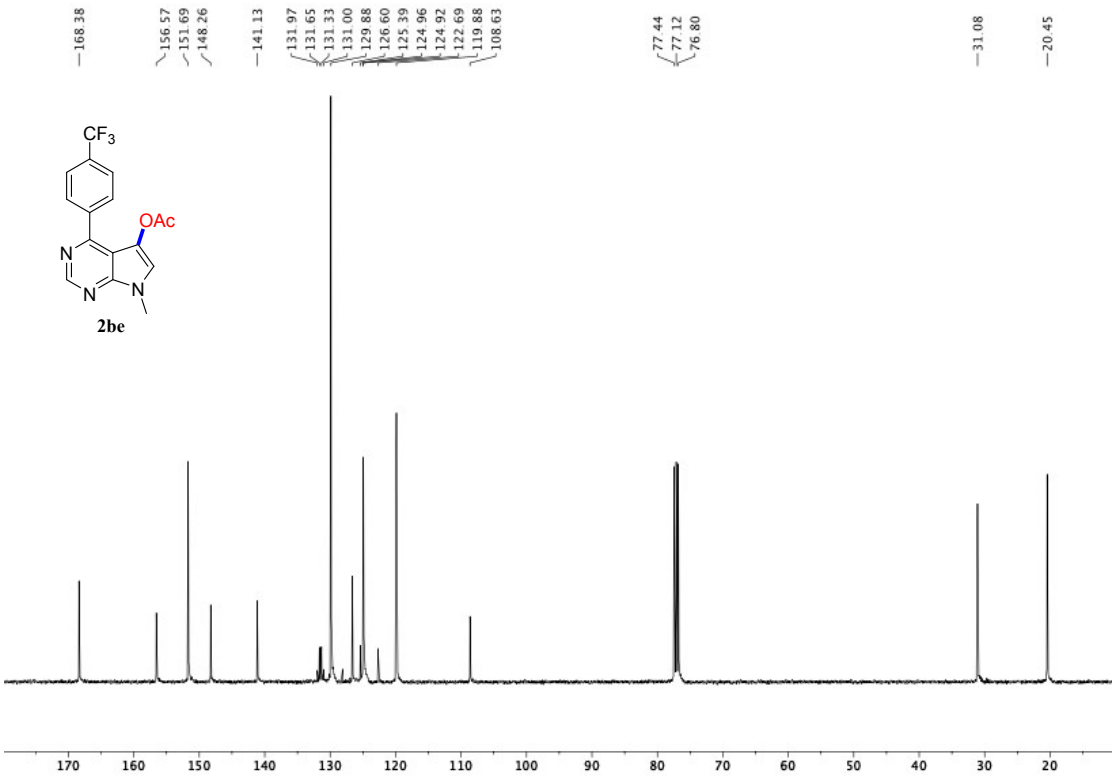

x10 5
+ Scan (0.2-0.3 min, 5 scans) MNJ-20180709-6.d Subtract
298.1192
320.1003
OAc
2bc
Counts vs. Mass-to-Charge (m/z)

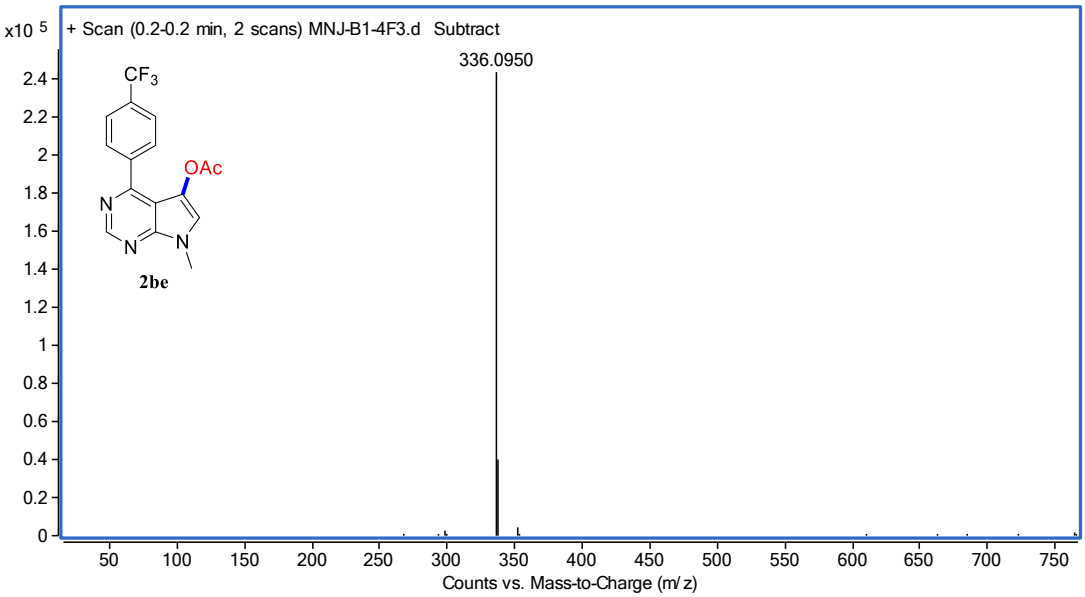

8.9988
8.0128
8.0091
7.9996
7.9958
7.8352
7.8314
7.8218
7.8181
7.3806
7.2765
3.9412
2.0830
CN
OAc
2bd
2.17
2.22
1.01
1.00
3.38
3.24

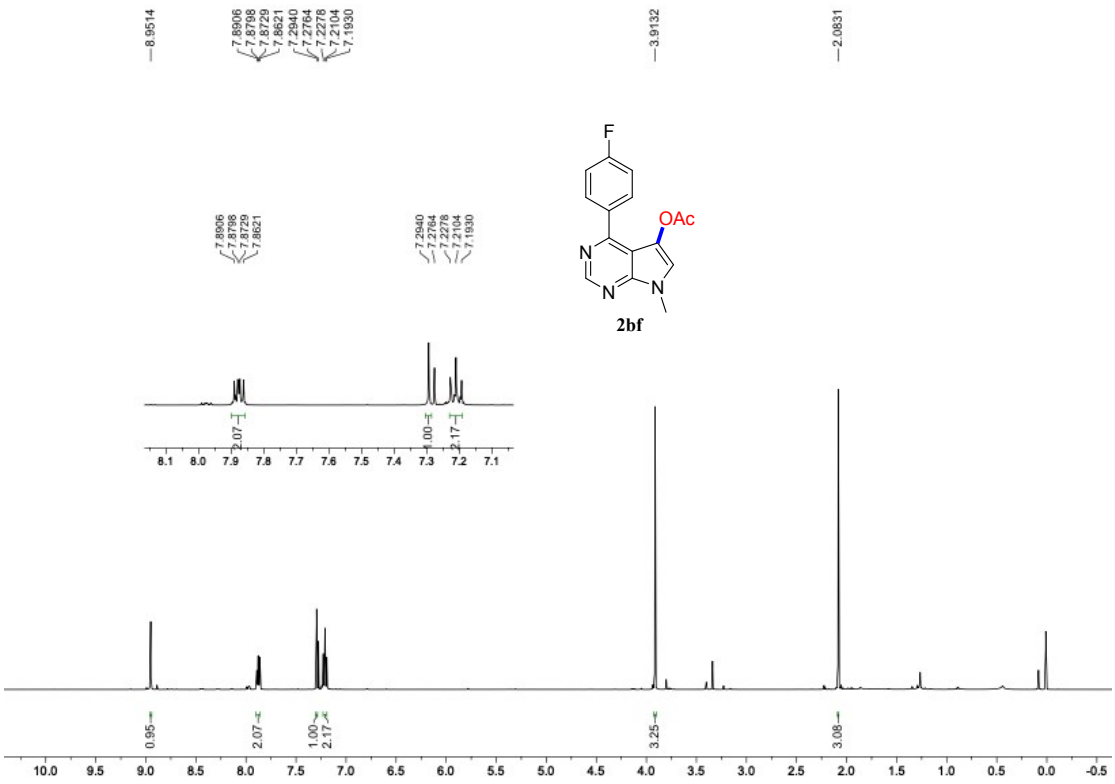

168.26
163.57
155.95
151.78
142.10
132.33
131.81
130.40
130.25
126.56
120.14
113.34
31.23
20.64
CN
OAc
N
N
N
2bd
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

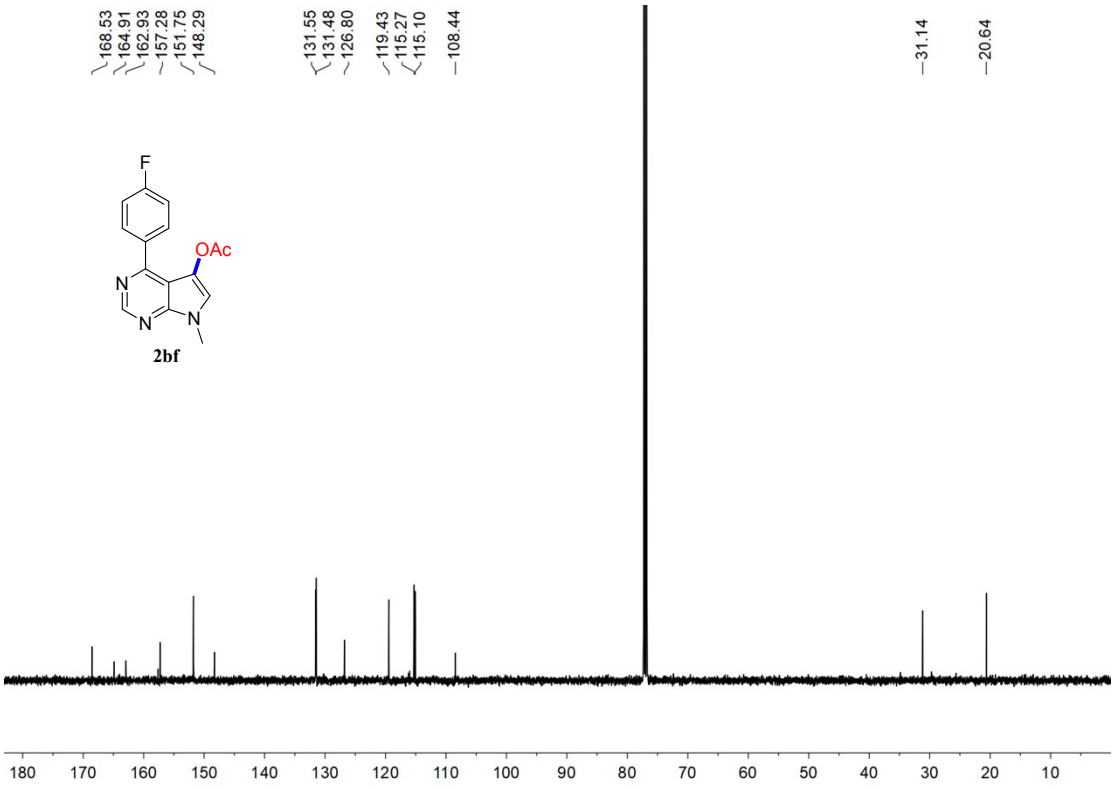

x10 4
+ Scan (0.2-0.2 min, 4 scans) MNJ-B1-4CN.d Subtract
293.1035
360.3235
315.0854
437.1931
377.1058
413.2652
CN
OAc
N
N
N
2bd
Counts vs. Mass-to-Charge (m/z)

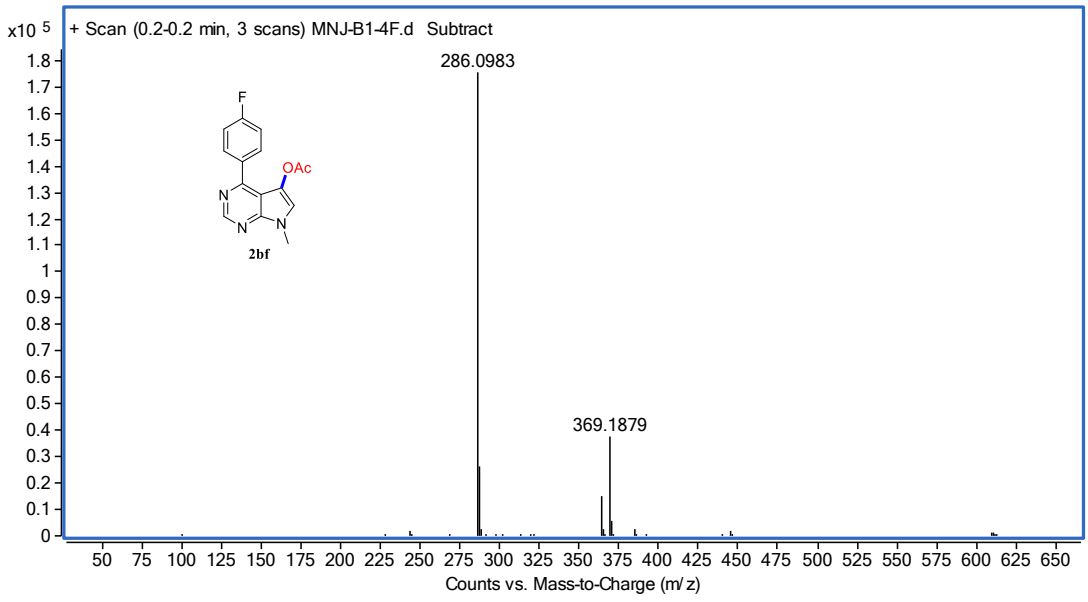

8.9506
7.9643
7.9442
7.7646
7.7444
7.3004
3.8773
1.9999
CF3
OAc
N
N
N
2be
0.94
1.94
1.92
1.00
2.99
3.01

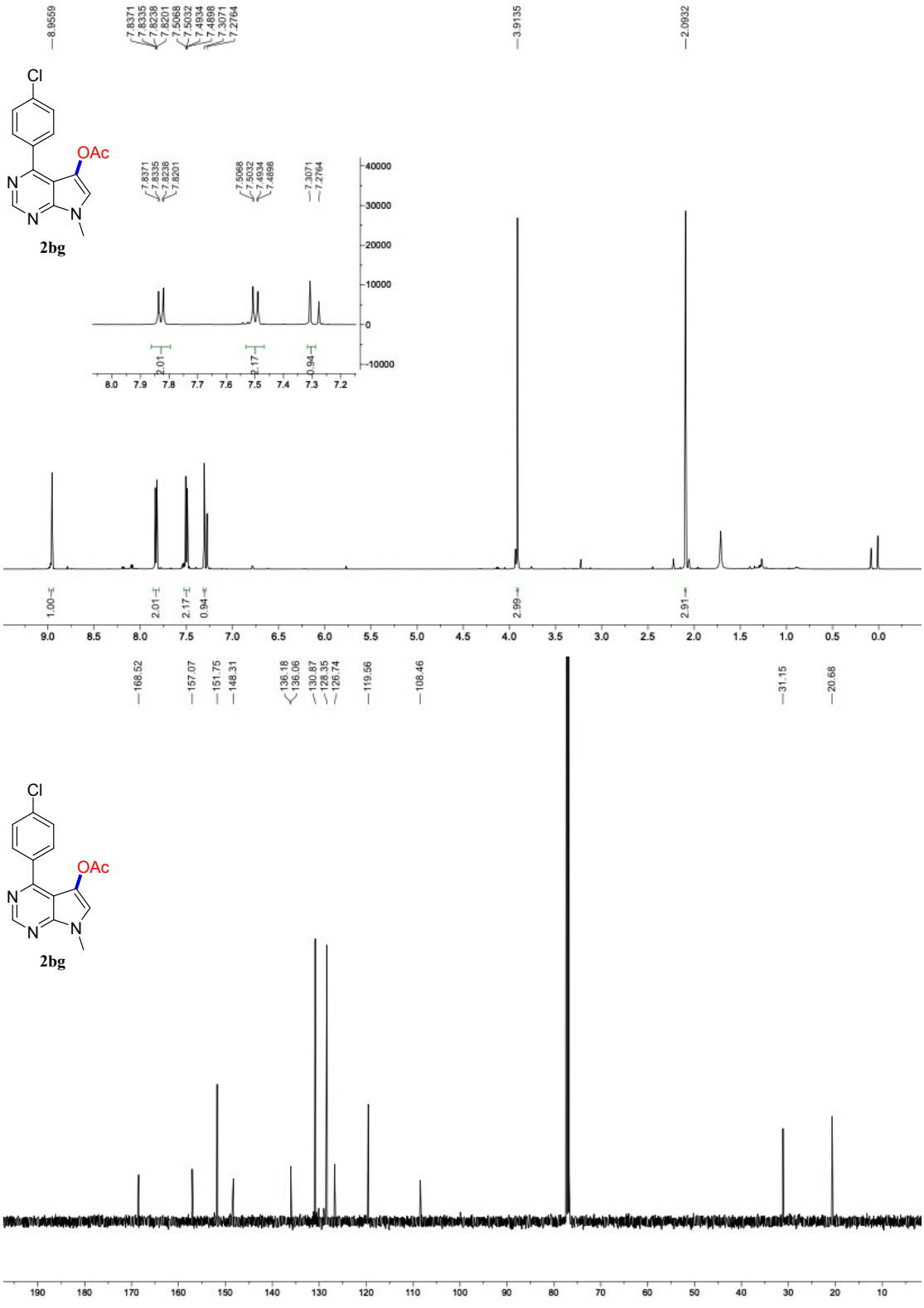

168.38
156.57
151.69
148.26
141.13
131.97
131.65
131.33
131.00
129.88
126.60
125.39
124.96
124.92
122.69
119.88
108.63
77.44
77.12
76.80
31.08
20.45
CF3
OAc
N
N
N
2be

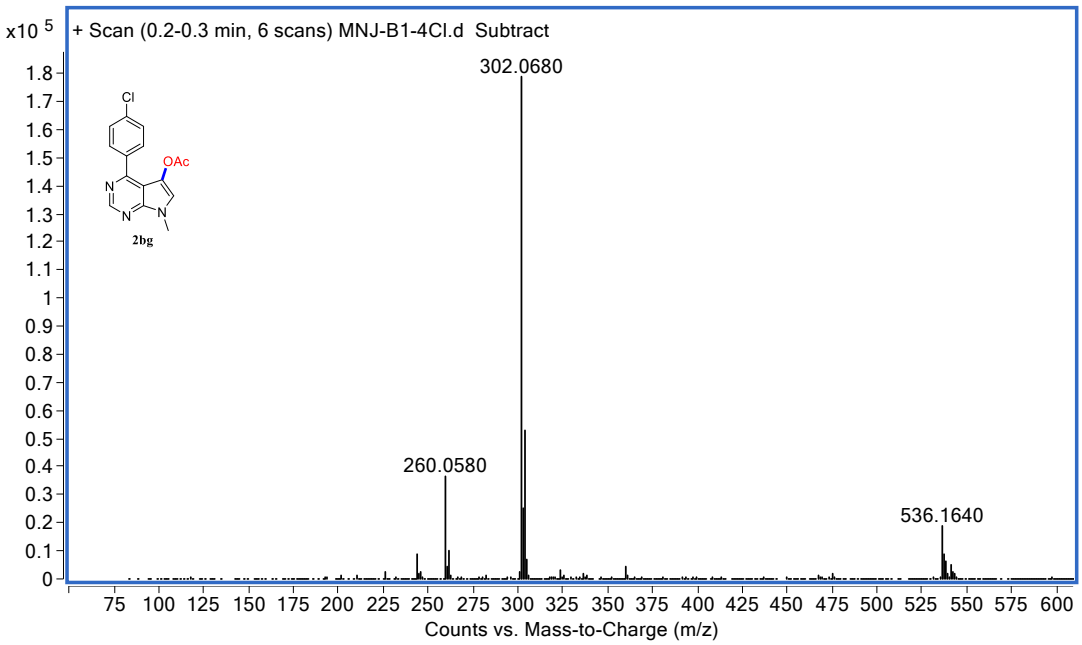

x10 5
+ Scan (0.2-0.2 min, 2 scans) MNJ-B1-4F3.d Subtract
336.0950
CF3
OAc
N
N
N
2be
Counts vs. Mass-to-Charge (m/z)

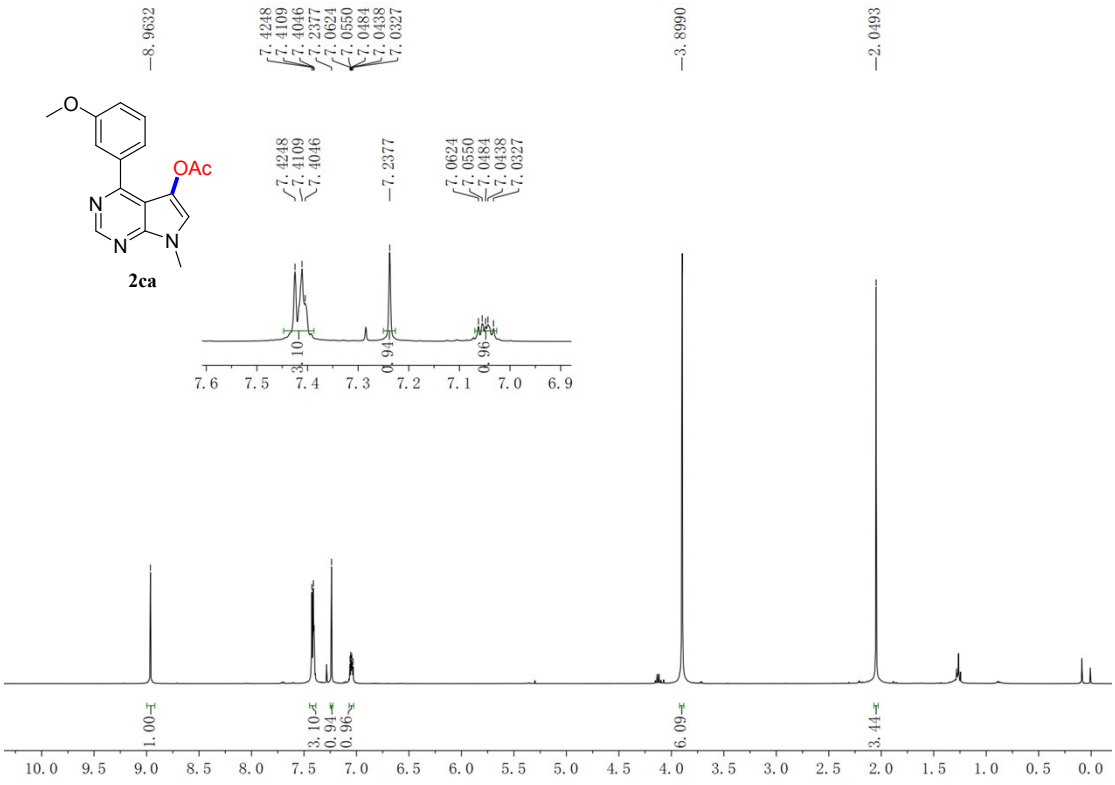

8.9514
7.8906
7.8798
7.8729
7.8621
7.2940
7.2764
7.2278
7.2104
7.1930
3.9132
2.0831
F
OAc
N
N
N
2bf

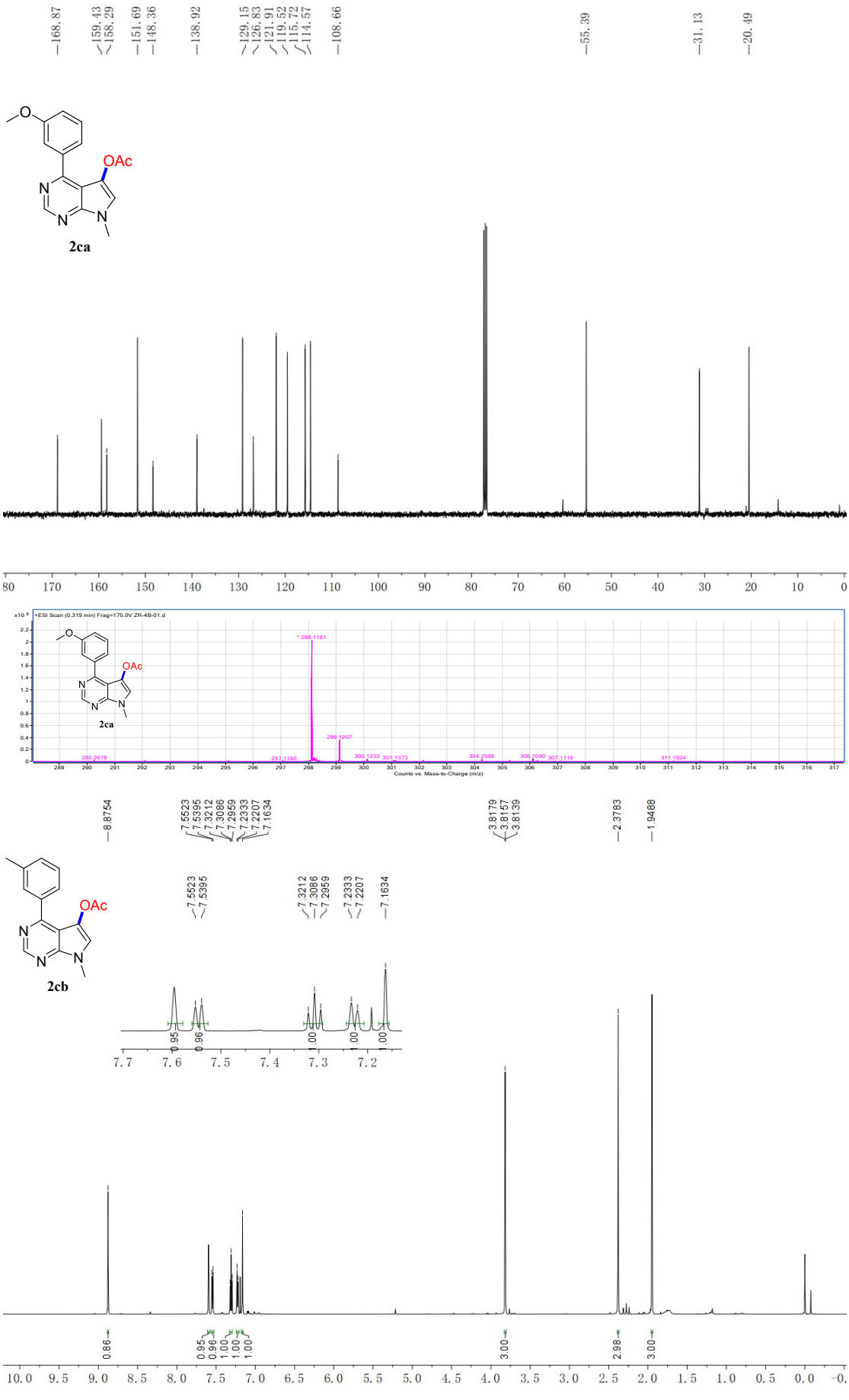

168.53
164.91
162.93
157.28
151.75
148.29
131.55
131.48
126.80
119.43
115.27
115.10
108.44
31.14
20.64
F
OAc
N
N
N
2bf
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

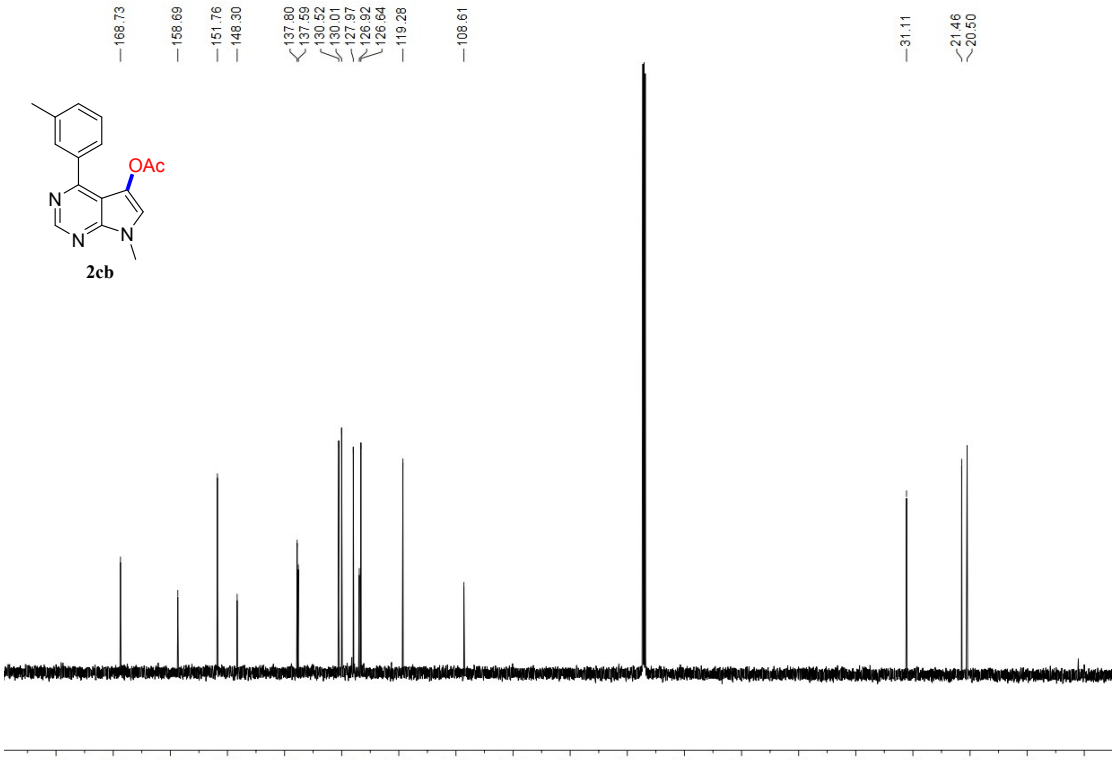

x10 5
+ Scan (0.2-0.2 min, 3 scans) MNJ-B1-4F.d Subtract
286.0983
369.1879
F
OAc
N
N
N
2bf
1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0
50 75 100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 625 650
Counts vs. Mass-to-Charge (m/z)

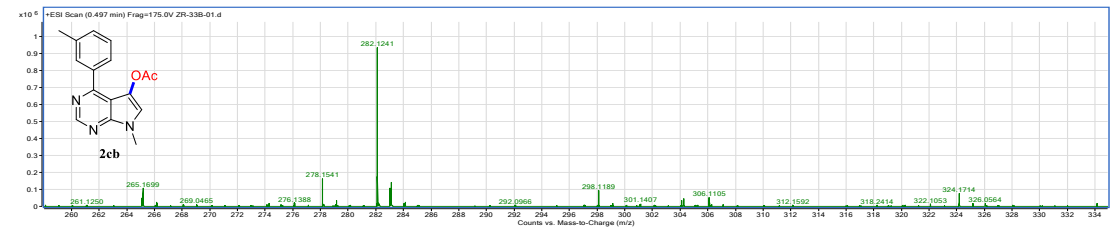

Cl
OAc
N
N
N
2bg
8.9559
7.8371
7.8335
7.8238
7.8201
7.5068
7.5032
7.4934
7.4898
7.3071
7.2764
3.9135
2.0932
1.00
2.01
2.17
0.94
2.99
2.91
168.52
157.07
151.75
148.31
136.18
136.06
130.87
128.35
126.74
119.56
108.46
31.15
20.68

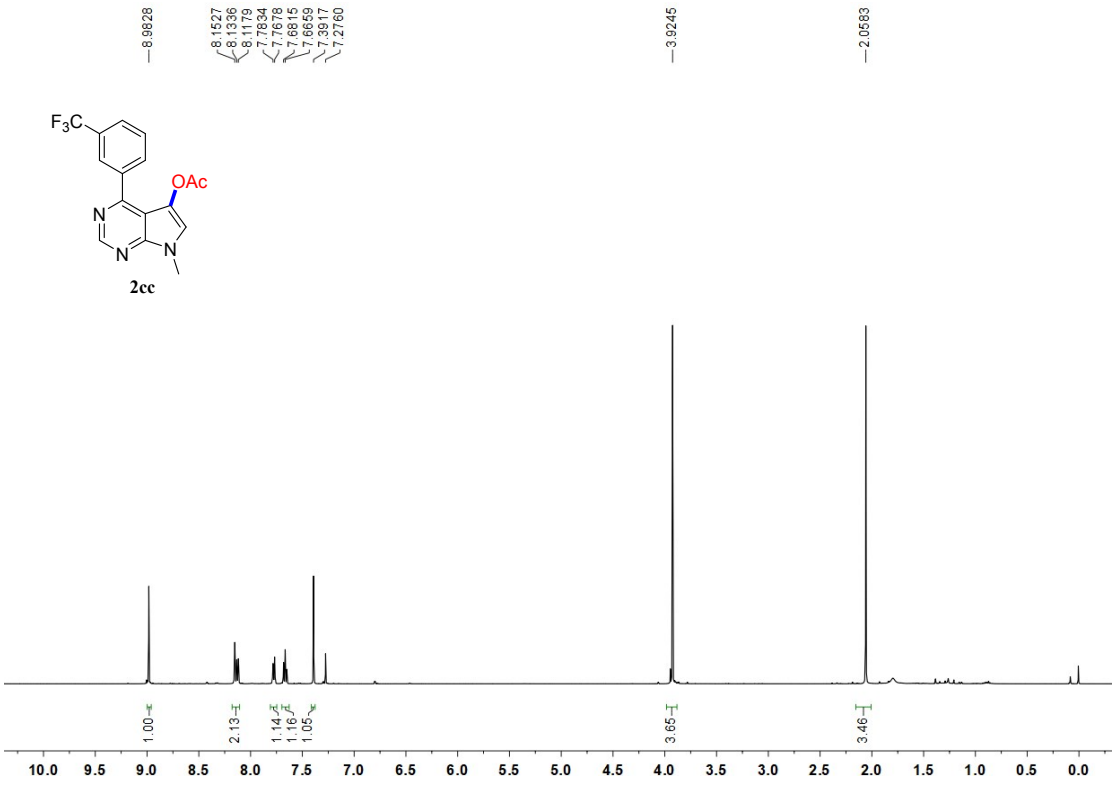

x10 5
+ Scan (0.2-0.3 min, 6 scans) MNJ-B1-4Cl.d Subtract
302.0680
260.0580
536.1640
Cl
OAc
2bg
Counts vs. Mass-to-Charge (m/z)

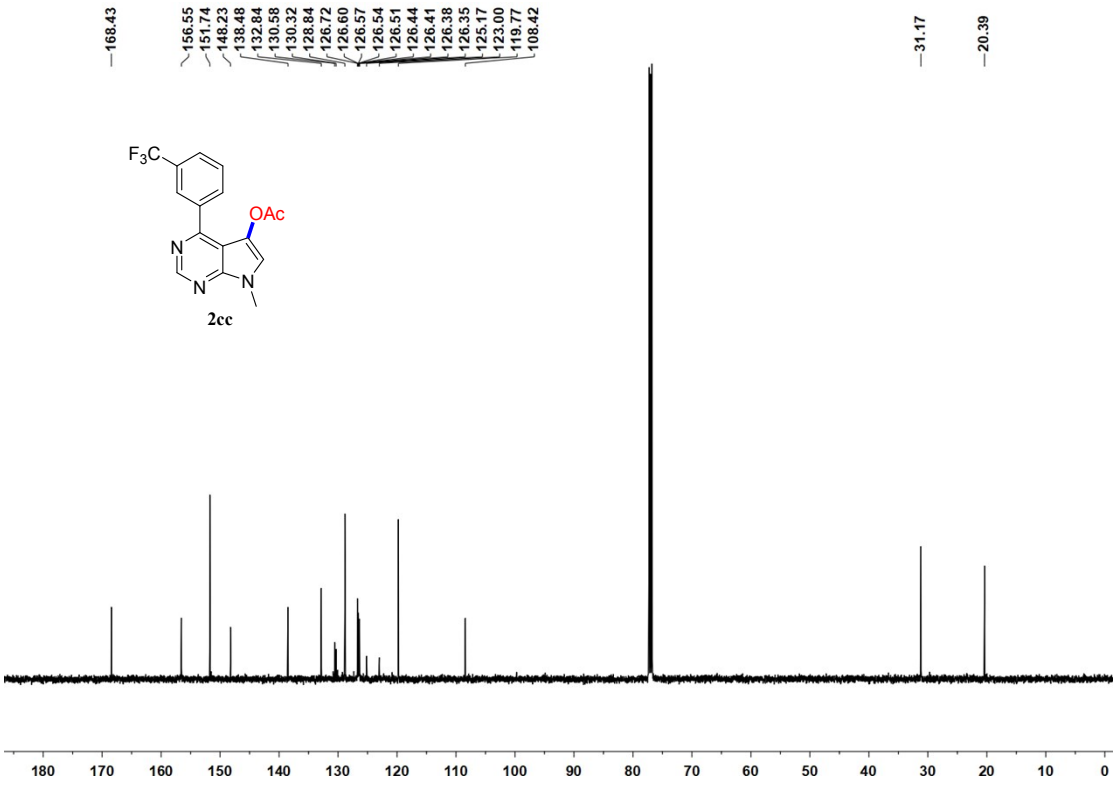

8.9632
7.4248
7.4109
7.4046
7.2377
7.0624
7.0550
7.0484
7.0438
7.0327
3.8990
2.0493
OAc
2ca
1.00
3.10
0.94
0.96
6.09
3.44

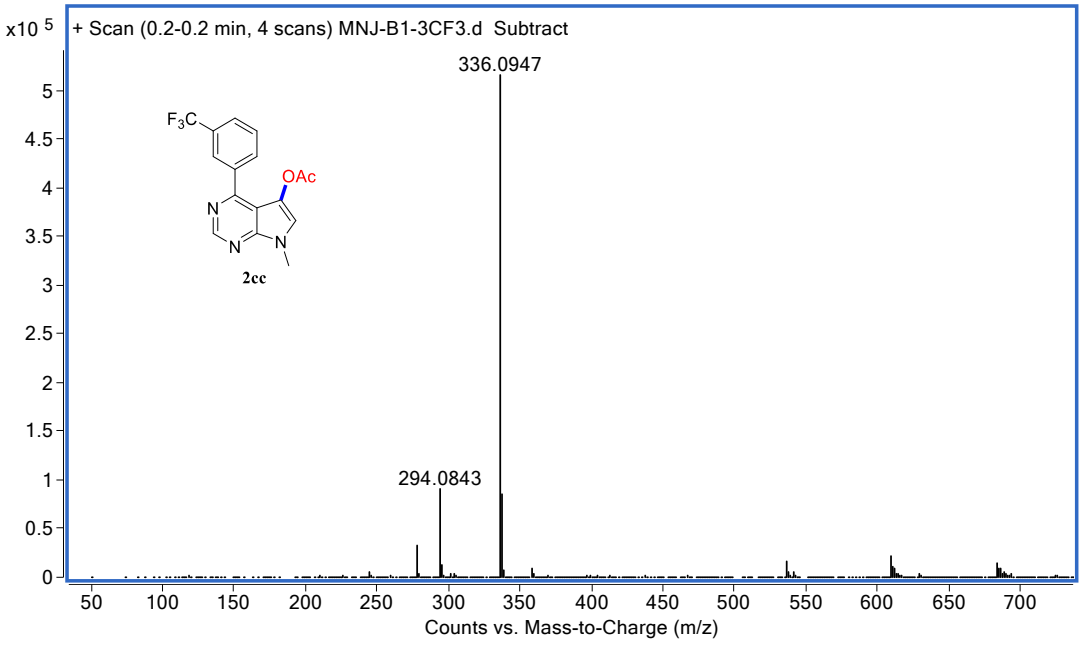

168.87
159.43
158.29
151.69
148.36
138.92
129.15
126.83
121.91
119.52
115.72
114.57
108.66
55.39
31.13
20.49
OAc
2ca
+ESI Scan (0.319 min) Frag=175.0V ZR-4B-01.d
298.1181
298.1207
Counts vs. Mass-to-Charge (m/z)
8.8754
7.5523
7.5395
7.3212
7.3086
7.2959
7.2333
7.2207
7.1634
3.8179
3.8157
3.8139
2.3783
1.9488
OAc
2cb
0.95
0.96
1.00
1.00
1.00
0.86
3.00
2.98
3.00

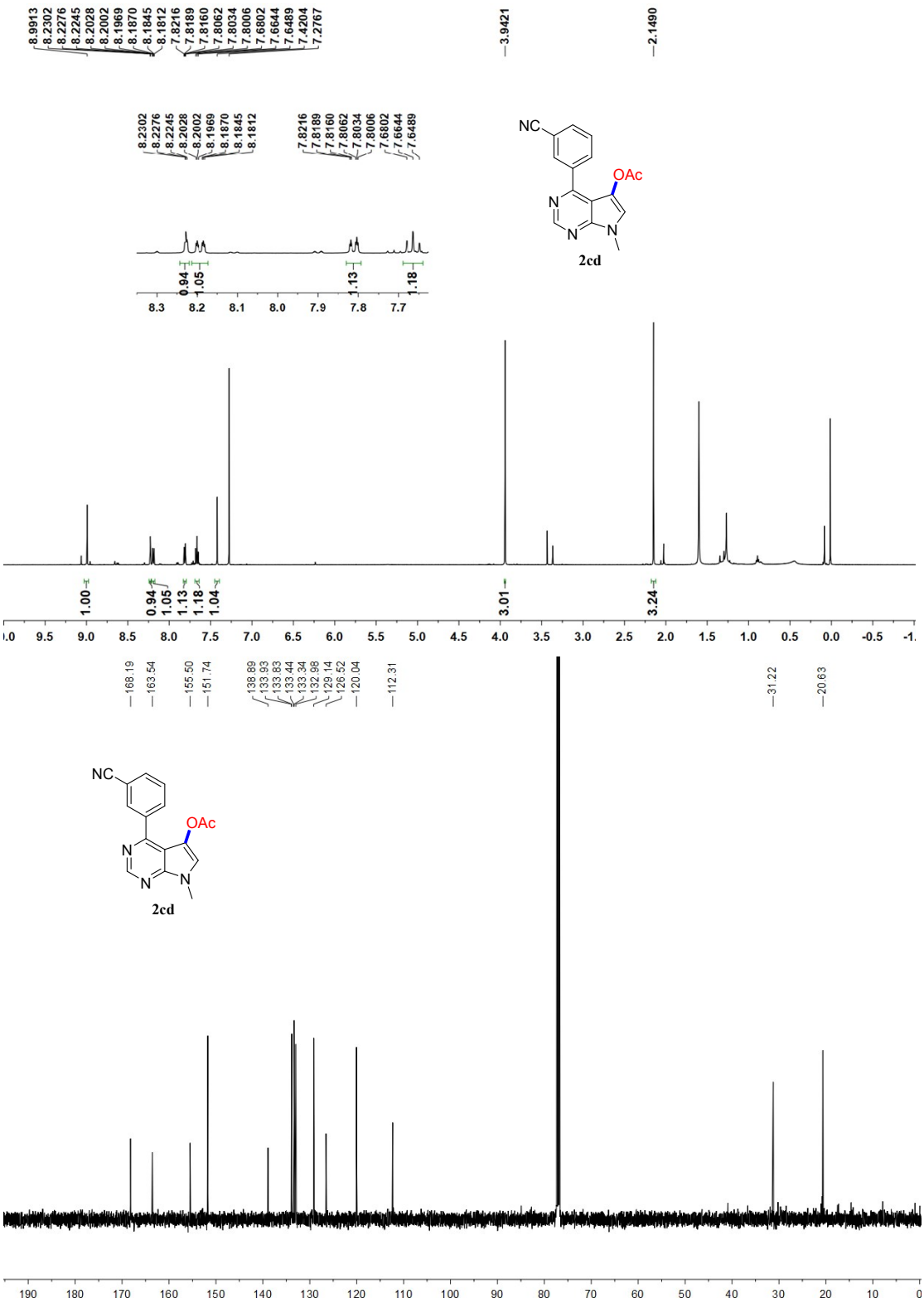

168.73
158.69
151.76
148.30
137.80
137.59
130.52
130.01
127.97
126.92
126.64
119.28
108.61
31.11
21.46
20.50
OAc
N
N
N
2cb

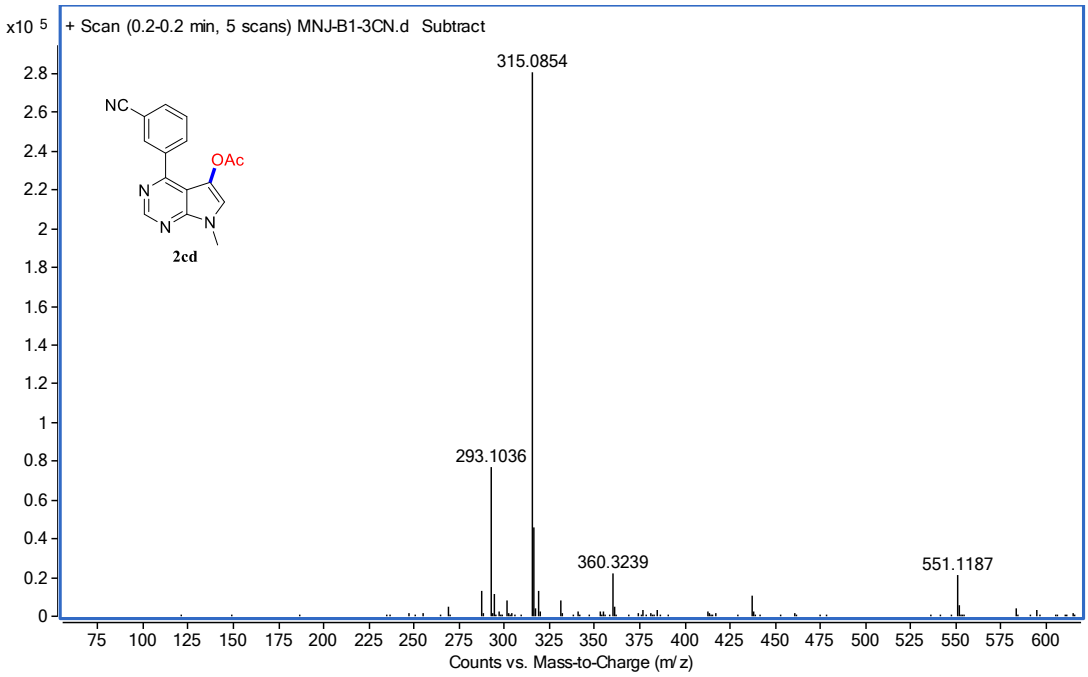

+ESI Scan (0.497 min) Frag=175.0V ZR-33B-01.d
282.1241
278.1541
265.1699
298.1189
306.1105
324.1714
OAc
N
N
N
2cb
Counts vs. Mass-to-Charge (m/z)

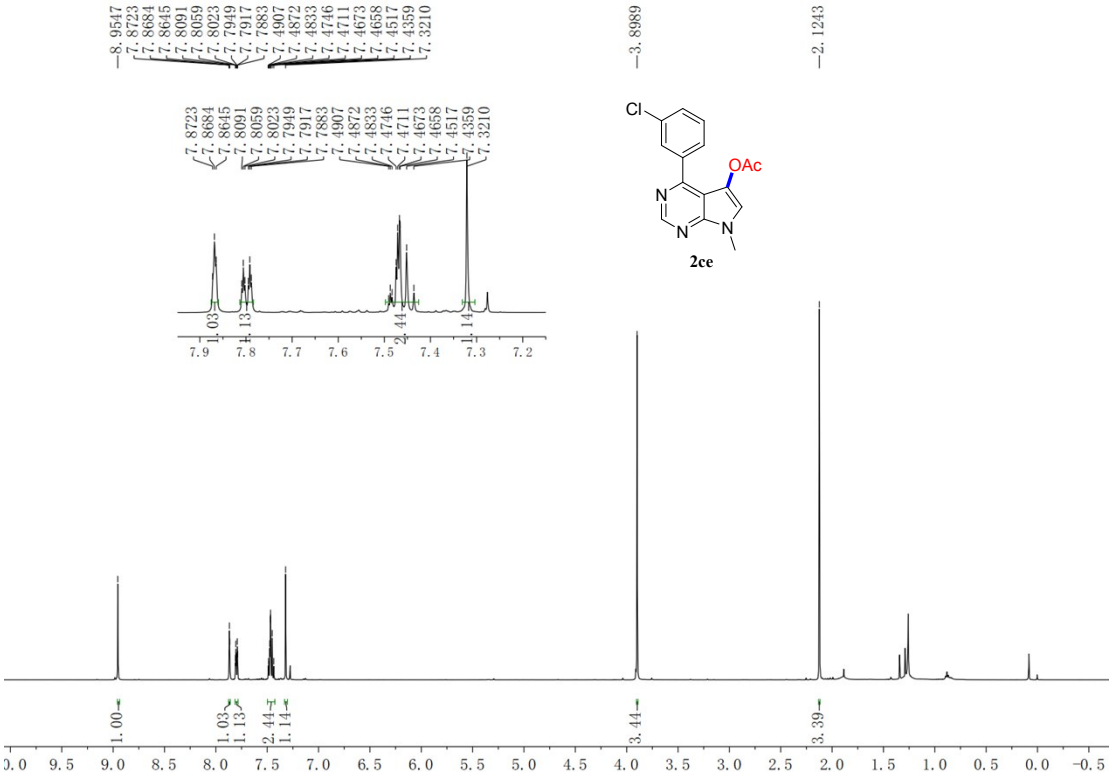

8.9828
8.1527
8.1336
8.1179
7.7834
7.7678
7.6815
7.6659
7.3917
7.2760
3.9245
2.0583
F3C
OAc
N
N
N
2cc
1.00
2.13
1.14
1.16
1.05
3.65
3.46

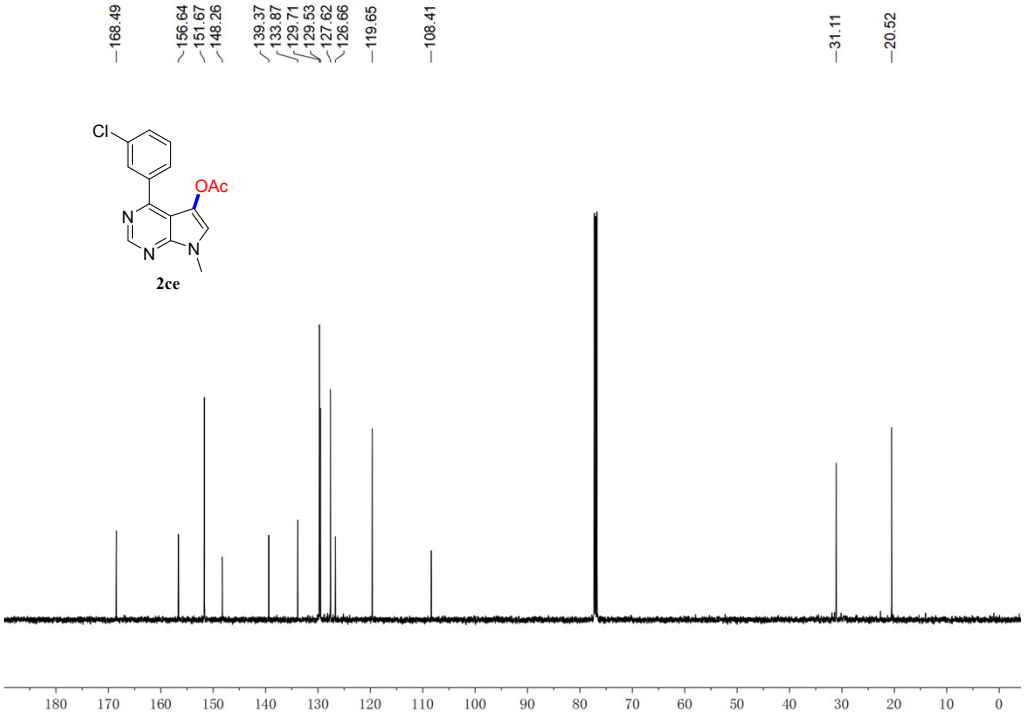

168.43
156.55
151.74
148.23
138.48
132.84
130.58
130.32
128.84
126.72
126.60
126.57
126.54
126.51
126.44
126.41
126.38
126.35
125.17
123.00
119.77
108.42
31.17
20.39
F3C
OAc
N
N
N
2cc
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

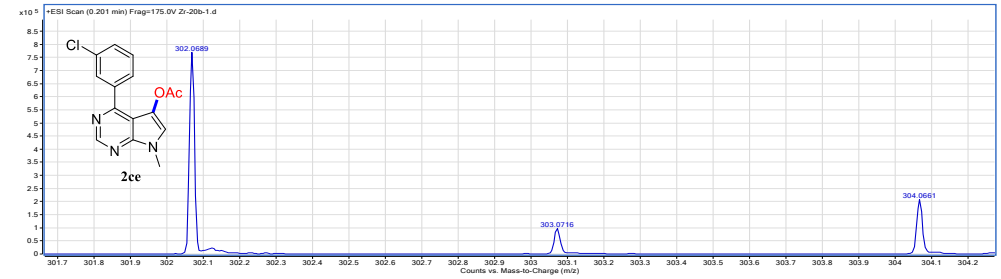

x10 5
+ Scan (0.2-0.2 min, 4 scans) MNJ-B1-3CF3.d Subtract
336.0947
294.0843
F3C
OAc
N
N
N
2cc
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
Counts vs. Mass-to-Charge (m/z)

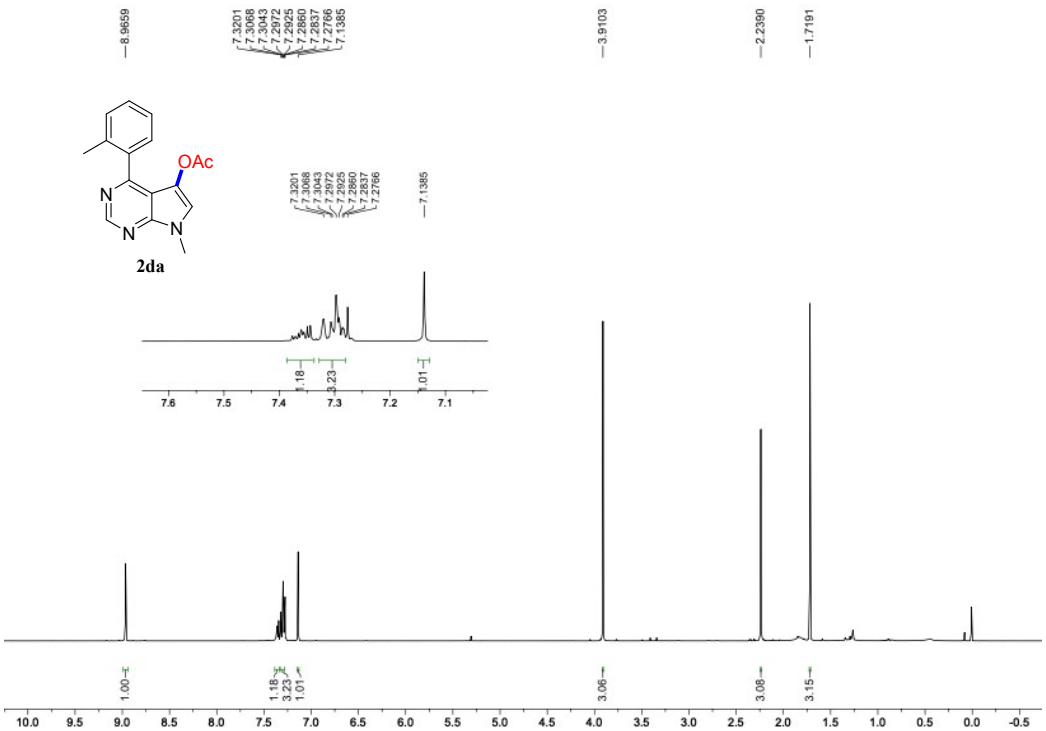

8.9913
8.2302
8.2276
8.2245
8.2028
8.2002
8.1969
8.1870
8.1845
8.1812
7.8216
7.8189
7.8160
7.8062
7.8034
7.8006
7.6802
7.6644
7.6489
7.4204
7.2767
3.9421
2.1490
NC
OAc
N
N
2cd
0.94
1.05
1.13
1.18
1.00
1.04
3.01
3.24
168.19
163.54
155.50
151.74
138.89
133.93
133.83
133.44
133.34
132.98
129.14
126.52
120.04
112.31
31.22
20.63

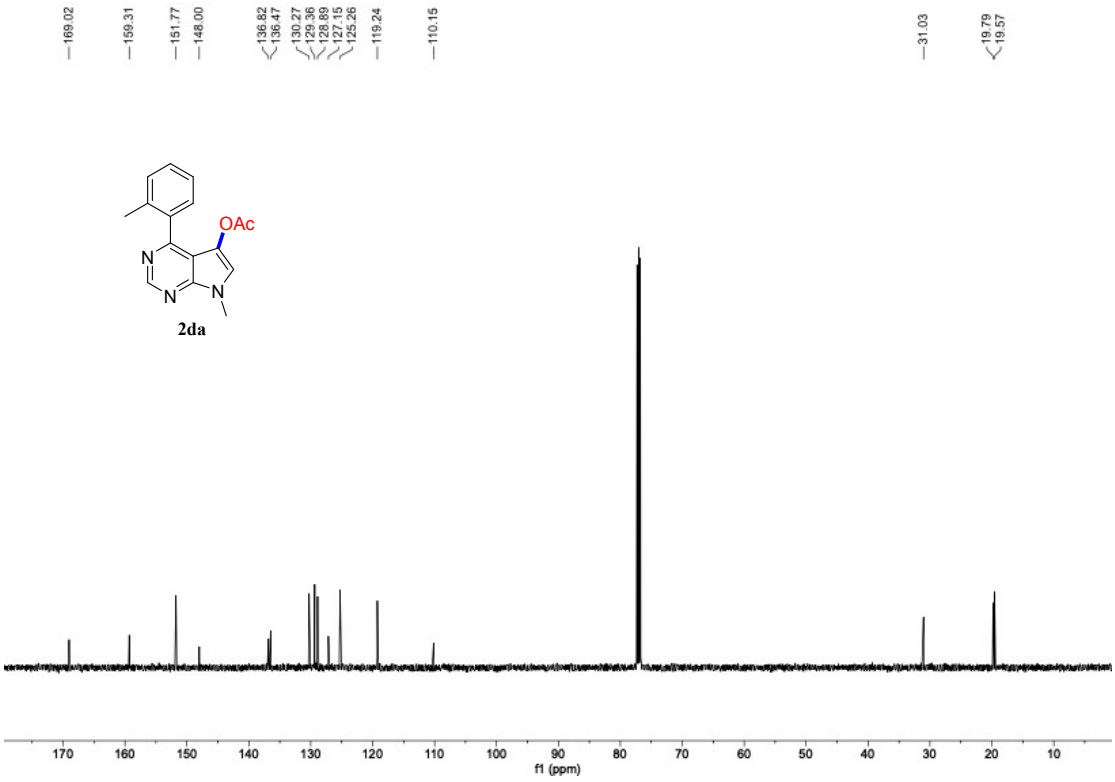

x10 5
+ Scan (0.2-0.2 min, 5 scans) MNJ-B1-3CN.d Subtract
315.0854
293.1036
360.3239
551.1187
NC
OAc
N
N
N
2cd
Counts vs. Mass-to-Charge (m/z)

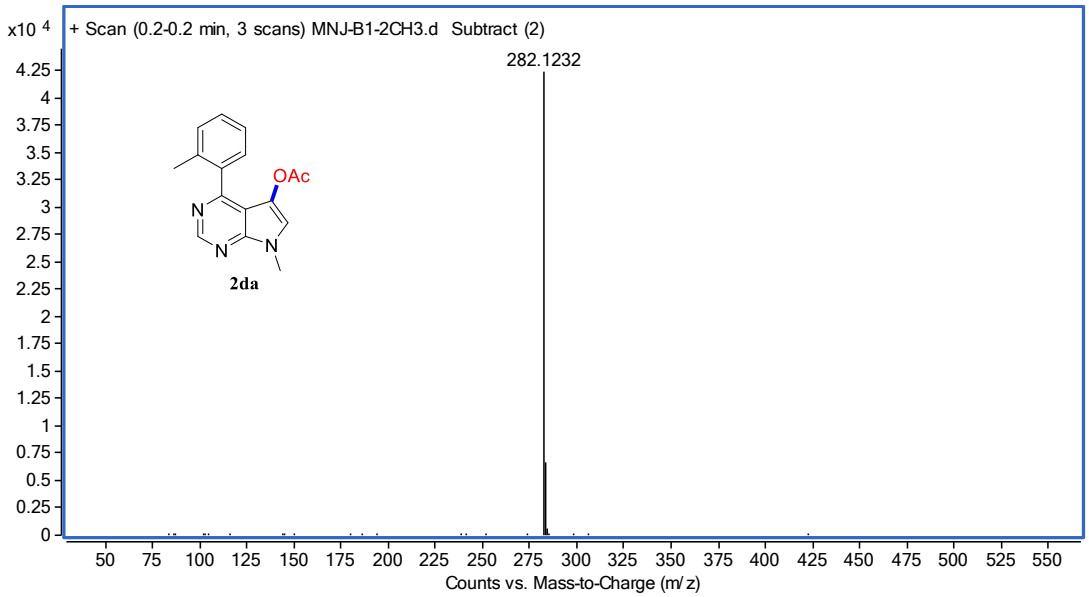

8.9547
7.8723
7.8684
7.8645
7.8091
7.8059
7.8023
7.7949
7.7917
7.7883
7.4907
7.4872
7.4833
7.4746
7.4711
7.4673
7.4658
7.4517
7.4359
7.3210
3.8989
2.1243
Cl
OAc
N
N
N
2ce
1.00
1.03
1.13
2.44
1.14
3.44
3.39

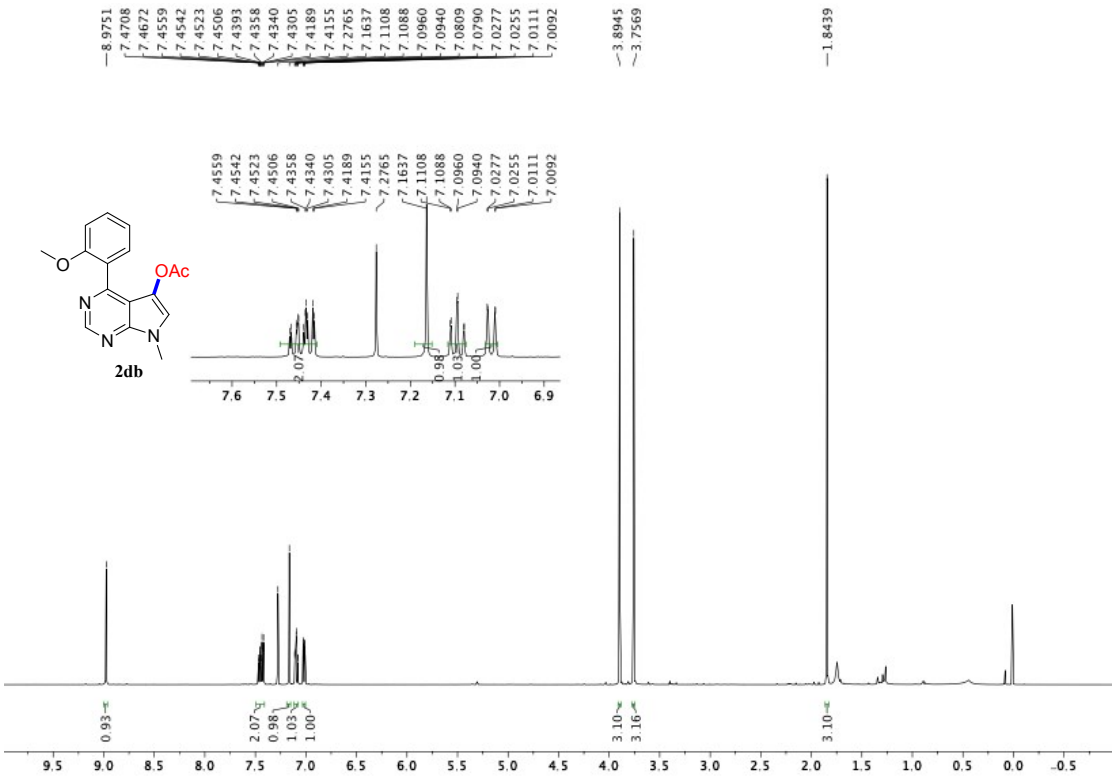

168.49
156.64
151.67
148.26
139.37
133.87
129.71
129.53
127.62
126.66
119.65
108.41
31.11
20.52
Cl
OAc
N
N
N
2ce
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

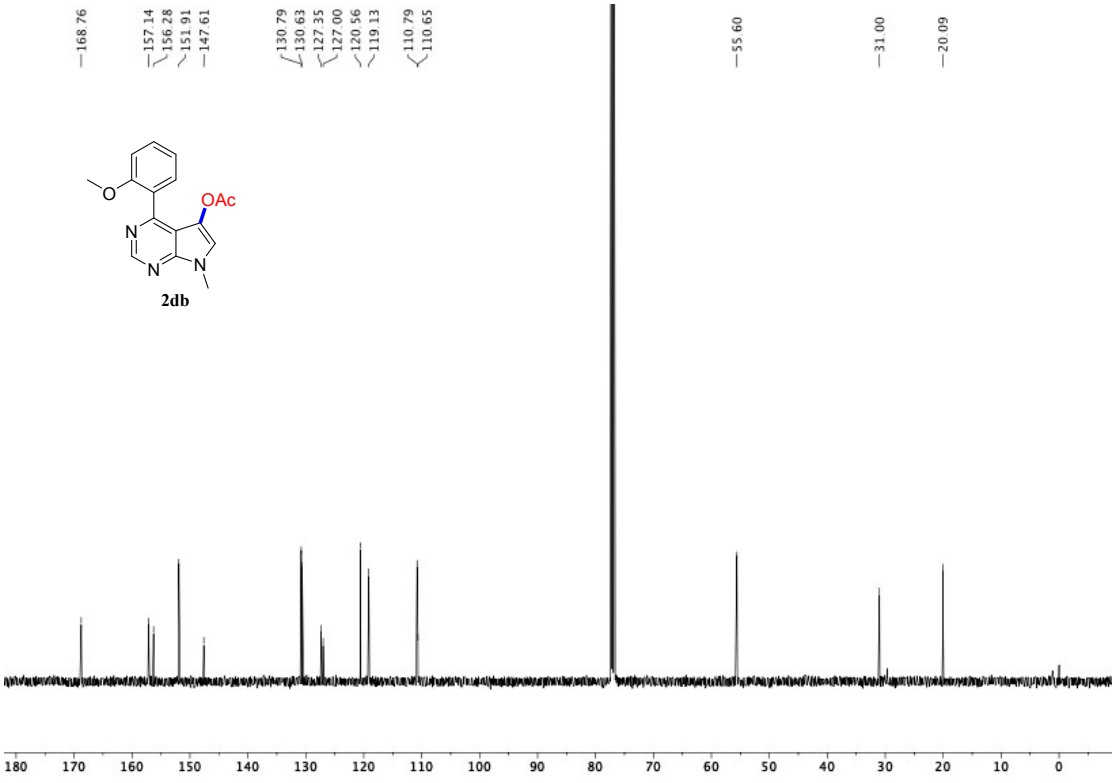

+ESI Scan (0.201 min) Frag=175.0V Zr-20b-1.d
302.0689
303.0716
304.0661
Cl
OAc
N
N
N
2ce
Counts vs. Mass-to-Charge (m/z)

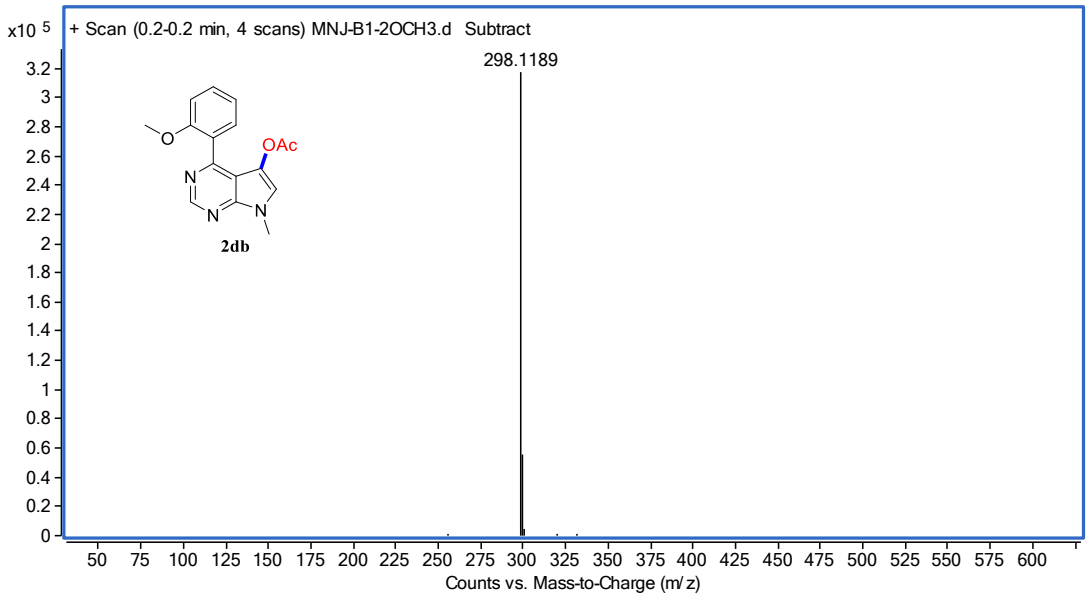

8.9659
7.3201
7.3068
7.3043
7.2972
7.2925
7.2860
7.2837
7.2766
7.1385
3.9103
2.2390
1.7191
OAc
N
N
N
2da
1.18
3.23
1.01
3.06
3.08
3.15
1.00

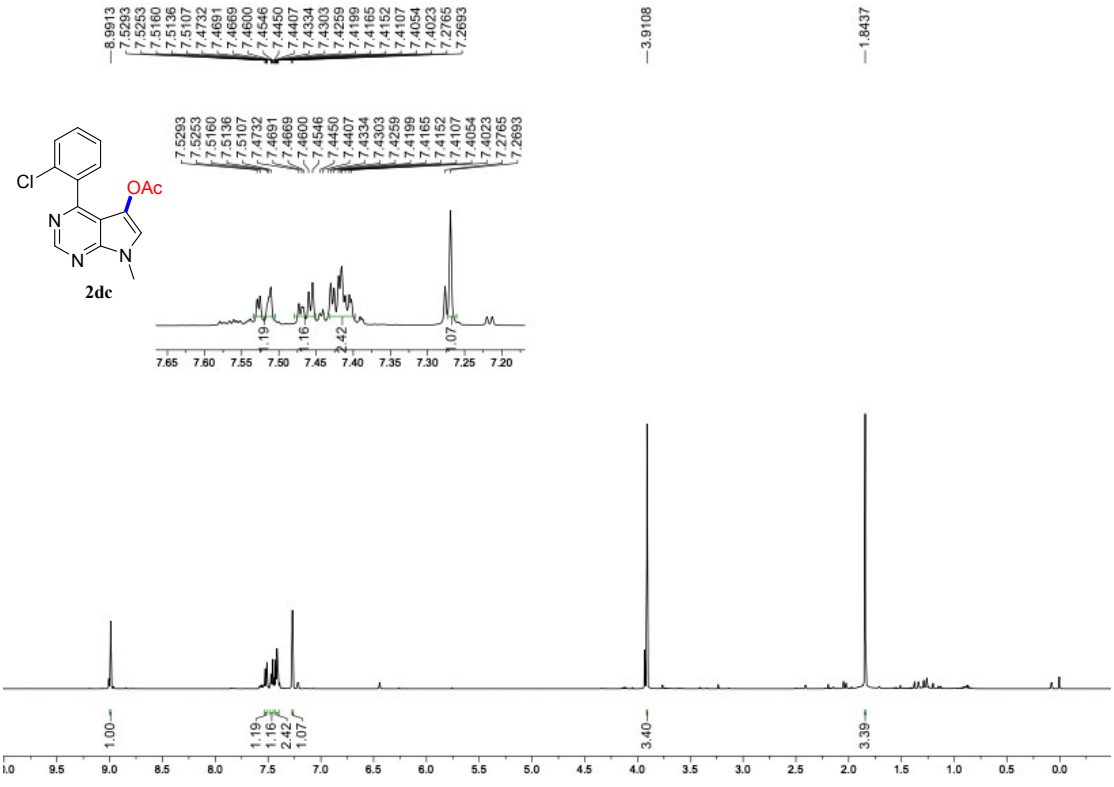

169.02
159.31
151.77
148.00
136.82
136.47
130.27
129.36
128.89
127.15
125.26
119.24
110.15
31.03
19.79
19.57
OAc
N
N
2da
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

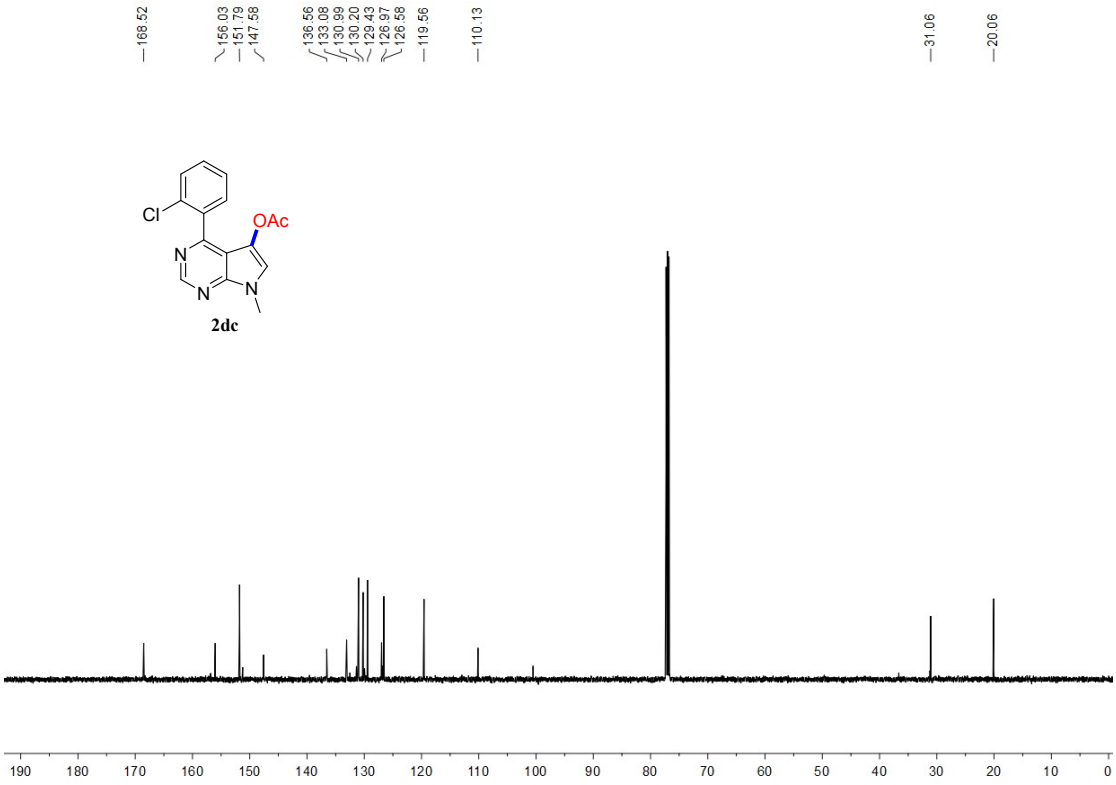

x10 4
+ Scan (0.2-0.2 min, 3 scans) MNJ-B1-2CH3.d Subtract (2)
282.1232
OAc
N
N
2da
4.25
4
3.75
3.5
3.25
3
2.75
2.5
2.25
2
1.75
1.5
1.25
1
0.75
0.5
0.25
0
50 75 100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550
Counts vs. Mass-to-Charge (m/z)

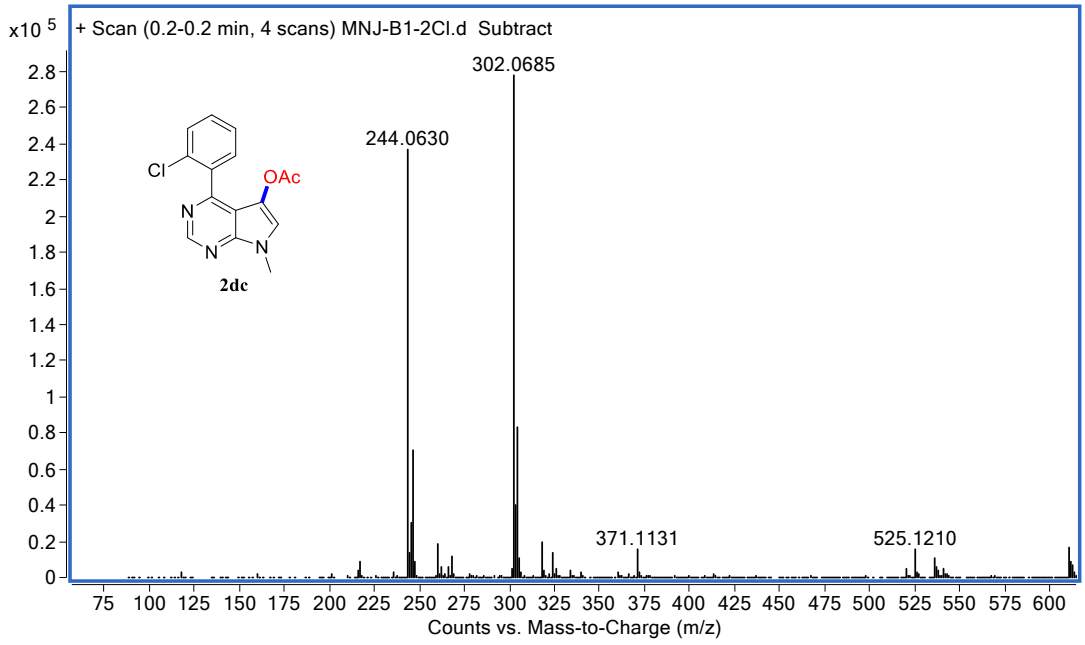

8.9751
7.4708
7.4672
7.4559
7.4542
7.4523
7.4506
7.4393
7.4358
7.4340
7.4305
7.4189
7.4155
7.2765
7.1637
7.1108
7.1088
7.0960
7.0940
7.0809
7.0790
7.0277
7.0255
7.0111
7.0092
3.8945
3.7569
1.8439
OAc
N
O
N
2db
0.93
2.07
0.98
1.03
1.00
3.10
3.16
3.10

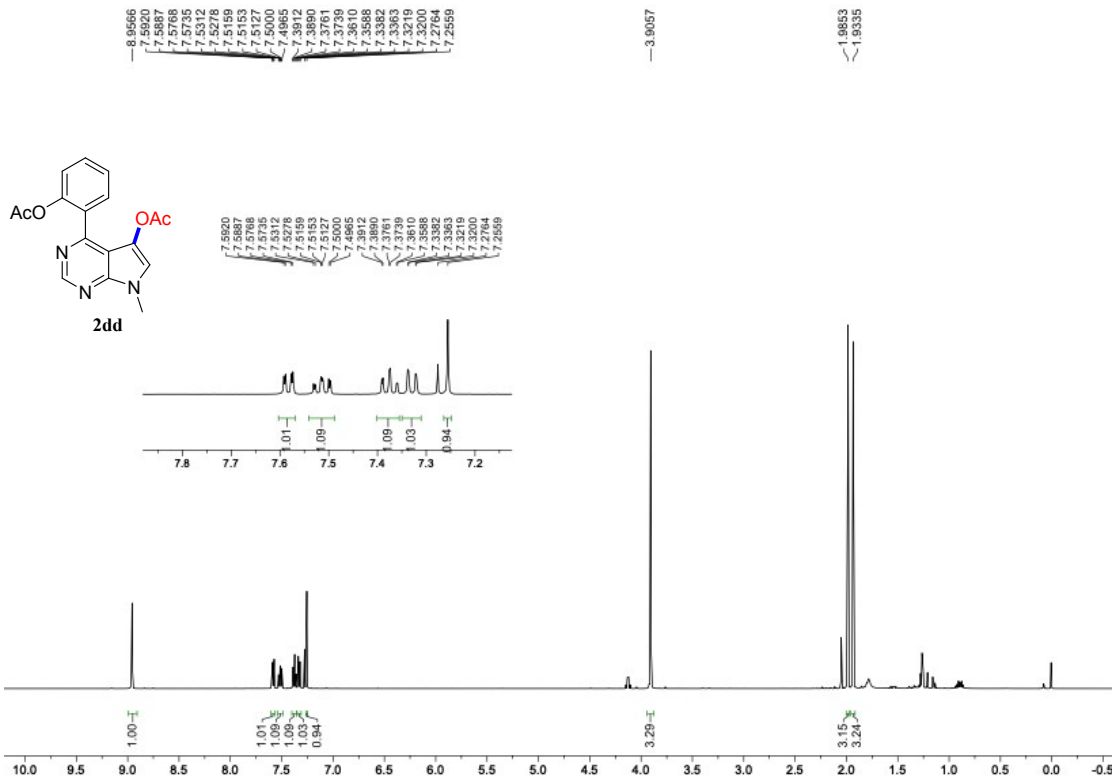

168.76
157.14
156.28
151.91
147.61
130.79
130.63
127.35
127.00
120.56
119.13
110.79
110.65
55.60
31.00
20.09
OAc
N
O
N
2db

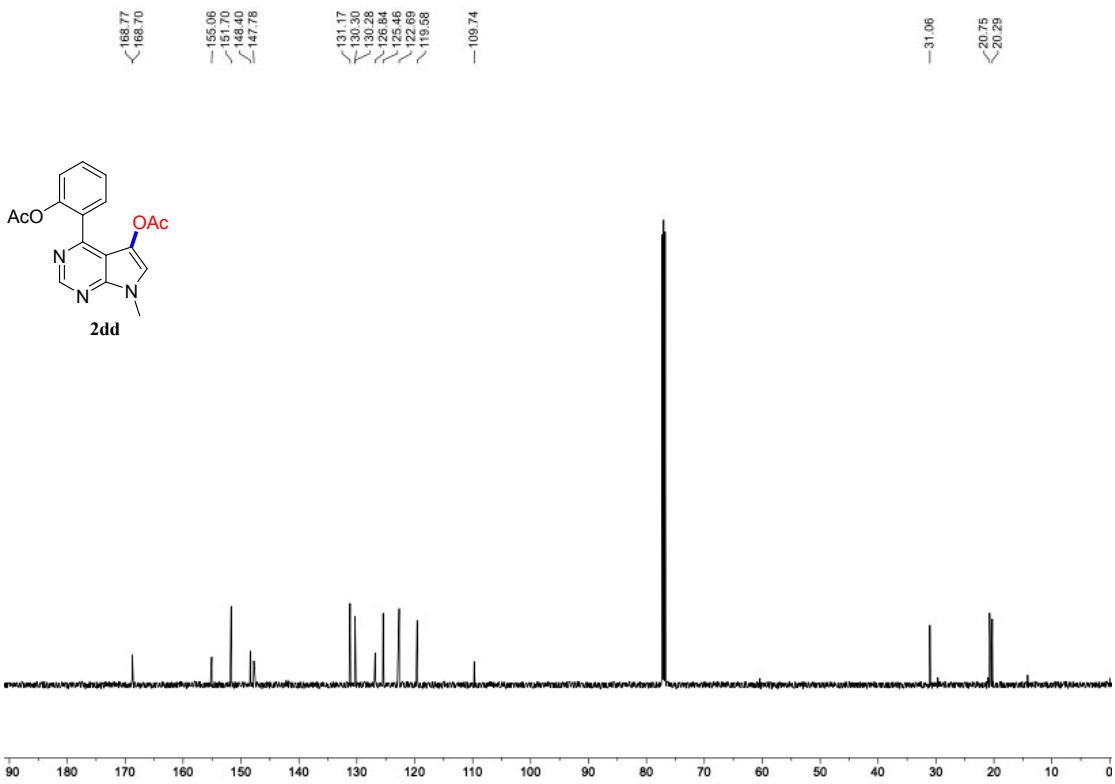

x10 5
+ Scan (0.2-0.2 min, 4 scans) MNJ-B1-2OCH3.d Subtract
298.1189
OAc
2db
Counts vs. Mass-to-Charge (m/z)

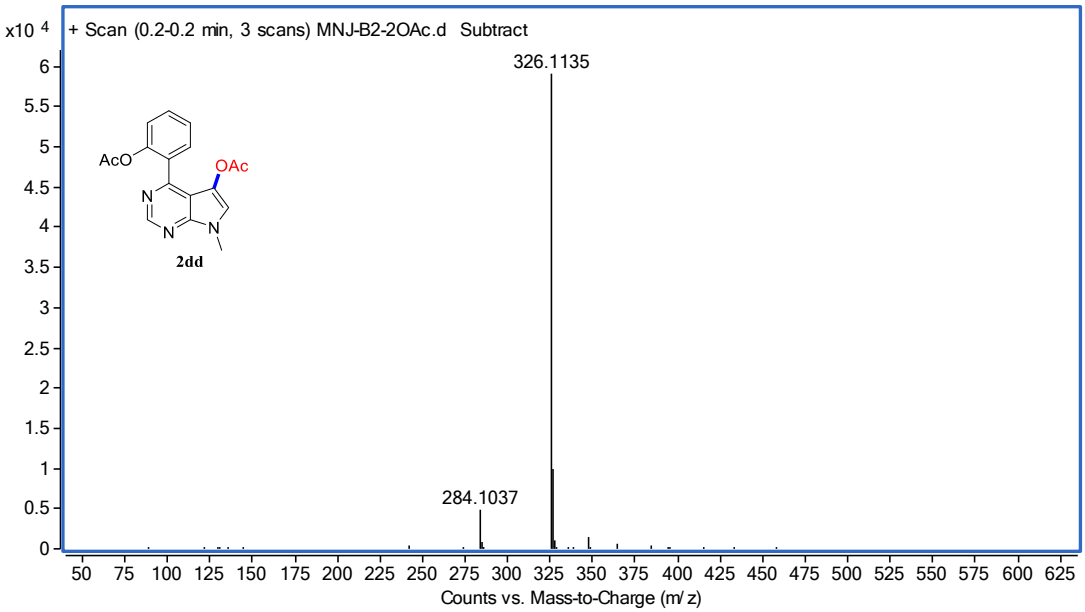

OAc
2dc


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
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

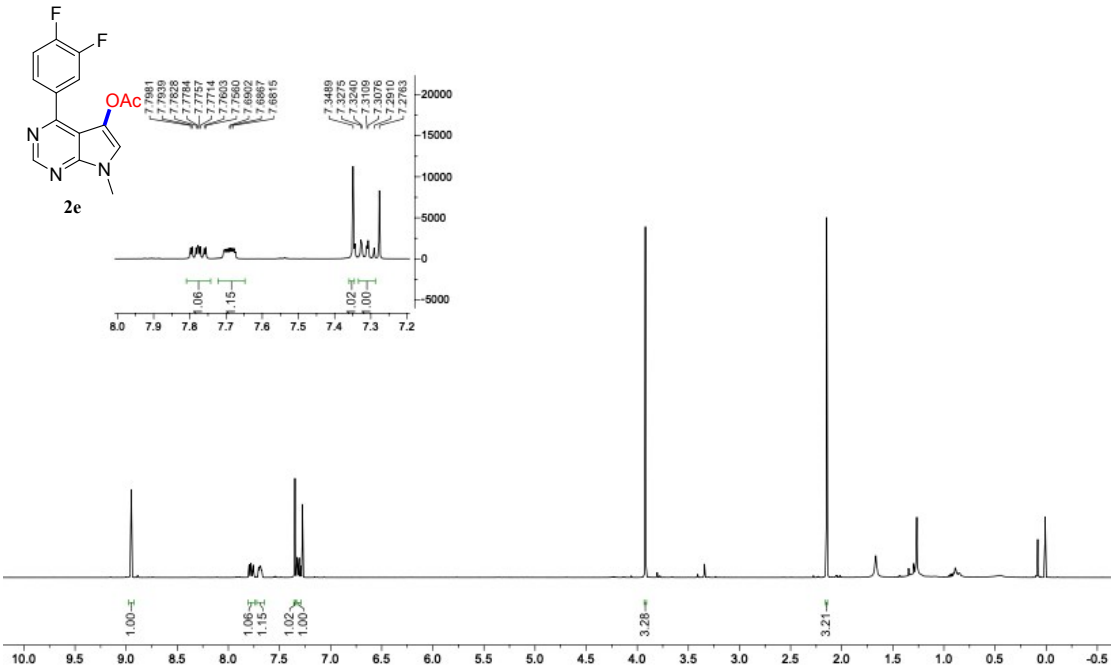

x10 5
+ Scan (0.2-0.2 min, 4 scans) MNJ-B1-2Cl.d Subtract
302.0685
244.0630
371.1131
525.1210
Cl
OAc
N
N
N
2dc
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
75 100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600
Counts vs. Mass-to-Charge (m/z)

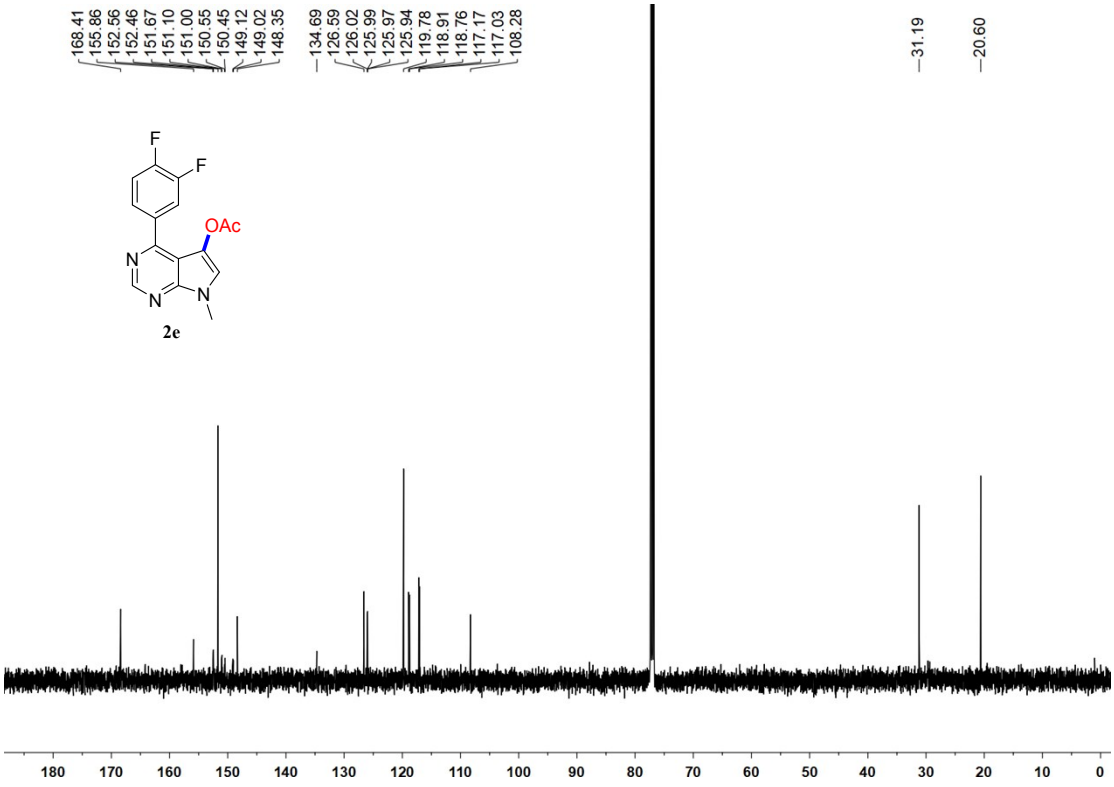

AcO
OAc
N
N
N
2dd

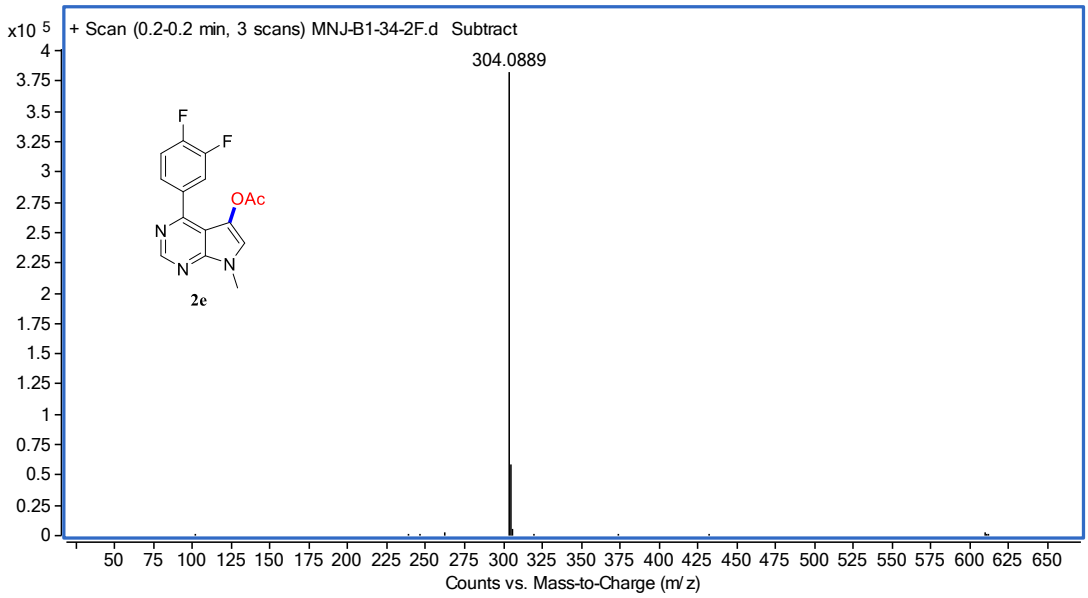

AcO
OAc
N
N
N
2dd

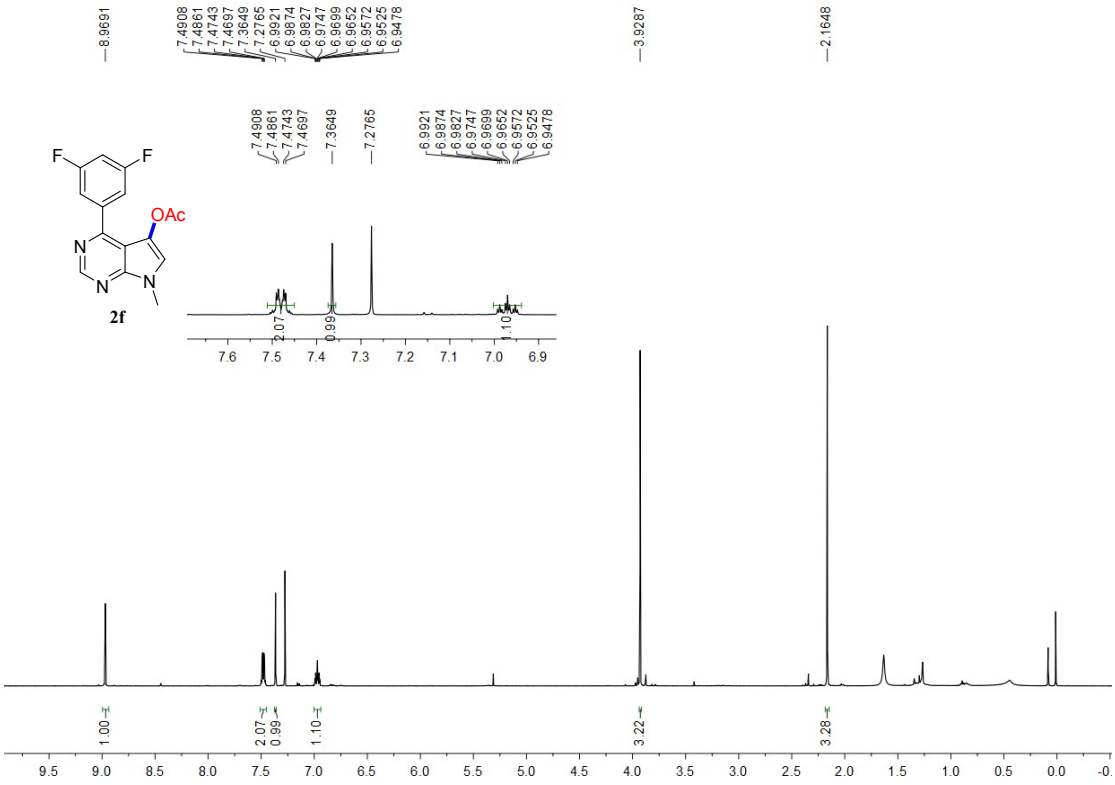

x10 4
+ Scan (0.2-0.2 min, 3 scans) MNJ-B2-2OAc.d Subtract
326.1135
284.1037
AcO
OAc
N
N
N
2dd
Counts vs. Mass-to-Charge (m/z)

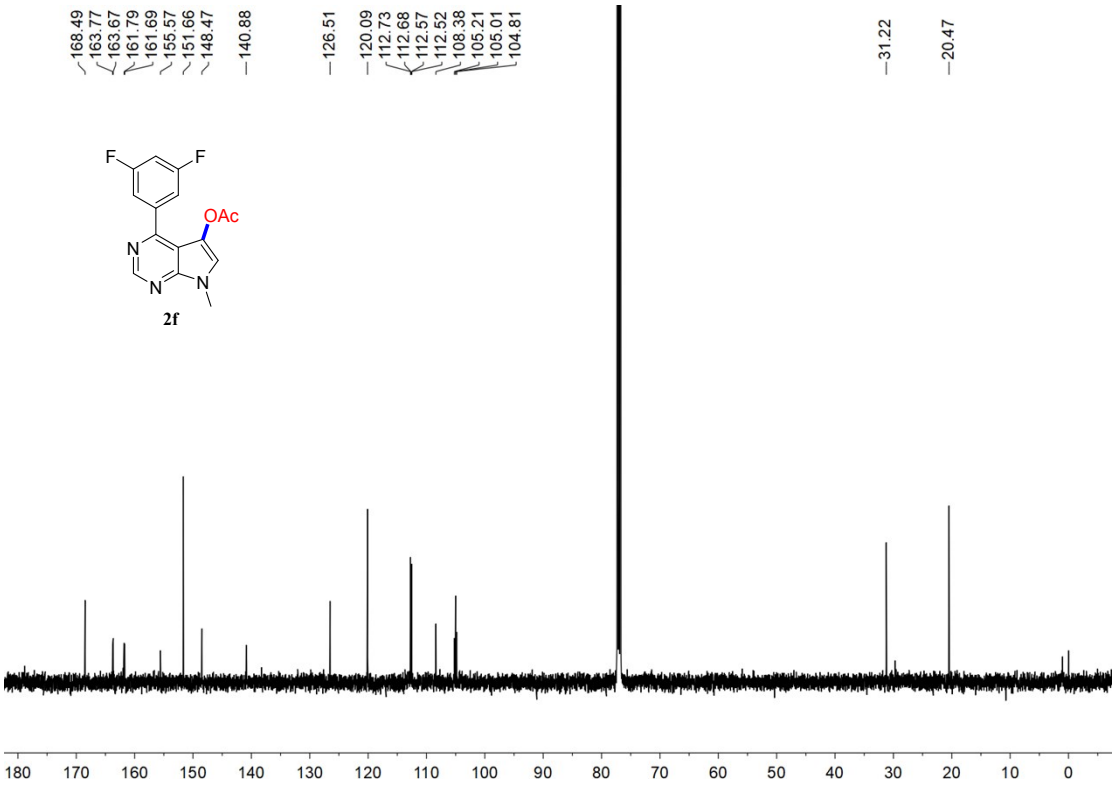

8.9503
7.7981
7.7939
7.7828
7.7784
7.7757
7.7714
7.7603
7.7560
7.6902
7.6867
7.6815
7.3489
7.3275
7.3240
7.3109
7.3076
7.2910
7.2763
3.9208
2.1480

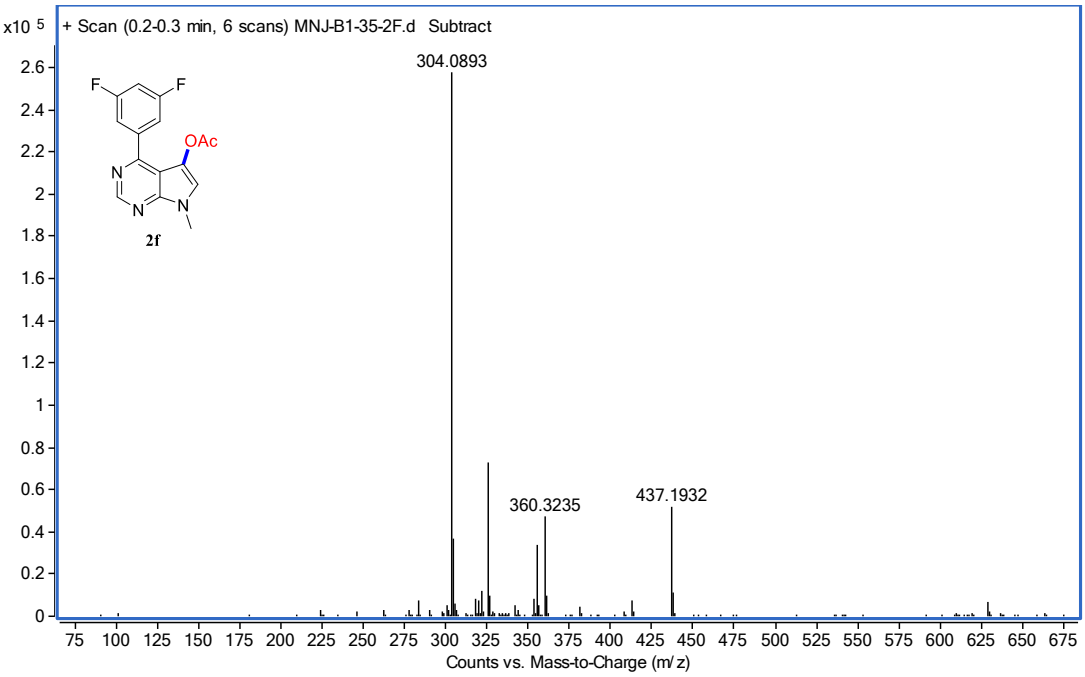

F
F
OAc
N
N
N
2e
1.06
1.15
1.02
1.00
3.28
3.21

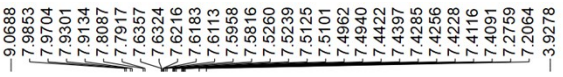

168.41
155.86
152.56
152.46
151.67
151.10
151.00
150.55
150.45
149.12
149.02
148.35
134.69
126.59
126.02
125.99
125.97
125.94
119.78
118.91
118.76
117.17
117.03
108.28
31.19
20.60
F
F
OAc
N
N
N
2e
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

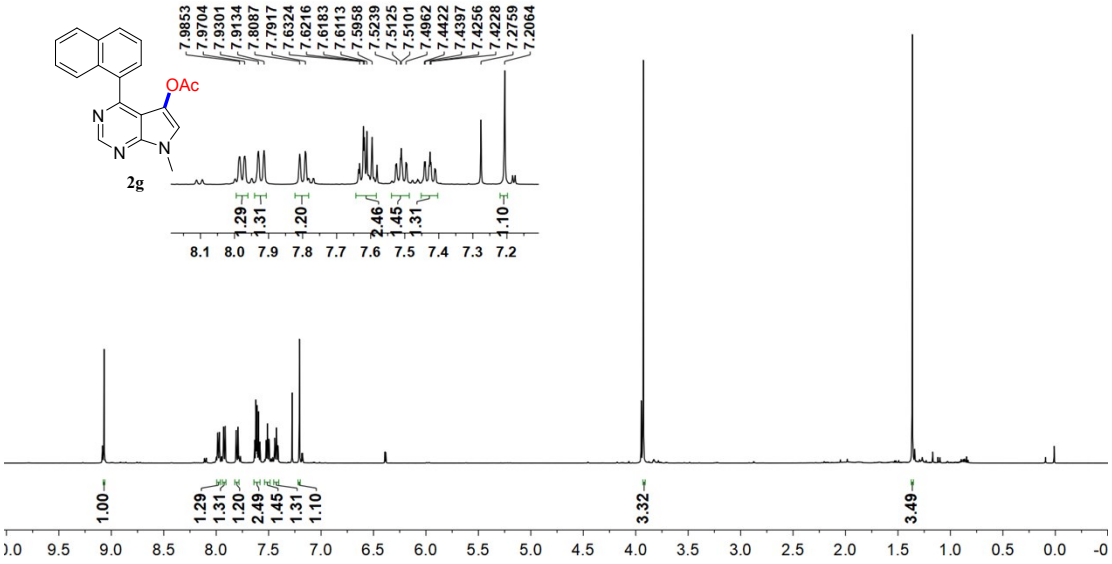

x10 5
+ Scan (0.2-0.2 min, 3 scans) MNJ-B1-34-2F.d Subtract
304.0889
4
3.75
3.5
3.25
3
2.75
2.5
2.25
2
1.75
1.5
1.25
1
0.75
0.5
0.25
0
F
F
OAc
N
N
N
2e
50 75 100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 625 650
Counts vs. Mass-to-Charge (m/z)

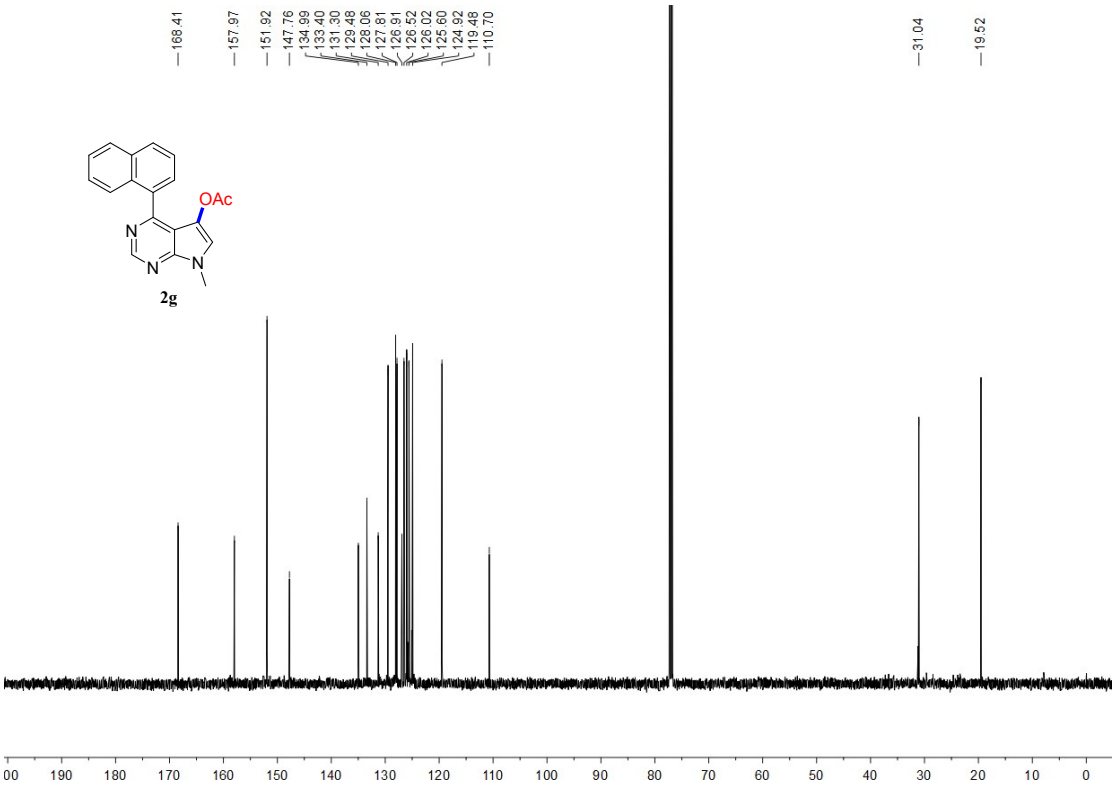

8.9691
7.4908
7.4861
7.4743
7.4697
7.3649
7.2765
6.9921
6.9874
6.9827
6.9747
6.9699
6.9652
6.9572
6.9525
6.9478
3.9287
2.1648
F
F
OAc
N
N
N
2f
2.07
0.99
1.10
1.00
3.22
3.28

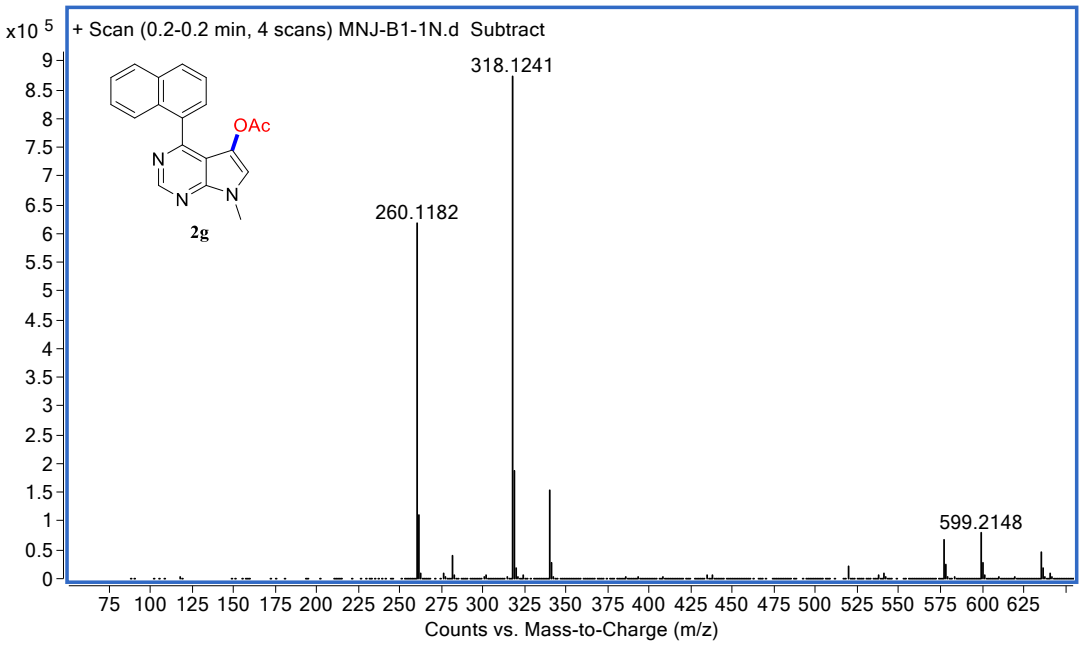

168.49
163.77
163.67
161.79
161.69
155.57
151.66
148.47
140.88
126.51
120.09
112.73
112.68
112.57
112.52
108.38
105.21
105.01
104.81
31.22
20.47
F
F
OAc
N
N
N
2f

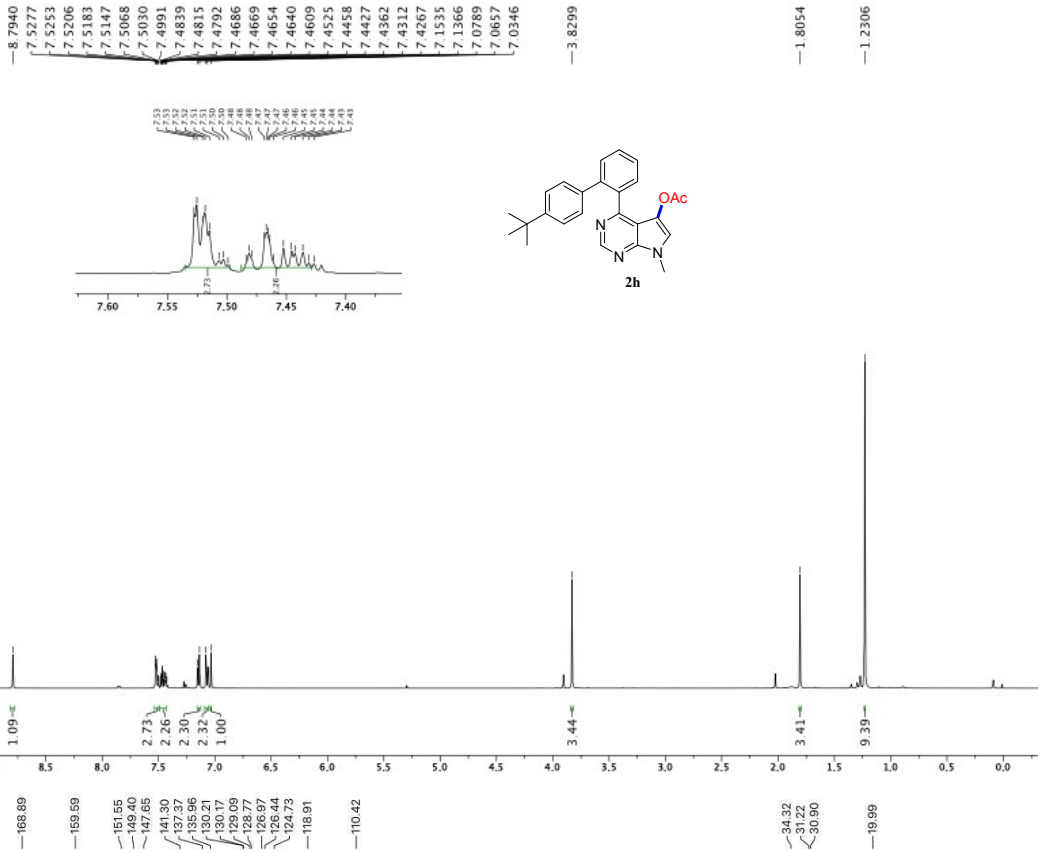

x10 5
+ Scan (0.2-0.3 min, 6 scans) MNJ-B1-35-2F.d Subtract
304.0893
360.3235
437.1932
F
F
OAc
N
N
N
2f
Counts vs. Mass-to-Charge (m/z)

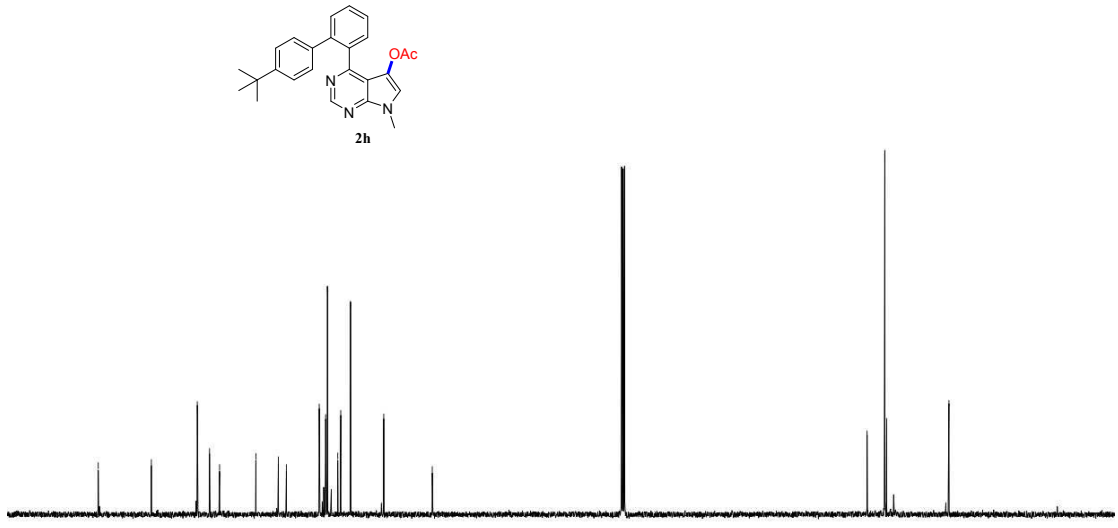

9.0688
7.9853
7.9704
7.9301
7.9134
7.8087
7.7917
7.6357
7.6324
7.6216
7.6183
7.6113
7.5958
7.5816
7.5260
7.5239
7.5125
7.5101
7.4962
7.4940
7.4422
7.4397
7.4285
7.4256
7.4228
7.4116
7.4091
7.2759
7.2064
3.9278
1.3633

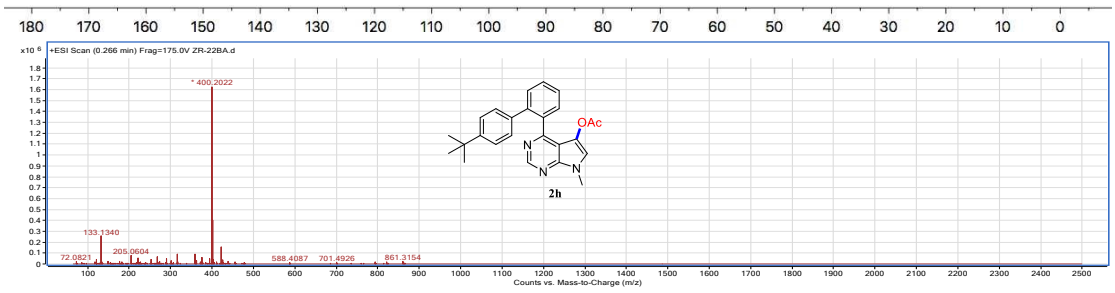

OAc
N
N
N
2g
7.9853
7.9704
7.9301
7.9134
7.8087
7.7917
7.6324
7.6216
7.6183
7.6113
7.5958
7.5239
7.5125
7.5101
7.4962
7.4422
7.4397
7.4256
7.4228
7.2759
7.2064
1.29
1.31
1.20
2.46
1.45
1.31
1.10
1.00
1.29
1.31
1.20
2.49
1.45
1.31
1.10
3.32
3.49

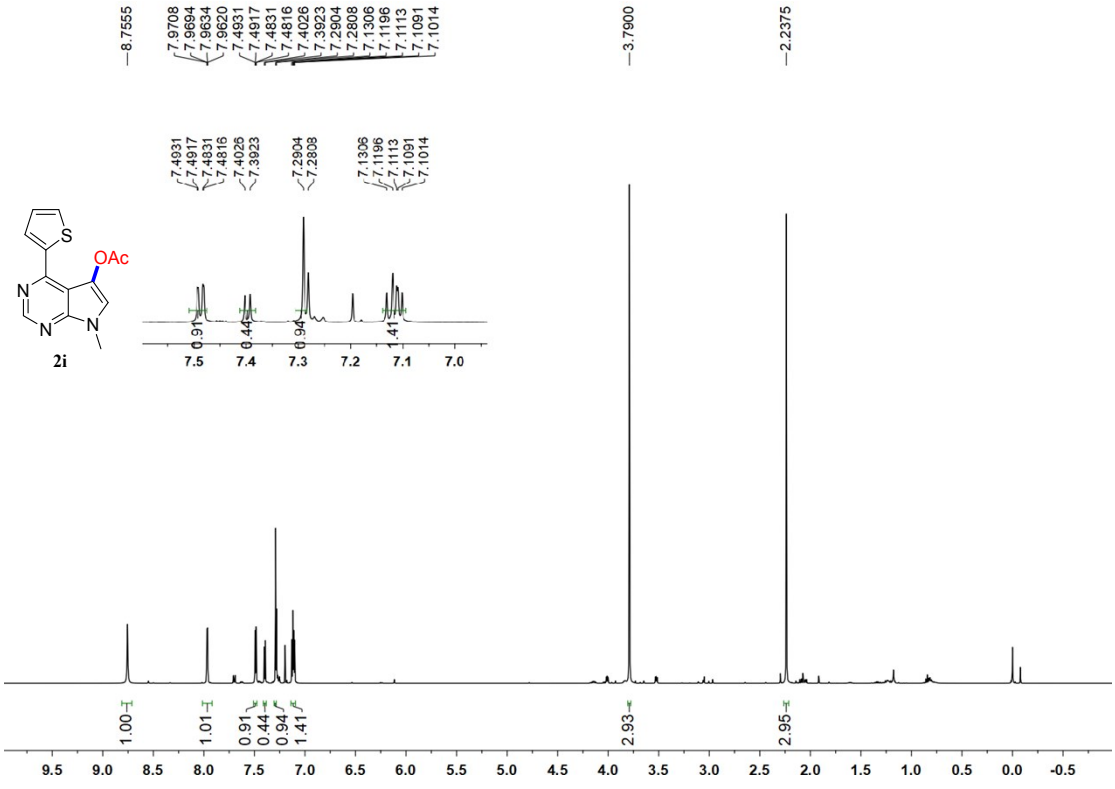

168.41
157.97
151.92
147.76
134.99
133.40
131.30
129.48
128.06
127.81
126.91
126.52
126.02
125.60
124.92
119.48
110.70
31.04
19.52
OAc
N
N
N
2g
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

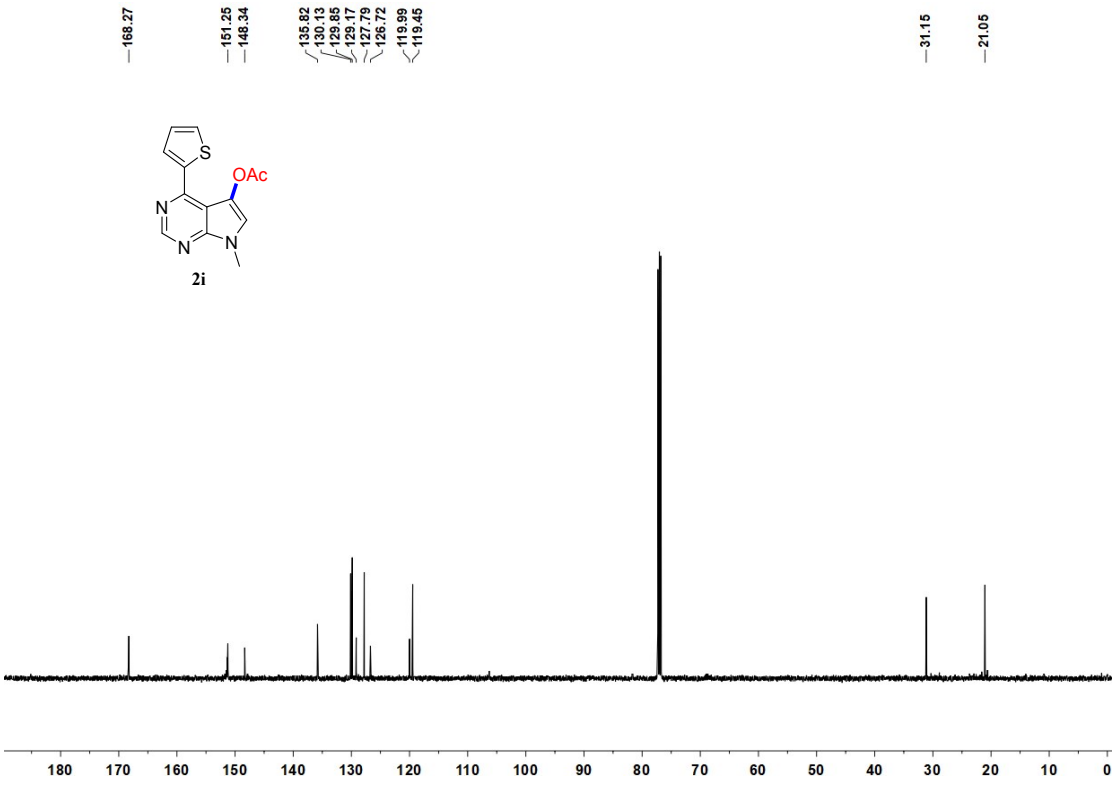

x10 5
+ Scan (0.2-0.2 min, 4 scans) MNJ-B1-1N.d Subtract
318.1241
260.1182
599.2148
OAc
N
N
N
2g
9
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
75 100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 625
Counts vs. Mass-to-Charge (m/z)

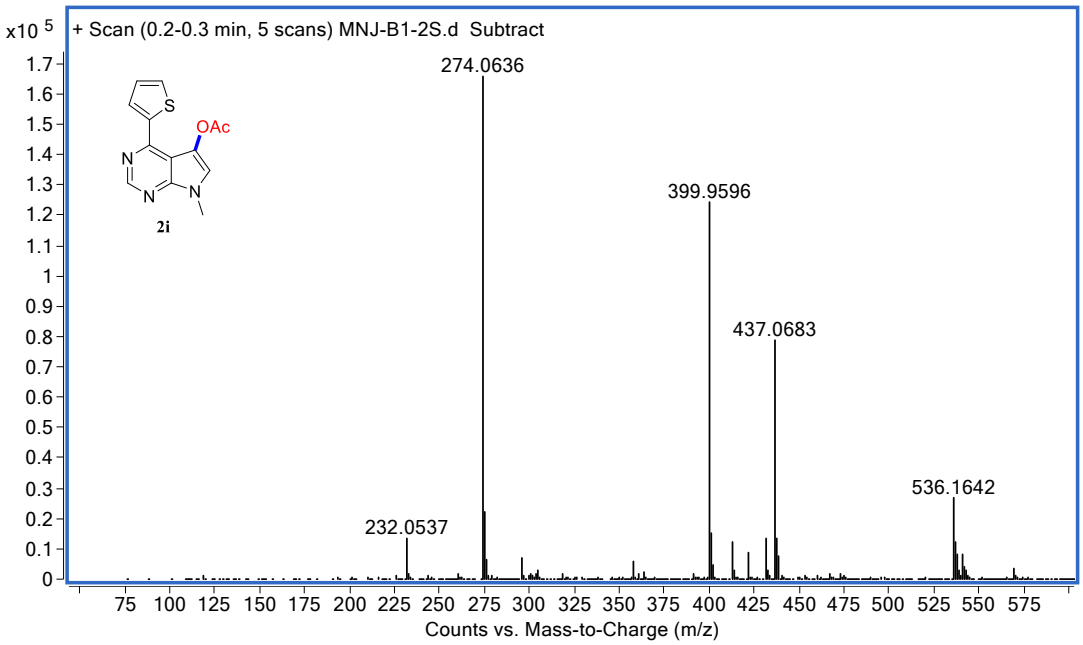

8.7940
7.5277
7.5253
7.5206
7.5183
7.5147
7.5068
7.5030
7.4991
7.4839
7.4815
7.4792
7.4686
7.4669
7.4654
7.4640
7.4609
7.4525
7.4458
7.4427
7.4362
7.4312
7.4267
7.1535
7.1366
7.0789
7.0657
7.0346
3.8299
1.8054
1.2306
OAc
2h
1.09
2.73
2.26
2.30
2.32
1.00
3.44
3.41
9.39
168.89
159.59
151.55
149.40
147.65
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

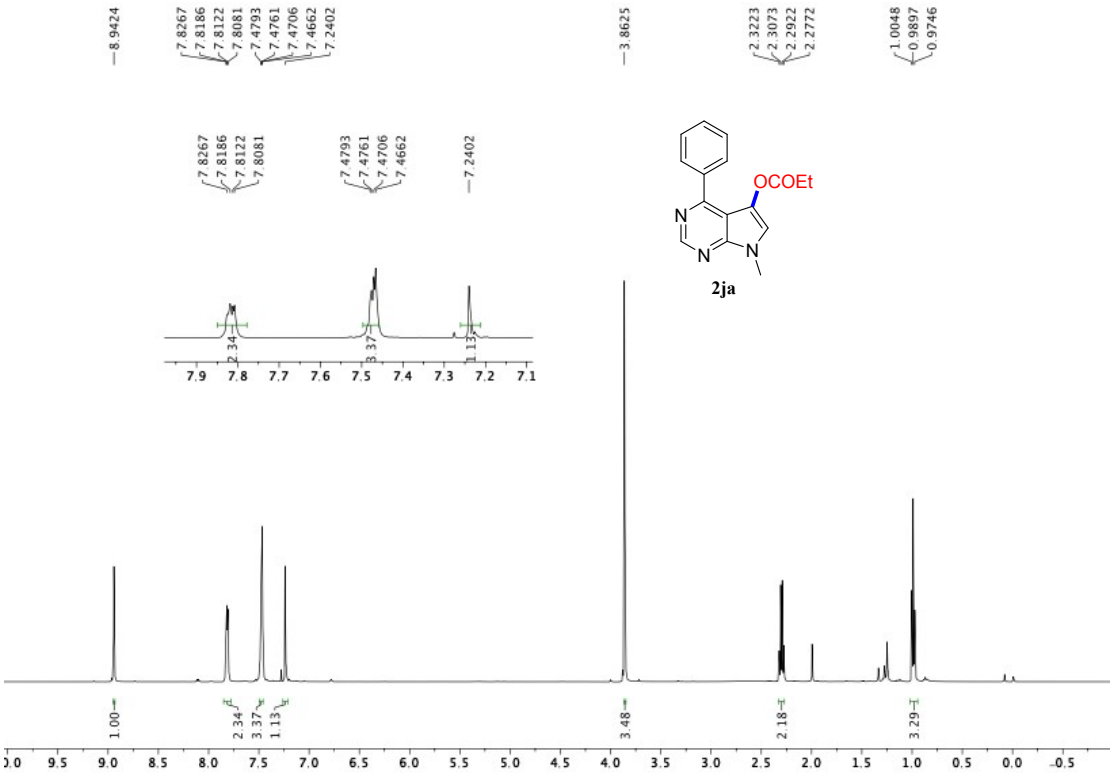

OAc
2h

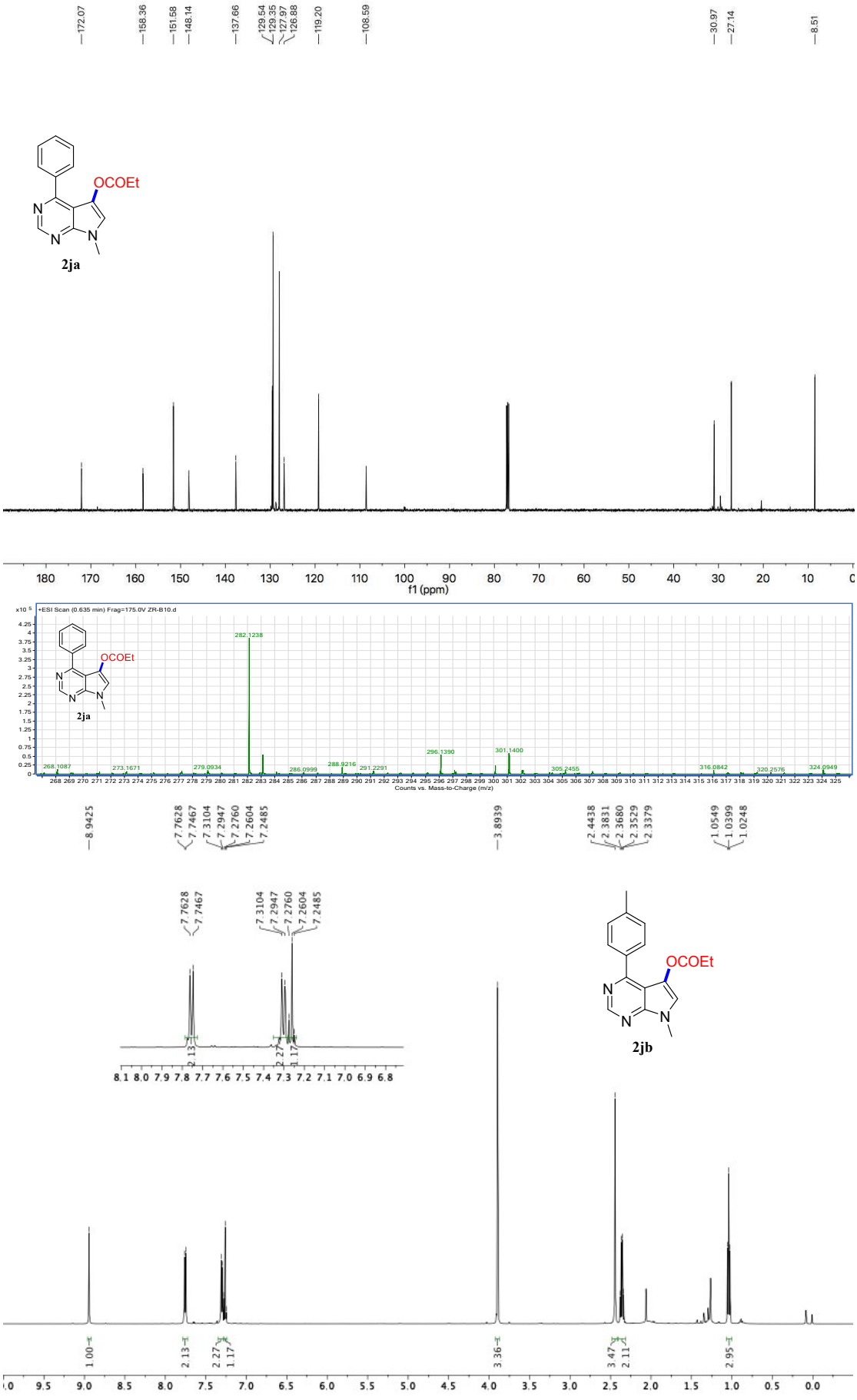

+ESI Scan (0.266 min) Frag=175.0V ZR-22BA.d
400.2022
133.1340
205.0604
72.0821
588.4087
701.4926
861.3154
OAc
2h
Counts vs. Mass-to-Charge (m/z)

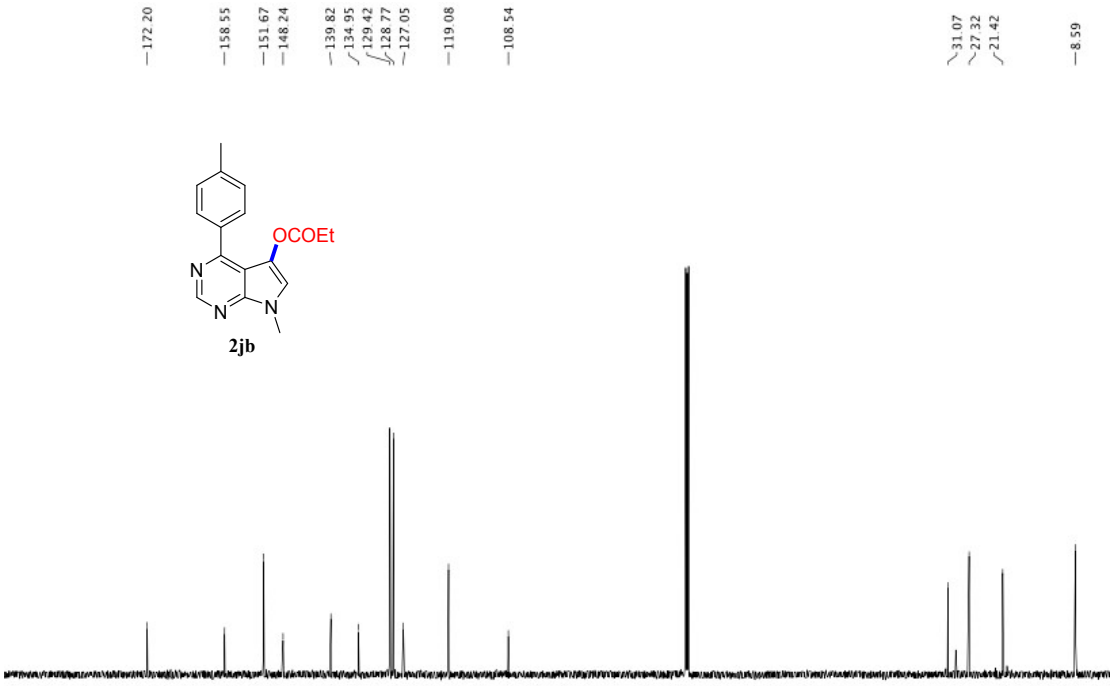

8.7555
7.9708
7.9694
7.9634
7.9620
7.4931
7.4917
7.4831
7.4816
7.4026
7.3923
7.2904
7.2808
7.1306
7.1196
7.1113
7.1091
7.1014
3.7900
2.2375
OAc
S
N
N
N
2i
0.91
0.44
0.94
1.41
7.5
7.4
7.3
7.2
7.1
7.0
1.00
1.01
0.91
0.44
0.94
1.41
2.93
2.95
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

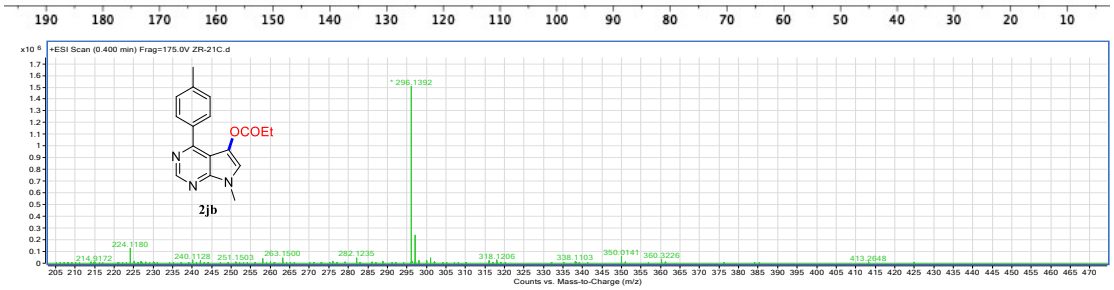

168.27
151.25
148.34
135.82
130.13
129.85
129.17
127.79
126.72
119.99
119.45
31.15
21.05
OAc
S
N
N
N
2i
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

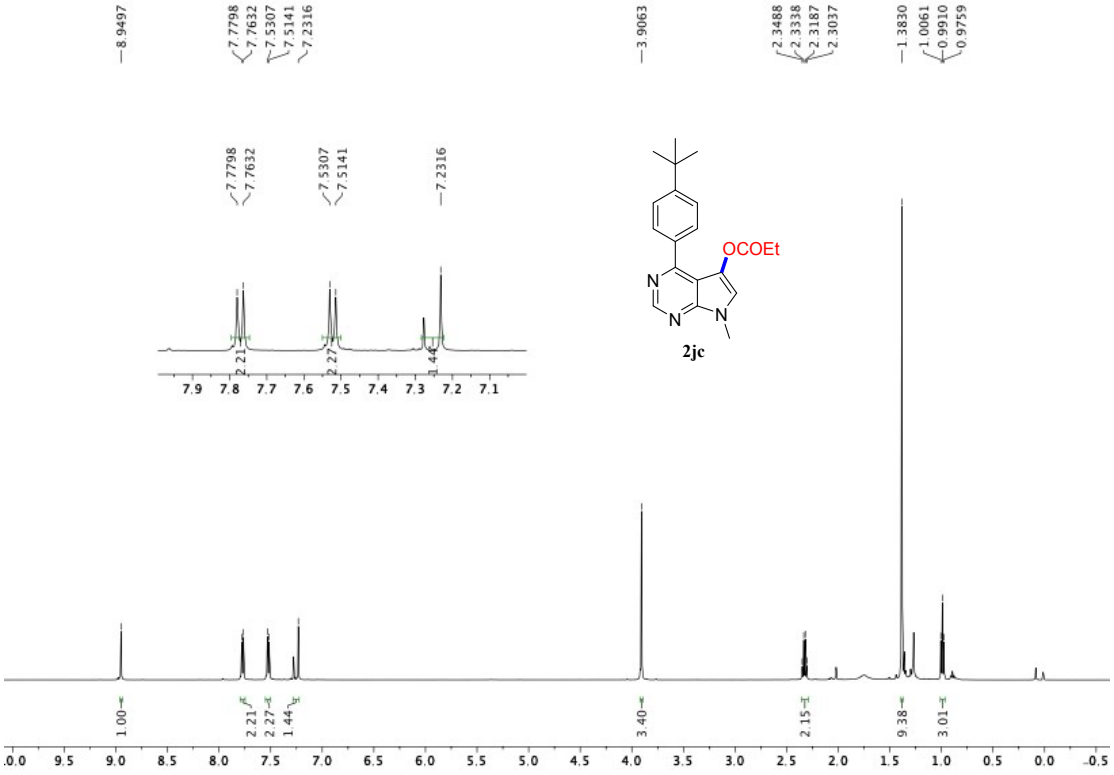

x10 5
+ Scan (0.2-0.3 min, 5 scans) MNJ-B1-2S.d Subtract
274.0636
399.9596
437.0683
536.1642
232.0537
OAc
2i
Counts vs. Mass-to-Charge (m/z)

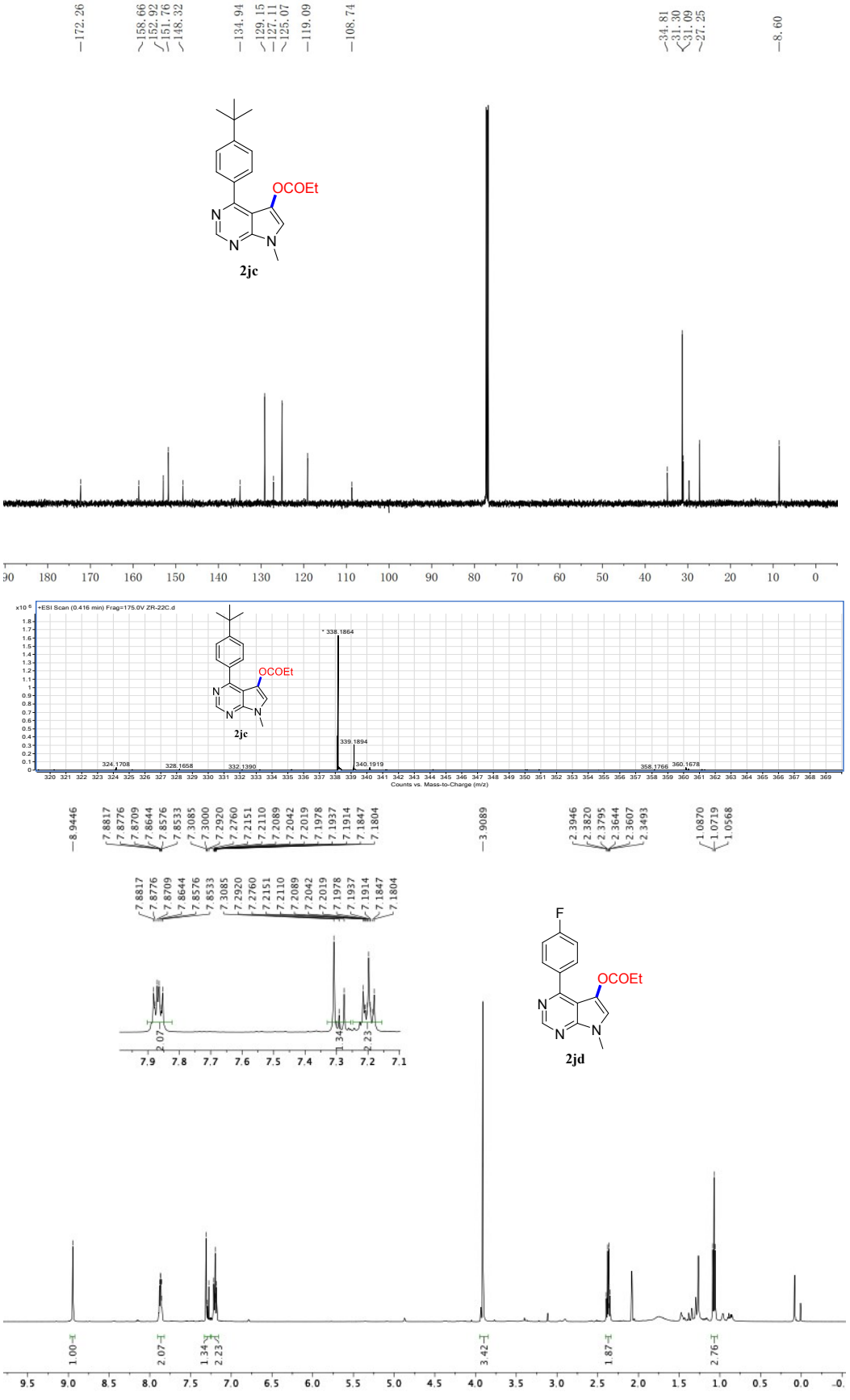

OCOEt
2ja


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
2ja
f1 (ppm)
+ESI Scan (0.635 min) Frag=175.0V ZR-B10.d
282.1238
296.1390
301.1400
Counts vs. Mass-to-Charge (m/z)
8.9425
7.7628
7.7467
7.3104
7.2947
7.2760
7.2604
7.2485
3.8939
2.4438
2.3831
2.3680
2.3529
2.3379
1.0549
1.0399
1.0248
OCOEt
2jb


172.20
158.55
151.67
148.24
139.82
134.95
129.42
128.77
127.05
119.08
108.54
31.07
27.32
21.42
8.59
OCOEt
N
N
N
2jb

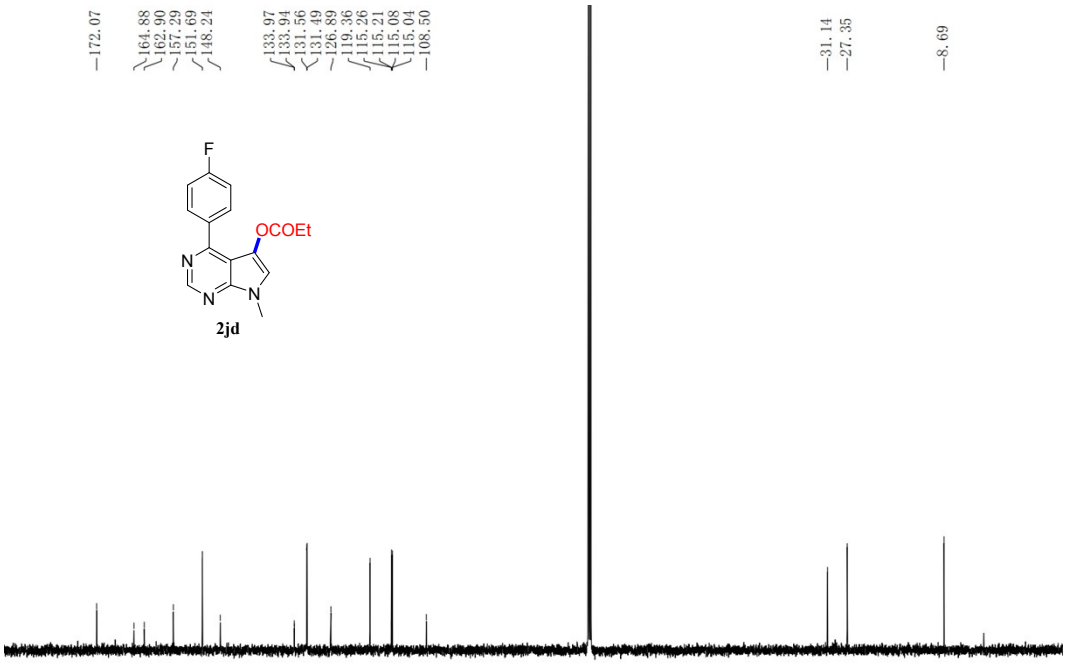

+ESI Scan (0.400 min) Frag=175.0V ZR-21C.d
OCOEt
2jb
* 296.1392
224.1180
214.9172
240.1128
251.1503
263.1500
282.1235
318.1206
338.1103
350.0141
360.3226
413.2648
Counts vs. Mass-to-Charge (m/z)

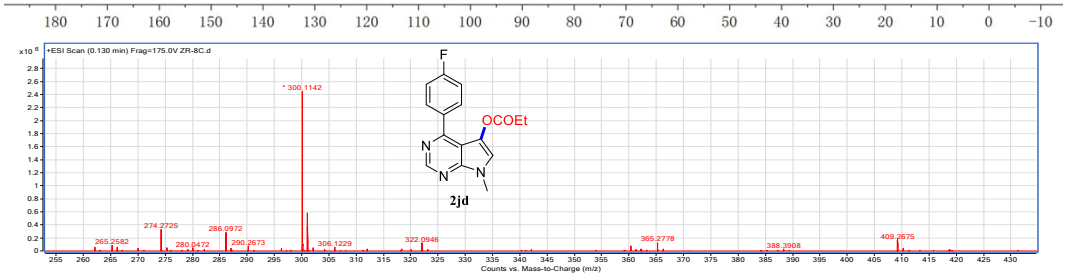

8.9497
7.7798
7.7632
7.5307
7.5141
7.2316
3.9063
2.3488
2.3338
2.3187
2.3037
1.3830
1.0061
0.9910
0.9759
OCOEt
N
N
N
2jc
1.00
2.21
2.27
1.44
3.40
2.15
9.38
3.01


172.26
158.66
152.92
151.76
148.32
134.94
129.15
127.11
125.07
119.09
108.74
34.81
31.30
31.09
27.25
8.60
OCOEt
2jc

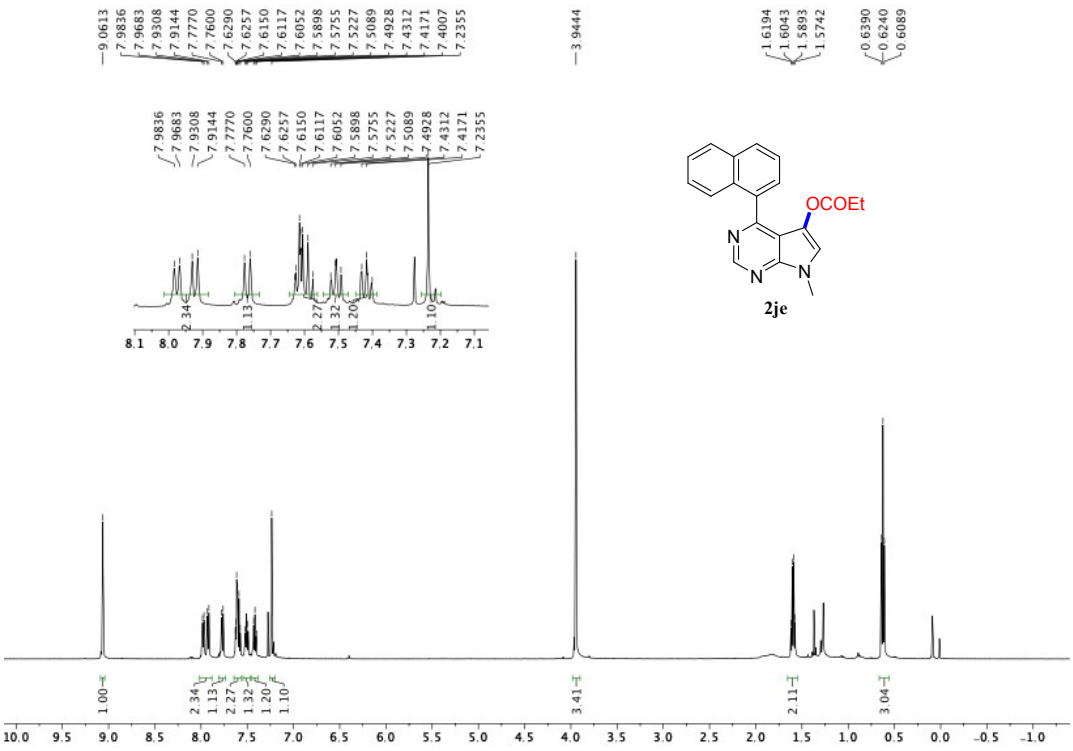
+ESI Scan (0.416 min) Frag=175.0V ZR-22C.d
* 338.1864
339.1894
340.1919
324.1708
328.1658
332.1390
358.1766
360.1678
OCOEt
2jc
Counts vs. Mass-to-Charge (m/z)

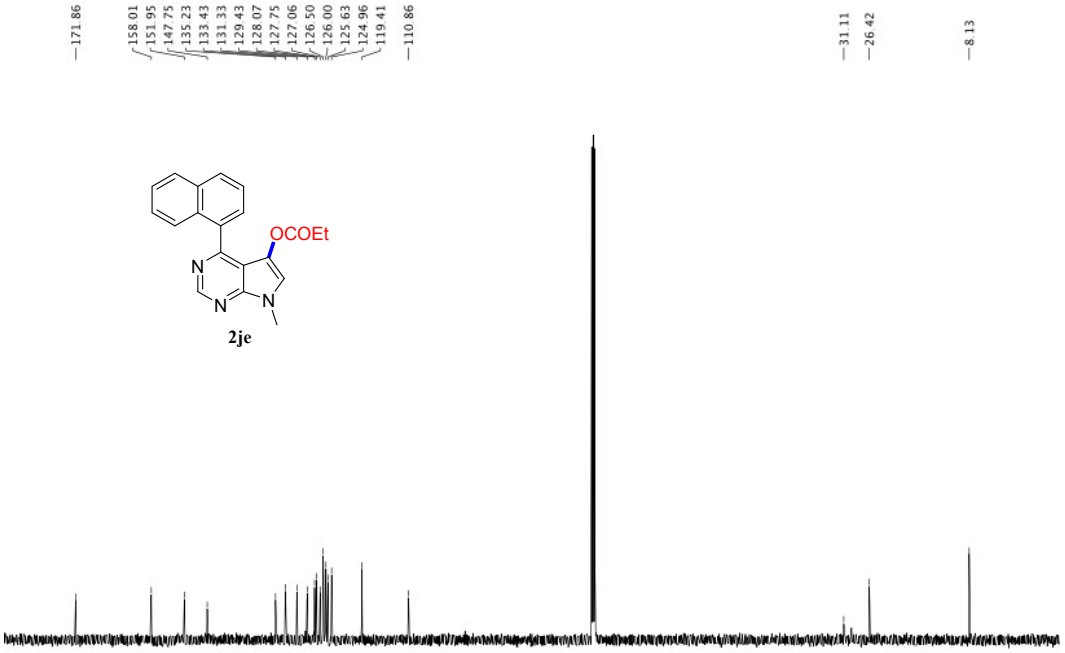
8.9446
7.8817
7.8776
7.8709
7.8644
7.8576
7.8533
7.3085
7.3000
7.2920
7.2760
7.2151
7.2110
7.2089
7.2042
7.2019
7.1978
7.1937
7.1914
7.1847
7.1804
3.9089
2.3946
2.3820
2.3795
2.3644
2.3607
2.3493
1.0870
1.0719
1.0568
F
OCOEt
2jd
1.00
2.07
1.34
2.23
3.42
1.87
2.76

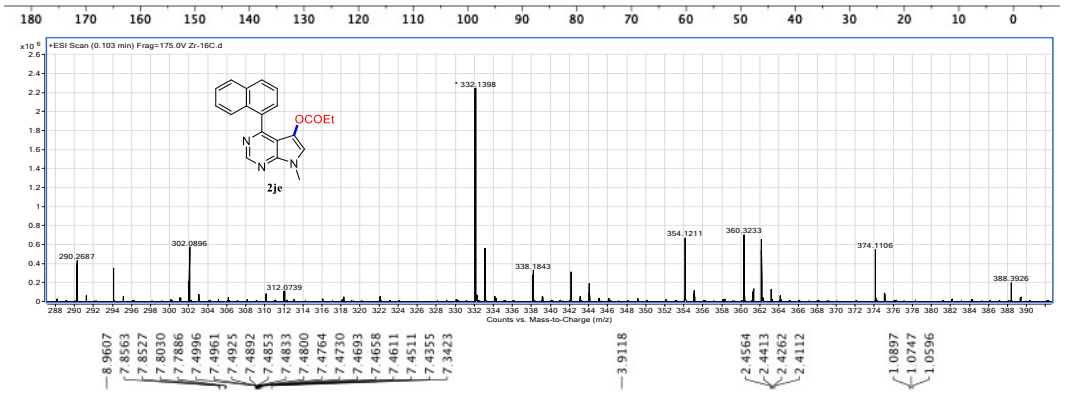

172.07
164.88
162.90
157.29
151.69
148.24
133.97
133.94
131.56
131.49
126.89
119.36
115.26
115.21
115.08
115.04
108.50
31.14
27.35
8.69
F
OCOEt
N
N
N
2jd

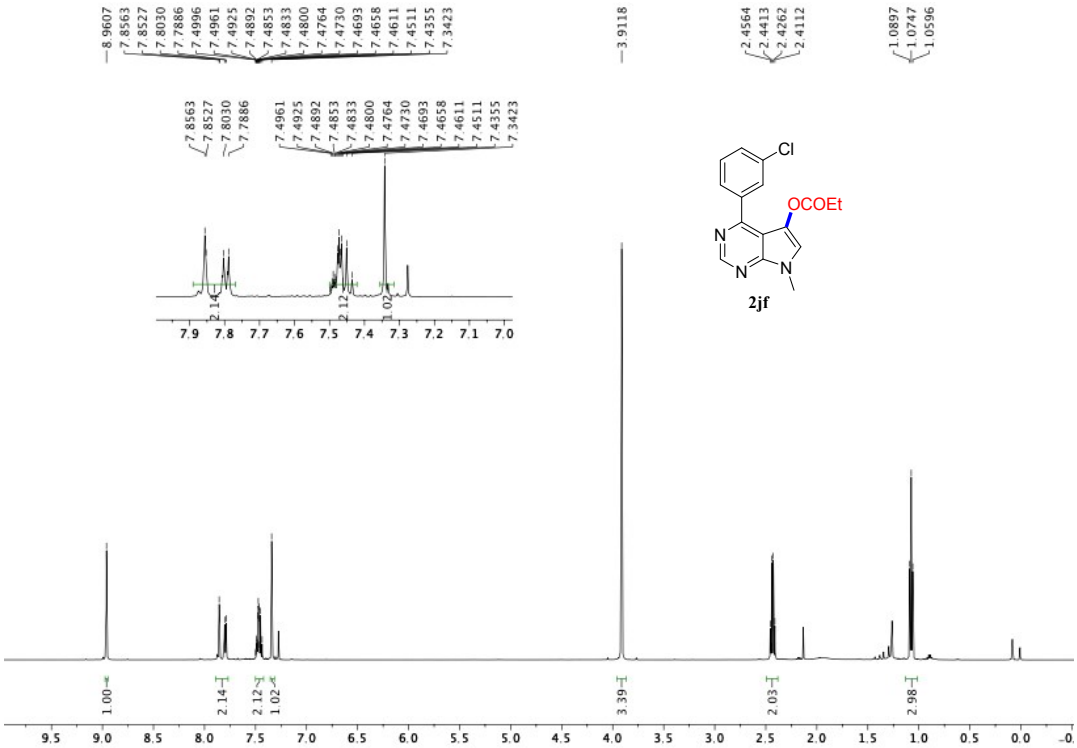

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

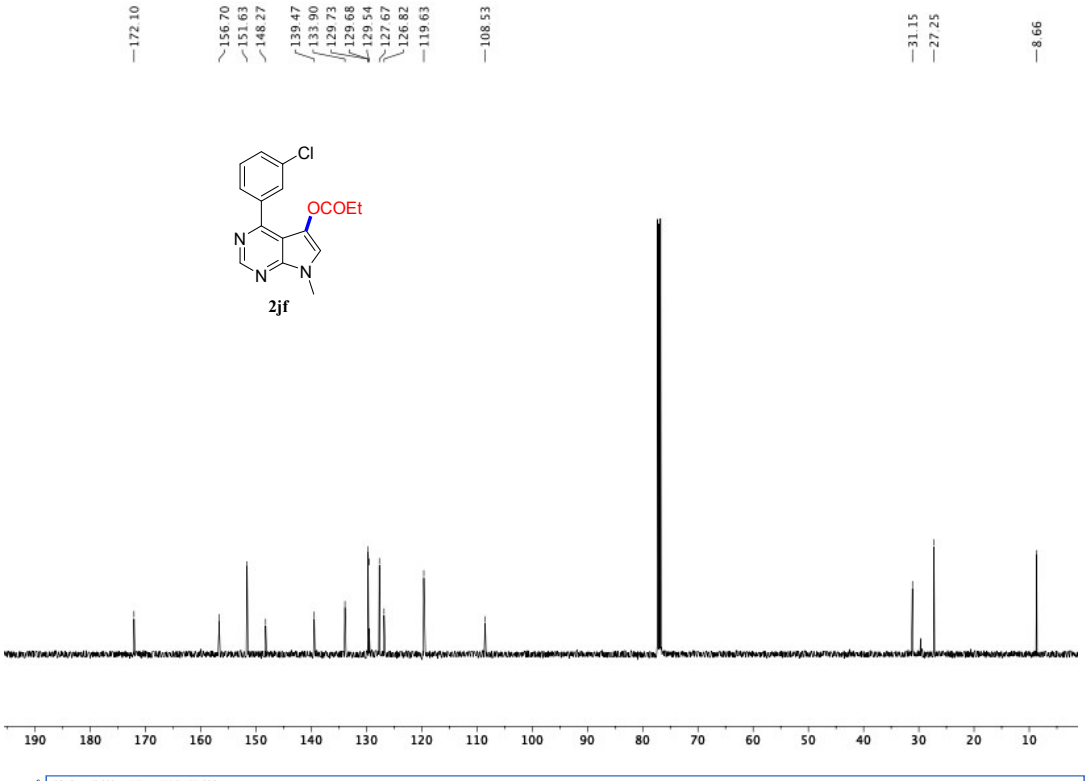
+ESI Scan (0.130 min) Frag=175.0V ZR-8C.d
300.1142
274.2725
265.2582
280.0472
286.0972
290.2673
306.1229
322.0946
365.2778
388.3908
409.2675
F
OCOEt
N
N
N
2jd
Counts vs. Mass-to-Charge (m/z)

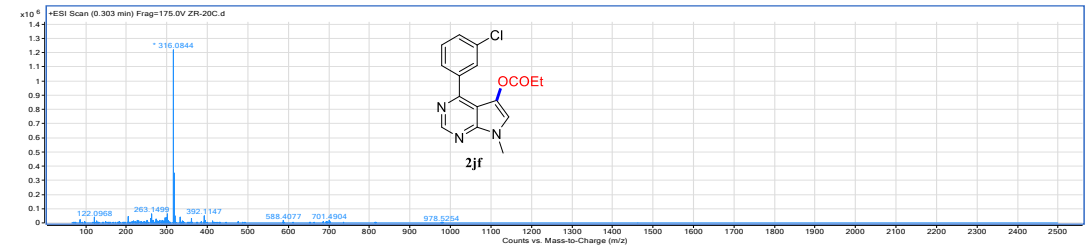

9.0613
7.9836
7.9683
7.9308
7.9144
7.7770
7.7600
7.6290
7.6257
7.6150
7.6117
7.6052
7.5898
7.5755
7.5227
7.5089
7.4928
7.4312
7.4171
7.4007
7.2355
3.9444
1.6194
1.6043
1.5893
1.5742
0.6390
0.6240
0.6089
OCOEt
N
N
N
2je
1.00
2.34
1.13
2.27
1.32
1.20
1.10
3.41
2.11
3.04

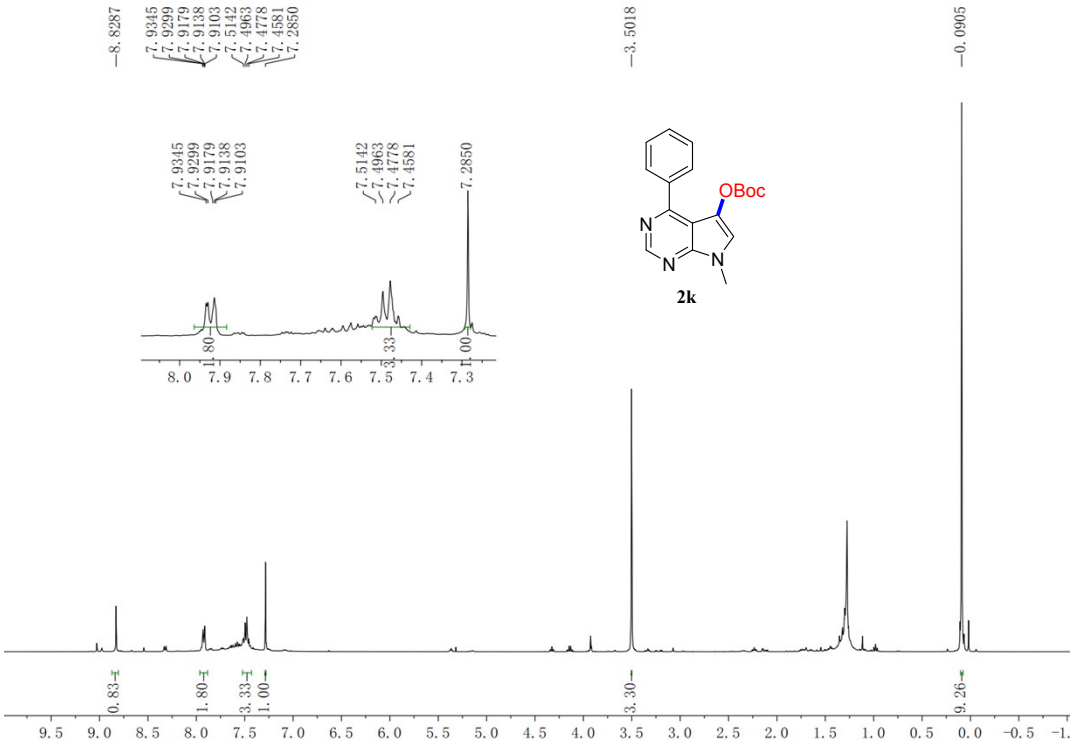

171.86
158.01
151.95
147.75
135.23
133.43
131.33
129.43
128.07
127.75
127.06
126.50
126.00
125.63
124.96
119.41
110.86
31.11
26.42
8.13
OCOEt
N
N
N
2je

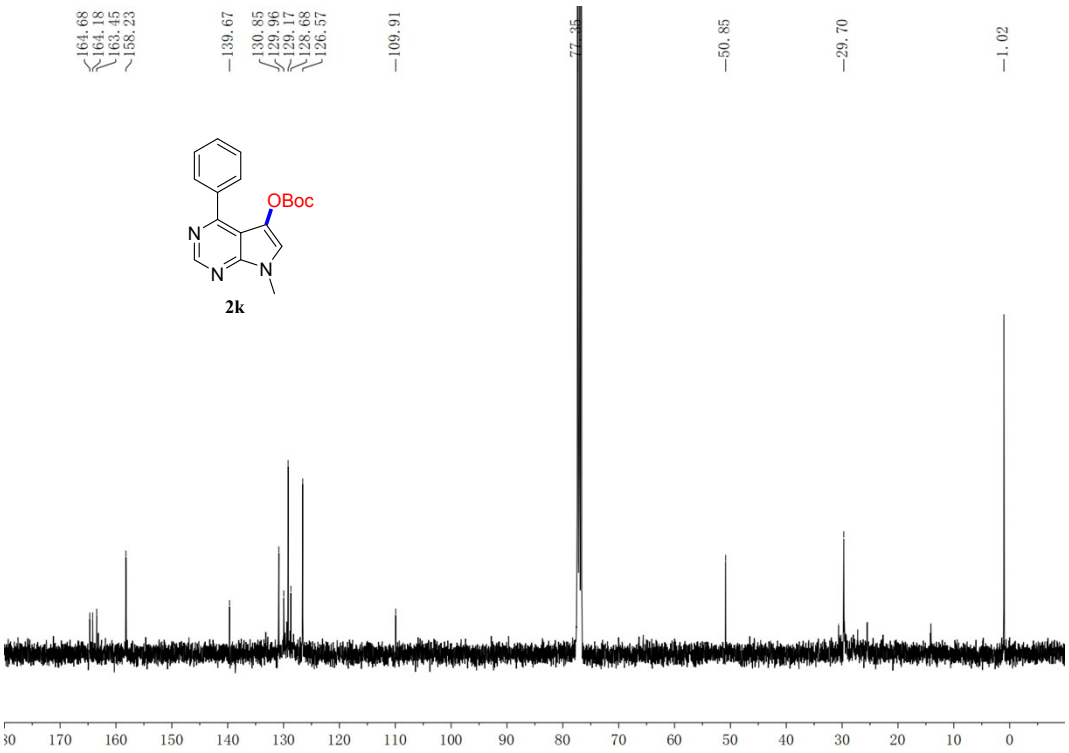

+ESI Scan (0.103 min) Frag=175.0V Zr-16C.d
OCOEt
2je
332.1398
354.1211
360.3233
374.1106
290.2687
302.0896
312.0739
338.1843
388.3926
Counts vs. Mass-to-Charge (m/z)

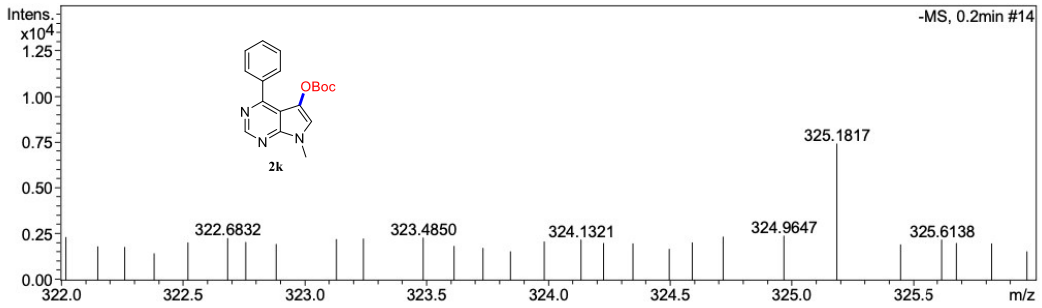

8.9607
7.8563
7.8527
7.8030
7.7886
7.4996
7.4961
7.4925
7.4892
7.4853
7.4833
7.4800
7.4764
7.4730
7.4693
7.4658
7.4611
7.4511
7.4355
7.3423
3.9118
2.4564
2.4413
2.4262
2.4112
1.0897
1.0747
1.0596
Cl
OCOEt
N
N
N
2jf
1.00
2.14
2.12
1.02
3.39
2.03
2.98

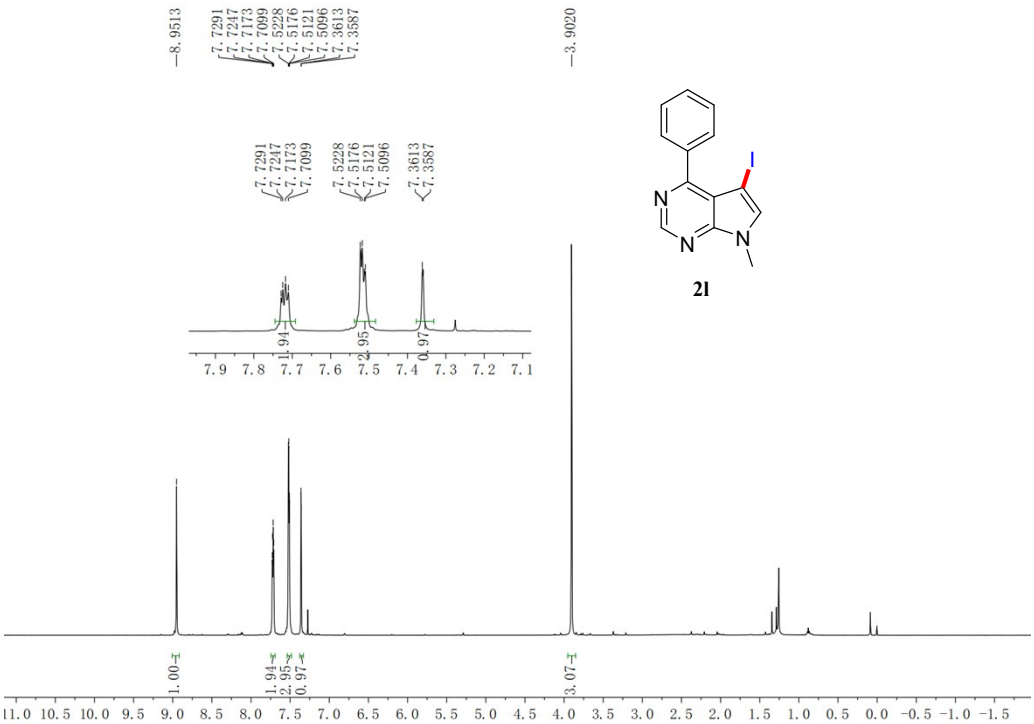

172.10
156.70
151.63
148.27
139.47
133.90
129.73
129.68
129.54
127.67
126.82
119.63
108.53
31.15
27.25
8.66
Cl
OCOEt
N
N
N
2jf

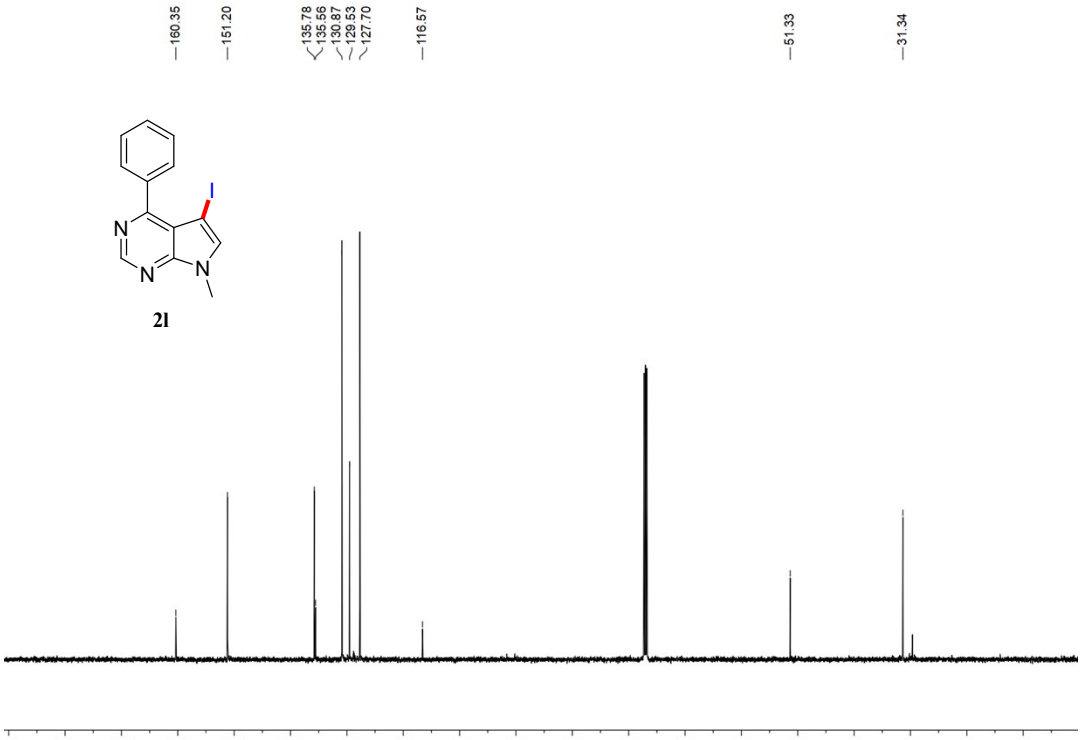

+ESI Scan (0.303 min) Frag=175.0V ZR-20C.d
316.0844
122.0968
263.1409
392.1147
588.4077
701.4904
978.5254
Counts vs. Mass-to-Charge (m/z)
Cl
OCOEt
N
N
N
2jf

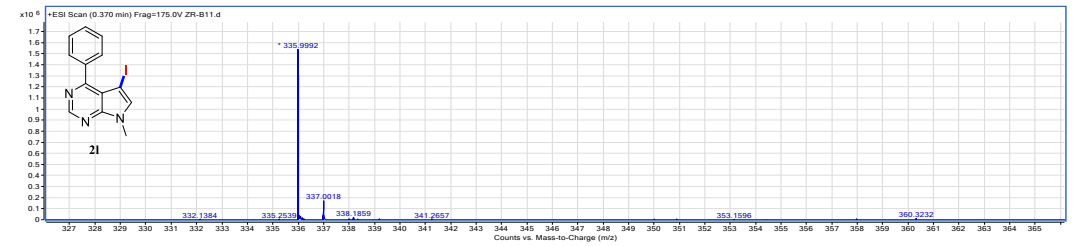

8.8287
7.9345
7.9299
7.9179
7.9138
7.9103
7.5142
7.4963
7.4778
7.4581
7.2850
3.5018
0.0905
OBoc
N
N
N
2k
0.83
1.80
3.33
1.00
3.30
9.26

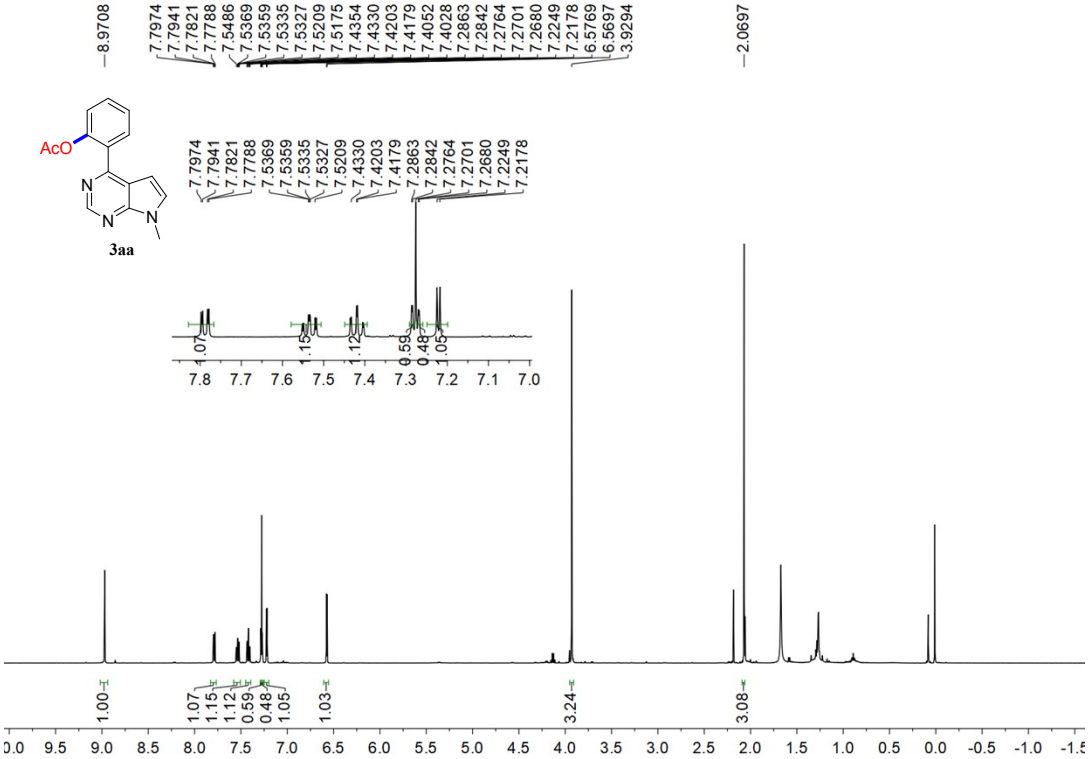

164.68
164.18
163.45
158.23
139.67
130.85
129.96
129.17
128.68
126.57
109.91
77.25
50.85
29.70
1.02
OBoc
N
N
N
2k

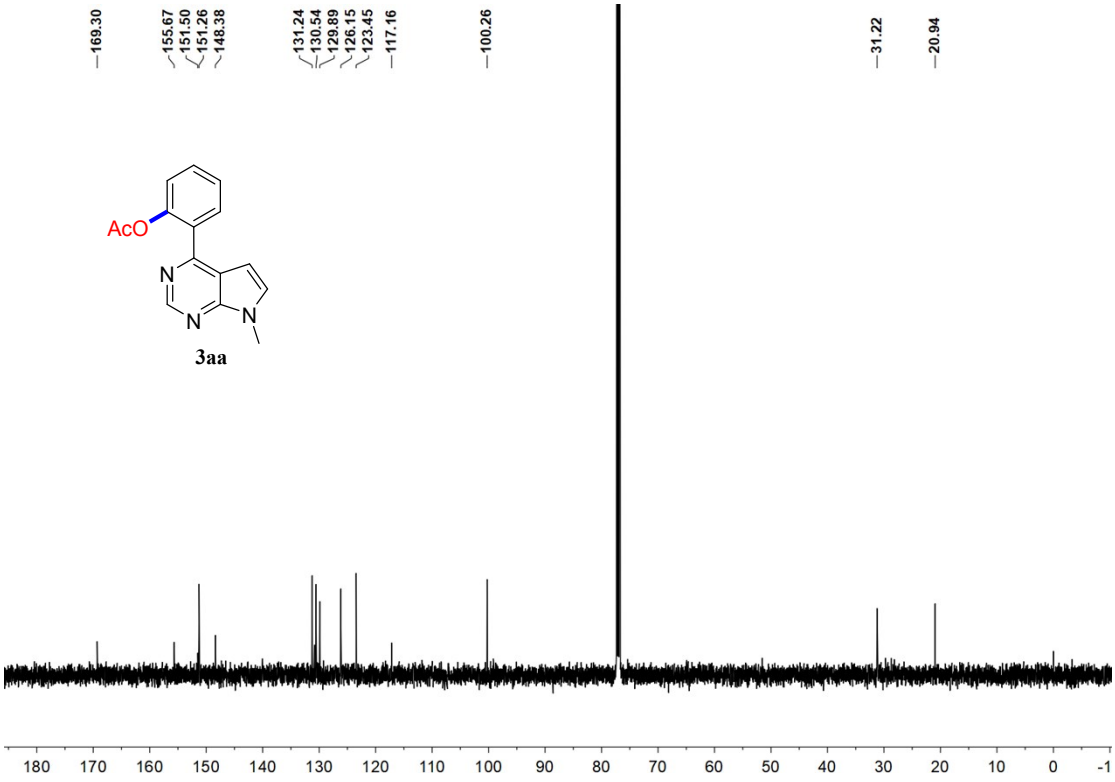

Intens.
x10^4
1.25
1.00
0.75
0.50
0.25
0.00
-MS, 0.2min #14
OBoc
2k
325.1817
322.6832
323.4850
324.1321
324.9647
325.6138
322.0
322.5
323.0
323.5
324.0
324.5
325.0
325.5
m/z

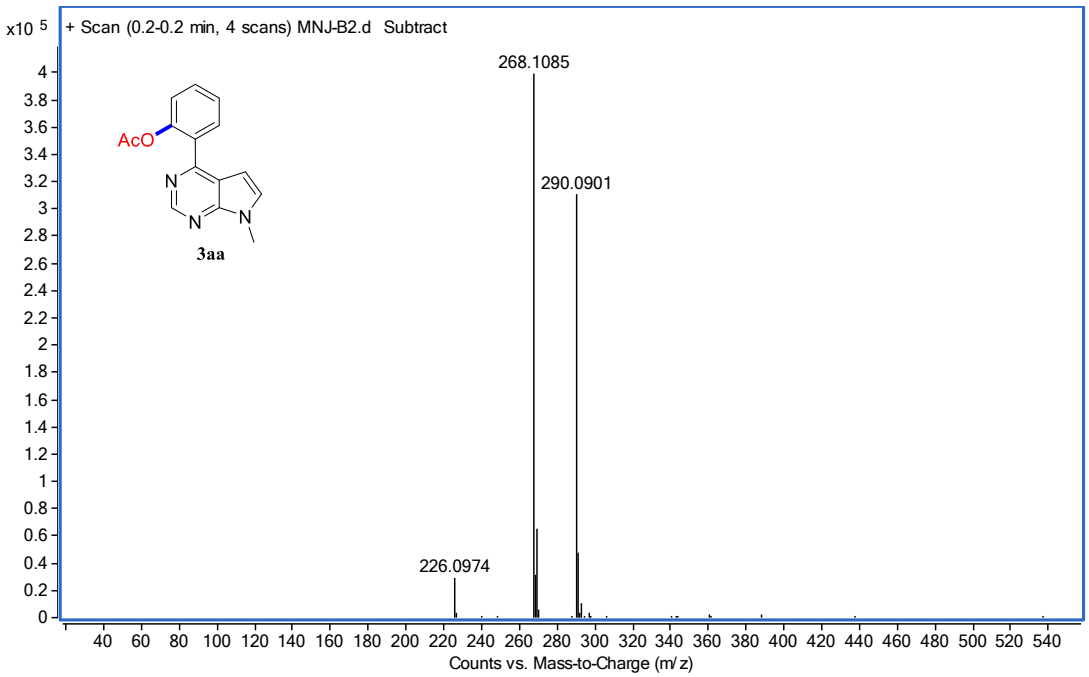

8.9513
7.7291
7.7247
7.7173
7.7099
7.5228
7.5176
7.5121
7.5096
7.3613
7.3587
3.9020
I
N
N
N
2l
1.94
2.95
0.97
1.00
3.07

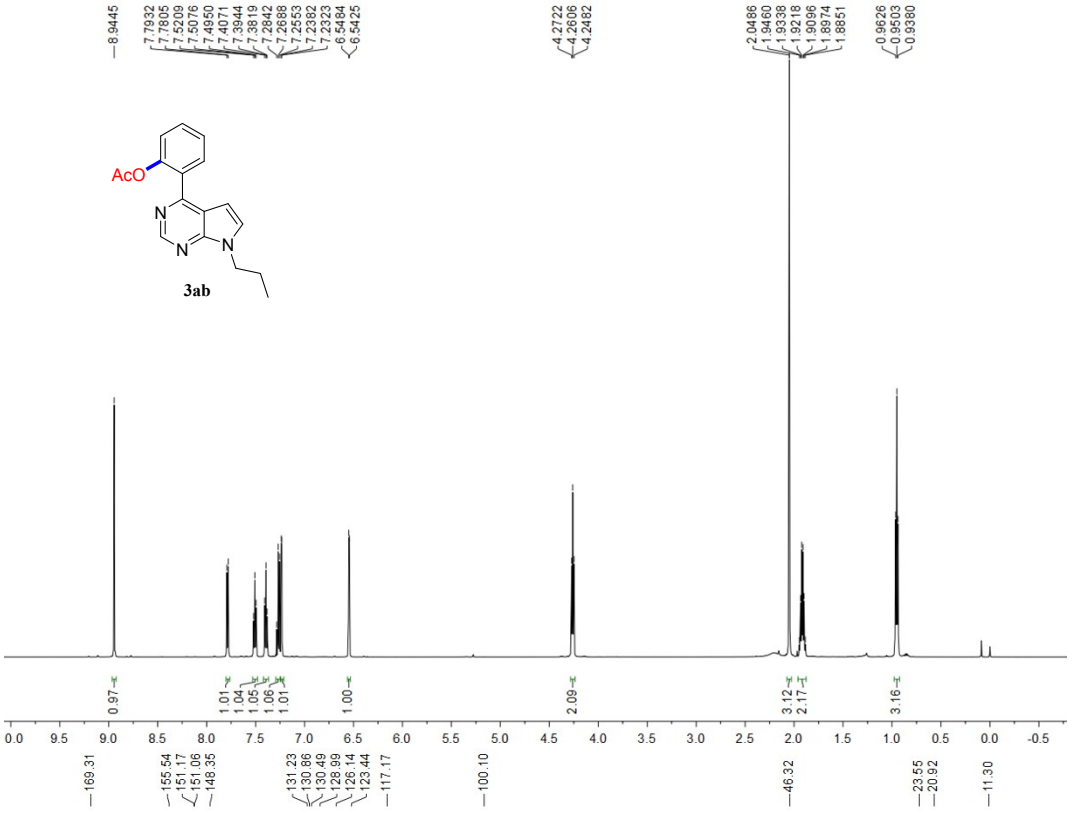

160.35
151.20
135.78
135.56
130.87
129.53
127.70
116.57
51.33
31.34
2l
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

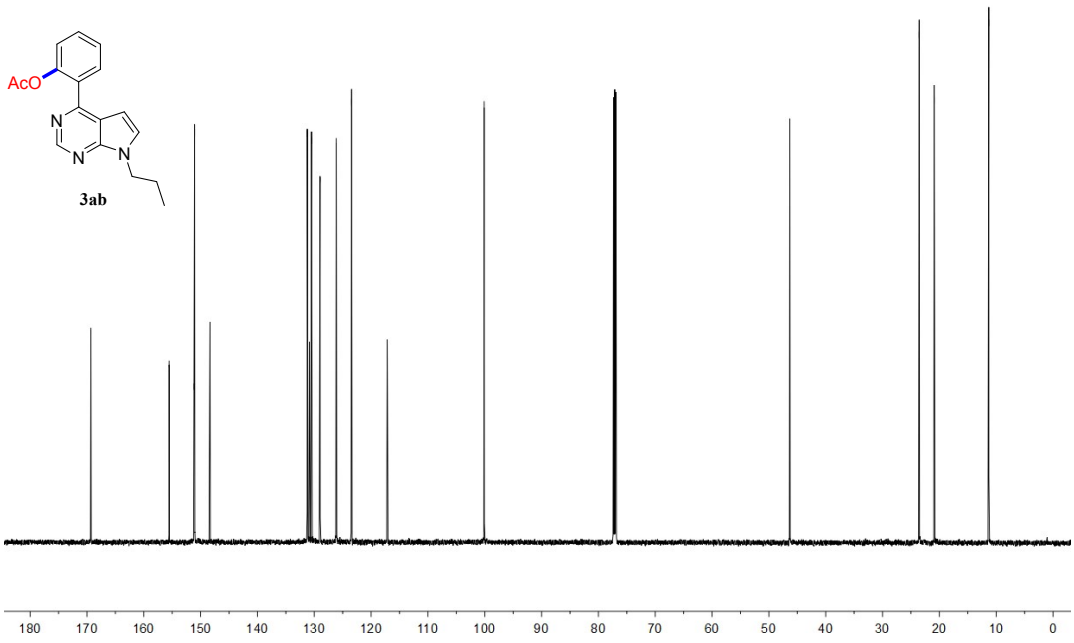

+ESI Scan (0.370 min) Frag=175.0V ZR-B11.d
335.9992
337.0018
332.1384
335.2539
338.1859
341.2657
353.1596
360.3232
2l
Counts vs. Mass-to-Charge (m/z)

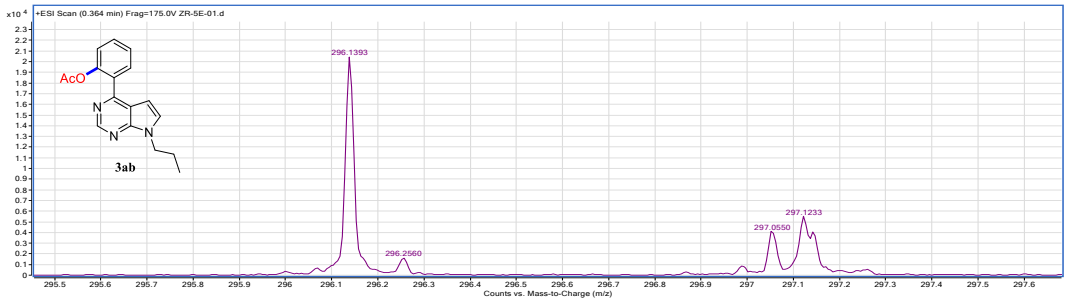

8.9708
7.7974
7.7941
7.7821
7.7788
7.5486
7.5369
7.5359
7.5335
7.5327
7.5209
7.5175
7.4354
7.4330
7.4203
7.4179
7.4052
7.4028
7.2863
7.2842
7.2764
7.2701
7.2680
7.2249
7.2178
6.5769
6.5697
3.9294
2.0697
AcO
3aa
1.00
1.07
1.15
1.12
0.59
0.48
1.05
1.03
3.24
3.08

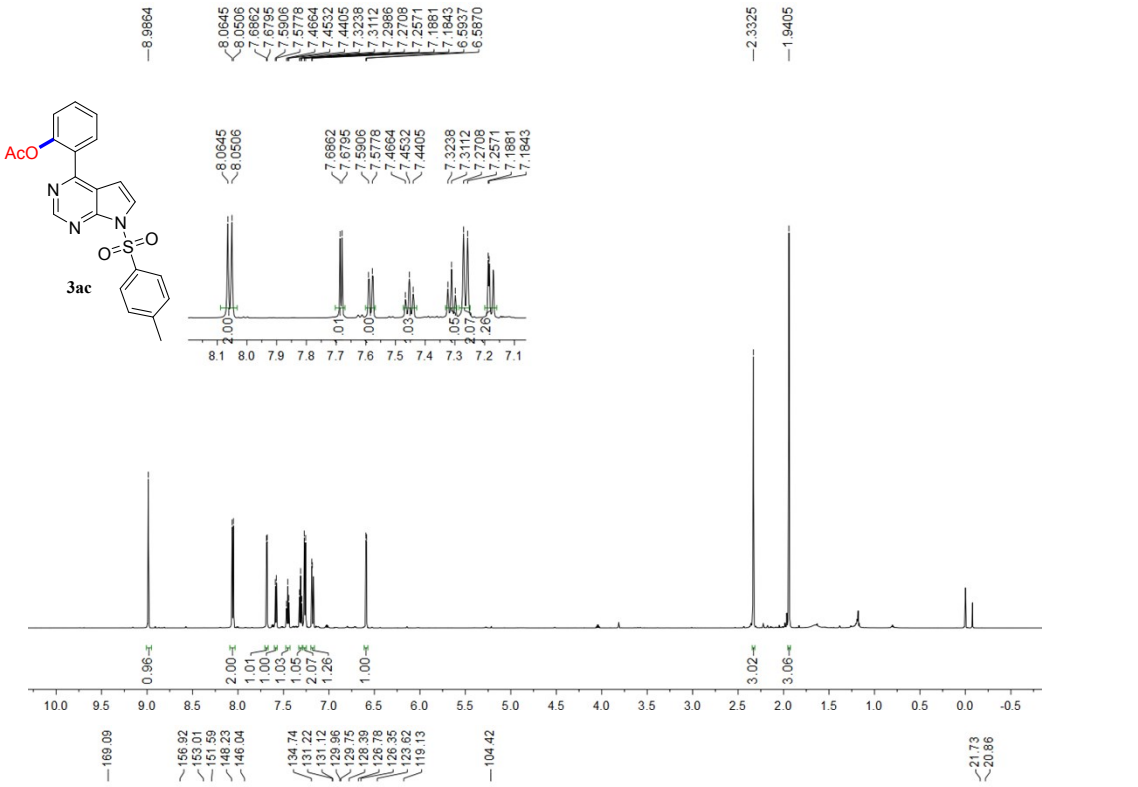

169.30
155.67
151.50
151.26
148.38
131.24
130.54
129.89
126.15
123.45
117.16
100.26
31.22
20.94
AcO
N
N
N
3aa
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

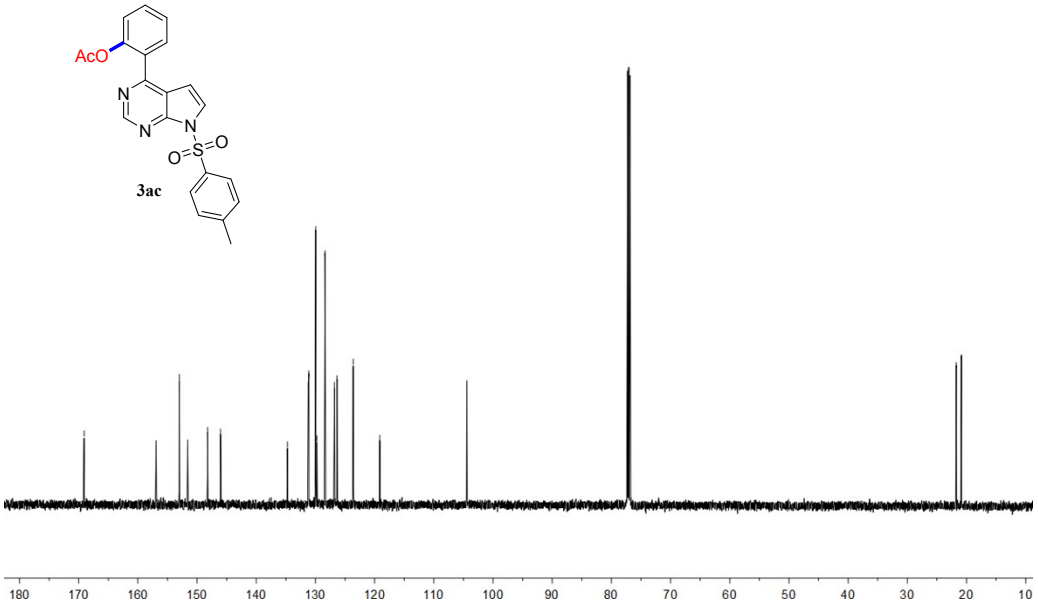

x10 5
+ Scan (0.2-0.2 min, 4 scans) MNJ-B2.d Subtract
268.1085
290.0901
226.0974
AcO
N
N
N
3aa
4 3.8 3.6 3.4 3.2 3 2.8 2.6 2.4 2.2 2 1.8 1.6 1.4 1.2 1 0.8 0.6 0.4 0.2 0
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540
Counts vs. Mass-to-Charge (m/z)

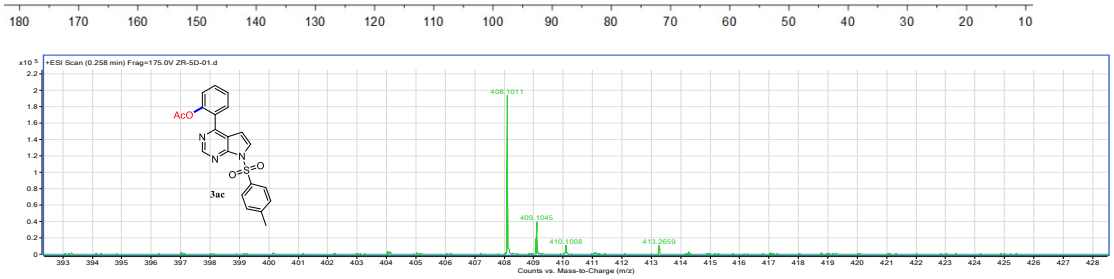

8.9445
7.7932
7.7805
7.5209
7.5076
7.4950
7.4071
7.3944
7.3819
7.2842
7.2688
7.2553
7.2382
7.2323
6.5484
6.5425
4.2722
4.2606
4.2482
2.0486
1.9460
1.9338
1.9218
1.9096
1.8974
1.8851
0.9626
0.9503
0.9380
AcO
N
N
N
3ab
0.97
1.01
1.04
1.05
1.06
1.01
1.00
2.09
3.12
2.17
3.16
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 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
169.31
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

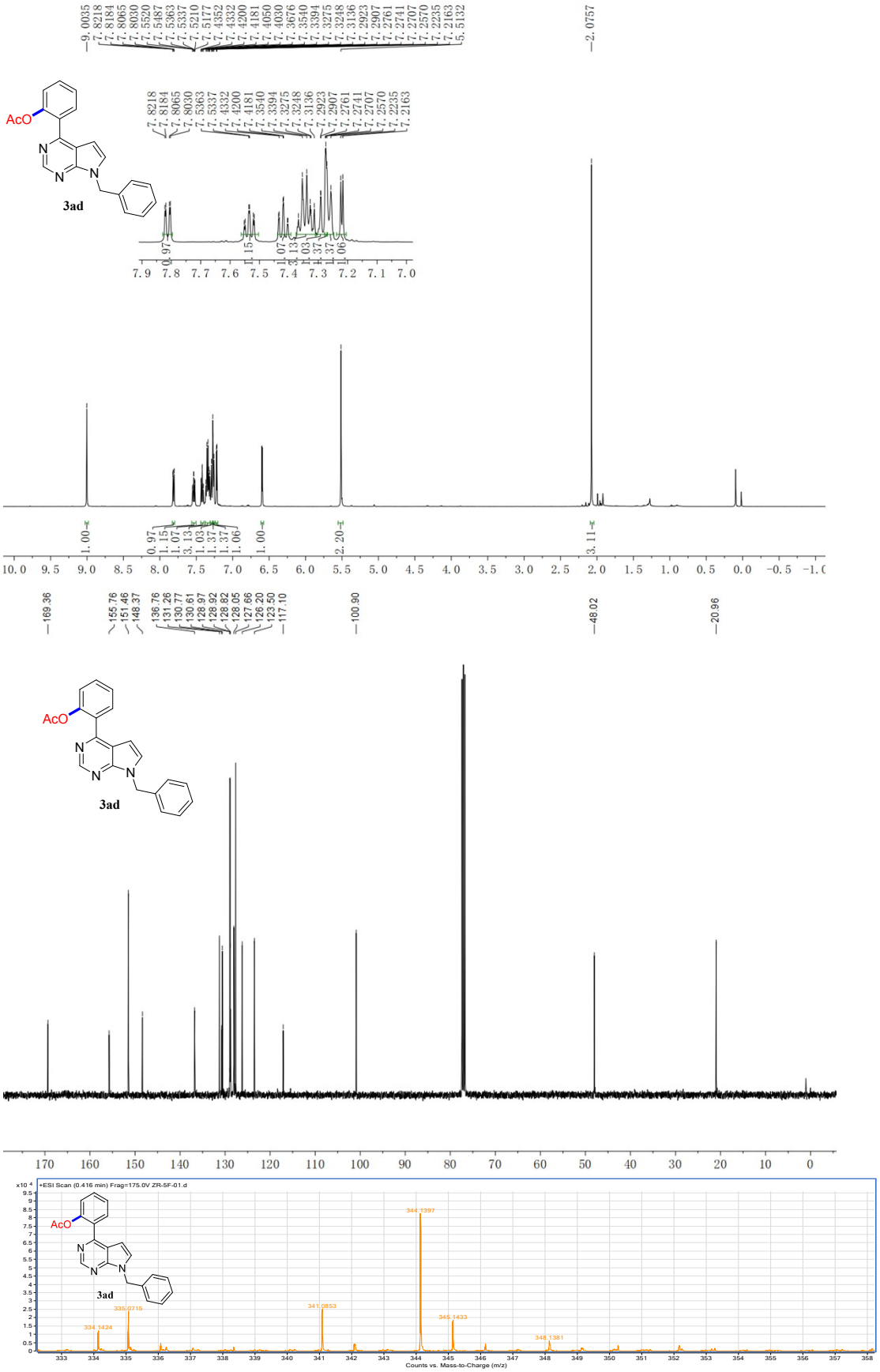

AcO
N
N
N
3ab
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

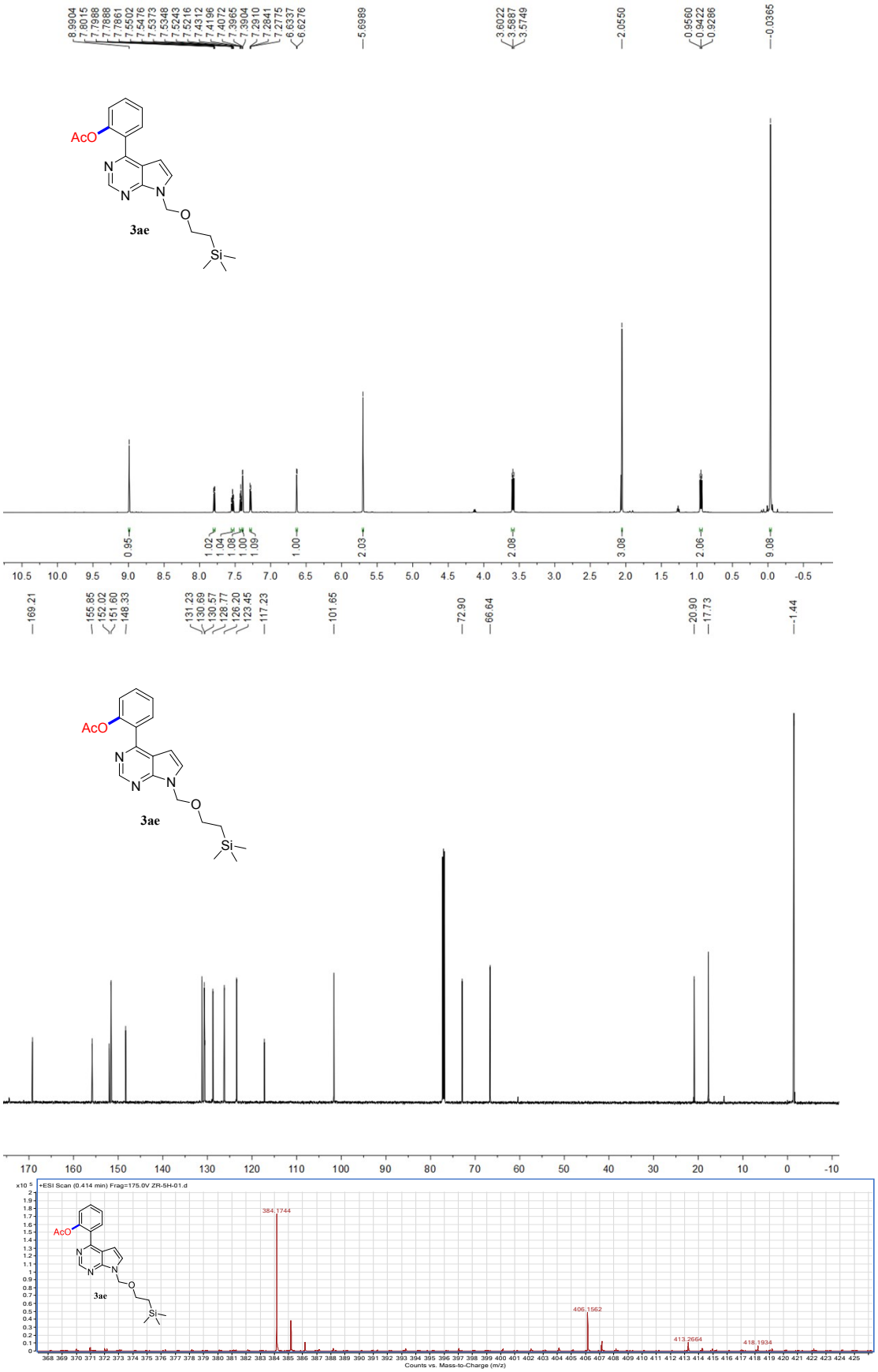

+ESI Scan (0.364 min) Frag=175.0V ZR-5E-01.d
AcO
N
N
N
3ab
296.1393
296.2560
297.0550
297.1233
Counts vs. Mass-to-Charge (m/z)

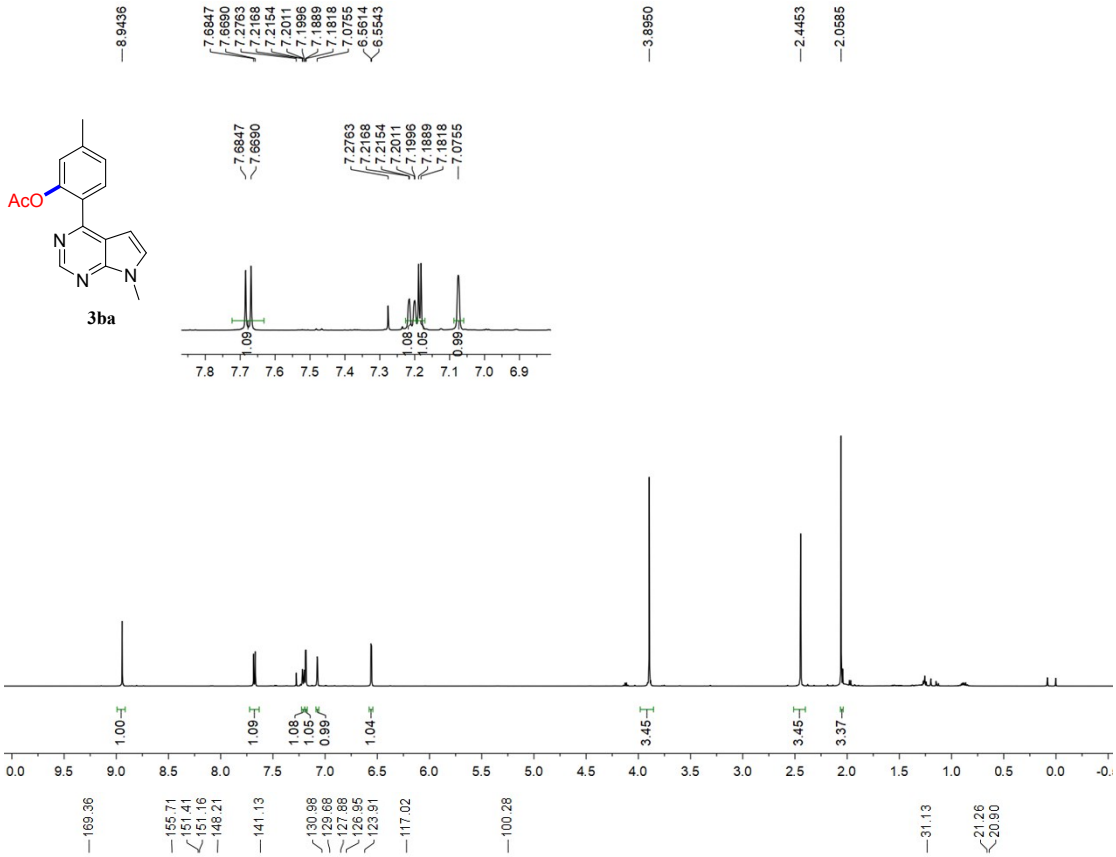

AcO
3ac

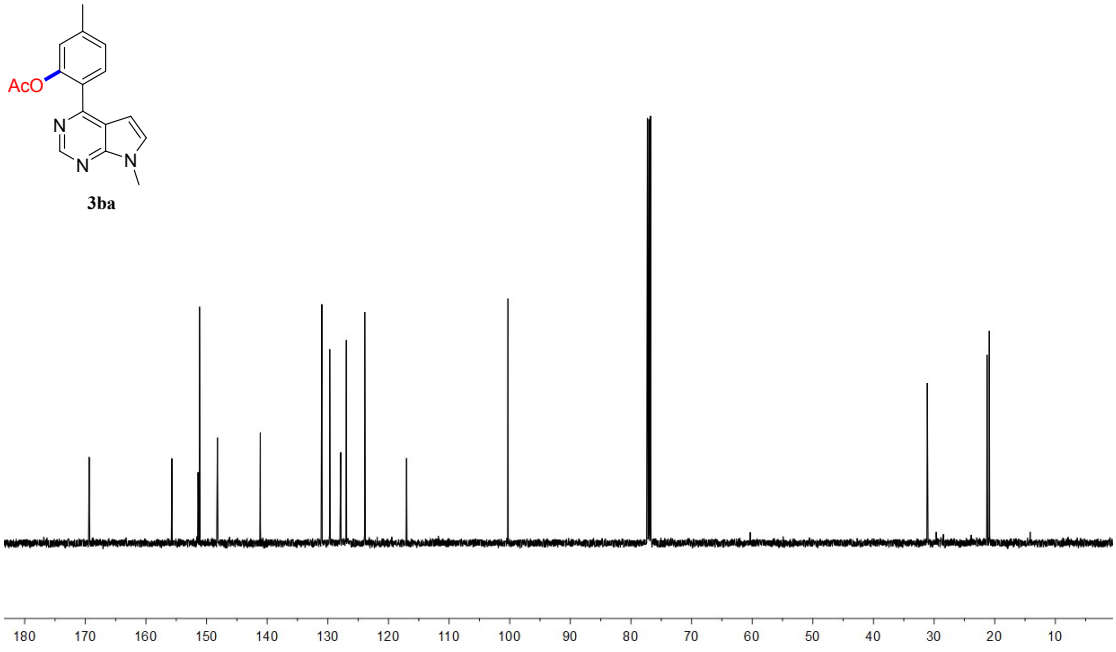

AcO
3ac

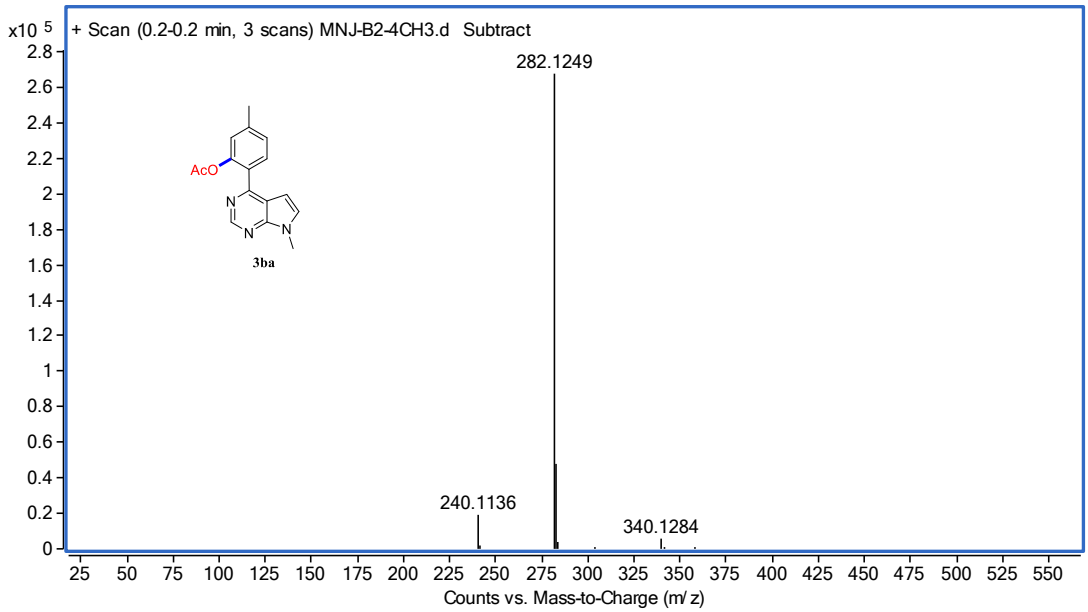

+ESI Scan (0.258 min) Frag=175.0V ZR-SD-01.d
AcO
3ac
408.1011
409.1045
410.1008
413.2659
Counts vs. Mass-to-Charge (m/z)

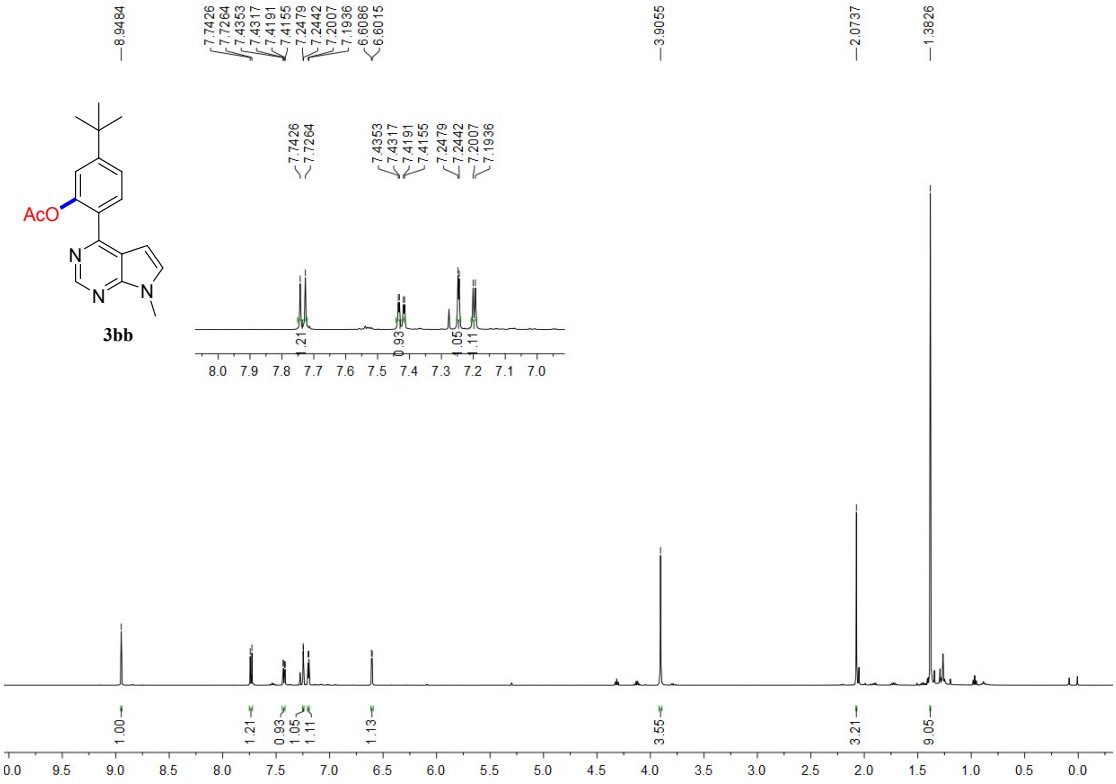

AcO
N
N
3ad
9.0035
7.8218
7.8184
7.8065
7.8030
7.5520
7.5487
7.5363
7.5337
7.5210
7.5177
7.4352
7.4332
7.4200
7.4181
7.4060
7.4030
7.3676
7.3540
7.3394
7.3275
7.3248
7.3136
7.2923
7.2907
7.2761
7.2741
7.2707
7.2570
7.2235
7.2163
5.5132
2.0757
0.97
1.15
1.07
3.13
1.03
1.37
1.37
1.06
1.00
2.20
3.11
169.36
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
+ESI Scan (0.416 min) Frag=175.0V ZR-5F-01.d
344.1397
341.0853
335.0715
345.1433
348.1381
334.1424
Counts vs. Mass-to-Charge (m/z)

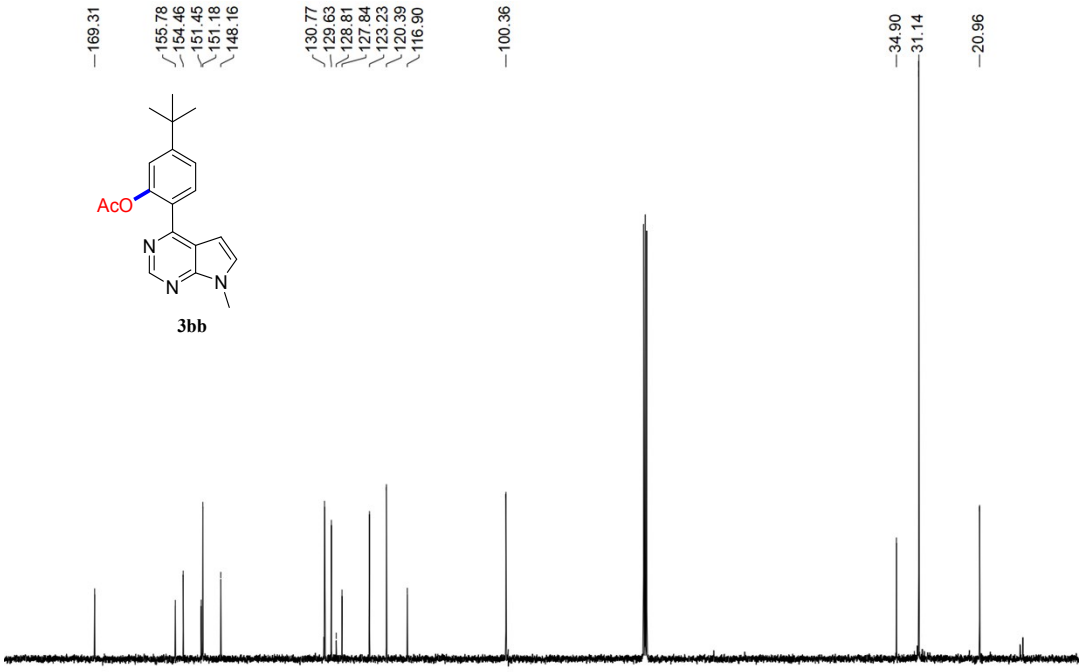

8.9904
7.8015
7.7988
7.7888
7.7861
7.5502
7.5476
7.5373
7.5348
7.5243
7.5216
7.4312
7.4196
7.4072
7.3965
7.3904
7.2910
7.2841
7.2775
6.6337
6.6276
5.6989
3.6022
3.5887
3.5749
2.0550
0.9560
0.9422
0.9286
0.0365
AcO
N
N
N
O
Si
3ae
0.95
1.02
1.04
1.08
1.00
1.09
1.00
2.03
2.08
3.08
2.06
9.08
10.5 10.0 9.5 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
x10 5
+ESI Scan (0.414 min) Frag=175.0V ZR-5H-01.d
AcO
N
N
N
O
Si
3ae
384.1744
406.1562
413.2664
418.1934
368 369 370 371 372 373 374 375 376 377 378 379 380 381 382 383 384 385 386 387 388 389 390 391 392 393 394 395 396 397 398 399 400 401 402 403 404 405 406 407 408 409 410 411 412 413 414 415 416 417 418 419 420 421 422 423 424 425
Counts vs. Mass-to-Charge (m/z)

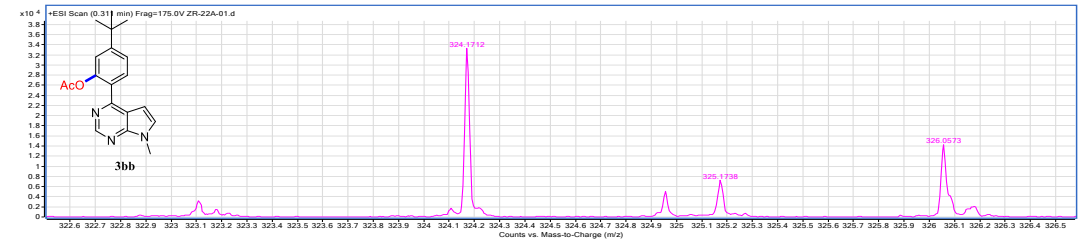

8.9436
7.6847
7.6690
7.2763
7.2168
7.2154
7.2011
7.1996
7.1889
7.1818
7.0755
6.5614
6.5543
3.8950
2.4453
2.0585
AcO
N
N
N
3ba
1.09
1.08
1.05
0.99
1.00
1.04
3.45
3.37
169.36
155.71
151.41
151.16
148.21
141.13
130.98
129.68
127.88
126.95
123.91
117.02
100.28
31.13
21.26
20.90

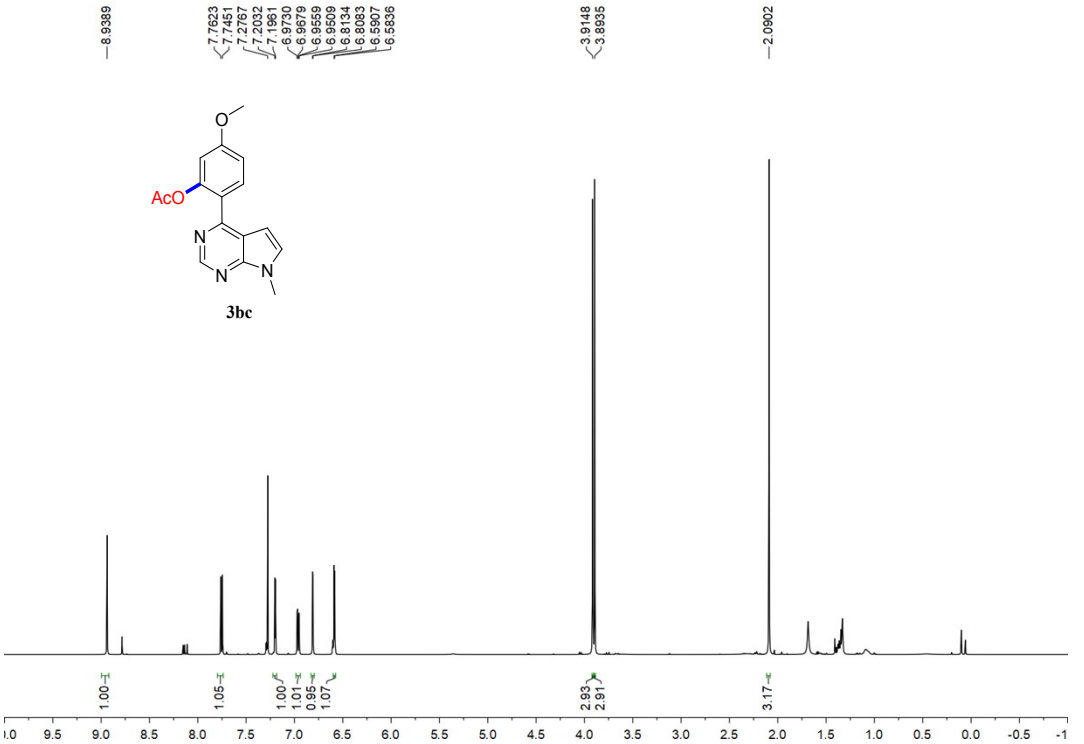

AcO
N
N
N
3ba

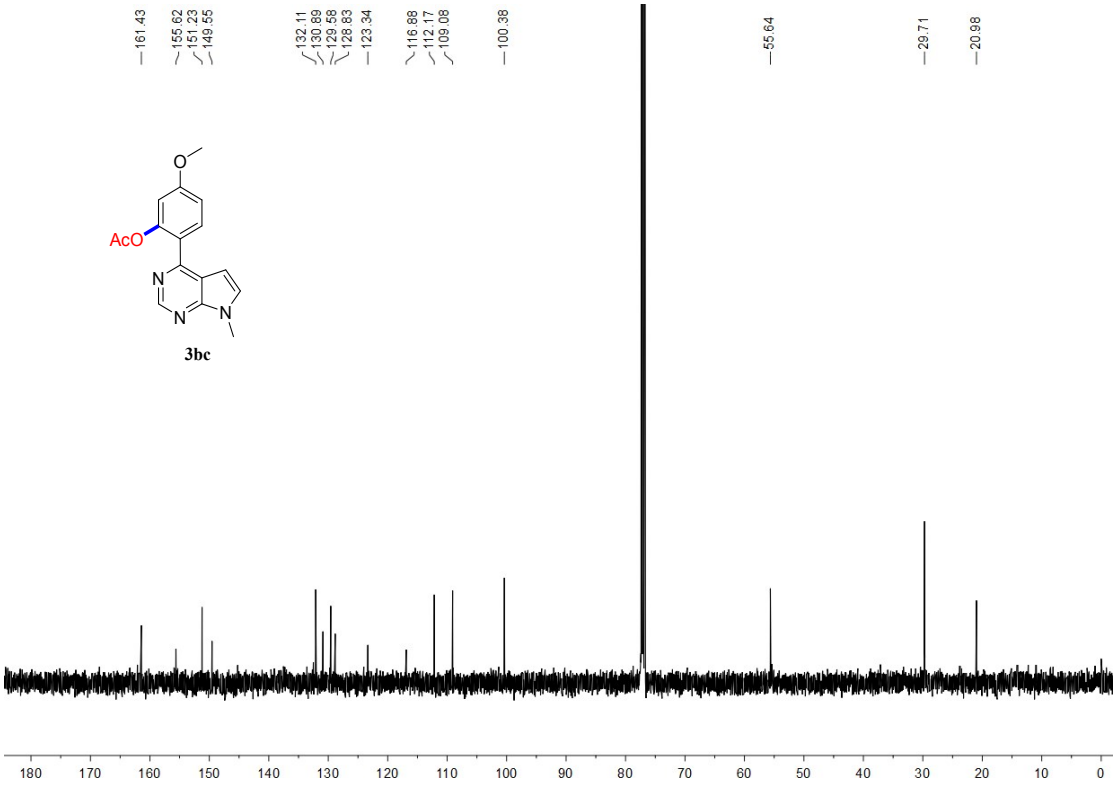

x10 5
+ Scan (0.2-0.2 min, 3 scans) MNJ-B2-4CH3.d Subtract
282.1249
240.1136
340.1284
AcO
N
N
N
3ba
Counts vs. Mass-to-Charge (m/z)

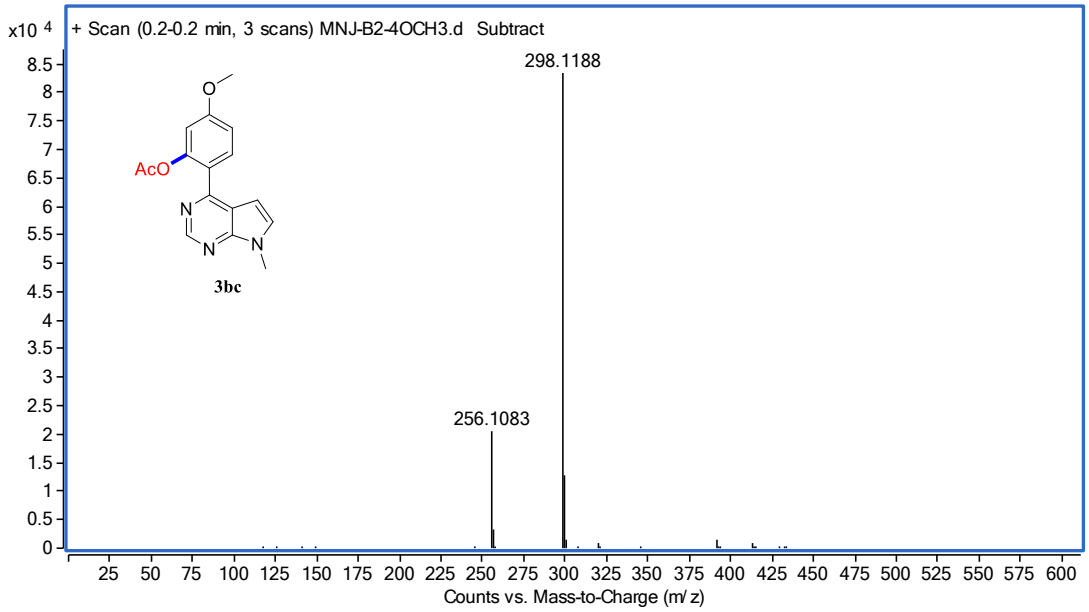

8.9484
7.7426
7.7264
7.4353
7.4317
7.4191
7.4155
7.2479
7.2442
7.2007
7.1936
6.6086
6.6015
3.9055
2.0737
1.3826
AcO
N
N
N
3bb
1.00
1.21
0.93
1.05
1.11
1.13
3.55
3.21
9.05

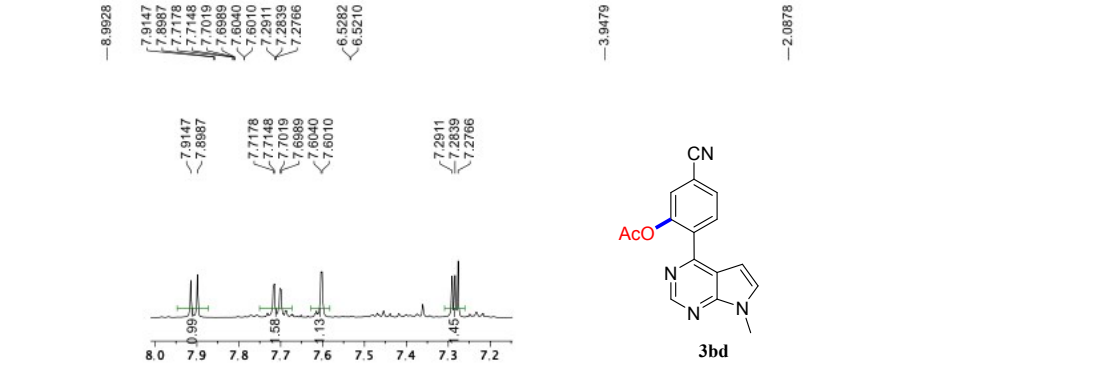

169.31
155.78
154.46
151.45
151.18
148.16
130.77
129.63
128.81
127.84
123.23
120.39
116.90
100.36
34.90
31.14
20.96
AcO
N
N
N
3bb

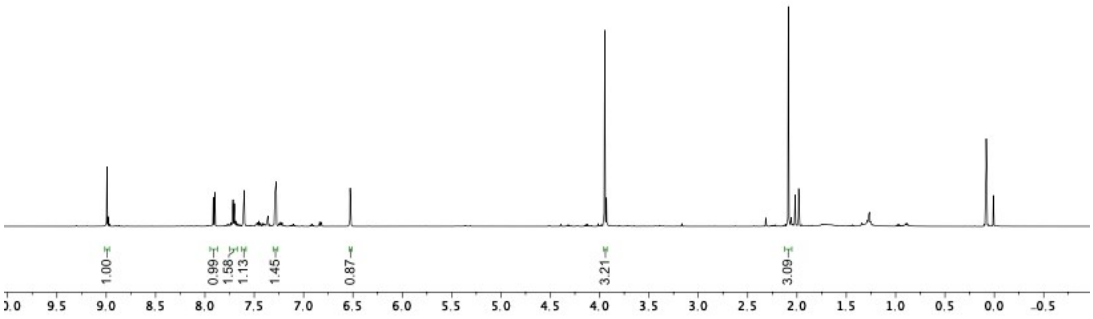

+ESI Scan (0.311 min) Frag=175.0V ZR-22A-01.d
AcO
N
N
N
3bb
324.1712
325.1738
326.0573
Counts vs. Mass-to-Charge (m/z)

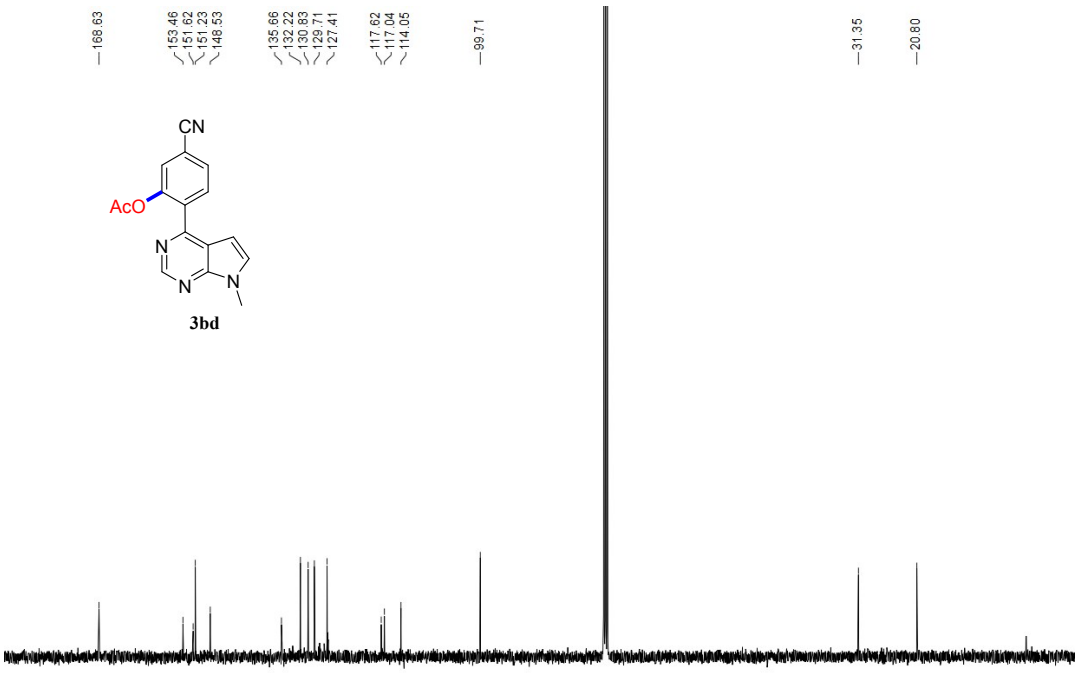

8.9389
7.7623
7.7451
7.2767
7.2032
7.1961
6.9730
6.9679
6.9559
6.9509
6.8134
6.8083
6.5907
6.5836
3.9148
3.8935
2.0902
O
AcO
N
N
N
3bc
1.00
1.05
1.00
1.01
0.95
1.07
2.93
2.91
3.17

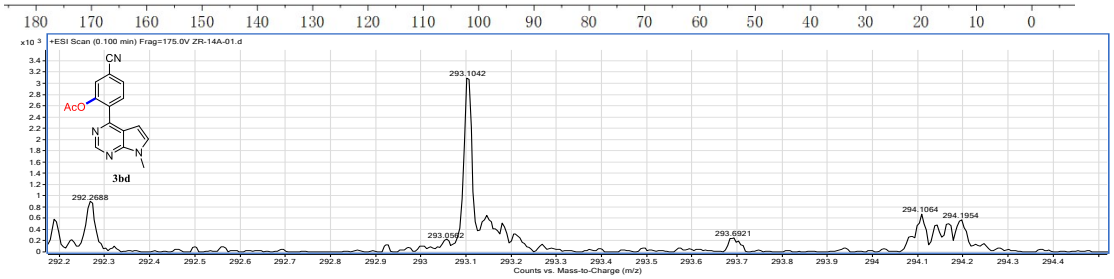

161.43
155.62
151.23
149.55
132.11
130.89
129.58
128.83
123.34
116.88
112.17
109.08
100.38
55.64
29.71
20.98
AcO
N
N
N
O
3bc
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

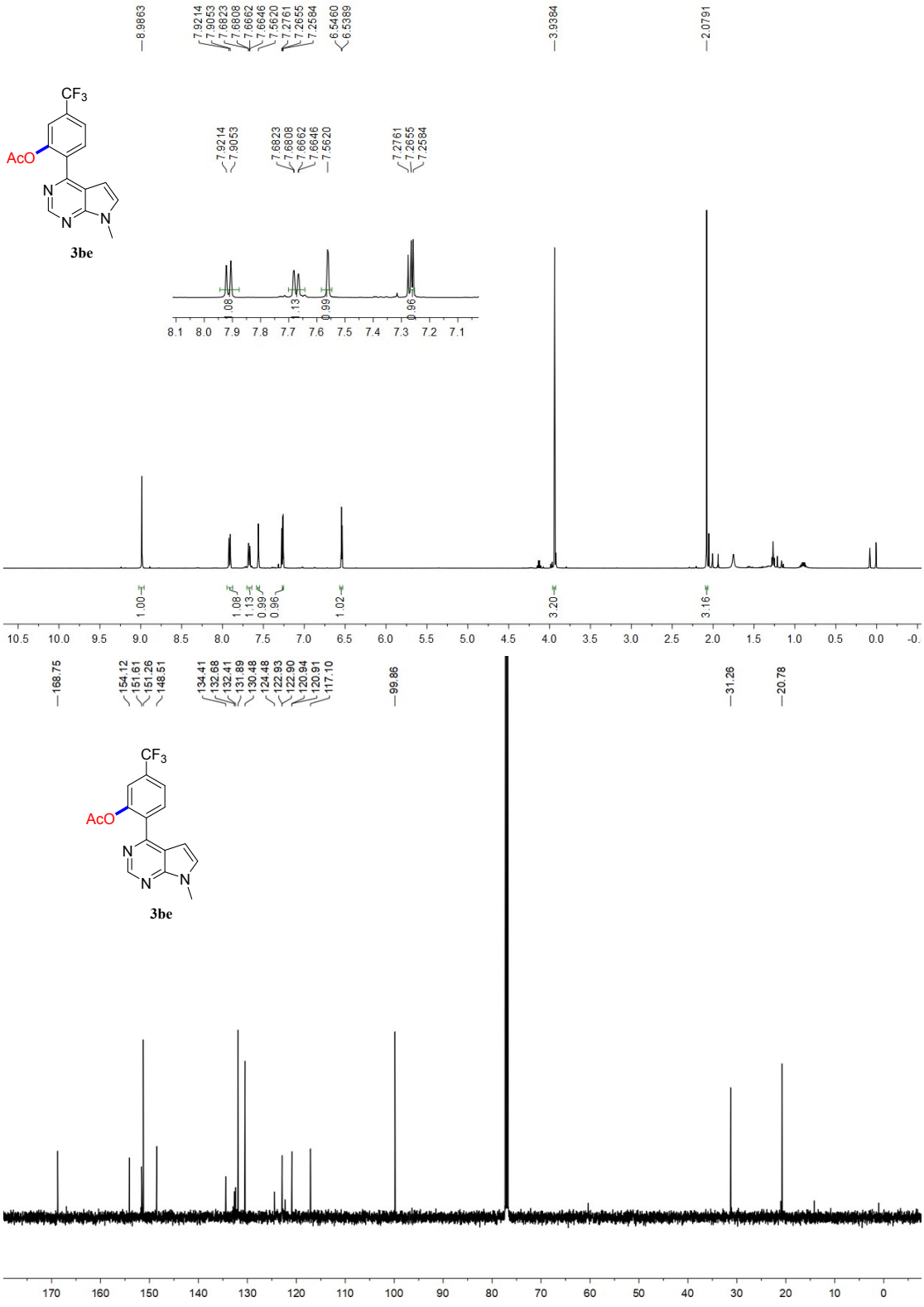

x10 4
+ Scan (0.2-0.2 min, 3 scans) MNJ-B2-4OCH3.d Subtract
298.1188
256.1083
AcO
N
N
N
O
3bc
8.5 8 7.5 7 6.5 6 5.5 5 4.5 4 3.5 3 2.5 2 1.5 1 0.5 0
25 50 75 100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600
Counts vs. Mass-to-Charge (m/z)

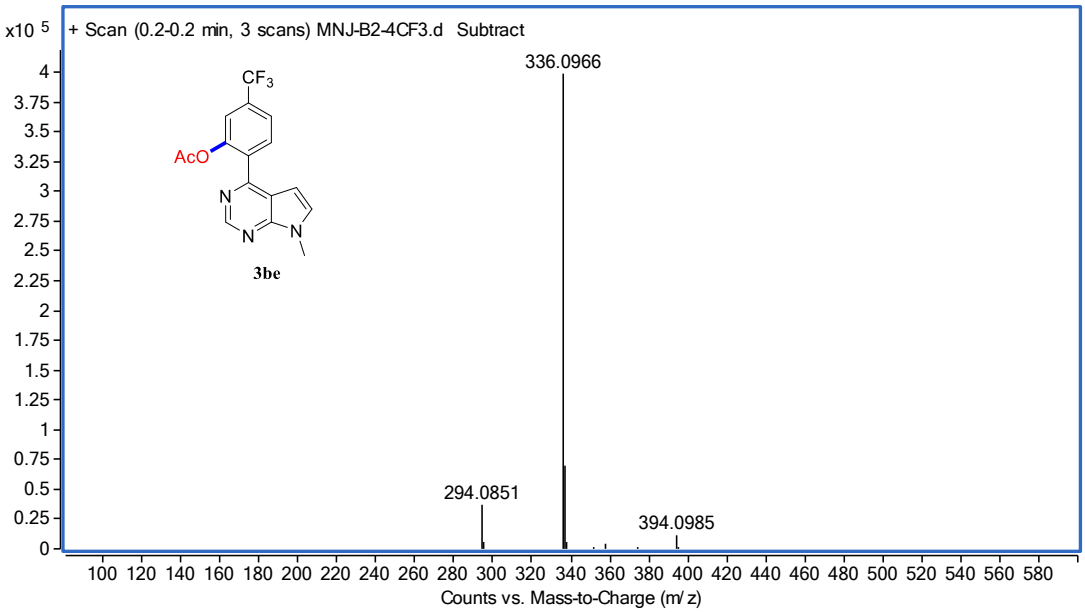

8.9928
7.9147
7.8987
7.7178
7.7148
7.7019
7.6989
7.6040
7.6010
7.2911
7.2839
7.2766
6.5282
6.5210
3.9479
2.0878
CN
AcO
N
N
N
3bd

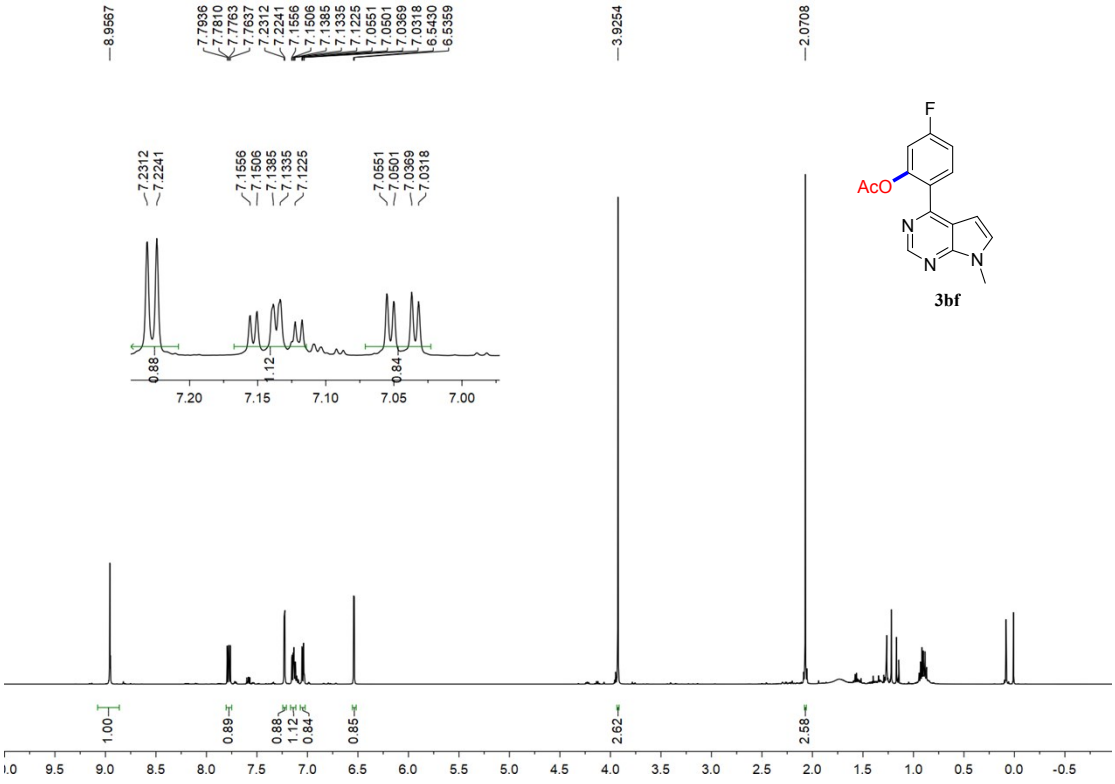

1.00
0.99
1.58
1.13
1.45
0.87
3.21
3.09

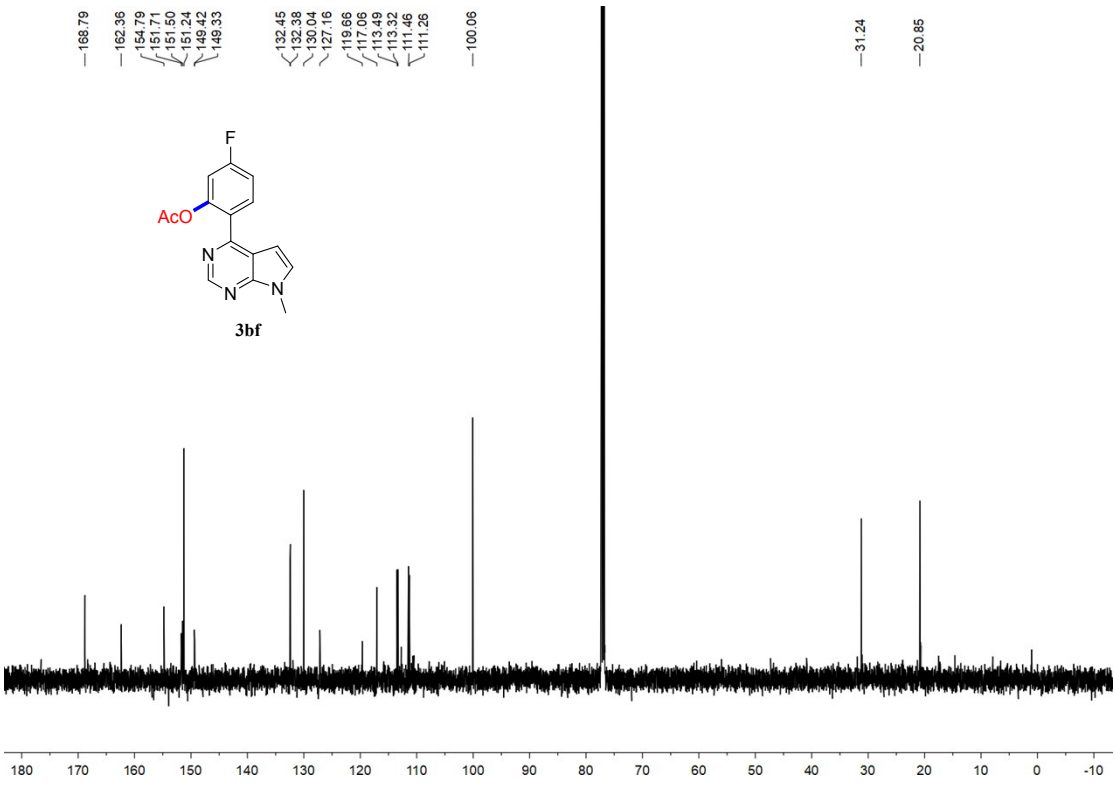

168.63
153.46
151.62
151.23
148.53
135.66
132.22
130.83
129.71
127.41
117.62
117.04
114.05
99.71
31.35
20.80
CN
AcO
N
N
N
3bd

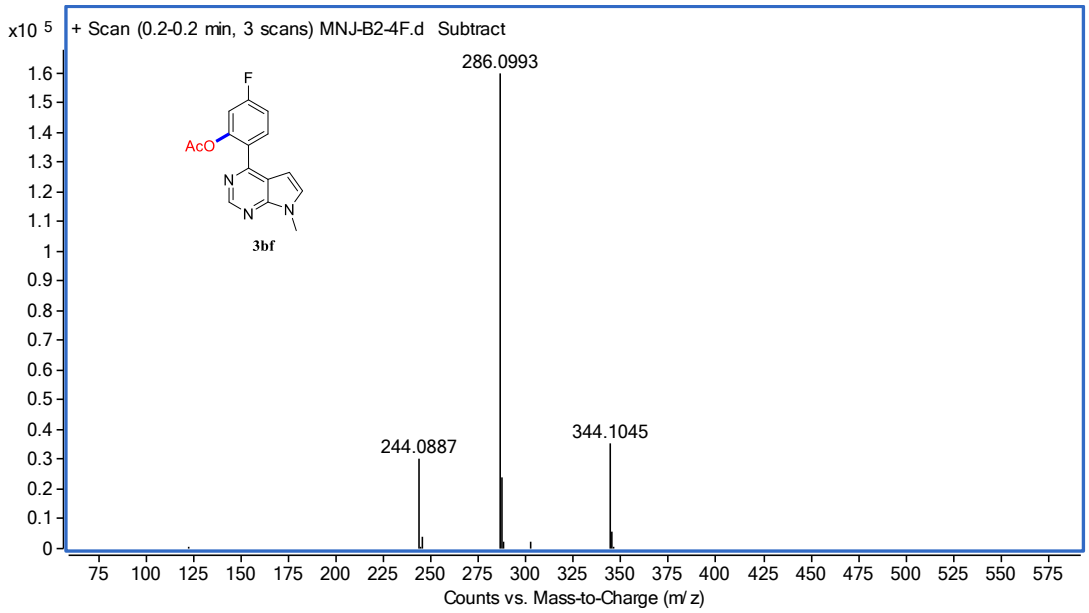

+ESI Scan (0.100 min) Frag=175.0V ZR-14A-01.d
CN
AcO
N
N
N
3bd
292.2688
293.0592
293.1042
293.6921
294.1064
294.1954
Counts vs. Mass-to-Charge (m/z)

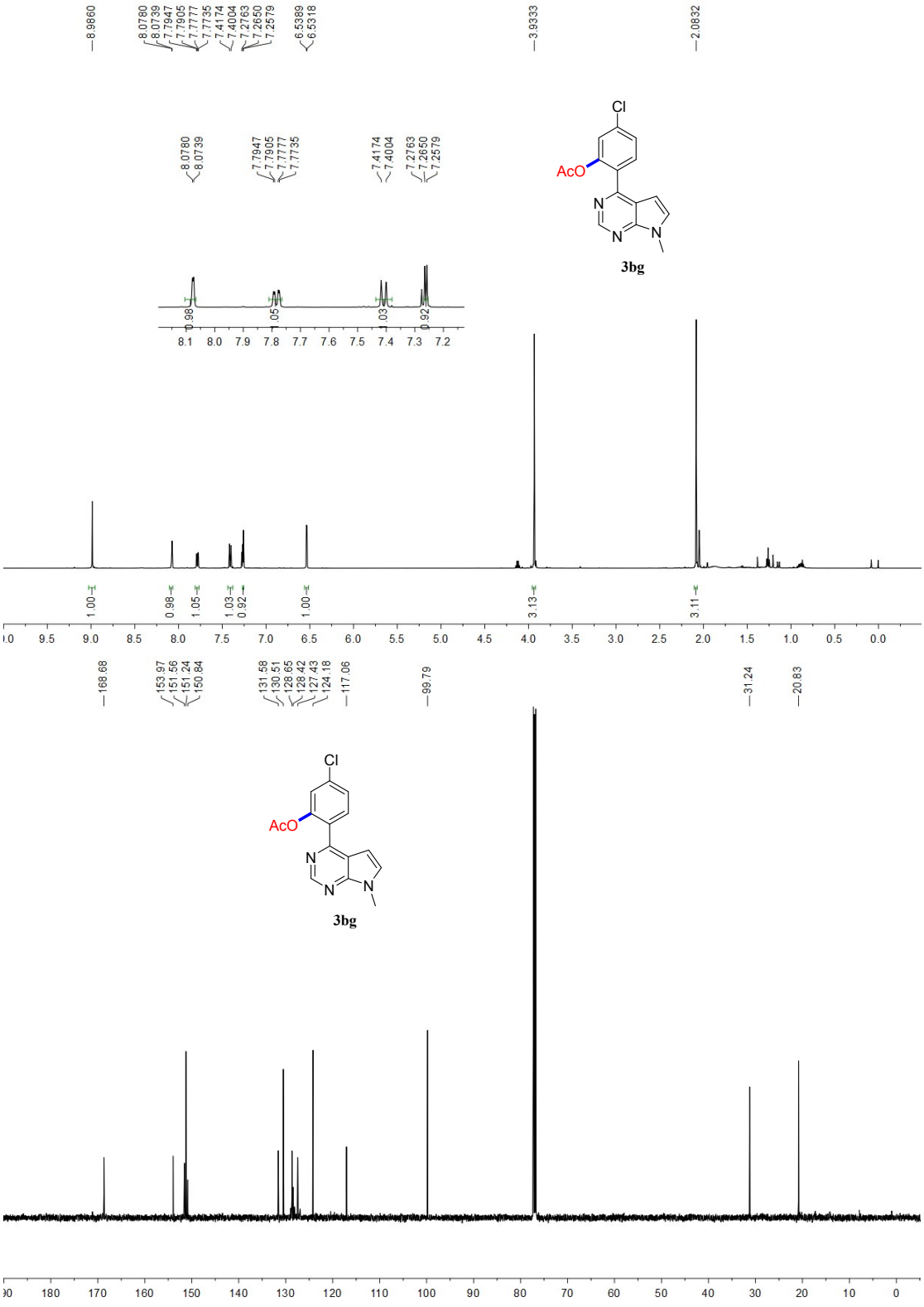

8.9863
7.9214
7.9053
7.6823
7.6808
7.6662
7.6646
7.5620
7.2761
7.2655
7.2584
6.5460
6.5389
3.9384
2.0791
CF3
AcO
N
N
N
3be
1.08
1.13
0.99
0.96
1.00
1.02
3.20
3.16
168.75
154.12
151.61
151.26
148.51
134.41
132.68
132.41
131.89
130.48
124.48
122.93
122.90
120.94
120.91
117.10
99.86
31.26
20.78

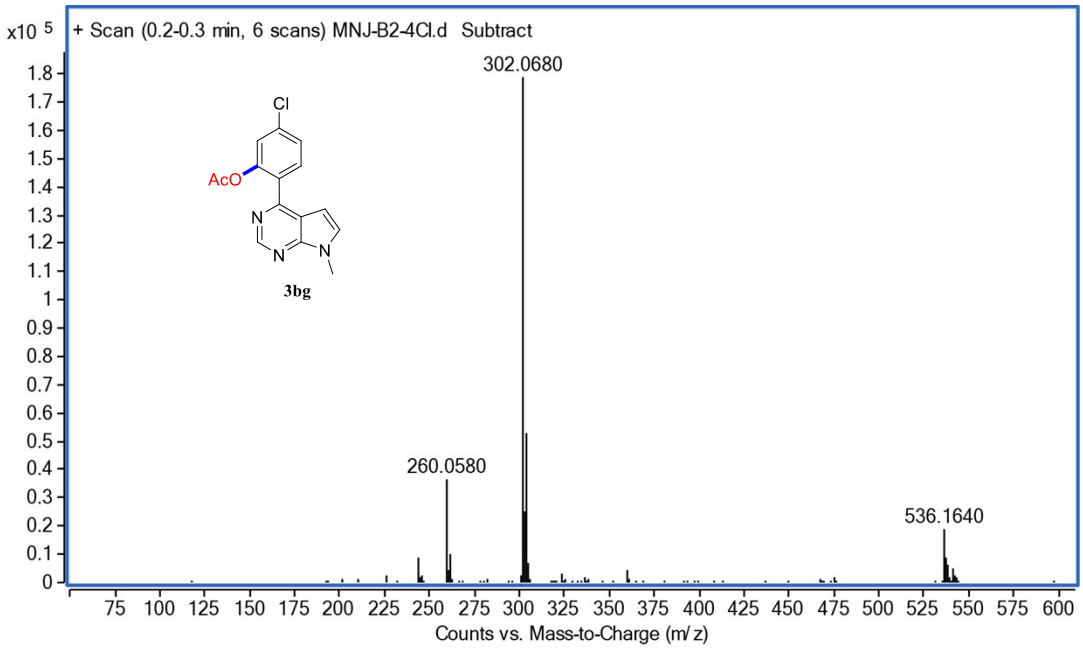

x10 5
+ Scan (0.2-0.2 min, 3 scans) MNJ-B2-4CF3.d Subtract
336.0966
294.0851
394.0985
CF3
AcO
N
N
N
3be
Counts vs. Mass-to-Charge (m/z)

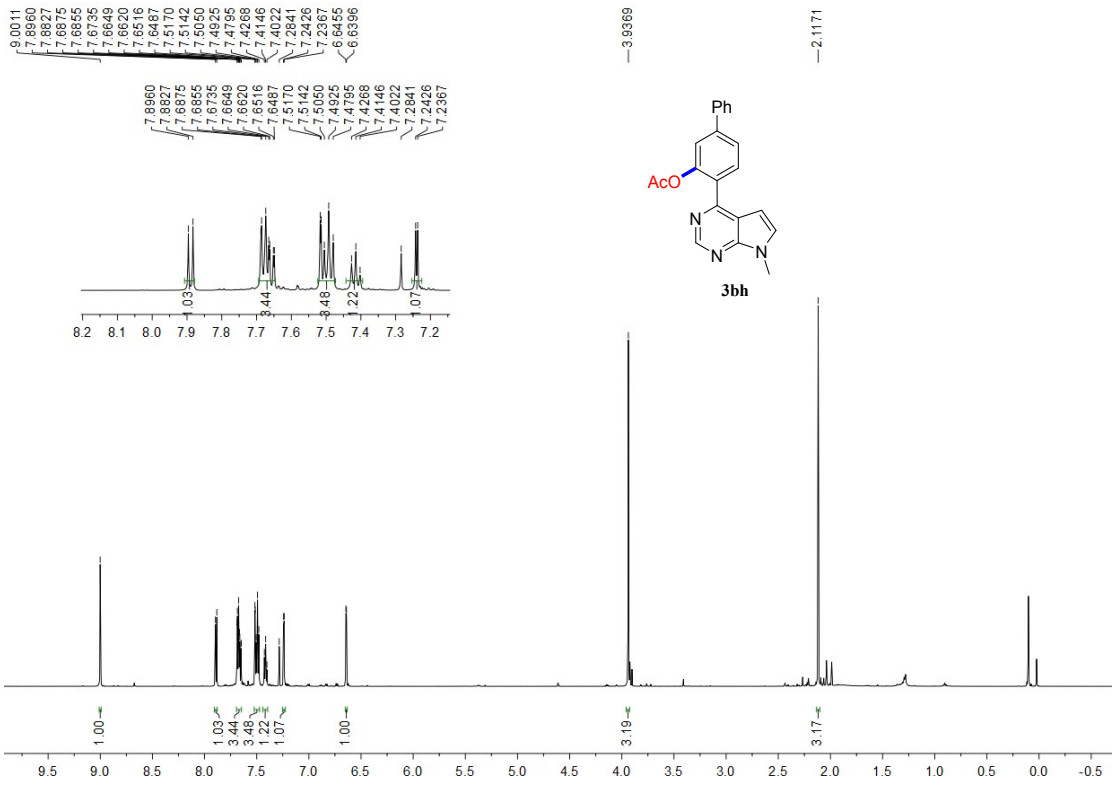

8.9567
7.7936
7.7810
7.7763
7.7637
7.2312
7.2241
7.1556
7.1506
7.1385
7.1335
7.1225
7.0551
7.0501
7.0369
7.0318
6.5430
6.5359
3.9254
2.0708
F
AcO
N
N
N
3bf
0.88
1.12
0.84
7.20
7.15
7.10
7.05
7.00
1.00
0.89
0.88
1.12
0.84
0.85
2.62
2.58

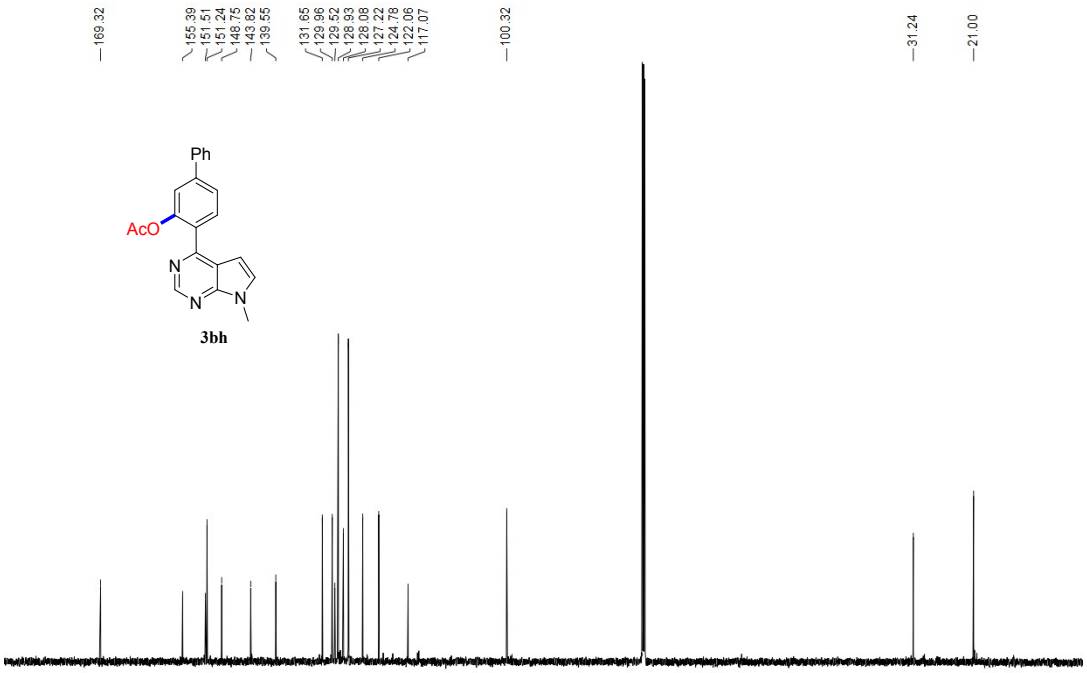

168.79
162.36
154.79
151.71
151.50
151.24
149.42
149.33
132.45
132.38
130.04
127.16
119.66
117.06
113.49
113.32
111.46
111.26
100.06
31.24
20.85
F
AcO
N
N
N
3bf
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

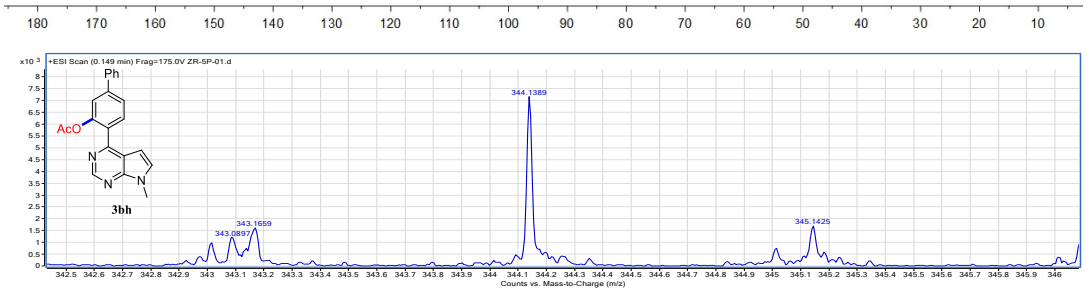

x10 5
+ Scan (0.2-0.2 min, 3 scans) MNJ-B2-4F.d Subtract
286.0993
244.0887
344.1045
F
AcO
N
N
N
3bf
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
75
100
125
150
175
200
225
250
275
300
325
350
375
400
425
450
475
500
525
550
575
Counts vs. Mass-to-Charge (m/z)


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
150.84
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)

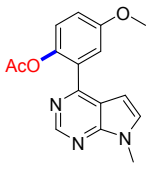

Ph
AcO
N
N
N
3bh

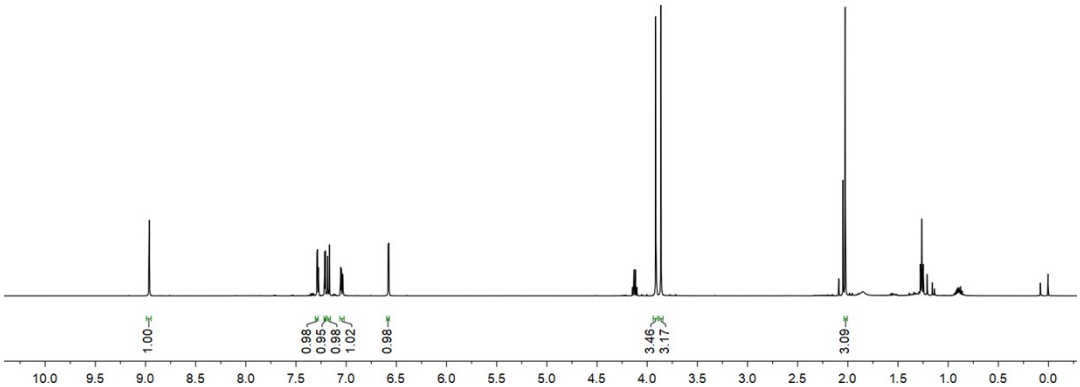

169.32
155.39
151.51
151.24
148.75
143.82
139.55
131.65
129.96
129.52
128.93
128.08
127.22
124.78
122.06
117.07
100.32
31.24
21.00
Ph
AcO
N
N
N
3bh

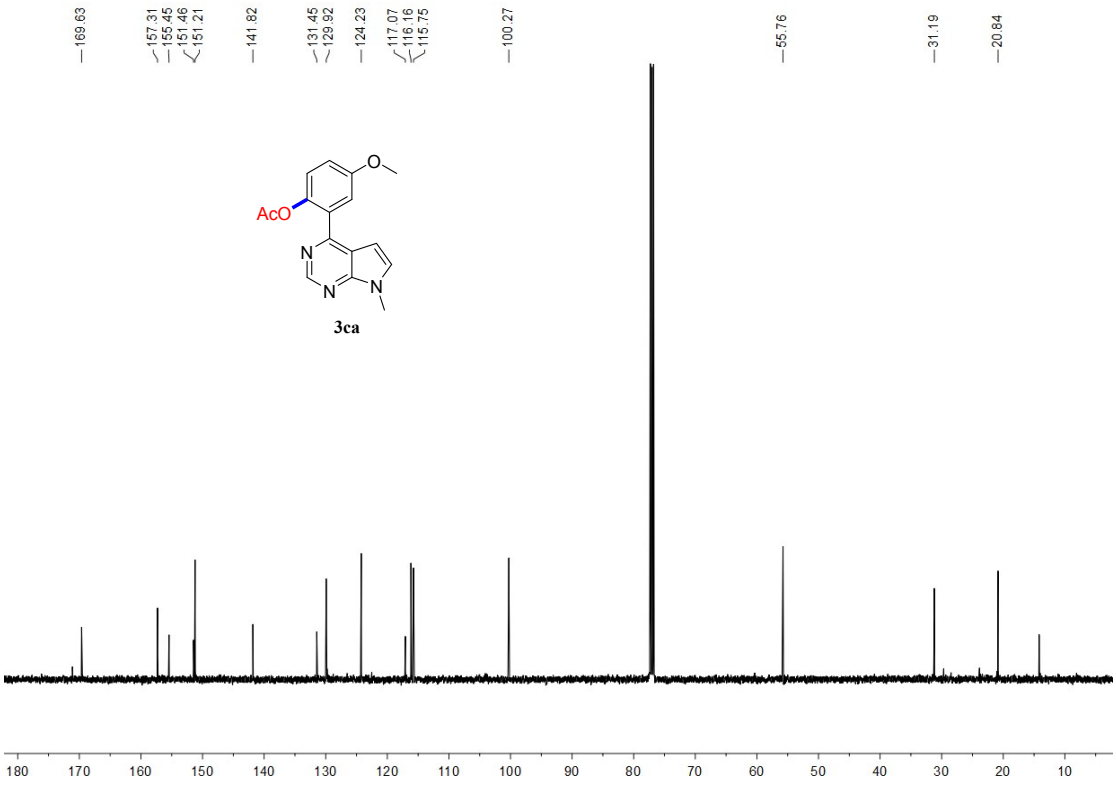

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

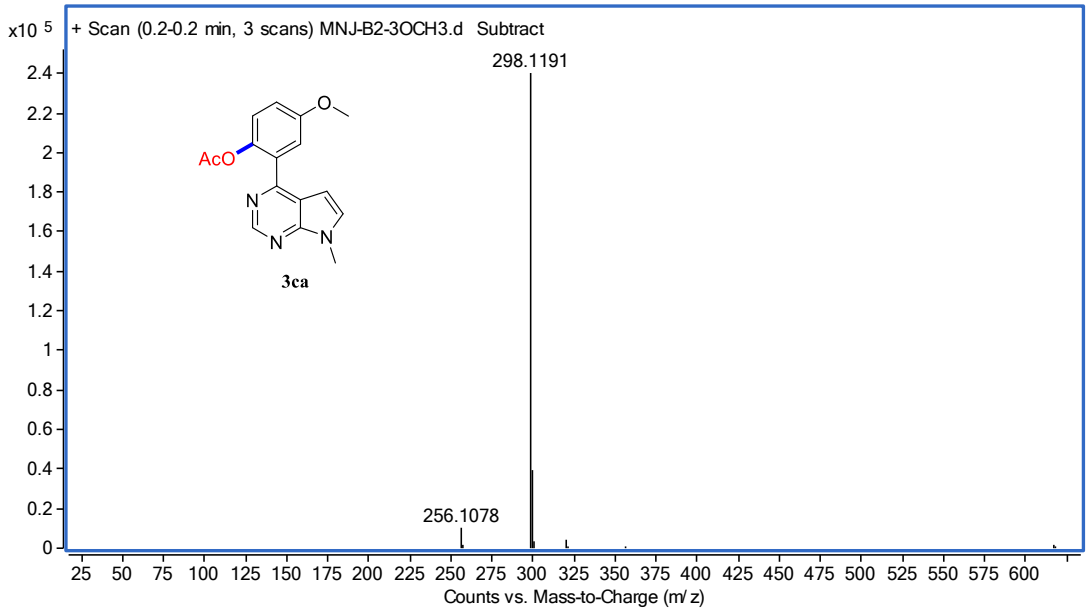
+ESI Scan (0.149 min) Frag=175.0V ZR-5P-01.d
Ph
AcO
N
N
N
3bh
344.1389
343.1659
343.0897
345.1425
Counts vs. Mass-to-Charge (m/z)

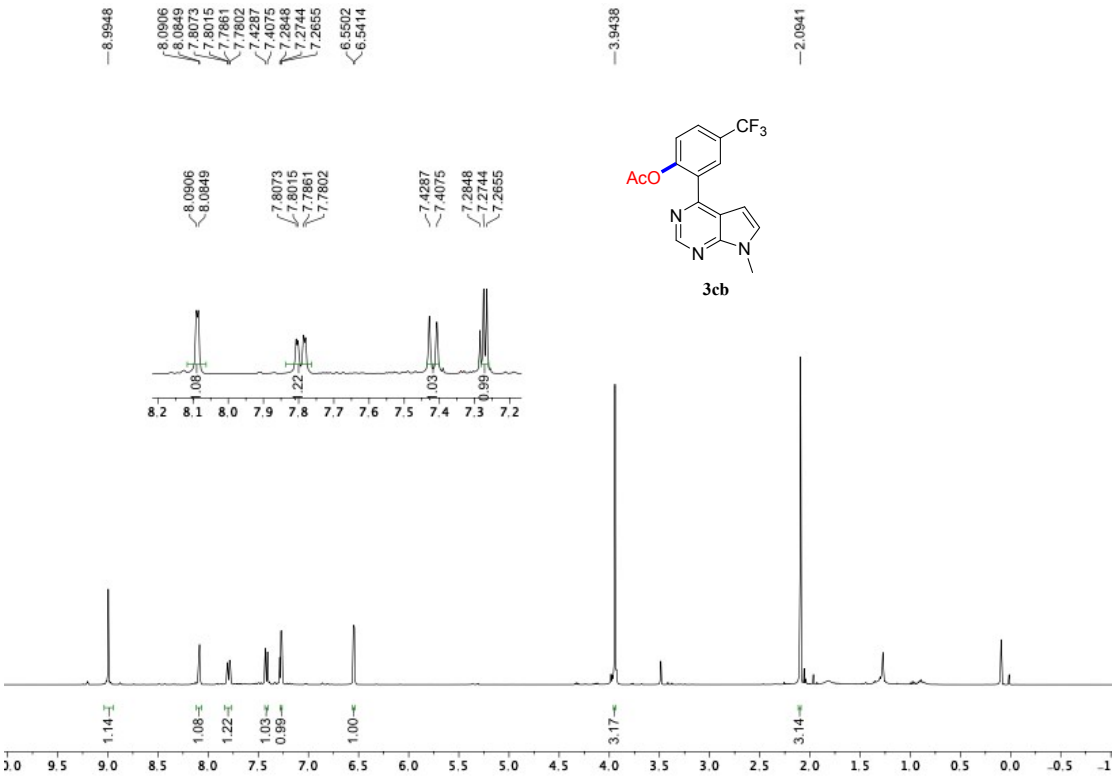

8.9634
7.2913
7.2851
7.2762
7.2149
7.2078
7.1849
7.1672
7.0556
7.0495
7.0378
7.0317
6.5817
6.5746
3.9148
3.8628
2.0283

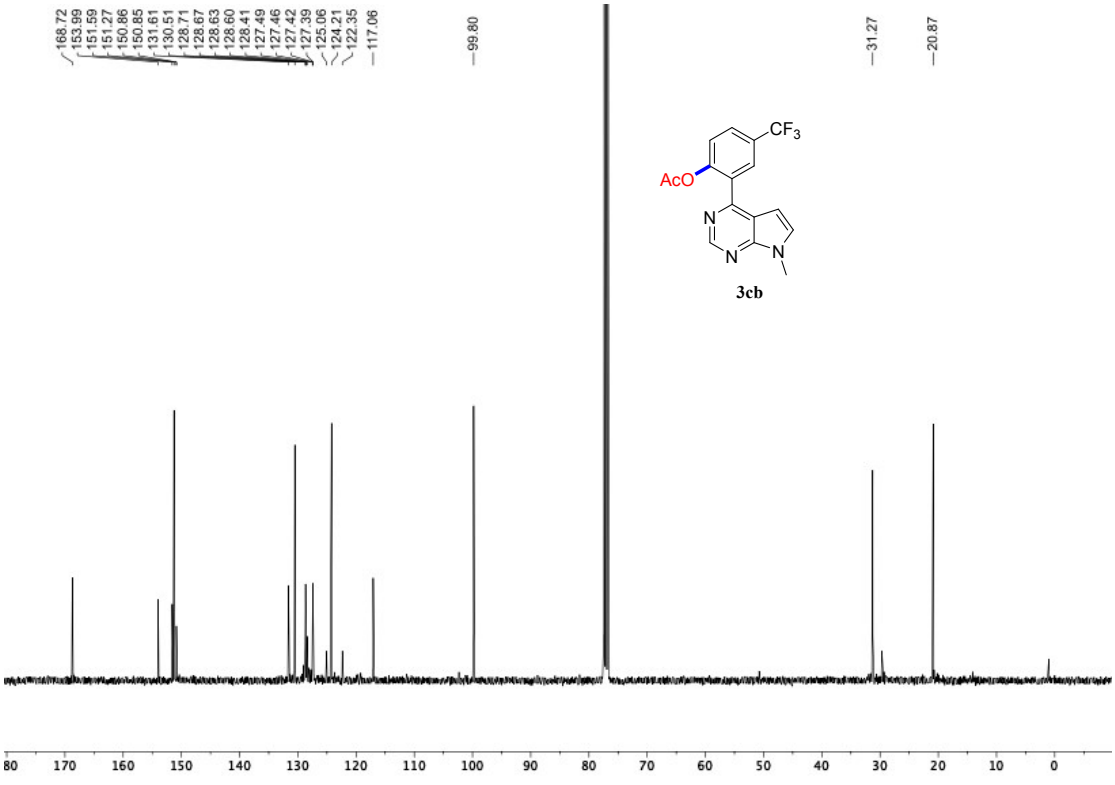

O
AcO
N
N
N
3ca

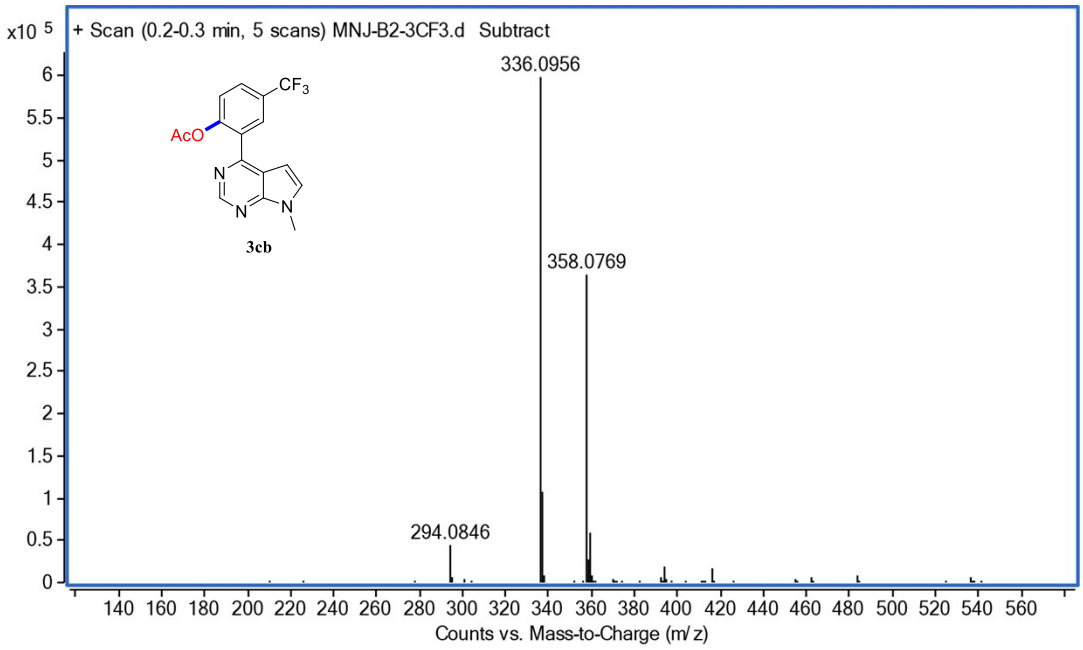

1.00
0.98
0.95
0.88
1.02
0.98
3.46
3.17
3.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

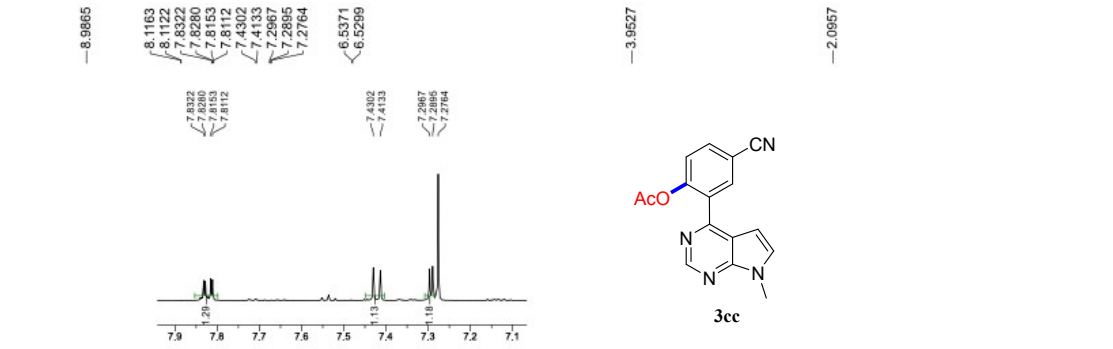

169.63
157.31
155.45
151.46
151.21
141.82
131.45
129.92
124.23
117.07
116.16
115.75
100.27
55.76
31.19
20.84
AcO
O
N
N
N
3ca
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

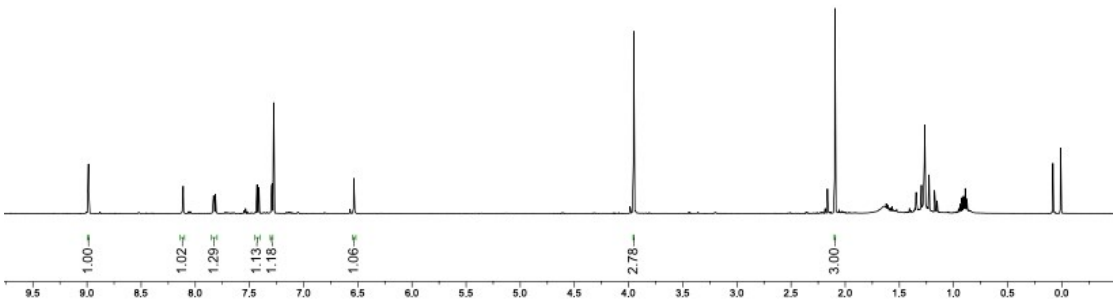

x10 5
+ Scan (0.2-0.2 min, 3 scans) MNJ-B2-3OCH3.d Subtract
298.1191
256.1078
AcO
O
N
N
N
3ca
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
25 50 75 100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600
Counts vs. Mass-to-Charge (m/z)

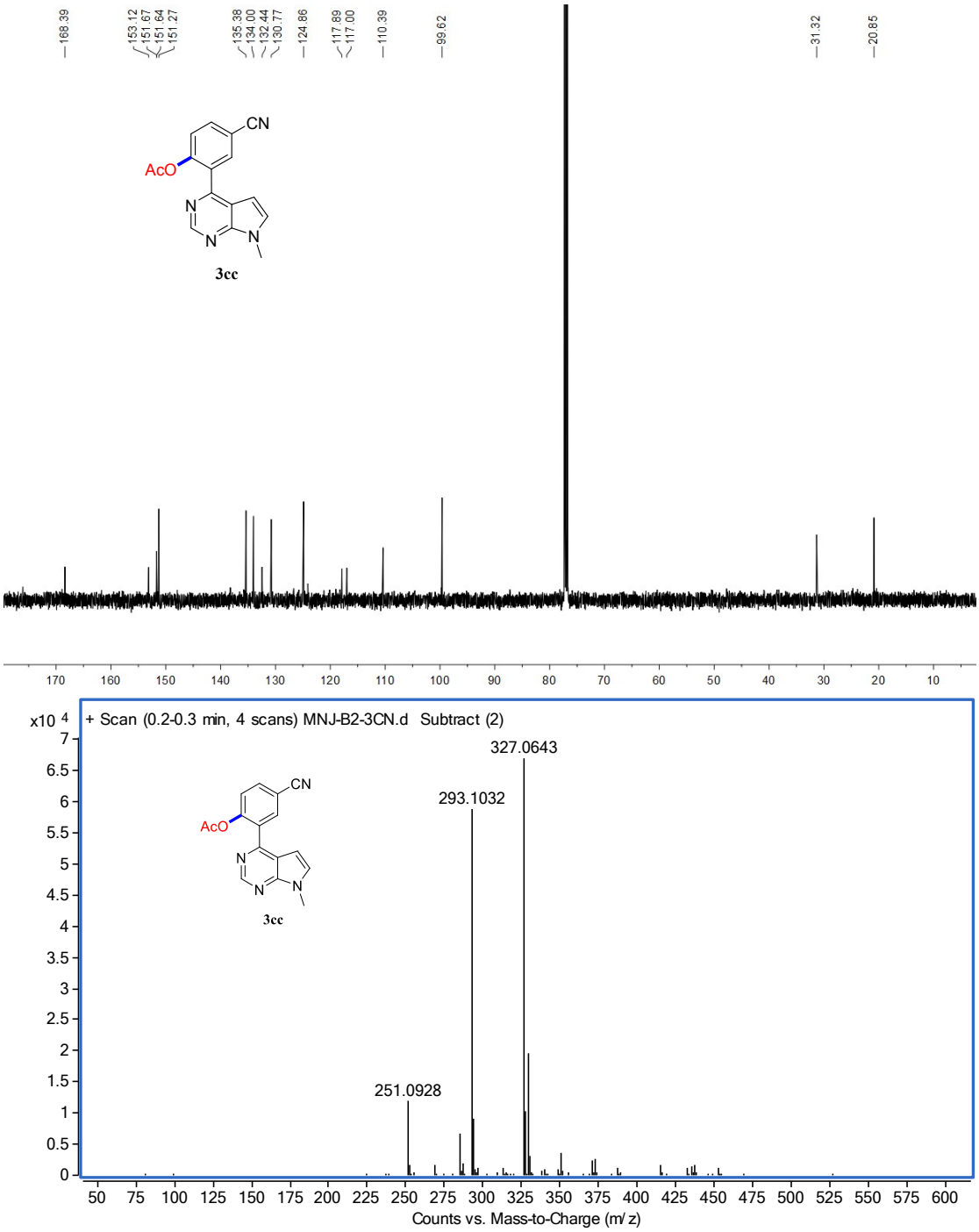

8.9948
8.0906
8.0849
7.8073
7.8015
7.7861
7.7802
7.4287
7.4075
7.2848
7.2744
7.2655
6.5502
6.5414
3.9438
2.0941
CF3
AcO
N
N
N
3cb
1.08
1.22
1.03
0.99
1.14
1.00
3.17
3.14

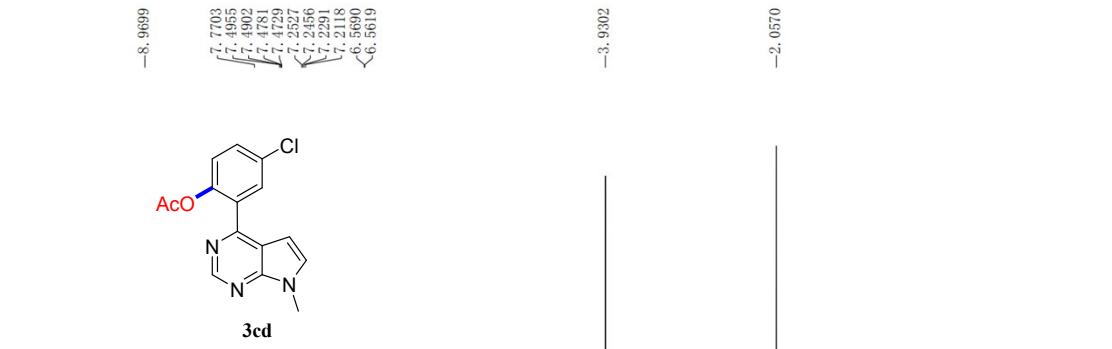

168.72
153.99
151.59
151.27
150.86
150.85
131.61
130.51
128.71
128.67
128.63
128.60
128.41
127.49
127.46
127.42
127.39
125.06
124.21
122.35
117.06
99.80
31.27
20.87
CF3
AcO
N
N
N
3cb

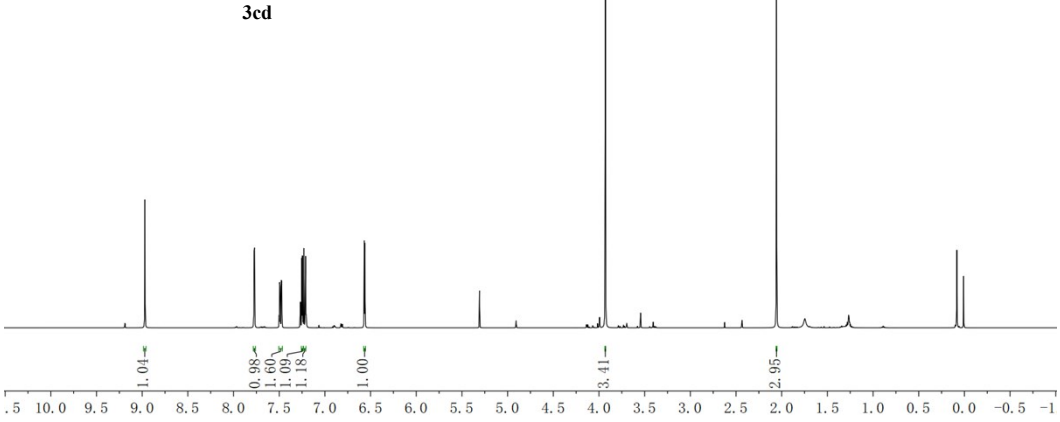

x10 5
+ Scan (0.2-0.3 min, 5 scans) MNJ-B2-3CF3.d Subtract
336.0956
358.0769
294.0846
CF3
AcO
N
N
N
3cb
Counts vs. Mass-to-Charge (m/z)

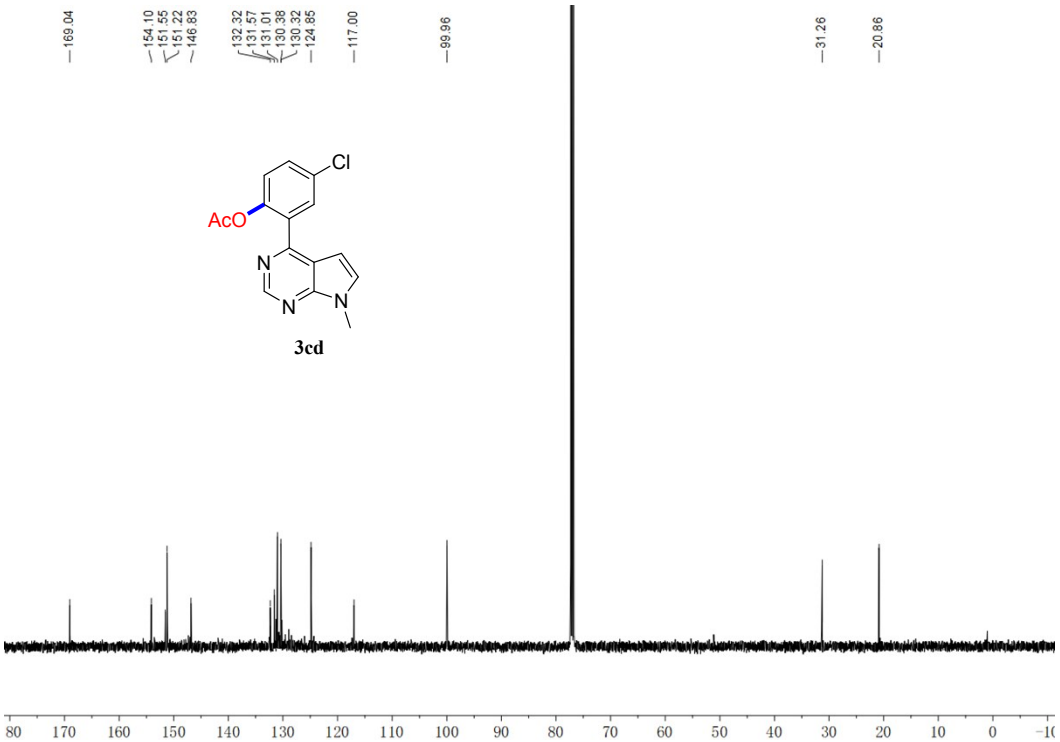

8.9865
8.1163
8.1122
7.8322
7.8280
7.8153
7.8112
7.4302
7.4133
7.2967
7.2895
7.2764
6.5371
6.5299
3.9527
2.0957
CN
AcO
N
N
N
3cc

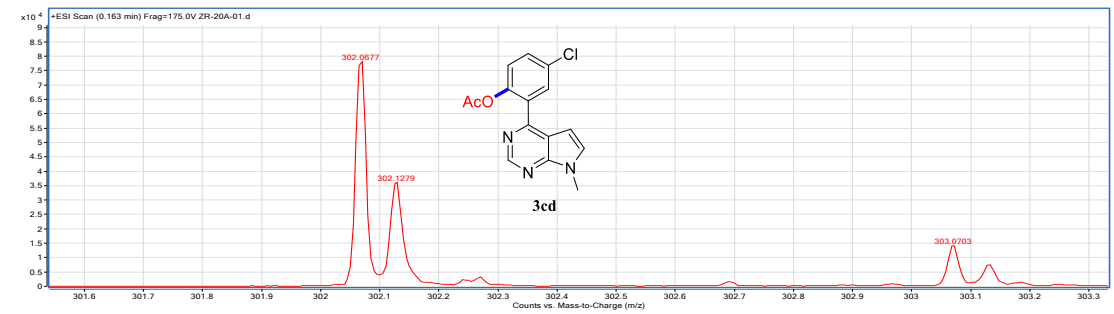

1.00
1.02
1.29
1.13
1.18
1.06
2.78
3.00


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
CN
AcO
N
N
N
3cc
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
x10 4
+ Scan (0.2-0.3 min, 4 scans) MNJ-B2-3CN.d Subtract (2)
327.0643
293.1032
251.0928
CN
AcO
N
N
N
3cc
7 6.5 6 5.5 5 4.5 4 3.5 3 2.5 2 1.5 1 0.5 0
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)


8.9699
7.7703
7.4955
7.4902
7.4781
7.4729
7.2527
7.2456
7.2291
7.2118
6.5690
6.5619
3.9302
2.0570
Cl
AcO
N
N
N
3cd

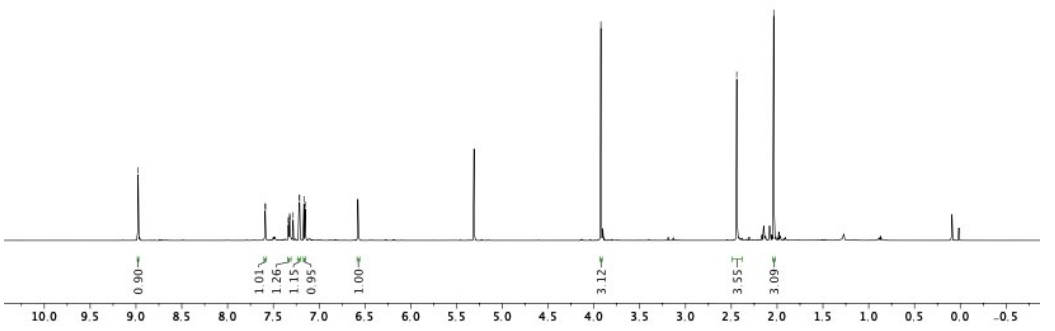

1.04
0.98
1.60
1.09
1.18
1.00
3.41
2.95

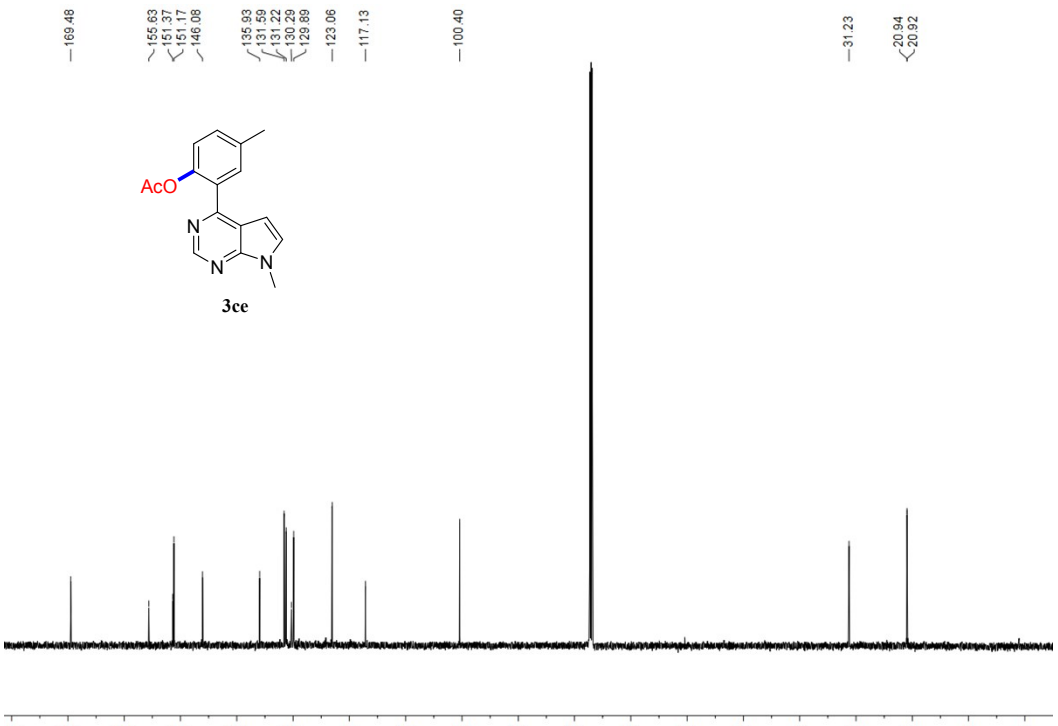

169.04
154.10
151.55
151.22
146.83
132.32
131.57
131.01
130.38
130.32
124.85
117.00
99.96
31.26
20.86
Cl
AcO
N
N
N
3cd


+ESI Scan (0.163 min) Frag=175.0V ZR-20A-01.d
302.0677
302.1279
303.0703
Cl
AcO
N
N
N
3cd
Counts vs. Mass-to-Charge (m/z)

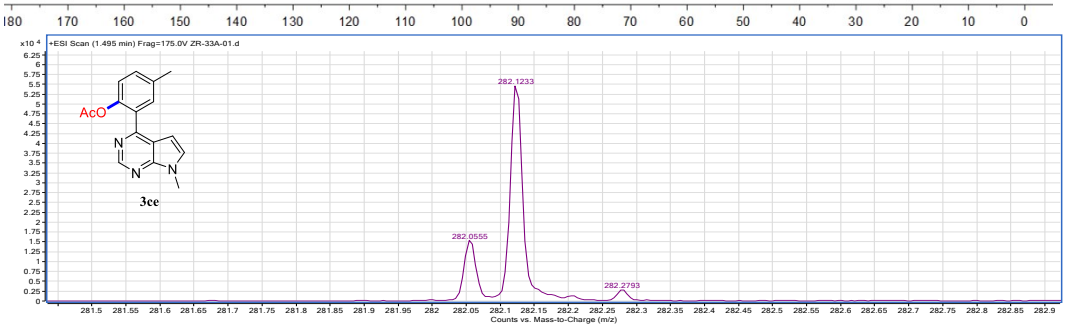

8.9767
7.5891
7.5854
7.3368
7.3331
7.3231
7.3192
7.2843
7.2191
7.2132
7.1661
7.1524
3.9243
2.4412
2.0374
AcO
N
N
N

3ce

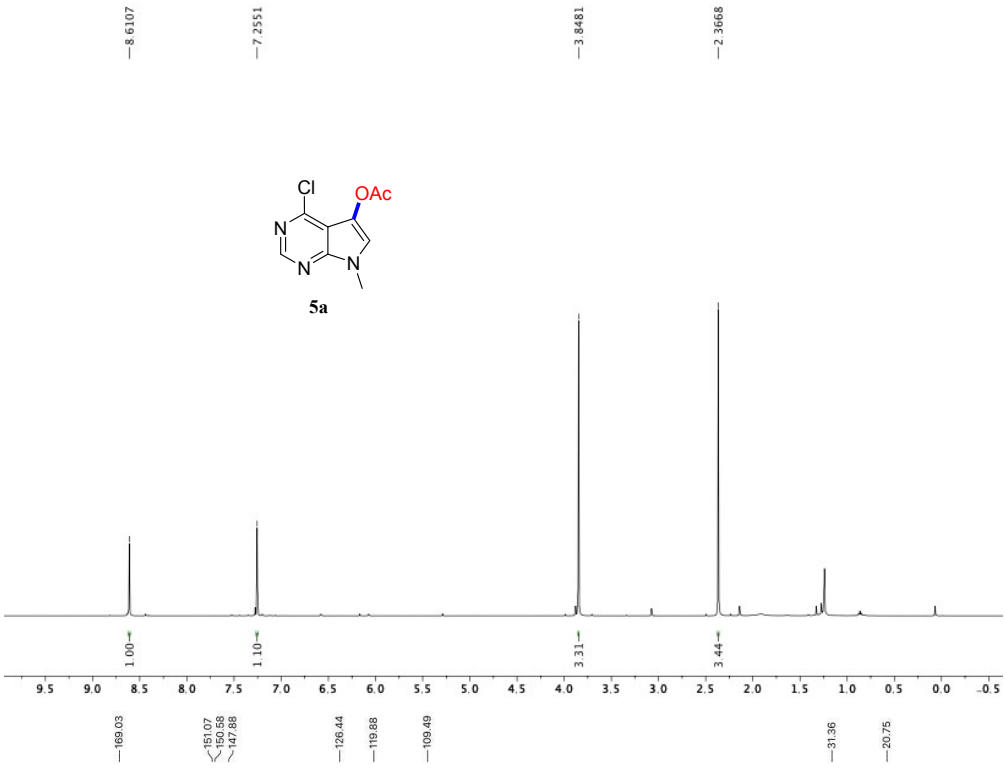

0.90
1.01
1.26
1.15
0.95
1.00
3.12
3.55
3.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

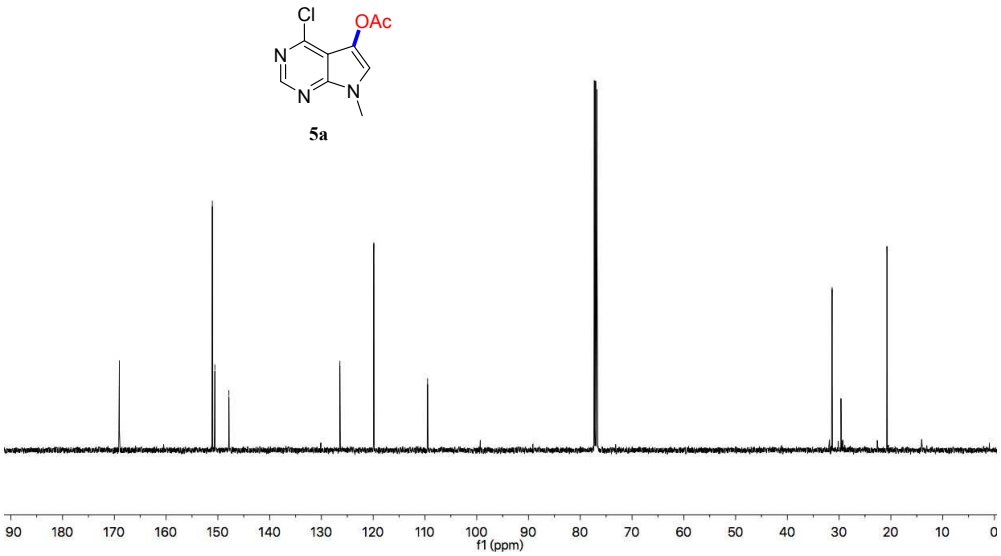

169.48
155.63
151.37
151.17
146.08
135.93
131.59
131.22
130.29
129.89
123.06
117.13
100.40
31.23
20.94
20.92
AcO
N
N
N

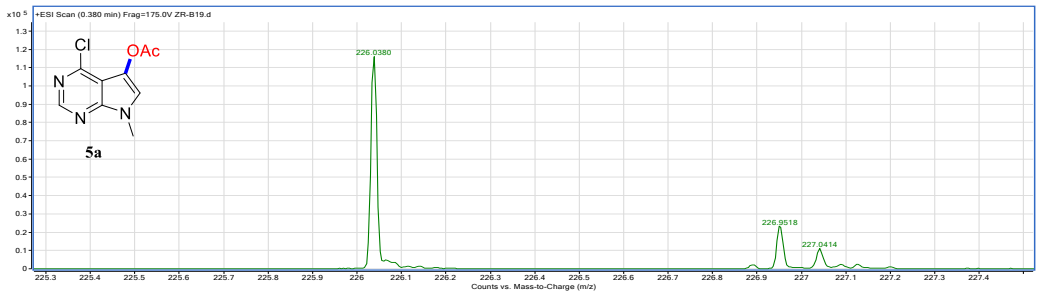
3ce

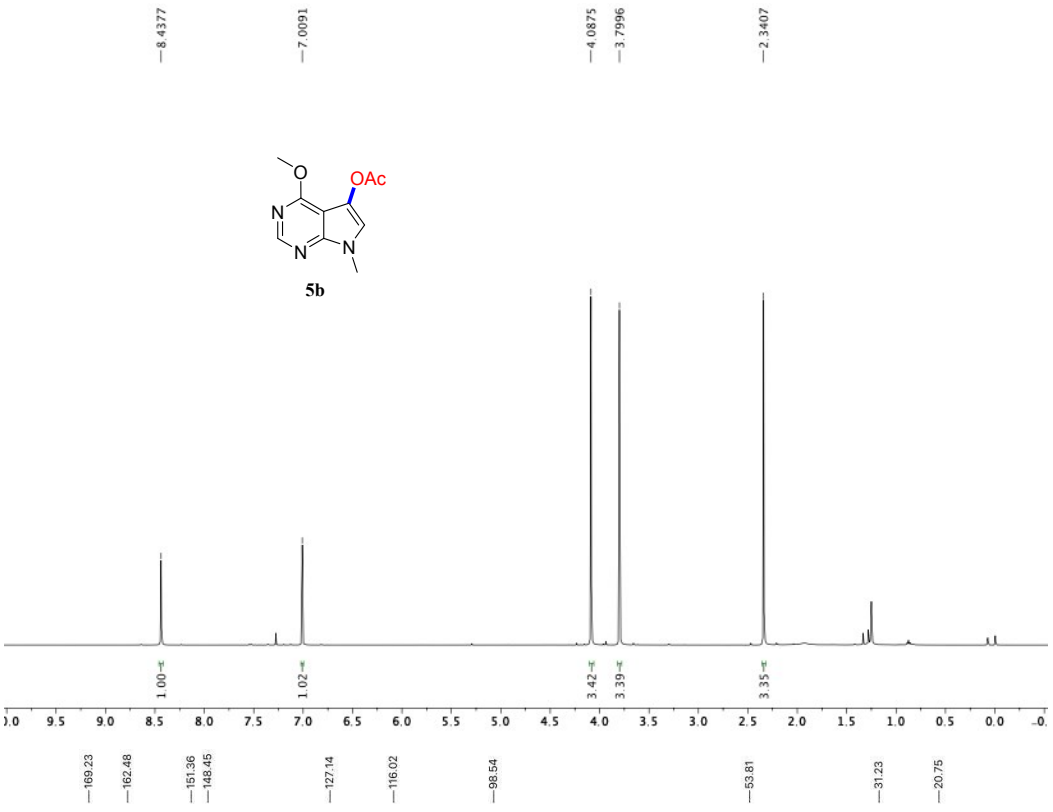

+ESI Scan (1.495 min) Frag=175.0V ZR-33A-01.d
282.1233
282.0555
282.2793
AcO
N
N
N
Counts vs. Mass-to-Charge (m/z)

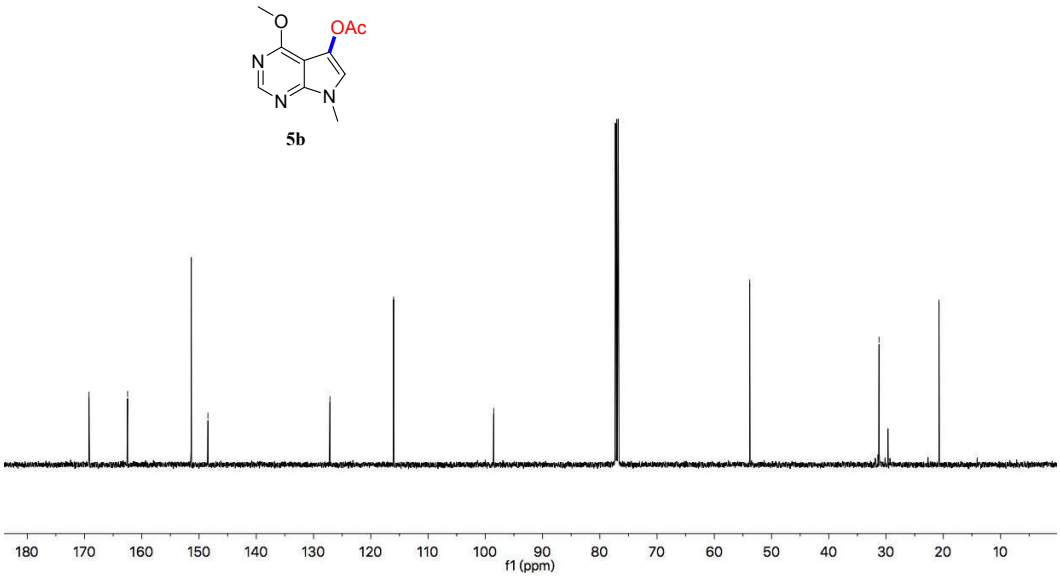
3ce

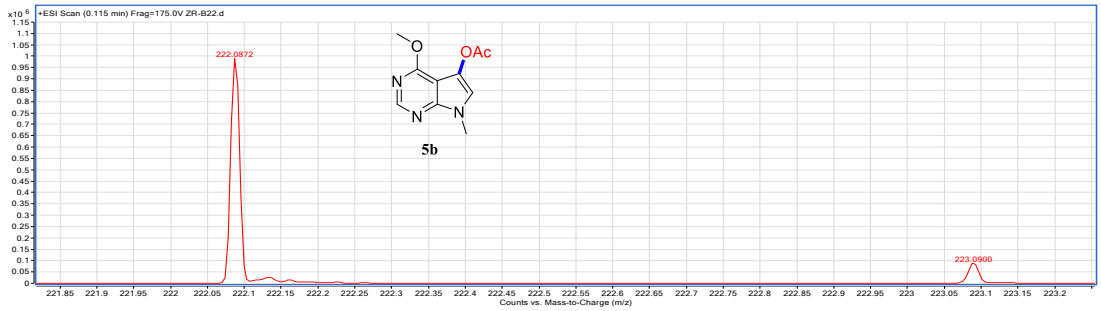

8.6107
7.2551
3.8481
2.3668
Cl
OAc
N
N
N
5a
1.00
1.10
3.31
3.44
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
169.03
161.07
150.58
147.88
126.44
119.88
109.49
31.36
20.75

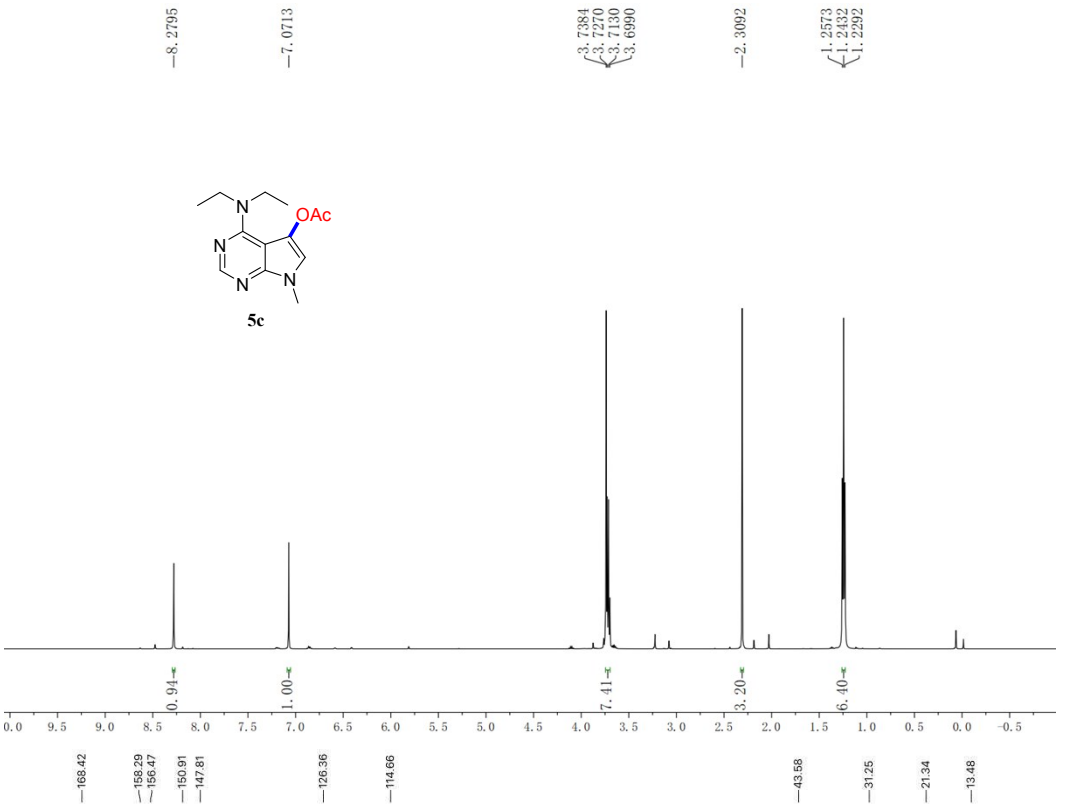

Cl
OAc
N
N
N
5a
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

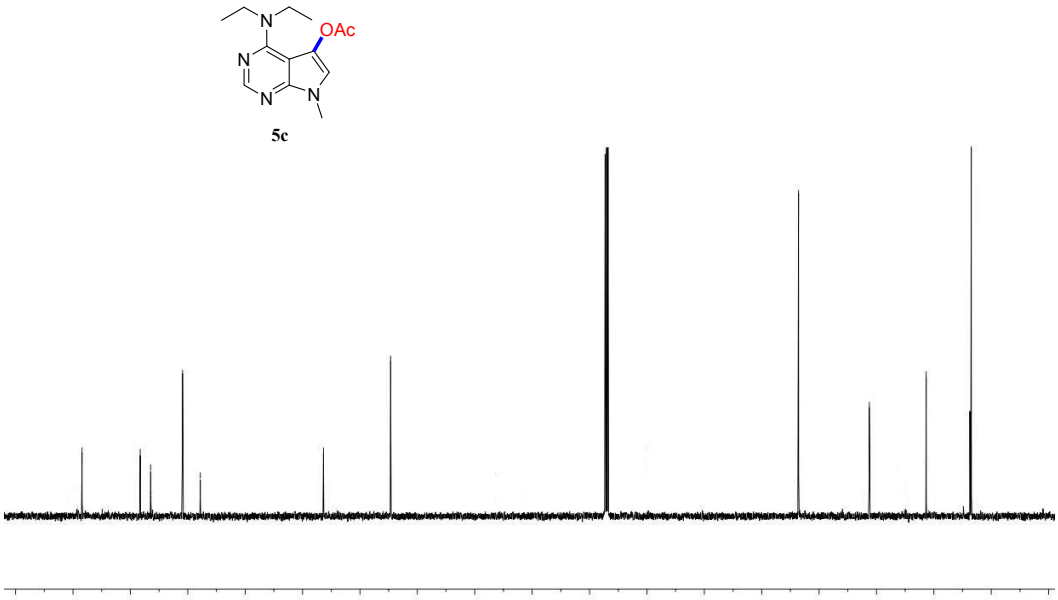

+ESI Scan (0.380 min) Frag=175.0V ZR-B19.d
Cl
OAc
N
N
N
5a
226.0380
226.9518
227.0414
Counts vs. Mass-to-Charge (m/z)

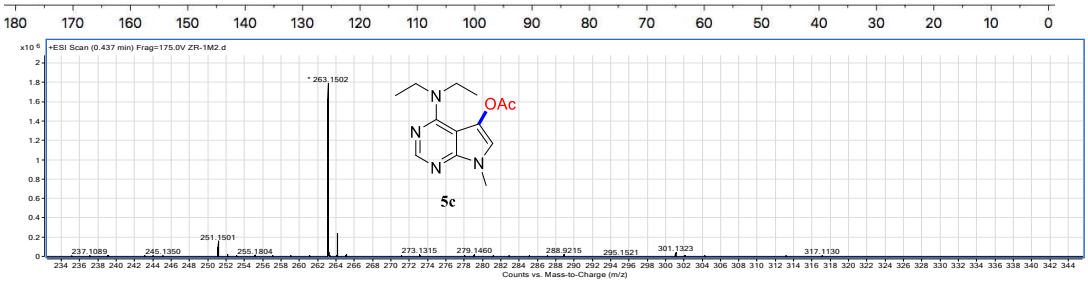

8.4377
7.0091
4.0875
3.7996
2.3407
OAc
5b
1.00
1.02
3.42
3.39
3.35


169.23
162.48
151.36
148.45
127.14
116.02
98.54
53.81
31.23
20.75
OAc
5b
f1 (ppm)

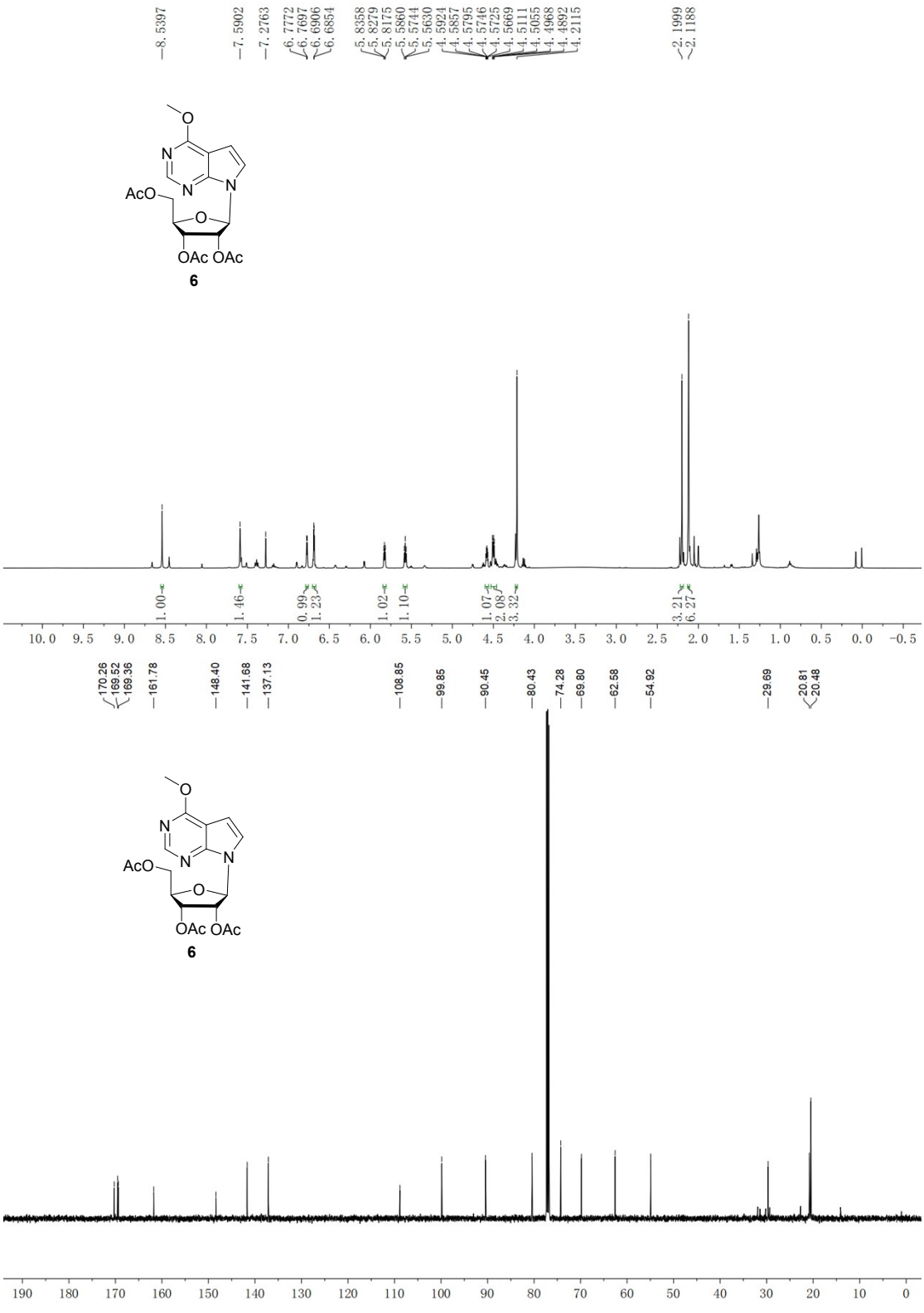

+ESI Scan (0.115 min) Frag=175.0V ZR-B22.d
222.0872
223.0900
OAc
5b
Counts vs. Mass-to-Charge (m/z)

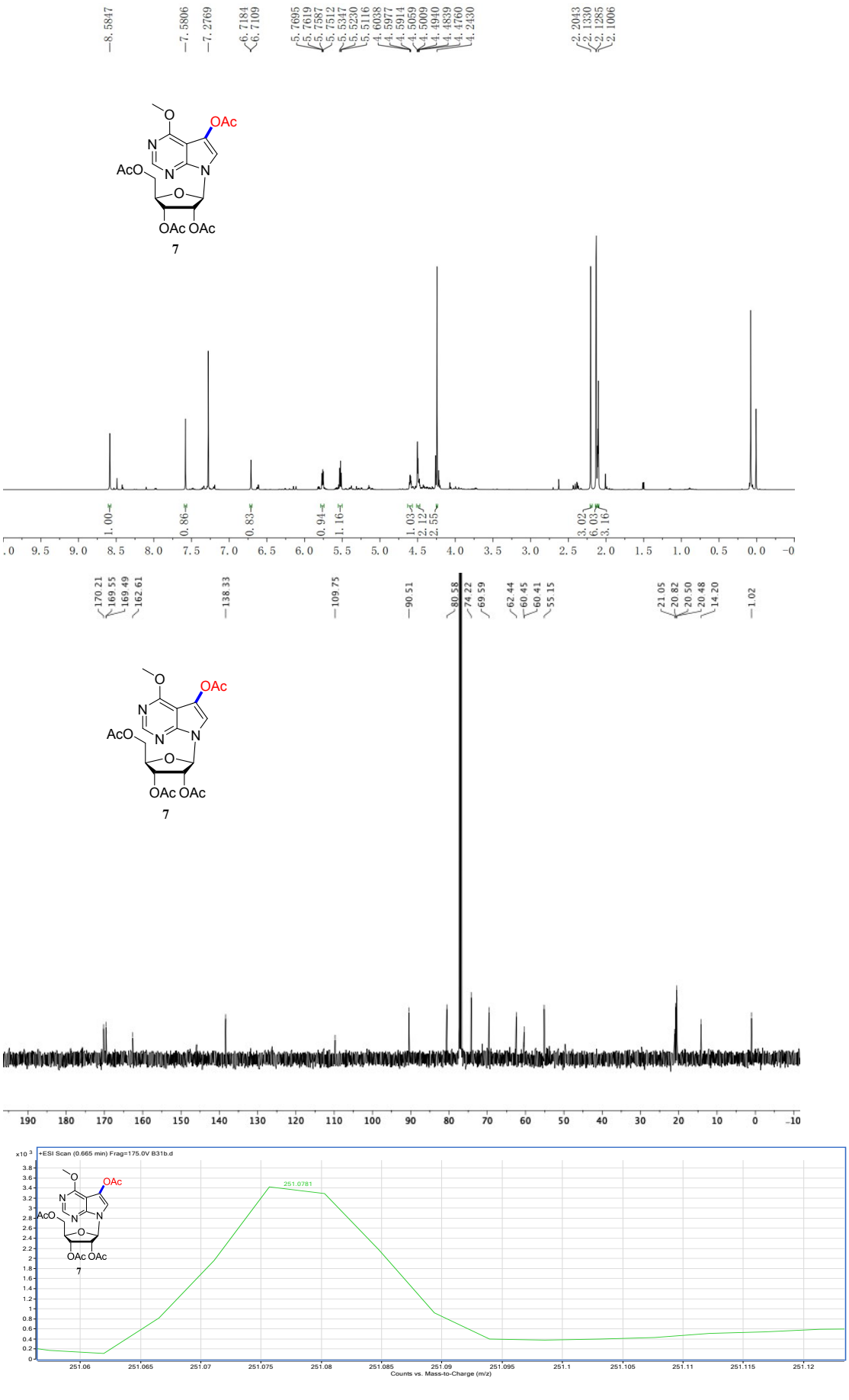

8.2795
7.0713
7.7384
7.7270
7.7130
7.6990
2.3092
1.2573
1.2432
1.2292
OAc
5c
0.94
1.00
7.41
3.20
6.40
168.42
158.29
156.47
150.91
147.81
126.36
114.66
43.58
31.25
21.34
13.48


OAc
5c

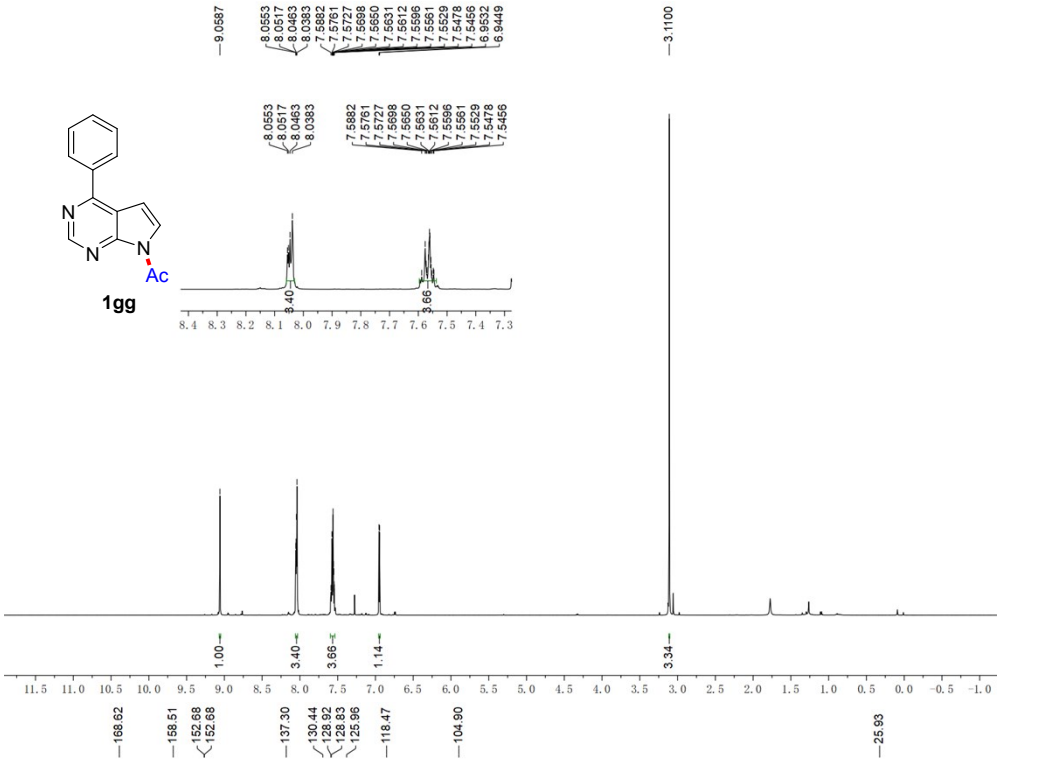


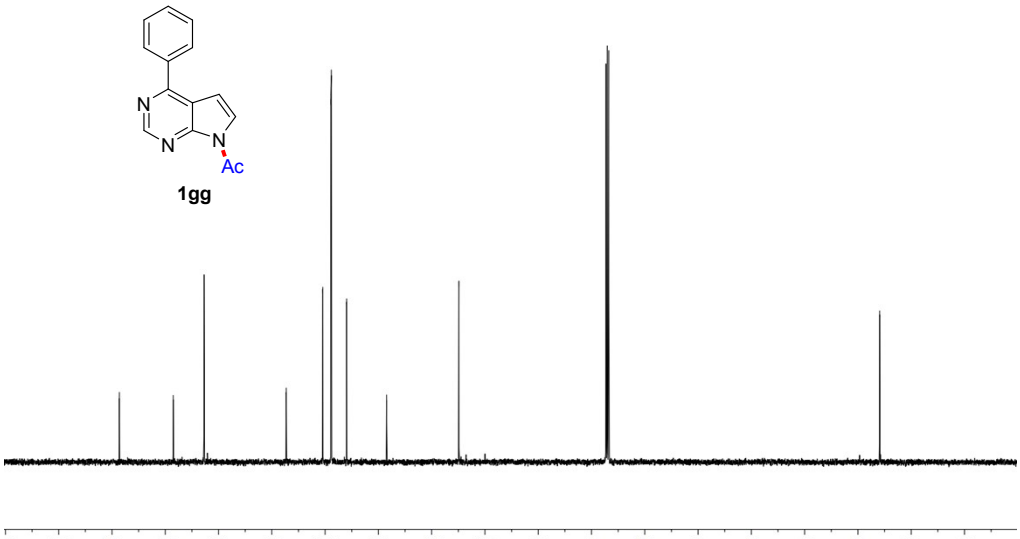
+ESI Scan (0.437 min) Frag=175.0V ZR-1M2.d
263.1502
OAc
5c
251.1501
237.1089
245.1350
255.1804
273.1315
279.1460
288.9215
295.1521
301.1323
317.1130
Counts vs. Mass-to-Charge (m/z)

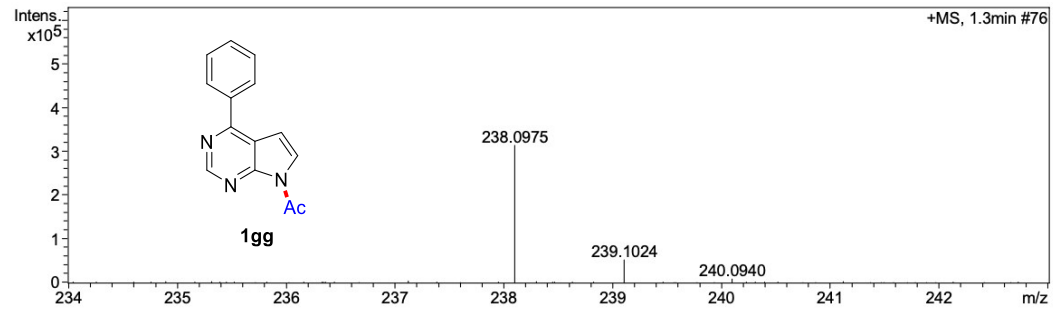

8.5397
7.5902
7.2763
6.7772
6.7697
6.6906
6.6854
5.8358
5.8279
5.8175
5.5860
5.5744
5.5630
4.5924
4.5857
4.5795
4.5746
4.5725
4.5669
4.5111
4.5055
4.4968
4.4892
4.2115
2.1999
2.1188
AcO
OAc OAc
6
1.00
1.46
0.99
1.23
1.02
1.10
1.07
2.08
3.32
3.21
6.27
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
170.26
169.52
169.36
161.78
148.40
141.68
137.13
108.85
99.85
90.45
80.43
74.28
69.80
62.58
54.92
29.69
20.81
20.48
AcO
OAc OAc
6
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


8.5847
7.5806
7.2769
6.7184
6.7109
5.7695
5.7619
5.7587
5.7512
5.5347
5.5230
5.5116
4.6038
4.5977
4.5914
4.5059
4.5009
4.4940
4.4839
4.4760
4.2430
2.2043
2.1330
2.1285
2.1006
OAc
AcO
OAc OAc
7
1.00
0.86
0.83
0.94
1.16
1.03
2.12
2.55
3.02
6.03
3.16
170.21
169.55
169.49
162.61
138.33
109.75
90.51
80.58
74.22
69.59
62.44
60.45
60.41
55.15
21.05
20.82
20.50
20.48
14.20
1.02
OAc
AcO
OAc OAc
7
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

+ESI Scan (0.665 min) Frag=175.0V B31b.d
x10 3
251.0781
OAc
AcO
OAc OAc
7
251.06
251.065
251.07
251.075
251.08
251.085
251.09
251.095
251.1
251.105
251.11
251.115
251.12
Counts vs. Mass-to-Charge (m/z)

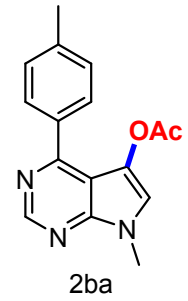

1gg


1gg


1gg
+MS, 1.3min #76
238.0975
239.1024
240.0940
m/z

6. Single Crystal X-ray Diffraction Data for Compounds 2ba

Figure S1. X-ray crystal structure of **2ba**



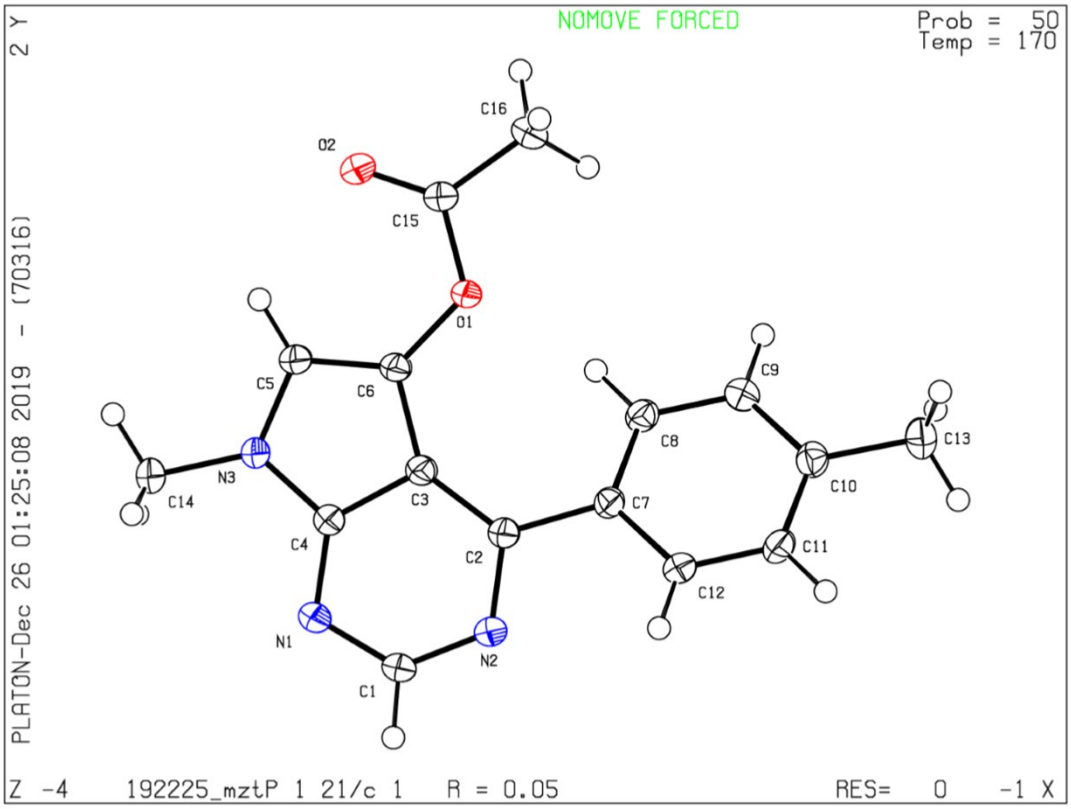


Table S2. Crystal data and structure refinement for 2ba.

Datablock: 192225_mzt_21b_0m_tw

```
Bond precision:  C-C = 0.0022 A          Wavelength=0.71073

Cell:            a=19.365(9)     b=10.189(4)          c=6.932(3)
                 alpha=90        beta=96.906(17)      gamma=90
Temperature:     170 K

                 Calculated                Reported
Volume           1357.8(10)                1357.8(9)
Space group      P 21/c                    P 1 21/c 1
Hall group       -P 2ybc                   -P 2ybc
Moiety formula   C16 H15 N3 O2             C16 H15 N3 O2
Sum formula      C16 H15 N3 O2             C16 H15 N3 O2
Mr               281.31                    281.31
Dx,g cm-3        1.376                     1.376
Z                4                         4
Mu (mm-1)        0.093                     0.093
F000             592.0                     592.0
F000'            592.25
h,k,lmax         24,13,8                   24,13,8
Nref             2999                      2970
Tmin,Tmax        0.975,0.982               0.671,0.746
Tmin'            0.955

Correction method= # Reported T Limits: Tmin=0.671 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.990          Theta(max)= 27.135

R(reflections)= 0.0516( 2566)     wR2(reflections)= 0.1361( 2970)

S = 1.060                 Npar= 194
```

7. HRMS of $PhI(OCOEt)_2$

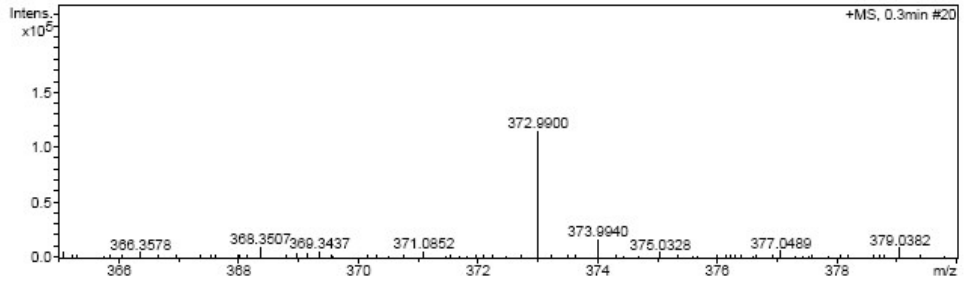
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\2020\0725\2_1-D,1_01_13693.d	Acquisition Date	7/25/2020 6:17:30 PM
Method	lc_pos_3min_hn.m	Operator	BDAL@DE
Sample Name	2	Instrument / Ser#	micrOTOF-Q II 10366
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.8 Bar
Focus	Not active	Set Capillary	5500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	950 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste



Meas. m/z	Formula	m/z	err [ppm]	mSigma
372.9900	C 12 H 15 I Na O 4	372.9907	2.1	13.0