*Supporting Information*

# Formamidine hydrochloride as an amino surrogate: $I_2$-catalyzed oxidative amidation of aryl methyl ketones leading to free (N-H) α-ketoamides

*Shan Liu, Qinghe Gao, Xia Wu, Jingjing Zhang, Kerong Ding and Anxin Wu**

*Key Laboratory of Pesticide & Chemical Biology, Ministry of Education; College of Chemistry, Central China Normal University, 152 Luoyu Road, Wuhan, Hubei, 430079, People's Republic of China*

*E-mail: chwuax@mail.ccnu.edu.cn*

Table of Contents

## 1. General Information

All substrates and reagents were commercially available and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200-300 mesh). IR spectra were recorded on a Perkin-Elmer PE-983 infrared spectrometer as KBr pellets with absorption in $cm^{-1}$. $^1H$ spectra were recorded in $CDCl_3$ or DMSO-$d_6$ on 400/600 MHz NMR spectrometers and resonances (δ) are given in parts per million relative to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. $^{13}C$ spectra were recorded in $CDCl_3$ or DMSO-$d_6$ on 100/150 MHz NMR spectrometers and resonances (δ) are given in ppm. HRMS were obtained on a Bruker 7-tesla FT-ICR MS equipped with an electrospray source. Melting points were determined using XT-4 apparatus and not corrected.

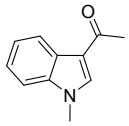
## 2. General Procedures for the Synthesis of 3

A mixture of acetophenone **1a** (1.0 mmol), formamidine hydrochloride **2** (1.0 mmol), iodine (0.8 mmol) in DMSO (2 mL) was stirred at 110 ℃ for 11 h till almost completed conversion of the substrates by TLC analysis, and added 50 mL water to the mixture, then extracted with EtOAc three times (3 × 50 mL). The extract was washed with 10% $Na_2S_2O_3$ solution (w/w), dried over anhydrous $Na_2SO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 5:1) to afford the desired product **3a** as a yellow solid (131.3 mg, 88% yield).

## 3. General Procedures for the Synthesis of 1s, 1t

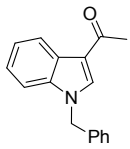
A mixture of **1r** (3.0 mmol), KOH (15.0 mmol), in acetone (5 mL) with five drops of water was stirred in the ice-water bath for 0.5 h, then methyl iodide (45.0 mmol) or benzyl bromide (12.0 mmol) in acetone (2 mL) was dropped into the mixture within 30 min. Ten minutes later, the mixture was stirred at room temperature for 3 h till almost completed conversion of the substrates by TLC analysis, then removed the acetone in vacuo, and added 50 mL water to the mixture, extracted with EtOAc three times (3 × 50 mL), dried over anhydrous $Na_2SO_4$ and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 3:1) to afford the product **1s** or **1t**.

**1-(1-methyl-*1H*-indol-3-yl)ethanone (1s)**

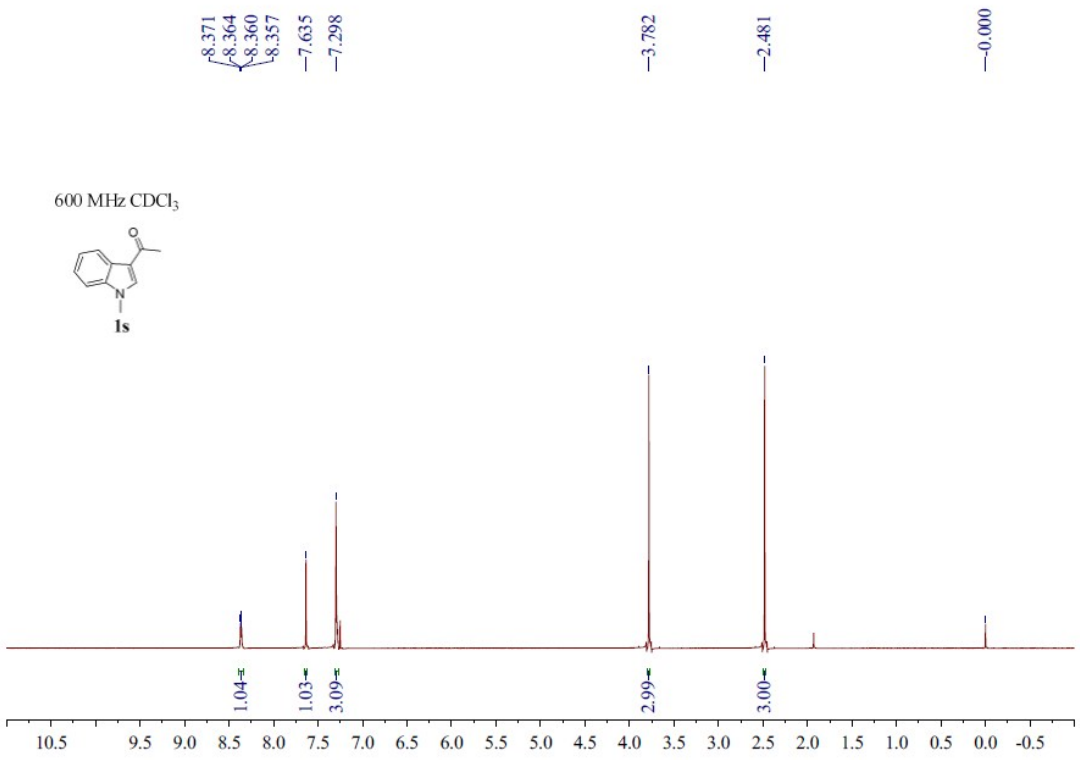


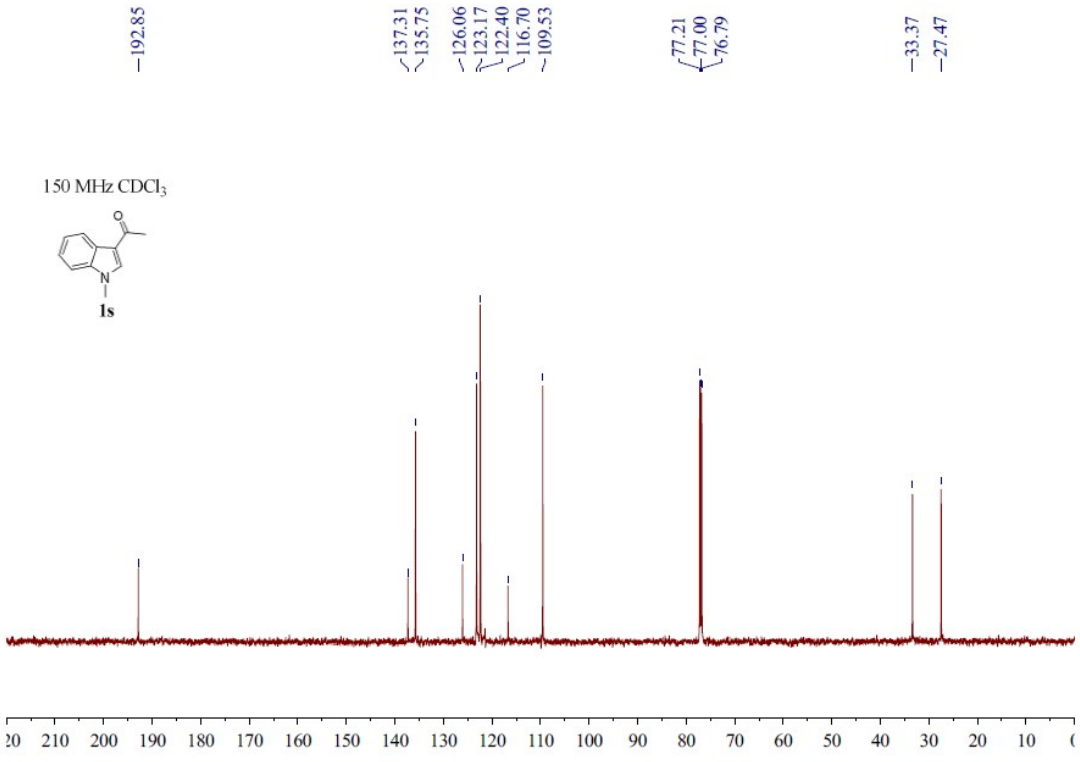

$^1H$ NMR (600 MHz, $CDCl_3$) 8.37-8.36 (m, 1H), 7.64 (s, 1H), 7.30 (s, 3H), 3.78 (s, 3H), 2.48 (s, 3H); $^{13}C$ NMR (150 MHz, $CDCl_3$) δ 192.9, 137.3, 135.8, 126.1, 123.2, 122.4 (x 2), 116.7, 109.5, 33.4, 27.5.

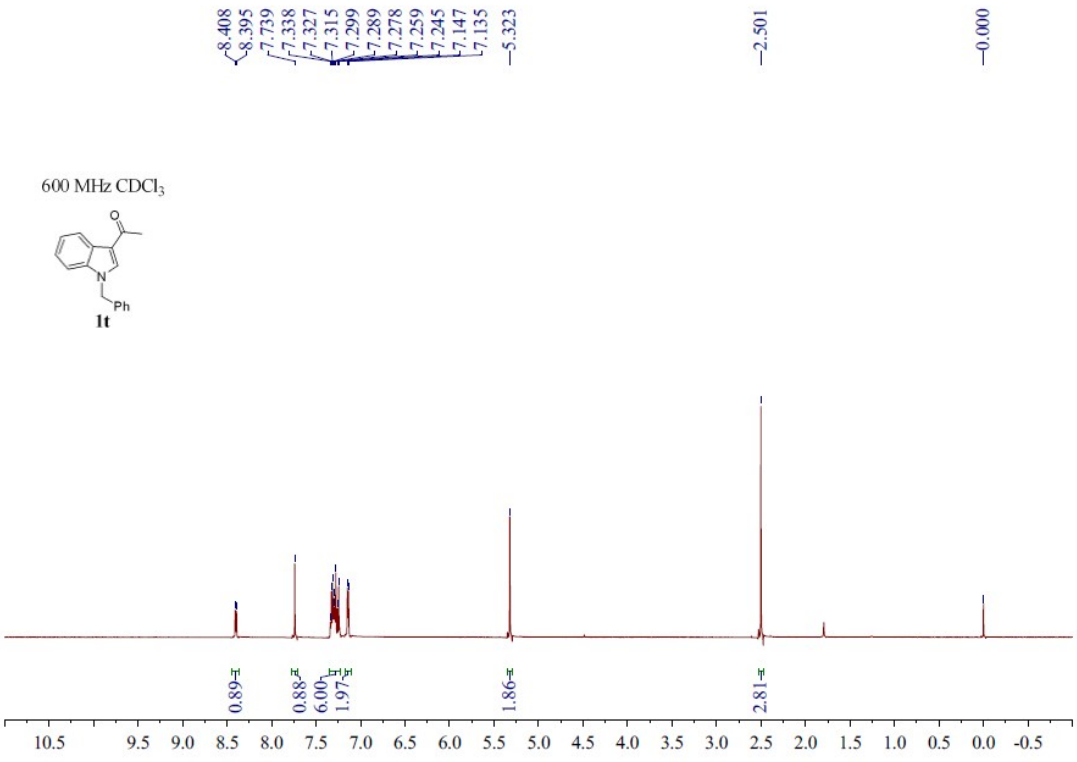
**1-(1-benzyl-*1H*-indol-3-yl)ethanone (1t)**

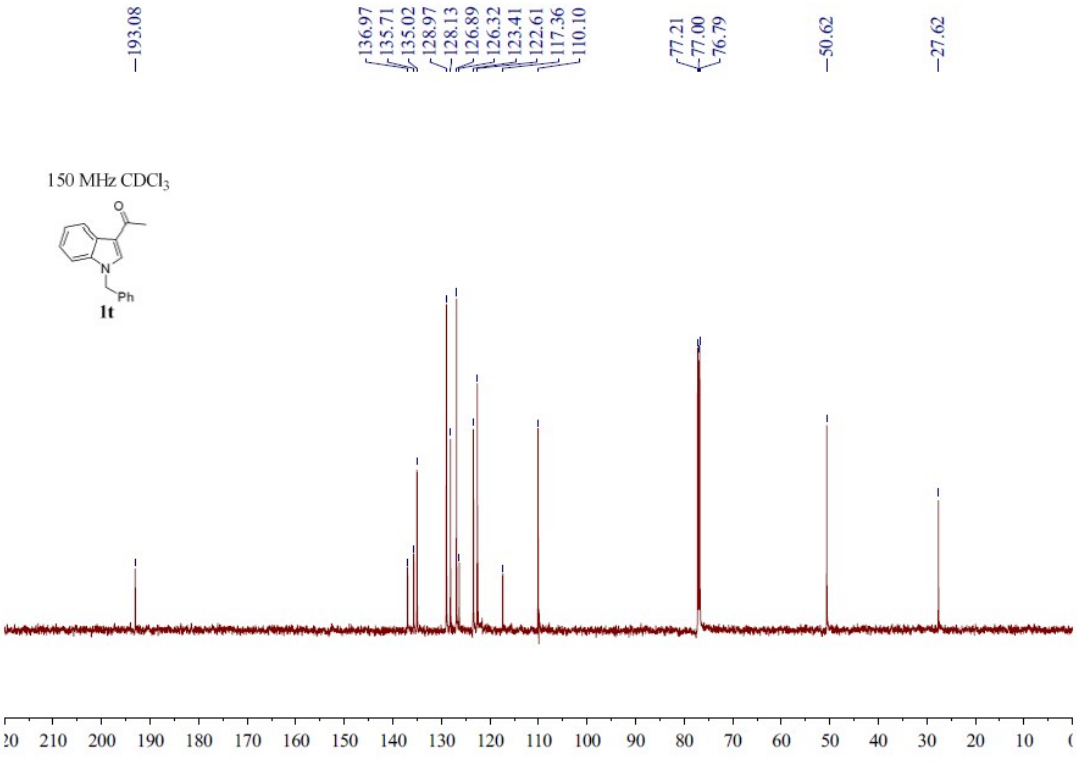



$^1H$ NMR (600 MHz, $CDCl_3$) δ 8.40 (d, $J$ = 7.8 Hz, 1H), 7.74 (s, 1H), 7.34-7.25 (m, 6H), 7.14 (d, $J$ = 7.2 Hz, 2H), 5.32 (s, 2H), 2.50 (s, 3H); $^{13}C$ NMR (150 MHz, $CDCl_3$) δ 193.1, 137.0, 135.7, 135.0, 129.0, 128.1, 126.9, 126.3, 123.4, 122.6 (x 2), 117.4, 110.1, 50.6, 27.6.


8.371
8.364
8.360
8.357
7.635
7.298
3.782
2.481
0.000
600 MHz CDCl3
1s
1.04
1.03
3.09
2.99
3.00
10.5 9.5 9.0 8.5 8.0 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 -0.5

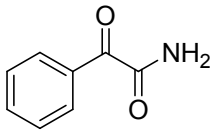

192.85
137.31
135.75
126.06
123.17
122.40
116.70
109.53
77.21
77.00
76.79
33.37
27.47
150 MHz CDCl3
1s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


8.408
8.395
7.739
7.338
7.327
7.315
7.299
7.289
7.278
7.259
7.245
7.147
7.135
5.323
2.501
0.000
600 MHz CDCl3
1t
0.89
0.88
6.00
1.97
1.86
2.81
10.5
9.5
9.0
8.5
8.0
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
-0.5


193.08
136.97
135.71
135.02
128.97
128.13
126.89
126.32
123.41
122.61
117.36
110.10
77.21
77.00
76.79
50.62
27.62
150 MHz CDCl3
1t
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

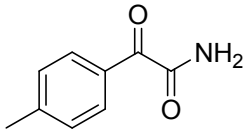
**4. Characterization Data of Compounds**

**2-oxo-2-phenylacetamide (3a)** [1]



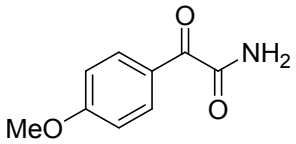
Yield 88%; Yellow solid; mp 69-71 ℃; IR (KBr): 3431, 3209, 1663, 1592, 1577, 1231; $^1$H NMR (600 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.8 Hz, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.05 (br, 1H), 6.32 (br, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 187.6, 164.4, 134.4, 132.8, 130.9, 128.5; MS (EI): m/z 150.09 (M + 1, 0.39%), 149.15 (M, 5.70), 105.05 (100).

**2-oxo-2-(*p*-tolyl)acetamide (3b)** [1]



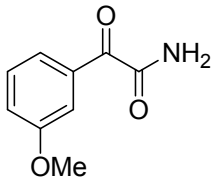
Yield 81%; White solid; mp 131-133 ℃; IR (KBr): 3403, 3199, 1686, 1636, 1603, 1237; $^1$H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.10 (br, 1H), 6.57 (br, 1H), 2.42 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 187.0, 164.7, 145.7, 131.2, 130.4, 129.3, 21.8; MS (EI): m/z 164.20 (M + 1, 0.18%), 163.16 (M, 5.53), 119.10 (100).

**2-(4-methoxyphenyl)-2-oxoacetamide (3c)** [1]



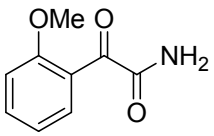
Yield 89%; Yellow solid; mp 145-147 ℃; IR (KBr): 3458, 3198, 1707, 1650, 1604, 1566, 1245, 1169; $^1$H NMR (600 MHz, DMSO-$d_6$) δ 8.27 (br, 1H), 7.97 (d, *J* = 9.0 Hz, 2H), 7.92 (br, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 3.86 (s, 3H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) δ 189.3, 167.6, 164.2, 132.3, 125.6, 114.4, 55.8; MS (EI): m/z 180.18 (M + 1, 1.04%), 179.25 (M, 8.76), 135.15 (100).

**2-(3-methoxyphenyl)-2-oxoacetamide (3d)**



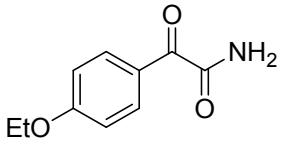
Yield 83%; Yellow solid; mp 96-97 ℃; IR (KBr): 3422, 3172, 1707, 1654, 1592, 1263; $^1$H NMR (600 MHz, DMSO-$d_6$) δ 8.34 (br, 1H), 8.00 (br, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.45 (s, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 3.82 (s, 3H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) δ 190.6, 167.2, 159.4, 134.1, 130.3, 122.6, 120.7, 113.5, 55.4; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_9H_9NNaO_3$: 202.0475; found: 202.0476.

**2-(2-methoxyphenyl)-2-oxoacetamide (3e)**



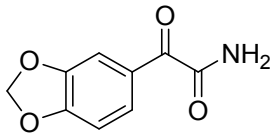
Yield 78%; Yellow solid; mp 120-121 ℃; IR (KBr): 3411, 3181, 1696, 1673, 1651, 1599, 1293; $^1$H NMR (600 MHz, DMSO-$d_6$) δ 8.02 (br, 1H), 7.64 (br, 1H), 7.61 (t, $J$ = 7.2 Hz, 2H), 7.18 (d, $J$ = 8.4 Hz, 1H), 7.09-7.07 (m, 1H), 3.80 (s, 3H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) δ 191.7, 167.8, 159.5, 135.2, 130.3, 124.1, 120.8, 112.8, 56.1; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_9H_9NNaO_3$: 202.0475; found: 202.0477.

**2-(4-ethoxyphenyl)-2-oxoacetamide (3f)**



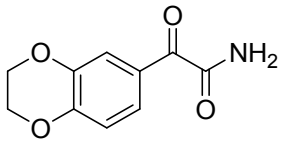

Yield 84%; Yellow solid; mp 111-113 ℃; IR (KBr): 3396, 3312, 3257, 1684, 1656, 1600, 1566; $^1$H NMR (600 MHz, DMSO-$d_6$) δ 8.26 (br, 1H), 7.96 (d, $J$ = 8.4 Hz, 2H), 7.92 (br, 1H), 7.08 (d, $J$ = 8.4 Hz, 2H), 4.13 (q, $J$ = 6.6 Hz, 2H), 1.34 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) δ 189.3, 167.6, 163.5, 132.3, 125.5, 114.7, 63.8, 14.5; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{10}H_{11}NNaO_3$: 216.0631; found: 216.0633.

**2-(benzo[*d*][1,3]dioxol-5-yl)-2-oxoacetamide (3g)**



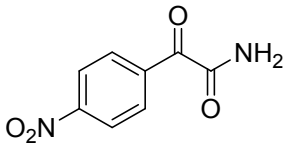

Yield 76%; Yellow solid; mp 174-176 ℃; IR (KBr): 3426, 3199, 1707, 1648, 1591, 1256; $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.26 (br, 1H), 7.91 (br, 1H), 7.64-7.62 (m, 1H), 7.41 (s, 1H), 7.09 (d, $J$ = 8.4 Hz, 1H), 6.17 (s, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 188.9, 167.3, 152.7, 148.1, 127.5, 127.3, 108.4, 107.8, 102.4; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_9H_7NNaO_4$: 216.0267; found: 216.0270.

**2-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-2-oxoacetamide (3h)**



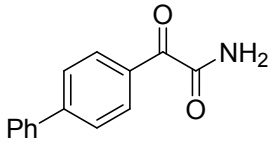

Yield 86%; Yellow solid; mp 158-161 ℃; IR (KBr): 3444, 3201, 1691, 1651, 1587, 1292, 1258; $^1$H NMR (600 MHz, DMSO-$d_6$) δ 8.26 (br, 1H), 7.91 (br, 1H), 7.53-7.51 (m, 1H), 7.46 (s, 1H), 7.03 (d, $J$ = 8.4 Hz, 1H), 4.36-4.35 (m, 2H), 4.30-4.29 (m, 2H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) δ 189.1, 167.3, 149.1, 143.4, 126.2, 124.1, 118.4, 117.6, 64.8, 64.0; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{10}H_9NNaO_4$: 230.0424; found: 230.0426.

**2-(4-nitrophenyl)-2-oxoacetamide (3i)**



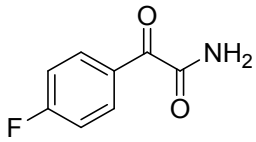

Yield 69%; Yellow solid; mp 157-159 ℃; IR (KBr): 3447, 3223, 1713, 1686, 1524, 1349, 1222; $^1$H NMR (600 MHz, $CDCl_3$) δ 8.52 (d, $J$ = 8.4 Hz, 2H), 8.33 (d, $J$ = 9.0 Hz, 2H), 7.08 (br, 1H), 6.15 (br, 1H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) δ 189.0, 165.7, 150.4, 137.6, 131.2, 123.9; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_8H_6N_2NaO_4$: 217.0220; found: 217.0218.

**2-([1,1'-biphenyl]-4-yl)-2-oxoacetamide (3j)**



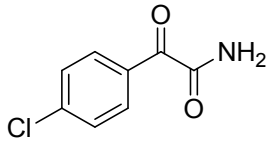
Yield 82%; White solid; mp 177-179 ℃; IR (KBr): 3426, 1662, 1599, 1405, 1241, 751; $^1$H NMR (600 MHz, DMSO-$d_6$) δ 8.36 (br, 1H), 8.07 (d, $J$ = 7.8 Hz, 2H), 8.03 (br, 1H), 7.90 (d, $J$ = 8.4 Hz, 2H), 7.77 (d, $J$ = 7.8 Hz, 2H), 7.53-7.51 (m, 2H), 7.46-7.44 (m, 1H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) δ 190.3, 167.2, 145.7, 138.7, 131.6, 130.4, 129.2, 128.7, 127.1 (x 2); HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{14}H_{11}NNaO_2$: 248.0682; found: 248.0683.

**2-(4-fluorophenyl)-2-oxoacetamide (3k)** [1]



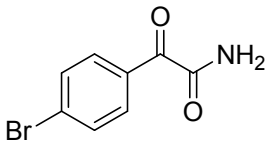
Yield 87%; Yellow solid; mp 150-151 ℃; IR (KBr): 3454, 3200, 1717, 1668, 1580, 1229; $^1$H NMR (600 MHz, DMSO-$d_6$) δ 8.35 (br, 1H), 8.09-8.07 (m, 2H), 8.04 (br, 1H), 7.42-7.39 (m, 2H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) δ 189.1, 166.8, 166.6, 164.9, 132.9, 129.6, 116.3, 116.1; MS (EI): m/z 168.16 (M + 1, 0.54%), 167.19 (M, 7.55), 123.07 (100).

**2-(4-chlorophenyl)-2-oxoacetamide (3l)**



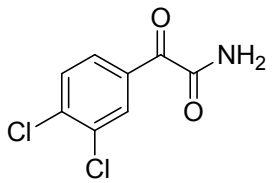
Yield 86%; Yellow solid; mp 130-131 ℃; IR (KBr): 3433, 3205, 1713, 1664, 1579, 1234; $^1$H NMR (600 MHz, $CDCl_3$) δ 8.30 (d, $J$ = 8.4 Hz, 2H), 7.46 (d, $J$ = 9.0 Hz, 2H), 7.07 (br, 1H), 6.31 (br, 1H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) δ 189.4, 166.5, 139.5, 131.6, 131.5, 129.2; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_8H_6ClNNaO_2$: 205.9979; found: 205.9978.

**2-(4-bromophenyl)-2-oxoacetamide (3m)** [1]



Yield 85%; Yellow solid; mp 123-125 ℃; IR (KBr): 3422, 3222, 1687, 1659, 1580, 1230; $^1$H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, $J$ = 8.4 Hz, 2H), 7.63 (d, $J$ = 7.8 Hz, 2H), 7.09 (br, 1H), 6.41 (br, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 186.1, 163.5, 132.6, 131.9, 131.7, 130.3; MS (EI): m/z 229.20 (M + 1, 6.38%), 228.63 (M, 1.18), 183.06 (100).

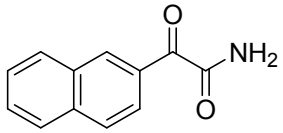
**2-(3,4-dichlorophenyl)-2-oxoacetamide (3n)**



Yield 67%; Yellow solid; mp 188-189 ℃; IR (KBr): 3453, 3210, 1709, 1668, 1222; $^1$H NMR (600

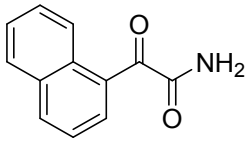
MHz, DMSO-$d_6$) δ 8.39 (br, 1H), 8.17 (s, 1H), 8.11 (br, 1H), 7.96 (d, $J$ = 8.4 Hz, 1H), 7.85 (d, $J$ = 8.4 Hz, 1H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) δ 187.8, 165.5, 137.3, 133.1, 131.9, 131.4, 131.3, 129.9; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_8H_5Cl_2NNaO_2$: 239.9590; found: 239.9590.

**2-(naphthalen-2-yl)-2-oxoacetamide (3o)** [1]



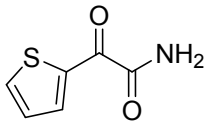
Yield 80%; Pink solid; mp 194-196 ℃; IR (KBr): 3409, 3208, 1694, 1665, 1595, 1222; $^1$H NMR (600 MHz, DMSO-$d_6$) δ 8.67 (s, 1H), 8.45 (br, 1H), 8.17 (d, $J$ = 7.8 Hz, 1H), 8.10 (br, 1H), 8.07 (d, $J$ = 8.4 Hz, 1H), 8.02-7.99 (m, 2H), 7.72-7.69 (m, 1H), 7.65-7.62 (m, 1H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) δ 190.9, 167.3, 135.6, 132.8, 132.0, 130.1, 129.9, 129.5, 128.8, 127.9, 127.3, 123.9; MS (EI): m/z 200.23 (M + 1, 2.71%), 199.25 (M, 20.83), 155.15 (100).

**2-(naphthalen-1-yl)-2-oxoacetamide (3p)**



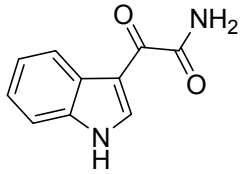
Yield 58%; Yellow solid; mp 159-160 ℃; IR (KBr): 3413, 3219, 1716, 1677, 1241; $^1$H NMR (600 MHz, DMSO-$d_6$) δ 8.81 (d, $J$ = 8.4 Hz, 1H), 8.45 (br, 1H), 8.27 (d, $J$ = 8.4 Hz, 1H), 8.08 (br, 1H), 8.08-8.07 (m, 2H), 7.73-7.63 (m, 3H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) δ 193.7, 167.6, 134.8, 133.5, 133.3 (1), 133.2 (7), 130.3, 128.9 (4), 128.8 (9), 128.8, 126.8, 124.9; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{12}H_9NNaO_2$: 222.0526; found: 222.0529.

**2-oxo-2-(thiophen-2-yl)acetamide (3q)**



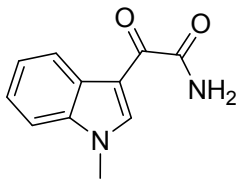
Yield 43%; Brown solid; mp 83-85 ℃; IR (KBr): 3443, 2923, 1707, 1648, 1410, 1348, 1244; $^1$H NMR (600 MHz, DMSO-$d_6$) δ 8.31 (br, 1H), 8.16 (d, $J$ = 4.8 Hz, 1H), 8.13 (d, $J$ = 4.2 Hz, 1H), 7.99 (br, 1H), 7.29-7.28 (m, 1H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) δ 180.6, 164.4, 138.8, 137.4, 137.3, 128.8; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_6H_5NNaO_2S$: 177.9933; found: 177.9932.

**2-(*1H*-indol-3-yl)-2-oxoacetamide (3r)**



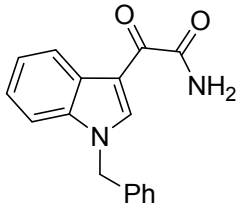
Yield 79%; Brown solid; mp 249-251 ℃; IR (KBr): 3396, 3258, 1667, 1615, 1598, 1580, 1408; $^1$H NMR (600 MHz, DMSO-$d_6$) δ 12.2 (br, 1H), 8.71 (d, $J$ = 3.6 Hz, 1H), 8.24-8.23 (m, 1H), 8.10 (br, 1H), 7.73 (br, 1H), 7.54-7.53 (m, 1H), 7.27-7.24 (m, 2H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) δ 183.0, 166.1, 136.4, 126.2, 123.5, 122.6, 121.4, 121.3, 112.6, 112.2; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{10}H_8N_2NaO_2$: 211.0478; found: 211.0481.

**2-(1-methyl-*1H*-indol-3-yl)-2-oxoacetamide (3s)**



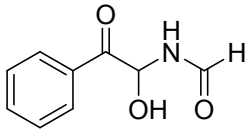
Yield 73%; Brown solid; mp 178-180 ℃; IR (KBr): 3373, 3220, 3056, 2908, 1705, 1626, 1591, 1519, 1347; $^1$H NMR (600 MHz, DMSO-$d_6$) δ 7.86 (s, 1H), 7.36 (d, $J$ = 7.8 Hz, 1H), 7.23 (br, 1H), 6.87 (br, 1H), 6.69 (d, $J$ = 7.8 Hz, 1H), 6.45-6.40 (m, 2H), 3.02 (s, 3H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) δ 182.4, 166.0, 141.7, 137.0, 126.7, 123.4, 122.9, 121.5, 121.3, 111.0, 33.3; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{11}H_{10}N_2NaO_2$: 225.0635; found: 225.0638.

**2-(1-benzyl-*1H*-indol-3-yl)-2-oxoacetamide (3t)**



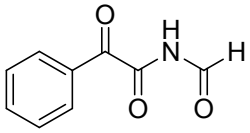
Yield 71%; Brown solid; mp 184-186 ℃; IR (KBr): 3392, 3191, 3128, 2922, 2852, 1697, 1624, 1593, 1515, 1355, 1175; $^1$H NMR (600 MHz, DMSO-$d_6$) δ 8.93 (s, 1H), 8.26-8.25 (m, 1H), 8.14 (br, 1H), 7.78 (br, 1H), 7.59-7.57 (m, 1H), 7.34 (t, $J$ = 7.2 Hz, 2H), 7.29-7.27 (m, 5H), 5.59 (s, 2H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) δ 182.7, 165.9, 136.8, 136.3, 129.3, 128.8, 128.7, 128.3, 127.8, 127.4, 127.3, 126.9, 123.5, 111.5, 49.8; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{17}H_{14}N_2NaO_2$: 301.0948; found: 301.0950.

***N*-(1-hydroxy-2-oxo-2-phenylethyl)formamide (A')**



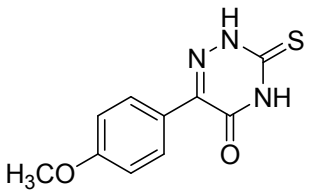
$^1$H NMR (600 MHz, DMSO-$d_6$) δ 9.00 (d, $J$ = 8.4 Hz, 1H), 8.12 (s, 1H), 8.00 (d, $J$ = 7.2 Hz, 2H), 7.67-7.64 (m, 1H), 7.54 (t, $J$ = 7.8 Hz, 2H), 6.77 (d, $J$ = 7.2 Hz, 1H), 6.43-6.40 (m, 1H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) δ 194.6, 161.2, 133.9, 133.8, 128.9, 128.8, 70.9; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_9H_9NNaO_3$: 202.0475; found: 202.0476.

***N*-formyl-2-oxo-2-phenylacetamide (B)**



$^1$H NMR (600 MHz, DMSO-$d_6$) δ 11.99 (s, 1H), 9.05 (s, 1H), 8.00 (d, $J$ = 7.8 Hz, 2H), 7.78 (t, $J$ = 7.2 Hz, 1H), 7.62 (t, $J$ = 7.8 Hz, 2H); HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_9H_7NNaO_3$: 200.0318; found: 200.0317.

**6-(4-methoxyphenyl)-3-thioxo-3,4-dihydro-1,2,4-triazin-5(*2H*)-one (4)** [2]



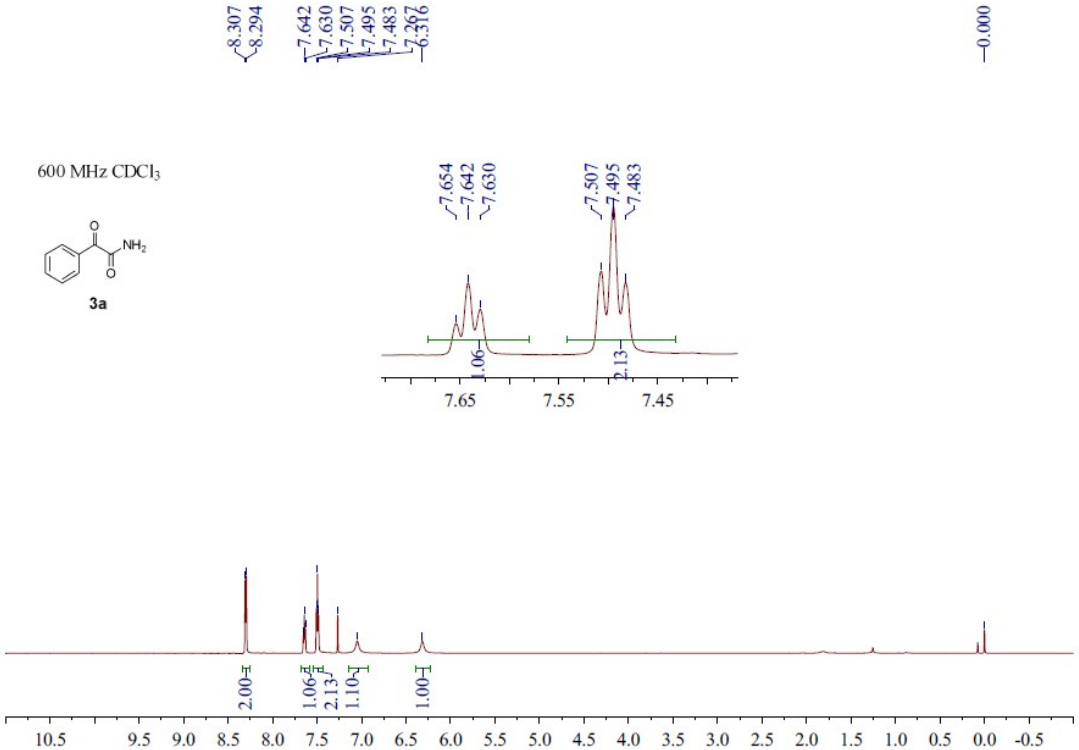
Yield 85%; Yellow solid; $^{1}$H NMR (600 MHz, DMSO-$d_6$) δ 13.61 (br, 1H), 13.20 (br, 1H), 7.92 (d, $J$ = 9.0 Hz, 2H), 7.01 (d, $J$ = 9.0 Hz, 2H), 3.80 (s, 3H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) δ 172.7, 160.8, 153.0, 145.2, 129.7, 124.1, 113.7, 55.4; MS (EI): m/z 237.08 (M + 2, 5.28%), 236.02 (M + 1, 12.73), 235.02 (100).

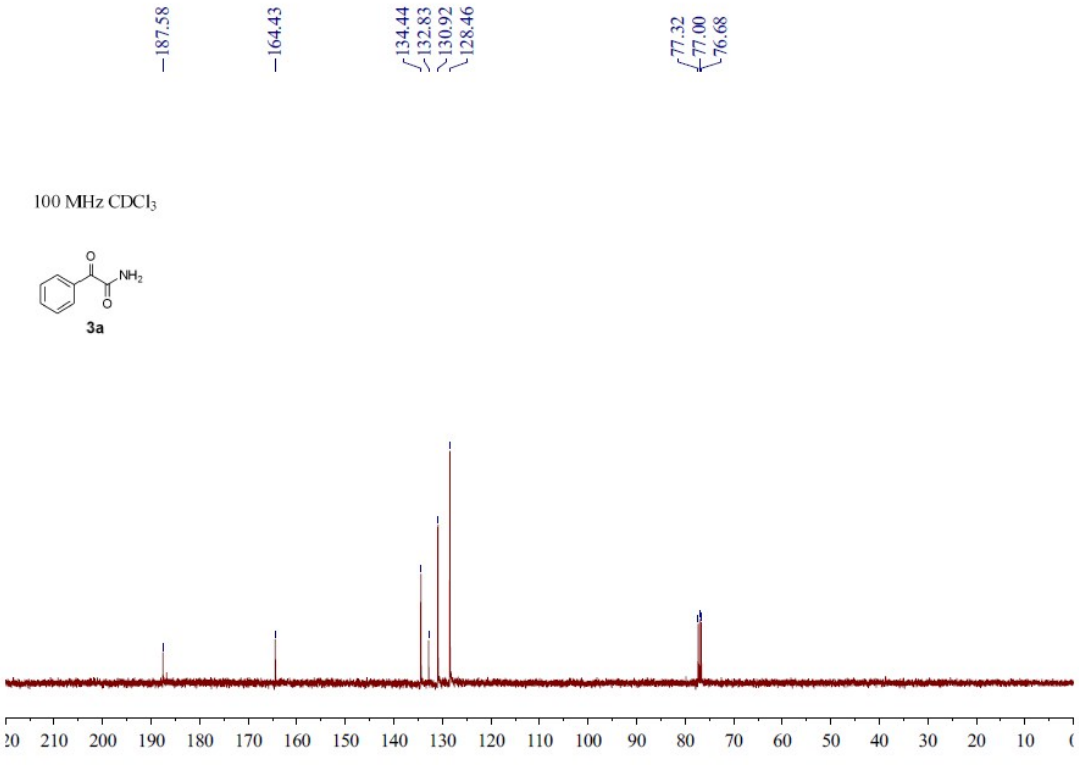
**Reference:**

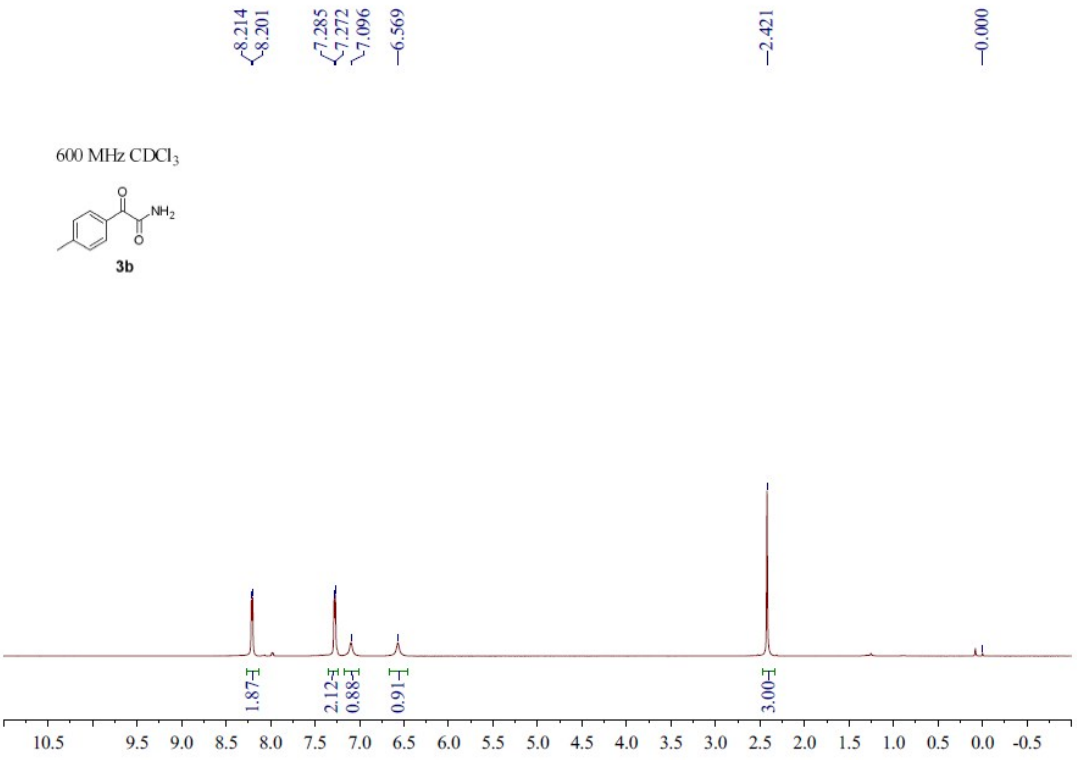
(1) Z. Zhang, J. Su, Z. Zha and Z. Wang, *Chem. Commun.*, 2013, **49**, 8982.

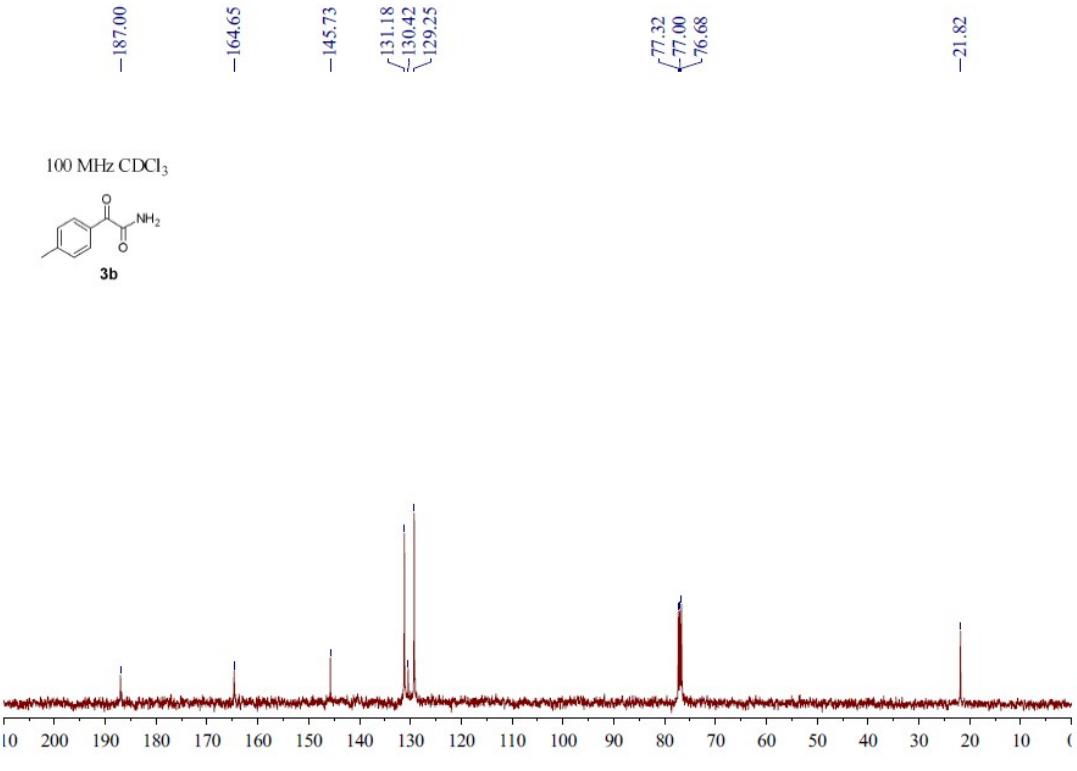
(2) F. M. Adam, A. J. Burton, K. S. Cardwell, R. A. Cox, R. A. Henson, K. Mills, J. C. Prodger, M. B. Schilling and D. T. Tape, *Tetrahedron Lett.*, 2003, **44**, 5657.

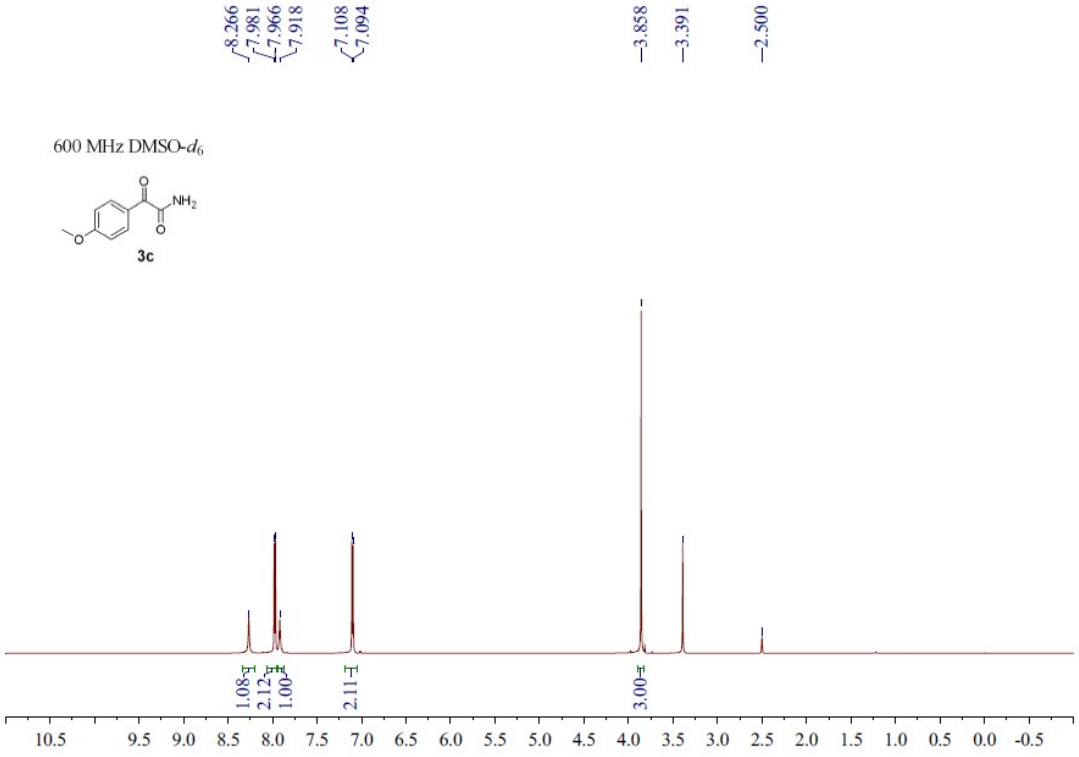
## 5. $^{1}H$ and $^{13}C$ NMR Spectra of Compounds

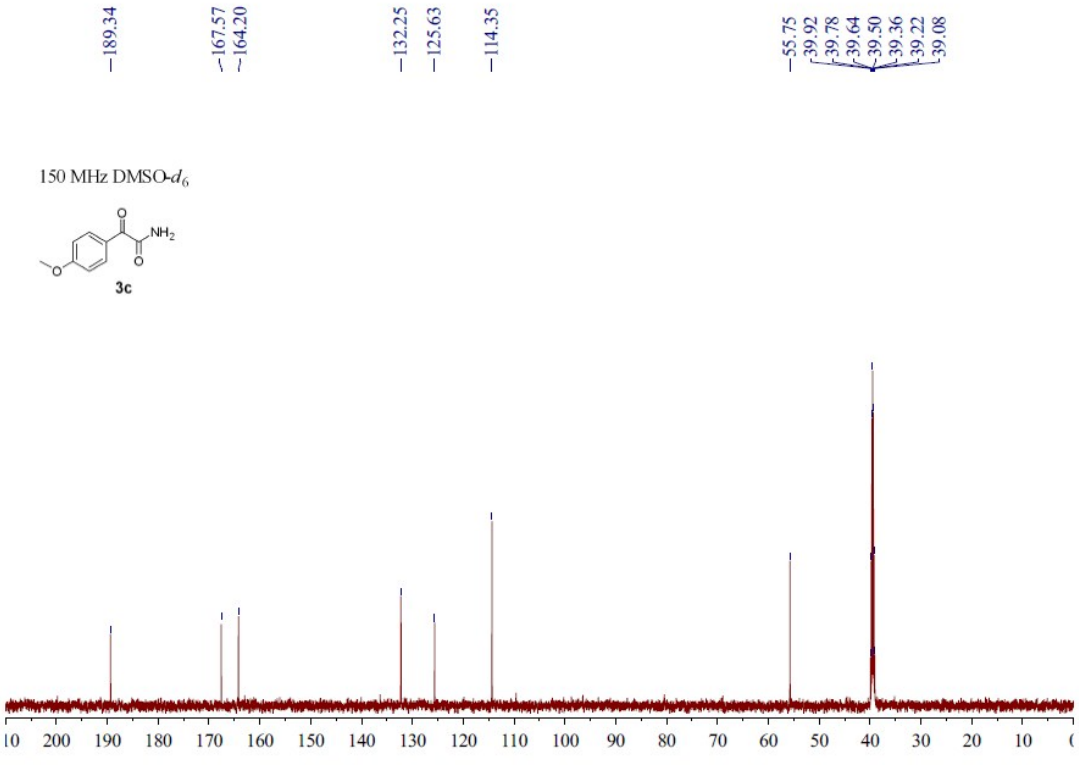


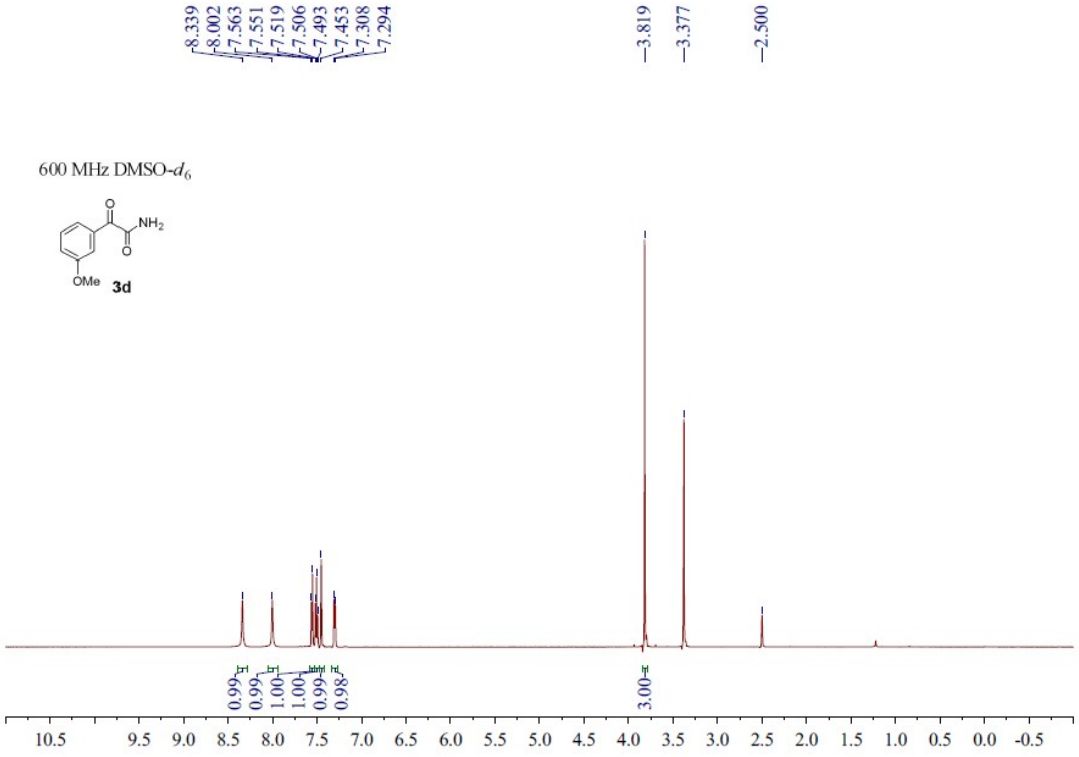



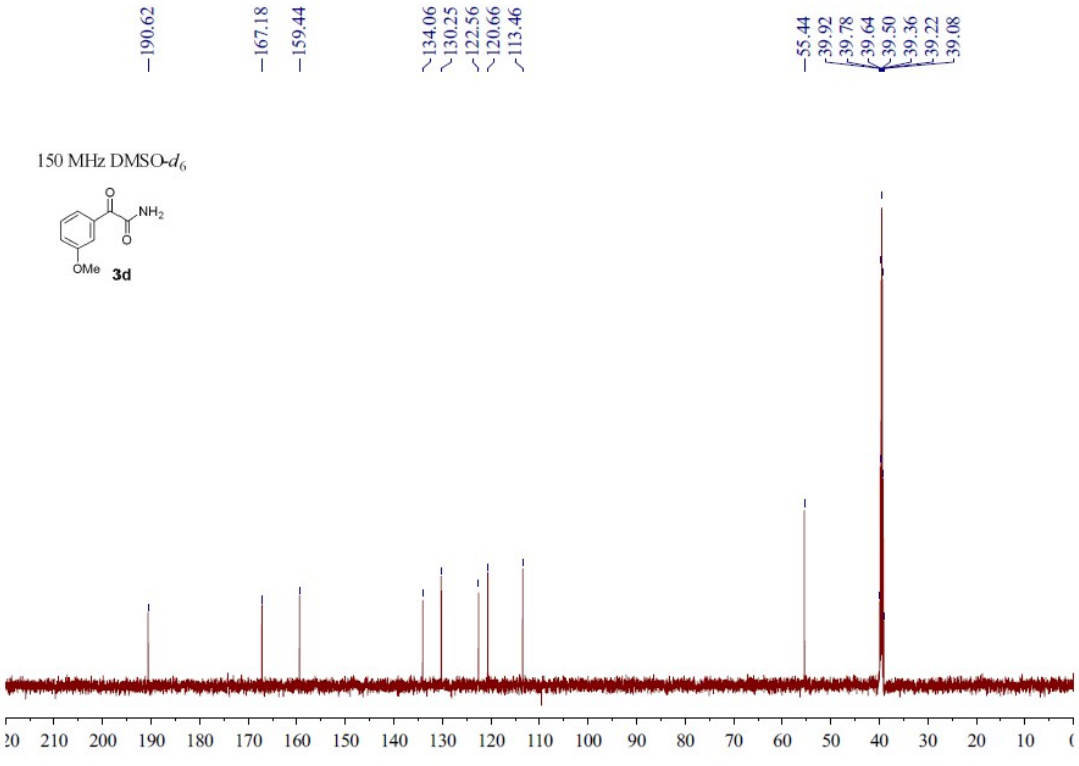

8.214
8.201
7.285
7.272
7.096
6.569
2.421
0.000
600 MHz CDCl3
NH2
3b
1.87
2.12
0.88
0.91
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

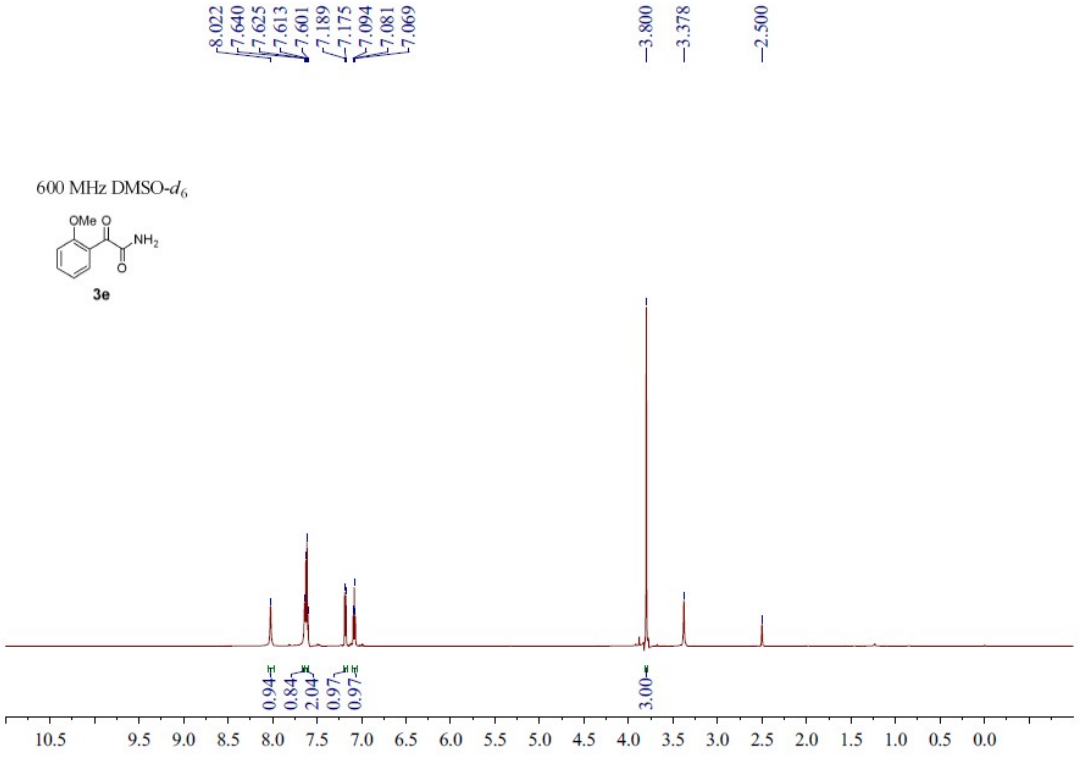

187.00
164.65
145.73
131.18
130.42
129.25
77.32
77.00
76.68
21.82
100 MHz CDCl3
NH2
3b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

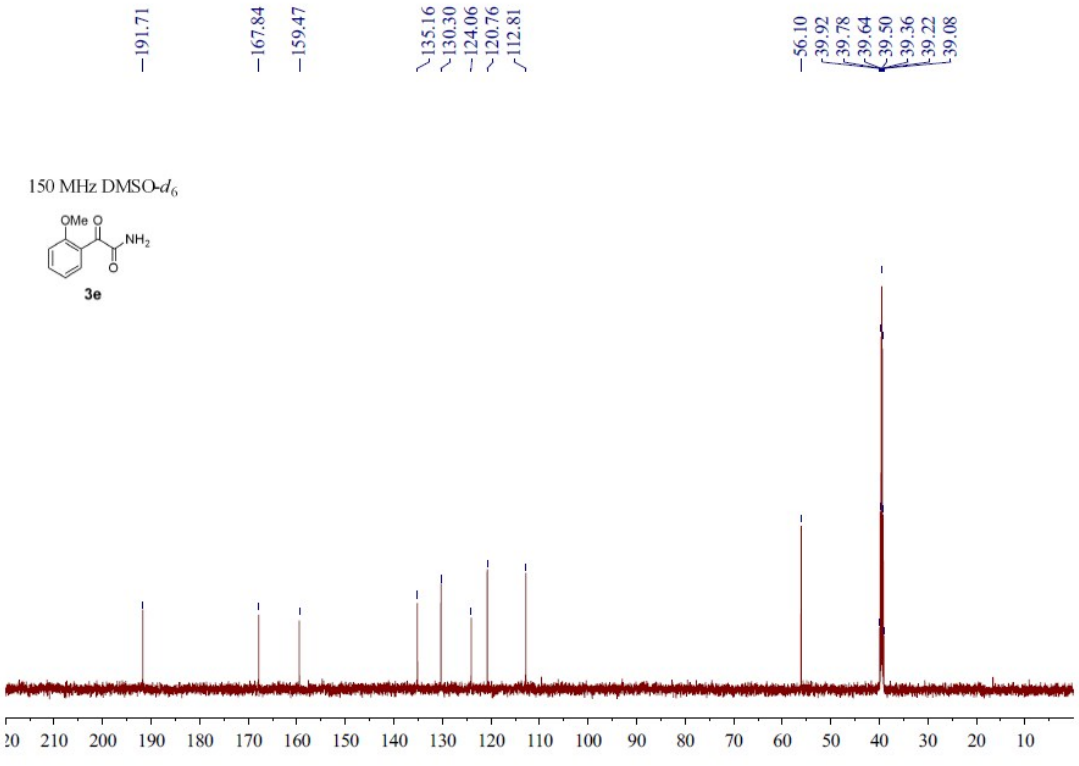

8.266
7.981
7.966
7.918
7.108
7.094
3.858
3.391
2.500
600 MHz DMSO-$d_6$
NH2
3c
1.08
2.12
1.00
2.11
3.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

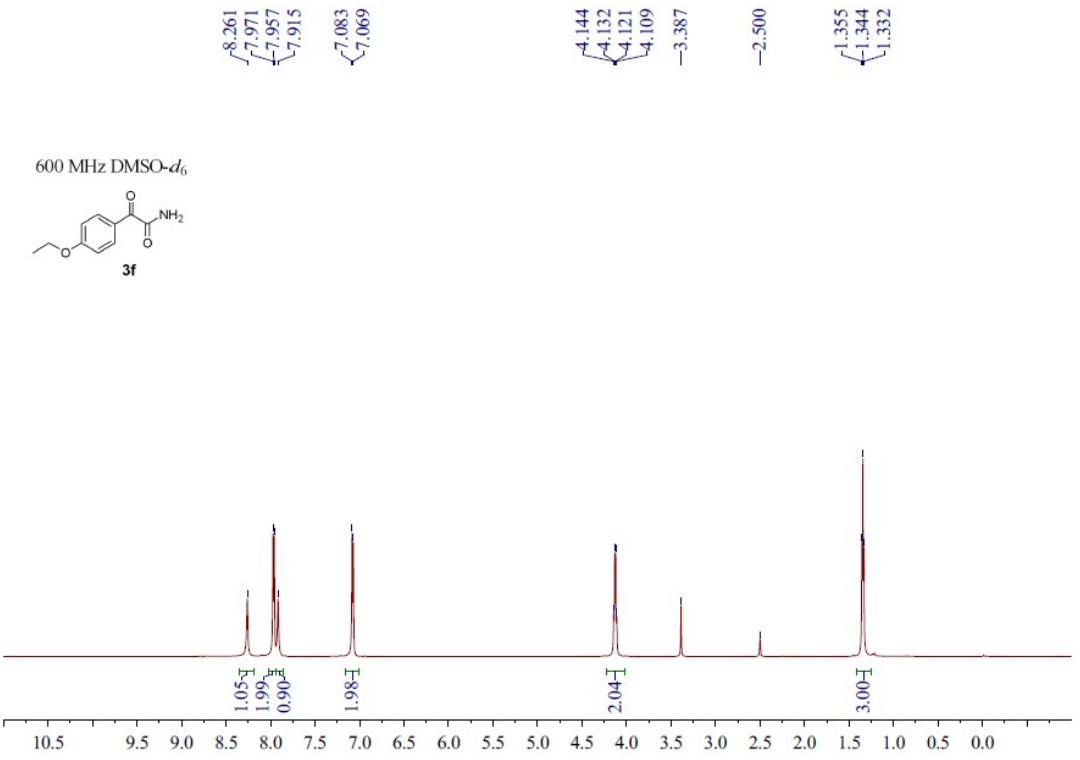

189.34
167.57
164.20
132.25
125.63
114.35
55.75
39.92
39.78
39.64
39.50
39.36
39.22
39.08
150 MHz DMSO-$d_6$
NH2
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

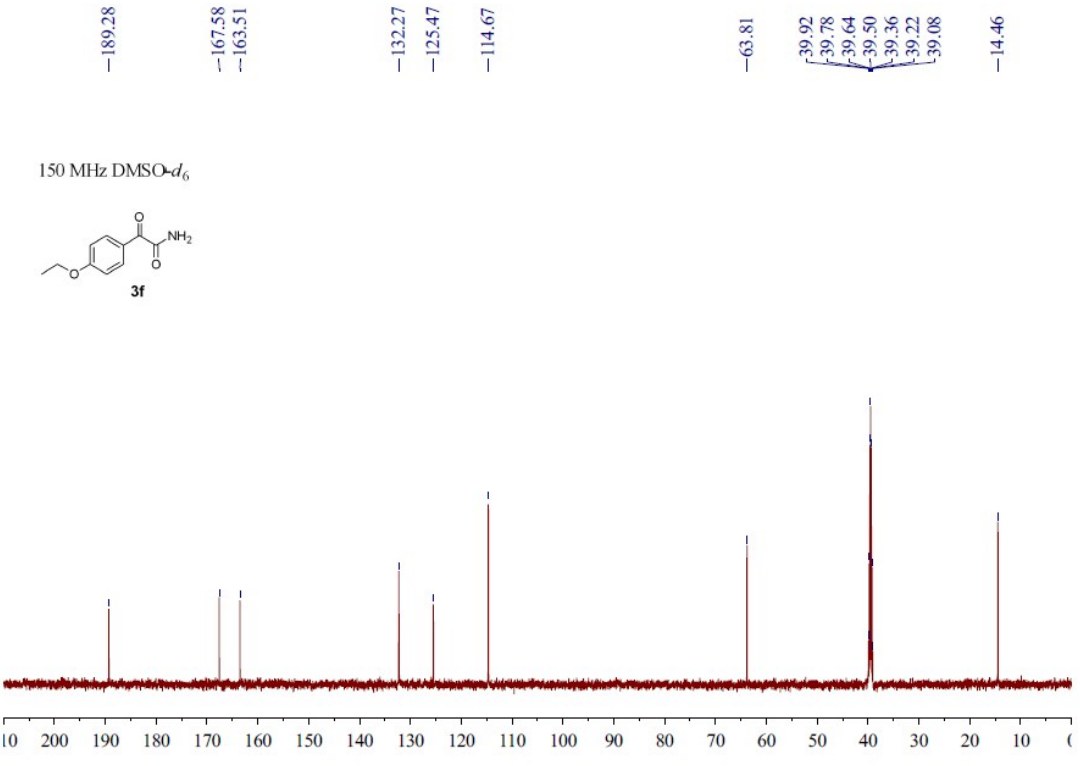

8.339
8.002
7.563
7.551
7.519
7.506
7.493
7.453
7.308
7.294
3.819
3.377
2.500
600 MHz DMSO-$d_6$
NH2
OMe
3d
0.99
0.99
1.00
1.00
0.99
0.98
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

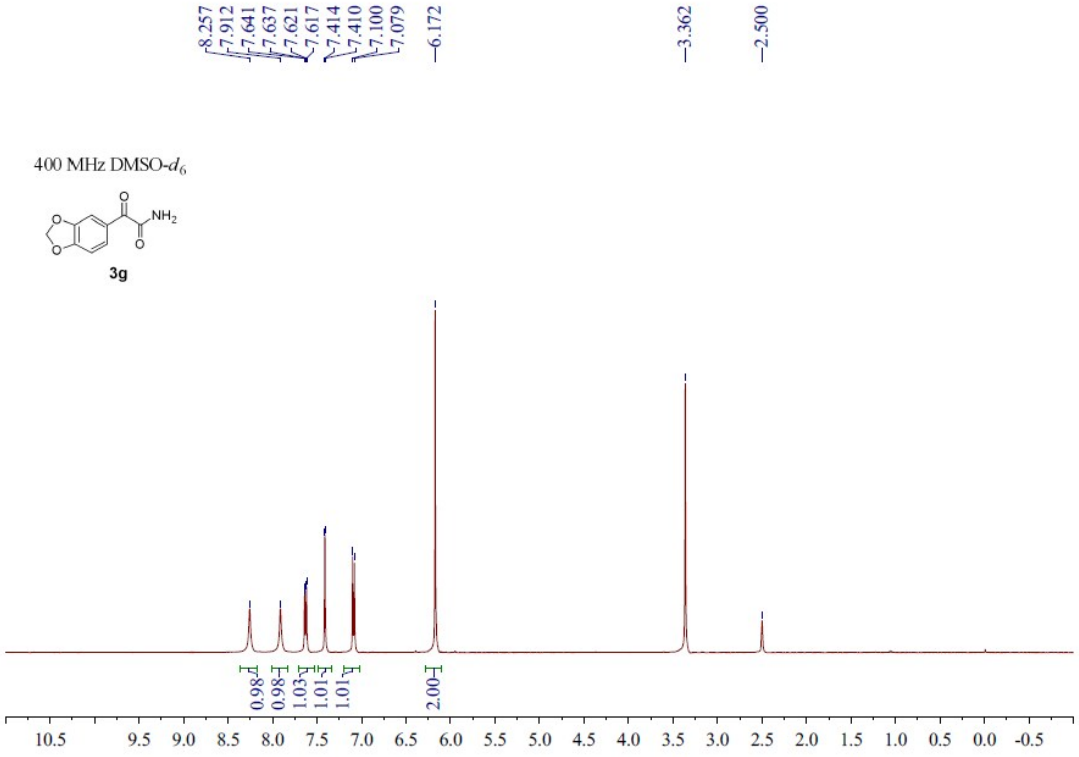

190.62
167.18
159.44
134.06
130.25
122.56
120.66
113.46
55.44
39.92
39.78
39.64
39.50
39.36
39.22
39.08
150 MHz DMSO-$d_6$
NH2
OMe
3d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

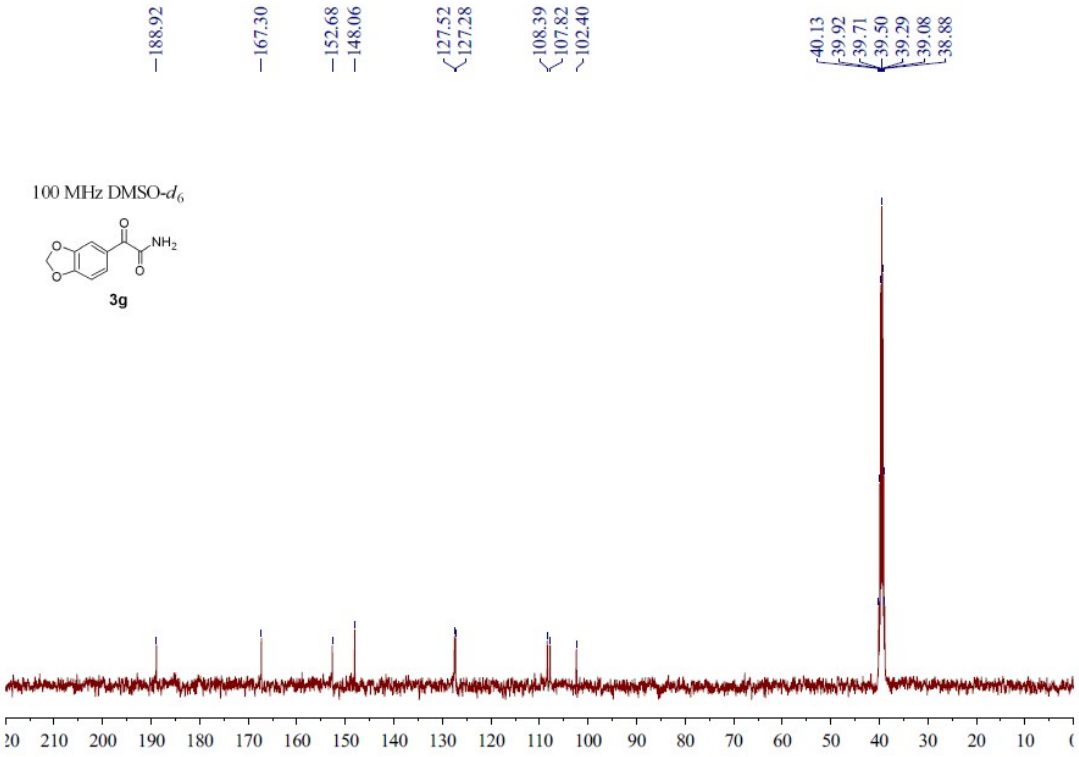

8.022
7.640
7.625
7.613
7.601
7.189
7.175
7.094
7.081
7.069
3.800
3.378
2.500
600 MHz DMSO-$d_6$
OMe O
NH2
O
3e
0.94
0.84
2.04
0.97
0.97
3.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

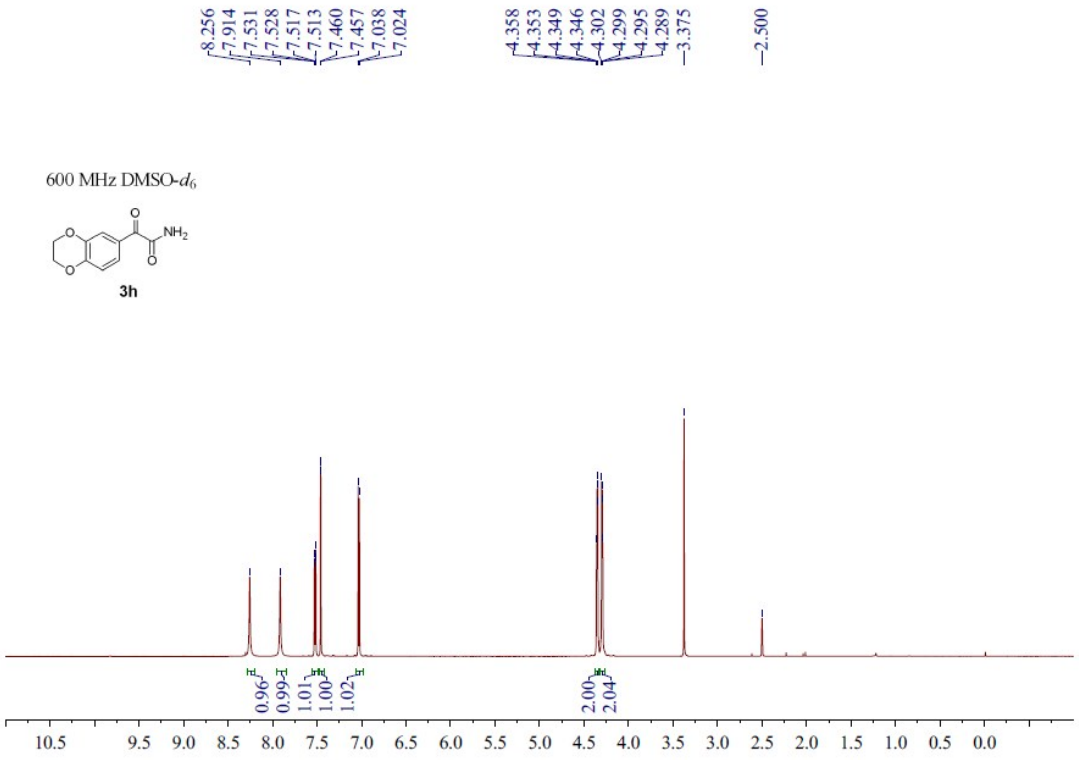

191.71
167.84
159.47
135.16
130.30
124.06
120.76
112.81
56.10
39.92
39.78
39.64
39.50
39.36
39.22
39.08
150 MHz DMSO-$d_6$
OMe O
NH2
O
3e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

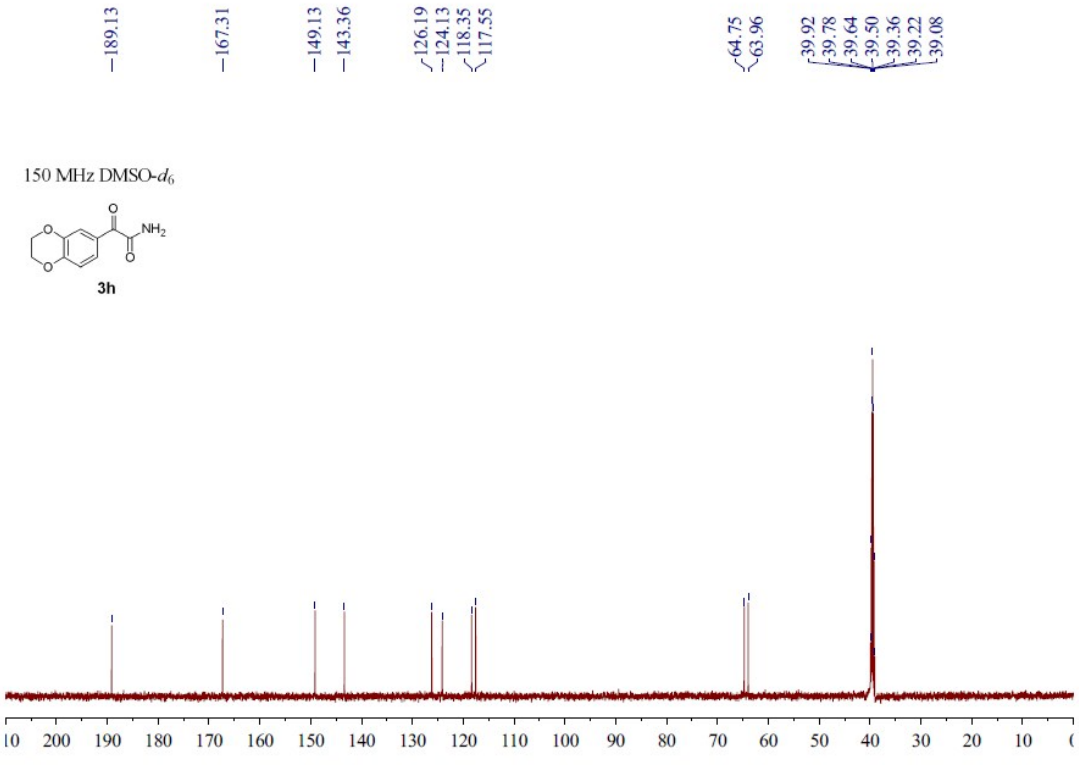

8.261
7.971
7.957
7.915
7.083
7.069
4.144
4.132
4.121
4.109
3.387
2.500
1.355
1.344
1.332
600 MHz DMSO-$d_6$
NH2
3f
1.05
1.99
0.90
1.98
2.04
3.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

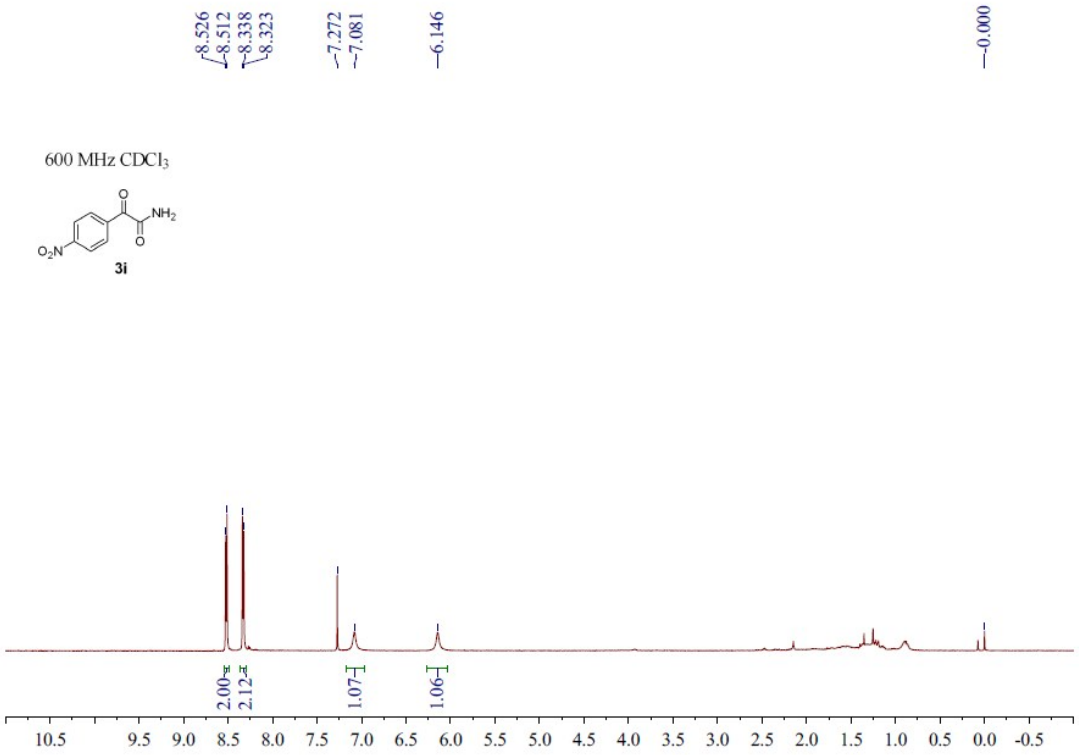

189.28
167.58
163.51
132.27
125.47
114.67
63.81
39.92
39.78
39.64
39.50
39.36
39.22
39.08
14.46
150 MHz DMSO-$d_6$
NH2
3f
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

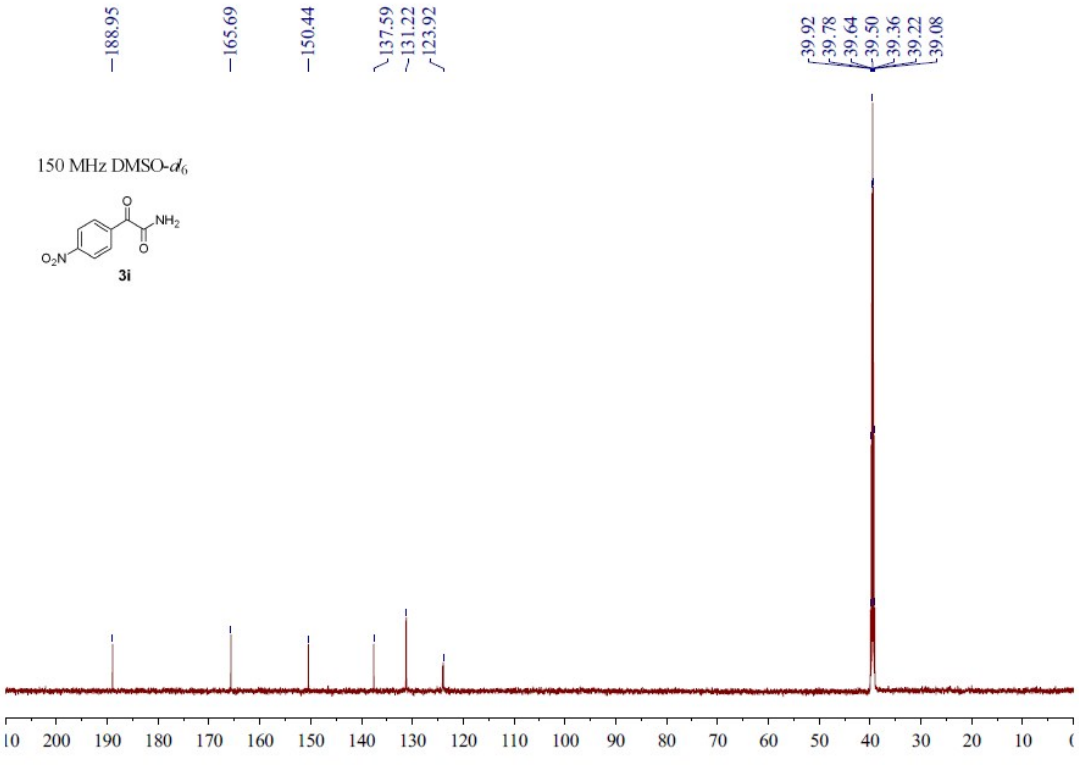

8.257
7.912
7.641
7.637
7.621
7.617
7.414
7.410
7.100
7.079
6.172
3.362
2.500
400 MHz DMSO-$d_6$
NH2
3g
0.98
0.98
1.03
1.01
1.01
2.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

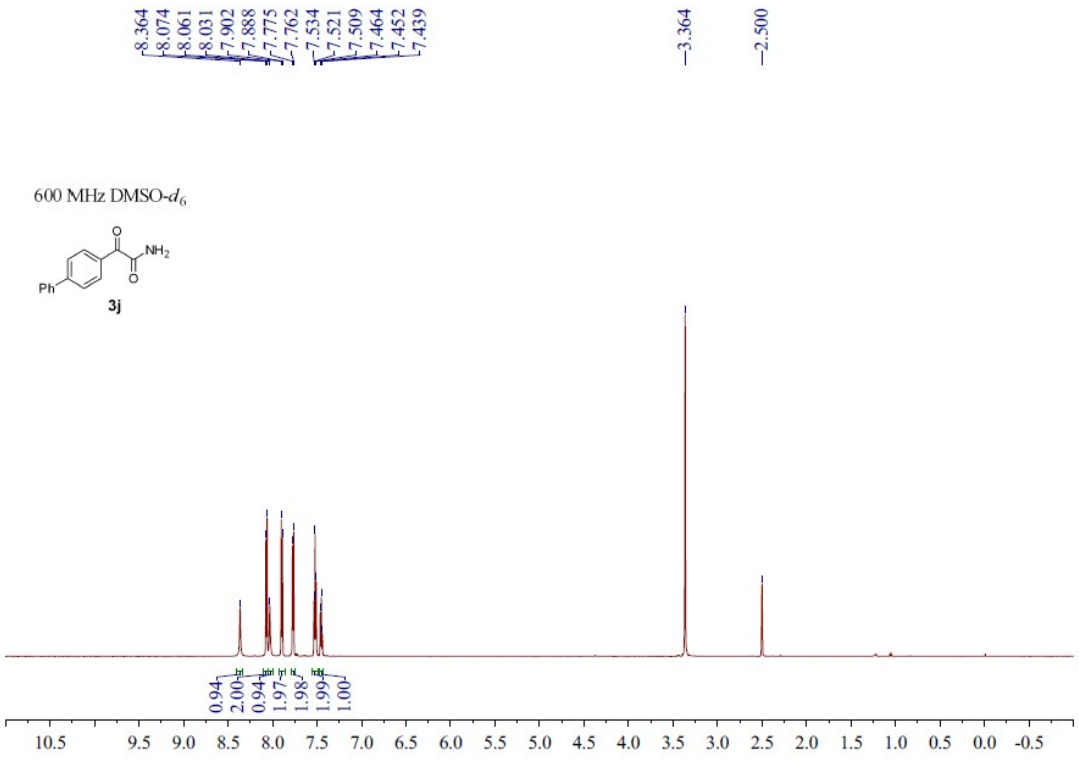

188.92
167.30
152.68
148.06
127.52
127.28
108.39
107.82
102.40
40.13
39.92
39.71
39.50
39.29
39.08
38.88
100 MHz DMSO-$d_6$
NH2
3g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

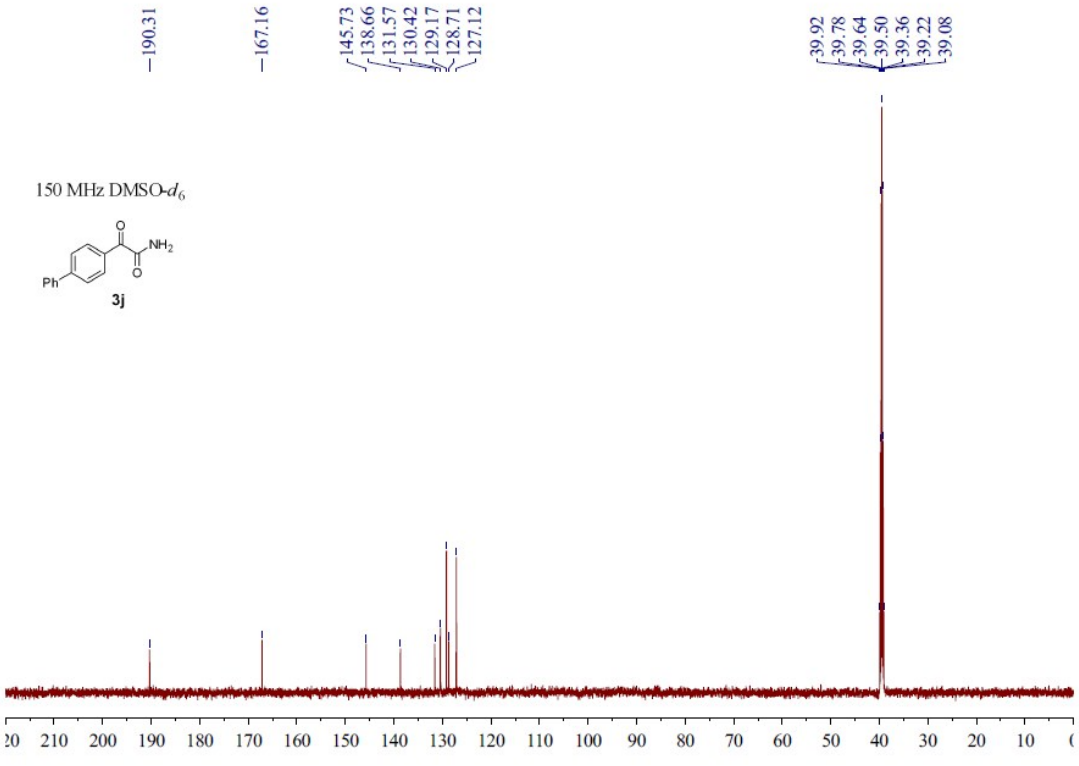

8.256
7.914
7.531
7.528
7.517
7.513
7.460
7.457
7.038
7.024
4.358
4.353
4.349
4.346
4.302
4.299
4.295
4.289
3.375
2.500
600 MHz DMSO-$d_6$
NH2
3h
0.96
0.99
1.01
1.00
1.02
2.00
2.04
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

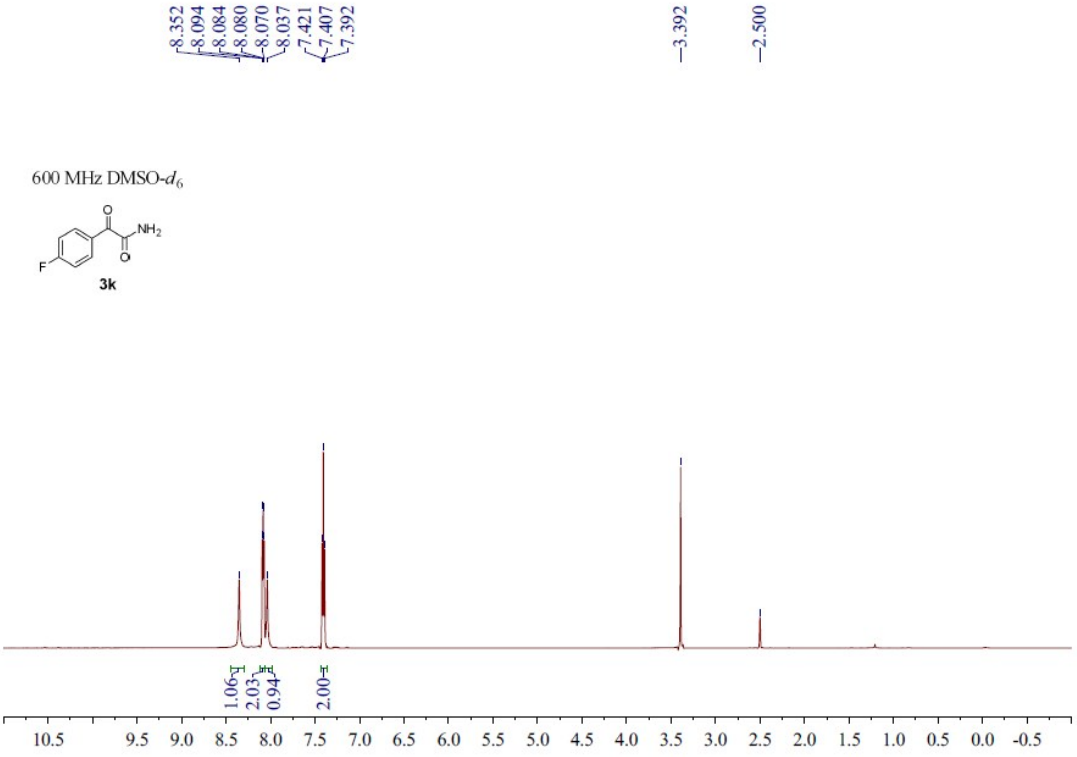

189.13
167.31
149.13
143.36
126.19
124.13
118.35
117.55
64.75
63.96
39.92
39.78
39.64
39.50
39.36
39.22
39.08
150 MHz DMSO-$d_6$
NH2
3h
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

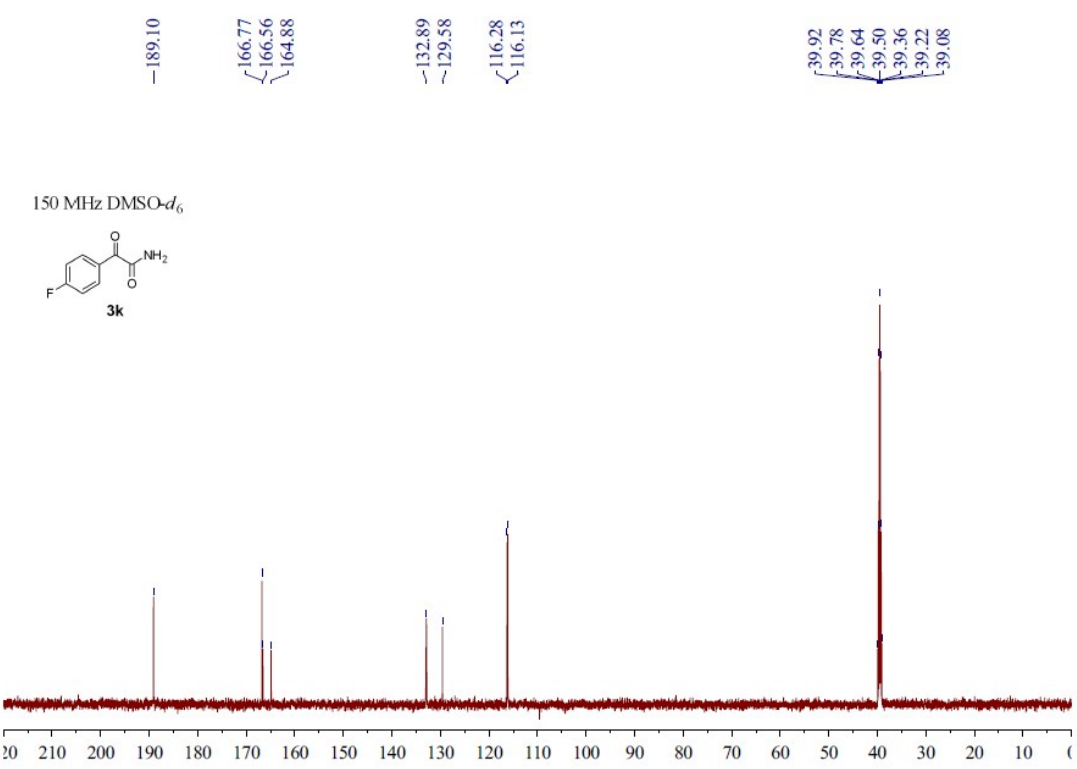

8.526
8.512
8.338
8.323
7.272
7.081
6.146
0.000
600 MHz CDCl3
NH2
O2N
3i
2.00
2.12
1.07
1.06
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

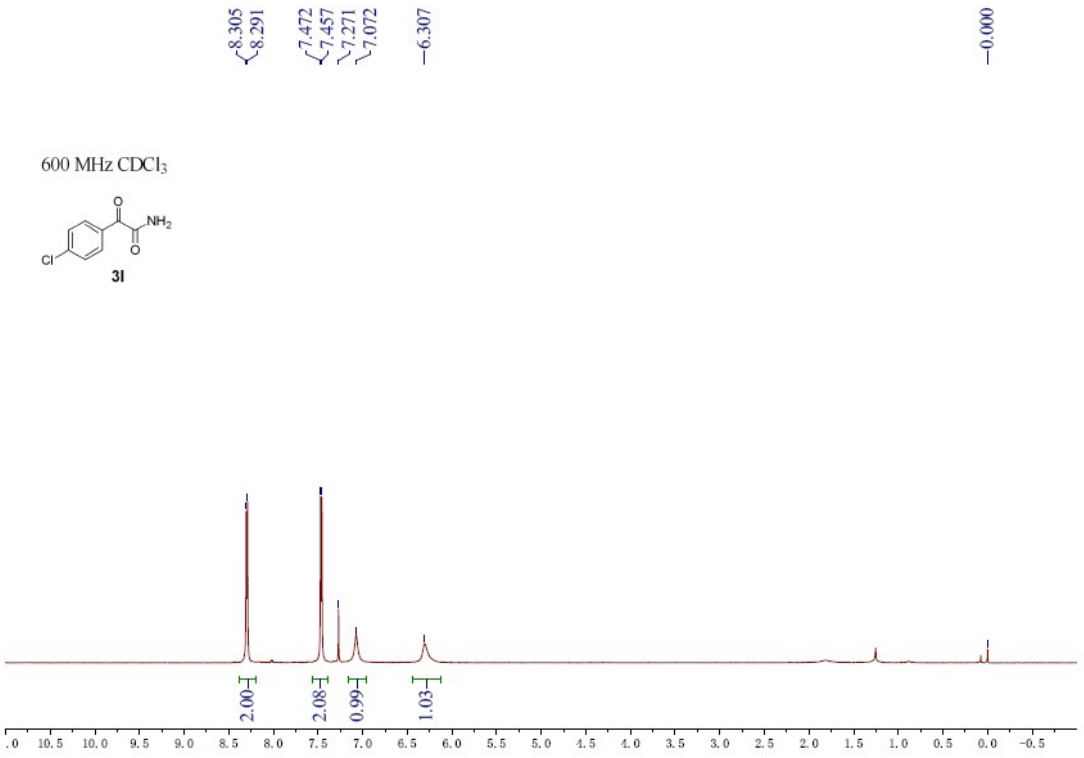

188.95
165.69
150.44
137.59
131.22
123.92
39.92
39.78
39.64
39.50
39.36
39.22
39.08
150 MHz DMSO-d6
NH2
O2N
3i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

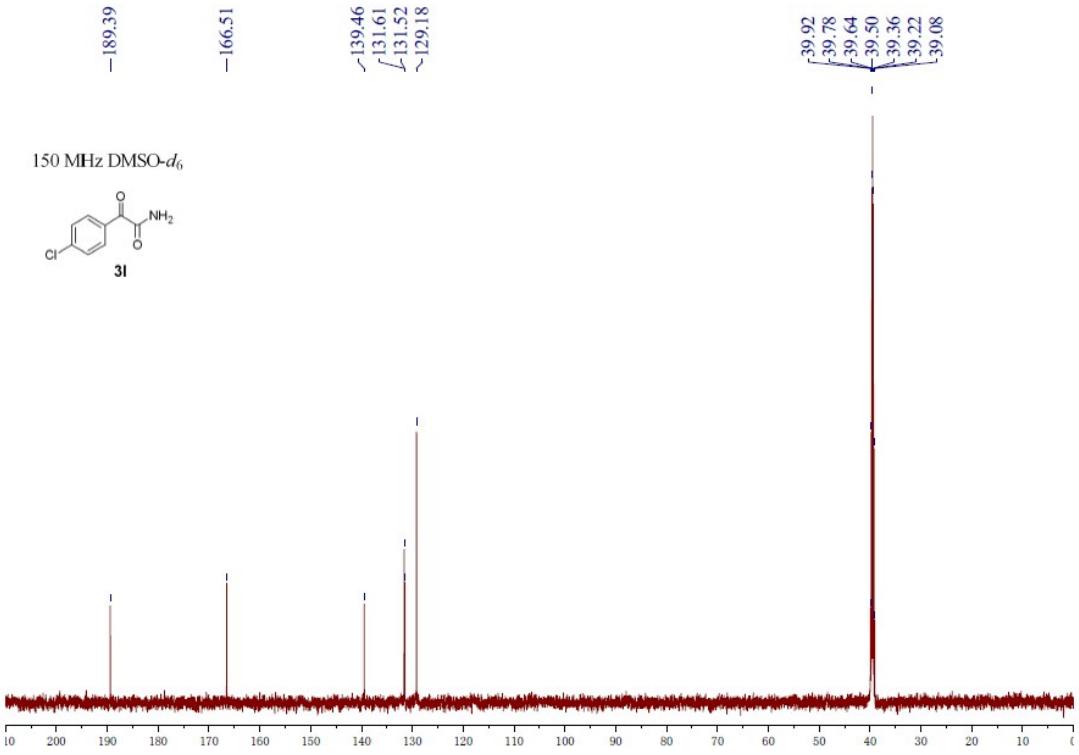

8.364
8.074
8.061
8.031
7.902
7.888
7.775
7.762
7.534
7.521
7.509
7.464
7.452
7.439
3.364
2.500
600 MHz DMSO-$d_6$
NH2
Ph
3j
0.94
2.00
0.94
1.97
1.98
1.99
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

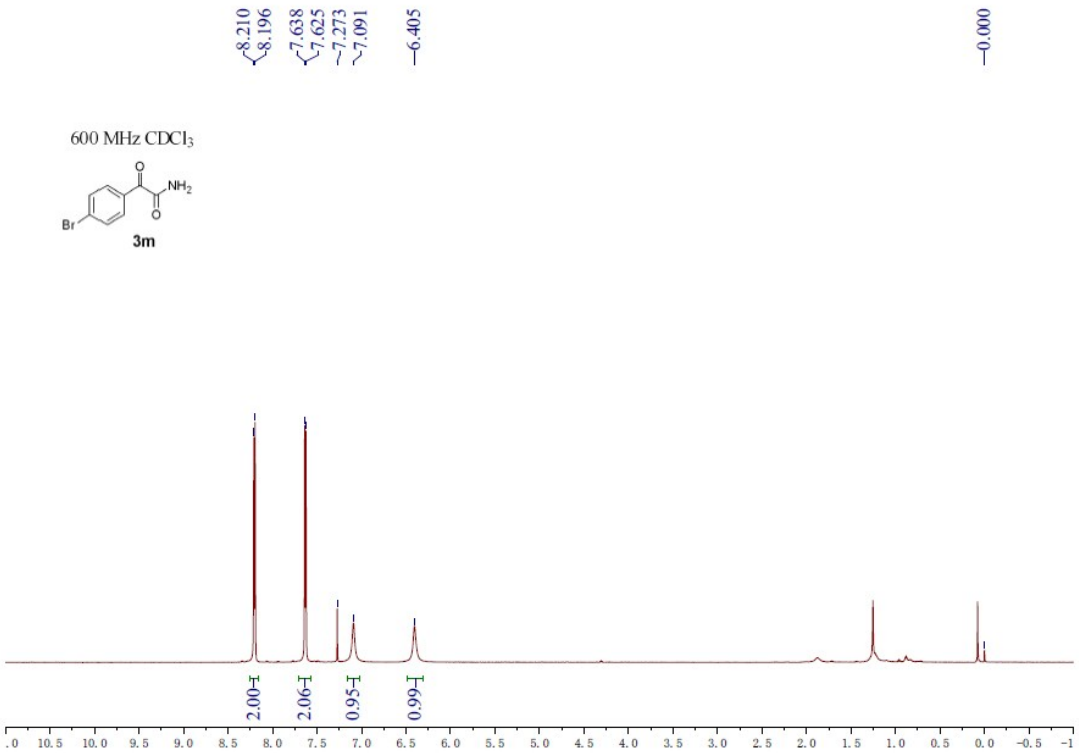

190.31
167.16
145.73
138.66
131.57
130.42
129.17
128.71
127.12
39.92
39.78
39.64
39.50
39.36
39.22
39.08
150 MHz DMSO-$d_6$
NH2
Ph
3j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

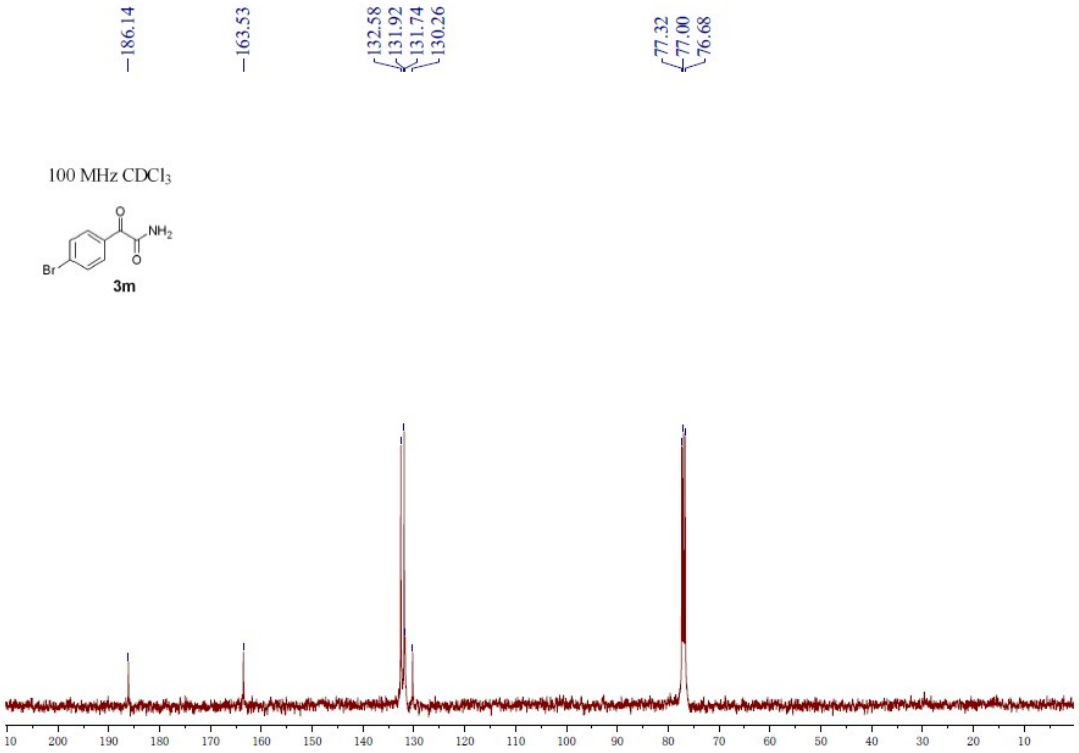

8.352
8.094
8.084
8.080
8.070
8.037
7.421
7.407
7.392
3.392
2.500
600 MHz DMSO-$d_6$
3k
1.06
2.03
0.94
2.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

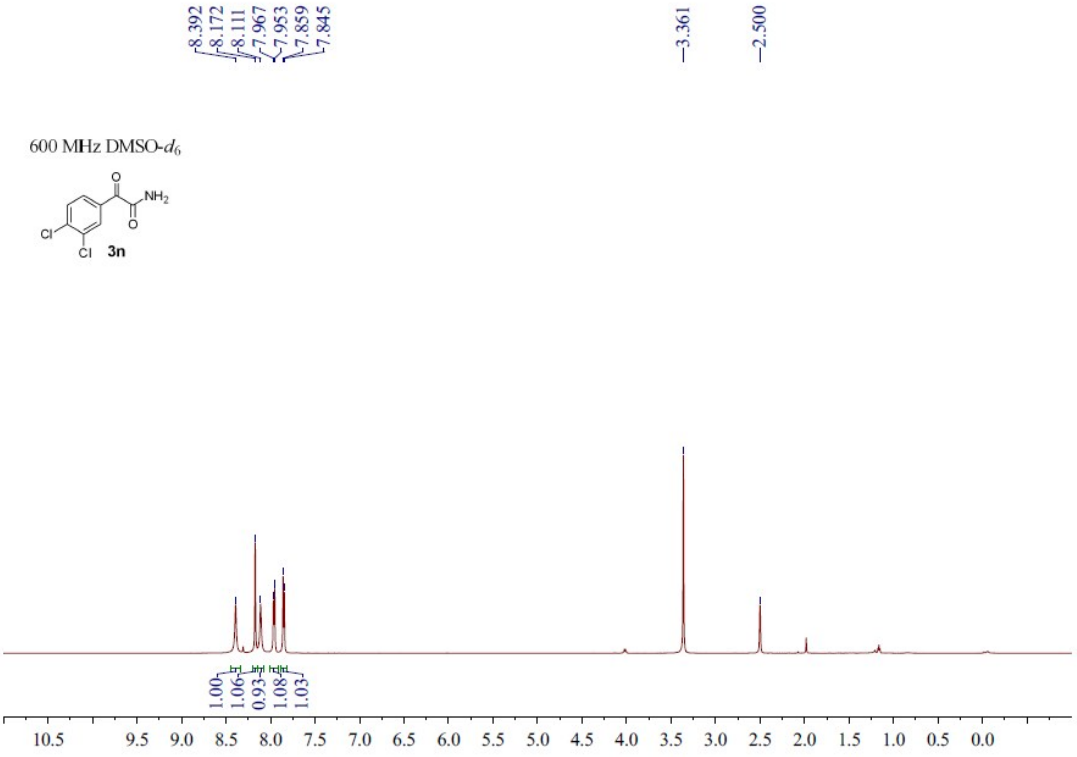

189.10
166.77
166.56
164.88
132.89
129.58
116.28
116.13
39.92
39.78
39.64
39.50
39.36
39.22
39.08
150 MHz DMSO-$d_6$
3k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

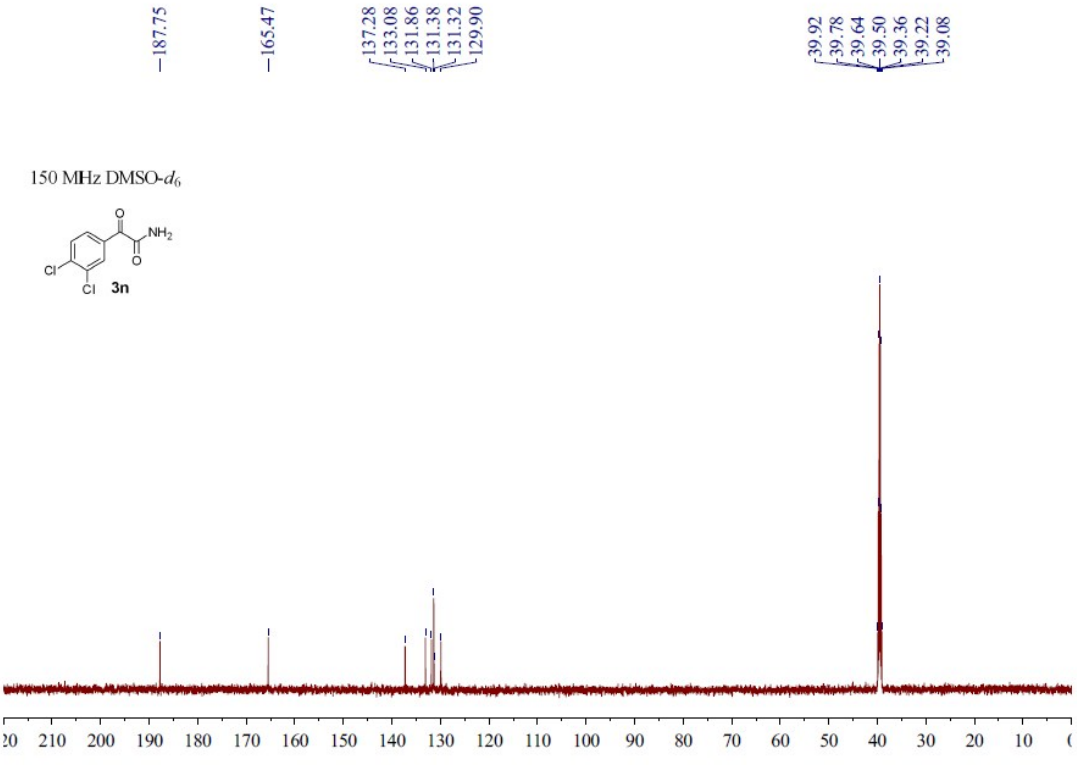

8.305
8.291
7.472
7.457
7.271
7.072
6.307
0.000
600 MHz CDCl3
NH2
O
O
Cl
3l
2.00
2.08
0.99
1.03


189.39
166.51
139.46
131.61
131.52
129.18
39.92
39.78
39.64
39.50
39.36
39.22
39.08
150 MHz DMSO-d6
NH2
O
O
Cl
3l

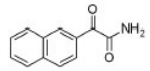

8.210
8.196
7.638
7.625
7.273
7.091
6.405
0.000
600 MHz CDCl3
NH2
Br
3m
2.00
2.06
0.95
0.99


186.14
163.53
132.58
131.92
131.74
130.26
77.32
77.00
76.68
100 MHz CDCl3
NH2
Br
3m

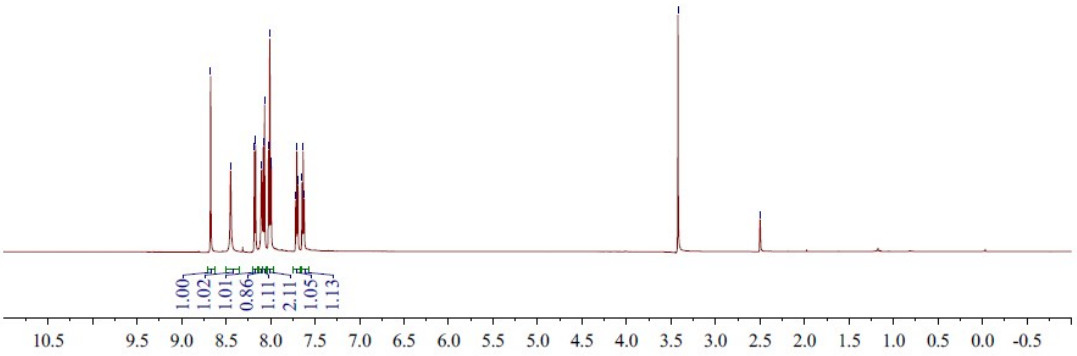

8.392
8.172
8.111
7.967
7.953
7.859
7.845
3.361
2.500
600 MHz DMSO-$d_6$
3n
1.00
1.06
0.93
1.08
1.03
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

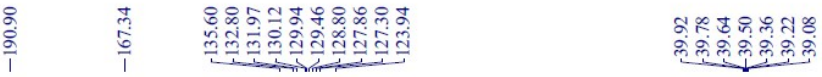

187.75
165.47
137.28
133.08
131.86
131.38
131.32
129.90
39.92
39.78
39.64
39.50
39.36
39.22
39.08
150 MHz DMSO-$d_6$
3n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


600 MHz DMSO-$d_6$

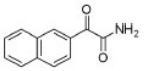


**3o**

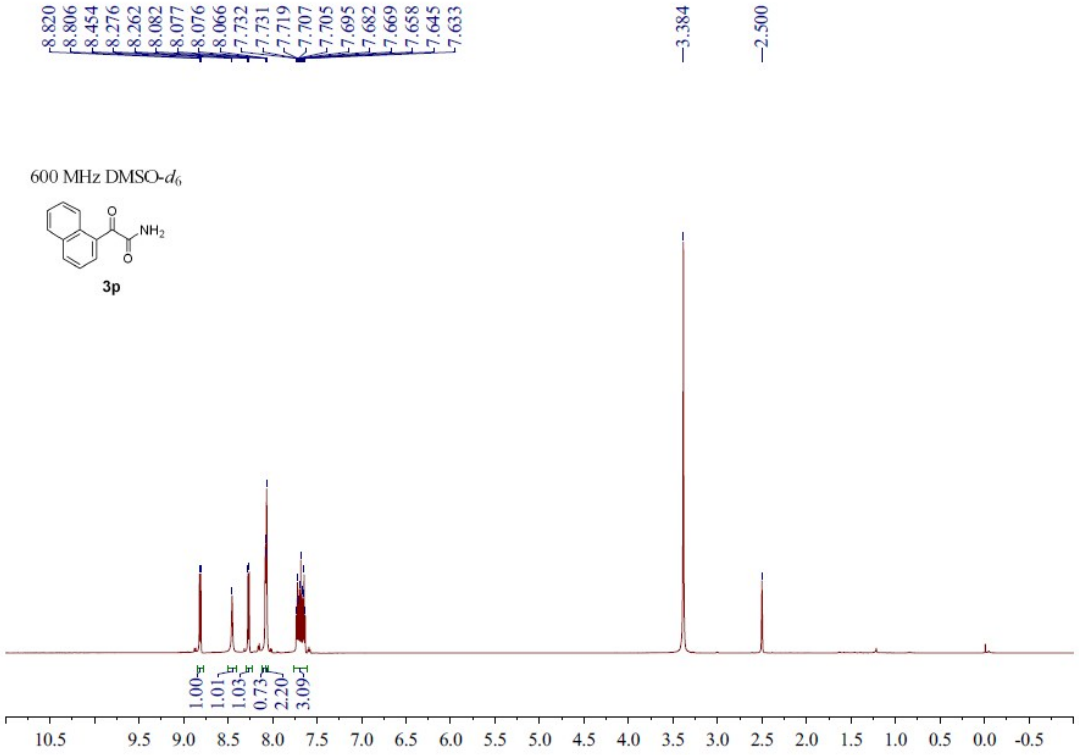


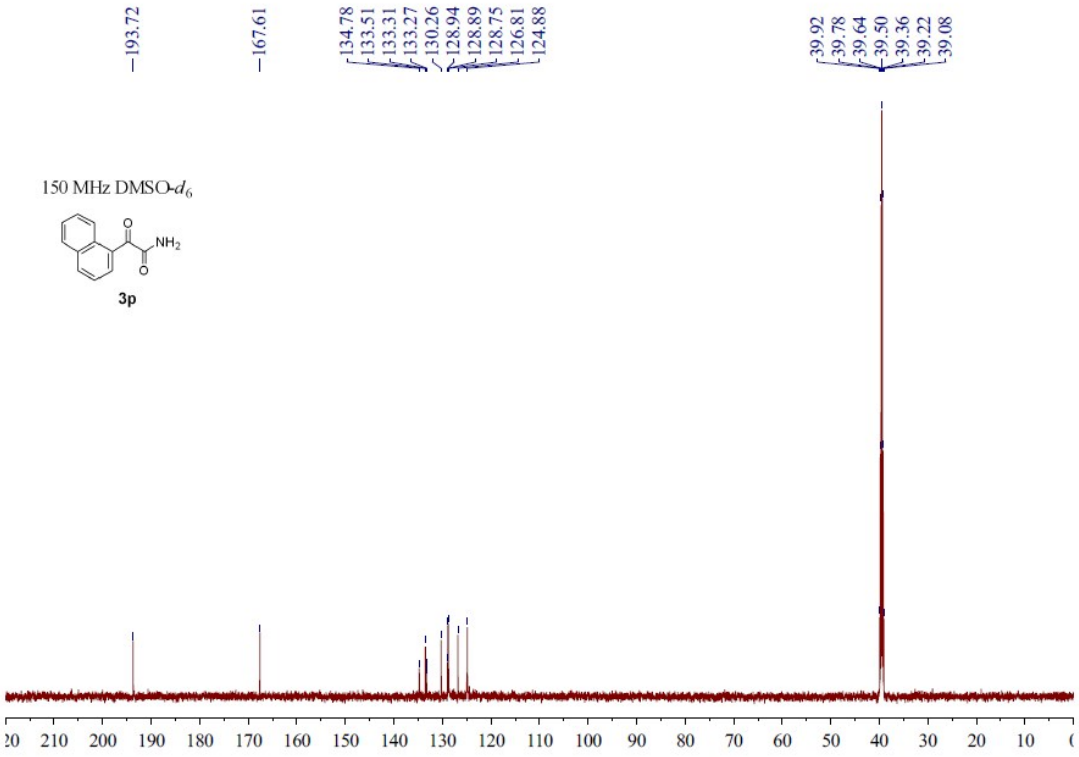



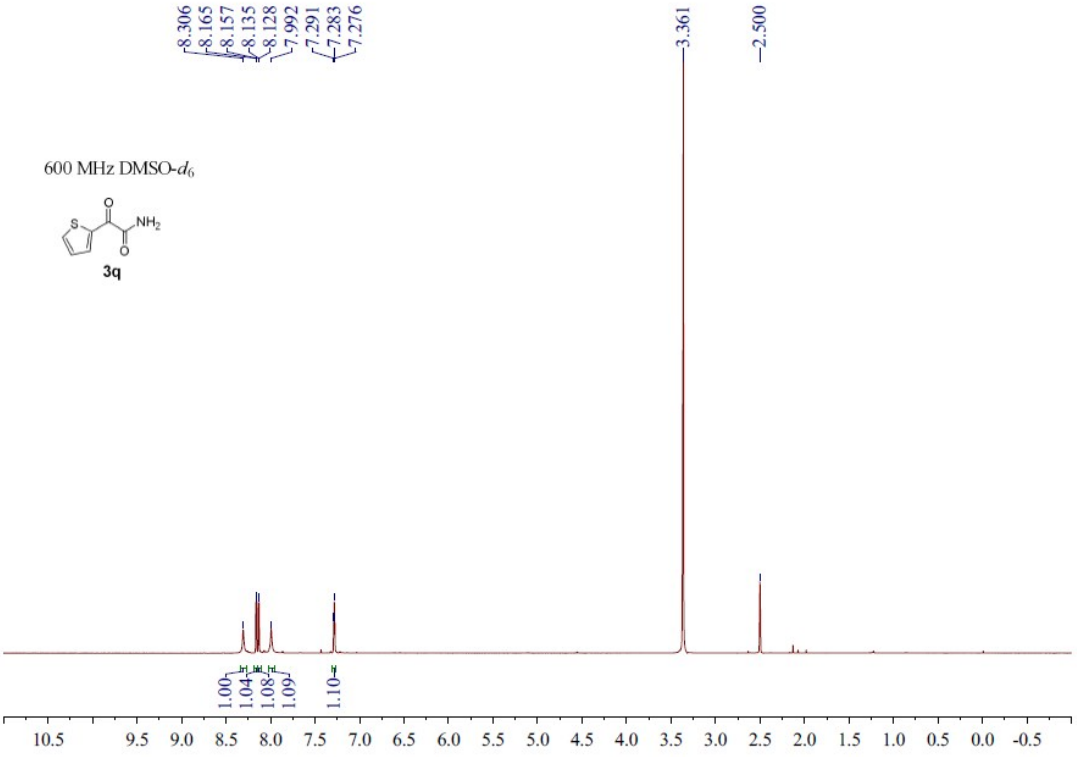

150 MHz DMSO-$d_6$

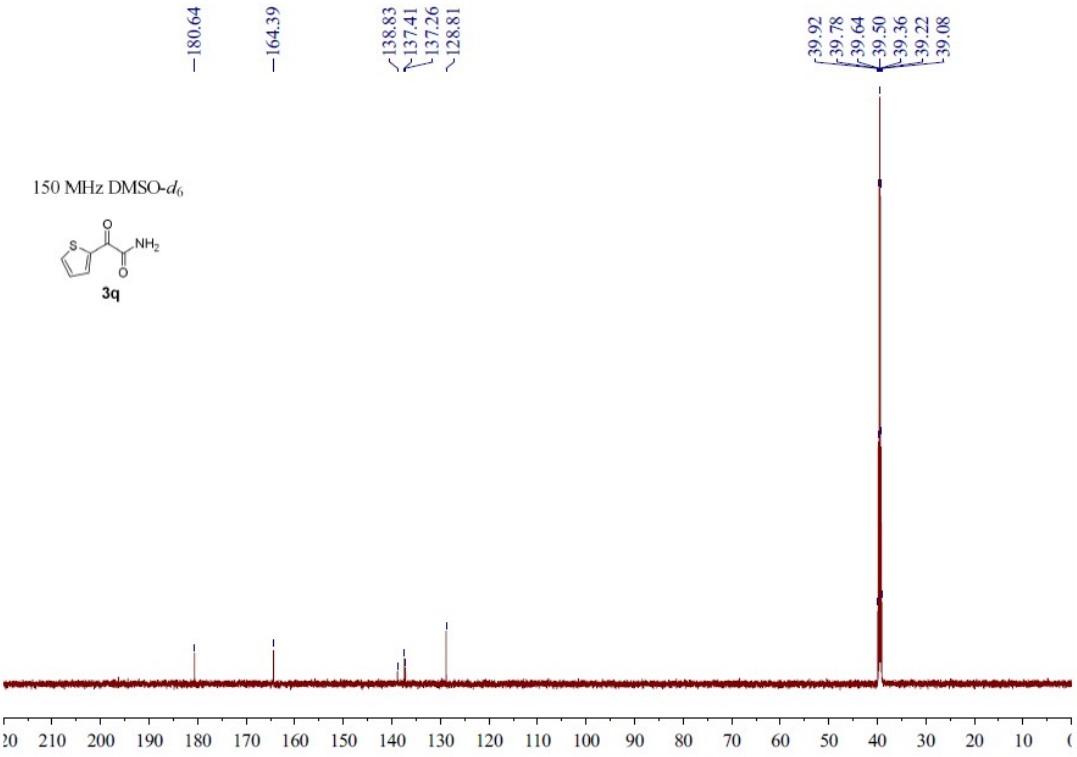


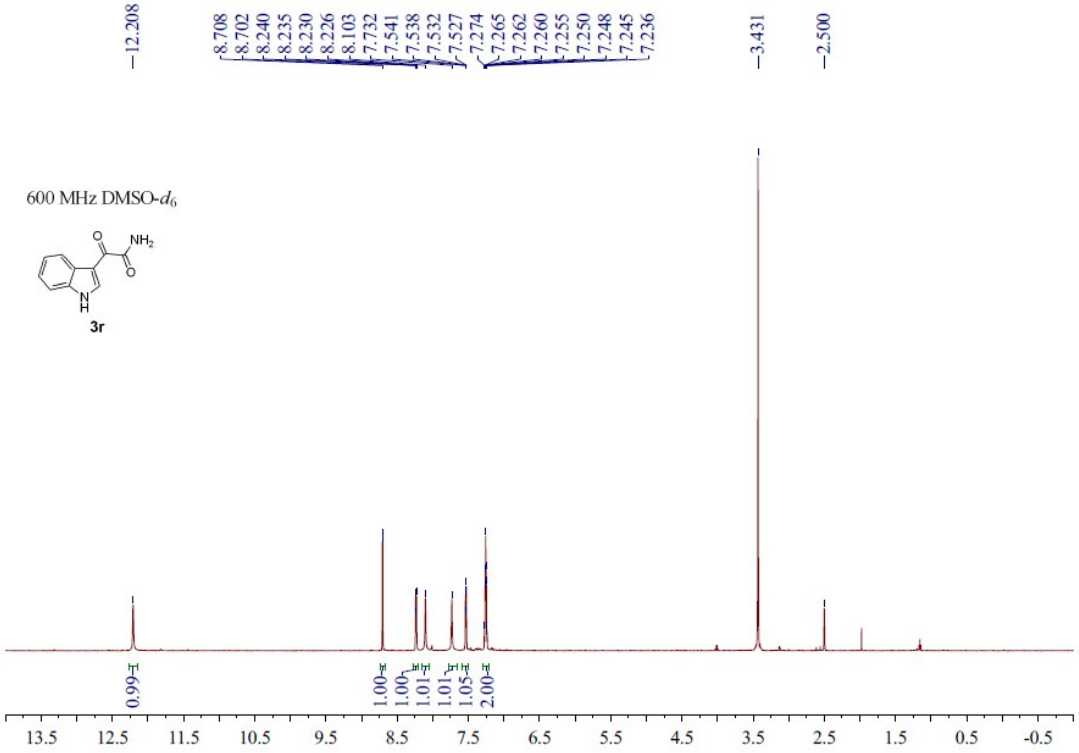
**3o**

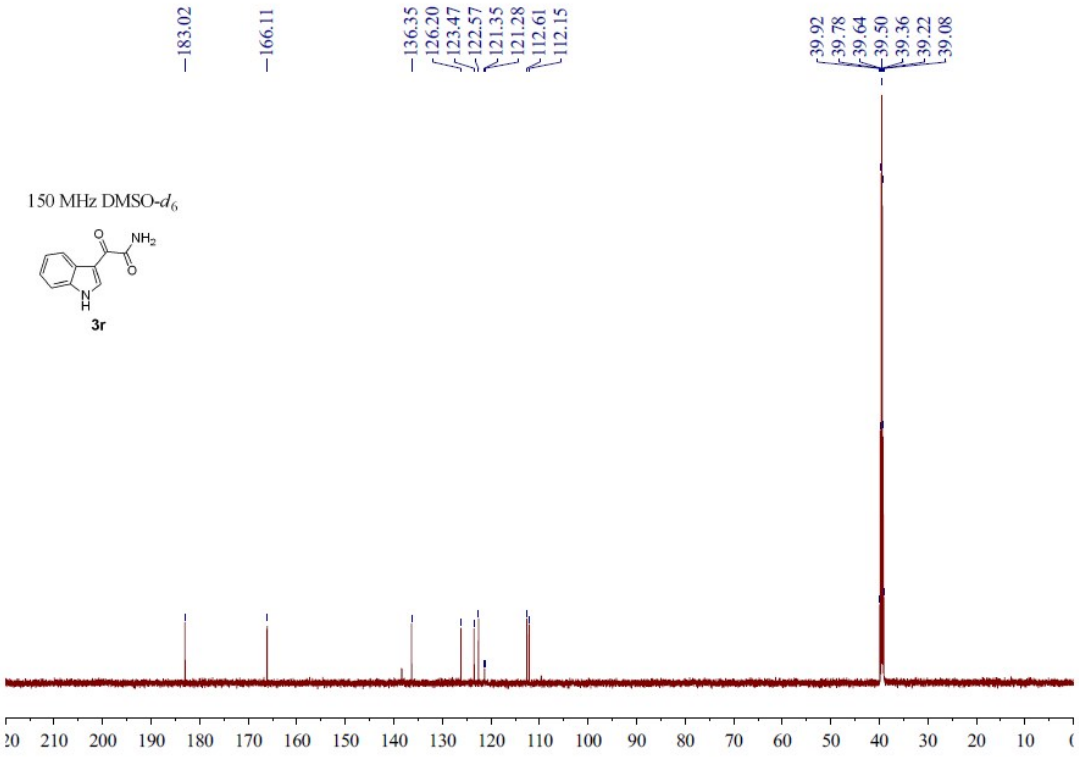

8.820
8.806
8.454
8.276
8.262
8.082
8.077
8.076
8.066
7.732
7.731
7.719
7.707
7.705
7.695
7.682
7.669
7.658
7.645
7.633
3.384
2.500
600 MHz DMSO-$d_6$
NH2
3p
1.00
1.01
1.03
0.73
2.20
3.09
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

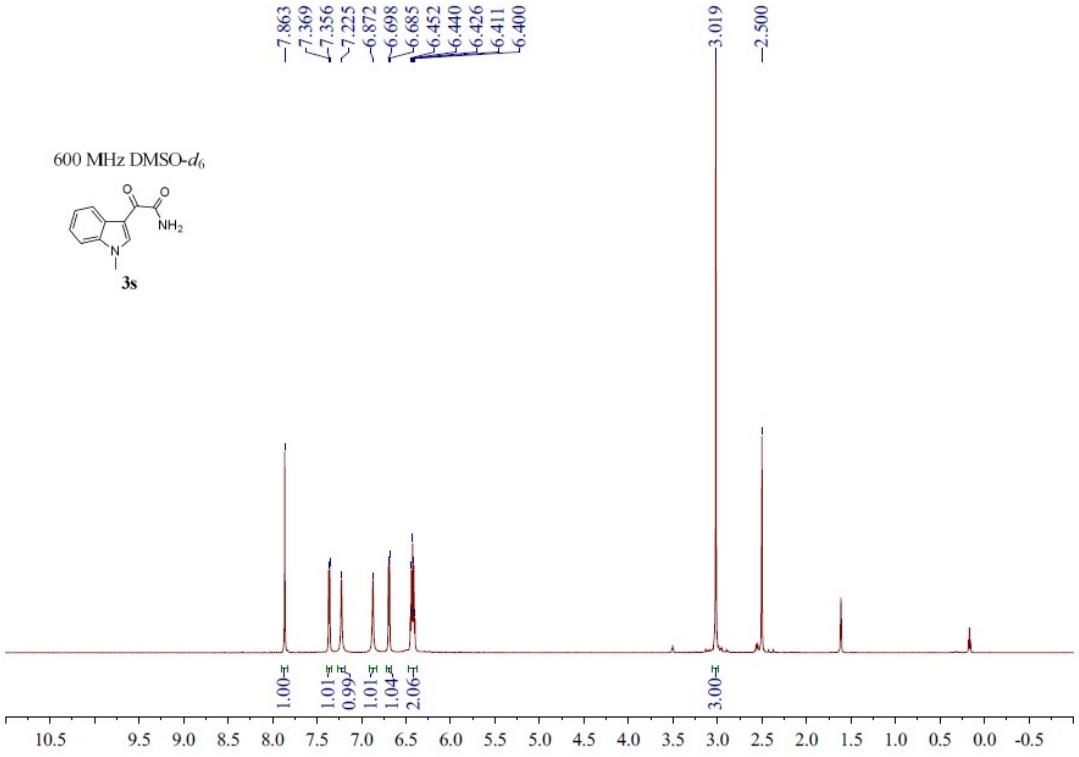

193.72
167.61
134.78
133.51
133.31
133.27
130.26
128.94
128.89
128.75
126.81
124.88
39.92
39.78
39.64
39.50
39.36
39.22
39.08
150 MHz DMSO-$d_6$
NH2
3p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

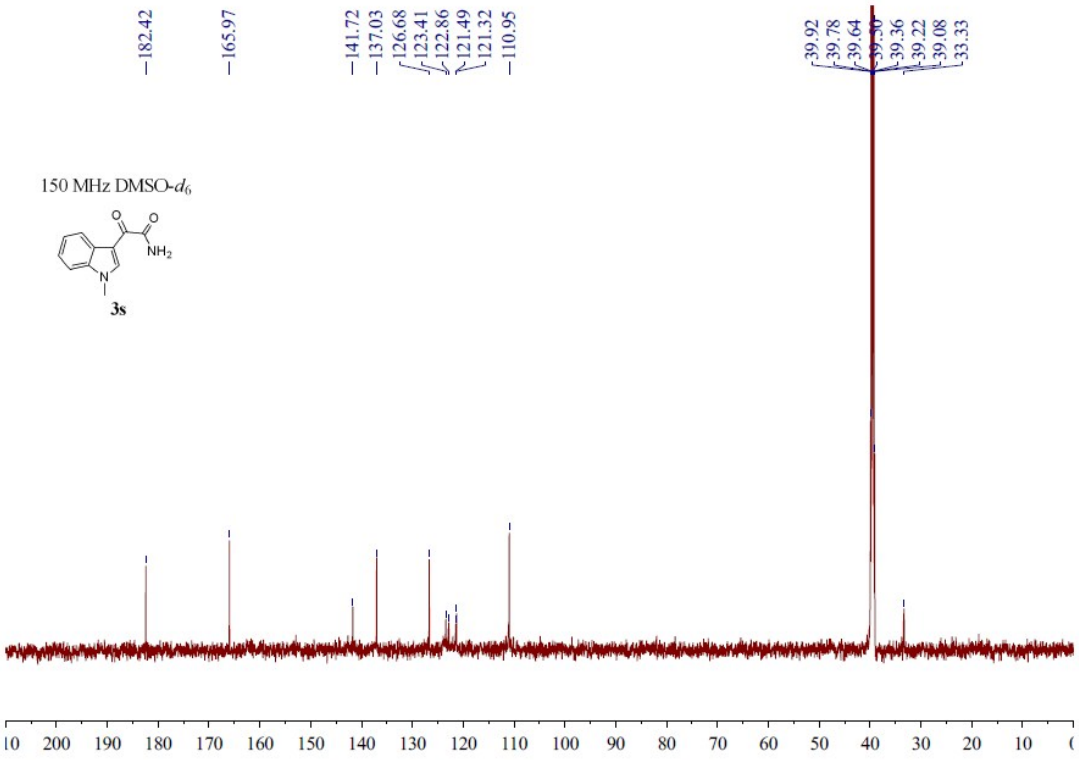

8.306
8.165
8.157
8.135
8.128
7.992
7.291
7.283
7.276
3.361
2.500
600 MHz DMSO-$d_6$
O
S
NH2
O
3q
1.00
1.04
1.08
1.09
1.10
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

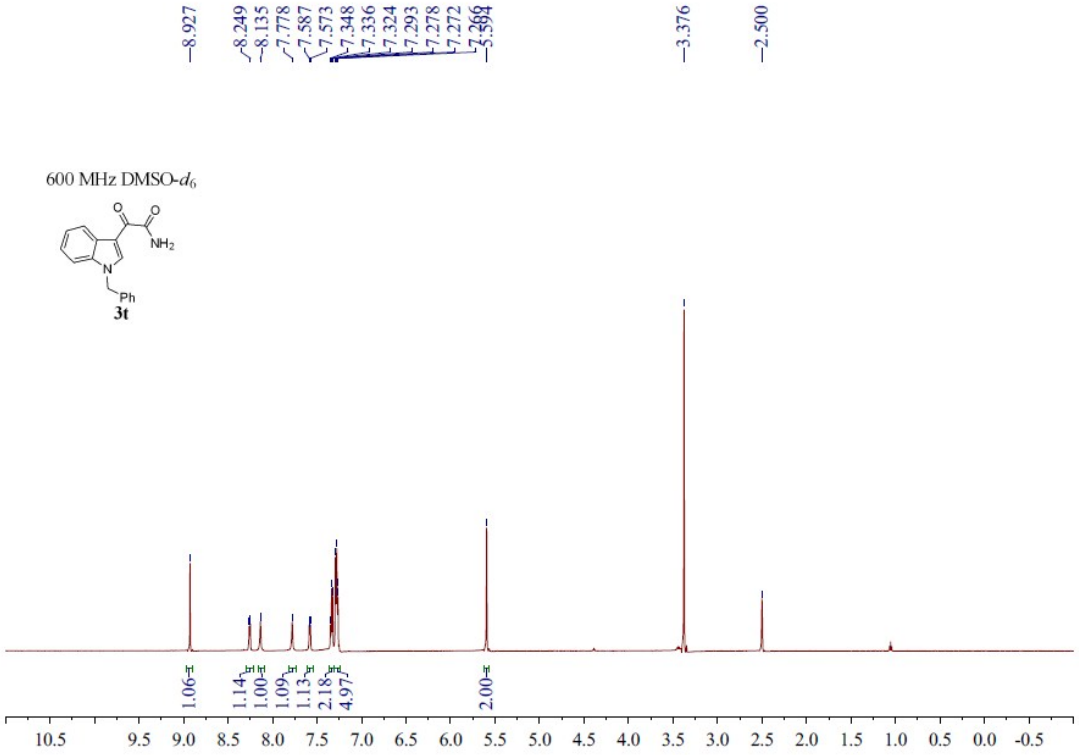

180.64
164.39
138.83
137.41
137.26
128.81
39.92
39.78
39.64
39.50
39.36
39.22
39.08
150 MHz DMSO-$d_6$
O
S
NH2
O
3q
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

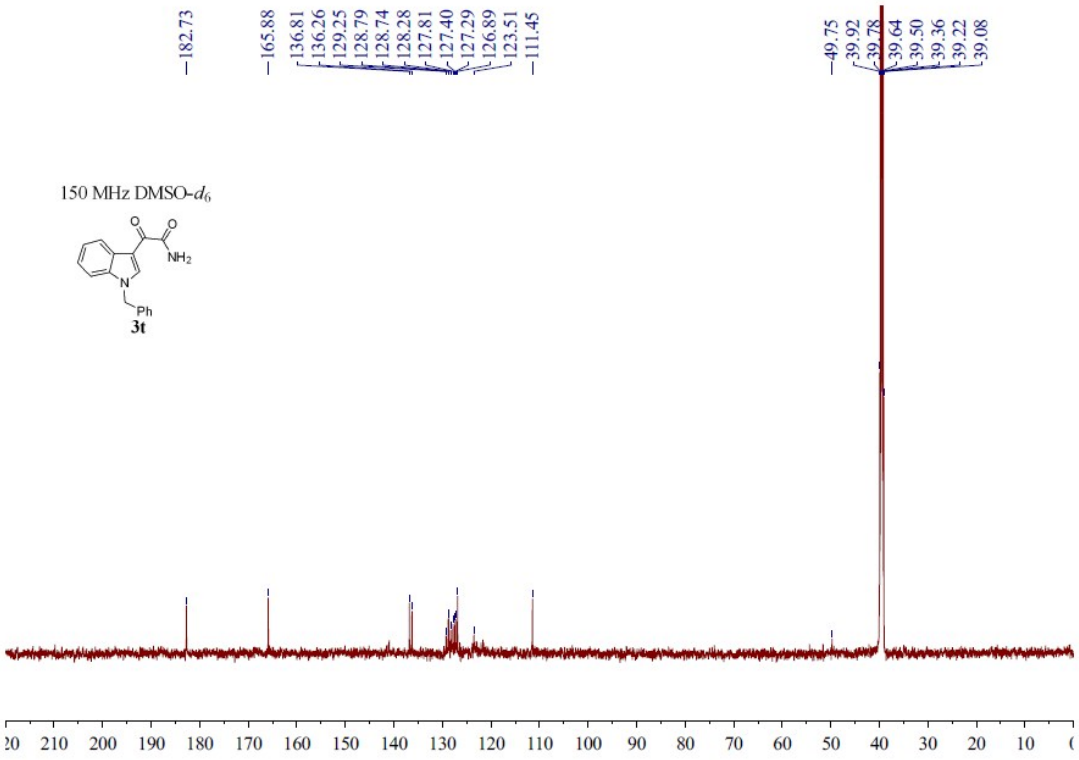

12.208
8.708
8.702
8.240
8.235
8.230
8.226
8.103
7.732
7.541
7.538
7.532
7.527
7.274
7.265
7.262
7.260
7.255
7.250
7.248
7.245
7.236
3.431
2.500
600 MHz DMSO-$d_6$
NH2
O
O
N
H
3r
0.99
1.00
1.00
1.01
1.01
1.05
2.00
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5

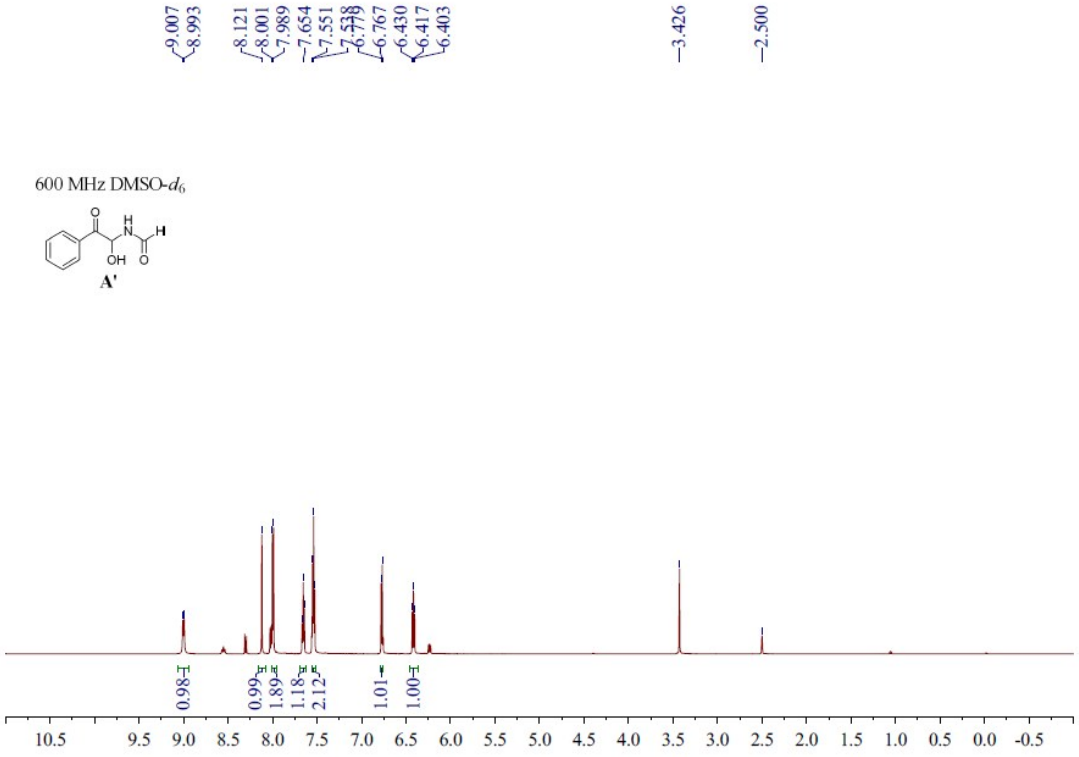

183.02
166.11
136.35
126.20
123.47
122.57
121.35
121.28
112.61
112.15
39.92
39.78
39.64
39.50
39.36
39.22
39.08
150 MHz DMSO-$d_6$
NH2
O
O
N
H
3r
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

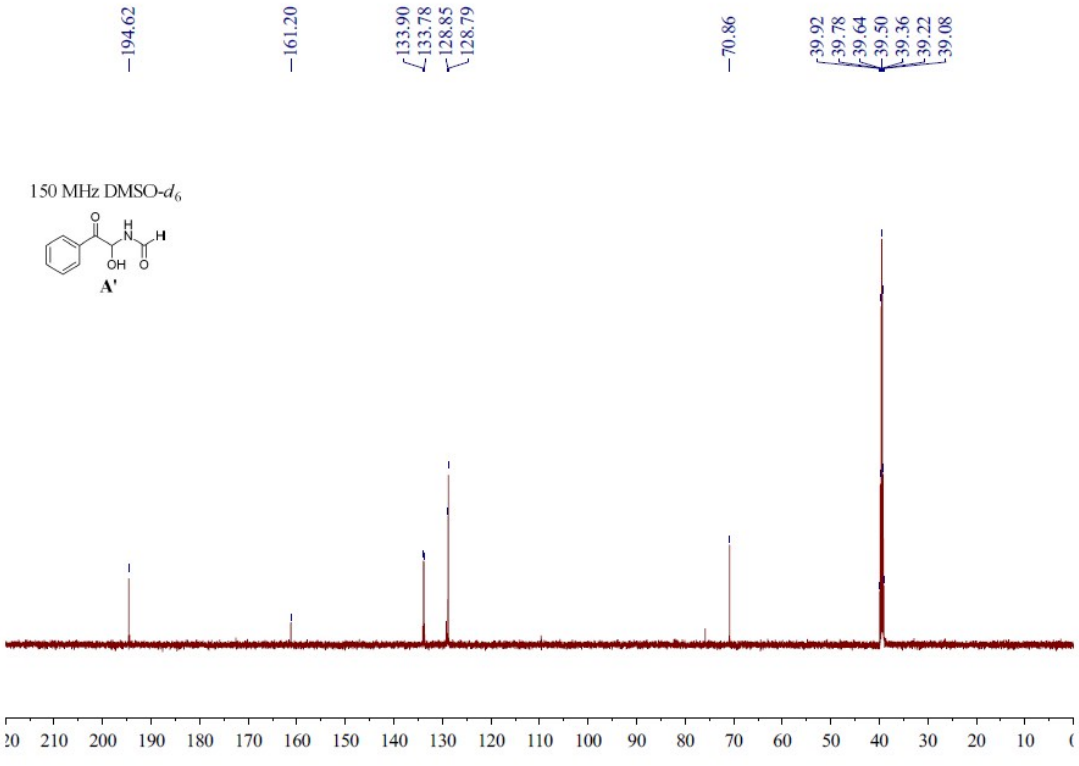

600 MHz DMSO-$d_6$
3s
7.863
7.369
7.356
7.225
6.872
6.698
6.685
6.452
6.440
6.426
6.411
6.400
3.019
2.500
1.00
1.01
0.99
1.01
1.04
2.06
3.00

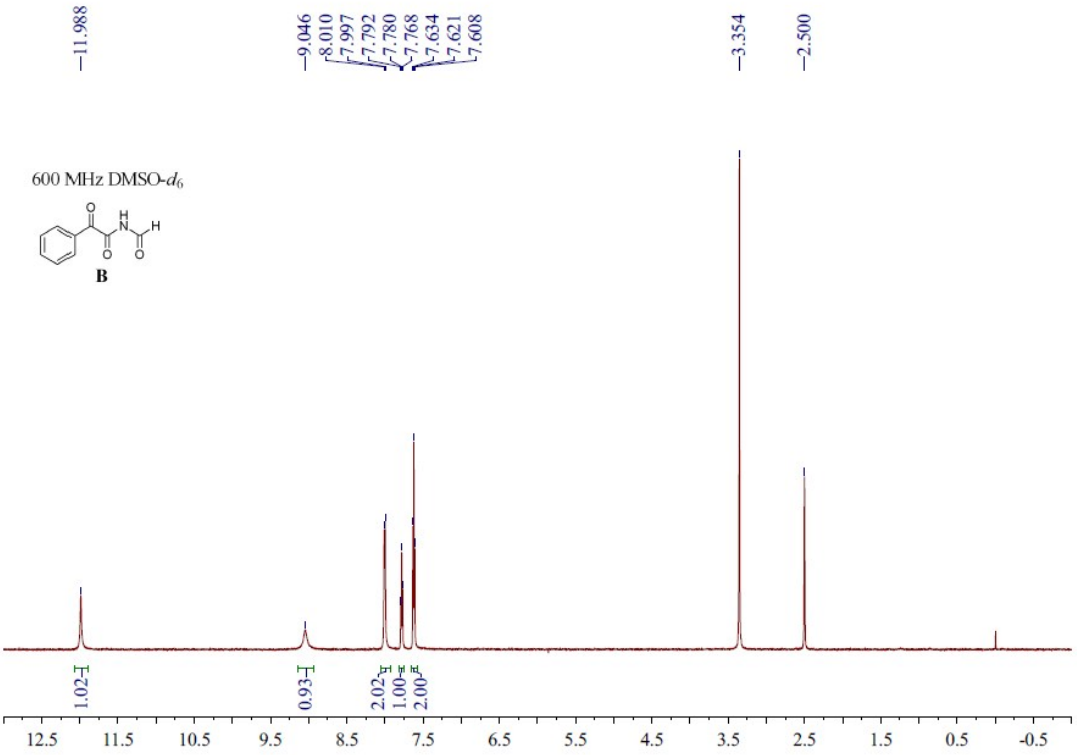

150 MHz DMSO-$d_6$
3s
182.42
165.97
141.72
137.03
126.68
123.41
122.86
121.49
121.32
110.95
39.92
39.78
39.64
39.50
39.36
39.22
39.08
33.33


8.927
8.249
8.135
7.778
7.587
7.573
7.348
7.336
7.324
7.293
7.278
7.272
3.376
2.500
600 MHz DMSO-$d_6$
NH2
Ph
3t
1.06
1.14
1.00
1.09
1.13
2.18
4.97
2.00


182.73
165.88
136.81
136.26
129.25
128.79
128.74
128.28
127.81
127.40
127.29
126.89
123.51
111.45
49.75
39.92
39.78
39.64
39.50
39.36
39.22
39.08
150 MHz DMSO-$d_6$
NH2
Ph
3t


9.007
8.993
8.121
8.001
7.989
7.654
7.551
6.767
6.430
6.417
6.403
3.426
2.500
600 MHz DMSO-$d_6$
A'
0.98
0.99
1.89
1.18
2.12
1.01
1.00
10.5 9.5 9.0 8.5 8.0 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 -0.5


194.62
161.20
133.90
133.78
128.85
128.79
70.86
39.92
39.78
39.64
39.50
39.36
39.22
39.08
150 MHz DMSO-$d_6$
A'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10



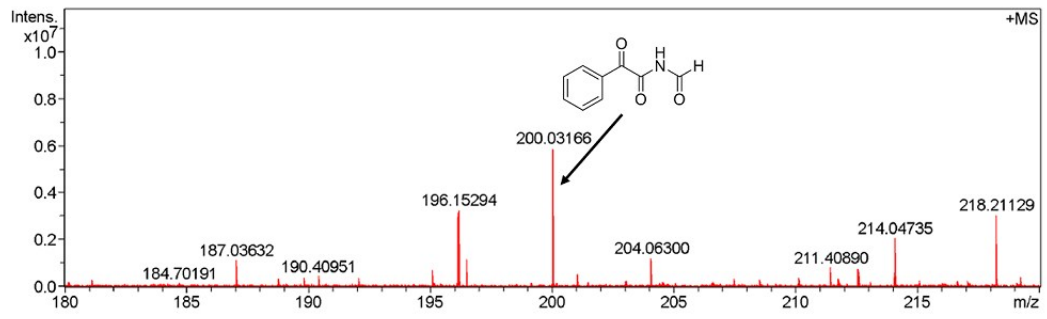

# Mass Spectrum SmartFormula Report

**Analysis Info**

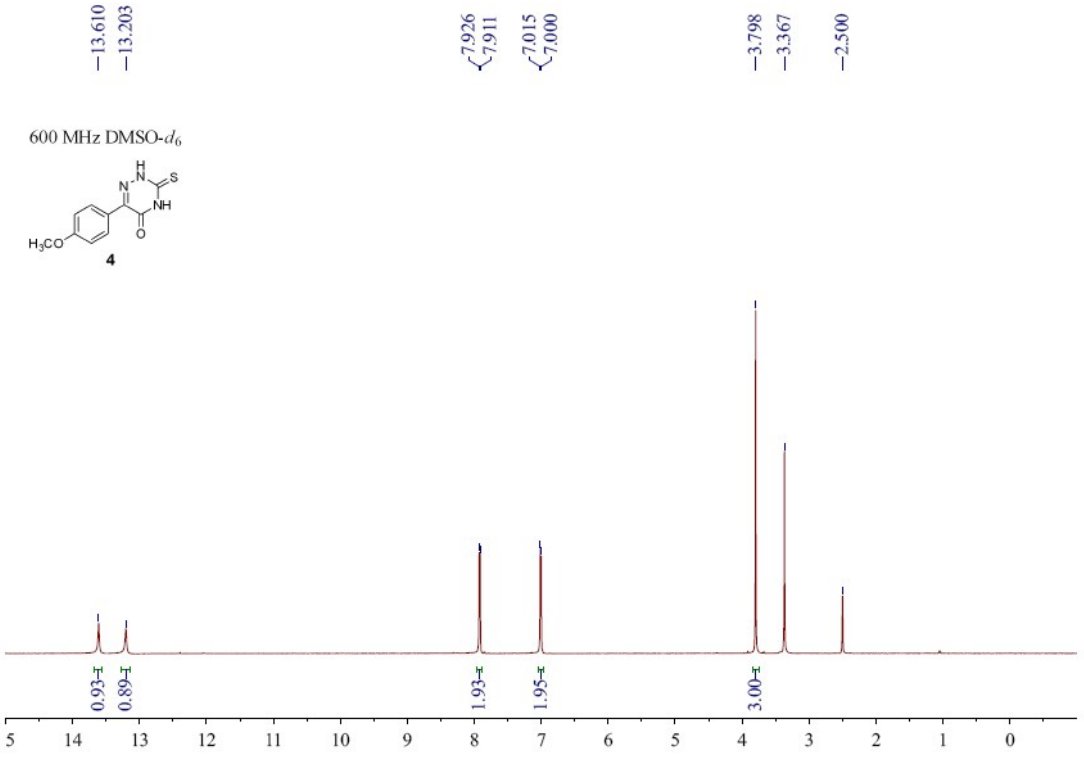
| | | | |
|---|---|---|---|
| Analysis Name | D:\Data\20141123\63136-B_000002.d | Acquisition Date | 11/23/2014 11:16:39 AM |
| Method | 20140812 | Operator | |
| Sample Name | | Instrument | apex-Ultra |
| Comment | | | |

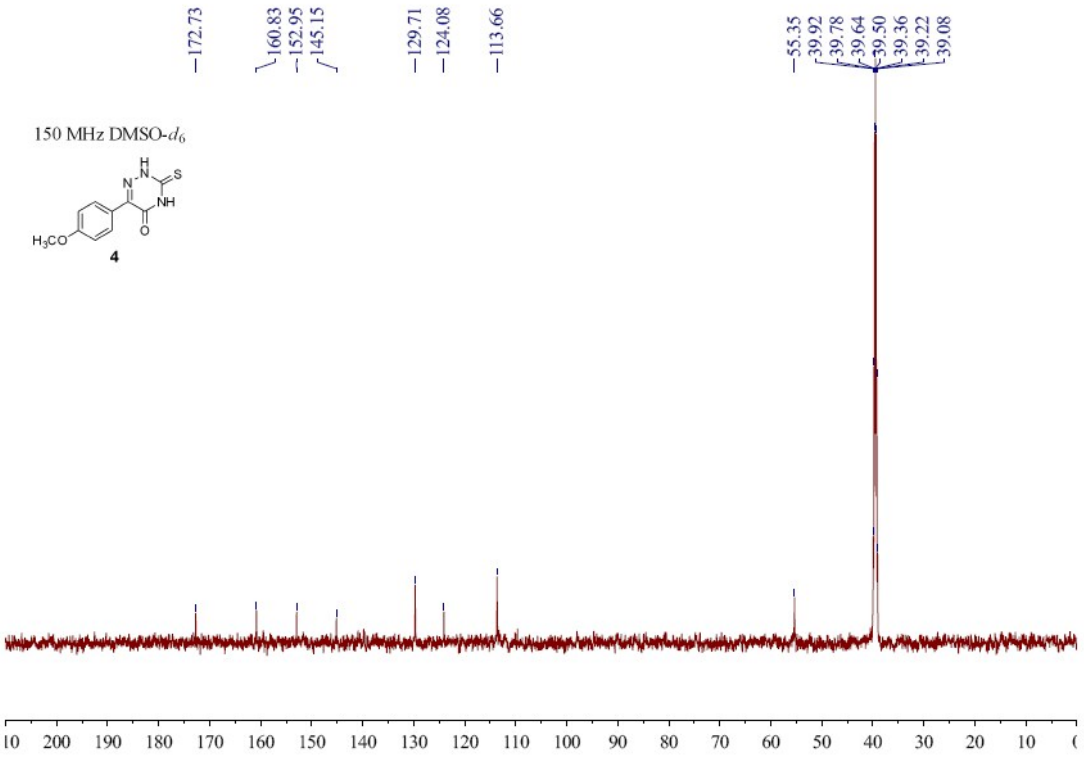
**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Polarity | Positive | Source | ESI | No. of Laser Shots | 20 |
| Averaged Scans | 2 | No. of Cell Fills | 1 | Laser Power | 51.0 % |
| Broadband Low Mass | 100.3 m/z | End Plate | 3500.0 V | MALDI Plate | 300.0 V |
| Broadband High Mass | 1200.0 m/z | Capillary Entrance | 4000.0 V | Imaging Spot Diameter | 2000.0 µm |
| Acquisition Mode | Single MS | Skimmer 1 | 20.0 V | | |
| Pulse Program | basic | Drying Gas Temperature | 180.0 °C | Calibration Date | Sat Nov 22 10:33:48 2014 |
| Source Accumulation | 0.0 sec | Drying Gas Flow Rate | 4.0 L/min | Data Acquisition Size | 131072 |
| Ion Accumulation Time | 0.1 sec | Nebulizer Gas Flow Rate | 1.0 L/min | Apodization | Sine-Bell Multiplication |
| Flight Time to Acq. Cell | 0.0 sec | | | | |




| Meas. m/z | # | Formula | m/z | err [mDa] | err [ppm] | rdb | N-Rule | e⁻ Conf | mSigma |
|---|---|---|---|---|---|---|---|---|---|
| 200.03166 | 1 | C 9 H 7 N Na O 3 | 200.03181 | 0.2 | 0.8 | 6.5 | ok | even | 8.2 |


13.610
13.203
7.926
7.911
7.015
7.000
3.798
3.367
2.500
600 MHz DMSO-$d_6$
4
0.93
0.89
1.93
1.95
3.00


172.73
160.83
152.95
145.15
129.71
124.08
113.66
55.35
39.92
39.78
39.64
39.50
39.36
39.22
39.08
150 MHz DMSO-$d_6$
4