Supporting Information

New Artificial Fluoro-Cofactor of Hydride Transfer with Novel Fluorescence assay for Redox Biocatalysis

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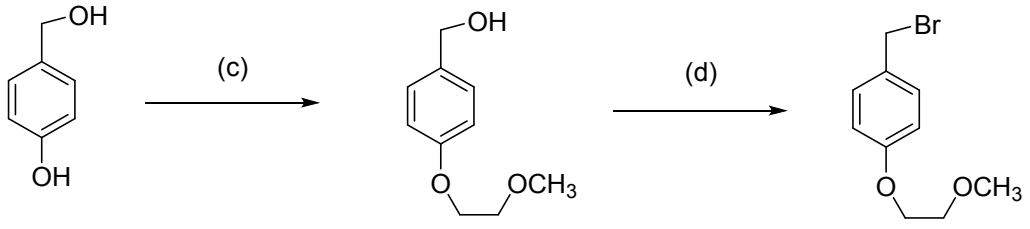
1 Materials and general methods

All chemical reagents were commercial products without further purification. Ultra-pure water was used to prepare all aqueous solutions and reactions. Other solvents were of analytic grade. All reactions were monitored by thin-layer chromatography (TLC). Column chromatography was performed using silica gel (Hailang, Qingdao) 300-400 mesh. ^{1}H and ^{13}C NMR spectra were recorded by employing a Bruker AV-400 spectrometer with chemical shifts expressed in parts per million (in DMSO-d_6, D_2O, Me_4Si as internal standard). High-resolution mass spectra (HRMS) were obtained on a Bruker EI TOF MS by Electrospray Ionization Mass Spectrometry (ESI). Fluorescence spectra were determined on a VARIAN CARY Eclipse Fluorescence spectrophotometer. Absorption spectra were determined on a VARIAN CARY 100 Bio UV-Visible spectrophotometer. Cyclic voltammetry was carried on Gamry Interface 1000.

2 Synthesis



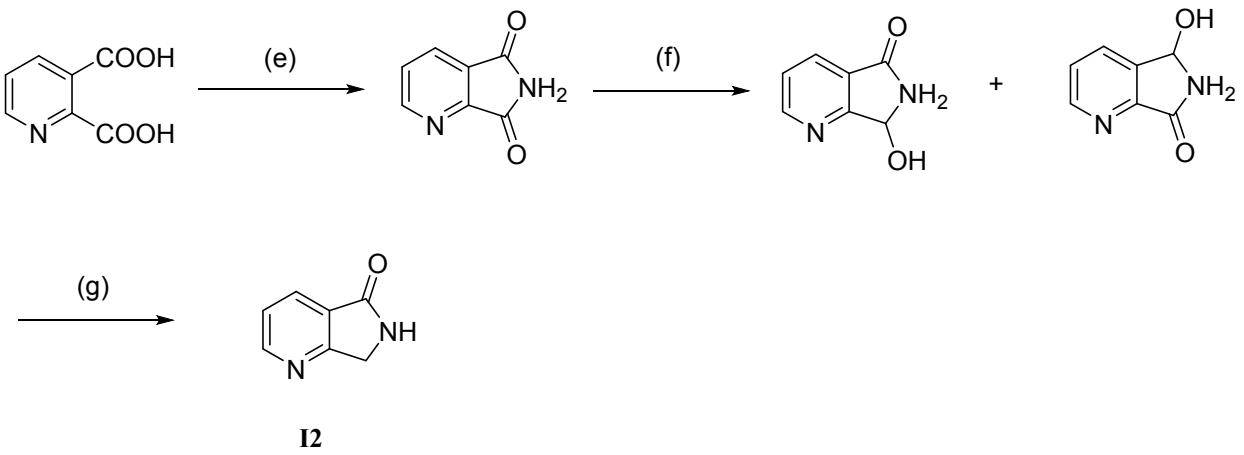
I1

Scheme S1 Synthesis of key intermediated **I1**

Reactions and conditions: (c) 1-Bromo-2-methoxyethane, 18-crown-6, K_2CO_3, acetone reflux for 72 h; (d) PBr_3, Et_2O , in Ar at rt for 6h.

Preparation of I1

Compounds **I1** was prepared according to the reported procedure.[1]



I2

Scheme S2 Synthesis of key intermediated **I2**

Reactions and conditions: (e) $AcNH_2$, Ac_2O, reflux; (f) -20 ^oC, $NaBH_4$, $CHCl_3$-MeOH(1:1, v/v); (g) Zn, CH_3COOH, 100 ^oC for 6 h;

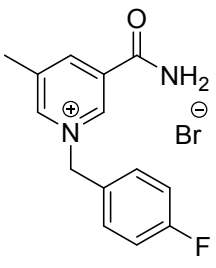
Preparation of I2

Compounds **I2** was prepared according to the reported procedure.[2]

Preparation of BNAH, 2b, 5b, 8b,9b

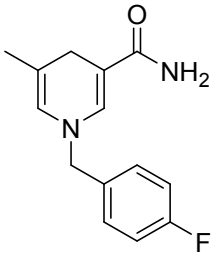
Compounds **BNAH, 2b, 5b, 8b,9b** was prepared according to the reported procedure.[3]

3-carbamoyl-1-(4-fluorobenzyl)-5-methylpyridin-1-ium bromide (3a)



To a solution of 5-methyl-nicotinamide 0.272 g (2 mmol) in acetonitrile (6 mL) was added a solution of 4-fluorobenzyl bromide 0.451 g (2.4 mmol) in acetonitrile (4 mL) dropwise. The reaction mixture was reflux for 8 h, yielding a white solid. After cooling to room temperature, the solution was added diethyl ether (3 mL) to further precipitate product. After filtering and washing with 3 × 3 mL diethyl ether, **3a** was obtained as a white solid with 70% yield. ^{1}H NMR (400 MHz, D_2O): δ (ppm) 9.14 (s, 1H), 8.87 (s, 1H), 8.72 (s, 1H), 7.51 (dd, J_1 =5.2 Hz, J_2 = 8.4 Hz, 2H), 7.21 (t, J = 8.8 Hz, 2H), 5.81 (s, 2H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 163.8, 162.8, 161.4, 145.7, 144.4, 142.0, 139.1, 133.4, 131.7, 131.6, 130.3, 130.2, 116.2, 116.0, 62.5, 17.9. HRMS (ESI) calcd for $C_{14}H_{14}N_2O$ $[M]^+$ 245.1090, found 245.1088.

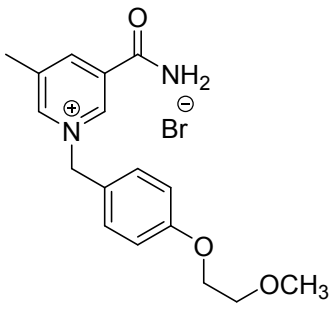
1-(4-fluorobenzyl)-5-methyl-1,4-dihydropyridine-3-carboxamide (3b)



To a solution of **3a** 0.162 g (0.5 mmol) in distilled water was added sodium bicarbonate 0.168 g (2 mmol) under Ar atmosphere. Sodium dithionite 0.348 g (2 mmol) was then added in small portions within 30 min. The reaction mixture was stirred in the dark at room tempeture for 3 h, until yellow precipitate appeared. After centrifuging, the solid was filtered and washed by ultrapure water and dried through vacuum freeze-drying equipment with 50% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.32 (dd, J_1 = 5.6 Hz, J_2 = 8.8 Hz, 2H), 7.19 (t, J = 8.8 Hz, 2H), 7.06 (s, 1H), 6.55 (s, 2H), 5.77 (s, 1H), 4.31 (s, 2H), 2.84 (s, 2H), 1.49 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ(ppm) 169.3, 162.7, 160.3, 137.2, 134.8, 129.3, 129.2, 123.7, 115.4, 115.2, 111.0, 99.4, 55.1, 28.1, 20.3. HRMS (ESI) calcd for $C_{14}H_{16}N_2OF$ $[M+H]^+$ 247.1247, found

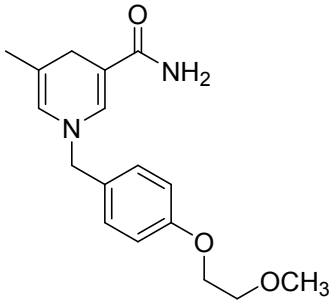
247.1209.

3-carbamoyl-1-(4-(2-methoxyethoxy)benzyl)-5-methylpyridin-1-ium bromide(4a)



To a solution of 5-methyl-nicotinamide 0.272 g (2 mmol) in acetonitrile (6 mL) was added to a solution of **I1** 0.537 g (2.2 mmol) in acetonitrile (4 mL) dropwise. After the reaction mixture was reflux for 8 h, excess solvent was removed in vacuo, following by methanol (1 mL) and diethyl ether (20 mL) and precipitate appeared. After filtering and washing with 3 × 3 mL diethyl ether, **4a** was obtained as a white solid with 71% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.70 (s, 1H), 9.26 (s, 1H), 8.85 (s, 1H), 8.56 (s, 1H), 8.17 (s, 1H), 7.57 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 5.78 (s, 2H), 4.10 (t, J = 4.4 Hz, 2H), 3.65 (t, J = 4.4 Hz,2H), 3.29 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 162.8, 159.3, 145.5, 144.3, 141.7, 139.0, 133.3, 130.8, 125.9, 114.9, 70.2, 67.0, 63.0, 58.2, 17.9. HRMS (ESI) calcd for $C_{17}H_{21}N_2O_3$ $[M]^+$ 301.1552, found 301.1546.

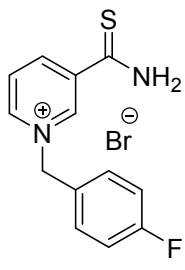
1-(4-(2-methoxyethoxy)benzyl)-5-methyl-1,4-dihydropyridine-3-carboxamide (4b)



To a solution of **4a** 0.190 g (0.5 mmol) in distilled water was added sodium bicarbonate 0.168 g (2 mmol) under Ar atmosphere. Sodium dithionite 0.348 g (2 mmol) was added in small portions within 30 min. The reaction mixture was stirred in the dark at room temperature for 3 h, precipitating brownish yellow product. After centrifuging, the solid (compound **4b**) was filtered and washed by ultrapure water and dried through vacuum

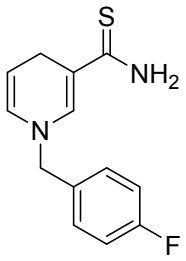
freeze-drying equipment with 50% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.18 (d, J = 8.4 Hz, 2H), 7.05 (s, 1H), 6.92 (d, J = 8.4 Hz, 2H), 6.52 (s, 2H), 5.75 (s, 1H), 4.23 (s, 2H), 4.07 (t, J = 4.8 Hz, 2H), 3.64 (t, J = 4.8 Hz, 2H), 3.30 (s, 3H), 2.84 (s, 2H), 1.48 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 169.3, 157.8, 137.3, 130.5, 128.7, 123.7, 114.5, 110.7, 99.1, 70.3, 66.8, 58.1, 55.4, 28.2, 20.3. HRMS (ESI) calcd for $C_{17}H_{22}N_2O_3Na$ $[M+Na]^+$ 325.1528, found 325.1519.

3-carbamothioyl-1-(4-fluorobenzyl)pyridin-1-ium bromide (6a)



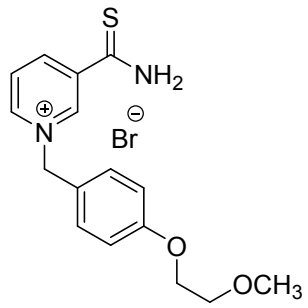
Under Ar atmosphere, a suspension of thionicotinamide (1.10 g, 8 mmol) in THF (16 mL) was heated and reflux to give a clear yellow solution, followed by adding a solution of 4-fluorobenzyl bromide (2.25 g, 12 mmol) in THF (12 mL) dropwise. The reaction mixture was allowed to reflux for another 3 h under Ar atmosphere, after which time the reaction flask was cooled in an ice-bath and the mixture was further concentrated in vacuo. The precipitate was then filtered washed with acetone and was further purified by column chromatography (DCM:MeOH = 15:1, v/v) and recrystallized by MeOH with 21% yield as yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 10.64 (s, 1H), 10.23 (s, 1H), 9.67 (s, 1H), 9.27 (d, J = 6.0 Hz, 1H), 8.87(d, J =8.0 Hz, 1H), 8.22 (dd, J_1 =6.0 Hz, J_2 = 8.0 Hz, 1H), 7.72 (dd, J_1 = 5.2 Hz, J_2 = 8.4 Hz, 2H), 7.32 (t, J = 8.8 Hz, 2H), 5.94 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ(ppm) 192.6, 163.8, 161.4, 145.5, 143.8, 142.8, 139.2, 131.8, 131.7, 130.1, 127.8, 116.2, 116.0, 62.6. HRMS(ESI)calcd for $C_{13}H_{12}N_2SF$ $[M]^+$ 247.0705, found 247.0698.

1-(4-fluorobenzyl)-1,4-dihydropyridine-3-carbothioamide (6b)



To a solution of **6a** 0.081 g (0.25 mmol) in distilled and deoxygenated water was added sodium bicarbonate 0.084 g (1 mmol) under Ar atmosphere. Sodium dithionite 0.174 g (1 mmol) was added in small portions within 30 min. The reaction mixture was stirred in the dark at room temperature for 3 h. When yellow oil appeared on the sidewall, the reaction solution was sucked away via syringe under argon and the yellow oil was washed with 3 × 3 mL deoxygenated water. Freeze-drying gets brwon solid with 19% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.33 (m, 2H)，7.20 (m, 2H), 7.00 (s, 1H), 6.58 (s, 2H), 5.94 (d, J = 7.6 Hz, 2H), 4.62 (t, J = 4.0 Hz,1H), 4.30 (s, 2H), 2.96 (s,2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ(ppm) 169.0, 162.7, 160.3, 137.7, 134.8, 134.7, 129.6, 129.3, 129.2, 115.4, 115.2, 101.9, 100.6, 55.0, 22.3. HRMS (ESI) calcd for $C_{13}H_{13}FN_2S$ $[M+H]^+$ 249.0862, found 249.0853.

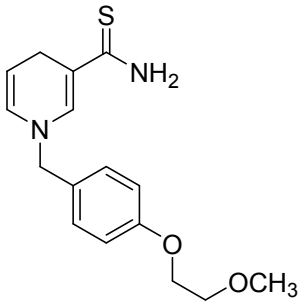
3-carbamothioyl-1-(4-(2-methoxyethoxy)benzyl)pyridin-1-ium bromide (7a)



Under Ar atmosphere, a suspension of thionicotinamide (1.10 g, 8 mmol) in THF (16 mL) was heated and reflux to give a clear yellow solution, followed by adding a solution of **I1** (2.66 g, 12 mmol) in THF (12 mL) dropwise. The reaction mixture was allowed to reflux for another 3 h under Ar atmosphere, after which time the reaction flask was cooled in an ice-bath and the mixture was further concentrated in vacuo. The precipitate was then filtered washed with acetone and was further purified by column chromatography (DCM:MeOH = 15:1, v/v) and recrystallized by MeOH with 22% yield as yellow solid. ^{1}H NMR (400 MHz, D_2O): δ (ppm) 10.64 (s, 1H), 10.21 (s, 1H), 9.61 (s, 1H),

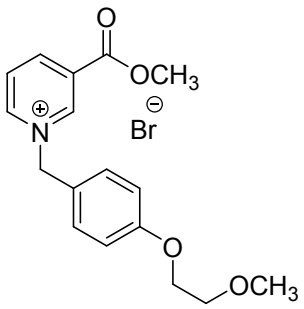
9.22 (d, J = 6 Hz, 2H), 8.83 (d, J = 8.4 Hz, 2H), 8.19 (dd, J_1 =6.0 Hz, J_2 = 8.0 Hz, 1H), 7.57 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 5.84 (s, 2H), 4.10 (t, J = 4.4 Hz, 2H), 3.65 (t, J = 4.4 Hz,2H), 3.29(s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ(ppm) 191.6, 156.5, 142.4, 140.8, 139.6, 137.0, 128.5, 125.2, 122.2, 112.8, 67.6, 64.3, 61.8, 55.4. HRMS (ESI) calcd for $C_{16}H_{19}N_2O_2S$ $[M]^+$ 303.1167, found 303.1154.

1-(4-(2-methoxyethoxy)benzyl)-1,4-dihydropyridine-3-carbothioamide (7b)



To a solution of **7a** 0.096 g (0.25 mmol) in distilled and deoxygenated water was added sodium bicarbonate 0.084 g (1 mmol) under Ar atmosphere. Sodium dithionite 0.174 g (1 mmol) was added in small portions within 30 min. The reaction mixture was stirred in the dark at room temperature for 3 h. When yellow oil appeared on the sidewall, the reaction solution was sucked away via syringe under argon and the yellow oil was washed with 3 × 3 mL deoxygenated water. Freeze-drying gets brwon solid with 22% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.20 (d, J = 8.4 Hz, 2H), 6.98 (s, 1H), 6.93 (d, J = 8.4 Hz, 2H), 6.55 (s, *2*H), 5.92 (d, J = 8.0 Hz, 1H), 4.59 (m, 1H), 4.22 (s, 2H), 4.07 (t, J = 4.8 Hz, 2H), 3.64 (t, J = 4.8 Hz, 2H), 3.30 (s, 3H), 2.95 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): 169.0, 157.8, 137.8, 130.4, 129.6, 128.7, 114.5, 101.7, 100.2, 70.3, 66.8, 58.1, 55.3, 22.4. HRMS (ESI) calcd for $C_{16}H_{20}N_2O_2S$ $[M+H]^+$ 305.1324, found 305.1326.

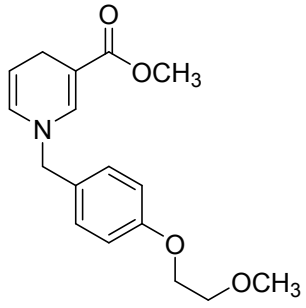
3-(methoxycarbonyl)-1-(4-(2-methoxyethoxy)benzyl)pyridin-1-ium bromide(10a)



To a solution of methyl nicotinate 0.274 g (2 mmol) in acetonitrile (6 mL) was added to a solution of **I1** 0.683 g (2.8 mmol) in acetonitrile (4

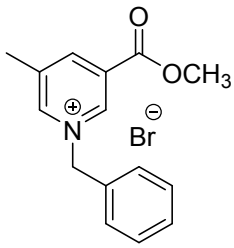
mL) dropwise. After the reaction mixture was reflux for 8 h, excess solvent was removed in vacuo, following by methanol (1 mL) and diethyl ether (20 mL) and precipitate appeared. After filtering and washing with 3 × 3 mL diethyl ether, **10a** was obtained as a white solid with 68% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.78 (s, 1H), 9.42 (d, J = 6.0 Hz, 1H), 9.00 (d, J = 8.0 Hz, 1H), 8.31 (dd, J_1 = 6.0 Hz, J_2 = 8.0 Hz, 1H), 7.59 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H), 5.94 (s, 2H), 4.13-4.10(m, 2H), 4.00 (s, 3H), 3.65-3.63 (m, 2H), 3.29 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): 162.1, 159.3, 147.6, 145.6, 145.4, 130.8, 130.1, 128.7, 125.8, 115.0, 70.2, 67.0, 63.0, 58.1, 53.5. HRMS (ESI) calcd for: $C_{17}H_{20}NO_4$ $[M]^+$ 302.1387, found 302.1393.

1-(4-(2-methoxyethoxy)benzyl)-1,4-dihydropyridine-3-carboxylate (10b)



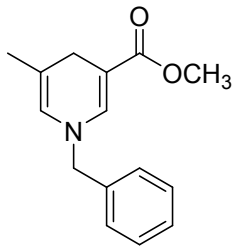
To a solution of **10a** 0.095 g (0.25 mmol) in distilled water was added sodium bicarbonate 0.084 g (1 mmol) under Ar atmosphere. Sodium dithionite 0.174 g (1 mmol) was then added in small portions within 30 min. The reaction mixture was stirred in the dark at room temperature for 3 h. When yellow oil appeared on the sidewall, the reaction solution was sucked away via syringe under argon and the yellow oil was washed with 3 × 3 mL deoxygenated water. Freeze-drying gets yellow solid with 31% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.21 (d, J =8.4 Hz, 2H), 7.21 (s, 1H), 6.93 (d, J =8.4 Hz, 2H), 5.93 (d, J =8.0 Hz, 1H), 4.73-4.70 (m, 1H), 4.31 (s, 2H), 4.07 (t, J = 4.4 Hz, 2H), 3.64 (t, J = 4.4 Hz, 2H), 3.56 (s, 3H), 3.30 (s, 3H), 2.97 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): 167.5, 157.9, 141.9, 130.0, 129.1, 128.8, 114.5, 103.7, 95.5, 70.3, 66.8, 58.1, 55.2, 50.5, 21.9. HRMS (ESI) calcd for $C_{17}H_{22}NO_4$ $[M+H]^+$ 304.1549, found 304.1556.

1-benzyl-3-(methoxycarbonyl)-5-methylpyridin-1-ium bromide(11a)



To a solution of methyl 5-methylnicotinate 0.151 g (1 mmol) in acetonitrile (1 mL) was added to a solution of benzyl bromide 0.187 g (1.1 mmol) in acetonitrile (1 mL) dropwise. After the reaction mixture was reflux for 8 h, excess solvent was removed in vacuo, following by methanol (1 mL) and diethyl ether (20 mL) and precipitate appeared. After filtering and washing with 3 × 3 mL diethyl ether, **11a** was obtained as a white solid with 85% yield. ^{1}H NMR (400 MHz, D_2O): δ (ppm) 9.25 (s, 1H), 8.87 (s, 1H), 8.82 (s, 1H), 7.43 (brs, 5H), 5.78 (s, 2H), 3.95 (s,3H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 162.2, 147.4, 145.9, 139.8, 134.0, 129.5, 129.4, 129.1, 128.9, 63.2, 53.5, 17.8. HRMS (ESI) calcd for $C_{15}H_{16}NO_2$ $[M]^+$ 242.1181, found 242.1181.

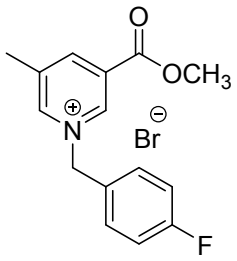
1-benzyl-5-methyl-1,4-dihydropyridine-3-carboxylate (11b)



To a solution of **11a** 0.161 g (0.5 mmol) in distilled water was added sodium bicarbonate 0.168 g (2 mmol) under Ar atmosphere. Sodium dithionite 0.348 g (2 mmol) was then added in small portions within 30 min. The reaction mixture was stirred in the dark at room temperature for 3 h. When yellow oil appeared on the sidewall, the reaction solution was sucked away via syringe under argon and the yellow oil was washed with 3 × 3 mL deoxygenated water. Freeze-drying gets yellow solid with 42% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.39-7.35 (m, 2H), 7.31-7.28 (m, 3H), 7.23 (s, 1H), 5.78 (s, 1H), 4.42 (s, 2H), 3.57 (s, 3H), 2.87 (s,2H), 1.50 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 167.6, 141.2, 138.2,

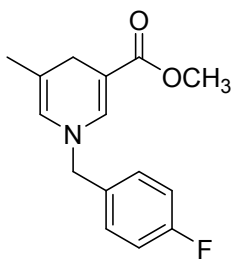
128.6, 127.4, 127.3, 123.3, 112.9, 94.6, 55.9, 50.4, 27.7, 20.1. HRMS (ESI) calcd for $C_{15}H_{18}NO_2$ $[M+H]^+$244.1338, found 244.1339.

1-(4-fluorobenzyl)-3-(methoxycarbonyl)-5-methylpyridin-1-ium bromide (12a)



To a solution of methyl 5-methylnicotinate 0.151 g (1 mmol) in acetonitrile (1 mL) was added to a solution of 4-fluorobenzyl bromide 0.207 g (1.1 mmol) in acetonitrile (1 mL) dropwise. After the reaction mixture was reflux for 8 h, excess solvent was removed in vacuo, following by methanol (1 mL) and diethyl ether (20 mL) and precipitate appeared. After filtering and washing with 3 × 3 mL diethyl ether, **12a** was obtained as a white solid with 49% yield. ^{1}H NMR (400 MHz, D_2O): δ (ppm) 9.24 (s, 1H), 8.86 (s, 1H), 8.83 (s, 1H), 7.45 (dd, J_1 = 5.2 Hz, J_2 = 8.8 Hz, 2H), 7.16 (d, J = 8.8 Hz, 2H), 5.77 (s,2H), 3.95 (s, 3H), 2.50(s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 163.8, 162.2, 161.4, 147.3, 145.8, 143.1, 139.8, 131.6, 131.5, 130.3, 130.2, 129.5, 116.1, 115.9, 62.4, 53.5, 17.8. HRMS (ESI) calcd for $C_{15}H_{15}NO_2F$ $[M]^+$ 260.1081, found 260.1074.

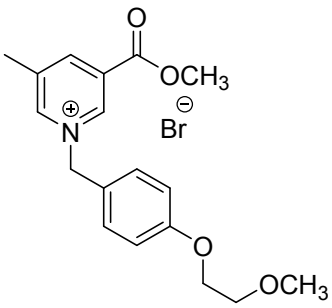
1-(4-fluorobenzyl)-5-methyl-1,4-dihydropyridine-3-carboxylate (12b)



To a solution of **12a** 0.169 g (0.5 mmol) in distilled water was added sodium bicarbonate 0.168 g (2 mmol) under Ar atmosphere. Sodium dithionite 0.348 g (2 mmol) was then added in small portions within 30 min. The reaction mixture was stirred in the dark at room temperature for 3 h. When yellow oil appeared on the sidewall, the reaction solution was sucked away via syringe under argon and the yellow oil was washed with 3 × 3 mL deoxygenated water.

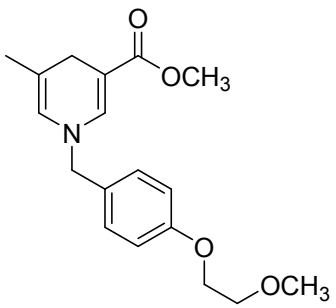
Freeze-drying gets yellow solid with 44% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.33 (dd, J_1 =5.6 Hz, J_2 = 8.0 Hz, 2H), 7.30 (s, 1H), 7.20 (t, J = 8.8 Hz, 2H), 5.78 (s, 1H), 4.41 (s, 2H), 3.58 (s, 3H), 2.87 (s,2H), 1.50 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 167.6, 162.8, 160.3, 141.1, 134.4, 129.4, 129.3, 123.1, 115.5, 115.3, 113.1, 94.8, 55.1, 50.4, 27.6, 20.1. HRMS (ESI) calcd for $C_{15}H_{17}NO_2F$ $[M+H]^+$ 262.1243, found 262.1236.

3-(methoxycarbonyl)-1-(4-(2-methoxyethoxy)benzyl)-5-methylpyridin-1-ium bromide (13a)



To a solution of methyl 5-methylnicotinate 0.302 g (2 mmol) in acetonitrile (1 mL) was added to a solution of I1 0.587 g (2.5 mmol) in acetonitrile (1 mL) dropwise. After the reaction mixture was reflux for 8 h, excess solvent was removed in vacuo, following by methanol (1 mL) and diethyl ether (20 mL) and vast precipitate appeared. After filtering and washing with 3 × 3 mL diethyl ether, **13a** was obtained as a white solid with 42% yield. ^{1}H NMR (400 MHz, D_2O): δ (ppm) 9.21 (s, 1H), 8.87 (s, 1H), 8.78 (s, 1H), 7.40 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 5.70 (s, 2H), 4.08-4.06 (m, 2H), 3.95 (s, 3H), 3.72-3.70 (m, 2H), 3.34 (s, 3H), 2.50 (s,3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 162.2, 159.3, 147.2, 145.7, 142.7, 139.7, 130.8, 129.4, 125.9, 114.9, 70.2, 67.0, 62.9, 58.1, 53.4, 17.8. HRMS (ESI) calcd for $C_{18}H_{22}NO_4$ $[M]^+$ 316.1549, found 316.1543.

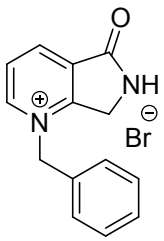
1-(4-(2-methoxyethoxy)benzyl)-5-methyl-1,4-dihydropyridine-3-carboxylate (13b)



To a solution of **13a** 0.098 g (0.25 mmol) in distilled and deoxygenated water was added sodium bicarbonate 0.084 g (1 mmol)

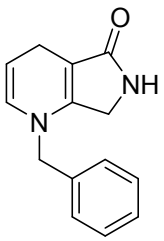
under Ar atmosphere. Sodium dithionite 0.174 g (1 mmol) was then added in small portions within 30 min. The reaction mixture was stirred in the dark at room temperature for 3 h. When yellow oil appeared on the sidewall, the reaction solution was sucked away via syringe under argon and the yellow oil was washed with 3 × 3 mL deoxygenated water. Freeze-drying gets yellow solid with 43% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.26 (s, 1H), 7.19 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 8.4 Hz, 2H), 5.77 (s, 2H), 4.33 (s, 2H), 4.07 (t, J = 4.4 Hz, 2H), 3.65 (t, J = 4.4 Hz,2H), 3.57 (s, 3H), 3.30 (s, 3H), 2.85 (s, 2H), 1.49 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 167.6, 157.9, 141.1, 130.0, 128.8, 123.2, 114.5, 112.9, 94.4, 70.3, 66.8, 58.1, 55.4, 50.4, 27.7, 20.1. HRMS (ESI) calcd for $C_{18}H_{24}NO_4$ $[M+H]^+$ 318.1705, found 318.1703.

1-benzyl-5-oxo-6,7-dihydro-5H-pyrrolo[3,4-b]pyridin-1-ium bromide (14a)



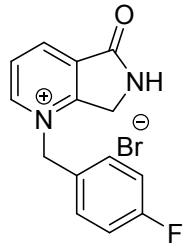
To a solution of 6,7-dihydro-5H-pyrrolo[3,4-b]pyridin-5-one 0.268 g (2 mmol) in acetonitrile (10 mL) was added to a solution of benzyl bromide 0.680 g (4 mmol) in acetonitrile (5 mL) dropwise. After the reaction mixture was reflux for 36 h yielding pink solid, following by filtering and washing with 3 × 3 mL diethyl ether, **14a** was obtained as pink solid with 37% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.54 (s, 1H), 9.27 (d, J = 6 Hz, 1H), 8.88 (d, J = 8 Hz, 1H), 8.28 (d, J = 7.2 Hz, 1H), 7.55-7.53 (m,2H), 7.48-7.46 (m, 3H), 6.00 (s, 2H), 4.93 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 164.6, 159.5, 146.4, 140.6, 132.5, 132.1, 129.4, 129.3, 129.2, 127.9, 59.6, 44.9. HRMS (ESI) calcd for $C_{14}H_{13}N_2O$ $[M]^+$ 225.1028, found 225.1018.

1-benzyl-1,4,6,7-tetrahydro-5H-pyrrolo[3,4-b]pyridin-5-one(14b)



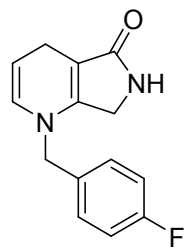
To a solution of **14a** 0.076 g (0.25 mmol) in distilled water was added sodium bicarbonate 0.084 g (1 mmol) under Ar atmosphere. Sodium dithionite 0.174 g (1 mmol) was added in small portions within 30 min. The reaction mixture was stirred in the dark at room temperature for 3 h, precipitating grey product. After centrifuging, the solid (compound **14b**) was filtered and washed by ultrapure water and dried through vacuum freeze-drying equipment with 50% yield as grey solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.40-7.36 (m, 2H), 7.30-7.27 (m, 3H), 7.15 (s, 1H), 6.06 (d, J = 8.4 Hz,1H), 4.65 (m, 1H), 4.39 (s, 2H), 3.78 (s, 2H), 2.95(s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 174.4, 154.4, 138.0, 131.0, 128.7, 127.3, 126.8, 101.6, 100.5, 51.7, 43.0, 19.7. HRMS (ESI) calcd for:$C_{14}H_{15}N_2O$ $[M+H]^+$ 227.1184, found 227.1182.

1-(4-fluorobenzyl)-5-oxo-6,7-dihydro-5H-pyrrolo[3,4-b]pyridin-1-ium bromide(15a)



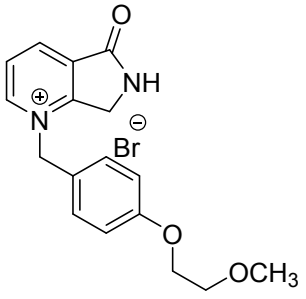
To a solution of 6,7-dihydro-5H-pyrrolo[3,4-b]pyridin-5-one 0.268 g (2 mmol) in acetonitrile (10 mL) was added to a solution of 4-fluorobenzyl bromide 0.752 g (4 mmol) in acetonitrile (5 mL) dropwise. After the reaction mixture was reflux for 24 h yielding pink solid, following by filtering and washing with 3 × 3 mL diethyl ether, **15a** was obtained as pink solid with 52% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.61 (s, 1H), 9.29 (d, J = 6 Hz 1H), 8.93 (d, J = 7.6 Hz, 1H), 8.31 (t, J = 7.2 Hz, 1H), 7.72 (dd,J_1 = 5.6 Hz, J_2 = 8.8 Hz, 2H), 7.39 (t, J = 8.8 Hz, 2H), 6.00 (s, 2H), 5.00 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ(ppm) 164.6, 163.8, 161.4, 159.5, 146.3, 140.6, 132.5, 132.0, 131.9, 128.3, 128.2, 127.8, 116.2, 116.0, 58.8, 44.9. HRMS (ESI) calcd for $C_{14}H_{12}N_2OF$ $[M]^+$ 243.0934, found 243.0926.

1-(4-fluorobenzyl)-1,4,6,7-tetrahydro-5H-pyrrolo[3,4-b]pyridin-5-one(15b)



To a solution of **15a** 0.122 g (0.5 mmol) in distilled water was added sodium bicarbonate 0.168 g (2 mmol) under Ar atmosphere. Sodium dithionite 0.348 g (2 mmol) was added in small portions within 30 min. The reaction mixture was stirred in the dark at room temperature for 3 h, precipitating grey product. After centrifuging, the solid (compound **15b**) was filtered and washed by ultrapure water and dried through vacuum freeze-drying equipment with 43% yield as grey solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.34-7.31 (m, 2H), 7.23 (s, 1H), 7.21-7.19 (m, 2H), 6.05 (d, J = 8.0 Hz,1H), 4.67-4.64 (m, 1H), 4.38 (s, 2H), 3.79 (s, 2H), 2.94(s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 174.4, 162.6, 160.2, 154.4, 134.1, 134.0, 130.8, 129.0, 128.9, 115.6, 115.4, 101.8, 100.6, 50.9, 43.0, 19.6. HRMS (ESI) calcd for $C_{14}H_{14}N_2OF$ $[M+H]^+$ 245.1090, found 245.1087.

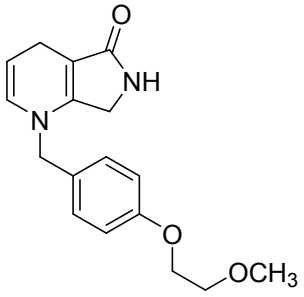
1-(4-(2-methoxyethoxy)benzyl)-5-oxo-6,7-dihydro-5H-pyrrolo[3,4-b]pyridin-1-ium bromide (16a)



To a solution of 6,7-dihydro-5H-pyrrolo[3,4-b]pyridin-5-one 0.268 g (2 mmol) in acetonitrile (10 mL) was added to a solution of **I1** 0.976 g (2.4 mmol) dissolved in acetonitrile (5 mL) in acetonitrile (5 mL) dropwise. After the reaction mixture was reflux for 24 h yielding pink solid, following by filtering and washing with 3 × 3 mL diethyl ether, **16a** was obtained as pink solid with 31% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.53 (s, 1H), 9.15 (d,J = 6.4 Hz, 1H), 8.85 (d, J = 7.6 Hz,1H), 8.23 (t, J = 6.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.05

(d, J =6.8 Hz, 2H), 5.82 (s, 2H), 4.92 (s, 2H), 4.13-4.11 (m, 2H), 3.67-3.65 (m, 2H), 3.30 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 164.6, 159.3, 159.2, 146.0, 140.4, 132.4, 131.3, 127.8, 123.8, 115.0, 70.2, 67.0, 59.3, 58.1, 44.9. HRMS (ESI) calcd for: $C_{17}H_{19}N_2O_3$ $[M]^+$ 299.1396, found 299.1396.

1-(4-(2-methoxyethoxy)benzyl)-1,4,6,7-tetrahydro-5H-pyrrolo[3,4-b]pyridin-5-one (16b)



To a solution of **16a** 0.095 g (0.25 mmol) in distilled water was added sodium bicarbonate 0.084 g (1 mmol) under Ar atmosphere. Sodium dithionite 0.174 g (1 mmol) was added in small portions within 30 min. The reaction mixture was stirred in the dark at room temperature for 3 h, precipitating grey product. After centrifuging, the solid (compound **16b**) was filtered and washed by ultrapure water and dried through vacuum freeze-drying equipment with 52% yield as grey solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.19 (d, J = 8.8 Hz, 2H), 7.15 (s, 1H), 6.94 (d, J = 8.8 Hz, 2H), 6.05 (d, J = 8 Hz, 1H), 4.65-4.59 (m, 1H), 4.30 (s, 2H), 4.06 (m, 2H), 3.79 (s, 2H), 3.65-3.63 (m, 2H), 3.30 (s, 3H), 2.93 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 174.5, 157.8, 154.5, 130.9, 129.7, 128.3, 114.6, 101.6, 100.4, 70.3, 66.8, 58.1, 51.2, 43.0, 19.7. HRMS (ESI) calcd for $C_{17}H_{21}N_2O_3$ $[M+H]^+$ 301.1552, found 301.1544.

3 Cyclic Voltammetry

Cyclic voltammetry was performed on a Gamry Interface 1000 electrochemical analyzer. A three-electrode arrangement in a single cell was used for the measurements: a

glassy carbon electrode as the working electrode, a Pt wire as the auxiliary electrode, and a SCE electrode as the reference electrode. The sample solutions contained a 10^{-3} M sample and 0.1 M KCl as a supporting electrolyte in 20% (v/v) DMSO, 80% (v/v) Tris-HCl buffer (10^{-2} M), and argon was bubbled for 10 min before each measurement. The voltage scan rate was 100 mV s^{-1}.

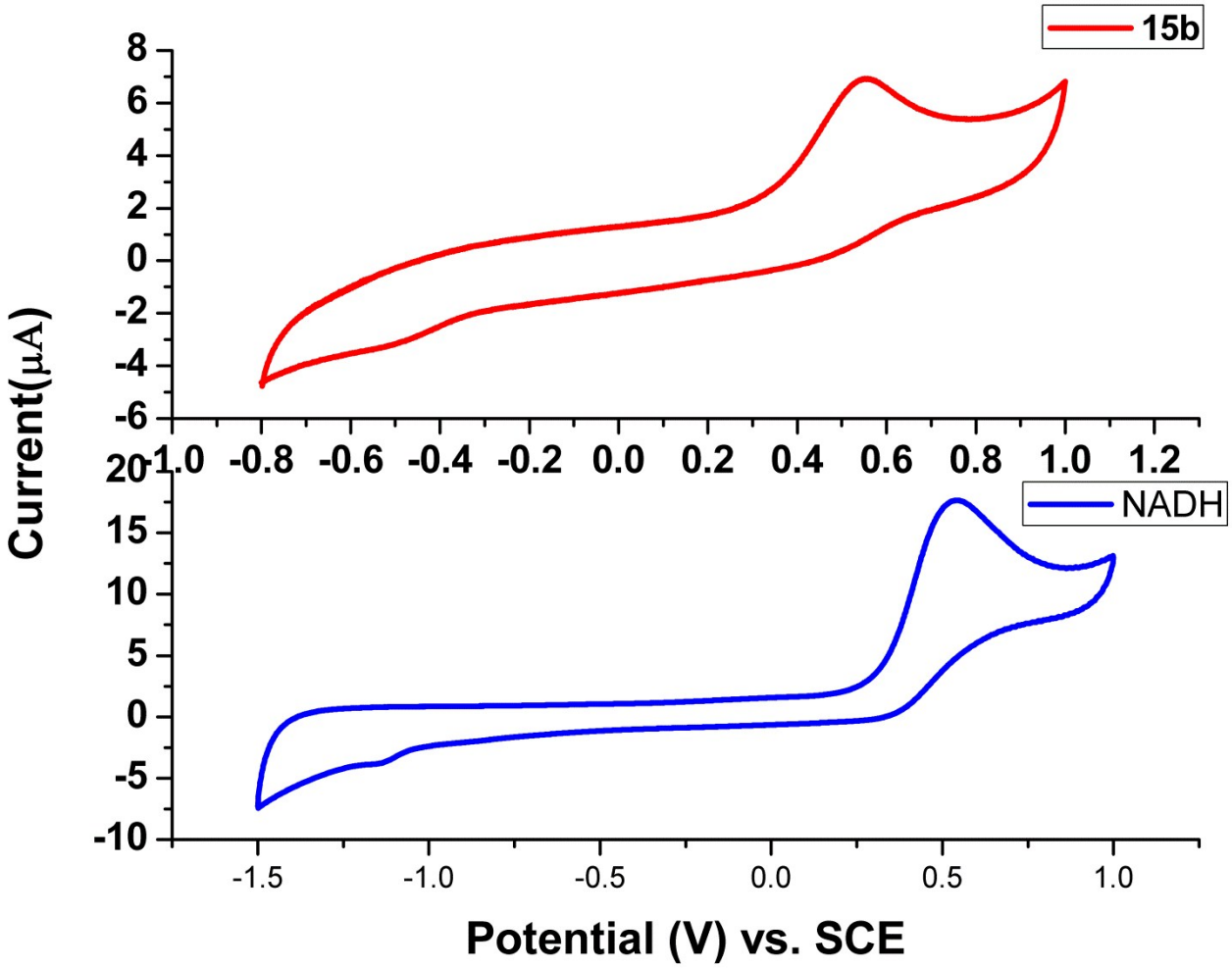


Figure S1 Potential of 15b and NADH (vs. SCE)

4 Determination of thermodynamic solubility

Weigh about 1 mg of the test compound into 1.5 mL centrifuge tube and add 1 mL PBS buffer (10^4 mM, pH = 7.4), sonicating for 5 min (if the compound is completely dissolved,

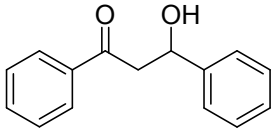
then added again 1 mg compound). After the suspension filtered by 0.22 μm PVDF, diluting the solution with methanol (v = 50%) and PBS (v = 50%) to a suitable concentration using and measuring absorbance values by UV spectrophotometer. Weigh about 2 mg compound accurately and add methanol to prepare 10^3 μg/mL mother solution. Take the above-described mother liquor to prepare the solution in concentrations of 30, 20, 10, 5, 2.5 μg /mL (diluted by PBS buffer) then measure absorbance value. With concentration c (μg/mL) as the abscissa, absorbance A as the ordinate, mapping and fitting line to get the standard curve. (The correlation coefficient should be greater than 0.998). Calculate solubility according to the standard curve of the linear equation.

5 Evaluation of biomimetic cofactors in chemistry system

A solution of α,β-epoxy ketones (1 mmol), Na_2CO_3 (5 mmol), $Na_2S_2O_4$ (3 mmol) and biomimetic cofactors (2b-16b) and BNAH (0.05 mmol) in 10 mL of CH_3CN/H_2O (v:v = 1:1) (deoxidized) was stirred under an argon atmosphere at room temperature for 24-48 h. The reaction mixture was extracted with dichloromethane and the combined extract dried with Na_2SO_4. After evaporation of the solvent, the residue was further purified by column chromatography (DCM : PE = 5:1, v/v) and identified by ^1H、^{13}C NMR and HRMS as corresponding β-hydroxy ketones. Reactant can be totally converted in this chemical catalysis system and reactions catalyzed by cofactors obtain the same product only the reaction time and yield are different.

Take the reaction catalyzed by **16b** for example

3-hydroxy-1,3-diphenylpropan-1-one



^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.97 (d, J = 7.2 Hz, 2H), 7.63

(t, J = 7.2 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.42 (d, J = 7.2 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.24 (t, J = 7.2 Hz, 1H), 5.15 (m, J = 4.4 Hz, 2H), 5.39 (d, J = 4.4 Hz, 1H), 3.43 (dd, J_1 = 8.8 Hz, J_2 = 16.0 Hz, 1H), 3.18 (dd, J_1 = 8.8 Hz, J_2 = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 198.3, 145.4, 137.1, 133.0, 128.6, 128.1, 128.0, 126.9, 125.9, 69.3, 47.9.

6 Evaluation of biomimetic cofactors in biology system

Evaluation of biomimetic cofactors catalytic were employed recombinant forms of Nitroreductase (expressed in Escherichia coli. purchased from Sigma-Aldrich). Stock solutions of probe **semi-CyHP** were prepared in pure DMSO (10^{-3} M). 10^{-5} M probe **semi-CyHP** diluted by 0.1 M phosphate buffered saline (pH 7.4) culture with 5×10^{-4} M different biomimetic cofactors and 2.5 μg/mL enzyme at 37 ºC. The emission intensity was collected from 500 nm to 700 nm with excitation at 490 nm.

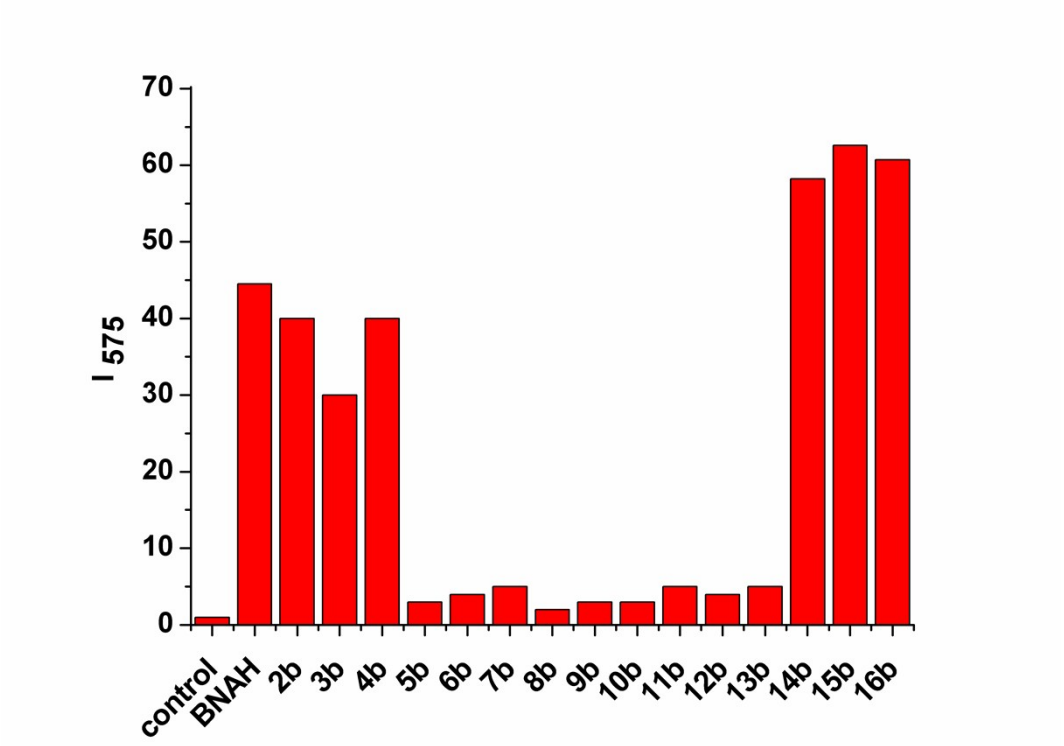


Figure S2 catalytic ability of artificial cofactors in nitroreductase system.

The fluorescence intensity data were collected after a certain time at

around 575 nm.

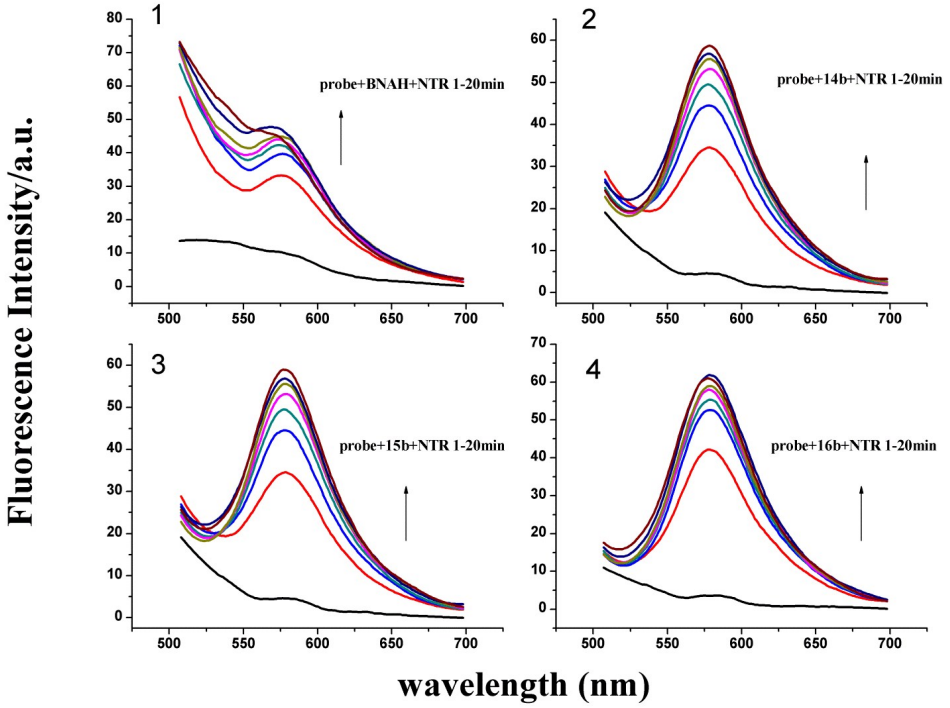
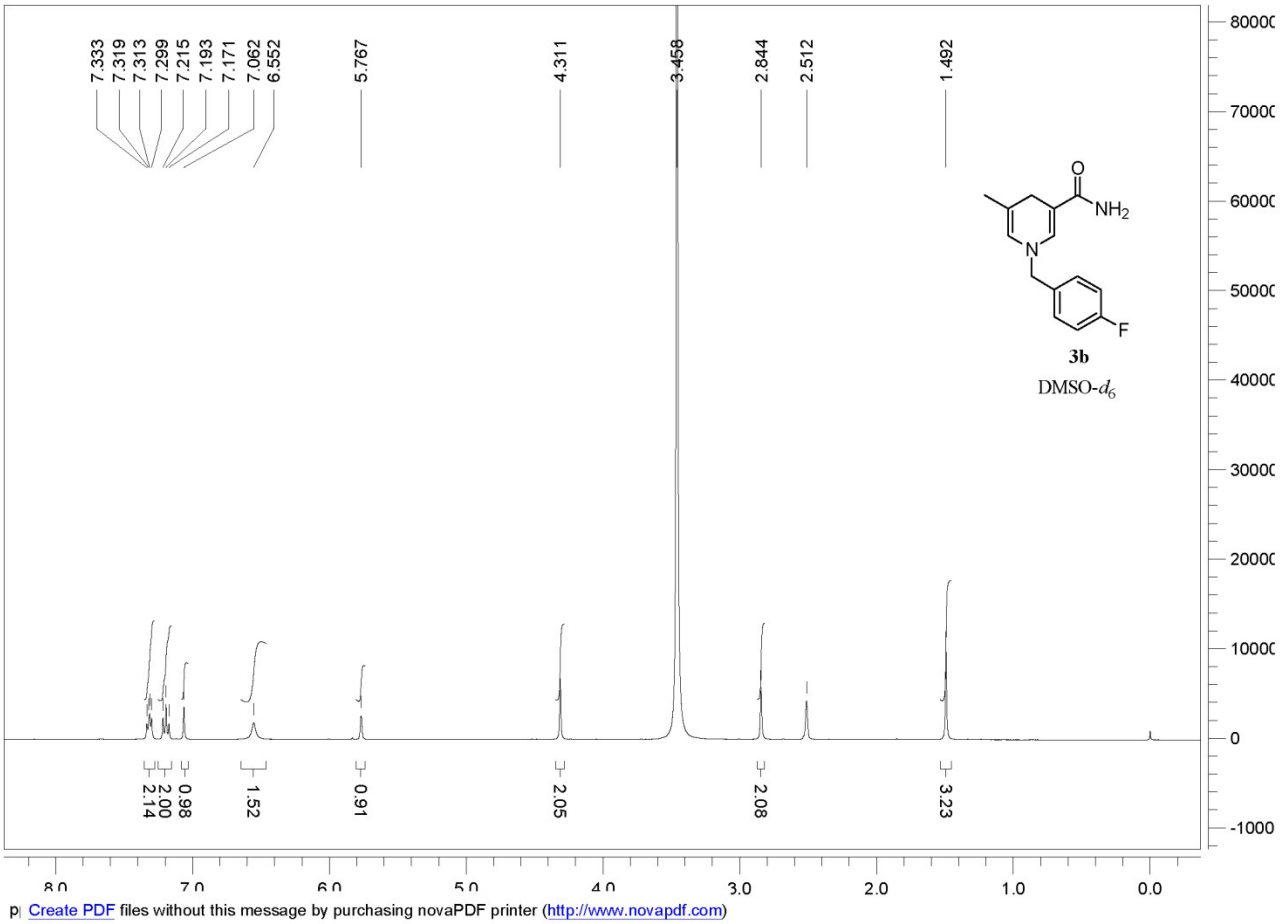
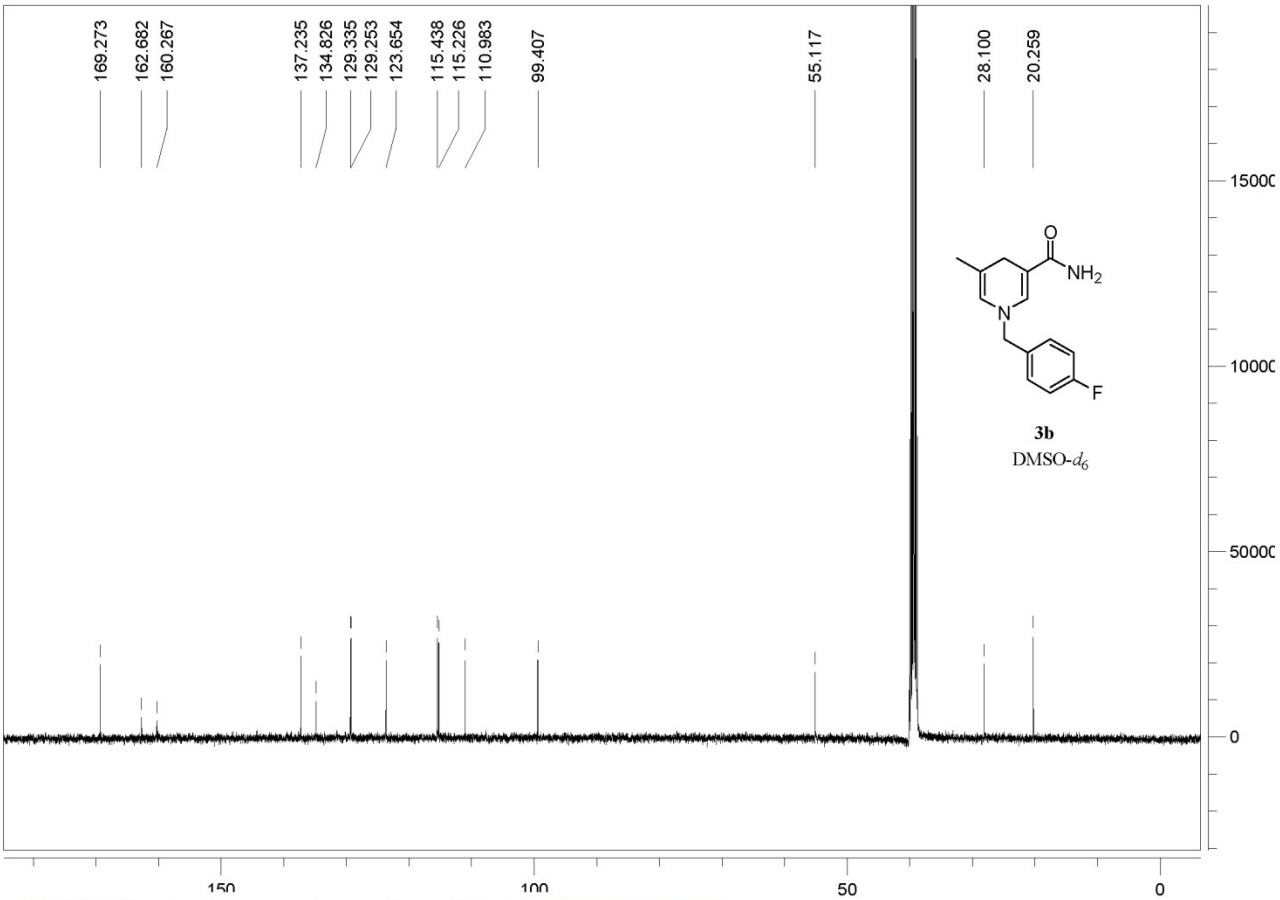


Fig S3 Fluorescence spectra of probe semi-CyHP (10 μM) after adding artificial cofactors (5×10^{-4} M) and NTR (2.5 μg mL^{-1}) in 0.1 M PBS buffer (pH 7.4) with 1% (v/v) DMSO at 37 ^{o}C. The fluorescent intensity data were collected after certain time intervals as indicated in the figure with excitation at 490 nm. Silt: 10, 10 nm. (1) BNAH acts as cofactor. (2) **14b** acts as cofactor. (3) **15b** acts as cofactor. (4) **16b** acts as cofactor.

7 NMR spectra and HRMS spectra





Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
13 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-14 H: 0-16 N: 0-2 O: 0-2 F: 0-1

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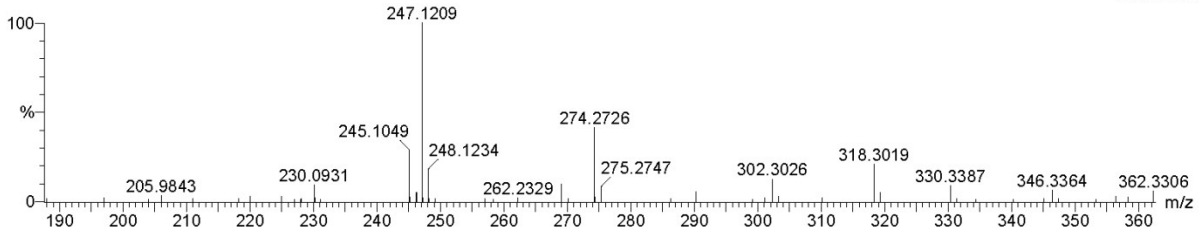
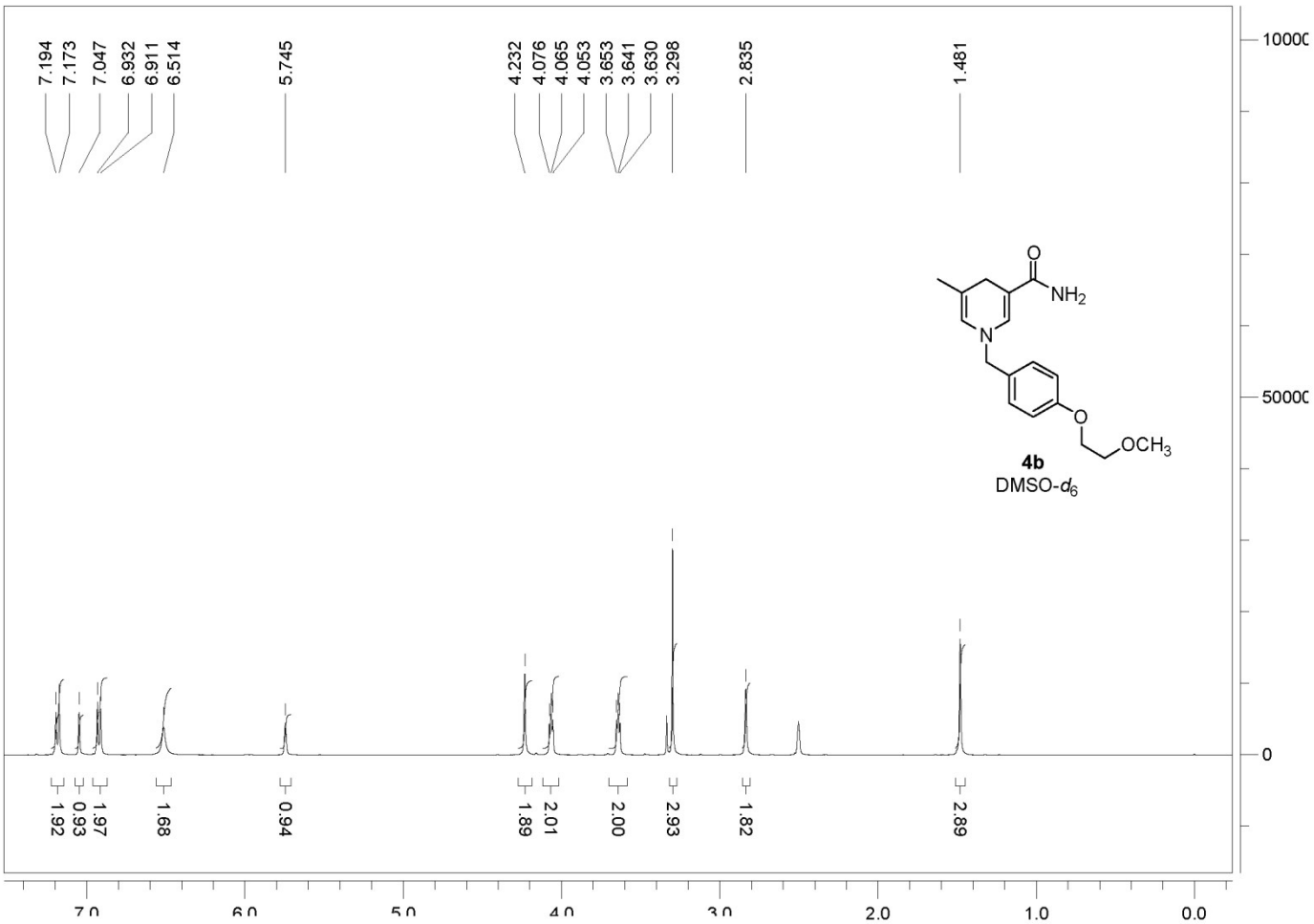
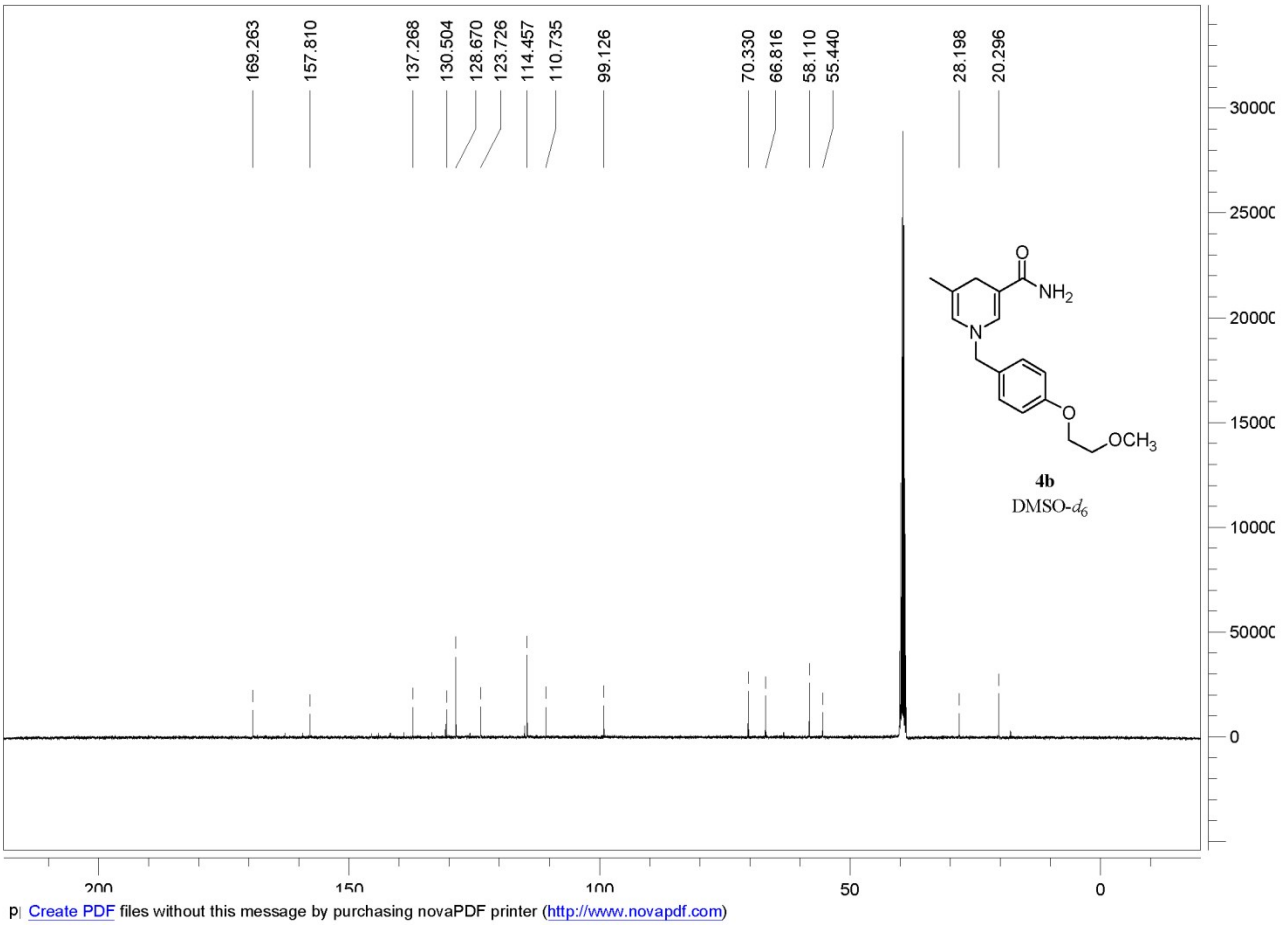
3b 14 (0.521) Cm (13:14) 1: TOF MS ES+ 2.53e+003



Minimum:				-1.5			
Maximum:		300.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
247.1209	247.1247	-3.8	-15.4	7.5	32.1	0.0	C14 H16 N2 O F





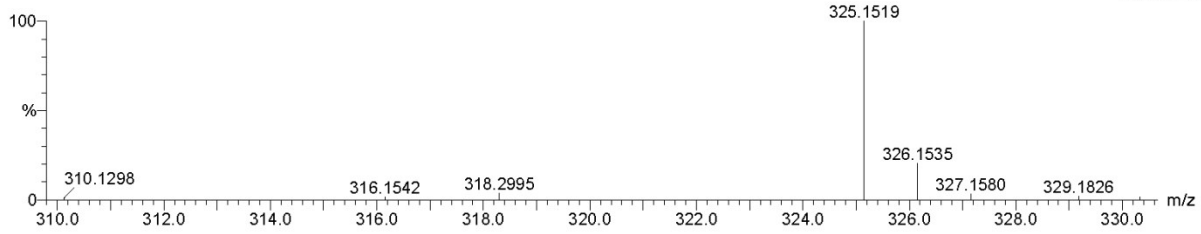
Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

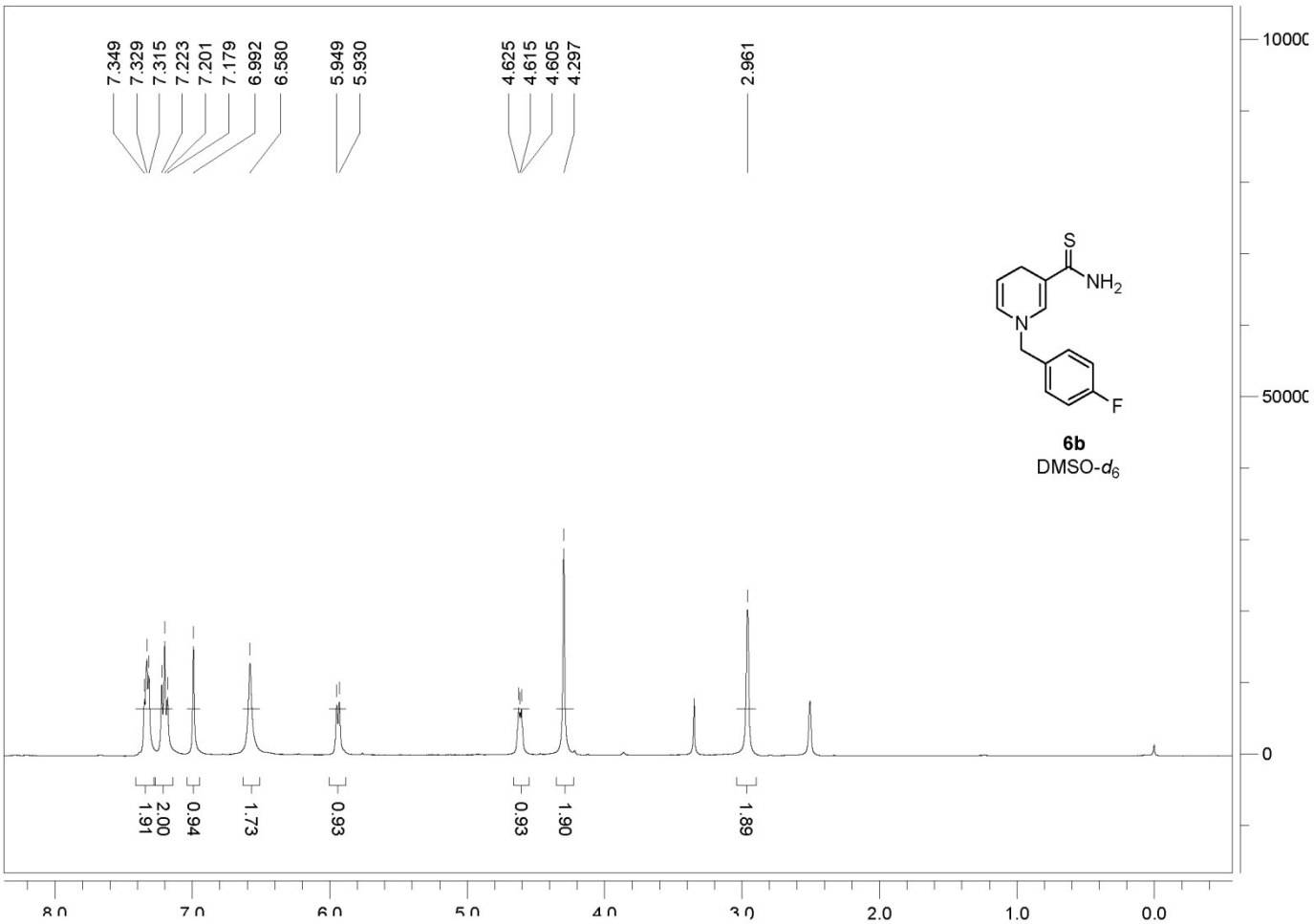
Monoisotopic Mass, Even Electron Ions
123 formula(e) evaluated with 7 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-28 H: 0-50 N: 0-2 O: 0-4 Na: 0-1

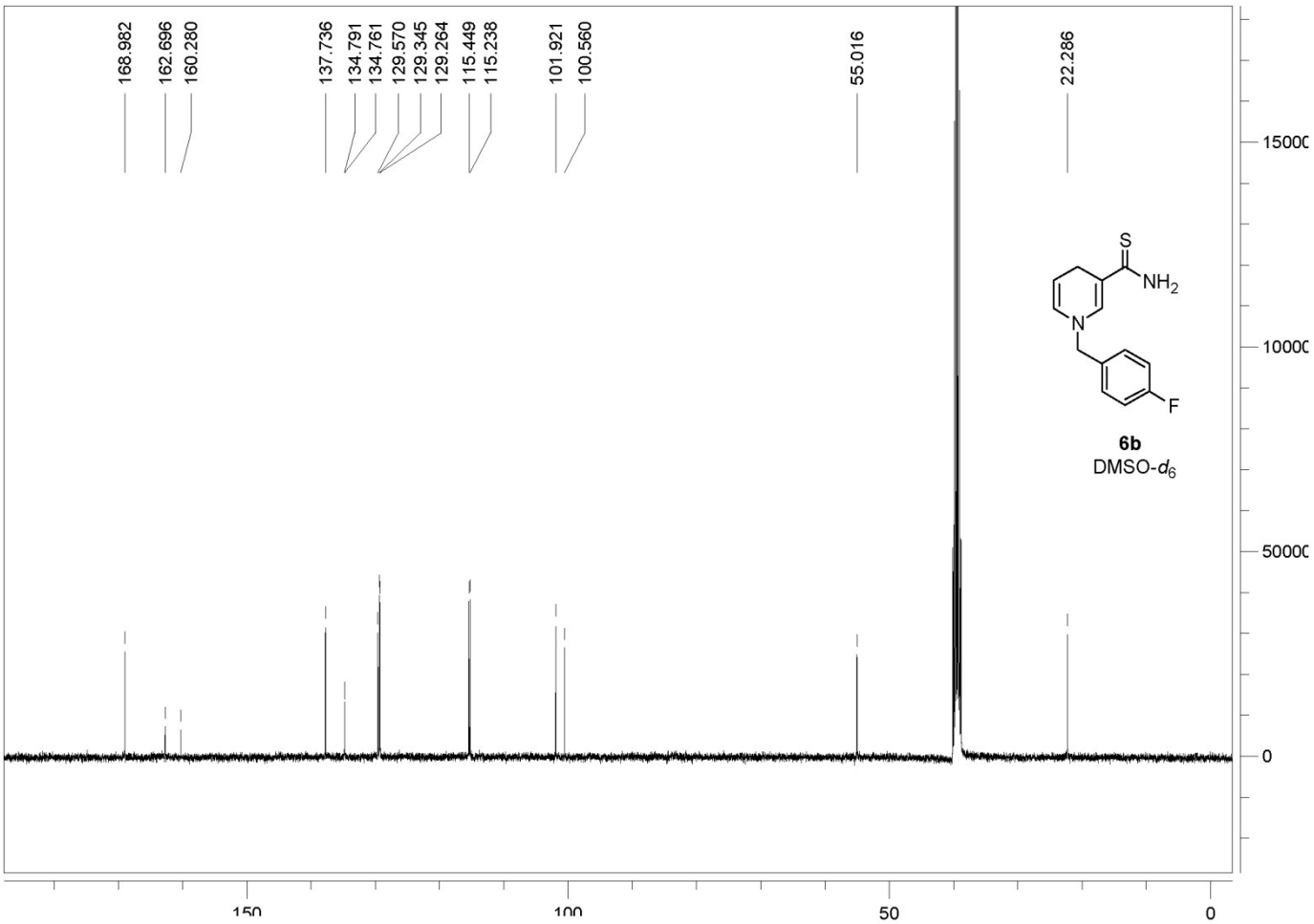
ZHU-WP ECUST institute of Fine Chem 30-May-2015 19:39:37

4b 87 (2.756) Cm (87:89) 1: TOF MS ES+ 3.97e+003



Minimum:				-1.5			
Maximum:		300.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
325.1519	325.1528	-0.9	-2.8	7.5	7.6	0.0	C17 H22 N2 O3 Na





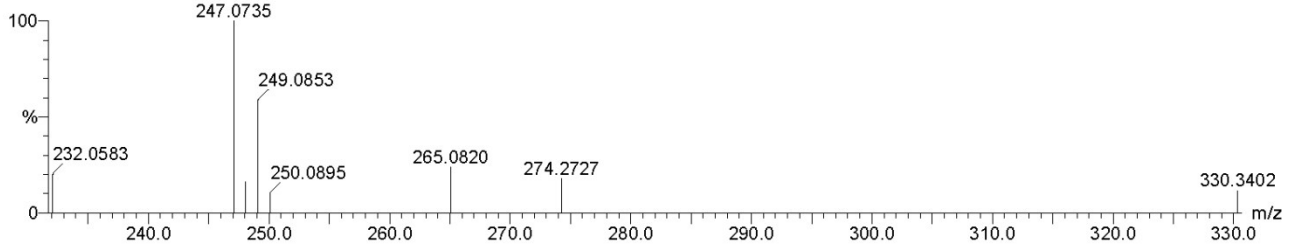
Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

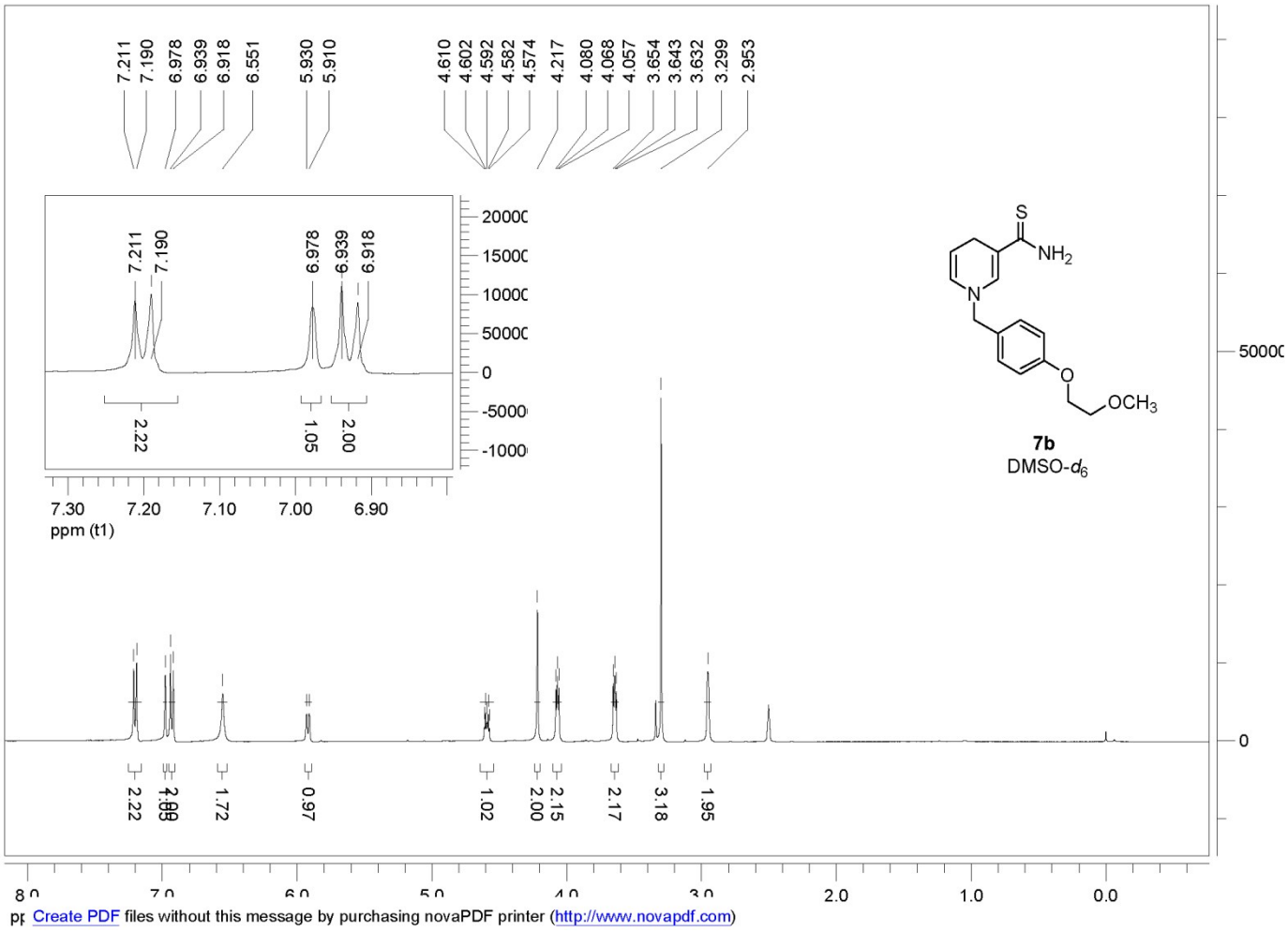
Monoisotopic Mass, Even Electron Ions
32 formula(e) evaluated with 3 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-44 H: 0-30 N: 0-2 S: 0-1 F: 0-1

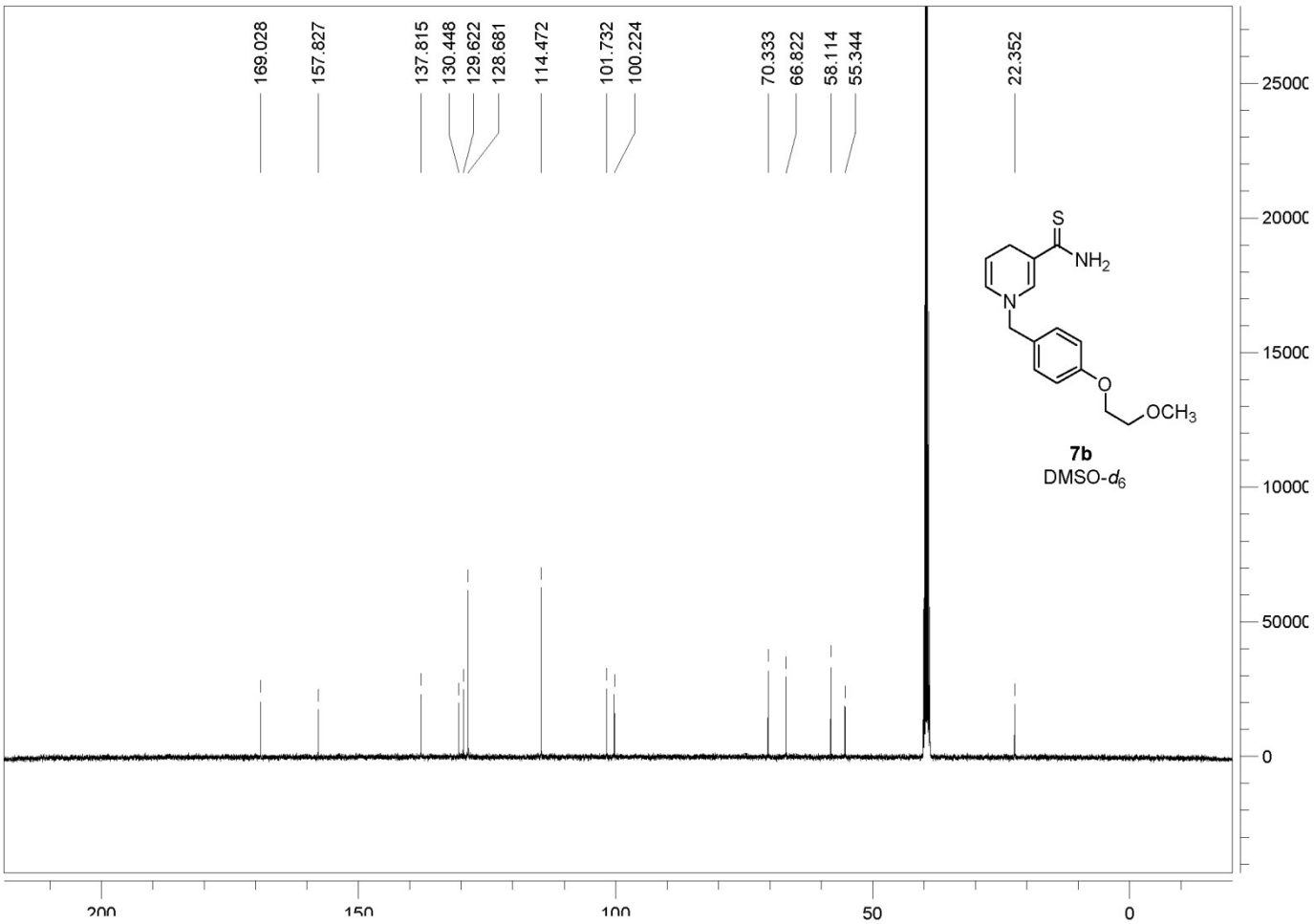
YYS ECUST institute of Fine Chem 06-Jan-2016 22:48:49

6b 205 (1.368) Cm (205) 1: TOF MS ES+ 2.23e+003



Minimum:				-1.5							
Maximum:		300.0	50.0	100.0							
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula				
249.0853	249.0862	-0.9	-3.6	7.5	20.2	0.0	C13	H14	N2	S	F





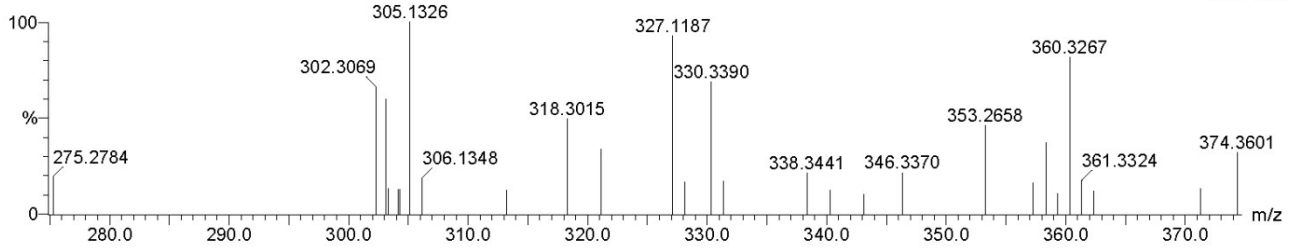
Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

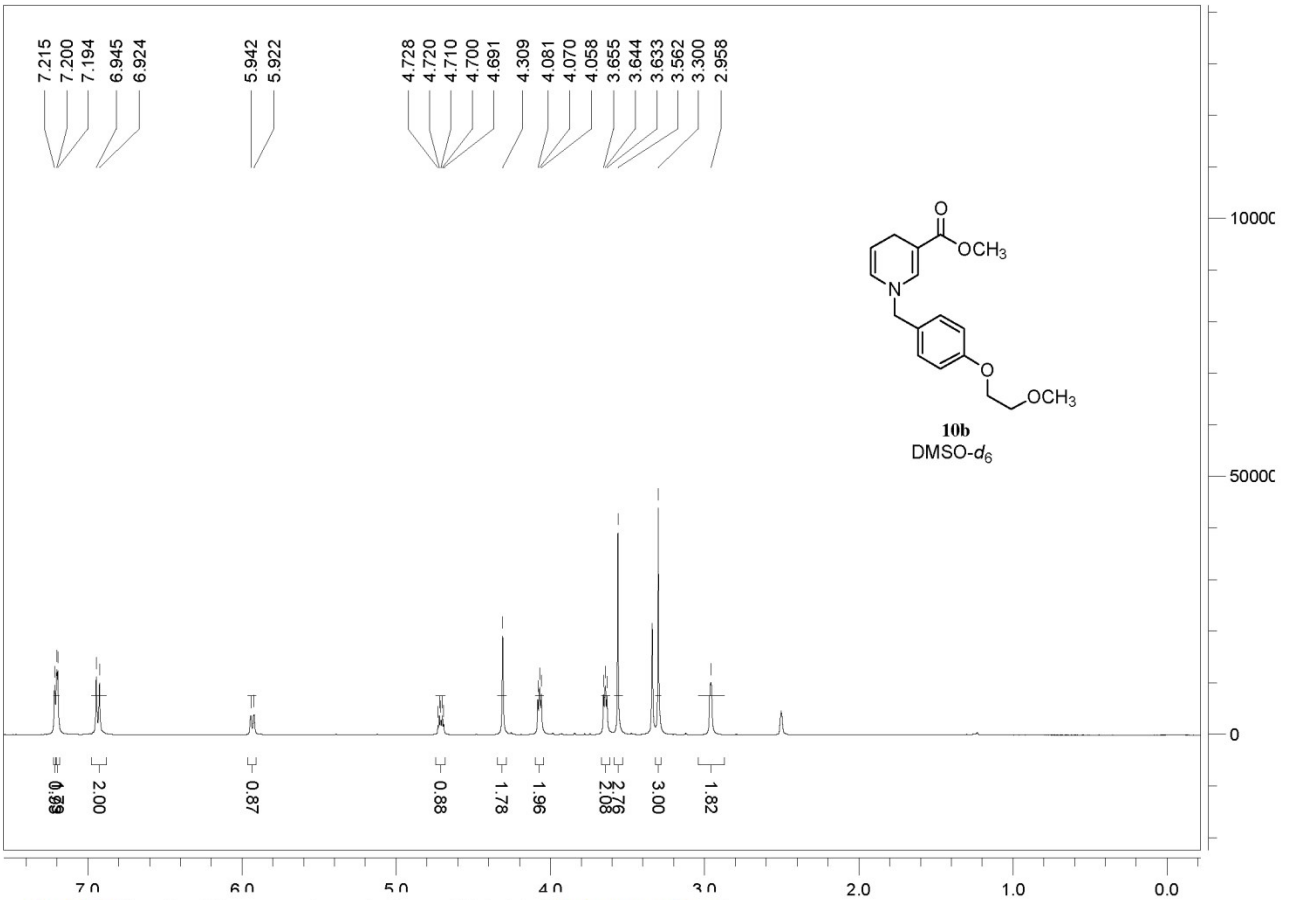
Monoisotopic Mass, Even Electron Ions
16 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-16 H: 0-30 N: 0-2 O: 0-2 S: 0-1

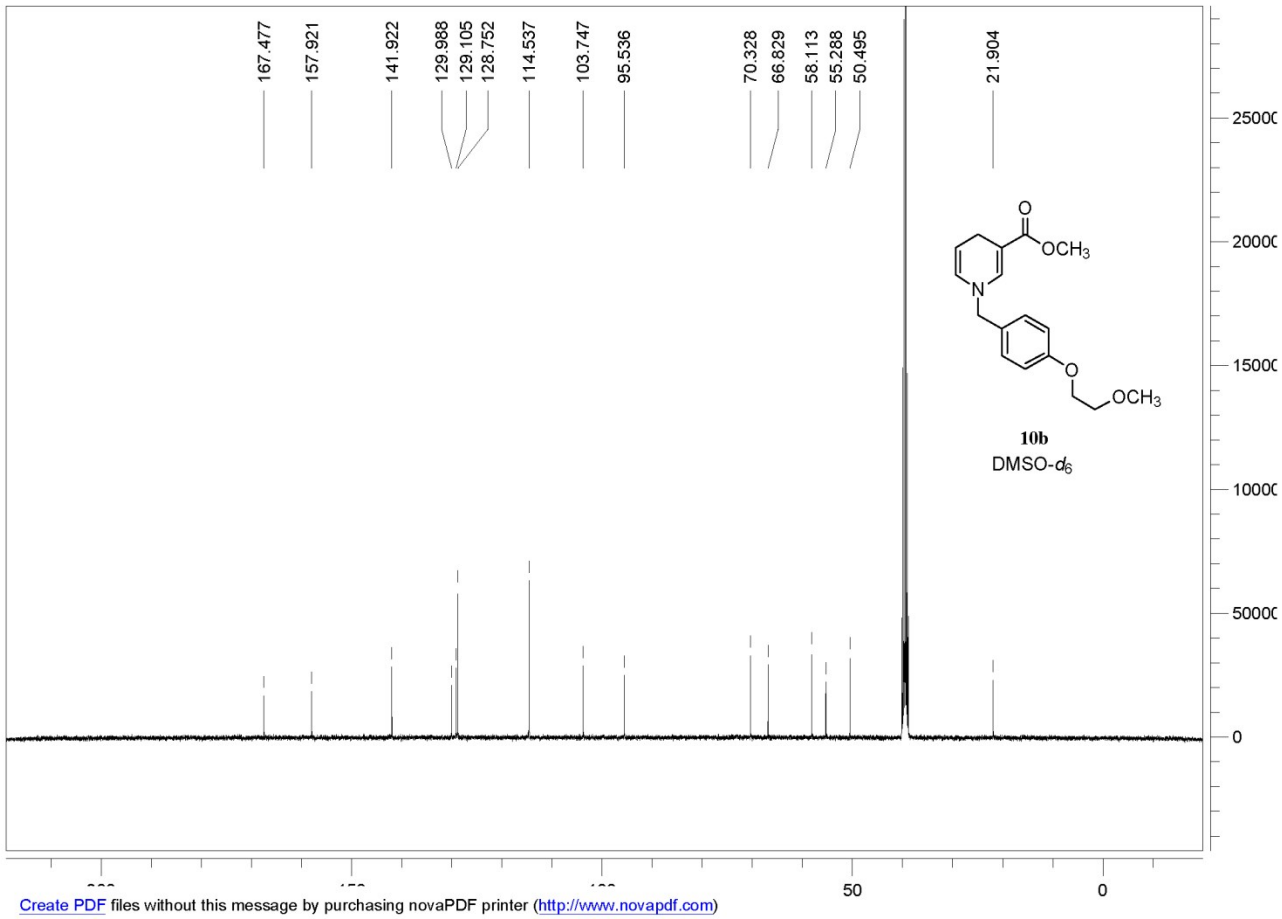
YYS ECUST institute of Fine Chem 06-Jan-2016 22:52:26

7b 65 (0.497) Cm (65) 1: TOF MS ES+ 4.92e+002



Minimum:				-1.5						
Maximum:		300.0	50.0	100.0						
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula			
305.1326	305.1324	0.2	0.7	7.5	17.7	0.0	C16	H21	N2	O2 S





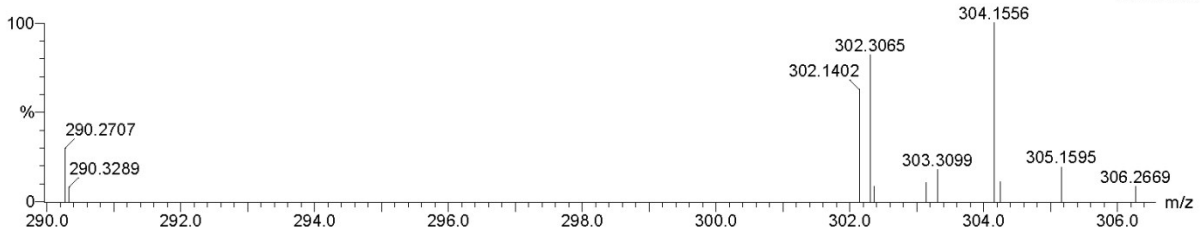
Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

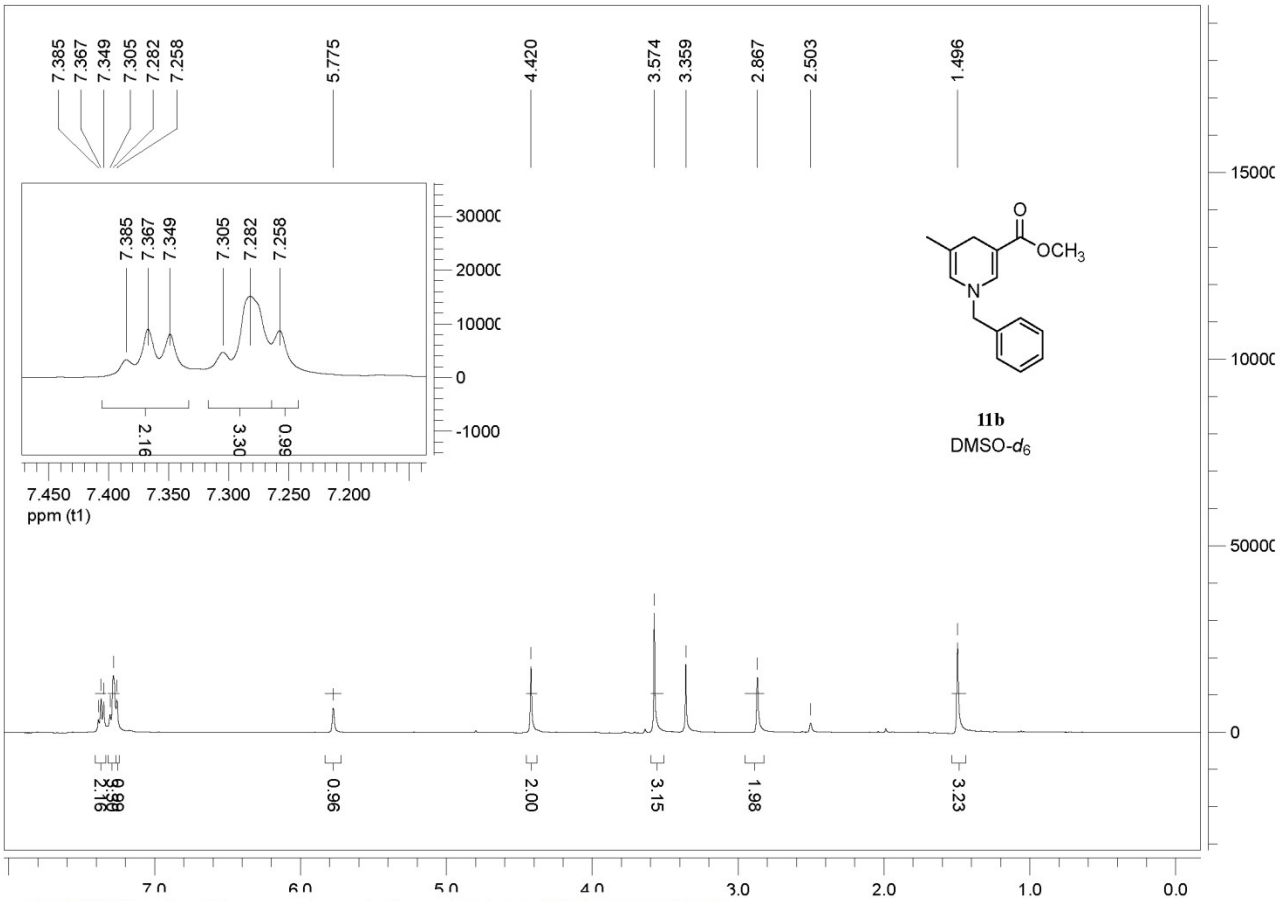
Monoisotopic Mass, Even Electron Ions
8 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-17 H: 0-22 N: 0-1 O: 0-4

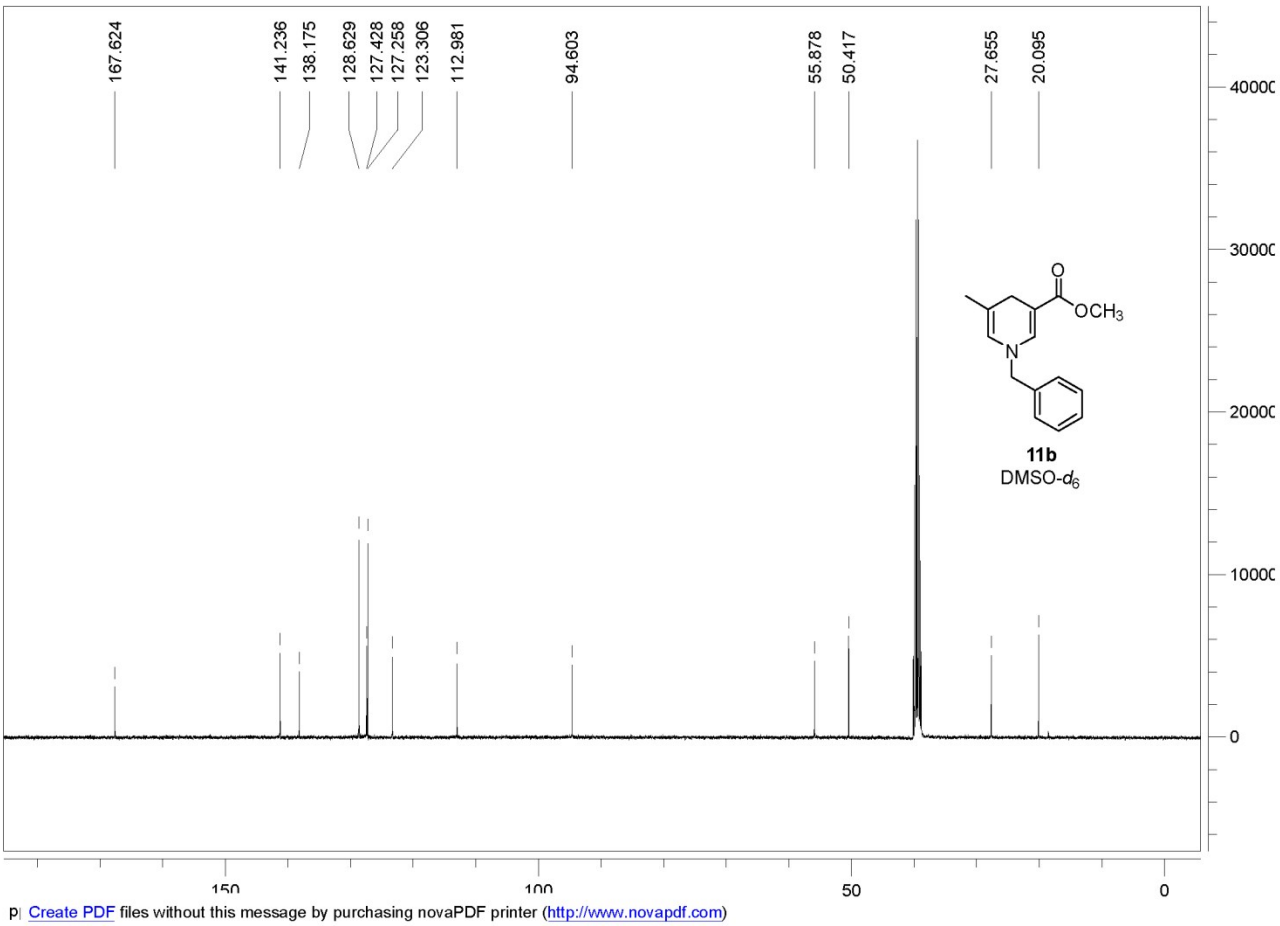
WP-ZHU ECUST institute of Fine Chem 20-Jul-2015 22:26:52

10b 142 (0.967) Cm (141:145) 1: TOF MS ES+ 2.22e+003



Minimum:				-1.5						
Maximum:		300.0	50.0	100.0						
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula			
304.1556	304.1549	0.7	2.3	7.5	17.2	0.0	C17	H22	N	O4





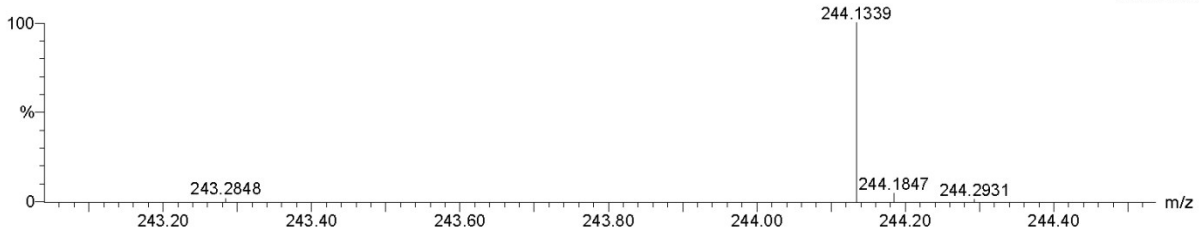
Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

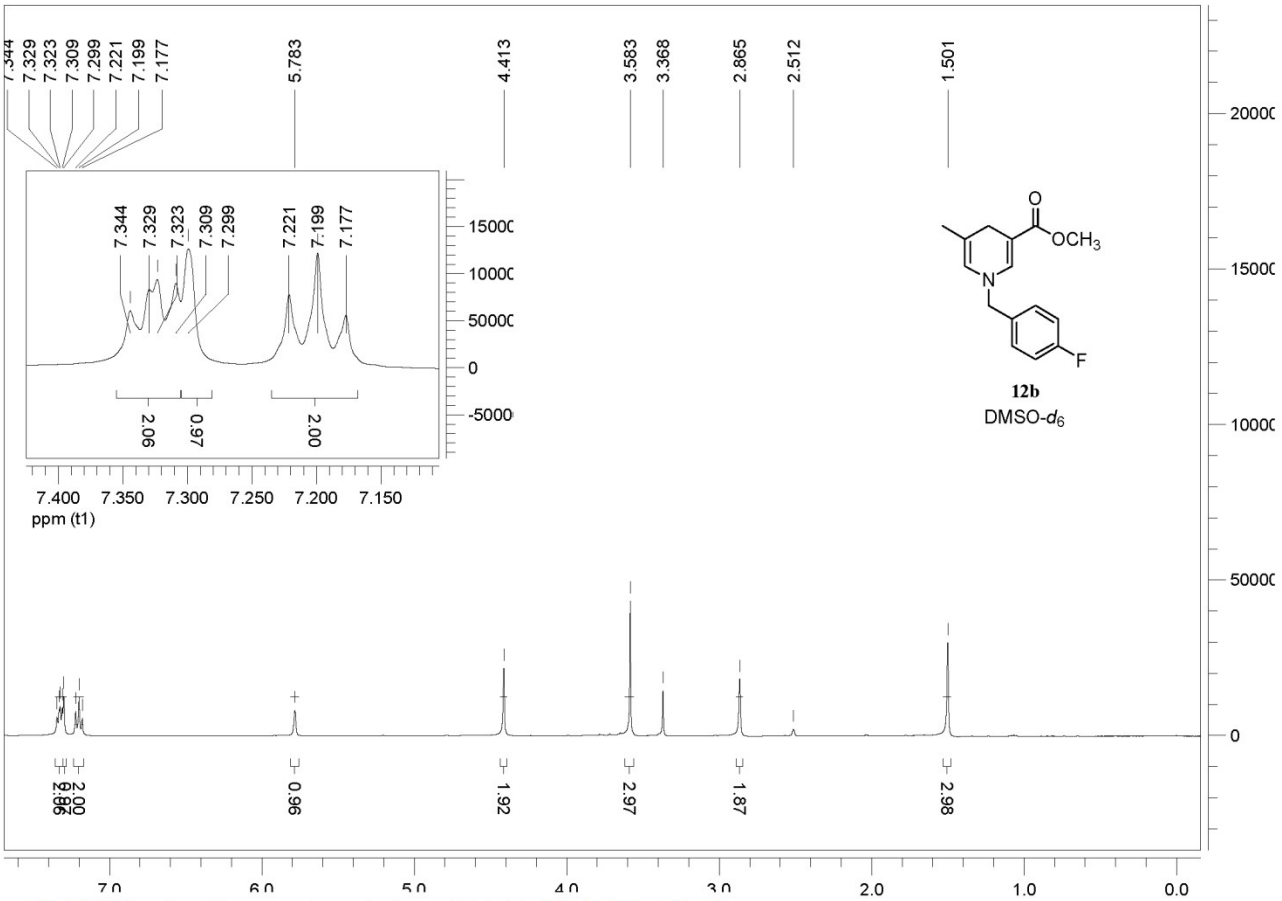
Monoisotopic Mass, Even Electron Ions
4 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-15 H: 0-18 N: 0-1 O: 0-2

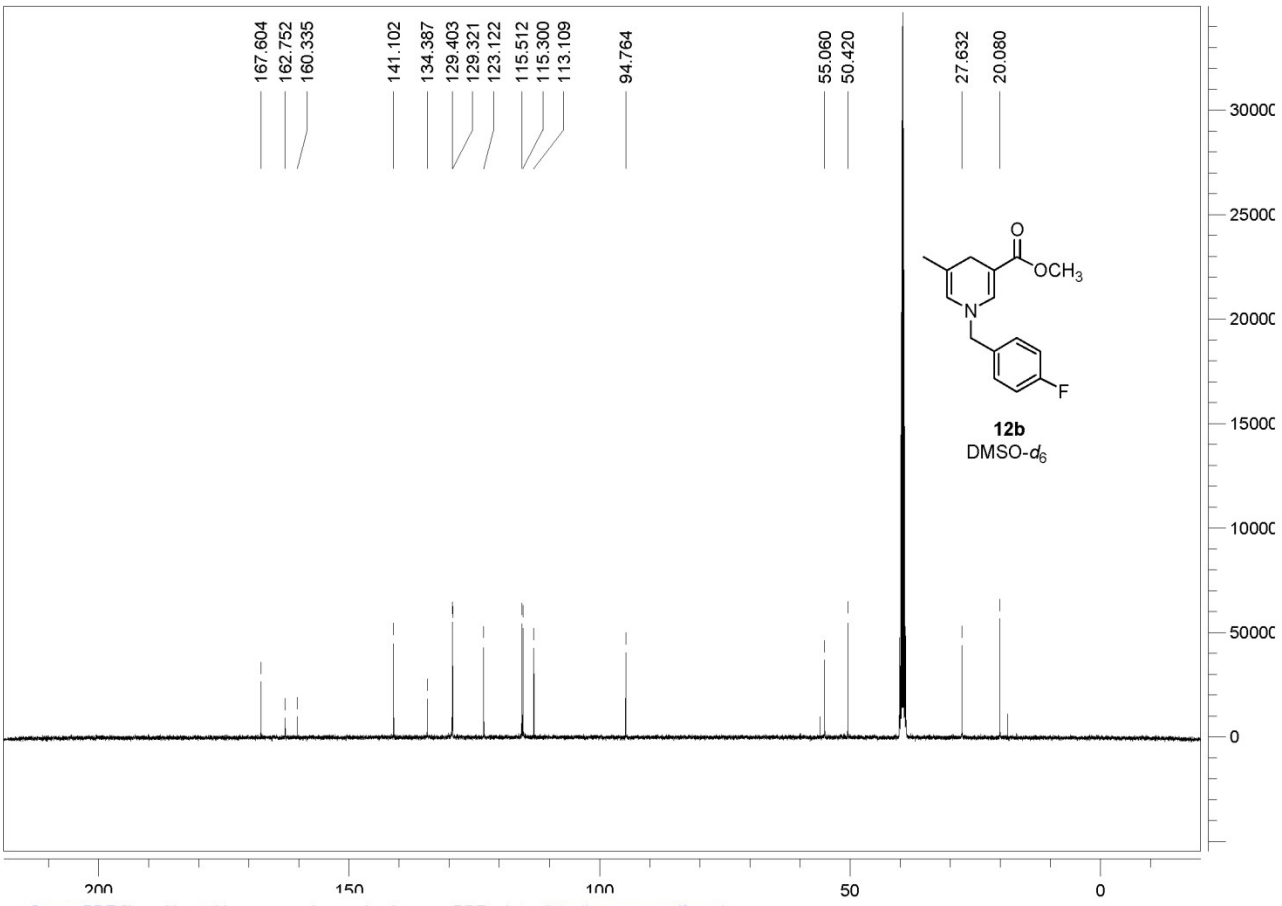
WP-ZHU ECUST institute of Fine Chem 25-May-2015 11:46:04

11b 128 (0.886) Cm (125:128) 1: TOF MS ES+ 3.61e+003



Minimum:				-1.5						
Maximum:		300.0	50.0	100.0						
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula			
244.1339	244.1338	0.1	0.4	7.5	39.4	0.0	C15	H18	N	O2





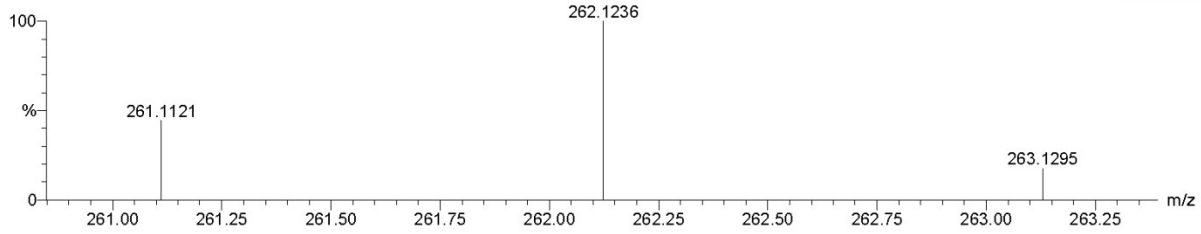
Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

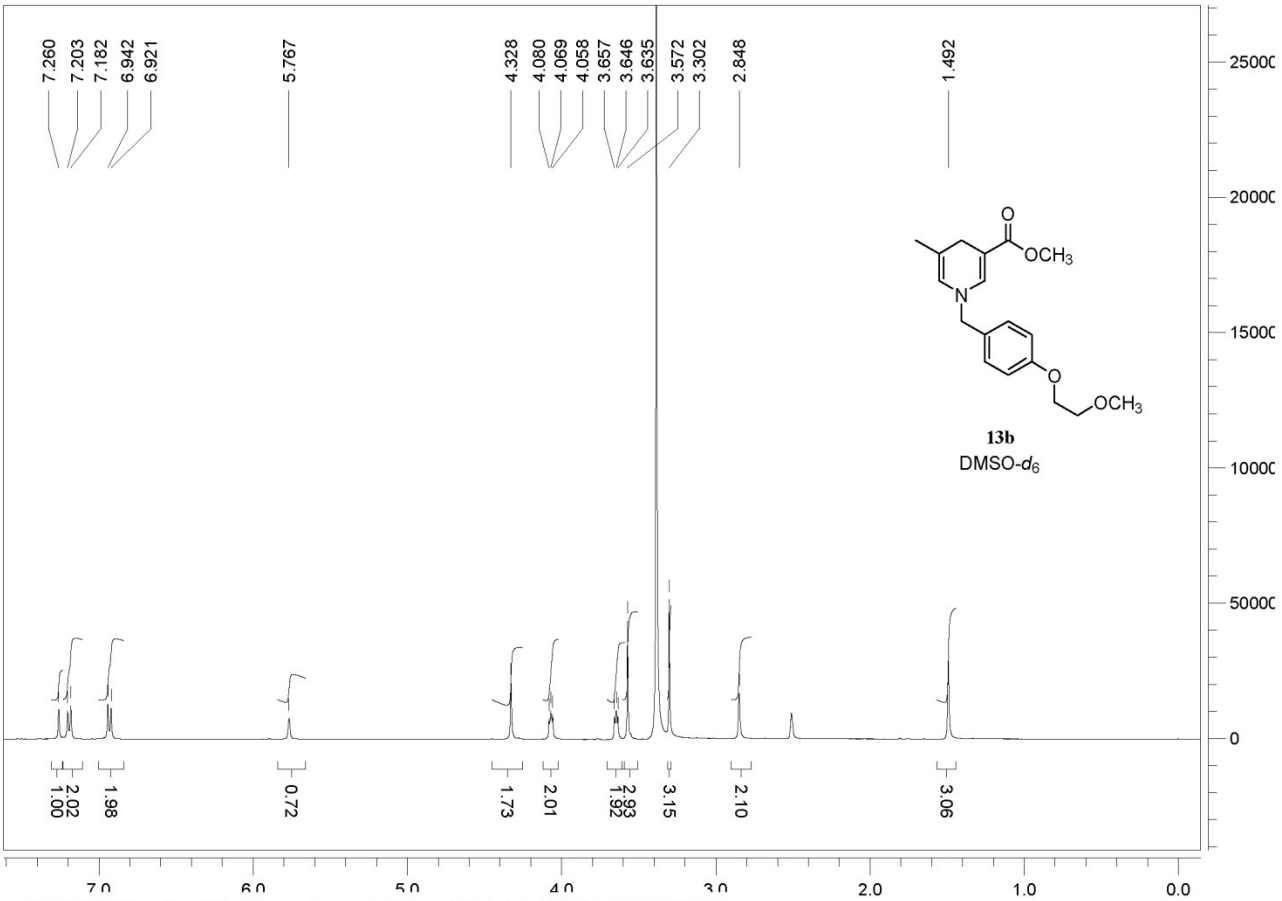
Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-15 H: 0-17 N: 0-1 O: 0-2 F: 0-1

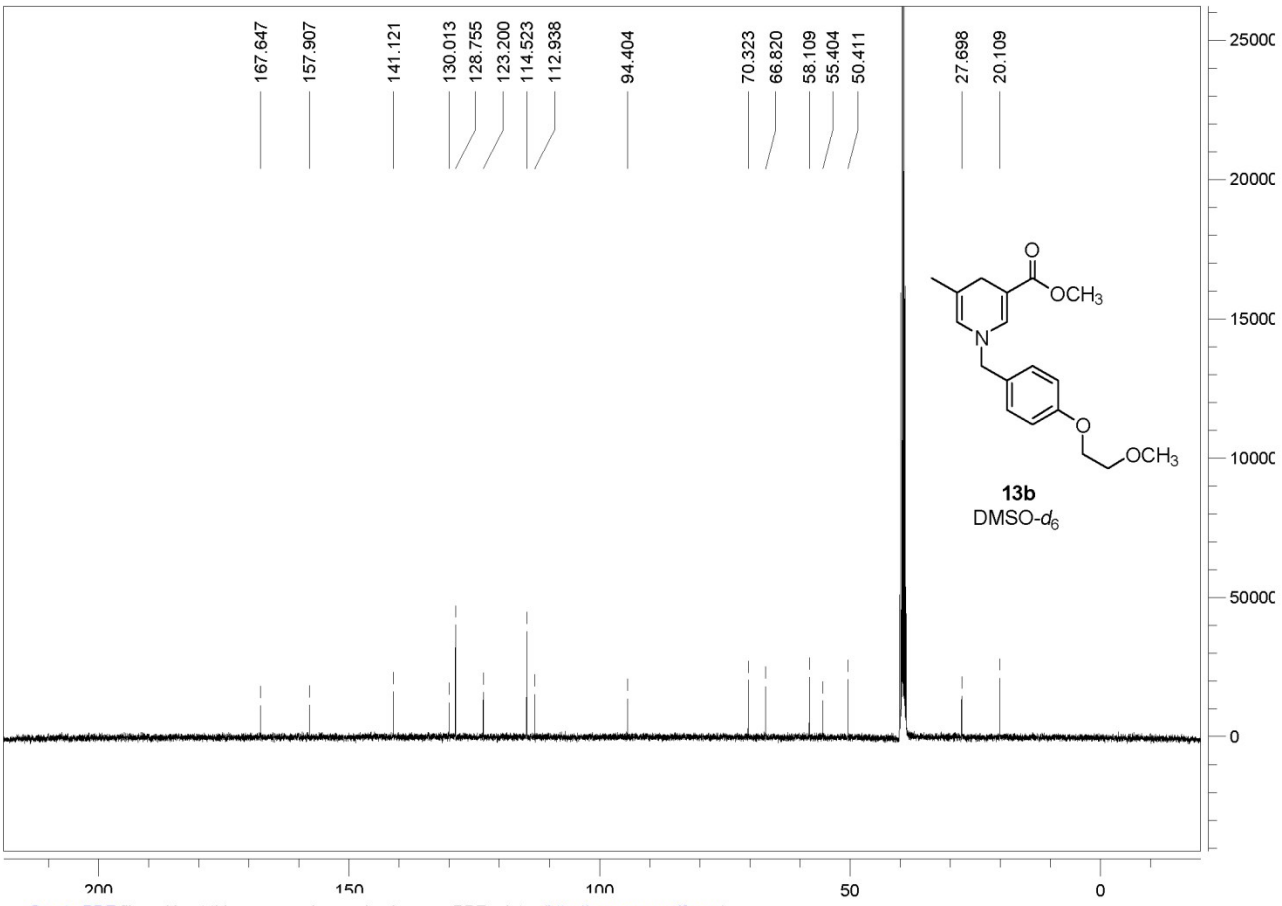
WP-ZHU ECUST institute of Fine Chem 25-May-2015 11:41:51

12b 59 (0.457) Cm (57:61) 1: TOF MS ES+ 1.48e+003



Minimum:				-1.5			
Maximum:		300.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
262.1236	262.1243	-0.7	-2.7	7.5	8.3	0.0	C15 H17 N O2 F





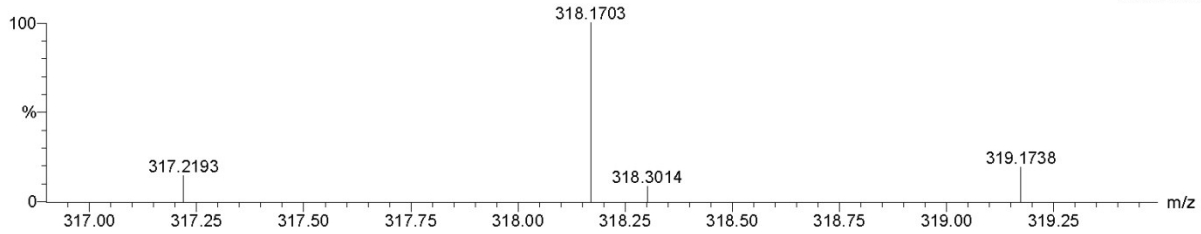
Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

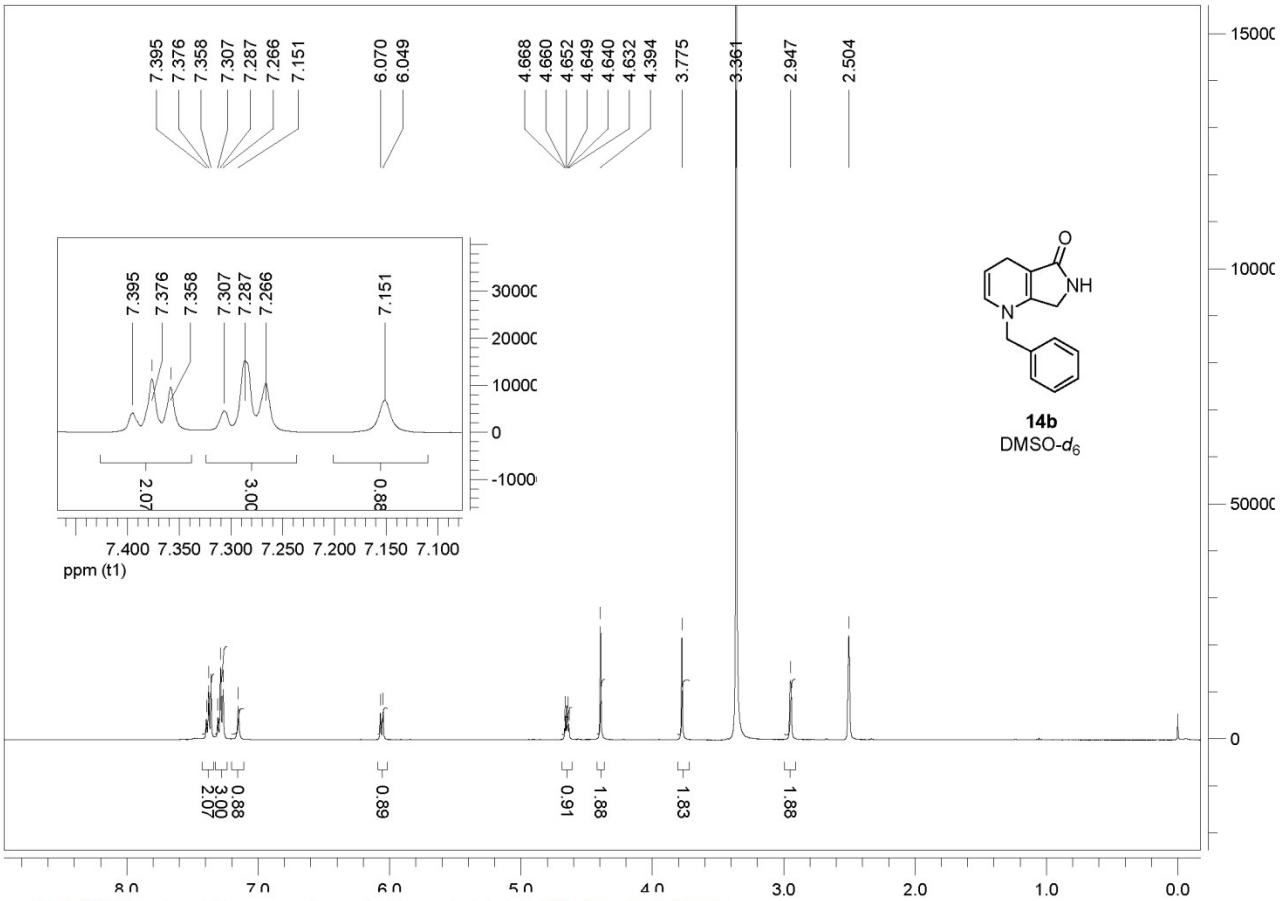
Monoisotopic Mass, Even Electron Ions
8 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-18 H: 0-24 N: 0-1 O: 0-4

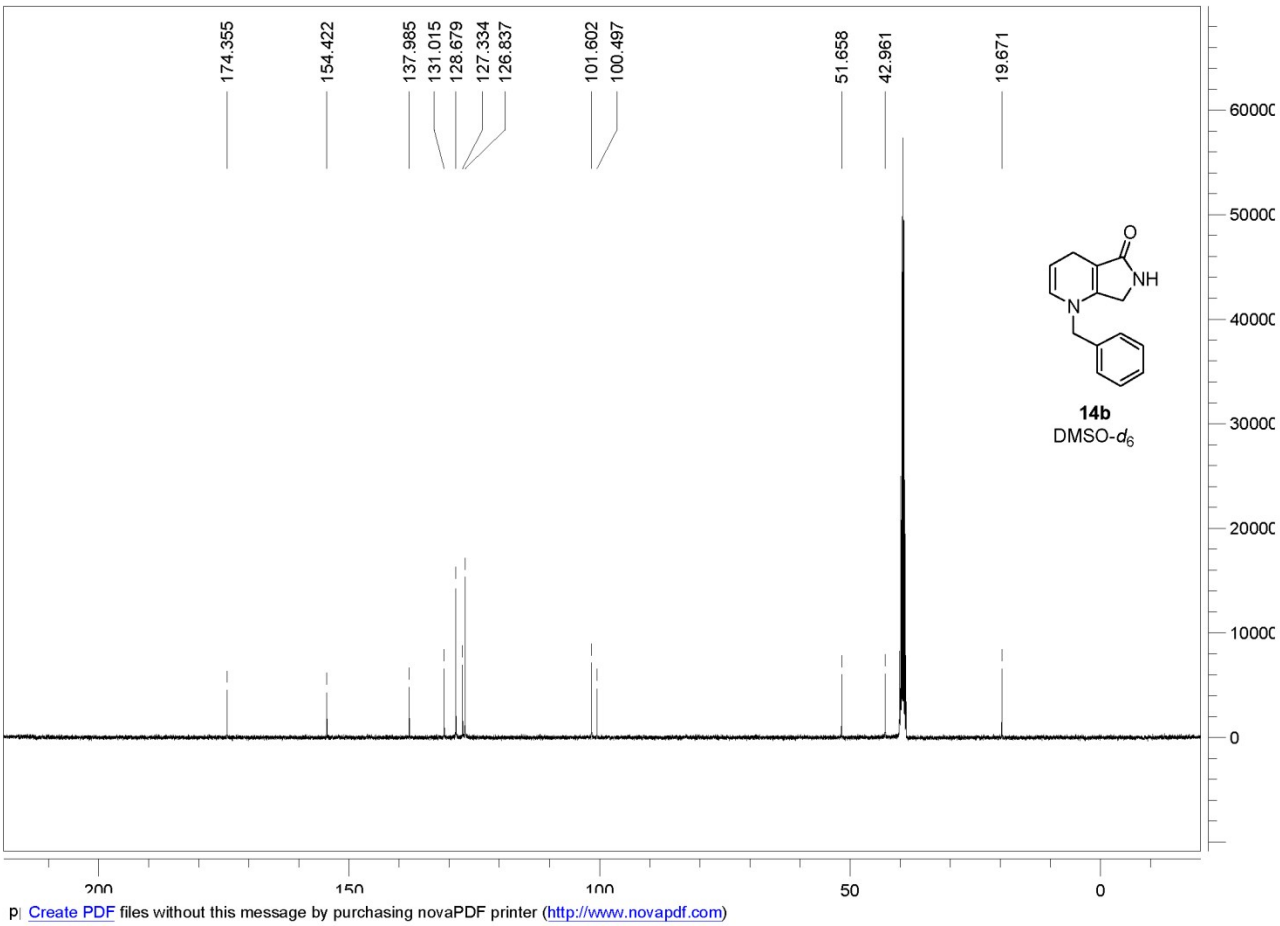
WP-ZHU ECUST institute of Fine Chem 25-May-2015 11:49:56

13b 75 (0.557) Cm (74:76) 1: TOF MS ES+ 3.35e+003



Minimum:				-1.5			
Maximum:		300.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
318.1703	318.1705	-0.2	-0.6	7.5	18.5	0.0	C18 H24 N O4





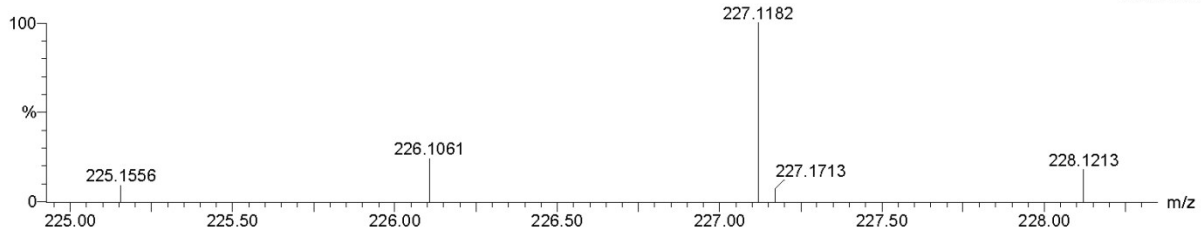
Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

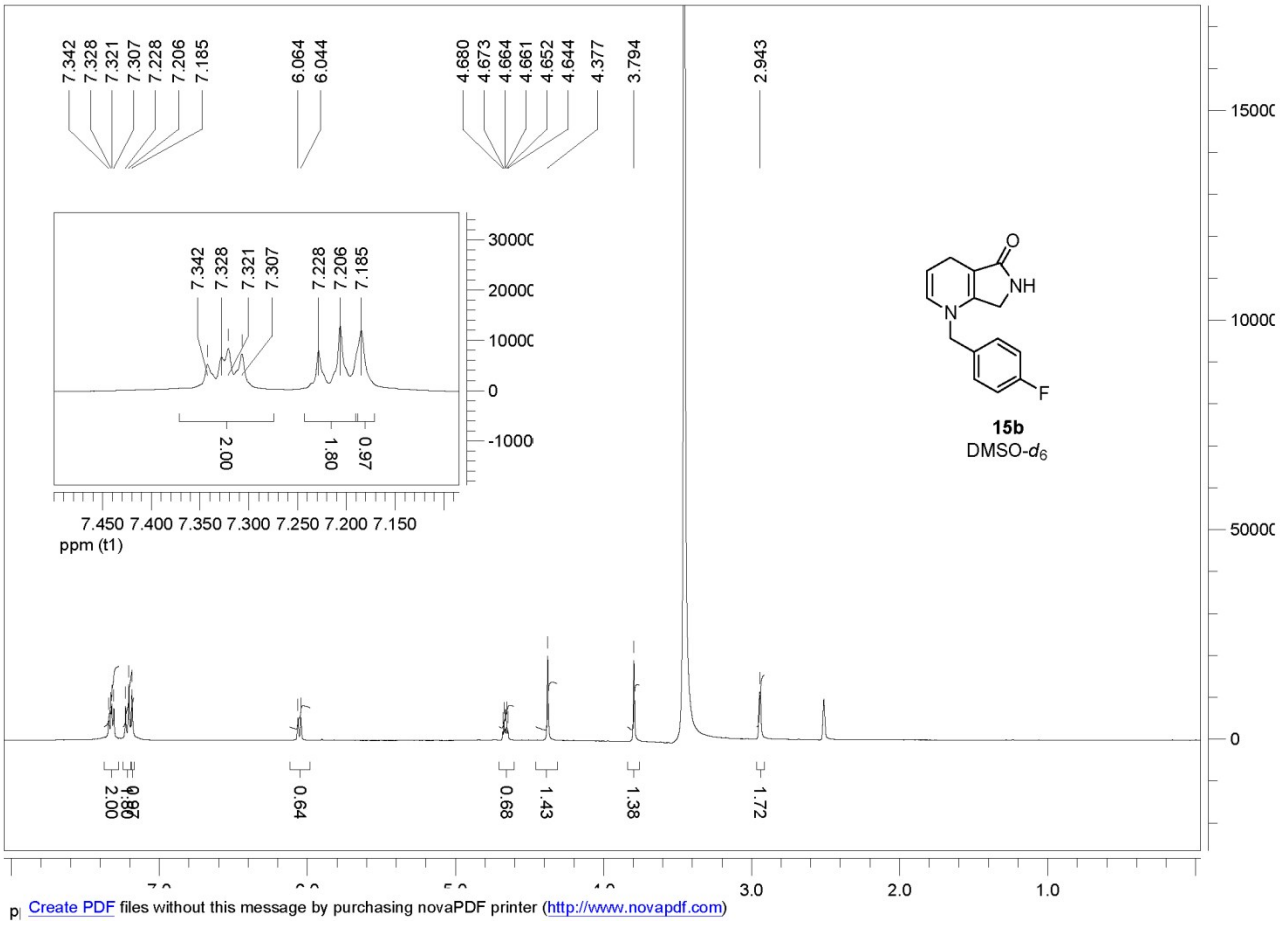
Monoisotopic Mass, Even Electron Ions
15 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-22 H: 0-30 N: 0-2 O: 0-1

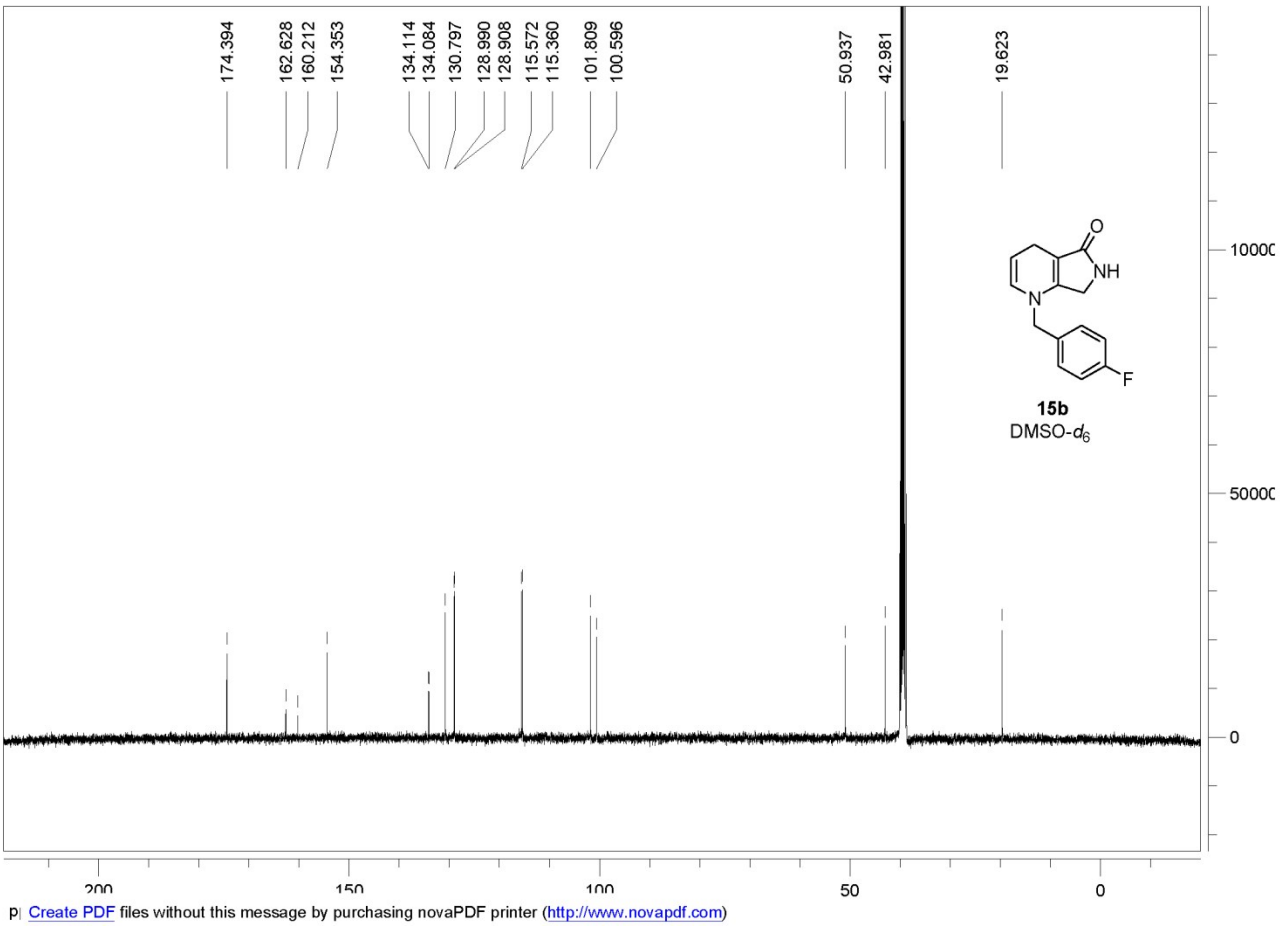
WP-ZHU ECUST institute of Fine Chem 27-Apr-2015 19:15:35

14b 191 (1.275) Cm (189:206) 1: TOF MS ES+ 7.54e+003



Minimum:				-1.5			
Maximum:		300.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
227.1182	227.1184	-0.2	-0.9	8.5	19.1	0.0	C14 H15 N2 O





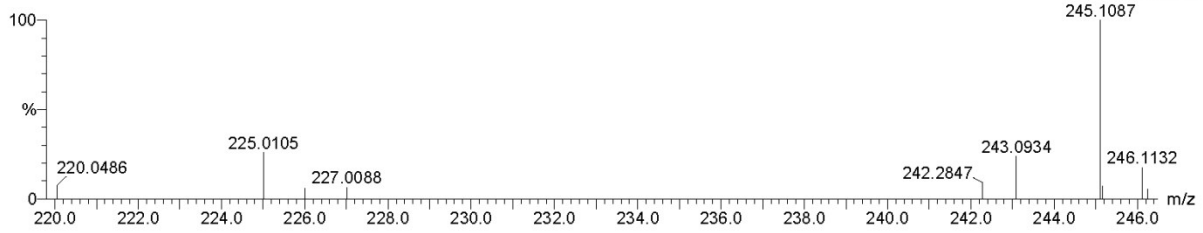
Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

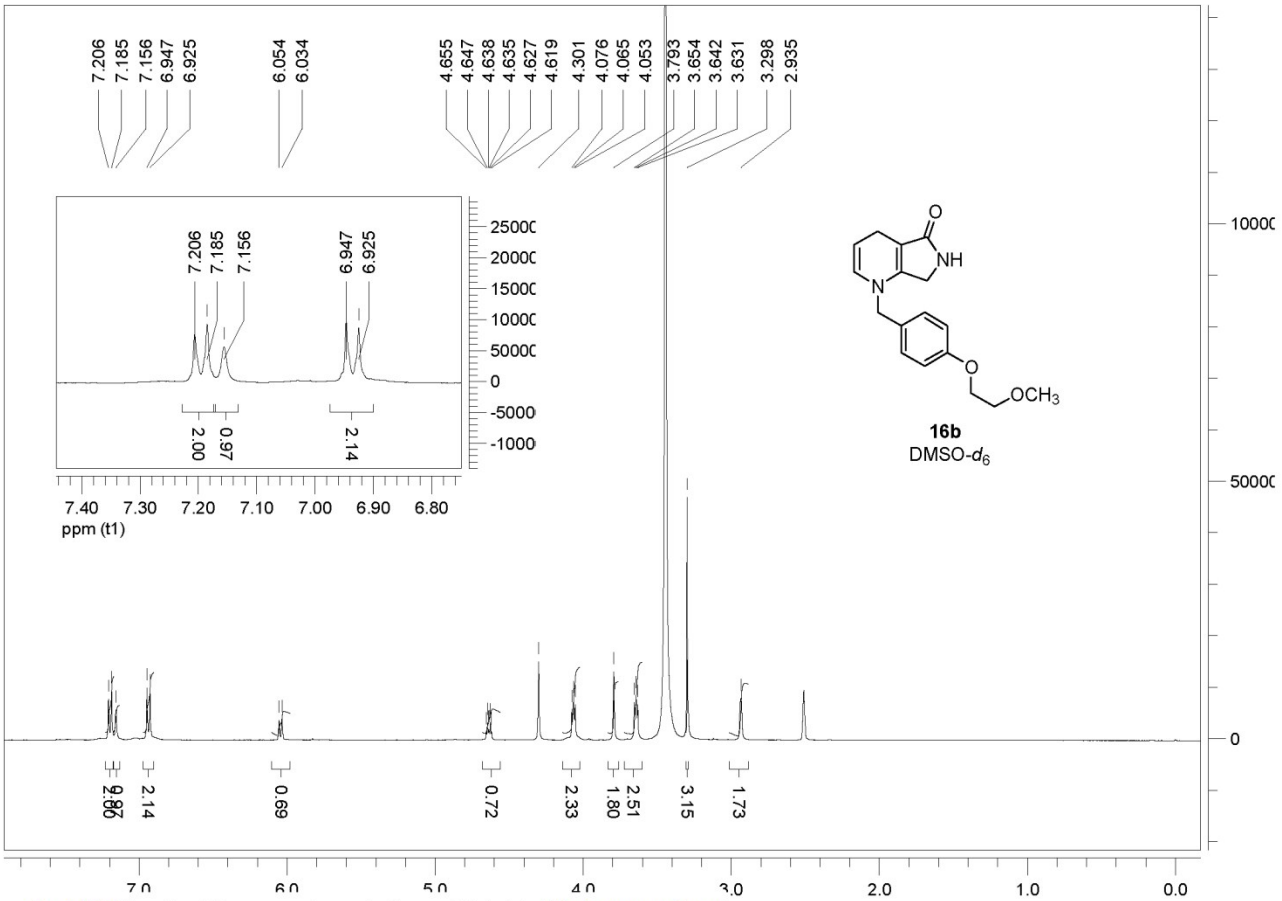
Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-14 H: 0-15 N: 0-2 O: 0-1 F: 0-1

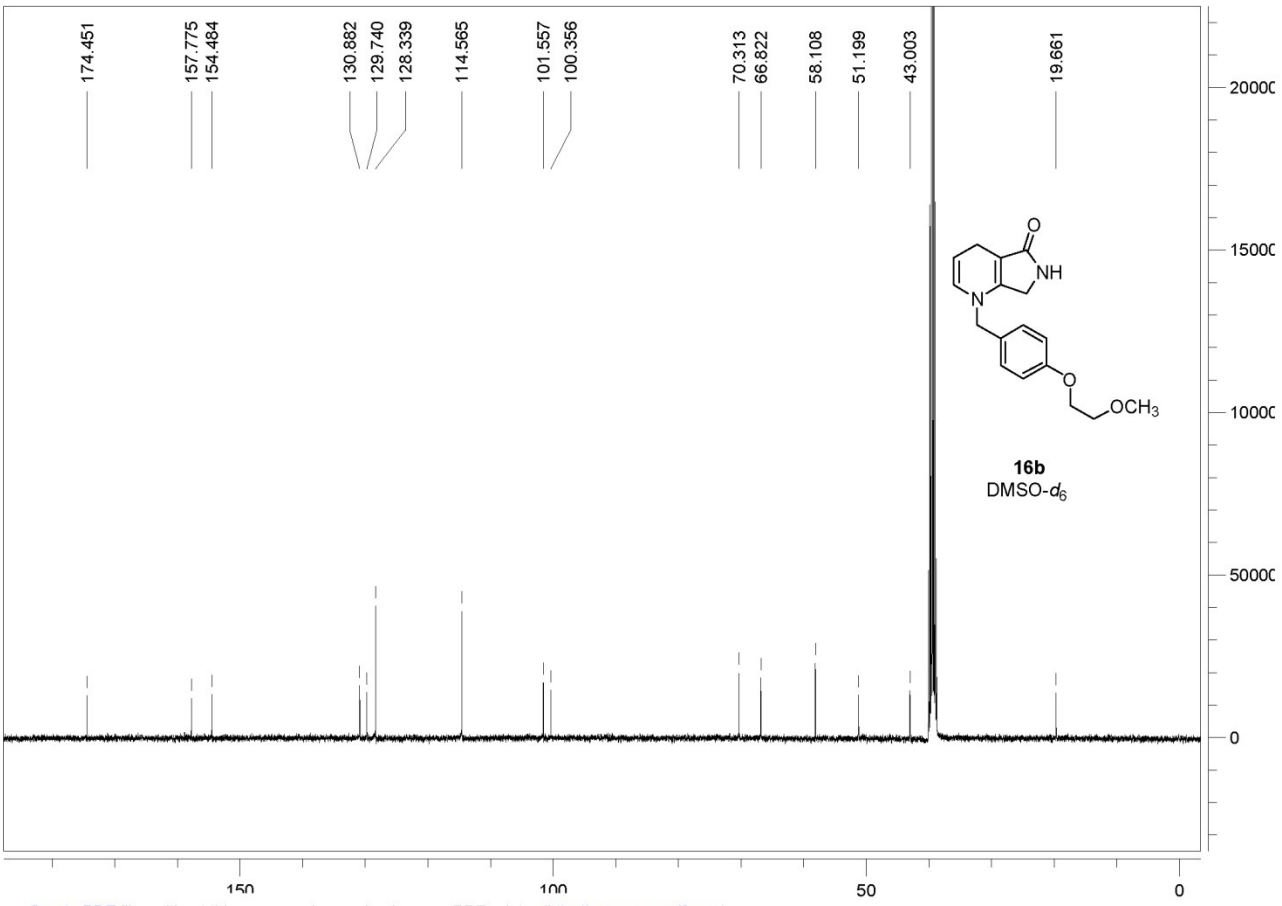
YF-XU ECUST institute of Fine Chem 19-May-2015 21:07:54

15b 63 (0.478) Cm (58:70) 1: TOF MS ES+ 2.93e+003



Minimum:				-1.5			
Maximum:		300.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
245.1087	245.1090	-0.3	-1.2	8.5	28.3	0.0	C14 H14 N2 O F





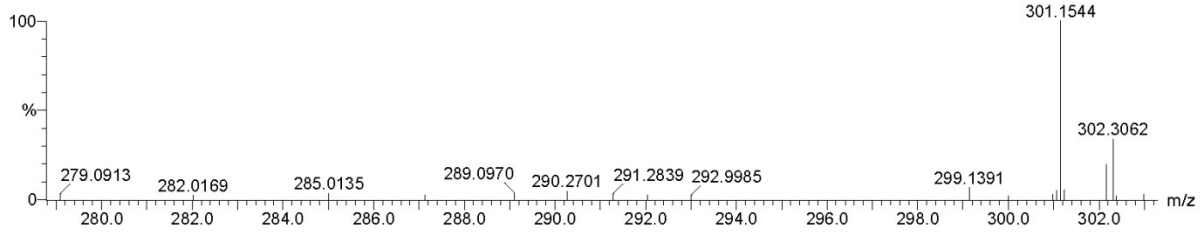
Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
10 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-17 H: 0-22 N: 0-2 O: 0-3

YF-XU ECUST institute of Fine Chem 19-May-2015 21:19:02

16b 65 (0.497) Cm (63:81) 1: TOF MS ES+ 4.05e+003



Minimum:				-1.5			
Maximum:		300.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
301.1544	301.1552	-0.8	-2.7	8.5	40.2	0.0	C17 H21 N2 O3

8 Supporting reference

1. Moutevelis-Minakakis, P.; Papavassilopoulou, E.; Mavromoustakos, T., *Molecules* **2012,** *18*, 50-73.
2. Galli, U.; Mesenzani, O.; Coppo, C.; Sorba, G.; Canonico, P. L.; Tron, G. C.; Genazzani, A. A., *Eur. J. Med. Chem.* **2012,** *55*, 58-66.
3. Zhu, X.-Q.; Tan, Y.; Cao, C.-T., *J. Phys. Chem. B.,* **2010,** *114*, 2058-2075.