A Domino Approach for the Synthesis of Pyrrolo[1,2-α]Pyrazine from Vinyl Azides

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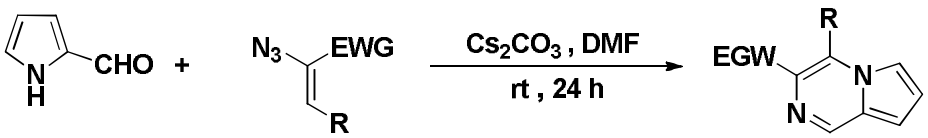

Supporting Information

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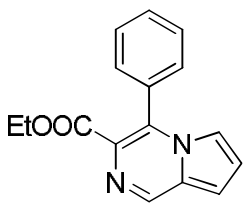
General Information:

All solvents were purified according to standard methods prior to use. Reactions were run under an atmosphere of nitrogen unless mentioned otherwise. Purifications of reaction products were carried out by chromatography using silica gel (200–300 mesh). Melting points were recorded on a BÜCHI B-540 melting point apparatus. Infrared spectra were recorded on FTIR spectrophotometer. NMR spectra were recorded for ^{1}H NMR at 500 MHz and for ^{13}C NMR at 125 MHz. For ^{1}H NMR, tetramethylsilane (TMS) served as internal standard (δ=0) and data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant(s) in Hz. For ^{13}C NMR , TMS(δ=0) or CDCl3 (δ=77.26) was used as internal standard and spectra were obtained with complete proton decoupling. Low-resolution MS and LC-MS data were obtained using ESI ionization. The starting material **1a, 1b, 1c, 1d, 1e, 1f, 1h, 1i, 1j, 1k, 1l, 1m, 1n, 1o, 1p, 1q, 1r** were prepared according to literature methods.[1, 2]

General Procedure for the Synthesis of 3

A mixture of vinyl azide **1** (1.0 mmol), 1H-pyrrole-2-carbaldehyde **2** (1.1 mmol) and Cs_2CO_3 (1.1 mmol) was stirred in anhydrous DMF (2 ml) at rt under nitrogen overnight. The reaction mixture was quenched with water (10 ml), and then extracted three times with EtOAc. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated. Purification of the crude product by chromatography (silica gel ; petroleum ether : ethyl acetate = 3 : 1) to afford **3**.

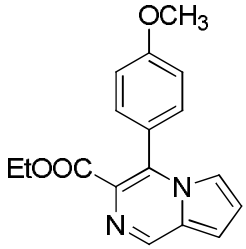
Characterization Data
Ethyl 4-phenylpyrrolo [1, 2-a] pyrazine-3-carboxylate (3a) :



3a

Pale yellow solid; m.p. 61-63 ^{0}C;IR(KBr) ν/ cm^{-1} 3050, 2980, 1725, 1380, 730, 708 ; ^{1}H NMR (500MHz, $CDCl_3$)δ 1.11 (3H, t, J=7.0Hz), 4.19 (2H, q, J=7.0Hz), 6.89-6.90 (1H,m), 6.94-6.95 (1H, m), 7.04 (1H, m), 7.41-7.43 (2H, m), 7.56-7.59 (3H, m), 8.91 (1H,s); ^{13}C NMR (125MHz, $CDCl_3$) δ 13.9, 61.2, 105.2, 116.0, 116.7, 126.6, 128.7, 129.2, 129.6, 132.4, 134.5, 143.5, 165.7; LC-MS(ESI): m/z $[M+H]^+$:267.0. HRMS (EI): m/z Calcd for $C_{16}H_{14}N_2O_2$ $(M)^+$ 266.1055 Found: *m/z* 266.1065.

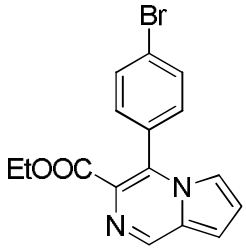
Ethyl 4-(4-methoxyphenyl)pyrrolo[1,2-a]pyrazine-3-carboxylate(3b):



3b

Pale yellow solid; m.p. 112-114^{o}C;IR(KBr) ν/ cm^{-1} 3118, 2972, 1716, 1375, 814 ; ^{1}H NMR (500MHz, $CDCl_3$)δ 1.17 (3H, t, J=7.5Hz), 3.90 (3H, s), 4.22 (2H, q, J=7.0Hz), 6.88-6.90 (1H,m), 6.92-6.94 (1H, m), 7.09 (2H, d, J=9.0Hz), 7.11-7.11 (1H, m), 7.34-7.36 (2H, d, J=9Hz), 8.82 (1H,s); ^{13}C NMR (125MHz, $CDCl_3$) δ 14.2, 55.5, 61.4, 105.3, 114.8, 116.1, 116.7, 124.5, 127.0, 128.9, 130.3, 134.5, 143.5, 160.7, 166.0; LC-MS(ESI): m/z $[M+H]^+$:297.0. HRMS (EI): m/z Calcd for $C_{17}H_{16}N_2O_3$ $(M)^+$ 296.1161 Found: *m/z* 296.1159.

Ethyl 4-(4-bromophenyl) pyrrolo [1, 2-a] pyrazine-3-carboxylate (3c):

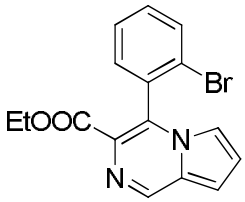


3c

Pale yellow solid; m.p. 81-83^{o}C; IR (KBr) ν/ cm^{-1} 3046, 2983, 1714, 810;^{1}H NMR (500MHz, $CDCl_3$)δ 1.18 (3H, t, J=7.5Hz), 4.23 (2H, q, J=7.0 Hz), 6.91-6.93 (1H, m), 6.96-6.97 (1H, m), 7.02-7.03 (1H, m), 7.31 (2H, d, J=8.5Hz), 7.72 (2H, d, J=8.5Hz), 8.92 (1H, s);^{13}C NMR (125MHz, $CDCl_3$)δ14.2, 61.6, 105.7, 116.0, 117.1, 124.2,

126.8, 128.9, 130.7, 131.5, 132.8, 133.6, 144.0, 165.6; LC-MS(ESI): m/z $[M+H]^+$:345.9. HRMS (EI): m/z Calcd for $C_{16}H_{13}N_2O_2Br$ $(M)^+$ 344.0160 Found: *m/z* 344.0164.

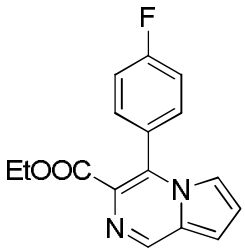
Ethyl 4-(2-bromophenyl)pyrrole[1,2-a]pyrazine-3-carboxylate (3d)



3d

Pale yellow solid; m.p. 115-117°C; IR(KBr) ν/ cm^{-1} 3058, 2971, 1721, 724;^{1}H NMR (500MHz, $CDCl_3$)δ1.14 (3H, t, J=7.0Hz), 4.23 (2H, q, J=7.0Hz), 6.90 (1H, m), 6.93-6.95 (1H, m), 6.98-6.99 (1H, m), 7.35 (1H, d, J=7.5Hz), 7.44(1H, t, J=7.5Hz), 7.52 (1H, t, J=7.5Hz), 7.79 (1H, d, J=8.0Hz), 8.96 (1H, s); ^{13}C NMR (125MHz, $CDCl_3$) δ14.1, 61.5, 105.6, 116.0, 117.3, 123.4, 126.9, 128.4, 128.6, 130.7, 131.3, 133.4, 133.9, 134.2, 144.0, 165.2;LC-MS(ESI): m/z $[M+H]^+$:345.2. HRMS (EI): m/z Calcd for $C_{16}H_{13}N_2O_2Br$ $(M)^+$ 344.0160 Found: *m/z* 344.0164.

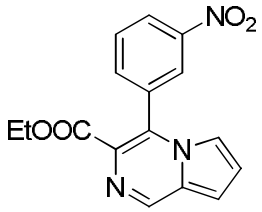
Ethyl 4-(4-fluorophenyl)pyrrolo[1,2-a]pyrazine-3-carboxylate (3e)



3e

Pale yellow solid ;m.p. 108-110°C; IR (KBr) ν/ cm^{-1} 3044, 2990, 1719, 838;^{1}H NMR (500MHz, $CDCl_3$)δ1.17 (3H, t, J=7.0Hz), 4.22 (2H, q, J=7.0Hz), 6.91-6.92 (1H, m), 6.96-6.97 (1H, m), 7.03 (1H,m), 7.27-7.30 (2H, m), 7.40-7.43 (2H, m), 8.91 (1H,s);^{13}C NMR (125MHz, $CDCl_3$) δ14.1, 61.4, 105.5, 115.9, 116.6(d, J=22), 116.9, 126.8, 128.4(d, J=4),128.8, 130.9(d, J=8), 133.6, 143.8, 163.4(d, J=249), 165.6 ;LC-MS(EI): m/z $[M+H]^+$:285.2. HRMS (EI): m/z Calcd for $C_{16}H_{13}N_2O_2F$ $(M)^+$ 284.0961 Found: *m/z* 284.0955.

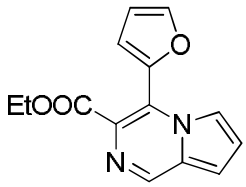
Ethyl 4-(3-nitrophenyl)pyrrolo[1,2-a]pyrazine-3-carboxylate (3f)



3f

Yellow solid; m.p. 162-163^{0}C;IR(KBr) ν/ cm^{-1}3051, 2973, 1723, 811, 735;^{1}H NMR (500MHz, $CDCl_3$)δ 1.20 (3H, t, J=7.0Hz), 4.24 (2H, q, J=7.5Hz), 6.95-6.97 (2H, m), 7.02-7.03 (1H, m), 7.77-7.83 (2H, m), 8.33 (1H, s), 8.45 (1H, d, J=7.5Hz), 8.98 (1H, s); ^{13}C NMR (125MHz, $CDCl_3$) δ 14.0, 61.6, 106.0, 115.6, 117.4, 124.3, 124.5, 126.7, 128.7, 130.4, 132.1, 134.1, 135.2, 144.3, 148.8, 165.1; LC-MS(EI): m/z $[M+H]^+$:311.9. HRMS (EI): m/z Calcd for $C_{16}H_{13}N_3O_4$ $(M)^+$ 311.0906 Found: *m/z* 311.0913.

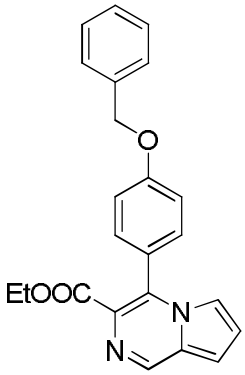
Ethyl 4-(furan-2-yl)pyrrolo[1,2-a]pyrazine-3-carboxylate(3g)



3g

Yellow liquid; IR(KBr) ν/ cm^{-1}3123, 2983, 1729; ^{1}H NMR (500MHz, $CDCl_3$)δ1.26 (3H, t, J=7.0Hz), 4.31 (2H, q, J=7.5Hz), 6.65-6.66 (1H, m), 6.83 (1H, m), 6.95-6.97 (2H, m), 7.52 (1H, m), 7.69 (1H, m), 8.86 (1H, s);^{13}C NMR (125MHz, $CDCl_3$) δ 14.2, 61.7, 105.8, 111.6, 113.1, 116.1, 117.0, 123.5, 128.6, 129.7, 143.8, 144.1, 144.3, 165.9; LC-MS(ESI): m/z $[M+H]^+$:257.1. HRMS (EI): m/z Calcd for $C_{14}H_{12}N_2O_3$ $(M)^+$ 256.0848 Found: *m/z* 256.0858.

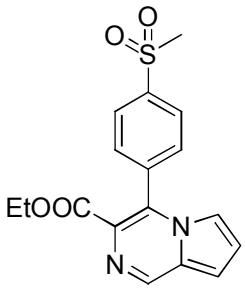
Ethyl 4-(4-(benzyloxy)phenyl)pyrrolo[1,2-a]pyrazine-3-carboxylate(3h)



3h

Pale yellow solid;m.p. 88-90^{0}C ;IR(KBr) ν/ cm^{-1}3067, 2981, 1715, 817, 736;^{1}H NMR (500MHz, $CDCl_3$)δ 1.14 (3H, t, J=7.0Hz), 4.21 (2H, q, J=7.0Hz), 5.15 (2H, s), 6.88-6.90 (1H, m), 6.93 (1H, m), 7.12 (1H, brs), 7.16 (2H, d, J=9.0Hz), 7.34-7.38 (3H, m), 7.42 (2H, t, J=7.0Hz), 7.48 (2H, d, J=7.0 Hz), 8.88 (1H, s) ; ^{13}C NMR (125MHz, $CDCl_3$) δ 14.0, 61.2, 70.1, 105.2, 115.5, 115.9, 116.6, 124.6, 126.8, 127.6, 128.2, 128.7, 130.2, 130.3, 134.3, 136.5, 143.4, 159.7, 165.9; LC-MS(ESI): m/z [M+H]$^+$:373.0. HRMS (EI): m/z Calcd for $C_{23}H_{20}N_2O_3$ $(M)^+$ 372.1474 Found: *m/z* 372.1481.

Ethyl 4-(4-(methylsulfonyl)phenyl)pyrrolo[1,2-a]pyrazine-3-carboxylate(3i)

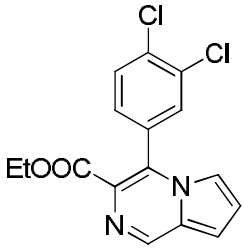


3i

Pale yellow solid;m.p. 182-184^{0}C ; IR(KBr) ν/ cm^{-1}3119, 2991, 1707, 818; ^{1}H NMR (500MHz, $CDCl_3$)δ 1.19(3H, t, J=7.0Hz), 3.19(3H, s), 4.23(2H, q, J=7.0Hz), 6.92-6.93(1H, m), 6.95-6.96(1H, m), 7.01-7.02(1H, m), 7.67(2H, d, J=8Hz), 8.19(2H, d, J=8Hz), 8.96(1H, s); ^{13}C NMR (125MHz, $CDCl_3$) δ14.1, 44.6, 61.7, 106.0, 115.9, 117.5, 126.6, 128.6, 128.8, 130.2, 132.9, 138.3, 141.8, 144.3, 165.3 ; LC-MS(ESI): m/z [M+H]$^+$:345.2. HRMS (EI): m/z Calcd for $C_{17}H_{16}N_2O_4S$ $(M)^+$ 344.0831 Found:

m/z 344.0829.

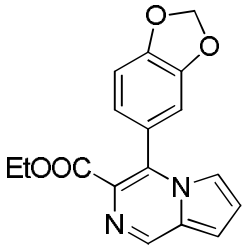
Ethyl 4-(3,4-dichlorophenyl)pyrrolo[1,2-a]pyrazine-3-carboxylate(3j)



3j

White solid;m.p. 169-171^{0}C ; IR(KBr) ν/ cm^{-1}3057, 2951, 1715, 1639, 866, 823, 772, 732 ;^{1}H NMR (500MHz, $CDCl_3$) 1.21(3H, t, J=7.0Hz), 4.25-4.26(2H, m), 6.94-6.95(1H, m), 6.98(1H, m), 7.03(1H, m), 7.28(1H, d, J=8.0Hz), 7.54(1H, s), 7.67(1H, d, J=8.0Hz), 8.92(1H, s);^{13}C NMR (125MHz, $CDCl_3$) δ 14.2, 61.7, 105.9, 116.0, 117.4, 126.9, 128.5, 128.9, 131.1, 131.6, 132.3, 132.4, 133.9, 134.4, 144.2, 165.4; LC-MS(ESI): m/z $[M+H]^+$:335.1. HRMS (EI): m/z Calcd for $C_{16}H_{12}N_2O_2Cl_2$ $(M)^+$ 334.0276 Found: *m/z* 334.0269.

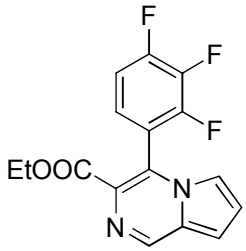
Ethyl 4-(benzo[d][1,3]dioxol-5-yl)pyrrolo[1,2-a]pyrazine-3-carboxylate(3k)



3k

Yellow solid;m.p. 104.5-106 ^{0}C ; IR(KBr) ν/ cm^{-1}3044, 2991, 1715, 884, 808, 714;^{1}H NMR (500MHz, $CDCl_3$)δδ1.22(3H, t, J=7.0Hz), 4.25(2H, q, J=7.0Hz), 6.07(2H, m), 6.88-6.90 (3H, m), 6.93(1H, brs), 6.98-7.00(1H, m), 7.15(1H, s), 8.88(1H, s); ^{13}C NMR (125MHz, $CDCl_3$) δ14.1, 61.3, 101.6, 105.3, 109.2, 109.3, 115.9, 116.7, 122.8, 125.6, 127.0, 128.8, 133.9, 143.5, 148.4, 148.8, 165.8; LC-MS(ESI): m/z $[M+H]^+$:311.2. HRMS (EI): m/z Calcd for $C_{17}H_{14}N_2O_4$ $(M)^+$ 310.0954 Found: *m/z* 310.0956.

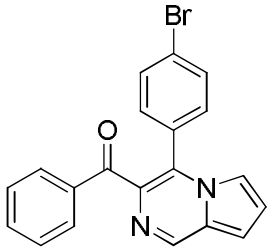
Ethyl 4-(2,3,4-trifluorophenyl)pyrrolo[1,2-a]pyrazine-3-carboxylate(3l)



3l

White solid;m.p. 88.5-90 ^{0}C ; IR(KBr) ν/ cm^{-1} 3069, 2993, 1718, 812, 733 ;^{1}H NMR (500MHz, $CDCl_3$)δ 1.27(3H, t, J=7.0Hz), 4.29(2H, q, J=7.0Hz), 6.97-9.98(1H, m), 7.00-7.01(1H, m), 7.06(1H, m), 7.12-7.17(1H, m), 7.18-7.23(1H, m), 8.96(1H, s);^{13}C NMR (125MHz, $CDCl_3$) δ 165.1, 152.5(ddd, J1=252,J2=10, J3=3), 149.6(ddd, J1=252, J2=10, J3=3), 144.6, 140.8(dt, J1=252, J2=15), 128.9, 128.0, 127.2, 124.5, 118.1(dd, J1=14, J2=4), 117.5, 115.7, 113.4(dd, J1=18, J2=4), 106.1, 61.8, 14.2; LC-MS(ESI): m/z $[M+H]^+$:321.2. HRMS (EI): m/z Calcd for $C_{16}H_{11}N_2O_2F_3$ $(M)^+$ 320.0773 Found: *m/z* 320.0776.

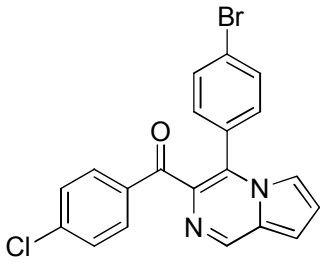
(4-(4-bromophenyl)pyrrolo[1,2-a]pyrazin-3-yl)(phenyl)methanone(3m)



3m

Brown solid;m.p. 215-217 ^{0}C ; IR(KBr) ν/ cm^{-1}3066, 2958, 1666, 803, 735 ; ^{1}H NMR (500MHz, $CDCl_3$)δ 6.64(1H, t, J=3.5Hz), 6.93-6.94(1H, m), 7.13-7.16(4H, m), 7.32-7.35(4H, m), 7.39(2H, d, J=7.0Hz) 8.91(1H, s); ^{13}C NMR (125MHz, $CDCl_3$) δ 113.3, 114.7, 120.2, 122.0, 124.9, 125.2, 125.9, 128.3, 128.7, 129.0, 132.2, 132.3, 133.0, 137.1, 155.0, 190.5 ;LC-MS(ESI): m/z $[M+NH_4]^+$:394.2. HRMS (EI): m/z Calcd for $C_{20}H_{13}N_2OBr$ $(M)^+$ 376.0211Found: *m/z* 376.0202.

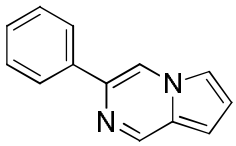
(4-(4-bromophenyl)pyrrolo[1,2-a]pyrazin-3-yl)(4-chlorophenyl)methanone(3n)



3n

Yellow solid;m.p. 130-132 ^{0}C ; IR(KBr) ν/ cm^{-1}3030, 2924, 1659, 817; ^{1}H NMR (500MHz, $CDCl_3$)δ6.96-6.97(1H, m), 6.99-7.00(1H, m), 7.22-7.23(1H, m), 7.35(2H, d, J=8.5Hz), 7.39(2H, d, J=8.5Hz), 7.63(2H, d, J=8.5Hz), 7.82(2H, d, J=8.5Hz), 8.85(1H, s); ^{13}C NMR (125MHz, $CDCl_3$) δ 105.7, 115.6, 117.1, 124.6, 128.7, 128.9, 130.1, 131.2, 131.6, 132.0, 132.9, 134.0, 135.8, 139.6, 143.0, 192.5; LC-MS(ESI): m/z $[M+H]^+$:411.1. HRMS (EI): m/z Calcd for $C_{20}H_{12}N_2OClBr$ $(M)^+$ 409.9822 Found: *m/z* 409.9814.

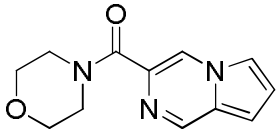
3-phenylpyrrolo[1,2-a]pyrazine(3o)



3o

Brown liquid; IR(KBr) ν/ cm^{-1} 3053, 1624, 730, 704; ^{1}H NMR (500MHz, $CDCl_3$)δ 6.88-6.89(2H, m), 7.45(1H, s), 7.52-7.56(4H, m), 7.65(2H, d, J=7.5Hz), 8.80(1H, s); ^{13}C NMR (125MHz, $CDCl_3$) δ 104.2, 113.4, 115.1, 126.9, 128.7, 129.4, 129.9, 130.6, 132.6, 144.3; LC-MS(ESI): m/z $[M+H]^+$:195.2. HRMS (EI): m/z Calcd for $C_{13}H_{10}N_2$ $(M)^+$ 194.0844 Found: *m/z* 194.0842.

Morpholino(pyrrolo[1,2-a]pyrazin-3-yl)methanone(3p)

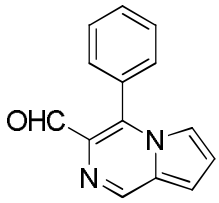


3p

White solid; m.p.100-102 ^{0}C IR(KBr) ν/ cm^{-1}3027, 2909, 2858, 1634 ; ^{1}H NMR (500MHz, $CDCl_3$)δ 3.78-3.89(8H, m), 6.85-6.86(1H, m), 6.97-6.98(1H, m),

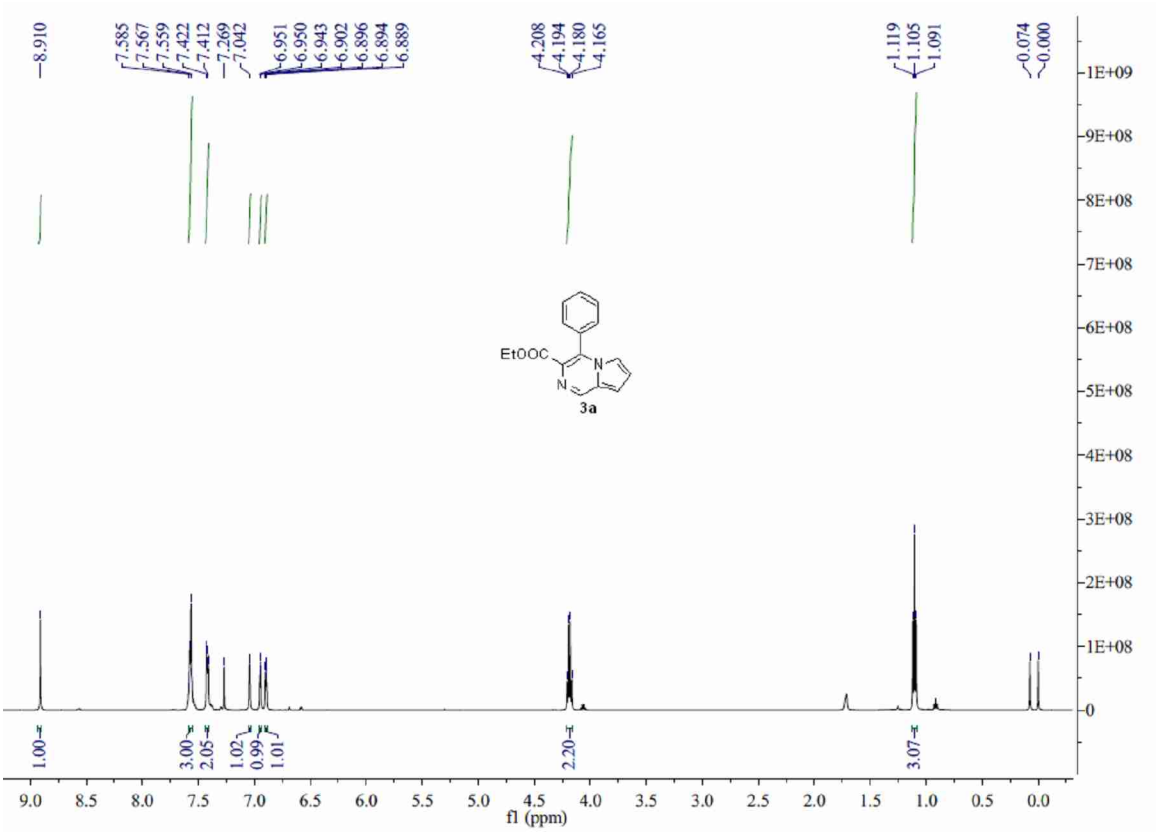
7.52-7.53(1H, m), 8.47(1H, s), 8.72(1H, s); ^{13}C NMR (125MHz, $CDCl_3$) δ43.4, 67.0, 104.5, 116.3, 116.6, 122.1, 127.6, 133.2, 142.8, 166.6; LC-MS(ESI): m/z $[M+H]^+$:232.2. HRMS (EI): m/z Calcd for $C_{12}H_{13}N_3O_2$ $(M)^+$ 231.1008 Found: *m/z* 231.1008.

4-phenylpyrrolo[1,2-a]pyrazine-3-carbaldehyde(3q)



3q

Brown liquid;IR(KBr) ν/ cm^{-1}3031, 2869, 1684, 736, 713; ^{1}H NMR (500MHz, $CDCl_3$)δ6.96-6.97(1H, m), 7.00-7.01(1H, m), 7.20-7.21(1H, m), 7.56-7.58(2H, m), 7.64-7.66(3H, m), 8.94(1H, s), 9.73(1H, s); ^{13}C NMR (125MHz, $CDCl_3$) δ 106.7, 116.3, 117.7, 128.7, 128.8, 129.7, 130.2, 131.0, 131.5, 140.2, 145.0, 189.2; LC-MS(ESI): m/z $[M+H]^+$:223.2. HRMS (EI): m/z Calcd for $C_{14}H_{10}N_2O$ $(M)^+$ 222.0793 Found: *m/z* 222.0795.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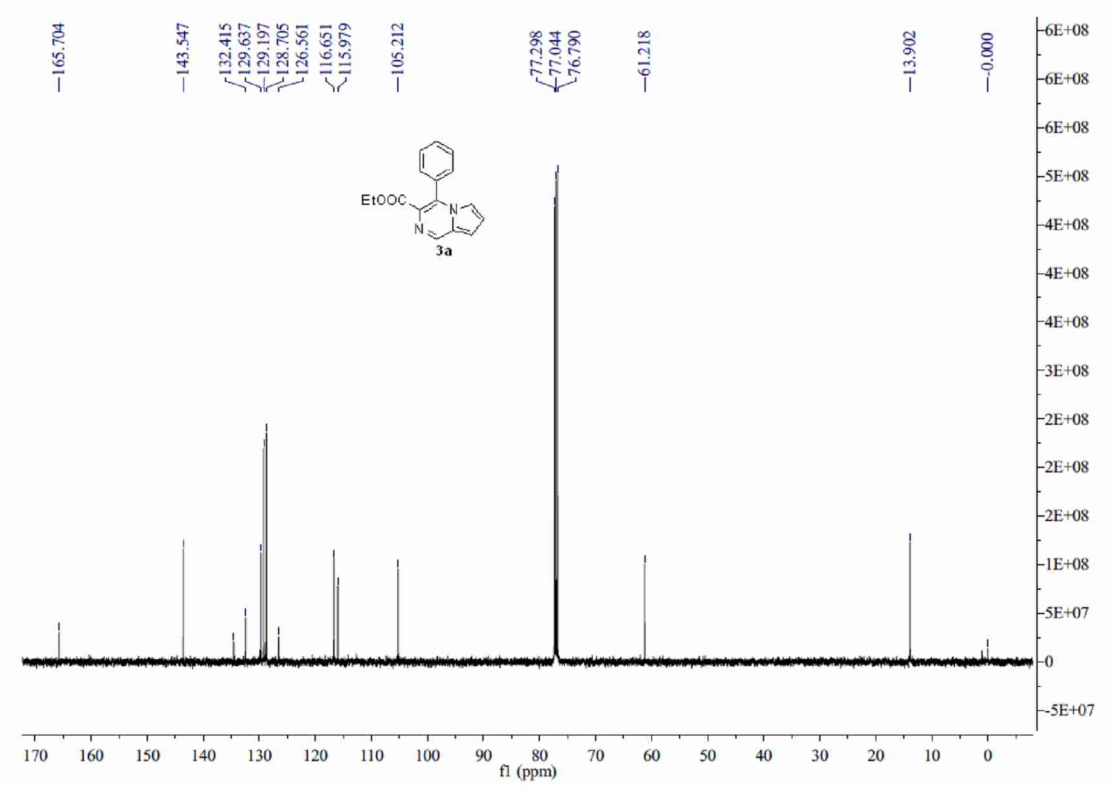
7.567
7.559
7.422
7.412
7.269
7.042
6.951
6.950
6.943
6.902
6.896
6.894
6.889
4.208
4.194
4.180
4.165
1.119
1.105
1.091
0.074
0.000
EtOOC
N
3a
1.00
3.00
2.05
1.02
0.99
1.01
2.20
3.07
fl (ppm)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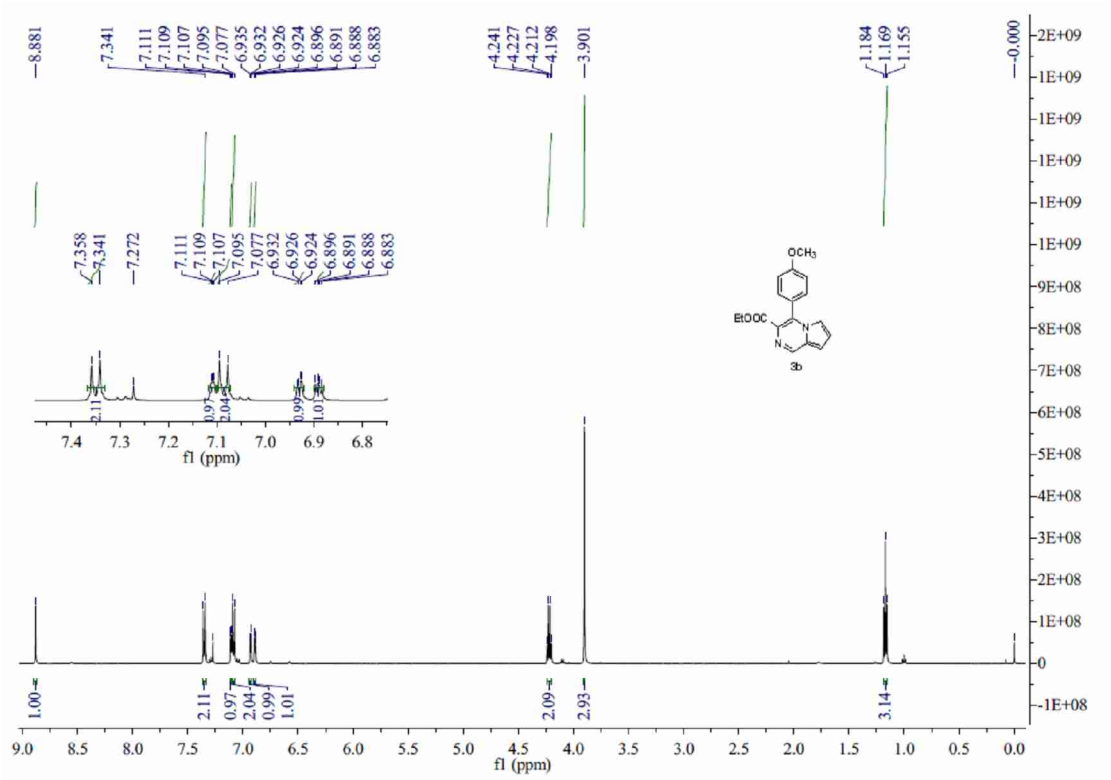
143.547
132.415
129.637
129.197
128.705
126.561
116.651
115.979
105.212
77.298
77.044
76.790
61.218
13.902
0.000
EtOOC
N
3a
fl (ppm)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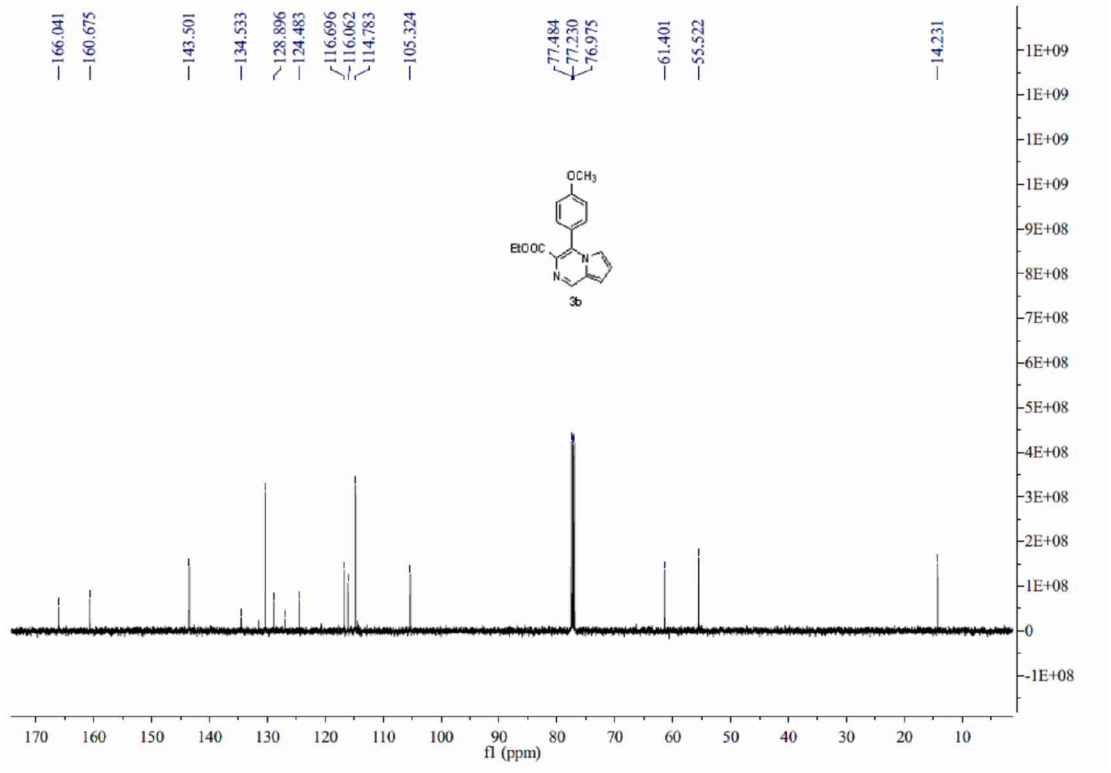
7.341
7.111
7.109
7.107
7.095
7.077
6.935
6.932
6.926
6.924
6.896
6.891
6.888
6.883
4.241
4.227
4.212
4.198
3.901
1.184
1.169
1.155
0.000
OCH3
EtOOC
N
3b
fl (ppm)
1.00
2.11
0.97
2.04
0.99
1.01
2.09
2.93
3.14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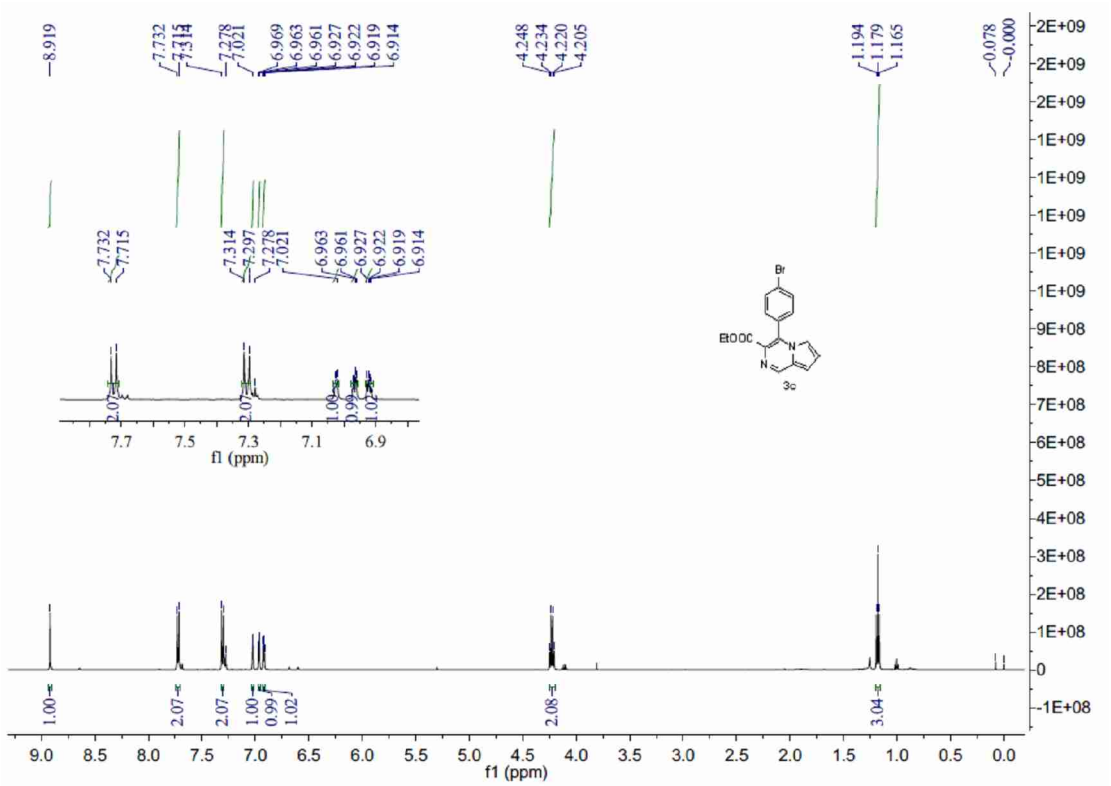
160.675
143.501
134.533
128.896
124.483
116.696
116.062
114.783
105.324
77.484
77.230
76.975
61.401
55.522
14.231
OCH3
EtOOC
N
3b
fl (ppm)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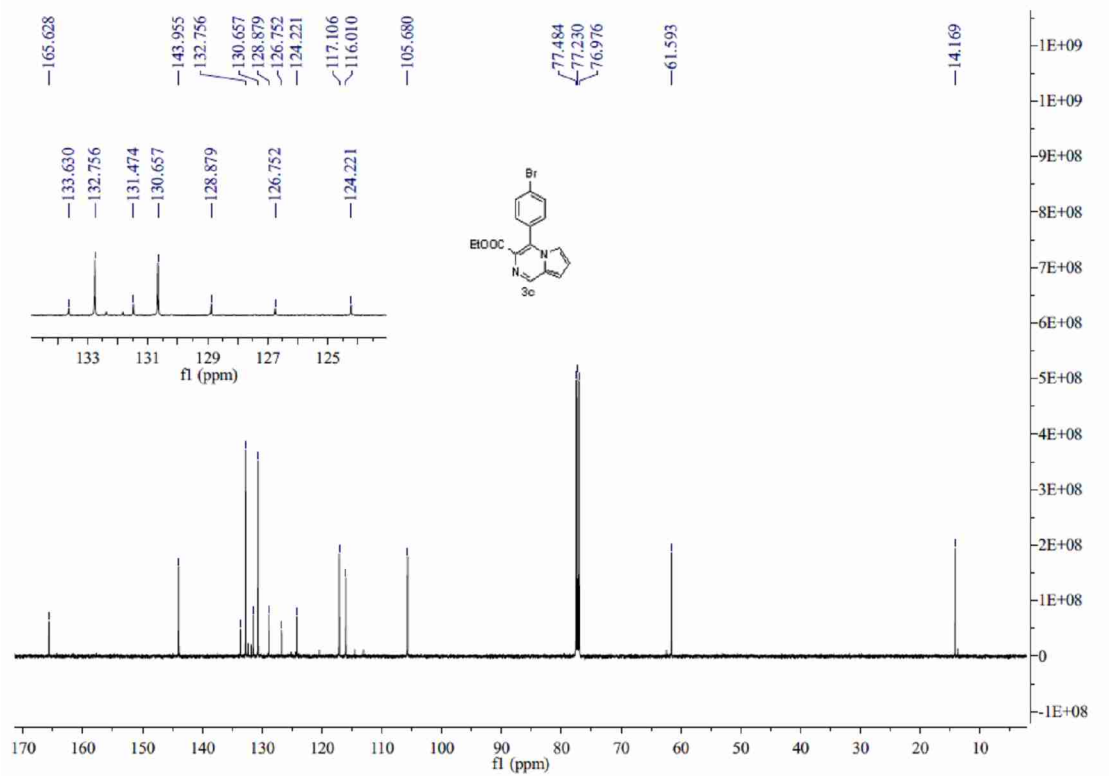
7.732
7.715
7.314
7.297
7.278
7.021
6.969
6.963
6.961
6.927
6.922
6.919
6.914
4.248
4.234
4.220
4.205
1.194
1.179
1.165
0.078
0.000
Br
EtOOC
N
3c
1.00
2.07
2.07
1.00
0.99
1.02
2.08
3.04
f1 (ppm)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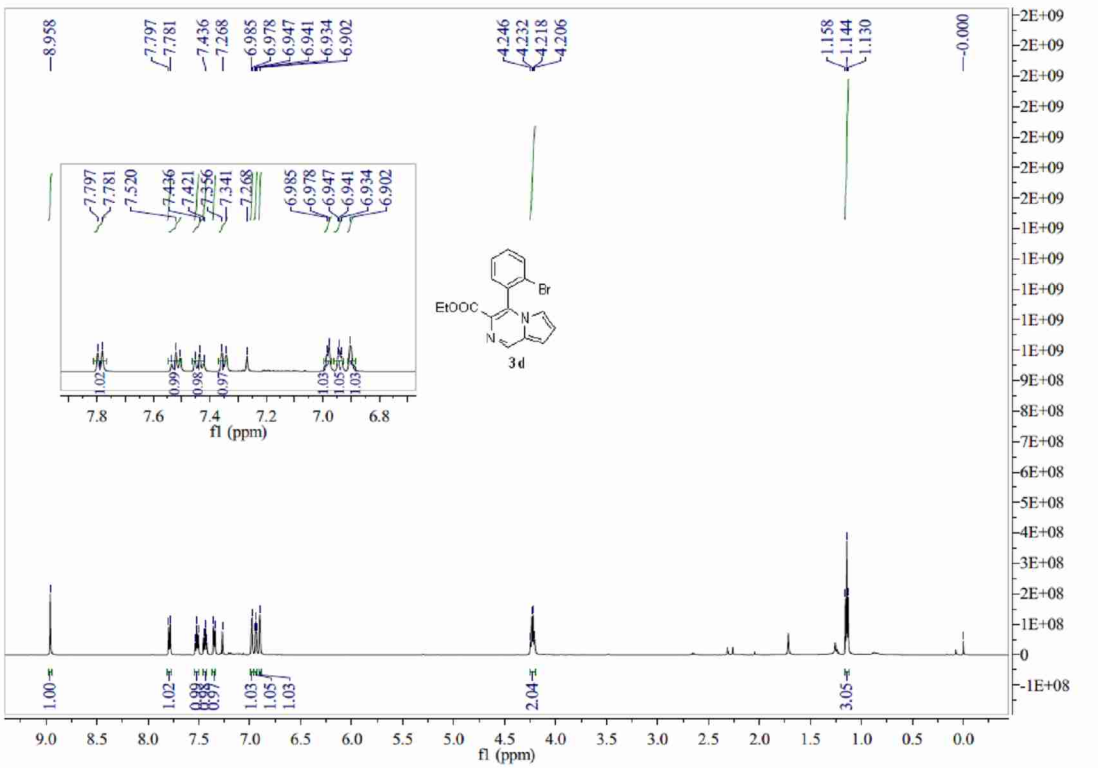
132.756
130.657
128.879
126.752
124.221
117.106
116.010
105.680
77.484
77.230
76.976
61.593
14.169
133.630
132.756
131.474
130.657
128.879
126.752
124.221
Br
EtOOC
N
3c
f1 (ppm)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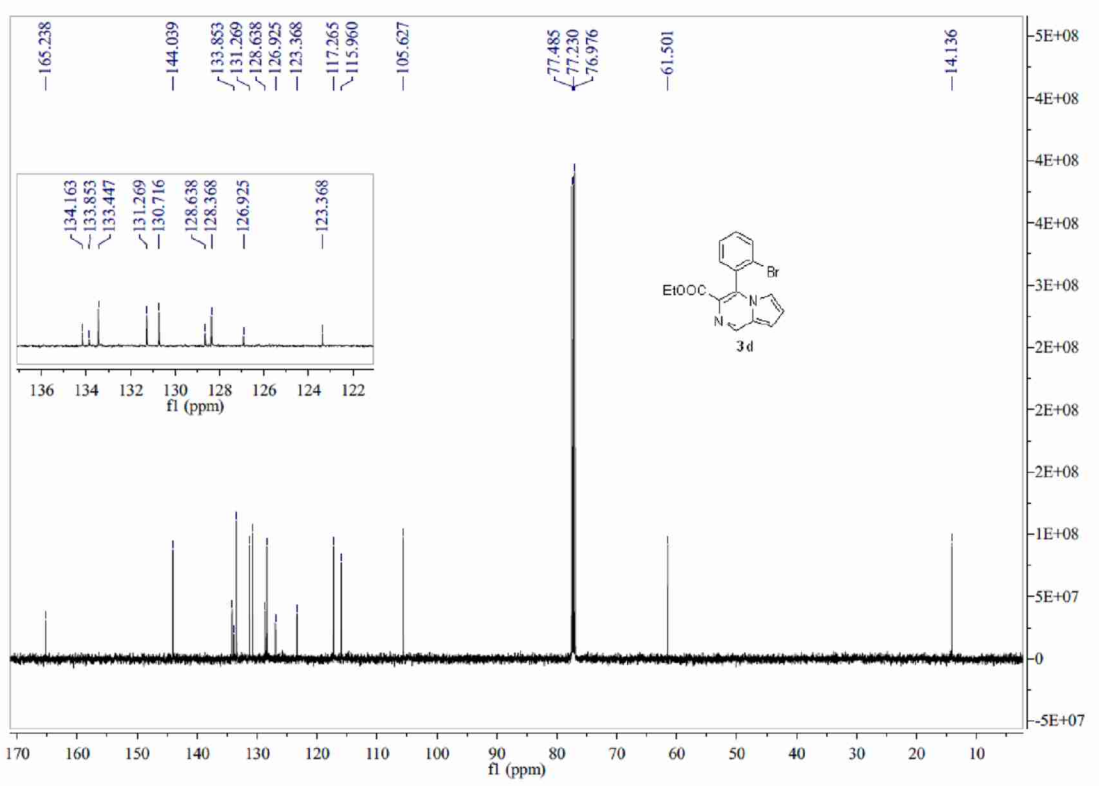
7.797
7.781
7.436
7.268
6.985
6.978
6.947
6.941
6.934
6.902
4.246
4.232
4.218
4.206
1.158
1.144
1.130
0.000
7.520
7.421
7.356
7.341
1.00
1.02
0.99
0.98
0.97
1.03
1.05
1.03
2.04
3.05
Br
EtOOC
N
3d
f1 (ppm)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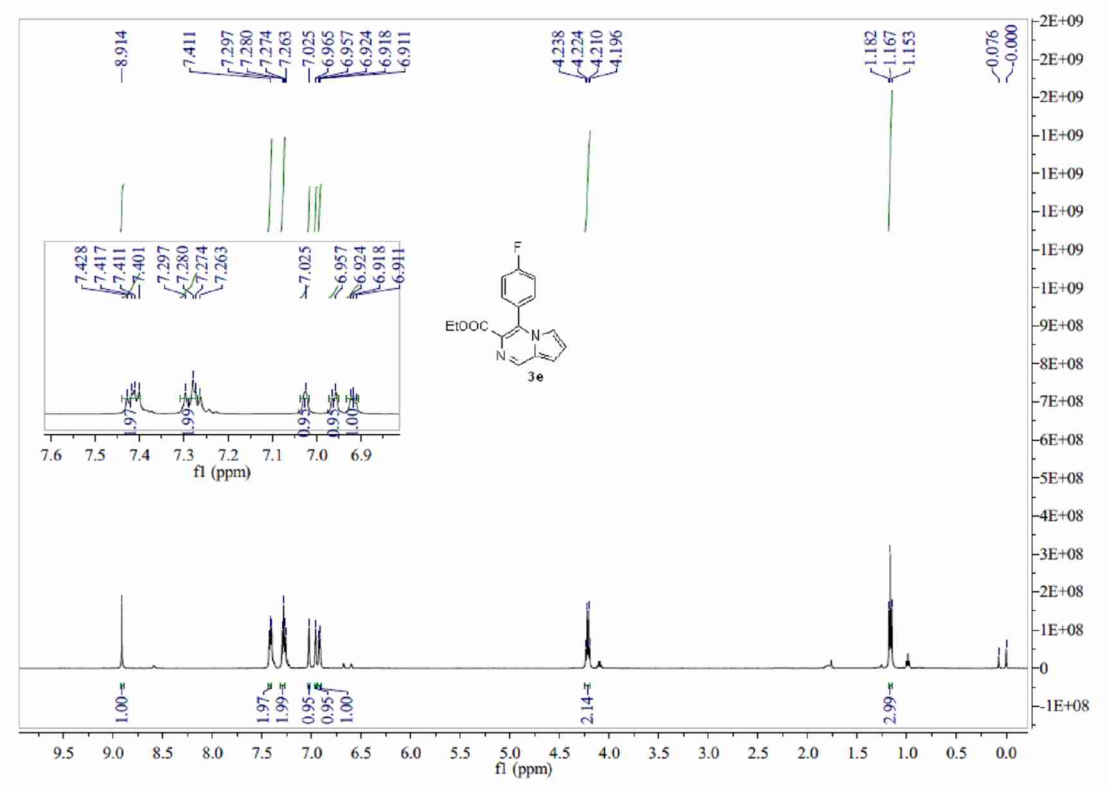
133.853
131.269
128.638
126.925
123.368
117.265
115.960
105.627
77.485
77.230
76.976
61.501
14.136
134.163
133.853
133.447
131.269
130.716
128.638
128.368
126.925
123.368
Br
EtOOC
N
3d
f1 (ppm)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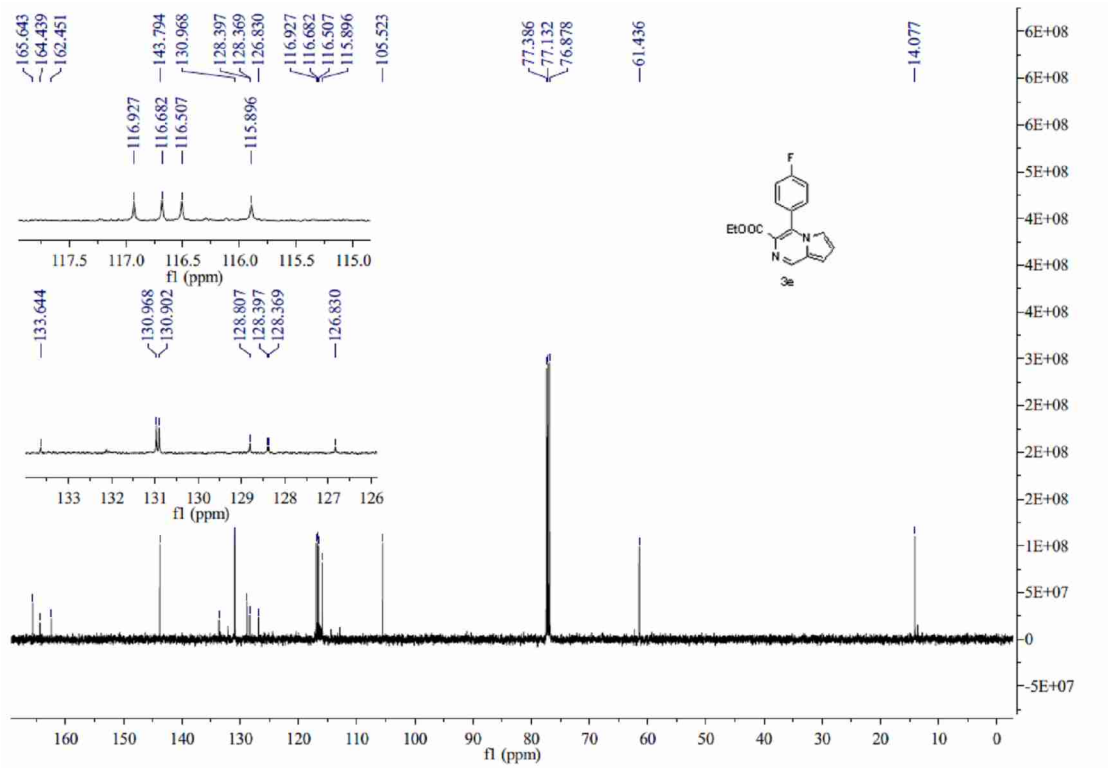
7.297
7.280
7.274
7.263
7.025
6.965
6.957
6.924
6.918
6.911
4.238
4.224
4.210
4.196
1.182
1.167
1.153
0.076
0.000
EtOOC
3e
fl (ppm)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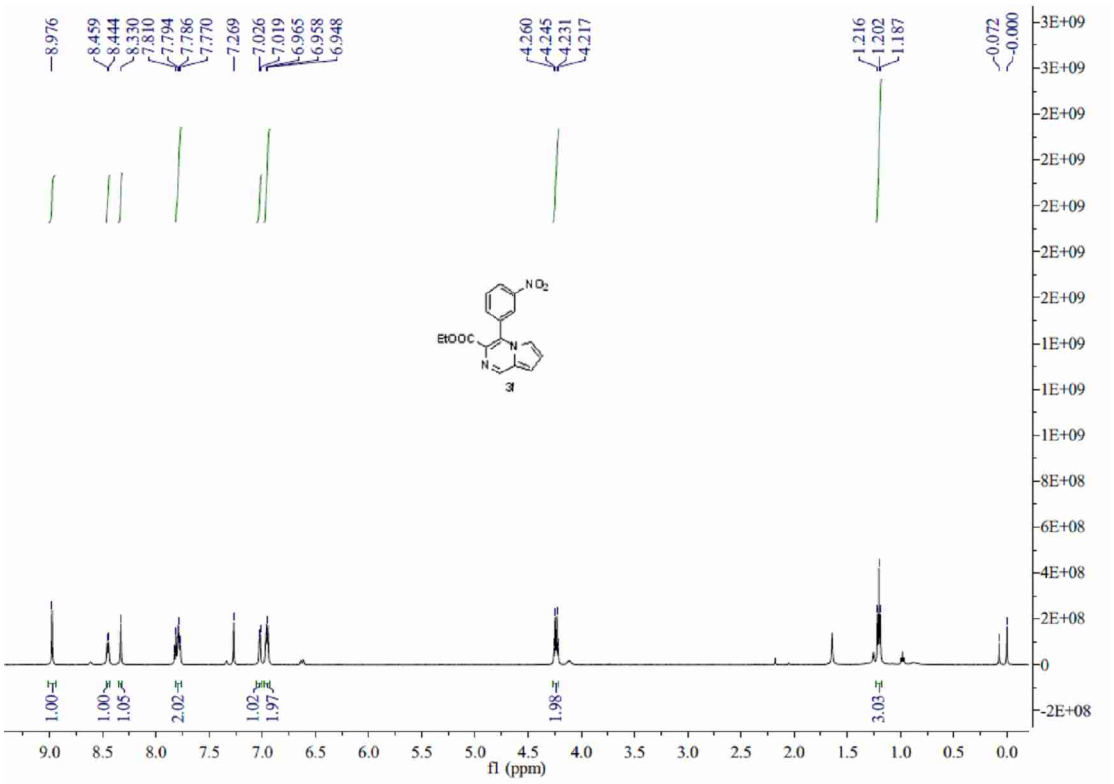
162.451
143.794
130.968
128.397
128.369
126.830
116.927
116.682
116.507
115.896
105.523
77.386
77.132
76.878
61.436
14.077
133.644
130.968
130.902
128.807
128.397
128.369
126.830
EtOOC
3e
fl (ppm)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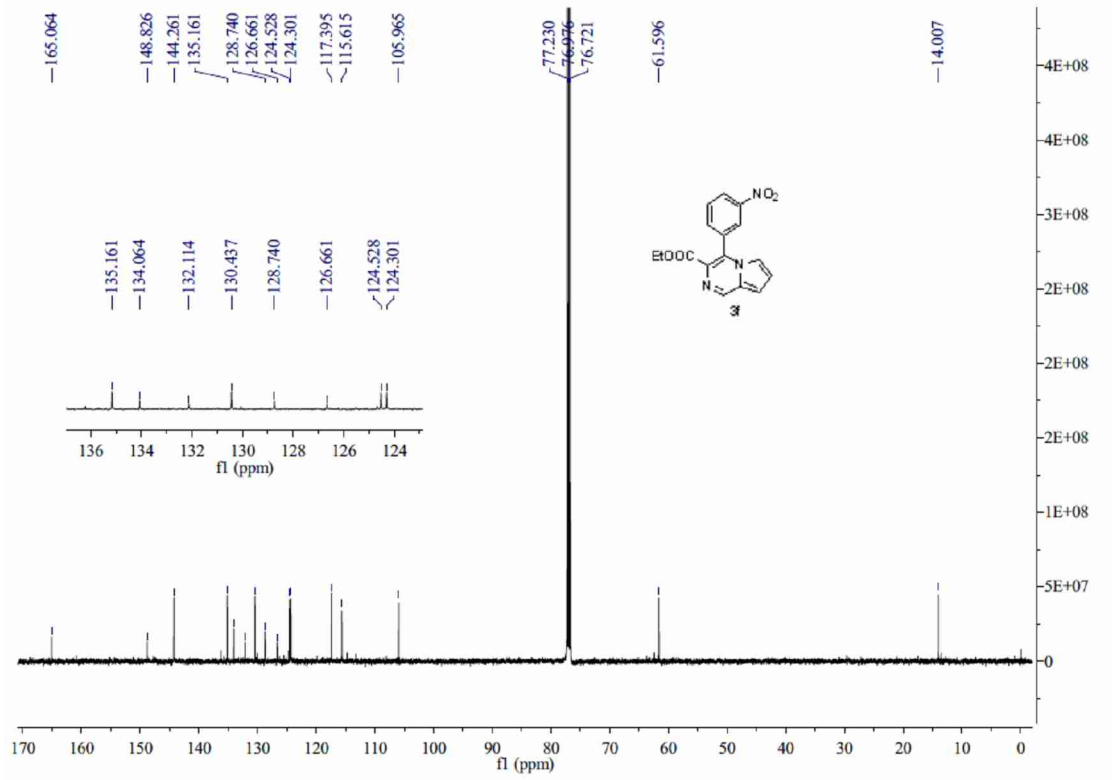
8.444
8.330
7.810
7.794
7.786
7.770
7.269
7.026
7.019
6.965
6.958
6.948
4.260
4.245
4.231
4.217
1.216
1.202
1.187
0.072
0.000
NO2
EtOOC
N
3f
1.00
1.00
1.05
2.02
1.02
1.97
1.98
3.03
fl (ppm)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135.161
128.740
126.661
124.528
124.301
117.395
115.615
105.965
77.230
76.976
76.721
61.596
14.007
135.161
134.064
132.114
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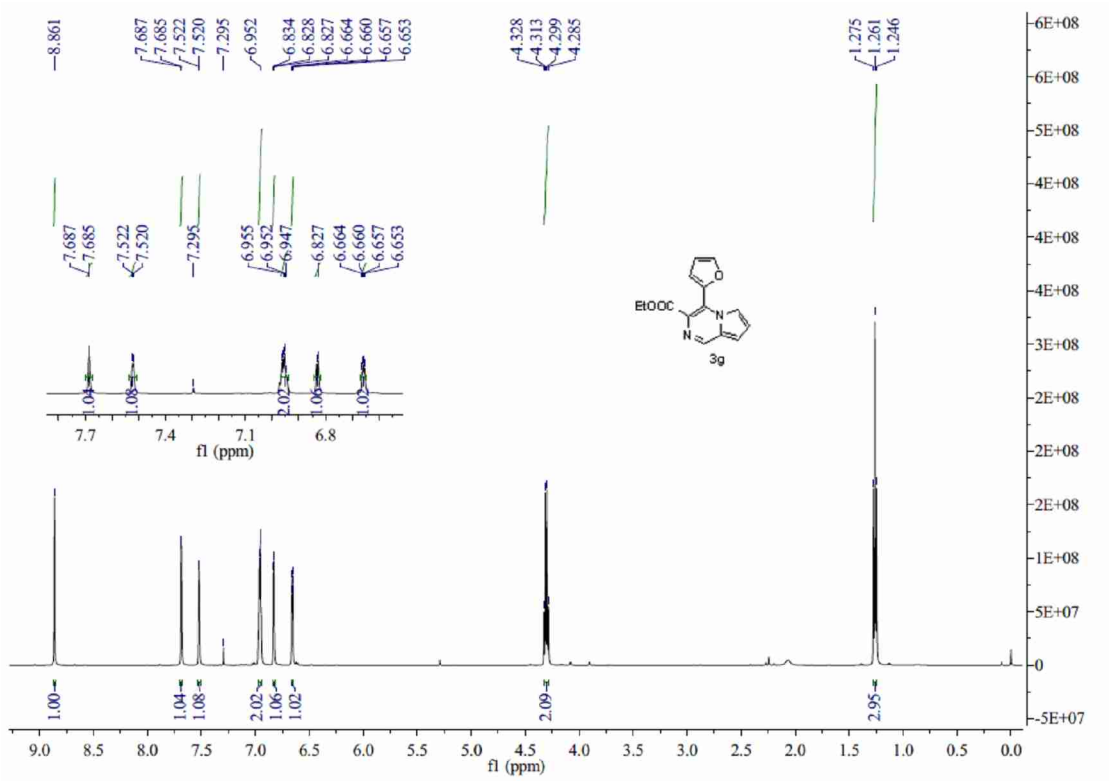
128.740
126.661
124.528
124.301
NO2
EtOOC
N
3f
fl (ppm)
fl (ppm)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7.685
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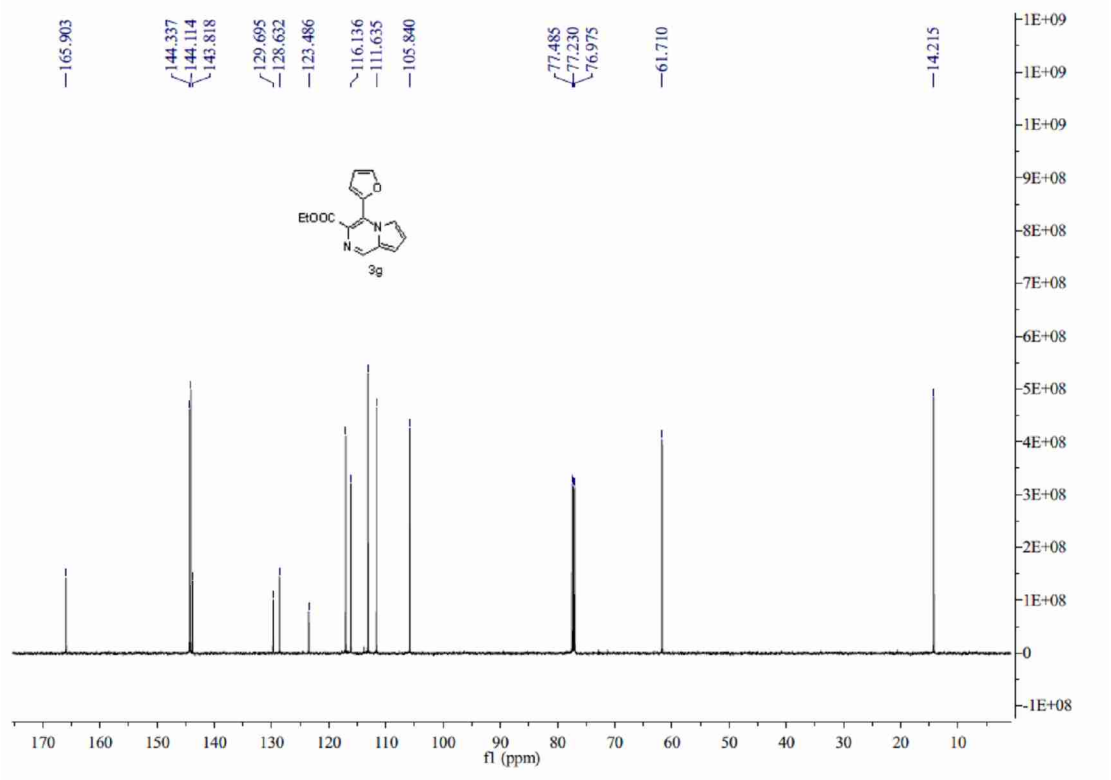
7.520
7.295
6.952
6.834
6.828
6.827
6.664
6.660
6.657
6.653
4.328
4.313
4.299
4.285
1.275
1.261
1.246
EtOOC
3g
1.00
1.04
1.08
2.02
1.06
1.02
2.09
2.95
fl (ppm)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128.632
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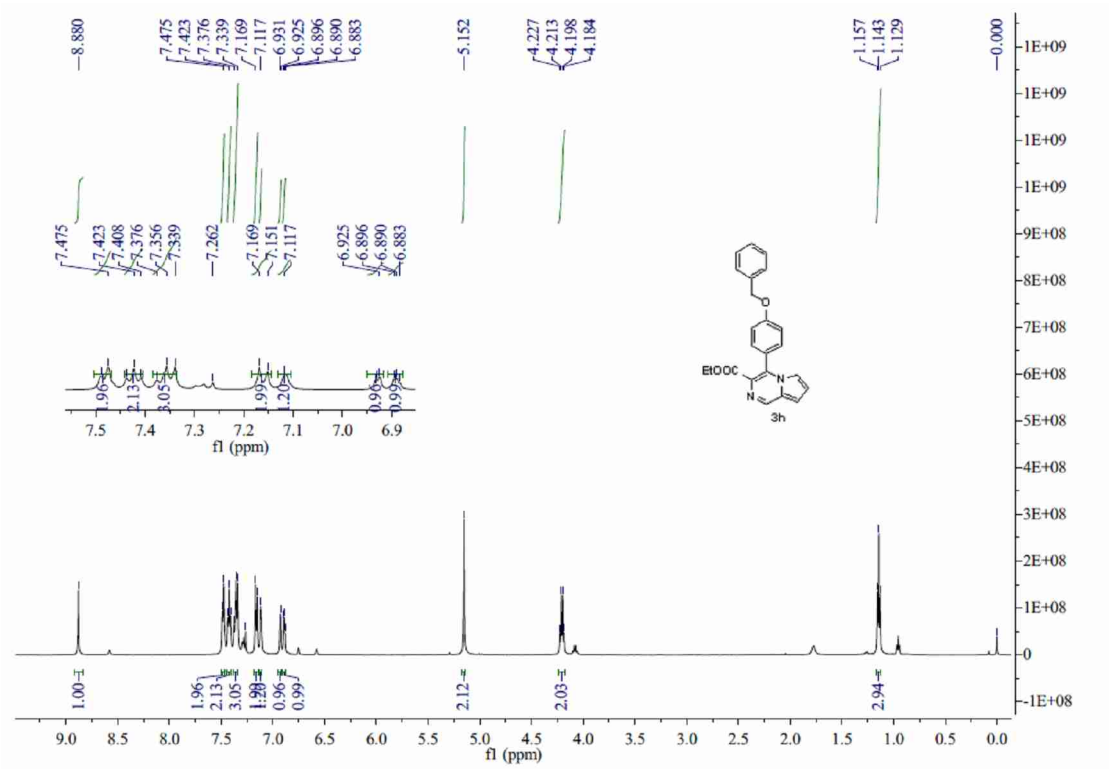
116.136
111.635
105.840
77.485
77.230
76.975
61.710
14.215
EtOOC
3g
fl (ppm)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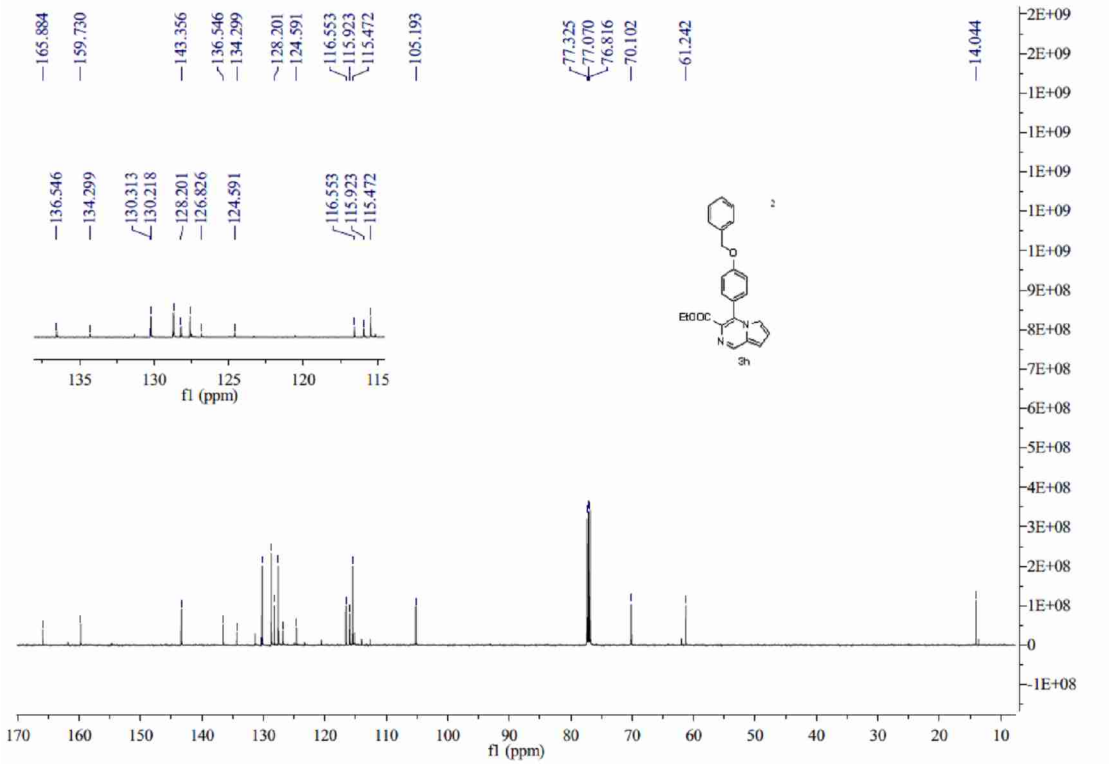
7.423
7.376
7.339
7.169
7.117
6.931
6.925
6.896
6.890
6.883
5.152
4.227
4.213
4.198
4.184
1.157
1.143
1.129
0.000
EtOOC
3h
f1 (ppm)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124.591
116.553
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115.472
105.193
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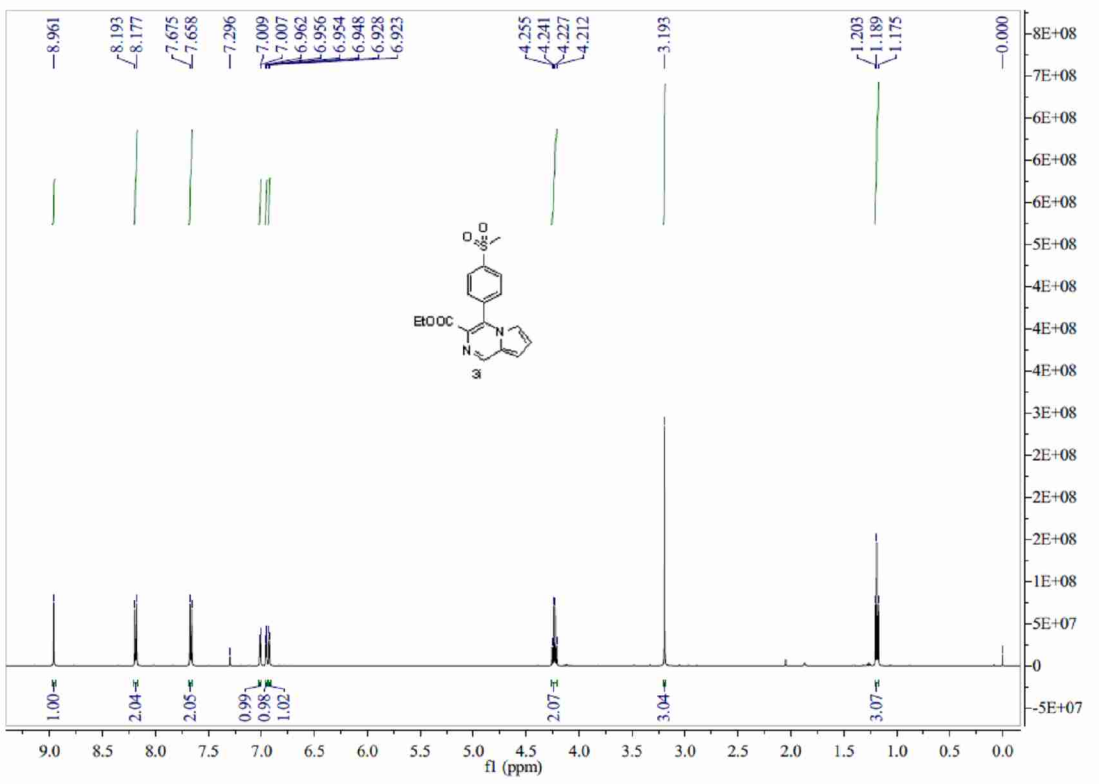
70.102
61.242
14.044
130.313
130.218
126.826
EtOOC
3h
f1 (ppm)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7.658
7.296
7.009
7.007
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6.956
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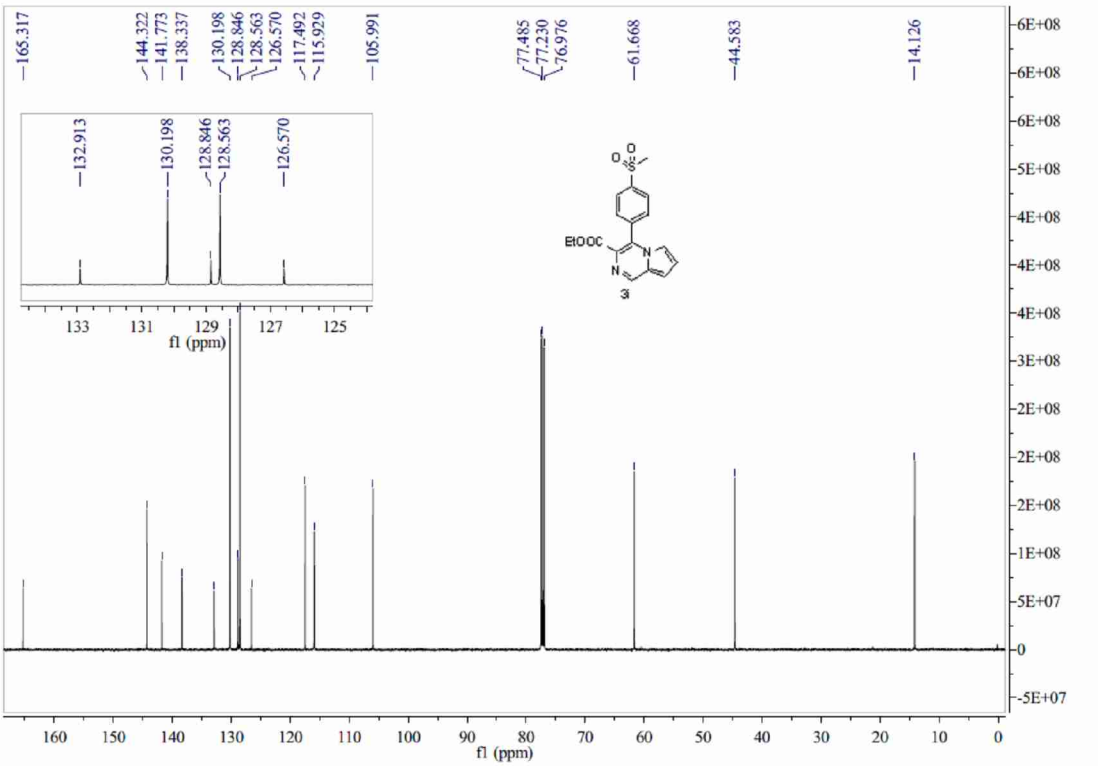
6.928
6.923
4.255
4.241
4.227
4.212
3.193
1.203
1.189
1.175
0.000
EtOOC
3i
1.00
2.04
2.05
0.99
0.98
1.02
2.07
3.04
3.07
f1 (ppm)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126.570
117.492
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105.991
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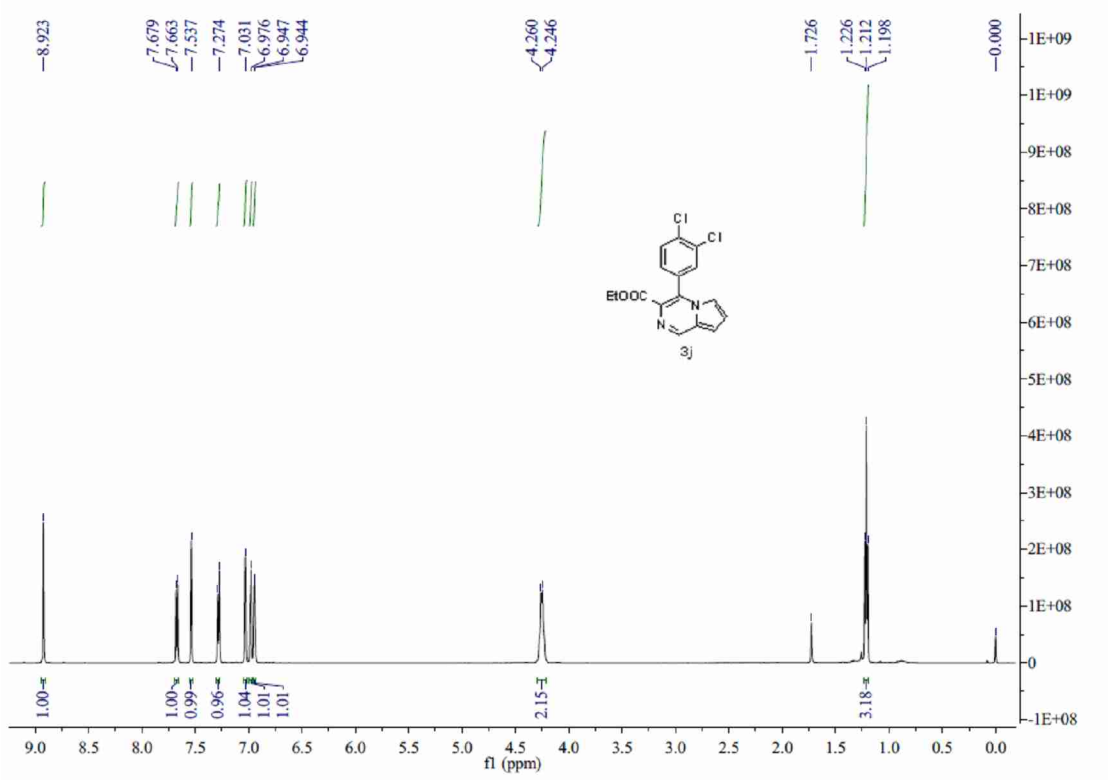
77.230
76.976
61.668
44.583
14.126
132.913
130.198
128.846
128.563
126.570
EtOOC
3i
f1 (ppm)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7.663
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7.031
6.976
6.947
6.944
4.260
4.246
1.726
1.226
1.212
1.198
0.000
Cl
Cl
EtOOC
N
N
3j
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1.00
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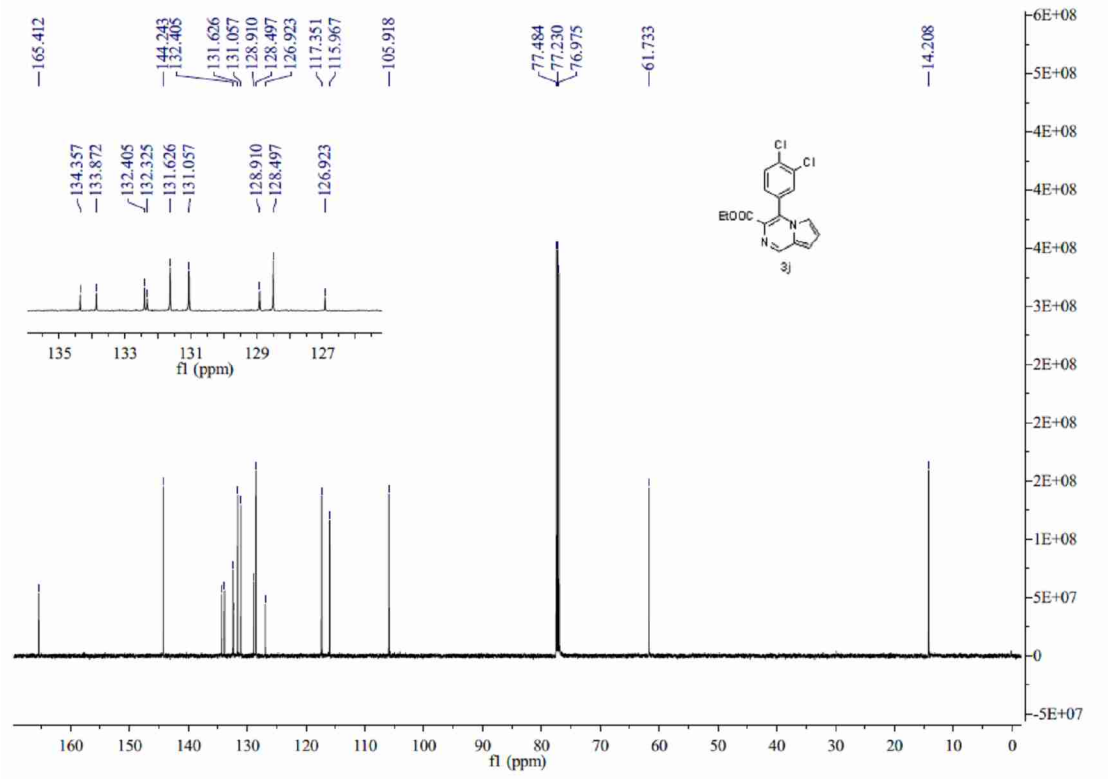
0.96
1.04
1.01
1.01
2.15
3.18
fl (ppm)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131.057
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128.497
126.923
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115.967
105.918
77.484
77.230
76.975
61.733
14.208
134.357
133.872
132.405
132.325
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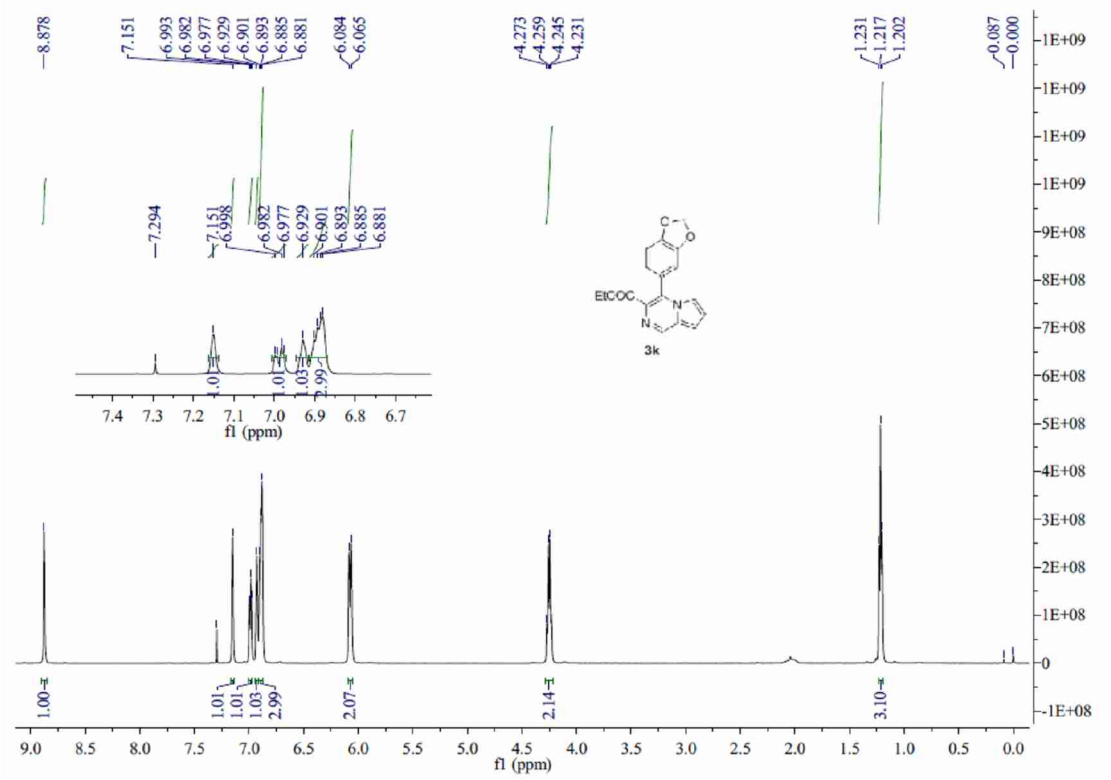
128.910
128.497
126.923
Cl
Cl
EtOOC
N
N
3j
fl (ppm)
fl (ppm)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6.893
6.885
6.881
6.084
6.065
4.273
4.259
4.245
4.231
1.231
1.217
1.202
0.087
0.000
7.294
EtCOC
3k
fl (ppm)
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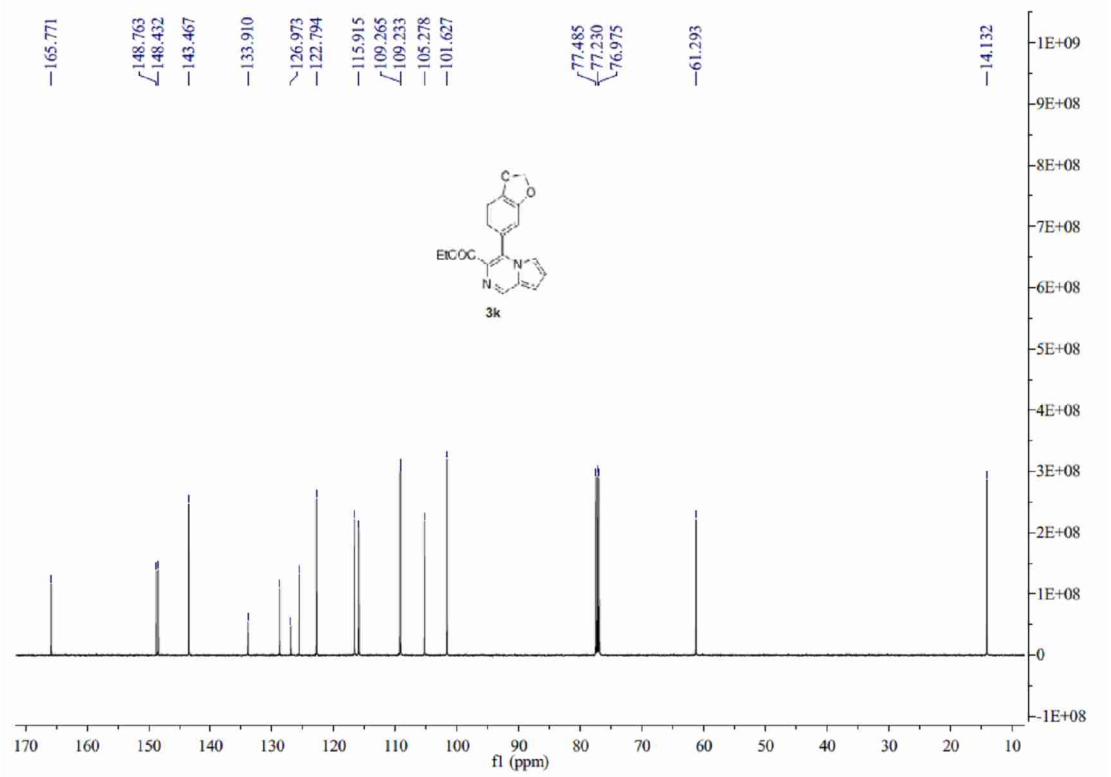
1.01
1.01
1.03
2.99
2.07
2.14
3.10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122.794
115.915
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101.627
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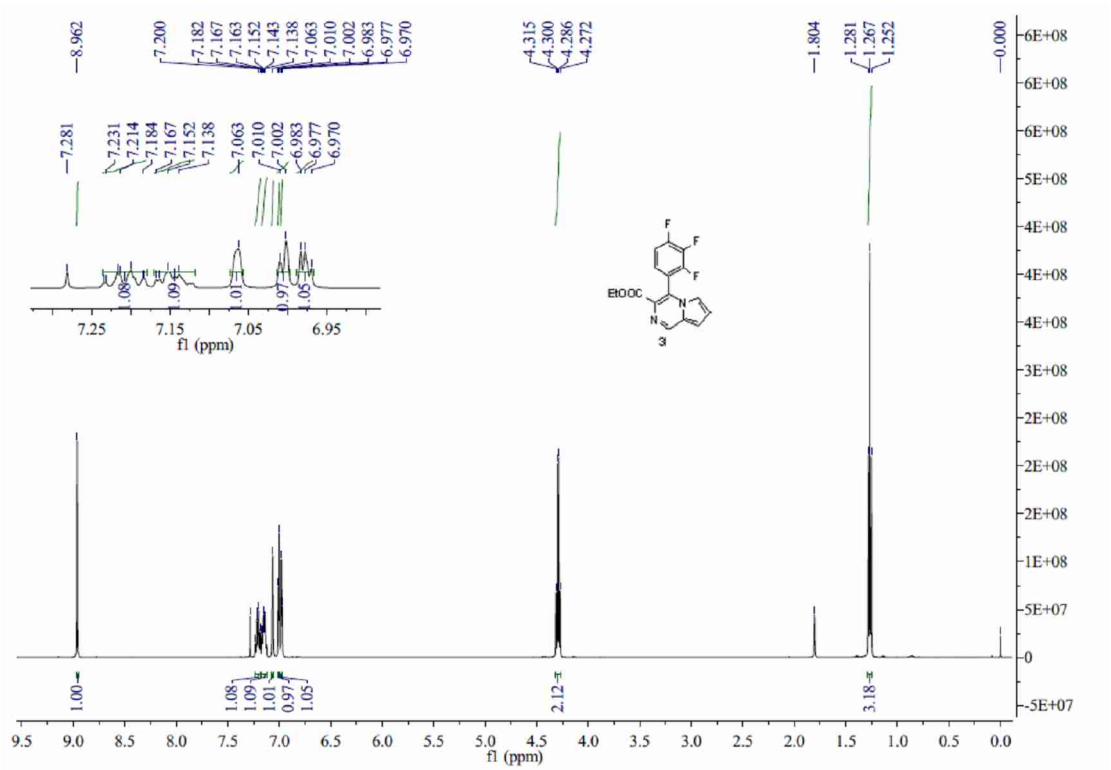
77.230
76.975
61.293
14.132
EtCOC
3k
fl (ppm)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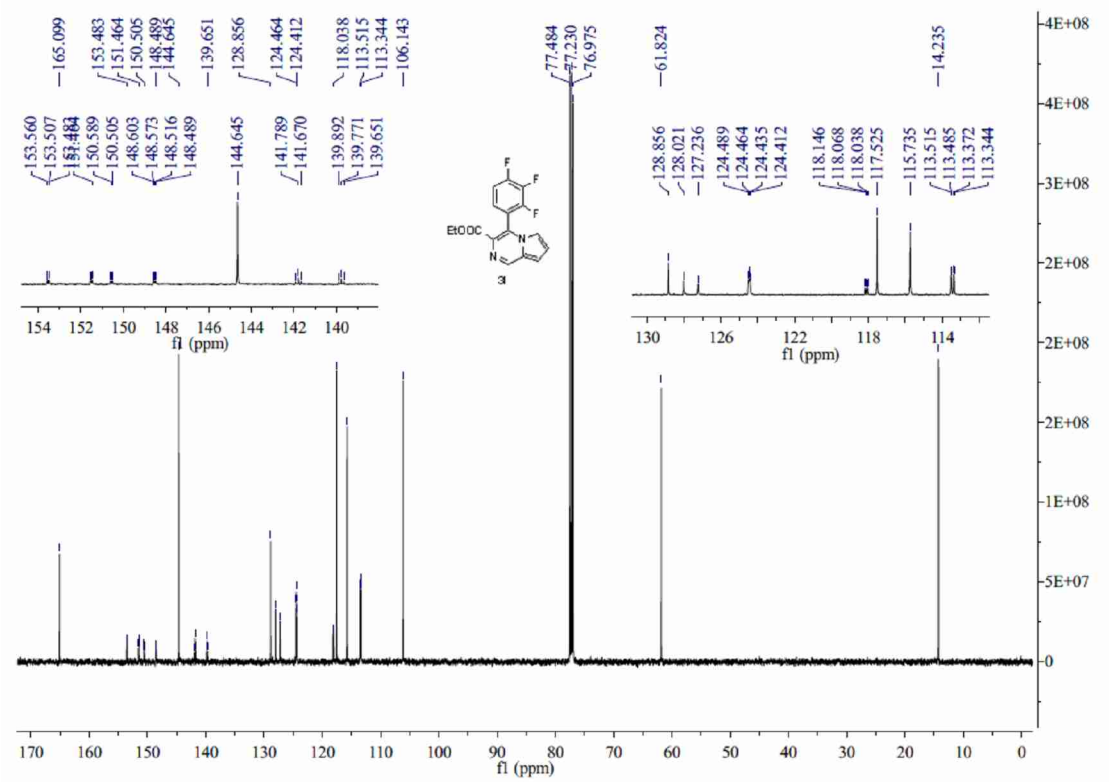
7.167
7.163
7.152
7.143
7.138
7.063
7.010
7.002
6.983
6.977
6.970
4.315
4.300
4.286
4.272
1.804
1.281
1.267
1.252
0.000
7.281
7.231
7.214
7.184
7.167
7.152
7.138
7.063
7.010
7.002
6.983
6.977
6.970
1.00
1.08
1.09
1.01
0.97
1.05
2.12
3.18
f1 (ppm)
EtOOC
3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118.038
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106.143
77.484
77.230
76.975
61.824
14.235
153.560
153.507
150.589
150.505
148.603
148.573
148.516
148.489
144.645
141.789
141.670
139.892
139.771
139.651
128.856
128.021
127.236
124.489
124.464
124.435
124.412
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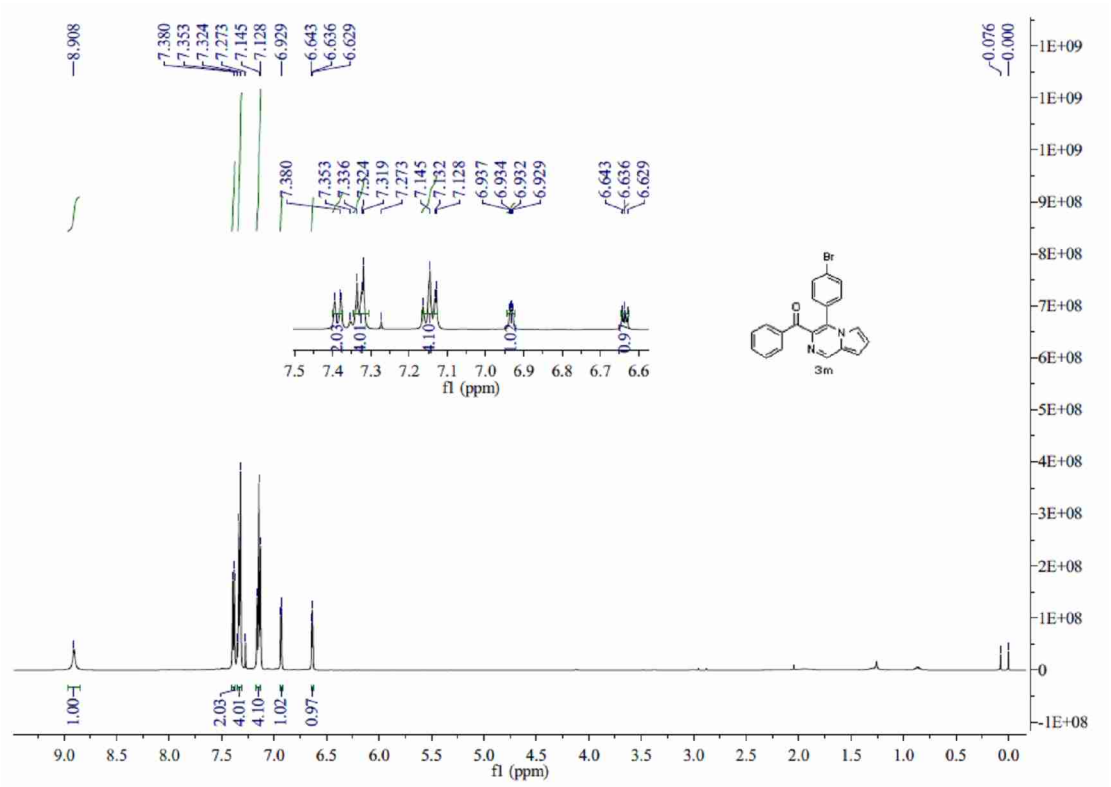
113.515
113.485
113.372
113.344
f1 (ppm)
EtOOC
3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7.324
7.273
7.145
7.128
6.929
6.643
6.636
6.629
0.076
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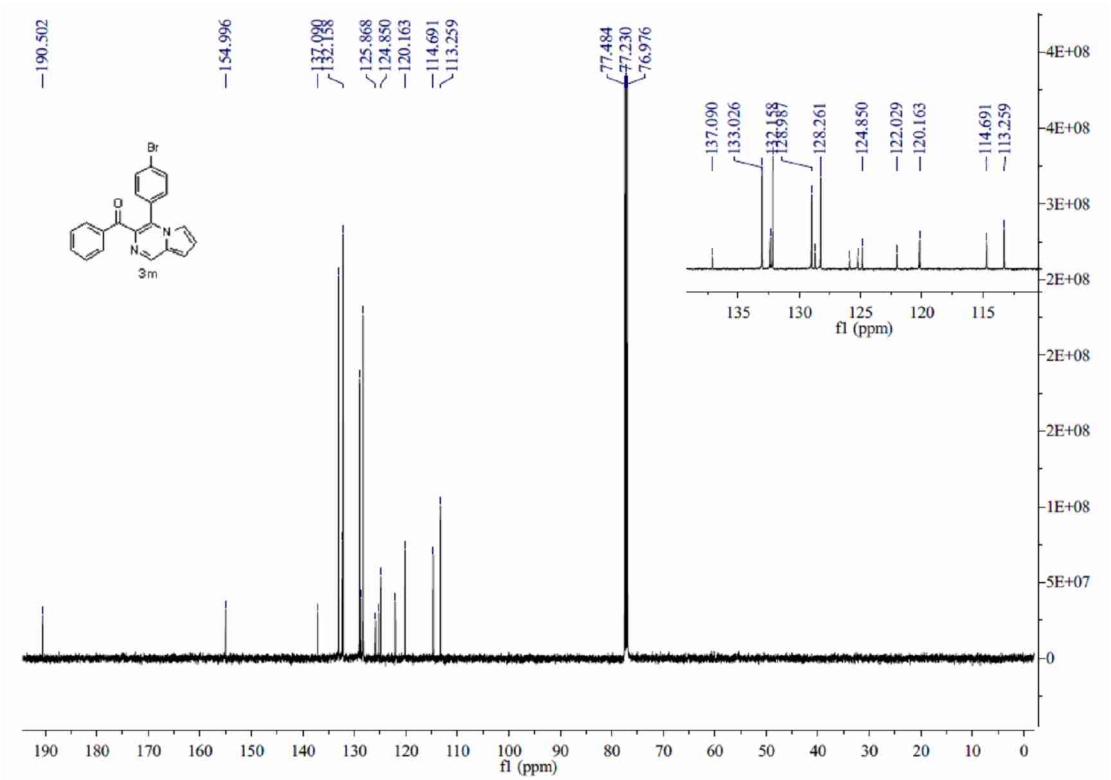
1.00
2.03
4.01
4.10
1.02
0.97
fl (ppm)
Br
O
N
3m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132.158
128.987
128.261
125.868
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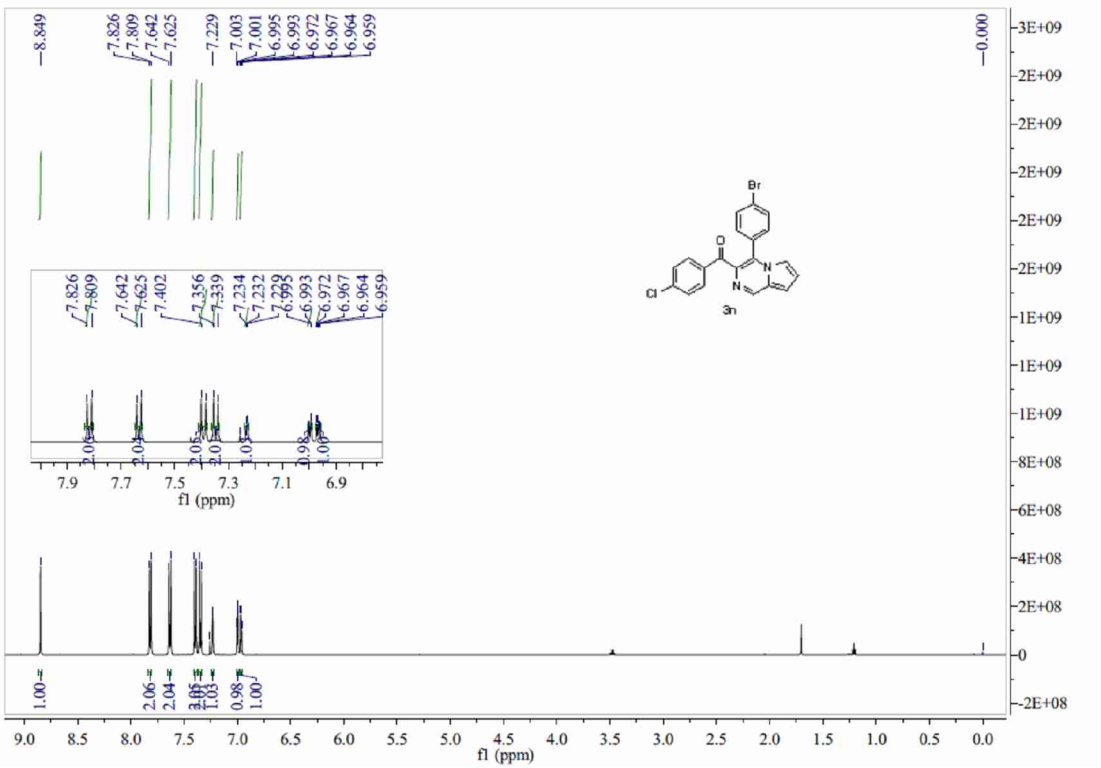
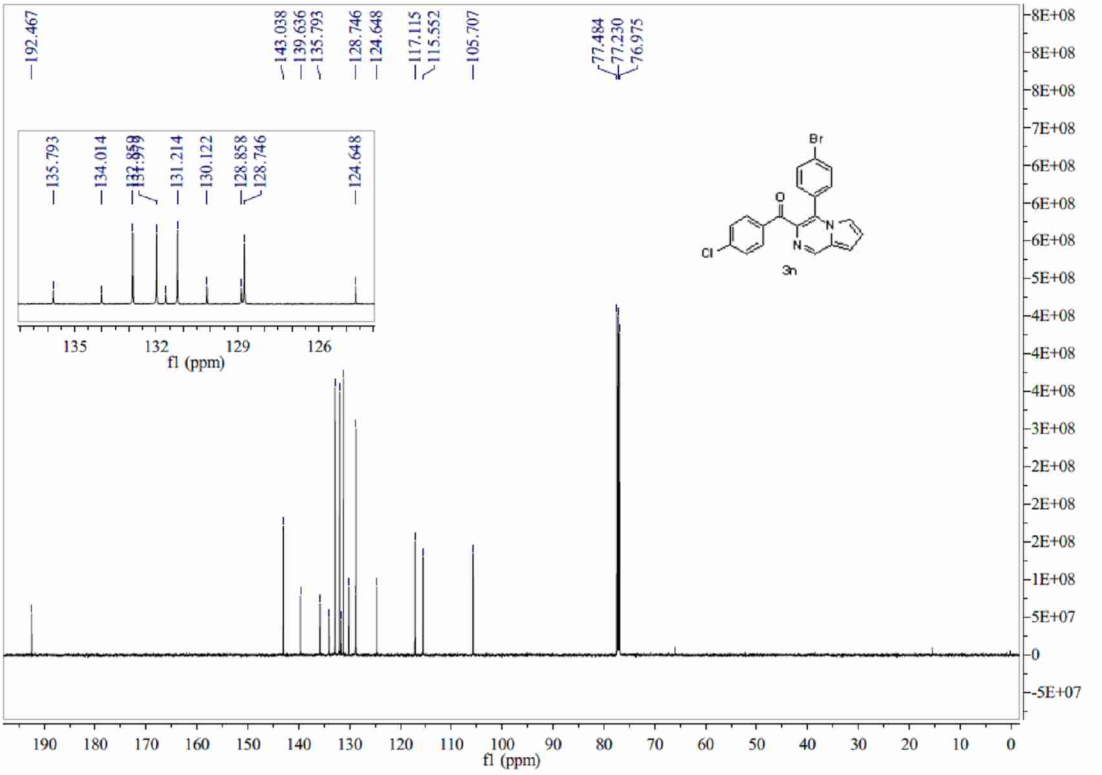
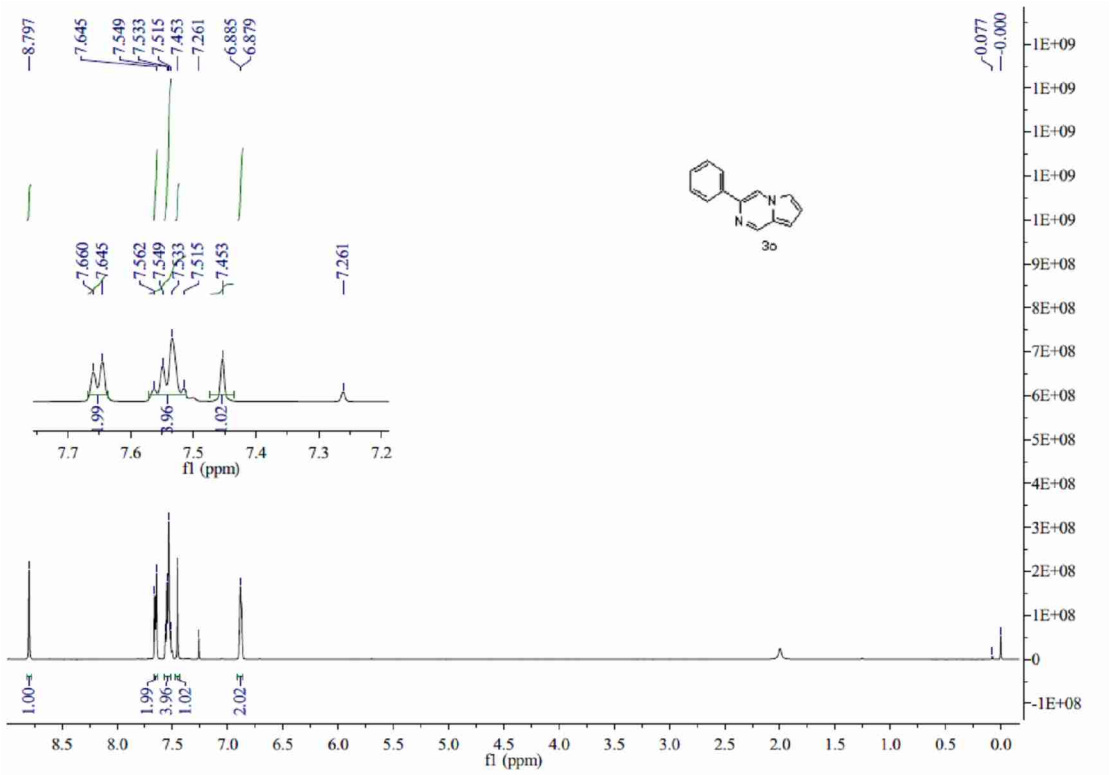
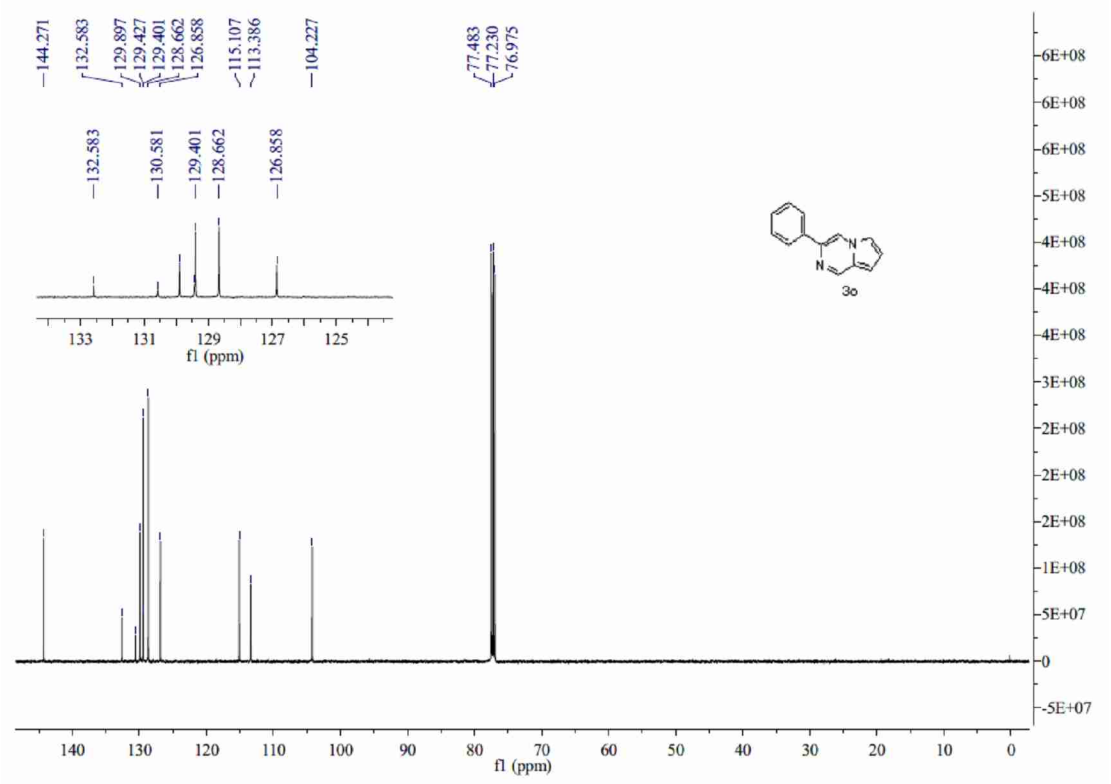
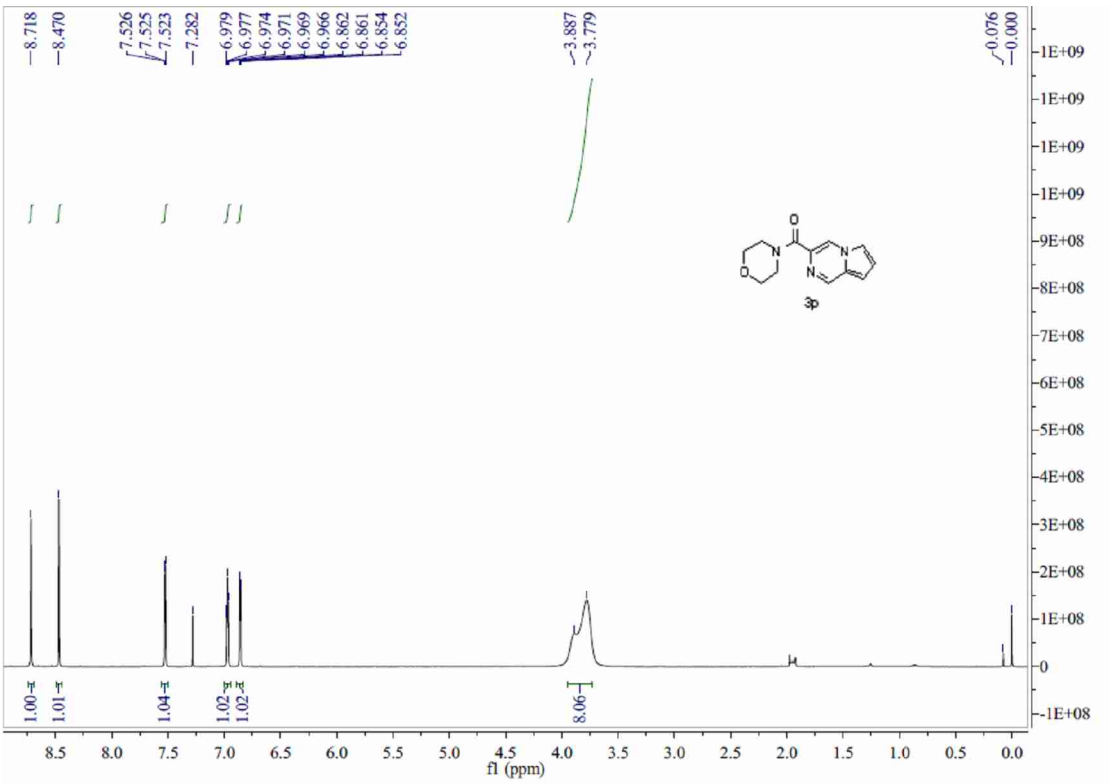
122.029
120.163
114.691
113.259
77.484
77.230
76.976
fl (ppm)
Br
O
N
3m

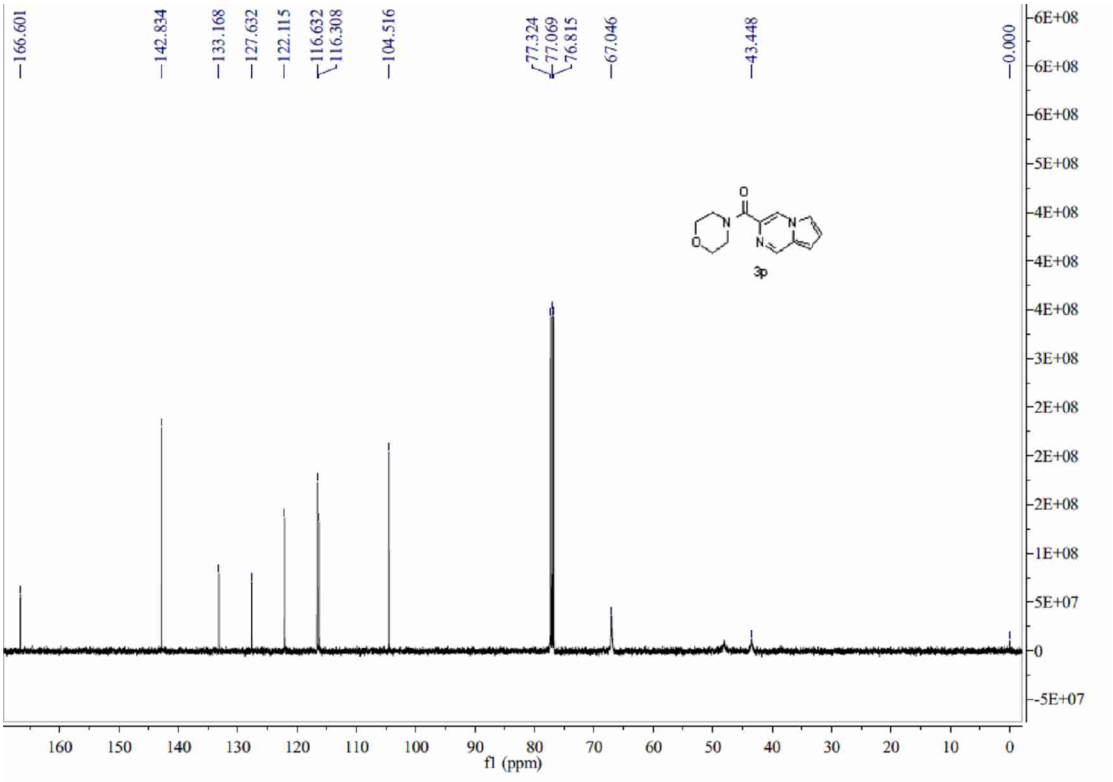

8.849
7.826
7.809
7.642
7.625
7.229
7.003
7.001
6.995
6.993
6.972
6.967
6.964
6.959
0.000
Br
O
Cl
N
3n
f1 (ppm)

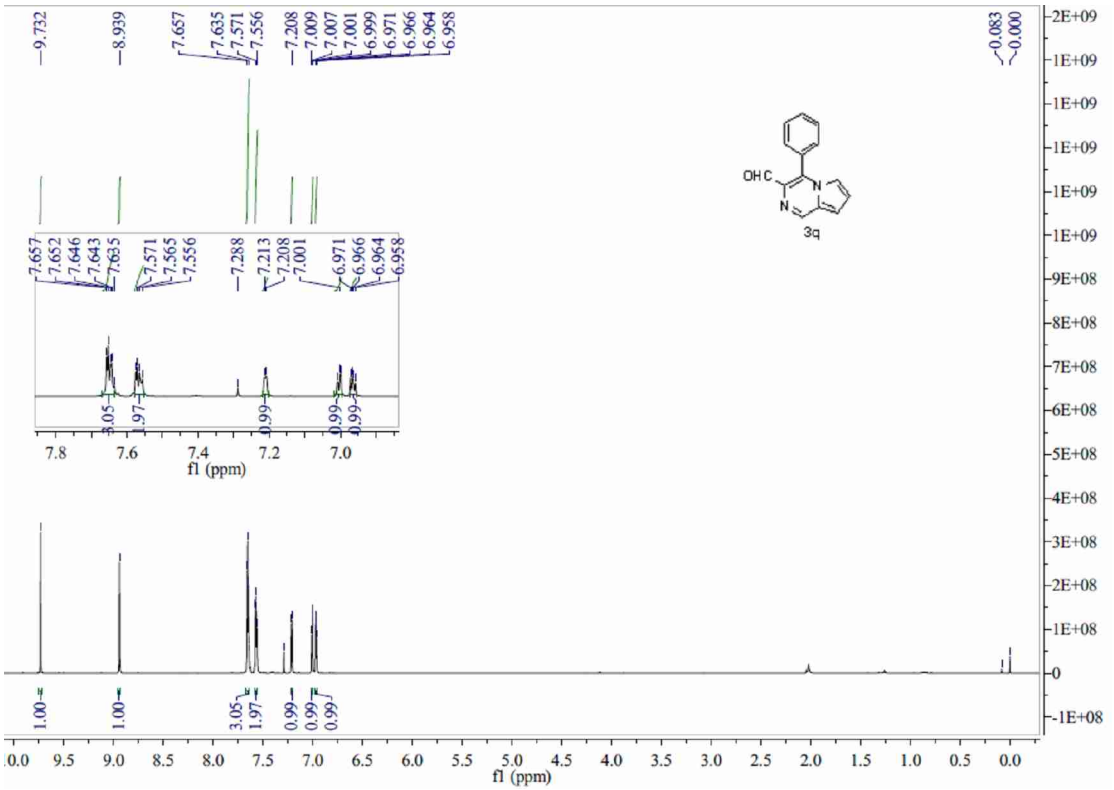

192.467
143.038
139.636
135.793
128.746
124.648
117.115
115.552
105.707
77.484
77.230
76.975
135.793
134.014
131.214
130.122
128.858
128.746
124.648
Br
O
Cl
N
3n
f1 (ppm)

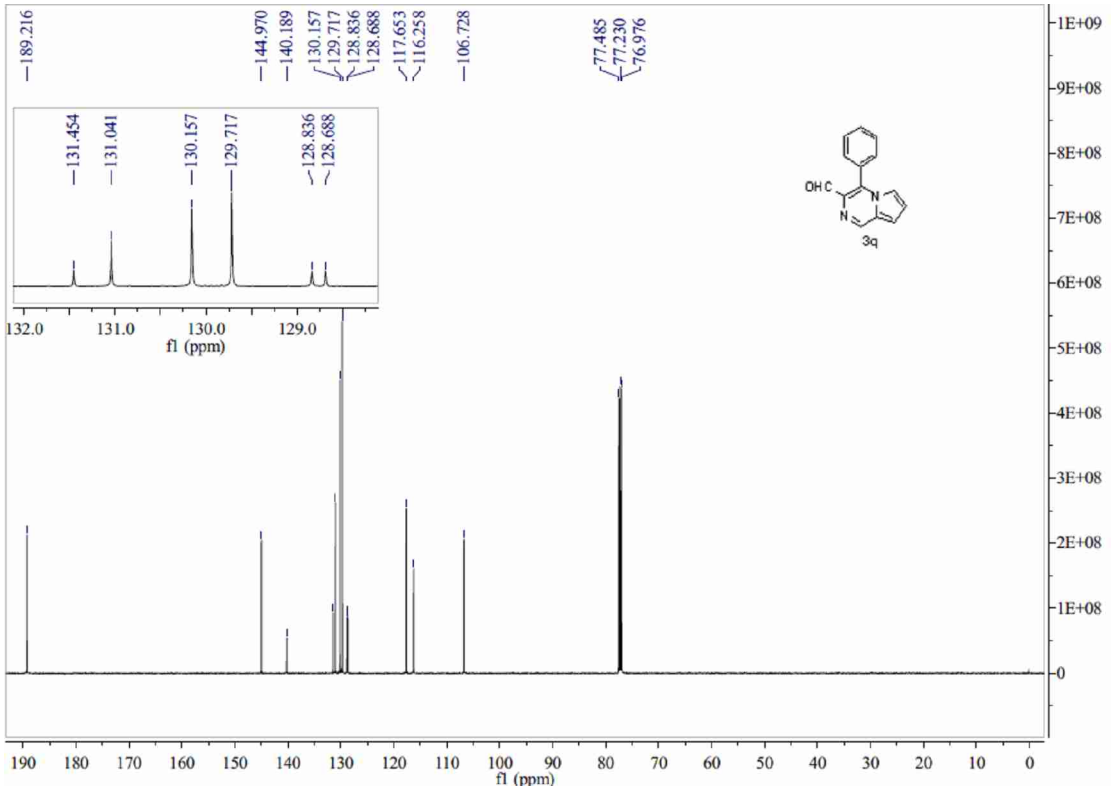

8.797
7.645
7.549
7.533
7.515
7.453
7.261
6.885
6.879
0.077
-0.000
7.660
7.645
7.562
7.549
7.533
7.515
7.453
7.261
1.99
3.96
1.02
f1 (ppm)
3o
1.00
1.99
3.96
1.02
2.02
f1 (ppm)


144.271
132.583
129.897
129.427
129.401
128.662
126.858
115.107
113.386
104.227
77.483
77.230
76.975
132.583
130.581
129.401
128.662
126.858
f1 (ppm)
3o
f1 (ppm)


8.718
8.470
7.526
7.525
7.523
7.282
6.979
6.977
6.974
6.971
6.969
6.966
6.862
6.861
6.854
6.852
3.887
3.779
0.076
0.000
1.00
1.01
1.04
1.02
1.02
8.06
fl (ppm)
3p


166.601
142.834
133.168
127.632
122.115
116.632
116.308
104.516
77.324
77.069
76.815
67.046
43.448
0.000
fl (ppm)
3p





Reference:

1. (a) Wang, Y.-F.; Toh, K. K.; Chiba, S.; Narasaka, K. *Org. Lett.* **2008**, 10, 5019. (b) Chiba, S.; Wang, Y.-F.; Lapointe, G.; Narasaka, K. *Org. Lett.* **2008**, 10, 313.(c)Wang, Y.-F.; Chiba, S. *J. Am. Chem. Soc.* **2009**, 131, 12570.(d) Subban K., Ekambaram R.,Raghavachary R. *Tetrahedron Lett*. **2009**, 50, 2389

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