Supporting Information

Palladium-Catalyzed C-H Acetoxylation of 2-Methoxyimino-2-Aryl-Acetates and Acetamides

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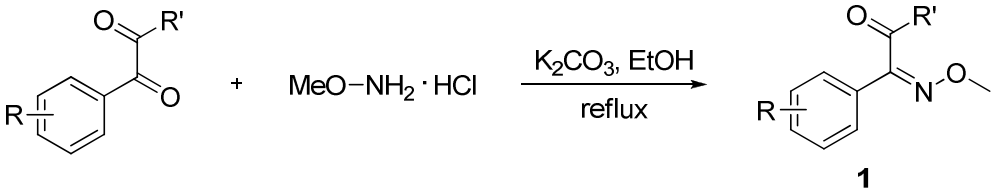
1. General

Unless otherwise noted, all reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Materials were purchased from commercial suppliers and used without further purification. All the solvents were treated prior to use according to the standard methods. Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H NMR spectra were recorded on Varian Mercury 400/600 (400/600 MHz) spectrophotometers. Chemical shifts (δ) are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on Varian Mercury 400/600 (100/150 MHz) with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). ^{19}F NMR spectra were recorded on Varian Mercury 400 (400 MHz) spectrophotometers. Chemical shifts are reported in ppm with C_6F_6 signal at -163 ppm as an external standard. Mass spectra were measured on a Finnigan Trace MS spectrometer (EI) or API 2000 LC/MS/MS (ESI-MS). Melting point was measured with BűCHI Melting Point B-545. IR spectra were measured on a BRUKER TENSOR 27 FT-IR spectrometer. Refractive index were measured on Abbé refractometer (2W).

2. General Procedure and Spectral Data of Substrates

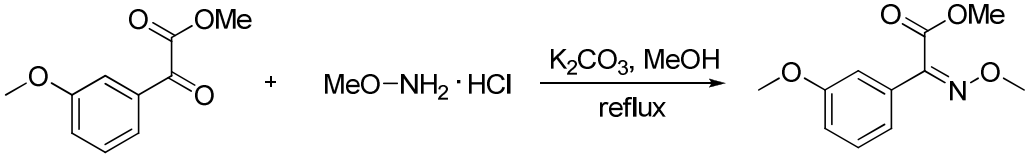
2.1 General Procedure



1

α-Ketoesters or ketoamides[1-3] (5 mmol, 1.0 equiv), methoxylamine hydrochloride (6-10 mmol, 1.2-2.0 equiv) and K_2CO_3 (6-10 mmol, 1.2-2.0 equiv) in EtOH (15 mL) were placed in a dried two-necked flask. The reaction system was stirred and refluxed until the reaction was completed by TLC analysis. After being cooled to room temperature, the reaction mixture was filtered through Celite. The filtrate was concentrated under reduced pressure, then the residue was purified by flash chromatography on silica gel to give the desired products.

Typical Procedure for Synthesis of compound 1m

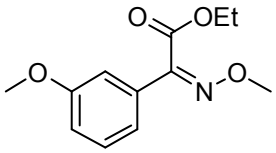


1m

α-Ketoester (5 mmol, 1.0 equiv), methoxylamine hydrochloride (6 mmol, 1.2 equiv) and K_2CO_3 (6 mmol, 1.2 equiv) in MeOH (15 mL) were placed in a dried two-necked flask. The reaction system was stirred and refluxed until the reaction was completed by TLC analysis. After being cooled to room temperature, the reaction mixture was filtered through Celite. The filtrate was concentrated under reduced pressure, then the residue was purified by flash chromatography on silica gel to give **1m**.

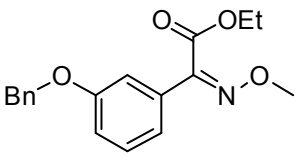
2.2 Spectral Data of Substrates

(*Z*)-ethyl 2-(methoxyimino)-2-(3-methoxyphenyl)acetate (1a)



Yield: 83%, colorless oil, $\mathbf{n}_{\mathbf{D}}^{25}$ = 1.5276; **IR** (KBr) ν_{max} 2981, 2941, 2904, 2837, 1738, 1608, 1575, 1490, 1465, 1432, 1331, 1292, 1251, 1207, 1030, 913, 883, 788, 734, 697, 654 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 1.4 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 6.95 (dd, *J* = 8.3, 1.7 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 4.01 (s, 3H), 3.81 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.5, 159.7, 150.5, 131.4, 129.7, 118.8, 116.5, 110.8, 62.9, 61.8, 55.2, 14.1; **MS**: m/z = 237.2 ([M^+]); **HRMS** m/z: Calcd for $C_{12}H_{15}NO_4Na^+$ [M+Na]$^+$: 260.0899, Found: 260.0864.

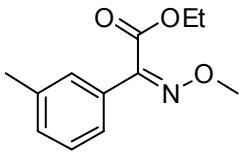
(*Z*)-ethyl 2-(3-(benzyloxy)phenyl)-2-(methoxyimino)acetate (1b)



Yield: 70%, white solid, **m.p.** 37-39 °C; **IR** (KBr) ν_{max} 2981, 2939, 2902, 1737, 1607, 1574, 1489, 1443, 1330, 1292, 1245, 1203, 1035, 884, 786, 738, 697 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.43-7.31 (m, 4H), 7.33-7.23 (m, 3H), 7.12 (d, *J* = 7.3 Hz, 1H), 7.01 (dd, *J* = 8.3, 0.9 Hz, 1H), 5.06 (s, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.01 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.5, 158.9, 150.5, 136.5, 131.4, 129.8,

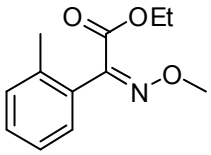
128.6, 128.0, 127.5, 119.1, 117.1, 111.9, 70.0, 63.0, 61.8, 14.1; **MS**: m/z = 313.1 ([M^+]); **HRMS** m/z: Calcd for $C_{18}H_{19}NO_4Na^+$ [M+Na]$^+$: 336.1212, Found: 336.1188.

(*Z*)-ethyl 2-(methoxyimino)-2-*m*-tolylacetate (1c)



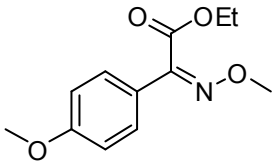
Yield: 63%, colorless oil, $\mathbf{n}_D^{25}$ = 1.5233; **IR** (KBr) ν_{max} 2982, 2940, 2904, 2821, 1738, 1611, 1464, 1445, 1369, 1327, 1238, 1177, 1064, 1034, 909, 885, 859, 792, 734, 699, 655 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.4 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 4.01 (s, 3H), 2.35 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.6, 150.8, 138.4, 131.1, 130.0, 128.6, 126.5, 123.3, 62.9, 61.7, 21.3, 14.1; **MS**: m/z = 221.0 ([M^+]).

(*Z*)-ethyl 2-(methoxyimino)-2-*o*-tolylacetate (1d)



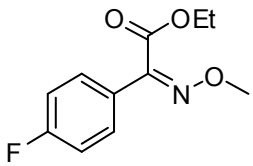
Yield: 50%, colorless oil, $\mathbf{n}_D^{25}$ = 1.5197; **IR** (KBr) ν_{max} 2978, 2939, 2902, 2821, 1737, 1603, 1459, 1368, 1322, 1280, 1220, 1048, 1024, 889, 859, 767, 725, 647 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.25–7.20 (m, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.01 (s, 3H), 2.46 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.4, 151.2, 137.3, 131.2, 129.8, 129.6, 128.8, 125.9, 62.9, 61.7, 20.9, 14.1; **MS:** m/z = 221.0 [M^+].

(*Z*)-ethyl 2-(methoxyimino)-2-(4-methoxyphenyl)acetate (1e)



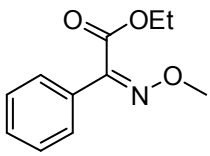
Yield: 73%, white solid, **m.p.** 33-34 ^{o}C; **IR** (KBr) ν_{max} 2981, 2940, 2905, 2840, 1737, 1611, 1515, 1464, 1331, 1307, 1258, 1223, 1176, 1058, 1032, 891, 859, 795, 610 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 7.2 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 3H), 3.79 (s, 3H), 1.37 (t, *J* = 6.7 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.8, 161.2, 150.3, 127.6, 122.6, 114.1, 62.6, 61.7, 55.2, 14.1; **MS**: m/z = 237.0 [M^+]; **HRMS** m/z: Calcd for $C_{12}H_{16}NO_4^+$ [M+H]$^+$: 238.1079, Found: 238.1042.

(*Z*)-ethyl 2-(4-fluorophenyl)-2-(methoxyimino)acetate (1f)



Yield: 49%, colorless oil, $\mathbf{n}_D^{25}$ = 1.5070; **IR** (KBr) ν_{max} 3078, 2983, 2942, 2904, 2822, 1738, 1600, 1511, 1465, 1370, 1330, 1227, 1160, 1056, 1028, 894, 860, 840, 811, 608, 554, 514 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.07 (t, *J* = 8.4 Hz, 2H), 4.42 (q, *J* = 7.3 Hz, 2H), 4.01 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.8, 163.4, 163.1, 149.6, 128.20, 128.15, 126.5, 116.0, 115.98, 115.8, 95.3, 62.9, 61.9, 14.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –111.1; **MS:** m/z = 225.0 [M^+].

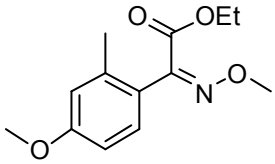
(*Z*)-ethyl 2-(methoxyimino)-2-phenylacetate (1g)



Yield: 69%, colorless oil, $\mathbf{n}_D^{25}$ = 1.5256; **IR** (KBr) ν_{max} 2981, 2940, 2903, 2821, 1738, 1605, 1464, 1447, 1370, 1331, 1222, 1186, 1058, 1034, 1023, 893, 858, 770, 691, 651 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 6.7 Hz, 2H), 7.40–7.36 (m, 3H), 4.42 (q, *J* = 7.1 Hz, 2H), 4.01 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.6, 150.6, 130.3, 130.1, 128.7, 126.1, 62.9,

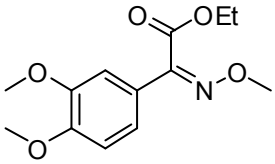
61.8, 14.1; **MS**: m/z = 207.2 [M^+]; **HRMS** m/z: Calcd for $C_{11}H_{13}NO_3Na$ [M+Na]$^+$: 230.0793, Found: 230.0750.

(*Z*)-ethyl 2-(4-methoxy-2-methylphenyl)-2-(methoxyimino)acetate (1h)



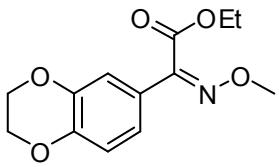
Yield: 56%, white solid, **m.p.** 45-46 ^oC; **IR** (KBr) ν_{max} 2990, 2936, 2843, 2819, 1733, 1609, 1561, 1504, 1454, 1326, 1302, 1252, 1224, 1171, 1132, 1045, 1024, 890, 818, 630 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.3 Hz, 1H), 6.76 – 6.73 (m, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.99 (s, 3H), 3.80 (s, 3H), 2.45 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.8, 160.3, 151.2, 139.3, 130.3, 122.2, 116.9, 111.1, 62.7, 61.6, 55.2, 21.5, 14.1; **MS**: m/z = 251.0 [M^+].

(*Z*)-ethyl 2-(3,4-dimethoxyphenyl)-2-(methoxyimino)acetate (1i)



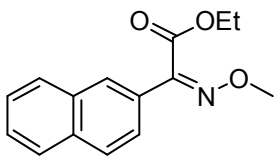
Yield: 80%, white solid, **m.p.** 51-52 ^oC; **IR** (KBr) ν_{max} 2964, 2939, 2912, 2840, 1739, 1604, 1515, 1466, 1445, 1423, 1329, 1255, 1211, 1170, 1151, 1028, 918, 891, 862, 817, 729, 642 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 1.7 Hz, 1H), 7.00 – 6.97 (m, 1H), 6.84 (dd, *J* = 8.2, 5.3 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 4.00 (d, *J* = 5.6 Hz, 3H), 3.91 (dd, *J* = 11.3, 6.7 Hz, 6H), 1.38 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.6, 151.0, 150.4, 149.2, 122.8, 120.0, 110.6, 107.9, 62.7, 62.6, 61.6, 55.8, 55.8, 14.1; **MS:** m/z = 267.0 [M^+].

(*Z*)-ethyl 2-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-2-(methoxyimino)acetate (1j)



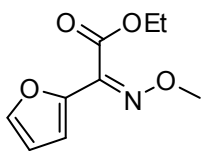
Yield: 83%, white solid, **m.p.** 66-67 ^oC; **IR** (KBr) ν_{max} 2989, 2942, 2908, 2828, 1731, 1591, 1573, 1511, 1469, 1433, 1365, 1333, 1296, 1261, 1247, 1216, 1174, 1129, 1058, 1027, 1009, 912, 887, 859, 831, 806, 732, 656, 624 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.10 (d, J = 1.9 Hz, 1H), 7.05 (dd, J = 8.5, 1.9 Hz, 1H), 6.85 (d, J = 8.5 Hz, 1H), 4.40 (q, J = 7.1 Hz, 2H), 4.25 (dd, J = 11.0, 5.1 Hz, 4H), 3.98 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.6, 150.1, 145.5, 143.7, 123.4, 119.6, 117.5, 115.1, 64.4, 64.1, 62.8, 61.7, 14.1; **MS:** m/z = 265.0 [M^+].

(*Z*)-ethyl 2-(methoxyimino)-2-(naphthalen-2-yl)acetate (1k)



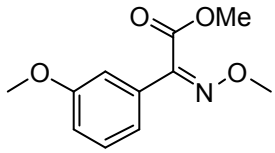
Yield: 55%, white solid, **m.p.** 70-71 ^oC; **IR** (KBr) ν_{max} 2993, 2975, 2943, 2909, 1729, 1601, 1468, 1446, 1367, 1307, 1250, 1219, 1181, 1131, 1054, 1031, 891, 858, 812, 754, 731 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85–7.80 (m, 5H), 7.50–7.46 (m, 2H), 4.48 (q, *J* = 7.1 Hz, 2H), 4.06 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 Hz, $CDCl_3$) δ 163.7, 150.7, 134.0, 132.8, 128.5, 127.7, 127.6, 127.2, 126.8, 126.7, 126.6, 122.5, 63.0, 61.9, 14.2; **MS**: m/z = 257.0 [M^+].

(*Z*)-ethyl 2-(furan-2-yl)-2-(methoxyimino)acetate (1l)



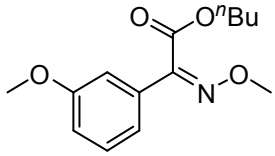
Yield: 88%, yellowish oil, **IR** (KBr) ν_{max} 2985, 2943, 2905, 2824, 1741, 1590, 1482, 1446, 1371, 1309, 1228, 1157, 1095, 1069, 1035, 932, 887, 861, 779, 759, 595 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) (ratio of isomers = 4:1, major isomer) δ 7.51 (d, *J* = 1.0 Hz, 1H), 7.29 (d, *J* = 3.4 Hz, 1H), 6.53 (dd, *J* = 3.4, 1.7 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 4.14 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 162.3, 144.7, 143.6, 142.4, 140.0, 119.1, 112.5, 111.7, 63.7, 62.2, 14.0; **MS:** m/z = 197.0 [M^+]; **HRMS** m/z: Calcd for $C_9H_{11}NO_4Na^+$ [M+Na]$^+$: 220.0586, Found: 220.0543.

(*Z*)-methyl 2-(methoxyimino)-2-(3-methoxyphenyl)acetate (1m)



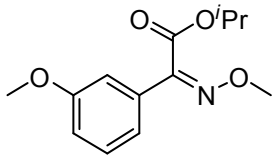
Yield: 65%, colorless oil, **n_D^{25}** = 1.5375; **IR** (KBr) ν_{max} 3004, 2942, 2838, 1743, 1608, 1575, 1490, 1464, 1432, 1333, 1290, 1252, 1212, 1173, 1044, 959, 913, 846, 787, 734, 699, 656 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 8.0 Hz, 1H), 7.15 (s, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 4.02 (s, 3H), 3.93 (s, 2H), 3.83 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.9, 159.7, 150.4, 131.3, 129.7, 118.9, 116.5, 110.9, 62.9, 55.3, 52.3; **MS:** m/z = 223.0 [M^+]; **HRMS** m/z: Calcd for $C_{11}H_{13}NO_4Na^+$ [M+Na]$^+$: 246.0742, Found: 246.0699.

(*Z*)-butyl 2-(methoxyimino)-2-(3-methoxyphenyl)acetate (1n)



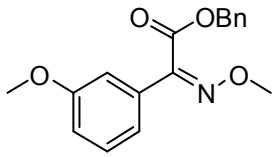
Yield: 73%, colorless oil, **n_D^{25}** = 1.5165; **IR** (KBr) ν_{max} 2962, 2939, 2875, 2838, 1739, 1608, 1575, 1490, 1465, 1432, 1331, 1290, 1250, 1206, 1046, 912, 866, 786, 734, 697, 655 cm^{-1}; **^{1}H NMR** (600 MHz, CDCl3) δ 7.28 (t, J = 8.0 Hz, 1H), 7.16 (s, 1H), 7.10 (d, J = 7.6 Hz, 1H), 6.94 (d, J = 8.2 Hz, 1H), 4.36 (t, J = 6.6 Hz, 2H), 4.01 (s, 3H), 3.81 (s, 3H), 1.74–1.70 (m, 2H), 1.46– 1.40 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.6, 159.7, 150.6, 131.4, 129.7, 118.8, 116.5, 110.7, 65.5, 62.9, 55.2, 30.4, 18.9, 13.5; **MS:** m/z = 265.0 [M^+].

(*Z*)-isopropyl 2-(methoxyimino)-2-(3-methoxyphenyl)acetate (1o)



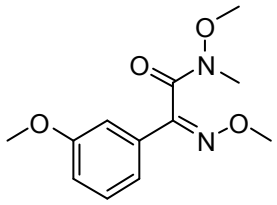
Yield: 85%, white solid, **m.p.** 46-47 °C; **IR** (KBr) ν_{max} 2982, 2940, 2837, 1734, 1608, 1575, 1490, 1465, 1432, 1325, 1288, 1253, 1212, 1105, 1045, 1027, 917, 871, 827, 785, 735, 692, 650 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 14.9, 7.0 Hz, 1H), 7.16 (s, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 5.35–5.29 (m, 1H), 4.01 (d, *J* = 0.5 Hz, 3H), 3.82 (s, 3H), 1.37 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.1, 159.7, 150.7, 131.5, 129.7, 118.8, 116.5, 110.8, 69.9, 62.8, 55.3, 21.8; **MS:** m/z = 251.0 [M^+].

(*Z*)-benzyl 2-(methoxyimino)-2-(3-methoxyphenyl)acetate (1p)



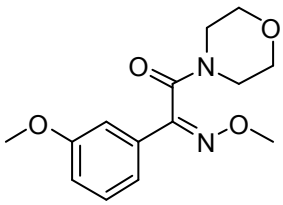
Yield: 66%, colorless oil, **n_D^{25}** = 1.5634; **IR** (KBr) ν_{max} 2939, 2840, 2822, 1744, 1613, 1574, 1488, 1456, 1437, 1322, 1284, 1251, 1207, 1180, 1044, 1025, 954, 902, 787, 743, 731, 696, 656 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.0 Hz, 2H), 7.37–7.31 (m, 3H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.06 (dd, *J* = 9.5, 4.8 Hz, 2H), 6.92 (dd, *J* = 8.3, 1.9 Hz, 1H), 5.38 (s, 2H), 4.00 (s, 3H), 3.71 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.3, 159.5, 150.1, 134.8, 131.1, 129.6, 128.44, 128.40, 118.7, 116.7, 110.3, 67.1, 62.8, 55.0; **MS:** m/z = 299.1 [M^+]; **HRMS** m/z: Calcd for $C_{17}H_{17}NO_4Na^+$ [M+Na]$^+$: 322.1055, Found: 322.1024.

(*Z*)-N-methoxy-2-(methoxyimino)-2-(3-methoxyphenyl)-*N*-methylacetamide (1q)



Yield: 88%, yellowish oil, $\mathbf{n}_{\mathbf{D}}^{25}$ = 1.5455; **IR** (KBr) ν_{max} 2940, 2821, 1667, 1607, 1574, 1489, 1463, 1427, 1387, 1321, 1302, 1231, 1181, 1043, 982, 900, 809, 790, 689 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) (ratio of isomers = 6:1, major isomer) δ 7.29 (dd, *J* = 14.7, 6.8 Hz, 1H), 7.24–7.16 (m, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 6.95 (t, *J* = 9.4 Hz, 1H), 4.02 (d, *J* = 7.2 Hz, 3H), 3.82 (s, 3H), 3.57 (s, 3H), 3.34 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.6, 159.7, 152.7, 132.1, 129.6, 118.9, 116.3, 110.7, 62.6, 61.8, 55.3, 31.5; **MS:** m/z = 252.0 [M^+].

(*Z*)-2-(methoxyimino)-2-(3-methoxyphenyl)-1-morpholinoethanone (1r)

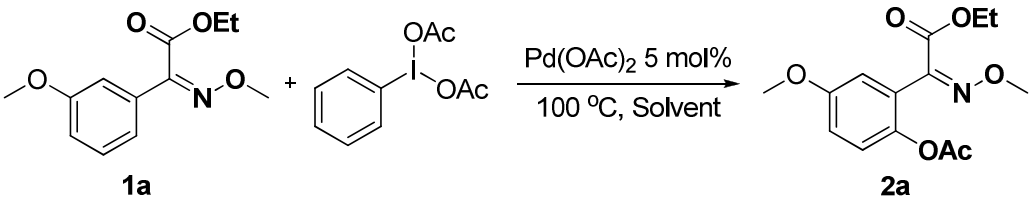


Yield: 78%, white solid, **m.p.** 88-89 °C; **IR** (KBr) ν_{max} 2976, 2932, 2856, 2824, 1639, 1606, 1493, 1464, 1443, 1427, 1327, 1275, 1251, 1177, 1112, 1058, 1007, 942, 902, 854, 818, 791, 753, 687, 639 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.36–7.25 (m, 1H), 7.22 (s, 1H), 7.14 (d, *J* = 6.7 Hz, 1H), 6.95 (d, *J* = 6.0 Hz, 1H), 4.01 (s, 3H), 3.82 (d, *J* = 7.6 Hz, 4H), 3.73 (s, 3H), 3.61 (d, *J* = 39.8 Hz, 2H), 3.33 (d, *J* = 39.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) 162.8, 159.6, 151.7, 131.6, 129.7, 118.7, 116.4, 110.5, 66.7, 66.5, 62. 7, 55.2, 46.1, 41.3; **MS:** m/z = 278.0 [M^+].

3. General Procedure and Spectral Data of Products

3.1 Reaction Optimization and Result Summary

Table 1. The Screening of Various Solvents.[a]

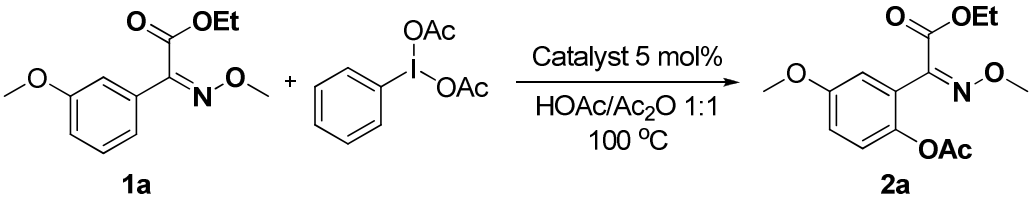


Entry	Solvent	Yield (%)[b]
1	HOAc	73
2	Ac_2O	66
3	CF_3COOH	-
4	$(CF_3CO)_2O$	-
5	DMF	-
6	CH_3CN	22
7	DMSO	-
8	Toluene	trace
9	HOAc/Ac_2O (1:1)	83
10	HOAc/Ac_2O (1:2)	80
11	HOAc/Ac_2O (2:1)	72

[a] The reactions were carried out with 0.30 mmol (1.0 equiv) of **1a**, 0.36 mmol (1.2 equiv) of $PhI(OAc)_2$ and 5 mol% $Pd(OAc)_2$ in 2.0 mL of solvent at 100 °C.

[b] Isolated yield.

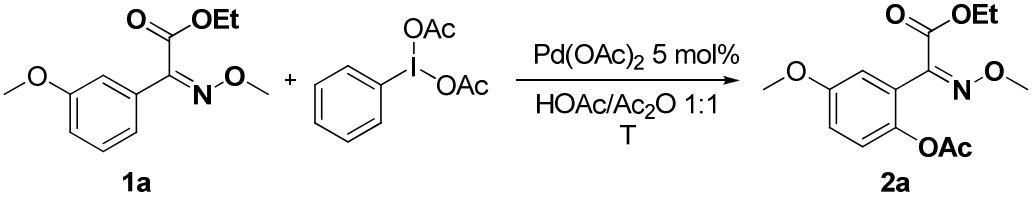
Table 2. The Screening of Various Catalysts.[a]



Entry	Catalyst	Yield (%)[b]
1	$Pd(OAc)_2$	83
2	$PdCl_2$	71
3	$Pd(PPh_3)_2Cl_2$	68
4	$Pd(CH_3CN)_2Cl_2$	65
5	$Pd(PPh_3)_4$	63
6	Pd_2dba_3	74
7	$Pd(TFA)_2$	73
8	$Pd(PhCN)_2Cl_2$	71
9[c]	-	-

[a] The reactions were carried out with 0.30 mmol (1.0 equiv) of **1a**, 0.36 mmol (1.2 equiv) of $PhI(OAc)_2$ and 5 mol% catalyst in 2.0 mL of $HOAc/Ac_2O$ (1:1) at 100 °C. [b] Isolated yield. [c] Without palladium.

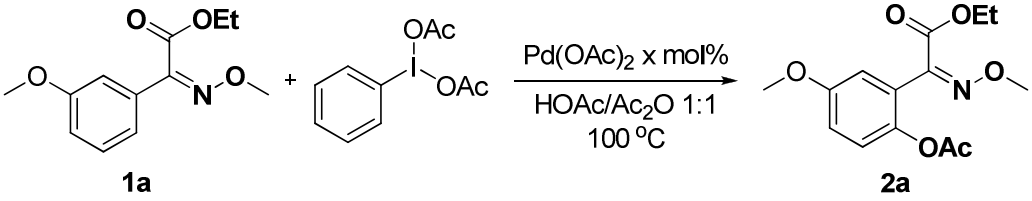
Table 3. The Screening of Temperature.[a]



Entry	Temp	Yield (%)[b]
1	100 °C	83
2	110 °C	80
3	120 °C	78
4	80 °C	66

[a] The reactions were carried out with 0.30 mmol (1.0 equiv) of **1a**, 0.36 mmol (1.2 equiv) of $PhI(OAc)_2$ and 5 mol% $Pd(OAc)_2$ in 2.0 mL of $HOAc/Ac_2O$ (1:1) . [b] Isolated yield.

Table 4. The Screening of catalyst loading.[a]

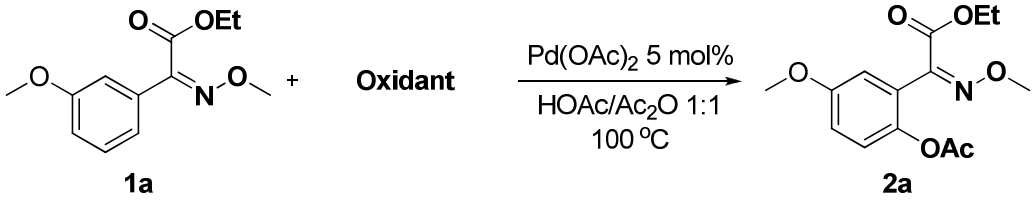


Entry	Loading	Yield (%)[b]
1	5 mol%	83

2	3 mol%	72
3	10 mol%	76

[a] The reactions were carried out with 0.30 mmol (1.0 equiv) of **1a**, 0.36 mmol (1.2 equiv) of $PhI(OAc)_2$ and $Pd(OAc)_2$ in 2.0 mL of $HOAc/Ac_2O$ (1:1) .
[b] Isolated yield.

Table 5. The Screening of Various Oxidants.[a]

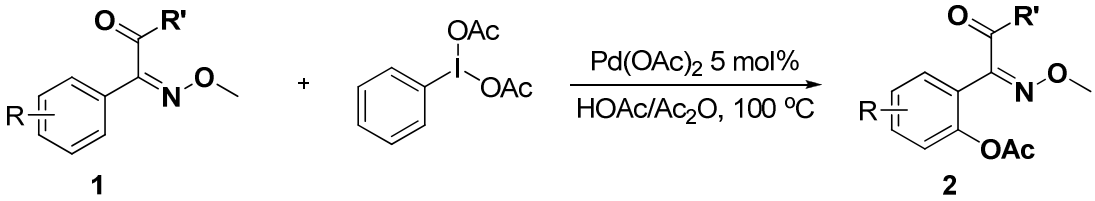


1a **2a**

Entry	Oxidant	Yield (%)[b]
1	$PhI(OAc)_2$	83
2	$K_2S_2O_8$	42
3	Oxone	21
4	Benzoyl peroxide	-
5	$3\text{-}ClPhCO_3H$	-
6[c]	-	-

[a] The reactions were carried out with 0.30 mmol (1.0 equiv) of **1a**, 0.36 mmol (1.2 equiv) of oxidant and 5 mol% $Pd(OAc)_2$ in 2.0 mL of $HOAc/Ac_2O$ (1:1).
[b] Isolated yield. [c] Without oxidant.

3.2 General Procedure

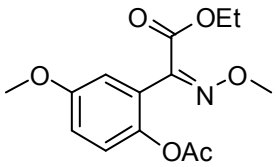


1 **2**

A mixture of substrate **1** (0.3 mmol, 1.0 equiv), iodobenzene diacetate (0.36 mmol, 1.2 equiv) and $Pd(OAc)_2$ (0.015 mmol, 0.05 equiv) were combined in AcOH (1.0 mL) and Ac_2O (1.0 mL) in a dried Schlenk tube under a nitrogen atmosphere. The reaction was stirred at 100 ºC and monitored by TLC. Upon completion or no further improvement of reaction, the reaction mixture was cooled to room temperature and was then diluted with ethyl acetate (50 mL). The organic layer was washed sequentially with saturated $NaHCO_3$ (2 x 30 mL), water (2 x 30 mL) and brine (1 x 30 mL) then dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the desired products.

3.3 Spectral Data of Products

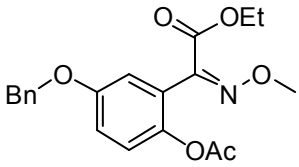
(*Z*)-ethyl 2-(2-acetoxy-5-methoxyphenyl)-2-(methoxyimino)acetate (2a)



Yield: 83%, white solid; **IR** (KBr) ν_{max} 2982, 2939, 2842, 1770, 1735, 1610, 1578, 1498, 1414, 1372, 1332, 1300, 1273, 1248, 1191, 1038, 1024, 923, 898, 883, 844, 820, 781, 595 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.14 (d, *J* = 3.0 Hz, 1H), 7.01 (d, *J* = 8.9 Hz, 1H), 6.96 (dd, *J* = 8.9, 3.0 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.02 (s, 3H), 3.81 (s, 3H),

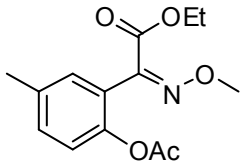
2.24 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.3, 162.3, 157.2, 147.4, 141.7, 124.4, 124.2, 117.0, 113.1, 63.1, 61.7, 55.7, 20.6, 14.0; **MS:** m/z = 295.2 [M^+]; **HRMS** m/z: Calcd for $C_{14}H_{17}NO_6K$ [M+K]$^+$: 334.0693, Found: 334.0686.

(*Z*)-ethyl 2-(2-acetoxy-5-(benzyloxy)phenyl)-2-(methoxyimino)acetate (2b)



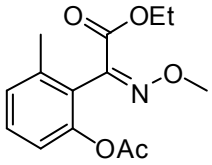
Yield: 74%, colorless oil; **IR** (KBr) ν_{max} 3033, 2983, 2940, 2903, 2822, 1767, 1739, 1607, 1572, 1493, 1456, 1241, 1368, 1180, 1036, 896, 742, 698, 650 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.43–7.38 (m, 4H), 7.33 (t, J = 6.9 Hz, 1H), 7.24 (s, 1H), 7.03–7.00 (m, 2H), 5.05 (s, 2H), 4.33 (q, J = 7.1 Hz, 2H), 4.02 (s, 3H), 2.24 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.3, 162.4, 156.4, 147.4, 141.9, 136.4, 128.6, 128.1, 127.5, 124.5, 124.3, 117.7, 114.2, 70.4, 63.1, 61.7, 20.7, 14.0; **MS:** m/z = 371.3 [M^+]; **HRMS** m/z: Calcd for $C_{20}H_{21}NO_6Na$ [M+Na]$^+$: 394.1267, Found: 394.1291.

(*Z*)-ethyl 2-(2-acetoxy-5-methylphenyl)-2-(methoxyimino)acetate (2c)



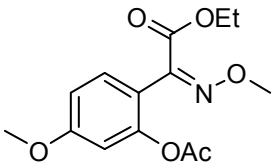
Yield: 80%, colorless oil; **IR** (KBr) ν_{max} 2984, 2940, 2902, 2822, 1762, 1739, 1493, 1464, 1368, 1328, 1266, 1238, 1192, 1039, 900, 860, 839, 743, 637 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.25–7.21 (m, 1H), 6.99 (d, J = 8.2 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 4.02 (s, 3H), 2.35 (s, 3H), 2.25 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.1, 162.5 147.6, 145.9, 136.0, 131.8, 129.5, 123.4, 123.1, 63.0, 61.6, 30.8, 20.7, 13.9; **MS:** m/z = 279.2 [M^+]; **HRMS** m/z: Calcd for $C_{14}H_{17}NO_5Na$ [M+Na]$^+$: 302.1004, Found: 302.0993.

(*Z*)-ethyl 2-(2-acetoxy-6-methylphenyl)-2-(methoxyimino)acetate (2d)



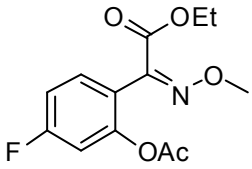
Yield: 80%, white solid; **IR** (KBr) ν_{max} 2983, 2942, 2833, 1770, 1738, 1608, 1463, 1372, 1309, 1201, 1096, 1045, 1024, 886, 793, 757, 689 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) (ratio of isomers = 10：1 , major isomer) δ 7.31 (t, J = 7.9 Hz, 1H), 7.14 (d, J = 7.6Hz, 1H), 6.96 (d, J = 8.1 Hz, 1H), 4.26(q, J = 7.1 Hz, 2H), 4.02 (s, 3H), 2.43 (s, 3H), 2.28 (s, 3H), 1.28(t, J = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.2, 161.7, 149.2, 146.1, 139.9, 130.0, 128.1, 124.2, 120.2, 63.1, 61.7, 20.8, 19.8, 13.9. **MS:** m/z = 279.2 [M^+]. **HRMS** m/z: Calcd for $C_{14}H_{17}NO_5Na$ [M+Na]$^+$: 302.1004, Found: 302.1035.

(*Z*)-ethyl 2-(2-acetoxy-4-methoxyphenyl)-2-(methoxyimino)acetate (2e)



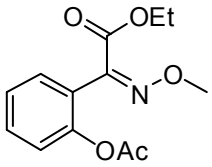
Yield: 61%, white solid; **IR** (KBr) ν_{max} 2981, 2940, 2905, 2842, 1773, 1737, 1615, 1508, 1463, 1369, 1331, 1298, 1220, 1161, 1122, 1034, 960, 891, 857, 819, cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) (ratio of isomers > 20:1, major isomer) δ 7.53 (d, J = 8.8 Hz, 1H), 6.81 (d, J = 8.8 Hz, 1H), 6.64 (s, 1H), 4.35 (q, J = 7.1 Hz, 2H), 3.99 (s, 3H), 3.80 (s, 3H), 2.27 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.8, 162.8, 161.6, 149.2, 147.5, 129.9, 116.1, 112.4, 108.9, 62.8, 61.6, 55.5, 20.7, 14.0; **MS:** m/z = 295.2 [M^+]; **HRMS** m/z: Calcd for $C_{14}H_{17}NO_6Na$ [M+Na]$^+$: 318.0954, Found: 318.0923.

(*Z*)-ethyl 2-(2-acetoxy-4-fluorophenyl)-2-(methoxyimino)acetate (2f)



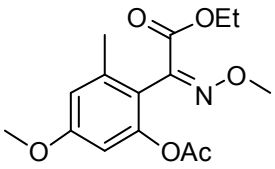
Yield: 47%, yellow oil; **IR** (KBr) ν_{max} 3082, 2985, 2942, 2905, 2823, 1777, 1740, 1606, 1503, 1419, 1369, 1328, 1189, 1147, 1102, 1049, 1027, 973, 893, 854, 822, 672, 628, 556, cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 8.8, 6.2 Hz, 1H), 6.99-7.03 (m, 1H), 6.90 (dd, *J* = 8.9, 2.5 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.02 (s, 3H), 2.27 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.4, 164.4, 162.7, 162.3, 149.1, 146.7, 130.5, 120.4, 113.8, 113.6, 111.4, 111.3, 63.2, 61.8, 20.7, 14.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –109.1; **MS:** m/z = 283.2 [M^+]; **HRMS** m/z: Calcd for $C_{13}H_{14}FNNaO_5$ [M+Na]$^+$: 306.0754, Found: 306.0753.

(*Z*)-ethyl 2-(2-acetoxyphenyl)-2-(methoxyimino)acetate (2g)



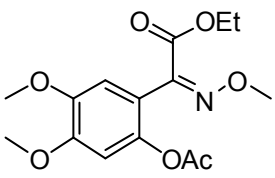
Yield: 66%, colorless oil; **IR** (KBr) ν_{max} 2984, 2941, 2904, 2823, 1772, 1738, 1606, 1487, 1446, 1369, 1327, 1263, 1184, 1109, 1038, 1023, 913, 893, 763, 677, 640, 540 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.37–7.33 (m, 1H), 7.19 (dd, *J* = 11.1, 4.2 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 3H), 2.18 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.9, 162.4, 148.2, 147.5, 131.1, 129.0, 126.3, 123.9, 123.4, 63.1, 61.7, 20.7, 14.0; **MS:** m/z = 265.2 [M^+]; **HRMS** m/z: Calcd for $C_{13}H_{15}NO_5Na$ [M+Na]$^+$: 288.0848, Found: 288.0782.

(*Z*)-ethyl 2-(2-acetoxy-4-methoxy-6-methylphenyl)-2-(methoxyimino)acetate (2h)



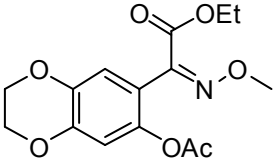
Yield: 85%, colorless oil; **IR** (KBr) ν_{max} 2979, 2941, 2843, 1774, 1737, 1614, 1574, 1493, 1465, 1368, 1329, 1302, 1202, 1145, 1034, 947, 887, 861, 764, 637, 590 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) (ratio of isomers = 6:1, major isomer) δ 6.68 (d, *J* = 1.9 Hz, 1H), 6.50 (d, *J* = 2.2 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 3H), 3.77 (s, 3H), 2.39 (s, 3H), 2.27 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, CDCl3) δ 169.0, 162.0, 160.5, 150.3, 146.3, 140.8, 116.7, 114.1, 106.0, 63.0, 61.6, 55.4, 20.8, 20.2, 13.9; **MS:** m/z = 309.2 [M^+]; **HRMS** m/z: Calcd for $C_{15}H_{19}NO_6Na$ [M+Na]$^+$: 332.1110, Found: 332.1132.

(*Z*)-ethyl 2-(2-acetoxy-4,5-dimethoxyphenyl)-2-(methoxyimino)acetate (2i)



Yield: 82%, colorless oil; **IR** (KBr) ν_{max} 2797, 2941, 2838, 1771, 1739, 1612, 1516, 1464, 1368, 1303, 1260, 1178, 1140, 1033, 980, 903, 797, 741, 590 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (s, 1H), 6.59 (s, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.01 (s, 3H), 3.91 (s, 3H), 3.88 (s, 3H), 2.25 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, DMSO) δ 169.16, 162.59, 151.38, 147.4, 146. 9, 142.5, 114.5, 109.1, 107.6, 62.8, 61.7, 56.0, 55.8, 20.6, 14.0; **MS:** m/z = 325.2 [M^+]; **HRMS** m/z: Calcd for $C_{15}H_{19}NO_7Na$ [M+Na]$^+$: 348.1059, Found: 348.1070.

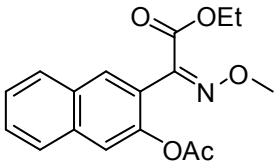
(*Z*)-ethyl 2-(7-acetoxy-2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-2-(methoxyimino)acetate (2j)



Yield: 56%, white solid, **m.p.** 69-70 °C; **IR** (KBr) ν_{max} 2989, 2941, 2899, 2829, 1773, 1726, 1620, 1577, 1515, 1462, 1415, 1375, 1350, 1307, 1281, 1217, 1174, 1144, 1054, 1033, 984, 931, 904, 882, 800,

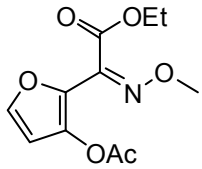
742, 597, 553 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.11 (s, 1H), 6.62 (s, 1H), 4.32-4.36 (m, 2H), 4.25 (dd, *J* = 15.8, 4.4 Hz, 4H), 3.98 (s, 3H), 2.24 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.2, 162.6, 147.2, 145.4, 142.0, 141.5, 116.9, 116.6, 112.2, 64.4, 64.0, 62.9, 61.7, 20.7, 14.0; **HRMS** m/z: Calcd for $C_{15}H_{17}NO_7Na$ $[M+Na]^+$: 346.0903, Found: 346.0905.

(*Z*)-ethyl 2-(3-acetoxynaphthalen-2-yl)-2-(methoxyimino)acetate (2k)



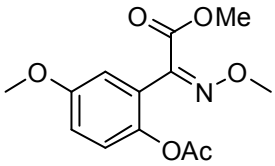
Yield: 73%, white solid, **m.p.** 60-62 °C; **IR** (KBr) ν_{max} 2987, 2942, 2831, 1765, 1724, 1632, 1599, 1469, 1441, 1369, 1326, 1273, 1233, 1198, 1156, 1123, 1036, 1012, 994, 895, 877, 747 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.56 (s, 1H), 7.43-7.49 (m, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 4.06 (s, 3H), 2.32 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, CDCl3) δ 169.2, 162.3, 147.9, 145.1, 133.9, 130.9, 129.9, 128.2, 127.7, 127.1, 126.3, 123.0, 120.7, 63.1, 61.7, 20.8, 13.9; **HRMS** m/z: Calcd for $C_{17}H_{18}NO_5$ $[M+H]^+$: 316.1185, Found: 316.1150.

(*Z*)-ethyl 2-(3-acetoxyfuran-2-yl)-2-(methoxyimino)acetate (2l)



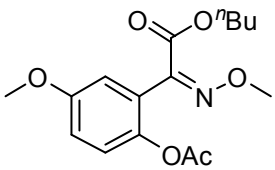
Yield: 17%, yellow oil; **IR** (KBr) ν_{max} 2985, 2943, 2906, 2825, 1796, 1740, 1606, 1572, 1522, 1464, 1446, 1372, 1308, 1221, 1174, 1079, 1023, 936, 861, 792 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) (ratio of isomers = 5:1, major isomer) δ 7.28 (d, *J* = 3.6 Hz, 1H), 6.11 (d, *J* = 3.7 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.13 (s, 3H), 2.32 (s, 3H), 1.39 (t, *J* = 6.7 Hz, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.6, 161.9, 151.6, 139.1, 135.0, 121.3, 94.8, 63.7, 62.2, 20.6, 14.0; **MS:** m/z = 255.2 $[M^+]$; **HRMS** m/z: Calcd for $C_{11}H_{13}NO_6Na$ $[M+Na]^+$: 278.0641, Found: 278.0618.

(*Z*)-methyl 2-(2-acetoxy-5-methoxyphenyl)-2-(methoxyimino)acetate (2m)



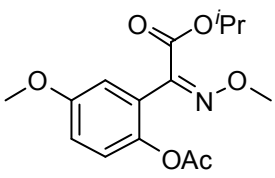
Yield: 83%, colorless oil; **IR** (KBr) ν_{max} 2943, 2906, 2840, 1768, 1743, 1608, 1573, 1494, 1464, 1427, 1368, 1248, 1182, 1033, 927, 896, 852, 824, 745, 654 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 2.8 Hz, 1H), 7.02 (d, *J* = 8.8 Hz, 1H), 6.96 (dd, *J* = 8.8, 2.8 Hz, 1H), 4.03 (s, 3H), 3.86 (s, 2H), 3.81 (s, 3H), 2.23 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.3, 162.8, 157.2, 147.1, 141.8, 124.4, 124.2, 117.2, 113.1, 63.2, 55.7, 52.3, 20.6; **MS:** m/z = 281.2 $[M^+]$; **HRMS** m/z: Calcd for $C_{13}H_{15}NO_6Na$ $[M+Na]^+$: 304.0797, Found: 304.0792.

(*Z*)-butyl 2-(2-acetoxy-5-methoxyphenyl)-2-(methoxyimino)acetate (2n)



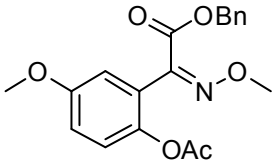
Yield: 83%, colorless oil; **IR** (KBr) ν_{max} 2962, 2941, 2875, 2841, 1770, 1741, 1608, 1572, 1494, 1465, 1368, 1247, 1186, 1037, 929, 896, 822, 747, 653 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.14 (s, 1H), 7.01 (d, *J* = 8.9 Hz, 1H), 6.96 (dd, *J* = 8.4, 3.5 Hz, 1H), 4.30-4.28 (m, 2H), 4.02 (s, 3H), 3.82 (s, 3H), 2.24 (s, 3H), 1.70–1.67 (m, 2H), 1.40–1.36 (m, 2H), 0.93 (d, *J* = 2.9 Hz, 1H), 0.92 (dd, *J* = 7.4, 2.9 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.4, 162.5, 157.1, 147.4, 141.7, 124.4, 124.2, 117.1, 112.9, 65.5, 63.1, 55.6, 30.3, 20.7, 18.9, 13.5; **MS:** m/z = 323.3 $[M^+]$; **HRMS** m/z: Calcd for $C_{16}H_{21}NO_6Na$ $[M+Na]^+$: 346.1267, Found: 346.1270.

(*Z*)-isopropyl 2-(2-acetoxy-5-methoxyphenyl)-2-(methoxyimino)acetate (2o)



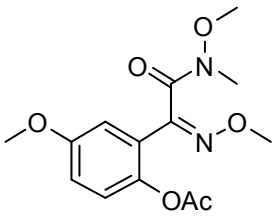
Yield: 75%, white solid, **m.p.** 55-56 ^{o}C; **IR** (KBr) ν_{max} 2983, 2940, 2841, 2824, 1768, 1729, 1614, 1577, 1499, 1459, 1415, 1375, 1272, 1256, 1191, 1174, 1097, 1040, 1015, 917, 895, 872, 825, 778, 745 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.12 (s, 1H), 7.01 (d, J = 8.9 Hz, 1H), 6.97-6.95 (m, 1H), 5.26-5,21 (m, 1H), 4.02 (s, 3H), 3.81 (s, 3H), 2.25 (s, 3H), 1.32 (d, J = 6.3 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.5, 161.9, 157.1, 147.7, 141.7, 124.4, 124.2, 117.0, 113.0, 69.8, 63.0, 55.6, 21.6, 20.7; **HRMS** m/z: Calcd for $C_{15}H_{19}NO_6Na$ $[M+Na]^+$: 332.1110, Found: 332.1136.

(*Z*)-benzyl 2-(2-acetoxy-5-methoxyphenyl)-2-(methoxyimino)acetate (2p)



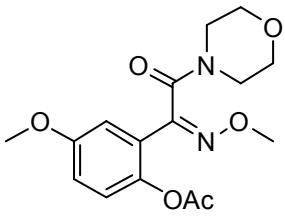
Yield: 72%, colorless oil; **IR** (KBr) ν_{max} 2941, 2839, 1768, 1741, 1608, 1572, 1494, 1463, 1368, 1262, 1246, 1187, 1036, 897, 823, 746, 699 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) (ratio of isomers = 5:1, major isomer) δ 7.41 – 7.27 (m, 5H), 7.08 (d, J = 2.9 Hz, 1H), 7.02 – 6.98 (m, 1H), 6.96 – 6.94 (m, 1H), 5.32 (s, 2H), 4.00 (s, 3H), 3.75 (s, 3H), 2.13 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.3, 162.3, 157.2, 147.2, 141.8, 134.8, 129.5, 128.4, 124.2, 117.3, 113.0, 67.2, 63.2, 55.6, 20.5. **MS:** m/z = 357.2 $[M^+]$. **HRMS** m/z: Calcd for $C_{19}H_{19}NO_6Na$ $[M+Na]^+$: 380.1110, Found: 380.1120.

(*Z*)-4-methoxy-2-(6-methyl-5-oxo-2,7-dioxa-3,6-diazaoct-3-en-4-yl)phenyl acetate (2q)



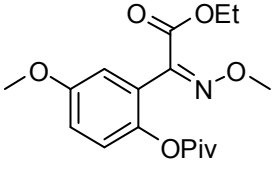
Yield: 85%, colorless oil; **IR** (KBr) ν_{max} 2941, 2839, 1766, 1667, 1608, 1571, 1494, 1463, 1368, 1298, 1188, 1045, 983, 900, 818, 788, 758, 627 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) (ratio of isomers = 6:1, major isomer) δ 7.13 (d, J = 2.9 Hz, 1H), 6.98 (d, J = 8.9 Hz, 1H), 6.96 – 6.92 (m, 1H), 4.00 (s, 3H), 3.80 (s, 3H), 3.50 (s, 3H), 3.27 (s, 3H), 2.26 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.6, 163.7, 157.2, 150.1, 141.6, 124.8, 124.6, 116.5, 113.1, 62.7, 61.5, 55.6, 31.4, 20.8; **MS:** m/z = 310.2 $[M^+]$; **HRMS** m/z: Calcd for $C_{14}H_{18}N_2O_6Na$ $[M+Na]^+$: 333.1063, Found: 333.1072.

(*Z*)-4-methoxy-2-(1-(methoxyimino)-2-morpholino-2-oxoethyl)phenyl acetate (2r)



Yield: 76%, colorless oil; **IR** (KBr) ν_{max} 2968, 2938, 2858, 1766, 1646, 1608, 1495, 1463, 1441, 1367, 1274, 1247, 1191, 1113, 1042, 1001, 900, 843, 819, 758, 595 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) (ratio of isomers = 9:1, major isomer) δ 7.12 (d, J = 2.9 Hz, 1H), 7.01 (d, J = 8.9 Hz, 1H), 6.94 (dd, J = 8.9, 2.9 Hz, 1H), 4.00 (s, 3H), 3.91–3.83 (m, 1H), 3.81 (s, 3H), 3.73 (t, J = 4.8 Hz, 2H), 3.62 (d, J = 22.4 Hz, 3H), 3.30 (d, J = 29.1 Hz, 2H), 2.26 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 169.7, 162.2, 157.2, 149.6, 141.5, 124.8, 123.7, 116.3, 113.6, 66.7, 66.4, 62.8, 55.6, 46.1, 41.4, 21.0. **MS:** m/z = 336.5 $[M^+]$; **HRMS** m/z: Calcd for $C_{16}H_{20}N_2O_6Na$ $[M+Na]^+$: 359.1219, Found: 359.1191.

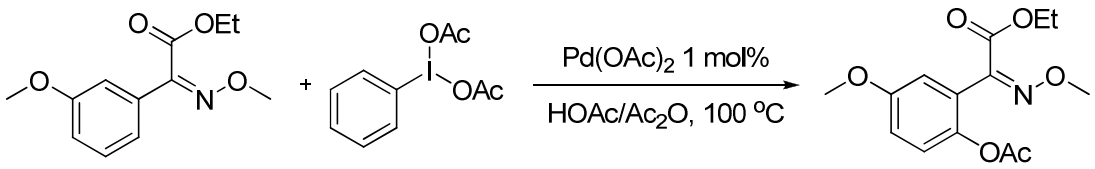
(*Z*)-2-(2-ethoxy-1-(methoxyimino)-2-oxoethyl)-4-methoxyphenyl pivalate (2s)



Yield: 57%, colorless oil; **IR** (KBr) ν_{max} 2977, 2940, 2908, 2839, 1753, 1607, 1577, 1496, 1481, 1464, 1417, 1368, 1246, 1204, 1107, 1032, 924, 887, 859, 827, 798, 758 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.03

(s, 1H), 6.94 (d, J = 1.1 Hz, 2H), 4.31 (q, J = 7.1 Hz, 2H), 4.01 (s, 3H), 3.81 (s, 3H), 1.34 (s, 9H), 1.30 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 177.0, 161.9, 156.9, 147.4, 142.4, 124.8, 124.0, 116.7, 114.0, 63.0, 61.7, 55.6, 39.1, 27.0, 14.1; **MS:** m/z = 337.3 [M^+]; **HRMS** m/z: Calcd for $C_{17}H_{23}NO_6Na$ [M+Na]$^+$: 360.1423, Found: 360.1426.

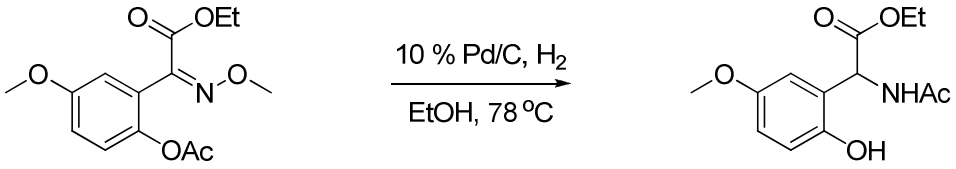
Procedure for a gram-scale experiment



1a (5 mmol 1.186 g) (6 mmol) **2a** 73% yield

A mixture of **1a** (5.0 mmol, 1.0 equiv), iodobenzene diacetate (6.0 mmol, 1.2 equiv) $Pd(OAc)_2$ (0.005 mmol, 0.01 equiv) was combined in AcOH (15 mL) and Ac_2O (15 mL) in a dried Schlenk tube under a nitrogen atmosphere. the reaction was stirred at 100 ºC and monitored by TLC. Upon completion or no further improvement of reaction, the reaction mixture was cooled to room temperature and was then diluted with ethyl acetate. the organic layer was washed sequentially with saturated $NaHCO_3$, water and brine then dried over anhydrous $MgSO_4$. Evaporation of the solvent and the resulting oil was purified by flash chromatography on silica gel to afford product **2a** as a white solid with 73% yield.

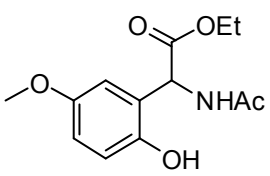
4. Typical Procedure for Synthesis of compound 3



2a **3** 99% yield

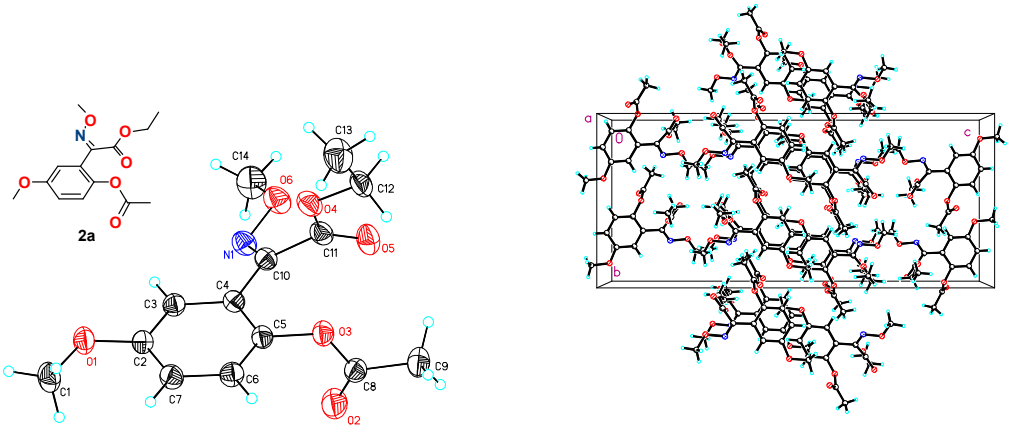
A suspension solution of **2a** (1 mmol) and 10% Pd/C (100 mg) in EtOH (2 mL) at a flask was transferred to stainless steel autoclave, which was charged with H_2 (50 atm). The hydrogenation was performed at 78 °C for 24 h. After carefully releasing the hydrogen, the reaction mixture was filtered through Celite. The filtrate was concentrated under reduced pressure to afford the product **3** as a white solid with 99% yield.

(*Z*)-ethyl 2-(2-acetoxy-5-methoxyphenyl)-2-(methoxyimino)acetate (3)



Yield: 99%, white solid, **m.p.** 103-104 °C; **IR** (KBr) ν_{max} 3406, 3101, 2832, 2747, 2595, 1743, 1644, 1605, 1513, 1467, 1435, 1377, 1311, 1213, 1159, 1116, 1035, 958, 858, 816, 754, 720, 646 cm-1; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.02 (d, *J* = 6.5 Hz, 1H), 6.95 (d, *J* = 8.9 Hz, 1H), 6.81 (dd, *J* = 8.9, 2.9 Hz, 1H), 6.51 (d, *J* = 2.9 Hz, 1H), 5.67 (d, *J* = 7.0 Hz, 1H), 4.34 – 4.20 (m, 2H), 3.72 (s, 3H), 2.05 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 170.8, 153.3, 148.8, 124.4, 119.2, 115.4, 112.8, 62.3, 55.6, 52.2, 22.6, 13.9; **HRMS** m/z: Calcd for $C_{13}H_{17}NO_5Na$ [M+Na]$^+$: 290.1004, Found: 290.0976.

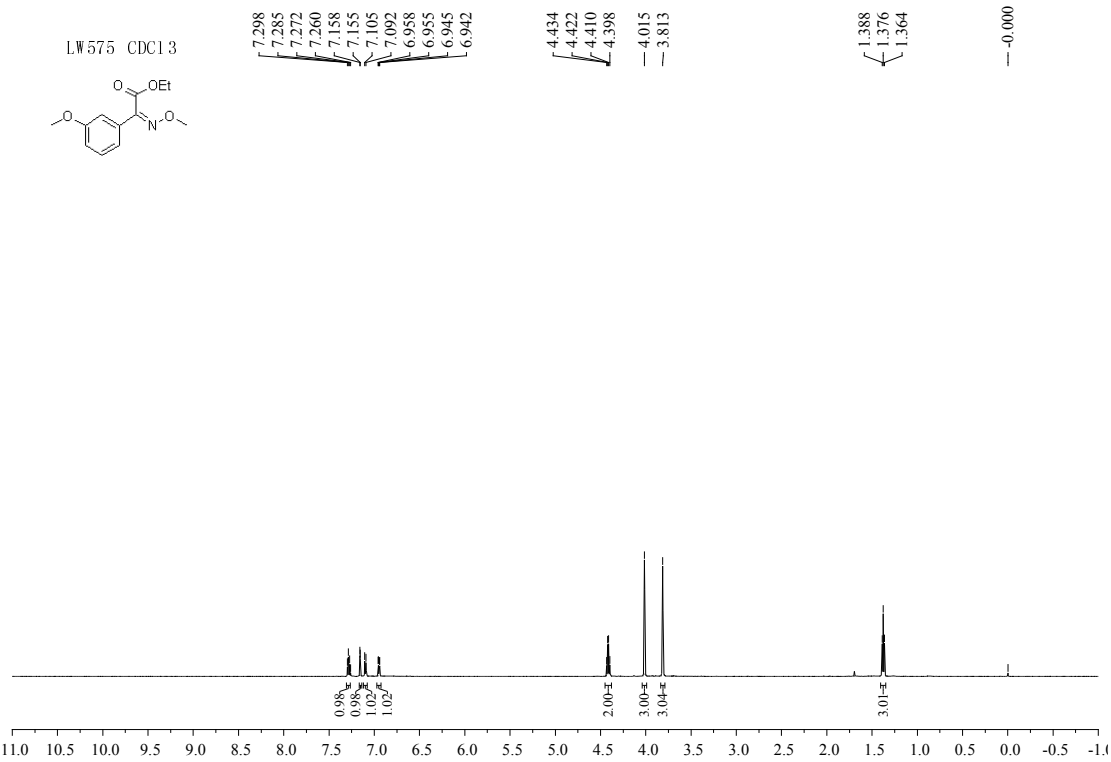
5. X-Ray structure of 2a

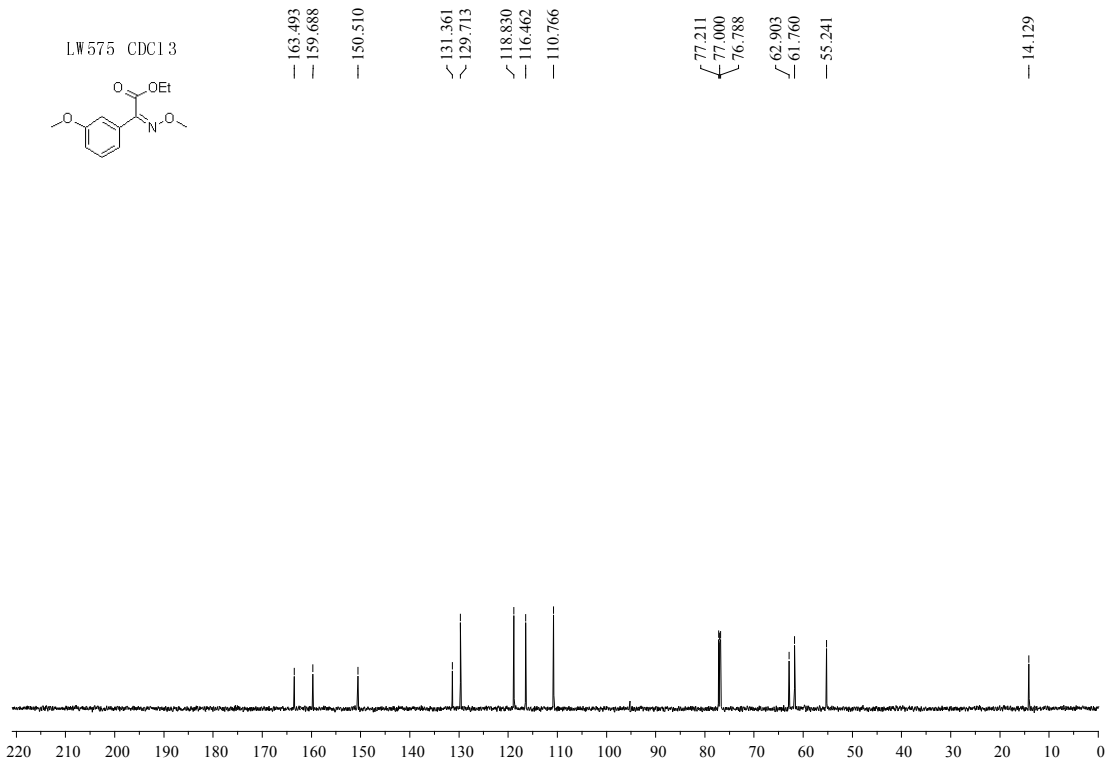


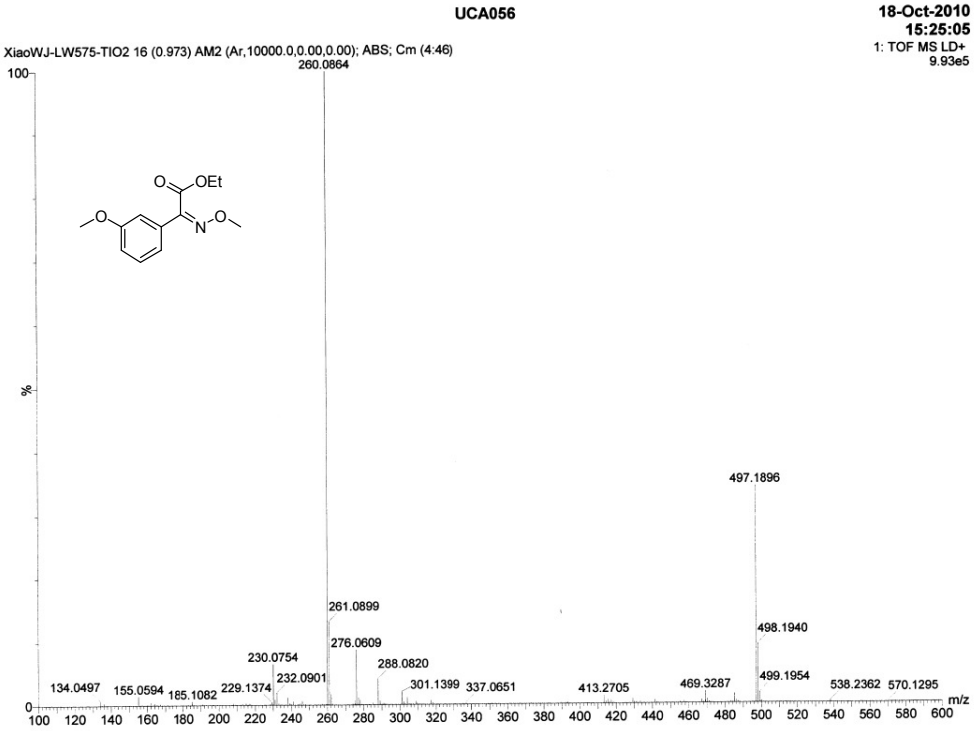
Crystal data for **2a**: Crystal data for **2a**: $C_{28}H_{34}N_2O_{12}$, M = 590.57, orthorhombic, *Pbca*, a = 7.6651(6) Å, b = 13.1131(9) Å, c = 29.874(2) Å, α = 90°, β = 90°, γ = 90°, V = 3002.7(4) Å^3, Z = 4, T = 298(2), *F000* = 1248, final R indices [I>2σ(I)]: R_1 = 0.0418, wR_2 = 0.1173, R indices (all data): R_1 = 0.0485, wR_2 = 0.1216. CCDC 814555. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

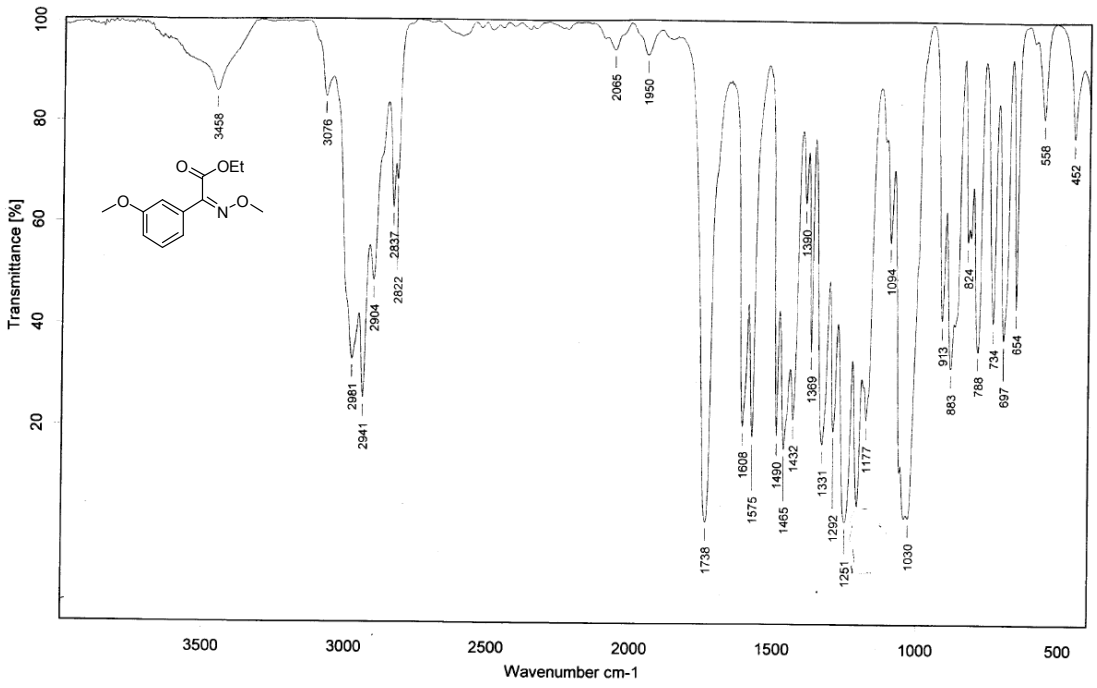
6. References

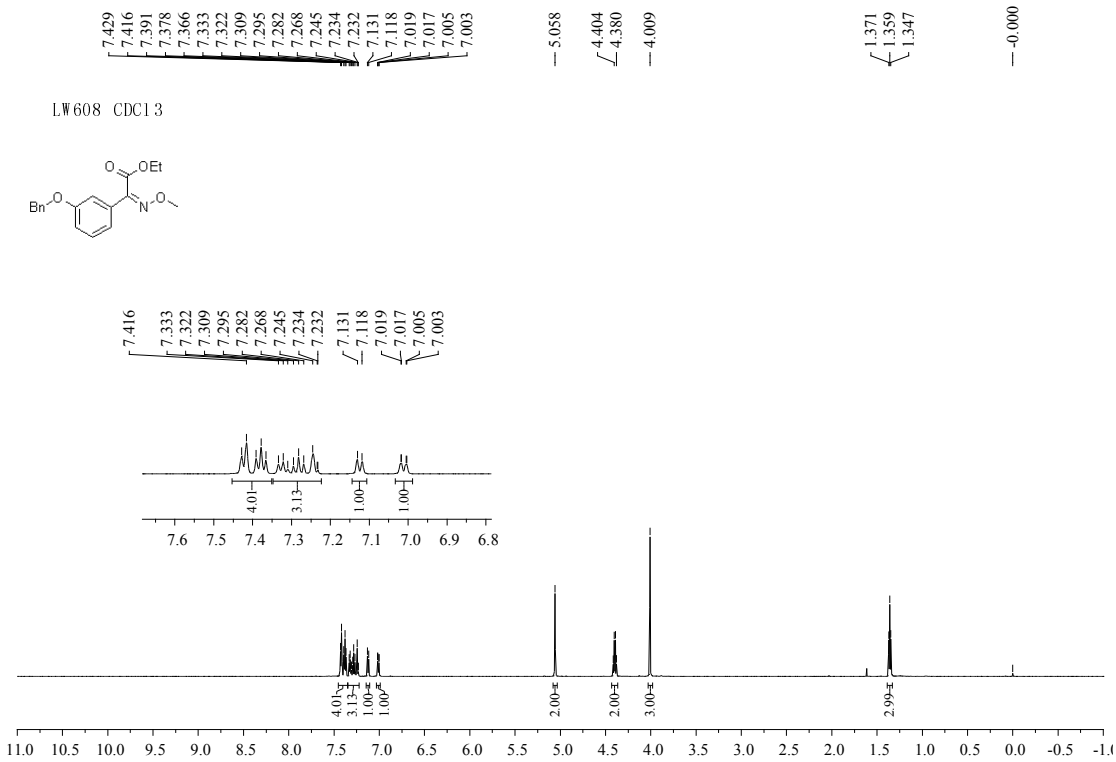
1. Q. Meng, Y. Sun, V. Ratovelomanana-Vidal, J. P. Genêt and Z. Zhang, *J. Org. Chem.*, 2008, **73**, 3842.
2. K. Wadhwa, C. Yang, P. R. West, K. C. Deming, S. R. Chemburkar and R. E. Reddy, *Syn. Comm.*, 2008, **38**, 4434.
3. C.-T. Chen, S. Bettigeri, S.-S. Weng, V. D. Pawar, Y.-H. Lin, C.-Y. Liu and Way-Zen Lee, *J. Org. Chem.*, 2007, **72**, 8175.

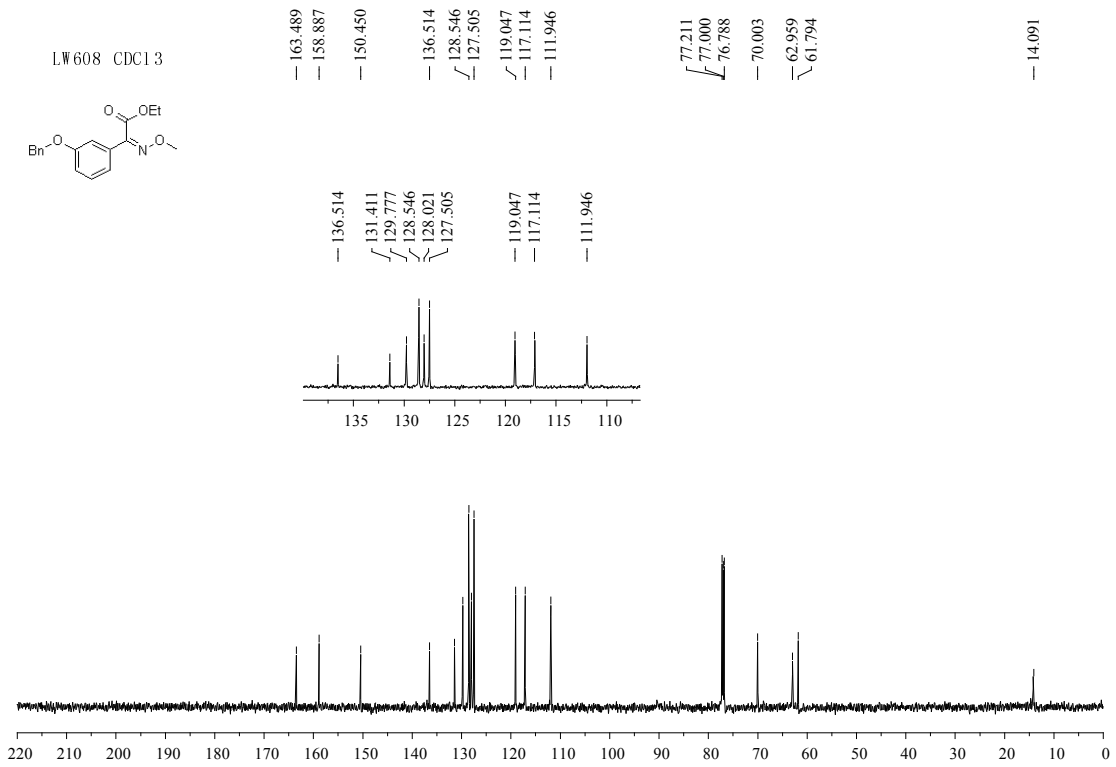


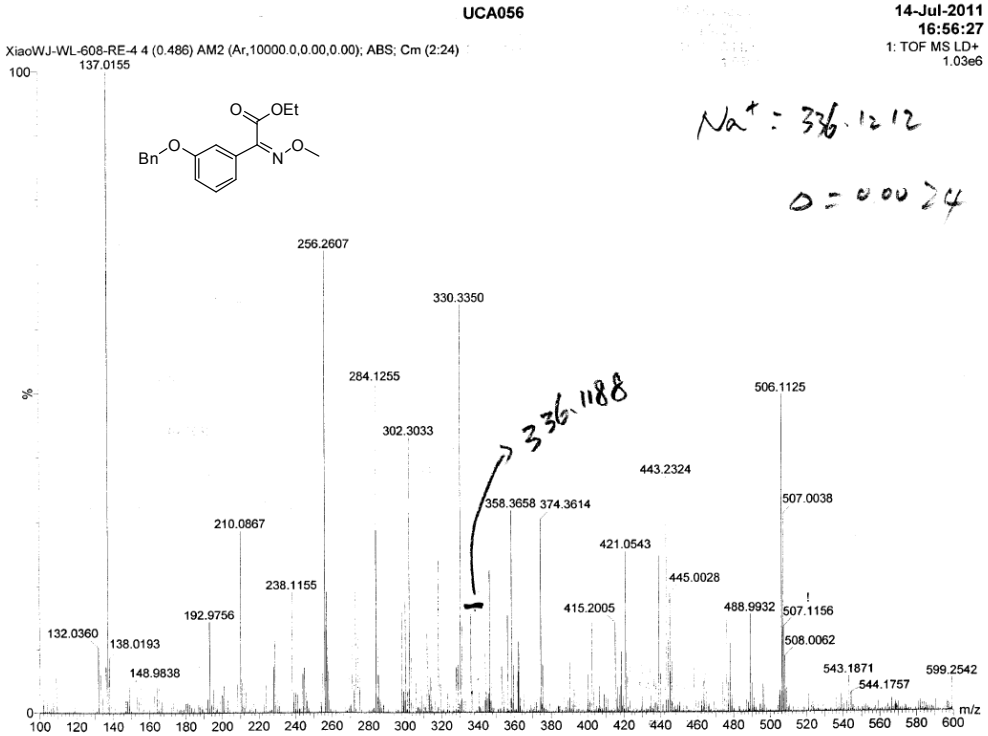


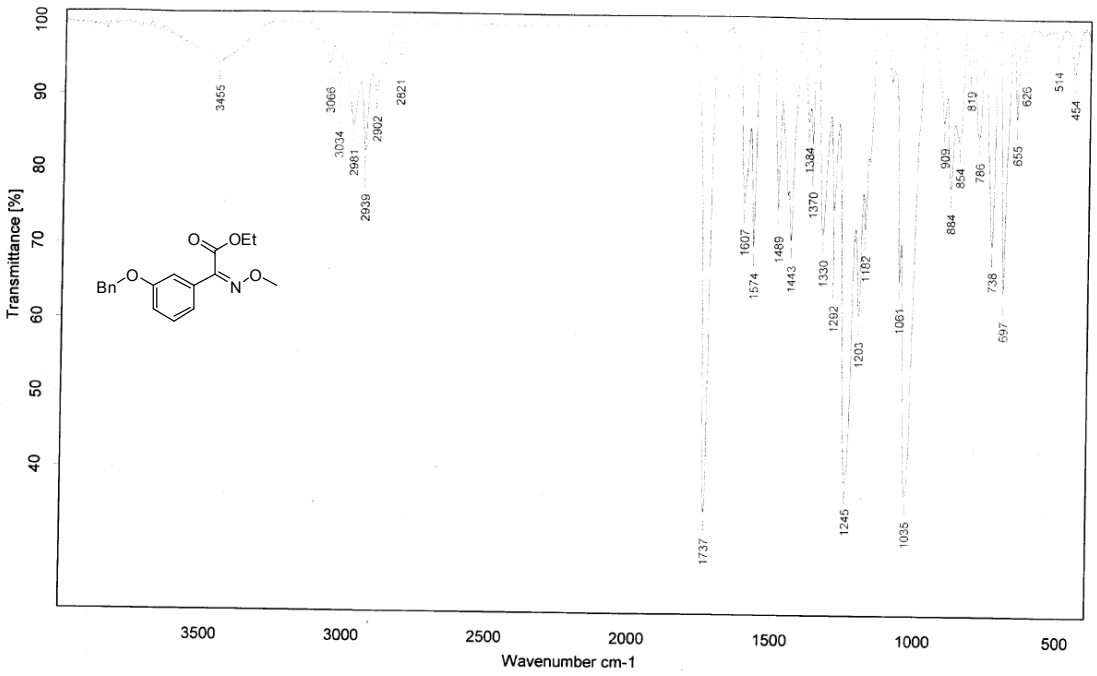


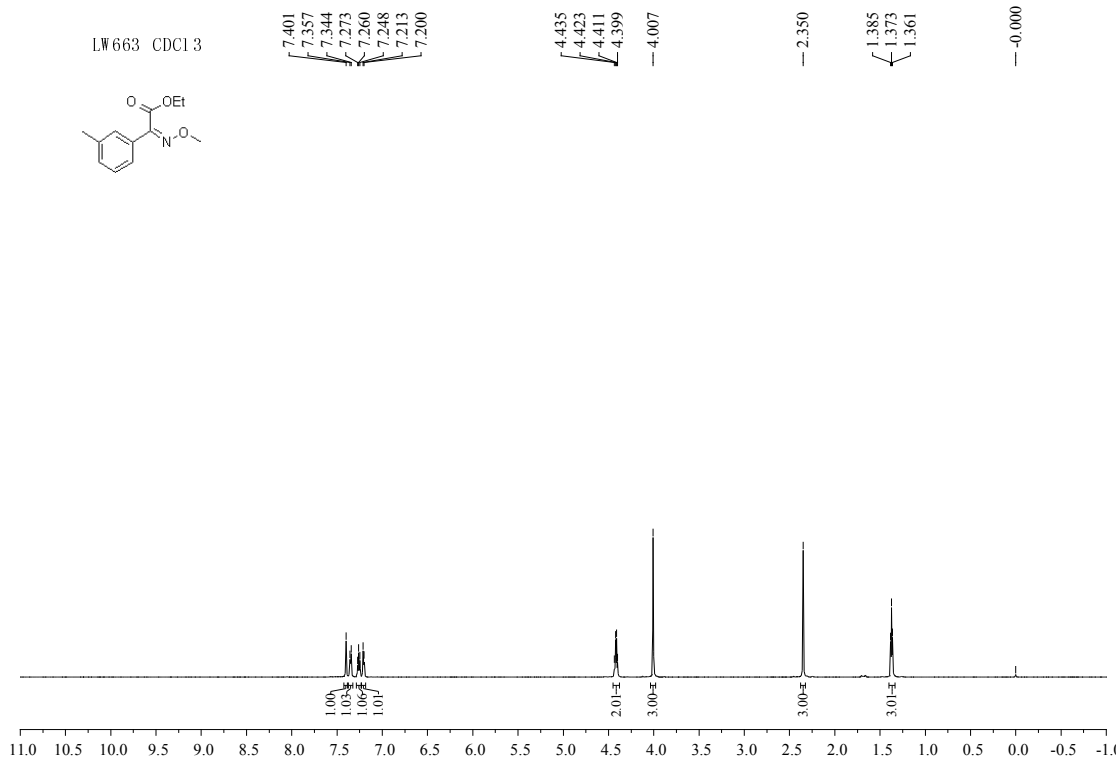


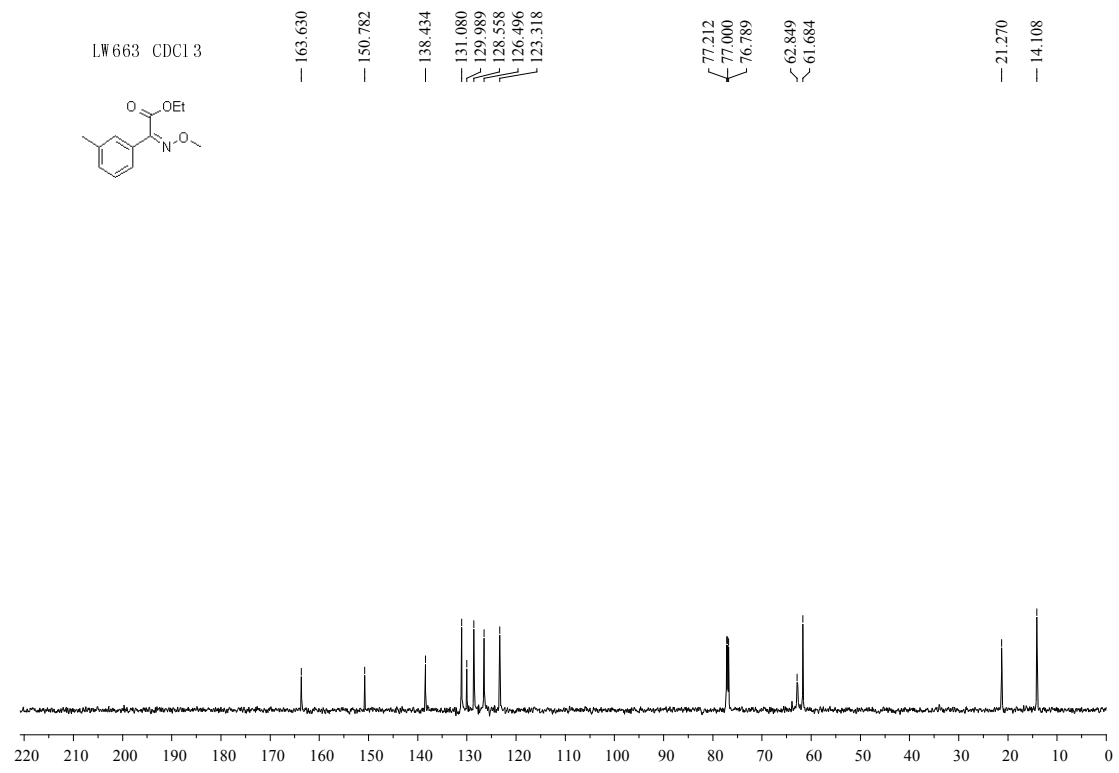


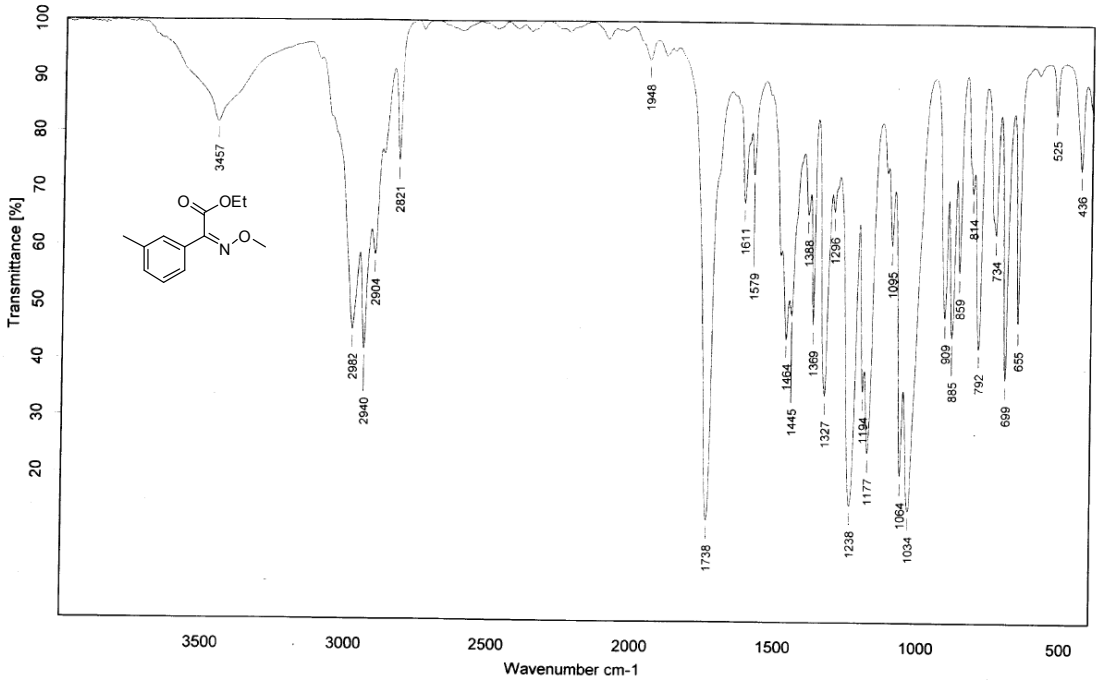


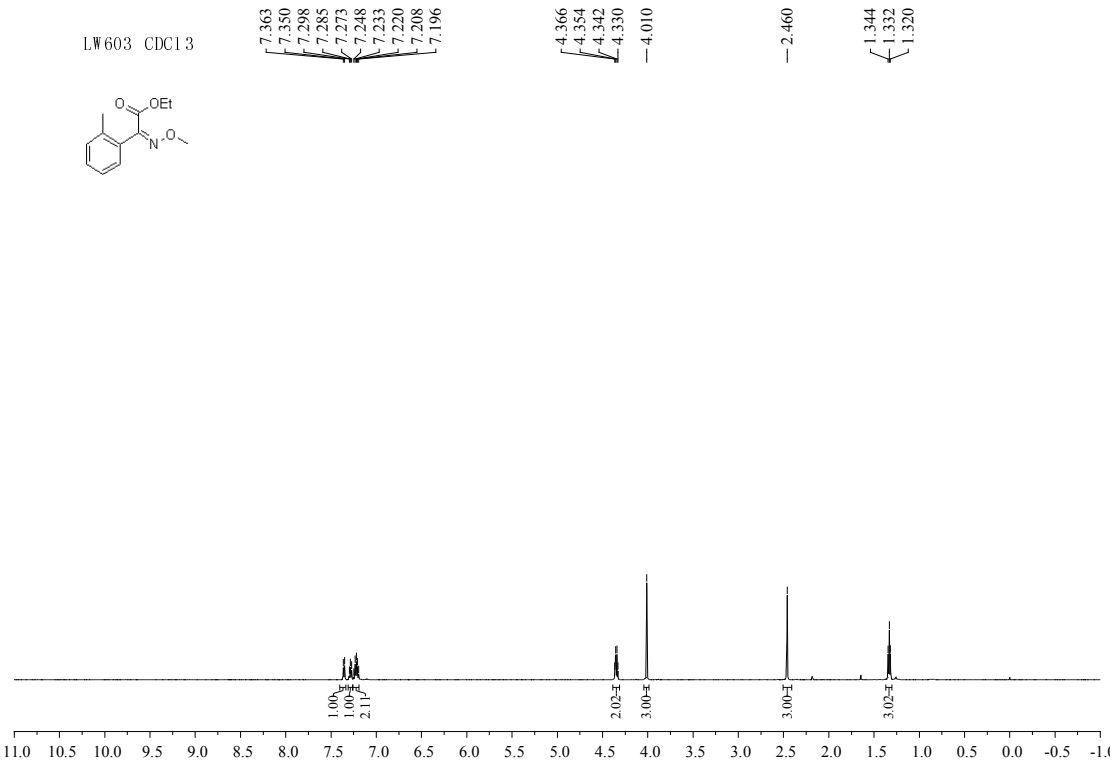


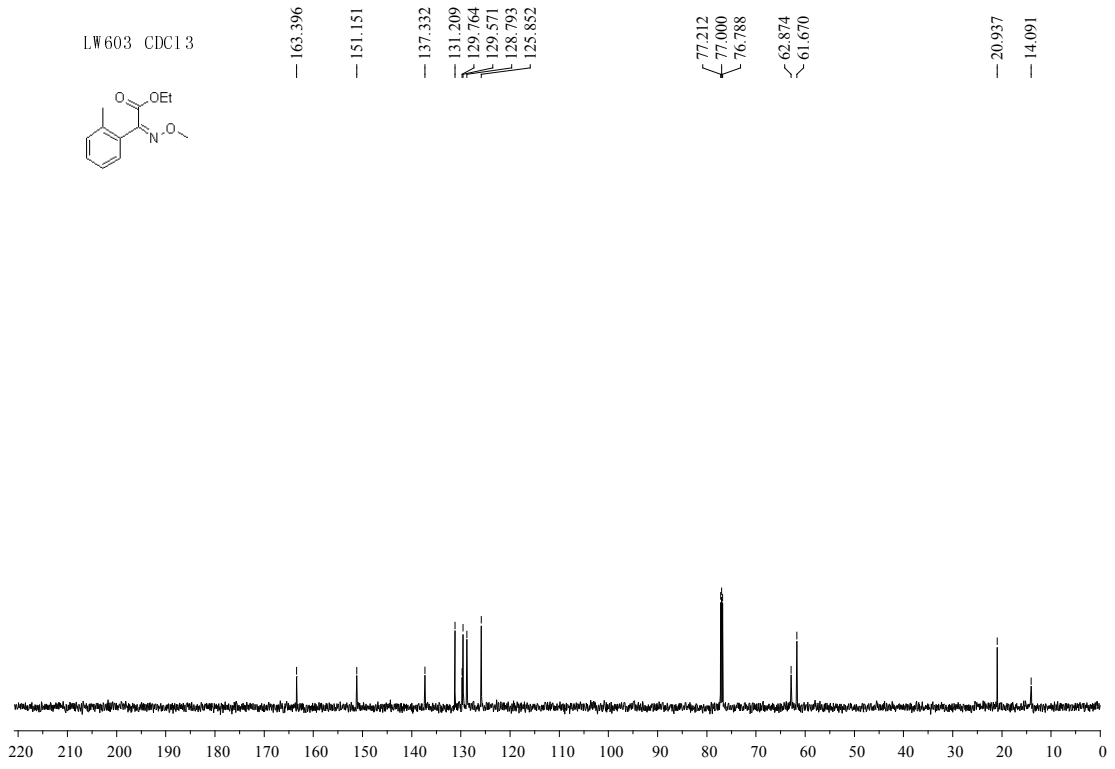


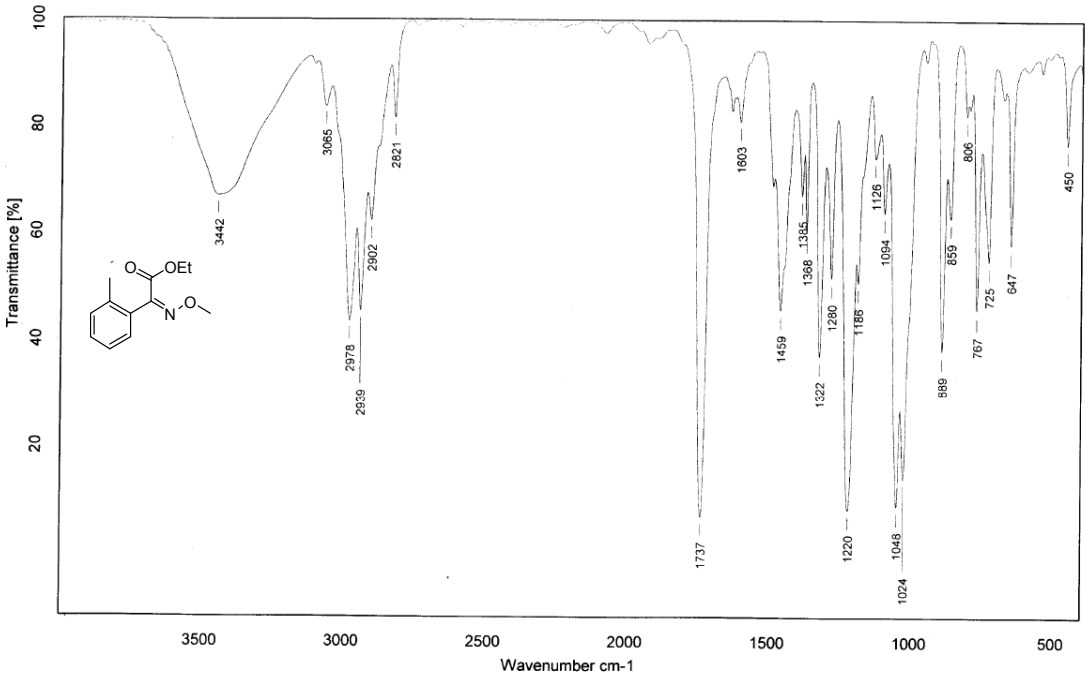


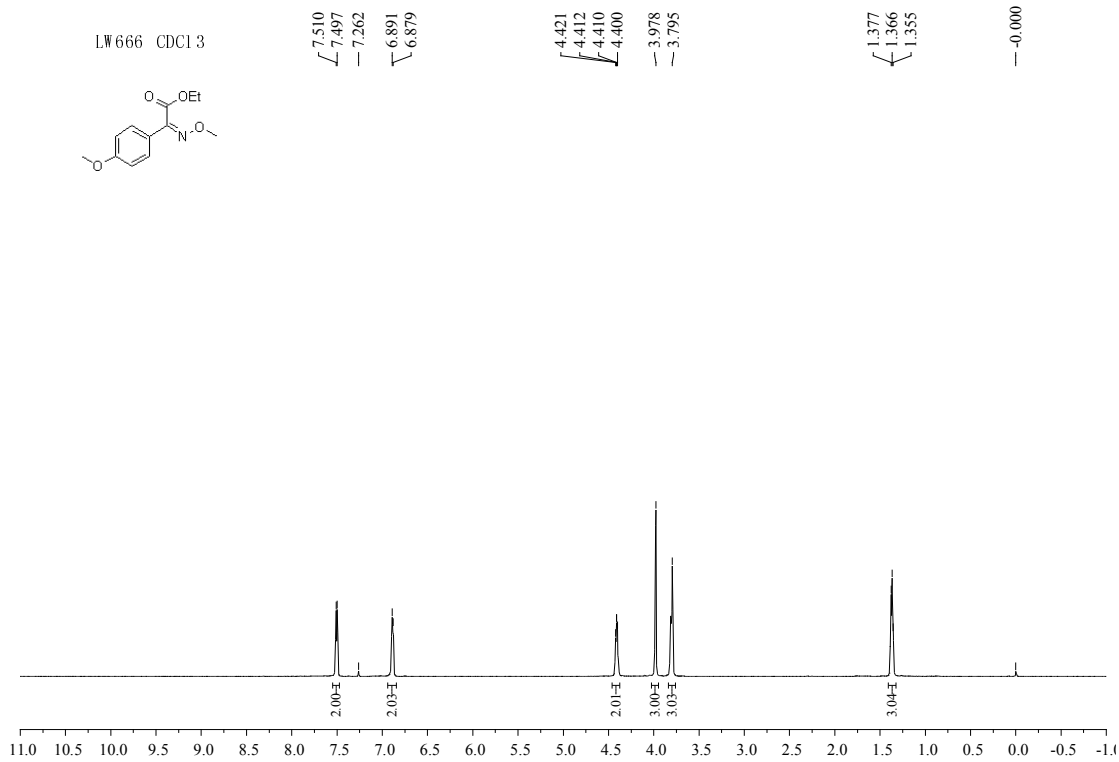


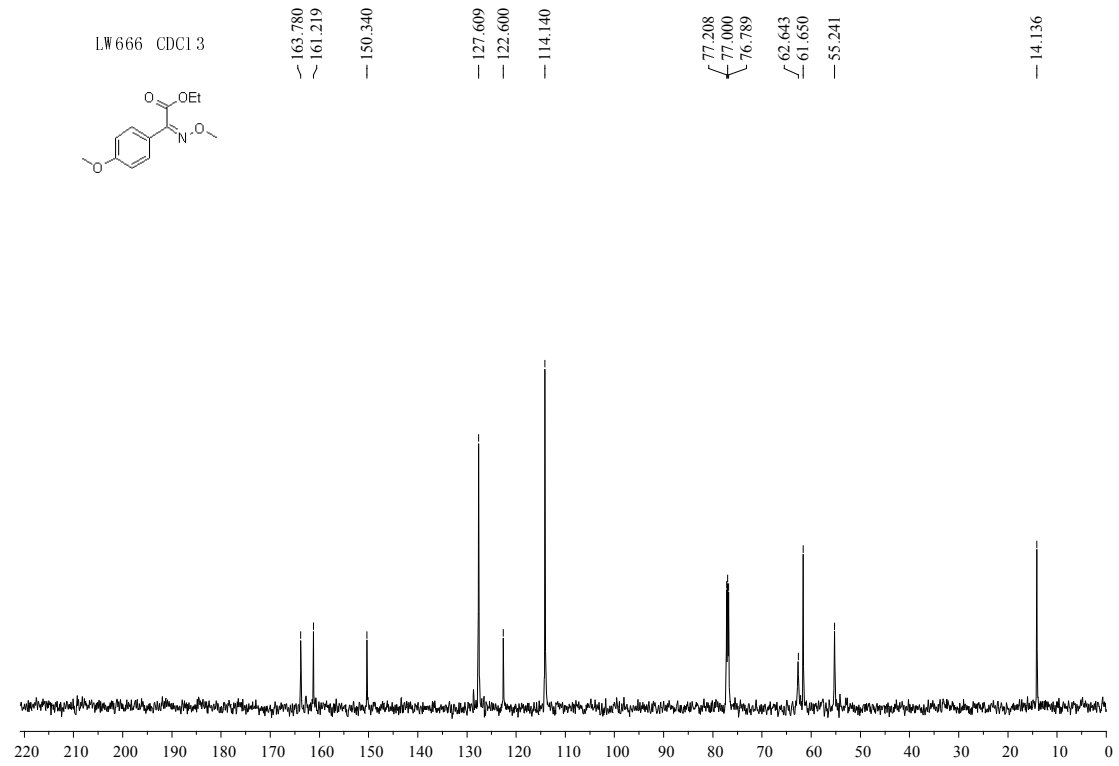


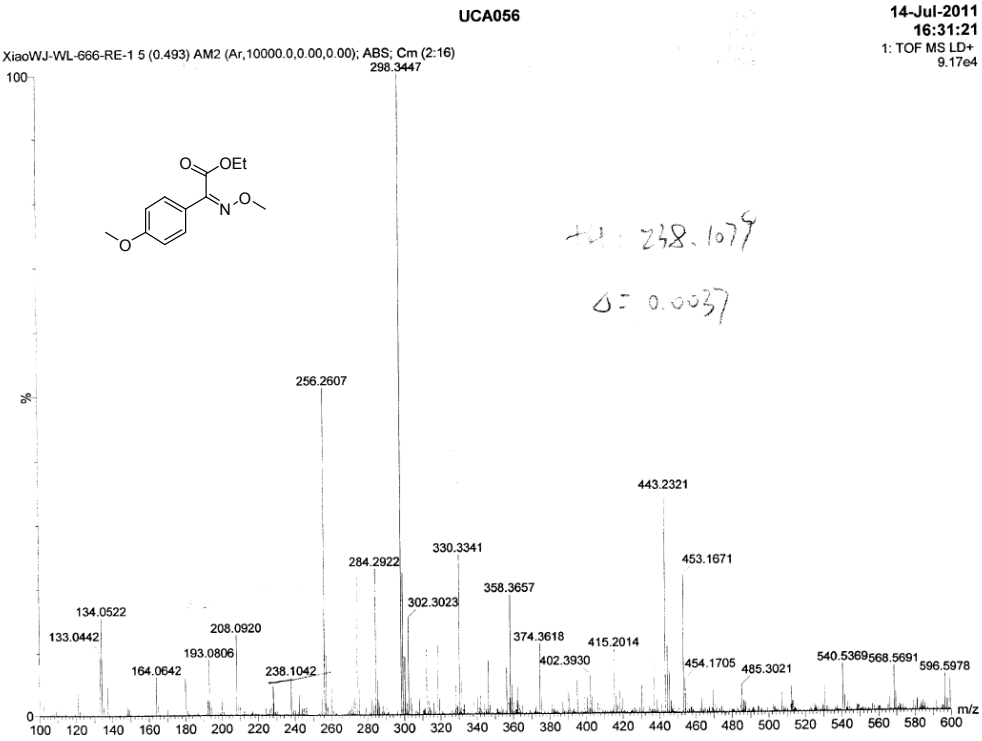


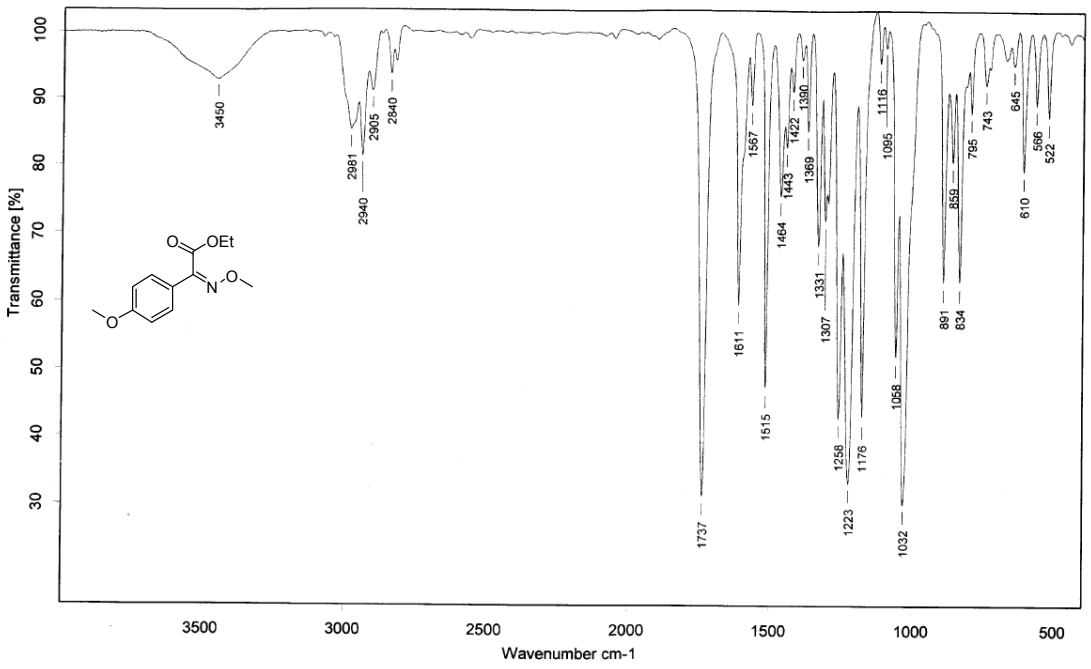


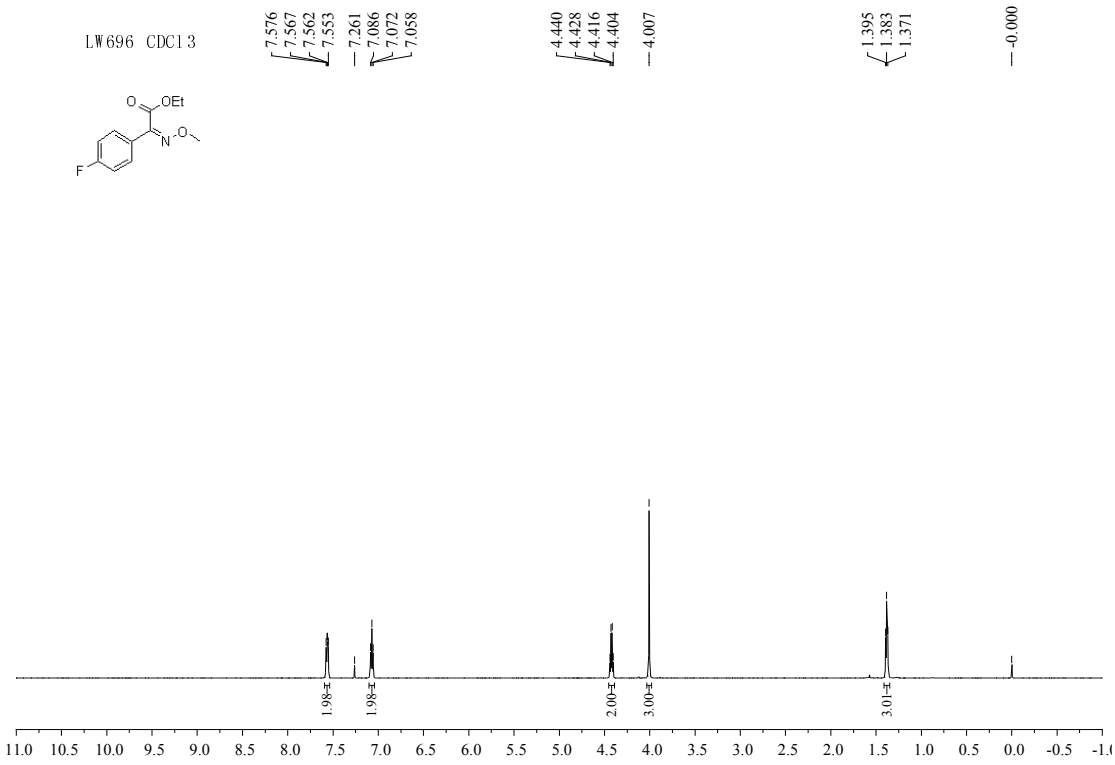


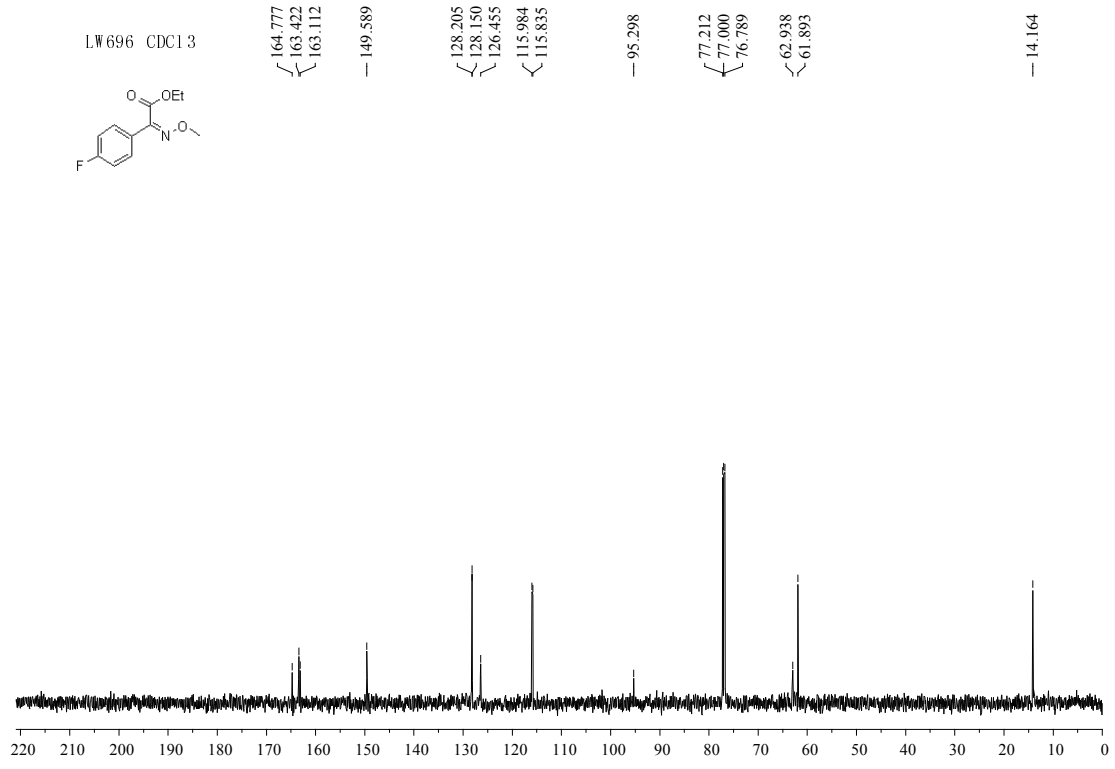


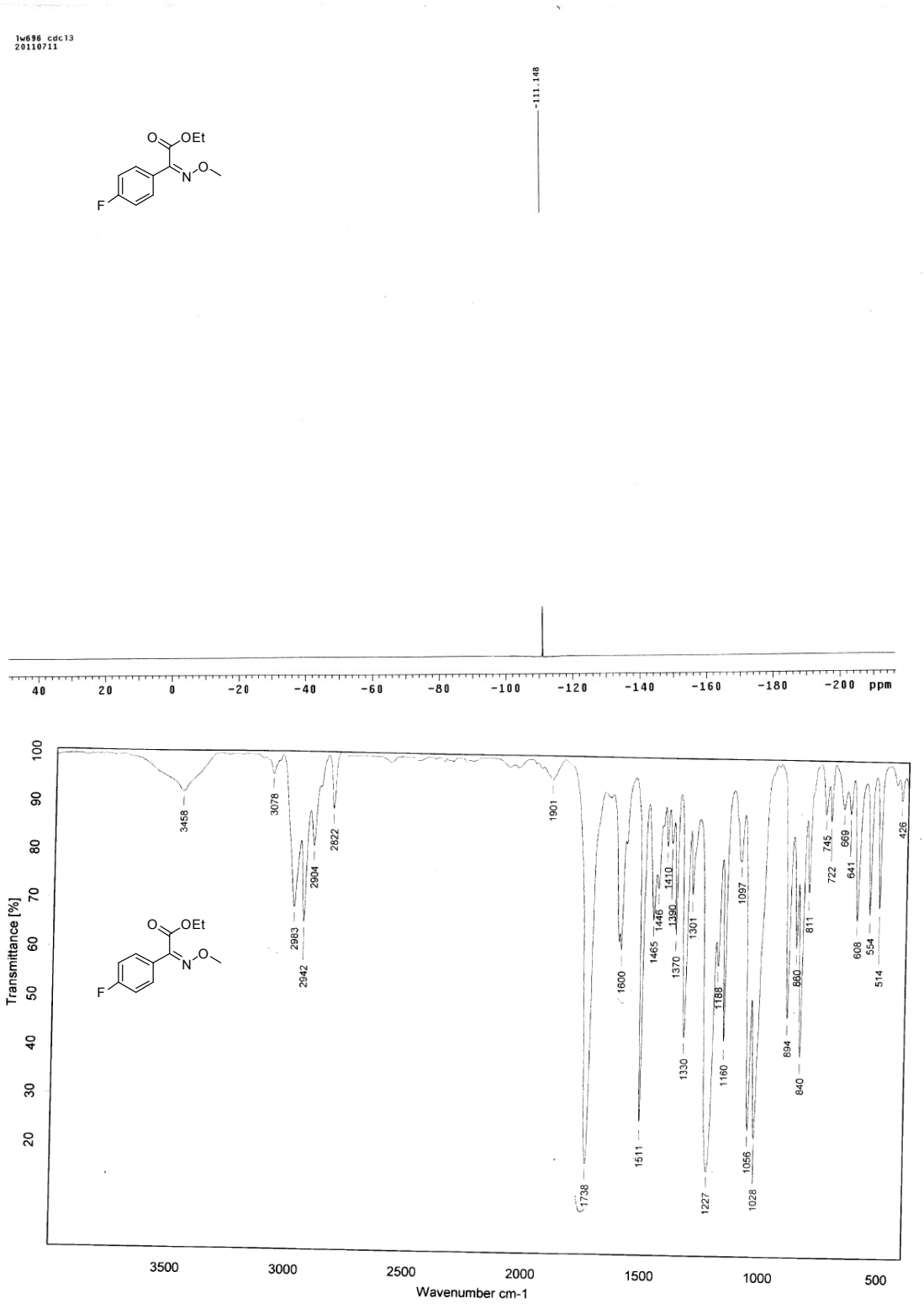












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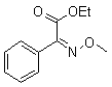

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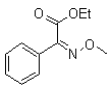

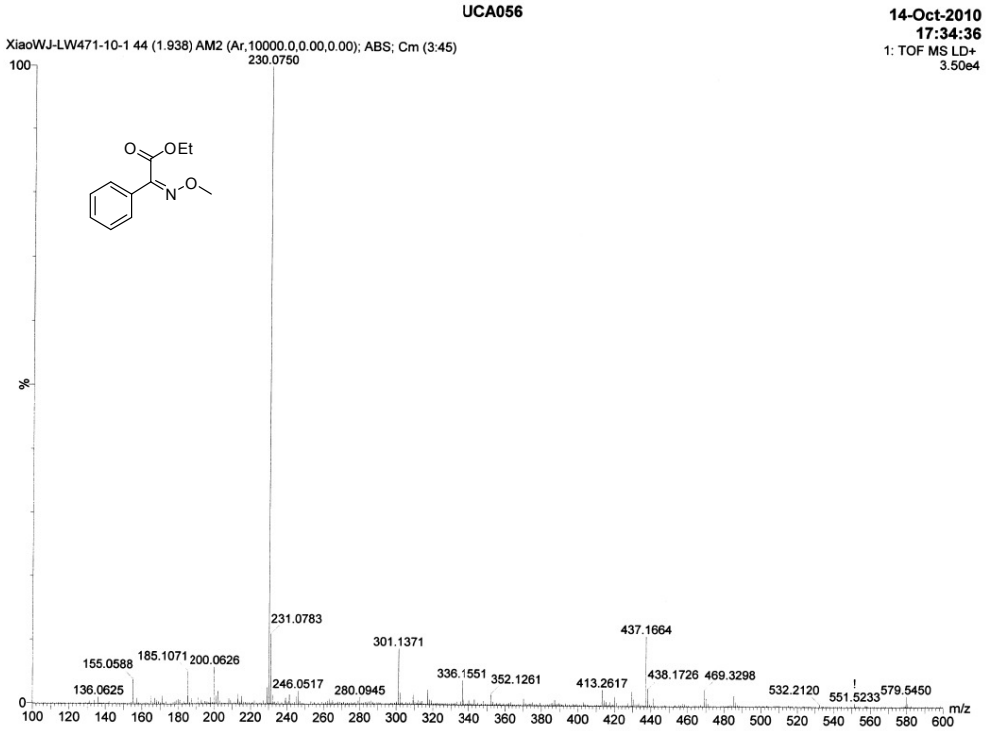

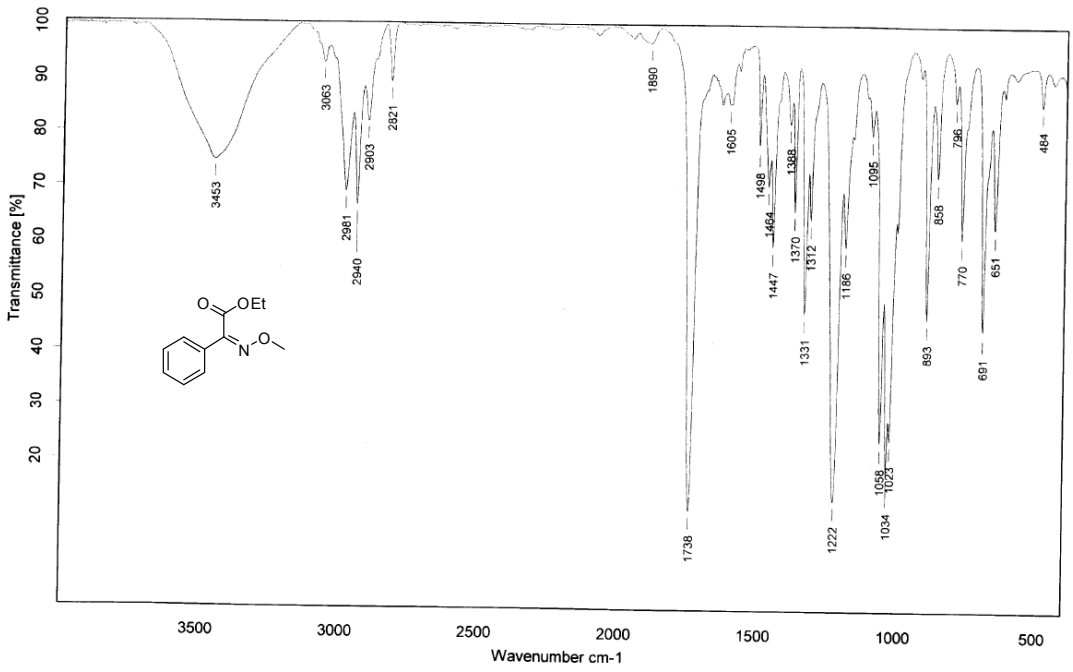

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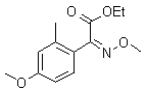

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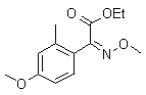

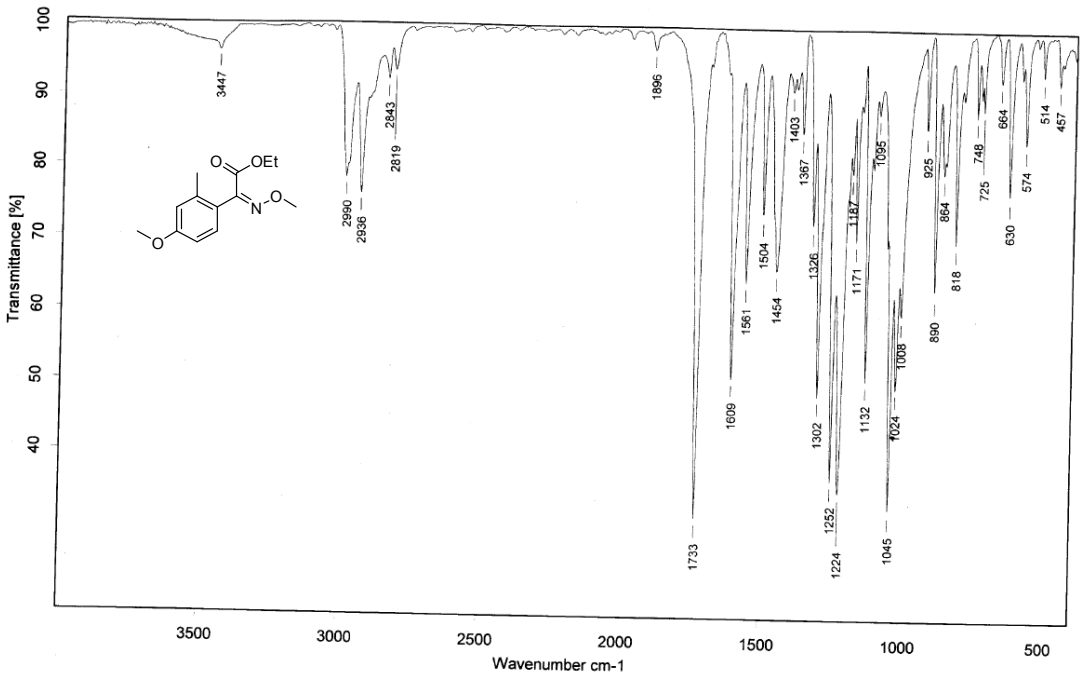

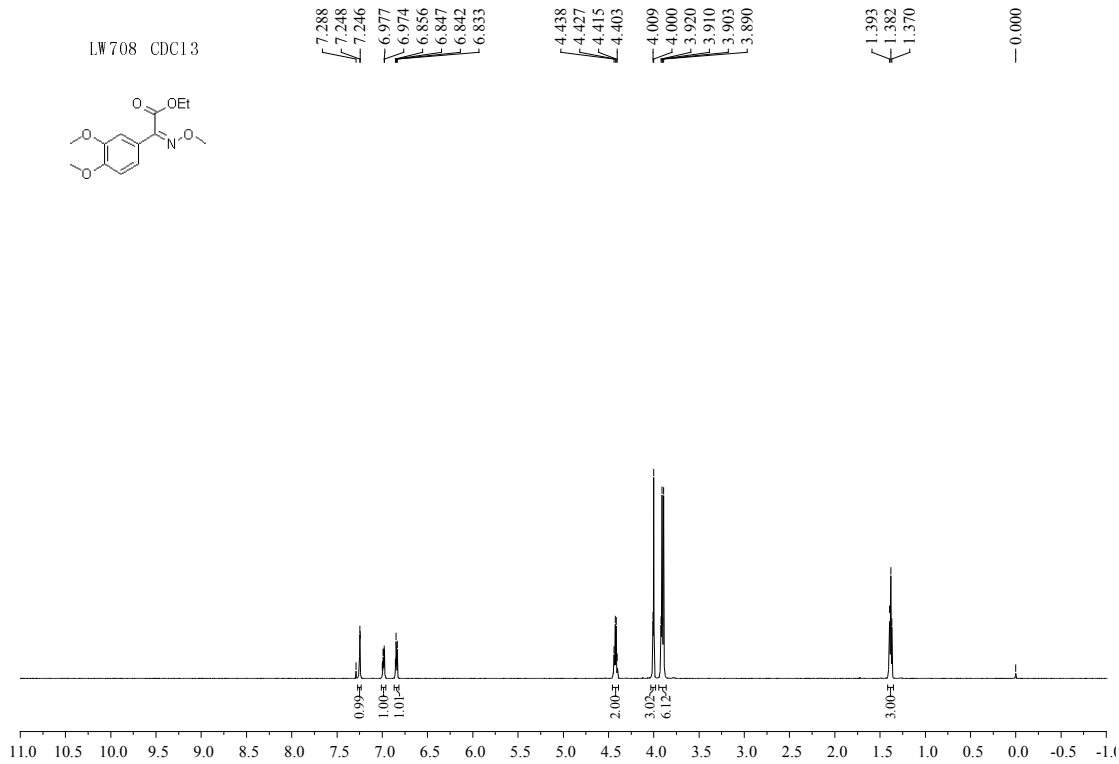

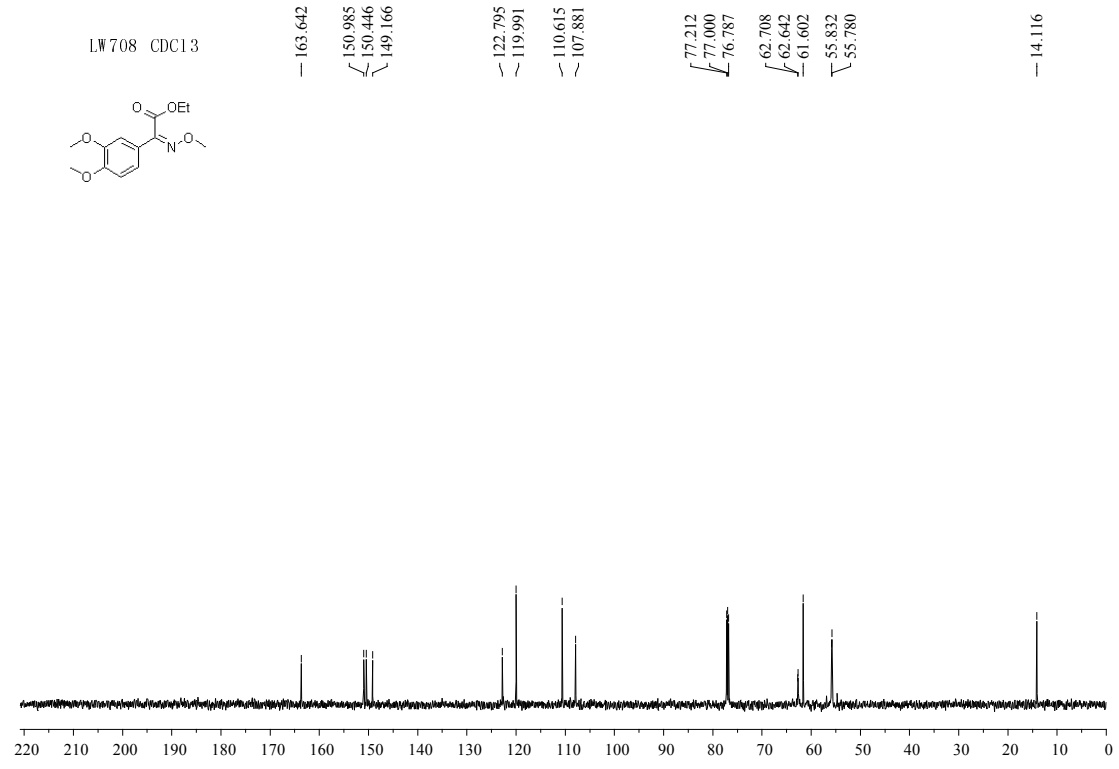

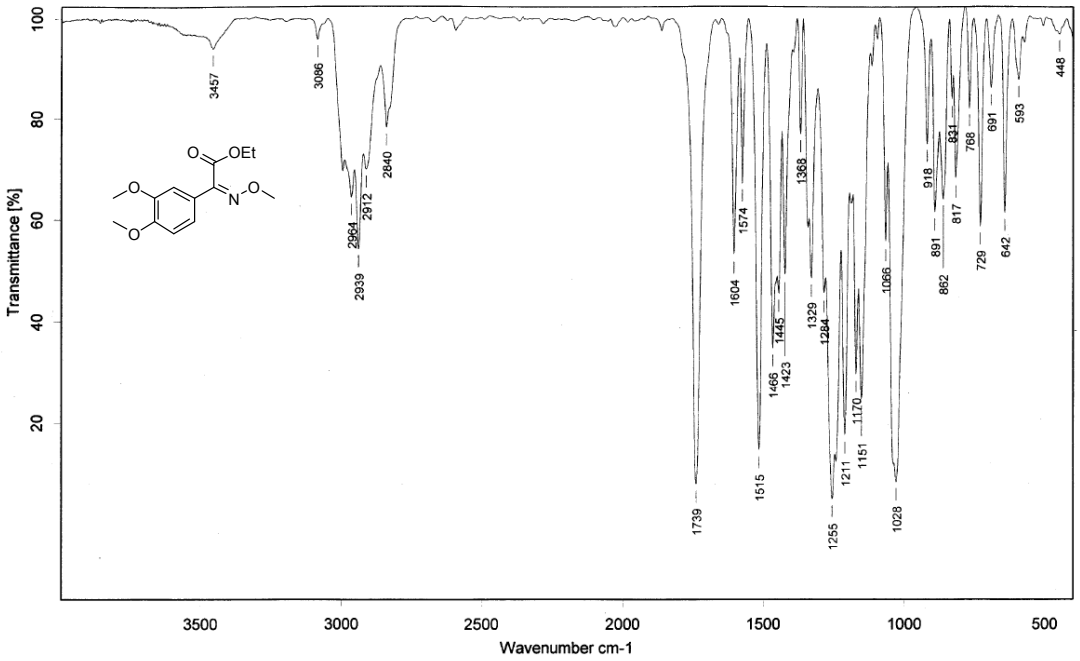

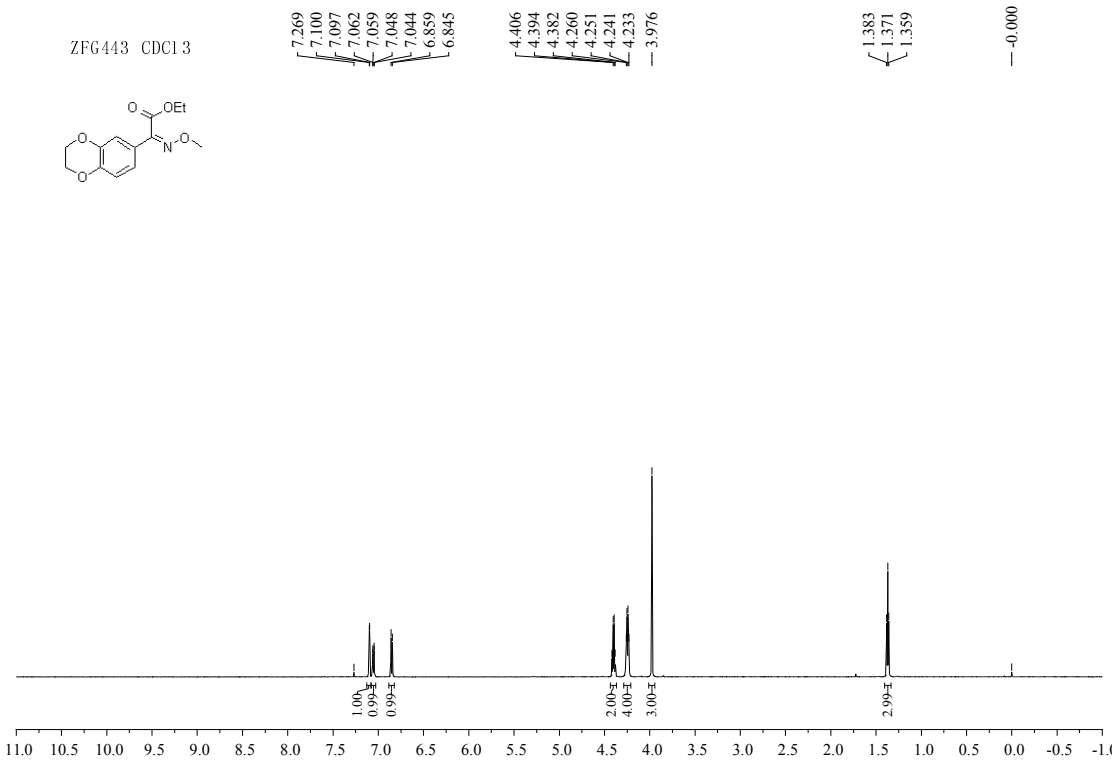

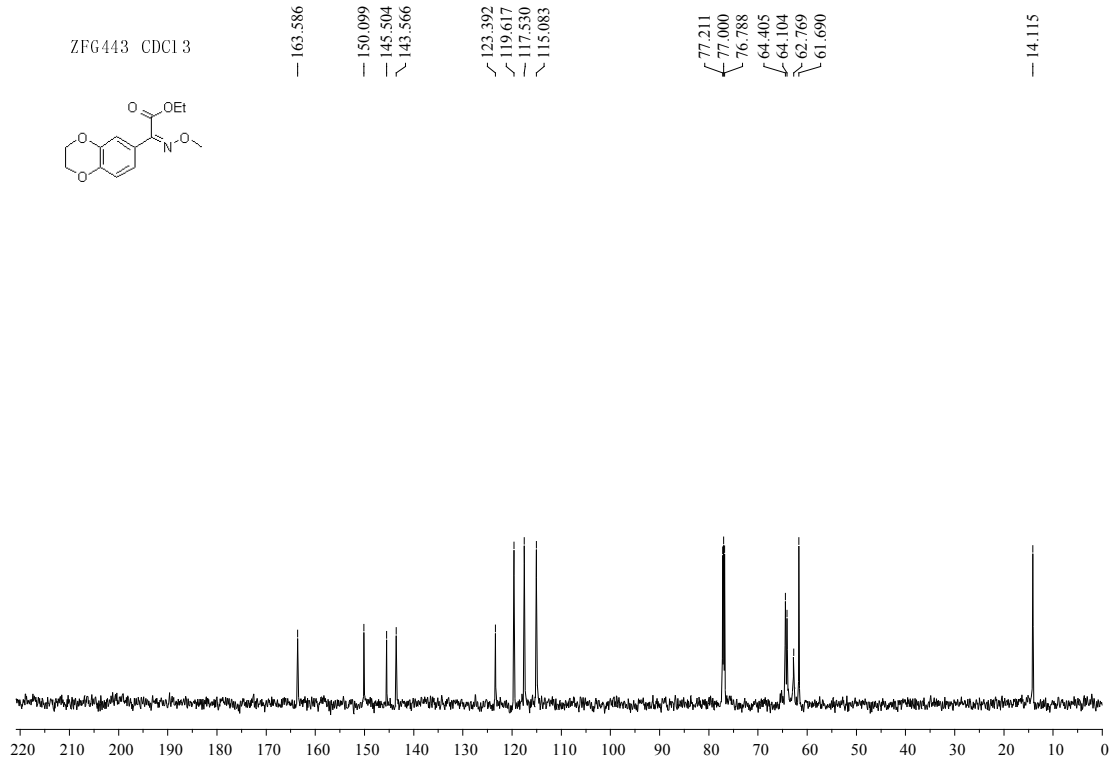

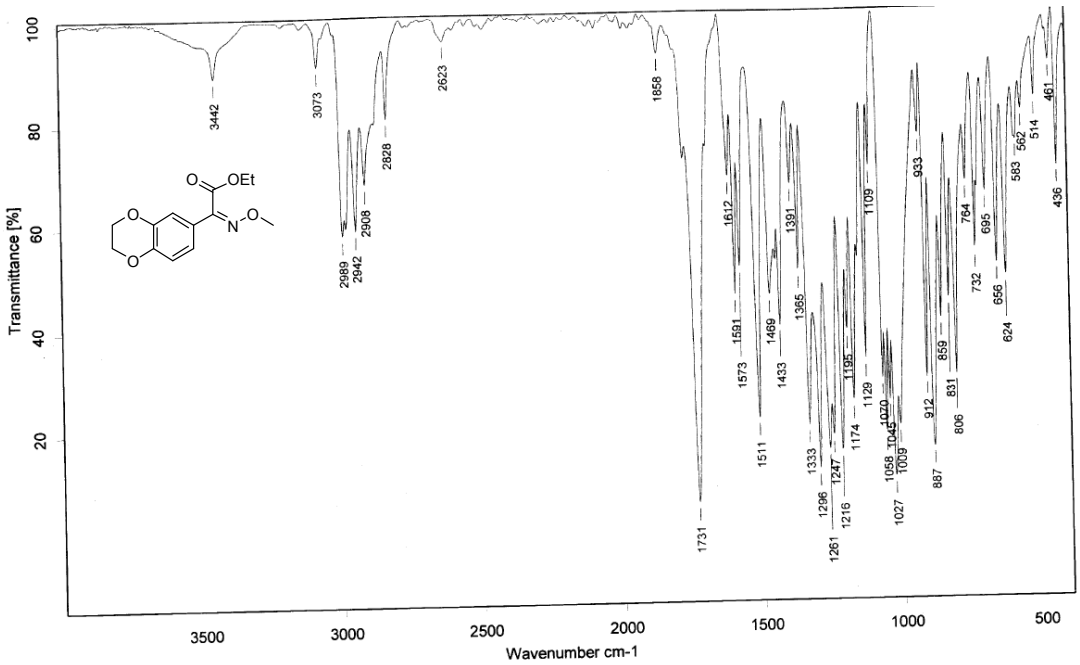

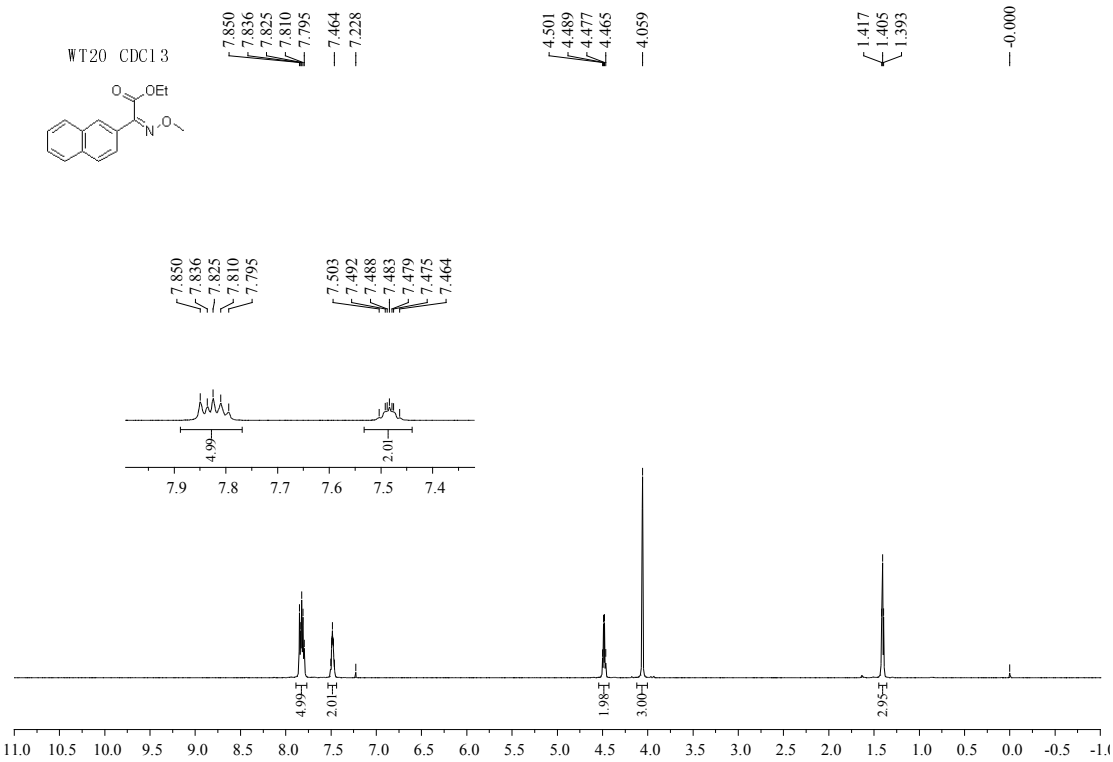

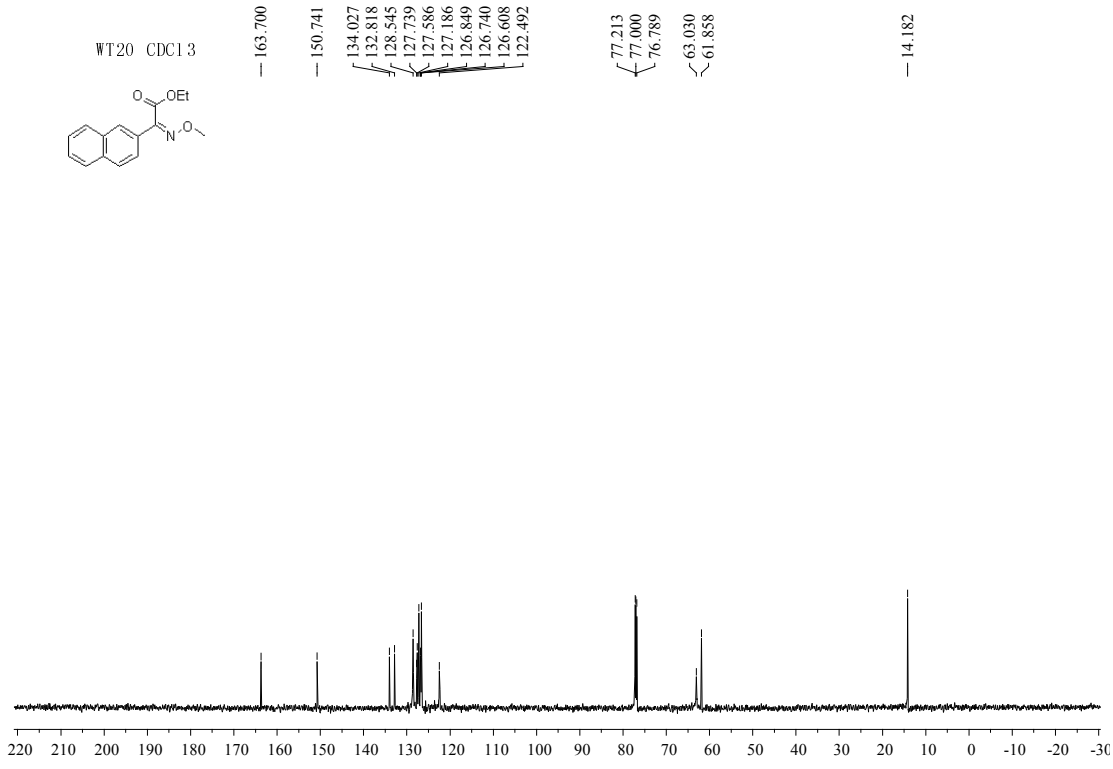

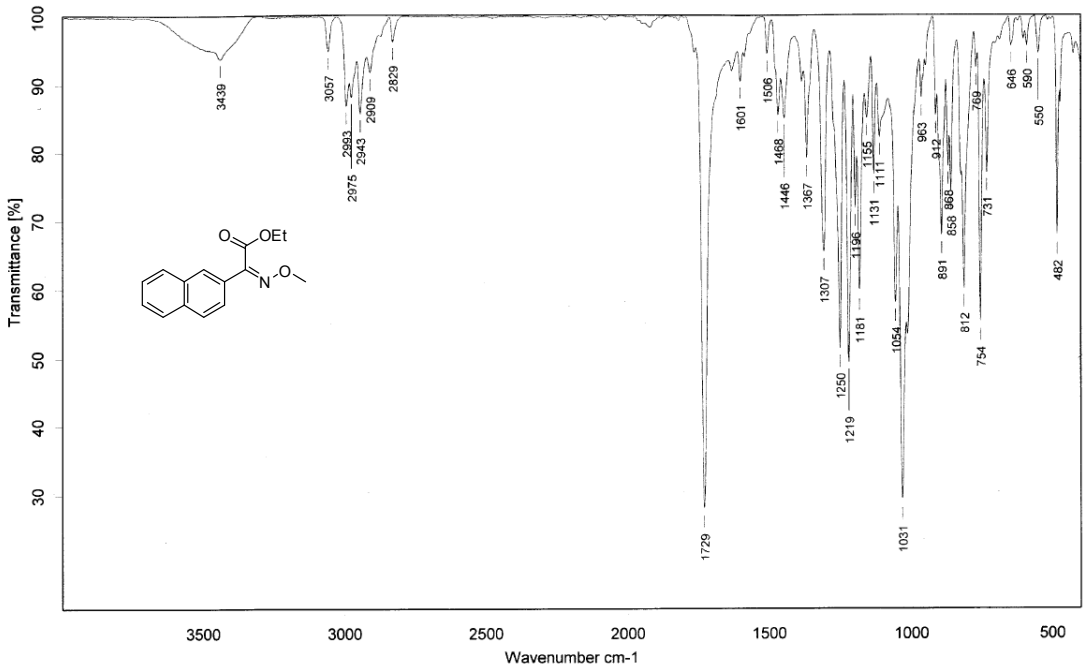

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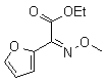

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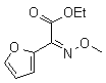

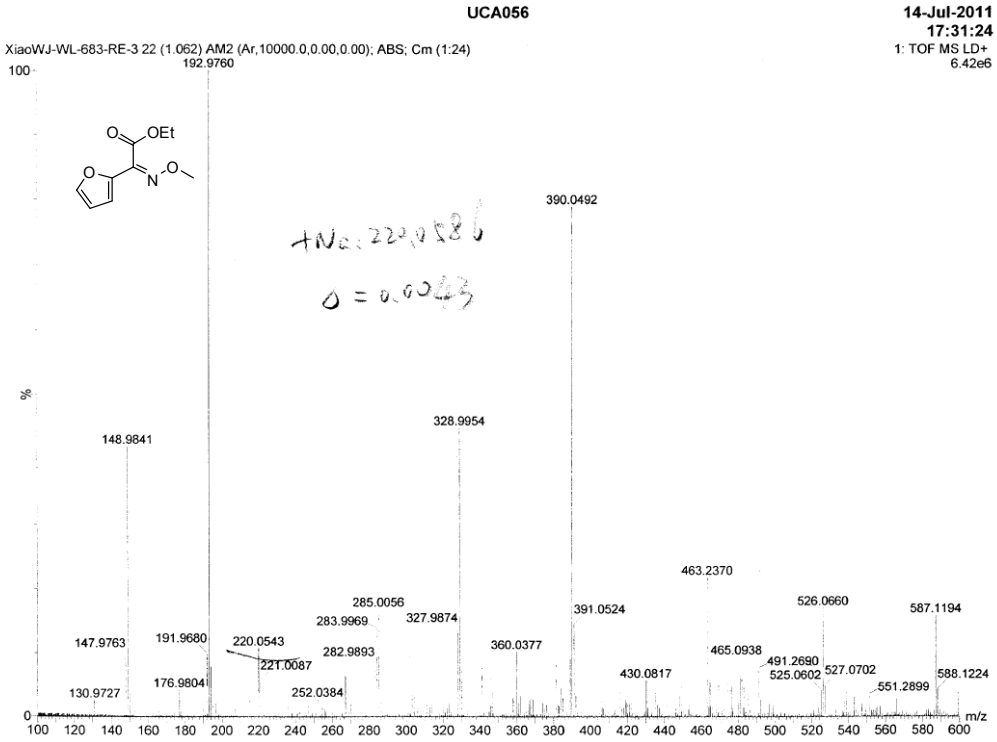

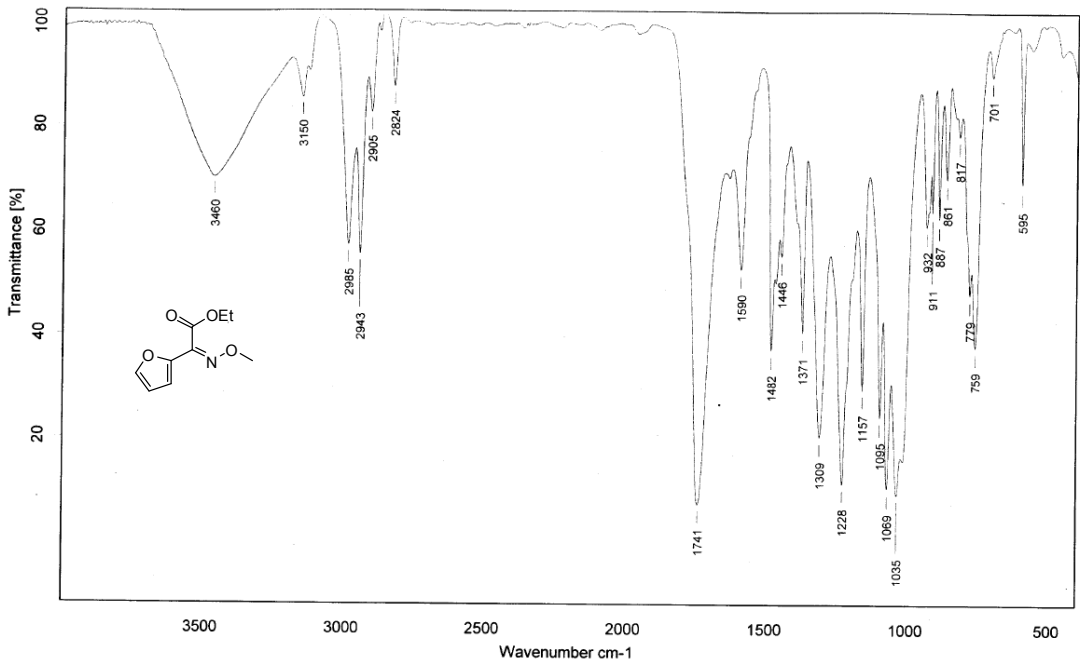

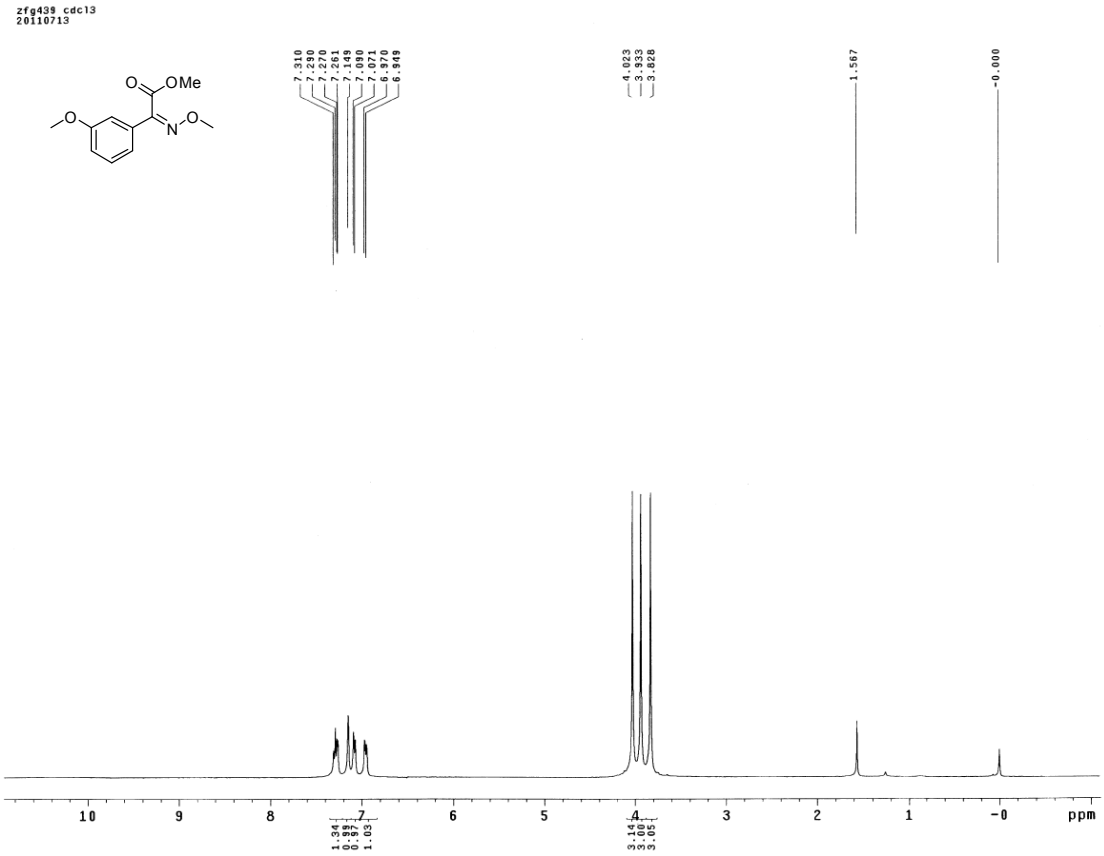

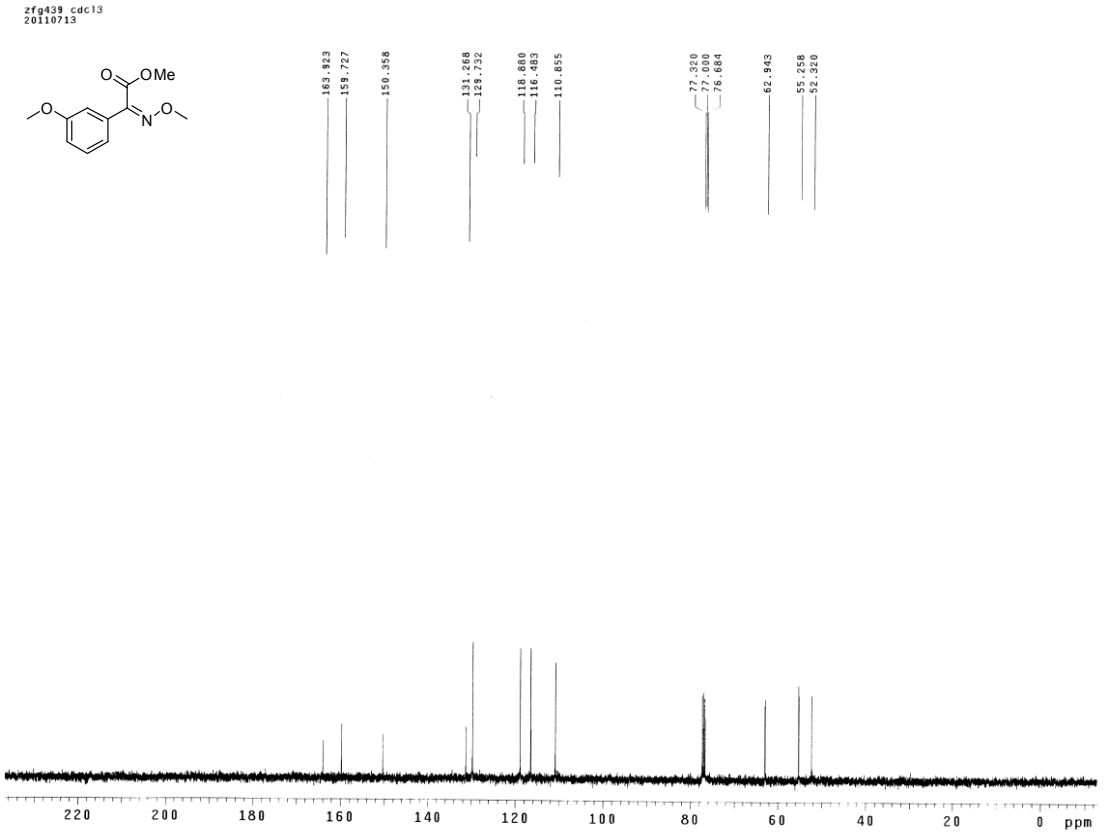

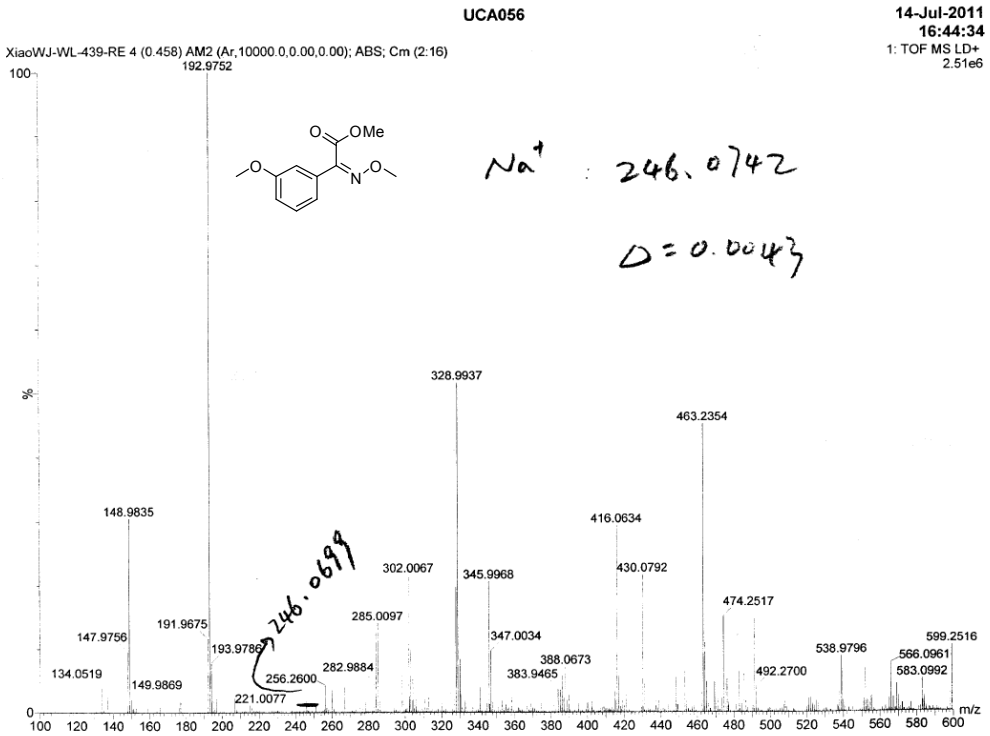

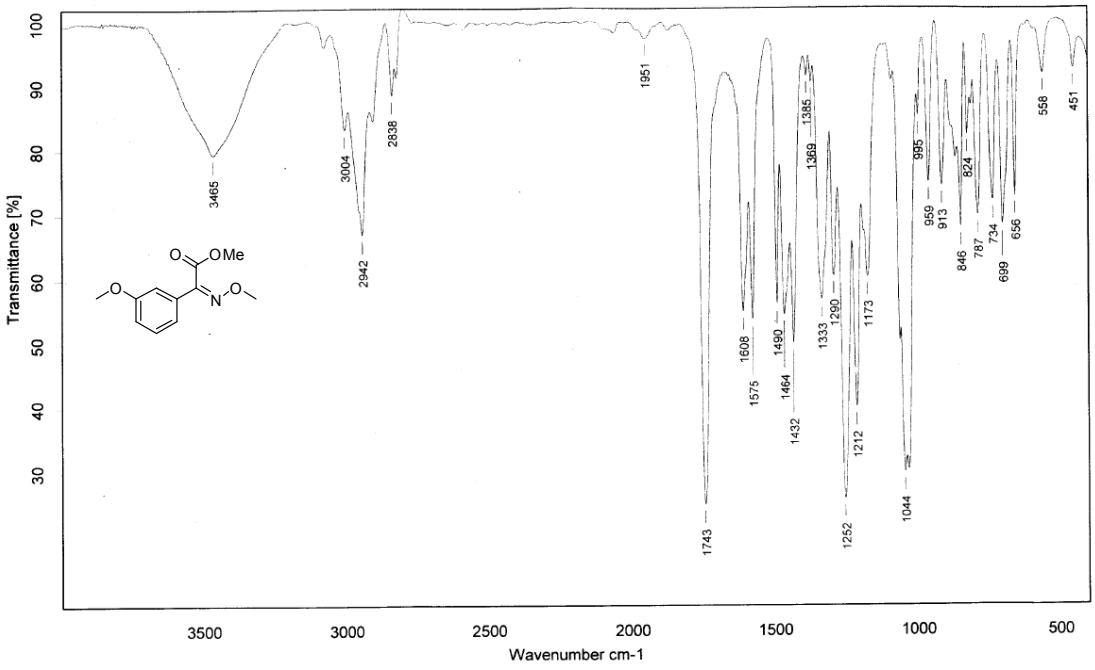

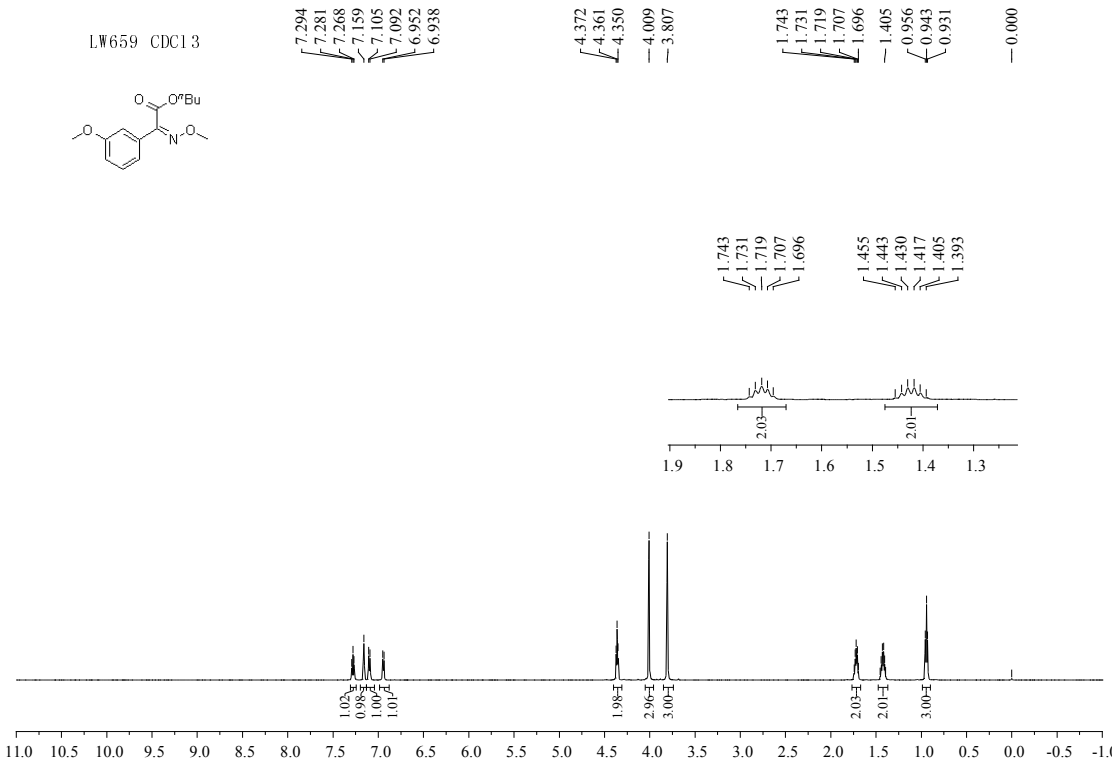

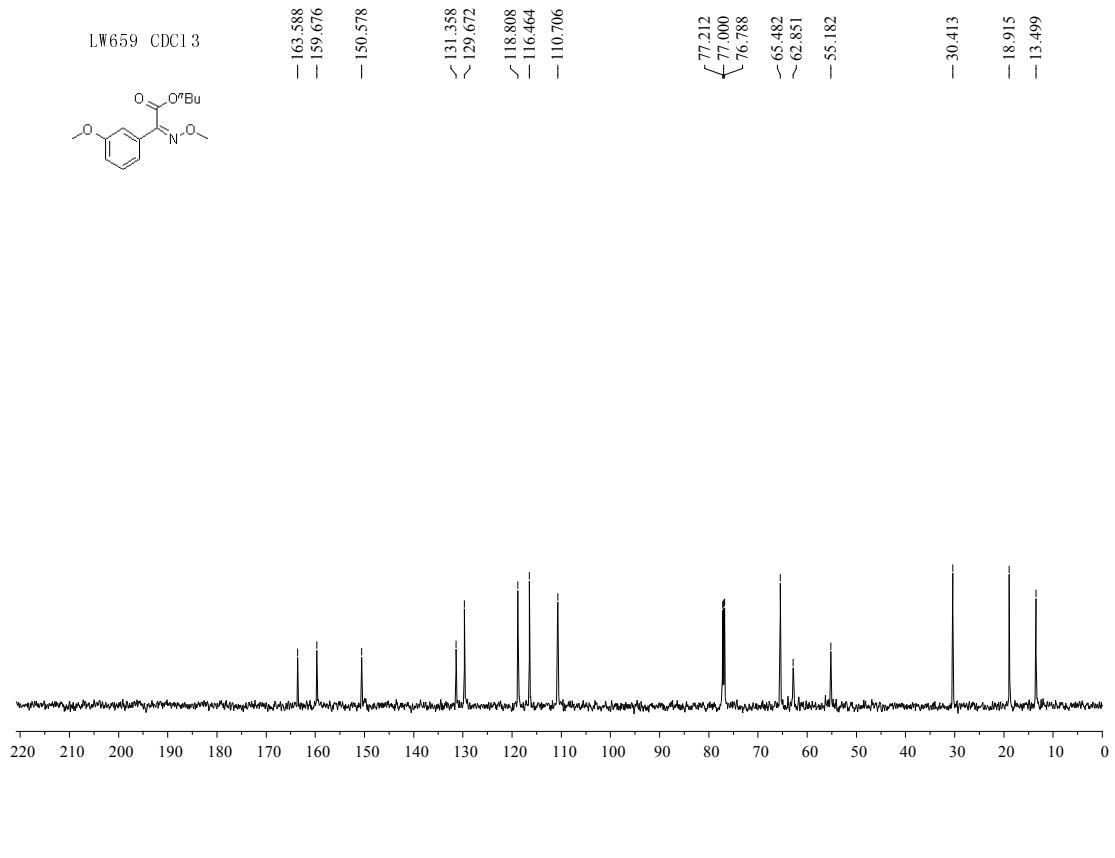

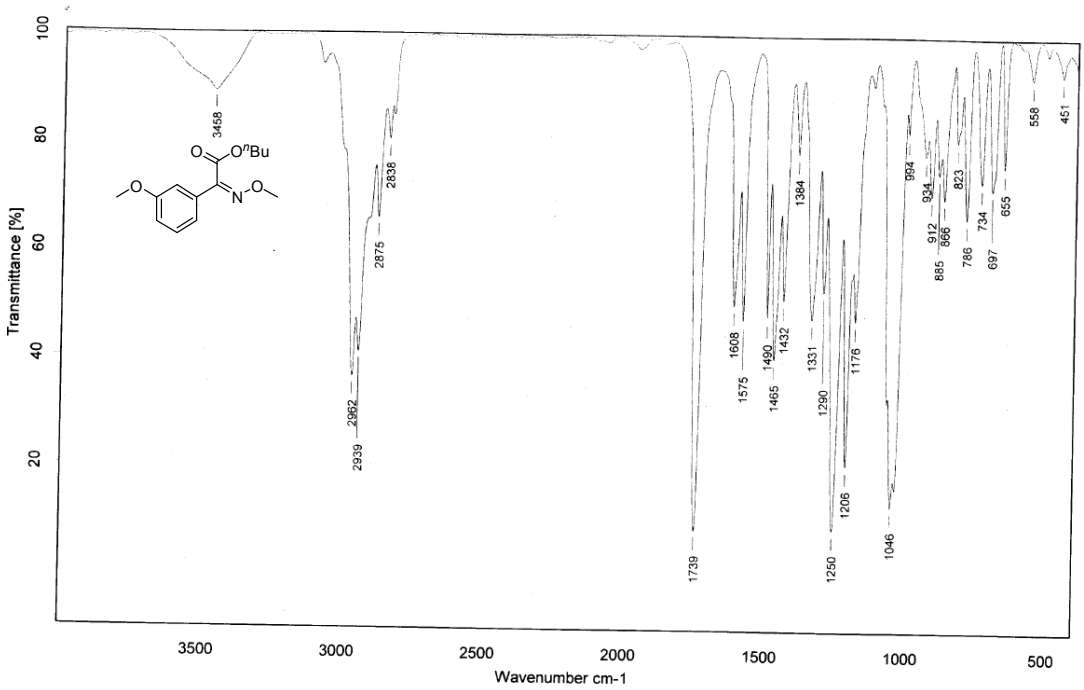

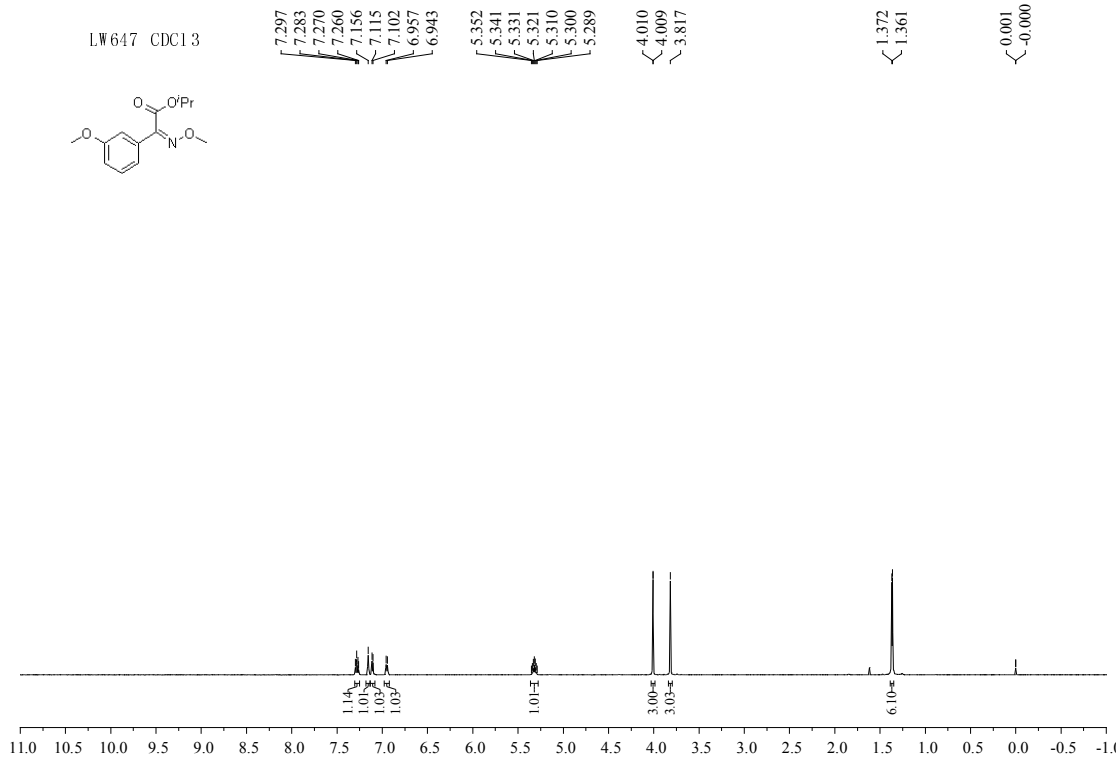

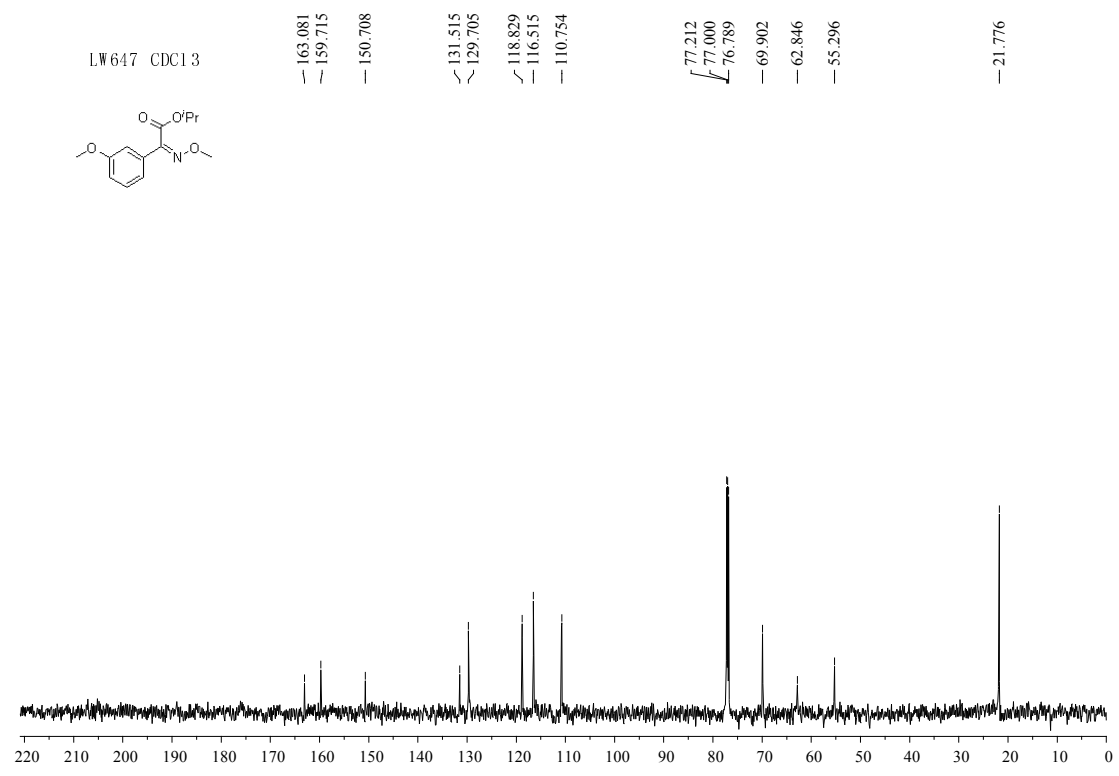

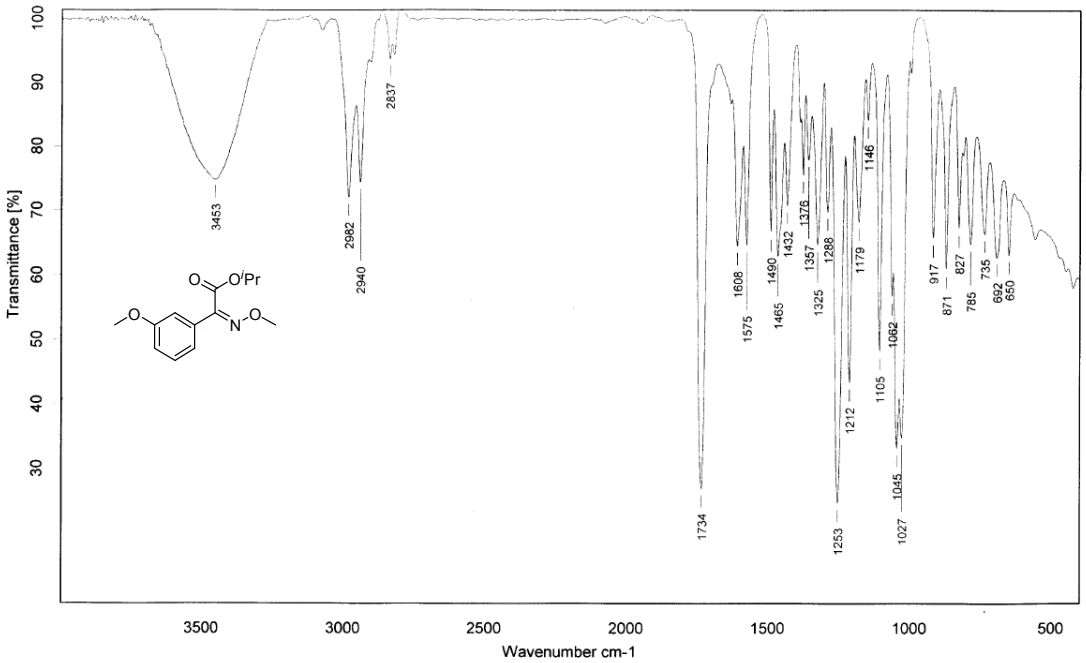

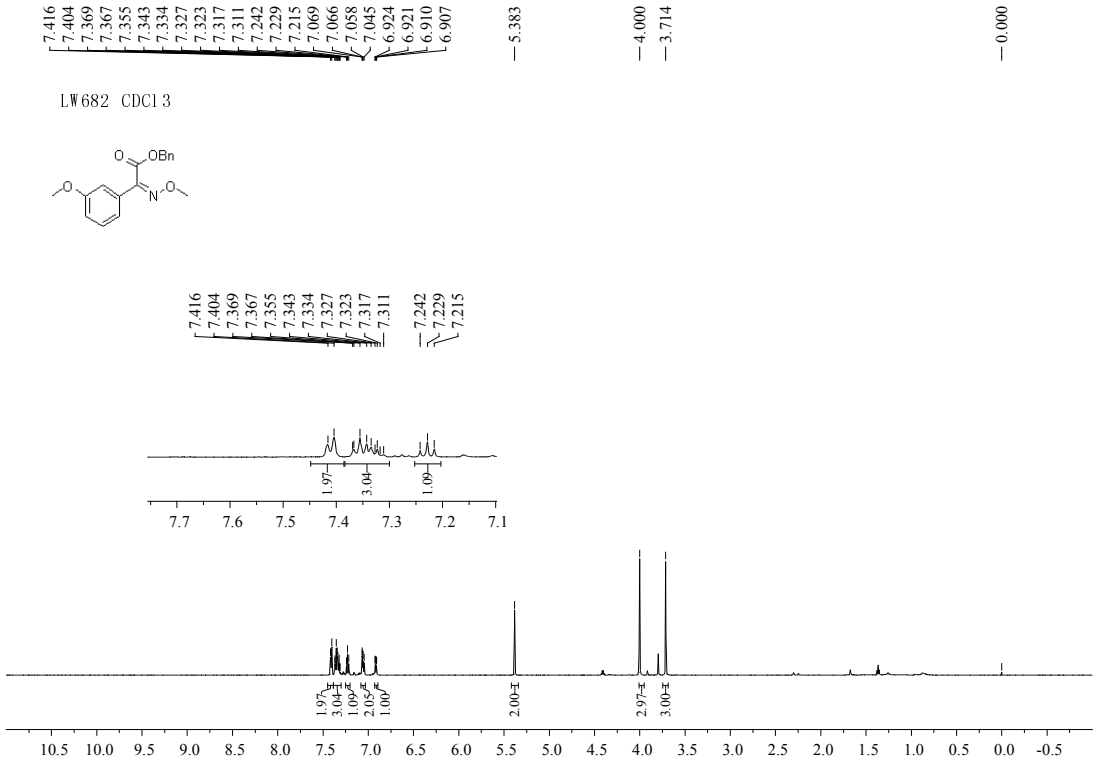

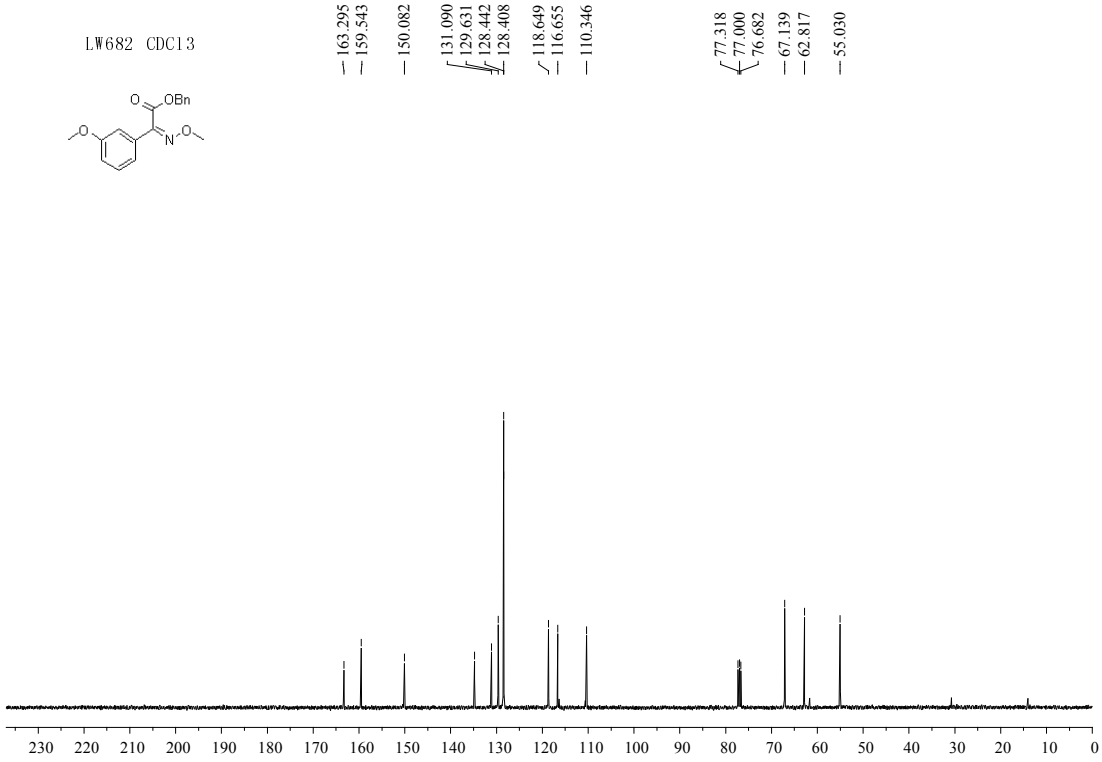

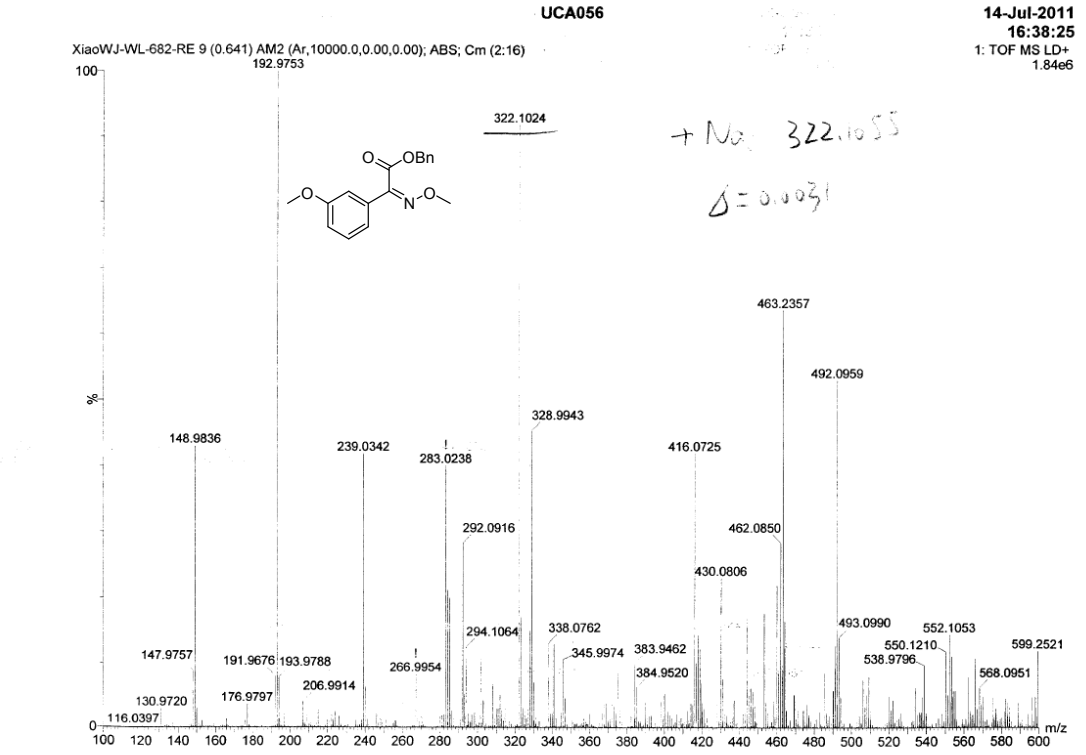

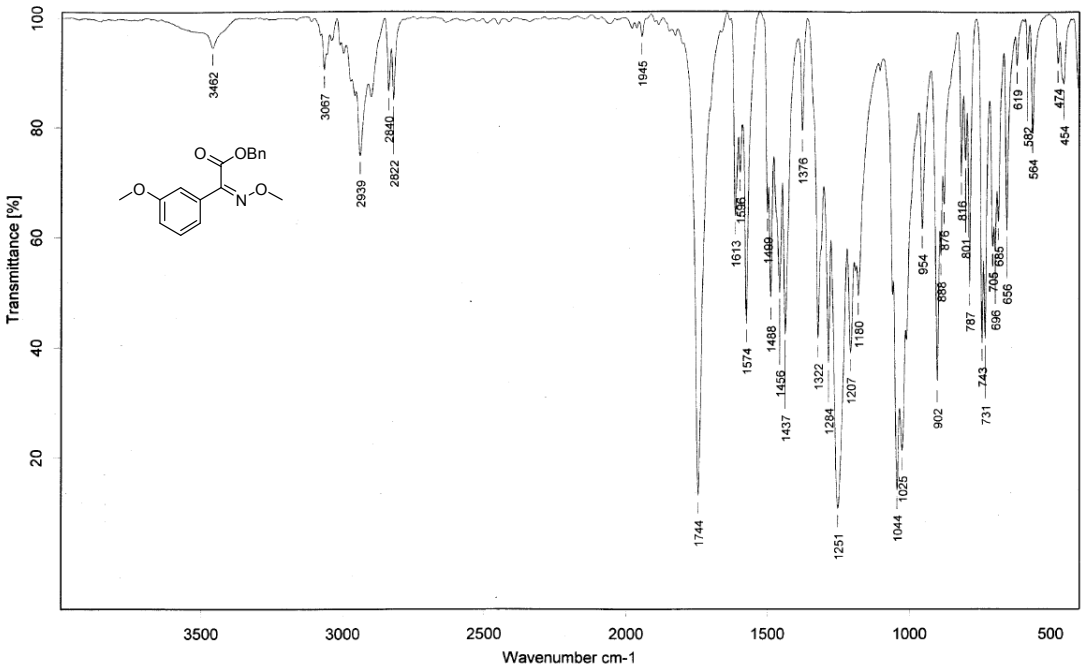

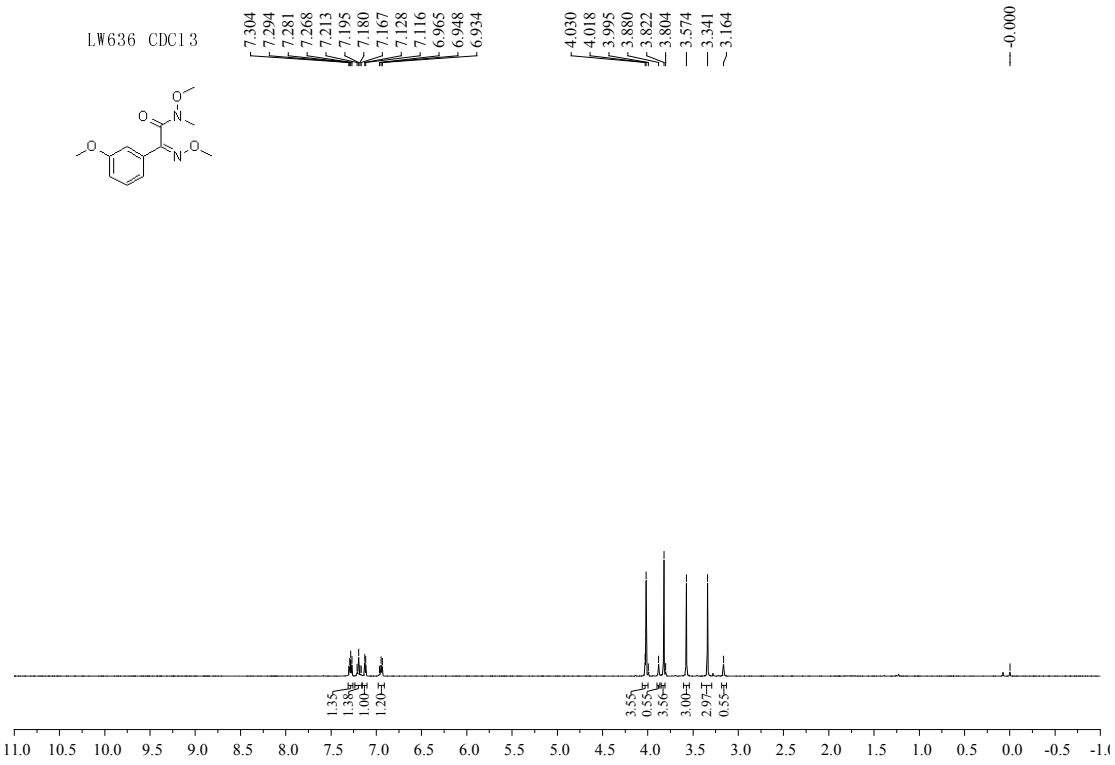

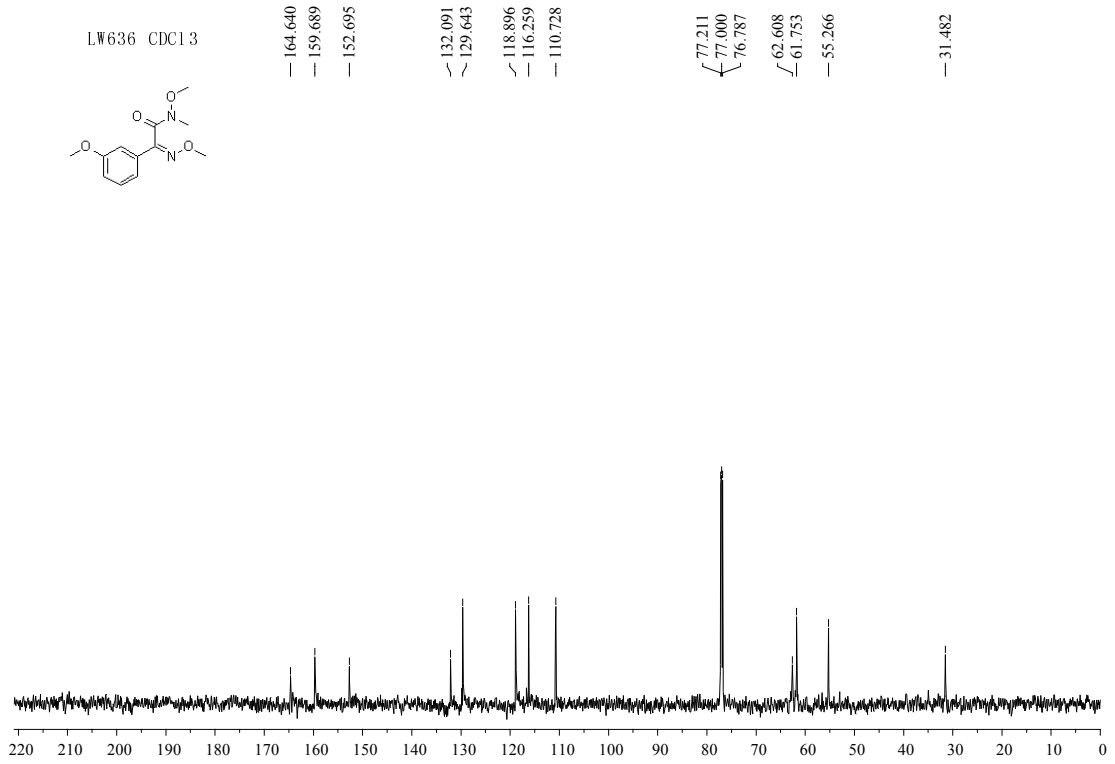

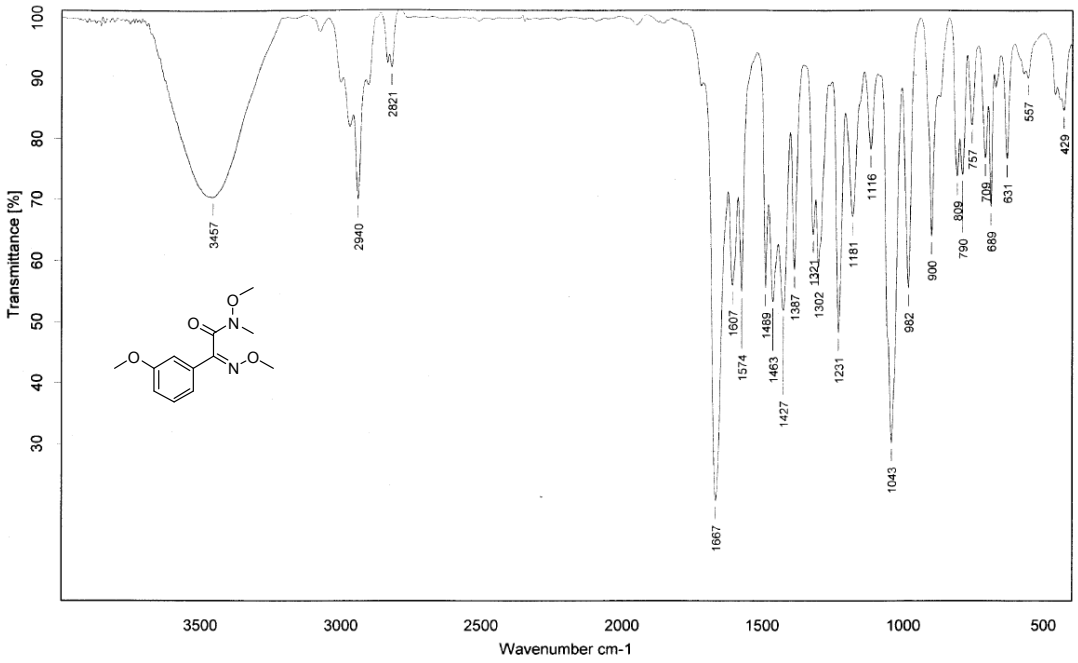

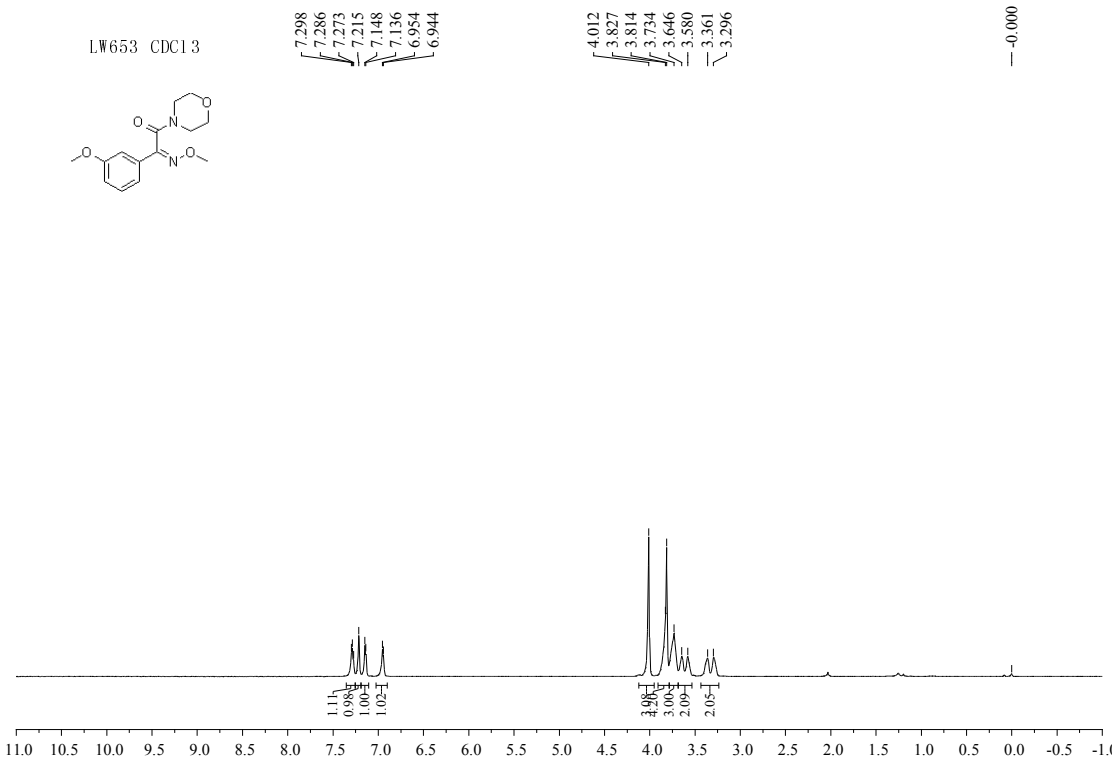

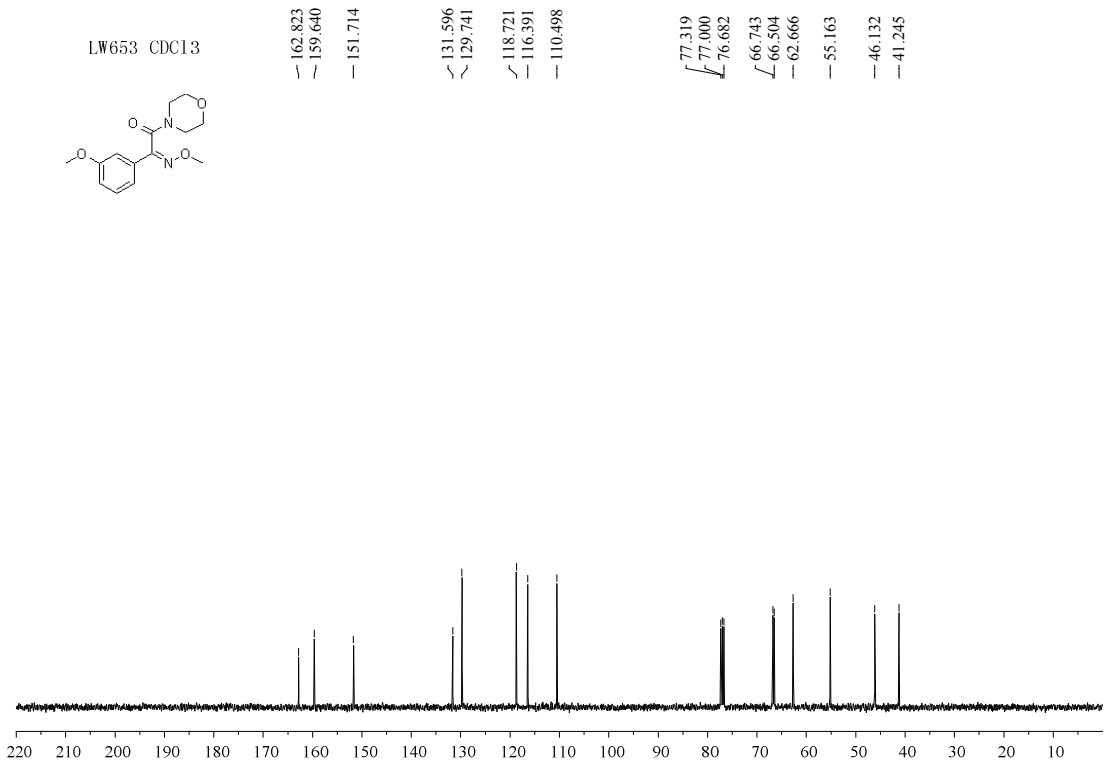

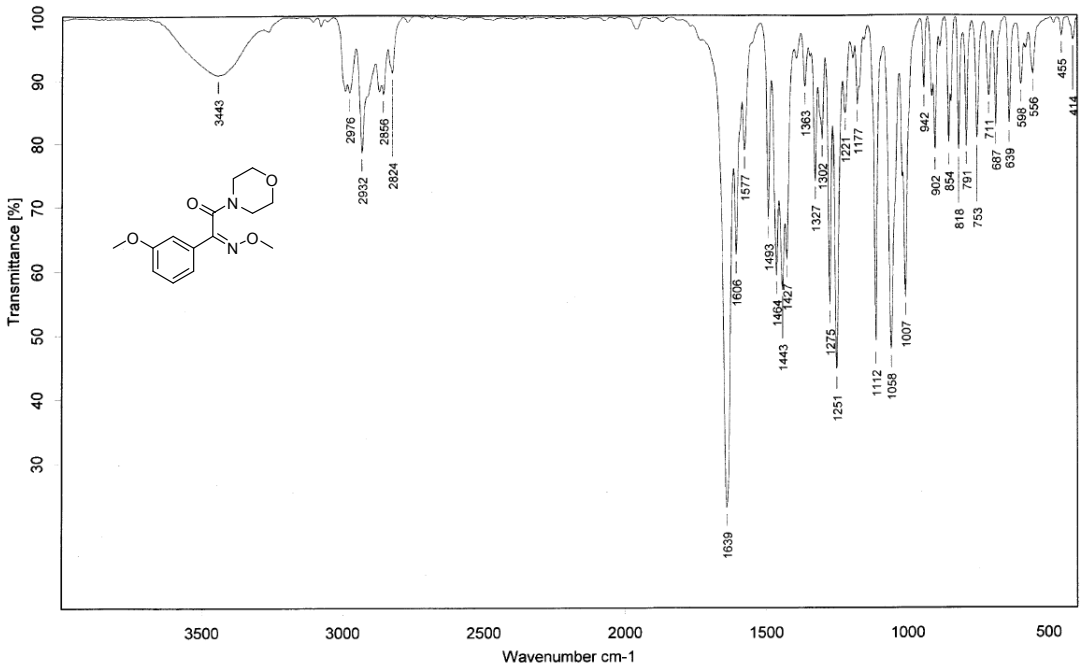

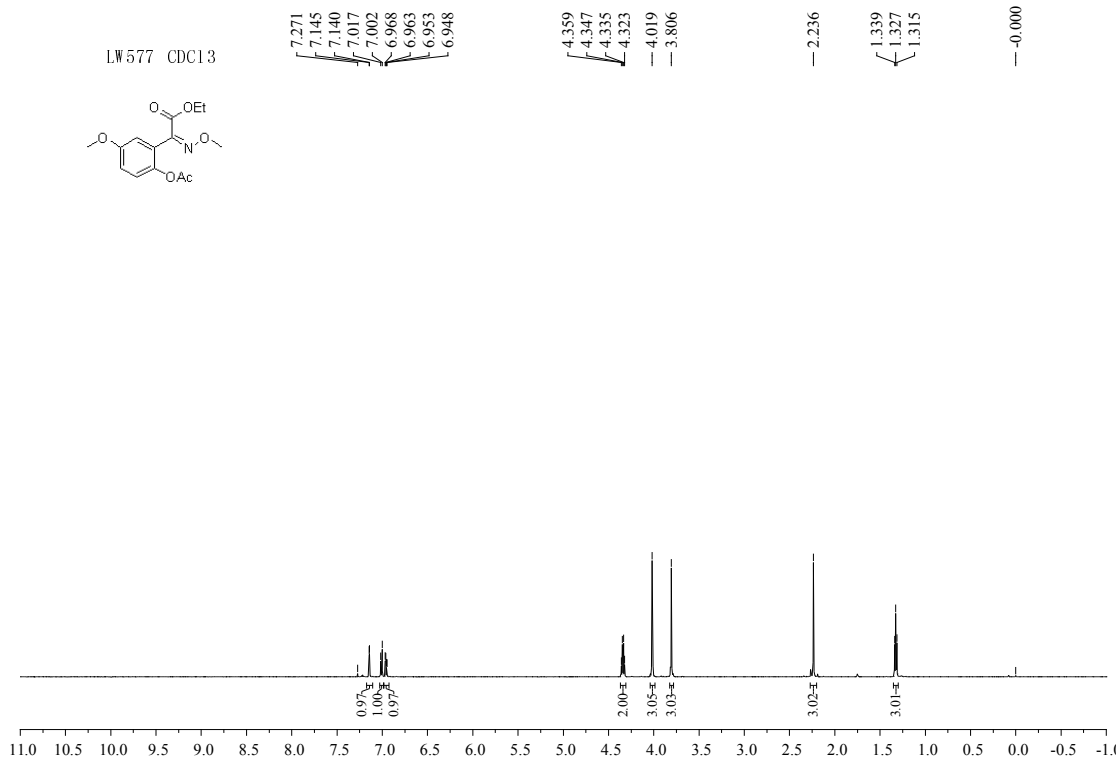

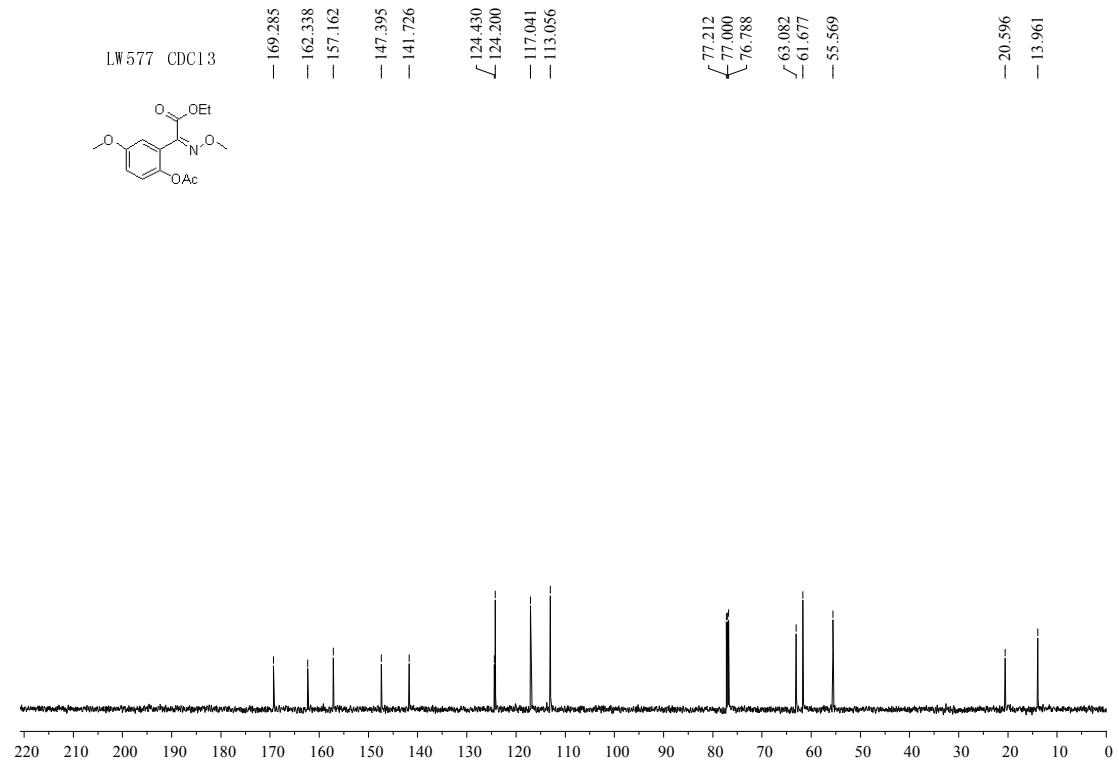

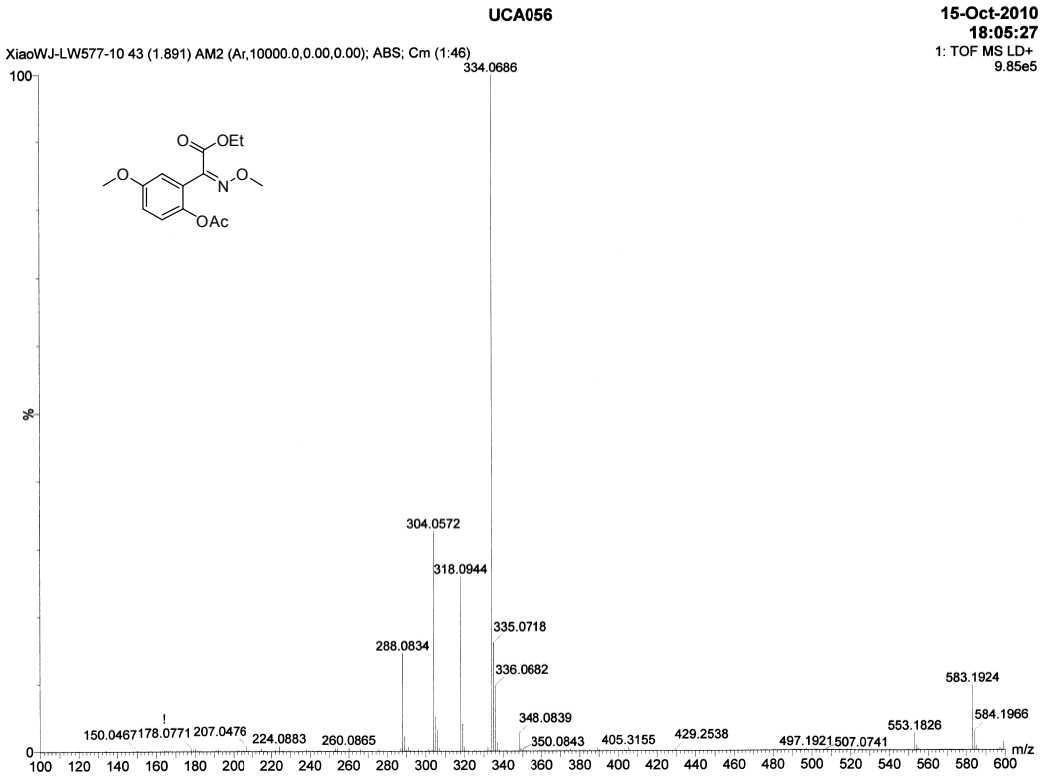

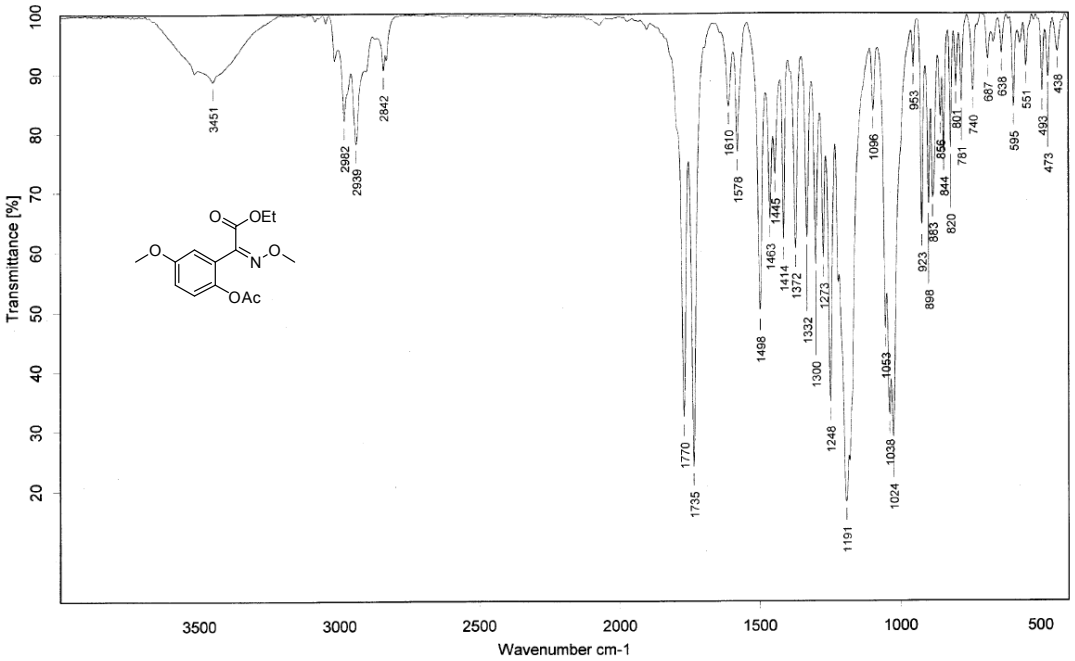

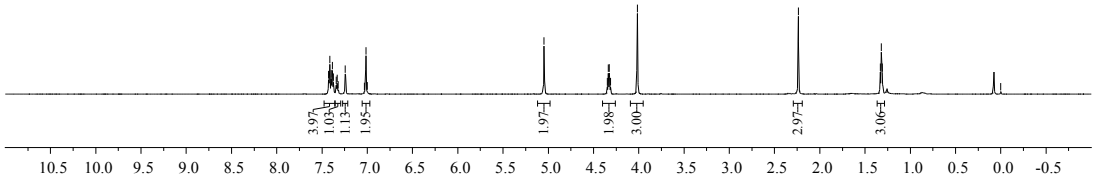

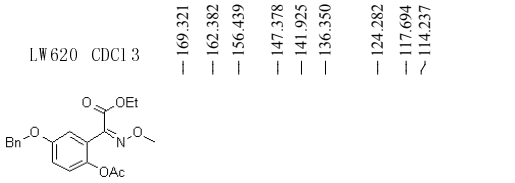

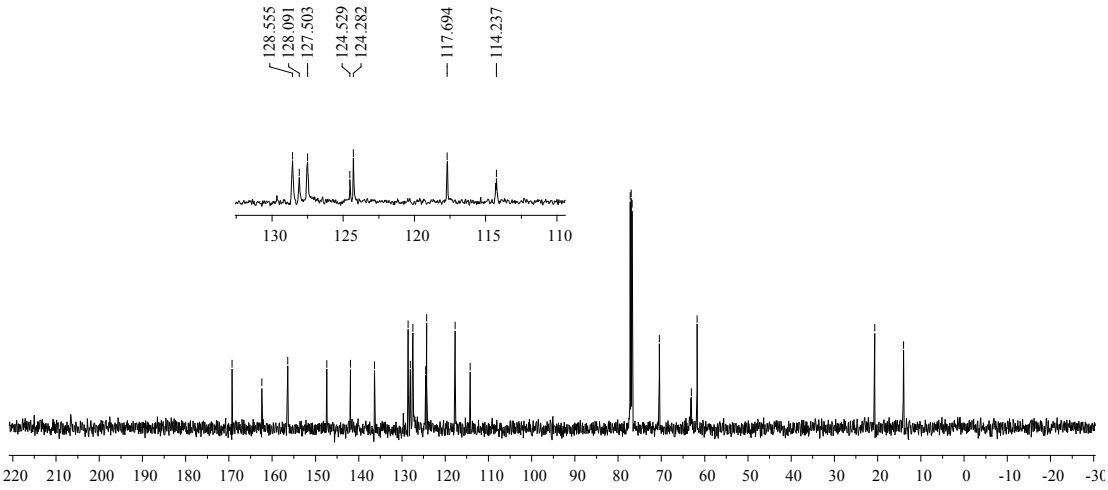

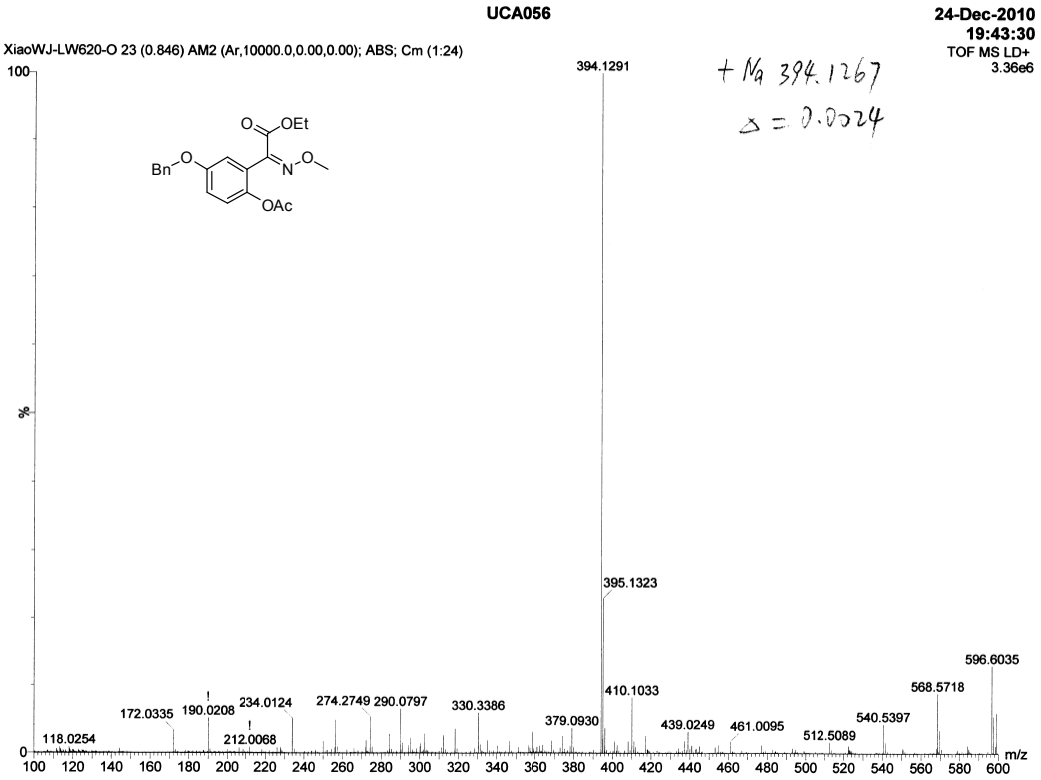

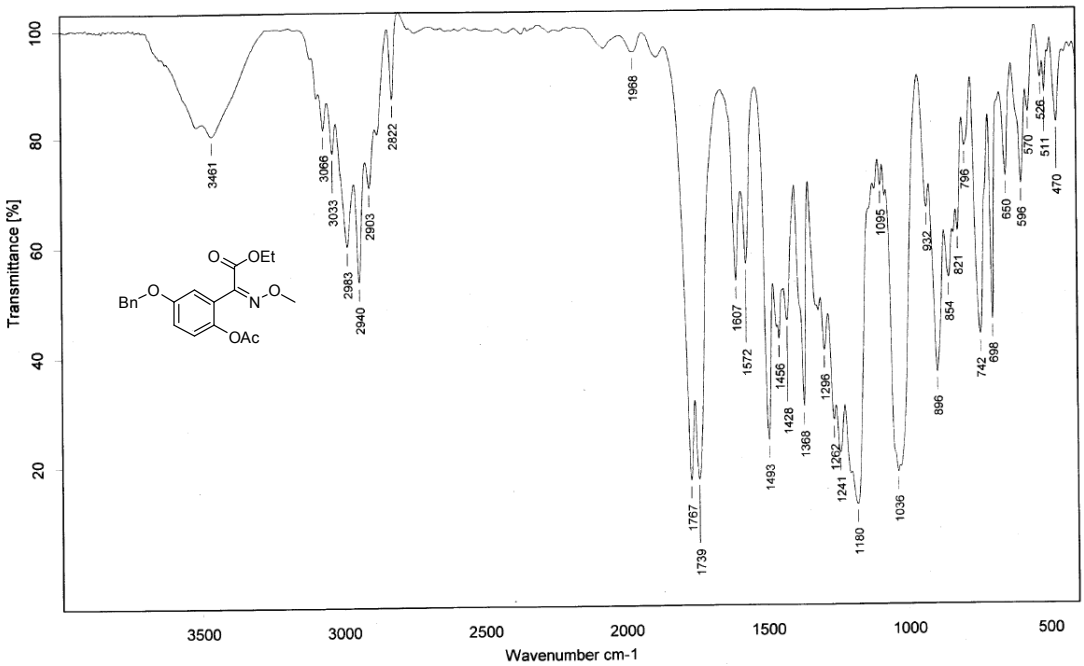

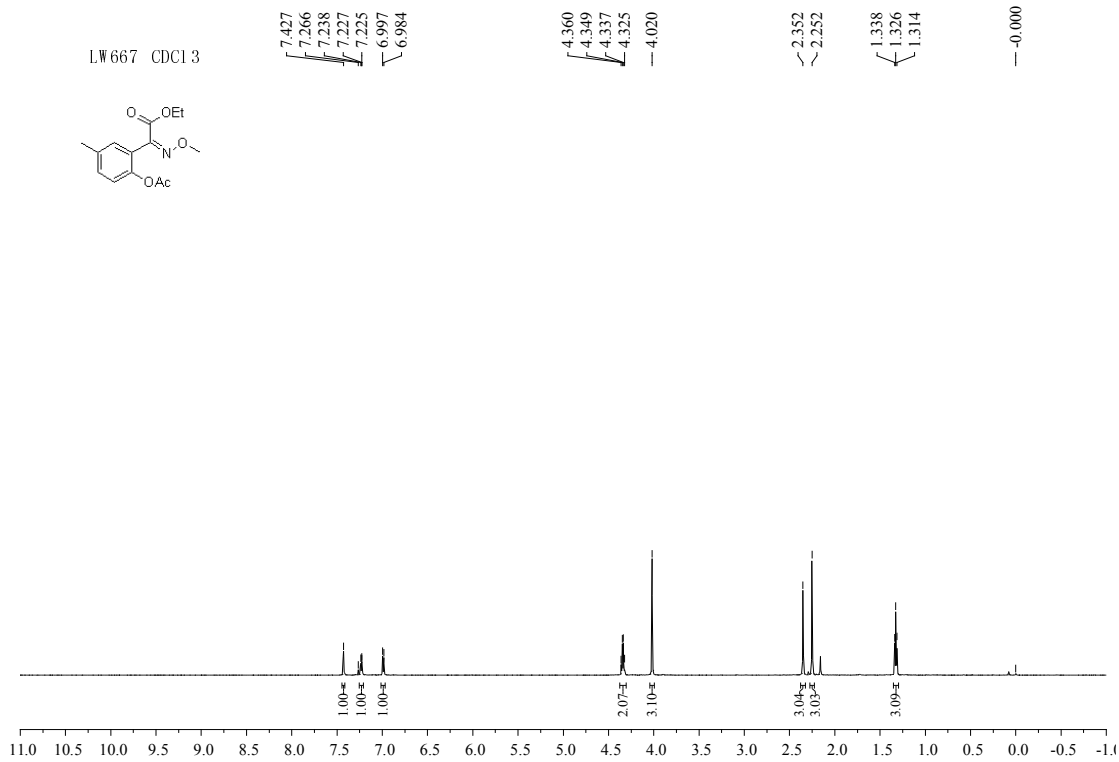

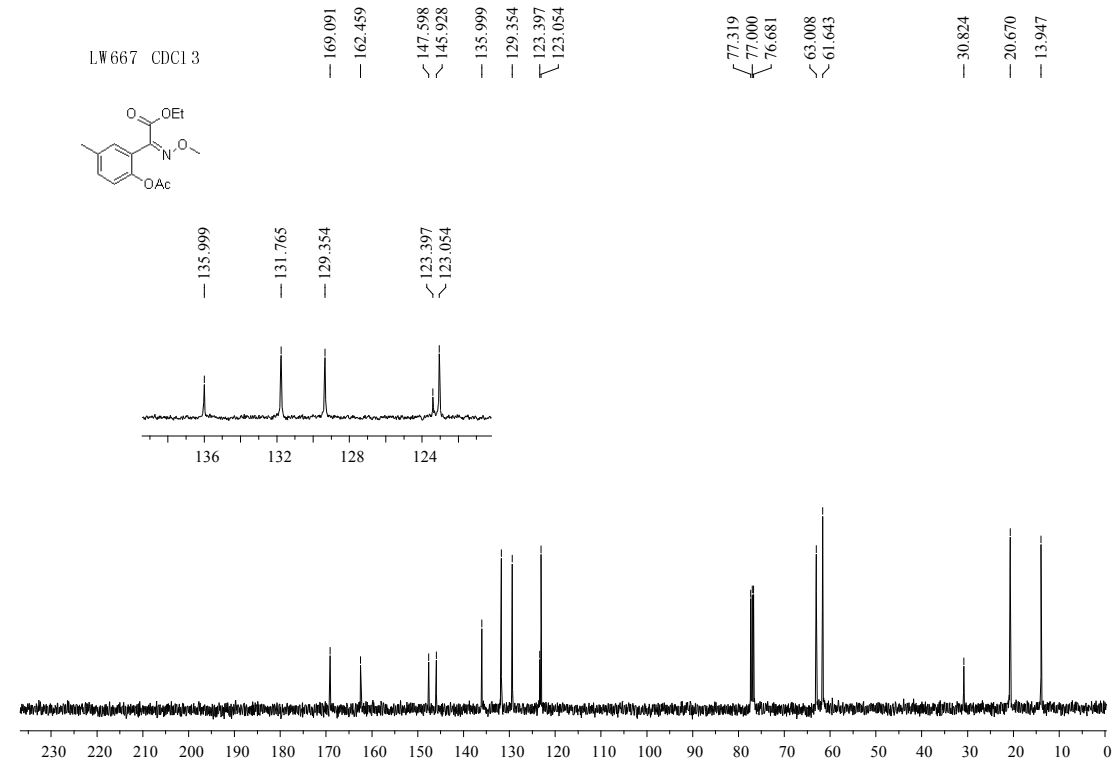

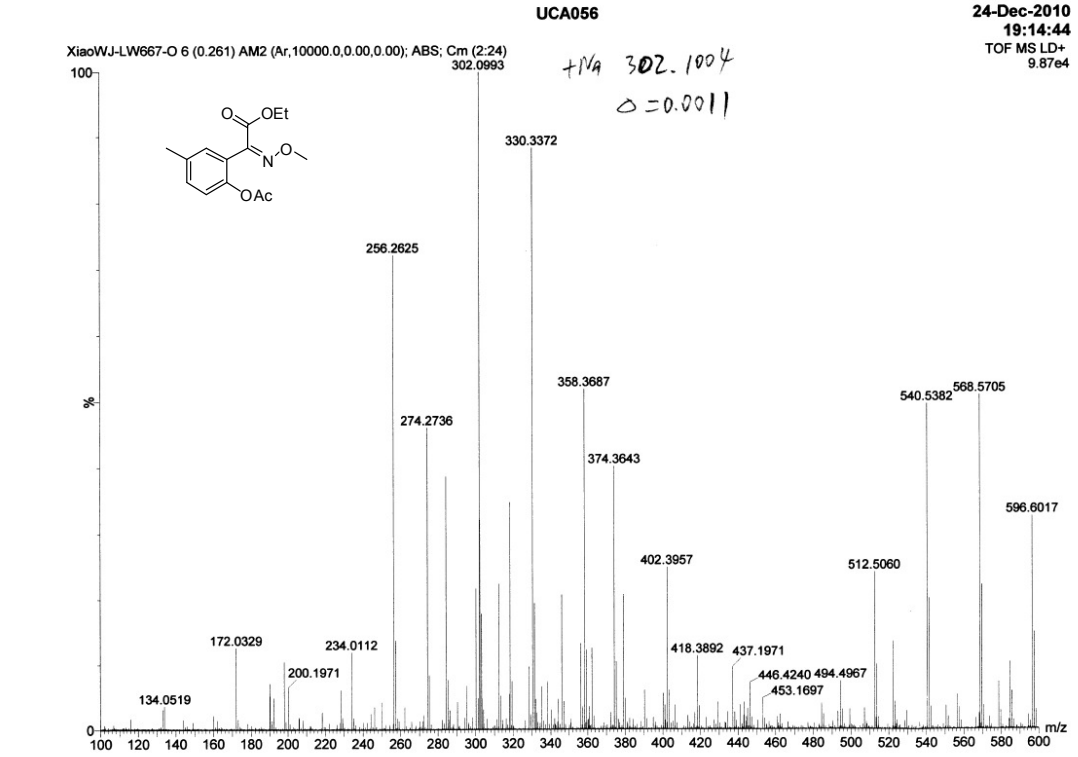

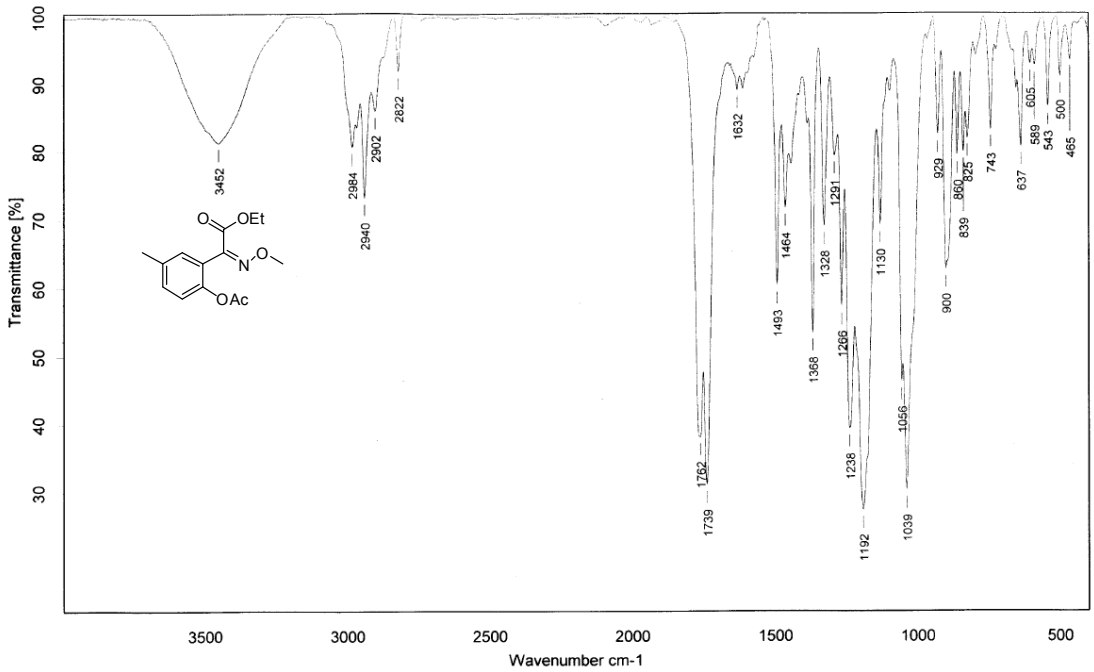

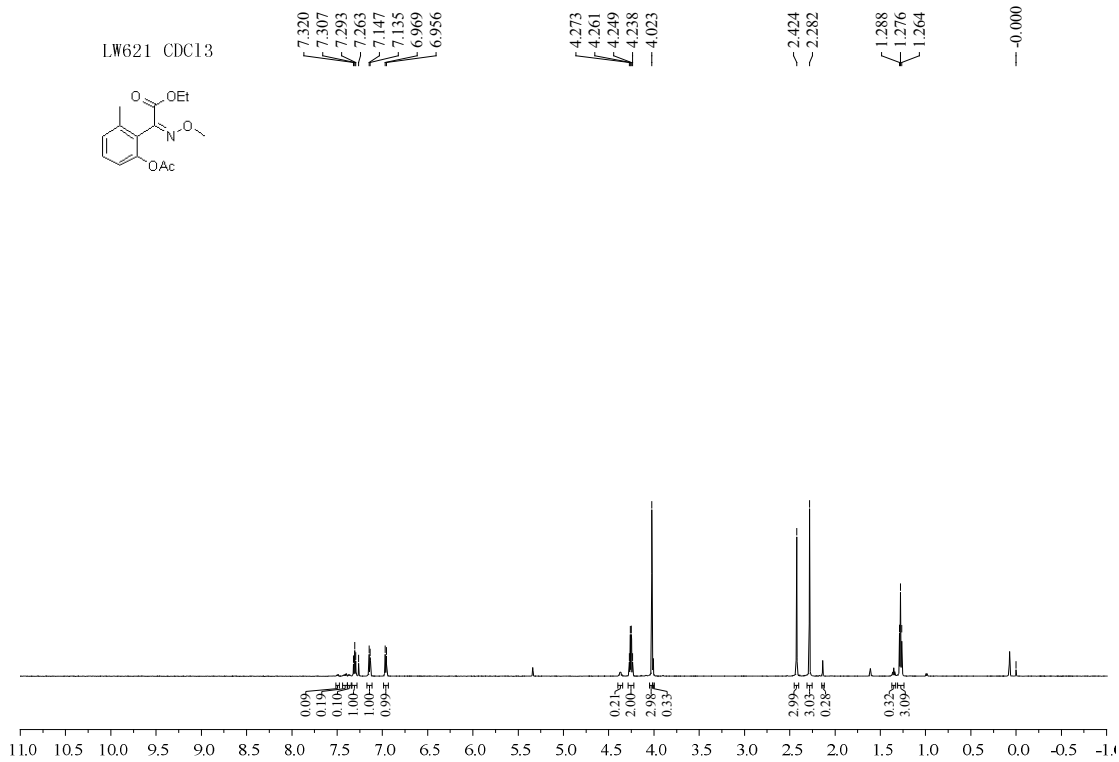

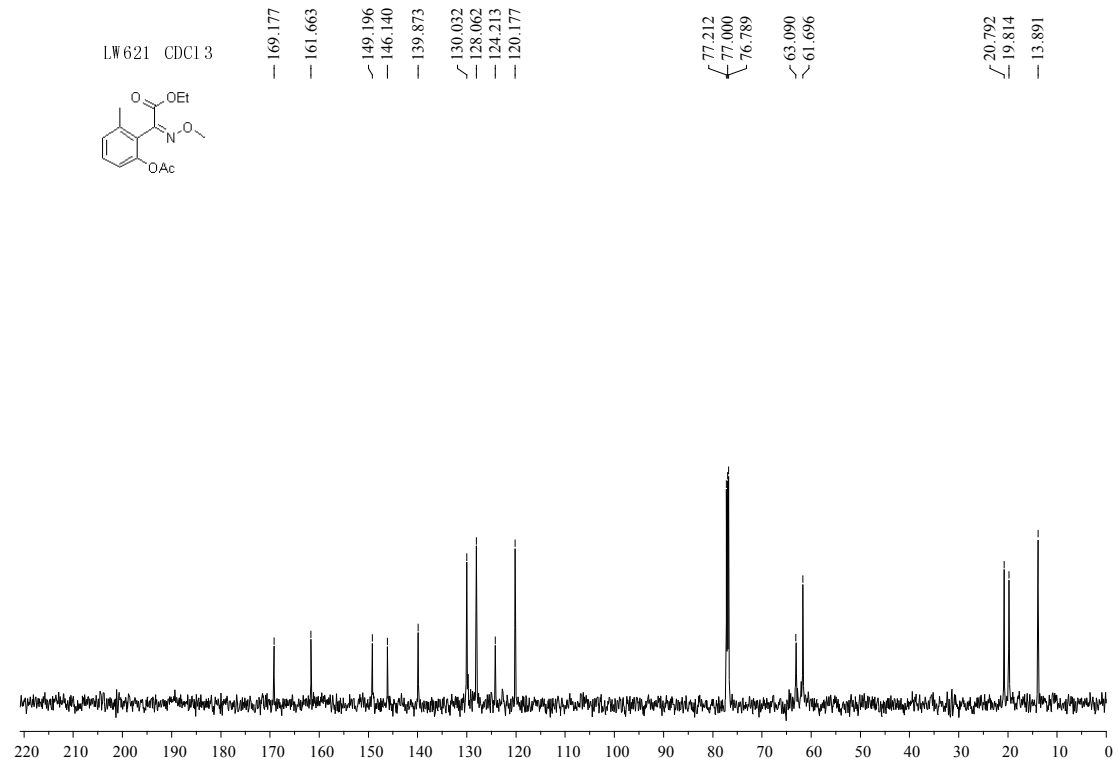

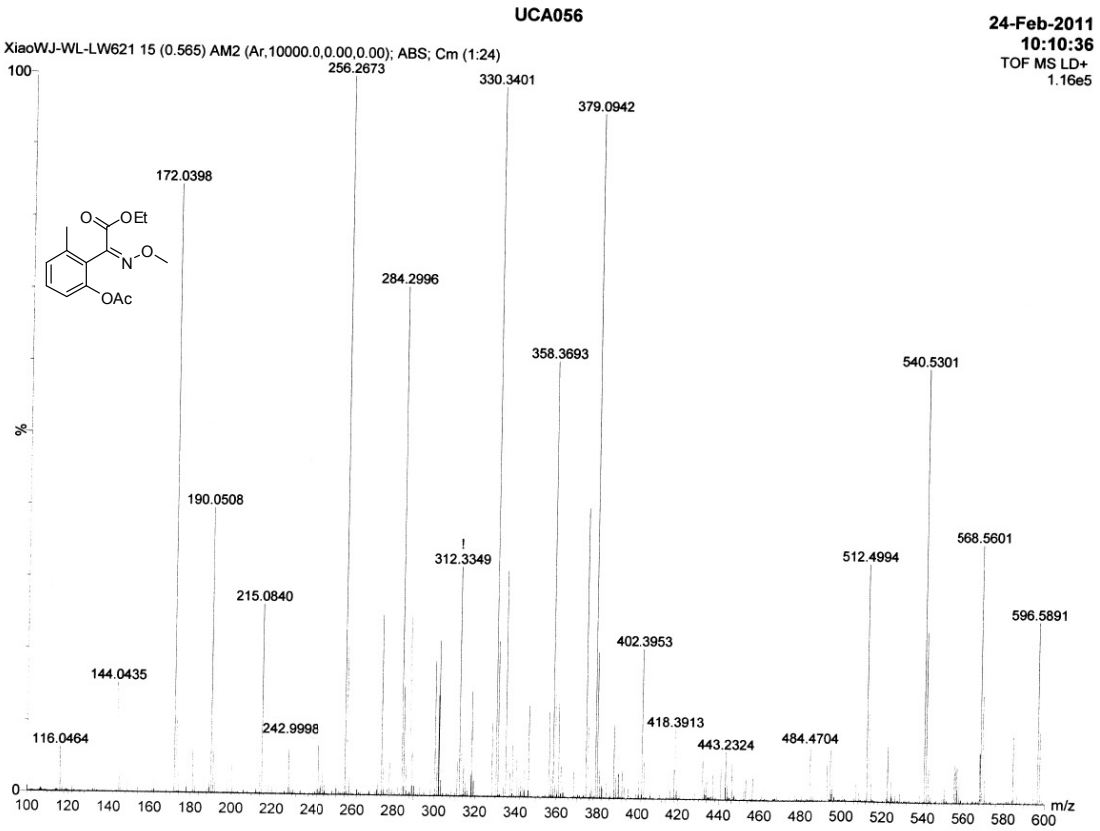

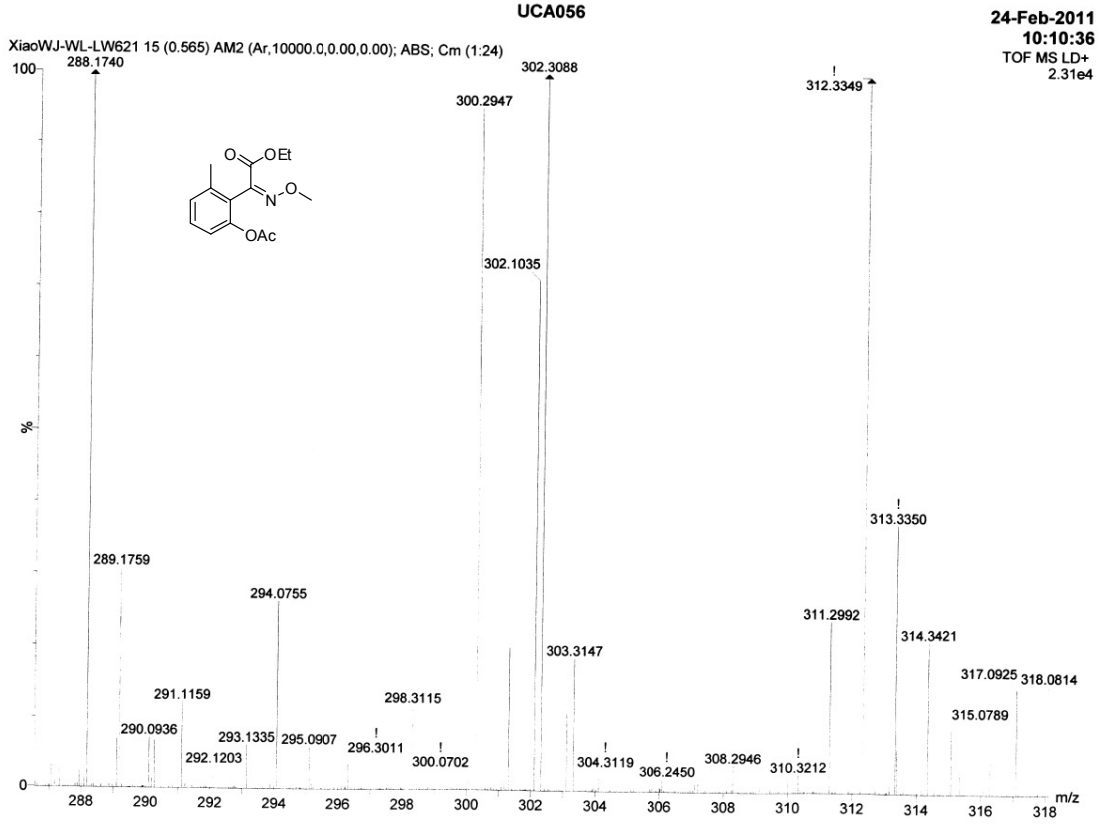

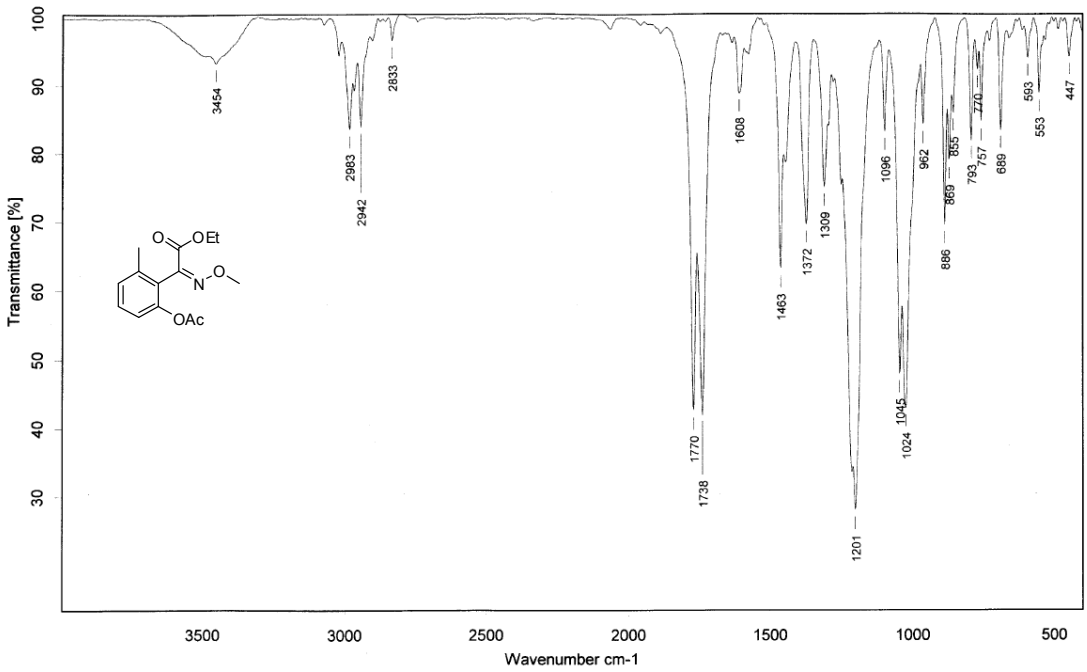

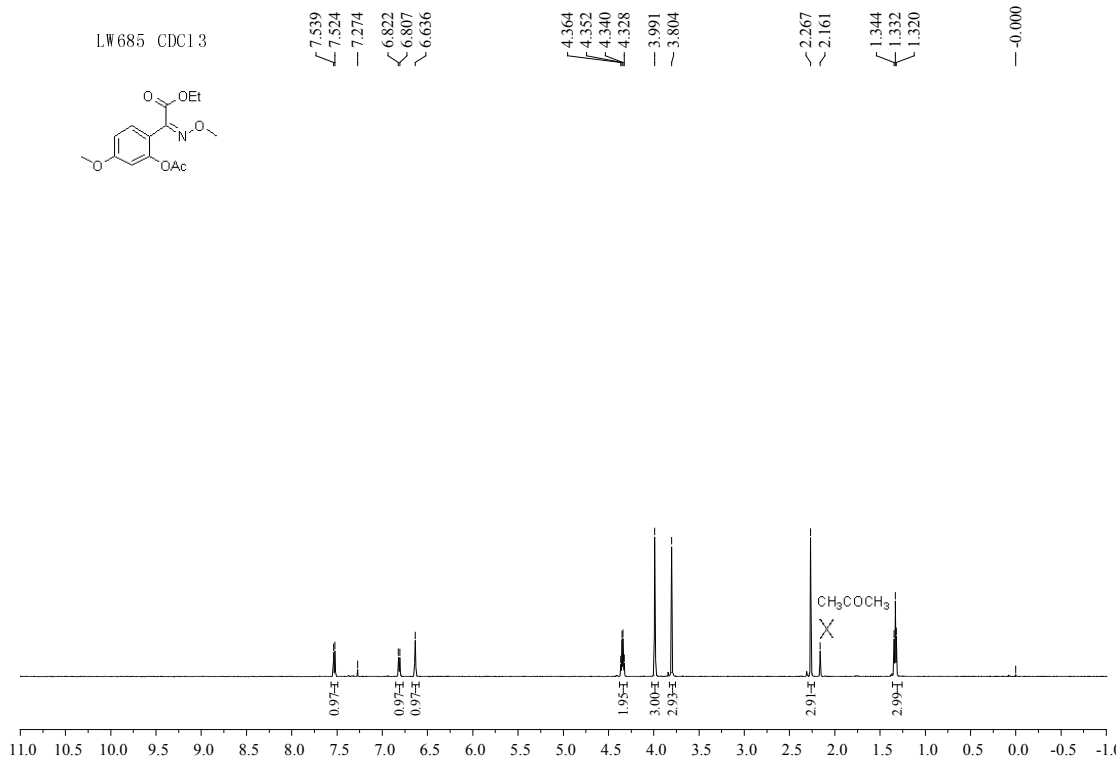

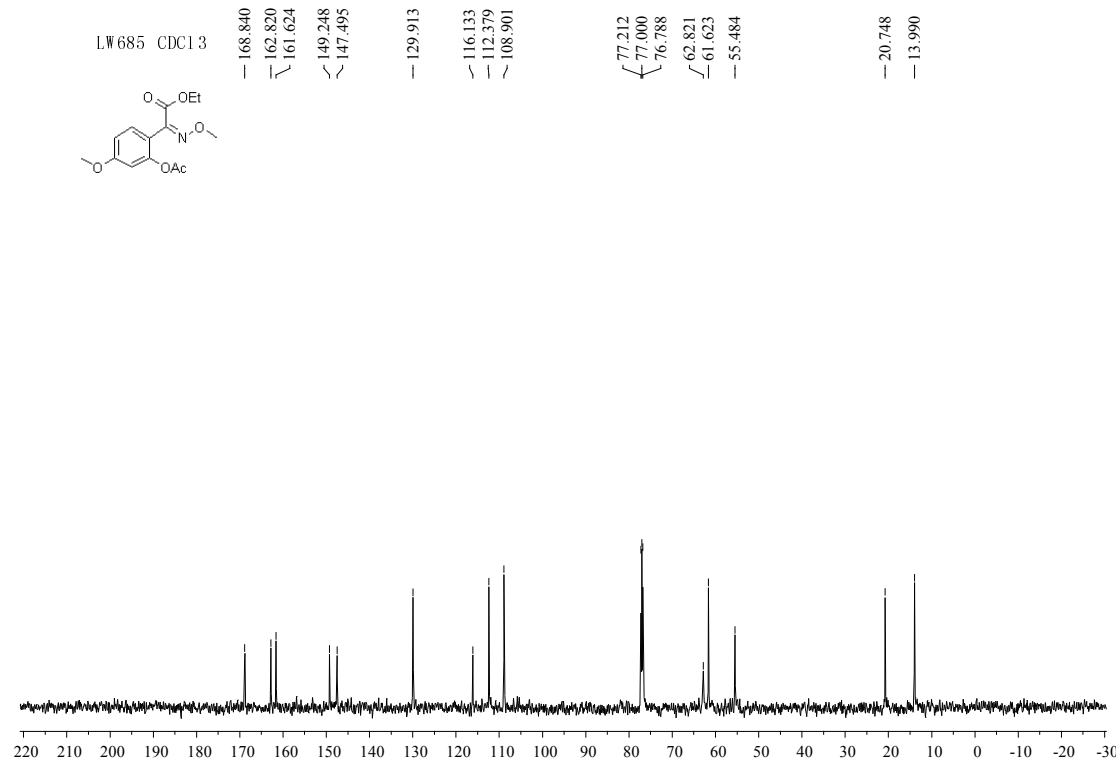

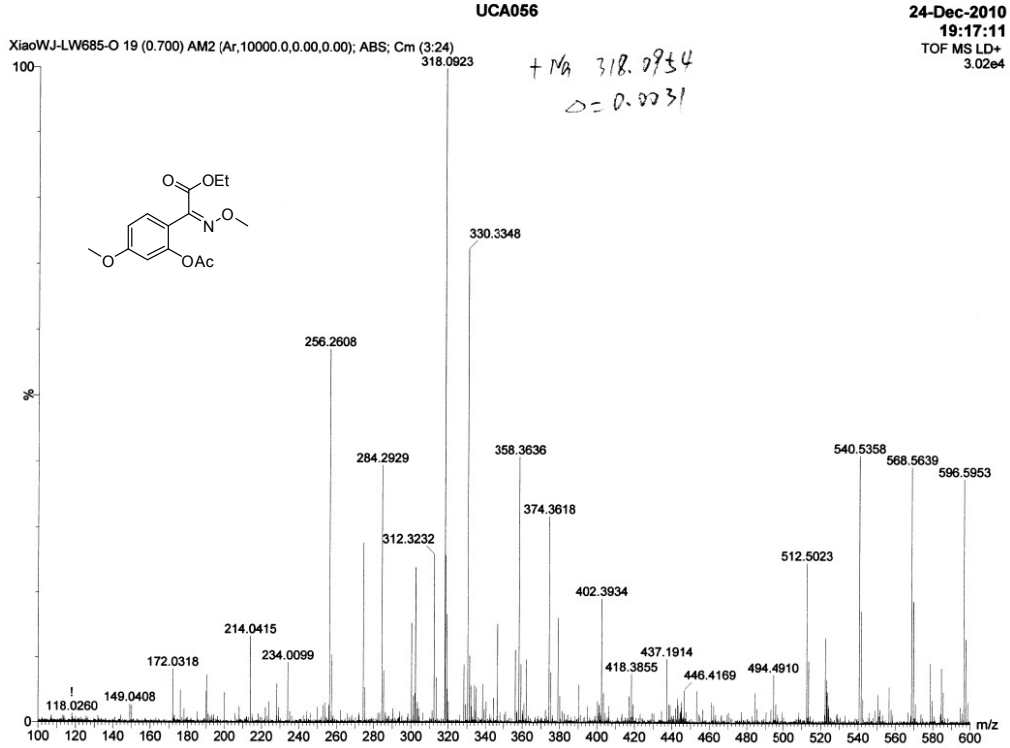

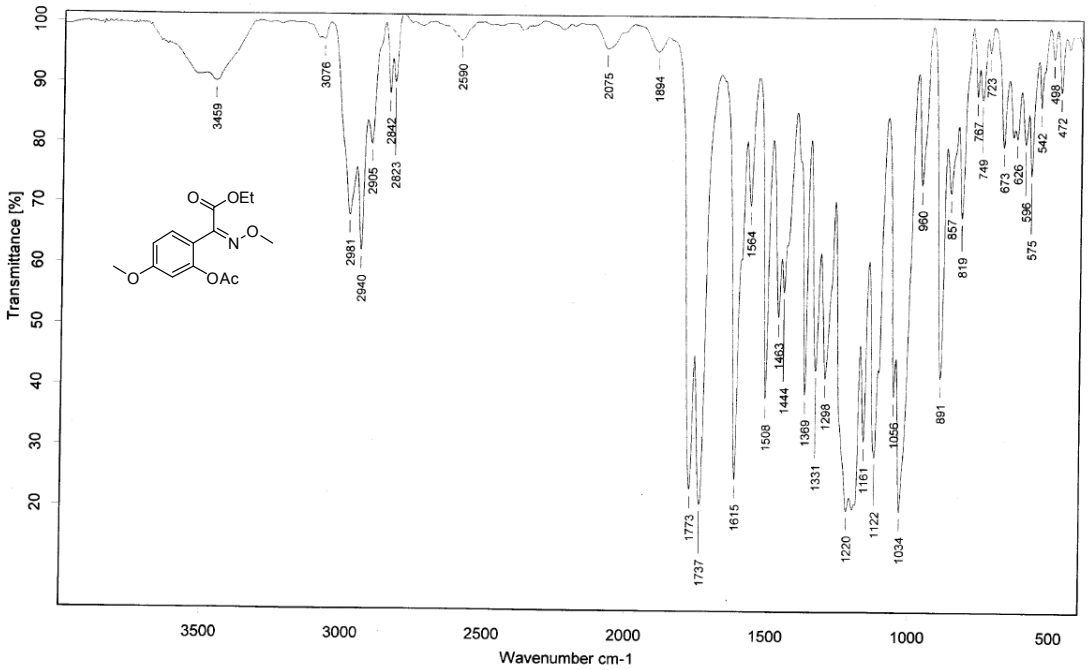

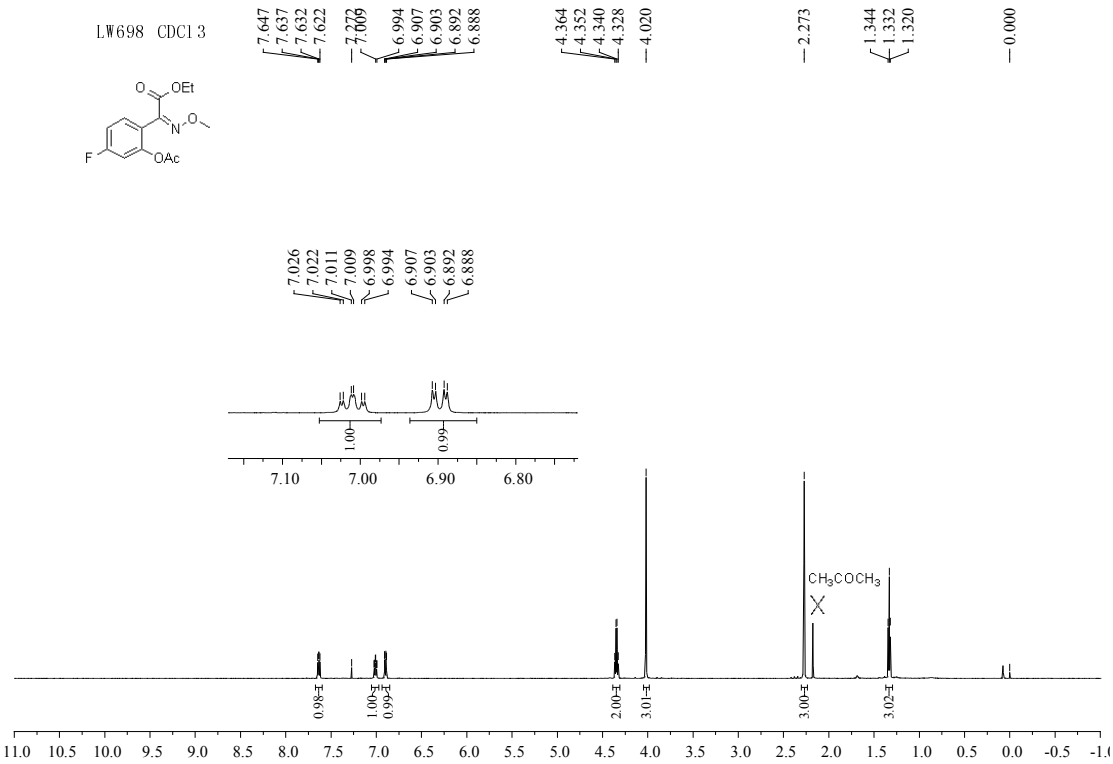

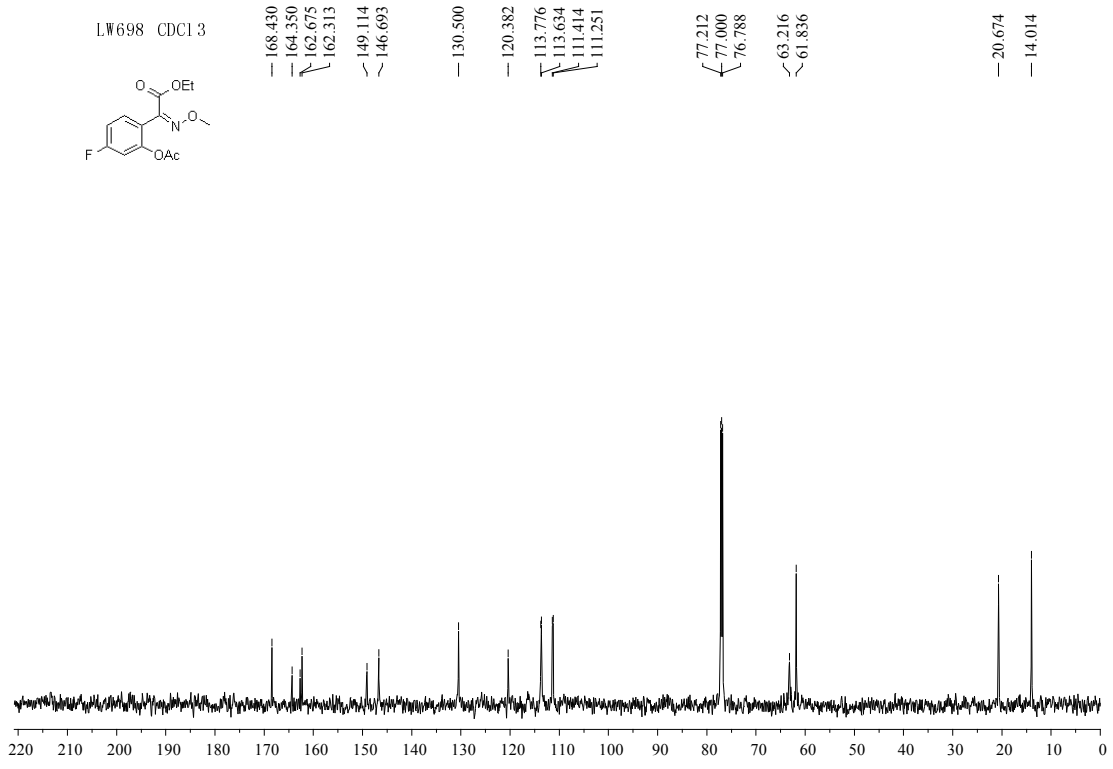

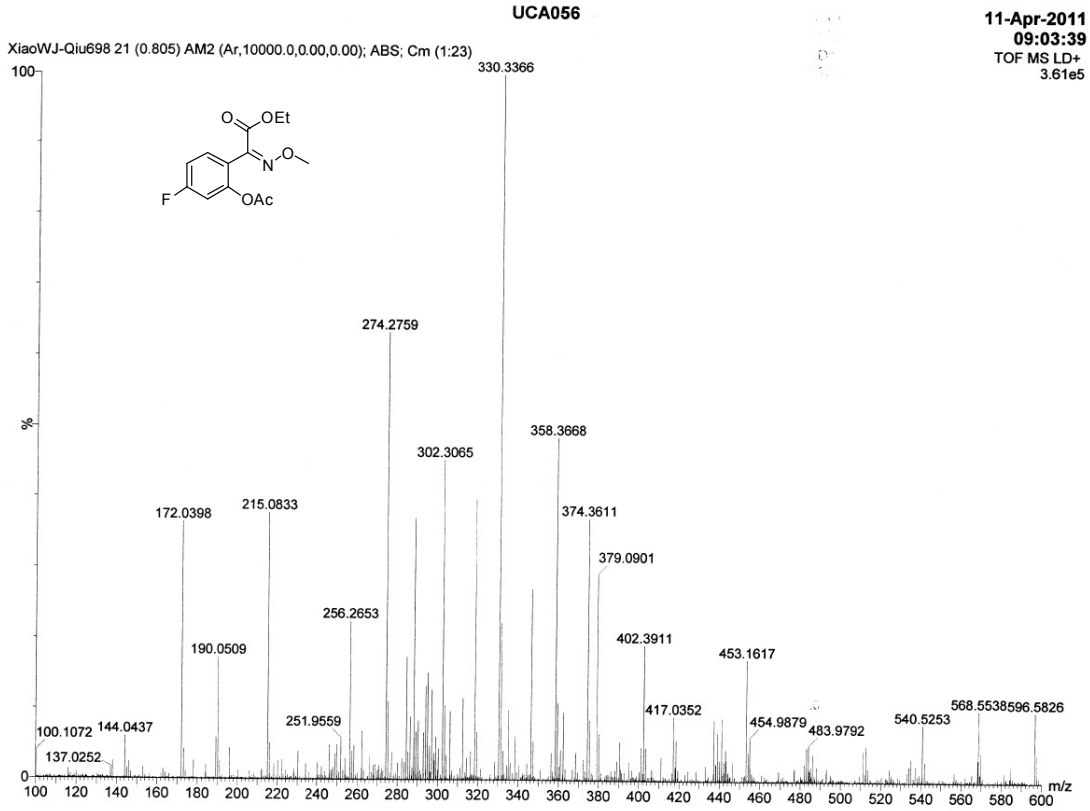

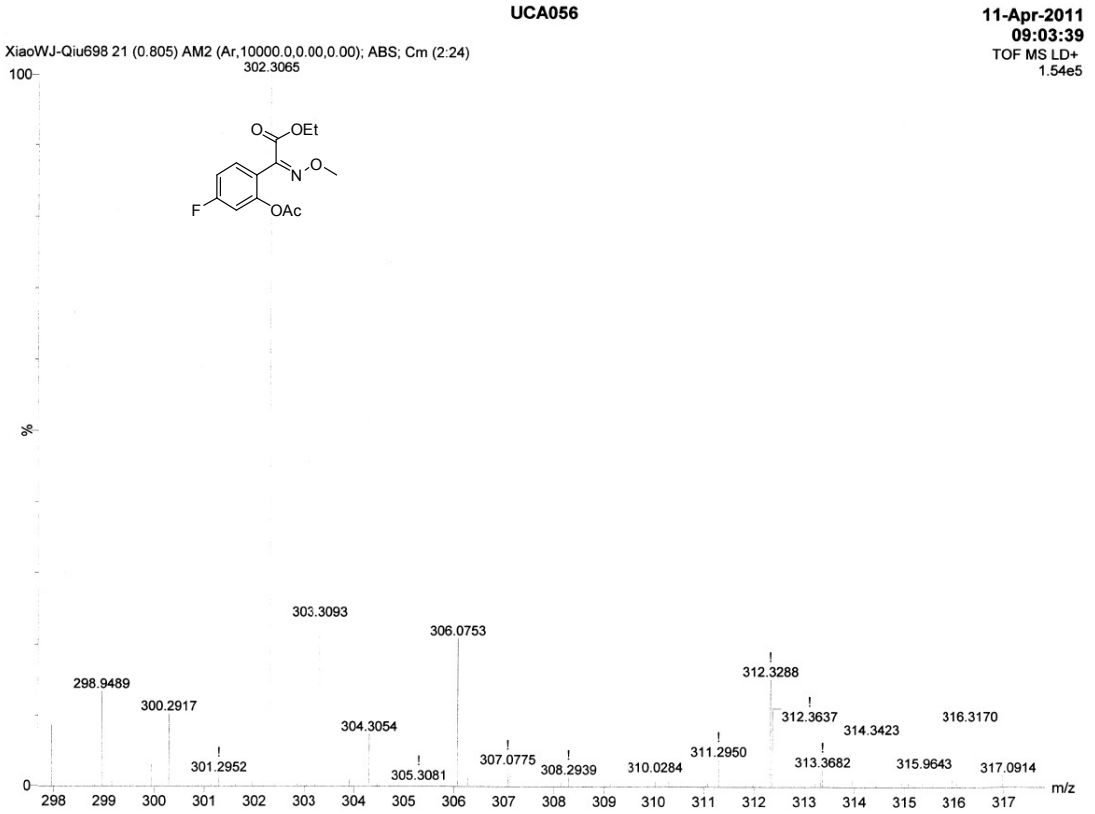

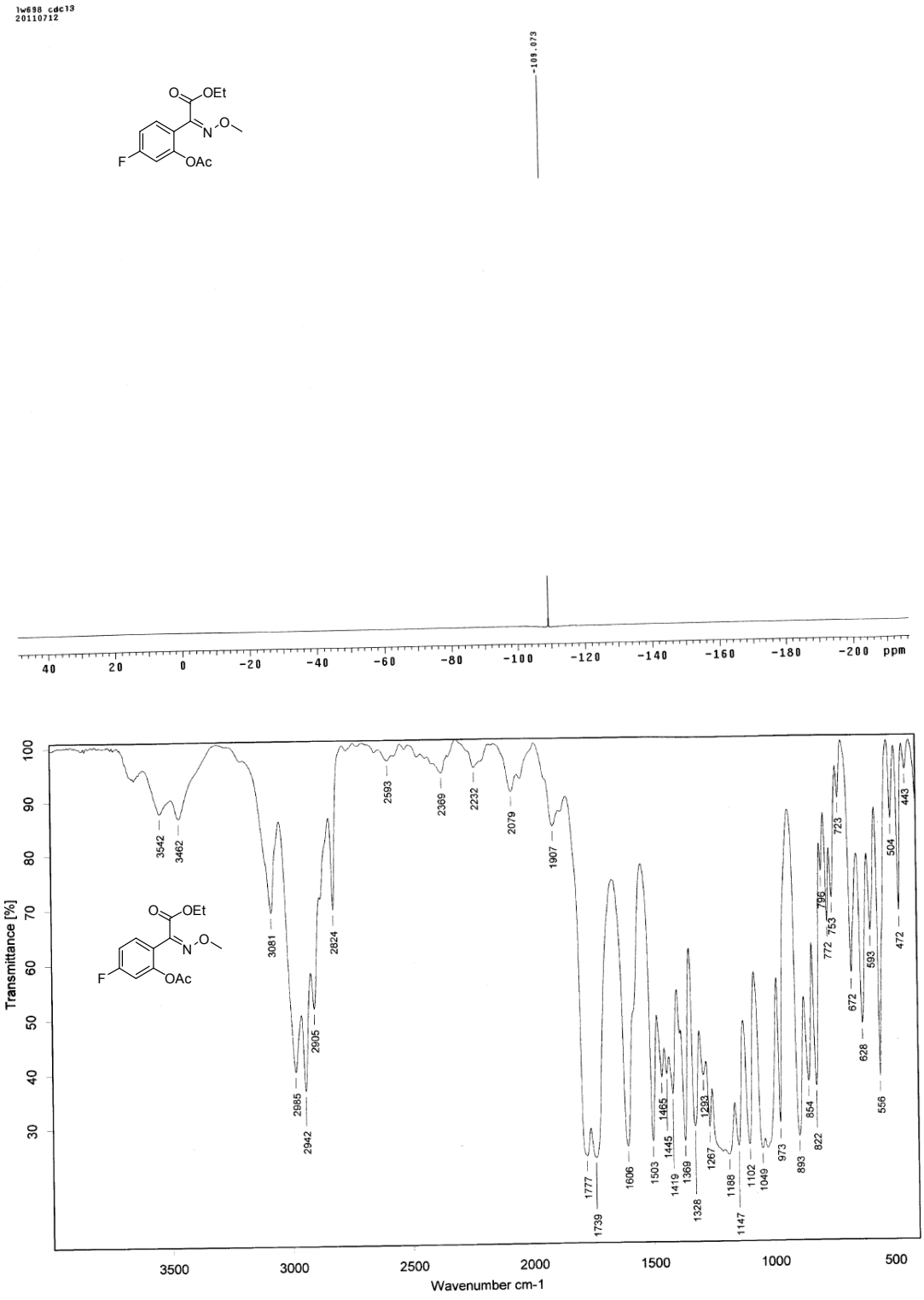

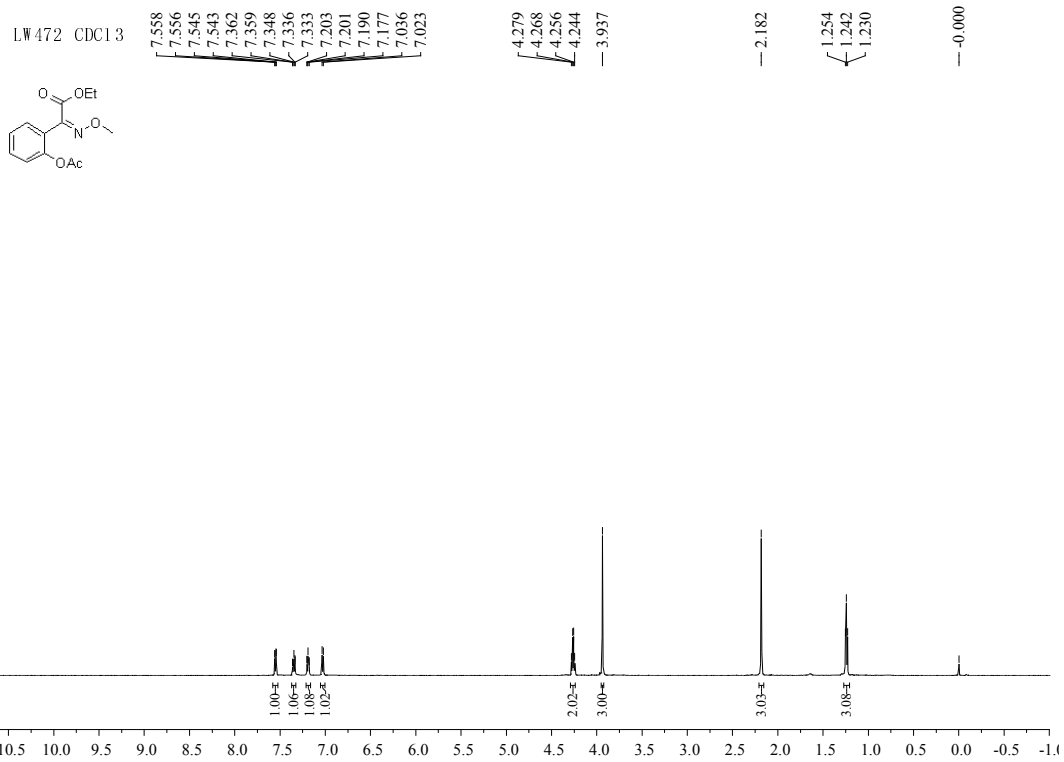

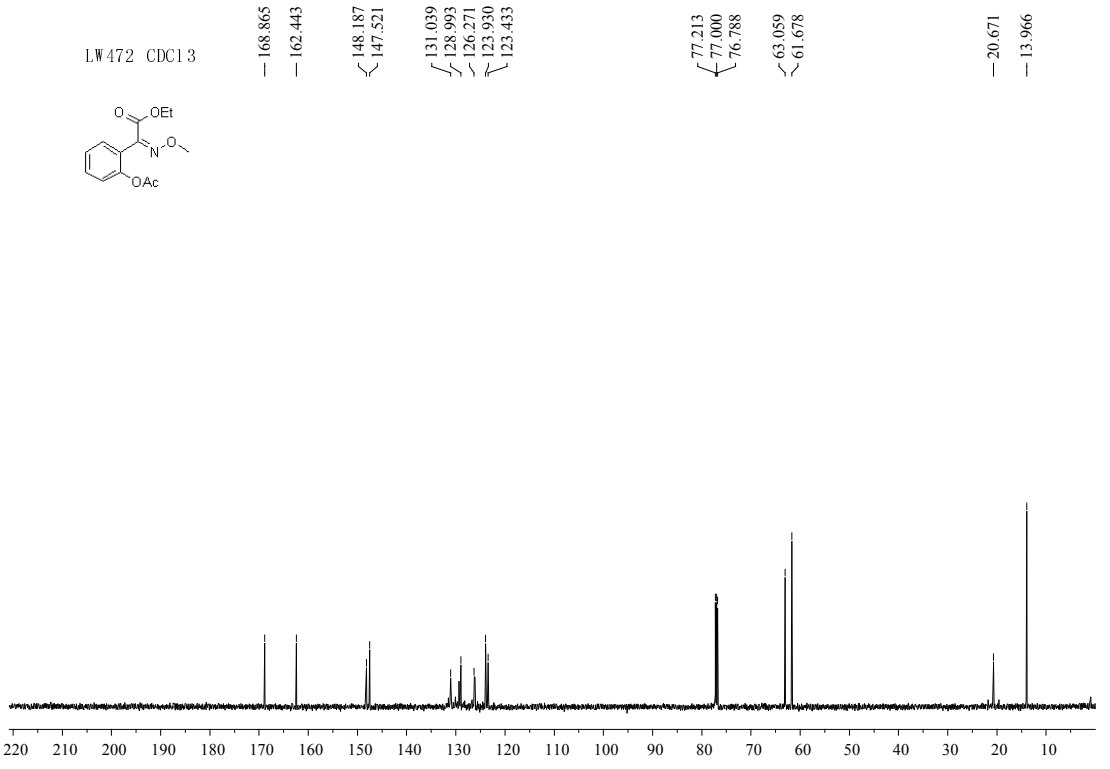

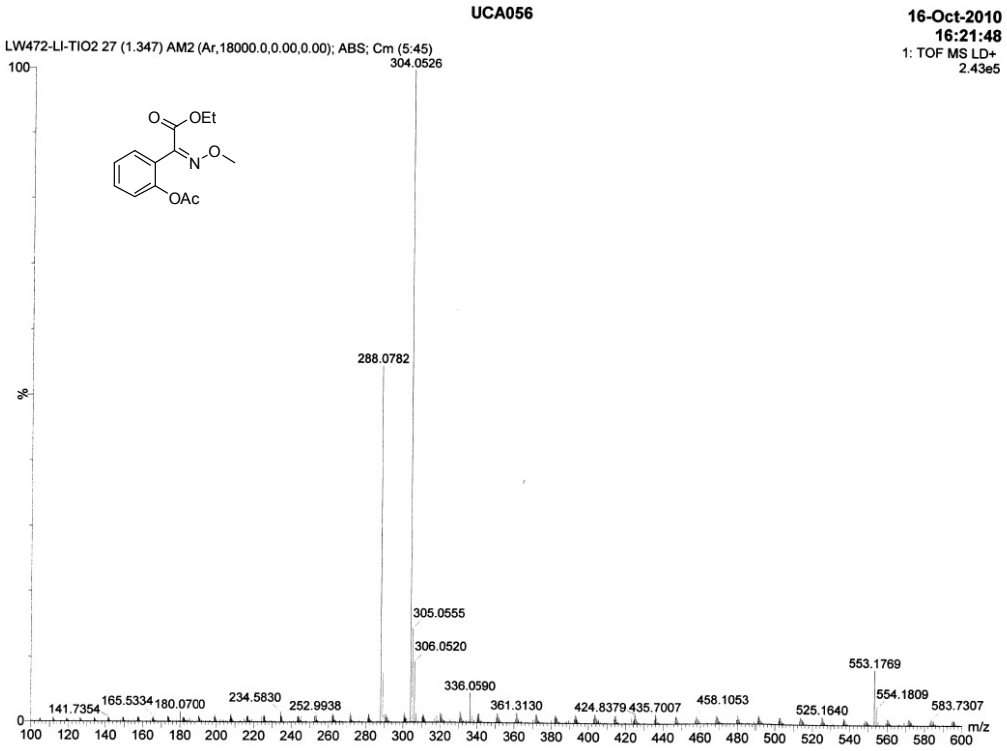

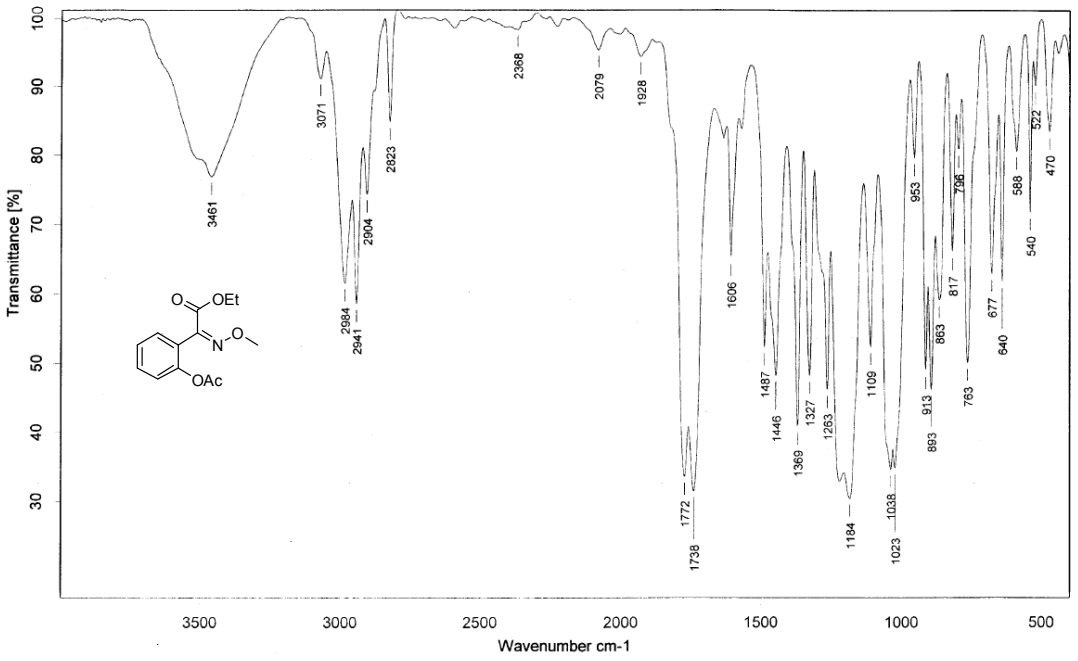

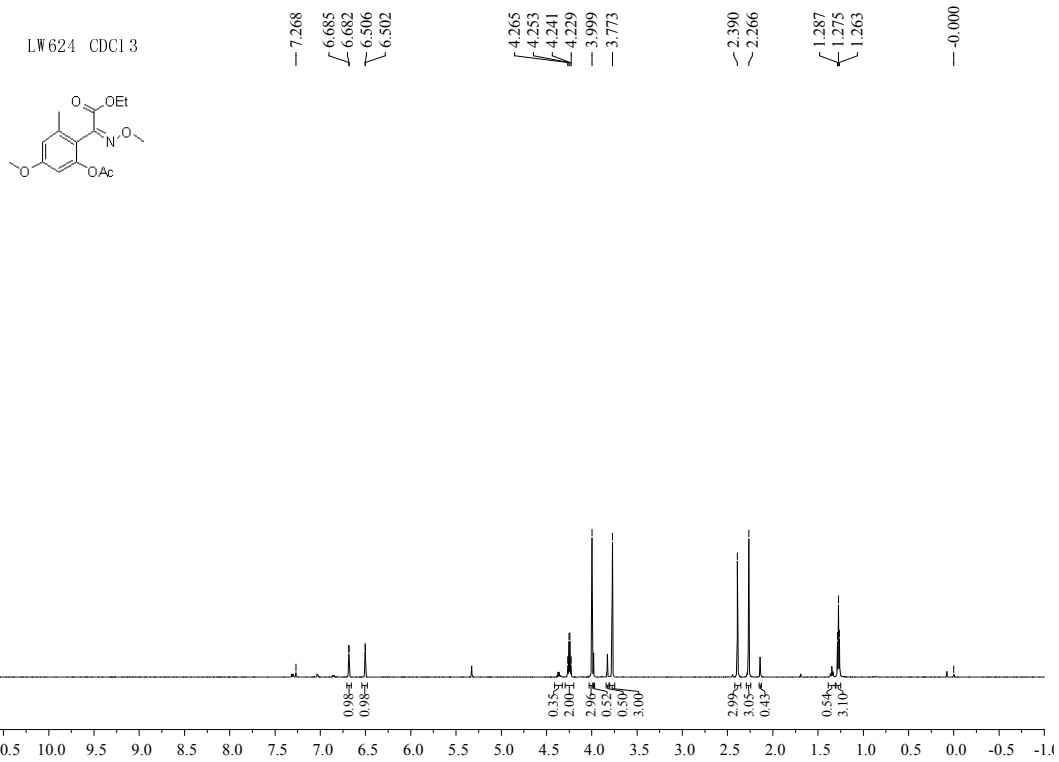

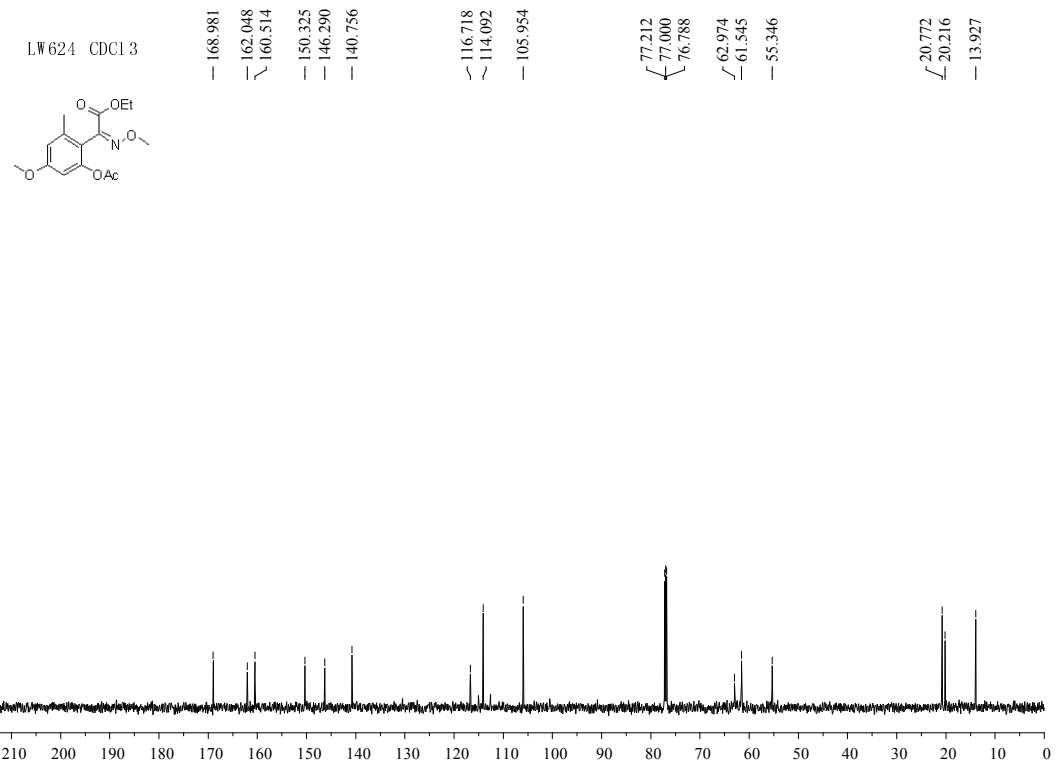

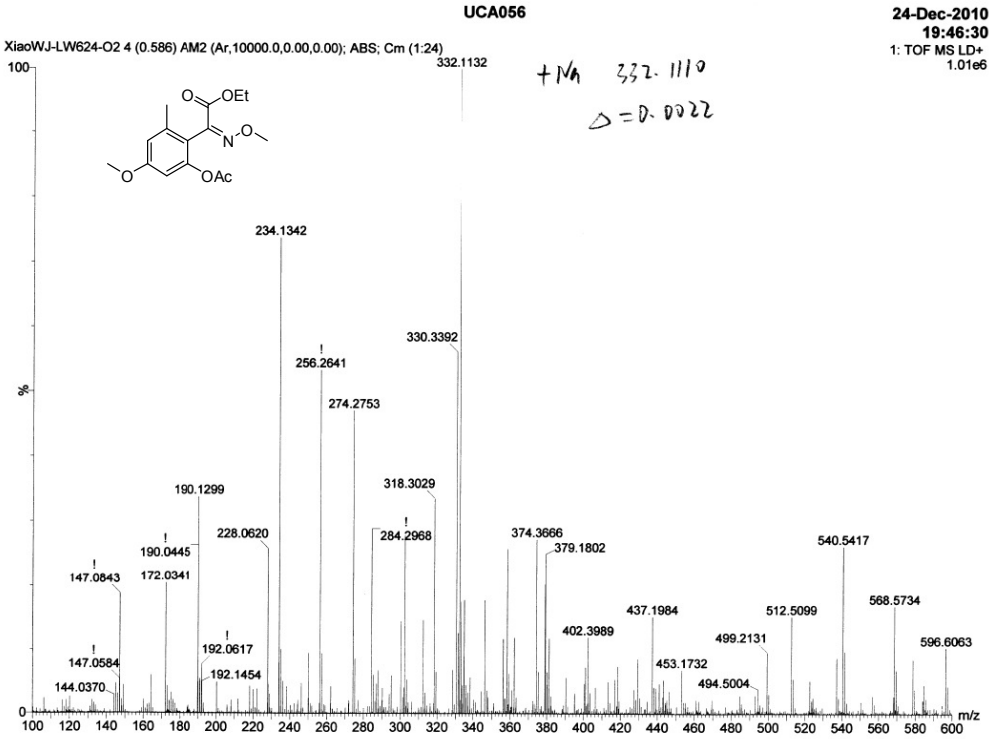

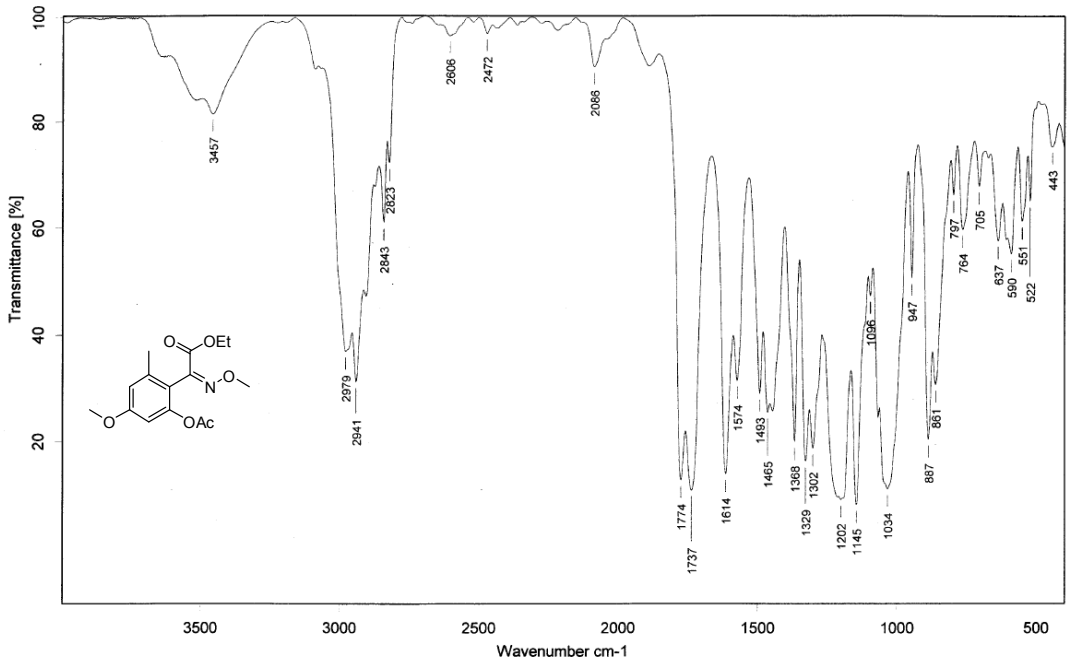

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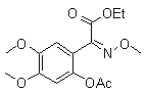

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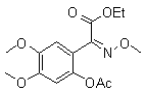
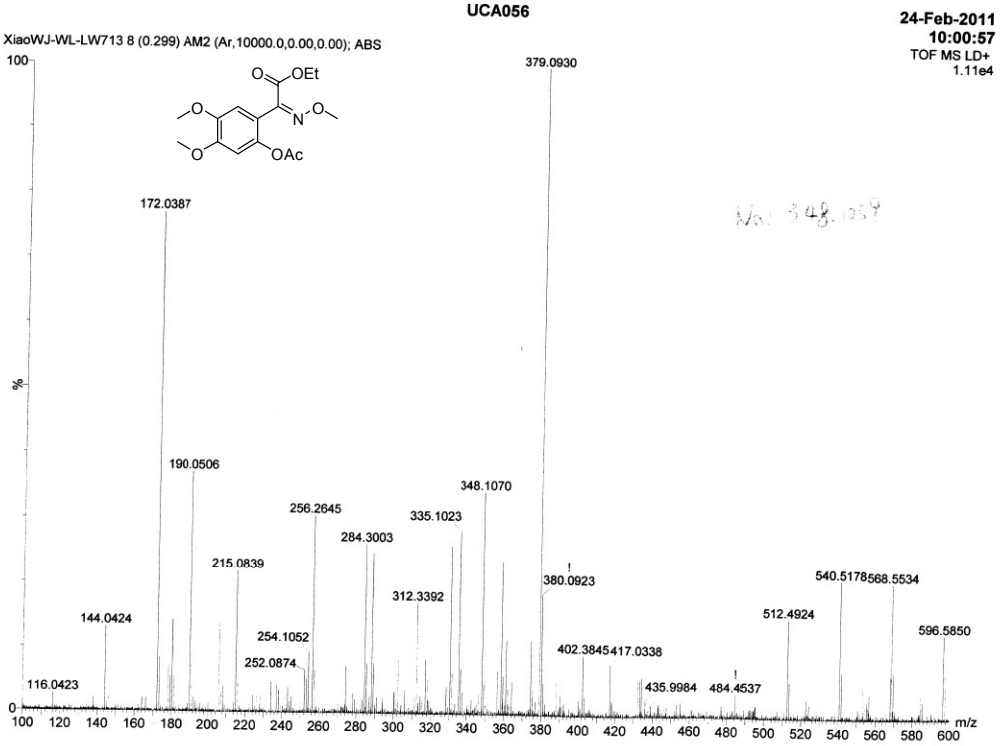
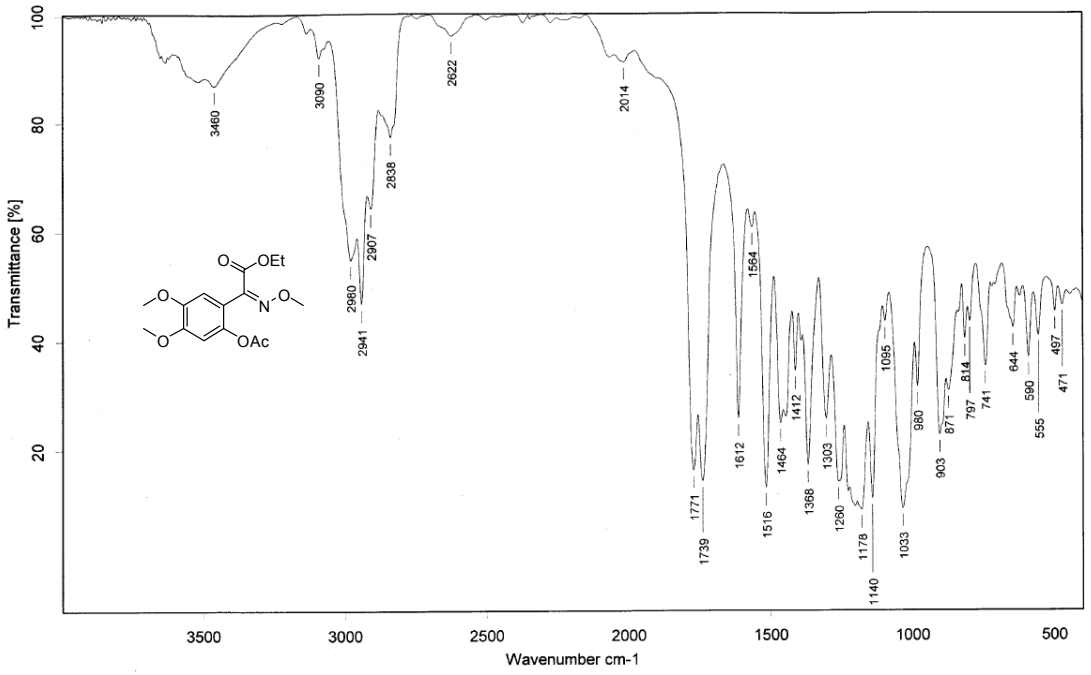
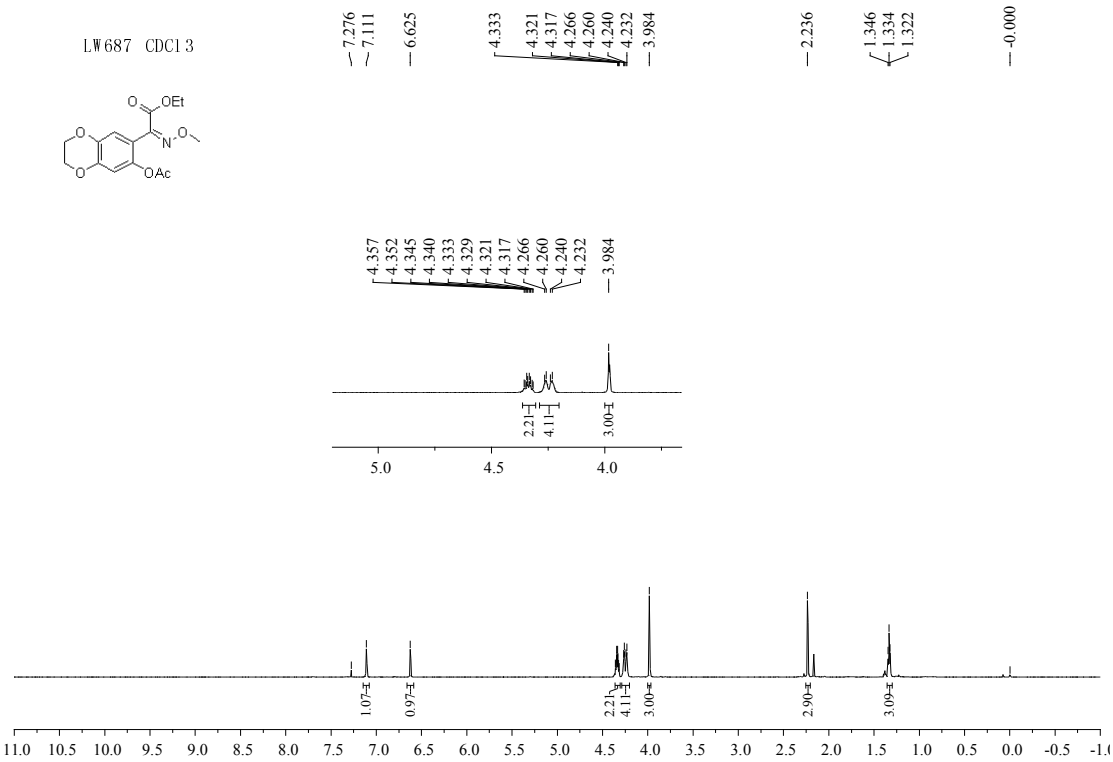
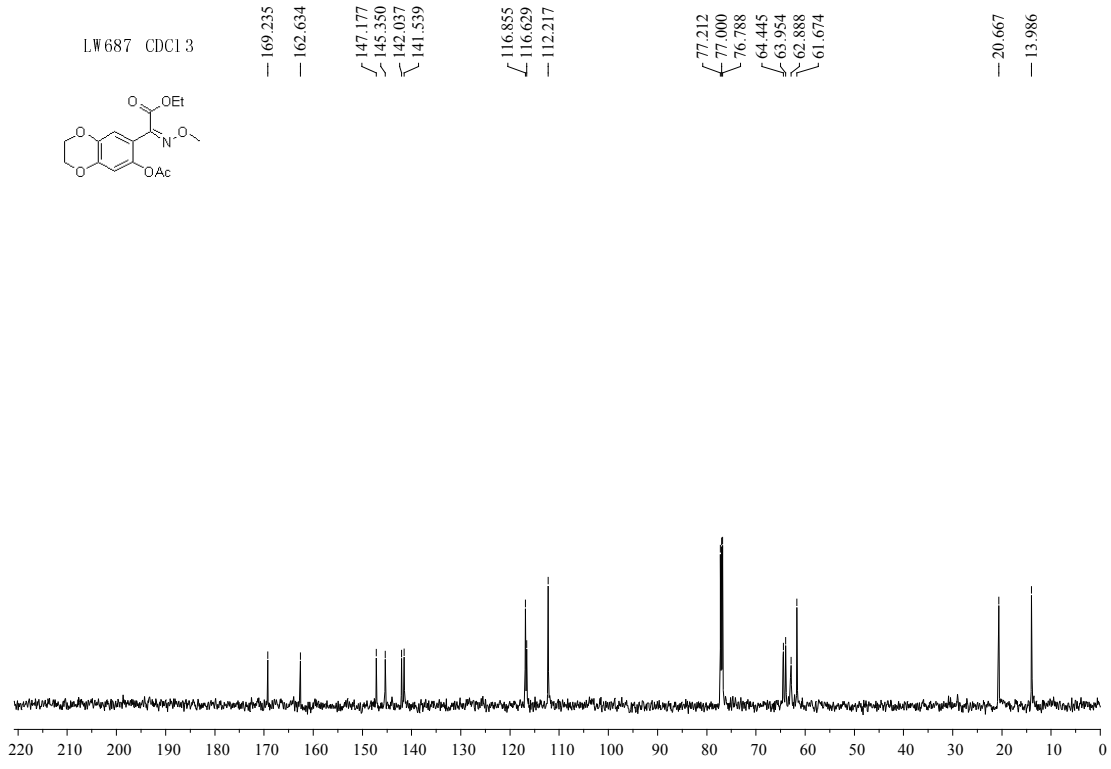
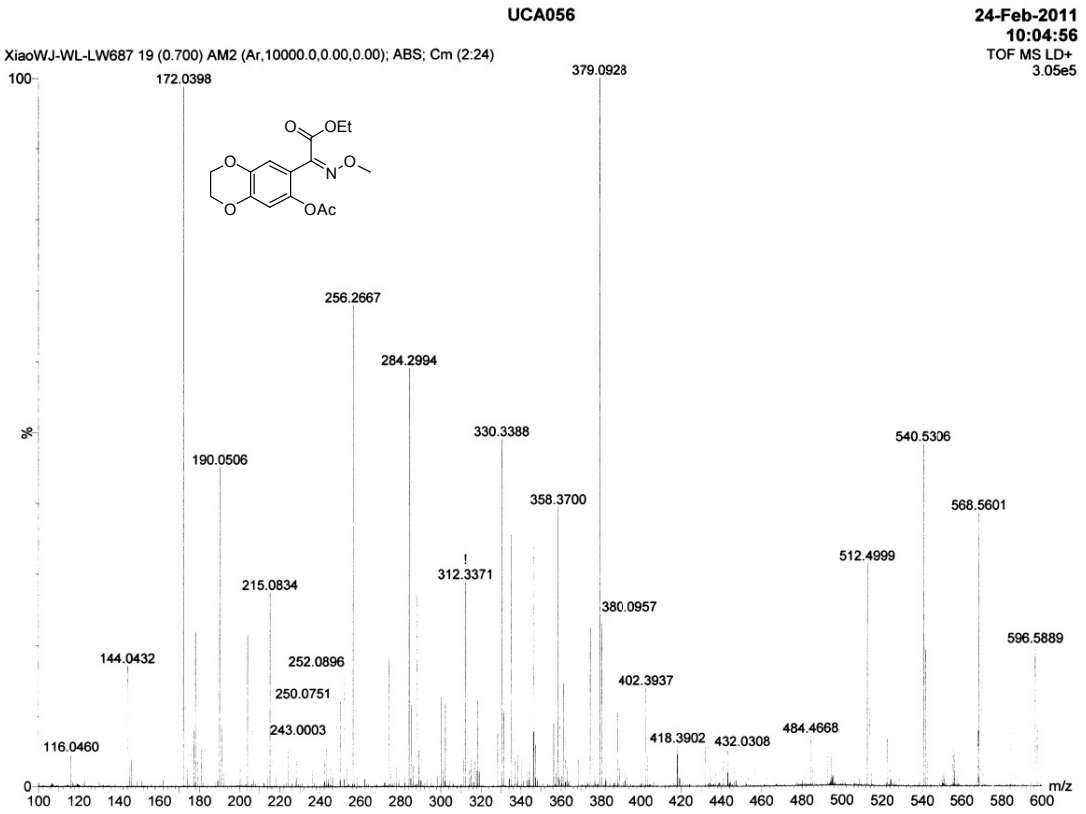


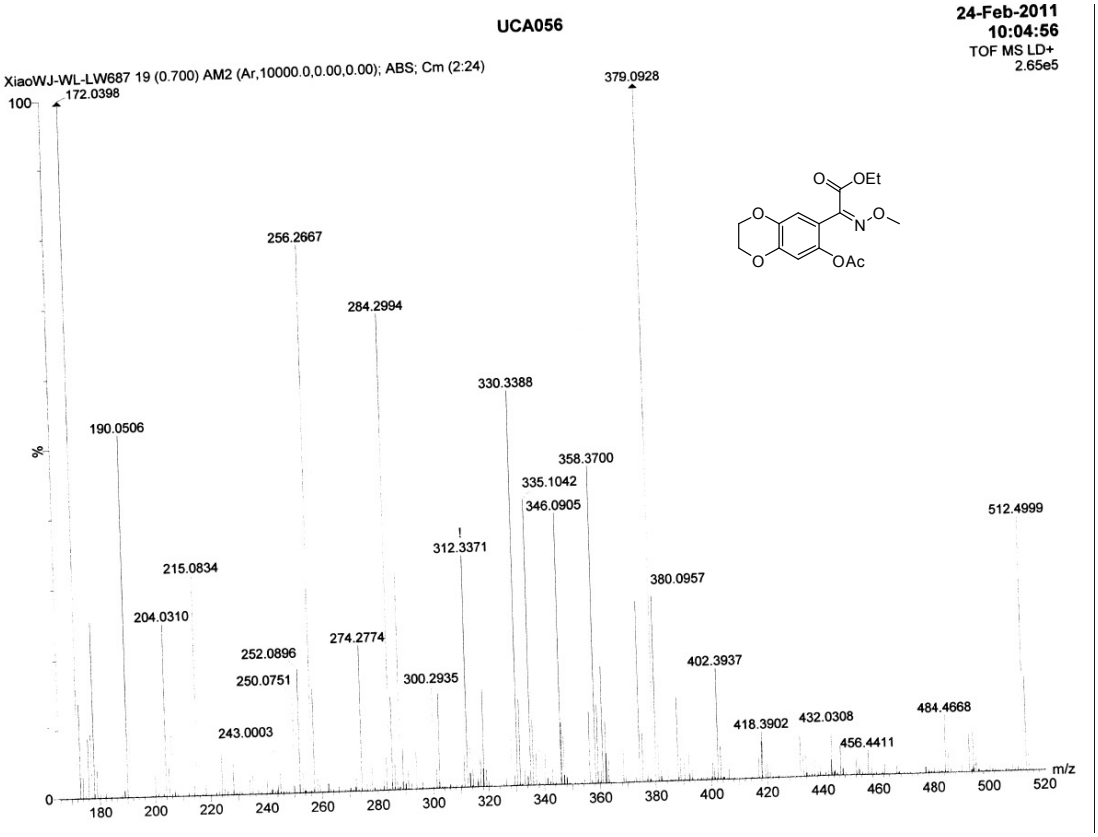


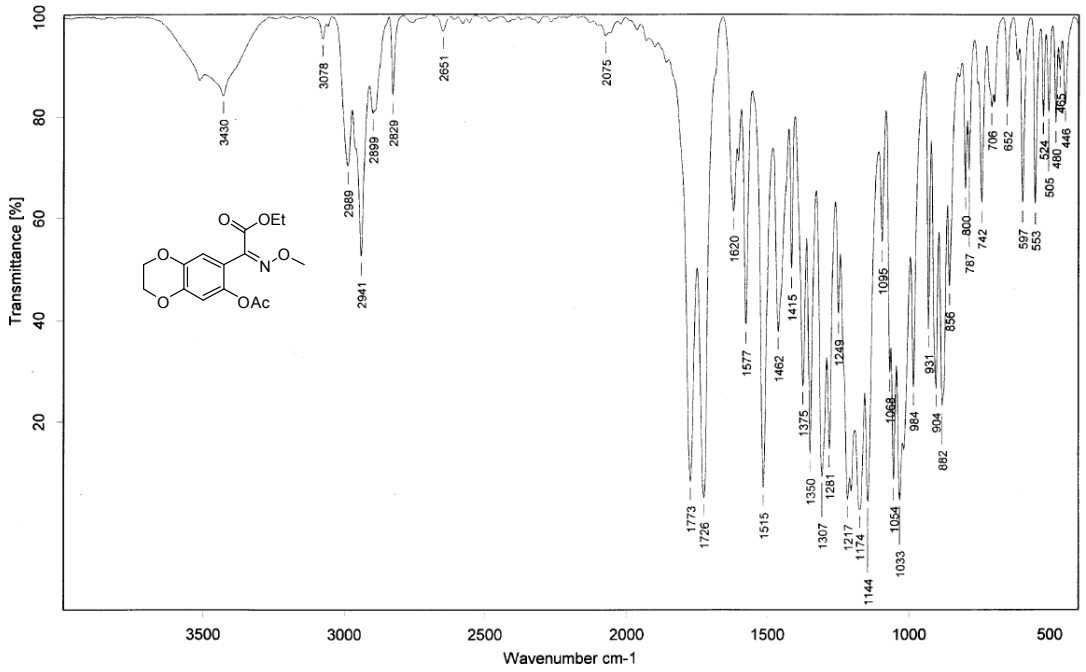


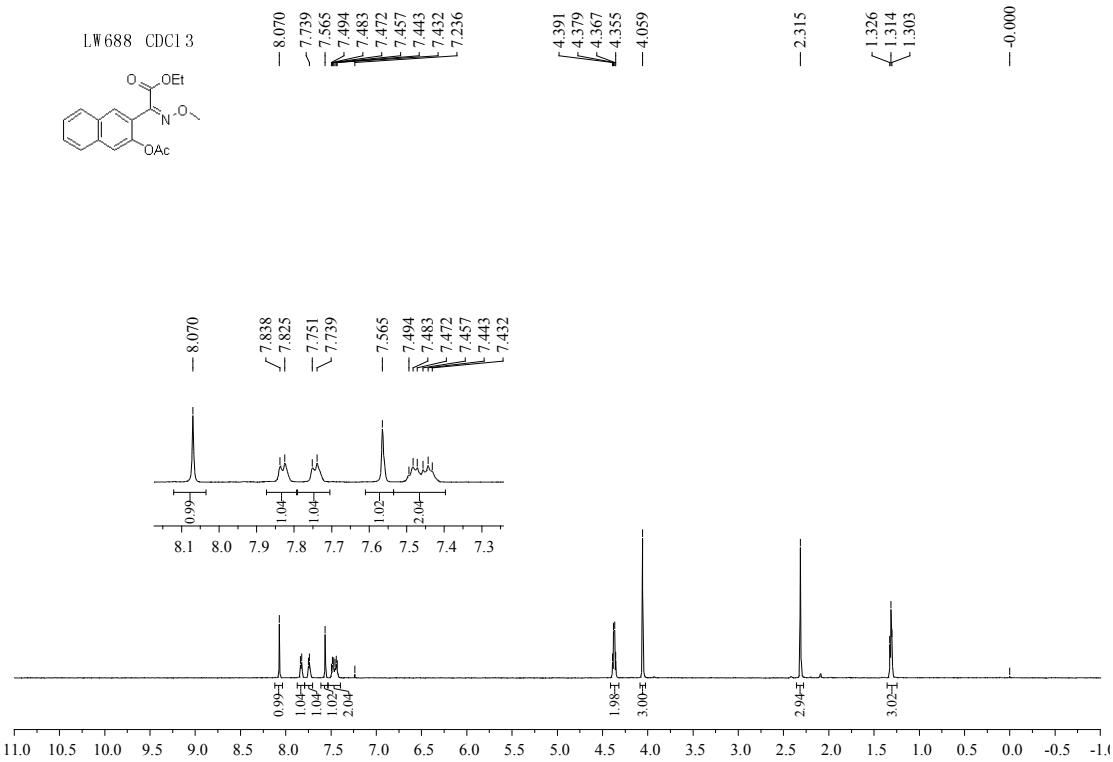


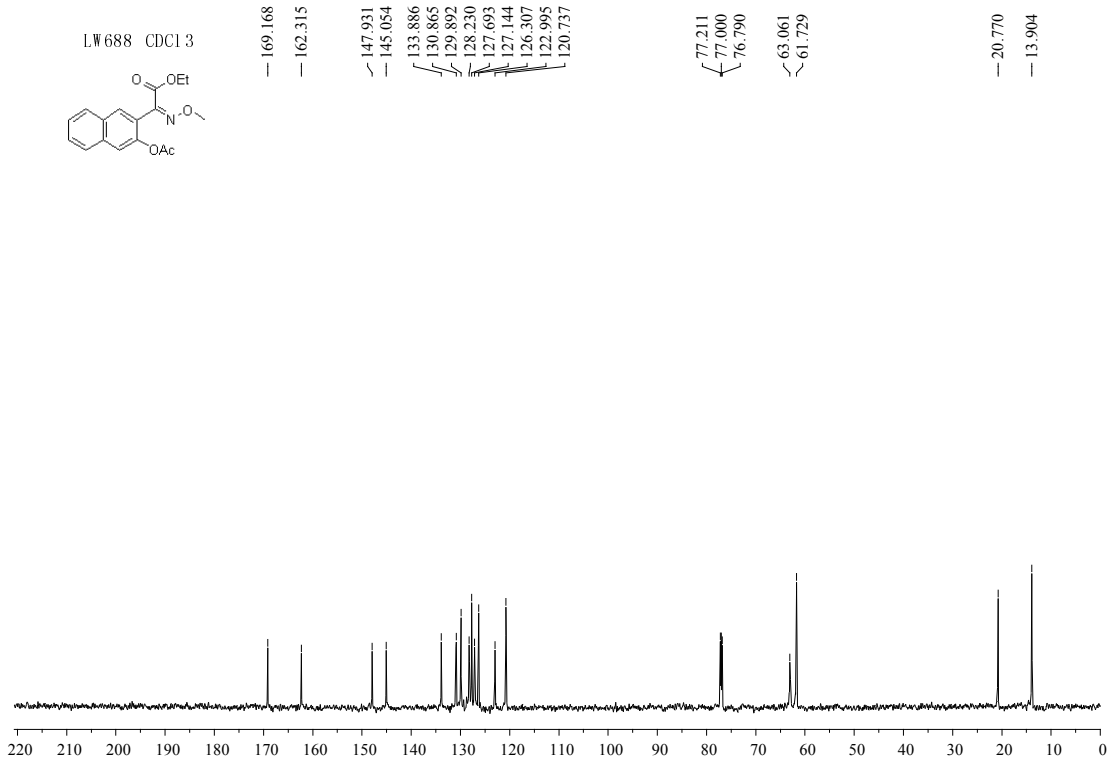












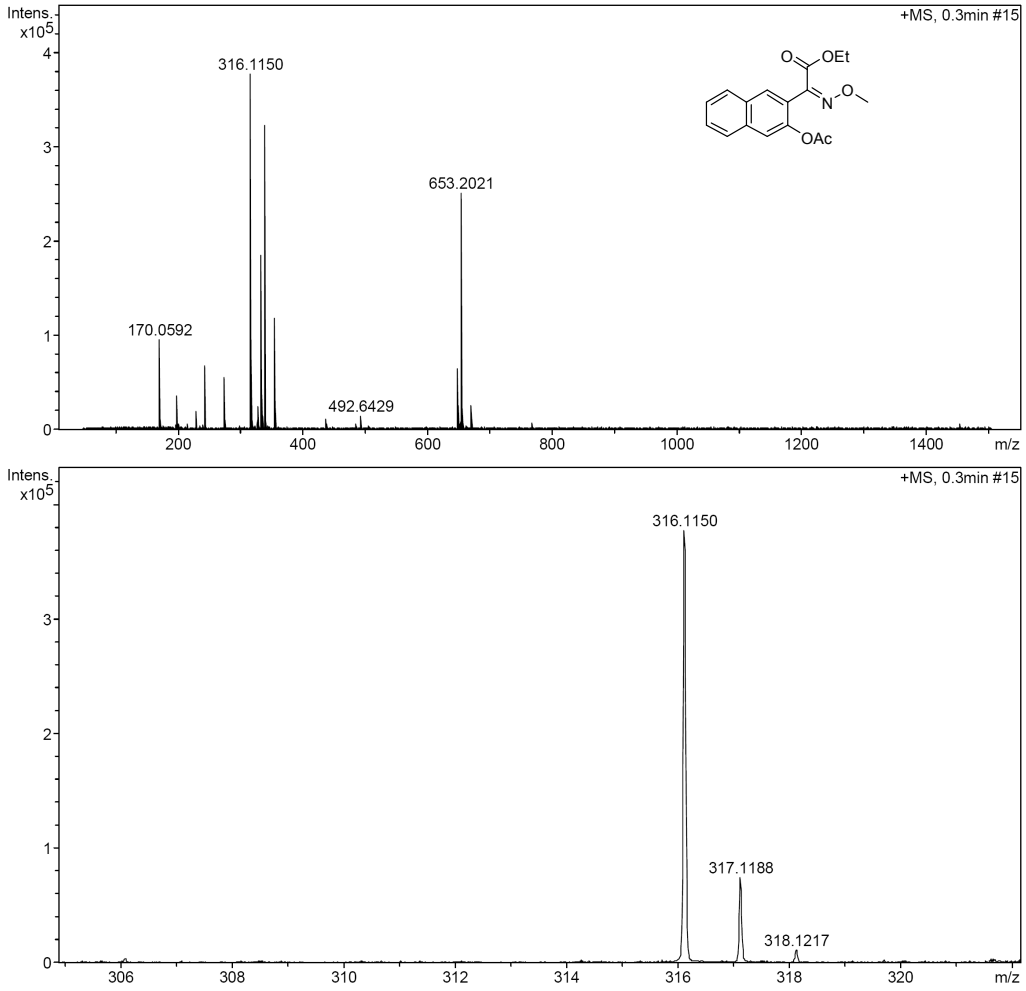
Display Report

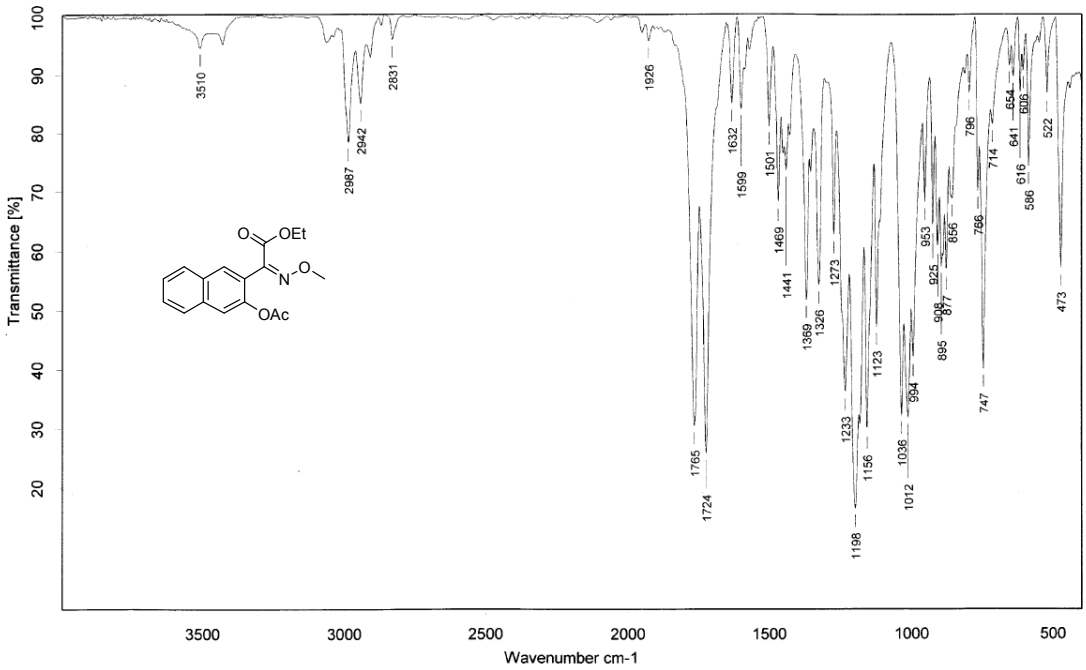
Analysis Info

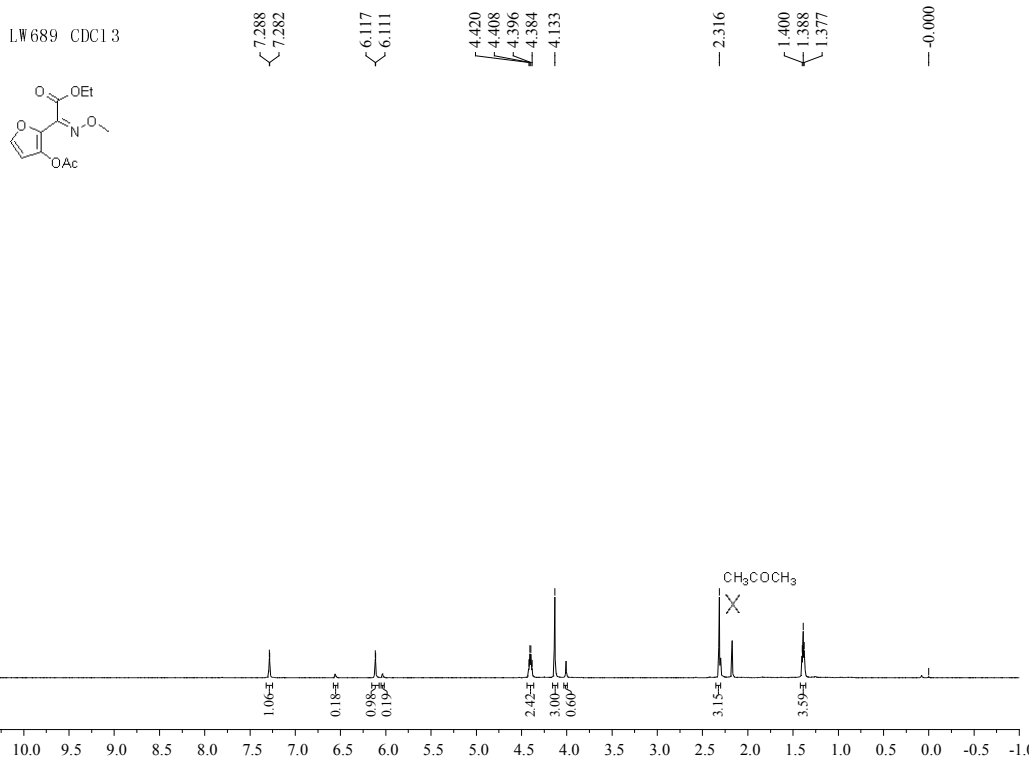
Analysis Name	D:\Data\MS\wj\0324\wc-ysq000007.d	Acquisition Date	3/24/2011 3:06:48 PM
Method	tune_200-800_hcoona-POS.m	Operator	gftang
Sample Name	lw688	Instrument / Ser#	micrOTOF II 10257
Comment			

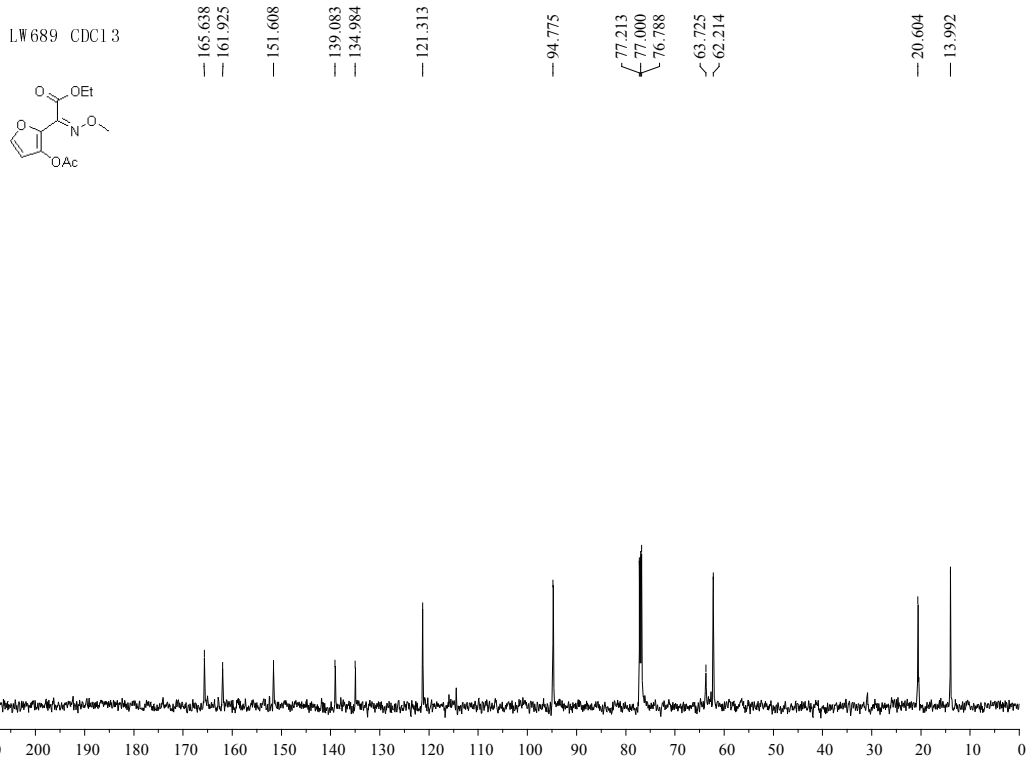
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active			Set Dry Heater	180 ℃
Scan Begin	50 m/z	Set Capillary	4000 V	Set Dry Gas	8.0 l/min
Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste









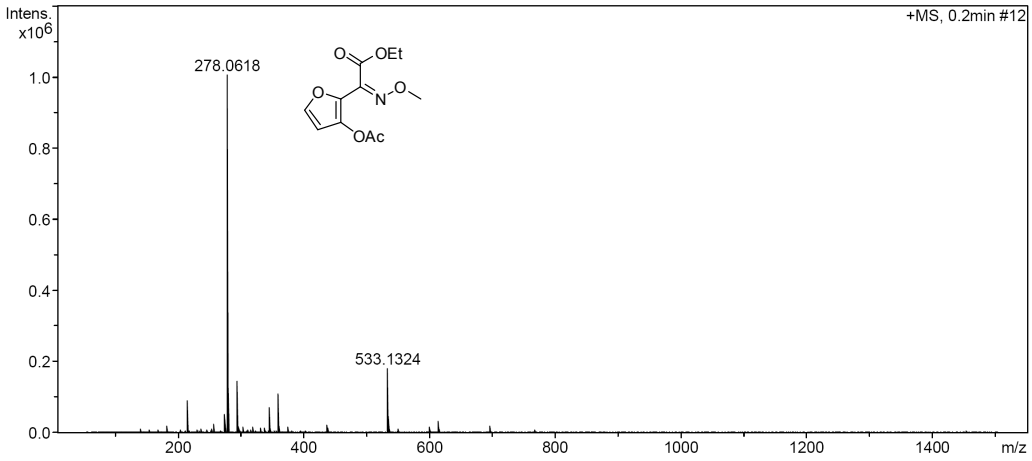
Display Report

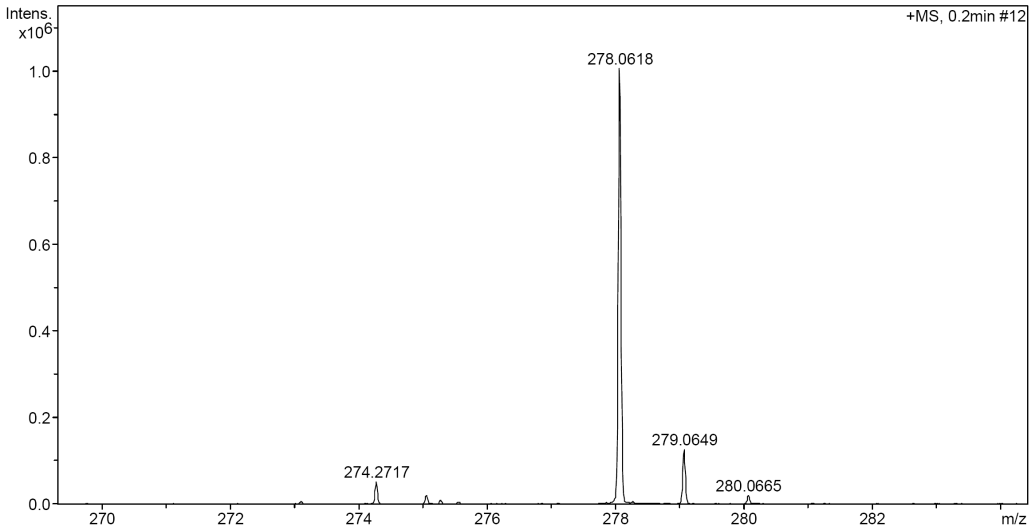
Analysis Info

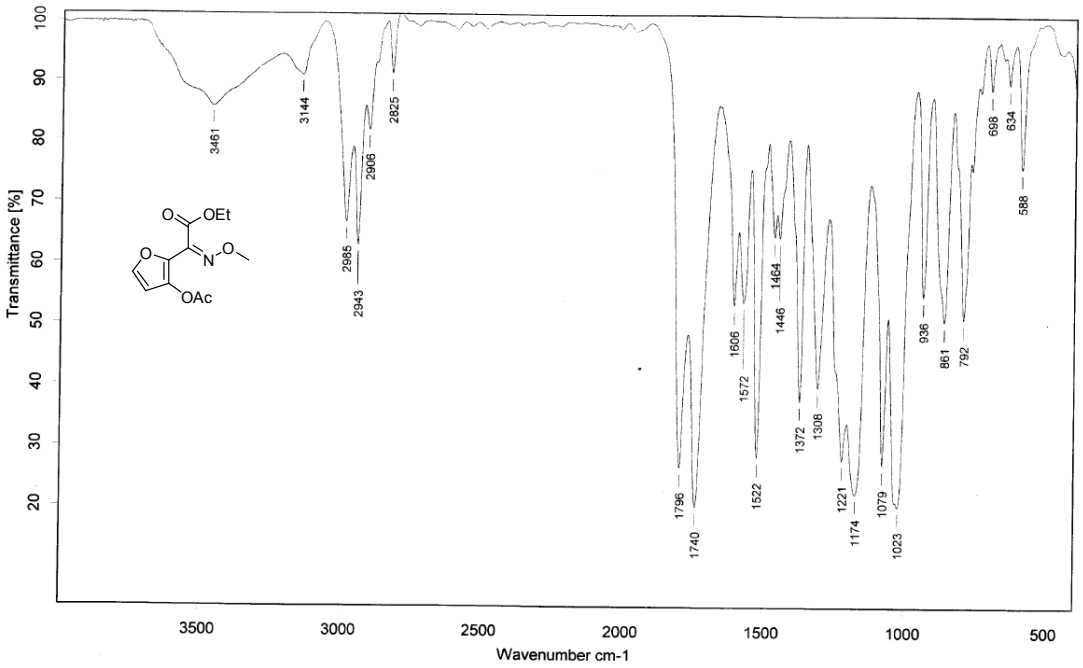
Analysis Name	D:\Data\MS\wj\0324\wc-ysq000005.d	Acquisition Date	3/24/2011 3:03:45 PM
Method	tune_200-800_hcoona-POS.m	Operator	gftang
Sample Name	lw689	Instrument / Ser#	micrOTOF II 10257
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4000 V	Set Dry Gas	8.0 l/min
Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste







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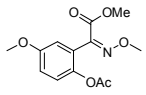

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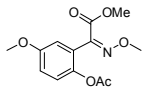
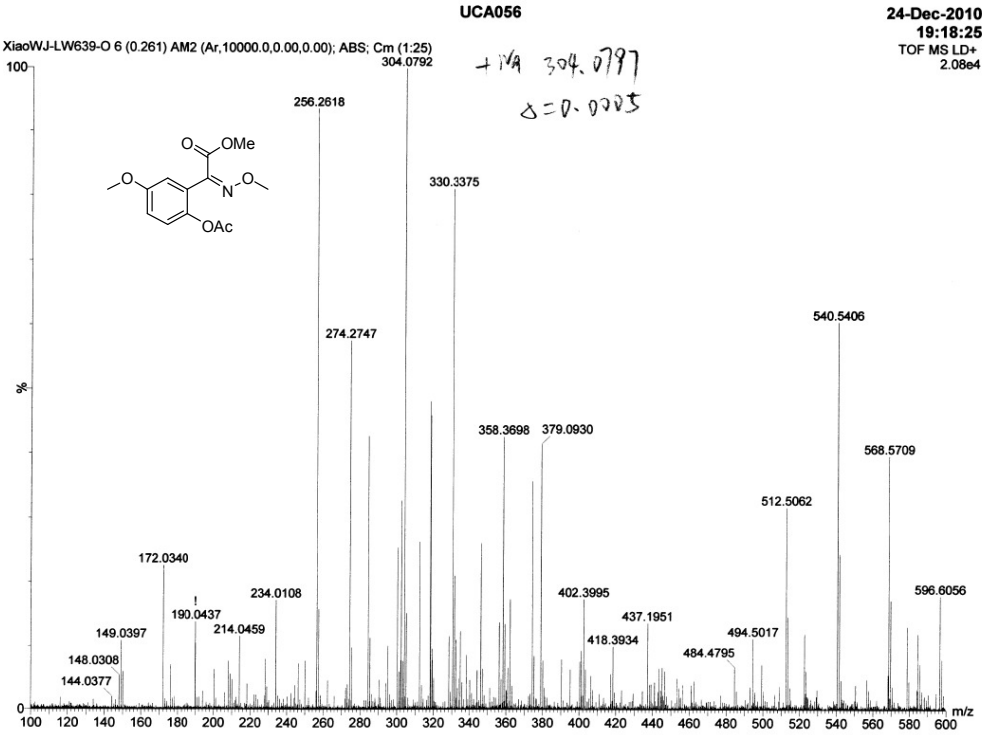
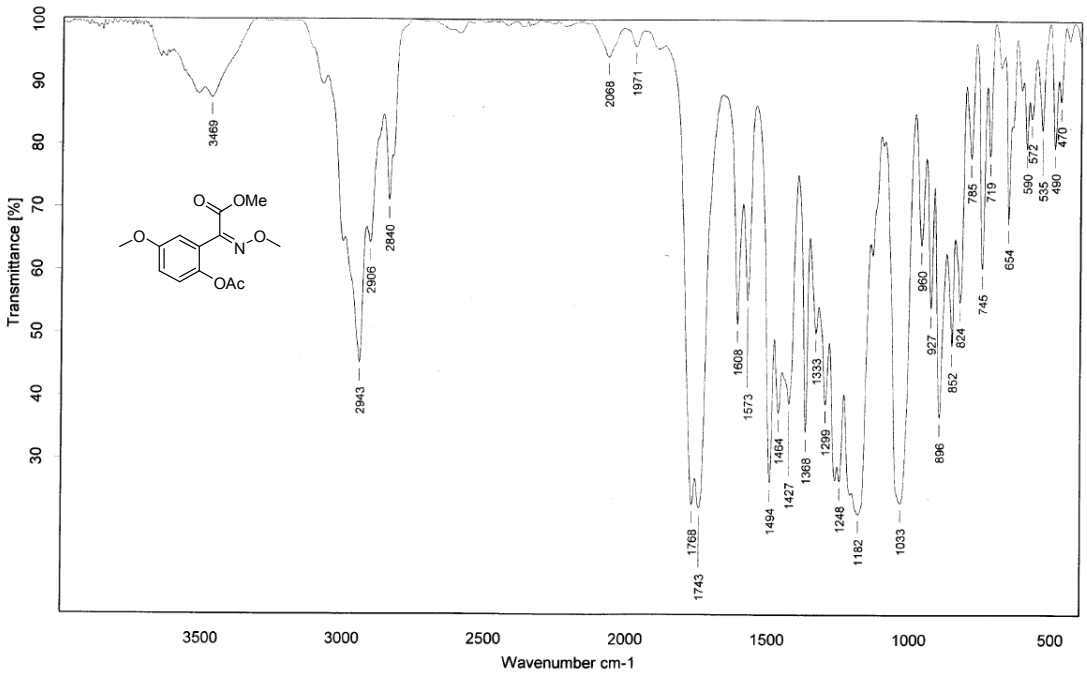
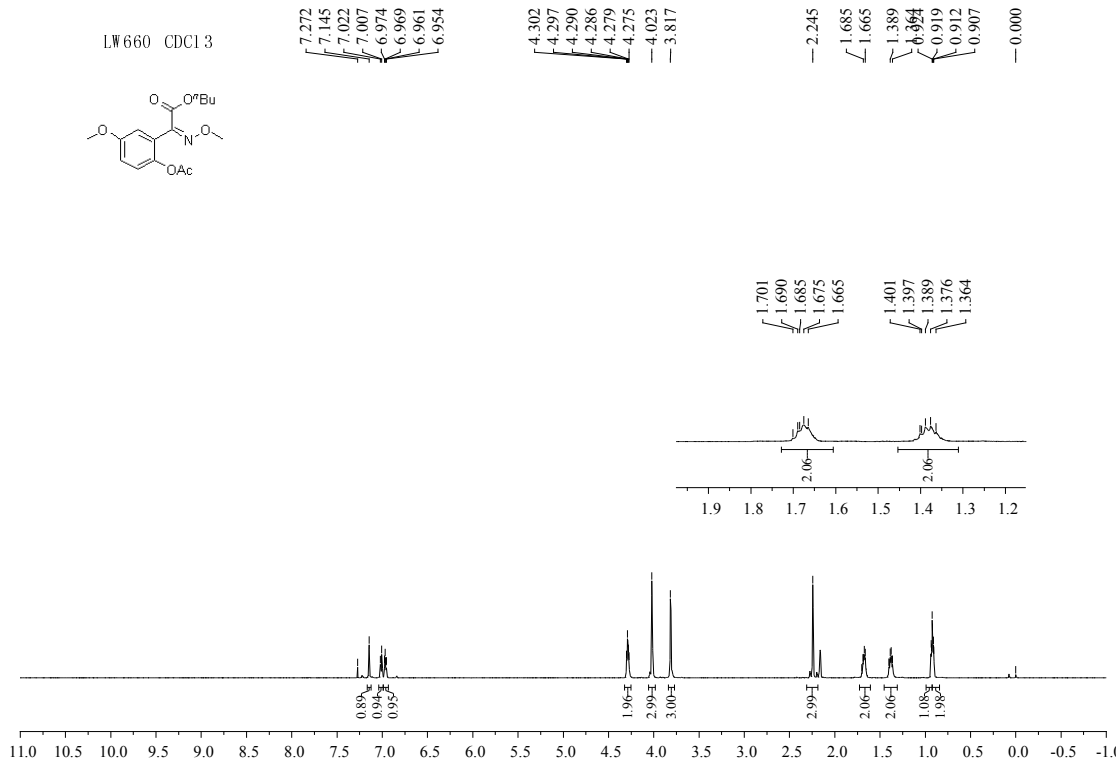
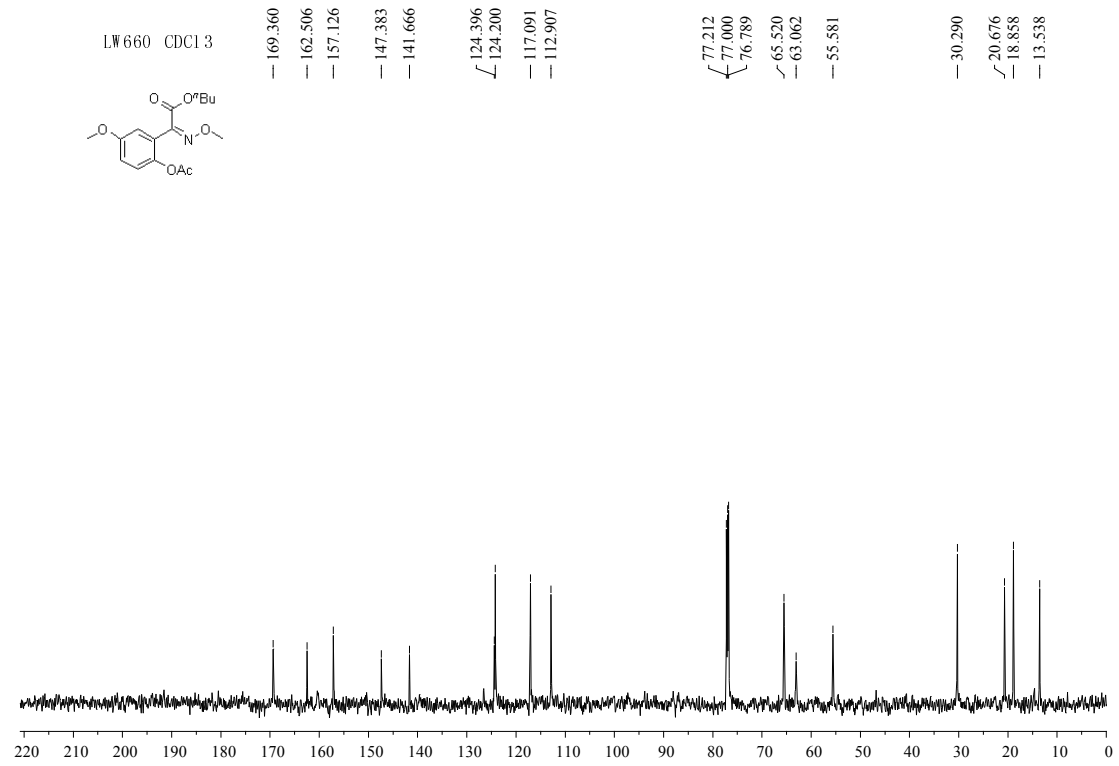
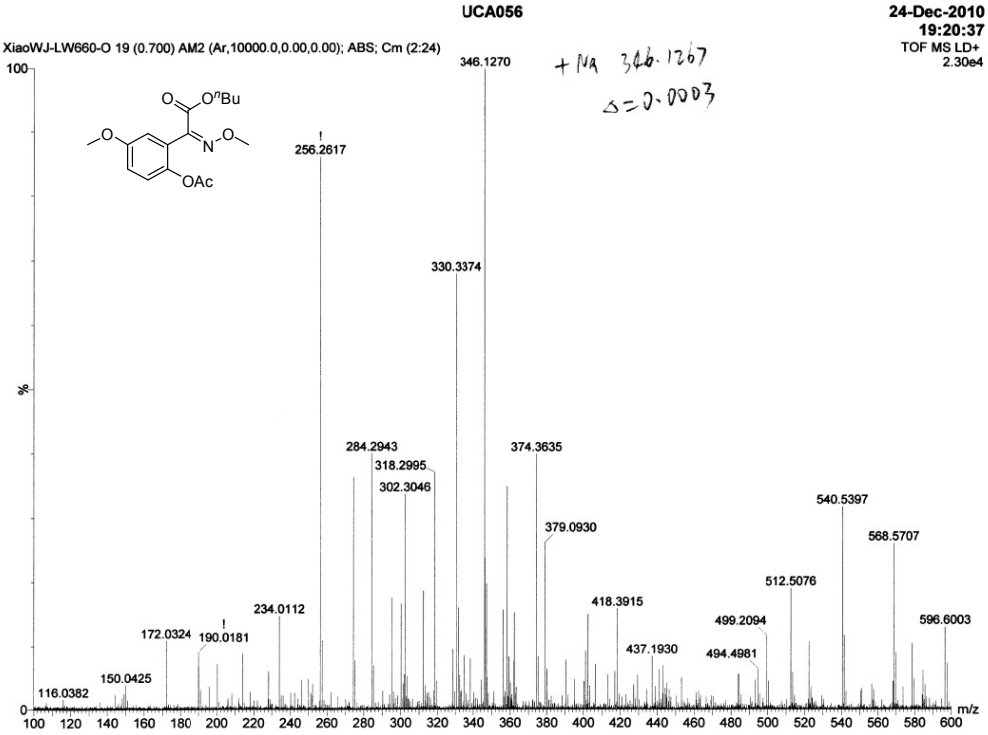


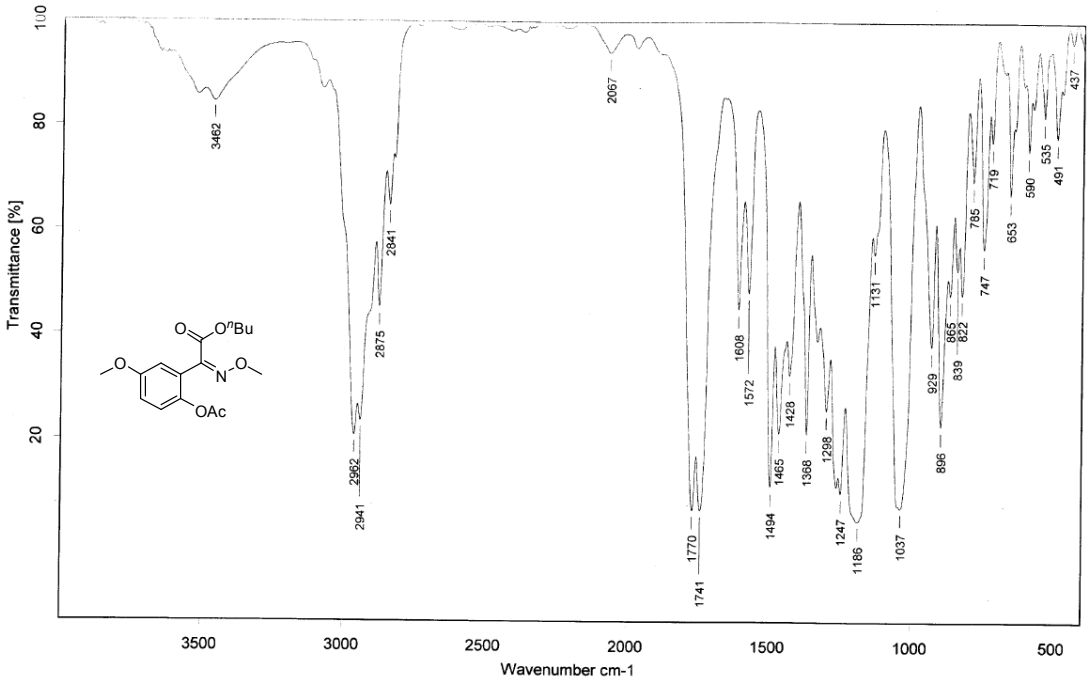


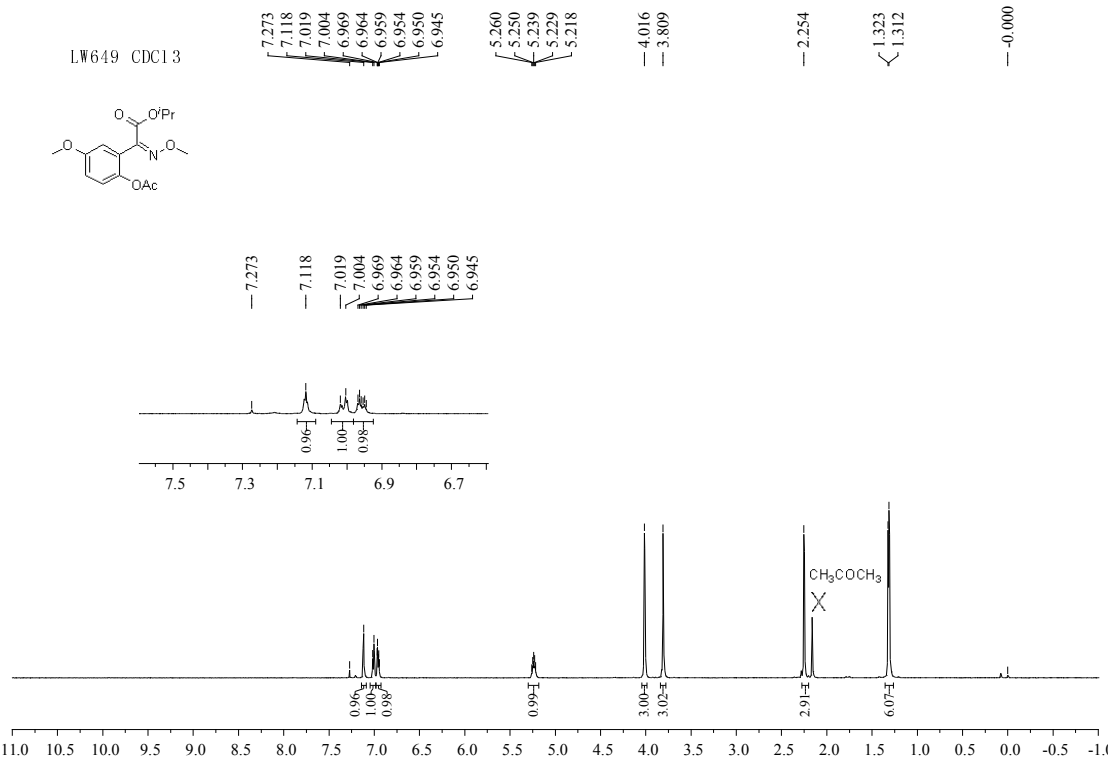


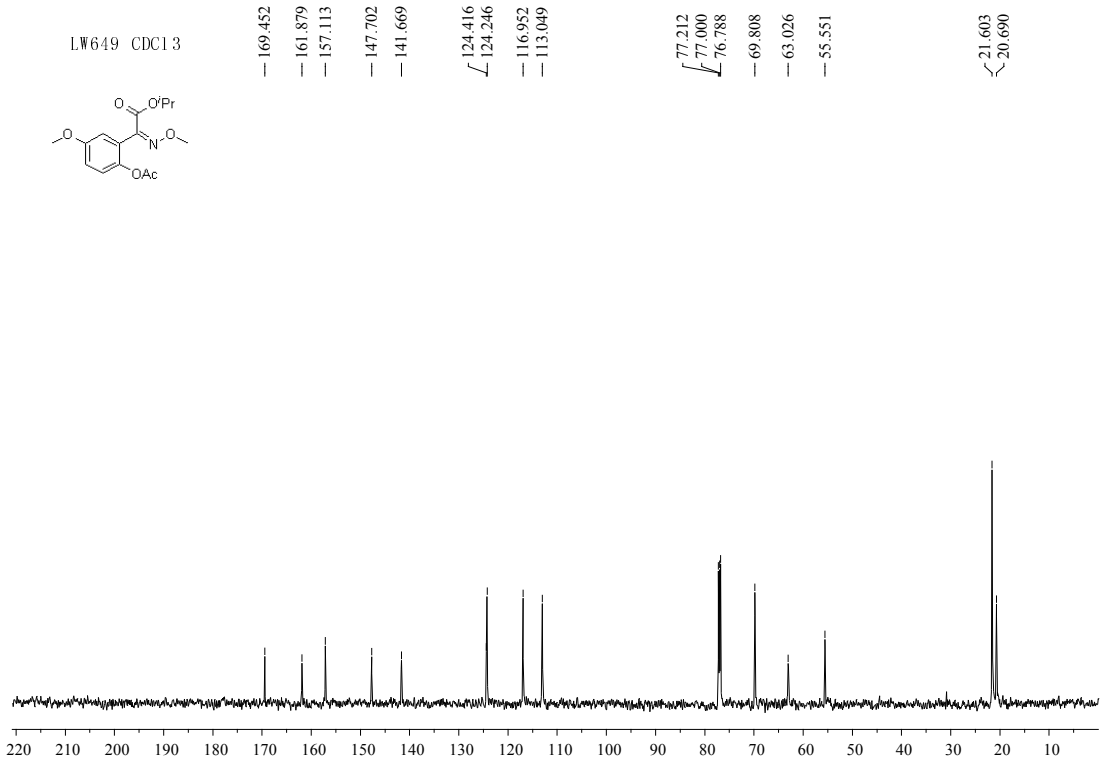


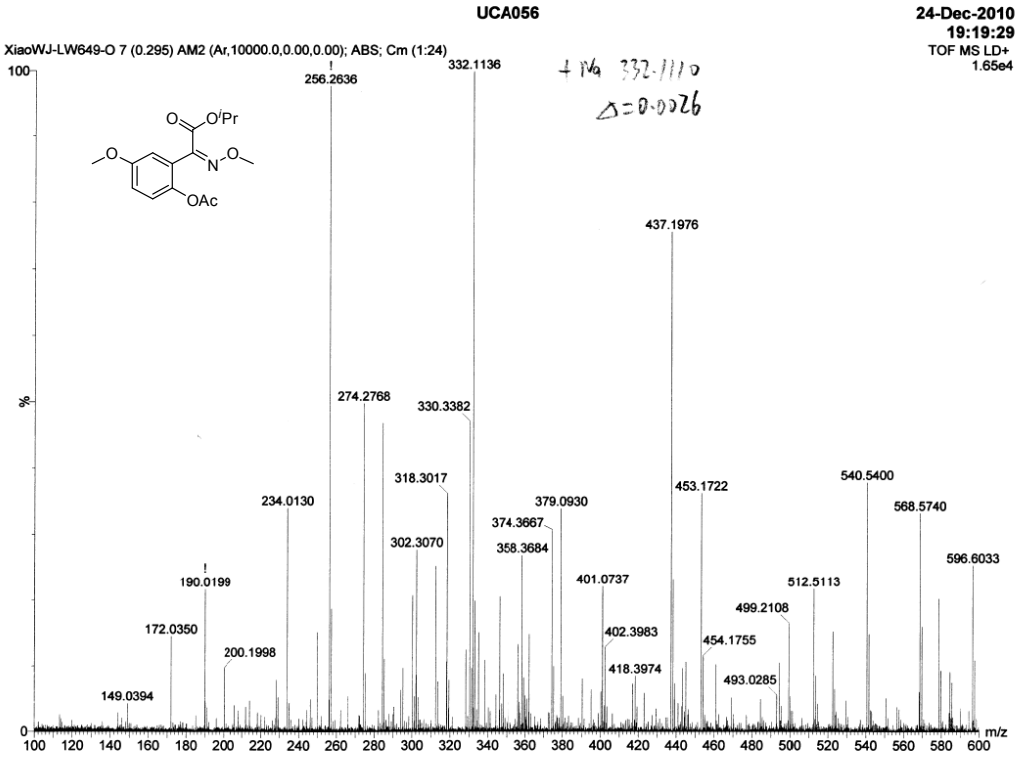


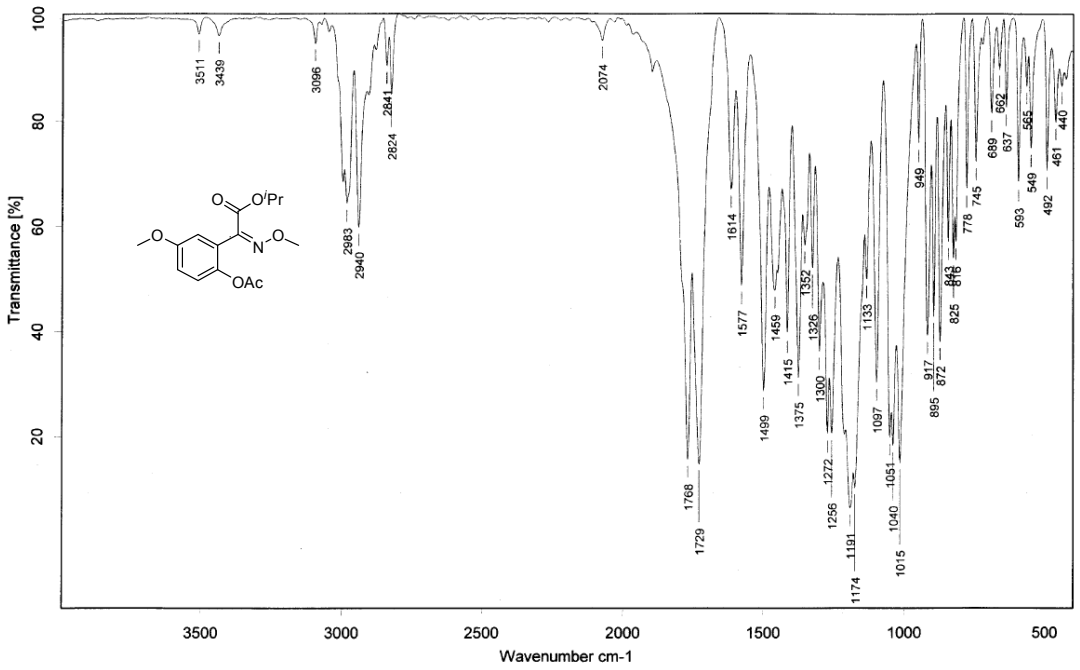


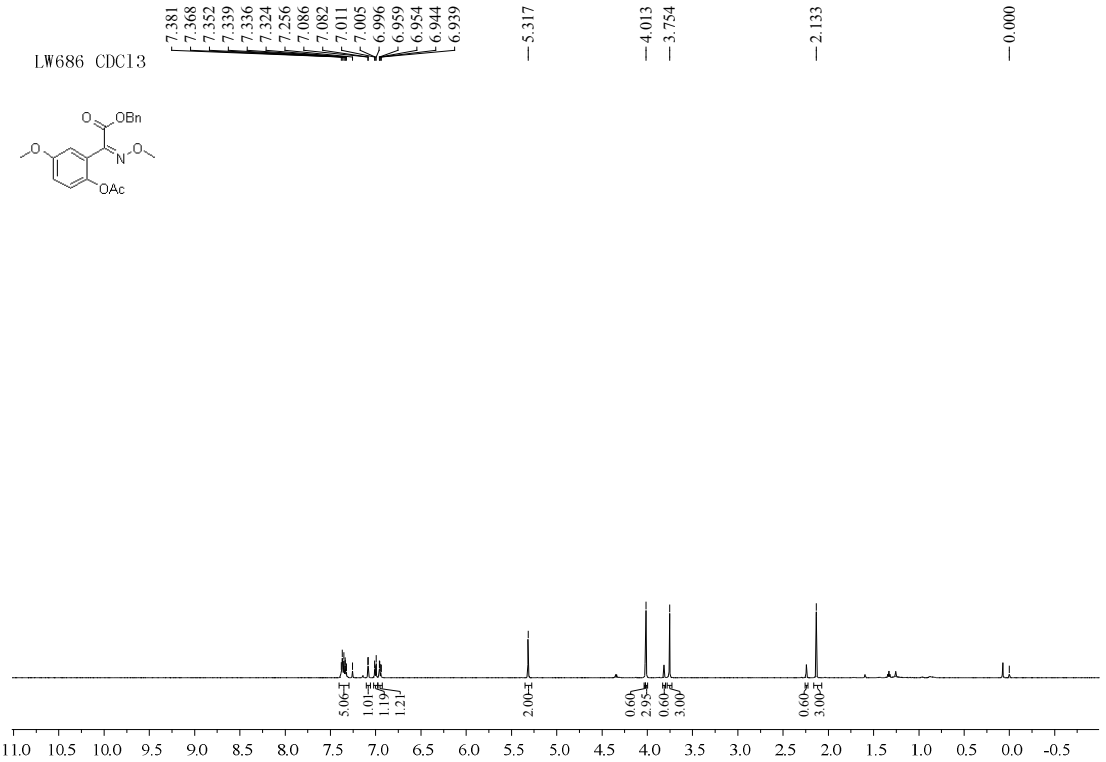


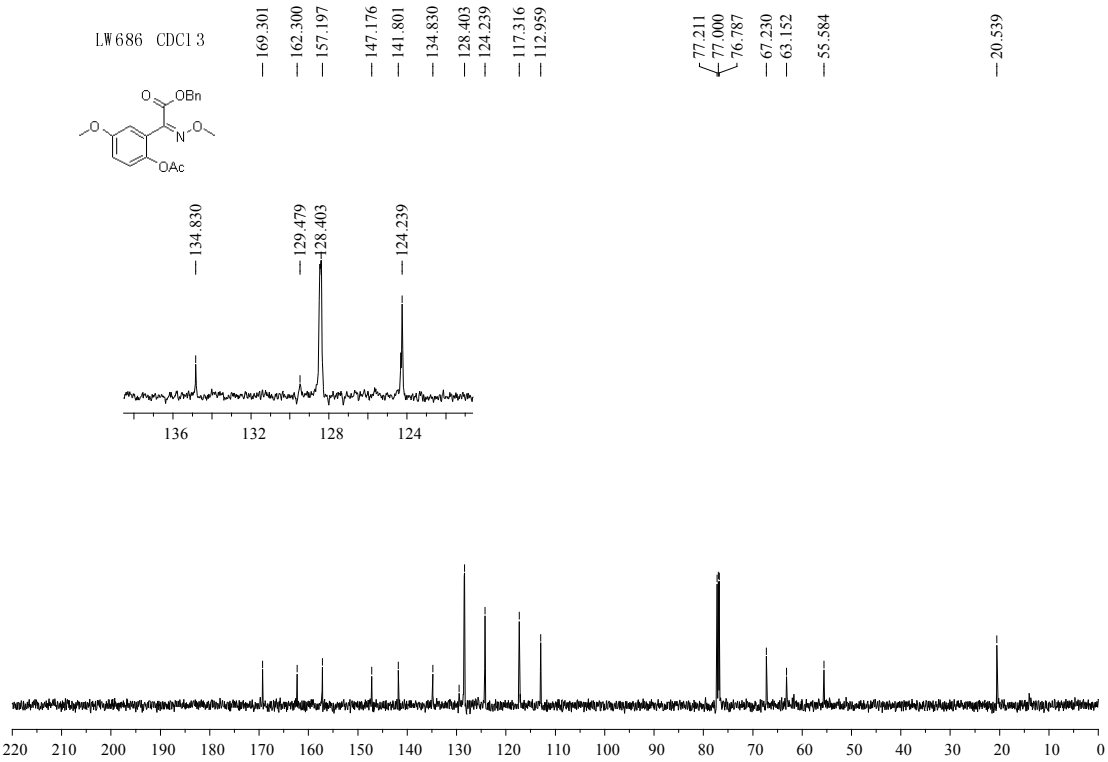


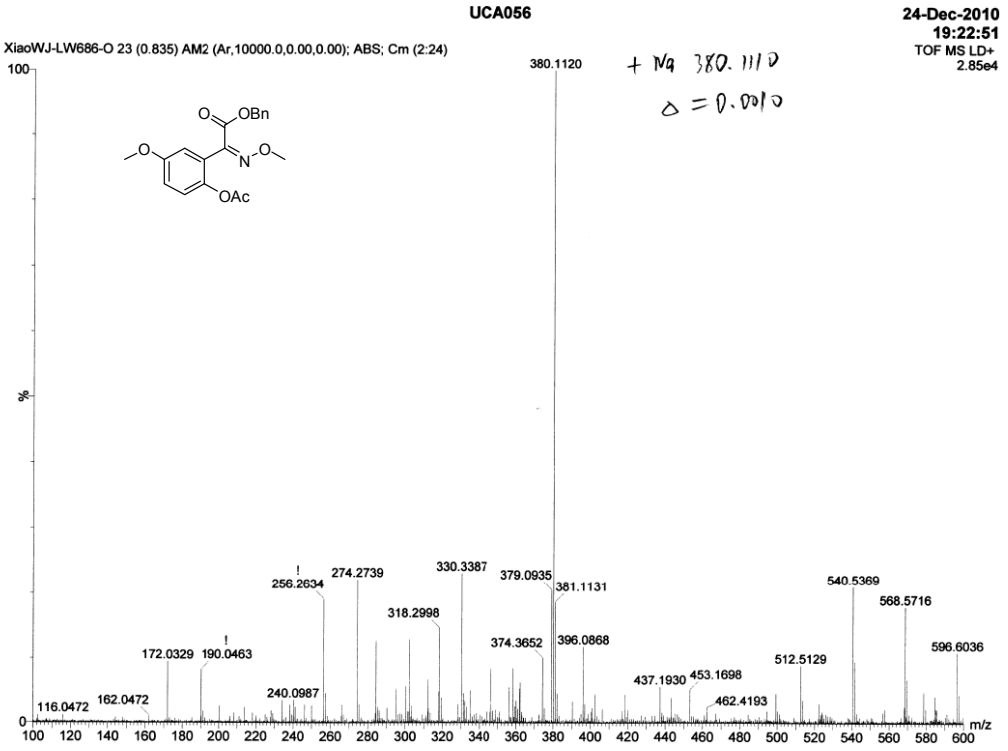


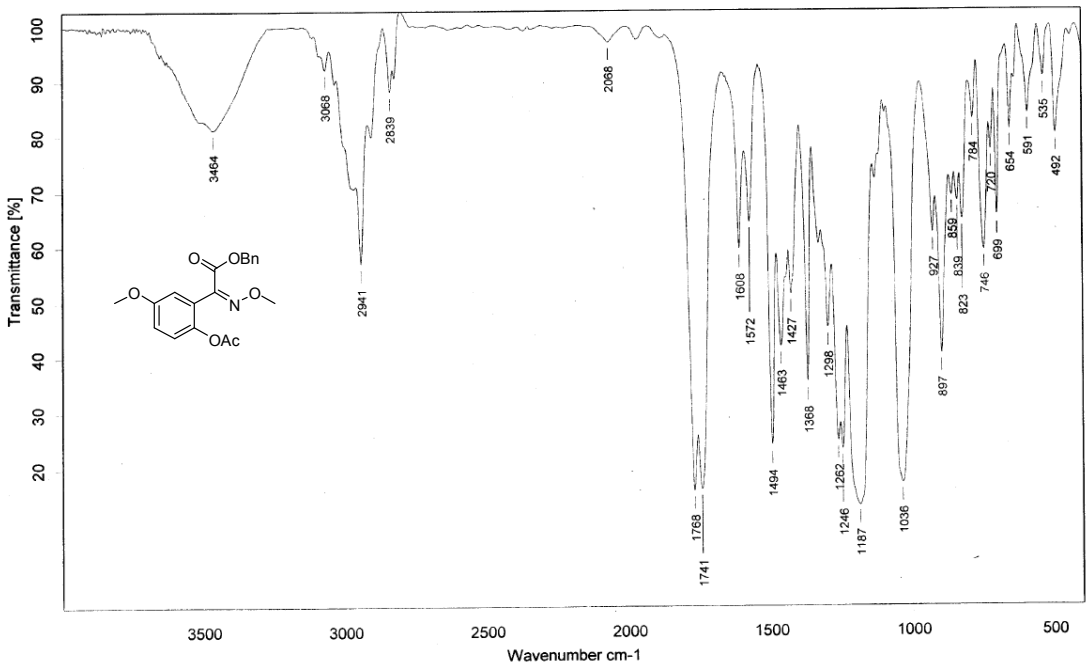


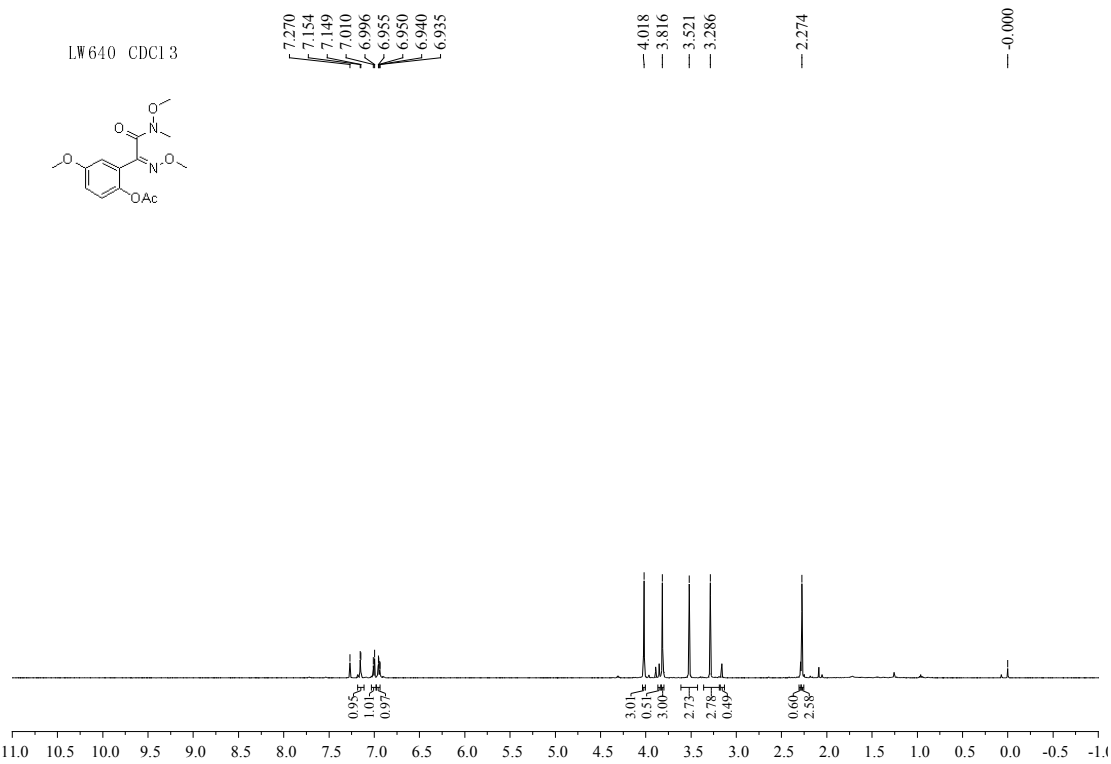


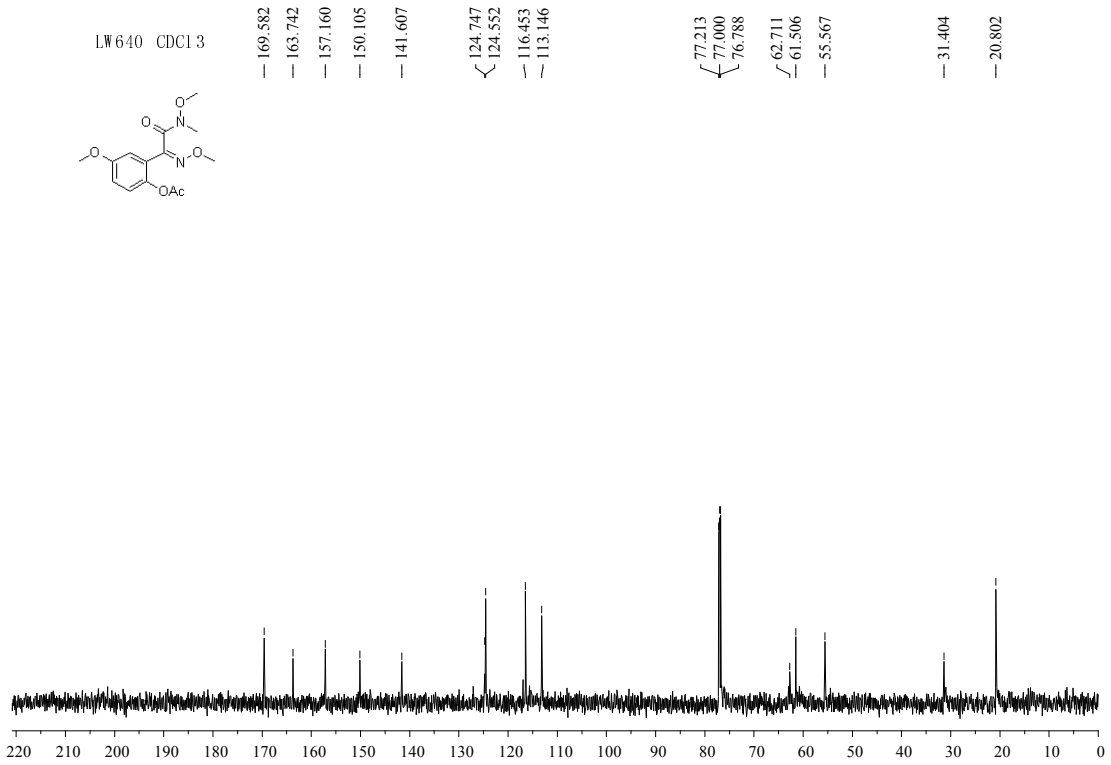


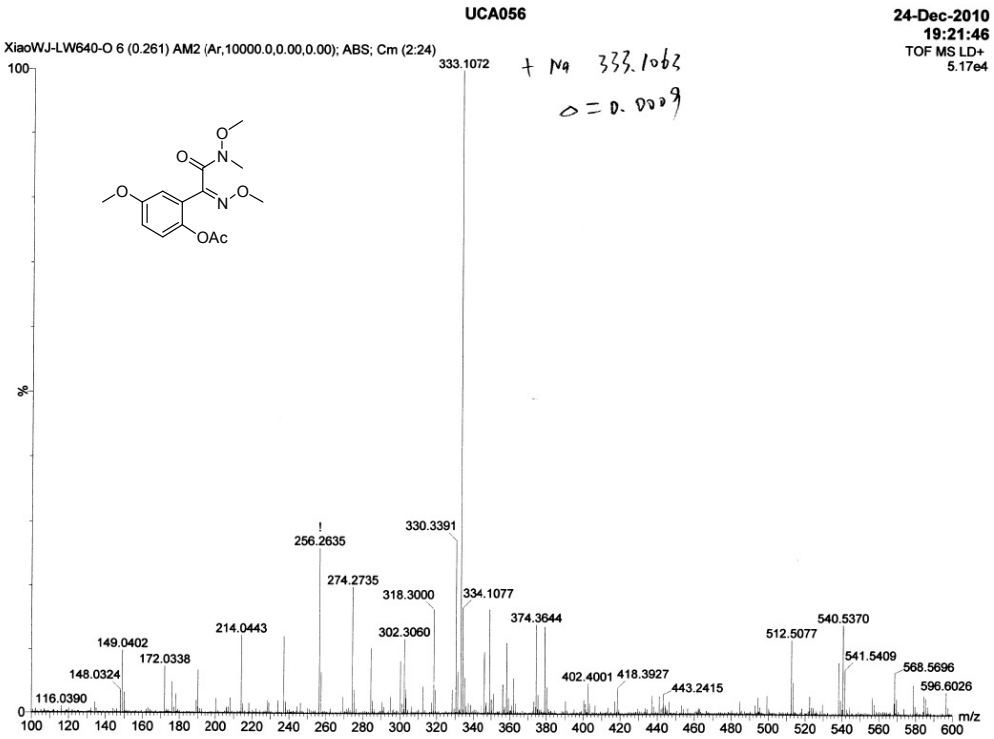


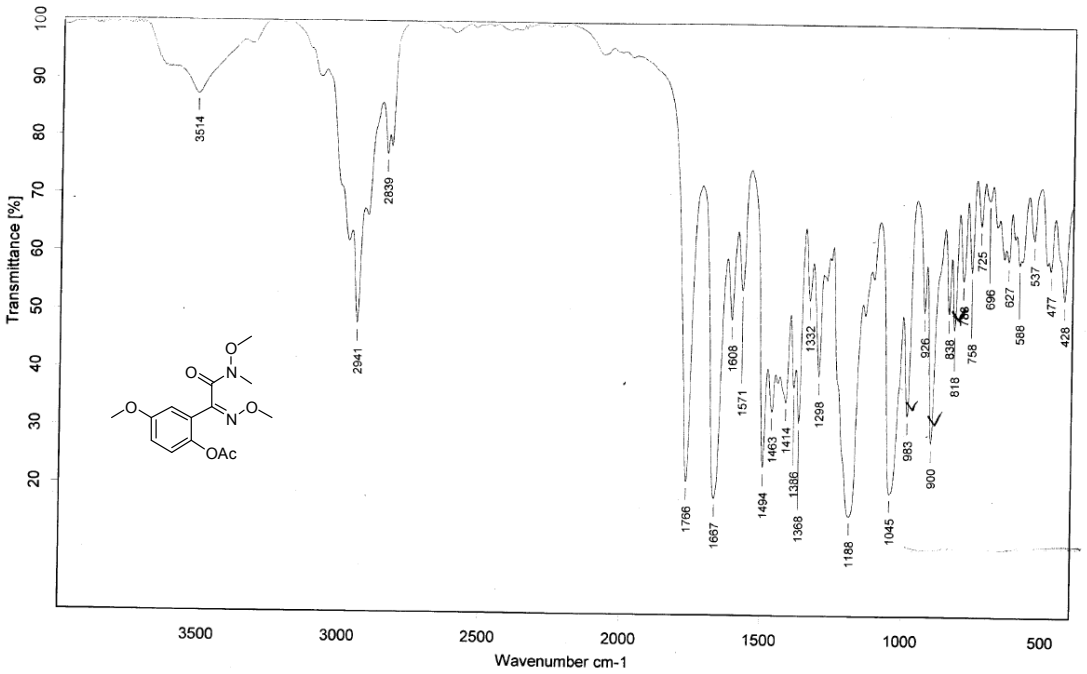


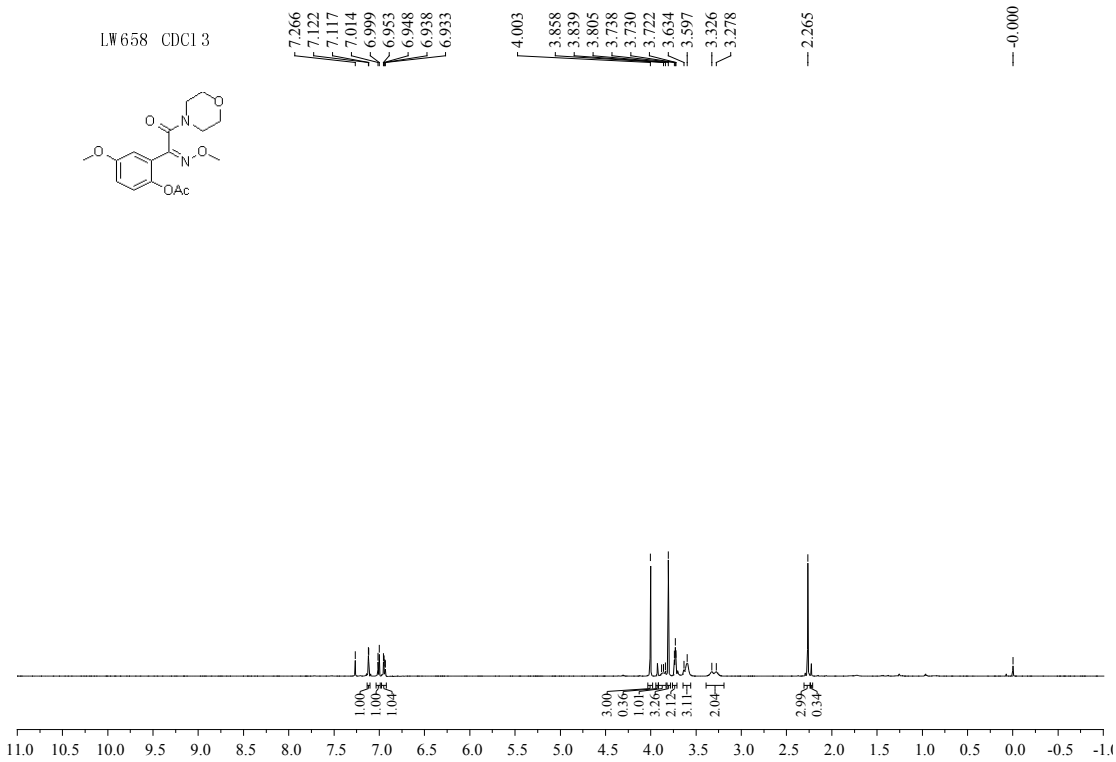


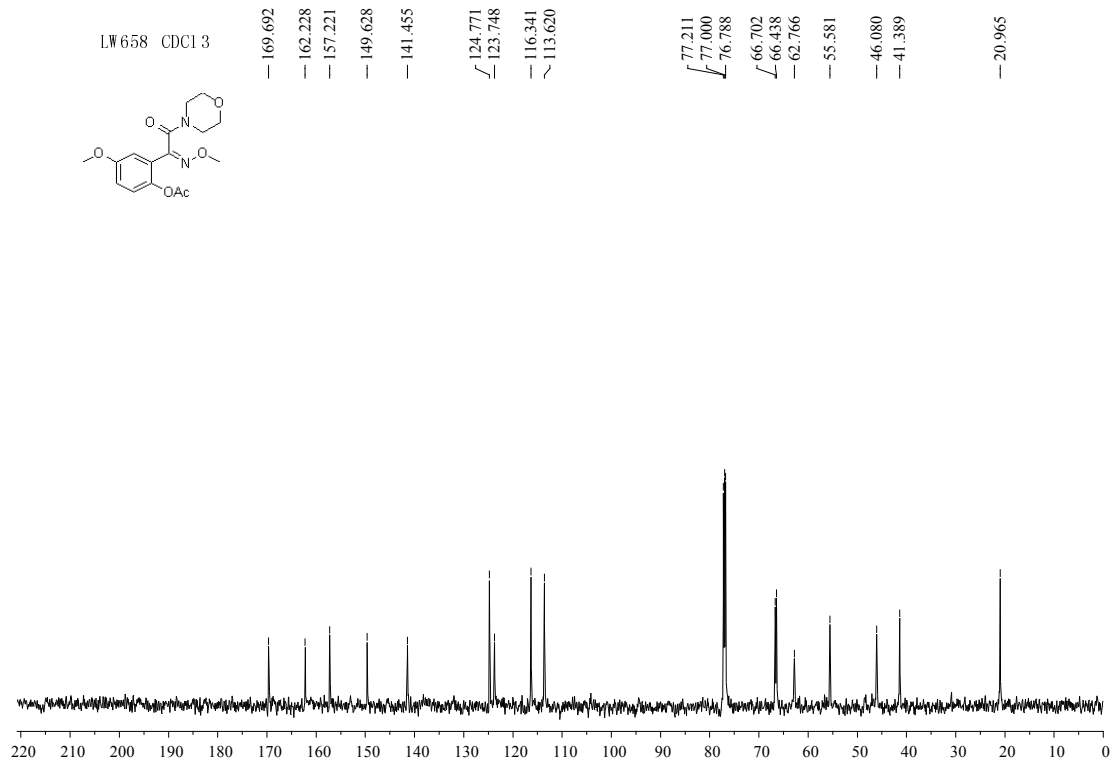












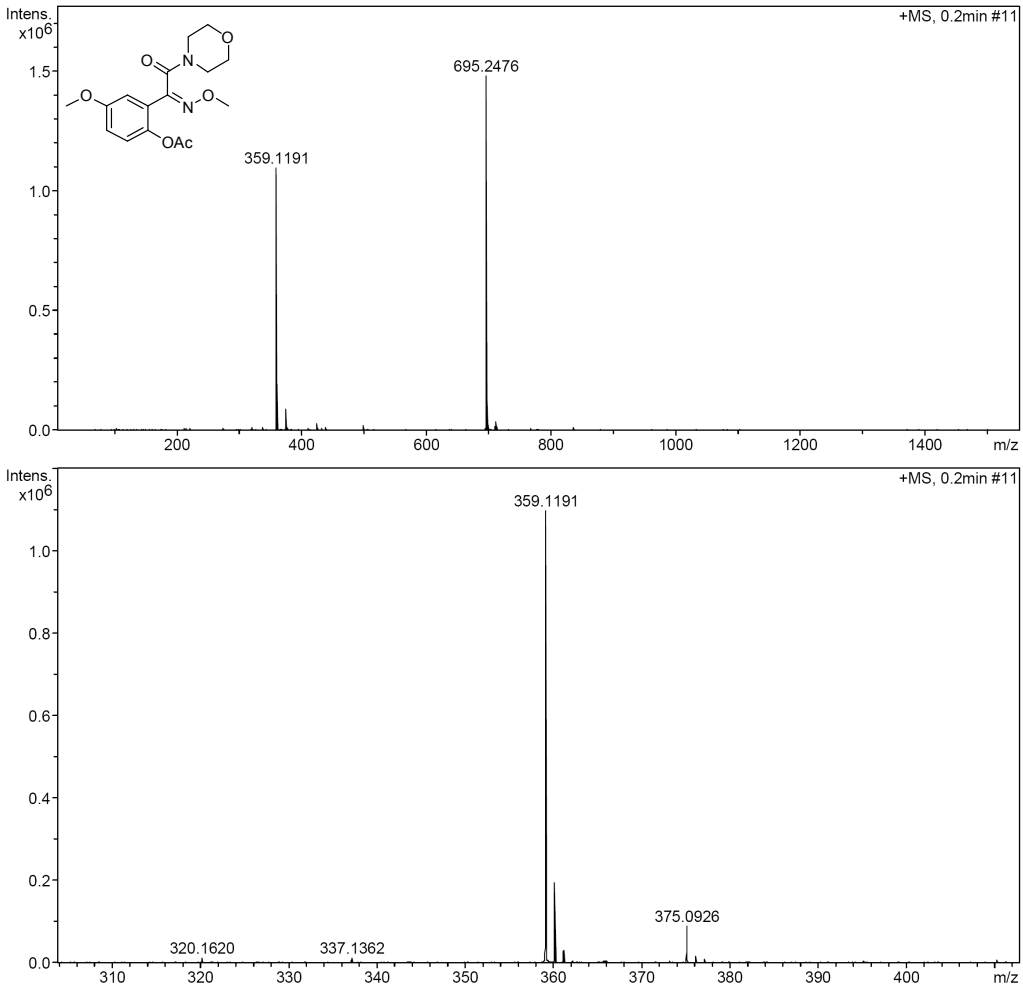
Display Report

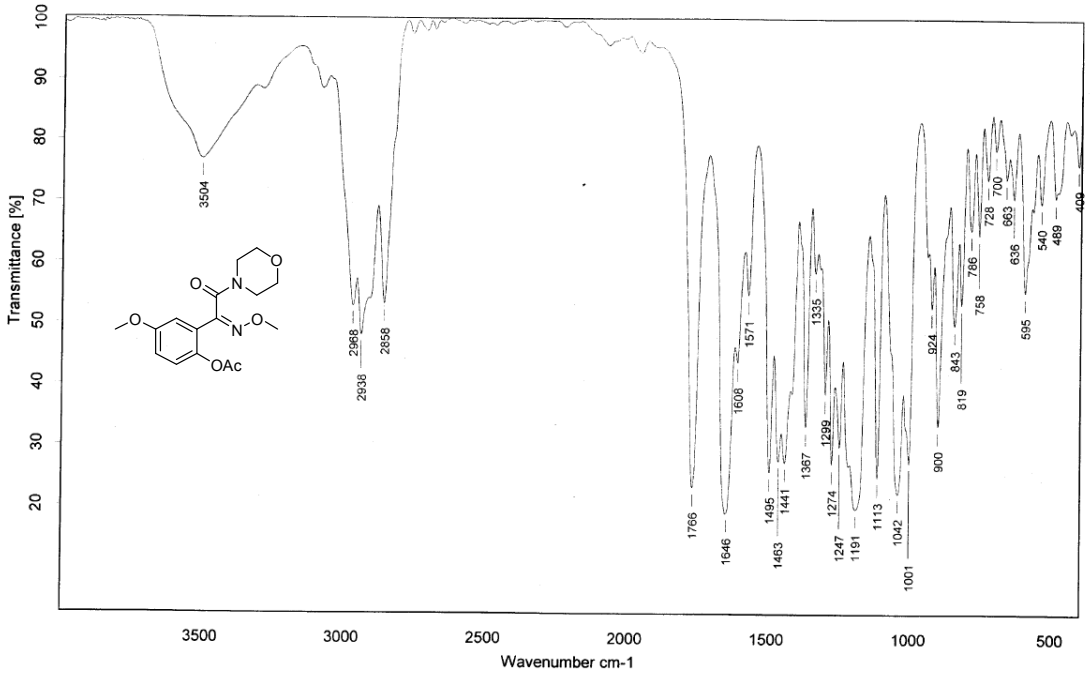
Analysis Info

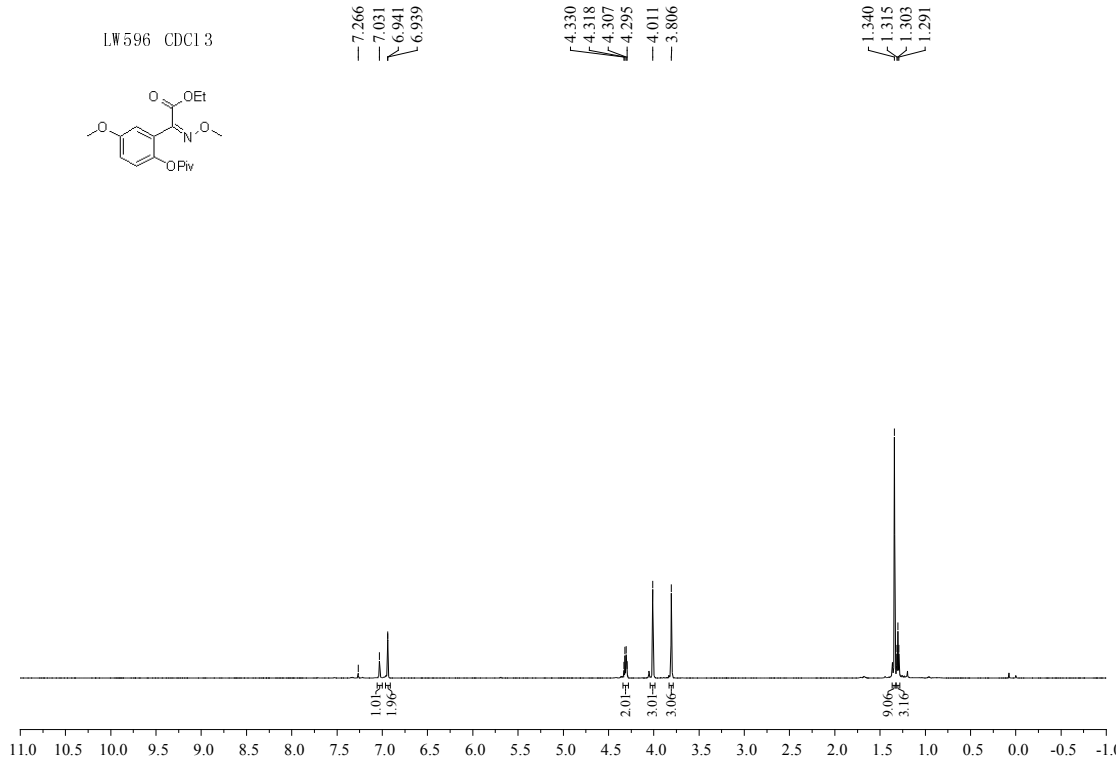
Analysis Name	D:\Data\MS\wj\0324\wc-ysq000002.d	Acquisition Date	3/24/2011 2:59:04 PM
Method	tune_200-800_hcoona-POS.m	Operator	gftang
Sample Name	lw658	Instrument / Ser#	micrOTOF II 10257
Comment			

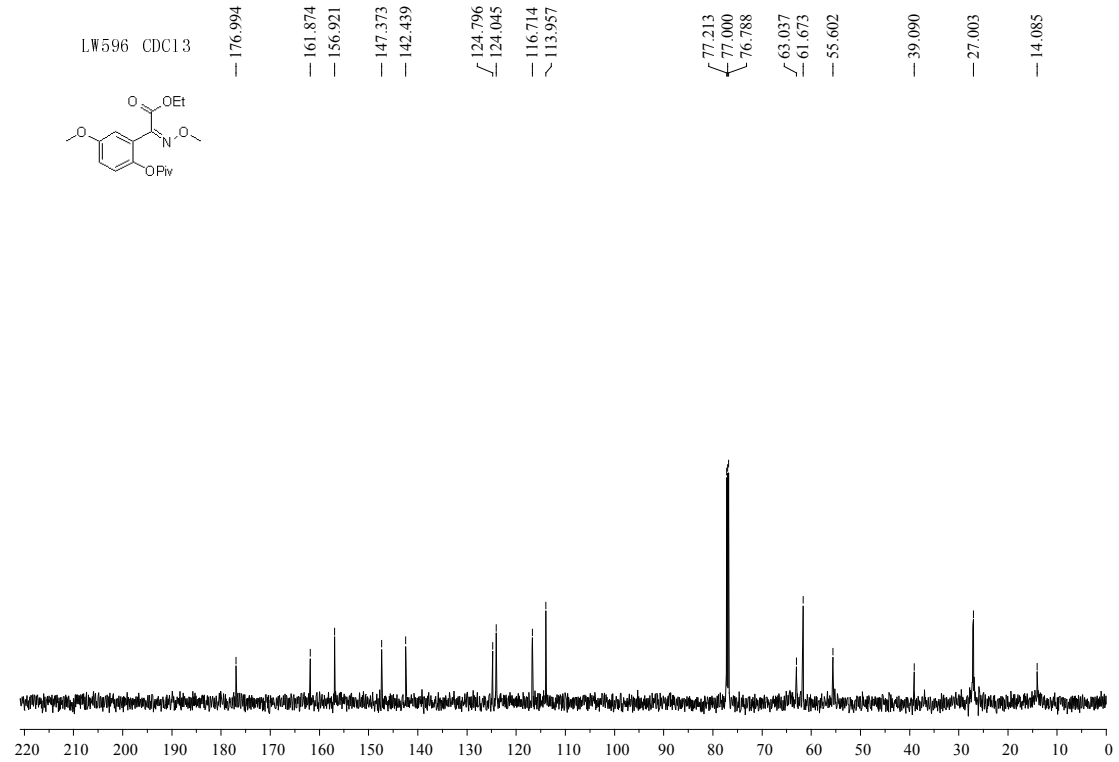
Acquisition Parameter

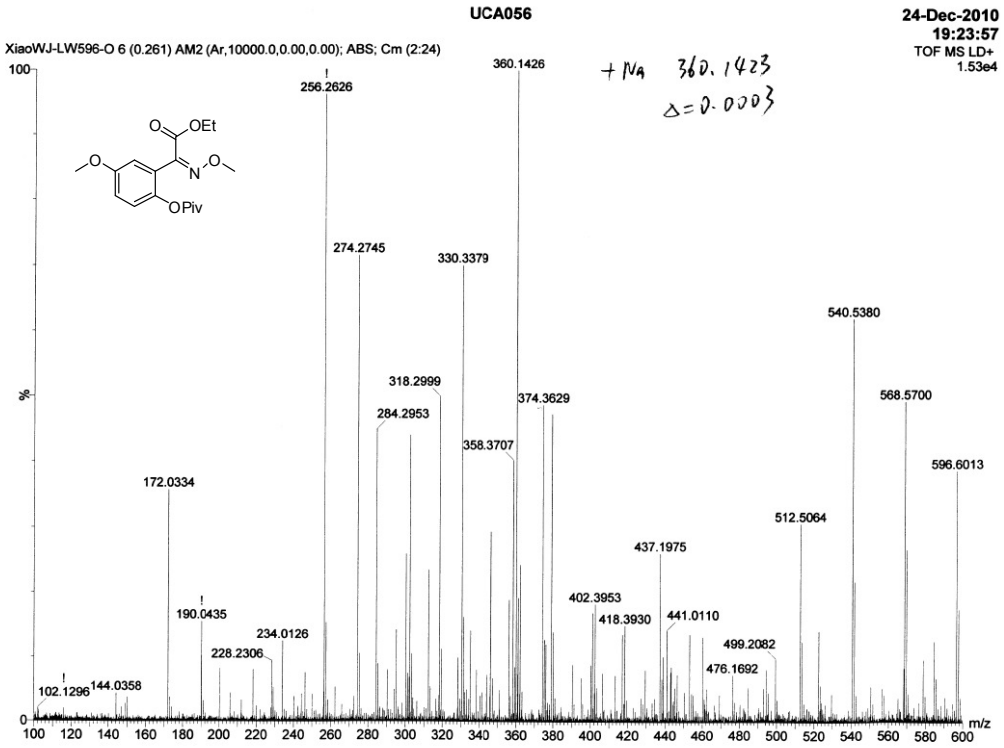
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active			Set Dry Heater	180 ℃
Scan Begin	50 m/z	Set Capillary	4000 V	Set Dry Gas	8.0 l/min
Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

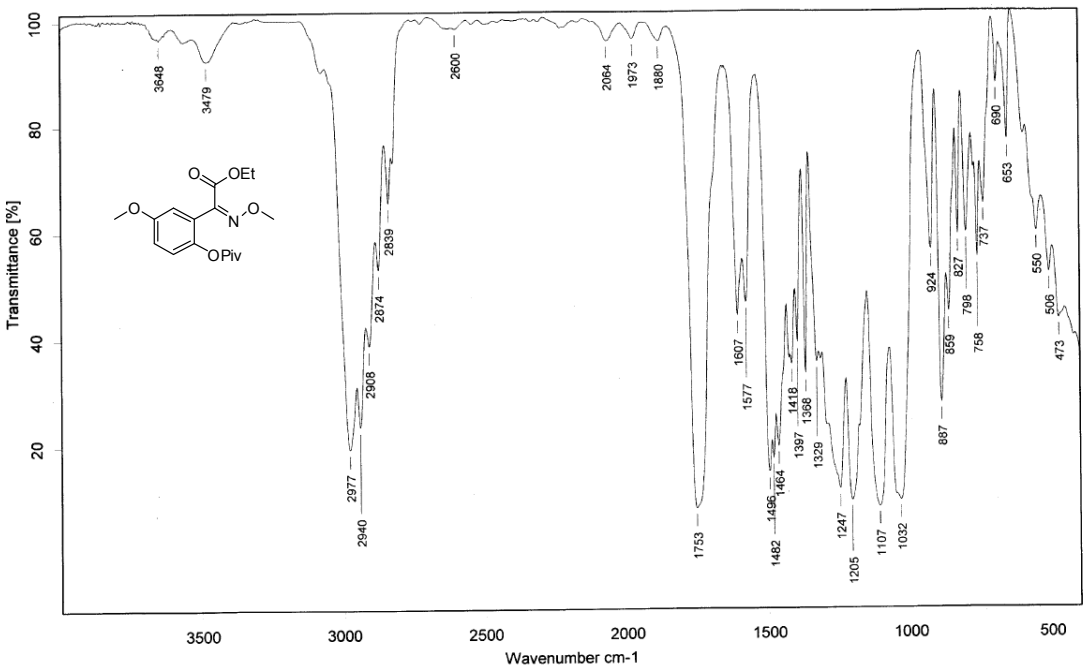


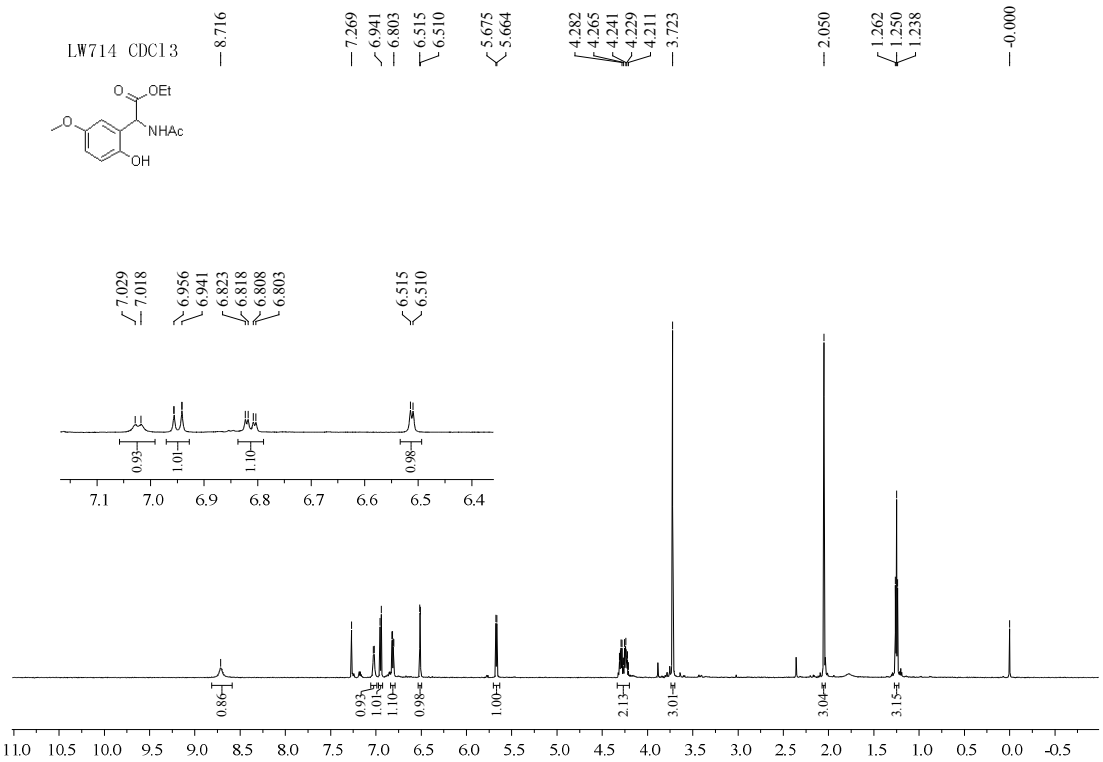


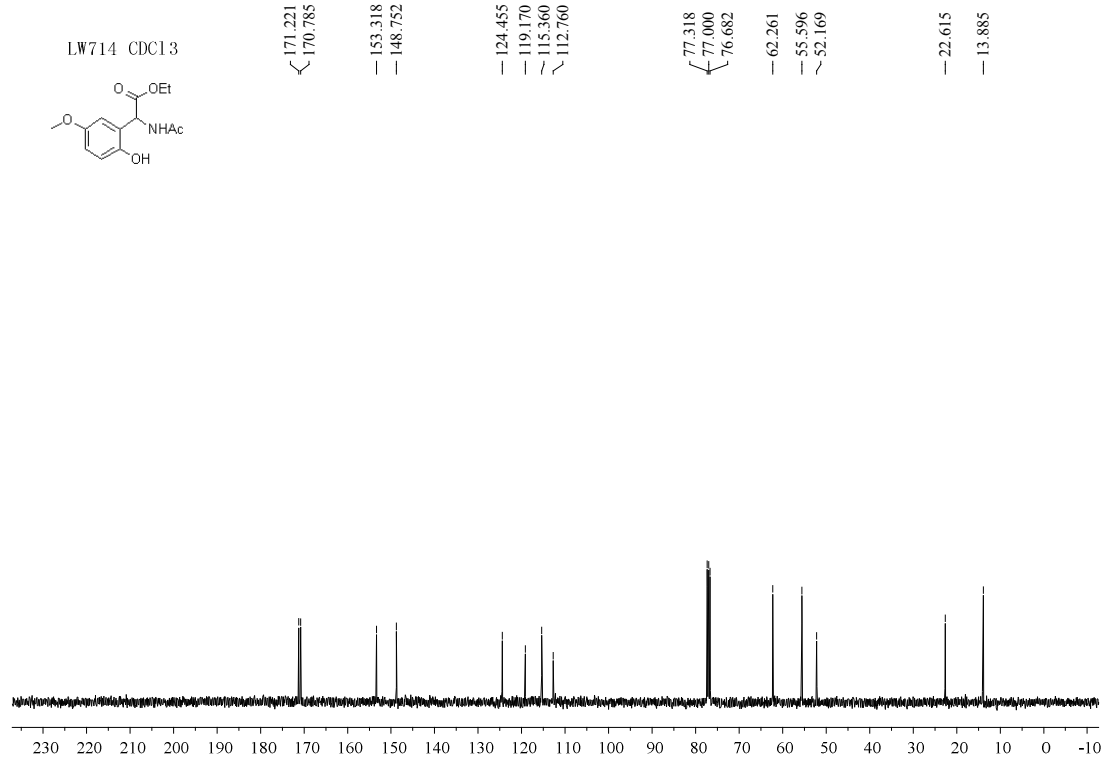












Display Report

Analysis Info

Analysis Name	D:\Data\MS\wj\0324\wc-ysq000003.d	Acquisition Date	3/24/2011 3:00:15 PM
Method	tune_200-800_hcoona-POS.m	Operator	gftang
Sample Name	lw714	Instrument / Ser#	micrOTOF II 10257
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active			Set Dry Heater	180 ℃
Scan Begin	50 m/z	Set Capillary	4000 V	Set Dry Gas	8.0 l/min
Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste