# Supporting Information

# Pd-Catalyzed Direct Oxidative *mono*-Aroyloxylation of *O*-Aralkyl Substituted Acetoxime Ethers

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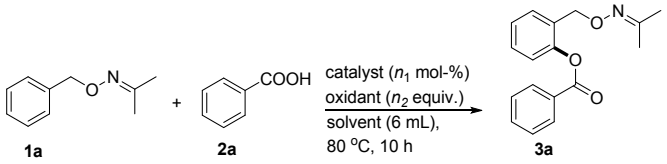
## Content

## 1. General Information

Unless otherwise indicated, all reagents were obtained from commercial sources and used as received without further purification. All reactions were carried out in oven-dried glassware and monitored by thin layer chromatography (TLC, pre-coated silica gel plates containing $HF_{254}$). All solvents were only dried over 4 Å molecular sieves. Reaction products were purified *via* column chromatography on silica gel (300–400 mesh). Melting points were determined using an open capillaries and uncorrected. NMR spectra were determined on Bruker AV400 in $CDCl_3$ with TMS as internal standard for $^1H$ NMR (400 MHz) and $^{13}C$ NMR (100 MHz), respectively. HRMS were measured on a QSTAR Pulsar I LC/TOF MS mass spectrometer or Micromass GCTTM gas chromatograph-mass spectrometer.

## 2. General Procedures and Characterization Data of Compounds

2.1 Investigations of the reaction parameters (Table 1).[a]



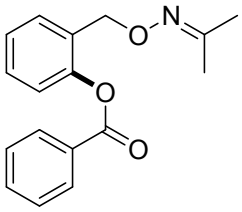

**1a** **2a** **3a**

| Entry | Catalyst ($n_1$ mol-%) | Oxidant ($n_2$ equiv.) | Solvent | Yield (%)[b] |
|---|---|---|---|---|
| 1 | $Pd(OAc)_2$ (10) | $K_2S_2O_8$ (2.0) | DCE | 67 |
| 2 | $Pd(OAc)_2$ (10) | oxone (2.0) | DCE | 65 |
| 3 | $Pd(OAc)_2$ (10) | $PhI(OAc)_2$ (2.0) | DCE | 61 |
| 4 | $Pd(OAc)_2$ (10) | $Na_2S_2O_8$ (2.0) | DCE | 59 |
| 5 | $Pd(OAc)_2$ (10) | TBHP (2.0) | DCE | 0 |
| 6 | $Pd(OAc)_2$ (10) | AgOAc (2.0) | DCE | 0 |
| 7 | $Pd(OAc)_2$ (10) | $K_2S_2O_8$ (2.0) | $CH_3CN$ | 71 |
| 8 | $Pd(OAc)_2$ (10) | $K_2S_2O_8$ (2.0) | DCM | 61 |
| 9 | $Pd(OAc)_2$ (10) | $K_2S_2O_8$ (2.0) | DMSO | 0 |
| **10** | **$Pd(OAc)_2$ (10)** | **$K_2S_2O_8$ (3.0)** | **$CH_3CN$** | **76** |
| 11 | $Pd(OAc)_2$ (10) | $K_2S_2O_8$ (4.0) | $CH_3CN$ | 76 |
| 12[c] | $Pd(OAc)_2$ (10) | $K_2S_2O_8$ (3.0) | $CH_3CN$ | 70 |
| 13[d] | $Pd(OAc)_2$ (10) | $K_2S_2O_8$ (3.0) | $CH_3CN$ | 55 |
| 14 | $(\eta^3\text{-}C_3H_5)_2Pd_2Cl_2$ (10) | $K_2S_2O_8$ (3.0) | $CH_3CN$ | 31 |
| 15 | $PdCl_2$ (10) | $K_2S_2O_8$ (3.0) | $CH_3CN$ | 0 |
| 16 | $(Ph_3P)_2PdCl_2$ (10) | $K_2S_2O_8$ (3.0) | $CH_3CN$ | 0 |
| 17 | $Pd(OAc)_2$ (15) | $K_2S_2O_8$ (3.0) | $CH_3CN$ | 67 |
| 18 | $Pd(OAc)_2$ (5) | $K_2S_2O_8$ (3.0) | $CH_3CN$ | 65 |

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (2.0 mmol), catalyst ($n_1$ mol- %), oxidant ($n_2$ equiv.), solvent (6 mL) at 80 °C for 10 h; [b] Isolated yields; [c] 60 °C; [d] 100 °C. DMSO = dimethylsulfoxide; DCM = dichloromethane; DCE = 1,2-dichloroethane.

**General procedure**: A mixture of substrate **1a** (1.0 mmol), **2a** (2.0 mmol), $Pd(OAc)_2$ ($n_1$ mol- %), oxidant ($n_2$ equiv.) and solvent (6 mL) was stirred at specific temperature for 10 h. Upon completion of the reaction, the mixture was dropped into the saturated $NaHCO_3$ solution (30 mL).

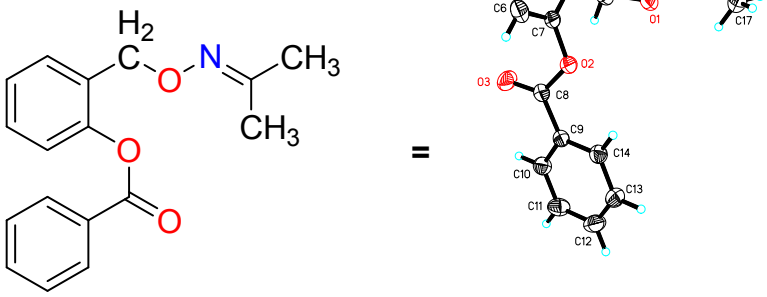
The solution was extracted with ethyl acetate (25 mL×3), and then the combined organic layers were dried over anhydrous $MgSO_4$. Finally, the solution was concentrated *in vacuo* to provide a crude product, which was purified *via* a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate 20:1) to supply the desired product **3a**.



**3a**

**2-(((propan-2-ylideneamino)oxy)methyl)phenyl benzoate (3a)**: white solid, 215.2 mg (76%), m.p. 72–74 °C; IR ($cm^{-1}$) $\bar{\upsilon}$ 3063, 2930, 2855, 1728, 1599, 1452, 1370, 1217, 1107, 954, 763, 703; $^1H$ NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.22 (s, 1H), 8.21 (s, 1H), 7.64 (t, $J$ = 7.6 Hz，1H), 7.53–7.50 (m, 2H), 7.49–7.48 (m, 1H), 7.39 (dt, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz, 1H), 7.29 (dd, $J_1$ = 7.6 Hz, $J_2$ = 1.2 Hz, 1H), 7.23 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.2 Hz, 1H), 5.12 (s, 2H), 1.77 (s, 3H), 1.76 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 165.0, 155.4, 149.1, 133.6, 130.5, 130.3 (2C), 129.9, 129.5, 128.9, 128.6 (2C), 126.0, 122.6, 70.7, 21.7, 15.6; HRMS (EI): *m/z* [$M^+$] calcd. for $C_{17}H_{17}NO_3$: 283.1208, found: 283.1204.

### 2.2 X-Ray crystallographic data of 3a



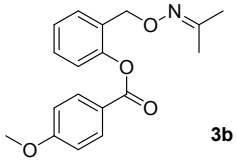

Crystal data and structure refinement for cd16181.

| | | |
|---|---|---|
| Identification code | cd16181 | |
| Empirical formula | C17 H17 N O3 | |
| Formula weight | 283.31 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | P b c a | |
| Unit cell dimensions | a = 12.049(3) Å | a= 90°. |
| | b = 7.1678(19) Å | b= 90°. |
| | c = 35.147(9) Å | g = 90°. |

| | |
|---|---|
| Volume | 3035.4(14) $Å^3$ |
| Z | 8 |
| Density (calculated) | 1.240 $Mg/m^3$ |
| Absorption coefficient | 0.085 $mm^{-1}$ |
| F(000) | 1200 |
| Crystal size | 0.180 x 0.150 x 0.120 $mm^3$ |
| Theta range for data collection | 2.049 to 25.499°. |
| Index ranges | -14<=h<=14, -8<=k<=6, -42<=l<=42 |
| Reflections collected | 16093 |
| Independent reflections | 2827 [R(int) = 0.0783] |
| Completeness to theta = 25.242° | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7456 and 0.6359 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 2827 / 0 / 193 |
| Goodness-of-fit on $F^2$ | 1.023 |
| Final R indices [I>2sigma(I)] | R1 = 0.0553, wR2 = 0.1462 |
| R indices (all data) | R1 = 0.0913, wR2 = 0.1661 |
| Largest diff. peak and hole | 0.172 and -0.154 $e.Å^{-3}$ |

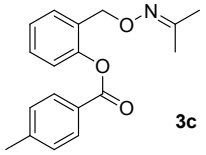
**2.3 Investigation on the substrate scope of aromatic acids (Scheme 3)**

**General procedure**: A mixture of substrate **1a** (1.0 mmol), **2** (2.0 mmol), $Pd(OAc)_2$ (0.10 mmol) , and $K_2S_2O_2$ (3.0 mmol) was dissolved in $CH_3CN$ (6 mL), then the reaction mixture was heated at 80 °C for 10 h, or a specific time of 15 h. Upon completion of the reaction, the mixture was dropped into the saturated $NaHCO_3$ solution (30 mL). The solution was extracted with ethyl acetate (25 mL×3), and then the combined organic layers were dried over anhydrous $MgSO_4$. Finally, the solution was concentrated *in vacuo* to provide a crude product, which was purified *via* a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate 20:1) to supply the desired product **3**.



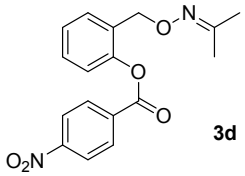
**3b**

**2-(((propan-2-ylideneamino)oxy)methyl)phenyl 4-methoxybenzoate (3b)**: white solid, 253.6 mg (81%), m.p. 74–76 °C; IR ($cm^{-1}$) $\bar{\upsilon}$ 3066, 2919, 2849, 1729, 1455, 1316, 1251, 1162, 1065, 918, 845, 749; $^1H$ NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.15 (d, $J$ = 9.2 Hz, 2H), 7.47 (d, $J$ = 7.6 Hz, 1H), 7.36 (t, $J$ = 8.0 Hz, 1H), 7.25 (t, $J$ = 7.6 Hz, 1H), 7.21 (d, $J$ = 8.0 Hz, 1H), 6.97 (d, $J$ = 8.8 Hz, 2H), 5.10 (s, 2H), 3.86 (s, 3H), 1.77 (s, 3H), 1.76 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 164.7, 163.9, 155.4, 149.2, 132.4 (2C), 130.6, 129.8, 128.9, 125.9, 122.7, 121.9, 113.9 (2C), 70.7, 55.6, 21.8, 15.7; HRMS (EI): *m/z* [$M^+$] calcd. for $C_{18}H_{19}NO_4$: 313.1314, found 313.1316.



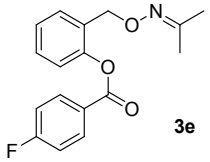
**3c**

**2-(((propan-2-ylideneamino)oxy)methyl)phenyl 4-methylbenzoate (3c)**: white solid, 226.8 mg (79%), m.p. 86–88 °C; IR ($cm^{-1}$) $\bar{\upsilon}$ 3063, 2929, 1726, 1655, 1492, 1446, 1374, 1217, 1107, 978, 879, 824, 781;$^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.09 (d, $J$ = 8.0 Hz, 2H), 7.49 (d, $J$ = 7.2 Hz, 1H), 7.38 (t, $J$ = 8.0 Hz, 1H), 7.32–7.26 (m, 3H), 7.22 (d, $J$ = 7.6 Hz, 1H), 5.11 (s, 2H), 2.45 (s, 3H), 1.78 (s, 3H) , 1.77 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 165.0, 155.4, 149.2, 144.4, 130.6, 130.4 (2C), 129.9, 129.3 (2C), 128.9, 126.8, 126.0, 122.7, 70.7, 21.84, 21.82, 15.7; HRMS (EI): *m/z* [$M^+$] calcd. for $C_{18}H_{19}NO_3$: 297.1365, found 297.1362.



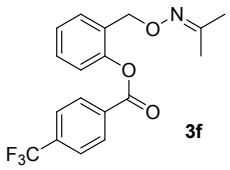
**3d**

**2-(((propan-2-ylideneamino)oxy)methyl)phenyl 4-nitrobenzoate (3d)**: yellow solid, 196.9 mg (60%), m.p. 65–67 °C; IR ($cm^{-1}$) $\bar{\upsilon}$ 3112, 2923, 2855, 1744, 1605, 1519, 1453, 1344, 1259, 1025, 988, 869, 750, 711; $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.37 (dd, $J_1$ = 14.4 Hz, $J_2$ = 9.2 Hz, 4H), 7.50 (dd, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz, 1H), 7.41 (td, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz, 1H), 7.32 (td, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz, 1H), 7.24 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.2 Hz, 1H), 5.09 (s, 2H), 1.75 (s, 3H), 1.74 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 163.2, 155.6, 151.0, 148.9, 135.1, 131.4 (2C), 130.4, 130.3, 129.7, 126.7, 123.8 (2C), 122.4, 70.8, 21.8, 15.7; HRMS (EI): *m/z* [$M^+$] calcd. for $C_{17}H_{16}N_2O_5$: 328.1059, found 328.1051.



**3e**

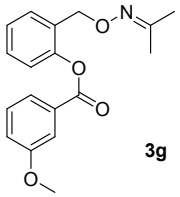
**2-(((propan-2-ylideneamino)oxy)methyl)phenyl 4-fluorobenzoate (3e)**: yellow oil, 201.7 mg (67%); IR ($cm^{-1}$) $\bar{\upsilon}$ 3073, 2921, 2851, 1737, 1601, 1505, 1453, 1366, 1261, 1152, 1066, 1014, 852, 749, 684; $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.25–8.21 (m, 2H), 7.74 (dd, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz, 1H), 7.38 (dt, $J_1$ = 8.0 Hz, $J_2$ = 1.6 Hz, 1H), 7.29 (dd, $J_1$ = 7.2 Hz, $J_2$ = 1.2 Hz, 1H), 7.23–7.15 (m, 3H), 5.10 (s, 2H), 1.77 (s, 3H), 1.76 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 166.2 (d, $^1J_{CF}$ = 254.9 Hz), 164.0, 155.4, 149.1, 132.9 (d, $^3J_{CF}$ = 9.4 Hz, 2C), 130.5, 130.1, 129.0, 126.2, 125.8 (d, $^4J_{CF}$ = 3.0 Hz), 122.6, 115.9 (d, $^2J_{CF}$ = 22.0 Hz, 2C), 70.8, 21.8, 15.7; HRMS (EI): *m/z* [$M^+$] calcd. for $C_{17}H_{16}FNO_3$: 301.1114, found 301.1119.



**3f**

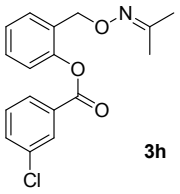
**2-(((propan-2-ylideneamino)oxy)methyl)phenyl 4-(trifluoromethyl)benzoate (3f)**: white solid, 228.2 mg (65%), m.p. 69–71 °C; IR ($cm^{-1}$) $\bar{\upsilon}$ 3080, 2951, 2915, 1740, 1267, 1166, 1109, 1077, 1006, 989, 860, 766, 701; $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.33 (d, $J$ = 8.0 Hz, 2H), 7.78 (d, $J$ = 8.0 Hz, 2H), 7.50 (dd, $J_1$ = 7.6 Hz, $J_2$ = 1.2 Hz, 1H), 7.41 (dt, $J_1$ = 8.0 Hz, $J_2$ = 1.6 Hz, 1H), 7.30 (dt, $J_1$ = 7.2 Hz, $J_2$ = 1.2 Hz, 1H), 7.23 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.2 Hz, 1H), 5.10 (s, 2H), 1.75 (s, 3H), 1.74 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 163.8, 155.4, 149.0, 135.0 (q, $^2J_{CF}$ = 32.5 Hz), 132.9, 130.7 (2C), 130.4, 130.3, 129.2, 123.7 (q, $^1J_{CF}$ = 271.1 Hz), 126.4, 125.7 (q, $^3J_{CF}$ = 3.6

Hz, 2C), 122.5, 70.8, 21.8, 15.6（$C_{18}H_{16}O_3NF_3$）; HRMS (EI): *m/z* [M-NO-$C_3H_6$]$^+$ calcd. for $C_{15}H_{10}O_2F_3$: 279.0633, found 279.0634.



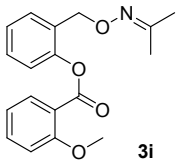
**3g**

**2-(((propan-2-ylideneamino)oxy)methyl)phenyl 3-methoxybenzoate (3g)**: yellow oil, 247.4 mg (79%); IR (cm$^{-1}$) $\bar{\upsilon}$ 3075, 2919, 2840, 1744, 1599, 1488, 1455, 1365, 1295, 1236, 1211, 1169, 1021, 880, 751, 694; $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.05 (d, $J$ = 8.0 Hz, 1H), 7.55 (t, $J$ = 8.0 Hz, 1H), 7.49 (d, $J$ = 7.2 Hz, 1H), 7.36 (t, $J$ = 7.6 Hz, 1H), 7.26 (t, $J$ = 6.8 Hz, 2H), 7.04 (t, $J$ = 6.4 Hz, 2H), 5.15 (s, 2H), 3.95 (s, 3H), 1.82 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 164.1, 159.8, 155.2, 149.0, 134.3, 132.3, 130.5, 129.6, 128.7, 125.8, 122.7, 120.1, 119.0, 112.1, 70.6, 55.9, 21.8, 15.6; HRMS (EI): *m/z* [M$^+$] calcd. for $C_{18}H_{19}NO_4$: 313.1314, found 313.1317.



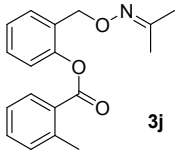
**3h**

**2-(((propan-2-ylideneamino)oxy)methyl)phenyl 3-chlorobenzoate (3h)**: white oil, 218.8 mg (69%); IR (cm$^{-1}$) $\bar{\upsilon}$ 3068, 2920, 2851, 1738, 1575, 1453, 1370, 1285, 1243, 1170, 1061, 882, 790, 739; $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.19 (s, 1H), 8.09 (d, $J$ = 7.6 Hz, 1H), 7.61 (d, $J$ = 8.0 Hz, 1H), 7.48 (t, $J$ = 8.4 Hz, 2H), 7.39 (t, $J$ = 7.6 Hz, 1H), 7.30 (d, $J$ = 7.2 Hz, 1H), 7.22 (d, $J$ = 8.0 Hz, 1H), 5.09 (s, 2H), 1.77 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 163.8, 155.5, 149.1, 134.8, 133.7, 131.4, 130.4, 130.3, 130.2, 130.0, 129.1, 128.4, 126.3, 122.5, 70.9, 21.8, 15.7 ($C_{17}H_{16}O_3NCl$); HRMS (EI): *m/z* [M-NO-$C_3H_6$]$^+$ calcd. for $C_{14}H_{10}O_2{}^{35}Cl$: 245.0369, found 245.0365.



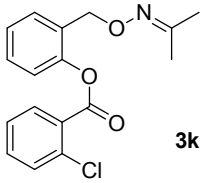
**3i**

**2-(((propan-2-ylideneamino)oxy)methyl)phenyl 2-methoxybenzoate (3i)**: yellow oil, 244.2 mg (78%); IR (cm$^{-1}$) $\bar{\upsilon}$ 3075, 2919, 2841, 1759, 1599, 1488, 1455, 1366, 1236, 1210, 1174, 1021, 880, 750; $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.05 (dd, $J$ = 8.0 Hz, $J$ = 1.6 Hz, 1H), 7.55 (dt, $J_1$ = 7.6 Hz, $J_2$ = 1.2 Hz, 1H), 7.49 (d, $J$ = 7.6 Hz, 1H), 7.36 (dt, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz, 1H), 7.28–7.26 (m, 1H), 7.26–7.23 (m, 1H), 7.04 (t, $J$ = 6.8 Hz, 2H), 5.16 (s, 3H), 3.94 (s, 3H), 1.82 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 164.2, 159.9, 155.4, 149.1, 134.3, 132.4, 130.6, 129.7, 128.8, 125.9, 122.8, 120.2, 119.1, 77.2, 70.7, 56.0, 21.9, 15.8; HRMS (EI): *m/z* [M$^+$] calcd. for $C_{18}H_{19}NO_4$: 313.1314, found 313.1315.



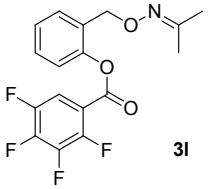
**3j**

**2-(((propan-2-ylideneamino)oxy)methyl)phenyl 2-methylbenzoate (3j)**: yellow oil, 219.9 mg (74%); IR ($cm^{-1}$) $\bar{\upsilon}$ 3066, 2919, 2851, 1736, 1487, 1454, 1453, 1362, 1239, 1212, 1175, 1040, 880, 735; $^1H$ NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.21 (d, $J$ = 8.0 Hz, 1H), 7.51–7.46 (m, 2H), 7.39 (t, $J$ = 7.6 Hz, 1H), 7.34–7.27 (m, 3H), 7.21 (d, $J$ = 7.6 Hz, 1H), 5.12 (s, 2H), 2.68 (s, 3H), 1.79 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 165.5, 155.3, 149.1, 141.4, 132.8, 132.0, 131.4, 130.5, 129.9, 128.9, 128.4, 126.0, 125.9, 122.7, 70.7, 22.0, 21.7, 15.6; HRMS (EI): *m/z* [$M^+$] calcd. for $C_{18}H_{19}N_2O_3$: 297.1365, found 297.1366.



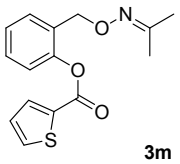
**3k**

**2-propanone,*O*-((2-(2-chloro-benoyloxy)phenyl)methy)oximes (3k)**: yellow oil, 193.4 mg (61%); IR ($cm^{-1}$) $\bar{\upsilon}$ 3066, 2921, 2871, 1747, 1590, 1489, 1366, 1284, 1213, 1239, 1174, 1111, 1032, 1071, 918, 879, 745; $^1H$ NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.11 (d, $J$ = 7.6 Hz, 1H), 7.55–7.47 (m, 3H), 7.41–7.36 (m, 2H), 7.30 (d, $J$ = 7.6 Hz, 1H), 7.27–7.24 (m, 1H), 5.13 (s, 2H), 1.80 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 162.7, 154.6, 148.0, 133.7, 132.3, 131.2, 130.5, 129.5, 129.2, 128.2, 128.1, 125.8, 125.3, 121.6, 60.8, 20.9, 14.8 ($C_{17}H_{16}O_3NCl$); HRMS (EI): *m/z* [M-NO-$C_3H_6$]$^+$ calcd. for $C_{14}H_{10}O_2{}^{35}Cl$: 245.0369, found 245.0366.



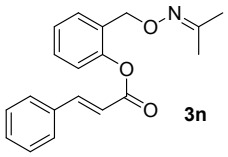
**3l**

**2-(((propan-2-ylideneamino)oxy)methyl)phenyl 2,3,4,5-tetrafluorobenzoate (3l)**: yellow oil, 181.1 mg (51%); IR ($cm^{-1}$) $\bar{\upsilon}$ 3081, 2923, 2854, 1741, 1627, 1524, 1484, 1367, 1192, 1087, 1016, 879, 742; $^1H$ NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.83–7.75 (m, 1H), 7.49 (dd, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz, 1H), 7.40 (dt, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz, 1H), 7.31 (dt, $J_1$ = 7.6 Hz, $J_2$ = 1.2 Hz,, 1H), 7.22 (dd, $J_1$ = 8.0 Hz, $J_2$ = 0.8 Hz, 1H), 5.08 (s, 2H), 1.78 (s, 3H), 1.77 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 160.3, 155.6, 149.8, 148.7, 147.2, 142.9, 130.6, 130.3, 129.2, 126.7, 122.3, 114.6, 113.8 (d, $J$ = 34.0 Hz), 113.6 (d, $J$ = 35.0 Hz), 70.77, 21.81, 15.65; HRMS (EI): *m/z* [$M^+$] calcd. for $C_{17}H_{13}NO_3F_4$: 355.0832, found 355.0834.



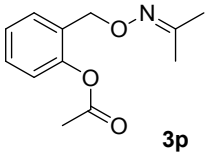
**3m**

**2-(((propan-2-ylideneamino)oxy)methyl)phenyl thiophene-2-carboxylate (2r)**: yellow oil, 176.3 mg (61%); IR ($cm^{-1}$) $\bar{\upsilon}$ 3102, 2963, 2930, 2865, 1707, 1491, 1218, 1006, 979, 875, 822, 732, 755; $^1H$ NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.91 (d, $J$ = 3.6 Hz, 1H), 7.59 (d, $J$ = 5.2 Hz, 1H), 7.41 (d, $J$ = 7.2 Hz, 1H), 7.31 (t, $J$ = 6.4 Hz, 1H), 7.23–7.15 (m, 2H), 7.11 (t, $J$ = 7.0 Hz, 1H), 5.05 (s, 2H), 1.73 (s, 3H), 1.71 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 159.5, 154.6, 147.8, 133.8, 132.6, 131.8, 129.6, 129.0, 128.0, 127.1, 125.2, 121.6, 69.7, 20.8, 14.7 ($C_{15}H_{15}O_3NS$); HRMS (EI): *m/z* [M-NO-$C_3H_6$]$^+$ calcd. for $C_{12}H_9O_2S$: 217.0323, found 217.0317.



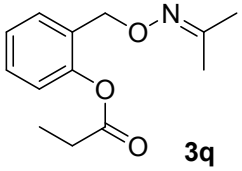
**3n**

**1-(2-acetoxyphenyl)-5-phenyl-4-propyl-1*H*-pyrazole-3-carboxylate (3n)**: white solid, 231.9 mg (75%); m.p. 62–64 °C; IR ($cm^{-1}$) $\bar{\upsilon}$ 3062, 2933, 2865, 1720, 1637, 1491, 1449, 1303, 1140, 974, 878, 825, 765, 704; $^1H$ NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.87 (d, $J$ = 16.0 Hz, 1H), 7.61–7.57 (m, 2H), 7.48 (dd, $J_1$ = 7.6 Hz, $J_2$ = 0.8 Hz,, 1H), 7.44–7.42 (m, 3H), 7.36 (dt, $J_1$ = 8.0 Hz, $J_2$ = 1.6 Hz,, 1H) , 7.28–7.26 (m, 1H), 7.17 (d, $J$ = 8.0 Hz, 1H), 7.65 (d, $J$ = 16.0 Hz, 1H), 5.10 (s, 2H), 1.85 (s, 3H), 1.83 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 165.3, 155.7, 148.9, 146.7, 134.2, 130.8, 130.4, 129.8, 129.1 (2C), 128.9, 128.4 (2C), 126.0, 122.5, 117.1, 70.6, 21.9, 15.8; HRMS (EI): *m/z* [$M^+$] calcd. for $C_{19}H_{19}NO_3$: 309.1365, found 309.1364.



**3p**

**2-(((propan-2-ylideneamino)oxy)methyl)phenyl acetate (3p)**: yellow oil, 163.6 mg (74%); IR ($cm^{-1}$) $\bar{\upsilon}$ 2921, 2852, 1764, 1488, 1453, 1366, 1203, 1166, 1010, 879, 750; $^1H$ NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.44 (dd, $J_1$ = 7.6 Hz, $J_2$ = 0.8 Hz,1H), 7.33 (dt, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz, 1H), 7.23 (t, $J$ = 7.6 Hz, 1H), 7.07 (d, $J$ = 8.0 Hz, 1H), 5.03 (s, 2H), 2.30 (s, 3H), 1.86 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 169.3, 155.4, 148.9, 130.3, 129.9, 128.9, 126.0, 122.4, 70.5, 21.8, 20.9, 15.6; HRMS (EI): *m/z* [$M^+$] calcd. for $C_{12}H_{15}NO_3$: 221.1052, found 221.1050.

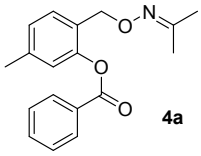


**3q**

**2-(((propan-2-ylideneamino)oxy)methyl)phenyl propionate (3q)**: yellow oil, 148.1 mg (63%); IR ($cm^{-1}$) $\bar{\upsilon}$ 2984, 2919, 2881, 1759, 1488, 1454, 1364, 1174, 1136, 1071, 878, 752; $^1H$ NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.43 (dd, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz, 1H), 7.32 (dt, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz,, 1H), 7.22 (dt, $J_1$ = 7.2 Hz, $J_2$ = 1.2 Hz, 1H), 7.07 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.2 Hz,, 1H), 5.02 (s, 2H), 2.60 (q, $J$ = 7.6 Hz, 2H), 1.86 (s, 3H) , 1.85 (s, 3H) , 1.27 (t, $J$ = 7.6 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 165.2, 157.3, 155.4, 142.4, 133.5, 131.5, 130.2, 129.6, 128.5, 123.2, 114.9, 113.7, 70.6, 55.6, 21.7, 15.6; HRMS (EI): *m/z* [$M^+$] calcd. for $C_{13}H_{17}NO_3$: 235.1208, found 235.1199.

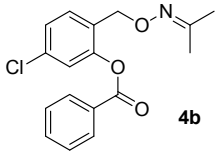
**2.4 Investigation on the substrate scope of masked aralkylalcohols (Scheme 4).**

**General procedure**: A mixture of substrate **1** (1.0 mmol), **2** (2.0 mmol), $Pd(OAc)_2$ (0.10 mmol) , and $K_2S_2O_2$ (3.0 mmol) was dissolved in $CH_3CN$ (6 mL), then the reaction mixture was heated at 80 °C for 10 h. Upon completion of the reaction, the mixture was dropped into the saturated $NaHCO_3$ solution (30 mL). The solution was extracted with ethyl acetate (25 mL×3), and then the combined organic layers were dried over anhydrous $MgSO_4$. Finally, the solution was concentrated *in vacuo* to provide a crude product, which was purified *via* a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate 20:1) to supply the desired product **4**.



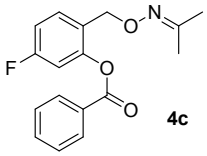
**4a**

**5-methyl-2-(((propan-2-ylideneamino)oxy)methyl)phenyl benzoate (4a)**: yellow solid, 243.7 mg (82%); m.p. 34–36 °C; IR ($cm^{-1}$) $\bar{\upsilon}$ 3060, 2921, 2854, 1735, 1450, 1365, 1237, 1115, 1060, 1024, 880, 705; $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.20 (d, $J$ = 7.2 Hz, 2H), 7.63 (t, $J$ = 7.6 Hz, 1H), 7.50 (t, $J$ = 7.6 Hz, 2H), 7.37 (d, $J$ = 7.6 Hz, 1H), 7.10–7.04 (m, 2H), 5.07 (s, 2H), 2.38 (s, 3H), 1.75 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 165.2, 155.4, 149.2, 139.4, 133.6, 130.3 (2C), 130.1, 129.7, 128.6 (2C), 127.4, 126.9, 123.3, 70.8, 21.8, 21.3, 15.7; HRMS (EI): *m/z* [$M^+$] calcd. for $C_{18}H_{19}NO_3$: 297.1365, found 297.1371.



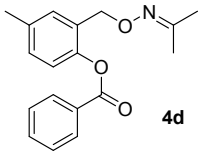
**4b**

**5-chloro-2-(((propan-2-ylideneamino)oxy)methyl)phenyl benzoate (4b)**: yellow solid, 197.0 mg (62%); m.p. 70–72 °C; IR ($cm^{-1}$) $\bar{\upsilon}$ 3069, 2966, 2923, 2866, 1734, 1601, 1485, 1451, 1255, 1217, 1058, 895, 699; $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.18 (d, $J$ = 7.6 Hz, 2H), 7.64 (t, $J$ = 7.6 Hz, 1H), 7.50 (t, $J$ = 7.6 Hz, 2H), 7.40 (d, $J$ = 7.6 Hz, 1H), 7.26–7.23 (m, 2H), 5.05 (s, 2H), 1.75 (s, 3H), 1.74 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 164.5, 155.7, 149.4, 133.9, 133.8, 130.7, 130.3 (2C), 129.3, 129.0, 128.7 (2C), 126.3, 123.1, 70.1, 21.7, 15.6 ($C_{17}H_{16}O_3NCl$); HRMS (EI): *m/z* [M-NO-$C_3H_6$]$^+$ calcd. for $C_{14}H_{10}O_2{}^{35}Cl$: 245.0369, found 245.0327.



**4c**

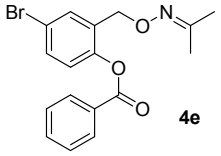
**5-fluoro-2-(((propan-2-ylideneamino)oxy)methyl)phenyl benzoate (4c):** white solid, 180.7 mg (60%); m.p. 68–70 °C; IR ($cm^{-1}$) $\bar{\upsilon}$ 3075, 2948, 2923, 2853, 1729, 1599, 1500, 1452, 1248, 1144, 1062, 986, 873, 823, 702; $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.22–8.18 (m, 2H), 7.65 (t, $J$ = 9.2 Hz, 1H), 7.52 (t, $J$ = 8.0 Hz, 2H), 7.47–7.43 (m, 1H), 7.04–7.69 (m, 2H), 5.06 (s, 2H), 1.76 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 164.5, 162.4 (d, $^1J_{CF}$ = 246.3 Hz), 155.5, 149.8 (d, $^3J_{CF}$ = 10.9 Hz), 133.8, 131.0 (d, $^3J_{CF}$ = 9.4 Hz), 130.3 (2C), 129.1, 128.6 (2C), 126.5 (d, $^4J_{CF}$ = 3.5 Hz), 113.0 (d, $^2J_{CF}$ = 20.9 Hz), 110.6 (d, $^2J_{CF}$ = 24.3 Hz), 70.2, 21.7, 15.6; HRMS (EI): *m/z* [$M^+$] calcd. for $C_{17}H_{16}NO_3F$: 301.1114, found 301.1119.



**4d**

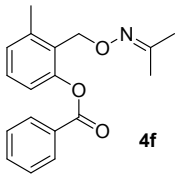
**4-methyl-2-(((propan-2-ylideneamino)oxy)methyl)phenyl benzoate (4d):** yellow solid, 222.8 mg (74%); m.p. 36–38 °C; IR ($cm^{-1}$) $\bar{\upsilon}$ 2920, 2858, 1734, 1498, 1450, 1262, 1194, 1059, 1024, 871, 705; $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.24–8.19 (m, 2H), 7.63 (t, $J$ = 7.2 Hz, 1H), 7.51 (q, $J$ = 7.6 Hz, 2H), 7.29 (s, 1H), 7.20–7.17 (m, 1H), 7.10 (d, $J$ = 8.0 Hz, 1H), 5.08 (s, 2H), 2.38 (s, 3H), 1.77 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 165.1, 155.3, 147.0, 135.7, 133.5, 130.6, 130.2

(2C), 129.9, 129.6, 129.5, 128.5 (2C), 122.3, 70.9, 21.8, 21.0, 15.6; HRMS (EI): *m/z* [$M^+$] calcd. for $C_{18}H_{19}NO_3$: 297.1368, found 297.1368.



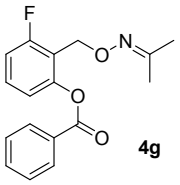
**4e**

**4-bromo-2-(((propan-2-ylideneamino)oxy)methyl)phenyl benzoate (4e):** yellow oil, 246.9 mg (68%); IR ($cm^{-1}$) $\bar{\upsilon}$ 3066, 2923, 2853, 1738, 1478, 1363, 1261, 1170, 1055, 1023, 877, 705; $^1H$ NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.19 (d, $J$ = 7.6 Hz, 2H), 7.67–7.60 (m, 2H), 7.53–7.46 (m, 3H), 7.11 (d, $J$ = 8.8 Hz, 1H), 5.06 (s, 2H), 1.80 (s, 3H), 1.77 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 164.6, 155.9, 147.9, 133.8, 132.9, 132.5, 131.7, 130.3 (2C), 129.1, 128.6 (2C), 124.3, 119.2, 69.9, 29.7, 21.7, 15.7; HRMS (EI): *m/z* [$M^+$] calcd. for $C_{17}H_{16}NO_3{}^{81}Br$: 363.0293, found 363.0300.



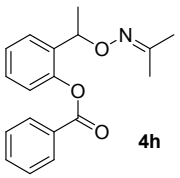
**4f**

**3-methyl-2-(((propan-2-ylideneamino)oxy)methyl)phenyl benzoate (4f):** white solid, 235.8 mg (81%); m.p. 96–98 °C; IR ($cm^{-1}$) $\bar{\upsilon}$ 3068, 2956, 2918, 2853, 1729, 1465, 1450, 1267, 1224, 1065, 985, 906, 780, 702; $^1H$ NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.22 (d, $J$ = 6.8 Hz, 2H), 7.63 (t, $J$ = 7.6 Hz, 1H), 7.51 (t, $J$ = 7.6 Hz, 2H), 7.29 (t, $J$ = 8.0 Hz, 1H), 7.13 (d, $J$ = 7.2 Hz, 1H), 7.07 (d, $J$ = 8.0 Hz, 1H), 5.12 (s, 2H), 2.48 (s, 3H), 1.73 (s, 3H), 1.70 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 165.3, 155.0, 150.4, 140.2, 133.5, 130.3 (2C), 129.7, 129.0 (2C), 128.6, 128.1, 128.0, 120.4, 67.1, 21.8, 20.0, 15.4; HRMS (EI): *m/z* [$M^+$] calcd. for $C_{18}H_{19}NO_3$: 297.1365, found 297.1364.



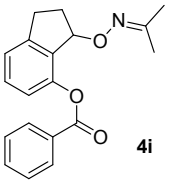
**4g**

**3-fluoro-2-(((propan-2-ylideneamino)oxy)methyl)phenyl benzoate (4g):** yellow solid, 189.7 mg (63%); m.p. 93–95 °C; IR ($cm^{-1}$) $\bar{\upsilon}$ 3065, 2990, 2958, 2922, 2852, 1731, 1618, 1468, 1365, 1250, 1070, 996, 922, 867, 786, 703; $^1H$ NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.15–8.12 (m, 2H), 7.56 (t, $J$ = 7.6 Hz, 1H), 7.43 (t, $J$ = 8.0 Hz, 2H), 7.32–7.27 (m, 1H), 7.00–6.92 (m, 2H), 5.07 (s, 2H), 1.59 (s, 3H), 1.57 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 164.8, 161.9 (d, $^1J_{CF}$ = 248.0 Hz), 155.3, 151.1 (d, $^3J_{CF}$ = 6.6 Hz), 133.7, 130.3 (2C), 129.7 (d, $^3J_{CF}$ = 10.0 Hz), 129.4,128.6 (2C), 118.8 (d, $^3J_{CF}$ = 3.5 Hz), 118.6 (d, $^2J_{CF}$ = 17.5 Hz), 113.1 (d, $^2J_{CF}$ = 22.3 Hz), 63.7, 21.7, 15.4; HRMS (EI): *m/z* [$M^+$] calcd. for $C_{17}H_{16}NO_3F$: 301.1114, found 301.1117.



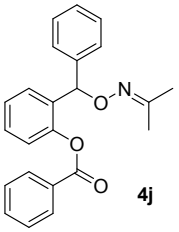
**4h**

**2-(1-((propan-2-ylideneamino)oxy)ethyl)phenyl benzoate (4h):** yellow oil, 216.8 mg (73%); IR ($cm^{-1}$) $\bar{\upsilon}$ 3070, 2977, 2928, 1734, 1487, 1449, 1257, 1213, 1061, 936, 751, 705, 670; $^1H$ NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.22 (d, $J$ = 7.6 Hz, 2H), 7.64 (t, $J$ = 7.6 Hz, 1H), 7.51 (t, $J$ = 8.0 Hz, 2H), 7.47 (dd, $J_1$ = 7.6 Hz, $J_2$ = 2.0 Hz, 1H), 7.34 (td, $J_1$ = 7.6 Hz, $J_2$ = 2.0 Hz, 1H), 7.29 (dd, $J_1$ = 7.6 Hz, $J_2$ = 1.2 Hz, 1H), 7.19 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.2 Hz, 1H), 5.45 (q, $J$ = 6.8 Hz, 1H), 1.83 (s, 3H), 1.76 (s, 3H) , 1.51 (d, $J$ = 6.8 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 165.0, 154.8, 148.0, 135.7, 133.6, 130.3 (2C), 129.6, 128.6 (2C), 128.1, 127.2, 126.1, 122.7, 75.3, 21.8, 21.1, 15.7 ($C_{18}H_{20}NO_3$); HRMS (EI): *m/z* $[M\text{-}NO\text{-}C_3H_6]^+$ calcd. for $C_{15}H_{14}O_2$: 226.0994, found 226.0967.



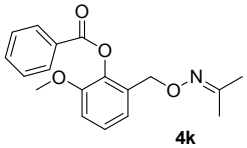
**4i**

**3-((propan-2-ylideneamino)oxy)-2,3-dihydro-1H-inden-4-yl benzoate (4i):** yellow solid, 219.5 mg (71%); m.p. 85–87 °C; IR ($cm^{-1}$) $\bar{\upsilon}$ 3061, 2921, 2851, 1736, 1469, 1450, 1263, 1226, 1170, 1065, 1024, 705; $^1H$ NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.20 (d, $J$ = 7.6 Hz, 2H), 7.61 (t, $J$ = 7.2 Hz, 1H), 7.49 (t, $J$ = 7.6 Hz, 2H), 7.34 (t, $J$ = 8.0 Hz, 1H), 7.18 (d, $J$ = 7.6 Hz, 1H), 7.07 (d, $J$ = 8.0 Hz, 1H), 5.79–5.76 (m, 1H), 3.19–3.11 (m, 1H), 2.93–2.85 (m, 1H), 2.52–2.42 (m, 1H), 2.27–2.18 (m, 1H), 1.55 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 164.7, 154.4, 148.4, 147.3, 134.1, 133.2, 130.3 (2C), 130.0, 129.9, 128.4 (2C), 122.5, 120.2, 84.6, 32.3, 30.5, 21.5, 15.4; HRMS (EI): *m/z* $[M^+]$ calcd. for $C_{19}H_{19}NO_3$: 309.1365, found 309.1367.



**4j**

**2-(phenyl((propan-2-ylideneamino)oxy)methyl)phenyl benzoate (4j):** yellow oil, 214.9 mg (71%); IR ($cm^{-1}$) $\bar{\upsilon}$ 3065, 3028, 2910, 1735, 1484, 1450, 1258, 1210, 1170, 1059, 1023, 927, 753, 699; $^1H$ NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.07 (d, $J$ = 7.2 Hz, 2H), 7.60 (t, $J$ = 7.2 Hz, 1H), 7.46 (t, $J$ = 8.0 Hz, 2H), 7.40–7.34 (m, 3H), 7.28–7.26 (m, 1H), 7.25–7.20 (m, 4H), 6.42 (s, 1H), 1.86 (s, 3H), 1.71 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 164.7, 155.6, 148.7, 140.5, 133.9, 133.5, 130.3 (2C), 129.5, 128.7, 128.6, 128.4 (2C), 128.2 (2C), 127.5, 127.5 (2C), 125.9, 123.0, 81.4, 21.8, 16.0 ($C_{23}H_{22}NO_3$); HRMS (EI): *m/z* $[M\text{-}NO\text{-}C_3H_6]^+$ calcd. for $C_{20}H_{16}O_2$: 288.1150, found 288.1114.



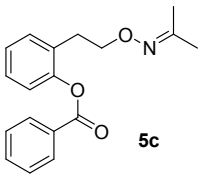
**4k**

**2-methoxy-6-(((propan-2-ylideneamino)oxy)methyl)phenyl benzoate (4k)**: yellow oil, 279.8 mg (84%); IR ($cm^{-1}$) $\bar{\upsilon}$ 3063, 2919, 2851, 1734, 1497, 1450, 1262, 1174, 1060, 1031, 878, 706; $^1H$ NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.20 (d, $J$ = 7.2 Hz, 2H), 7.63 (t, $J$ = 7.6 Hz, 1H), 7.50 (t, $J$ = 7.6 Hz, 2H), 7.13 (d, $J$ = 8.8 Hz, 1H), 7.02 (d, $J_1$ = 3.2 Hz, 1H), 6.89 (dd, $J_1$ = 8.8 Hz, $J_2$ = 3.2 Hz, 1H),

5.07 (s, 2H), 3.83 (s, 3H), 1.79 (s, 3H) , 1.77 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 172.7, 155.3, 149.0, 130.3, 129.9, 128.8, 125.9, 122.4, 70.5, 27.6, 21.8, 15.6, 9.1; HRMS (EI): *m/z* [$M^+$] calcd. for $C_{18}H_{19}NO_4$: 333.1314, found 333.1313.

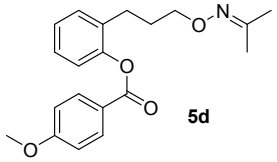
**2.5 Investigation on the substrate scope of extended aralkylalcohols (Scheme 5)**

**General procedure**: A mixture of substrate **1** (1.0 mmol), **2** (2.0 mmol), $Pd(OAc)_2$ (0.10 mmol) and $K_2S_2O_2$ (3.0 mmol) was dissolved in $CH_3CN$ (6 mL), then the reaction mixture was heated at 80 $^oC$ for 10 h. Upon completion of the reaction, the mixture was dropped into the saturated $NaHCO_3$ solution (30 mL). The solution was extracted with ethyl acetate (25 mL×3), and then the combined organic layers were dried over anhydrous $MgSO_4$. Finally, the solution was concentrated *in vacuo* to provide a crude product, which was purified *via* a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate 20:1) to supply the desired product **5**.



**5c**

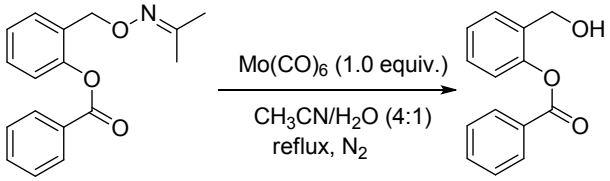
**2-(2-((propan-2-ylideneamino)oxy)ethyl)phenyl benzoate (5c):** yellow oil, 204.9 mg (69%); IR ($cm^{-1}$) $\bar{\upsilon}$ 2972, 2930, 2877, 1655, 1451, 1365, 1263, 1215, 1171, 1063, 831, 753; $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.25 (d, $J$ = 6.8 Hz, 2H), 7.65 (t, $J$ = 7.6 Hz, 1H), 7.52 (t, $J$ = 8.0 Hz, 2H), 7.35 (dd, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz, 1H), 7.30 (dt, $J_1$ = 7.6 Hz, $J_2$ = 1.6 Hz, 1H), 7.23 (dd, $J_1$ = 7.2 Hz, $J_2$ = 1.2 Hz, 1H), 7.18 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.2 Hz, 1H), 4.24 (dt, $J_1$ = 6.8 Hz, $J_2$ = 2.4 Hz, 2H), 2.96 (t, $J$ = 7.2 Hz, 2H), 1.79 (s, 3H), 1.77 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 165.1, 155.0, 149.5, 133.6, 131.1, 131.0, 130.3 (2C), 129.6, 128.6 (2C), 127.5, 126.1, 122.4, 72.6, 30.3, 21.8, 15.7; HRMS (EI): *m/z* [$M^+$] calcd. for $C_{18}H_{19}NO_3$: 297.1365, found 297.1367.



**5d**

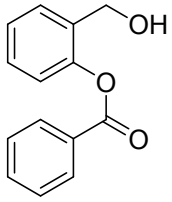
**2-(3-((propan-2-ylideneamino)oxy)propyl)phenyl 4-methoxybenzoate (5d):** yellow oil, 143.3 mg (42%); IR ($cm^{-1}$) $\bar{\upsilon}$ 3209, 2921, 2853, 1728, 1605, 1510, 1456, 1252, 1162, 1068, 1017, 846, 763; $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.17 (d, $J$ = 9.2 Hz, 2H), 7.30 (dd, $J_1$ = 7.2 Hz, $J_2$ = 1.6 Hz, 1H), 7.22 (td, $J_1$ = 8.8 Hz, $J_2$ = 1.6 Hz, 2H), 7.13 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.2 Hz, 1H), 6.99 (d, $J$ = 9.2 Hz, 2H), 4.01 (t, $J$ = 6.4 Hz, 2H), 3.90 (s, 3H), 2.67 (t, $J$ = 7.6 Hz, 2H), 1.94 (t, $J$ = 8.0 Hz, 2H), 1.80 (s, 3H), 1.71 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 164.7, 163.8, 154.4, 149.2, 134.0, 132.2 (2C), 130.3, 127.0, 125.9, 122.4, 121.8, 113.8 (2C), 72.4, 55.4, 29.6, 26.8, 21.7, 15.3; HRMS (EI): *m/z* [$M^+$] calcd. for $C_{20}H_{23}NO_4$: 341.1627, found 341.1605.

## 3. Selectively removal of the acetoxime directing group (Scheme 6)




**3a** **6**, 79%

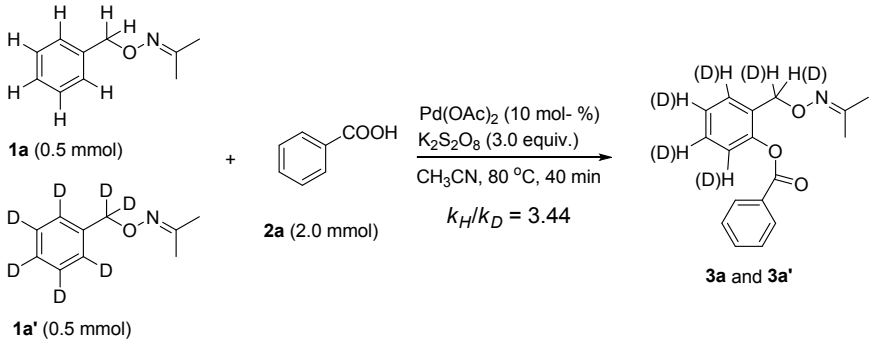
**Procedure**: To a mixture of compound **3a** (141.5mg, 0.5 mmol) in acetonitrile (4.0 mL) containing water (1.0 mL), molybdenum hexacarbony (132.0 mg, 0.5 mmol) was added. The flask was evacuated and backfilled with $N_2$ three times and then heated at reflux. The reaction was nonitored by TLC (silica gel, eluent: EtOAc/hexanes = 1:5). On completion of the reaction, silica gel (0.3 g) was added to the cooled mixture. After removal of the solvent *in vacuo,* the residue was purified by flash column chramatography on silica gel (eluents: petroleum ether/ethyl acetate 20:1) to give the corresponding product **6**.




**6**

**2-(hydroxymethyl)phenyl benzoate (6):** white solid, 90.1 mg (79%); m.p. 71–73 $^{o}$C; IR ($cm^{-1}$) $\bar{\upsilon}$ 3338, 3064, 3036, 2957, 1685, 1598, 1455, 1373, 1273, 1180, 1107, 869, 749, 707; $^{1}$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 8.13 (s, 1H), 8.07 (d, $J$ = 7.2 Hz, 2H), 7.58 (t, $J$ = 7.2 Hz, 1H), 7.44 (t, $J$ = 7.6 Hz, 2H), 7.37 (dd, $J_1$ = 1.2 Hz, $J_2$ = 7.6 Hz, 1H), 7.30 (t, $J$ = 8.4 Hz, 1H), 6.98 (d, $J$ = 8.0 Hz, 1H), 6.93 (t, $J$ = 7.6 Hz, 1H), 5.38 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, ppm): $\delta$ 168.8, 155.6, 133.6, 132.3, 131.2, 130.0 (2C), 129.2, 128.5 (2C), 121.7, 120.6, 117.8, 63.7; HRMS (EI): *m/z* [$M^+$] calcd. for $C_{14}H_{12}O_3$: 228.0786, found 228.0785.

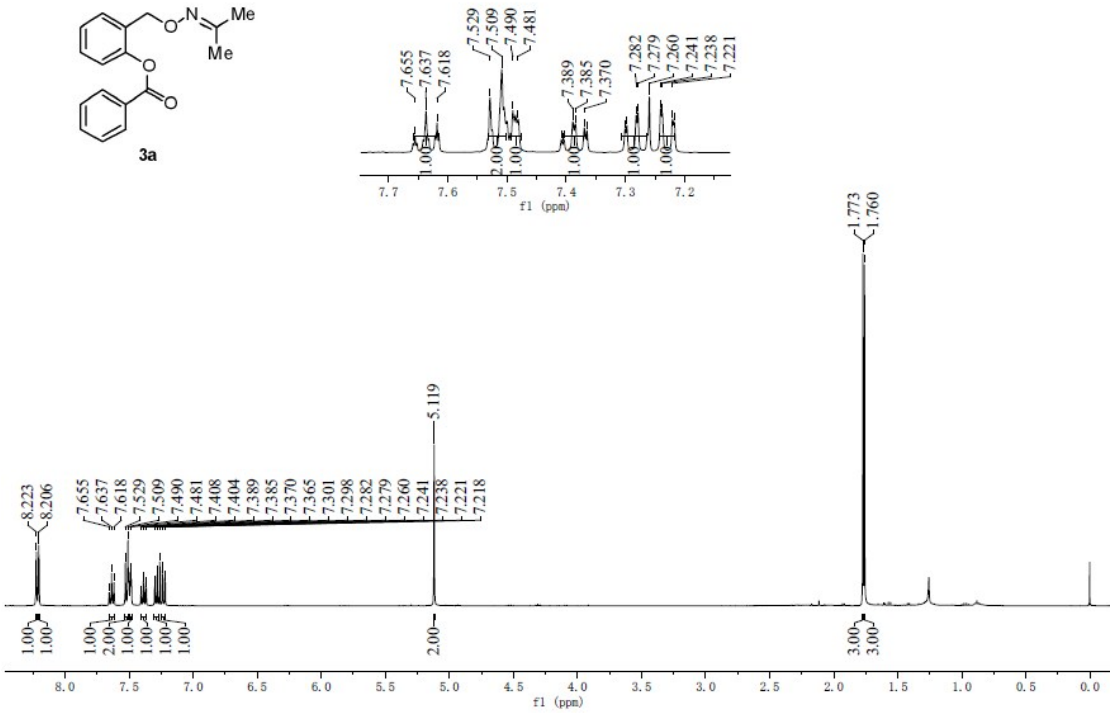
## 4. Kinetic isotope effect experiment (Scheme 7)

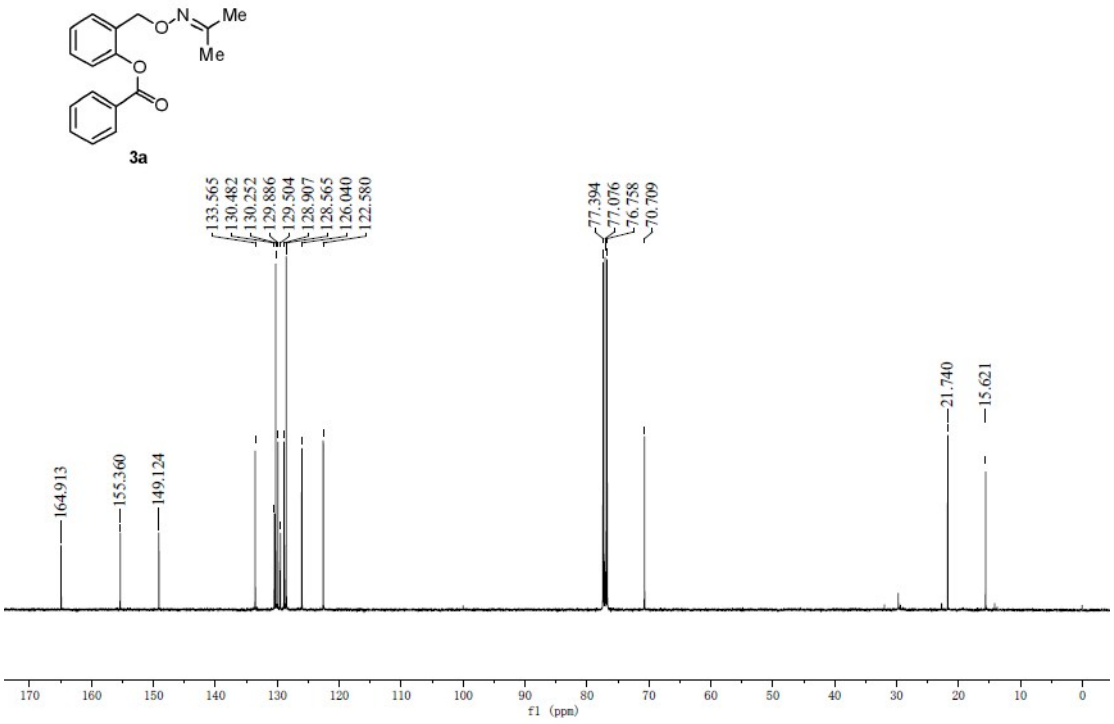



**Procedure**: A mixture of substrate **1a** (0. 5 mmol), **1a'**- $d_7$ (0. 5 mmol) , $Pd(OAc)_2$ (0.1 mmol) and $K_2S_2O_8$ (3.0 mmol) was dissolved in $CH_3CN$ (6 mL), then the reaction mixture was heated at 80 °C for 40 min. Upon completion of the reaction, the mixture was dropped into the saturated $NaHCO_3$ solution (30 mL). The solution was extracted with ethyl acetate (25 mL×3), and then combined organic layers were dried over anhydrous $MgSO_4$. Finally, the solution was concentrated *in vacuo* to provide a crude product, which was purified *via* a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate 20:1) to supply the desired product. The product distribution ($k_H/k_D$ = 3.44) was analyzed by $^1$H NMR.

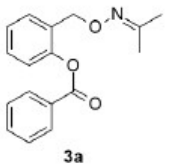
# 5. All Copies of Spectra

## 5.1 Copies of the spectra for Scheme 3



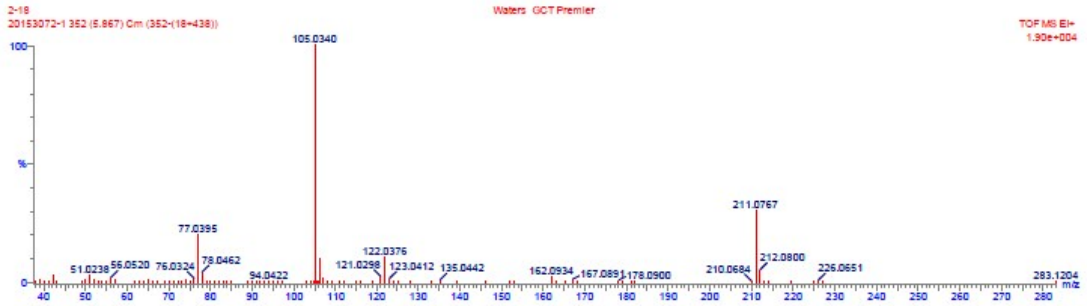
**Elemental Composition Report**



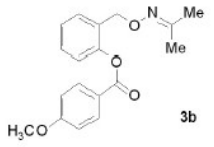
3a

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

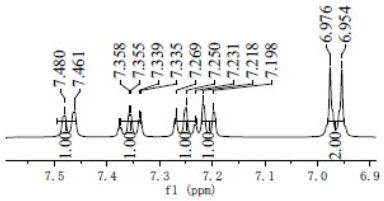
Monoisotopic Mass, Odd and Even Electron Ions
1392 formula(e) evaluated with 89 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-17 H: 0-17 N: 0-1 O: 0-3

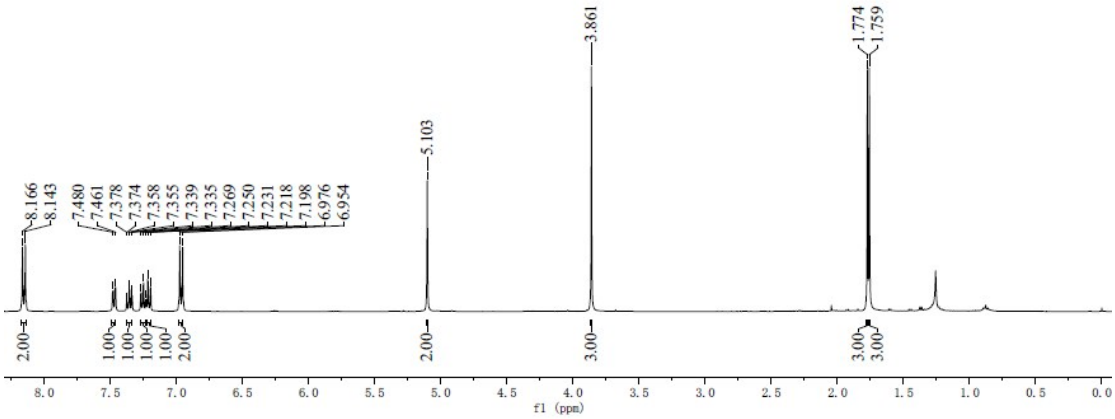


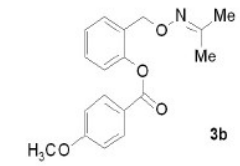

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | 0.10 | | | | | | -1.5 |
| Maximum: | 100.00 | | | | 5.0 | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 283.1204 | 0.11 | 283.1208 | -0.4 | -1.4 | 10.0 | 5546028.0 | C17 H17 N O3 |



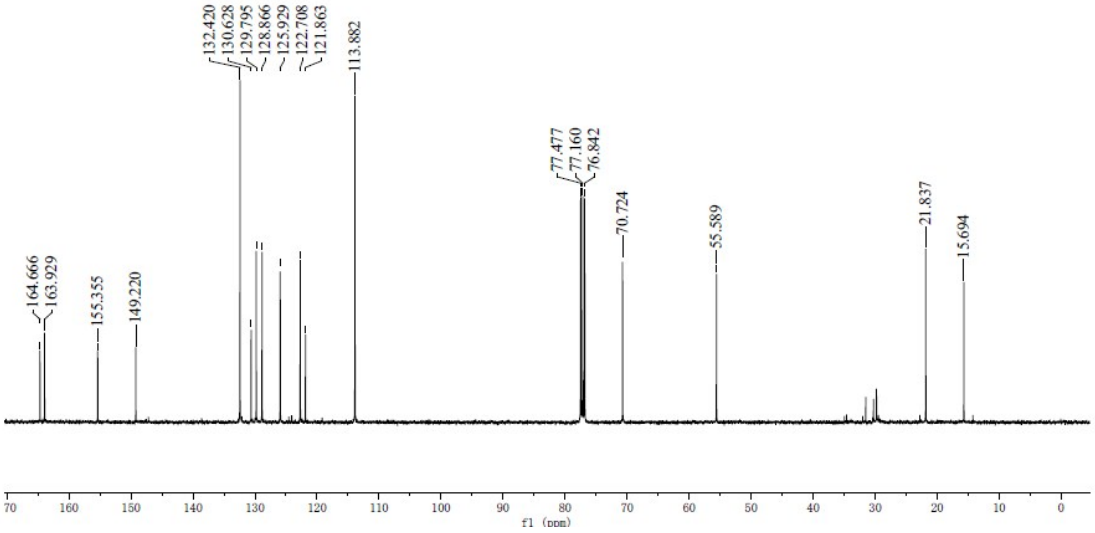
3b



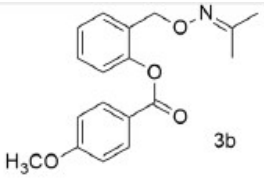






3b




**Elemental Composition Report**




3b

**Single Mass Analysis**
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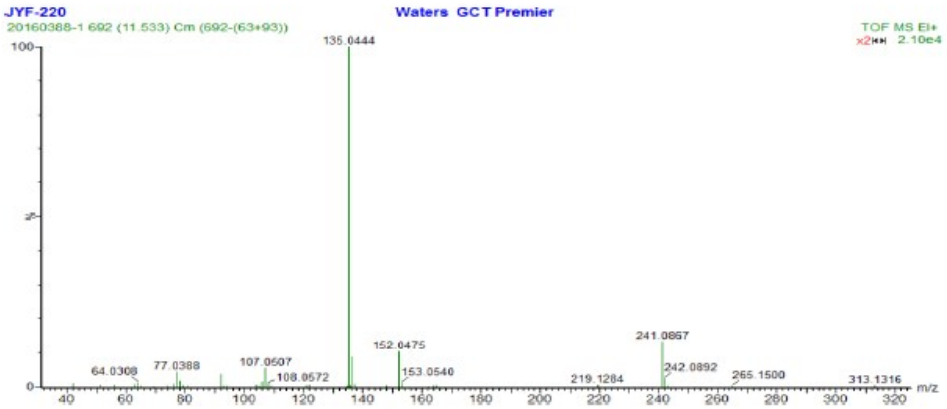
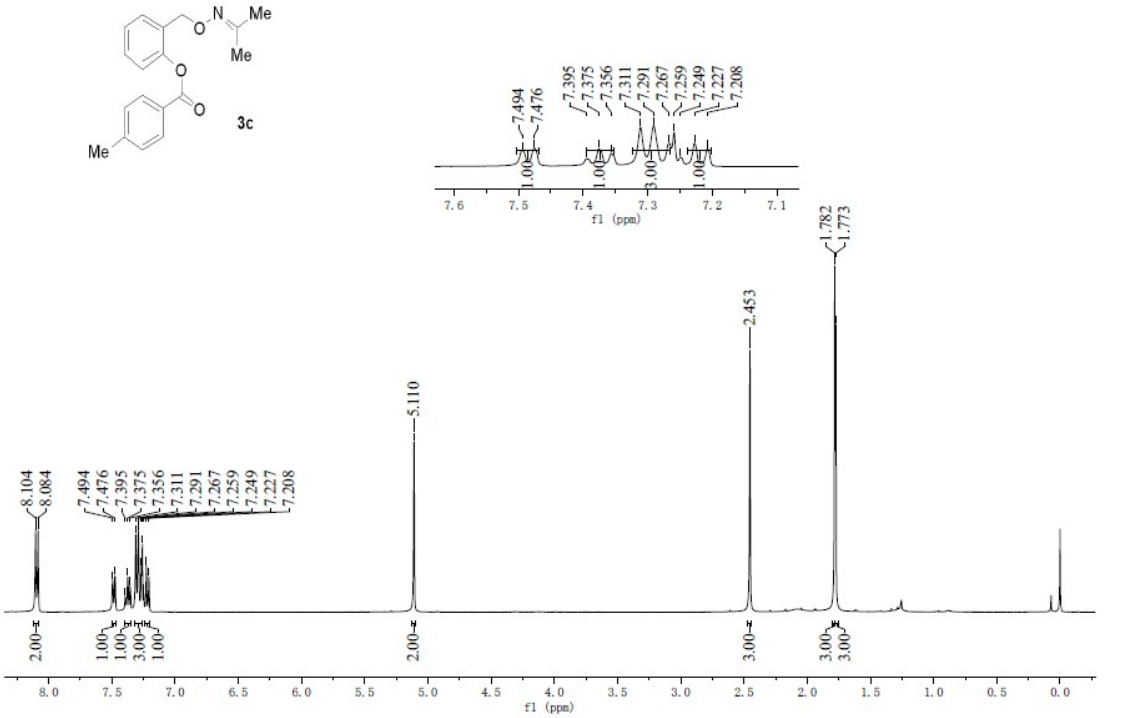
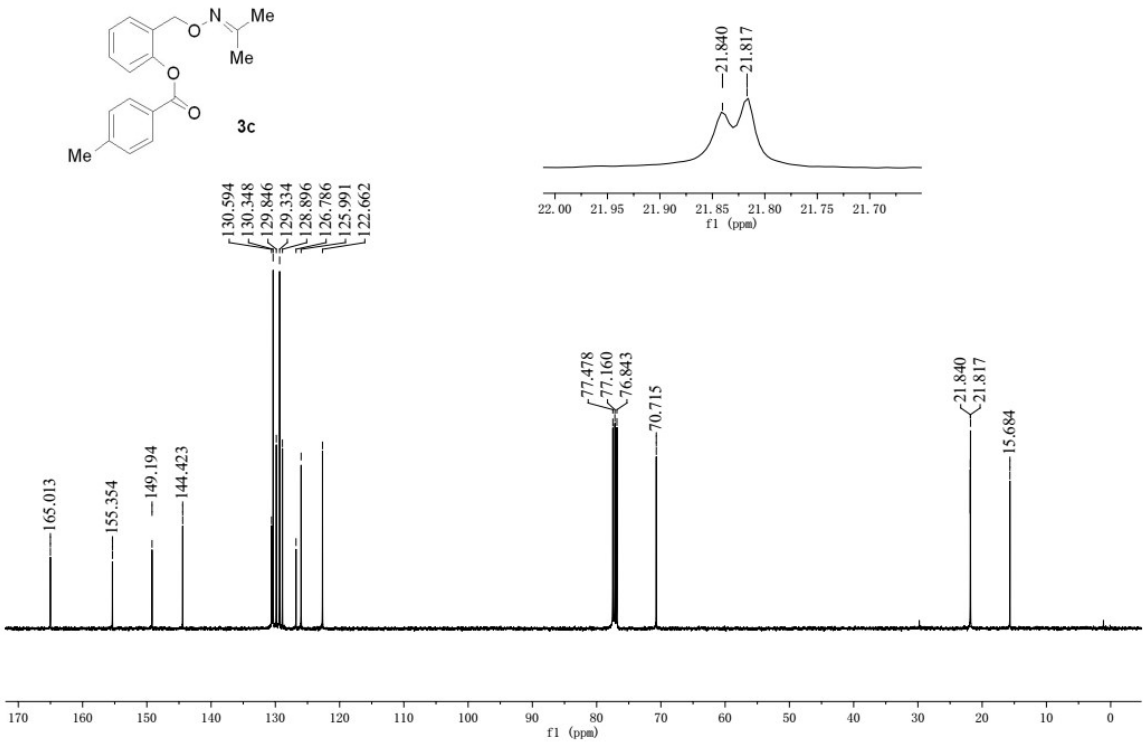
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
8 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-18 H: 0-19 N: 0-1 O: 0-4




| | | | | | | |
|---|---|---|---|---|---|---|
| Minimum: | | | | | | -1.5 |
| Maximum: | | 5.0 | | 10.0 | | 50.0 |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 313.1316 | 313.1314 | 0.2 | 0.6 | 10.0 | n/a | C18 H19 N O4 |


3c
Me
N
O
Me
Me
7.494
7.476
7.395
7.375
7.356
7.311
7.291
7.267
7.259
7.249
7.227
7.208
f1 (ppm)
8.104
8.084
5.110
2.453
1.782
1.773
2.00
1.00
1.00
3.00
1.00
2.00
3.00
3.00
3.00
f1 (ppm)


3c
Me
N
O
Me
Me
21.840
21.817
f1 (ppm)
130.594
130.348
129.846
129.334
128.896
126.786
125.991
122.662
77.478
77.160
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21.817
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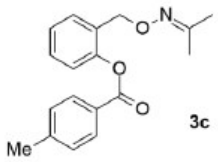
155.354
149.194
144.423
f1 (ppm)

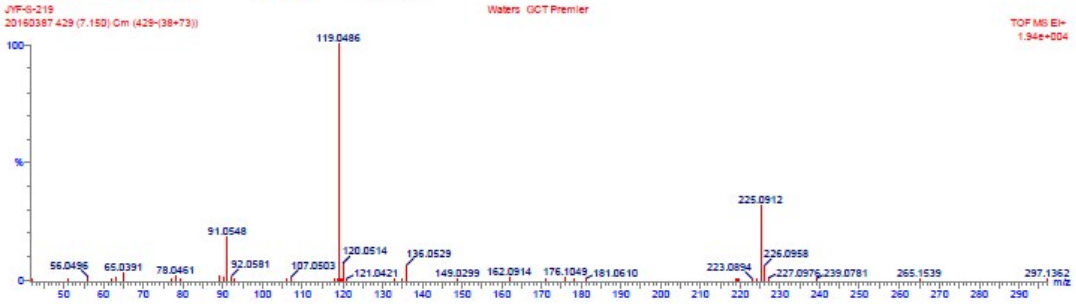
**Elemental Composition Report**



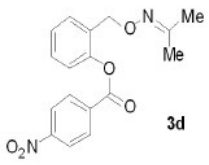
**3c**

**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

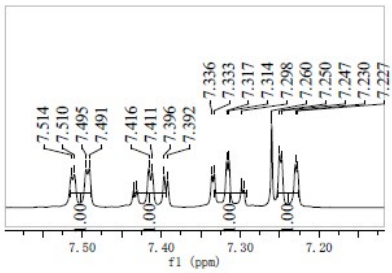
Monoisotopic Mass, Odd and Even Electron Ions
838 formula(e) evaluated with 34 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-18 H: 0-19 N: 0-1 O: 0-3

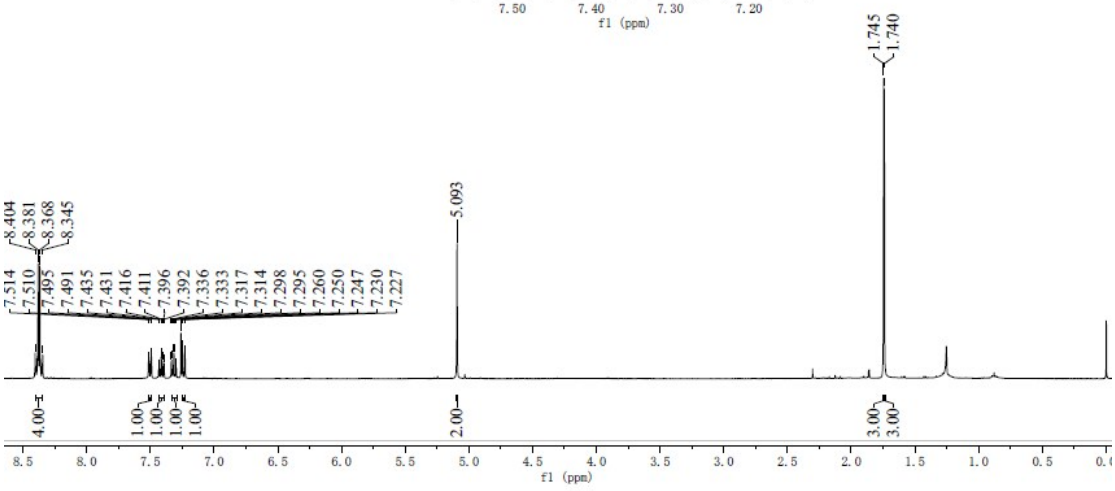


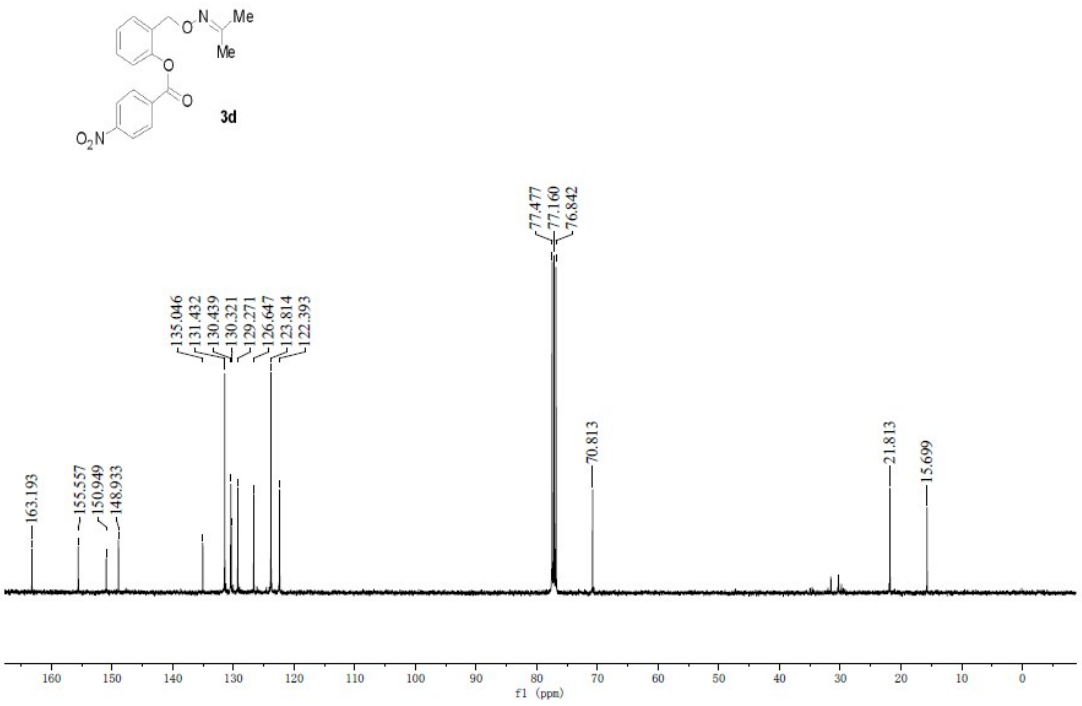

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | | 0.10 | | | | | -1.5 |
| Maximum: | | 100.00 | | | 5.0 | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 297.1362 | 0.11 | 297.1365 | -0.3 | -1.0 | 10.0 | 5546028.5 | C18 H19 N O3 |



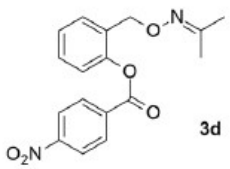
**3d**




3d
163.193
155.557
150.949
148.933
135.046
131.432
130.439
130.321
129.271
126.647
123.814
122.393
77.477
77.160
76.842
70.813
21.813
15.699
f1 (ppm)

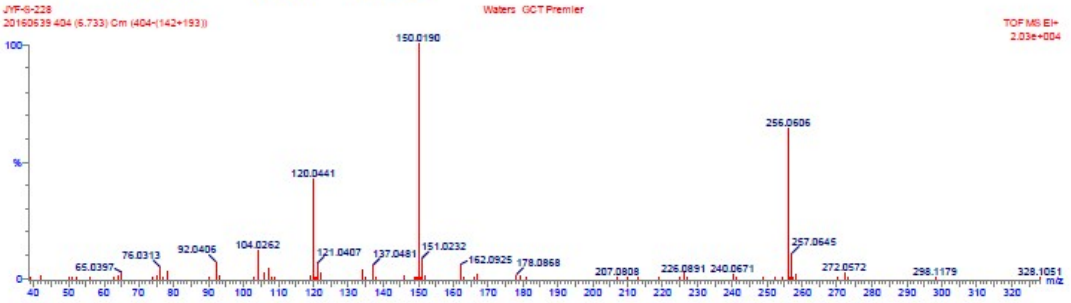
**Elemental Composition Report**



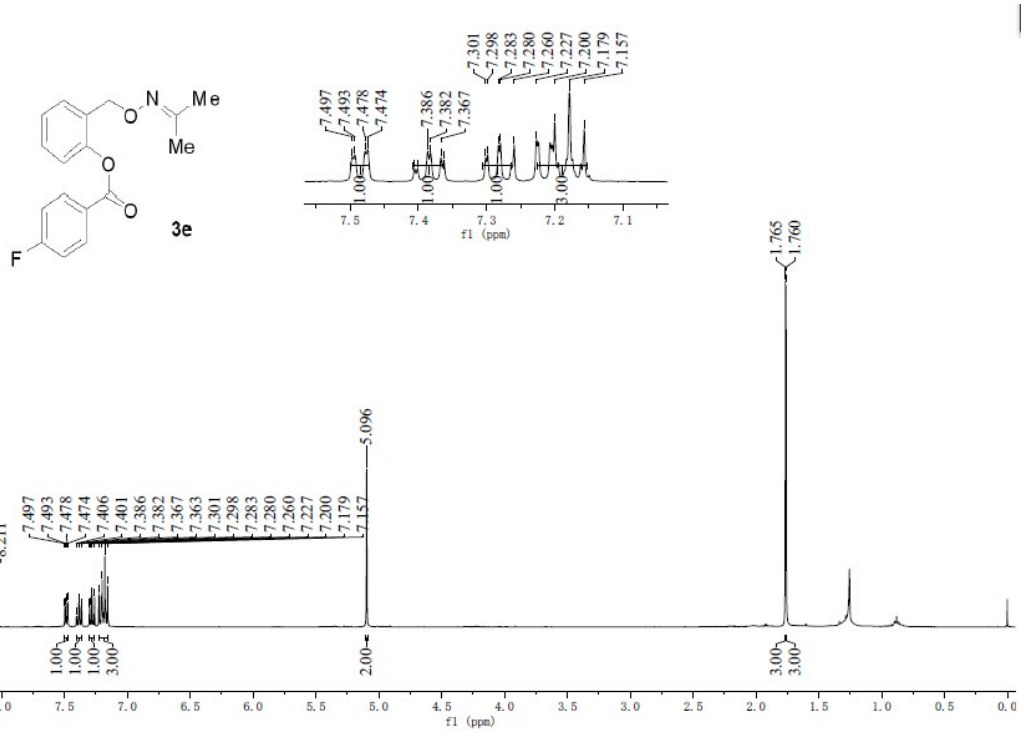
3d

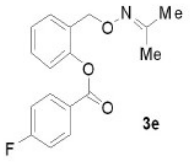
**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
1947 formula(e) evaluated with 103 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-17 H: 0-16 N: 0-2 O: 0-5

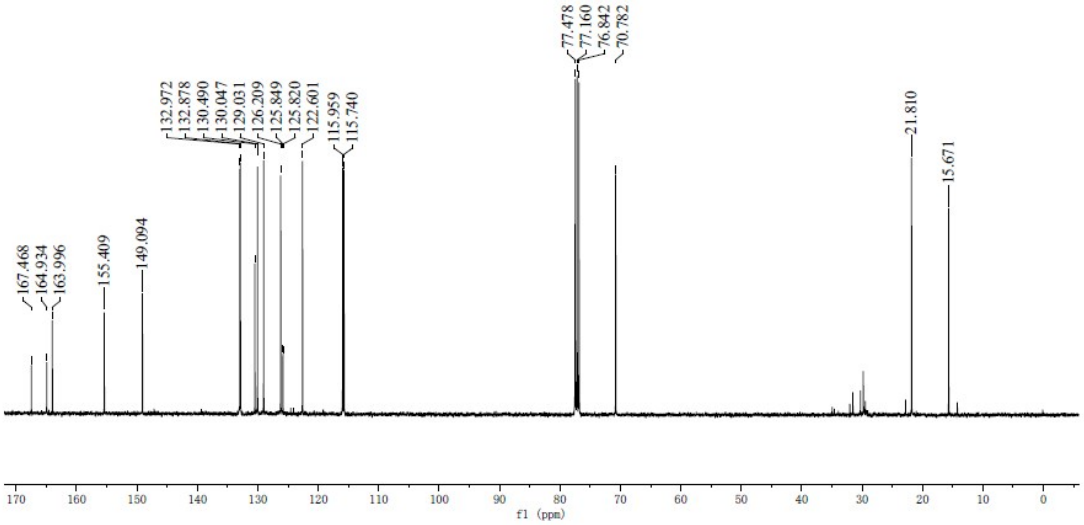



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | 0.11 | | | | | | -1.5 |
| Maximum: | 100.00 | | | | 5.0 | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 328.1051 | 0.12 | 328.1059 | -0.8 | -2.4 | 11.0 | 5546028.5 | C17 H16 N2 O5 |

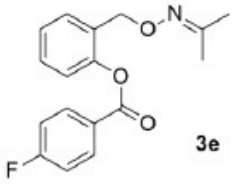





3e




**Elemental Composition Report**

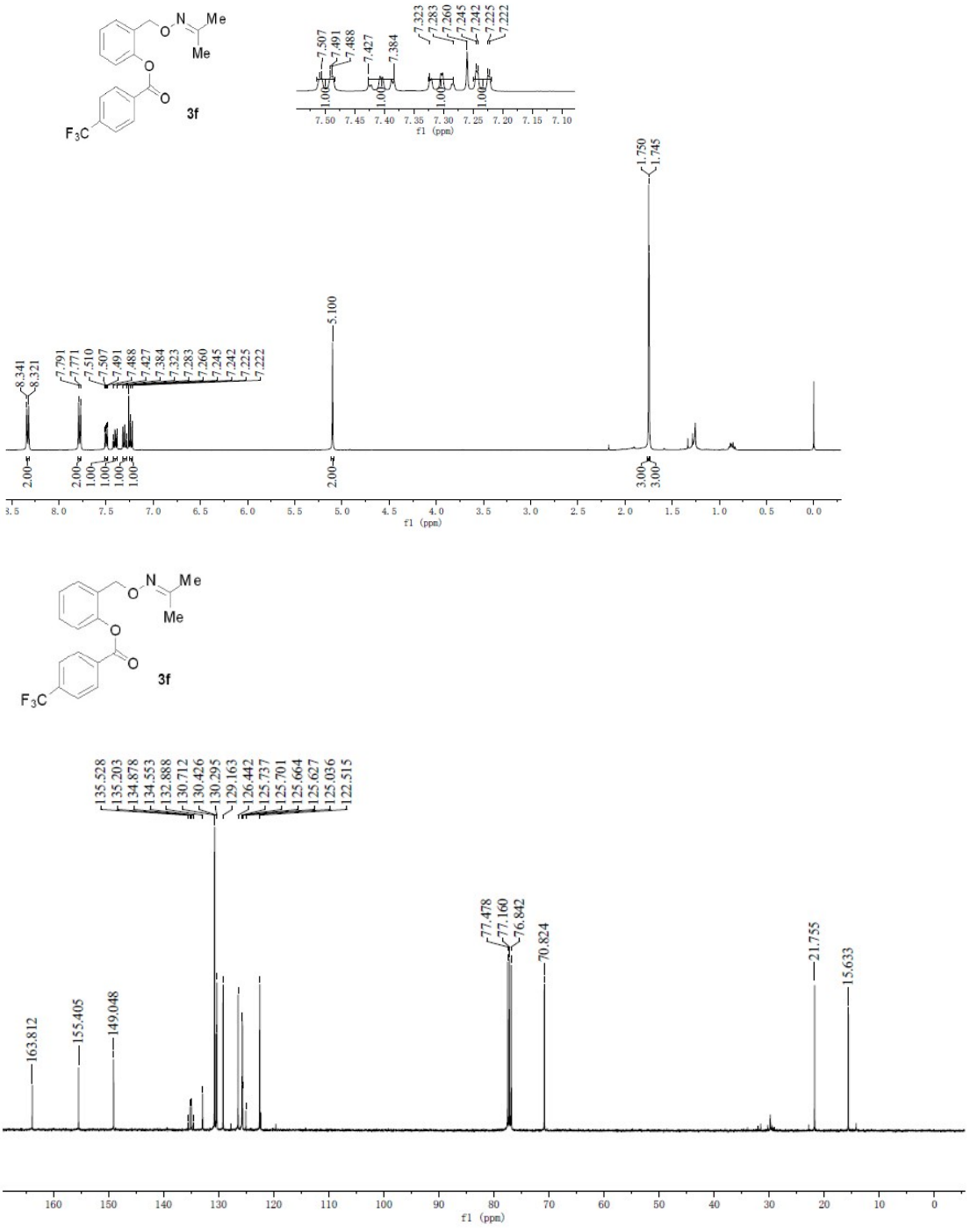



3e

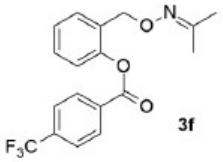
**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
13 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-17 H: 0-16 N: 0-1 O: 0-3 F: 0-1


| | | | | | | |
|---|---|---|---|---|---|---|
| Minimum: | | | | | | -1.5 |
| Maximum: | | | 5.0 | | 10.0 | 50.0 |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 301.1119 | 301.1114 | 0.5 | 1.7 | 10.0 | n/a | C17 H16 N O3 F |


3f
3f
f1 (ppm)

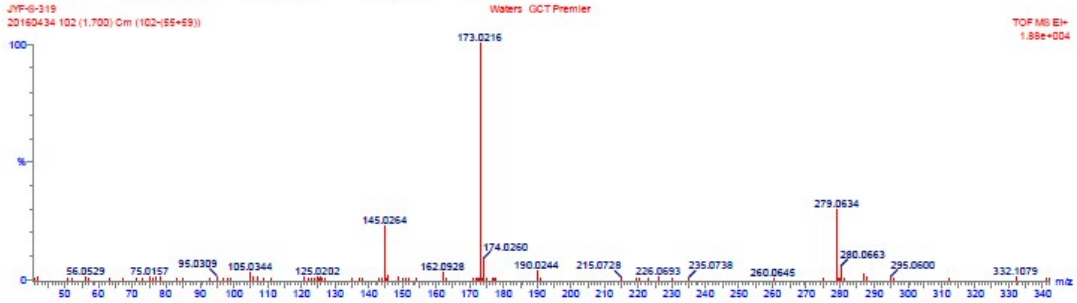
**Elemental Composition Report**



3f

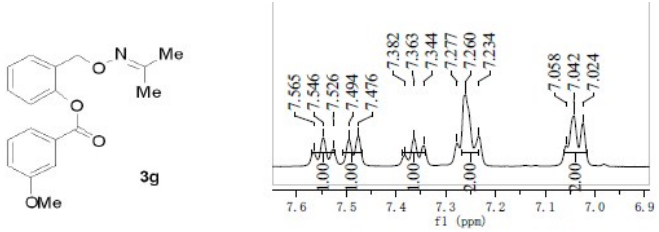
**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
254 formula(e) evaluated with 17 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-18 H: 0-16 N: 0-1 O: 0-3 F: 0-3



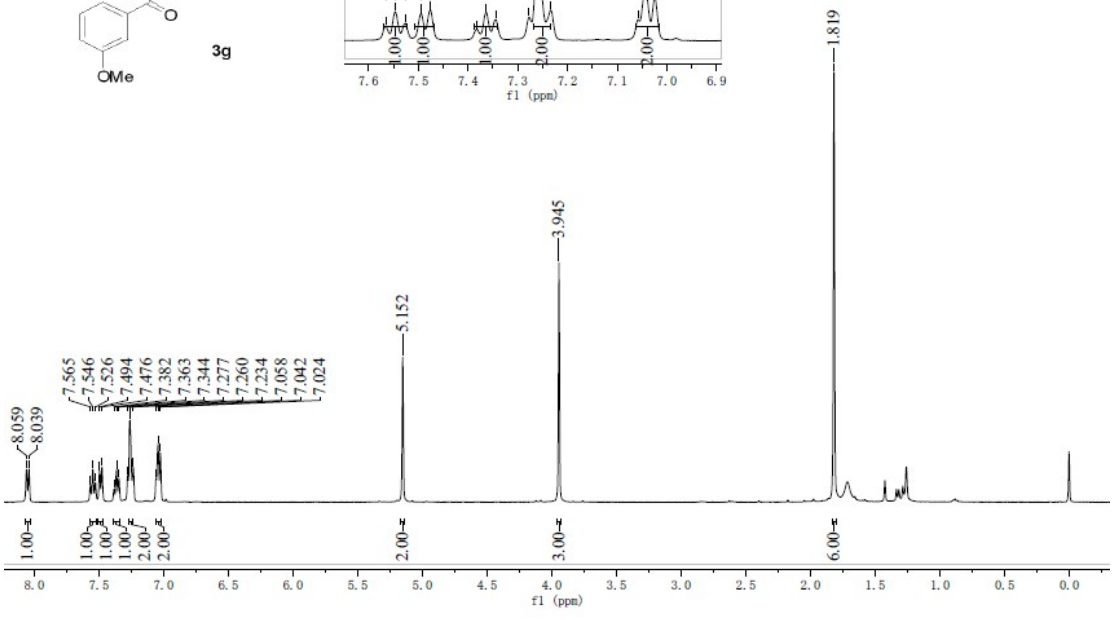

| | | | | | | |
|---|---|---|---|---|---|---|
| Minimum: | 3.00 | | | | | -1.5 |
| Maximum: | 100.00 | | 5.0 | 10.0 | | 50.0 |

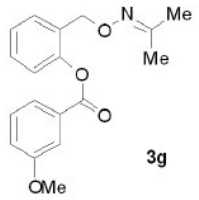
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
|---|---|---|---|---|---|---|---|
| 279.0634 | 29.77 | 279.0633 | 0.1 | 0.4 | 9.5 | 0.1 | C15 H10 O2 F3 |



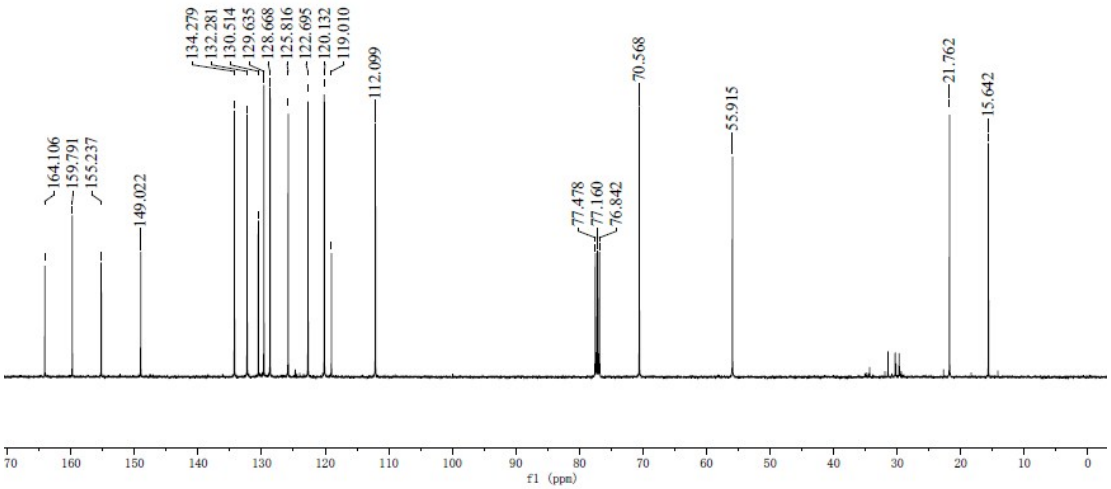




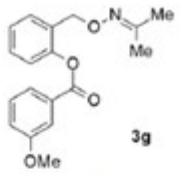





3g




**Elemental Composition Report**

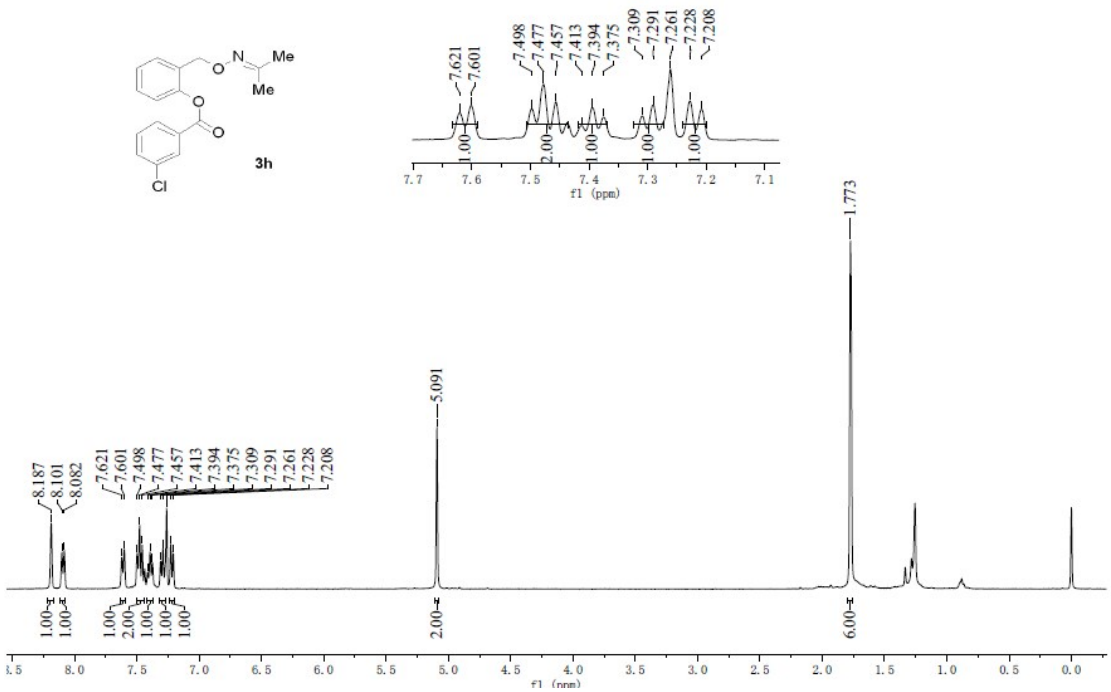


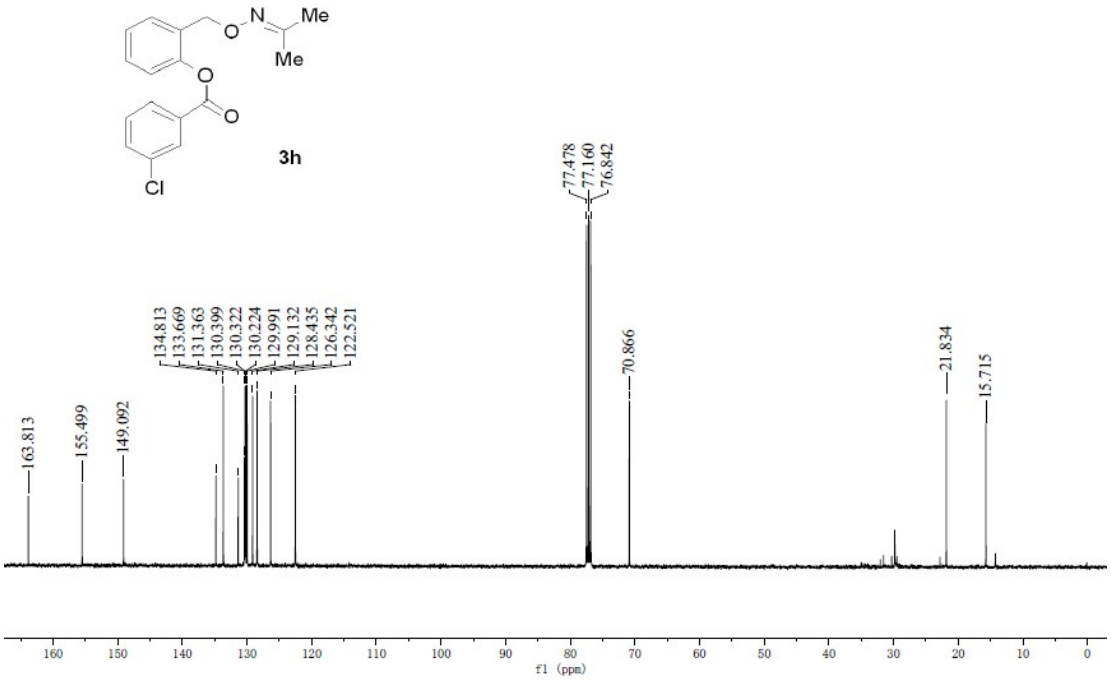

3g

**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

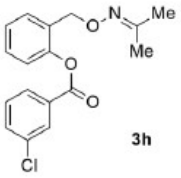
Monoisotopic Mass, Odd and Even Electron Ions
781 formula(e) evaluated with 49 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-18 H: 0-19 N: 0-1 O: 0-4


| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | | 0.22 | | | | | -1.5 |
| Maximum: | | 100.00 | | | 5.0 | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 313.1317 | 0.23 | 313.1314 | 0.3 | 1.0 | 10.0 | 5546035.5 | C18 H19 N O4 |


3h
Cl
7.621
7.601
7.498
7.477
7.457
7.413
7.394
7.375
7.309
7.291
7.261
7.228
7.208
f1 (ppm)
8.187
8.101
8.082
5.091
1.773
1.00
2.00
6.00
f1 (ppm)


3h
Cl
77.478
77.160
76.842
134.813
133.669
131.363
130.399
130.322
130.224
129.991
129.132
128.435
126.342
122.521
70.866
21.834
15.715
163.813
155.499
149.092
f1 (ppm)

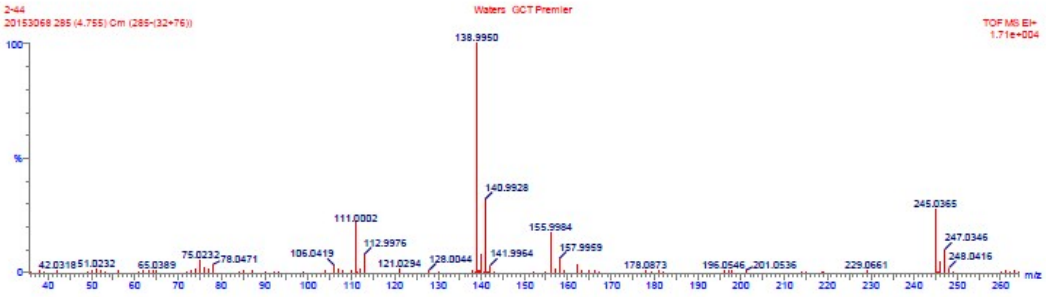
**Elemental Composition Report**



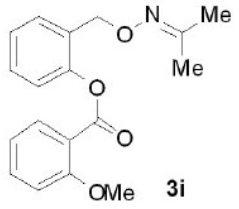
**3h**

**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

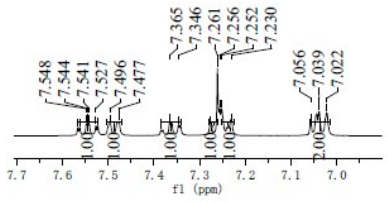
Monoisotopic Mass, Odd and Even Electron Ions
462 formula(e) evaluated with 29 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-17 H: 0-16 N: 0-1 O: 0-3 35Cl: 0-1 37Cl: 0-1

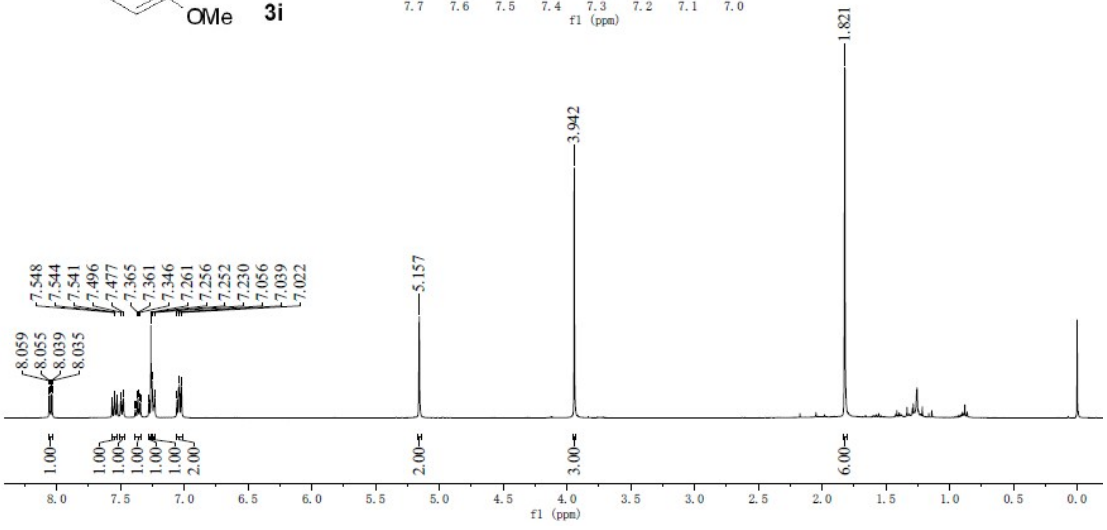


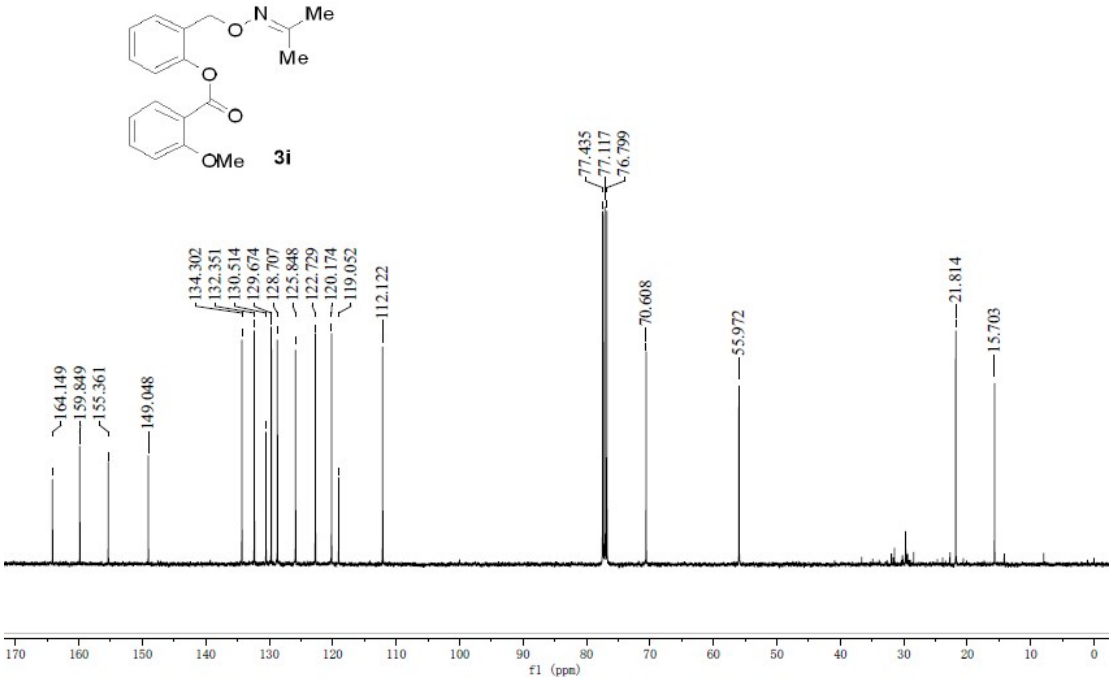

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | 3.00 | | | | | | -1.5 |
| Maximum: | 100.00 | | | 5.0 | | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 245.0365 | 27.44 | 245.0369 | -0.4 | -1.6 | 9.5 | 0.5 | C14 H10 O2 35Cl |



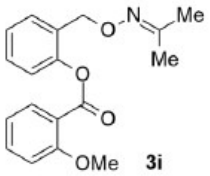
**3i**



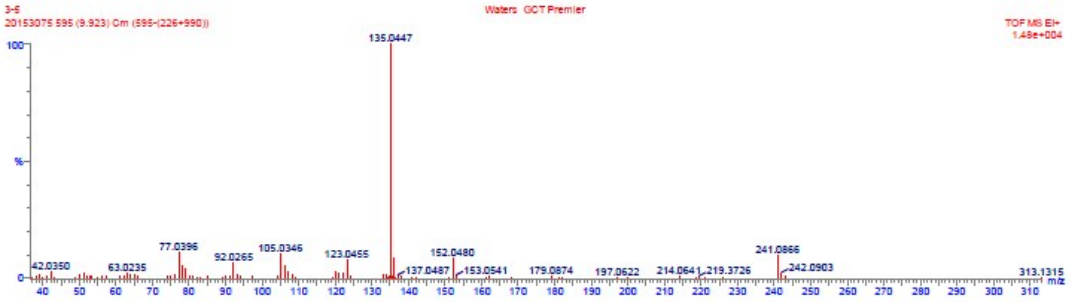



**Elemental Composition Report**

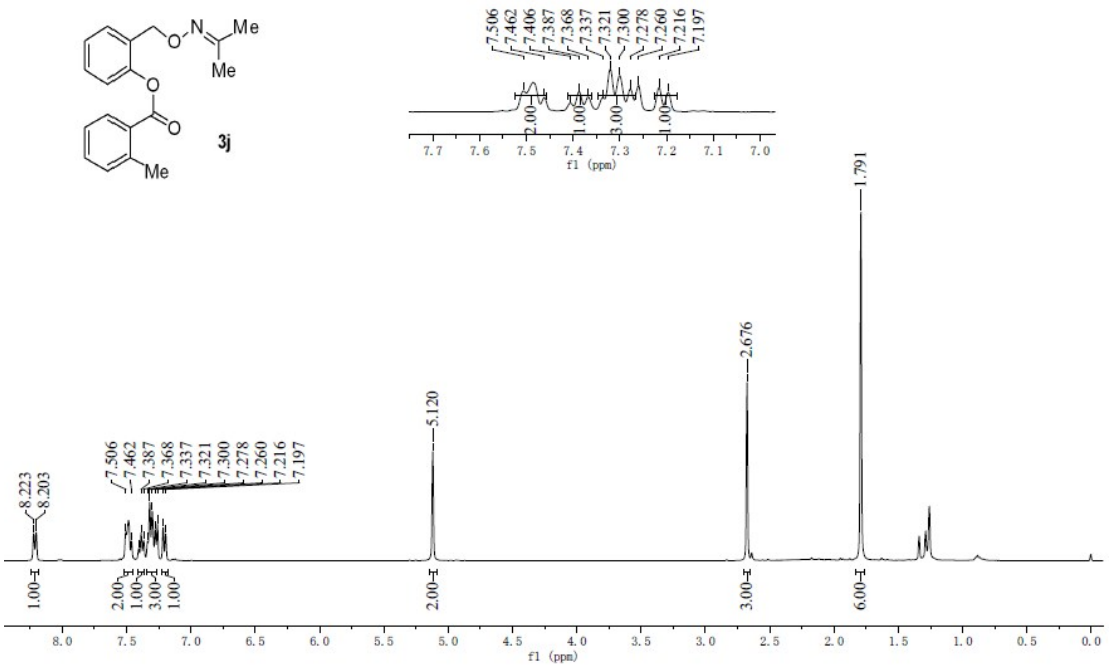


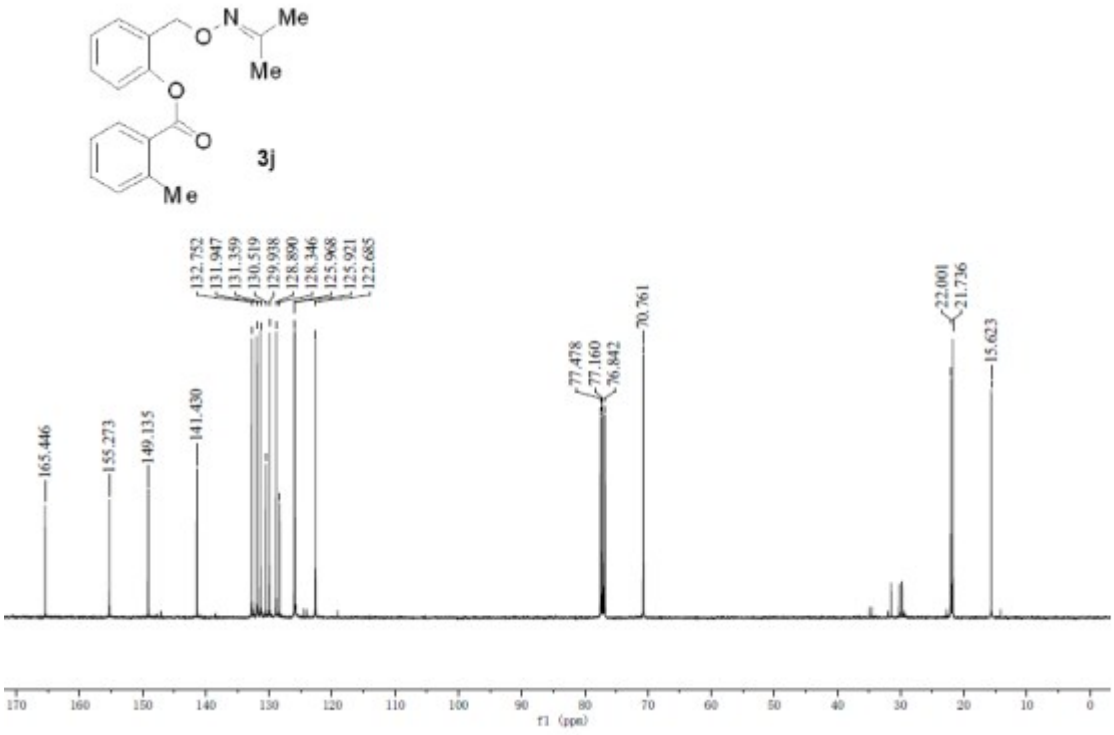

**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
1345 formula(e) evaluated with 75 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-18 H: 0-19 N: 0-1 O: 0-4

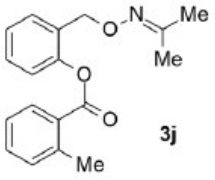



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | 0.13 | | | | | | -1.5 |
| Maximum: | 100.00 | | | | 5.0 | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 313.1315 | 0.14 | 313.1314 | 0.1 | 0.3 | 10.0 | 5546028.5 | C18 H19 N O4 |


3j
7.506
7.462
7.406
7.387
7.368
7.337
7.321
7.300
7.278
7.260
7.216
7.197
2.00
1.00
3.00
1.00
f1 (ppm)
8.223
8.203
7.506
7.462
7.387
7.368
7.337
7.321
7.300
7.278
7.260
7.216
7.197
5.120
2.676
1.791
1.00
2.00
1.00
3.00
1.00
2.00
3.00
6.00
f1 (ppm)


3j
132.752
131.947
131.359
130.519
129.938
128.890
128.346
125.968
125.921
122.685
165.446
155.273
149.135
141.430
77.478
77.160
76.842
70.761
22.001
21.736
15.623
f1 (ppm)

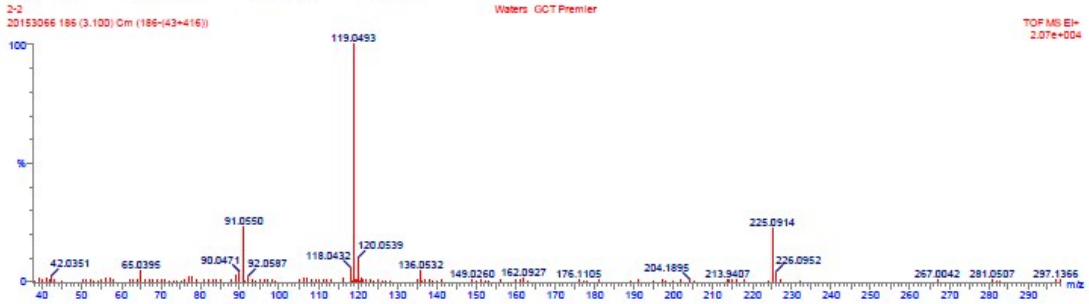
**Elemental Composition Report**



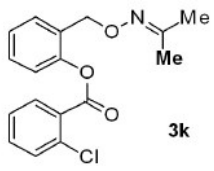

3j

**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

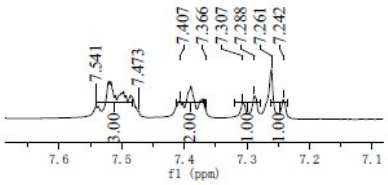
Monoisotopic Mass, Odd and Even Electron Ions
333 formula(e) evaluated with 29 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-18 H: 0-19 N: 0-1 O: 0-3

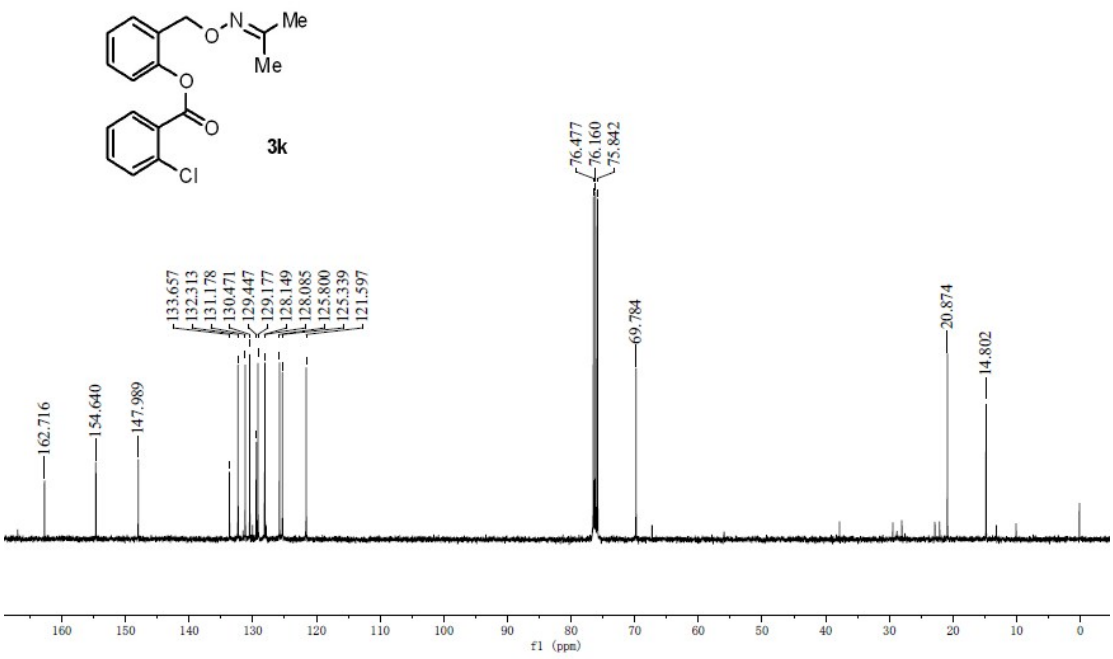



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | 0.80 | | | | | | -1.5 |
| Maximum: | 100.00 | | | | 5.0 | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 297.1366 | 0.89 | 297.1365 | 0.1 | 0.3 | 10.0 | 2773019.3 | C18 H19 N O3 |

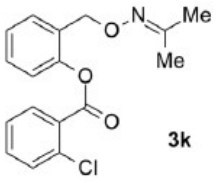



3k



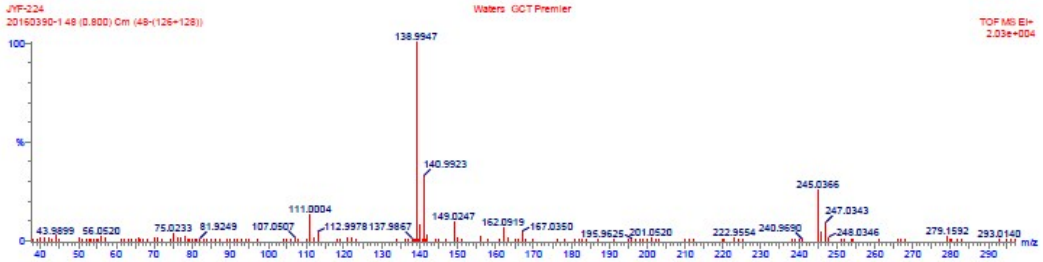



**Elemental Composition Report**

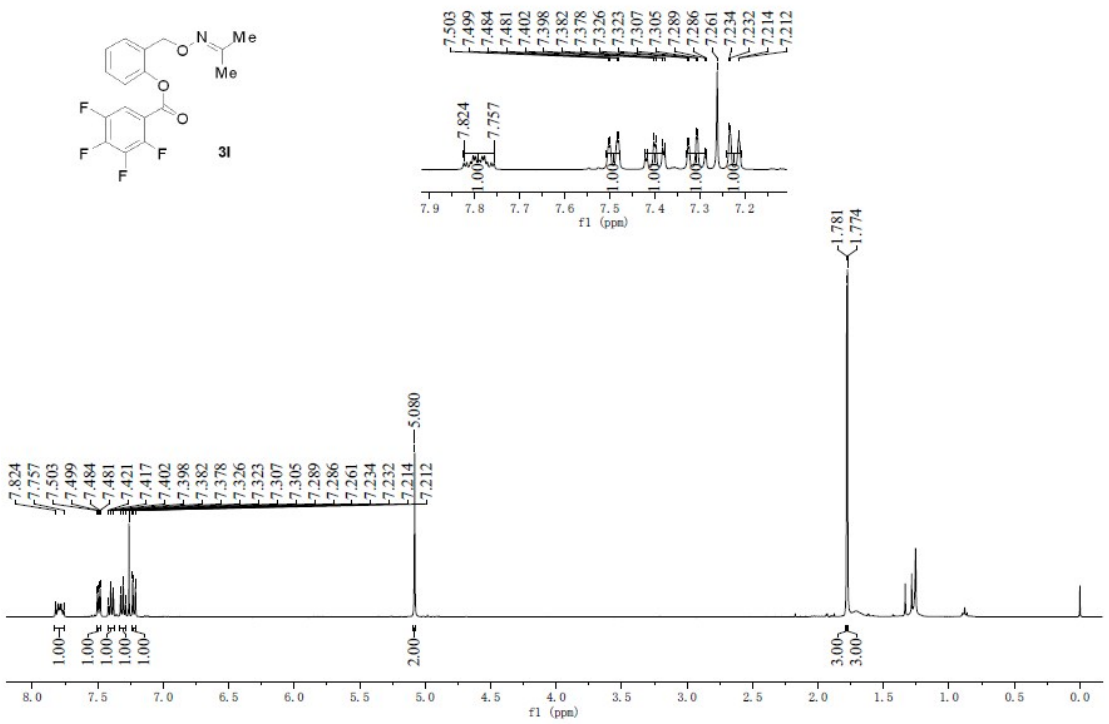


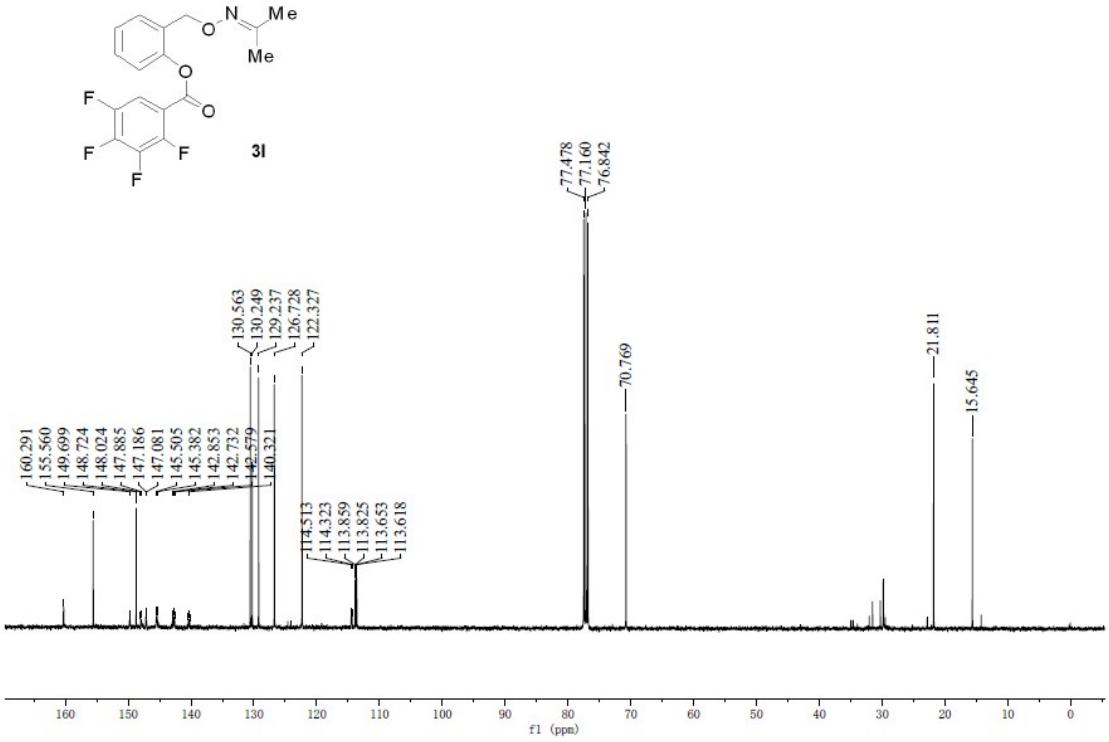

**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
504 formula(e) evaluated with 27 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-17 H: 0-16 N: 0-1 O: 0-3 35Cl: 0-1 37Cl: 0-1

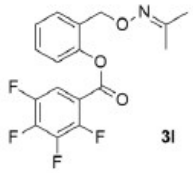



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | 3.00 | | | | | | -1.5 |
| Maximum: | 100.00 | | | 5.0 | | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 245.0366 | 25.52 | 245.0369 | -0.3 | -1.2 | 9.5 | 2.0 | C14 H10 O2 35Cl |


3l
7.824
7.757
7.503
7.499
7.484
7.481
7.421
7.417
7.402
7.398
7.382
7.378
7.326
7.323
7.307
7.305
7.289
7.286
7.261
7.234
7.232
7.214
7.212
5.080
1.781
1.774
f1 (ppm)


3l
160.291
155.560
149.699
148.724
148.024
147.885
147.186
147.081
145.505
145.382
142.853
142.732
142.579
140.321
130.563
130.249
129.237
126.728
122.327
114.513
114.323
113.859
113.825
113.653
113.618
77.478
77.160
76.842
70.769
21.811
15.645
f1 (ppm)

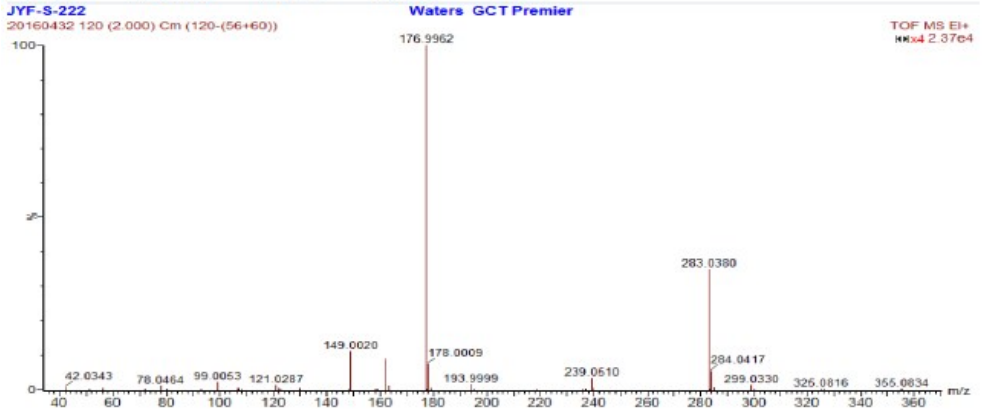
**Elemental Composition Report**



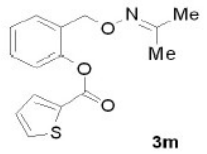
3l

**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

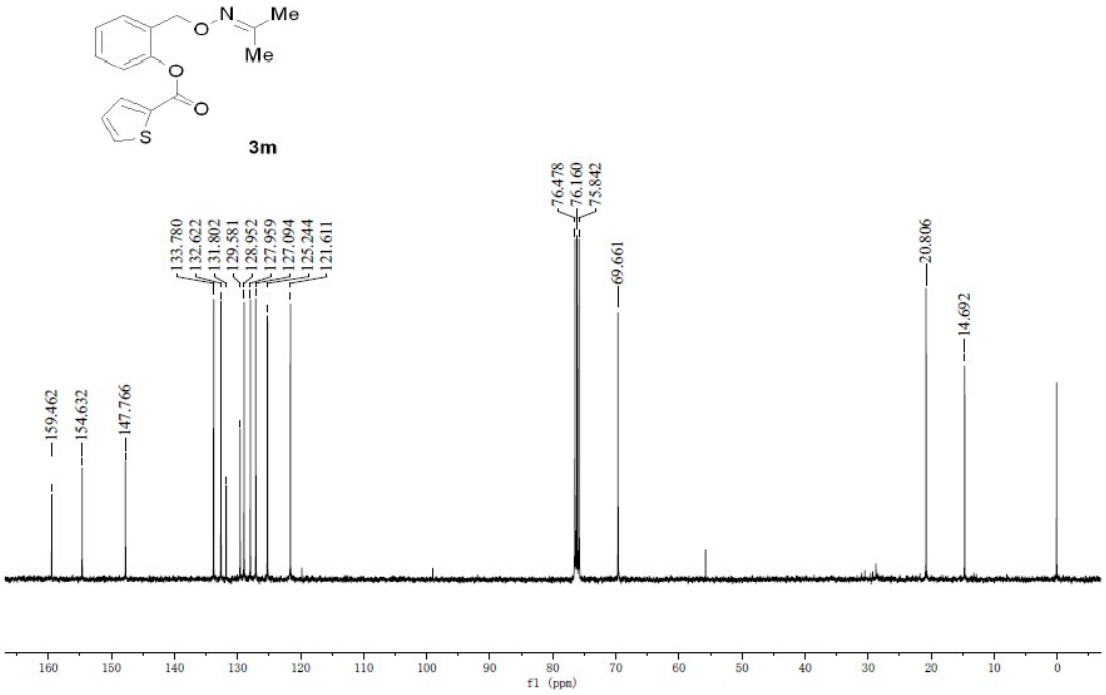
Monoisotopic Mass, Odd and Even Electron Ions
37 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-17 H: 0-13 N: 0-1 O: 0-3 F: 0-4



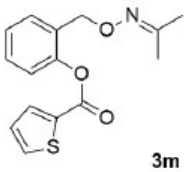

| | | | | | | |
|---|---|---|---|---|---|---|
| Minimum: | | | | | | -1.5 |
| Maximum: | | | 5.0 | 10.0 | | 50.0 |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 355.0834 | 355.0832 | 0.2 | 0.6 | 10.0 | n/a | C17 H13 N O3 F4 |



3m

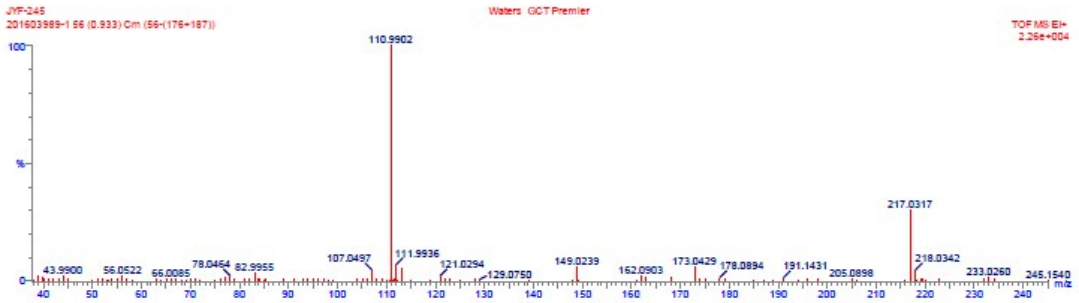



**Elemental Composition Report**

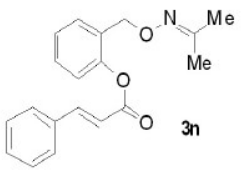


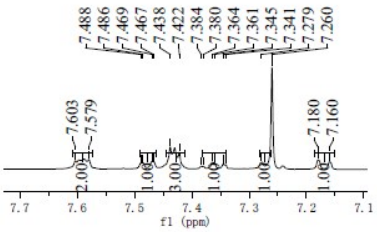

**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

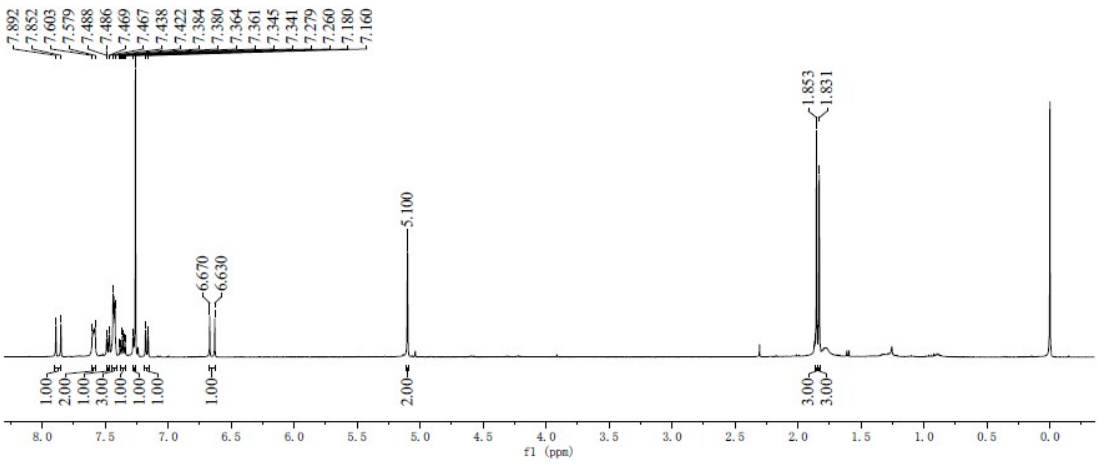
Monoisotopic Mass, Odd and Even Electron Ions
196 formula(e) evaluated with 15 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-15 H: 0-15 N: 0-1 O: 0-3 S: 0-1

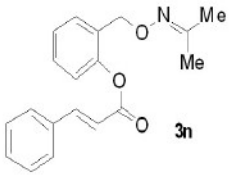


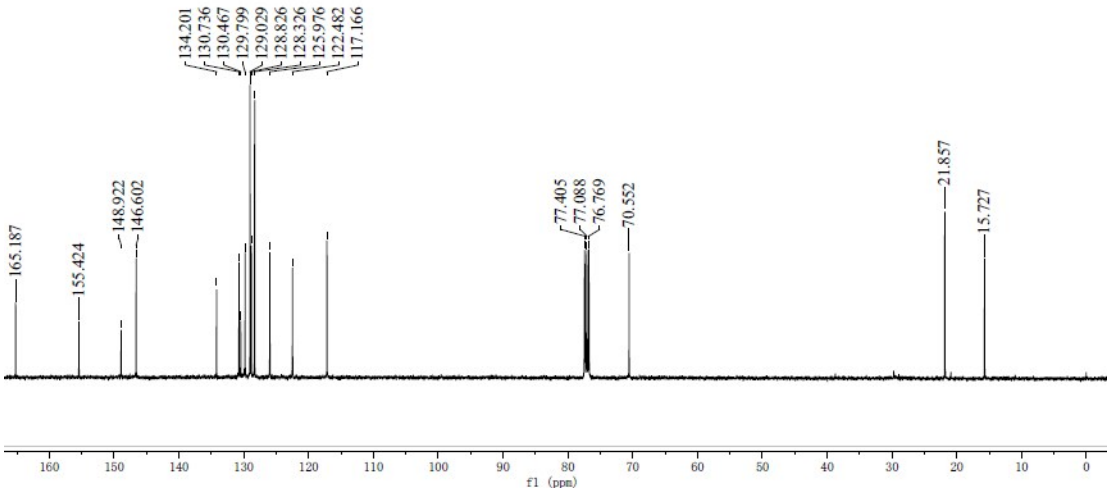

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | 3.00 | | | | | | -1.5 |
| Maximum: | 100.00 | | | 5.0 | | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 217.0317 | 29.71 | 217.0323 | -0.6 | -2.8 | 8.5 | 2776597.0 | C12 H9 O2 S |


N
Me
Me
O
O
O
3n

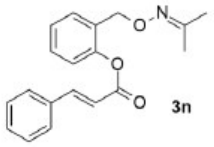

7.488
7.486
7.469
7.467
7.438
7.422
7.384
7.380
7.364
7.361
7.345
7.341
7.279
7.260
7.603
7.579
7.180
7.160
f1 (ppm)


7.892
7.852
7.603
7.579
7.488
7.486
7.469
7.467
7.438
7.422
7.384
7.380
7.364
7.361
7.345
7.341
7.279
7.260
7.180
7.160
1.853
1.831
6.670
6.630
5.100
f1 (ppm)


N
Me
Me
O
O
O
3n

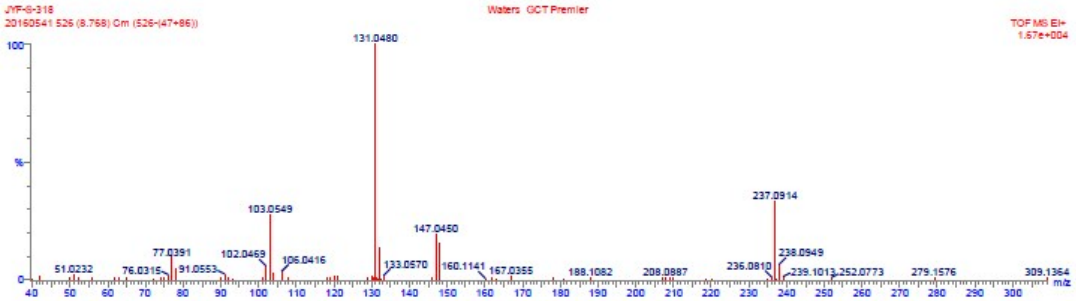

134.201
130.736
130.467
129.799
129.029
128.826
128.326
125.976
122.482
117.166
165.187
155.424
148.922
146.602
77.405
77.088
76.769
70.552
21.857
15.727
f1 (ppm)

**Elemental Composition Report**



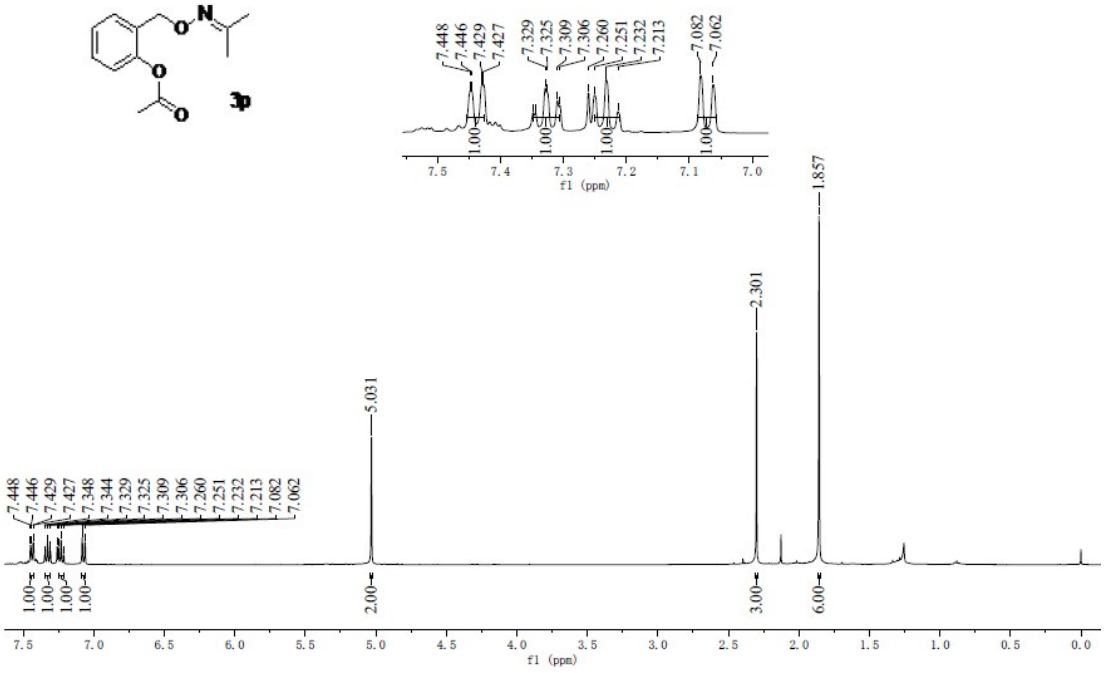

**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

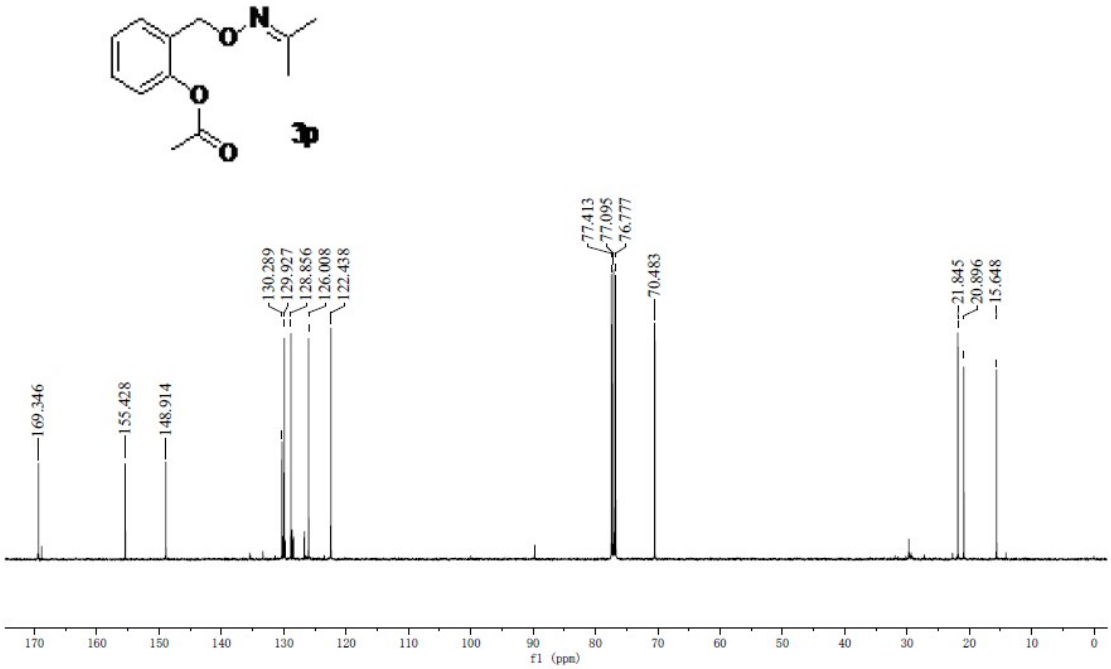
Monoisotopic Mass, Odd and Even Electron Ions
702 formula(e) evaluated with 48 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-19 H: 0-19 N: 0-1 O: 0-3



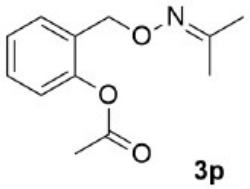

| | | | | | | |
|---|---|---|---|---|---|---|
| Minimum: | 0.18 | | | | | -1.5 |
| Maximum: | 100.00 | | | 5.0 | 10.0 | 50.0 |

| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
|---|---|---|---|---|---|---|---|
| 309.1364 | 0.19 | 309.1365 | -0.1 | -0.3 | 11.0 | 5546032.0 | C19 H19 N O3 |



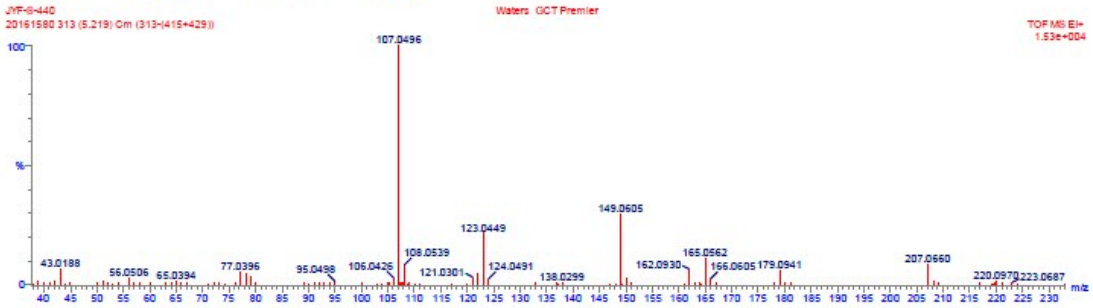



**Elemental Composition Report**

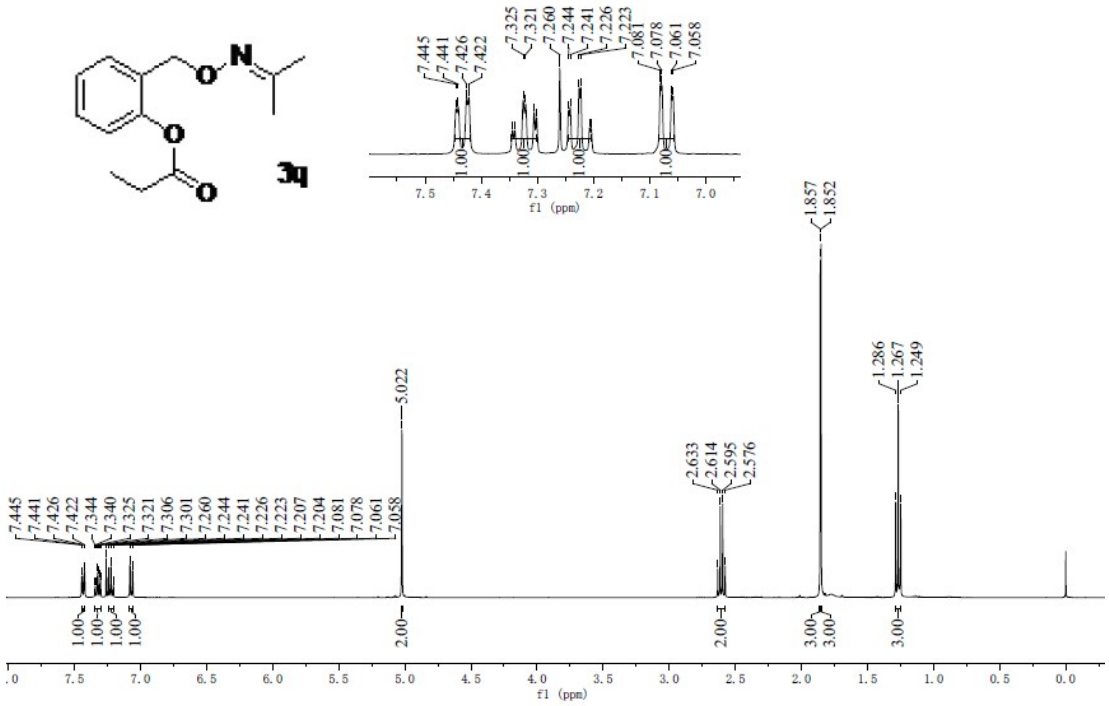


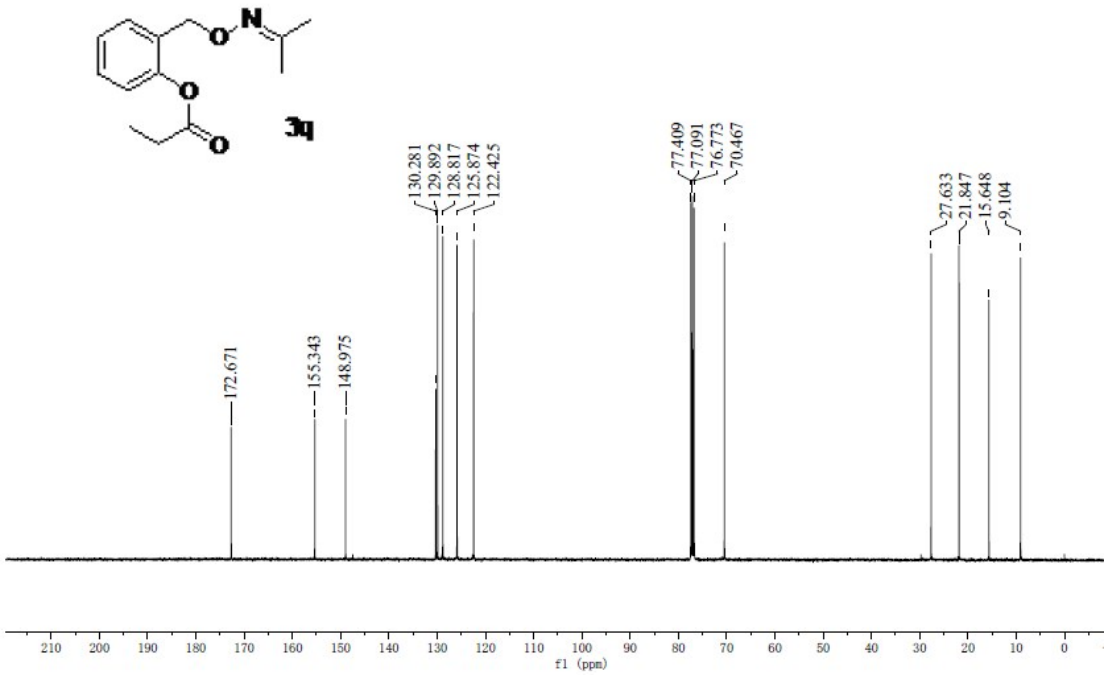

**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
290 formula(e) evaluated with 28 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-12 H: 0-15 N: 0-1 O: 0-3

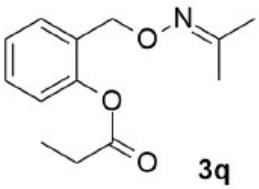



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | | 0.70 | | | | | -1.5 |
| Maximum: | | 100.00 | | | 5.0 | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 221.1050 | 0.74 | 221.1052 | -0.2 | -0.9 | 6.0 | 2773065.3 | C12 H15 N O3 |


3q
7.445
7.441
7.426
7.422
7.344
7.340
7.325
7.321
7.306
7.301
7.260
7.244
7.241
7.226
7.223
7.207
7.204
7.081
7.078
7.061
7.058
5.022
2.633
2.614
2.595
2.576
1.857
1.852
1.286
1.267
1.249
1.00
1.00
1.00
1.00
2.00
2.00
3.00
3.00
3.00
f1 (ppm)


3q
172.671
155.343
148.975
130.281
129.892
128.817
125.874
122.425
77.409
77.091
76.773
70.467
27.633
21.847
15.648
9.104
f1 (ppm)

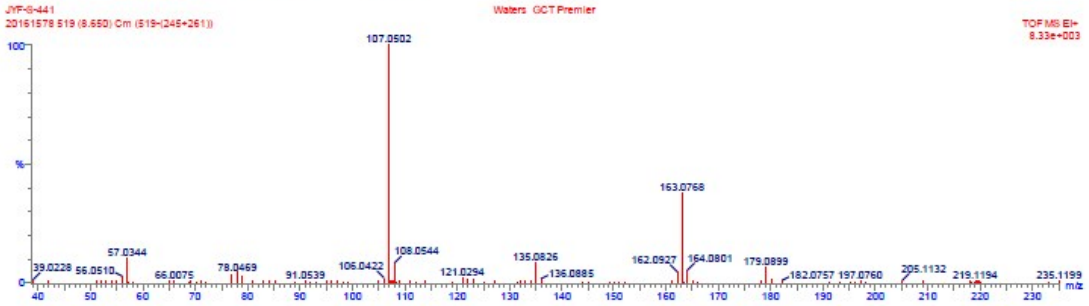
**Elemental Composition Report**



3q

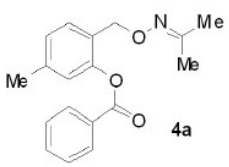
**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

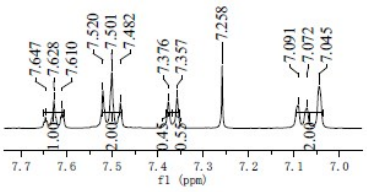
Monoisotopic Mass, Odd and Even Electron Ions
766 formula(e) evaluated with 49 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-13 H: 0-17 N: 0-1 O: 0-3

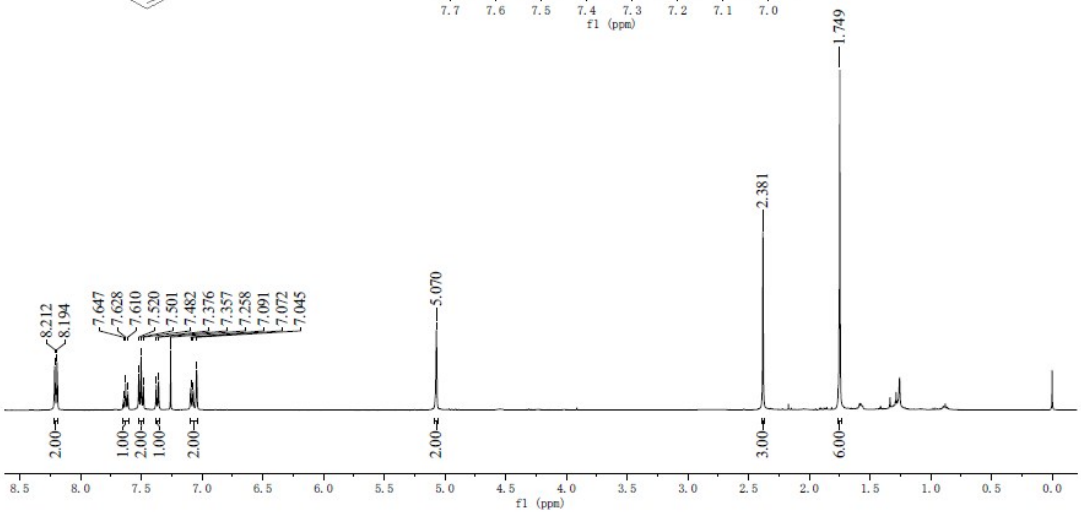


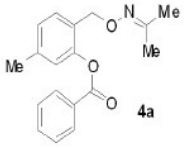

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | | 0.20 | | | | | -1.5 |
| Maximum: | | 100.00 | | | 5.0 | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 235.1199 | 0.21 | 235.1208 | -0.9 | -3.8 | 6.0 | 5546026.0 | C13 H17 N O3 |

## 5.2 Copies of the spectra for Scheme 4

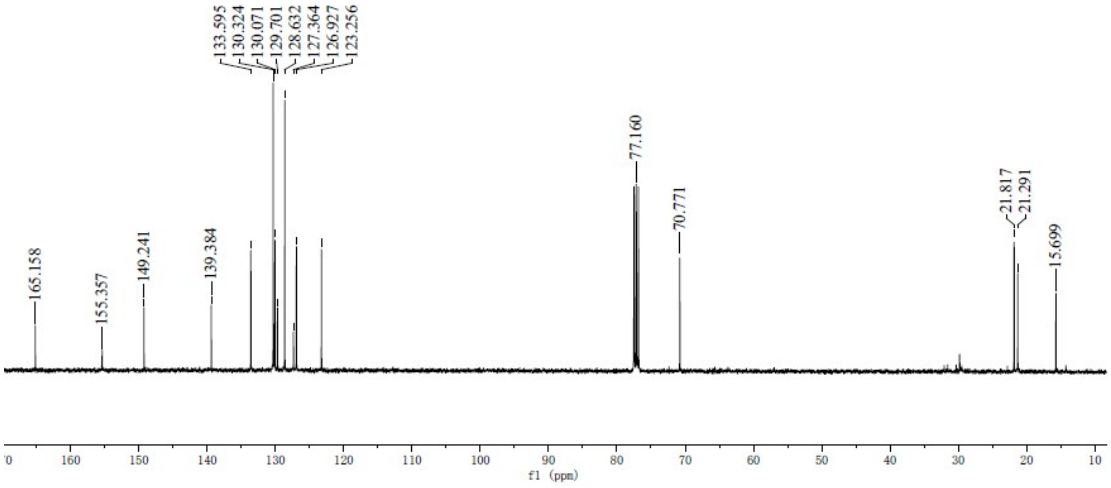


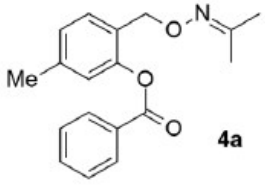






4a



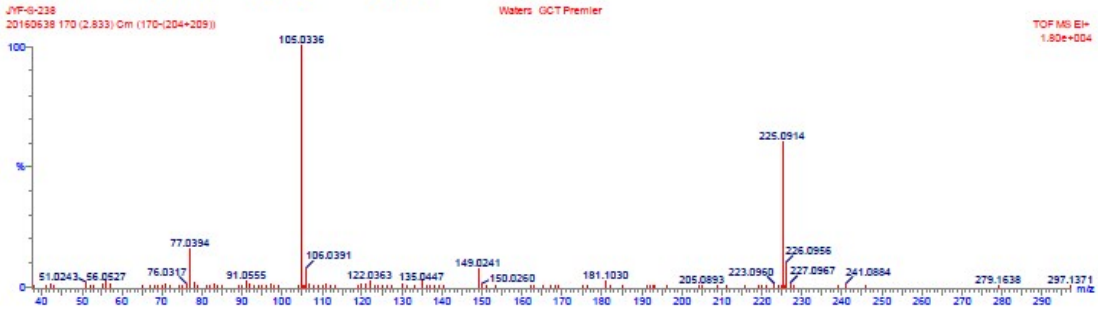

**Elemental Composition Report**



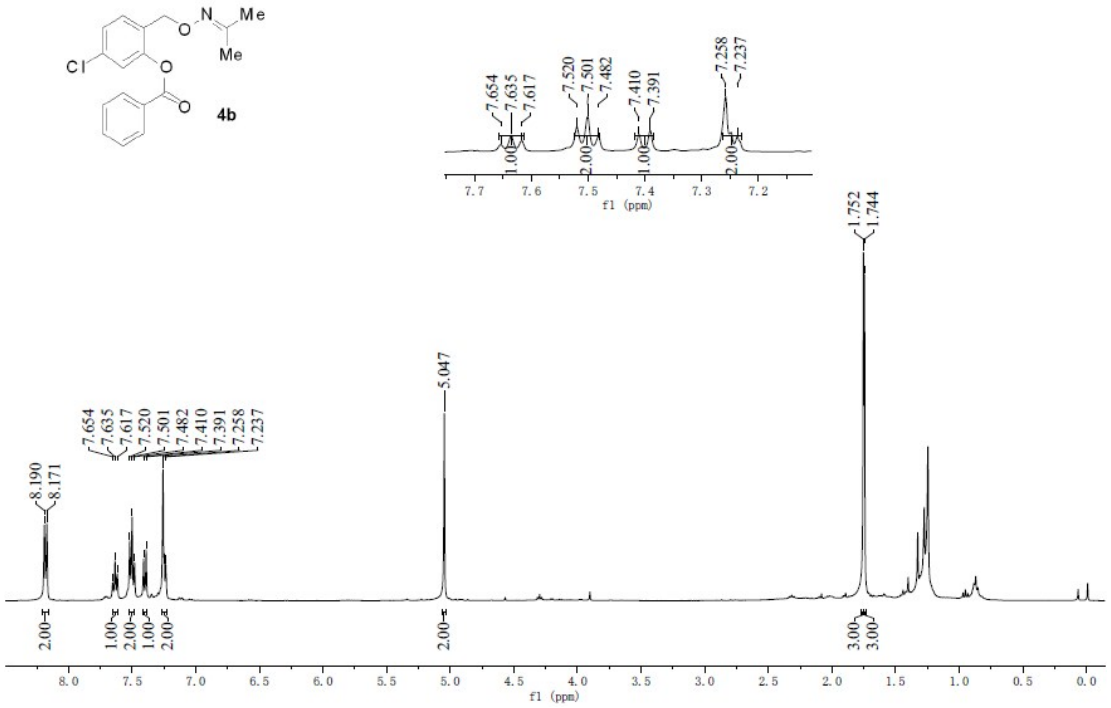

4a

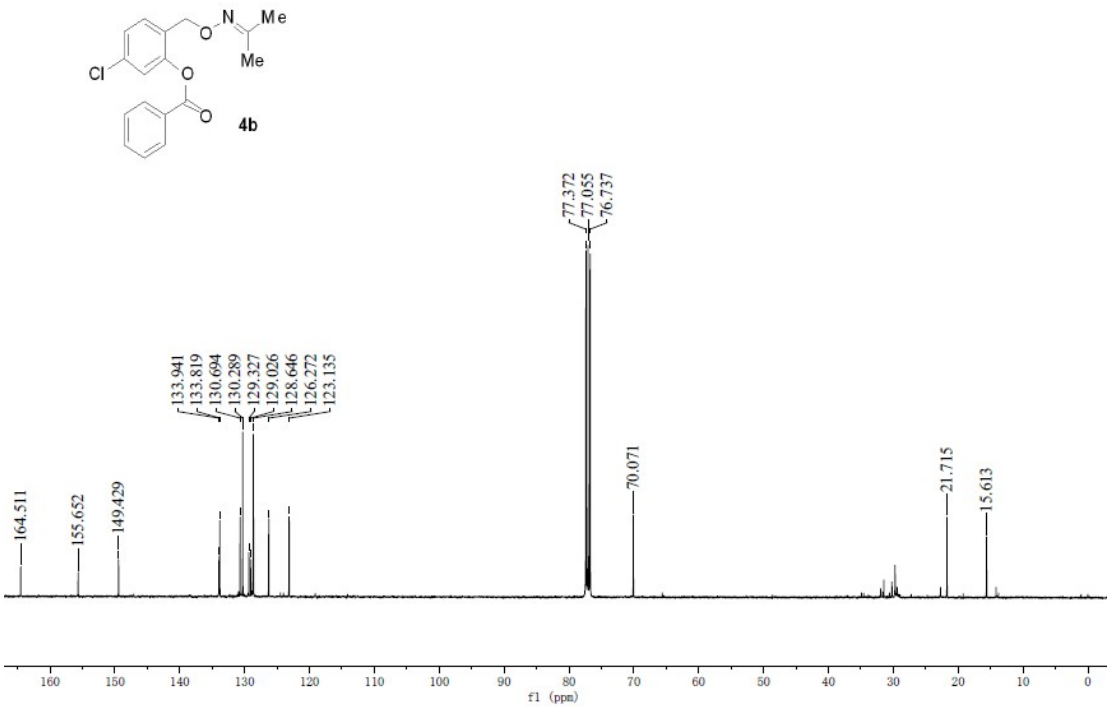
**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
1453 formula(e) evaluated with 86 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-18 H: 0-19 N: 0-1 O: 0-3

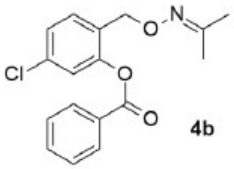



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | | 0.12 | | | | | -1.5 |
| Maximum: | | 100.00 | | | 5.0 | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 297.1371 | 0.13 | 297.1365 | 0.6 | 2.0 | 10.0 | 5546029.0 | C18 H19 N O3 |


4b
7.654
7.635
7.617
7.520
7.501
7.482
7.410
7.391
7.258
7.237
f1 (ppm)
8.190
8.171
5.047
1.752
1.744
2.00
1.00
2.00
1.00
2.00
2.00
3.00
3.00
f1 (ppm)


4b
77.372
77.055
76.737
133.941
133.819
130.694
130.289
129.327
129.026
128.646
126.272
123.135
164.511
155.652
149.429
70.071
21.715
15.613
f1 (ppm)

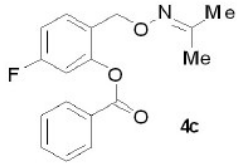
**Elemental Composition Report**

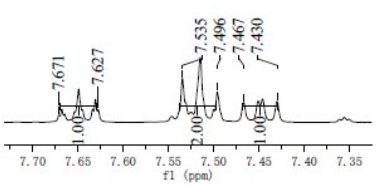


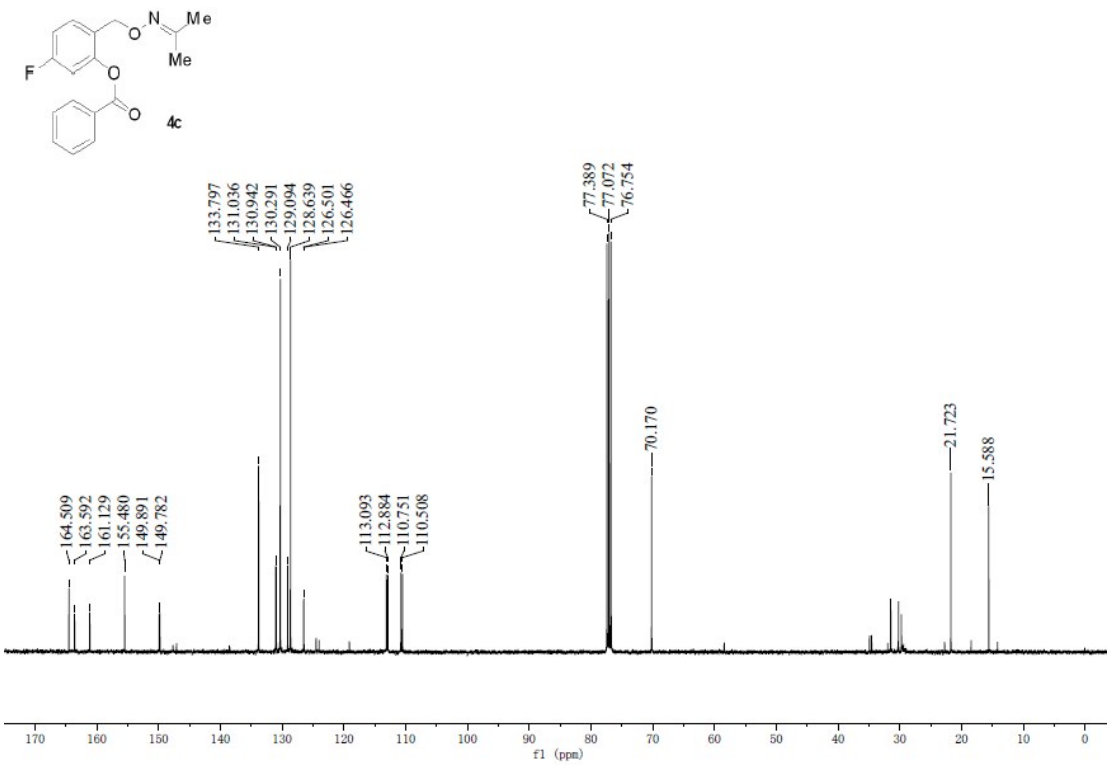

**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
991 formula(e) evaluated with 58 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-17 H: 0-16 N: 0-1 O: 0-3 35Cl: 0-1 37Cl: 0-1

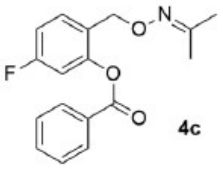

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | 0.29 | | | | | | -1.5 |
| Maximum: | 100.00 | | | 5.0 | | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 245.0372 | 34.32 | 245.0369 | 0.3 | 1.2 | 9.5 | 0.4 | C14 H10 O2 35Cl |



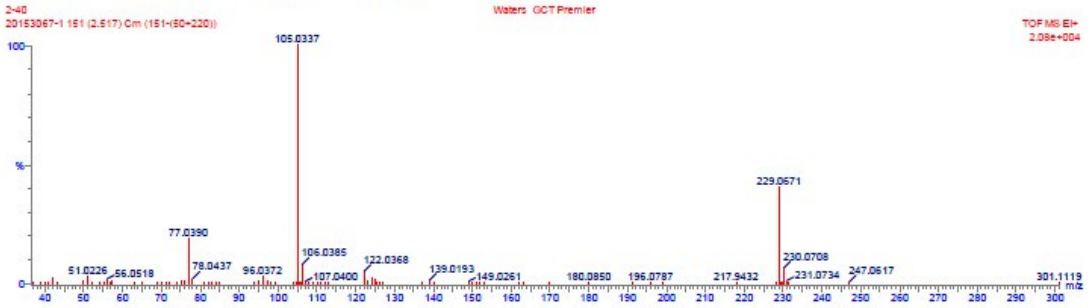



**Elemental Composition Report**

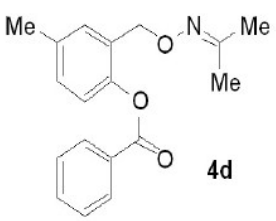


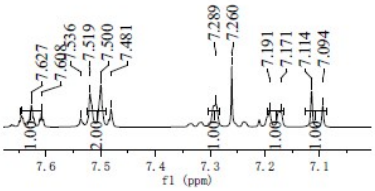

**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

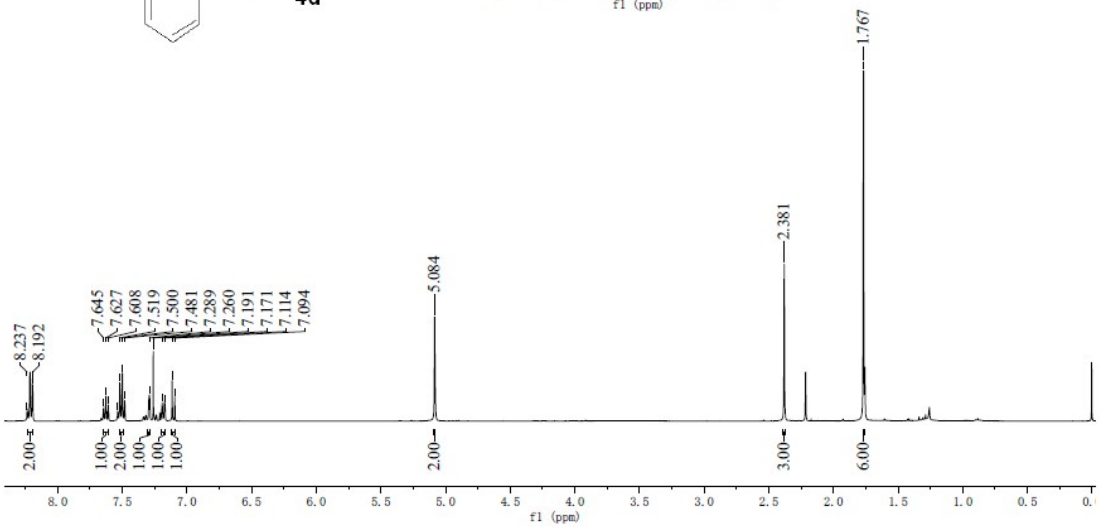
Monoisotopic Mass, Odd and Even Electron Ions
2386 formula(e) evaluated with 131 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-17 H: 0-16 N: 0-1 O: 0-3 F: 0-1

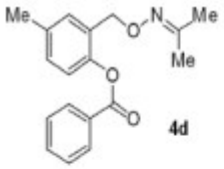


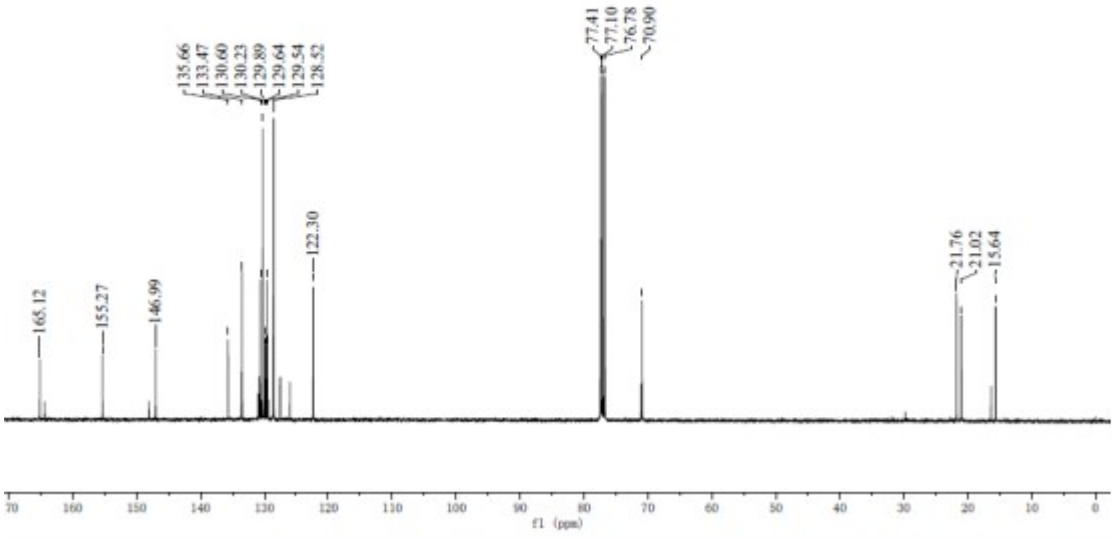

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | 0.10 | | | | | | -1.5 |
| Maximum: | 100.00 | | | | 5.0 | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 301.1119 | 0.11 | 301.1114 | 0.5 | 1.7 | 10.0 | 5546028.5 | C17 H16 N O3 F |


Me
N
Me
Me
O
O
O
4d

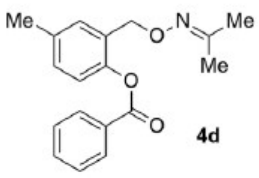

7.627
7.608
7.536
7.519
7.500
7.481
7.289
7.260
7.191
7.171
7.114
7.094
f1 (ppm)


8.237
8.192
7.645
7.627
7.608
7.519
7.500
7.481
7.289
7.260
7.191
7.171
7.114
7.094
5.084
2.381
1.767
f1 (ppm)


Me
N
Me
Me
O
O
4d

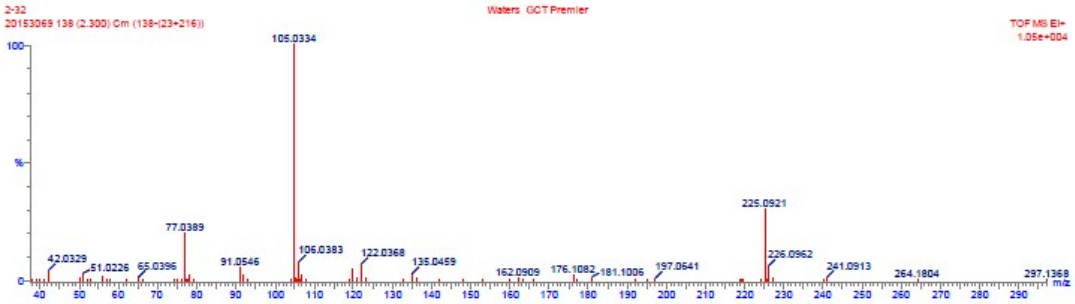

165.12
155.27
146.99
135.66
133.47
130.60
130.23
129.89
129.64
129.54
128.52
122.30
77.41
77.10
76.78
70.90
21.76
21.02
15.64
f1 (ppm)

Elemental Composition Report

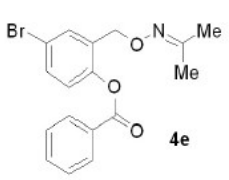


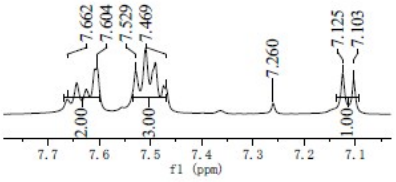

**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

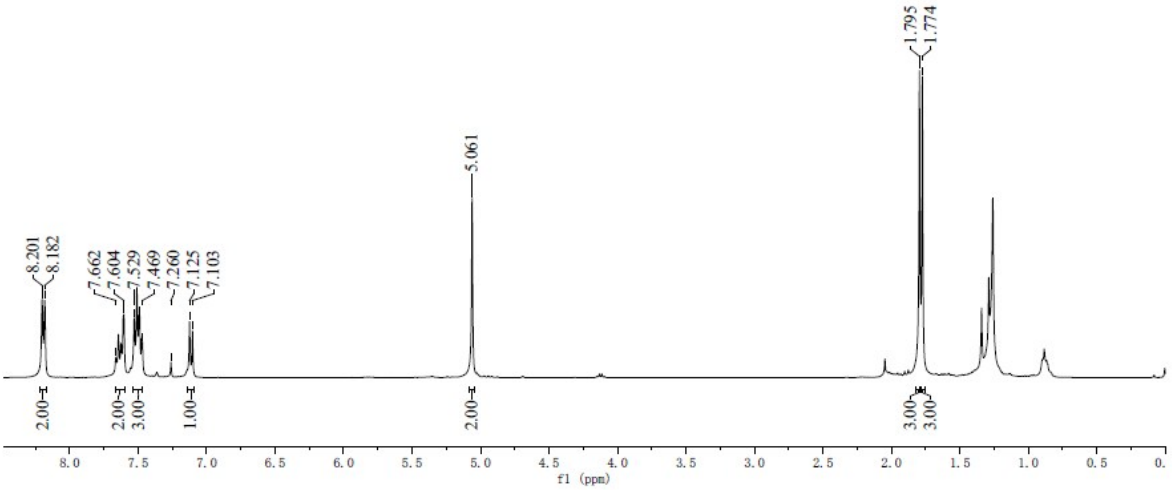
Monoisotopic Mass, Odd and Even Electron Ions
384 formula(e) evaluated with 31 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-18 H: 0-19 N: 0-1 O: 0-3

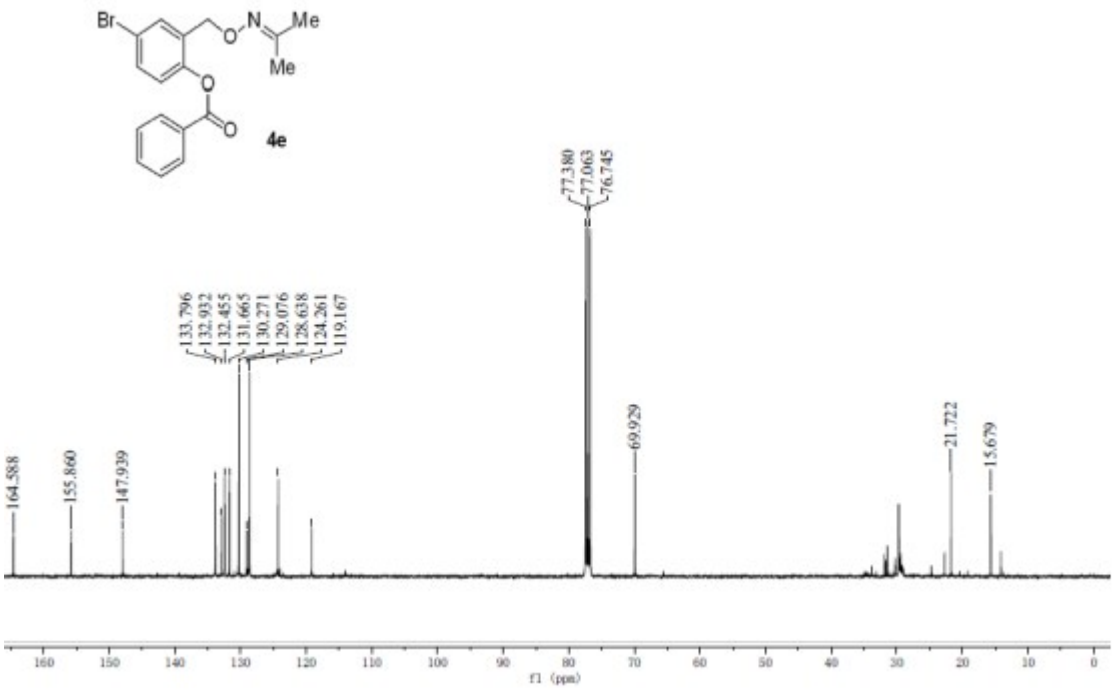



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | 0.50 | | | | | | -1.5 |
| Maximum: | 100.00 | | | | 5.0 | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 297.1368 | 0.52 | 297.1365 | 0.3 | 1.0 | 10.0 | 5546041.0 | C18 H19 N O3 |

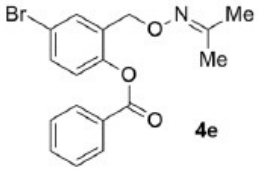




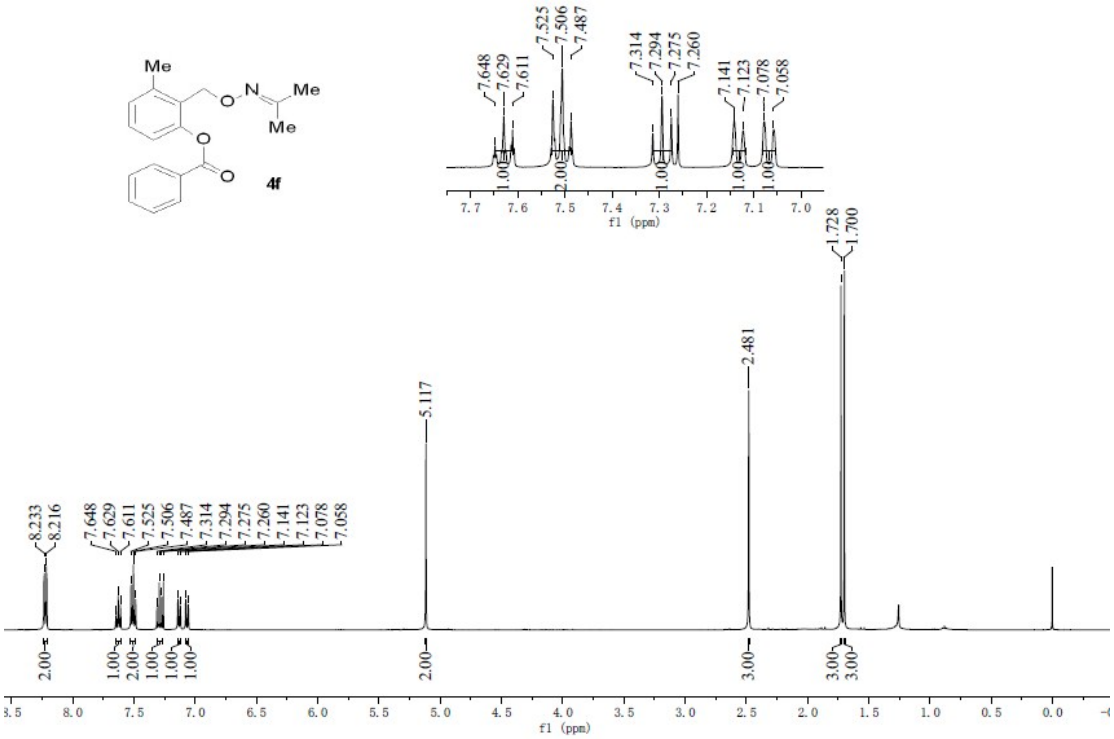

**Elemental Composition Report**

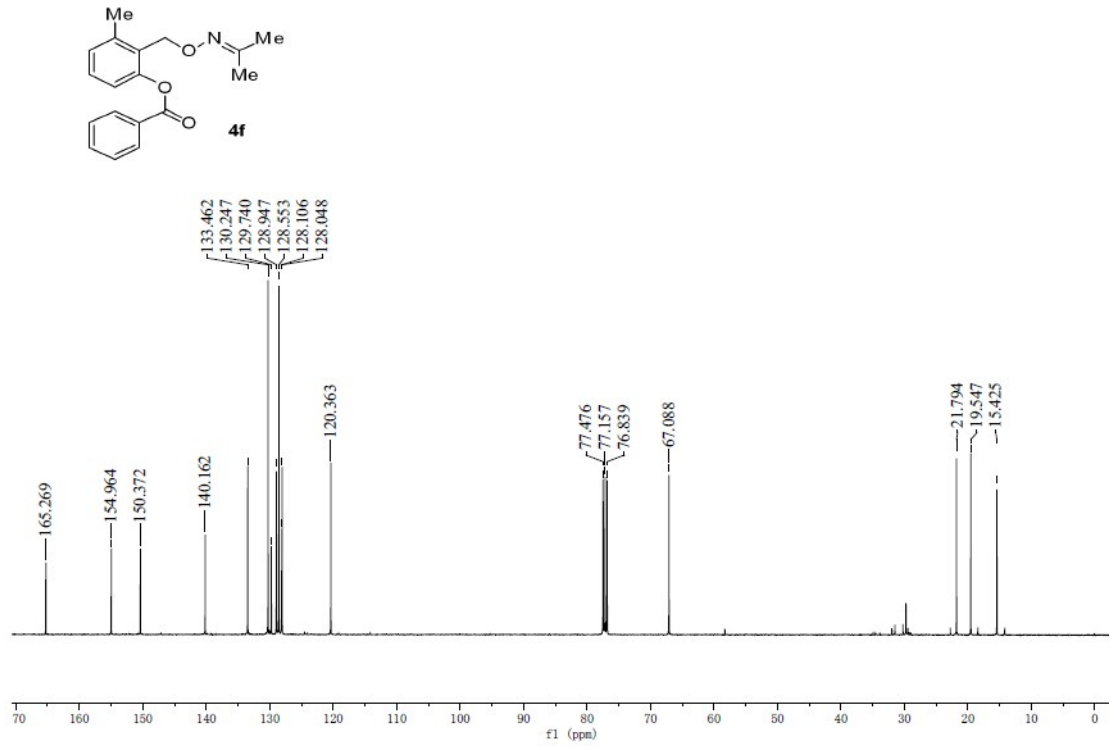



**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

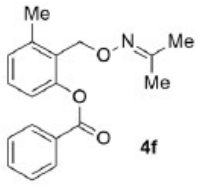
Monoisotopic Mass, Odd and Even Electron Ions
1890 formula(e) evaluated with 88 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-17 H: 0-16 N: 0-1 O: 0-3 79Br: 0-1 81Br: 0-1


| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | | 0.20 | | | | | -1.5 |
| Maximum: | | 100.00 | | | 5.0 | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 363.0300 | 0.32 | 363.0293 | 0.7 | 1.9 | 10.0 | 5546037.5 | C17 H16 N O3 81Br |


Me
N
Me
Me
O
O
O
4f
7.648
7.629
7.611
7.525
7.506
7.487
7.314
7.294
7.275
7.260
7.141
7.123
7.078
7.058
1.728
1.700
2.481
5.117
8.233
8.216
f1 (ppm)


Me
N
Me
Me
O
O
O
4f
133.462
130.247
129.740
128.947
128.553
128.106
128.048
120.363
77.476
77.157
76.839
67.088
21.794
19.547
15.425
165.269
154.964
150.372
140.162
f1 (ppm)

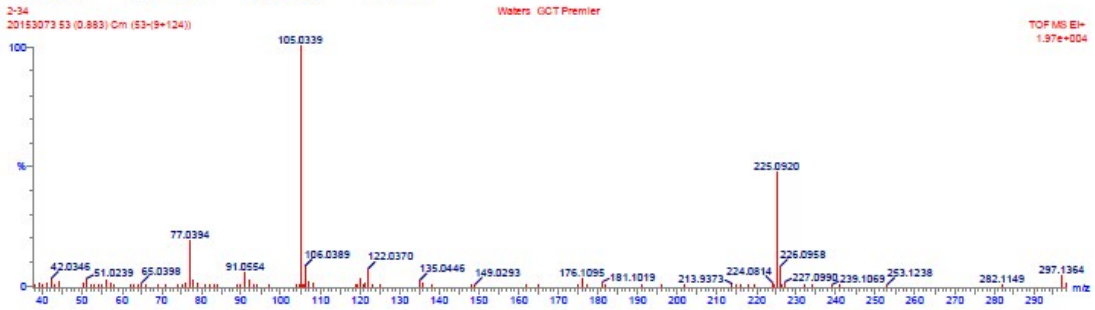
**Elemental Composition Report**



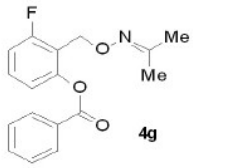
4f

**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

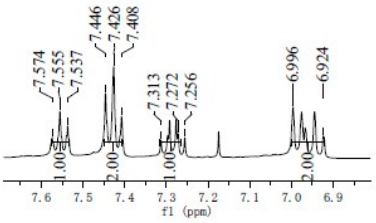
Monoisotopic Mass, Odd and Even Electron Ions
96 formula(e) evaluated with 8 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-18 H: 0-19 N: 0-1 O: 0-3

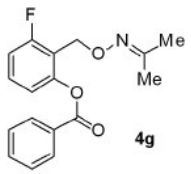



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | 3.00 | | | | | | -1.5 |
| Maximum: | 100.00 | | | 5.0 | | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 297.1364 | 4.17 | 297.1365 | -0.1 | -0.3 | 10.0 | 2773157.8 | C18 H19 N O3 |

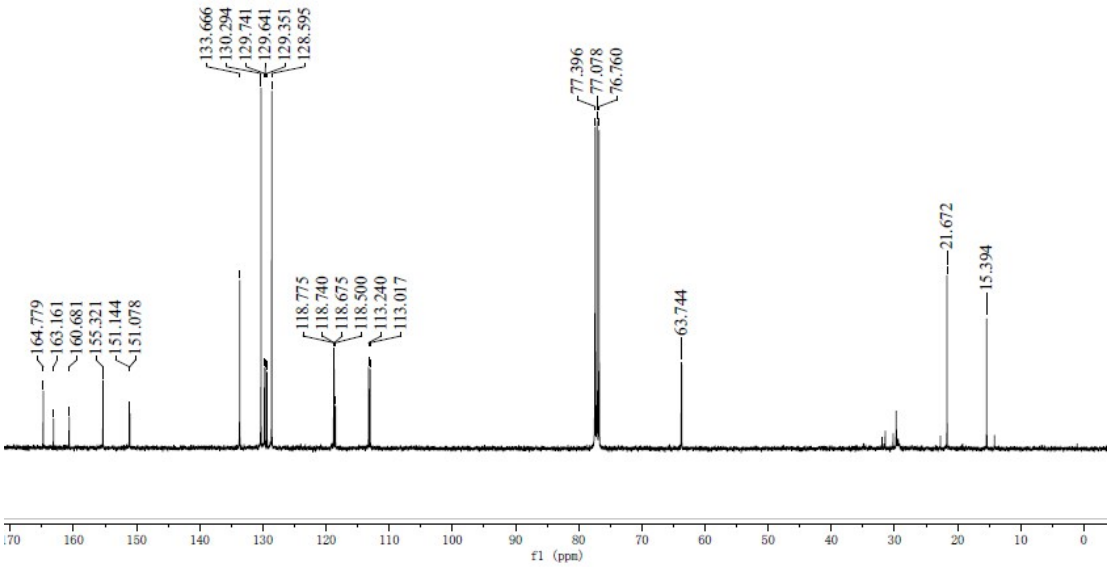


4g

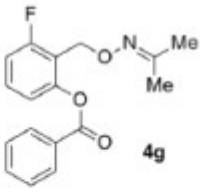





**4g**




**Elemental Composition Report**

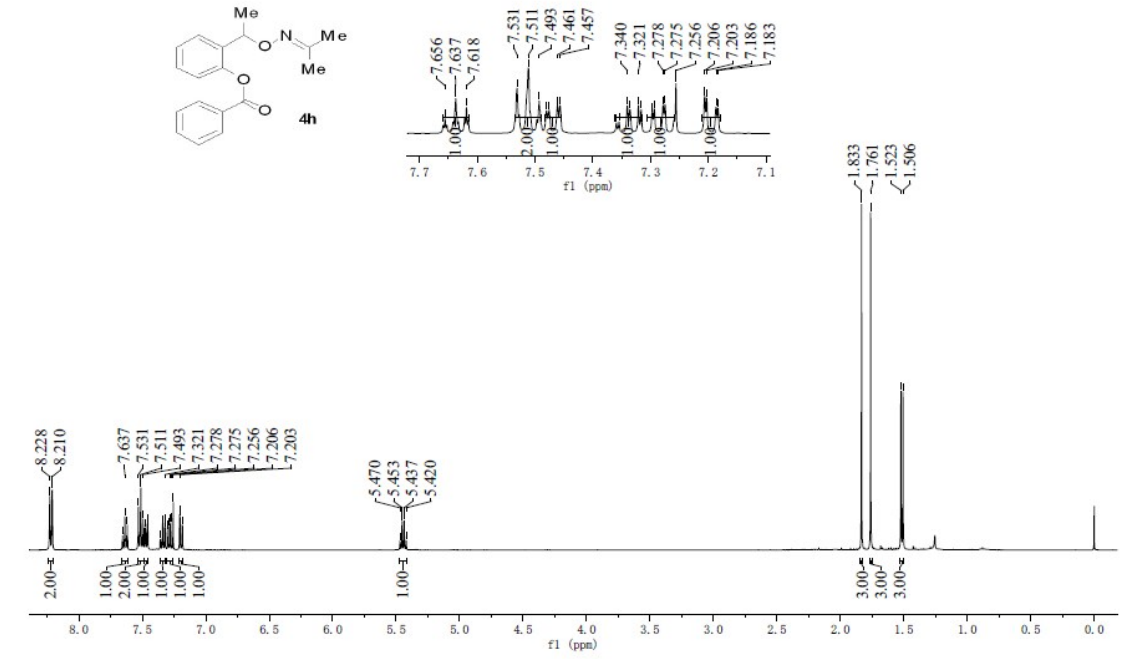


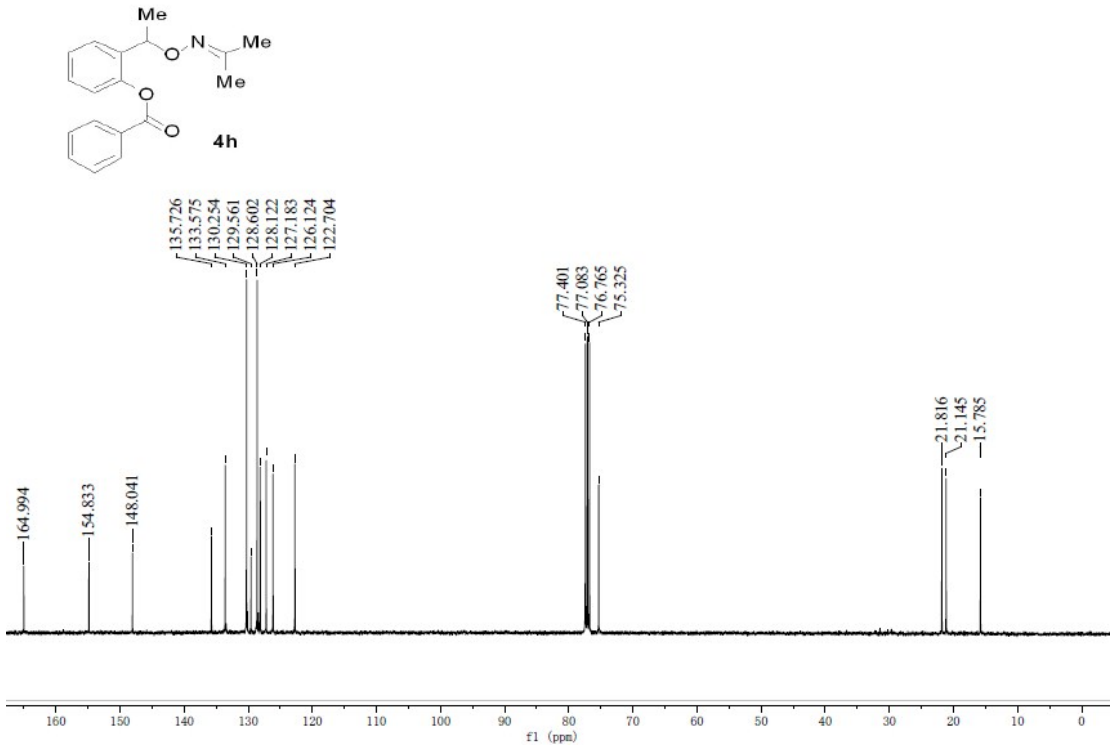

**4g**

**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

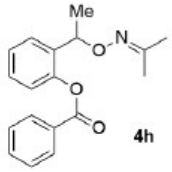
Monoisotopic Mass, Odd and Even Electron Ions
361 formula(e) evaluated with 34 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-17 H: 0-16 N: 0-1 O: 0-3 F: 0-1


| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | 0.70 | | | | | | -1.5 |
| Maximum: | 100.00 | | | 5.0 | | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 301.1117 | 0.72 | 301.1114 | 0.3 | 1.0 | 10.0 | 2773014.8 | C17 H16 N O3 F |


Me
N
Me
Me
O
O
4h
7.656
7.637
7.618
7.531
7.511
7.493
7.461
7.457
7.340
7.321
7.278
7.275
7.256
7.206
7.203
7.186
7.183
1.833
1.761
1.523
1.506
8.228
8.210
7.637
7.531
7.511
7.493
7.321
7.278
7.275
7.256
7.206
7.203
5.470
5.453
5.437
5.420
f1 (ppm)


Me
N
Me
Me
O
O
4h
135.726
133.575
130.254
129.561
128.602
128.122
127.183
126.124
122.704
77.401
77.083
76.765
75.325
21.816
21.145
15.785
164.994
154.833
148.041
f1 (ppm)

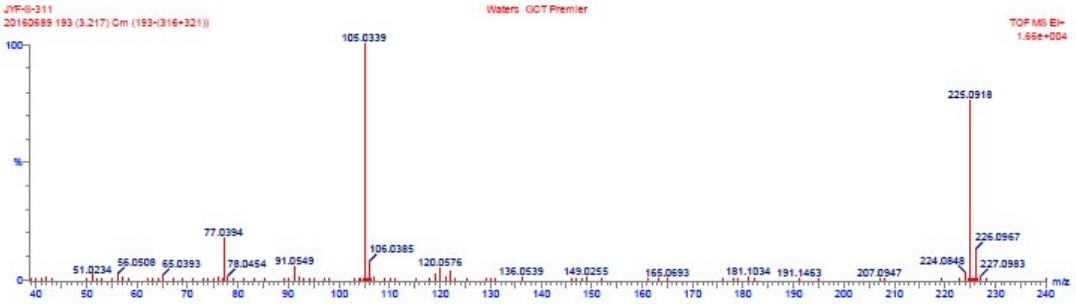
Elemental Composition Report



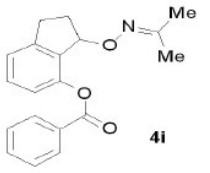
4h

**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

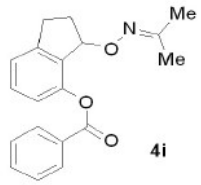
Monoisotopic Mass, Odd and Even Electron Ions
103 formula(e) evaluated with 8 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-18 H: 0-19 N: 0-1 O: 0-3



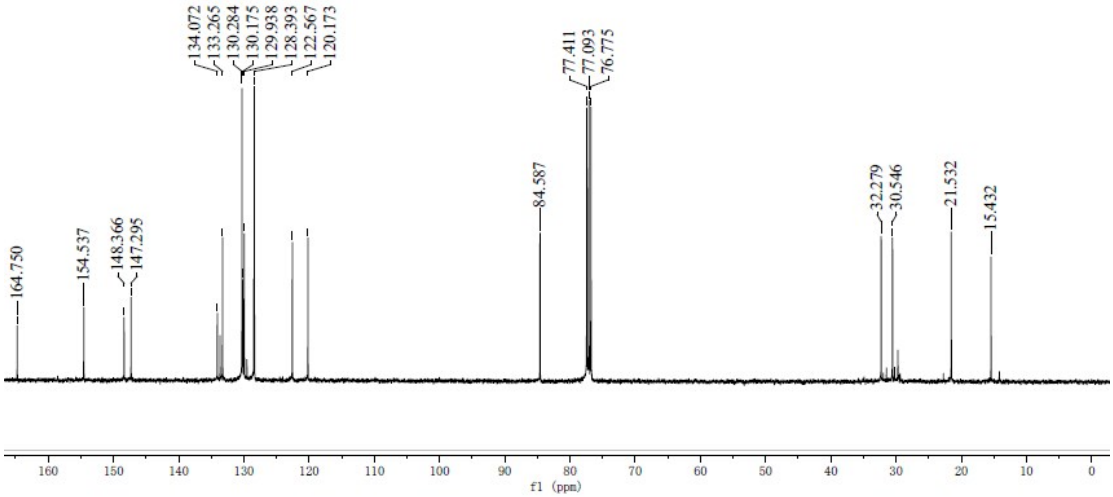

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | 3.00 | | | | | | -1.5 |
| Maximum: | 100.00 | | | 5.0 | | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 226.0967 | 12.50 | 226.0994 | -2.7 | -11.9 | 9.0 | 38.0 | C15 H14 O2 |



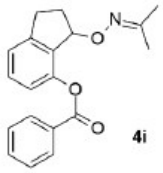
4i




4i



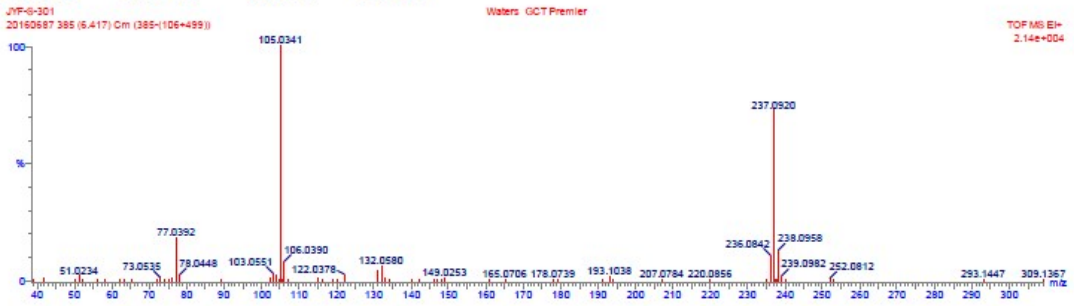

**Elemental Composition Report**



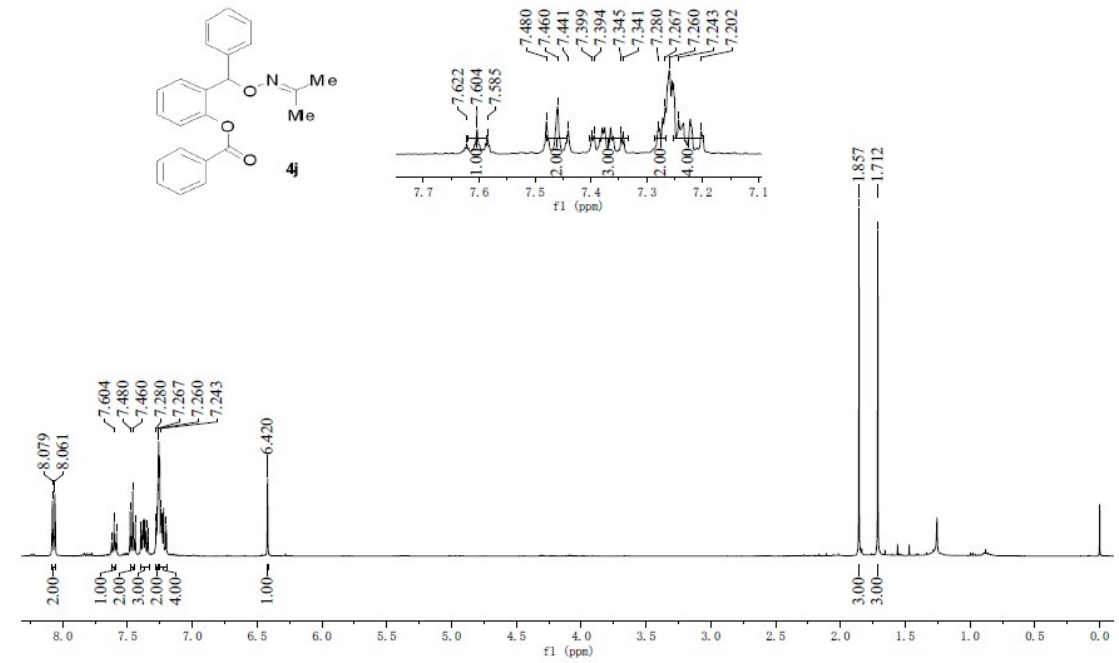

4i

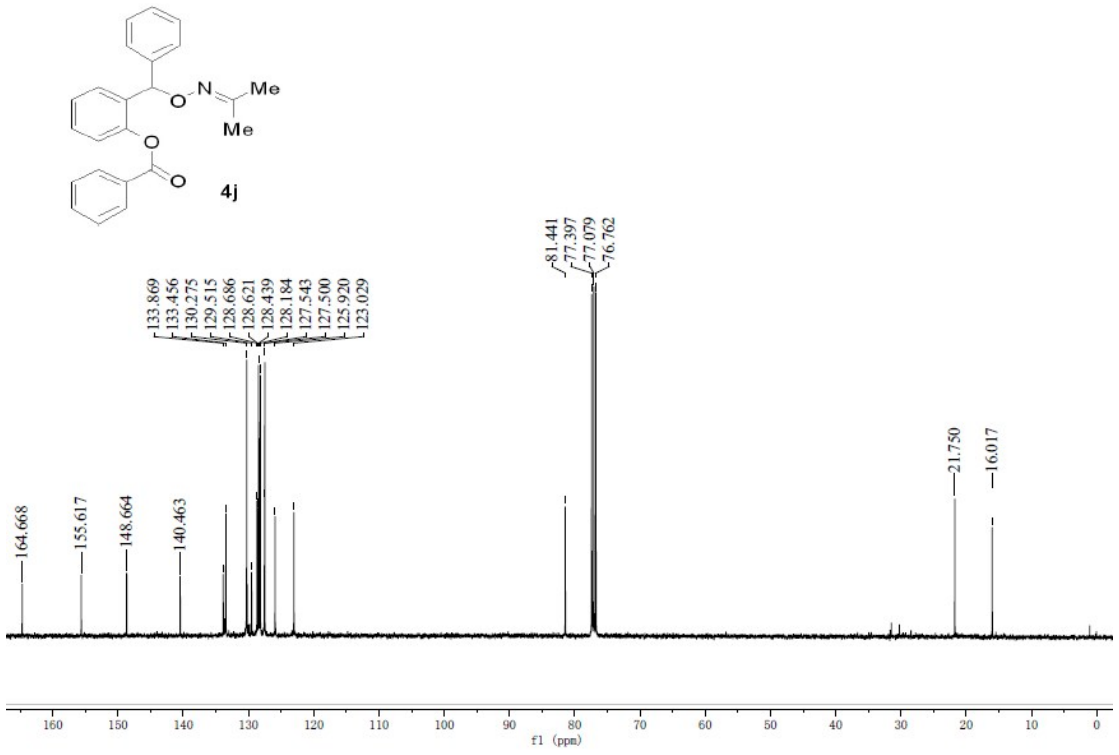
**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
763 formula(e) evaluated with 48 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-19 H: 0-19 N: 0-1 O: 0-3

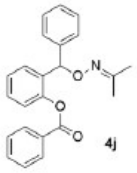



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | 0.14 | | | | | | -1.5 |
| Maximum: | 100.00 | | | | 5.0 | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 309.1367 | 0.15 | 309.1365 | 0.2 | 0.6 | 11.0 | 5546032.5 | C19 H19 N O3 |


4j
7.622
7.604
7.585
7.480
7.460
7.441
7.399
7.394
7.345
7.341
7.280
7.267
7.260
7.243
7.202
f1 (ppm)
8.079
8.061
7.604
7.480
7.460
7.280
7.267
7.260
7.243
6.420
1.857
1.712
f1 (ppm)

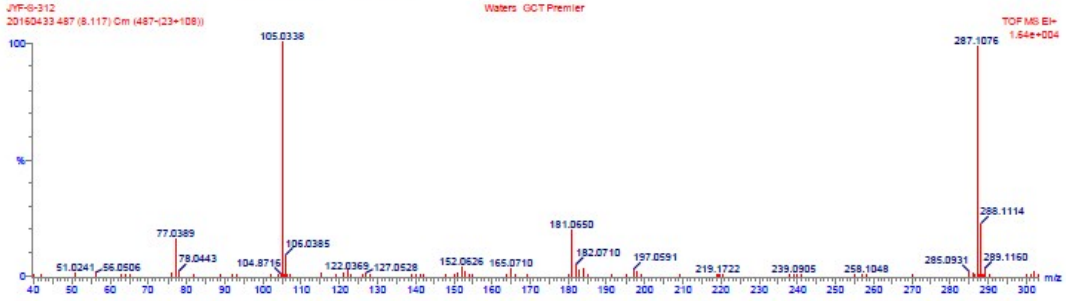

4j
164.668
155.617
148.664
140.463
133.869
133.456
130.275
129.515
128.686
128.621
128.439
128.184
127.543
127.500
125.920
123.029
81.441
77.397
77.079
76.762
21.750
16.017
f1 (ppm)

Elemental Composition Report

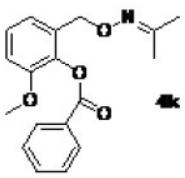


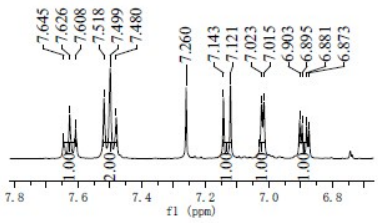

**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

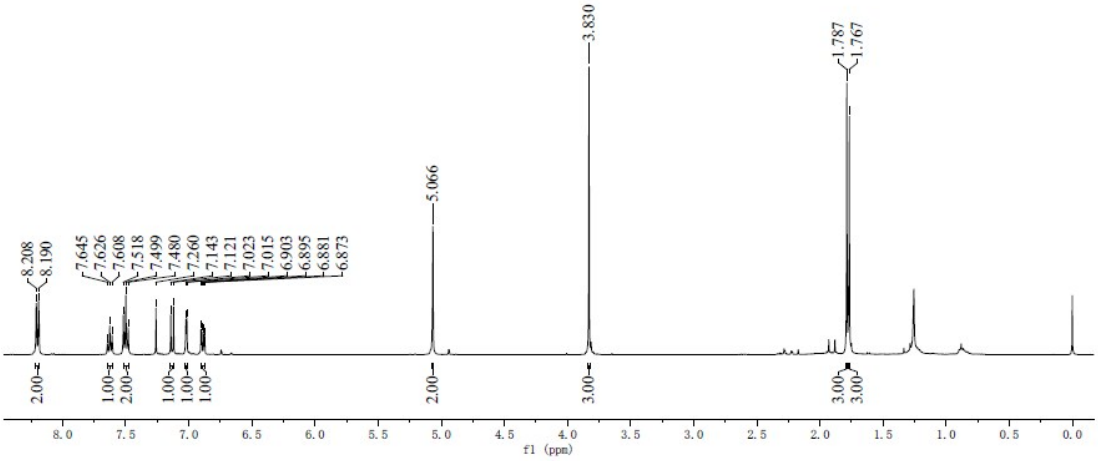
Monoisotopic Mass, Odd and Even Electron Ions
113 formula(e) evaluated with 8 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-23 H: 0-21 N: 0-1 O: 0-3

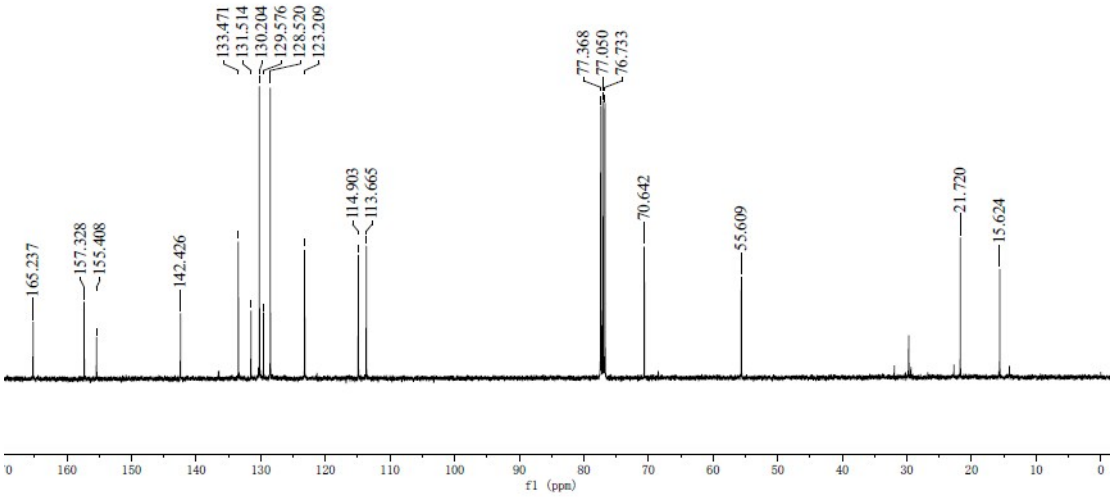



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | 3.00 | | | | | | -1.5 |
| Maximum: | 100.00 | | | 5.0 | | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 288.1114 | 21.80 | 288.1150 | -3.6 | -12.5 | 13.0 | 121.1 | C20 H16 O2 |

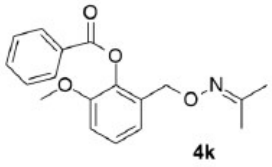




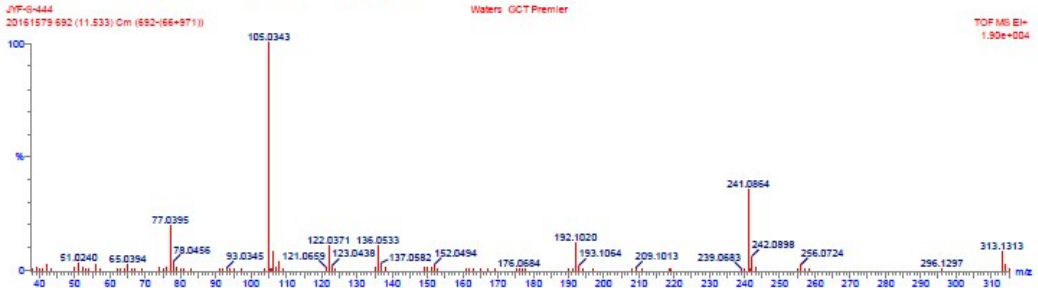

**Elemental Composition Report**



**4k**

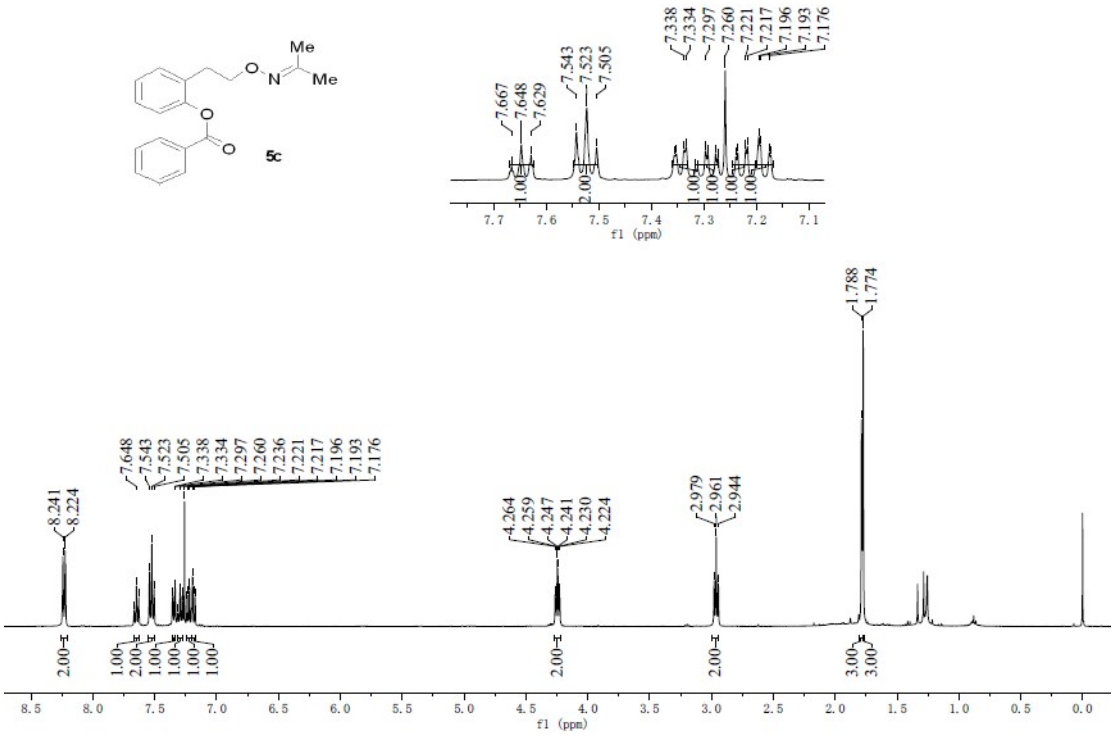
**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

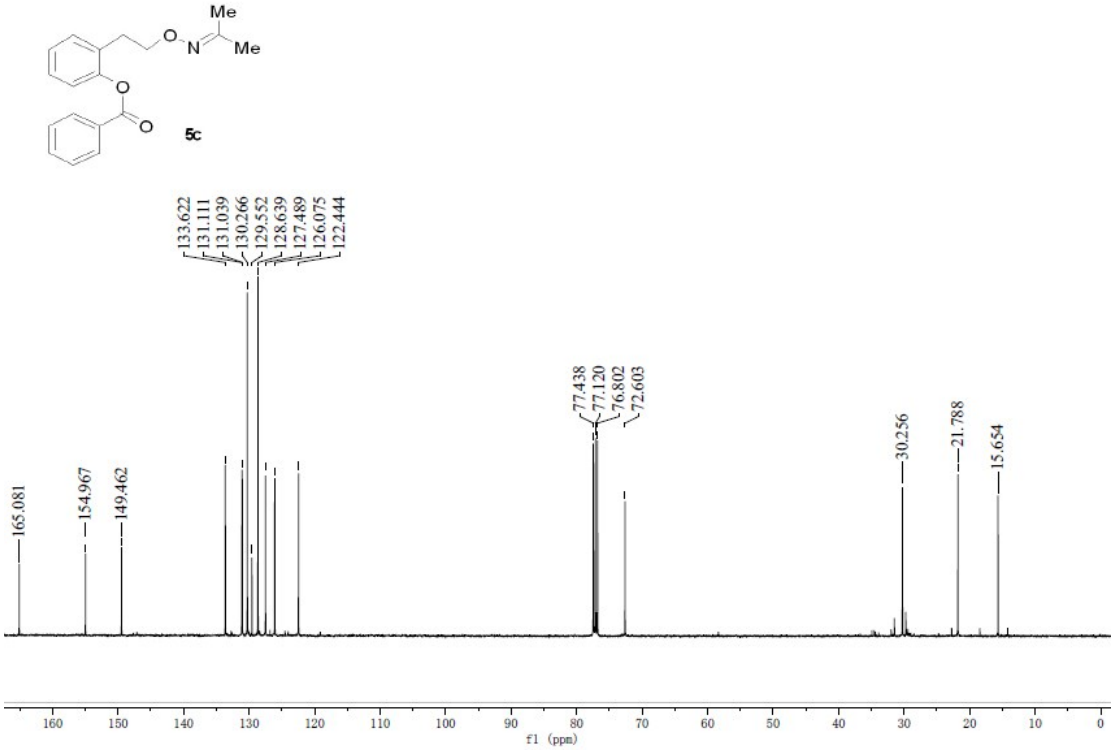
Monoisotopic Mass, Odd and Even Electron Ions
157 formula(e) evaluated with 12 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-18 H: 0-19 N: 0-1 O: 0-4



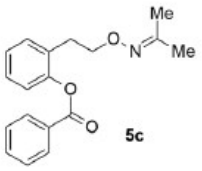

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | 3.00 | | | | | | -1.5 |
| Maximum: | 100.00 | | | 5.0 | | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 313.1313 | 7.51 | 313.1314 | -0.1 | -0.3 | 10.0 | 0.8 | C18 H19 N O4 |

## 5.3 Copies of the spectra for Scheme 5


Me
O
N
Me
O
O
5c
7.667
7.648
7.629
7.543
7.523
7.505
7.338
7.334
7.297
7.260
7.221
7.217
7.196
7.193
7.176
f1 (ppm)
1.788
1.774
8.241
8.224
7.648
7.543
7.523
7.505
7.338
7.334
7.297
7.260
7.236
7.221
7.217
7.196
7.193
7.176
4.264
4.259
4.247
4.241
4.230
4.224
2.979
2.961
2.944
f1 (ppm)

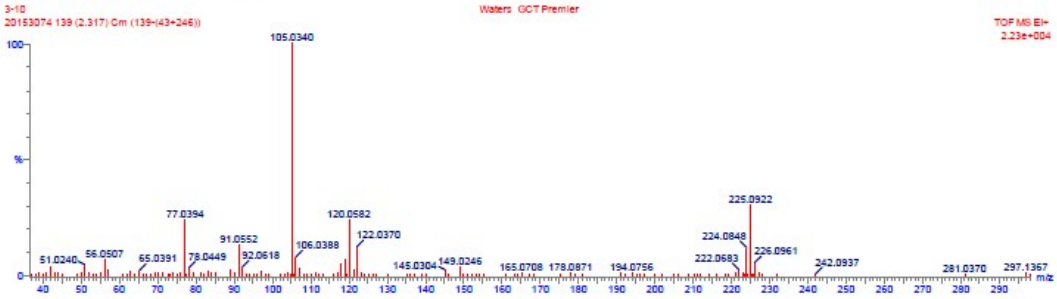



**Elemental Composition Report**

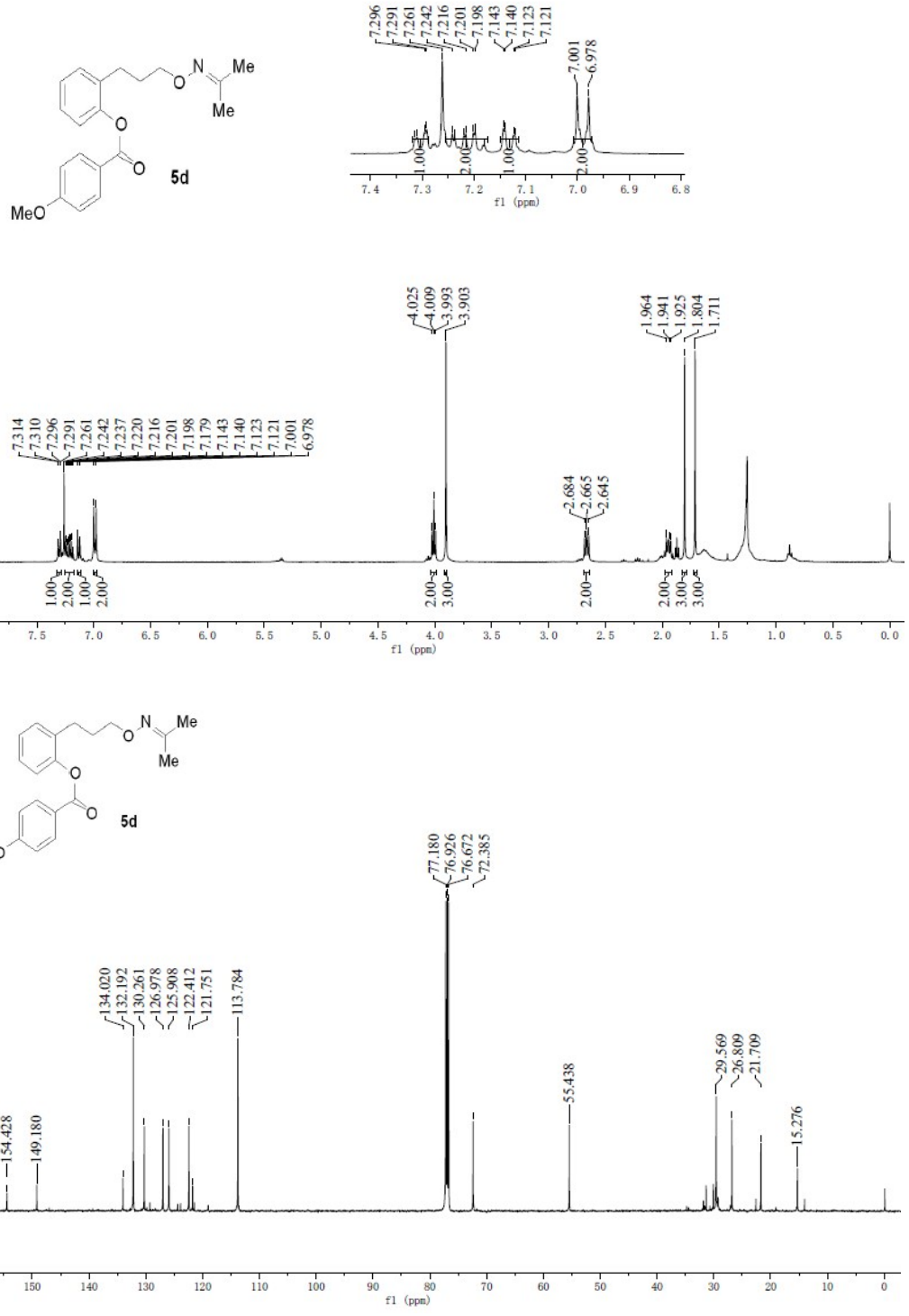



Multiple Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

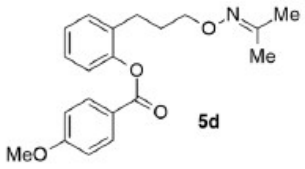
Monoisotopic Mass, Odd and Even Electron Ions
584 formula(e) evaluated with 46 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-18 H: 0-19 N: 0-1 O: 0-3




| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | 0.69 | | | | | | -1.5 |
| Maximum: | 100.00 | | | | 5.0 | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 297.1367 | 0.70 | 297.1365 | 0.2 | 0.7 | 10.0 | 2773017.0 | C18 H19 N O3 |


5d
MeO
7.296
7.291
7.261
7.242
7.216
7.201
7.198
7.143
7.140
7.123
7.121
7.001
6.978
f1 (ppm)
4.025
4.009
3.993
3.903
1.964
1.941
1.925
1.804
1.711
8.180
8.157
7.314
7.310
7.296
7.291
7.261
7.242
7.237
7.220
7.216
7.201
7.198
7.179
7.143
7.140
7.123
7.121
7.001
6.978
2.684
2.665
2.645
f1 (ppm)
5d
MeO
77.180
76.926
76.672
72.385
134.020
132.192
130.261
126.978
125.908
122.412
121.751
113.784
55.438
29.569
26.809
21.709
164.735
163.792
154.428
149.180
15.276
f1 (ppm)

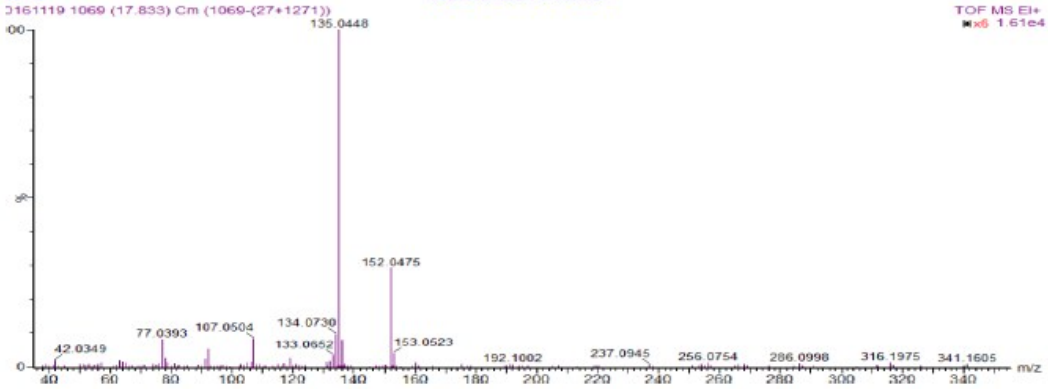
**Elemental Composition Report**



**5d**

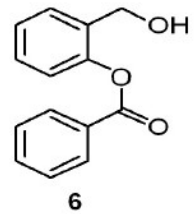
Multiple Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
3398 formula(e) evaluated with 162 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-20 H: 0-23 N: 0-1 O: 0-4

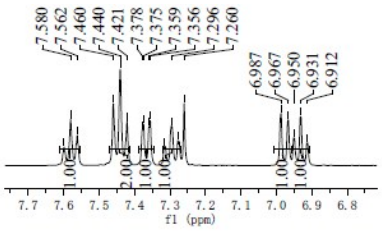


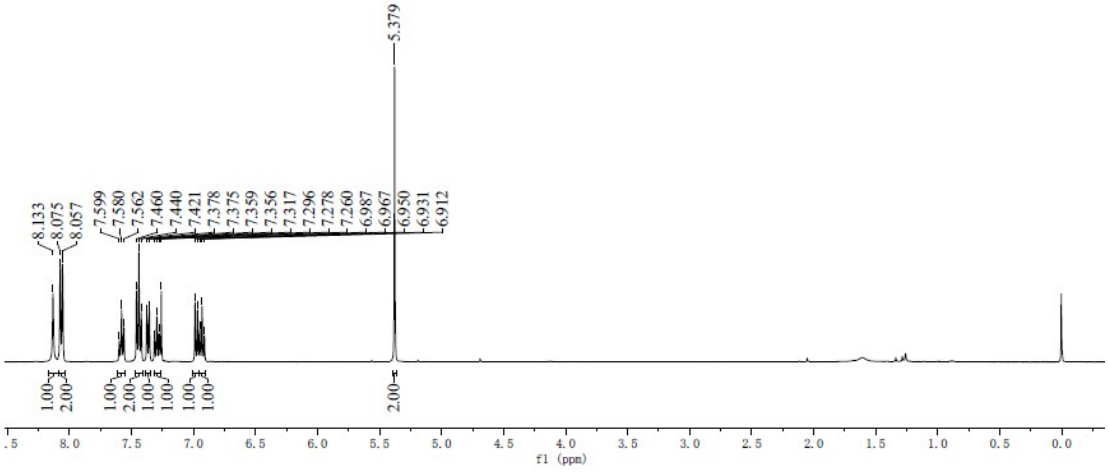

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | | 0.10 | | | | | -1.5 |
| Maximum: | | 100.00 | | | 5.0 | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 341.1605 | 0.11 | 341.1627 | -2.2 | -6.4 | 10.0 | 5546028.0 | C20 H23 N O4 |

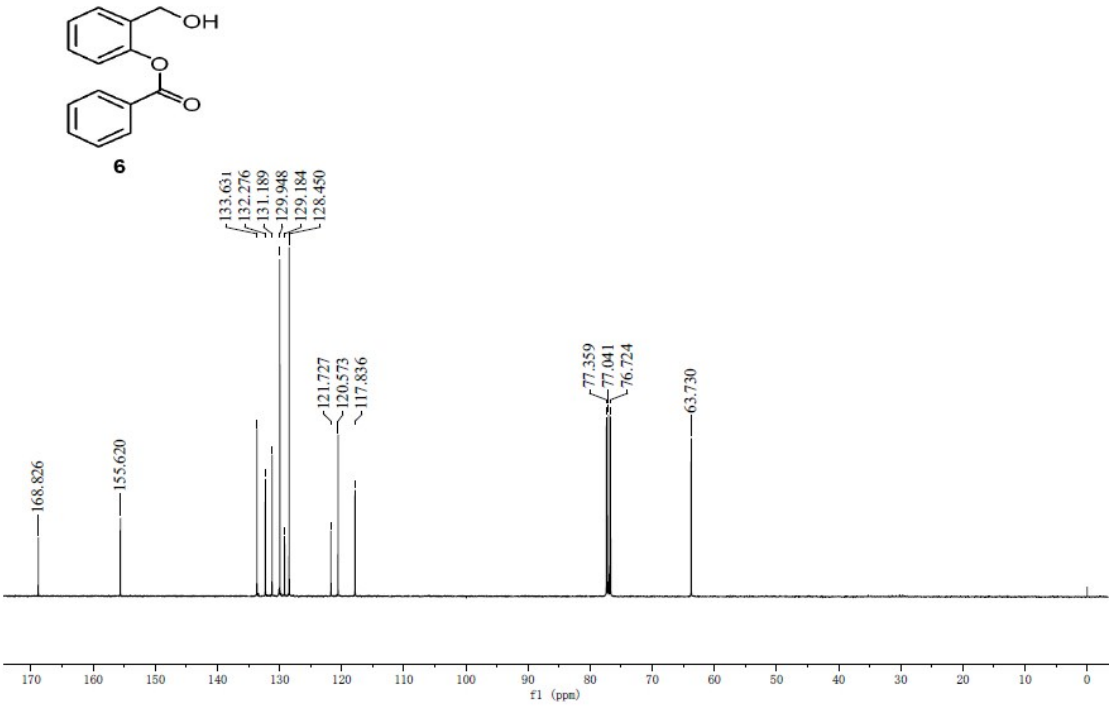
## 5.4 Copies of the spectra for Scheme 6



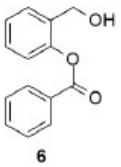
**6**



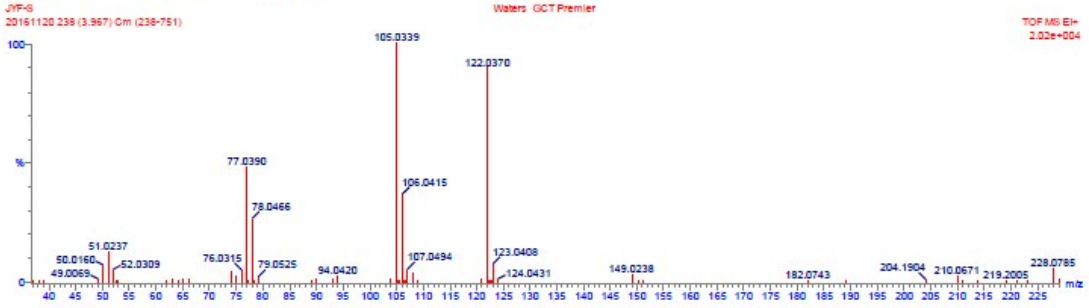



**Elemental Composition Report**



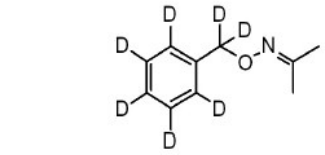

Multiple Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
63 formula(e) evaluated with 14 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-14 H: 0-12 O: 0-3

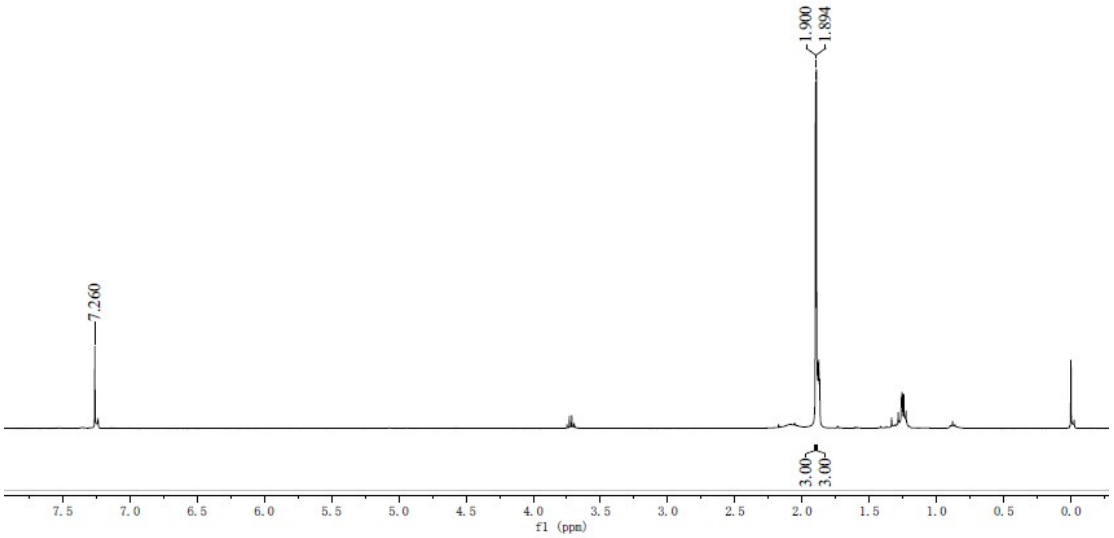


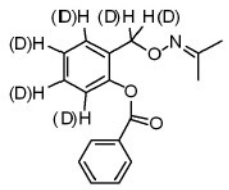

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | 3.00 | | | | | | -1.5 |
| Maximum: | 100.00 | | | | 5.0 | 10.0 | 50.0 |
| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 228.0785 | 5.38 | 228.0786 | -0.1 | -0.4 | 9.0 | 2773137.5 | C14 H12 O3 |

## 5.5 Copies of the spectra for Scheme 7

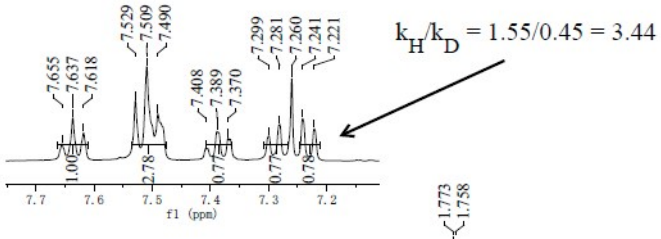


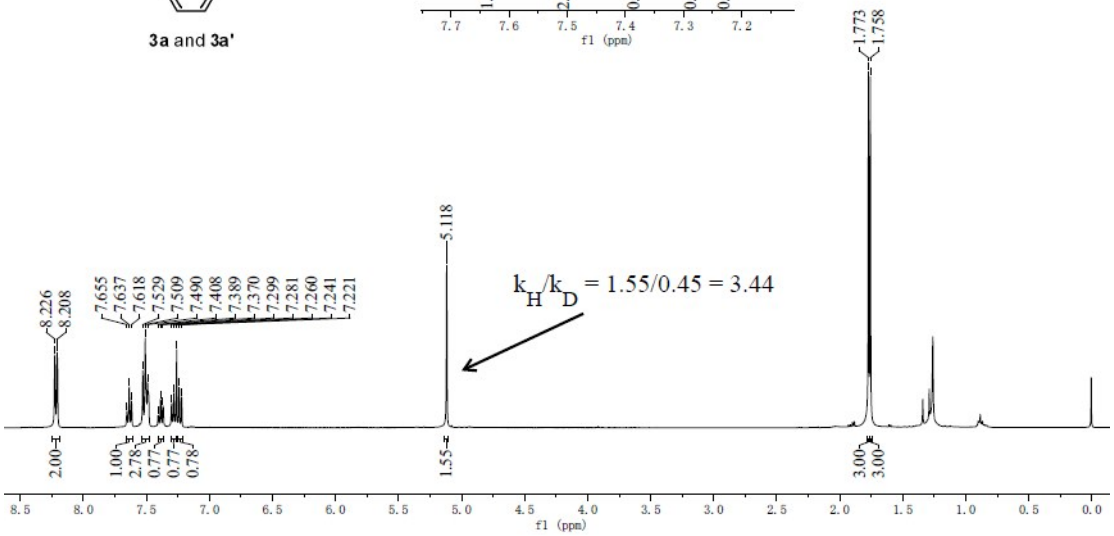
**1a'**


1.900
1.894
7.260
3.00
3.00
f1 (ppm)



**3a** and **3a'**


7.655
7.637
7.618
7.529
7.509
7.490
7.408
7.389
7.370
7.299
7.281
7.260
7.241
7.221
$k_H/k_D$ = 1.55/0.45 = 3.44
f1 (ppm)


8.226
8.208
7.655
7.637
7.618
7.529
7.509
7.490
7.408
7.389
7.370
7.299
7.281
7.260
7.241
7.221
5.118
1.773
1.758
$k_H/k_D$ = 1.55/0.45 = 3.44
2.00
1.00
2.78
0.77
0.77
0.78
1.55
3.00
3.00
f1 (ppm)