Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

(Supporting Information)

Zn/Sc bimetallic relay catalysis: one pot cycloisomerization/ carbonyl–ene reaction toward oxazole derivatives

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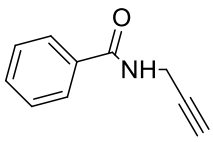
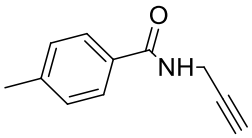
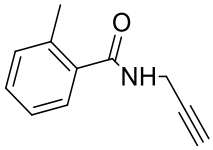
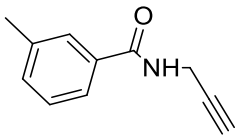
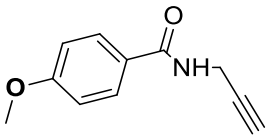
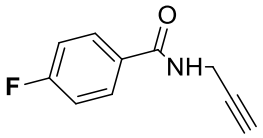
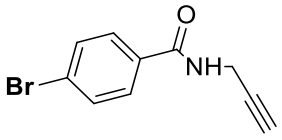
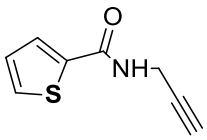
Contents

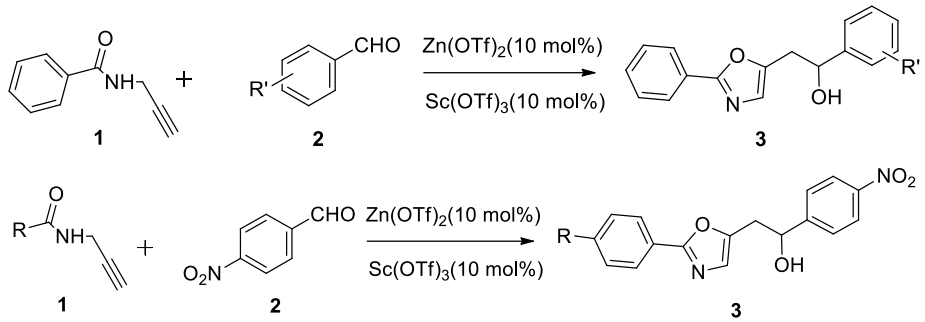
1. General Information

All NMR spectra were recorded on Bruker-400 or 300 MHz spectrometer. HRMS were measured on the Q-TOF6510 instruments. Routine monitoring of the reaction was performed by TLC using precoated silica gel plates. All the reagents and Solvents used in this reaction such as DCM were purchased from Acros or local company and used directly.

2. Synthesis and Characterization of Starting Materials

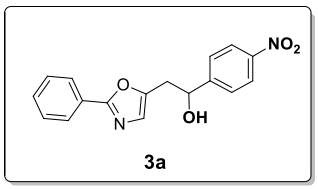
No.	Structures	References
1a		*Organic Letters*. 2004, **6,** 4391-4394.
1m		*Journal of Organic Chemistry.* 2014, **79,** 1254-1264.
1n		*Journal of Organic Chemistry.* 2014, **79,** 1254-1264.
1o		*Journal of Organic Chemistry.* 2012, **77,** 6394-6408.
1p		*Organic & Biomolecular Chemistry.* 2011**,** **9**, 4429-4431.
1q		*Chemistry - A European Journal.* 2010, **16,** 956-963.
1r		U.S., 5846990, 08 Dec 1998.
1s		*Journal of Organic Chemistry.* 2008, **73,** 4746-4749.

3. General procedure of 3



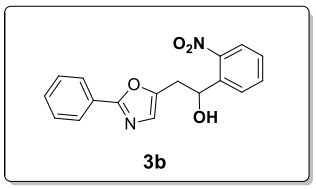
1 (1 equiv), **2** (1.2 equiv), $Zn(OTf)_2$ (10 mol%) and $Sc(OTf)_3$ (10 mol%) were dissolved in DCM. The mixture was kept stirring at 45°C overnight in a sealed tube. After the reaction was completed (monitored by TLC), the solution was filtered on celite and then evaporated under reduced pressure. Purification by flash column chromatography afforded the desired product.

4. Characterization Data of Products



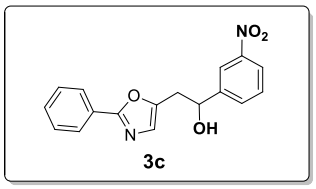
3a

Yield: 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.7 Hz, 2H), 7.85 (dd, J = 7.8, 1.5 Hz, 2H), 7.57 (d, J = 8.6 Hz, 2H), 7.46–7.36 (m, 3H), 6.86 (s, 1H), 5.16 (t, J = 6.3 Hz, 1H), 3.90 (s, 1H), 3.11 (d, J = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.37, 150.46, 148.47, 147.47, 130.44, 128.82, 126.99, 126.59, 126.04, 125.96, 123.78, 71.38, 36.01. HRMS exact mass calcd for ($C_{17}H_{14}N_2O_4$+H) requires m/z 311.1026, found m/z 311.1028.



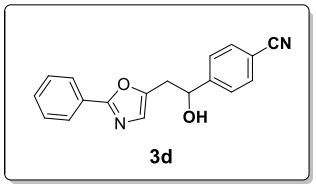
3b

Yield(71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.1 Hz, 1H), 7.94–7.83 (m, 3H), 7.66 (t, J = 7.6 Hz, 1H), 7.51–7.33 (m, 4H), 6.93 (s, 1H), 5.63 (dd, J = 8.5, 3.1 Hz, 1H), 3.77 (s, 1H), 3.31 (dd, J = 15.2, 3.1 Hz, 1H), 3.09 (dd, J = 15.2, 8.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.31, 149.03, 147.52, 138.91, 133.74, 130.22, 128.72, 128.50, 128.13, 127.14, 126.07, 125.86, 124.51, 67.85, 35.26. HRMS exact mass calcd for ($C_{17}H_{14}N_2O_4$+H) requires m/z 311.1026, found m/z 311.1009.



3c

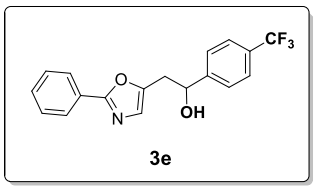
Yield(39%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.30 (s, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.90 (dd, J = 11.9, 6.9 Hz, 3H), 7.68 (t, J = 7.9 Hz, 1H), 7.54 (d, J = 5.1 Hz, 3H), 7.03 (s, 1H), 5.98 (d, J = 4.7 Hz, 1H), 5.18 (dd, J = 11.2, 5.8 Hz, 1H), 3.20 (d, J = 6.2 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.12, 150.24, 148.18, 147.63, 133.18, 130.63, 130.07, 129.49, 127.63, 126.17, 125.95, 122.47, 121.00, 70.27, 35.60. HRMS exact mass calcd for ($C_{17}H_{14}N_2O_4$+H) requires m/z 311.1026, found m/z 311.1025.



3d

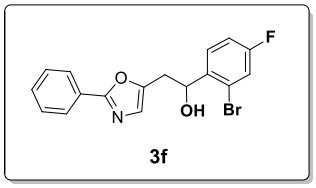
Yield(48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.82 (m, 2H), 7.64 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 6.7 Hz, 3H), 6.85 (s, 1H), 5.10 (t, J = 6.3 Hz, 1H), 3.57 (s, 1H), 3.10 (d, J = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.48, 132.38, 130.39, 128.81, 127.12, 126.50, 126.49, 126.05, 125.98, 118.66, 111.60, 71.61, 35.93. HRMS exact mass calcd for ($C_{18}H_{14}N_2O_2$+H) requires m/z 291.1134,

found m/z 291.1128.



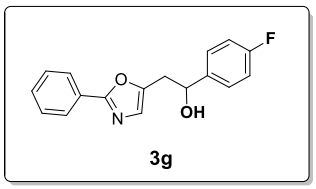
3e

Yield(60%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.81 (dd, *J* = 6.2, 2.5 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.51–7.41 (m, 3H), 6.96 (s, 1H), 5.80 (d, *J* = 4.5 Hz, 1H), 5.04 (dd, *J* = 11.1, 5.8 Hz, 1H), 3.11 (d, *J* = 6.1 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) *δ* 160.07, 150.31, 149.97, 149.96, 130.60, 129.44, 128.34, 128.03, 127.71, 127.66, 127.16, 126.19, 126.07, 125.94, 125.42, 125.38, 125.35, 125.31, 123.48, 70.72, 35.70. HRMS exact mass calcd for ($C_{18}H_{14}NF_3O_2$+H) requires m/z 334.1055, found m/z 334.1046.



3f

Yield(71%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.85 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.62 (dd, *J* = 8.7, 6.4 Hz, 1H), 7.54–7.41 (m, 4H), 7.28 (td, *J* = 8.6, 2.5 Hz, 1H), 6.96 (s, 1H), 5.86 (d, *J* = 4.6 Hz, 1H), 5.17 (dt, *J* = 9.8, 4.9 Hz, 1H), 3.10–2.94 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) *δ* 162.57, 160.17, 160.11, 150.14, 140.31, 140.28, 130.62, 129.80, 129.72, 129.50, 127.68, 126.08, 125.95, 121.70, 121.60, 119.55, 119.31, 115.52, 115.31, 69.81, 34.55. HRMS exact mass calcd for ($C_{17}H_{13}FBrNO_2$+H) requires m/z 361.0192, found m/z 361.0184.



3g

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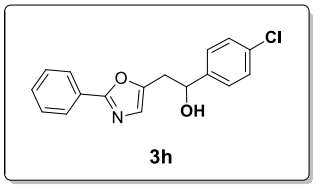
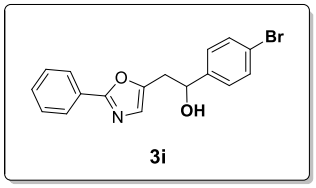
Yield(59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.45–7.28 (m, 5H), 7.03 (t, *J* = 8.6 Hz, 2H), 6.81 (s, 1H), 5.01 (dd, *J* = 7.4, 5.5 Hz, 1H), 3.30 (s, 1H), 3.09 (qd, *J* = 15.3, 6.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 163.59, 161.14, 149.17, 139.04, 139.01, 130.20, 128.75, 127.50, 127.42, 127.33, 126.07, 125.65, 115.51, 115.29, 71.77, 35.99. HRMS exact mass calcd for ($C_{17}H_{14}FNO_2$+H) requires m/z 284.1087, found m/z 284.1090.



3h

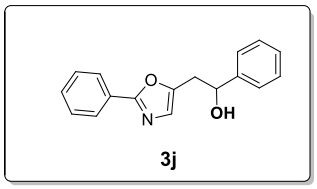
Yield(53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.44–7.37 (m, 3H), 7.35–7.27 (m, 4H), 6.84 (s, 1H), 5.05–4.98 (m, 1H), 3.16–3.06 (m, 2H), 3.04 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 161.22, 148.93, 141.66, 133.65, 130.22,

128.76, 128.73, 127.33, 127.16, 126.08, 125.81, 71.80, 35.93. HRMS exact mass calcd for ($C_{17}H_{14}ClNO_2$+H) requires m/z 300.0791, found m/z 300.0784.



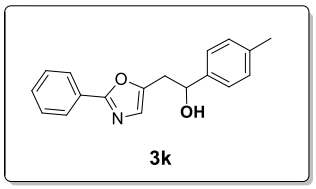
3i

Yield(38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 6.2, 2.6 Hz, 2H), 7.55–7.35 (m, 5H), 7.25 (d, *J* = 8.3 Hz, 2H), 6.82 (s, 1H), 5.04–4.95 (m, 1H), 3.23 (s, 1H), 3.16–3.00 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 161.21, 148.94, 142.22, 131.67, 130.23, 128.77, 127.51, 127.29, 126.08, 125.77, 121.73, 71.81, 35.87. HRMS exact mass calcd for ($C_{17}H_{14}BrNO_2$+H) requires m/z 344.0286, found m/z 344.0281.



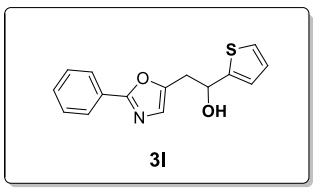
3j

Yield(48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.95 (m, 2H), 7.45–7.31 (m, 8H), 6.89 (s, 1H), 5.08 (dd, *J* = 7.6, 5.4 Hz, 1H), 3.23–3.11 (m, 2H), 2.41 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 155.90, 143.97, 137.79, 124.85, 123.48, 123.39, 122.80, 122.28, 120.84, 120.54, 120.50, 67.34, 30.60. HRMS exact mass calcd for ($C_{17}H_{15}NO_2$+H) requires m/z 266.1181, found m/z 266.1178.



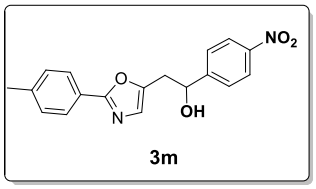
3k

Yield(52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.95 (m, 2H), 7.44–7.42 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.88 (s, 1H), 5.05–5.02 (m, 1H), 3.22–3.09 (m, 2H), 2.35 (s, 3H), 2.32 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 161.09, 158.01, 149.36, 140.10, 137.79, 130.07, 129.30, 128.72, 127.57, 126.09, 125.71, 72.45, 35.80, 21.14. HRMS exact mass calcd for ($C_{18}H_{17}NO_2$+H) requires m/z 280.1338, found m/z 280.1336.



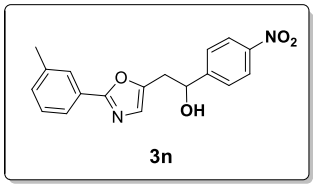
3l

Yield(51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.90 (m, 2H), 7.42–7.40 (m, 3H), 7.28–7.26 (m, 1H), 7.00–6.87 (m, 2H), 6.87 (s, 1H), 5.32 (t, *J* = 5.8 Hz, 1H), 3.46 (s, 1H), 3.26–3.23 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 161.15, 148.84, 147.02, 130.19, 128.76, 127.32, 126.78, 126.09, 125.86, 124.94, 123.99, 68.48, 36.09. HRMS exact mass calcd for ($C_{15}H_{13}NO_2S$+H) requires m/z 272.0745, found m/z 272.0735.



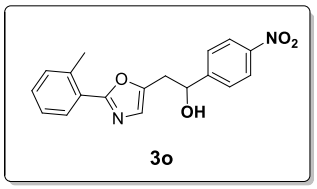
3m

Yield(52%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.18 (d, *J* = 8.7 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.92 (s, 1H), 5.89 (d, *J* = 4.7 Hz, 1H), 5.08 (dd, *J* = 11.2, 6.1 Hz, 1H), 3.10 (d, *J* = 6.3 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) *δ* 160.28, 153.06, 149.75, 147.06, 140.45, 130.04, 127.63, 125.95, 125.02, 123.70, 70.50, 35.54, 21.44. HRMS exact mass calcd for ($C_{18}H_{16}N_2O_4$+H) requires m/z 325.1188, found m/z 325.1202.



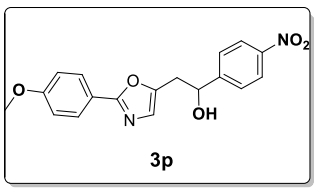
3n

Yield(49%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.6 Hz, 2H), 7.66 (s, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.32–7.20 (m, 2H), 6.85 (s, 1H), 5.16 (t, *J* = 6.4 Hz, 1H), 3.71 (s, 1H), 3.11 (d, *J* = 6.4 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 161.58, 150.41, 148.26, 147.51, 138.58, 131.23, 128.71, 126.94, 126.64, 126.59, 125.97, 123.77, 123.22, 71.43, 36.03, 21.31. HRMS exact mass calcd for ($C_{18}H_{16}N_2O_4$+H) requires m/z 325.1188, found m/z 325.1195.



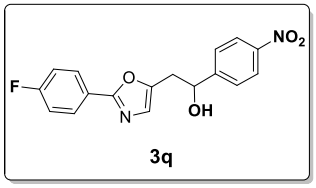
3o

Yield(53%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.17 (d, *J* = 8.7 Hz, 2H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.37–7.22 (m, 3H), 6.98 (s, 1H), 5.94 (d, *J* = 4.5 Hz, 1H), 5.08 (dd, *J* = 10.8, 5.9 Hz, 1H), 3.12 (d, *J* = 6.2 Hz, 2H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) *δ* 160.46, 152.98, 149.47, 147.06, 136.81, 132.05, 130.22, 128.47, 127.62, 126.54, 125.94, 123.71, 70.57, 35.44, 21.87. HRMS exact mass calcd for ($C_{18}H_{16}N_2O_4$+H) requires m/z 325.1188, found m/z 325.1198.



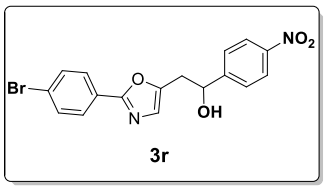
3p

Yield(64%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.18 (d, *J* = 8.7 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.7 Hz, 2H), 7.02 (d, *J* = 8.9 Hz, 2H), 6.88 (s, 1H), 5.89 (d, *J* = 4.7 Hz, 1H), 5.07 (dd, *J* = 11.1, 6.1 Hz, 1H), 3.79 (s, 3H), 3.09 (d, *J* = 6.3 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) *δ* 161.20, 160.22, 153.07, 149.40, 147.06, 127.68, 127.62, 125.82, 123.69, 120.38, 114.90, 70.53, 55.80, 35.53. HRMS exact mass calcd for ($C_{18}H_{16}N_2O_5$+H) requires m/z 341.1137, found m/z 341.1157.



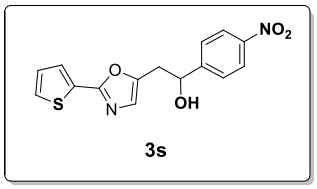
3q

Yield(46%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.18 (d, *J* = 8.7 Hz, 2H), 7.92–7.84 (m, 2H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.32 (t, *J* = 8.8 Hz, 2H), 6.94 (s, 1H), 5.91 (d, *J* = 4.7 Hz, 1H), 5.09 (dd, *J* = 11.2, 6.1 Hz, 1H), 3.10 (d, *J* = 6.3 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) *δ* 164.82, 162.36, 159.36, 159.35, 152.98, 150.26, 150.25, 147.07, 128.44, 128.36, 127.61, 126.14, 124.33, 124.30, 123.71, 116.76, 116.54, 70.46, 35.52. HRMS exact mass calcd for ($C_{17}H_{13}FN_2O_4$+H) requires m/z 329.0938, found m/z 329.0953.



3r

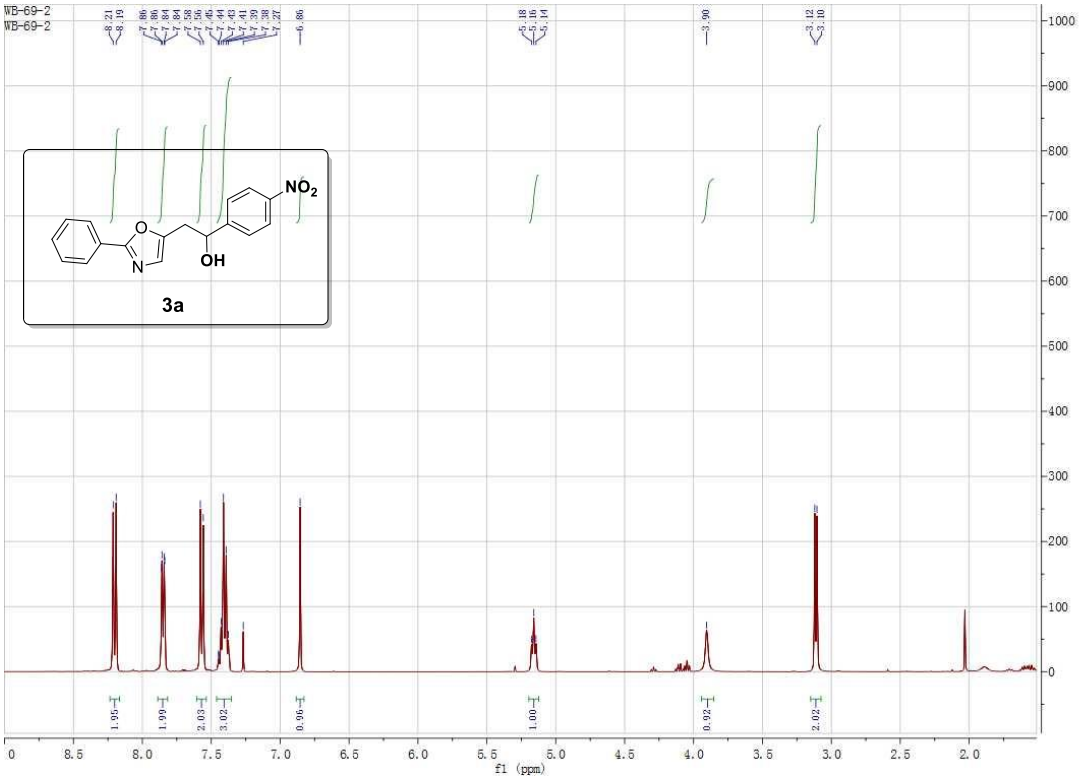
Yield(64%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.18 (d, *J* = 8.7 Hz, 2H), 7.77 (d, *J* = 8.6 Hz, 2H), 7.66 (dd, *J* = 16.8, 8.6 Hz, 4H), 6.98 (s, 1H), 5.91 (d, *J* = 4.7 Hz, 1H), 5.09 (dd, *J* = 11.3, 6.0 Hz, 1H), 3.11 (d, *J* = 6.2 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) *δ* 164.05, 157.70, 155.34, 151.83, 137.33, 132.64, 132.34, 131.50, 131.12, 128.82, 128.47, 75.17, 40.29. HRMS exact mass calcd for ($C_{17}H_{13}BrN_2O_4$+H) requires m/z 389.0137, found m/z 389.0132.

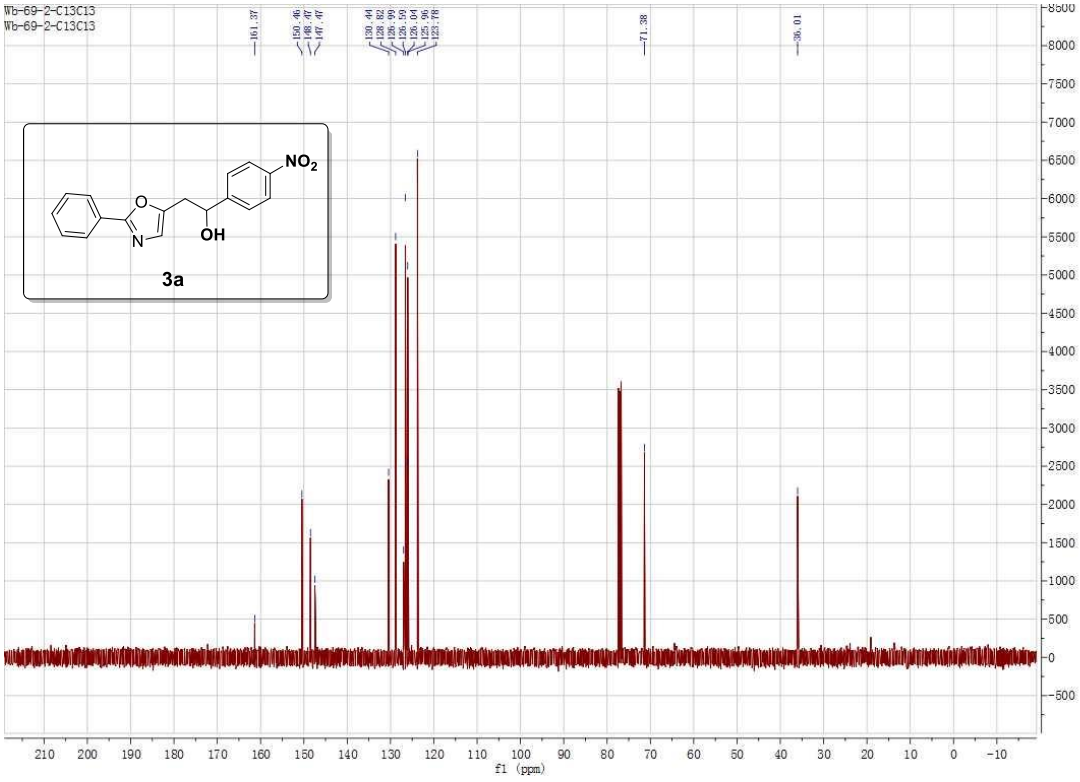


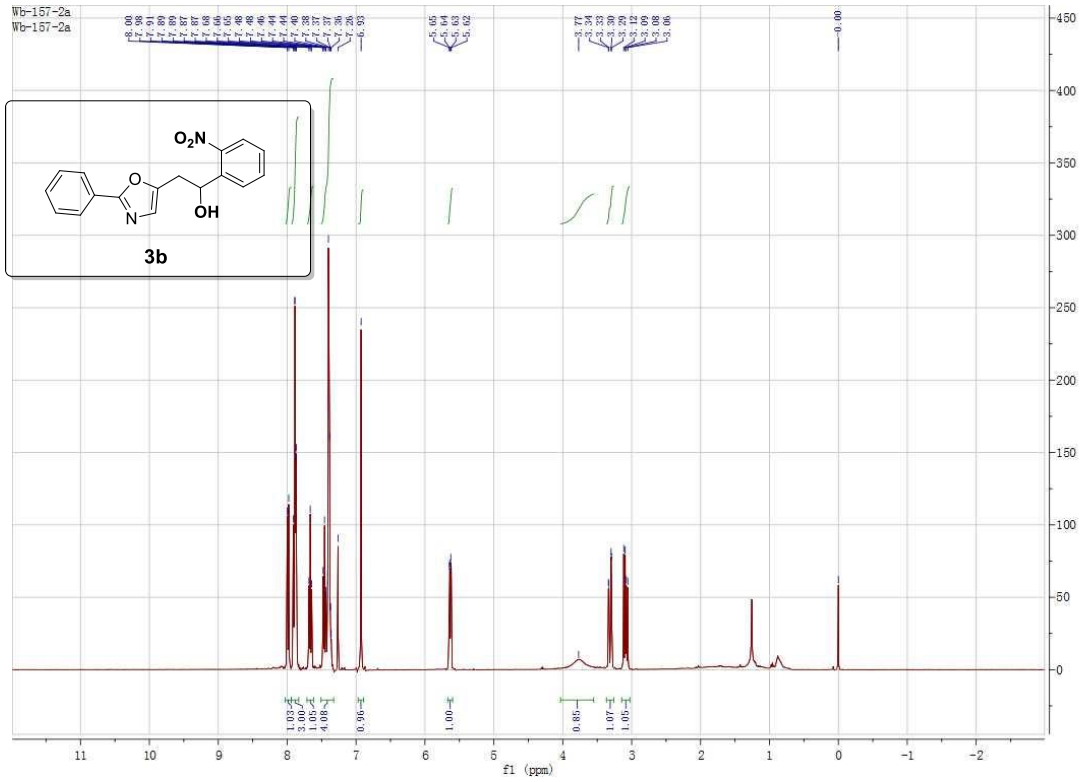
3s

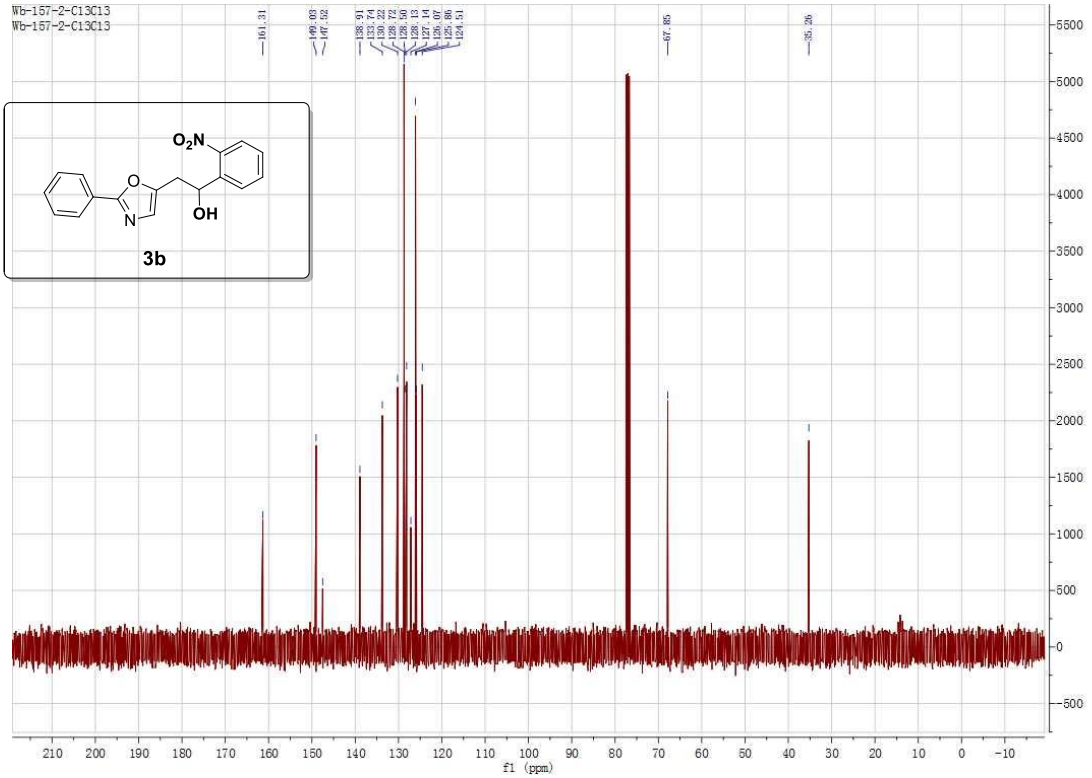
Yield(43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.51 (s, 1H), 7.40 (d, *J* = 4.9 Hz, 1H), 7.13–7.03 (m, 1H), 6.82 (s, 1H), 5.19 (t, *J* = 6.1 Hz, 1H), 3.61 (s, 1H), 3.11 (d, *J* = 5.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 157.59, 150.29, 147.91, 147.52, 129.57, 128.32, 127.99, 127.57, 126.60, 125.98, 123.81, 71.36, 35.93. HRMS exact mass calcd for ($C_{15}H_{12}SN_2O_4$+H) requires m/z 317.0596, found m/z 317.0606.

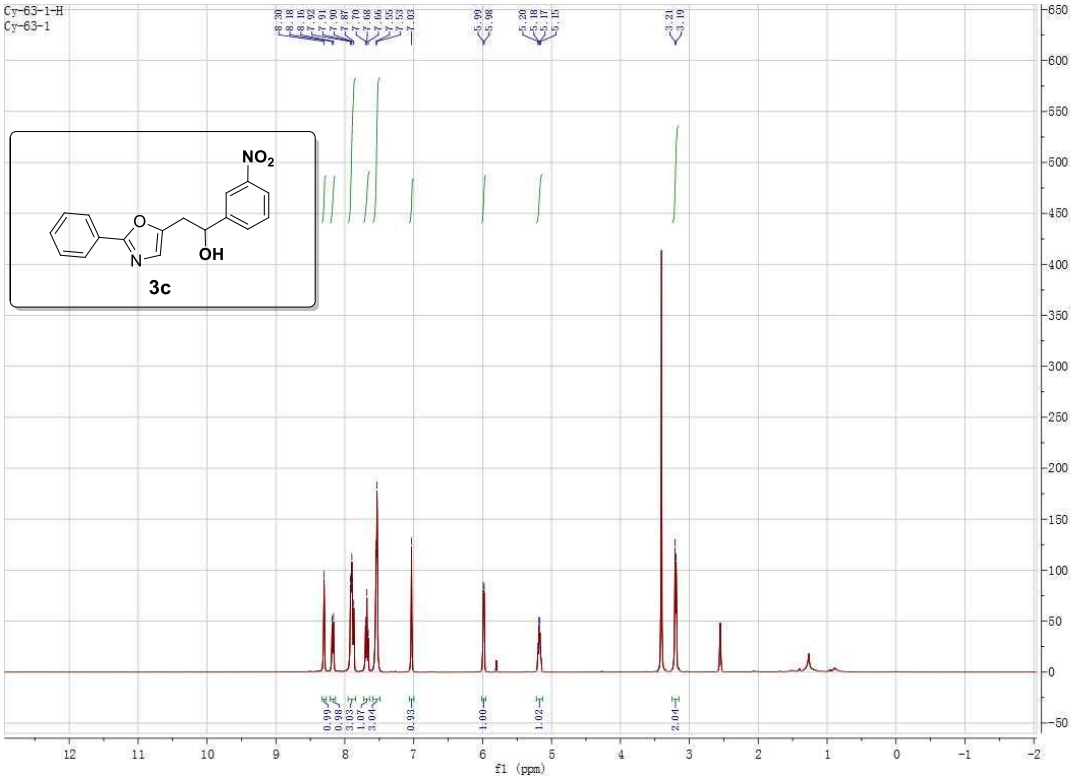
5. ^{1}H NMR and ^{13}C NMR Spectra of Products






Wb-157-2a
Wb-157-2a
3b


Wb-157-2-C13C13
Wb-157-2-C13C13
3b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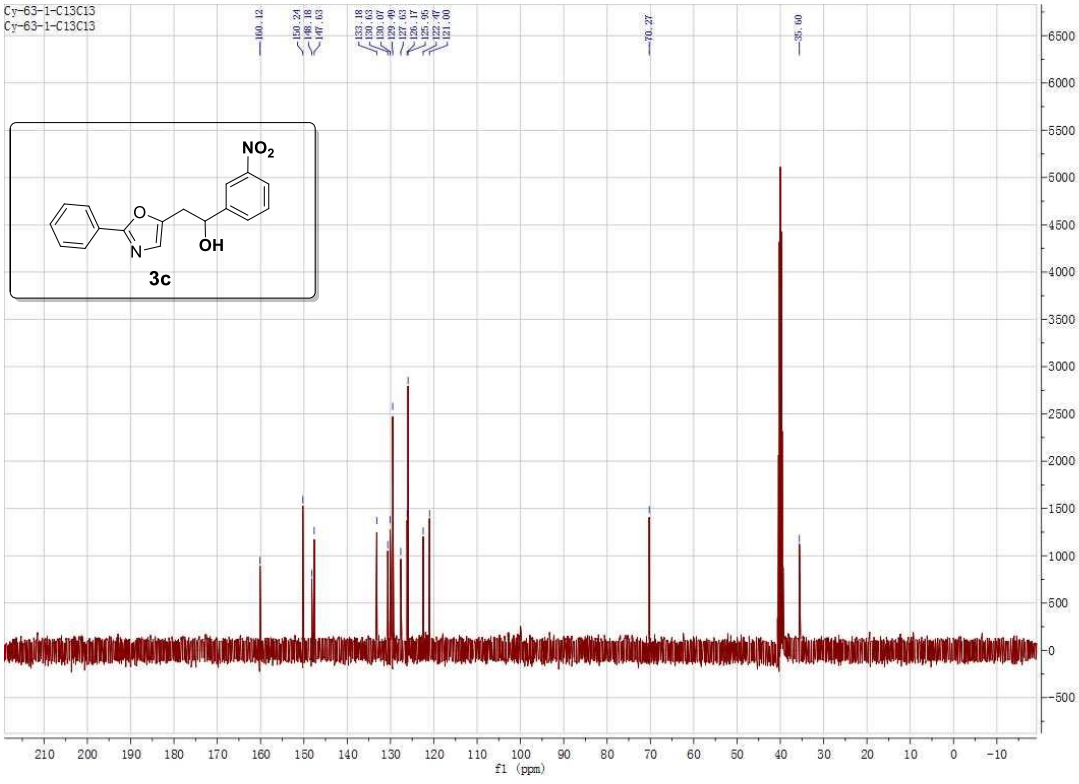
Cy-63-1
NO2
OH
N
O
3c
f1 (ppm)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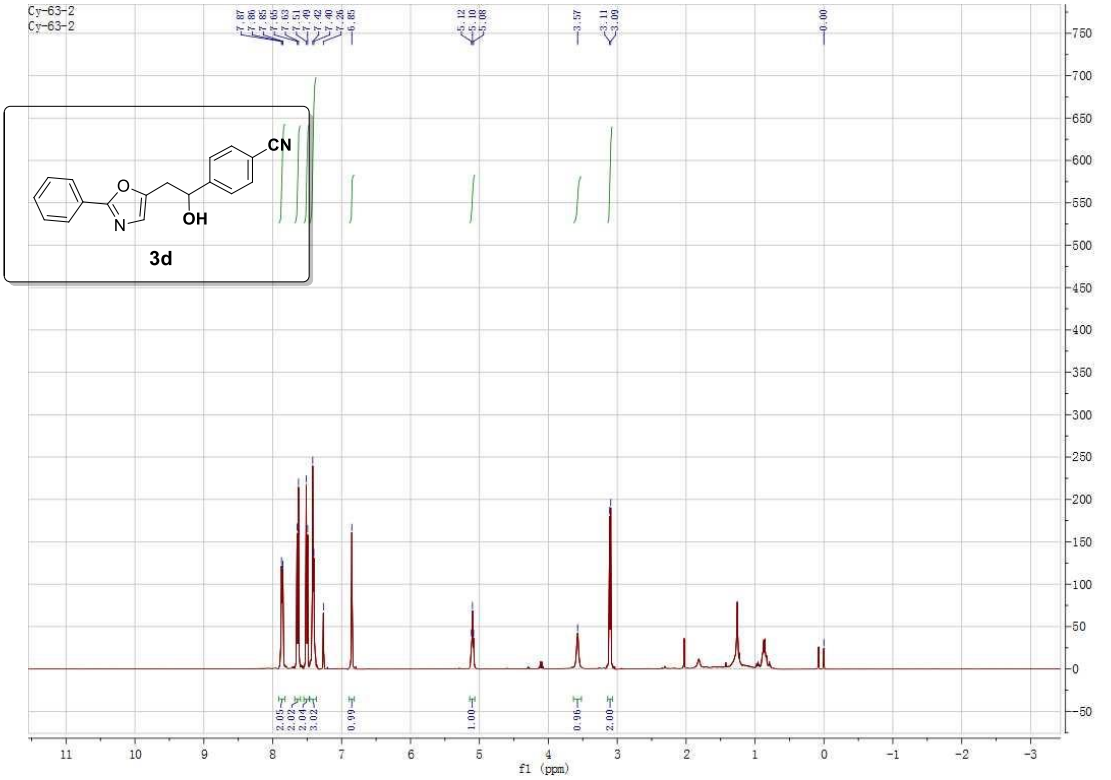
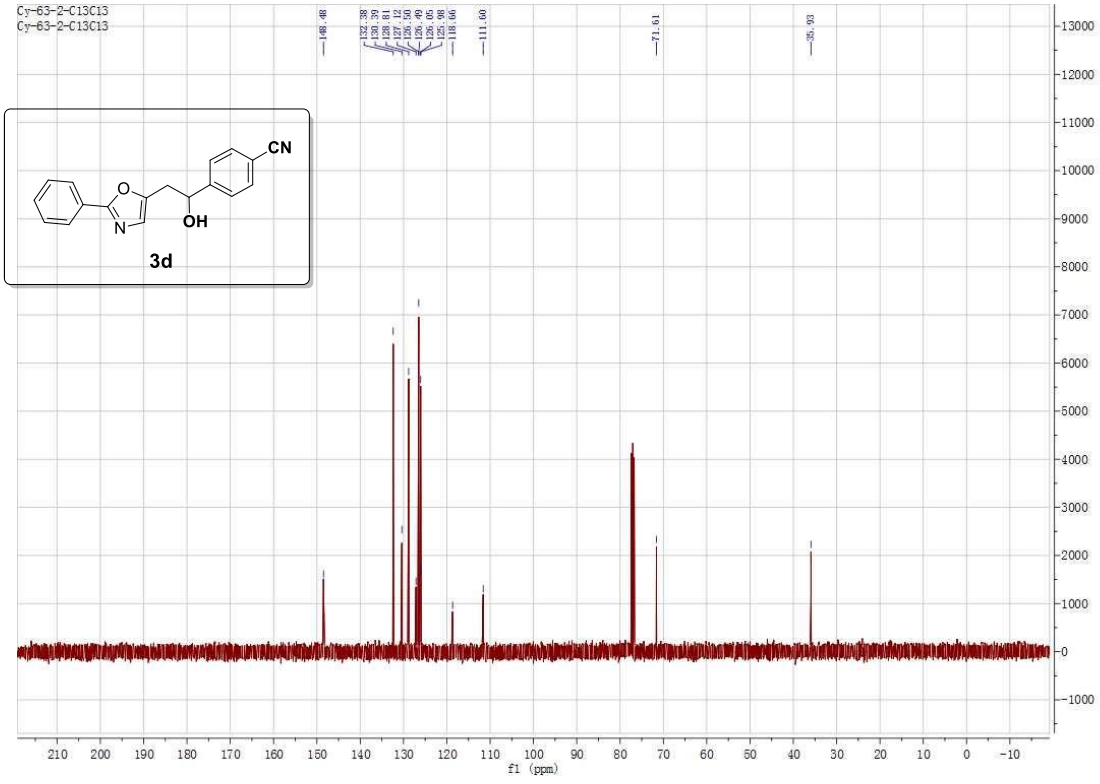
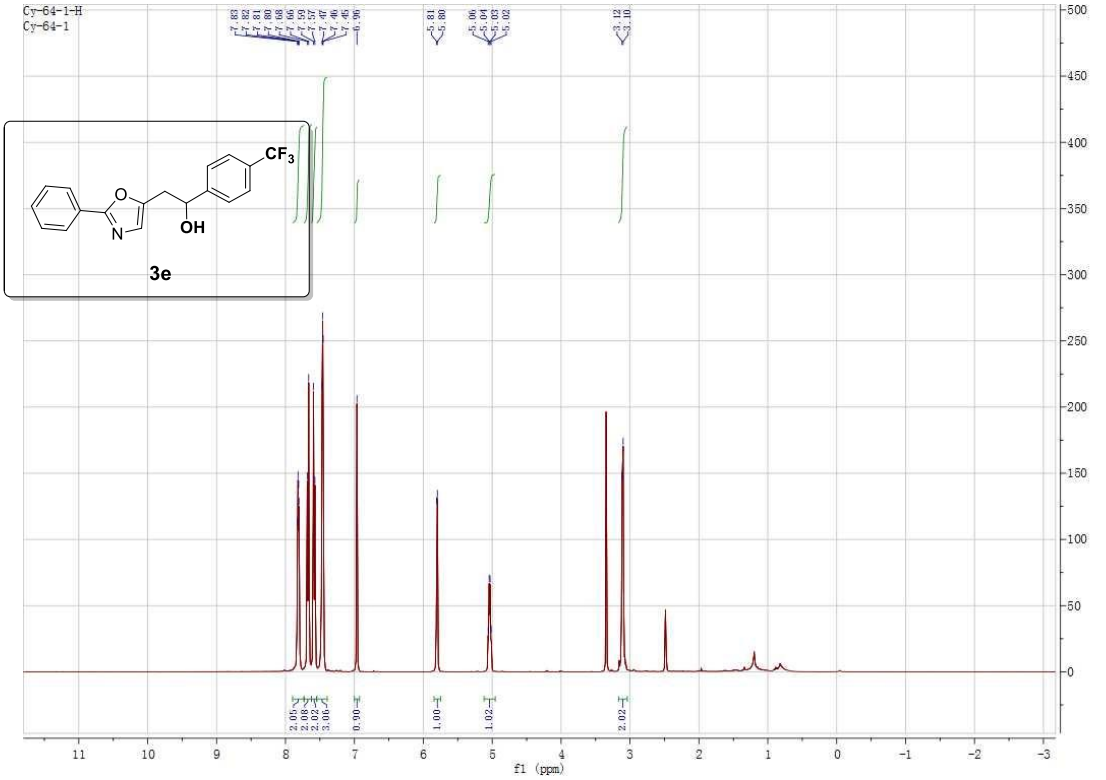
Cy-63-1-C13C13
NO2
OH
N
O
3c
f1 (ppm)


Cy-63-2
Cy-63-2
CN
O
N
OH
3d
f1 (ppm)


Cy-63-2-C13C13
Cy-63-2-C13C13
CN
O
N
OH
3d
f1 (ppm)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Cy-64-1
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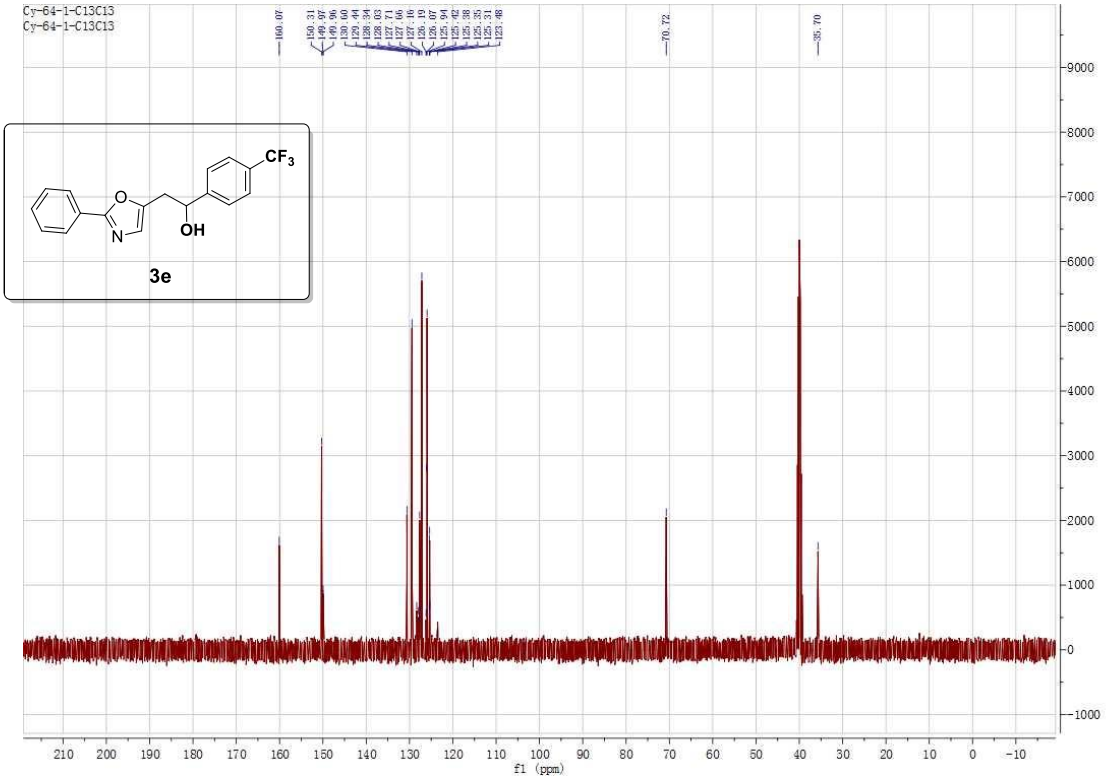
O
N
OH
3e
f1 (ppm)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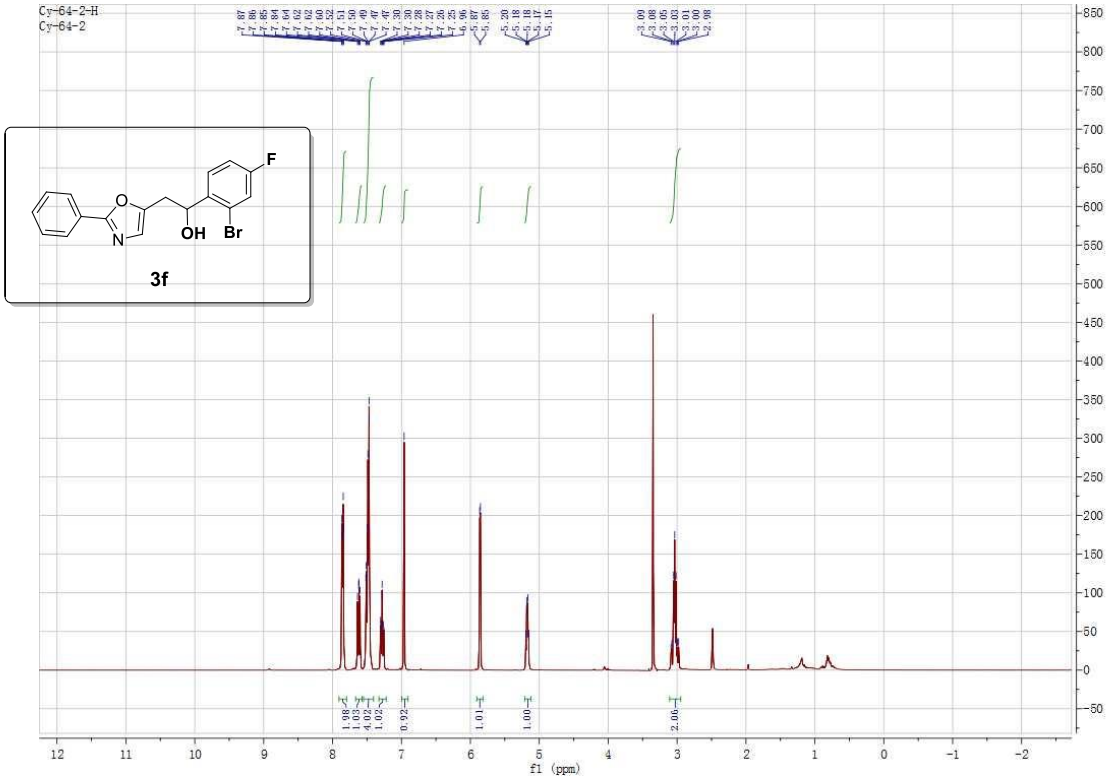
Cy-64-1-C13C13
CF3
O
N
OH
3e
f1 (ppm)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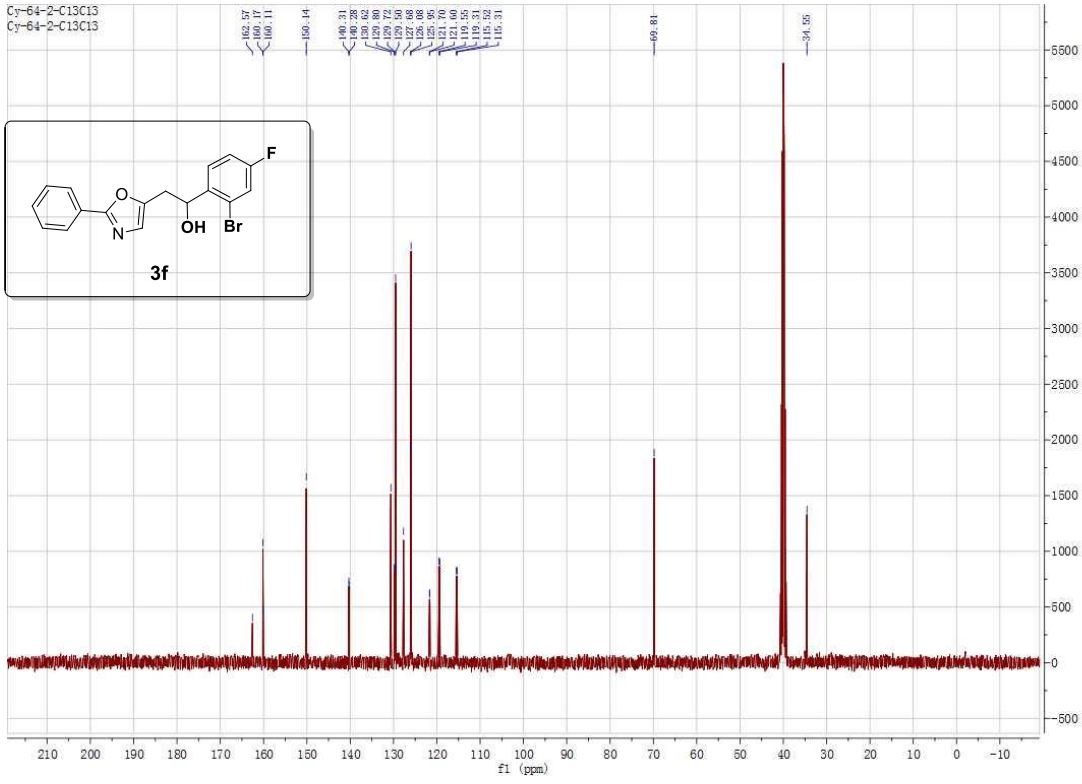
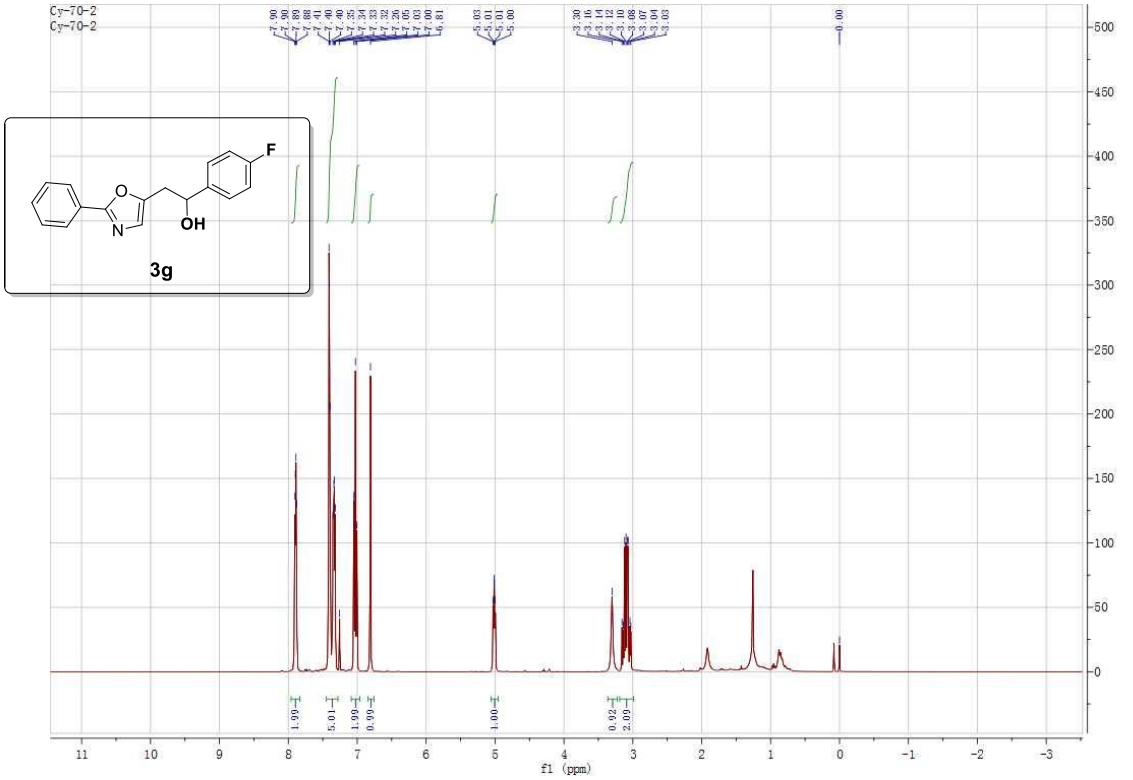
Cy-64-2
F
O
N
OH
Br
3f
f1 (ppm)


Cy-64-2-C13C13
Cy-64-2-C13C13
F
O
N
OH
Br
3f
f1 (ppm)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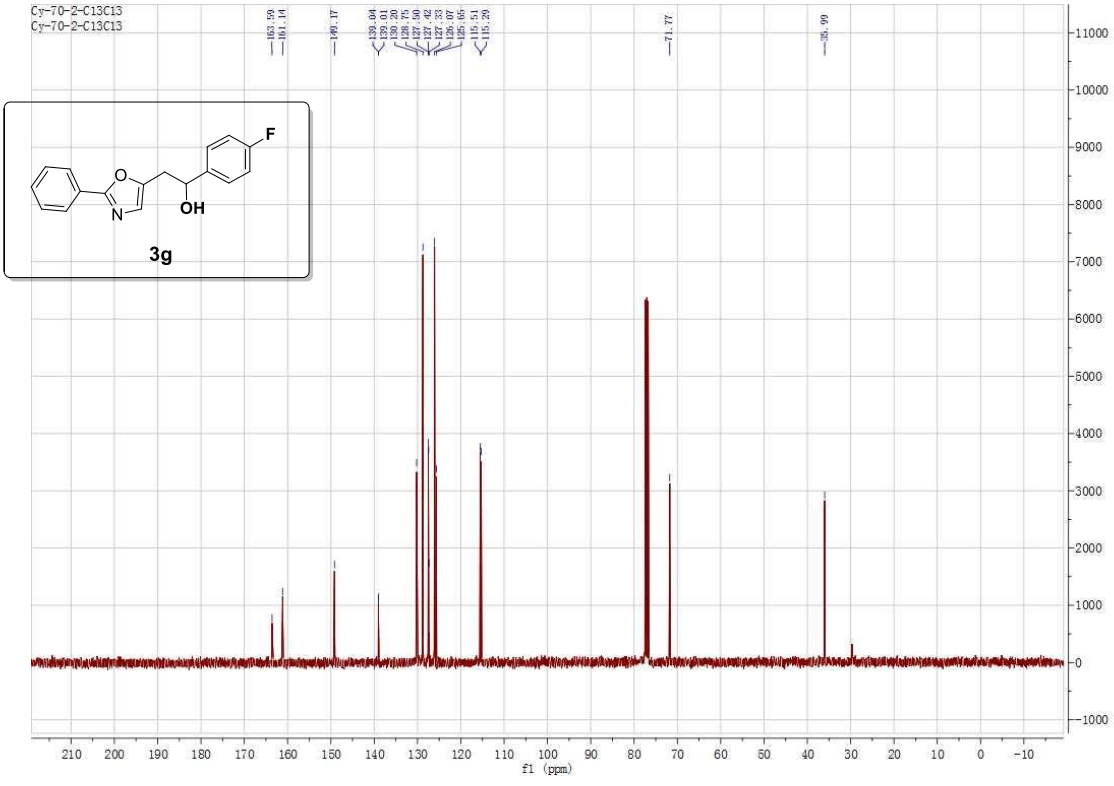
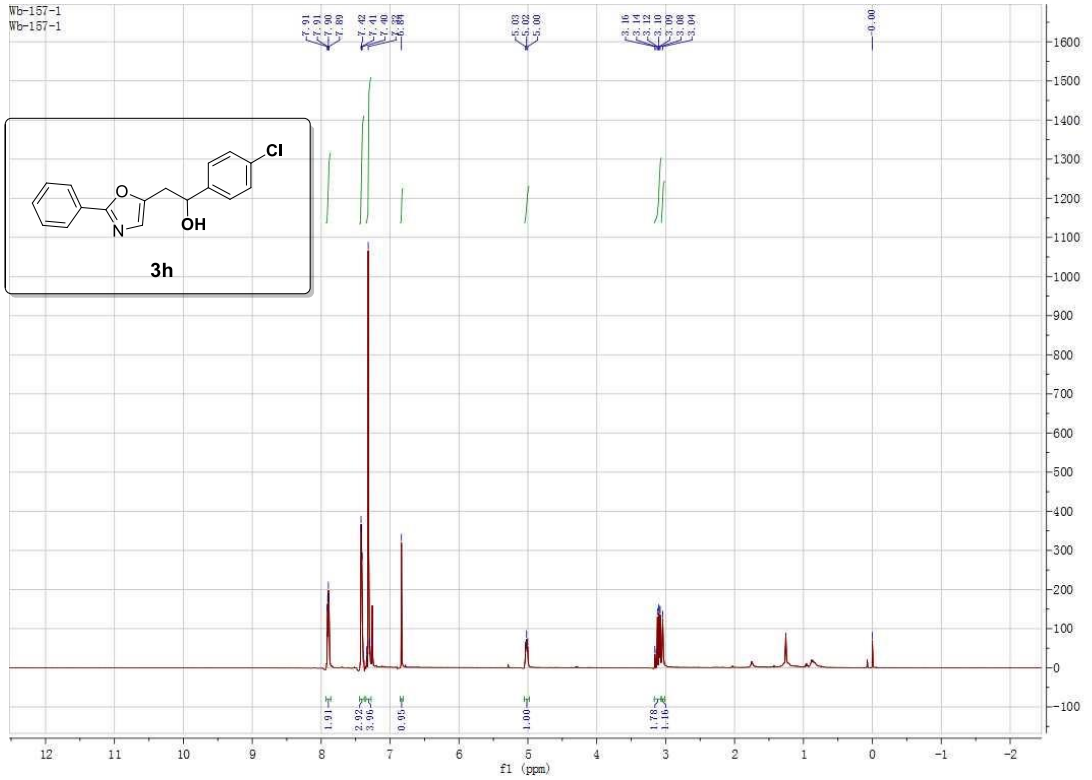
Cy-70-2
F
O
N
OH
3g
f1 (ppm)


Cy-70-2-C13C13
Cy-70-2-C13C13
F
O
N
OH
3g
f1 (ppm)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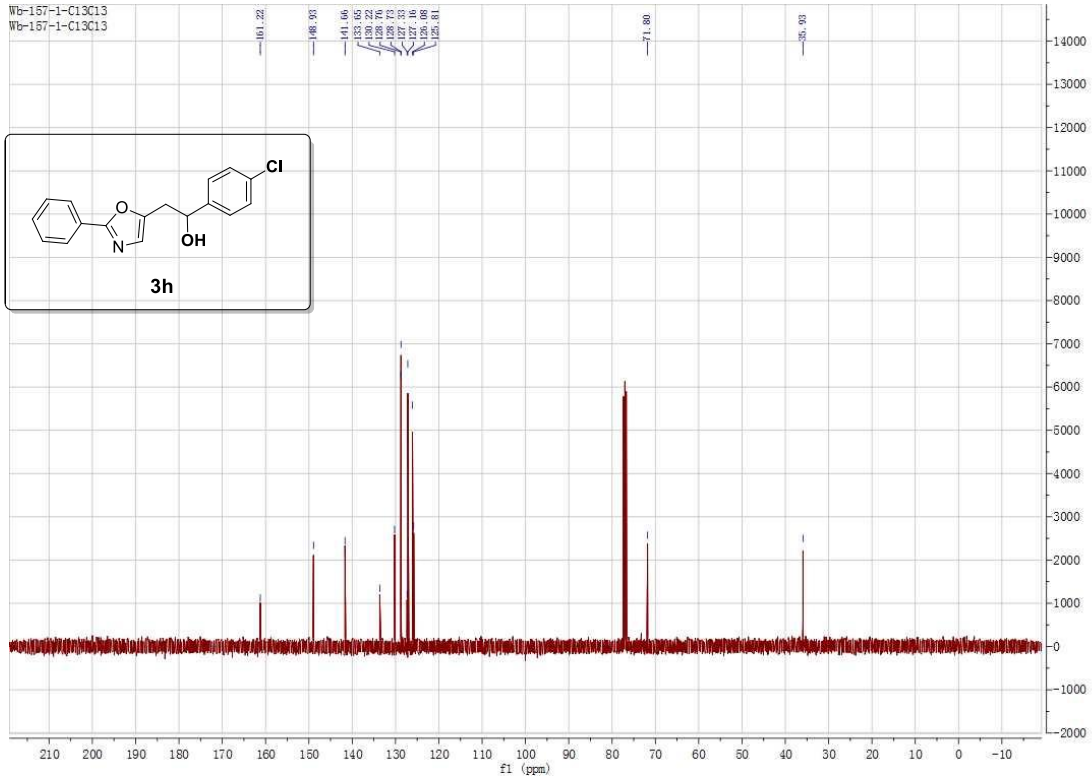
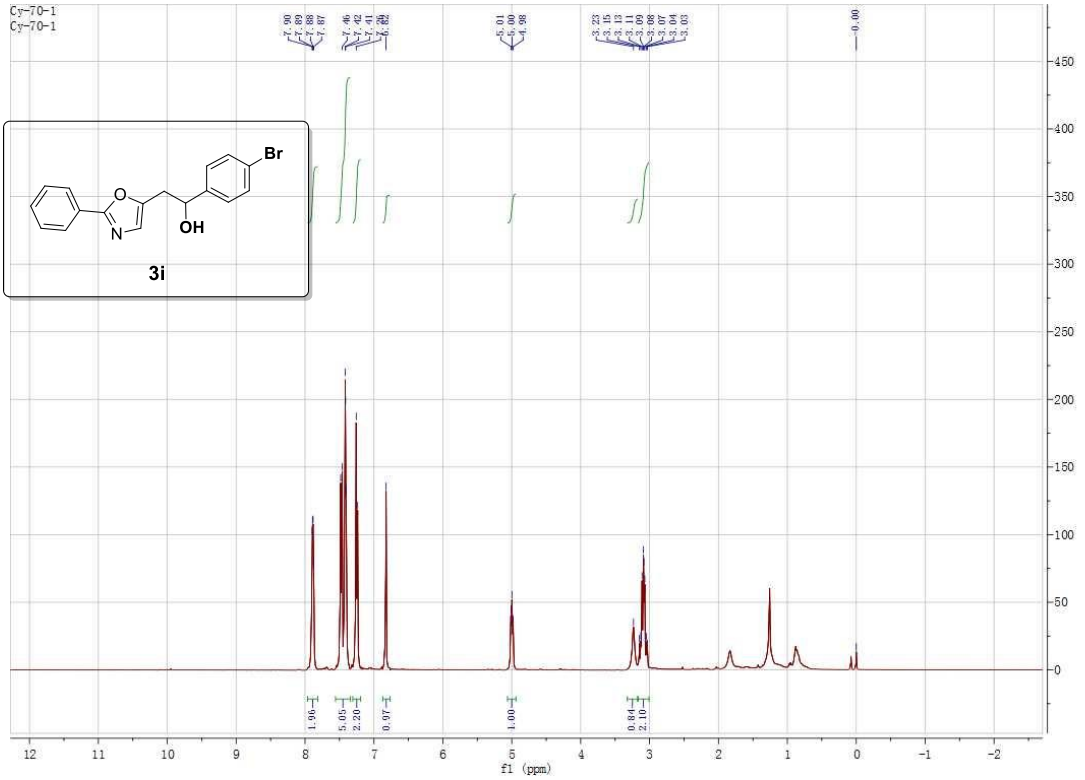
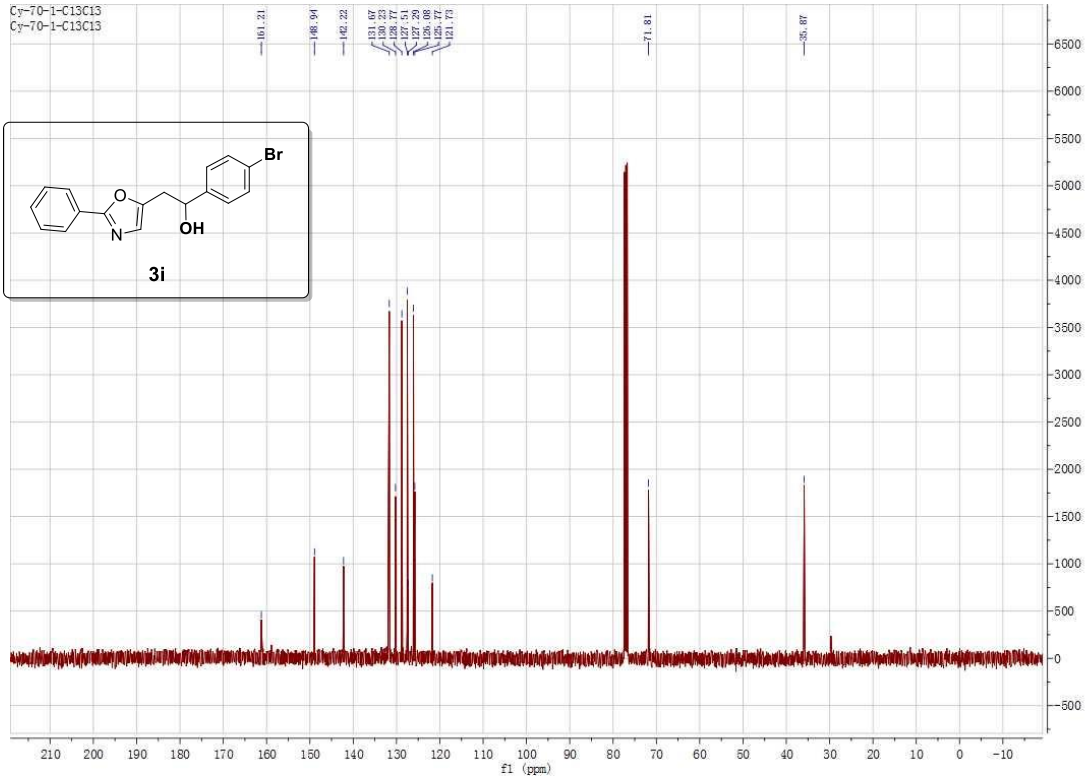
Wb-157-1
Cl
O
N
OH
3h
f1 (ppm)


Wb-157-1-C13C13
Wb-157-1-C13C13
Cl
O
N
OH
3h
f1 (ppm)


Cy-70-1
Cy-70-1
Br
OH
3i
f1 (ppm)


Cy-70-1-C13C13
Cy-70-1-C13C13
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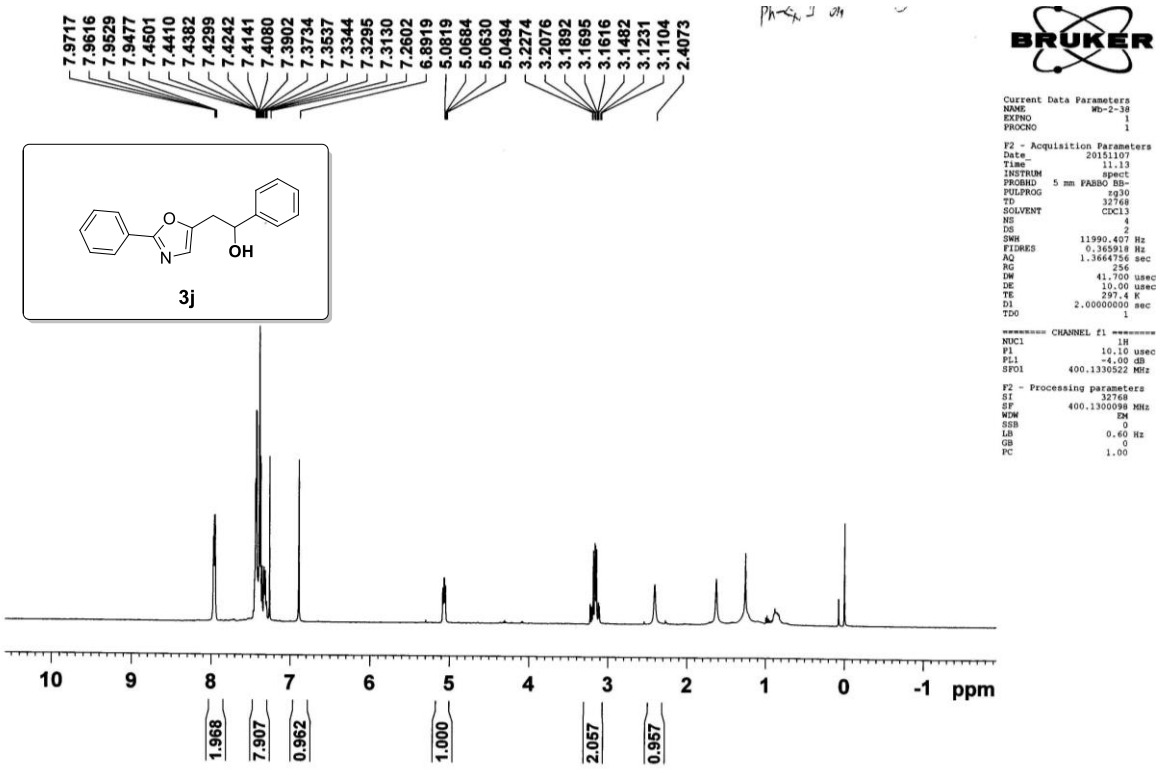
148.94
142.22
131.67
130.23
128.77
127.51
127.29
126.88
125.47
121.73
71.81
35.87
Br
OH
3i
f1 (ppm)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7.4299
7.4242
7.4141
7.4080
7.3902
7.3734
7.3537
7.3344
7.3295
7.3130
7.2602
6.8919
5.0819
5.0684
5.0630
5.0494
3.2274
3.2076
3.1892
3.1695
3.1616
3.1482
3.1231
3.1104
2.4073
3j
Current Data Parameters
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PROCNO 1
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PULPROG zg30
TD 32768
SOLVENT CDCl3
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DS 2
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FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 256
DW 41.700 usec
DE 10.00 usec
TE 297.4 K
D1 2.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 10.10 usec
PL1 -4.00 dB
SFO1 400.1330522 MHz
F2 - Processing parameters
SI 32768
SF 400.1300098 MHz
WDW EM
SSB 0
LB 0.60 Hz
GB 0
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7.907
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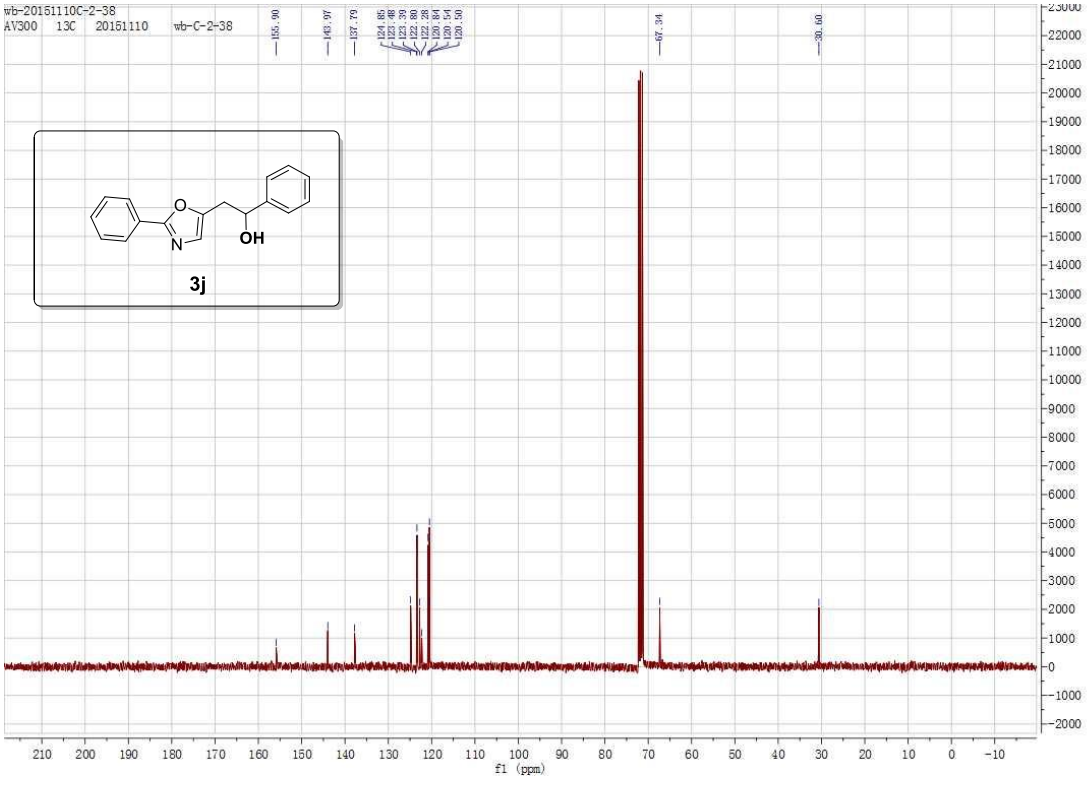
1.000
2.057
0.957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AV300 13C 20151110 wb-C-2-38
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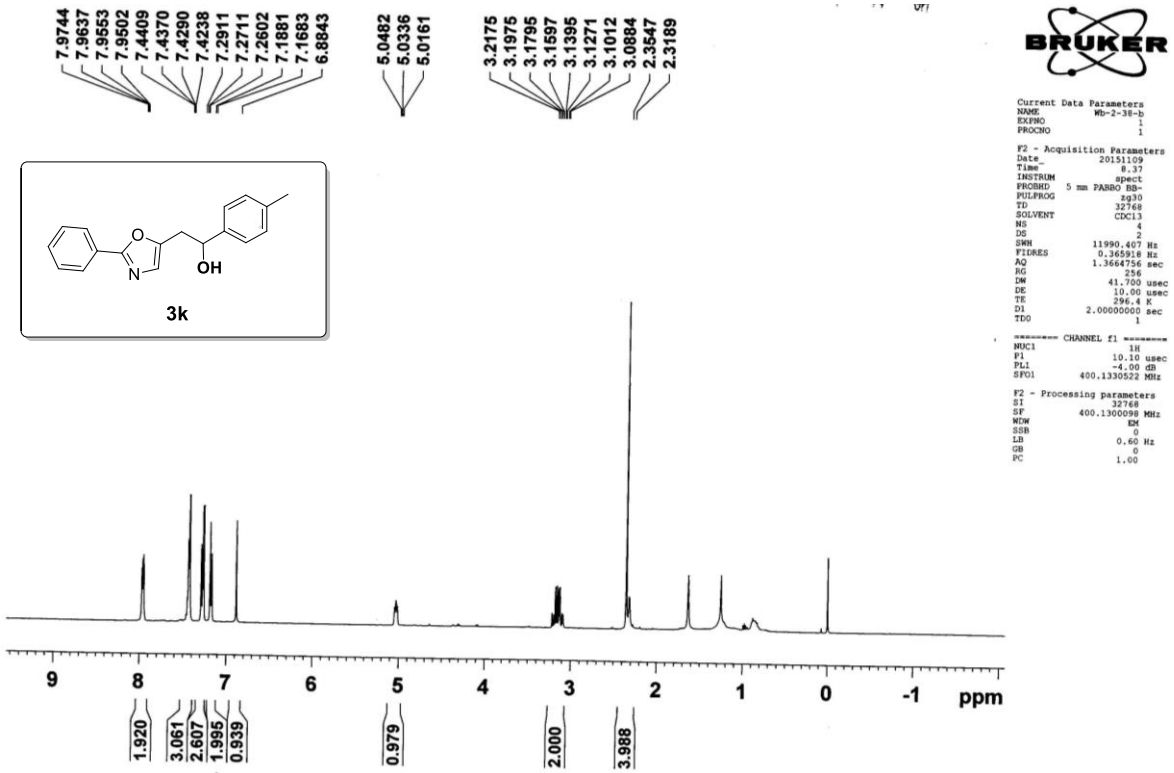
137.79
124.85
123.49
123.39
122.80
122.28
120.94
120.54
120.50
67.34
30.60
3j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.9637
7.9553
7.9502
7.4409
7.4370
7.4290
7.4238
7.2911
7.2711
7.2602
7.1881
7.1683
6.8843
5.0482
5.0336
5.0161
3.2175
3.1975
3.1795
3.1597
3.1395
3.1271
3.1012
3.0884
2.3547
2.3189
OH
3k
BRUKER
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PROCNO 1
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Time 8.37
INSTRUM spect
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SOLVENT CDCl3
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DS 2
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FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 256
DW 41.700 usec
DE 10.00 usec
TE 296.4 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.10 usec
PL1 -4.00 dB
SFO1 400.1330522 MHz
F2 - Processing parameters
SI 32768
SF 400.1300098 MHz
WDW EM
SSB 0
LB 0.60 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
0
-1
ppm
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3.061
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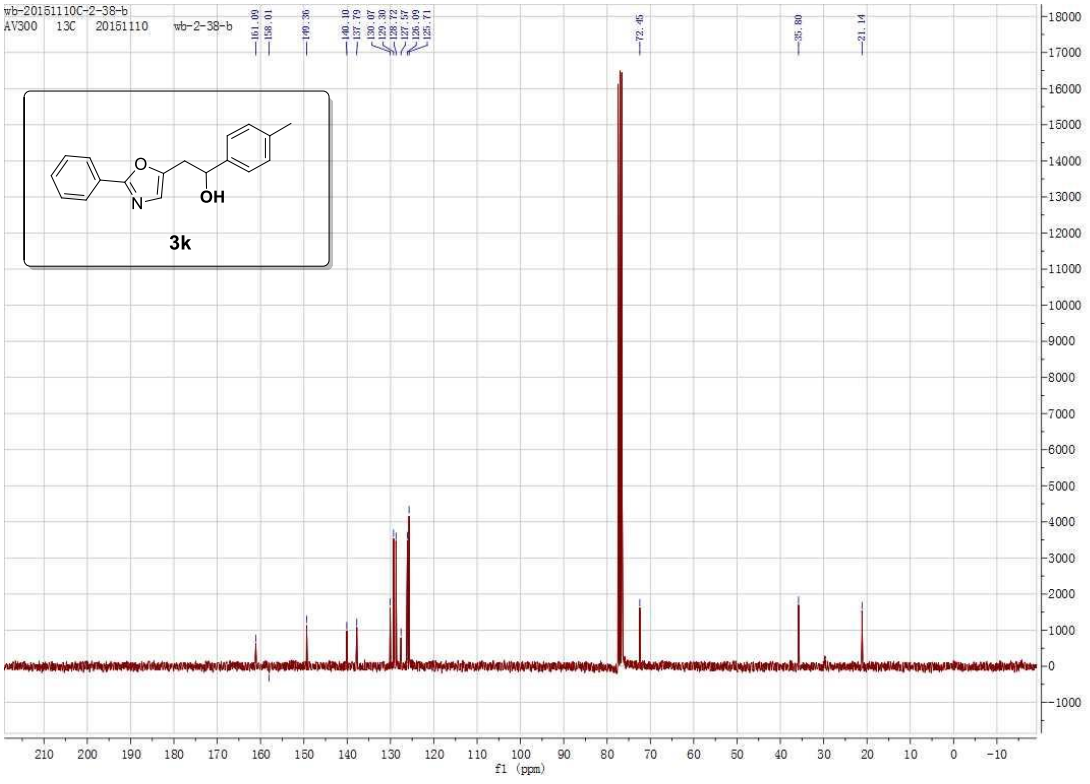
2.000
3.988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127.57
126.09
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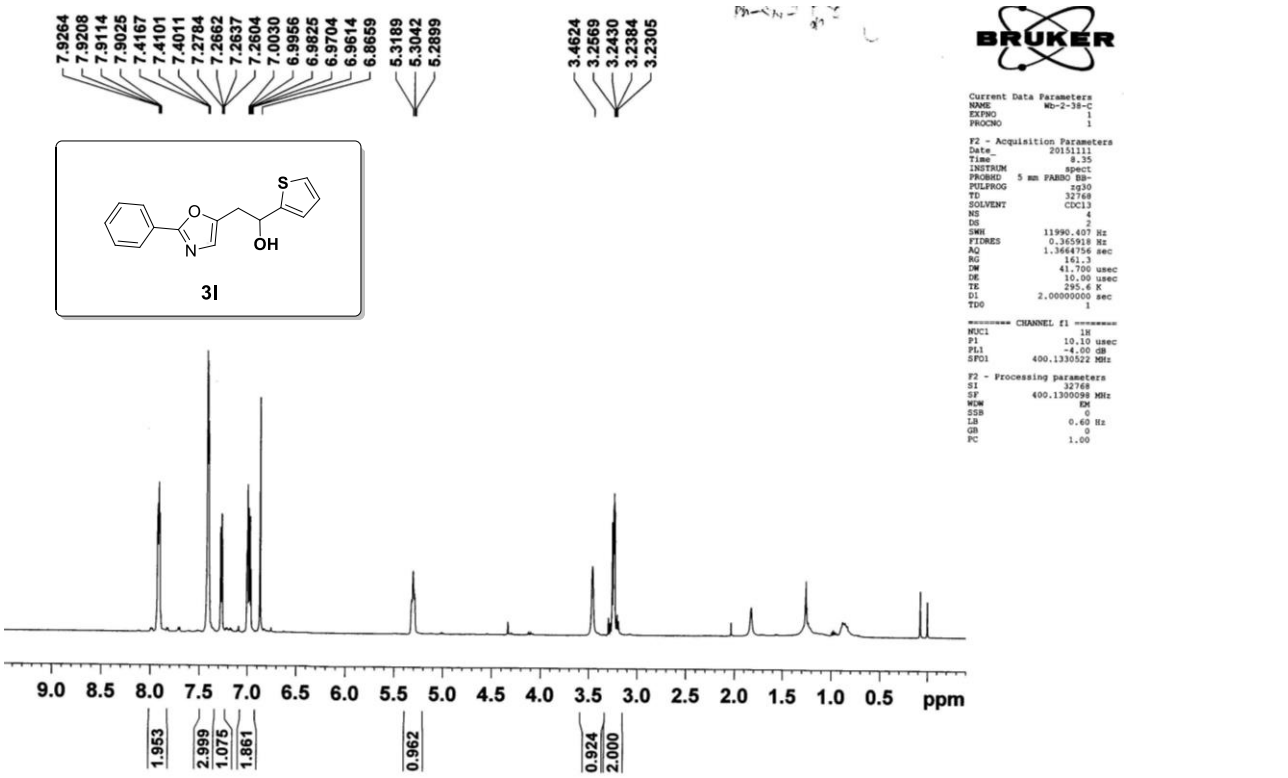
35.80
21.14
OH
3k
f1 (ppm)



BRUKER

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EXPNO                         1
PROCNO                        1

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Time                      8.35
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                  zg30
TD                      32768
SOLVENT                 CDCl3
NS                          4
DS                          2
SWH                 11990.407 Hz
FIDRES              0.365918 Hz
AQ                  1.3664756 sec
RG                      161.3
DW                     41.700 usec
DE                     10.00 usec
TE                     295.6 K
D1                  2.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      10.10 usec
PL1                     -4.00 dB
SFO1                400.1330522 MHz

F2 - Processing parameters
SI                      32768
SF                  400.1300098 MHz
WDW                        EM
SSB                         0
LB                      0.60 Hz
GB                          0
PC                       1.00
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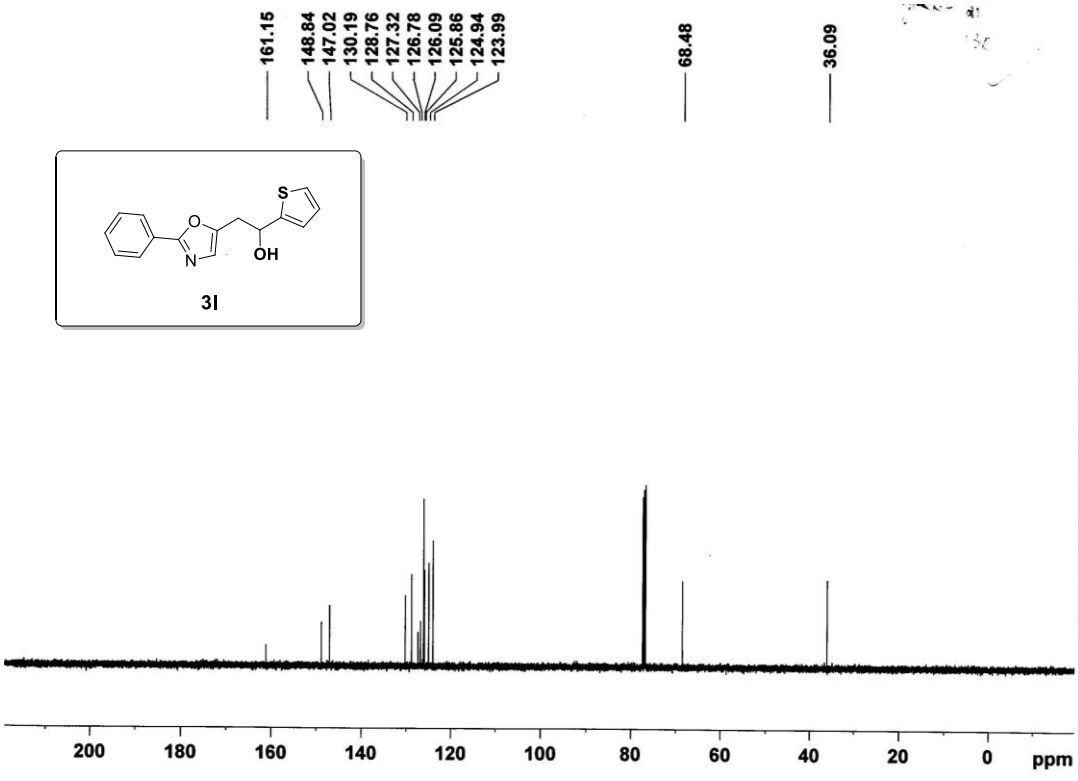

BRUKER

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Current Data Parameters
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PROCNO                        1

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PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                        125
DS                          4
SWH                 23980.814 Hz
FIDRES              0.365918 Hz
AQ                  1.3664756 sec
RG                     20642.5
DW                     20.850 usec
DE                      8.00 usec
TE                     296.1 K
D1                  2.00000000 sec
d11                 0.03000000 sec
DELTA               1.89999998 sec
TD0                         2

======== CHANNEL f1 ========
NUC1                       13C
P1                      8.30 usec
PL1                     -3.00 dB
SFO1                100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  80.00 usec
PL12                   12.93 dB
PL13                   12.80 dB
PL2                    -1.00 dB
SFO2                400.1316005 MHz

F2 - Processing parameters
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SF                  100.6127690 MHz
WDW                        no
SSB                         0
LB                      0.00 Hz
GB                          0
PC                       1.40
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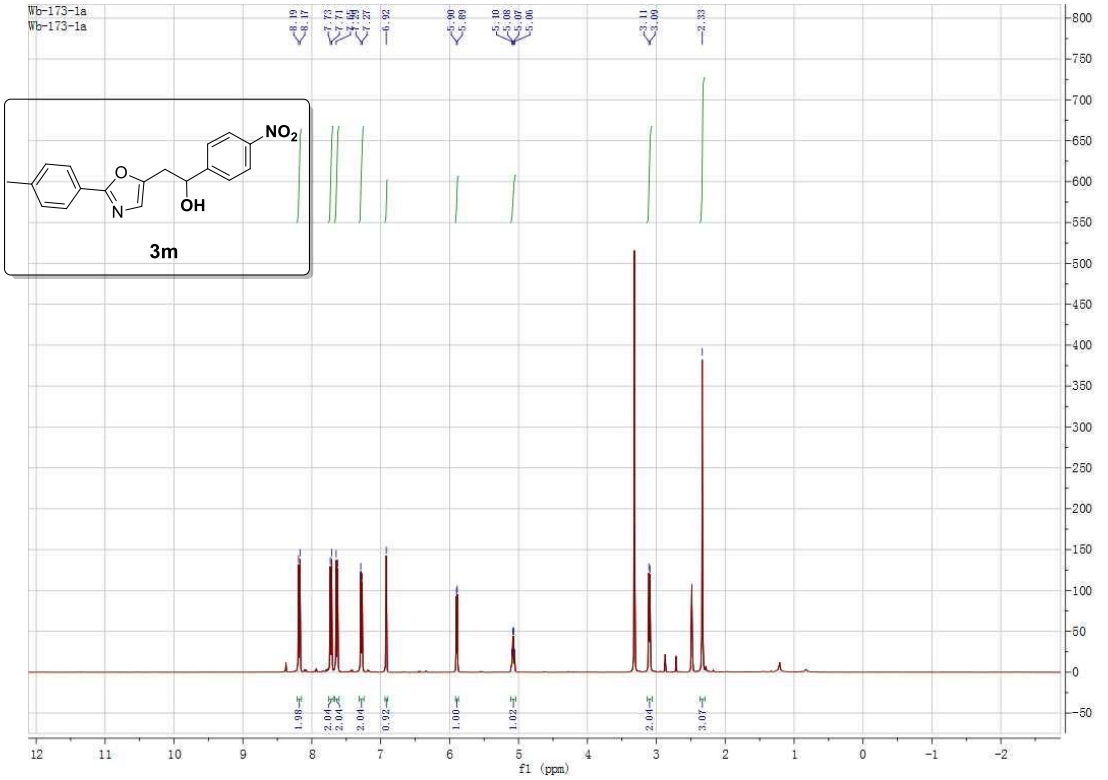
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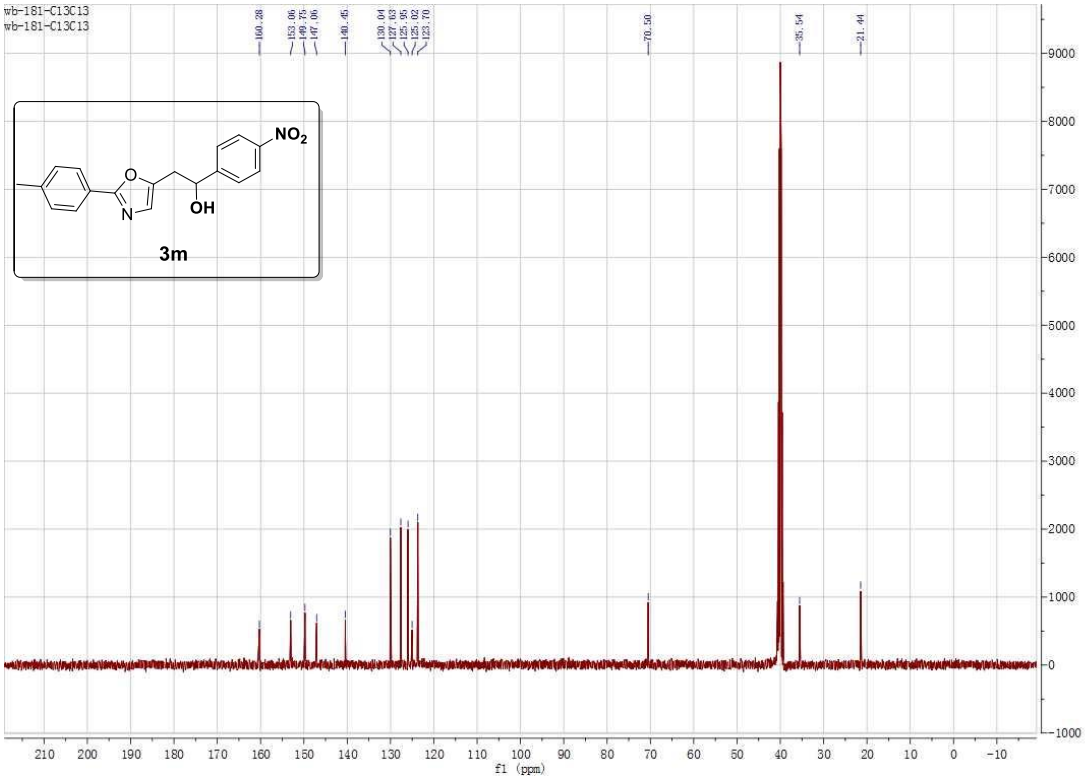
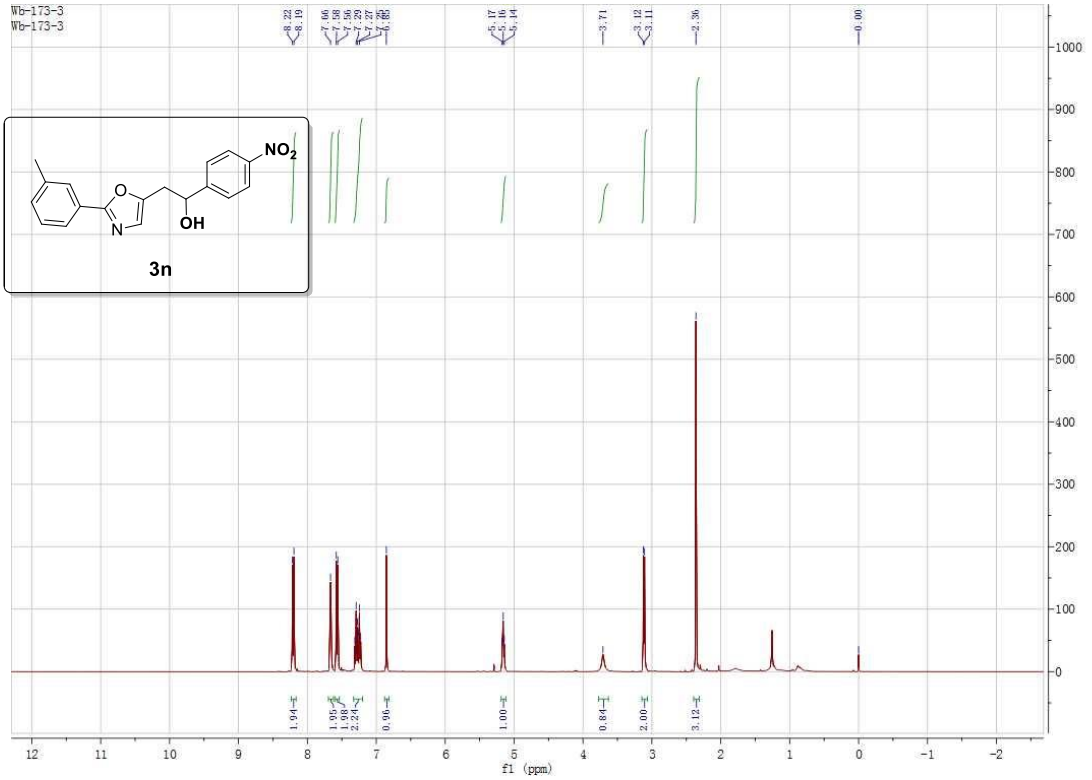
Wb-173-1a
NO2
O
N
OH
3m
f1 (ppm)


wb-181-C13C13
wb-181-C13C13
NO2
O
N
OH
3m
f1 (ppm)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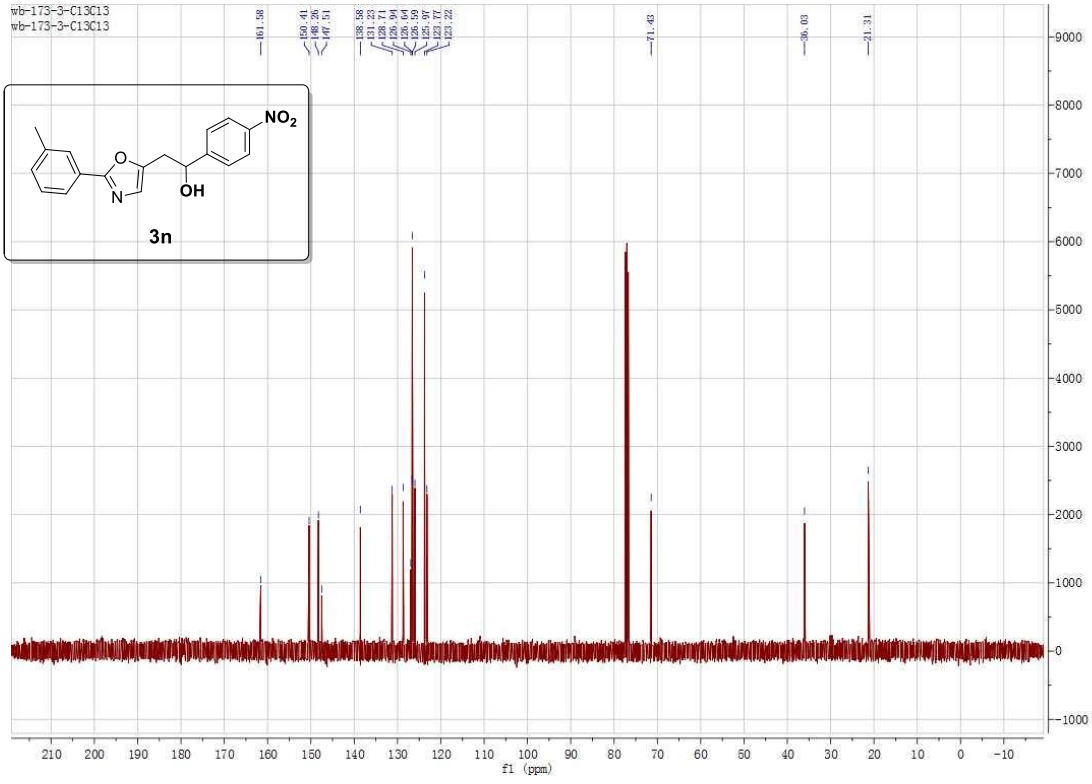
Wb-173-3
NO2
OH
3n
f1 (ppm)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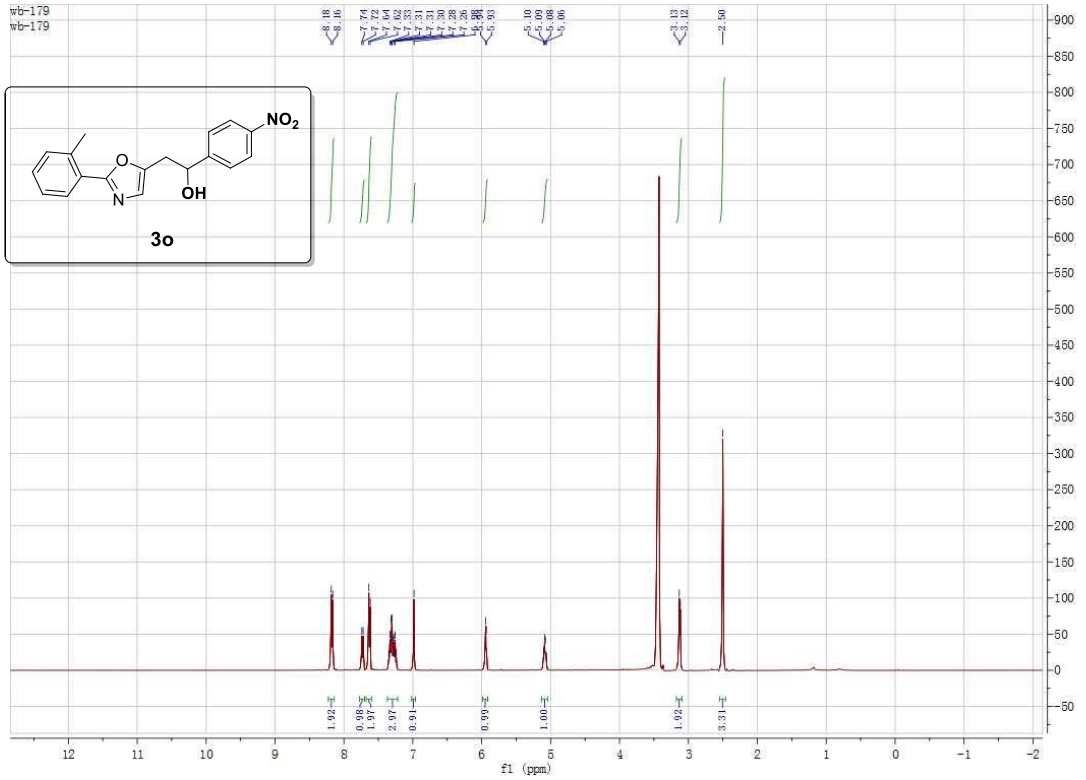
wb-173-3-C13C13
NO2
OH
3n
f1 (ppm)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wb-179
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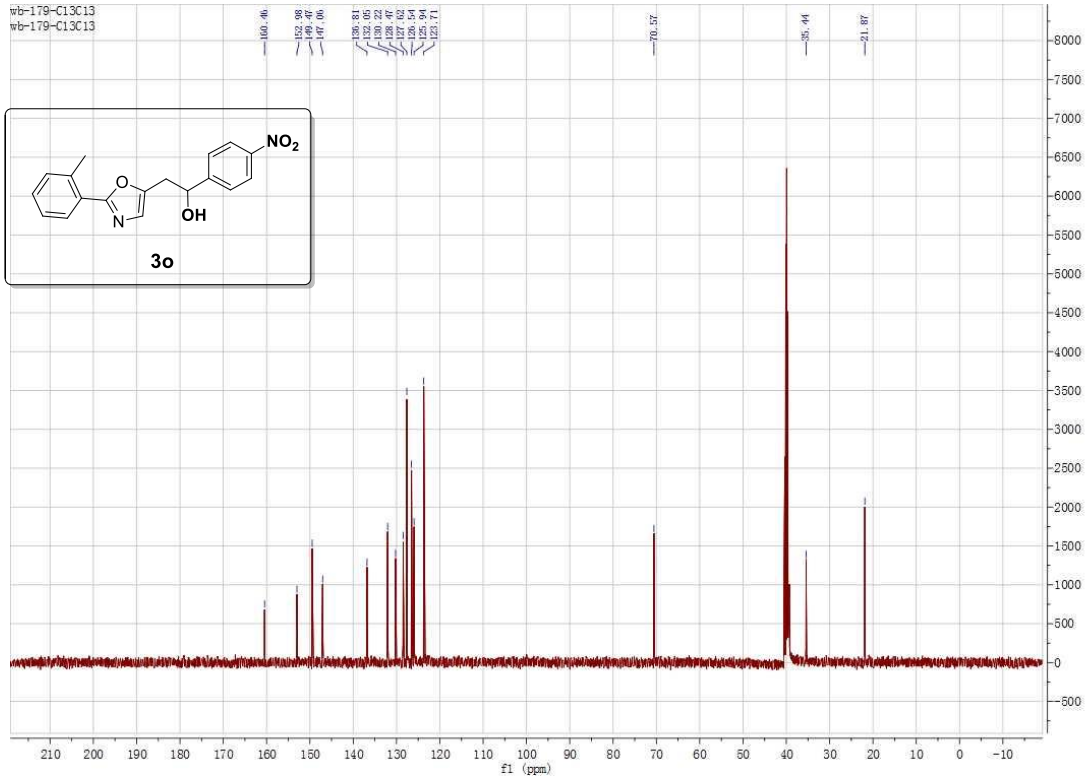
O
N
OH
3o
f1 (ppm)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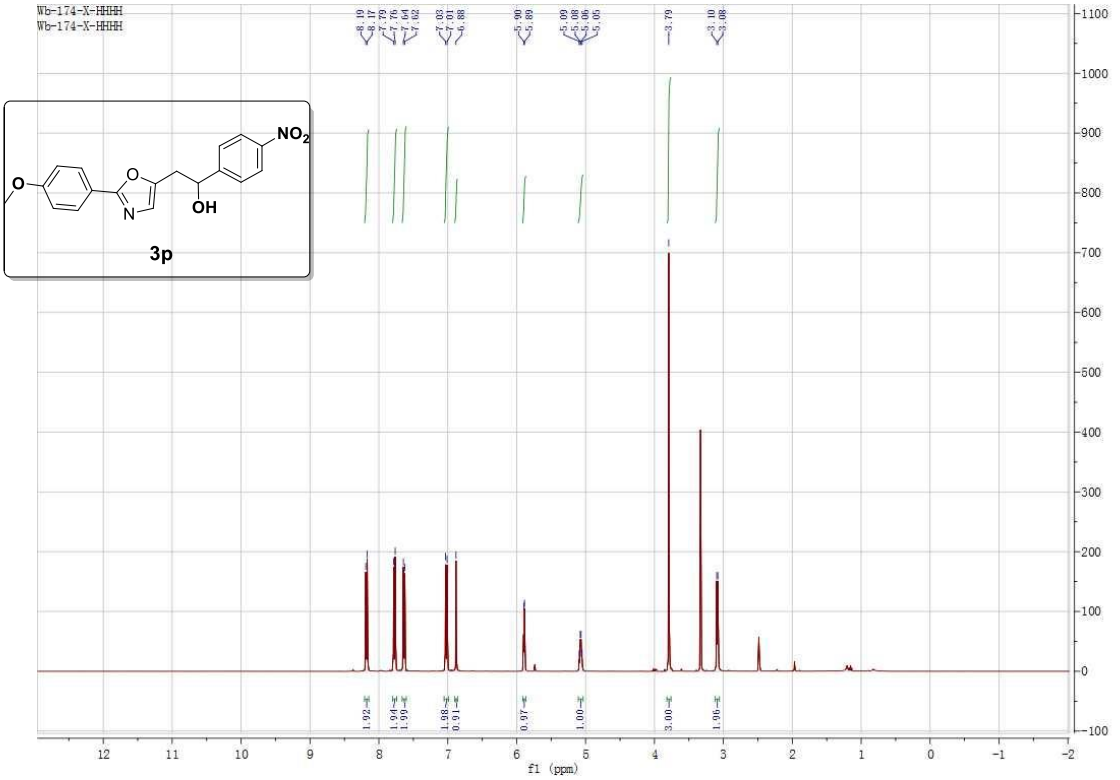
wb-179-C13C13
NO2
O
N
OH
3o
f1 (ppm)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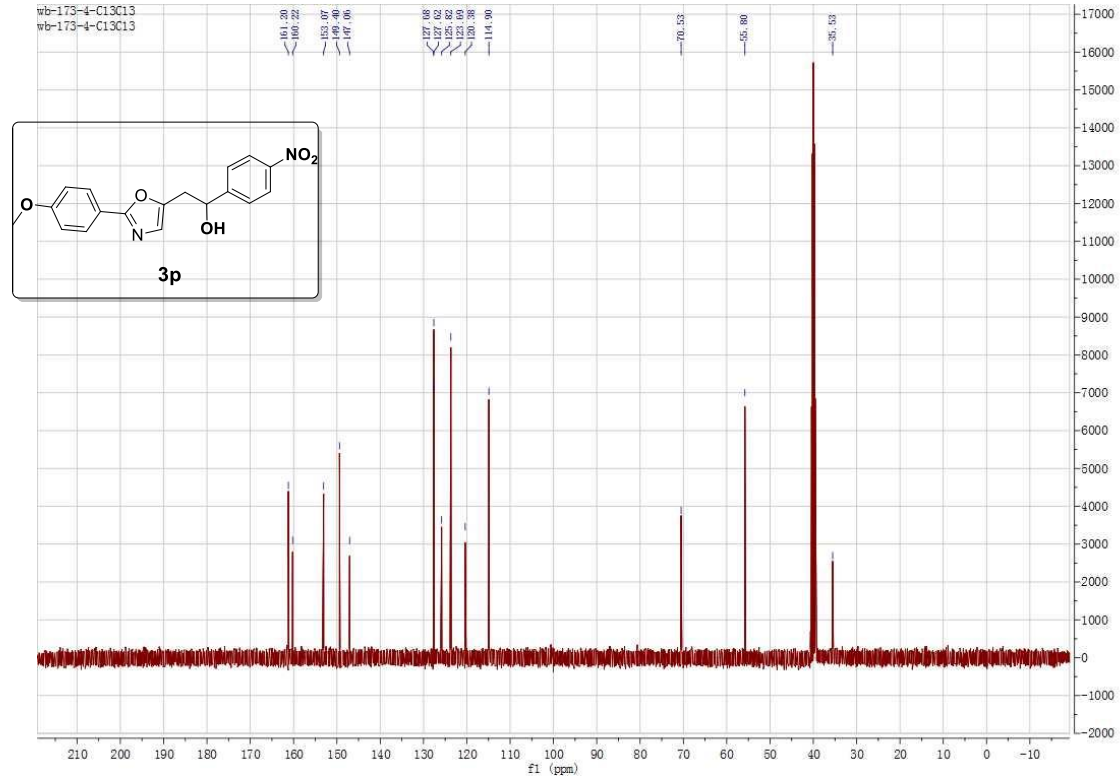
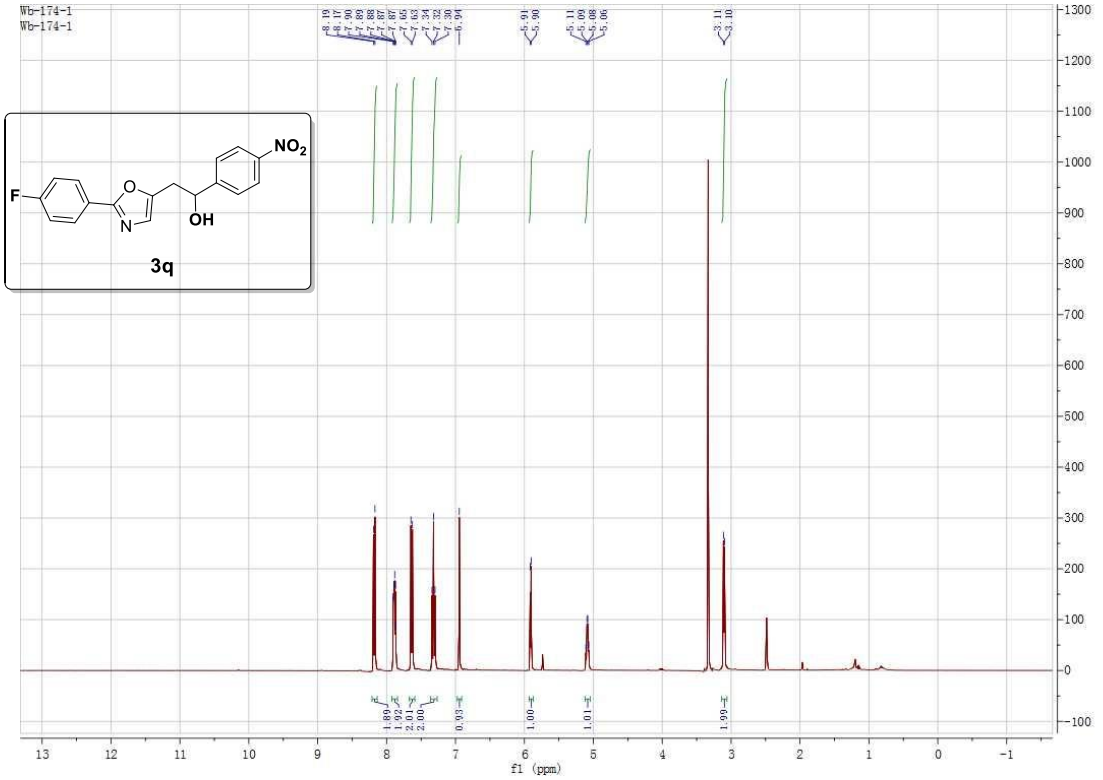
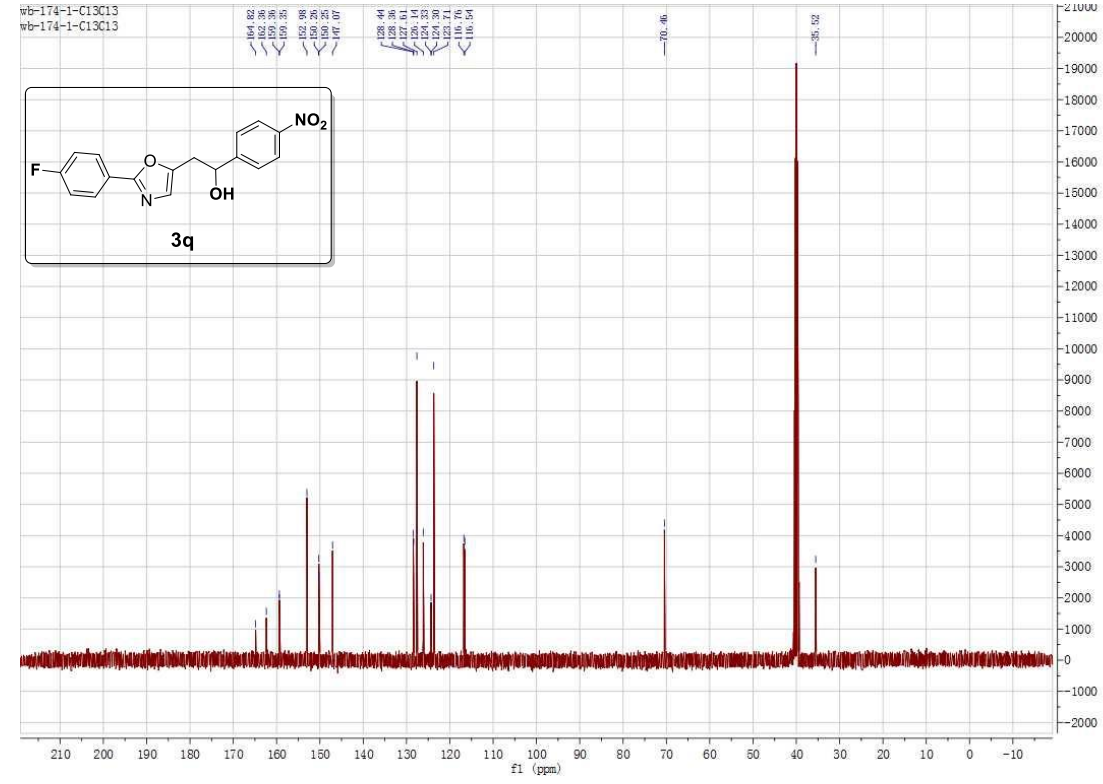
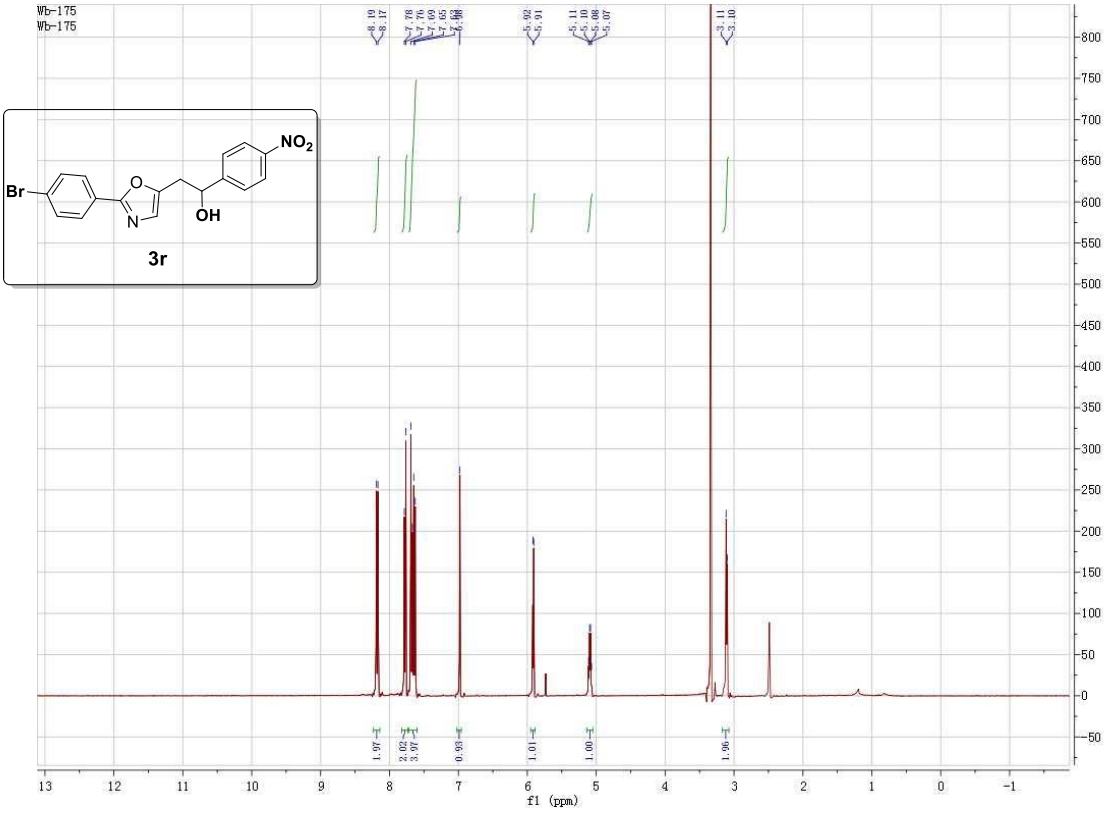
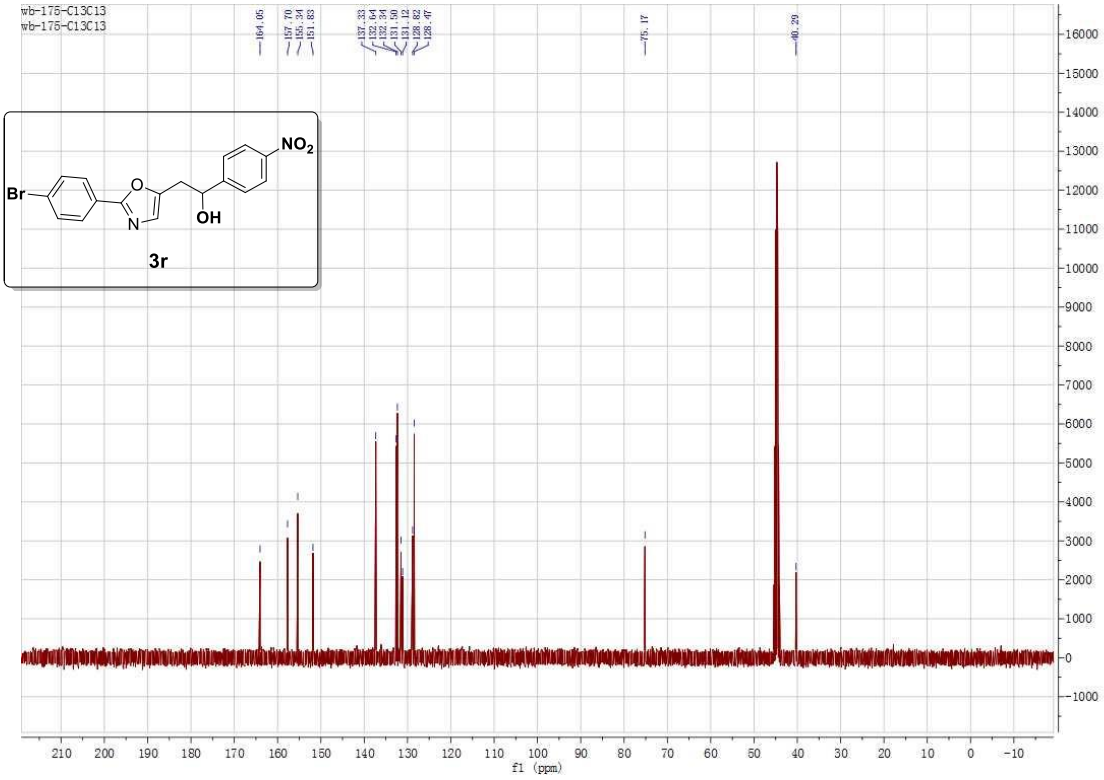
Wb-174-X-HHHH
8.19
8.17
7.79
7.76
7.64
7.62
7.03
7.01
6.88
5.90
5.89
5.09
5.08
5.06
5.05
3.79
3.10
3.08
1.92
1.94
1.99
1.98
0.91
0.97
1.00
3.00
1.96
f1 (ppm)
NO2
O
O
N
OH
3p

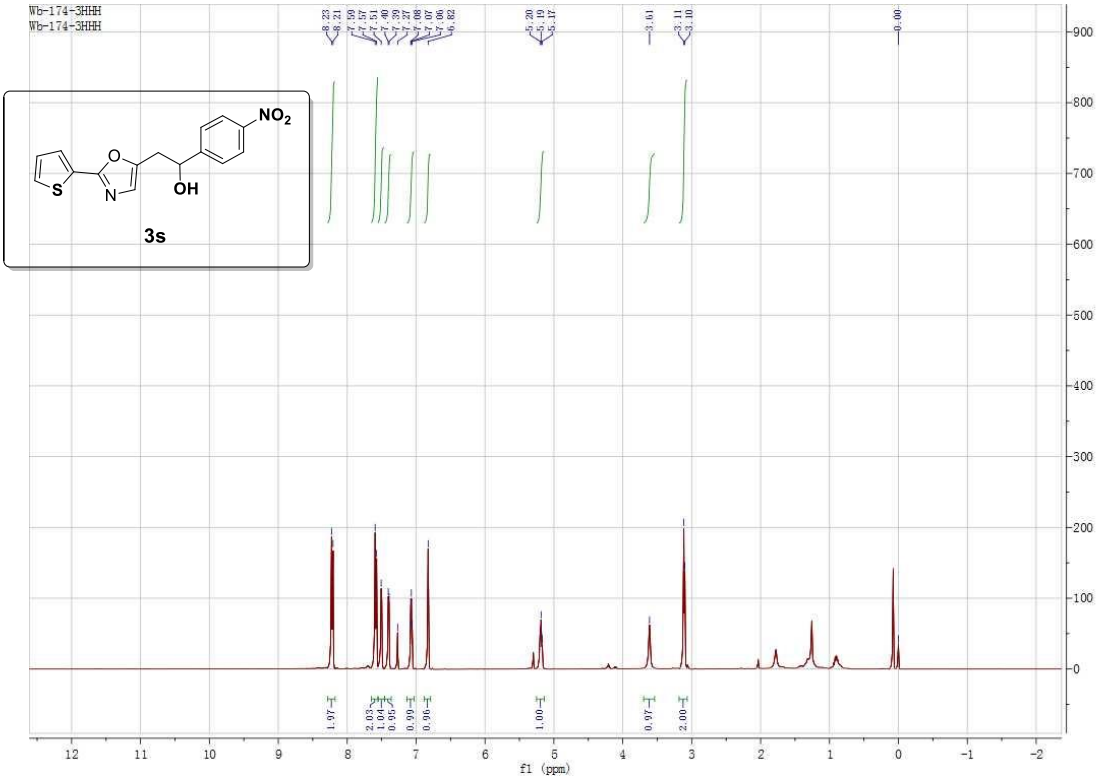

wb-173-4-C13C13
wb-173-4-C13C13
161.20
160.22
153.07
149.40
147.06
127.68
127.62
125.82
123.69
120.38
114.90
70.53
55.80
35.53
f1 (ppm)
NO2
O
O
N
OH
3p

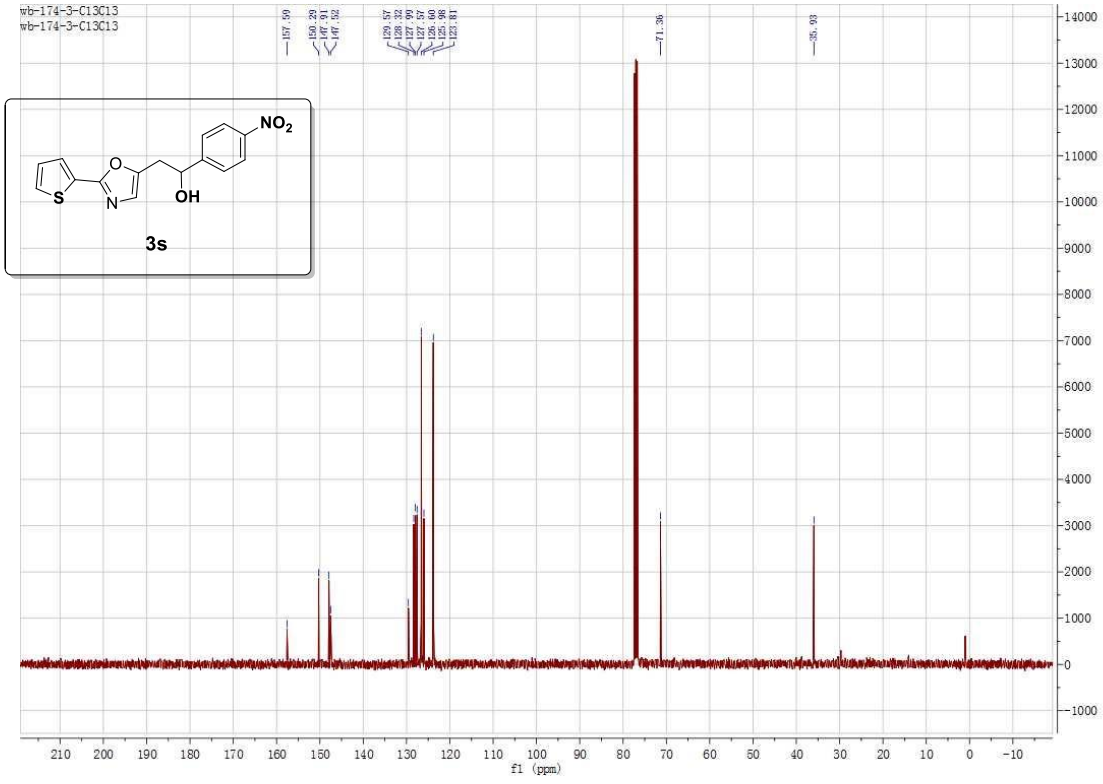

Wb-174-1
Wb-174-1
NO2
F
O
N
OH
3q
f1 (ppm)


wb-174-1-C13C13
wb-174-1-C13C13
NO2
F
O
N
OH
3q
f1 (ppm)


Wb-175
Wb-175
Br
O
N
OH
NO2
3r
fl (ppm)

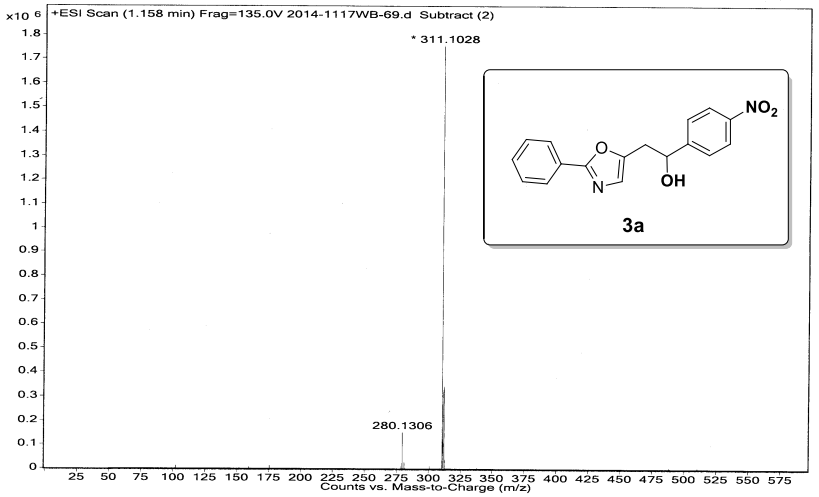

wb-175-C13C13
wb-175-C13C13
Br
O
N
OH
NO2
3r
fl (ppm)


Wb-174-3HHH
Wb-174-3HHH
NO2
O
S
N
OH
3s
f1 (ppm)

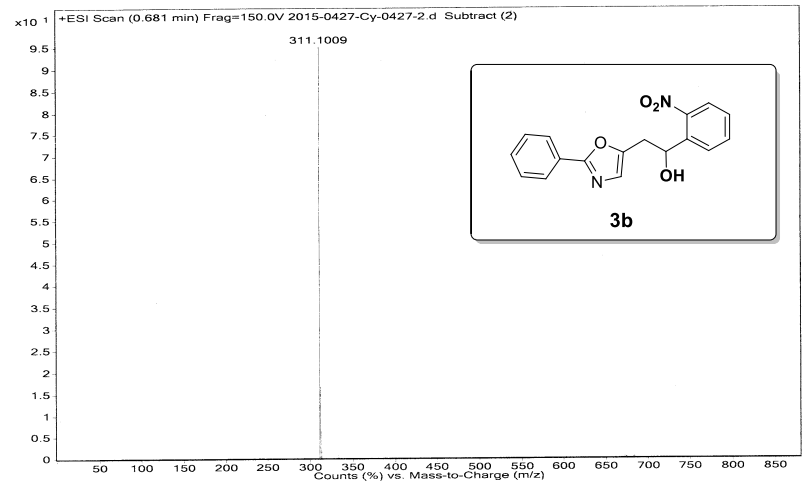

wb-174-3-C13C13
wb-174-3-C13C13
NO2
O
S
N
OH
3s
f1 (ppm)

6. HRMS Spectra of Products

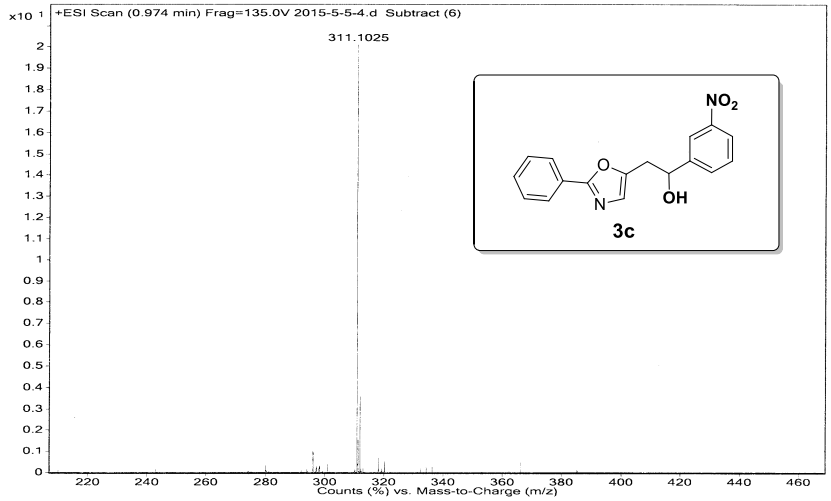
Sample Name	2014-1117WB-69	**Position**	P1-B9	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	2014-1117WB-69.d	**ACQ Method**	0103.m	**Comment**		**Acquired Time**	11/17/2014 10:13:51 AM



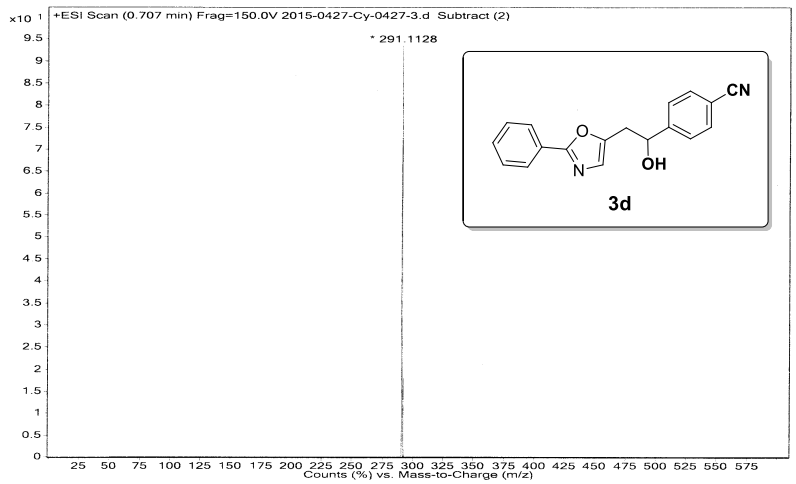
Sample Name	2015-0427-Cy-0427-2	**Position**	P1-C8	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	2015-0427-Cy-0427-2.	**ACQ Method**	0103.m	**Comment**		**Acquired Time**	4/27/2015 4:33:39 PM



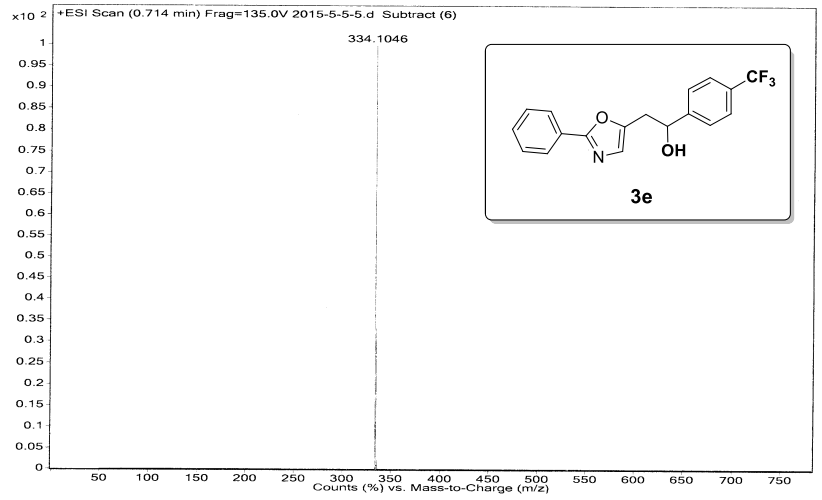
Sample Name	2015-5-5-4	**Position**	P1-E8	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	2015-5-5-4.d	**ACQ Method**	0103.m	**Comment**		**Acquired Time**	5/9/2015 3:42:13 PM



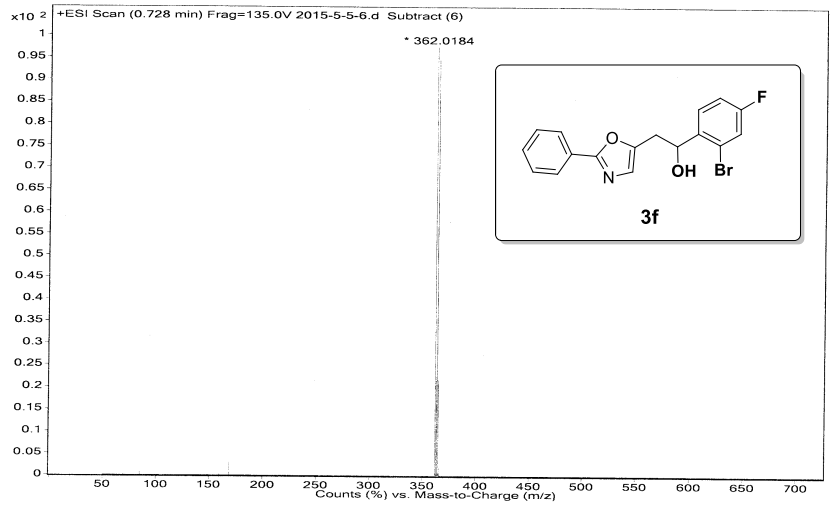
Sample Name	2015-0427-Cy-0427-3	**Position**	P1-B8	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	2015-0427-Cy-0427-3.	**ACQ Method**	0103.m	**Comment**		**Acquired Time**	4/27/2015 4:35:52 PM



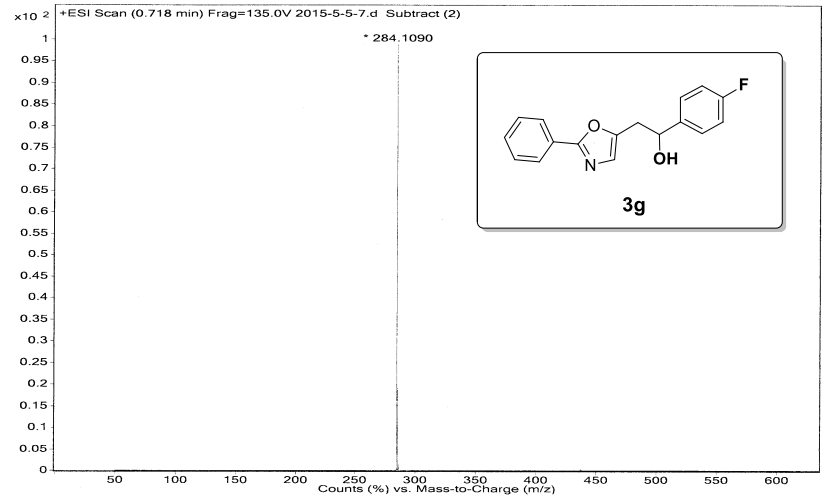
Sample Name	2015-5-5-5	**Position**	P1-D8	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	2015-5-5-5.d	**ACQ Method**	0103.m	**Comment**		**Acquired Time**	5/9/2015 3:44:27 PM



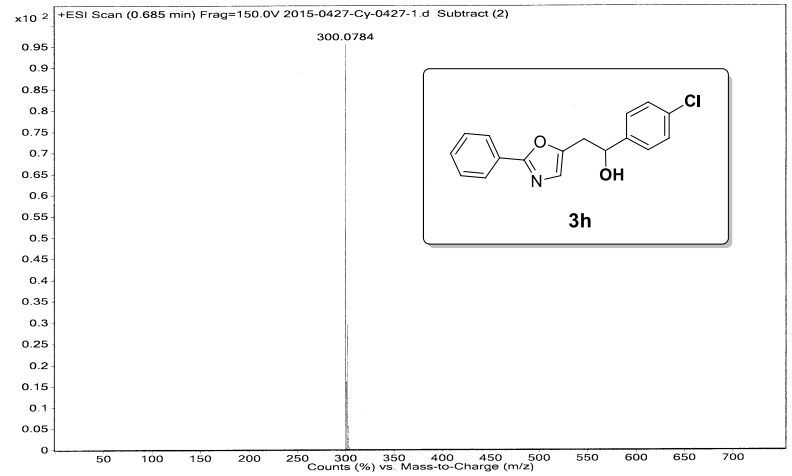
Sample Name	2015-5-5-6	**Position**	P1-C8	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	2015-5-5-6.d	**ACQ Method**	0103.m	**Comment**		**Acquired Time**	5/9/2015 3:49:06 PM



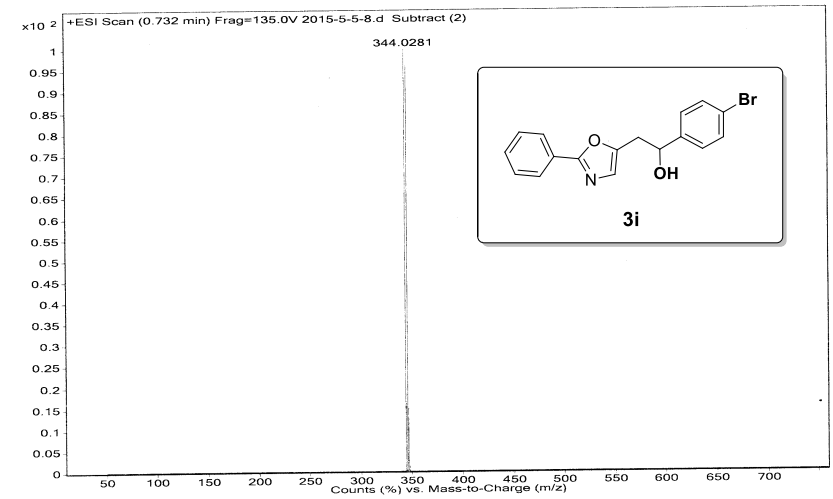
Sample Name	2015-5-5-7	**Position**	P1-B8	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	2015-5-5-7.d	**ACQ Method**	0103.m	**Comment**		**Acquired Time**	5/9/2015 3:51:22 PM



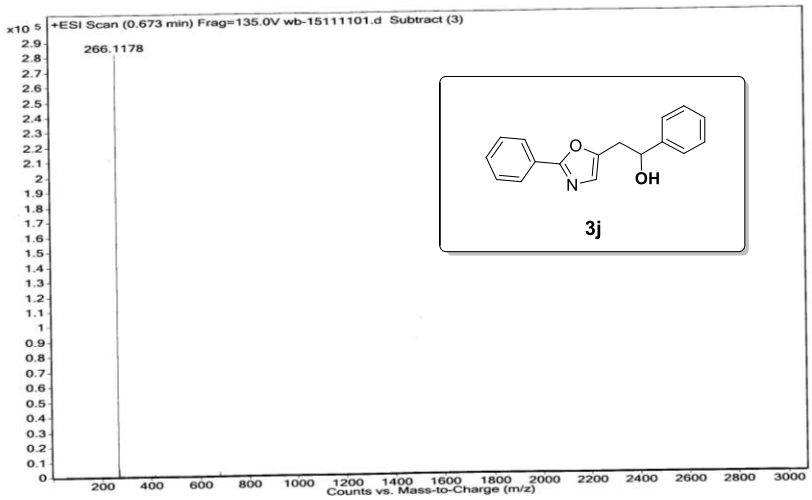
Sample Name	2015-0427-Cy-0427-1	**Position**	P1-D8	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	2015-0427-Cy-0427-1.	**ACQ Method**	0103.m	**Comment**		**Acquired Time**	4/27/2015 4:31:26 PM



Sample Name	2015-5-5-8	**Position**	P1-A8	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	2015-5-5-8.d	**ACQ Method**	0103.m	**Comment**		**Acquired Time**	5/9/2015 3:53:36 PM

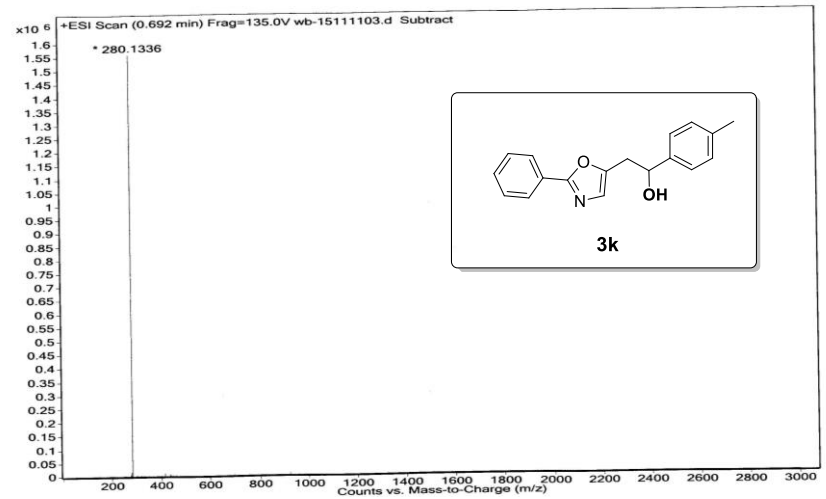


Sample Name	wb-15111101	**Position**	P1-E8	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	wb-15111101.d	**ACQ Method**	0103.m	**Comment**		**Acquired Time**	11/13/2015 9:24:18 AM



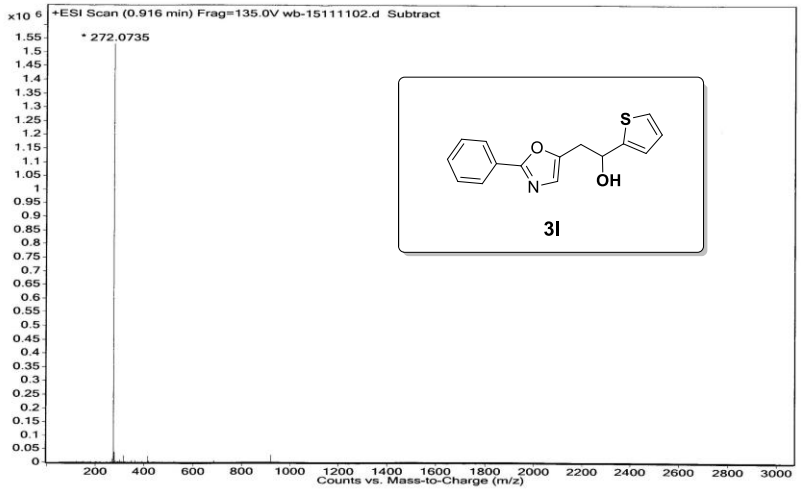
3j

Sample Name	wb-15111103	**Position**	P1-D8	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	wb-15111103.d	**ACQ Method**	0103.m	**Comment**		**Acquired Time**	11/13/2015 9:39:10 AM



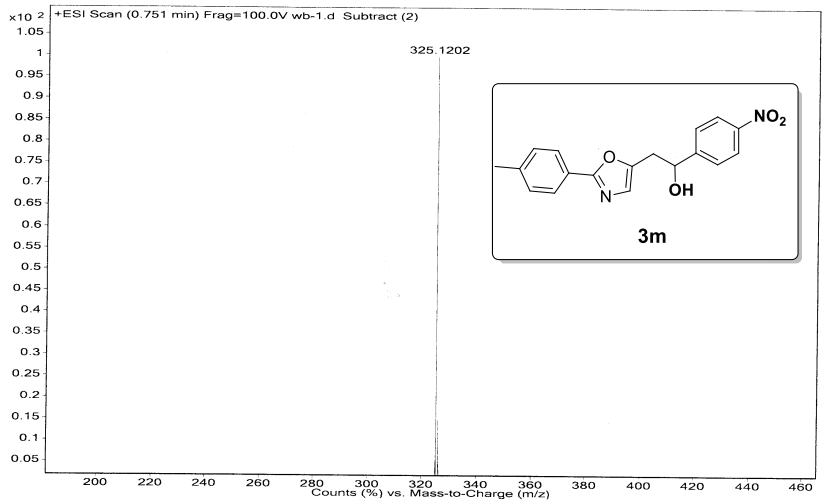
3k

Sample Name	wb-15111102	**Position**	P1-F8	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	wb-15111102.d	**ACQ Method**	0103.m	**Comment**		**Acquired Time**	11/13/2015 9:15:48 AM

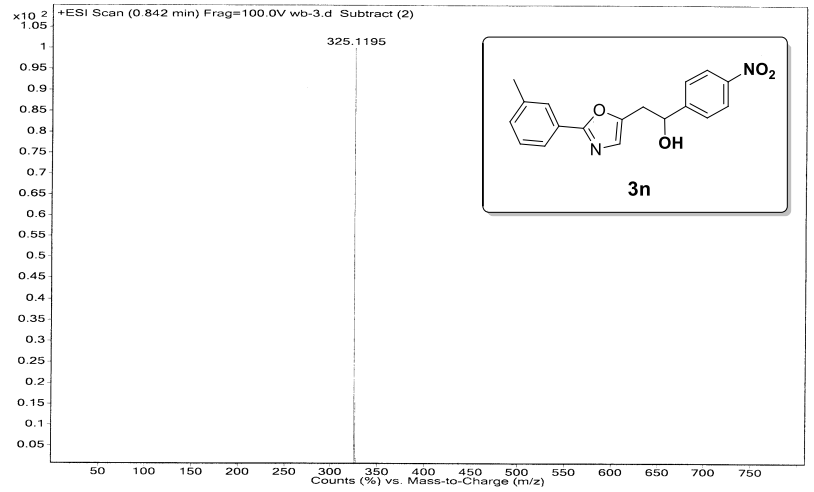


3l

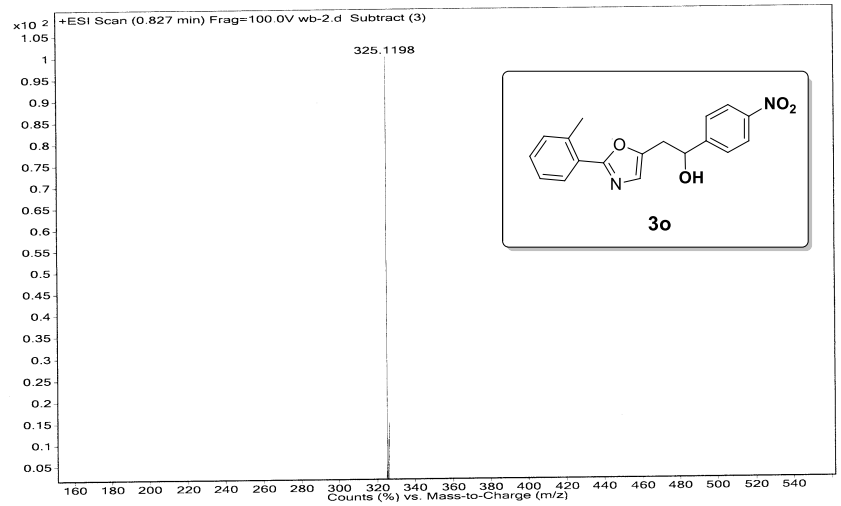
Sample Name	wb-1	**Position**	P1-F1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	wb-1.d	**ACQ Method**	0103.m	**Comment**		**Acquired Time**	6/5/2015 3:08:00 PM



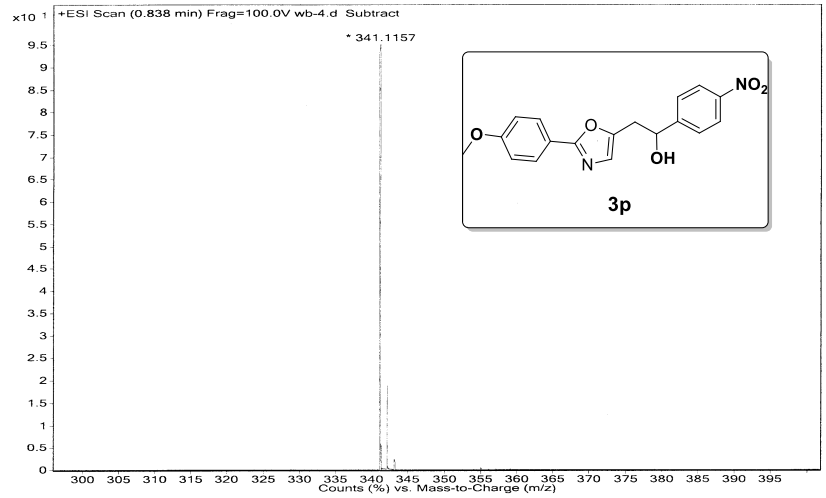
Sample Name	Unavailable	**Position**	Unavailable	**Instrument Name**	Unavailable	**User Name**	Unavailable
Inj Vol	Unavailable	**InjPosition**	Unavailable	**SampleType**	Unavailable	**IRM Calibration Status**	Success
Data Filename	wb-3.d	**ACQ Method**		**Comment**	Sample information is unavailable	**Acquired Time**	Unavailable



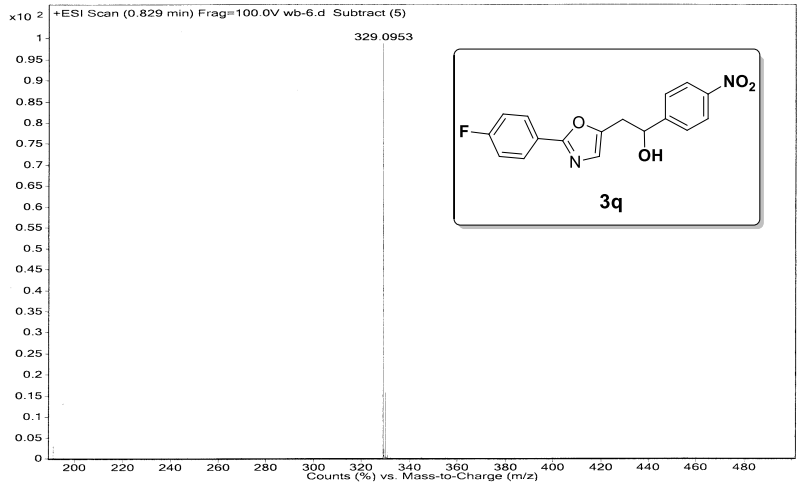
Sample Name	wb-2	**Position**	P1-E1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	wb-2.d	**ACQ Method**	0103.m	**Comment**		**Acquired Time**	6/5/2015 3:10:38 PM



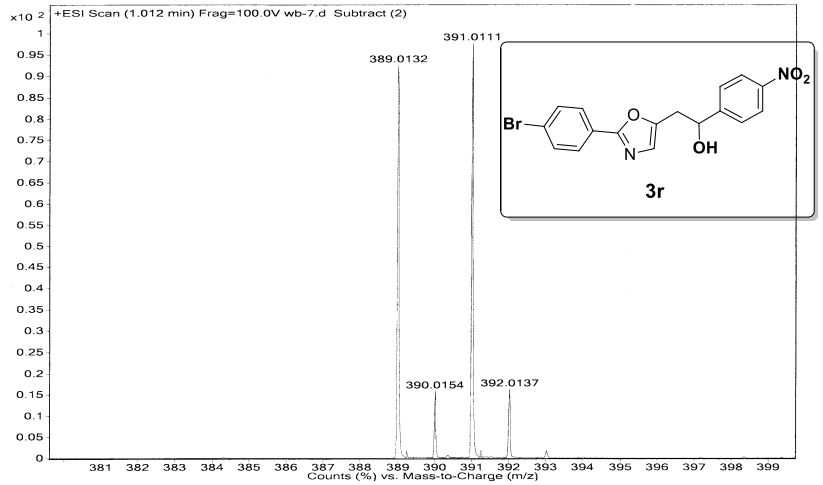
Sample Name	wb-4	**Position**	P1-C1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	wb-4.d	**ACQ Method**	0103.m	**Comment**		**Acquired Time**	6/5/2015 3:15:58 PM



Sample Name	Unavailable	**Position**	Unavailable	**Instrument Name**	Unavailable	**User Name**	Unavailable
Inj Vol	Unavailable	**InjPosition**	Unavailable	**SampleType**	Unavailable	**IRM Calibration Status**	Success
Data Filename	wb-6.d	**ACQ Method**		**Comment**	Sample information is unavailable	**Acquired Time**	Unavailable



Sample Name	Unavailable	**Position**	Unavailable	**Instrument Name**	Unavailable	**User Name**	Unavailable
Inj Vol	Unavailable	**InjPosition**	Unavailable	**SampleType**	Unavailable	**IRM Calibration Status**	Success
Data Filename	wb-7.d	**ACQ Method**		**Comment**	Sample information is unavailable	**Acquired Time**	Unavailable



Sample Name	wb-5	**Position**	P1-B1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	wb-5.d	**ACQ Method**	0103.m	**Comment**		**Acquired Time**	6/5/2015 3:18:39 PM