Supporting Information

TBN-promoted regioselective C-C bond cleavage: a new strategy for the synthesis of unsymmetrically substituted *N*-aryl oxalamides

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Contents

1. General remarks

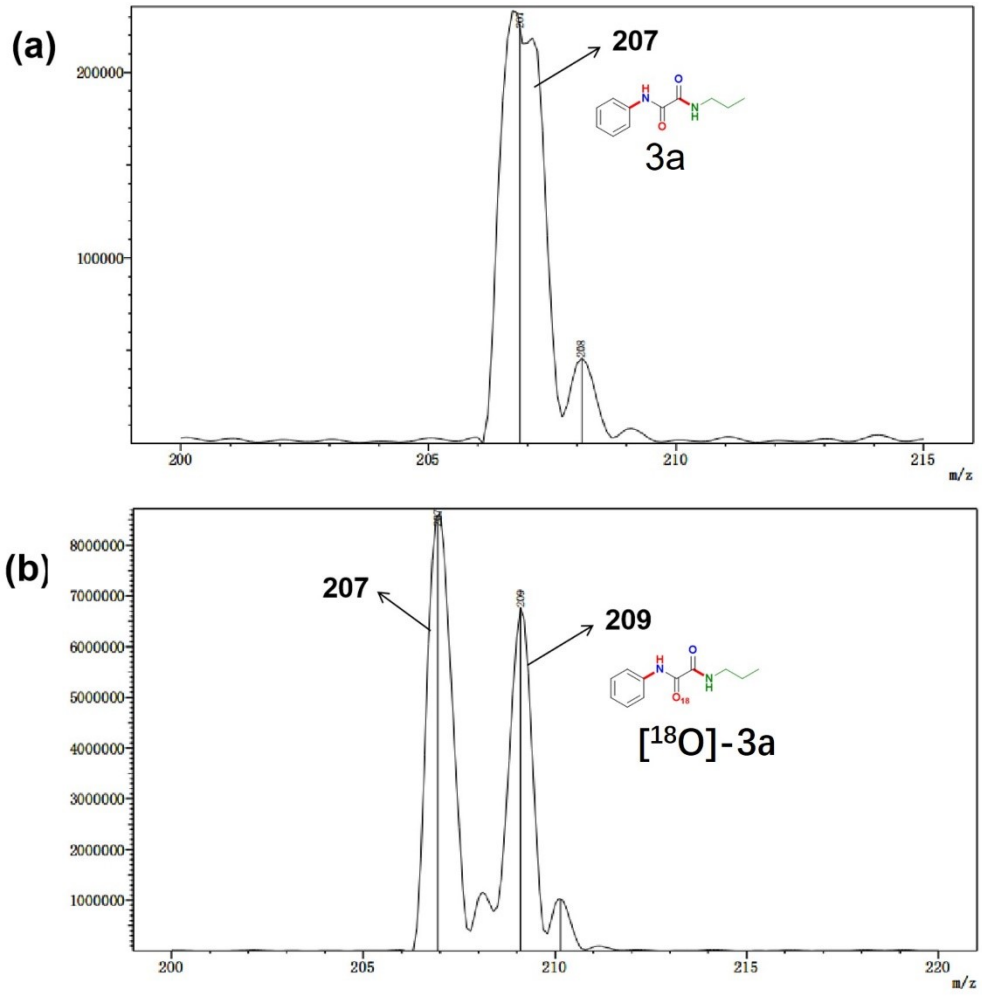
All non-aqueous reactions and manipulations were performed in oxygen atmosphere. The reactions were monitored by GC and LC-MS. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brucker ADVANCE III spectrometer at 400 MHz and 100 MHz, respectively, and chemical shifts were reported in parts per million (ppm). Flash column chromatography was performed using silica gel 300-400 μm. LC-MS results were recorded on LC-MS JINDAO804, and GC analysis was performed on GC 7820A. Hydrazines were purchased from Energy Chemical, Alfa Aesar, Aladdin or Maya Reagent; amines were purchased from Aladdin, dried by standard methods before using.

2. General experimental procedure for the synthesis of amides

A 25 ml Schlenk-type tube equipped with a magnetic stir bar was charged with substrate 1 (**1a-1p**) (0.2 mmol), TBN (0.44 mmol), $CuCl_2$ (0.04 mmol). The reaction tube was evacuated and back-filled with N_2. Amine 2 (**2a-2q**) (0.26 mmol) and C_2H_5OH (2 mL, H_2O 0.2 mmol) were added at room temperature under N_2 atmosphere, then the reaction mixture was stirred at 120 ºC for 12 h. The reaction was monitored by GC or LC-MS. After completion of the reaction, the resulting solution was cooled to room temperature, and neutralized with saturated solution of NaCl. The product was extracted with EtOAc, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel to give analytically pure product.

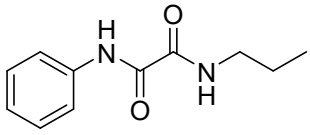
3. Control experiment with H_2O^{18}, LC-MS spectrum (+)

To obtain the source of oxygen atoms, since the reaction did not proceed under oxygen conditions, we added H_2O^{18} to reaction system under otherwise identical conditions (all raw materials and solvents were treated via standard anhydrous procedures), the ^{18}O labelled product **[^{18}O]-3**a was generated in 75% yield, as determined by LC-MS. MS (207) is the molecular weight of **3a** with H_2O reaction system **(a)**, MS (209) is the molecular weight of **3a** with H_2O^{18} reaction system **(b)**. The results showed that even 2 equivalent H_2O^{18} was added to reaction system, only one O^{18} was detected in the product of **3a**, because all systems are absolutely waterless, so the other oxygen comes from TBN.



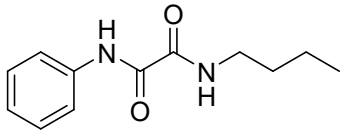
4. ^{1}H NMR and ^{13}C NMR data of products

N^1-phenyl-N^2-propyloxalamide (3a)[1]



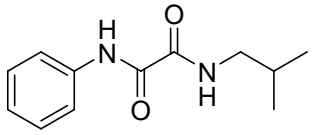
Following the general procedure (EtOAc/Petroleum ether 1:15), **3a** was obtained as a white solid, isolated yield: 78%, m.p. 113-115 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.20 (s, 1H), 8.74 (s, 1H), 7.95 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.0 Hz, 2H), 3.34 (q, *J* = 7.2 Hz, 2H), 1.69-1.60 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 154.3, 133.2, 132.6, 128.9, 127.8, 41.8, 23.0, 11.6. LC-MS: m/z = 207.

N^1-butyl-N^2-phenyloxalamide (3b)[1]



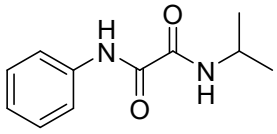
Following the general procedure (EtOAc/Petroleum ether 1:15), **3b** was obtained as a white solid, isolated yield: 75%, m.p. 102-105 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (s, 1H), 8.66 (s, 1H), 7.91 (d, *J* = 7.2 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 3.40 (q, *J* = 7.2 Hz, 2H), 1.62-1.57 (m, 2H), 1.47-1.38 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 153.9, 133.2, 132.6, 129.1, 127.7, 39.8, 31.8, 20.2, 13.9. LC-MS: m/z = 221.

N^1-isobutyl-N^2-phenyloxalamide (3c)[4]



Following the general procedure (EtOAc/Petroleum ether 1:15), **3c** was obtained as a white solid, isolated yield: 70%, m.p. 115-117 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.77 (s, 1H), 8.88 (s, 1H), 8.02 (d, *J* = 6.8 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 3.20 (t, *J* = 6.4 Hz, 2H), 1.93-1.87 (m, 1H), 0.99 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 154.8, 133.1, 132.6, 128.8, 128.0, 47.5, 28.7, 20.3. LC-MS: m/z = 221.

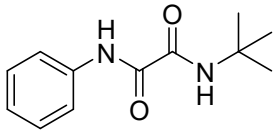
N^1-isopropyl-N^2-phenyloxalamide (3d)[1]



Following the general procedure (EtOAc/Petroleum ether 1:15), **3d** was obtained as a white solid, isolated yield: 73%, m.p. 107-109 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.76 (s, 1H), 8.68 (s, 1H), 8.01 (d, *J* =6.8 Hz, 2H), 7.58 (t, *J* =7.4 Hz, 1H), 7.48 (t, *J* =7.6 Hz, 2H), 4.15-4.02 (m,

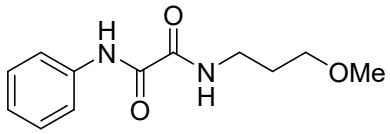
1H), 1.27 (d, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 153.9, 133.1, 132.7, 128.8, 128.0, 42.3, 22.8. LC-MS: m/z = 206.

N^1-(tert-butyl)-N^2-phenyloxalamide (3e)[1]



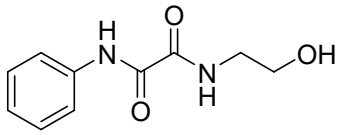
Following the general procedure (EtOAc/Petroleum ether 1:15), **3e** was obtained as a white solid, isolated yield: 76%, m.p. 112-115 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.64 (s, 1H), 8.83 (s, 1H), 8.01 (d, J = 6.8 Hz, 2H), 7.60 (t, J = 8.0 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 153.2, 133.0, 132.8, 128.8, 128.0, 51.1, 29.0. LC-MS: m/z = 221.

N^1-(3-methoxypropyl)-N^2-phenyloxalamide (3f)[1]



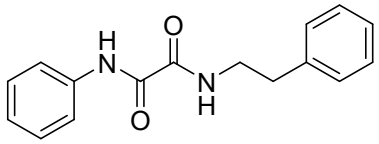
Following the general procedure (EtOAc/Petroleum ether 1:15), **3f** was obtained as a white solid, isolated yield: 73%, m.p. 102-105 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.49 (s, 1H), 8.89 (s, 1H), 7.98 (d, J = 6.8 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H), 3.51-3.45 (m, 4H), 3.37 (s, 3H), 1.92-1.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 155.1, 133.0, 132.5, 128.6, 128.2, 70.5, 58.8, 37.4, 29.5. LC-MS: m/z = 237.

N^1-(2-hydroxyethyl)-N^2-phenyloxalamide (3g)[1]



Following the general procedure (EtOAc/Petroleum ether 1:15), **3g** was obtained as a white solid, isolated yield: 70%, m.p. 106-109 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.24 (s, 1H), 9.02 (s, 1H), 7.92 (d, J = 7.2 Hz, 2H), 7.60 (t, J = 8.2 Hz ,1H), 7.50 (t, J = 7.8 Hz, 2H), 3.82 (t, J = 5.0 Hz, 2H), 3.57 (q, J = 5.6 Hz, 2H), 2.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 155.4, 133.4, 132.4, 129.0, 127.8, 62.5, 42.9. LC-MS: m/z = 209.

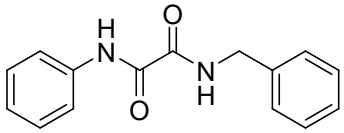
N^1-phenethyl-N^2-phenyloxalamide (3h)[1]



Following the general procedure (EtOAc/Petroleum ether 1:15), **3h** was obtained as a white solid, isolated yield: 72%, m.p. 249-251 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.63

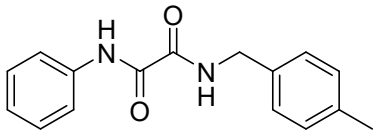
(s, 1H), 8.85 (s, 1H), 7.98 (d, *J* = 6.8 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.23 (d, *J* = 5.6 Hz, 3H), 3.62 (q, *J* = 6.8 Hz, 2H), 2.92 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 154.8, 138.9, 133.1, 132.5, 128.9, 128.8, 128.7, 128.1, 126.7, 41.6, 36.1. LC-MS: m/z = 269.

N^1-benzyl-N^2-phenyloxalamide (3i)[2]



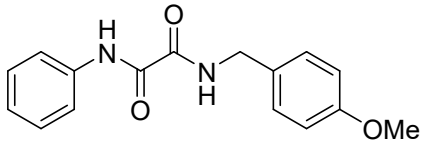
Following the general procedure (EtOAc/Petroleum ether 1:15), **3i** was obtained as a white solid, isolated yield: 78%, m.p. 237-238 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.16 (s, 1H), 9.10 (s, 1H), 7.93 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.36-7.28 (m, 5H), 4.58 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 154.3, 138.2, 133.3, 132.5, 129.0, 128.9, 127.8, 127.7, 127.6, 44.0. LC-MS: m/z = 255.

N^1-(4-methylbenzyl)-N^2-phenyloxalamide (3j)[1]



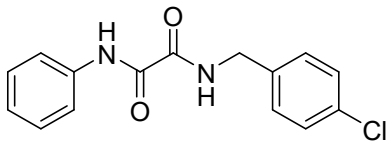
Following the general procedure (EtOAc/Petroleum ether 1:15), **3j** was obtained as a white solid, isolated yield: 76%, m.p. 244-247 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.52 (s, 1H), 9.11 (s, 1H), 7.96 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 10 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.53 (d, *J* = 6.0 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 154.5, 137.3, 135.2, 133.2, 132.5, 129.5, 128.9, 127.9, 127.7,43.7, 21.2. LC-MS: m/z = 269.

N^1-(4-methoxybenzyl)-N^2-phenyloxalamide (3k)[1]



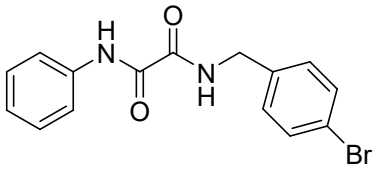
Following the general procedure (EtOAc/Petroleum ether 1:15), **3k** was obtained as a white solid, isolated yield: 78%, m.p. 251-253 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 (s, 1H), 9.01 (s, 1H), 7.92 (d, *J* = 7.2 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 4.50 (d, *J* = 5.6 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 159.1, 154.0, 133.1, 132.4, 130.2, 129.0, 128.9, 127.6, 114.1, 55.3, 43.3. LC-MS: m/z = 285.

***N*^{1}-(4-chlorobenzyl)-*N*^{2}-phenyloxalamide (3l)**[5]



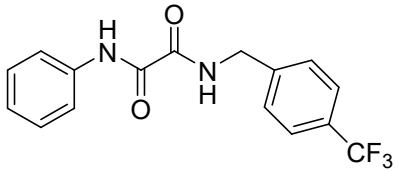
Following the general procedure (EtOAc/Petroleum ether 1:15), **3l** was obtained as a white solid, isolated yield: 77%, m.p. 240-242 ℃. ^{1}H NMR(400 MHz, $CDCl_3$): δ 9.09 (s, 1H), 9.02 (s, 1H), 7.91 (d, *J* = 7.2 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.32-7.28 (m, 4H), 4.54 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 154.2, 136.8, 133.4, 132.4, 129.4, 129.1, 129.0, 127.7, 127.1, 43.4. LC-MS: m/z = 289.

***N*^{1}-(4-bromobenzyl)-*N*^{2}-phenyloxalamide (3m)**[5]



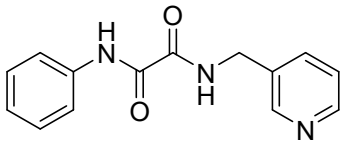
Following the general procedure (EtOAc/Petroleum ether 1:15), **3m** was obtained as a white solid, isolated yield: 79%, m.p. 235-238 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.81 (s, 1H), 9.13 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.0 Hz, 1H), 7.53 (q, *J* = 8.0 Hz, 4H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.43 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ168.7, 154.2, 139.4, 133.2, 133.0, 131.7, 130.0, 129.0, 128.6, 120.4, 42.6. LC-MS: m/z = 333.

***N*^{1}-phenyl-*N*^{2}-(4-(trifluoromethyl)benzyl)oxalamide (3n)**[5]



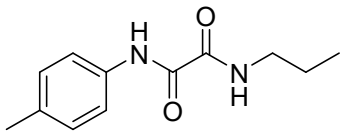
Following the general procedure (EtOAc/Petroleum ether 1:15), **3y** was obtained as a white solid, isolated yield: 72%, m.p. 223-226 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.85 (s, 1H), 9.22 (t, *J* = 6.2 Hz, 1H), 7.99 (d, *J* = 7.2 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 6.8 Hz, 1H), 7.56-7.49 (m, 4H), 4.55 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.7, 154.3, 144.9, 133.3 (d, $J_{c\text{-}f}$ = 29.0 Hz), 129.0, 128.6, 128.3, 128.1 (q, $J_{c\text{-}f}$ = 32.0 Hz), 126.2 (d, $J_{c\text{-}f}$ = 270.0 Hz), 125.7 ((q, $J_{c\text{-}f}$ = 4.0 Hz), 42.8;. LC-MS: m/z = 323.

***N*^{1}-phenyl-*N*^{2}-(pyridin-3-ylmethyl)oxalamide (3o)**[5]



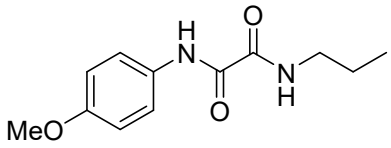
Following the general procedure (EtOAc/Petroleum ether 1:10), **3o** was obtained as a white solid, isolated yield: 84%, m.p. 212-215 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.84 (s, 1H), 9.27 (s, 1H), 8.63 (d, *J* = 32.8 Hz, 2H), 7.97 (d, *J* = 7.2 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H),7.45 (t, *J* = 7.8 Hz, 2H), 7.27 (t, *J* = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 154.9, 149.3, 149.1, 135.4, 134.0, 133.4, 132.4, 128.9, 128.0, 123.8, 41.5. LC-MS: m/z = 256.

N^1-propyl-N^2-(p-tolyl)oxalamide (3p)[1]



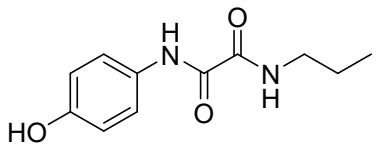
Following the general procedure (EtOAc/Petroleum ether 1:10), **3p** was obtained as a white solid, isolated yield: 81%, m.p. 127-129 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.46 (s, 1H), 8.80 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 3.36 (q, *J* = 6.8 Hz, 2H), 2.42 (s, 3H), 1.69-1.59 (m, 2H), 1.01 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 154.6, 143.9, 129.8, 129.6, 128.0, 41.8, 23.0, 21.7, 11.6. LC-MS: m/z = 221.

N^1-(4-methoxyphenyl)-N^2-propyloxalamide (3q)[1]



Following the general procedure (EtOAc/Petroleum ether 1:15), **3q** was obtained as a white solid, isolated yield: 75%, m.p. 121-124 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.17 (s, 1H), 8.79 (s, 1H), 7.94 (d, *J* = 9.2 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H), 3.34 (q, *J* = 6.8 Hz 2H), 1.68-1.59 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 163.6, 154.6, 130.0, 124.8, 114.2, 55.7, 41.8, 23.0, 11.6. LC-MS: m/z = 237.

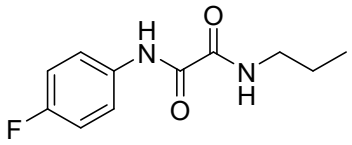
N^1-(4-hydroxyphenyl)-N^2-propyloxalamide (3r)[1]



Following the general procedure (EtOAc/Petroleum ether 1:15), **3r** was obtained as a faint yellow solid, isolated yield: 73%, m.p. 108-111 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.72 (s, 1H), 7.18 (s, 1H), 6.29 (d, *J* = 8.4 Hz, 2H), 5.32 (d, *J* = 8.4 Hz, 2H), 1.63 (q, *J* = 6.8 Hz,

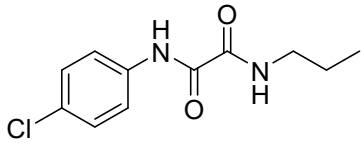
2H), 1.00 (s, 1H), -0.006--0.096 (m, 2H), -0.67 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ168.6, 162.3, 154.9, 131.1, 123.6, 116.1, 40.2, 23.1, 11.9. LC-MS: m/z = 223.

N^1-(4-fluorophenyl)-N^2-propyloxalamide (3s)[2]



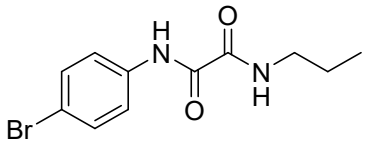
Following the general procedure (EtOAc/Petroleum ether 1:15), **3s** was obtained as a faint yellow solid, isolated yield: 70%, m.p. 113-115 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.98 (s, 1H), 8.76 (s, 1H), 7.92 (d, J = 9.2 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 3.34 (q, J = 7.2 Hz, 2H), 1.68-1.59 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 167.0 (d, $J_{c\text{-}f}$ = 253.0 Hz), 155.3, 131.0 (d, $J_{c\text{-}f}$ = 9.0 Hz), 128.8 (d, $J_{c\text{-}f}$ = 3.0 Hz), 115.9 (d, $J_{c\text{-}f}$ = 21.0 Hz), 41.7, 23.0, 11.6. LC-MS: m/z = 225.

N^1-(4-chlorophenyl)-N^2-propyloxalamide (3t)[2]



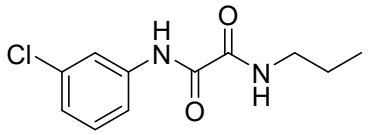
Following the general procedure (EtOAc/Petroleum ether 1:15), **3t** was obtained as a faint yellow solid, isolated yield: 73%, m.p. 117-119 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.08 (s, 1H), 8.80 (s, 1H), 7.99 (d, J = 8.8 Hz, 2H), 7.46 (d, J = 8.8 Hz, 2H), 3.35 (q, J = 7.2 Hz, 2H), 1.67-1.59 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 155.1, 139. 5, 131.0, 129.8, 129.0, 41.8, 23.0, 11.6. LC-MS: m/z = 241.

N^1-(4-bromophenyl)-N^2-propyloxalamide (3u)[2]



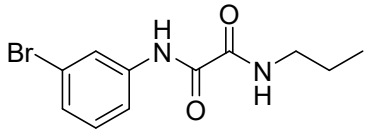
Following the general procedure (EtOAc/Petroleum ether 1:15), **3u** was obtained as a faint yellow solid, isolated yield: 70%, m.p. 113-115 ℃. ^{1}H NMR(400 MHz, $CDCl_3$): δ 9.18 (s, 1H), 8.67 (s, 1H), 7.83 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.8 Hz, 2H), 3.38 (q, J = 7.2 Hz, 2H), 1.68-1.60 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 154.3, 132.3, 131.5, 129.5, 128.3, 41.9, 23.0, 11.5. LC-MS: m/z = 286.

N^1-(3-chlorophenyl)-N^2-propyloxalamide (3v)[2]



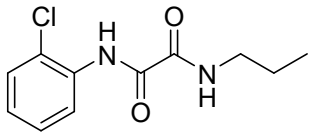
Following the general procedure (EtOAc/Petroleum ether 1:15), **3v** was obtained as a faint yellow solid, isolated yield: 72%, m.p. 109-112 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.12 (s, 1H), 8.77 (s, 1H), 8.11 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 3.39 (q, *J* = 5.6 Hz, 2H), 1.70-1.60 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 154.7, 135.1, 134.4, 133.1, 130.1, 128.4, 126.4, 41.8, 23.0, 11.5. LC-MS: m/z = 241.

N^1-(3-bromophenyl)-N^2-propyloxalamide (3w)[2]



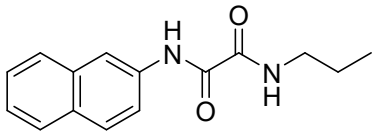
Following the general procedure (EtOAc/Petroleum ether 1:15), **3w** was obtained as a faint yellow solid, isolated yield: 78%, m.p. 116-119 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ ^{1}H NMR (400 MHz, Chloroform-*d*): δ 10.02 (s, 1H), 8.76 (s, 1H), 8.24 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 6.8 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 3.40 (q, *J* = 6.8 Hz, 2H), 1.70-1.60 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 154.6, 136.0, 134.6, 131.2, 130.3, 126.8, 123.0, 41.8, 23.0, 11.6. LC-MS: m/z = 286.

N^1-(2-chlorophenyl)-N^2-propyloxalamide (3x)[2]



Following the general procedure (EtOAc/Petroleum ether 1:15), **3x** was obtained as a faint yellow solid, isolated yield: 70%, m.p. 103-106 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (s, 1H), 8.37 (s, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.38-7.36 (m, 2H), 7.31-7.27 (m, 1H), 3.20 (q, *J* = 7.2 Hz, 2H), 1.58-1.48 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.6, 153.5, 133.5, 132.6, 131.3, 130.8, 130.0, 127.2, 41.8, 22.9, 11.5. LC-MS: m/z = 241.

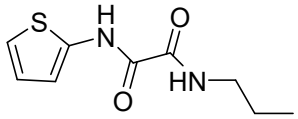
N^1-(naphthalen-2-yl)-N^2-propyloxalamide (3z)



Following the general procedure (EtOAc/Petroleum ether 1:15), **3z** was obtained as a white solid, isolated yield: 77%, m.p. 128-131 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.53 (s, 1H), 8.83 (s, 1H), 8.55 (s, 1H), 8.00-7.90 (m, 4H), 7.64-7.55 (m, 2H), 3.39 (q, *J* = 6.8 Hz, 2H), 1.71-

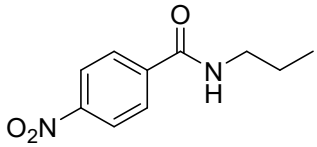
1.62 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 154.5, 135.6, 132.7, 129.8, 129.5, 129.1, 128.9, 128.7, 128.0, 127.2, 123.8, 41.9, 23.0, 11.6. LC-MS: m/z = 257. HRMS (EI): calcd for $C_{15}H_{16}N_2O_2$: 256.1212; found: 256.1219.

N^1-propyl-N^2-(thiophen-2-yl)oxalamide (3z1)[2]



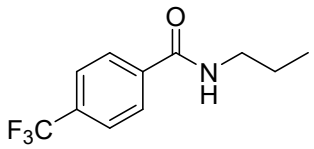
Following the general procedure (EtOAc/Petroleum ether 1:15), **3z1** was obtained as a white solid, isolated yield: 81%, m.p. 121-123 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.82 (s, 1H), 8.81 (s, 1H), 8.23 (d, J = 4.0 Hz, 1H), 7.65 (d, J = 6.0 Hz, 1H), 7.13 (t, J = 4.4 Hz, 1H), 3.37 (q, J = 6.8 Hz, 2H), 1.69-1.60 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2, 155.3, 137.9, 133.3, 131.1, 128.2, 41.7, 22.9, 11.6. LC-MS: m/z = 213.

4-nitro-*N*-propylbenzamide (4a)[3]



Following the general procedure (EtOAc/Petroleum ether 1:15), **4a** was obtained as a faint yellow solid, isolated yield: 66%, m.p. 80-83 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 8.8 Hz, 2H), 7.95 (d, J = 8.8 Hz, 2H), 6.51 (s, 1H), 3.45 (q, J = 8.0 Hz, 2H), 1.71-1.62 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 149.6, 140.6, 128.2, 123.9, 42.2, 22.9, 11.5. LC-MS: m/z = 209.

***N*-propyl-4-(trifluoromethyl)benzamide (4b)**[3]



Following the general procedure (EtOAc/Petroleum ether 1:15), **4b** was obtained as a white solid, isolated yield: 79%, m.p. 84-86 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 6.29 (s, 1H), 3.45 (q, J = 6.0 Hz, 2H), 1.70-1.61 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 138.3, 133.4 (d, $J_{c\text{-}f}$ = 32.0 Hz), 127.5, 125.8 (d, $J_{c\text{-}f}$ = 4.0 Hz), 125.2 (d, $J_{c\text{-}f}$ = 271.0 Hz), 42.1, 23.0, 11.6. LC-MS: m/z = 232.

5. References

(1) A. Jayaram, V. T. Seenivasan, K. Govindan, Y. M. Liu, N. Q. Chen, and T. W.

Yeh, Base-promoted triple cleavage of CCl_2Br: a direct one-pot synthesis of unsymmetrical oxalamide derivatives. *Chem. Commun.* 2024, **60**, 3079-3082.

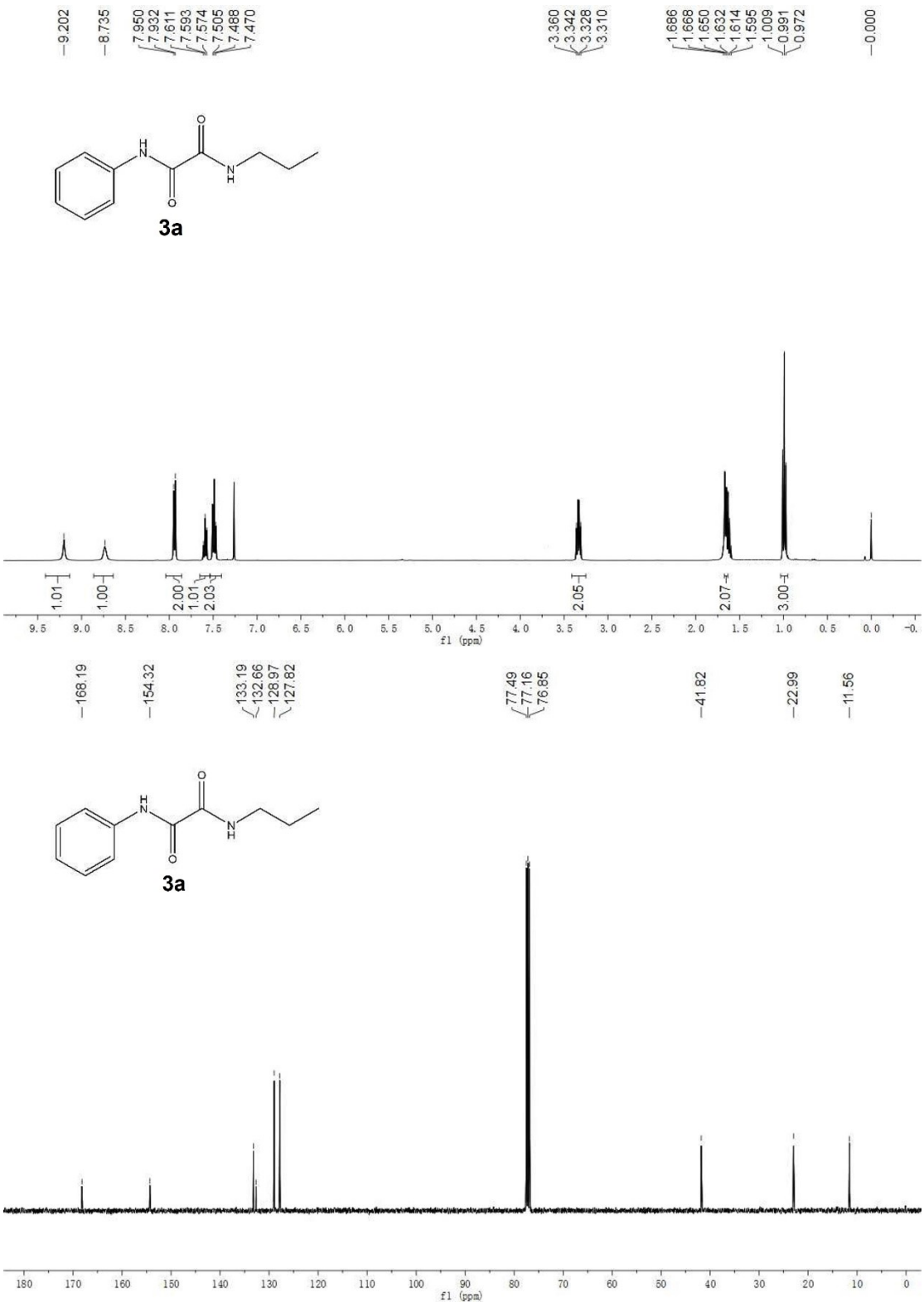
(2) D. Ghosh, R. Nandi, S**.** Khamarui, D. K. Maiti, Selective amidation by a photocatalyzed umpolung reaction. *Chem. Commun.* 2019, **55** , 3883-3886.

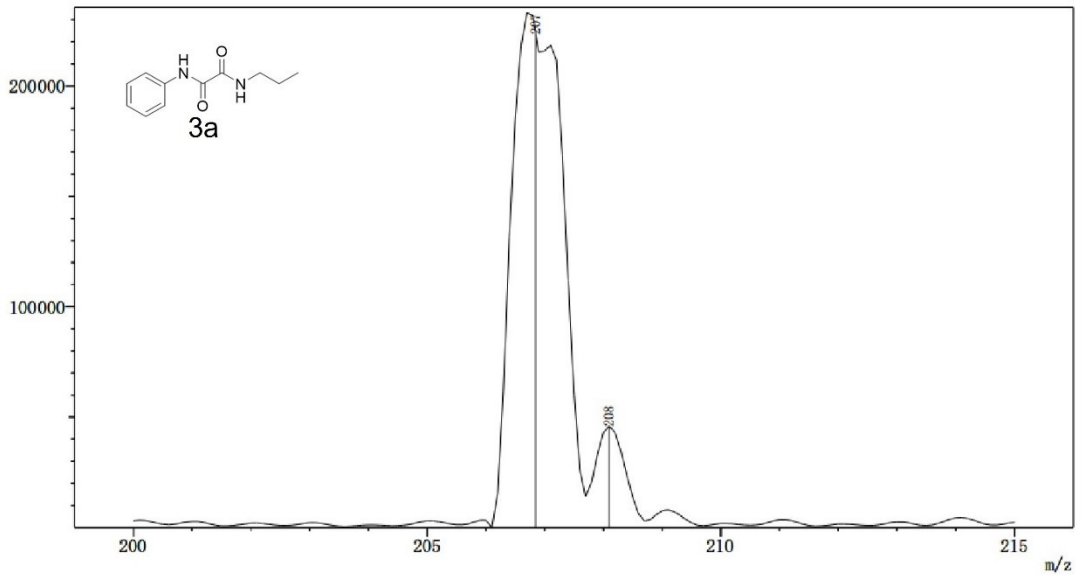
(3) S. Yang, H. Tian, L. Li, Y. Wang, C. Xie, X. Chen, $PhI(OAc)_2$-mediated C–N bond cleavage of acylhydrazines with amines for the synthesis of amides, *New J. Chem*., 2023, **47**, 3663-3667.

(4) X. Zhuang, L. Ling, Y. Wang, B. Li, and B. Sun, Photoinduced cascade C–N/C═O bond formation from bromodifluoroalkyl reagents, amines, and H_2O via a triple-cleavage process, *Org. Lett.*, 2022, **24**, 1668-1672.

(5) X. Y. Zhang, L. P. Cheng, Z. J. Zhong, W. Pang, X. Song, Design, synthesis and biological evaluation of oxalamide derivatives as potent neuraminidase inhibitors, *New J. Chem*., 2022, **46**, 13533-13539.

6. Copies of ^{1}H NMR and ^{13}C NMR spectrum

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100000
207
208
200
205
210
215
m/z


8.819
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7.910
7.892
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7.599
7.581
7.515
7.495
7.477
3.427
3.379
3.365
3.347
1.621
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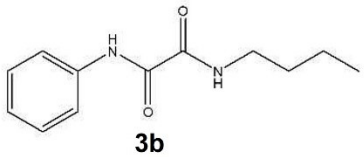
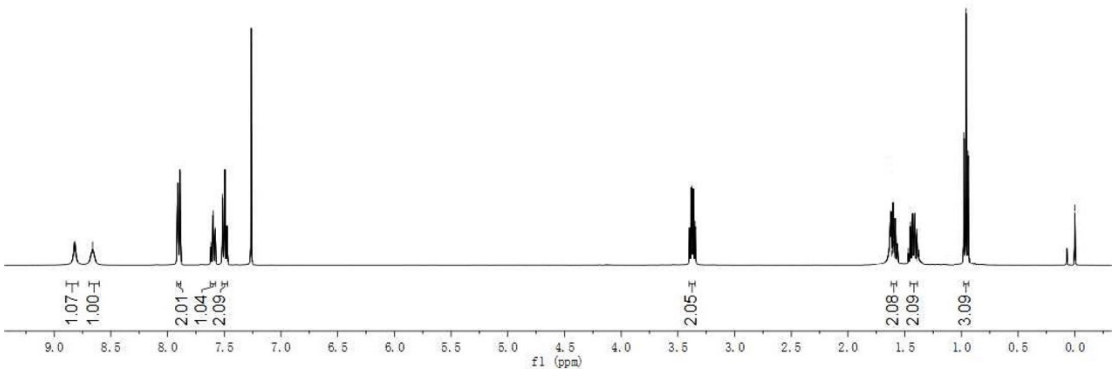


3b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2.05
2.08
2.09
3.09
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


168.04
153.97
133.24
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129.05
127.67
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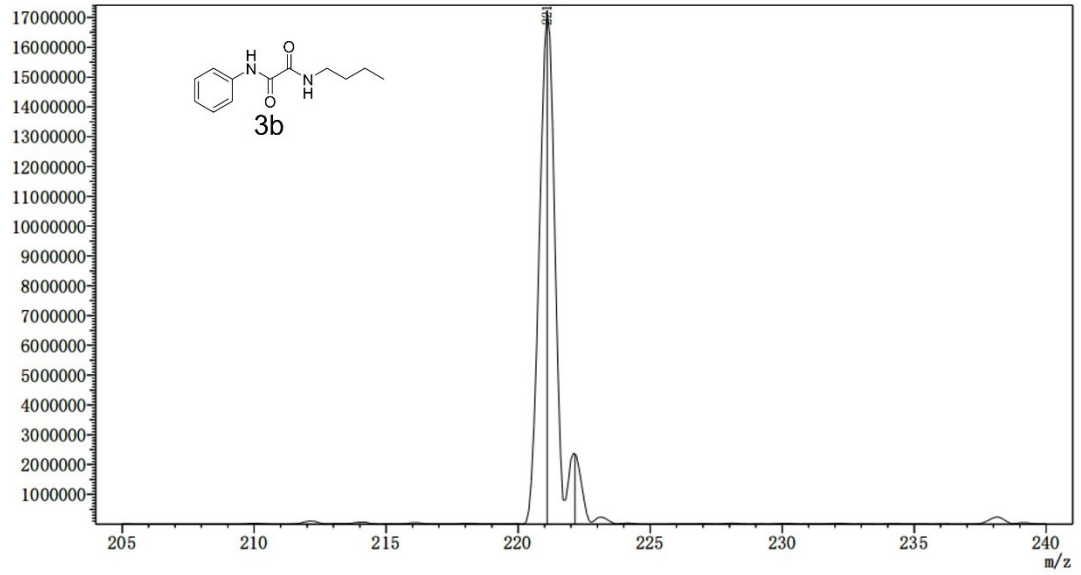
39.82
31.77
20.25
13.89
3b
f1 (ppm)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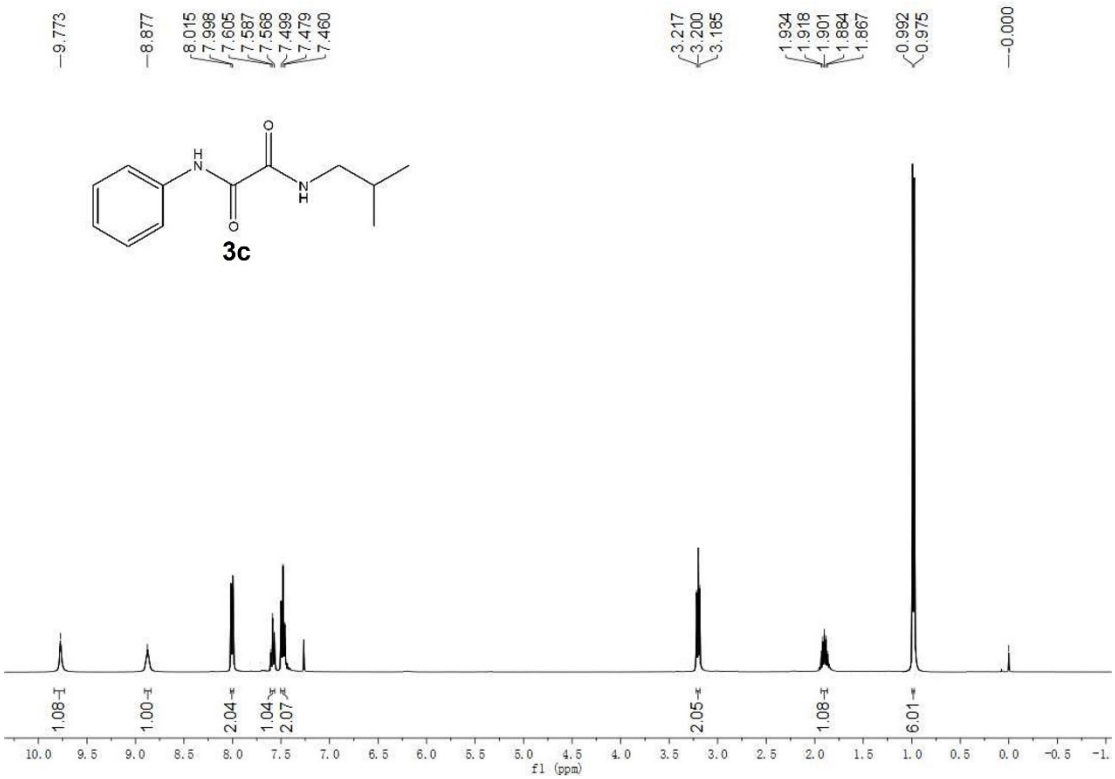
m/z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3.185
1.934
1.918
1.901
1.884
1.867
0.992
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1.00
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1.04
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2.05
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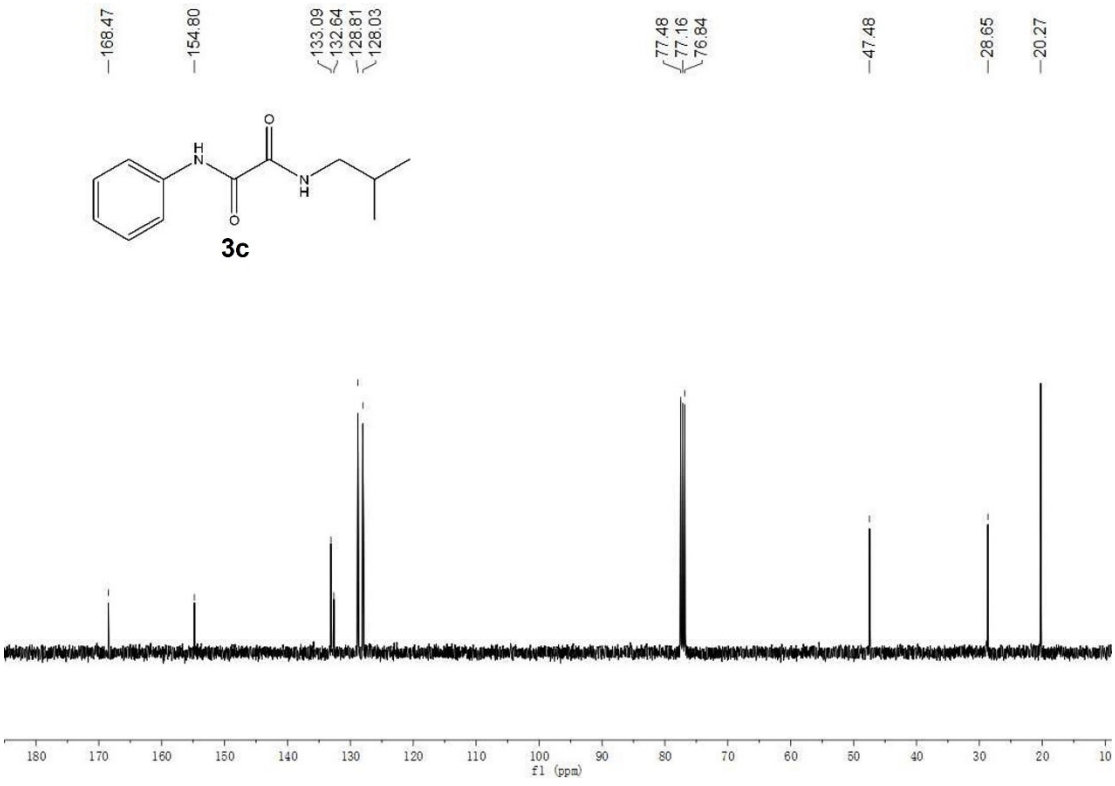
f1 (ppm)

3c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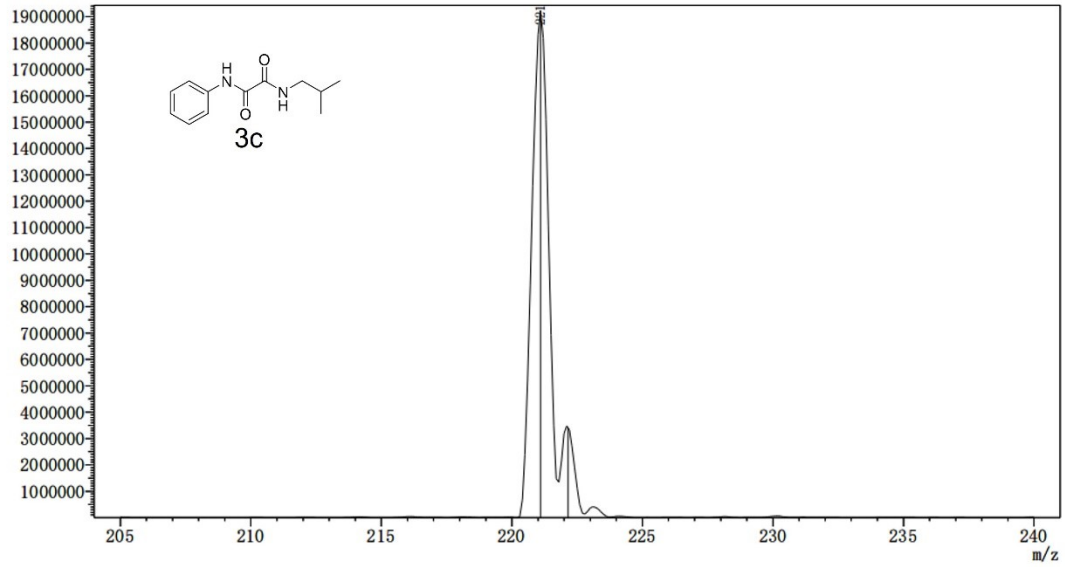
f1 (ppm)

3c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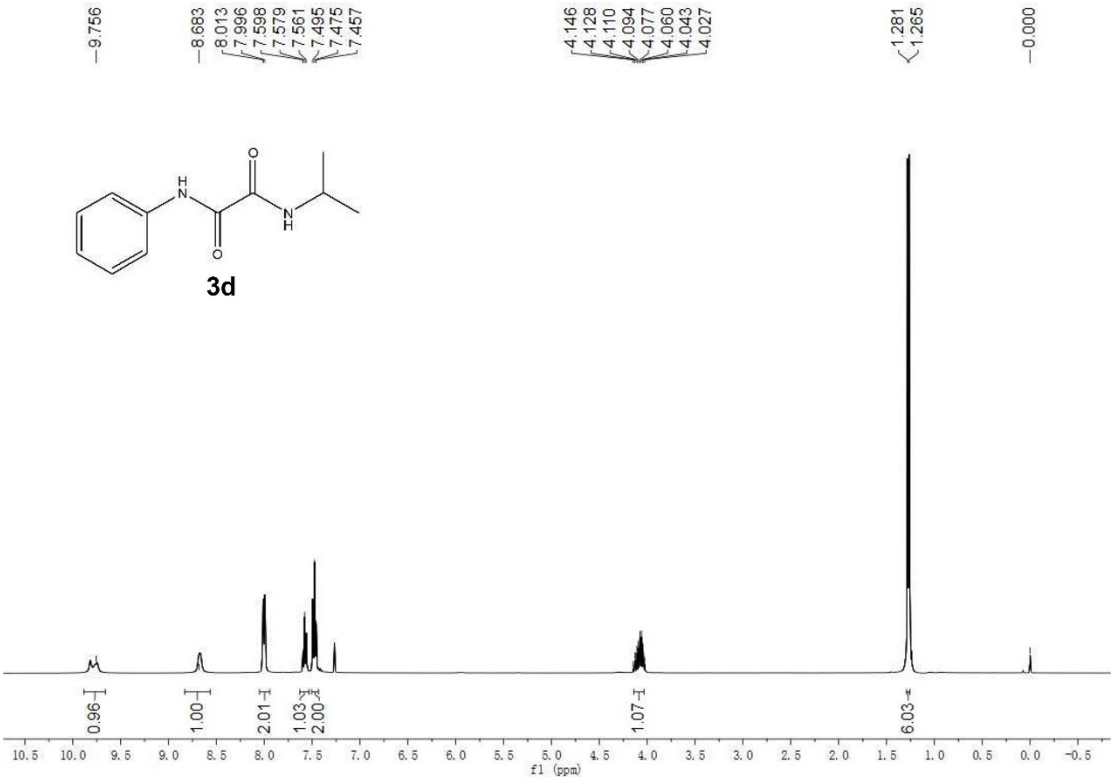
m/z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4.094
4.077
4.060
4.043
4.027
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3d
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1.00
2.01
1.03
2.00
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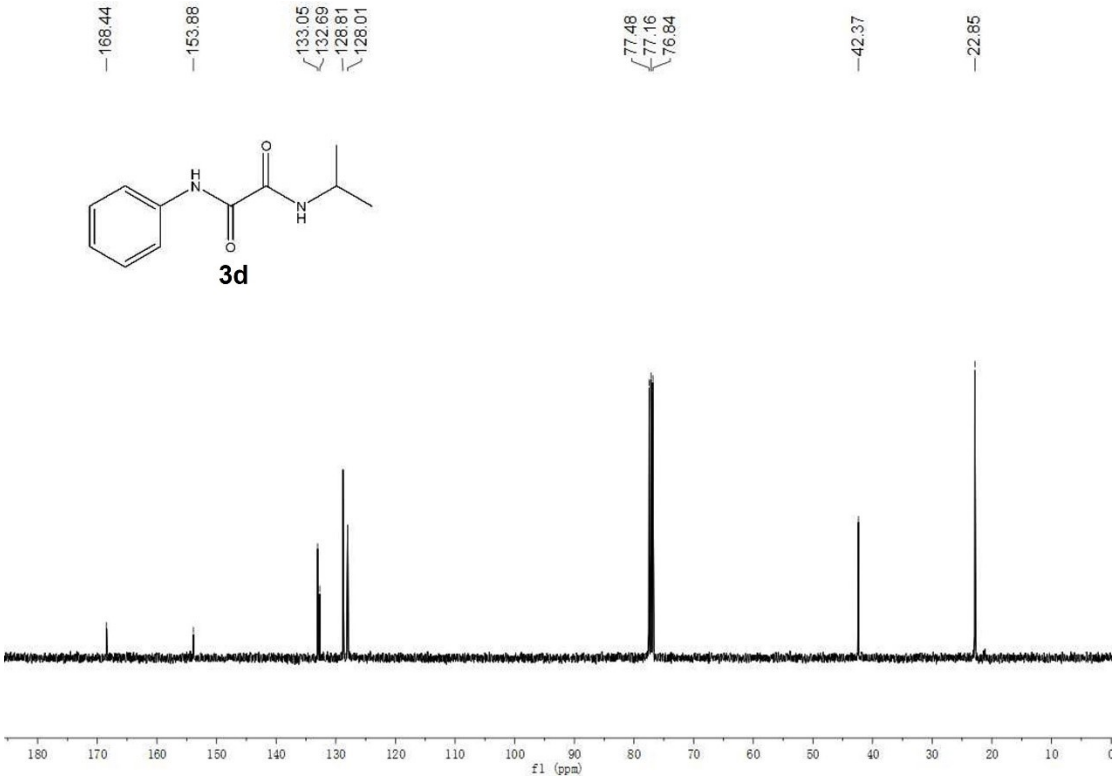
f1 (ppm)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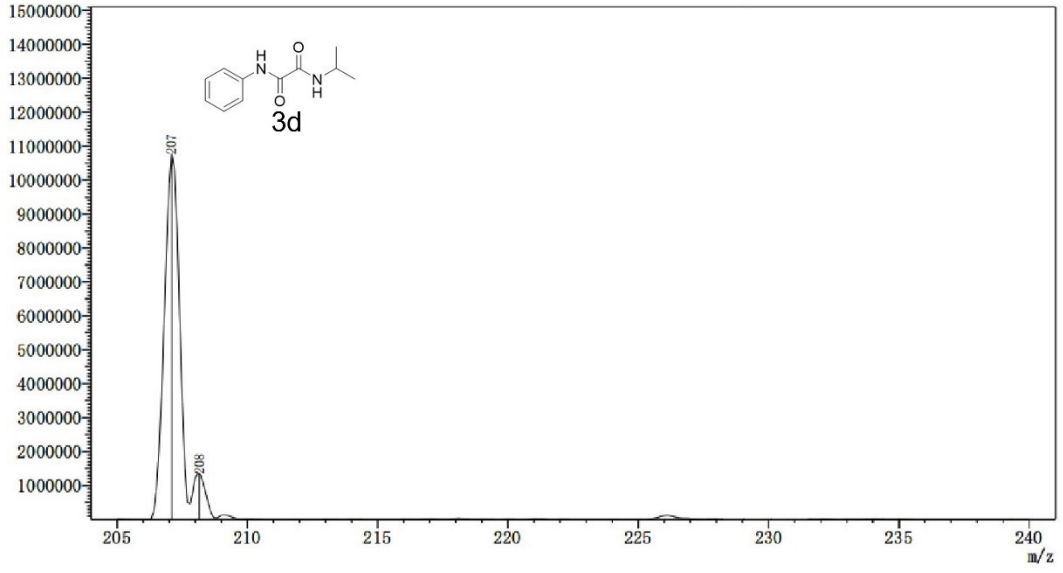
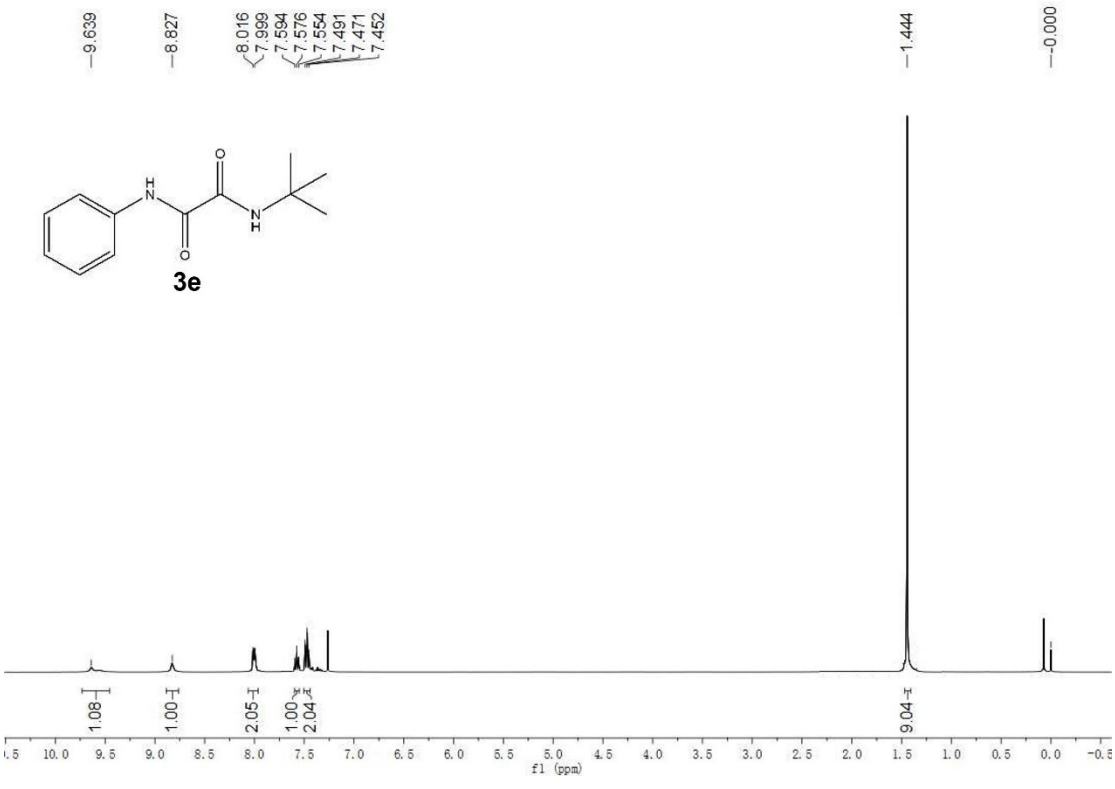
3d
f1 (ppm)


3d
207
208
m/z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2.05
1.00
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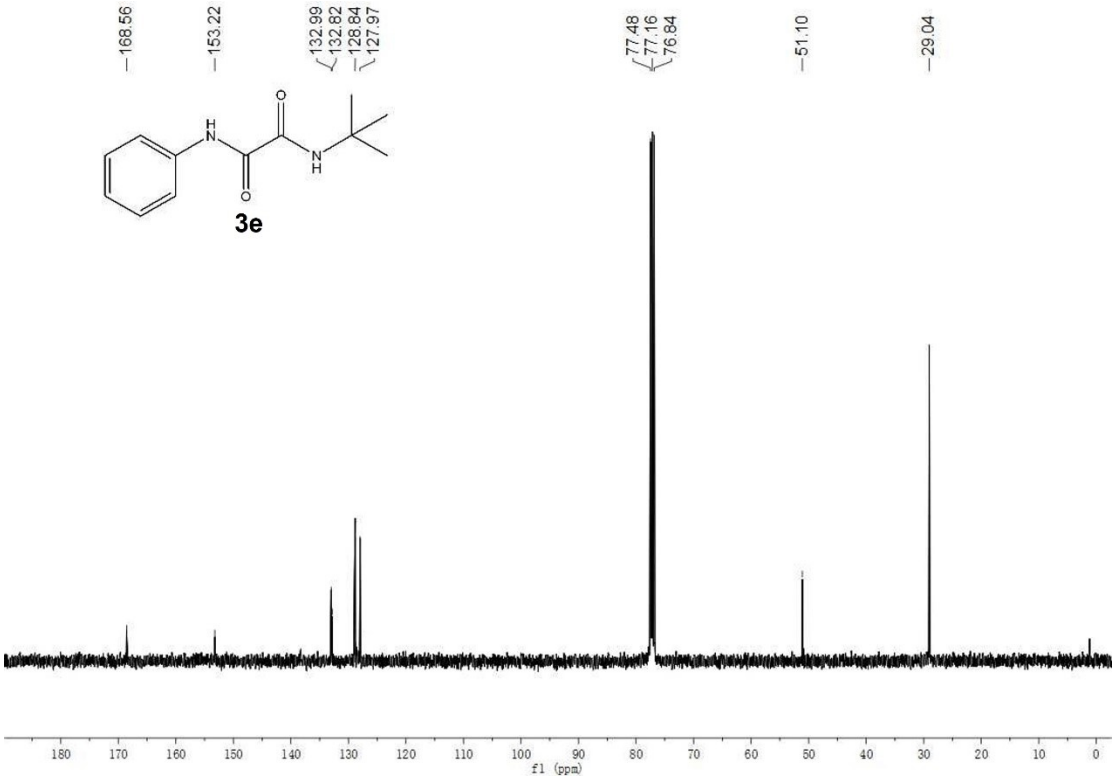
9.04
f1 (ppm)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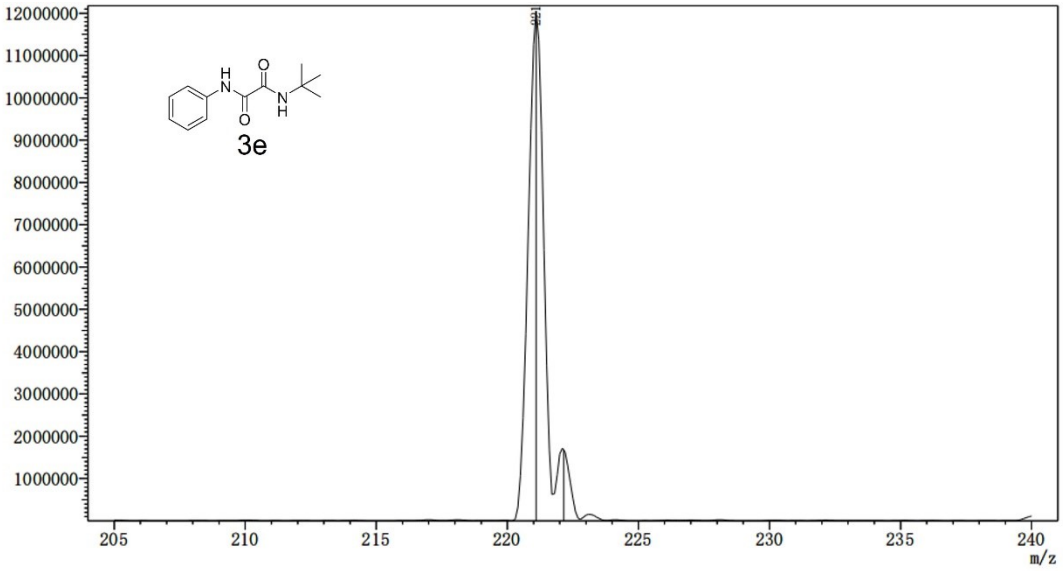
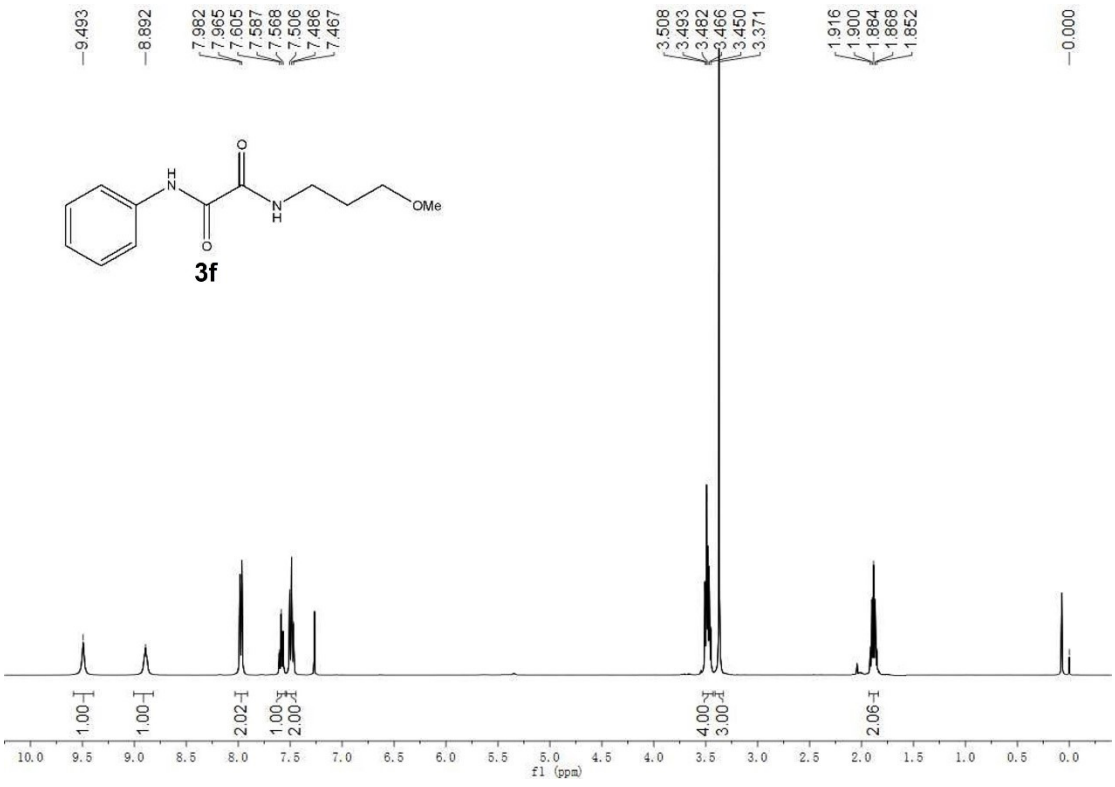
3e
f1 (ppm)


3e
m/z


3f
OMe
f1 (ppm)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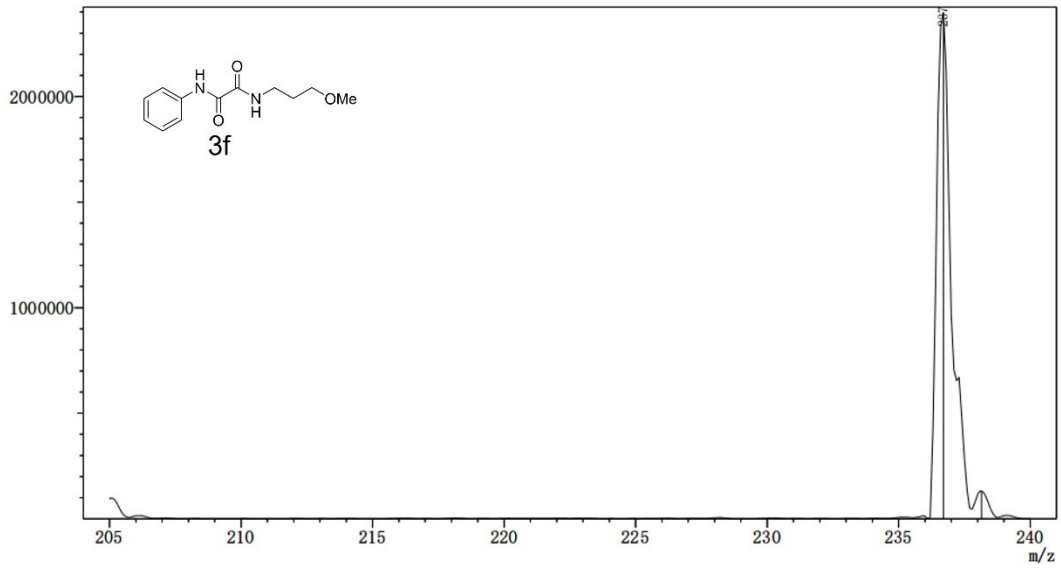
OMe
3f
f1 (ppm)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OMe
3f
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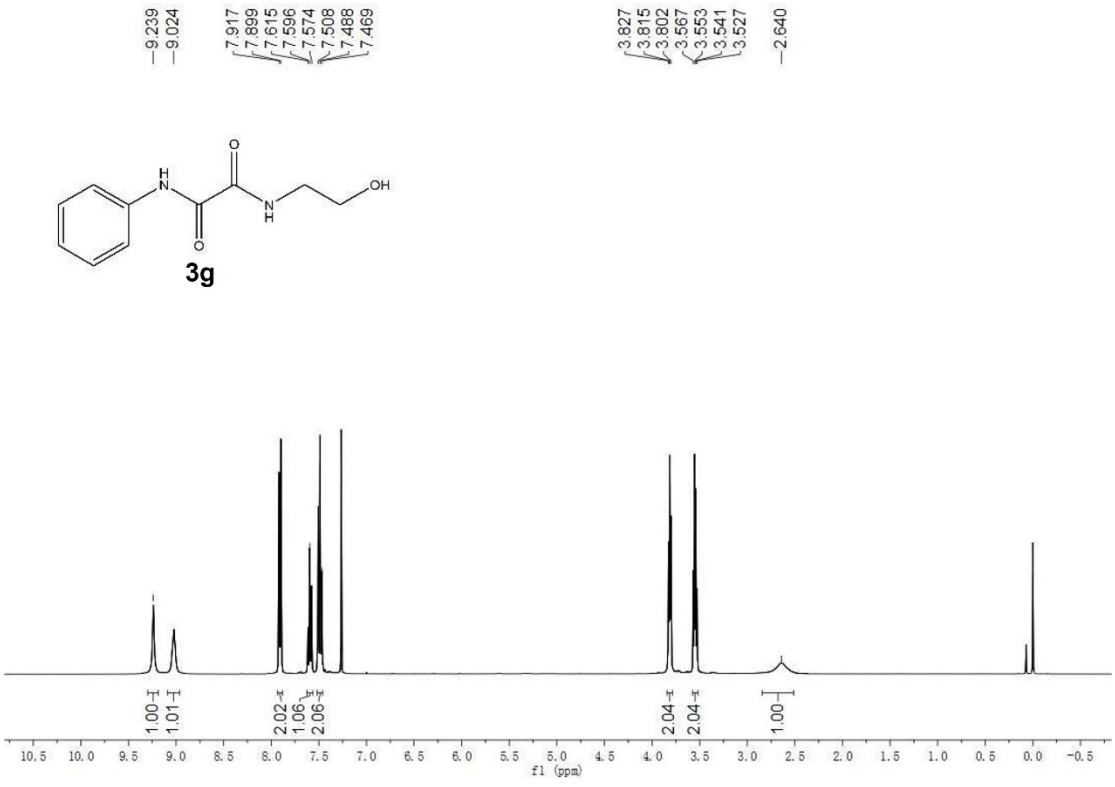
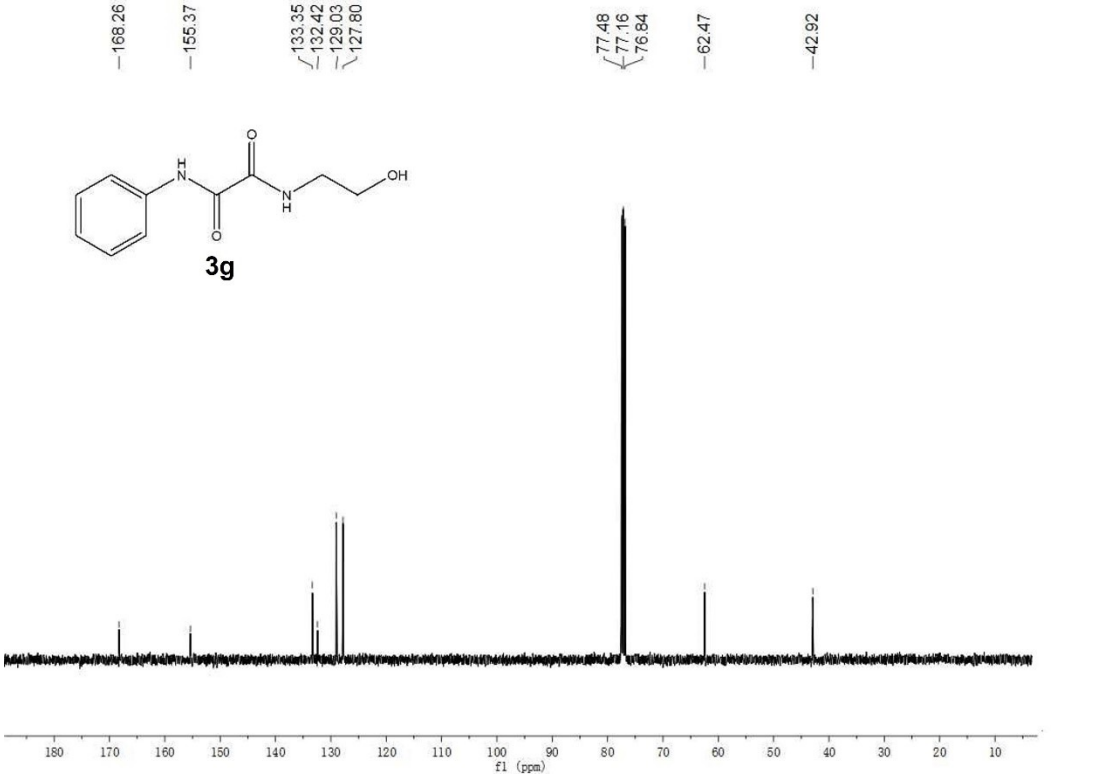
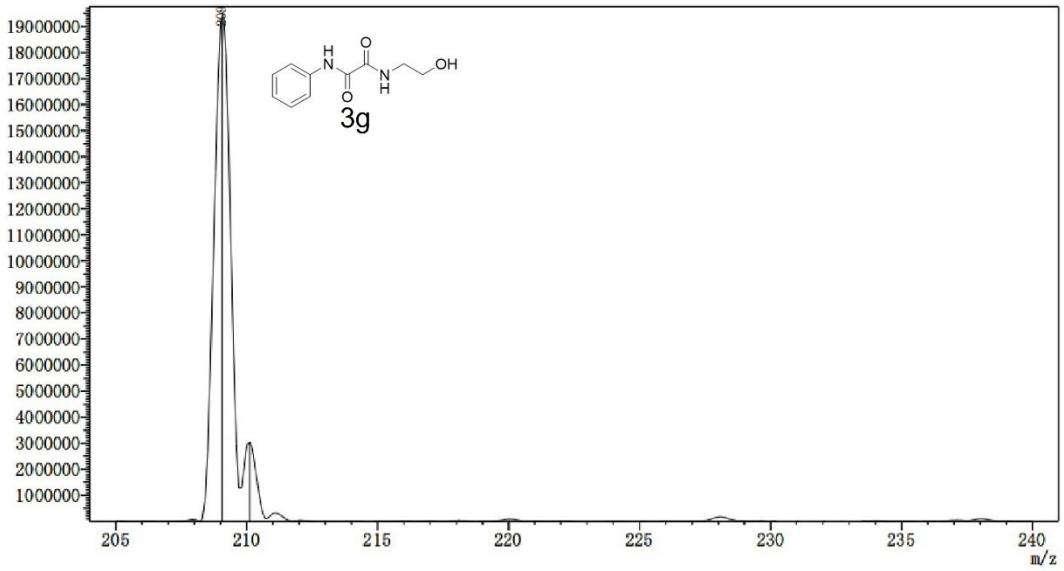
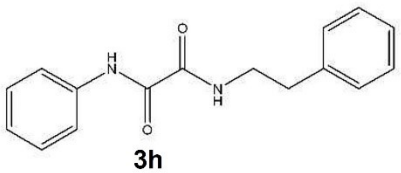
210
215
220
225
230
235
240
m/z


9.239
9.024
7.917
7.899
7.615
7.596
7.574
7.508
7.488
7.469
3.827
3.815
3.802
3.567
3.553
3.541
3.527
2.640
3g
1.00
1.01
2.02
1.06
2.06
2.04
2.04
1.00
f1 (ppm)

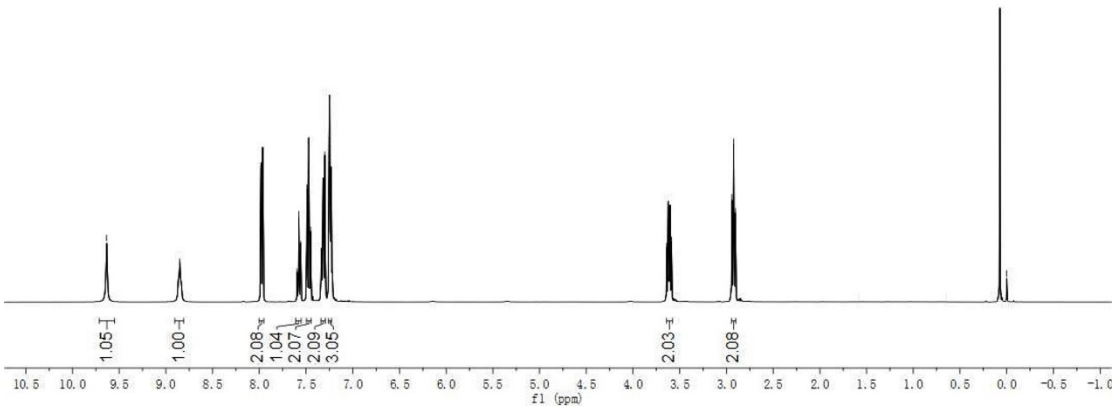

168.26
155.37
133.35
132.42
129.03
127.80
77.48
77.16
76.84
62.47
42.92
3g
f1 (ppm)

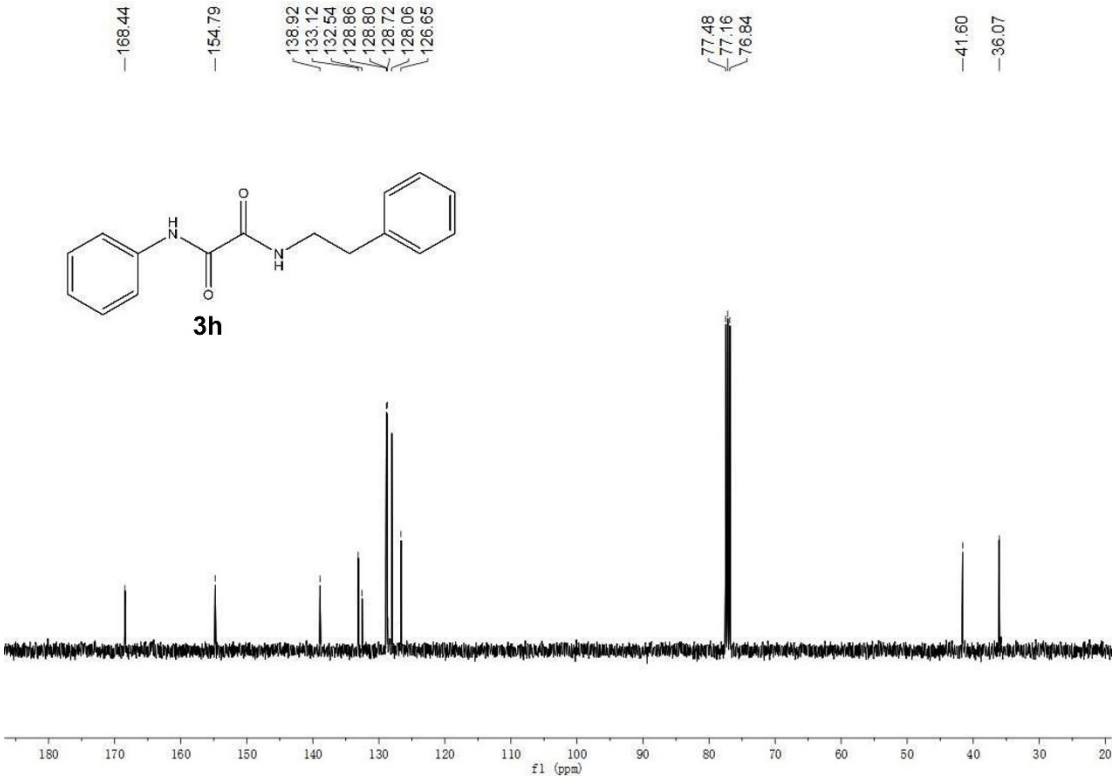

3g
m/z

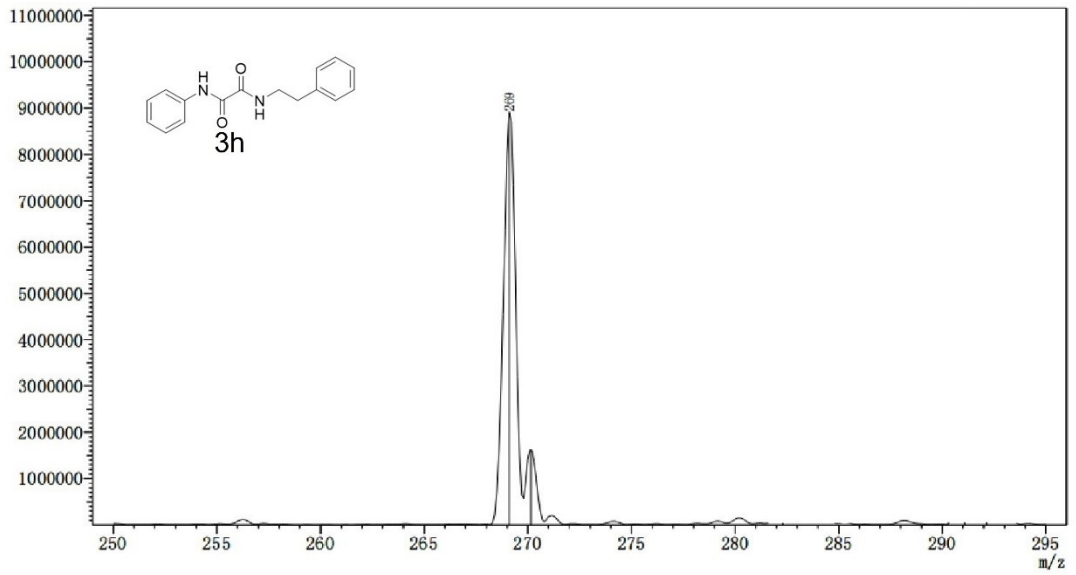

9.634
8.851
7.981
7.964
7.595
7.576
7.558
7.490
7.470
7.452
7.336
7.317
7.299
7.248
7.234
7.229
3.639
3.622
3.607
3.588
2.941
2.923
2.904
0.000



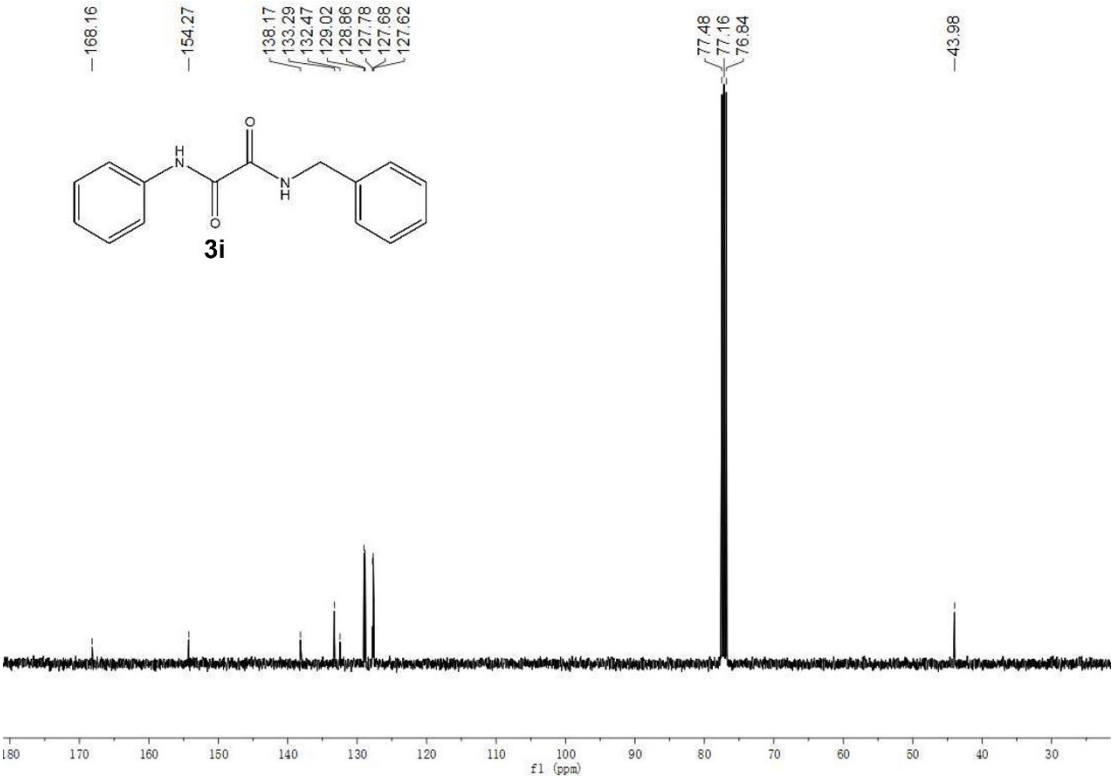
3h

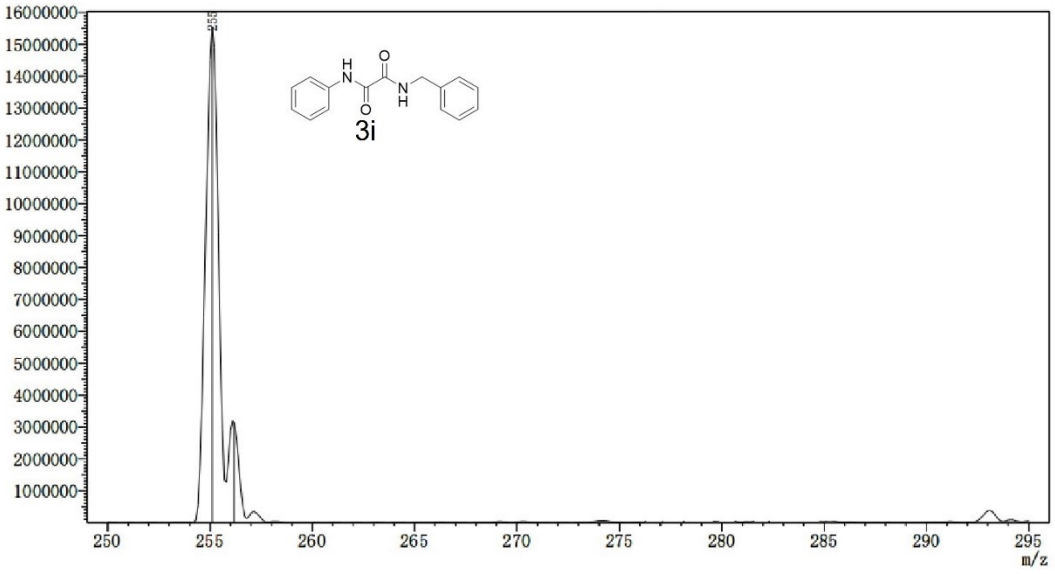

1.05
1.00
2.08
1.04
2.07
2.09
3.05
2.03
2.08
f1 (ppm)

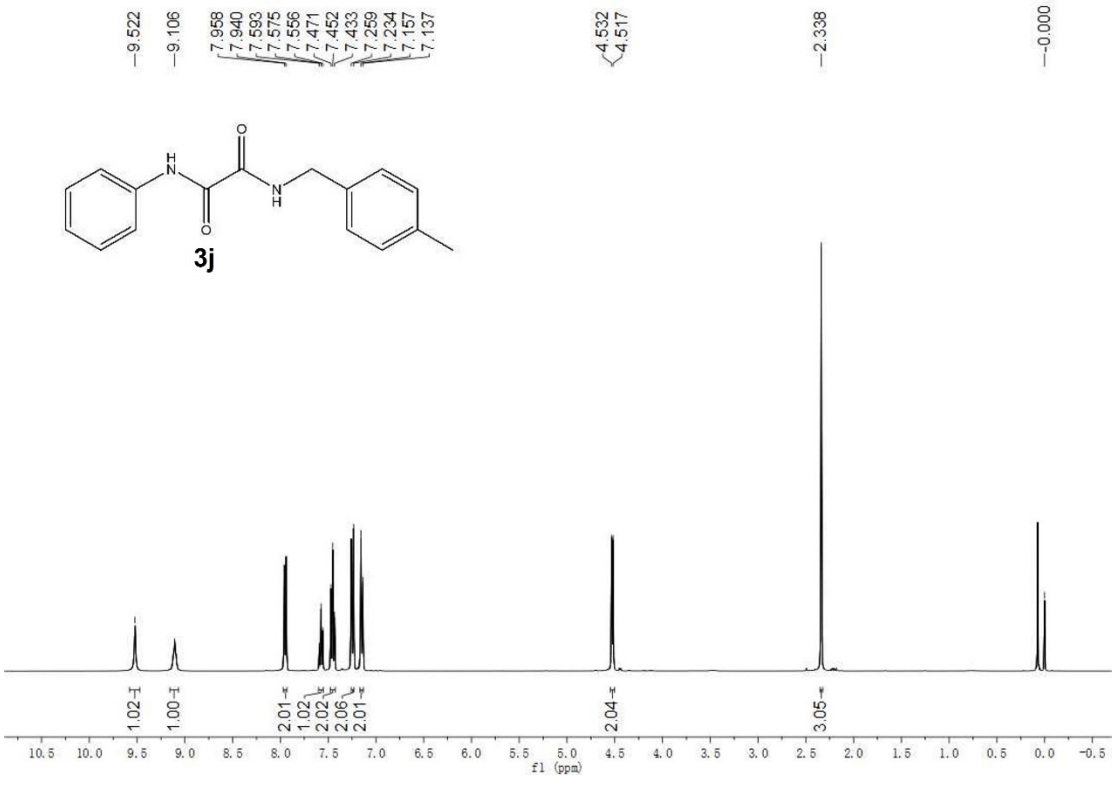

168.44
154.79
138.92
133.12
132.54
128.86
128.80
128.72
128.06
126.65
77.48
77.16
76.84
41.60
36.07
3h
f1 (ppm)


3h
2069
m/z


9.158
9.096
7.926
7.908
7.600
7.585
7.563
7.480
7.464
7.450
7.359
7.350
7.304
7.292
7.261
4.582
4.567
0.000
3i
1.09
1.00
2.04
1.00
2.09
5.08
2.05
f1 (ppm)


168.16
154.27
138.17
133.29
132.47
129.02
128.86
127.78
127.68
127.62
77.48
77.16
76.84
43.98
3i
f1 (ppm)


3i
m/z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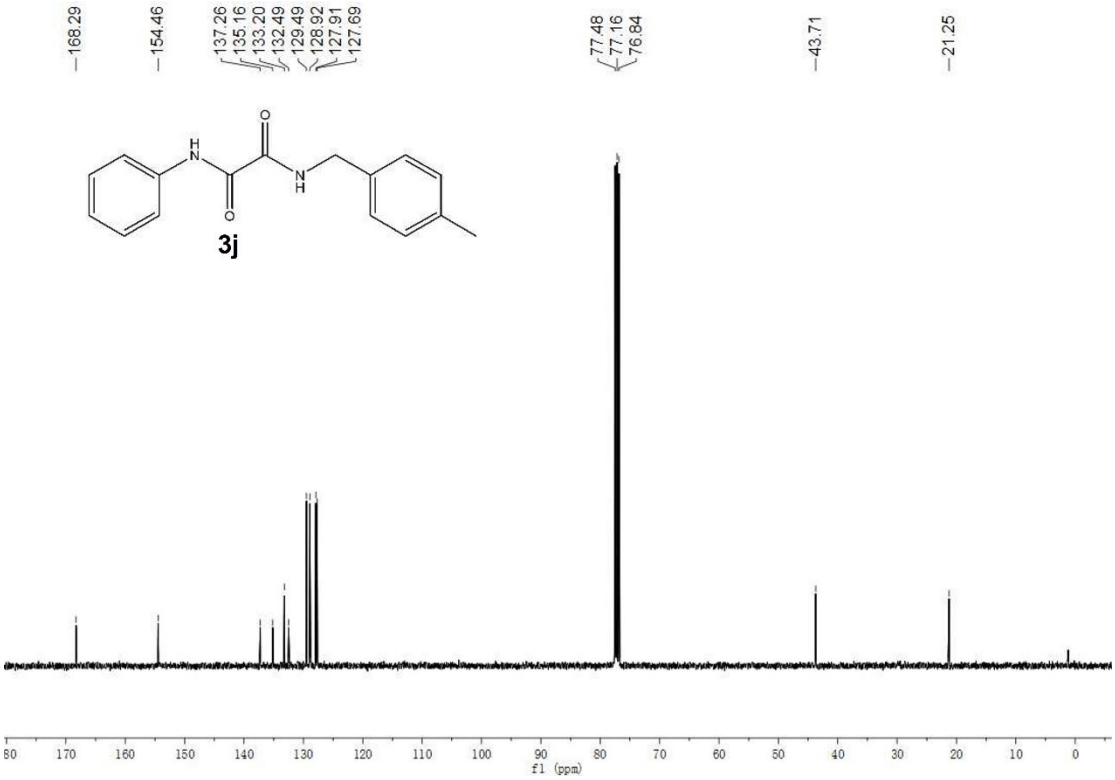
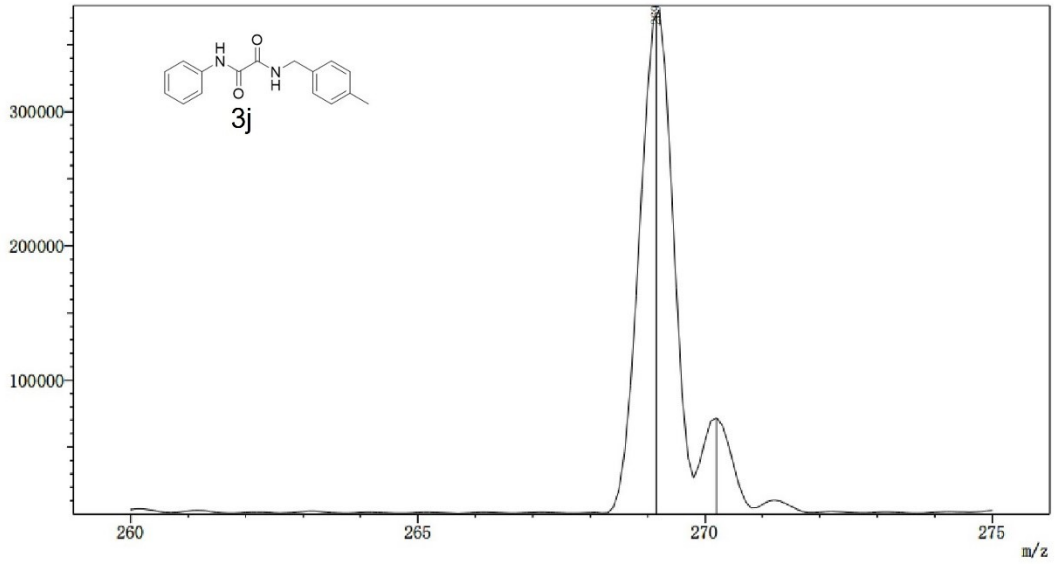
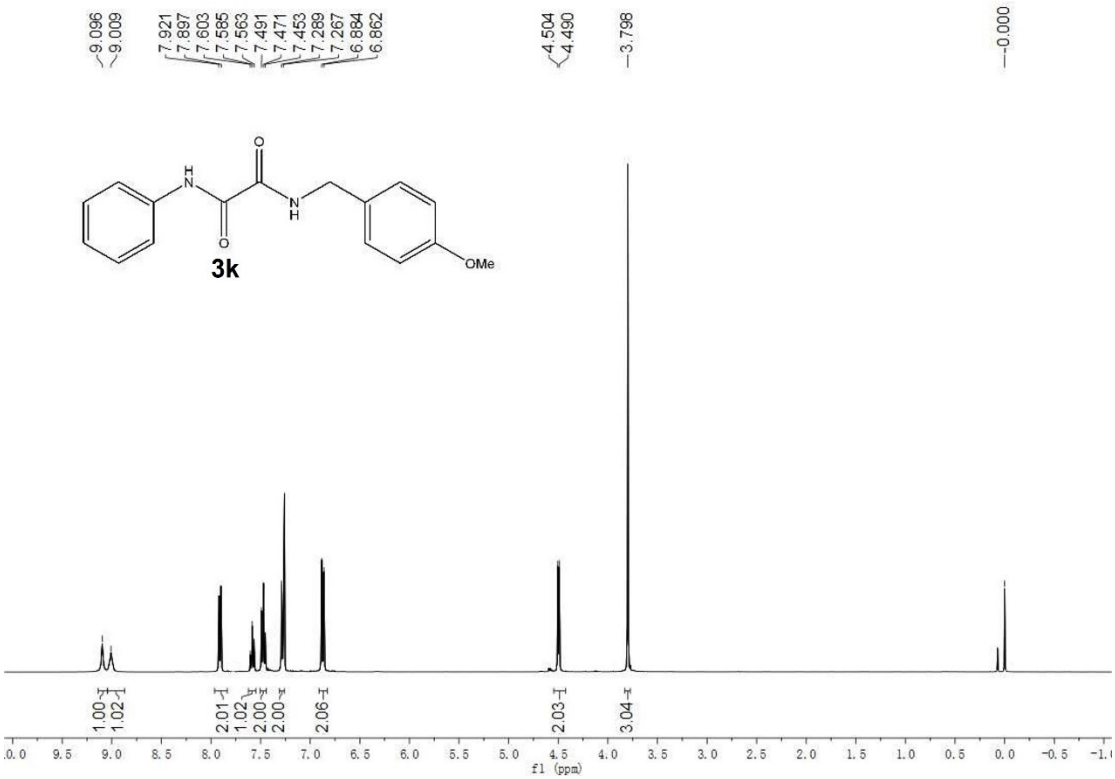
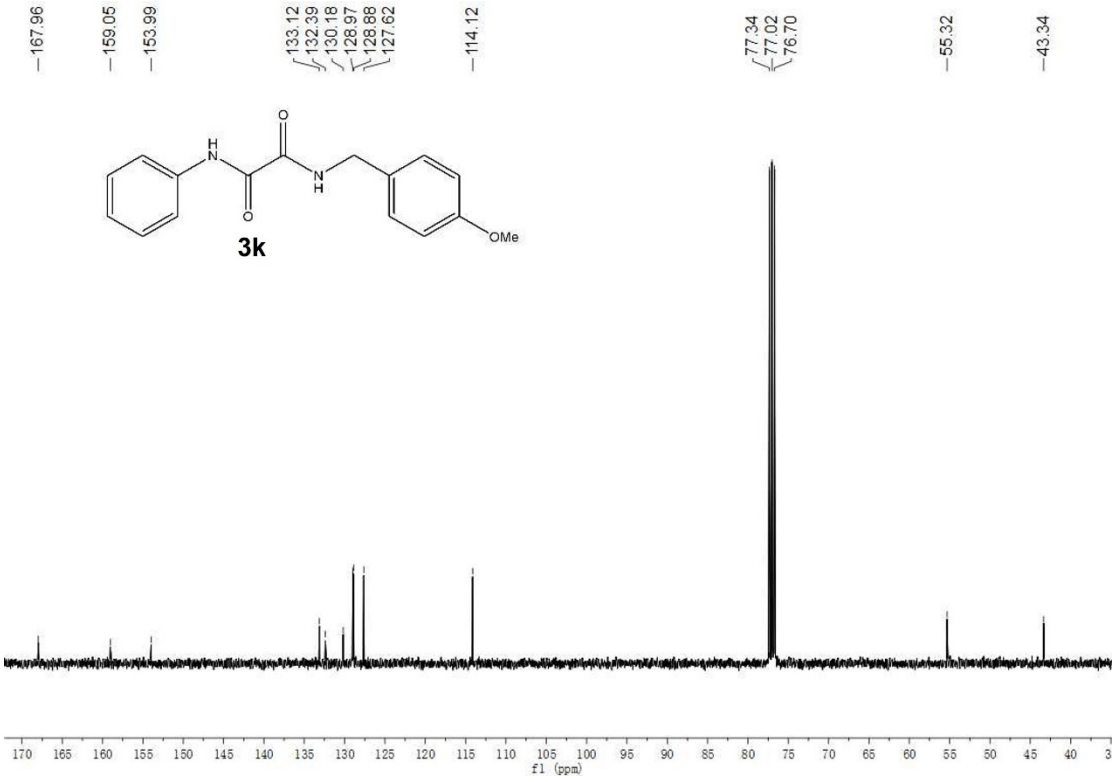
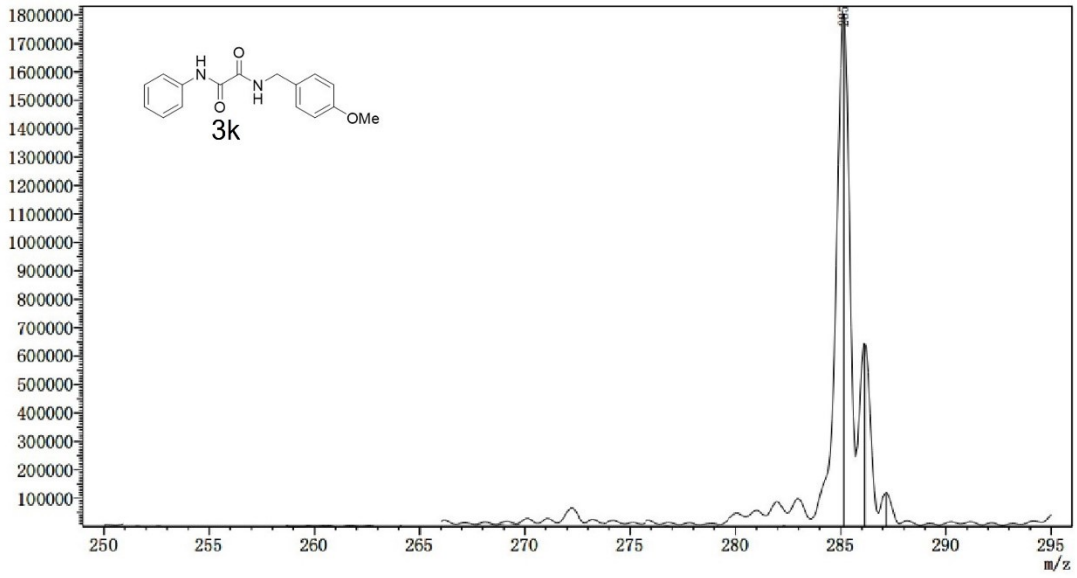
9.106
7.958
7.940
7.593
7.575
7.556
7.471
7.452
7.433
7.259
7.234
7.157
7.137
4.532
4.517
2.338
0.000
3j
1.02
1.00
2.01
1.02
2.02
2.06
2.01
2.04
3.05
f1 (ppm)


168.29
154.46
137.26
135.16
133.20
132.49
129.49
128.92
127.91
127.69
77.48
77.16
76.84
43.71
21.25
3j
f1 (ppm)

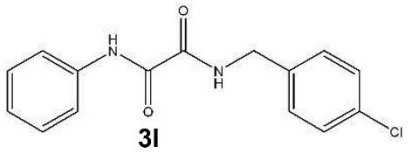

3j
300000
200000
100000
260
265
270
275
m/z

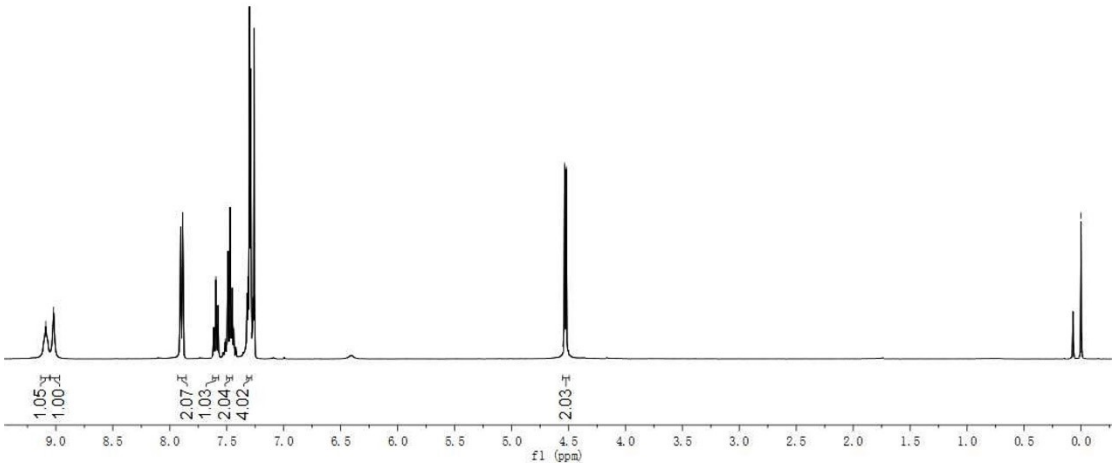

9.096
9.009
7.921
7.897
7.603
7.585
7.563
7.491
7.471
7.453
7.289
7.267
6.884
6.862
4.504
4.490
3.798
0.000
3k
OMe
1.00
1.02
2.01
1.02
2.00
2.00
2.06
2.03
3.04
f1 (ppm)

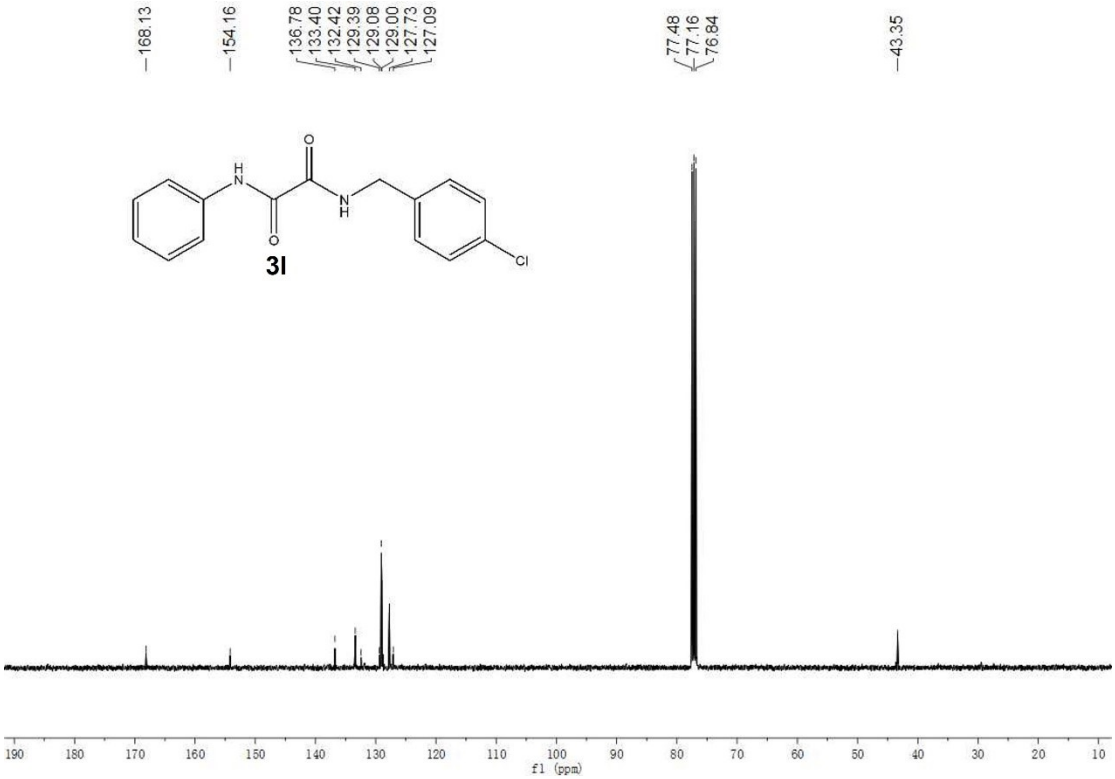

167.96
159.05
153.99
133.12
132.39
130.18
128.97
128.88
127.62
114.12
77.34
77.02
76.70
55.32
43.34
3k
OMe
f1 (ppm)

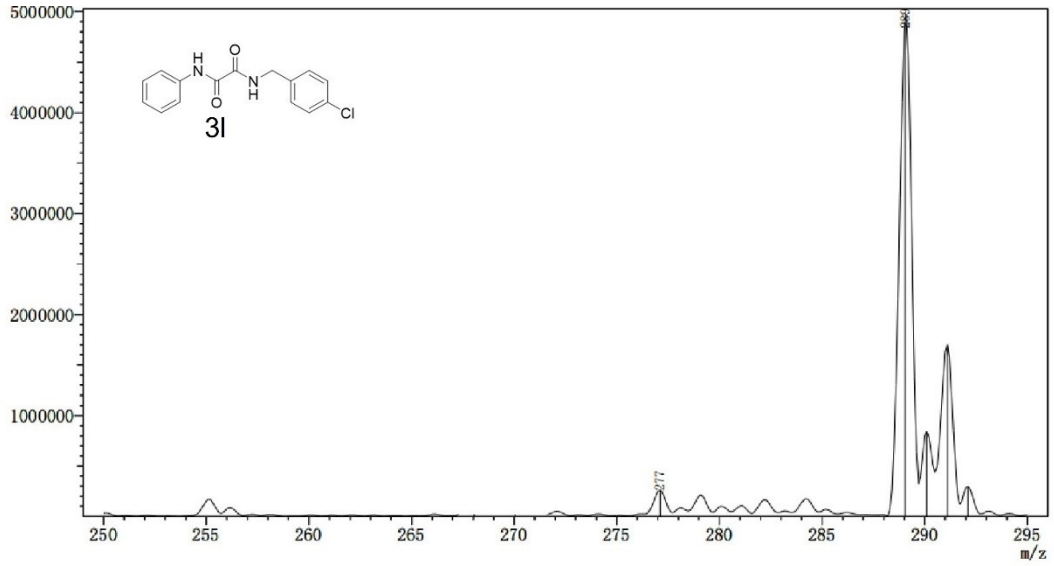

3k
OMe
m/z

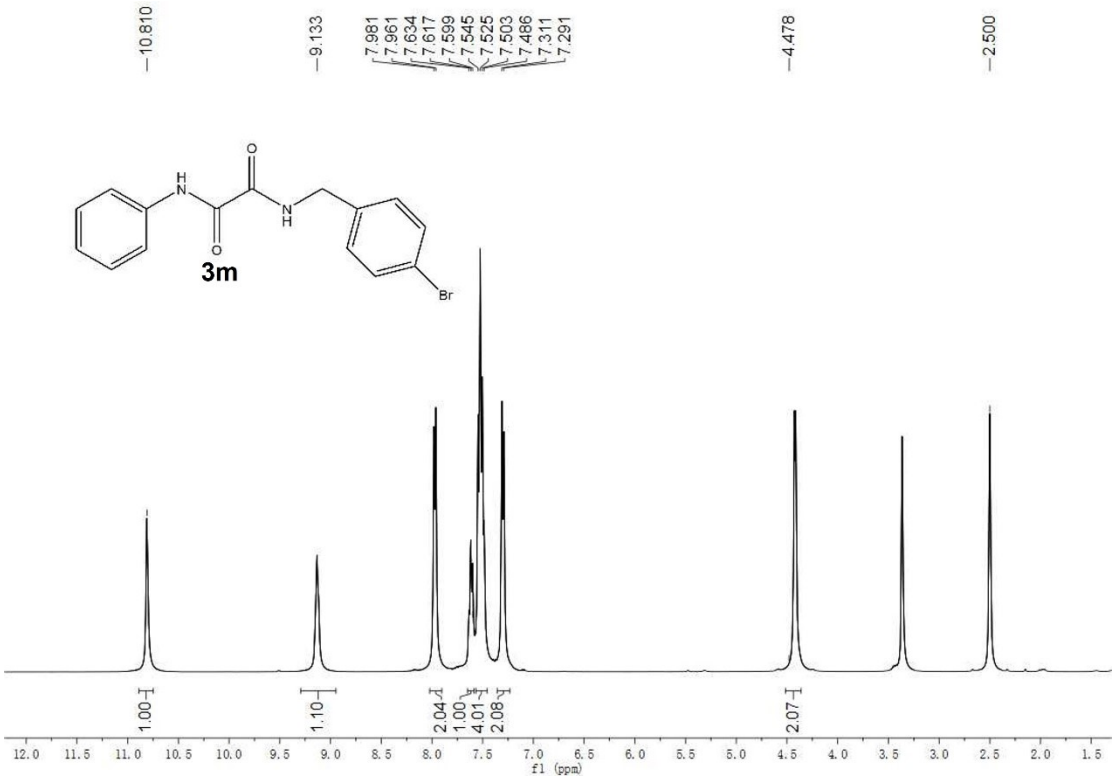

9.089
9.021
7.906
7.888
7.614
7.596
7.577
7.514
7.490
7.470
7.451
7.438
7.322
7.314
7.301
7.290
7.283
4.535
4.520
0.000

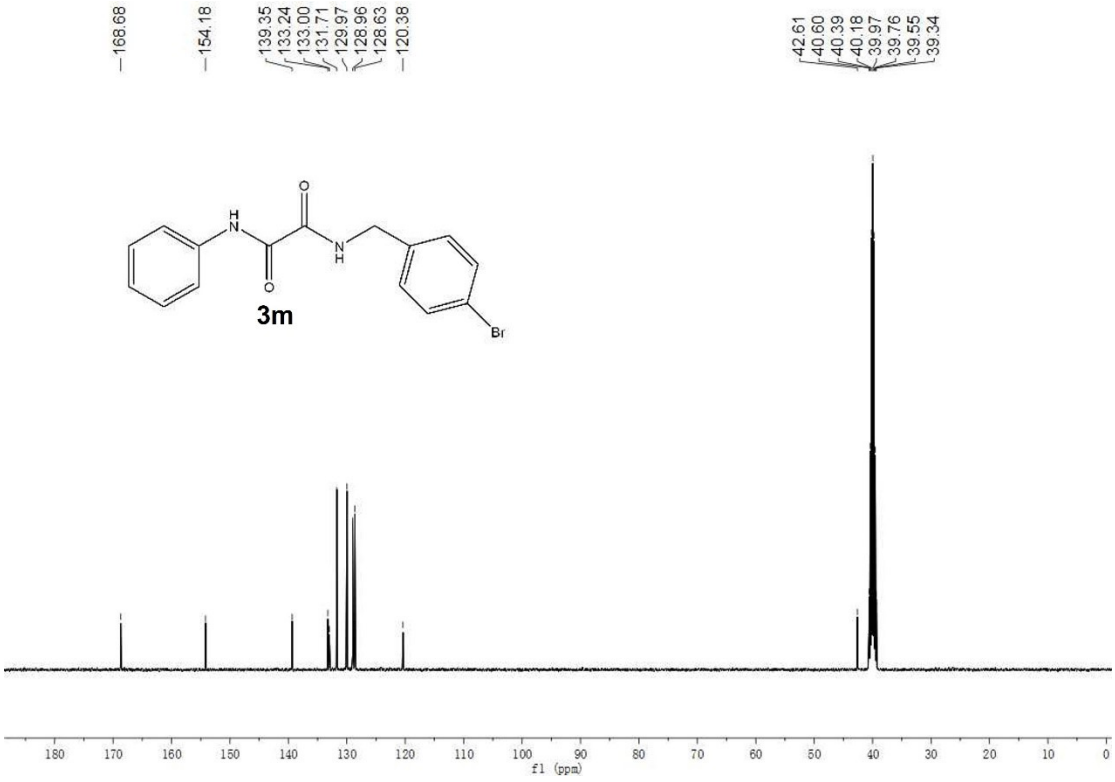

3l
Cl

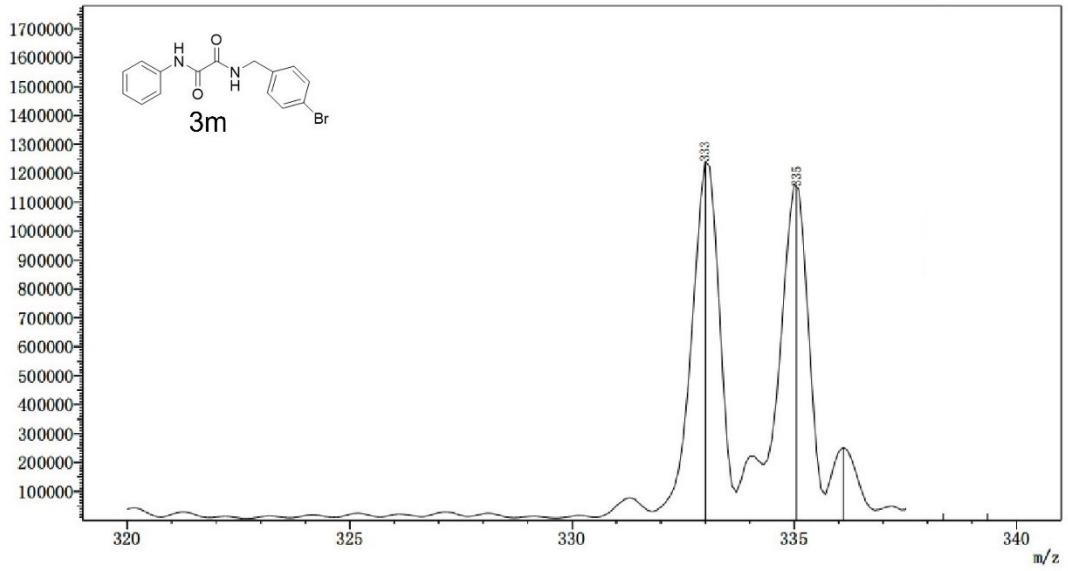

1.05
1.00
2.07
1.03
2.04
4.02
2.03
f1 (ppm)

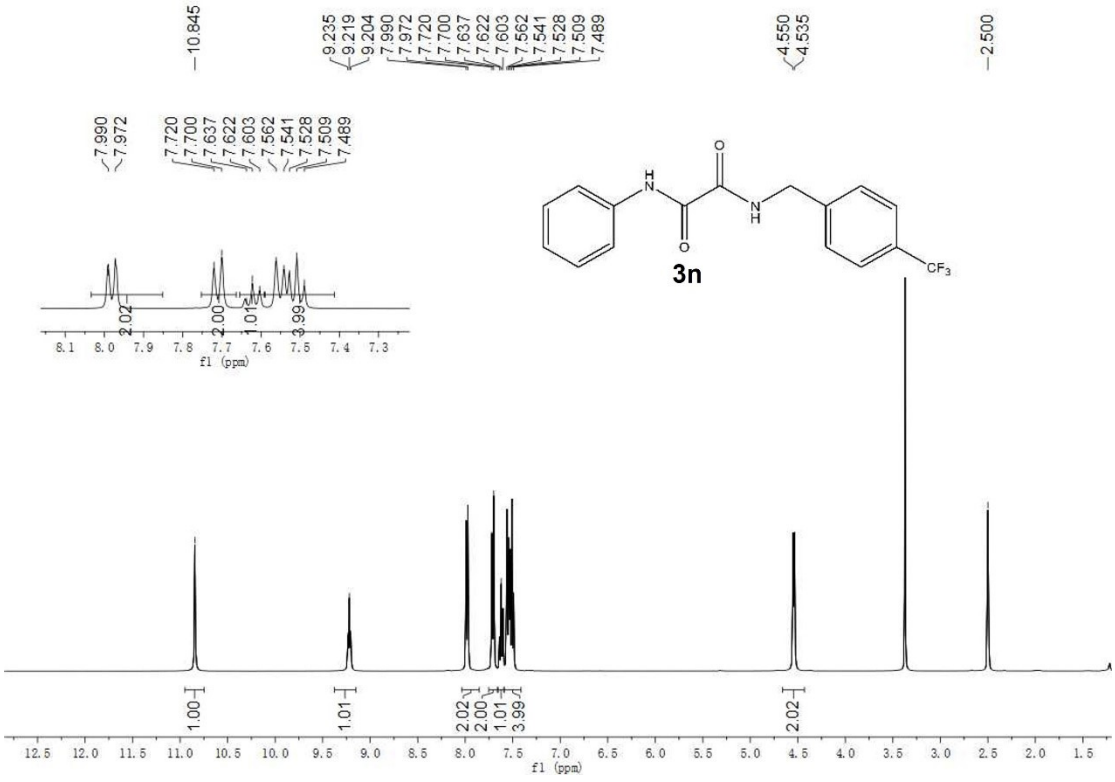

168.13
154.16
136.78
133.40
132.42
129.39
129.08
129.00
127.73
127.09
77.48
77.16
76.84
43.35
3l
f1 (ppm)

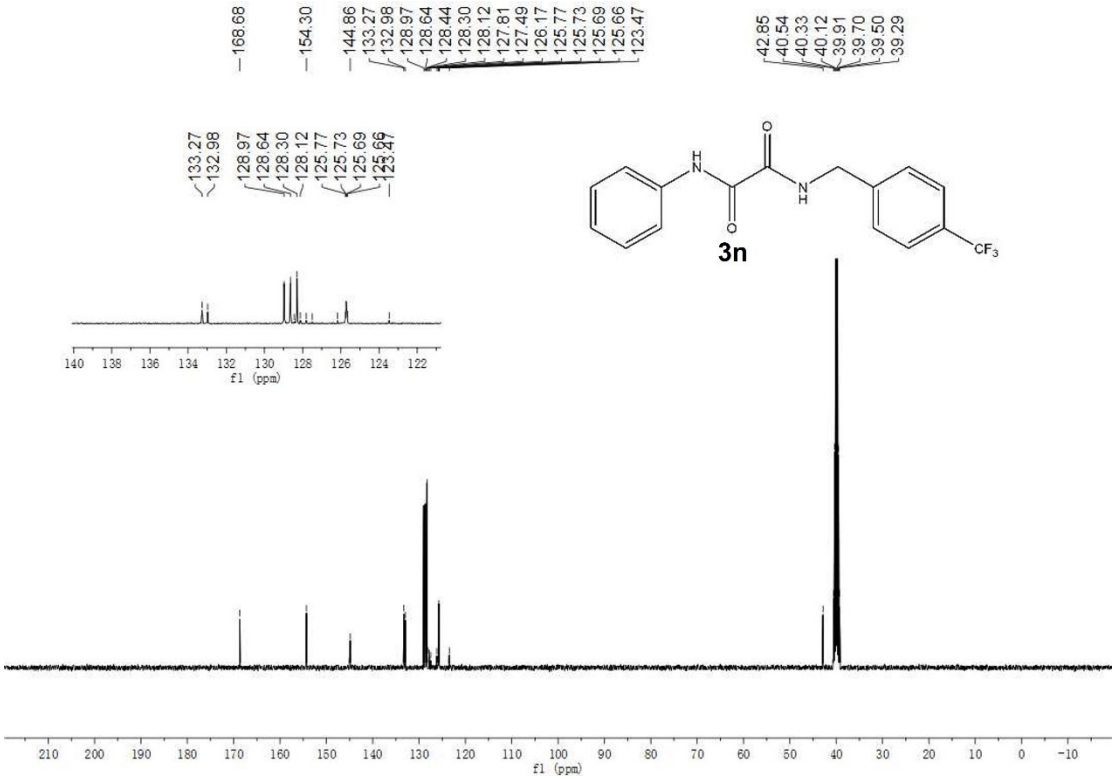

3l
m/z

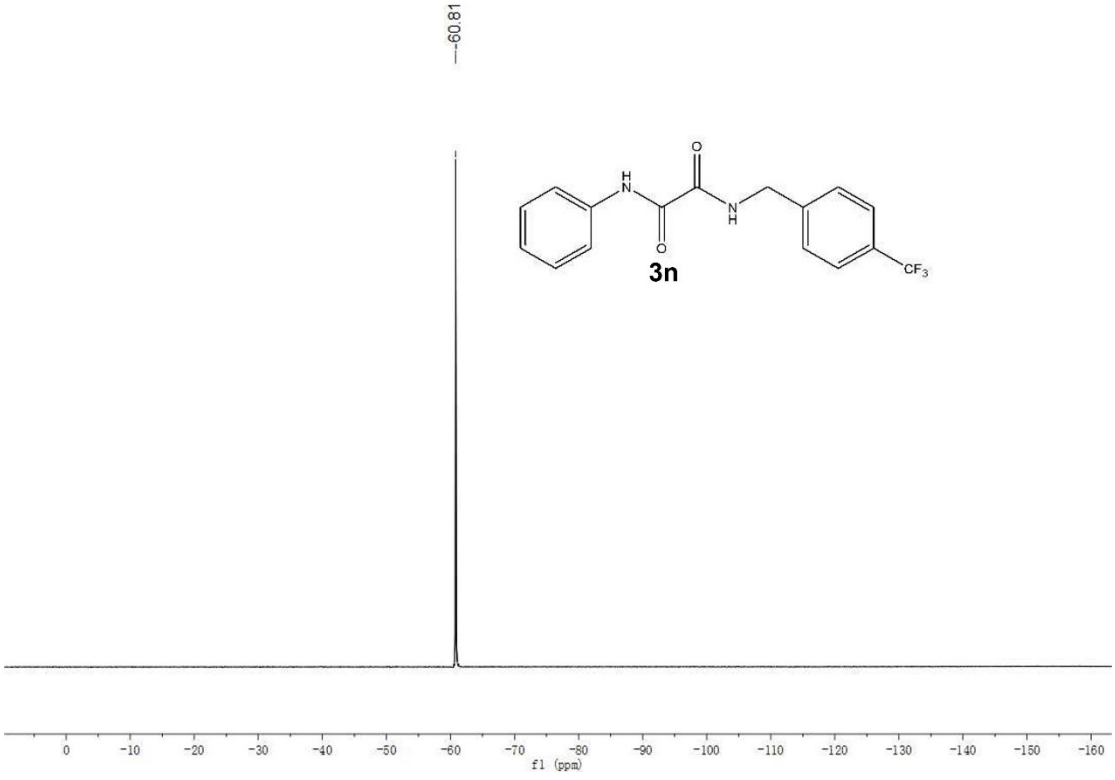

10.810
9.133
7.981
7.961
7.634
7.617
7.599
7.545
7.525
7.503
7.486
7.311
7.291
4.478
2.500
3m
Br
1.00
1.10
2.04
1.00
4.01
2.08
2.07
f1 (ppm)

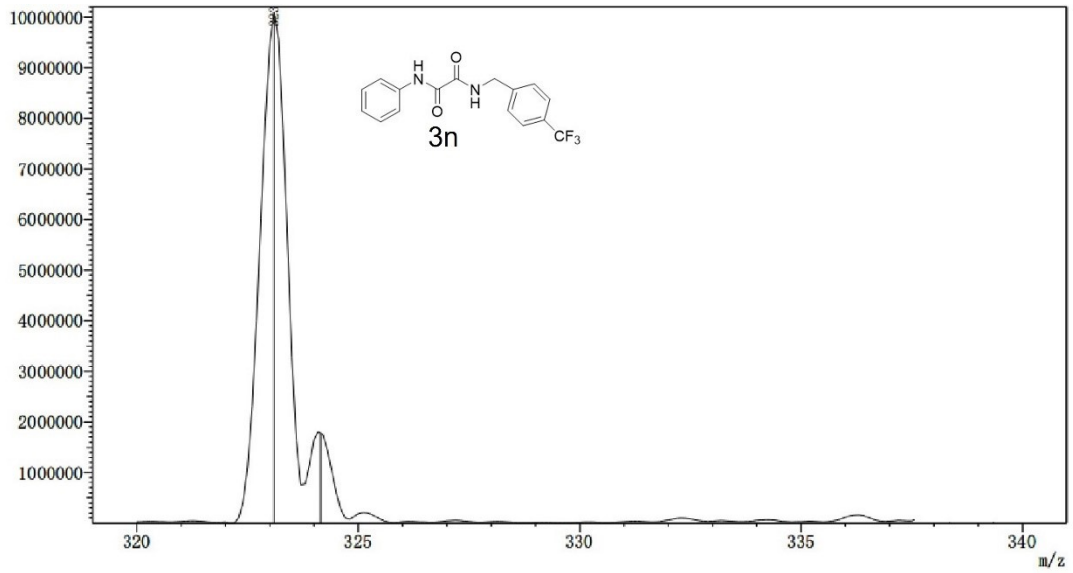

168.68
154.18
139.35
133.24
133.00
131.71
129.97
128.96
128.63
120.38
42.61
40.60
40.39
40.18
39.97
39.76
39.55
39.34
3m
Br
f1 (ppm)


3m
Br
333
335
m/z

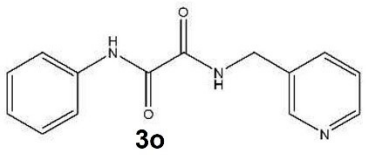

10.845
9.235
9.219
9.204
7.990
7.972
7.720
7.700
7.637
7.622
7.603
7.562
7.541
7.528
7.509
7.489
4.550
4.535
2.500
3n
CF3
f1 (ppm)

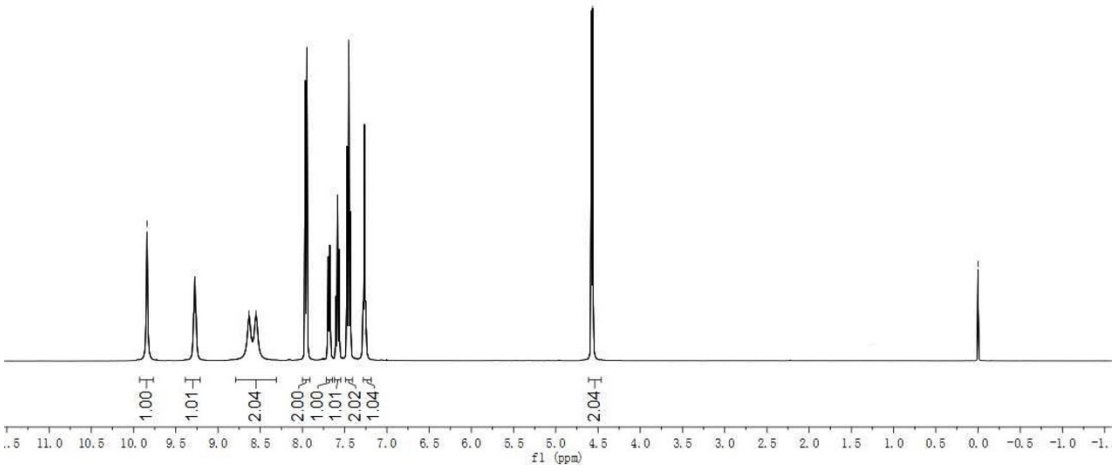

168.68
154.30
144.86
133.27
132.98
128.97
128.64
128.44
128.30
128.12
127.81
127.49
126.17
125.77
125.73
125.69
125.66
123.47
42.85
40.54
40.33
40.12
39.91
39.70
39.50
39.29
3n
f1 (ppm)

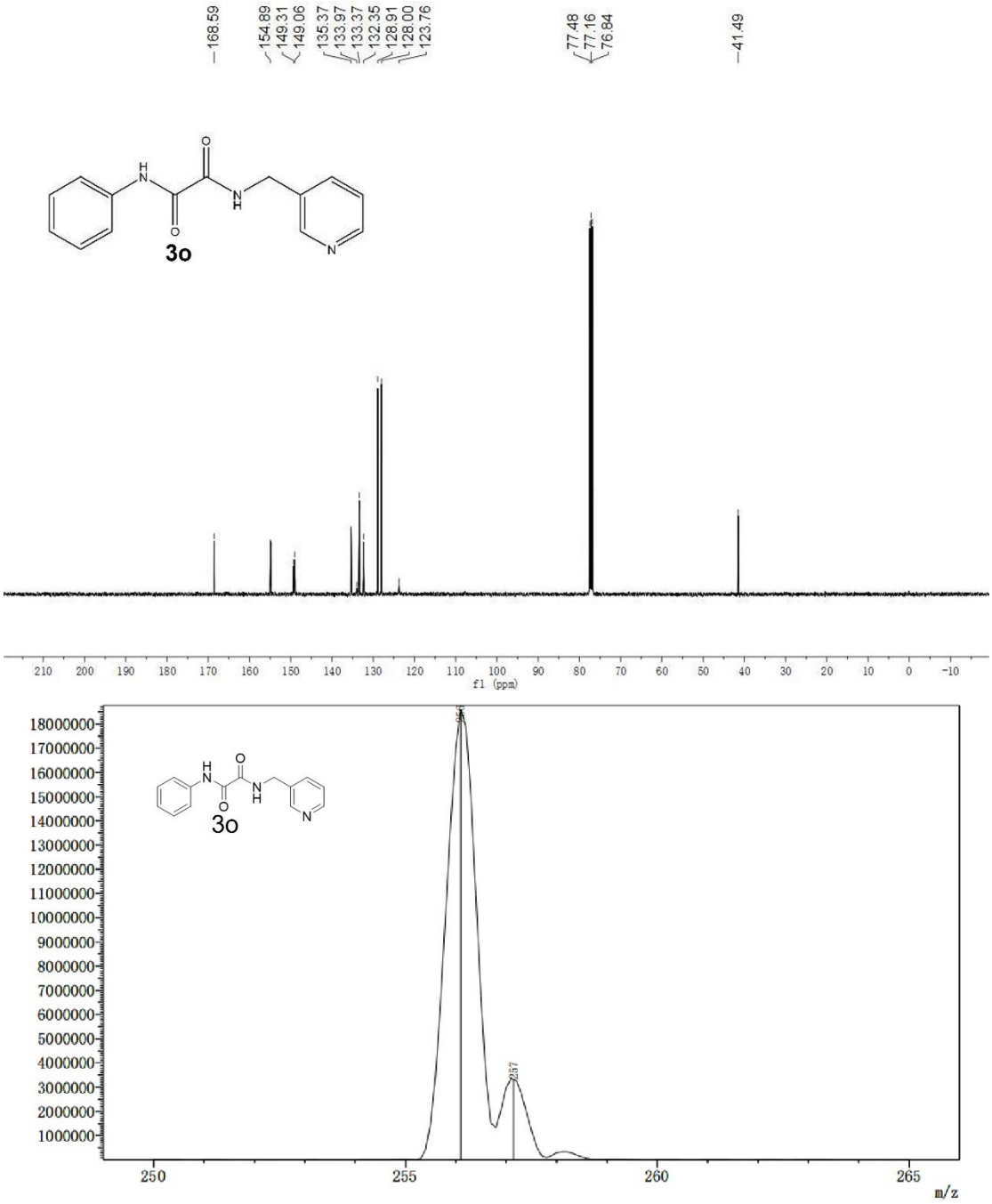

-60.81
3n
f1 (ppm)

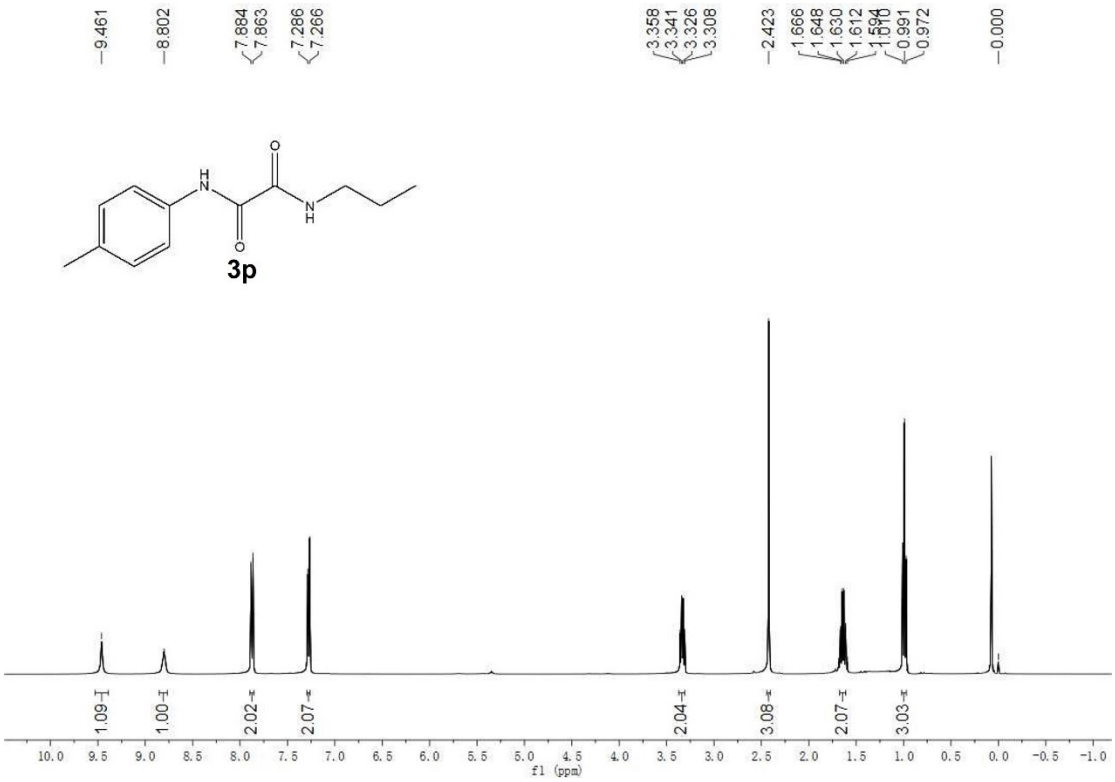

10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
320
325
330
335
340
m/z
3n
CF3

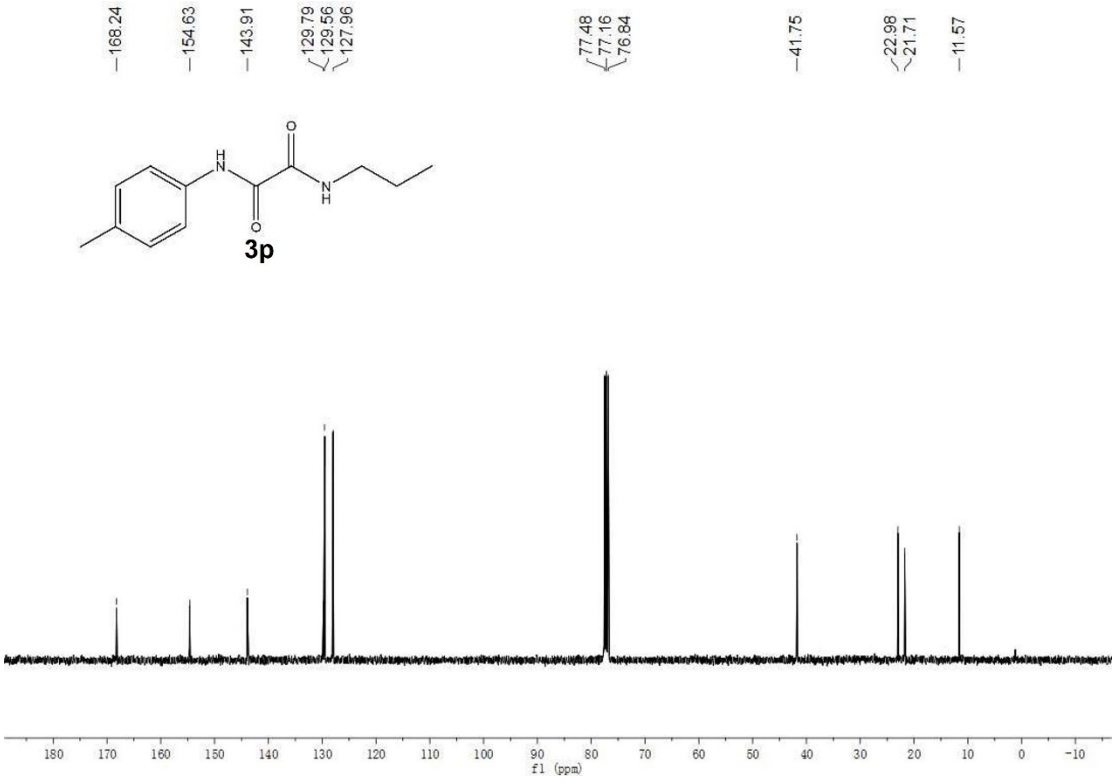

9.841
9.274
8.632
8.550
7.966
7.948
7.696
7.676
7.603
7.585
7.566
7.472
7.452
7.433
7.282
7.267
7.252
4.579
4.564
0.000

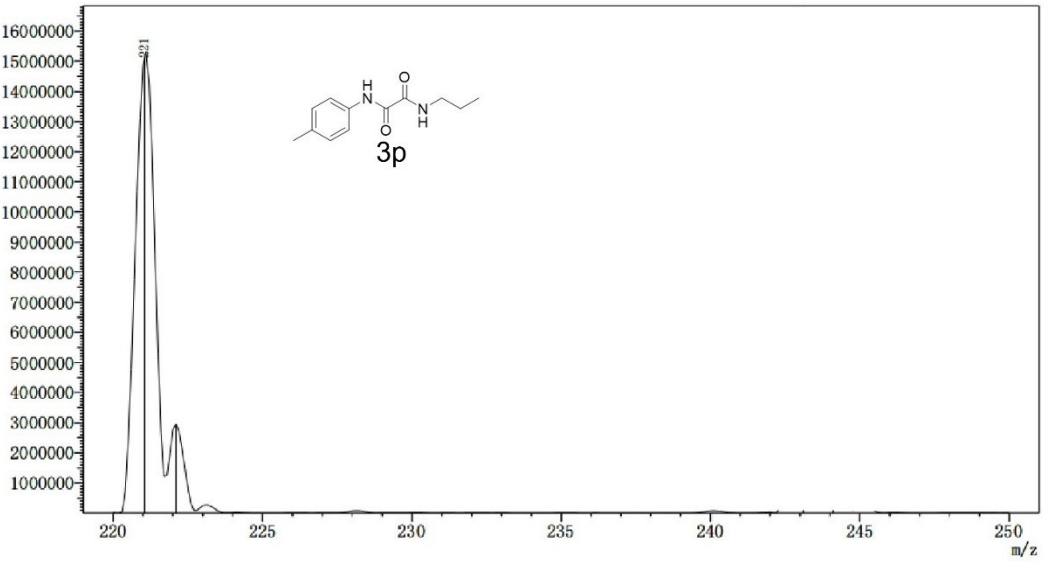

3o

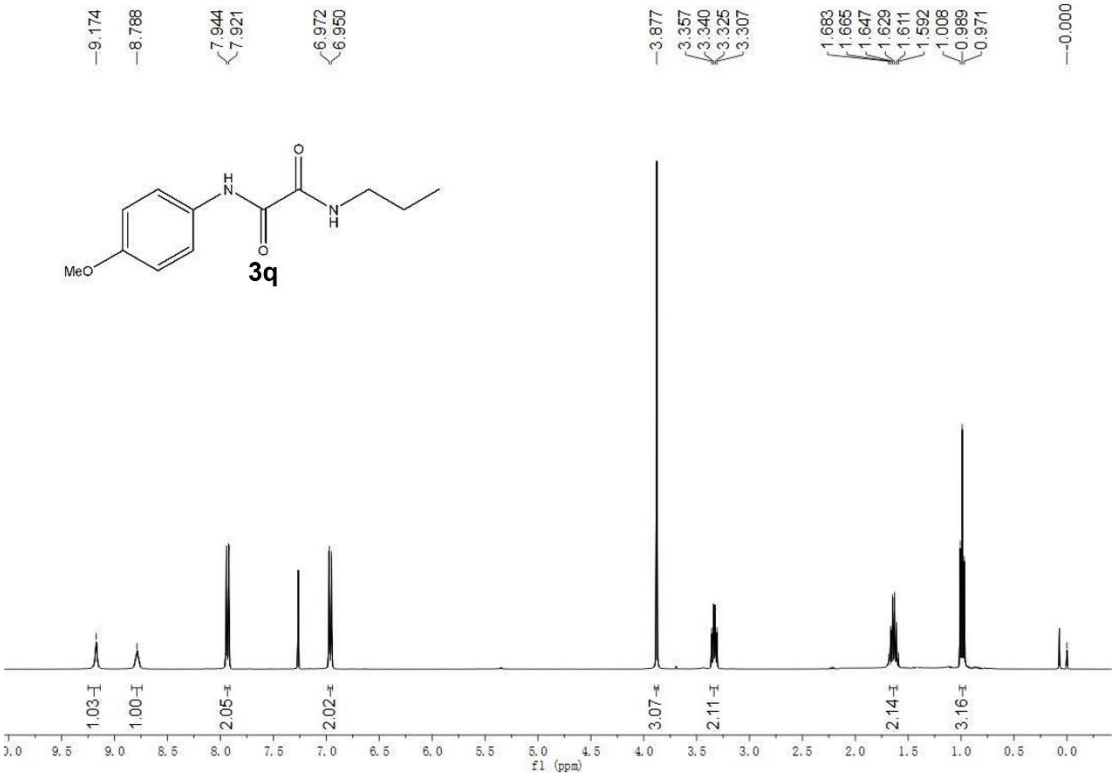

1.00
1.01
2.04
2.00
1.00
1.01
2.02
1.04
2.04
f1 (ppm)

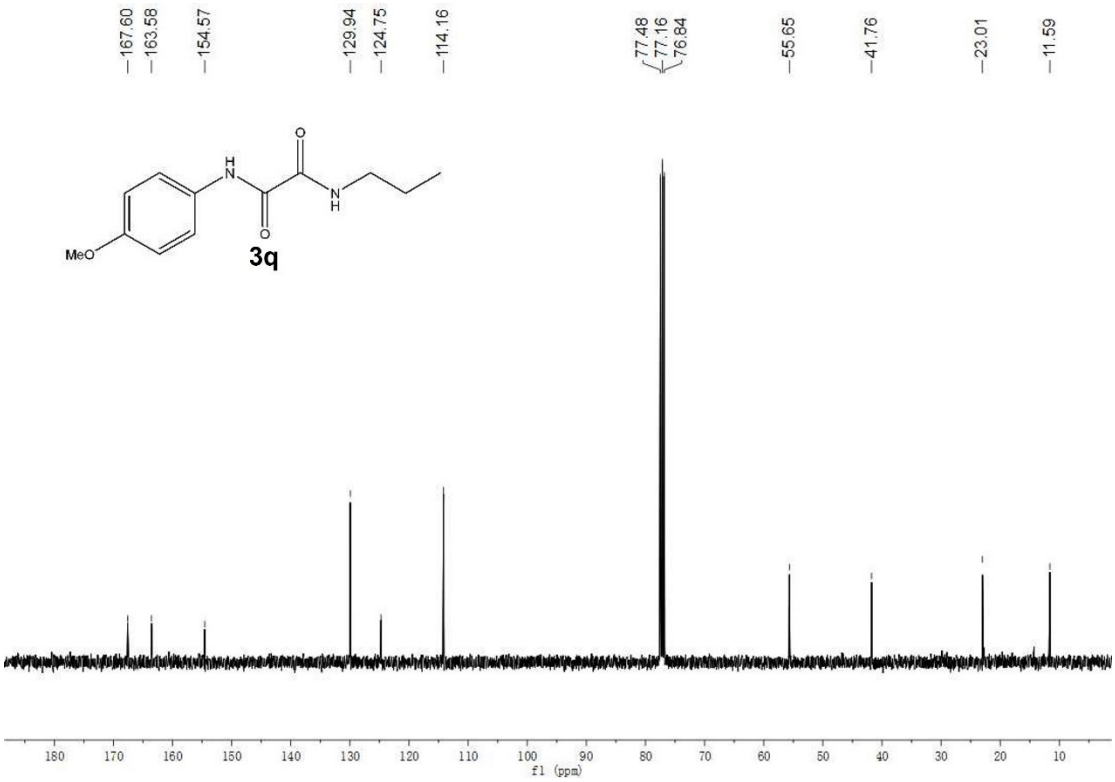

168.59
154.89
149.31
149.06
135.37
133.97
133.37
132.35
128.91
128.00
123.76
77.48
77.16
76.84
41.49
3o
f1 (ppm)
3o
m/z

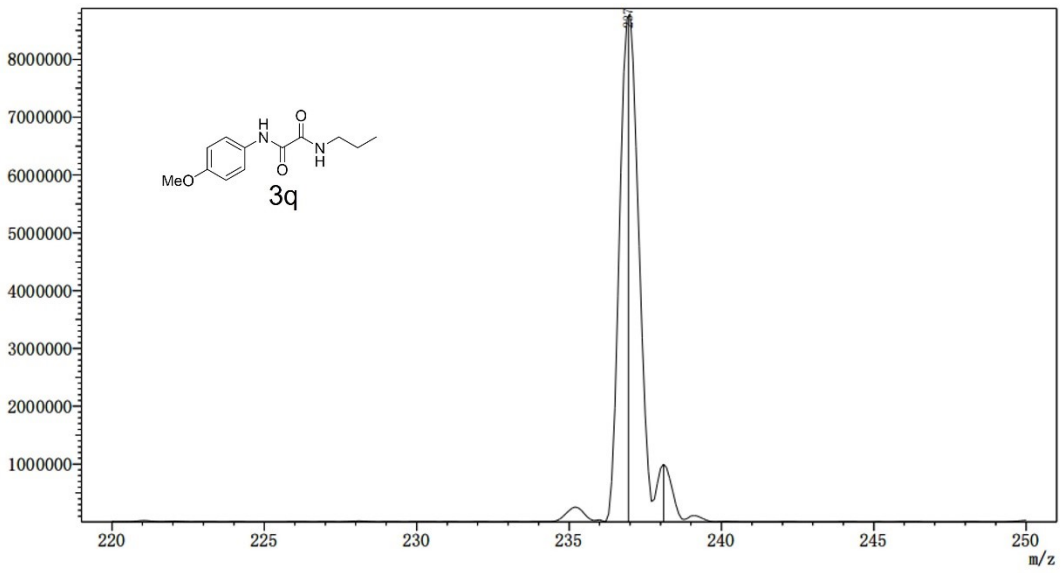

9.461
8.802
7.884
7.863
7.286
7.266
3.358
3.341
3.326
3.308
2.423
1.666
1.648
1.630
1.612
1.594
1.010
0.991
0.972
0.000
3p
1.09
1.00
2.02
2.07
2.04
3.08
2.07
3.03
f1 (ppm)

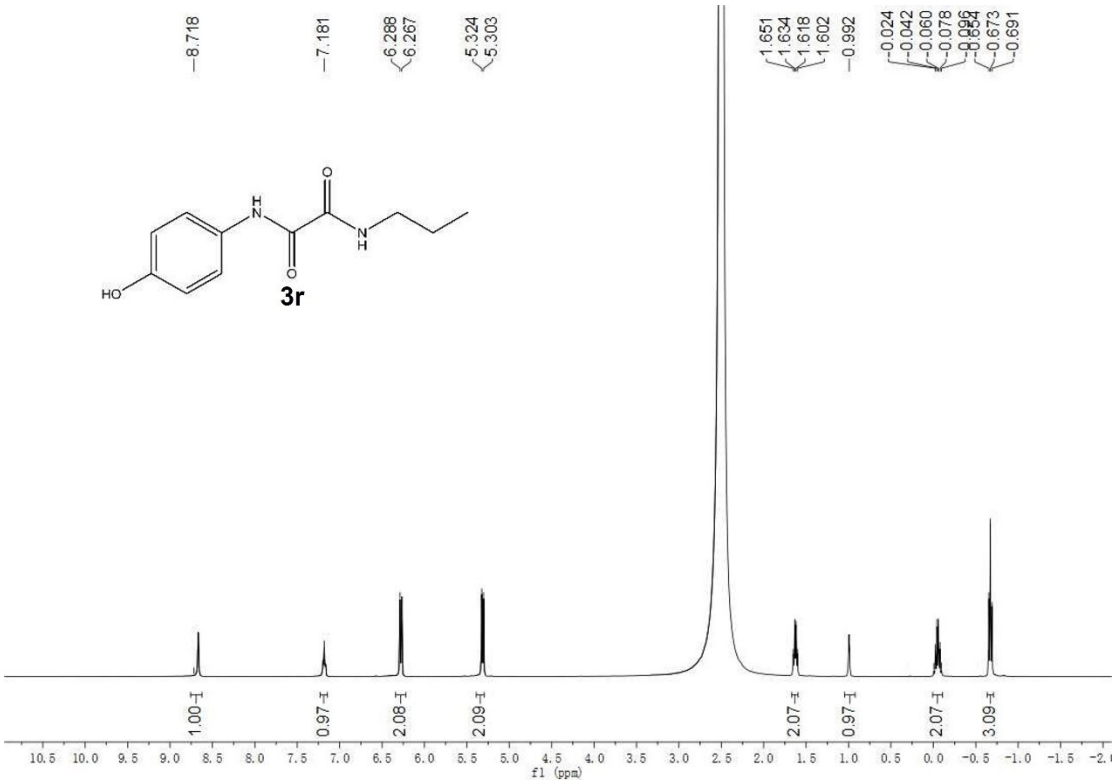

168.24
154.63
143.91
129.79
129.56
127.96
77.48
77.16
76.84
41.75
22.98
21.71
11.57
3p
f1 (ppm)

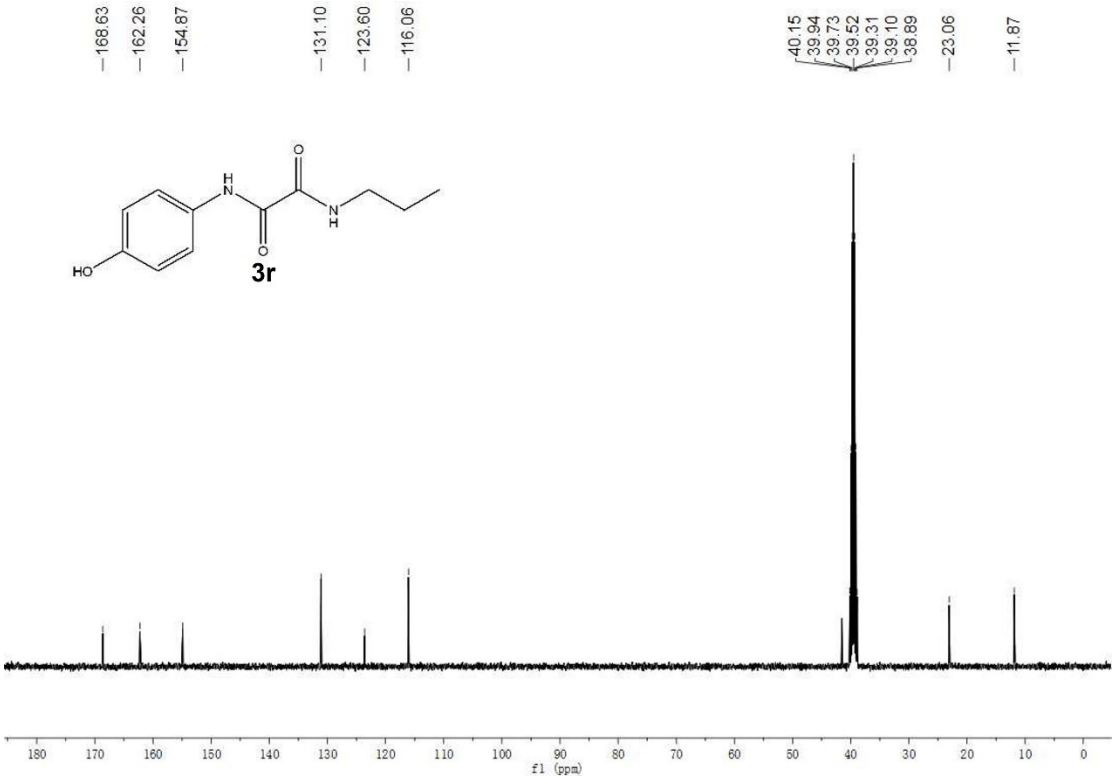

221
3p
m/z

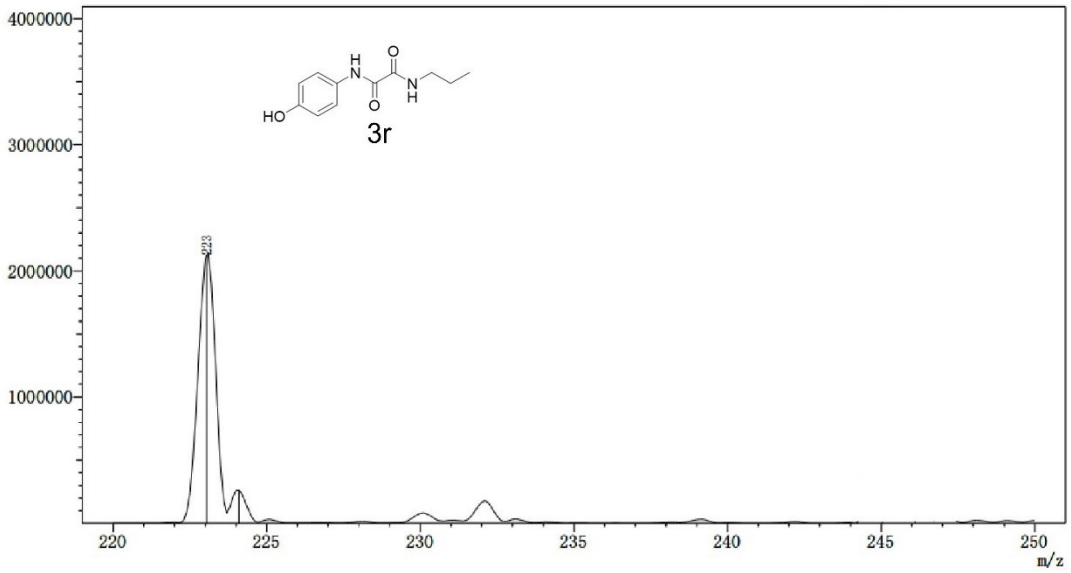

9.174
8.788
7.944
7.921
6.972
6.950
3.877
3.357
3.340
3.325
3.307
1.683
1.665
1.647
1.629
1.611
1.592
1.008
0.989
0.971
0.000
MeO
3q
1.03
1.00
2.05
2.02
3.07
2.11
2.14
3.16
f1 (ppm)


167.60
163.58
154.57
129.94
124.75
114.16
77.48
77.16
76.84
55.65
41.76
23.01
11.59
MeO
3q
f1 (ppm)

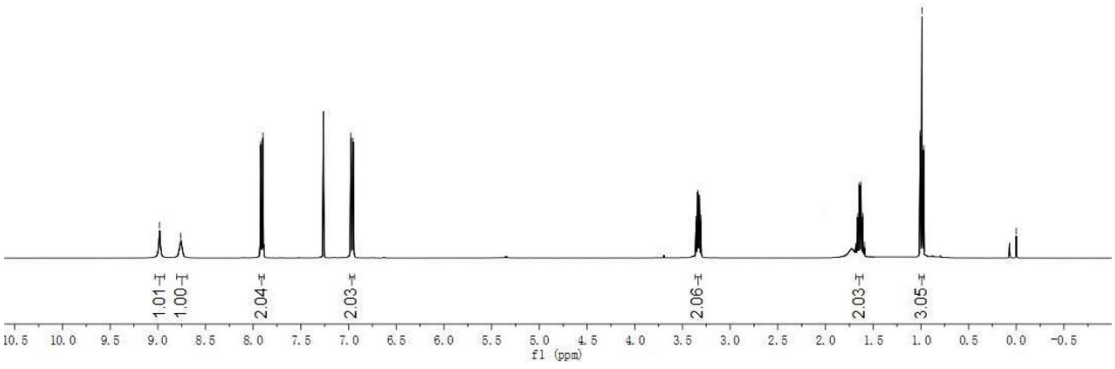

8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
MeO
3q
220
225
230
235
240
245
250
m/z

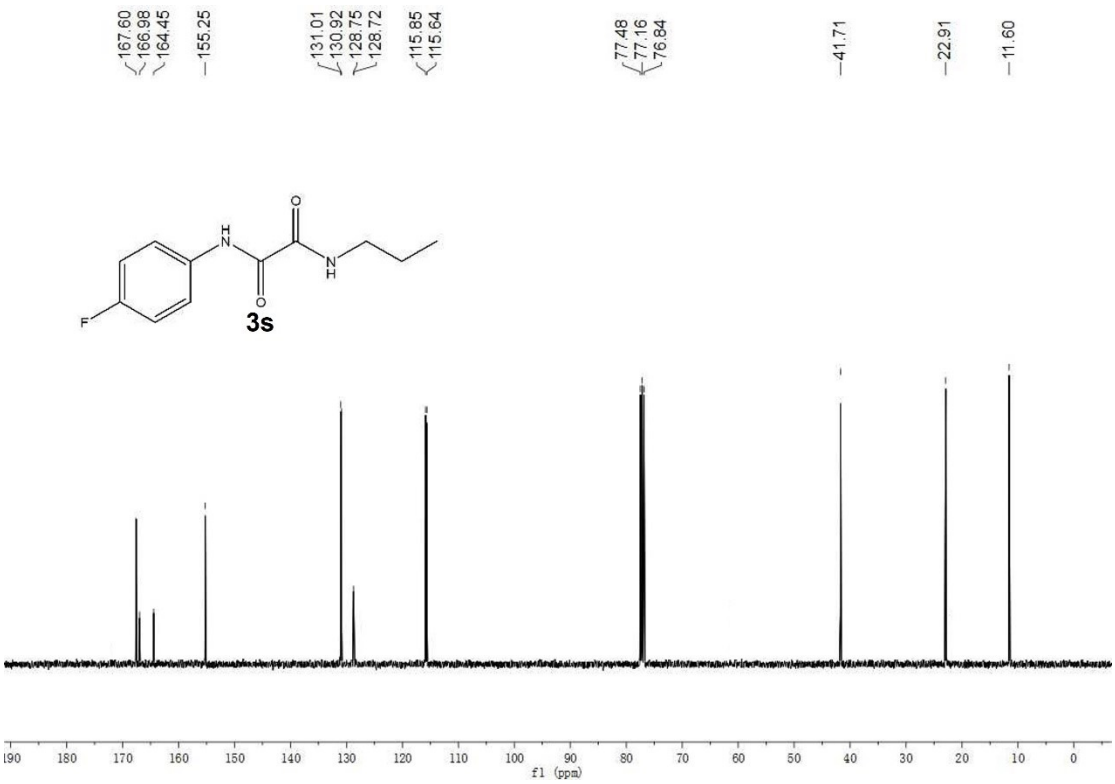

8.718
7.181
6.288
6.267
5.324
5.303
1.651
1.634
1.618
1.602
0.992
0.024
0.042
0.060
0.078
0.673
0.691
HO
3r
1.00
0.97
2.08
2.09
2.07
0.97
2.07
3.09
f1 (ppm)

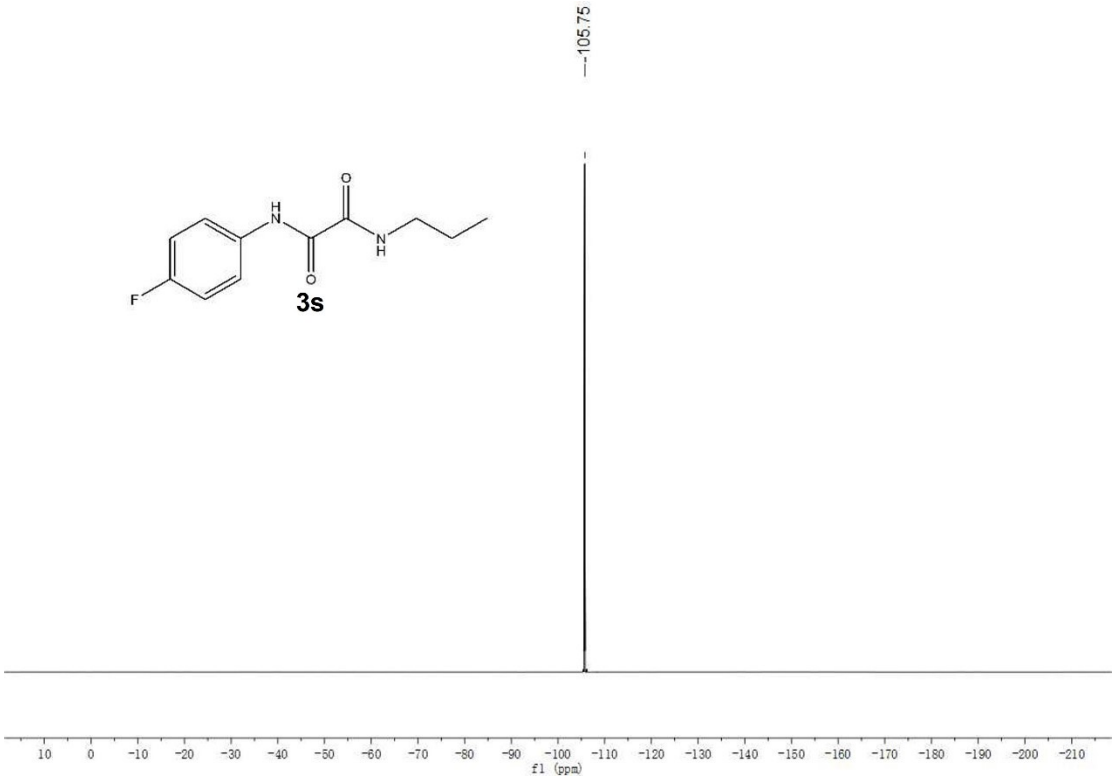

168.63
162.26
154.87
131.10
123.60
116.06
40.15
39.94
39.73
39.52
39.31
39.10
38.89
23.06
11.87
HO
3r
f1 (ppm)

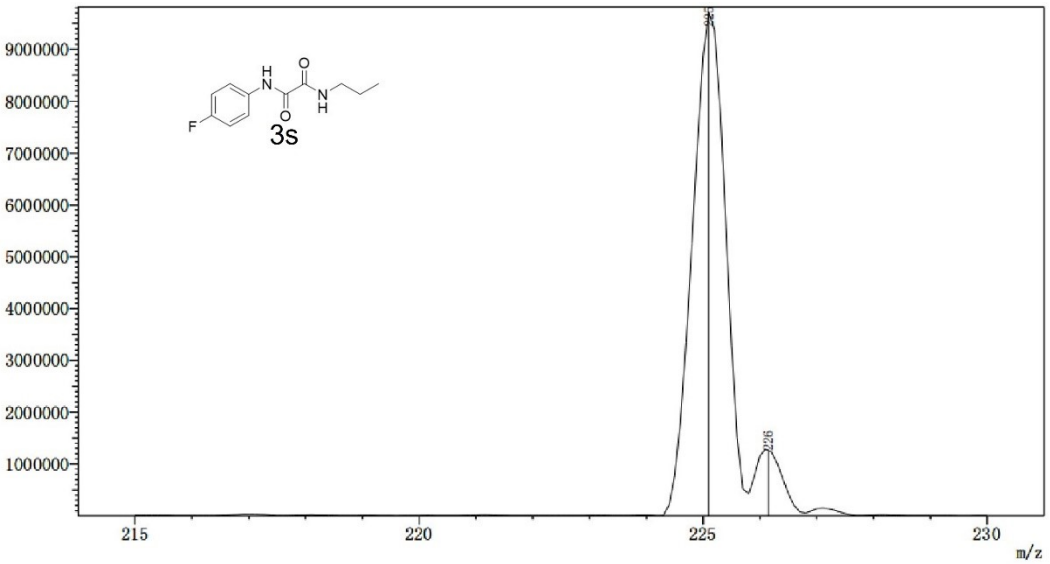

4000000
3000000
2000000
1000000
223
220
225
230
235
240
245
250
m/z
HO
3r

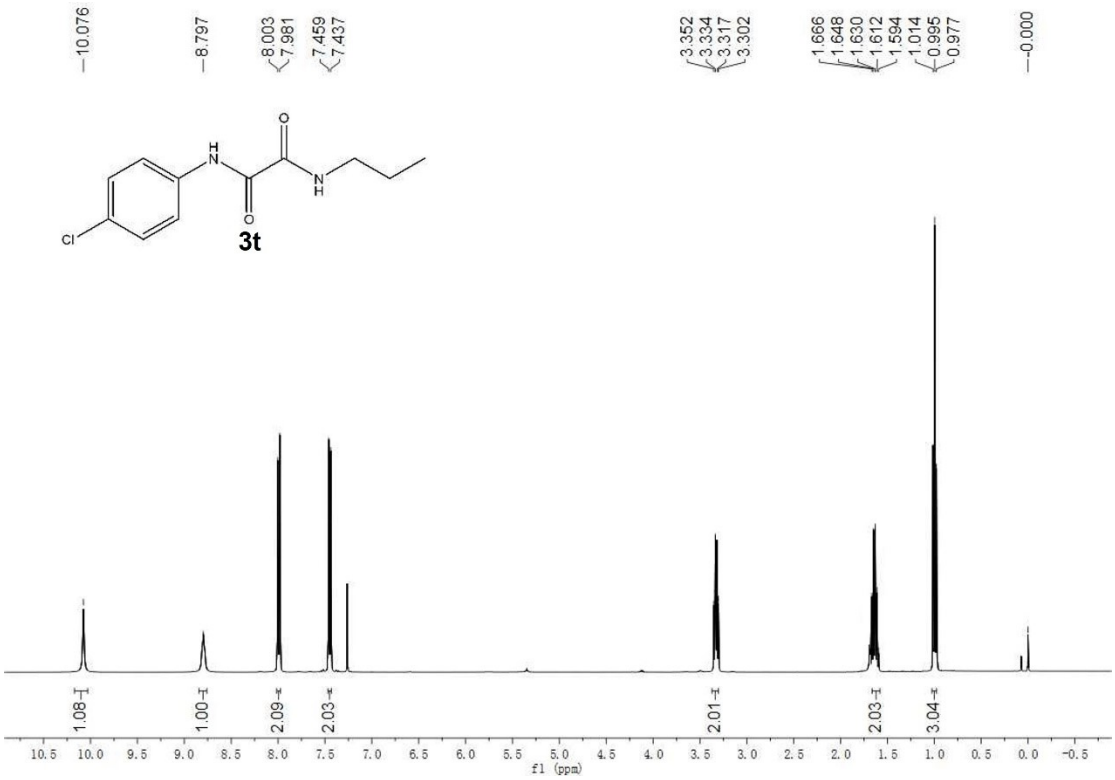

8.981
8.759
7.921
7.898
6.975
6.953
3.357
3.339
3.325
3.307
1.682
1.664
1.646
1.628
1.610
1.592
1.007
0.989
0.970
0.000
F
3s

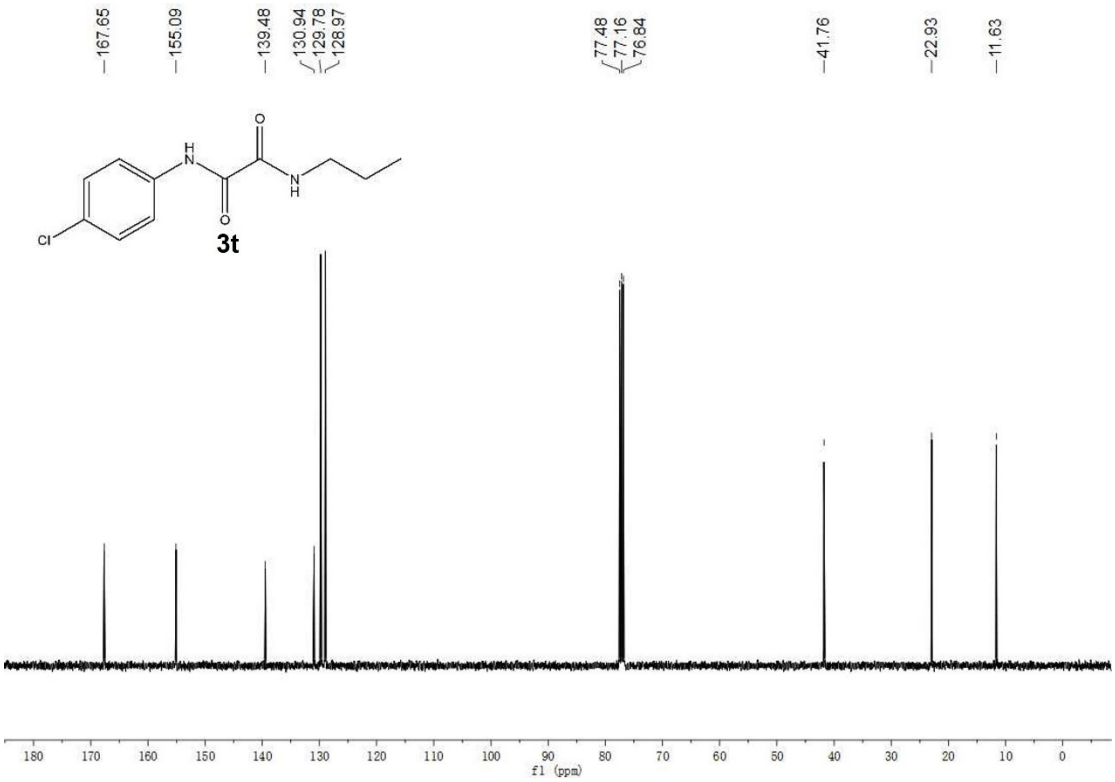

1.01
1.00
2.04
2.03
2.06
2.03
3.05
f1 (ppm)

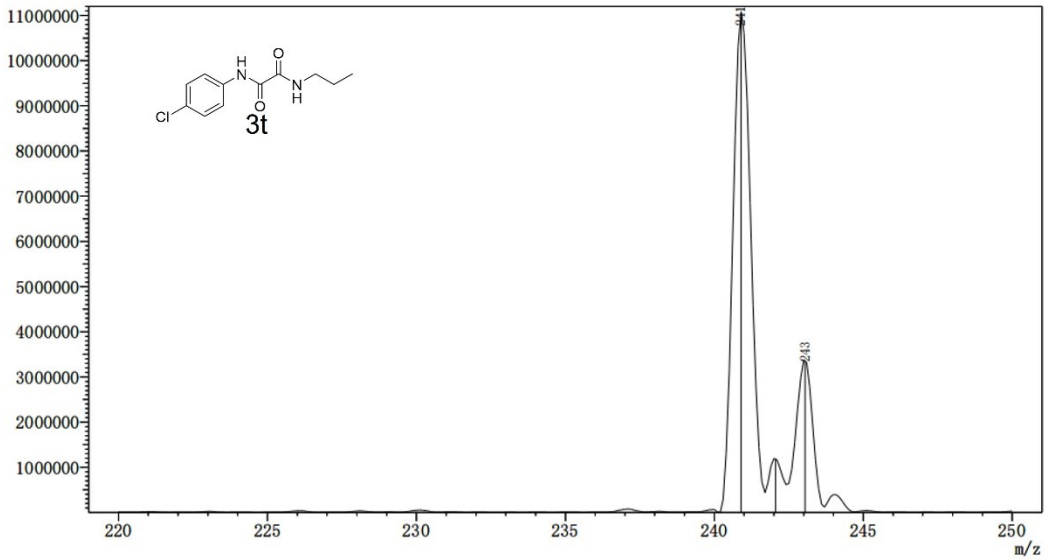

167.60
166.98
164.45
155.25
131.01
130.92
128.75
128.72
115.85
115.64
77.48
77.16
76.84
41.71
22.91
11.60
3s
f1 (ppm)

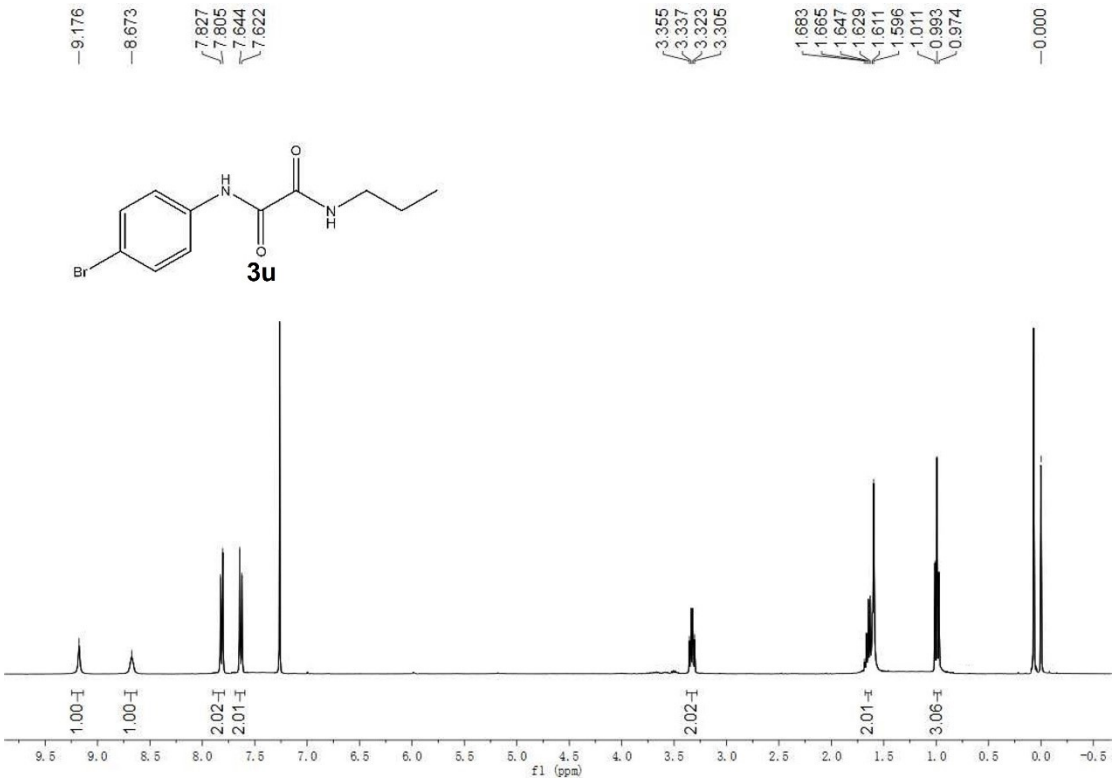

105.75
3s
f1 (ppm)

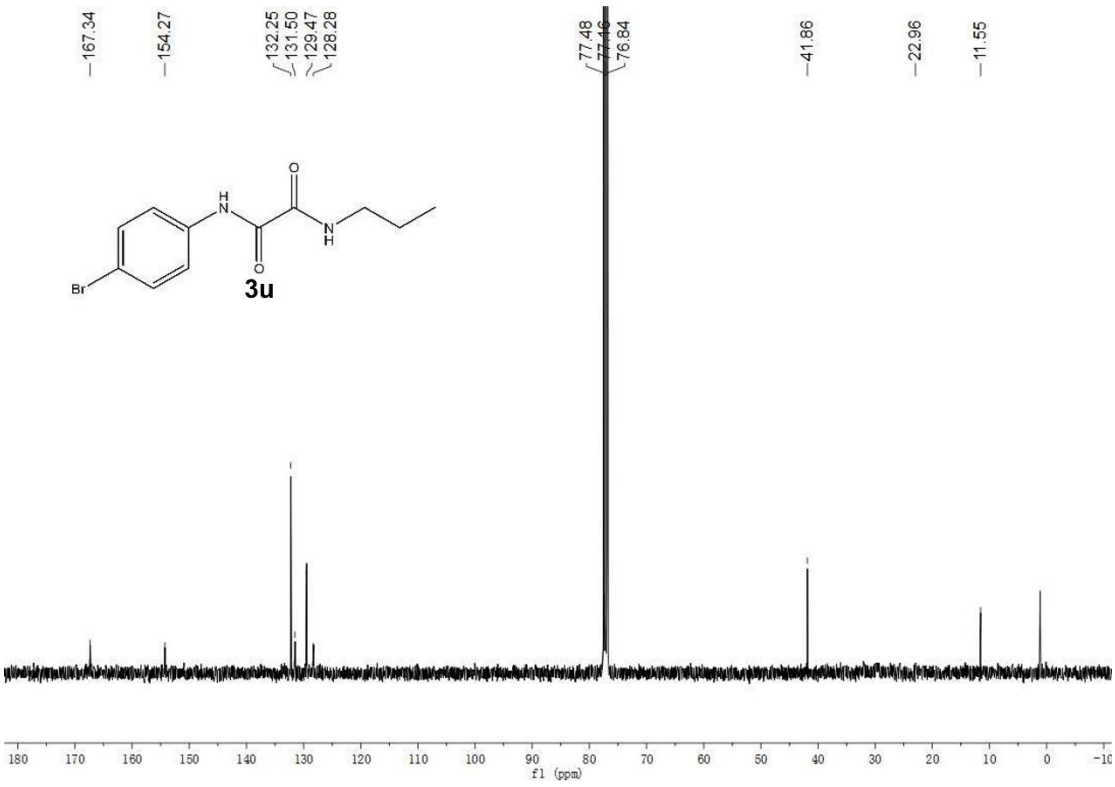

3s
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
215
220
225
230
m/z
226

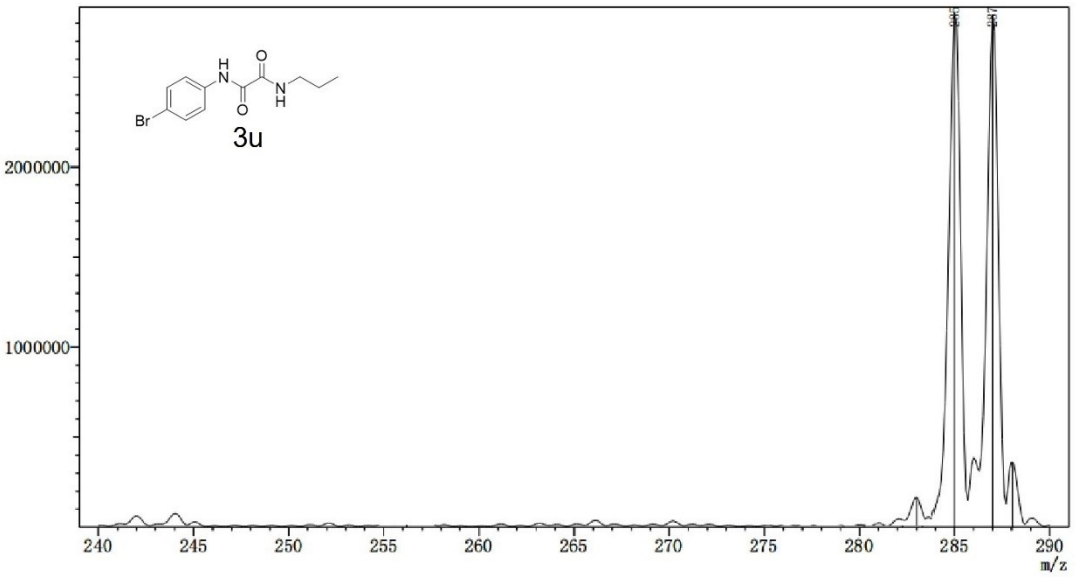

10.076
8.797
8.003
7.981
7.459
7.437
3.352
3.334
3.317
3.302
1.666
1.648
1.630
1.612
1.594
1.014
0.995
0.977
0.000
3t
1.08
1.00
2.09
2.03
2.01
2.03
3.04
f1 (ppm)

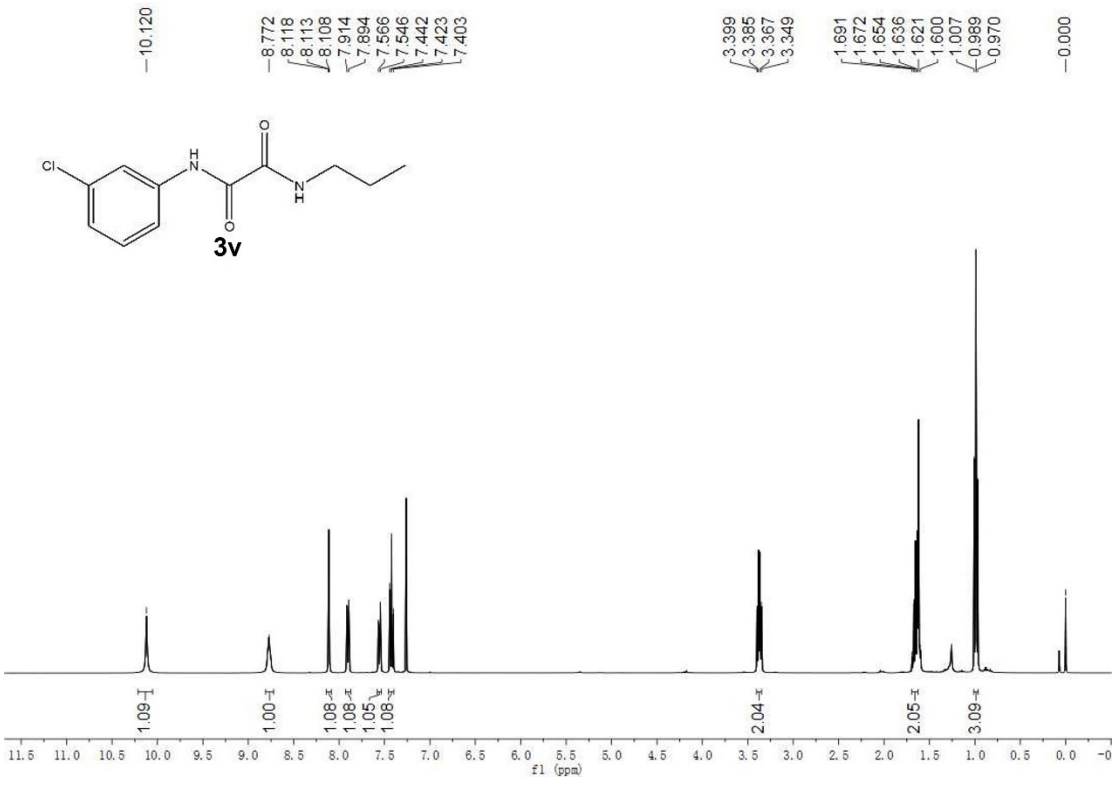

167.65
155.09
139.48
130.94
129.78
128.97
77.48
77.16
76.84
41.76
22.93
11.63
3t
f1 (ppm)

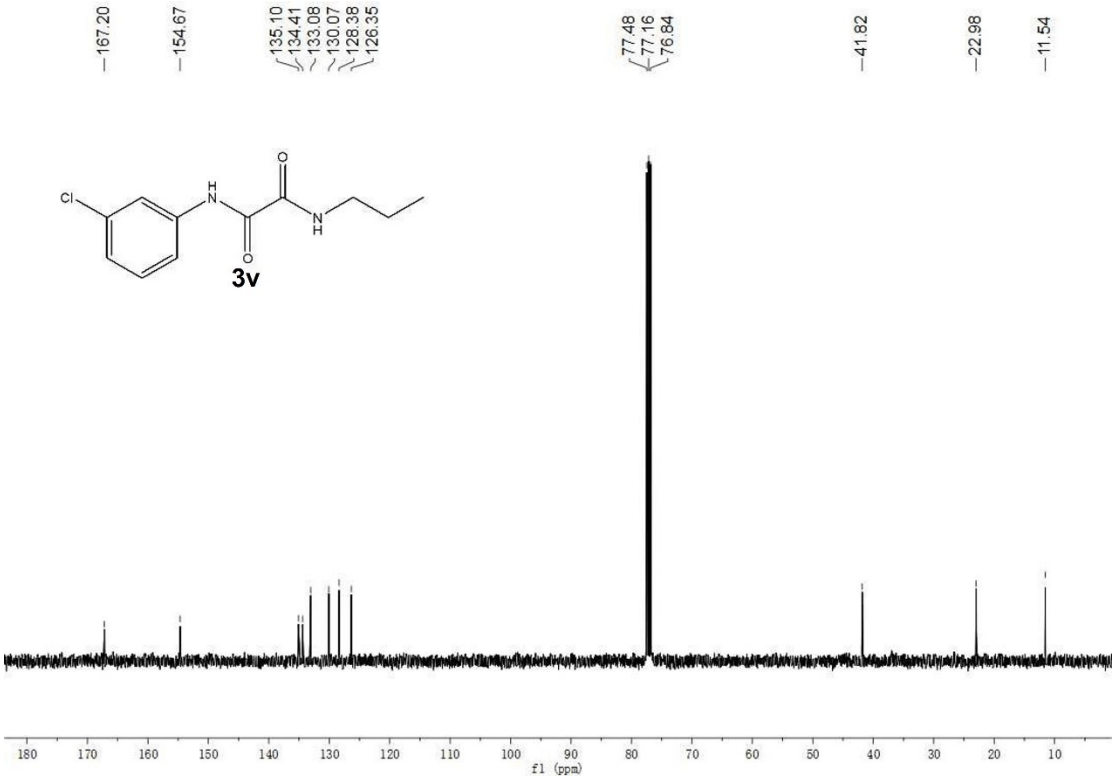

3t
241
243
m/z

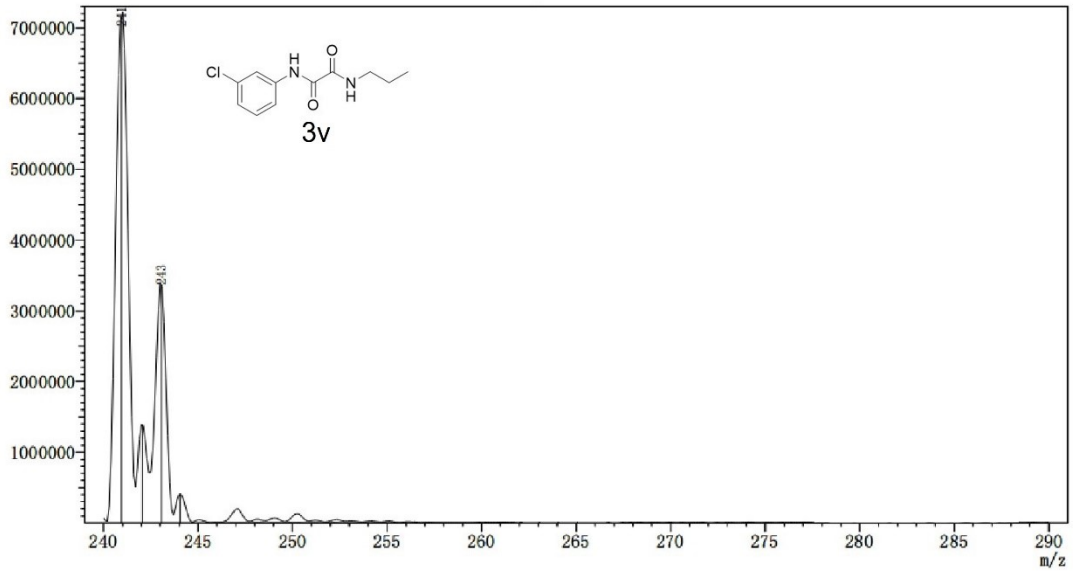

9.176
8.673
7.827
7.805
7.644
7.622
3.355
3.337
3.323
3.305
1.683
1.665
1.647
1.629
1.611
1.596
1.011
0.993
0.974
0.000
3u
1.00
1.00
2.02
2.01
2.02
2.01
3.06
f1 (ppm)


167.34
154.27
132.25
131.50
129.47
128.28
77.48
77.16
76.84
41.86
22.96
11.55
3u
f1 (ppm)

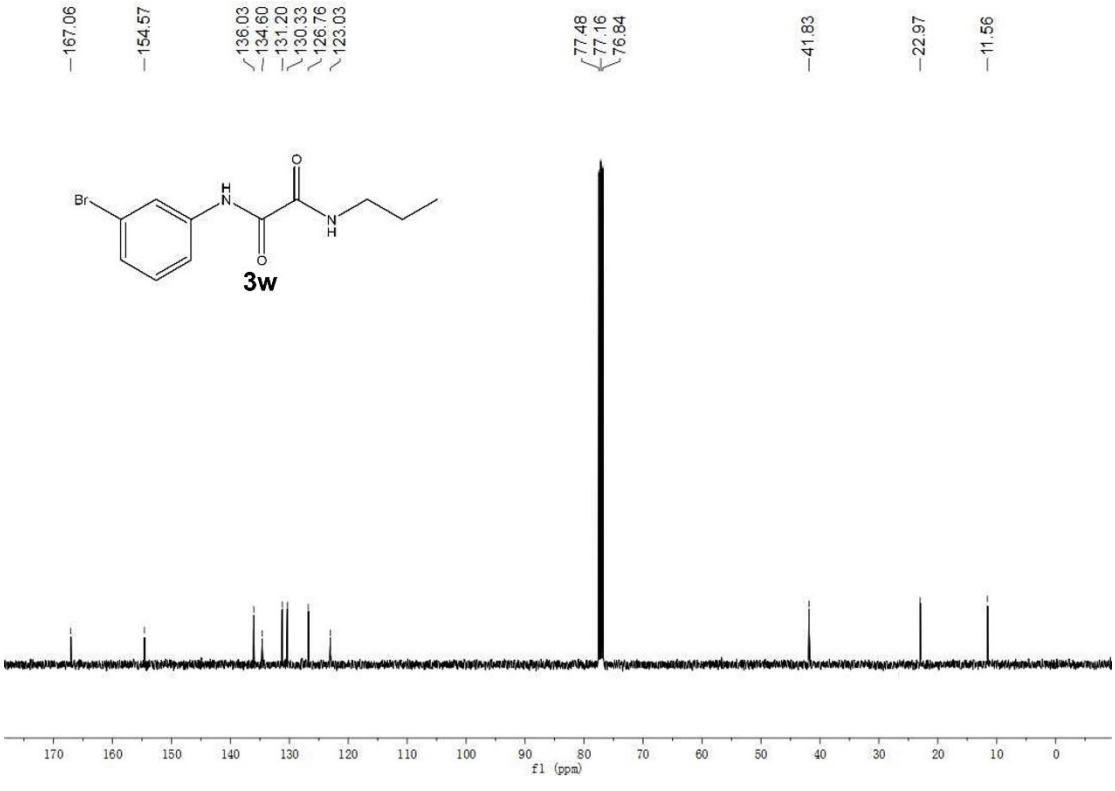

3u
2000000
1000000
240
245
250
255
260
265
270
275
280
285
290
m/z

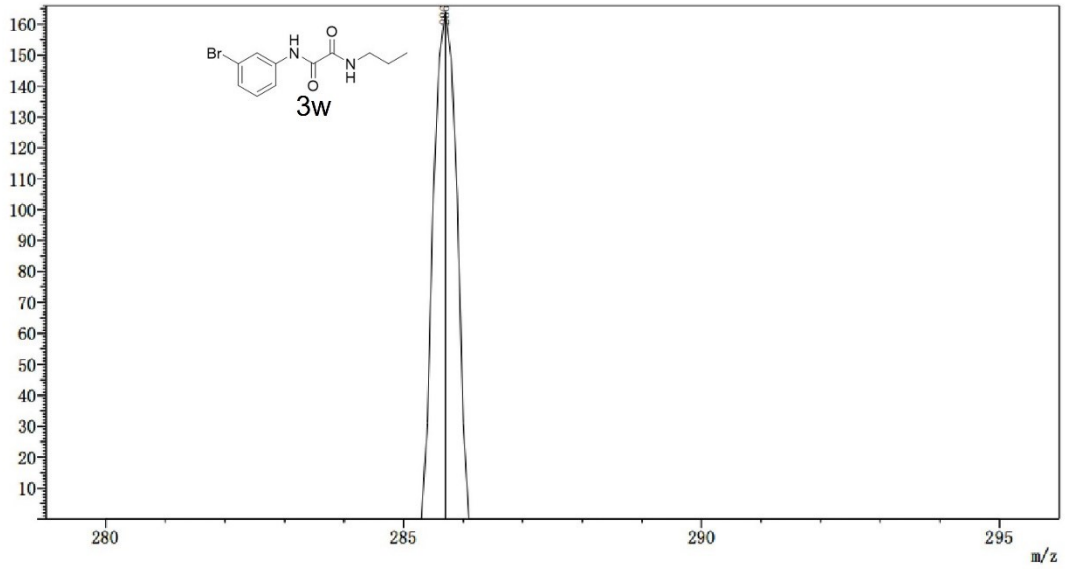

10.120
8.772
8.118
8.113
8.108
7.914
7.894
7.566
7.546
7.442
7.423
7.403
3.399
3.385
3.367
3.349
1.691
1.672
1.654
1.636
1.621
1.600
1.007
0.989
0.970
0.000
3v
1.09
1.00
1.08
1.08
1.05
1.08
2.04
2.05
3.09
f1 (ppm)


167.20
154.67
135.10
134.41
133.08
130.07
128.38
126.35
77.48
77.16
76.84
41.82
22.98
11.54
Cl
H
N
O
O
N
H
3v
f1 (ppm)

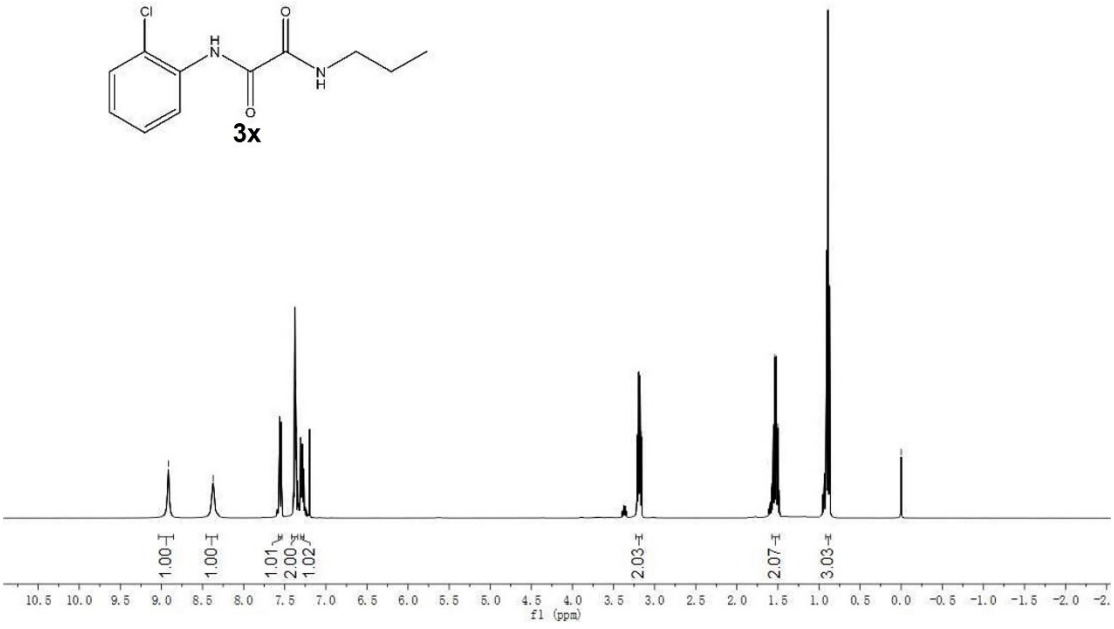

7000000
6000000
5000000
4000000
3000000
2000000
1000000
Cl
H
N
O
O
N
H
3v
m/z

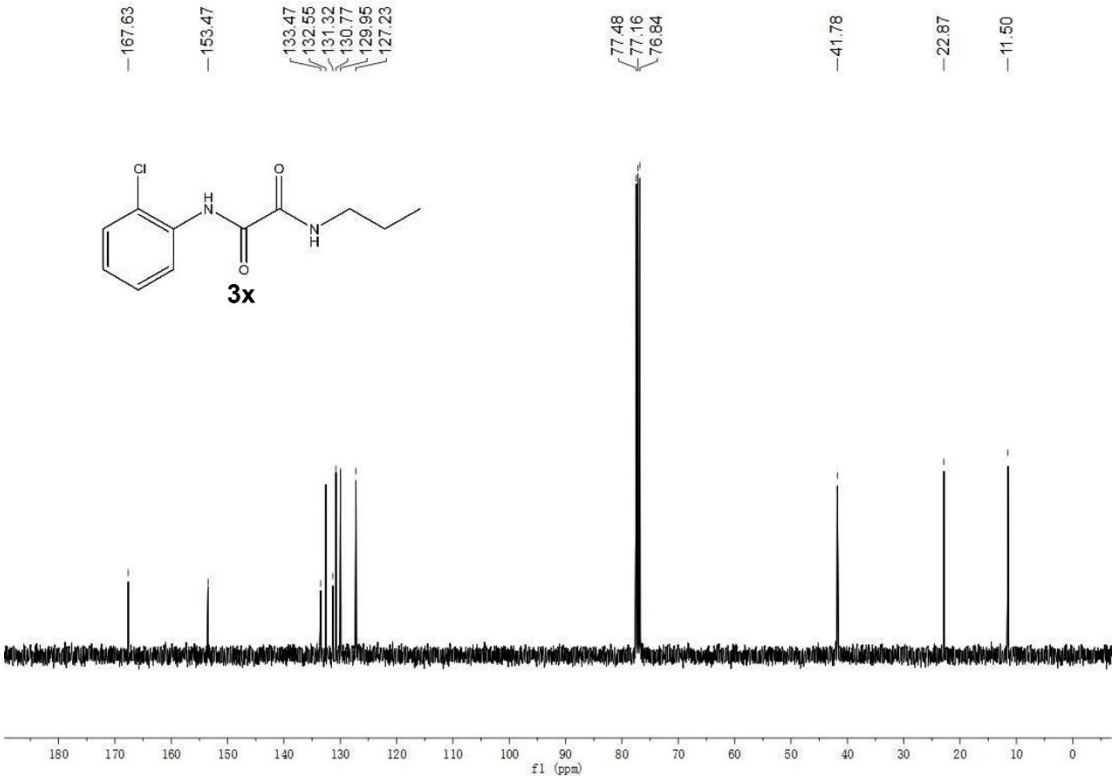

10.021
8.760
8.237
7.947
7.926
7.722
7.705
7.382
7.362
7.343
3.407
3.390
3.375
3.358
1.689
1.670
1.652
1.634
1.626
1.616
1.598
1.008
0.989
0.971
-0.000
Br
N
H
O
O
N
H
3w
1.06
1.00
1.00
1.01
1.01
1.05
2.08
2.16
3.09
f1 (ppm)

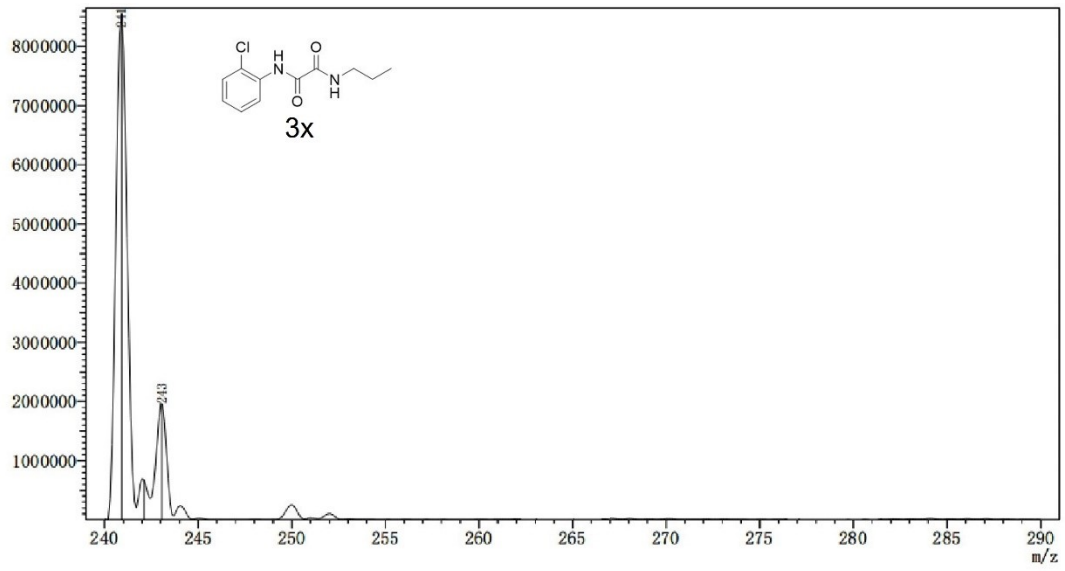

167.06
154.57
136.03
134.60
131.20
130.33
126.76
123.03
77.48
77.16
76.84
41.83
22.97
11.56
Br
N
H
O
O
N
H
3w
f1 (ppm)

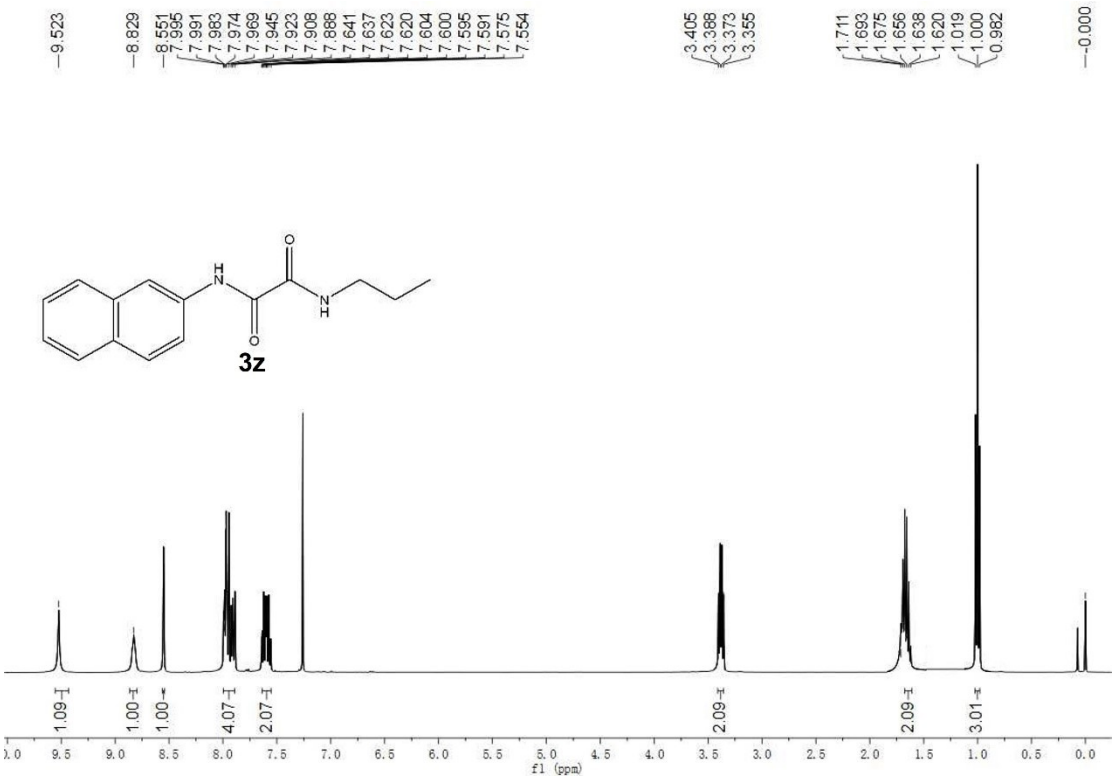

Br
3w
m/z

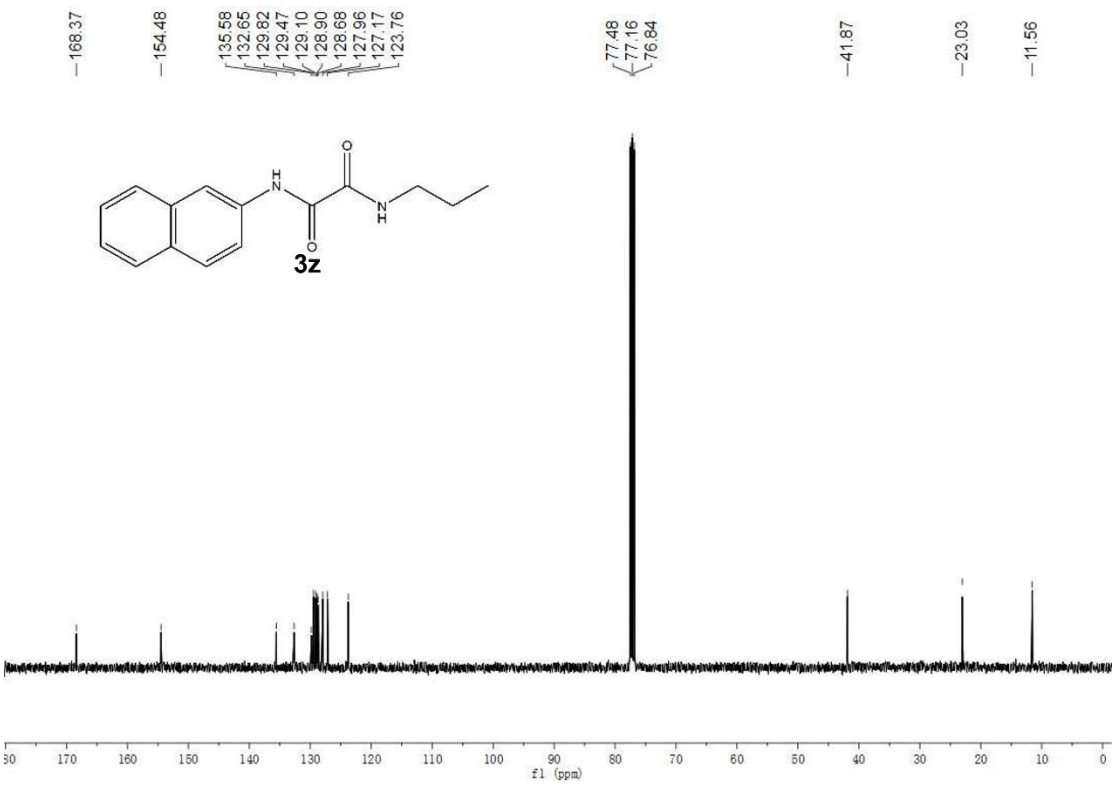

8.916
8.372
7.562
7.544
7.379
7.376
7.370
7.365
7.361
7.306
7.299
7.292
7.287
7.285
7.281
7.272
7.266
3.211
3.193
3.179
3.161
1.575
1.556
1.537
1.519
1.501
1.483
0.908
0.890
0.871
0.000

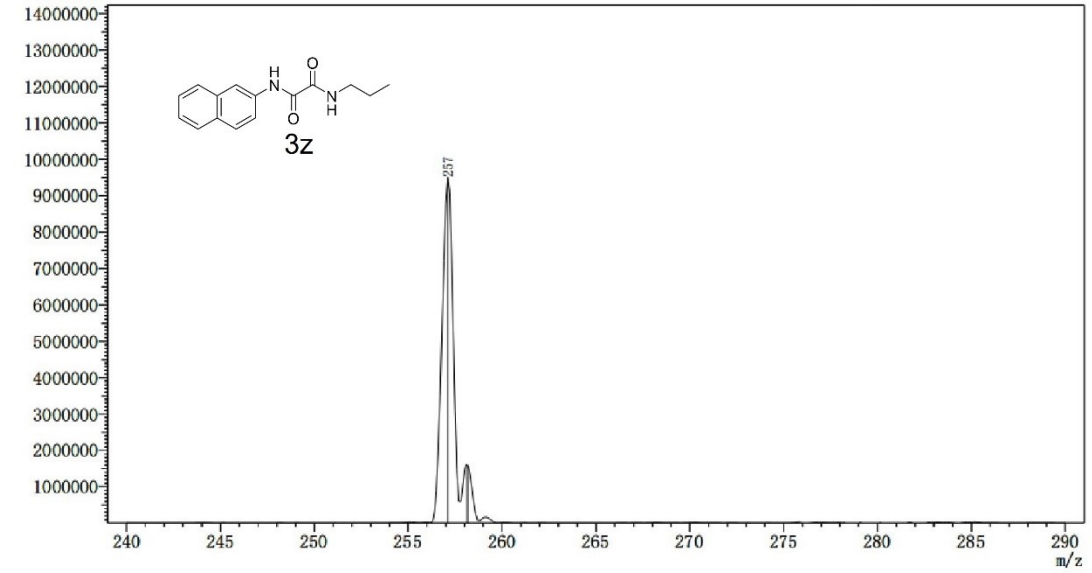

Cl
3x
1.00
1.00
1.01
2.00
1.02
2.03
2.07
3.03
f1 (ppm)

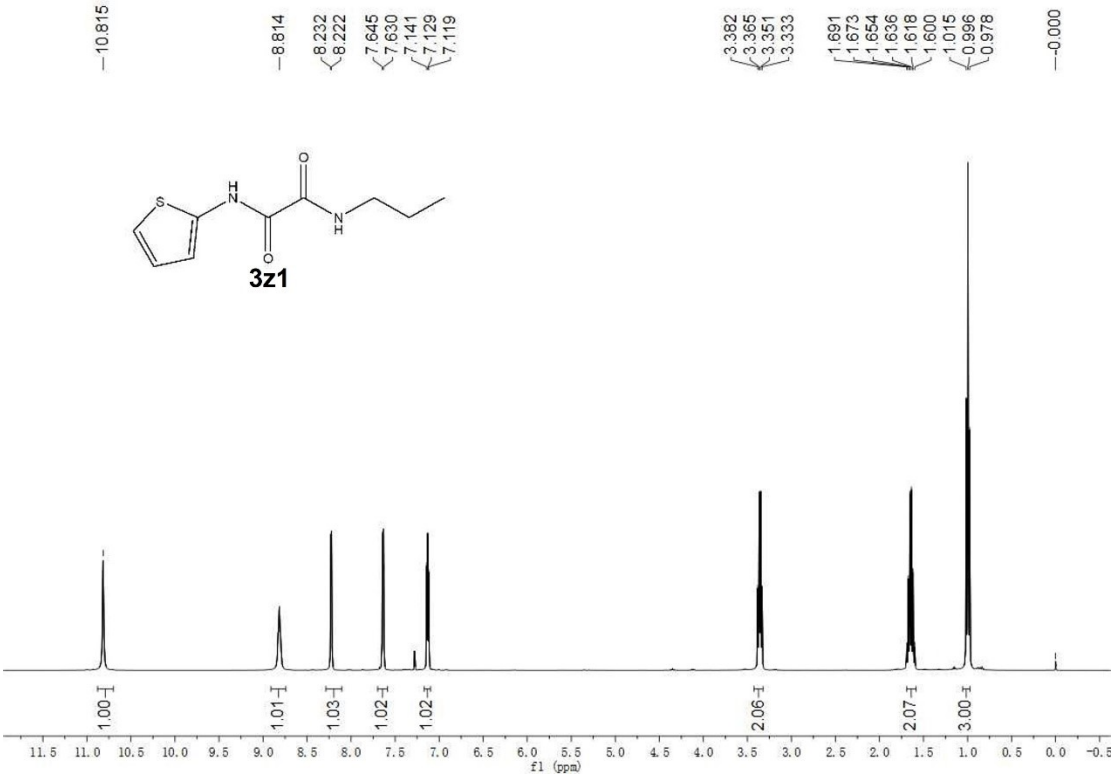

167.63
153.47
133.47
132.55
131.32
130.77
129.95
127.23
77.48
77.16
76.84
41.78
22.87
11.50
Cl
H
N
O
O
H
N
3x
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

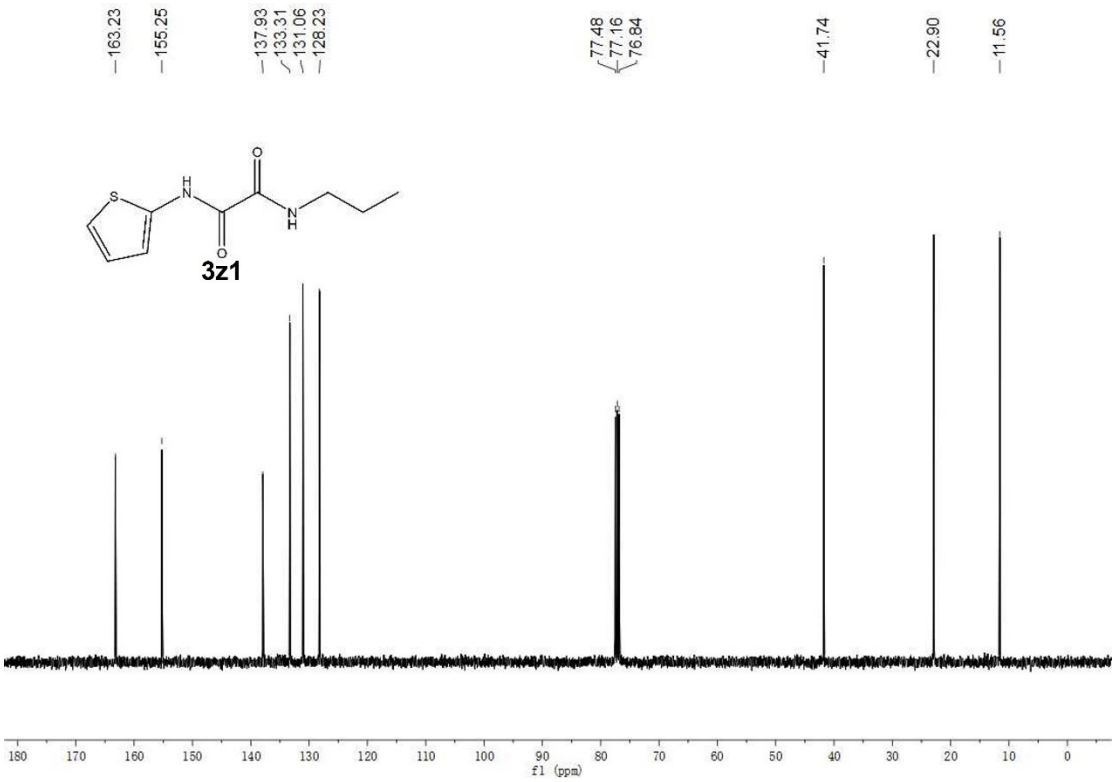

8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
241
243
Cl
H
N
O
O
H
N
3x
240 245 250 255 260 265 270 275 280 285 290
m/z

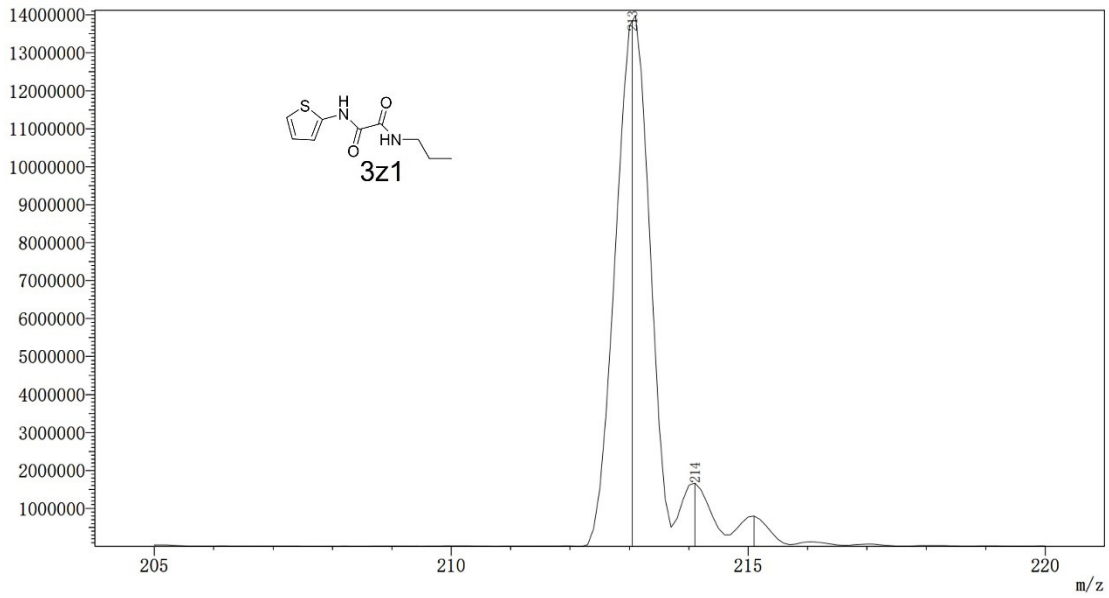

9.523
8.829
8.551
7.995
7.991
7.983
7.974
7.969
7.945
7.923
7.908
7.888
7.641
7.637
7.623
7.620
7.604
7.600
7.595
7.591
7.575
7.554
3.405
3.388
3.373
3.355
1.711
1.693
1.675
1.656
1.638
1.620
1.019
1.000
0.982
0.000
3z
1.09
1.00
1.00
4.07
2.07
2.09
2.09
3.01
f1 (ppm)

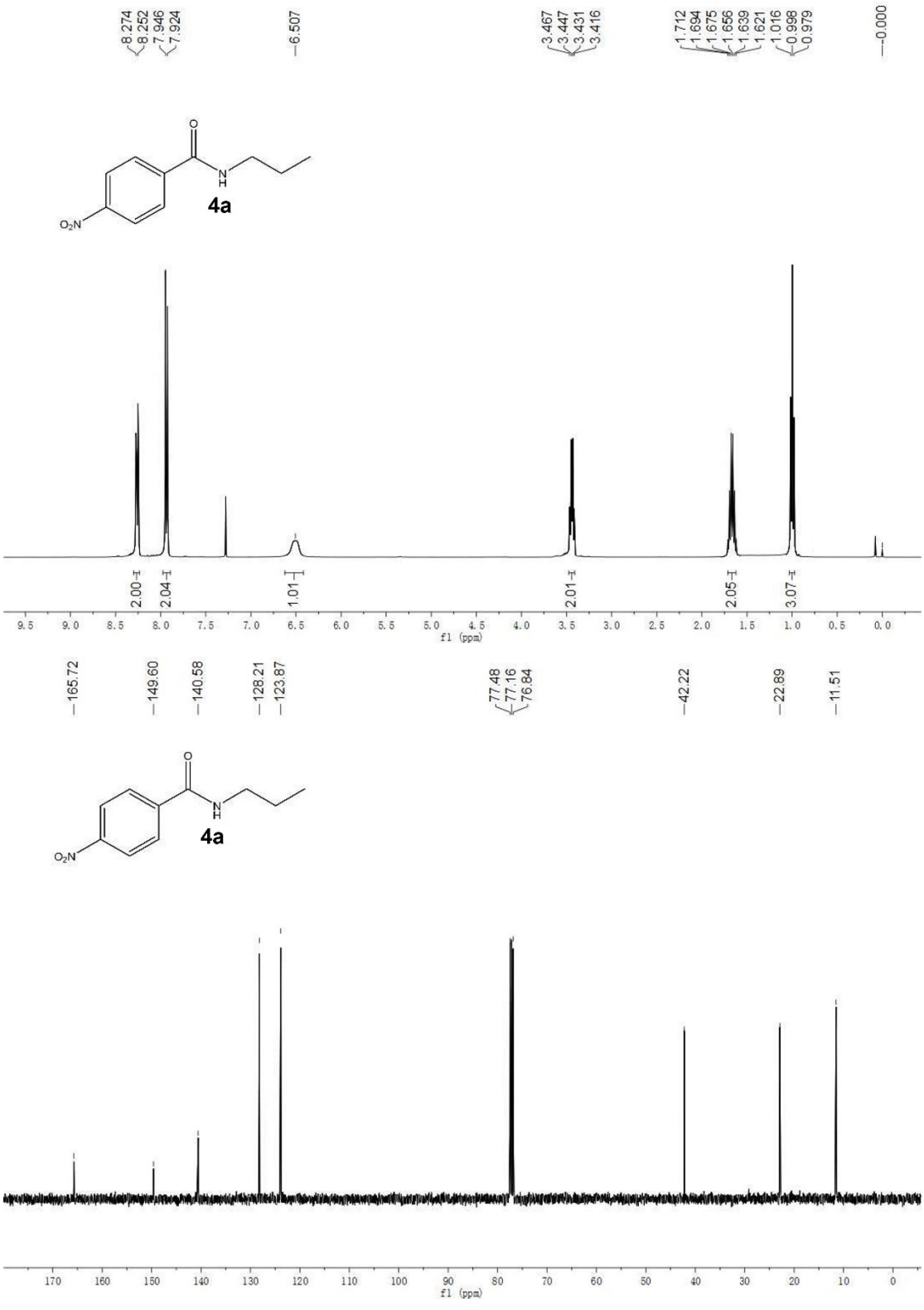

168.37
154.48
135.58
132.65
129.82
129.47
129.10
128.90
128.68
127.96
127.17
123.76
77.48
77.16
76.84
41.87
23.03
11.56
3z
f1 (ppm)


3z
257
m/z


10.815
8.814
8.232
8.222
7.645
7.630
7.141
7.129
7.119
3.382
3.365
3.351
3.333
1.691
1.673
1.654
1.636
1.618
1.600
1.015
0.996
0.978
0.000
3z1
1.00
1.01
1.03
1.02
1.02
2.06
2.07
3.00
f1 (ppm)


163.23
155.25
137.93
133.31
131.06
128.23
77.48
77.16
76.84
41.74
22.90
11.56
3z1
f1 (ppm)


3z1
213
214
m/z


8.274
8.252
7.946
7.924
6.507
3.467
3.447
3.431
3.416
1.712
1.694
1.675
1.656
1.639
1.621
1.016
0.998
0.979
0.000
4a
2.00
2.04
1.01
2.01
2.05
3.07
f1 (ppm)
165.72
149.60
140.58
128.21
123.87
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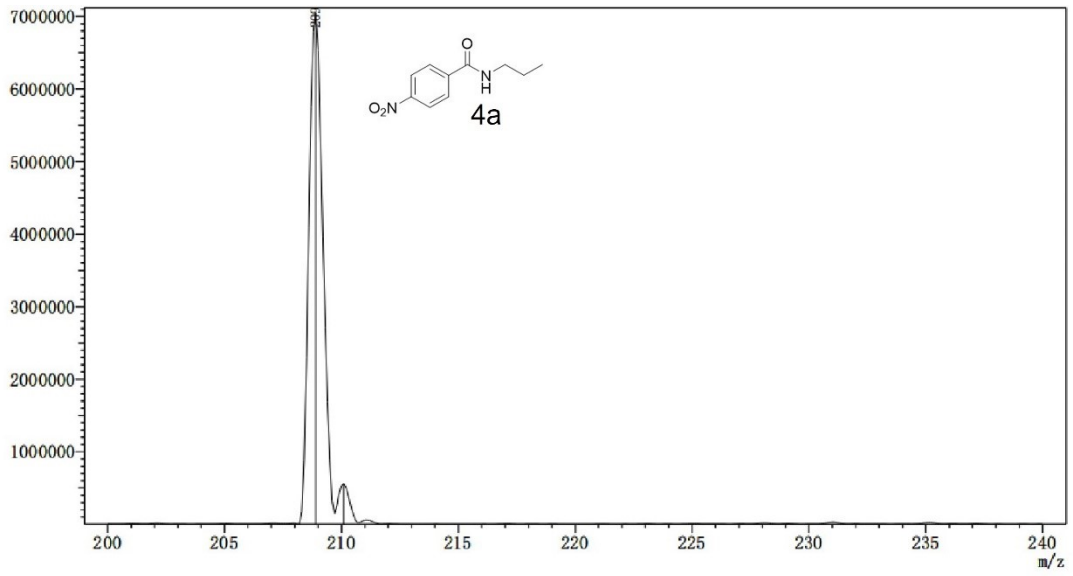
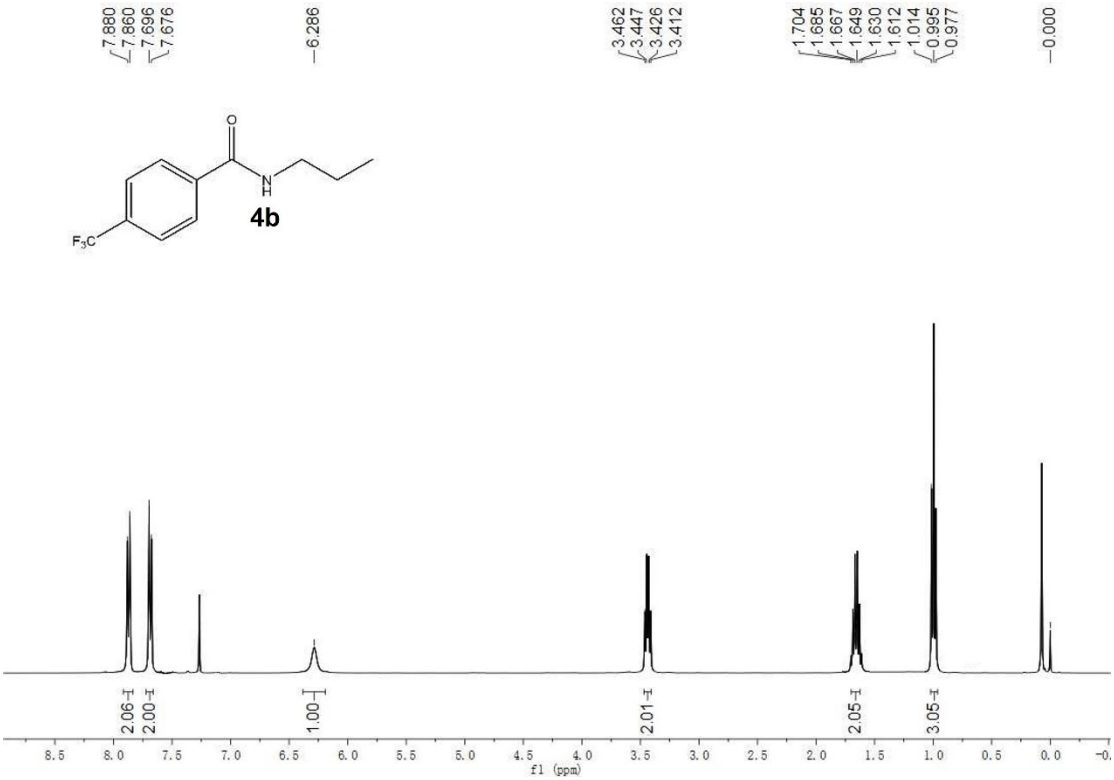
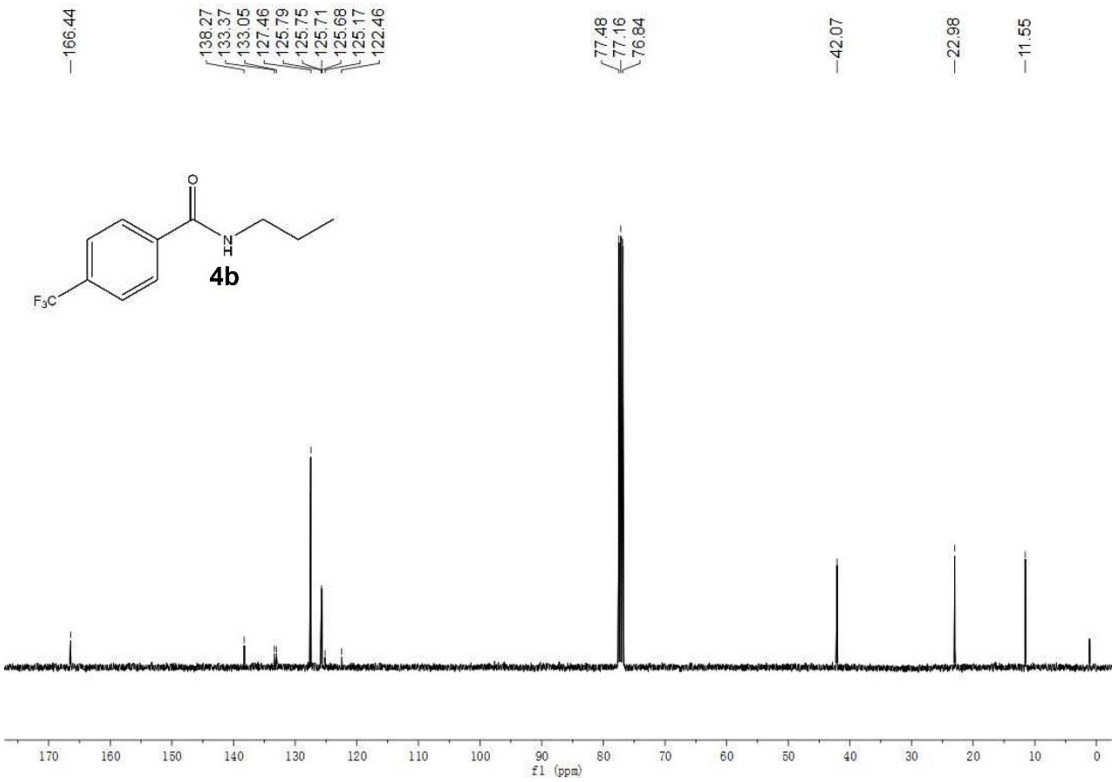
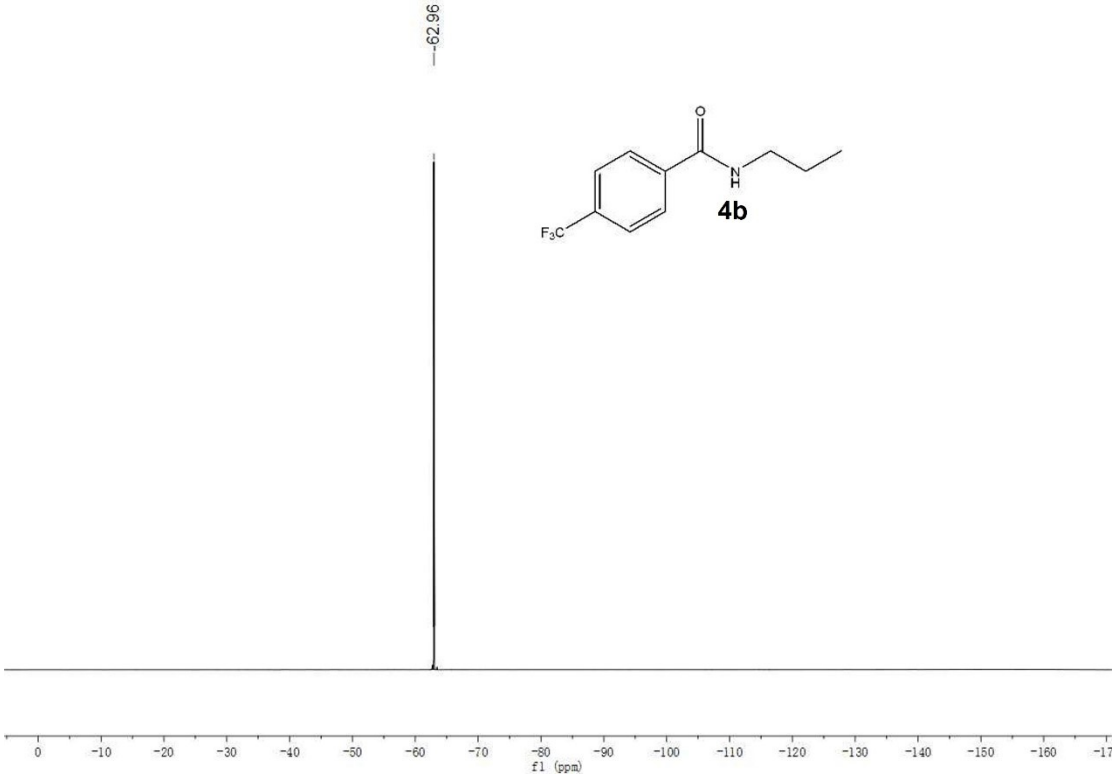
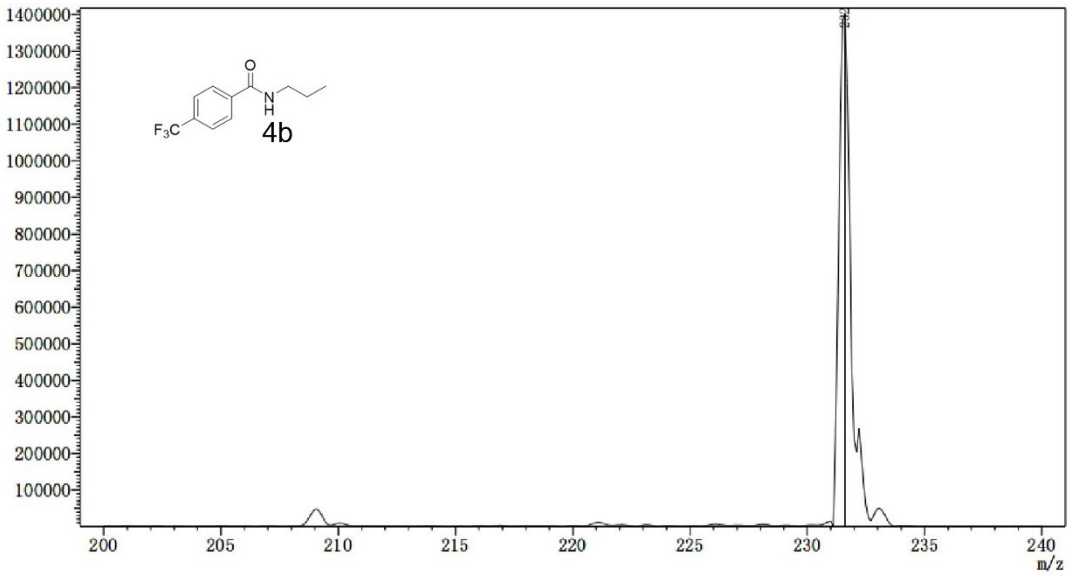
76.84
42.22
22.89
11.51
4a
f1 (ppm)


4a
m/z


4b
f1 (ppm)


166.44
138.27
133.37
133.05
127.46
125.79
125.75
125.71
125.68
125.17
122.46
77.48
77.16
76.84
42.07
22.98
11.55
4b
F3C
f1 (ppm)


-62.96
4b
F3C
f1 (ppm)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900000
800000
700000
600000
500000
400000
300000
200000
100000
200
205
210
215
220
225
230
235
240
m/z
O
N
H
F3C
4b