SUPPORTING INFORMATION

Visible light-mediated decarboxylative amination of indoline-2-carboxylic acids catalyzed by Rose Bengal

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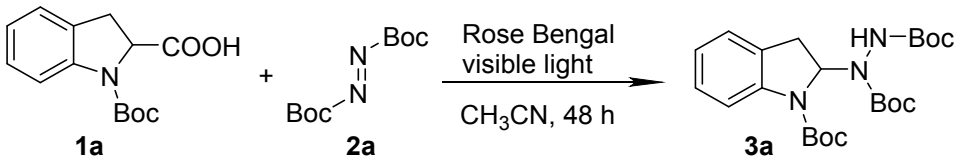
1. General Information

N-protected indoline-2-carboxylate acids and *N*-Boc-1,2,3,4-tetrahydroisoquinoline-1-carboxylic acid (**1**) were prepared according to the literature[1]. Rose Bengal was purchased from Aladdin, Shanghai, China (R104993-1 G, Lot#L15040, 95%). Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) with Haiyang GF254 silica gel plates (Qingdao Haiyang chemical industry Co Ltd. Qingdao, China) using UV light and vanillic aldehyde as visualizing agents. Flash column chromatography was performed using 200-300 mesh silica gel at increased pressure. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AM 600 (600 MHz) (Bruker BioSpin AG Ltd., Beijing, China). Chemical shifts were reported in ppm from TMS with the solvent resonance as the internal standard. Data were reported as follows: chemical shifts (δ) in ppm, coupling constants (J) in Hz, and solvent ($CDCl_3$). High-resolution mass spectra were obtained by using ESI ioniza-tion sources (Varian 7.0T FTICR-MS). Melting points were taken on a WPX-4 apparatus and were uncorrected (Yice instrument equipment Co Ltd, Shanghai).

2. Extra information for optimization of the reaction conditions

Table S1 Effect of molar ratio of substrates on the model reaction [a]

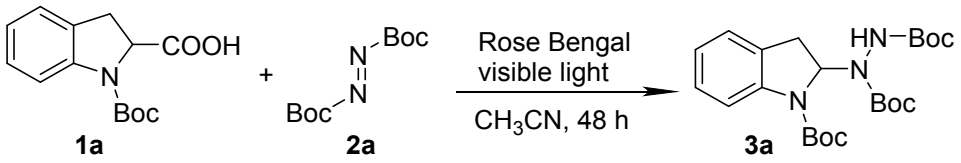


Entry	Molar ratio (1a : 2a)	Yield (%)[b]
1	3 : 1	55
2	2.5 : 1	54
3	**2 : 1**	**52**
4	1.5 : 1	46
5	1 : 1	41
6	1 : 1.5	49
7	1 : 2	50

[a] Reaction conditions: **1a** (0.2-0.6 mmol), **2a** (0.2-0.4 mmol), CH_3CN (1.0 mL), and Rose Bengal (2 mol%) under irradiation of 32 W fluorescent bulb at rt for 48 h.

[b] Isolated yield.

Table S2 Effect of solvent volume on the model reaction [a]

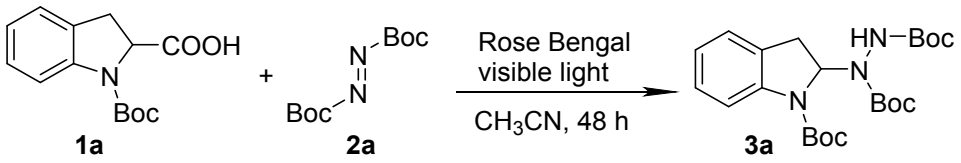


Entry	CH_3CN (mL)	Yield (%)[b]
1	**0.5**	**54**
2	1	52
3	1.5	47
4	2	50
5	2.5	48

[a] Reaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), CH_3CN, and Rose Bengal (2 mol%) under irradiation of 32 W fluorescent bulb at rt for 48 h.

[b] Isolated yield.

Table S3 Effect of visible light on the model reaction [a]

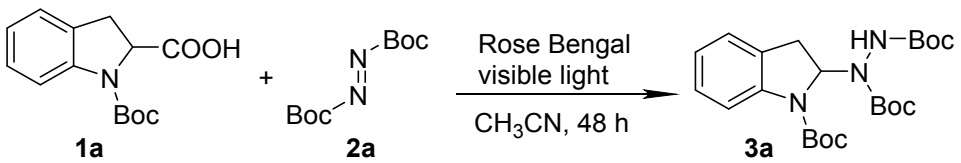


Entry	Visible light (W)	Yield (%)[b]
1	5	25
2	12	34
3	**23**	**52**
4	32	54
5	45	54

[a] Reaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), CH_3CN (0.5 mL), and Rose Bengal (2 mol%) under irradiation of fluorescent bulb at rt for 48 h.

[b] Isolated yield.

Table S4 Effect of photocatalyst loading on the model reaction [a]



Entry	Rose Bengal (x mol%)	Yield (%)[b]
1	0.5	58
2	**1**	**66**

3	2	53
4	4	48
5	7.5	39
6	10	32

[a] Reaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), CH_3CN (0.5 mL), and Rose Bengal (x mol%) under irradiation of 23 W fluorescent bulb at rt for 48 h.

[b] Isolated yield.

3. Fluorescence of 2a

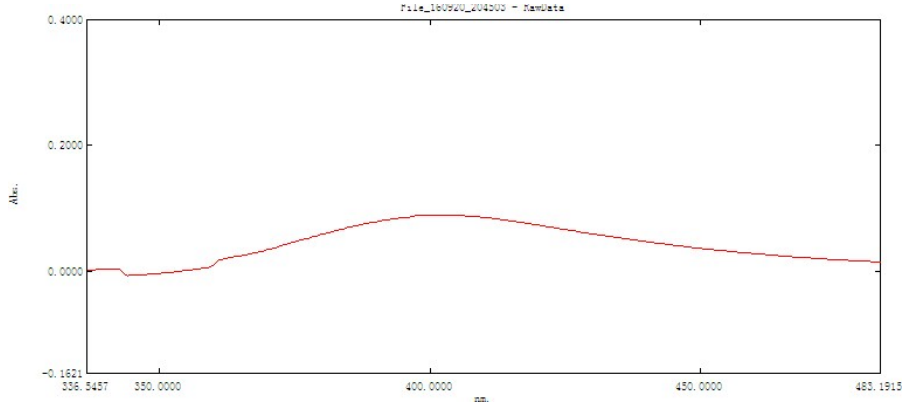
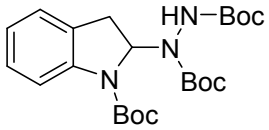


Figure 1. Fluorescence response of **2a** (2.5 mM in CH_3CN).

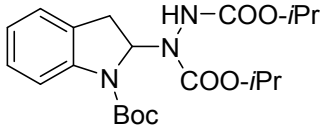
4. Characterization data of the products

Di-*tert*-butyl 1-(1-(*tert*-butoxycarbonyl)indolin-2-yl)hydrazine-1,2-dicarboxylate (3a)



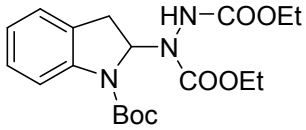
White solid; mp 174-175 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.73 (m, 1H), 7.11 (m, 2H), 6.92 (t, *J*=7.3, 1H), 6.51 (br, 1H), 5.85 (d, *J*=179.1, 1H), 3.30 (m, 2H), 1.50 (m, 27H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 155.3, 153.0, 152.1, 142.2, 129.5, 127.1, 124.2, 123.9, 122.5, 114.3, 81.6, 81.1, 70.7, 34.6, 32.9, 28.5, 28.2, 28.2, 28.1. HRMS(ESI) m/z 472.2422 ($M+Na^+$), Cal. $C_{23}H_{35}N_3O_6Na$, 472.2418.

Di-*iso*-propyl 1-(1-(*tert*-butoxycarbonyl)indolin-2-yl)hydrazine-1,2-dicarboxylate (3b)



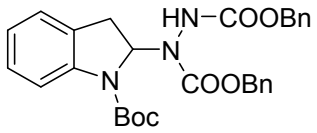
White solid; mp 139-140 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.60 (m, 1H), 7.12 (m, 2H), 6.92 (t, *J*=7.2, 1H), 6.54(br, 1H), 6.04 (d, *J*=94.7, 1H), 4.89 (m, 2H), 3.32 (m, 2H), 1.54 (s, 9H), 1.17 (m, 12H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 155.9, 151.9, 142.0, 127.1, 123.9, 122.5, 114.2, 81.8, 70.7, 70.0, 69.7, 28.4, 21.8. HRMS(ESI) m/z 444.2113 ($M+Na^+$), Cal. $C_{21}H_{31}N_3O_6Na$, 444.2105.

Diethyl 1-(1-(*tert*-butoxycarbonyl)indolin-2-yl)hydrazine-1,2-dicarboxylate (3c)



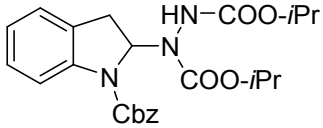
Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.71 (m, 1H), 7.12 (m, 2H), 6.93 (t, *J*=7.1, 1H), 6.60 (br, 1H), 6.23 (d, *J*=89.0, 1H), 4.12 (m, 4H), 3.33 (m, 2H), 1.54 (s, 9H), 1.21 (dd, *J*=41.5, 35.3, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 156.4, 154.5, 151.9, 141.9, 129.0, 127.2, 123.9, 122.6, 114.3, 81.9, 62.6, 62.0, 29.6, 28.4, 14.3. HRMS(ESI) m/z 416.1800 ($M+Na^+$), Cal. $C_{19}H_{27}N_3O_6Na$, 416.1792.

Dibenzyl 1-(1-(*tert*-butoxycarbonyl)indolin-2-yl)hydrazine-1,2-dicarboxylate (3d)



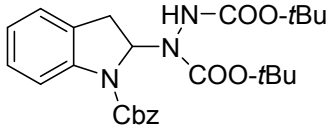
White solid; mp 123-124 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.66 (m, 1H), 7.31 (dd, *J*=33.0, 9.9, 8H), 7.08 (dd, *J*=96.7, 59.9, 5H), 6.62 (br, 1H), 6.34 (d, *J*=124.1, 1H), 5.06 (m, 4H), 3.19 (m, 2H), 1.46 (d, *J*=37.9, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 156.2, 153.9, 151.9, 141.9, 135.7, 128.6, 128.5, 128.2, 127.9, 127.3, 126.9, 124.0, 122.7, 114.4, 82.0, 68.2, 67.6, 28.4. HRMS(ESI) m/z 540.2112 ($M+Na^+$), Cal. $C_{29}H_{31}N_3O_6Na$, 540.2105.

Di-*iso*-propyl 1-(1-((benzyloxy)carbonyl)indolin-2-yl)hydrazine-1,2-dicarboxylate (3e)



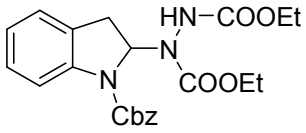
White solid; mp 120-122 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.72 (m, 1H), 7.37 (m, 5H), 7.13 (m, 2H), 6.96 (d, *J*=6.7, 1H), 6.67 (br, 1H), 6.19 (d, *J*=115.2, 1H), 5.29 (m, 2H), 4.86 (m, 2H), 3.38 (m, 2H), 1.21 (m, 12H); ^{13}C NMR (151 MHz, CDCl3) δ = 156.2, 154.1, 153.9, 152.7, 141.6, 135.9, 128.6, 128.3, 127.3, 123.9, 122.9, 114.4, 69.8, 67.6, 29.7, 21.8. HRMS(ESI) m/z 478.1956 ($M+Na^+$), Cal. $C_{24}H_{29}N_3O_6Na$, 478.1949.

Di-*tert*-butyl 1-(1-((benzyloxy)carbonyl)indolin-2-yl)hydrazine-1,2-dicarboxylate (3f)



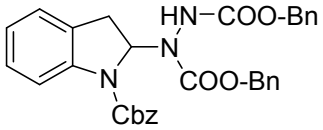
White solid; mp 153-154 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.75 (m, 1H), 7.37 (m, 5H), 7.12 (dd, *J*=17.0, 6.9, 2H), 6.95 (t, *J*=7.3, 1H), 6.61 (br, 1H), 5.82 (d, *J*=192.4, 1H), 5.30 (d, *J*=51.7, 2H), 3.30 (m, 2H), 1.35 (dd, *J*=73.0, 28.7, 18H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 155.3, 153.1, 152.7, 141.8, 136.1, 128.7, 128.6, 128.1, 127.2, 124.0, 122.9, 114.4, 81.6, 81.0, 70.8, 67.3, 33.4, 28.0. HRMS(ESI) m/z 506.2266 ($M+Na^+$), Cal. $C_{26}H_{23}N_3O_6Na$, 506.2262.

Diethyl 1-(1-((benzyloxy)carbonyl)indolin-2-yl)hydrazine-1,2-dicarboxylate (3g)



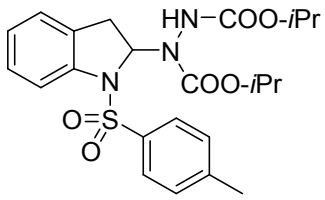
White solid; mp 93-94 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.81 (m, 1H), 7.37 (dd, *J*=18.5, 11.6, 5H), 7.13 (m, 2H), 6.96 (t, *J*=7.2, 1H), 6.66 (br, 1H), 6.29 (d, *J*=113.6, 1H), 5.26 (s, 2H), 4.07 (s, 4H), 3.35 (m, 2H), 1.19 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 156.6, 154.5, 152.8, 141.6, 135.9, 128.6, 128.4, 127.4, 124.0, 123.0, 114.4, 67.8, 62.9, 62.7, 62.0, 29.7, 14.3. HRMS(ESI) m/z 450.1643 ($M+Na^+$), Cal. $C_{22}H_{25}N_3O_6Na$, 450.1636.

Dibenzyl 1-(1-((benzyloxy)carbonyl)indolin-2-yl)hydrazine-1,2-dicarboxylate (3h)



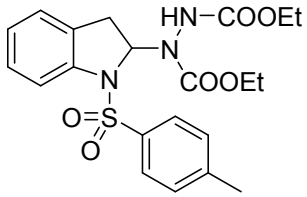
White solid; mp 143-144°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.76 (m, 1H), 7.13 (m, 18H), 6.72 (m, 1H), 6.36 (d, *J*=139.9, 1H), 5.06 (m, 6H), 3.41 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 156.4, 152.7, 135.8, 135.6, 128.6, 128.5, 128.2, 127.8, 128.5, 124.1, 123.1, 114.4, 67.6, 29.7. HRMS(ESI) m/z 574.1957 ($M+Na^+$), Cal. $C_{32}H_{29}N_3O_6Na$, 574.1949.

Di-*iso*-propyl 1-(1-tosylindolin-2-yl)hydrazine-1,2-dicarboxylate (3i)



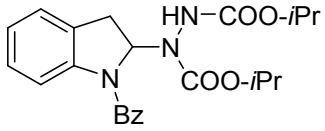
Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.73 (m, 3H), 7.25 (m, 2H), 7.19 (t, *J*=7.7, 1H), 7.00 (m, 2H), 6.42 (d, *J*=25.1, 1H), 4.97 (m, 2H), 3.10 (m, 2H), 2.37 (s, 3H), 1.26 (m, 12H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 156.2, 144.4, 141.0, 129.8, 127.6, 124.6, 123.8, 114.4, 70.9, 69.9, 26.9, 21.9, 21.8, 21.7, 21.5. HRMS(ESI) m/z 498.1677 ($M+Na^+$), Cal. $C_{23}H_{29}N_3O_6SNa$, 498.1669.

Diethyl 1-(1-tosylindolin-2-yl)hydrazine-1,2-dicarboxylate (3j)



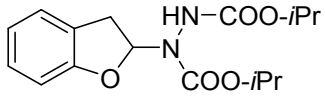
White solid; mp 141-142 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.73 (d, *J*=40.7, 3H), 7.22 (dt, *J*=15.5, 8.6, 3H), 7.00 (m, 2H), 6.42 (m, 2H), 4.19 (m, 4H), 3.21 (s, 2H), 2.37 (s, 3H), 1.26 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 156.5, 144.5, 141.0, 129.8, 127.7, 124.6, 123.9, 114.4, 63.1, 62.1, 26.9, 21.5, 14.3. HRMS(ESI) m/z 470.1361 ($M+Na^+$), Cal. $C_{21}H_{25}N_3O_6SNa$, 470.1356.

Di-*iso*-propyl 1-(1-benzoylindolin-2-yl)hydrazine-1,2-dicarboxylate (3k)



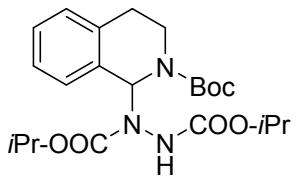
White solid; mp 175-176 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.30 (m, 9H), 6.29 (m, 2H), 4.92 (m, 2H), 3.40 (m, 2H), 1.26 (d, *J*=6.2, 12H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 169.9, 155.9, 142.3, 130.6, 128.8, 127.0, 124.4, 123.9, 115.6, 69.9, 64.3, 29.7, 21.9, 21.8. HRMS(ESI) m/z 448.1850 ($M+Na^+$), Cal. $C_{23}H_{27}N_3O_5Na$, 448.1843.

Di-*iso*-propyl 1-(2,3-dihydrobenzofuran-2-yl)hydrazine-1,2-dicarboxylate (3l)



Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.12 (m, 2H), 6.82 (m, 2H), 6.11 (d, *J*=129.1, 1H), 4.99 (dd, *J*=33.4, 27.4, 2H), 3.37 (m, 2H), 1.25 (m, 12H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 157.3, 155.2, 153.5, 126.9, 123.5, 119.8, 107.8, 99.0, 69.1, 28.6, 20.7, 21.0, 20.9, 20.7. HRMS(ESI) m/z 345.1429 ($M+Na^+$), Cal. $C_{16}H_{22}N_2O_5Na$, 345.1421.

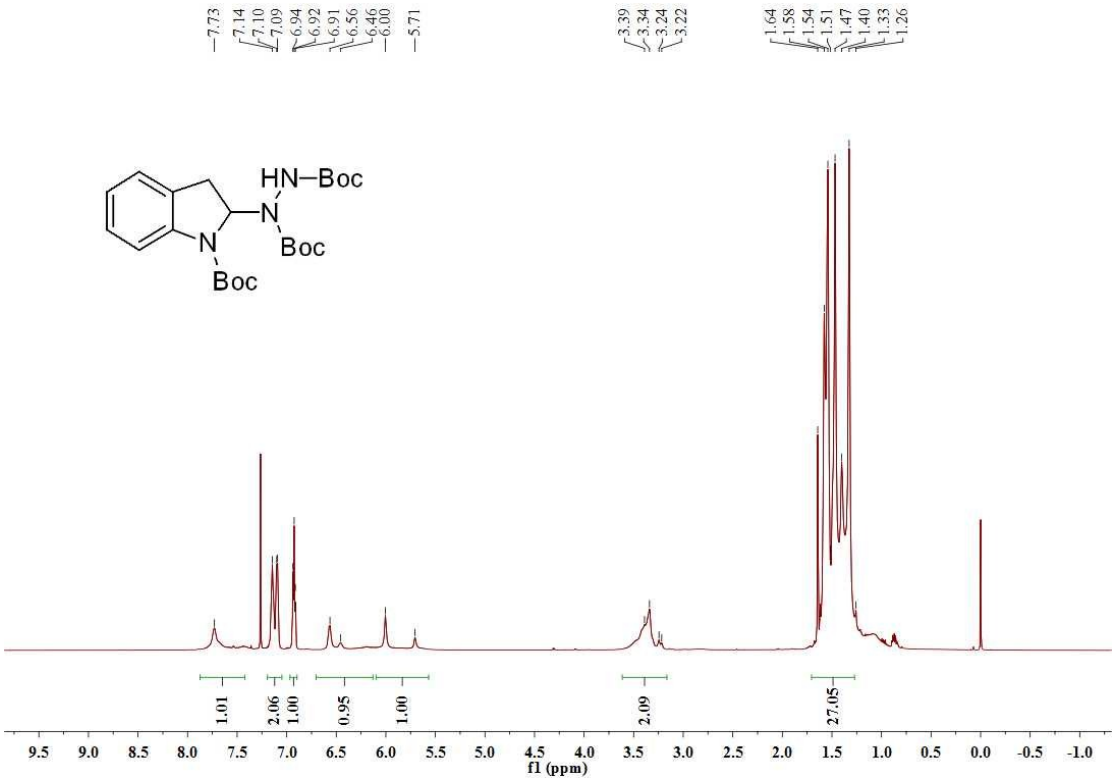
Di-*iso*-propyl 1-(2-(*tert*-butoxycarbonyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)hydrazine-1,2-dicarboxylate (3m)

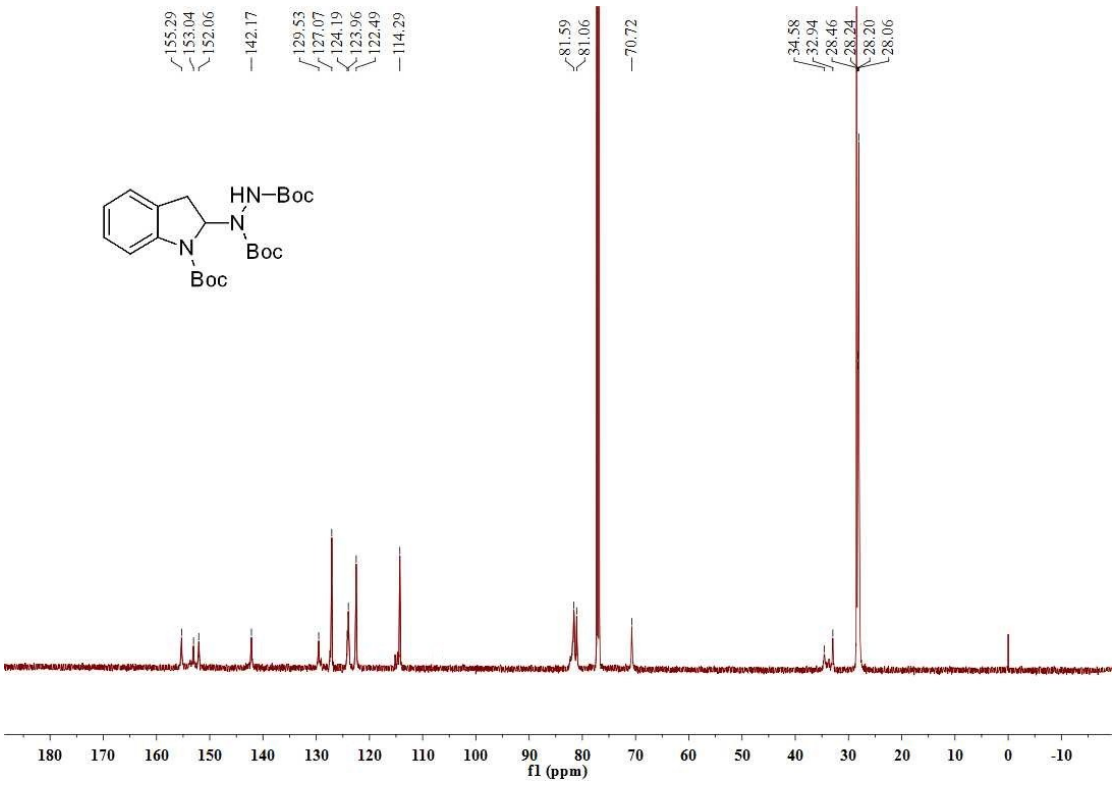


Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.57 (s, 1H), 7.17 (m, 3H), 6.22 (dd, *J*=416.6, 316.2, 2H), 4.84 (d, *J*=201.0, 2H), 4.25 (d, *J*=110.9, 1H), 3.33 (d, *J*=130.6, 1H), 2.77 (d, *J*=30.9, 2H), 1.42 (m, 21H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 154.9, 134.4, 128.6, 127.8, 126.6, 80.8, 70.0, 28.9, 28.4, 21.9. HRMS(ESI) m/z 458.2269 ($M+Na^+$), Cal. $C_{22}H_{33}N_3O_6Na$, 458.2262.

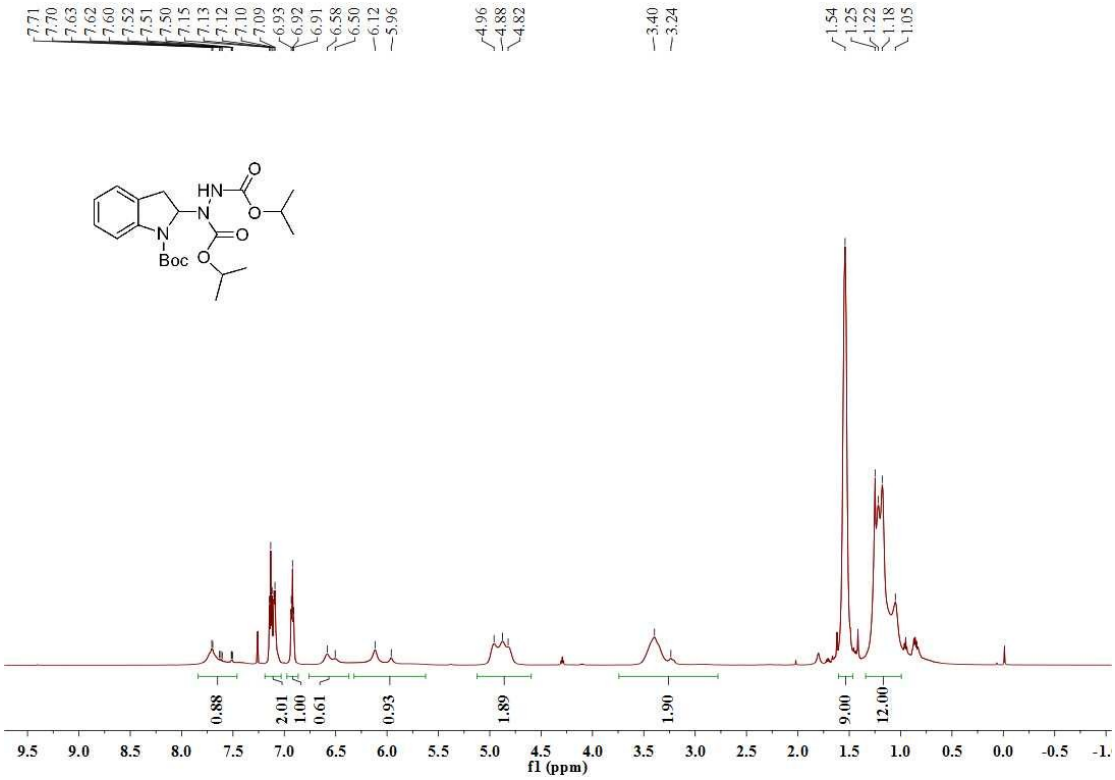
5. ^{1}H NMR and ^{13}C NMR spectra of the products

3a





3b


7.71
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7.52
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6.92
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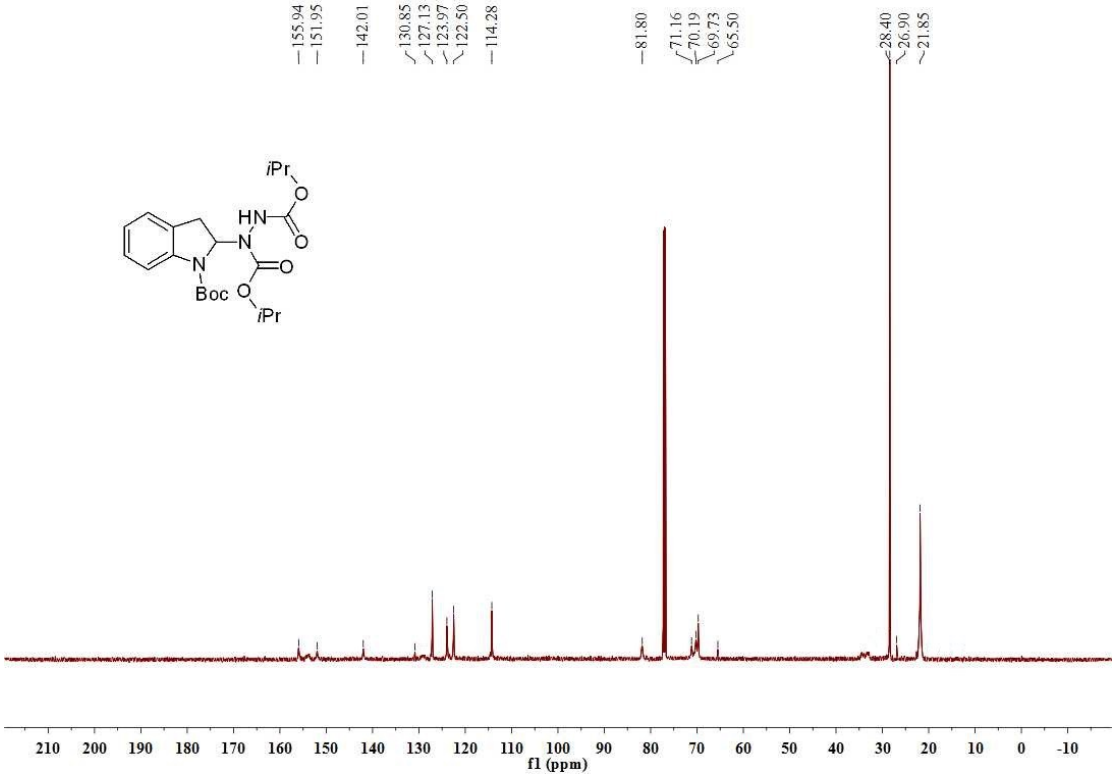
4.88
4.82
3.40
3.24
1.54
1.25
1.22
1.18
1.05
HN
N
O
Boc
0.88
2.01
1.00
0.61
0.93
1.89
1.90
9.00
12.00
f1 (ppm)


155.94
151.95
142.01
130.85
127.13
123.97
122.50
114.28
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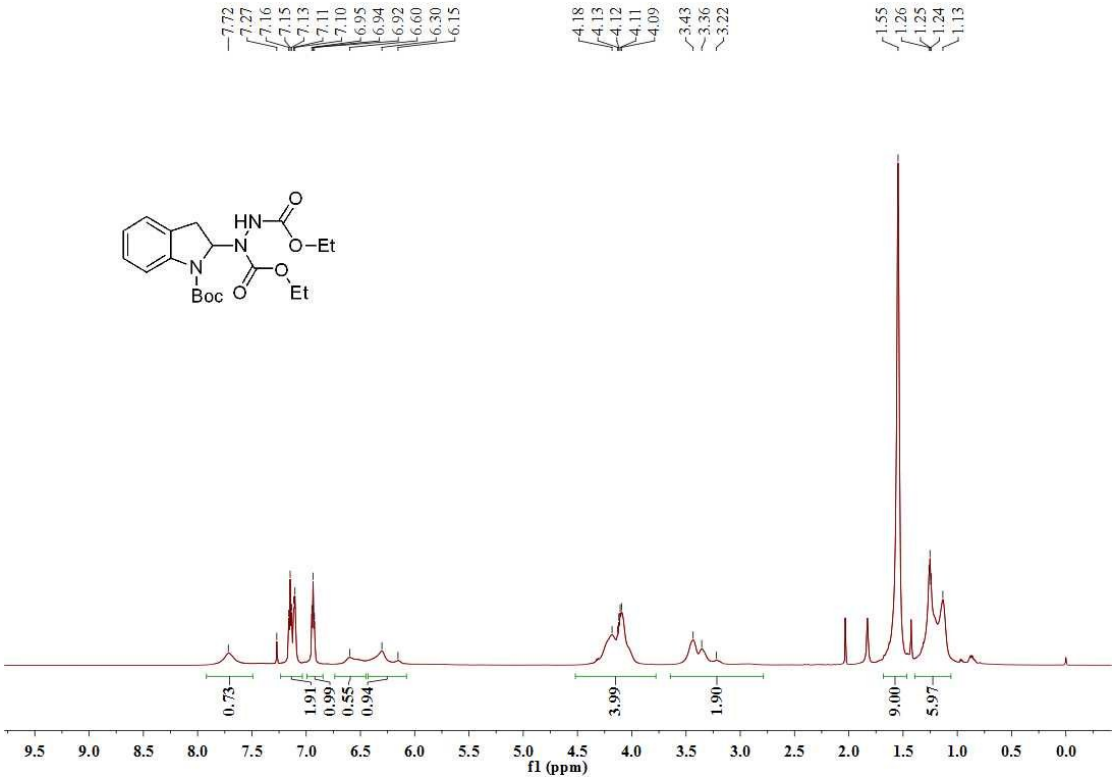
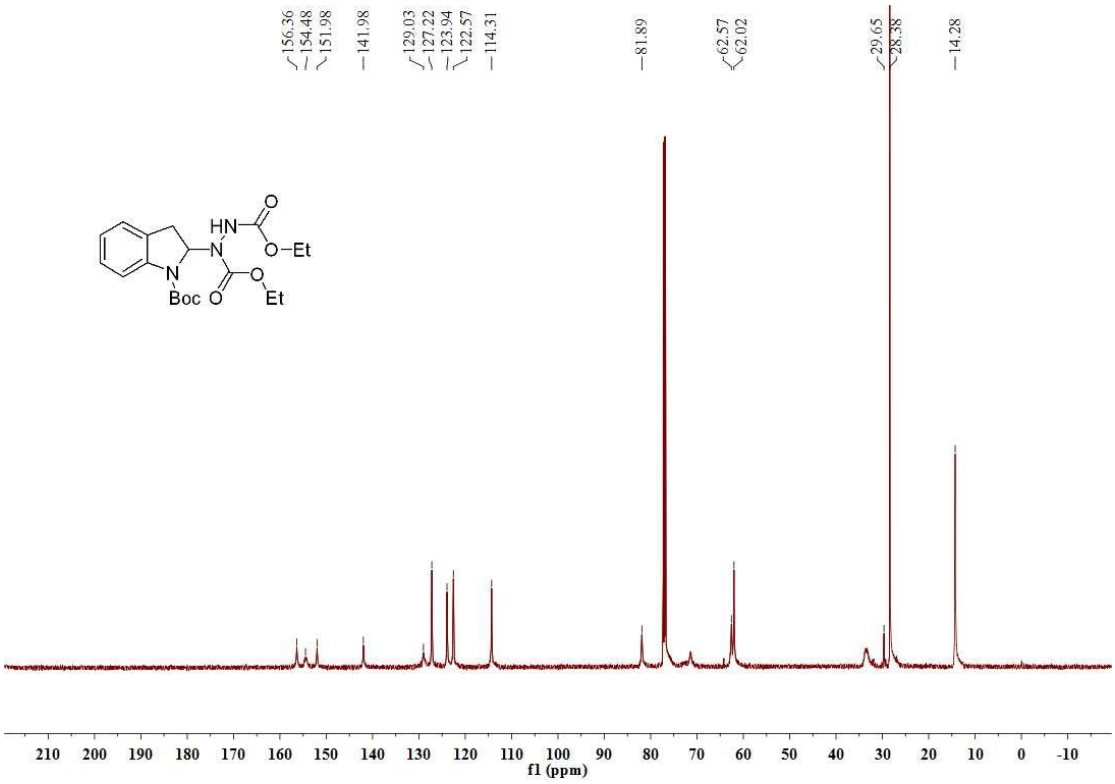
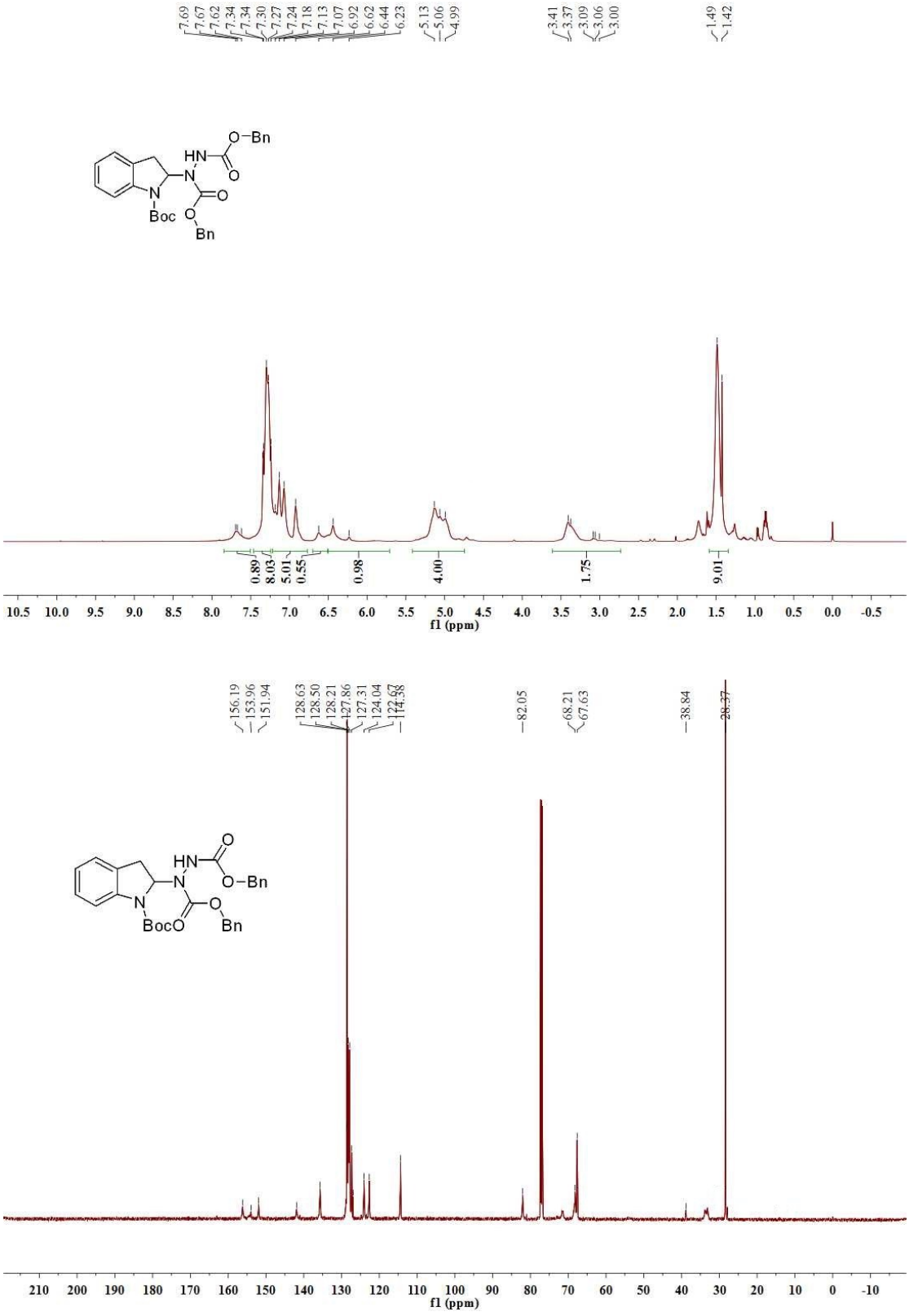
71.16
70.19
69.73
65.50
28.40
26.90
21.85
iPr
HN
N
O
Boc
f1 (ppm)

3c

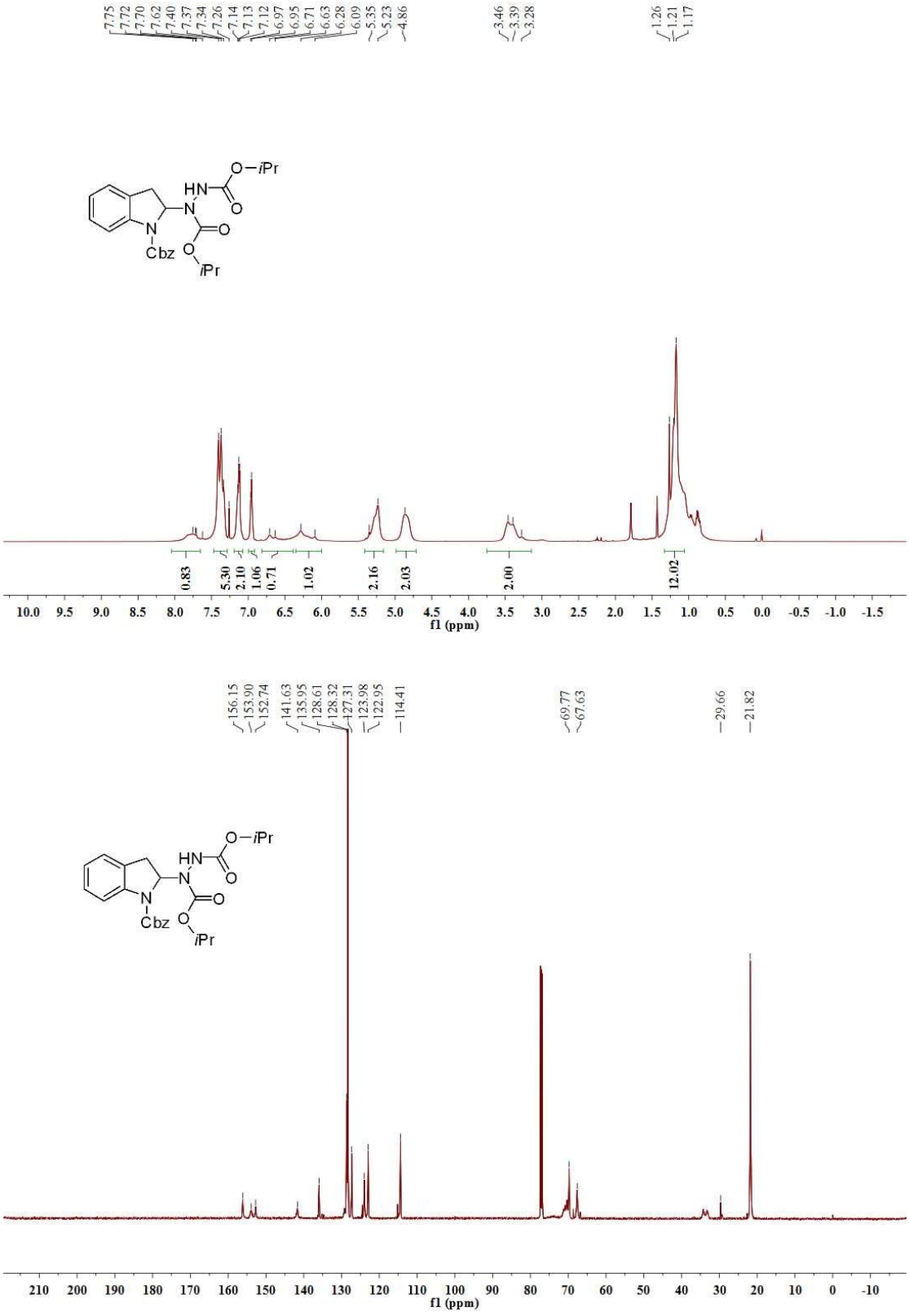

7.72
7.27
7.16
7.15
7.13
7.11
7.10
6.95
6.94
6.92
6.60
6.30
6.15
4.18
4.13
4.12
4.11
4.09
3.43
3.36
3.22
1.55
1.26
1.25
1.24
1.13
HN
O
O–Et
N
N
Boc
O
O
Et
0.73
1.91
0.99
0.55
0.94
3.99
1.90
9.00
5.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


156.36
154.48
151.98
141.98
129.03
127.22
123.94
122.57
114.31
81.89
62.57
62.02
29.65
28.38
14.28
HN
O
O–Et
N
N
Boc
O
O
Et
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

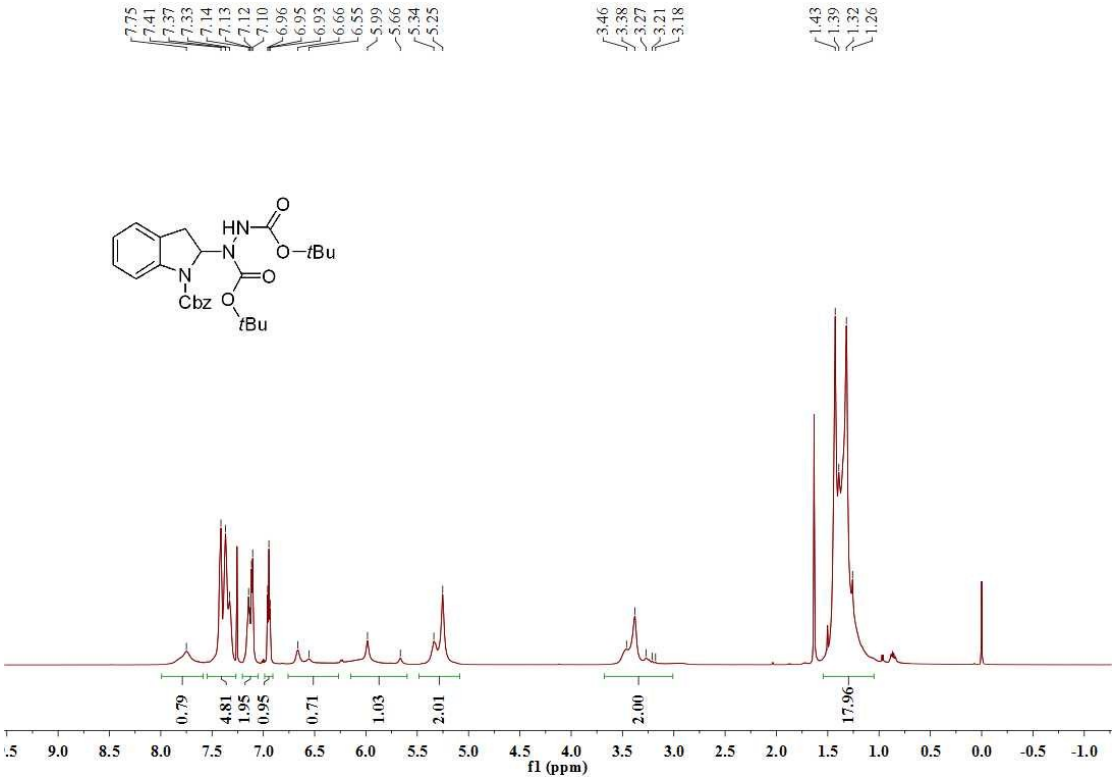
3d

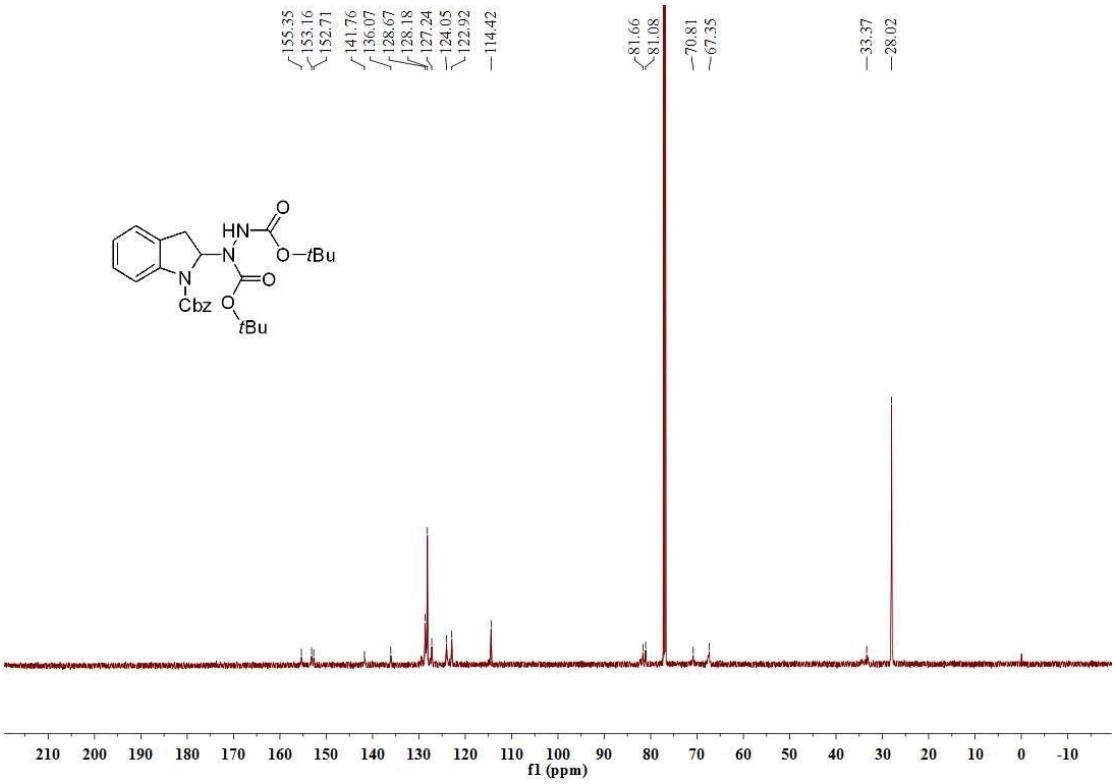

7.69
7.67
7.62
7.34
7.30
7.27
7.24
7.18
7.13
7.07
6.92
6.62
6.44
6.23
5.13
5.06
4.99
3.41
3.37
3.09
3.06
3.00
1.49
1.42
O–Bn
HN
N
O
Boc
O
Bn
0.89
8.03
5.01
0.55
0.98
4.00
1.75
9.01
fl (ppm)
156.19
153.96
151.94
128.63
128.50
128.21
127.86
127.31
124.04
82.05
68.21
67.63
38.84
28.37
BocO
fl (ppm)

3e

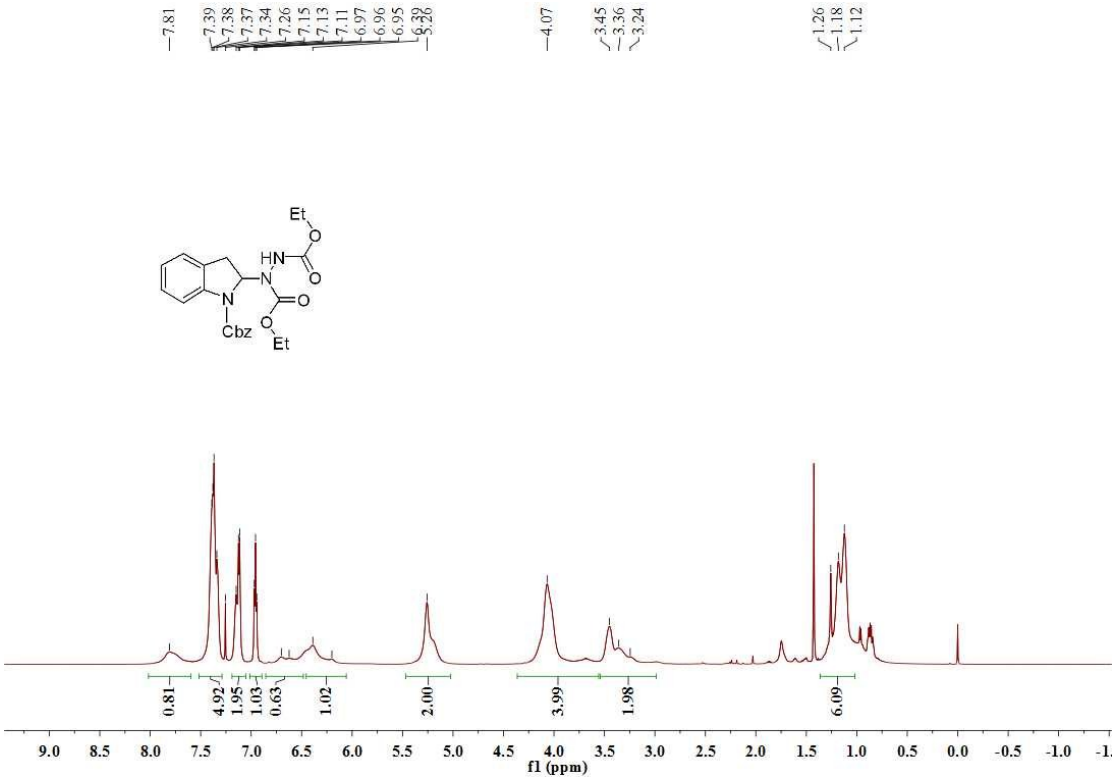

7.75
7.72
7.70
7.62
7.40
7.37
7.34
7.26
7.14
7.13
7.12
6.97
6.95
6.71
6.63
6.28
6.09
5.35
5.23
4.86
3.46
3.39
3.28
1.26
1.21
1.17
O–iPr
HN
N
O
N
Cbz
O
iPr
0.83
5.30
2.10
1.06
0.71
1.02
2.16
2.03
2.00
12.02
f1 (ppm)
156.15
153.90
152.74
141.63
135.95
128.61
128.32
127.31
123.98
122.95
114.41
69.77
67.63
29.66
21.82
f1 (ppm)

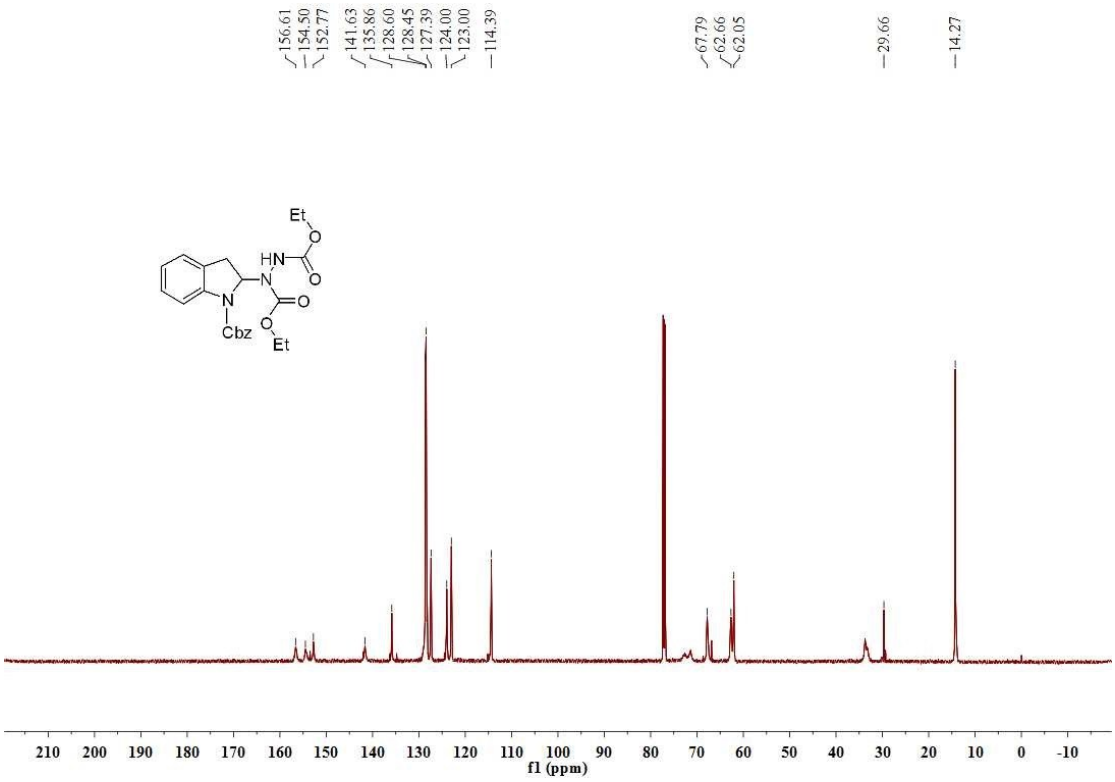
3f


7.75
7.41
7.37
7.33
7.14
7.13
7.12
7.10
6.96
6.95
6.93
6.66
6.55
5.99
5.66
5.34
5.25
3.46
3.38
3.27
3.21
3.18
1.43
1.39
1.32
1.26
HN
O
O–tBu
N
N
O
Cbz
O
tBu
0.79
4.81
1.95
0.95
0.71
1.03
2.01
2.00
17.96
f1 (ppm)

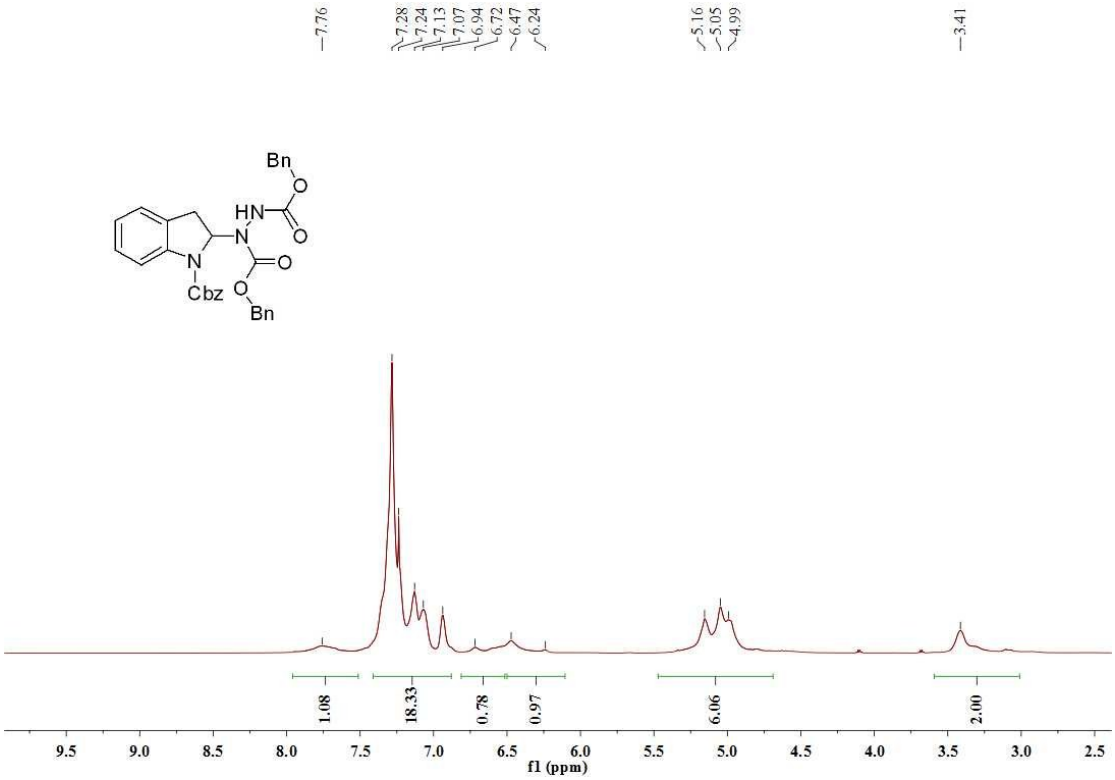

155.35
153.16
152.71
141.76
136.07
128.67
128.18
127.24
124.05
122.92
114.42
81.66
81.08
70.81
67.35
33.37
28.02
HN
O
O–tBu
N
N
O
Cbz
O
tBu
f1 (ppm)

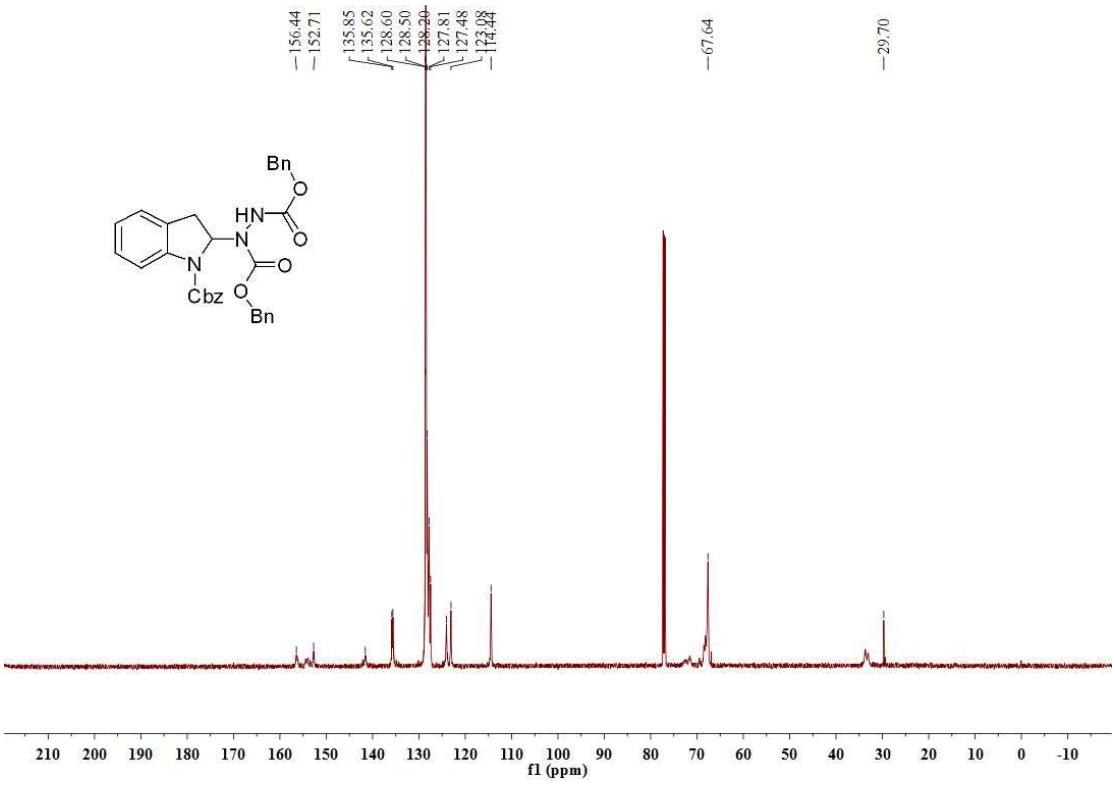
3g


7.81
7.39
7.38
7.37
7.34
7.26
7.15
7.13
7.11
6.97
6.96
6.95
6.39
5.28
4.07
3.45
3.36
3.24
1.26
1.18
1.12
Et
O
HN
N
O
O
N
Cbz
O
Et
0.81
4.92
1.95
1.03
0.63
1.02
2.00
3.99
1.98
6.09
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 -1.0
f1 (ppm)

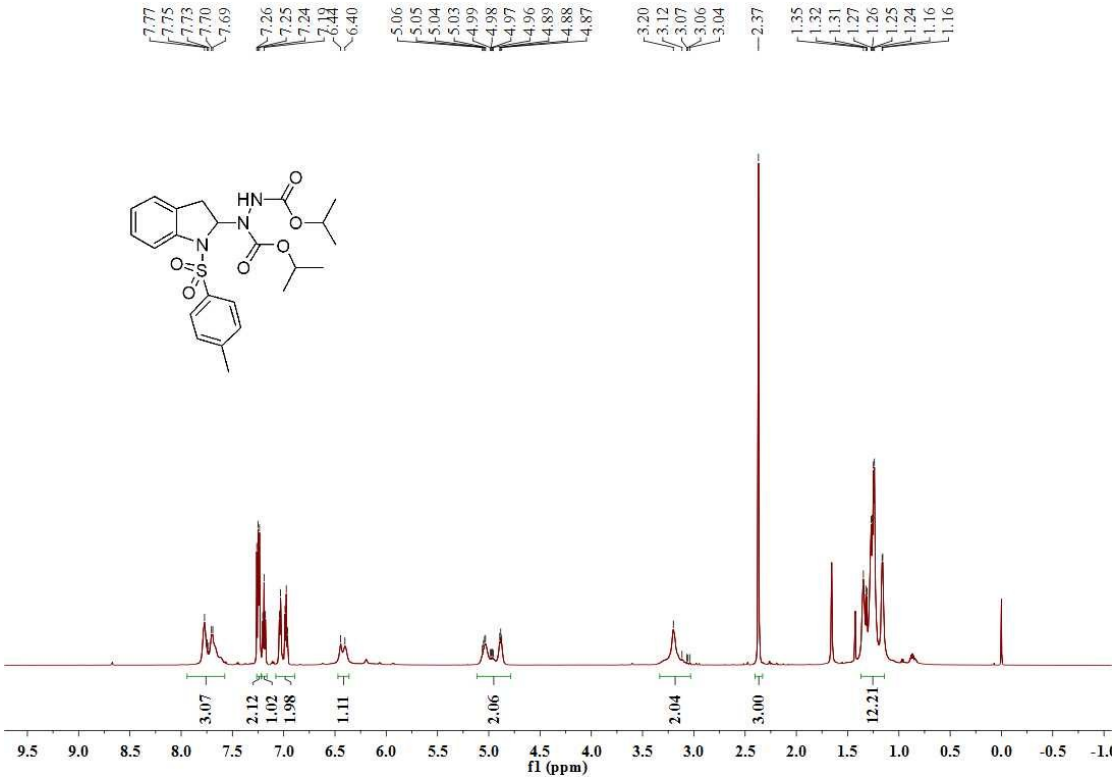

156.61
154.50
152.77
141.63
135.86
128.60
128.45
127.39
124.00
123.00
114.39
67.79
62.66
62.05
29.66
14.27
Et
O
HN
N
O
O
N
Cbz
O
Et
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

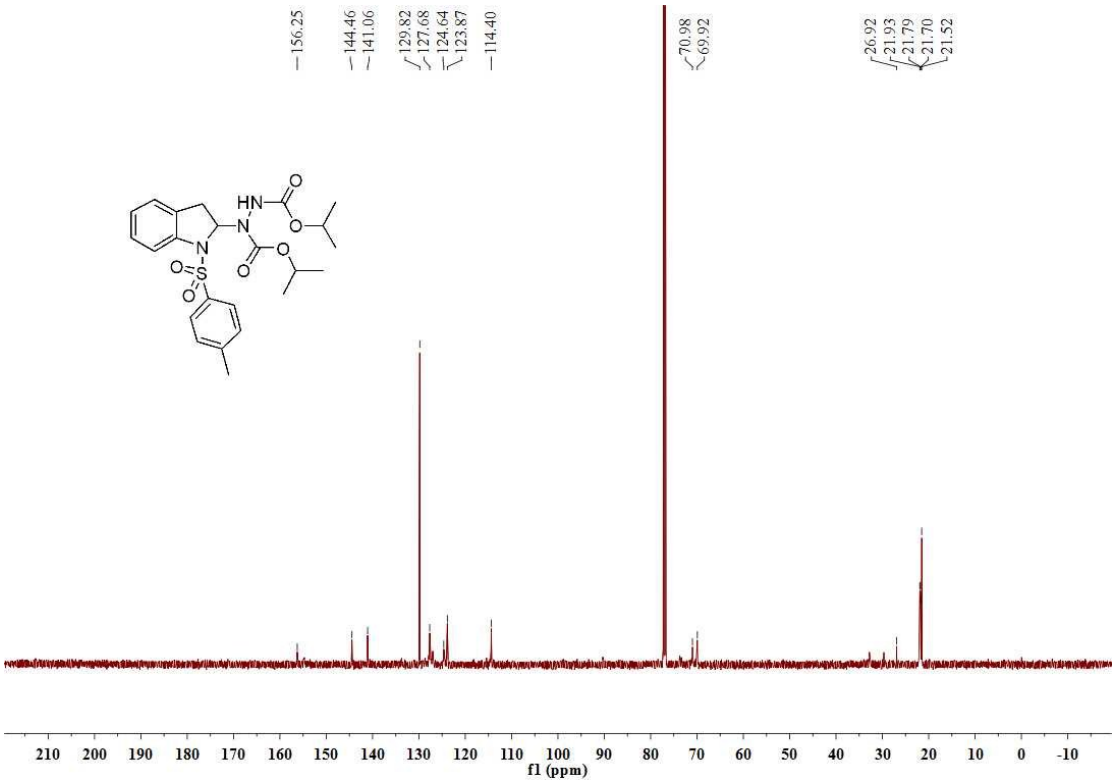
3h


7.76
7.28
7.24
7.13
7.07
6.94
6.72
6.47
6.24
5.16
5.05
4.99
3.41
Bn
HN
N
O
Cbz
Bn
1.08
18.33
0.78
0.97
6.06
2.00
f1 (ppm)

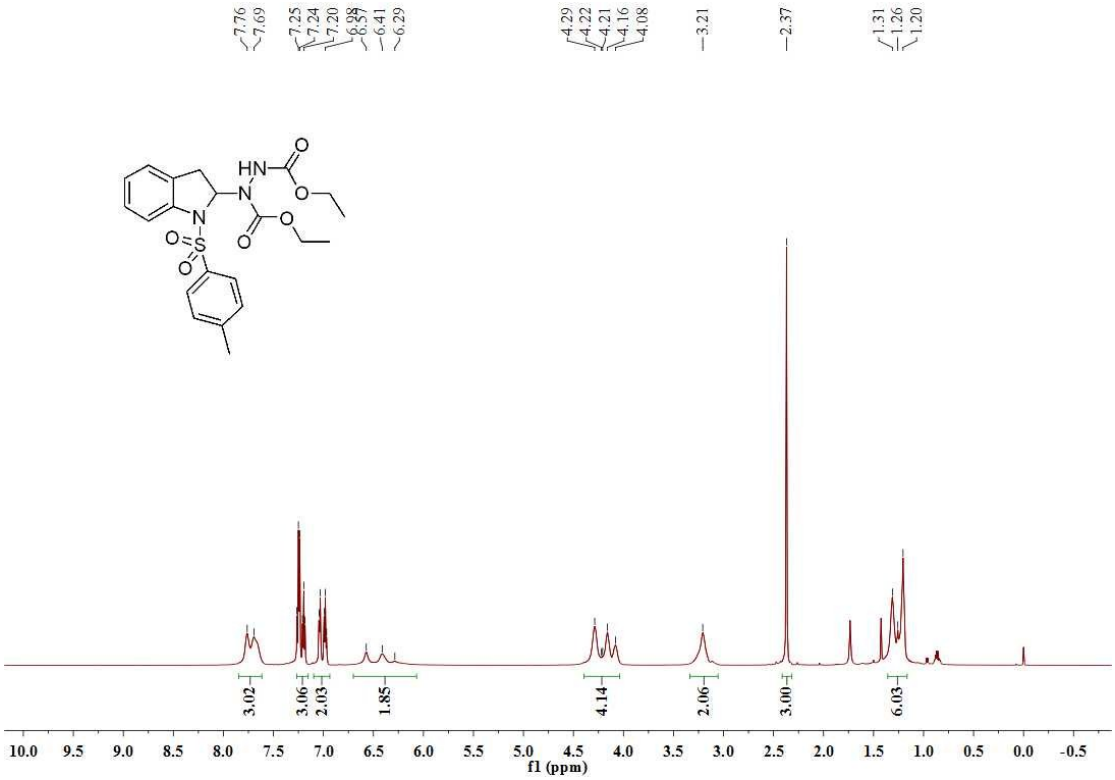

156.44
152.71
135.85
135.62
128.60
128.50
128.20
127.81
127.48
67.64
29.70
Bn
HN
N
O
Cbz
Bn
f1 (ppm)

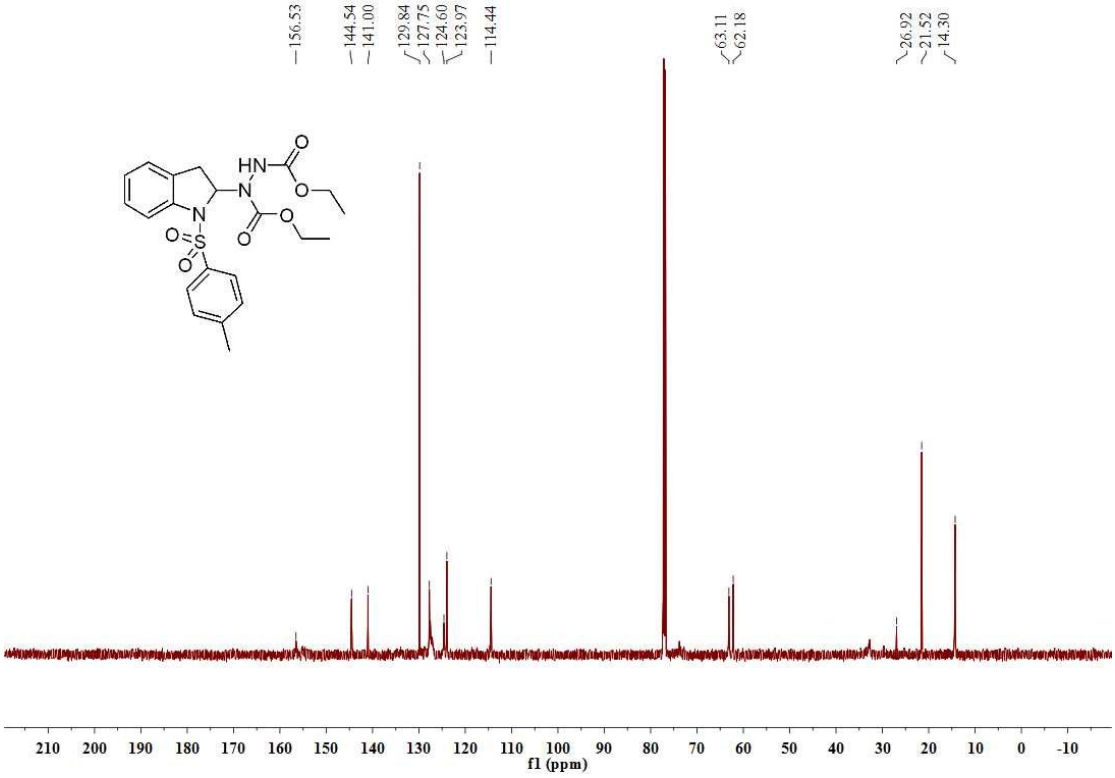
3i


7.77
7.75
7.73
7.70
7.69
7.26
7.25
7.24
7.19
6.44
6.40
5.06
5.05
5.04
5.03
4.99
4.98
4.97
4.96
4.89
4.88
4.87
3.20
3.12
3.07
3.06
3.04
2.37
1.35
1.32
1.31
1.27
1.26
1.25
1.24
1.16
1.16
HN
N
O
O
O
O
S
O
3.07
2.12
1.02
1.98
1.11
2.06
2.04
3.00
12.21
f1 (ppm)

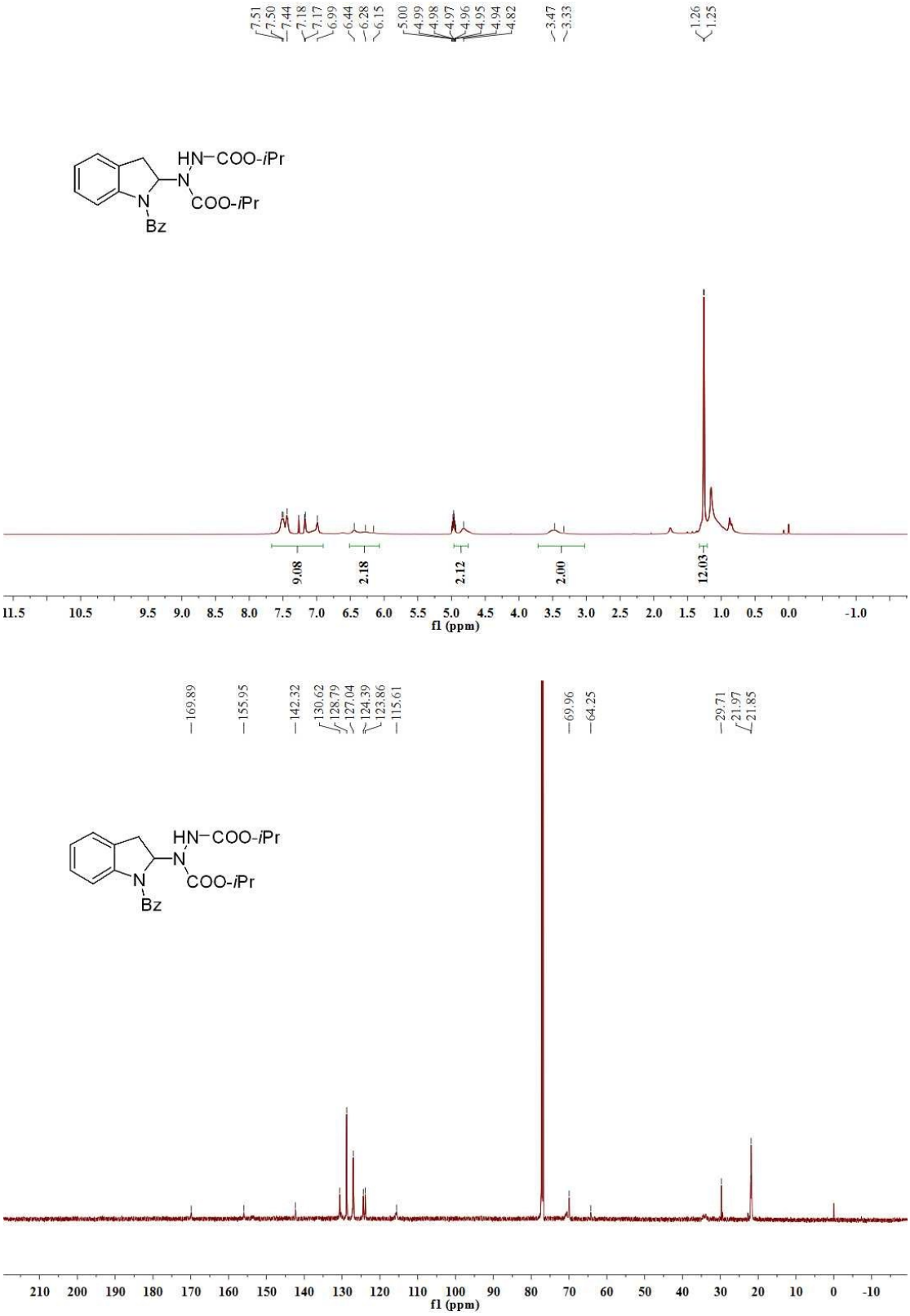

156.25
144.46
141.06
129.82
127.68
124.64
123.87
114.40
70.98
69.92
26.92
21.93
21.79
21.70
21.52
HN
N
O
O
O
O
S
O
f1 (ppm)

3j

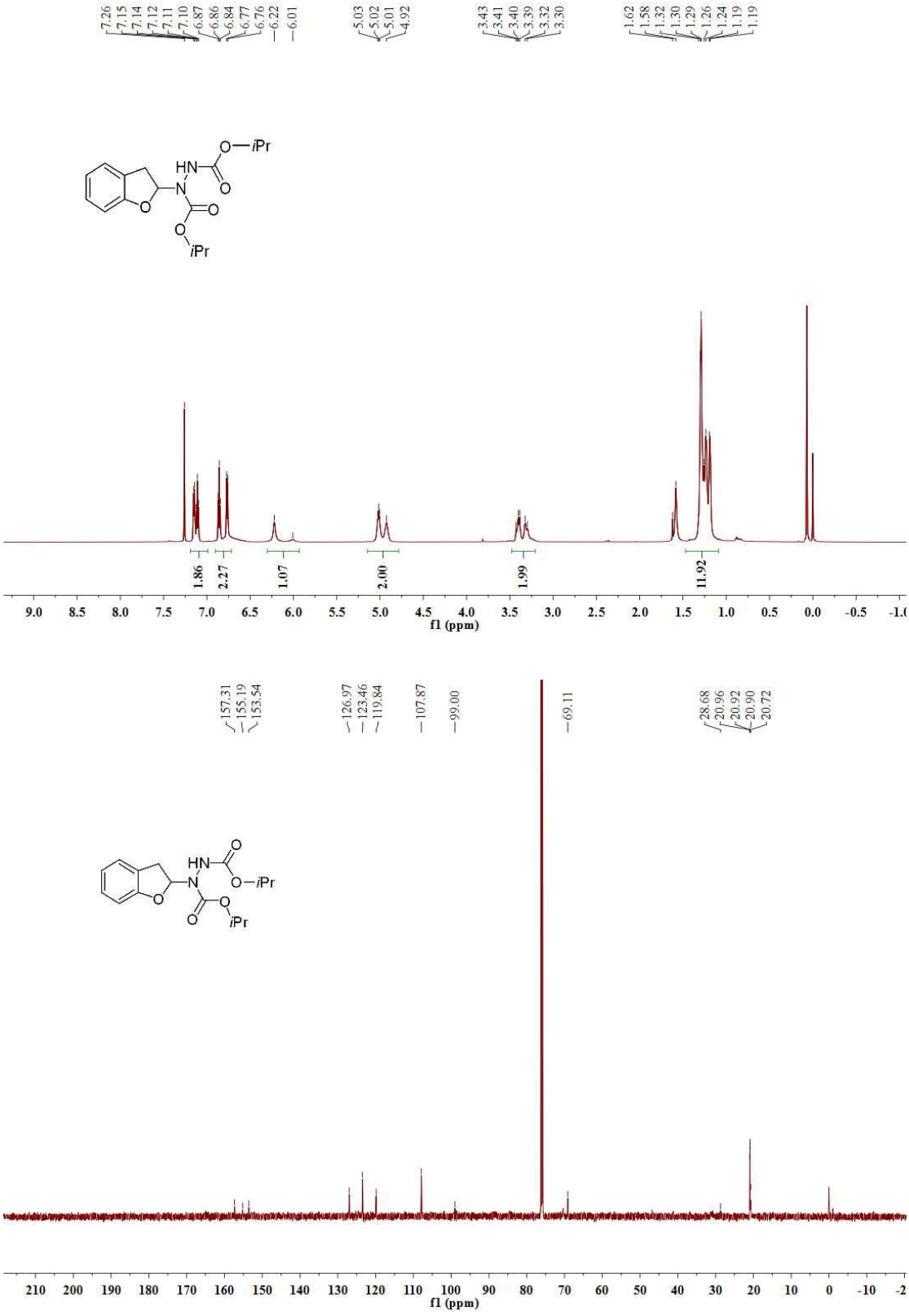

7.76
7.69
7.25
7.24
7.20
6.98
6.59
6.41
6.29
4.29
4.22
4.21
4.16
4.08
3.21
2.37
1.31
1.26
1.20
HN
N
O
O
N
O
S
O
O
3.02
3.06
2.03
1.85
4.14
2.06
3.00
6.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


156.53
144.54
141.00
129.84
127.75
124.60
123.97
114.44
63.11
62.18
26.92
21.52
14.30
HN
N
O
O
N
O
S
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

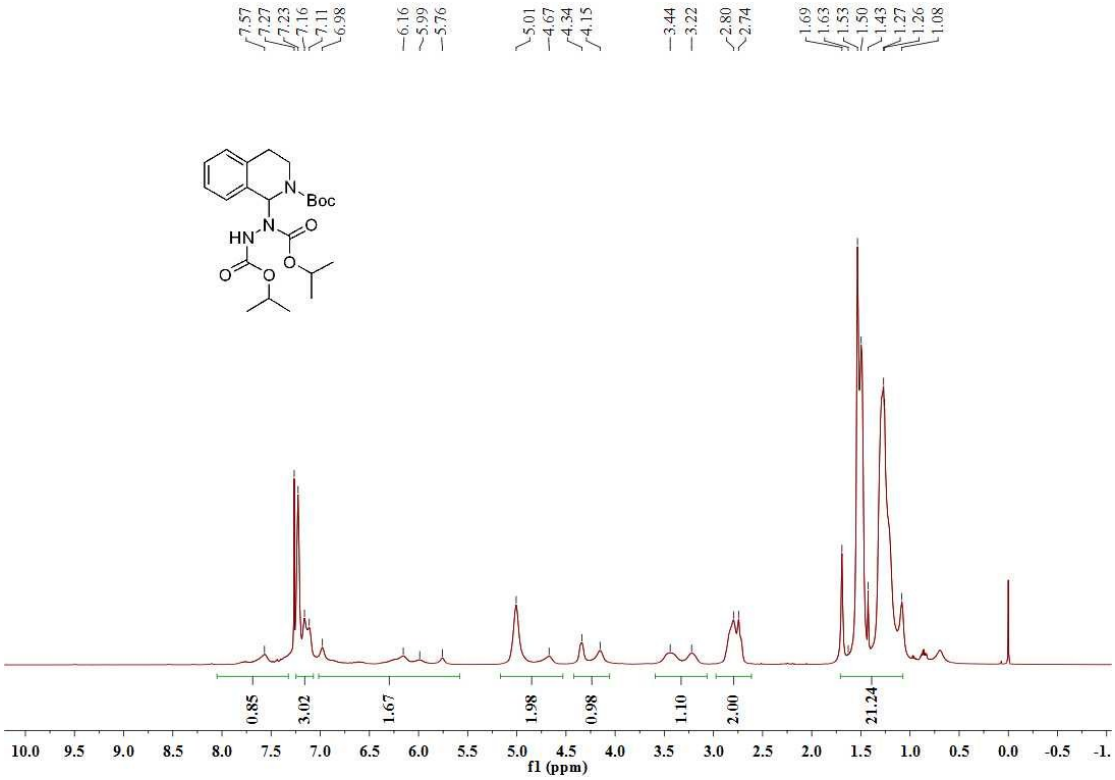
3k

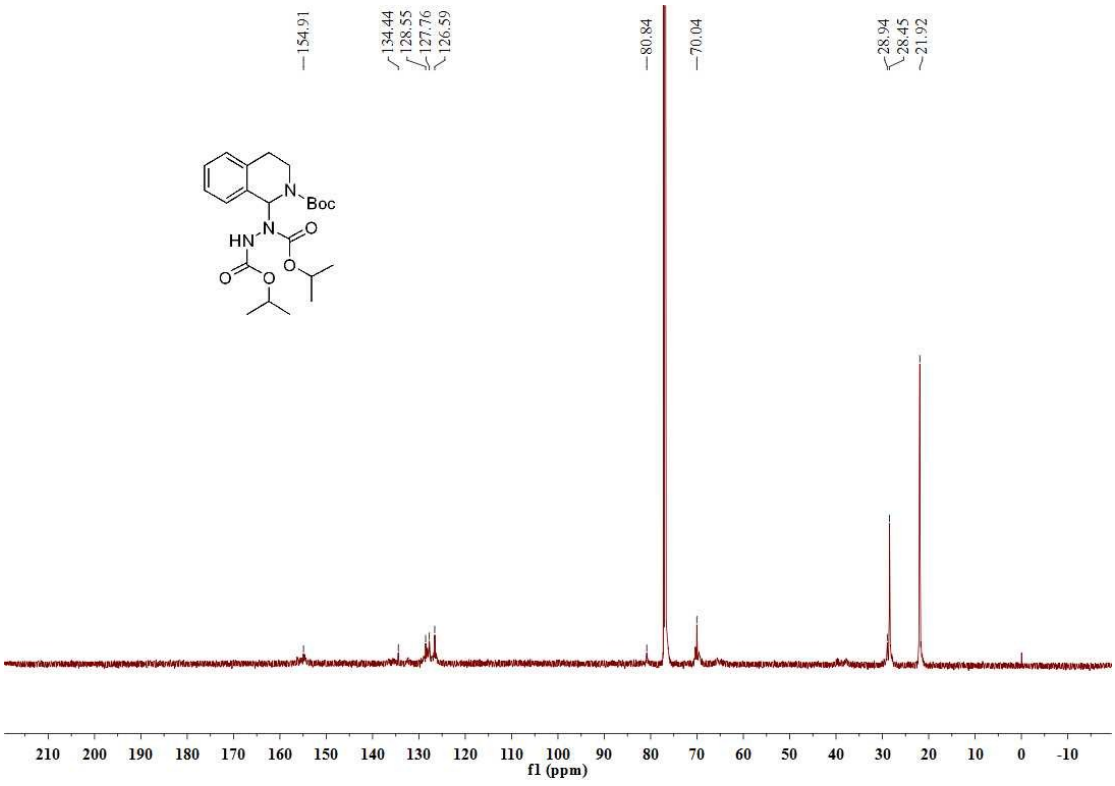

7.51
7.50
7.44
7.18
7.17
6.99
6.44
6.28
6.15
5.00
4.99
4.98
4.97
4.96
4.95
4.94
4.82
3.47
3.33
1.26
1.25
HN−COO-iPr
N
N
COO-iPr
Bz
9.08
2.18
2.12
2.00
12.03
f1 (ppm)
169.89
155.95
142.32
130.62
128.79
127.04
124.39
123.86
115.61
69.96
64.25
29.71
21.97
21.85
HN−COO-iPr
N
N
COO-iPr
Bz
f1 (ppm)

3l


7.26
7.15
7.14
7.12
7.11
7.10
6.87
6.86
6.84
6.77
6.76
6.22
6.01
5.03
5.02
5.01
4.92
3.43
3.41
3.40
3.39
3.32
3.30
1.62
1.58
1.32
1.30
1.29
1.26
1.24
1.19
1.19
O—iPr
HN
N
O
O
O
iPr
1.86
2.27
1.07
2.00
1.99
11.92
f1 (ppm)
157.31
155.19
153.54
126.97
123.46
119.84
107.87
99.00
69.11
28.68
20.96
20.92
20.90
20.72
HN
N
O—iPr
O
O
iPr
f1 (ppm)

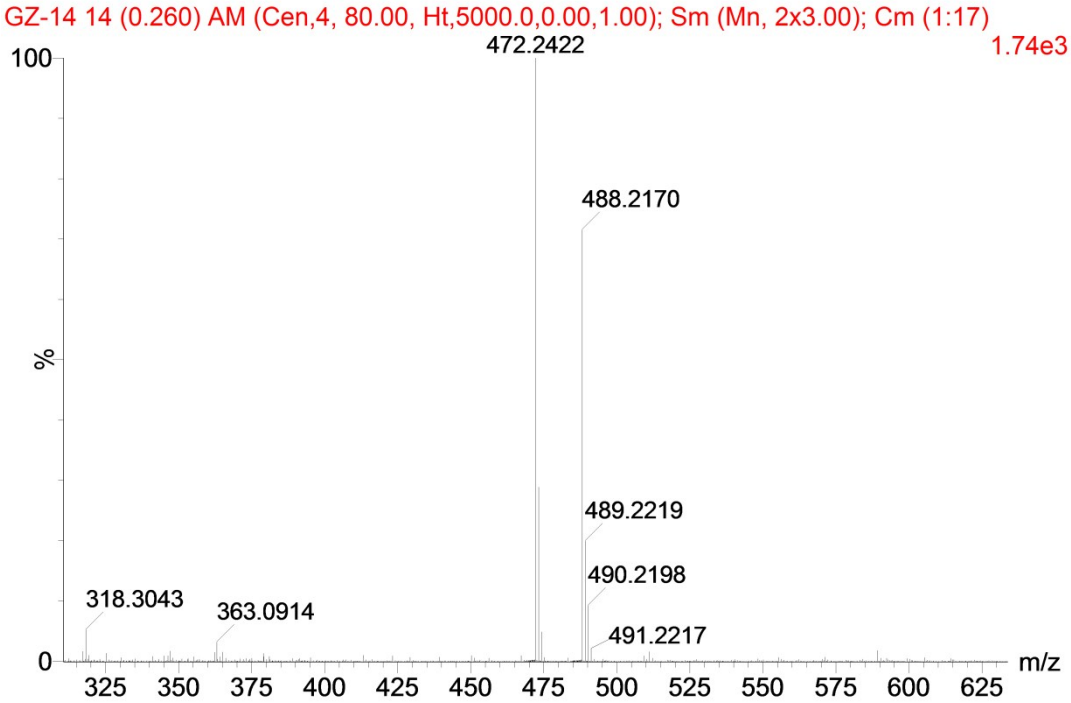
3m


7.57
7.27
7.23
7.16
7.11
6.98
6.16
5.99
5.76
5.01
4.67
4.34
4.15
3.44
3.22
2.80
2.74
1.69
1.63
1.53
1.50
1.43
1.27
1.26
1.08
Boc
HN
0.85
3.02
1.67
1.98
0.98
1.10
2.00
21.24
f1 (ppm)

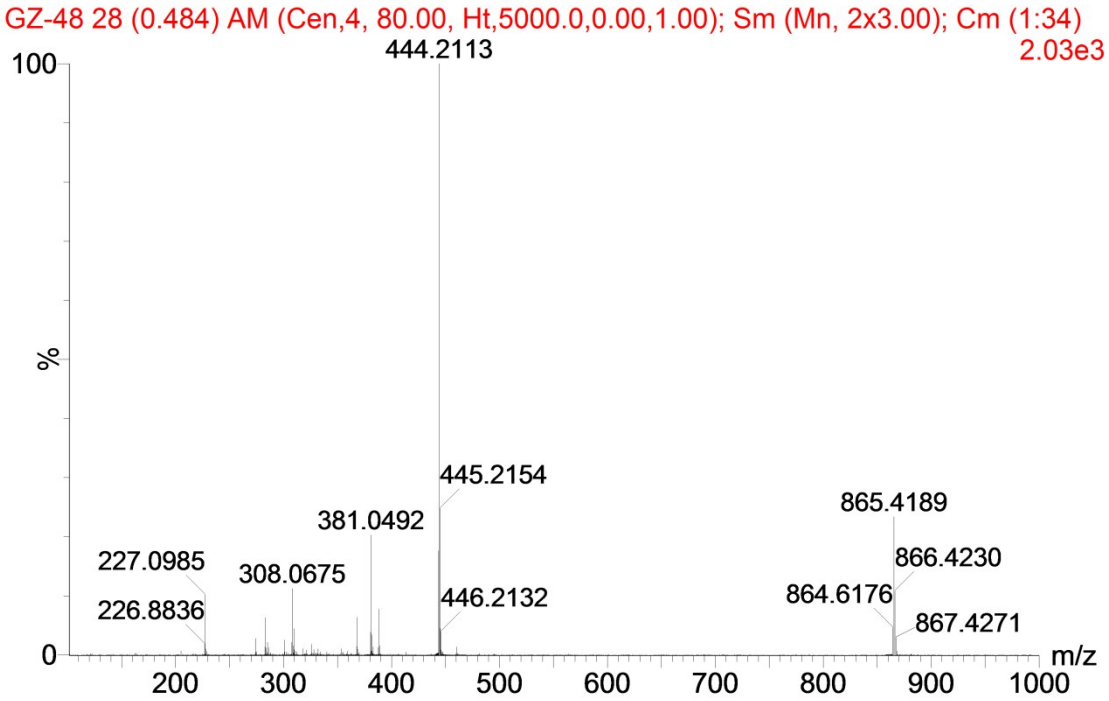

154.91
134.44
128.55
127.76
126.59
80.84
70.04
28.94
28.45
21.92
Boc
HN
f1 (ppm)

6. HRMS spectra

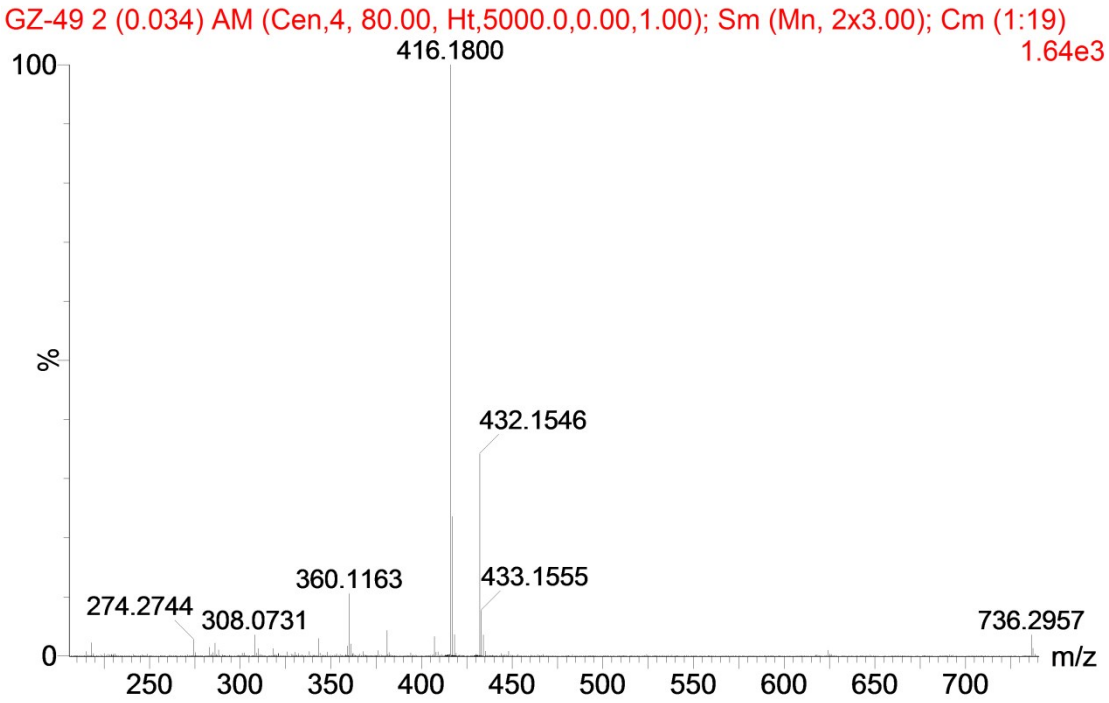
3a



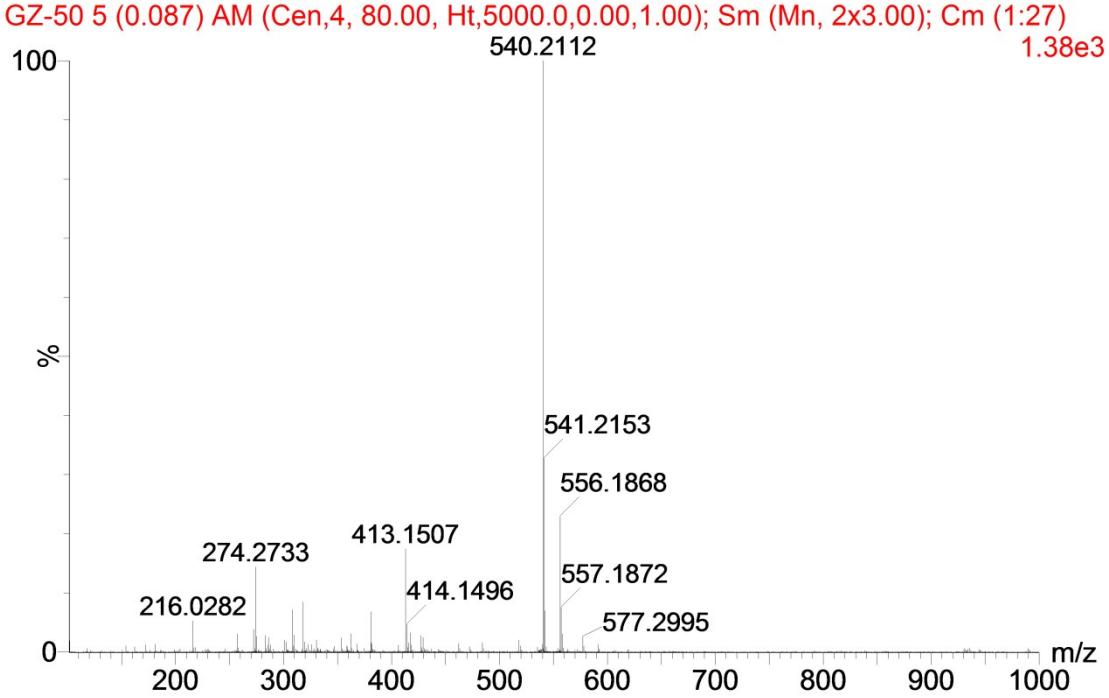
3b



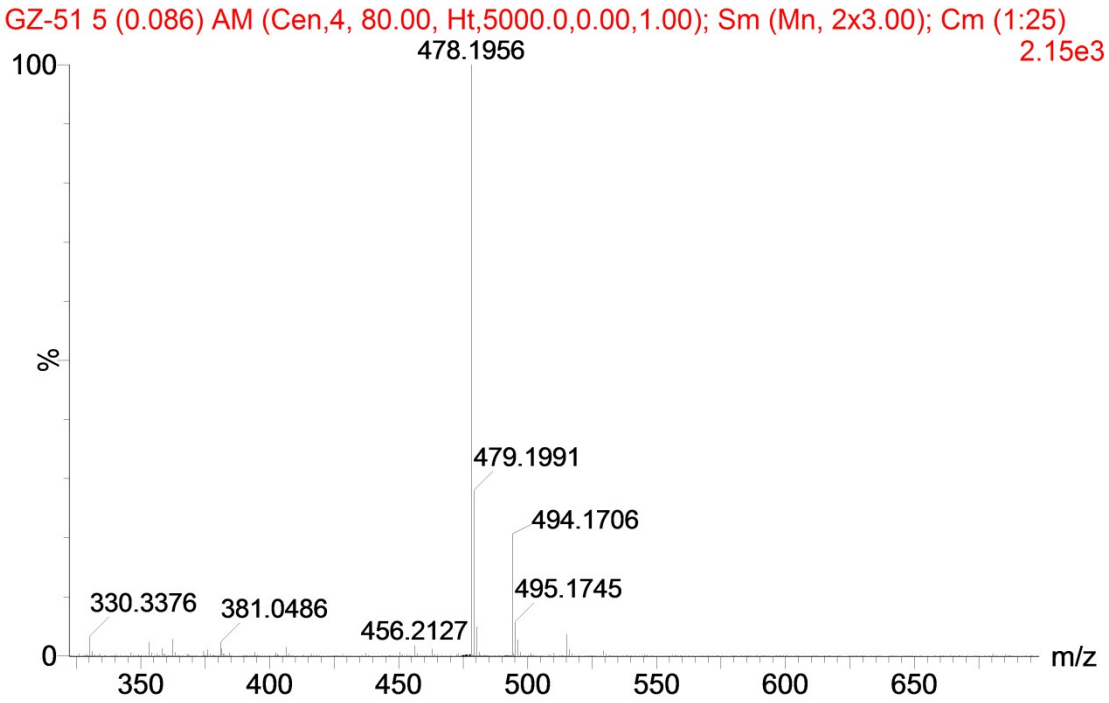
3c


GZ-49 2 (0.034) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (1:19)
1.64e3
416.1800
100
%
0
432.1546
360.1163
433.1555
274.2744
308.0731
736.2957
m/z
250
300
350
400
450
500
550
600
650
700

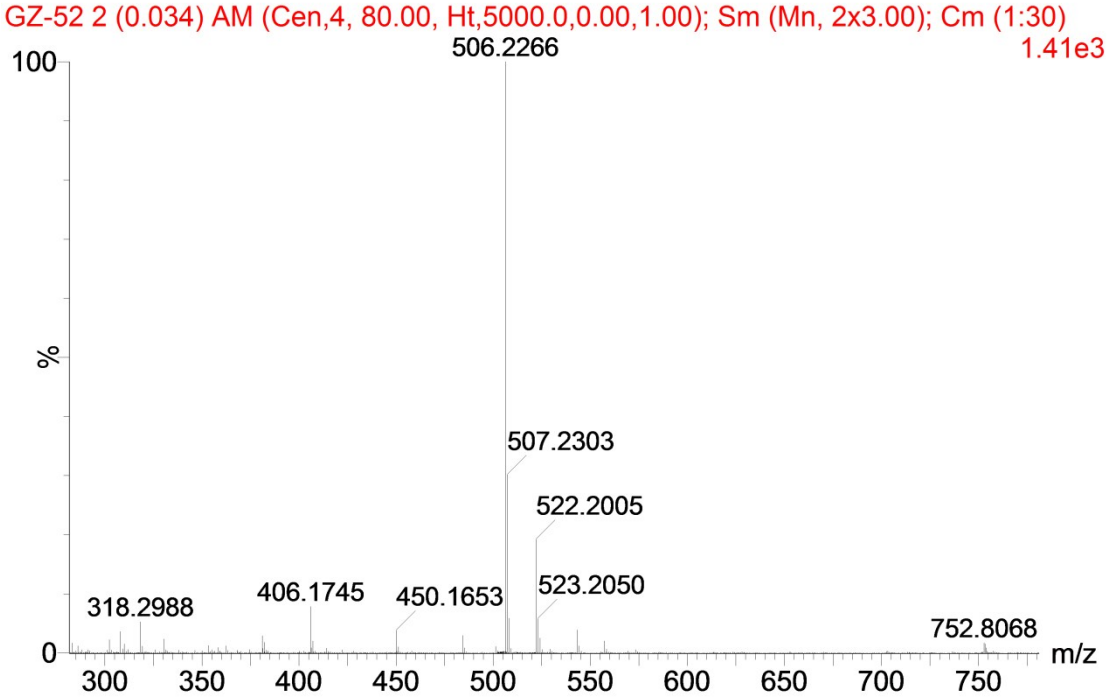
3d


GZ-50 5 (0.087) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (1:27)
1.38e3
540.2112
100
%
0
541.2153
556.1868
413.1507
274.2733
557.1872
414.1496
216.0282
577.2995
m/z
200
300
400
500
600
700
800
900
1000

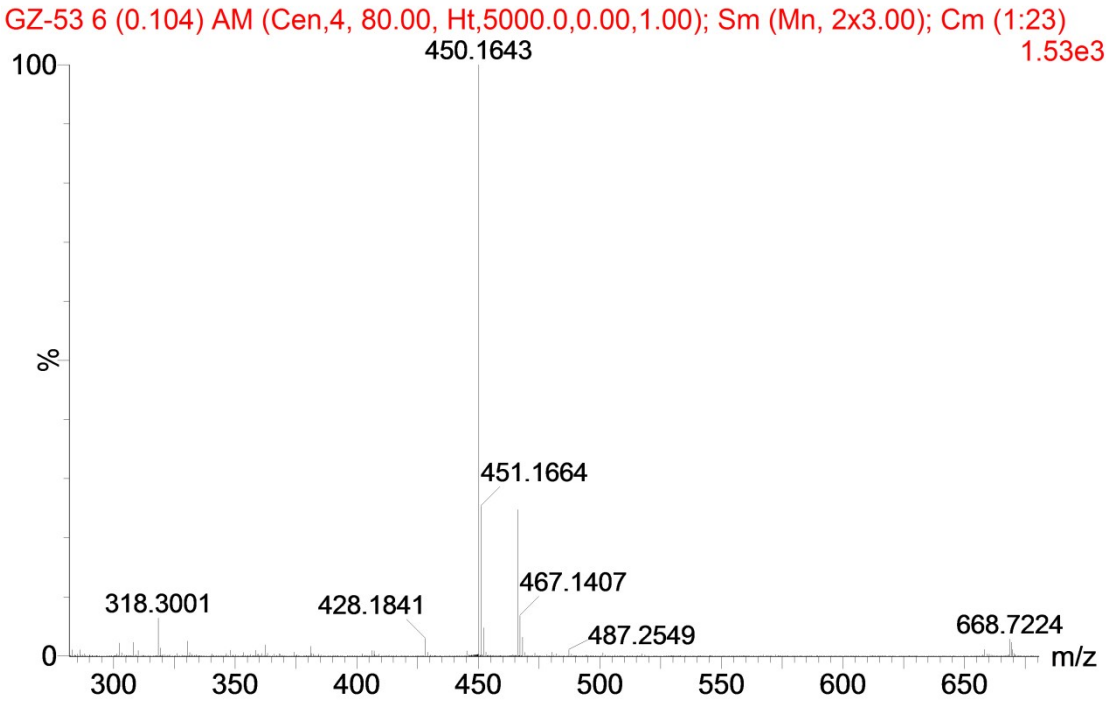
3e


GZ-51 5 (0.086) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (1:25)
2.15e3
478.1956
100
%
479.1991
494.1706
495.1745
330.3376
381.0486
456.2127
0
350
400
450
500
550
600
650
m/z

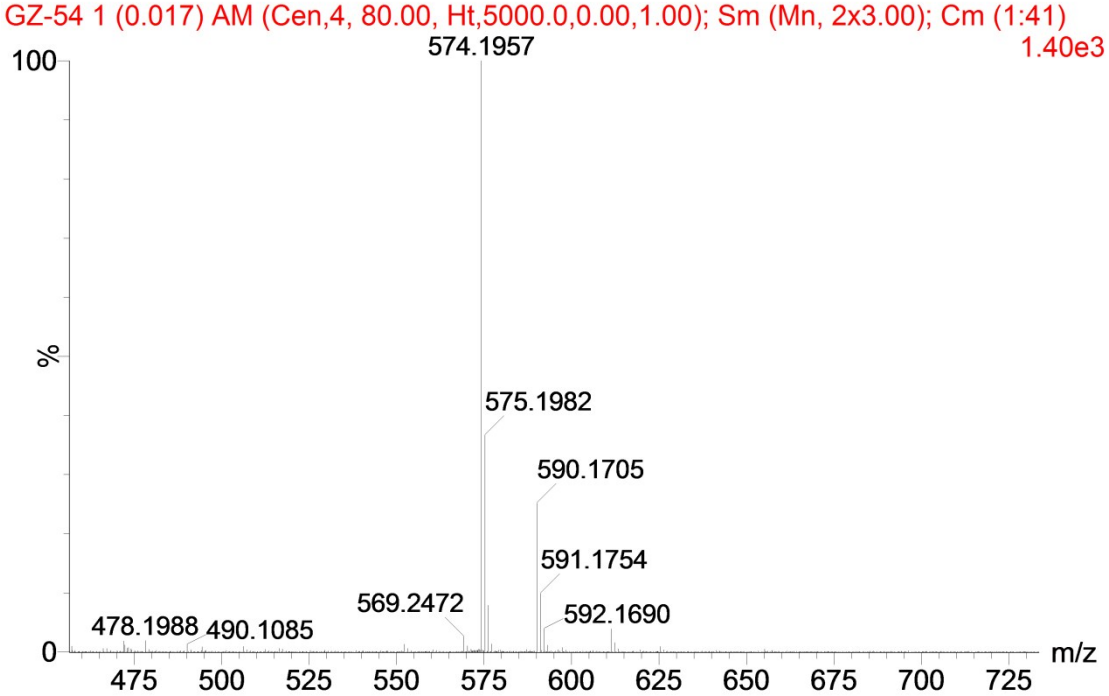
3f


GZ-52 2 (0.034) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (1:30)
1.41e3
506.2266
100
%
507.2303
522.2005
523.2050
318.2988
406.1745
450.1653
752.8068
0
300
350
400
450
500
550
600
650
700
750
m/z

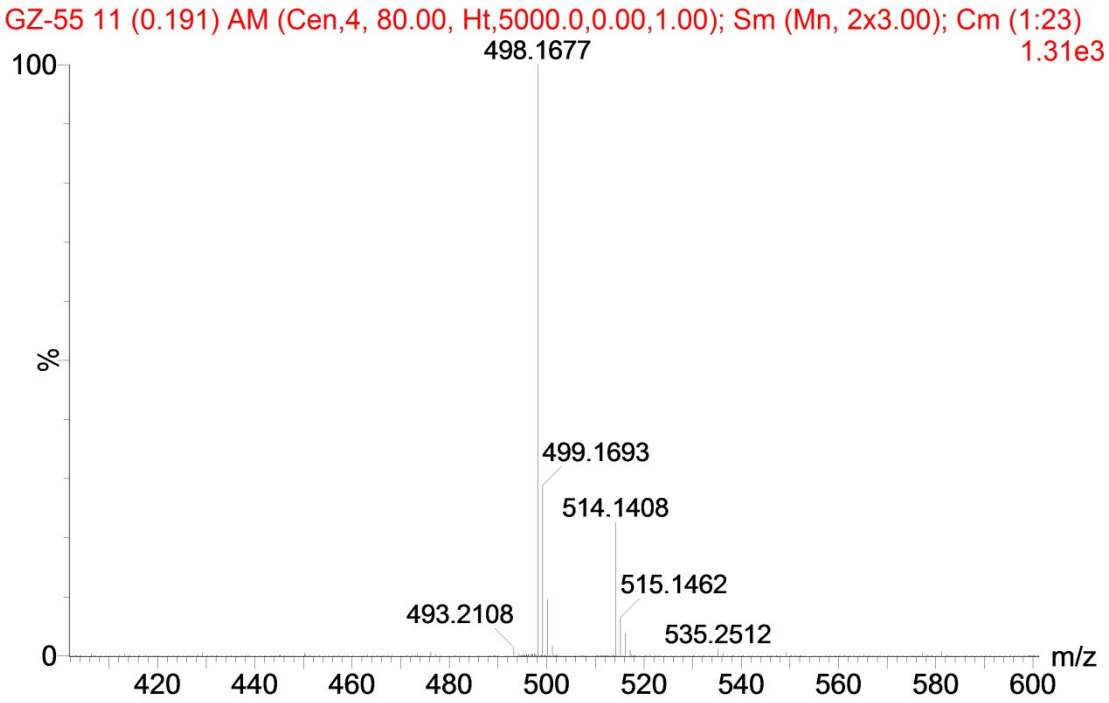
3g


GZ-53 6 (0.104) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (1:23)
1.53e3
450.1643
100
%
451.1664
467.1407
318.3001
428.1841
487.2549
668.7224
0
m/z
300
350
400
450
500
550
600
650

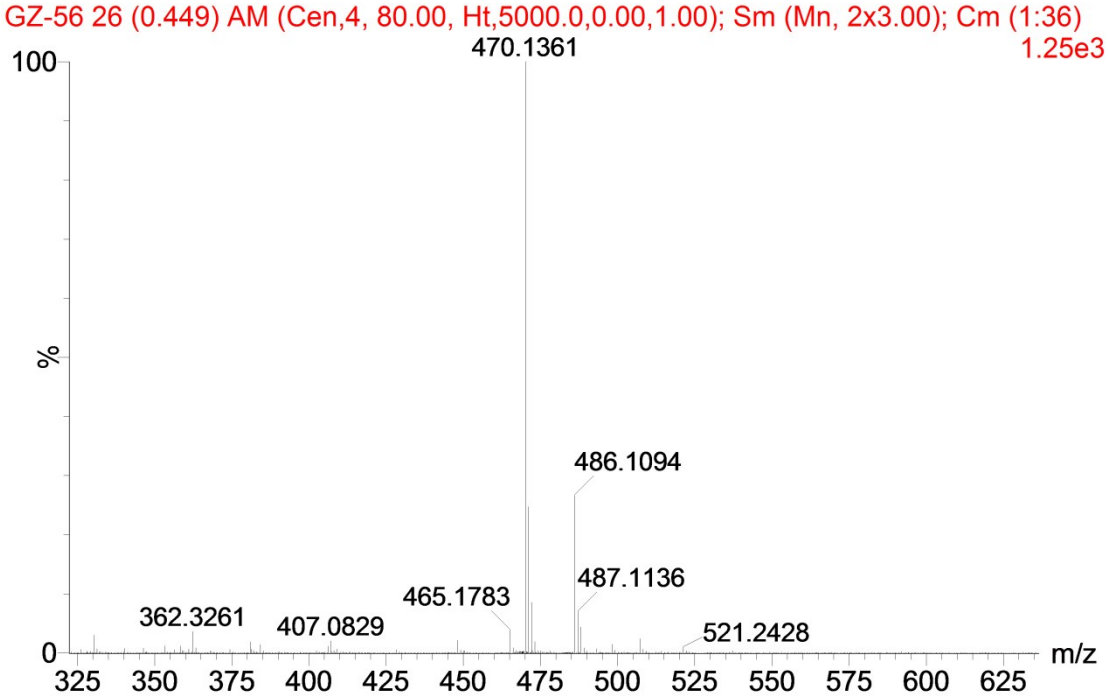
3h


GZ-54 1 (0.017) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (1:41)
1.40e3
574.1957
100
%
575.1982
590.1705
591.1754
569.2472
592.1690
478.1988
490.1085
0
m/z
475
500
525
550
575
600
625
650
675
700
725

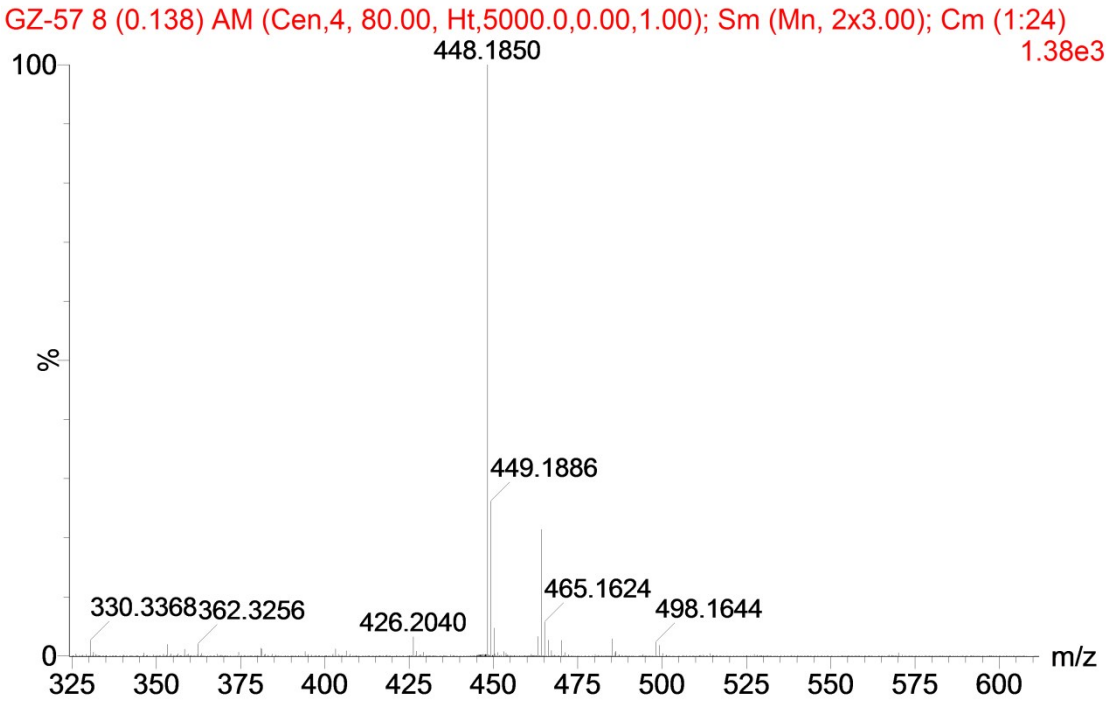
3i


GZ-55 11 (0.191) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (1:23)
1.31e3
498.1677
499.1693
514.1408
515.1462
493.2108
535.2512
100
%
0
420
440
460
480
500
520
540
560
580
600
m/z

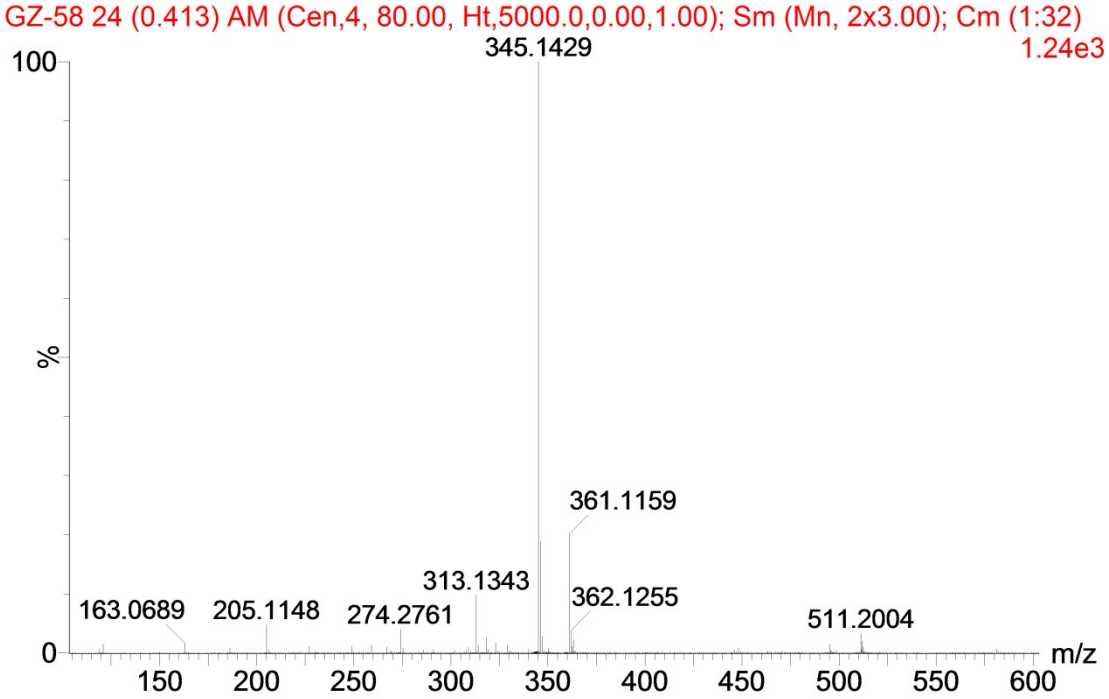
3j


GZ-56 26 (0.449) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (1:36)
1.25e3
470.1361
486.1094
487.1136
465.1783
362.3261
407.0829
521.2428
100
%
0
325
350
375
400
425
450
475
500
525
550
575
600
625
m/z

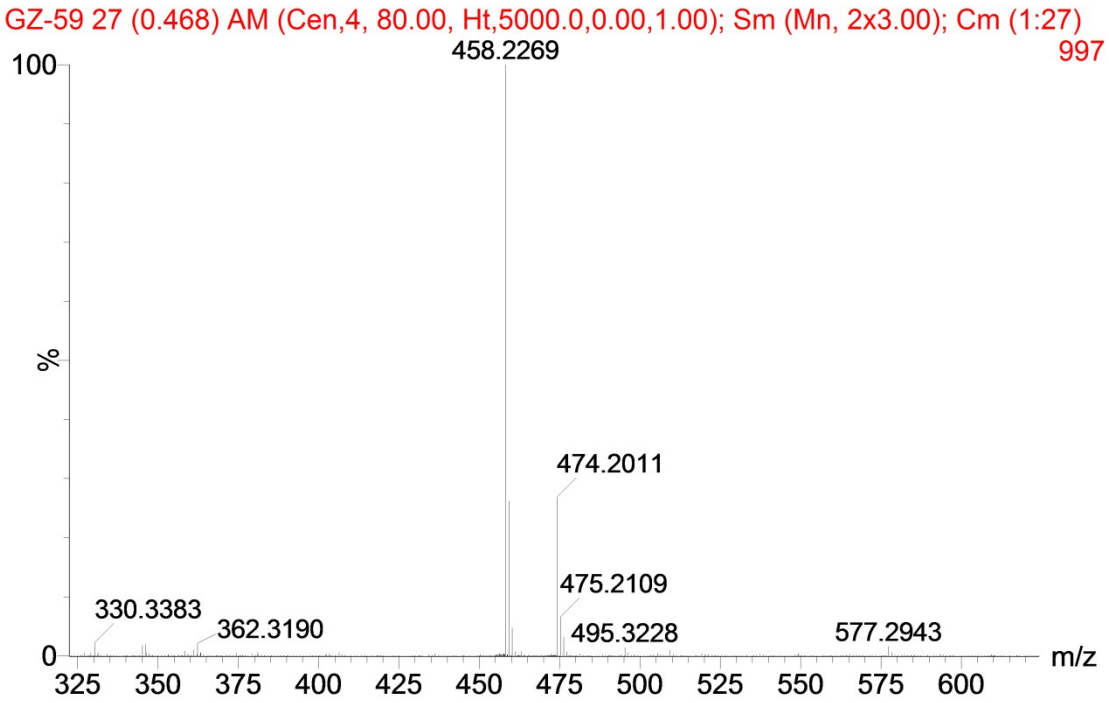
3k


GZ-57 8 (0.138) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (1:24)
1.38e3
448.1850
449.1886
465.1624
498.1644
330.3368
362.3256
426.2040
100
%
0
325 350 375 400 425 450 475 500 525 550 575 600
m/z

3l


GZ-58 24 (0.413) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (1:32)
1.24e3
345.1429
361.1159
313.1343
362.1255
163.0689
205.1148
274.2761
511.2004
100
%
0
150 200 250 300 350 400 450 500 550 600
m/z

3m


GZ-59 27 (0.468) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 2x3.00); Cm (1:27)
997
458.2269
100
%
474.2011
475.2109
330.3383
362.3190
495.3228
577.2943
0
m/z
325 350 375 400 425 450 475 500 525 550 575 600

7. References

1. a) M. Kurokawa and T. Sugai, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 1021–1025. b) J. Charton, A. C. Gassiot, S. G. Mizzi, M. A. D. Fontaine, P. Melnyk and C. Sergheraert, *Bioorg. Med. Chem. Lett.,* 2005, **15**, 4833–4837. c) A. Hartikka, A. T. S′ lo′sarczyka and P. I. Arvidsson, *Tetrahedron: Asymmetry*, 2007, **18**, 1403–1409. d) S.-J. Zhang, W.-W. Sun, P. Cao, X.-P. Dong, J.-K. Liu, B. Wu, *J. Org. Chem.*, 2016, **81**, 956−968. e) Y. Sasano, S. Nagasawa, M. Yamazaki, M.Shibuya, J. Park and Y. Iwabuchi, *Angew. Chem. Int. Ed.*, 2014, **53**, 3236 –3240.